Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Palladium-Catalyzed Direct Arylation of Benzoxazoles with Unactivated Simple Arenes

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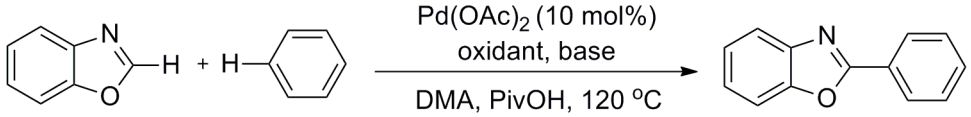
General Information

5-fluorobenzoxazole,[1] 5-bromobenzoxazole,[1] 5-phenylbenzoxazole,[1] naphtha[1,2-d]oxazole,[1] 5-acetylbenzoxazole,[1] 6-methylbenzoxazole,[1] benzoxazole-5-carboxylic acid methyl ester,[1] 4-methylbenzoxazole,[1] 5-tert-butylbenzoxazole,[1] 5-methoxybenzoxazole,[1] 5-nitrobenzisoxazole,[1] 5-trifluoromethylbenzoxazole[1] benzoxazole-6-carboxylic acid methyl ester[1] and 2-deuterated 5-methylbenzoxazole[2] were prepared according to the reported procedures. ^{1}H and ^{13}C spectra of known compounds were in accordance with those described in the literatures. All other reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros, and Meryer and used without further purification. DMA was distilled from CaH_2 under nitrogen and stored under nitrogen. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (377 MHz) spectra were recorded in $CDCl_3$ solutions using a Burker AVANCE 400 spectrometer. Elemental analysis was done on the CHNOS Elemental Analyzer (Vario MICRO). Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and 1200LC.

General Experimental Procedures

Table 1 Selected Results from the Optimization Studies for Palladium-Catalyzed Direct Arylation of Benzoxazole with Simple Benzene[a]



1a 3a

Entry	Base (equiv)	Oxidant (equiv)	Solvent(mL)	Yield (%)[b]
1	K_2CO_3 (2.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
2	Cs_2CO_3 (2.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
3	K_3PO_4 (2.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	trace
4	NaOAc (2.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
5	tBuOLi (2.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
6	Pyridine (0.2)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
7	K_2CO_3 (2.0) +PivOH (3.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
8	K_3PO_4 (2.0) +PivOH (3.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	14
9	PivOK (2.0) +PivOH (1.0)	$Cu(OAc)_2$ (2.0)	DMA (2.0)	none
10	K_3PO_4 (2.0) +PivOH (3.0)	$CuCl_2$ (2.0)	DMA (2.0)	62
11	K_3PO_4 (2.0) +PivOH (3.0)	$Cu(OTf)_2$ (2.0)	DMA (2.0)	27
12	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (2.0)	85(79)[c]
13[d]	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (2.0)	65
14[e]	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (2.0)	12
15[f]	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (2.0)	none
16	K_3PO_4 (2.0) +PivOH (3.0)	Ag_2CO_3 (2.0)	DMA (2.0)	none
17	K_3PO_4 (2.0) +PivOH (3.0)	AgOAc (2.0)	DMA (2.0)	none
18	K_3PO_4 (2.0) +PivOH (3.0)	Ag_2O (2.0)	DMA (2.0)	none
19	K_3PO_4 (2.0) +PivOH (3.0v)	AgF (2.0)	DMA (2.0)	none
20	K_3PO_4 (2.0) +PivOH (3.0)	BQ (2.0)	DMA (2.0)	trace
21[g]	K_3PO_4 (2.0)	$CuBr_2$ (2.0)	DMA (2.0)	26
22[h]	K_3PO_4 (2.0)	$CuBr_2$ (2.0)	DMA (2.0)	70
23[i]	K_3PO_4 (2.0)	$CuBr_2$ (2.0)	DMA (2.0)	60
24[j]	PivOH (3.0)	$CuBr_2$ (2.0)	DMA (2.0)	none
25	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMF (2.0)	28
26	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMSO (2.0)	24
27	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	Dioxane (2.0)	14
28	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	NMP (2.0)	36
29	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (0)	none
30	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (0.5)	10
31	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (1.0)	28
32	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (2.0)	DMA (1.5)	60
33	K_3PO_4 (1.2) +PivOH (1.8)	$CuBr_2$ (2.0)	DMA (2.0)	14
34	K_3PO_4 (1.6) +PivOH (2.4)	$CuBr_2$ (2.0)	DMA (2.0)	30

35	K_3PO_4 (2.4) +PivOH (3.6)	$CuBr_2$ (2.0)	DMA (2.0)	32
36	K_3PO_4 (2.8) +PivOH (4.2)	$CuBr_2$ (2.0)	DMA (2.0)	14
37	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (1.6)	DMA (2.0)	71
38	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (1.2)	DMA (2.0)	50
39	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (1.0)	DMA (2.0)	38
40	K_3PO_4 (2.0) +PivOH (3.0)	$CuBr_2$ (0.2)	DMA (2.0)	8

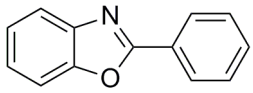
[a] Reaction conditions: benzoxazole **1** (0.2 mmol), benzene **2** (4.0 mL), base (2.0 equiv), acid (3.0 equiv), oxidant (2 equiv), solvent (2.0 mL), O_2 (1 atm), 120 ℃, 24 h. [b] GC yields. [c] isolated yield. [d] Reaction was carried out under air. [e] Reaction was carried out under nitrogen. [f] In the absence of palladium. [g] acetic acid (3.0 equiv). [h] *tert*-butylacetic acid (3.0 equiv). [i] Isobutyric acid (3.0 equiv). [j] in the absence of K_3PO_4. Note: BQ = benzoquinone.

General Procedure of Palladium-Catalyzed Direct Arylation of Benzoxazoles with Simple Arenes：

In a glove box, a 25 mL Schlenk tube equipped with a stir bar was charged with $CuBr_2$ (2 equiv), K_3PO_4 (2 equiv), PivOH (3 equiv), $Pd(OAc)_2$ (10 mol %). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMA (2 mL), arene (4 mL), and benzoxazoles (0.2 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. The reaction mixture was stirred at 120 □ for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (20 mL). The filtrate was washed with water (3×15 mL). The organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

Characterization of Products in Details :

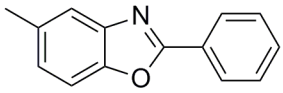
2-phenylbenzoxazole[3]



3a

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (79% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

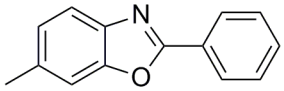
5-methyl-2-phenylbenzoxazole[3]



3b

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (93% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

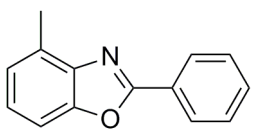
6-methyl-2-phenylbenzoxazole[3]



3c

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (65% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

4-methyl-2-phenylbenzoxazole[3]

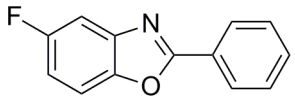


3d

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a

white solid (69% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

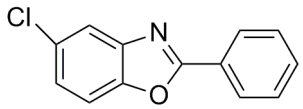
5-fluoro-2-phenylbenzoxazole[4]



3e

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (91% yield). The ^{1}H, ^{13}C,^{19}F NMR spectra were in accordance with those described in the literature.

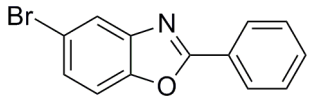
5-chloro-2-phenylbenzoxazole[4]



3f

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (83% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

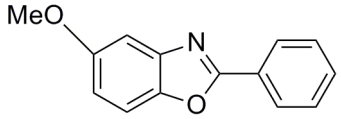
5-bromo-2-phenylbenzoxazole[4]



3g

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (52% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

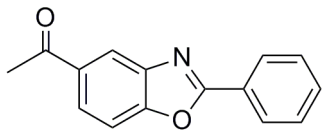
5-methoxy-2-phenylbenzoxazole[3]



3h

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (74% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

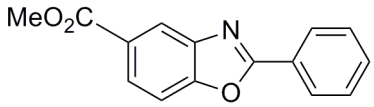
5-acetyl-2-phenylbenzoxazole



3i

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (65% yield) in 48h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 1.5 Hz, 1 H), 8.27 - 8.25 (m, 2H), 8.05 (dd, *J* =8.5, 1.7 Hz, 1H), 7.63 (d, *J=8.5* Hz, 1H), 7.58-7.53(m, 3H), 2.69(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$):δ 197.1, 164.5, 153.7, 142.3, 134.4, 132.1, 129.0, 127.8, 126.6, 125.8, 120.9, 110.6, 26.8; Anal. Calcd. For $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.88; H, 5.18; N, 5.61.

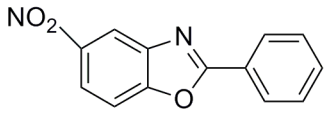
2-phenyl-benzoxazole-5-carboxylic acid methyl ester



3j

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (77% yield) in 48h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.4 (d, *J* =1.4 Hz, 1H), 8.25-8.23 (m, 2 H), 8.09 (dd, *J* =8.5, 1.6 Hz, 1H), 7.6(d, *J* =8.5 Hz, 1H), 7.55-7.49(m, 3H), 3.95(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 166.7, 164.3, 153.6, 142.2, 131.9, 128.9, 127.8, 127.0, 126.6, 121.9, 110.3, 52.3; Anal. Calcd. For $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.14; H, 4.57; N, 5.47.

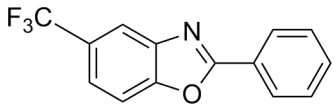
5-nitro-2-phenylbenzoxazole[5]



3k

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (63% yield) in 48h. The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

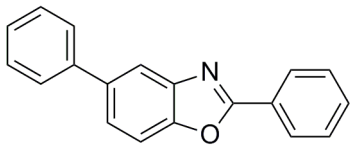
5-trifluoromethyl-2-phenylbenzoxazole[6]



3l

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (66% yield) in 48h. The ^{1}H, ^{13}C, ^{19}F NMR spectra were in accordance with those described in the literature.

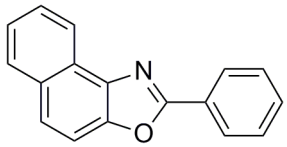
2,5-diphenyl-benzooxazole[7]



3m

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (75% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

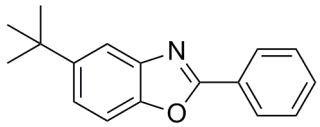
2-phenyl-naphth[1,2-d]oxazole[3]



3n

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (86% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

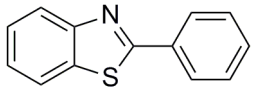
5-tert-butyl-2-phenylbenzoxazole[8]



3o

Following the general procedure, using 9:1 hexane-EtOAc as the eluant afforded a white solid (94% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

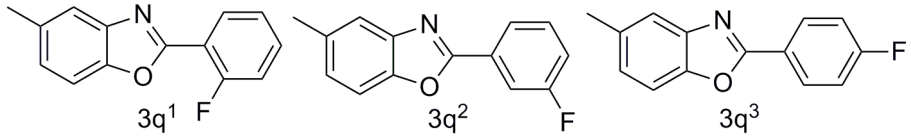
2-phenylbenzothiazole[9]



3p

Follow the general procedures, 2.0 equiv $Cu(OAc)_2$ and 1.5 equiv PivOH was used at 130℃ for 48h, using 9:1 hexane-EtOAc as the eluant afforded a white solid (52% yield). The ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature.

5-methyl-2-(o-fluorophenyl)benzoxazole, 5-methyl-2-(m-fluorophenyl)benzoxazole and 5-methyl-2-(p-fluorophenyl)benzoxazole



$3q^1$ $3q^2$ $3q^3$

Following the general procedure for 48h, using hexane as the eluant afforded a white solid (80% yield) containing (1:1.2:4) isomers (determined by ^{19}F NMR， for two isomers had the same retention time on GC).

Anal. Calcd. For $C_{14}H_{10}FNO$: C, 74.00; H, 4.44; N, 6.16. Found: C, 74.14; H, 4.47; N, 6.32.

Assignments of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR respectively.

$3q^1$

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.22 (m, 2H), 7.54 (s, 1H), 7.44(d, *J* =8.3Hz, 1H), 7.22-7.15(m, 3H), 2.48(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 164.8(d,

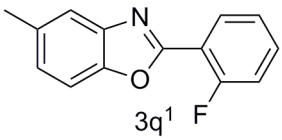
J_F=252.6Hz), 162.2, 149.0, 142.1, 134.6, 129.8(d, J_F=8.9Hz), 128.9, 127.6, 126.3, 123.6(d, J_F=3.1Hz), 119.9, 116.1(d, J_F=22.3Hz), 110.0, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -107.66 (s, 1F).

3q^2

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dm, J=7.8 Hz, 1H), 7.94 (dm, J=9.5 Hz, 1H), 7.58(s, 1H), 7.53-7.47(m, 2H), 7.25-7.18(m, 2H), 2.50(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 162.9(d, J_F=246.7Hz), 161.8(d, J_F=3.5Hz), 149.0, 142.0, 134.7, 130.5(d, J_F=8.2Hz), 129.3(d, J_F=8.6Hz), 126.7, 123.3(d, J_F=3.2Hz), 120.0, 118.4(d, J_F=21.3Hz), 114.4(d, J_F=24.0Hz), 110.0, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -111.9 (s, 1F).

3q^3

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (td, J=7.6, 1.8 Hz, 1H), 7.61-7.60 (m, 1H), 7.54-7.47(m, 2H), 7.32-7.23(m, 2H), 7.20-7.18(m, 1H), 2.49(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 160.8(d, J_F=258.4Hz), 159.9, 148.7, 141.9, 134.5, 133.0(d, J_F=8.7Hz), 130.5 (d, J_F=1.3Hz), 126.7, 124.4(d, J_F=3.9Hz), 120.2, 117.0(d, J_F=21.7Hz), 115.7(d, J_F=10.4Hz), 110.0, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -110.2 (s, 1F).



3q[1]

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Vail#	:
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Batch Filename	:
Report Filename	: Default.lcr
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Chromatogram
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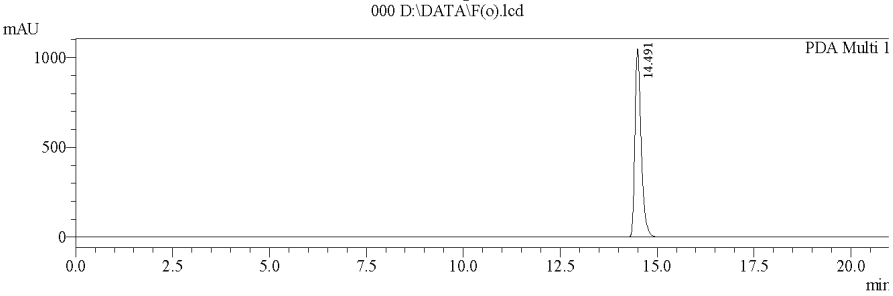
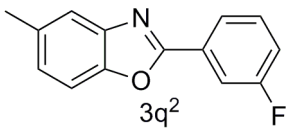


1 PDA Multi 1 / 310nm 4nm

PeakTable

PDA Ch1 310nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	o	14.491	11692901	1048164	100.000	0.000
Total			11692901	1048164	100.000	

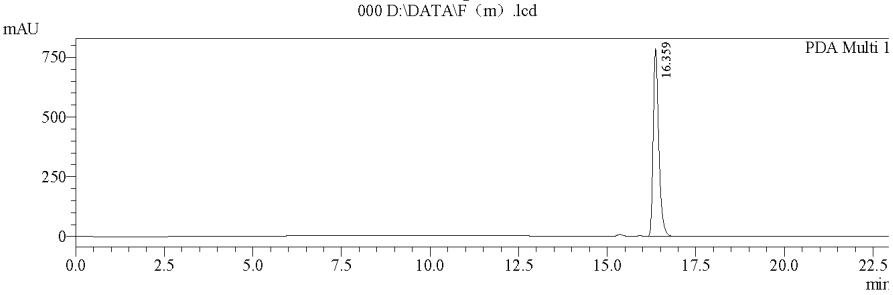


3q^2

Sample Information

Acquired by	: Admin
Sample Name	: 000
Sample ID	: 000
Vail#	:
Injection Volume	: 20 uL
Data Filename	: F（m）.lcd
Method Filename	: 50-100%20min.lcm
Batch Filename	:
Report Filename	: Default.lcr
Date Acquired	: 2012-7-10 17:09:43
Data Processed	: 2012-7-10 17:47:52Unknown

Chromatogram
000 D:\DATA\F（m）.lcd

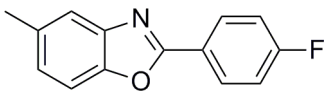


1 PDA Multi 1 / 310nm 4nm

PeakTable

PDA Ch1 310nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	m	16.359	8576365	785137	100.000	0.000
Total			8576365	785137	100.000	

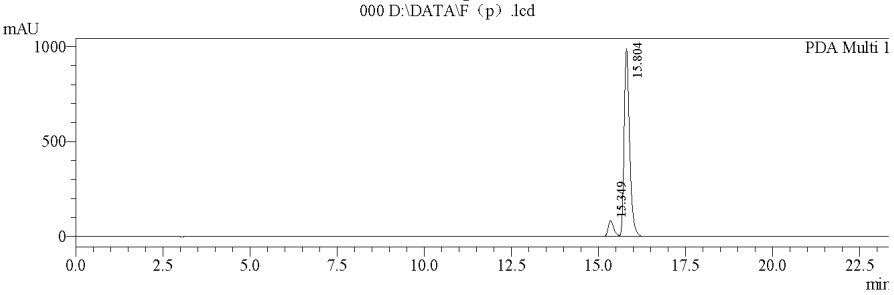


$3q^3$

Sample Information

Acquired by	: Admin
Sample Name	: 000
Sample ID	: 000
Vail#	:
Injection Volume	: 20 uL
Data Filename	: F（p）.lcd
Method Filename	: 50-100%20min.lcm
Batch Filename	:
Report Filename	: Default.lcr
Date Acquired	: 2012-7-10 17:42:10
Data Processed	: 2012-7-10 18:07:20Unknown

Chromatogram
000 D:\DATA\F（p）.lcd

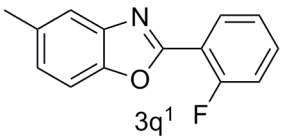


1 PDA Multi 1 / 310nm 4nm

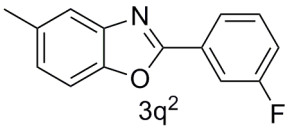
PeakTable

PDA Ch1 310nm 4nm

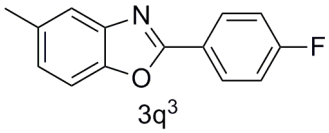
Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1		15.349	893390	82119	7.660	0.000
2	p	15.804	10769793	988560	92.340	1.550
Total			11663183	1070679	100.000	



3q^1



3q^2

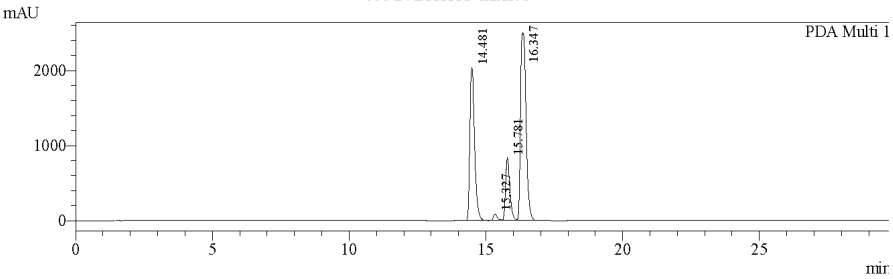


3q^3

Sample Information

Acquired by	: Admin
Sample Name	: 000
Sample ID	: 000
Vail#	:
Injection Volume	: 20 uL
Data Filename	: F-mix.lcd
Method Filename	: 50-100%20min.lcm
Batch Filename	:
Report Filename	: Default.lcr
Date Acquired	: 2012-7-10 16:07:50
Data Processed	: 2012-7-10 18:11:28Unknown

Chromatogram
000 D:\DATA\F-mix.lcd



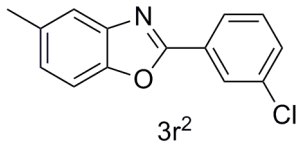
1 PDA Multi 1 / 310nm 4nm

PeakTable

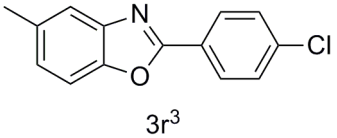
PDA Ch1 310nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	o	14.481	24411513	2038983	34.855	0.000
2		15.327	978921	88309	1.398	2.767
3	p	15.781	9304507	840560	13.285	1.527
4	m	16.347	35342105	2502116	50.462	1.769
Total			70037046	5469968	100.000	

2-(4-chloro-phenyl)-5-methylbenzoxazole and 2-(3-chloro-phenyl)-5-methylbenzoxazole



$3r^2$



$3r^3$

Following the general procedure and 1.8 equiv $CuBr_2$, 2.5 equiv K_3PO_4, 3.75 equiv PivOH was used for 48h, using hexane as the eluant afforded a white solid (68% yield) containing (1.4:1) isomers (determined by ^1H NMR, for they had the same retention time on GC).

Anal. Calcd. For $C_{14}H_{10}ClNO$: C, 69.00; H, 4.14; N, 5.75. Found: C, 69.47; H, 4.20; N, 5.80.

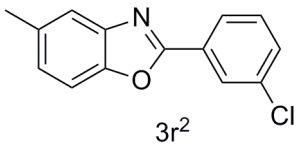
Assignments of ^1H NMR, ^{13}C NMR respectively.

$3r^2$

^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.10-8.08 (m, 1H), 7.54(s, 1H), 7.48-7.40(m, 3H), 7.16(d, *J*= 8.3 Hz, 1H), 2.47(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 161.6, 149.0, 142.1, 135.0, 134.7, 131.3, 130.2, 129.0, 127.5, 126.7, 125.5, 120.0, 110.0, 21.5

$3r^3$

^1H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (m, *2*H), 7.55 (s, 1H), 7.50-7.48(m, 2H), 7.44(d, *J*= 8.3 Hz, 1H), 7.17(d, *J*= 8.3 Hz, 1H), 2.49(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 162.1, 149.0, 142.1, 137.7, 134.7, 129.3, 128.8, 126.5, 125.8, 120.0, 110.0, 21.5;

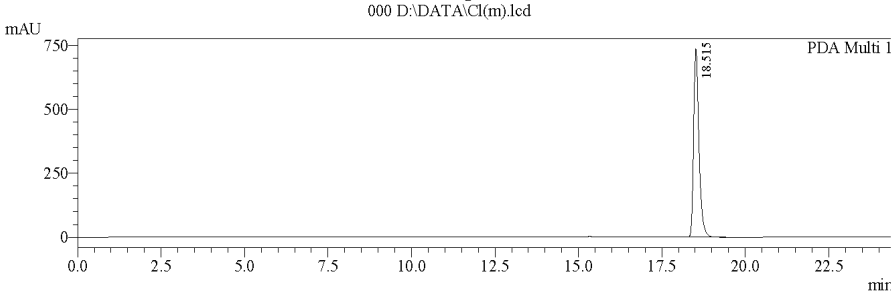


$3r^2$

Sample Information

Acquired by	: Admin
Sample Name	: 000
Sample ID	: 000
Vail#	:
Injection Volume	: 20 uL
Data Filename	: Cl(m).lcd
Method Filename	: 50-100%20min.lcm
Batch Filename	:
Report Filename	: Default.lcr
Date Acquired	: 2012-7-10 10:55:06
Data Processed	: 2012-7-10 17:39:43Unknown

Chromatogram
000 D:\DATA\Cl(m).lcd

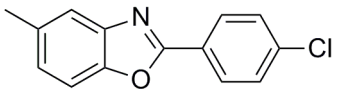


1 PDA Multi 1 / 310nm 4nm

PeakTable

PDA Ch1 310nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	m	18.515	8159918	736668	100.000	0.000
Total			8159918	736668	100.000	

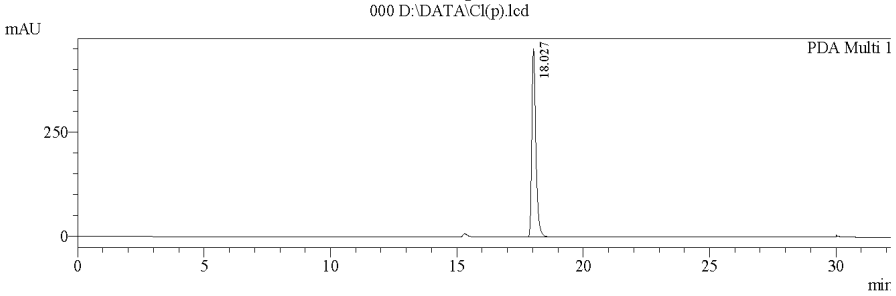


$3r^3$

Sample Information

Acquired by	: Admin
Sample Name	: 000
Sample ID	: 000
Vail#	:
Injection Volume	: 20 uL
Data Filename	: Cl(p).lcd
Method Filename	: 50-100%20min.lcm
Batch Filename	:
Report Filename	: Default.lcr
Date Acquired	: 2012-7-10 10:16:56
Data Processed	: 2012-7-10 17:44:29Unknown

Chromatogram
000 D:\DATA\Cl(p).lcd

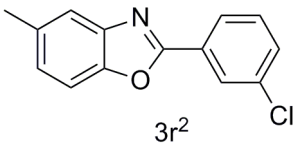


1 PDA Multi 1 / 310nm 4nm

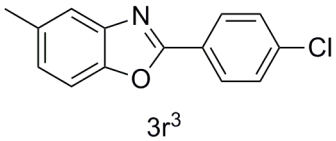
PeakTable

PDA Ch1 310nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	p	18.027	5004049	450620	100.000	0.000
Total			5004049	450620	100.000	



$3r^2$

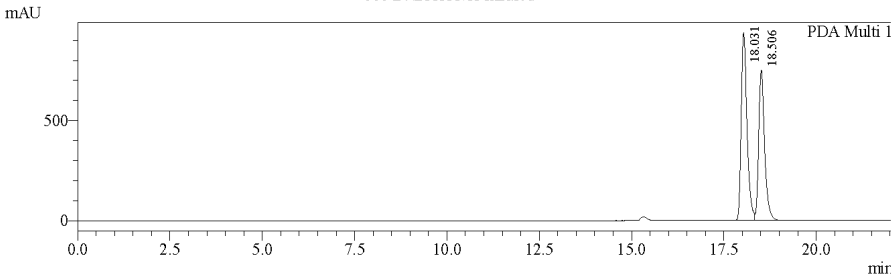


$3r^3$

Sample Information

Acquired by	: Admin
Sample Name	: 000
Sample ID	: 000
Vail#	:
Injection Volume	: 20 uL
Data Filename	: Cl-mix.lcd
Method Filename	: 50-100%20min.lcm
Batch Filename	:
Report Filename	: Default.lcr
Date Acquired	: 2012-7-10 11:27:24
Data Processed	: 2012-7-10 17:45:43Unknown

Chromatogram
000 D:\DATA\Cl-mix.lcd



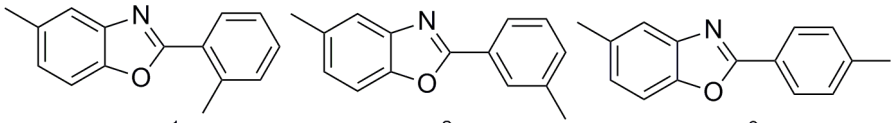
1 PDA Multi 1 / 310nm 4nm

PeakTable

PDA Ch1 310nm 4nm

Peak#	Name	Ret. Time	Area	Height	Area %	Resolution
1	p	18.031	10204399	937771	54.927	0.000
2	m	18.506	8373585	751197	45.073	1.621
Total			18577985	1688968	100.000	

2-(o-tolyl)-5-methyl-benzoxazole, 2-(m-tolyl)-5-methyl-benzoxazole and 2-(p-tolyl)-5-methyl-benzoxazole



3S[1] 3S[2] 3S[3]

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140 ℃ for 48h, using hexane as the eluant afforded a white solid (74% yield) containing (1:1.8:1.6) isomers (determined by GC).

Anal. Calcd. For $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.26; H, 5.91; N, 6.26.

Assignments of ^{1}H NMR, ^{13}C NMR respectively.

3s[1]

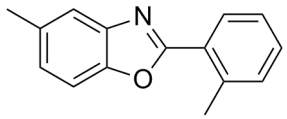
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J*= 7.4 Hz, 1H), 7.60 (s, 1H), 7.55(s, 1H), 7.46(d, *J*= 8.2 Hz, 1H), 7.42-7.32(m, 3H), 7.17(d, *J*= 8.2 Hz, 1H), 2.81(s, 3H), 2.50(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 163.6, 148.6, 142.3, 138.8, 134.2, 131.8, 130.8, 129.9, 126.4, 126.1, 126.0, 120.1, 109.8, 22.2, 21.5.

3s[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 8.04 (d, *J*= 7.6 Hz, 1H), 7.55(s, 1H), 7.45-7.38(m, 2H), 7.33(d, *J*= 7.5 Hz, 1H), 7.15(d, *J*= 8.2 Hz, 1H), 2.49(s, 3H), 2.45(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 163.3, 149.0, 142.3, 138.6, 134.2, 132.1, 128.7, 128.0, 127.2, 126.1, 124.7, 119.9, 109.9, 21.5, 21.3.

3s[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J*= 8.2 Hz, *2*H), 7.54 (s, 1H), 7.43(d, *J*= 8.0 Hz, 1H), 7.32(d, *J*= 8.0 Hz, 2H), 7.14(d, *J*= 8.2 Hz, 1H), 2.48(s, 3H), 2.44(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 163.4, 148.9, 142.1, 142.0, 134.4, 129.6, 127.6, 126.0, 124.4, 119.7, 109.9, 21.6, 21.5.

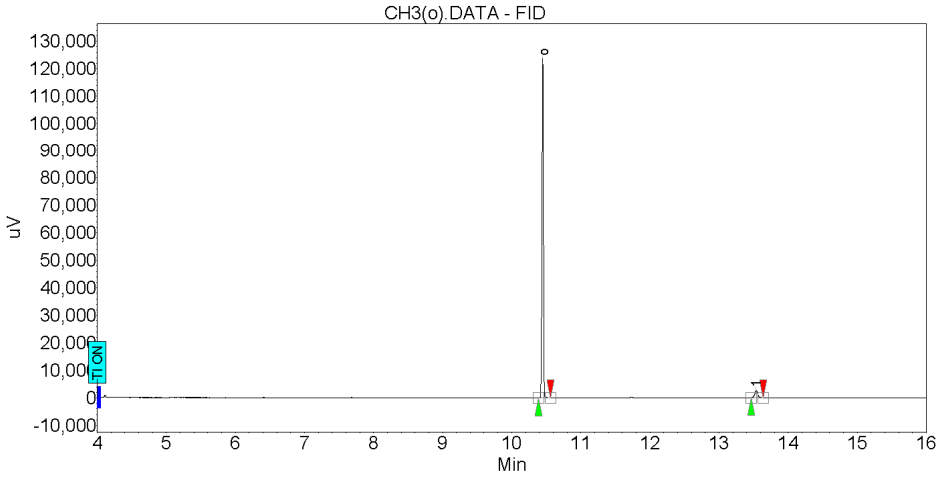


3S[1]

Chromatogram : CH3(o)_channel1

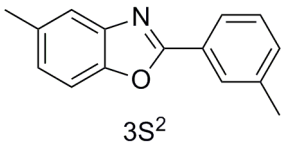
System : 430GC
Method : wuge-CH3
User : 430

Acquired : 2012-7-9 16:09:45
Processed : 2012-7-10 16:03:22
Printed : 2012-7-10 16:05:17



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]	Res. USP
1	o	10.45	95.59	123902.4	2988.6	95.587	0.00
2	1	13.54	4.41	2573.2	138.0	4.413	51.34
Total			100.00	126475.6	3126.6	100.000	

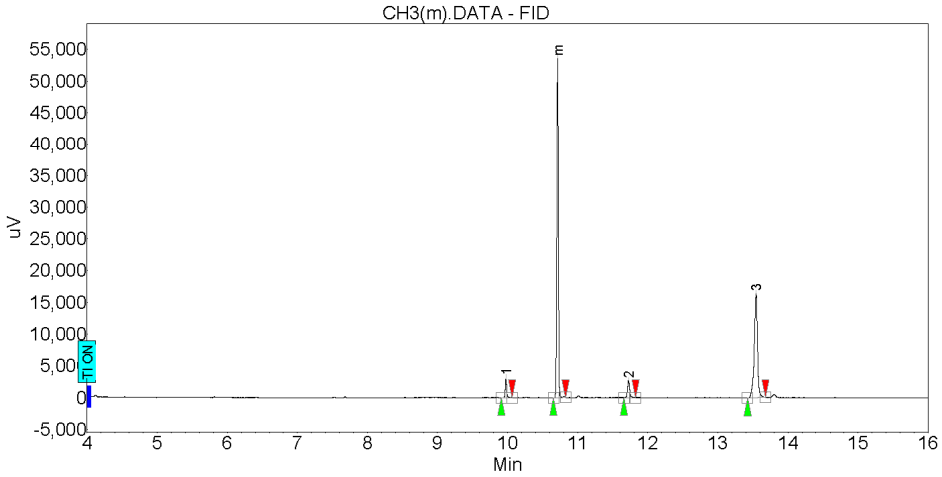


$3S^2$

Chromatogram : CH3(m)_channel1

System : 430GC
Method : wuge-CH3
User : 430

Acquired : 2012-7-9 16:32:43
Processed : 2012-7-10 16:03:06
Printed : 2012-7-10 16:05:30



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]	Res. USP
1	1	9.98	2.95	2936.9	70.6	2.948	0.00
2	m	10.71	56.34	53659.5	1348.4	56.339	19.00
3	2	11.73	4.03	2724.4	96.5	4.030	21.18
4	3	13.55	36.68	16418.7	877.9	36.683	26.43
Total			100.00	75739.5	2393.4	100.000	

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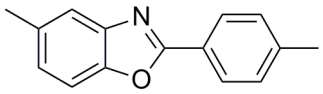
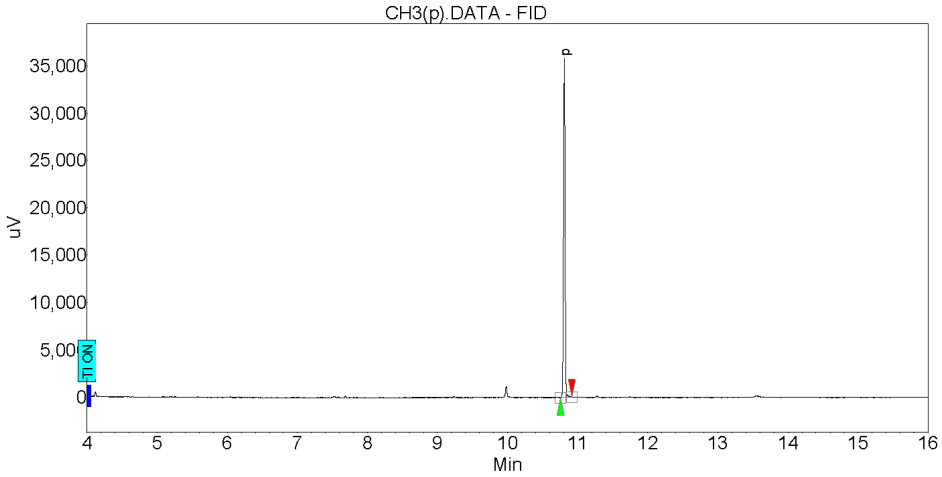


3S^3

Chromatogram : CH3(p)_channel1

System : 430GC
Method : wuge-CH3
User : 430

Acquired : 2012-7-9 15:46:42
Processed : 2012-7-10 16:03:40
Printed : 2012-7-10 16:05:42



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]	Res. USP
1	p	10.81	100.00	35876.9	918.1	100.000	0.00
Total			100.00	35876.9	918.1	100.000	

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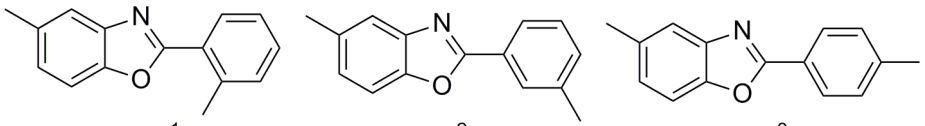
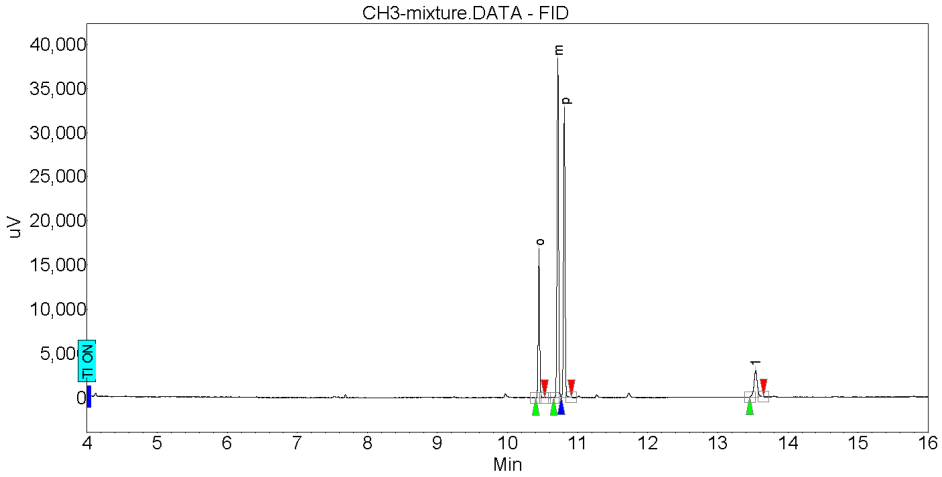


3S[1] 3S[2] 3S[3]

Chromatogram : CH3-mixture_channel1

System : 430GC
Method : wuge-CH3
User : 430

Acquired : 2012-7-9 16:57:08
Processed : 2012-7-10 16:04:00
Printed : 2012-7-10 16:04:58



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]	Res. USP
1	o	10.45	17.14	16841.8	408.8	17.139	0.00
2	m	10.72	41.18	38409.5	982.2	41.183	6.78
3	p	10.81	34.84	32906.1	830.9	34.837	2.27
4	1	13.54	6.84	3018.7	163.1	6.840	44.80
Total			100.00	91176.1	2385.0	100.000	

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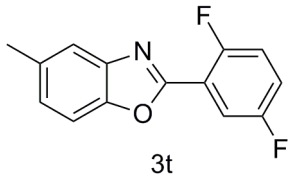
2-(2,5-difluorophenyl)-5- methylbenzoxazole

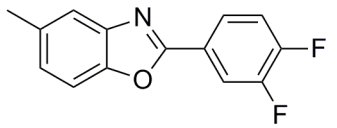


3t

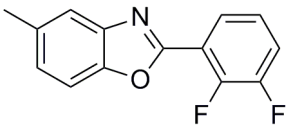
Following the general procedure for 48h, using hexane as the eluant afforded a white solid (76% yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 -7.89 (m, 1H), 7.61 (s, 1 H), 7.48(d, J =8.3 Hz, 1H), 7.24-7.16(m, 3H), 2.49(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 158.5 (dd, J_F=243.6, 2.5 Hz), 158.3(dd, J_F=6.0, 2.7 Hz), 156.8(dd, J_F=255.2, 2.5 Hz), 148.7(d, J_F=1.1 Hz), 141.8, 134.8, 127.1, 120.4, 119.5(dd, J_F=24.2, 8.8Hz), 118.4(dd, J_F=24.4, 8.3Hz), 116.7(dd, J_F=13.0, 8.7Hz), 116.4(d, J_F=2.1Hz), 110.1, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -117.7 (d, J_F= 17.7 Hz, 1F), -116.1 (d, J_F= 17.7 Hz, 1F); Anal.Calcd. For $C_{14}H_9F_2NO$: C, 68.57; H, 3.70; N, 5.71. Found: C, 68.74; H, 3.75; N, 6.03.

