Electronic Supplementary Material (ESI) for Chemical Communications

Macrocyclic aromatic pyridone pentamer as a highly efficient organocatalyst for the direct arylations of unactivated arenes

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Supporting Information

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1. General remarks

^{1}H NMR and ^{13}C NMR data were obtained on a Bruker AMX500 (500 MHz) nuclear resonance spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm (chloroform, 7.26 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from tetramethylsilane using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Mass spectra were obtained using instrumentation which includes Finnigan MAT95XL-T and Micromass VG7035. Flash column chromatography was performed using 200 - 300 mesh silica with the indicated solvent system according to standard techniques. Analytical thin layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification in advance before use.

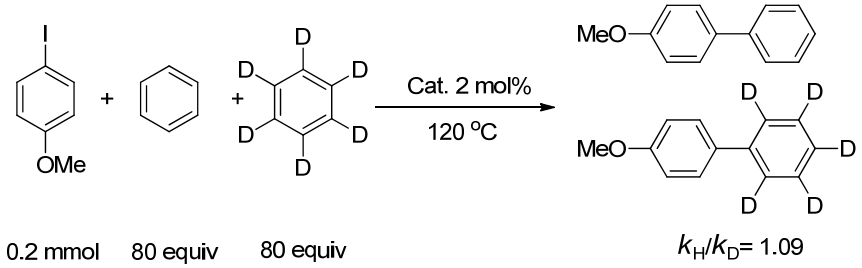
2. Synthesis of catalysts P5 had been reported in the following journal article

Zhiyun Du, Changliang Ren, Ruijuan Ye, Jie Shen, Victor Maurizot, Yujin Lu, Jian Wang, Huaqiang Zeng ***Chem. Commun.*** 2011, 47, 12488-12490.

3. General experimental procedures for the arylation reactions

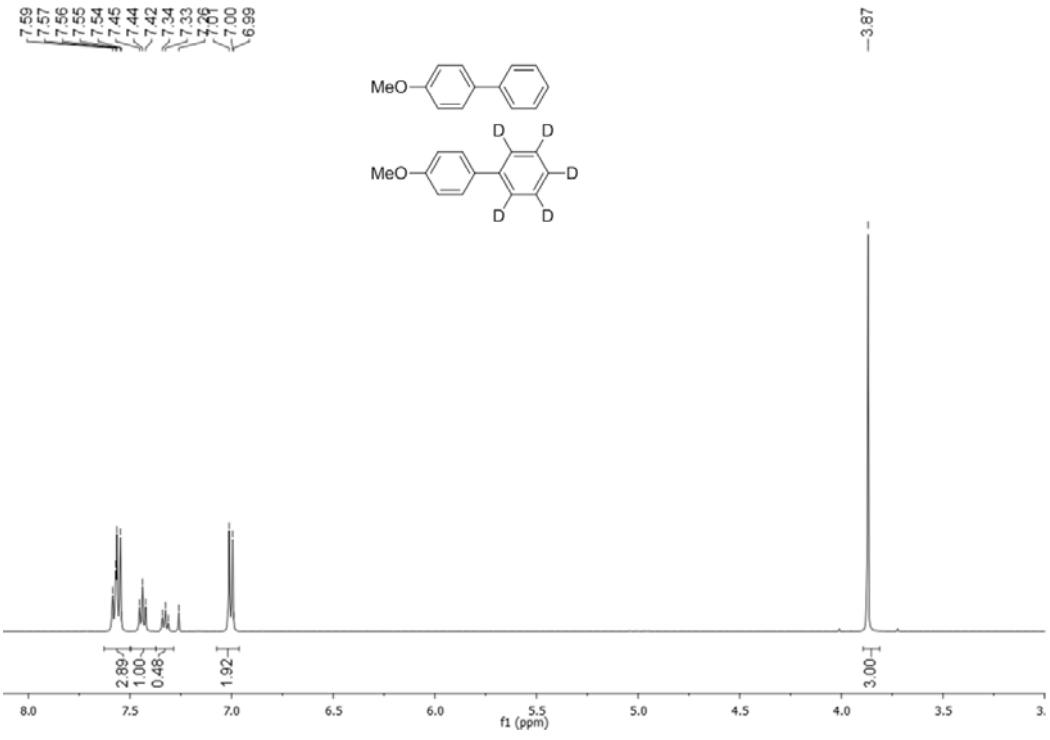
Aryl iodides (0.2 mmol, if solid) and **P5** (0.004 mmol, 2 mol %) were added in dried Schlenk tubes. KO*t*-Bu (0.6mmol, 3.0 equiv) was added. Benzene (3 mL) and aryl iodides (0.2 mmol, if liquid) were added into tubes by syringe. The septum-sealed tube was evacuated and refilled with Argon three times. The mixture was stirred under an argon atmosphere in sealed Schlenk tubes at 120 °C for 24 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200 -300 mesh silica gel with hexane/ethyl acetate as eluent.

4. Kinetic isotope effect experiments



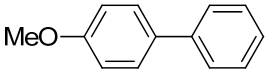
0.2 mmol 80 equiv 80 equiv k_H/k_D= 1.09

4-iodoanisole (0.2 mmol), KO*t*-Bu (0.6 mmol) and **P5a** (2 mol%) were added to a Schlenk tube, and then benzene-H_6 (1.4 mL) and benzene-D_6 (1.4 mL) were added into the tube by syringe. The septum-sealed tube was evacuated and refilled with Ar three times. The mixture was stired under an argon atmosphere at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched and extracted with ether (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph to yield the desired product. The product distribution (k_H/k_D = 1.09) was analyzed by ^{1}HNMR.



5. The characterization of products

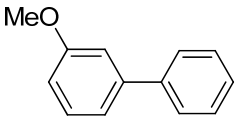
The spectroscopic data of all the products are presented. All the known compounds were in accordance with the data reported in the literatures.



4-Methoxybiphenyl (3a)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 -7.55 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H).

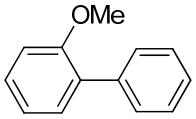
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.18, 140.85, 133.81, 128.70, 128.13, 126.72, 126.64, 114.22, 55.32.



3-Methoxylbiphenyl (3b)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.61 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.35 (m, 2H), 7.22 – 7.15 (m, 2H), 6.93 – 6.91 (m, 1H), 3.89 (s, 2H).

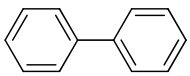
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.90, 142.74, 141.07, 129.72, 128.70, 127.38, 127.17, 119.65, 112.86, 112.64, 55.26.



2-Methoxylbiphenyl (3c)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 -7.34 (m, 3H), 7.08 – 7.01 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.51, 138.59, 130.93, 130.77, 129.59, 128.65, 128.02, 126.95, 120.87, 111.28, 55.59.

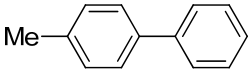


Biphenyl (3d)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 4H), 7.47 – 7.44 (m, 4H), 7.38 – 7.34

(m, 2H).

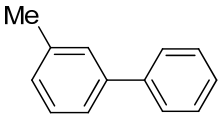
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.31, 128.76, 127.26, 127.18.



4-Methylbiphenyl (3e)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.57 (m, 2H), 7.50 – 7.48 (m, 2H), 7.44 – 7.40 (m, 2H), 7.33 – 7.30 (m, 1H), 7.26 – 7.24 (m, 2H), 2.39 (s, 3H).

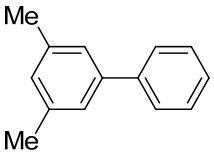
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.19, 138.38, 137.03, 129.49, 128.72, 127.01, 126.99, 21.11



3-Methylbiphenyl (3f)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.45 – 7.29 (m, 6H), 7.17 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 2H).

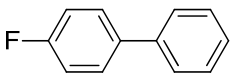
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.34, 141.22, 138.31, 128.67, 127.97, 127.16, 124.25, 21.53.



3,5-Dimethylbiphenyl (3g)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.45 – 7.42 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.23 (s, 2H), 7.01 (s, 1H), 2.40 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.45, 141.25, 138.23, 128.87, 128.61, 127.17, 127.05, 125.09, 21.40.

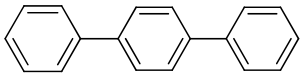


4 - Fluorobiphenyl (3h)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 4H), 7.46 – 7.43 (m, 2H), 7.37 – 7.34

(m, 1H), 7.15 – 7.12 (m, 2H).

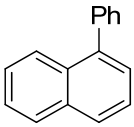
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.50 (d, J = 245.7 Hz), 140.29, 137.37 (d, J = 2.5 Hz), 128.83, 128.70 (d, J = 7.56 Hz), 127.27, 127.04, 115.62 (d, J = 21.42 Hz).



p **- Terphenyl (3i)[1]**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 8H), 7.50 -7.47 (m, 4H), 7.40 – 7.37 (m, 2H).

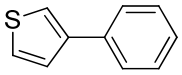
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.68, 140.10, 128.80, 127.48, 127.32, 127.03.



1 - Phenylnaphthalene (3j)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 3H), 7.57– 7.46 (m, 6H), 7.45 – 7.44(m, 3H).

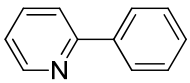
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.74, 140.24, 133.77, 131.59, 130.05, 128.23, 127.60, 127.21, 126.90, 126.00, 125.99, 125.74, 125.35.



3-Phenylthiophene (3k)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.60 (m, 2H), 7.46 – 7.45 (m, 1H), 7.43 – 7.35 (m, 4H), 7.30 (t, J = 7.4 Hz, 1H).

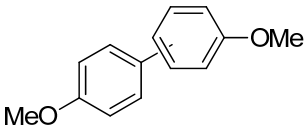
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.36, 135.85, 128.79, 127.11, 126.44, 126.33, 126.17, 120.25.



2-Phenylpyridine (3l)[2]

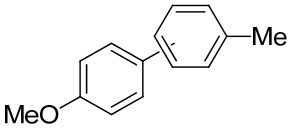
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.6 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.84 – 7.64 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.24 – 7.21 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.62, 149.81, 139.56, 136.83, 129.06, 128.86, 127.04, 122.19, 120.66.



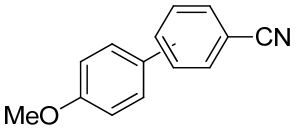
(p-Methoxyphenyl)anisole (3l)[1] (the mixture of o/m/p)

MS(EI) Calcd for $C_{14}H_{14}O_2$: 214.0994; Found:214.0993.



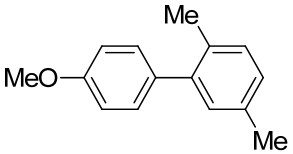
(p-Methoxyphenyl)toluene (3m)[1] (the mixture of o/m/p)

MS(EI) Calcd for $C_{14}H_{14}O$: 198.1045; Found:198.1045.



(p-Methoxyphenyl)benzonitrile (3n)[2] (the mixture of o/m/p)

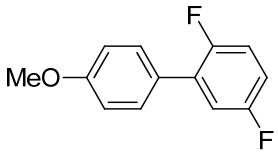
MS(EI) Calcd for $C_{14}H_{14}ON$: 209.0841; Found:209.0841.



2,5 - dimethyl - 4' - methoxybiphenyl (3o)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 6.94 (m, 7H), 3.86 (s,3H), 2.35 (s,3H), 2.24 (s,3H).

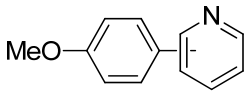
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.44, 141.35, 135.13, 134.51, 132.28, 130.63, 130.20, 127.64, 113.44, 55.27, 20.89, 20.00.



2,5−difluoro−4'−methoxybiphenyl (3p)[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.14 – 7.06 (m, 2H), 7.01 – 6.93 (m, 3H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.76 (d, *J* = 241.25 Hz), 159.58, 155.70 (d, *J* = 241.25 Hz), 130.03 (d, *J* = 3.75 Hz), 128.12, 127.13, 117.16 – 116.41 (m), 114.62 – 114.36 (m), 114.03, 55.30.



