Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

A tertiary phosphine oxide ligand-based recyclable system for the Suzuki-Miyaura and Negishi reactions: Evidence for pseudo-homogeneous catalysis

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Experimental methods

General considerations:
Reagents were purchased from Sigma Aldrich or Alfa Aesar and used without further purification. Laboratory grade Tetrahydrofuran (THF) was purchased from Fisher Scientific and dried over sodium/benzophenone and distilled prior to use. NMR data was collected at 400 or 500 MHz on Jeol or Varian instruments in $CDCl_3$ at 298 K and referenced to tetramethylsilane. Gas Chromatography-Mass Spectrometry (GC-MS) data was collected using Thermo Scientific ISQ Single Quadrupole system. Ligands **L1**-**L7** were purchased from Sigma Aldrich or Alfa Aesar and used without further purification. Heated and anhydrous reactions were performed in screw cap vials or Teflon-sealed reaction tubes. All manipulations were carried out under an inert atmosphere using standard Schlenk and glovebox techniques, unless otherwise stated.

General procedure for palladium-catalysed Suzuki Miyaura coupling:
Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $Pd(OAc)_2$ (3.2 mg, 0.015 mmol) and cyclohexyldiphenyl phosphine oxide (**L3**) (8.5 mg, 0.03 mmol) with anhydrous THF (3 mL) as solvent. Subsequently, 4-Iodotoluene (65 mg, 0.3 mmol) was added followed by potassium tert-butoxide (67.6 mg, 0.6 mmol) and phenylboronic acid (73.16 mg, 0.6 mmol). The reaction mixture was removed from the glovebox and stirred at RT under an argon atmosphere for 24 hours. The reaction solvent was removed under reduced pressure and the resulting residue was extracted with hexane and dried *in vacuo* to afford the product (**1a**) as a white powder (92 % yield).

General procedure for palladium-catalysed Negishi coupling:
Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol) and cyclohexyldiphenyl phosphine oxide (**L3**) (8.5 mg, 0.03 mmol) with anhydrous THF (3 mL) as solvent. Subsequently, 4-Iodotoluene (65 mg, 0.3 mmol) was added followed by Tolylzinc iodide (1.2 ml, 0.6 mmol, 0.5 M in THF). The reaction mixture was removed from the glovebox and stirred at RT under an argon atmosphere for 24 hours. The reaction solvent was removed under reduced pressure and the resulting residue was extracted with hexane and dried *in vacuo* to afford the product (**2a**) as a white powder (83 % yield).

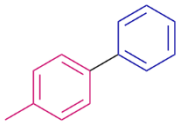
General procedure for Pd catalyst recycling:
Following the end point of the reaction, the solvent was evaporated in a vacuum and the resulting residue was extracted with hexane. The precipitate was re-dissolved in THF and the reagents were added. This methodology was repeated for each subsequent catalytic cycle.

Procedure for Pd catalyst recycling with aqueous work-up:
Following the end point of the reaction the solvent was evaporated in vacuum and the resulting residue was extracted with hexane. The precipitate was then washed with de-ionized water, filtered, and subsequently dried in a vacuum oven overnight (30 mmHg, 120 °C). The precipitate was re-dissolved in THF and the reagents were added. This methodology was repeated for subsequent catalytic cycles.

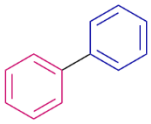
Active catalyst studies – Homogenous catalysis test:
$Pd(OAc)_2$ (5 mol%) and cyclohexyldiphenyl phosphine oxide (**L3**) (10 mol%) were stirred under the reaction conditions with KOtBu (5 mol%) and 4-Iodotoluene (5 mol%) for 3 hours,

filtered, and the filtrate was used as catalyst in the test reaction. High reactivity was observed providing completion of the reaction under the standard conditions (24 hrs). Pd black was observed as a precipitate, however the reaction proceeded to completion suggesting a homogenous Pd active species.

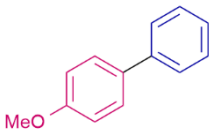
Experimental Data (^{1}H, ^{13}C{^{1}H} and Mass spec.)



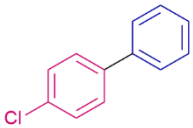
1a - ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.55 (d, 2H, J_{HH} = 7.8 Hz, o-Ar-H), 7.50-7.47 (d, 2H, J_{HH} = 8.4 Hz, m-Ar-H), 7.42 (t, J= 7.8 Hz, 2H, J_{HH} = 7.8 Hz, m-Ar-H), 7.31 (t, 1H, J_{HH} = 7.8 Hz, p-Ar-H), 7.23-7.21 (d, 2H, J_{HH} = 7.8 Hz, o-Ar-H), 2.40 (s, 3H).^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 141.3, 138.5, 137.2, 129.6, 128.9, 127.2, 127.1, 21.2. GC-MS: calcd. for $C_{13}H_{12}$, (m/z) = 168.09; found 168 (M·+).



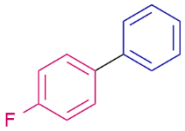
1b- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.60 (dd, 4H, J_{HH} = 7.8 Hz, o-Ar-H), 7.48-7.44 (t, 4H, J_{HH} = 7.8 Hz, m-Ar-H), 7.38-7.34 (t, 2H, J_{HH} = 7.8 Hz, p-Ar-H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 141.4, 128.9, 127.4, 127.3. GC-MS: calcd. for $C_{12}H_{10}$, (m/z) = 154.08; found 154 (M·+).



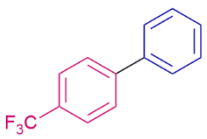
1c- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.53 (m, 4H), 7.44-7.40 (t, 2H, J_{HH} = 7.6 Hz, m-Ar′-H), 7.33-7.29 (t, 1H, J_{HH} = 7.3 Hz, pAr′-H), 6.99-6.95 (d, 2H, J_{HH} = 9.0 Hz, o-Ar-H), 3.86 (s, 3H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 159.3, 141.0, 133.7, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5. GC-MS: calcd. for $C_{13}H_{12}O$, (m/z) = 184.09; found 184 (M·+).



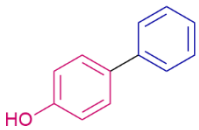
1d- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.54 (m, 4H), 7.49-7.39 (m, 5H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 140.4, 140.0, 133.8, 129.3, 129.1, 128.8, 128.0, 127.4. GC-MS: calcd. for $C_{12}H_9Cl$, (m/z) = 188.04; found 188 (M·+)



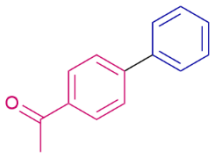
1e- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.47 (m, 4H), 7.45-7.36 (m, 3H), 7.16-7.11 (m, 2H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 162.4 (d, J = 246.3 Hz), 140.4, 137.3 (d, J = 3.3 Hz), 129.0, 128.8 (d, J = 8.0 Hz), 127.4, 127.3, 115.7 (d, J = 21.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -115.9. GC-MS: calcd. for $C_{12}H_9F$, (m/z) = 172.07; found 172 (M·+)



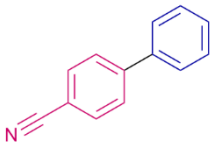
1f- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (bs, 4H), 7.62-7.60 (d, 2H, J_{HH} = 7.8 Hz, oAr′-H), 7.50-7.46 (t, 2H, J_{HH} = 7.8 Hz, m-Ar′-H), 7.43-7.42 (t, 1H, J_{HH} = 7.8 Hz, p-Ar′- H).^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 144.8, 139.9, 129.8 (q, J = 32.6 Hz), 129.5, 128.3, 127.5, 127.4, 126.2 (q, J = 3.6 Hz), 124.9 (q, J= 271.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.4. GC-MS: calcd. for $C_{13}H_9F_3$, (m/z) = 222.07; found 222 (M·+)



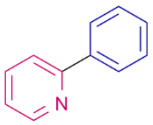
1i- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 4H), 7.40 (t, 2H, J_{HH} = 7.6 Hz), 7.31-7.27 (m, 1H), 6.96 (d, 2H, J_{HH} = 8.4 Hz), 3.84 (s, 1H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 155.2, 140.8, 134.0, 128.7, 128.4, 126.7, 115.7. GC-MS: calcd. for $C_{12}H_{10}O$, (m/z) = 170.07; found 170 (M·+).



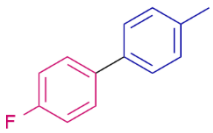
1l- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 8.0 Hz), 7.65 (d, 2H, J = 7.6 Hz), 7.50 (t, 2H, J = 7.6 Hz), 7.41 (d, 1H, J = 7.6 Hz), 2.65 (s, 3H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): *δ* = 198.0, 146.0, 140.0, 136.0, 129.1, 129.0, 128.4, 127.4, 127.3, 26.8. GC-MS: calcd. for $C_{14}H_{12}O$, (m/z) = 196.09; found 196 (M·+).



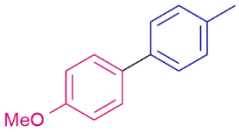
1n- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.66 (m, 4H), 7.60-7.57 (m, 2H), 7.50-7.41 (m, 3H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 146.8, 139.3, 132.7, 129.2, 128.8, 127.8, 127.3, 119.1, 111.0. GC-MS: calcd. for calcd. for $C_{13}H_{9}N$, (m/z) = 179.07; found 179 (M·+).



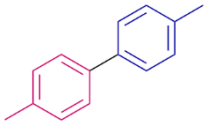
1s- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73-8.71 (m, 1H) , 8.02-8.00 (m, 2H), 7.81-7.74 (m, 2H), 7.51-7.42 (m, 3H), 7.27-7.24 (m, 1H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 157.5, 149.6, 139.3, 136.9, 129.0, 128.8, 126.9, 121.1, 120.6. GC-MS: calcd. for calcd. for $C_{11}H_{9}N$, (m/z) = 155.07; found 155 (M·+).



2a- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, 2H, J = 6.8, 3.4 Hz), 7.48 (d, 2H, J = 8 Hz), 7.27 (m, 4H), 2.41 (s, 3H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 162.8, 160.4, 136.6, 136.2, 129.5, 128.5, 126.9, 115.5 (d, J = 21.2 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -116.3. GC-MS: calcd. for $C_{13}H_{11}F$, (m/z) = 186.08; found 186 (M·+).

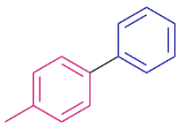


2b- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.41 (m, 4H), 7.27-7.23 (m, 2H), 6.99-6.96 (m, 2H), 3.86 (s, 3H), 2.40 (s, 3H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 158.9, 138.0, 136.4, 133.8, 129.4, 128.0, 126.6, 114.2, 55.4, 21.1. GC-MS: calcd. for for $C_{14}H_{14}O$, (m/z) = 198.1; found 198 (M·+).



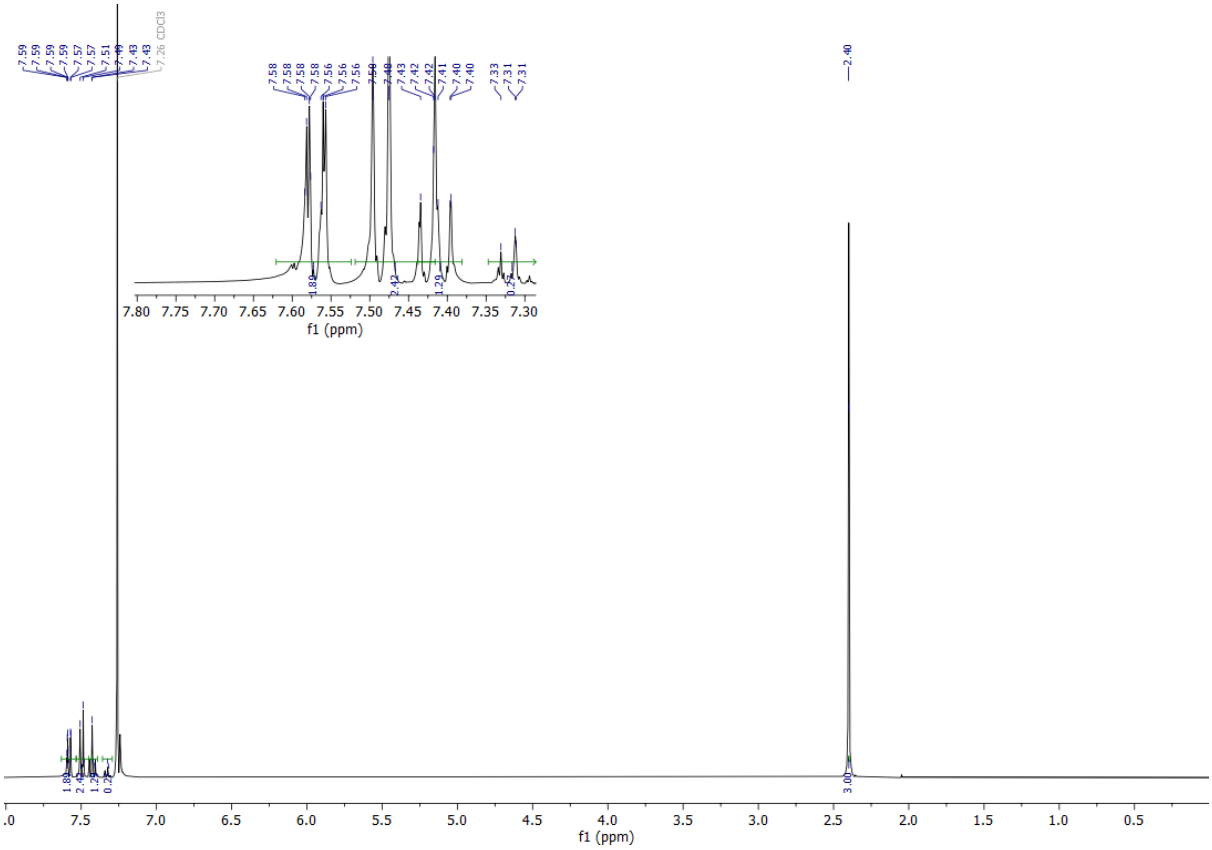
2c- ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8 Hz, 4H), 7.26 (d, *J* = 8 Hz, 4H), 2.42 (s, 6H). ^{13}C[^{1}H] NMR (100 MHz, $CDCl_3$): δ = 138.6, 137.1, 129.5, 126.8, 21.1. GC-MS: calcd. for $C_{14}H_{14}$, (m/z) = 182.11; found 182 (M·+).

NMR Spectra:

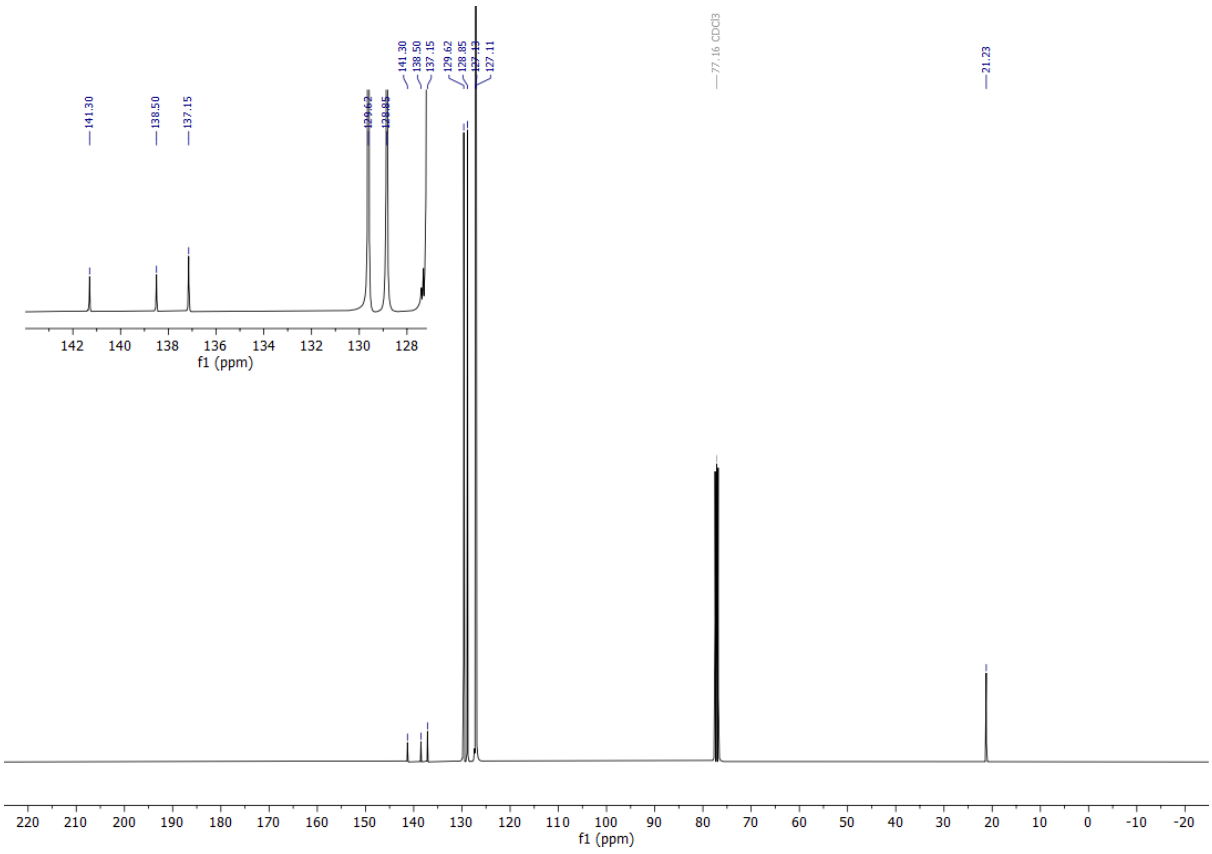


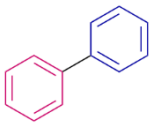
1a

^{1}H


7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

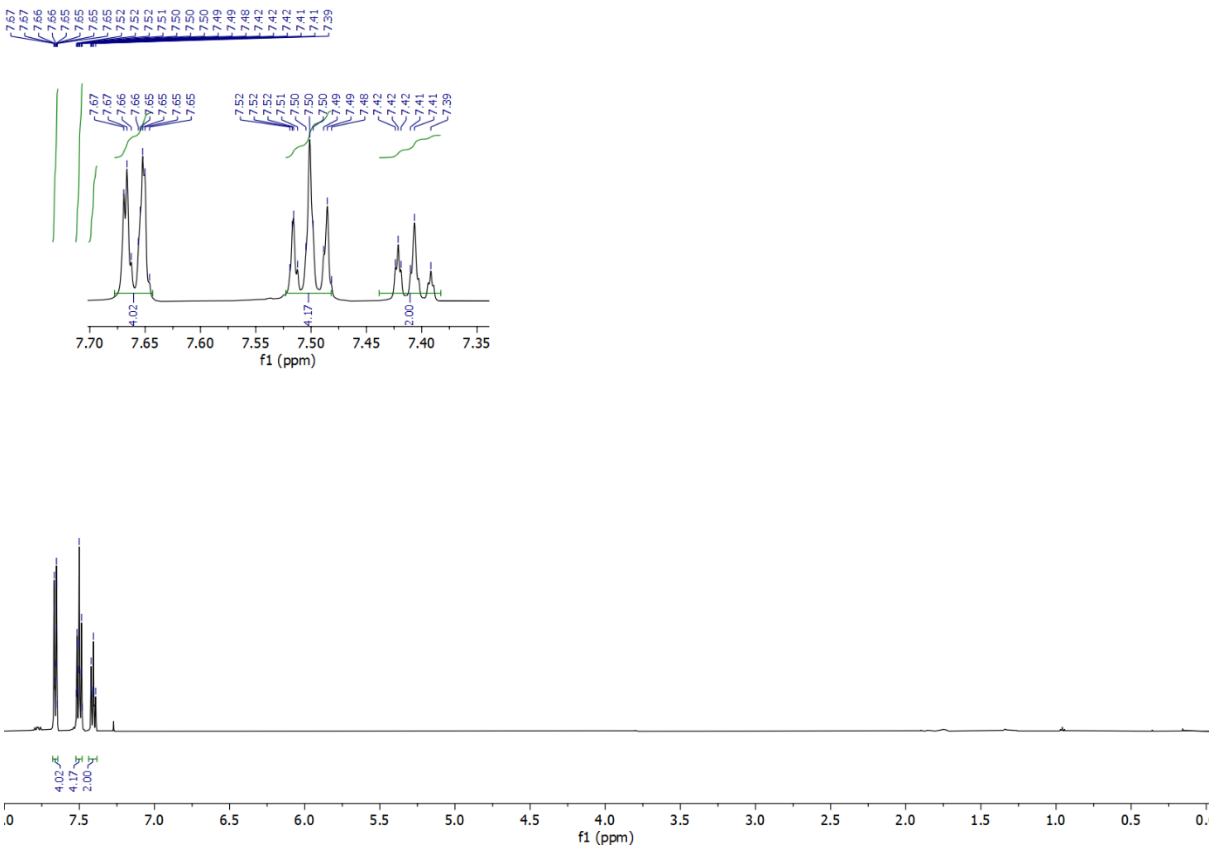
^{13}C [^{1}H]