2-(3,4-difluorophenyl)-5-methylbenzoxazole and 2-(2,3-difluorophenyl)-5-methylbenzoxazole



3u^1



3u^2

Following the general procedure for 48h, using hexane as the eluant afforded **3u^1** and **3u^2** in 46% and 38% yield, respectively, they were both white solids.

Anal. Calcd. For $C_{14}H_9F_2NO$: C, 68.57; H, 3.70; N, 5.71. Found: C, 68.44; H, 3.97; N, 5.82.

Assignments of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR respectively.

3u^1

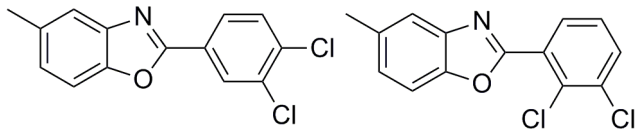
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 -7.95 (m, 2H), 7.52 (s, 1 H), 7.42(d, J =8.3 Hz, 1H), 7.31-7.25(m, 1H), 7.17-7.15(m, 1H), 2.47(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 161.0, 152.4(dd, J_F=254.6, 12.8 Hz), 150.6(dd, J_F=249.6, 13.2 Hz), 149.0, 142.1, 134.7, 126.6, 124.4(dd, J_F=6.7, 3.8Hz), 119.5(dd, J_F=7.0, 3.8Hz), 120.0, 118.0(d, J_F=18.1Hz), 116.7(d, J_F=19.8Hz), 110.0, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ

-132.4 (d, J_F= 21.5 Hz, 1 F), -136.1 (d, J_F= 20.6 Hz, 1 F).

3u^2

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.94 (m, 1H), 7.59(s, 1 H), 7.46(d, *J* =8.3 Hz, 1H), 7.34-7.26(m, 1H), 7.23-7.18(m, 2H), 2.48(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 158.5, 151.3(dd, J_F=248.0, 11.4 Hz), 149.2(dd, J_F=258.6, 11.5 Hz), 148.8, 141.8, 134.8, 127.0, 125.0(d, J_F=3.7Hz), 124.3(dd, J_F=6.5, 5.3Hz), 120.3, 119.8(d, J_F=17.3Hz), 117.7(d, J_F=7.3Hz), 110.1, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -136.0 (d, J_F= 19.7 Hz, 1 F), -136.5 (d, J_F= 20.0Hz, 1 F).

2-(3,4-dichlorophenyl)-5-methylbenzoxazole and 2-(2,3-dichlorophenyl)-5-methylbenzoxazole



3v^1 3v^2

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140 ℃ for 48h, using hexane as the eluant afforded **3v^1** and **3v^2** in 52% and 17% yield, respectively, they were both white solids.

Anal. Calcd. For $C_{14}H_9Cl_2NO$: C, 60.46; H, 3.26; N, 5.04. Found: C, 60.89; H, 3.34; N, 5.07.

Assignments of ^{1}H NMR, ^{13}C NMR respectively.

3v^1

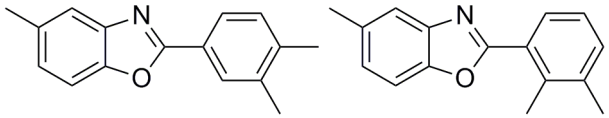
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J*= 2.0 Hz, 1H), 8.01 (dd, *J*=8.4, 2.0 Hz, 1H), 7.55(d, *J*= 8.4 Hz, 1H), 7.52(s, 1H), 7.41(d, *J*= 8.4 Hz, 1H), 7.18-7.15(m, 1H), 2.47(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 160.8, 149.0, 142.0, 135.6, 134.8, 133.4, 131.0, 129.2, 127.1, 126.8, 126.4, 120.1, 110.0, 21.5.

3v^2

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J*= 7.9, 1.5 Hz, 1H), 7.62-7.60 (m, 2H), 7.48(d, *J*= 8.3 Hz, 1H), 7.33(t, *J*= 7.9 Hz, 1H), 7.22-7.20(m, 1H), 2.49(s, 3H); **^{13}C**

NMR (100MHz, $CDCl_3$): δ 160.4, 148.9, 141.7, 135.0, 134.7, 132.6, 132.0, 130.1, 128.7, 127.3, 127.0, 120.4, 110.2, 21.5.

2-(3,4-dimethylphenyl)-5-methylbenzoxazole and 2-(2,3-dimethylphenyl)-5-methylbenzoxazole



$3w^1$ $3w^2$

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140℃ for 48h, using hexane as the eluant afforded **$3w^1$** and **$3w^2$** in 55% and 10% yield, respectively, they were both white solids.

Anal. Calcd. For $C_{15}H_{13}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.11; H, 6.49; N, 5.77.

Assignments of ^{1}H NMR, ^{13}C NMR respectively.

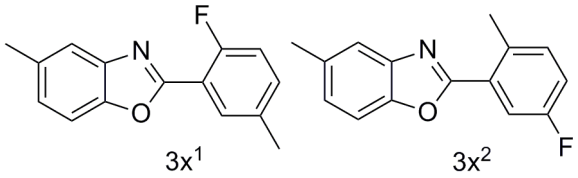
$3w^1$

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.93 (d, *J*=7.8Hz, 1H), 7.52(s, 1H), 7.41-7.38(m, 1H), 7.25-7.23(m, 1H), 7.10(d, *J*=8.0Hz, 1H), 2.46(s, 3H), 2.33-2.29(m, 6H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 163.5, 148.9, 142.3, 140.7, 137.3, 134.2, 130.0, 128.6, 125.9, 125.1, 124.8, 119.7, 109.8, 21.5, 19.9, 19.7.

$3w^2$

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*=7.7Hz, 1H), 7.48 (s, 1H), 7.33(d, *J*=8.3Hz, 1H), 7.18(d, *J*=7.3Hz, 1H), 7.11(t, *J*=7.8Hz, 1H), 7.05-7.03(m, 1H), 2.56(s, 3H), 2.38(s, 3H), 2.27(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 164.0, 148.6, 142.2, 138.1, 137.1, 134.0, 132.3, 128.0, 127.0, 126.0, 125.5, 120.0, 21.4, 20.7, 17.1.

2-(2-fluoro-5-methylphenyl)-5-methylbenzoxazole and 2-(5-fluoro-2-methylphenyl)-5-methylbenzoxazole



3x[1] 3x[2]

Following the general procedure for 48h, using hexane as the eluant afforded **3x[1]** and **3x[2]** in 64% and 10% yield, respectively, they were both light yellow solids.

Anal. Calcd. For $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 74.74; H, 5.32; N, 5.83.

Assignments of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR respectively.

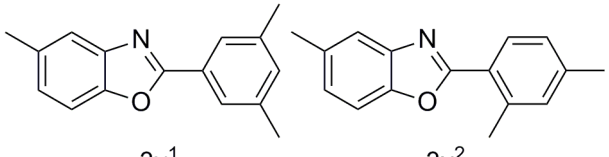
3x[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 -8.00 (m, 1H), 7.60 (s, 1 H), 7.47(d, J =8.3 Hz, 1H), 7.30-7.26(m, 1H), 7.19-7.10(m, 2H), 2.48(s, 3H), 2.40(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 159.8(d, J_F=5.2 Hz), 159.0(d, J_F=256.0Hz), 148.7(d, J_F=1.1Hz), 141.9, 134.5, 134.0(d, J_F=3.7Hz), 133.5(d, J_F=8.3Hz), 130.5(d, J_F=1.1Hz), 126.6, 120.1, 116.7(d, J_F=21.7Hz), 115.0(d, J_F=10.6Hz), 110.0, 21.5, 20.6; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -115.6 (s, 1F).

3x[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J =9.7, 2.8Hz 1H), 7.59 (s, 1 H), 7.45(d, J =8.3 Hz, 1H), 7.31-7.27(m, 1H), 7.19-7.17(m, 1H), 7.09(td, J =8.2, 2.8Hz , 1H)2.76(s, 3H), 2.49(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 162.2(d, J_F=2.9 Hz), 160.9(d, J_F=244.1Hz), 148.5, 142.2, 134.4, 134.4, 133.2(d, J_F=7.7 Hz), 127.6(d, J_F=8.0 Hz), 126.5, 120.2, 117.6(d, J_F=20.8 Hz), 116.3(d, J_F=23.7 Hz), 110.0, 21.5, 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -117.0 (s, 1F).

5-methyl-2-(3,5-dimethylphenyl)benzoxazole[10] and 5-methyl -2(2,4-dimethylphenyl) benzoxazole[11]



3y[1] 3y[2]

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140℃ for 48h, using hexane as the eluant afforded **3y**^{1} and **3y**^{2} in 54% and 23% yield, respectively, they were both white solids.

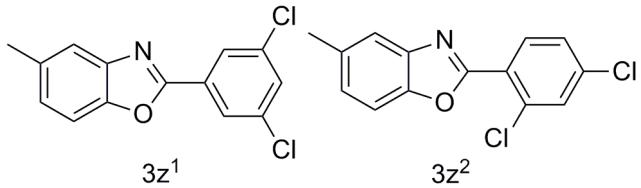
Anal. Calcd. For $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.11; H, 6.49; N, 5.77.

Assignments of ^{1}H NMR, ^{13}C NMR respectively.

The ^{1}H, ^{13}C NMR spectra of **3y**^{1} in accordance with those described in the literature.[11]

The ^{1}H, ^{13}C NMR spectra of **3y**^{2} in accordance with those described in the literature.[12]

5-methyl-2-(3,5-dichlorophenyl)benzoxazole and 5-methyl-2- (2,4-dichlorophenyl) benzoxazole



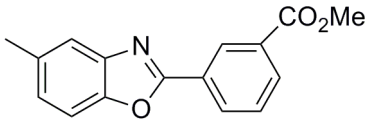
Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140℃ for 48h, using hexane as the eluant mixture of regioisomers **3z**^{1}:**3z**^{2} (17:1) determined by GC and 78% yield seperated by column chromatography. Due to the low yield of the **3z**^{2} isomer, it is not possible to report its spectroscopic data. The following data belongs to the major regioisomer.

Anal. Calcd. For $C_{14}H_9Cl_2NO$: C, 60.46; H, 3.26; N, 5.04. Found: C, 60.50; H, 3.42; N, 5.32.

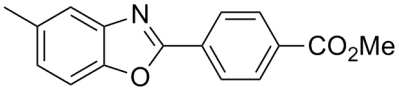
Assignments of ^{1}H NMR, ^{13}C NMR of **3z**^{1} major product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.93 (d, *J*=7.8Hz, 1H), 7.52(s, 1H), 7.41-7.38(m, 1H), 7.25-7.23(m, 1H), 7.10(d, *J*=8.0Hz, 1H), 2.46(s, 3H), 2.33-2.29(m, 6H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 163.5, 148.9, 142.3, 140.7, 137.3, 134.2, 130.0, 128.6, 125.9, 125.1, 124.8, 119.7, 109.8, 21.5, 19.9, 19.7.

2-(3-Methoxycarbonyl-phenyl) -5-methylbenzoxazole and2-(4-Meth oxycar bony l-phenyl) -5-methylbenzoxazole



3aa[2]



3aa[1]

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140 ℃ for 48h, using hexane as the eluant afforded a white solid (73% yield) containing (2:1) isomers (determined by GC).

Anal. Calcd. For $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.96; H, 5.01; N, 5.26.

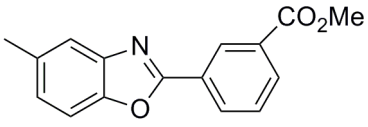
Assignments of ^{1}H NMR, ^{13}C NMR respectively.

3aa[1]

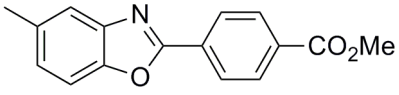
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J*=7.7Hz, 2H), 8.14 (d, *J*=7.7Hz, 2H), 7.54 (s, 1H), 7.43 (d, *J*=8.0Hz, 1H), 7.16 (d, *J*=8.0Hz, 1H), 3.94(s, 3H), 2.47(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 166.3, 161.9, 142.3, 149.1, 142.2, 134.7, 132.3, 131.1, 130.0, 126.9, 120.2, 110.1, 52.3, 21.5.

3aa[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.43 (d, *J*=7.8Hz, 1H), 8.20 (d, *J*=7.8Hz, 1H), 7.61 (t, *J*=7.8Hz, 1H), 7.58 (s, 1H), 7.47 (d, *J*=8.3Hz, 1H), 7.18 (d, *J*=8.3Hz, 1H), 3.98(s, 3H), 2.49(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 166.3, 162.1, 149.0, 142.1, 134.7, 132.3, 131.6, 131.1, 128.6, 127.7, 126.7, 120.0, 110.1, 52.4, 21.5.



3aa^2



3aa^1

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Method : wuge-酯
User : 430

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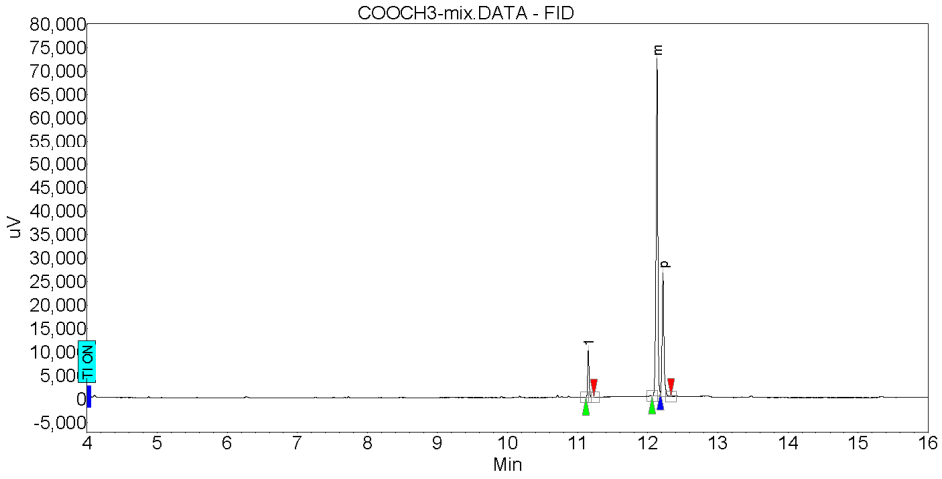

Peak results :

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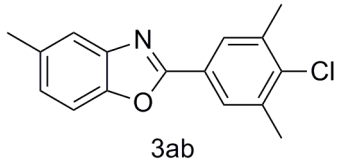
2	m	12.13	67.10	72265.7	2125.1	67.105	24.34
3	p	12.22	25.61	26466.3	811.1	25.610	1.86
Total			100.00	108792.8	3166.9	100.000	

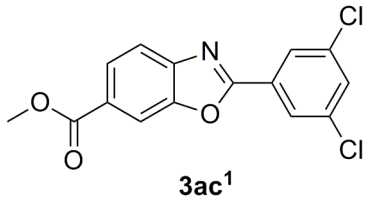
2-(4-chloro-3,5-dimethylphenyl) -5-methylbenzoxazole



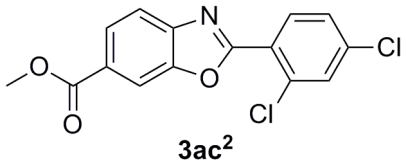
3ab

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140 ℃ for 48h, using hexane as the eluant afforded a white solid (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* =8.0 Hz, 1H), 7.48 (s, 1H), 7.33 (d, *J* =8.3Hz, 1H), 7.11(d, *J* =8.0 Hz, 1H), 7.06(d, *J* =8.3 Hz, 1H), 2.75(s, 3H), 2.39(s, 3H), 2.36(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 163.0, 148.6, 142.2, 139.5, 136.7, 136.5, 134.3, 128.1, 128.0, 126.3, 126.1, 120.1, 109.8, 21.5, 21.5, 18.5; Anal. Calcd. For $C_{15}H_{12}ClNO$: C, 69.91; H, 4.69; N, 5.43. Found: C, 70.05; H, 4.75; N, 5.50.

methyl 2-(3,5-dichlorophenyl) benzoxazole-6-carboxylate and methyl 2-(2,4-dichlorophenyl) benzoxazole-6-carboxylate



3ac^1



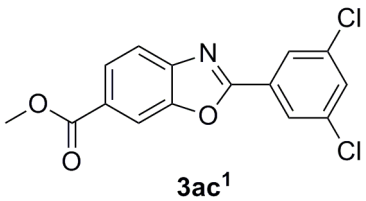
3ac^2

Following the general procedure and 1.8 equiv $CuBr_2$ was used at 140 ℃ for 48h, using hexane as the eluant mixture of regioisomers **3ac^1**:**3ac^2** (12:1) determined by GC and 43% yield seperated by column chromatography. Due to the low yield of the **3ac^2** isomer, it is not possible to report its spectroscopic data. The following data belongs to the major regioisomer.

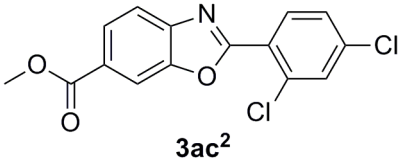
Anal. Calcd. For $C_{15}H_9Cl_2NO_3$: C, 55.93; H, 2.82; N, 4.35. Found: C, 56.01; H, 2.91; N, 4.38.

Assignments of ^{1}H NMR, ^{13}C NMR of **3ac^1** major product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.12 (t, *J*=7.8Hz, 2H), 7.83(d, *J*=8.4Hz, 1H), 7.58(s, 1H), 7.41(d, *J*=8.4Hz, 1H), 3.96(s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 166.5, 162.6, 150.2, 145.4, 138.2, 134.6, 132.7, 131.5, 127.8, 127.6, 126.5, 124.2, 120.1, 112.5, 52.4.



3ac[1]



3ac[2]

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Batch Filename	:
Report Filename	: Default.lcr
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Chromatogram
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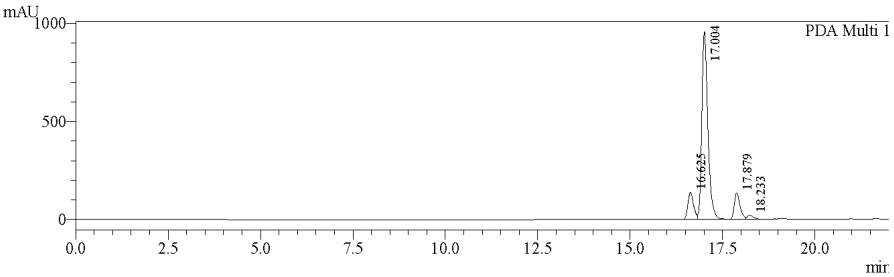

1 PDA Multi 1 / 310nm 4nm

PeakTable

PDA Ch1 310nm 4nm

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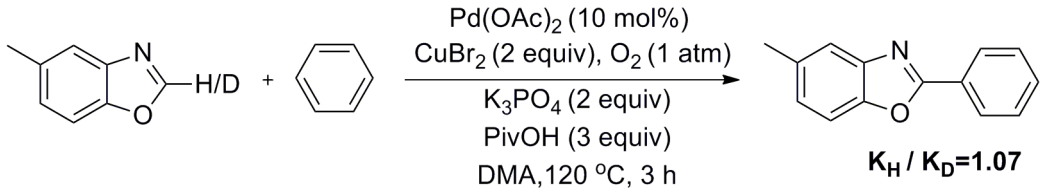
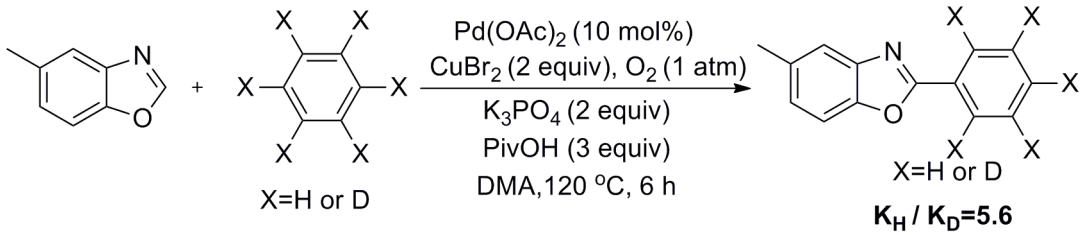
2		17.004	10842166	957228	77.557	1.273
3		17.879	1429956	133952	10.229	2.982
4		18.233	242395	20060	1.734	1.069
Total			13979531	1248143	100.000	

Kinetic Isotope Effect Experiment:

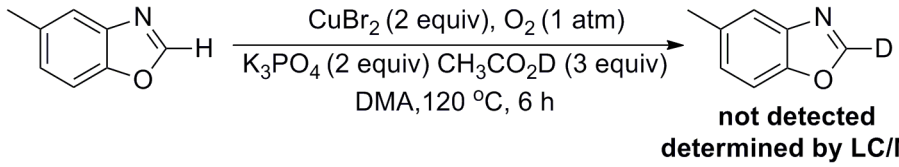


Initially, the target product, 5-methyl-2-phenylbenzoxazole was used as a standard compound to make a curve involving the product concentration and peak area (external standard method, GC-MS). Then an intermolecular competition reaction between 5-methylbenzoxazole and deuterated 5-methylbenzoxazole was carried out.

In a glove box, two 25 mL of Schlenk tubes equipped with a stir bar were charged with 5-methybenzoxazole (0.2 mmol), $CuBr_2$ (2 equiv), K_3PO_4 (2 equiv), PivOH (3 equiv), $Pd(OAc)_2$ (10 mol %). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. In one tube, under dioxygen, DMA (2 mL), and benzene (4 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. In another tube, under dioxygen, DMA (2 mL), benzene (4mL), and deuterated 5-methylbenzoxazole (0.2 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. The reaction mixture was stirred at 120 □ for 3 h (conversion approximately 20% yield) and When measuring the values of KIE, the reaction was quenched at (3 h, 6 h, 9 h and 12 h, no significant difference in the KIE value was observed for different reaction time). After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether, filtered through a pad of silica gel, Finally, the mixture was analyzed by GC, and the GC yield of the target product was calculated according to the pre-established curve. The ratio of the two target products represents the KIE value.



In a glove box, two 25 mL of Schlenk tubes equipped with a stir bar were charged with 5-methybenzoxazole (0.2 mmol), $CuBr_2$ (2 equiv), K_3PO_4 (2 equiv), PivOH (3 equiv), $Pd(OAc)_2$(10 mol %). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. In one tube, under dioxygen, DMA (2 mL) and benzene (4 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. In another tube, under dioxygen, DMA (2 mL), benzene-d_6 (4 mL), and 5-methylbenzoxazole (0.2 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. The reaction mixture was stirred at 120 □ for 6 h, The reaction was then cooled and an aliquot was removed and analyzed by GC/MS.

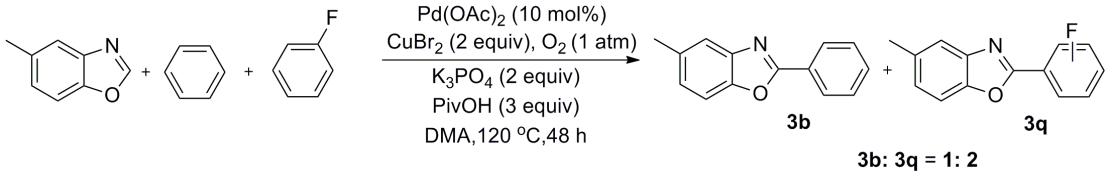


In a glove box, a 25 mL of Schlenk tube equipped with a stir bar were charged with $CuBr_2$ (2 equiv), K_3PO_4 (2 equiv), 5-methybenzoxazole (0.2 mmol), the tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. In one tube, under dioxygen, DMA (2 mL) and CH_3CO_2D (3 equiv) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. The reaction mixture was stirred at 120 □ for 6 h, The reaction was then cooled and an aliquot was removed and analyzed by LC/MS.

Note: no deuterium incorporation into the 5-methybenzoxazole substrate was observed in the presence or in the absence of $Pd(OAc)_2$ catalyst , or $CuBr_2$

(2equiv) CH_3CO_2D (3equiv), O_2, DMA and in the absence of K_3PO_4 base as catalyst system , corresponding experiments results also analyzed by LC/MS.

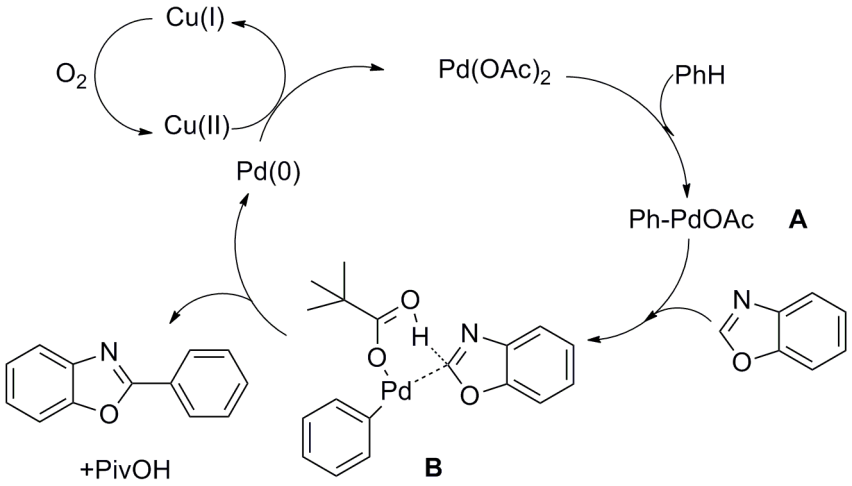
Competition investigation:



In a glove box, a 25 mL of Schlenk tube equipped with a stir bar was charged with 5-methylbenzoxazole (0.2 mmol), $CuBr_2$ (2 equiv), K_3PO_4 (0.75 equiv), PivOH (3 equiv), $Pd(OAc)_2$(10 mol %). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMA (2 mL), benzene (2 mL), and fluorobenzene (2 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under a oxygen flow. The reaction mixture was stirred at 120 □ for 48 h. The solution was then extracted and analyzed by GC to determine the product distribution.

Plausible Mechanism to Approach Oxidative Cross-Coupling of Benzoxazole

with Arenes



On the basis of the data above and precedent literature, a plausible catalytic cycle is proposed. Taking the coupling of benzoxazole with benzene for example, the initial palladation of benzene afforded A via an intramolecular abstraction process (This hypothesis is supported by the fact that electron-rich arenes such as anisole failed to react, while benzene and methyl benzoate readily coupled with benzoxazole), followed by coordination of benzoxazole to Pd through N atom and subsequent via concerted metalation-deprotonation to form an ArPd(benzoxazole) intermediate, which underwent reductive elimination to generate the product ,along with Pd(0) which is reoxidized by the excess Cu(II)/O_2 regenerated the catalytically active Pd(II) species to complete the catalytic cycle.

References:

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(2) For the synthesis of 2-deuterated oxazoles, see: E. Crowe, F. Hossner, M. J. Hughes, *Tetrahedron* **1995**, *51*, 8889-8900.

