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Combined Experimental/theoretical Study on D-Glucosamine Promoted Regioselective Sulfenylation of Indoles Catalyzed by Copper

Xin Ge [ab], Fengli Sun [a], Xuemin Liu [a], Xinzhi Chen [b], Chao Qian [b]* and Shaodong Zhou [b]*

[a] *School of Chemical and Material Engineering, Jiangnan University, Wuxi, P.R China*

[b] *Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College ofChemical and Biological Engineering, Zhejiang University, Hangzhou, P.R China.*

* Corresponding author. Chao Qian, E-mail: qianchao@zju.edu.cn and Shaodong Zhou, E-mail: shaodong.zhou@campus.tu-berlin.de

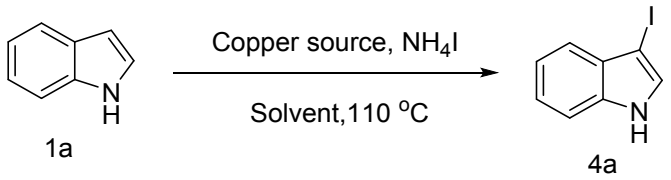
General methods

Melting points were determined on an X4-Data microscopic melting point apparatus and were uncorrected. Nuclear magnetic resonance (NMR) spectra were measured at 400 MHz (^{1}H) or at 100 MHz (^{13}C) on a Bruker Avance DRX-400 spectrometer. All reactions were monitored by analytical thin-layer chromatography (TLC) from Merck with detection by UV. The products were purified by column chromatography through silica gel (300-400 mesh). All reagents and solvents were general reagent grade unless otherwise stated.

General procedure of $Cu(OAc)_2$/D-Glucosamine catalyzed regioselective sulfenylation of indoles with sodium benzenesulfinate.

To a stirred solution of DMSO (5 ml) were added $Cu(OAc)_2$ (0.1 mmol, 20 mg), indole (1.0 mmol), sodium benzenesulfinate (1.2 mmol), NH_4I (3 mmol, 435 mg) and D-Glucosamine (0.1 mmol) were added to the solution, subsequently the mixture was heated to 110 ^{o}C under air and stirred for 6 h. When the reaction was finished, the mixture was cooled and partitioned by adding the ethyl acetate (20 ml) and water (20 ml). Then, the organic phase was separated and the aqueous phase was extracted with ethyl acetate (20 ml) twice. The combined organic phases were washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuo. Then the crude product was purified by column chromatography through silica gel, eluting with ethyl acetate/petroleum ether solvent mixture, to give the pure product.

Table S1. Optimization of *C*3-iodization of indoles[a]



1a 4a

Entry	Copper Source	Solvent	Yield (%) [b]
1	$Cu(OAc)_2$	DMSO	45
2	$CuSO_4 \cdot 5H_2O$	DMSO	45
3	$Cu(OAc)_2$	toluene	0
4	$Cu(OAc)_2$	hexane	0

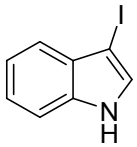
[a] Reaction conditions: 1a (1 mmol), catalyst (0.1 mmol), NH_4I (3 mmol), Solvent (5 mL), 110 ^{o}C, 6 h. [b] Isolated yield.

General procedure of the reduction of sodium benzenesulfinate to diphenyldisulfide.

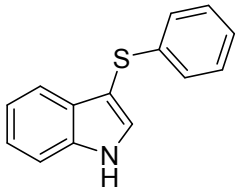
To a stirred solution of DMSO (5 ml) were added $Cu(OAc)_2$ (0.1 mmol, 20 mg), sodium benzenesulfinate (1.2 mmol), NH_4I (3 mmol, 435 mg) were added to the solution, subsequently the mixture was heated to 110 ^{o}C under air and stirred for 6 h. When the reaction was finished, the mixture was cooled and partitioned by adding the ethyl acetate (20 ml) and water (20 ml). Then, the organic

phase was separated and the aqueous phase was extracted with ethyl acetate (20 ml) twice. The combined organic phases were washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuo. Then the crude product was purified by column chromatography through silica gel, eluting with ethyl acetate/petroleum ether solvent mixture, to give the pure diphenyldisulfide (89% yield).

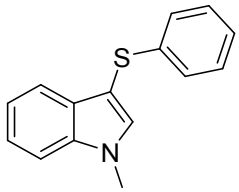
The spectral data of the products



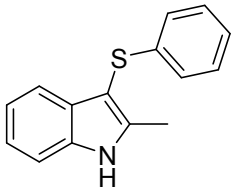
3-Iodoindole. Light yellow solid, m.p.: 72-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.50 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.39 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.31 (t, *J* = 2.4 Hz, 1H), 7.28 (s, 1H), 7.27 – 7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.63, 129.81, 128.41, 123.20, 121.02, 120.82, 111.27, 57.58. MS (EI): m/z = 243 $[M]^+$.



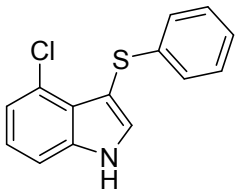
3-(Phenylthio)-1*H*-indole. White solid, m.p.: 149-150 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.40 (d, J = 2.6 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.22 - 7.14 (m, 1H), 7.13 - 7.05 (m, 3H), 7.03 (t, J = 4.2 Hz, 2H), 6.97 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.19, 135.47, 129.66, 128.07, 127.66, 124.82, 123.74, 122.01, 119.87, 118.64, 110.55, 101.78. MS (EI): m/z = 225 $[M]^+$.



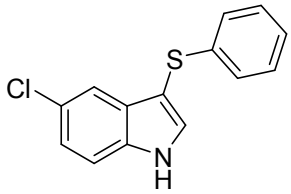
N-methyl-3-phenylthio-1*H*-indole. White solid, m.p.: 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.9 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.19 (dd, J = 14.2, 7.1 Hz, 3H), 7.14 – 7.10 (m, 2H), 7.08 (d, J = 7.1 Hz, 1H), 3.88 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.68, 137.56, 135.05, 129.85, 128.65, 125.74, 124.67, 122.57, 120.50, 119.76, 109.71, 100.57, 33.15. MS (EI): m/z = 239 $[M]^+$.



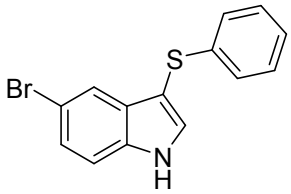
2-Methyl-3-(phenylthio)-1*H*-indole. White solid, m.p.: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.08 – 7.03 (m, 3H), 6.94-6.99 (m, 3H), 2.44 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.68, 137.56, 135.05, 129.85, 128.65, 125.74, 124.67, 122.57, 120.50, 119.76, 109.71, 100.57, 33.15. MS (EI): m/z = 239 $[M]^+$.



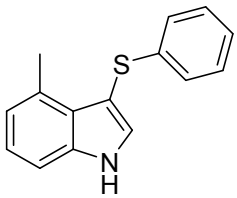
4-chloro-3-(phenylthio)-1*H*-indole. White solid, m.p.: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.38 (d, J = 2.7 Hz, 1H), 7.24 (m, 1H), 7.14 - 7.06 (m, 3H), 7.04 (m, 3H), 6.99 (dt, J = 9.0, 4.2 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.76, 136.96, 131.65, 127.64, 125.91, 124.84, 124.17, 123.73, 122.60, 121.25, 109.44, 101.87. MS (EI): m/z = 259 $[M]^+$.



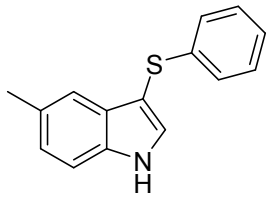
5-chloro-3-(phenylthio)-1*H*-indole. White solid, m.p.: 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 2.6 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.26 (dd, J = 10.9, 8.9 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.14 – 7.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.71, 134.84, 131.99, 130.42, 128.82, 126.95, 125.97, 125.06, 123.56, 119.17, 112.67, 102.97. MS (EI): m/z = 259 $[M]^+$.



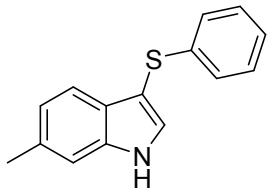
5-Bromo-3-(phenylthio)-1*H*-indole. White solid, m.p.: 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.78 (s, 1H), 7.51 (d, J = 2.6 Hz, 1H), 7.38 (dd, J = 8.6, 1.7 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 7.20 (dd, J = 9.7, 5.4 Hz, 2H), 7.15 – 7.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.70, 135.14, 131.82, 131.02, 128.83, 126.15, 125.94, 125.06, 122.29, 114.52, 113.05, 102.93. MS (EI): m/z = 303 $[M]^+$.



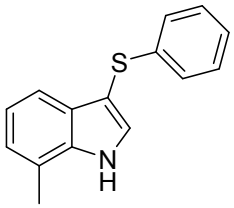
4-Methyl-3-(phenylthio)-1*H*-indole. Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.49 (dd, J = 6.4, 2.8 Hz, 1H), 7.44 (d, J = 2.7 Hz, 1H), 7.29 (d, J = 7.1 Hz, 1H), 7.19 - 7.12 (m, 2H), 7.11 - 7.06 (m, 3H), 6.92 (d, J = 7.1 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.56, 137.07, 132.11, 131.86, 128.76, 127.01, 125.25, 124.51, 123.11, 122.48, 109.49, 102.33, 18.57. MS (EI): m/z = 239 $[M]^+$.



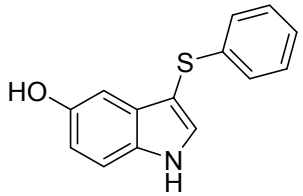
5-Methyl-3-(phenylthio)-1*H*-indole. White solid, m.p.: 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.38-7.31 (m, 2H), 7.24 (d, J = 8.3 Hz, 1H), 7.12-7.05 (m, 2H), 7.04-6.98 (m, 3H), 6.99-6.93 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.47, 133.74, 129.87, 129.38, 128.37, 127.66, 124.60, 123.68, 123.62, 118.12, 110.20, 100.91, 20.41. MS (EI): m/z = 239 $[M]^+$.



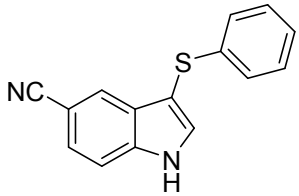
6-Methyl-3-(phenylthio)-1*H*-indole. White solid, m.p.:156-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 2.6 Hz, 1H), 7.14 (s, 1H), 7.07 (dd, J = 10.1, 4.9 Hz, 2H), 7.02 (dd, J = 5.4, 3.2 Hz, 2H), 6.99 - 6.94 (m, 1H), 6.92 (d, J = 8.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.33, 135.91, 131.98, 129.02, 127.64, 125.88, 124.73, 123.65, 121.66, 118.26, 110.48, 101.51, 20.67. MS (EI): m/z = 239 $[M]^+$.



7-Methyl-3-(phenylthio)-1*H*-indole. White solid, m.p.: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.56 – 7.46 (m, 2H), 7.25 – 7.00 (m, 7H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.35, 136.10, 130.42, 128.74, 128.71, 125.87, 124.76, 123.61, 121.09, 120.80, 117.39, 103.23, 16.46. MS (EI): m/z = 239 $[M]^+$.

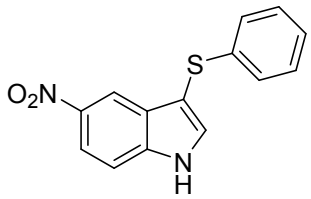


5-Hydroxy-3-(phenylthio)-1*H*-indole. Brown oil. ^{1}H NMR (400 MHz, DMSO) δ 11.41 (s, 1H), 8.89 (s, 1H), 7.64 (d, J = 2.7 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.23 - 7.15 (m, 2H), 7.08 - 6.96 (m, 3H), 6.77 – 6.69 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 152.12, 139.85, 132.99, 131.49, 130.16, 129.26, 125.59, 125.10, 113.34, 112.98, 102.65, 98.45. MS (EI): m/z = 241 $[M]^+$.

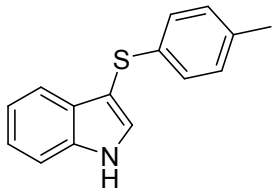


5-Cyano-3-(phenylthio)-1*H*-indole. White solid, m.p.: 183-184 °C. ^{1}H NMR (400 MHz, DMSO) δ

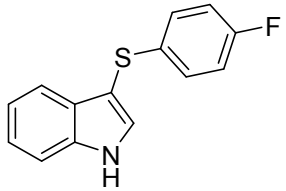
12.25 (s, 1H), 8.00 (s, 1H), 7.82 (d, J = 0.9 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.54 (dd, J = 8.5, 1.5 Hz, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.09 (s, 1H), 7.07 – 7.01 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 139.08, 138.59, 135.60, 129.47, 129.03, 126.34, 125.76, 125.47, 124.04, 120.61, 114.32, 102.90, 101.76. MS (EI): m/z = 250 $[M]^+$.



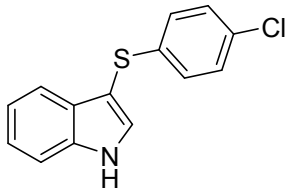
5-Nitro-3-(phenylthio)-1*H*-indole. Yellow solid, m.p.: 155-1156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.59 (d, J = 2.2 Hz, 1H), 8.18 (dd, J = 9.0, 2.2 Hz, 1H), 7.64 (d, J = 2.6 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.16 – 7.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.58, 137.91, 133.74, 128.95, 126.45, 125.53, 124.77, 124.04, 118.63, 116.85, 111.97, 106.45. MS (EI): m/z = 270 $[M]^+$.



3-(4-Tolylthio)-1H-indole. White solid, m.p.: 125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.34-7.26 (m, 1H), 7.24-7.17 (m, 1H), 7.12-7.05 (m, 2H), 7.02 (d, J = 8.1 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.51, 135.51, 134.70, 130.44, 129.51, 129.14, 126.35, 122.98, 120.84, 119.70, 111.56, 103.55, 20.86. MS (EI): m/z = 239 $[M]^+$.

