Supporting Information

Assembly of Indole-2-Carboxylic Acid Esters through a Ligand-Free Copper-Catalysed Cascade Process

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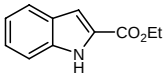
Content:

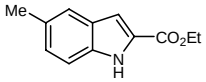
Typical procedure for the preparation of Indole-2-Carboxylic Acid Esters: The aryl halides, base, copper salts and solvent were added together into a reacting tube under nitrogen atmosphere. Then ethyl isocyanoacetate was slowly added and the mixtures were stirred at certain temperature. After the reactions were finished, ethyl acetate and water were added. The organic phase was separated, dried over sodium sulphate and evaporated in vacuum. The residues were loaded on silica gel column and purified to get the final products.

Ethyl 1*H*-indole-2-carboxylate (5) [1]



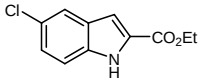
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.99 (br, 1H), 7.68 (m, 1H), 7.13-7.42 (m, 4H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ESI-MS *m/z* 189.9 $(M+H)^+$.

Ethyl 5-methyl-1*H*-indole-2-carboxylate (7a) [2]



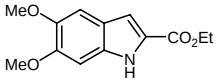
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.88 (br, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.19 (m, 2H), 7.00 (d, *J* = 8.0 Hz 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). ESI-MS *m/z* 204.1 $(M+H)^+$.

Ethyl 5-chloro-1*H*-indole-2-carboxylate (7b) [3]



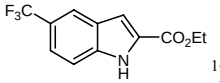
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.25 (br, 1H), 7.65 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.15 (s, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H), ESI-MS *m/z* 222.0 $(M-H)^-$.

Ethyl 5, 6-dimethoxy-1*H*-indole-2-carboxylate (7c) [4]



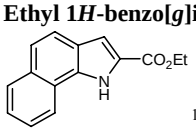
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.06 (br, 1H), 7.11 (s, 1H), 7.03 (s, 1H), 6.84 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), ESI-MS *m/z* 250.0 $(M+H)^+$.

Ethyl 5-(trifluoromethyl)-1*H*-indole-2-carboxylate (7d) [5]



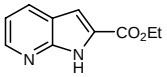
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.55 (br, 1H), 8.00(s, 1H), 7.55-7.50 (m, 2H), 7.30 (s, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), ESI-MS *m/z* 256.0 $(M-H)^-$.

Ethyl 1*H*-benzo[*g*]indole-2-carboxylate (7e) [6]



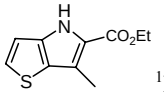
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.95 (br, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.59-7.49 (m, 3H), 7.35 (s, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), ESI-MS *m/z* 240.0 $(M+H)^+$.

Ethyl 1*H*-pyrrolo [2, 3-*b*] pyridine-2-carboxylate (7f) [7]



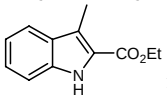
^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.58 (br, 1H), 8.61 (m, 1H), 8.05 (m, 1H), 7.19-7.15 (m, 2H), 4.46 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 6.8 Hz, 3H). ESI-MS *m/z* 191.1 $(M+H)^+$.

Ethyl 6-methyl-4*H*-thieno [3, 2-*b*] pyrrole-5-carboxylate (7g) [8]



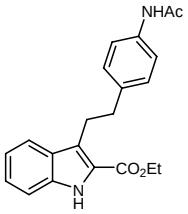
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.18 (br, 1H), 7.29 (d, *J* = 5.6 Hz, 1H), 6.89 (d, *J* = 5.6 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.4, 139.6, 129.1, 126.5, 123.1, 120.2, 111.3, 60.3, 14.5, 12.1, ESI-MS *m/z* 209.9 $(M+H)^+$.

Ethyl 3-methyl-1*H*-indole-2-carboxylate (7h) [9]



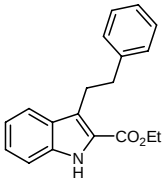
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79 (br, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.38-7.30 (m, 2H), 7.16-7.13 (m, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ESI-MS *m/z* 204.1 $(M+H)^+$.

Ethyl 3-(4-acetamidophenethyl)-1*H*-indole-2-carboxylate (7i)



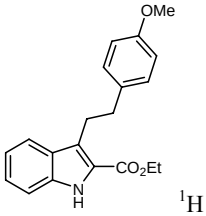
^{1}H NMR (DMSO, 400 MHz) δ 11.47 (br, 1H), 9.82 (br, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.24 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.05 (m, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.02 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (DMSO, 100 MHz) δ 168.4, 162.2, 137.2, 136.9, 136.7, 128.8, 127.4, 125.2, 123.5, 123.0, 120.7, 119.8, 119.4, 112.8, 60.6, 36.8, 27.2, 24.4, 14.8; EI-MS *m/z* 350 (M^+), 202, 156, 128, 106; HR-MS (EI) calcd for $C_{21}H_{22}N_2O_3$ requires 350.1630, found 350.1626.

Ethyl 3-phenethyl-1*H*-indole-2-carboxylate (7j) [10]



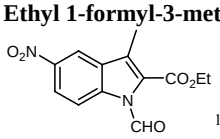
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (br, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.40-7.12 (m, 8H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 8.0 Hz, 2H), 2.96(t, *J* = 8.0 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ESI-MS *m/z* 294.2 $(M+H)^+$.

Ethyl 3-(4-methoxyphenethyl)-1*H*-indole-2-carboxylate (7k)



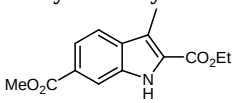
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.80 (br, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33 (m, 1H), 7.17-7.12 (m, 3H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.91(t, *J* = 6.8 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ 162.4, 157.8, 135.9, 134.4, 129.3, 127.8, 125.5, 124.1, 123.3, 120.7, 120.0, 113.7, 111.7, 60.7, 55.3, 36.4, 27.4, 14.5; EI-MS *m/z* 323 (M^+), 202, 156, 128, 121; HR-MS (EI) calcd. for $C_{20}H_{21}NO_3$ requires 323.1521, found 323.1517.

Ethyl 1-formyl-3-methyl-5-nitro-1*H*-indole-2-carboxylate (7l)



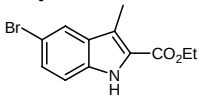
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 6.51 (s, 1H), 4.26 (q, *J* = 5.2 Hz, 2H), 2.72 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H); ESI-MS *m/z* 277.1 $(M+H)^+$.

2-ethyl 6-methyl 3-methyl-1*H*-indole-2,6-dicarboxylate (7m) [11]



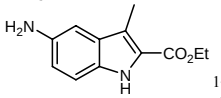
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.15 (br, 1H), 8.14 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 2.60 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 162.4, 135.0, 131.7, 126.9, 126.2, 120.4, 119.7, 114.2, 61.1, 52.1, 14.4, 9.92; ESI-MS *m/z* 262.5 $(M+H)^+$.

Ethyl 6-bromo-3-methyl-1*H*-indole-2-carboxylate (7n) [12]



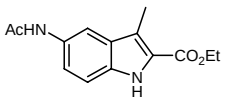
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71 (br, 1H), 7.51 (m, 2H), 7.23 (m, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.58 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ESI-MS *m/z* 282.0 $(M+H)^+$.

Ethyl 5-amino-3-methyl-1*H*-indole-2-carboxylate （7o) [13]



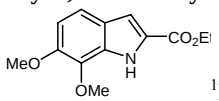
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (br, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.89 (s, 1H), 6.80 (d, *J* = 8.4 Hz 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.56 (br, 2H), 2.53 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ESI-MS *m/z* 219.0 $(M+H)^+$.

Ethyl 5-acetamido-3-methyl-1*H*-indole-2-carboxylate (7p)



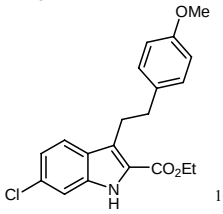
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (br, 1H), 7.88 (s, 1H), 7.31-7.22 (m, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.20 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (DMSO, 100 MHz) δ 168.2, 162.3, 133.5, 132.3, 127.8, 124.1, 119.6, 118.4, 112.7, 110.2, 60.5, 24.3, 14.8, 10.2; EI-MS *m/z* 260 (M^+), 214, 172, 144, 116; HR-MS (EI) calcd for $C_{14}H_{16}N_2O_3$ requires 260.1161, found 260.1158.

Ethyl 6,7-dimethoxy-1*H*-indole-2-carboxylate (9a)



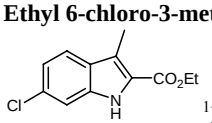
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.93 (br, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.16 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.01 (s, 3H), 3.94 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 161.8, 149.0, 132.0, 127.5, 124.0, 117.6, 109.9, 109.2, 61.0, 60.9, 57.2, 14.4; ESI-MS *m/z* 250.1 $(M+H)^+$; HR-MS (EI) calcd for $C_{13}H_{15}NO_4$ requires 249.2625, found 249.2629.

Ethyl 6-chloro-3-(4-methoxyphenethyl)-1*H*-indole-2-carboxylate (9b)



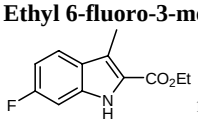
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81 (br, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (s, 1H), 7.12-7.06 (m, 2H), 6.81 (m, 2H), 4.41 (q, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 3.32(t, *J* = 8.0 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 1.44 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1, 157.9, 136.0, 134.0, 131.4, 129.3, 126.5, 124.1, 123.9, 121.7, 121.0, 113.7, 111.5, 60.9, 55.3, 36.3, 27.2, 14.4; EI-MS *m/z* 357 (M^+), 236, 190, 162, 121; HR-MS (EI) calcd for $C_{20}H_{20}ClNO_3$ requires 357.1132, found 357.1123.

Ethyl 6-chloro-3-methyl-1*H*-indole-2-carboxylate (9c) [14]



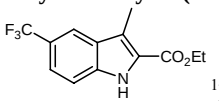
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (br, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.35 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.58 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H); ESI-MS *m/z* 238.1 $(M+H)^+$.

Ethyl 6-fluoro-3-methyl-1*H*-indole-2-carboxylate (9d) [15]



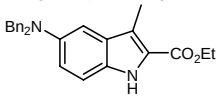
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65 (br, 1H), 7.58 (m, 1H), 7.03 (m, 1H), 6.90 (m, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H); ESI-MS *m/z* 222.0 $(M+H)^+$.

Ethyl 3-methyl-5-(trifluoromethyl)-1*H*-indole-2-carboxylate (9e) [16]



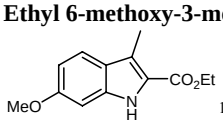
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.99 (br, 1H), 7.96 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.8 Hz 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H); ESI-MS *m/z* 270.0 $(M-H)^-$.

Ethyl 5-(dibenzylamino)-3-methyl-1*H*-indole-2-carboxylate (9f)



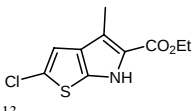
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (br, 1H), 7.31-7.24 (m, 10H), 7.18 (m, 1H), 6.99 (m, 1H), 6.89 (s, 1H), 4.61(s, 4H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{3}C NMR ($CDCl_3$, 100 MHz) δ 162.6, 144.0, 139.1, 130.2, 129.3, 128.4, 127.2, 126.8, 123.7, 119.2, 116.7, 112.1, 103.3, 60.4, 55.5, 14.4, 9.93; EI-MS *m/z* 398 (M^+), 352, 307, 261, 233,128, 91; HR-MS (EI) calcd for $C_{26}H_{26}N_2O_2$ requires 398.1994, found 398.1990.

Ethyl 6-methoxy-3-methyl-1*H*-indole-2-carboxylate (9g) [17]



^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (br, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 6.81-6.77 (m, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 2.58(s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.6, 159.1, 136.9, 123.1, 122.4.1, 121.6, 120.7, 111.2, 93.5, 60.4, 55.4, 14.5, 10.0; ESI-MS *m/z* 234.1 $(M+H)^+$.

Ethyl 2-chloro-4-methyl-6*H*-thieno[2,3-b]pyrrole-5-carboxylate (9h)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.45 (br, 1H), 6.87 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.0, 133.3, 130.3, 123.9, 123.7, 120.1, 116.5, 60.5, 14.5, 11.6; ESI-MS *m/z* 244.5 $(M+H)^+$; HR-MS (EI) calcd for $C_{10}H_{10}ClNO_2S$ requires 243.0121, found 243.0119.