(p-Methoxyphenyl)pyridine (3q)[3]

***o*-3q**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.7 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 2H), 7.72 – 7.65 (m, 2H), 7.18 – 7.15 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H)**.**

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.48, 157.14, 149.54, 136.68, 132.04, 128.18, 121.42, 119.84, 114.14, 55.37.

***m*-3q**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.55 (s, 1H), 7.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.34 (dd, *J* = 7.8, 4.8 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.79, 147.96, 147.83, 133.89, 130.27, 128.24, 123.54, 114.58, 55.40.

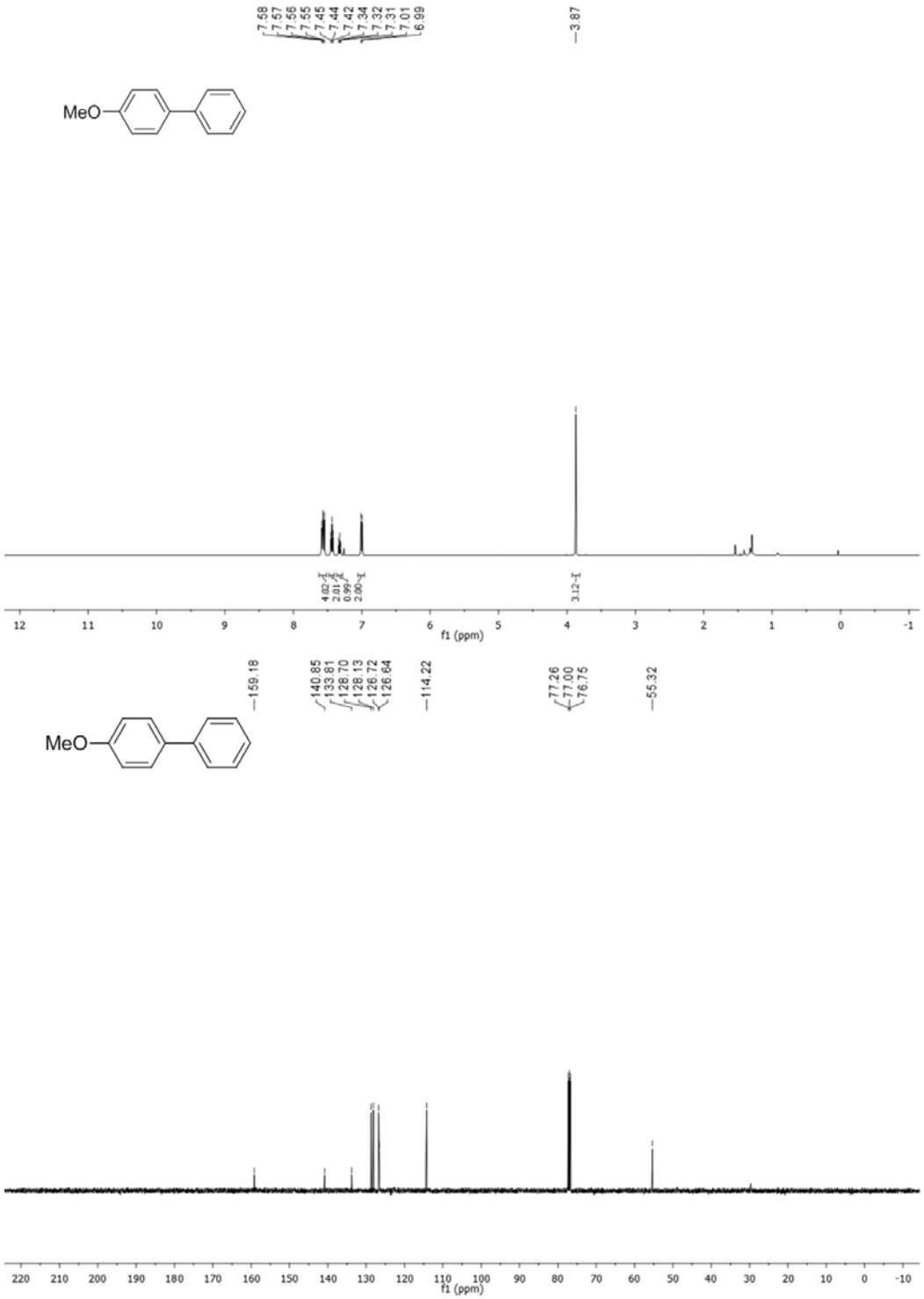
***p*-3q**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 6.0 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.58, 150.15, 147.87, 130.39, 128.16, 121.08, 114.58, 55.41.

References:

1. Sun, C.-L.; Hu, L.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* **2010**, *2*, 1042.
2. Tanimoro, K.; Ueno, M.; Takeda, K.; Kirihata, M.; Tanimori, S. *J. Org. Chem.* **2012**, *77*, 7844.
3. Chen, W.-C.; Hsu, Y.-C.; Shih, W.-C.; Lee, C.-Y.; Chuang, W.-H.; Tsai, Y.-F.; Chen, P. P.-Y.; Ong, T.-G. *Chem. Commun.* **2012**, *48*, 6702.

^{1}H and ^{13}C Spectra:

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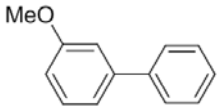
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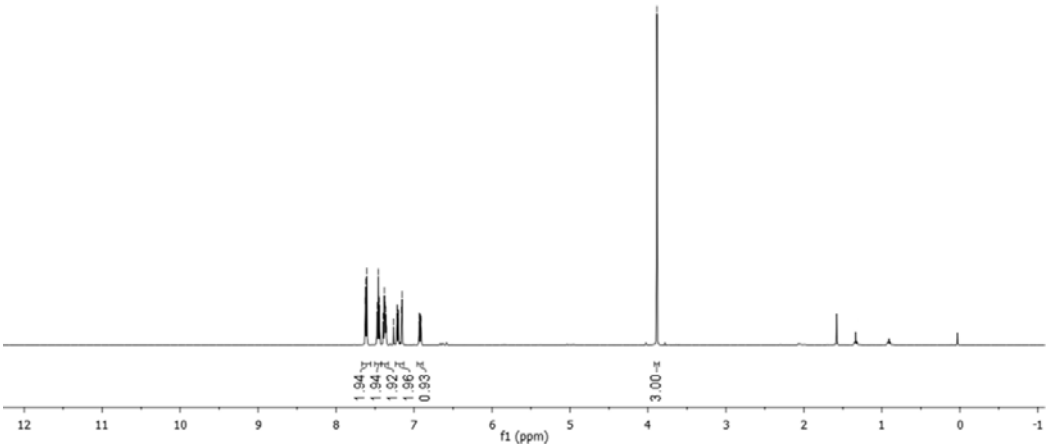
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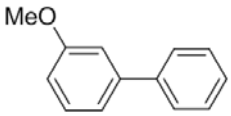
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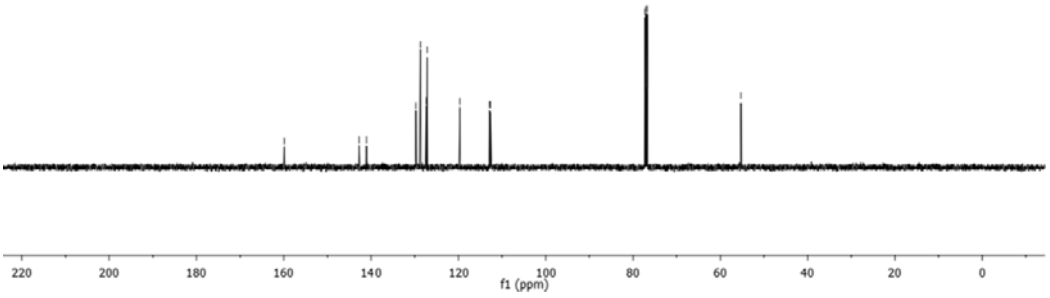
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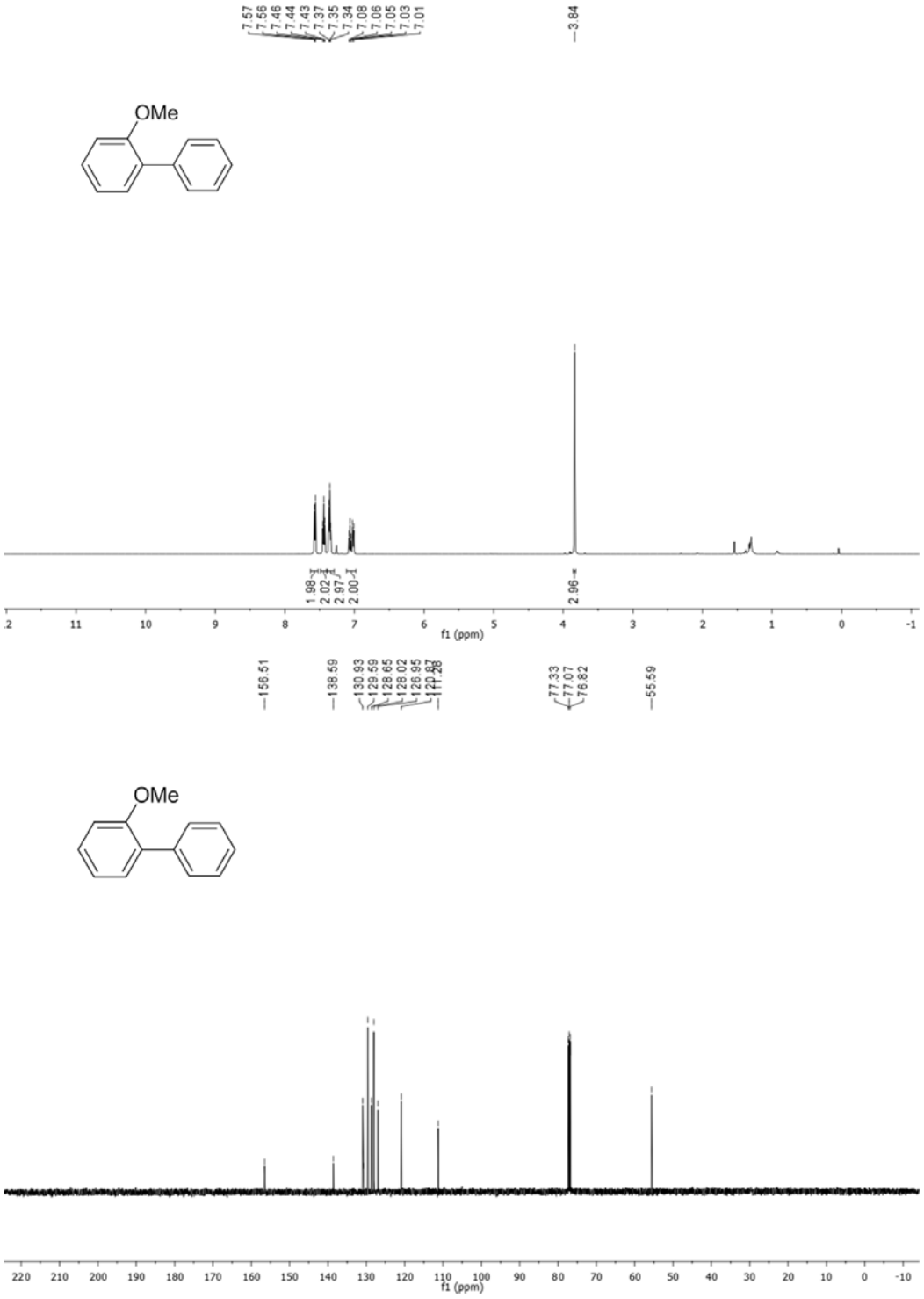
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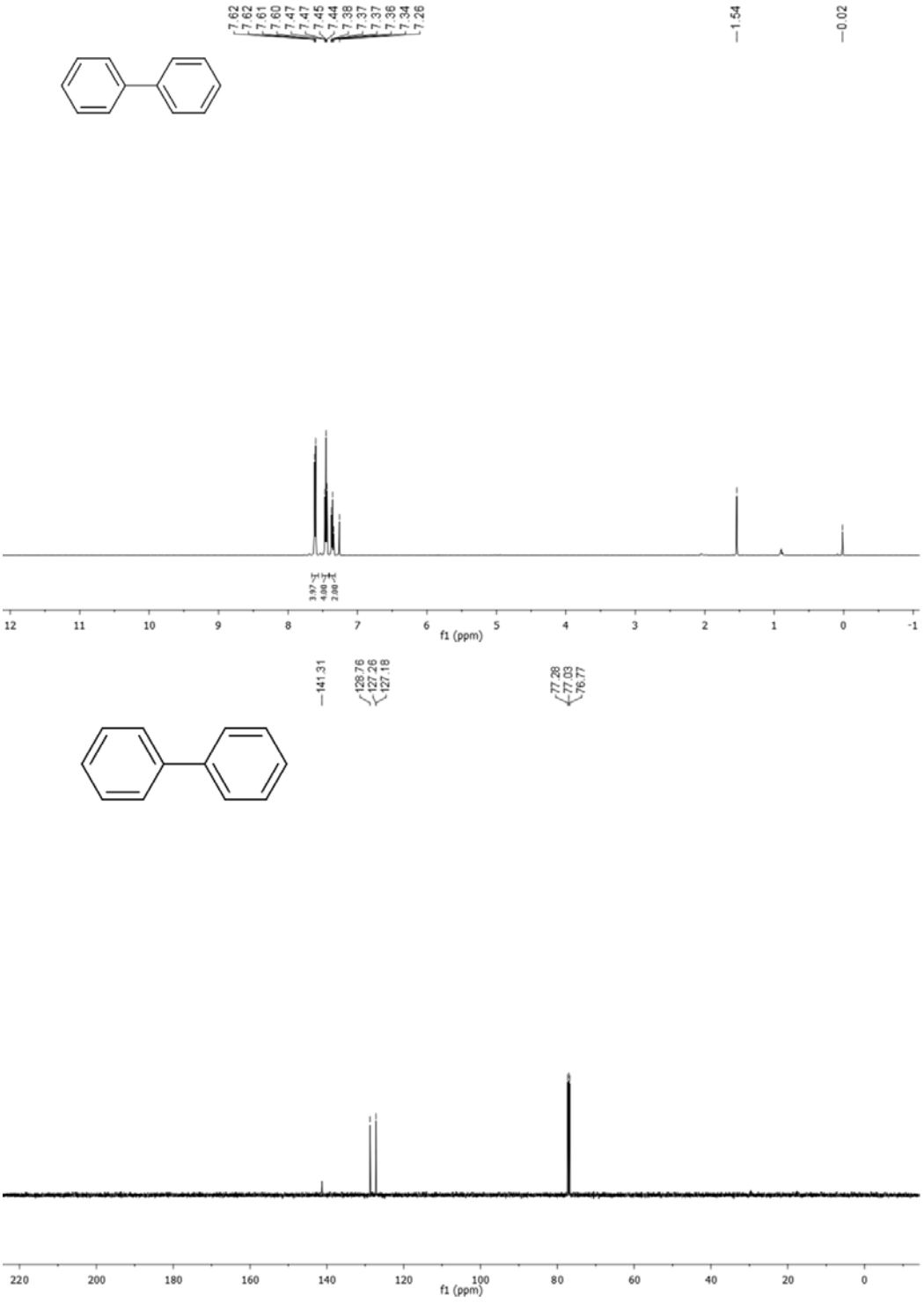
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f1 (ppm)
141.31
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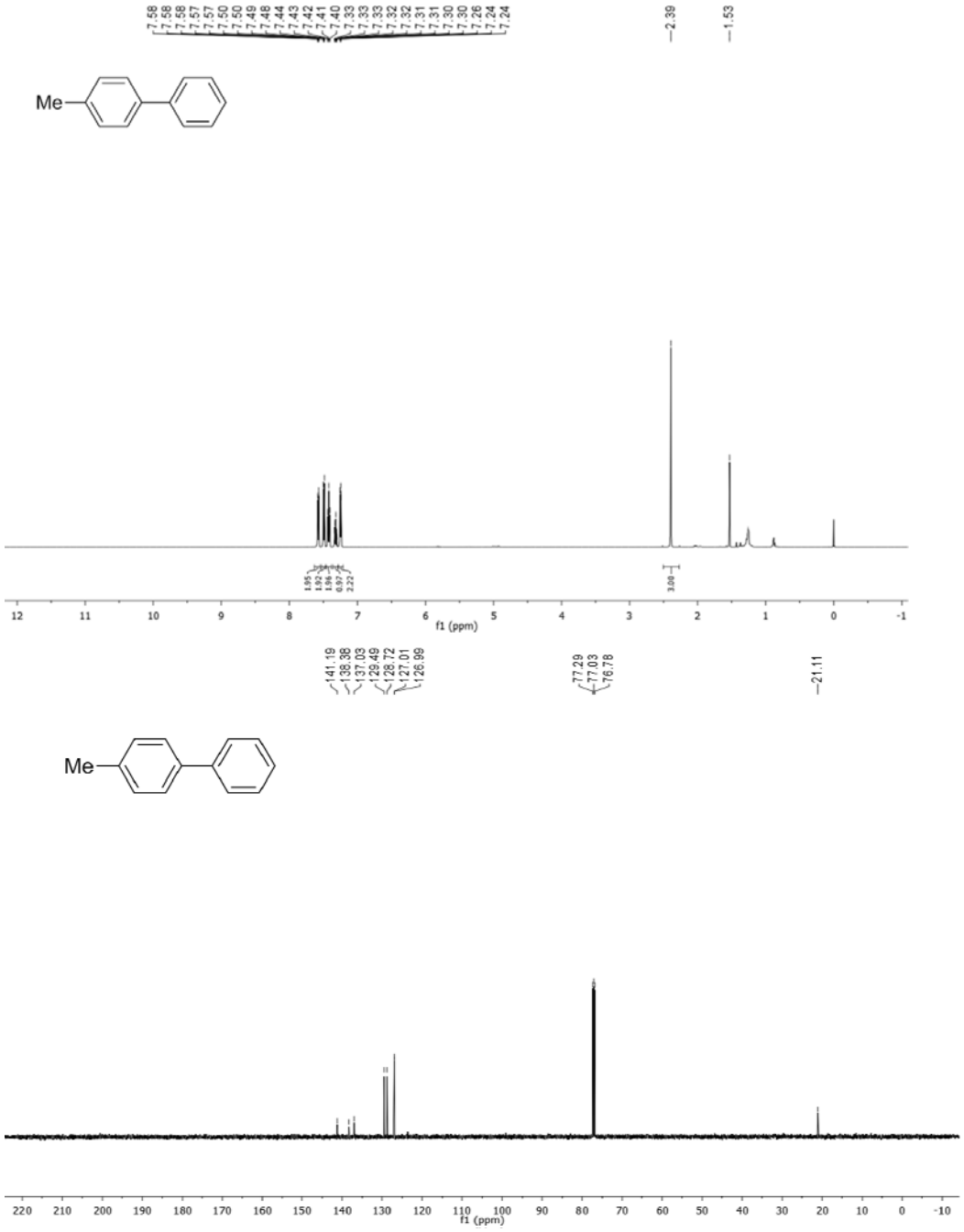
127.26
127.18
77.28
77.03
76.77
f1 (ppm)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7.43
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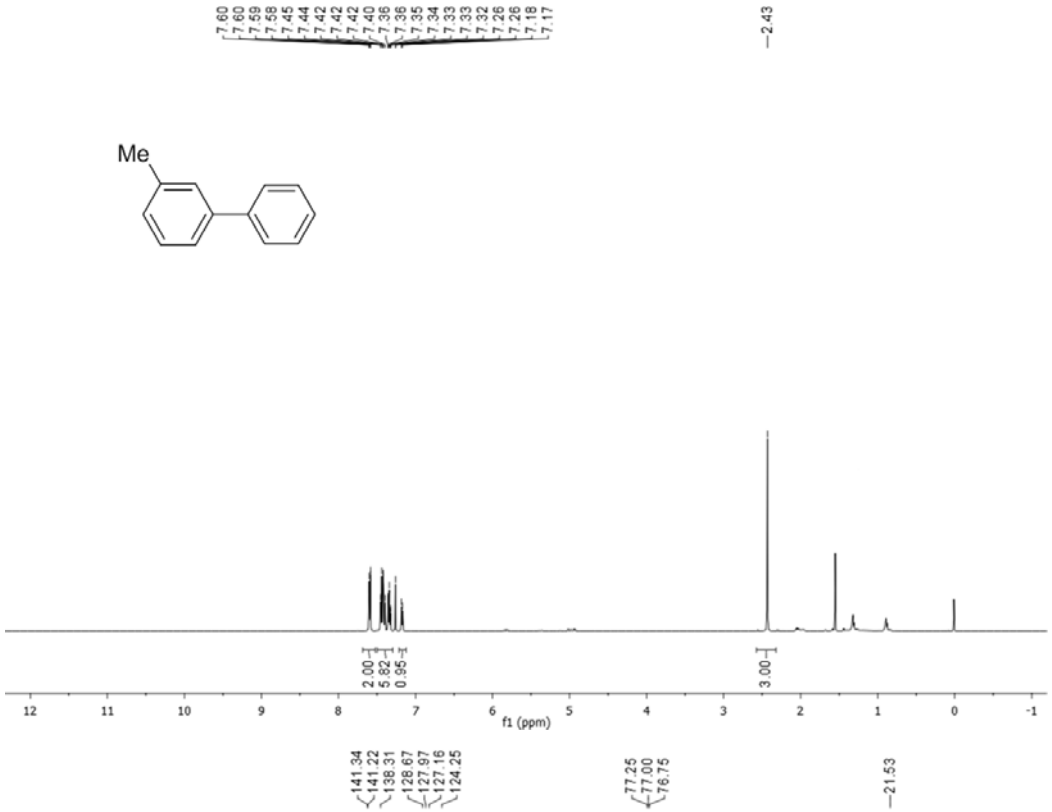
7.40
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.26
7.24
7.24
2.39
1.53
Me
1.95
1.92
1.86
0.97
2.22
3.00
f1 (ppm)
141.19
138.38
137.03
129.49
128.72
127.01
126.99
77.29
77.03
76.78
21.11
Me
f1 (ppm)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7.60
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7.42
7.42
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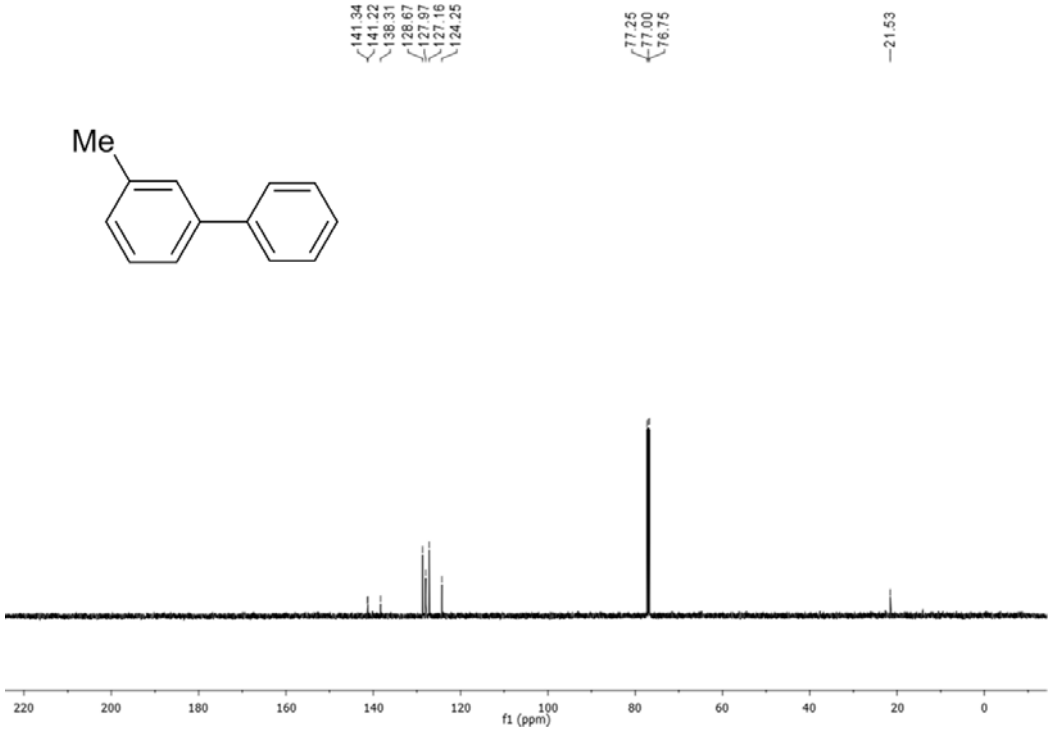
7.36
7.35
7.34
7.33
7.32
7.26
7.18
7.17
2.43
Me
2.00
5.82
0.95
3.00
f1 (ppm)