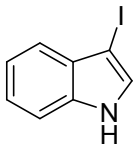


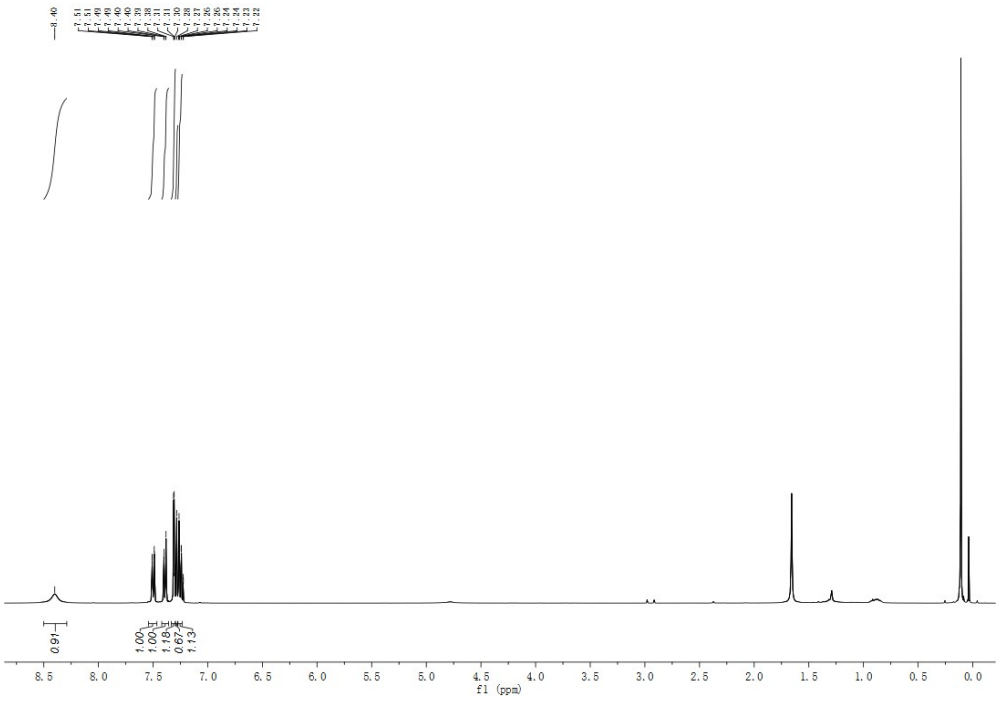
3-((4-Fluorophenyl)thio)-1H-indole. White solid, m.p.: 137-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 2.6 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.31 (m, 1H), 7.24-7.17 (m, 1H), 7.16-7.08 (m, 2H), 6.94-6.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.52, 134.05, 134.02, 130.50, 128.88, 127.95, 127.87, 123.14, 120.98, 119.53, 115.86, 115.64, 111.65, 103.42. MS (EI): m/z = 243 $[M]^+$.

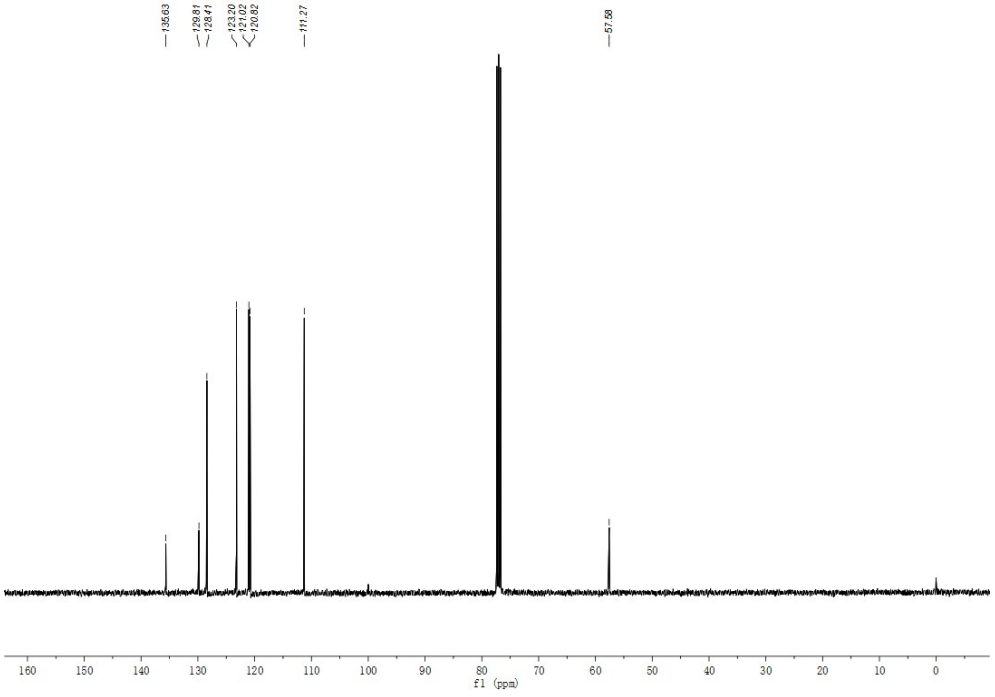


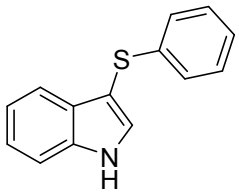
3-((4-Chlorophenyl)thio)-1H-indole. White solid, m.p.: 127-128 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.26 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.84, 136.53, 130.72, 130.56, 128.82, 128.76, 127.13, 123.22, 121.07, 119.52, 111.68, 102.46. MS (EI): m/z = 259 $[M]^+$.

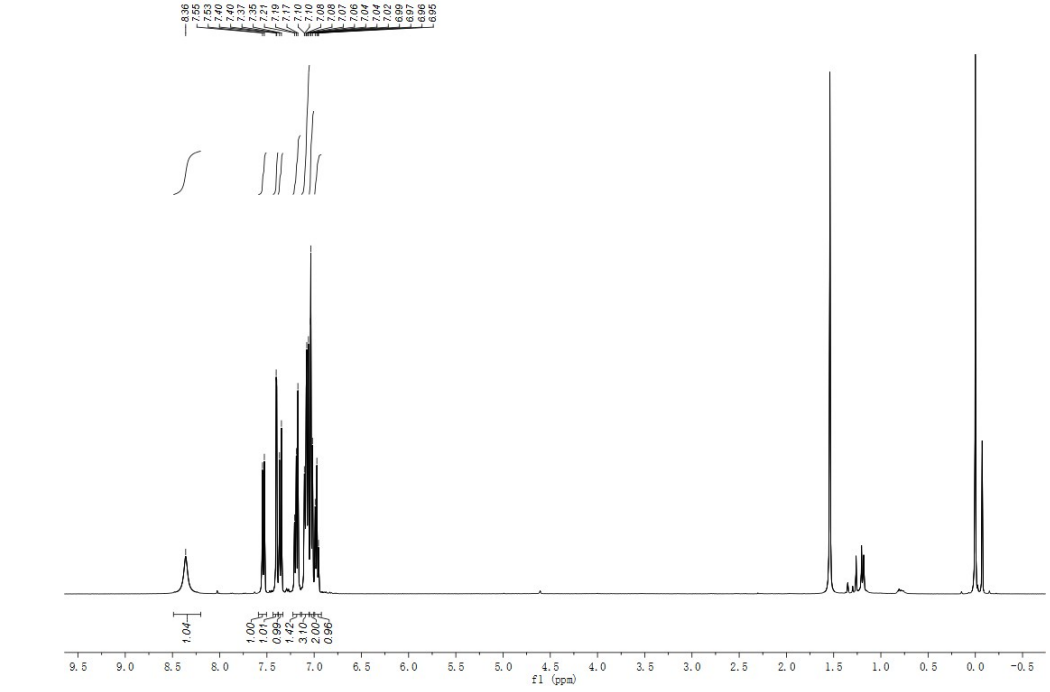
NMR Spectra of All Products








S
N
H


8.36
7.55
7.53
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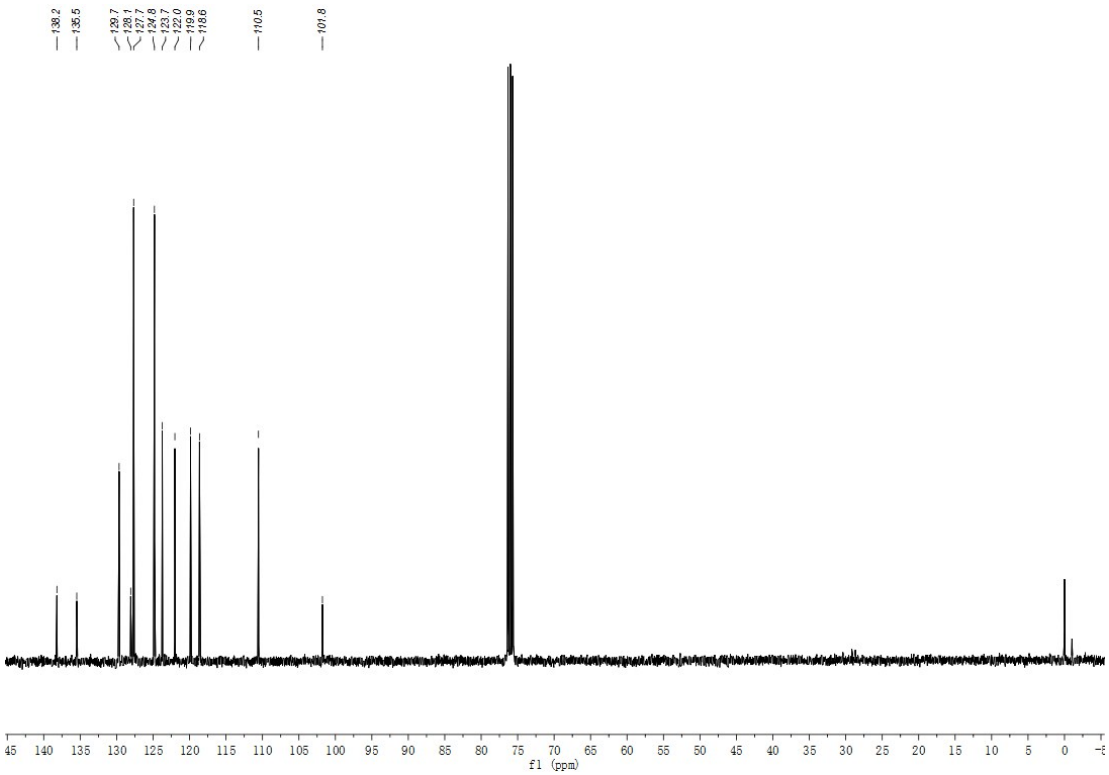
7.37
7.35
7.21
7.19
7.17
7.10
7.10
7.08
7.08
7.07
7.06
7.04
7.04
7.02
6.99
6.97
6.96
6.95
1.04
1.00
1.01
0.99
1.42
3.10
2.00
0.96
f1 (ppm)


138.2
135.5
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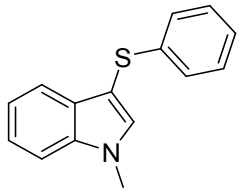
127.7
124.8
123.7
122.0
119.9
118.6
110.5
101.8
f1 (ppm)


