Supporting Information

Palladium-Catalyzed Regio-selective Oxidative C-H Bond Acylation of Azoxybenzenes with Alcohols

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Contents:

1. General methods.

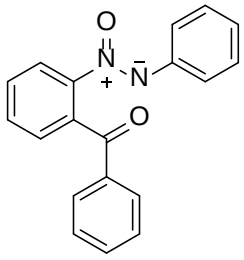
All reactions involving air- and moisture-sensitive reagents were carried out under a nitrogen atmosphere. Toluene, DMF, 1, 2-dichloroethane, DMSO, 1, 4- dioxane and CH_3CN were distilled from appropriate drying agents prior to use. All chemicals were purchased from Aldrich and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230~400 mesh) was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker

INOVA-400. NMR Spectrums were recorded on a 400 instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. Azoxybenzenes were prepared from arylamines, according to the literature[1].

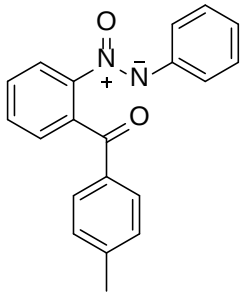
General Catalytic Procedure for *Ortho*-acylation of Azoxybenzenes with Alcohol Derivatives.

$Pd(TFA)_2$ (6.6 mg, 0.02 mmol, 10 mol %), azoxybenzene (39.6 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (64.8 mg, 0.6 mmol, 3.0 equiv), TBHP (196μl, 70%, 1.4 mmol, 7.0 equiv) and DCE (1.0 mL) were added in a 10 mL sealed tube with a Teflon-lined cap. The vessel was heated in an oil bath at 100 ^{o}C for 20 h followed by cooling. The contents were subjected to flash chromatography (eluent: petroleum ether/EtOAc = 20:1) to give the corresponding product (73%) as a pale yellow oil. The purified material was dried under an oil-pump vacuum..

2. Characterization of the Products

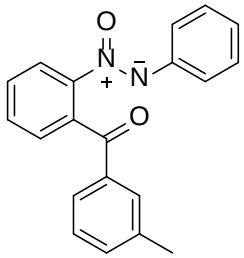


3aa: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24-8.23 (d, *J* = 4.0 Hz, 1 H), 7.78-7.76 (d, *J* = 8.0 Hz, 2 H), 7.68 (dd, *J* = 4.0 Hz, *J* = 4.0 Hz, 4 H), 7.53 -7.45 (m, 2 H), 7.38-7.28 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.00, 147.12, 143.05, 136.82, 134.67, 133.05, 131.33, 130.49, 129.89, 128.81, 128.76, 128.47, 128.45, 124.92, 123.29. HRMS (ESI) ($[M+Na]^{+}$) Calcd. for $C_{19}H_{14}N_2O_2$: 325.0953, Found: 325.0962.

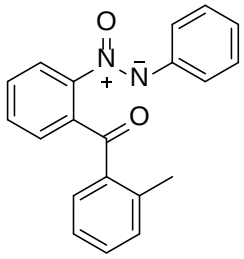


3ab: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1 H), 7.74-7.72 (d, *J* = 8.0 Hz, 2 H), 7.68-7.66 (d, *J* = 8.0Hz, 4 H), 7.51 (s, 1 H), 7.31-7.29 (d, *J* = 8.0Hz, 3 H), 7.17-7.16 (d, *J* = 4.0 Hz,

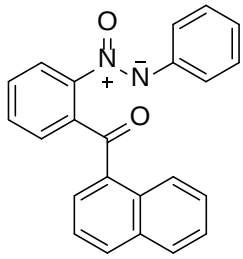
2 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.80, 147.04, 143.96, 143.12, 134.92, 134.35, 131.25, 130.31, 129.85, 129.20, 128.99, 128.75, 128.44, 124.99, 123.30, 21.63. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{16}N_2O_2$: 339.1109, Found: 339.1121.



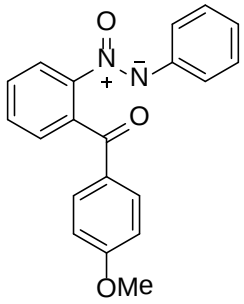
3ac: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23-8.21 (d, *J* = 8.0 Hz, 1 H), 7.72-7.70 (d, *J* = 8.0 Hz, 2 H), 7.66-7.65 (d, *J* = 4.0 Hz, 2 H), 7.60 (s, 1 H), 7.53-7.51 (d, *J* = 8.0 Hz, 2 H), 7.31-7.22 (m, 5 H), 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.20, 147.11, 143.04, 138.26, 136.77, 134.77, 133.83, 131.22, 130.40, 129.81, 129.14, 128.77, 128.38, 128.28, 126.08, 124.89, 123.24, 21.15. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{16}N_2O_2$: 339.1109, Found: 339.1118.



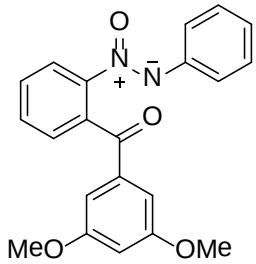
3ad: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06-8.05 (d, *J* = 4.0 Hz, 1 H), 7.63 (s, 3 H), 7.57-7.55 (d, *J* = 8.0 Hz, 2 H), 7.29-7.27 (m, 5 H), 7.15-7.10 (m, 2 H), 2.53 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.39, 147.87, 143.28, 139.81, 136.18, 135.69, 131.85, 131.77, 131.06, 130.90, 130.25, 129.60, 128.36, 125.27, 124.66, 123.38, 21.19. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{16}N_2O_2$: 339.1109, Found: 339.1124.



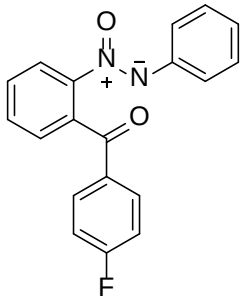
3ae: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97-8.95 (d, *J* = 8.0 Hz, 1 H), 8.09-8.08 (d, *J* = 4.0 Hz, 1 H), 7.90-7.88 (d, *J* = 8.0 Hz, 1 H), 7.78-7.76 (d, *J* = 8.0 Hz, 1 H), 7.69-7.65 (m, 3 H), 7.58-7.51 (m, 2 H), 7.49-7.45 (t, *J* = 8.0 Hz, 1 H), 7.42-7.41 (d, *J* = 4.0 Hz, 2 H), 7.33-7.30 (t, *J* = 8.0 Hz, 1 H),7.12 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.26, 147.99, 143.02, 135.94, 133.92, 133.76, 133.44, 131.01, 130.98, 130.70, 130.17, 129.86, 129.46, 128.12, 126.46, 126.24, 124.64, 123.89, 123.48. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{23}H_{16}N_2O_2$: 375.1109, Found: 375.1111.



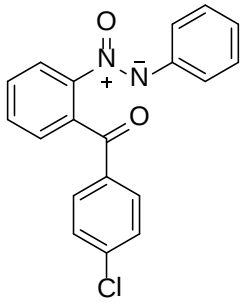
3af: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.21 (d, *J* = 4.0 Hz, 1 H), 7.76-7.74 (d, *J* = 8.0 Hz, 4 H), 7.63-7.62 (d, *J* = 4.0 Hz, 2 H), 7.49 (s, 1 H), 7.32-7.30 (d, *J* = 8.0 Hz, 3 H), 6.86-6.84 (d, *J* = 8.0 Hz, 2 H), 3.79 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.88, 163.50, 147.01, 143.19, 135.03, 131.23, 131.20, 130.21, 129.91, 129.86, 128.71, 128.48, 125.02, 123.35, 113.75, 55.42. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{20}H_{16}N_2O_3$: 355.1059, Found: 355.1072.



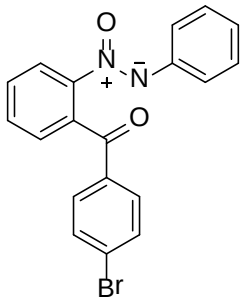
3ag: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.21 (t, *J* = 4.0 Hz, 1 H), 7.78-7.76 (d, *J* = 8.0 Hz, 2 H), 7.65-7.64 (m, 2 H), 7.53 (s, 1 H), 7.33-7.31 (d, *J* = 8.0 Hz, 3 H), 6.88 (s, 2 H), 6.55 (s, 1 H), 3.72 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.64, 160.65, 147.15, 143.10, 138.83, 134.57, 131.25, 130.52, 129.91, 128.81, 128.45, 125.00, 123.29, 106.55, 105.52, 55.49. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{21}H_{18}N_2O_4$: 385.1164, Found: 385.1175.



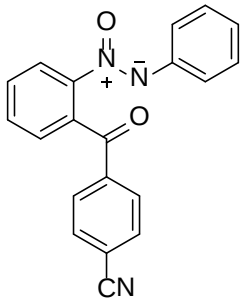
3ah: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25-8.24 (d, *J* = 4.0 Hz, 1 H), 7.79-7.75 (m, 4 H), 7.68-7.66 (d, *J* = 8.0 Hz, 2 H), 7.52-7.51 (d, *J* = 4.0 Hz, 1 H), 7.33-7.32 (d, *J* = 4.0 Hz, 3 H), 7.06-7.02 (t, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.51, 165.56 (d, *J* = 254.0 Hz), 147.01, 143.00, 134.34, 133.32 (d, *J* = 3.0 Hz), 131.38, 131.29, 130.59, 130.09, 128.65, 128.53, 124.96, 123.36, 115.65 (d, *J* = 22.0 Hz). HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{13}FN_2O_2$: 343.0859, Found: 343.0873.



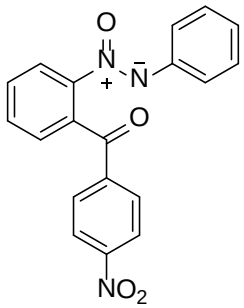
3ai: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25-8.24 (m, 1 H), 7.76-7.75 (d, *J* = 4.0 Hz, 2 H), 7.71-7.66 (m, 4 H), 7.50-7.49 (d, *J* = 4.0 Hz, 1 H), 7.34-7.32 (d, *J* = 8.0 Hz, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.79, 146.99, 142.97, 139.41, 135.27, 134.17, 131.43, 130.66, 130.14, 130.07, 128.81, 128.65, 128.55, 124.99, 123.36. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{13}ClN_2O_2$: 359.0563, Found: 359.0578.



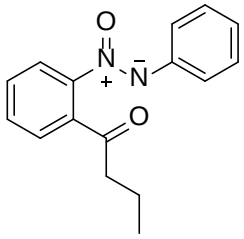
3aj: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25-8.24 (d, *J* = 4.0 Hz, 1 H), 7.76-7.74 (d, *J* = 8.0 Hz, 2 H), 7.67-7.61 (m, 4 H), 7.51-7.49 (d, *J* = 8.0 Hz, 3 H), 7.34-7.32 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.97, 147.02, 142.98, 135.71, 134.15, 131.80, 131.44, 130.68, 130.18, 130.15, 128.66, 128.56, 128.18, 124.99, 123.38. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{13}BrN_2O_2$: 403.0058, Found: 403.0070.



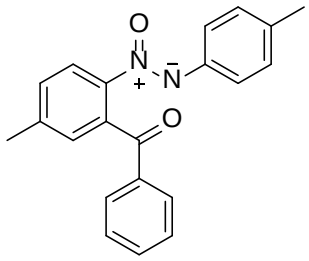
3ak: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28-8.27 (d, *J* = 4.0 Hz, 1 H), 7.83-7.82 (d, *J* = 4.0 Hz, 2 H), 7.74-7.71 (m, 4 H), 7.65-7.63 (d, *J* = 8.0 Hz, 2 H), 7.55 (s, 1 H), 7.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.29, 147.10, 142.78, 140.07, 133.40, 132.32, 131.71, 131.18, 130.47, 128.79, 128.76, 128.64, 124.98, 123.39, 117.87, 115.97. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{20}H_{13}N_3O_2$: 350.0905, Found: 350.0918.



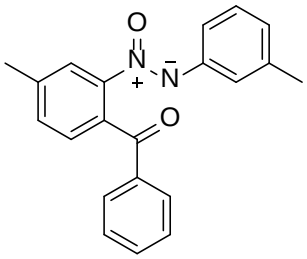
3al: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30-8.29 (d, *J* = 4.0 Hz, 1 H), 8.20-8.18 (d, *J* = 8.0 Hz, 2 H), 7.90-7.88 (d, *J* = 8.0 Hz, 2 H), 7.77-7.72 (m, 4 H), 7.56 (s, 1 H), 7.32 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.03, 149.99, 147.07, 142.78, 141.61, 133.44, 131.78, 131.26, 130.54, 129.35, 128.76, 128.67, 125.05, 123.71, 123.45. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{13}N_3O_4$: 370.0804, Found: 370.0816.



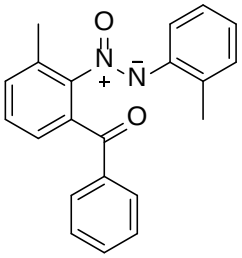
3am: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12-8.11 (d, *J* = 4.0 Hz, 3 H), 7.57-7.56 (d, *J* = 4.0 Hz, 2 H), 7.49-7.46 (t, *J* = 8.0 Hz, 2 H), 7.42-7.41 (d, *J* = 4.0 Hz, 2 H), 2.75-2.71 (t, *J* = 8.0 Hz, 2 H), 1.74-1.69 (m, 2 H), 0.94-0.91 (t, *J* = 8.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.03, 146.19, 143.47, 136.74, 131.18, 130.25, 130.18, 128.74, 127.34, 125.35, 123.46, 44.88, 17.68, 13.67. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{16}H_{16}N_2O_2$: 291.1109, Found: 291.1123.



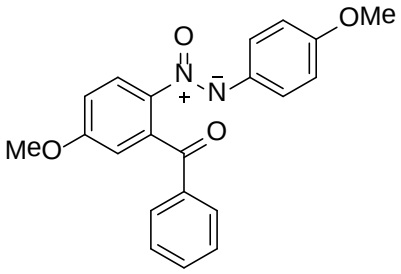
3ba: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14-8.12 (d, *J* = 8.0 Hz, 1 H), 7.77-7.75 (d, *J* = 8.0 Hz, 2 H), 7.66-7.64 (d, *J* = 8.0 Hz, 2 H), 7.46-7.41 (m, 2 H), 7.36-7.32 (t, *J* = 8.0 Hz, 2 H), 7.28 (s, 1 H), 7.09-7.07 (d, *J* = 8.0 Hz, 2 H). 2.47 (s, 3 H), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.27, 144.81, 142.01, 140.88, 140.37, 136.97, 134.50, 132.89, 130.89, 129.02, 128.69, 128.40, 125.04, 123.07, 21.47, 21.20. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{21}H_{18}N_2O_2$: 353.1266, Found: 353.1277.



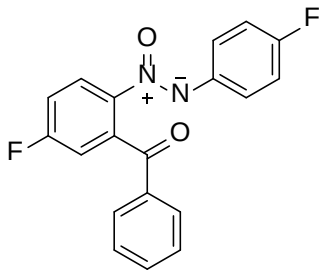
3ca: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (s, 1 H), 7.76-7.74 (m, 2 H), 7.47-7.41 (m, 5 H), 7.36-7.33 (m, 2 H), 7.19-7.15 (t, *J* = 8.0 Hz, 1 H), 7.08-7.07 (d, *J* = 4.0 Hz, 1 H), 2.53 (s, 3 H), 2.28 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.12, 147.35, 143.14, 141.35, 138.14, 137.12, 132.85, 131.85, 131.83, 130.54, 128.89, 128.72, 128.39, 128.19, 125.23, 123.62, 121.88, 21.32, 21.26. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{21}H_{18}N_2O_2$: 353.1266, Found: 353.1269.



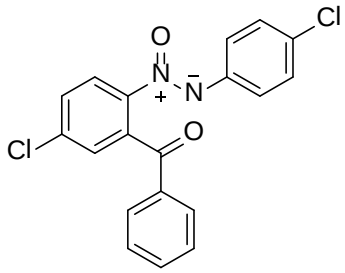
3da: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80-7.77 (m, 2 H), 7.63-7.61 (d, *J* = 8.0 Hz, 1 H), 7.53-7.36 (m, 6 H), 7.19-7.13 (m, 2 H), 7.10-7.06 (m, 1 H), 2.53 (s, 3 H), 2.21 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.12, 147.78, 142.02, 136.49, 135.05, 134.01, 133.82, 133.29, 131.91, 130.49, 129.68, 129.10, 128.89, 128.29, 127.25, 125.62, 121.08, 18.28, 18.05. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{21}H_{18}N_2O_2$: 353.1266, Found: 353.1267.



3ea: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23-8.20 (d, *J* = 12.0 Hz, 1 H), 7.85-7.83 (d, *J* = 8.0 Hz, 2 H), 7.78-7.77 (d, *J* = 4.0 Hz, 2 H), 7.46-7.44 (d, *J* = 8.0 Hz, 1 H), 7.37-7.33 (t, *J* = 8.0 Hz, 2 H), 7.11-7.09 (d, *J* = 12.0 Hz, 1 H), 6.94 (s, 1 H), 6.79-6.77 (d, *J* = 8.0 Hz, 2 H), 3.89 (s, 3 H), 3.79 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.83, 161.43, 160.35, 140.00, 137.03, 136.84, 136.15, 132.95, 128.67, 128.45, 127.27, 124.79, 115.56, 113.47, 113.08, 55.90, 55.36. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{21}H_{18}N_2O_4$: 385.1164, Found: 385.1166.

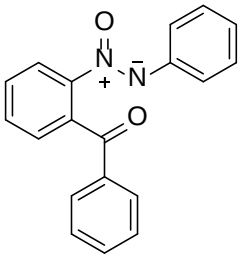


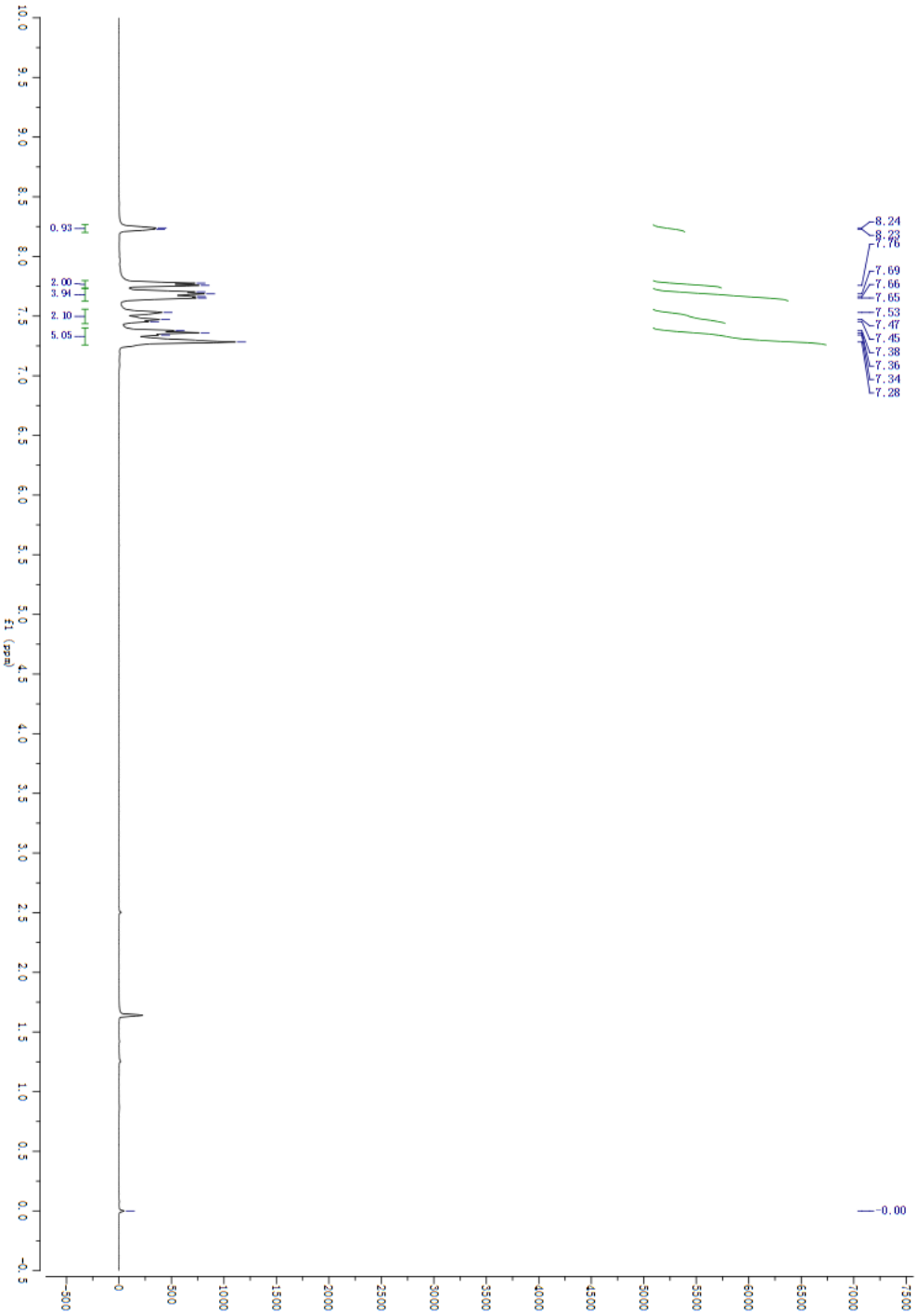
3fa: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28-8.26 (t, *J* = 4.0 Hz, 1 H), 7.80-7.75 (m, 4 H), 7.52-7.49 (m, 1 H), 7.41-7.32 (m, 3 H), 7.22-7.20 (d, *J* = 8.0 Hz, 1 H), 7.00-6.96 (t, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.33, 163.69 (d, *J* = 254.0 Hz), 162.67 (d, *J* = 252.0 Hz), 142.93, 139.39, 137.02 (d, *J* = 7.0 Hz), 136.21, 133.44, 128.71 (d, *J* = 9.0 Hz), 127.49 (d, *J* = 8.0 Hz), 125.76 (d, *J* = 9.0 Hz), 117.29 (d, *J* = 22.0 Hz), 115.92 (d, *J* = 24.0 Hz), 115.52 (d, *J* = 23.0 Hz). HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{12}F_2N_2O_2$: 361.0765, Found: 361.0769.

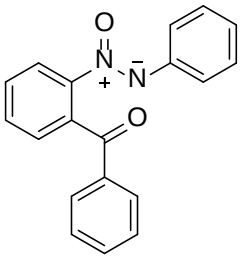


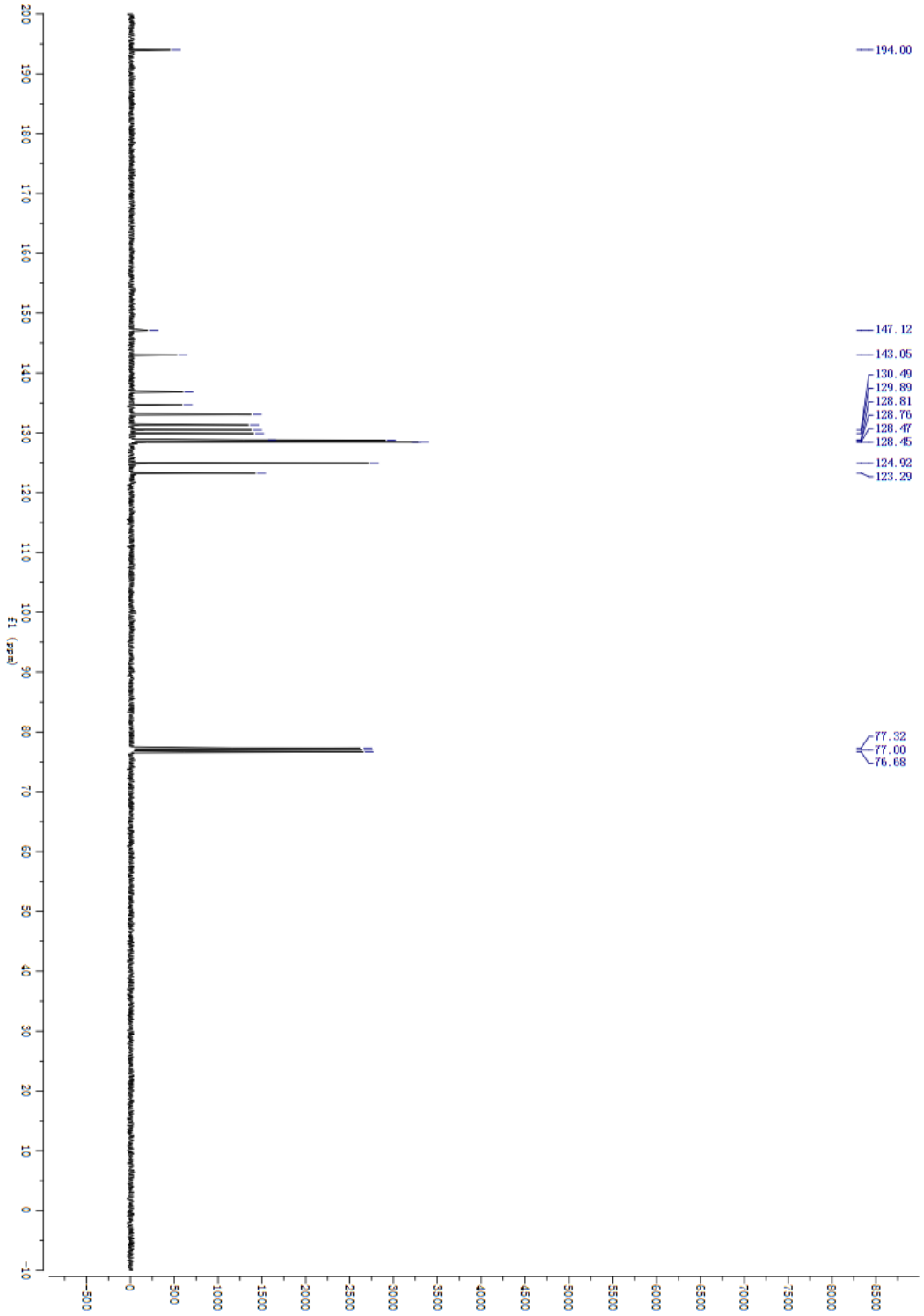
3ga: Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21-8.19 (d, *J* = 8.0 Hz, 1 H), 7.77-7.75 (d, *J* = 8.0 Hz, 2 H), 7.71-7.69 (d, *J* = 8.0 Hz, 2 H), 7.63-7.61 (d, *J* = 8.0 Hz, 1 H), 7.51-7.49 (d, *J* = 8.0 Hz, 2 H), 7.41-7.38 (m, 2 H), 7.28-7.26 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.30, 145.16, 141.28, 137.93, 136.22, 136.13, 135.61, 133.49, 130.44, 128.77, 128.73, 128.68, 126.47, 124.76. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{12}Cl_2N_2O_2$: 393.0173, Found: 393.0173.

