Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

The transition-metal-catalyst-free oxidative homocoupling of organomanganese reagents prepared by the insertion of magnesium into organic halides in the presence of $MnCl_2$•2LiCl

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CONTENT :

TP1: Typical procedure for the preparation of aromatic manganese reagents (2a-q).

LiCl (2.2 equiv.) was placed in an argon-flushed flask and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). After cooled to room temperature, this flask was charged with manganese chloride (1.1 equiv.), and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). The flask was evacuated and backfilled with argon three times and THF (5-10 mL) was added. The mixture was stirred until the clear solution was formed. Magnesium turning (2.5 equiv.) was placed in an argon-flushed flask and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). The flask was evacuated and backfilled with argon three times. The solution of $MnCl_2$•LiCl in THF was transferred with syringe at 10 °C. The solution of organic halide (1 equiv.) was then added at the appropriate temperature (-5 °C to 15 °C) and the reaction mixture was stirred until the conversion of the organic halide reached > 95% (monitored by GC-analysis of hydrolyzed reaction aliquots). Yields of these resulting aromatic manganese reagents were determined by iodolysis or allylation with allyl bromide in THF.

Phenylmanganese(II) chloride (2a). According to **TP1**, bromobenzene (**1a**, 471 mg, 3 mmol) reacted with magnesium turning (180 mg, 2.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3.5 h at 10 °C affording the corresponding aryl manganese reagent **2a** in 63% yield.

(3-Methoxyphenyl)manganese(II) chloride (2b). According to **TP1**, 1-bromo-3-methoxybenzene (**1b**, 561 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3 h at 10 °C affording the corresponding aryl manganese reagent **2b** in 52% yield.

(4-Methoxyphenyl)manganese(II) chloride (2c). According to **TP1**, 1-iodo-4-methoxybenzene (**1c**, 351 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (10 mL) within 1.5 h at 10 °C affording the corresponding aryl manganese reagent **2c** in 42% yield.

(4-(Trifluoromethoxy)phenyl)manganese(II) chloride (2d). According to **TP1**, 1-bromo-4-(trifluoromethoxy)benzene (**1d**, 723 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3.5 h at 10 °C affording the corresponding aryl manganese reagent **2d** in 53% yield.

(5-Fluoro-2-methoxyphenyl)manganese(II) chloride (2e). According to **TP1**, 2-bromo-4-fluoro-1-methoxybenzene (**1e**, 615 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3 h at 10 °C affording the corresponding aryl manganese reagent **2e** in 66% yield.

(2-Fluorophenyl)manganese(II) chloride (2f). According to **TP1**, 1-fluoro-2-iodobenzene (**1f**, 666 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3 h at 10 °C affording the corresponding aryl manganese reagent **2f** in 63% yield.

(2,4-Difluorophenyl)manganese(II) chloride (2g). According to **TP1**, 1-bromo-2,4-difluorobenzene (**1g**, 579 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3.5 h at 10 °C affording the corresponding aryl manganese reagent **2g** in 64% yield.

(2-(Trifluoromethyl)phenyl)manganese(II) chloride (2h). According to **TP1**, 1-bromo-2-(trifluoromethyl)benzene (**1h**, 675 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3.5 h at 10 °C affording the corresponding aryl manganese reagent **2h** in 87% yield (Yield of the aromatic manganese reagents **2h** was determined by allylation with allyl bromide in THF).

(3,5-Bis(trifluoromethyl)phenyl)manganese(II) chloride (2i). According to **TP1**, 1-bromo-3,5-bis(trifluoromethyl)benzene (**1i**, 879 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3.5 h at 10 °C affording the corresponding aryl manganese reagent **2i** in 40% yield (Yield of the aromatic manganese reagents **2i** was

52% when determined by allylation with allyl bromide in THF).

(2-Cyanophenyl)manganese(II) chloride (2j). According to **TP1**, 2-bromobenzonitrile (**1j**, 546 mg, 3 mmol) reacted with magnesium turning (180 mg, 7.5 mmol), $MnCl_2$ (415 mg, 3.3 mmol), LiCl (280 mg, 6.6 mmol) in THF (10 mL) within 3 h at 10 °C affording the corresponding aryl manganese reagent **2j** in 54% yield.

Thiophen-3-ylmanganese(II) chloride (2k). According to **TP1**, 3-bromothiophene (**1k**, 245 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (5 mL) within 5 h at 10 °C affording the corresponding aryl manganese reagent **2k** in 30% yield.

Thiophen-2-ylmanganese(II) chloride (2l). According to **TP1**, 2-bromobenzonitrile (**1l**, 245 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (5 mL) within 5 h at 10 °C affording the corresponding aryl manganese reagent **2l** in 50% yield.

Pyridin-3-ylmanganese(II) chloride (2m). According to **TP1**, 3-chloropyridine (**1m**, 170 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (10 mL) within 15 h at 15 °C affording the corresponding aryl manganese reagent **2m** in 80% yield (Yield of the aromatic manganese reagents **2m** was determined by allylation with allyl bromide in THF).

Pyridin-2-ylmanganese(II) chloride (2n). According to **TP1**, 2-bromopyridine (**1n**, 237 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (10 mL) within 2.5 h at 10 °C affording the corresponding aryl manganese reagent **2n** in 39% yield (Yield of the aromatic manganese reagents **2n** was determined by allylation with allyl bromide in THF).

(3,4,5-Trichlorophenyl)manganese(II) chloride (2o). According to **TP1**, 5-bromo-1,2,3-trichlorobenzene (**1o**, 390 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (10 mL) within 3 h at 10 °C affording the corresponding aryl manganese reagent **2o** in 33% yield (Yield of the aromatic manganese reagents **2o** was 42% when determined by

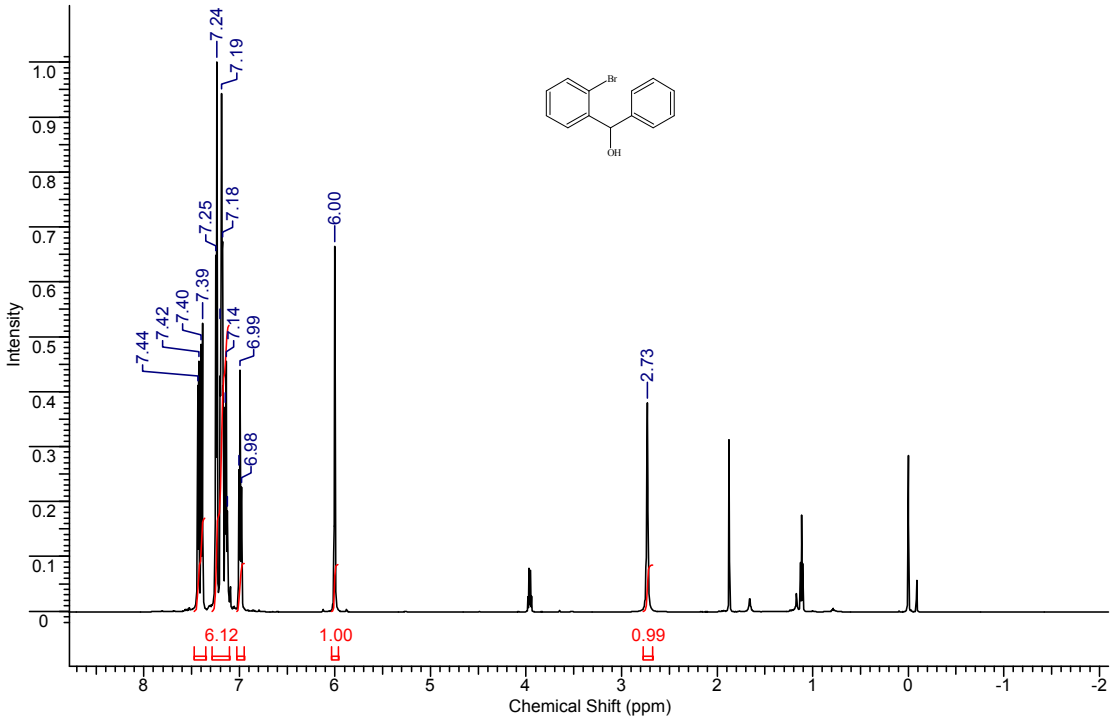
allylation with allyl bromide in THF).

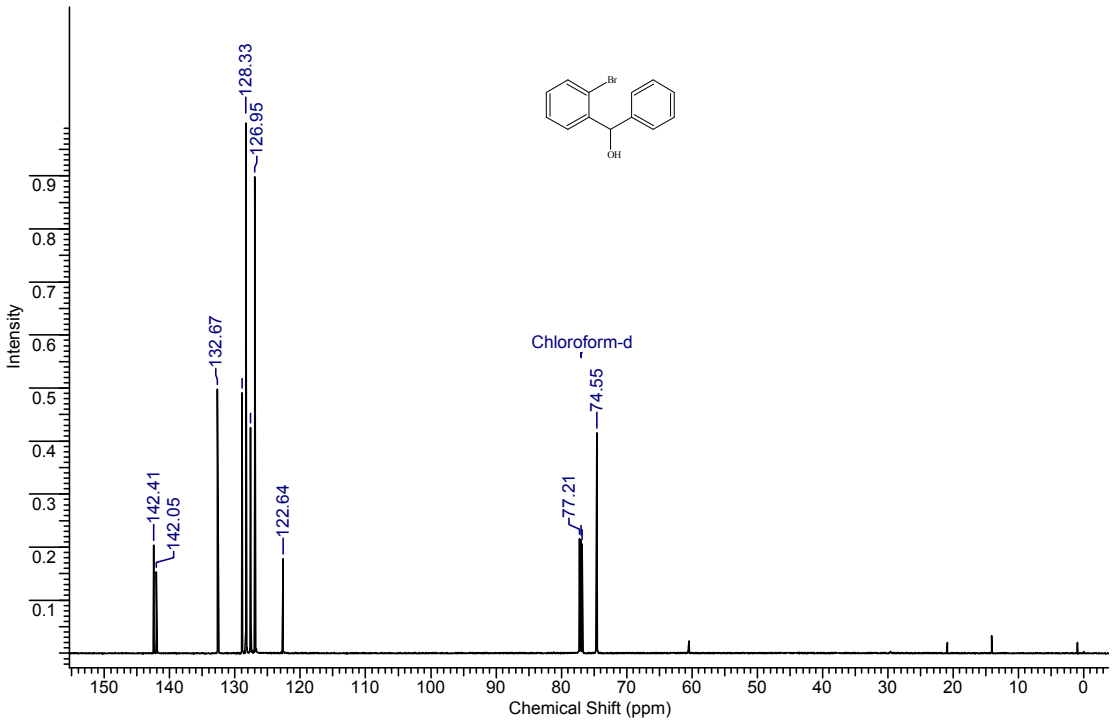
(4-Cyano-3-fluorophenyl)manganese(II) chloride (2p). According to **TP1**, 4-bromo-2-fluorobenzonitrile (**1p**, 300 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (10 mL) within 3 h at 10 °C affording the corresponding aryl manganese reagent **2p** in 26% yield (Yield of the aromatic manganese reagents **2p** was 40% when determined by allylation with allyl bromide in THF).

(4-(Ethoxycarbonyl)phenyl)manganese(II) chloride (2q). According to **TP1**, ethyl 4-iodobenzoate (**1q**, 414 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (10 mL) within 2 h at -5 °C affording the corresponding aryl manganese reagent **2q** in 44% yield (Yield of the aromatic manganese reagents **2q** was determined by allylation with allyl bromide in THF).

^{1}H NMR and ^{13}C NMR

Compound **4a**





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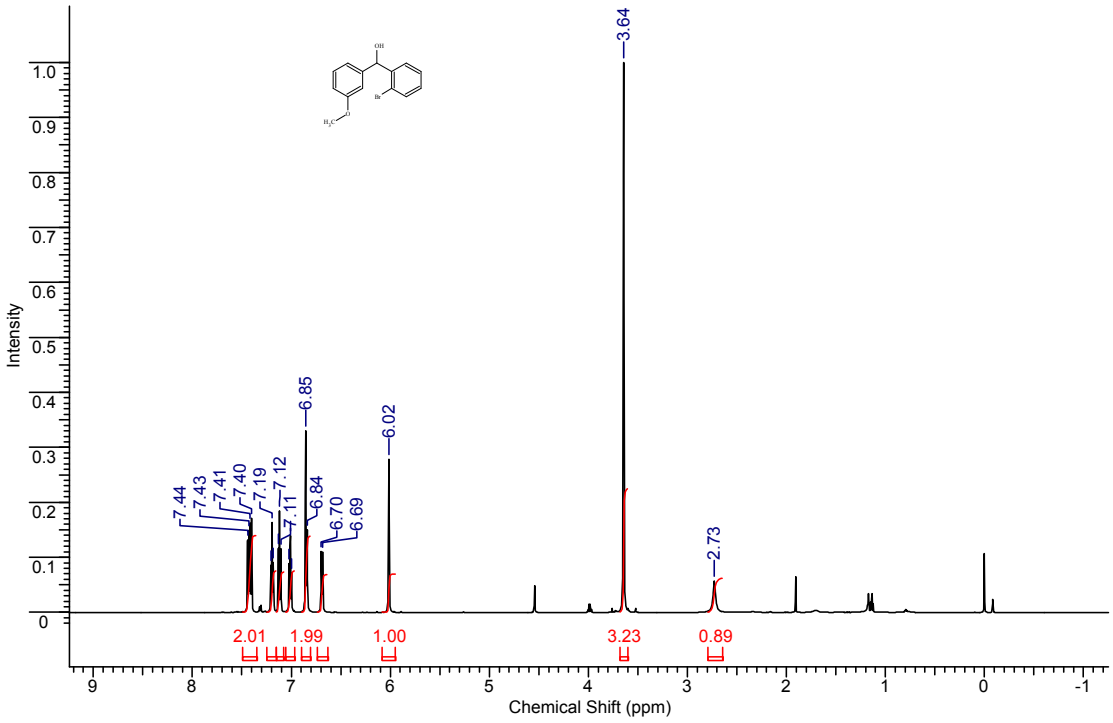
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6.85
6.02
7.44
7.43
7.41
7.40
7.19
7.12
7.11
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6.69
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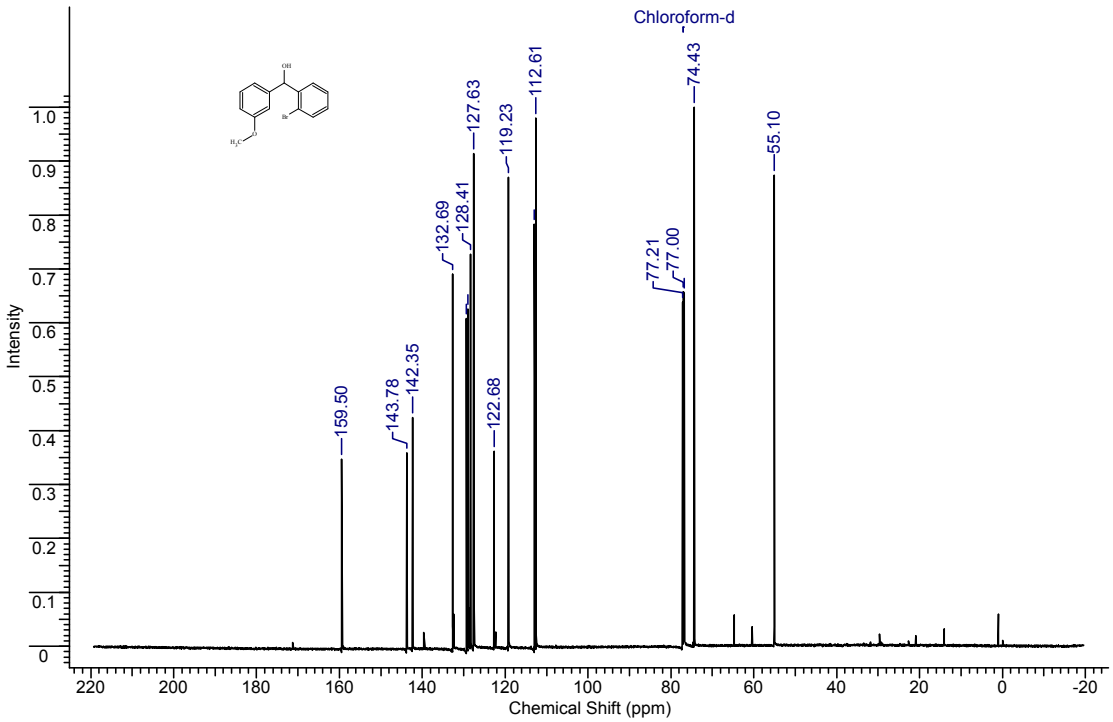
2.01
1.99
1.00
3.23
0.89
Intensity
Chemical Shift (ppm)