Reference:

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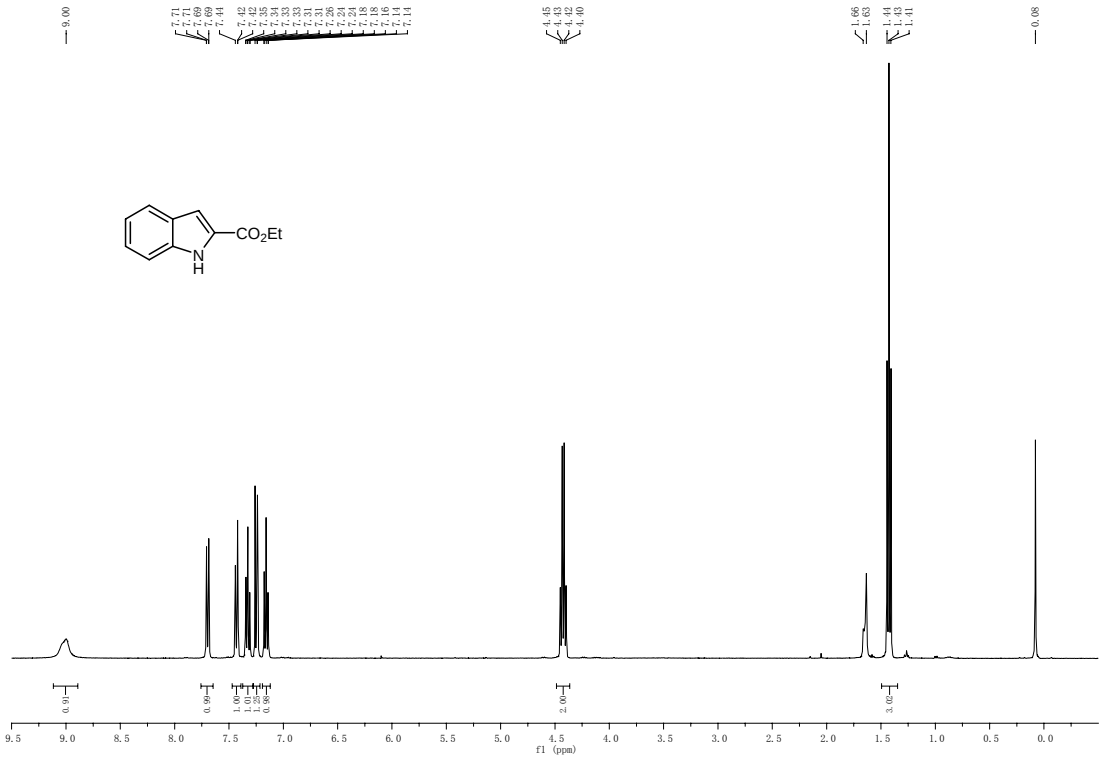
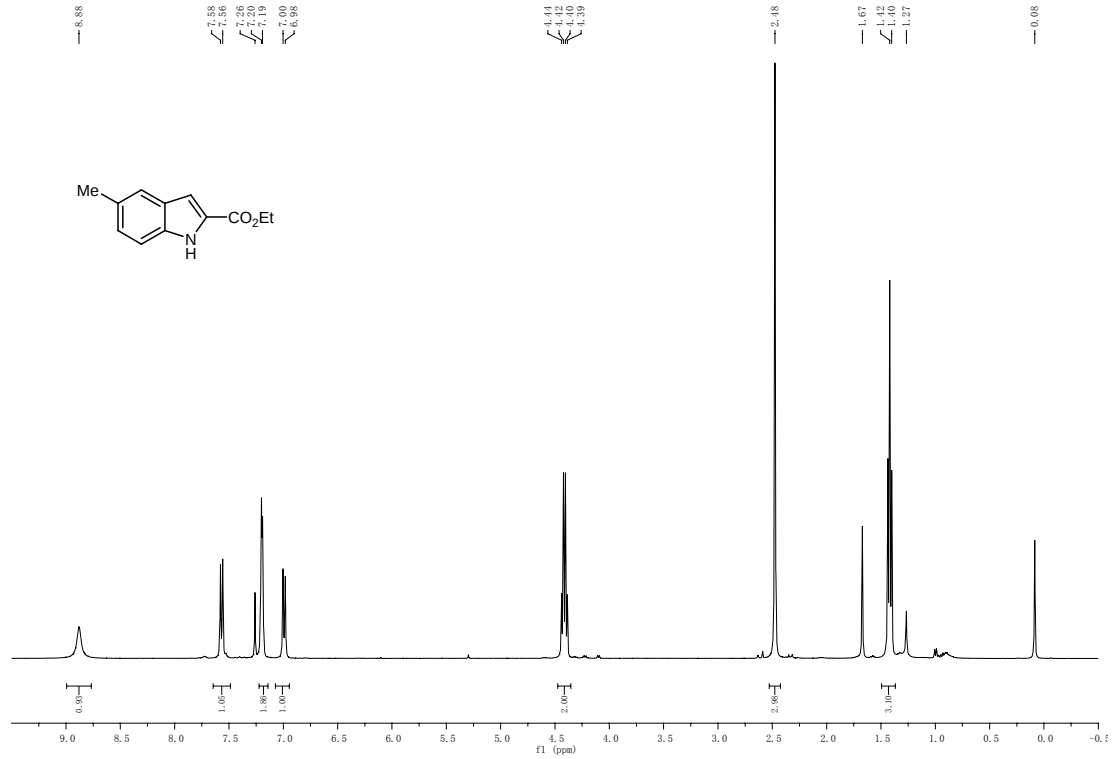
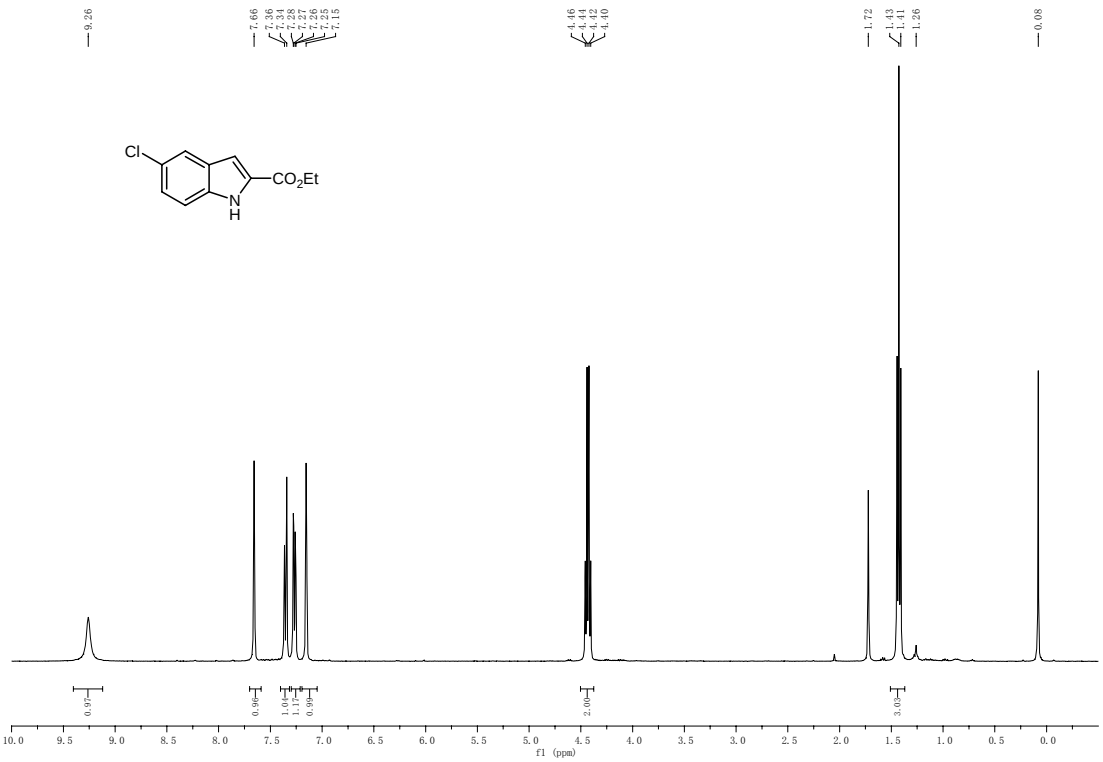
NMR Spectrum:



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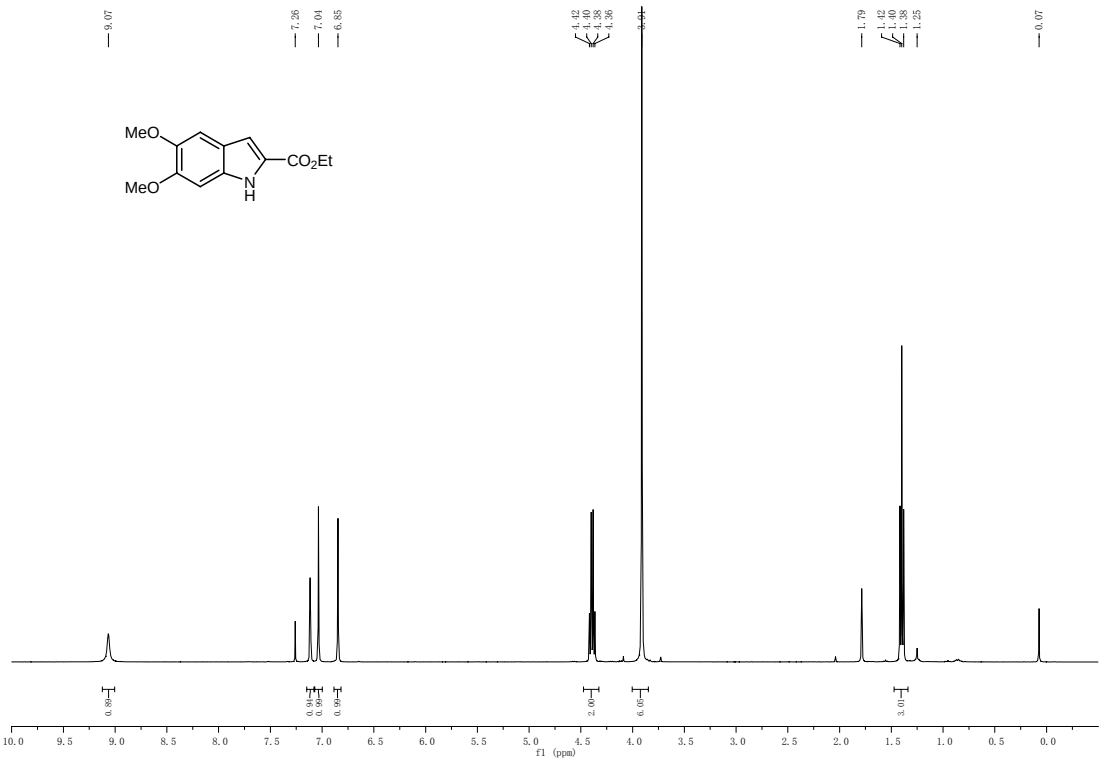
7.34
7.28
7.27
7.26
7.25
7.15
4.46
4.44
4.42
4.40
1.72
1.43
1.41
1.26
0.08
Cl
CO2Et
N
H
0.97
0.96
1.01
1.17
0.99
2.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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4.36
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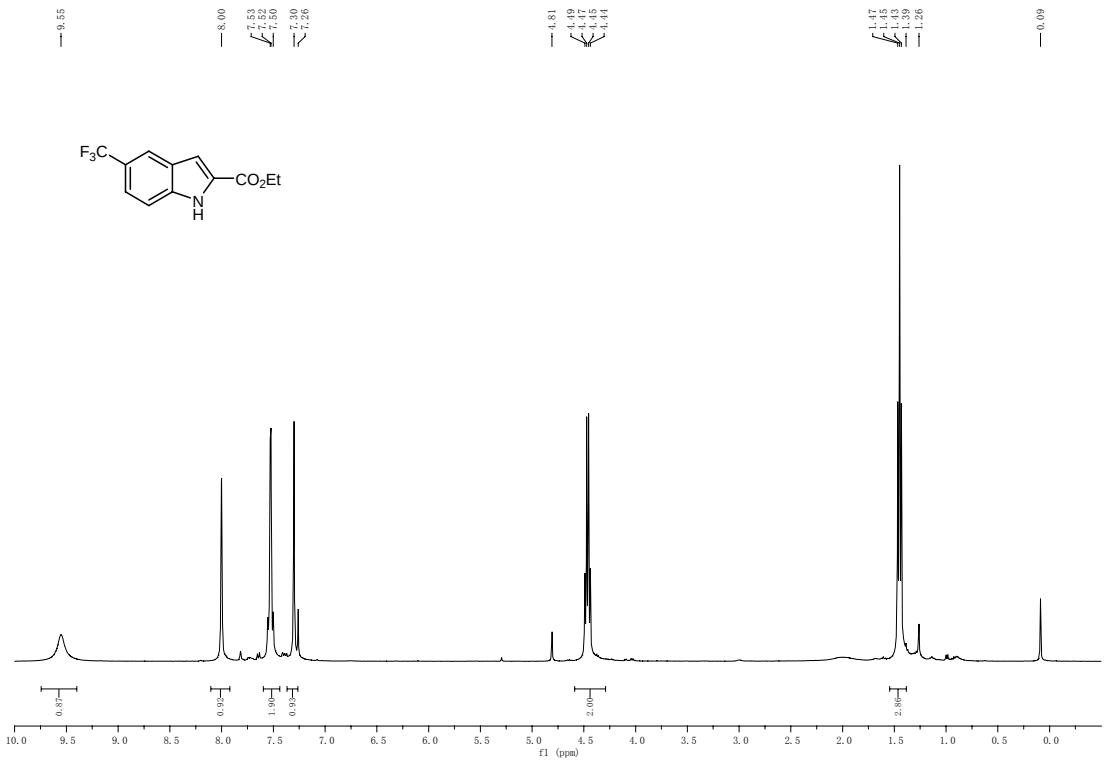
1.38
1.25
0.07
MeO
MeO
CO2Et
N
H
0.80
0.94
0.98
0.98
2.00
6.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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1.45
1.43
1.39
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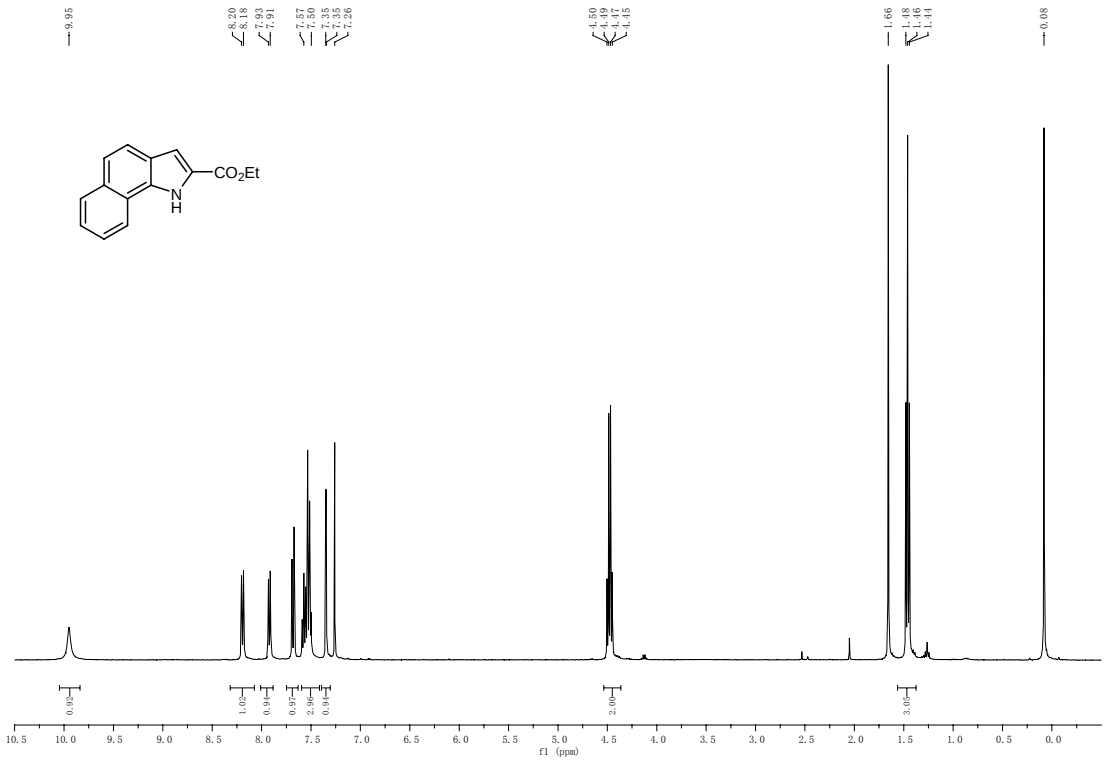
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4.47
4.45
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1.48
