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Supplementary Material

N,S-Chelating triazole-thioether palladium for the one-pot synthesis of biaryls

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Supporting Information

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Table of Contents

1. General Information

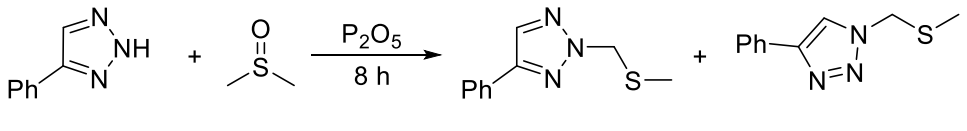
^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz spectrometers. Chemical shifts were recorded in $CDCl_3$, or DMSO-d_6 solutions referenced to tetramethylsilane (TMS) (0.00 ppm) or $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.50 ppm) for ^{1}HNMR, $CDCl_3$ (77 ppm) and DMSO-d_6 (39.5 ppm) for ^{13}CNMR. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates. All other reagents were purchased from commercial suppliers and used without further purification.

2. Experimental Procedure

2.1 Ligand syntheses

Previously, we developed a highly efficient one-pot synthesis of *NH*-1,2,3-triazoles[1]. With these *NH*-1,2,3-triazoles in hand, a series of *N*-substituted sulfur-containing 1,2,3-triazoles **L1-L2** were designed as ligands[2]. We also designed and synthesized a large steric ligand 4-phenyl-2-((p-tolylthio)methyl)-2H-1,2,3-triazole **L3**. Derivation of 1,2,3-triazole-thioether was realized by our work to form **L4**[3].

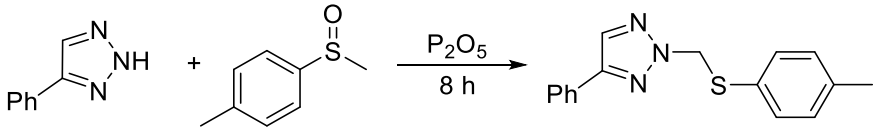
2.1.1 The synthesis of 1,2,3-triazole-thioether ligands:



L1 **L2**

In a 250 mL round-bottomed flask, *NH*-1,2,3-triazole (10.0 g) was accurately added, and then dried solvent DMSO (100 mL) was added. P_2O_5 (24 g) was added slowly. The resulting mixture was stirred at 70 °C in a sealed vessel under air. After disappearance of the reactant (monitored by TLC), the reaction mixture was cooled and added water (500 mL) slowly, and extracted with ethyl acetate (3 × 100 mL). The combined organic layer was washed with brine (1 × 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether as eluent) to yield the product. The small polarity N^2-substitution product was 9.5 g (yield 67%), and the large polarity N^1- substitution product was 3.0 g (yield 21%). The total yield was 88%.

2.1.2 The synthesis of 4-phenyl-2-((p-tolylthio) methyl)-2H-1,2,3-triazole ligands:

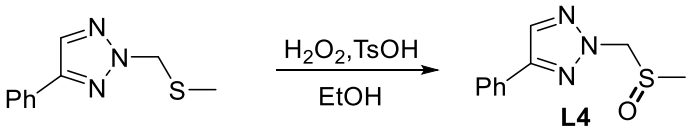


L3

To a 250 mL round-bottomed flask, *NH*-1,2,3-triazoles (5.0 g), 1-methyl-4-(methylsulfinyl)benzene (50 mL) and P_2O_5 (12 g) were accurately added in turn. Then, the mixture was stirred at 70 °C in a sealed vessel under air. After the

reaction was completed (monitored by TLC), the mixture was cooled and extracted with ethyl acetate (100 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtered and concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether as eluent) to yield the product. The small polarity N^2-substitution product was 4.8 g (yield 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.69 (s, 2H), 2.33 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 138.5, 133.0, 131.9, 130.1, 129.9, 129.3, 128.8, 128.6, 126.0, 59.3, 21.2.HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{16}H_{16}N_3S$: 282.1059, found 282.1063.

2.1.3 The synthesis of 2-((methylsulfinyl) methyl)-4-phenyl-2H-1,2,3-triazole ligands:



In a 250 mL round-bottomed flask, 5.0 g N^2-substitution product 2-((methylsulfinyl)methyl)-4-phenyl-2H-1,2,3-triazole was added, 8 mL of hydrogen peroxide with 30% concentration, TsOH (0.2 mL) and ethanol (50 mL) were added, and the reaction temperature was 70 ^{o}C. The reaction was basically completed in about 8 hours through TLC monitoring. After the reaction was completed, sodium bisulfite was added to remove excess hydrogen peroxide and solvent ethanol was decompressed. The residues were added with 150 mL of water, and then extracted with ethyl acetate (3 × 50 mL). The combined organic layer was washed with brine (1 × 50 mL). The obtained organic layer was dried with anhydrous Na_2SO_4, and ethyl acetate was removed by decompression to obtain 5.2 g white solid with a yield of 90%.

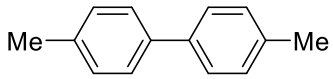
2.2 One-pot coupling procedure

An oven-dried Schlenk tube was charged with bis(pinacolato)diboron (1 mmol), $Pd(CH_3CN)_2Cl_2$ (1 mol %), **L2**(1 mol %), anhydrous *t*-BuOK (2.5 mmol). The

Schlenk tube was backfilled with argon for three times. Then, DMF (3 mL) was added by syringe, followed by addition of arylhalides (2.2 mmol) in a similar manner (solids were added with other reagents before evacuation). The reaction was stirred in 50 °C and was monitored by TLC. After 4 hours, the reaction mixture was added water (50 mL), and then extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with brine and was dried over anhydrous Na_2SO_4. After filtered and concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum ether as eluent) to yield the product.

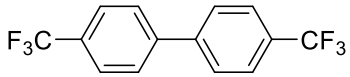
3. Cross-coupling Product Characterization Data

4,4'-dimethyl-1,1'-biphenyl (3a) [4]



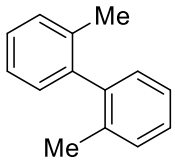
White solid. Mp: 125 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6(s), 137.0 (s), 129.7 (s), 127.1 (s), 21.4 (s).

4,4'-bis(trifluoromethyl)-1,1'-biphenyl (3b) [5]



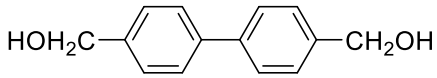
White solid. Mp: 92 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 4H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 131.0, 128.2, 126.7, 126.1.

2,2'-dimethyl-1,1'-biphenyl (3c) [4]



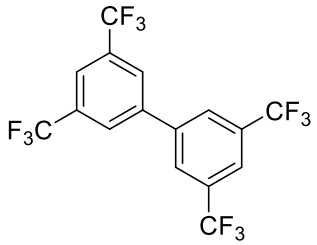
Light yellow liquid. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 6H). ^{13}CNMR(100 MHz, $CDCl_3$) δ 141.9 (s), 138.9 (s), 129.2 (s), 128.6 (s), 128.5 (s), 124.9 (s), 22.2 (s).

[1,1'-biphenyl]-4,4'-diyldimethanol (3d) [6]



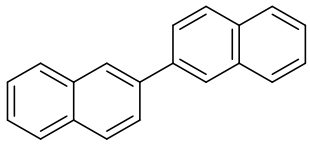
White solid. Mp: 188 ^{o}C. Eluent: EtOAc/Petroleum ether (V/V = 1:10). ^{1}H NMR (400 MHz, DMSO) δ 7.64 – 7.58 (m, 4H), 7.39 (d, J = 8.4 Hz, 4H), 5.26 (t, J = 5.6 Hz, 2H), 4.53 (d, J = 5.7 Hz, 4H). ^{13}C NMR (100 MHz, DMSO) δ 141.9, 138.8, 127.3, 126.5, 62.9.

3,3',5,5'-tetrakis(trifluoromethyl)-1,1'-biphenyl (3e) [7]



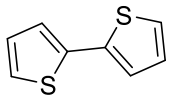
White solid. Mp: 68 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 4H), 7.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 133.4, 133.0, 132.7, 132.4, 127.5, 124.4, 122.6, 121.6.

2,2'-binaphthalene (3f) [7]



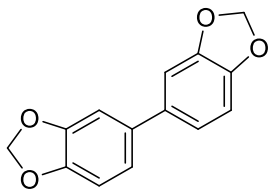
White solid. Mp: 188 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 2H), 7.99 (d, J = 8.8 Hz, 4H), 7.94 – 7.88 (m, 4H), 7.59 – 7.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 133.7, 132.7, 128.5, 128.2, 127.7, 126.4, 126.1, 126.0, 125.7.

2,2'-bithiophene (3g) [5]



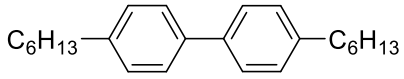
White solid. Mp: 33 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H), 7.20 – 7.17 (m, 2H), 7.02 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ137.7(s), 128.1(s), 124.7(s), 124.1(s).

5,5'-bibenzo[d][1,3]dioxole (3h) [8]



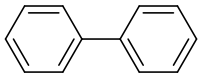
White solid. Mp: 145 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (m, 3H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.86 (s, 1H), 6.84 (s, 1H), 5.99 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.4, 135.0, 119.9, 108.2, 107.2, 100.8.

4,4'-dihexyl-1,1'-biphenyl (3i) [9]



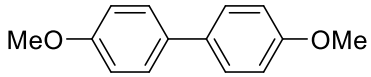
Colorless liquid. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 4H), 2.68 – 2.62 (m, 4H), 1.65 (m, 4H), 1.42 – 1.26 (m, 12H), 0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.8, 129.1, 127.1, 35.9, 32.1, 31.8, 29.4, 22.9, 14.4.

1,1'-biphenyl (3j) [4]



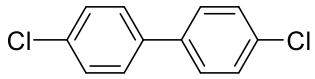
White solid. Mp: 69 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.7, 127.2, 127.2.

4,4'-dimethoxy-1,1'-biphenyl (3k) [4]



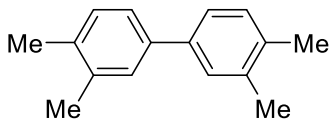
White solid. Mp: 175 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 4H), 6.97 – 6.95 (m, 4H), 3.85 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 134.5, 128.7, 115.1, 56.3.

4,4'-dichloro-1,1'-biphenyl (3l) [5]



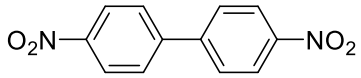
White solid. Mp: 149 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 133.4, 128.7, 127.9.

3, 3', 4, 4'-tetramethyl-1,1'-biphenyl (3m) [10]



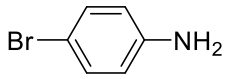
White solid. Mp: 76 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 7.32 (m, 2H), 7.19 (d, J = 7.8Hz, 2H), 2.33 (s, 6H), 2.30 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ138.9, 136.8, 135.3, 129.9, 128.2, 124.3, 19.9, 19.4.

4, 4'-dinitro-1, 1'-biphenyl (3n) [5]



Orange yellow solid. Mp: 240 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 4H), 6.66 – 6.53 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6 (s), 129.7 (s), 123.8 (s), 116.8 (s).

4-bromoaniline (4n) [11]



Yellow solid. Mp: 55 ^{o}C. Eluent: Petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.57 – 6.54 (m, 2H), 3.66 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 132.6, 117.3, 110.8).