141.34
141.22
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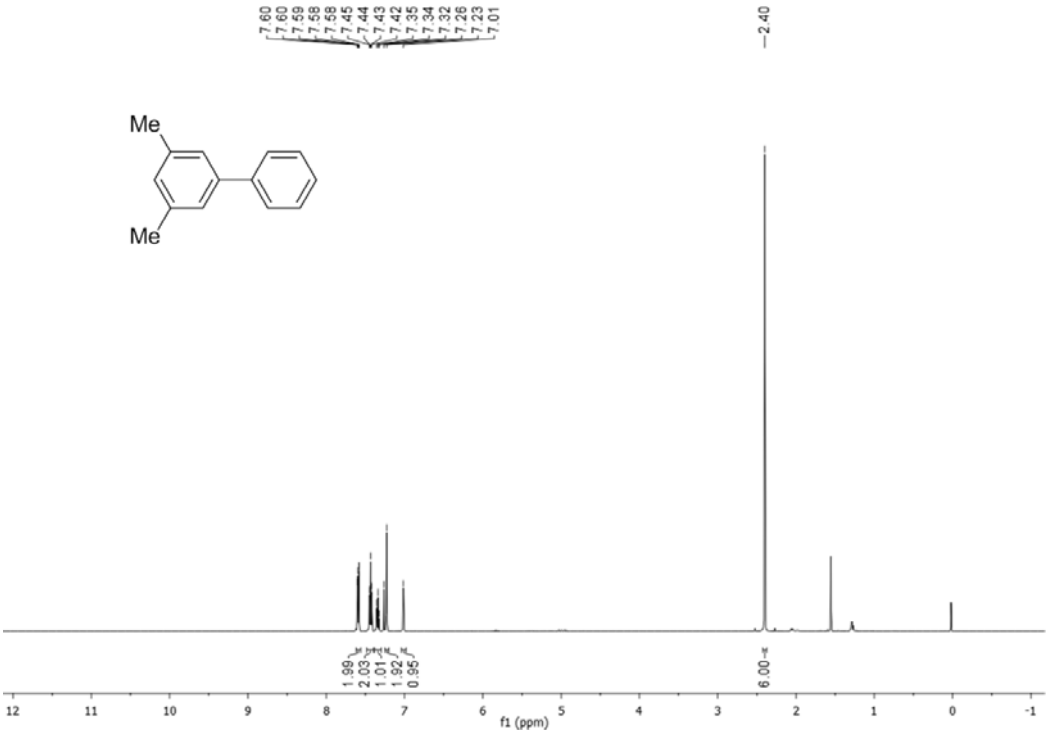
127.97
127.16
124.25
77.25
77.00
76.75
21.53
Me
f1 (ppm)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7.58
7.45
7.44
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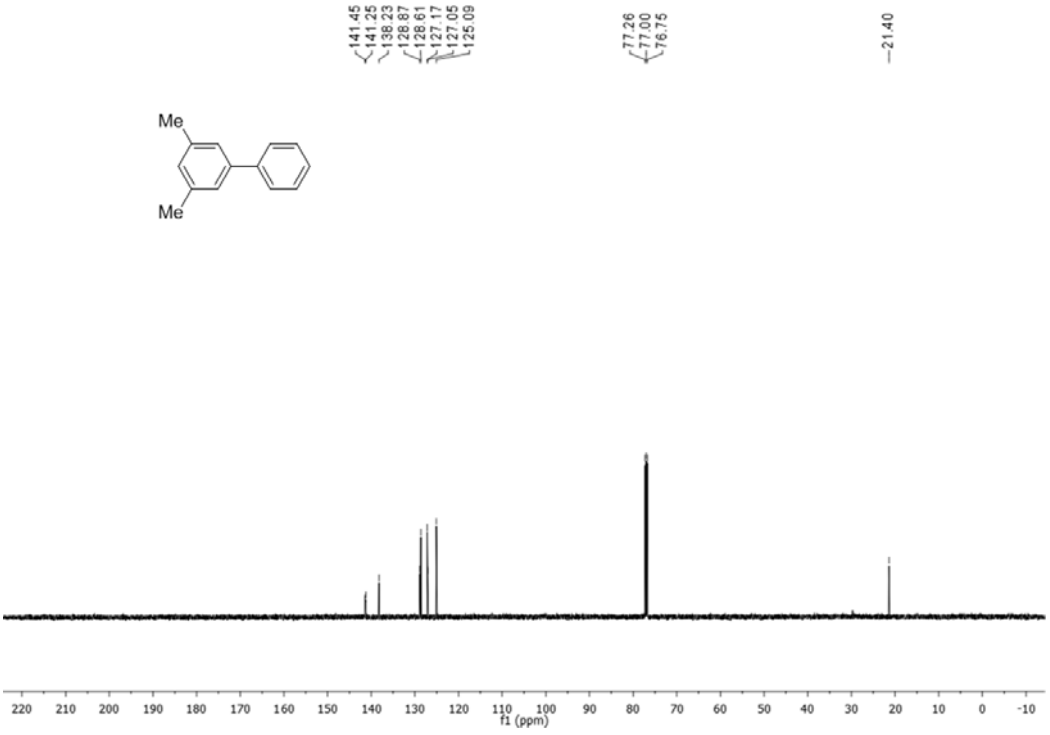
7.42
7.35
7.34
7.32
7.26
7.23
7.01
2.40
Me
Me
1.99
2.03
1.01
1.92
0.95
6.00
f1 (ppm)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141.25
138.23
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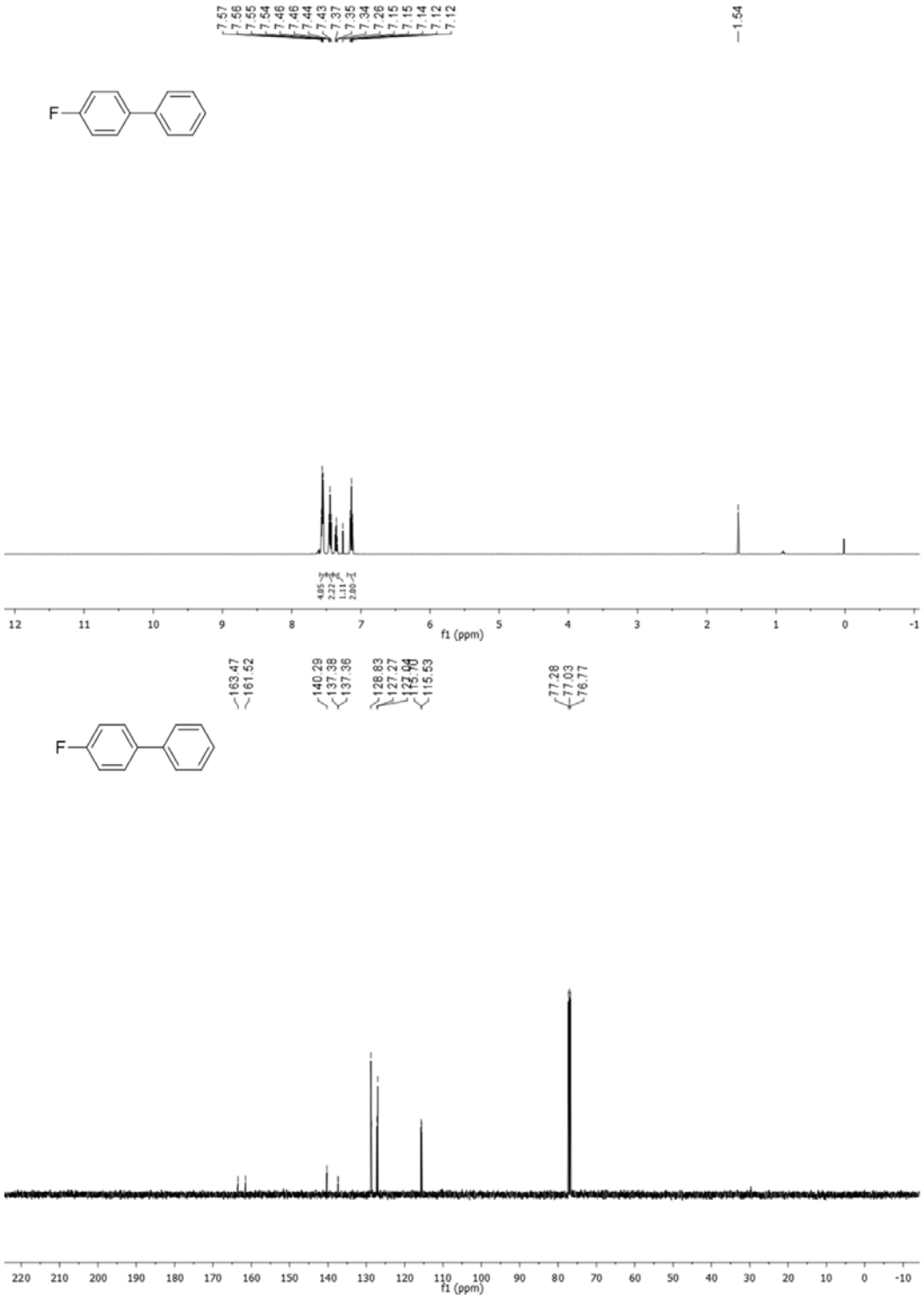
127.17
127.05
125.09
77.26
77.00
76.75
21.40
Me
Me
f1 (ppm)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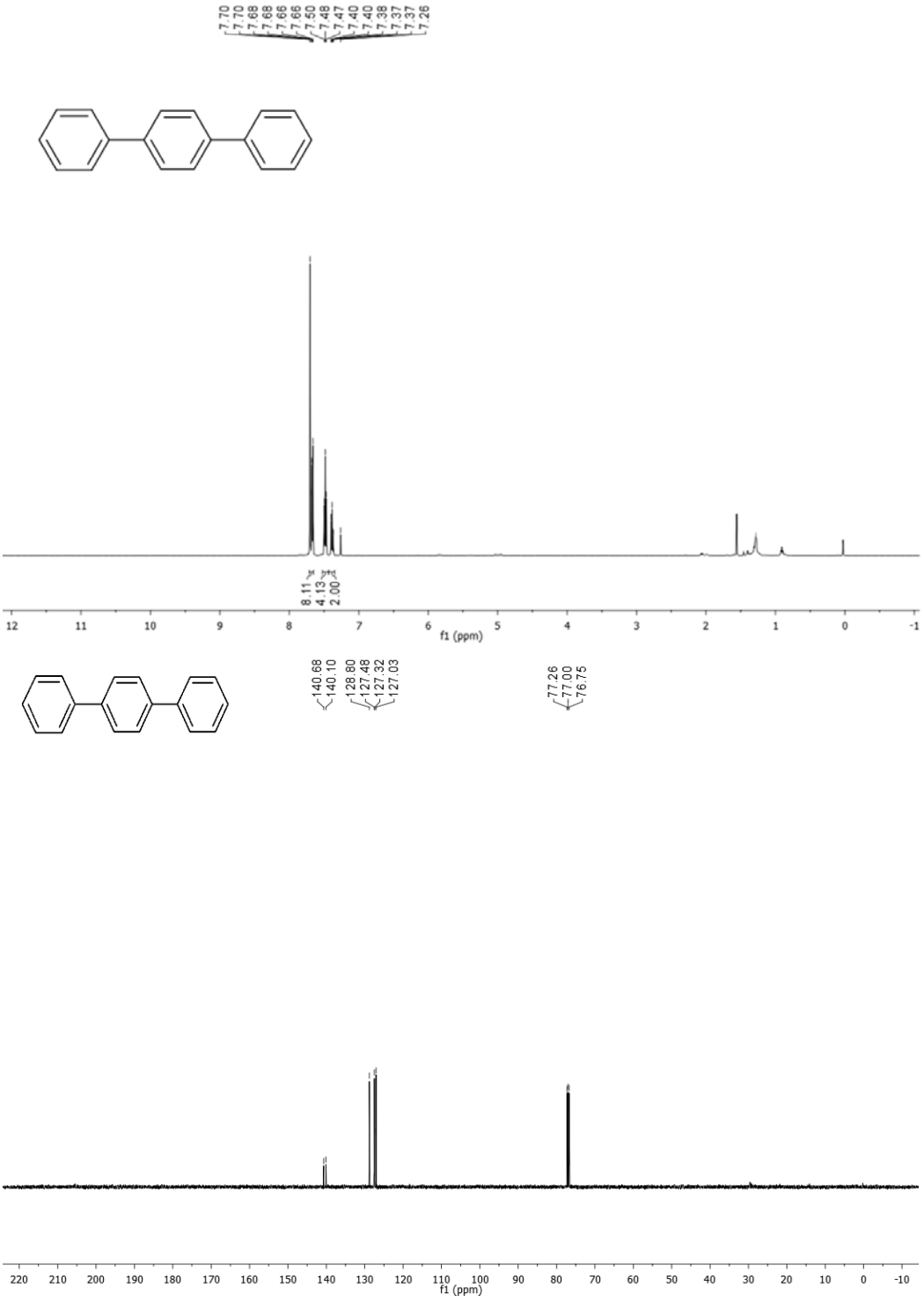
7.46
7.44
7.43
7.37
7.35
7.34
7.26
7.15
7.15
7.14
7.12
7.12
1.54
F
f1 (ppm)
163.47
161.52
140.29
137.38
137.36
128.83
127.27
115.53
77.28
77.03
76.77
F
f1 (ppm)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7.68
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7.66
7.50
7.48
7.47
7.40
7.40
7.38
7.37
7.37
7.26
8.11
4.13
2.00
f1 (ppm)