Chloroform-d
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127.63
119.23
112.61
132.69
128.41
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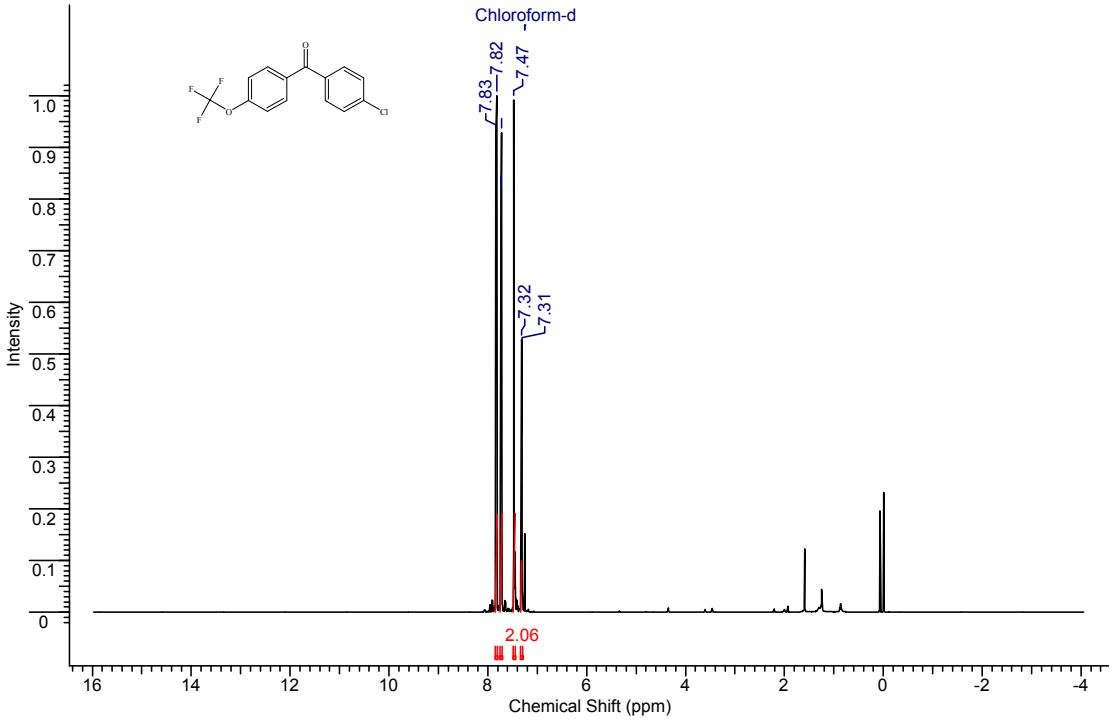
142.35
122.68
Intensity
Chemical Shift (ppm)

Compound **4d**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7.82
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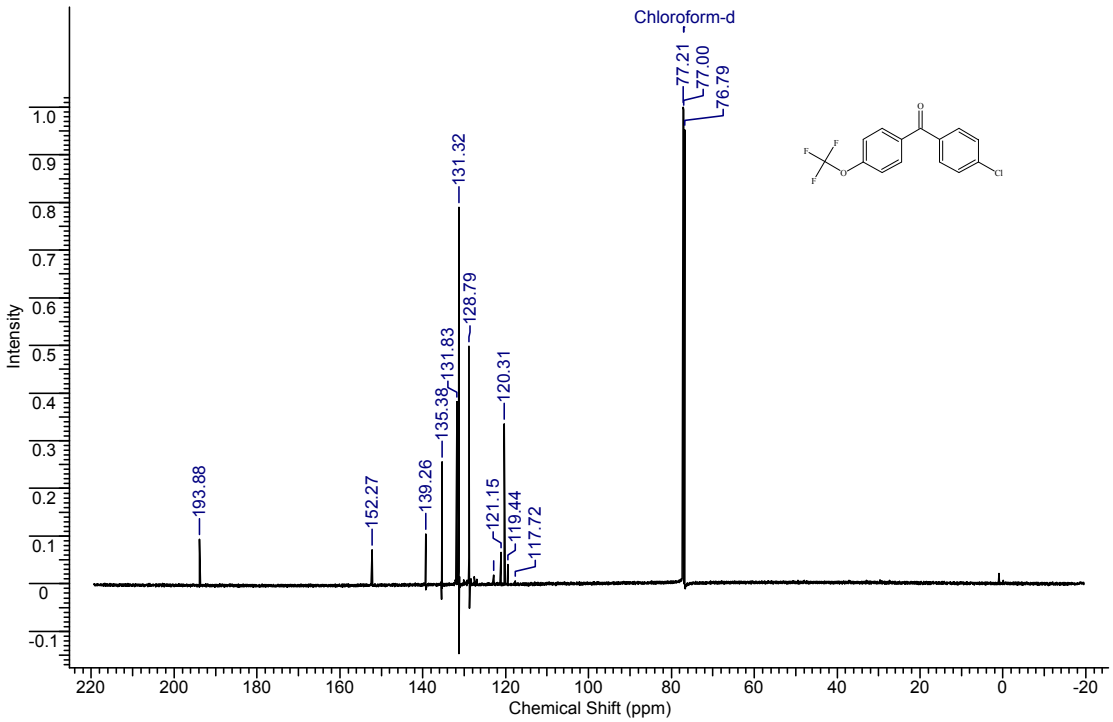
7.32
7.31
2.06
Intensity
Chemical Shift (ppm)


Chloroform-d
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77.00
76.79
131.32
128.79
131.83
135.38
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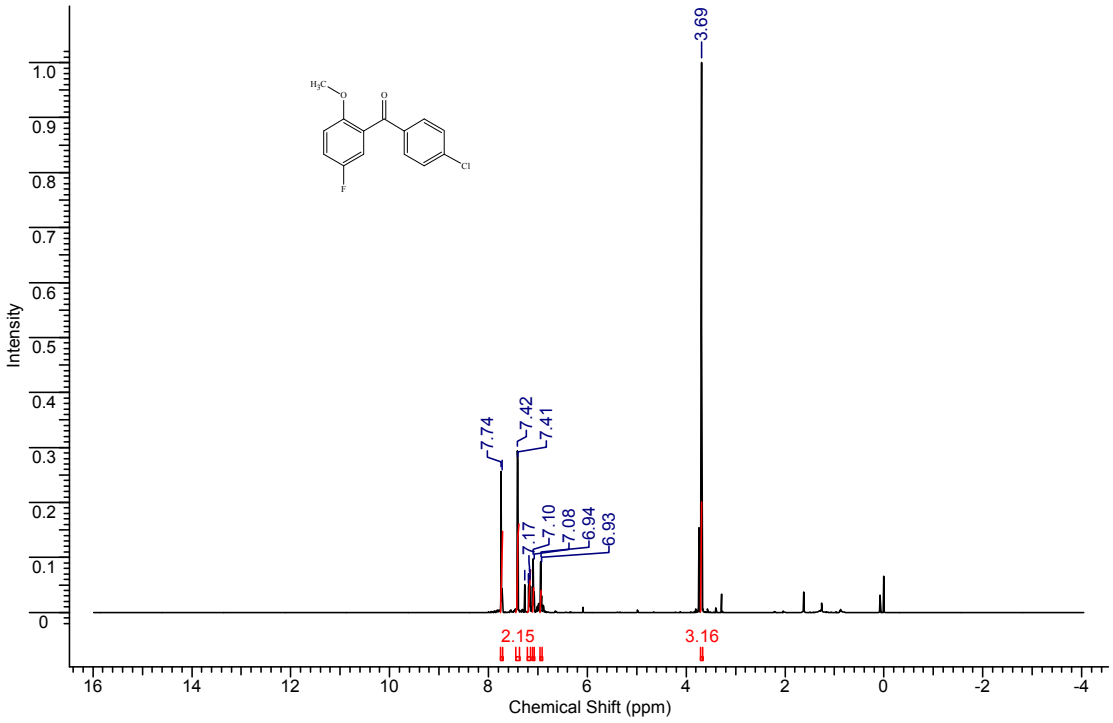
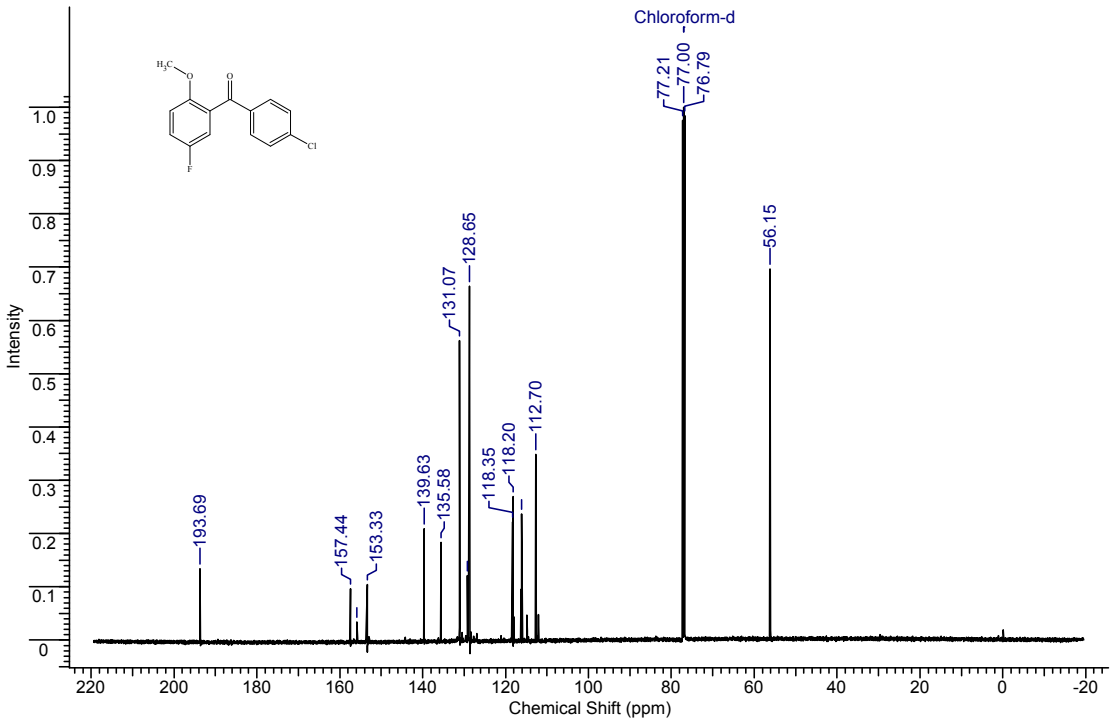
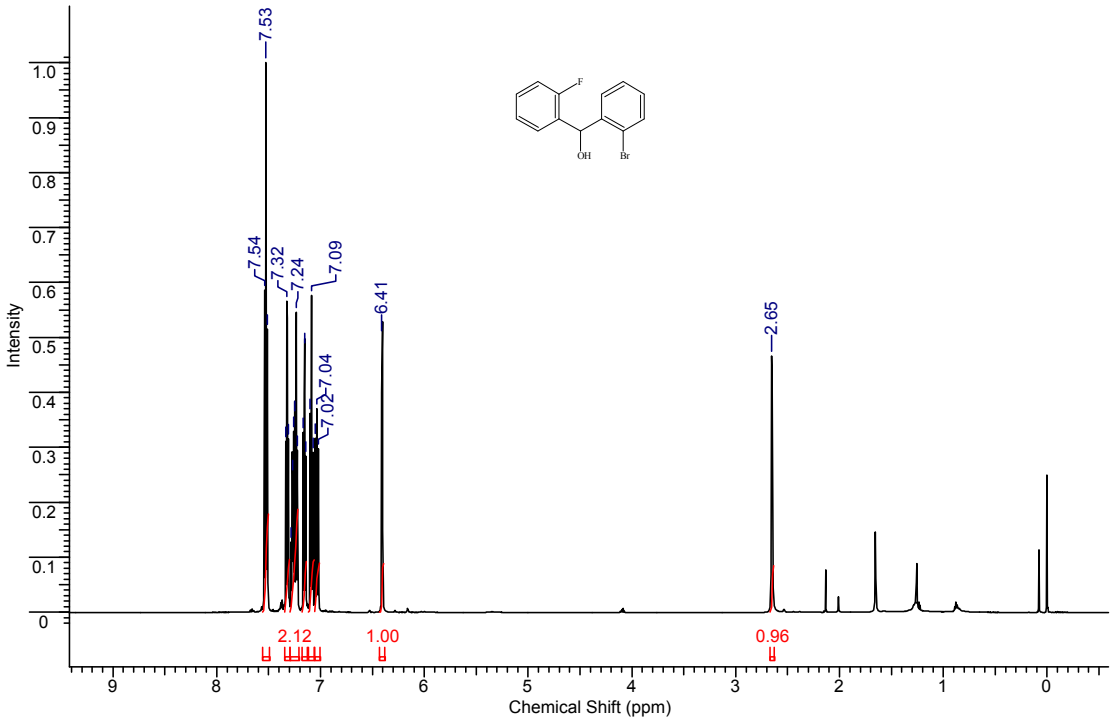
193.88
152.27
139.26
121.15
119.44
117.72
Intensity
Chemical Shift (ppm)

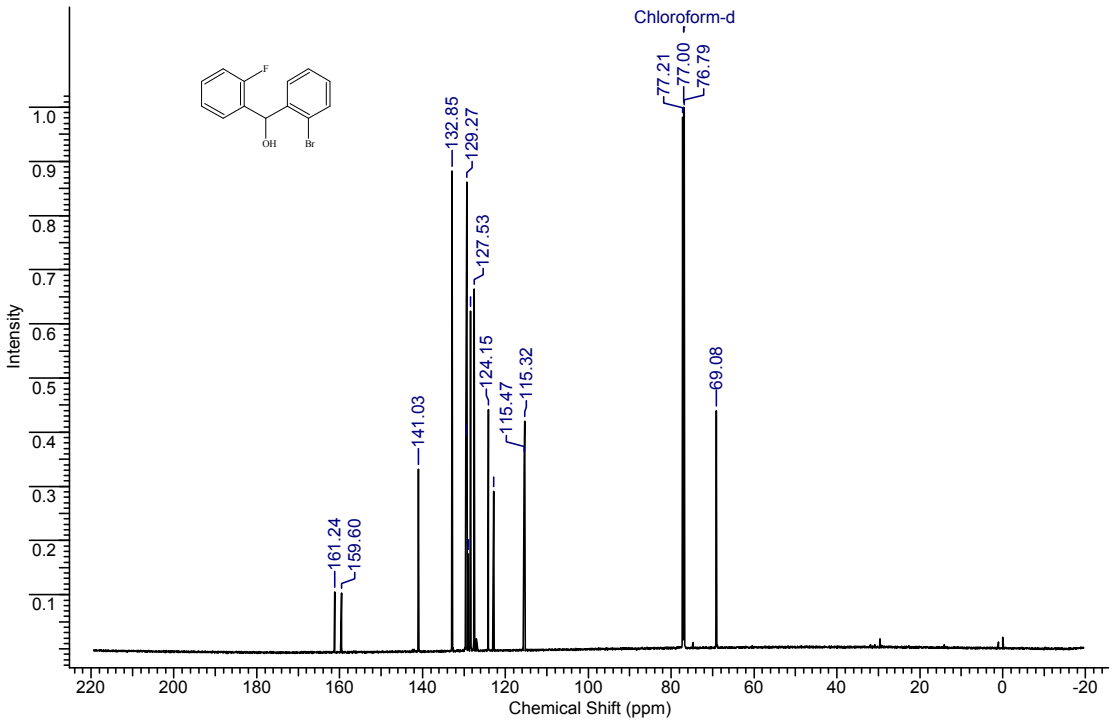
Compound **4e**


3.69
7.74
7.42
7.41
7.17
7.10
7.08
6.94
6.93
2.15
3.16
Intensity
Chemical Shift (ppm)