141.30
138.50
137.15
129.62
128.85
127.13
127.11
77.16 CDCl3
21.23
142 140 138 136 134 132 130 128
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



1b

^{1}H


7.67
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7.41
7.41
7.41
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7.50
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7.40
7.35
f1 (ppm)
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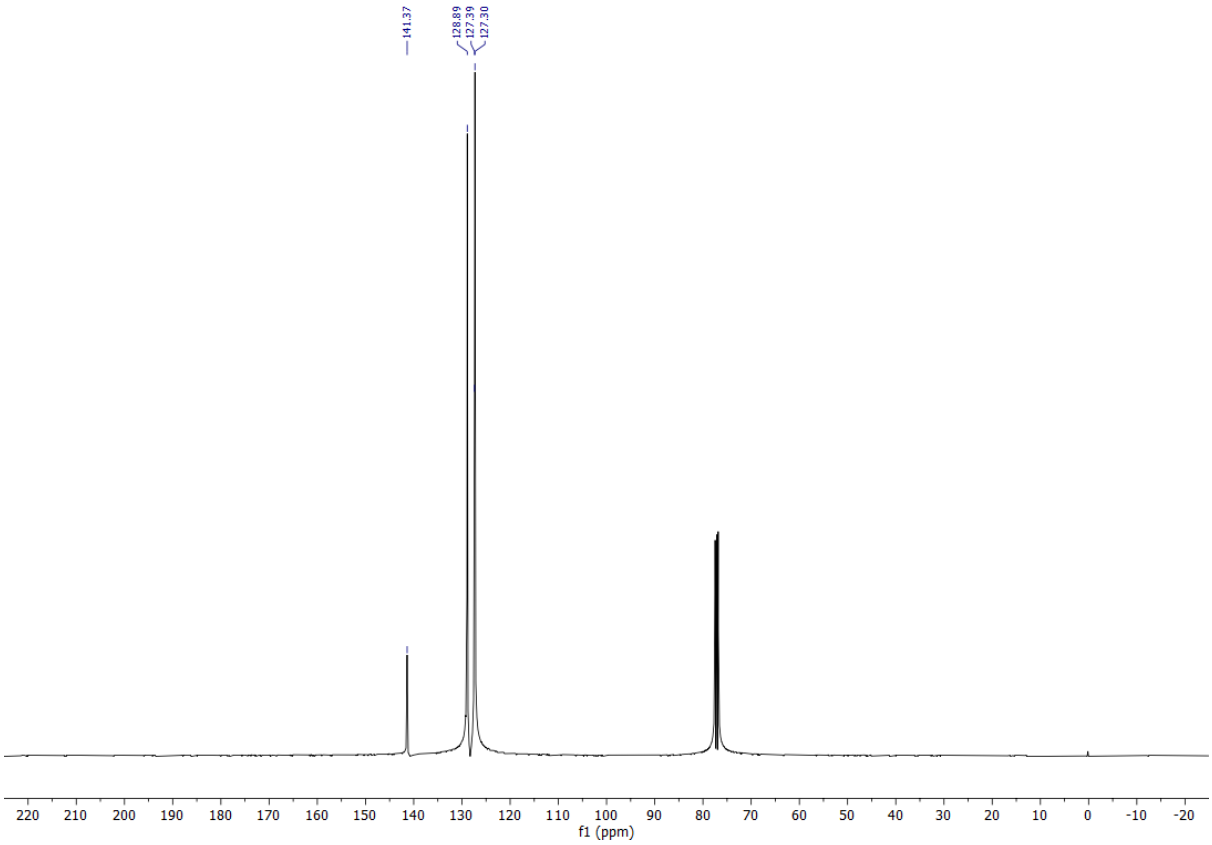
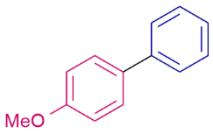
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

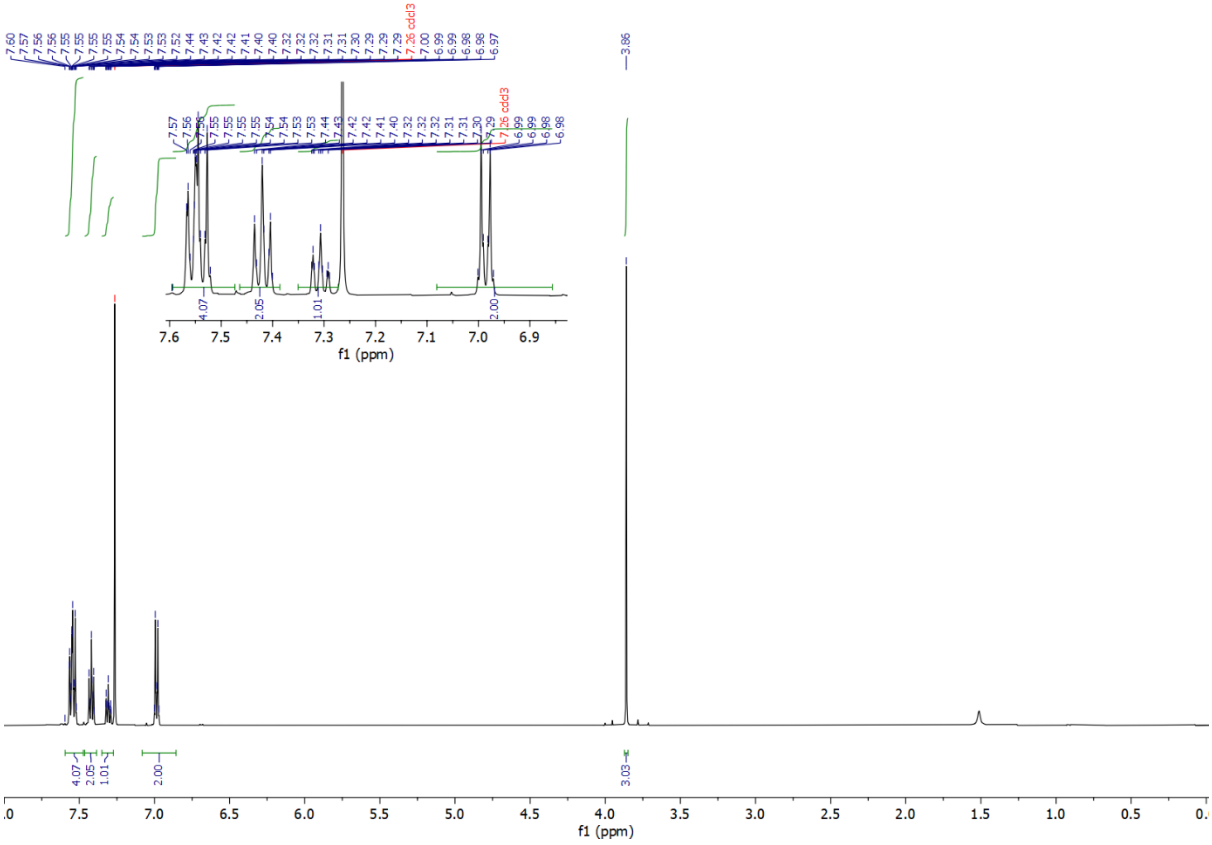
^{13}C [^{1}H]


141.37
128.89
127.39
127.30
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

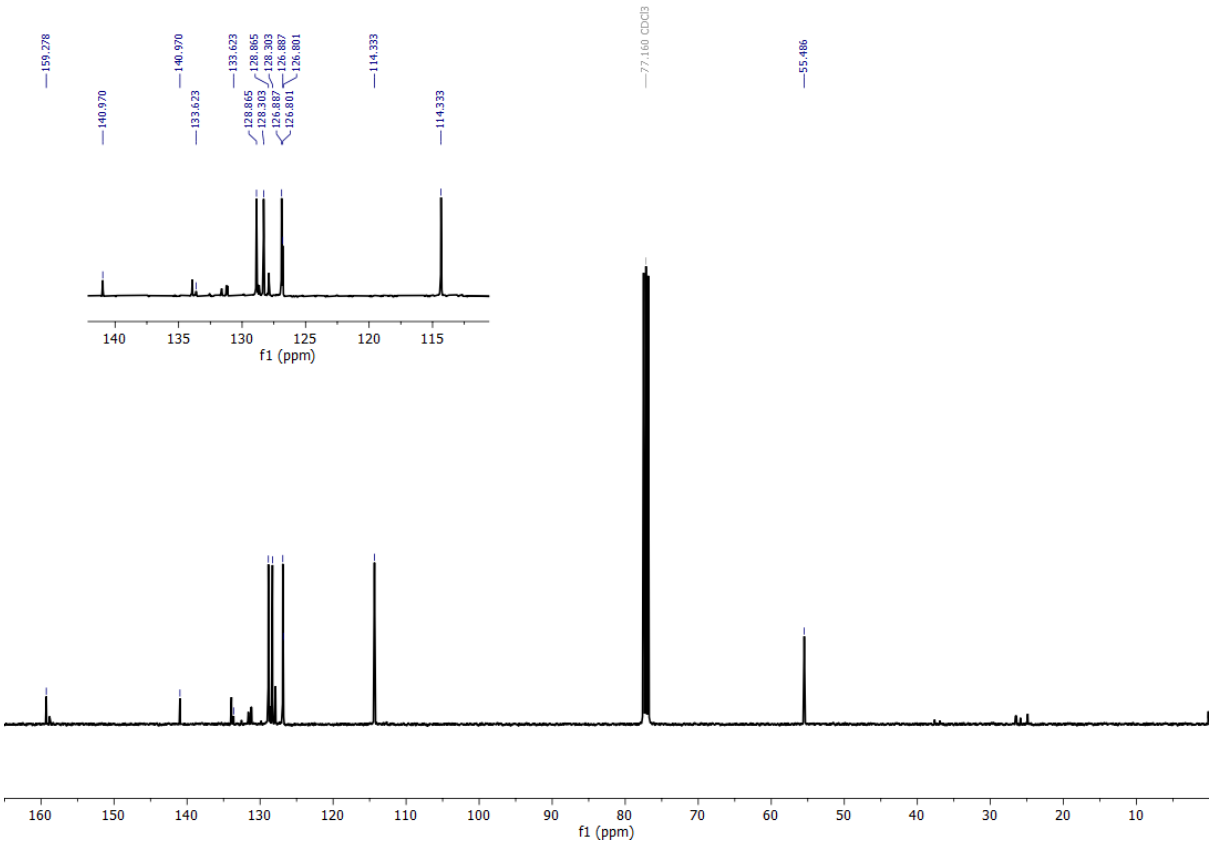

MeO

1c

^{1}H



^{13}C [^{1}H]


159.278
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128.303
126.887
126.801
114.333
77.160 CDCl3
55.486
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133.623
128.865
128.303
126.887
126.801
114.333
140
135
130
125
120
115
f1 (ppm)
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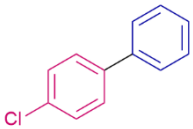
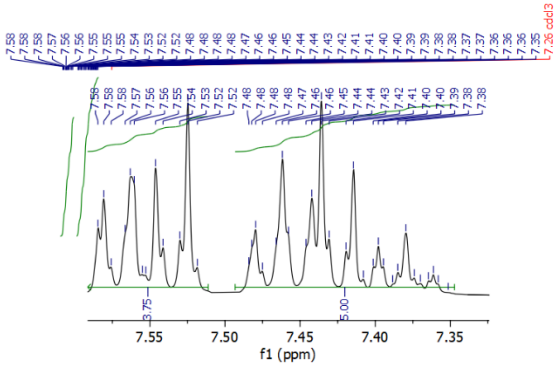
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl

1d

^{1}H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5.00
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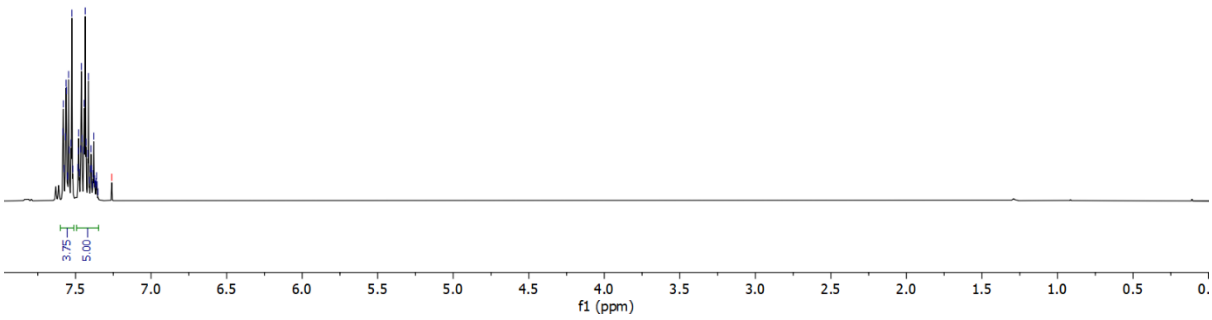
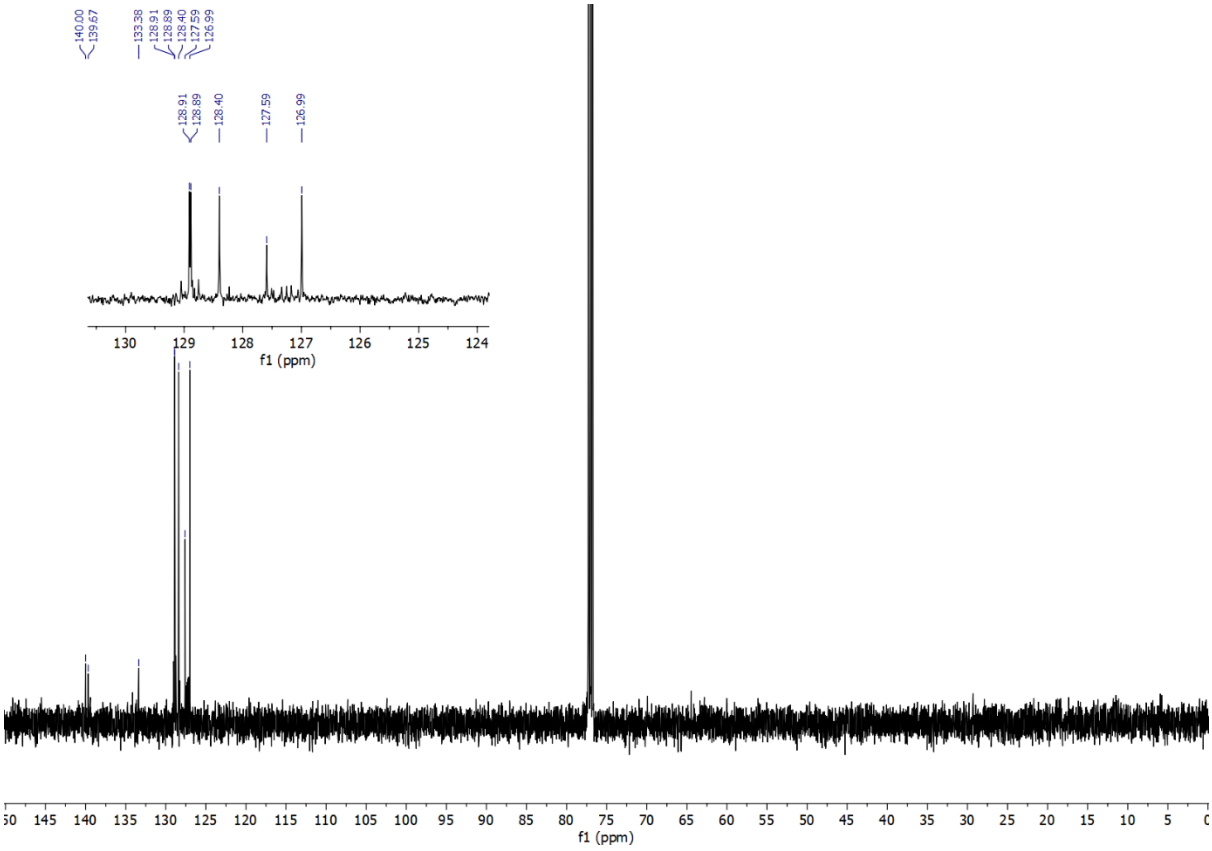
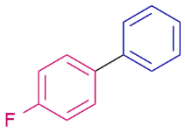
7.50
7.45
7.40
7.35
f1 (ppm)


3.75
5.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

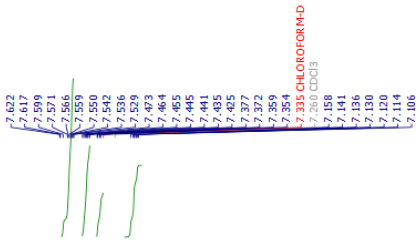
^{13}C [^{1}H]

