Supporting Information

Direct Intermolecular C-H Arylation of Unactivated Arenes with Aryl Bromides Catalysed by 2-Pyridyl Carbinol

Yinuo Wu,[a,b*] Pui Ying Choy[a] and Fuk Yee Kwong[a*]

[a]The Hong Kong Polytechnic University Shenzhen Research Institute (SZRI), Shenzhen, China; and State Key Laboratory of Chirosciences and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China.

[b]School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou, China.

E-mail: fuk-yee.kwong@polyu.edu.hk

Table of Contents

1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All the reactions were performed in Rotaflo®(England) resealable screw-cap Schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). Benzene and toluene were freshly distilled from sodium under nitrogen.[1] Thin layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (230-400 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with TMS (δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer and the spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a ESIMS mass spectrometer. GC-MS analysis was conducted on a GCD system. Products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system.

2. General procedures for reaction condition screenings

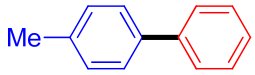
4-Bromotoluene (1.0 mmol), 2-pyridyl carbinol (as indicated in Table 1) and KO*t*-Bu (2.0 mmol) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar under N_2 atmosphere. Benzene (8.0 mL) was then added into the tube. The tube was stirred at room temperature for 3-5 minutes and then placed into a preheated oil bath (80-120 °C) for 24 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (~10 mL), dodecane (227 μL, internal standard) and water (~3 ml) were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

3. General procedures for direct C-H bond arylation

Substituted aryl bromides (1.0 mmol), 2-pyridyl carbinol (10 mol%) and KO*t*-Bu (2.0 mmol) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. Unactivated arenes (8.0 mL or 80 *equiv.*) was added into the tube. The tube was stirred at room temperature for 3-5 minutes and then placed into a preheated oil bath at 80 ^{o}C for 24 hours. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with water and diluted with ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired biaryl product.

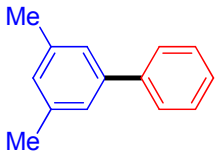
4. Characterization data

4-Methyl-1,1'-biphenyl (Table 2, entry 1 and 2, compound 1)[2]



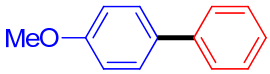
Eluents (Hexane, R_f = 0.55), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.51 (m, 4H), 7.46–7.40 (m, 2H), 7.35-7.25 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.47, 138.36, 136.88, 128.81, 128.21, 126.85, 21.32.

3,5-Dimethyl-1,1'-biphenyl (Table 2, entry 3, compound 2)[2]



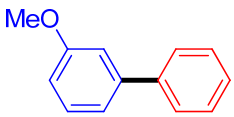
Eluents (Hexane, R_f = 0.55), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.27 (s, 2H), 7.05 (s, 1H), 2.44 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.54, 141.34, 138.29, 128.95, 128.69, 127.13, 125.17, 21.46.

4-Methoxy-1,1'-biphenyl (Table 2, entry 4, compound 3)[2]



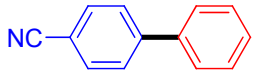
Eluents (Hexane, R_f = 0.20), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 8.3 Hz, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.22, 140.56, 133.63, 128.81, 128.21, 126.69, 114.28, 55.63.

3-Methoxy-1,1'-biphenyl (Table 2, entry 5, compound 4)[2]



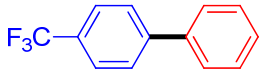
Eluents (Hexane, R_f = 0.20), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39–7.31 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 1H), 6.90 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.96, 142.80, 141.13, 129.74, 128.73, 127.41, 127.20, 119.70, 112.93, 112.70, 55.31.

[1,1'-Biphenyl]-4-carbonitrile (Table 2, entry 6, compound 5)[2]



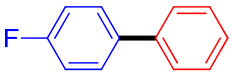
Eluents (EA/Hexane = 1:10, R_f = 0.30), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 17.2, 8.2 Hz, 4H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.46–7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.69, 139.19, 132.60, 129.13, 128.68, 127.75, 127.24, 118.94, 110.92.

4-(Trifluoromethyl)-1,1'-biphenyl (Table 2, entry 7, compound 6)[3]



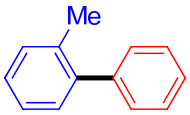
Eluents (EA/Hexane = 1:100, R_f = 0.35), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.66, 139.79, 128.99, 128.43, 128.19, 127.43, 127.29, 125.71(d, *J* = 4 Hz), 122.94.

4-(Trifluoromethyl)-1,1'-biphenyl (Table 2, entry 8, compound 7)[2]



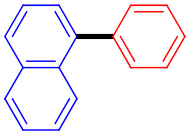
Eluents (EA/Hexane = 1:10, R_f = 0.45), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 5.6, 2.1 Hz, 4H), 7.52–7.43 (m, 2H), 7.42–7.34 (m, 1H), 7.24–7.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.47 (d, *J* = 260.58 Hz), 140.31, 137.40 (d, *J* = 3.34.04 Hz), 128.8, 128.73 (d, *J* =8.08 Hz), 127.31, 127.07, 115.7 (d, *J* = 22.4 Hz).

2-Methyl-1,1'-biphenyl (Table 2, entry 9, compound 8)[2]



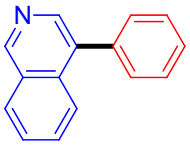
Eluents (Hexane, R_f = 0.55), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 3H), 7.31–7.21 (m, 4H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.99, 135.36, 130.31, 129.81, 129.21, 128.07, 127.26, 126.77, 125.77, 20.48.

1-Phenylnaphthalene (Table 2, entry 10, compound 9)[2]



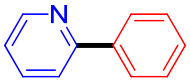
Eluents (Hexane, R_f = 0.50), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 3H), 7.54 – 7.36 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.83, 140.32, 133.86, 131.69, 130.13, 128.31, 127.93, 127.68, 127.28, 127.22, 126.97, 126.08, 125.87, 125.43.

4-Phenylisoquinoline (Table 2, entry 11, compound 10)[2]



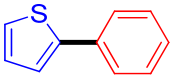
Eluents (EA/Hexane = 1:100, R_f = 0.55), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.50 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.72–7.59 (m, 2H), 7.50 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.00, 142.74, 136.95, 134.25, 133.38, 130.59, 130.11, 128.60, 128.41, 127.95, 127.91, 127.22, 124.78.

2-Phenylpyridine (Table 2, entry 12, compound 11)[3]



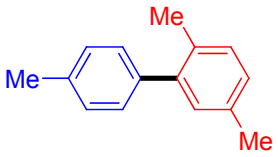
Eluents (EA/Hexane = 1:100, R_f = 0.40), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.59 (d, *J* = 4.6 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.44–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.46, 148.34, 137.85, 136.67, 134.38, 129.09, 128.12, 127.17, 123.56.

2-Phenylthiophene (Table 2, entry 13, compound 12)[4]



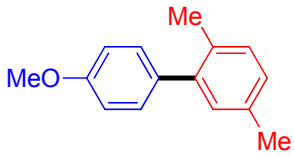
Eluents (EA/Hexane = 1:100, R_f = 0.45), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.34–7.23 (m, 3H), 7.13–7.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.42, 134.43, 128.88, 128.00, 127.46, 125.97, 124.80, 123.08.

2,4',5-Trimethyl-1,1'-biphenyl (Table 3, entry 1, compound 14)[3]



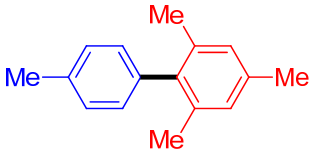
Eluents (Hexane, R_f = 0.35), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.36 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.73, 139.20, 136.29, 135.16, 132.24, 130.63, 130.24, 129.08, 128.76, 127.78, 126.74, 21.19, 20.94, 20.02.

4'-Methoxy-2,5-dimethyl-1,1'-biphenyl (Table 3, entry 2, compound 15)[2]



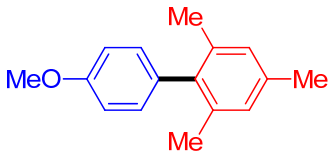
Eluents (EA/Hexane = 1:100, R_f = 0.35), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 2.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.11–7.03 (m, 3H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.47, 141.49, 135.12, 134.57, 132.30, 130.89, 130.65, 130.23, 127.67, 113.44, 55.40, 20.85, 20.03.

2,4,4',6-Tetramethyl-1,1'-biphenyl (Table 3, entry 3, compound 16)[3]



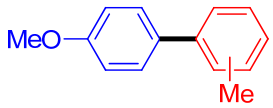
Eluents (Hexane, R_f = 0.45), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.93 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.00, 138.00, 136.37, 136.11, 135.93, 129.14, 129.04, 128.00, 21.21, 20.99, 20.75.

4'-Methoxy-2,4,6-trimethyl-1,1'-biphenyl (Table 3, entry 4, compound 17)[2]



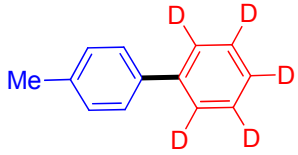
Eluents (EA/Hexane = 1:100, R_f = 0.35), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.92 (m, 4H), 2.32 (s, 3H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.46, 138.00, 136.19, 133.29, 130.17, 127.74, 114.05, 55.41, 21.31, 20.85.

Mixture of 4'-methoxy-2-methyl-1,1'-biphenyl, 4'-methoxy-3-methyl-1,1'-biphenyl, 4'-methoxy-4-methyl-1,1'-biphenyl (Table 3, entry 5, compound 18)[2]



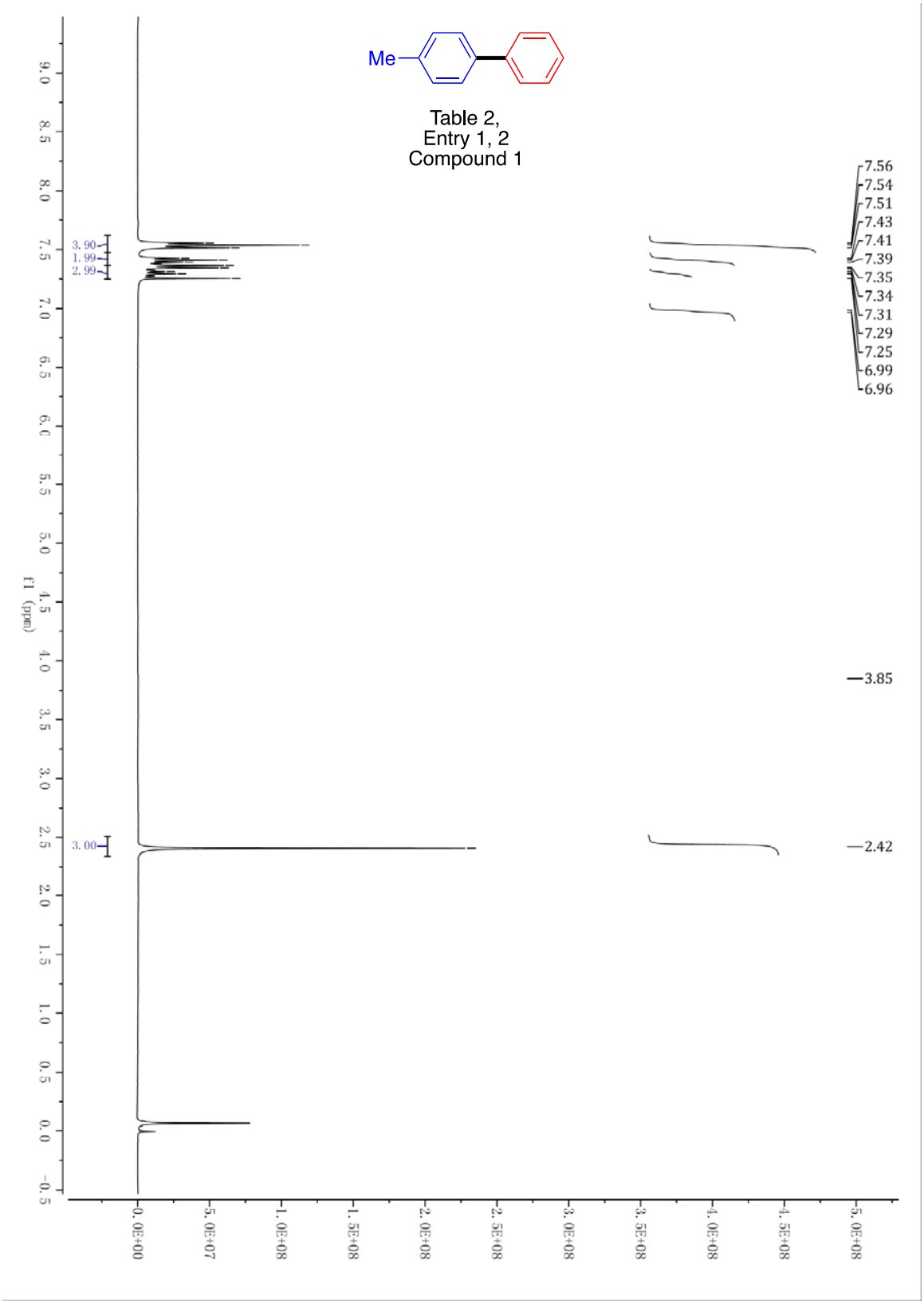
Eluents (EA/Hexane = 1:100, R_f = 0.45), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.25 (m, 6H), 7.23-6.97 (m 2H), 3.87 (m, 3H), 2.31-2.44 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.12, 158.56, 141.59, 138.30, 135.51, 134.42, 130.33, 130.28, 129.94, 129.48, 128.67, 128.19, 127.98, 127.60, 127.45, 127.01, 126.62, 125.79, 123.89, 116.40, 114.18, 113.53, 55.36, 55.30, 21.59, 20.57.

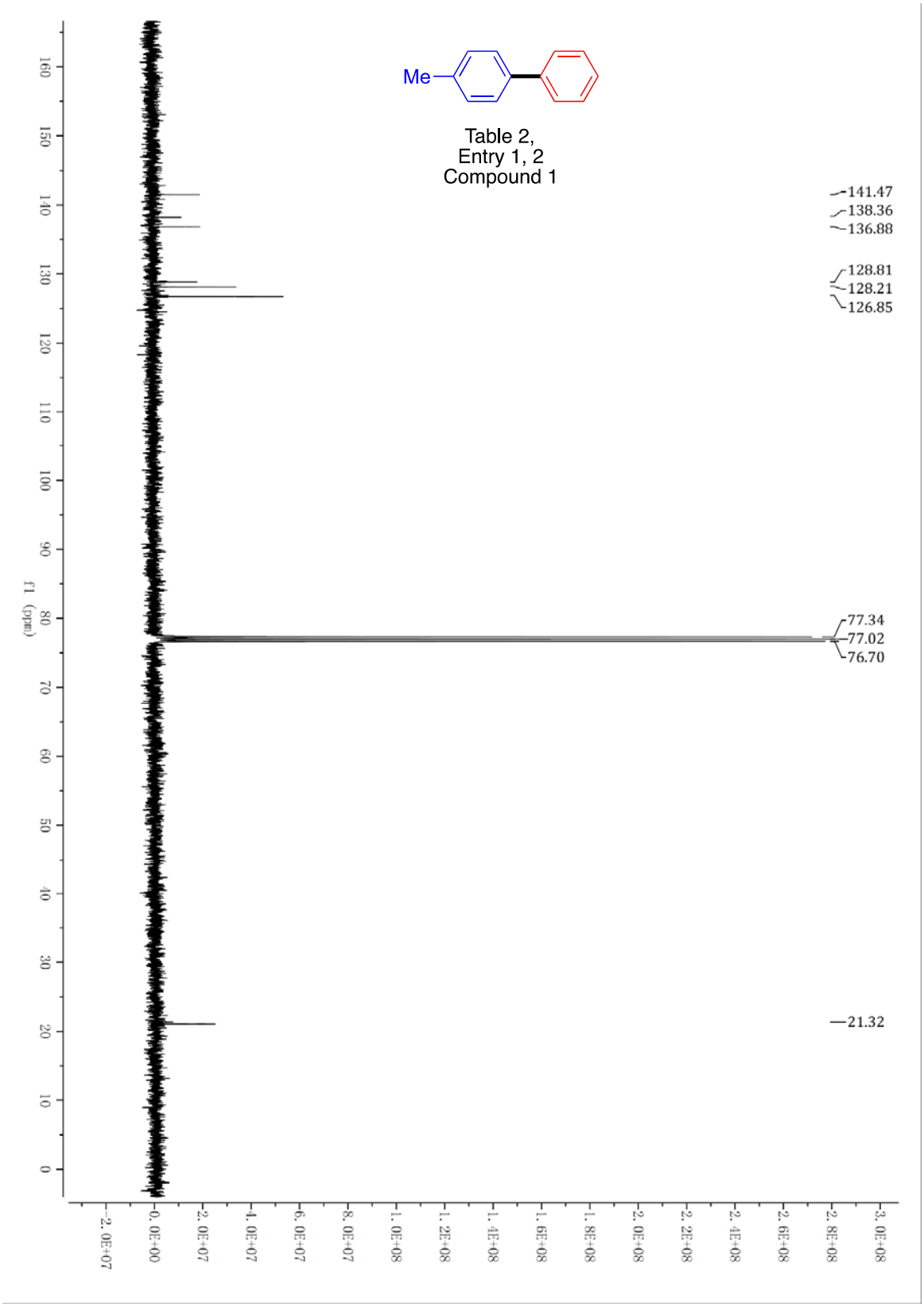
4'-Methyl-1,1'-biphenyl-2,3,4,5,6-d_5 (Scheme 1, compound 19)[5]