Chloroform-d
77.21
77.00
76.79
193.69
157.44
153.33
139.63
135.58
131.07
128.65
118.35
118.20
112.70
56.15
Intensity
Chemical Shift (ppm)

Compound **4f**


7.53
7.54
7.32
7.24
7.09
6.41
7.04
7.02
2.65
2.12
1.00
0.96
Intensity
Chemical Shift (ppm)


Chloroform-d
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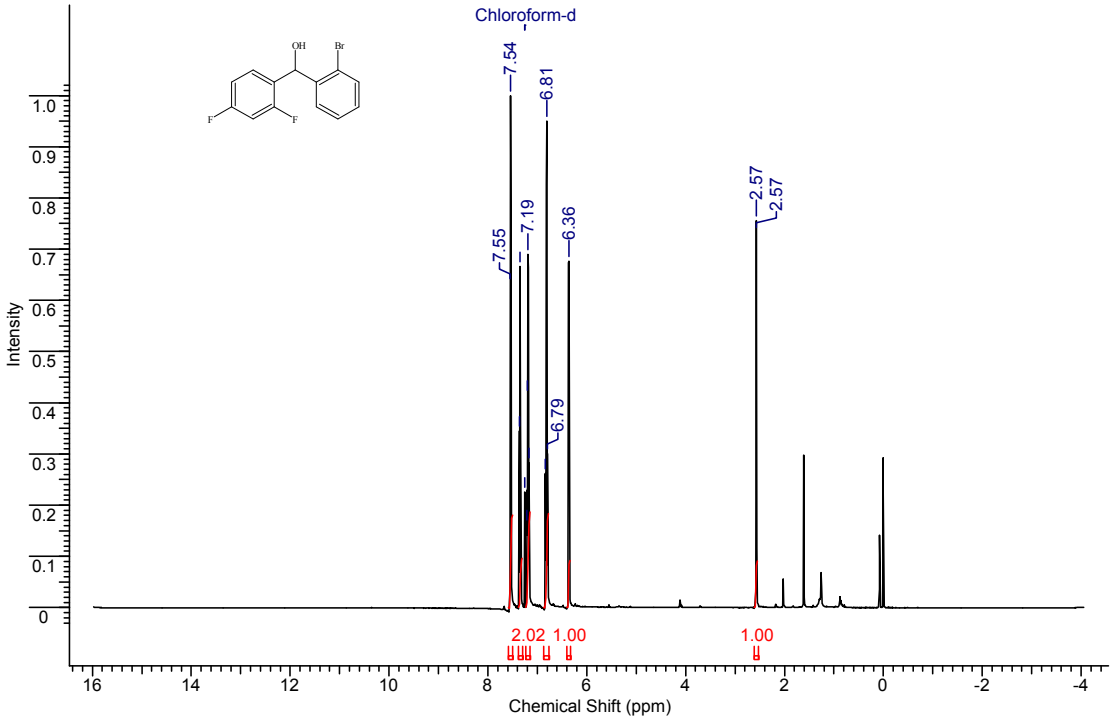
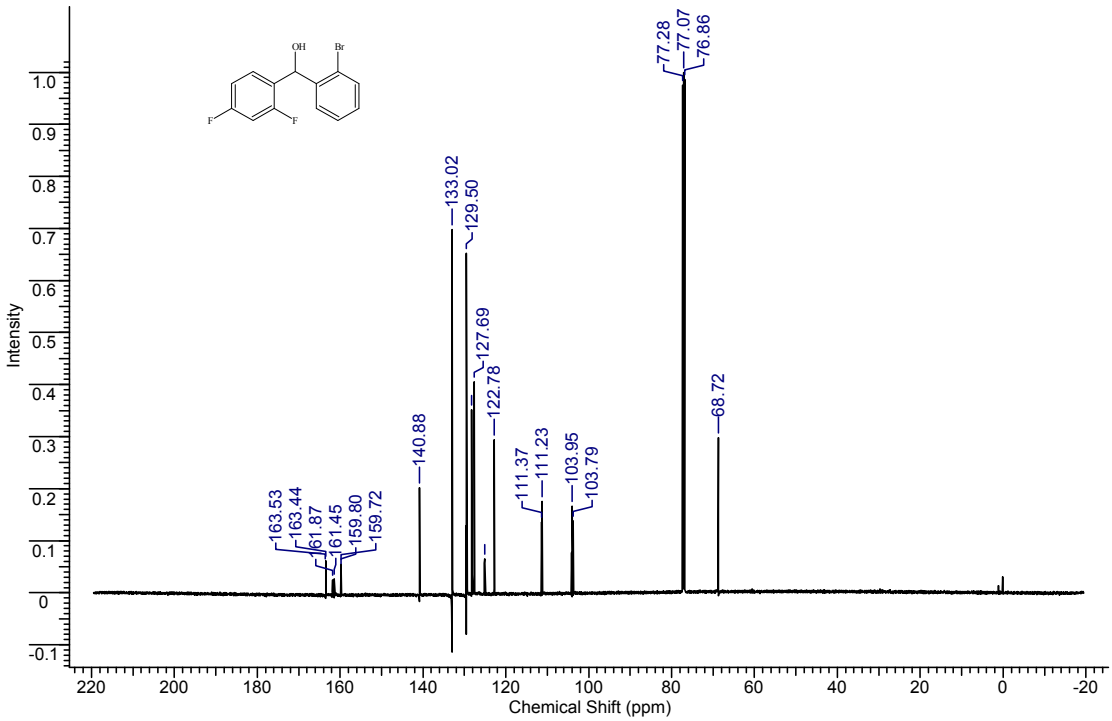
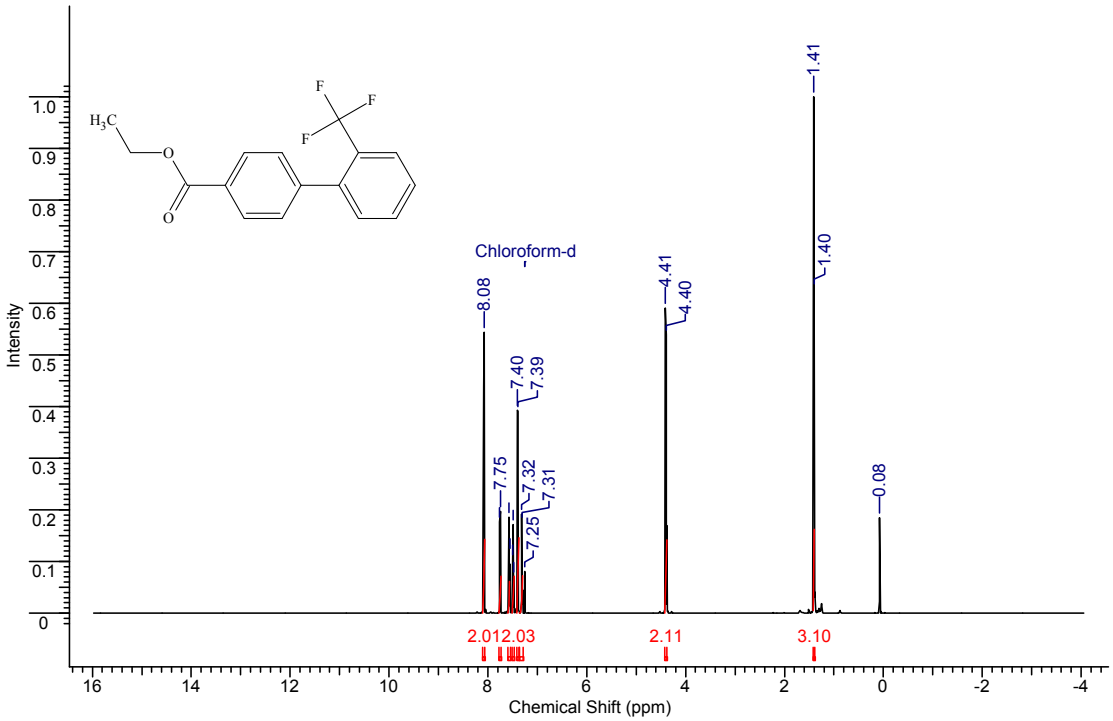
77.00
76.79
132.85
129.27
127.53
124.15
115.47
115.32
141.03
69.08
161.24
159.60
Intensity
Chemical Shift (ppm)

Compound **4g**


Chloroform-d
7.54
6.81
7.55
7.19
6.36
2.57
2.57
6.79
2.02
1.00
1.00
Intensity
Chemical Shift (ppm)


77.28
77.07
76.86
133.02
129.50
127.69
122.78
68.72
140.88
111.37
111.23
103.95
103.79
163.53
163.44
161.87
161.45
159.80
159.72
Intensity
Chemical Shift (ppm)

Compound **4h**


Chloroform-d
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7.75
7.40
7.39
7.32
7.31
7.25
4.41
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1.41
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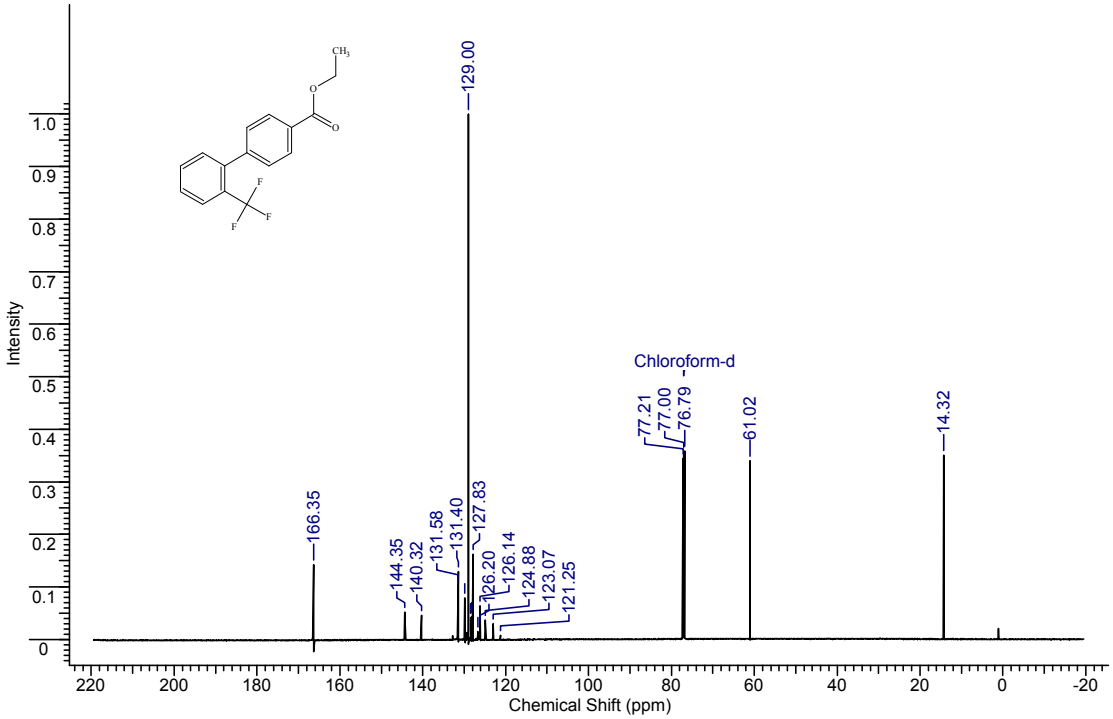
0.08
2.01
2.03
2.11
3.10
Intensity
Chemical Shift (ppm)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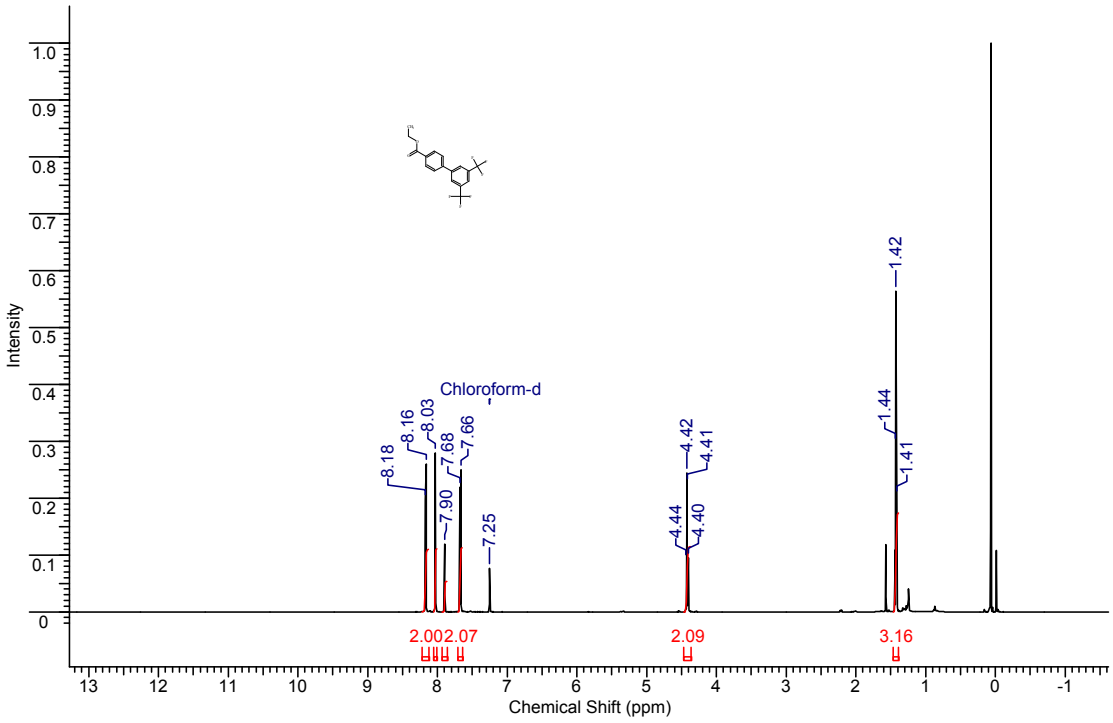
166.35
144.35
140.32
131.58
131.40
127.83
126.20
126.14
124.88
123.07
121.25
Chloroform-d
77.21
77.00
76.79
61.02
14.32
Intensity
Chemical Shift (ppm)