1.46
1.44
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H
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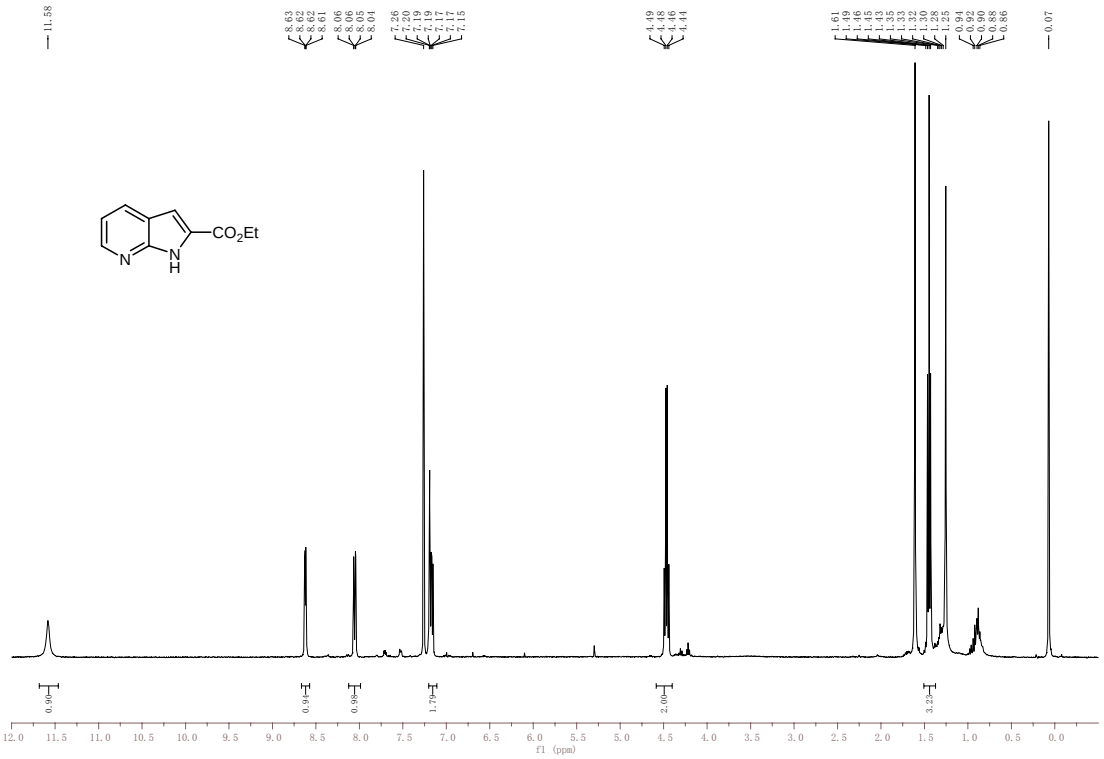
0.94
2.00
3.05
f1 (ppm)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1.49
1.46
1.45
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1.33
1.32
1.30
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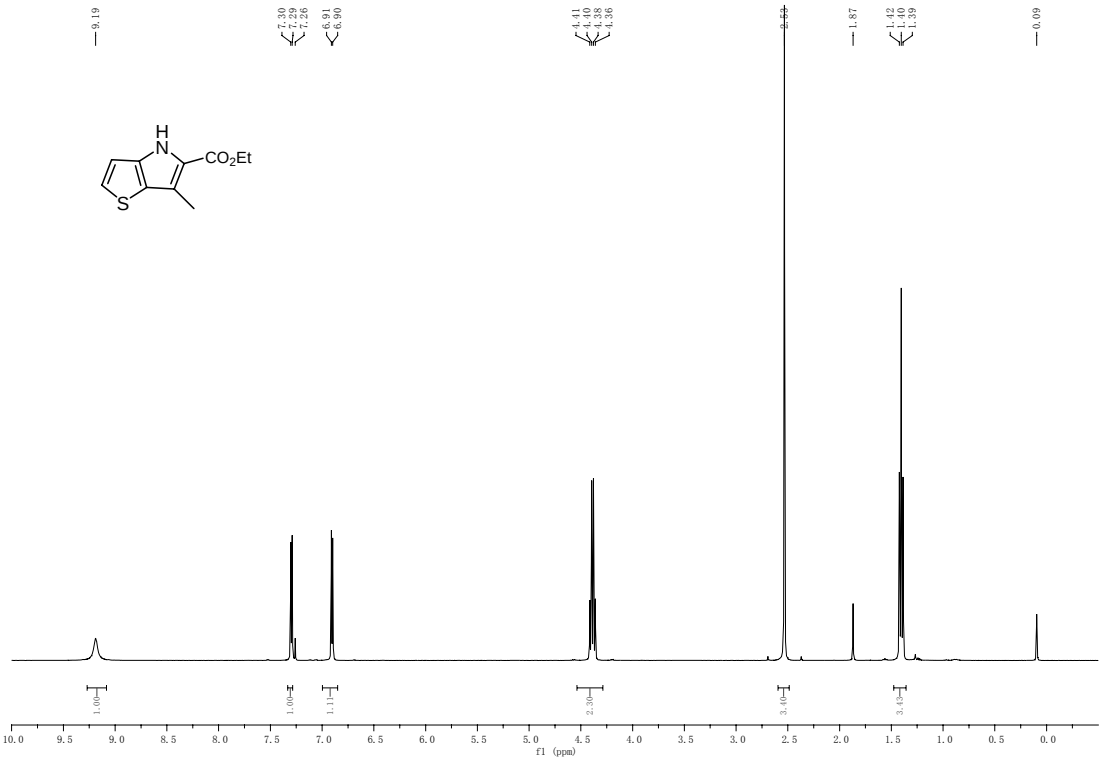
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1.40
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S
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1.00
1.11
2.30
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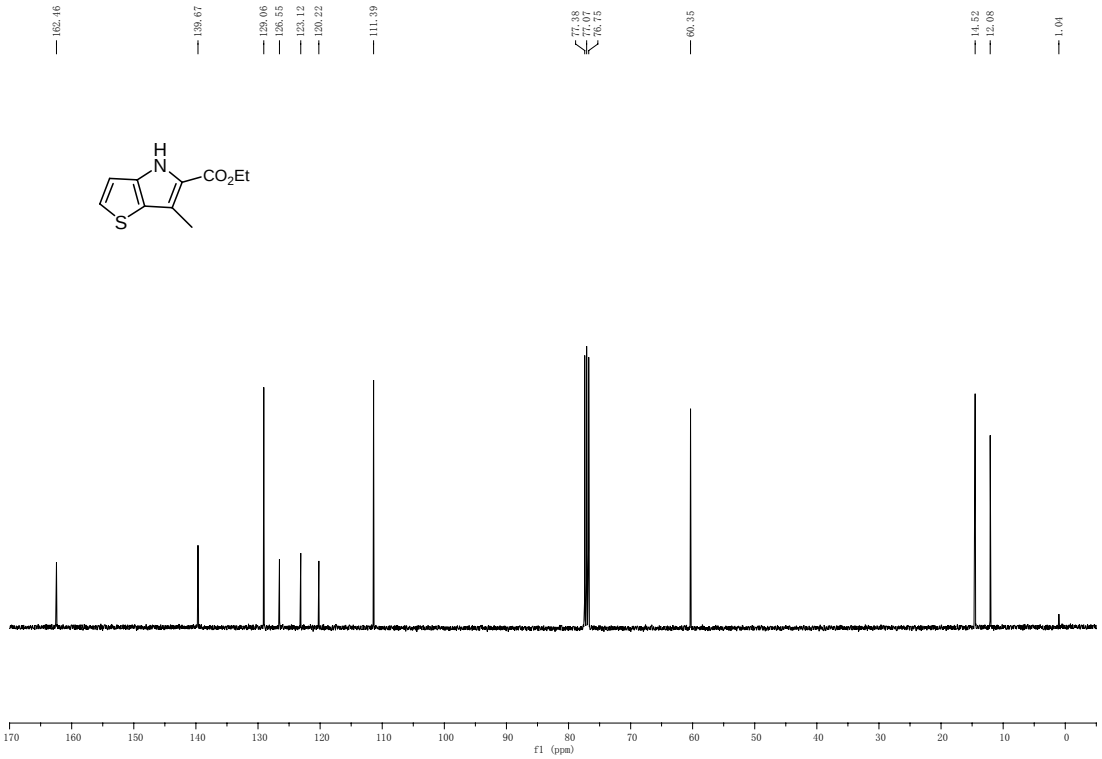
f1 (ppm)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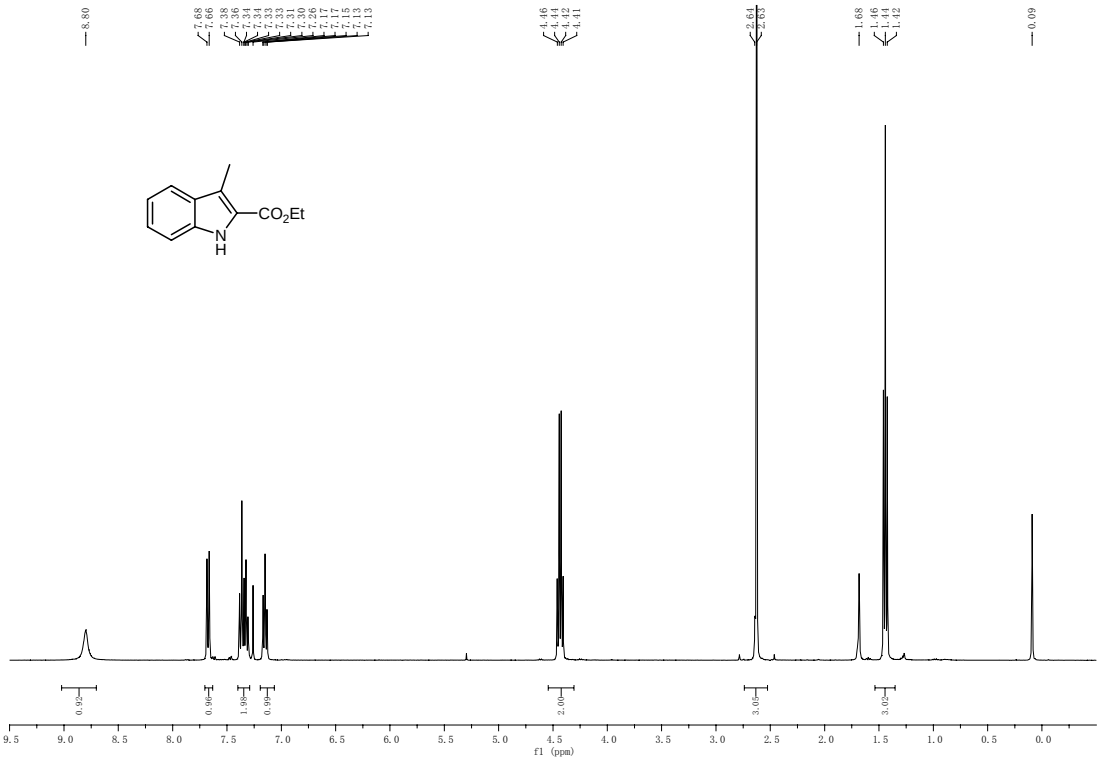