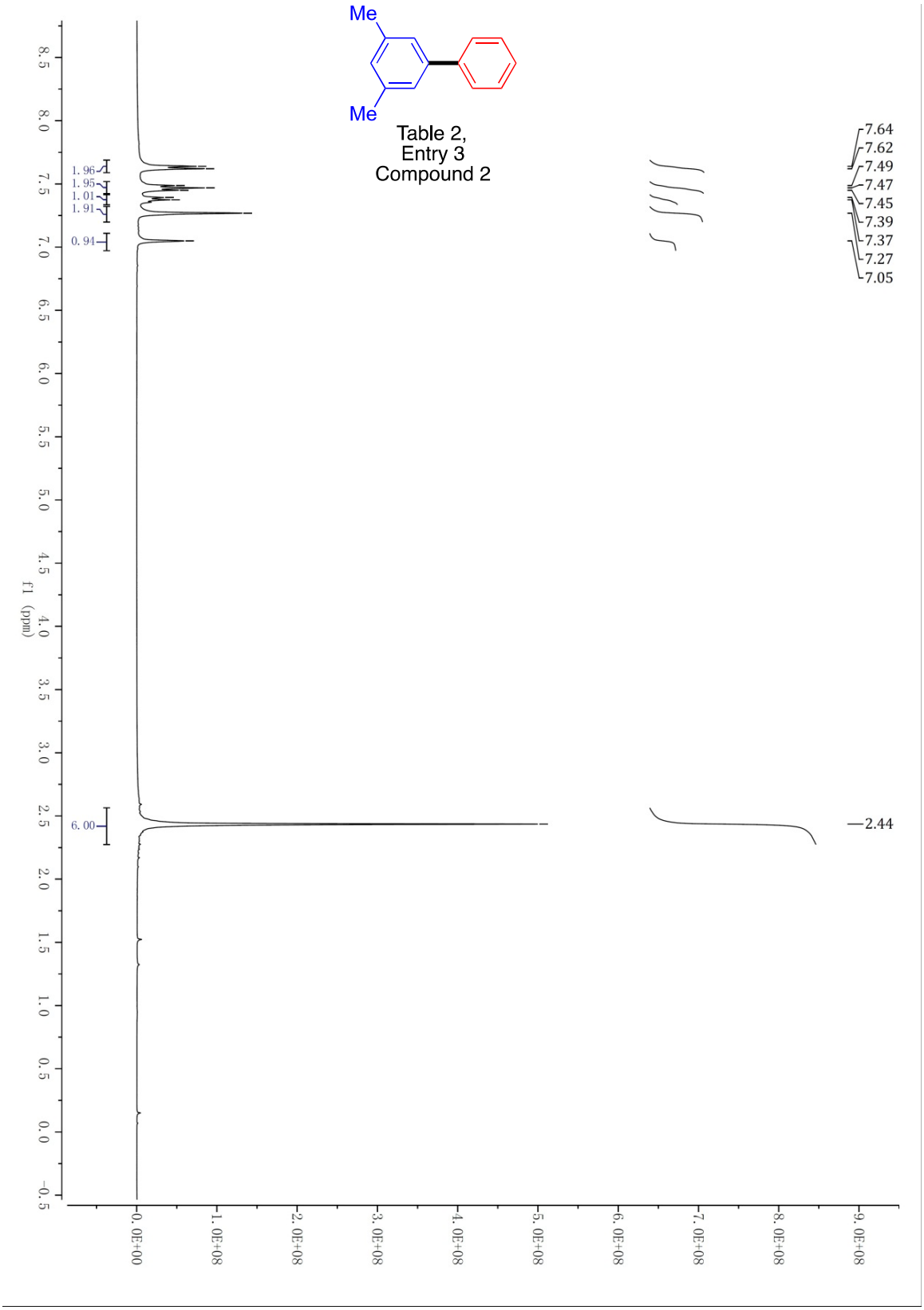


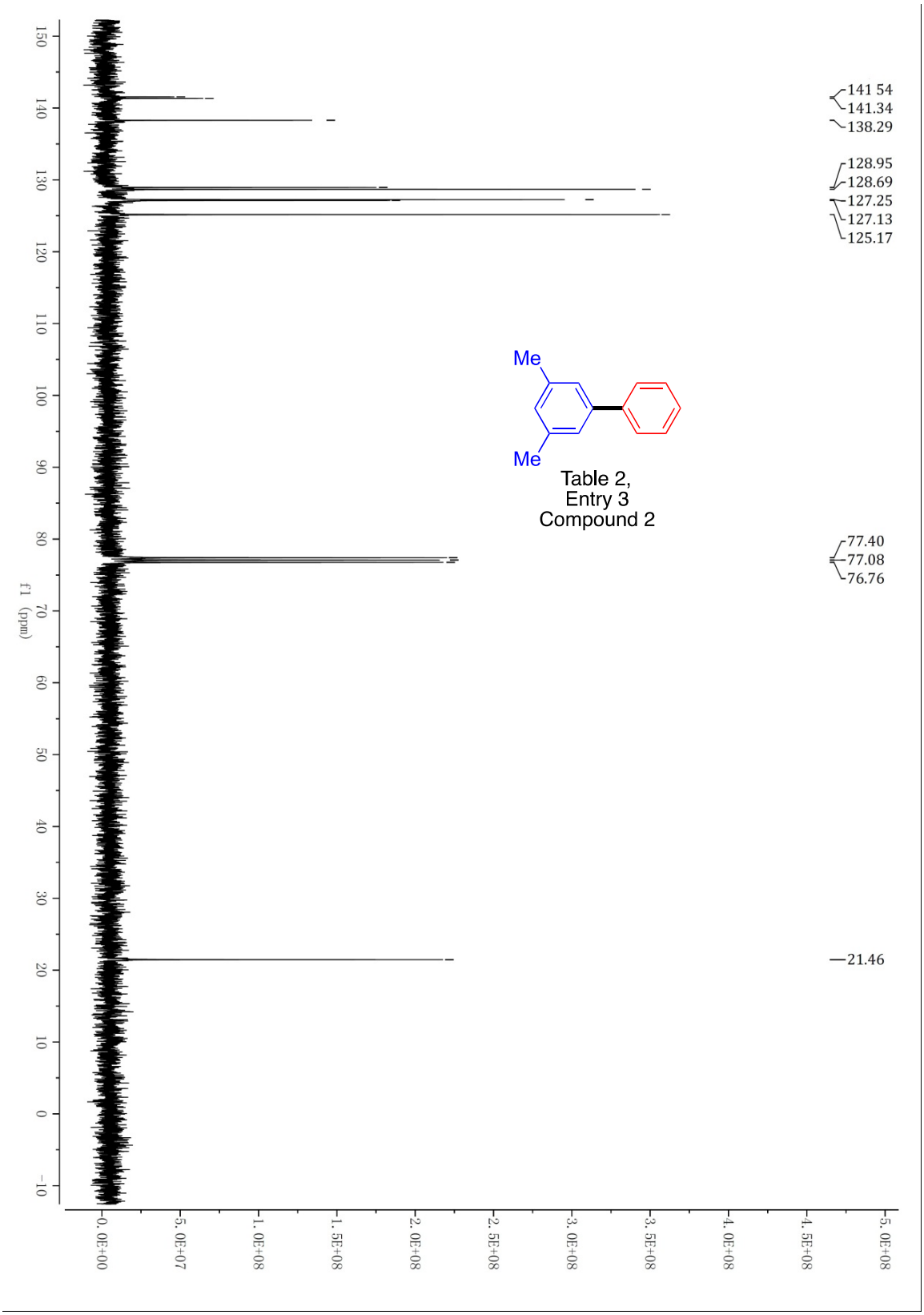
Eluents (Hexane, R_f = 0.55), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7,33 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.04, 138.36, 137.04, 129.53, 127.03, 21.14.

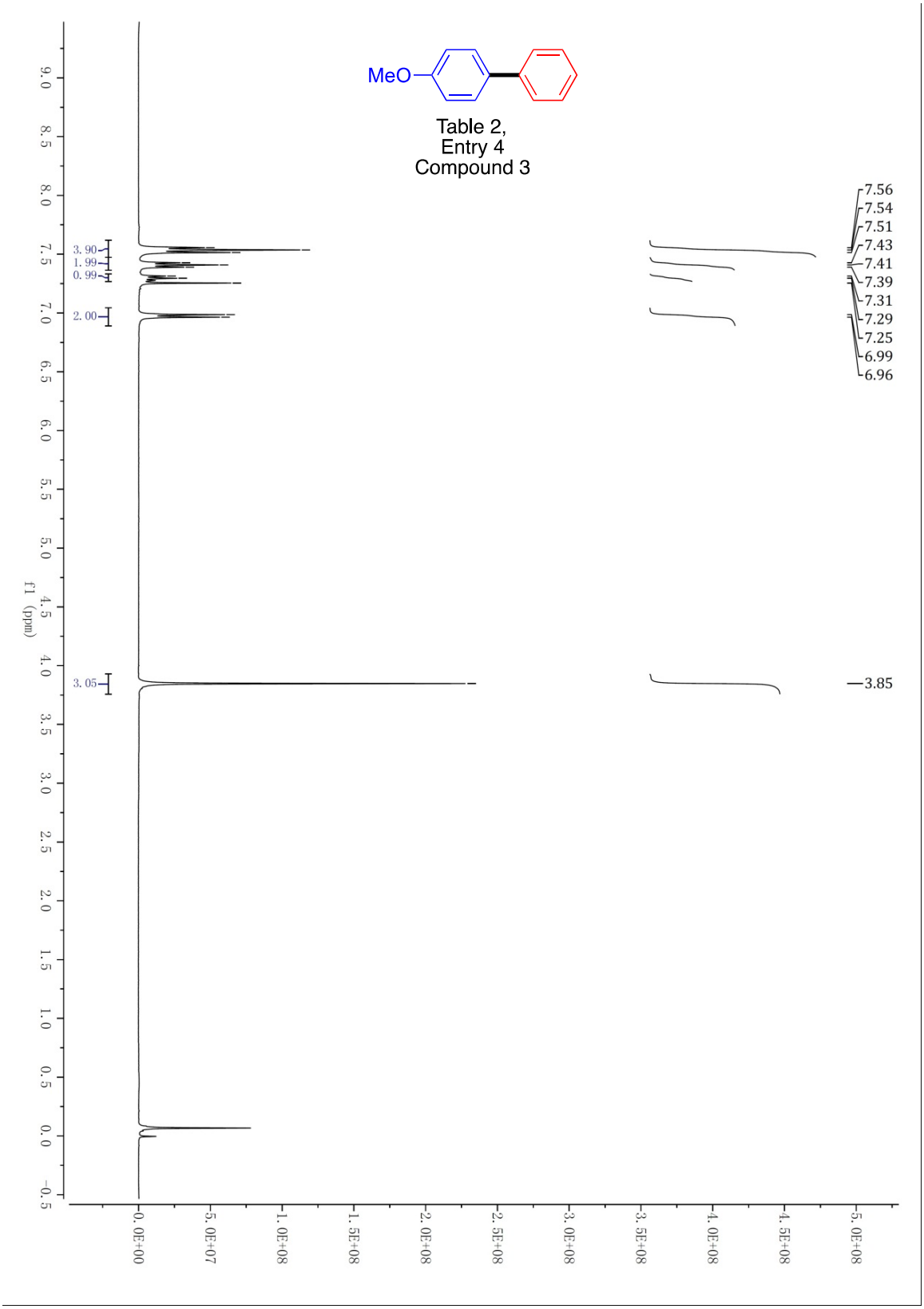
5. ^{1}H, ^{13}C spectra

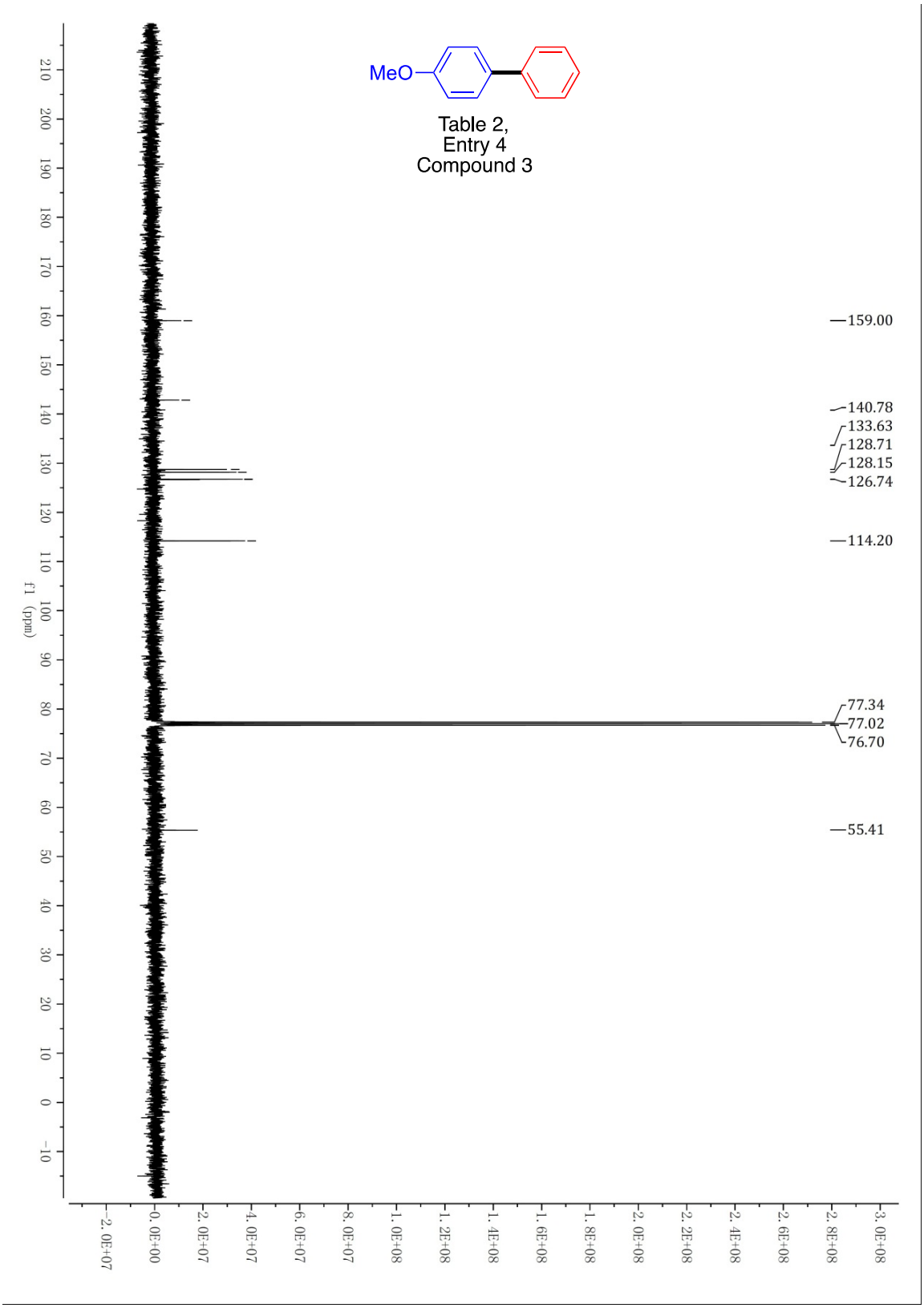


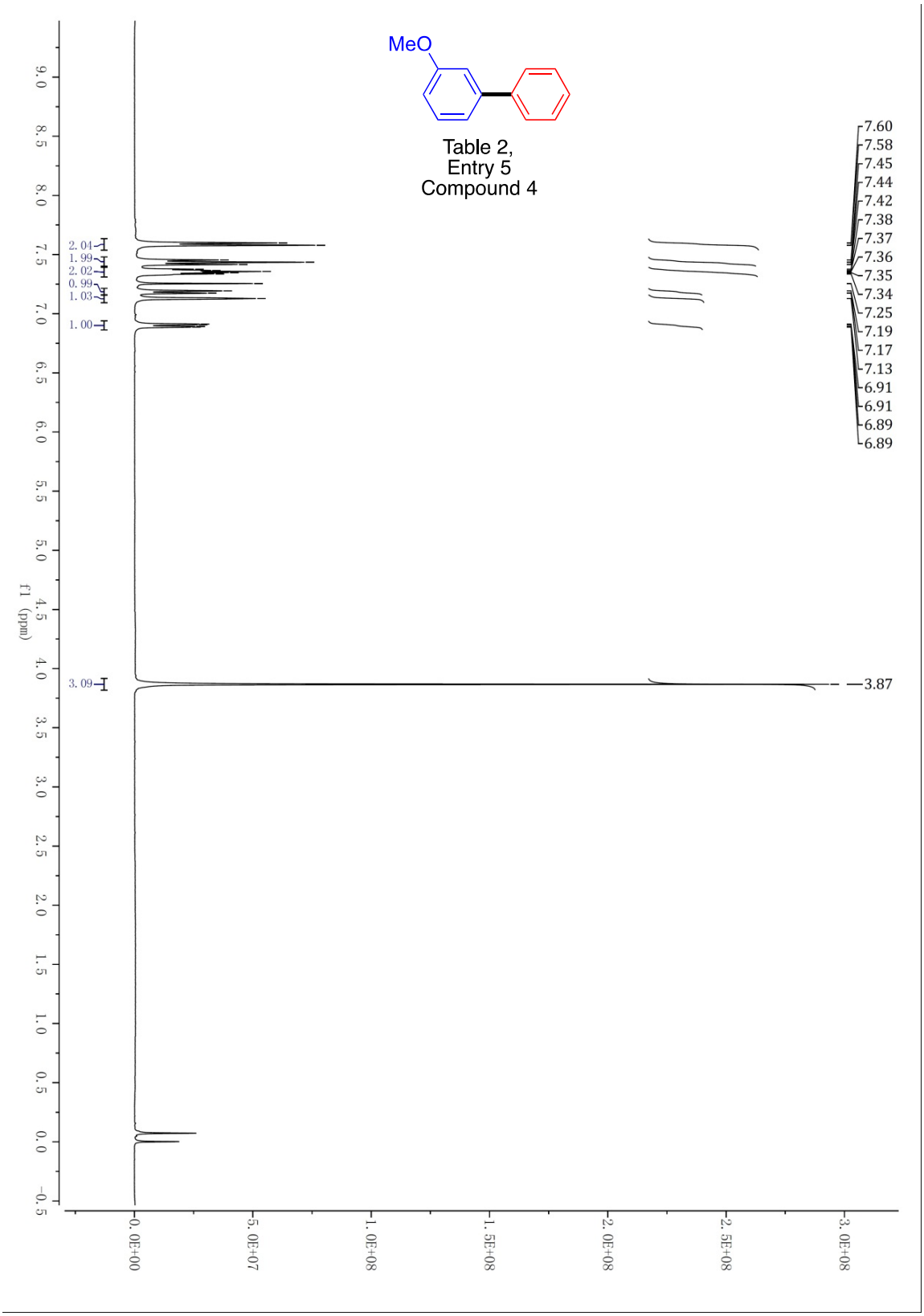

Me
Table 2,
Entry 1, 2
Compound 1
141.47
138.36
136.88
128.81
128.21
126.85
77.34
77.02
76.70
21.32
f1 (ppm)