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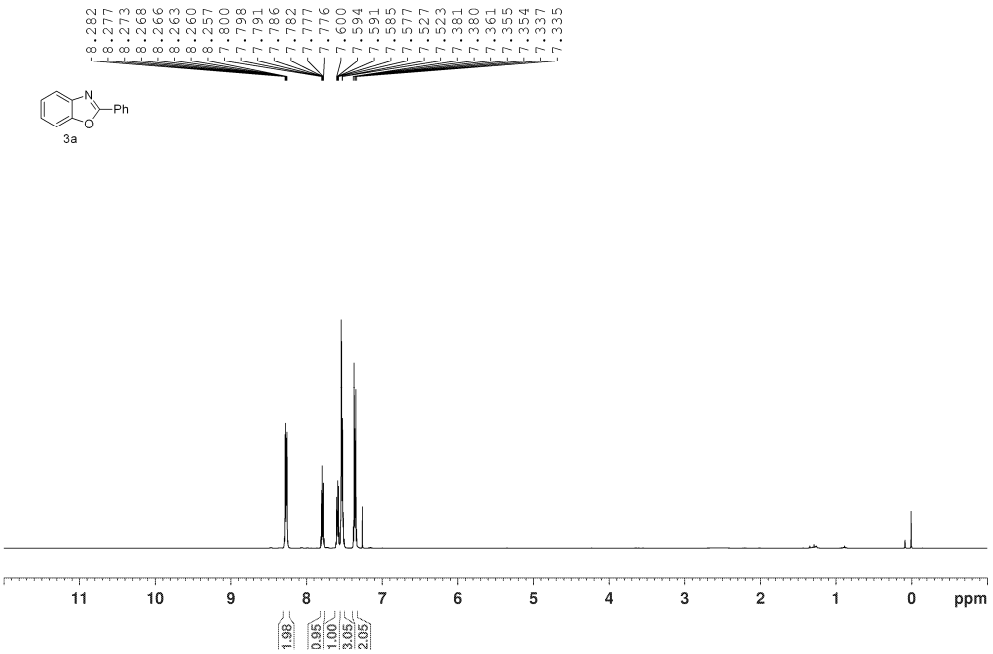
(11) Ö. Temiz, İ. Ören, E. Şener, İ. Yalçin, N. Uçartürk, Farmaco **1998**, *53*, 337 - 341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8.266
8.263
8.260
8.257
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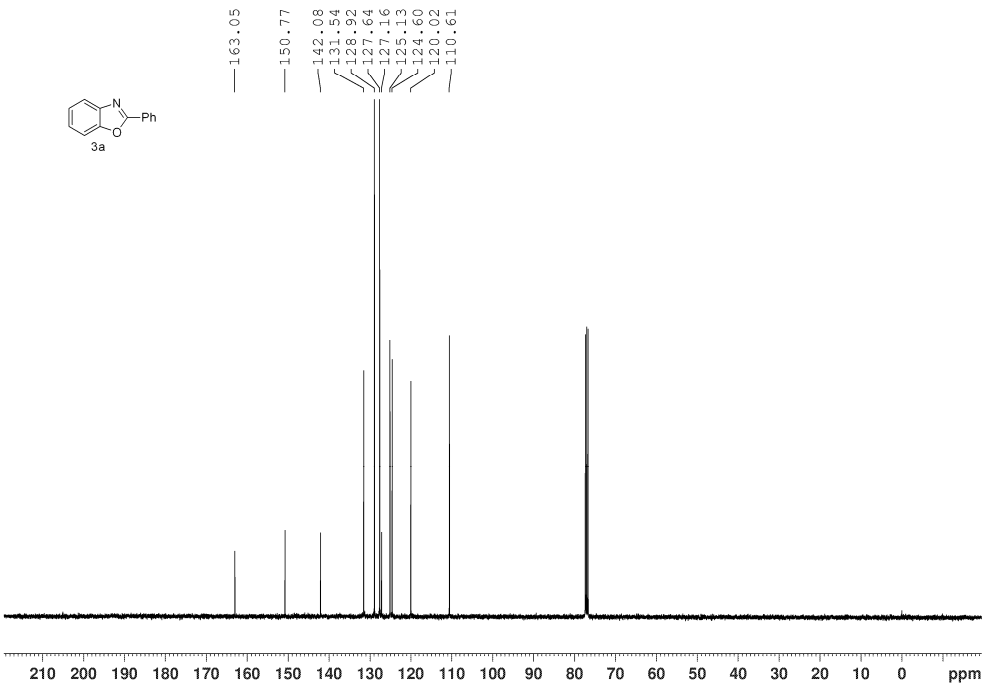
7.798
7.791
7.786
7.782
7.777
7.776
7.600
7.594
7.591
7.585
7.577
7.527
7.523
7.381
7.380
7.361
7.355
7.354
7.337
7.335
N
Ph
O
3a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
0.95
1.00
3.05
2.05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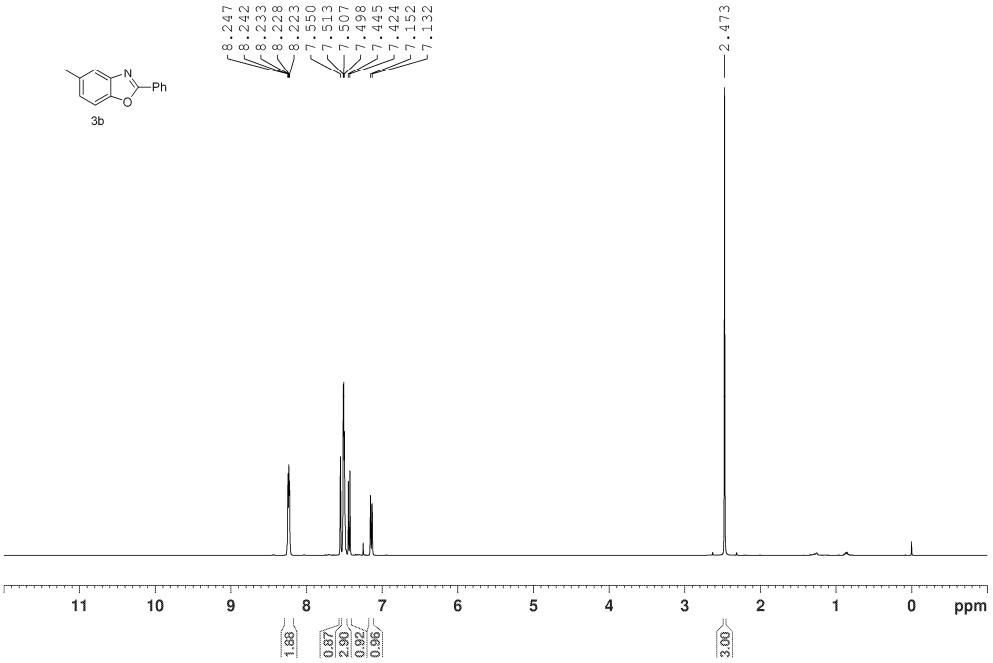
150.77
142.08
131.54
128.92
127.64
127.16
125.13
124.60
120.02
110.61
N
Ph
O
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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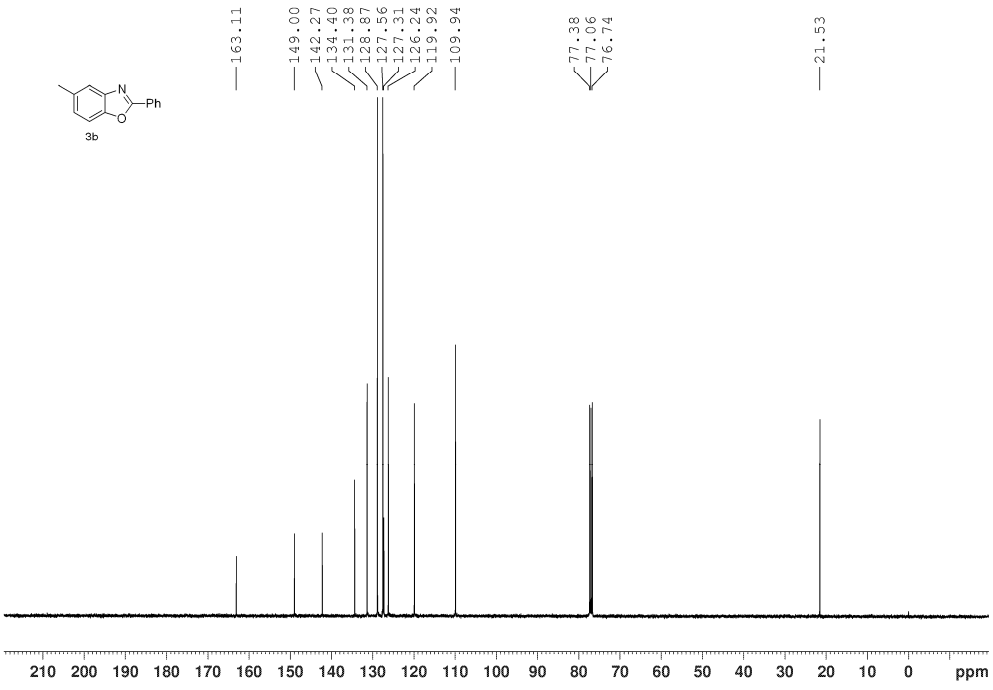
8.242
8.233
8.228
8.223
7.550
7.513
7.507
7.498
7.445
7.424
7.152
7.132
2.473
N
O
Ph
3b
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.88
0.87
2.90
0.92
0.96
3.00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126.24
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76.74
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O
Ph
3b
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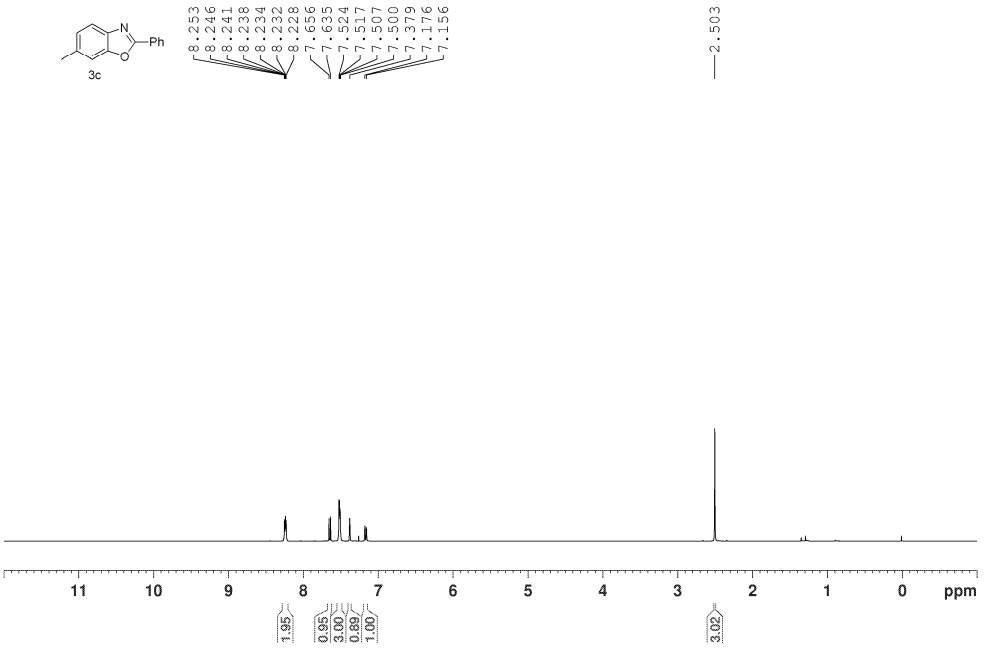
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7.517
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7.500
7.379
7.176
7.156
2.503
11
10
9
8
7
6
5
4
3
2
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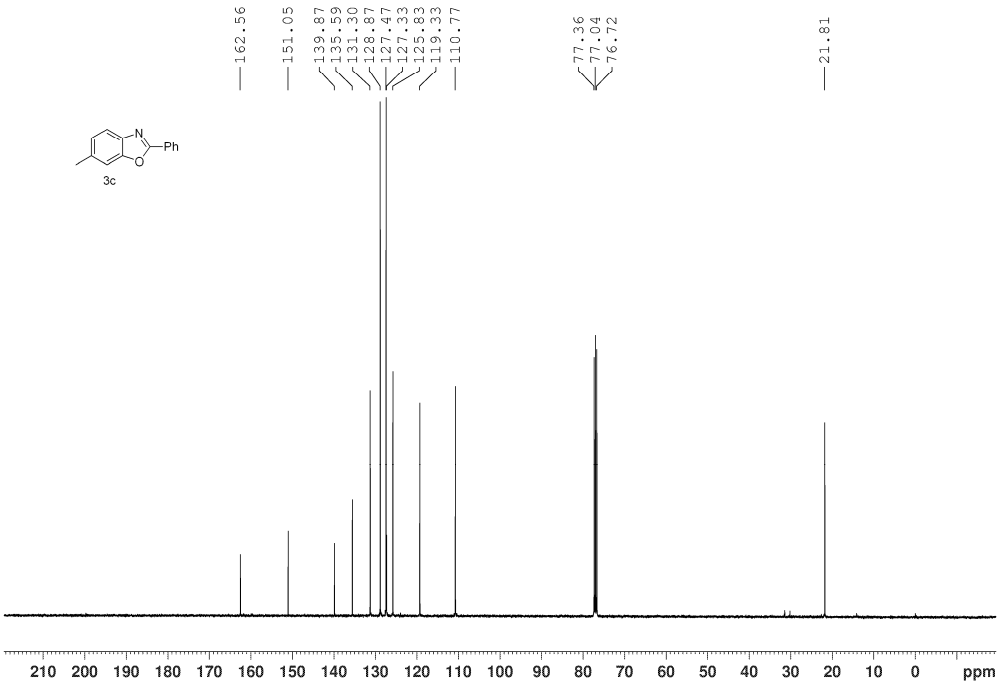
0
ppm
1.95
0.95
3.00
0.89
1.00
3.02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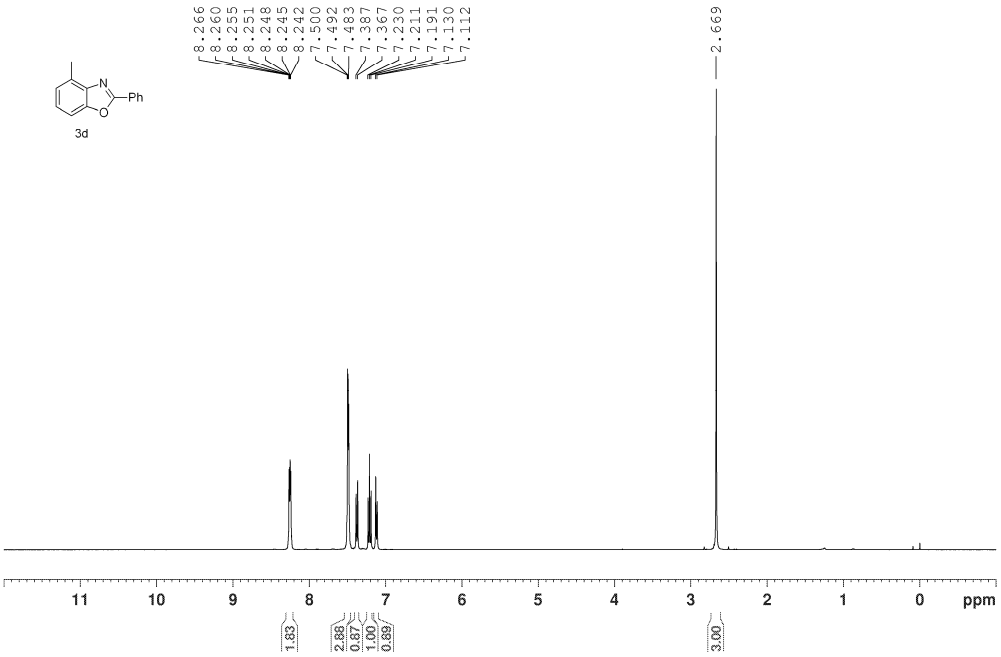
77.36
77.04
76.72
21.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.245
8.242
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7.483
7.387
7.367
7.230
7.211
7.191
7.130
7.112
2.669
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O
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3d
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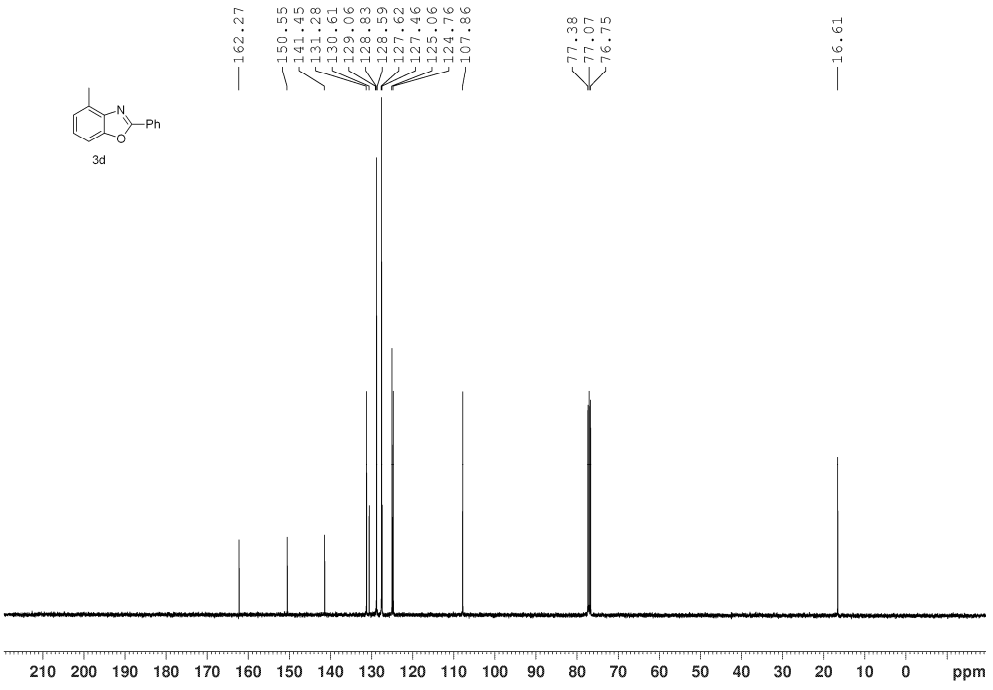
2.88
0.87
1.00
0.89
3.00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128.59
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127.46
125.06
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76.75
16.61
N
O
Ph
3d
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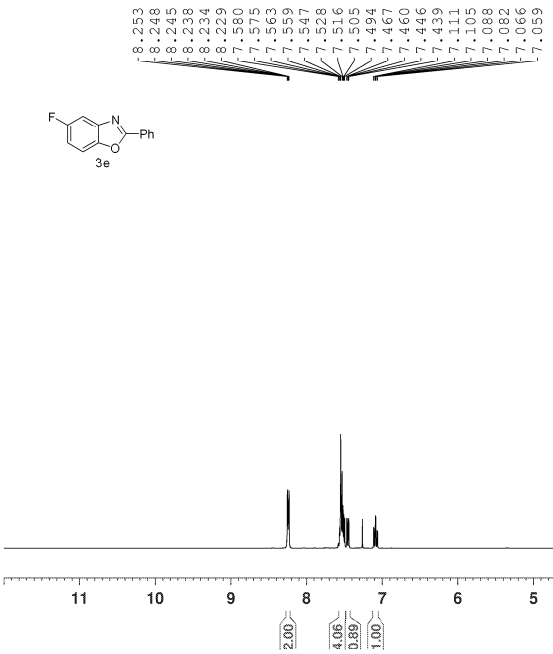
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8.234
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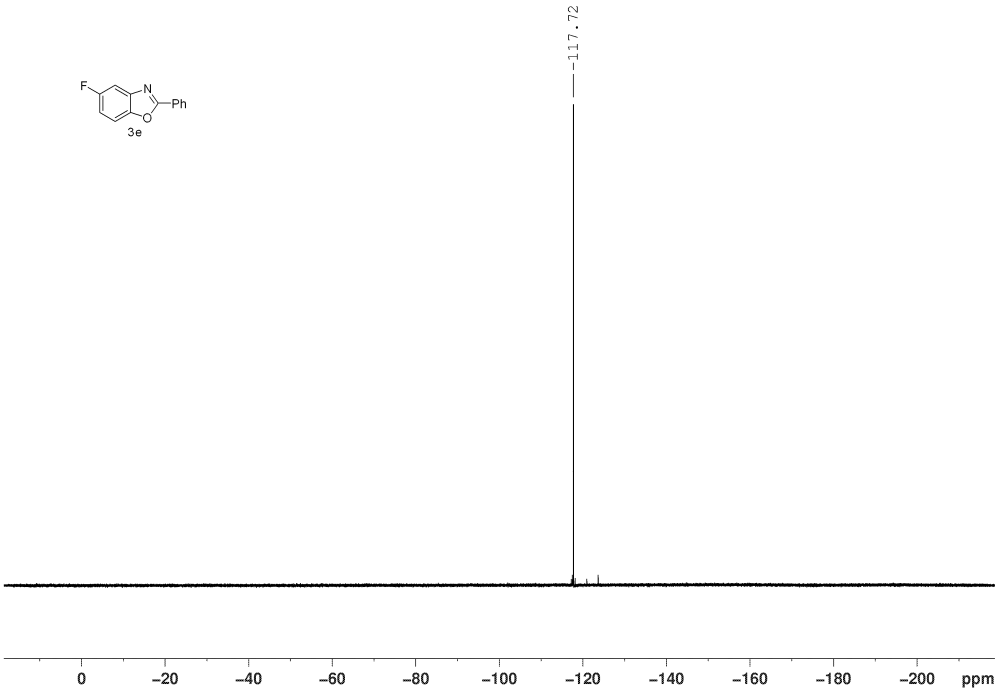
7.516
7.505
7.494
7.467
7.460
7.446
7.439
7.111
7.105
7.088
7.082
7.066
7.059
F
N
O
Ph
3e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.06
0.89
1.00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-100
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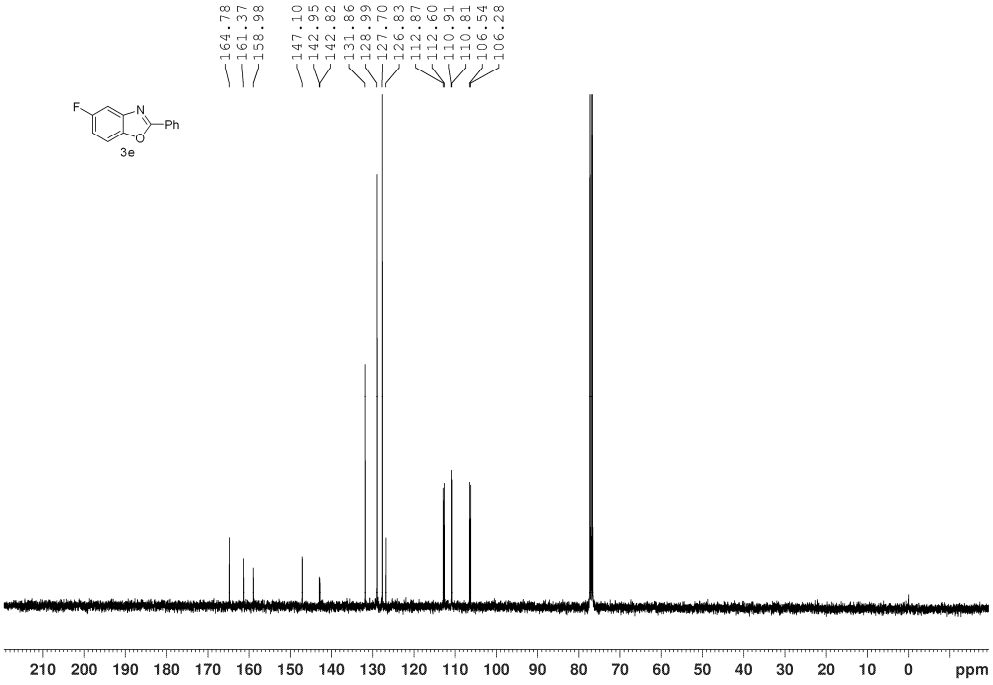
-160
-180
-200
ppm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129.99
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112.60
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F
N
O
Ph
3e
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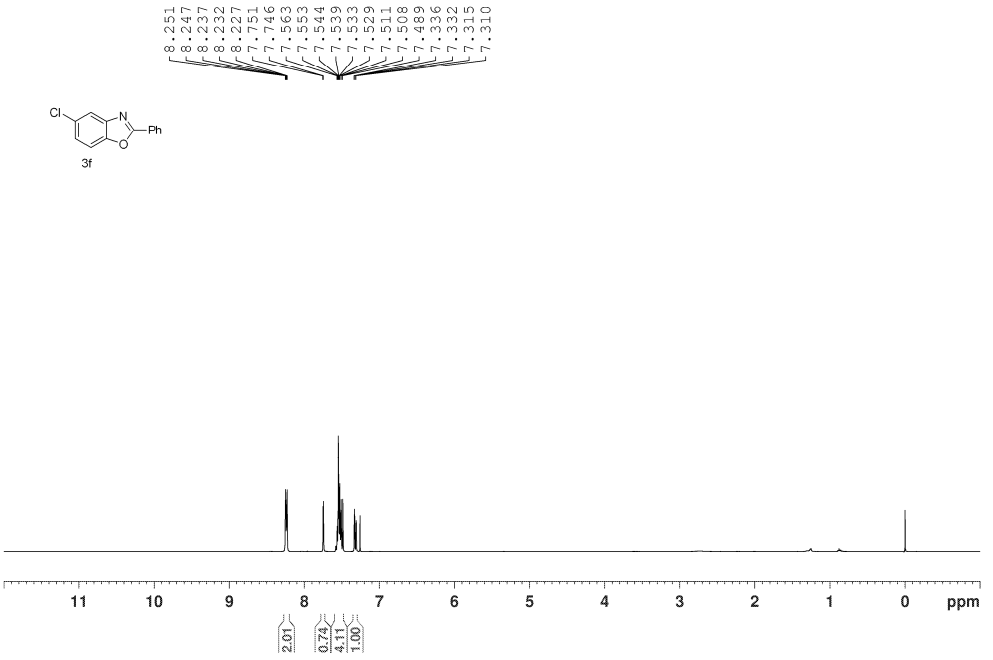
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7.544
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7.529
7.511
7.508
7.489
7.336
7.332
7.315
7.310
Cl
N
O
Ph
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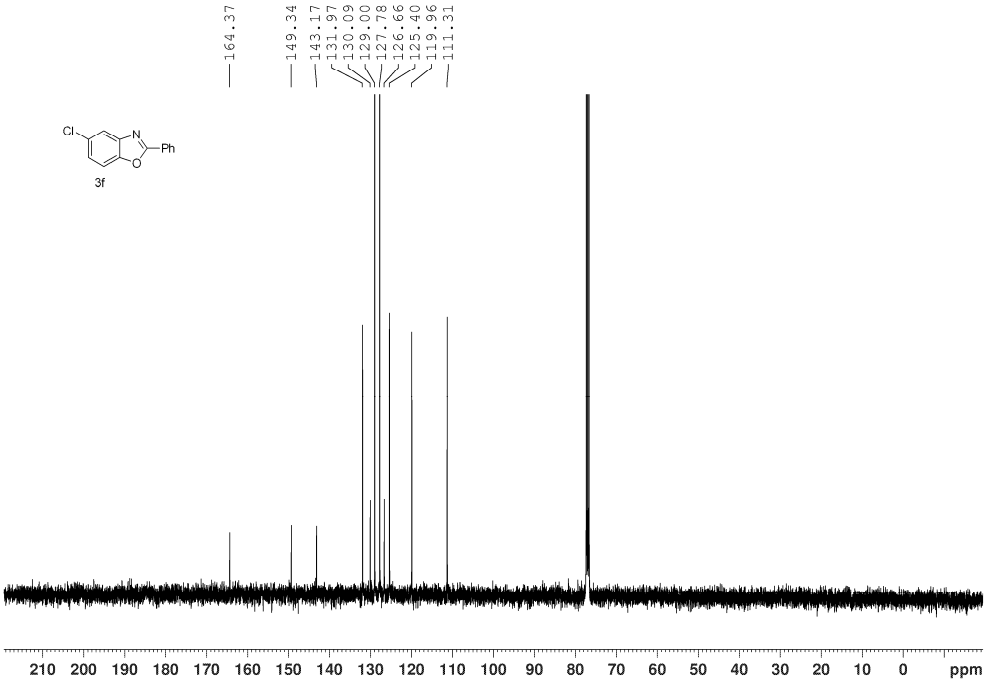
4.11
1.00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111.31
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O
Ph
3f
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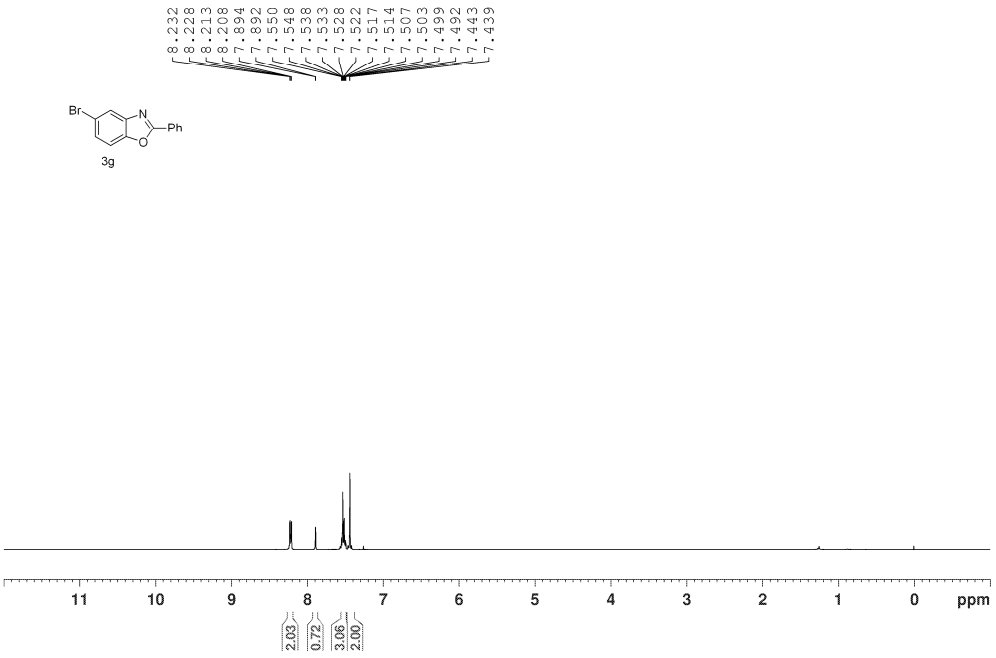
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7.507
7.503
7.499
7.492
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O
Ph
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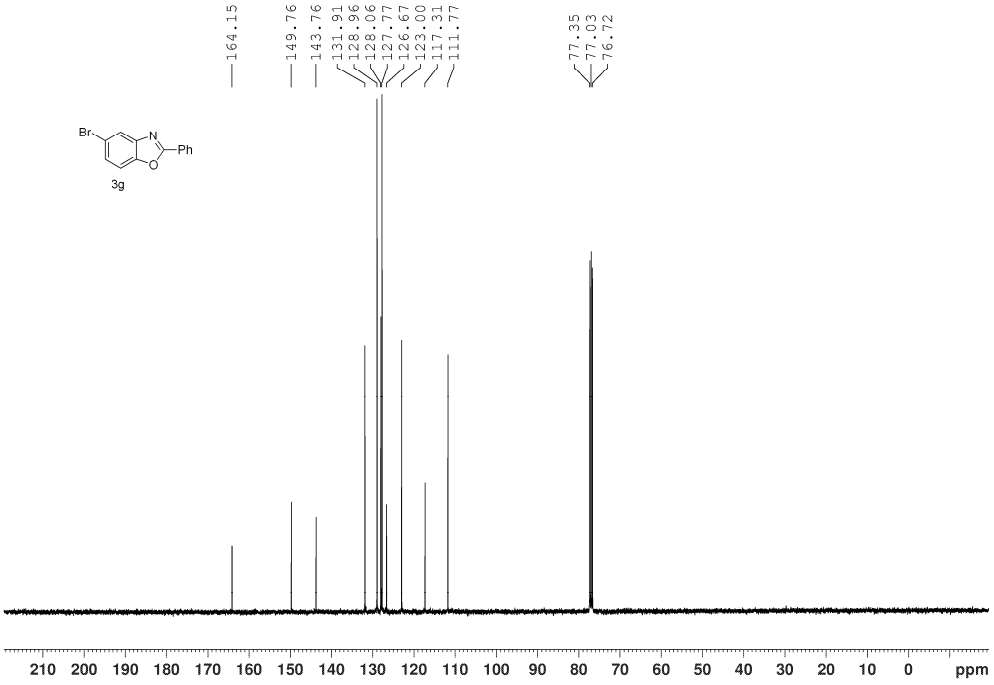
3.06
2.00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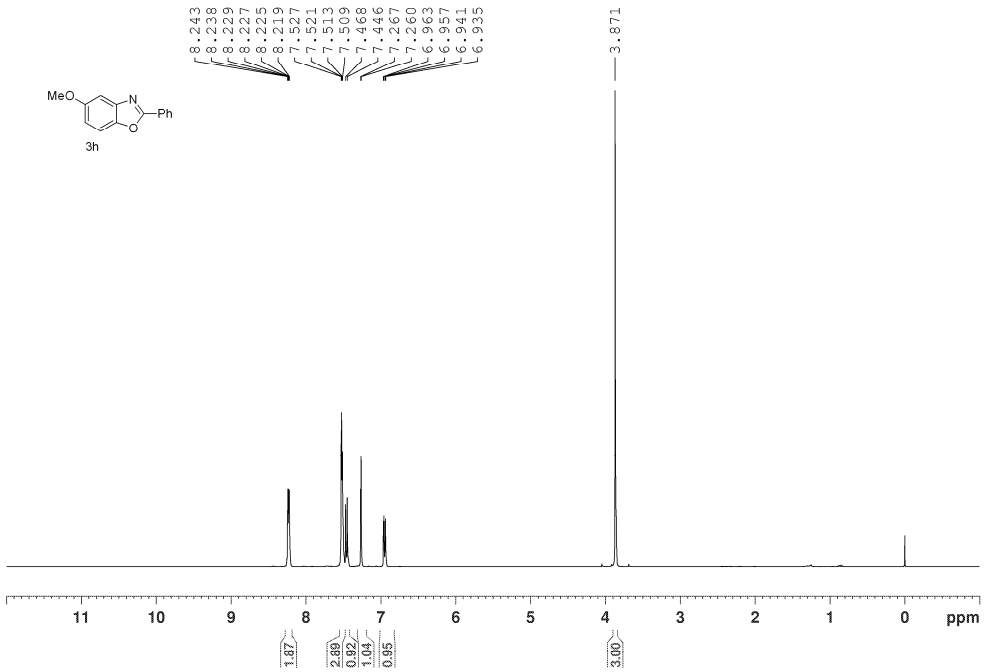
Br
N
O
Ph
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.446
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6.957
6.941
6.935
3.871
MeO
N
O
Ph
3h
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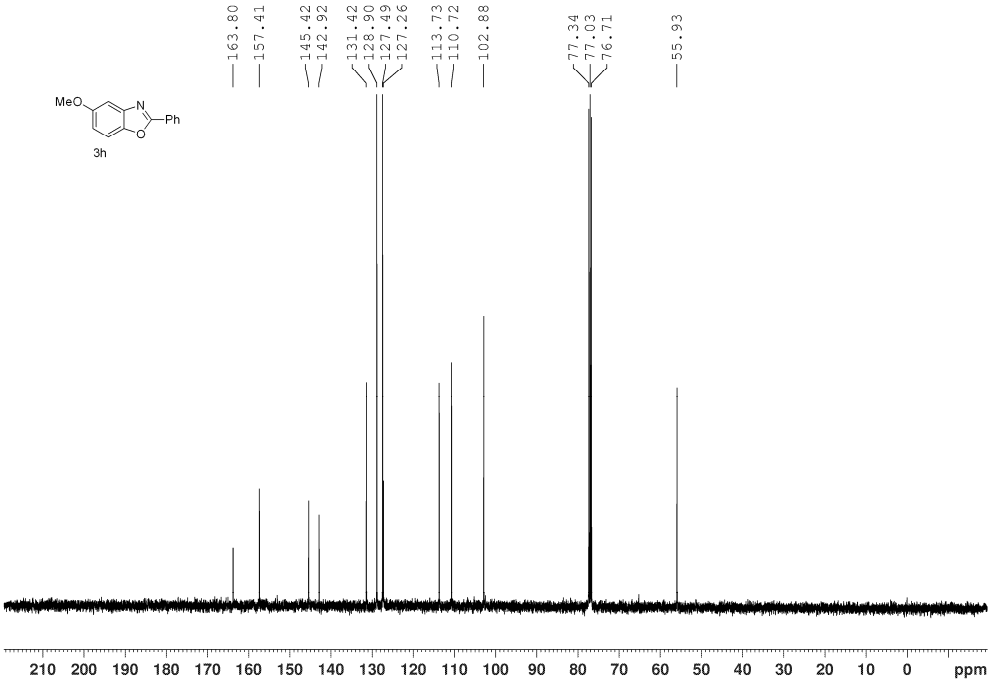
1.04
0.95
3.00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Ph
O
3h
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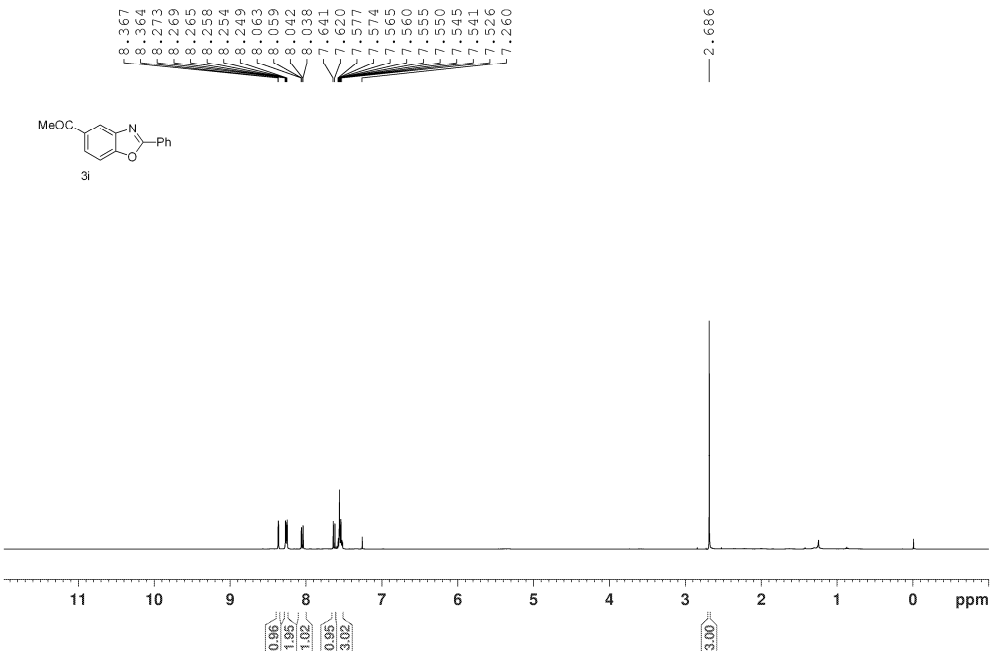
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8.059
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7.620
7.577
7.574
7.565
7.560
7.555
7.550
7.545
7.541
7.526
7.260
2.686
MeOC
N
Ph
O
3i
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0.96
1.95
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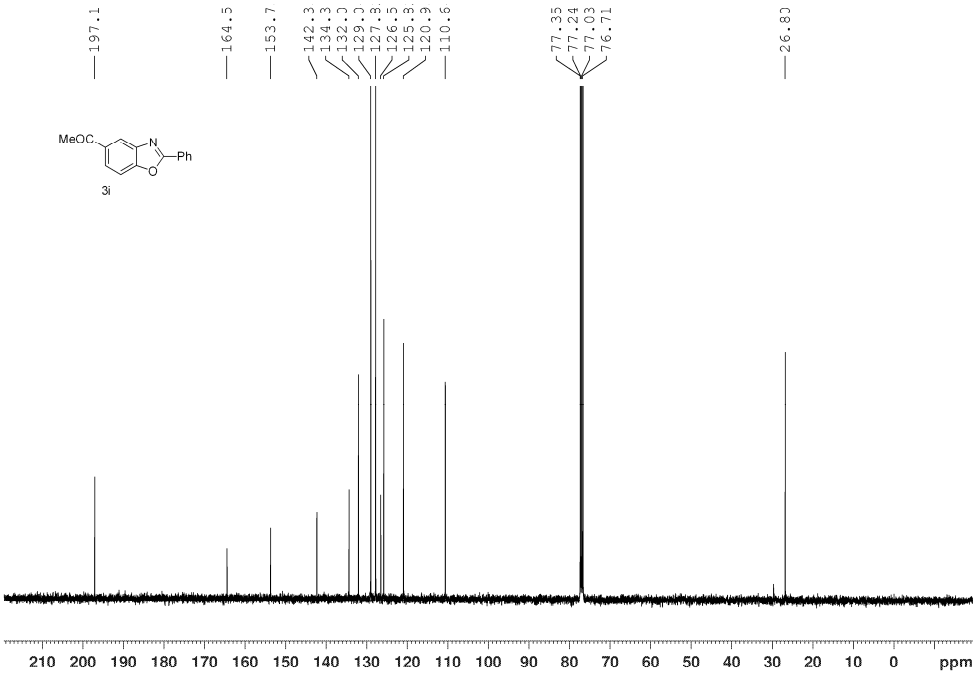
0.95
3.02
3.00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125.8
120.9
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77.24
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76.71
26.80
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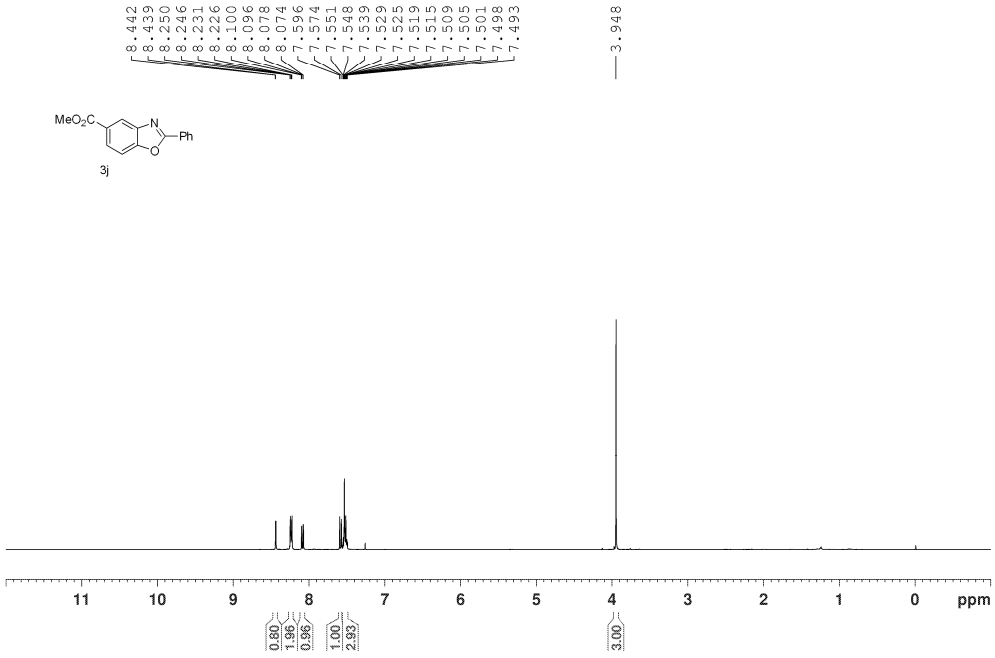
N
Ph
O
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.539
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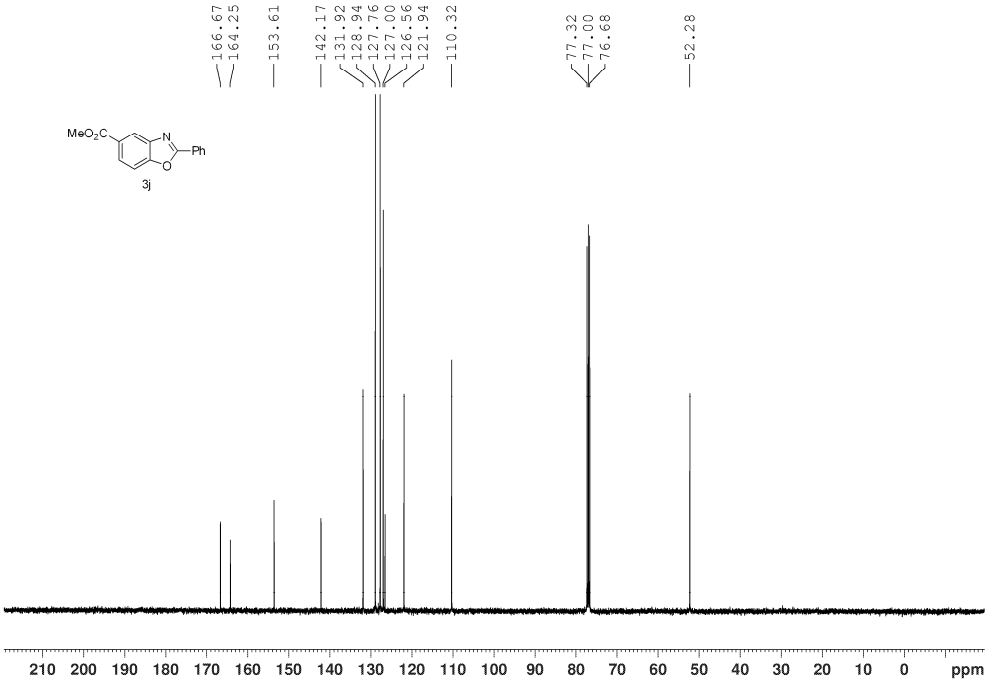
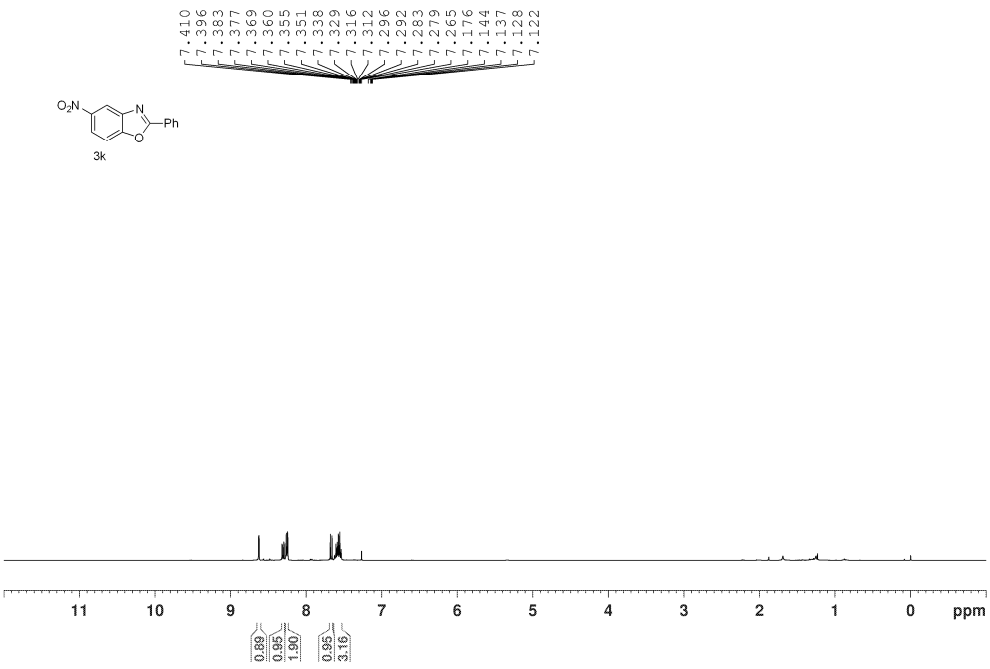
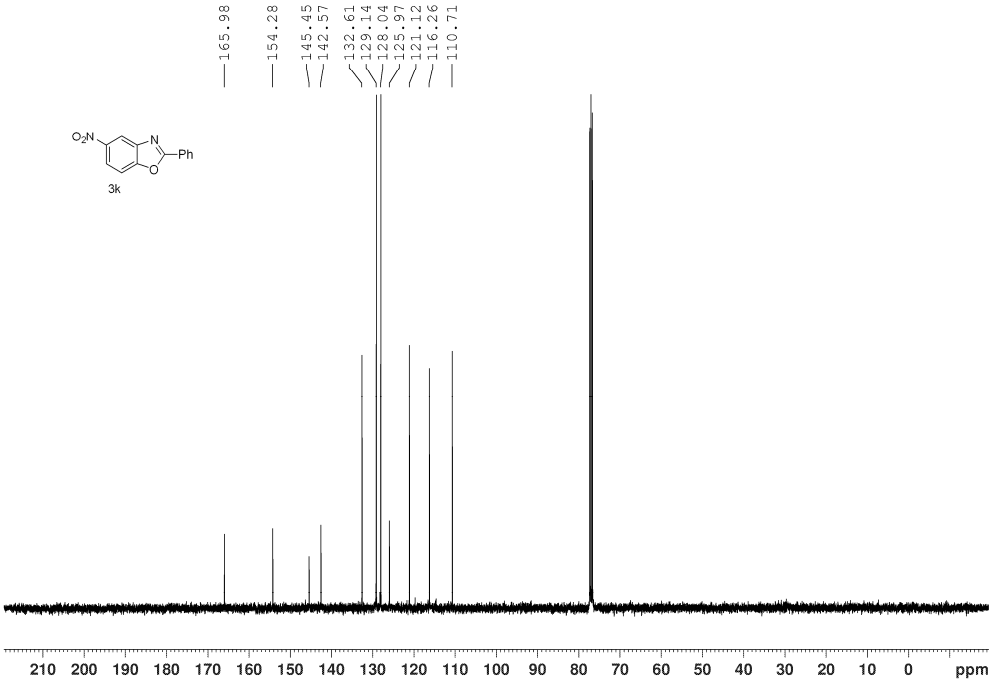
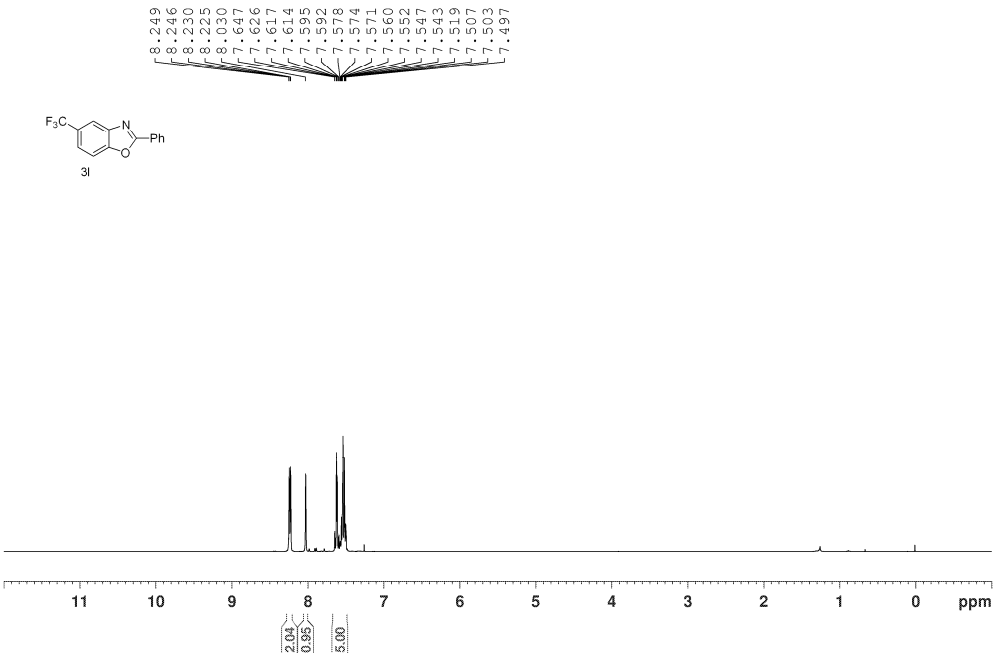
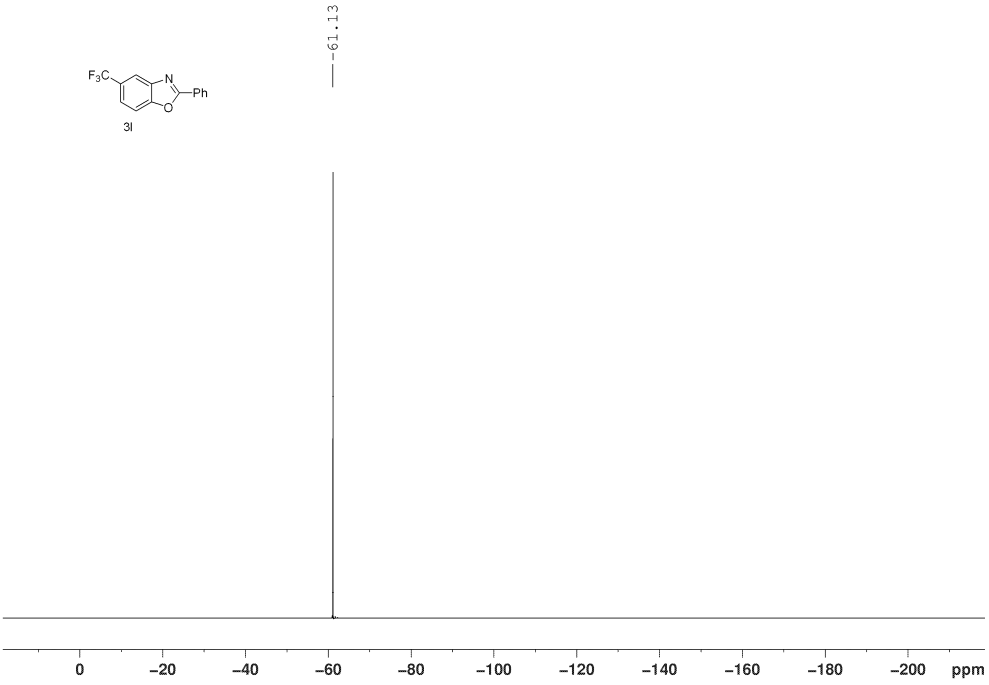
7.515
7.509
7.505
7.501
7.498
7.493
3.948
MeO2C
N
Ph
O
3j
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.80
1.96
0.96
1.00
2.93
3.00