H
N
CO2Et
S
f1 (ppm)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4.44
4.42
4.41
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1.46
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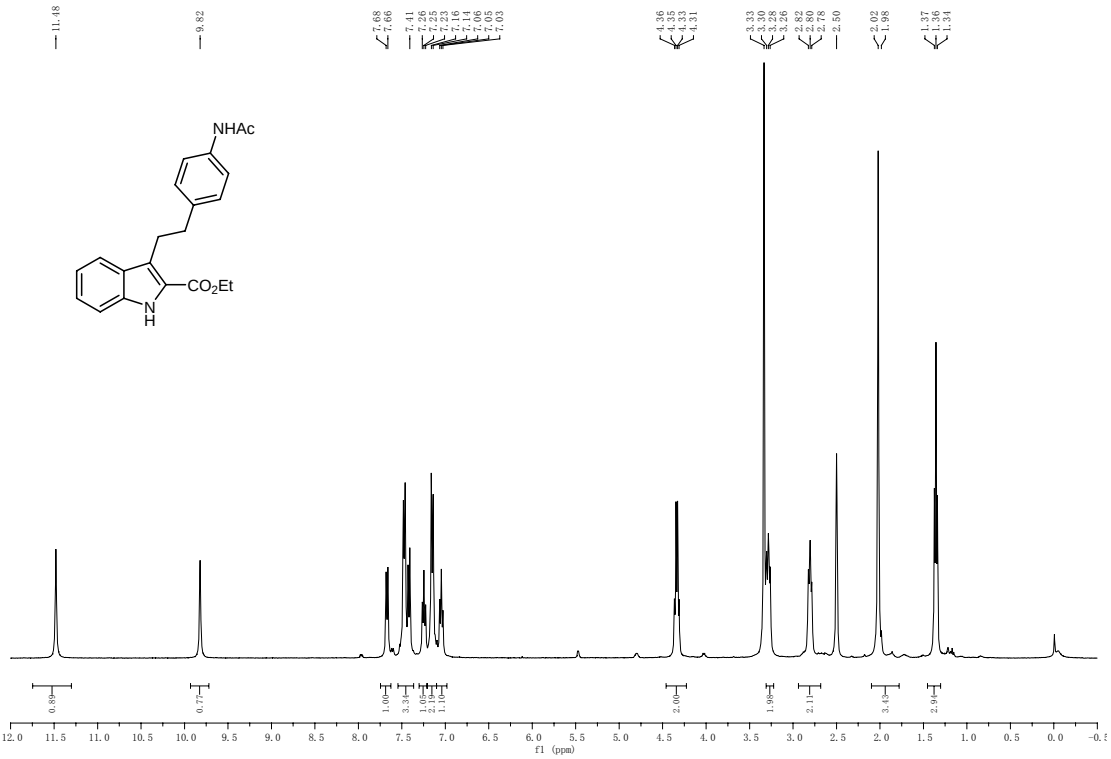
f1 (ppm)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3.28
3.26
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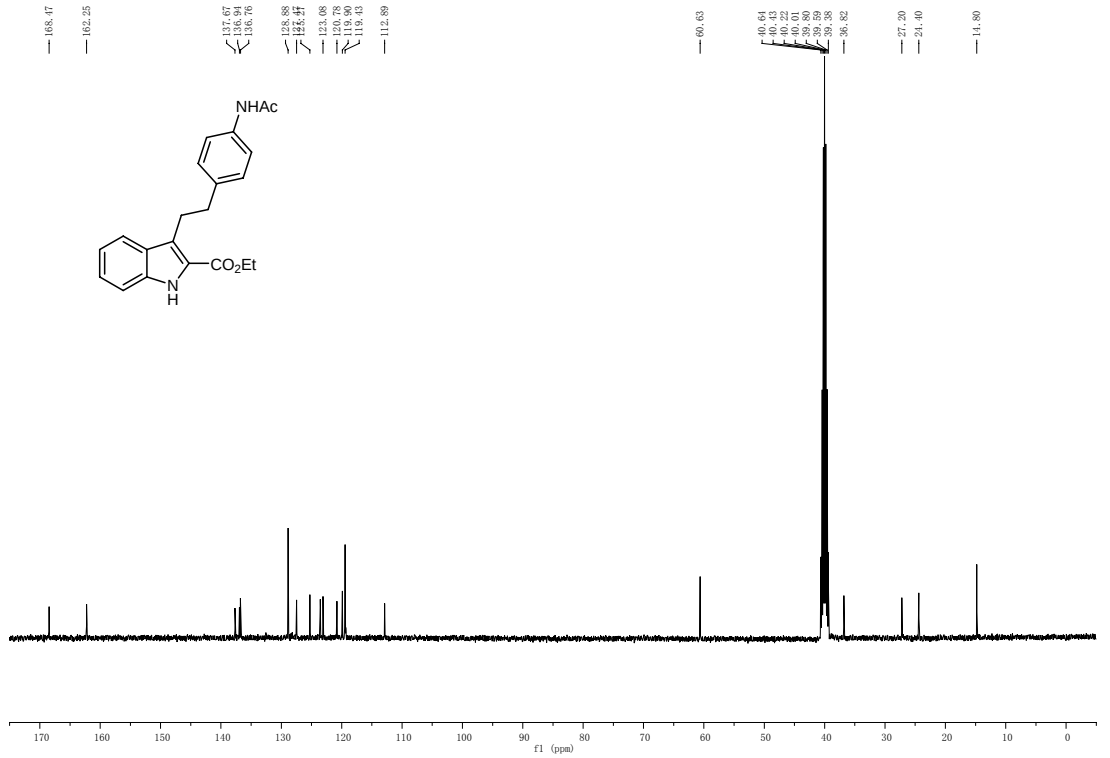
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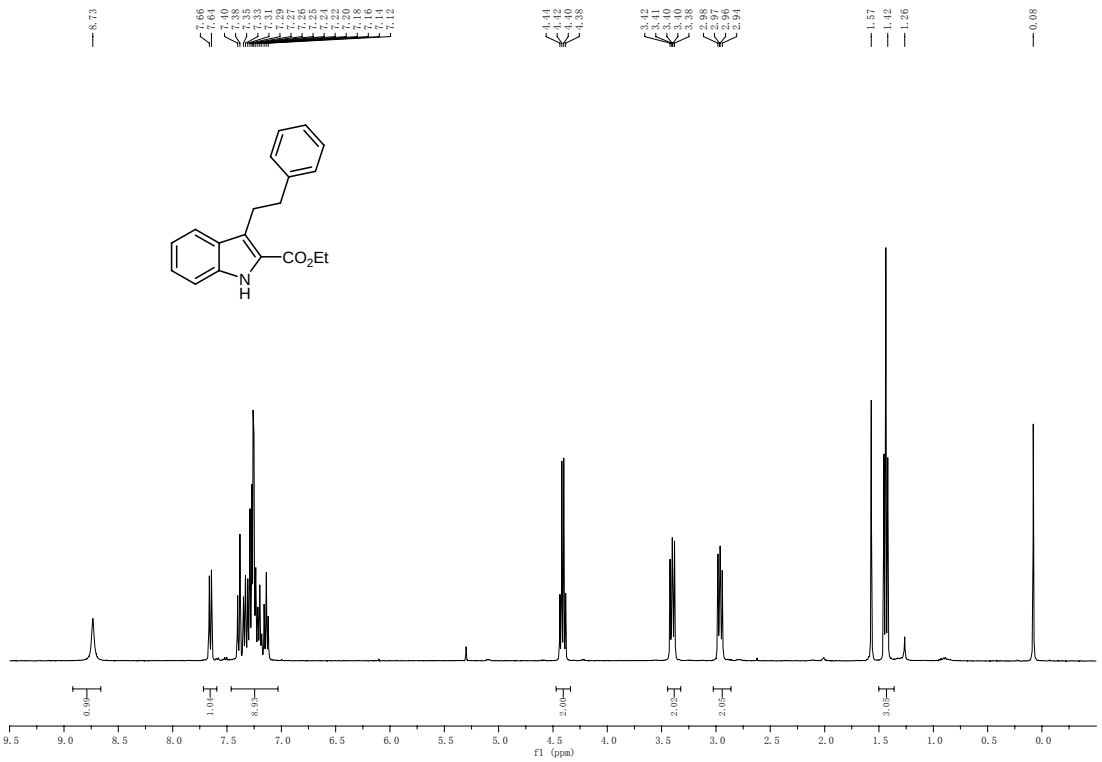
N
H
f1 (ppm)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7.12
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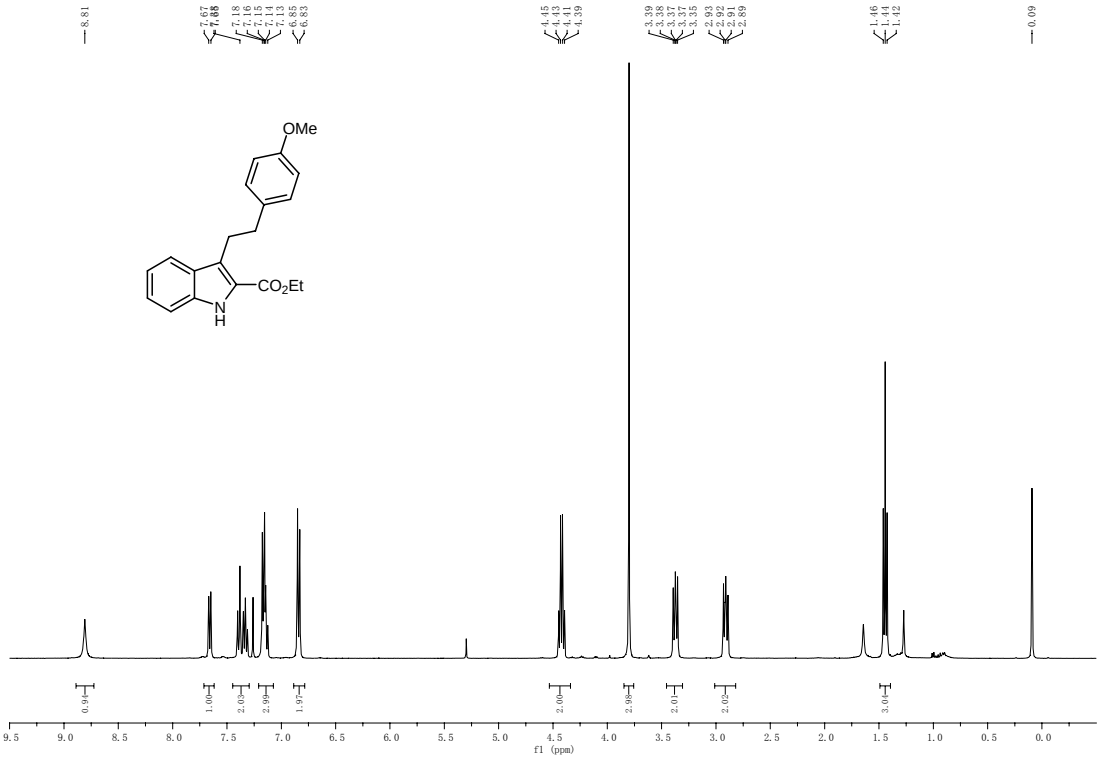
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3.37
3.35
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2.89