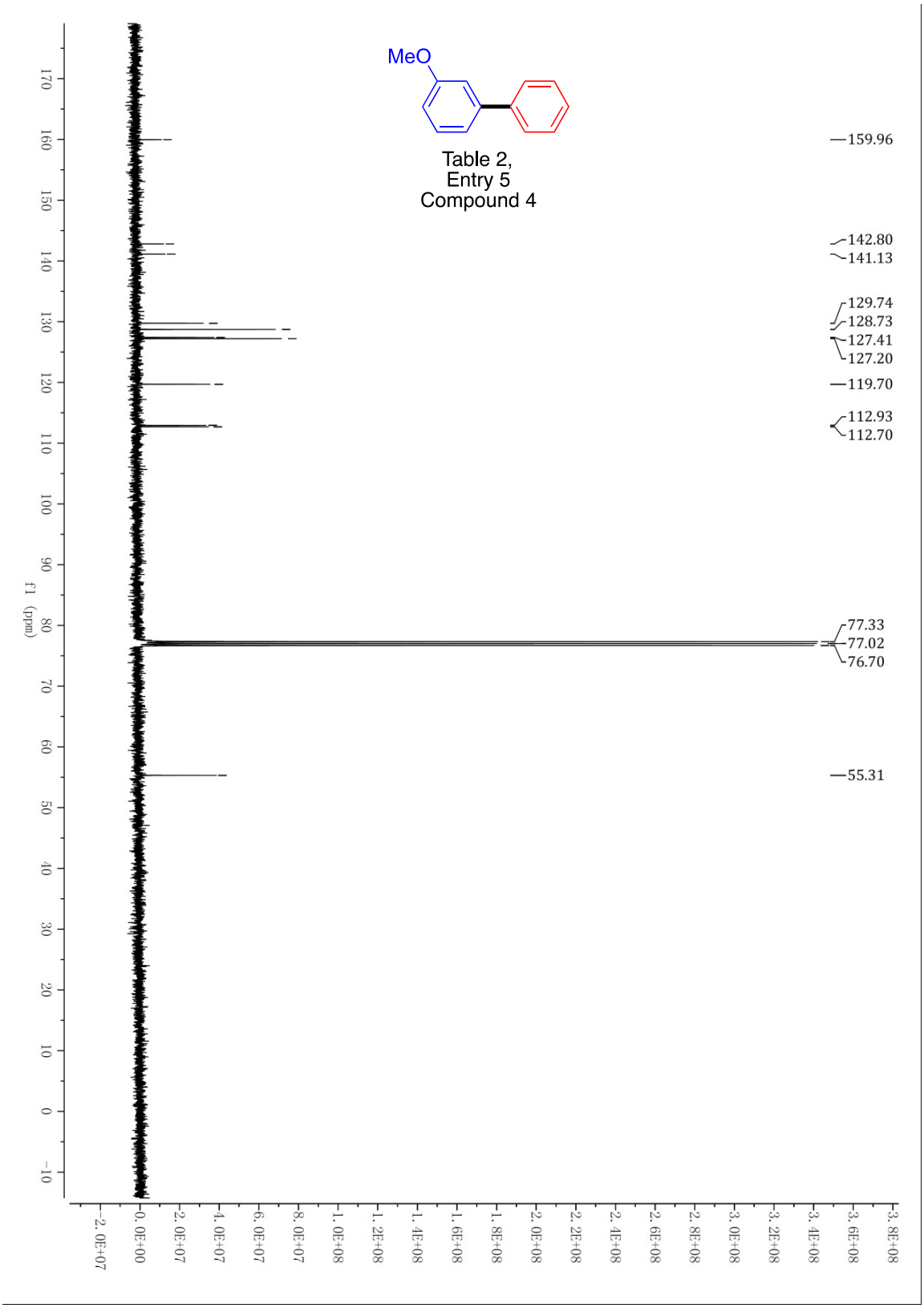

Me
Me
Table 2,
Entry 3
Compound 2
1.96
1.95
1.01
1.91
0.94
6.00
7.64
7.62
7.49
7.47
7.45
7.39
7.37
7.27
7.05
2.44
f1 (ppm)


141 54
141.34
138.29
128.95
128.69
127.25
127.13
125.17
77.40
77.08
76.76
21.46
Me
Me
Table 2,
Entry 3
Compound 2
f1 (ppm)


MeO
Table 2,
Entry 4
Compound 3
7.56
7.54
7.51
7.43
7.41
7.39
7.31
7.29
7.25
6.99
6.96
3.85
3.90
1.99
0.99
2.00
3.05
f1 (ppm)


MeO
Table 2,
Entry 4
Compound 3
159.00
140.78
133.63
128.71
128.15
126.74
114.20
77.34
77.02
76.70
55.41
f1 (ppm)


MeO
Table 2,
Entry 5
Compound 4
2.04
1.99
2.02
0.99
1.03
1.00
3.09
3.87
7.60
7.58
7.45
7.44
7.42
7.38
7.37
7.36
7.35
7.34
7.25
7.19
7.17
7.13
6.91
6.91
6.89
6.89
f1 (ppm)


MeO
Table 2,
Entry 5
Compound 4
159.96
142.80
141.13
129.74
128.73
127.41
127.20
119.70
112.93
112.70
77.33
77.02
76.70
55.31
f1 (ppm)

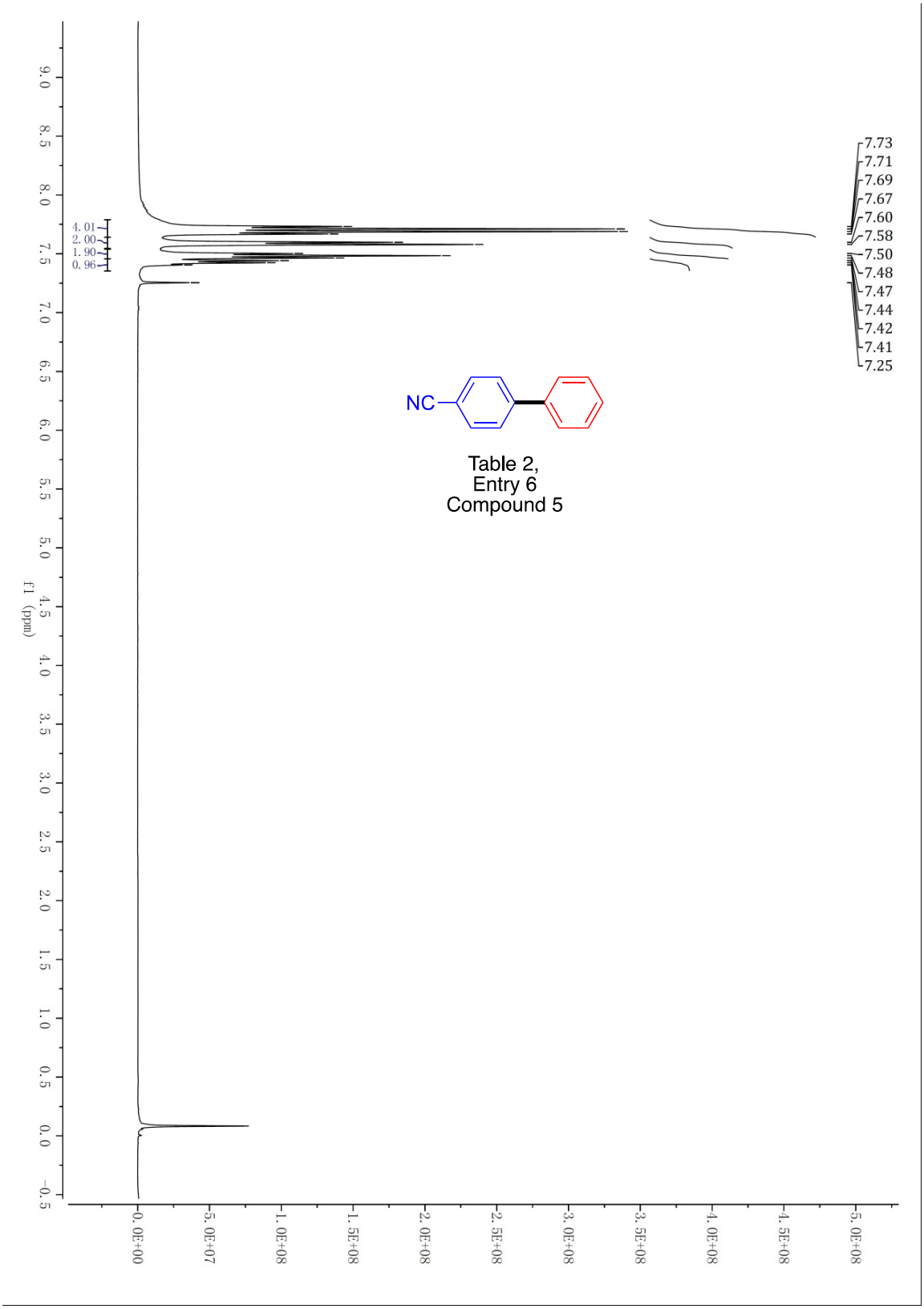
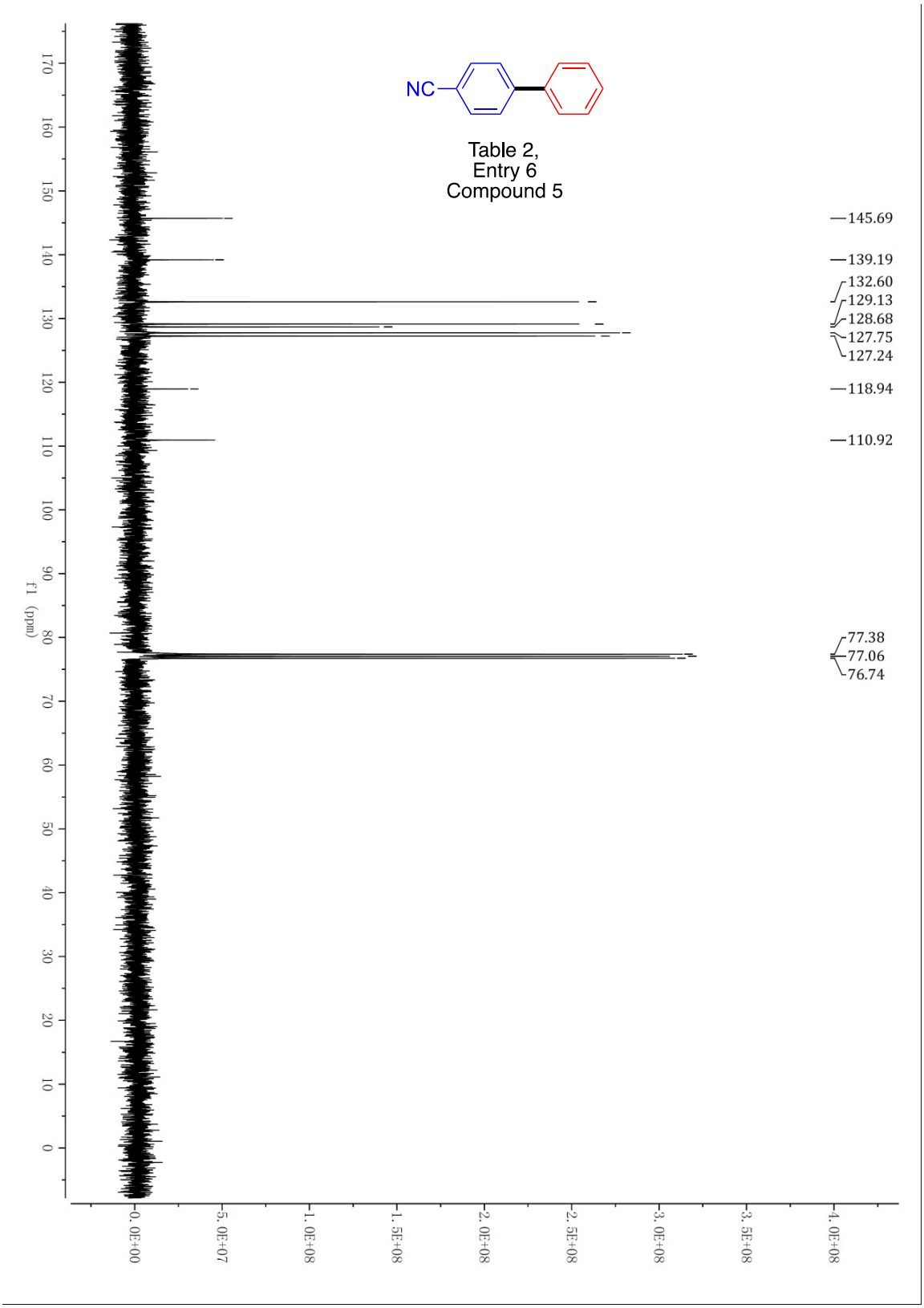


Table 2,
Entry 6
Compound 5


NC
Table 2,
Entry 6
Compound 5
145.69
139.19
132.60
129.13
128.68
127.75
127.24
118.94
110.92
77.38
77.06
76.74
f1 (ppm)

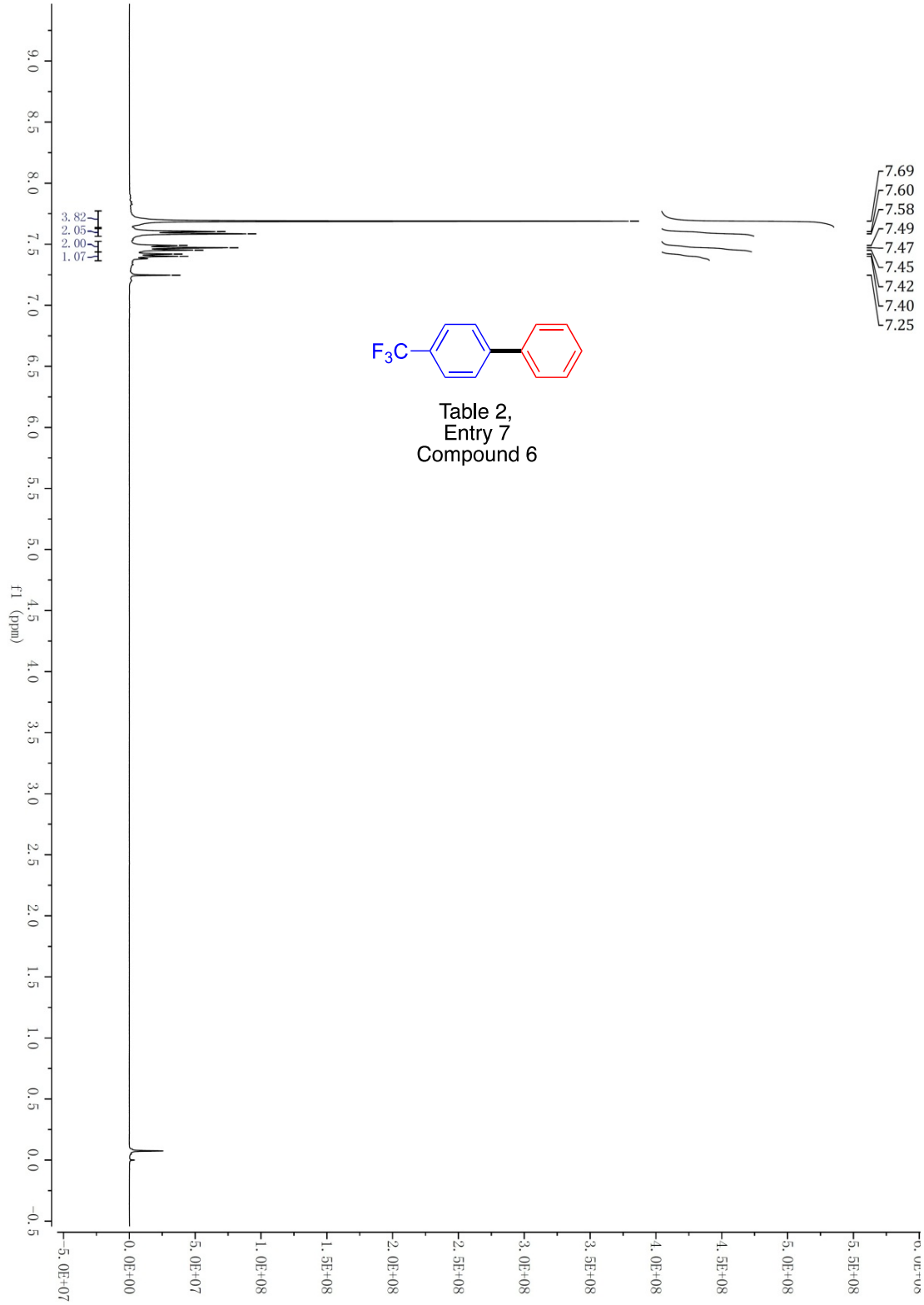
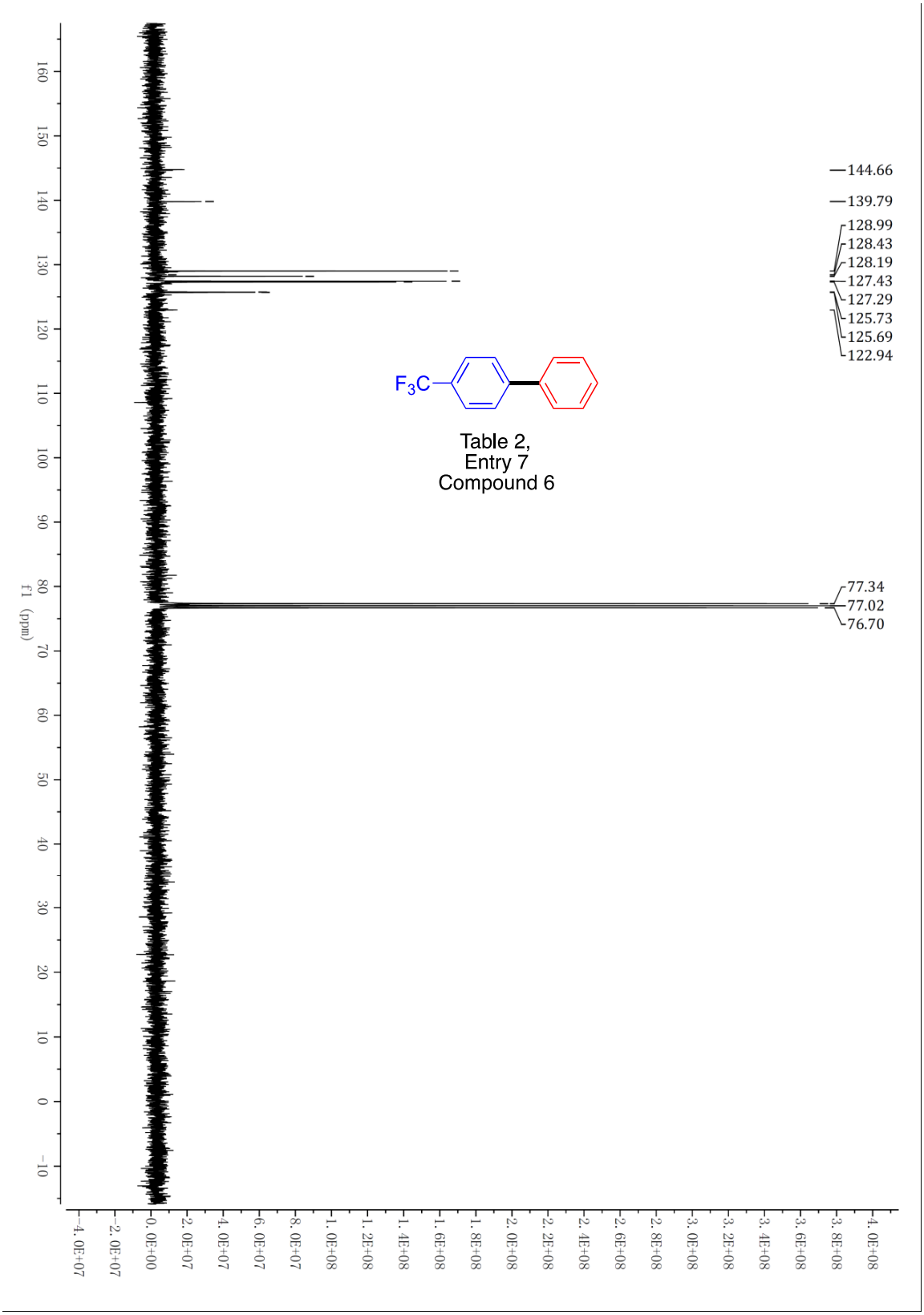


Table 2,
Entry 7
Compound 6


144.66
139.79
128.99
128.43
128.19
127.43
127.29
125.73
125.69
122.94
77.34
77.02
76.70
F3C
Table 2,
Entry 7
Compound 6
f1 (ppm)

