

Supporting Information for

**Pd-Catalyzed Highly Selective C(sp²)-Br Bond
Coupling Reactions of *o*-(or *m*-, or *p*-)
Chloromethyl Bromobenzene with Arylboronic
Acids**

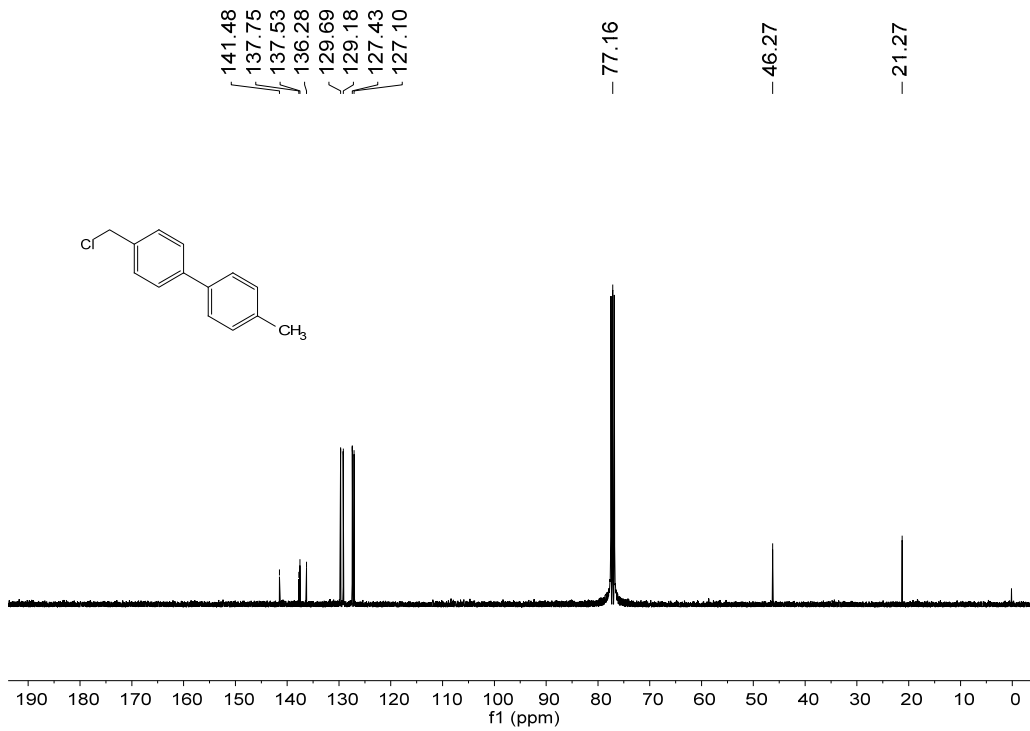
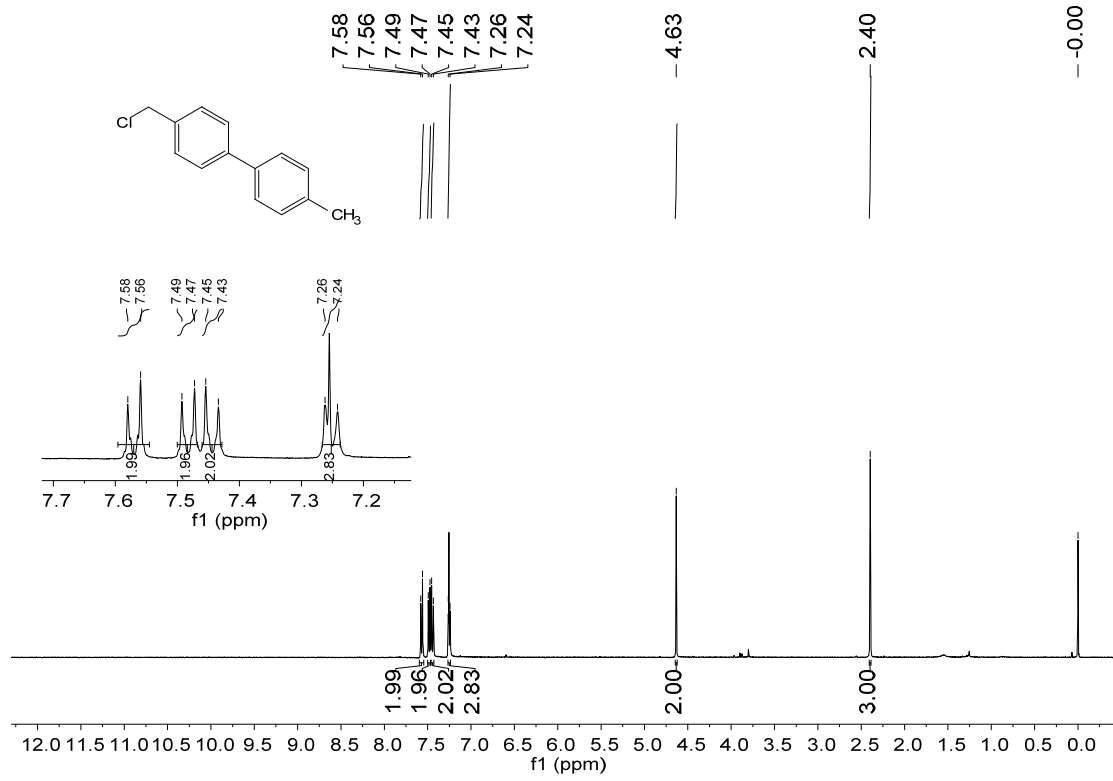
Ming-ming Pei, Ping Liu*, Yan Liu, Xin-ming Lv, Xiao-wei Ma*, and Bin Dai

School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, China; peimiming@163.com; liuyan1979810@aliyun.com; ciqlxm@163.com; db_tea@shzu.edu.cn.

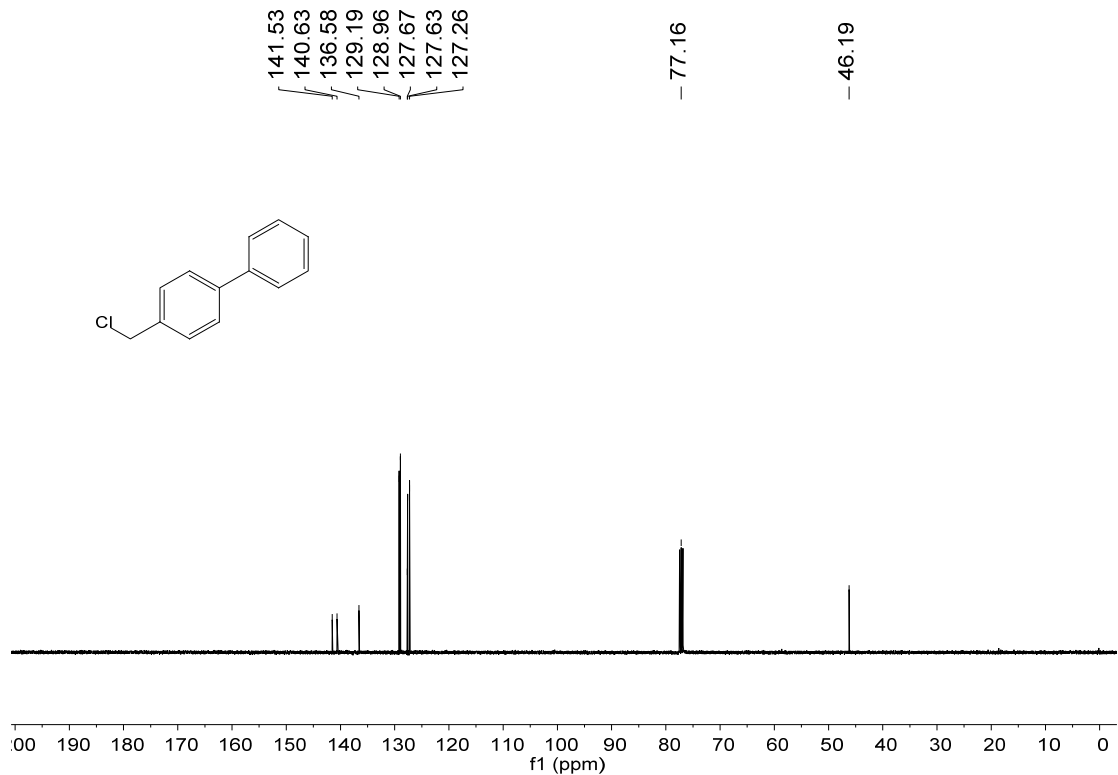
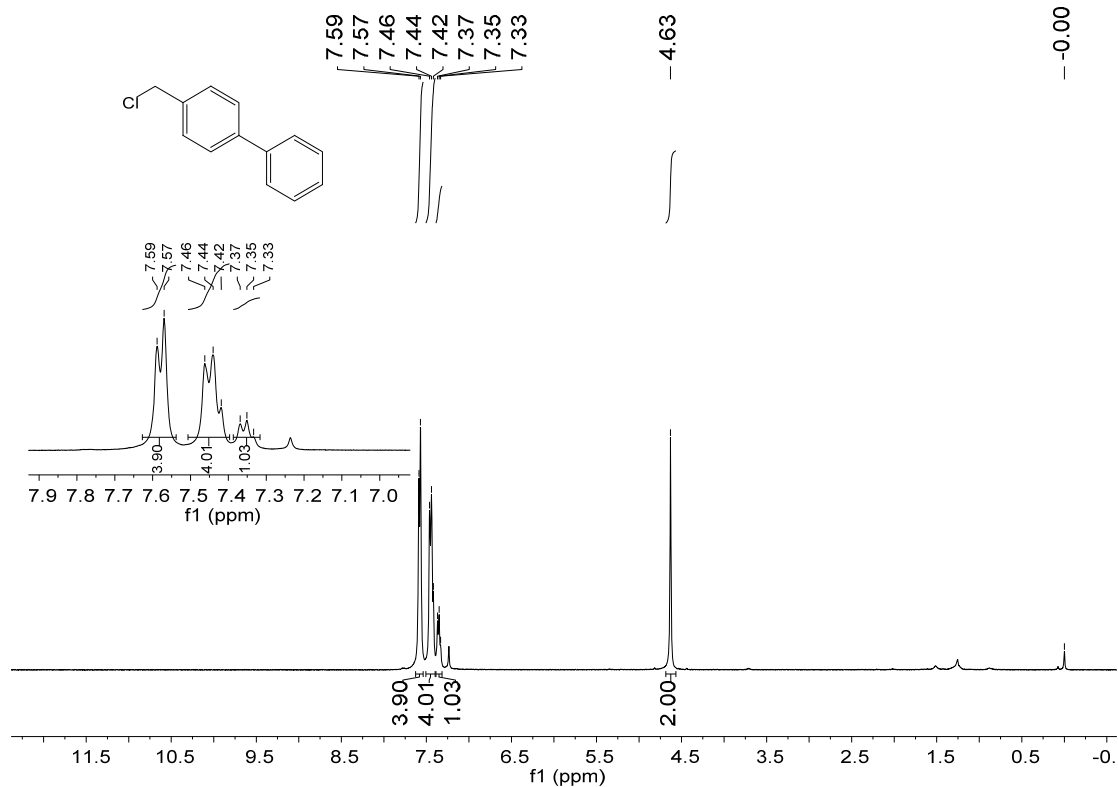
* Correspondence: e-mail: liuping1979112@aliyun.com, mxw_tea@shzu.edu.cn. Tel.: +86 0993 2057213.

Copies of ¹H NMR, ¹³C NMR and HRMS Spectra.....S2–S45

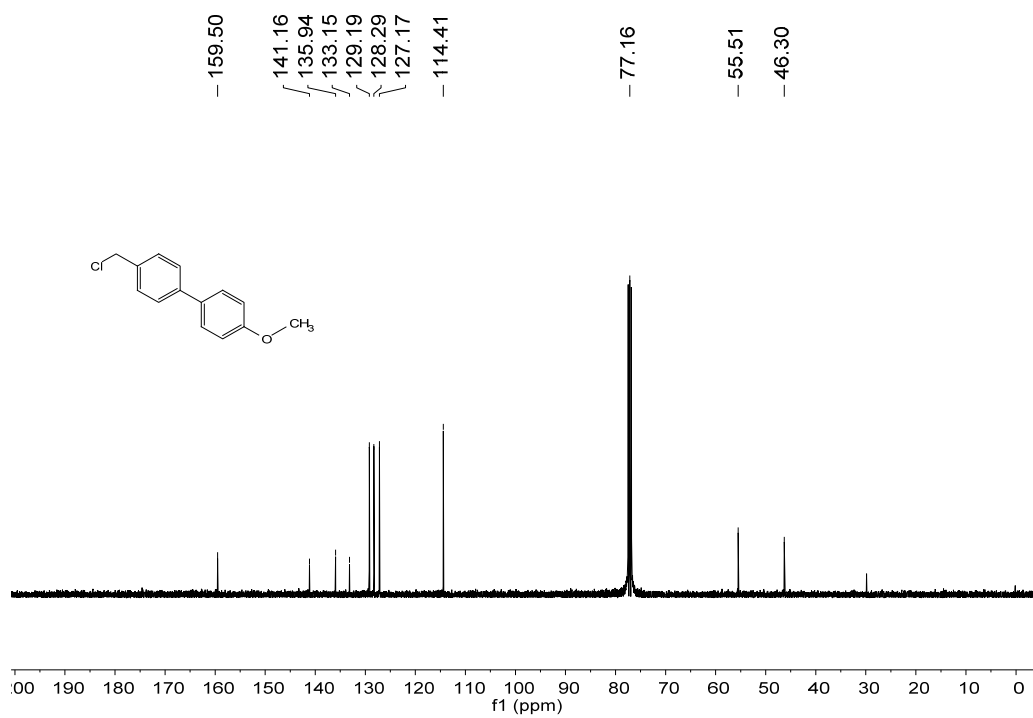
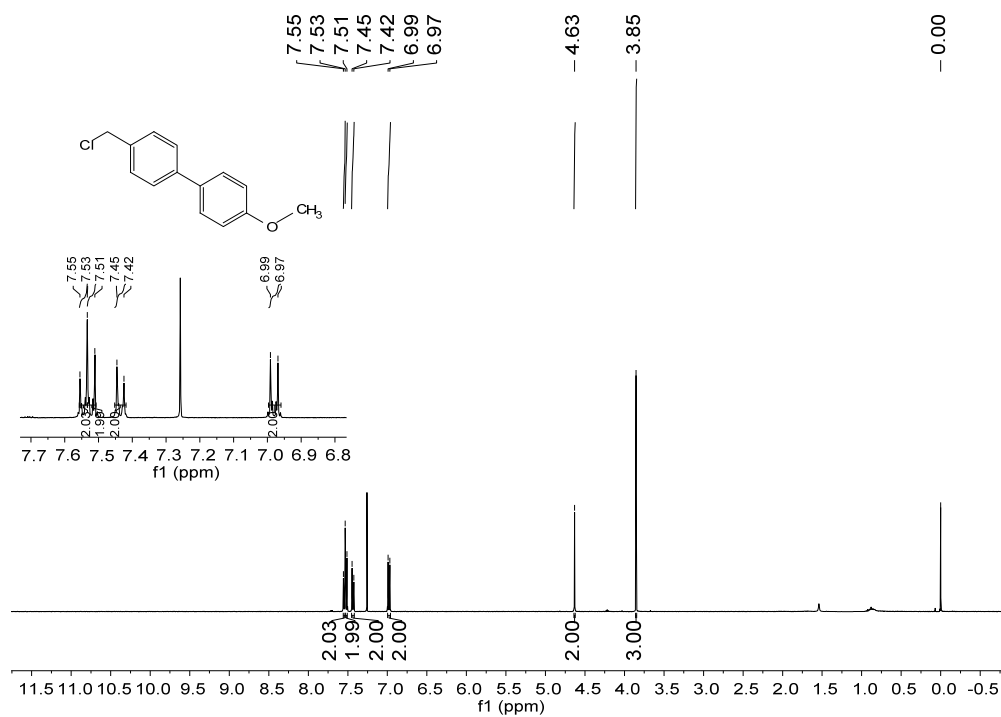
4-(chloromethyl)-4'-methyl-1,1'-biphenyl[3a]



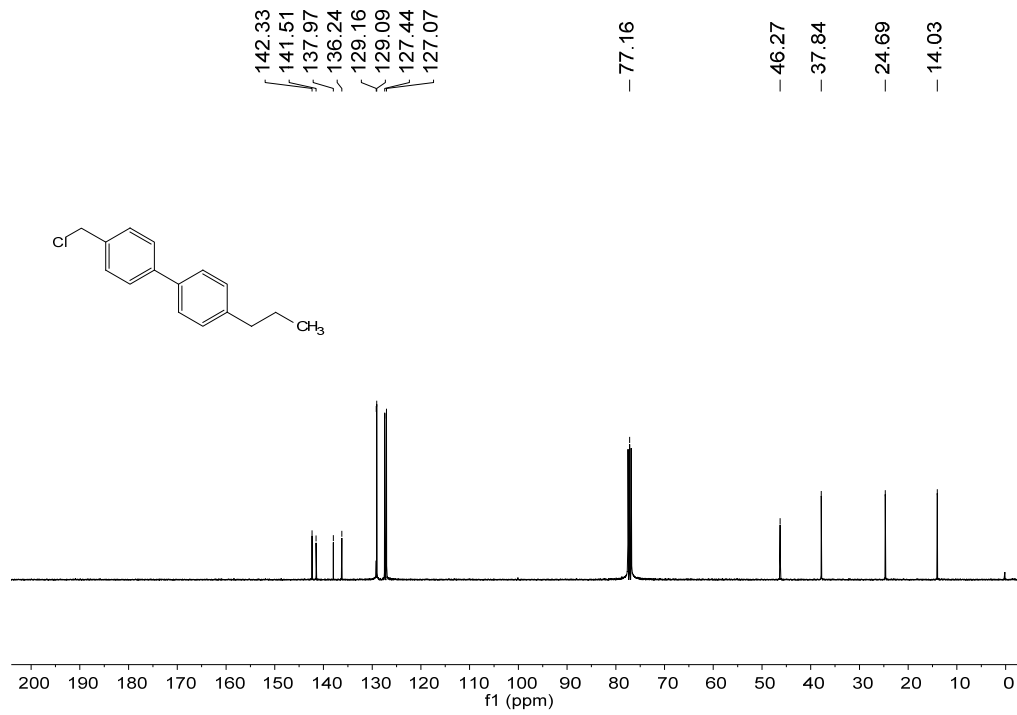
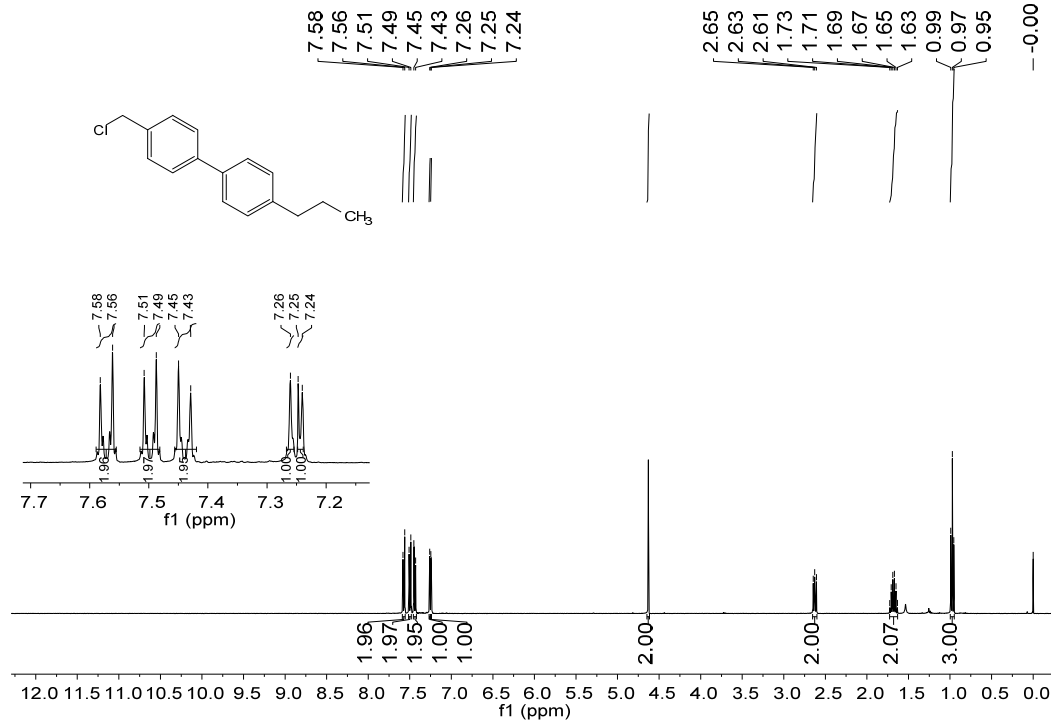
4-(chloromethyl)-1,1'-biphenyl[3b]



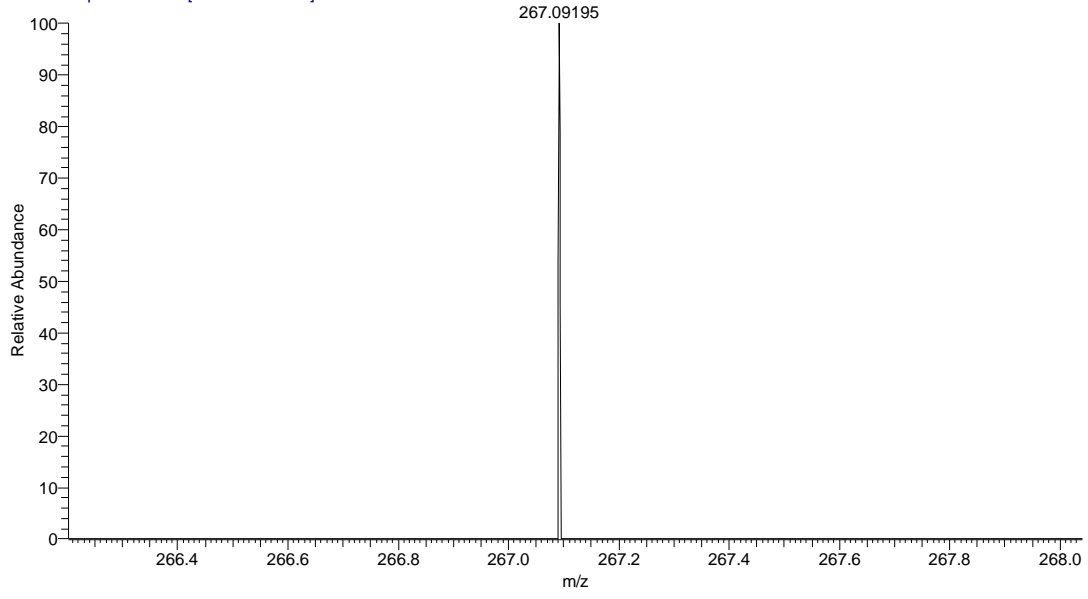
4-(chloromethyl)-4'-methoxy-1,1'-biphenyl[3c]



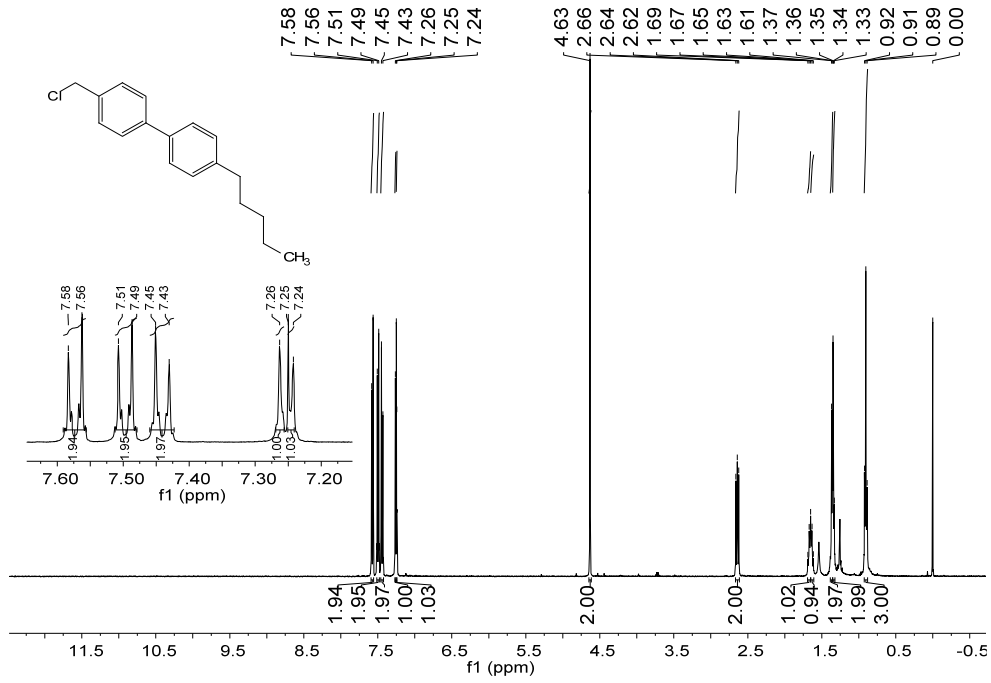
4-(chloromethyl)-4'-propyl-1,1'-biphenyl[3d]

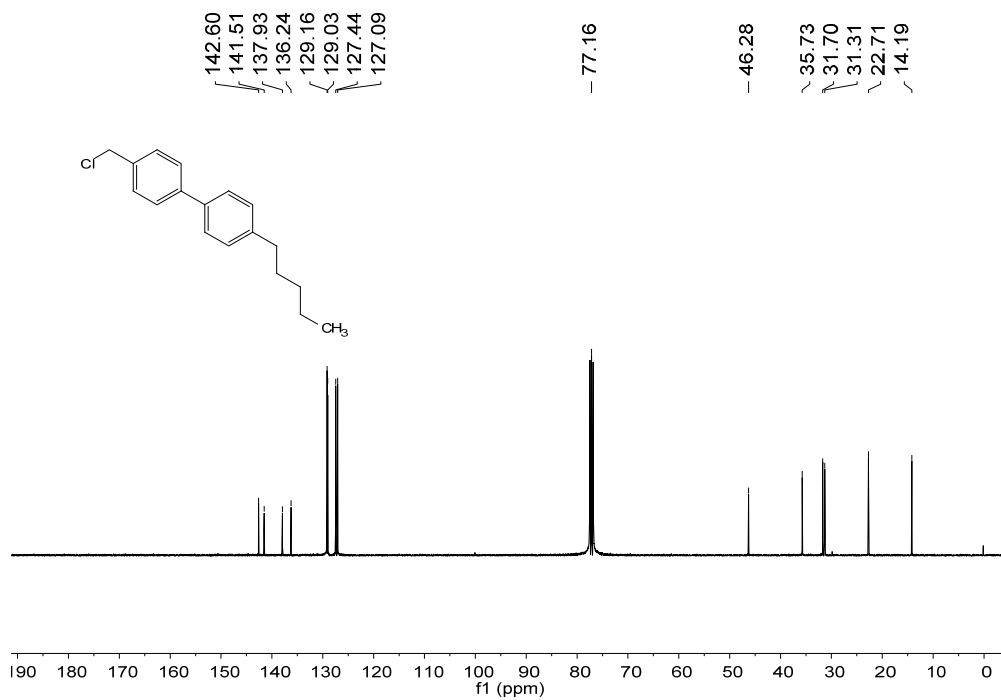


1 #15 RT: 0.27 AV: 1 NL: 6.39E2
T: FTMS + p ESI Full ms [150.00-2000.00]