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1.44
1.42
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CO2Et
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2.03
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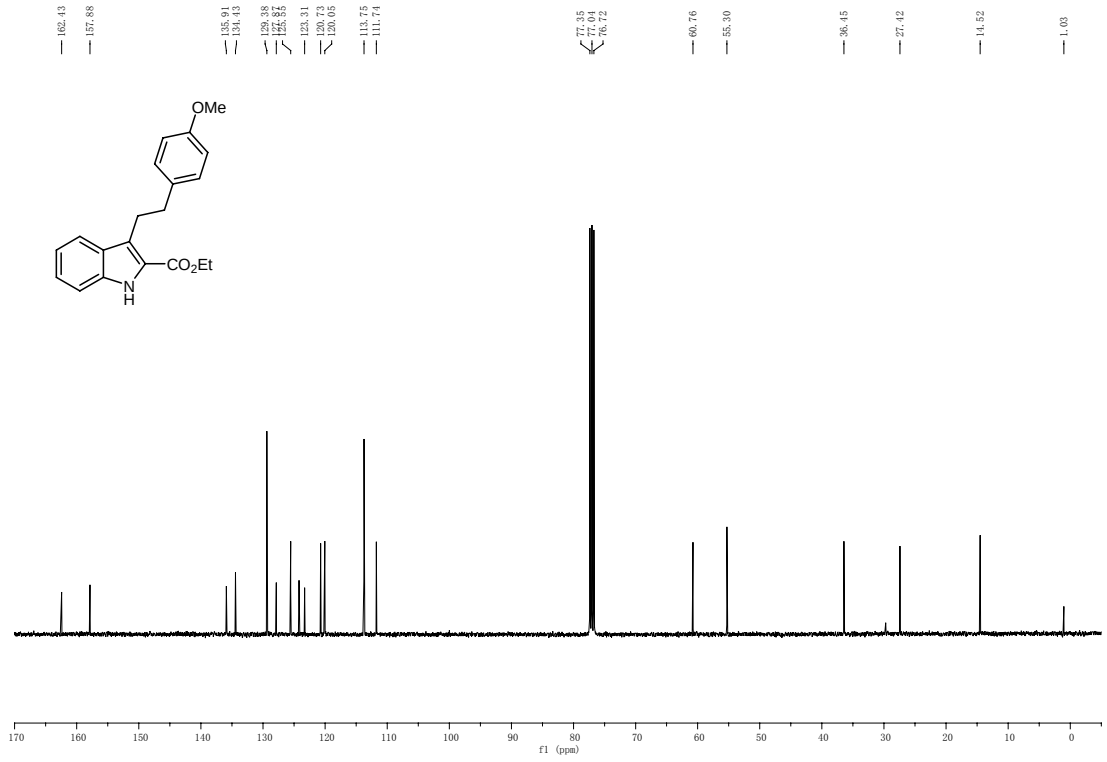
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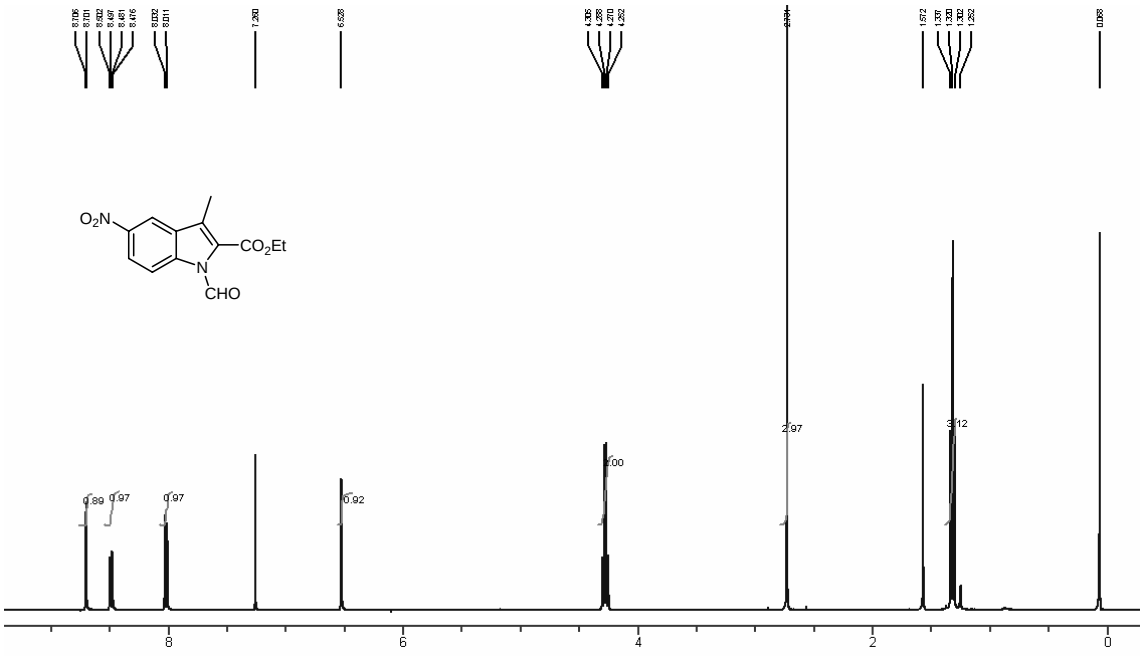
H
f1 (ppm)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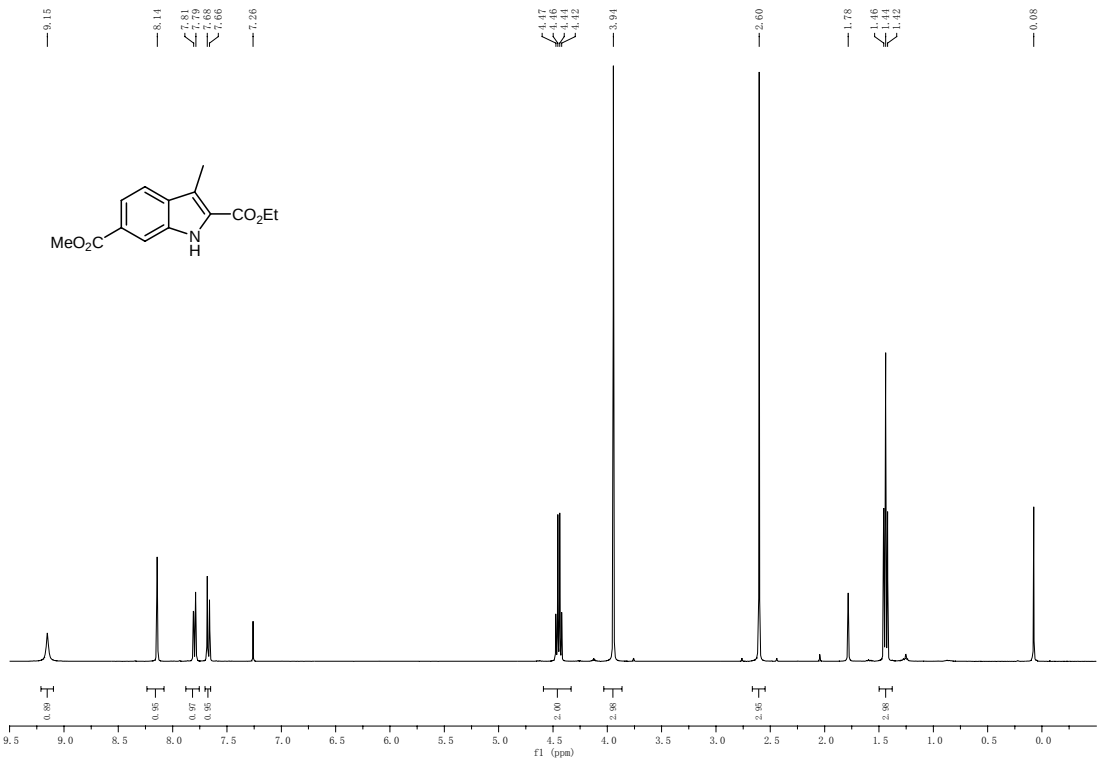
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1.46
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MeO2C
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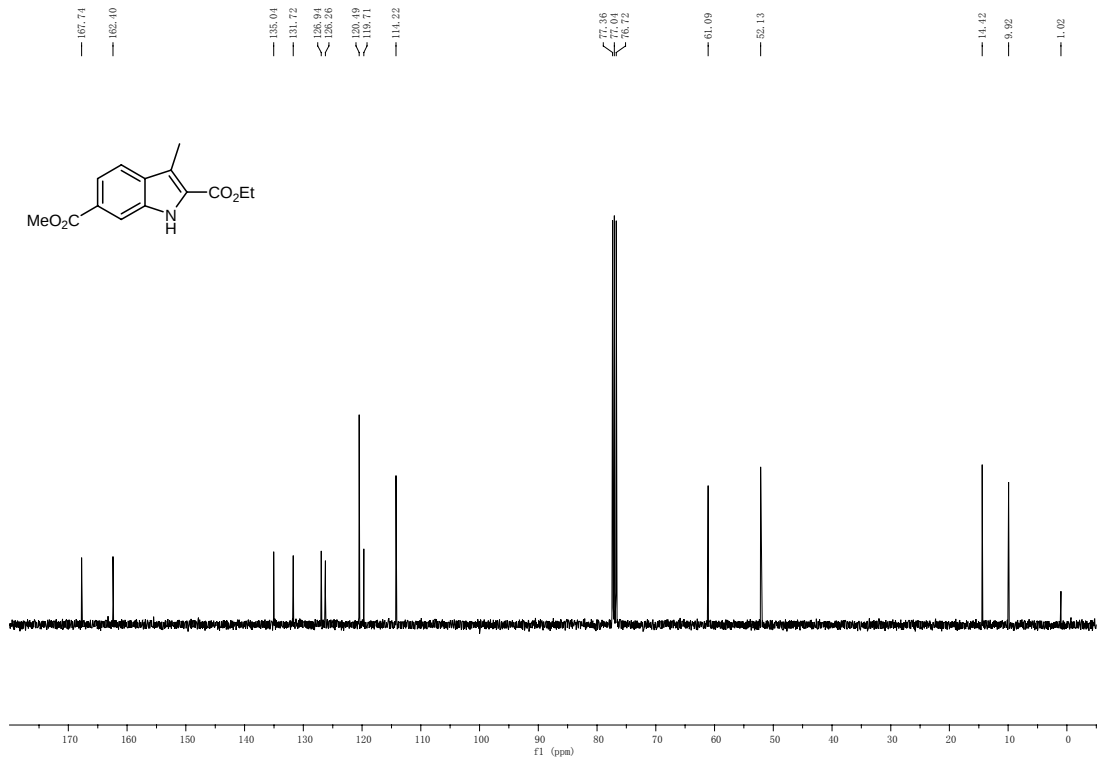
f1 (ppm)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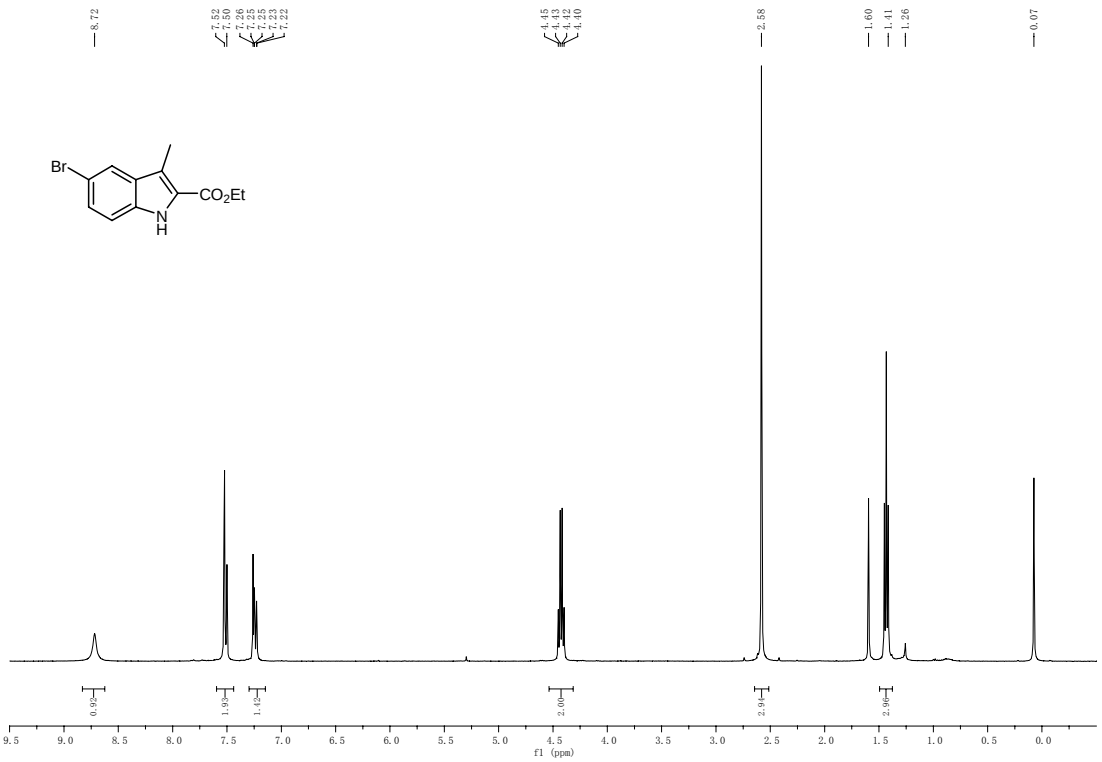