Compound **4i**


Intensity
Chloroform-d
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8.03
7.68
7.66
7.90
7.25
4.44
4.42
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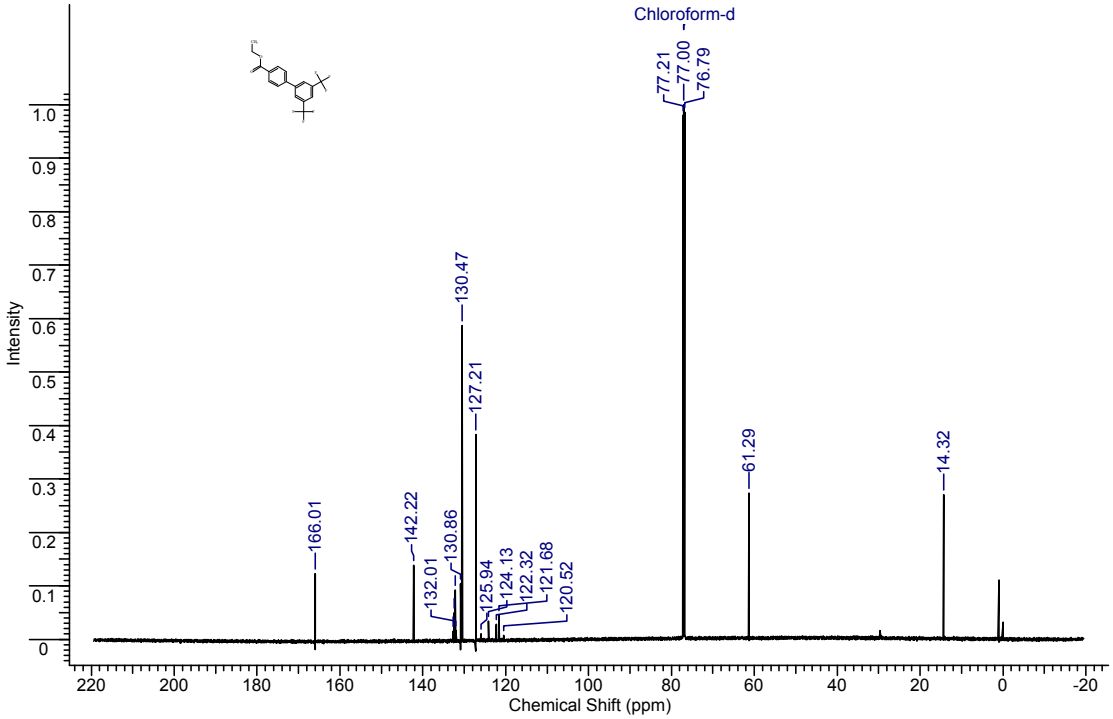
4.40
1.44
1.42
1.41
2.00
2.07
2.09
3.16
Chemical Shift (ppm)


Intensity
Chloroform-d
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166.01
142.22
132.01
130.86
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127.21
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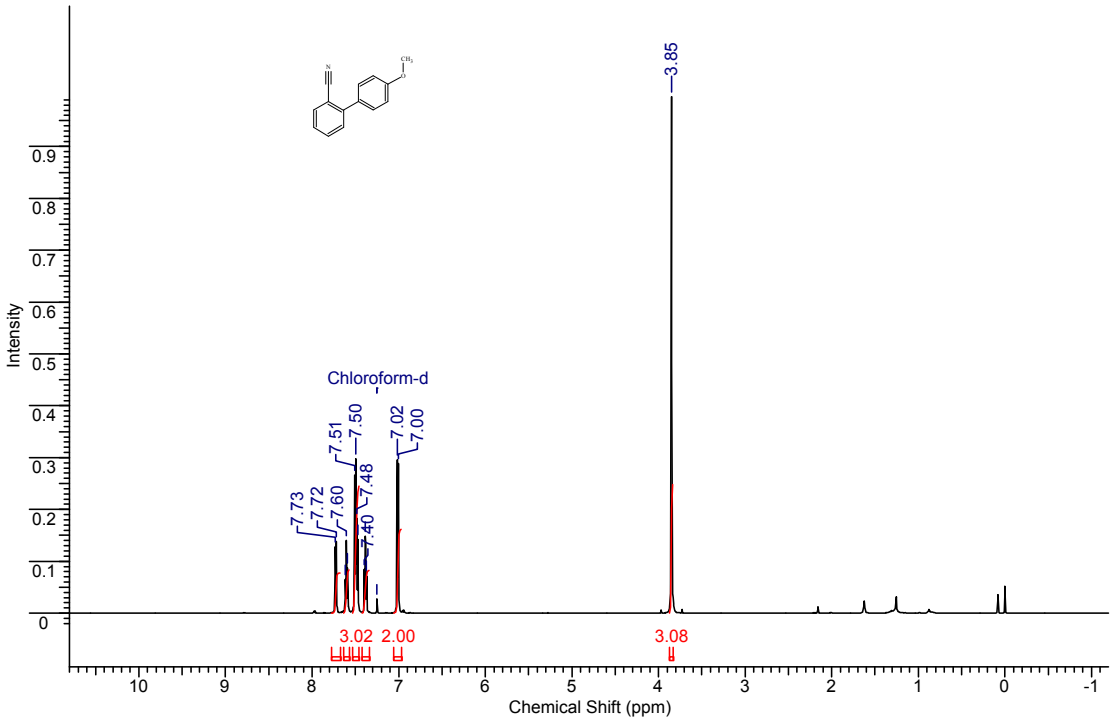
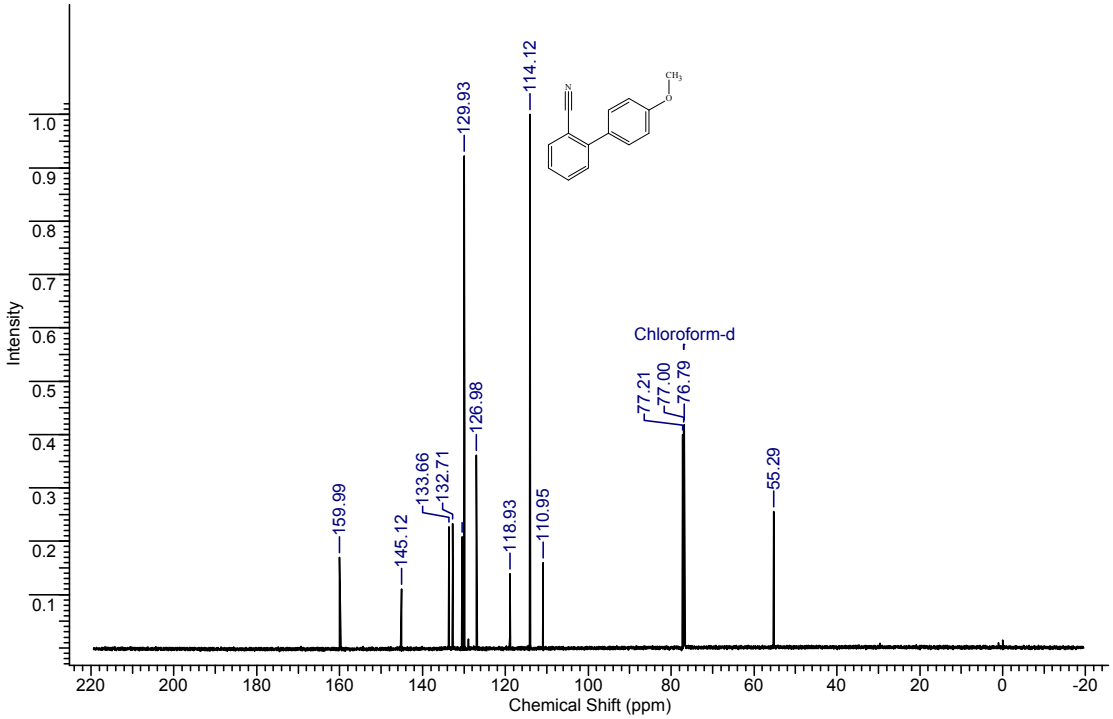
124.13
122.32
121.68
120.52
61.29
14.32
Chemical Shift (ppm)

Compound **4j**


3.85
Chloroform-d
7.73
7.72
7.60
7.51
7.50
7.48
7.40
7.02
7.00
3.02
2.00
3.08
Intensity
Chemical Shift (ppm)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126.98
159.99
145.12
133.66
132.71
118.93
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Chloroform-d
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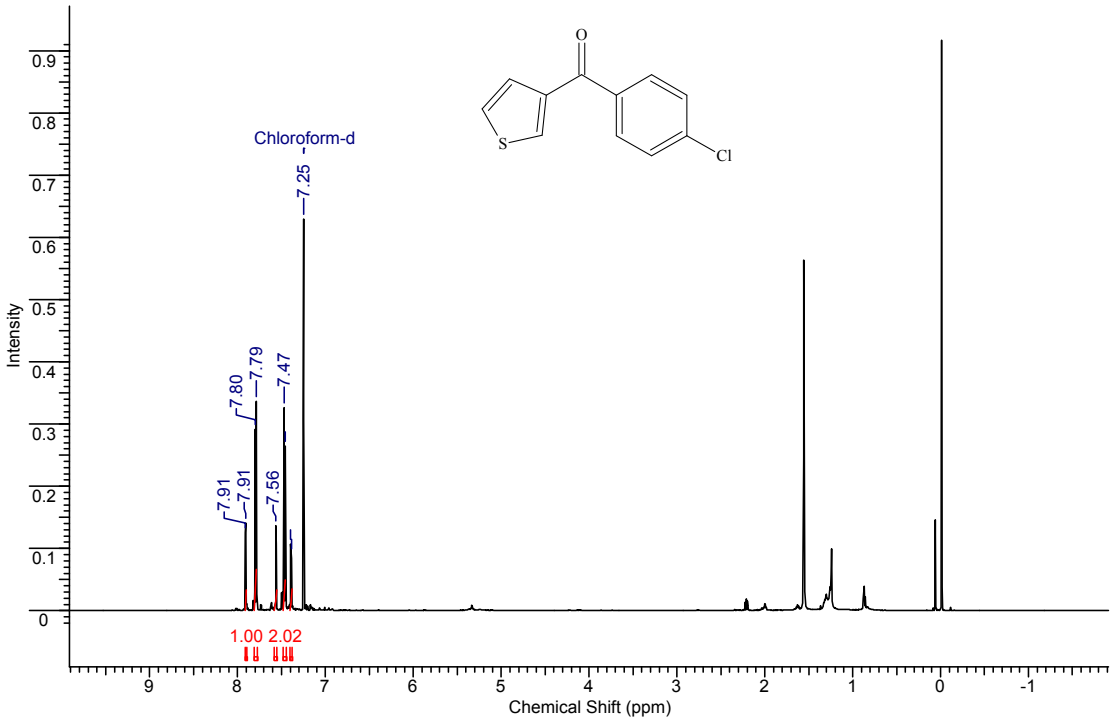
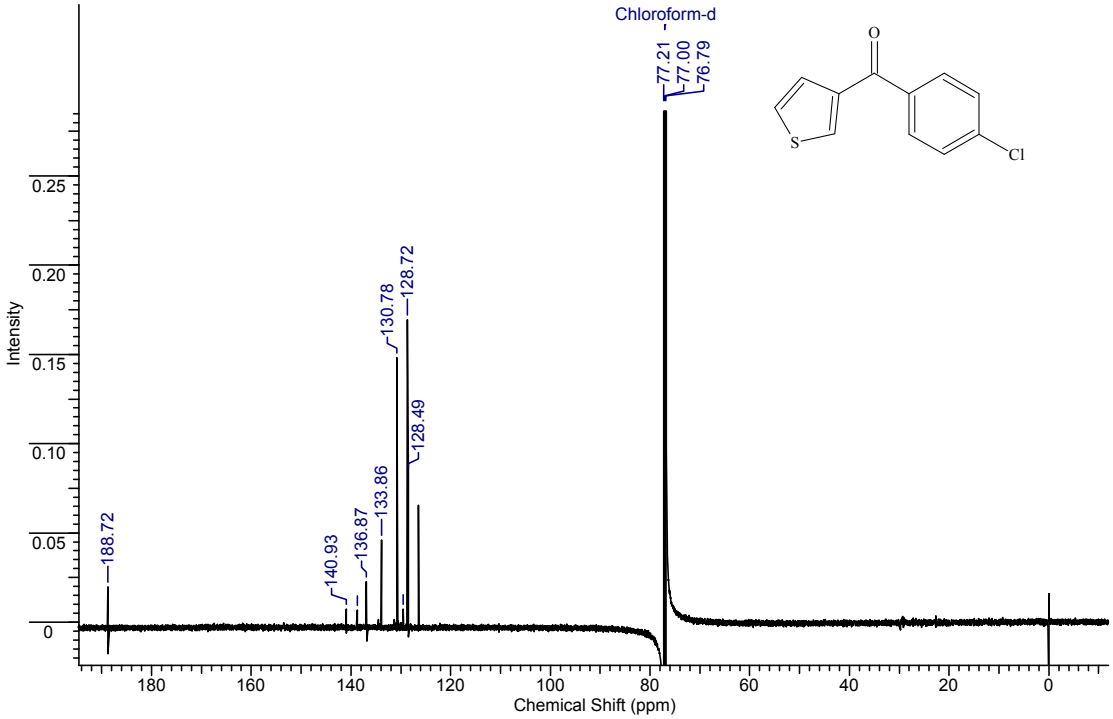
76.79
55.29
Intensity
Chemical Shift (ppm)

Compound **4k**


Chloroform-d
7.25
7.80
7.79
7.47
7.91
7.91
7.56
1.00 2.02
Intensity
Chemical Shift (ppm)
O
S
Cl


Chloroform-d
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77.00
76.79
188.72
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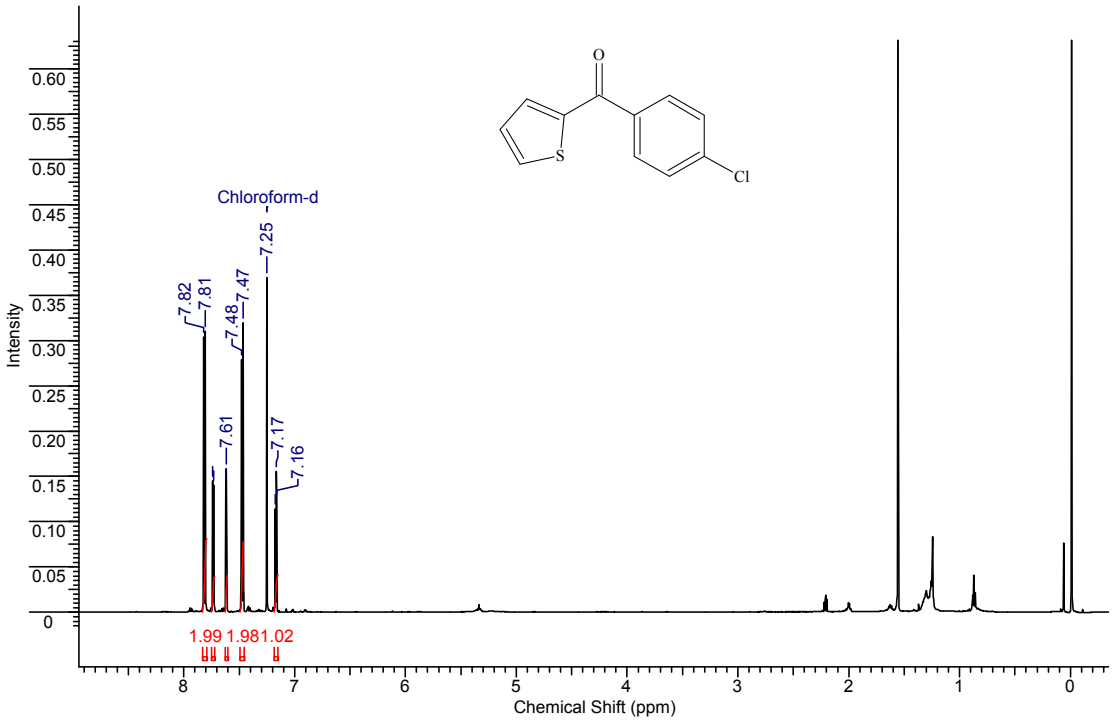
130.78
128.72
128.49
Intensity
Chemical Shift (ppm)
O
S
Cl