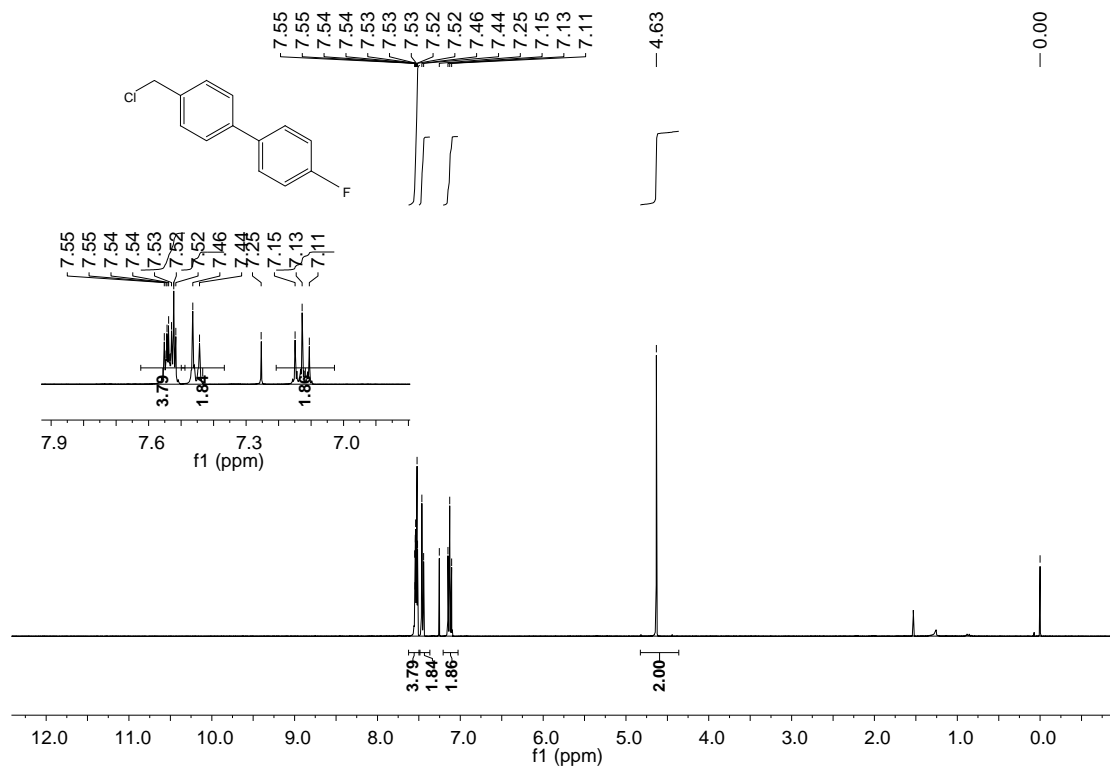


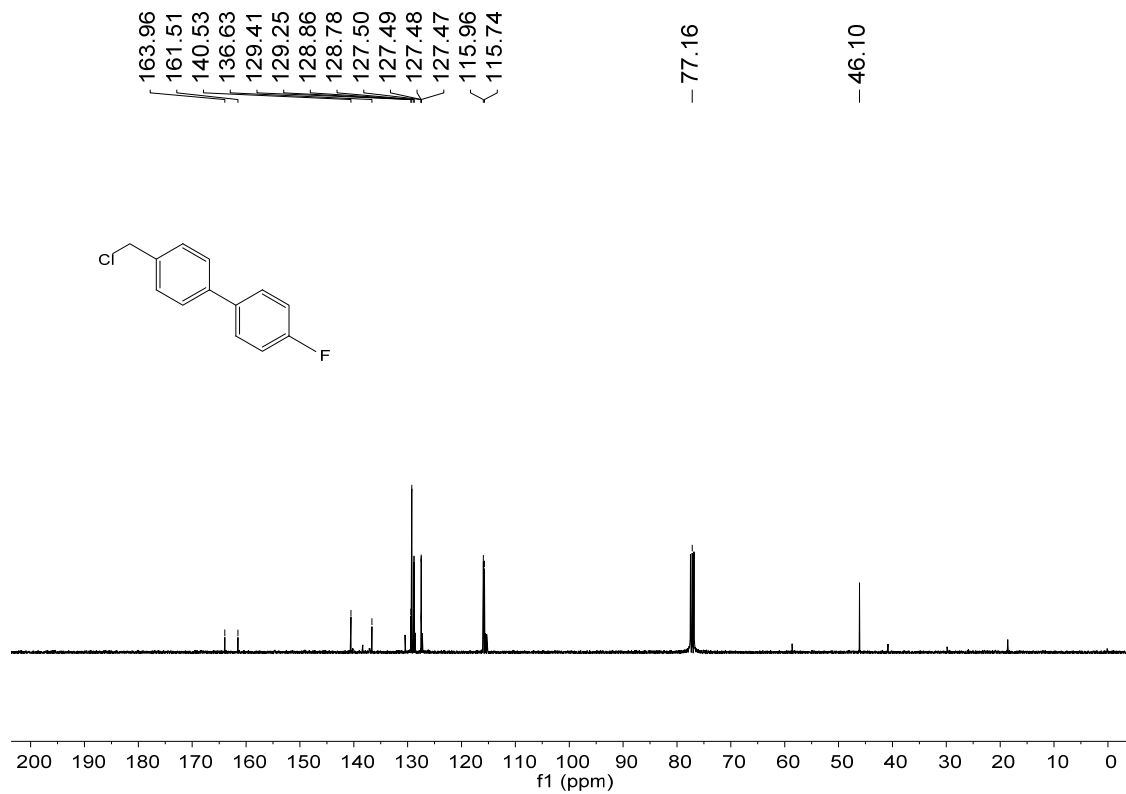
4-(chloromethyl)-4'-pentyl-1,1'-biphenyl[3e]



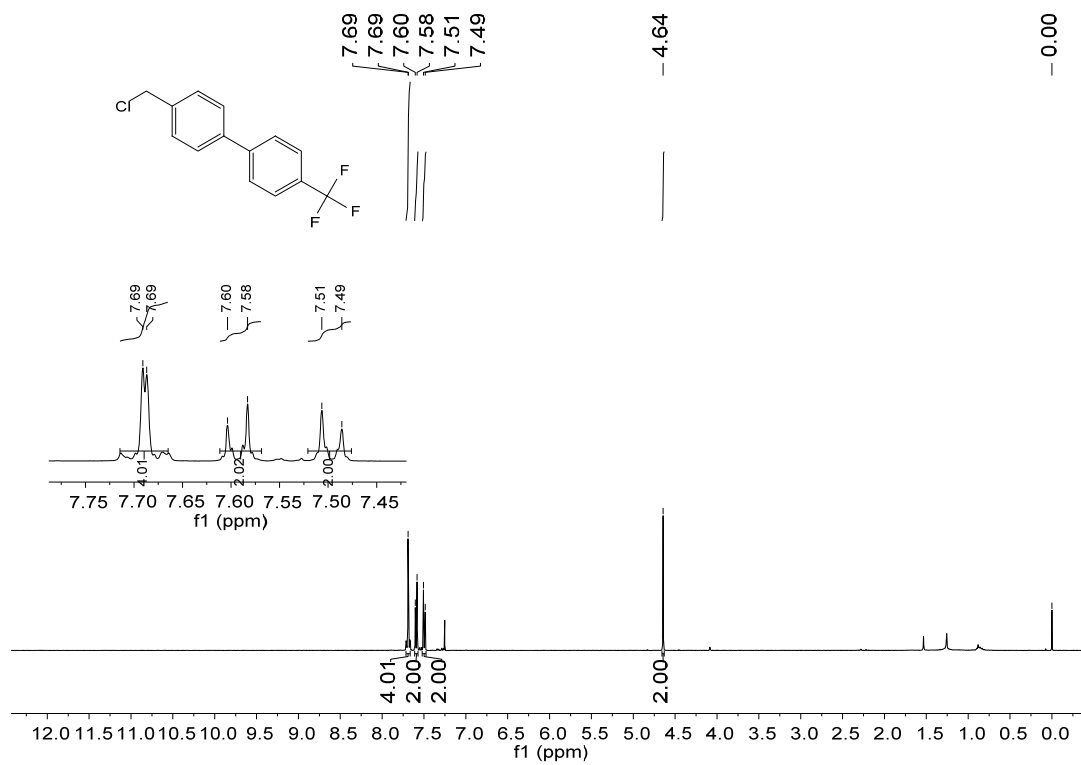


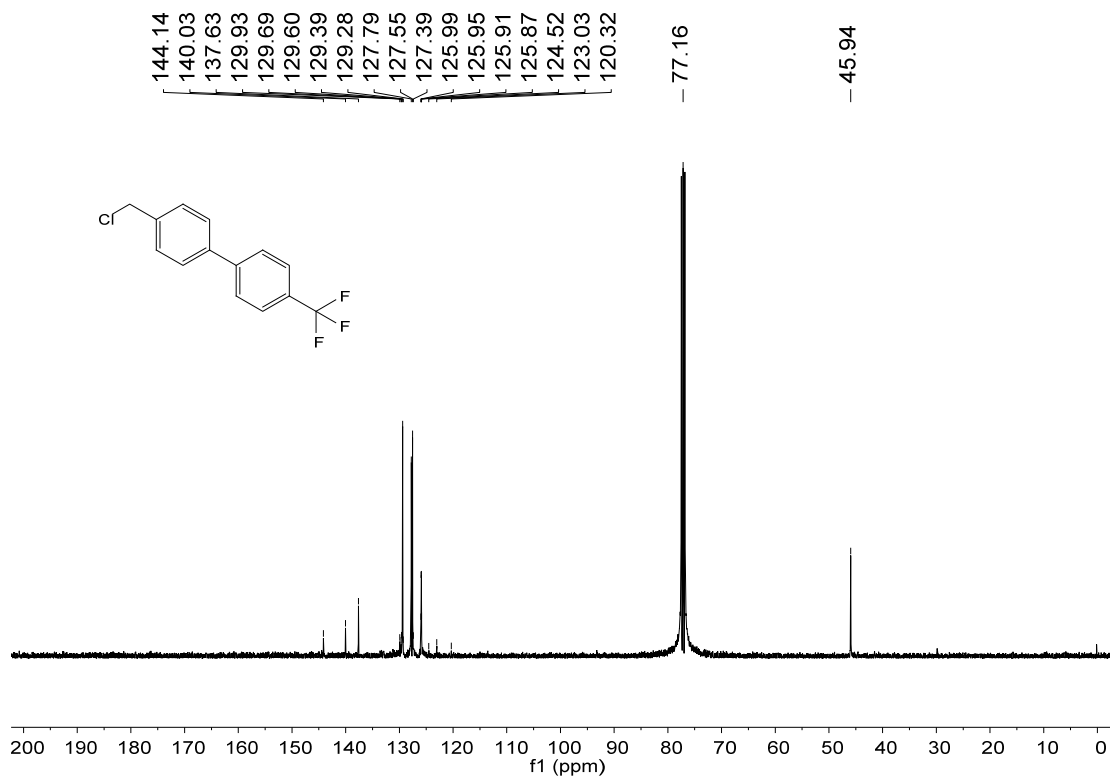
4-(chloromethyl)-4'-fluoro-1,1'-biphenyl[3f]



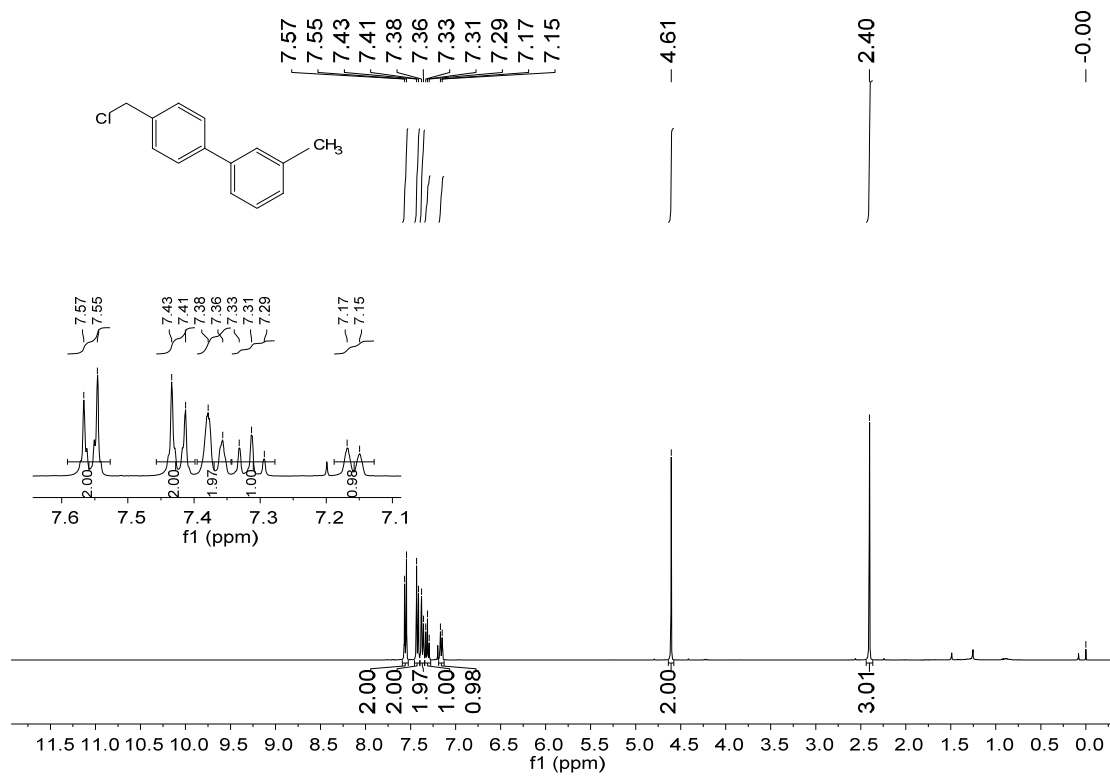


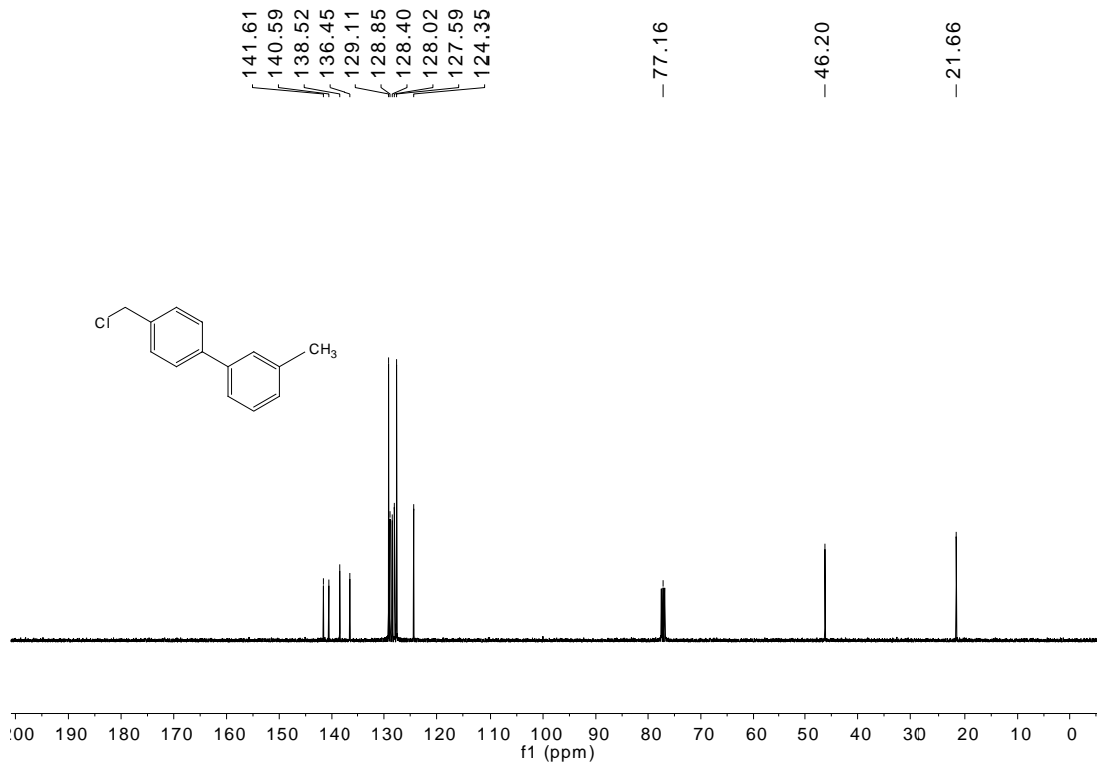
4-(chloromethyl)-4'-(trifluoromethyl)-1,1'-biphenyl[3g]





4'-(chloromethyl)-3-methyl-1,1'-biphenyl[3h]





Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

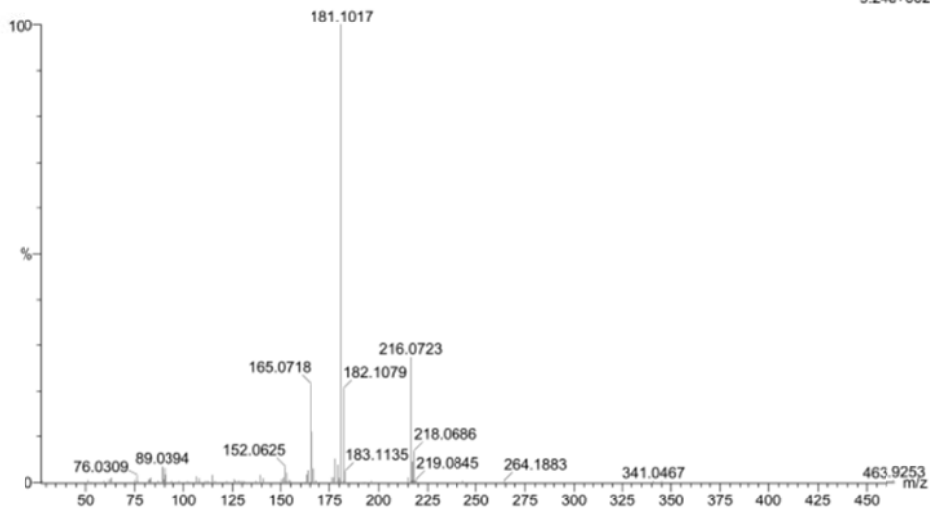
Elements Used:

C: 0-15 H: 0-15 F: 0-3 Cl: 0-2

default file

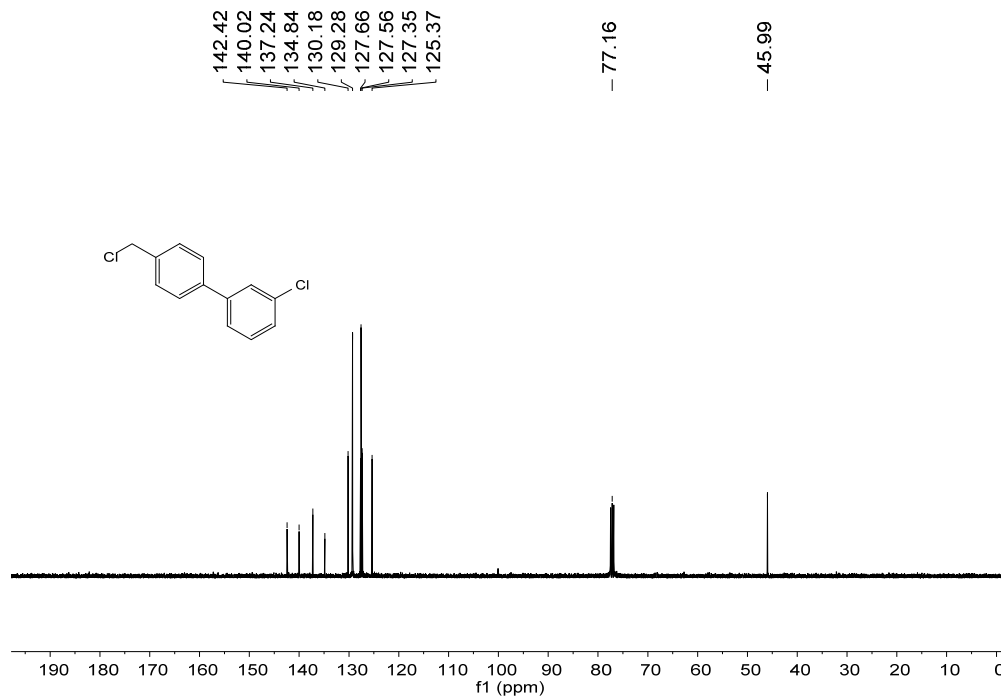
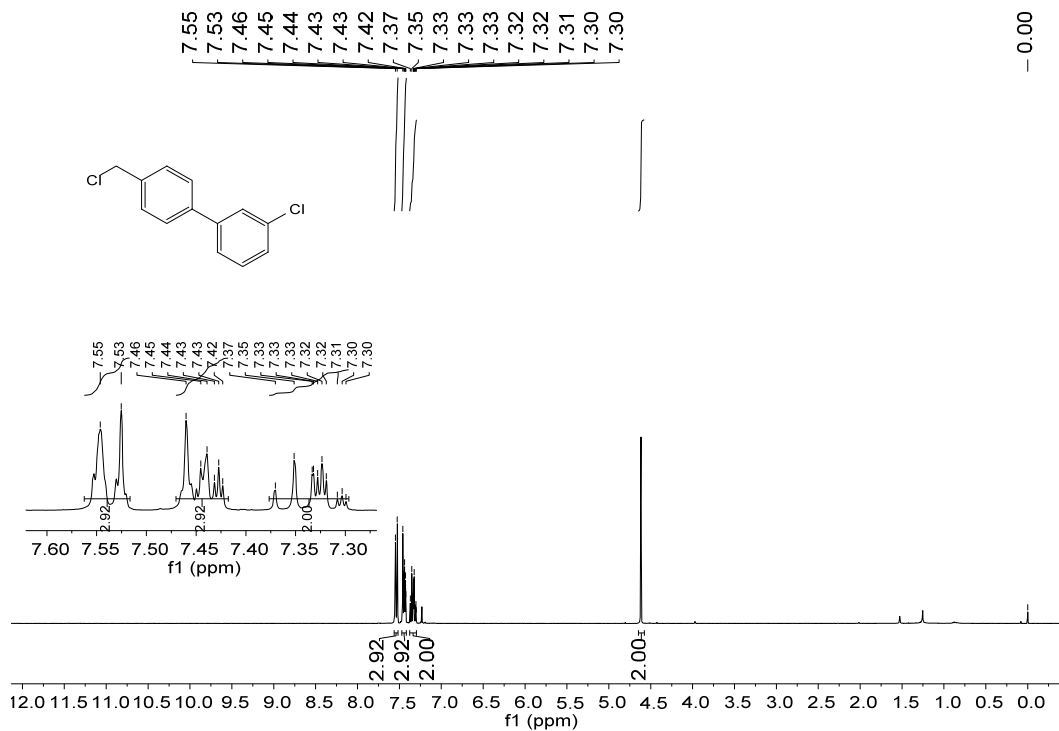
HR-3-1 1943 (12.058) Cm (1943-(1934:1938+1965:1968))

TOF MS EI+
9.24e+002



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
216.0723	216.0706	1.7	7.9	8.0	2.7	C14 H13 Cl

3-chloro-4'-(chloromethyl)-1,1'-biphenyl[3i]



Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 14 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

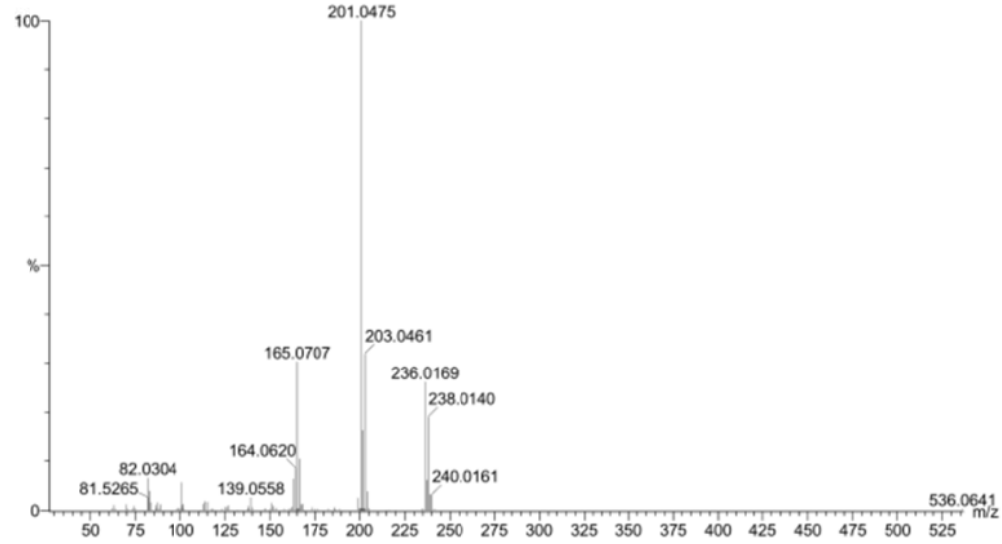
Elements Used:

C: 0-15 H: 0-15 F: 0-3 Cl: 0-2

default file

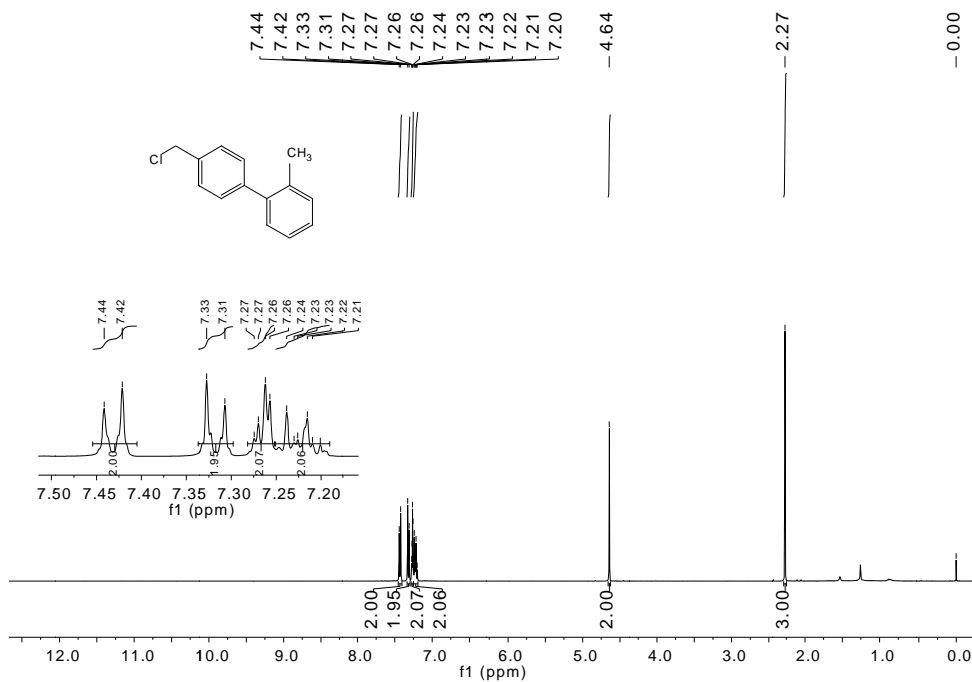
HR-3-1 2045 (12.602) Cm (2045-(2028:2036+2057:2068))