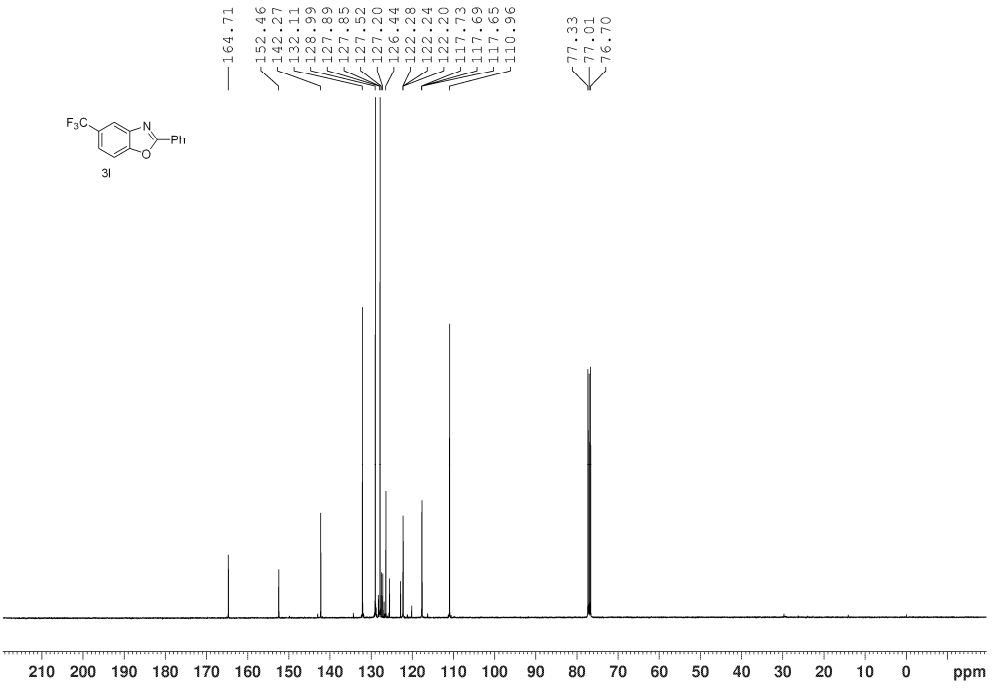

166.67
164.25
153.61
142.17
131.92
128.94
127.76
127.00
126.56
121.94
110.32
77.32
77.00
76.68
52.28
MeO2C
N
Ph
O
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

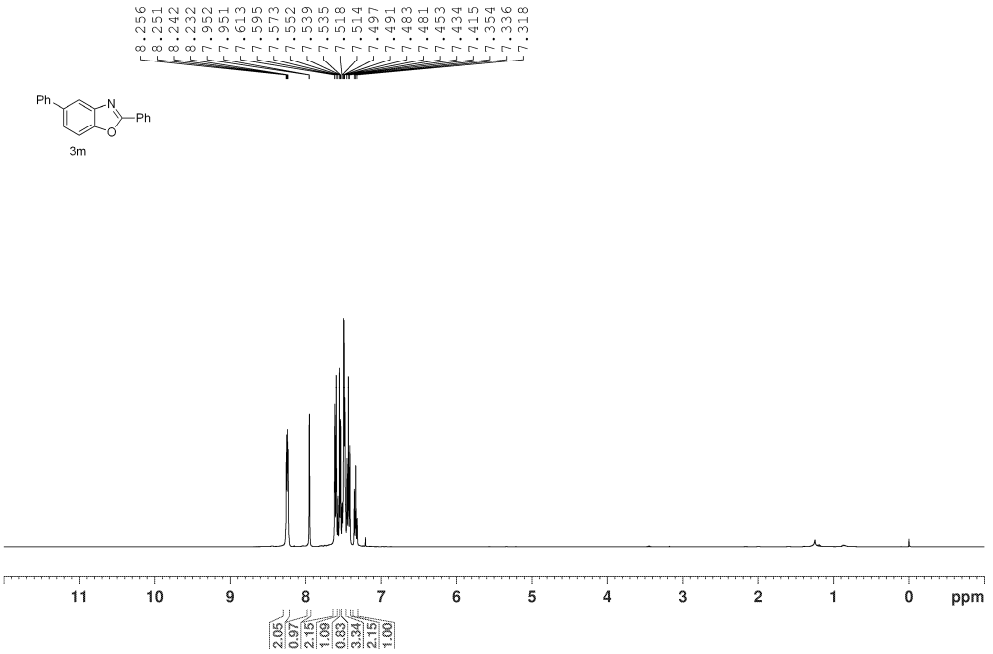

7.410
7.396
7.383
7.377
7.369
7.360
7.355
7.351
7.338
7.329
7.316
7.312
7.296
7.292
7.283
7.279
7.265
7.176
7.144
7.137
7.128
7.122
O2N
N
Ph
O
3k
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.69
0.95
1.90
0.95
3.16

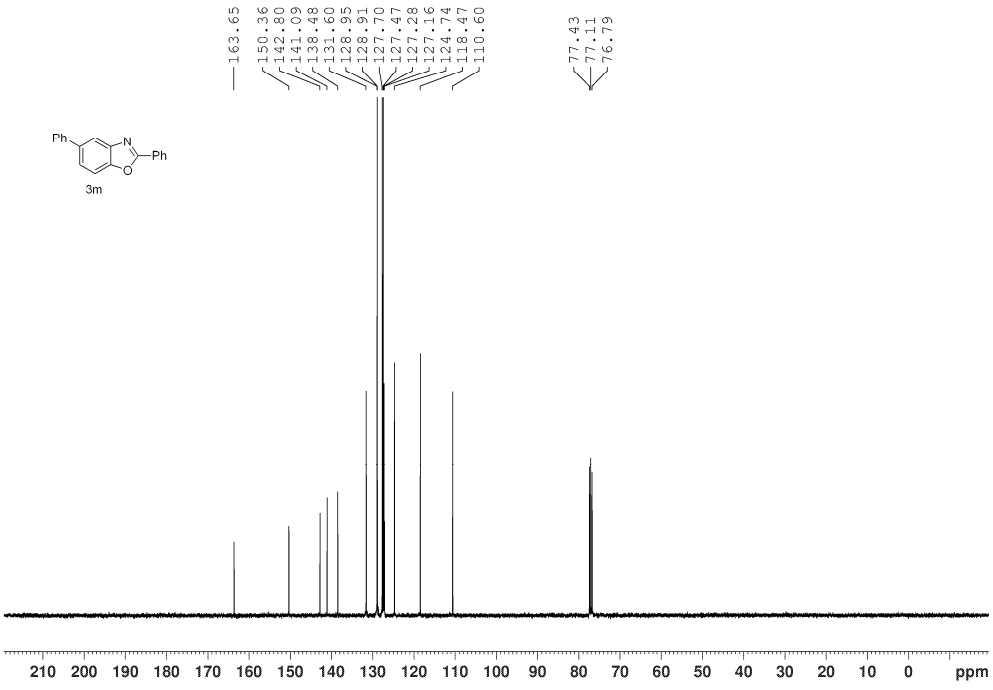

165.98
154.28
145.45
142.57
132.61
129.14
128.04
125.97
121.12
116.26
110.71
O2N
N
O
Ph
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

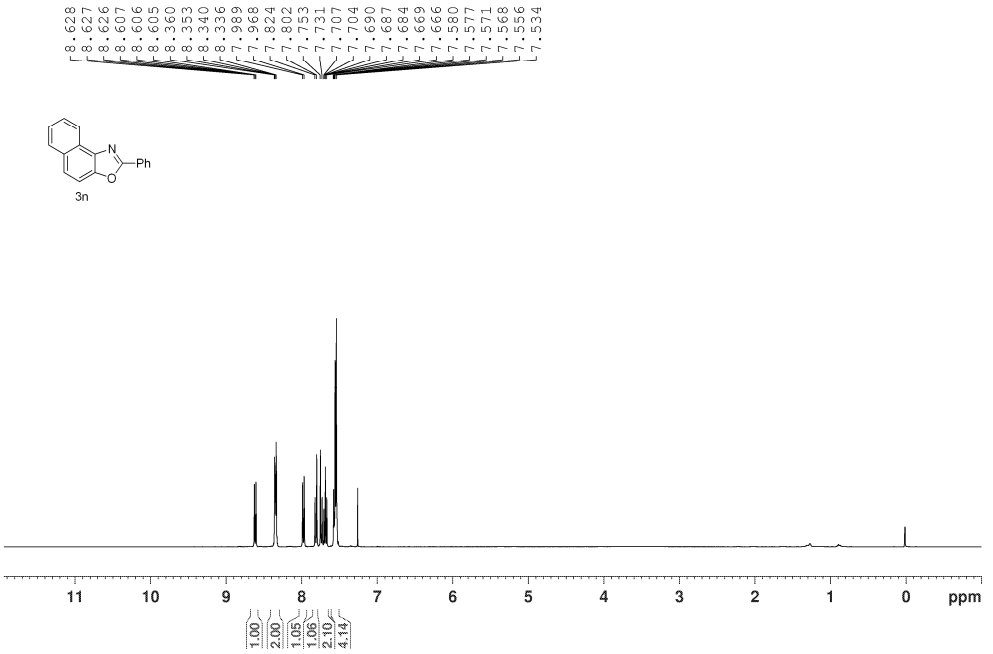

8.249
8.246
8.230
8.225
8.030
7.647
7.626
7.617
7.614
7.595
7.592
7.578
7.574
7.571
7.560
7.552
7.547
7.543
7.519
7.507
7.503
7.497
F3C
N
O
Ph
3l
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.04
0.95
5.00

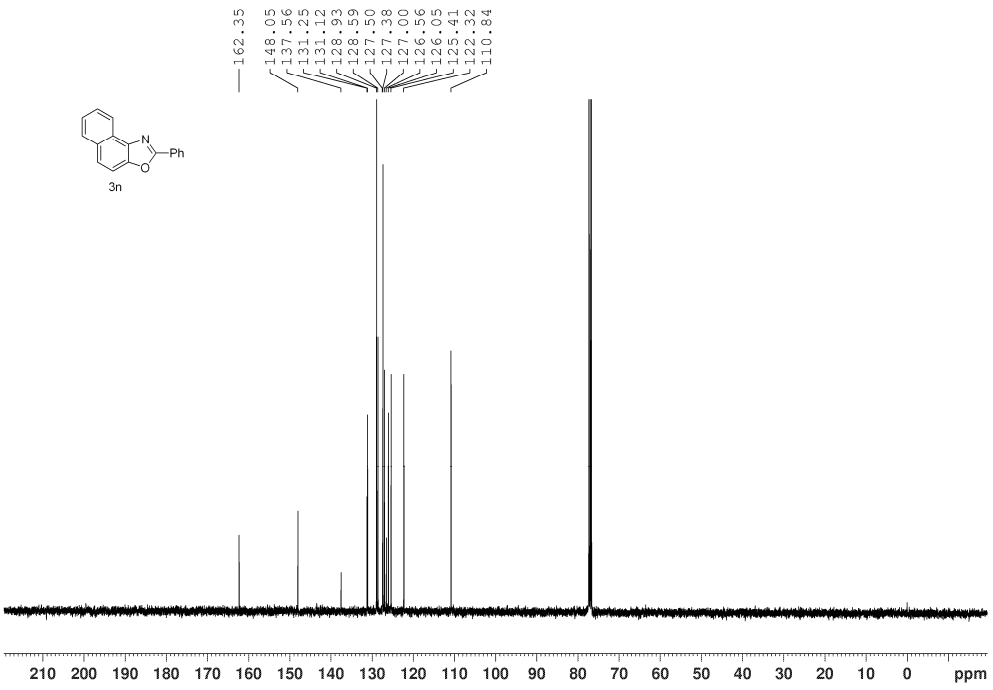

-61.13
3l
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

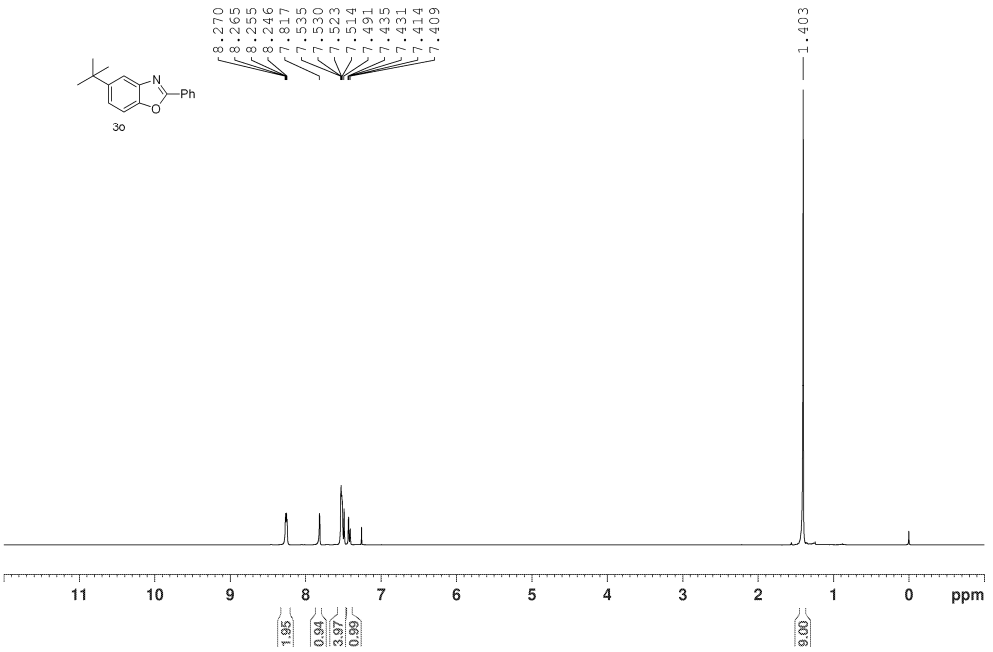

164.71
152.46
142.27
132.11
128.99
127.89
127.85
127.52
127.20
126.44
122.28
122.24
122.20
117.73
117.69
117.65
110.96
77.33
77.01
76.70
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

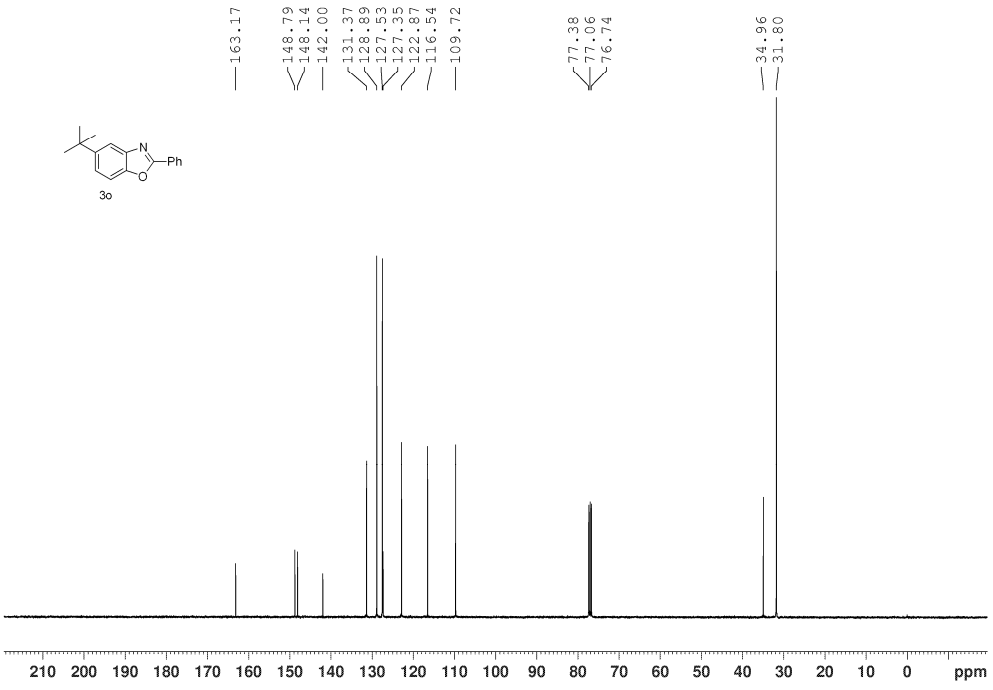

8.256
8.251
8.242
8.232
7.952
7.951
7.613
7.595
7.573
7.552
7.539
7.535
7.518
7.514
7.497
7.491
7.483
7.481
7.453
7.434
7.415
7.354
7.336
7.318
Ph
N
O
Ph
3m
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
0.97
2.15
1.69
0.83
3.34
2.15
1.00

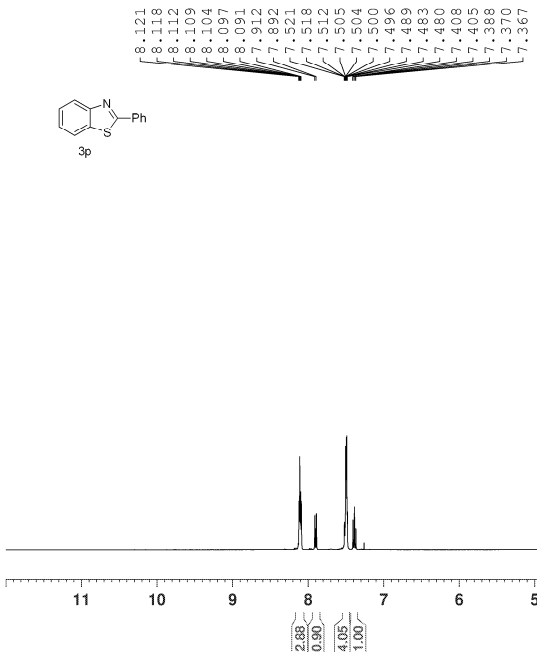

163.65
150.36
142.80
141.09
138.48
131.60
128.95
128.91
127.70
127.47
127.28
127.16
124.74
118.47
110.60
77.43
77.11
76.79
Ph
N
O
Ph
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

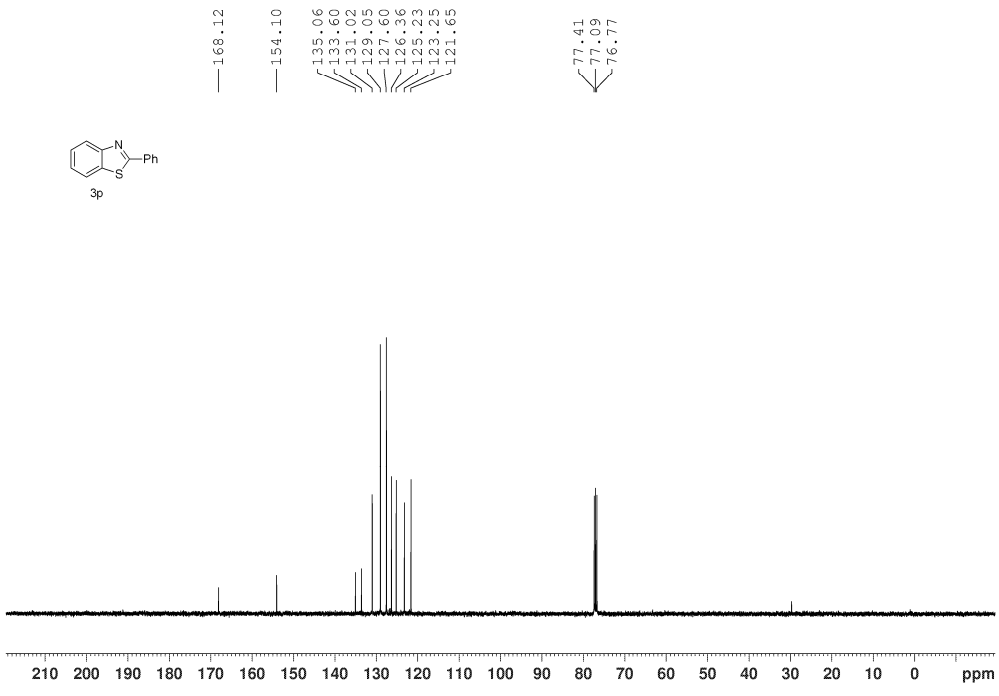

8.628
8.627
8.626
8.607
8.606
8.605
8.360
8.353
8.340
8.336
7.989
7.968
7.824
7.802
7.753
7.731
7.707
7.704
7.690
7.687
7.684
7.669
7.666
7.580
7.577
7.571
7.568
7.556
7.534
N
Ph
O
3n
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.00
1.05
1.06
2.10
4.14