Compound **4l**


Chloroform-d
7.82
7.81
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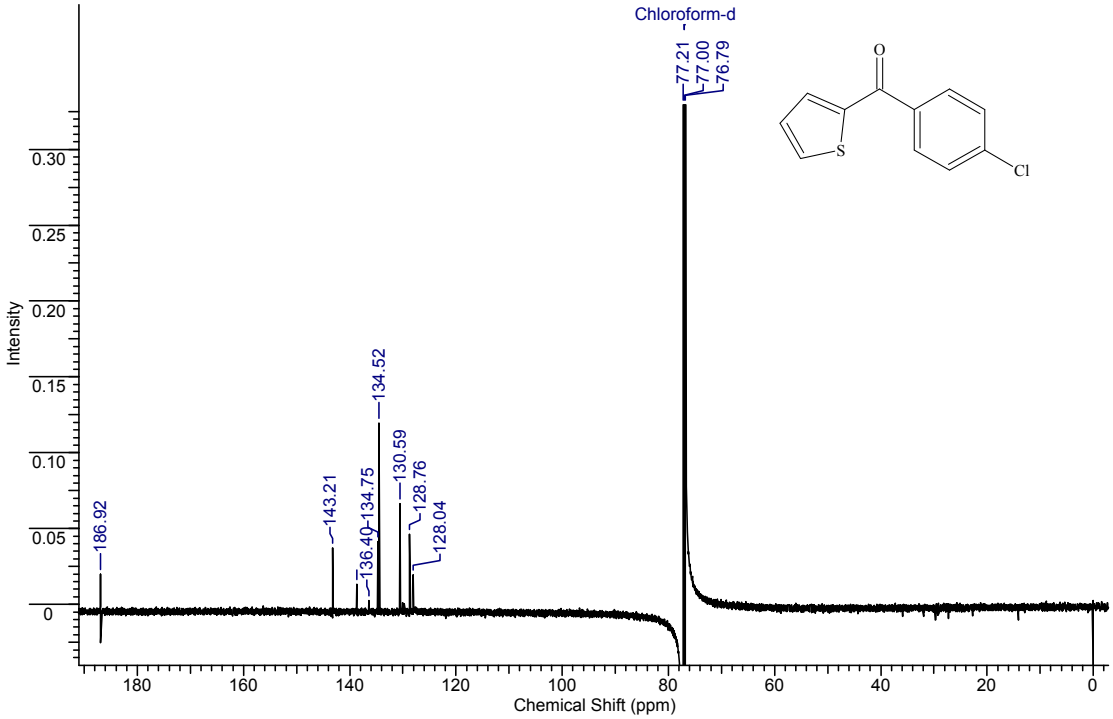
7.47
7.25
7.17
7.16
1.99 1.98 1.02
Intensity
Chemical Shift (ppm)
O
S
Cl


Chloroform-d
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76.79
186.92
143.21
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130.59
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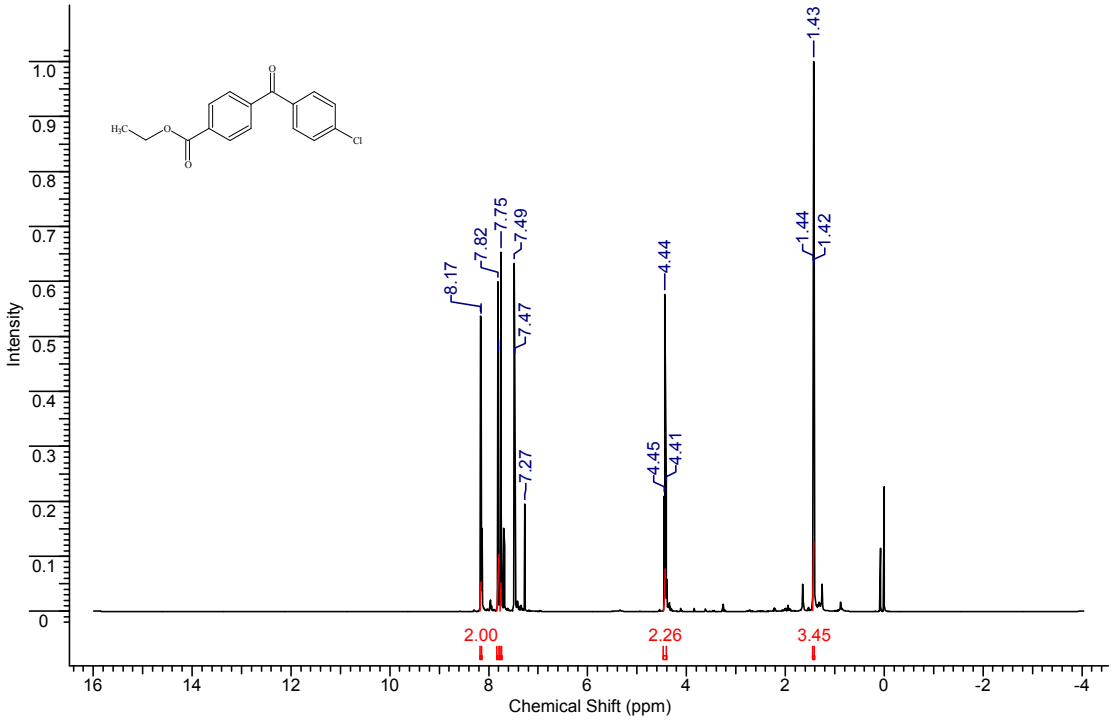
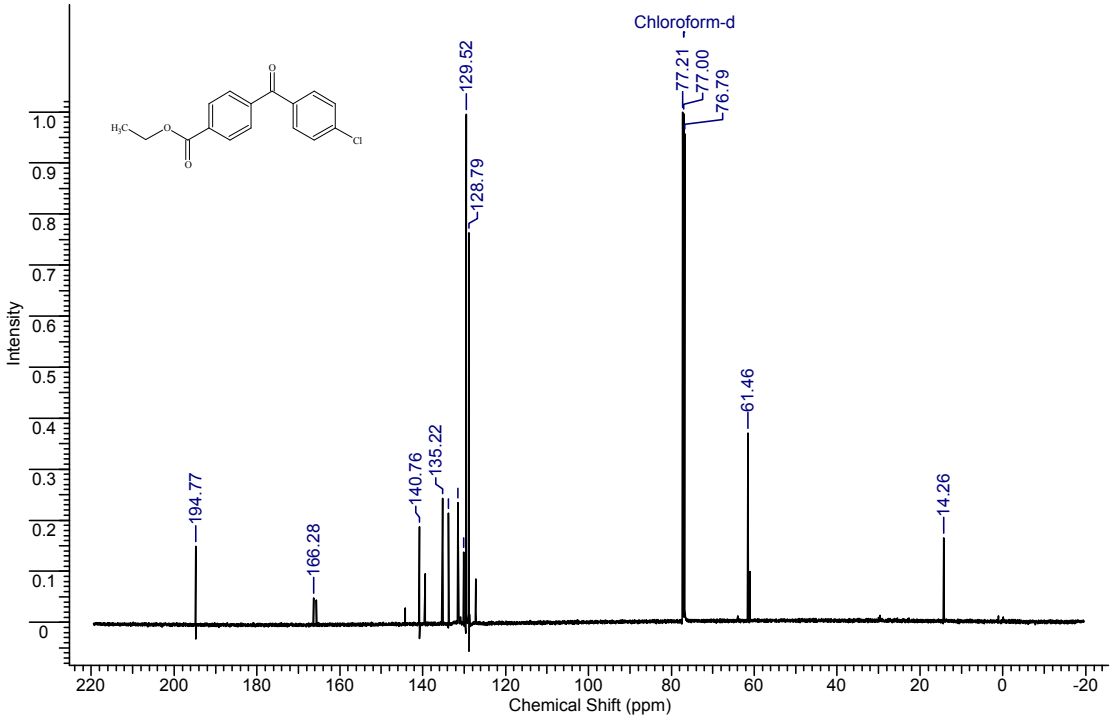
128.04
Intensity
Chemical Shift (ppm)
O
S
Cl

Compound **4q**


8.17
7.82
7.75
7.49
7.47
7.27
4.44
4.45
4.41
1.44
1.43
1.42
2.00
2.26
3.45
Intensity
Chemical Shift (ppm)


Chloroform-d
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128.79
77.21
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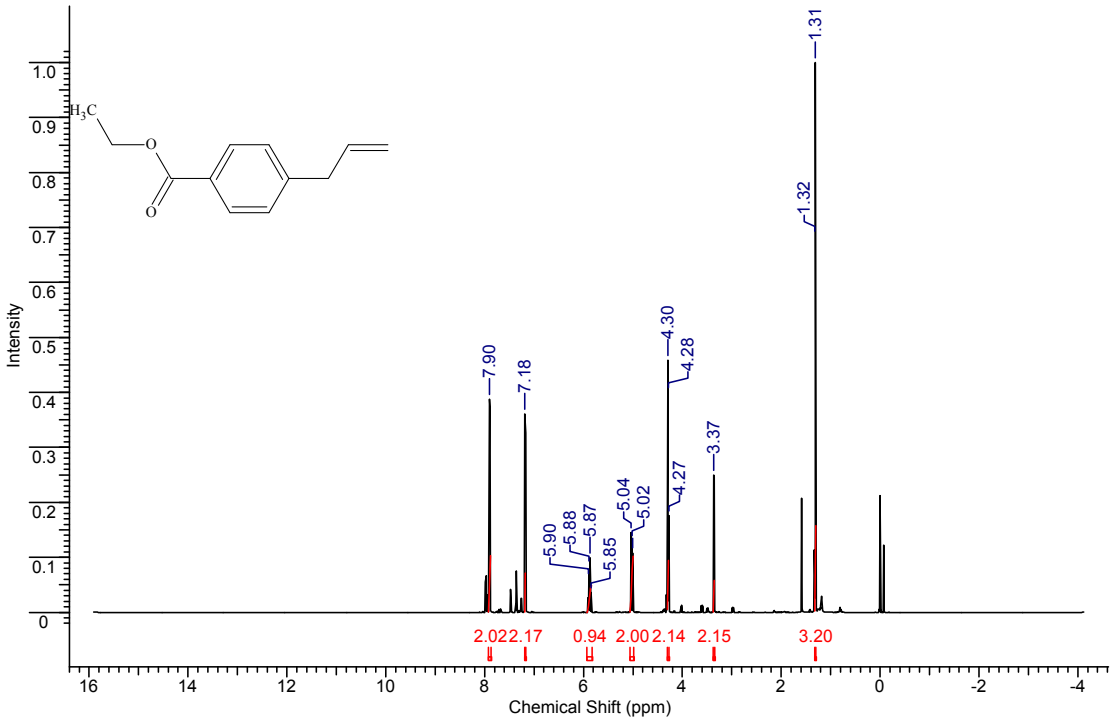
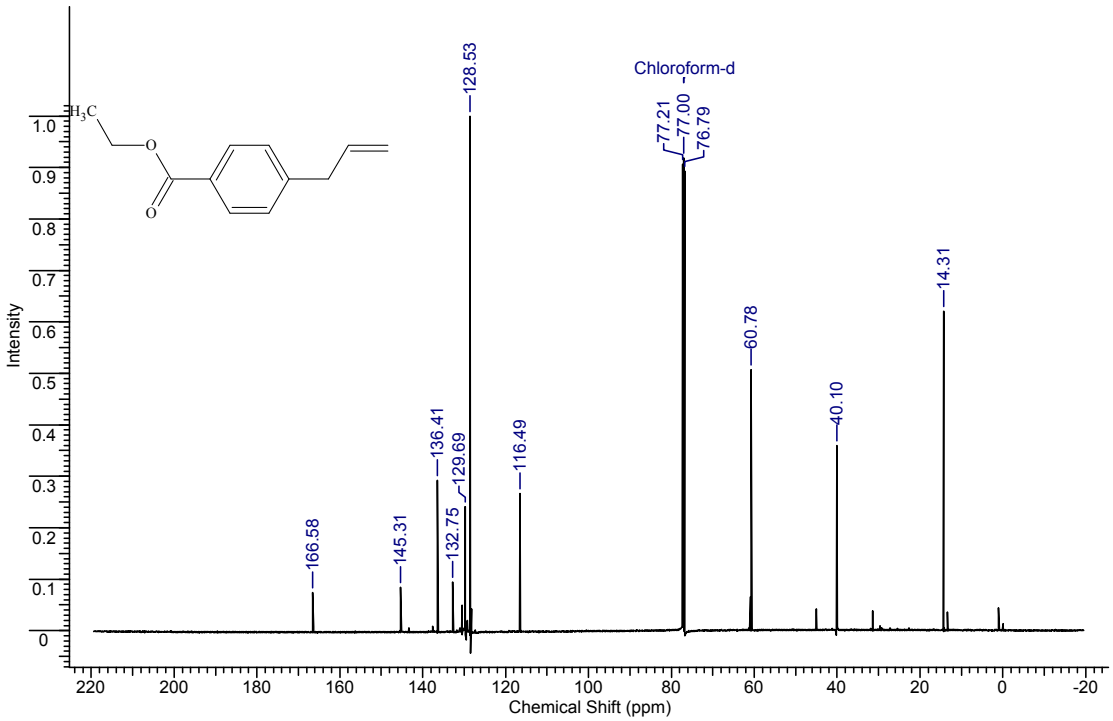
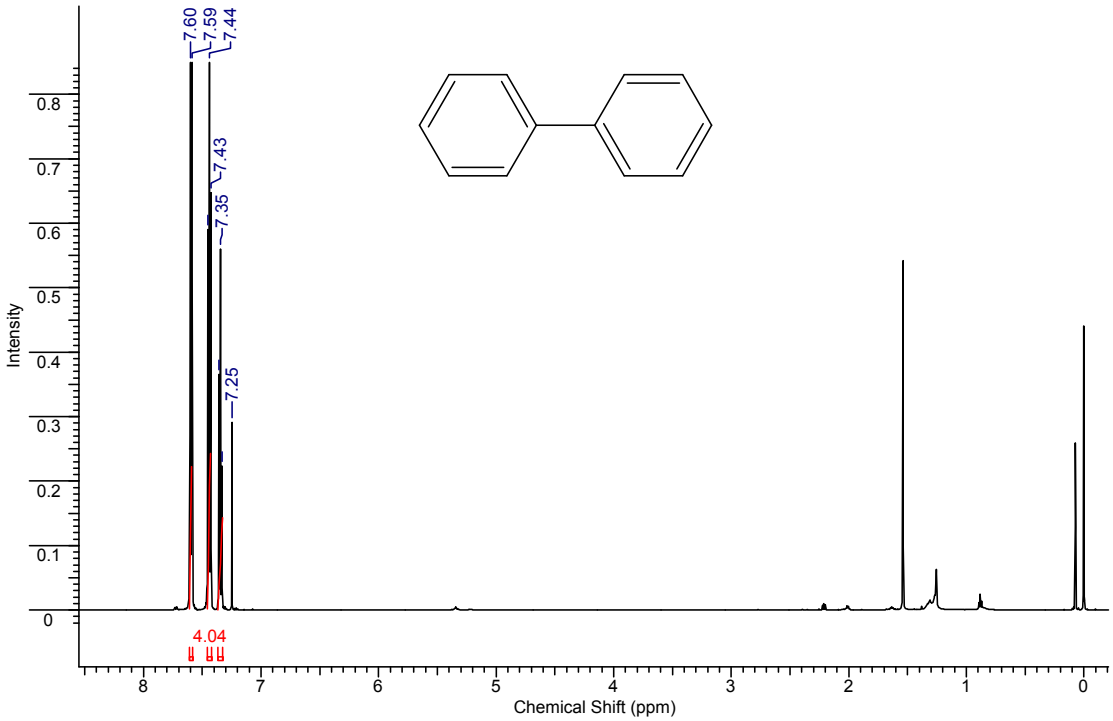
76.79
61.46
194.77
166.28
140.76
135.22
14.26
Intensity
Chemical Shift (ppm)