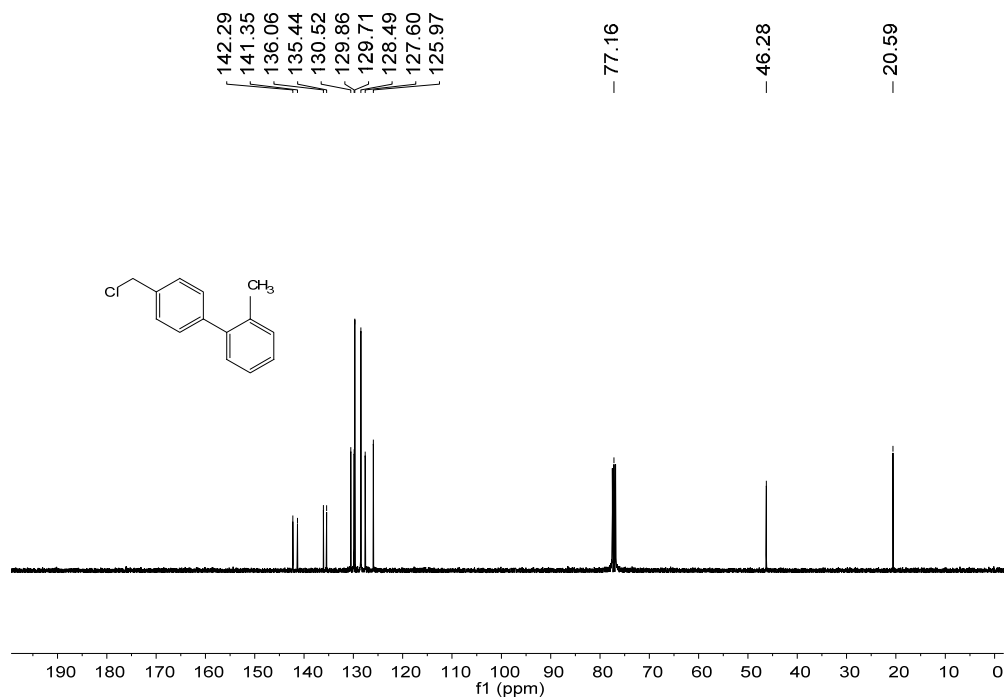
TOF MS EI+
 1.30e+003



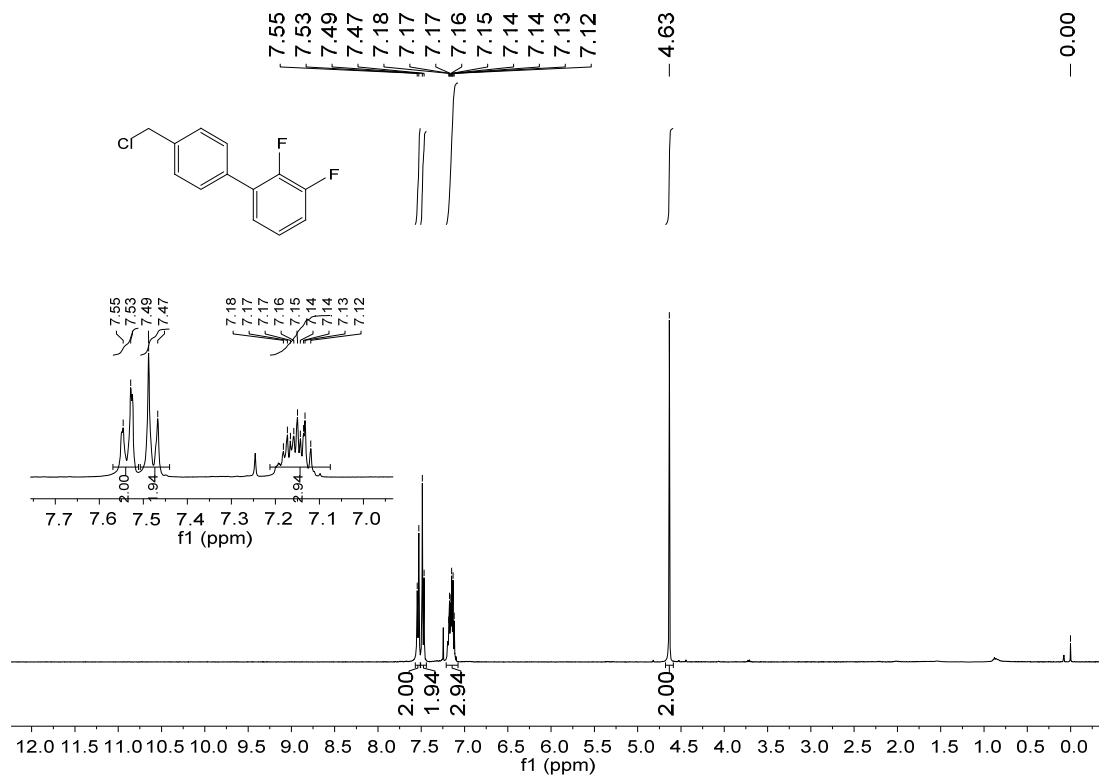
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
236.0169	236.0160	0.9	3.8	8.0	5.4	C13 H10 Cl2

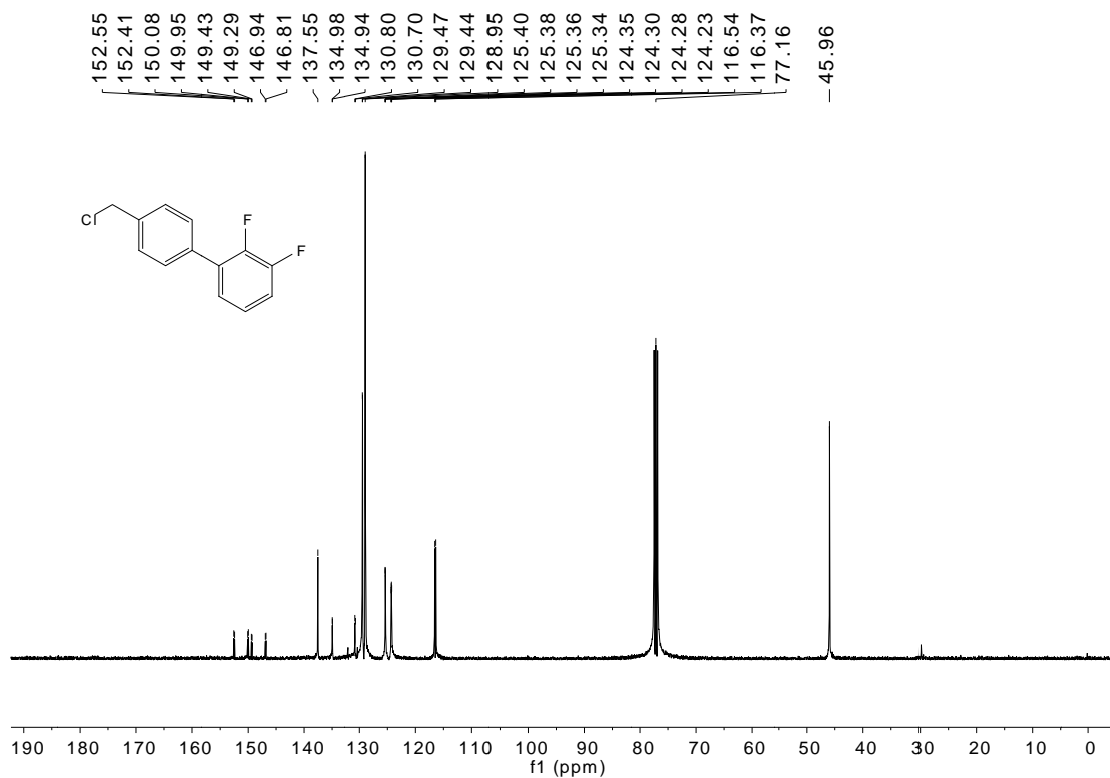
4'-(chloromethyl)-2-methyl-1,1'-biphenyl[3j]





4'-(chloromethyl)-2,3-difluoro-1,1'-biphenyl[3k]





Elemental Composition Report

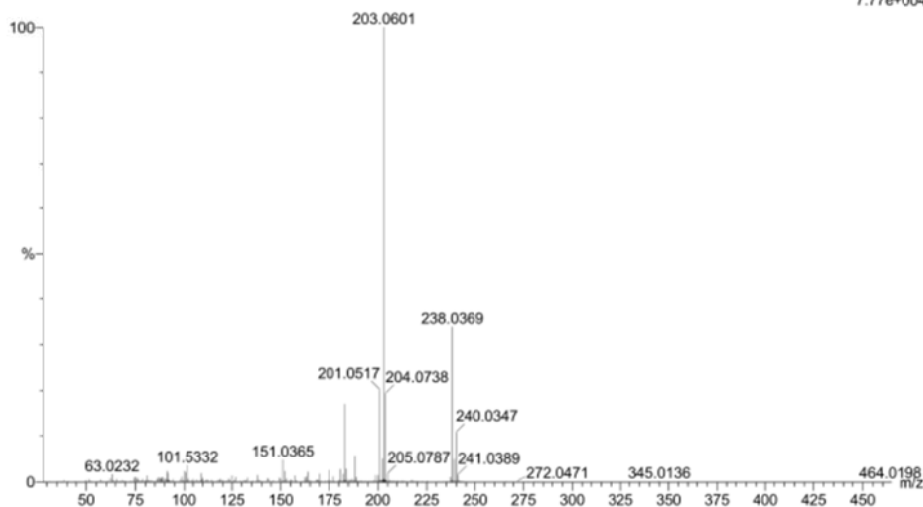
Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 13 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 0-15 H: 0-15 Cl: 0-2 F: 0-3

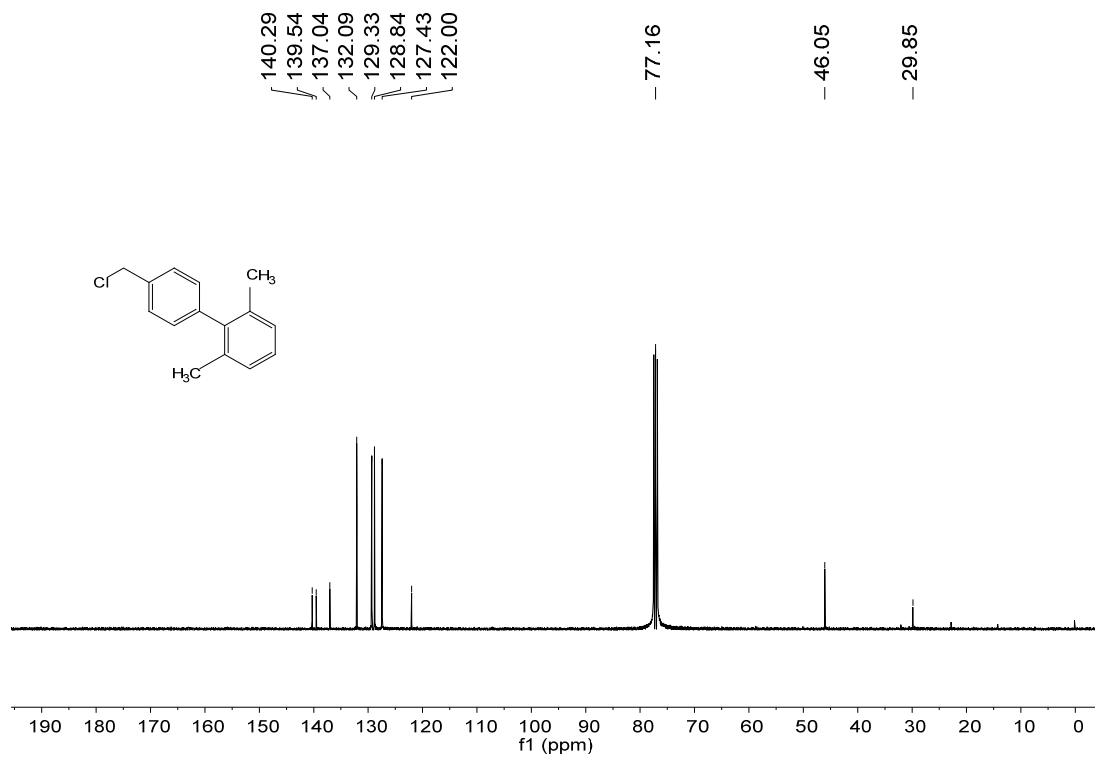
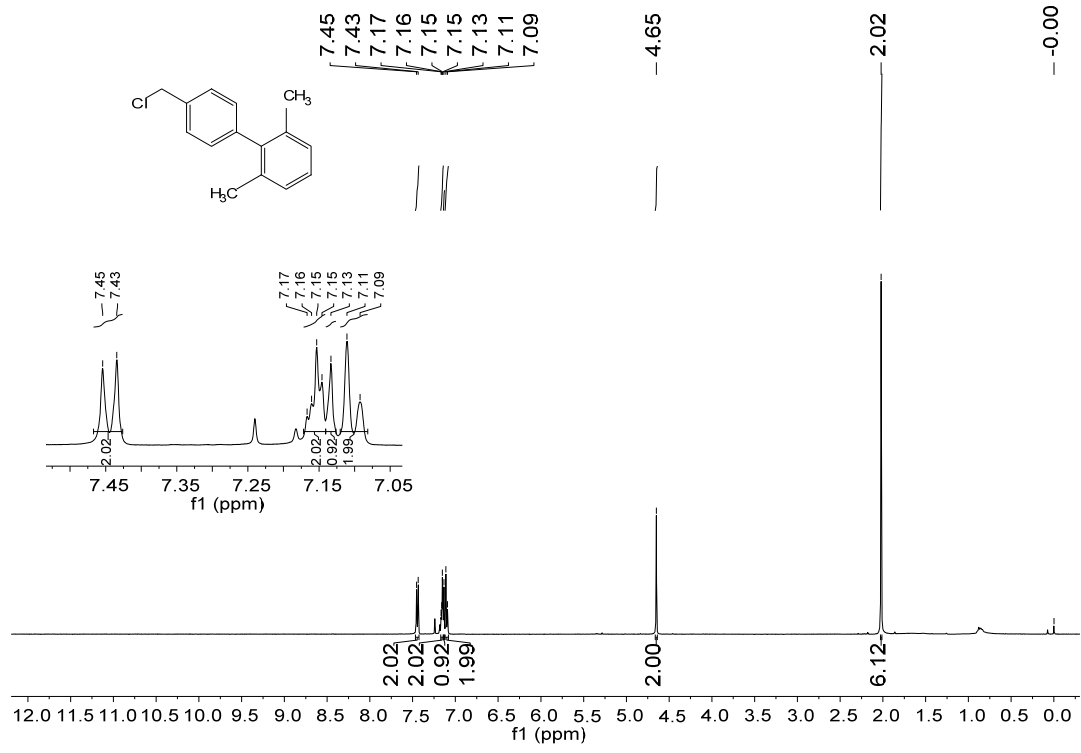
default file
 HR-3-1 1820 (11.402) Cm (1817:1825-(1803:1813+1842:1852))

TOF MS EI+
 7.77e+004

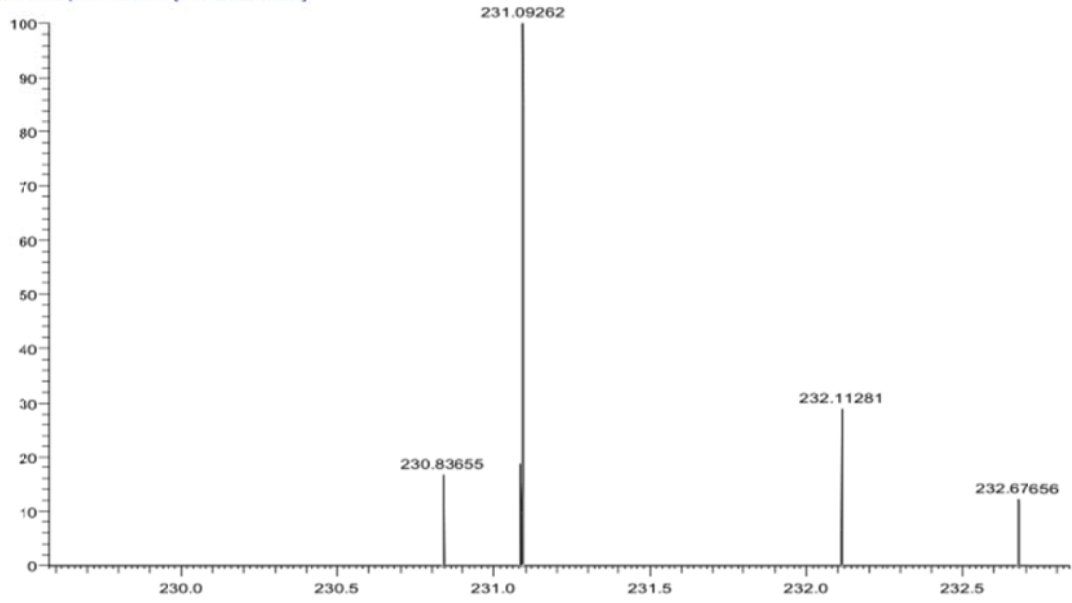


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
238.0369	238.0361	0.8	3.4	8.0	6.4	C13 H9 Cl F2

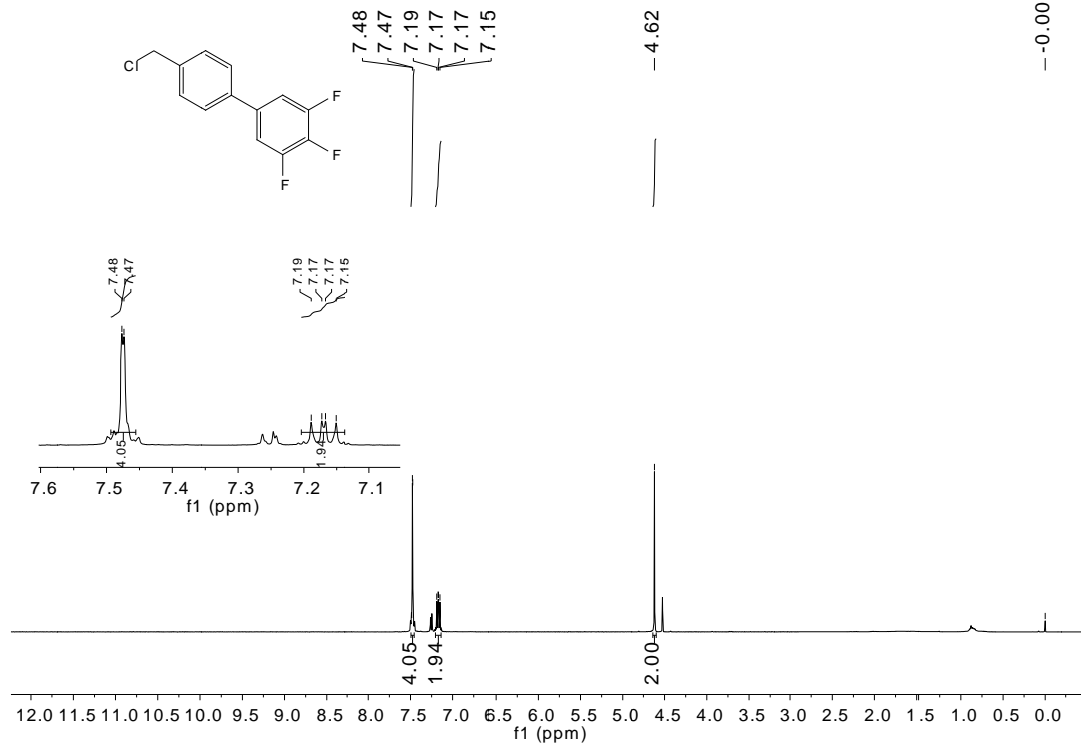
4'-(chloromethyl)-2,6-dimethyl-1,1'-biphenyl[3]

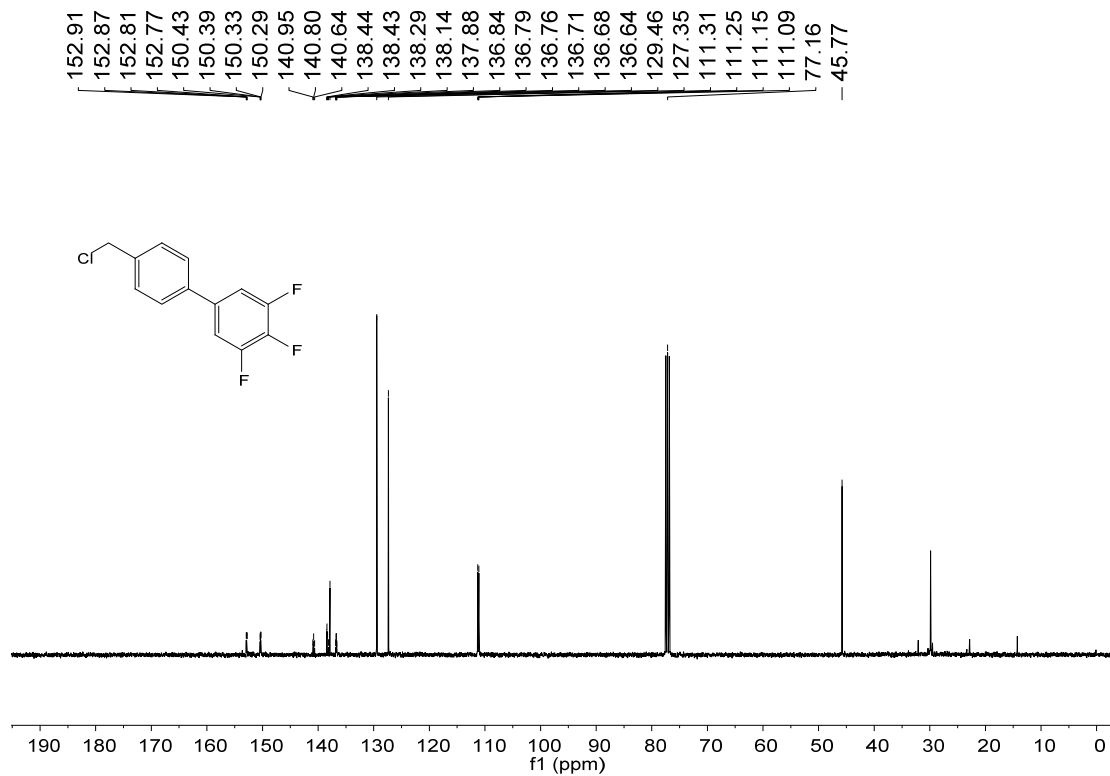


00016 #24 RT: 0.36 AV: 1 NL: 1.17E4
T: FTMS + p ESI Full ms [150.00-2000.00]

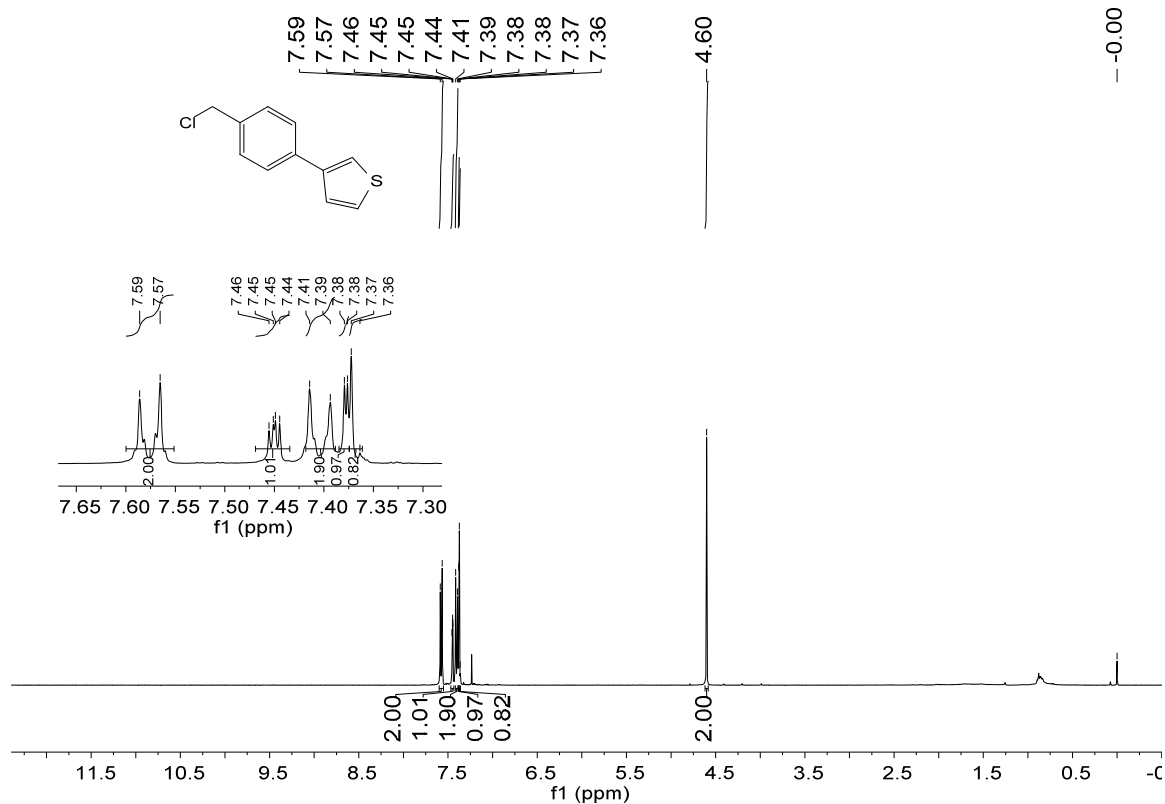


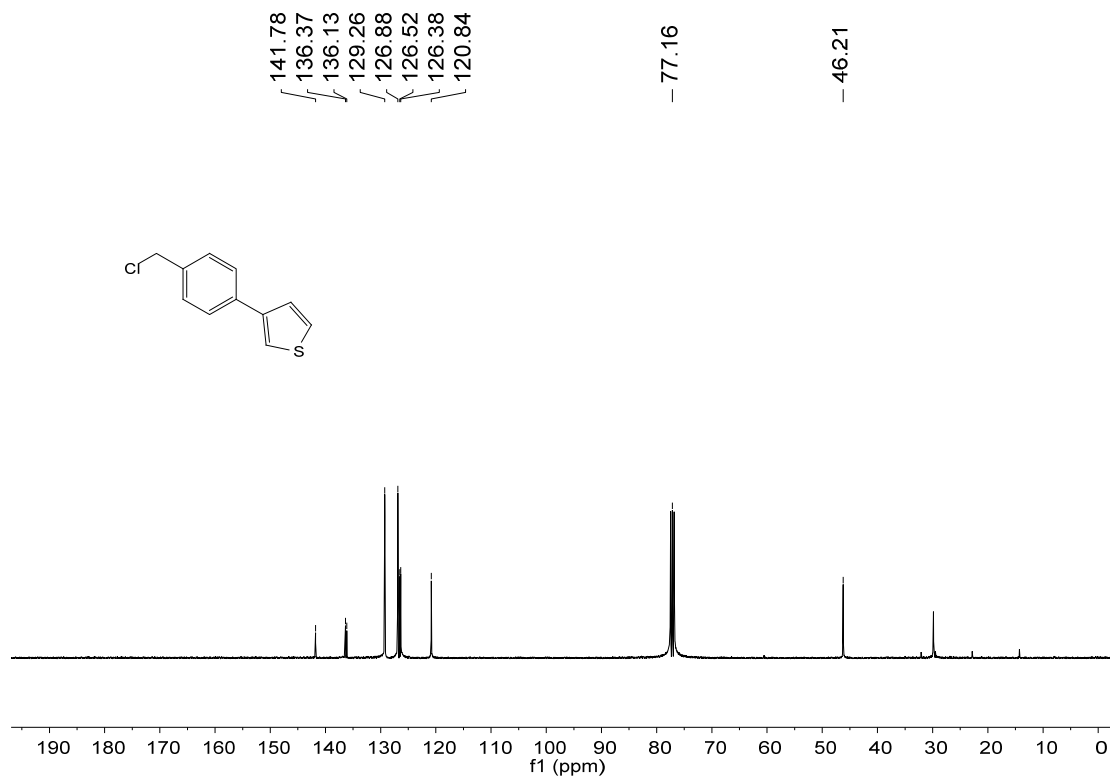
4'-(chloromethyl)-3,4,5-trifluoro-1,1'-biphenyl[3m]



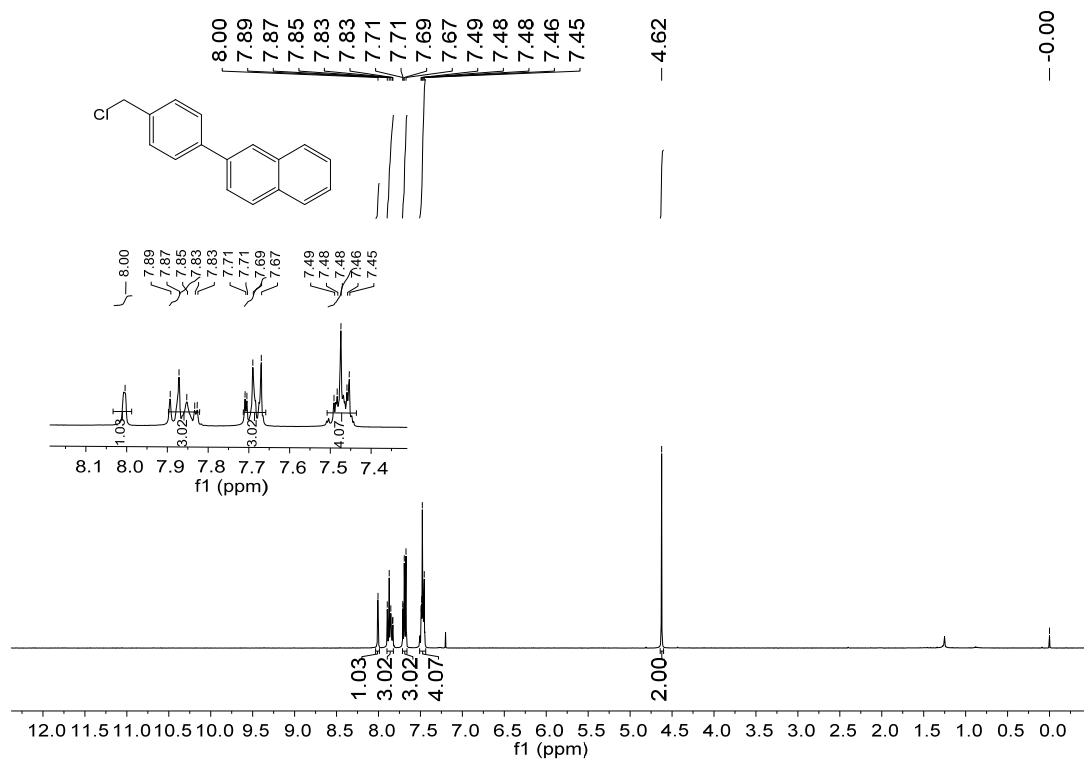


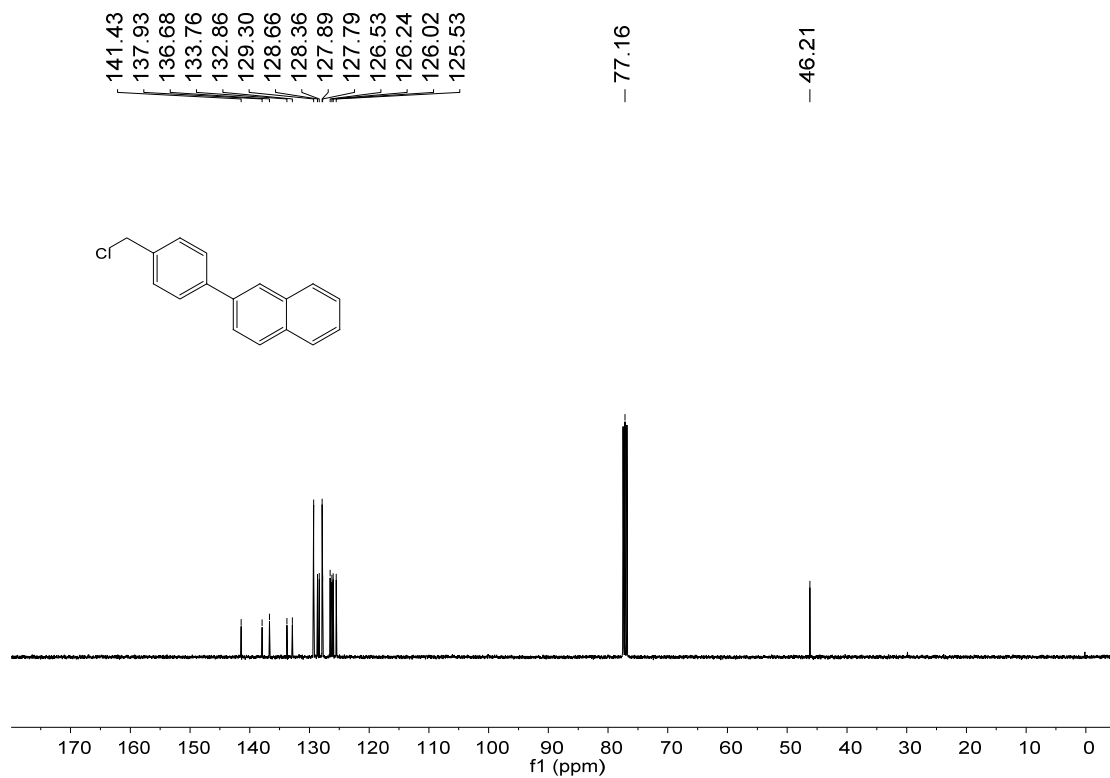
3-(4-(chloromethyl)phenyl)thiophene[3n]



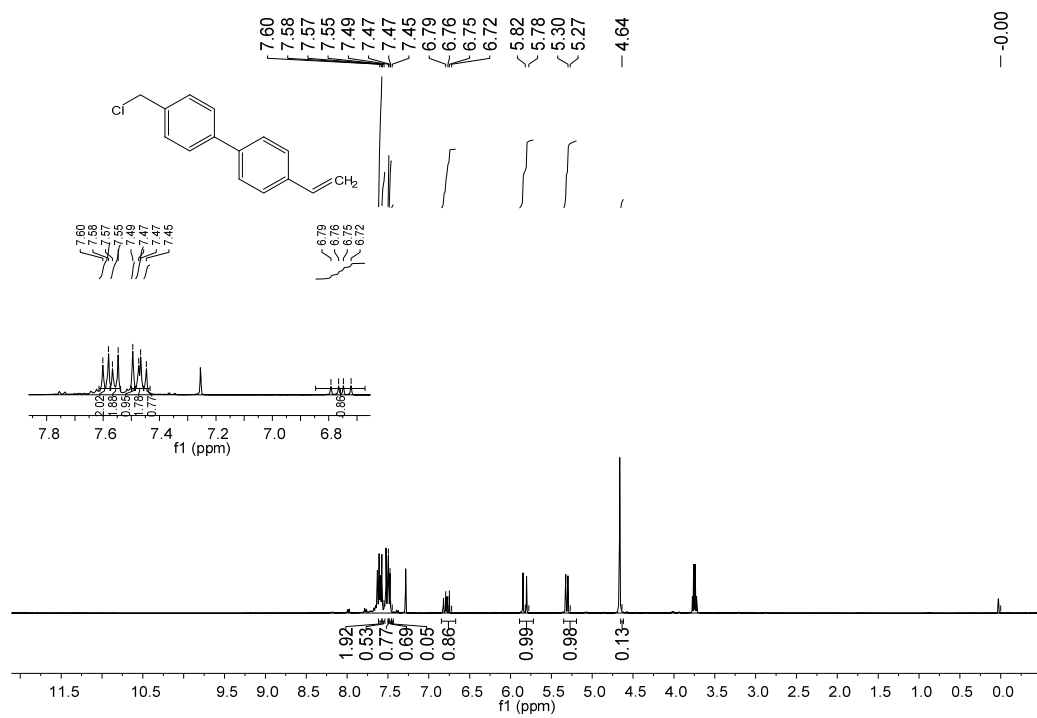


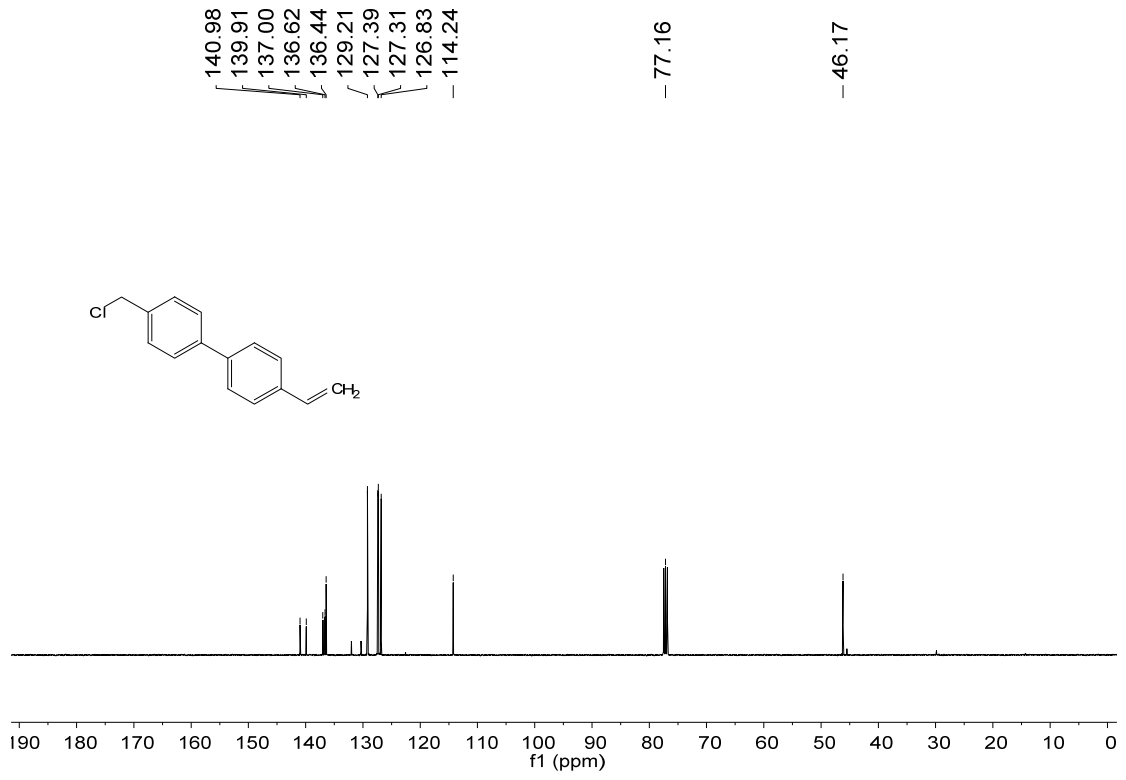
2-(4-(chloromethyl)phenyl)naphthalene[3o]



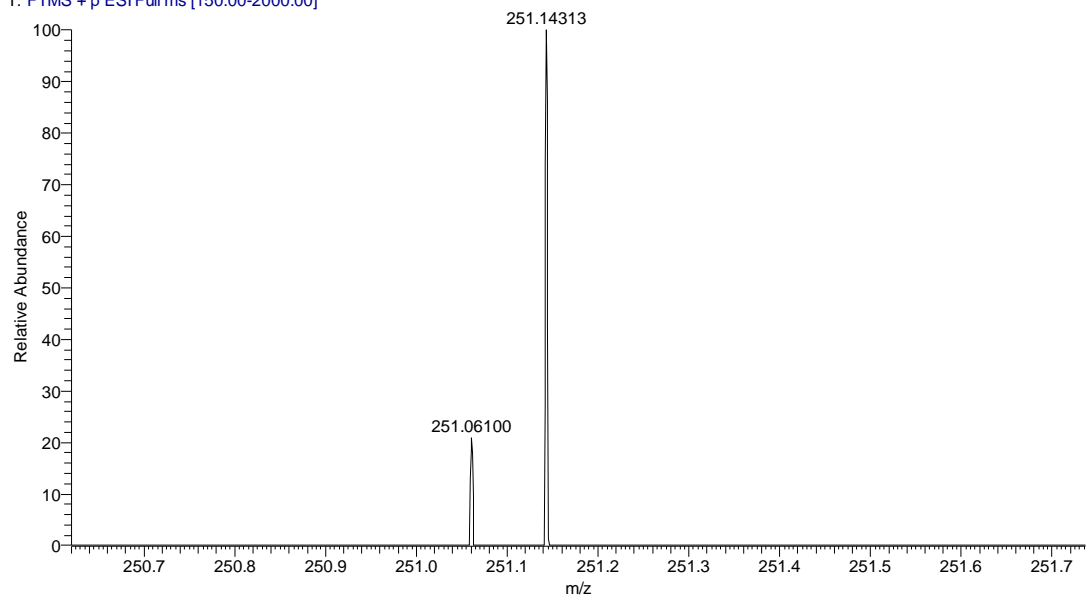


4-(chloromethyl)-4'-vinyl-1,1'-biphenyl[3p]

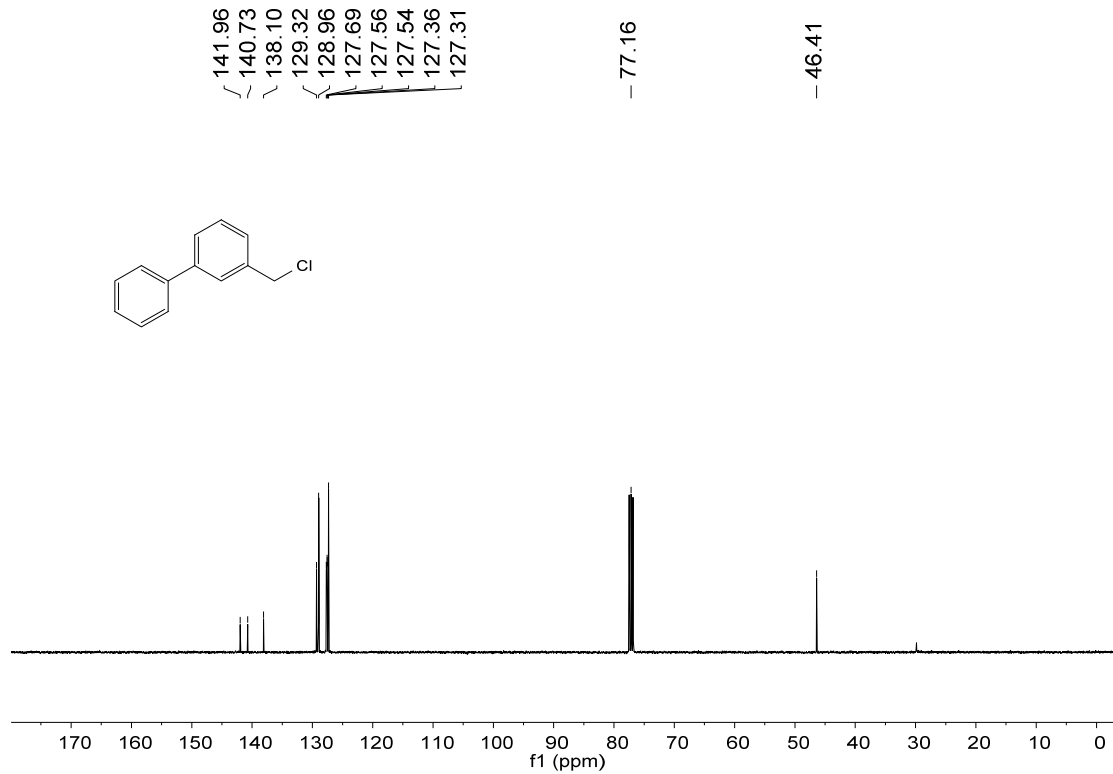
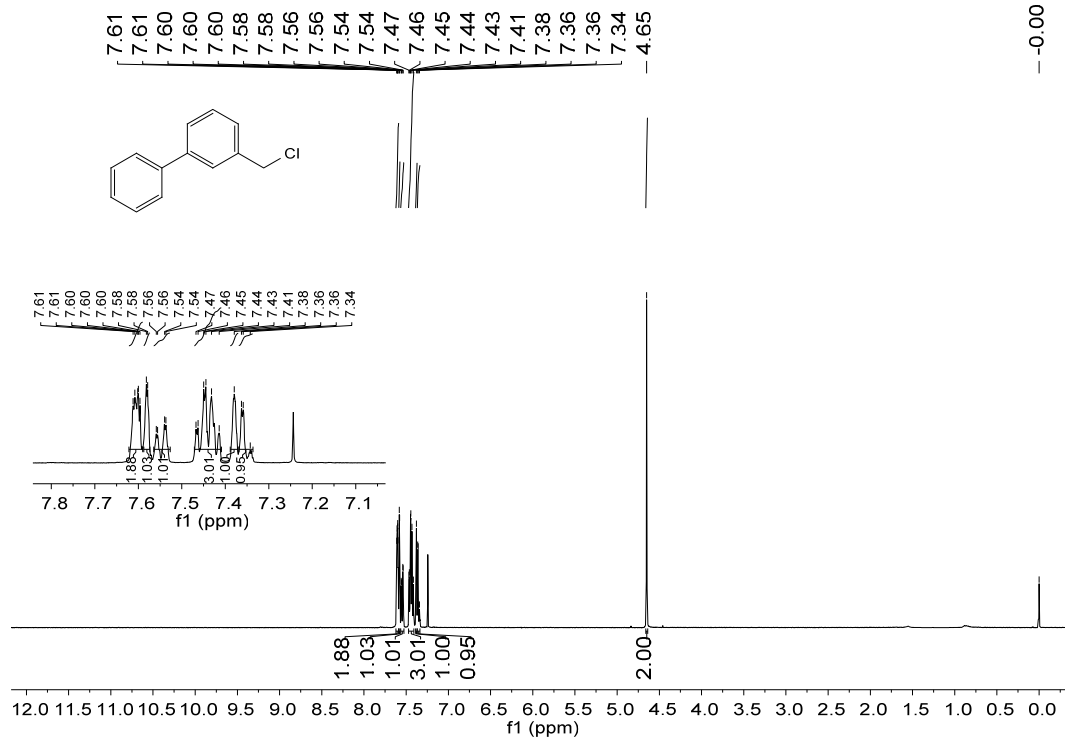




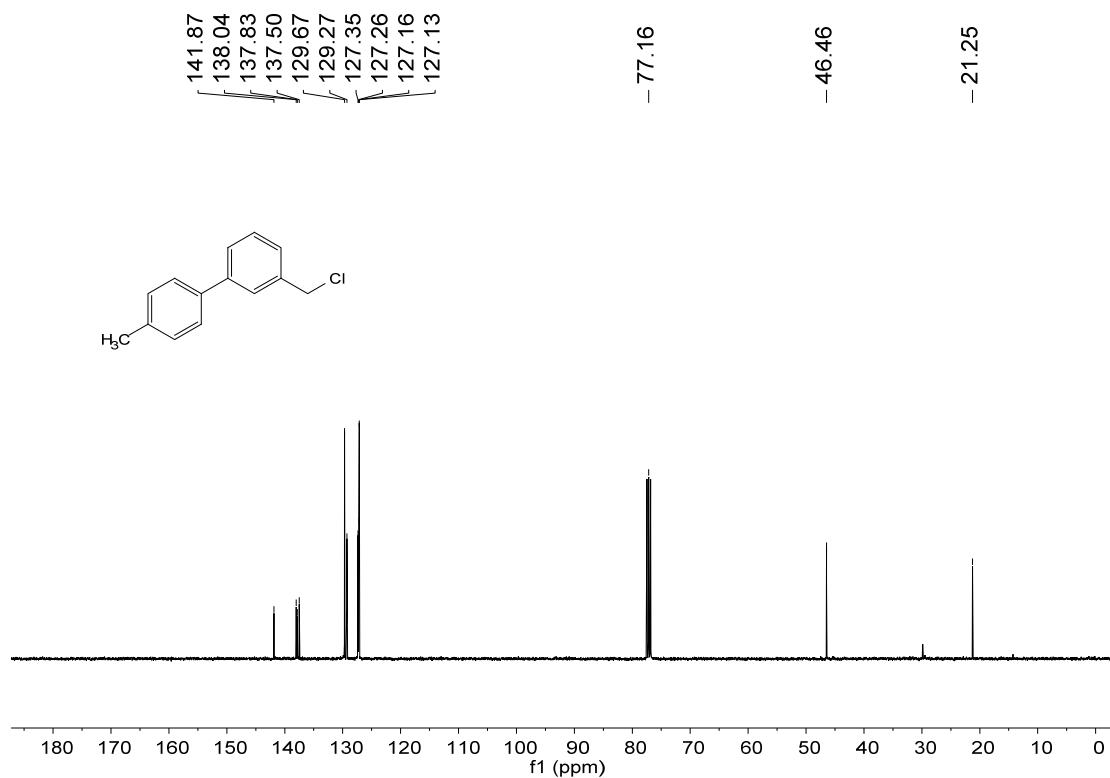
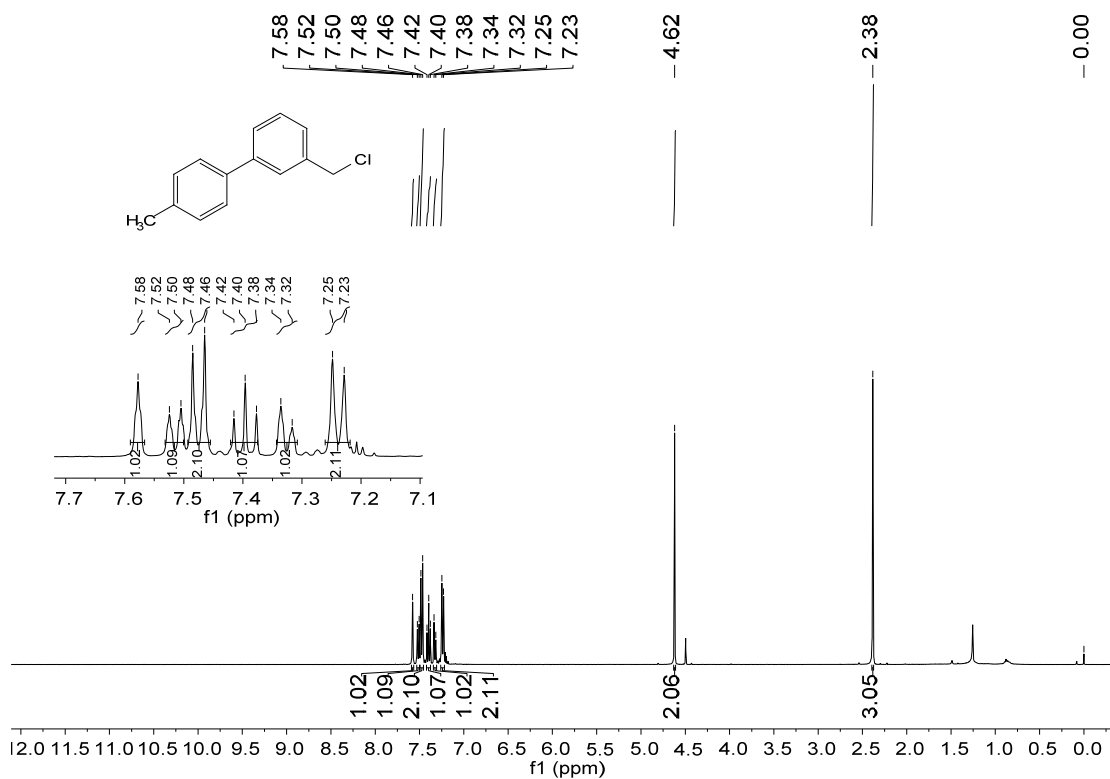
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T: FTMS + p ESI Full ms [150.00-2000.00]



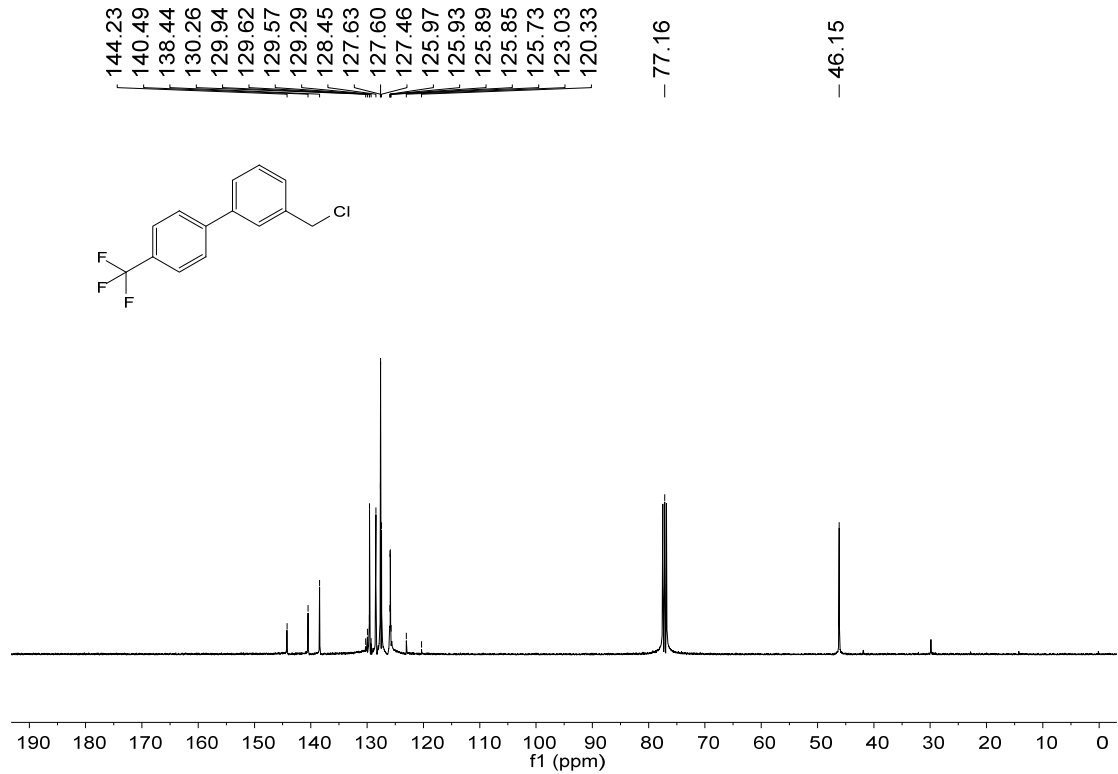
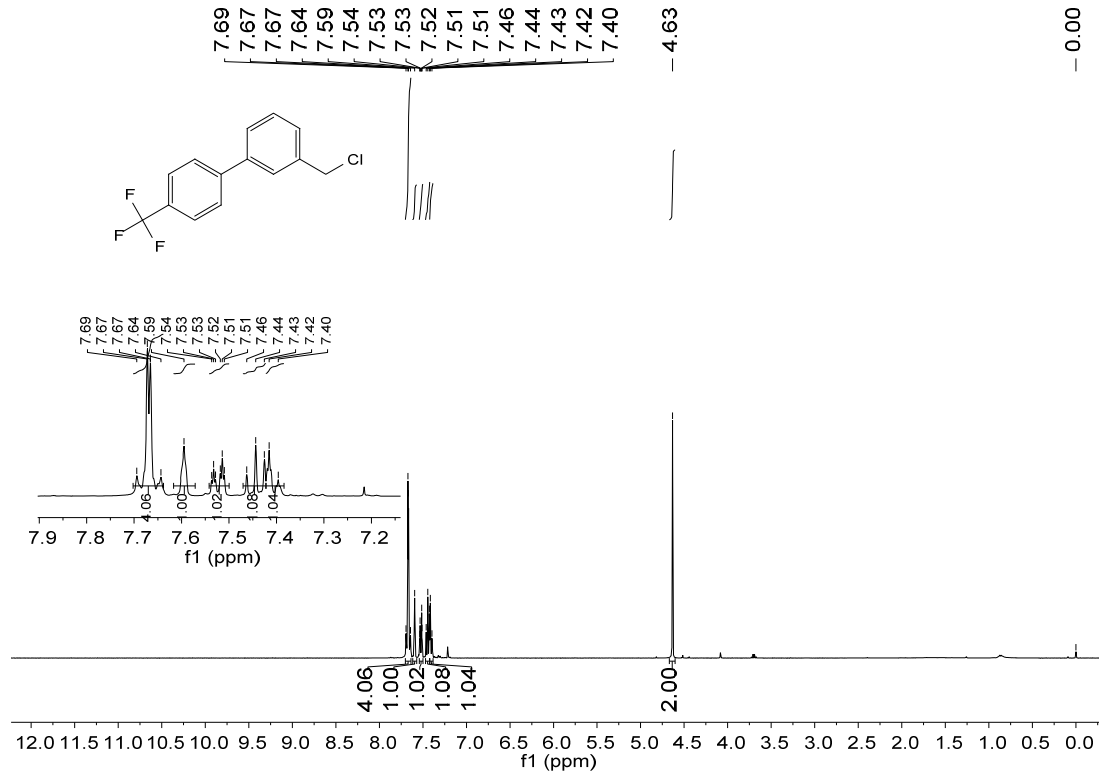
3-(chloromethyl)-1,1'-biphenyl[4a]



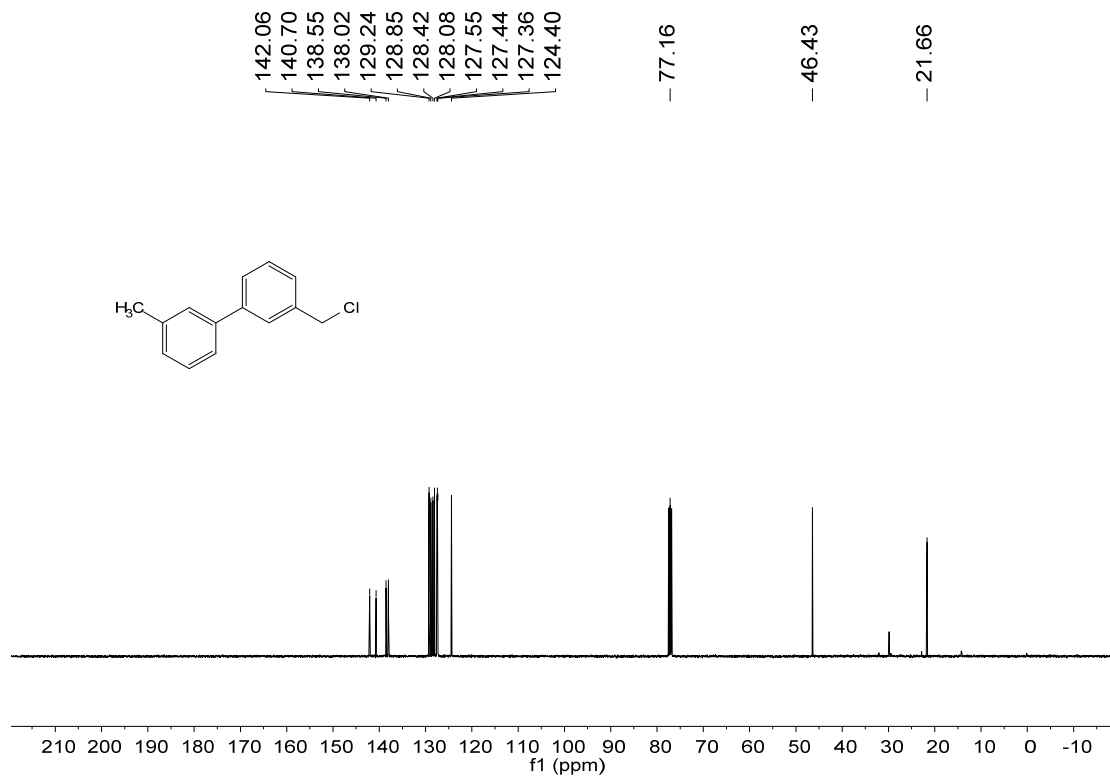
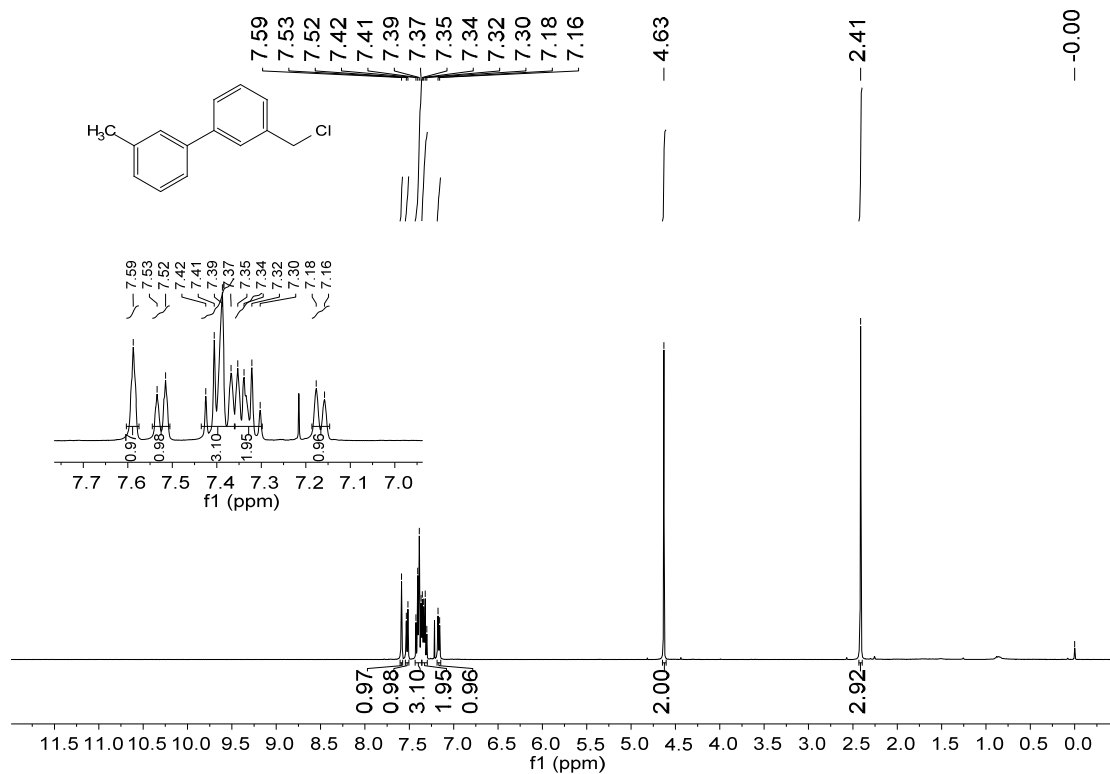
3-(chloromethyl)-4'-methyl-1,1'-biphenyl[4b]

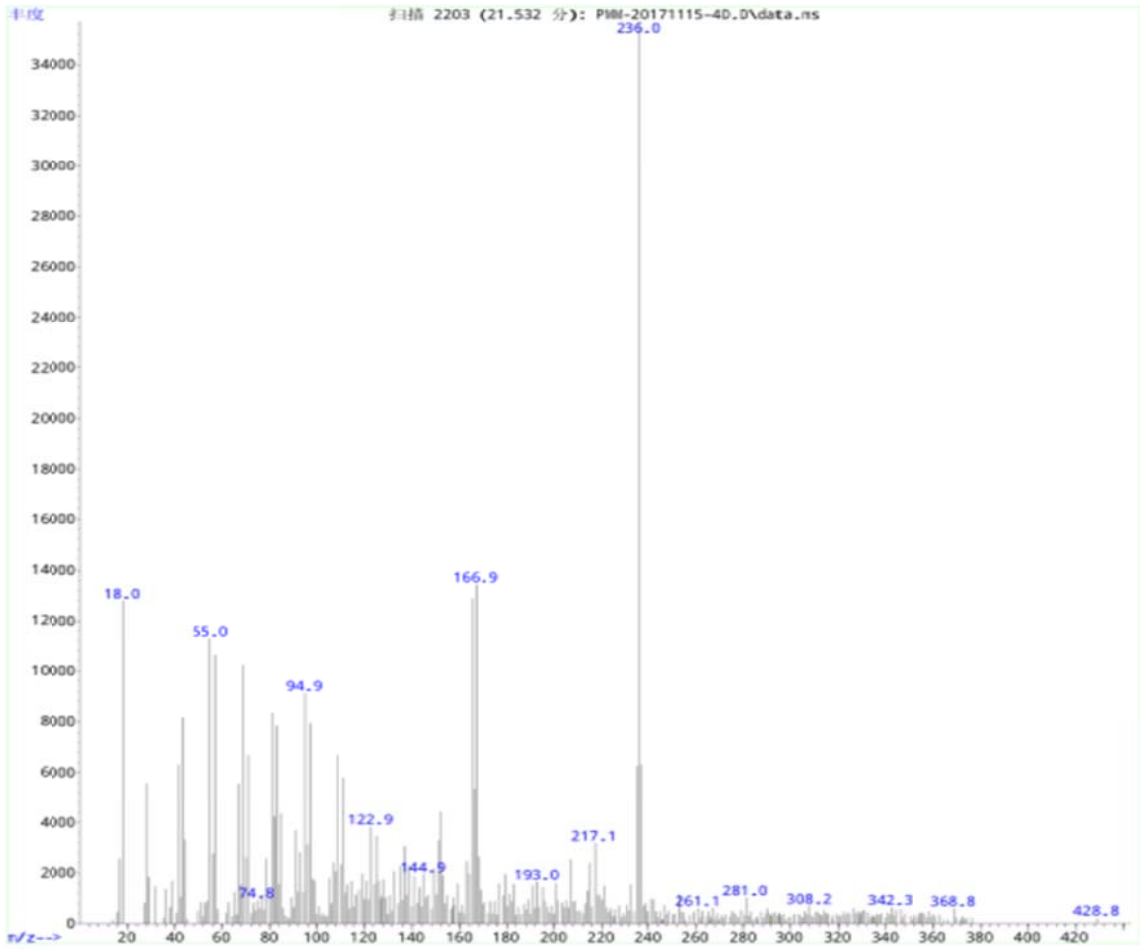


3-(chloromethyl)-4'-(trifluoromethyl)-1,1'-biphenyl[4c]

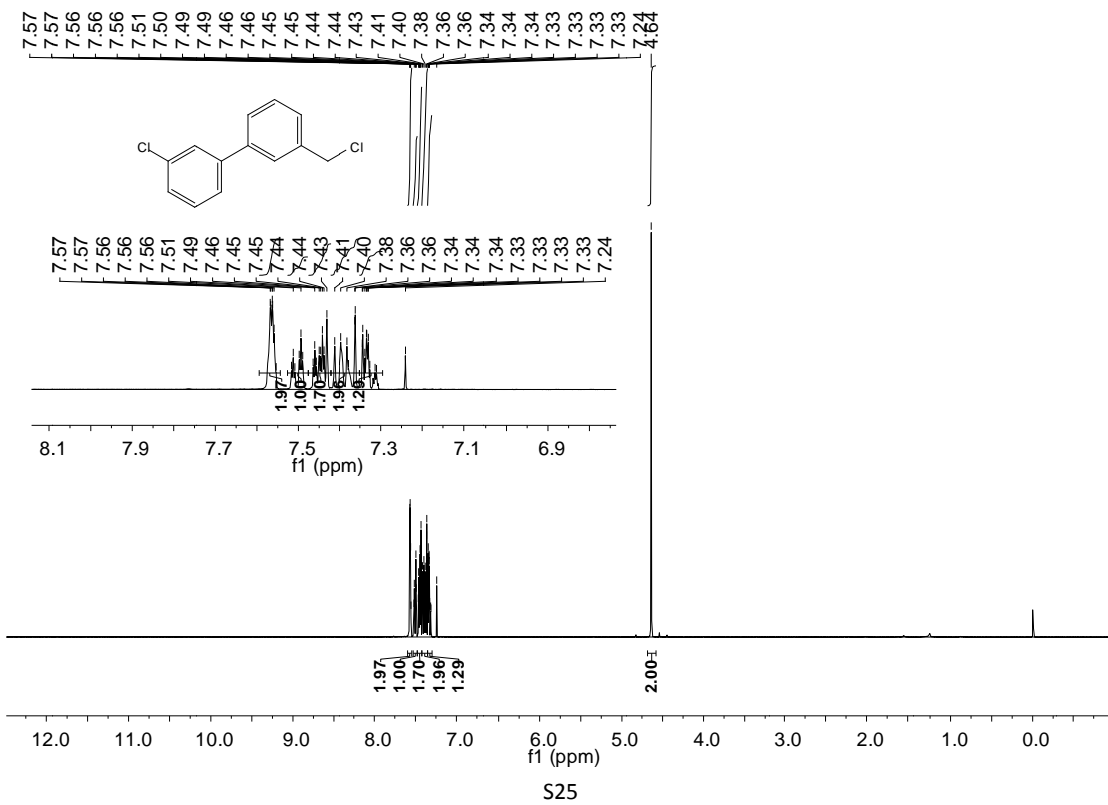


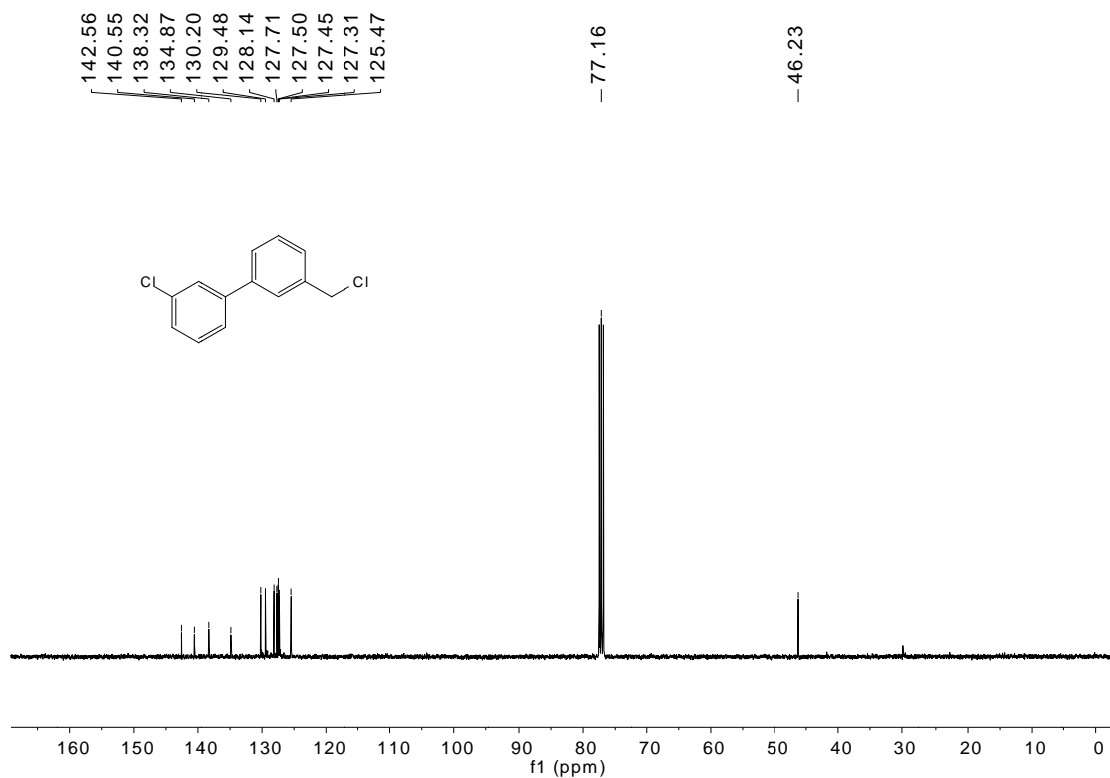
3-(chloromethyl)-3'-methyl-1,1'-biphenyl[4d]





3-chloro-3'-(chloromethyl)-1,1'-biphenyl[4e]





Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

20 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

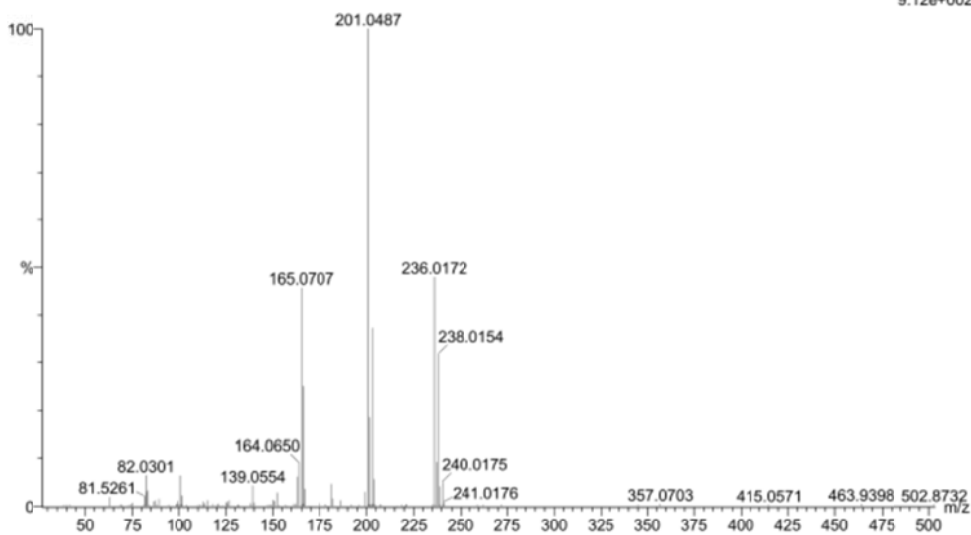
Elements Used:

C: 0-15 H: 0-15 F: 0-3 Cl: 0-3

default file

HR-4 1857 (12.464) Cm(1854:1857-(1844:1852+1875:1886))

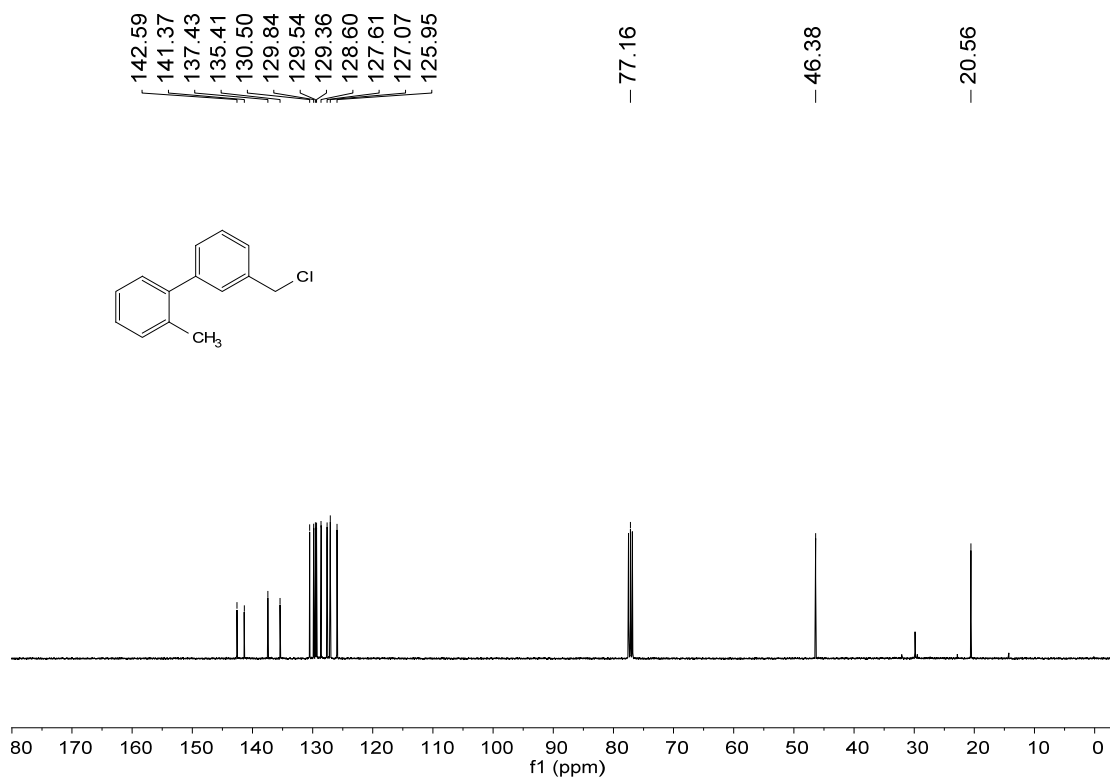
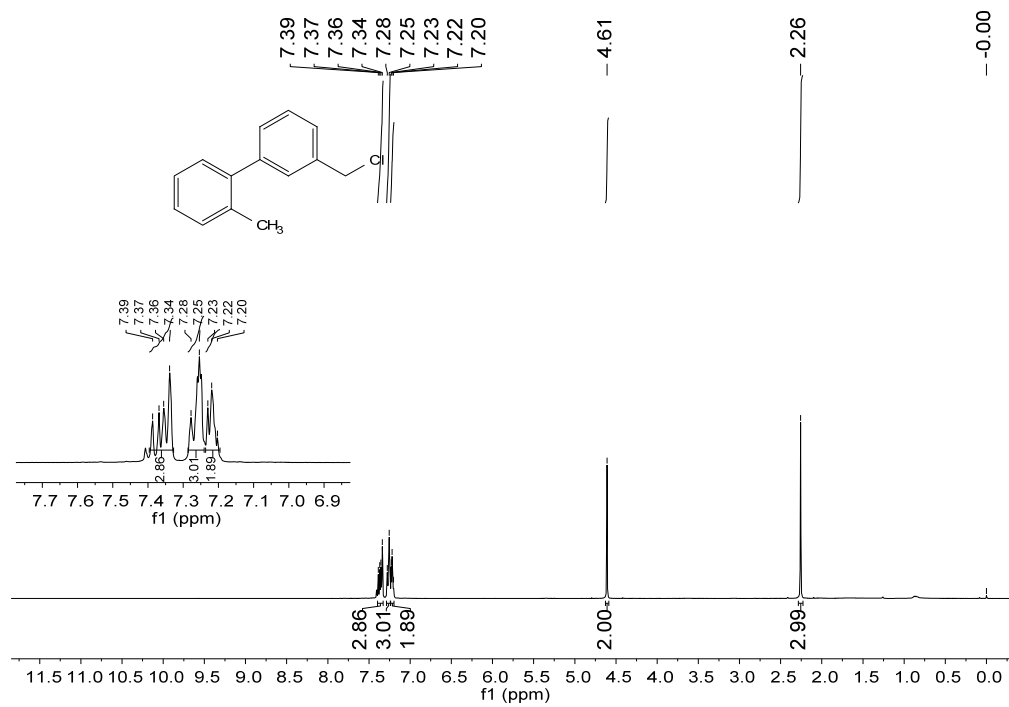
TOF MS EI+
9.12e+002



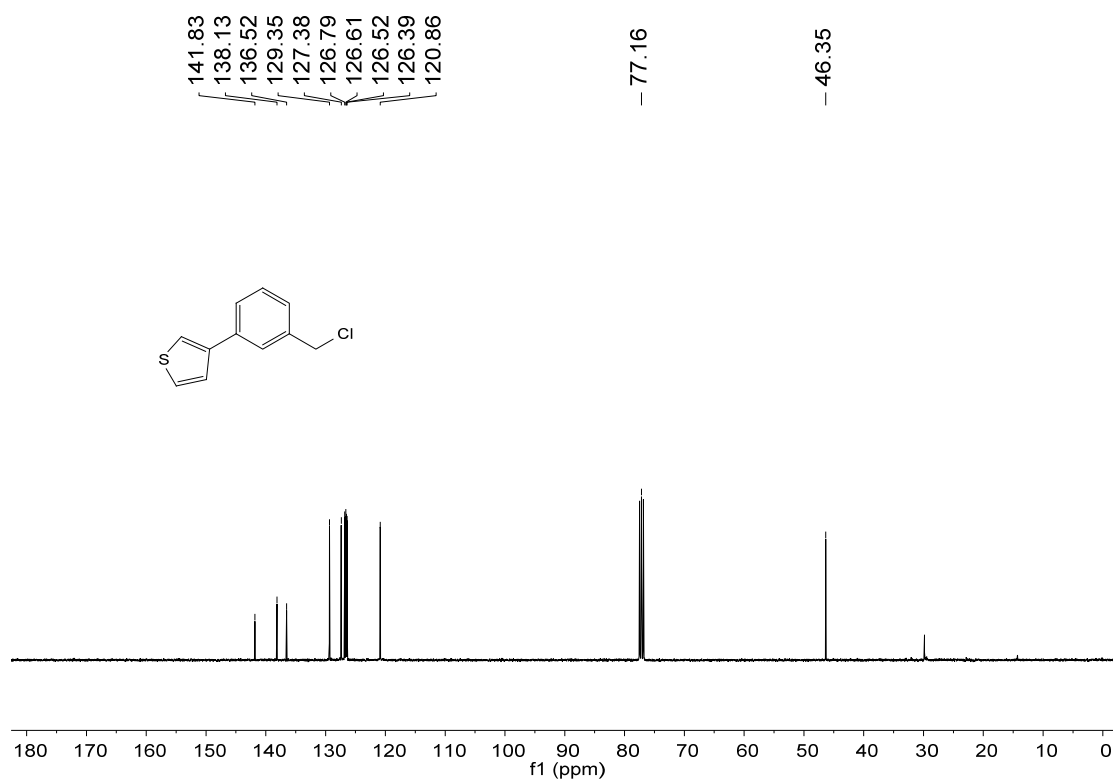
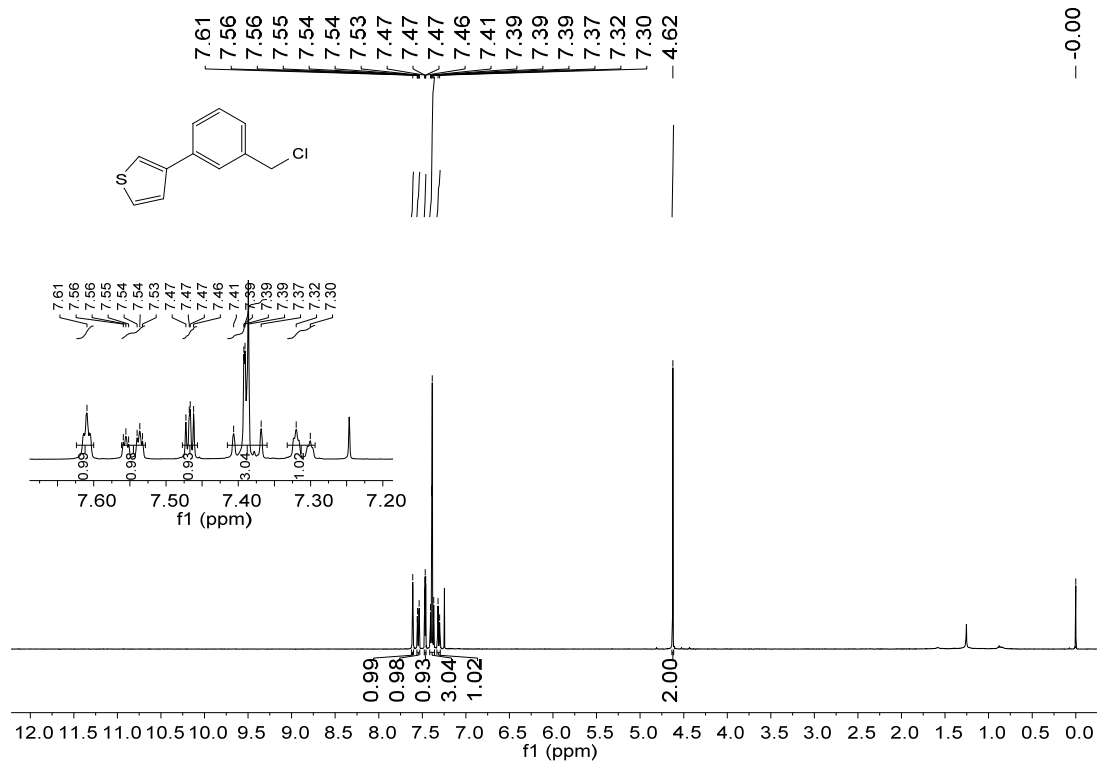
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
236.0172	236.0160	1.2	5.1	8.0	2.2	C13 H10 Cl2

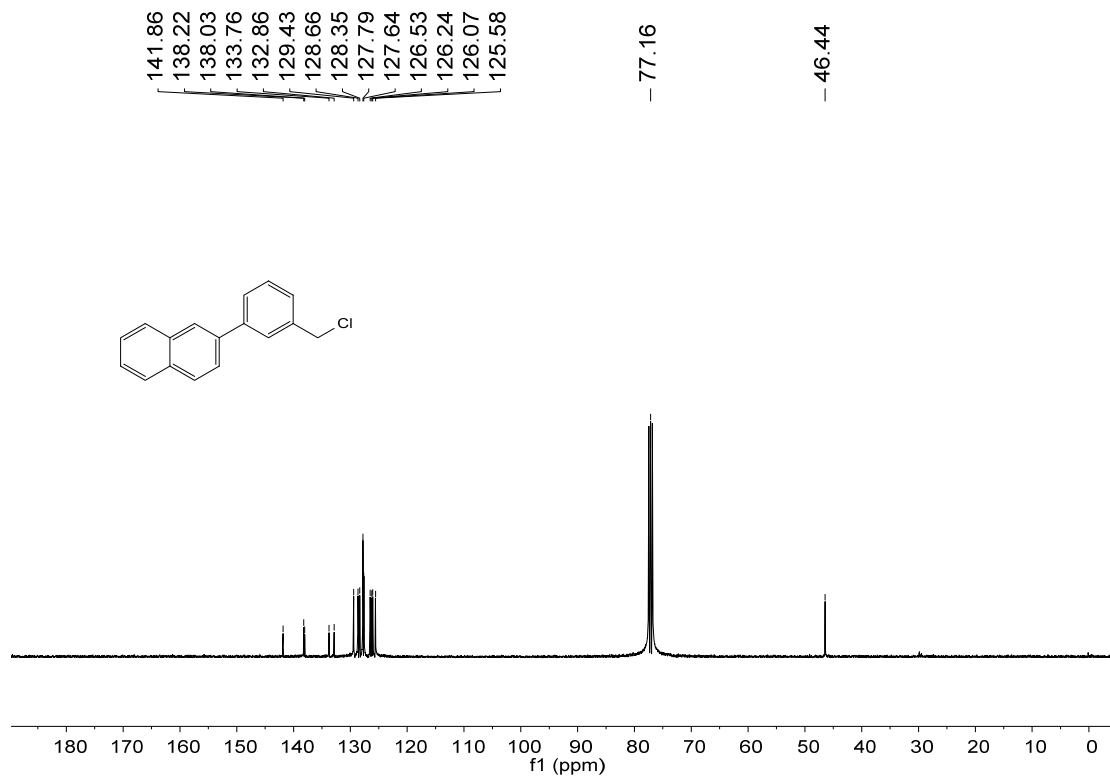
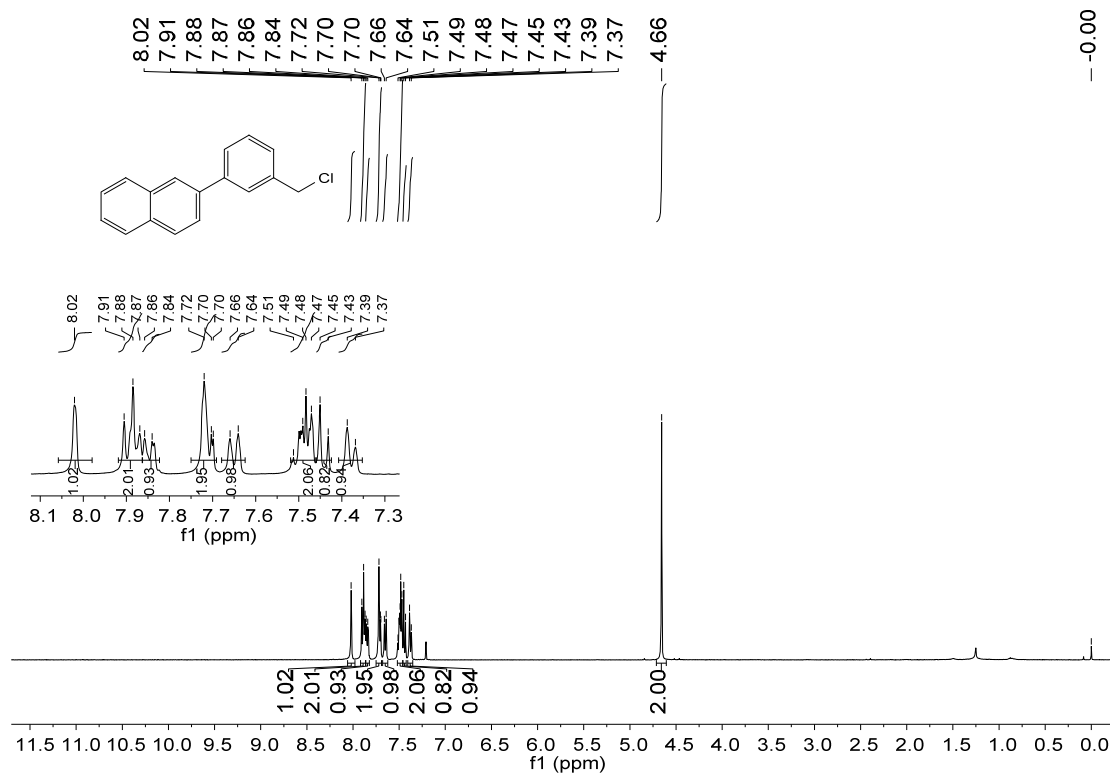
3'-(chloromethyl)-2-methyl-1,1'-biphenyl[4f]



3-(3-(chloromethyl)phenyl)thiophene[4g]



2-(3-(chloromethyl)phenyl)naphthalene[4h]



Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

49 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

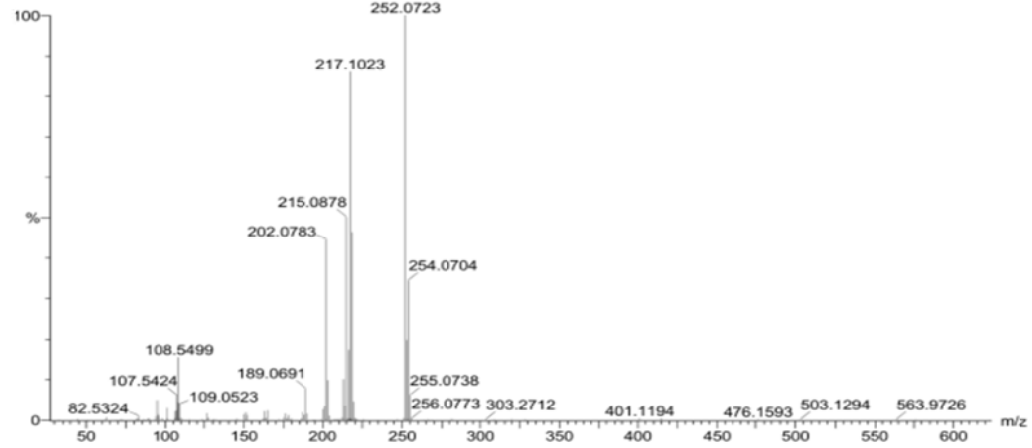
Elements Used:

C: 0-30 H: 0-30 F: 0-4 Cl: 0-3

default file

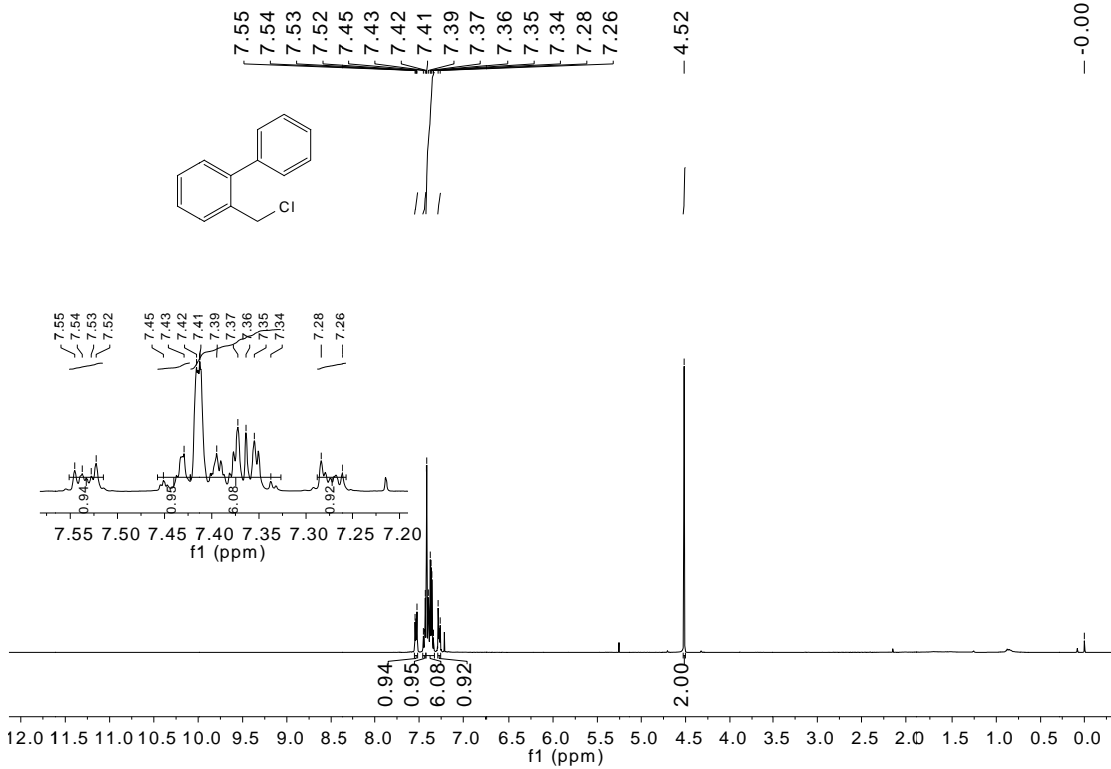
HR-4h-2 1413 (10.096) Cm (1408:1415-(1385:1400+1436:1470))

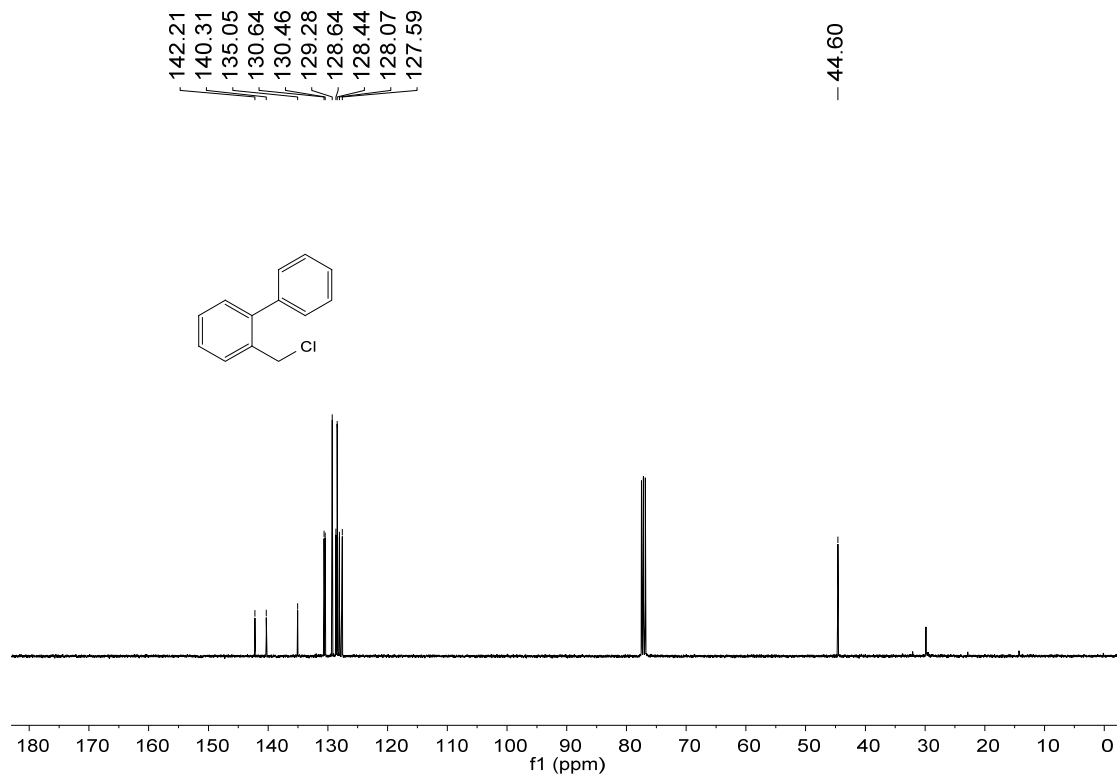
TOF MS EI+
2.17e+003



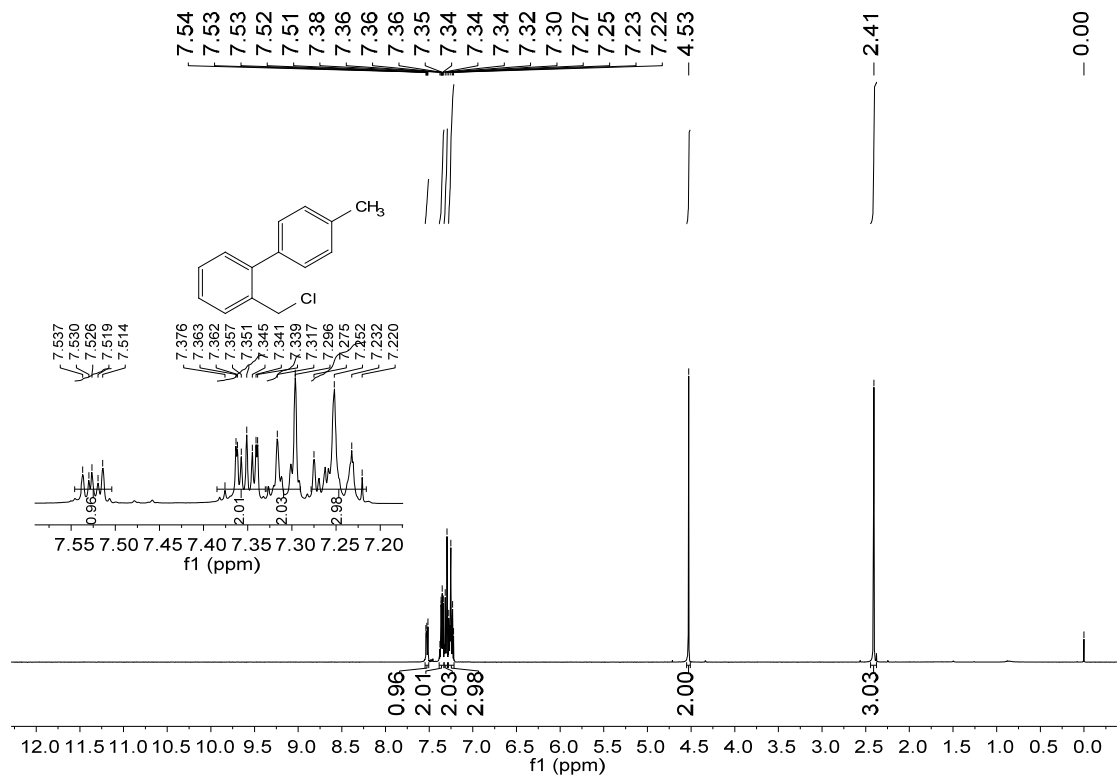
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
252.0723	252.0706	1.7	6.7	11.0	0.8	C17 H13 Cl

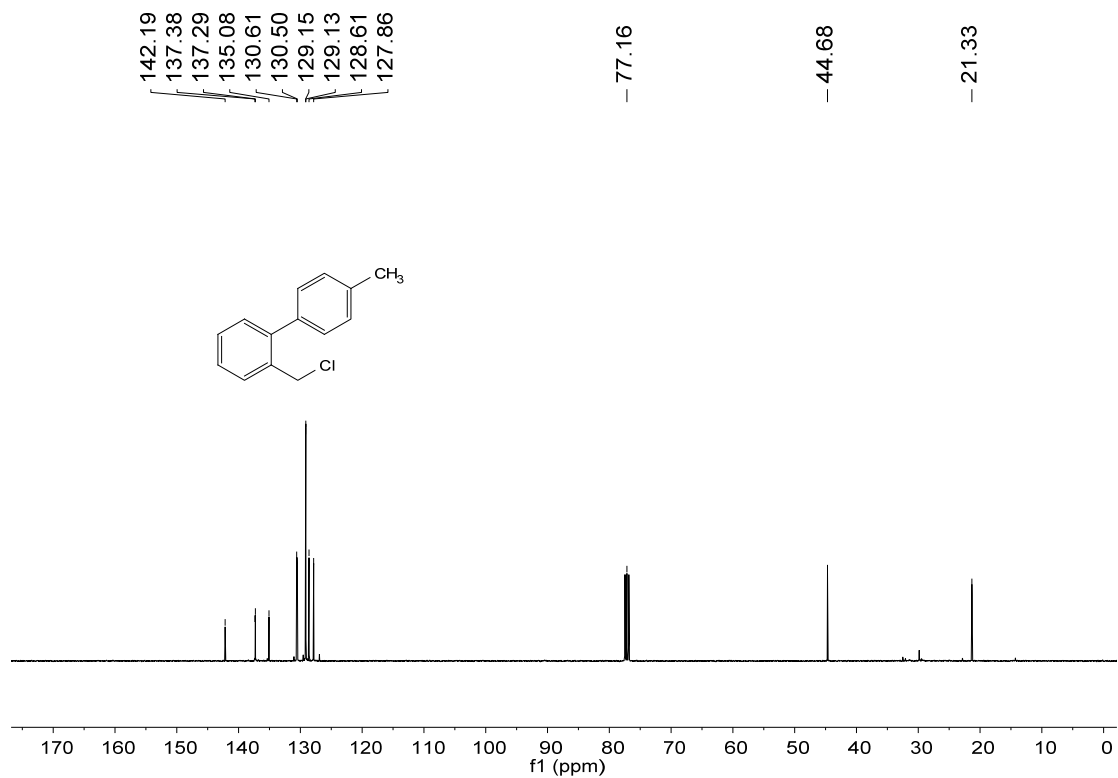
2-(chloromethyl)-1,1'-biphenyl[5a]



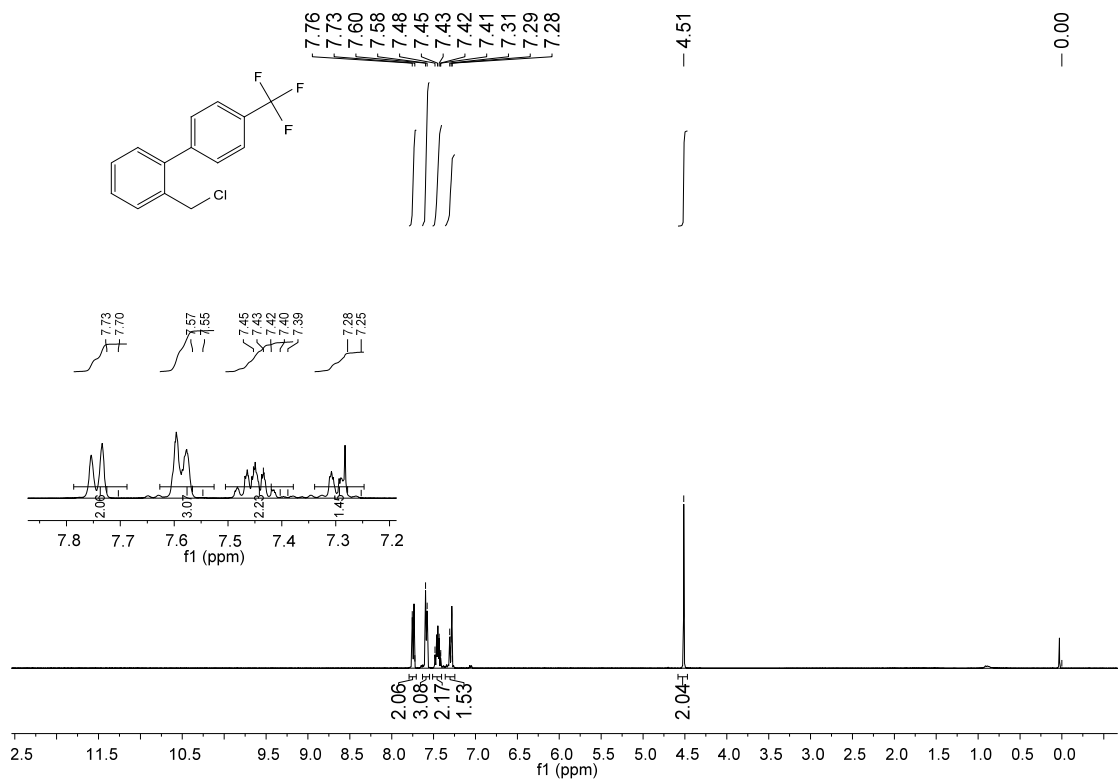


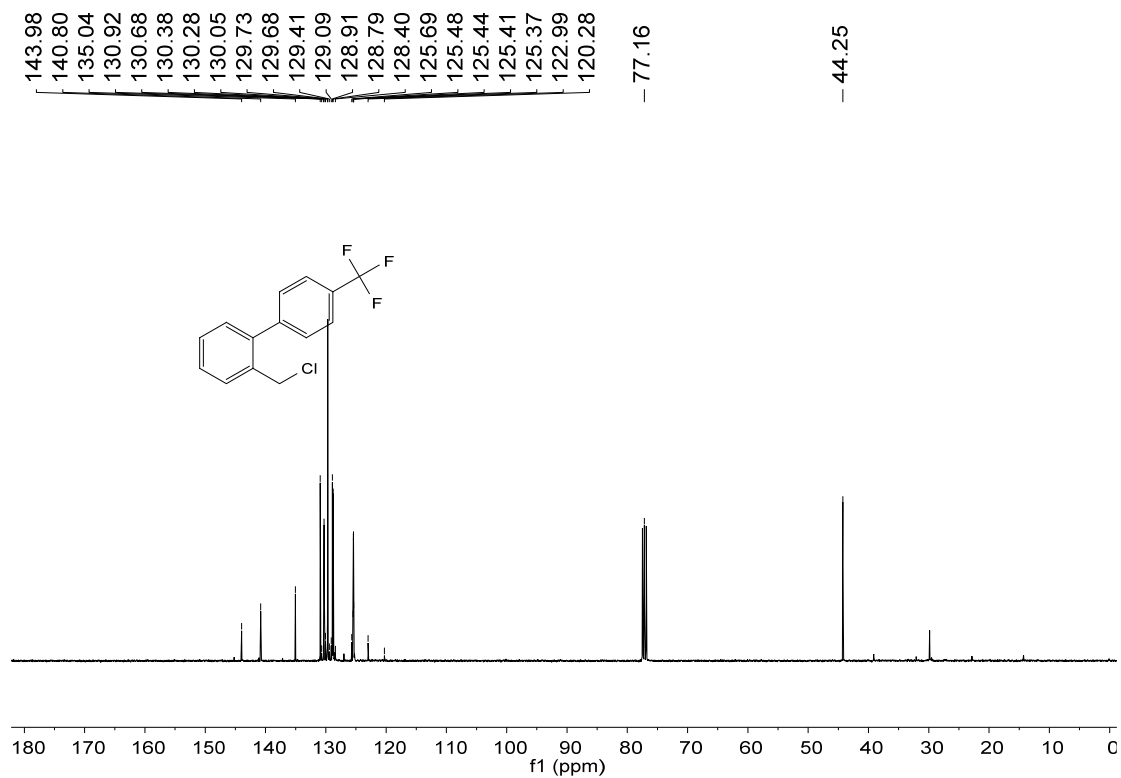
2-(chloromethyl)-4'-methyl-1,1'-biphenyl[5b]



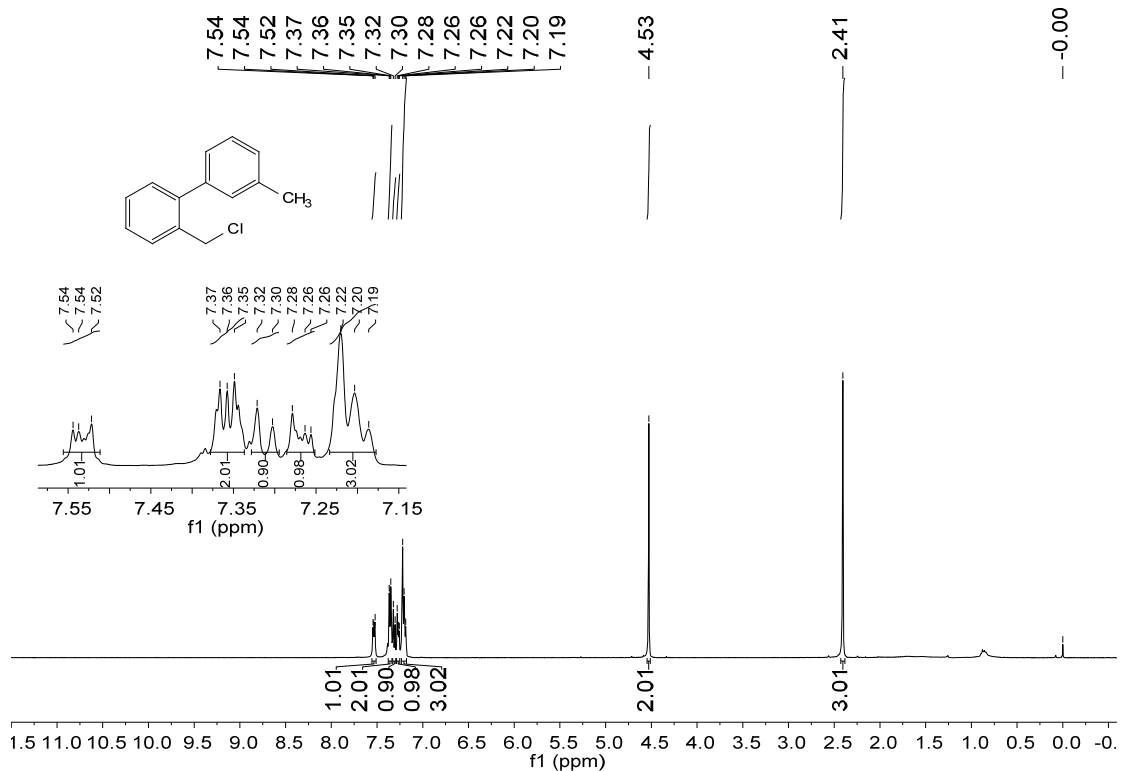


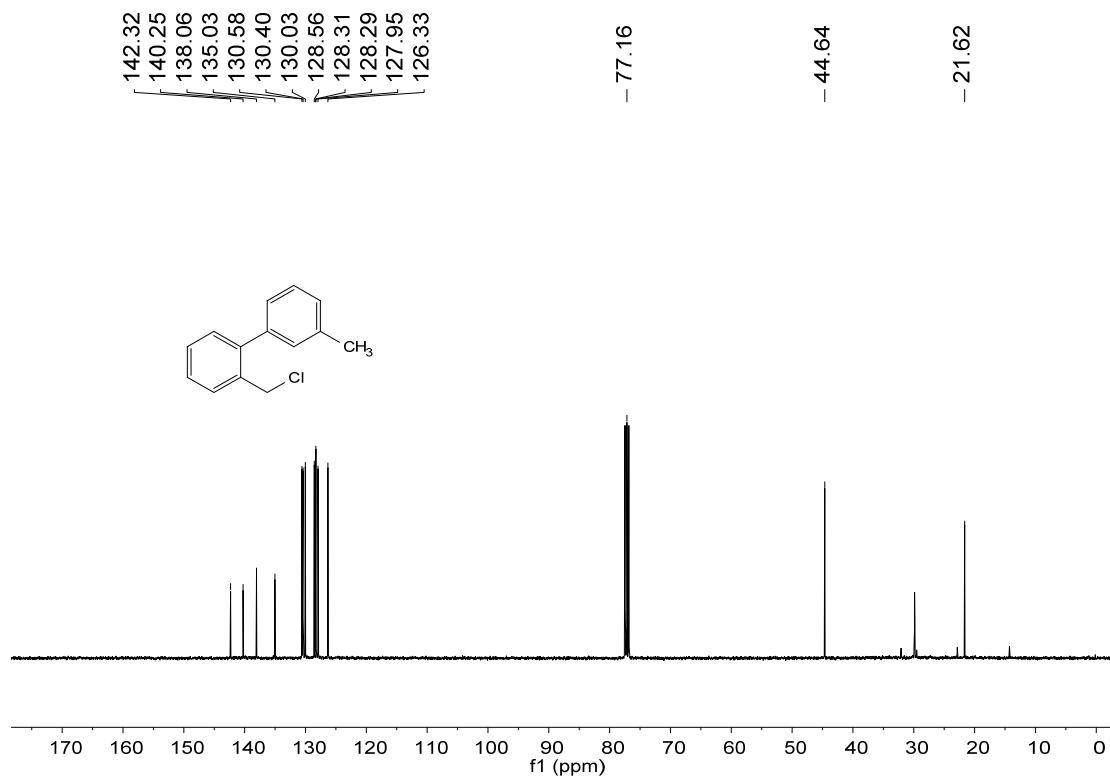
2-(chloromethyl)-4'-(trifluoromethyl)-1,1'-biphenyl[5c]