4. References

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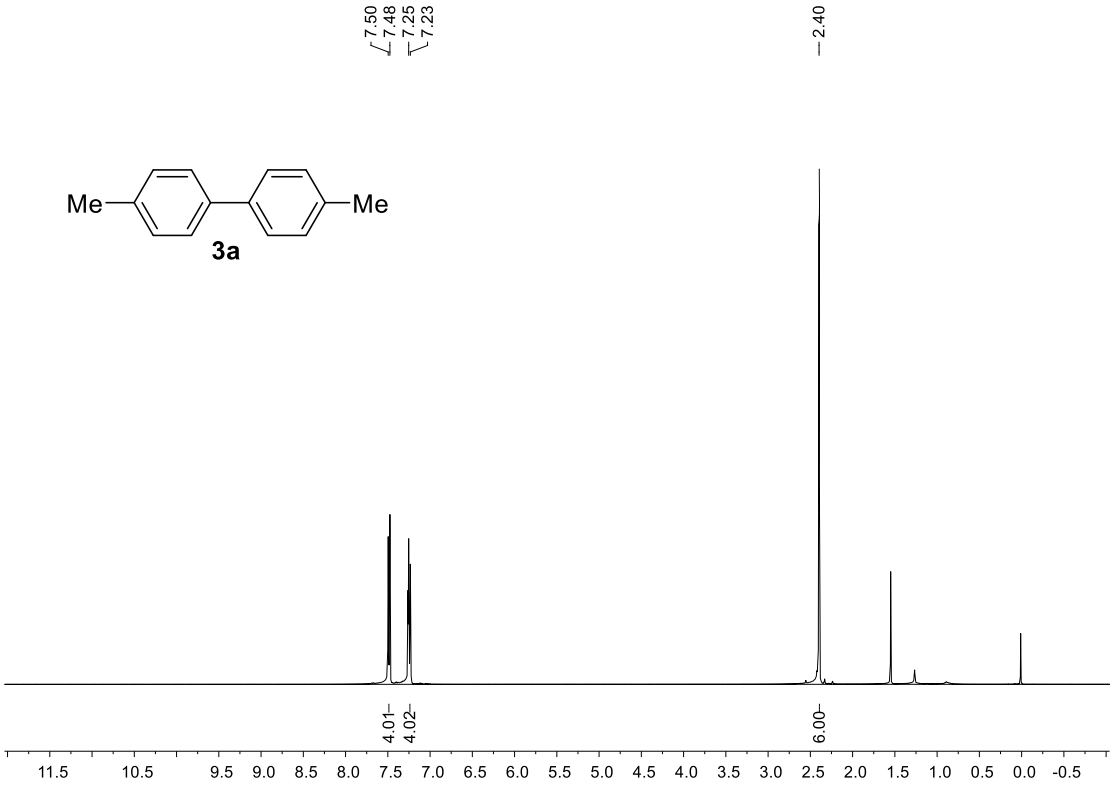
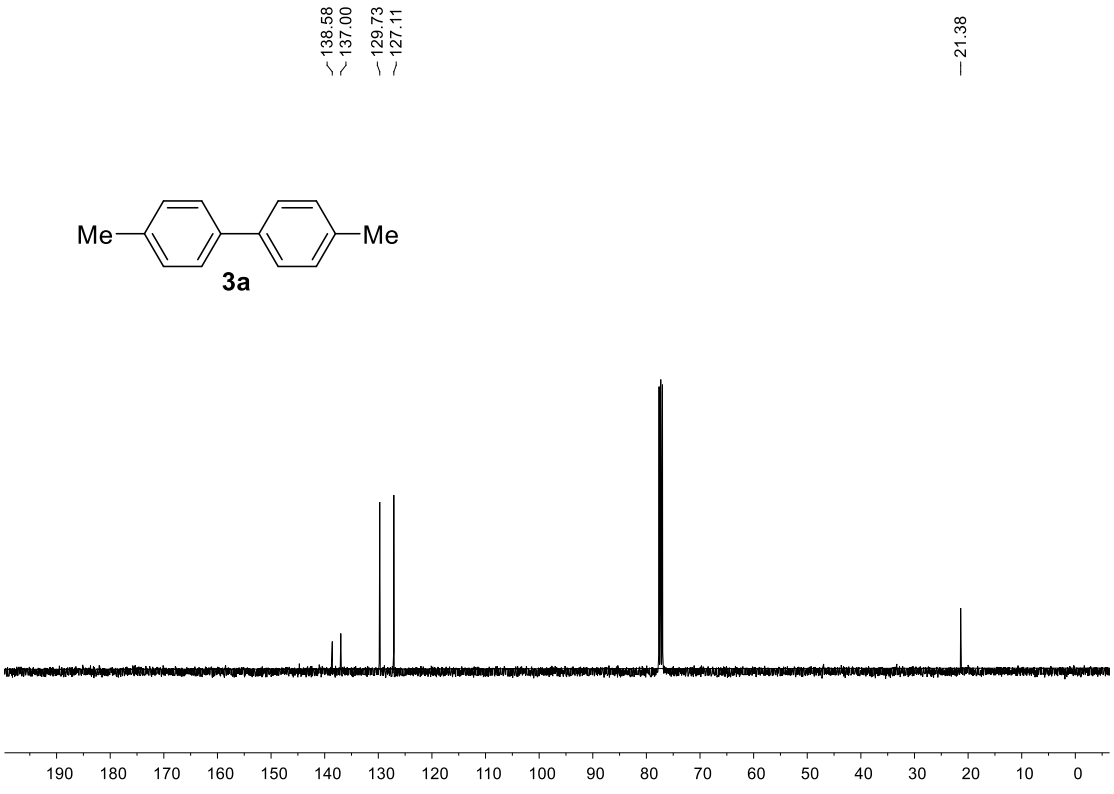
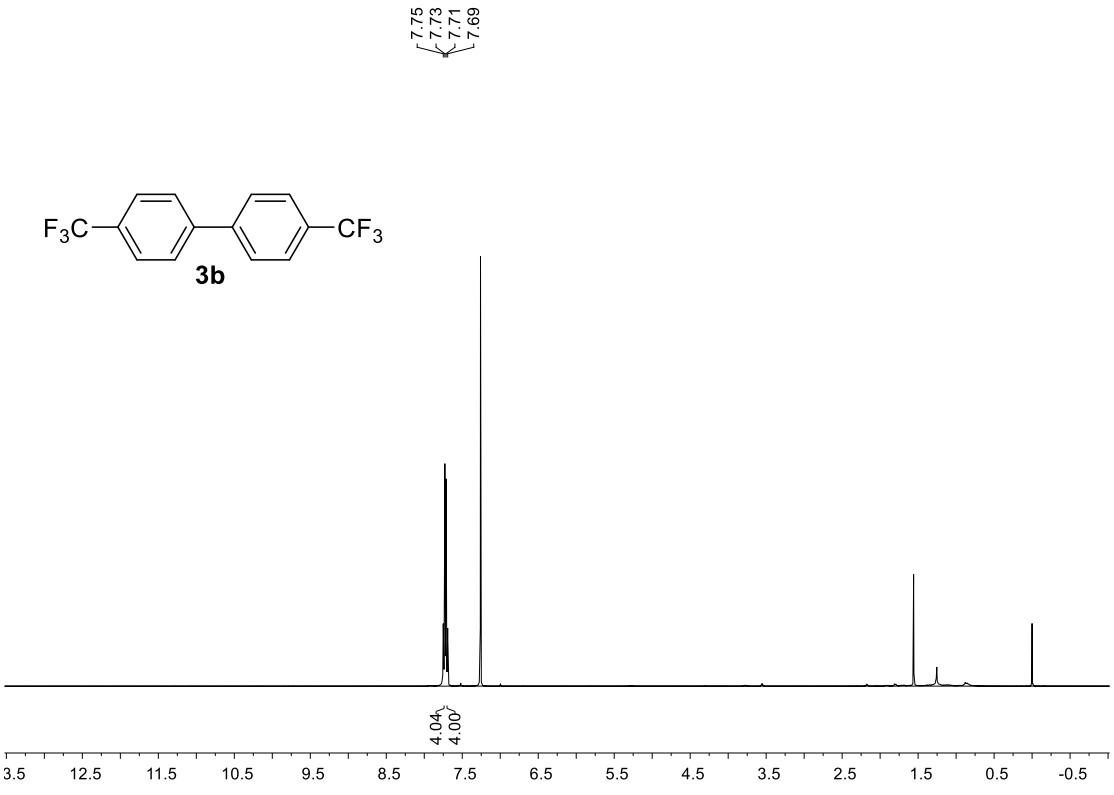
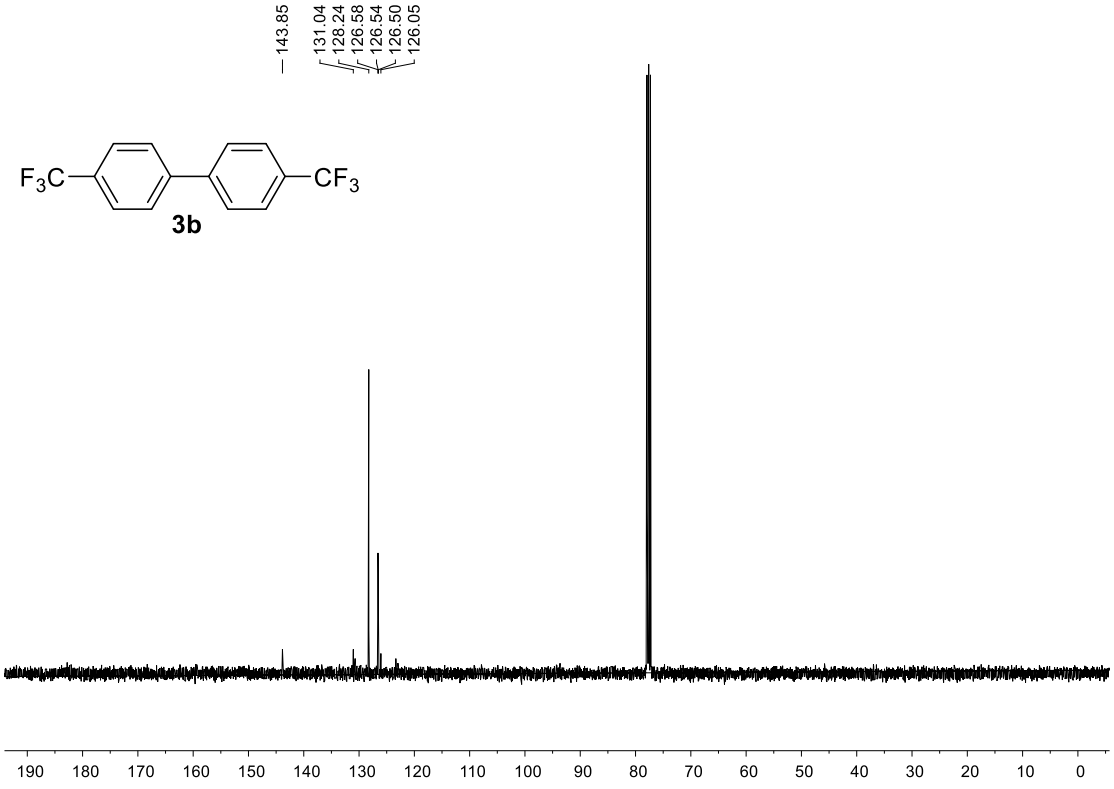
5. ^{1}H NMR and ^{13}C NMR Spectra