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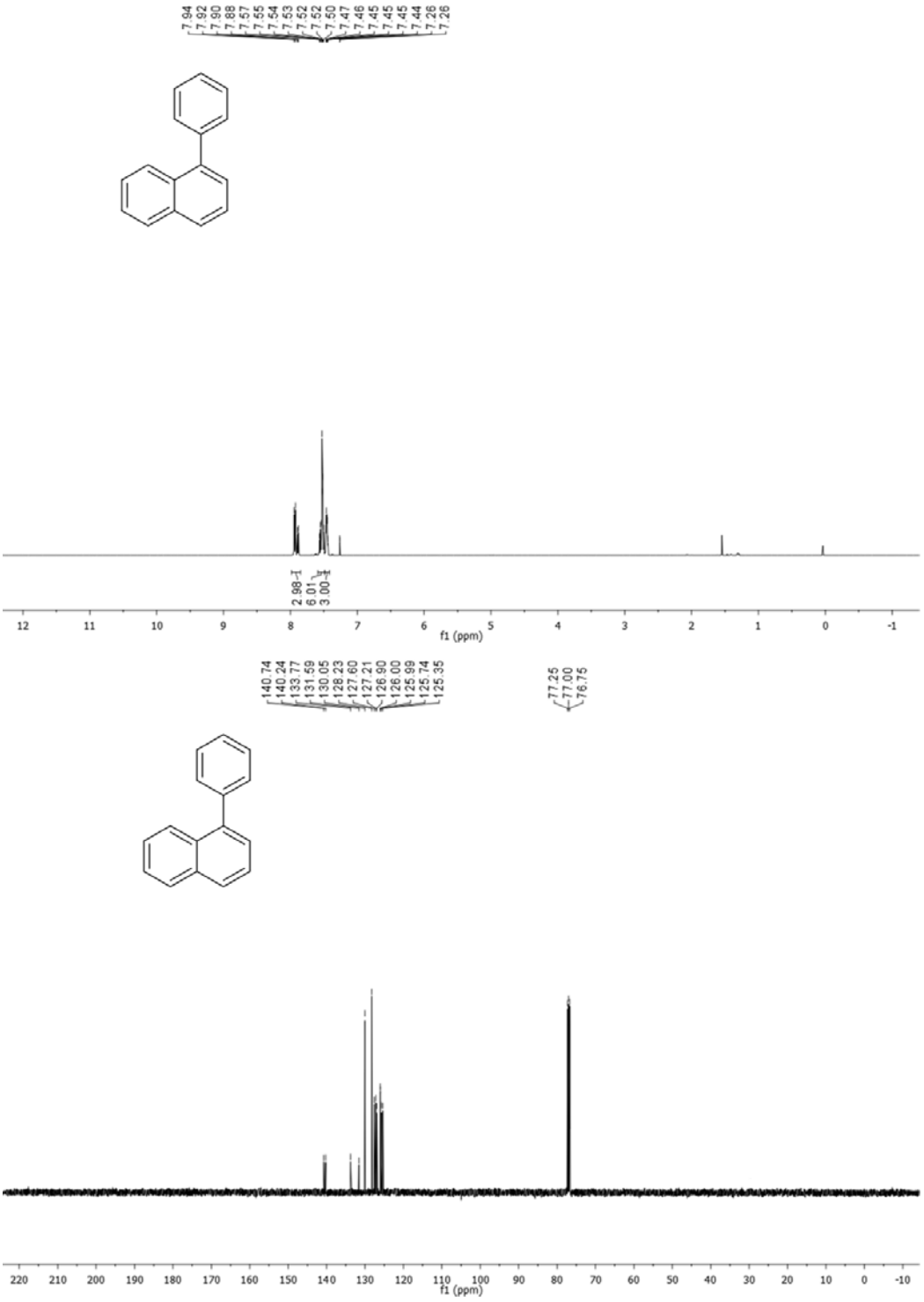
140.10
128.80
127.48
127.32
127.03
77.26
77.00
76.75
f1 (ppm)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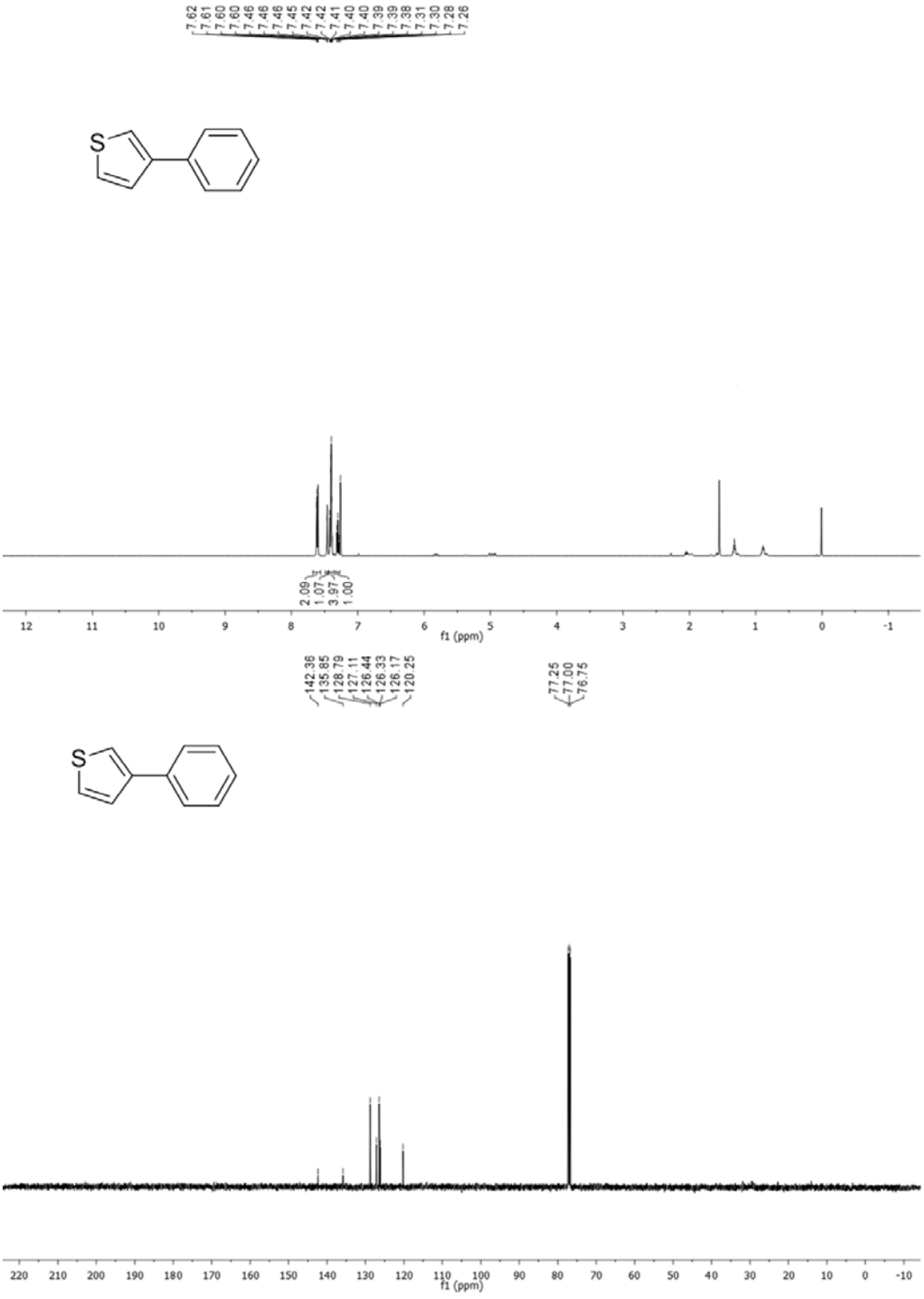
7.92
7.90
7.88
7.57
7.55
7.54
7.53
7.52
7.52
7.50
7.47
7.46
7.45
7.45
7.45
7.44
7.26
7.26
2.98
6.01
3.00
f1 (ppm)
140.74
140.24
133.77
131.59
130.05
128.23
127.60
127.21
126.90
126.00
125.99
125.74
125.35
77.25
77.00
76.75
f1 (ppm)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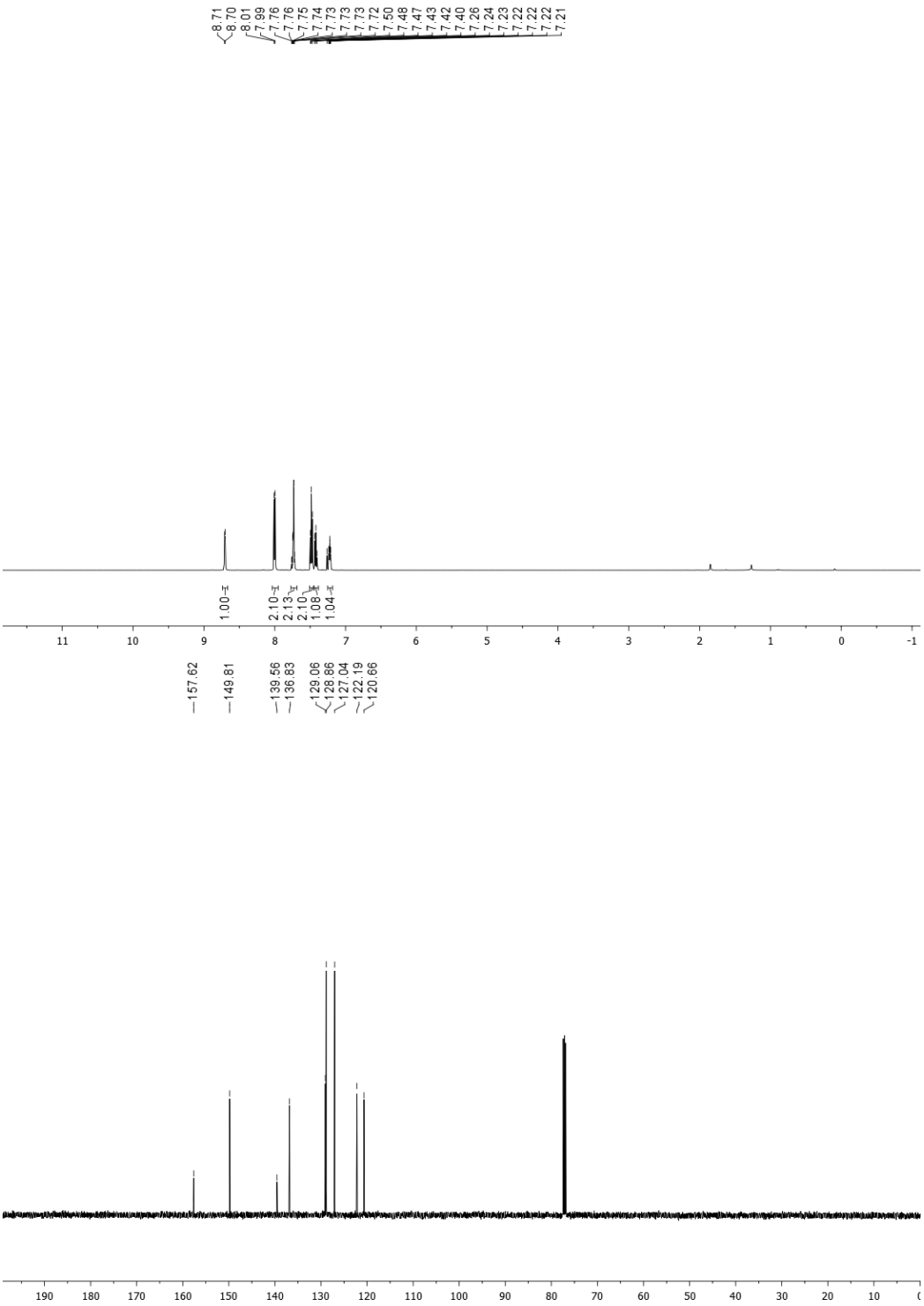
7.46
7.45
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.31
7.30
7.28
7.26
S
2.09
1.07
3.97
1.00
f1 (ppm)
142.36
135.85
128.79
127.11
126.44
126.33
126.17
120.25
77.25
77.00
76.75
S
f1 (ppm)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7.73
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7.50
7.48
7.47
7.43
7.42
7.40
7.26
7.24
7.23
7.22
7.22
7.22
7.21
1.00
2.10
2.13
2.10
1.08
1.04
11
10
9
8
7
6
5
4
3
2
1
0
-1
157.62
149.81
139.56
136.83
129.06
128.86
127.04
122.19
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190