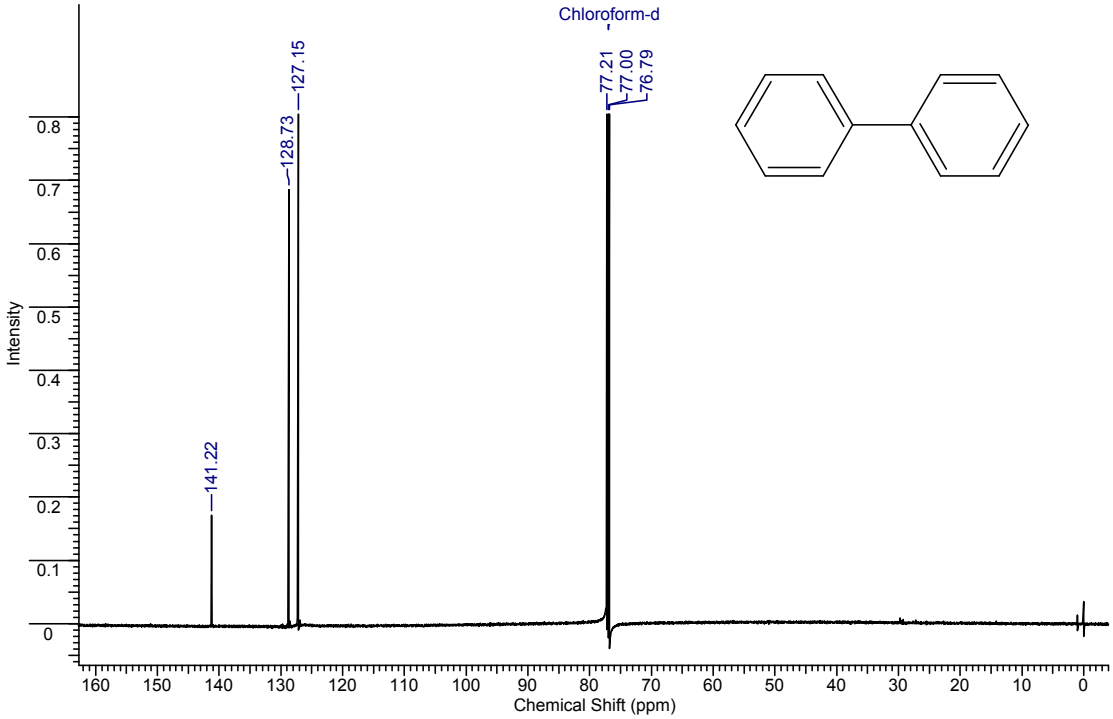
Compound **4r**


1.31
1.32
4.30
4.28
3.37
4.27
5.04
5.02
5.90
5.88
5.87
5.85
7.90
7.18
2.02 2.17 0.94 2.00 2.14 2.15 3.20
Intensity
Chemical Shift (ppm)

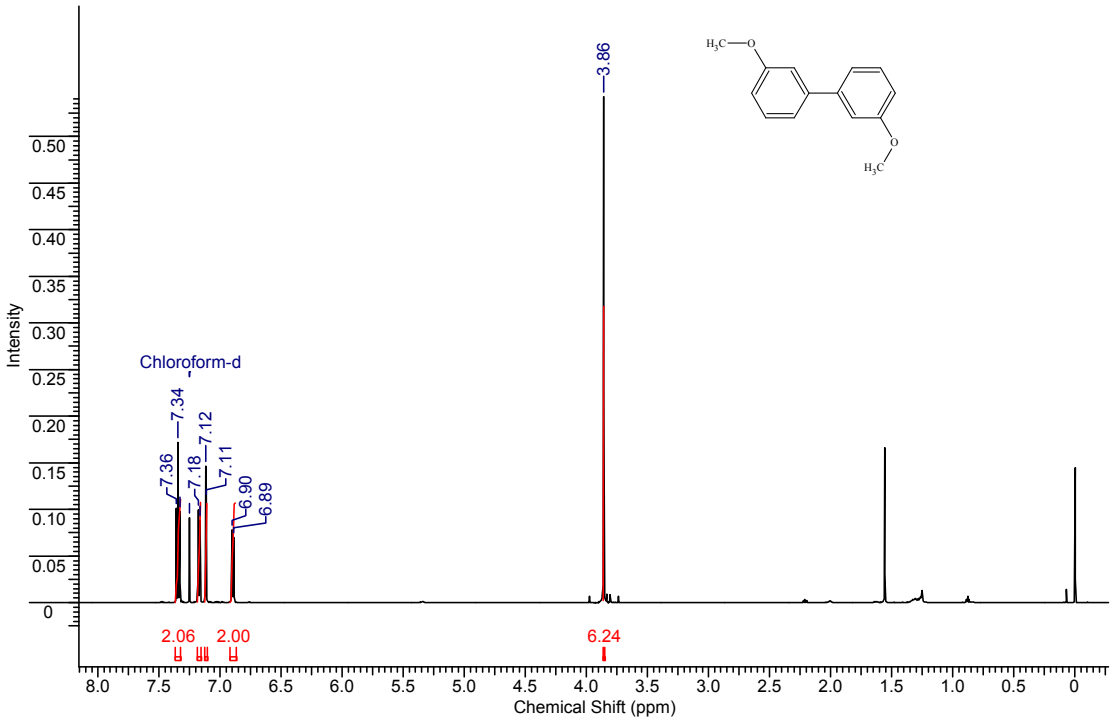

128.53
Chloroform-d
77.21
77.00
76.79
60.78
14.31
40.10
136.41
129.69
116.49
166.58
145.31
132.75
Intensity
Chemical Shift (ppm)

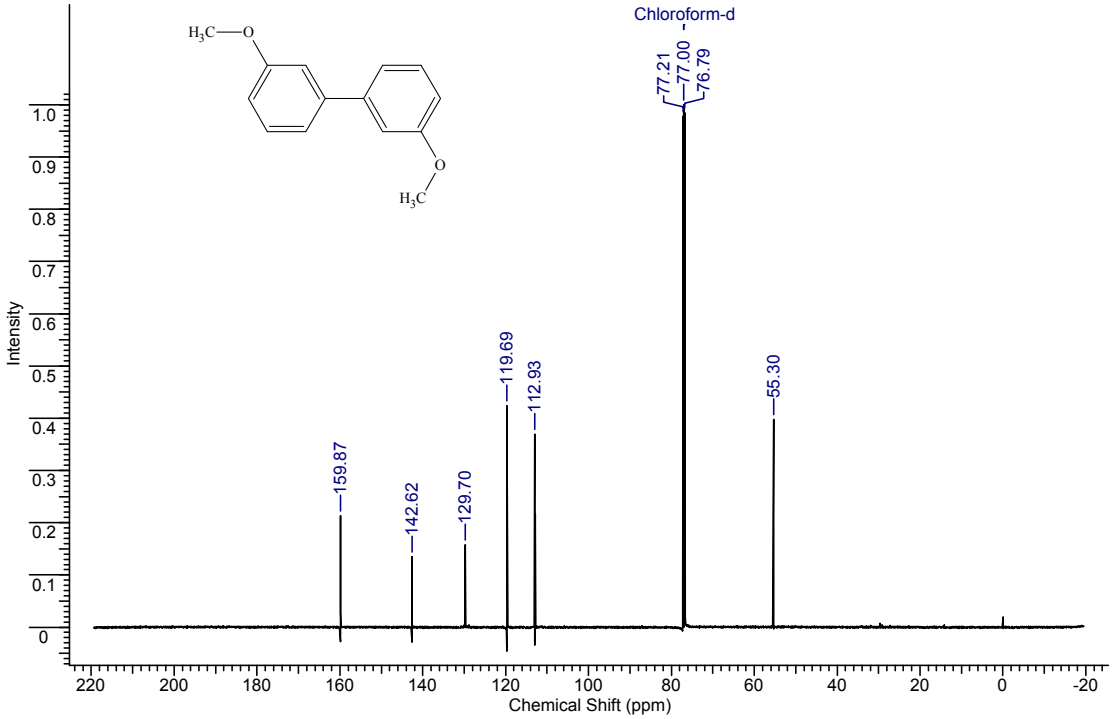
Compound **5a**


7.60
7.59
7.44
7.43
7.35
7.25
4.04
Intensity
Chemical Shift (ppm)

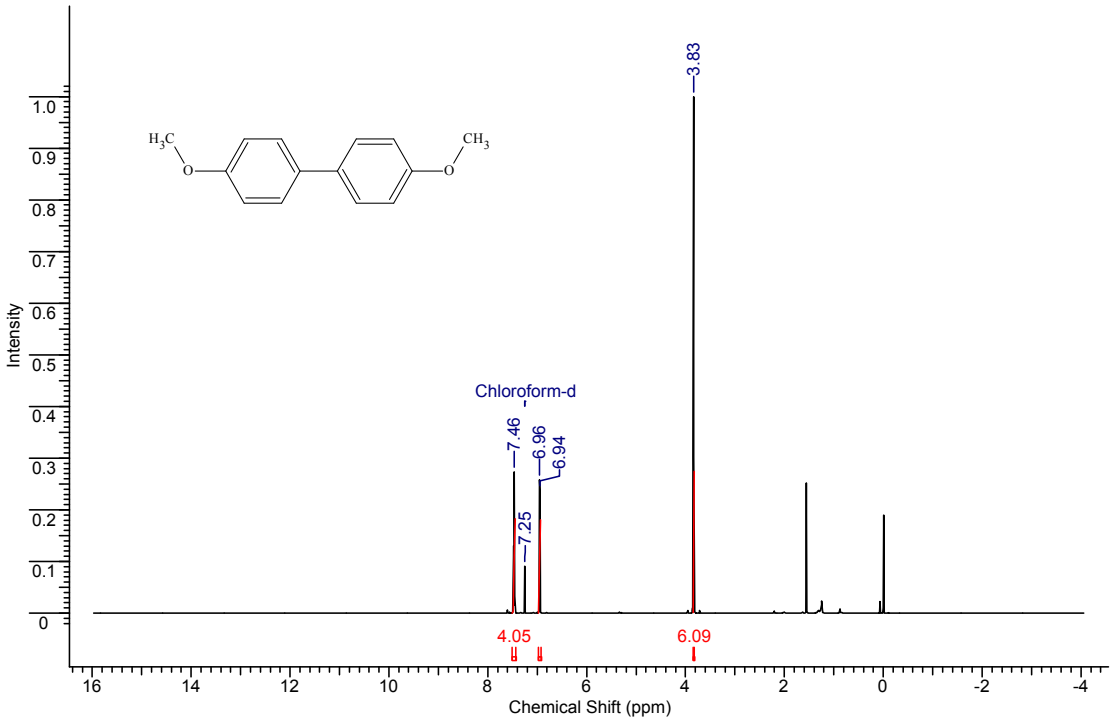

Chloroform-d
77.21
77.00
76.79
127.15
128.73
141.22
Intensity
Chemical Shift (ppm)

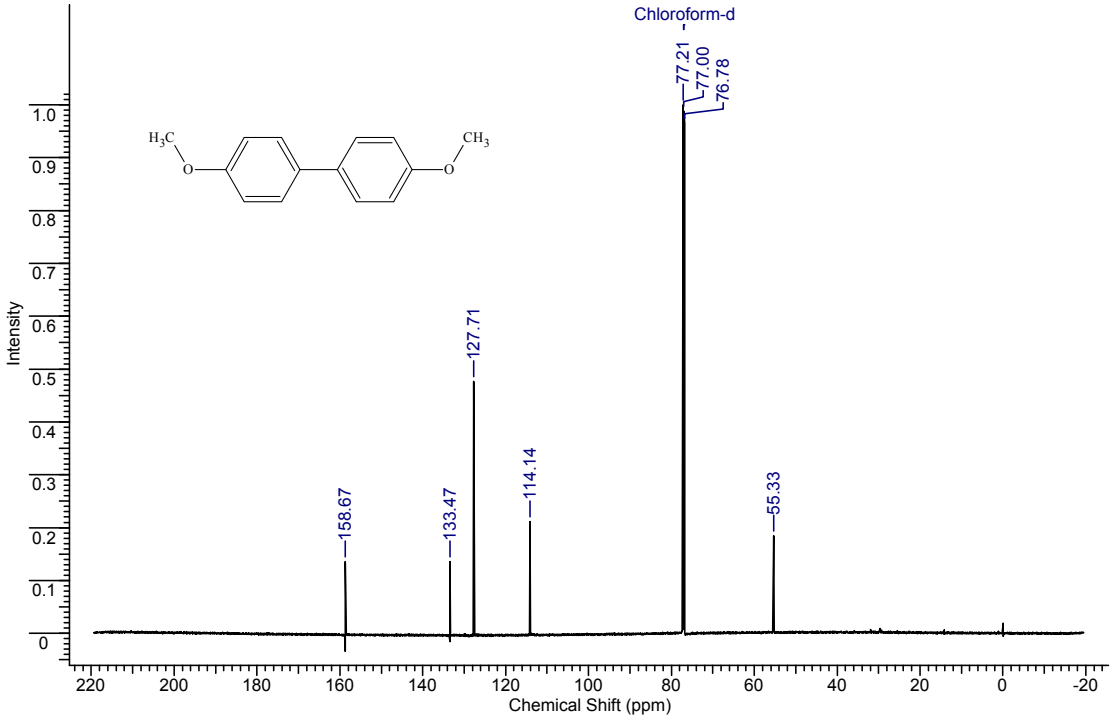
Compound **5b**


Chloroform-d
7.36
7.34
7.18
7.12
7.11
6.90
6.89
3.86
2.06
2.00
6.24
Intensity
Chemical Shift (ppm)

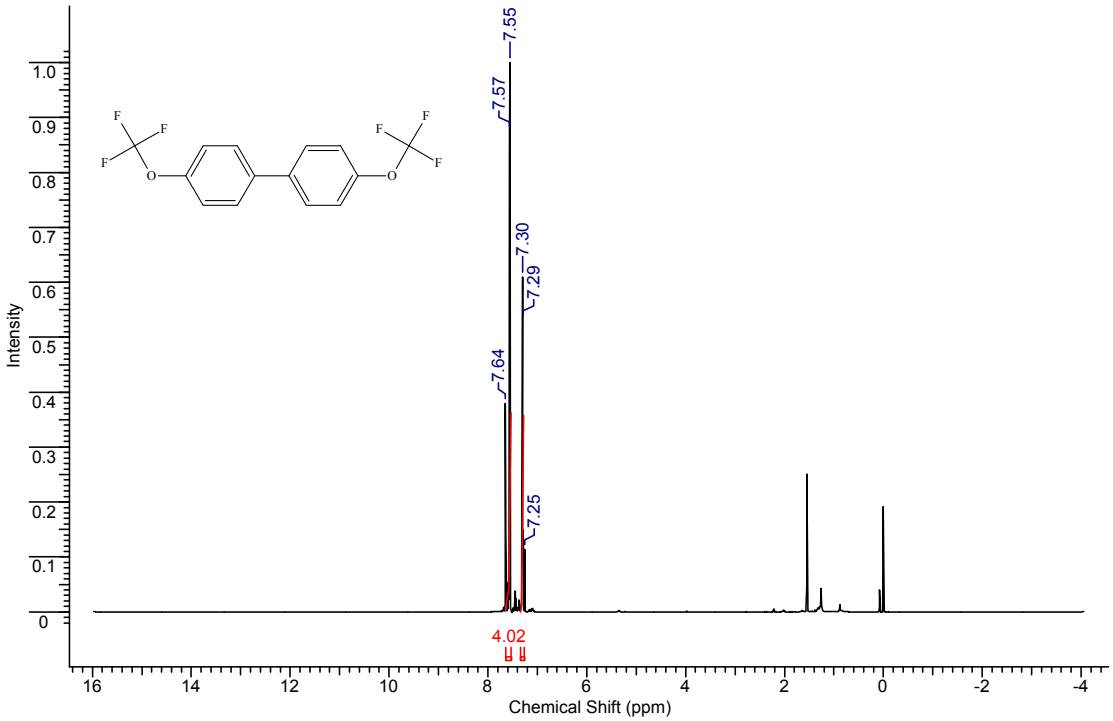

Chloroform-d
77.21
77.00
76.79
159.87
142.62
129.70
119.69
112.93
55.30
Intensity
Chemical Shift (ppm)