7.75
7.73
7.71
7.69
F3C
CF3
3b
4.04
4.00
3.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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131.04
128.24
126.58
126.54
126.50
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F3C
CF3
3b
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180
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70
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10
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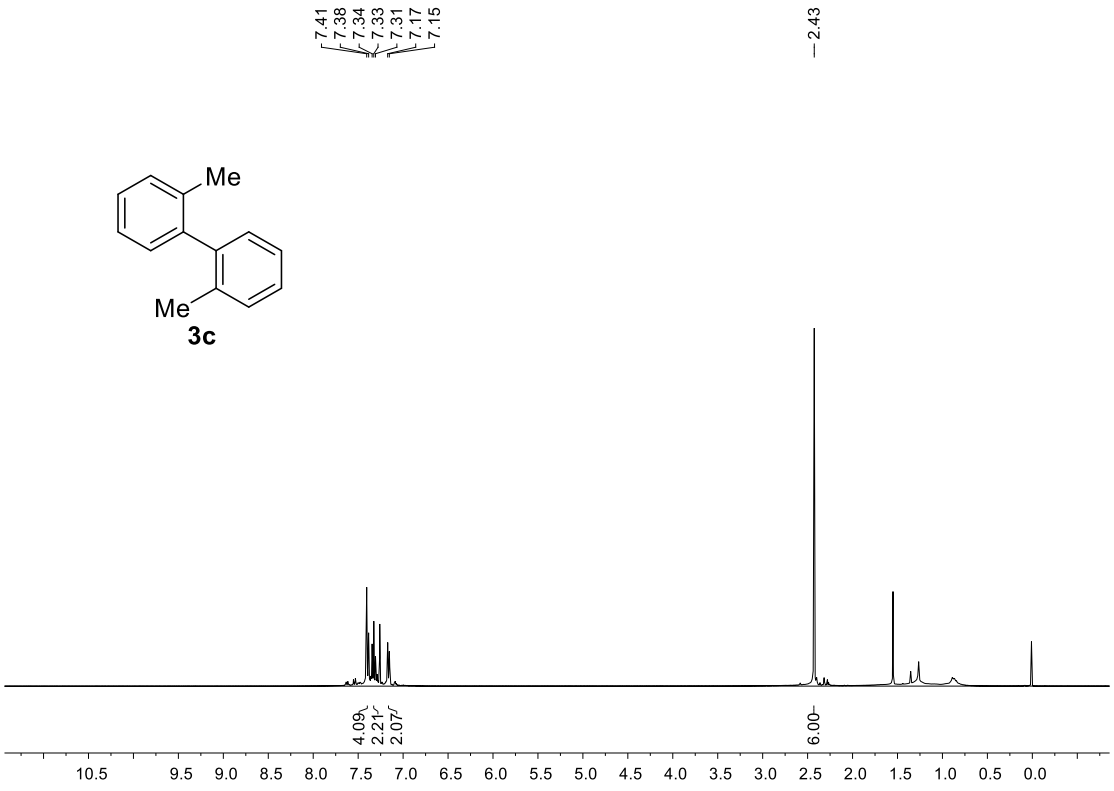
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7.38
7.34
7.33
7.31
7.17
7.15
2.43
Me
Me
3c
4.09
2.21
2.07
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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1.0
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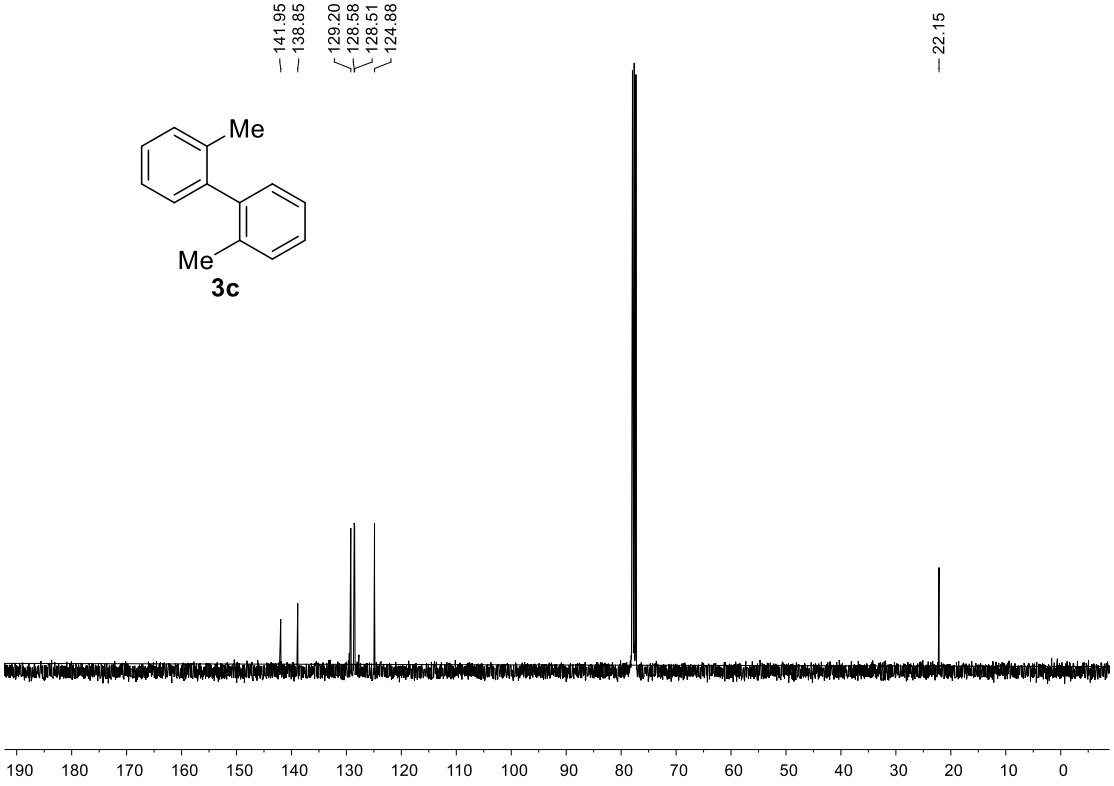
141.95
138.85
129.20
128.58
128.51
124.88
22.15
Me
Me
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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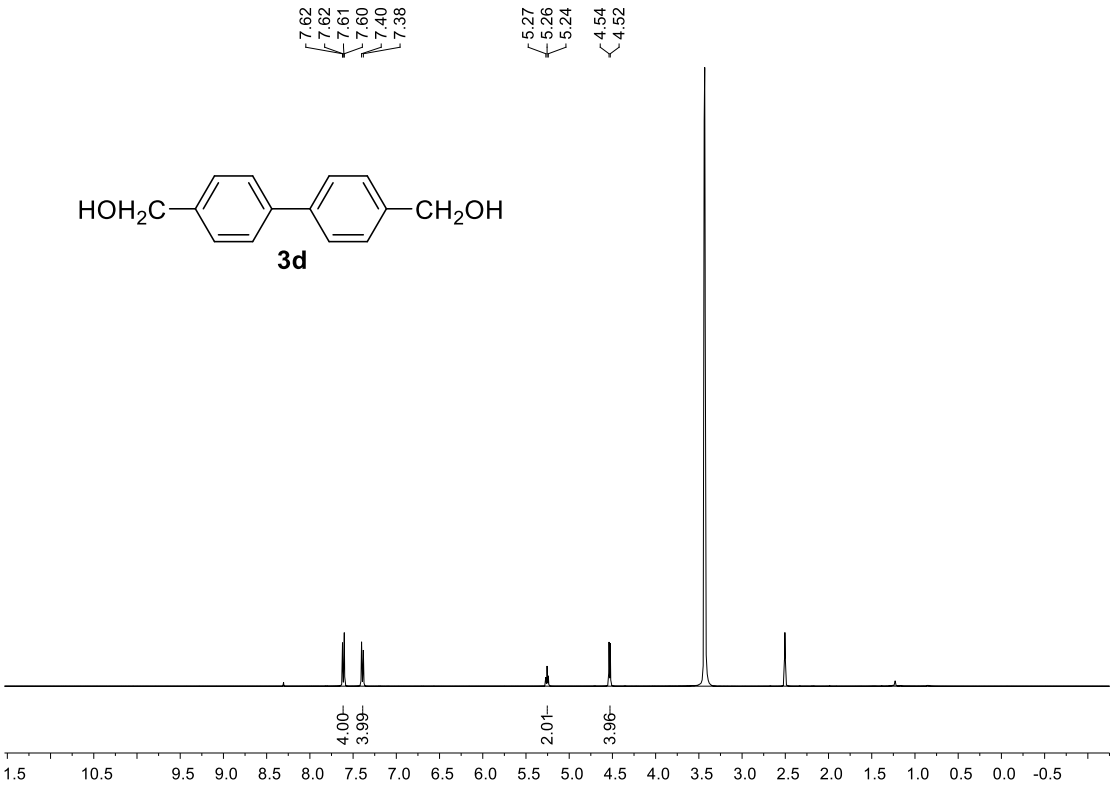
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5.27
5.26
5.24
4.54
4.52
HOH2C
CH2OH
3d
4.00
3.99
2.01
3.96
1.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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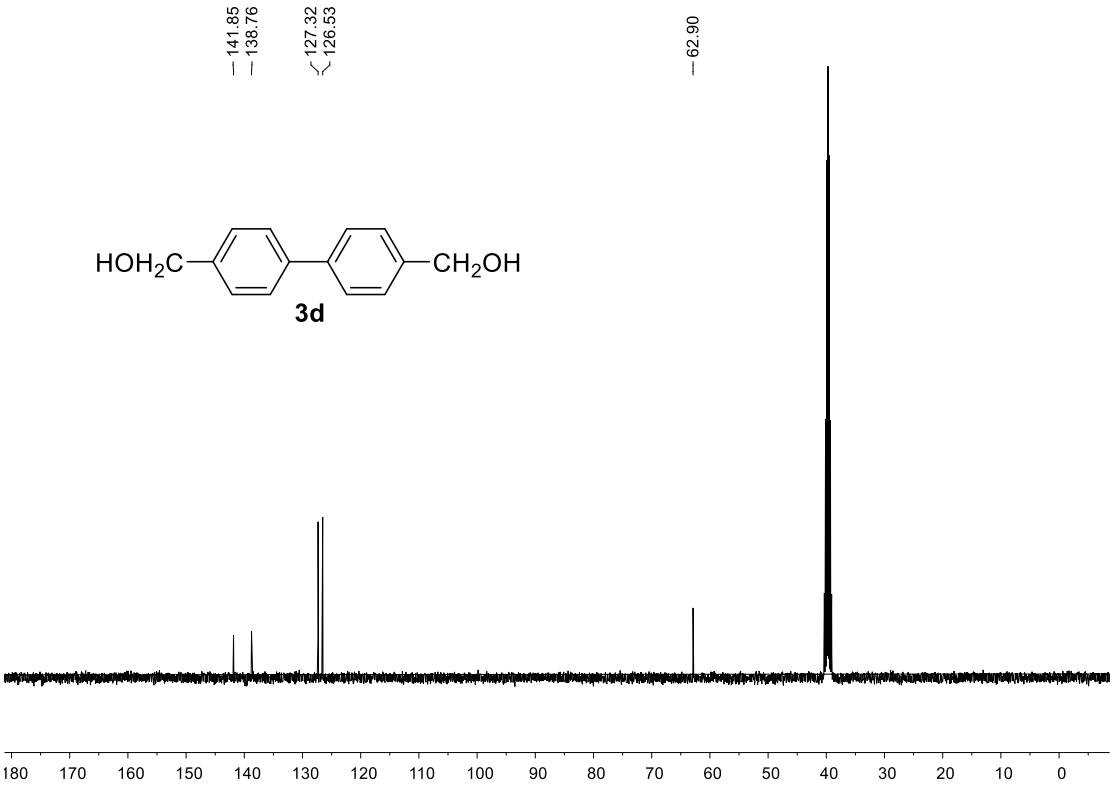
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138.76
127.32
126.53
62.90
HOH2C
CH2OH
3d
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70