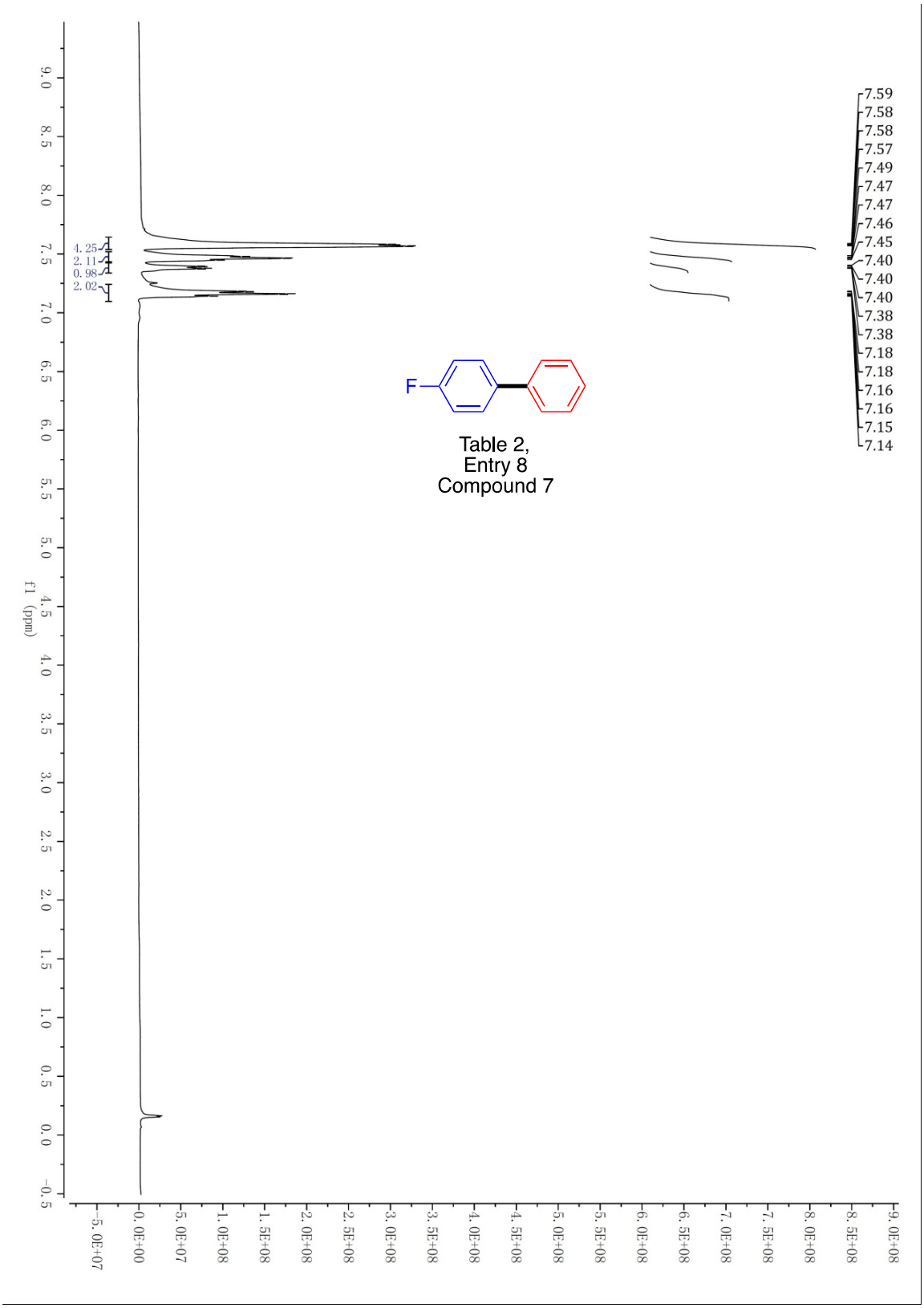
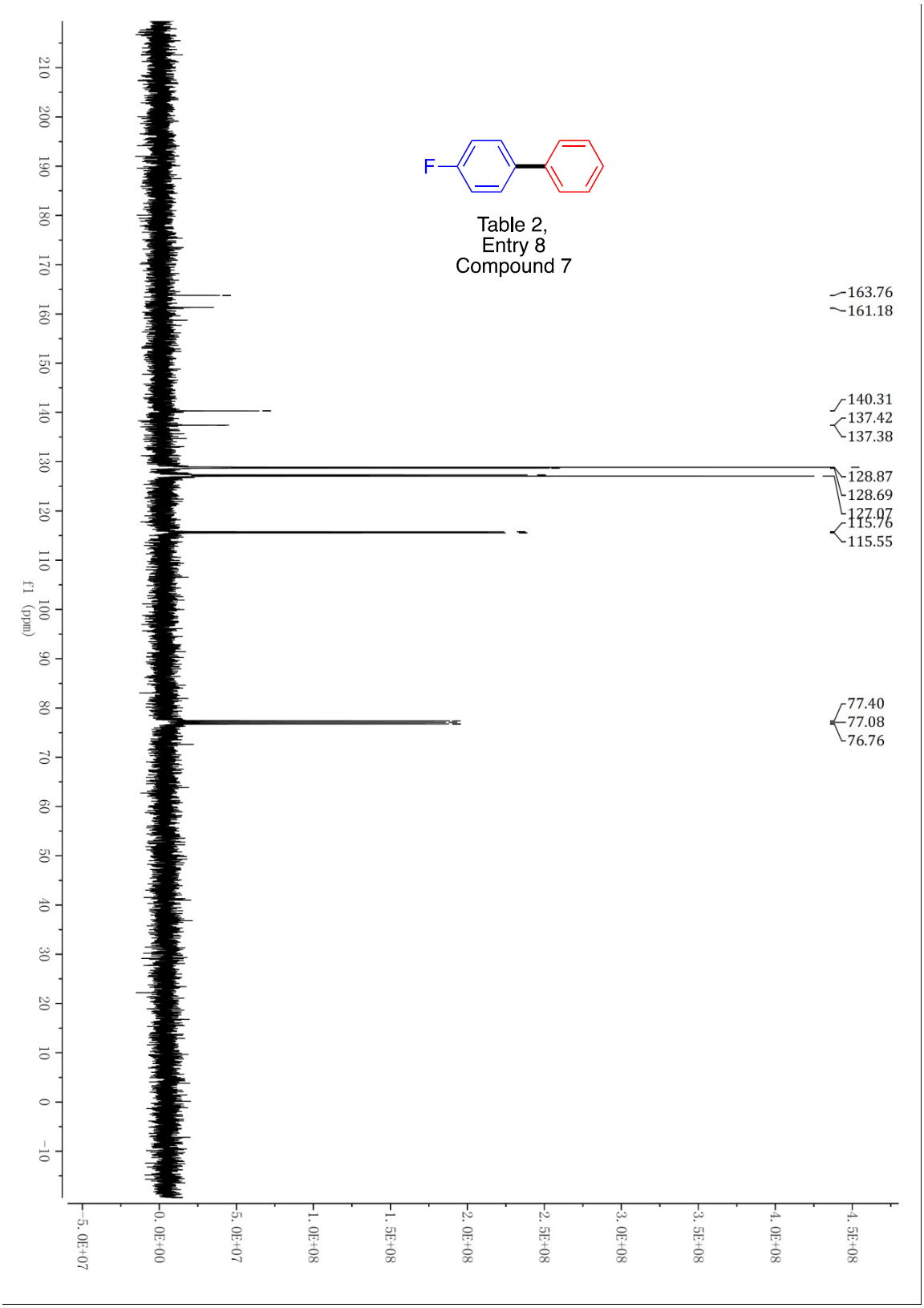
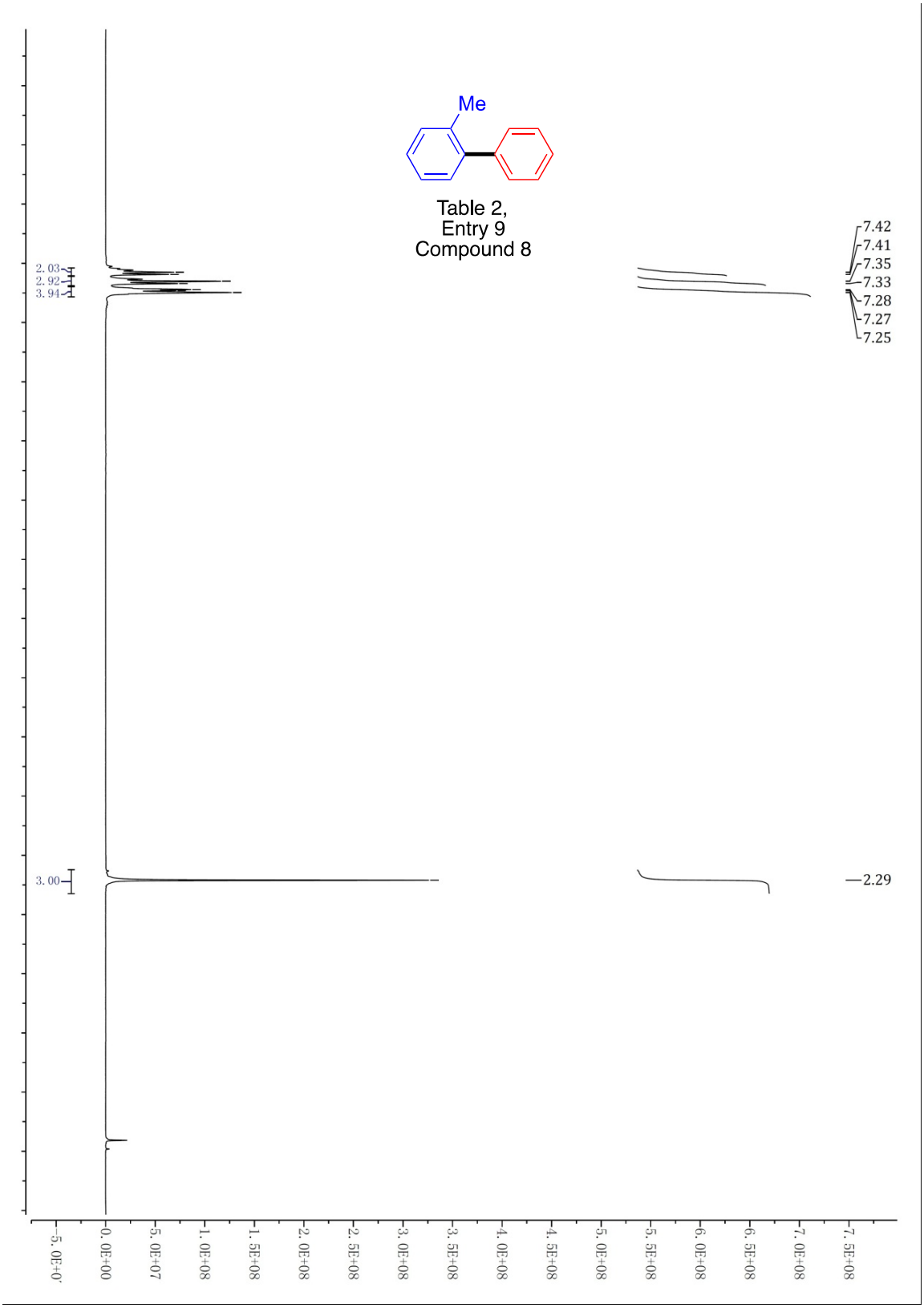
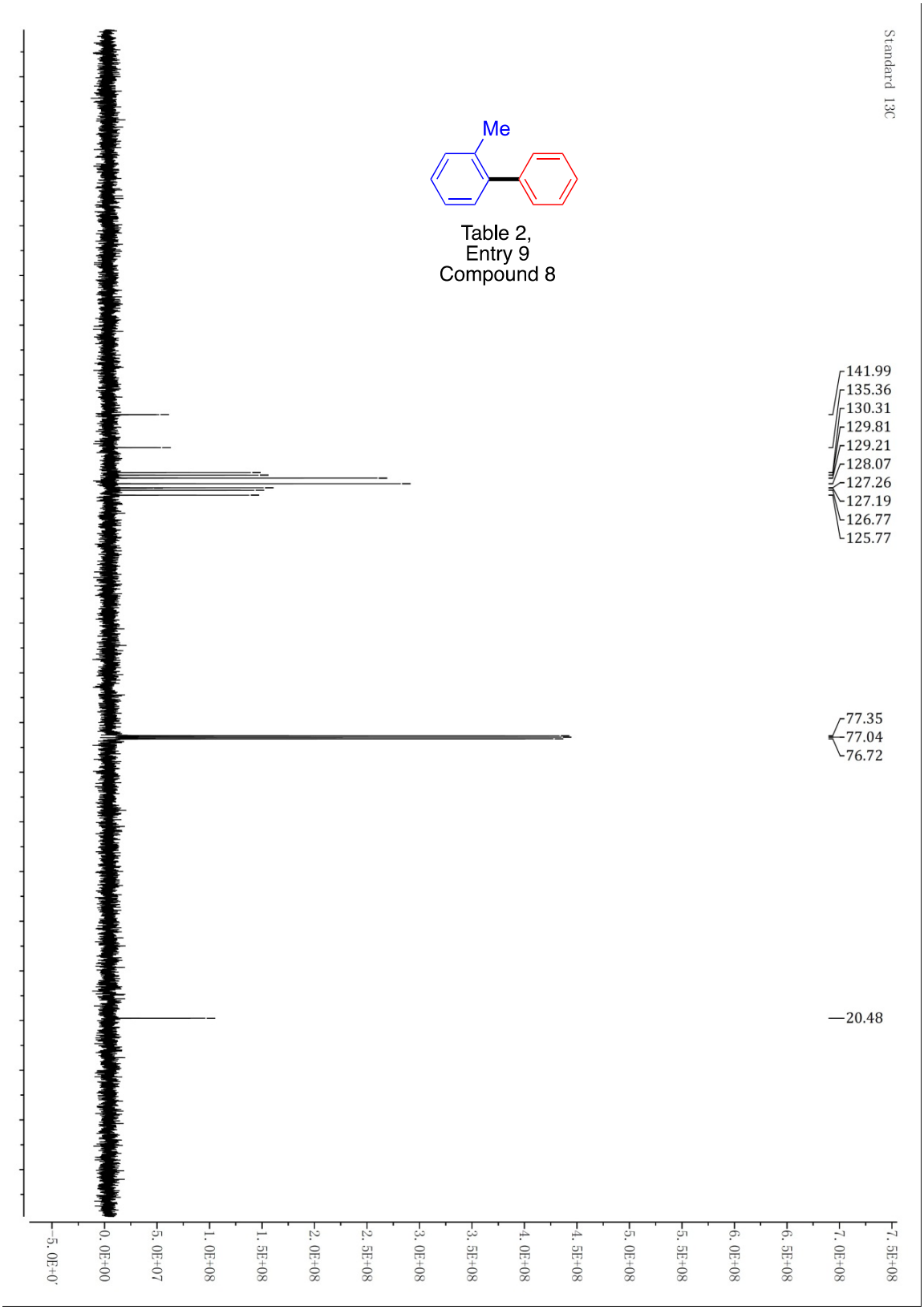


Table 2,
Entry 8
Compound 7


F
Table 2,
Entry 8
Compound 7
163.76
161.18
140.31
137.42
137.38
128.87
128.69
127.07
115.76
115.55
77.40
77.08
76.76
f1 (ppm)


Me
Table 2,
Entry 9
Compound 8
2.03
2.92
3.94
3.00
7.42
7.41
7.35
7.33
7.28
7.27
7.25
2.29


Standard 13C
Me
Table 2,
Entry 9
Compound 8
141.99
135.36
130.31
129.81
129.21
128.07
127.26
127.19
126.77
125.77
77.35
77.04
76.72
20.48
-5.0E+07
0.0E+00
5.0E+07
1.0E+08
1.5E+08
2.0E+08
2.5E+08
3.0E+08
3.5E+08
4.0E+08
4.5E+08
5.0E+08
5.5E+08
6.0E+08
6.5E+08
7.0E+08
7.5E+08