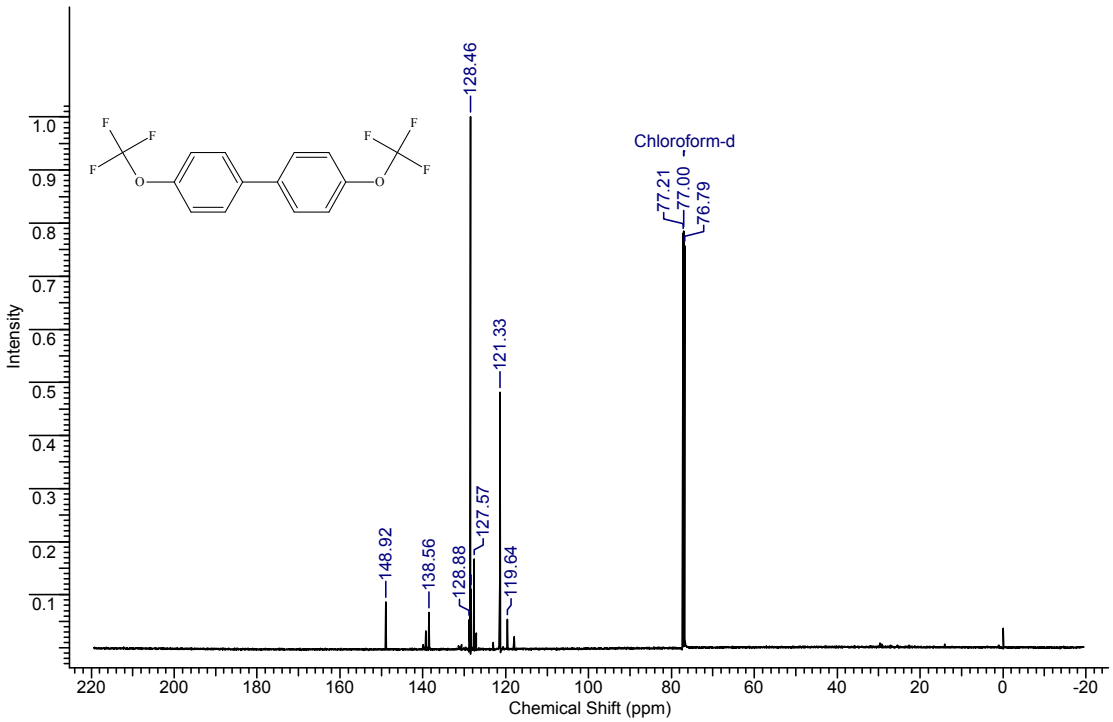
Compound **5c**


3.83
Chloroform-d
7.46
6.96
6.94
7.25
4.05
6.09
Intensity
Chemical Shift (ppm)

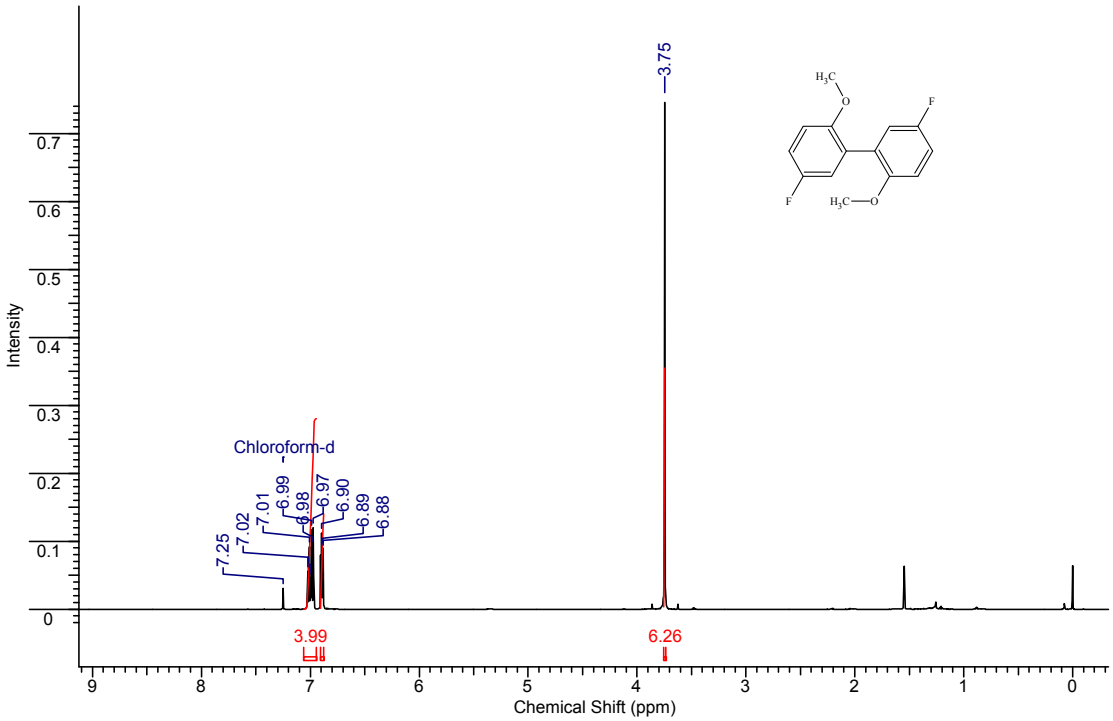

Chloroform-d
77.21
77.00
76.78
127.71
158.67
133.47
114.14
55.33
Intensity
Chemical Shift (ppm)

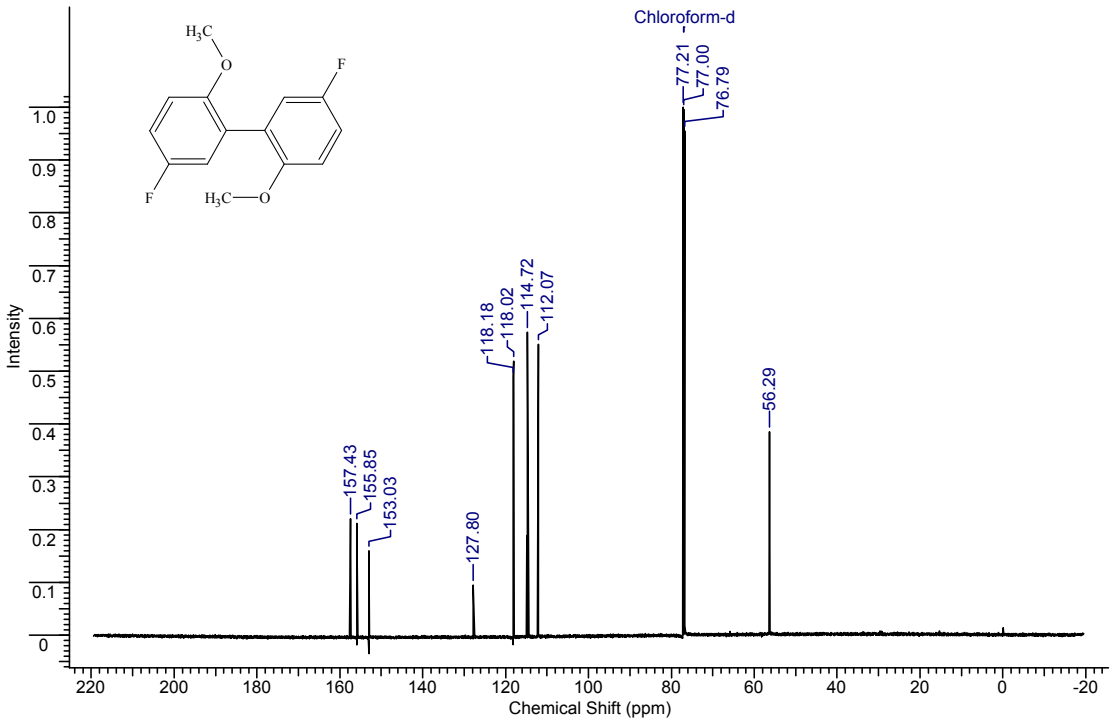
Compound **5d**


7.55
7.57
7.30
7.29
7.64
7.25
4.02
Intensity
Chemical Shift (ppm)

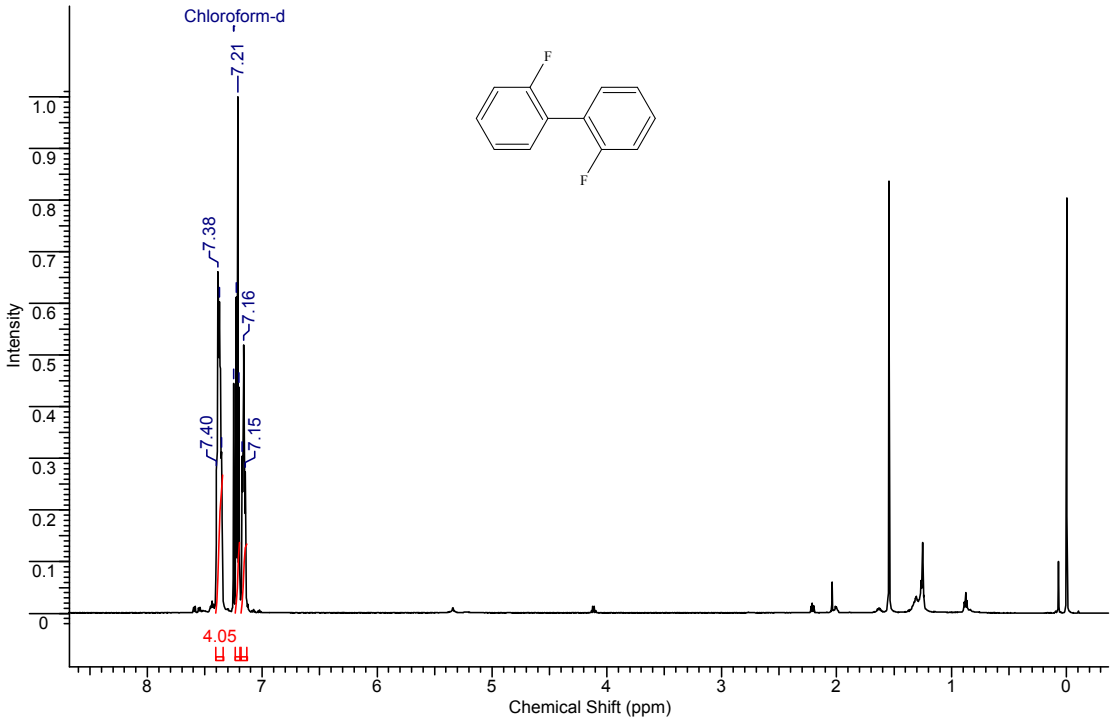

128.46
Chloroform-d
77.21
77.00
76.79
121.33
148.92
138.56
128.88
127.57
119.64
Intensity
Chemical Shift (ppm)

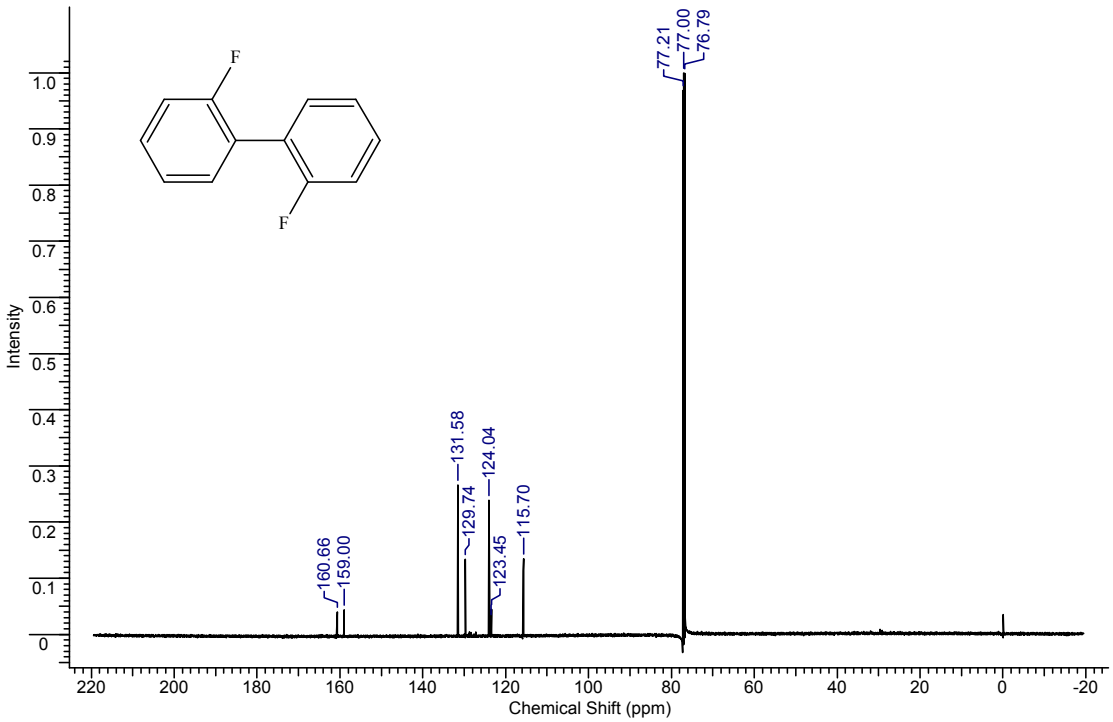
Compound **5e**


3.75
Chloroform-d
7.25
7.02
7.01
6.99
6.98
6.97
6.90
6.89
6.88
3.99
6.26
Intensity
Chemical Shift (ppm)

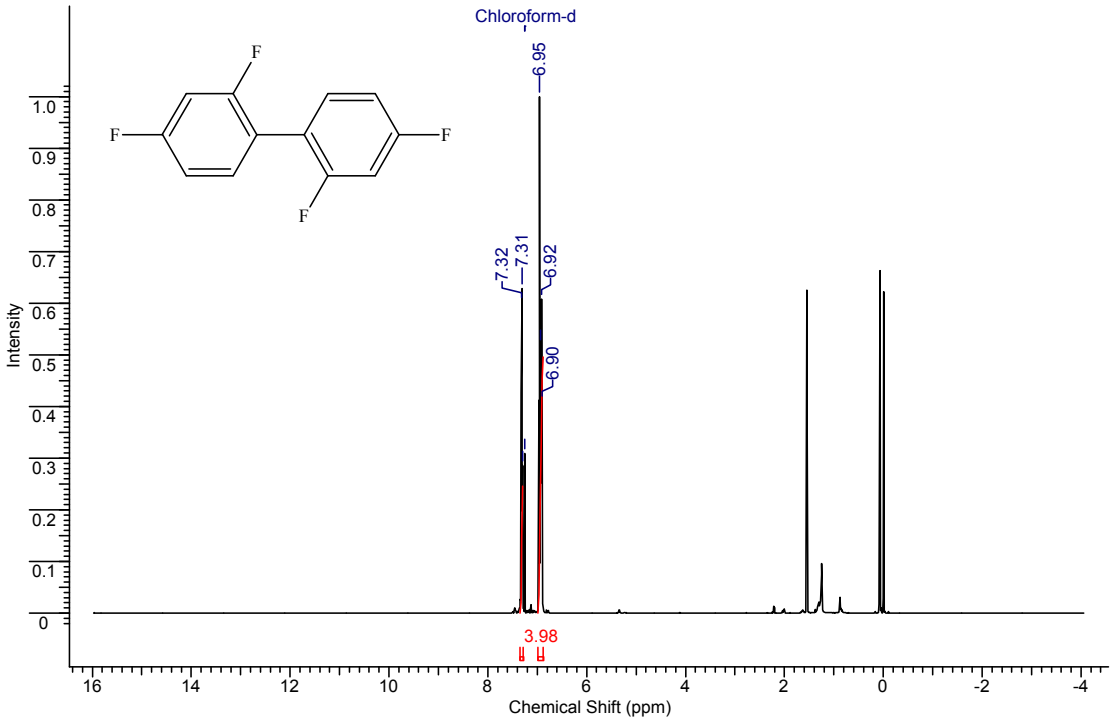

Chloroform-d
77.21
77.00
76.79
118.18
118.02
114.72
112.07
157.43
155.85
153.03
127.80
56.29
Intensity
Chemical Shift (ppm)