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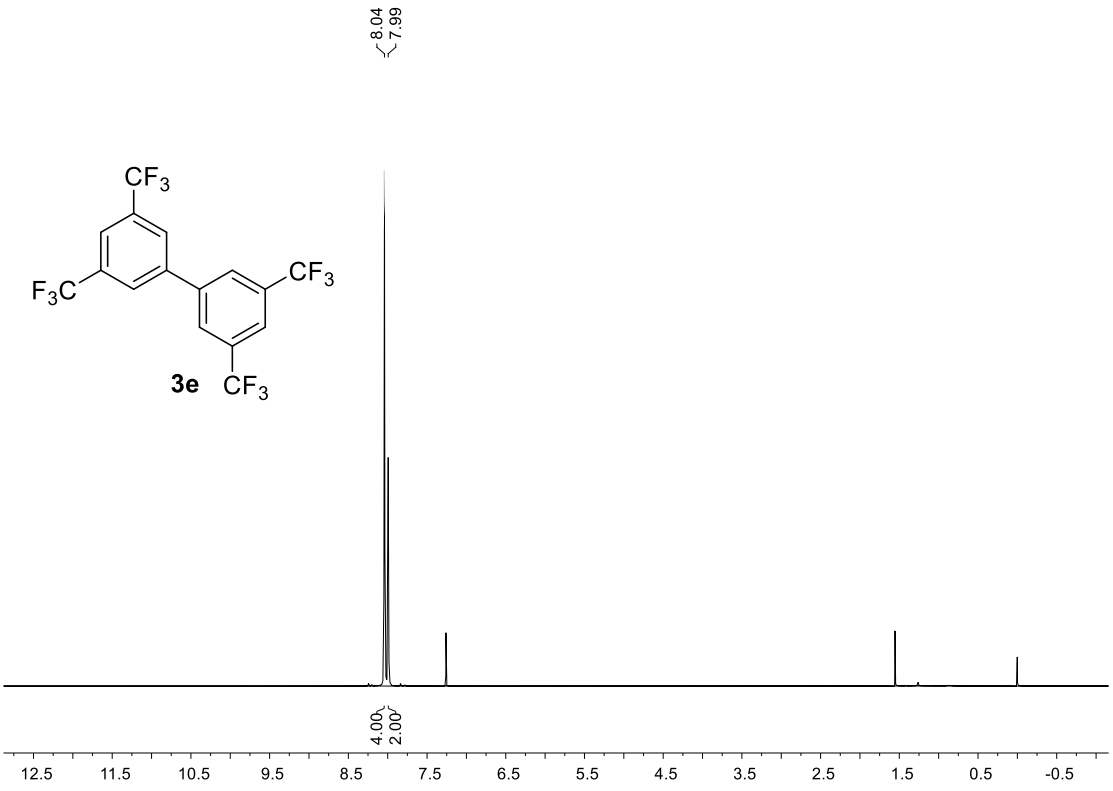
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CF3
F3C
CF3
3e
CF3
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2.00
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5.5
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1.5
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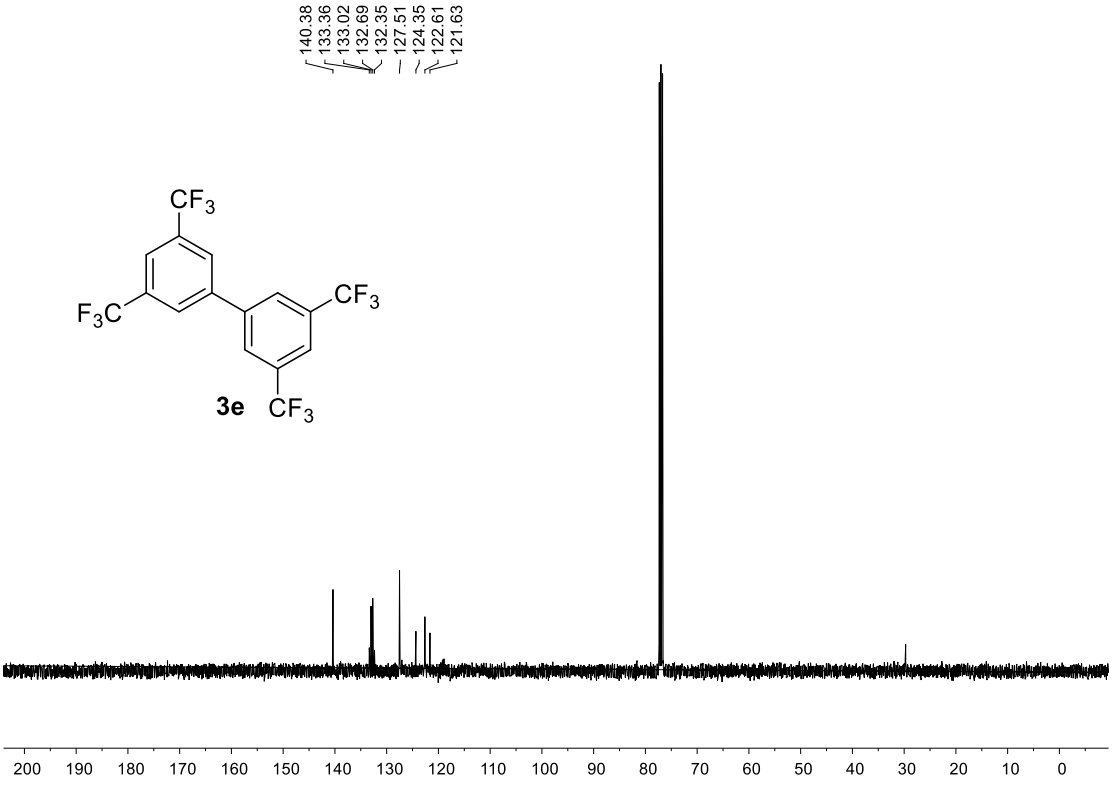
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133.02
132.69
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127.51
124.35
122.61
121.63
CF3
F3C
CF3
3e
CF3
200
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150
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100
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10
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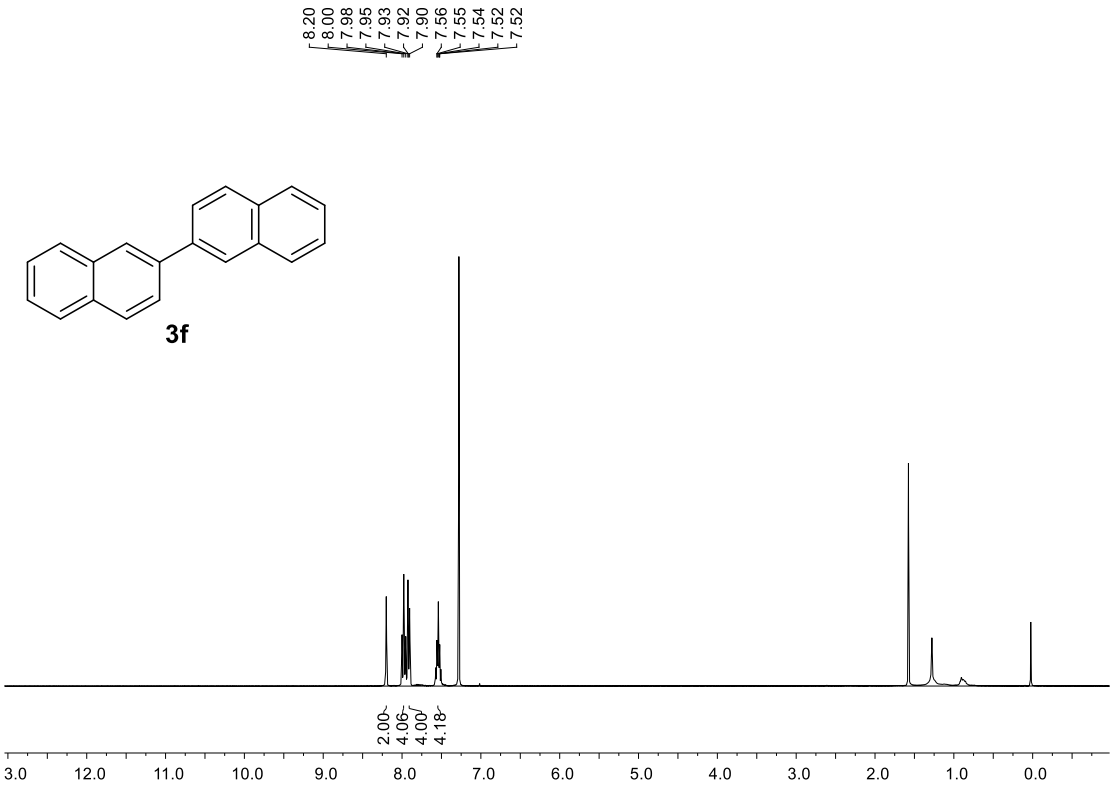
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7.90
7.56
7.55
7.54
7.52
7.52
3f
2.00
4.06
4.00
4.18
3.0
12.0
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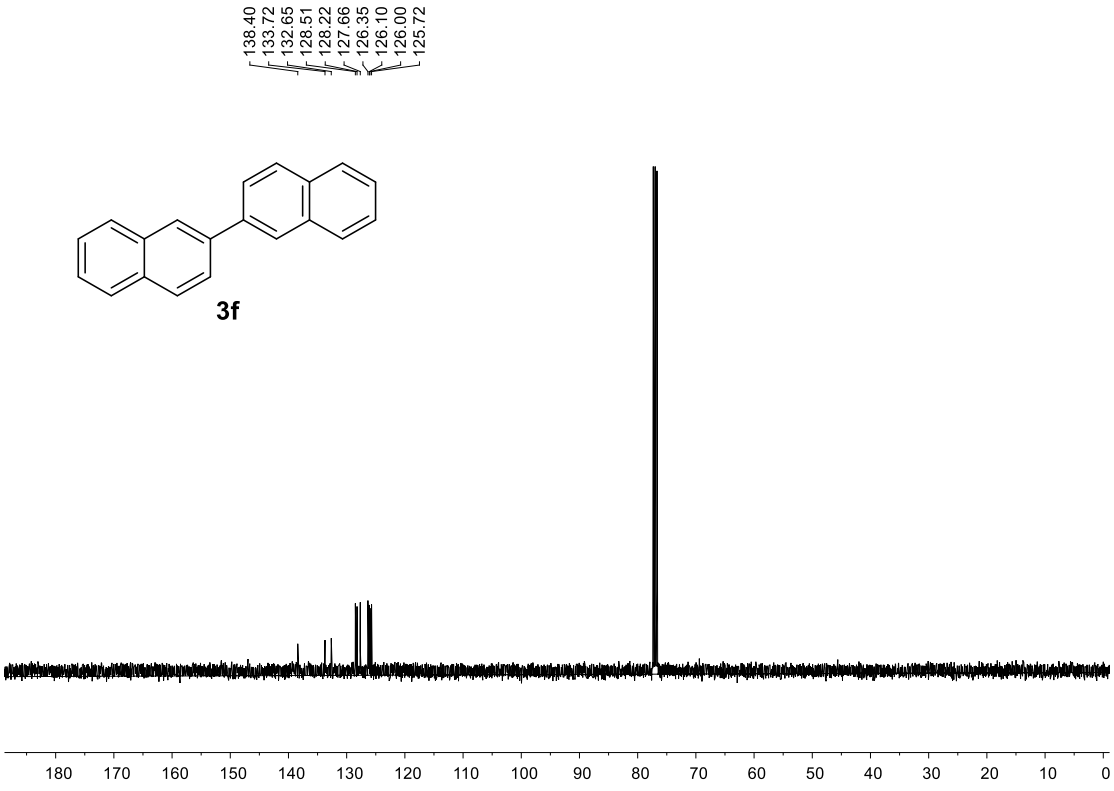
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128.51
128.22
127.66
126.35
126.10
126.00
125.72
3f
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170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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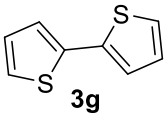
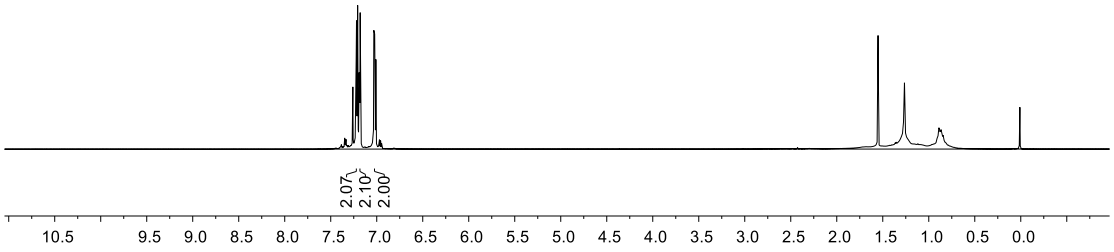
7.22
7.21
7.21
7.19
7.19
7.18
7.03
7.02
7.02
7.01