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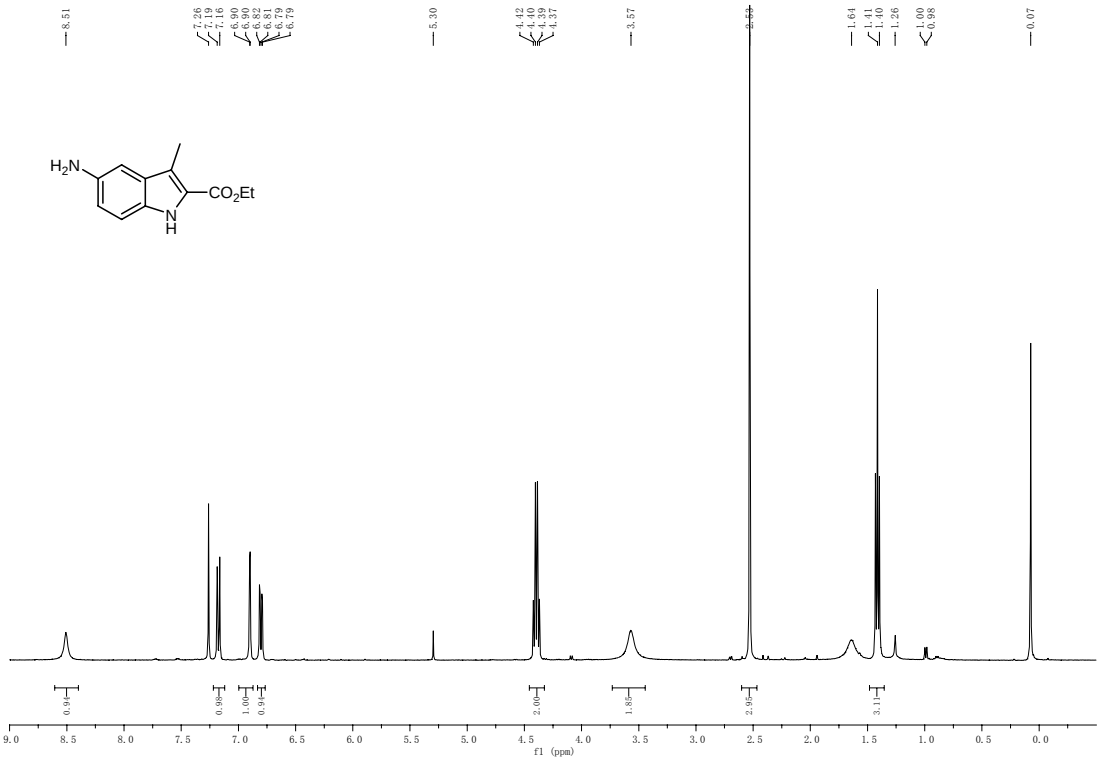
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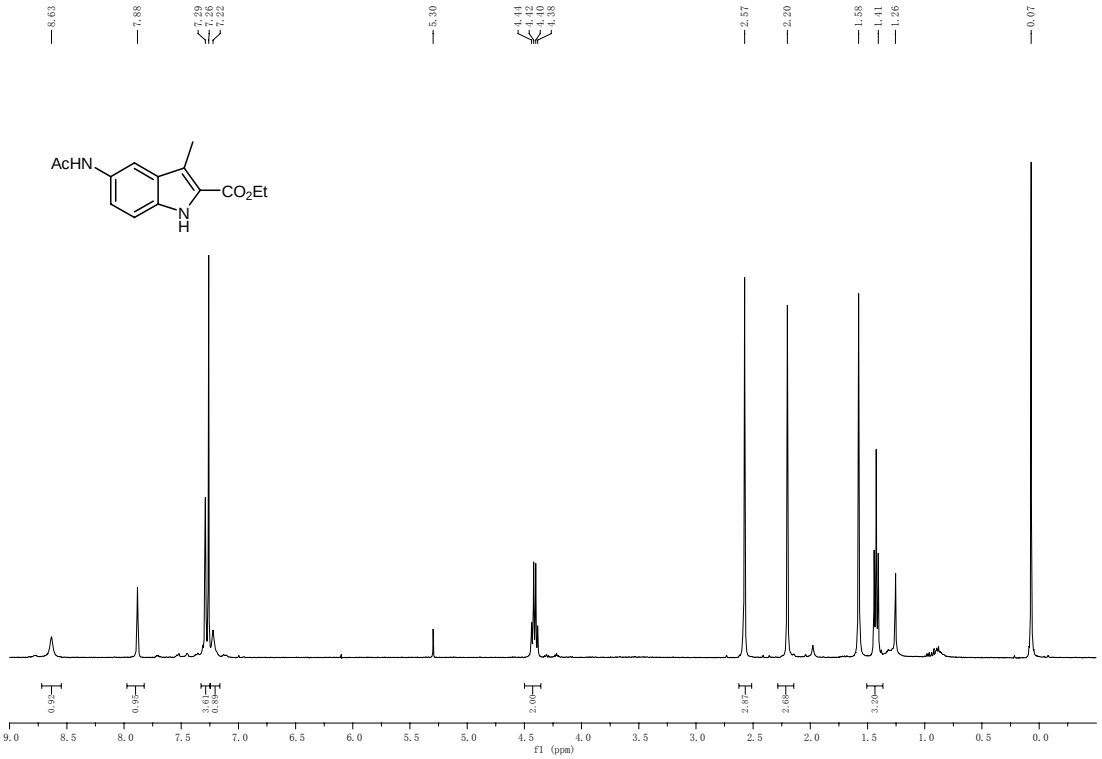
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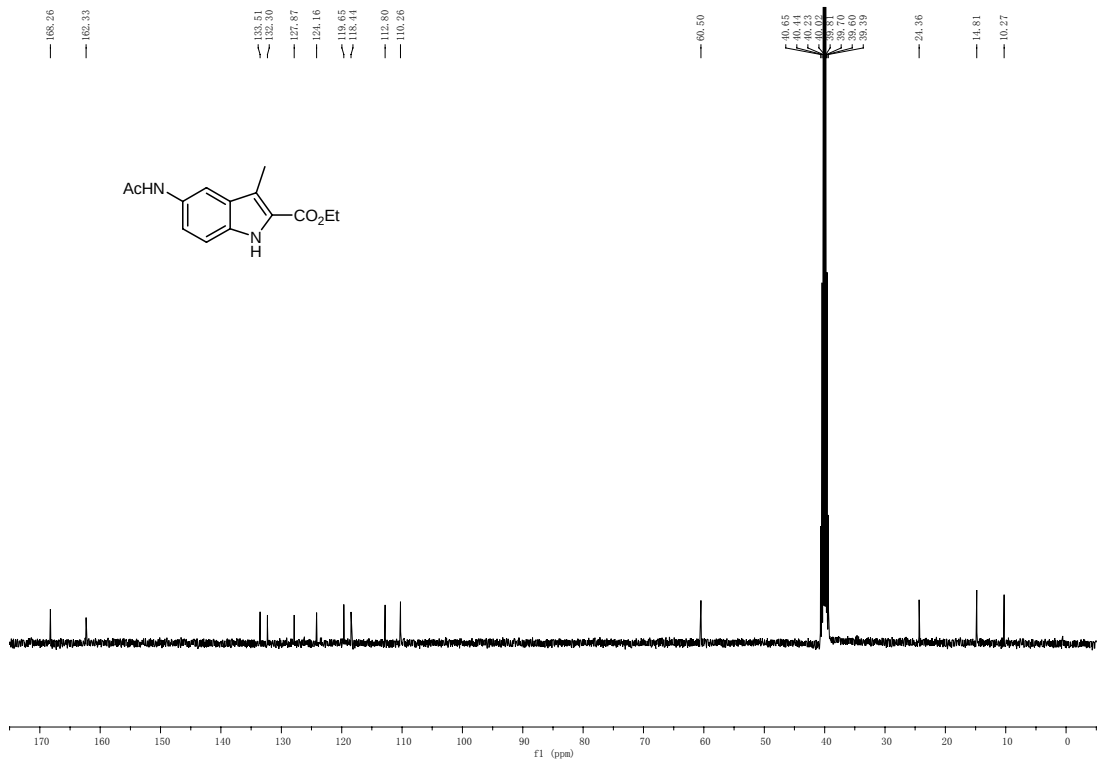
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H
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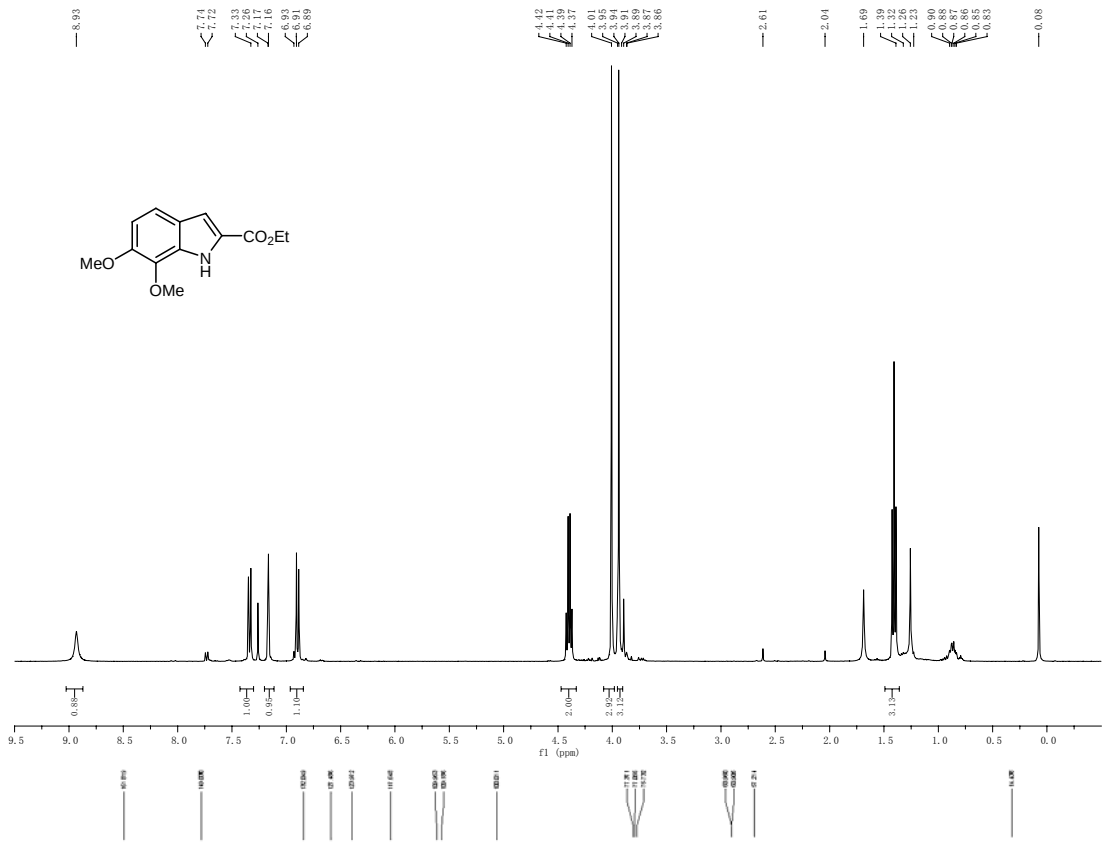
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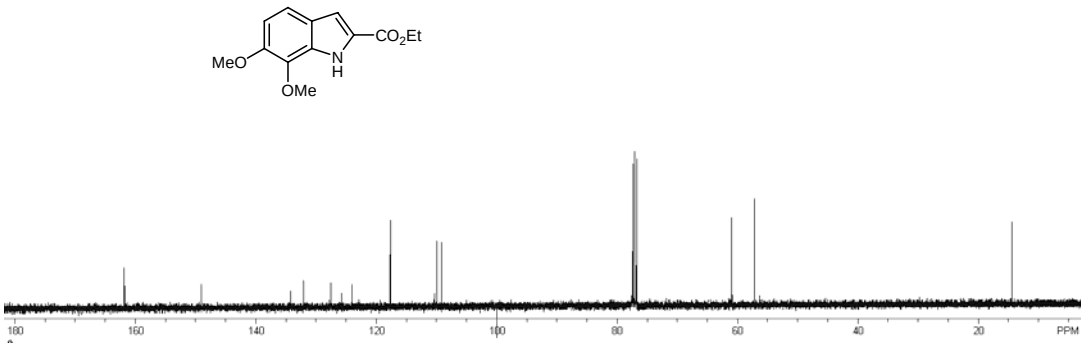
MeO
N
H
OMe
f1 (ppm)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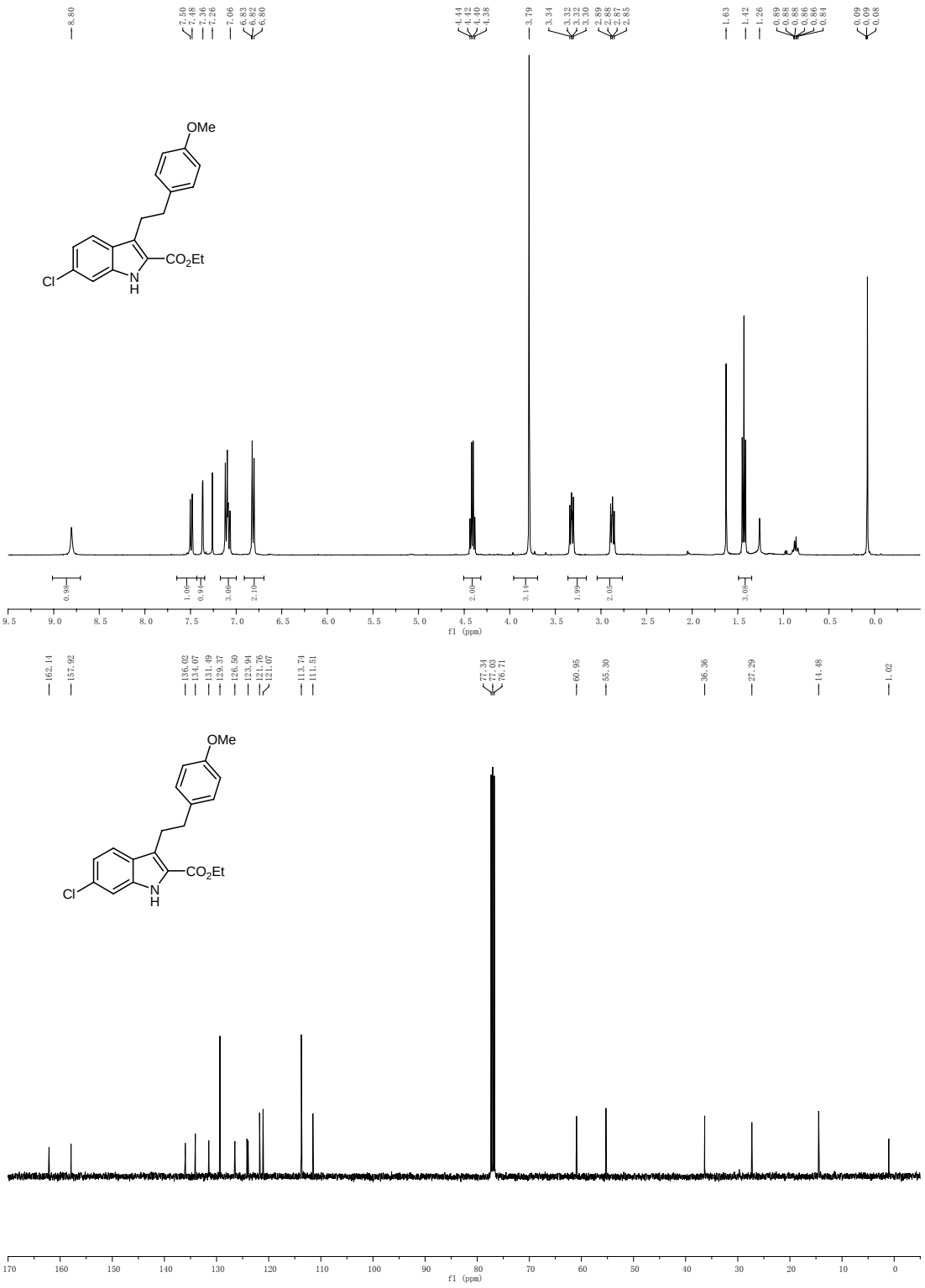
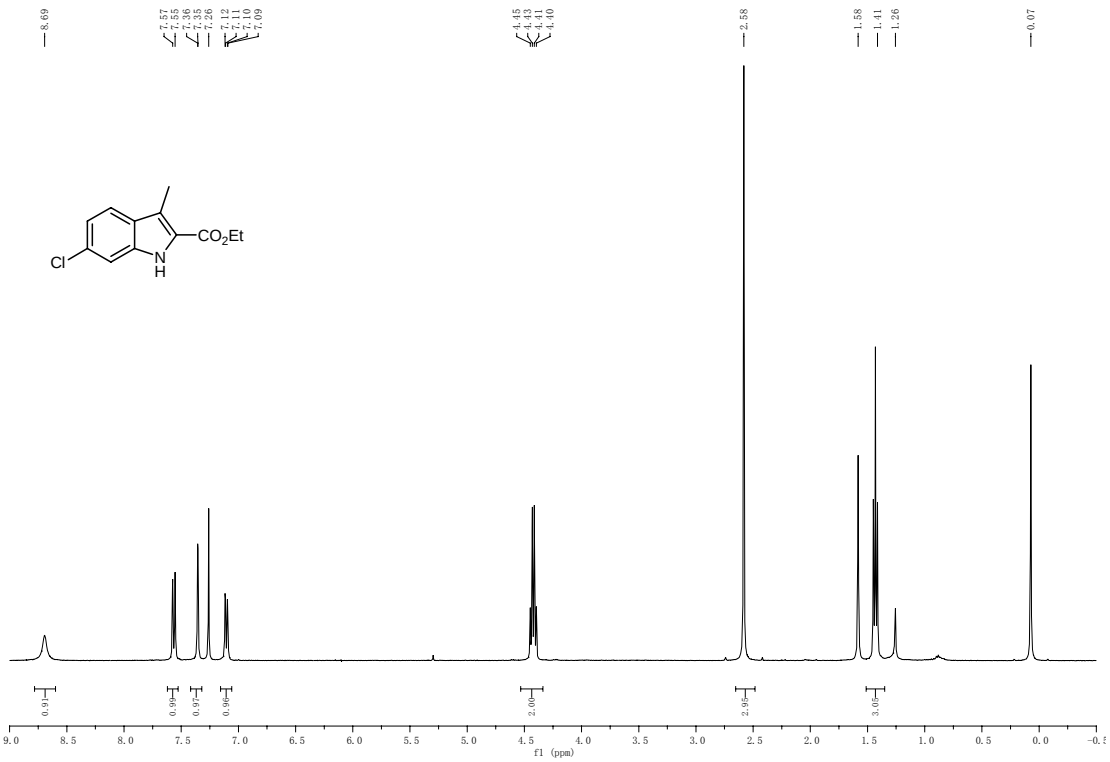
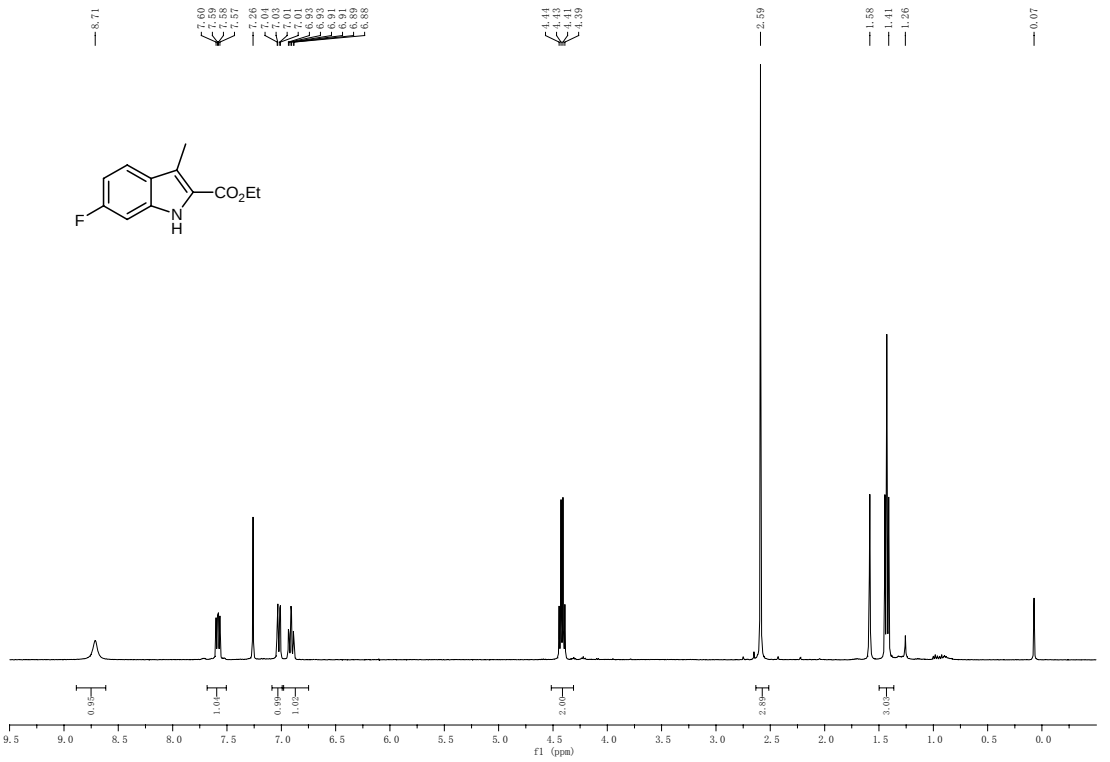
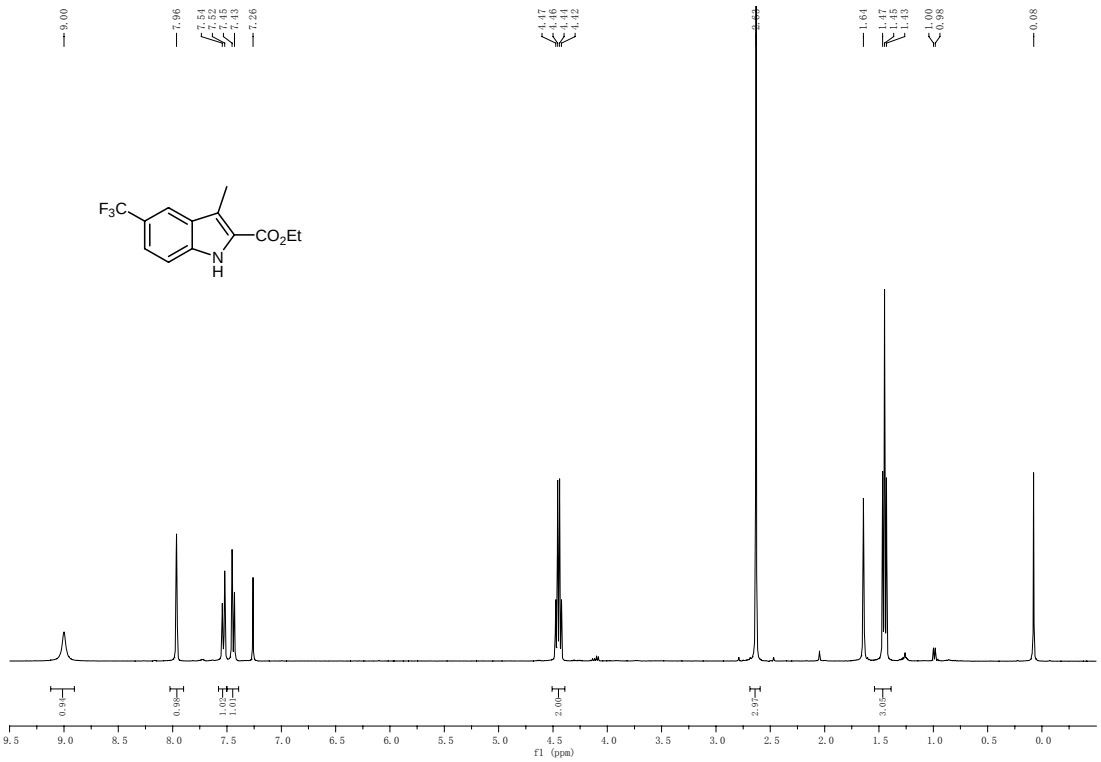
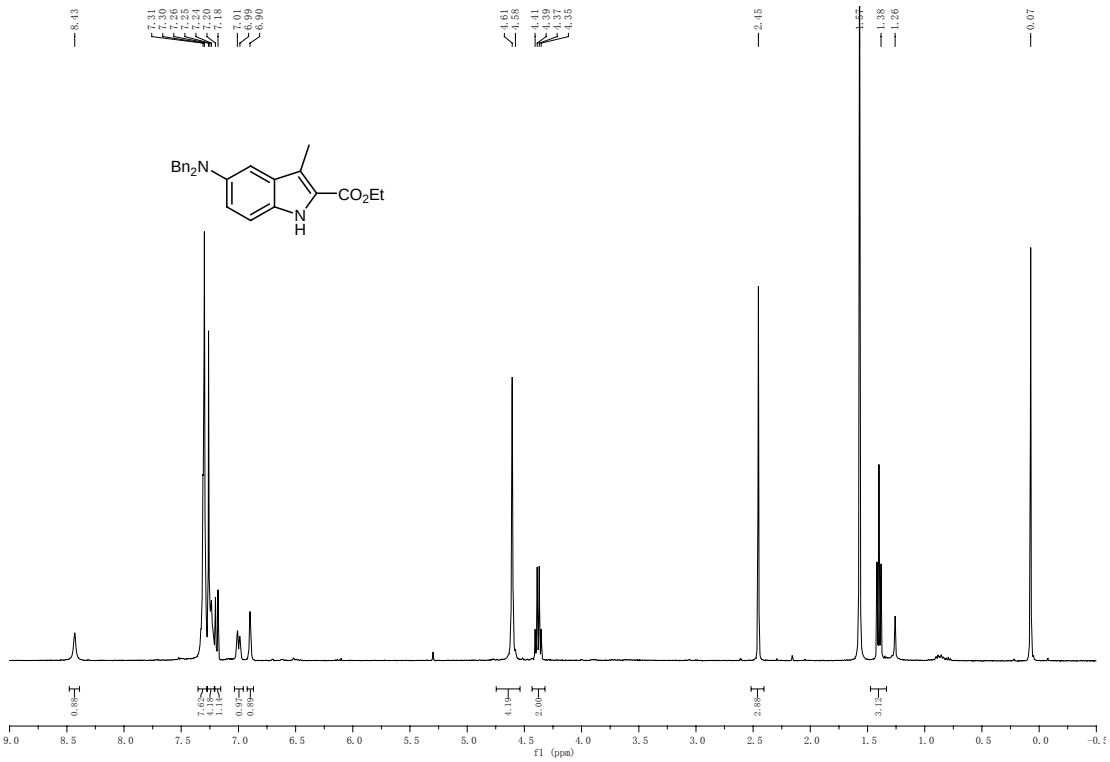
OMe
PPM