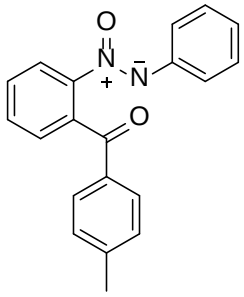
3. NMR Charts

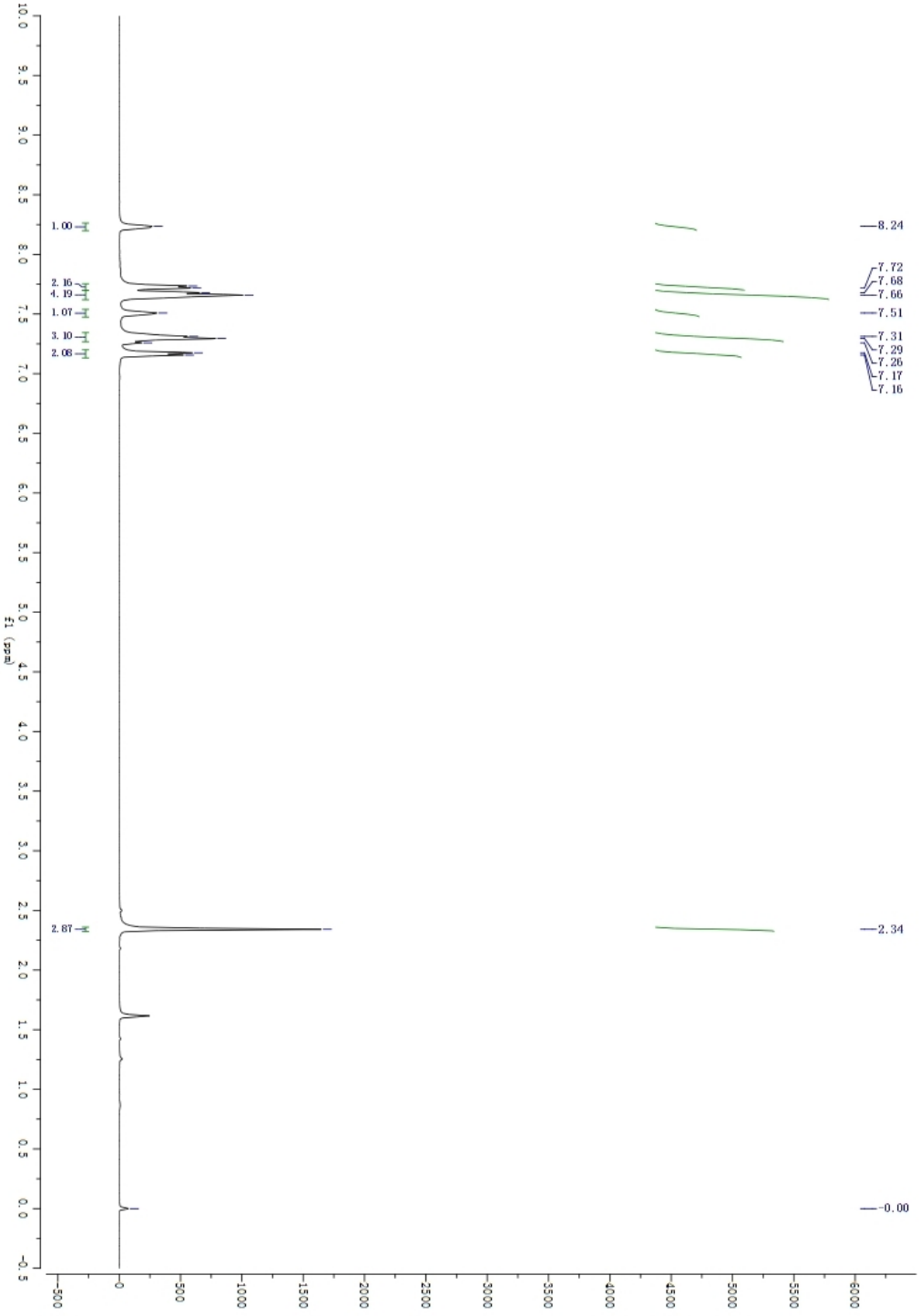


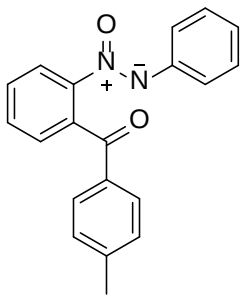

0.93
2.00
3.94
2.10
5.05
8.24
8.23
7.76
7.69
7.66
7.65
7.53
7.47
7.45
7.38
7.36
7.34
7.28
0.00
f1 (ppm)

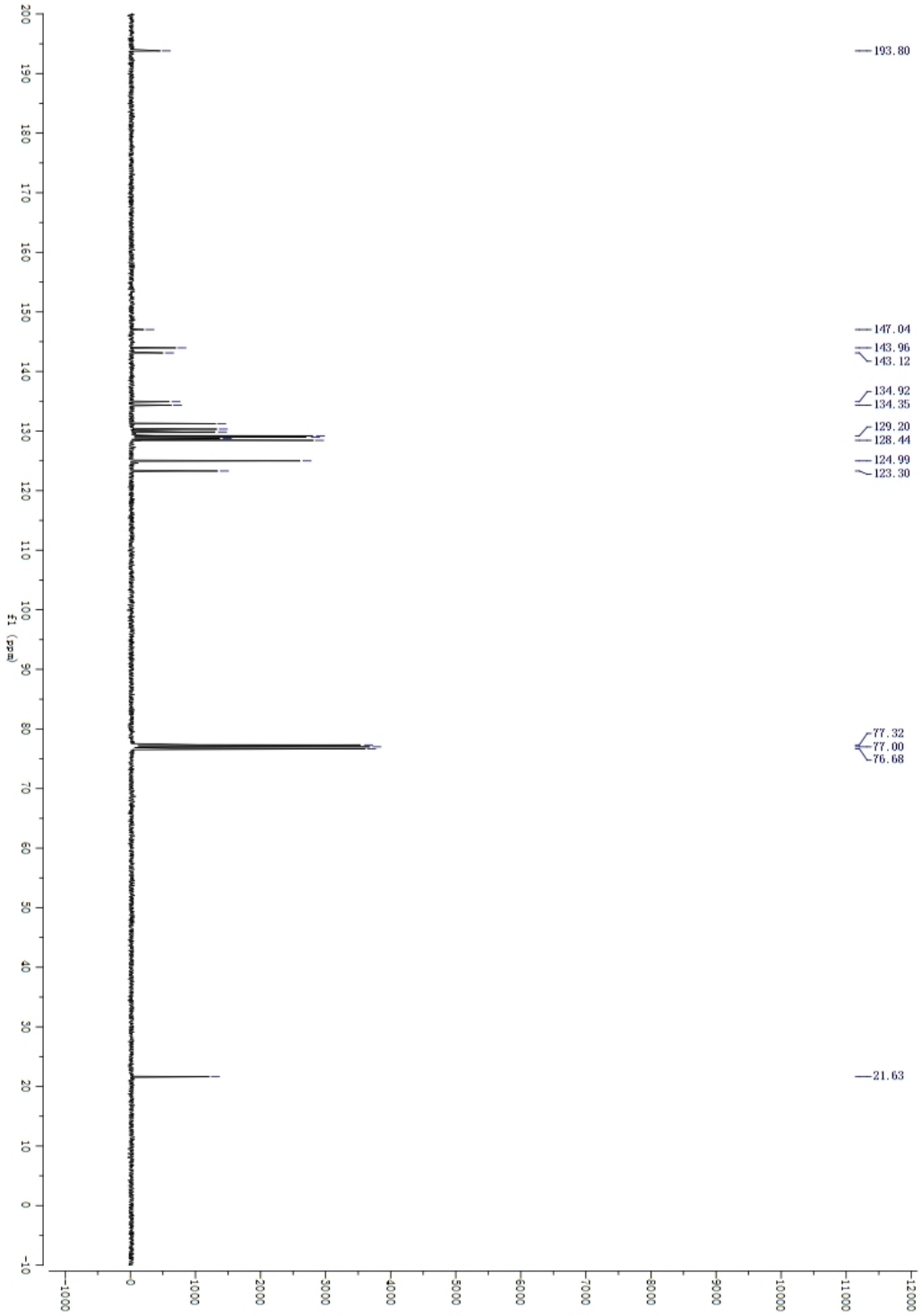

O
N
+
N
−
O

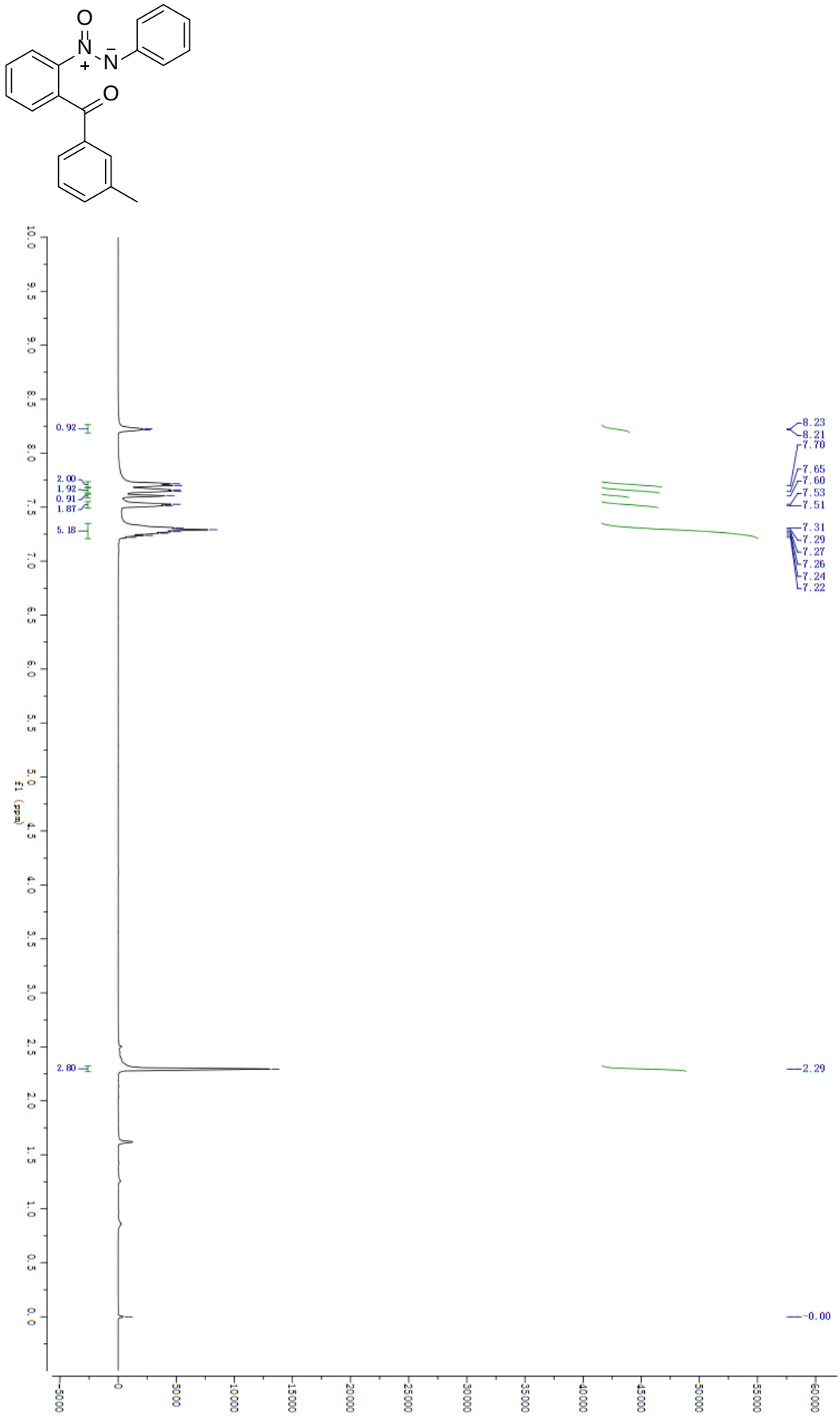

194.00
147.12
143.05
130.49
129.89
128.81
128.76
128.47
128.45
124.92
123.29
77.32
77.00
76.68
f1 (ppm)

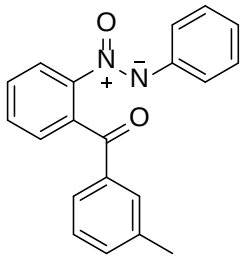


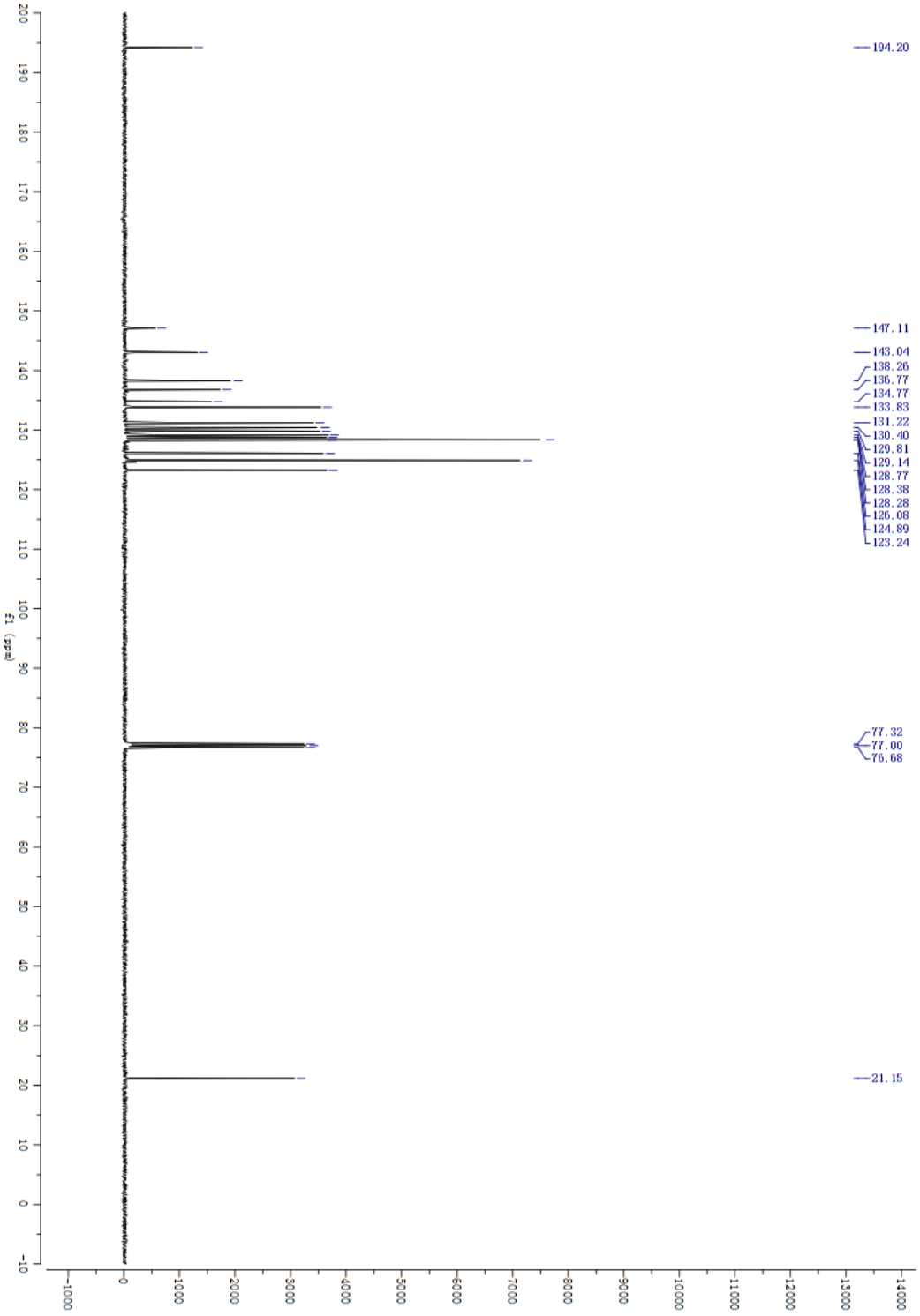

1.00
2.16
4.19
1.07
3.10
2.08
2.87
8.24
7.72
7.68
7.66
7.51
7.31
7.29
7.26
7.17
7.16
2.34
0.00
f1 (ppm)




193.80
147.04
143.96
143.12
134.92
134.35
129.20
128.44
124.99
123.30
77.32
77.00
76.68
21.63
f1 (ppm)


O
N
N
O
0.92
2.00
1.92
0.91
1.87
5.18
2.80
8.23
8.21
7.70
7.65
7.60
7.53
7.51
7.31
7.29
7.27
7.26
7.24
7.22
2.29
0.00
f1 (ppm)




194.20
147.11
143.04
138.26
136.77
134.77
133.83
131.22
130.40
129.81
129.14
128.77
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126.08
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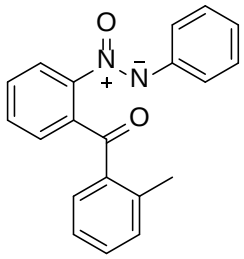
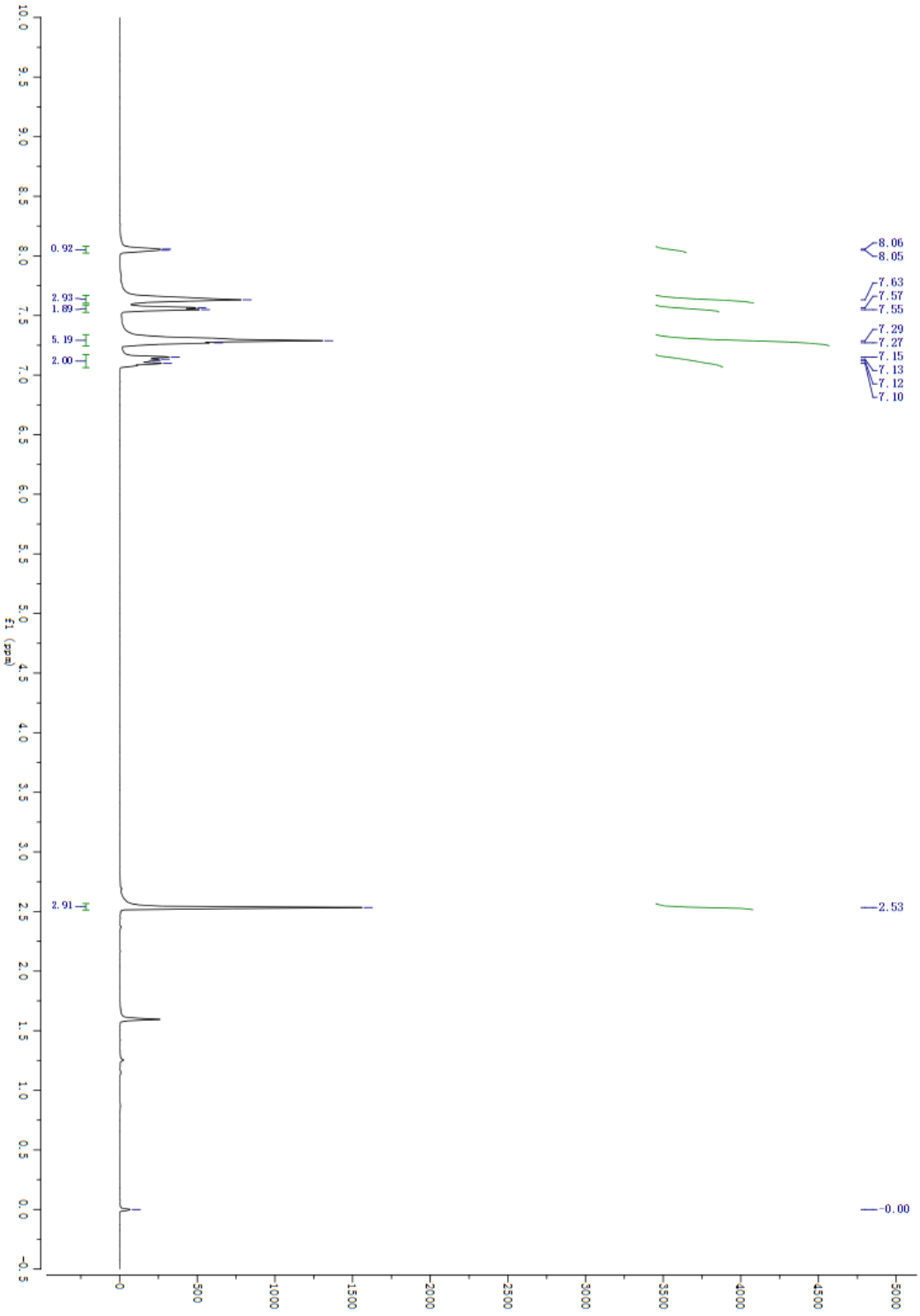
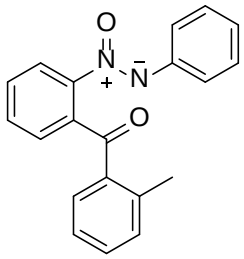
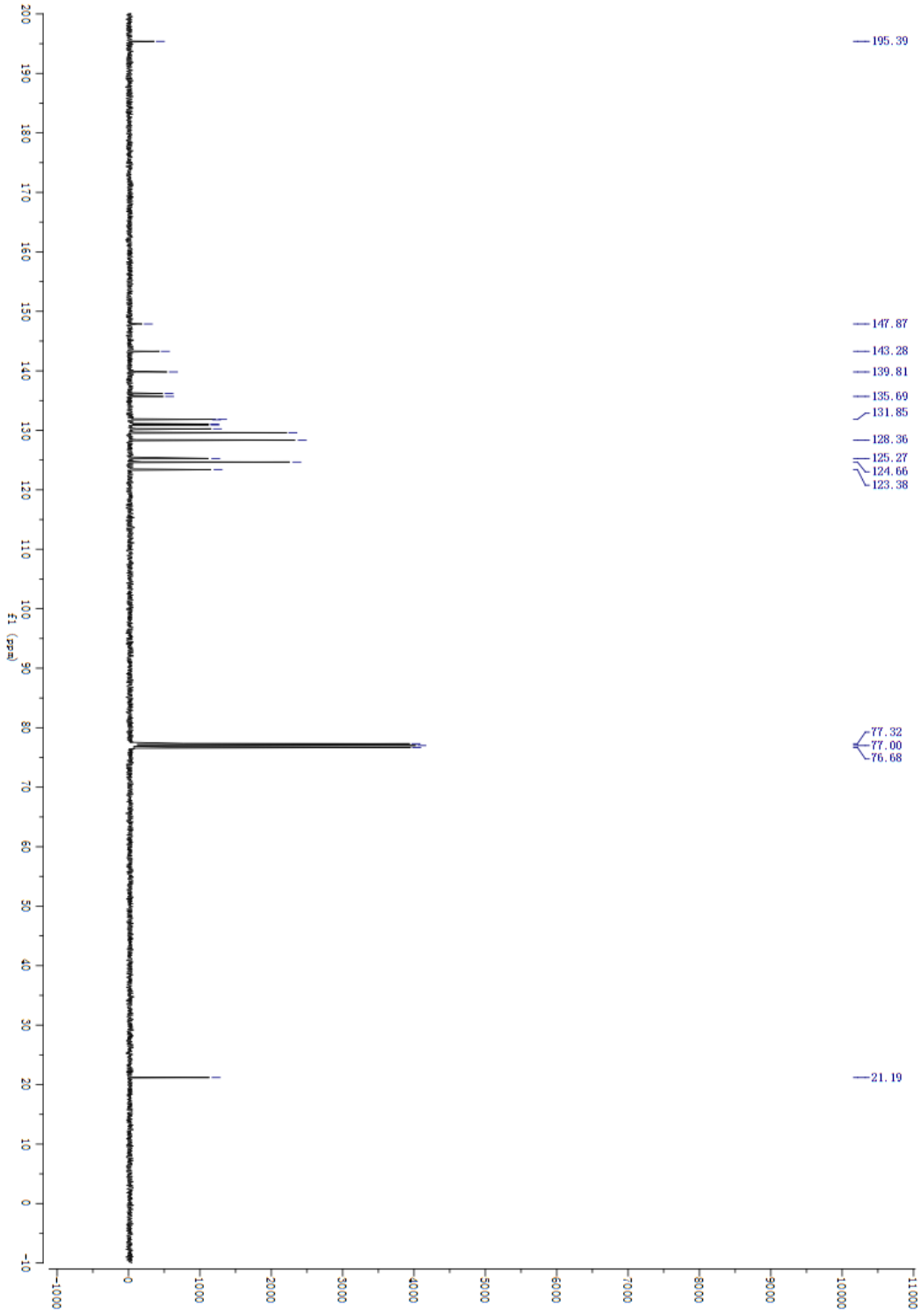
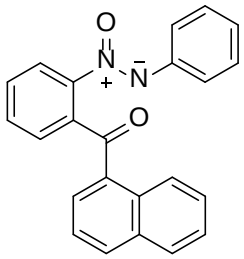
123.24
77.32
77.00
76.68
21.15
f1 (ppm)