S
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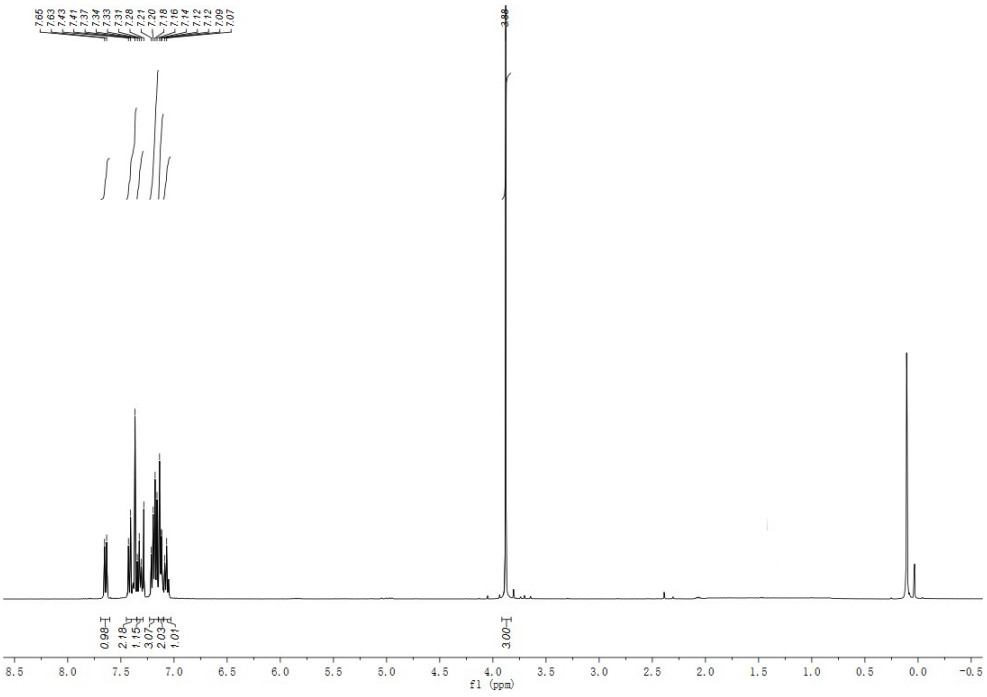
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7.31
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7.20
7.18
7.16
7.14
7.13
7.12
7.09
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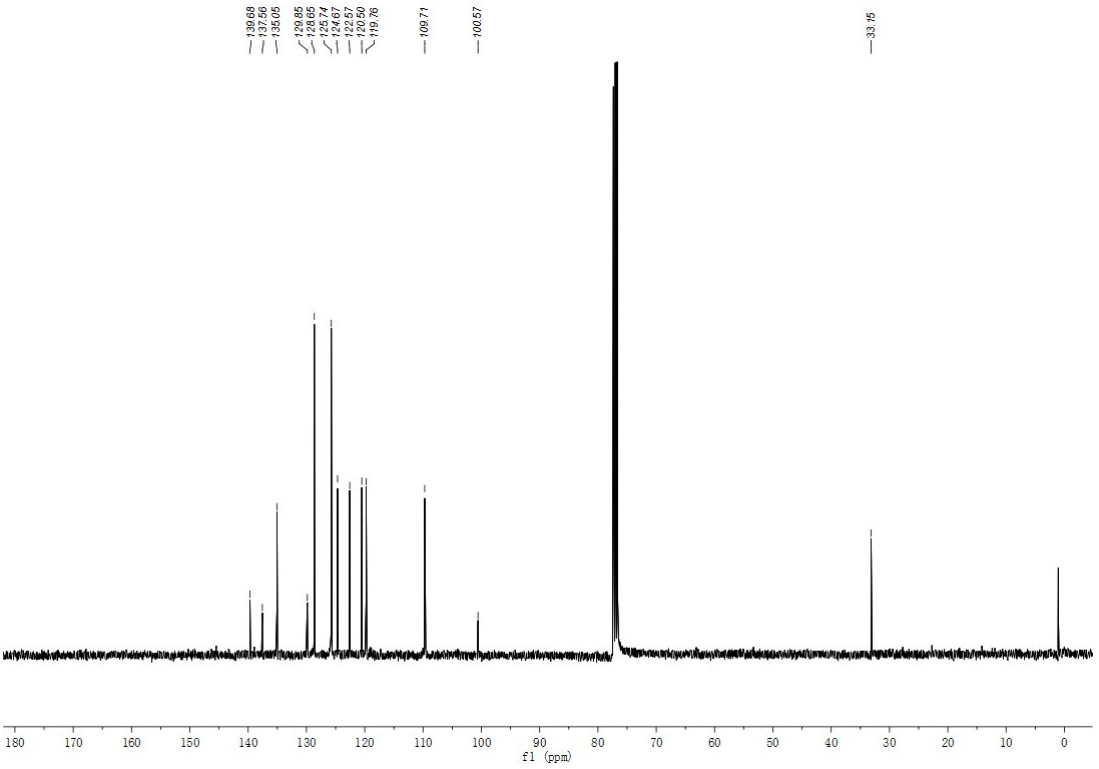
0.98
2.18
1.15
3.07
2.03
1.01
3.00
f1 (ppm)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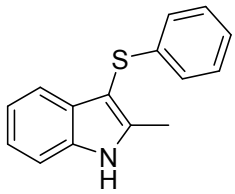
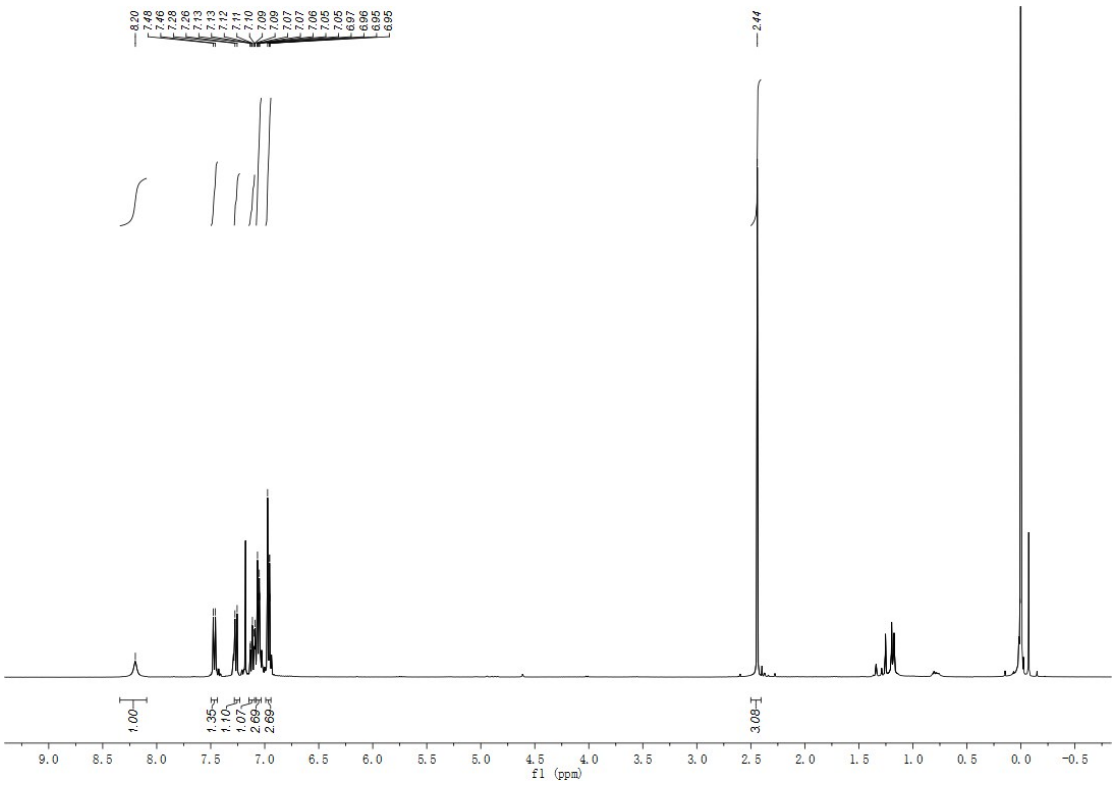
109.71
100.57
33.15
f1 (ppm)


S
N
H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7.11
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7.09
7.07
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7.06
7.05
7.05
6.97
6.96
6.95
6.95
2.44
1.00
1.35
1.10
1.07
2.69
2.69
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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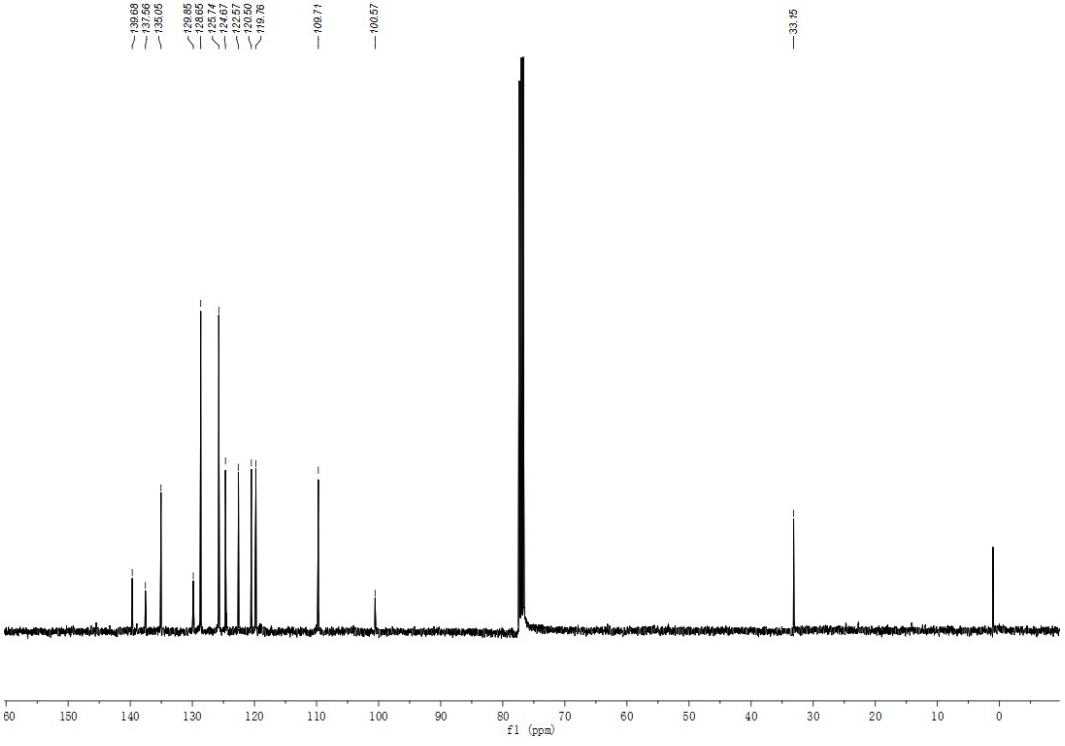
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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124.67
122.57
120.50
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109.71
100.57
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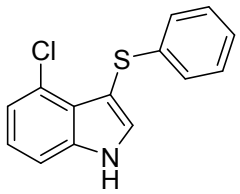
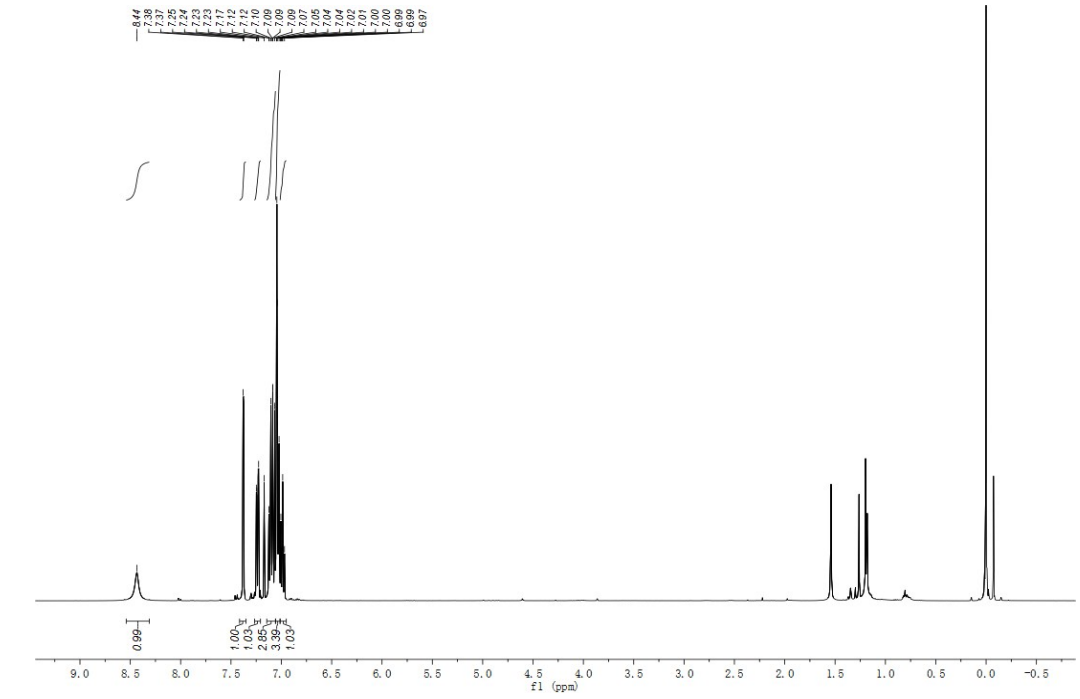
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
S
N
H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7.23
7.17
7.12
7.12
7.10
7.09
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7.09
7.07
7.05
7.04
7.04
7.02
7.01
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7.00
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0.99
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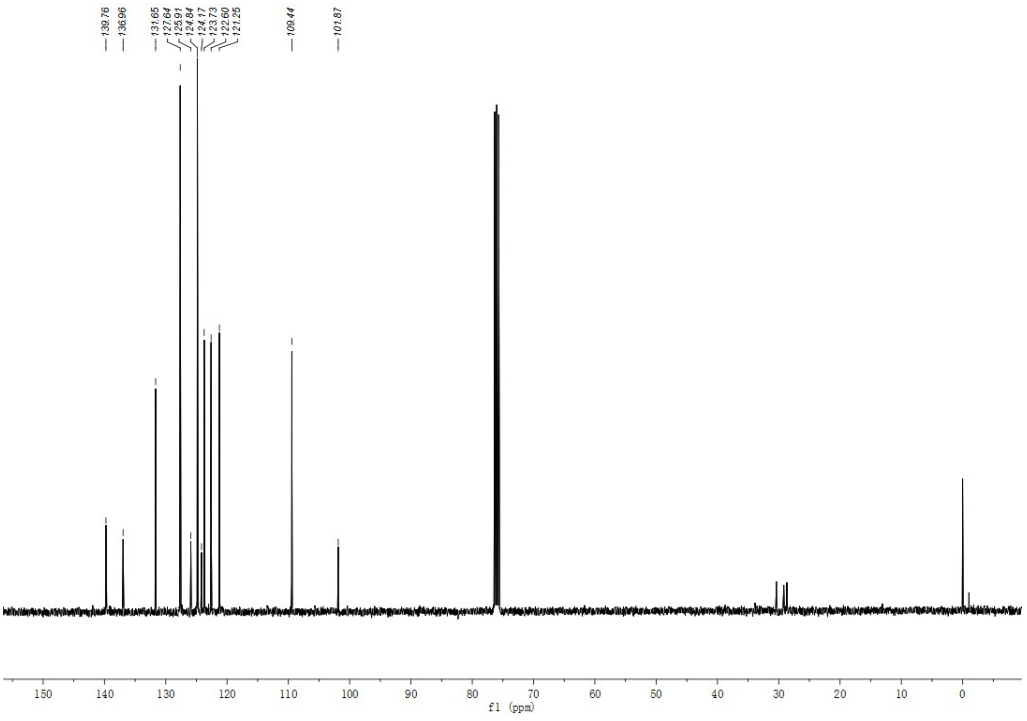
1.03
2.85
3.39
1.03
f1 (ppm)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124.17
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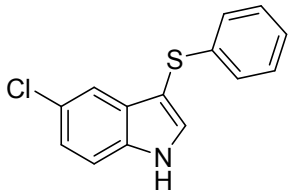
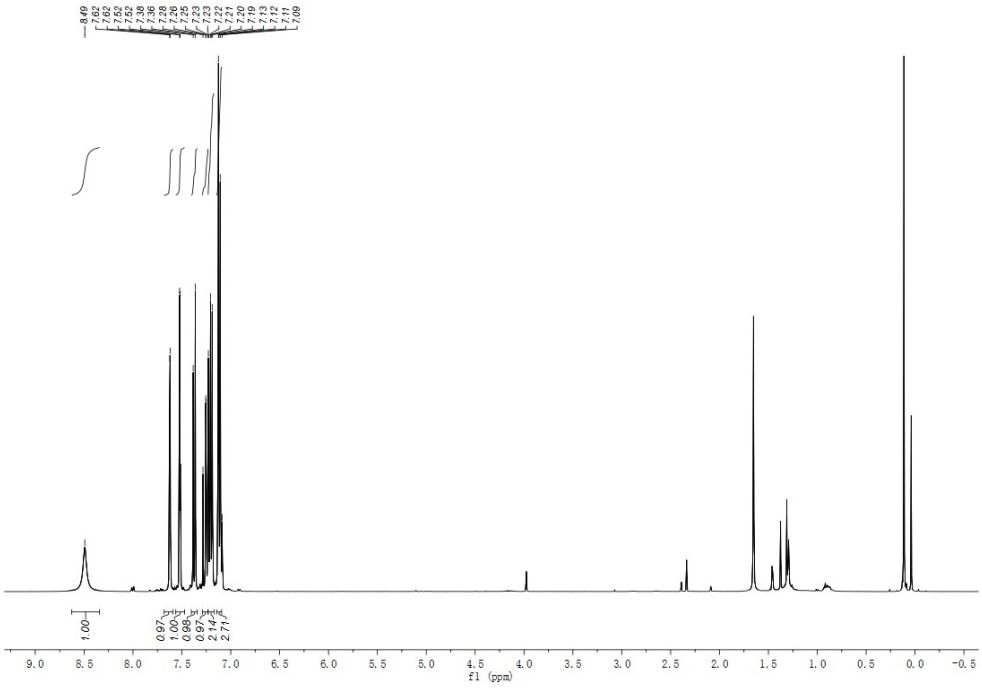
121.60
121.25
109.44
101.87
f1 (ppm)