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160
150
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120
110
100
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80
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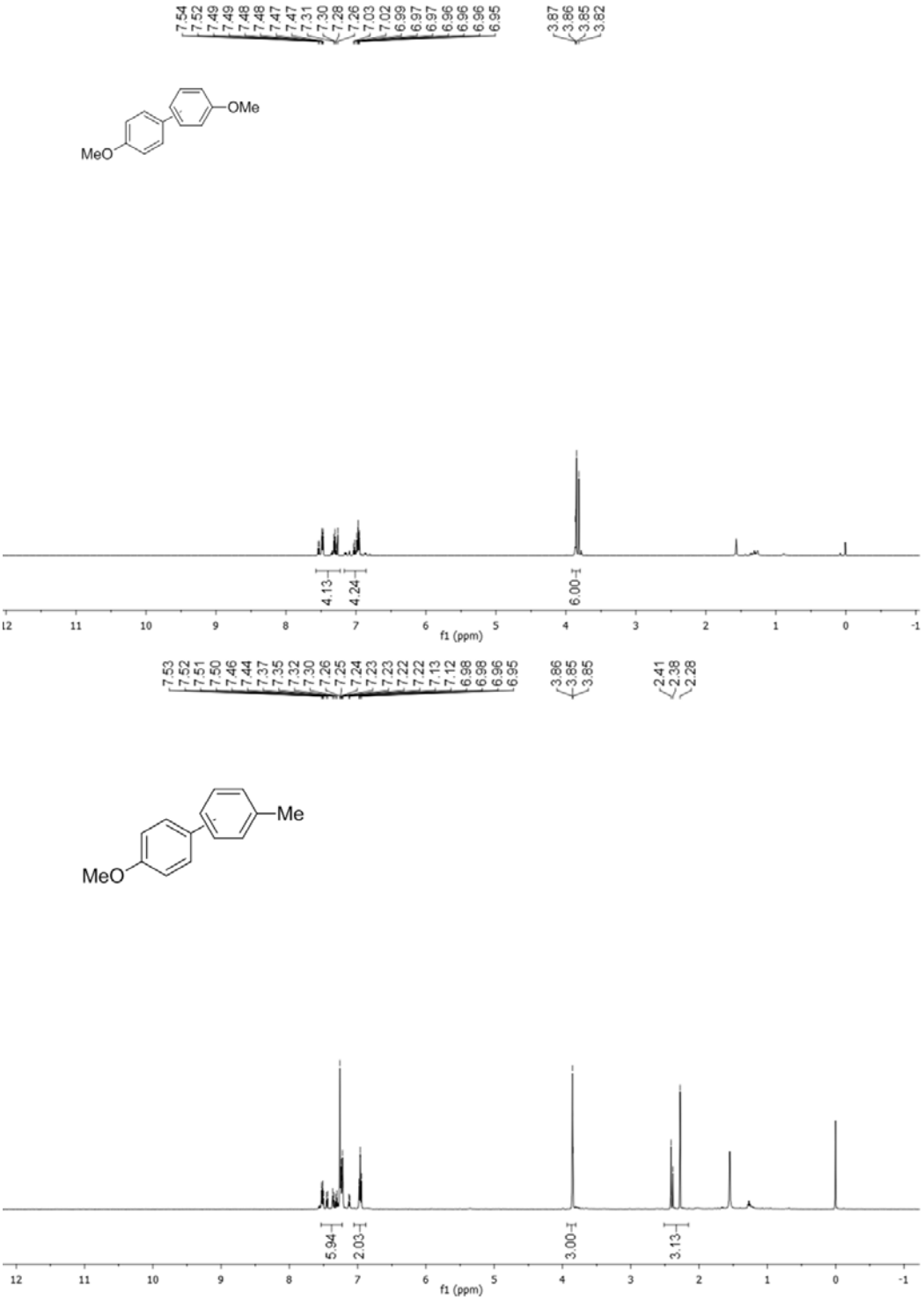
20
10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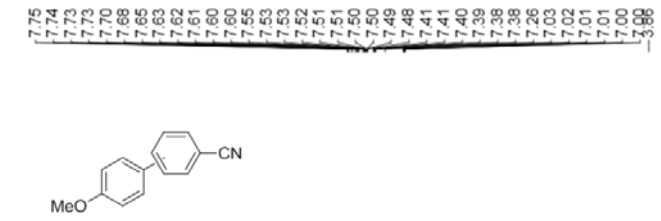
7.48
7.47
7.47
7.31
7.30
7.28
7.26
7.03
7.02
6.99
6.97
6.97
6.96
6.96
6.96
6.95
3.87
3.86
3.85
3.82
OMe
MeO
4.13
4.24
6.00
f1 (ppm)
7.53
7.52
7.51
7.50
7.46
7.44
7.37
7.35
7.32
7.30
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.13
7.12
6.98
6.98
6.96
6.95
3.86
3.85
3.85
2.41
2.38
2.28
Me
MeO
5.94
2.03
3.00
3.13
f1 (ppm)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7.55
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.41
7.41
7.40
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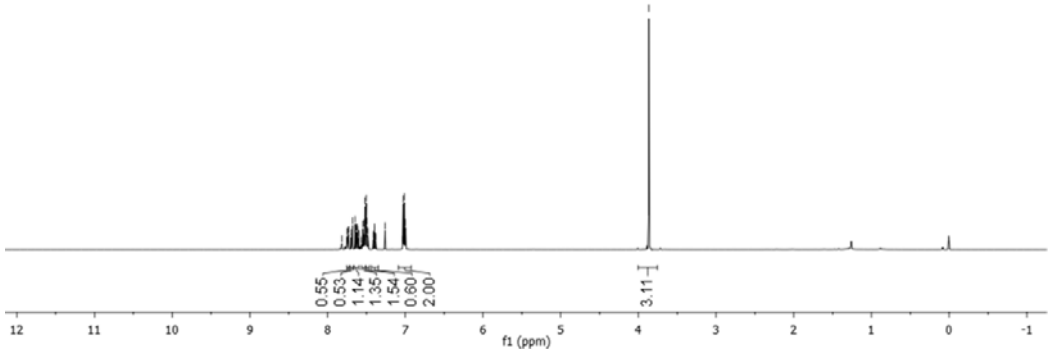
7.38
7.26
7.03
7.02
7.01
7.01
7.00
3.88
CN
MeO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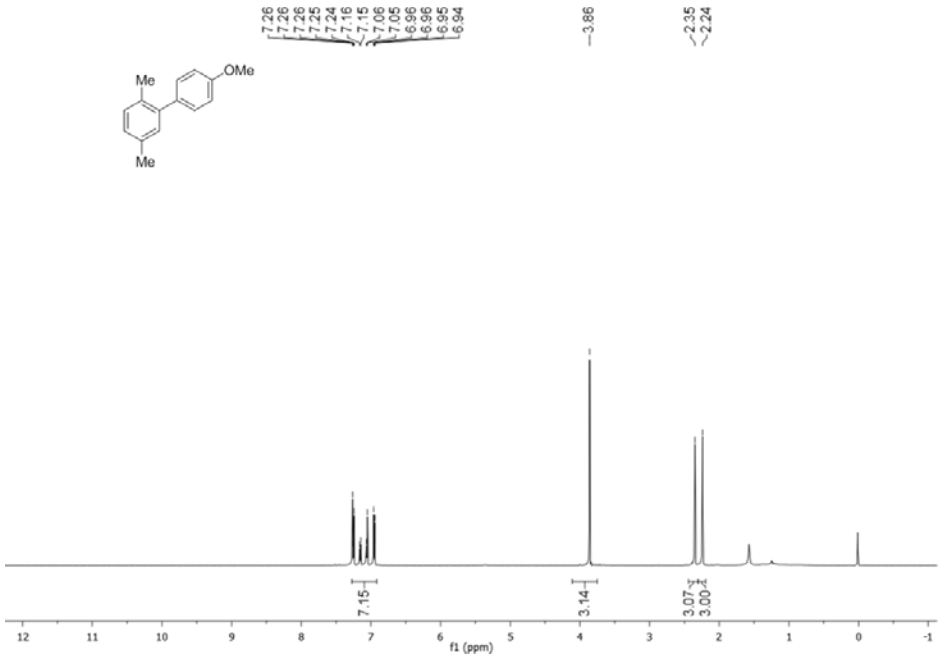
0.53
1.14