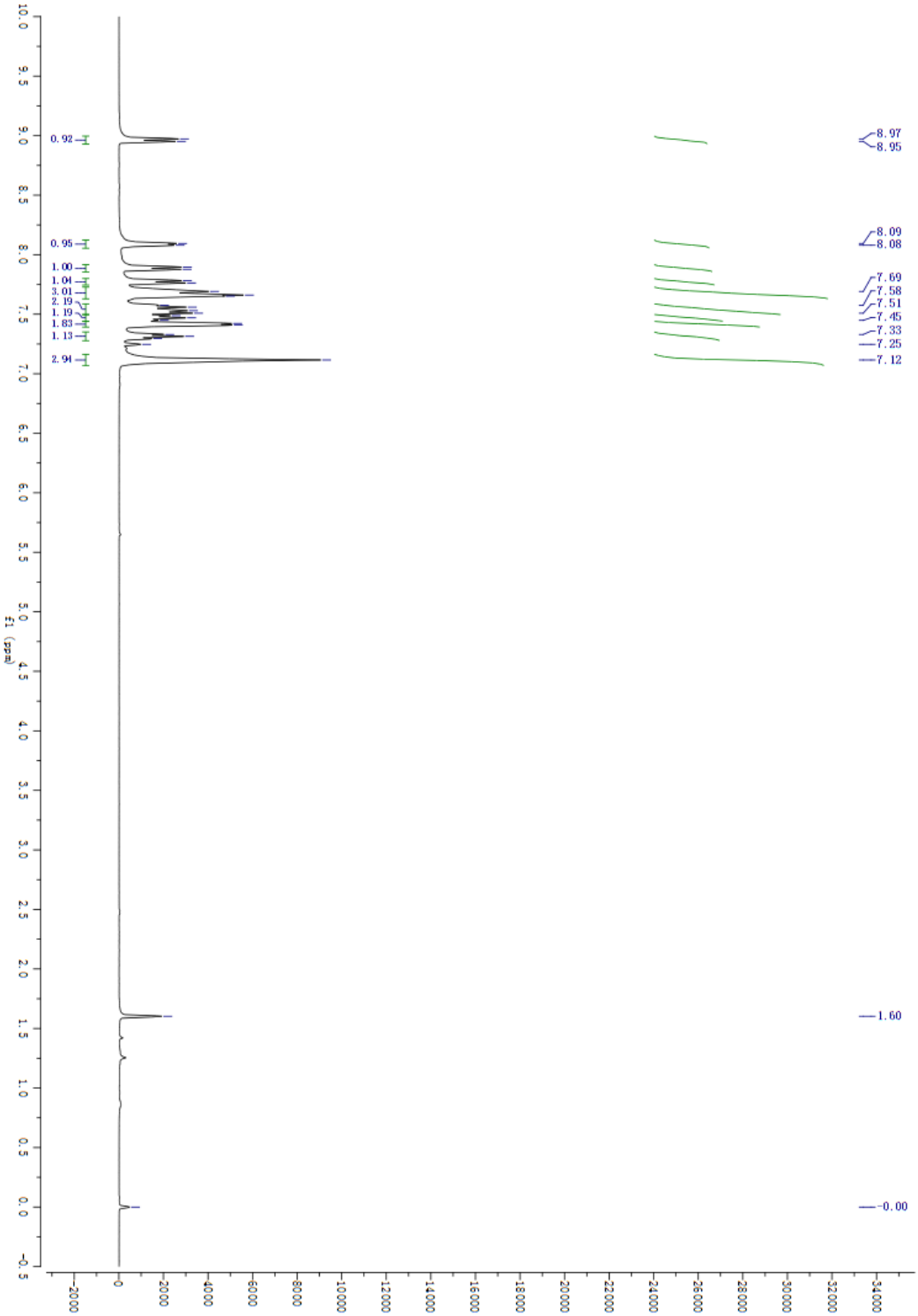


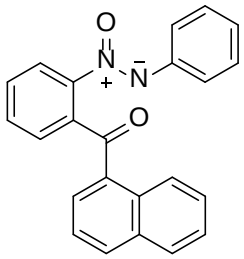

0.92
2.93
1.89
5.19
2.00
2.91
8.06
8.05
7.63
7.57
7.55
7.29
7.27
7.15
7.13
7.12
7.10
2.53
0.00
f1 (ppm)

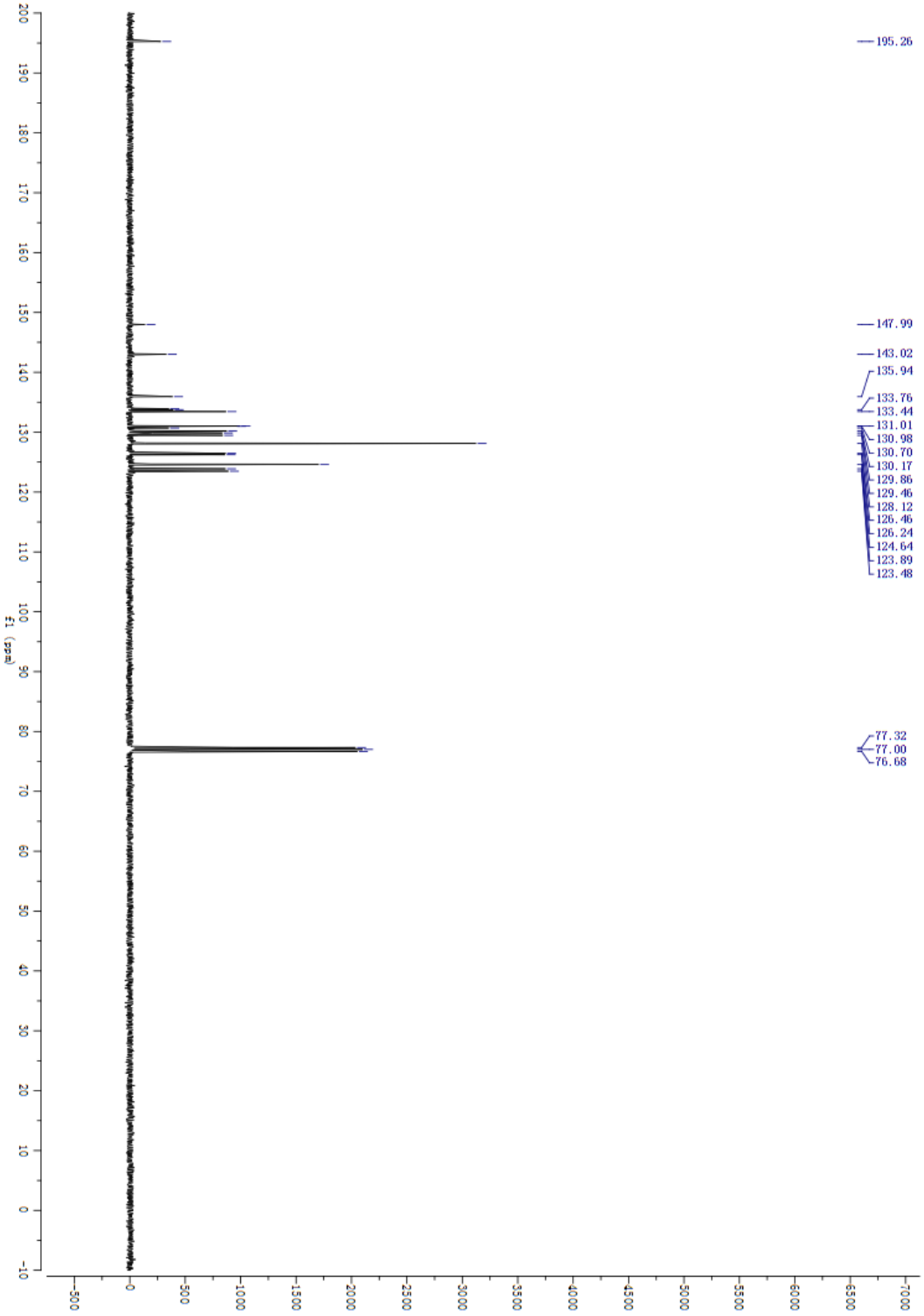

O
N
+
N
−
O


195.39
147.87
143.28
139.81
135.69
131.85
128.36
125.27
124.66
123.38
77.32
77.00
76.68
21.19
f1 (ppm)




0.92
0.95
1.00
1.04
3.01
2.19
1.19
1.83
1.13
2.94
8.97
8.95
8.09
8.08
7.69
7.58
7.51
7.45
7.33
7.25
7.12
1.60
0.00
f1 (ppm)




195.26
147.99
143.02
135.94
133.76
133.44
131.01
130.98
130.70
130.17
129.86
129.46
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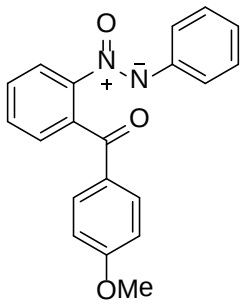
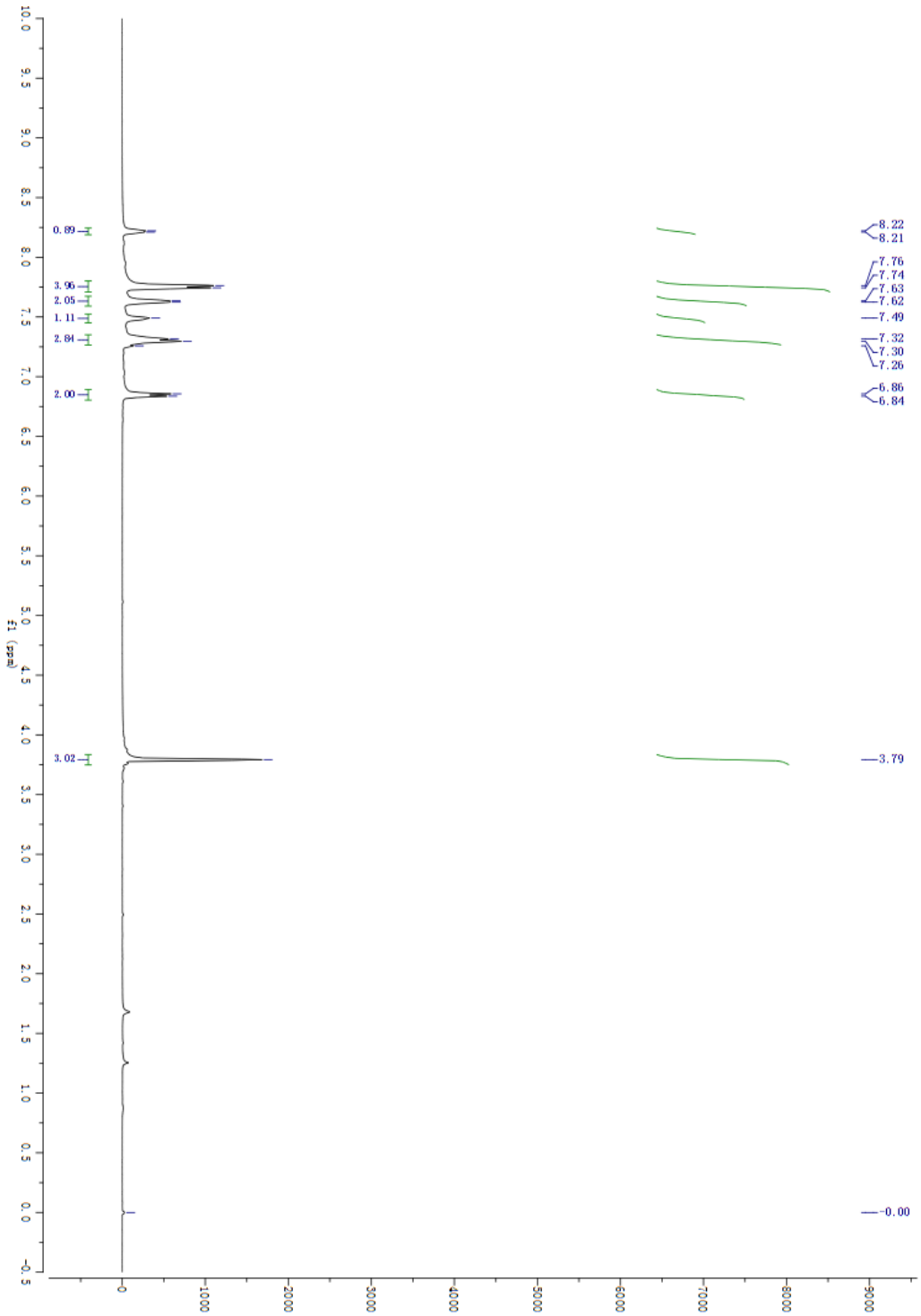
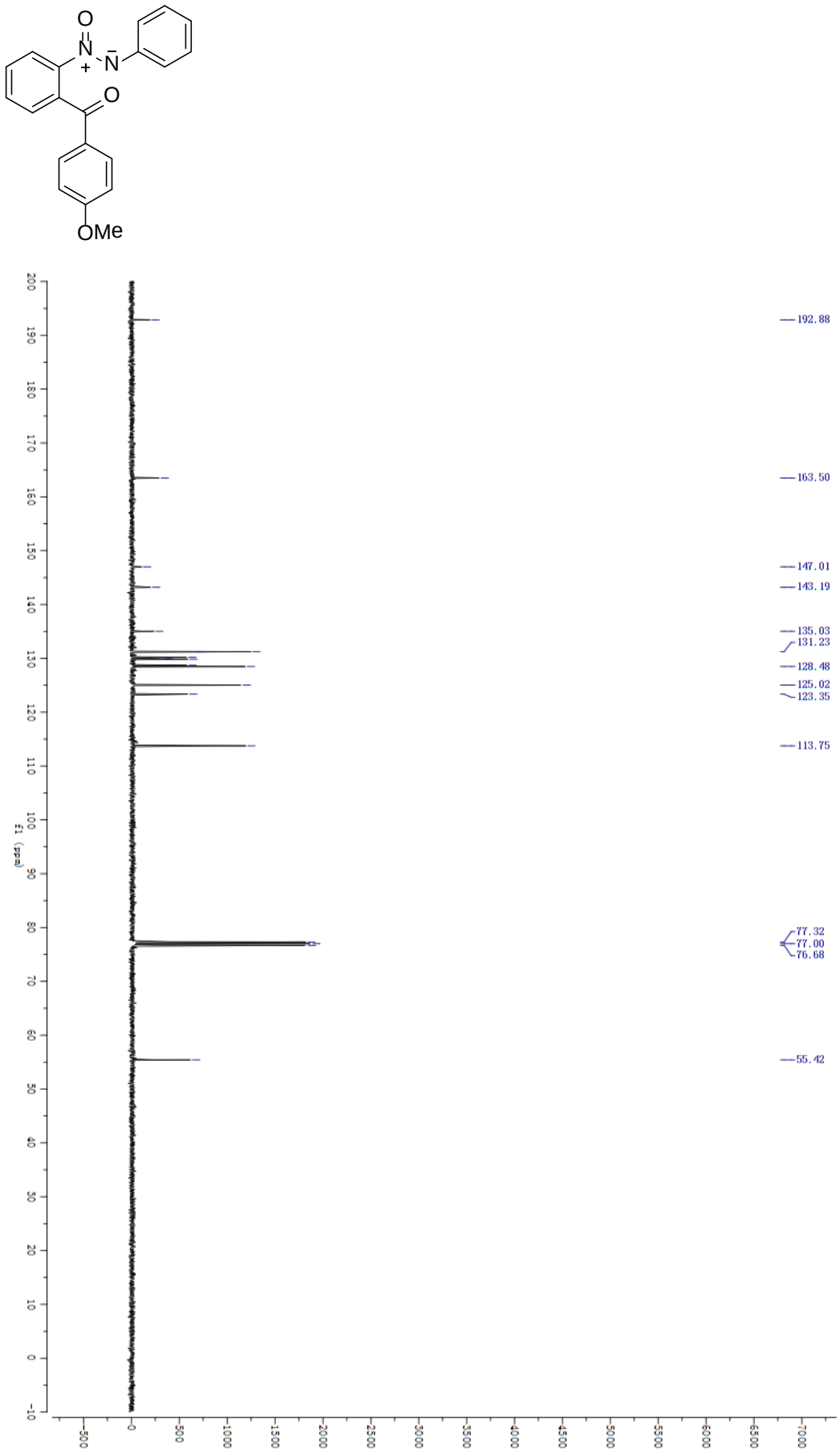
123.89
123.48
77.32
77.00
76.68
f1 (ppm)


O
N
N
O
OMe


0.89
3.96
2.05
1.11
2.84
2.00
3.02
8.22
8.21
7.76
7.74
7.63
7.62
7.49
7.32
7.30
7.26
6.86
6.84
3.79
0.00
f1 (ppm)


O
N
N
O
OMe
192.88
163.50
147.01
143.19
135.03
131.23
128.48
125.02
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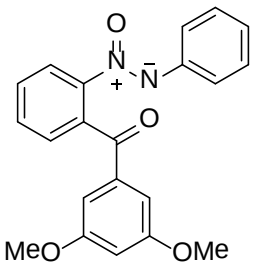
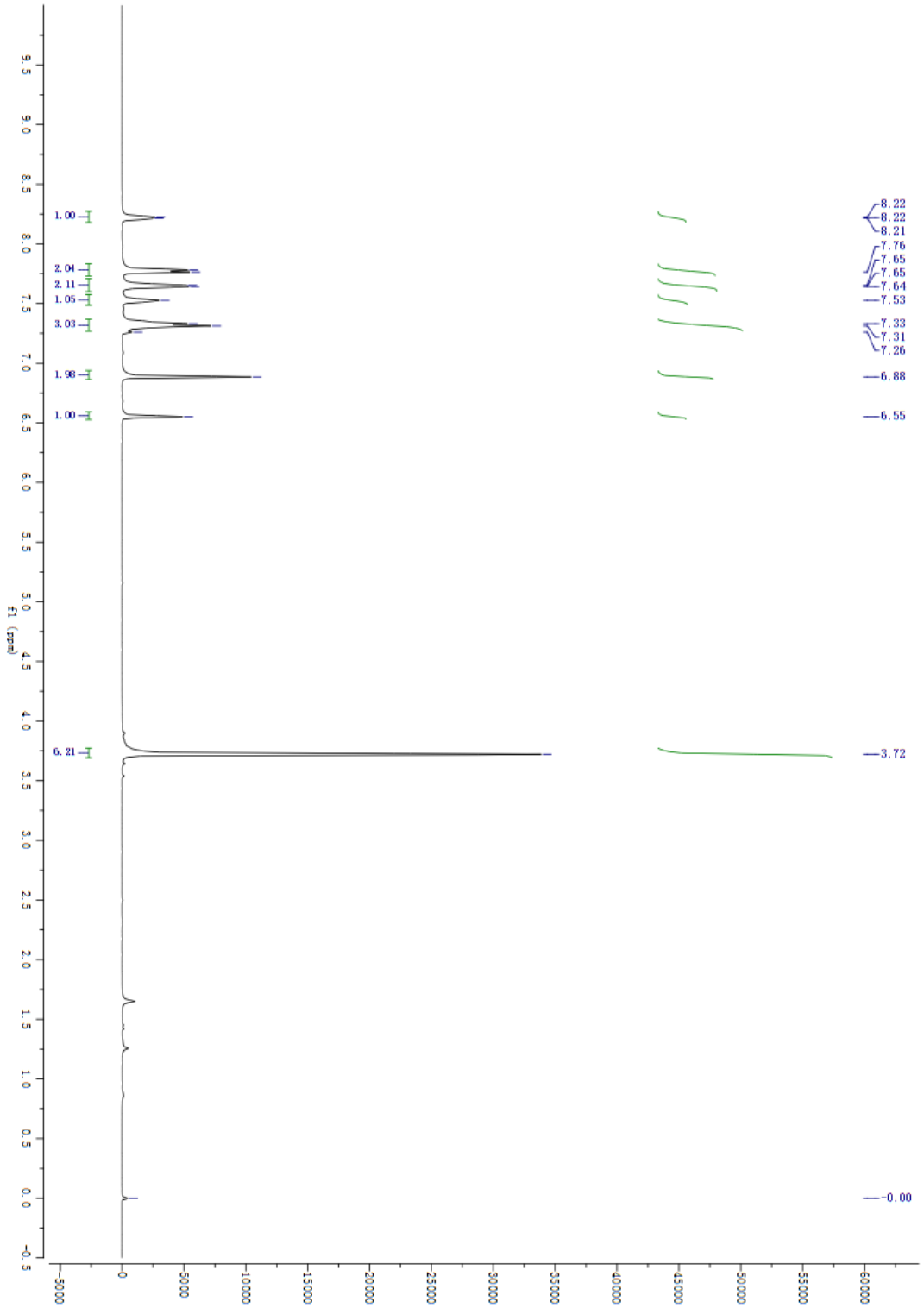
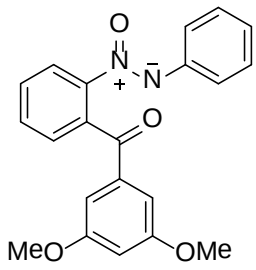
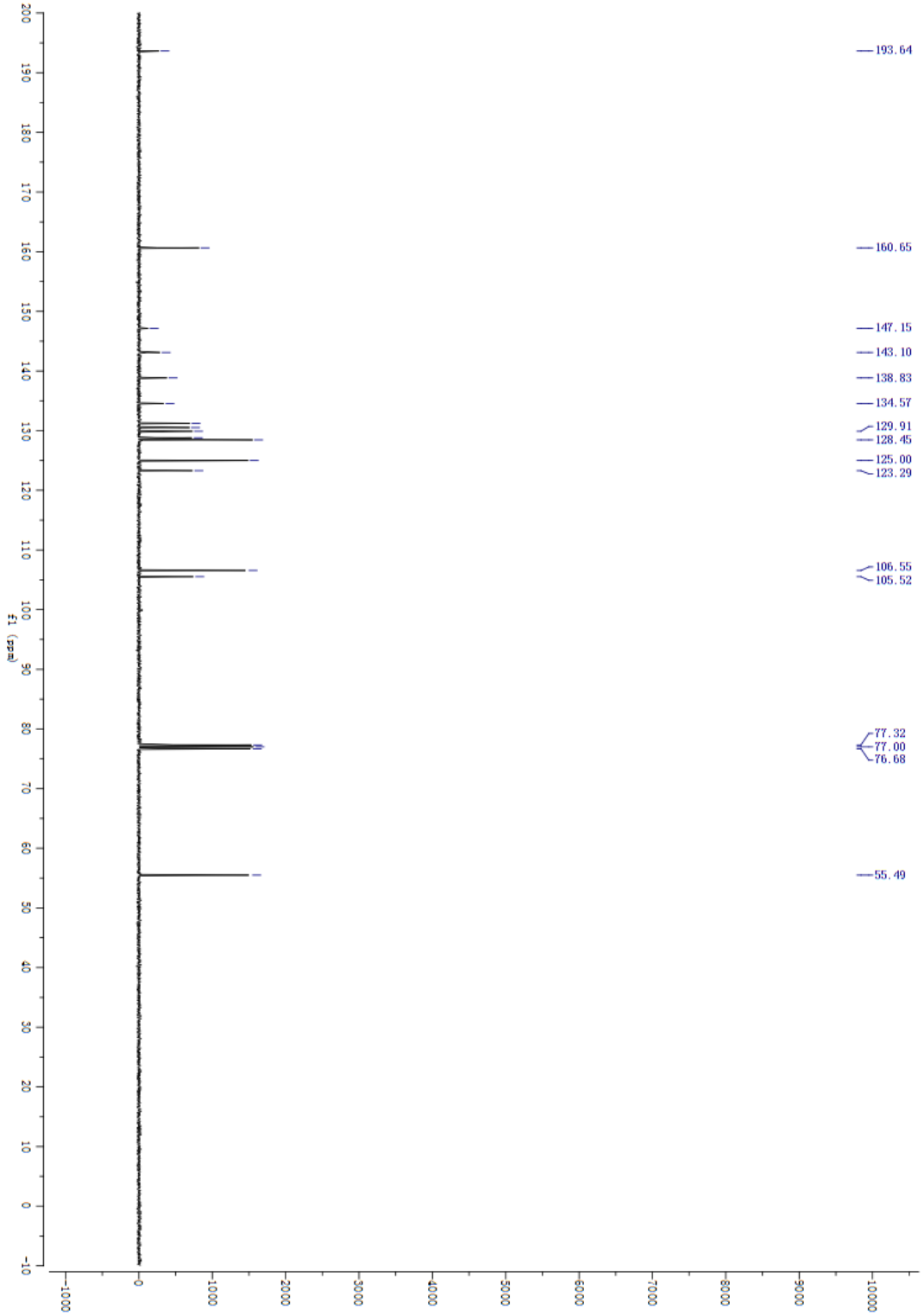
113.75
77.32
77.00
76.68
55.42
f1 (ppm)