S
S

3g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2.10
2.00
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8.0
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7.0
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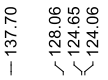
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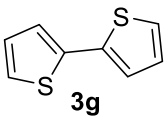
124.65
124.06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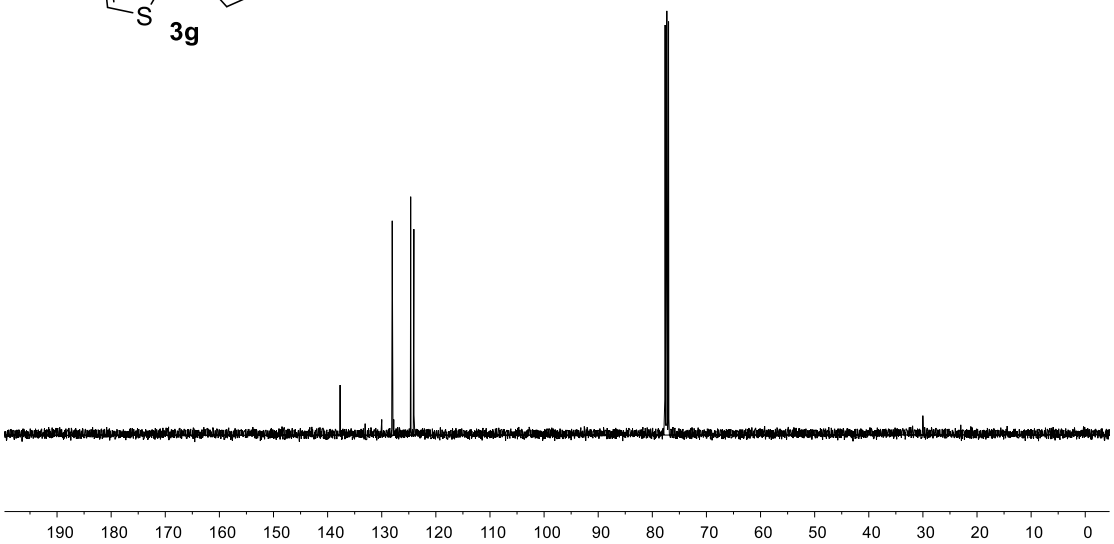
S

3g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110
100
90
80
70
60
50
40
30
20
10
0