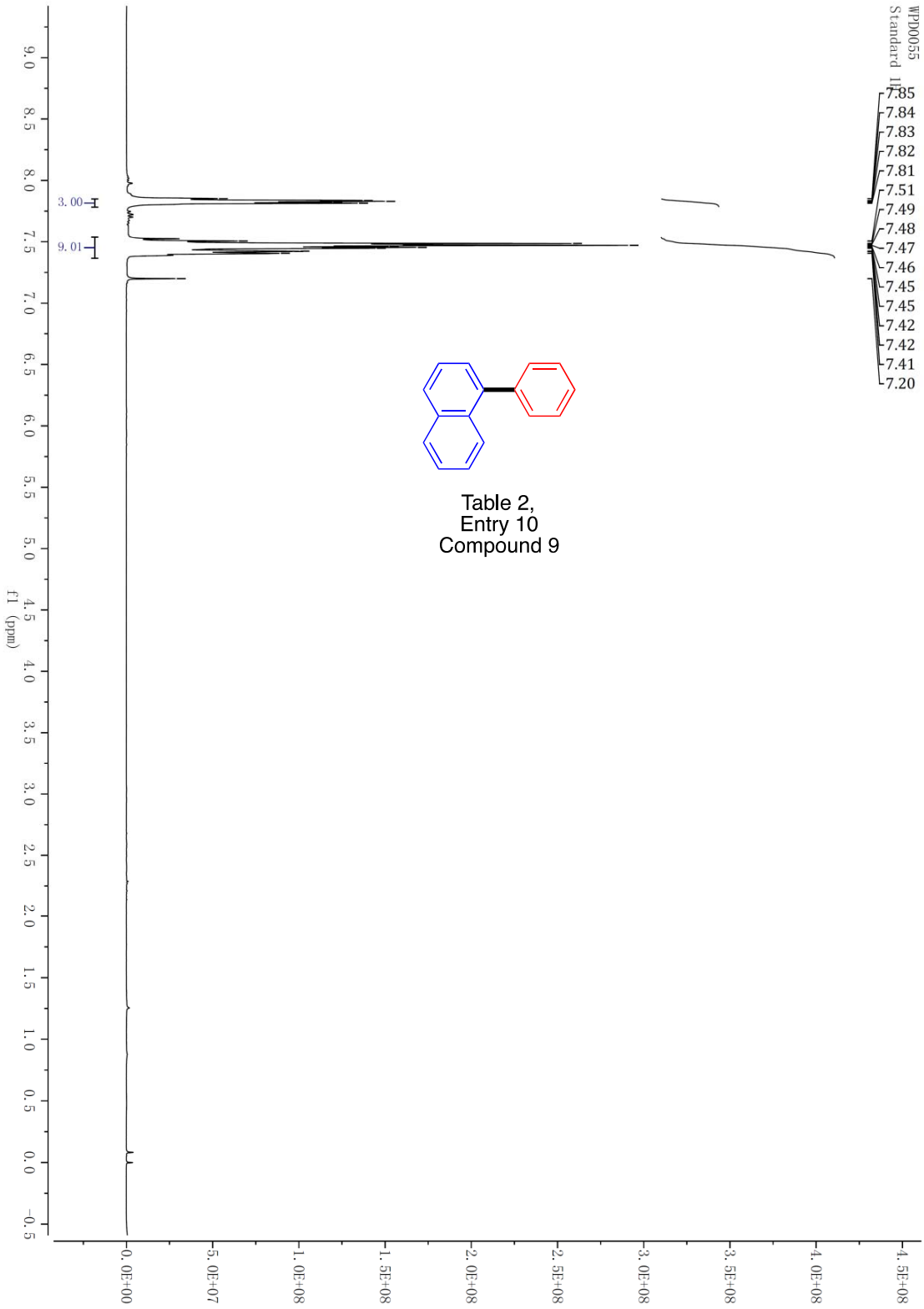


Table 2,
Entry 10
Compound 9

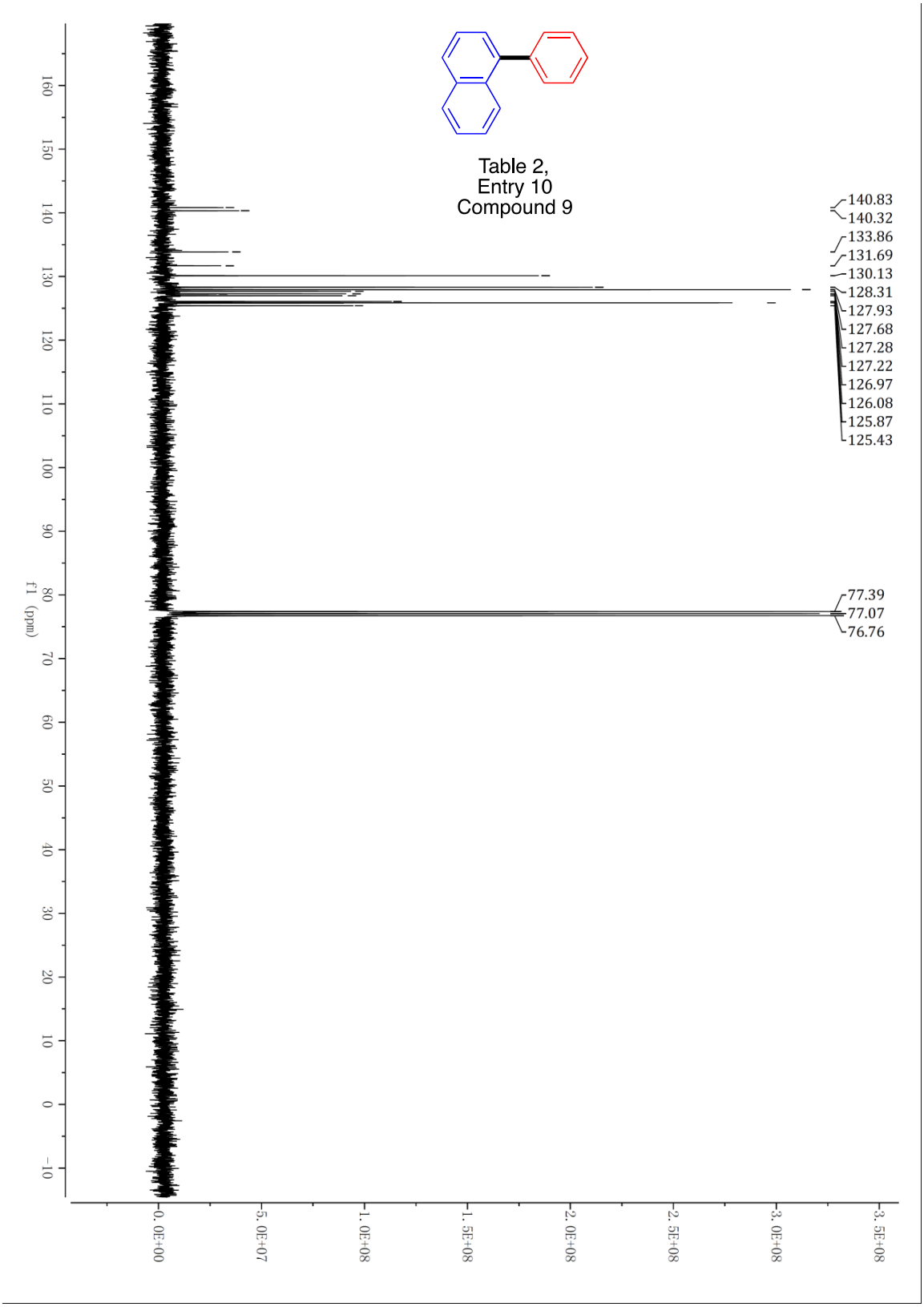


Table 2,
Entry 10
Compound 9
140.83
140.32
133.86
131.69
130.13
128.31
127.93
127.68
127.28
127.22
126.97
126.08
125.87
125.43
77.39
77.07
76.76
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0.0E+00
5.0E+07
1.0E+08
1.5E+08
2.0E+08
2.5E+08
3.0E+08
3.5E+08

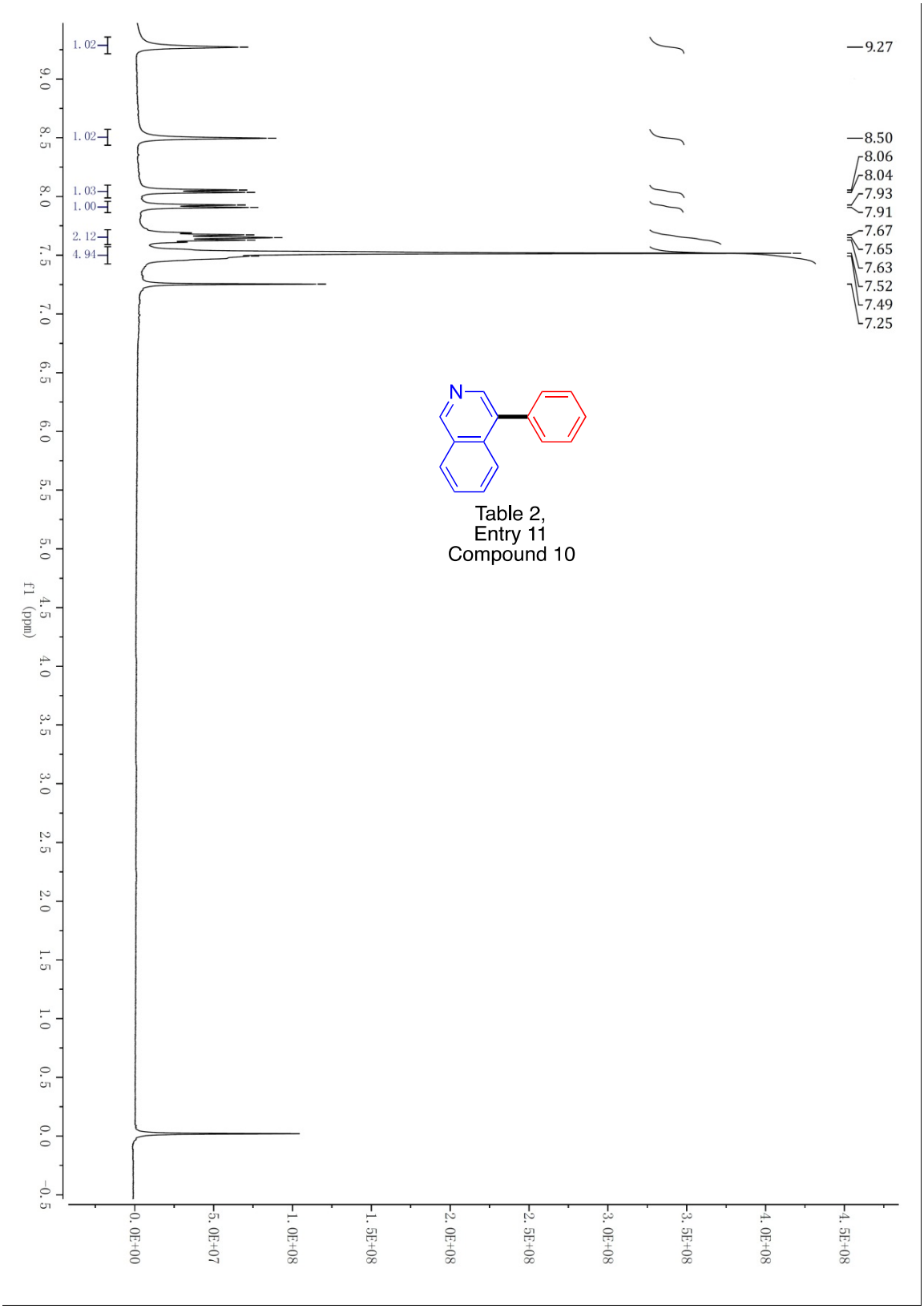
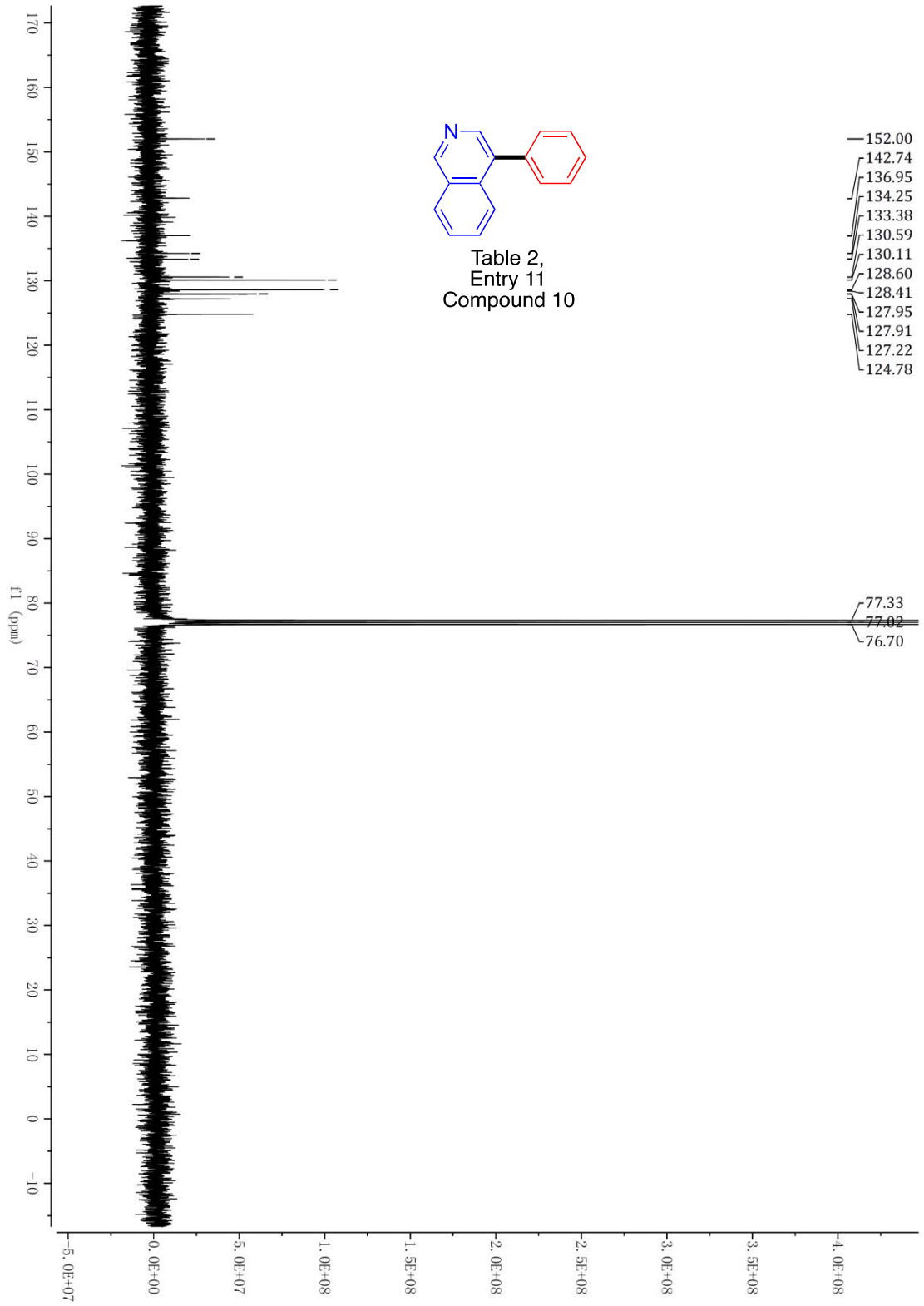


Table 2,
Entry 11
Compound 10


N
Table 2,
Entry 11
Compound 10
152.00
142.74
136.95
134.25
133.38
130.59
130.11
128.60
128.41
127.95
127.91
127.22
124.78
77.33
77.02
76.70
f1 (ppm)