O
N
N
O
MeO
OMe


1.00
2.04
2.11
1.05
3.03
1.98
1.00
6.21
8.22
8.22
8.21
7.76
7.65
7.65
7.64
7.53
7.33
7.31
7.26
6.88
6.55
3.72
0.00
f1 (ppm)


O
N
+
N
O
MeO
OMe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160.65
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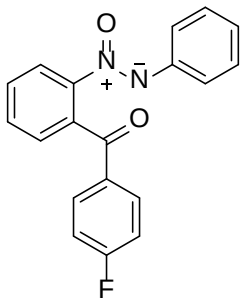
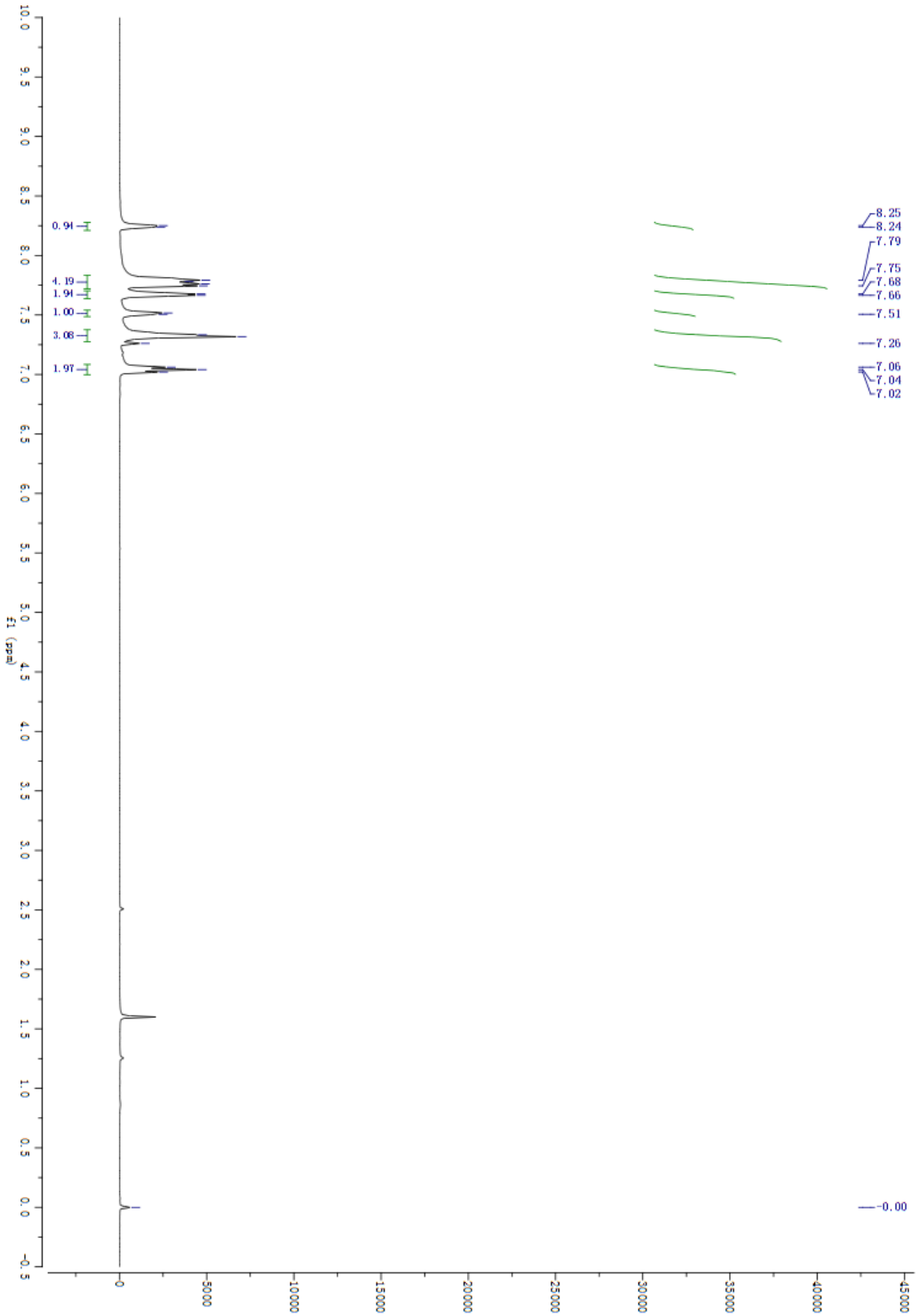
143.10
138.83
134.57
129.91
128.45
125.00
123.29
106.55
105.52
77.32
77.00
76.68
55.49
f1 (ppm)


O
N
N
O
F


0.94
4.19
1.94
1.00
3.08
1.97
8.25
8.24
7.79
7.75
7.68
7.66
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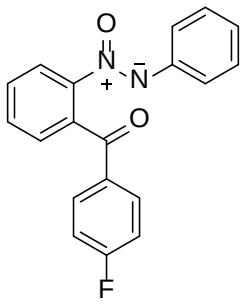
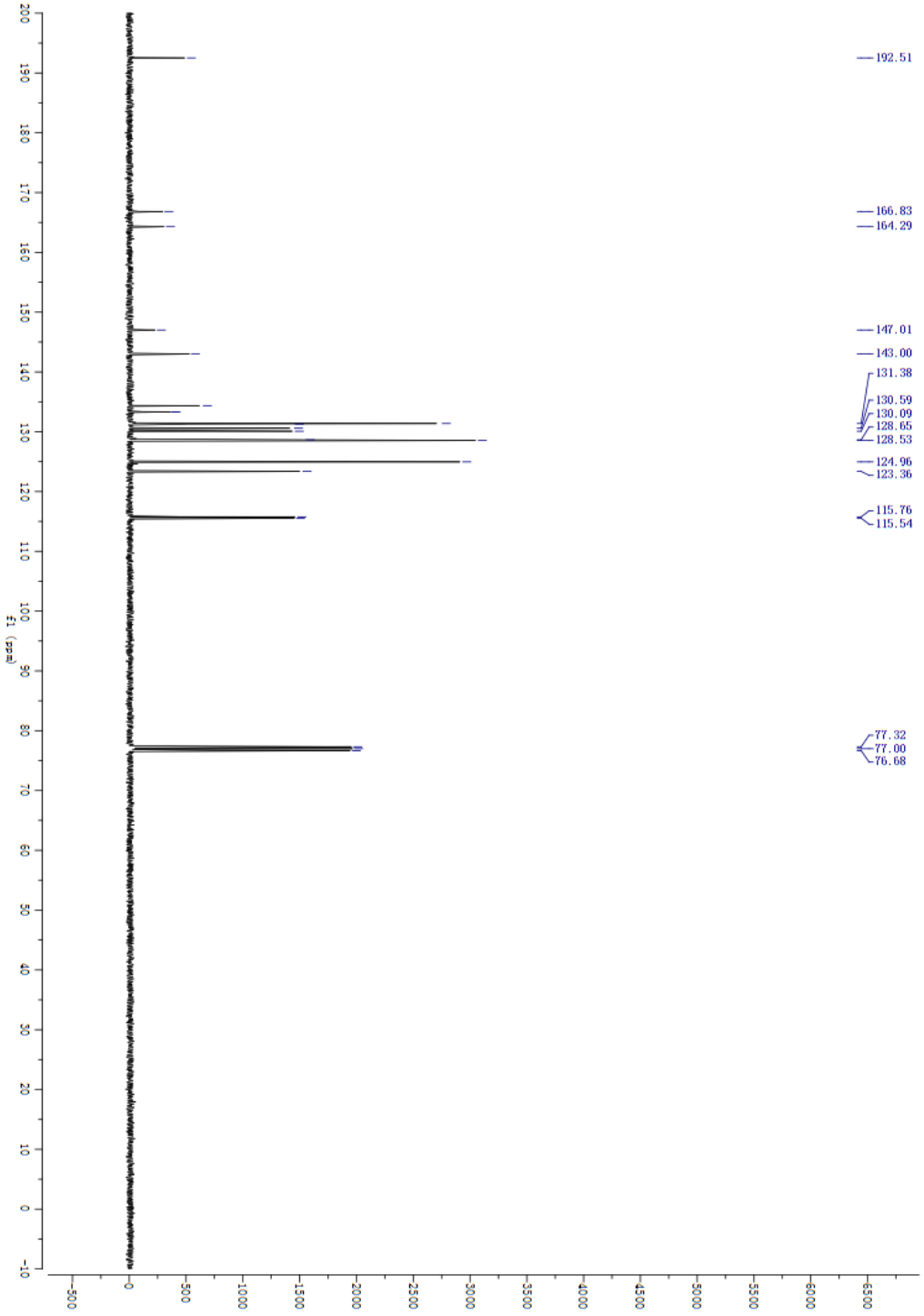
7.06
7.04
7.02
0.00
f1 (ppm)


O
N
+
N
O
F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166.83
164.29
147.01
143.00
131.38
130.59
130.09
128.65
128.53
124.96
123.36
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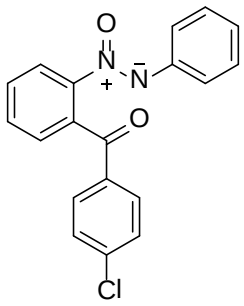
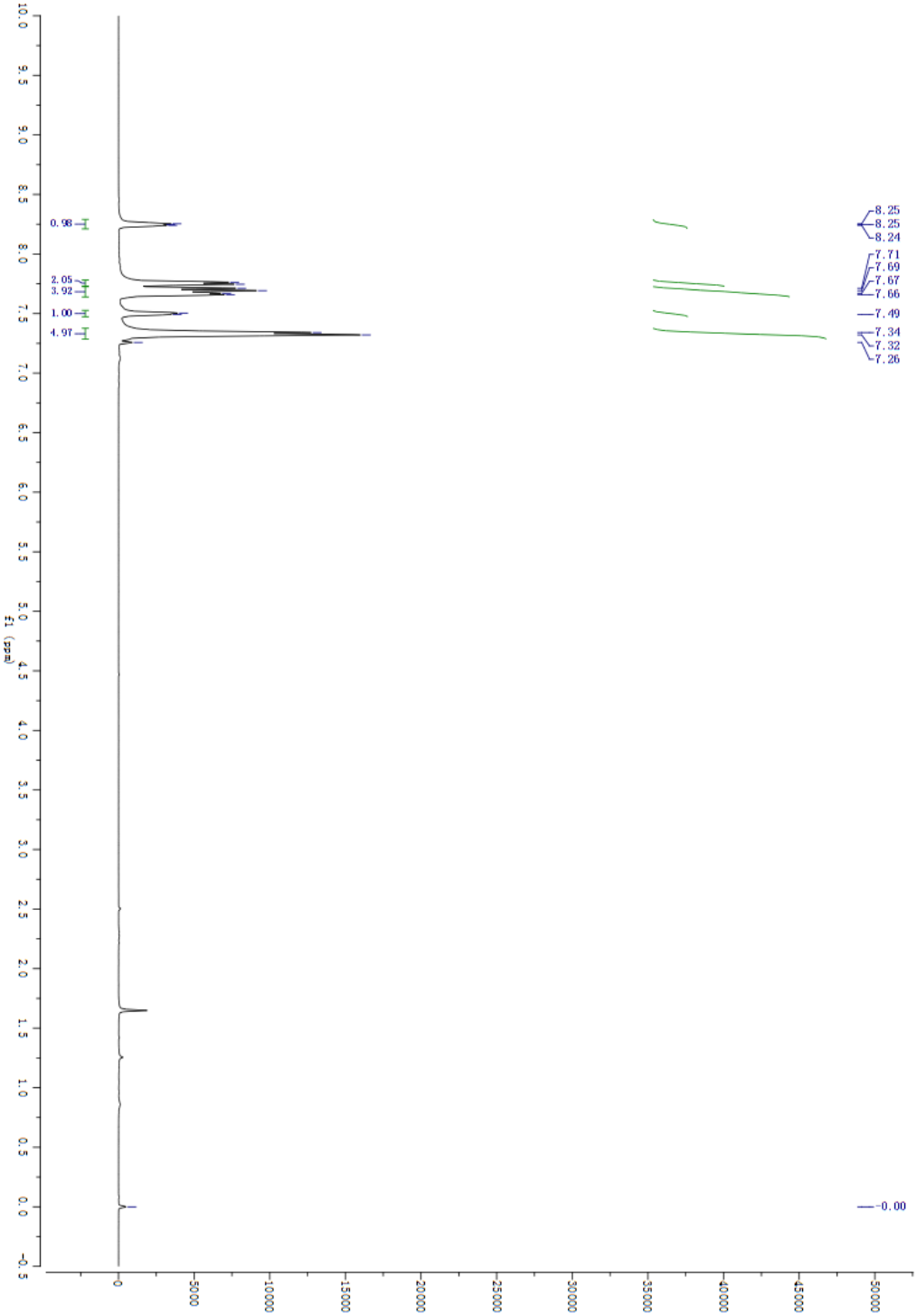
115.54
77.32
77.00
76.68
f1 (ppm)


O
N
N
O
Cl


0.98
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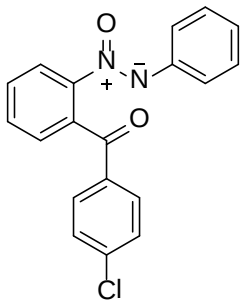
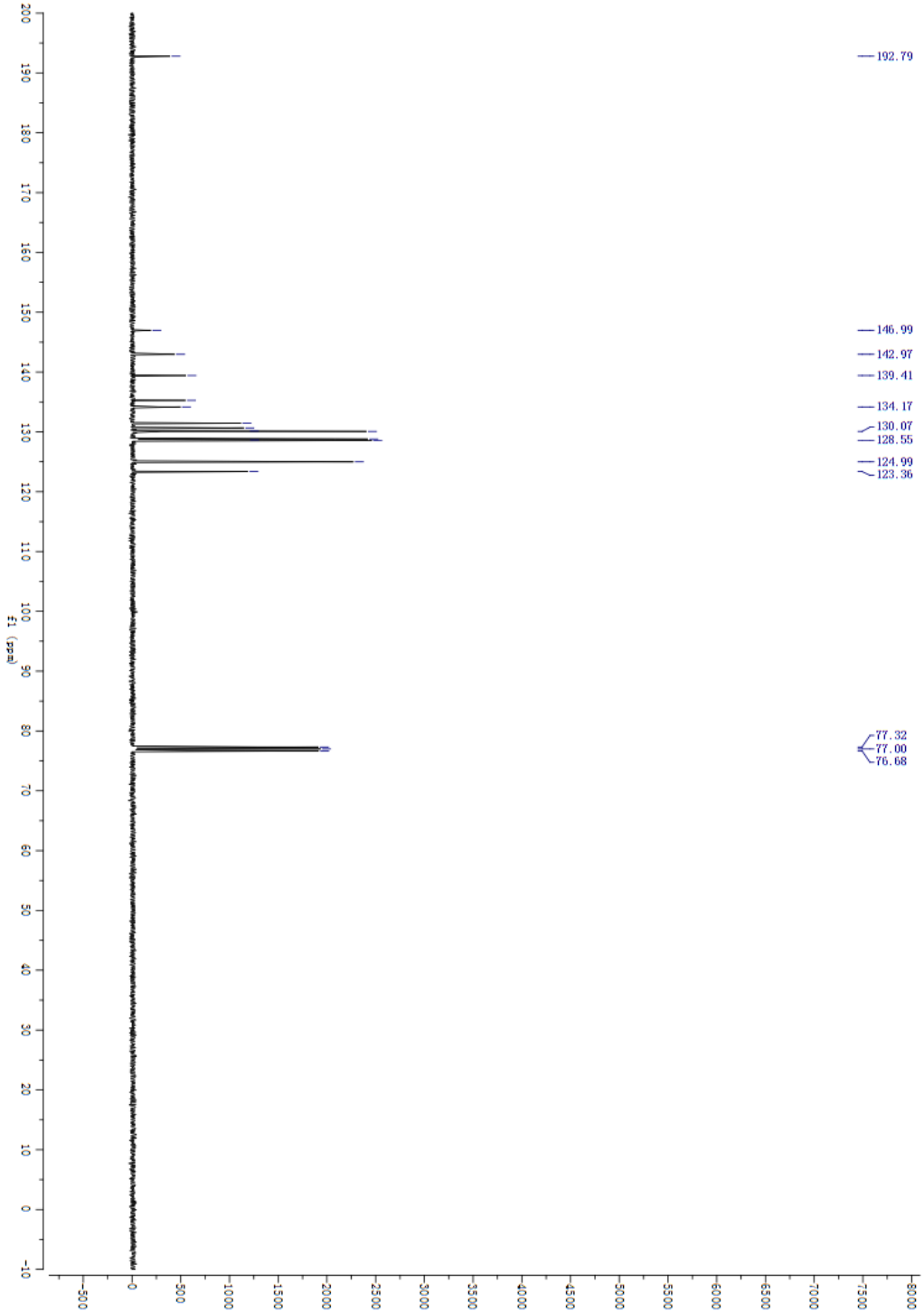
3.92
1.00
4.97
8.25
8.25
8.24
7.71
7.69
7.67
7.66
7.49
7.34
7.32
7.26
0.00
f1 (ppm)


O
N
N
O
Cl


192.79
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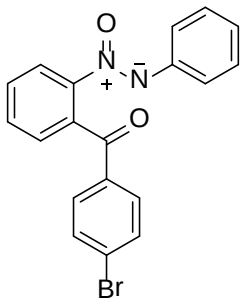
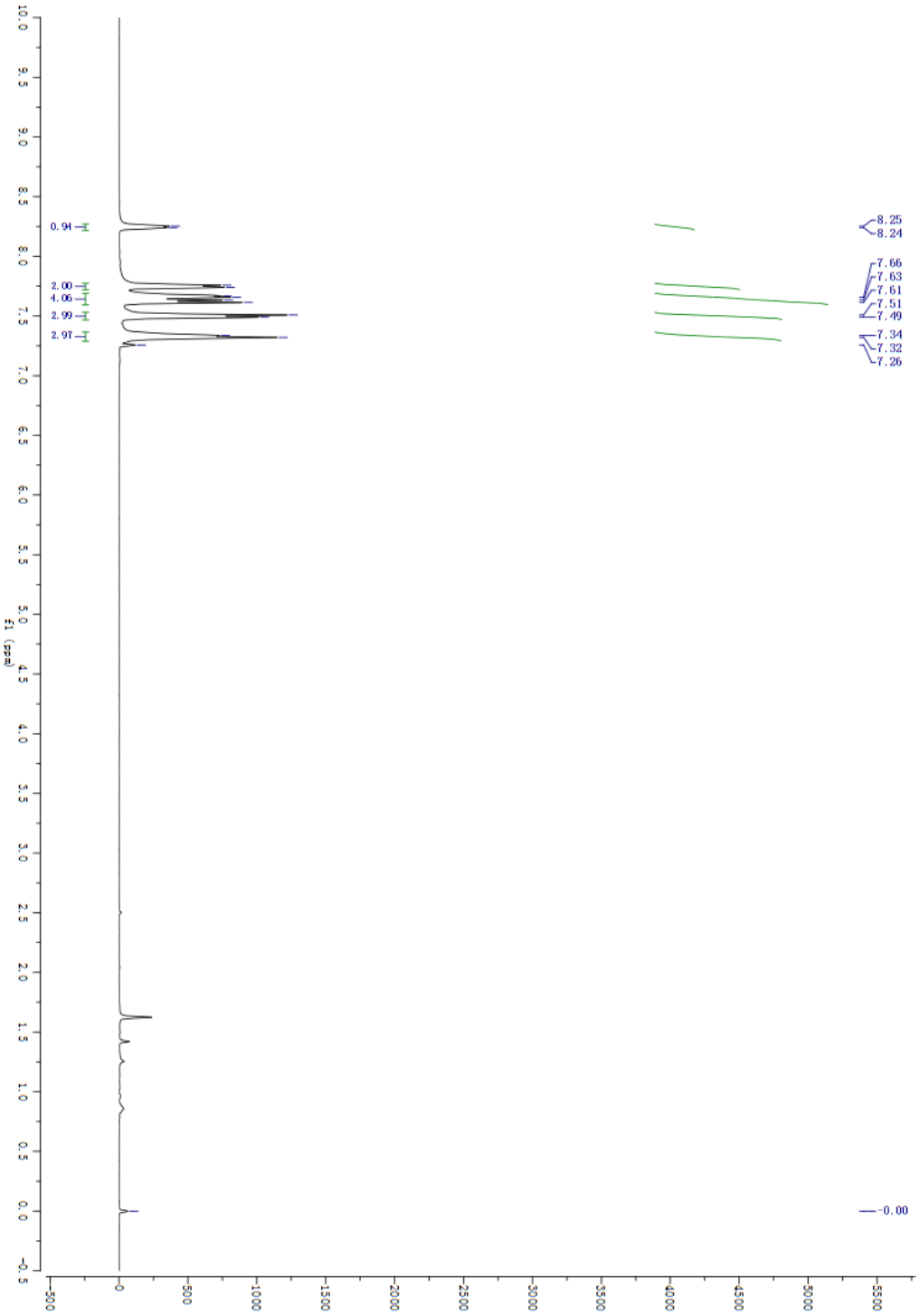
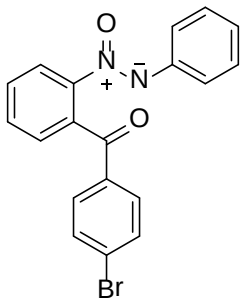
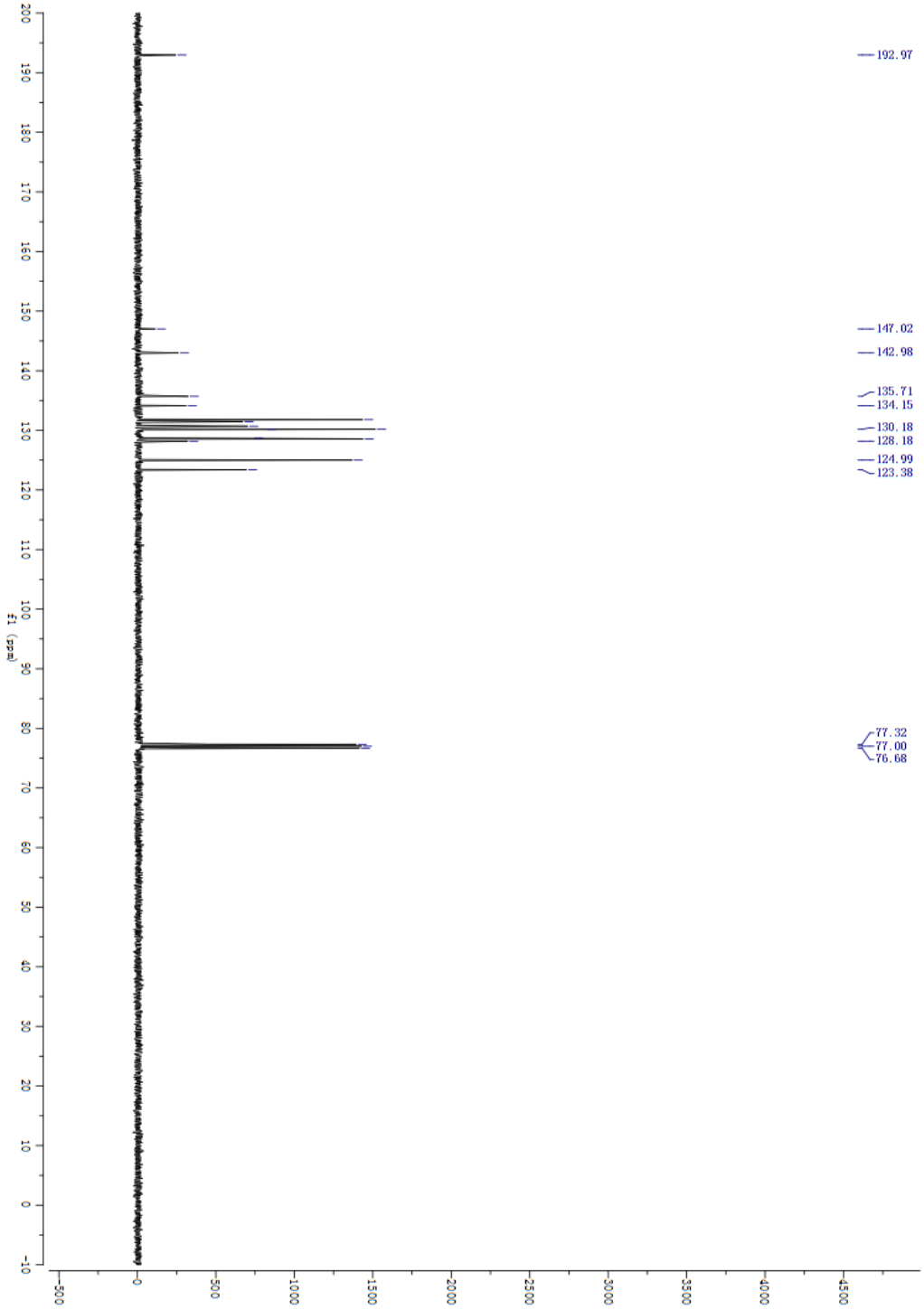
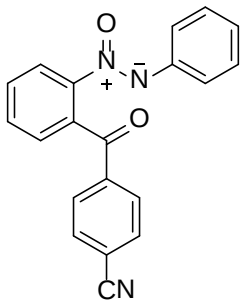
142.97
139.41
134.17
130.07
128.55
124.99
123.36
77.32
77.00
76.68
f1 (ppm)

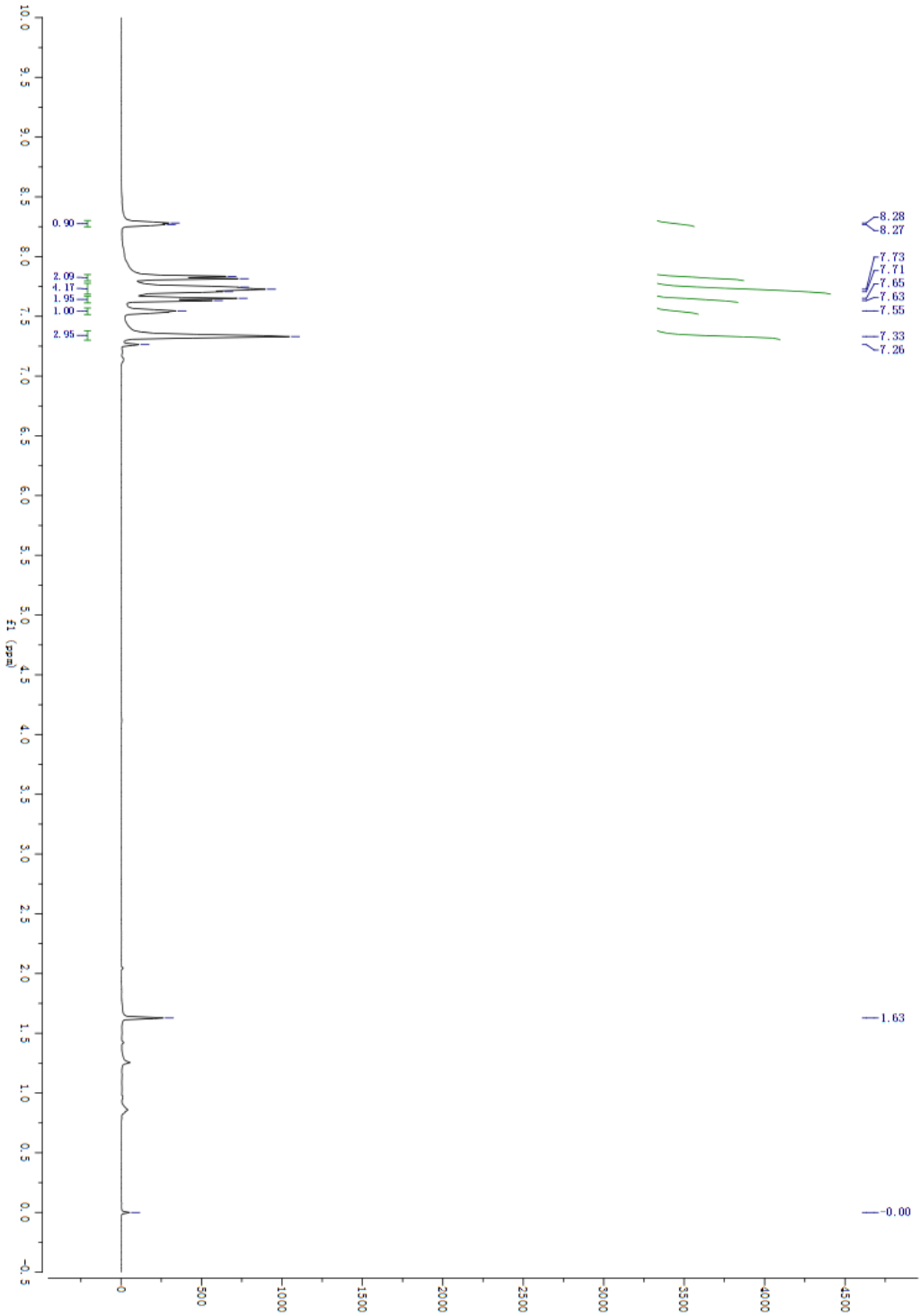

O
N
N
O
Br


0.94
2.00
4.06
2.99
2.97
8.25
8.24
7.66
7.63
7.61
7.51
7.49
7.34
7.32
7.26
0.00
f1 (ppm)


O
N
+
N
O
Br


192.97
147.02
142.98
135.71
134.15
130.18
128.18
124.99
123.38
77.32
77.00
76.68
f1 (ppm)


O
N
N
O
CN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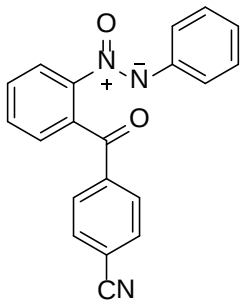
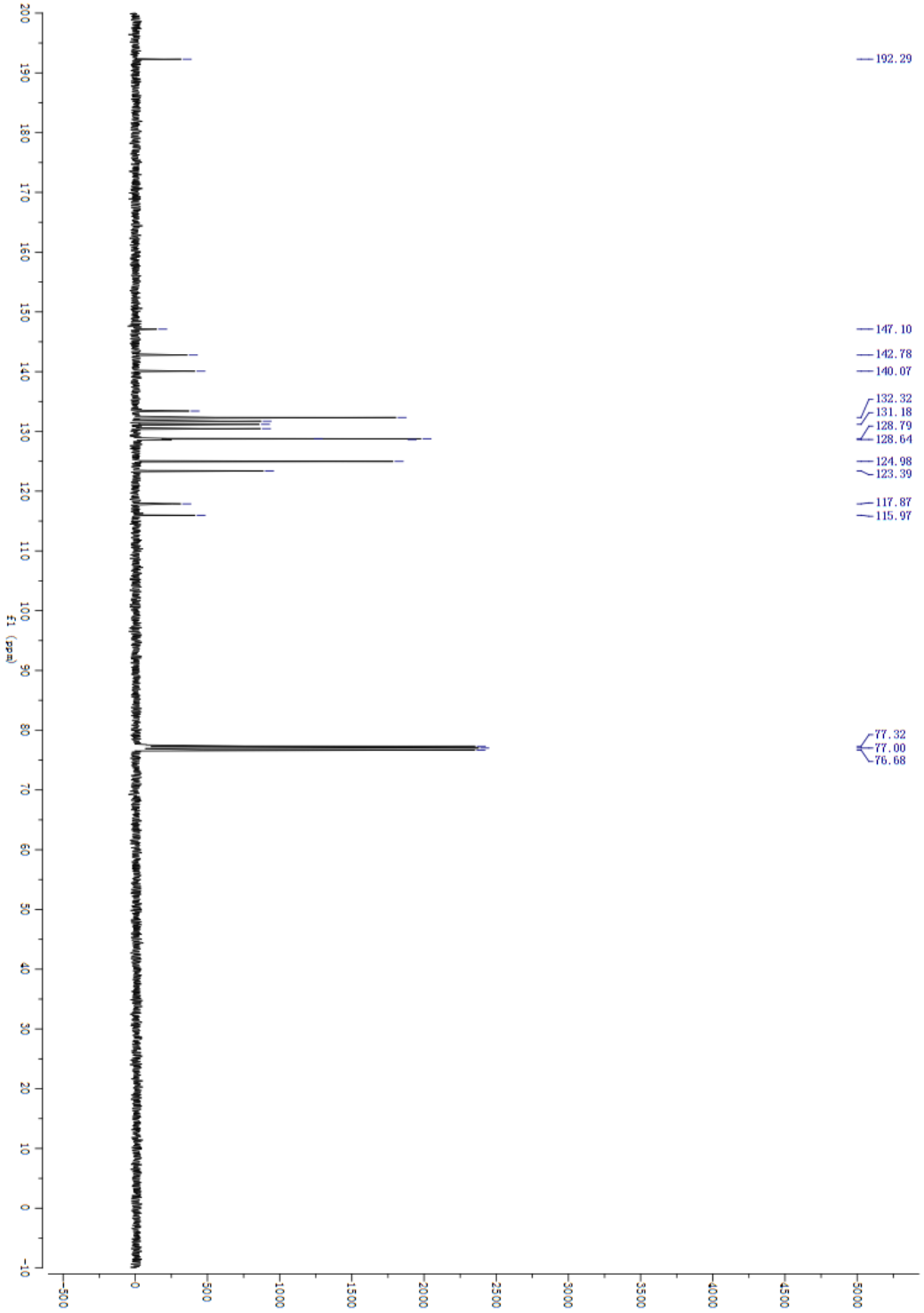
2.09
4.17
1.95
1.00
2.95
8.28
8.27
7.73
7.71
7.65
7.63
7.55
7.33
7.26
1.63
0.00
f1 (ppm)


O
N
+
N
O
CN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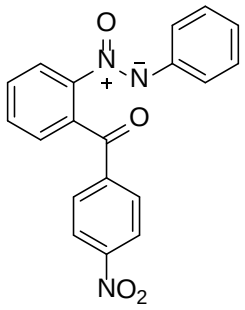
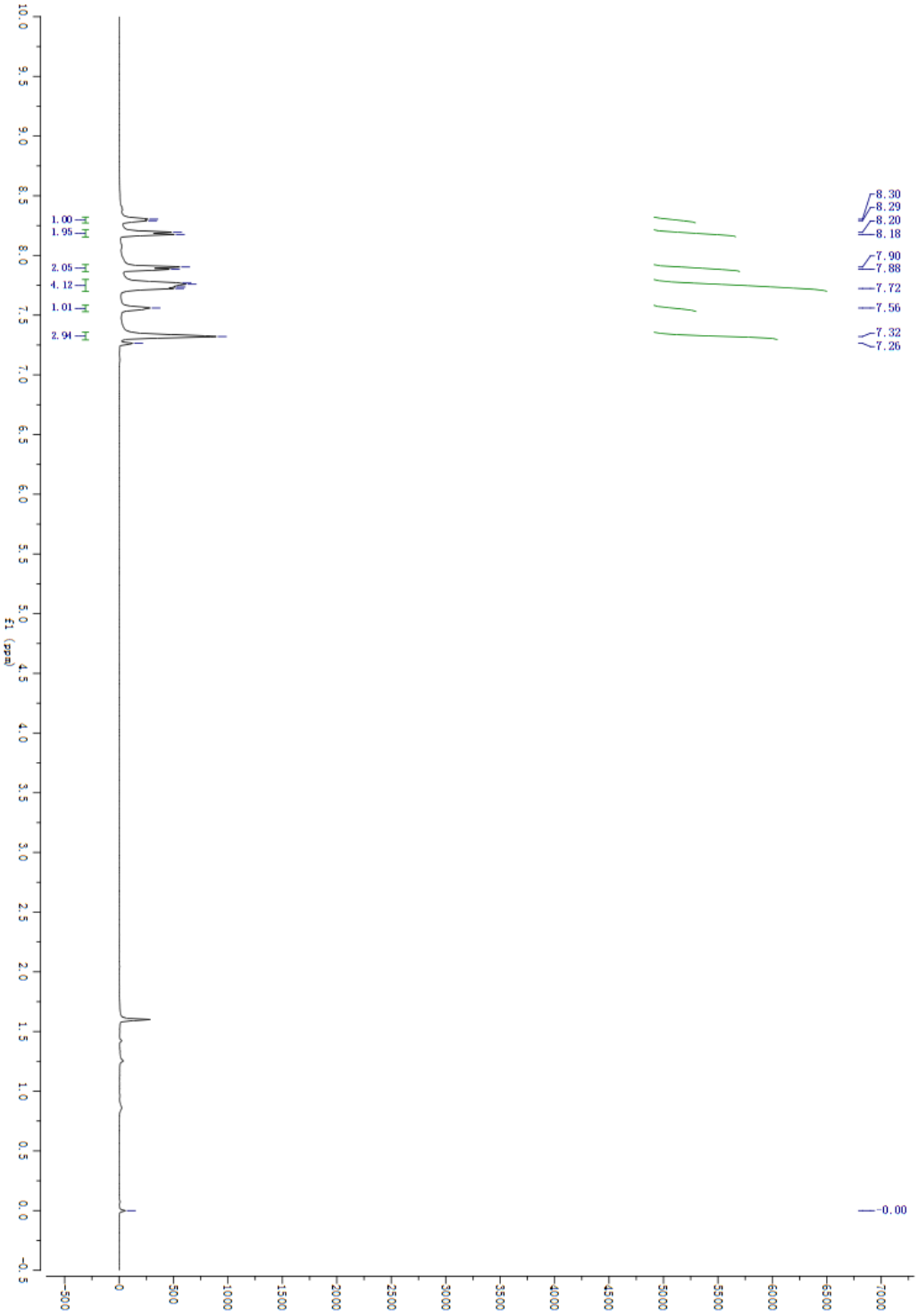
147.10
142.78
140.07
132.32
131.18
128.79
128.64
124.98
123.39
117.87
115.97
77.32
77.00
76.68
f1 (ppm)


O
N
+
N
O
NO2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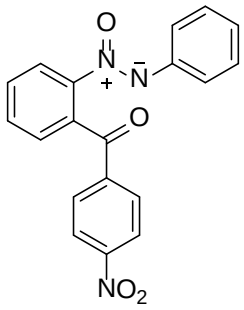
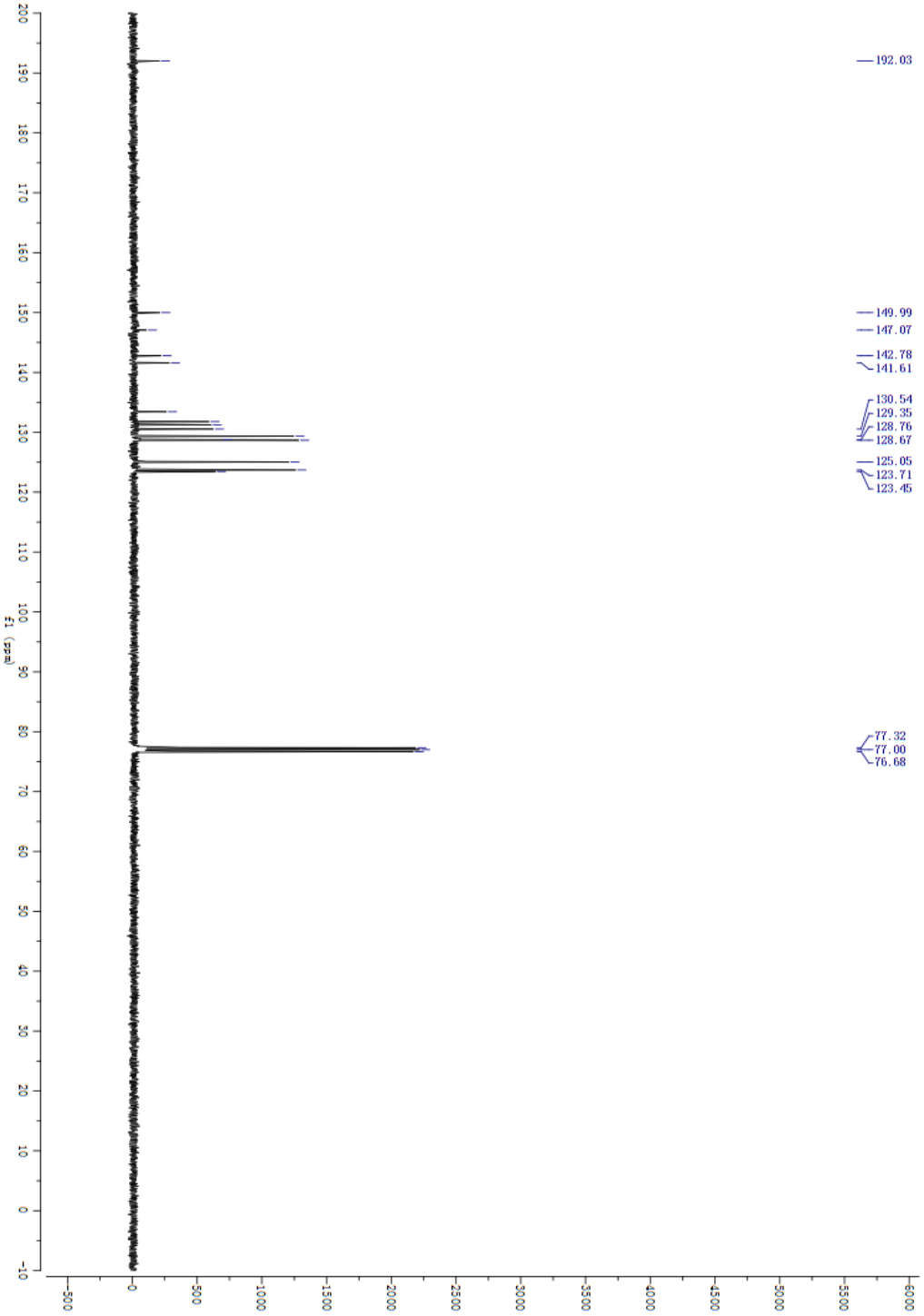
1.95
2.05
4.12
1.01
2.94
8.30
8.29
8.20
8.18
7.90
7.88
7.72
7.56
7.32
7.26
0.00
f1 (ppm)


O
N
+
N
O
NO2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147.07
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130.54
129.35
128.76
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125.05
123.71
123.45
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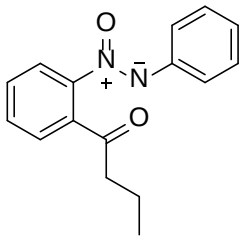
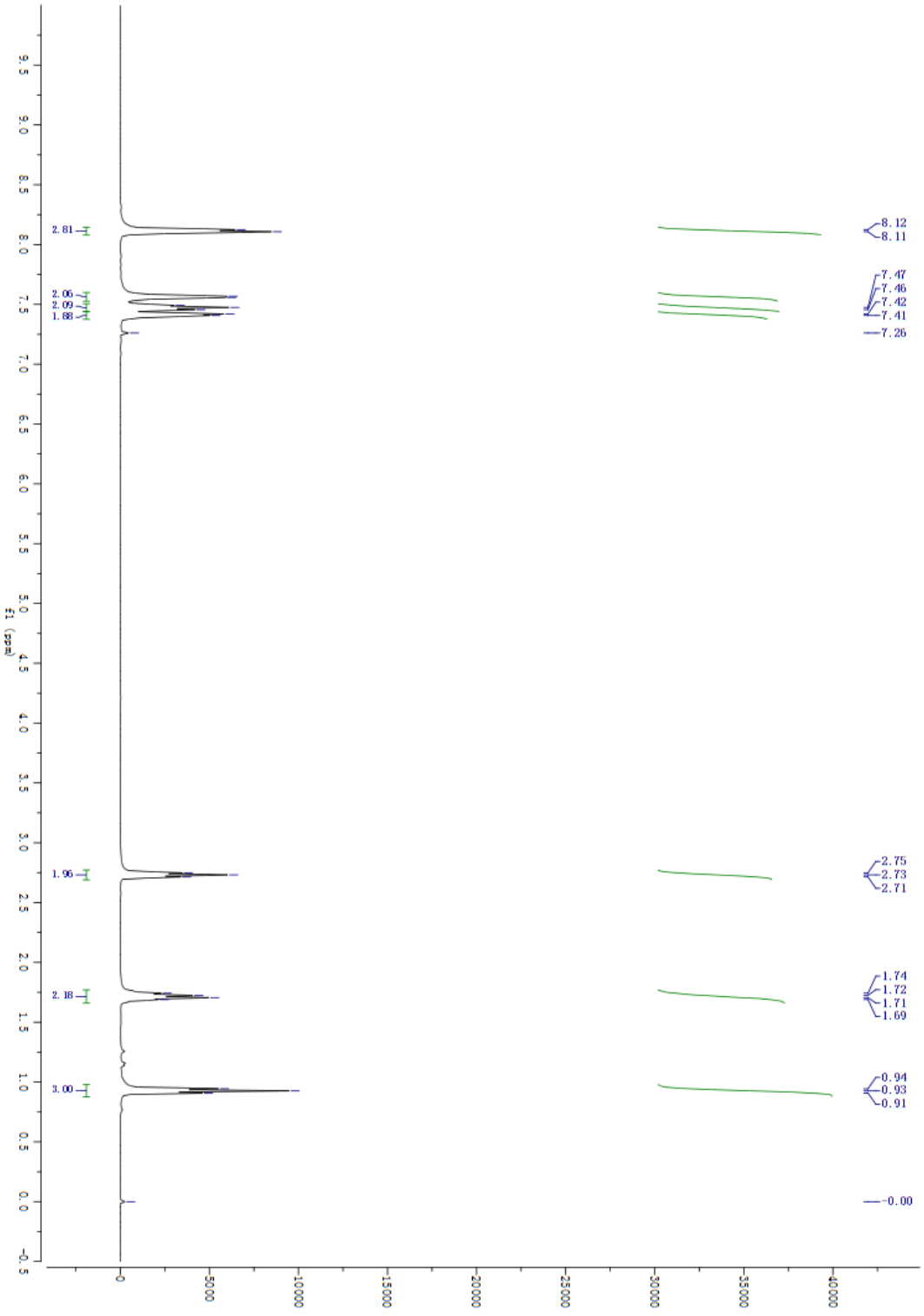
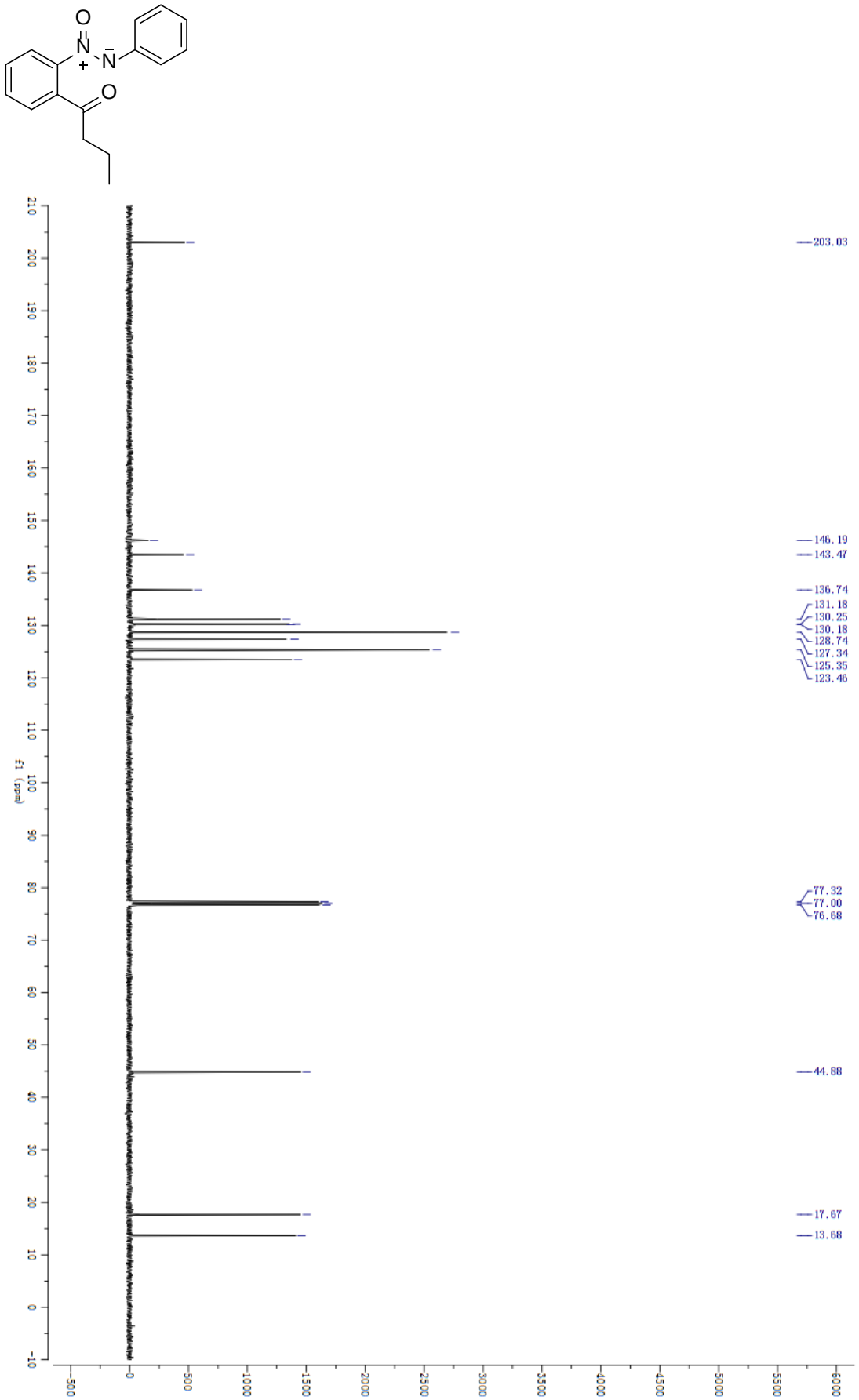
77.00
76.68
f1 (ppm)