6.99
6.99
6.98
6.98
6.96
6.96
6.86
6.84
5.99
3h
3.00
1.18
1.08
0.89
4.38
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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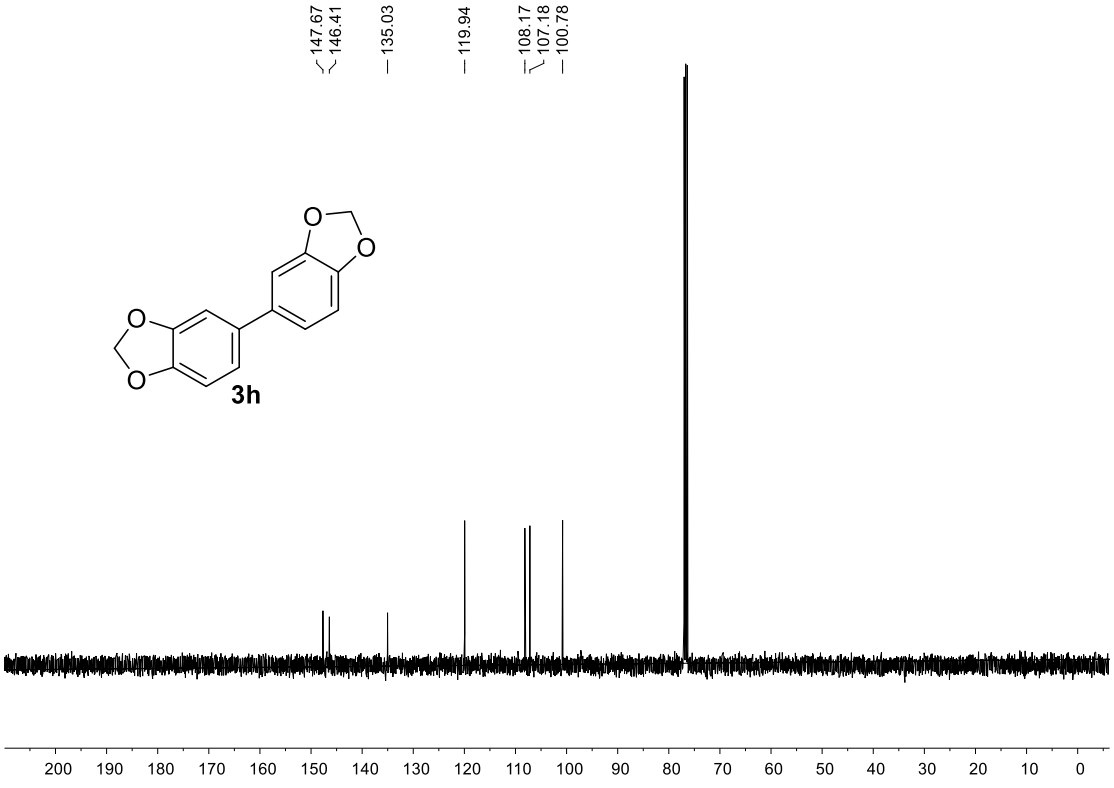
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119.94
108.17
107.18
100.78
3h
200
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150
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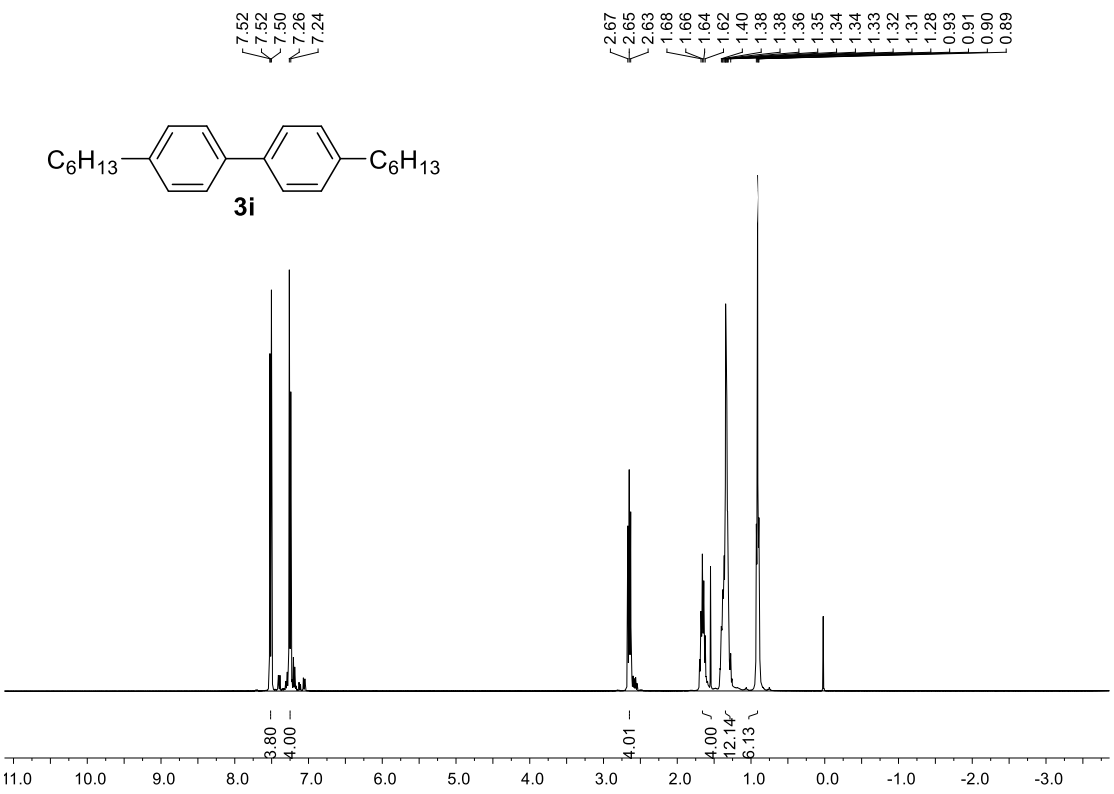
0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2.65
2.63
1.68
1.66
1.64
1.62
1.40
1.38
1.38
1.36
1.35
1.34
1.34
1.33
1.32
1.31
1.28
0.93
0.91
0.90
0.89
C6H13
C6H13
3i
3.80
4.00
4.01
4.00
12.14
6.13
11.0
10.0
9.0
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5.0
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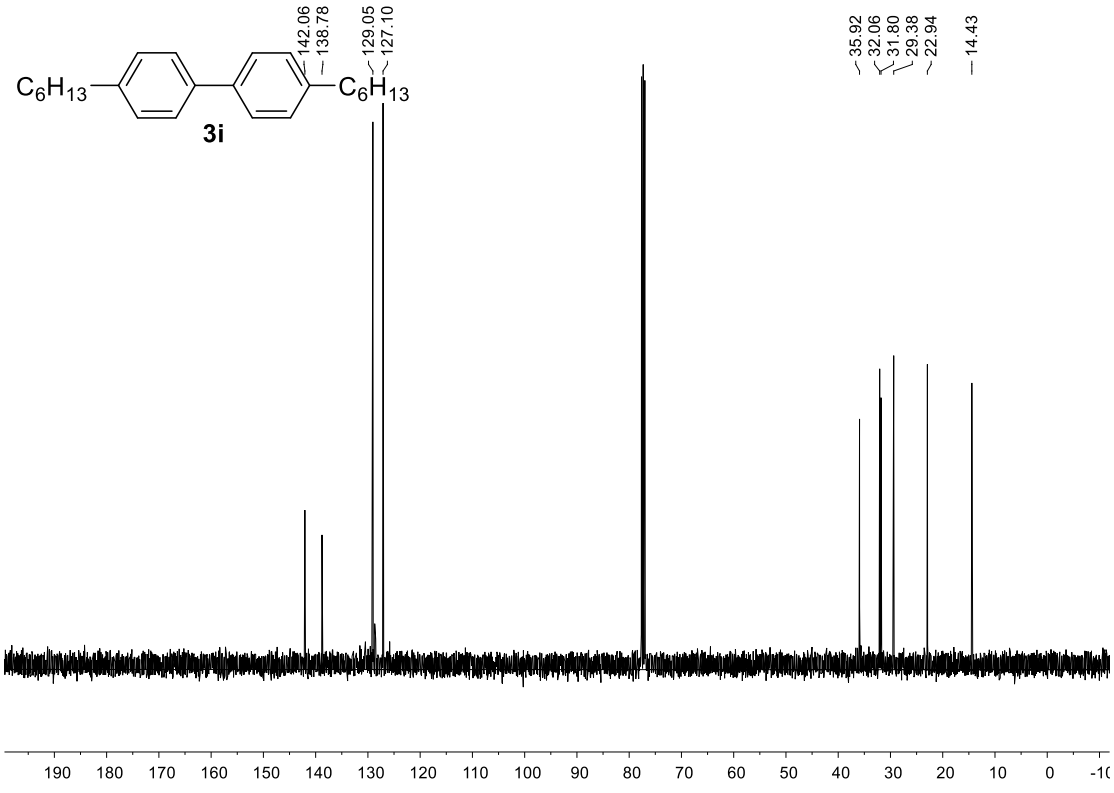
-2.0
-3.0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35.92
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31.80
29.38
22.94
14.43
C6H13
C6H13
3i
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150
140
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120
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100
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30
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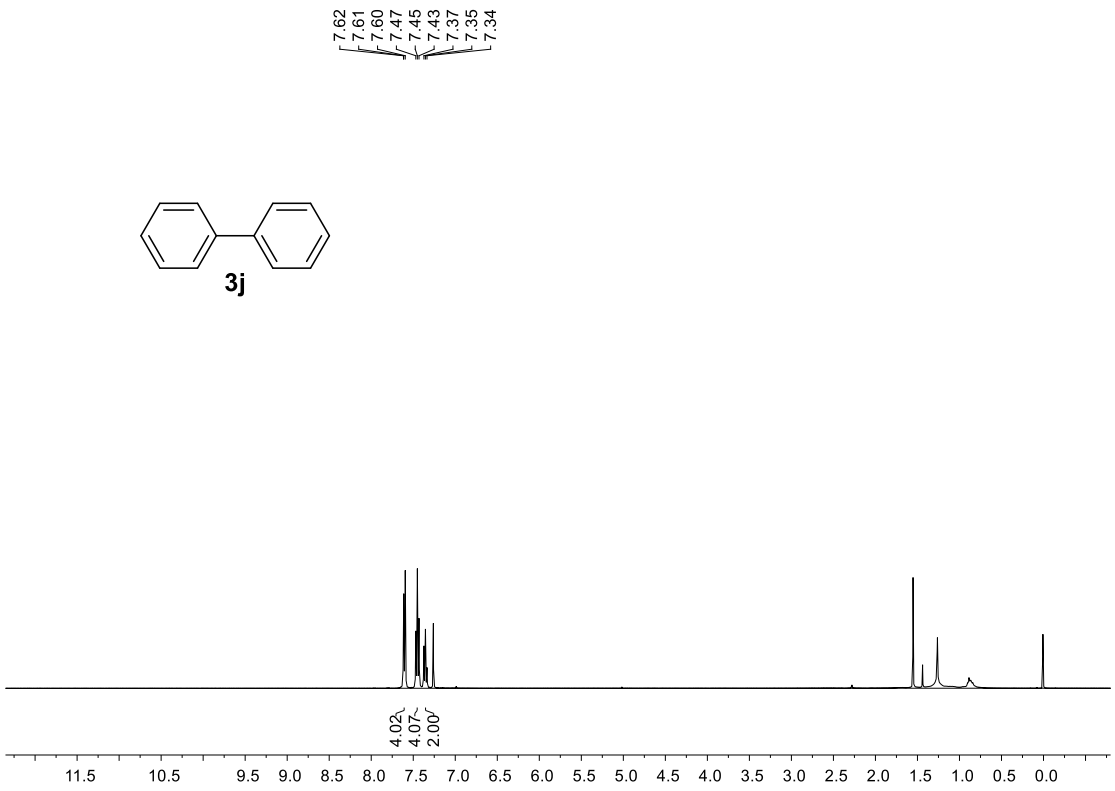
10
0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7.60
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7.45
7.43
7.37
7.35
7.34
3j
4.02
4.07
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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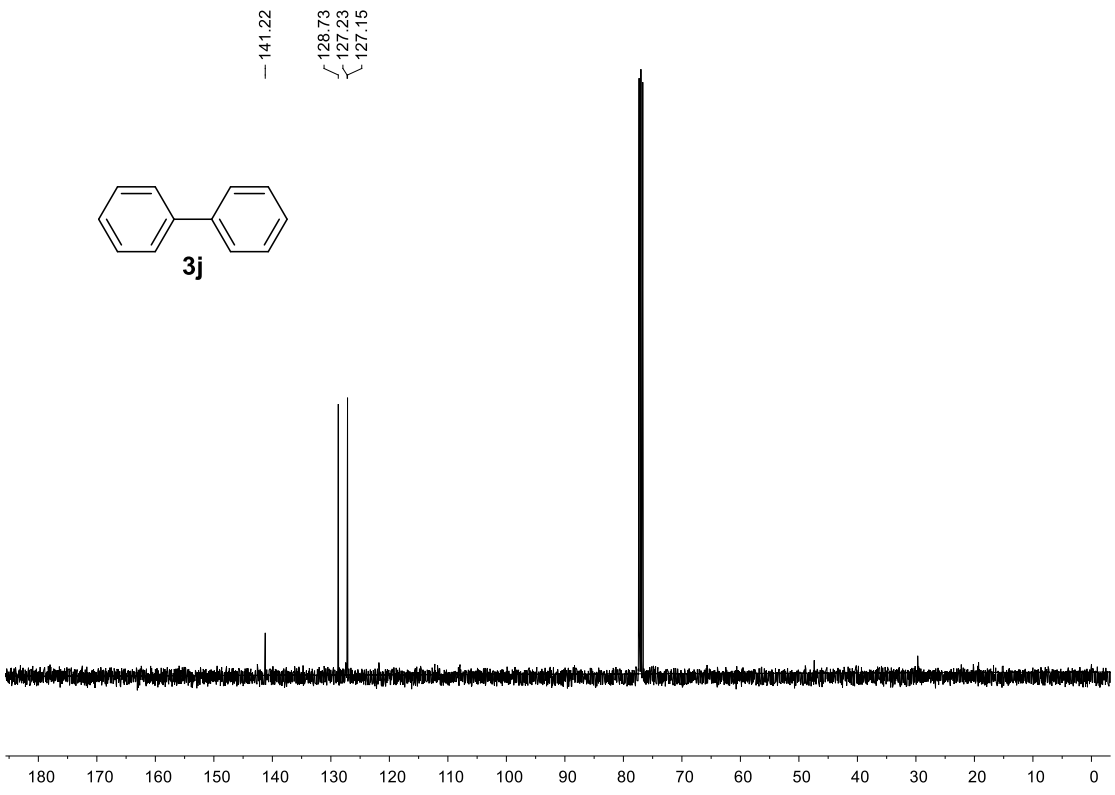
0.0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127.15
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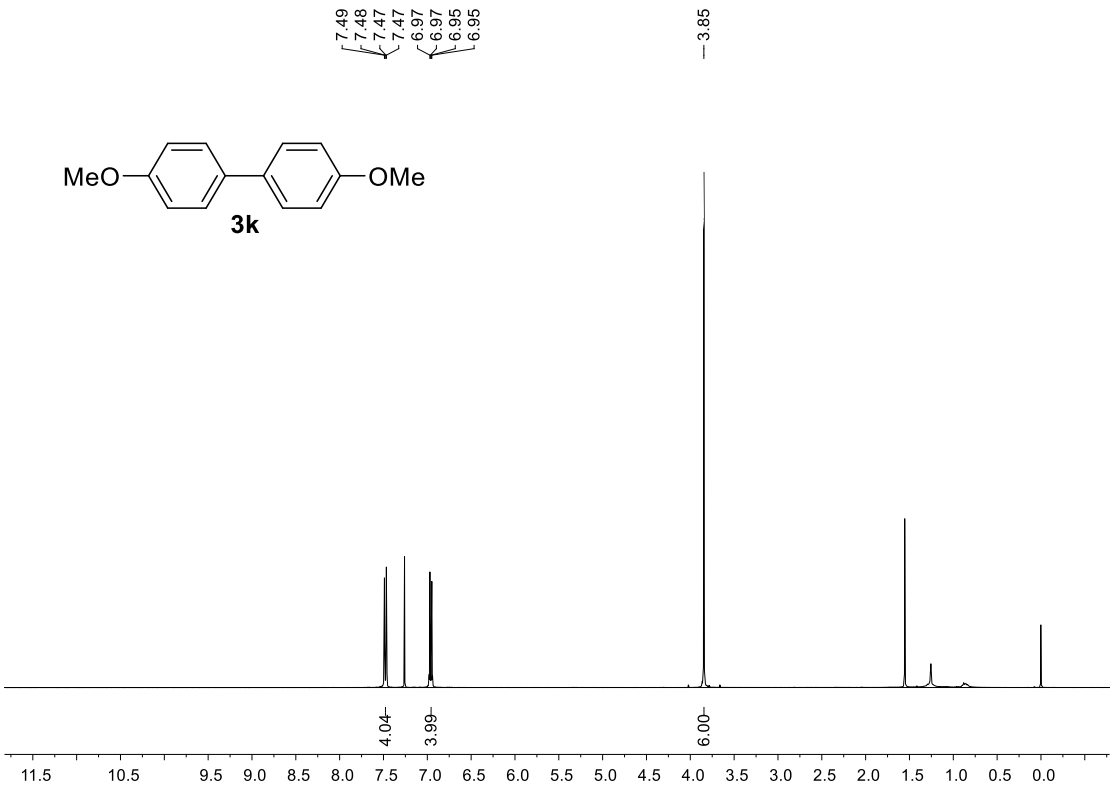