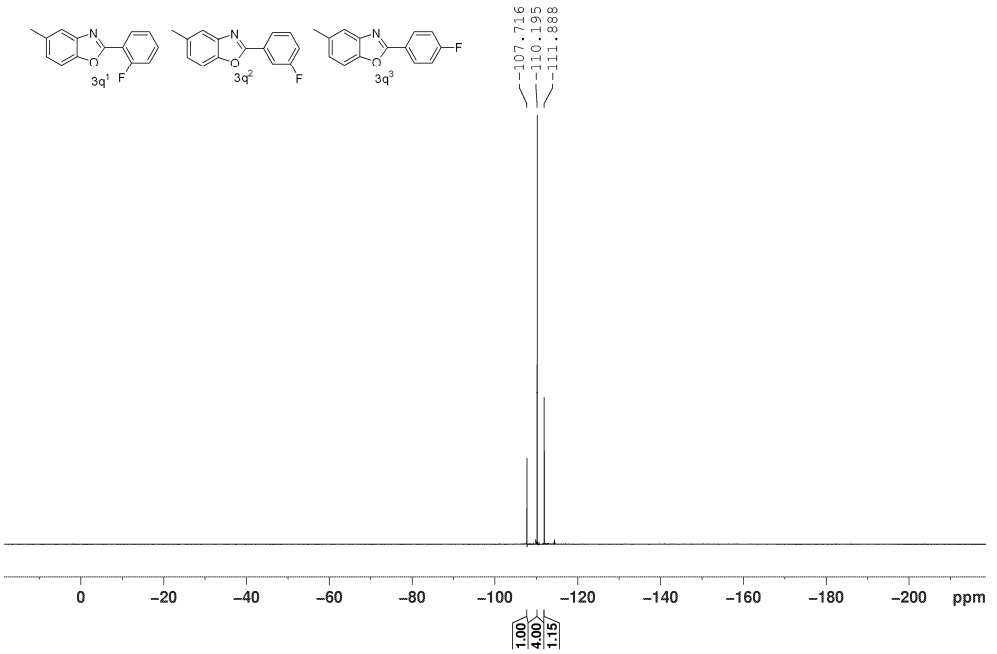

162.35
148.05
137.56
131.25
131.12
128.93
128.59
127.50
127.38
127.00
126.56
126.05
125.41
122.32
110.84
N
Ph
O
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

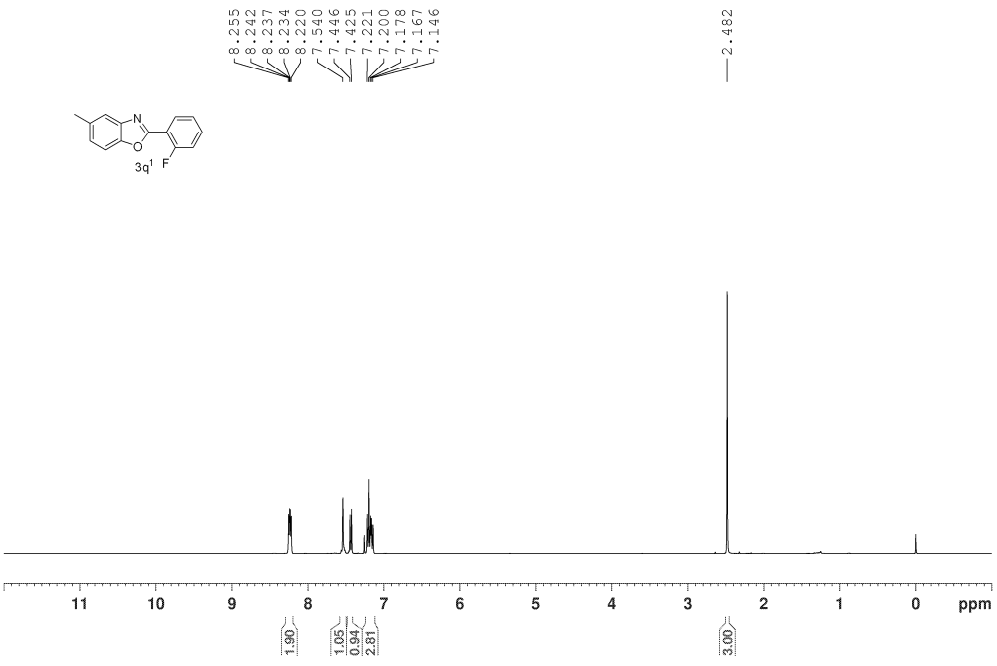

8.270
8.265
8.255
8.246
7.817
7.535
7.530
7.523
7.514
7.491
7.435
7.431
7.414
7.409
1.403
N
O
Ph
3o
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
0.94
2.97
0.99
9.00

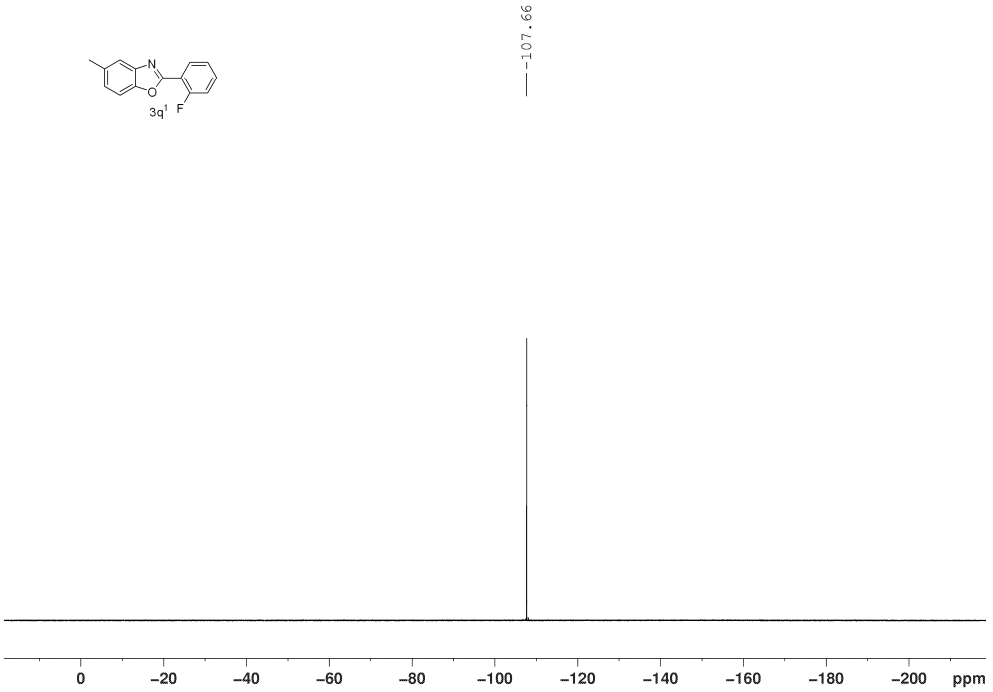

163.17
148.79
148.14
142.00
131.37
128.89
127.53
127.35
122.87
116.54
109.72
77.38
77.06
76.74
34.96
31.80
N
O
Ph
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

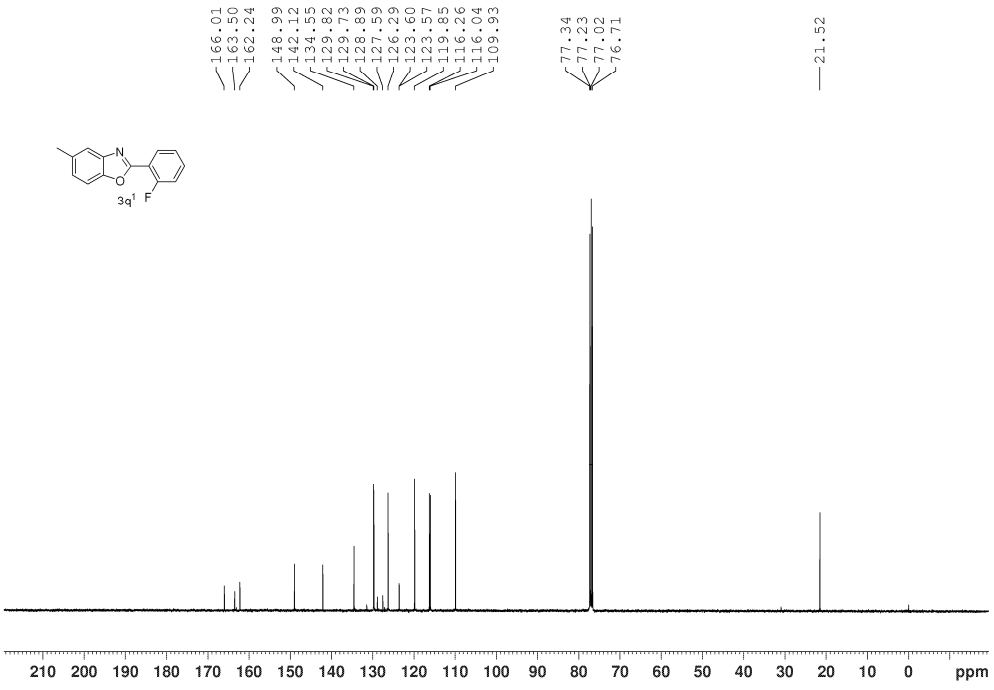

8.121
8.118
8.112
8.109
8.104
8.097
8.091
7.912
7.892
7.521
7.518
7.512
7.505
7.504
7.500
7.496
7.489
7.483
7.480
7.408
7.405
7.388
7.370
7.367
N
S
Ph
3p
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.88
0.90
4.05
1.00

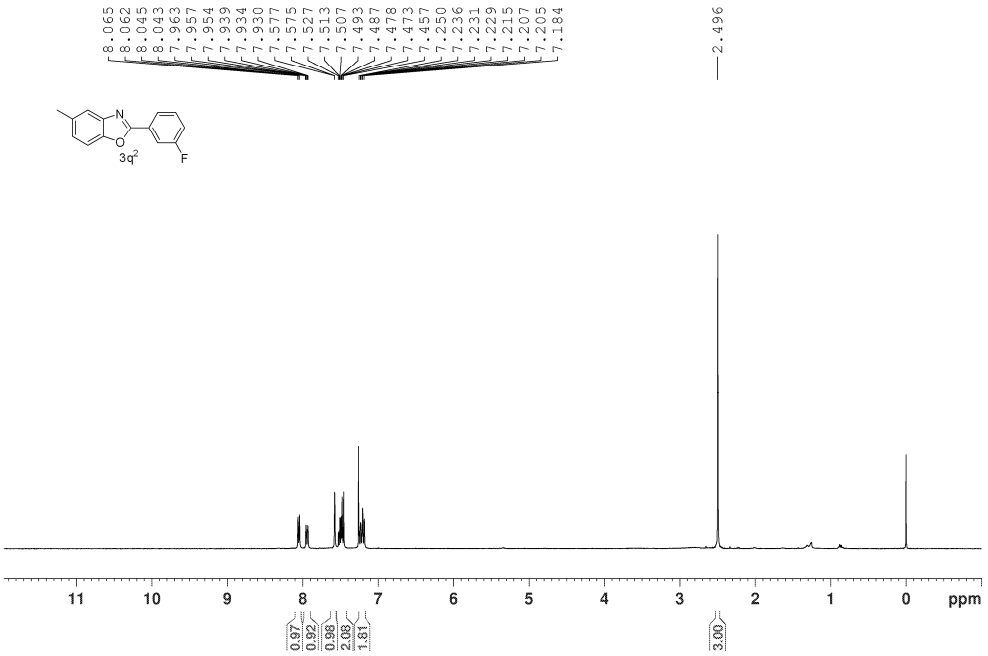

168.12
154.10
135.06
133.60
131.02
129.05
127.60
126.36
125.23
123.25
121.65
77.41
77.09
76.77
N
S
Ph
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

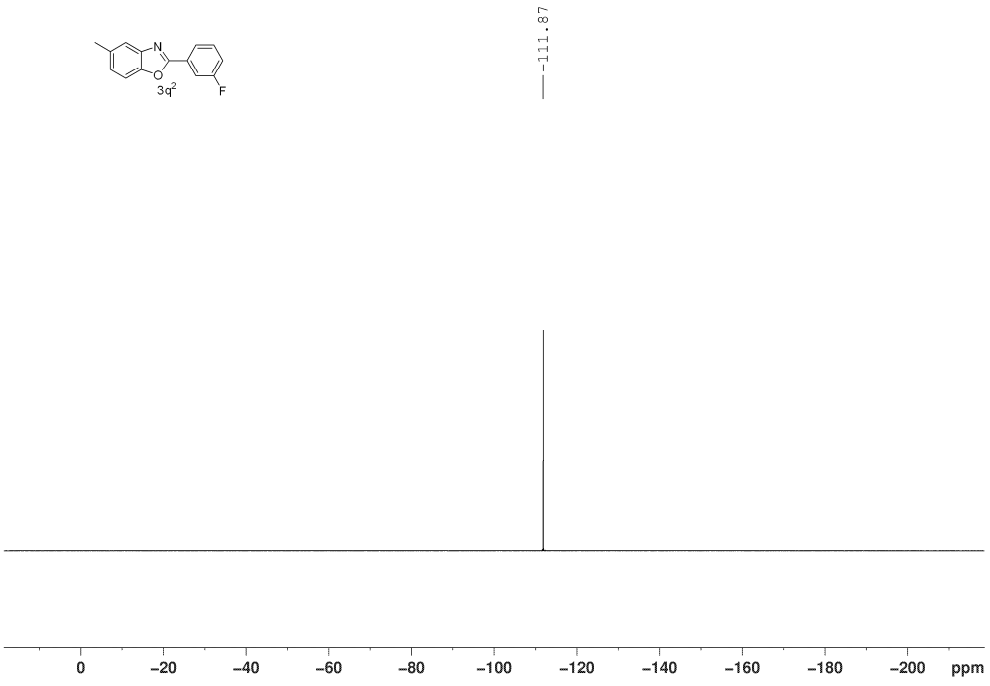

3q1
F
3q2
F
3q3
F
-107.716
-110.195
-111.888
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
4.00
1.15

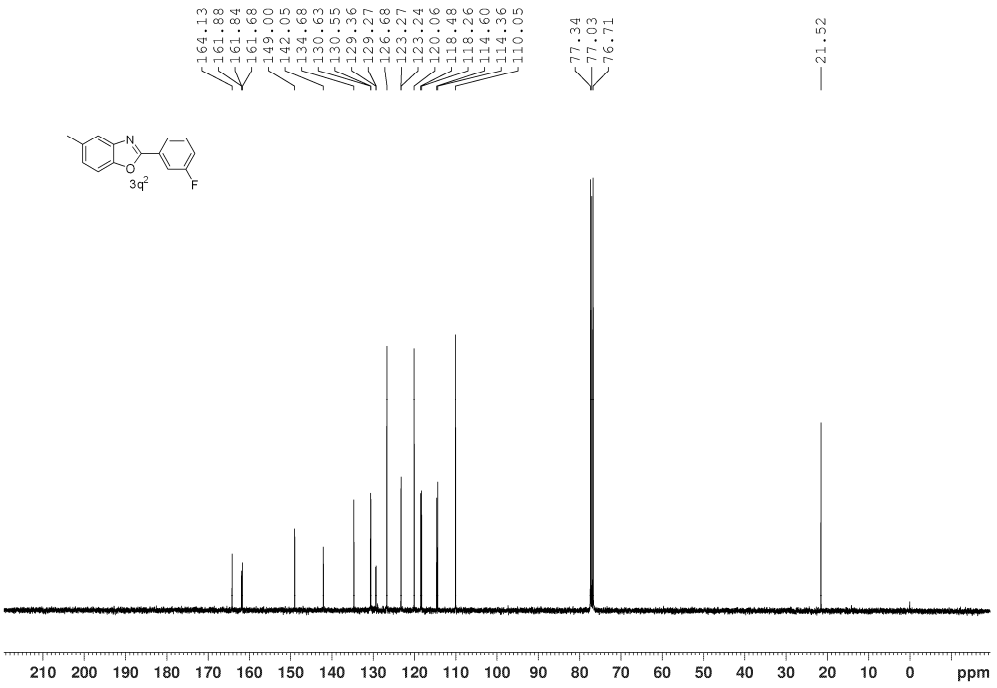

8.255
8.242
8.237
8.234
8.220
7.540
7.446
7.425
7.221
7.200
7.178
7.167
7.146
2.482
3q1
F
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.90
1.05
0.94
2.81
3.00

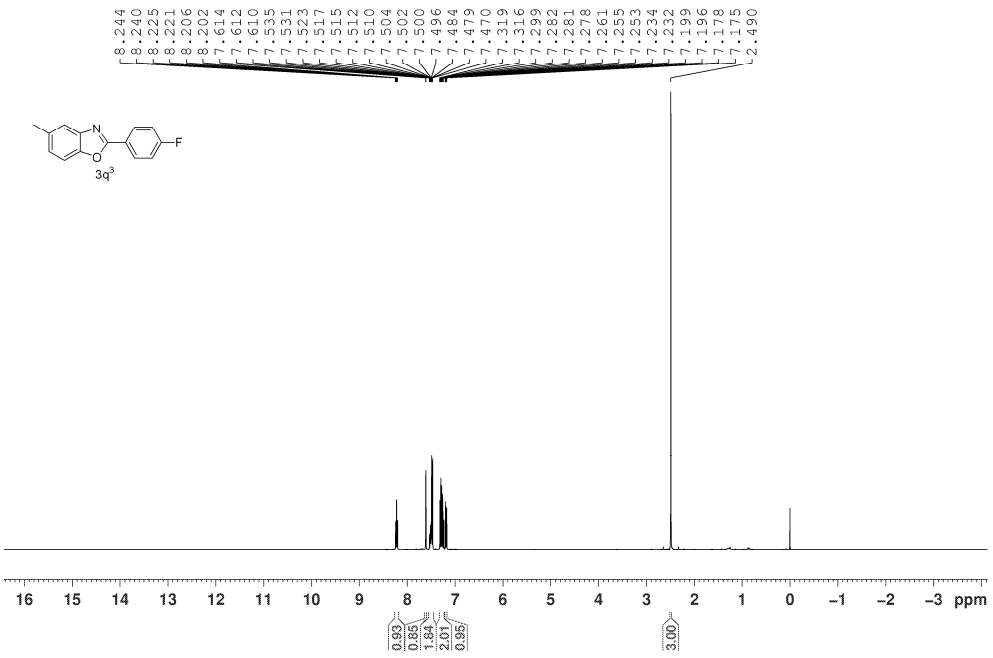

3q1
F
-107.66
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

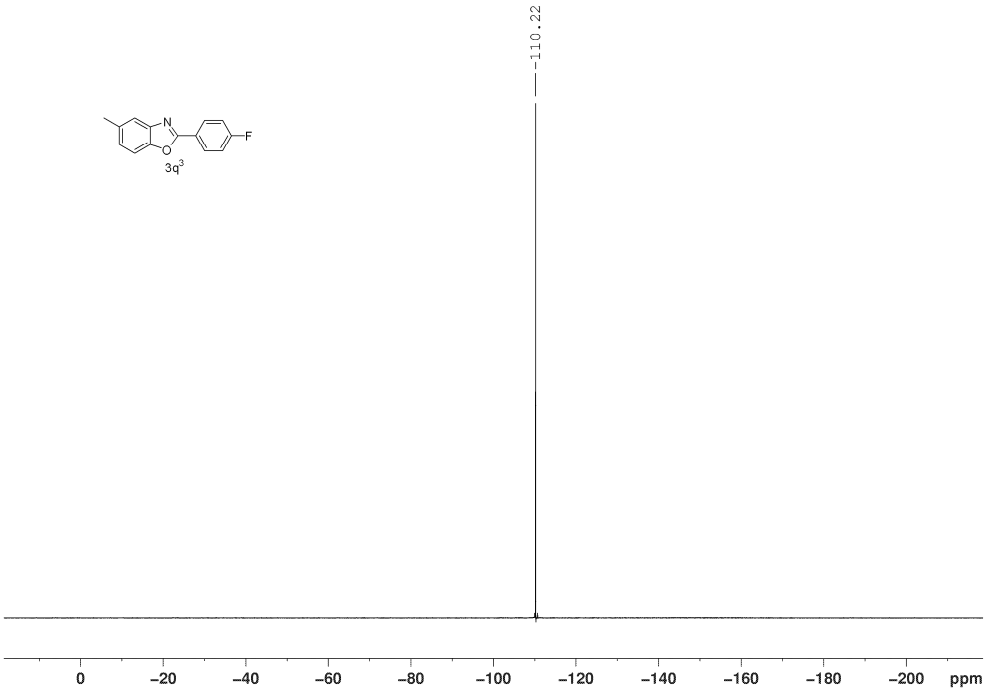

166.01
163.50
162.24
148.99
142.12
134.55
129.82
129.73
128.89
127.59
126.29
123.60
123.57
119.85
116.26
116.04
109.93
77.34
77.23
77.02
76.71
21.52
3q1
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

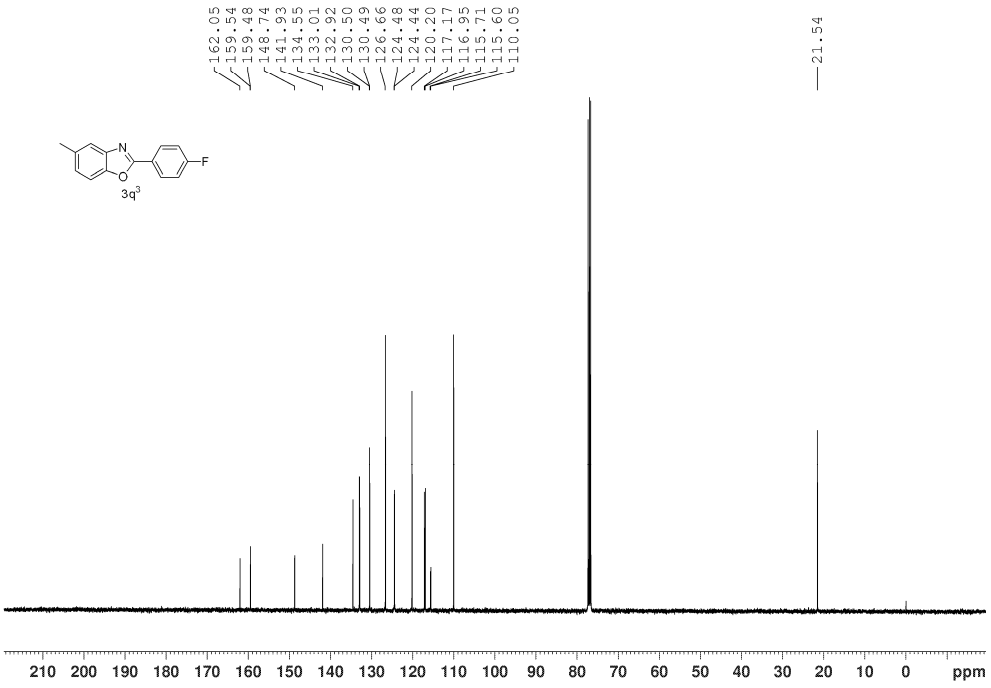

8.065
8.062
8.045
8.043
7.963
7.957
7.954
7.939
7.934
7.930
7.577
7.575
7.527
7.513
7.507
7.493
7.487
7.478
7.473
7.457
7.250
7.236
7.231
7.229
7.215
7.207
7.205
7.184
2.496
3q2
F
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
0.92
0.98
2.08
1.81
3.00

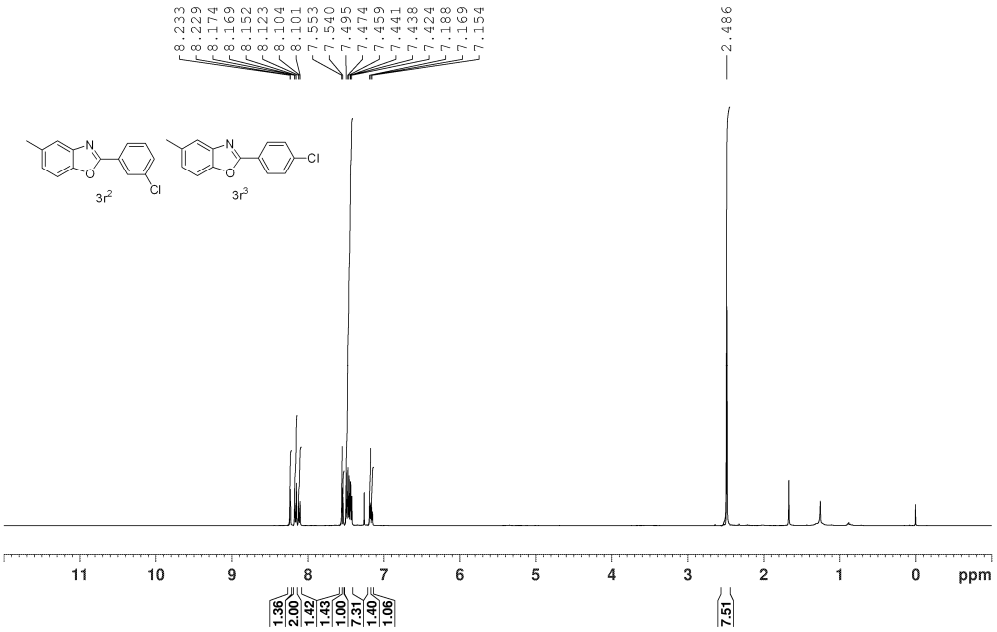

-111.87
3q2
F
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

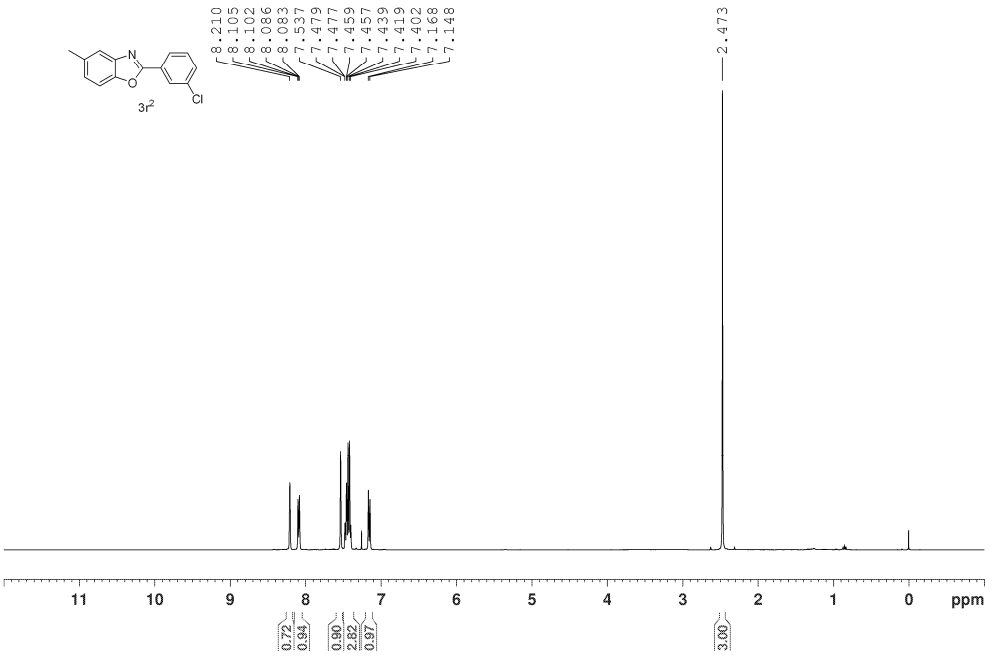

164.13
161.88
161.84
161.68
149.00
142.05
134.68
130.63
130.55
129.36
129.27
126.68
123.27
123.24
120.06
118.48
118.26
114.60
114.36
110.05
77.34
77.03
76.71
21.52
3q2
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

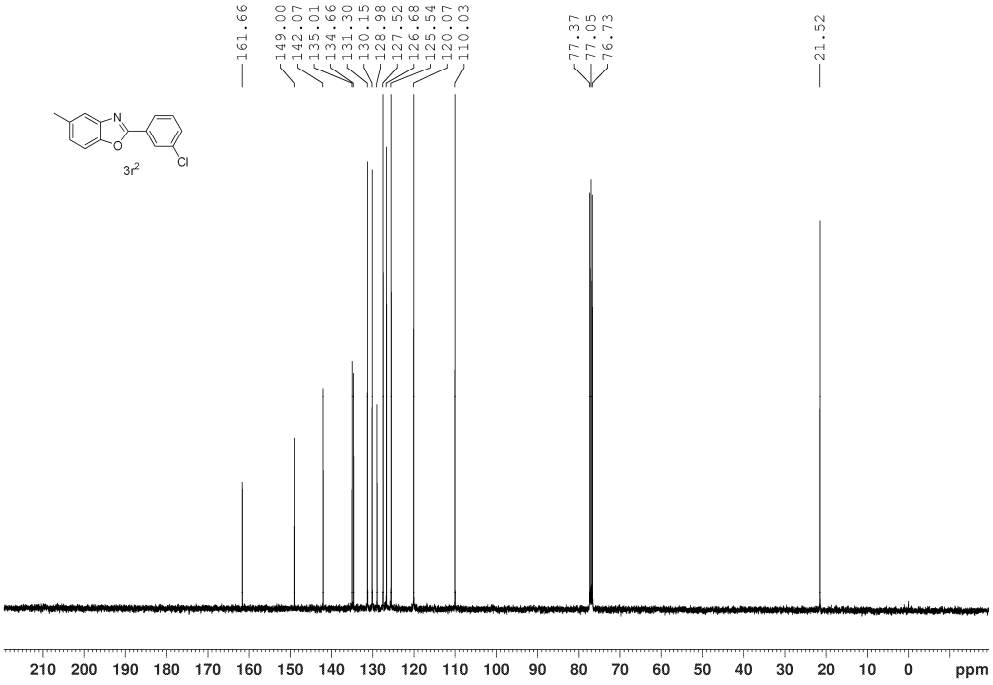

8.244
8.240
8.225
8.221
8.206
8.202
7.614
7.612
7.610
7.535
7.531
7.523
7.517
7.515
7.512
7.510
7.504
7.502
7.500
7.496
7.484
7.479
7.470
7.319
7.316
7.299
7.282
7.281
7.278
7.261
7.255
7.253
7.234
7.232
7.199
7.196
7.178
7.175
2.490
3q3
F
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 ppm
0.93
0.85
1.84
2.01
0.95
3.00

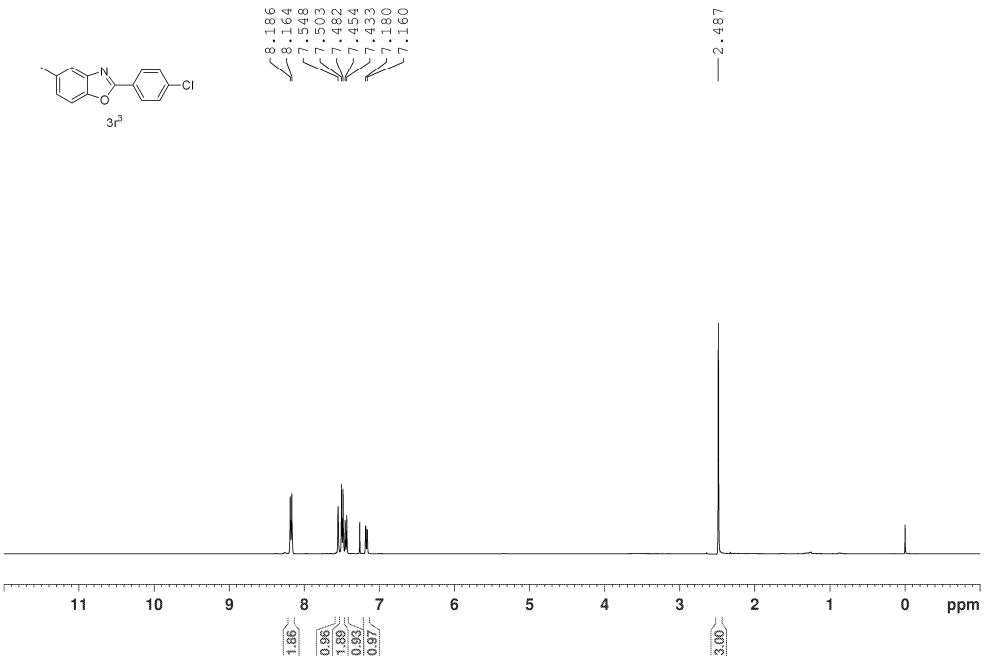

-110.22
N
O
F
3q3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

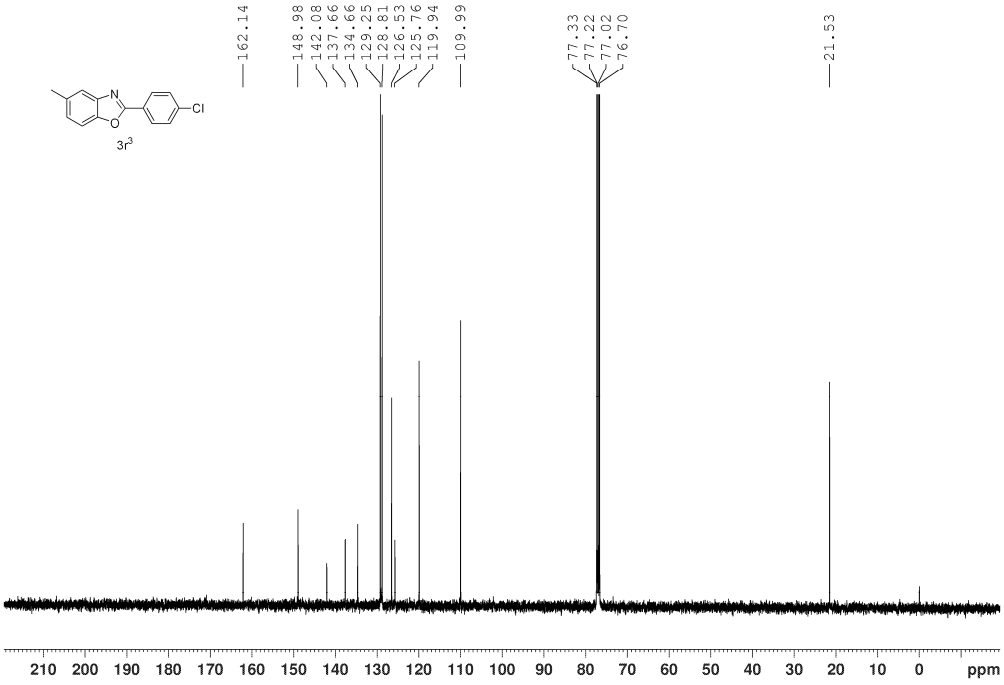

162.05
159.54
159.48
148.74
141.93
134.55
133.01
132.92
130.50
130.49
126.66
124.48
124.44
120.20
117.17
116.95
115.71
115.60
110.05
21.54
N
O
F
3q3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