2.81
2.06
2.09
1.88
1.96
2.18
3.00
8.12
8.11
7.47
7.46
7.42
7.41
7.26
2.75
2.73
2.71
1.74
1.72
1.71
1.69
0.94
0.93
0.91
-0.00
f1 (ppm)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131.18
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123.46
77.32
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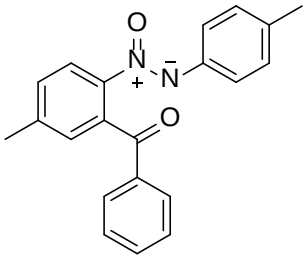
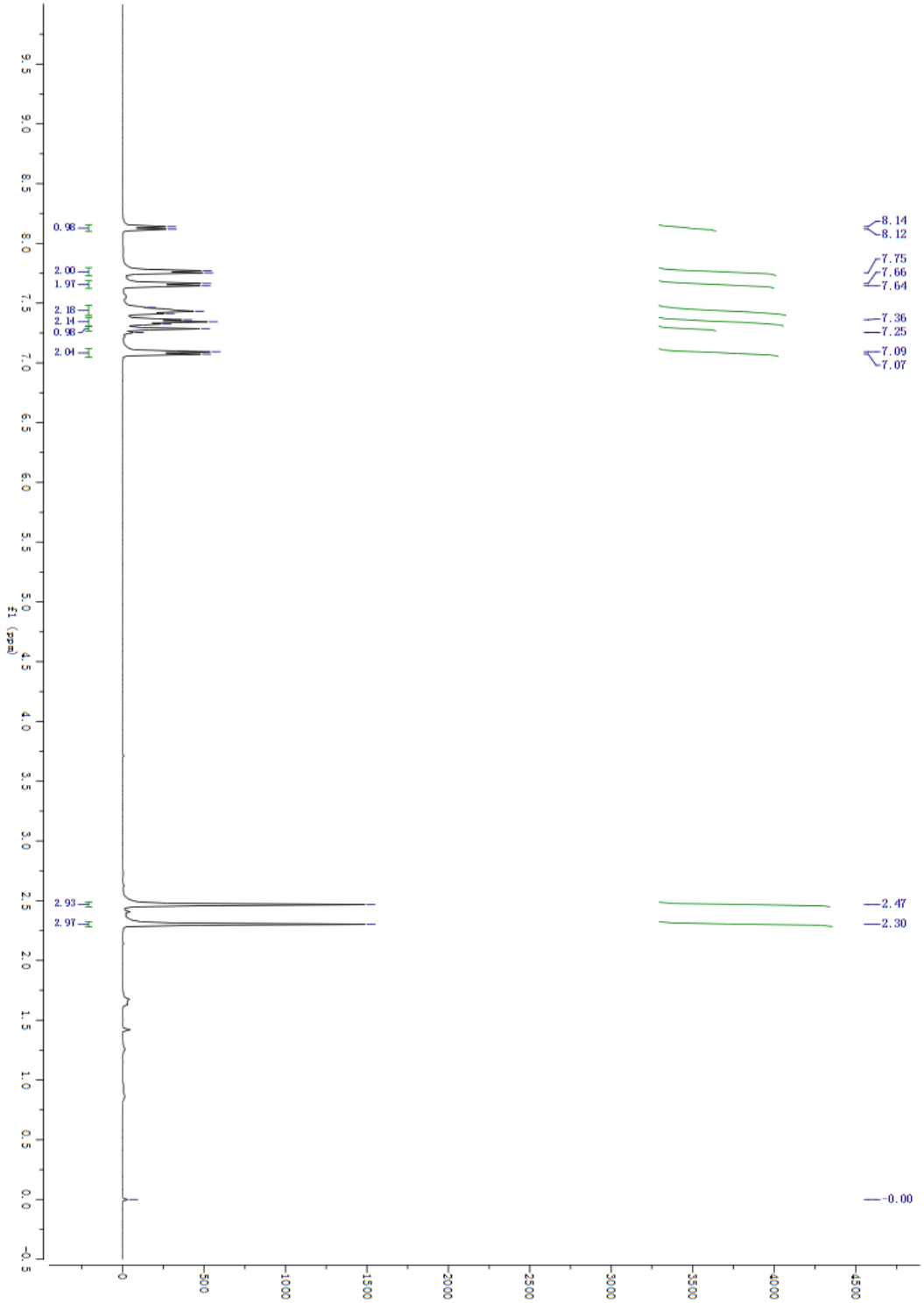
76.68
44.88
17.67
13.68
f1 (ppm)

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2.00
1.97
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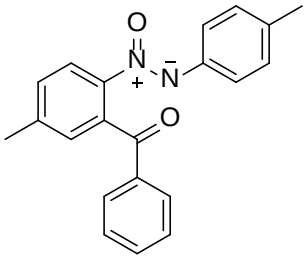
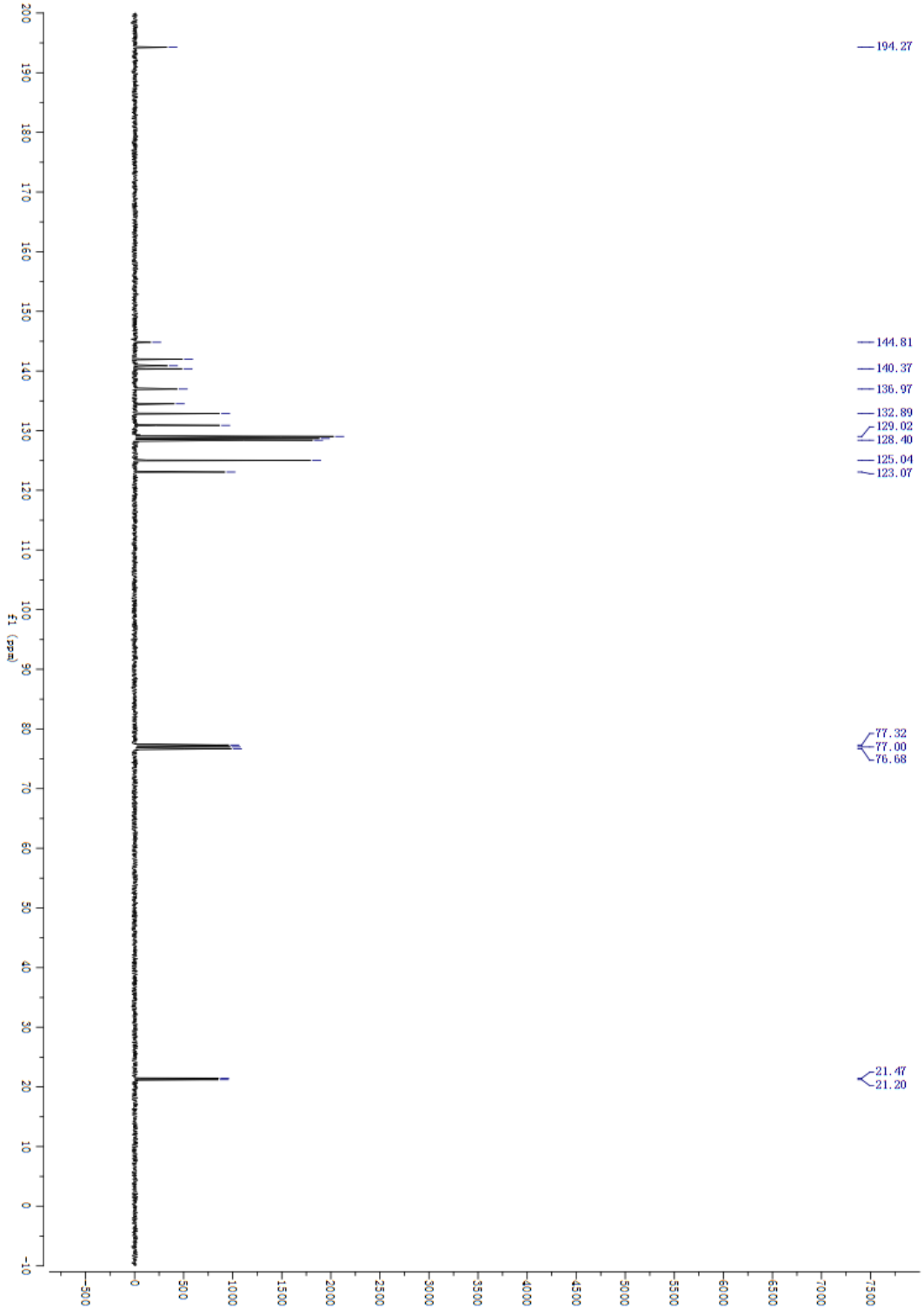
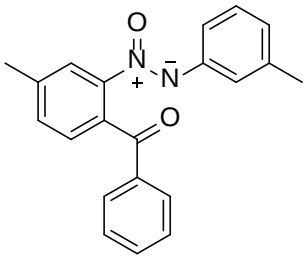
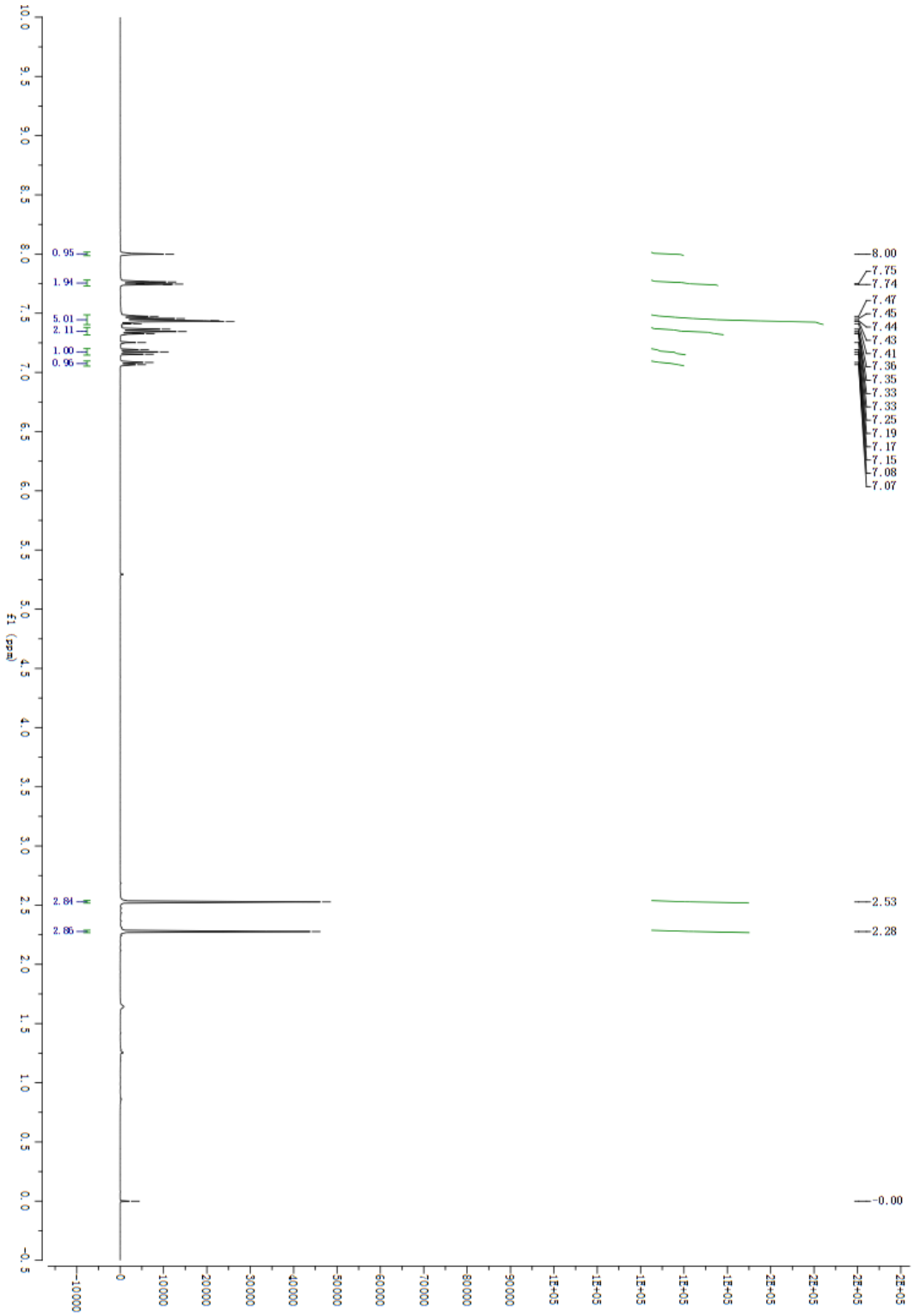
2.14
0.98
2.04
2.93
2.97
8.14
8.12
7.75
7.66
7.64
7.36
7.25
7.09
7.07
2.47
2.30
0.00
f1 (ppm)




194.27
144.81
140.37
136.97
132.89
129.02
128.40
125.04
123.07
77.32
77.00
76.68
21.47
21.20
f1 (ppm)

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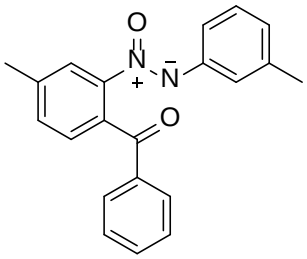
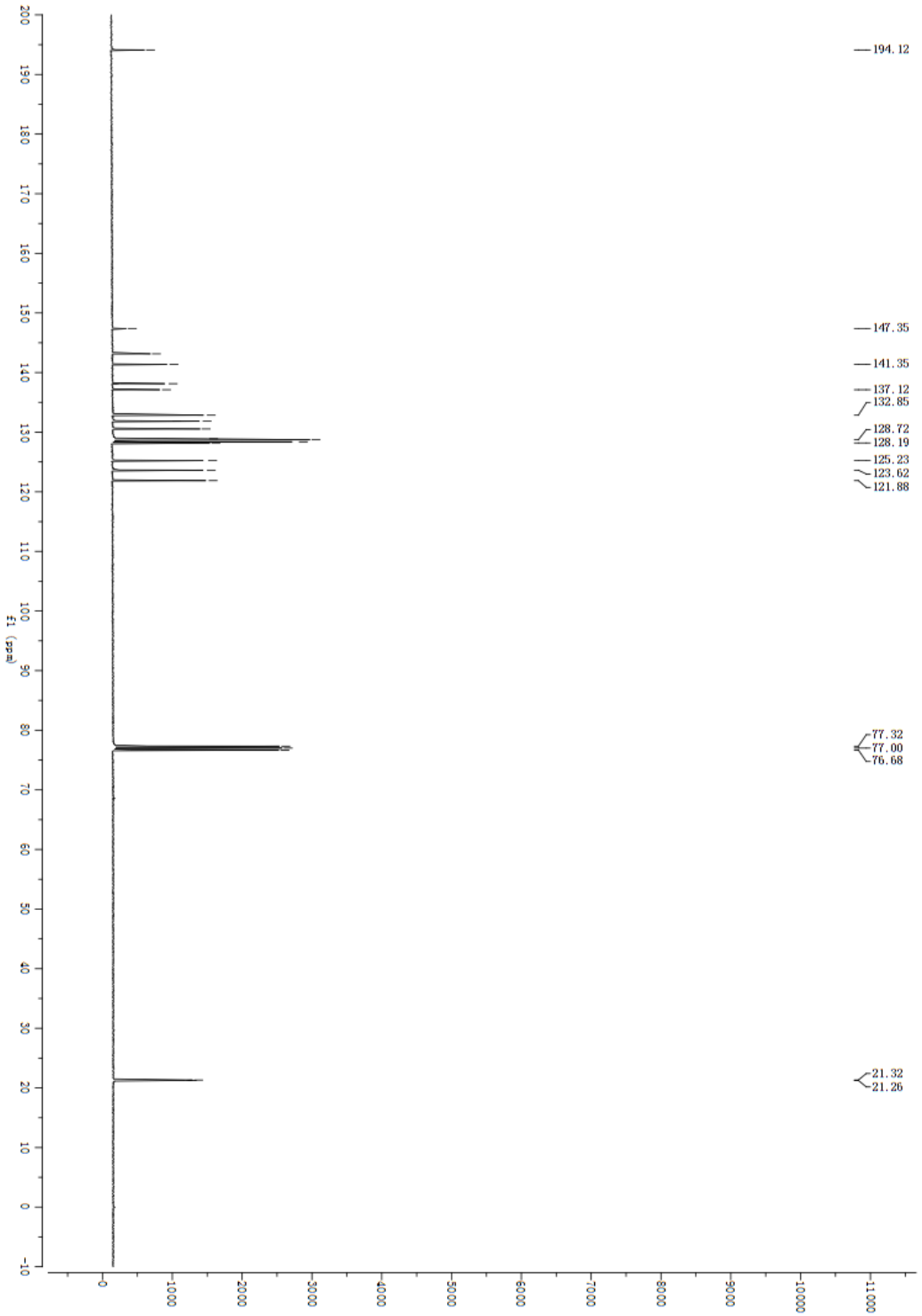
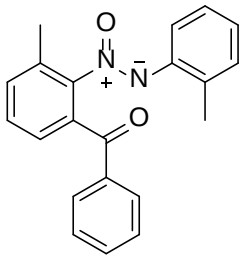
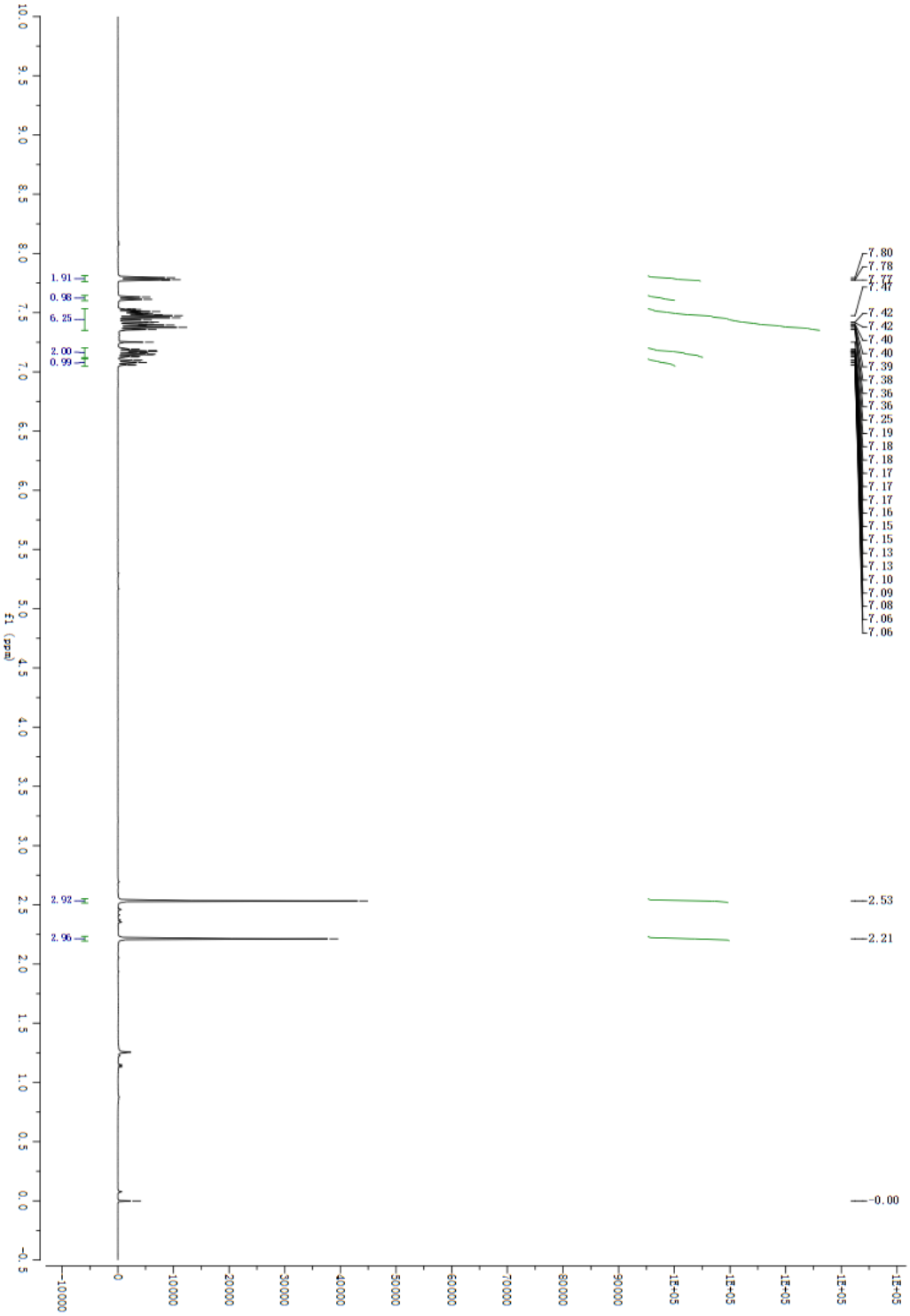
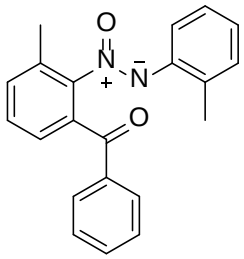
1.94
5.01
2.11
1.00
0.96
2.84
2.86
8.00
7.75
7.74
7.47
7.45
7.44
7.43
7.41
7.36
7.35
7.33
7.33
7.25
7.19
7.17
7.15
7.08
7.07
2.53
2.28
0.00
f1 (ppm)