Cl
S
N
H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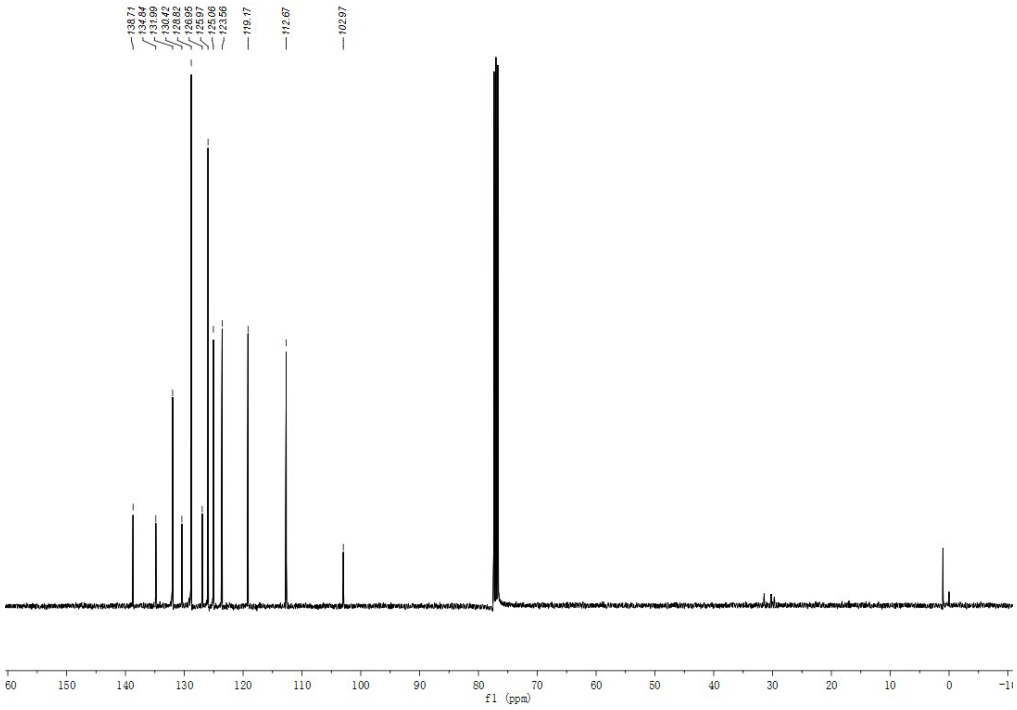
7.36
7.26
7.25
7.23
7.22
7.21
7.10
7.10
7.13
7.12
7.11
7.09
1.00
0.97
1.00
0.96
0.97
2.14
2.71
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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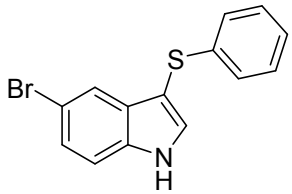
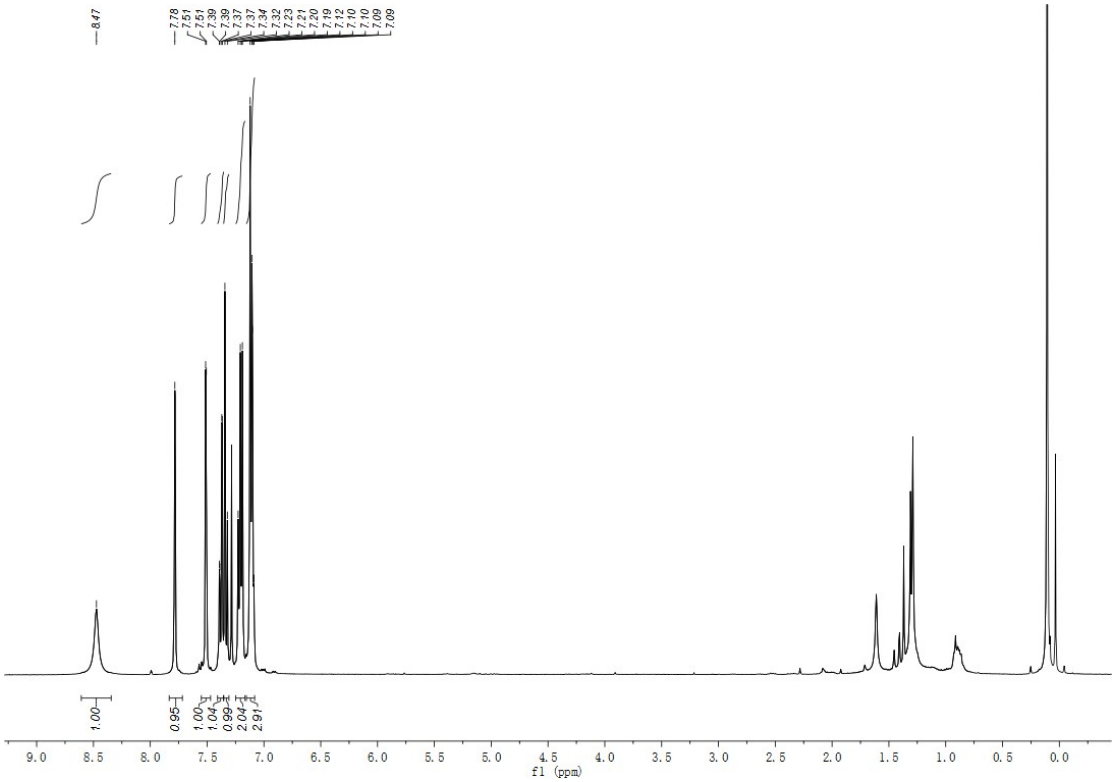
131.99
130.42
128.83
126.95
125.97
125.06
123.56
119.17
112.67
102.97
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
S
N
H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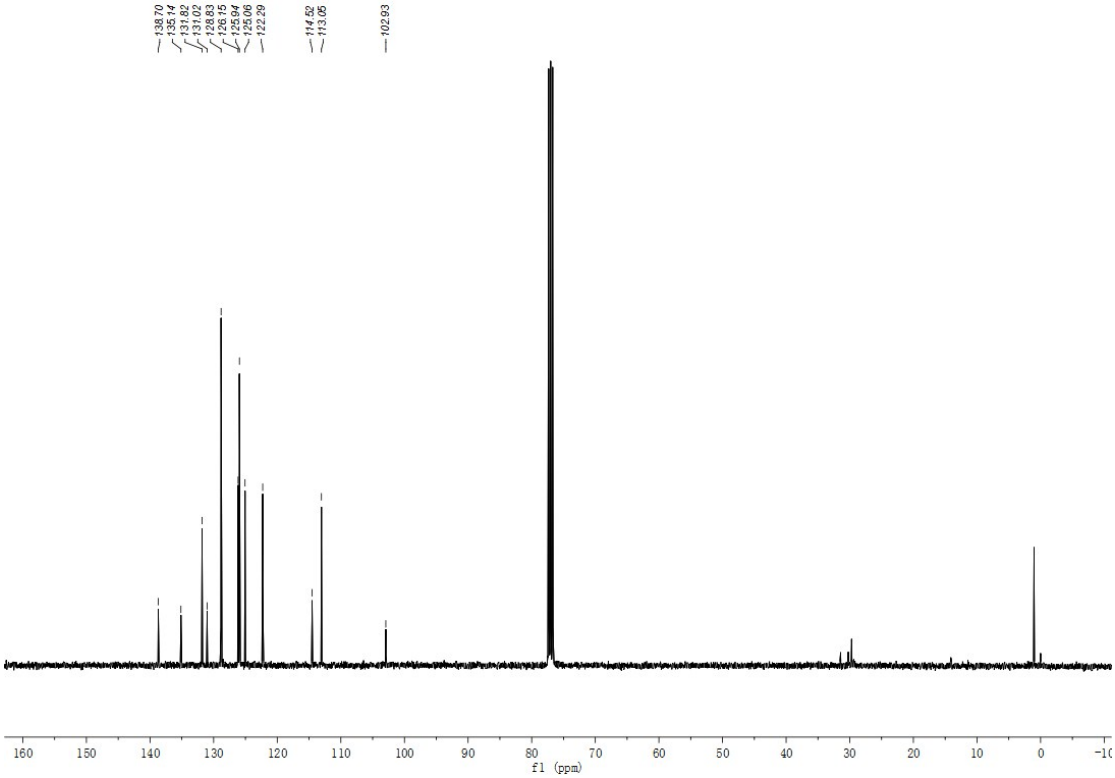
7.37
7.34
7.32
7.23
7.21
7.20
7.19
7.12
7.10
7.10
7.09
7.09
1.00
0.95
1.00
1.04
0.99
2.04
2.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.06
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114.52
113.05
102.93
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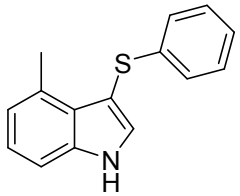
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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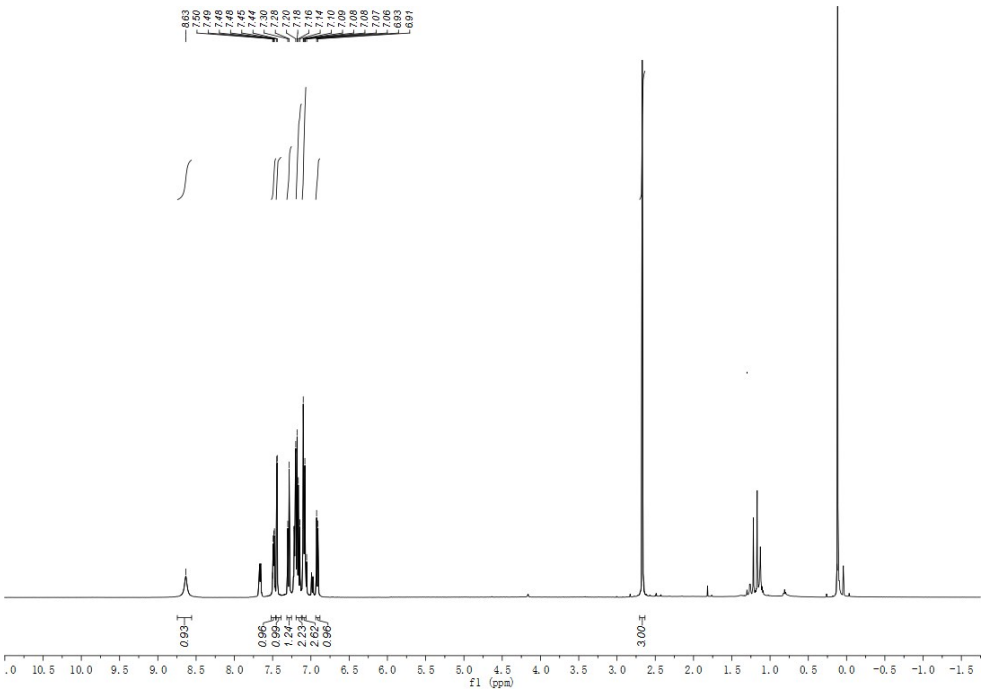
N
H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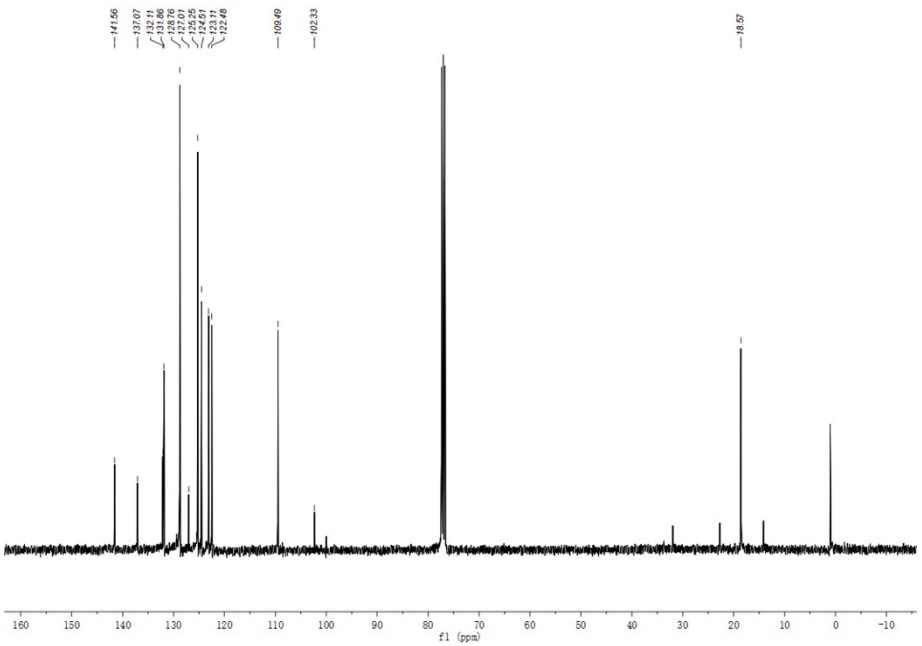
7.45
7.44
7.30
7.28
7.20
7.18
7.16
7.14
7.10
7.09
7.08
7.06
7.07
7.06
6.93
6.91
0.93
0.96
0.99
1.24
2.23
2.62
0.96
3.00
f1 (ppm)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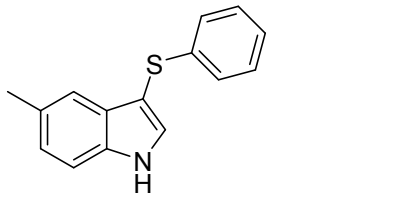
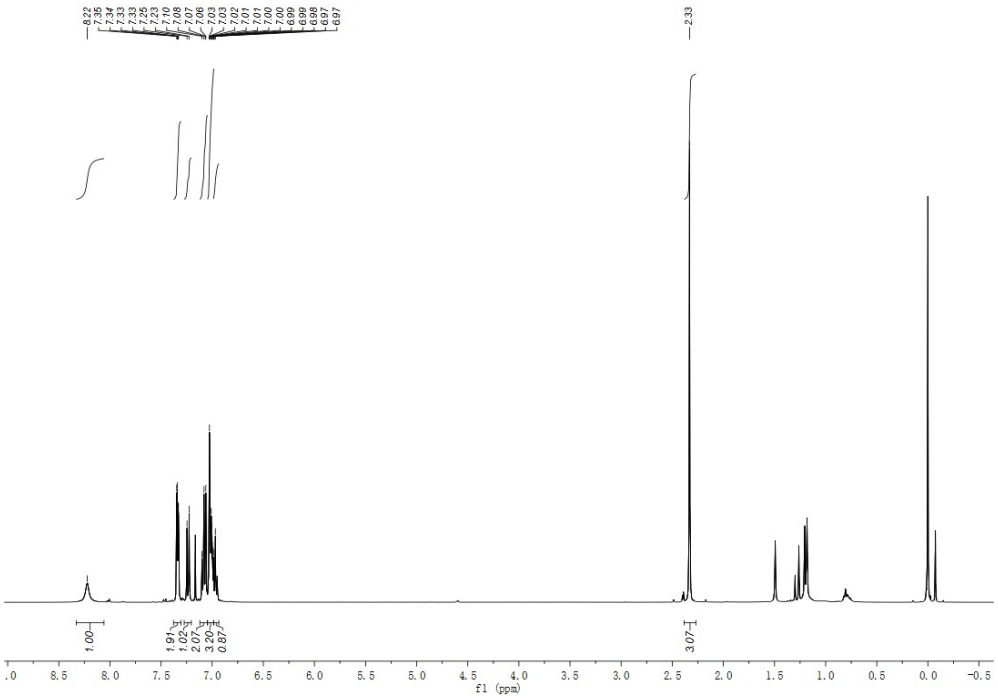
127.01
125.25
124.61
123.11
122.46
109.49
102.33
18.57
f1 (ppm)