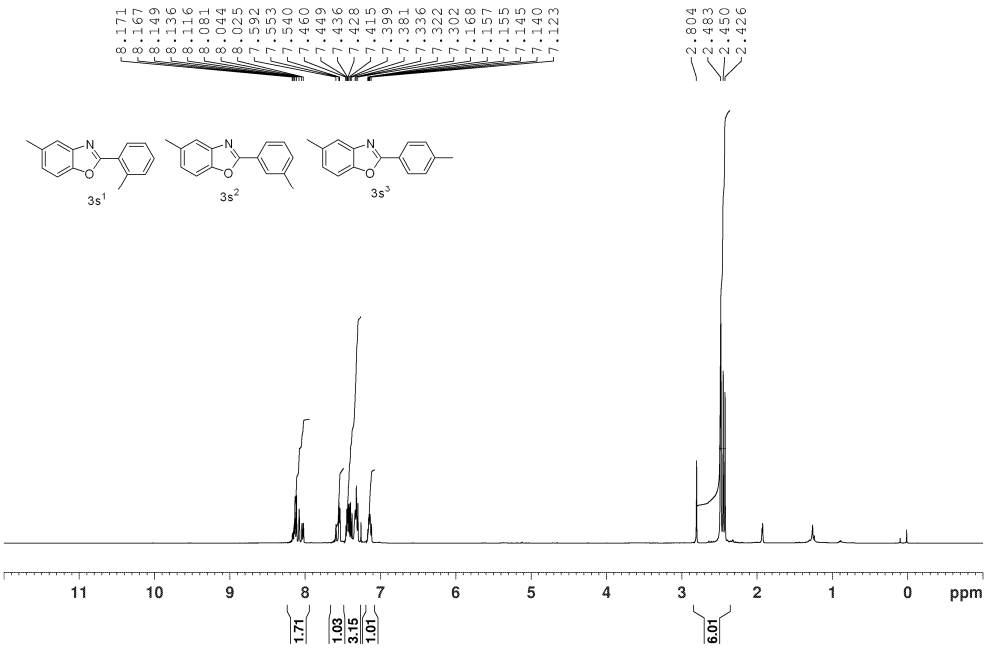

8.233
8.229
8.174
8.169
8.152
8.123
8.104
8.101
7.553
7.540
7.495
7.474
7.459
7.441
7.438
7.424
7.188
7.169
7.154
2.486
3r2
3r3
Cl
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.36 2.00 1.42 1.43 1.00 7.31 1.40 1.06
7.51


8.210
8.105
8.102
8.086
8.083
7.537
7.479
7.477
7.459
7.457
7.439
7.419
7.402
7.168
7.148
2.473
3r2
Cl
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.72 0.94 0.90 2.82 0.97
3.00


161.66
149.00
142.07
135.01
134.66
131.30
130.15
128.98
127.52
126.68
125.54
120.07
110.03
77.37
77.05
76.73
21.52
N
O
Cl
3r2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.186
8.164
7.548
7.503
7.482
7.454
7.433
7.180
7.160
2.487
N
O
Cl
3r3
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.66
0.96
1.89
0.53
0.97
3.00


162.14
148.98
142.08
137.66
134.66
129.25
128.81
126.53
125.76
119.94
109.99
77.33
77.22
77.02
76.70
21.53
Cl
3r3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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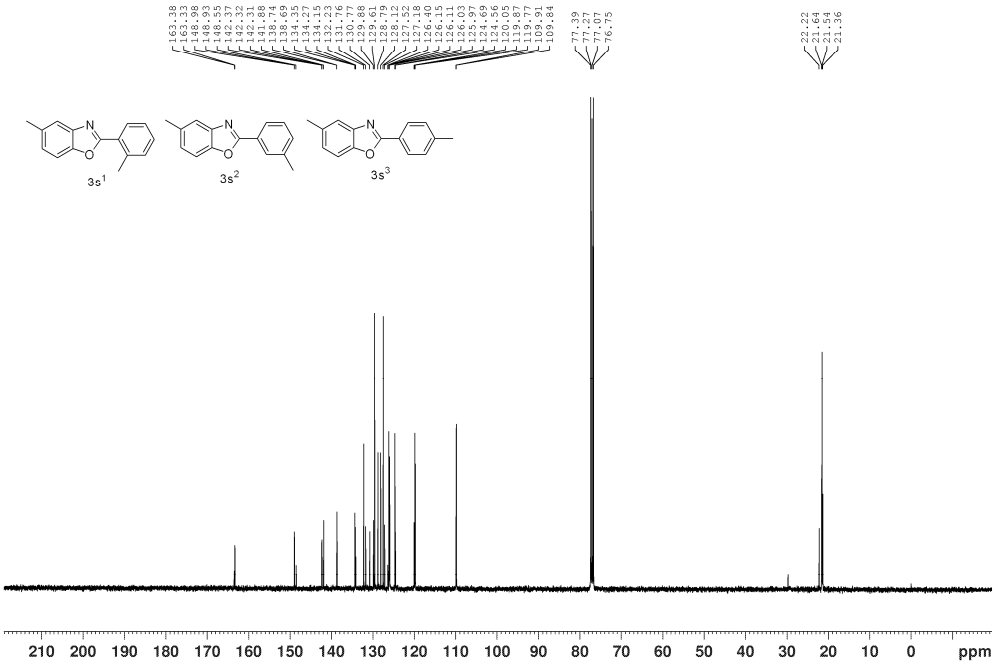
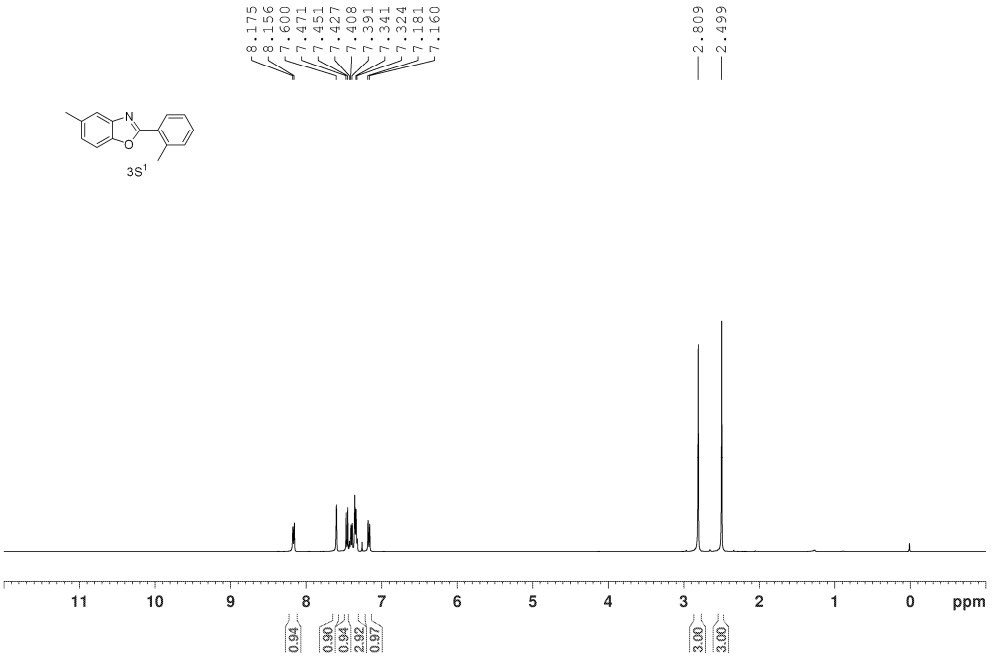
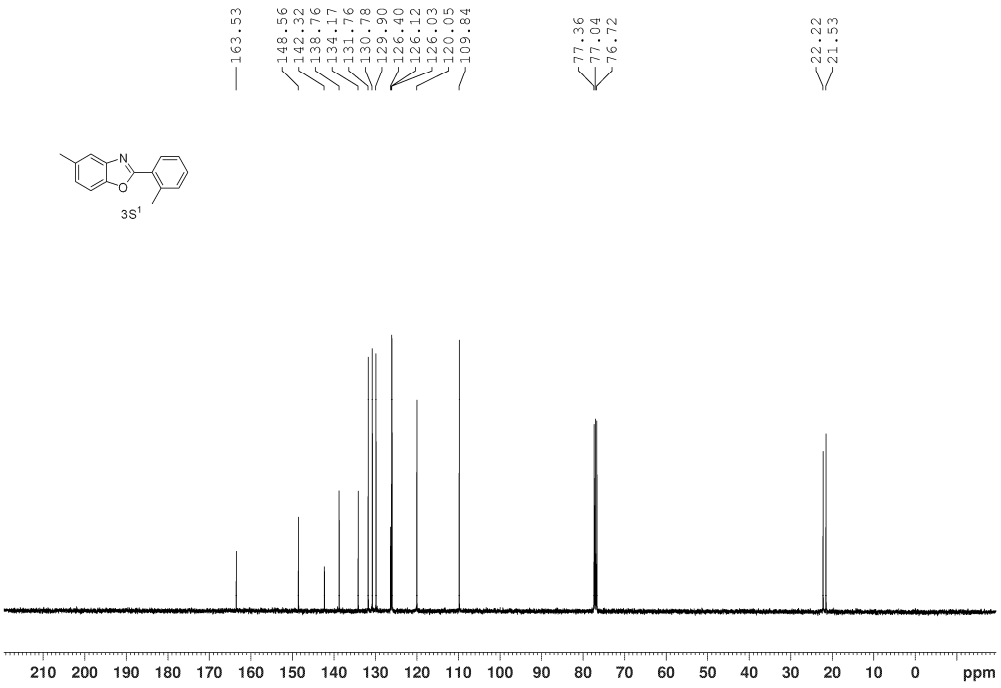
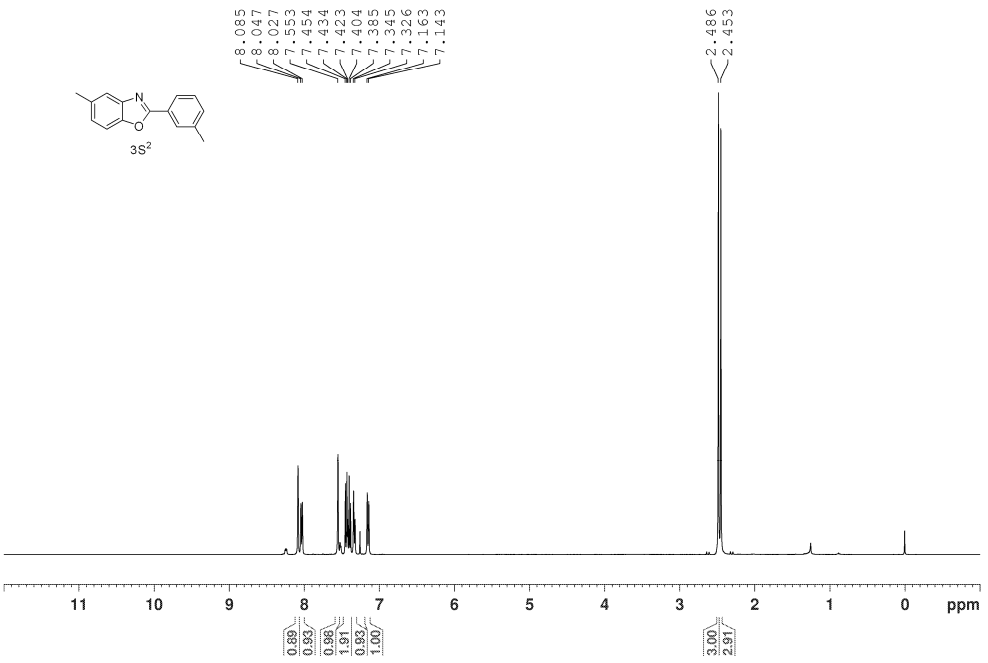
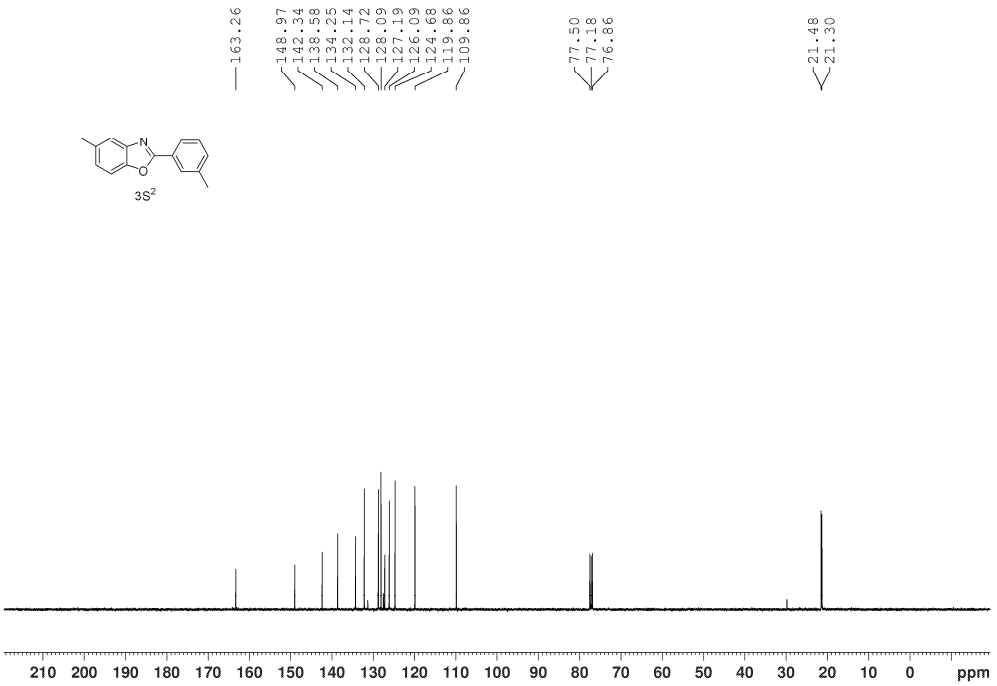
8.167
8.149
8.136
8.116
8.081
8.044
8.025
7.592
7.553
7.540
7.460
7.449
7.436
7.428
7.415
7.399
7.381
7.336
7.322
7.302
7.168
7.157
7.155
7.145
7.140
7.123
2.804
2.483
2.450
2.426
3s1
3s2
3s3
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.71
1.08
3.15
1.01
6.01

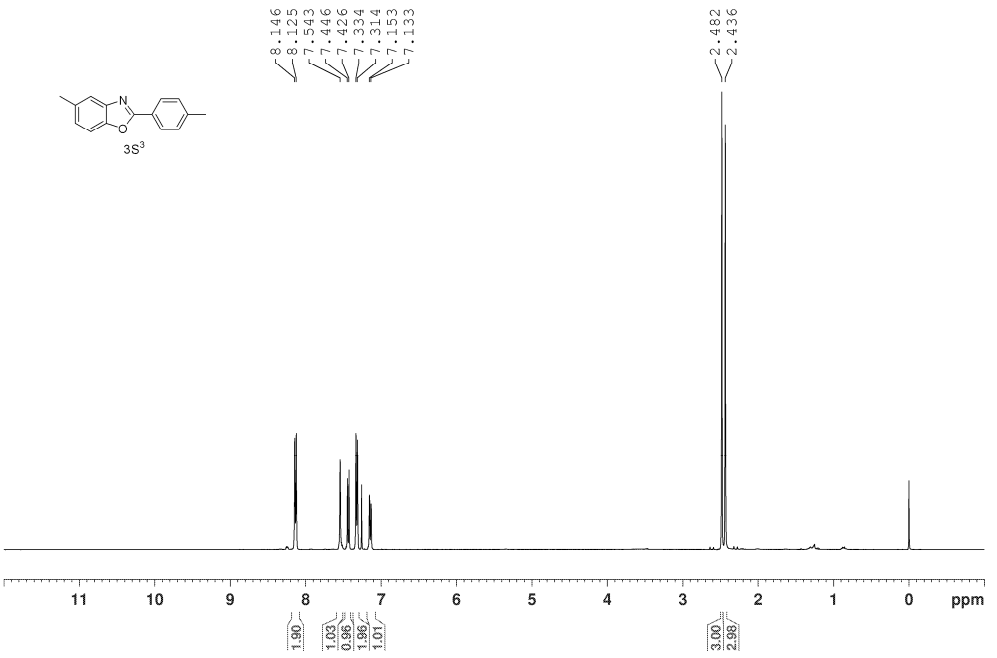

163.38
163.33
148.98
148.93
148.55
142.37
142.32
142.31
141.88
138.74
138.69
134.35
134.27
134.15
132.23
131.76
131.77
129.88
129.61
128.79
128.12
127.52
127.18
126.40
126.15
126.11
126.03
125.97
124.69
124.56
120.55
119.87
119.77
109.91
109.84
77.39
77.27
77.07
76.75
21.64
21.54
21.36
3s1
3s2
3s3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

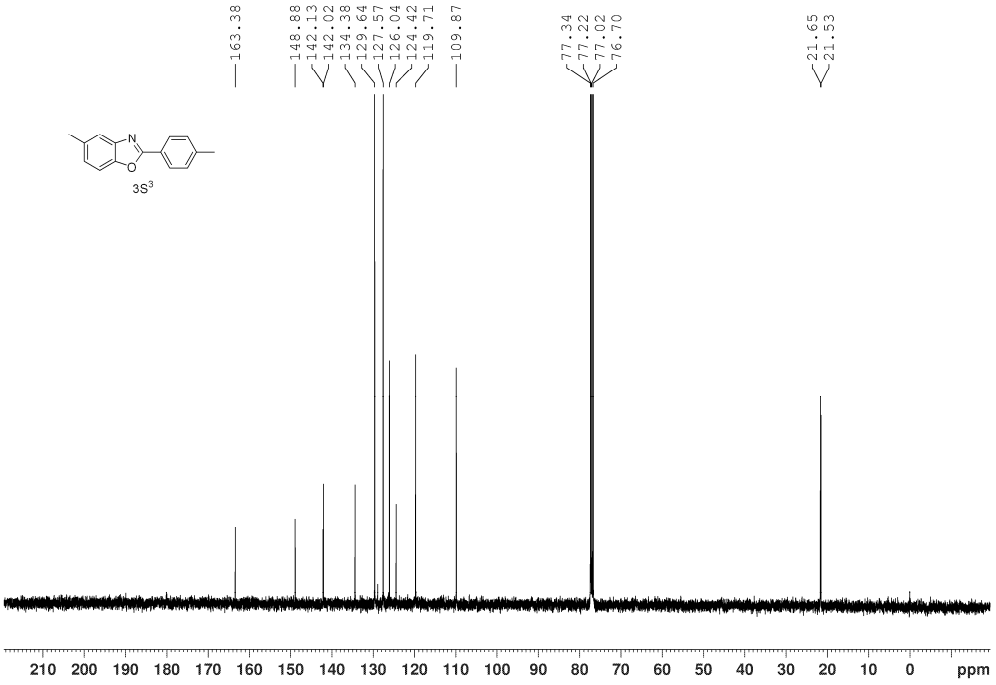

8.175
8.156
7.600
7.471
7.451
7.427
7.408
7.391
7.341
7.324
7.181
7.160
2.809
2.499
3S1
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.94
0.90
0.94
2.92
0.97
3.00
3.00

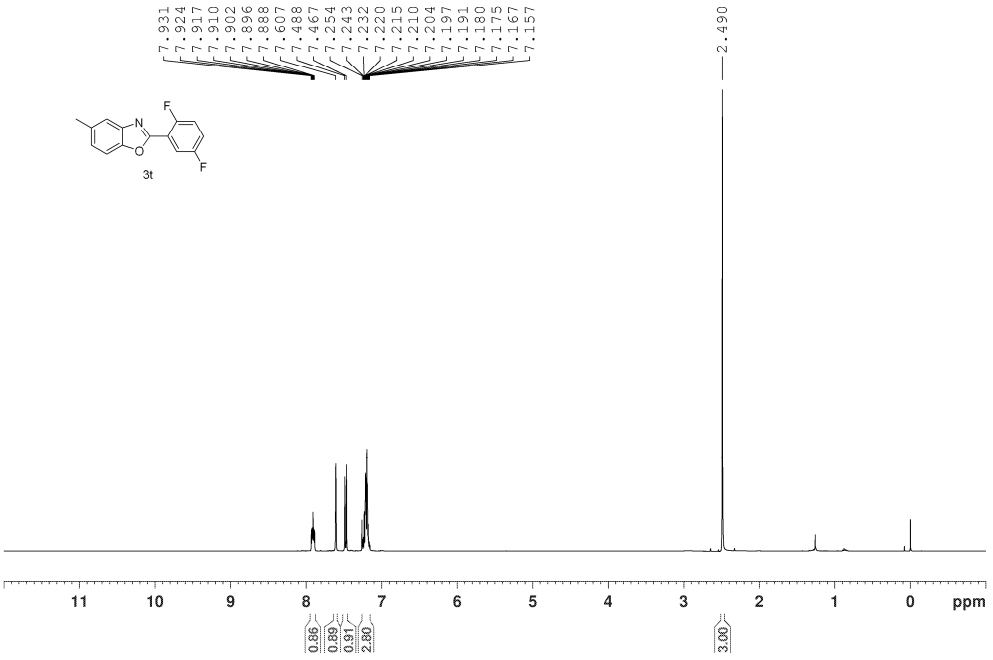

163.53
148.56
142.32
138.76
134.17
131.76
130.78
129.90
126.40
126.12
126.03
120.05
109.84
77.36
77.04
76.72
22.22
21.53
3S1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

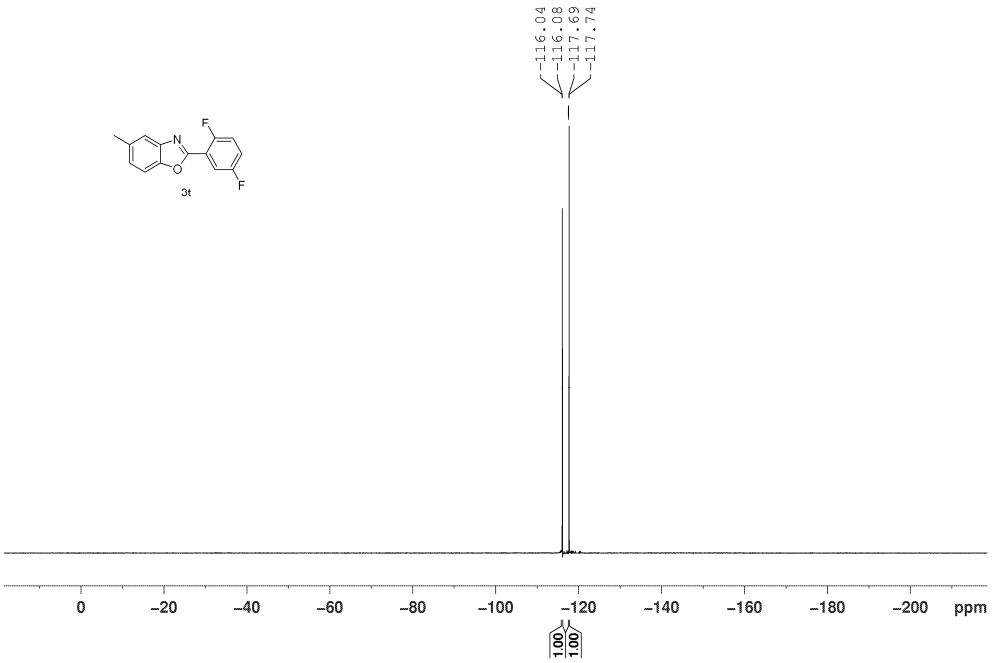

8.085
8.047
8.027
7.553
7.454
7.434
7.423
7.404
7.385
7.345
7.326
7.163
7.143
2.486
2.453
3S2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.89
0.93
0.98
1.91
0.93
1.00
3.00
2.91

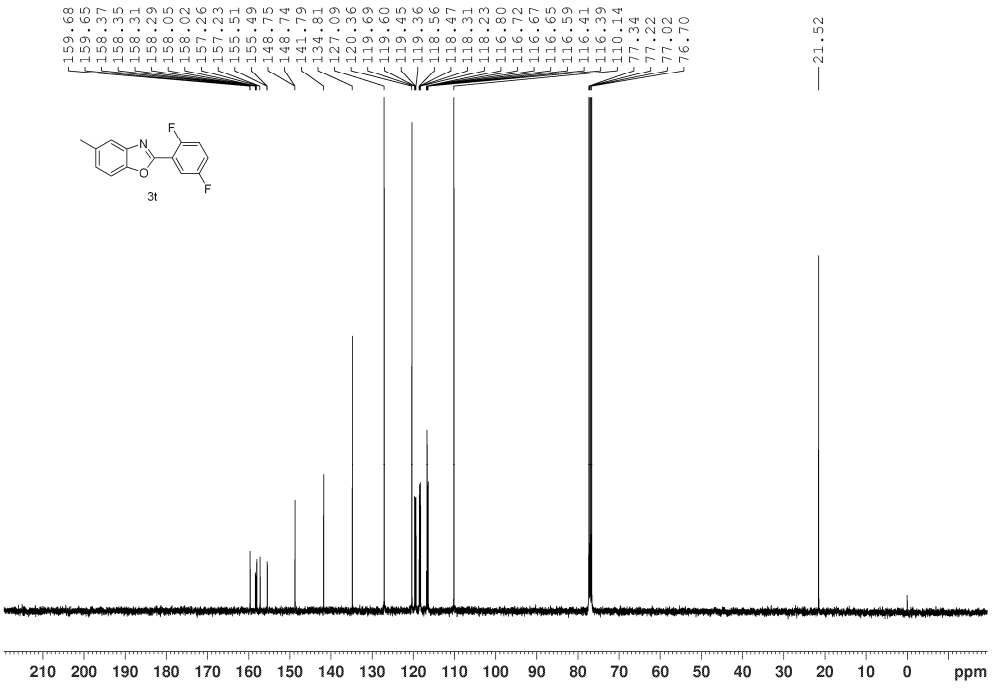

163.26
148.97
142.34
138.58
134.25
132.14
128.72
128.09
127.19
126.09
124.68
119.86
109.86
77.50
77.18
76.86
21.48
21.30
3S2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

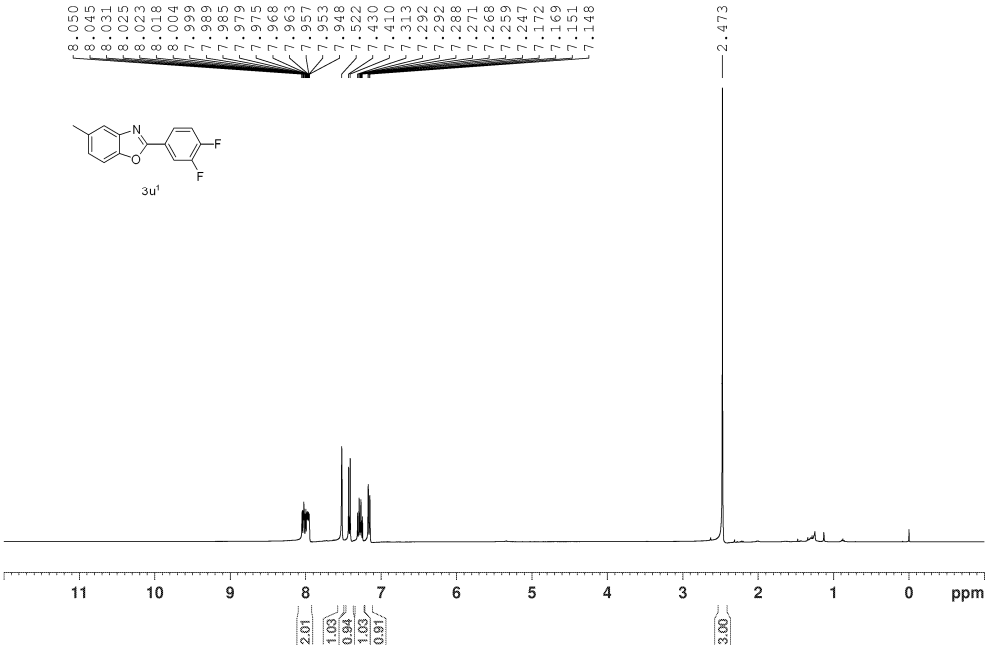

8.146
8.125
7.543
7.446
7.426
7.334
7.314
7.153
7.133
2.482
2.436
3S3
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.90
1.03
0.96
1.96
1.01
3.00
2.98

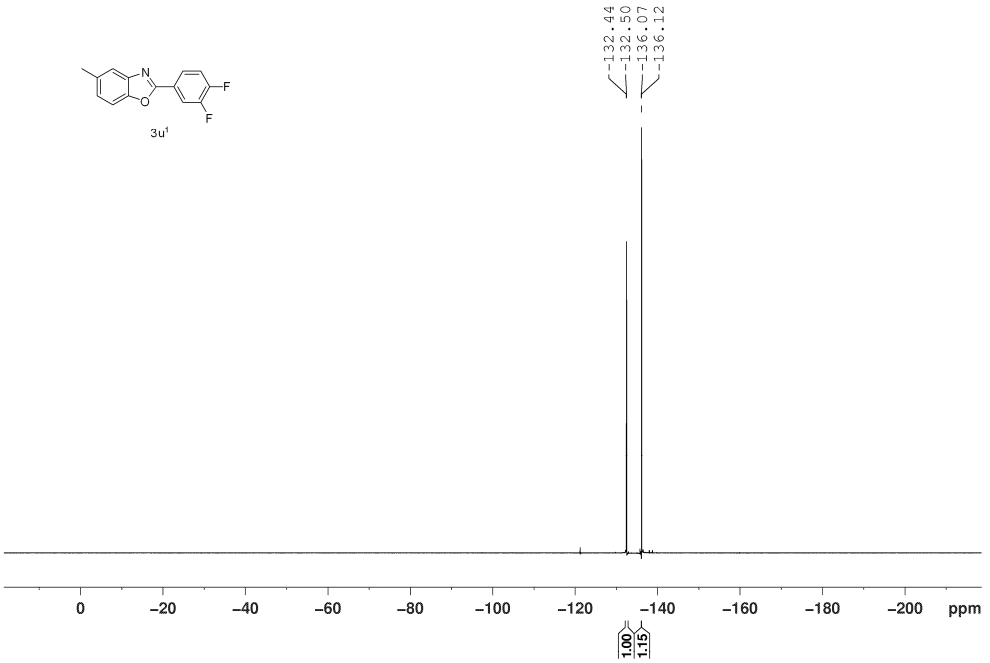

163.38
148.88
142.13
142.02
134.38
129.64
127.57
126.04
124.42
119.71
109.87
77.34
77.22
77.02
76.70
21.65
21.53
3S3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

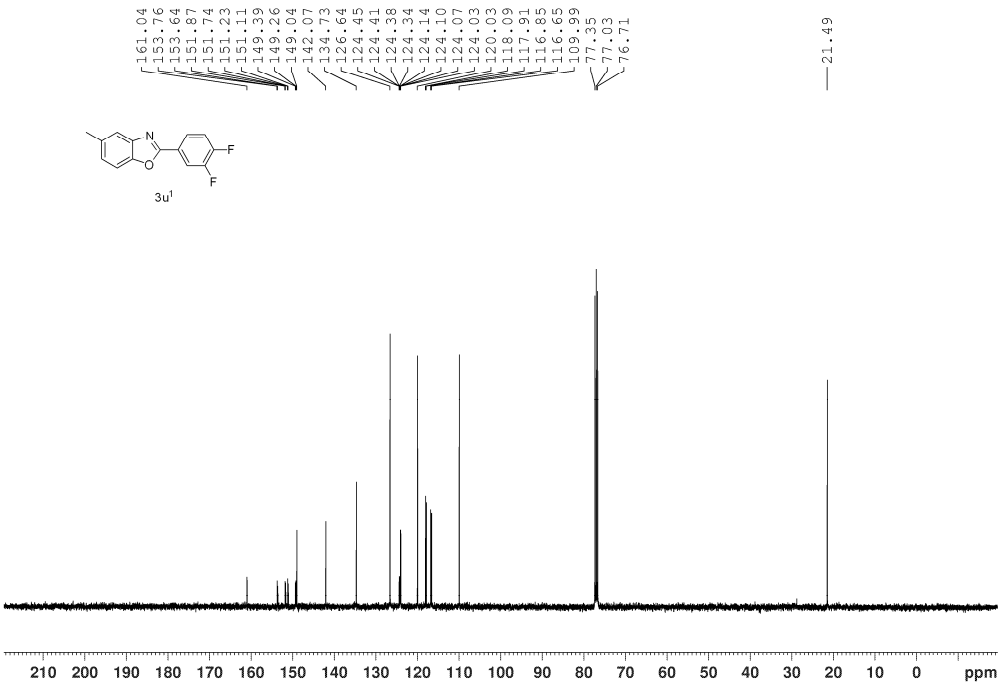

7.931
7.924
7.917
7.910
7.902
7.896
7.888
7.607
7.488
7.467
7.254
7.243
7.232
7.220
7.215
7.210
7.204
7.197
7.191
7.180
7.175
7.167
7.157
2.490
3t
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.86
0.89
0.91
2.80
3.00

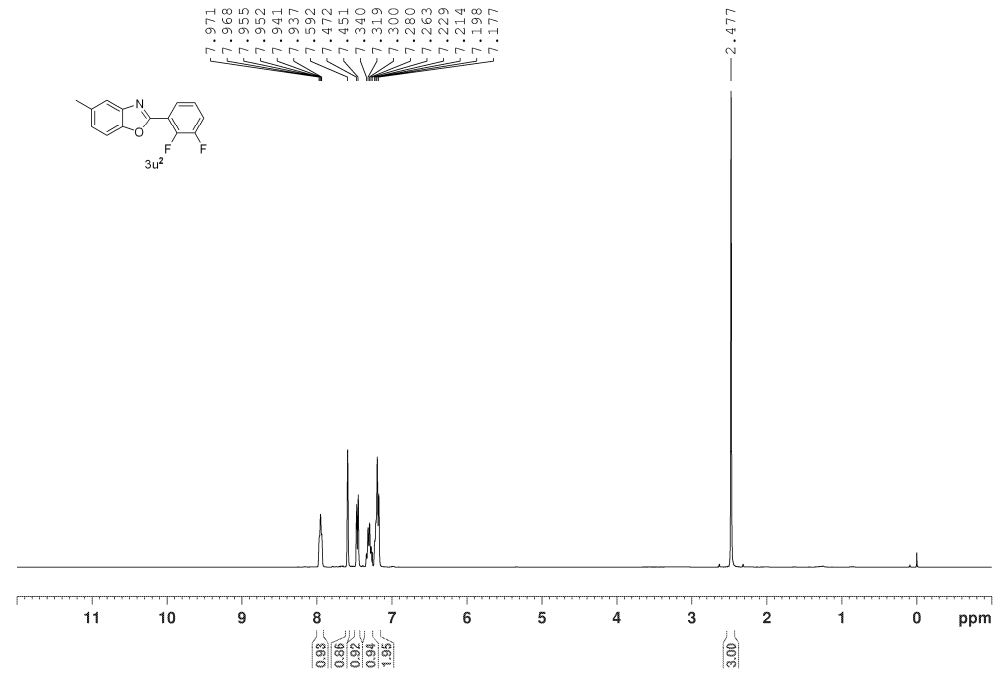

-116.04
-116.08
-117.69
-117.74
F
N
O
F
3t
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.00