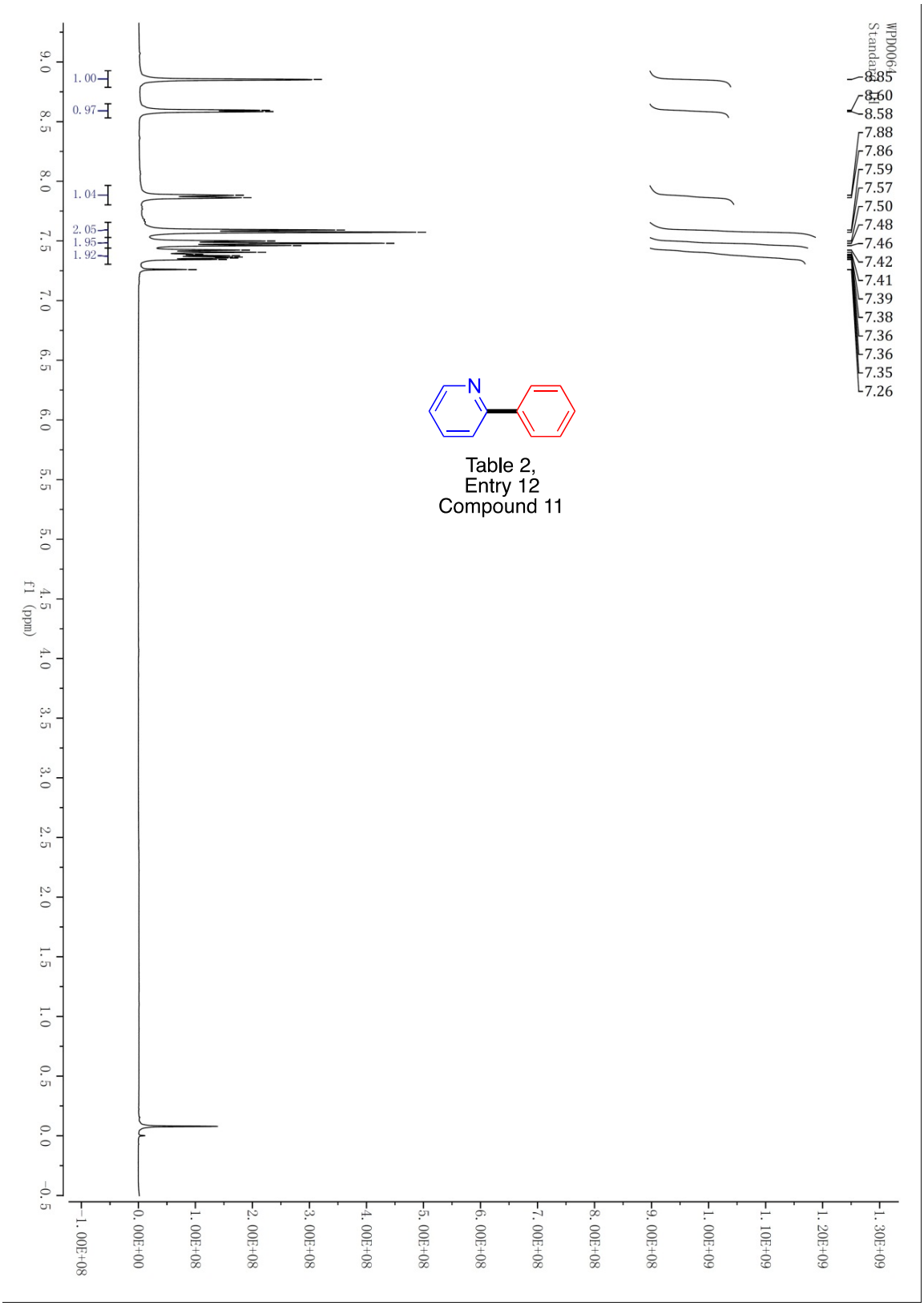


Table 2,
Entry 12
Compound 11

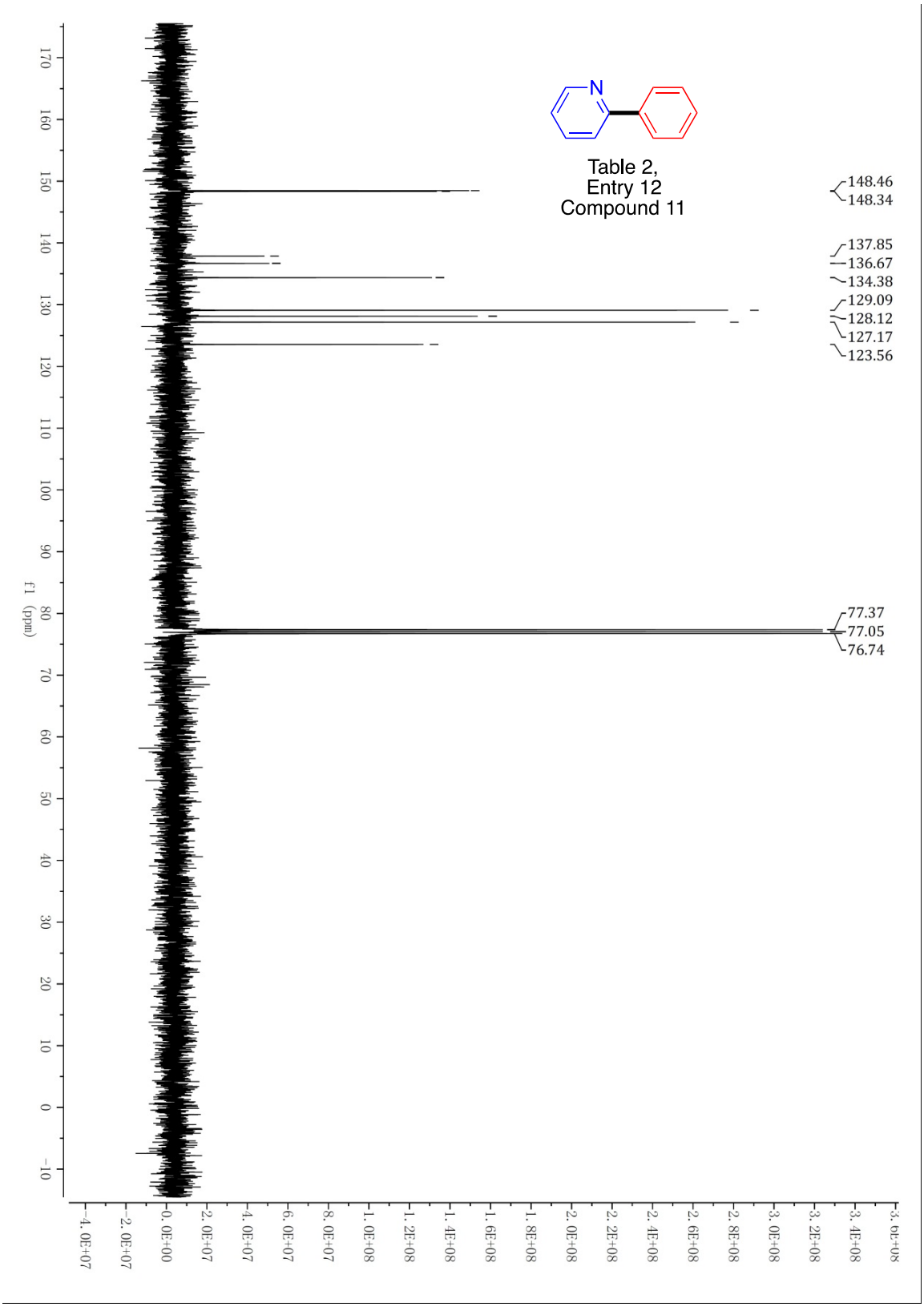
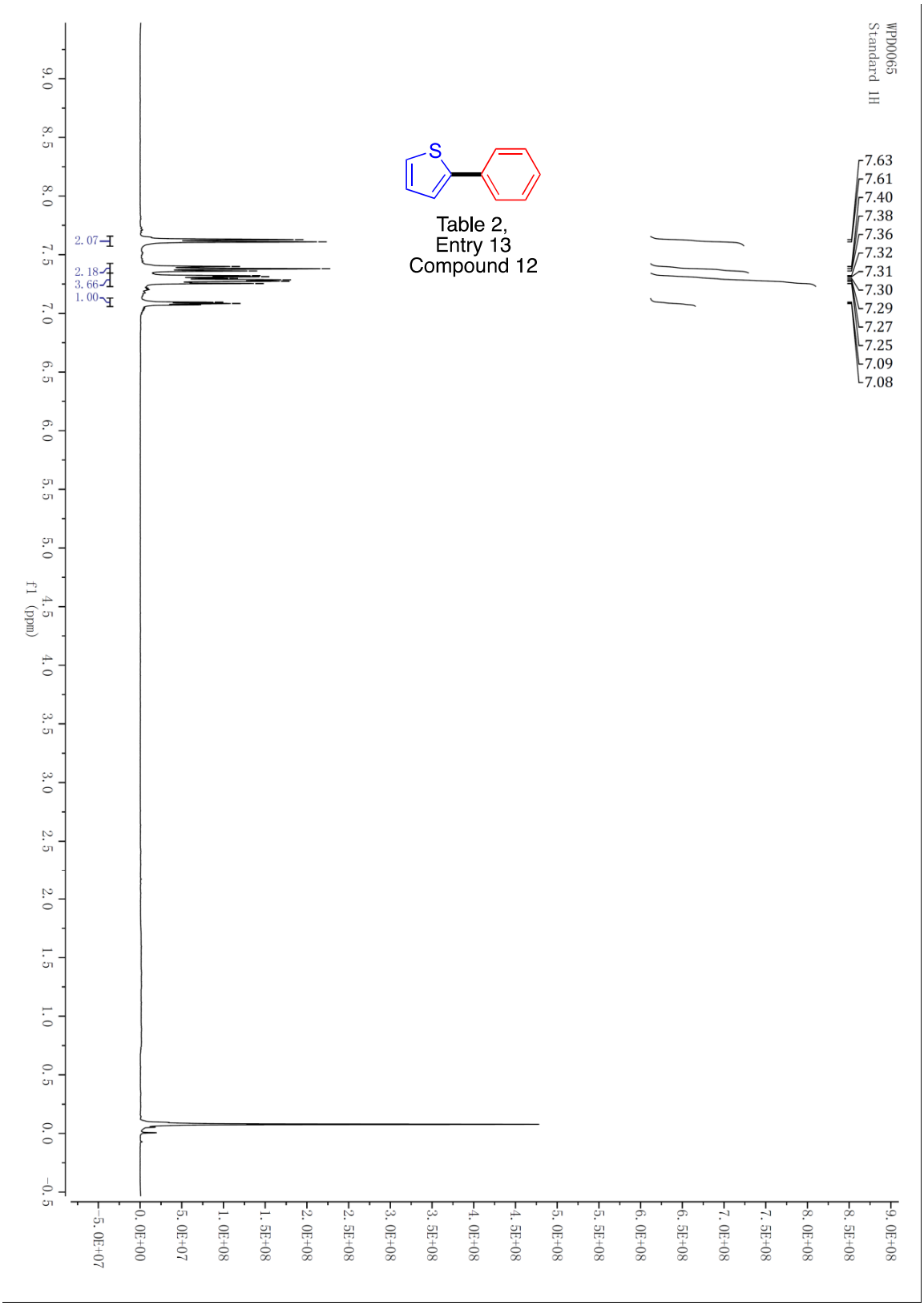
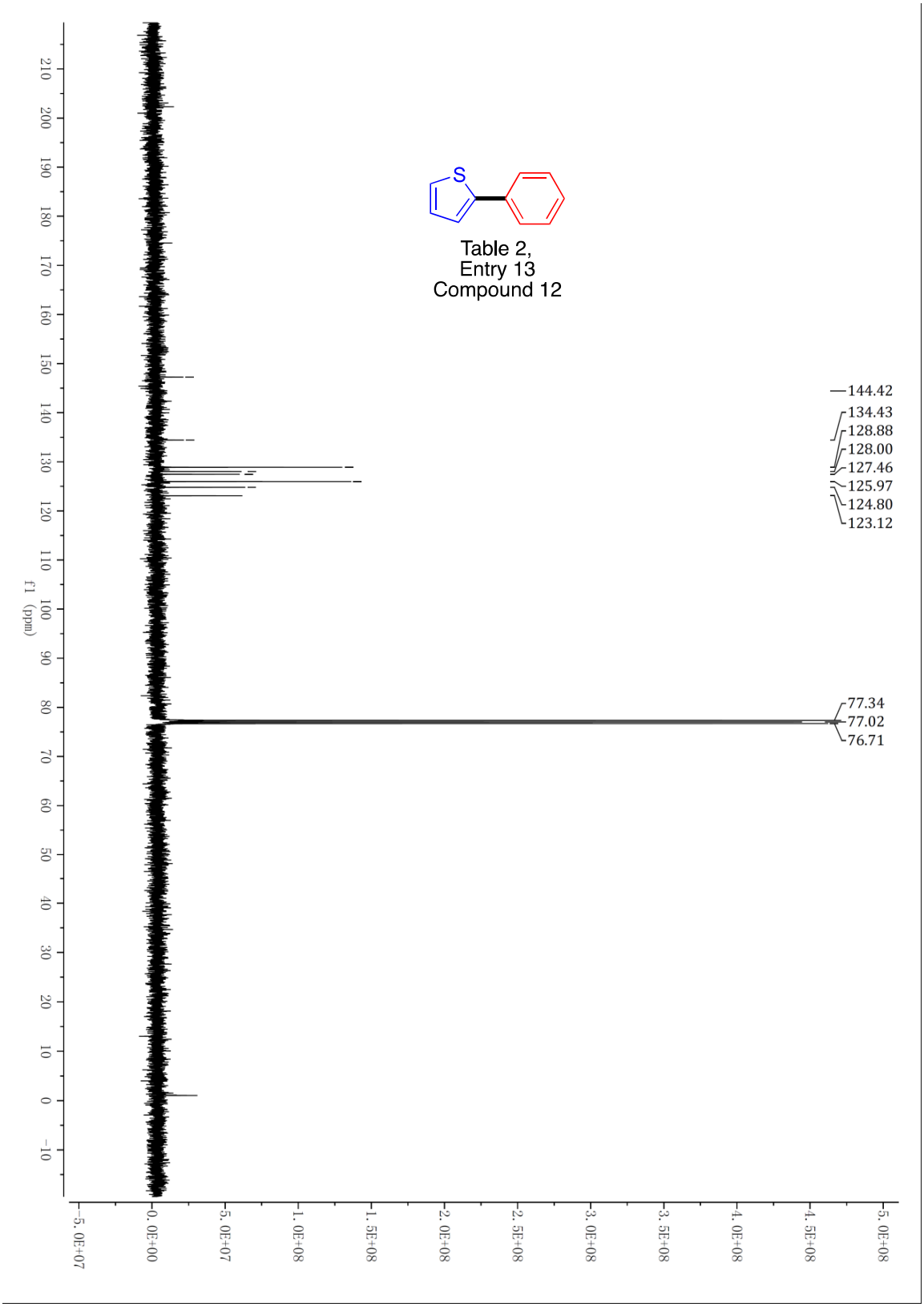
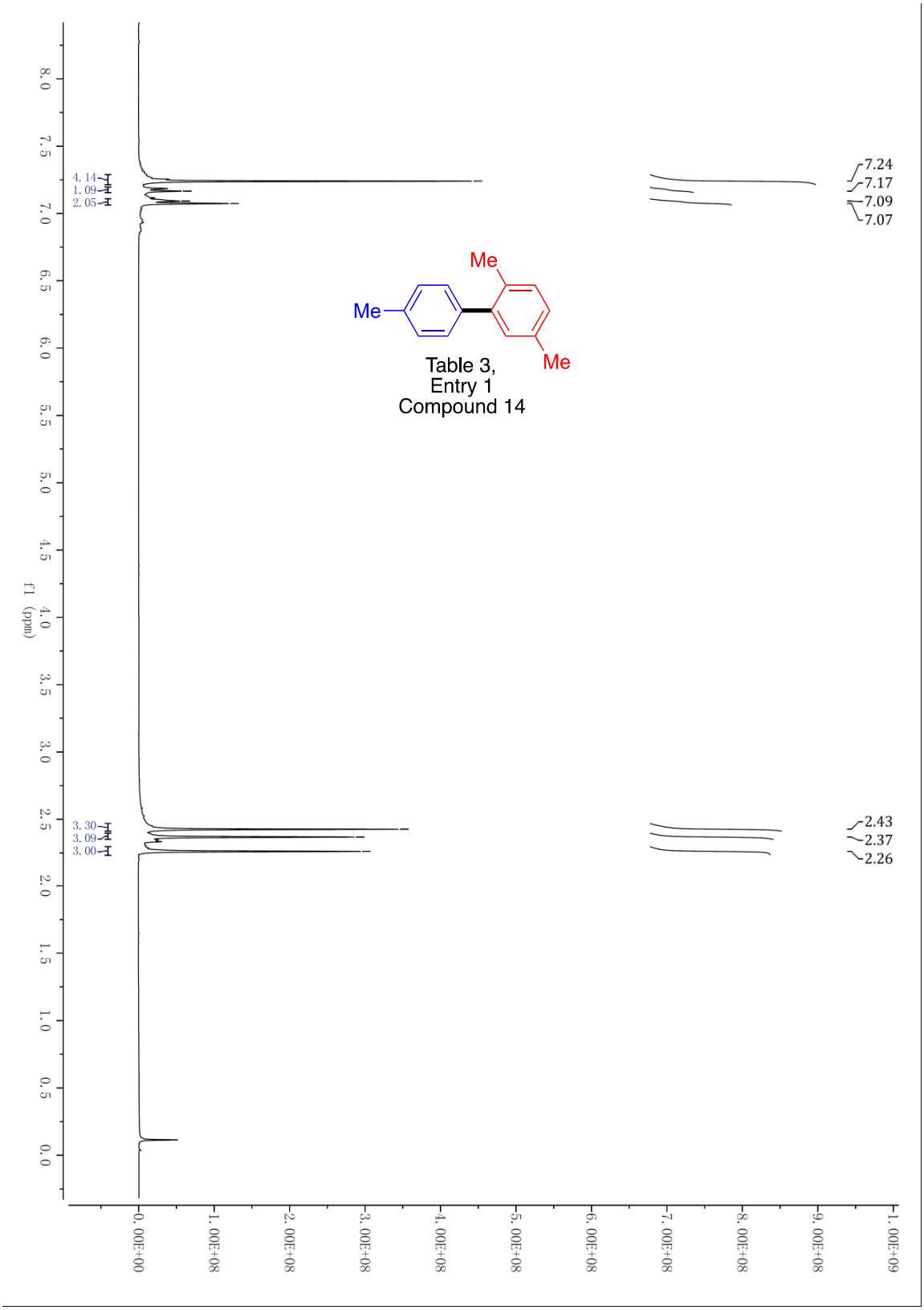
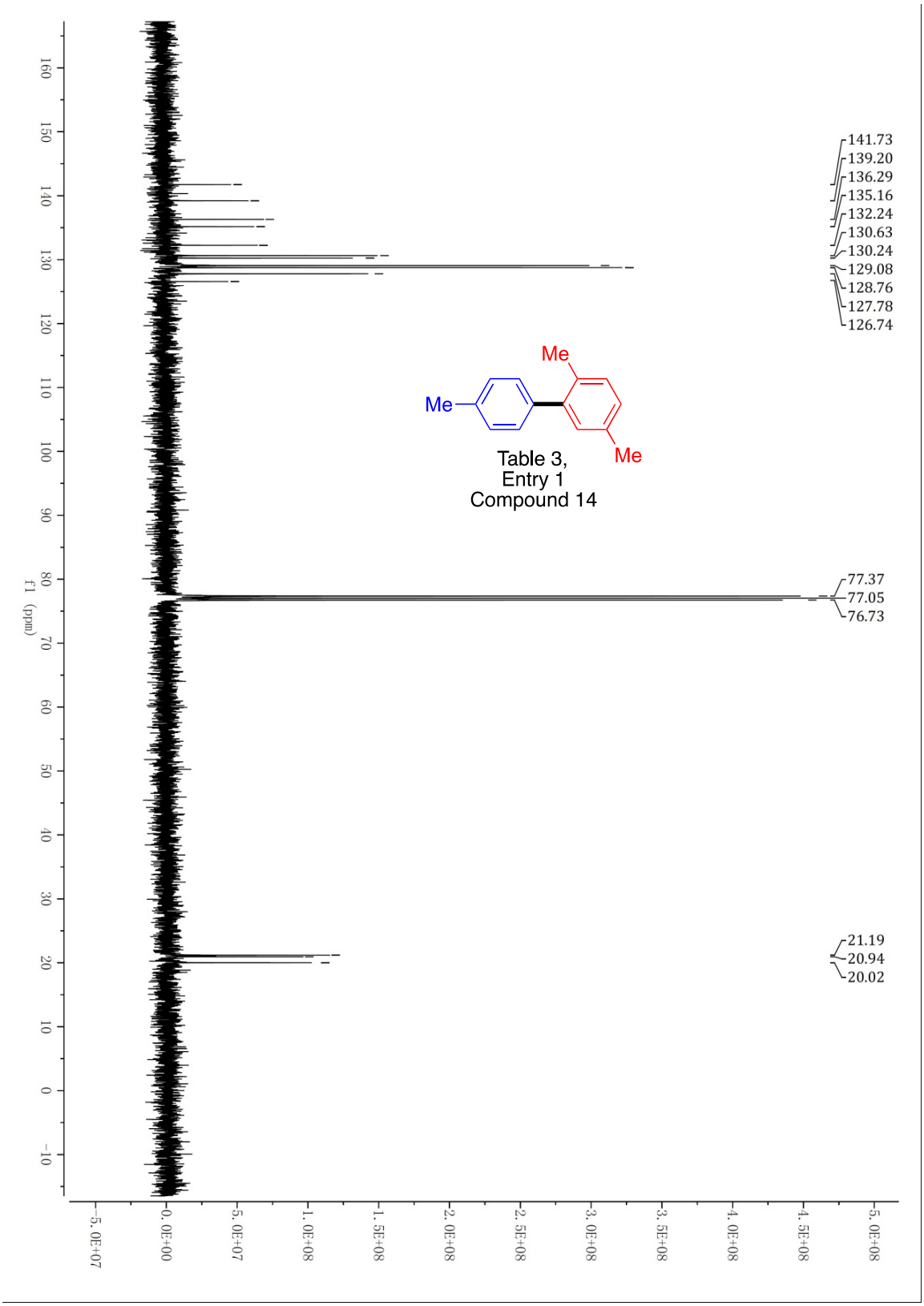


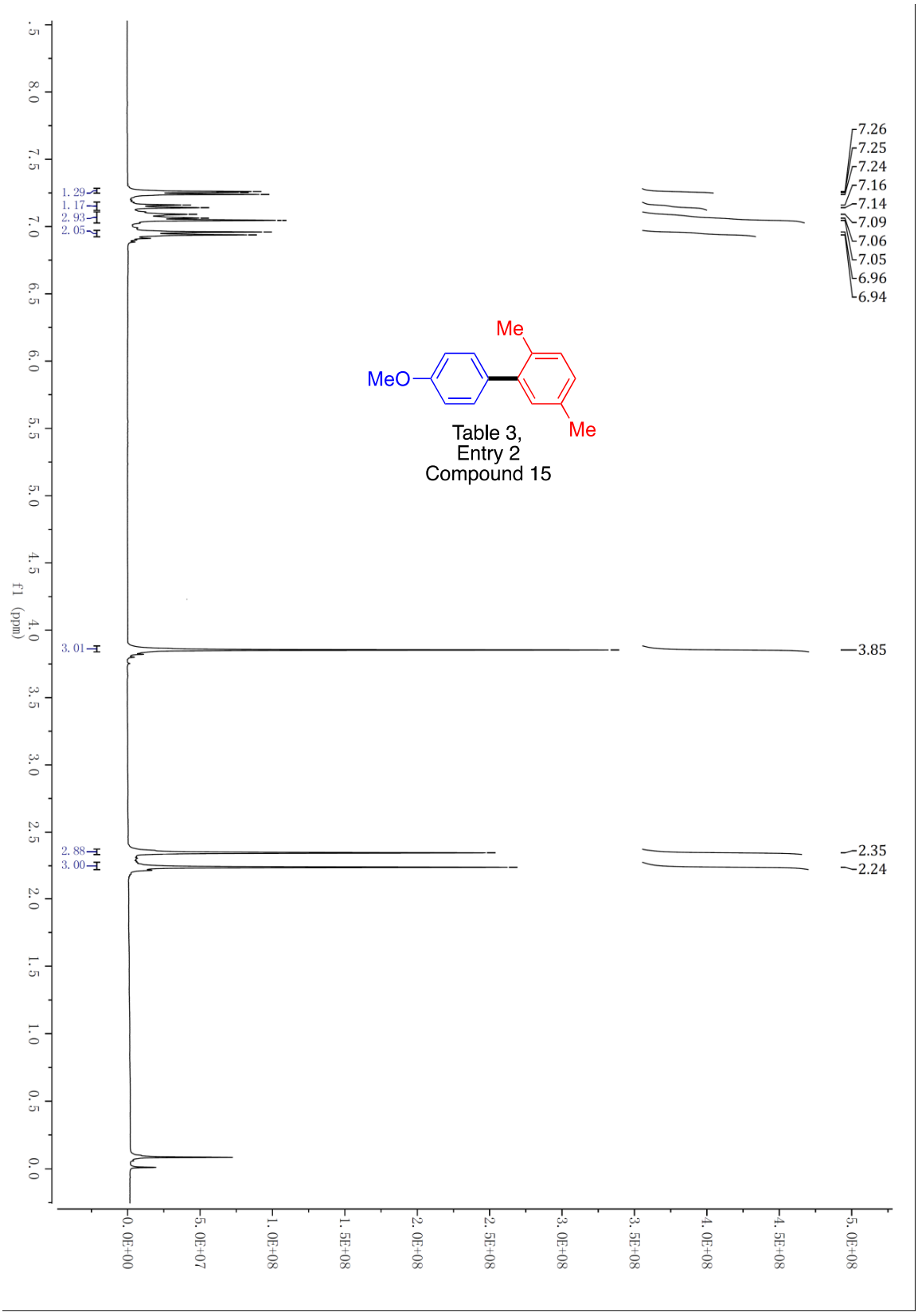
Table 2,
Entry 12
Compound 11
148.46
148.34
137.85
136.67
134.38
129.09
128.12
127.17
123.56
77.37
77.05
76.74
f1 (ppm)