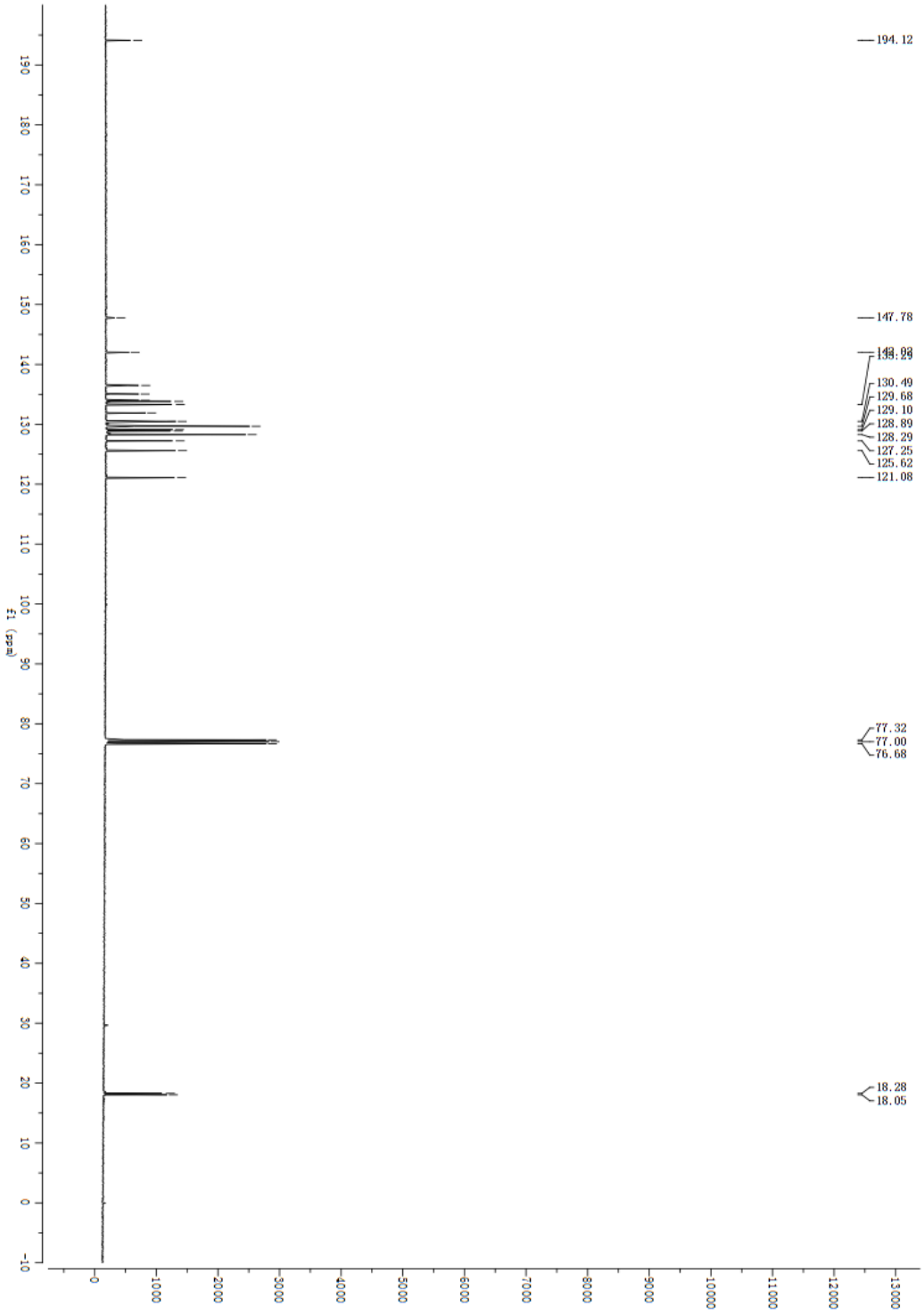



194.12
147.35
141.35
137.12
132.85
128.72
128.19
125.23
123.62
121.88
77.32
77.00
76.68
21.32
21.26
f1 (ppm)




1.91
0.98
6.25
2.00
0.99
2.92
2.96
7.80
7.78
7.77
7.47
7.42
7.42
7.40
7.40
7.39
7.38
7.36
7.36
7.25
7.19
7.18
7.18
7.17
7.17
7.17
7.16
7.15
7.15
7.13
7.13
7.10
7.09
7.08
7.06
7.06
2.53
2.21
0.00
f1 (ppm)

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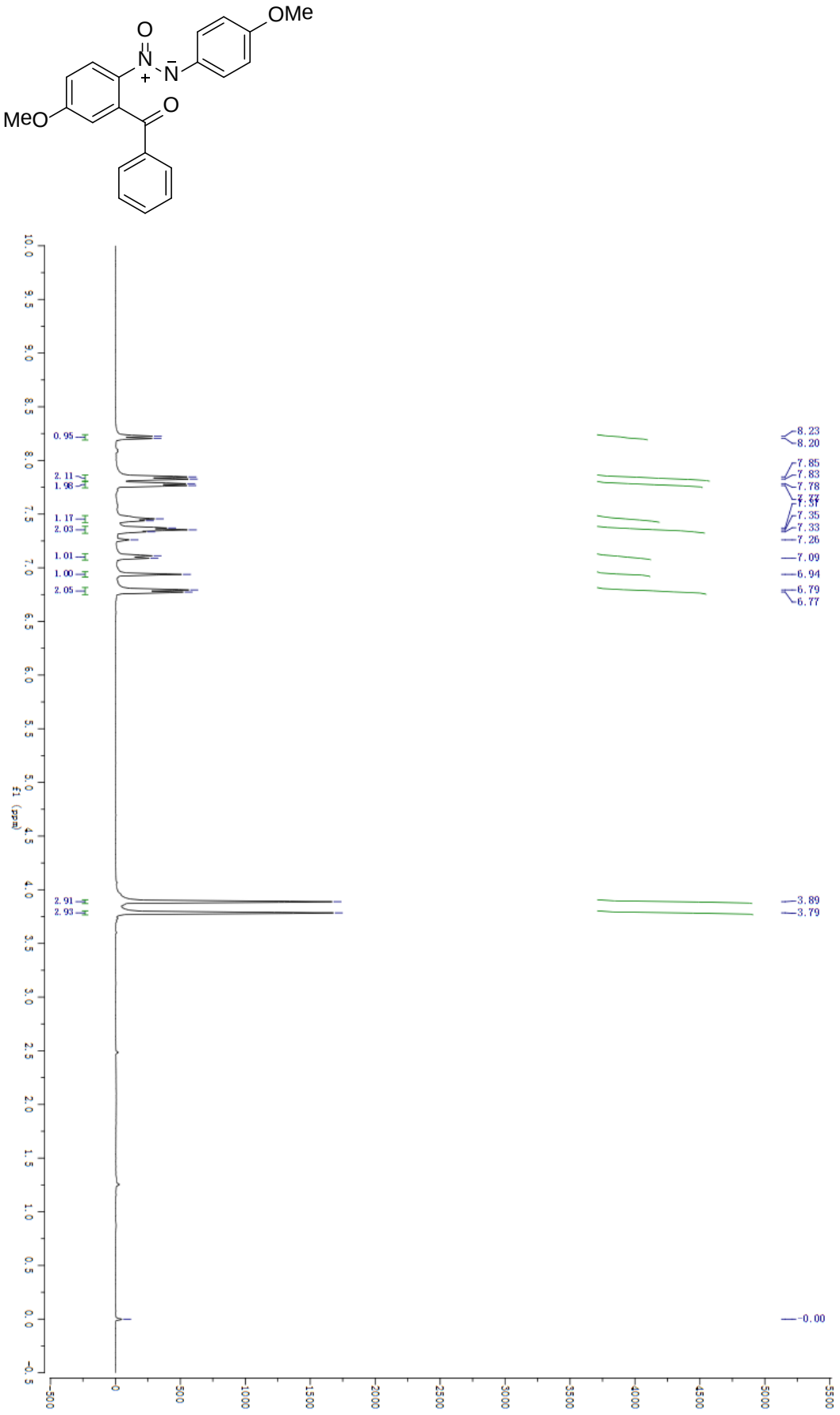
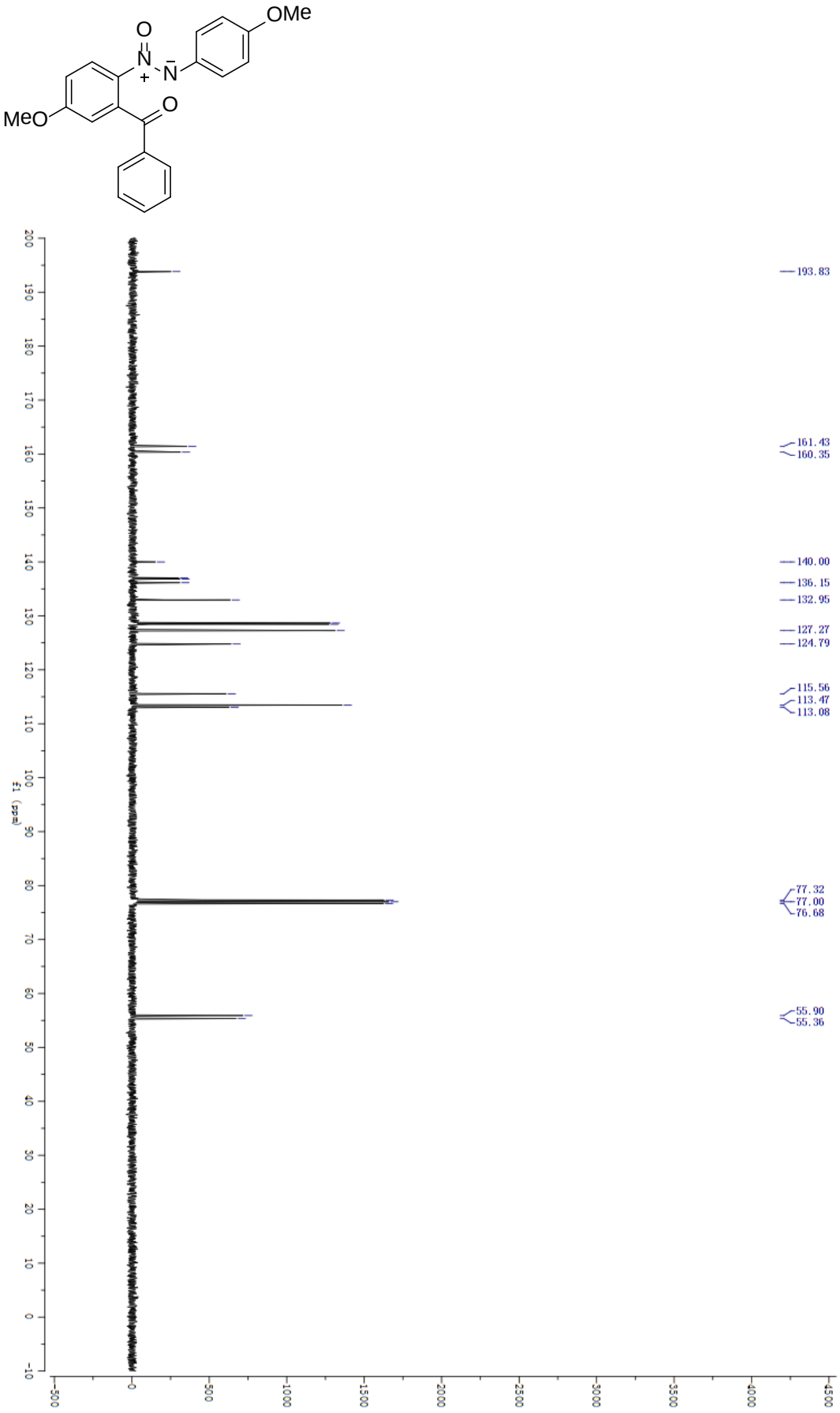
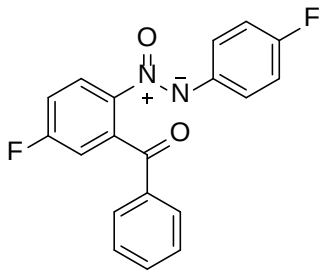
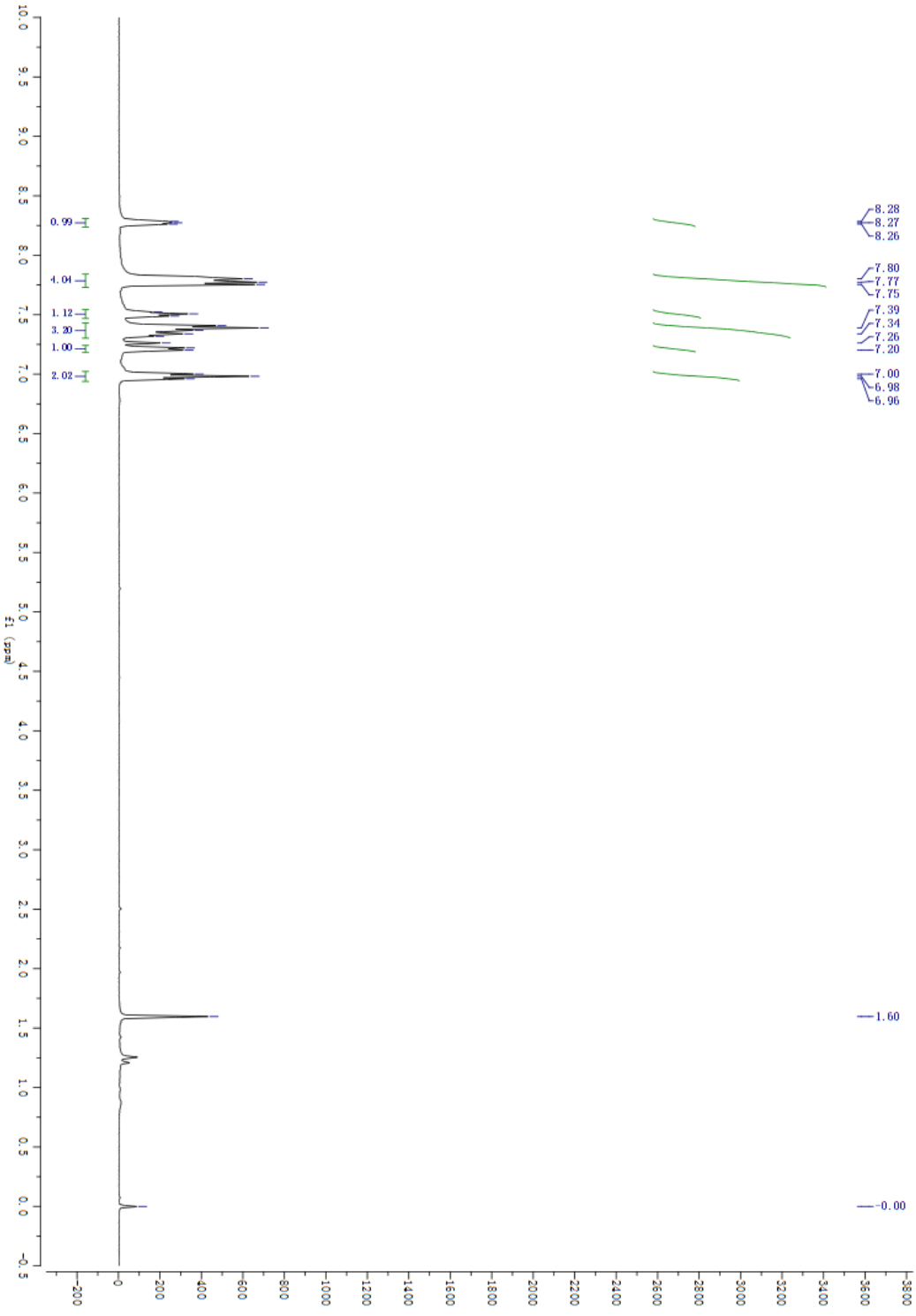
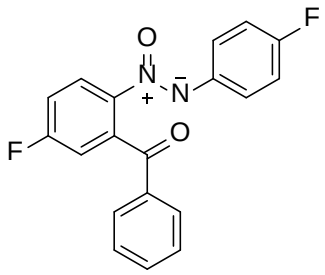
147.78
130.49
129.68
129.10
128.89
128.29
127.25
125.62
121.08
77.32
77.00
76.68
18.28
18.05

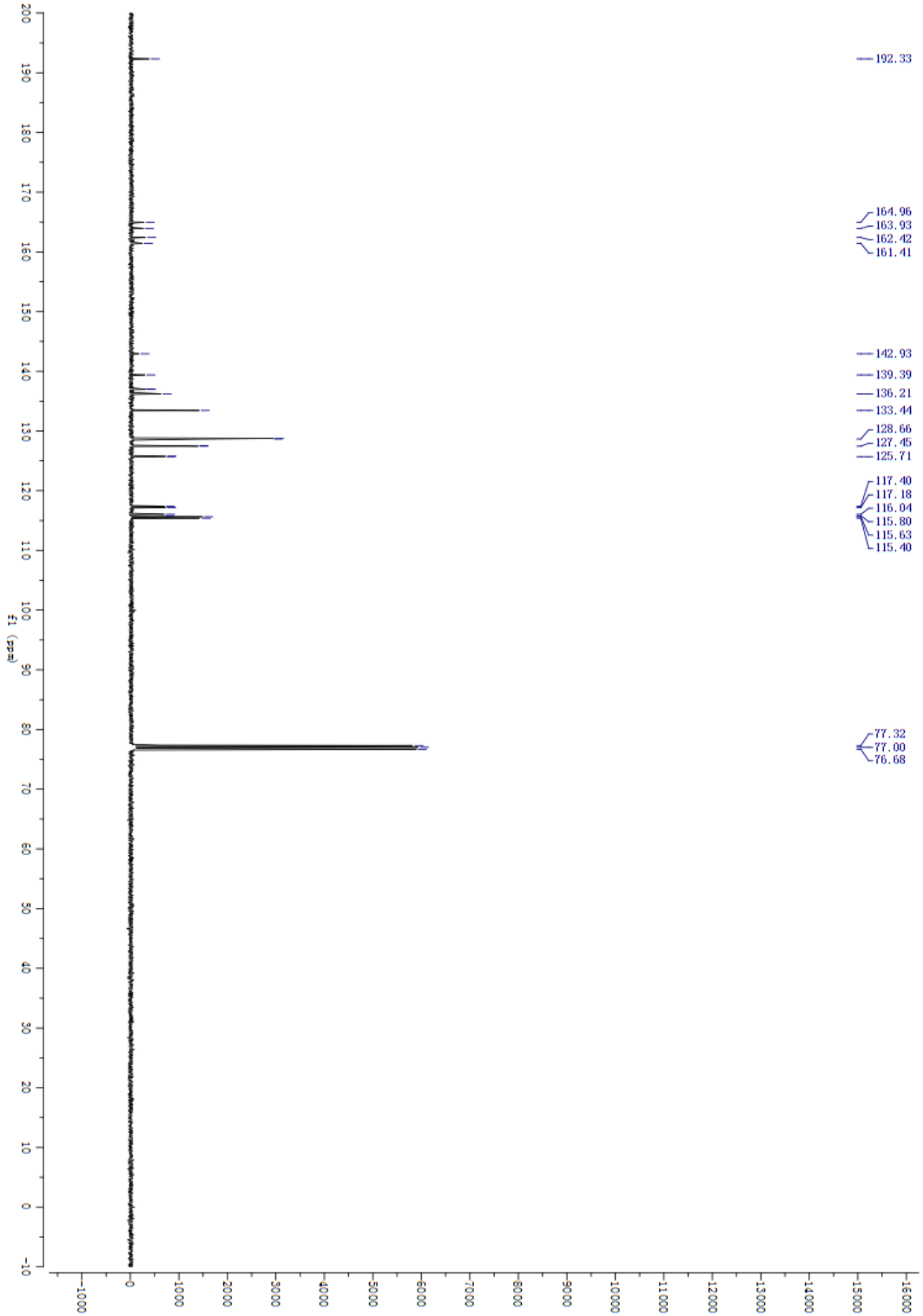

OMe
O
N
N
O
MeO
f1 (ppm)
0.95
2.11
1.98
1.17
2.03
1.01
1.00
2.05
2.91
2.93
8.23
8.20
7.85
7.83
7.78
7.35
7.33
7.26
7.09
6.94
6.79
6.77
3.89
3.79
0.00


OMe
O
N
N
MeO
O
193.83
161.43
160.35
140.00
136.15
132.95
127.27
124.79
115.56
113.47
113.08
77.32
77.00
76.68
55.90
55.36
f1 (ppm)


O
N
+
N
F
O
F


0.99
4.04
1.12
3.20
1.00
2.02
8.28
8.27
8.26
7.80
7.77
7.75
7.39
7.34
7.26
7.20
7.00
6.98
6.96
1.60
0.00
f1 (ppm)


O
N
+
N
F
O
F


192.33
164.96
163.93
162.42
161.41
142.93
139.39
136.21
133.44
128.66
127.45
125.71
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117.18
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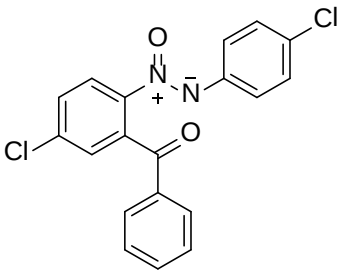
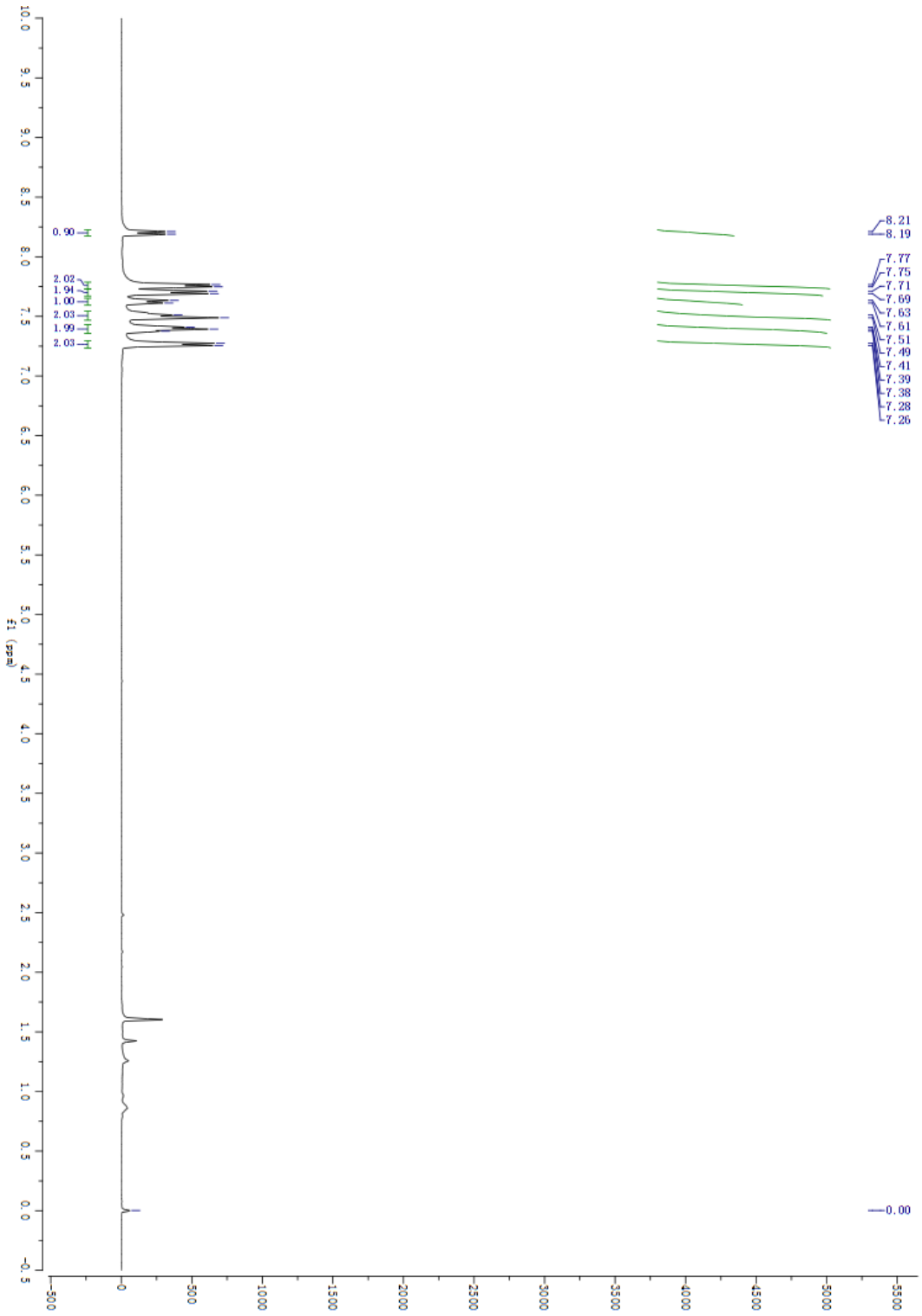
115.63
115.40
77.32
77.00
76.68
f1 (ppm)