1.35
1.54
0.60
2.00
3.11
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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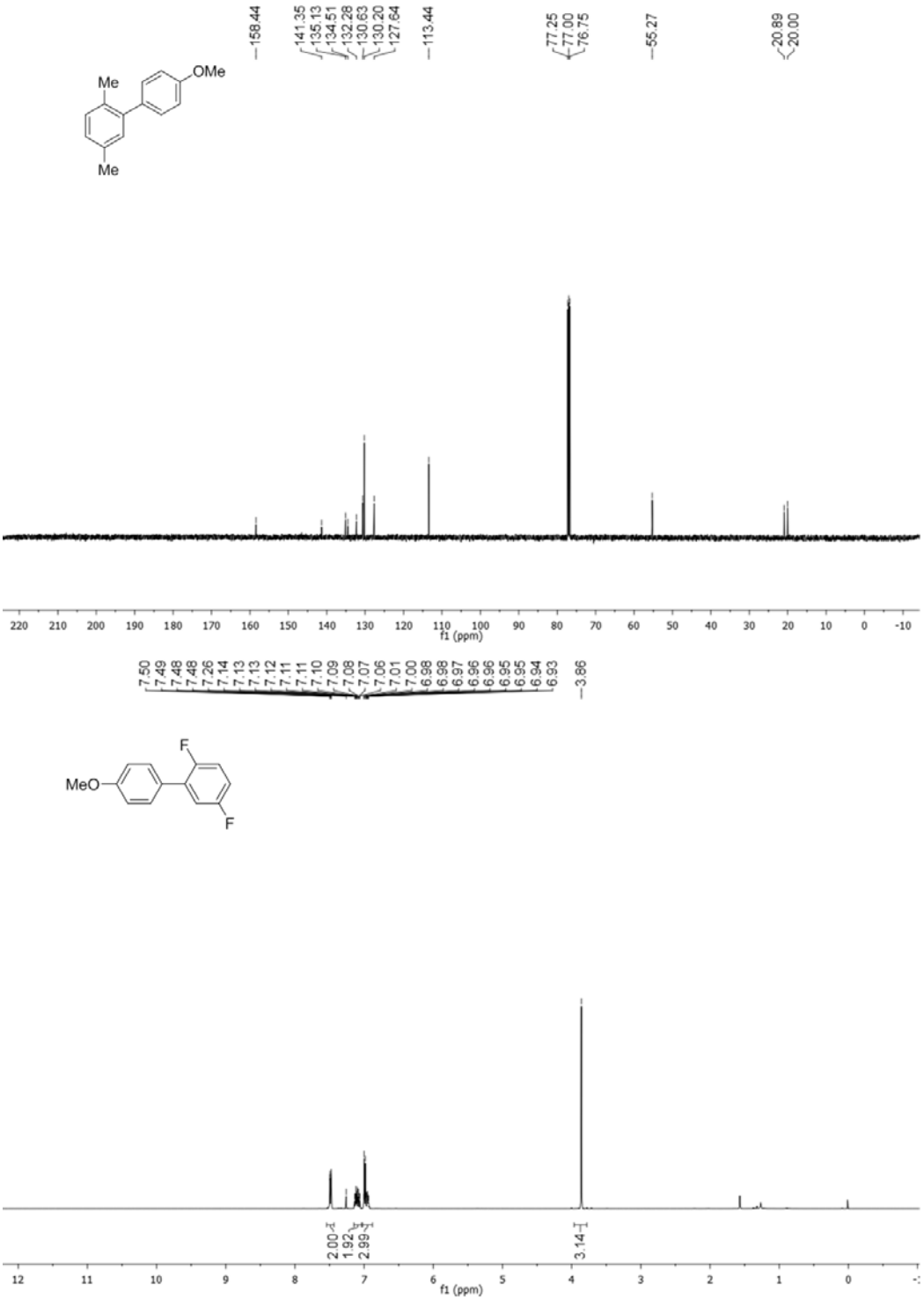
7.26
7.26
7.25
7.24
7.16
7.15
7.06
7.05
6.96
6.96
6.95
6.94
3.86
2.35
2.24
OMe
Me
Me
7.15
3.14
3.07
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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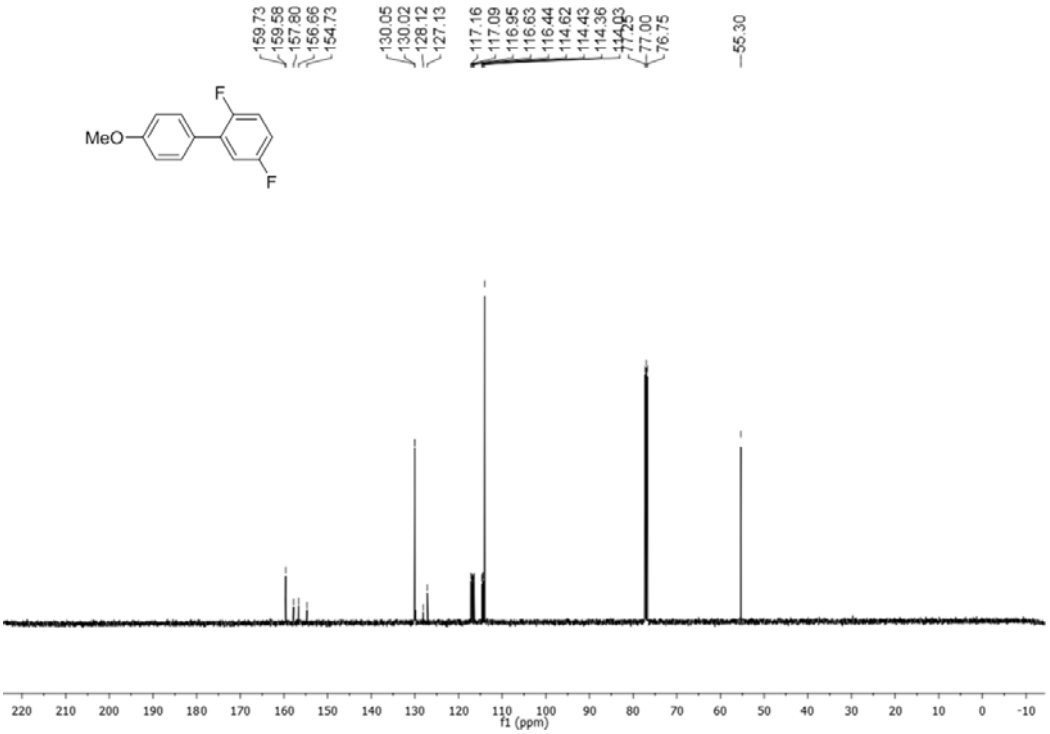
130.63
130.20
127.64
113.44
77.25
77.00
76.75
55.27
20.89
20.00
OMe
Me
Me
f1 (ppm)
7.50
7.49
7.48
7.48
7.26
7.14
7.13
7.13
7.12
7.11
7.11
7.10
7.09
7.08
7.07
7.06
7.01
7.00
6.98
6.98
6.97
6.96
6.96
6.95
6.95
6.94
6.93
3.86
F
MeO
F
2.00
1.92
2.99
3.14
f1 (ppm)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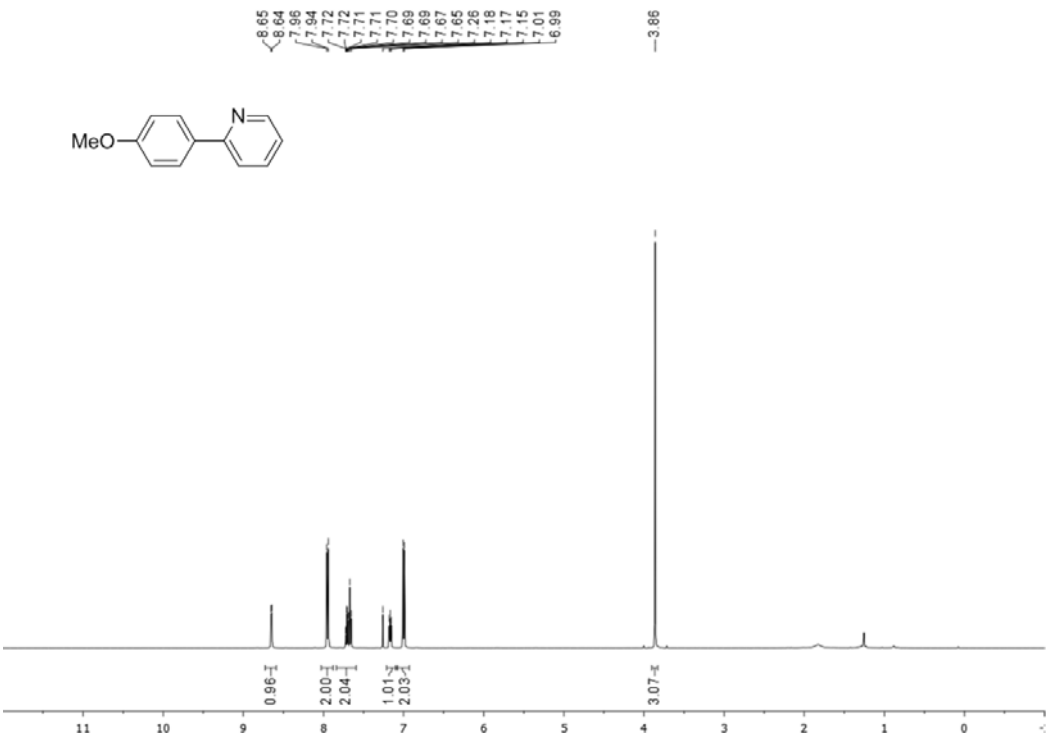
128.12
127.13
117.16
117.09
116.95
116.63
116.44
114.62
114.43
114.36
114.03
77.20
77.00
76.75
55.30
F
MeO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.71
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7.69
7.69
7.67
7.65
7.26
7.18
7.17
7.15
7.01
6.99
3.86