S
N
H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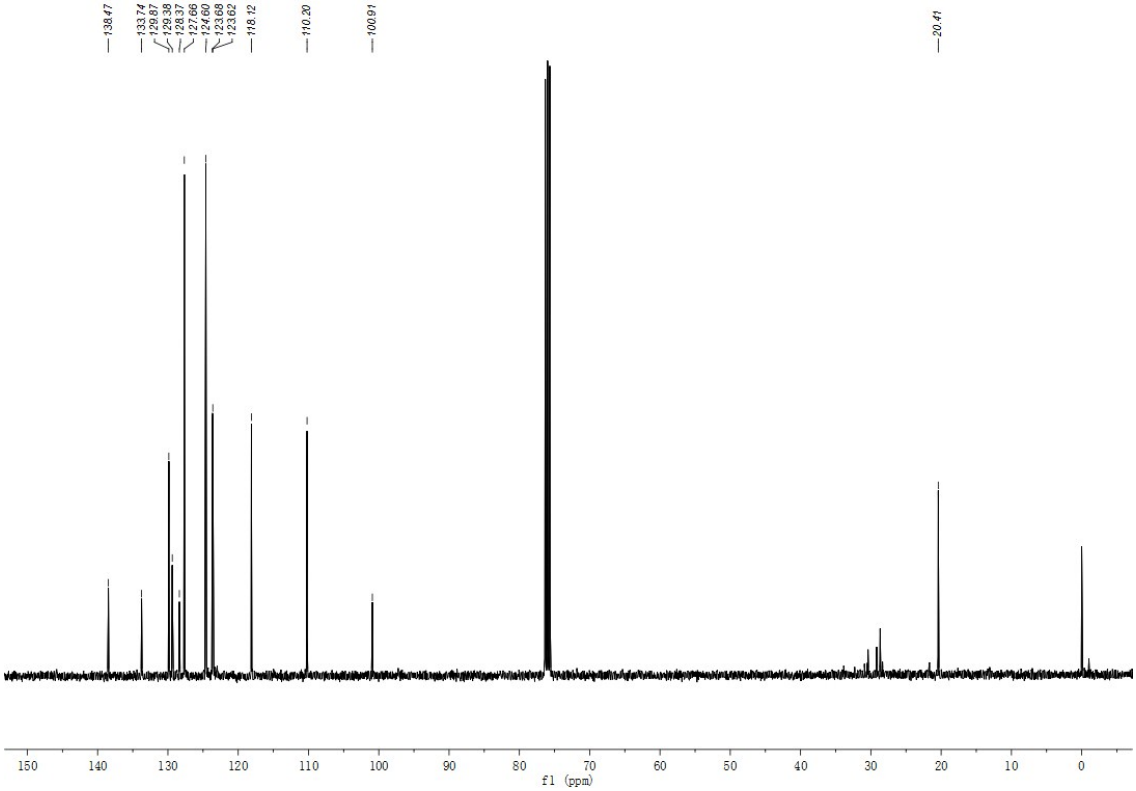
7.23
7.10
7.08
7.07
7.06
7.03
7.03
7.02
7.01
7.01
7.00
7.00
6.99
6.98
6.97
6.97
2.33
1.00
1.91
1.02
2.07
3.09
0.87
3.07
f1 (ppm)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123.62
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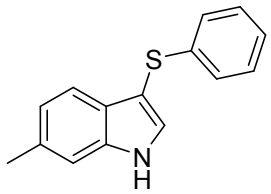
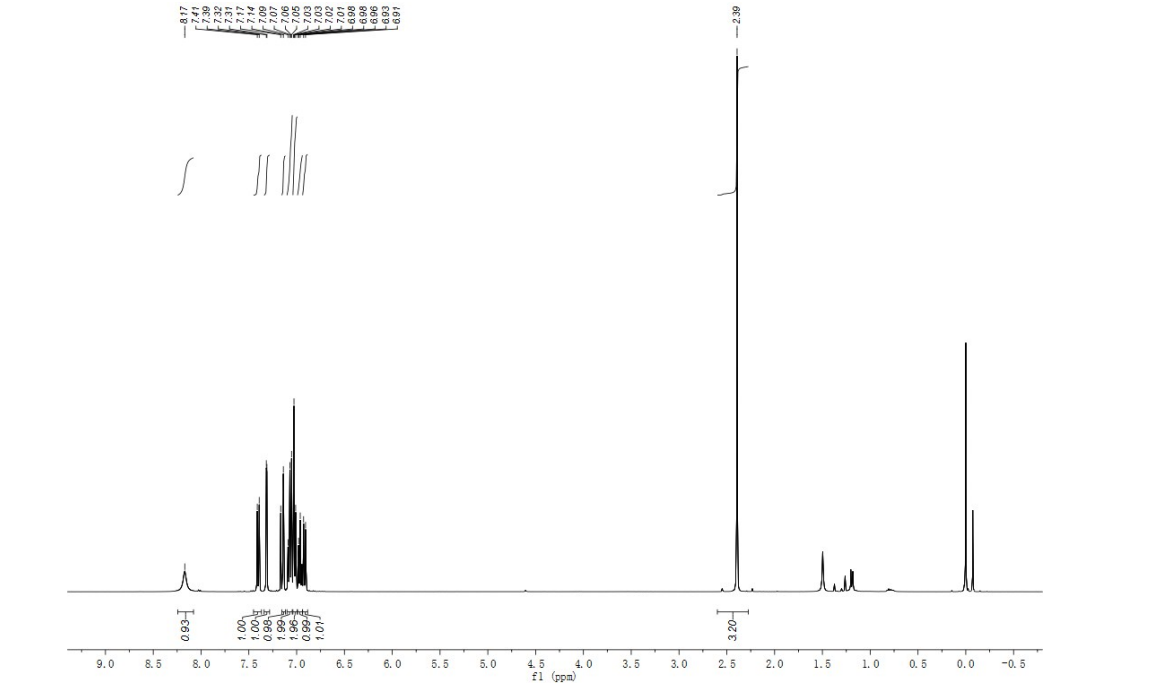
110.20
100.91
20.41
f1 (ppm)


S
N
H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7.17
7.14
7.09
7.07
7.06
7.05
7.03
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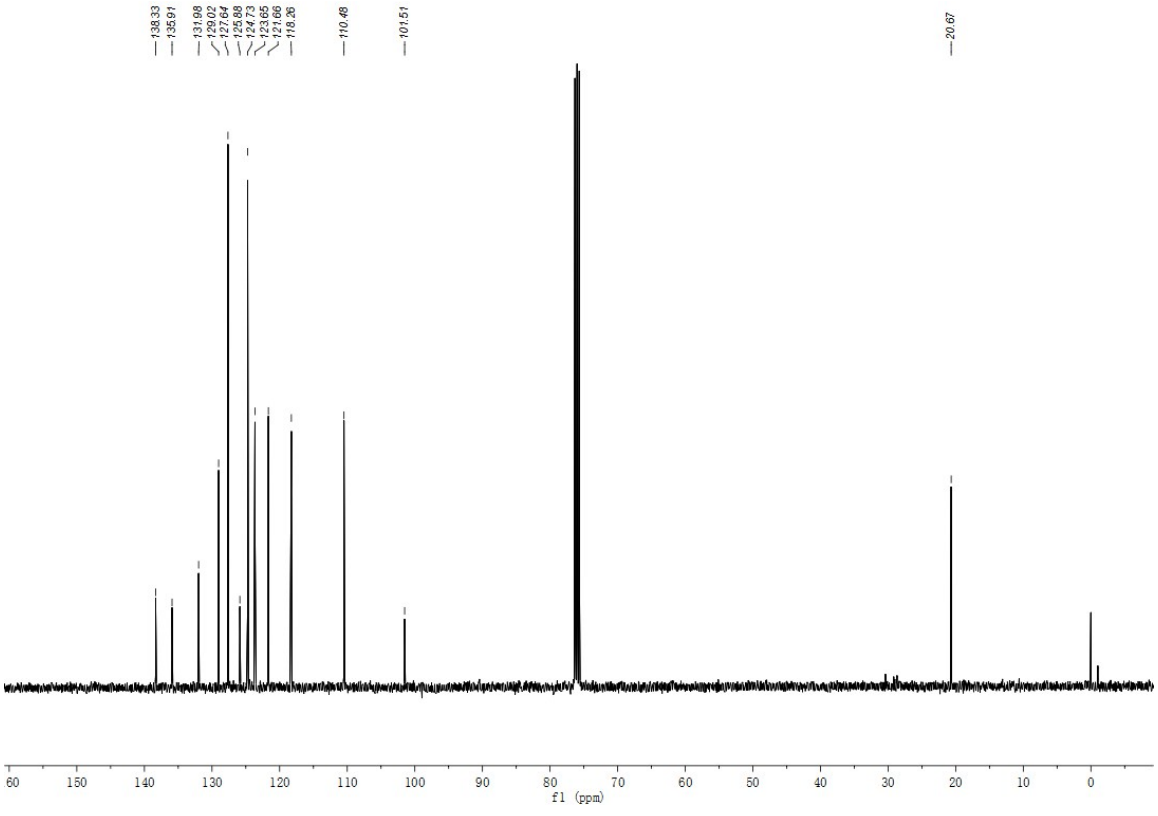
7.01
6.98
6.98
6.96
6.93
6.91
2.39
0.93
1.00
1.00
0.98
1.99
0.99
0.97
1.01
3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.02
127.64
125.88
124.73
123.65
121.66
118.26
110.48
101.51
20.67
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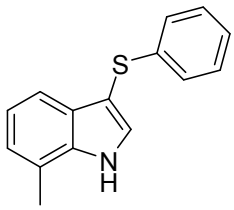
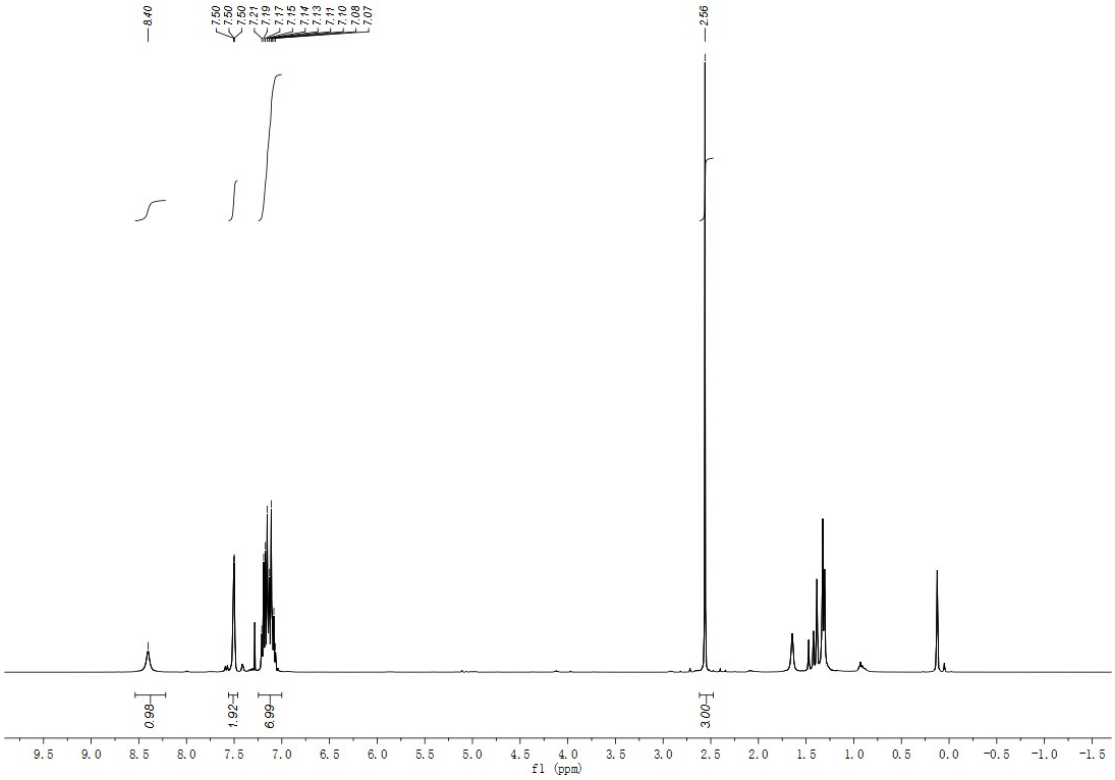
f1 (ppm)