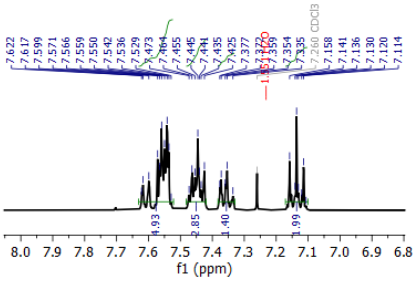

140.00
139.67
133.38
128.91
128.89
128.40
127.59
126.99
130
129
128
127
126
125
124
f1 (ppm)
f1 (ppm)

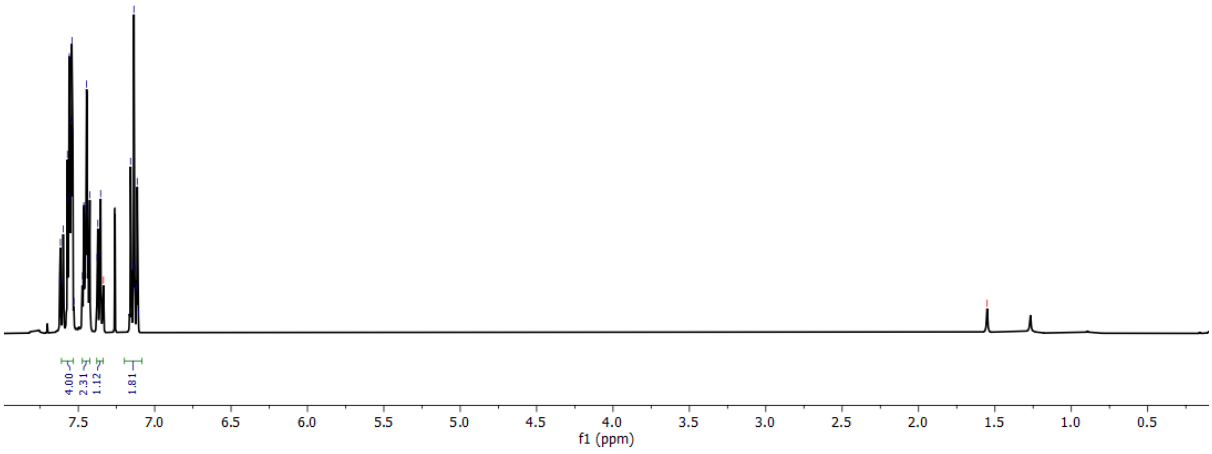

F

1e

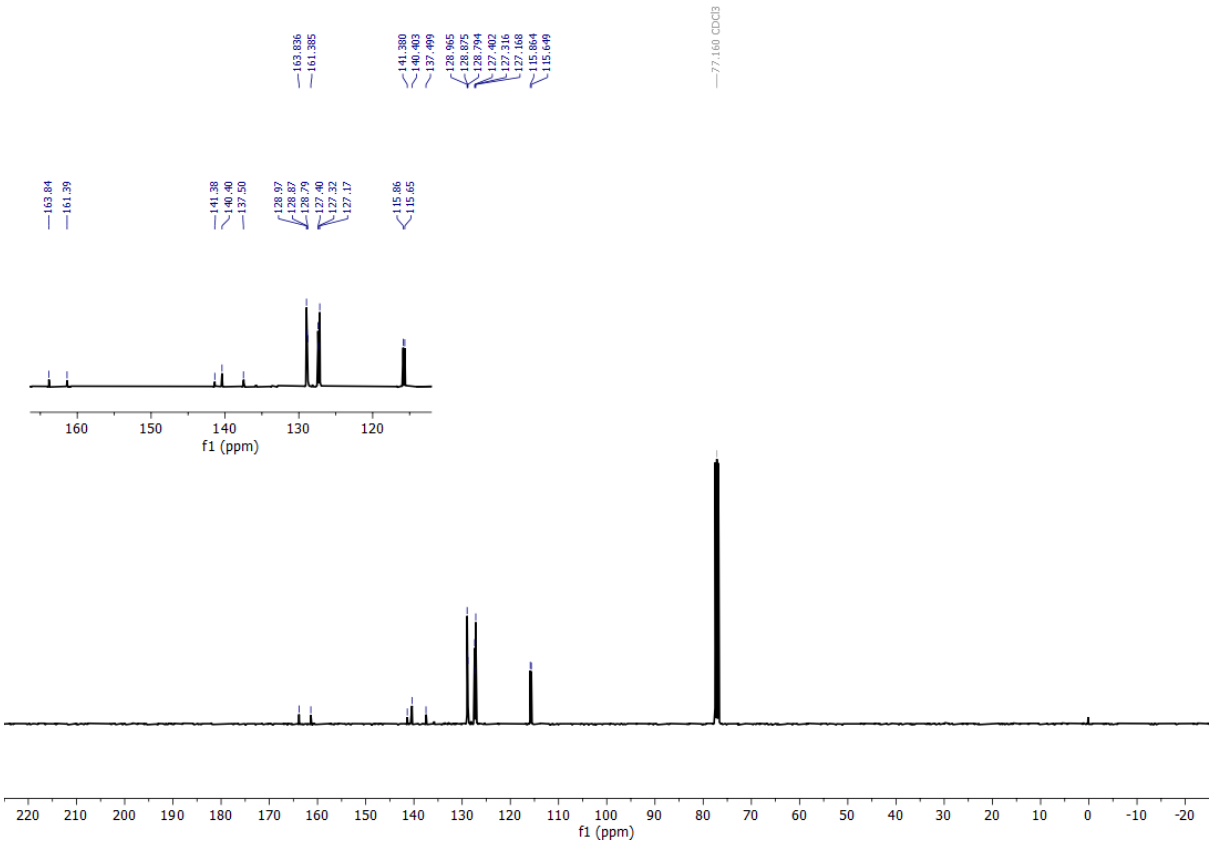
^{1}H


7.622
7.617
7.599
7.571
7.566
7.559
7.550
7.542
7.536
7.529
7.473
7.464
7.455
7.445
7.441
7.435
7.425
7.377
7.372
7.359
7.354
7.335 CHLOROFORM-D
7.260 CDCl3
7.158
7.141
7.136
7.130
7.120
7.114
7.106

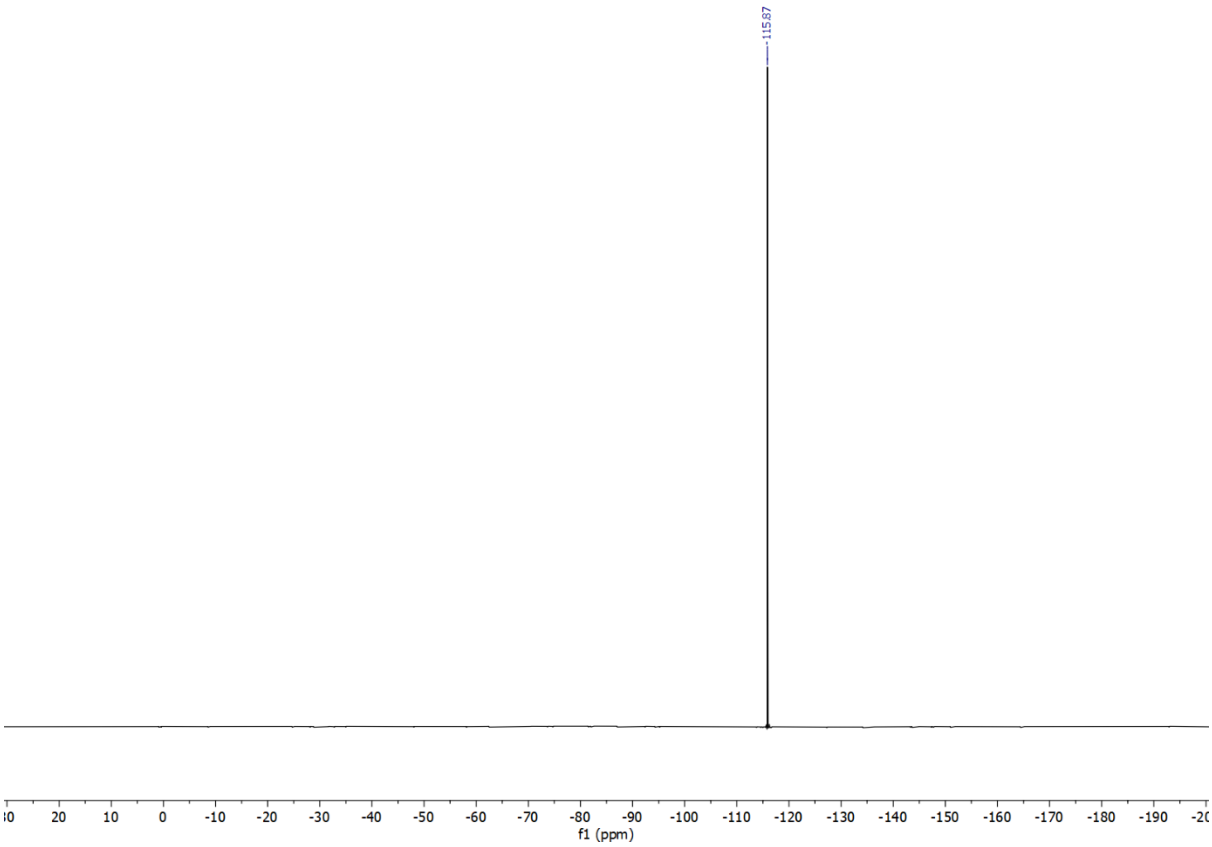

7.622
7.617
7.599
7.571
7.566
7.559
7.550
7.542
7.536
7.529
7.473
7.464
7.455
7.445
7.441
7.435
7.425
7.377
7.372
7.359
7.354
7.335
7.260 CDCl3
7.158
7.141
7.136
7.130
7.120
7.114
1.93
2.85
1.40
1.99
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)

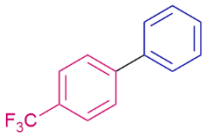

4.00
2.31
1.12
1.81
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

^{13}C [^{1}H]


163.836
161.385
141.380
140.403
137.499
128.965
128.875
128.794
127.402
127.316
127.168
115.864
115.649
77.160 CDCl3
163.84
161.39
141.38
140.40
137.50
128.97
128.87
128.79
127.40
127.32
127.17
115.86
115.65
160
150
140
130
120
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

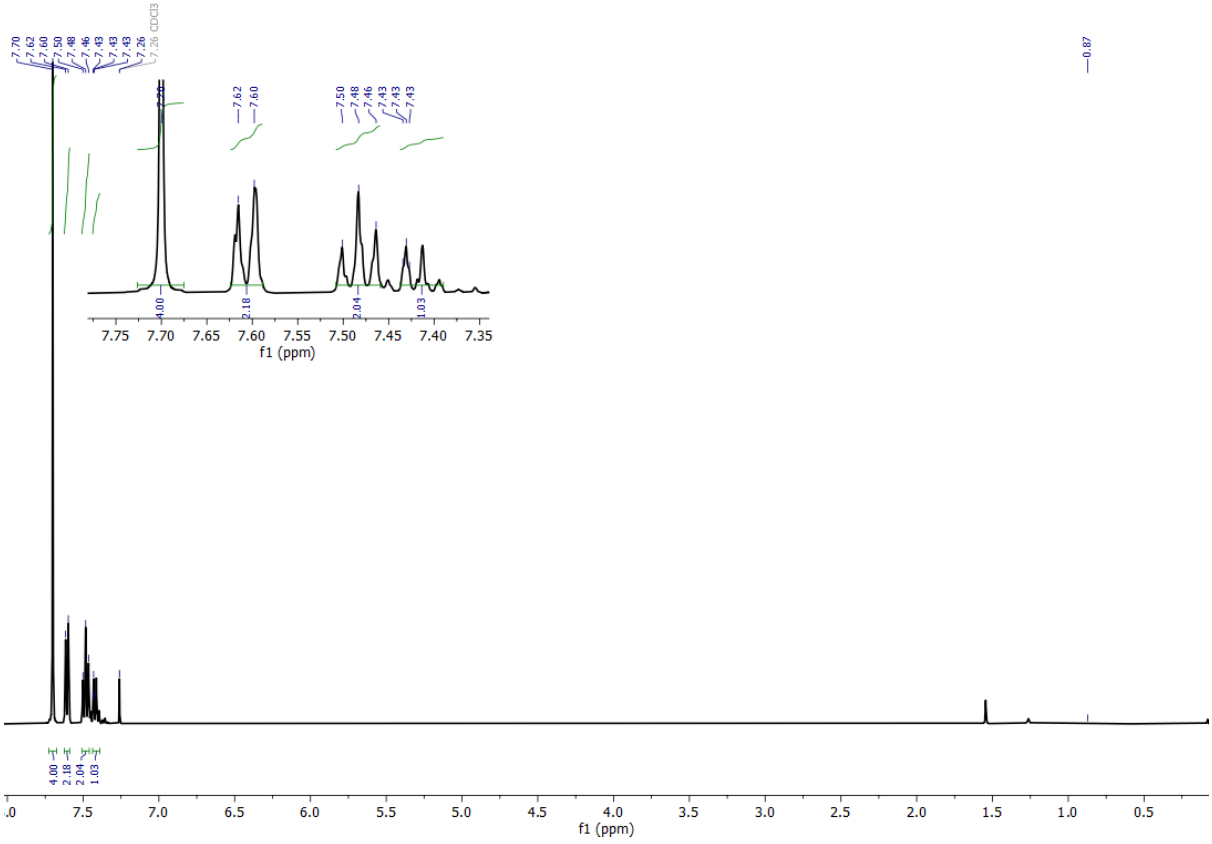
^{19}F


-115.87
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

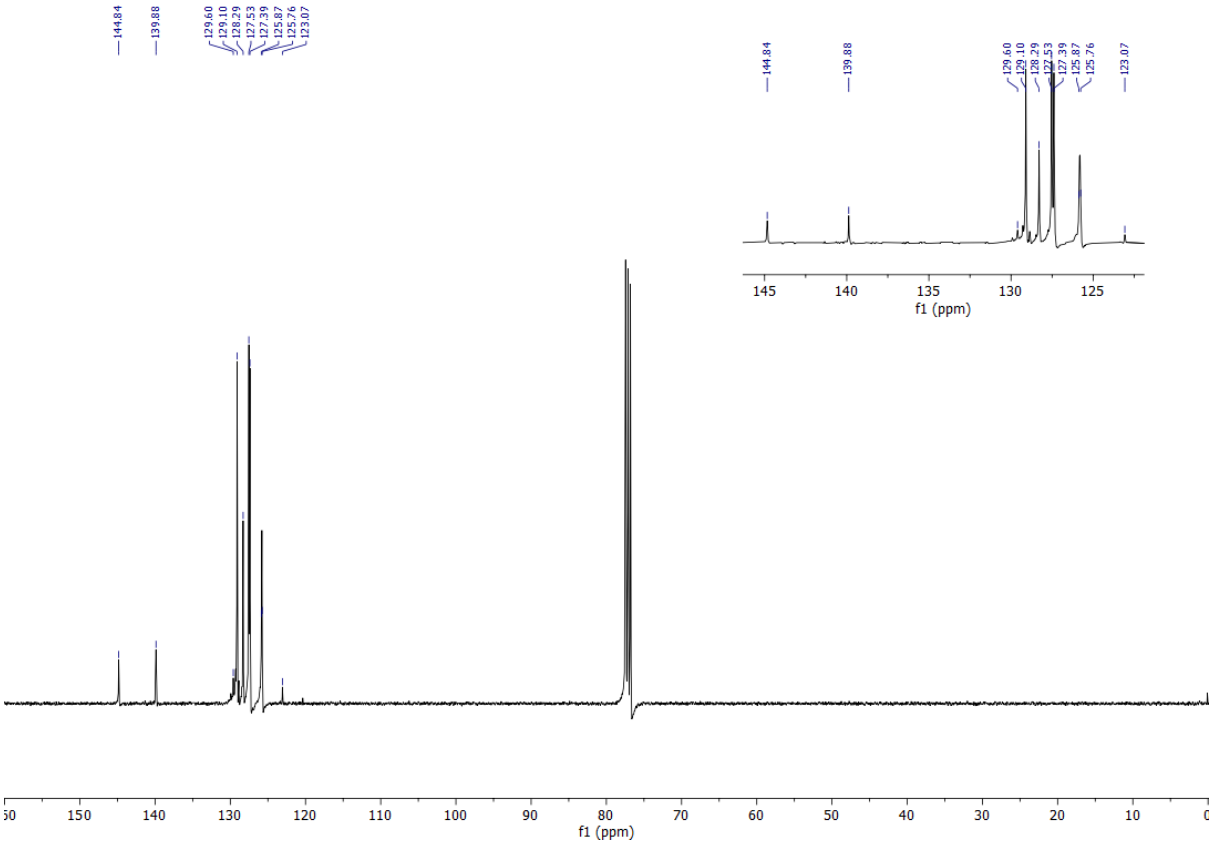

F3C

1f

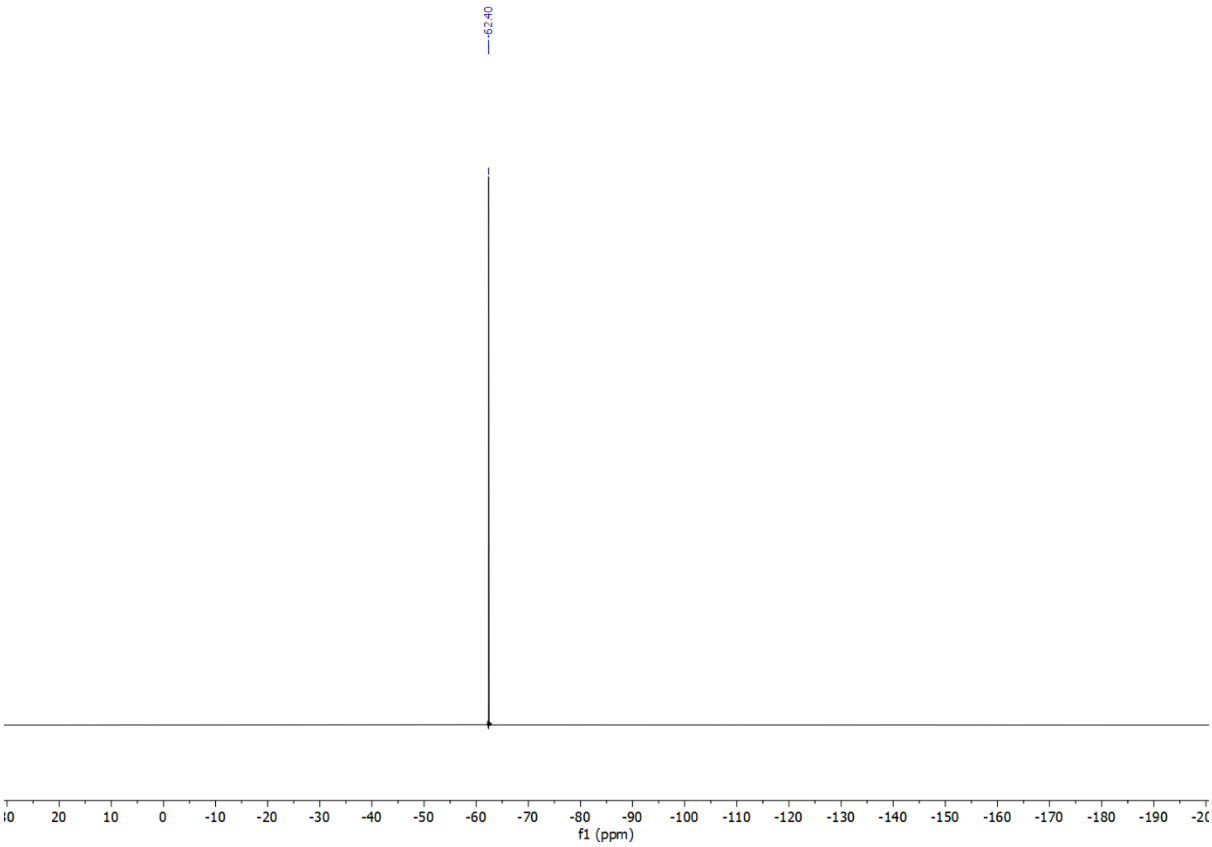
^{1}H

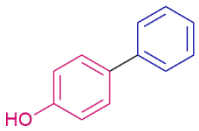

7.70
7.62
7.60
7.50
7.48
7.46
7.43
7.43
7.43
7.26
7.26 CDCl3
7.62
7.60
7.50
7.48
7.46
7.43
7.43
7.43
0.87
4.00
2.18
2.04
1.03
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