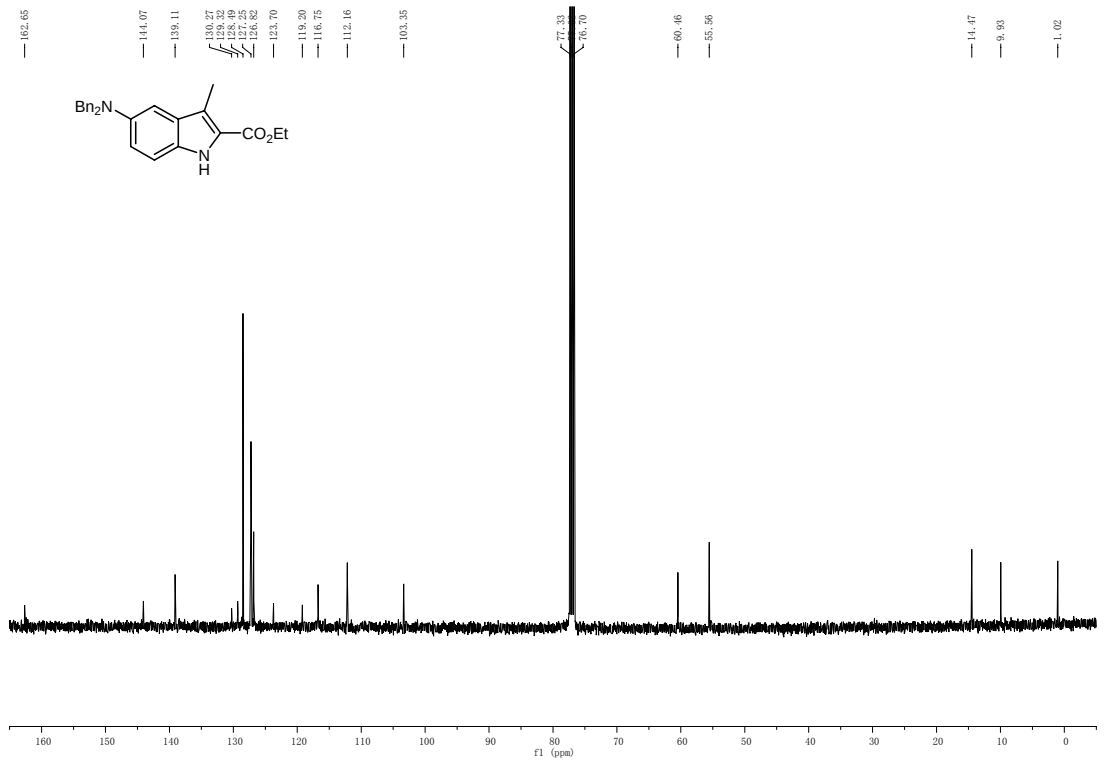

OMe
CO2Et
Cl
N
H
f1 (ppm)

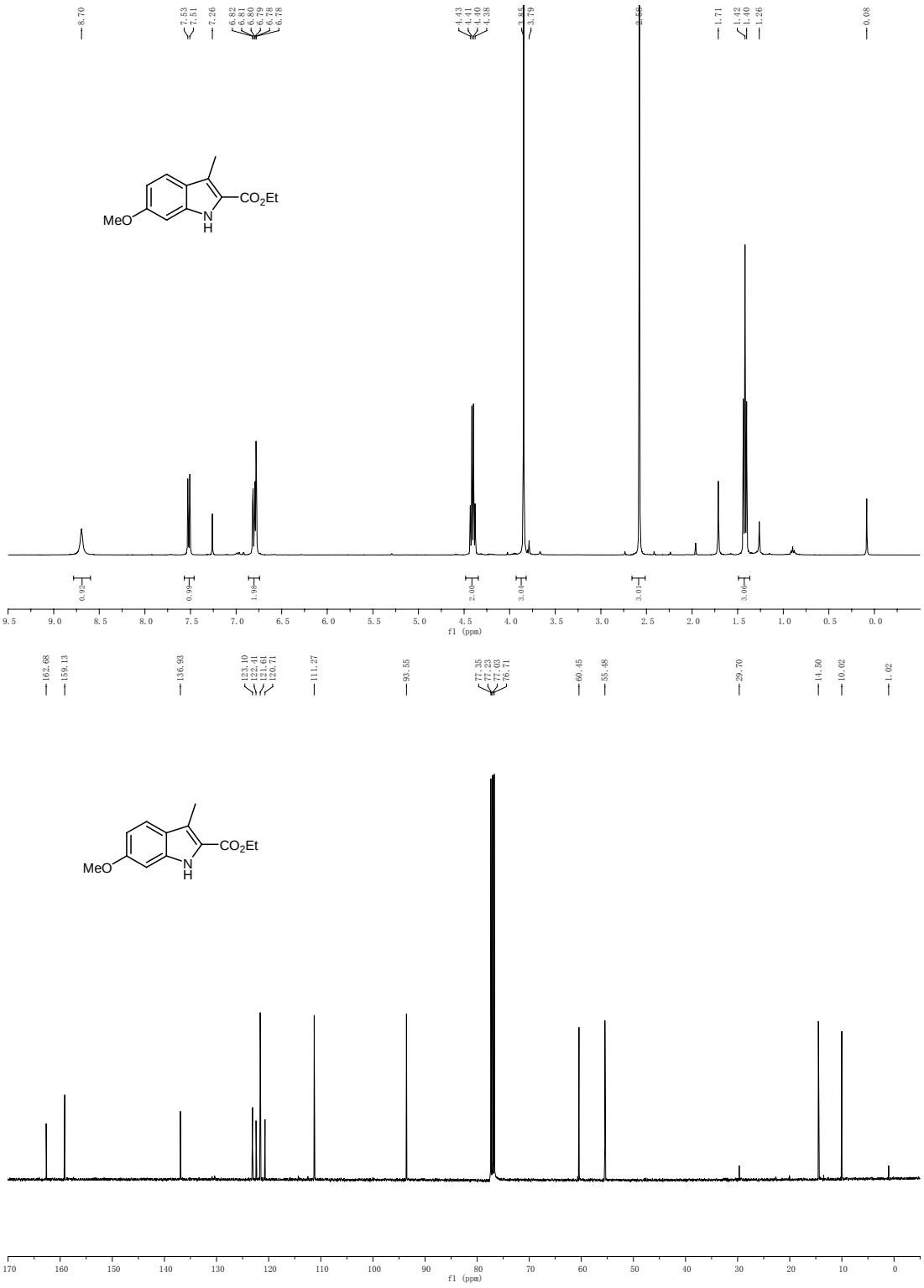

8.69
7.57
7.55
7.36
7.35
7.26
7.12
7.11
7.10
7.09
4.45
4.43
4.41
4.40
2.58
1.58
1.41
1.26
0.07
CO2Et
Cl
N
H
0.91
0.99
0.97
0.96
2.00
2.90
3.03
f1 (ppm)

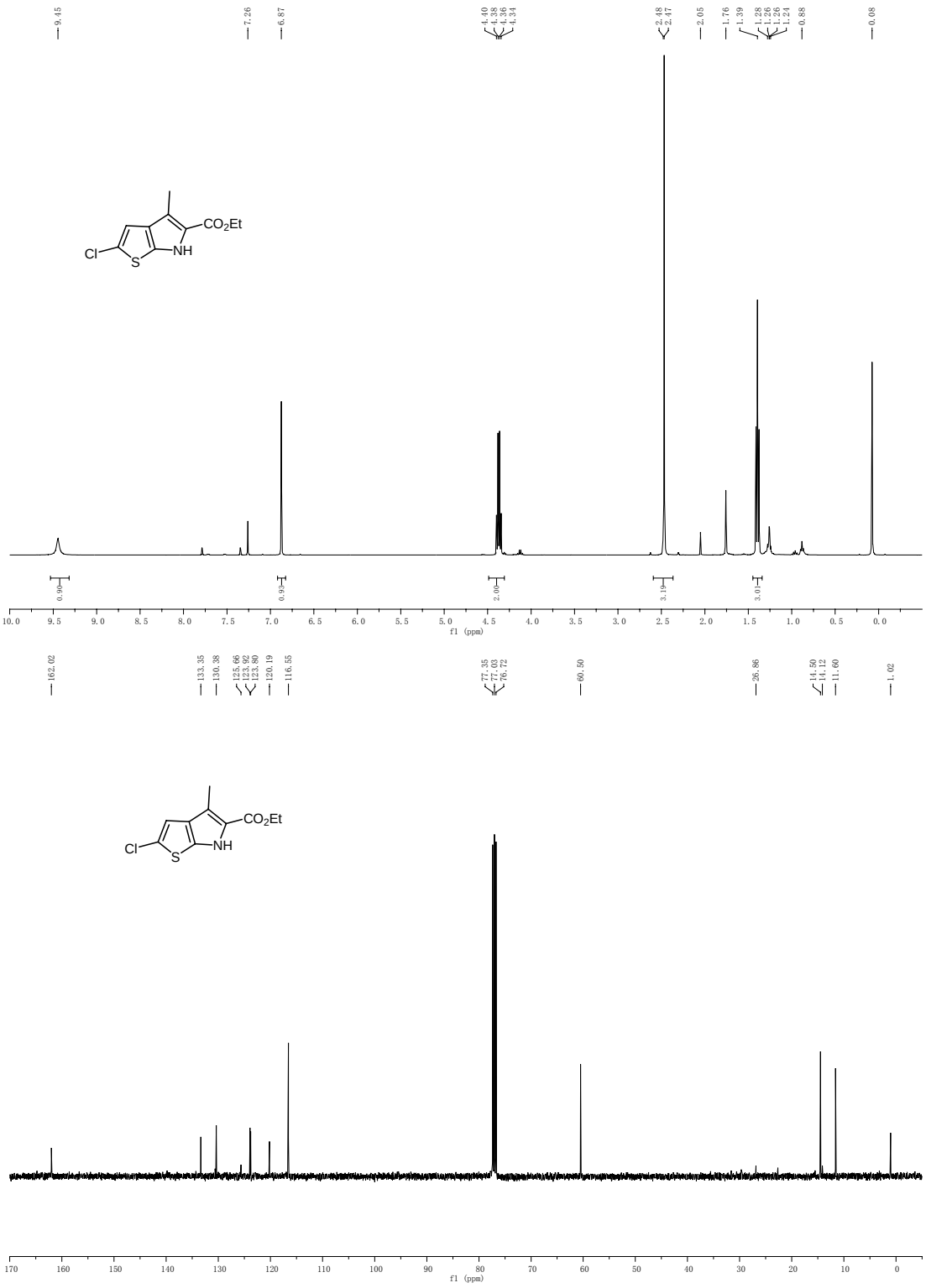

8.71
7.60
7.59
7.58
7.57
7.26
7.04
7.03
7.01
7.01
6.93
6.93
6.91
6.91
6.89
6.88
4.44
4.43
4.41
4.39
2.59
1.58
1.41
1.26
0.07
CO2Et
F
N
H
0.95
1.04
0.99
1.02
2.00
2.89
3.03
f1 (ppm)


9.00
7.96
7.54
7.52
7.45
7.43
7.26
4.47
4.46
4.44
4.42
2.69
1.64
1.47
1.45
1.43
1.00
0.98
0.08
F3C
CO2Et
N
H
0.94
0.98
1.00
1.07
2.00
2.97
3.00
f1 (ppm)


8.43
7.31
7.30
7.26
7.25
7.24
7.20
7.18
7.01
6.99
6.90
4.61
4.58
4.41
4.39
4.37
4.35
2.45
1.57
1.38
1.26
0.07
Bn2N
CO2Et
N
H
f1 (ppm)


162.65
144.07
139.11
130.27
129.32
128.49
127.25
126.82
123.70
119.20
116.75
112.16
103.35
77.33
76.70
60.46
55.56
14.47
9.93
1.02
Bn2N
CO2Et
N
H
f1 (ppm)


8.70
7.53
7.51
7.26
6.82
6.81
6.80
6.79
6.78
6.78
4.43
4.41
4.40
4.38
3.85
3.79
2.65
1.71
1.42
1.40
1.26
0.08
CO2Et
MeO
N
H
0.92
0.99
1.98
2.00
3.01
3.01
3.00
f1 (ppm)
162.68
159.13
136.93
123.10
122.41
121.61
120.71
111.27
93.55
77.35
77.23
77.03
76.71
60.45
55.48
29.70
14.50
10.02
1.02
f1 (ppm)


9.45
7.26
6.87
4.40
4.38
4.36
4.34
2.48
2.47
2.05
1.76
1.39
1.28
1.26
1.26
1.24
0.88
0.08
CO2Et
Cl
S
NH
0.90
0.99
2.00
3.19
3.01
f1 (ppm)
162.02
133.35
130.38
125.66
123.92
123.80
120.19
116.55
77.35
77.03
76.72
60.50
26.86
14.50
14.12
11.60
1.02
CO2Et
Cl
S
NH
f1 (ppm)