S
N
H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7.50
7.50
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7.17
7.15
7.14
7.13
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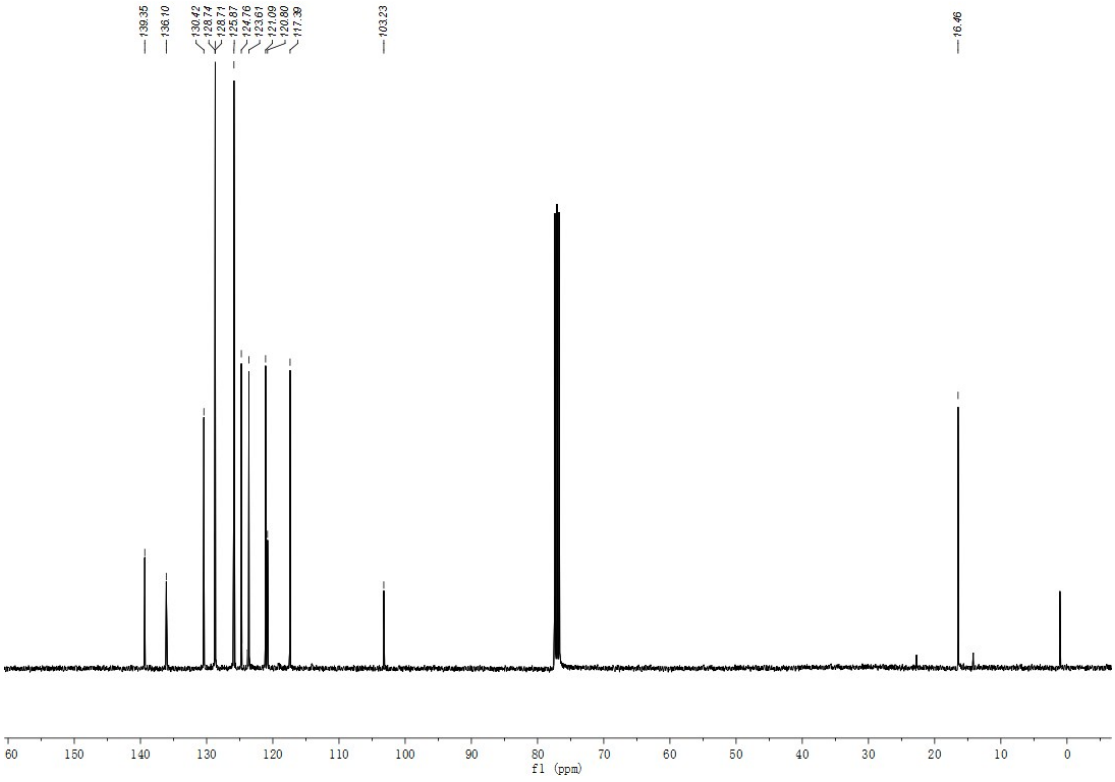
7.10
7.08
7.07
2.56
0.98
1.92
6.99
3.00
f1 (ppm)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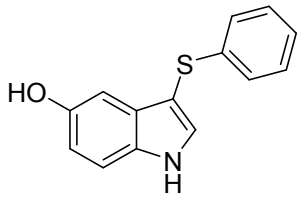
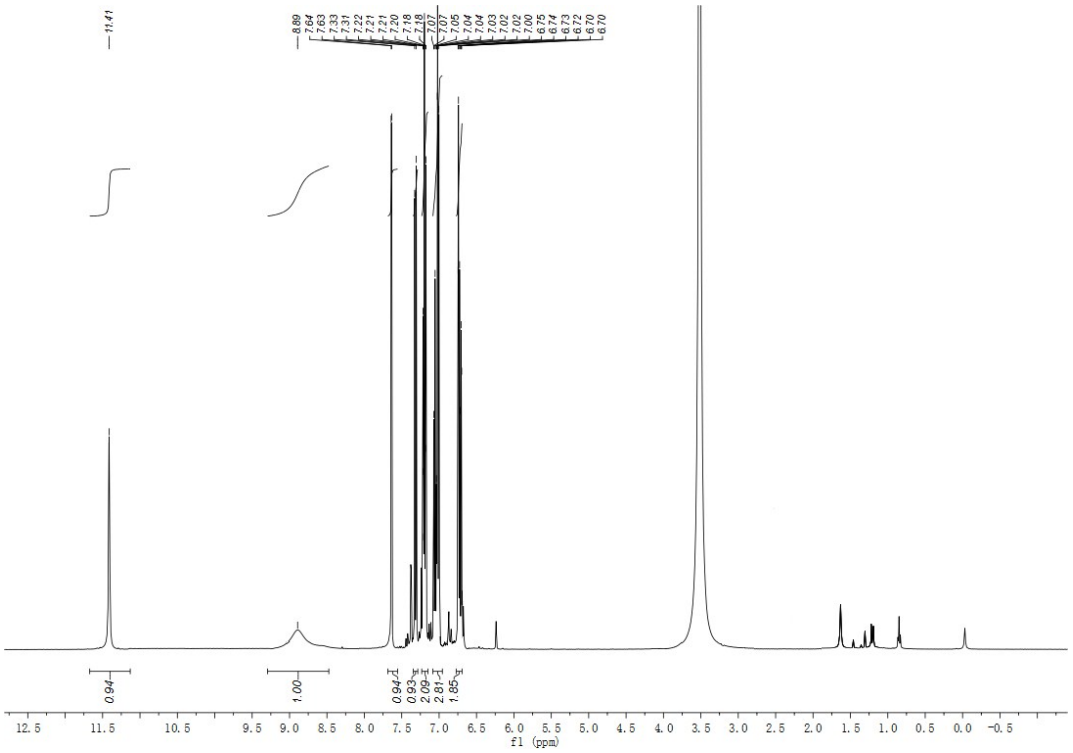
128.71
125.87
124.76
123.61
121.09
120.80
117.30
103.23
16.46
f1 (ppm)


HO
S
N
H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7.20
7.18
7.18
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7.07
7.05
7.04
7.04
7.03
7.02
7.02
7.00
6.75
6.74
6.73
6.72
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6.70
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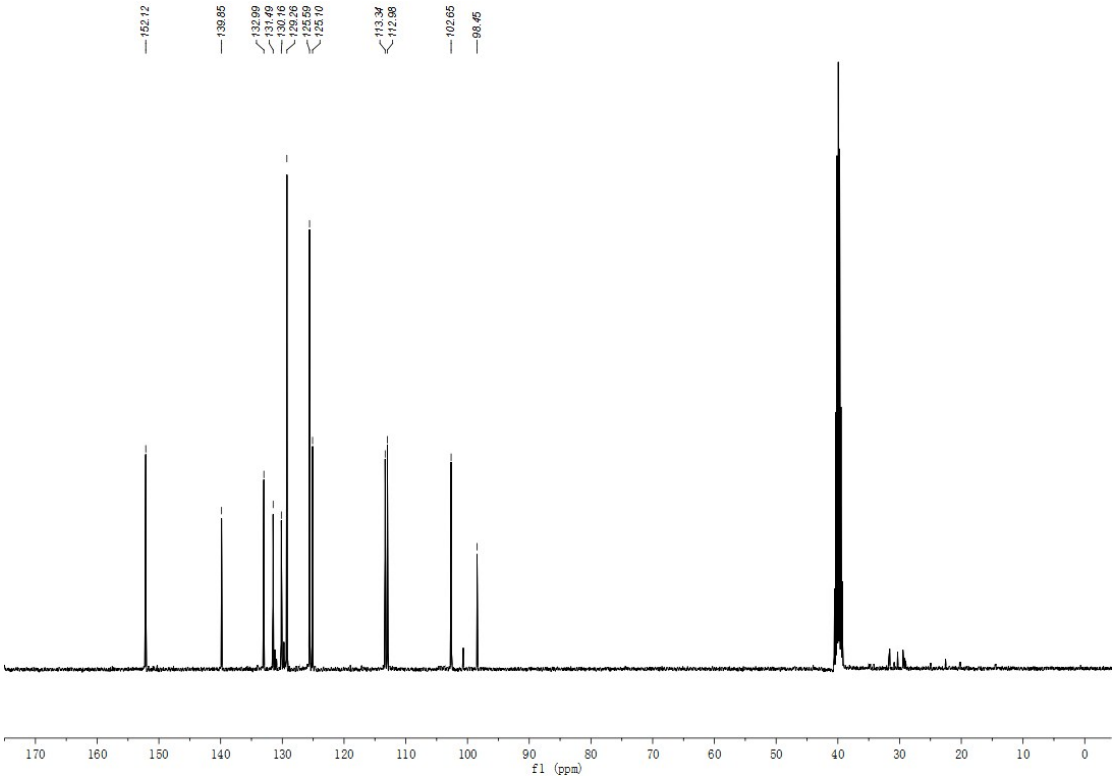
1.00
0.94
0.93
2.09
2.81
1.85
f1 (ppm)


152.12
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129.26
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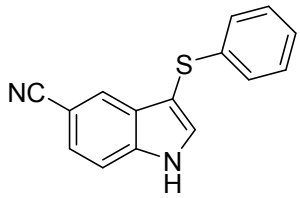
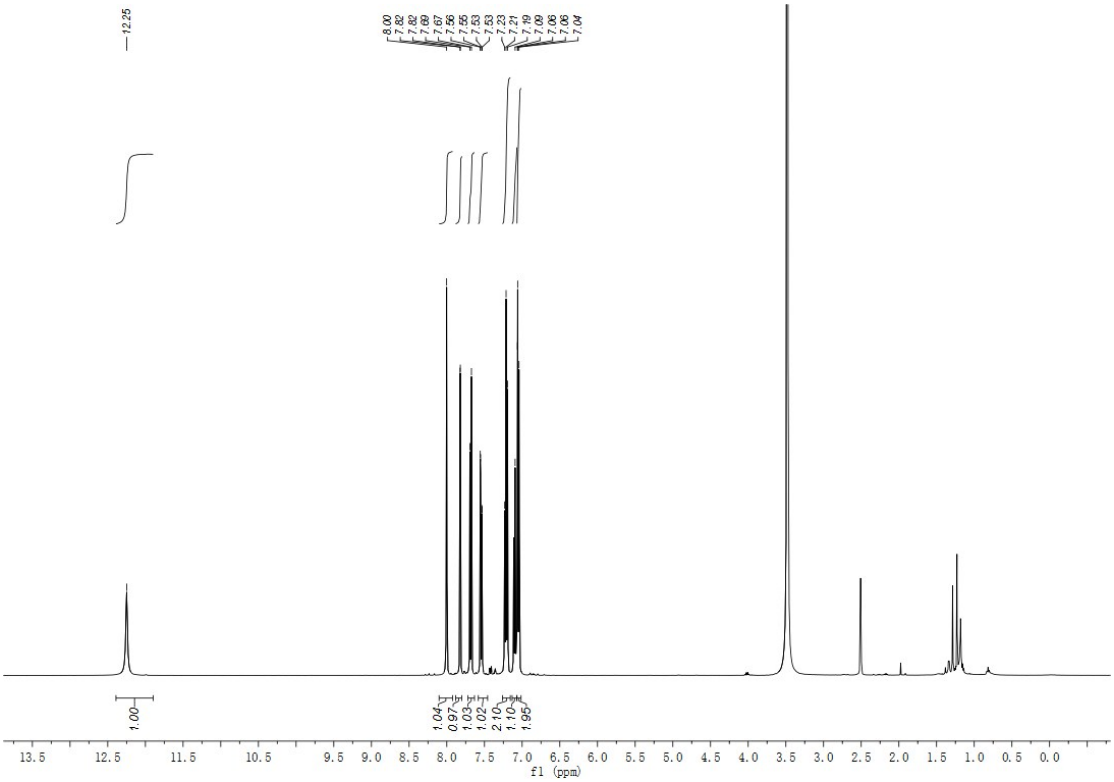
125.10
113.34
112.98
102.65
98.45
f1 (ppm)