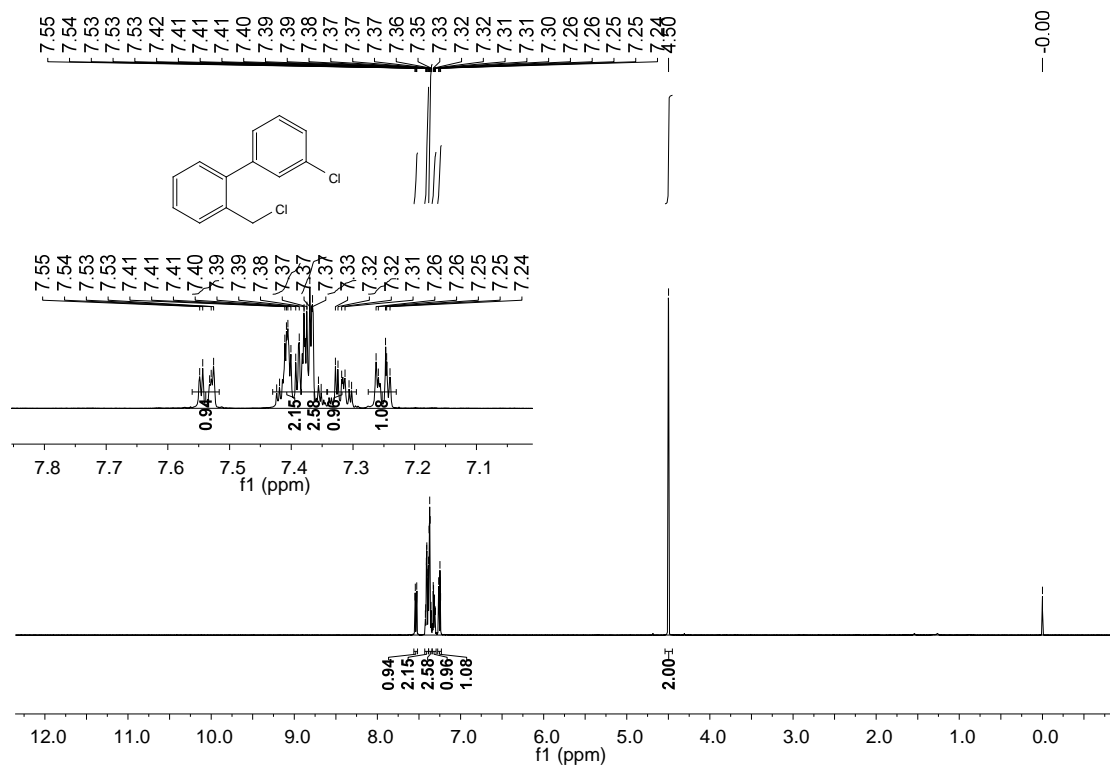


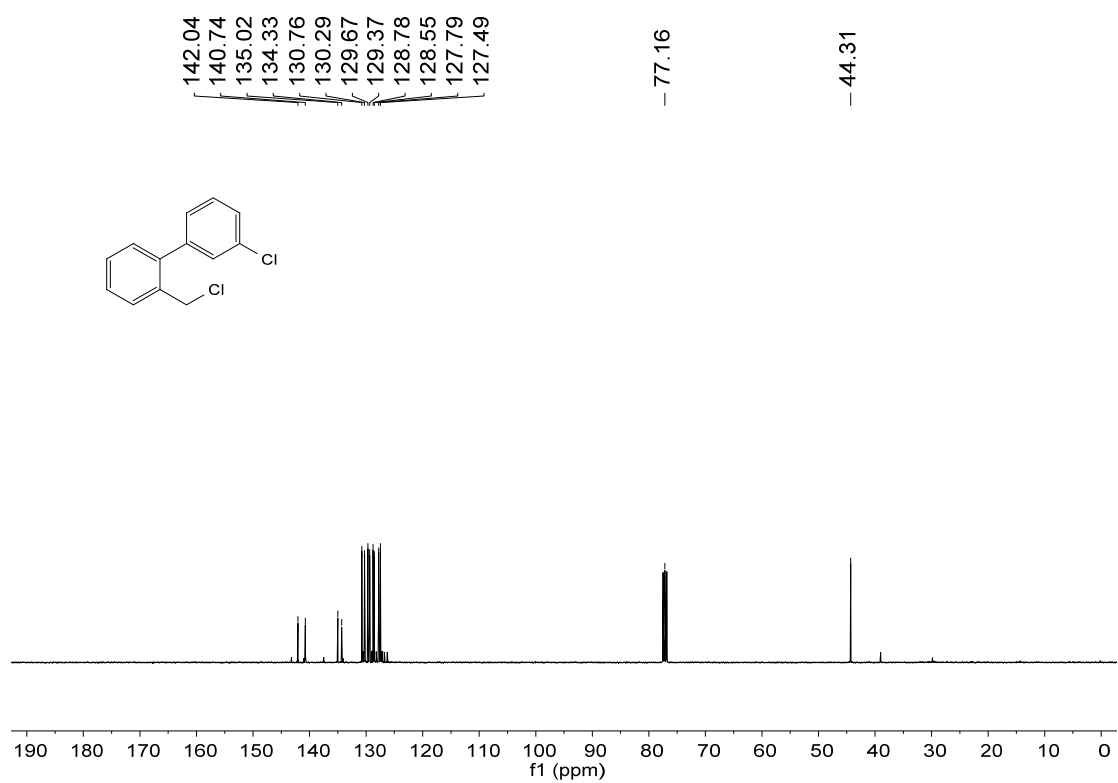
2-(chloromethyl)-3'-methyl-1,1'-biphenyl[5d]



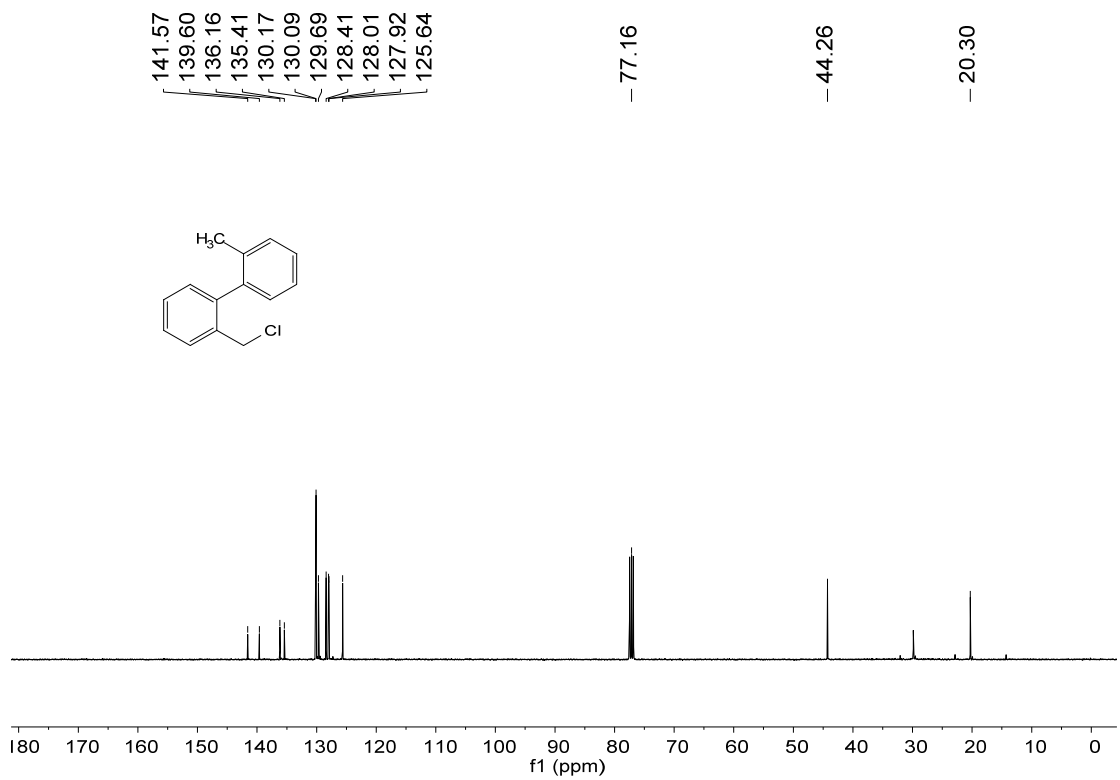
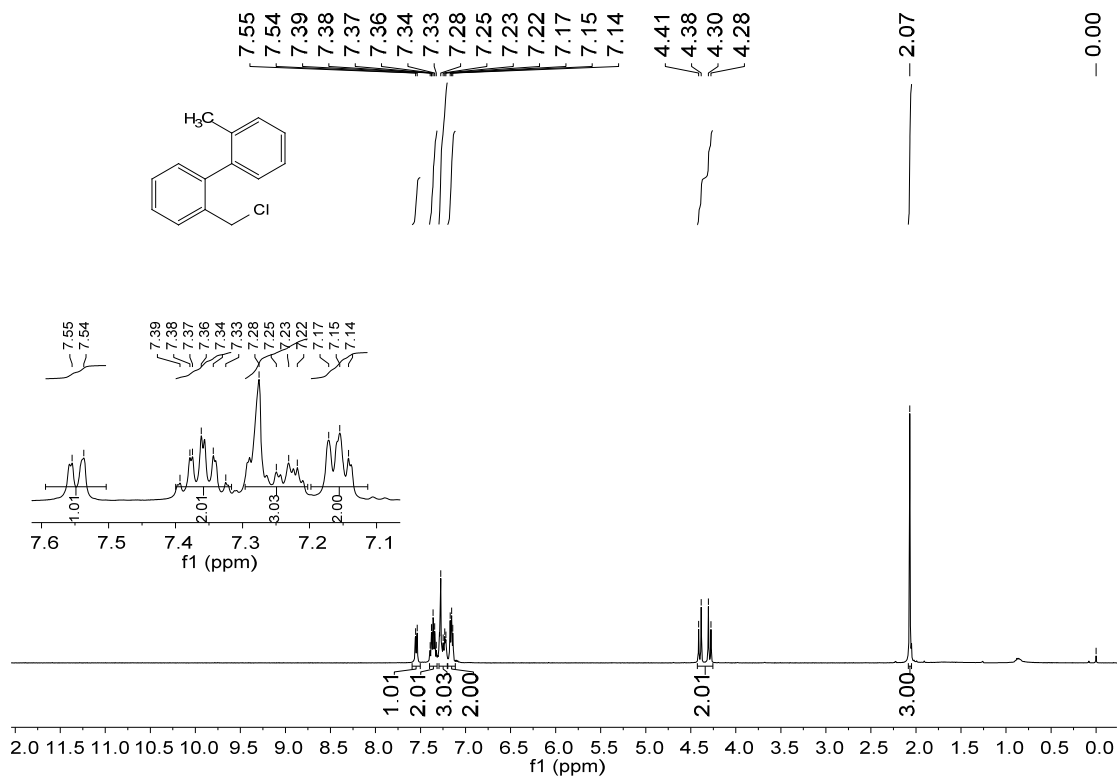


3'-chloro-2-(chloromethyl)-1,1'-biphenyl[5e]

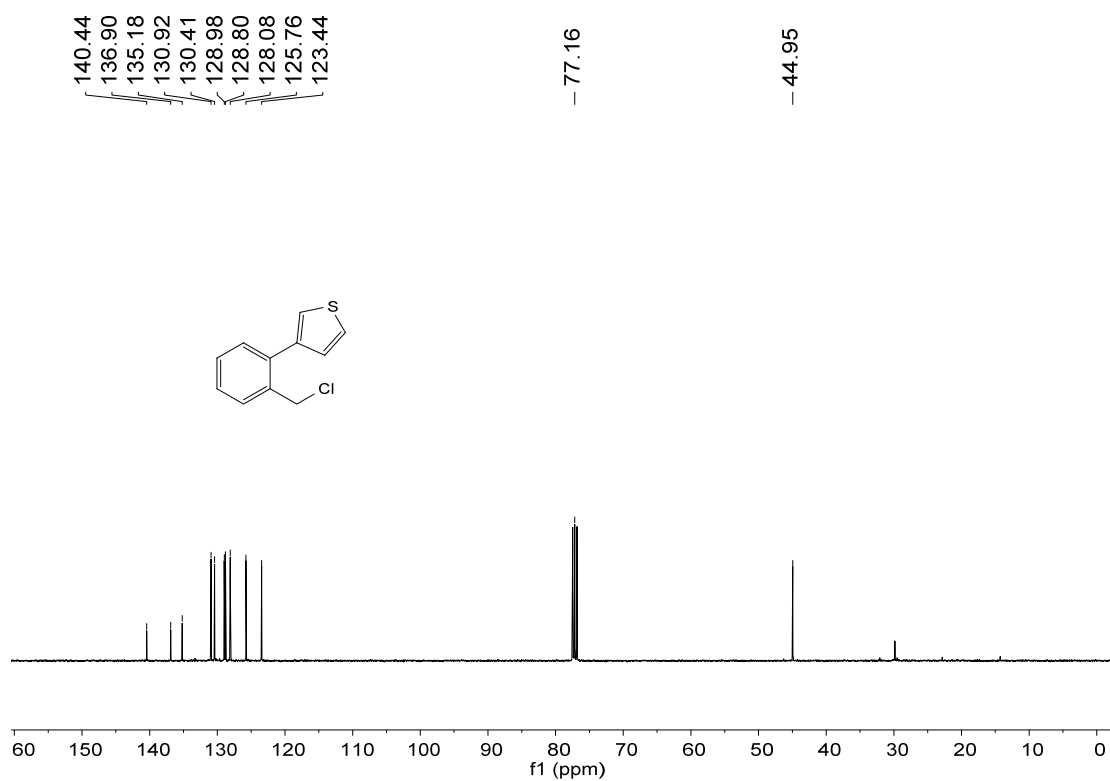
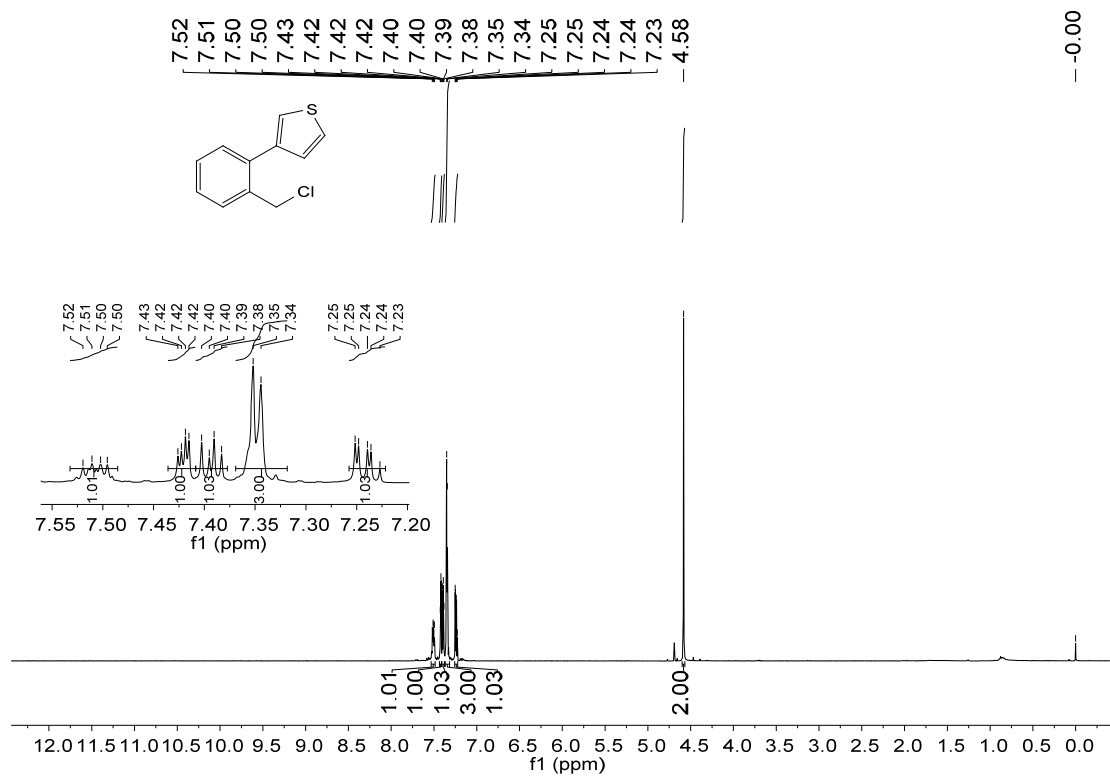




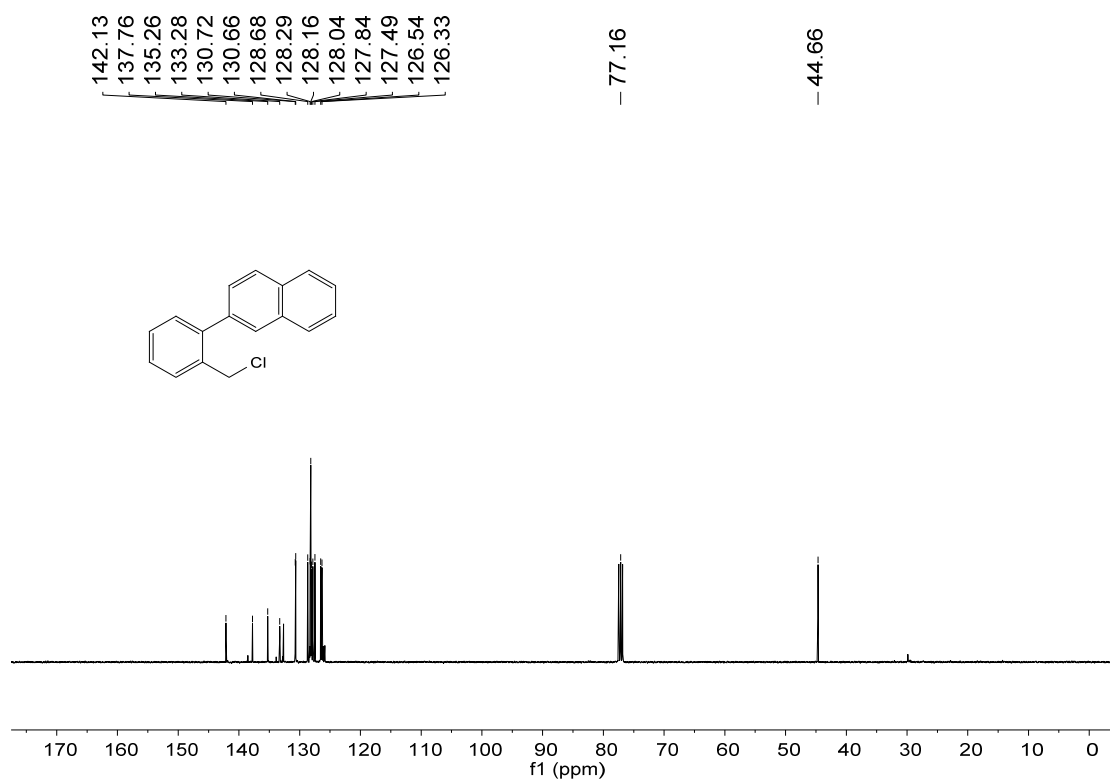
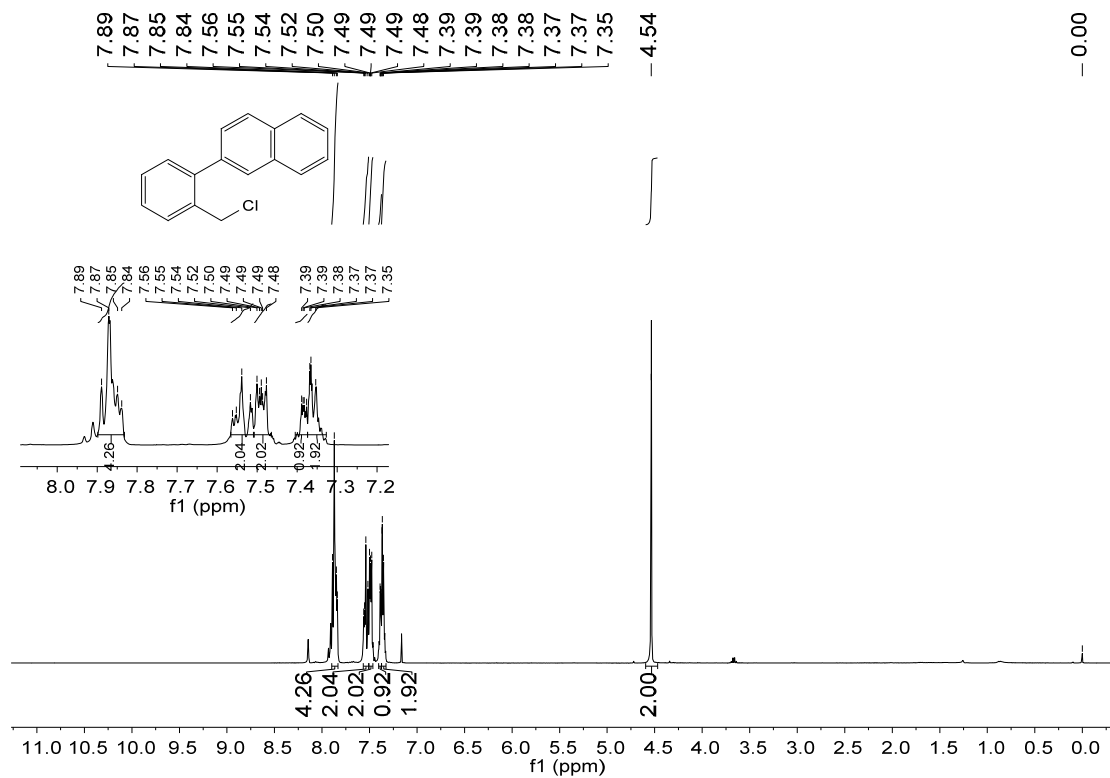
2-(chloromethyl)-2'-methyl-1,1'-biphenyl[5f]



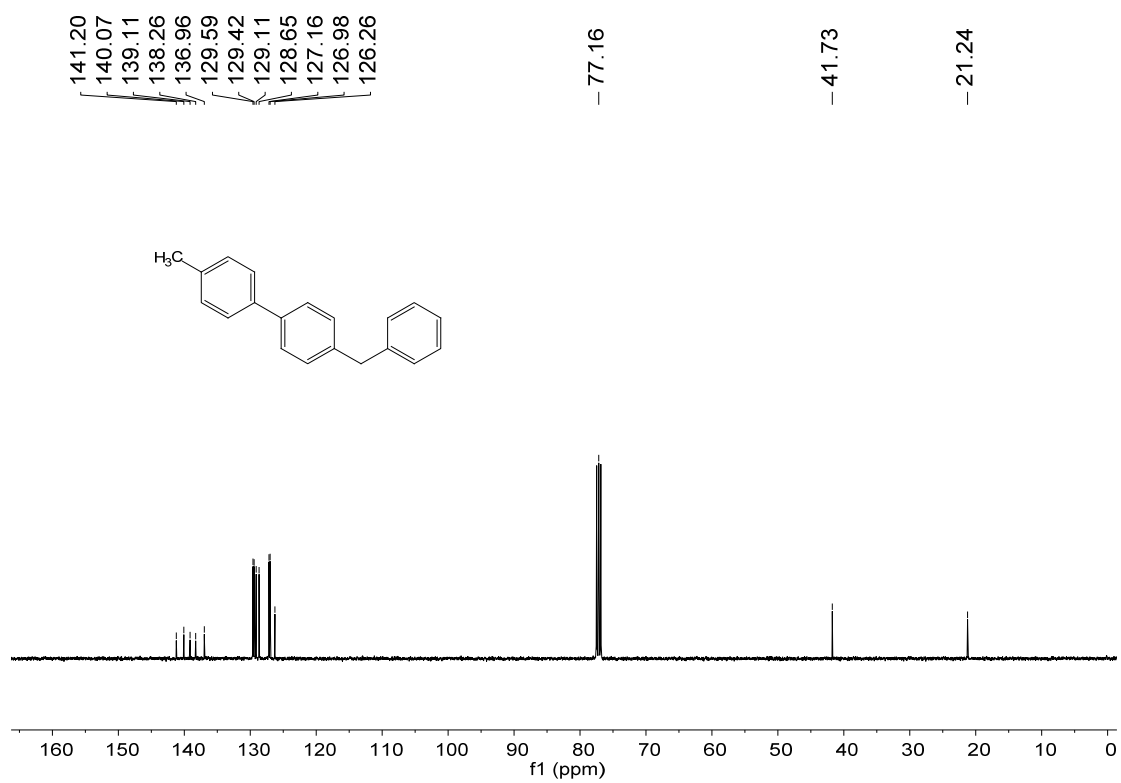
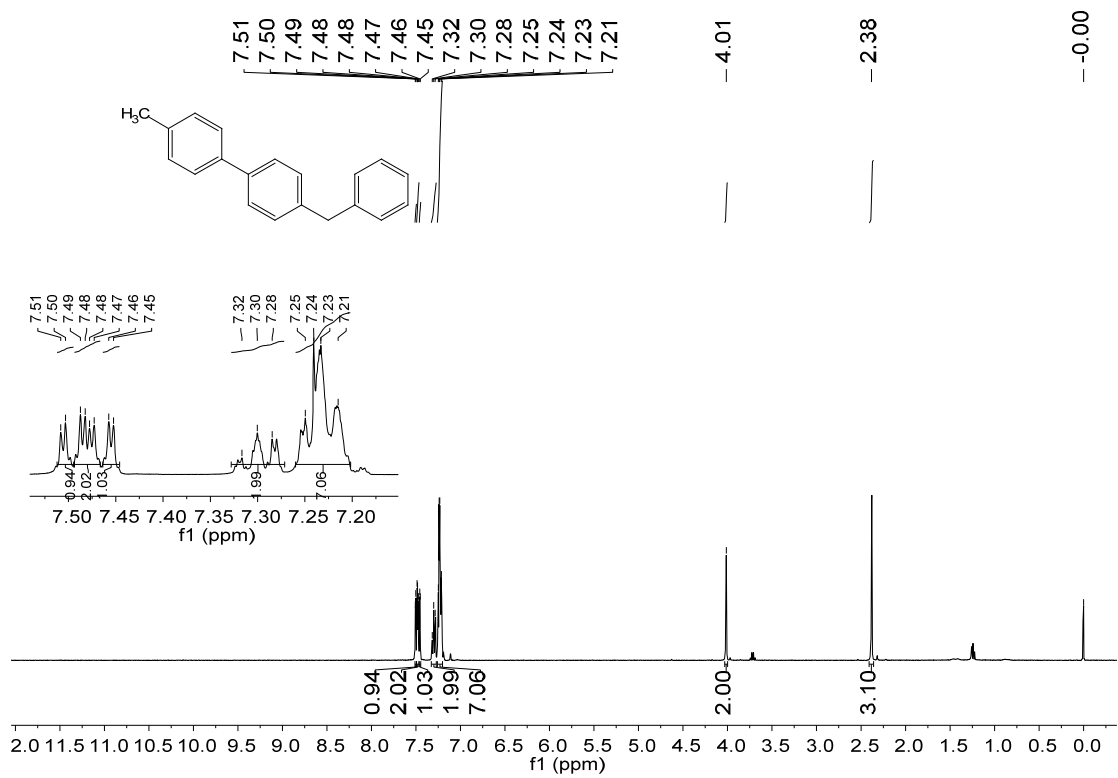
3-(2-(chloromethyl)phenyl)thiophene[5g]



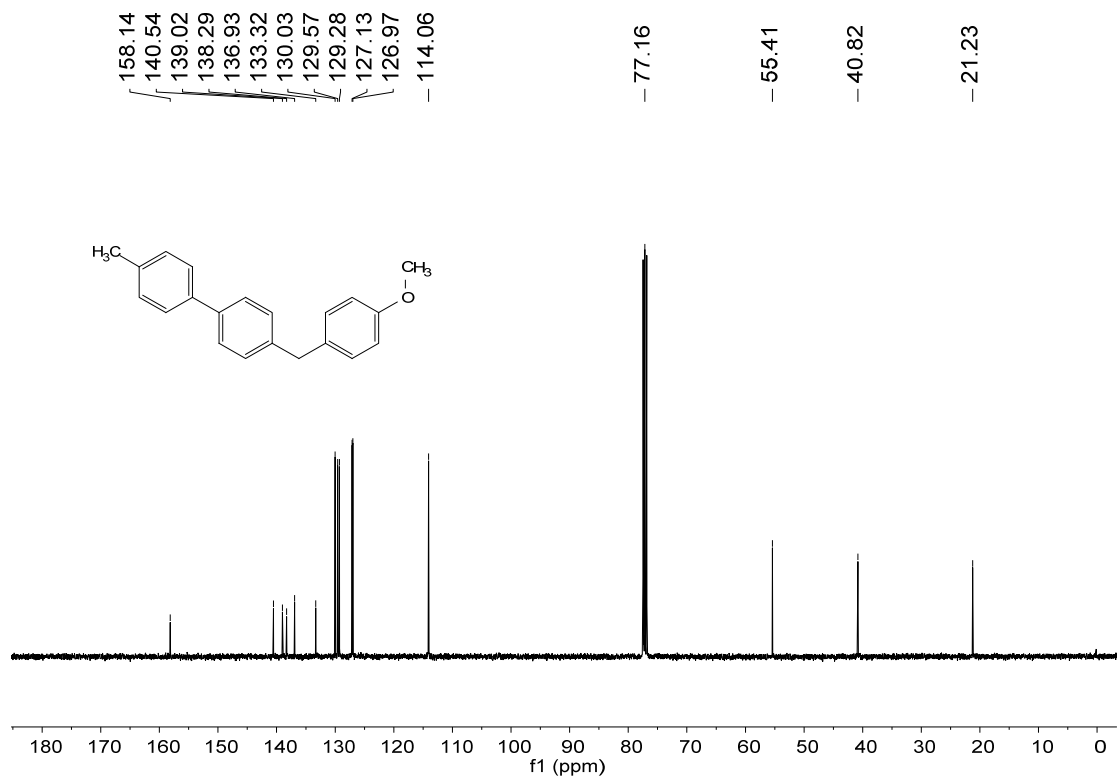
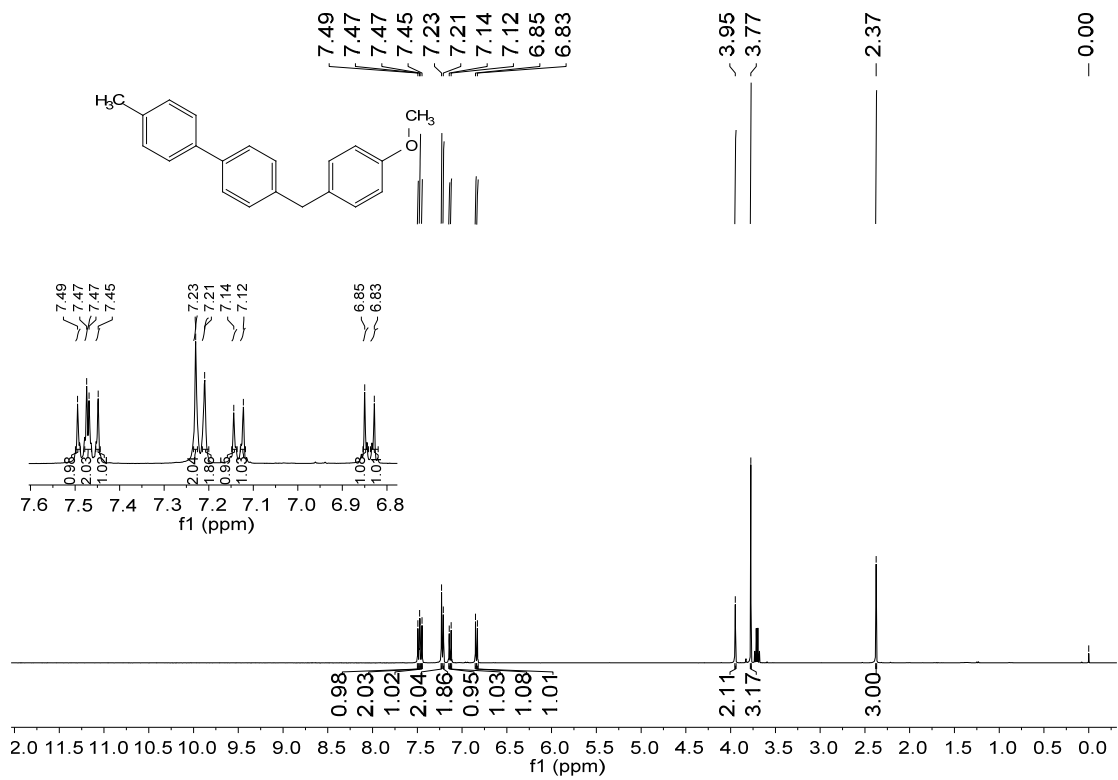
2-(2-(chloromethyl)phenyl)naphthalene[5h]