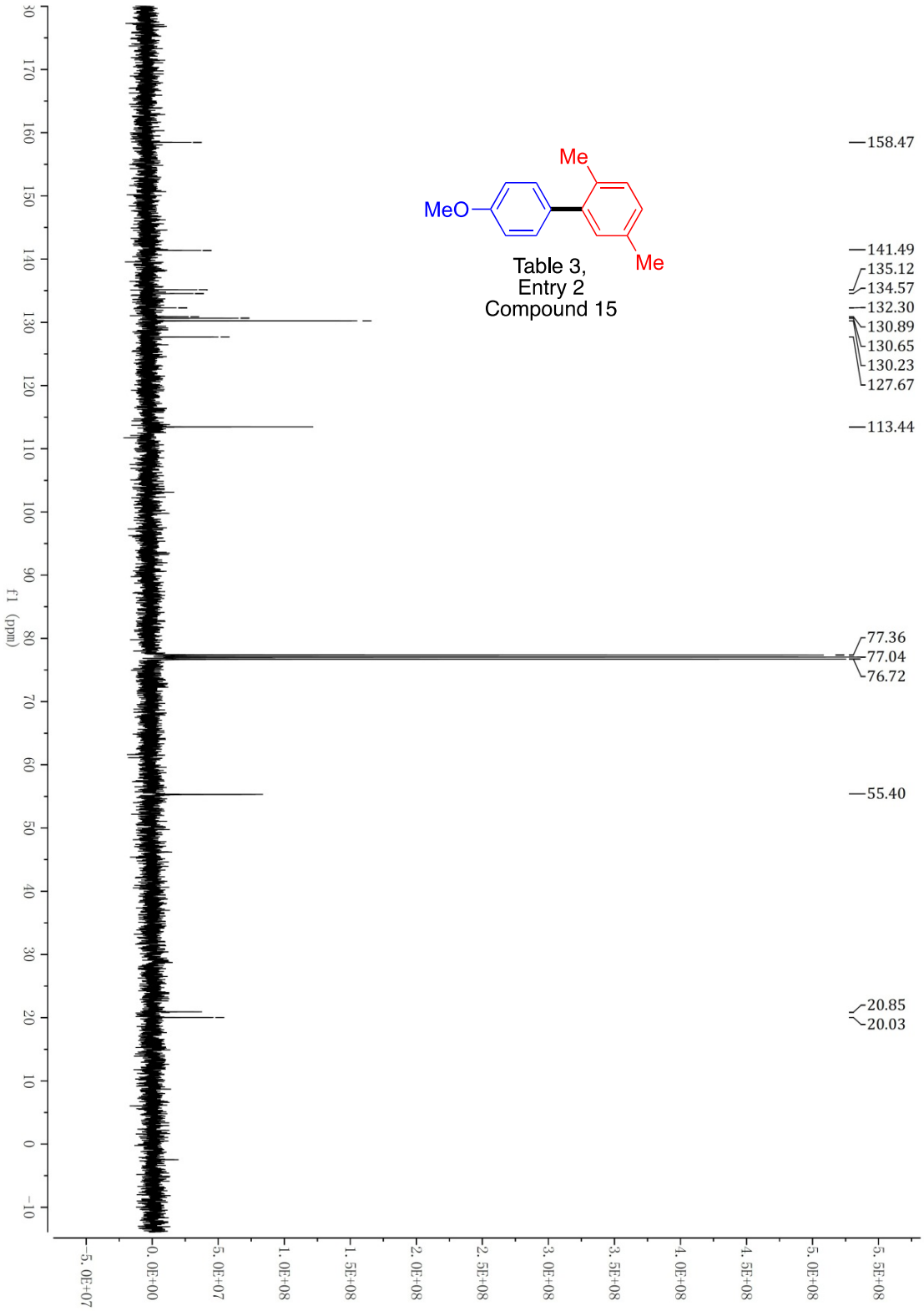

WPD0065
Standard 1H
Table 2,
Entry 13
Compound 12
S
7.63
7.61
7.40
7.38
7.36
7.32
7.31
7.30
7.29
7.27
7.25
7.09
7.08
2.07
2.18
3.66
1.00
f1 (ppm)

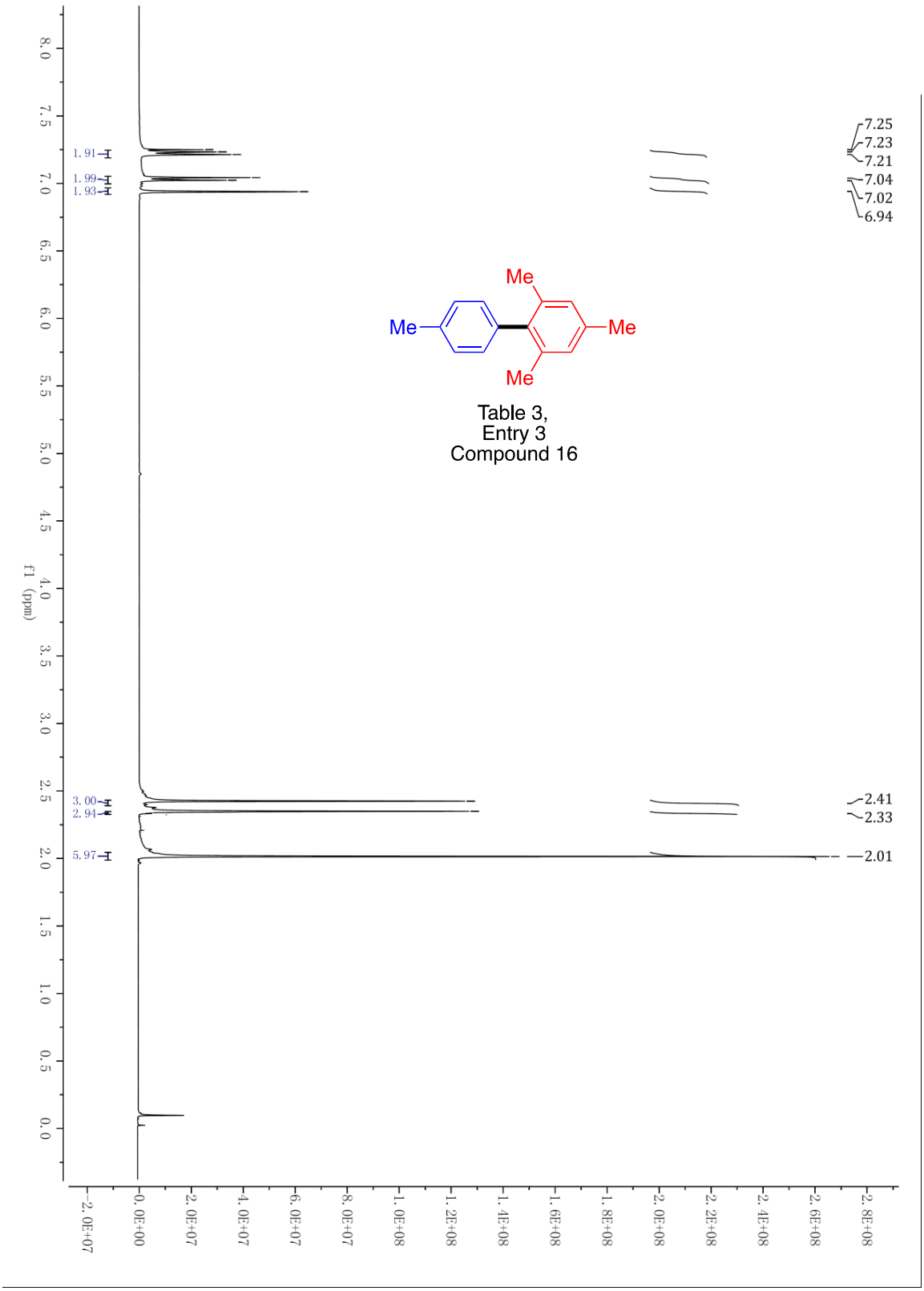

S
Table 2,
Entry 13
Compound 12
144.42
134.43
128.88
128.00
127.46
125.97
124.80
123.12
77.34
77.02
76.71
f1 (ppm)

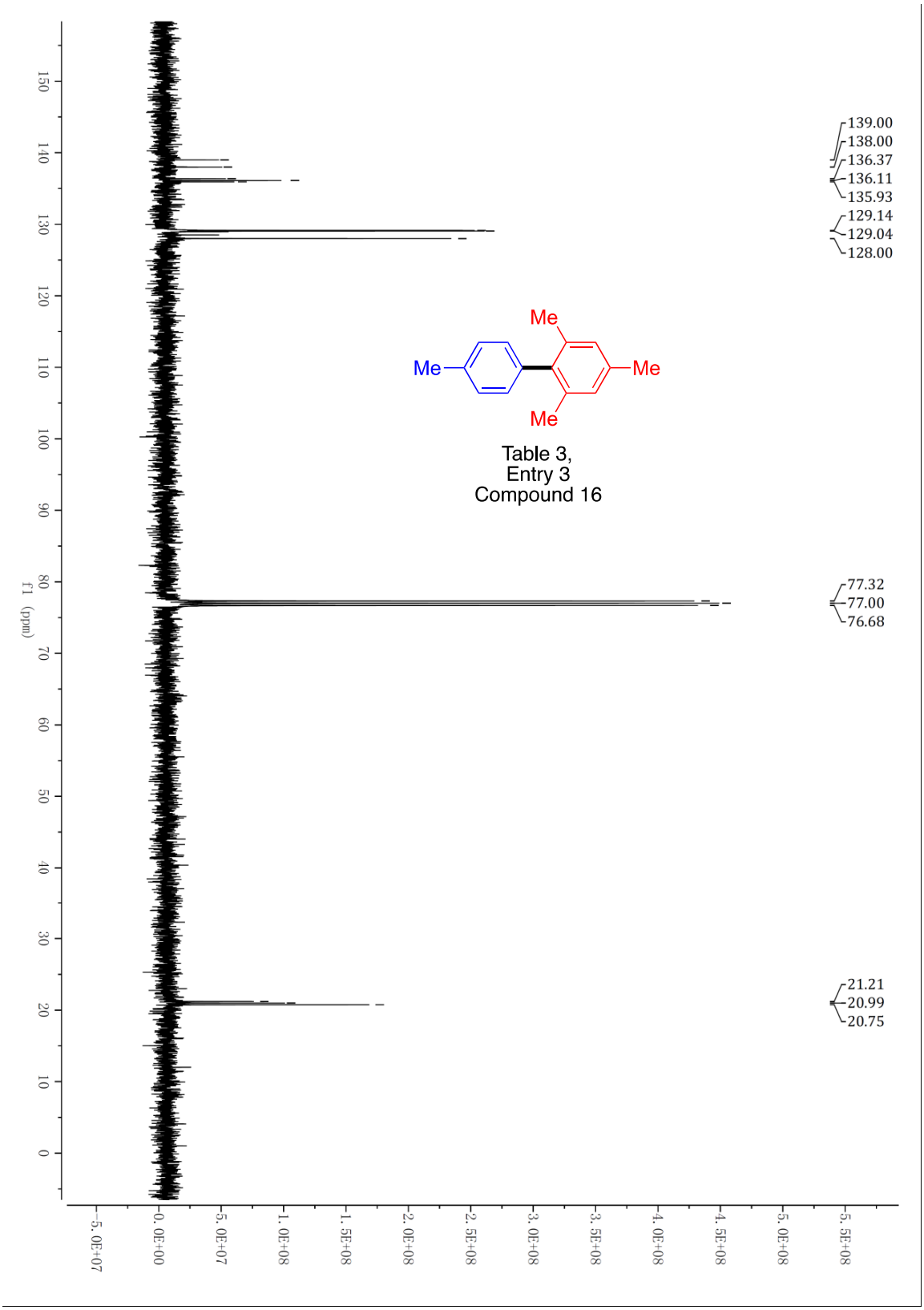

Me
Me
Me
Table 3,
Entry 1
Compound 14
4.14
1.09
2.05
3.30
3.09
3.00
7.24
7.17
7.09
7.07
2.43
2.37
2.26
f1 (ppm)

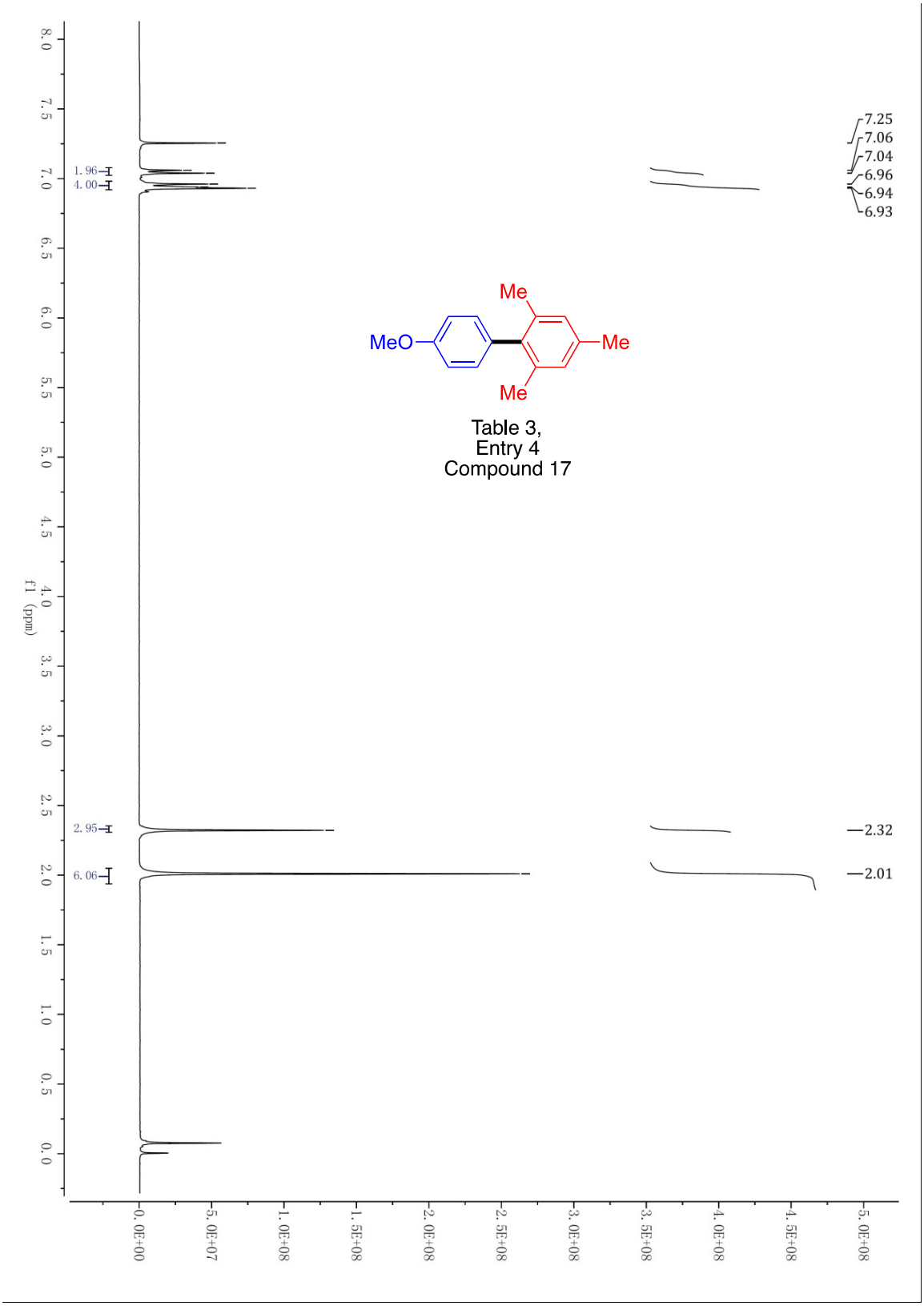

141.73
139.20
136.29
135.16
132.24
130.63
130.24
129.08
128.76
127.78
126.74
77.37
77.05
76.73
21.19
20.94
20.02
Me
Me
Me
Table 3,
Entry 1
Compound 14
f1 (ppm)

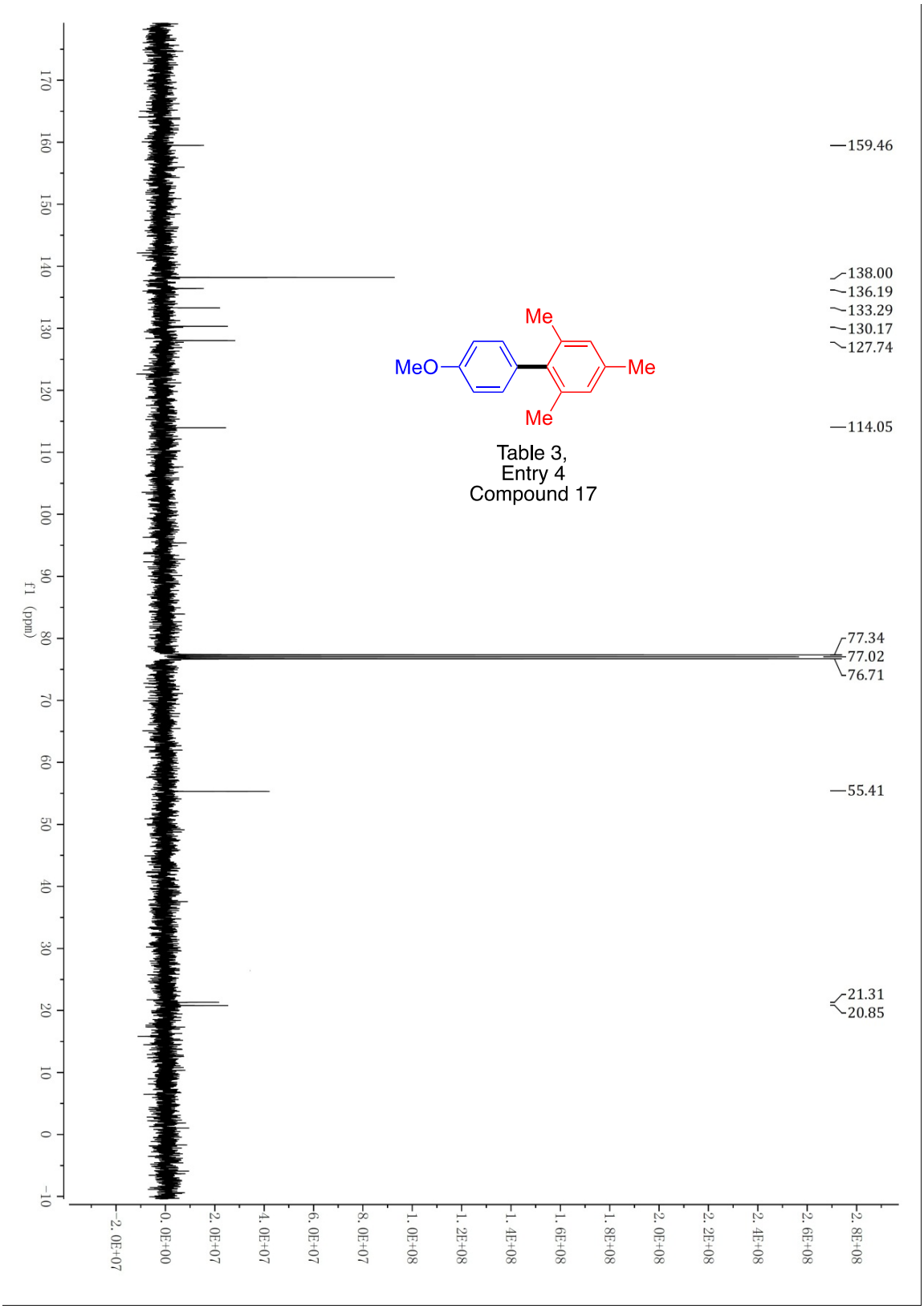

7.26
7.25
7.24
7.16
7.14
7.09
7.06
7.05
6.96
6.94
1.29
1.17
2.93
2.05
3.01
2.88
3.00
3.85
2.35
2.24
Me
MeO
Me
Table 3,
Entry 2
Compound 15
f1 (ppm)