NC
S
N
H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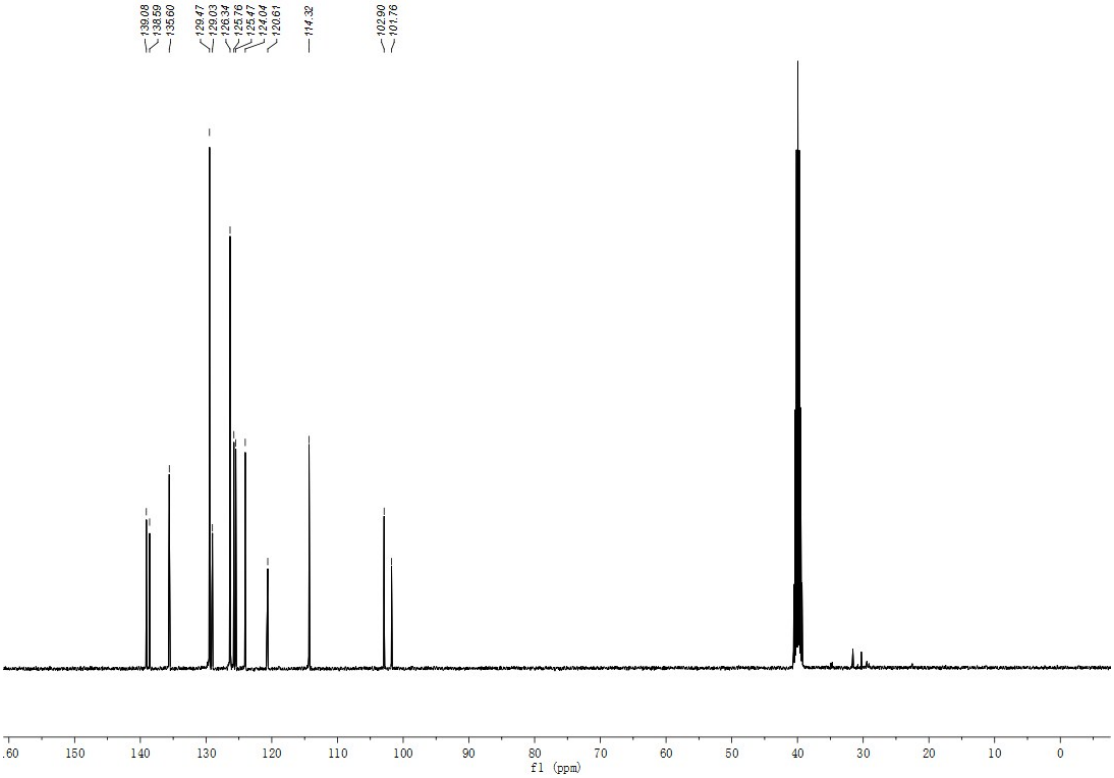
7.19
7.09
7.06
7.06
7.04
1.00
1.04
0.97
1.03
1.02
2.10
1.10
1.95
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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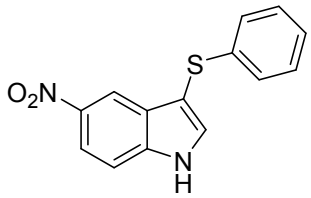
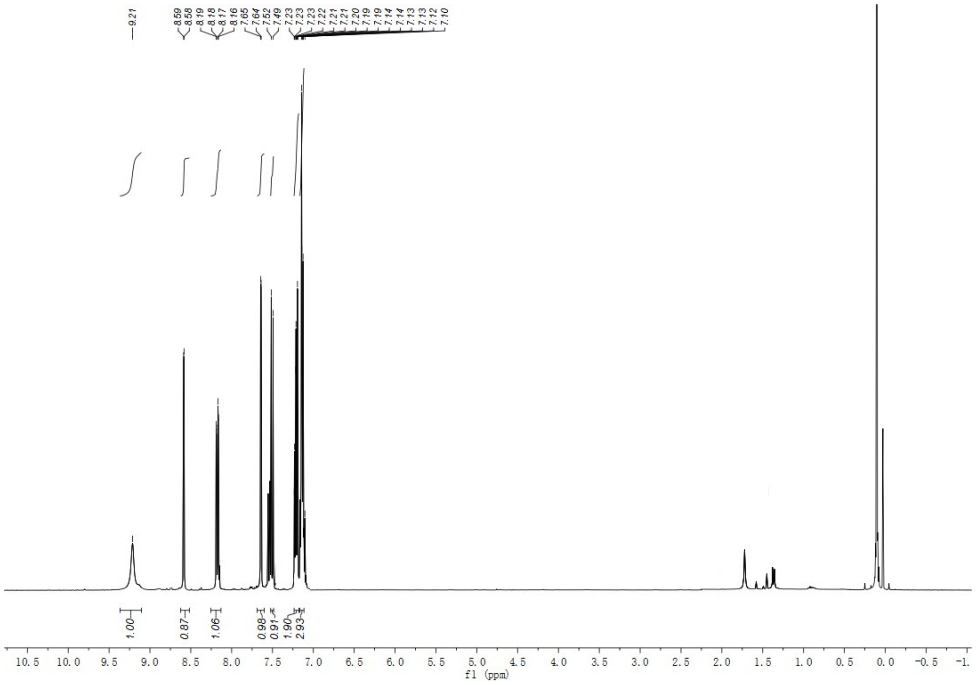
129.47
129.03
126.34
125.76
125.47
124.04
120.61
114.32
102.90
101.76
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O_2N
S
N
H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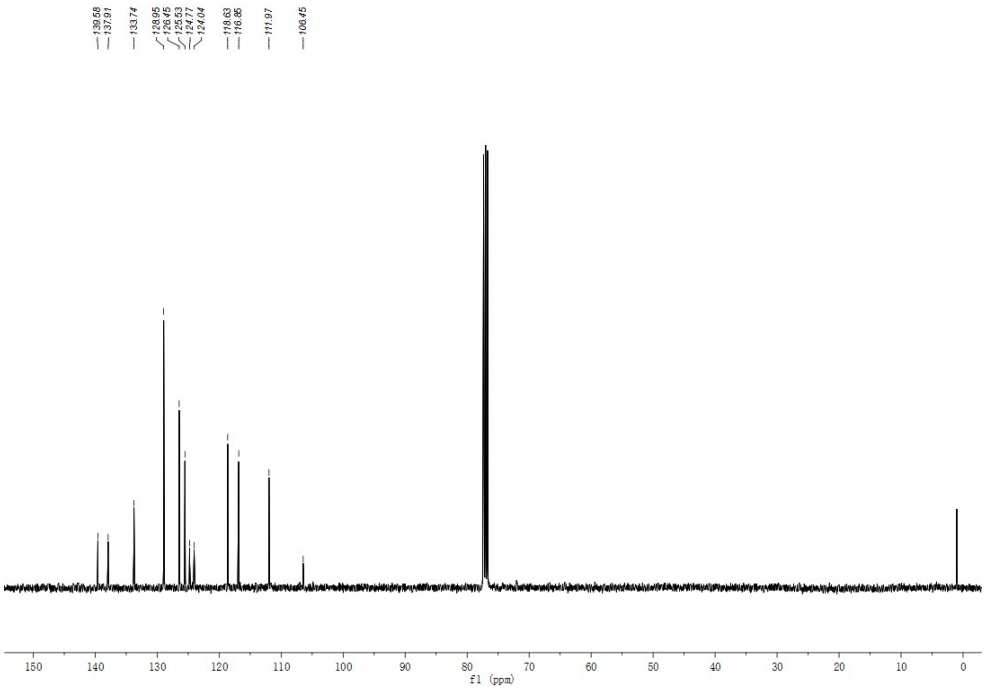
8.16
7.65
7.64
7.62
7.49
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.14
7.14
7.13
7.13
7.12
7.10
1.00
0.87
1.06
0.98
0.91
1.90
2.93
f1 (ppm)


139.58
137.91
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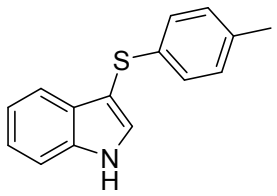
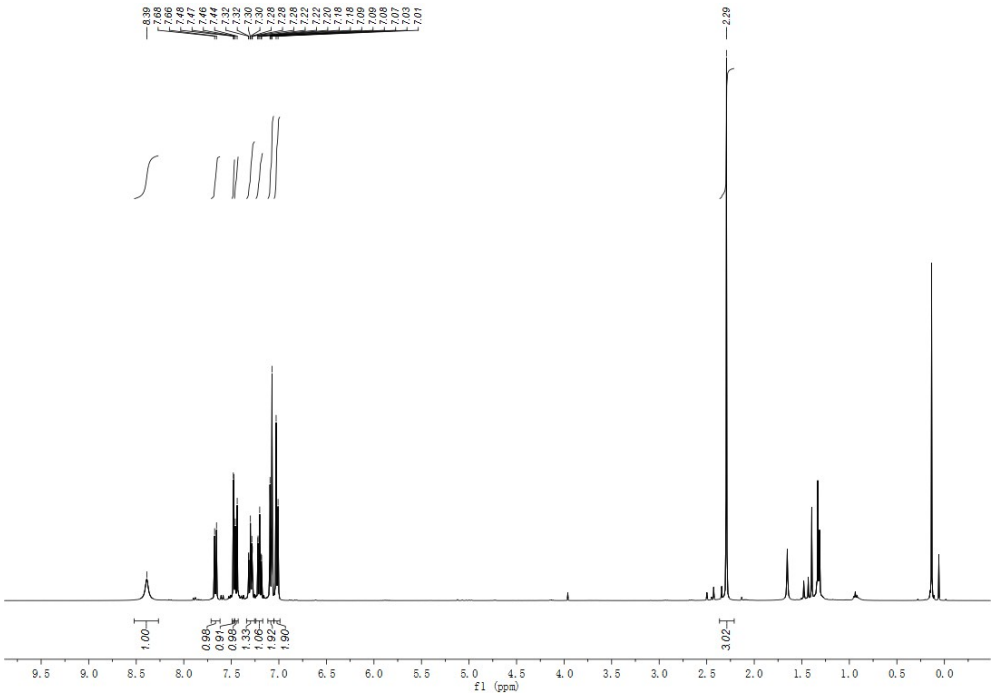
128.95
126.45
125.53
124.77
124.04
118.63
118.06
111.97
106.45
f1 (ppm)


S
N
H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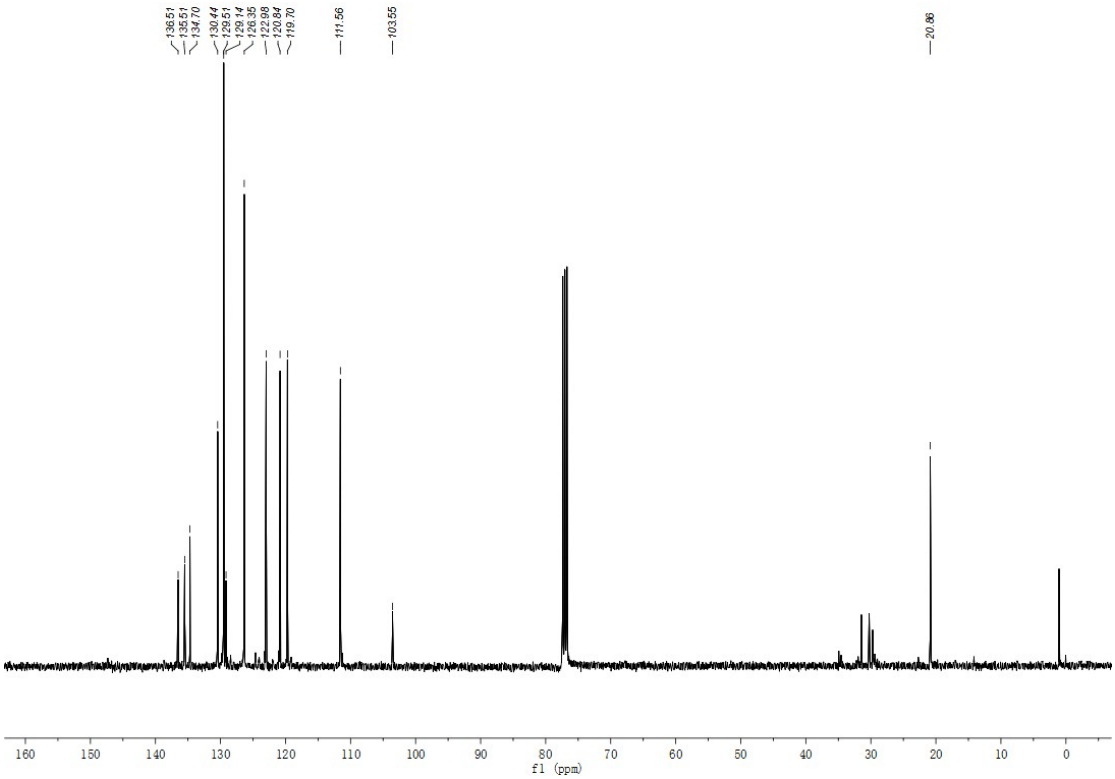
7.68
7.66
7.48
7.47
7.46
7.44
7.33
7.32
7.30
7.30
7.28
7.28
7.23
7.22
7.20
7.18
7.18
7.09
7.09
7.08
7.07
7.03
7.01
2.29
1.00
0.98
0.91
0.98
1.33
1.06
1.92
1.90
3.02
f1 (ppm)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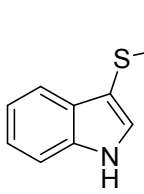
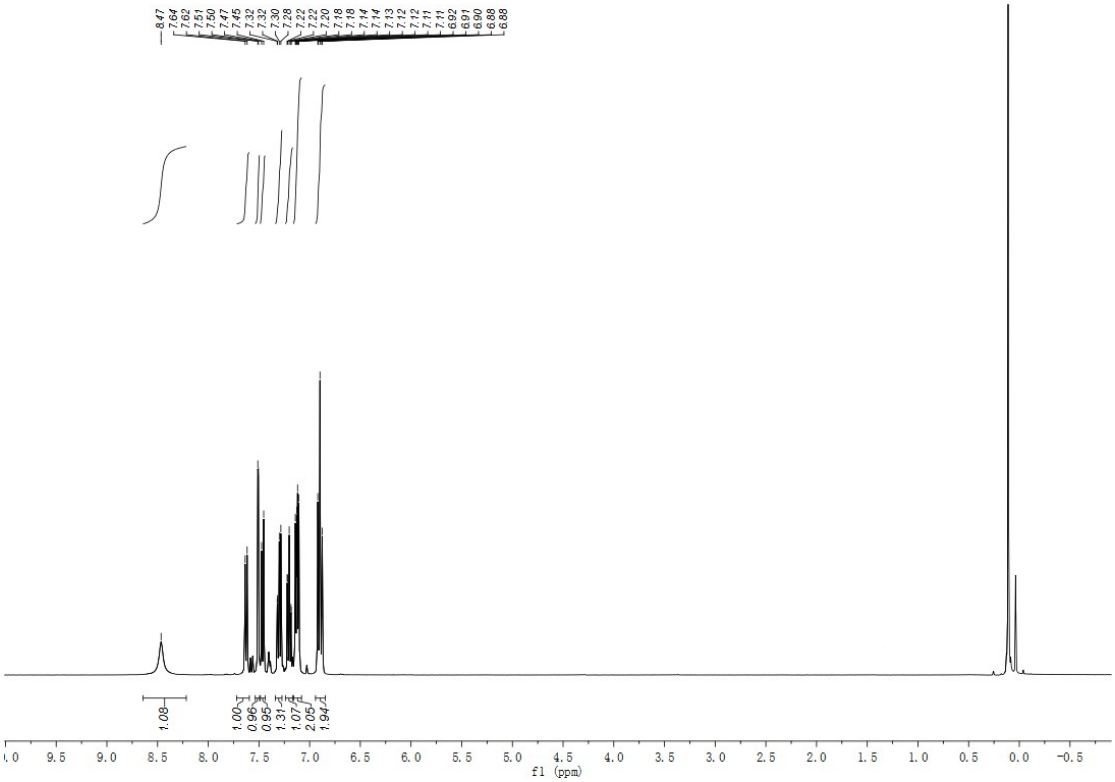
135.51
134.70
130.44
129.51
129.14
126.35
122.98
120.84
119.70
111.56
103.55
20.86
f1 (ppm)