10
0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7.48
7.47
7.47
6.97
6.97
6.95
6.95
3.85
MeO
OMe
3k
4.04
3.99
6.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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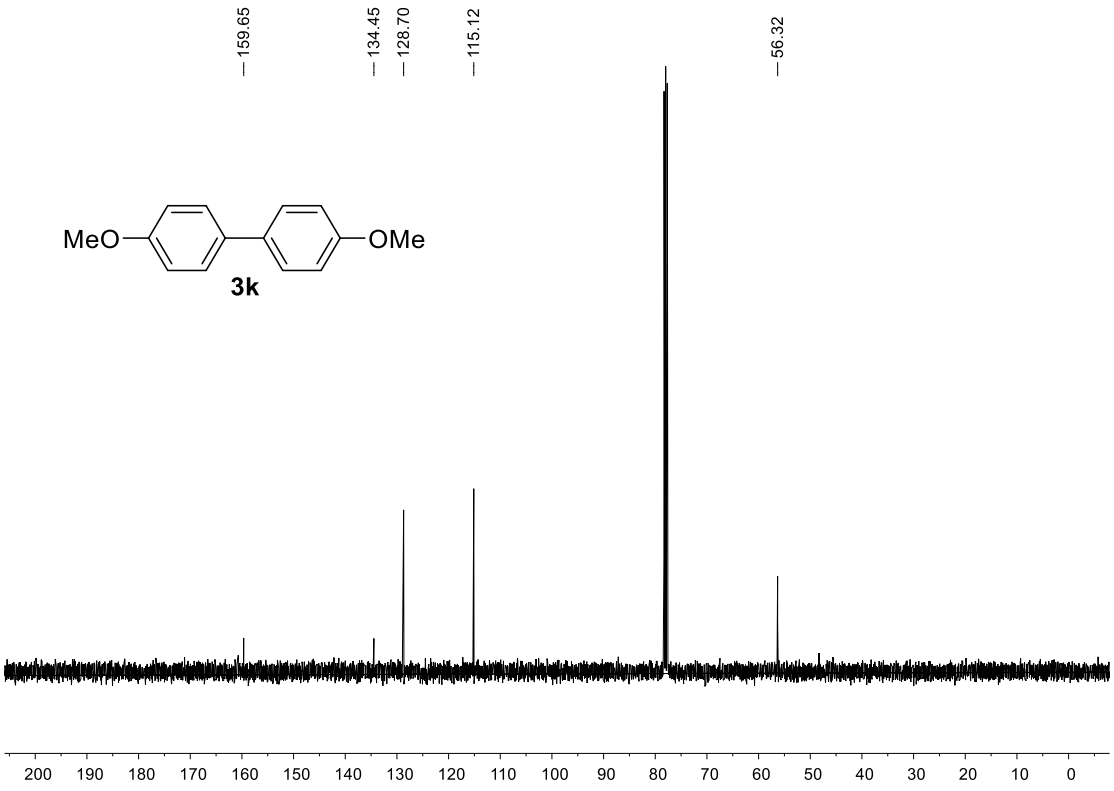
159.65
134.45
128.70
115.12
56.32
MeO
OMe
3k
200
190
180
170
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140
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120
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100
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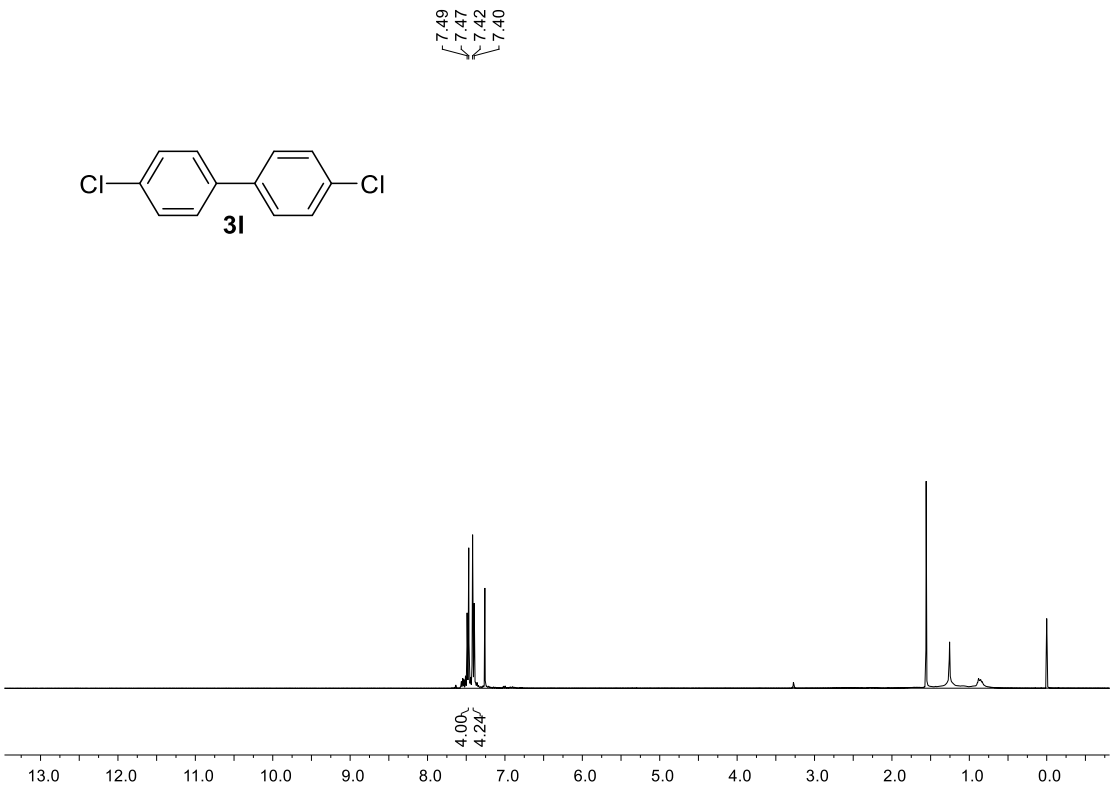
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7.40
Cl
Cl
3l
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4.24
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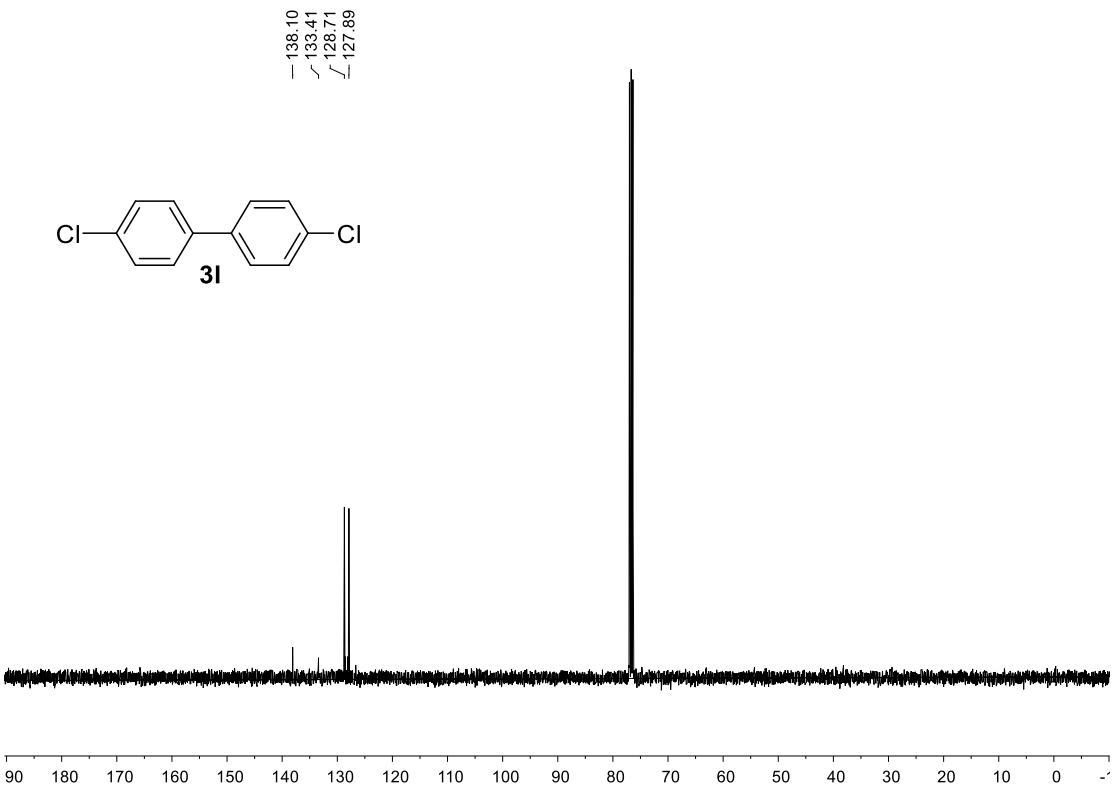
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133.41
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127.89
Cl
Cl
3l
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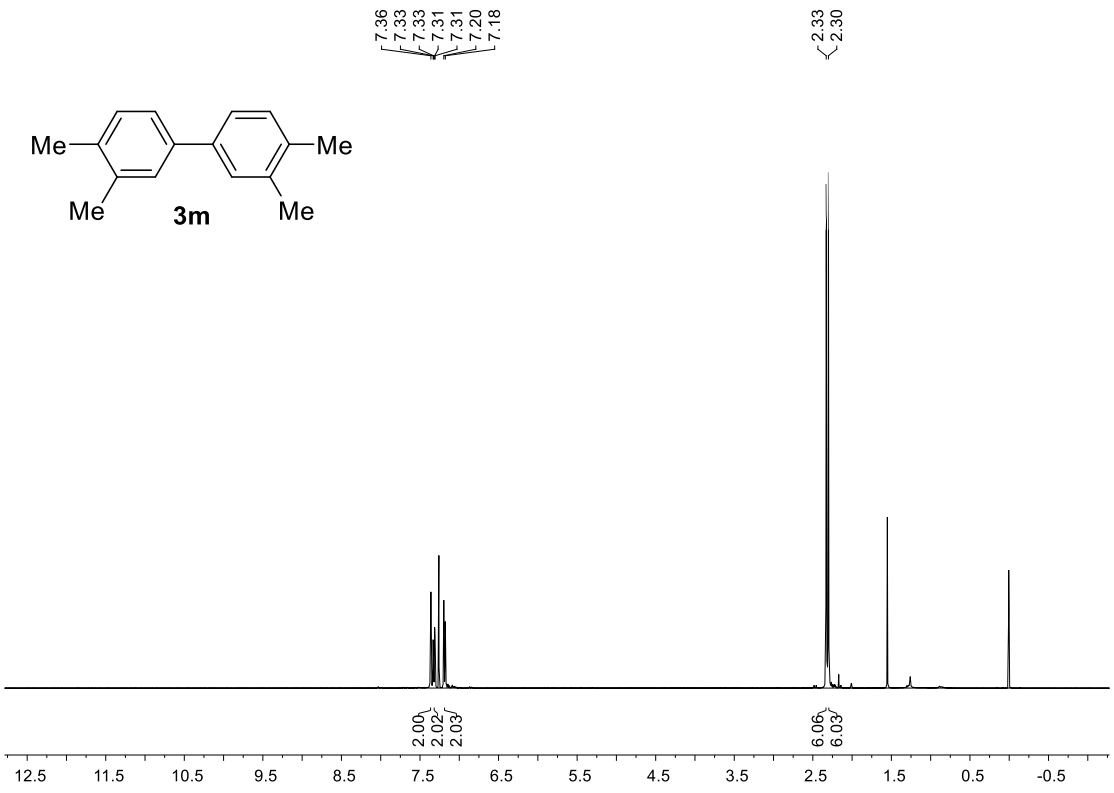
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7.20
7.18
2.33
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Me
Me
Me
Me
3m
2.00
2.02
2.03
6.06
6.03
12.5
11.5
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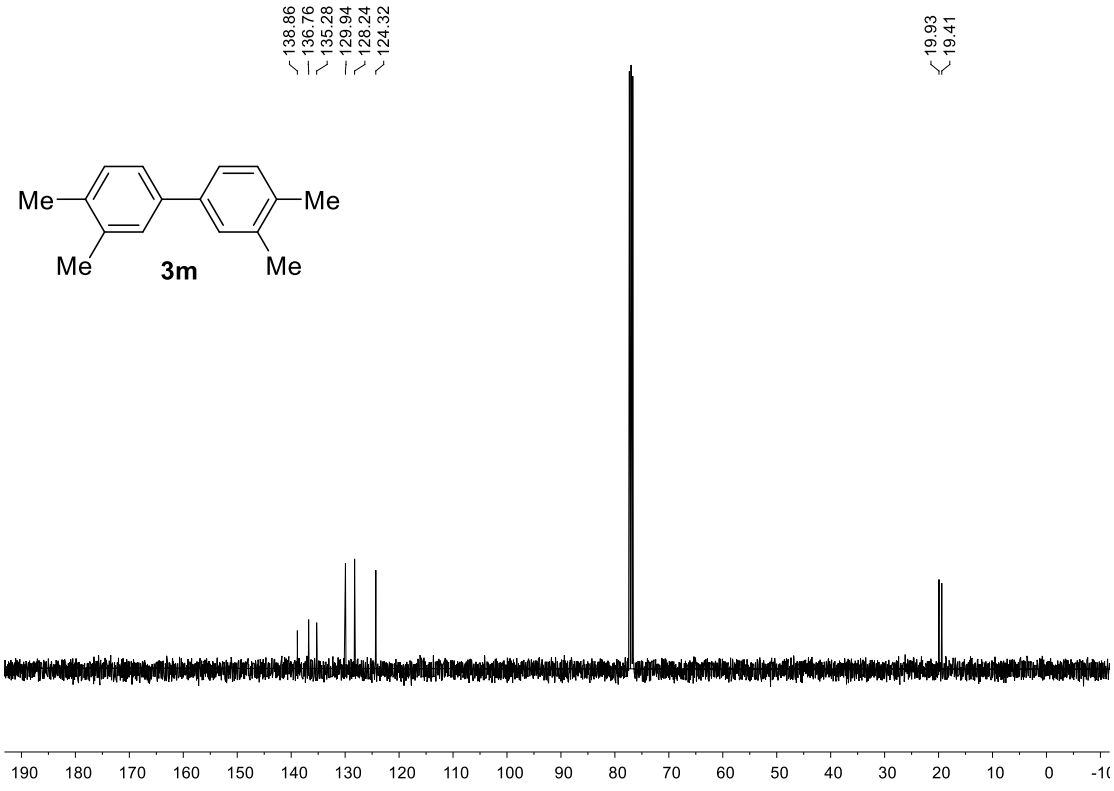
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124.32
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19.41
Me
Me
Me
Me
3m
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30
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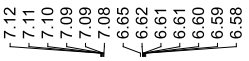
10
0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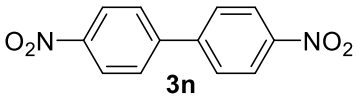
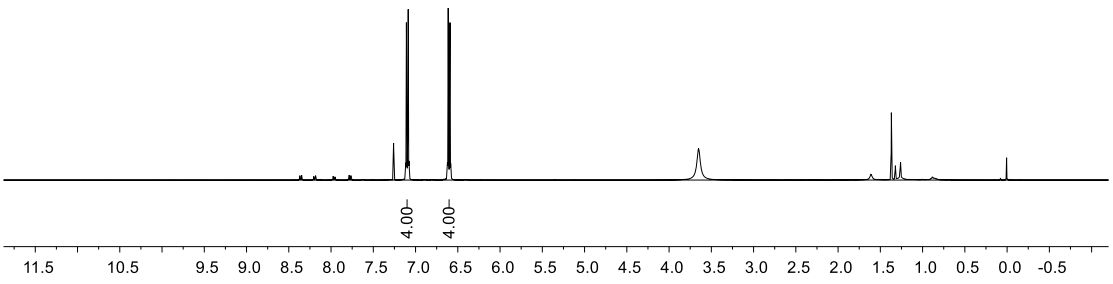
6.60
6.59
6.58