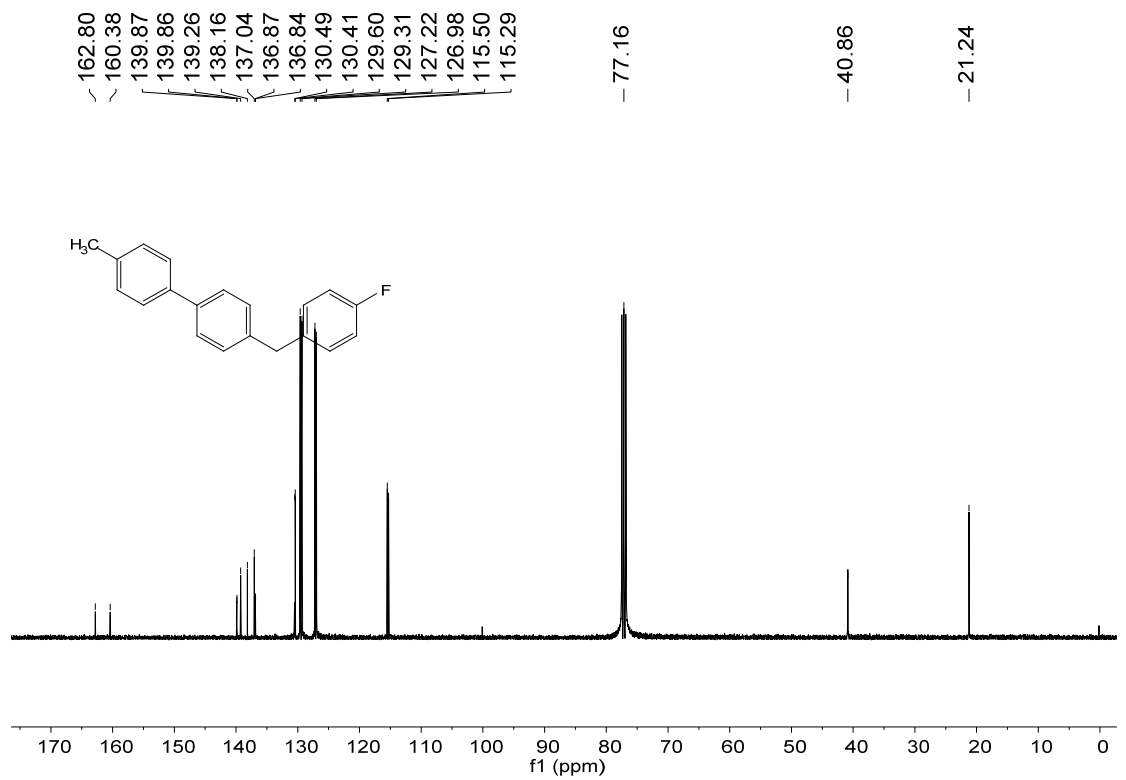
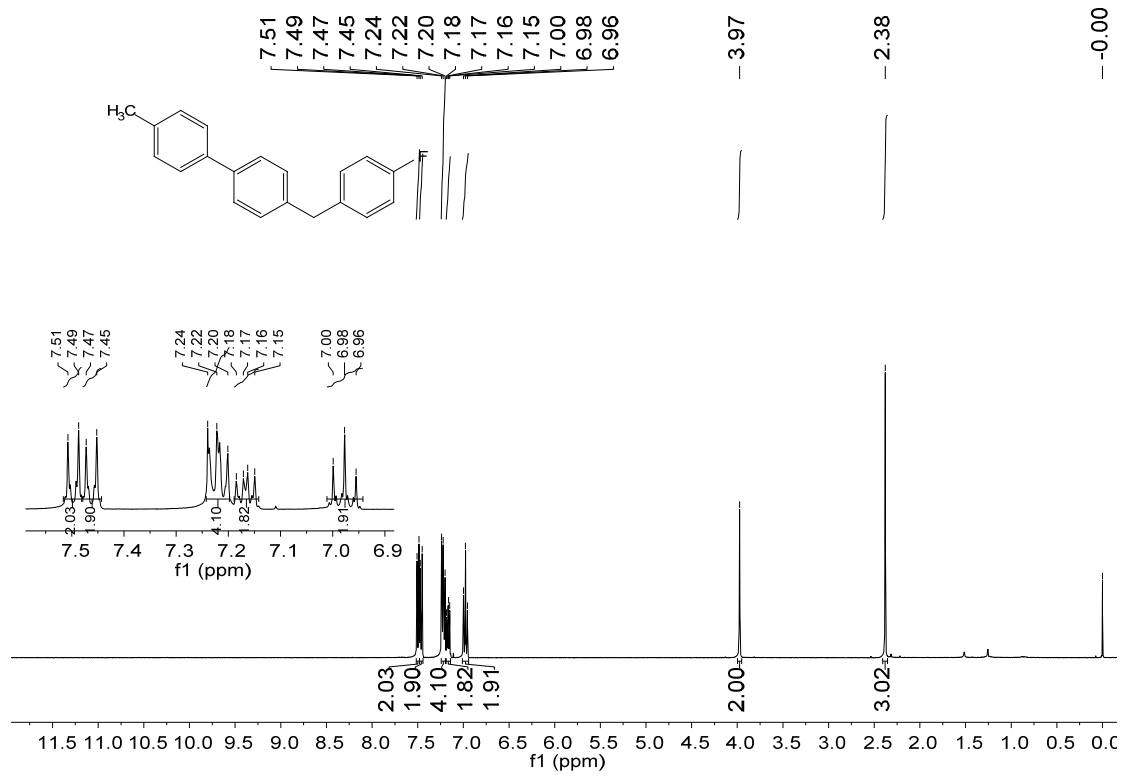
4-benzyl-4'-methyl-1,1'-biphenyl[6a]



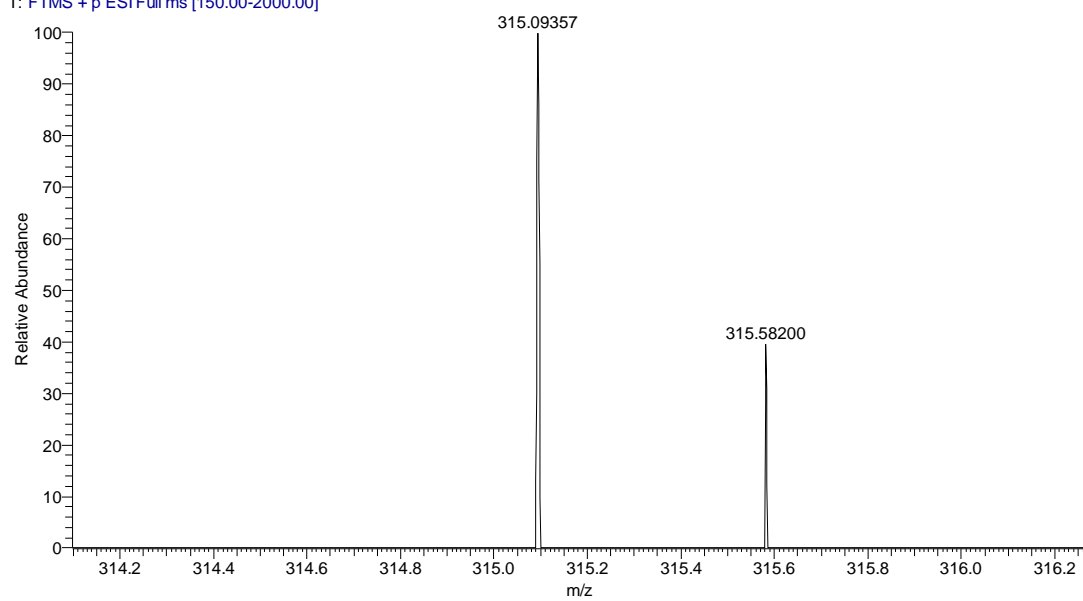
4-(4-methoxybenzyl)-4'-methyl-1,1'-biphenyl[6b]



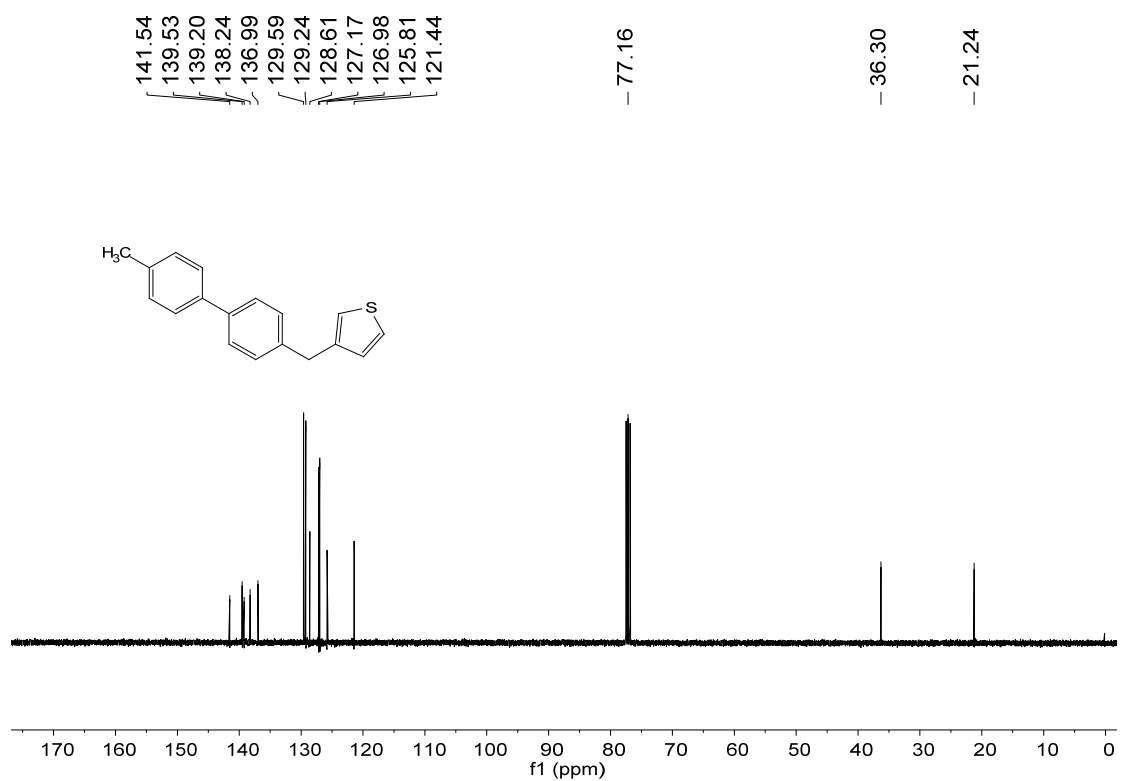
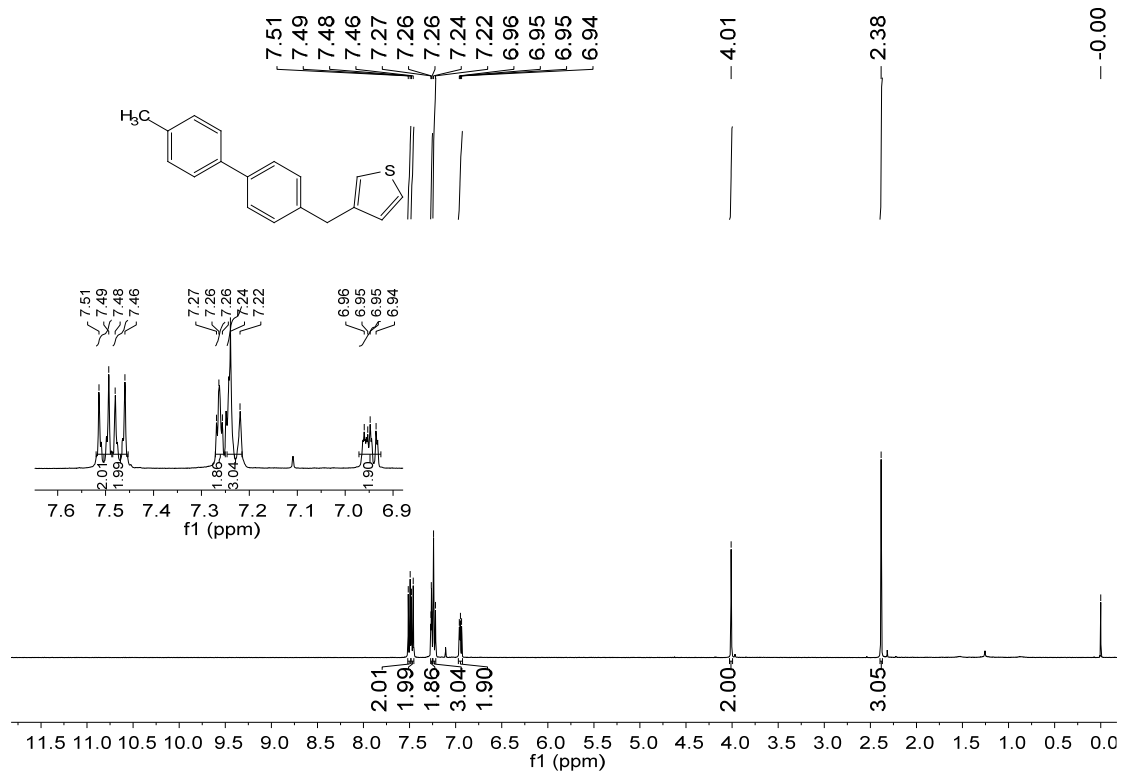
4-(4-fluorobenzyl)-4'-methyl-1,1'-biphenyl[6c]



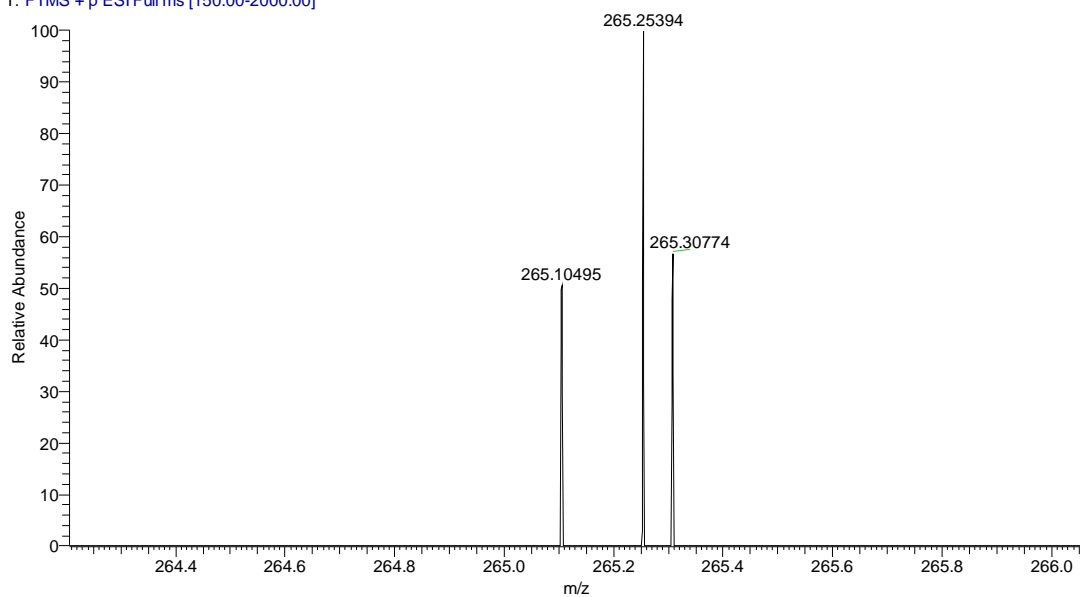
6 #4 RT: 0.06 AV: 1 NL: 1.24E3
T: FTMS + p ESI Full ms [150.00-2000.00]



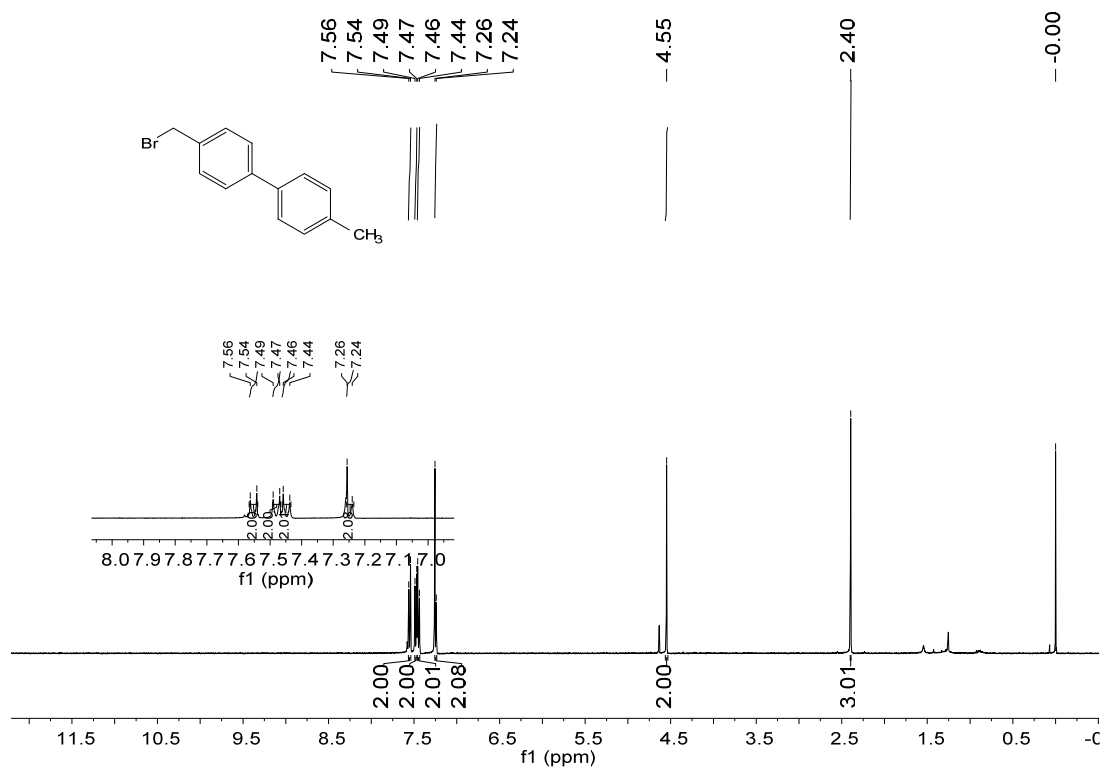
3-((4'-methyl-[1,1'-biphenyl]-4-yl)methyl)thiophene[6d]

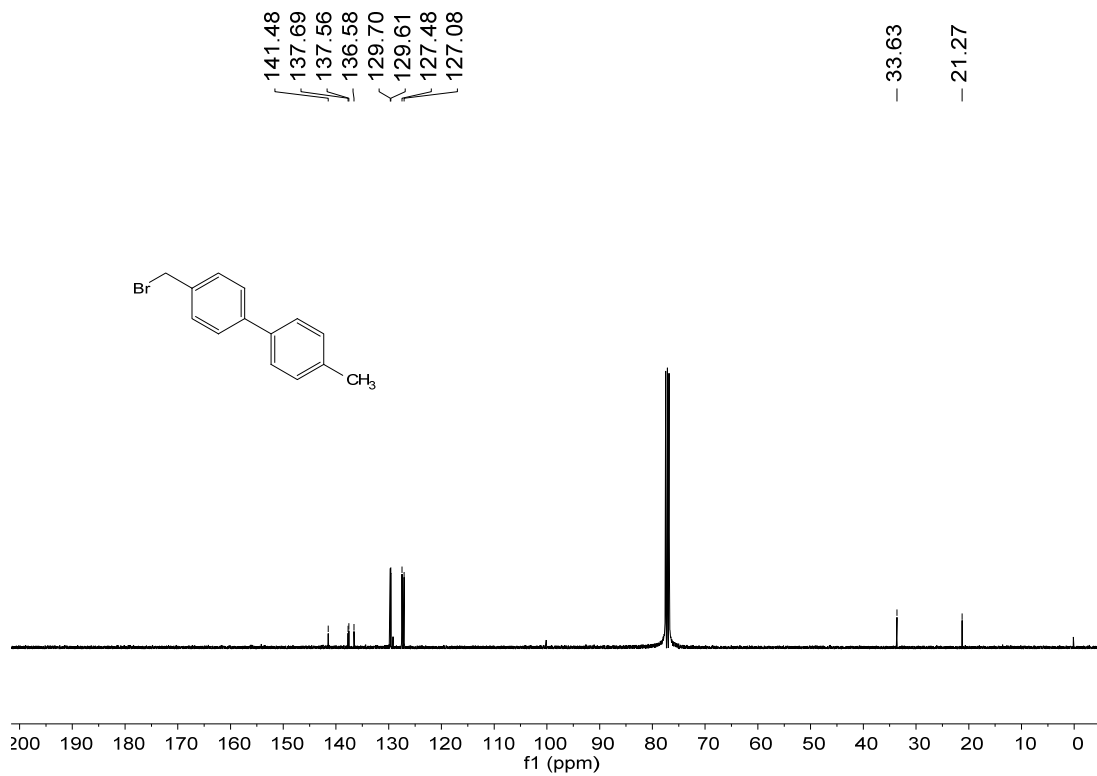


7 #1 RT: 0.01 AV: 1 NL: 1.51E3
T: FTMS + p ESI Full ms [150.00-2000.00]

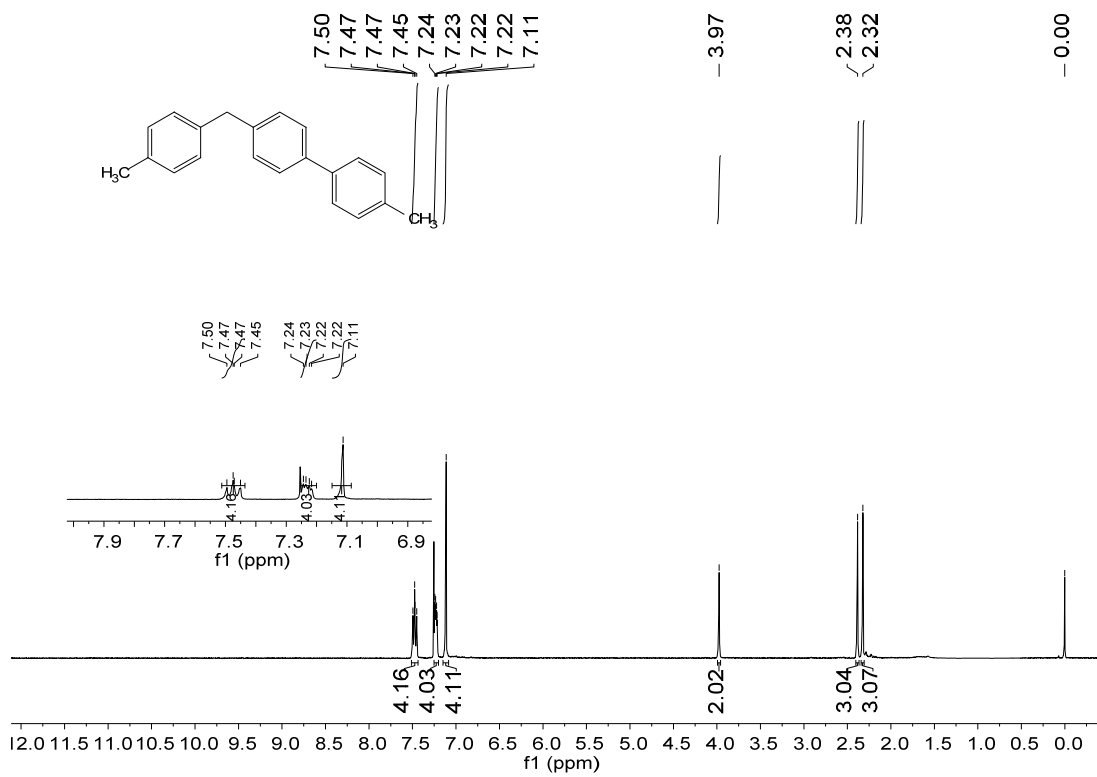


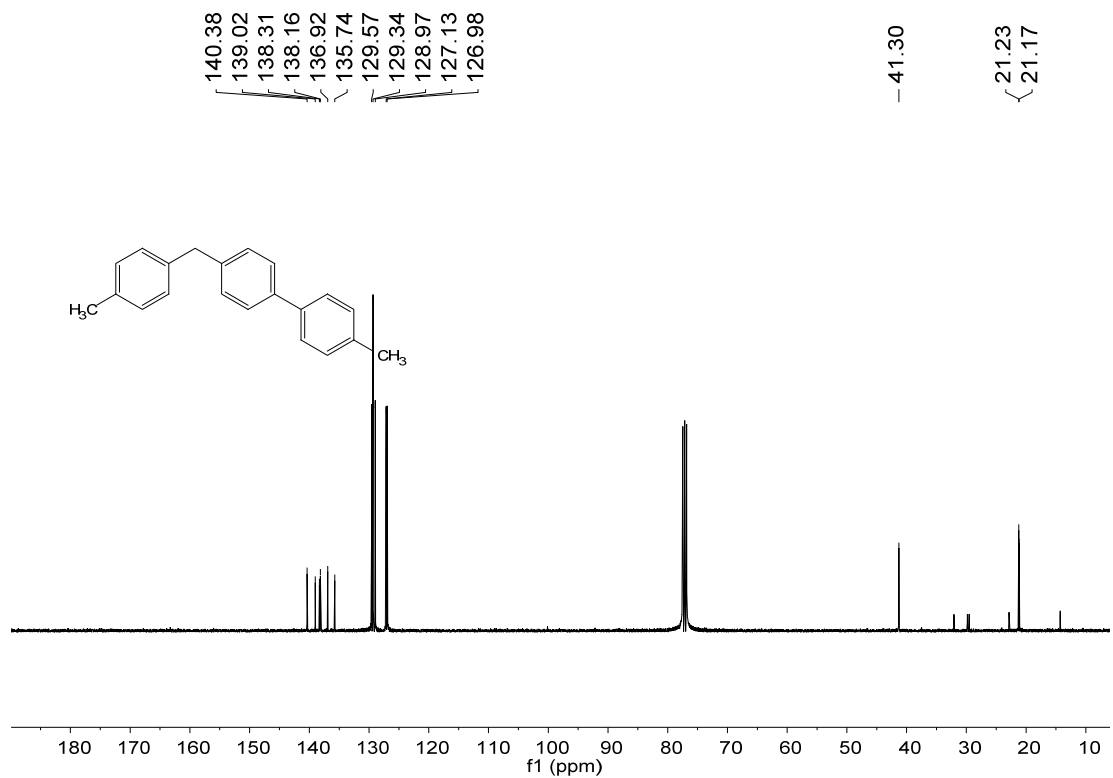
4-(bromomethyl)-4'-methyl-1,1'-biphenyl [7a]





4-methyl-4'-(4-methylbenzyl)-1,1'-biphenyl [7b]





4-methyl-1,1'-biphenyl [7c]