F
S
N
H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7.64
7.62
7.51
7.50
7.47
7.45
7.32
7.32
7.30
7.28
7.22
7.22
7.20
7.18
7.18
7.14
7.14
7.13
7.12
7.12
7.11
7.11
6.92
6.91
6.90
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6.88
1.08
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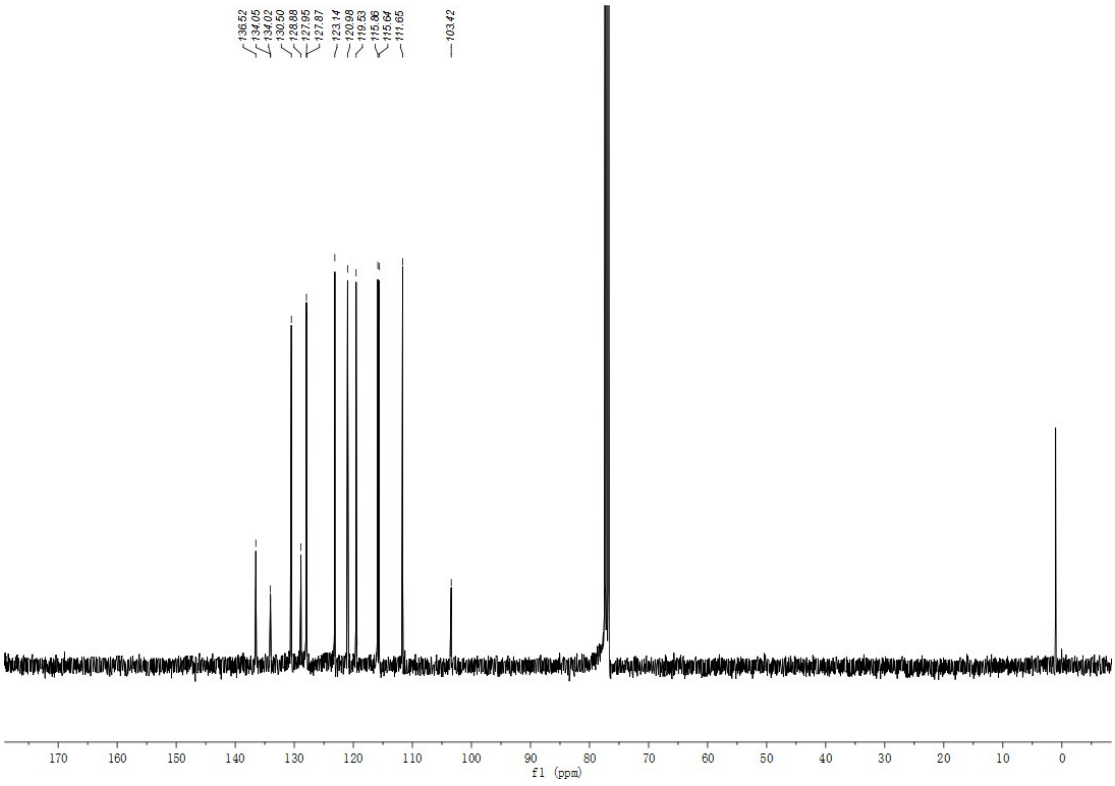
0.96
0.95
1.31
1.07
2.05
1.94
f1 (ppm)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134.05
134.02
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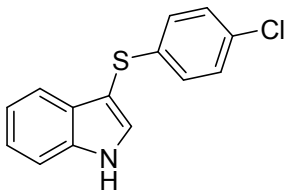
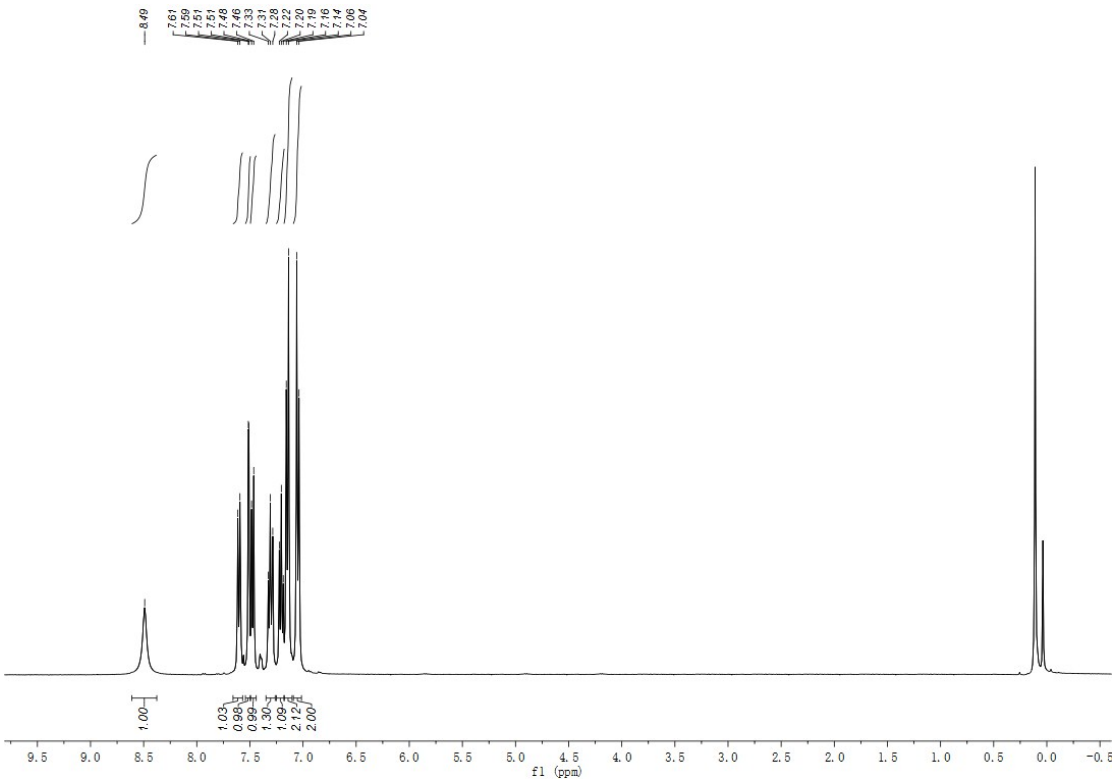
119.53
115.86
115.64
111.65
103.42
f1 (ppm)


Cl
S
N
H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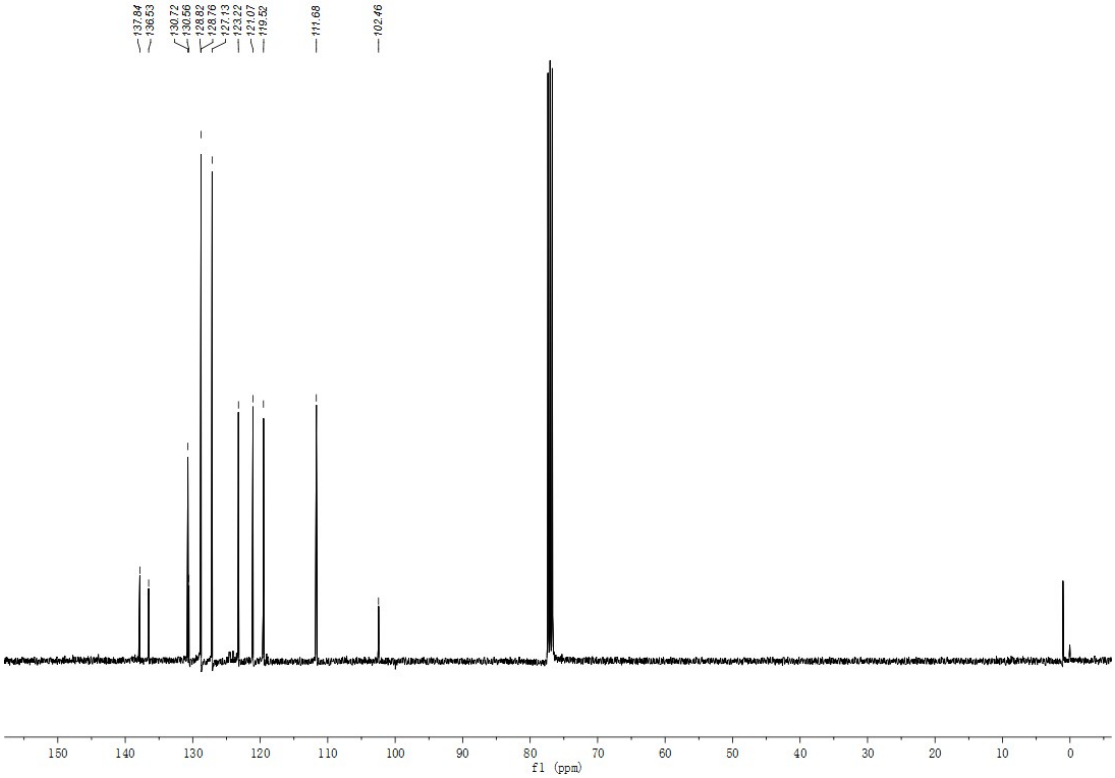
7.61
7.59
7.51
7.51
7.48
7.46
7.33
7.31
7.28
7.22
7.20
7.19
7.16
7.14
7.06
7.04
1.00
1.03
0.98
0.99
1.30
1.09
2.12
2.00
f1 (ppm)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128.82
128.76
127.13
123.22
121.07
119.52
111.68
102.46
f1 (ppm)

Computational details

The theoretical work was performed using the Gaussian 09 program.[1] For geometry optimization and frequency analysis, the cc-pVDZ-pp basis set[2] were used for the I and Cu atoms, and the 6-31g(d) all-electron basis[3] was used for all the other atoms (BSI); for sing-point energy calculation, the aug-cc-pVTZ(PP) basis set[2,4] (BSII) was used for all atoms. The Polarizable Continuum Model using the integral equation formalism variant (IEFPCM)[5] was employed to evaluate the solvation energies. The B97-1 functional[6] was employed, and this functional has been proven to be reliable for calculating Cu complex-containing systems.[7] Stationary points were optimized without symmetry constraint, and their nature confirmed by vibrational frequency analysis. Intrinsic reaction coordinate[8] calculations were performed to link transition structures with the respective intermediates. Unscaled vibrational frequencies were used to correct the relative energies for zero-point energy (ZPE) contributions.

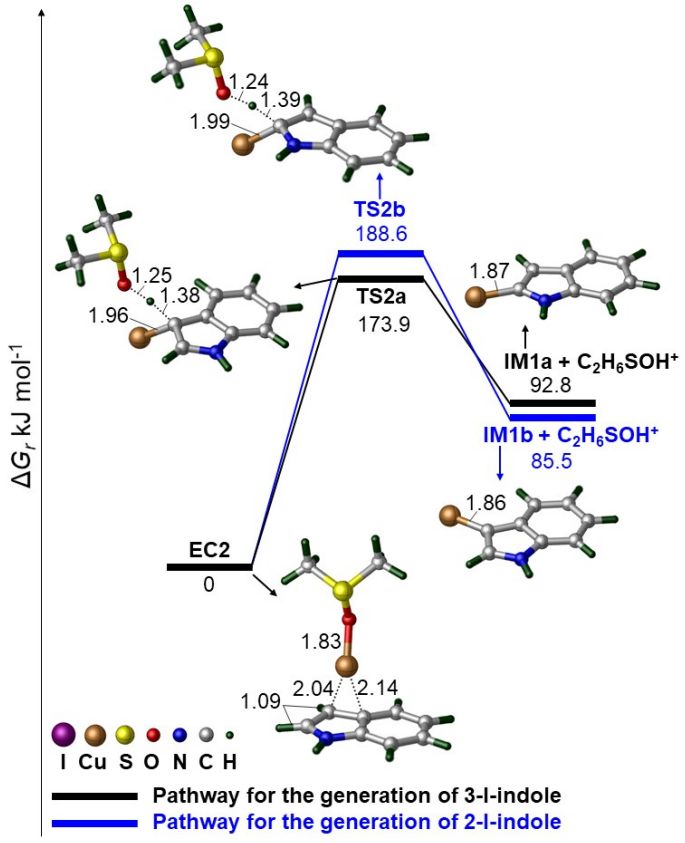

Figure 1. Simplified PESs for the generation of 2-I-indole and 3-I-indole starting from the encounter complex **EC2** as calculated at the B97-1/BSII//B97-1/BSI level of theory. Zero-point corrected, relative energies are given in kJ mol^{-1} and bond lengths in Å; charges are omitted for the sake of clarity.

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