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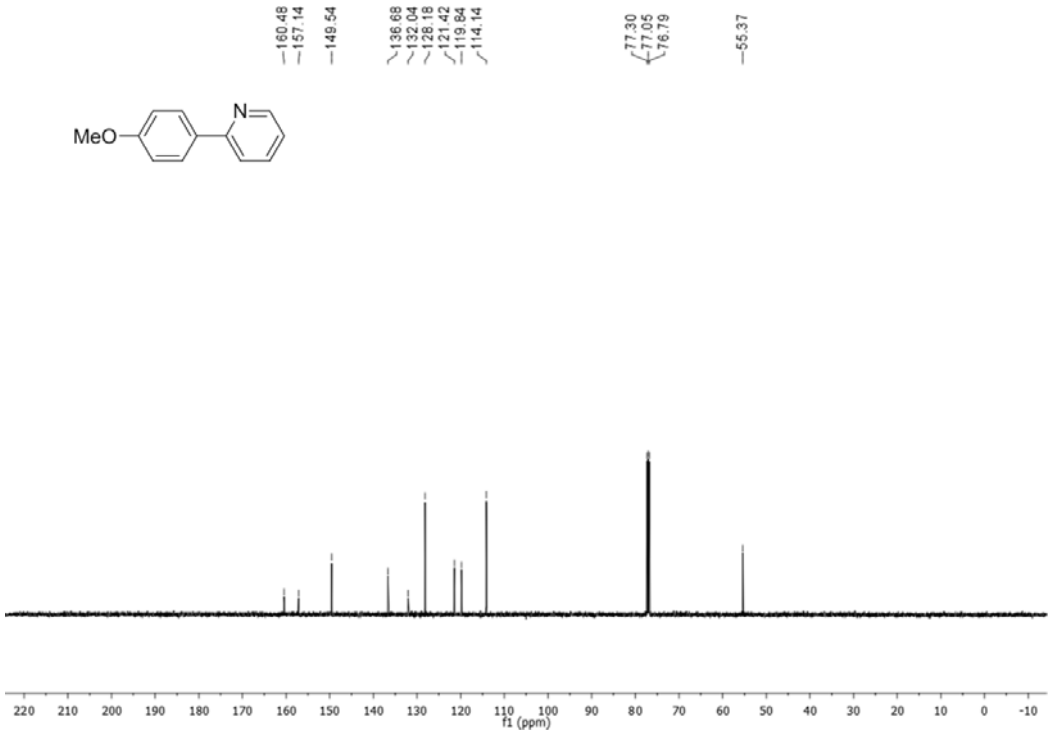
MeO
0.96
2.00
2.04
1.01
2.03
3.07
11 10 9 8 7 6 5 4 3 2 1 0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136.68
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119.84
114.14
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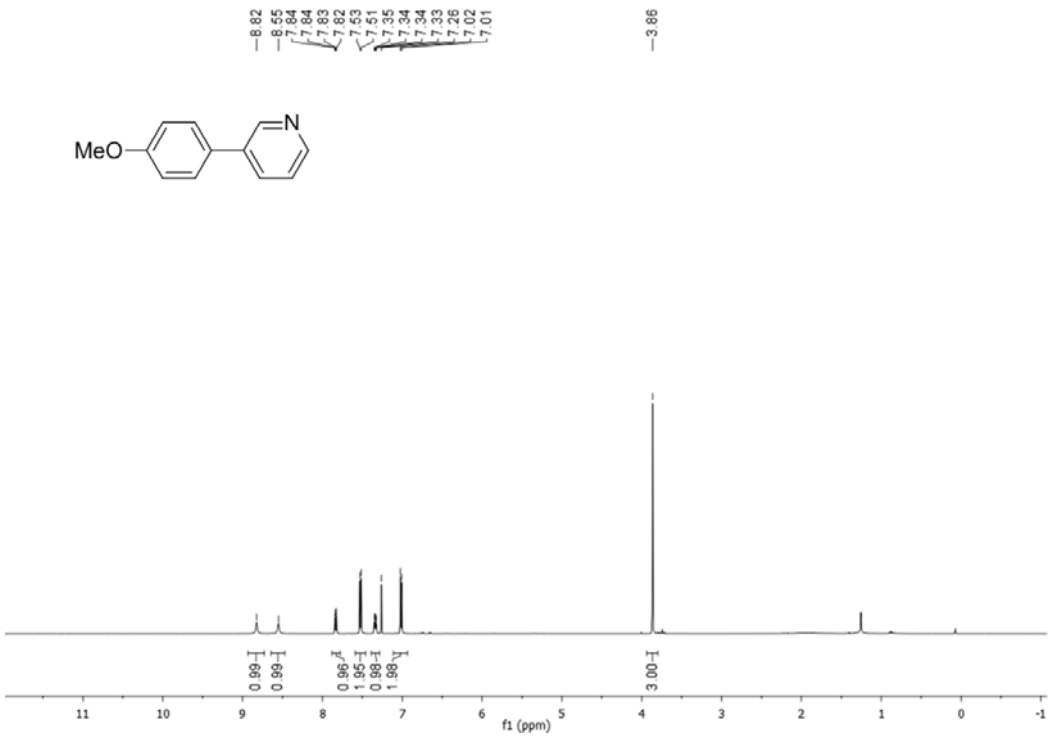
77.05
76.79
55.37
MeO
N
f1 (ppm)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7.34
7.34
7.33
7.26
7.02
7.01
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MeO
N
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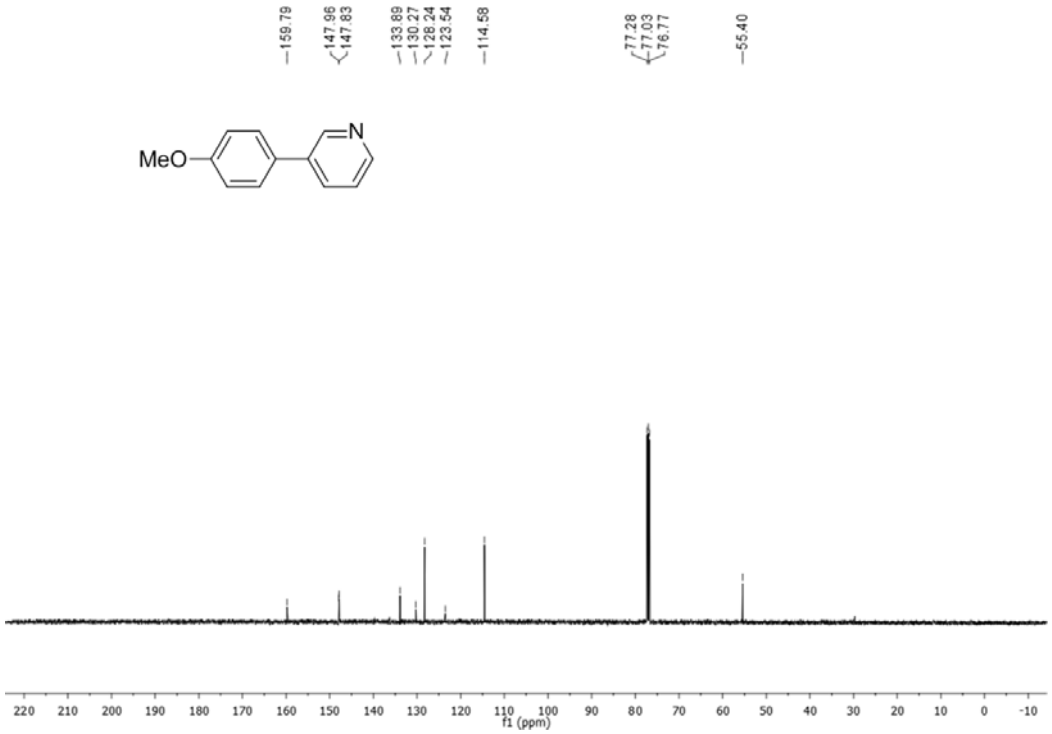
0.99
0.96
1.95
0.98
1.98
3.00
f1 (ppm)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76.77
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MeO
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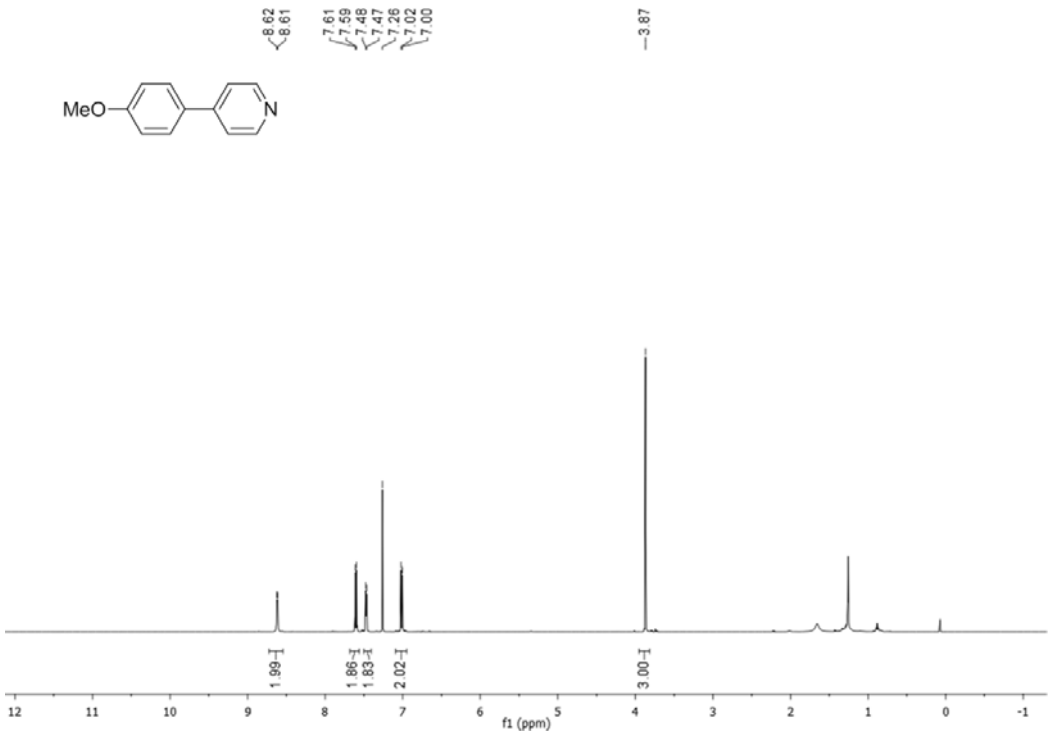
f1 (ppm)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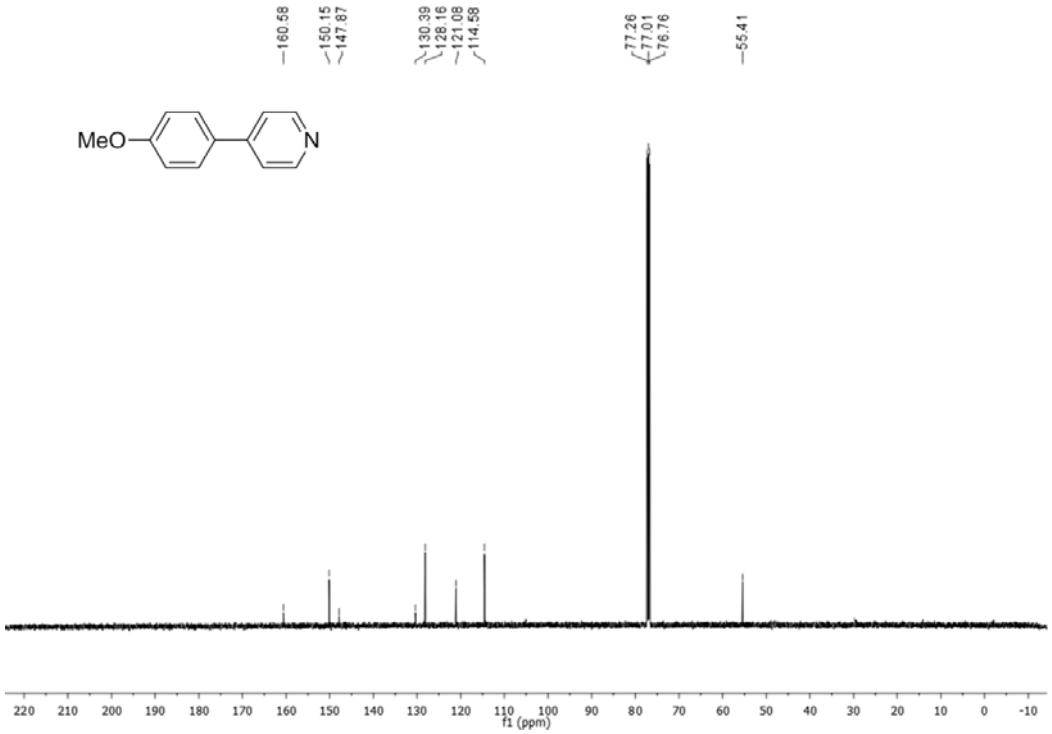
3.00
f1 (ppm)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77.01
76.76
55.41
MeO
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)