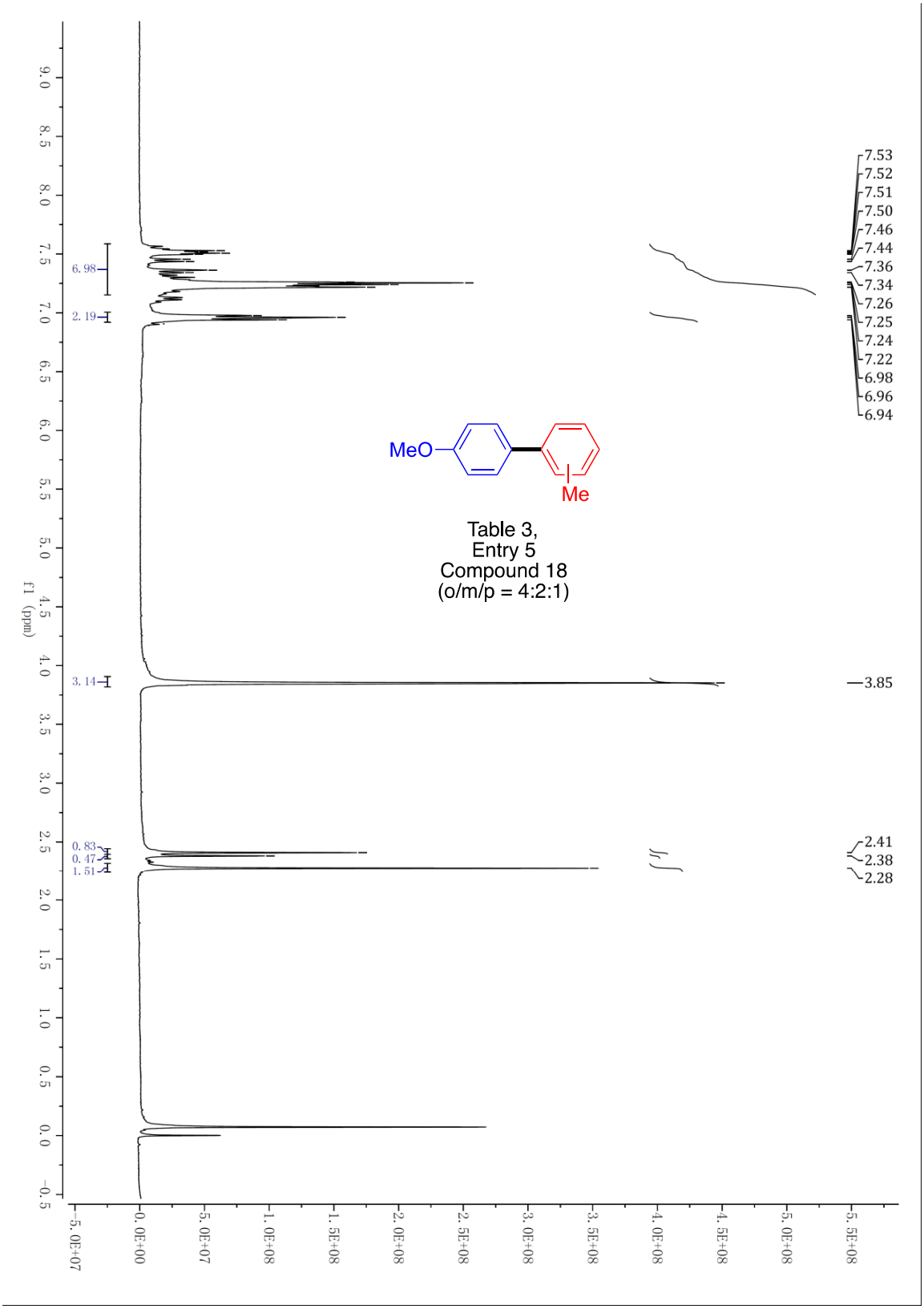

Me
MeO
Me
Table 3,
Entry 2
Compound 15
158.47
141.49
135.12
134.57
132.30
130.89
130.65
130.23
127.67
113.44
77.36
77.04
76.72
55.40
20.85
20.03
f1 (ppm)

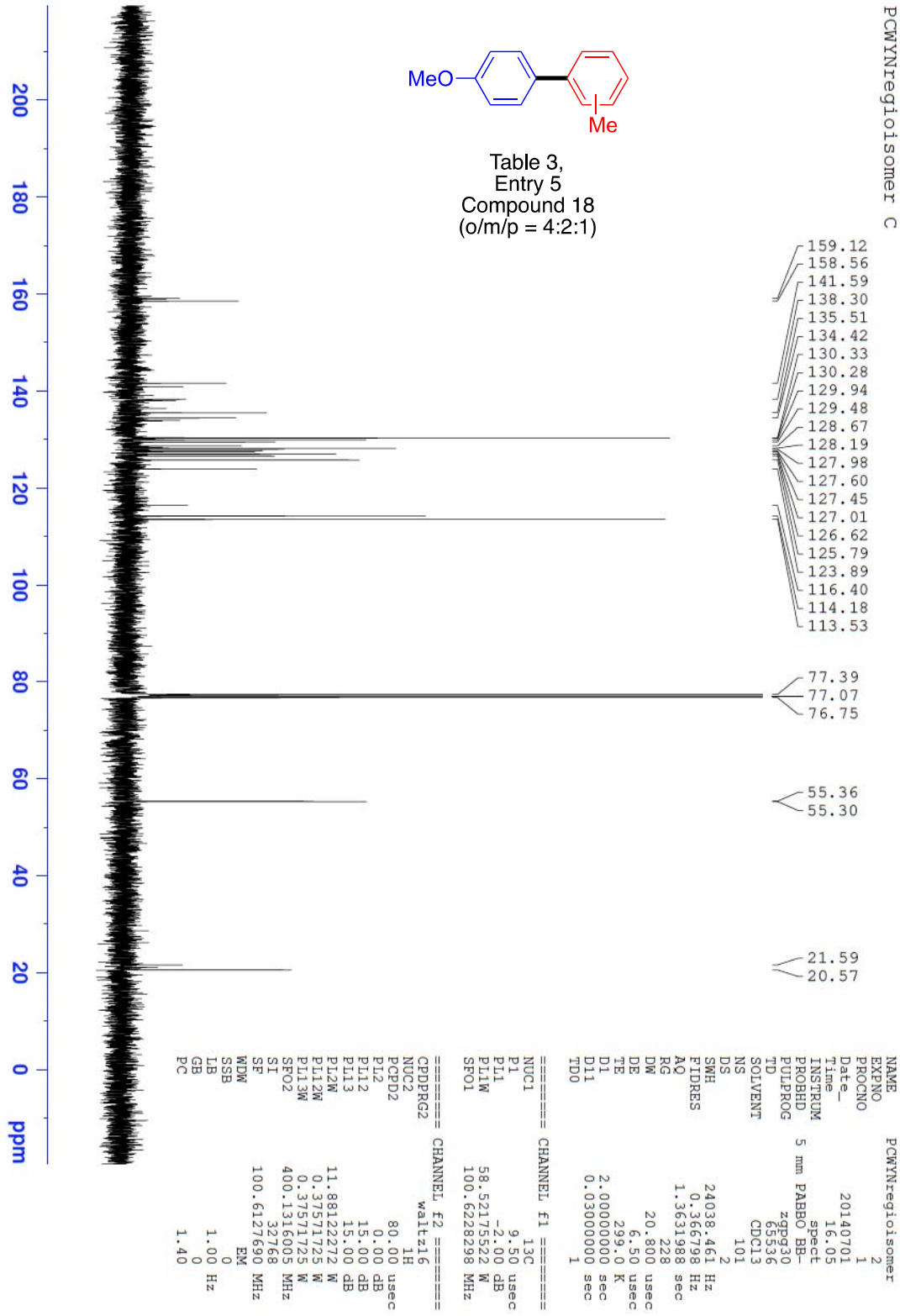

Me
Me
Me
Table 3,
Entry 3
Compound 16
7.25
7.23
7.21
7.04
7.02
6.94
2.41
2.33
2.01
1.91
1.99
1.93
3.00
2.94
5.97
f1 (ppm)

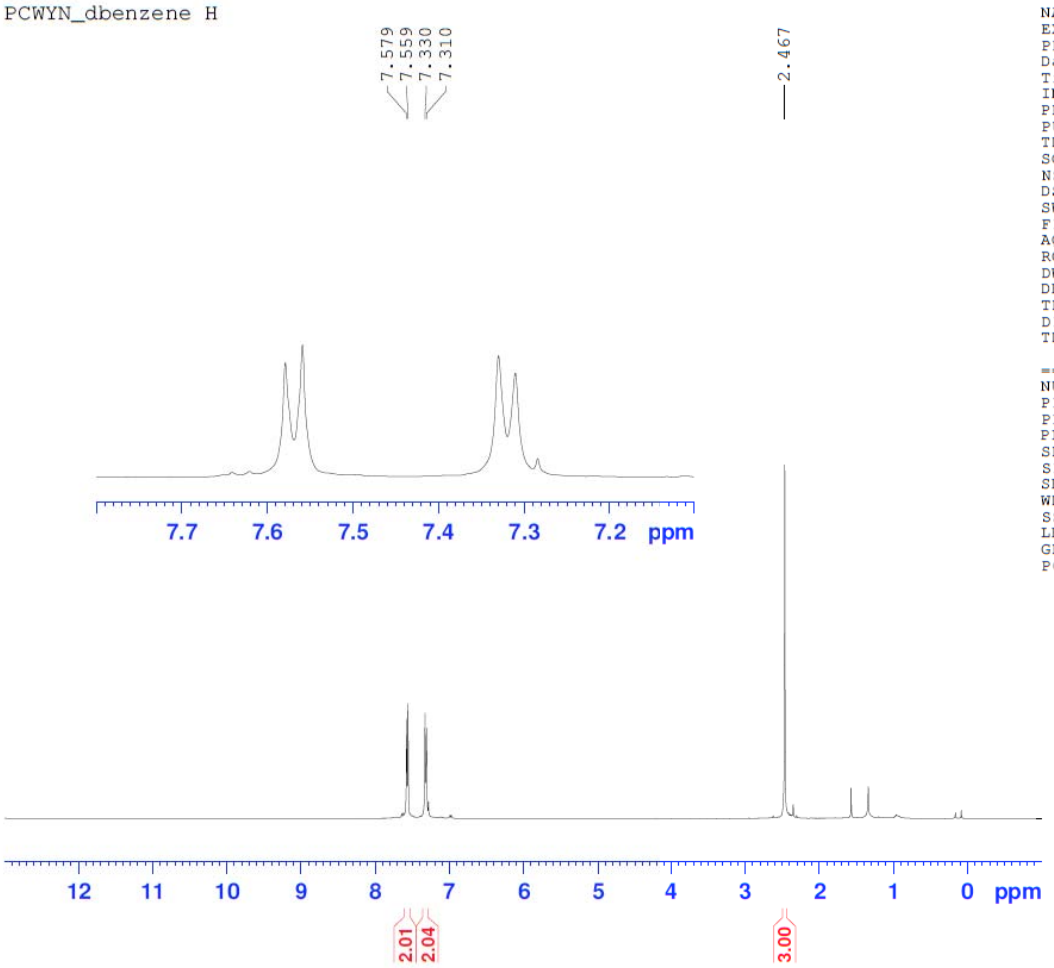

139.00
138.00
136.37
136.11
135.93
129.14
129.04
128.00
77.32
77.00
76.68
21.21
20.99
20.75
Me
Me
Me
Table 3,
Entry 3
Compound 16
f1 (ppm)


Me
MeO
Me
Me
Table 3,
Entry 4
Compound 17
7.25
7.06
7.04
6.96
6.94
6.93
1.96
4.00
2.95
6.06
2.32
2.01
f1 (ppm)


159.46
138.00
136.19
133.29
130.17
127.74
114.05
77.34
77.02
76.71
55.41
21.31
20.85
MeO
Me
Me
Me
Table 3,
Entry 4
Compound 17
f1 (ppm)

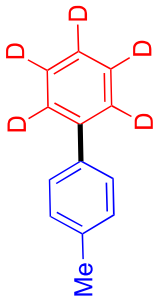

MeO
Me
Table 3,
Entry 5
Compound 18
(o/m/p = 4:2:1)
7.53
7.52
7.51
7.50
7.46
7.44
7.36
7.34
7.26
7.25
7.24
7.22
6.98
6.96
6.94
3.85
2.41
2.38
2.28
6.98
2.19
3.14
0.83
0.47
1.51
f1 (ppm)


MeO
Me
Table 3,
Entry 5
Compound 18
(o/m/p = 4:2:1)
PCWYNregioisomer C
159.12
158.56
141.59
138.30
135.51
134.42
130.33
130.28
129.94
129.48
128.67
128.19
127.98
127.60
127.45
127.01
126.62
125.79
123.89
116.40
114.18
113.53
77.39
77.07
76.75
55.36
55.30
21.59
20.57
NAME PCWYNregioisomer
EXPNO 2
PROCNO 1
Date_ 20140701
Time_ 16.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 101
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 228
DW 20.800 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm



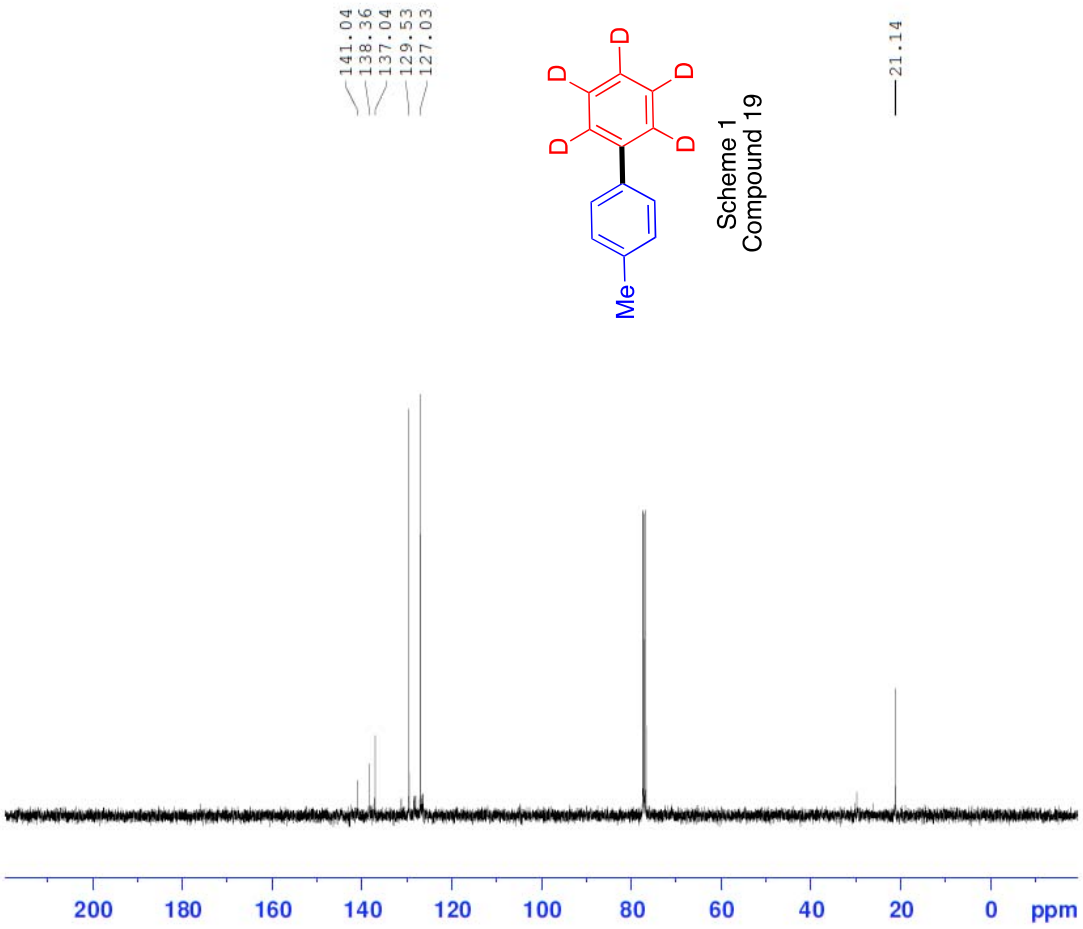

```
NAME        PCWYN_dbenzene
EXPNO                    1
PROCNO                   1
Date_             20140519
Time                 10.44
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               5597.015 Hz
FIDRES           0.170807 Hz
AQ               2.9273248 sec
RG                    90.5
DW                  89.333 usec
DE                    6.50 usec
TE                  298.5 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.70 usec
PL1                   0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                   32768
SF           400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



Scheme 1
Compound 19

PCWYN_dbenzene C



Scheme 1
Compound 19

NAME	PCWYN_dbenzene
EXPNO	2
PROCNO	1
Date_	20140519
Time	10.48
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	40
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	228
DW	20.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

References

(1) W. L. F. Armarego and D. D. Perrin, *In Purification of Laboratory Chemicals*, 4th, Ed. Butterworth-Heinemann: Oxford UK: 1996.

(2) C. L. Sun, H. Li, D. G. Yu, M. Yu, X. Y. Lu, K. Haung, S. F. Zheng, B. J. Li and Z. J. Shi, *Nat. Chem.,* 2010, **2**, 1044.

(3) F. Vallée, J. J. Mousseau and A. B. Charette, *J. Am. Chem. Soc.,* 2010, **132**, 1514.

(4) M. L. N. Rao, D. Banerjee and R. J. Dhanorkar, *Synlett,* 2011, **9**, 1324.

(5) Y. Qiu, Y. Liu, K. Yang, W. Hong, Z. Li, Z. Wang, Z. Yao and S. Jiang, *Org. Lett.,* 2011, **13**, 3556.