^{13}C [^{1}H]


144.84
139.88
129.60
129.10
128.29
127.53
127.39
125.87
125.76
123.07
f1 (ppm)

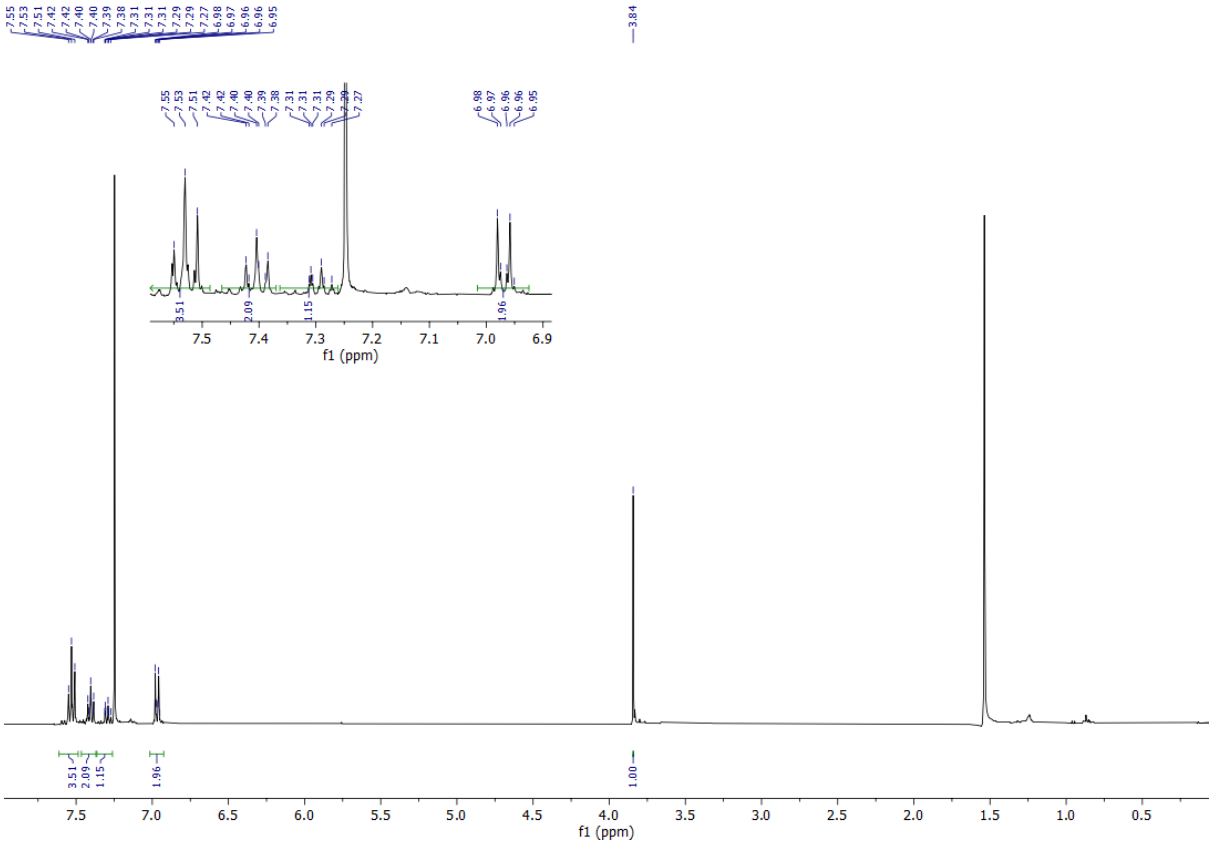
^{19}F


-62.40
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

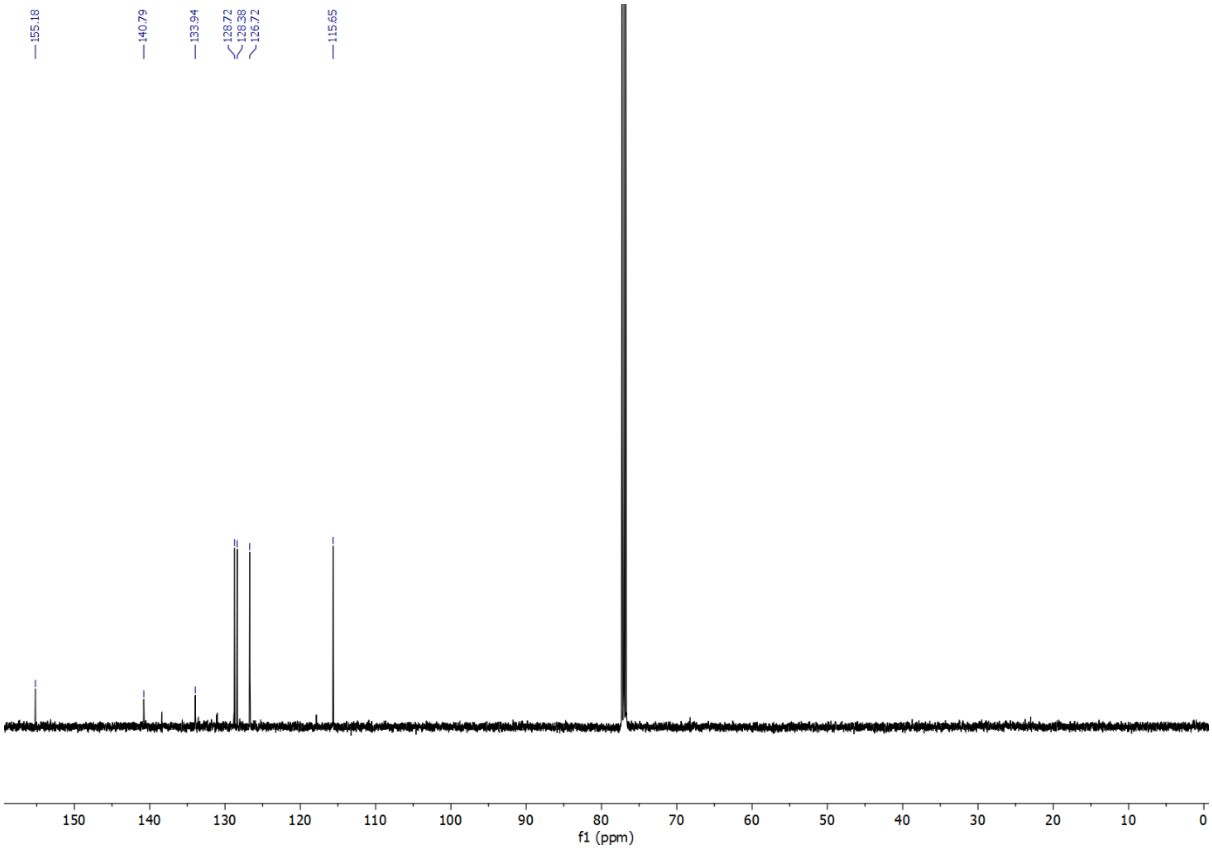

HO

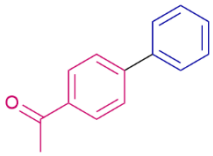
1i

^{1}H


7.55
7.53
7.51
7.42
7.42
7.40
7.40
7.39
7.38
7.31
7.31
7.31
7.29
7.29
7.27
6.98
6.97
6.96
6.96
6.95
3.84
3.51
2.09
1.15
1.96
1.00
f1 (ppm)

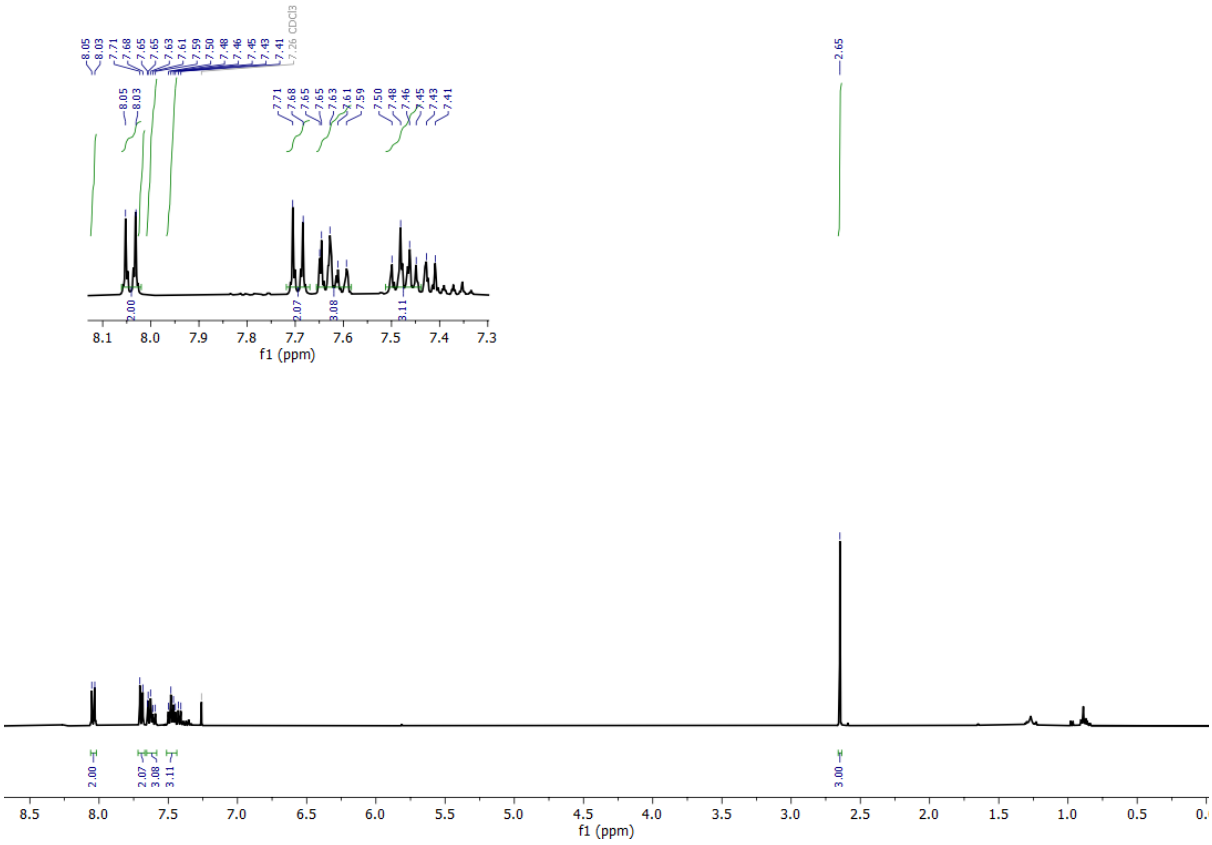
^{13}C [^{1}H]


155.18
140.79
133.94
128.72
128.38
126.72
115.65
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

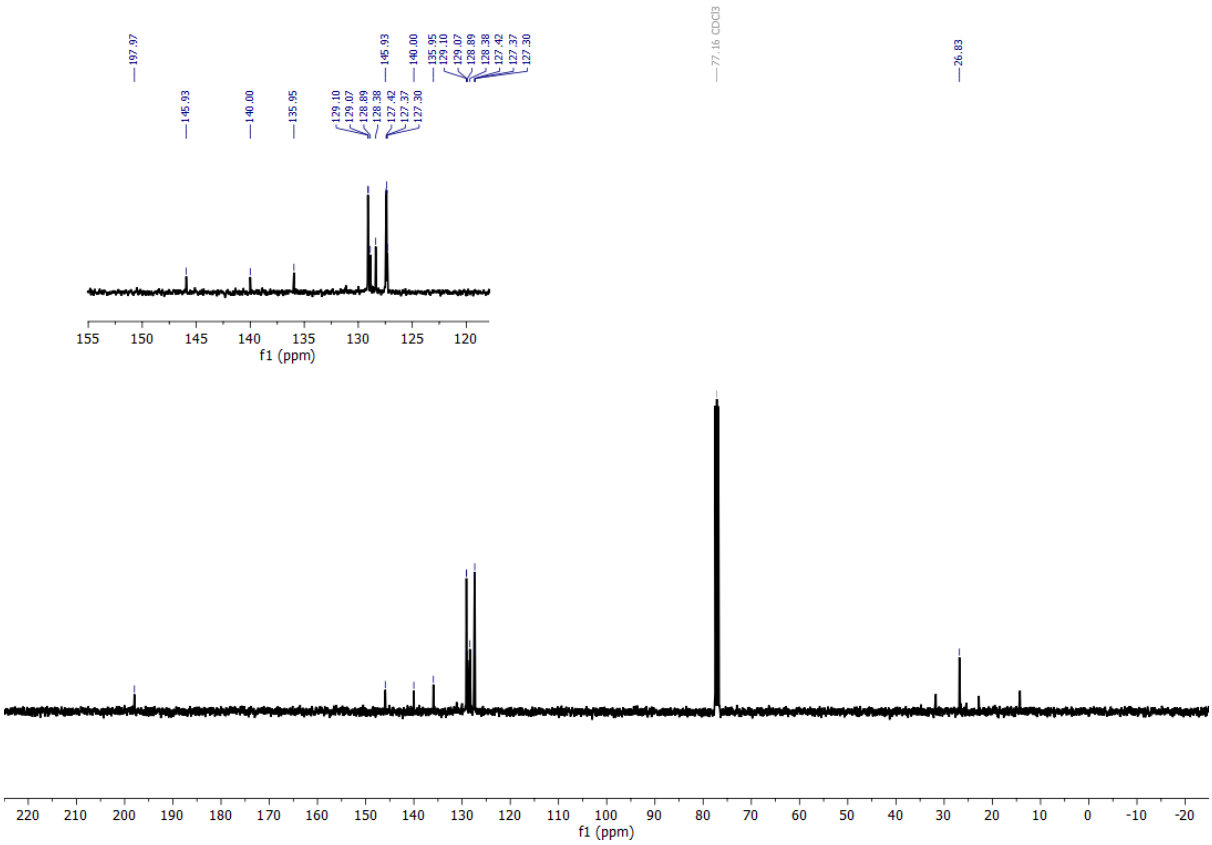


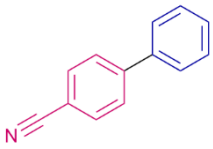
1l

^{1}H


8.05
8.03
7.71
7.68
7.65
7.65
7.63
7.61
7.59
7.50
7.48
7.46
7.45
7.43
7.41
7.26 CDCl3
2.65
2.00
2.07
3.08
3.11
3.00
f1 (ppm)

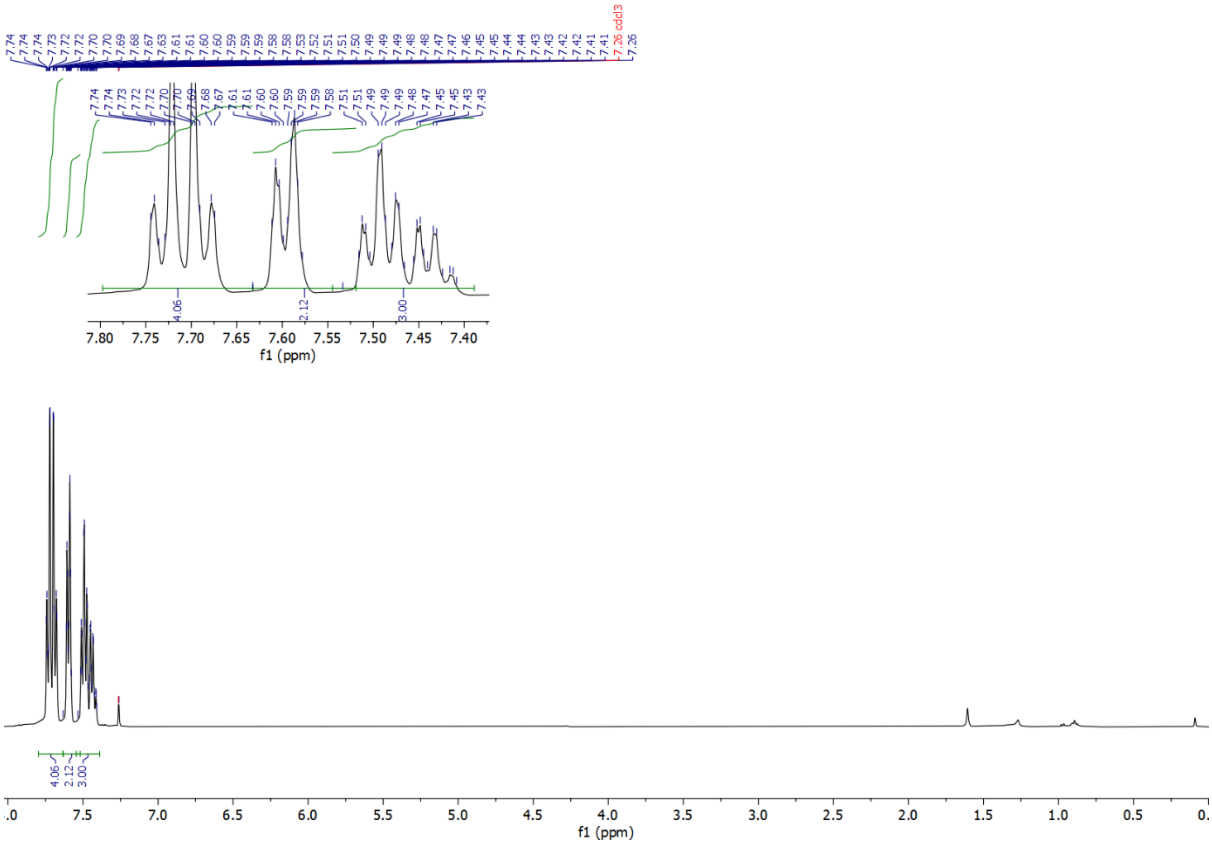
^{13}C [^{1}H]