Cl
O
N
N
O
Cl


0.90
2.02
1.94
1.00
2.03
1.99
2.03
8.21
8.19
7.77
7.75
7.71
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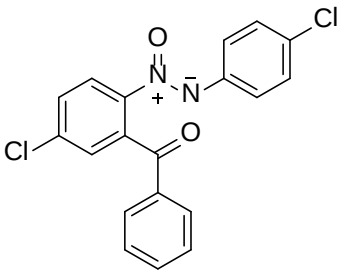
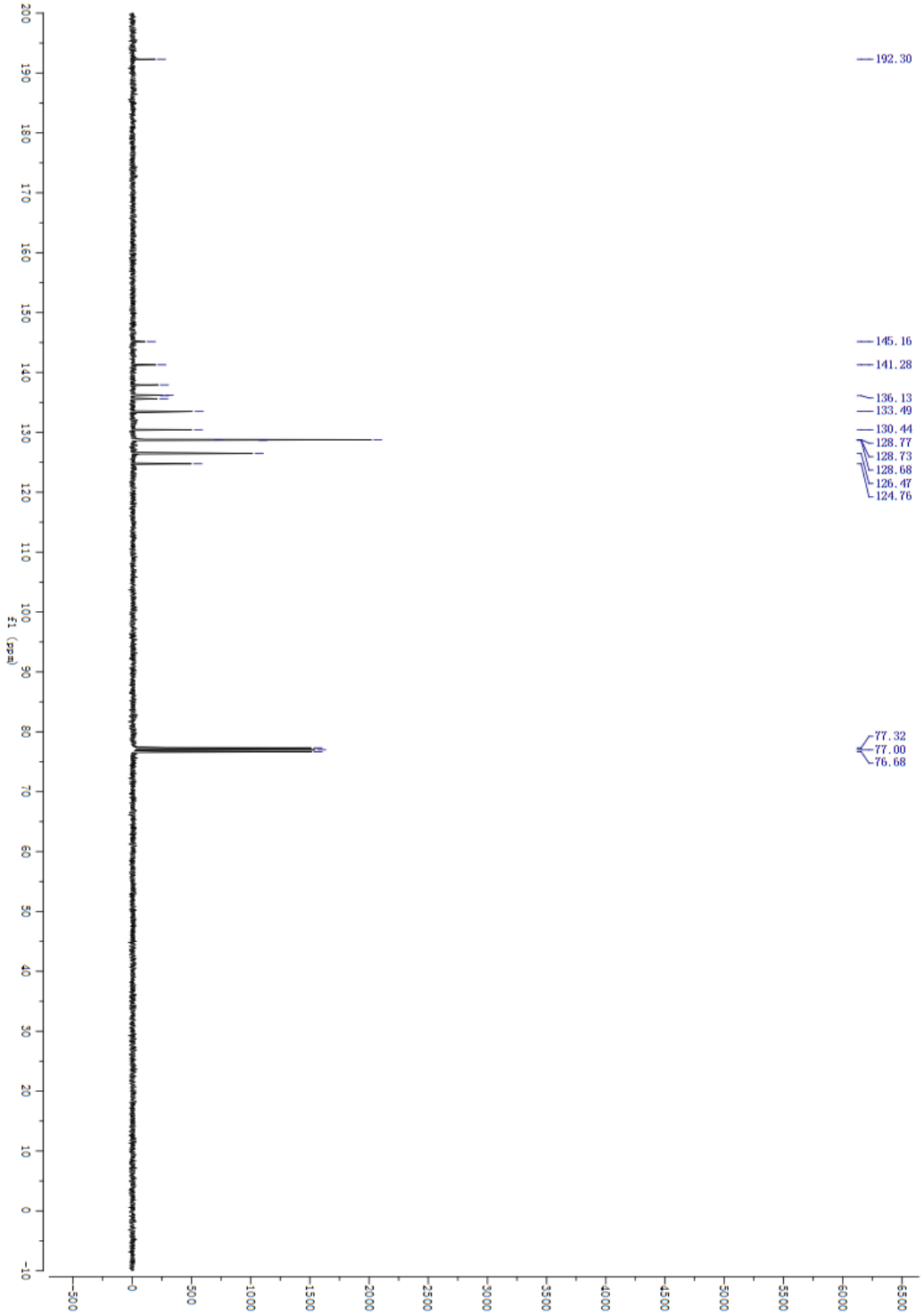
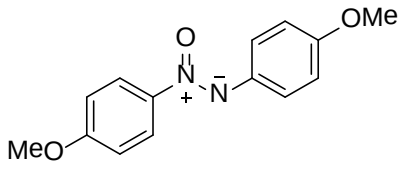
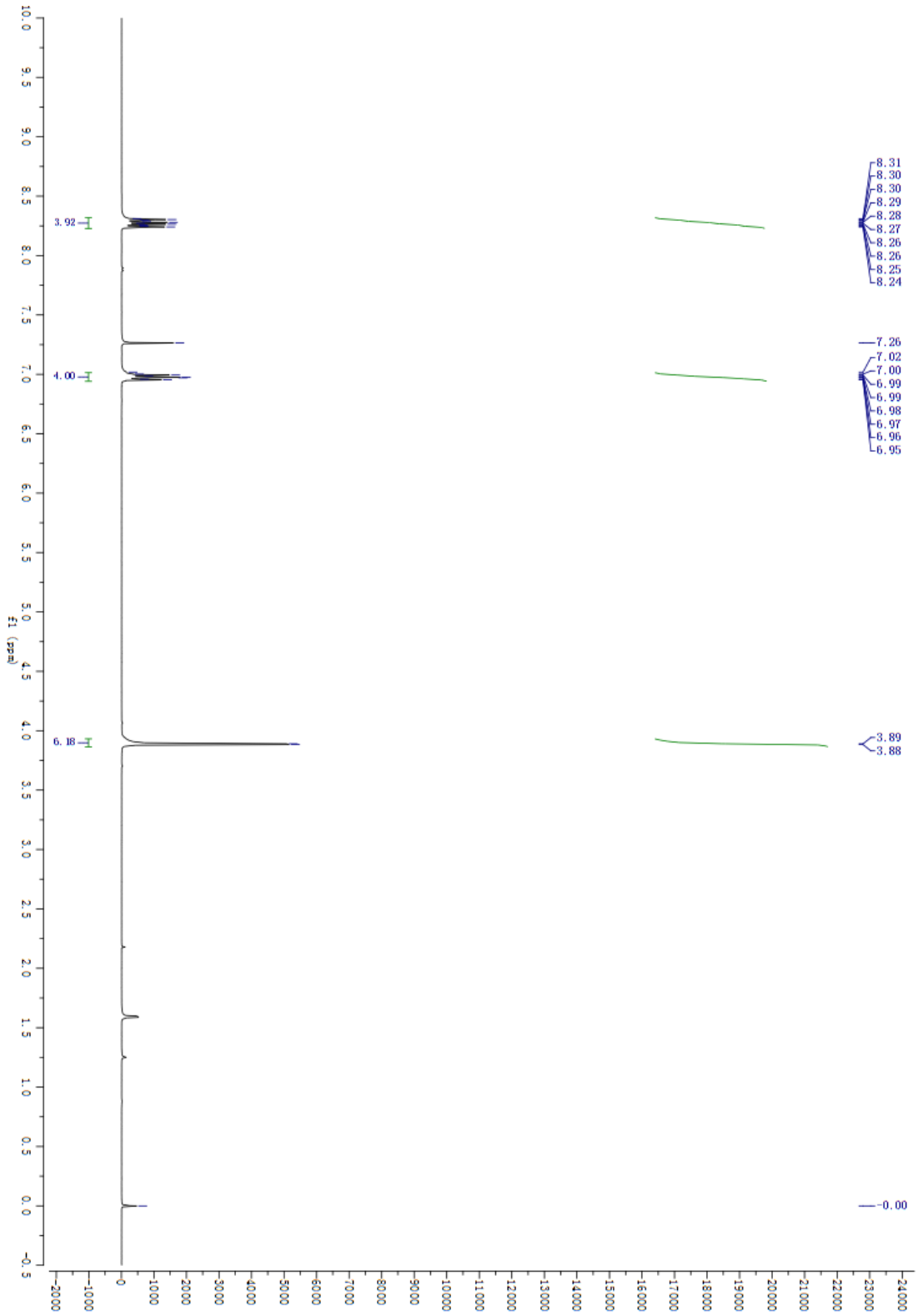
7.38
7.28
7.26
0.00
f1 (ppm)

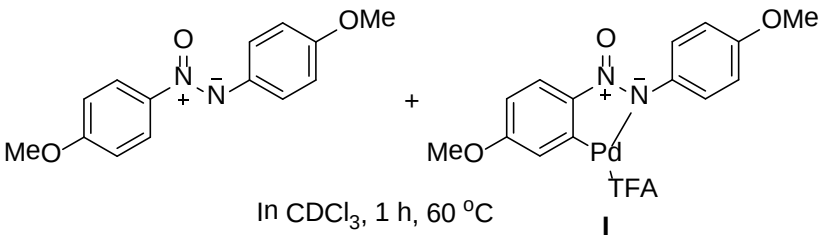

Cl
O
N
N
O
Cl


192.30
145.16
141.28
136.13
133.49
130.44
128.77
128.73
128.68
126.47
124.76
77.32
77.00
76.68
f1 (ppm)

4. In-situ NMR Chart.

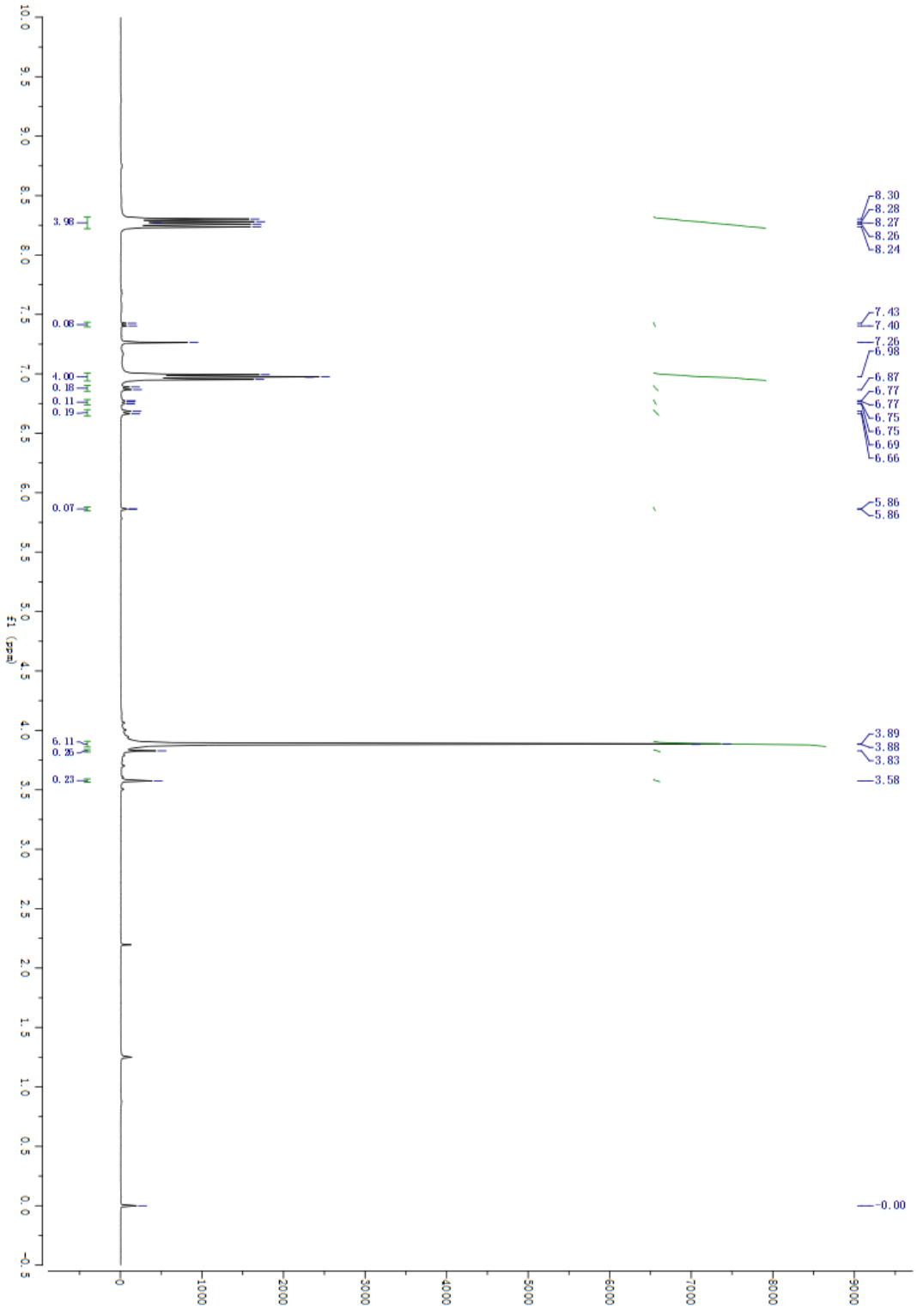


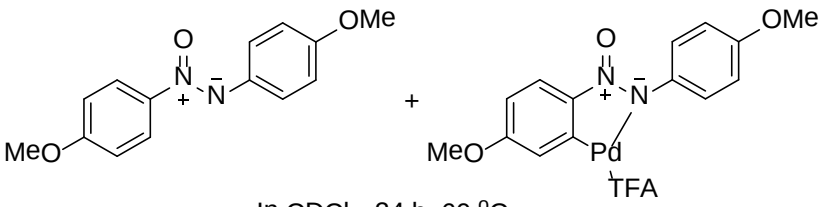




In $CDCl_3$, 1 h, 60 ^oC

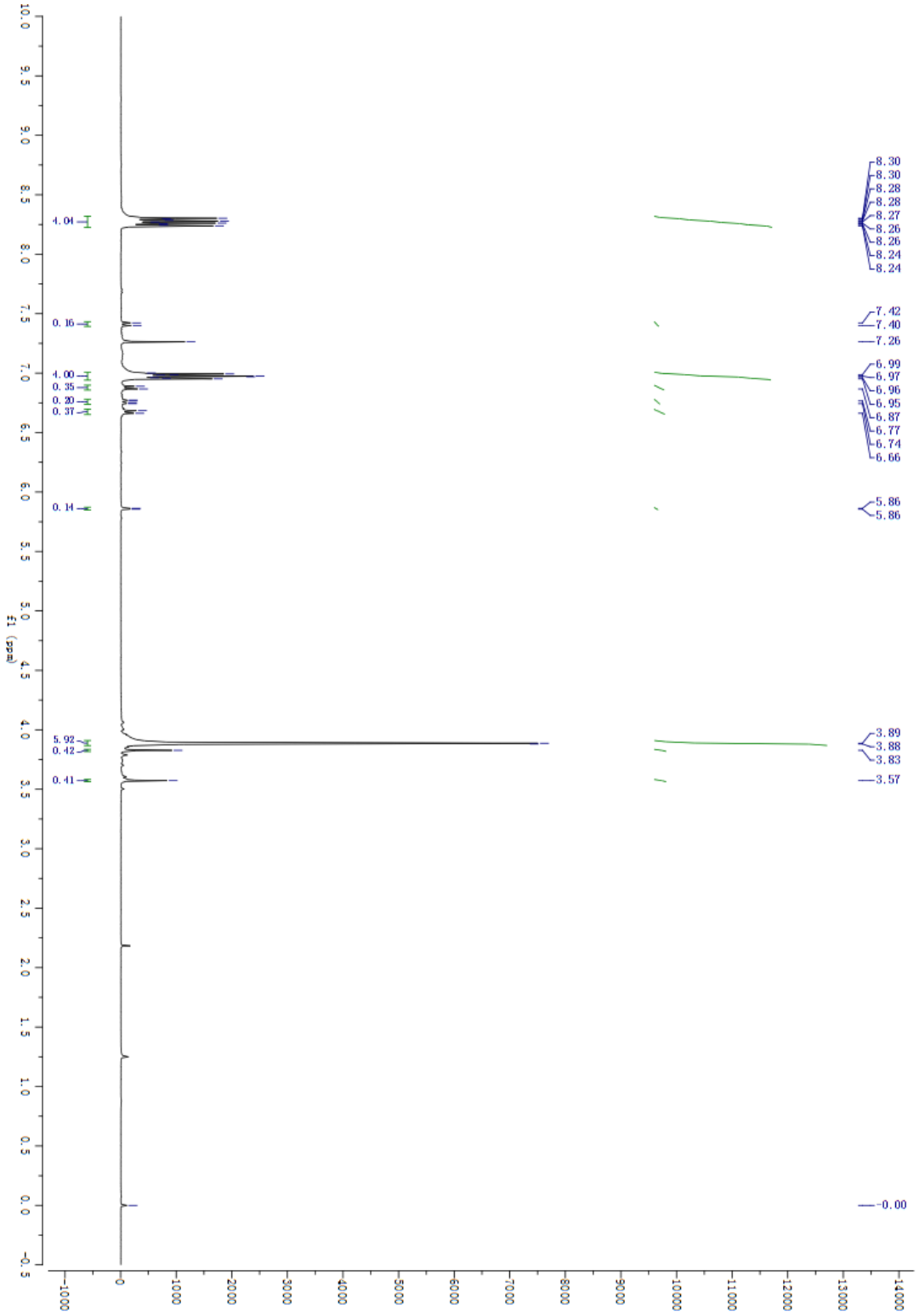
I

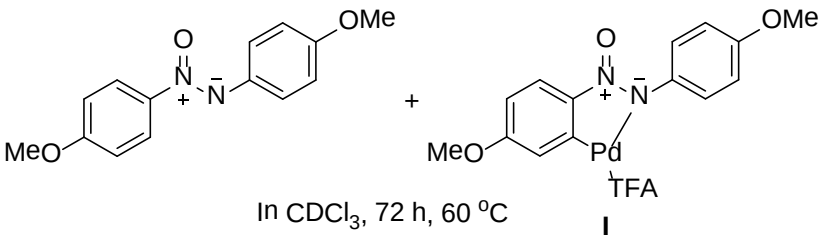




In $CDCl_3$, 24 h, 60 ^oC

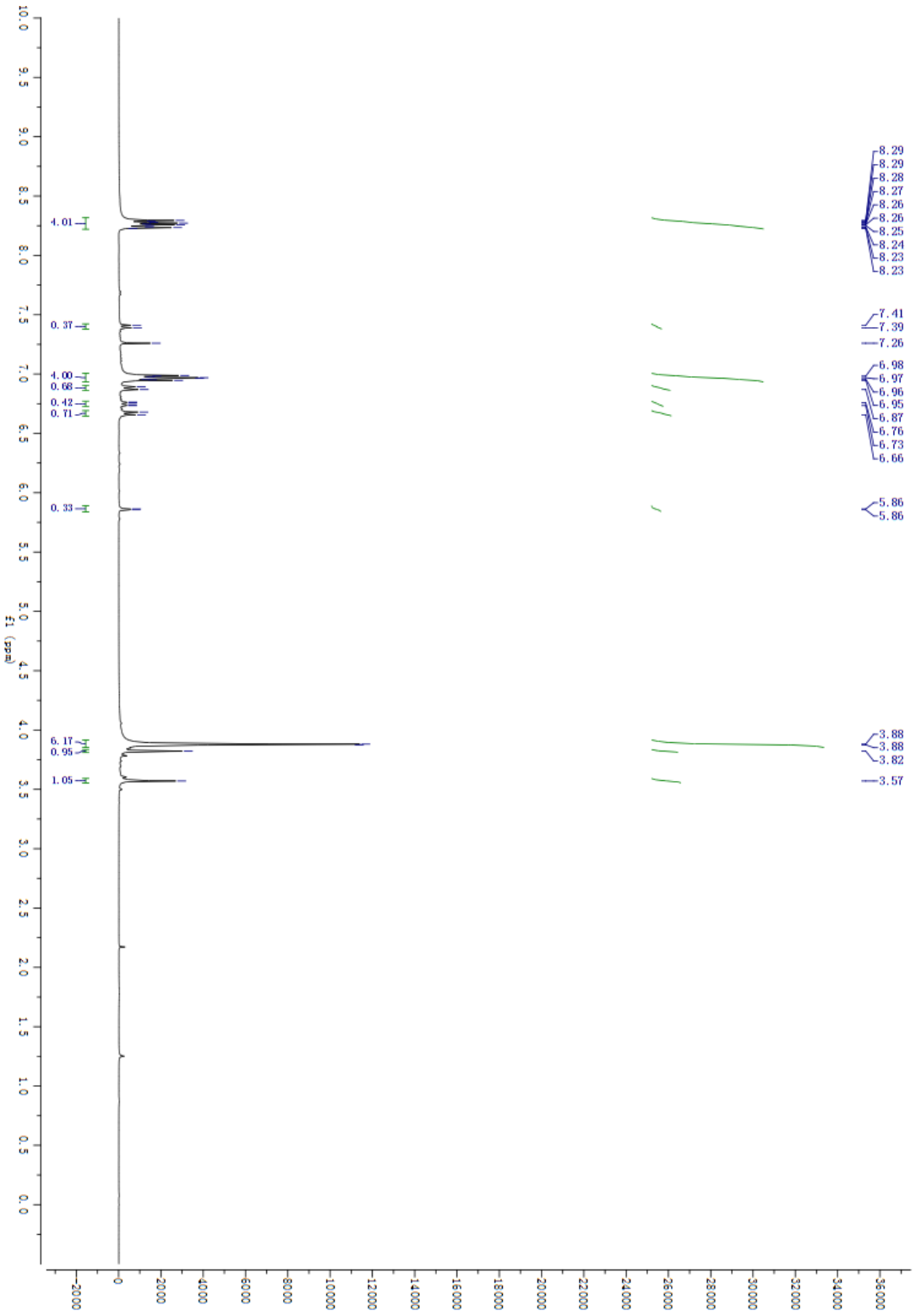
I





In $CDCl_3$, 72 h, 60 ^oC

I



5. Crystal structure.

X-ray single-crystal for acylated azoxybenzene **3ai** (CCDC 1037307)

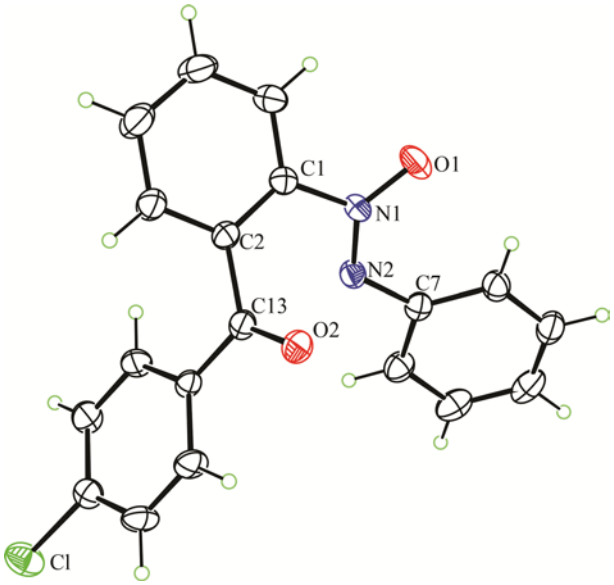


Table 1. Crystal and Refinement Data for 3ai

compound	**3ai**
empirical formula	$C_{19}H_{13}ClN_2O_2$
Fw	336.76
crystal system	Monoclinic
space group	*P*2(1)/*n*
a /Å	6.021(2)
b /Å	16.358(6)
c /Å	16.457(6)
α /°	90
β /°	96.874(4)
γ /°	90
V /Å^3	1609.4(10)
Z	4
D_{calc} /g cm^{-3}	1.390
F (000)	696
μ /mm^{-1}	0.251
θ range	1.76 −25.00
reflns collected	2812
independent reflns	2045
observed reflns [$I > 2\sigma(I)$]	2812
R(int)	0.0384
R_1; wR_2 [$I > 2\sigma(I)$]	0.0532, 0.1464
R_1; wR_2 (all data)	0.0797, 0.1676
GOF (F^2)	1.074

6. References

[1] G. Christin, P. Beate, I. Elisabeth, R.-B. Karola, *Synthesis*, 2008, **2008**, 1889.