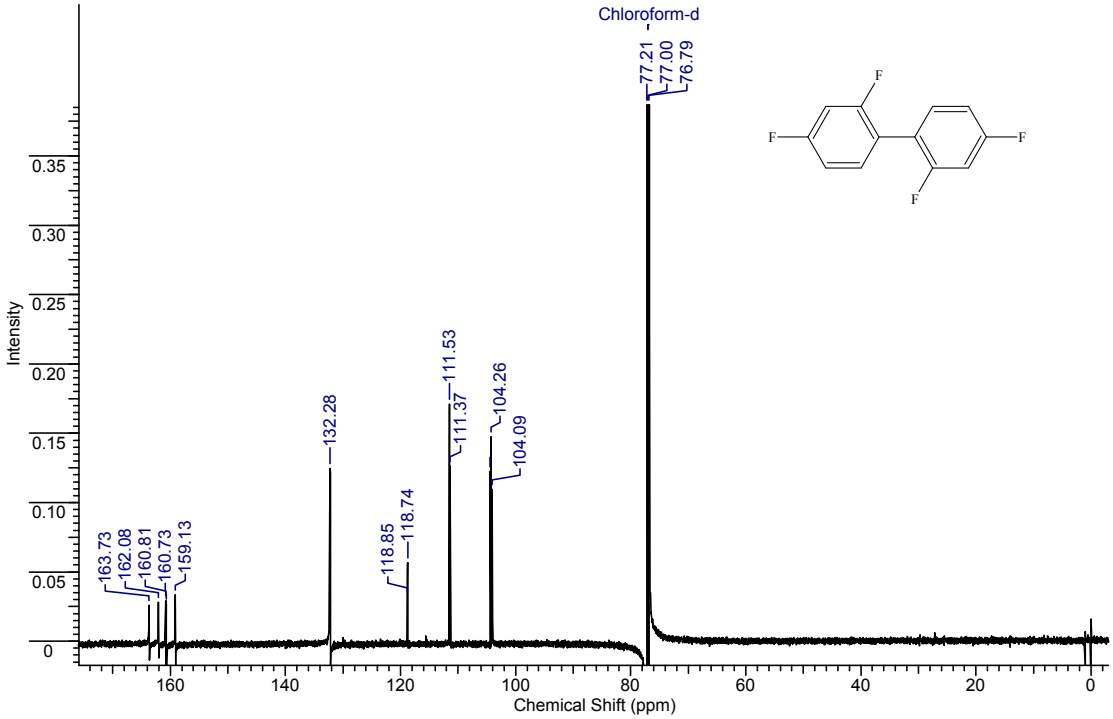
Compound **5f**


Chloroform-d
7.21
7.38
7.16
7.40
7.15
4.05
Intensity
Chemical Shift (ppm)

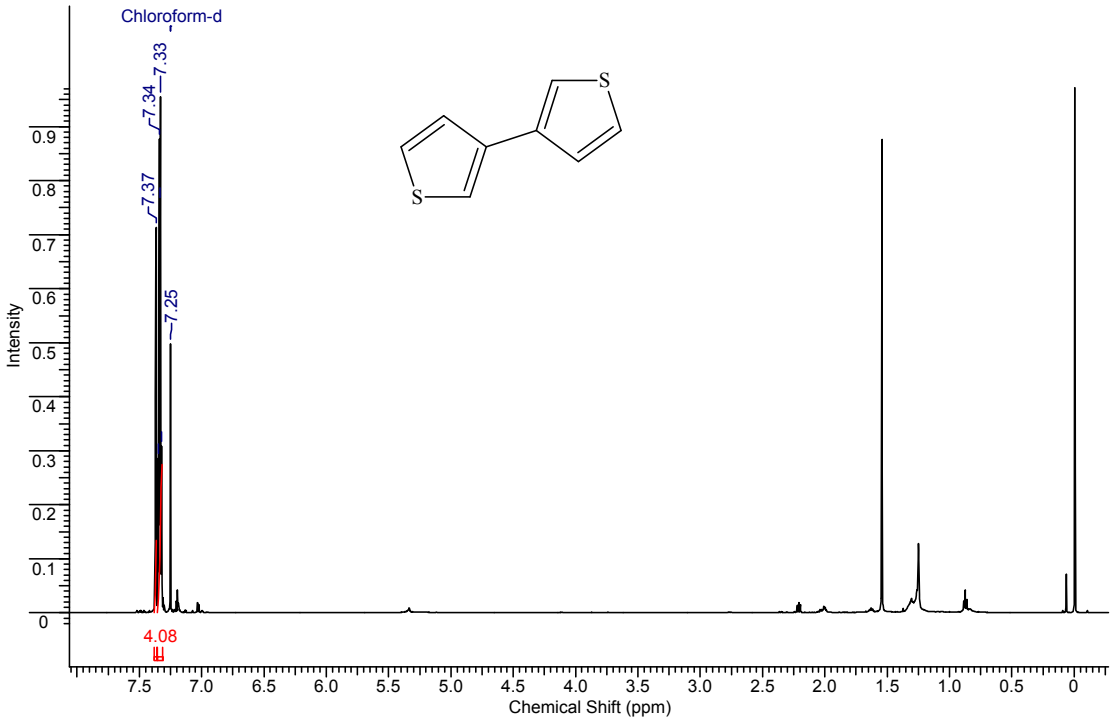

77.21
77.00
76.79
131.58
124.04
129.74
115.70
123.45
160.66
159.00
Intensity
Chemical Shift (ppm)

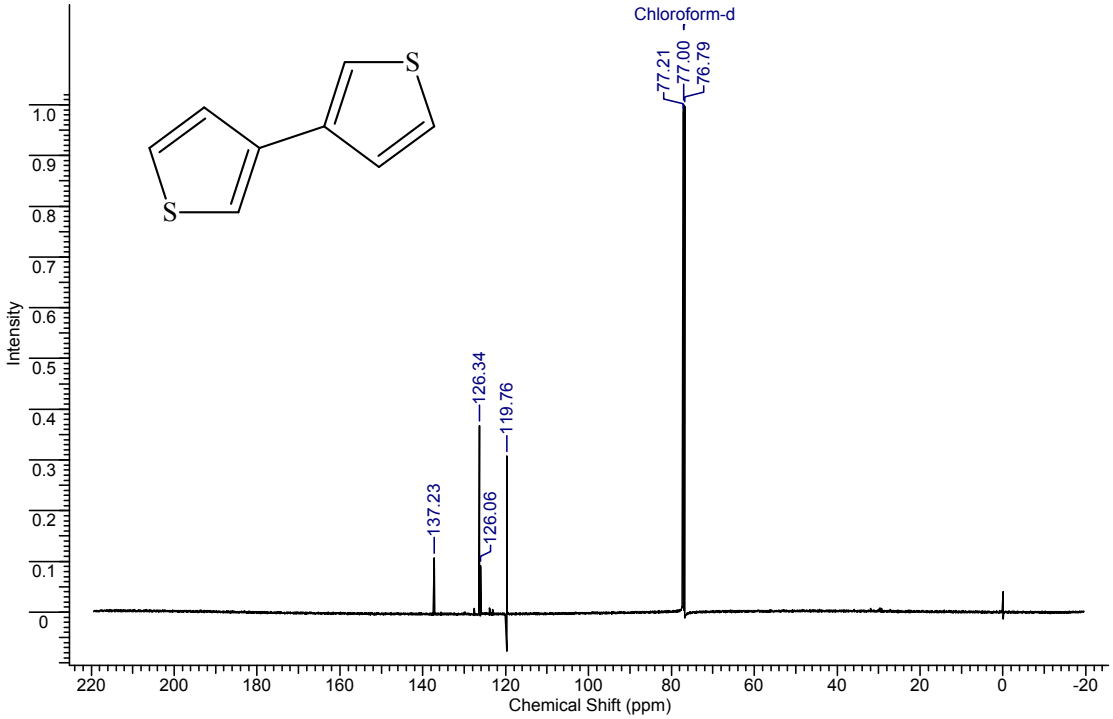
Compound **5g**


Chloroform-d
6.95
7.32
7.31
6.92
6.90
3.98
Intensity
Chemical Shift (ppm)

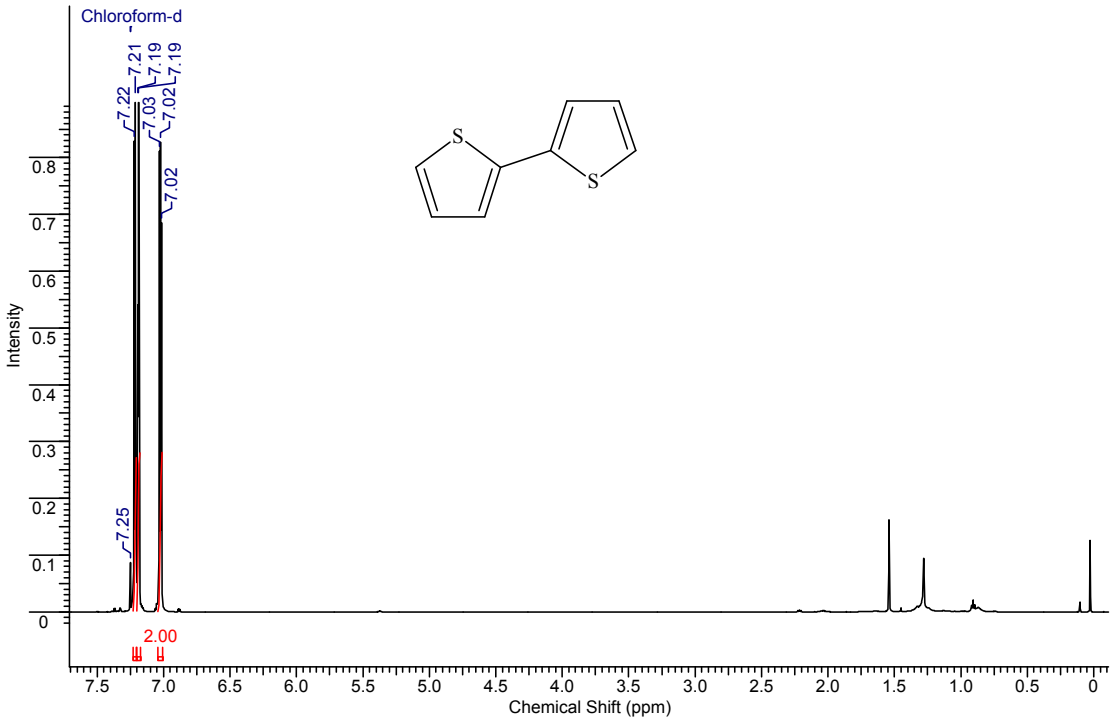

Chloroform-d
77.21
77.00
76.79
163.73
162.08
160.81
160.73
159.13
132.28
118.85
118.74
111.53
111.37
104.26
104.09
Intensity
Chemical Shift (ppm)

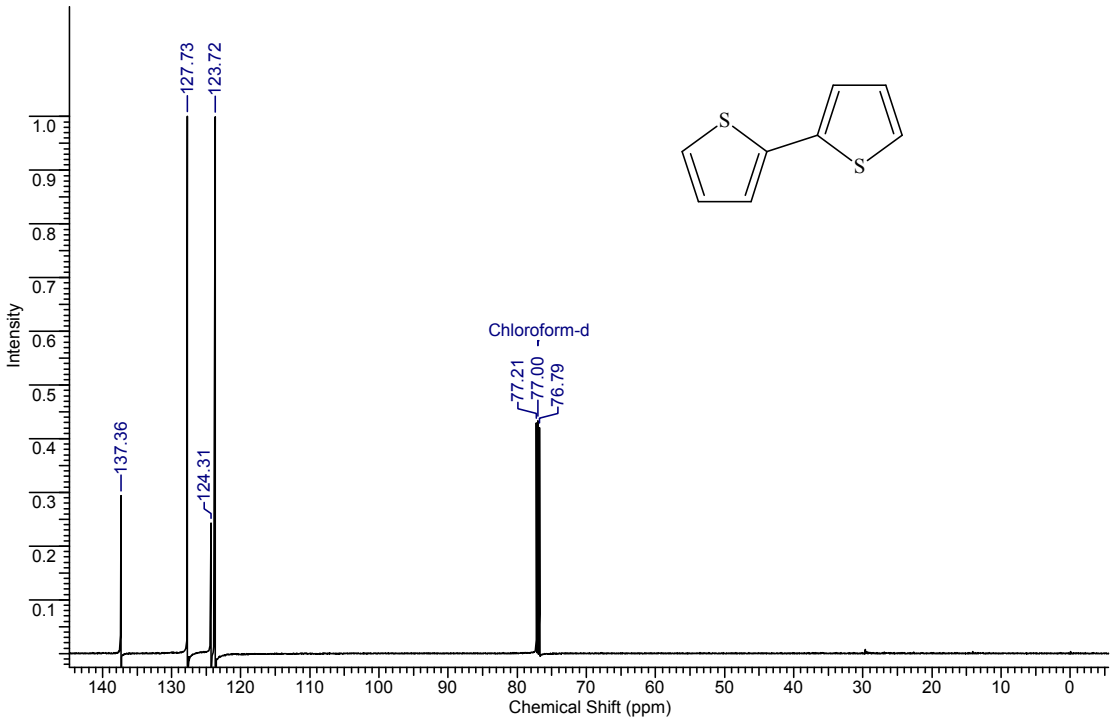
Compound **5k**


Chloroform-d
7.33
7.34
7.37
7.25
4.08
S
S
Intensity
Chemical Shift (ppm)


Chloroform-d
77.21
77.00
76.79
126.34
119.76
137.23
126.06
S
S
Intensity
Chemical Shift (ppm)

Compound **5l**


Chloroform-d
7.22
7.21
7.19
7.19
7.03
7.02
7.19
7.02
7.25
2.00
Intensity
Chemical Shift (ppm)
S
S


127.73
123.72
137.36
124.31
Chloroform-d
77.21
77.00
76.79
Intensity
Chemical Shift (ppm)
S
S