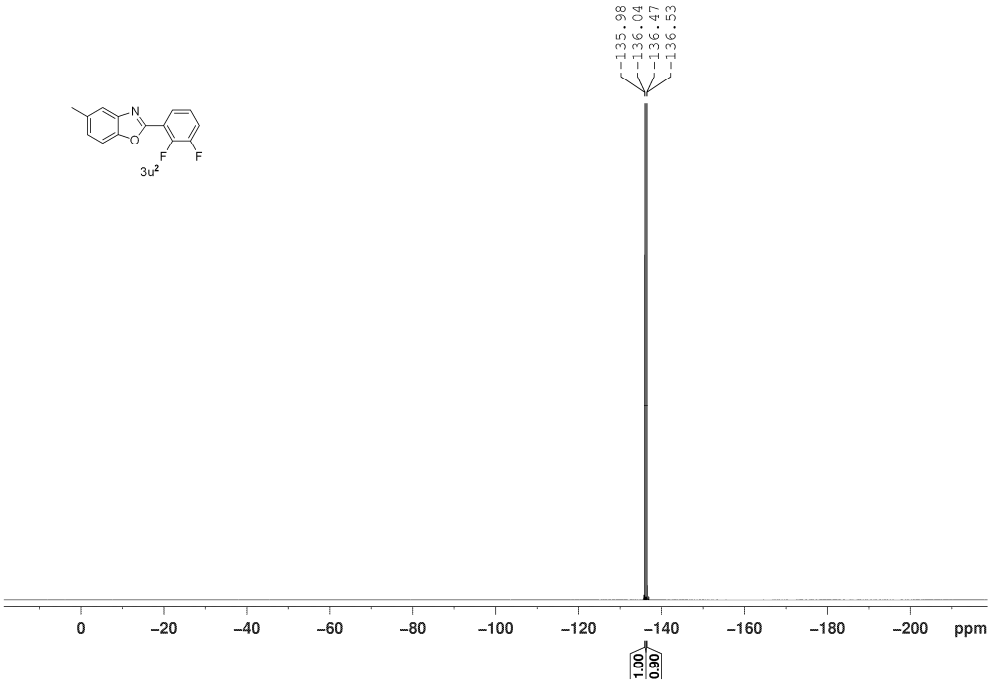

159.68
159.65
158.37
158.35
158.31
158.29
158.05
158.02
157.26
157.23
155.51
155.49
148.75
148.74
141.79
134.81
127.09
120.36
119.69
119.60
119.45
119.36
118.56
118.47
118.31
118.23
116.80
116.72
116.67
116.65
116.59
116.41
116.39
110.14
77.34
77.22
77.02
76.70
21.52
F
N
O
F
3t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

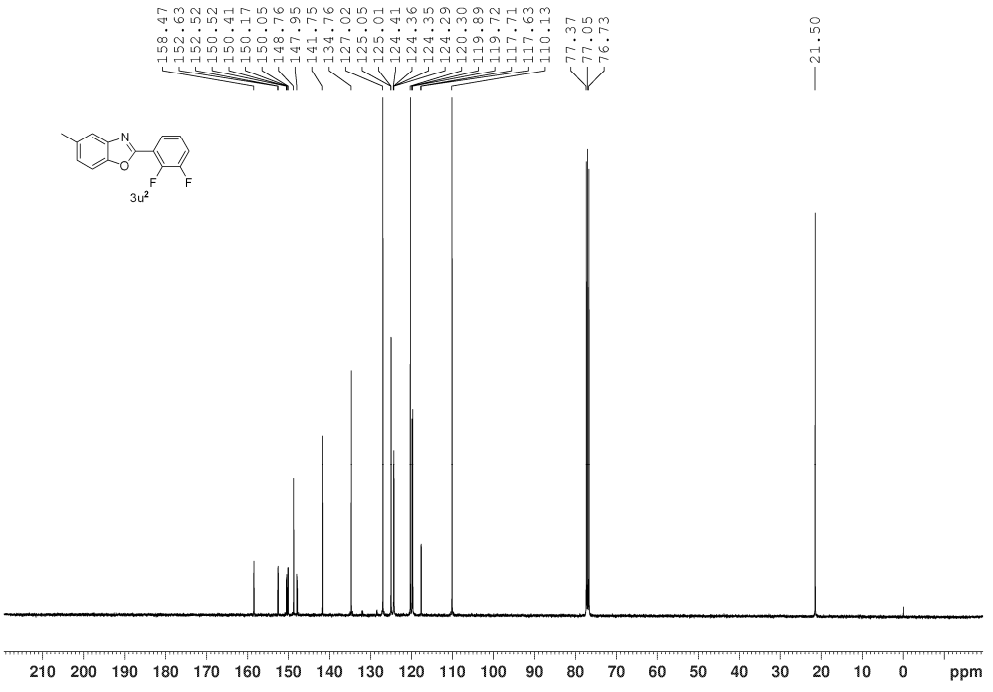

8.050
8.045
8.031
8.025
8.023
8.018
8.004
7.999
7.989
7.985
7.979
7.975
7.968
7.963
7.957
7.953
7.948
7.522
7.430
7.410
7.313
7.292
7.288
7.271
7.268
7.259
7.247
7.172
7.169
7.151
7.148
2.473
3u1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.03
0.94
1.03
0.91
3.00

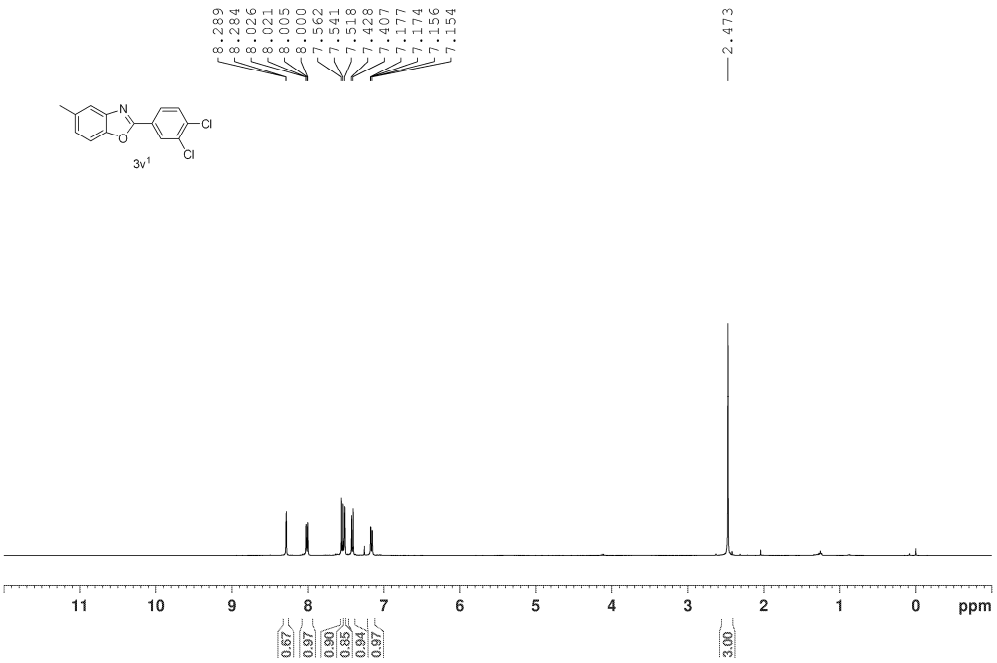

-132.44
-132.50
-136.07
-136.12
3u1
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.15


161.04
153.76
153.64
151.87
151.74
151.23
151.11
149.39
149.26
149.04
142.07
134.73
126.64
124.45
124.41
124.38
124.34
124.14
124.10
124.07
124.03
120.03
118.09
117.91
116.85
116.65
109.99
77.35
77.03
76.71
21.49
3u1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.971
7.968
7.955
7.952
7.941
7.937
7.592
7.472
7.451
7.340
7.319
7.300
7.280
7.263
7.229
7.214
7.198
7.177
2.477
3u2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.93
0.86
0.92
0.94
1.95
3.00


-135.98
-136.04
-136.47
-136.53
3u²
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
0.90


158.47
152.63
152.52
150.52
150.41
150.17
150.05
148.76
147.95
141.75
134.76
127.02
125.05
125.01
124.41
124.36
124.35
124.29
120.30
119.89
119.72
117.71
117.63
110.13
77.37
77.05
76.73
21.50
3u²
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.284
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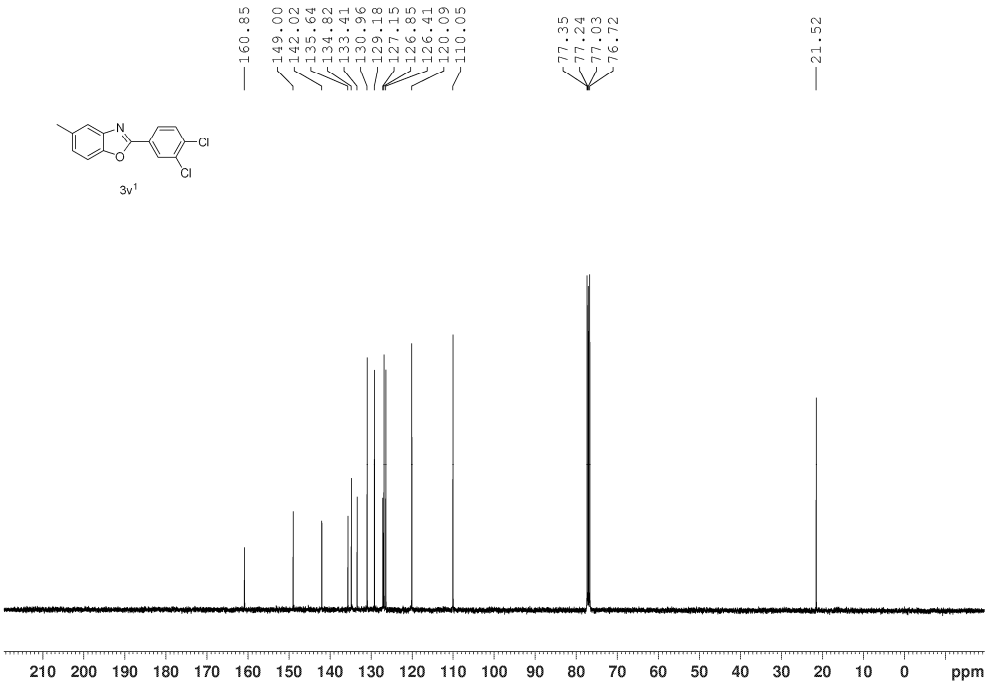
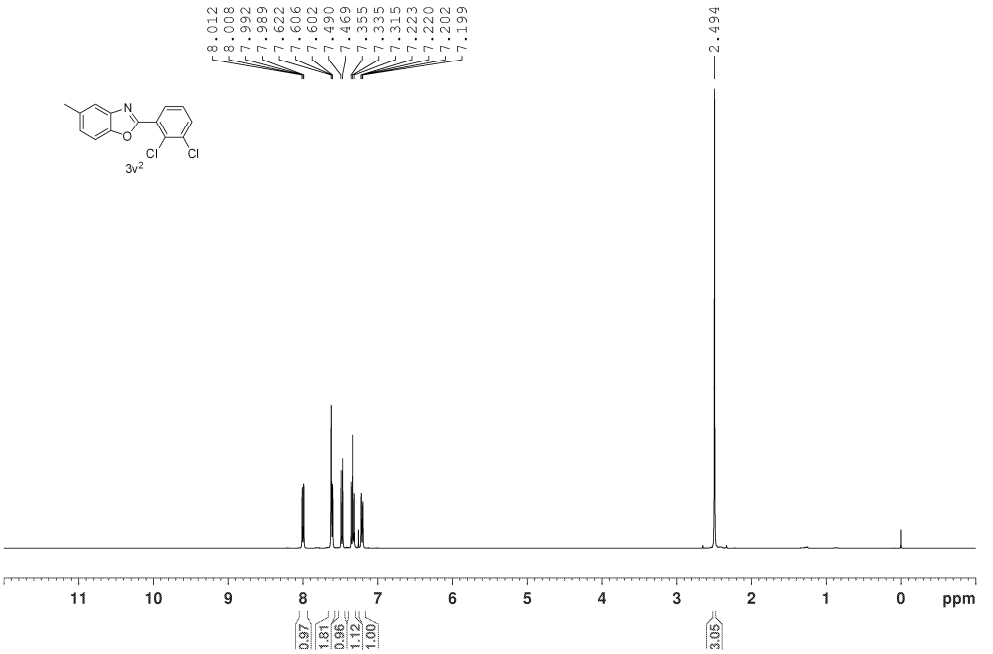
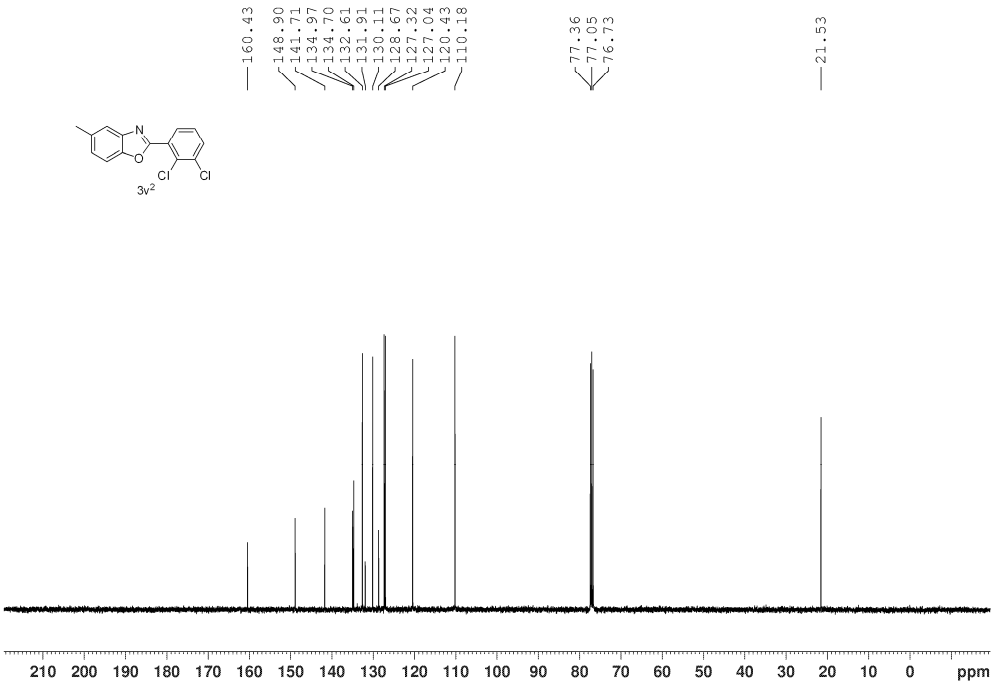
8.021
8.005
8.000
7.562
7.541
7.518
7.428
7.407
7.177
7.174
7.156
7.154
2.473
Cl
Cl
N
O
3v1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.67
0.97
0.90
0.85
0.94
0.97
3.00


160.85
149.00
142.02
135.64
134.82
133.41
130.96
129.18
127.15
126.85
126.41
120.09
110.05
77.35
77.24
77.03
76.72
21.52
Cl
Cl
N
O
3v1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.012
8.008
7.992
7.989
7.622
7.606
7.602
7.490
7.469
7.355
7.335
7.315
7.223
7.220
7.202
7.199
2.494
Cl
Cl
3v2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.81
0.96
1.12
1.00
3.05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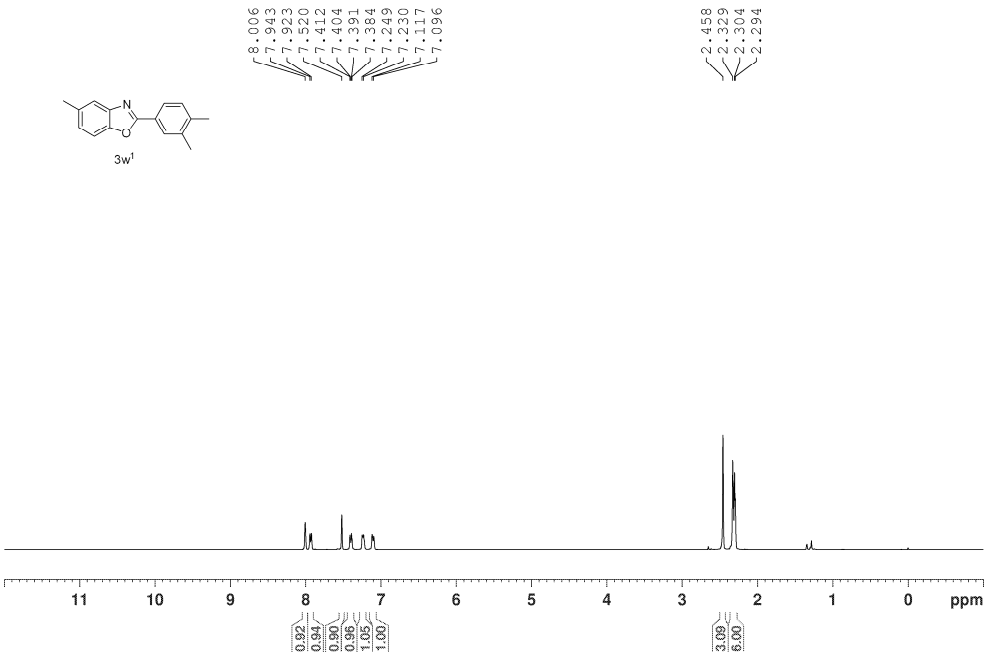
134.97
134.70
132.61
131.91
130.11
128.67
127.32
127.04
120.43
110.18
77.36
77.05
76.73
21.53
Cl
Cl
3v2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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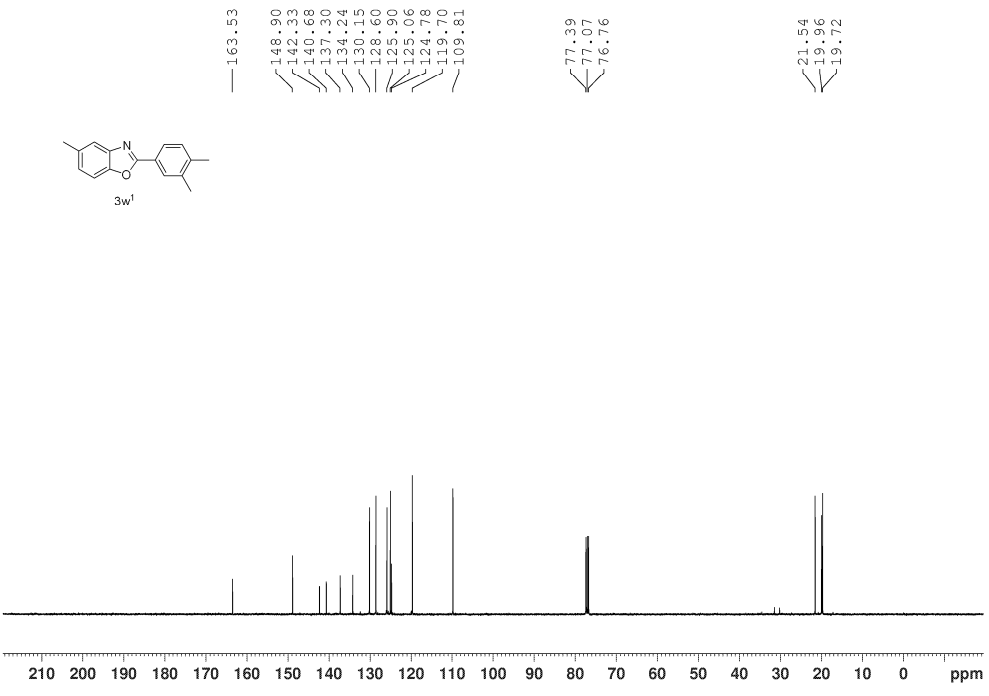
7.943
7.923
7.520
7.412
7.404
7.391
7.384
7.249
7.230
7.117
7.096
2.458
2.329
2.304
2.294
3w1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
0.94
0.90
0.96
1.05
1.00
3.09
6.00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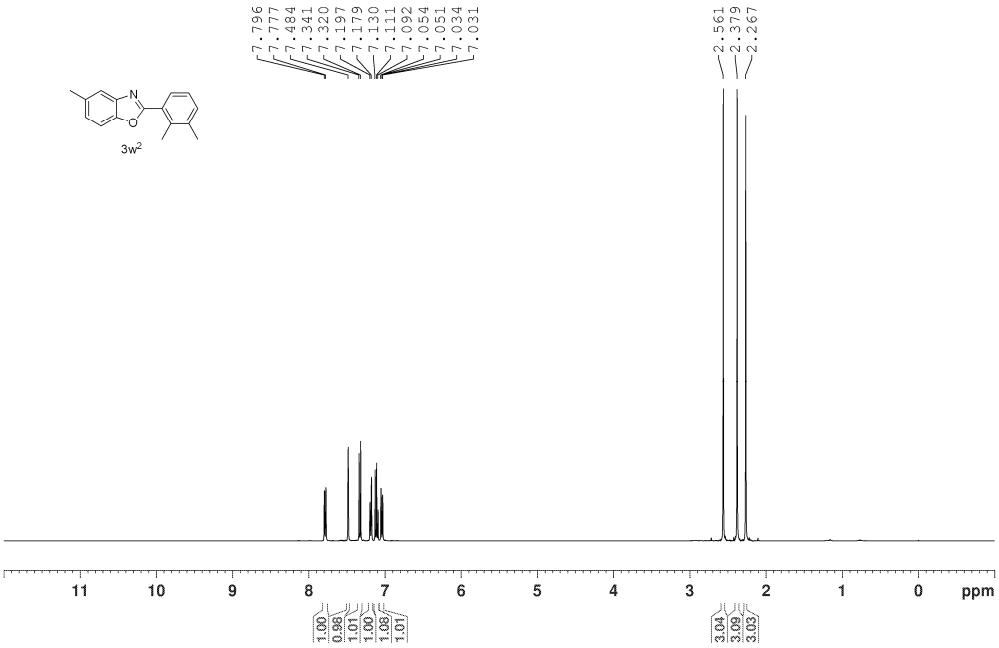
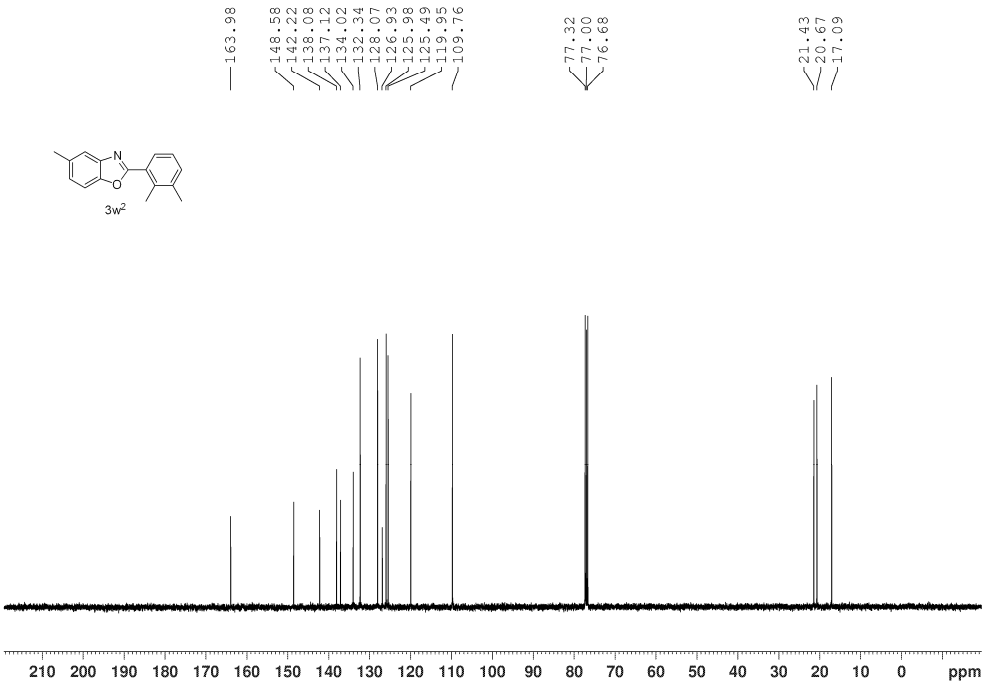
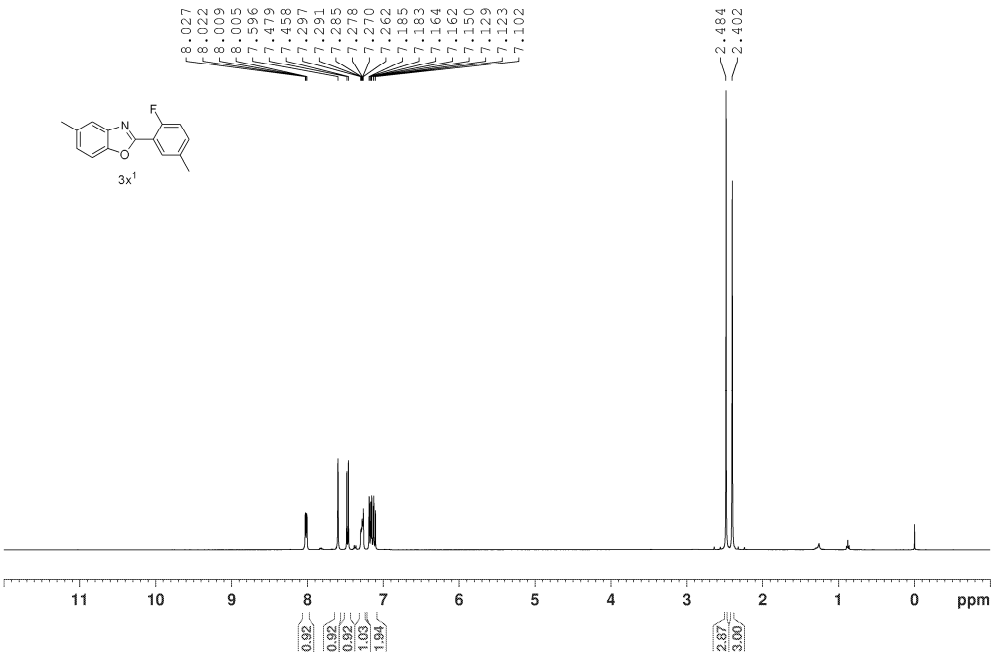
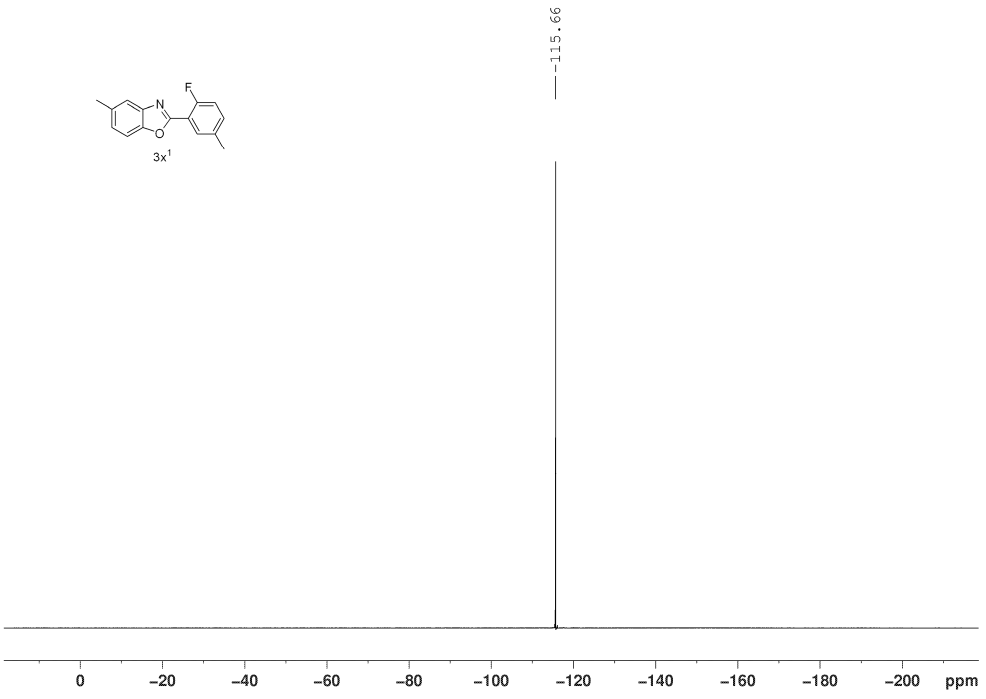
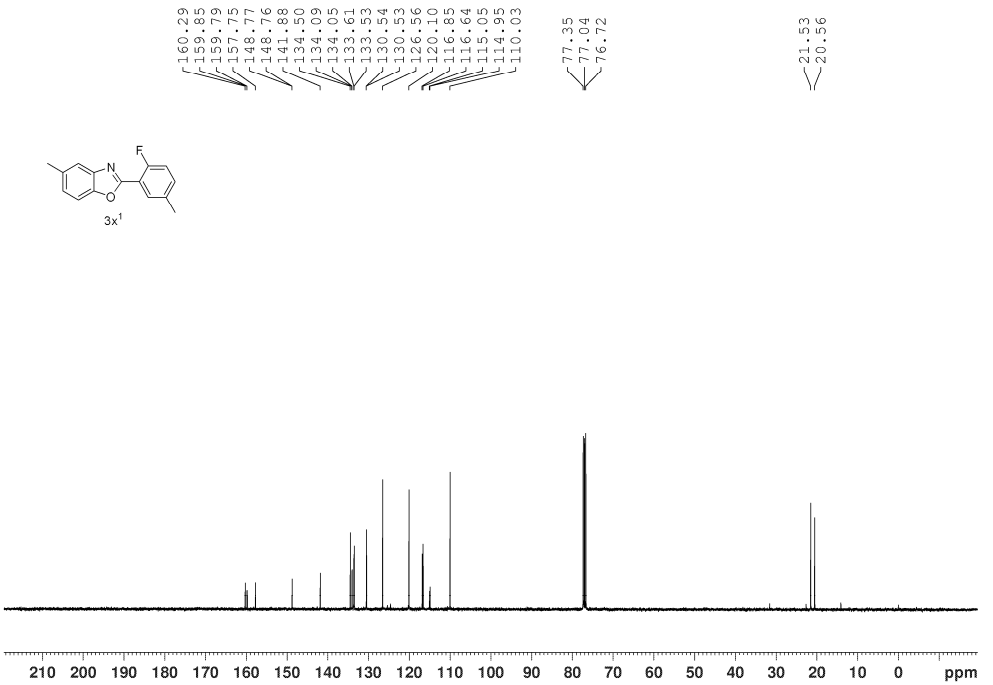
148.90
142.33
140.68
137.30
134.24
130.15
128.60
125.90
125.06
124.78
119.70
109.81
77.39
77.07
76.76
21.54
19.96
19.72
3w1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.796
7.777
7.484
7.341
7.320
7.197
7.179
7.130
7.111
7.092
7.054
7.051
7.034
7.031
2.561
2.379
2.267
3w2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 0.98 1.01 1.00 1.08 1.01
3.04 3.09 3.03


163.98
148.58
142.22
138.08
137.12
134.02
132.34
128.07
126.93
125.98
125.49
119.95
109.76
77.32
77.00
76.68
21.43
20.67
17.09
3w2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.027
8.022
8.009
8.005
7.596
7.479
7.458
7.297
7.291
7.285
7.278
7.270
7.262
7.185
7.183
7.164
7.162
7.150
7.129
7.123
7.102
2.484
2.402
F
N
O
3x1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
0.92
0.92
1.03
1.94
2.87
3.00