197.97
145.93
140.00
135.95
129.10
129.07
128.89
128.38
127.42
127.37
127.30
77.16 CDCl3
26.83
155 150 145 140 135 130 125 120
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

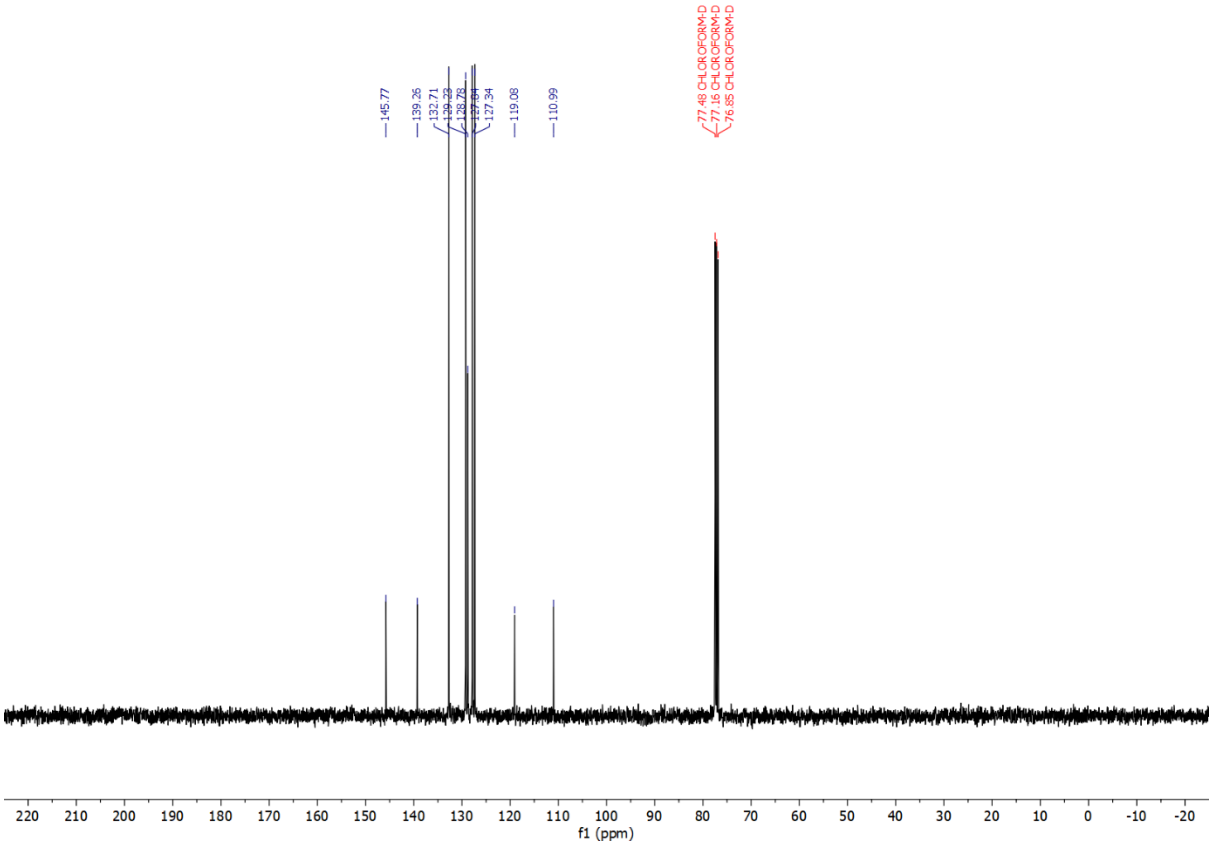


1n

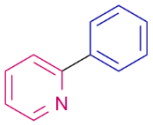
^{1}H


7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40
f1 (ppm)
4.06
2.12
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

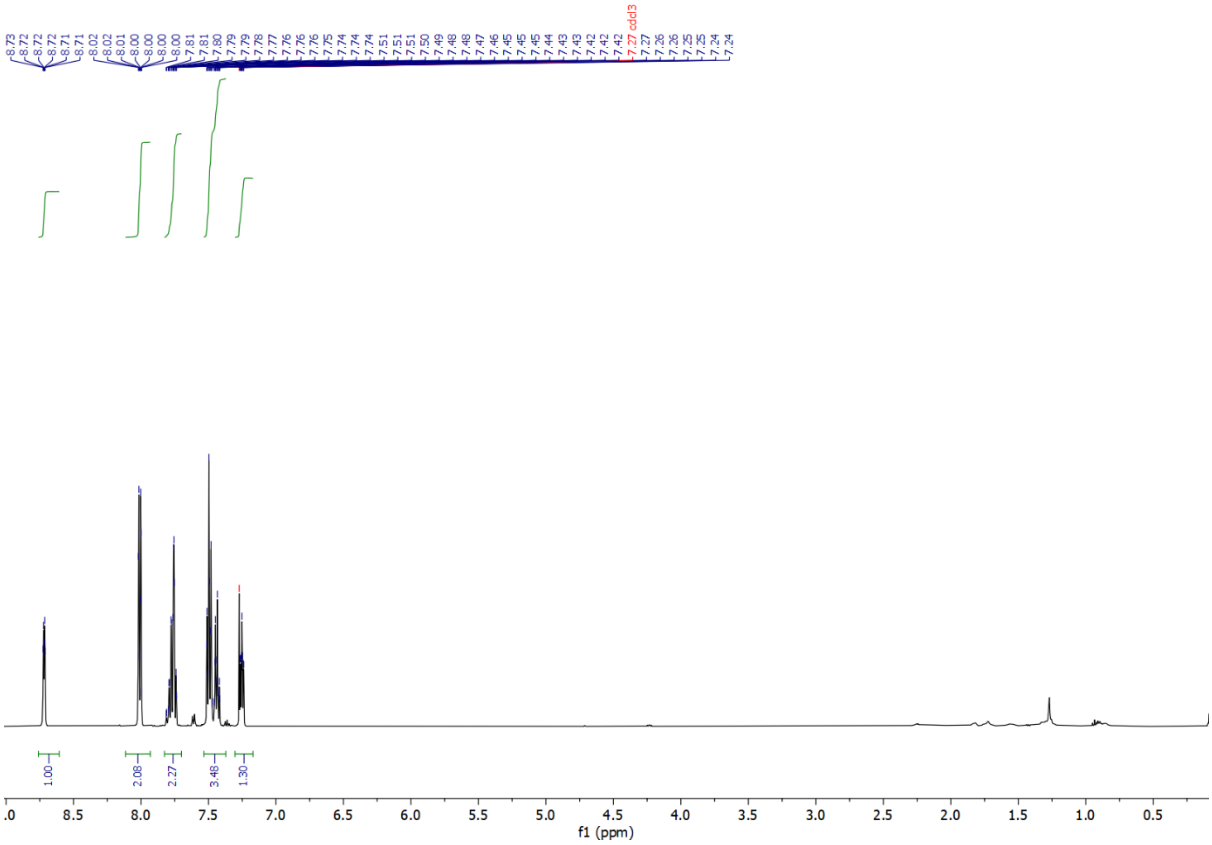
$^{13}C[^{1}H]$


145.77
139.26
132.71
129.23
128.78
127.84
127.34
119.08
110.99
77.48 CHLOROFORM-D
77.16 CHLOROFORM-D
76.85 CHLOROFORM-D
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

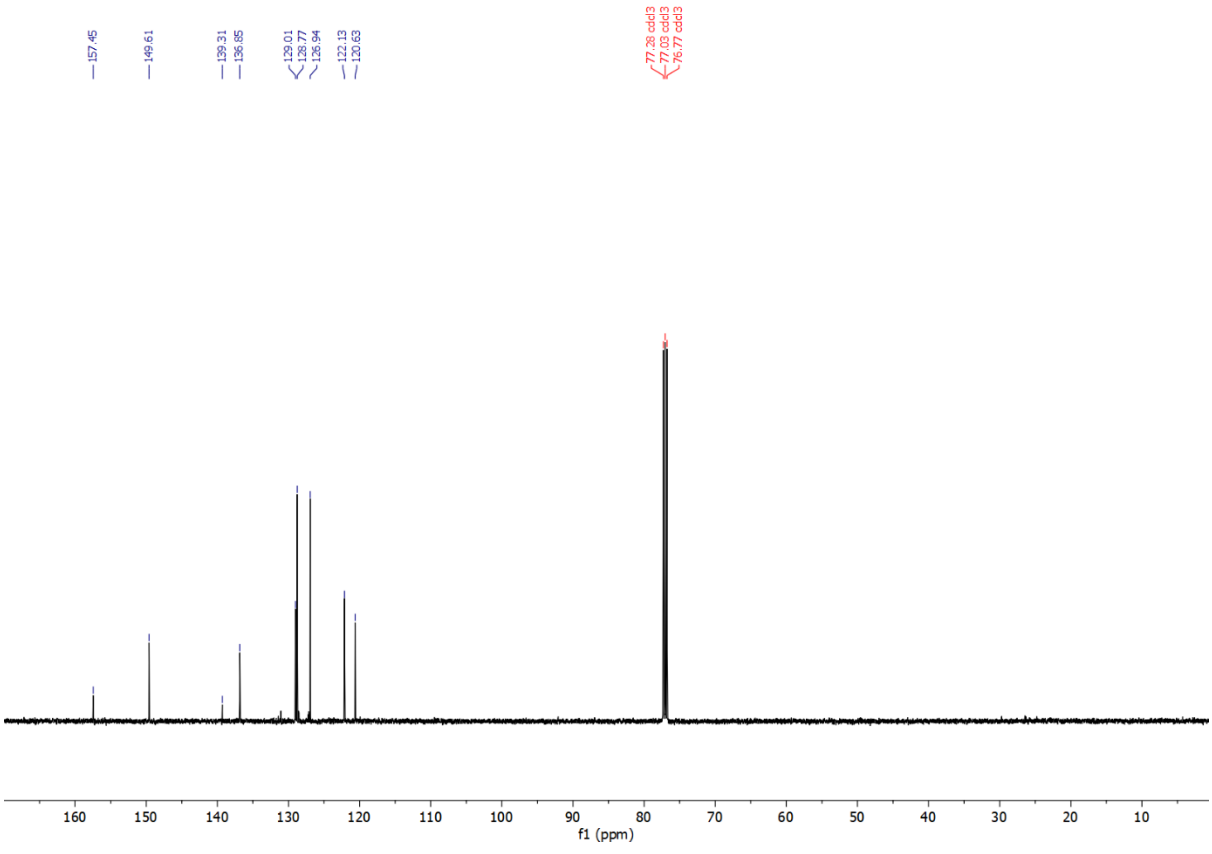
1s


N

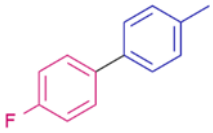
^{1}H


8.73
8.72
8.72
8.72
8.72
8.71
8.71
8.02
8.02
8.01
8.00
8.00
8.00
8.00
8.00
7.81
7.81
7.80
7.79
7.79
7.78
7.77
7.76
7.76
7.76
7.75
7.74
7.74
7.74
7.51
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.42
7.42
7.27 cdcl3
7.27
7.26
7.26
7.25
7.25
7.24
7.24
1.00
2.08
2.27
3.48
1.30
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

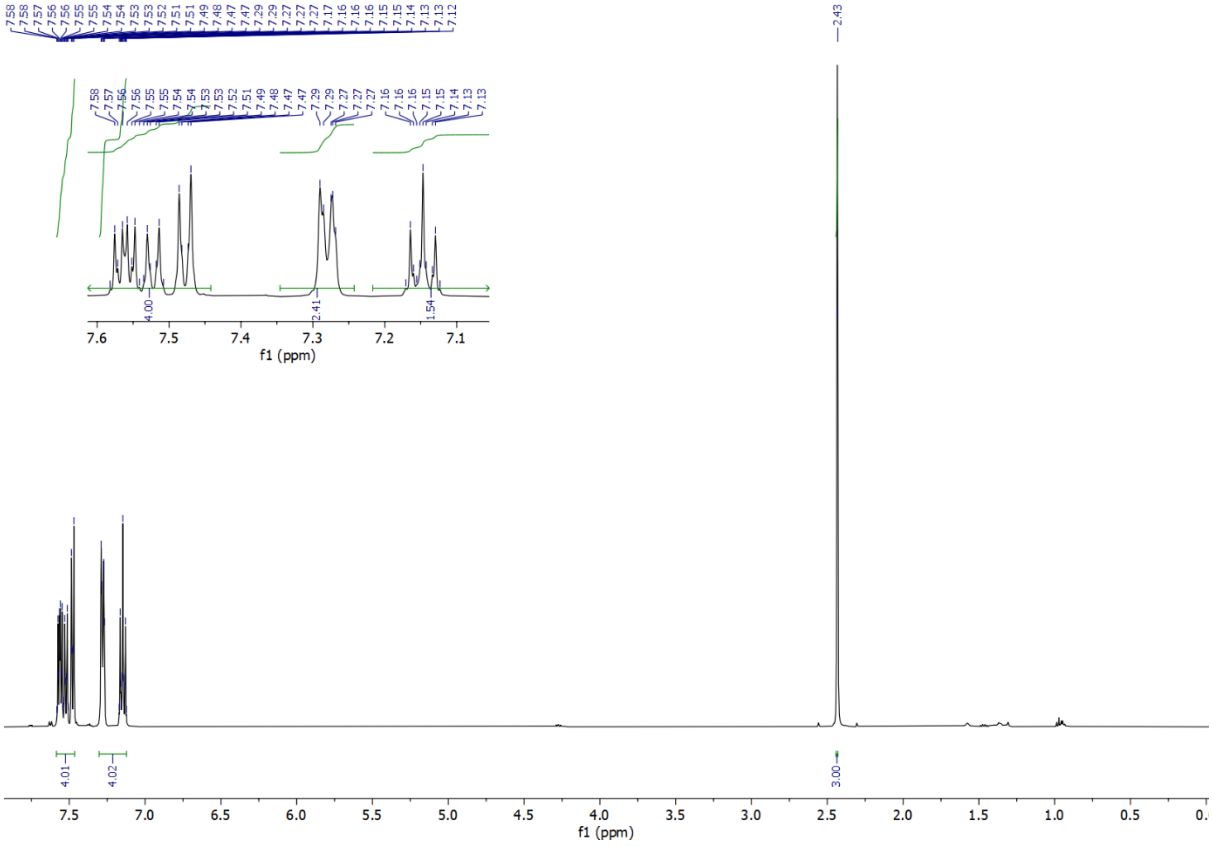
^{13}C [^{1}H]


157.45
149.61
139.31
136.85
129.01
128.77
126.94
122.13
120.63
77.28 cdcl3
77.03 cdcl3
76.77 cdcl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

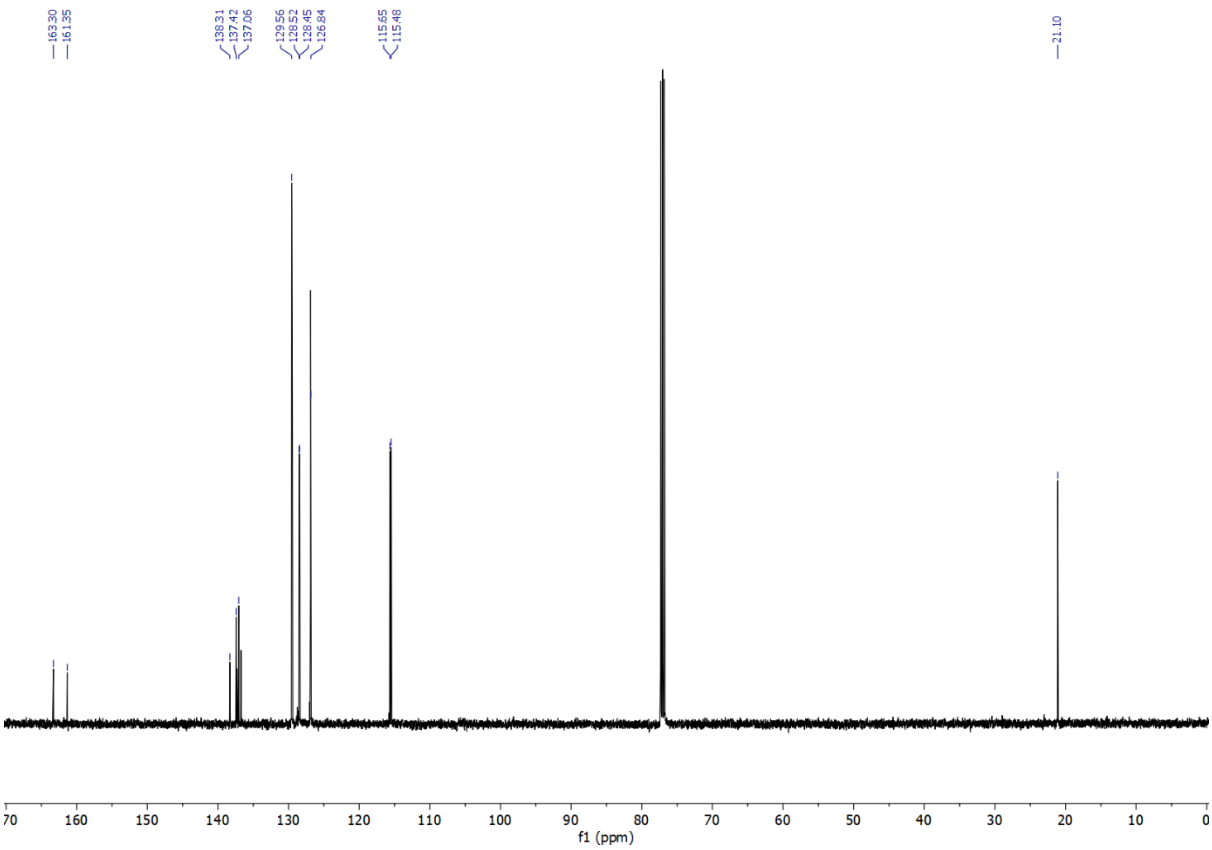
2a


F

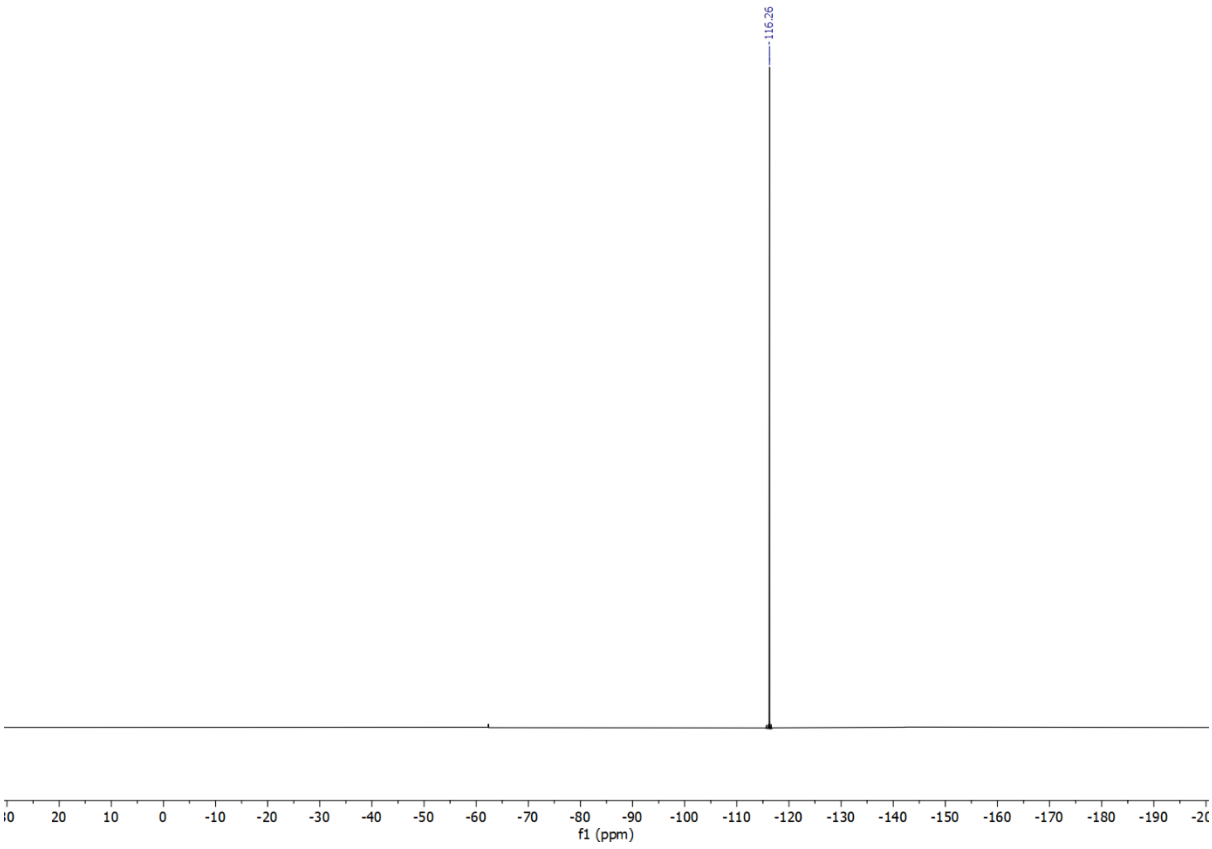
^{1}H


7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.49
7.48
7.47
7.47
7.29
7.27
7.27
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.12
2.43
4.00
2.41
1.54
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
4.01
4.02
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

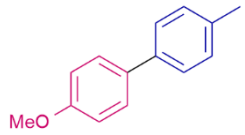
^{13}C[^{1}H]


163.30
161.35
138.31
137.42
137.06
129.56
128.52
128.45
126.84
115.65
115.48
21.10
f1 (ppm)

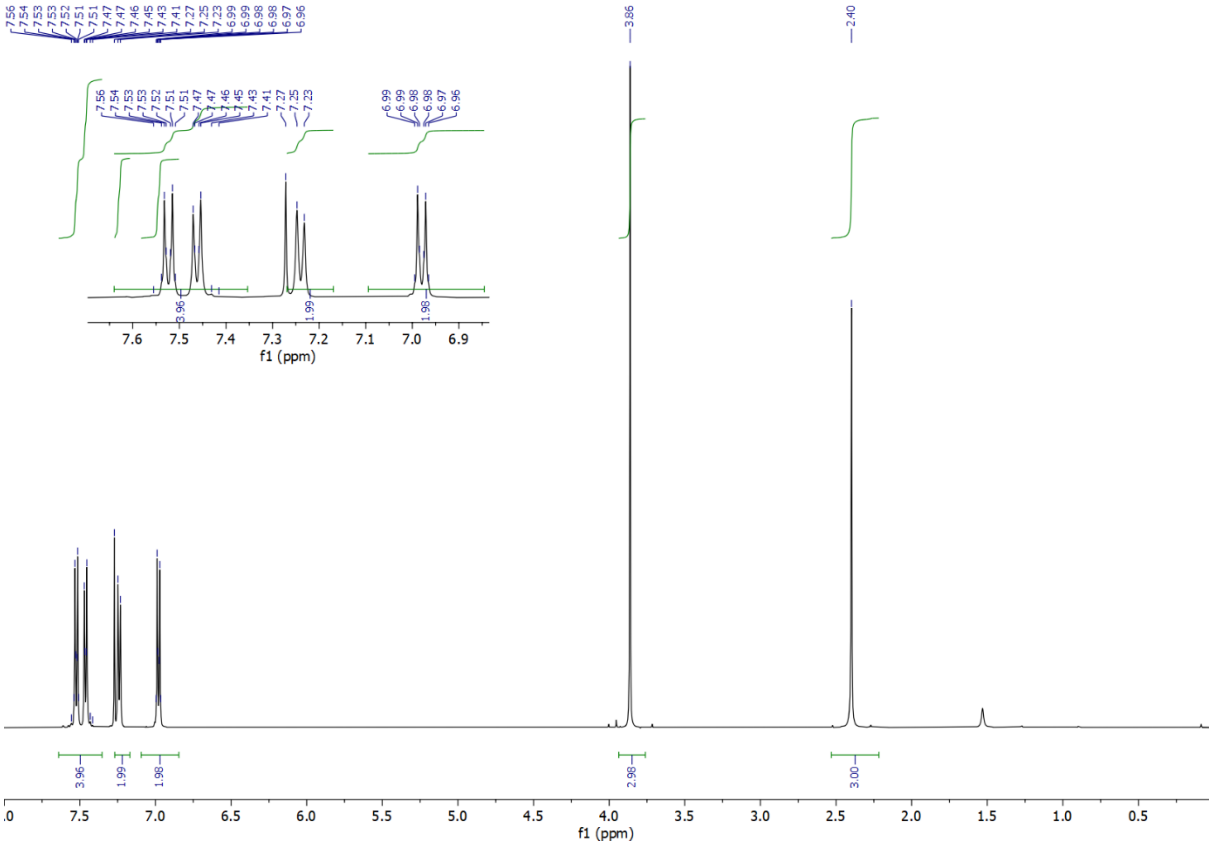
^{19}F


116.26
f1 (ppm)

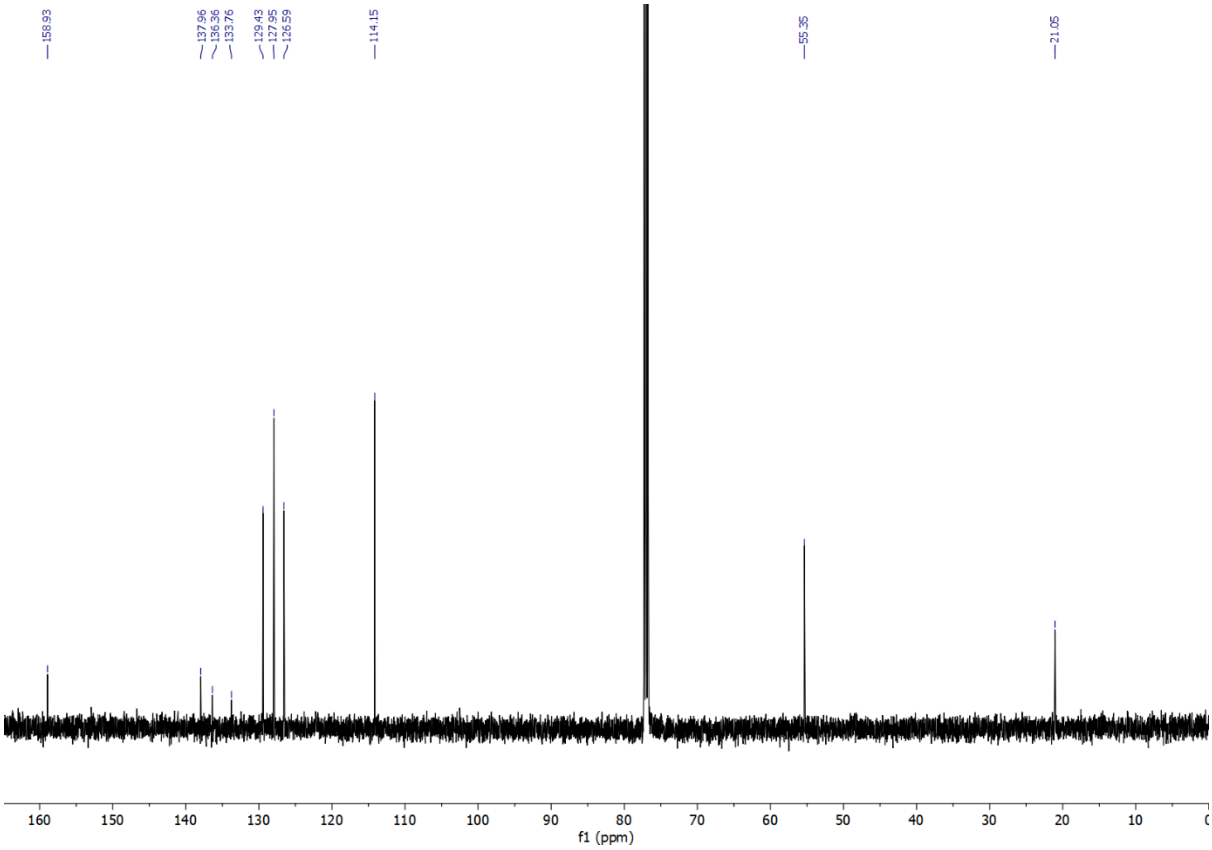
2b


MeO

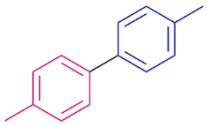
^{1}H


7.56
7.54
7.53
7.53
7.52
7.51
7.51
7.47
7.47
7.46
7.45
7.43
7.41
7.27
7.25
7.23
6.99
6.99
6.98
6.98
6.97
6.96
3.86
2.40
3.96
1.99
1.98
2.98
3.00
f1 (ppm)

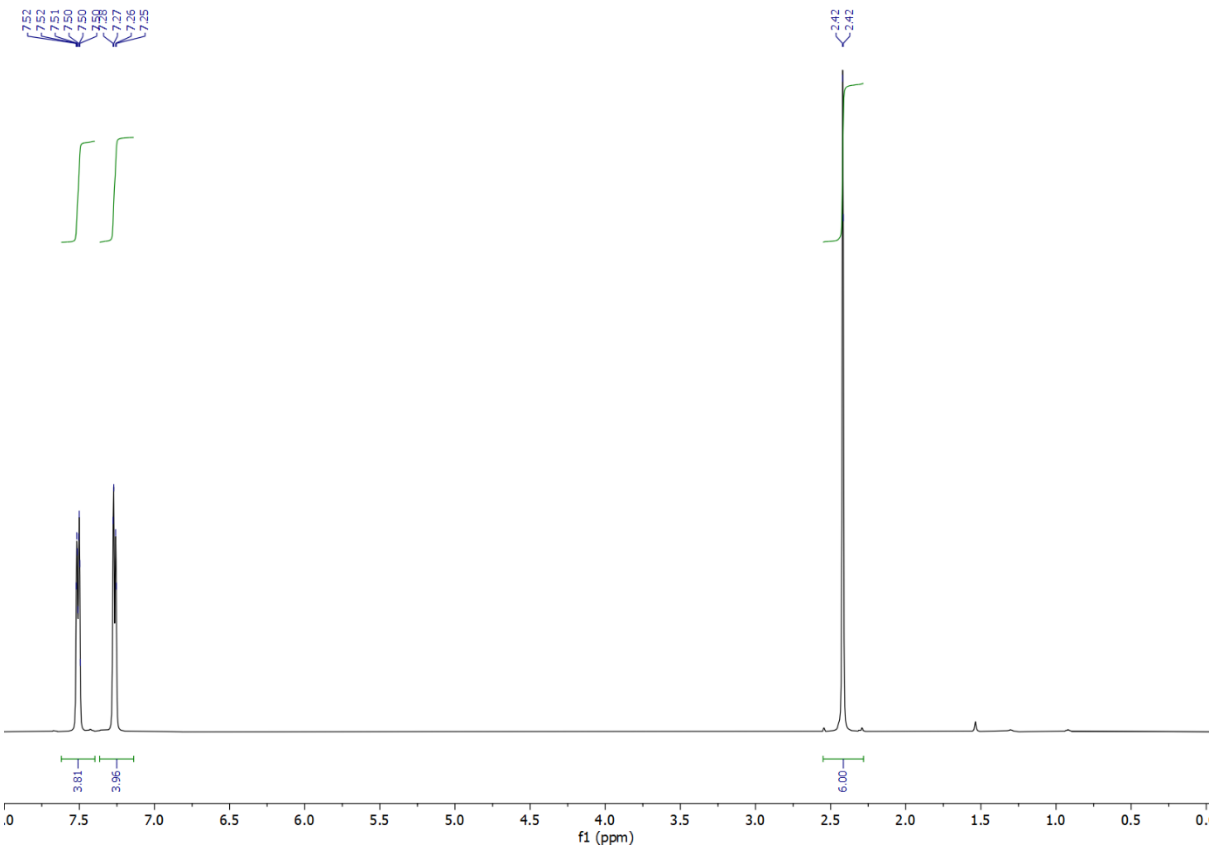
^{13}C[^{1}H]


158.93
137.96
136.36
133.76
129.43
127.95
126.59
114.15
55.35
21.05
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

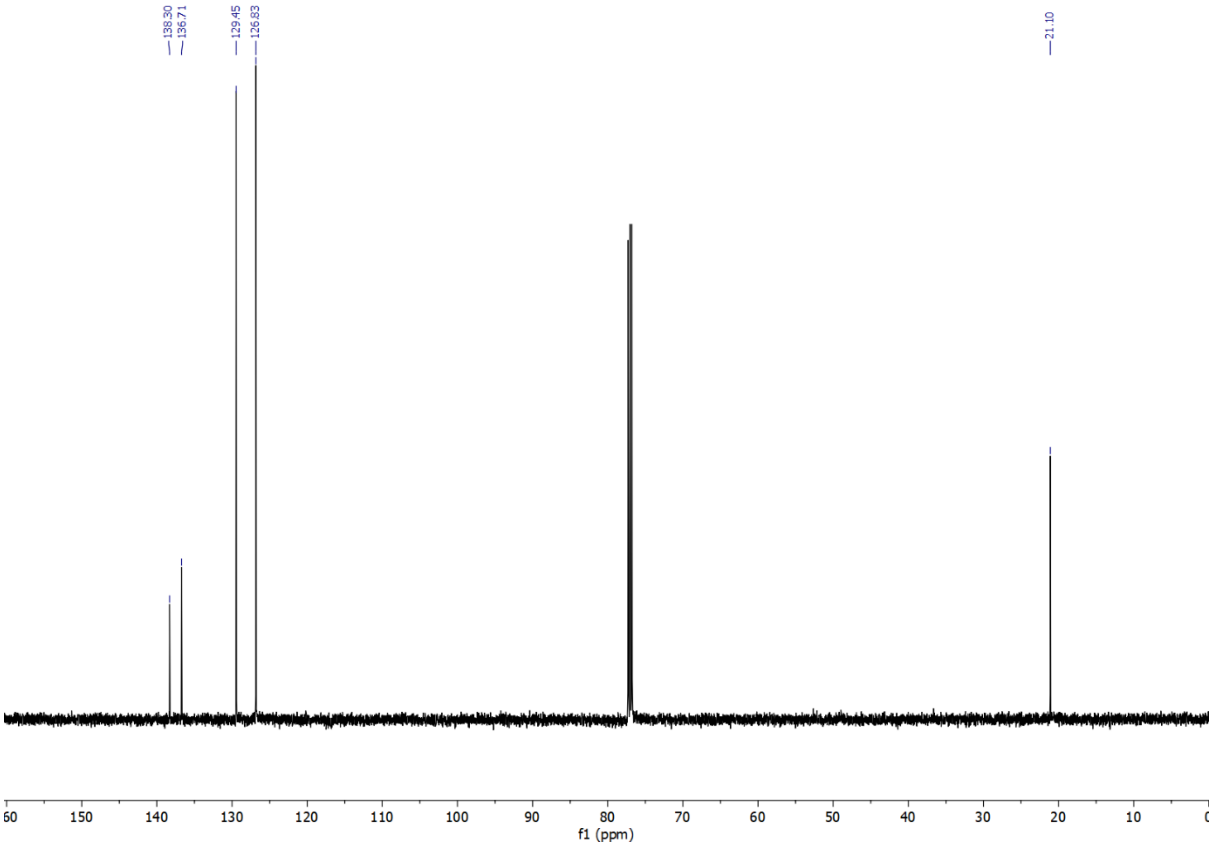
2c



^{1}H


7.52
7.52
7.51
7.50
7.50
7.27
7.26
7.25
2.42
2.42
3.81
3.96
6.00
f1 (ppm)

$^{13}C[^{1}H]$

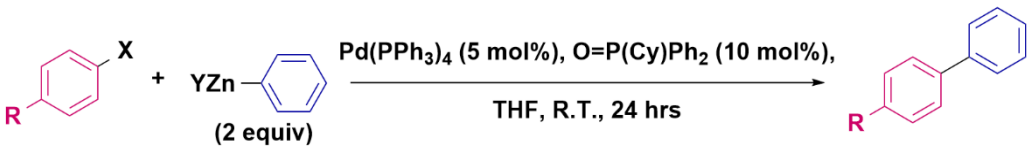

138.30
136.71
129.45
126.83
21.10
f1 (ppm)

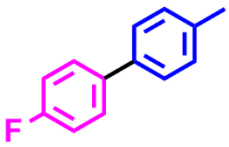
Ligand Optimisation (Table S1):

Entry	L (Phosphine oxide)	Spec. Conversion (%)
1	Tricyclohexyl phosphine oxide	92
2	Tri-octyl phosphine oxide	96
3	Cyclohexyl diphenylphosphine oxide	>99
4	Triphenyl phosphine oxide	91
5	Triphenyl phosphine oxide*	97
6	Diphenyl(2,4,6-trimethyl benzoyl) phosphine oxide	89
7	3-methyl-2-phenyl-2-phospholene oxide	86
8	1,2-bis diphenylphosphinoethane monoxide	7

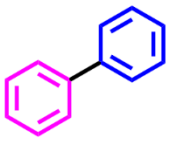
Conditions: 0.3 mmol 4-Iodotoluene, 0.6 mmol KO^tBu, 0.6 mmol Phenyl boronic acid, 10 mol% Phosphine oxide, 5 mol% Pd $(OAc)_2$, 3ml THF, R.T., 24 hrs.(*5 mol% $PdCl_2$).

Negishi Substrates (Table S2):

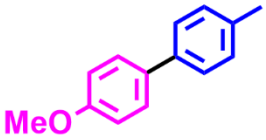




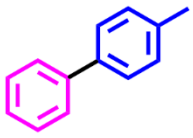
X= Y= I, [99%], (78%)



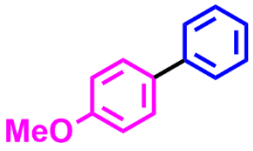
X= I Y= Br, [99%], (74%)



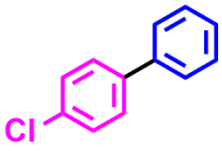
X= Y= I, [98%], (85%)
X= I, Y= Br, [81%], (57%)



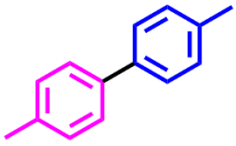
X= Y= I, [99%], (80%)



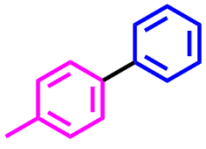
X= I, Y= Br, [98%], (65%)
X=Y=Br, [19%]



X= I,Y= Br, [99%], (56%)



X= Y= I, [99%], (83%)



X= I Y= Br, [81%], (60%)

Conditions: 0.3 mmol Ar-X, 0.6 mmol Negishi reagent, 10 mol% Phosphine oxide, 5 mol% Pd $(PPh_3)_4$, 3ml THF, R.T., 24 hrs.

Pd catalysed Negishi recyclability (Table S3):

Table 2. Recyclability of Pd Negishi Catalyst

Cycle[a]	Temperature (°C)	Yield (%) (Spectroscopic (Isolated))	Selectivity (2c: 2c')
1	R.T.	>99	10:1
2	R.T.	>99	11:1
3	R.T.	>99	10:1
4	R.T.	>99	16:1
5	R.T.	75	25:1
6	R.T.	88	16:1
7	R.T.[b]	90	25:1
8	R.T.[c]	96	25:1
9	R.T.[c]	94	25:1
10	R.T.[c]	92	25:1

Conditions: Recyclability studies w/ $O{=}PCyPh_2$, $Pd(PPh_3)_4$. [a] $Pd(PPh_3)_4$ (0.015mmol), Ligand (0.03mmol), 4-Iodoanisole (0.3 mmol), Tolylzinc iodide (0.6mmol), Solvent = 2ml, Reaction time = 24 hrs. Spectroscopic yield calculated with tetramethylsilane as an internal standard. Ratio of heterocoupled product 4-methoxy-4'-methyl-1,1'-biphenyl (2c) to homocoupled product 4,4'-dimethoxy-1,1'-biphenyl (2c'). [b] Reaction time = 36 hrs. [c] Reaction time = 48 hrs.

EDAX data:

EDAX analyses were carried out on an Talos F200C G2 Transmission Electron Microscope at the University of California, Merced Imaging and Microscopy Facility. Specifications: Gun type: X-FEG Gun brightness at 200 kV [A/cm2 /sr] $1.8 \cdot 10^9$ accelerating voltage: 200kv TEM information limit: 0.18 nm, TEM point to point resolution: 0.30 nm, STEM resolution: 0.20 nm, Oxford EDAX: AZtec Energy TEM Advanced with X-MaxN TSR 80mm^2 with 127eV resolution.

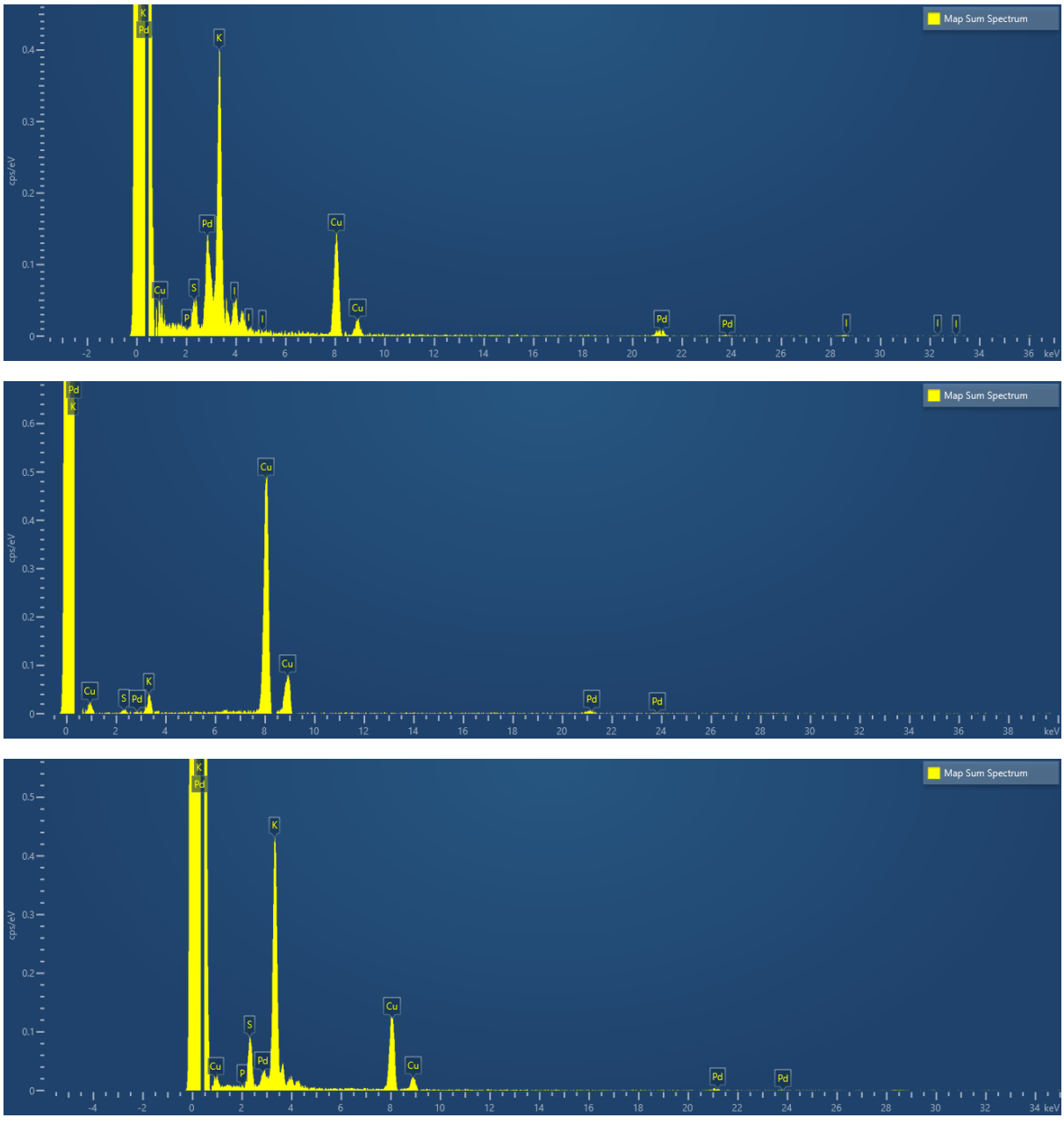


Figure S1: EDAX data for Pd Nanocomposites.

SSNMR:

Solid state NMR spectroscopy was carried out on a 500 MHz Agilent Propulse instrument with a Phoenix NMR HX Solid state NMR probe.

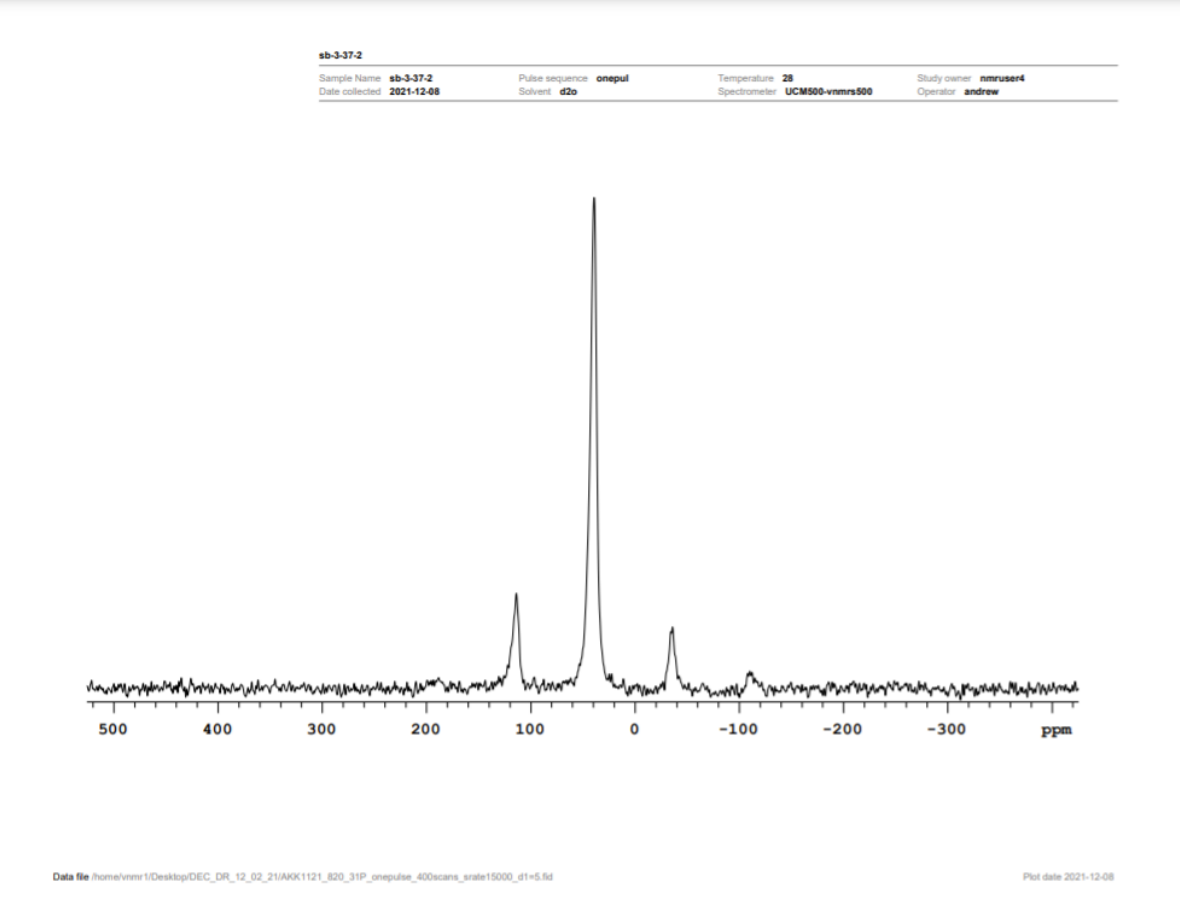
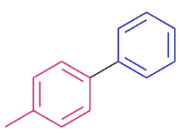


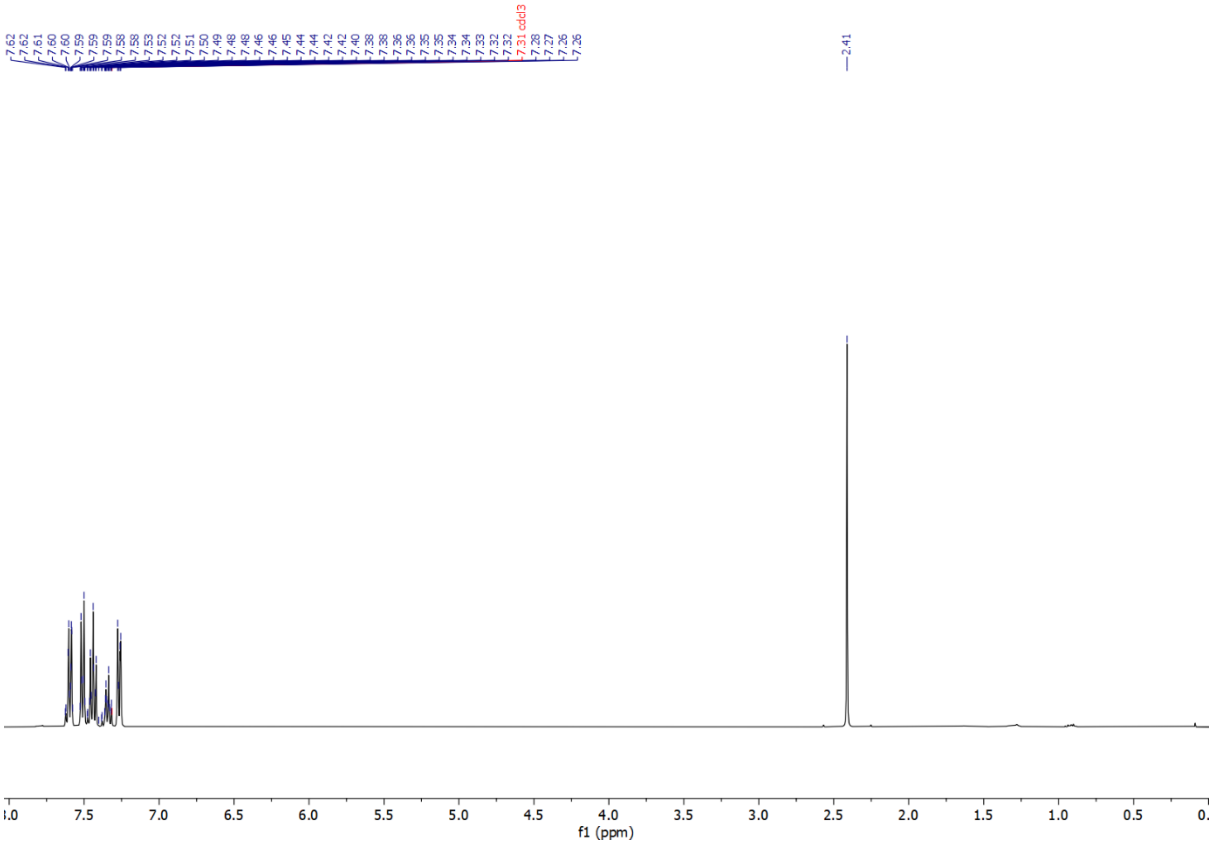
Figure S2: Solid state NMR of Pd catalyst.

Additional Negishi substrate NMR



1a

^{1}H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7.42
7.40
7.38
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7.36
7.36
7.35
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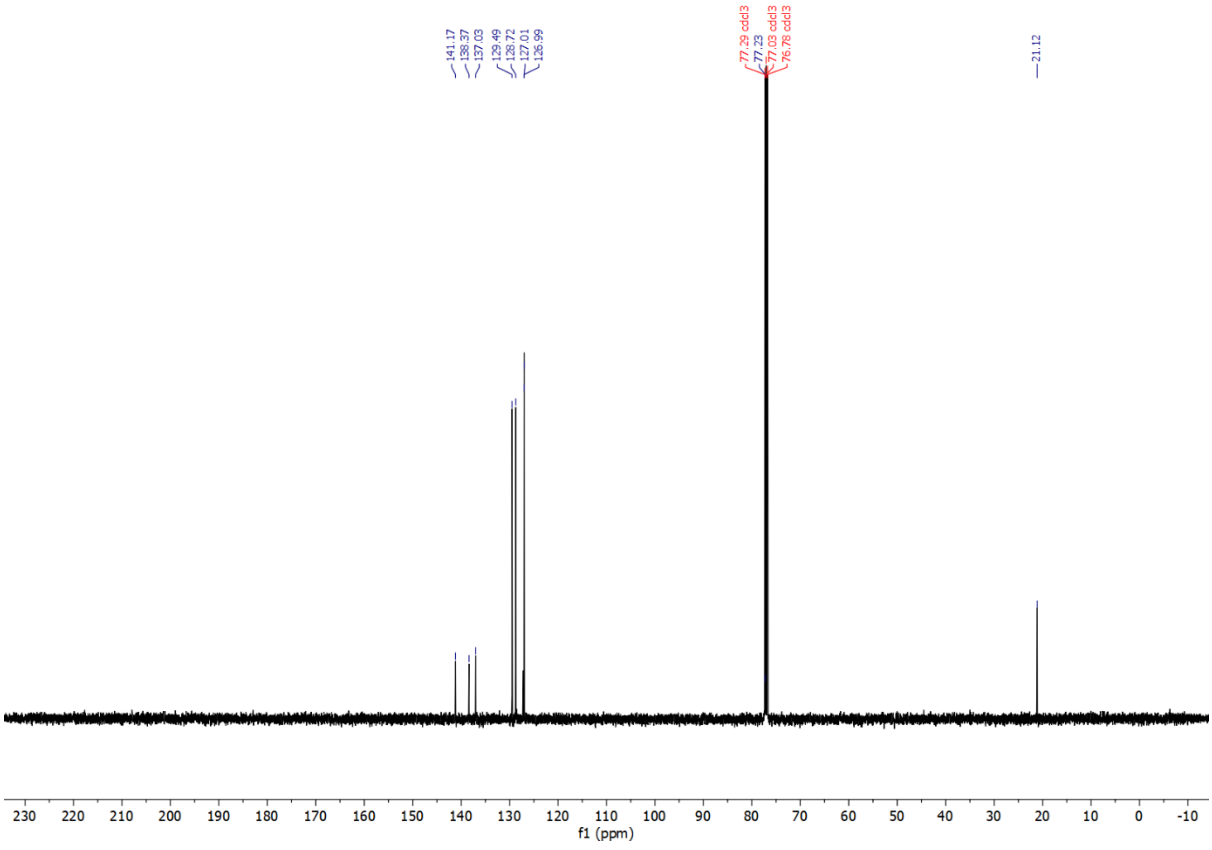
7.34
7.34
7.33
7.32
7.31 cdcl3
7.28
7.27
7.26
7.26
2.41
f1 (ppm)

^{13}C [^{1}H]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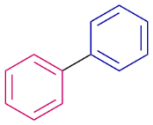
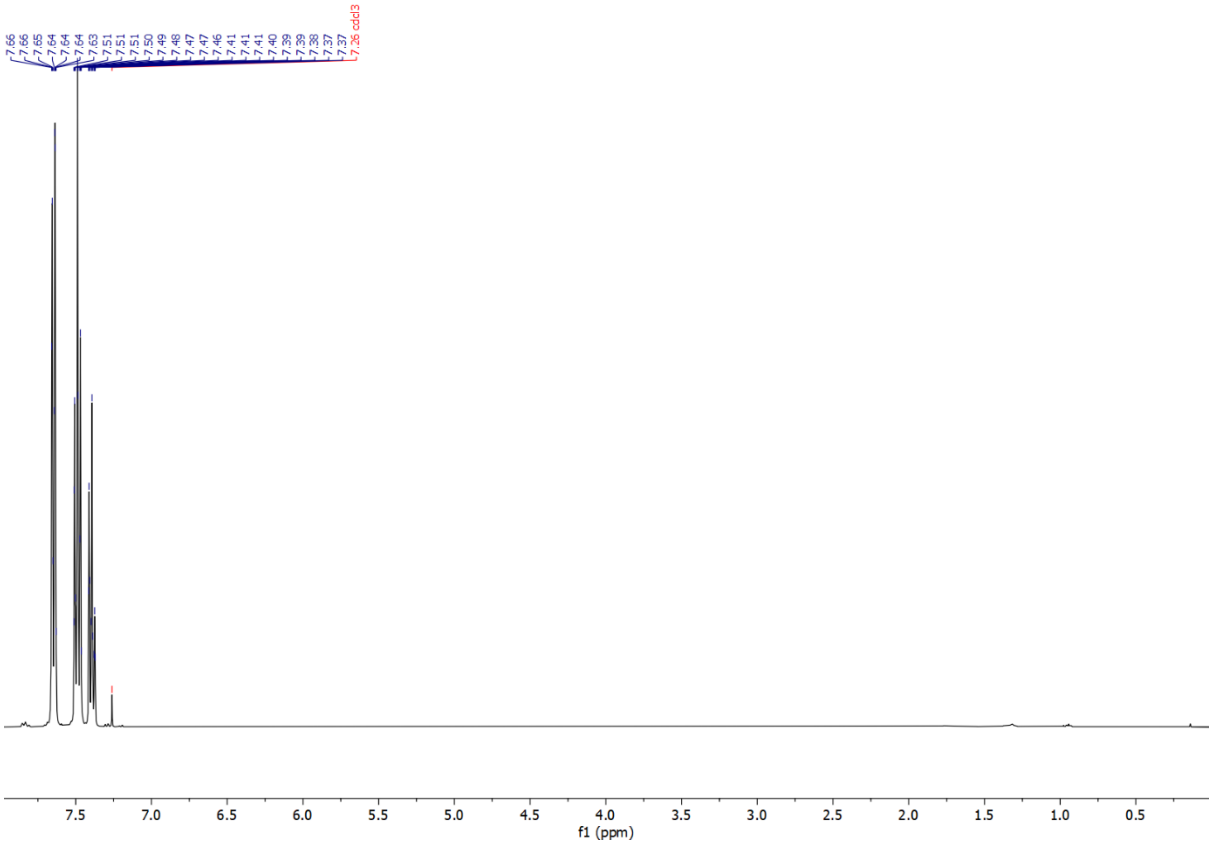
128.72
127.01
126.99
77.29 cdcl3
77.23
77.03 cdcl3
76.78 cdcl3
21.12
f1 (ppm)



1b

^{1}H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7.32
7.26 cdcl3
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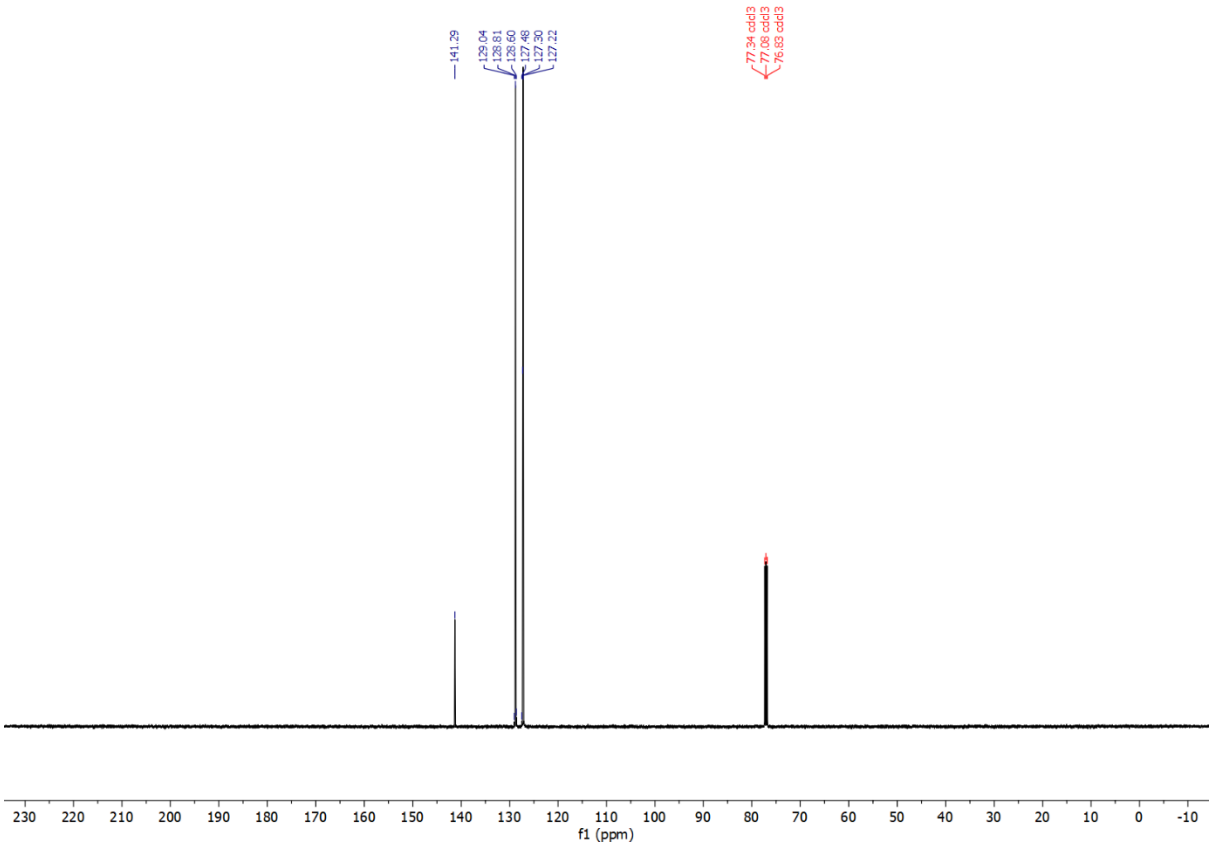
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

^{13}C [^{1}H]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127.30
127.22
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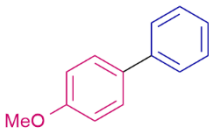
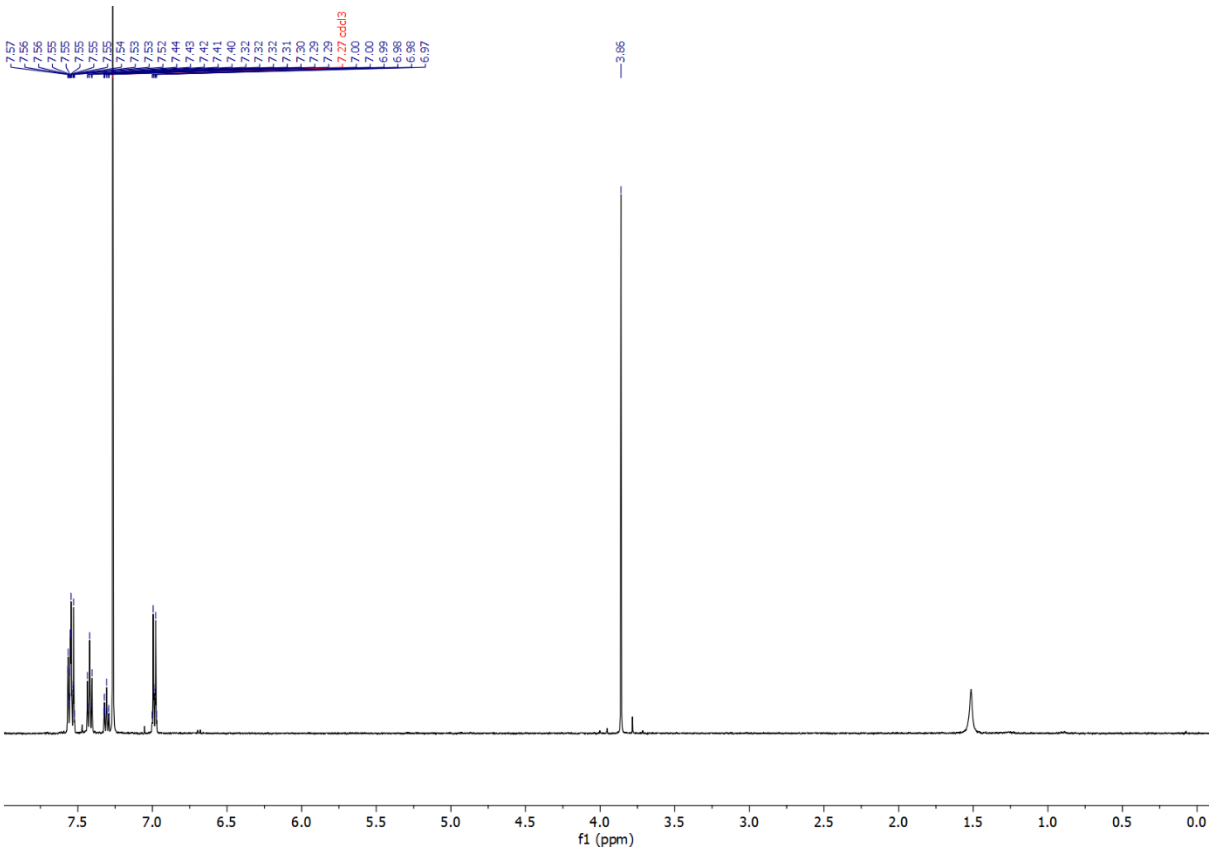
77.08 cdcl3
76.83 cdcl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO

1c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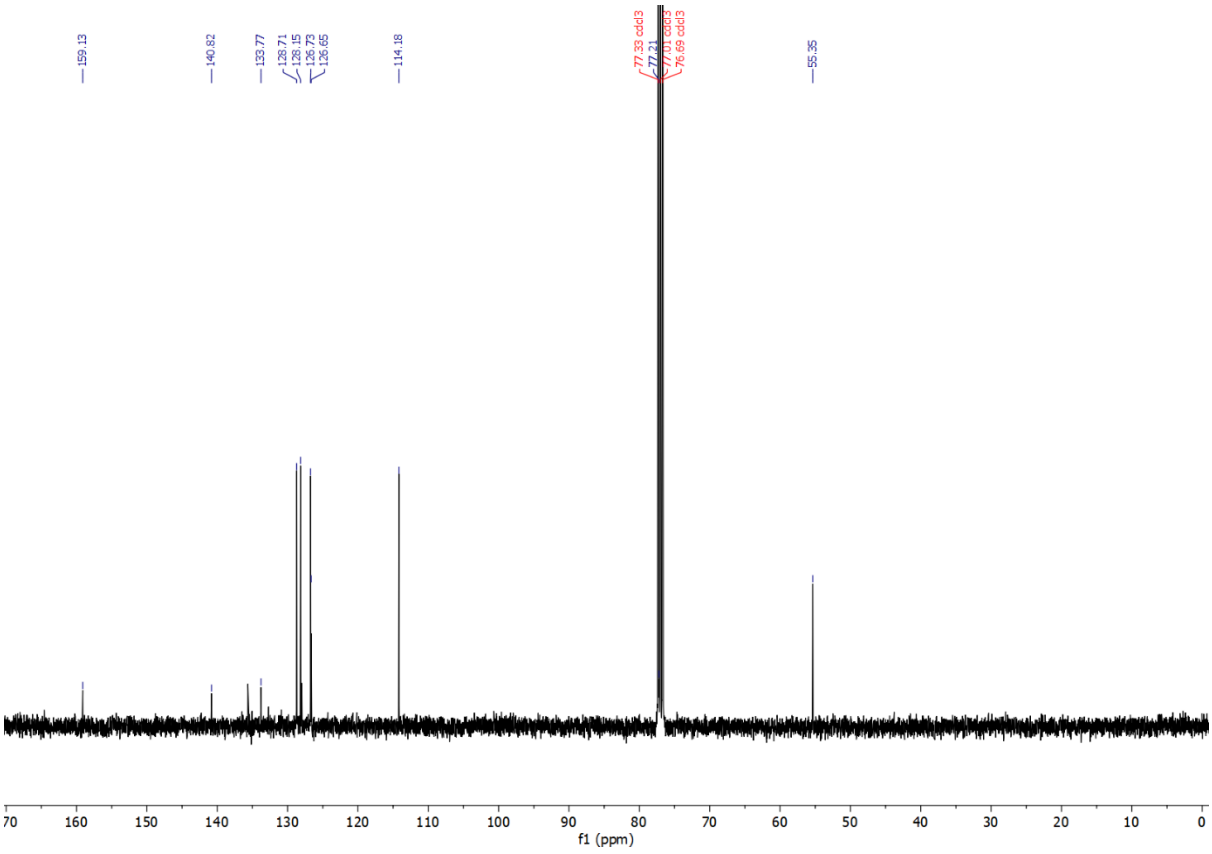
0.0
f1 (ppm)

^{13}C [^{1}H]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114.18
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77.01 cdcl3
76.69 cdcl3
55.35
70
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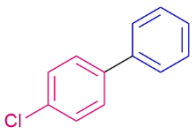
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl

1d

^{1}H


7.58
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7.37
7.36
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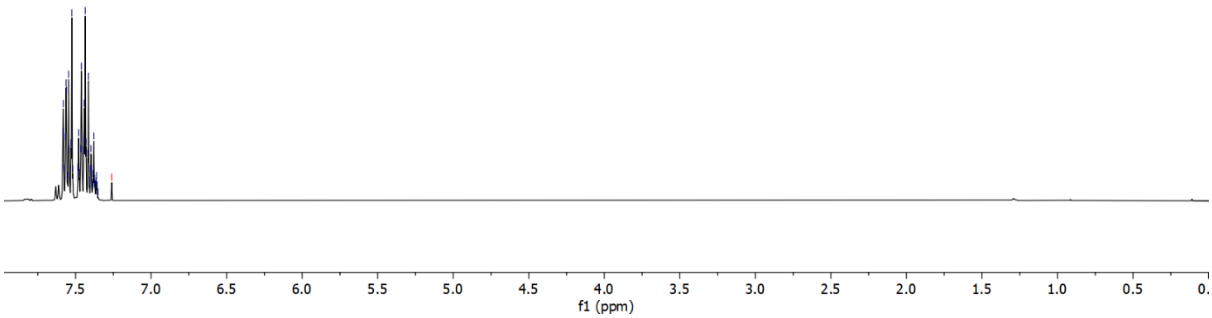
7.35
7.26 cdcl3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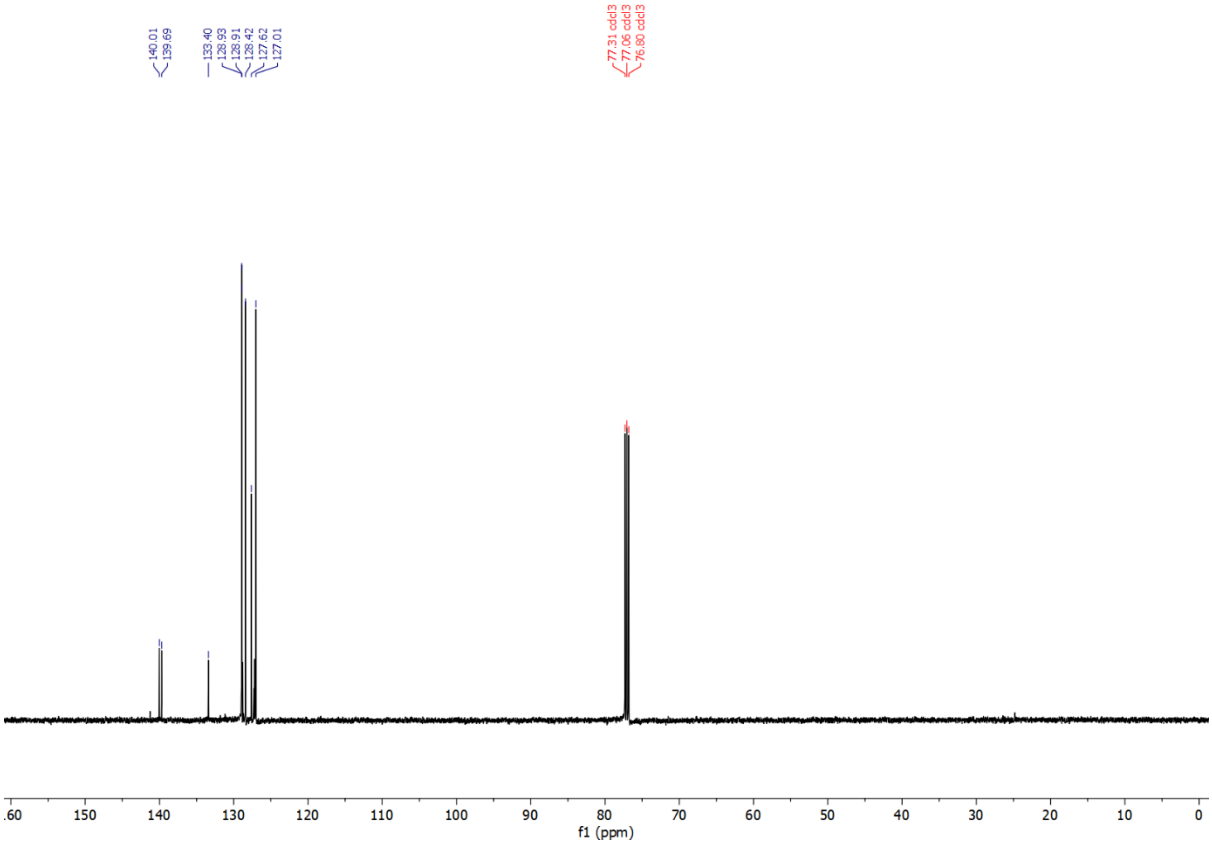
2.0
1.5
1.0
0.5
0.
f1 (ppm)

^{13}C [^{1}H]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133.40
128.93
128.91
128.42
127.62
127.01
77.31 cdcl3
77.06 cdcl3
76.80 cdcl3
f1 (ppm)