O2N
NO2

3n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4.00
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8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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4.0
3.5
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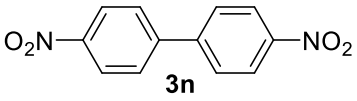
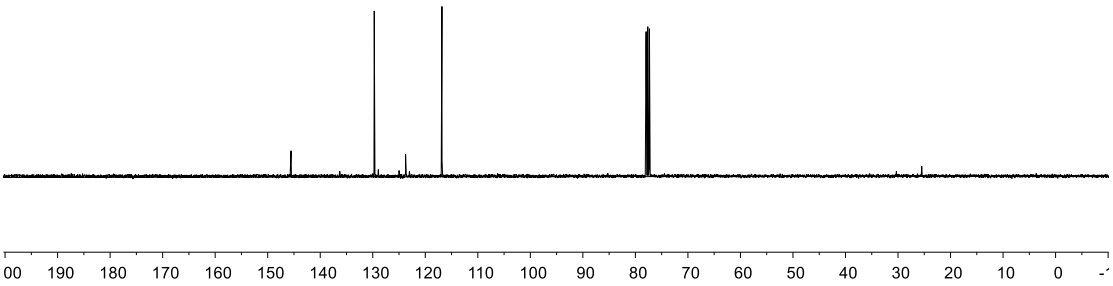
1.5
1.0
0.5
0.0
-0.5


145.55
129.72
123.75
116.83


O2N
NO2

3n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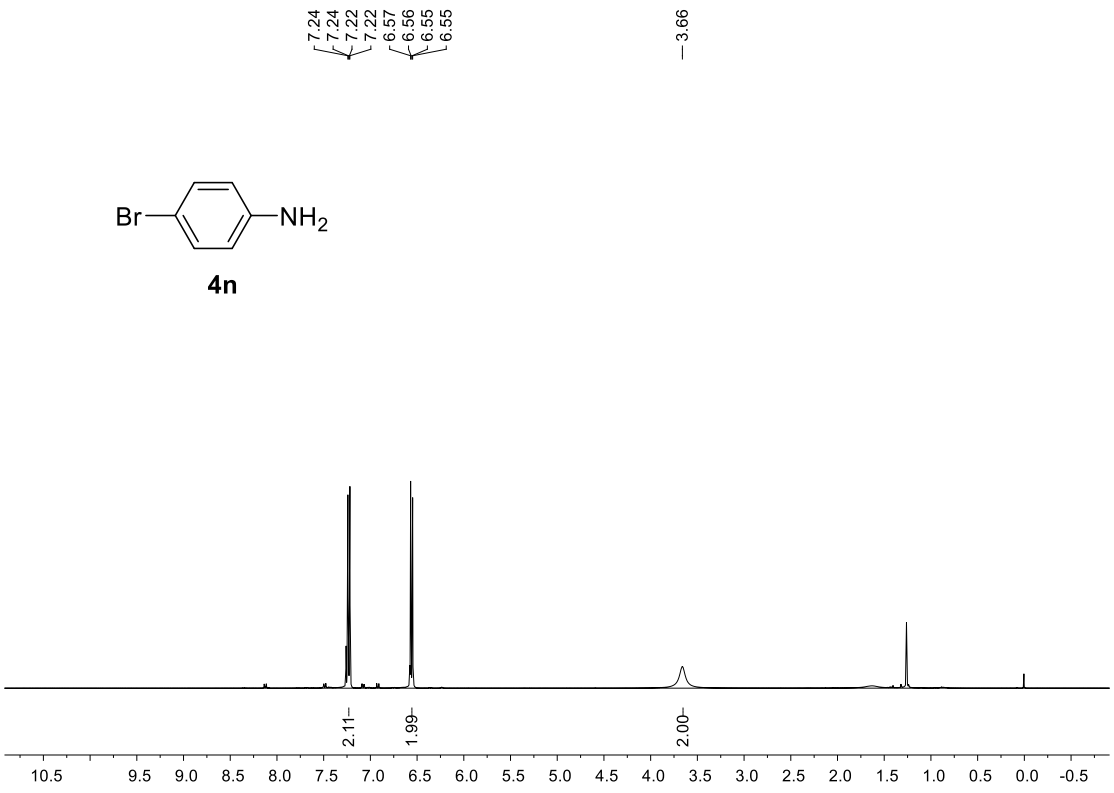
10
0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6.55
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Br
NH2
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1.99
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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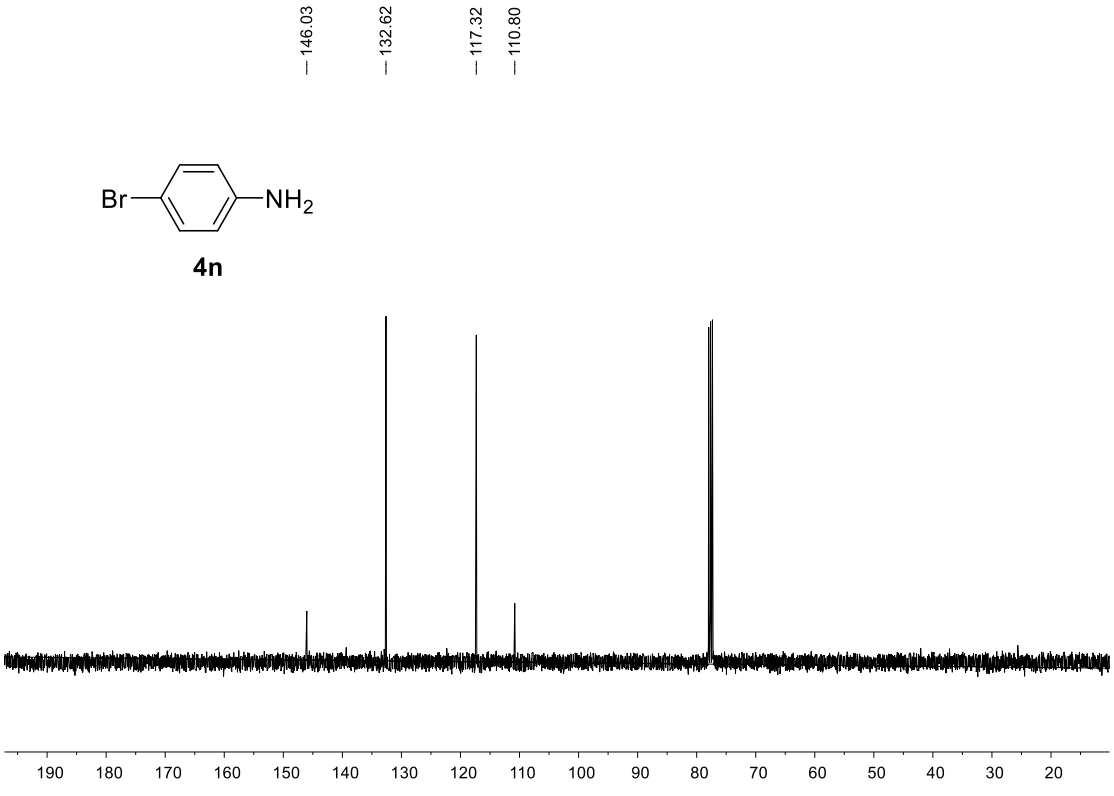
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Br
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4n
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140
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70
60
50
40
30
20