-115.66
F
N
O
3x1
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


160.29
159.85
159.79
157.75
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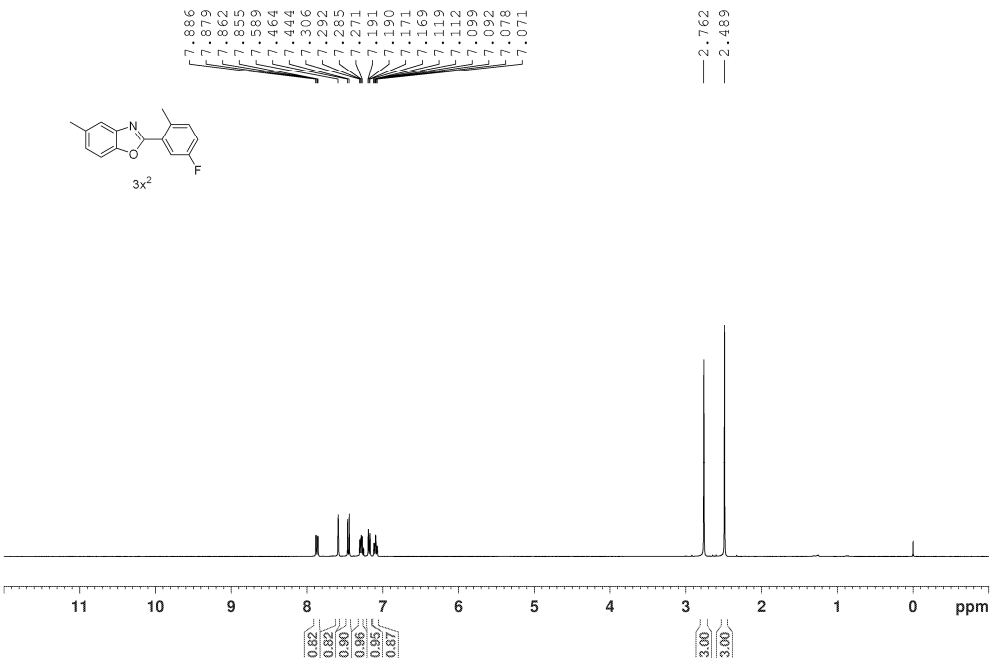
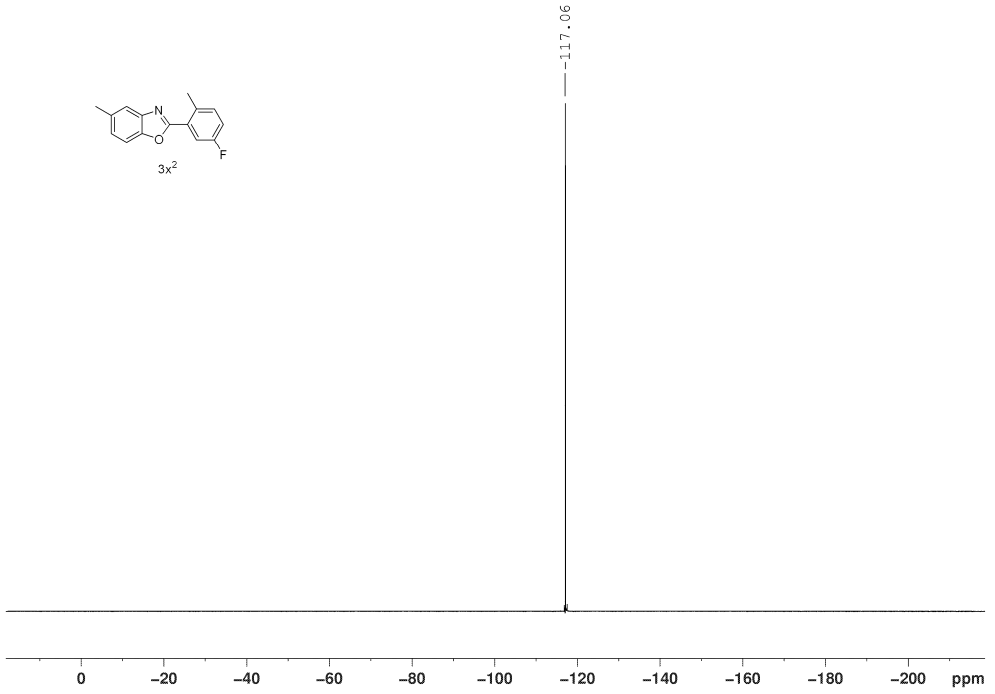
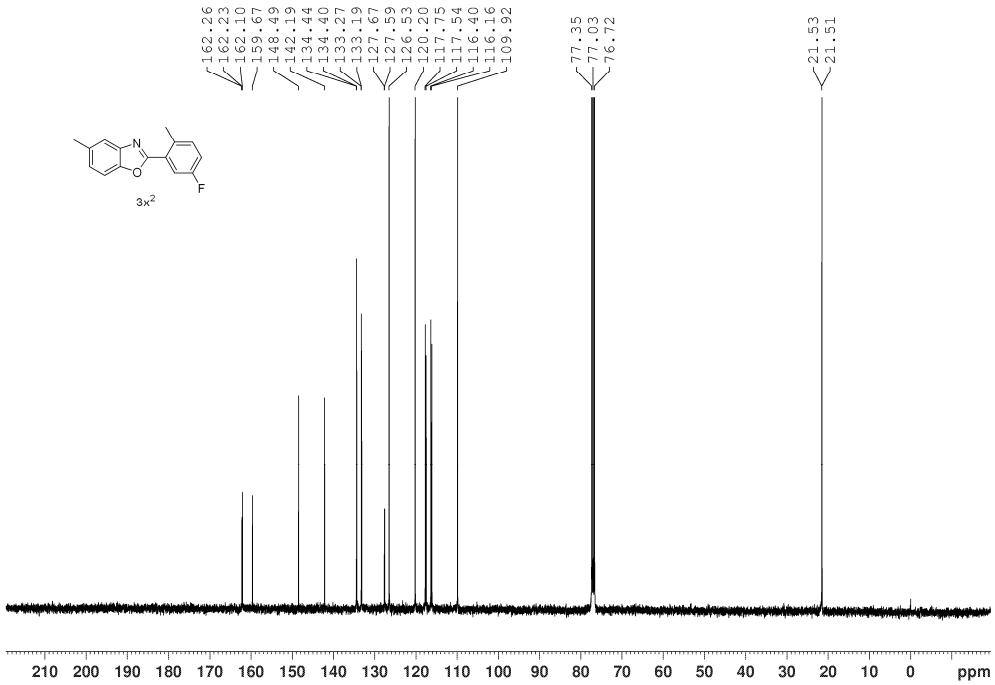
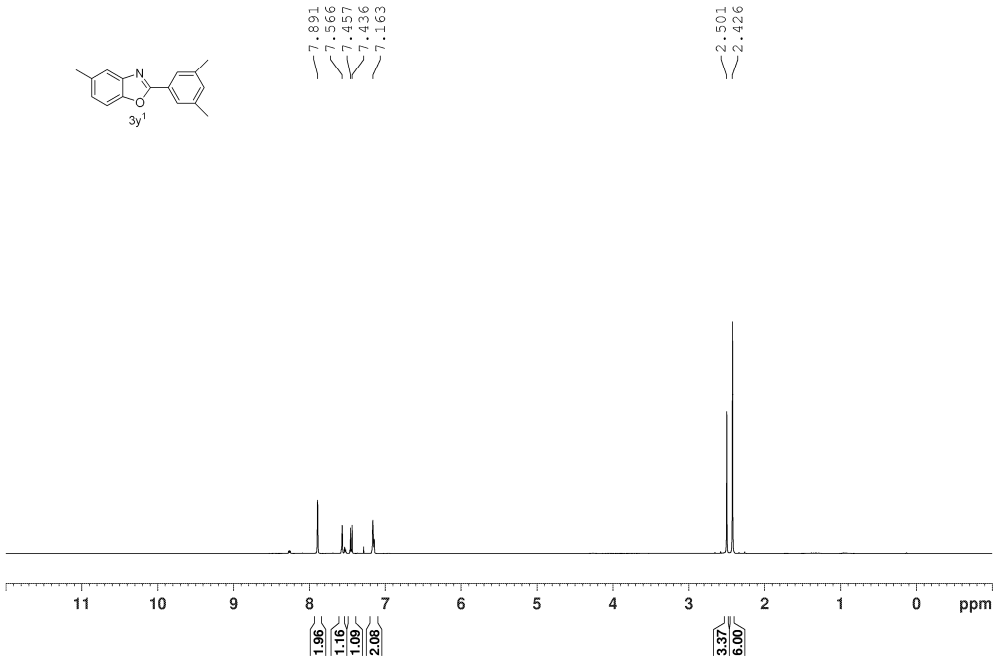
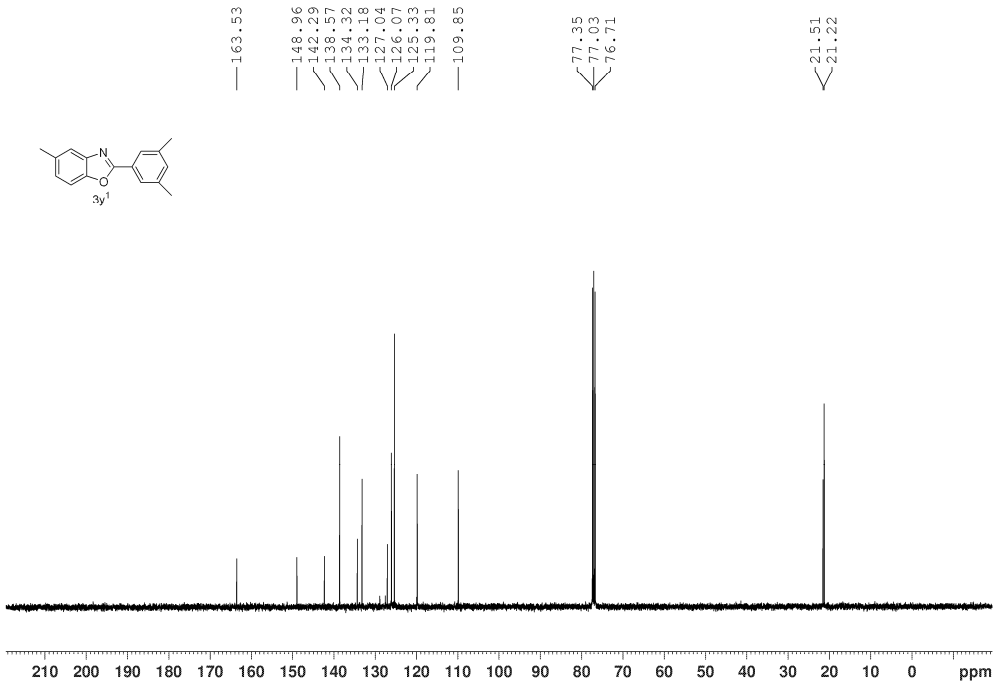
148.76
141.88
134.50
134.09
134.05
133.61
133.53
130.54
130.53
126.56
120.10
116.85
116.64
115.05
114.95
110.03
77.35
77.04
76.72
21.53
20.56
F
N
O
3x1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

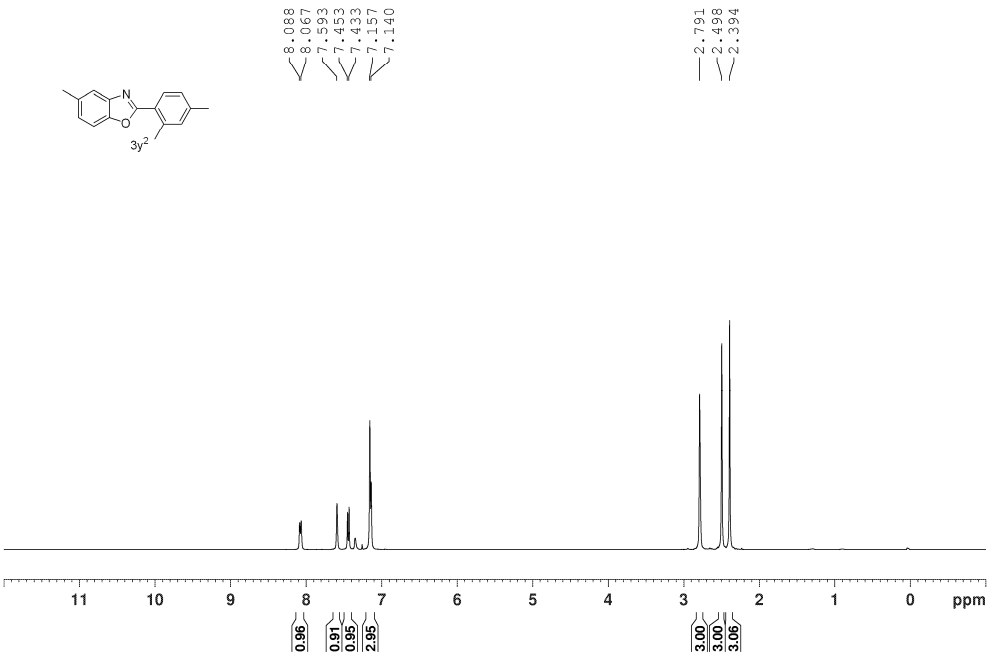

7.886
7.879
7.862
7.855
7.589
7.464
7.444
7.306
7.292
7.285
7.271
7.191
7.190
7.171
7.169
7.119
7.112
7.099
7.092
7.078
7.071
2.762
2.489
N
O
F
3x2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.82
0.82
0.90
0.96
0.95
0.87
3.00
3.00

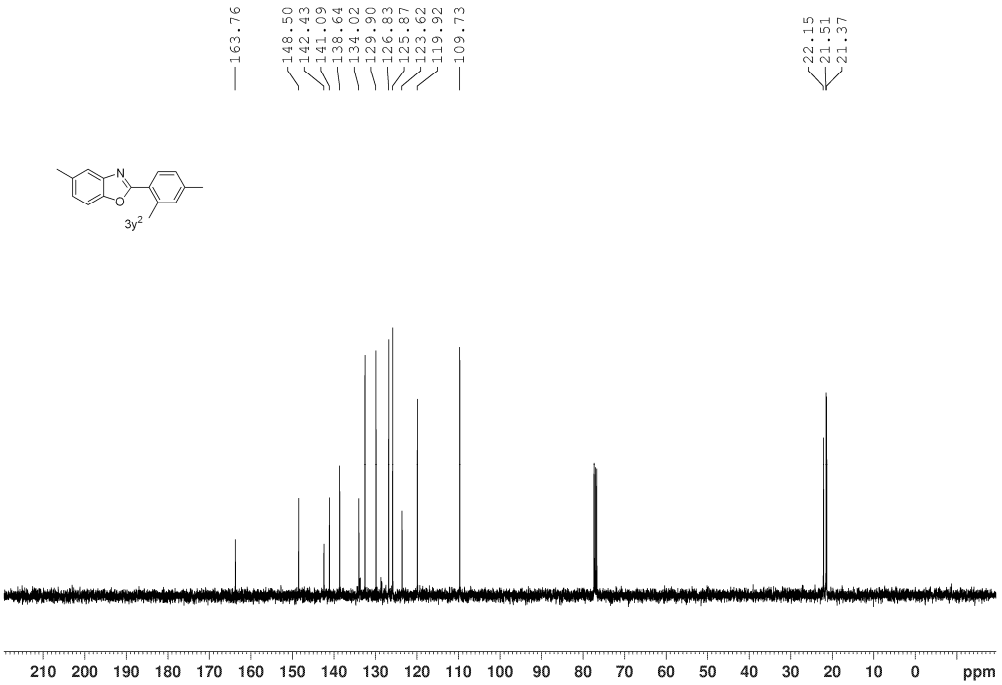

-117.06
3x2
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

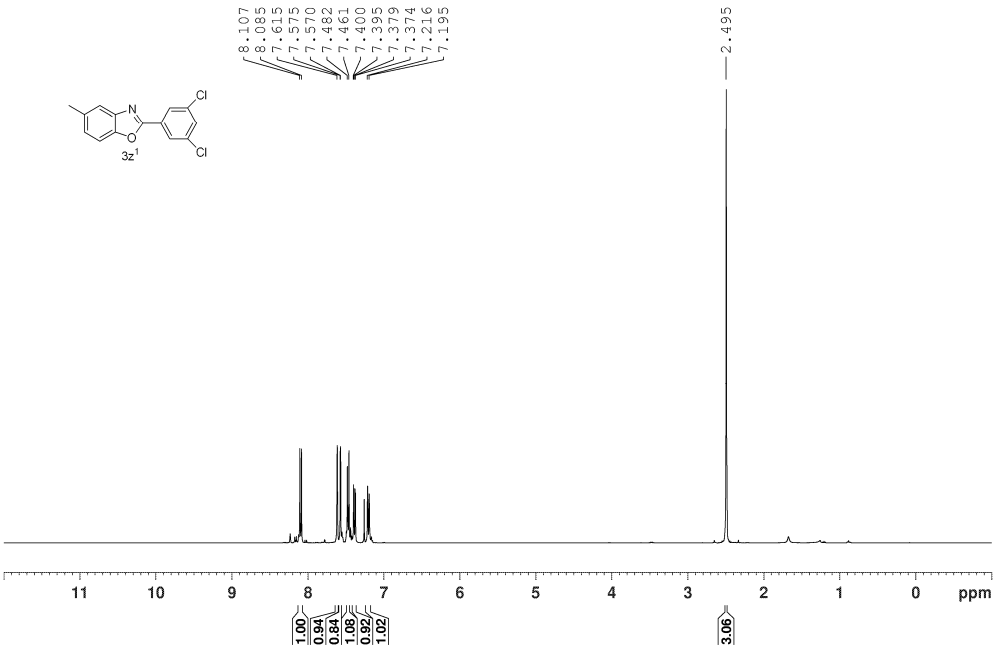

162.26
162.23
162.10
159.67
148.49
142.19
134.44
134.40
133.27
133.19
127.67
127.59
126.53
120.20
117.75
117.54
116.40
116.16
109.92
77.35
77.03
76.72
21.53
21.51
3x2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

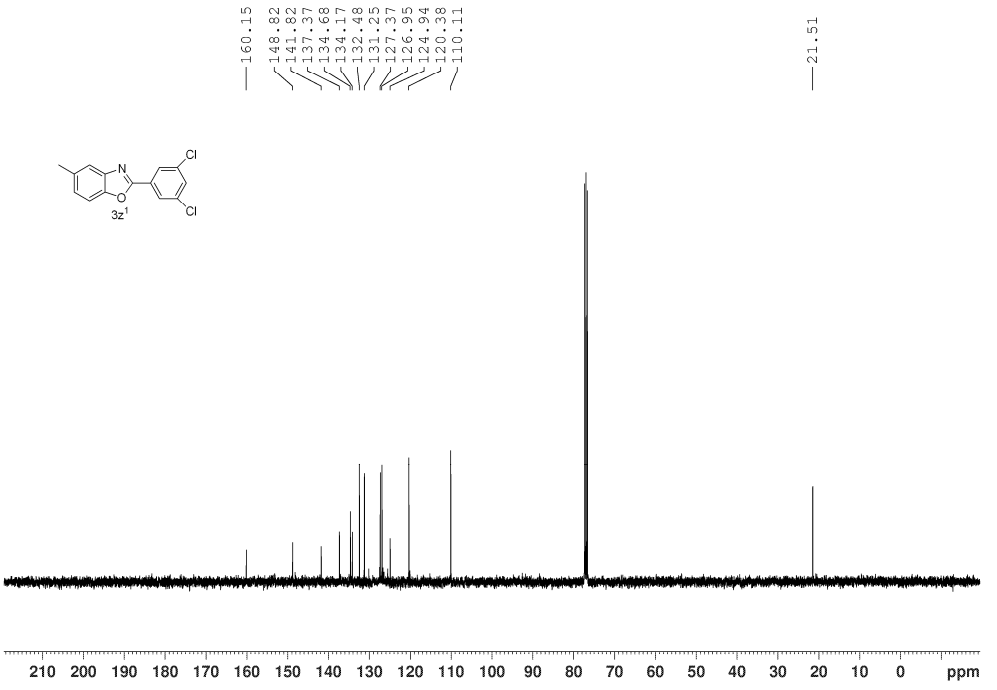

7.891
7.566
7.457
7.436
7.163
2.501
2.426
3y1
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.96
1.16
1.09
2.08
3.37
6.00

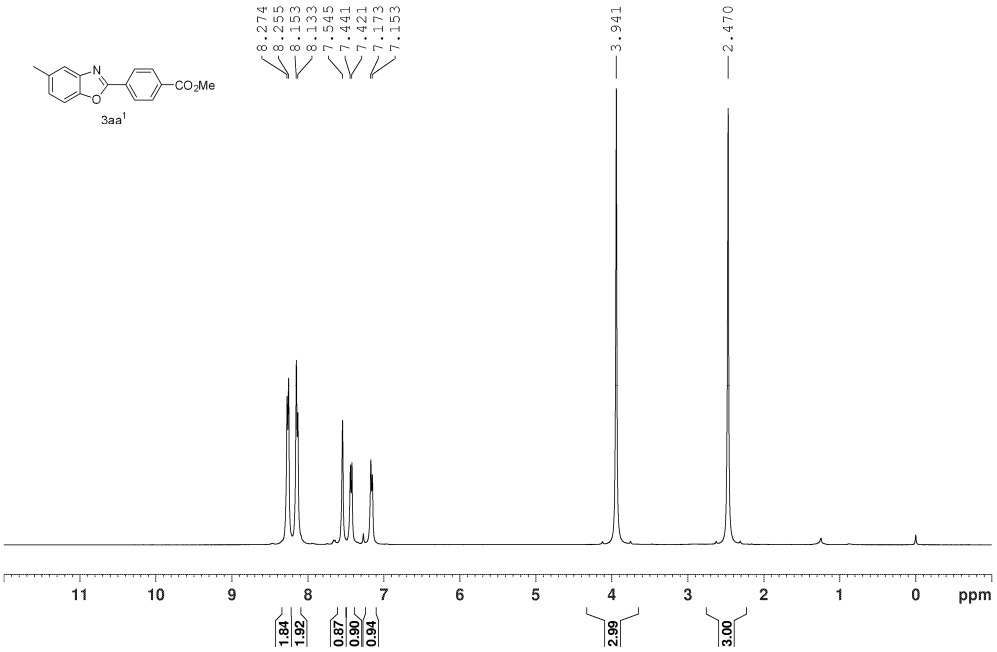

163.53
148.96
142.29
138.57
134.32
133.18
127.04
126.07
125.33
119.81
109.85
77.35
77.03
76.71
21.51
21.22
3y1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

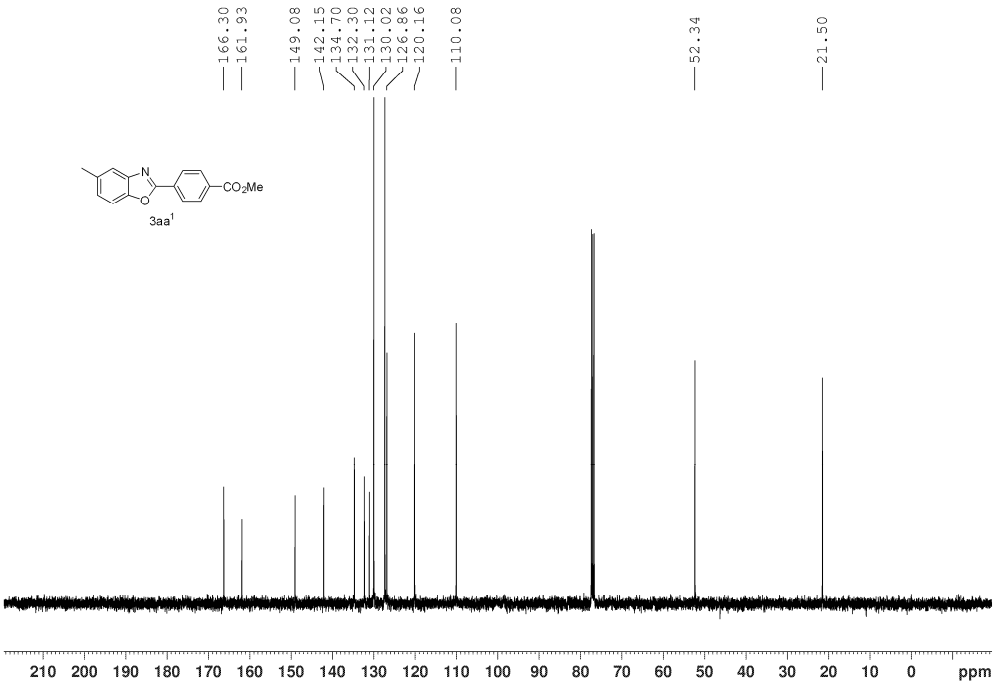

8.088
8.067
7.593
7.453
7.433
7.157
7.140
2.791
2.498
2.394
3y2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.96
0.91
0.95
2.95
3.00
3.00
3.06

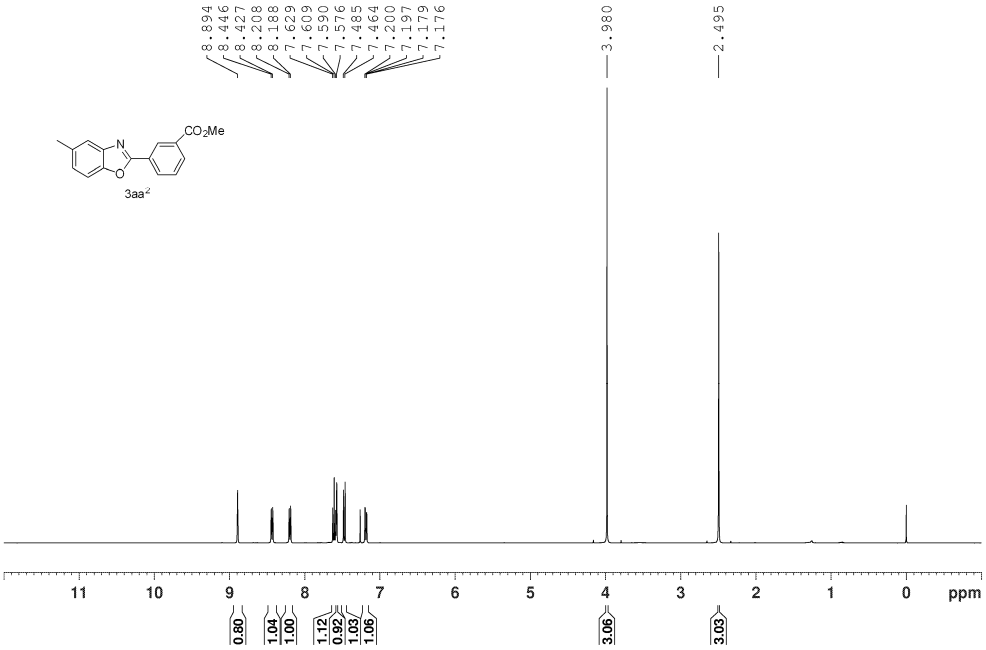

163.76
148.50
142.43
141.09
138.64
134.02
129.90
126.83
125.87
123.62
119.92
109.73
22.15
21.51
21.37
3y2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

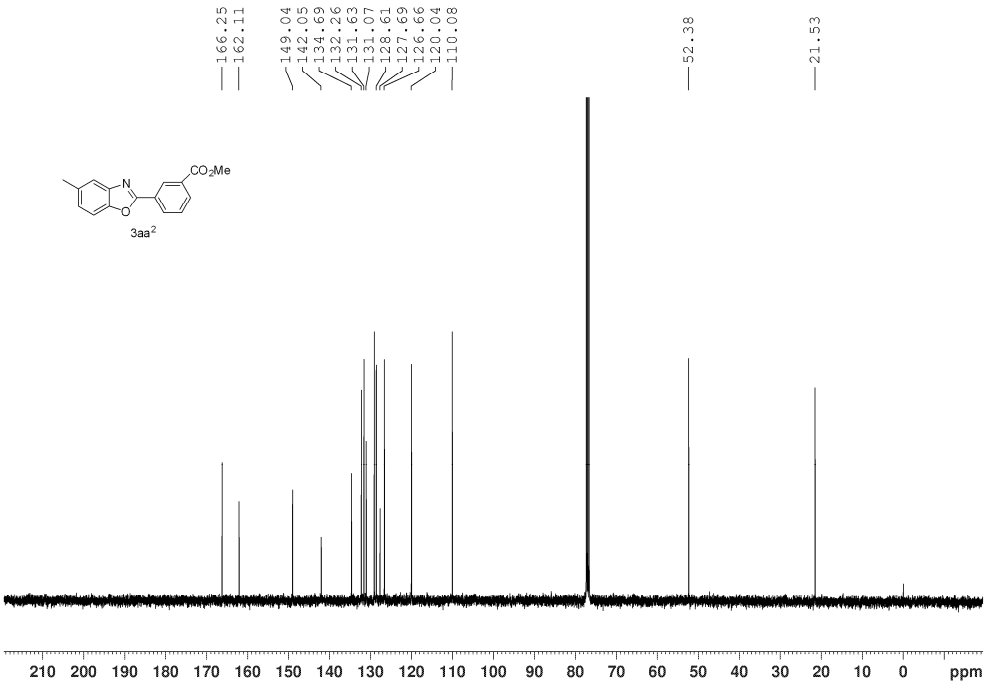

8.107
8.085
7.615
7.575
7.570
7.482
7.461
7.400
7.395
7.379
7.374
7.216
7.195
2.495
Cl
N
O
Cl
3z1
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.94
0.84
1.08
0.92
1.02
3.06

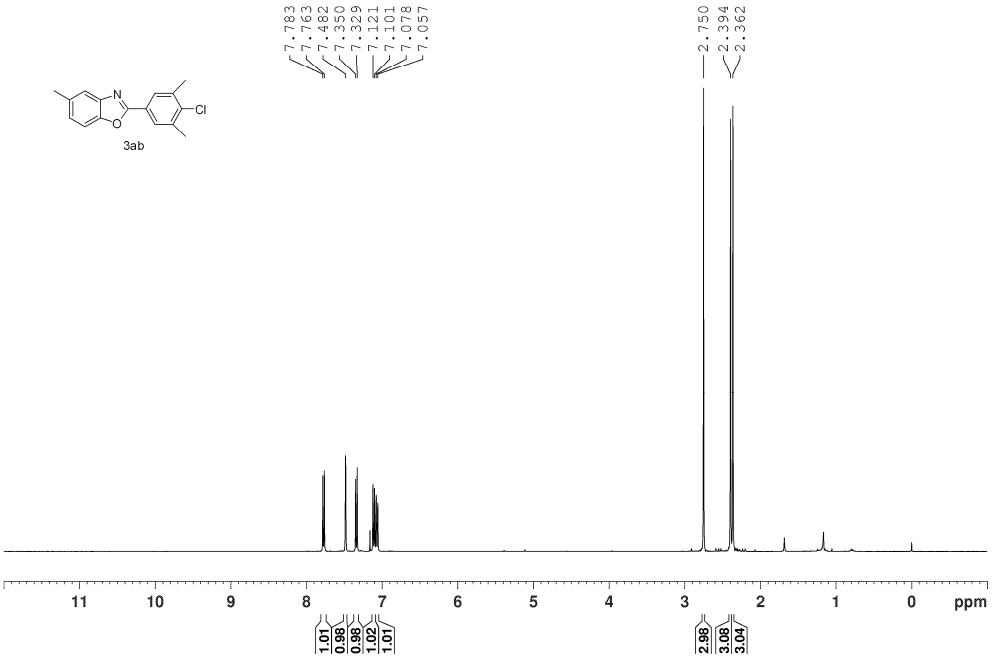

160.15
148.82
141.82
137.37
134.68
134.17
132.48
131.25
127.37
126.95
124.94
120.38
110.11
21.51
Cl
N
O
Cl
3z1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

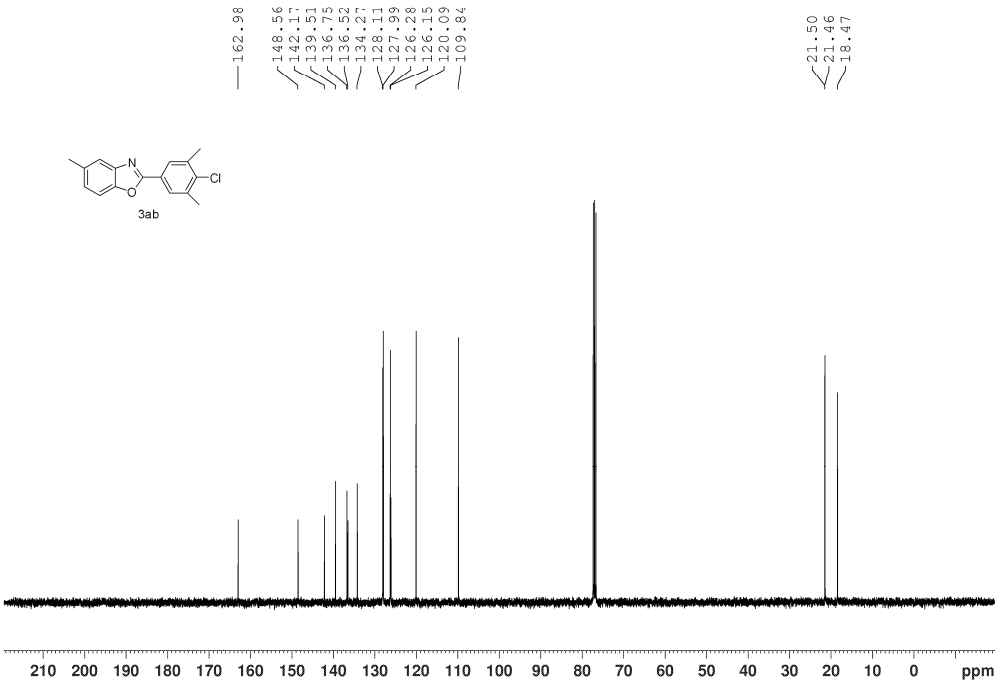

8.274
8.255
8.153
8.133
7.545
7.441
7.421
7.173
7.153
3.941
2.470
CO2Me
3aa1
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.84
1.92
0.87
0.90
0.94
2.99
3.00

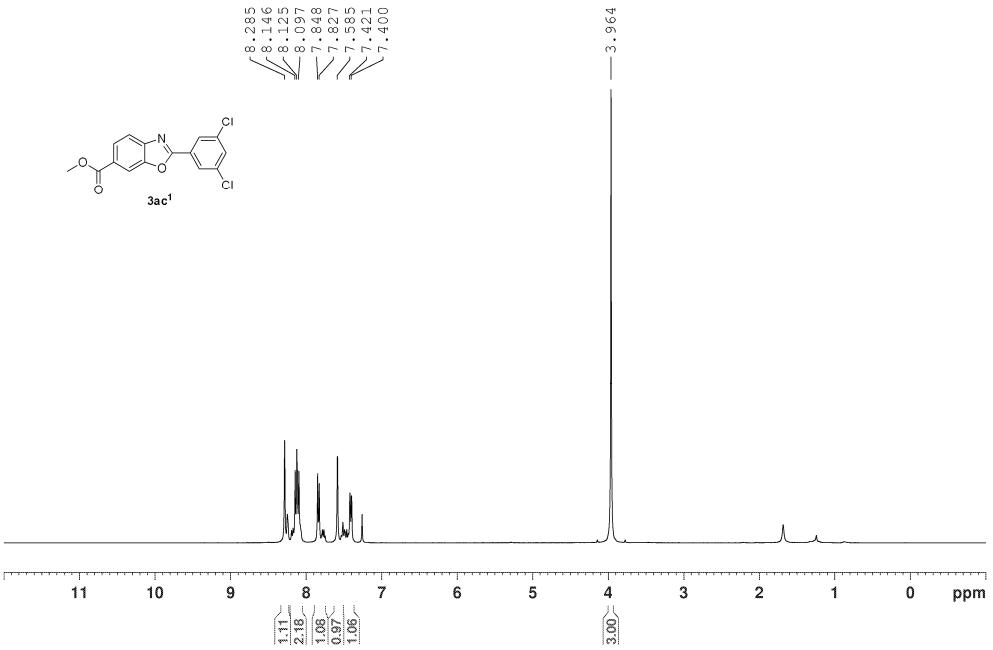

166.30
161.93
149.08
142.15
134.70
132.30
131.12
130.02
126.86
120.16
110.08
52.34
21.50
CO2Me
3aa1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

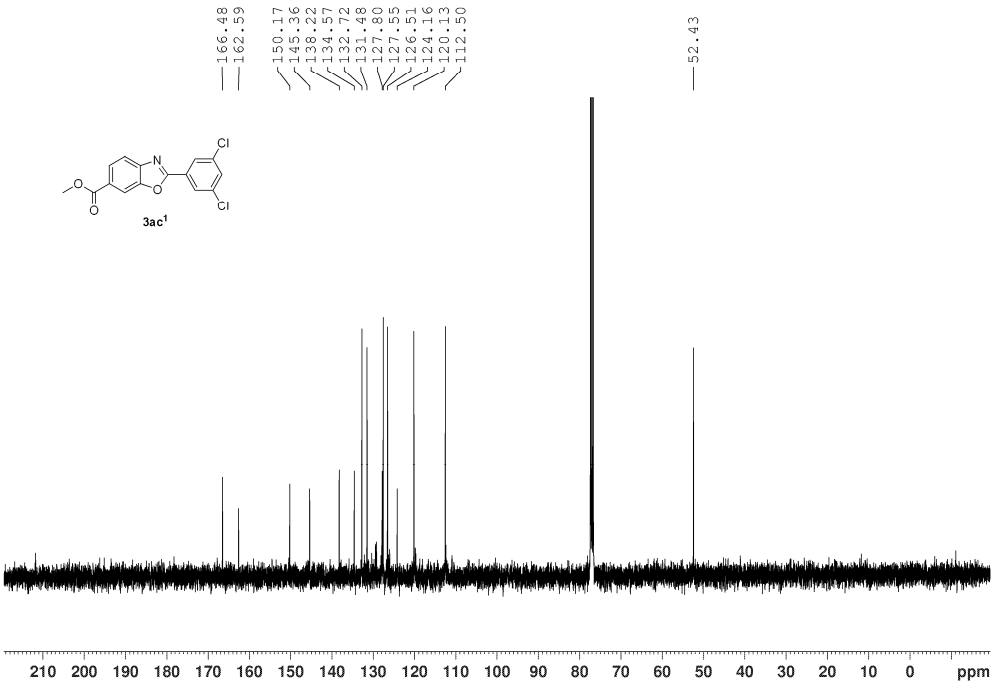

8.894
8.446
8.427
8.208
8.188
7.629
7.609
7.590
7.576
7.485
7.464
7.200
7.197
7.179
7.176
3.980
2.495
CO2Me
3aa2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.80 1.04 1.00 1.12 0.92 1.03 1.06 3.06 3.03


166.25
162.11
149.04
142.05
134.69
132.26
131.63
131.07
128.61
127.69
126.66
120.04
110.08
52.38
21.53
CO2Me
3aa2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.783
7.763
7.482
7.350
7.329
7.121
7.101
7.078
7.057
2.750
2.394
2.362
N
O
Cl
3ab
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.98
0.98
1.02
1.01
2.98
3.08
3.04


162.98
148.56
142.17
139.51
136.75
136.52
134.27
128.11
127.99
126.28
126.15
120.09
109.84
21.50
21.46
18.47
N
O
Cl
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.285
8.146
8.125
8.097
7.848
7.827
7.585
7.421
7.400
3.964
Cl
Cl
O
O
N
O
3ac1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.11
2.18
1.08
0.97
1.06
3.00


166.48
162.59
150.17
145.36
138.22
134.57
132.72
131.48
127.80
127.55
126.51
124.16
120.13
112.50
52.43
Cl
Cl
O
O
N
O
3ac1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm