Supporting Information for

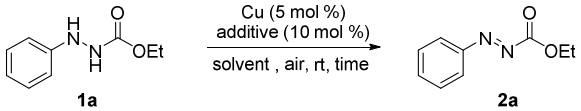
Aerobic Oxidation of Alkyl 2-Phenylhydrazinecarboxylates Catalyzed by CuCl and DMAP

Min Hye Kim and Jinho Kim*

Department of Chemistry, and Research Institute of Natural Sciences, Incheon National University, 119 Academy-ro, Yeonsu-gu, Incheon 22012, Republic of Korea.
jinho@inu.ac.kr

Table of Contents

1. Optimization for Cu-catalyzed aerobic oxidation of ethyl 2-phenylhydrazinecarboxylate.[a]



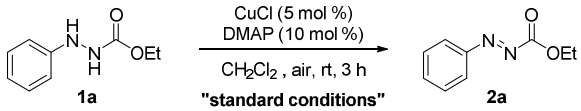
1a **2a**

entry	Cu	additive	solvent	RBF size (mL)	time (h)	yield (%)[b]
1	CuI	DMAP	DCM	50	3	18
2	CuBr	DMAP	DCM	50	3	91
3	CuCl	DMAP	DCM	50	3	95
4	CuCN	DMAP	DCM	50	3	3
5	$[(CH_3CN)_4Cu]PF_6$	DMAP	DCM	50	3	95
6	$CuBr_2$	DMAP	DCM	50	3	80
7	$CuCl_2$	DMAP	DCM	50	3	69
8	$Cu(acac)_2$	DMAP	DCM	50	3	85
9	$Cu(CH_3COO)_2$	DMAP	DCM	50	3	94
10	$(CF_3SO_3)_2Cu$	DMAP	DCM	50	3	75
11	$Cu(NO_3)_2{\cdot}H_2O$	DMAP	DCM	50	3	95
12	$Cu(OH)_2$	DMAP	DCM	50	3	27
13	CuCl	DBU	DCM	50	3	84
14	CuCl	1, 10-phenanthroline	DCM	50	3	16
15	CuCl	pyridine	DCM	50	3	75
16	CuCl	4-methoxypyridine	DCM	50	3	89
17	CuCl	2-fluoropyridine	DCM	50	3	6

18	CuCl	2,2'-bipyridine	DCM	50	3	36
19	CuCl	DMAP	DCM	50	3	95
20	CuCl	DMAP	chloroform	50	3	98
21	CuCl	DMAP	DCE	50	3	98
22	CuCl	DMAP	DCM	50	3	95
23	CuCl	DMAP	DMAc	50	3	88
24	CuCl	DMAP	DMF	50	3	84
25	CuCl	DMAP	DMSO	50	3	92
26	CuCl	DMAP	THF	50	3	93
27	CuCl	DMAP	1,4-dioxane	50	3	90
28	CuCl	DMAP	acetonitrile	50	3	86
29	CuCl	DMAP	toluene	50	3	95
30	CuCl	DMAP	DCM	10	3	53
31	CuCl	DMAP	DCM	25	3	65
32	CuCl	DMAP	DCM	50	3	95
33	CuCl	DMAP	DCM	20 (vial)	3	62
34[c]	CuCl	DMAP	DCM	10	1	95
35[c]	CuCl	DMAP	DCM	25	1	93
36[c]	CuCl	DMAP	DCM	50	1	93
37	CuCl	DMAP	DCM	50	1	96
38	CuCl	DMAP	DCM	50	2	91
39	CuCl	DMAP	DCM	50	3	95
40	CuCl	DMAP	DCM	50	4	94

[a]Reaction conditions: **1a** (0.5 mmol), Cu (5 mol %), additive (10 mol %) and solvent (2.0 mL) in 50 mL round-bottom flask under air at room temperature for the indicated time. [b]Yield determined by ^{1}H NMR spectroscopy (internal standard: 1,1,2,2-tetrachloroethane). [c]Under oxygen.

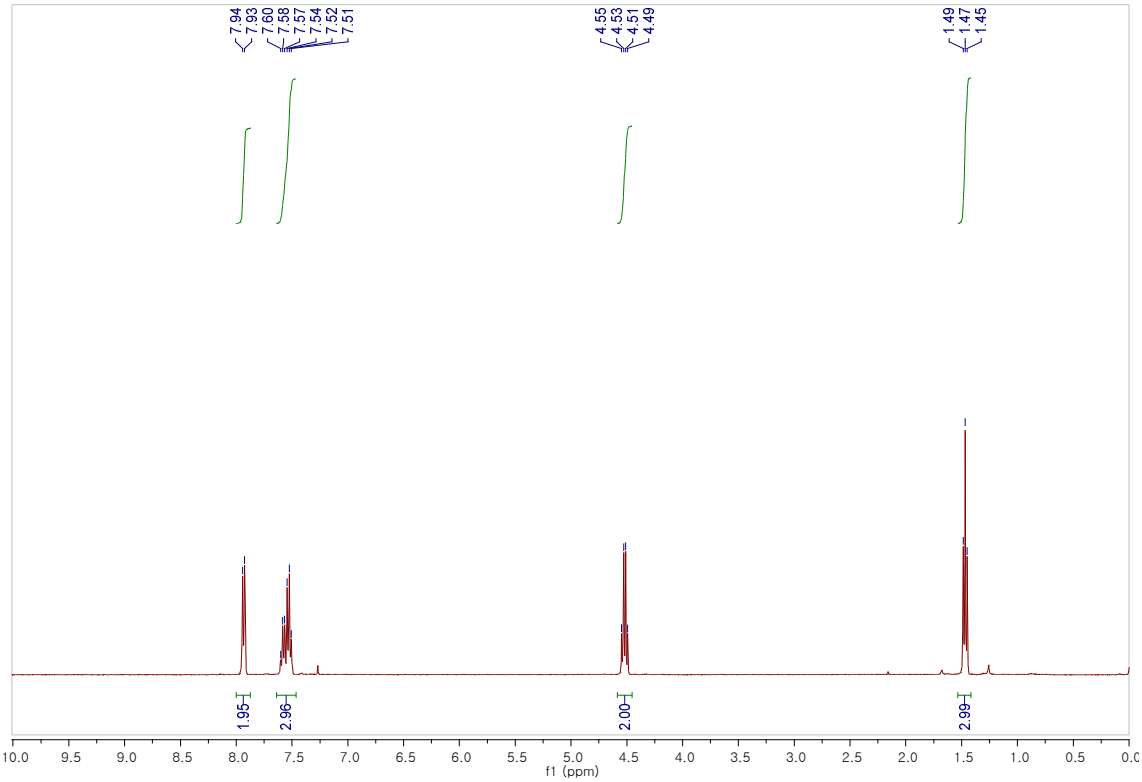
2. Control experiments

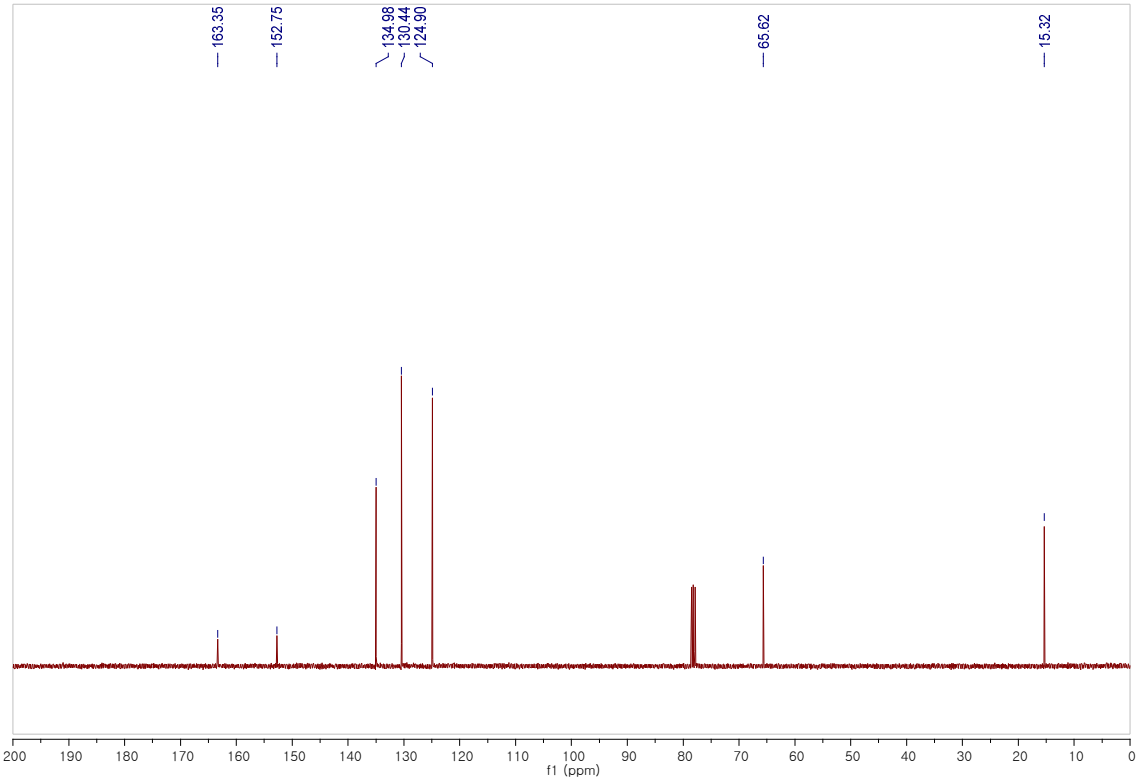


entry	change from "standard conditions"	yield (%)
1	no change	95
2	no Cu	0
3	no DMAP	0
4	N_2 instead of air	0

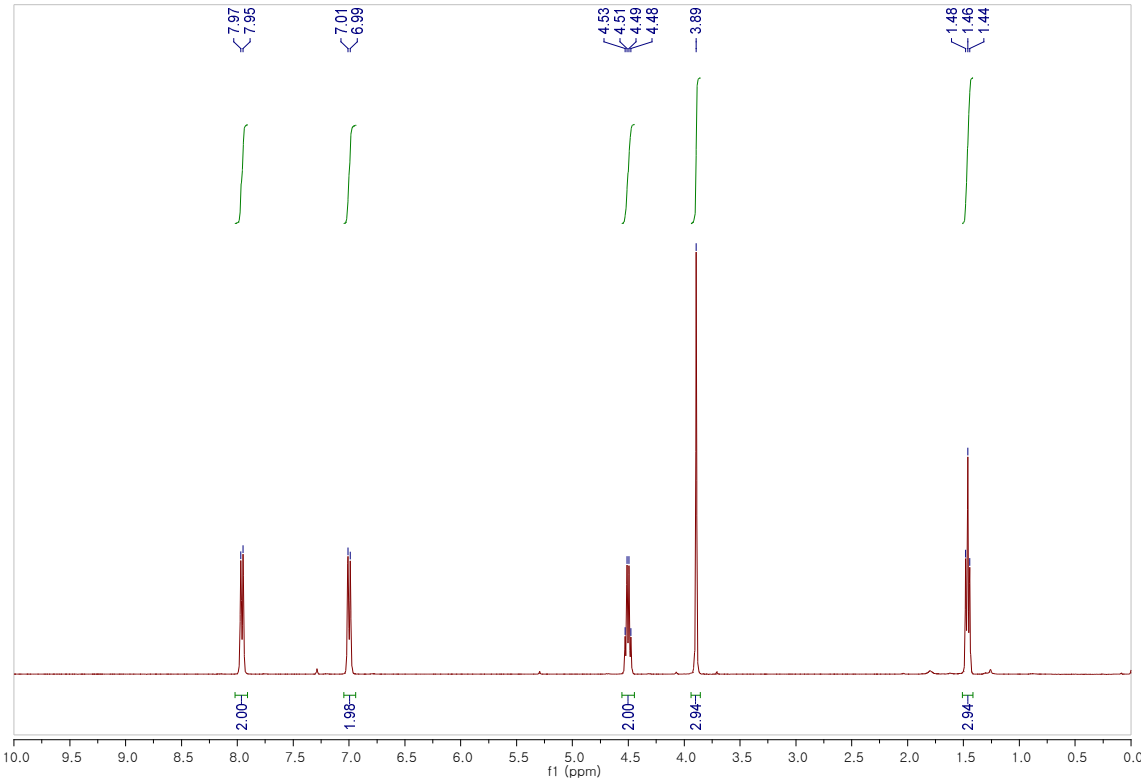
3. ^{1}H, ^{13}C, and ^{19}F NMR spectra of substrates

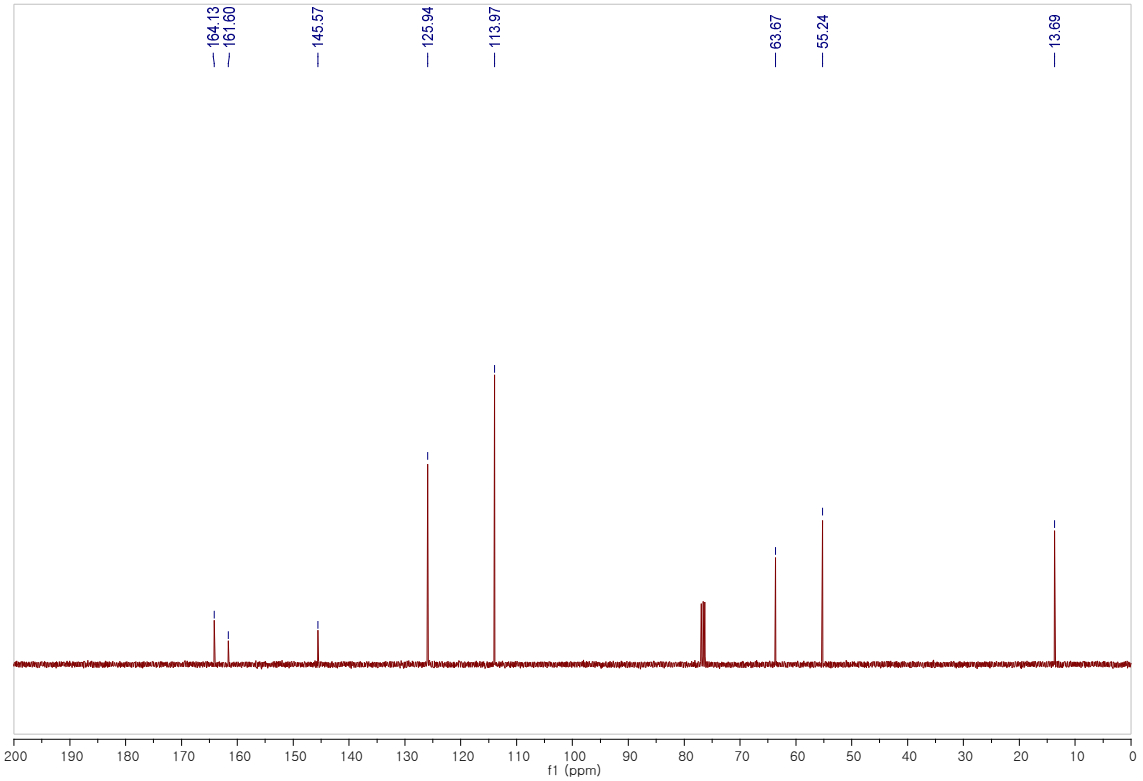
Ethyl 2-phenylazocarboxylate (2a)



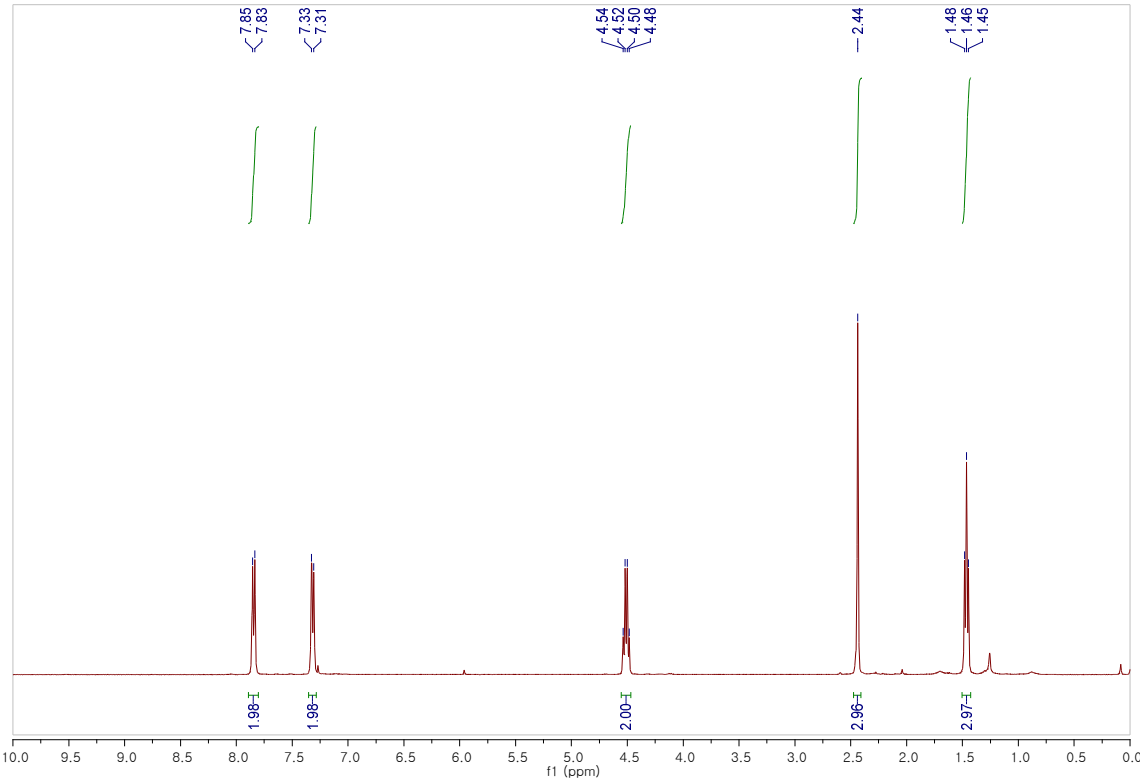


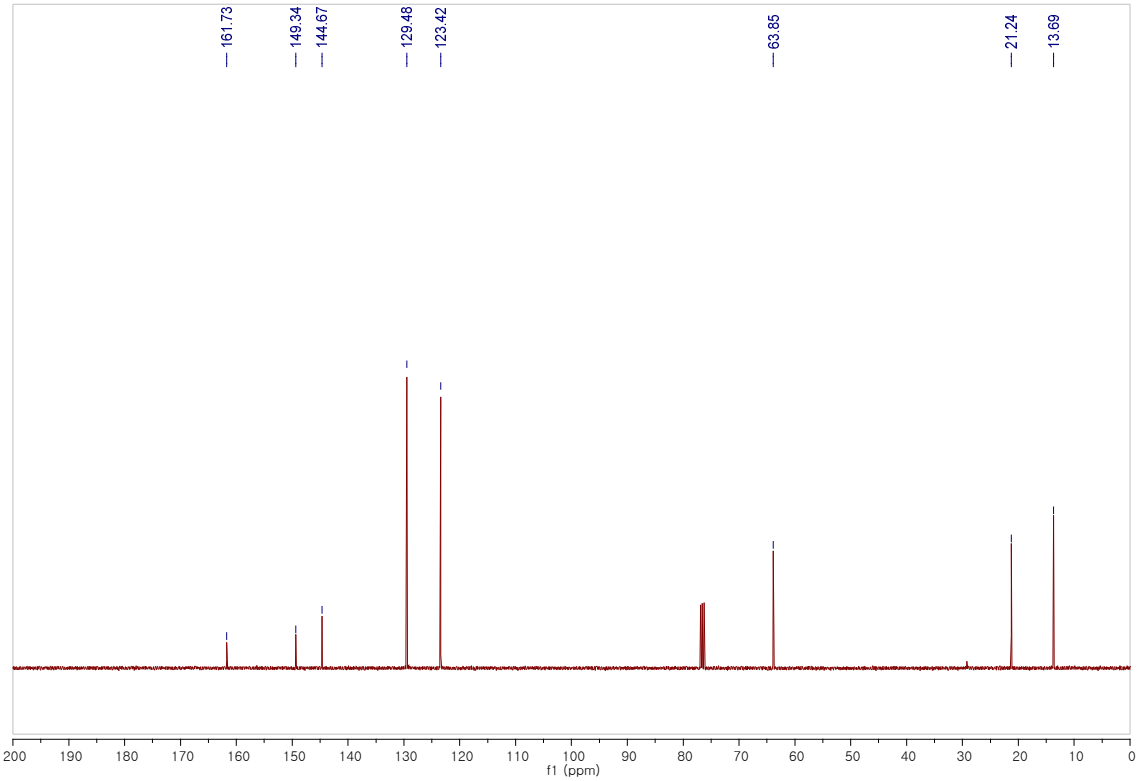
Ethyl 2-(4-methoxyphenyl)azocarboxylate (2b)



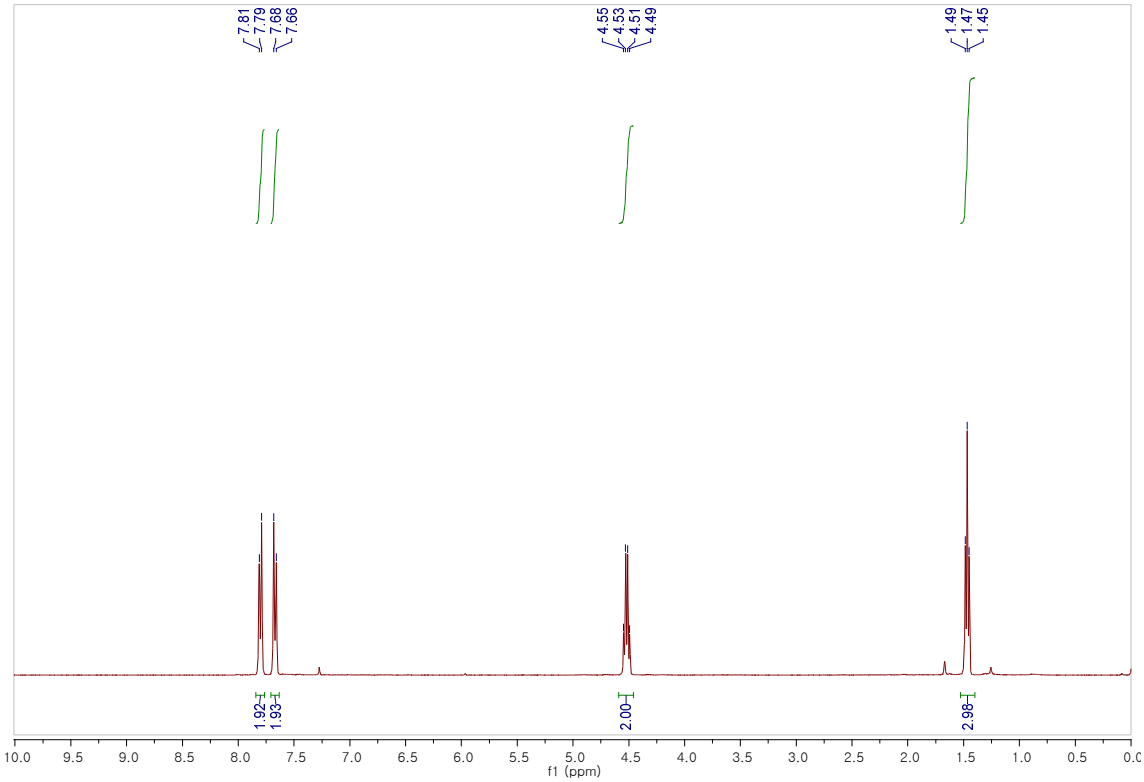


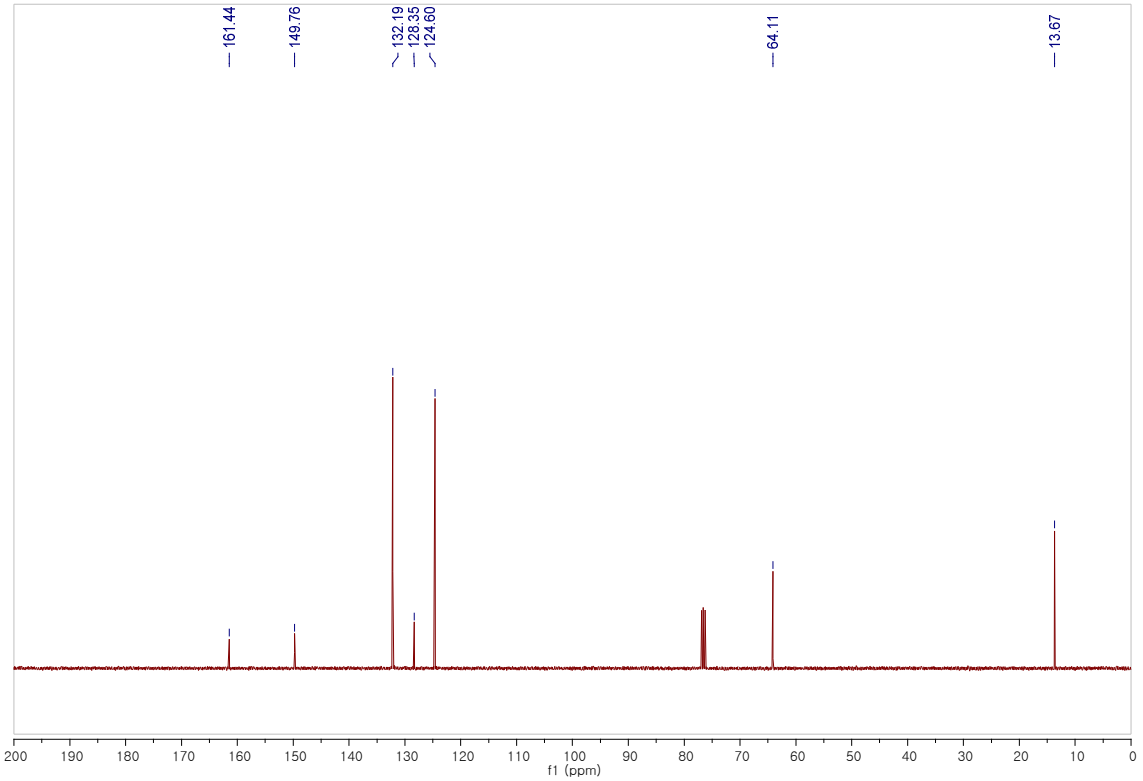
Ethyl 2-(4-methylphenyl)azocarboxylate (2c)



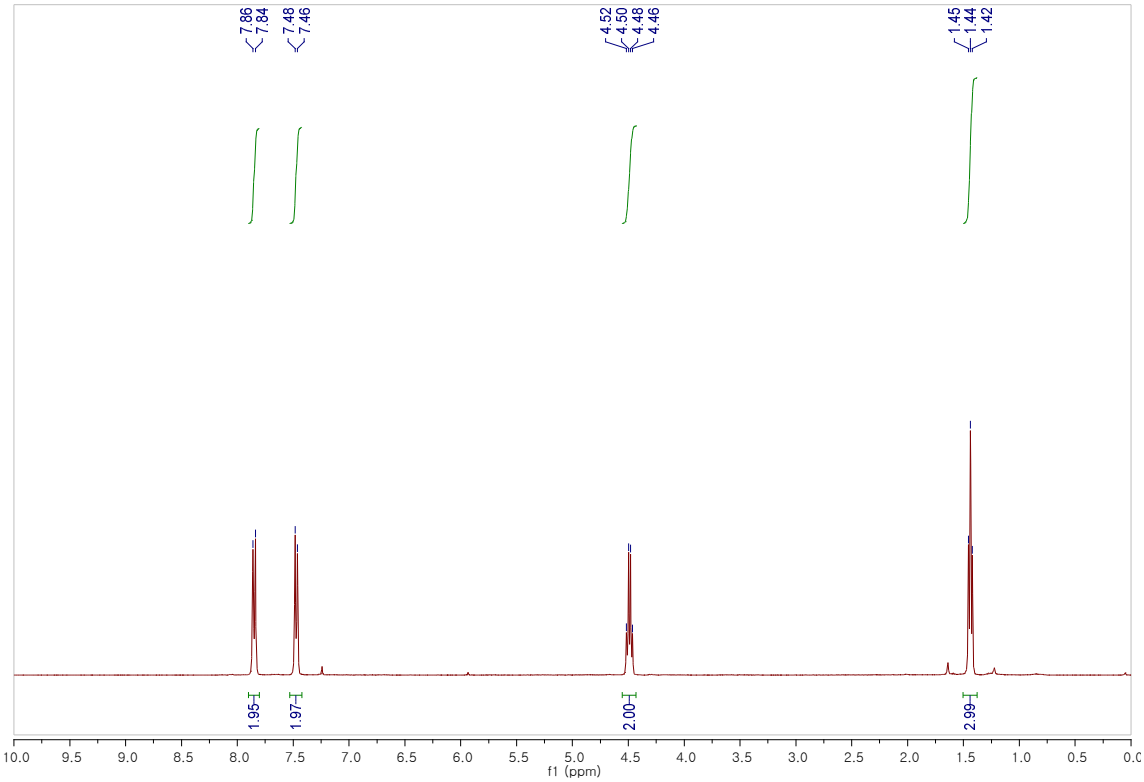


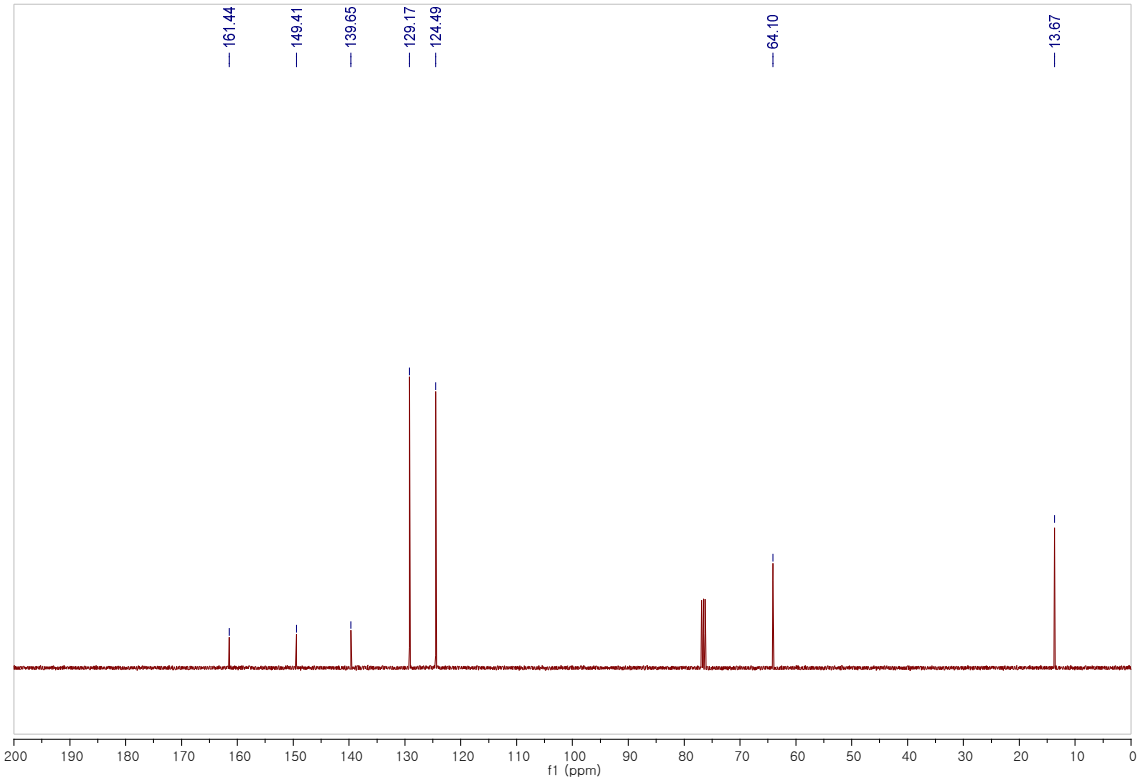
Ethyl 2-(4-bromophenyl)azocarboxylate (2d)



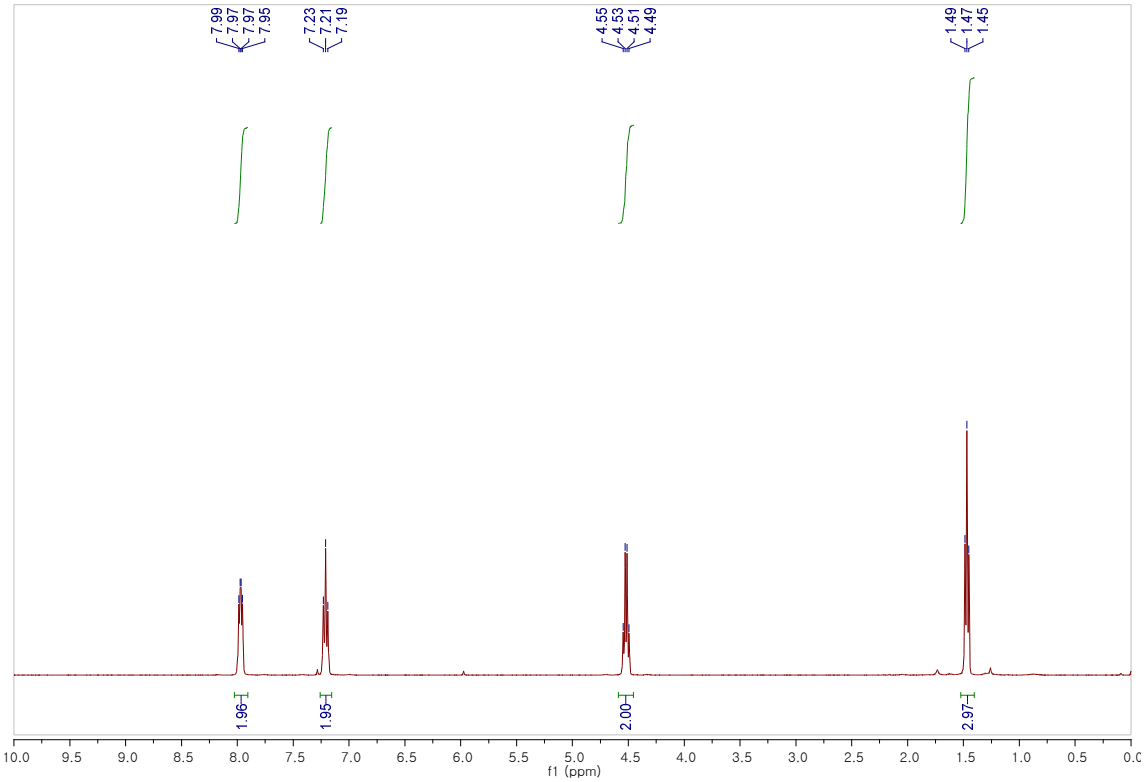


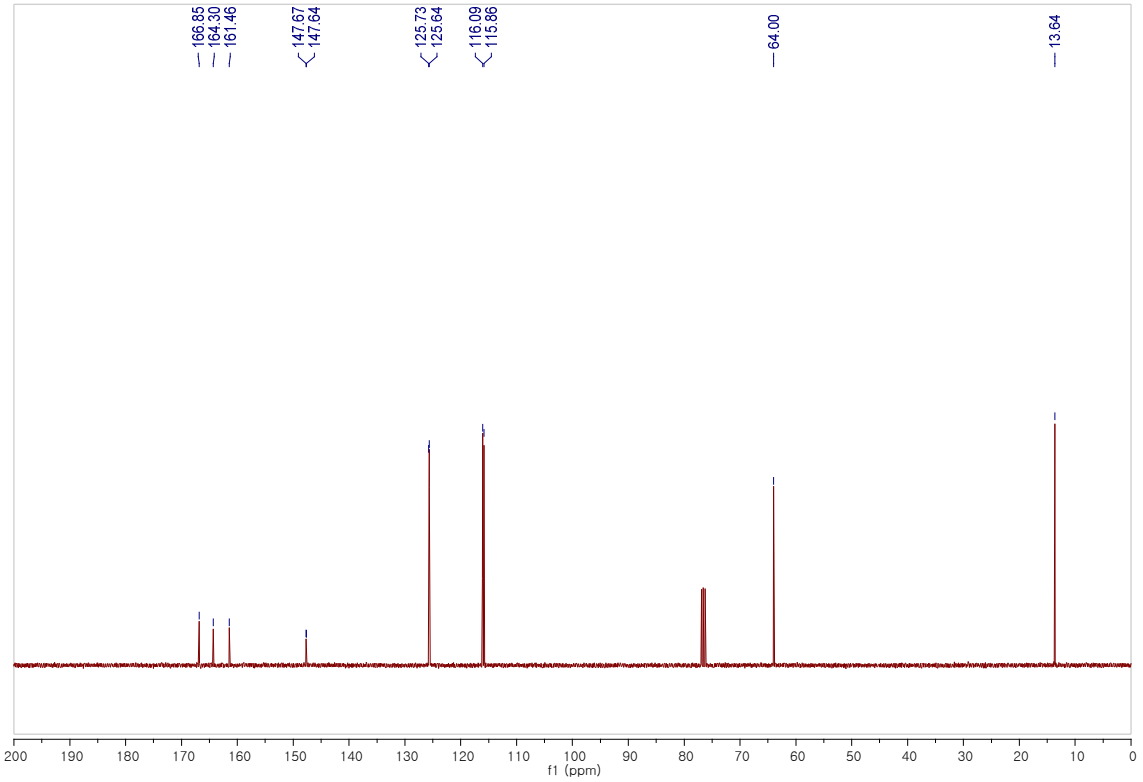
Ethyl 2-(4-chlorophenyl)azocarboxylate (2e)

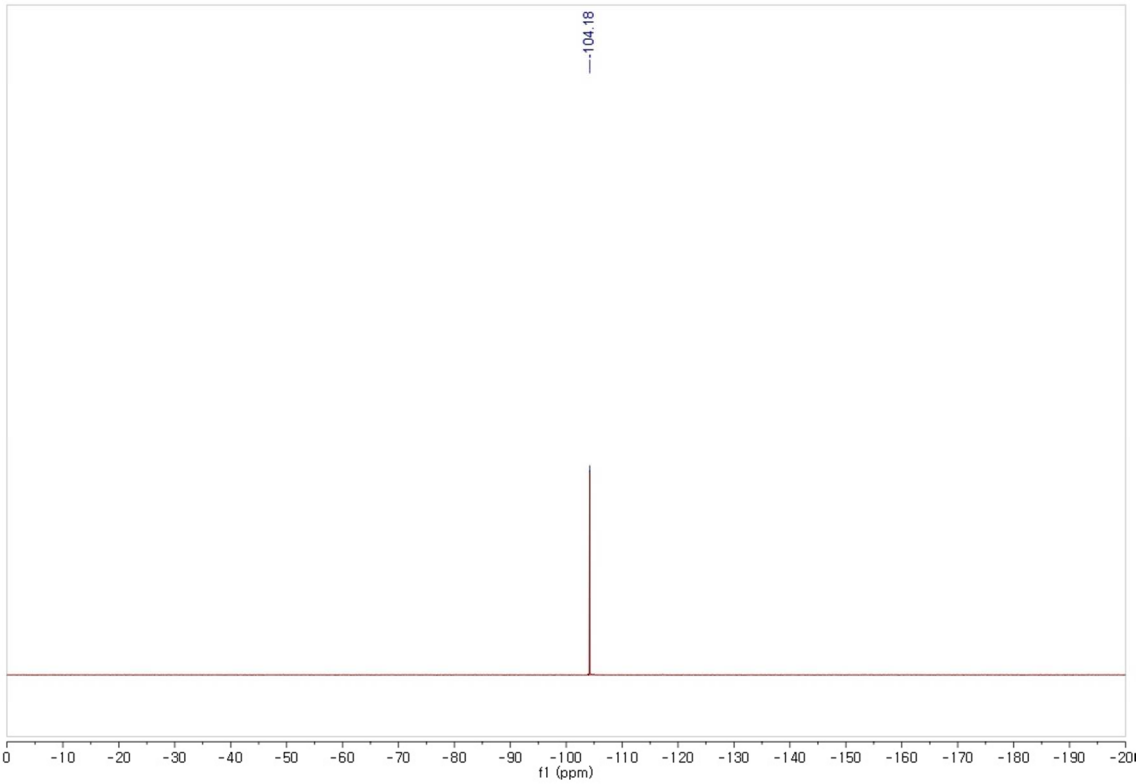




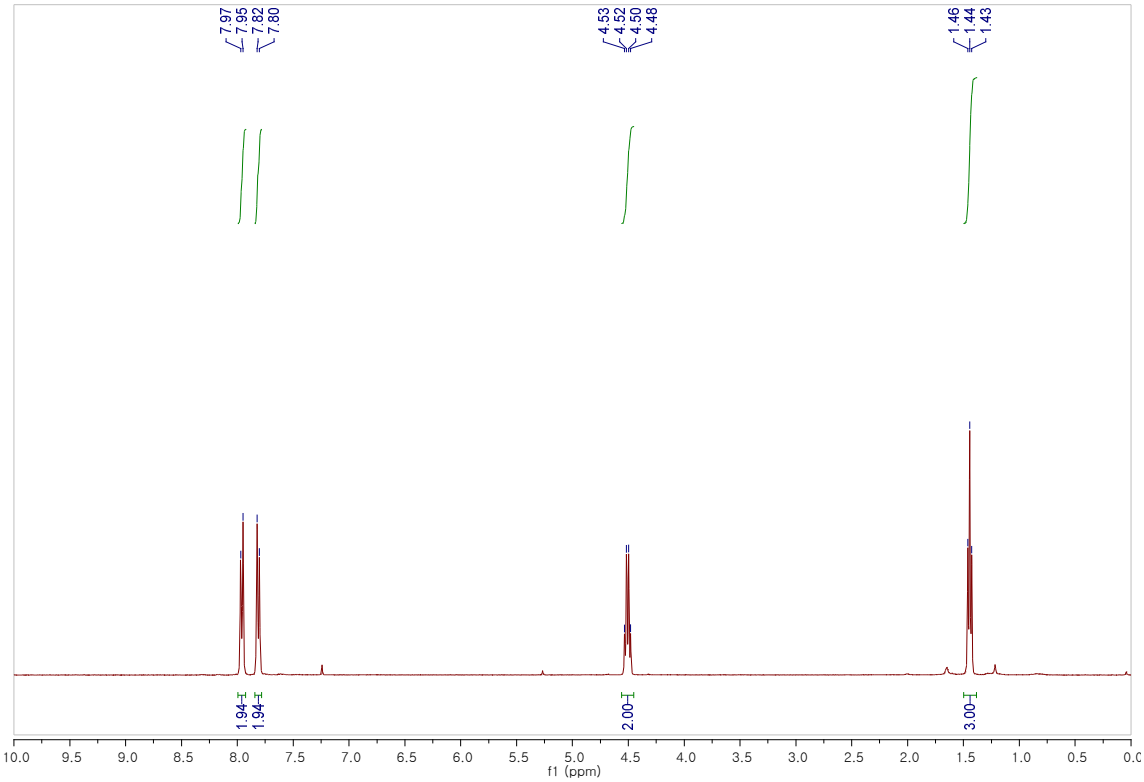
Ethyl 2-(4-fluorophenyl)azocarboxylate (2f)

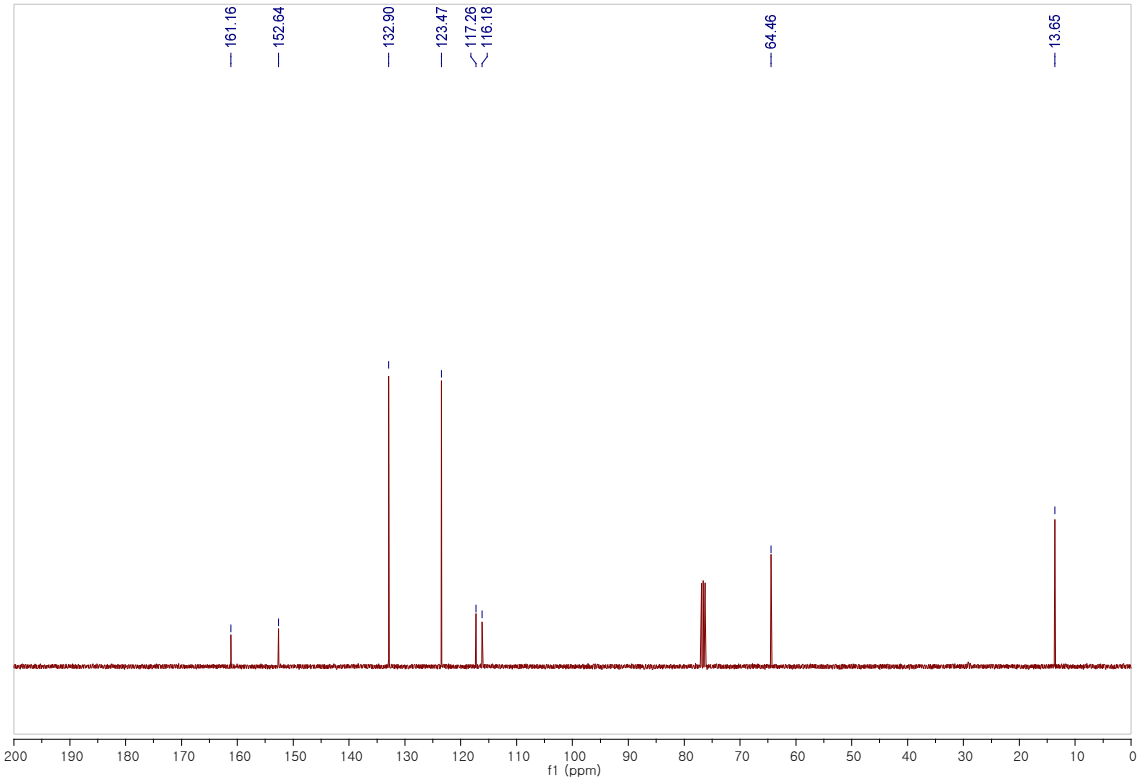




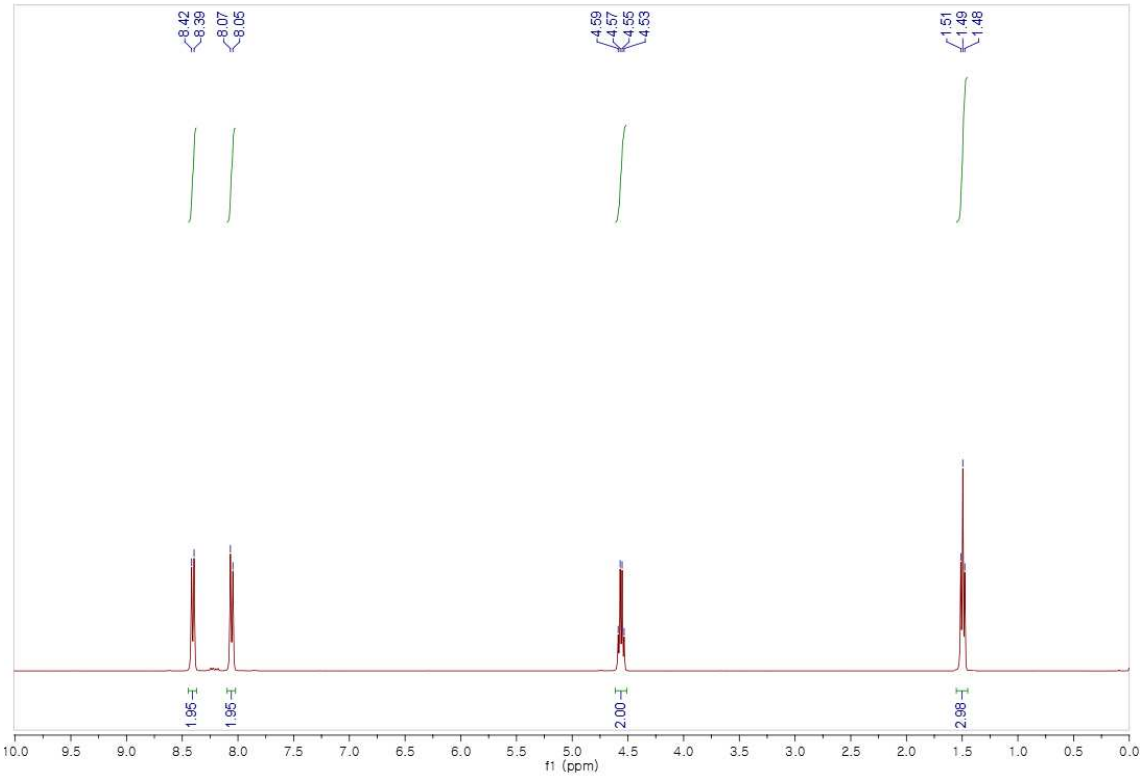

-104.18
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

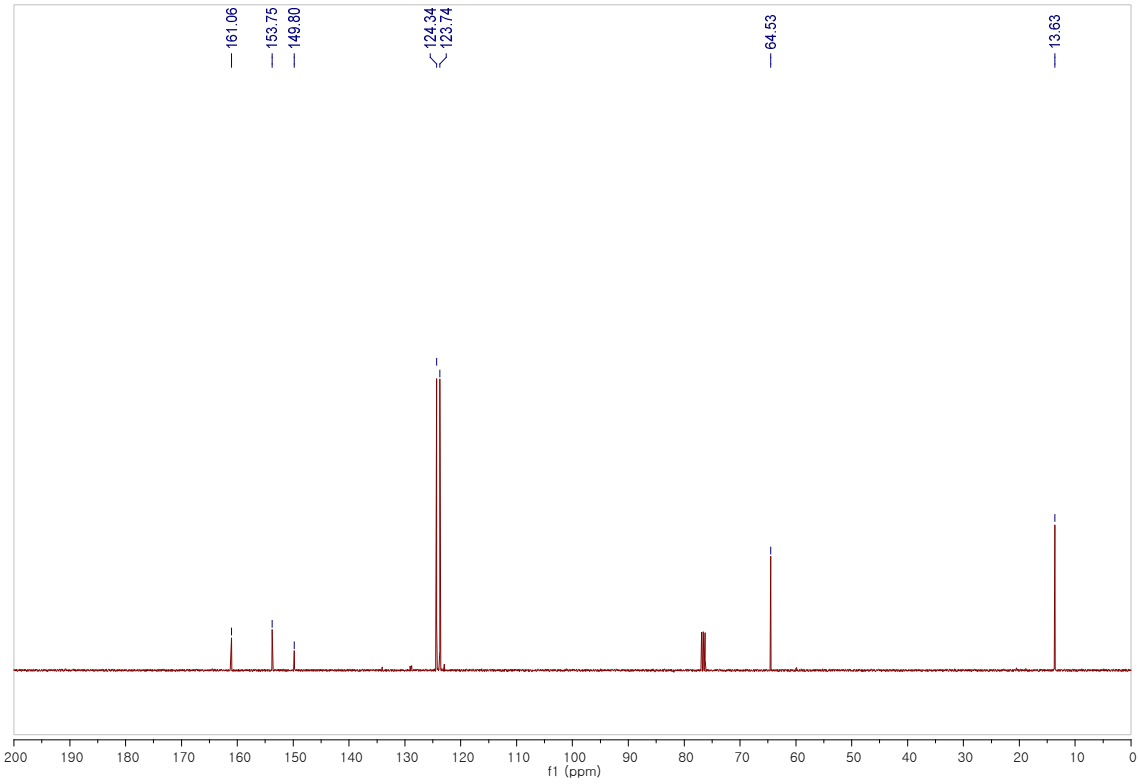
Ethyl 2-(4-cyanophenyl)azocarboxylate (2g)



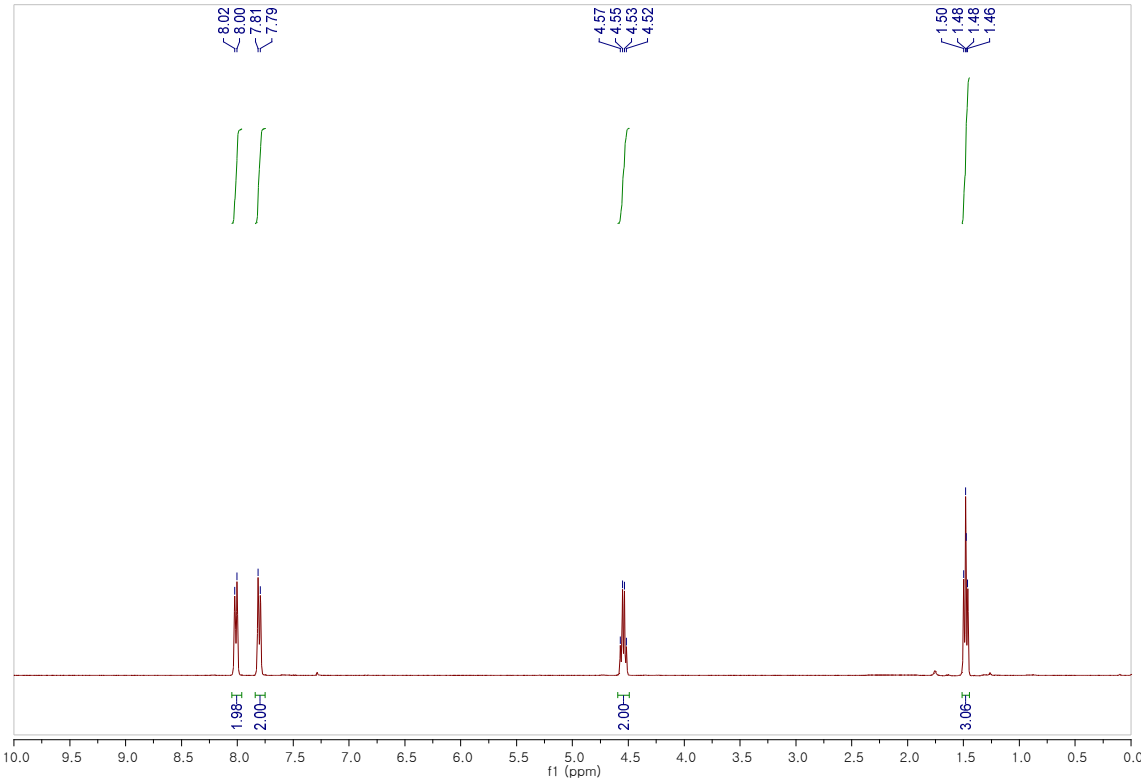


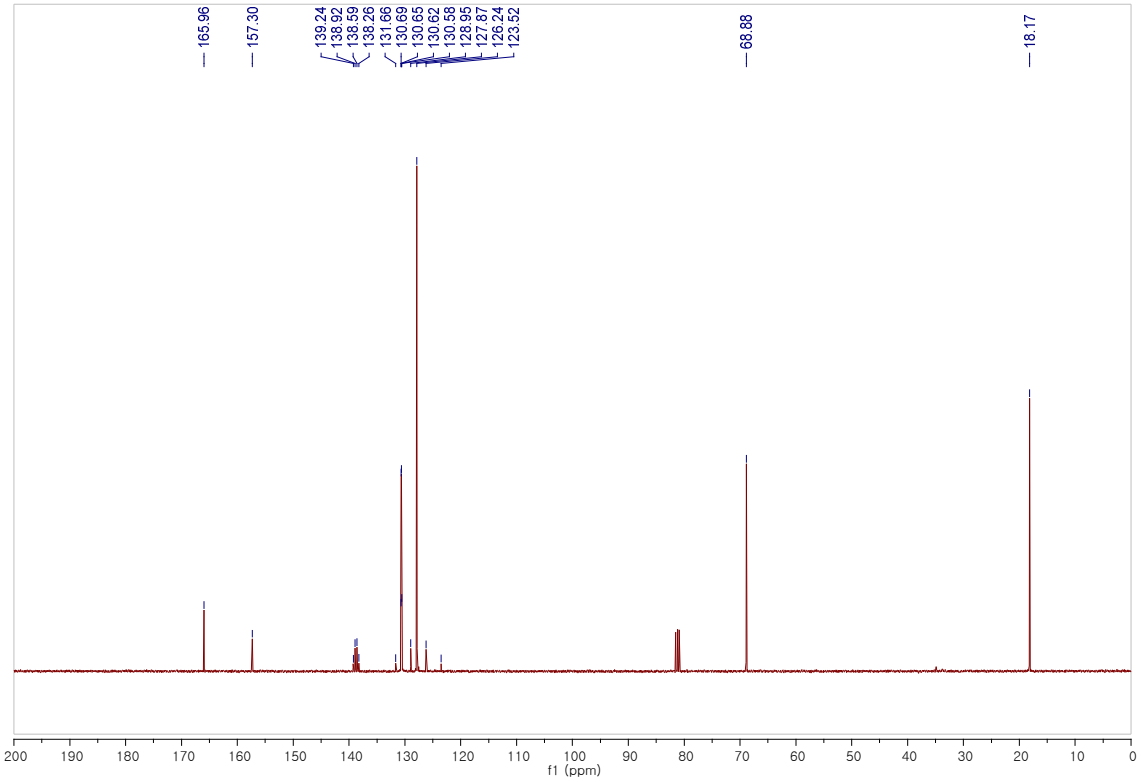
Ethyl 2-(4-nitrophenyl)azocarboxylate (2h)

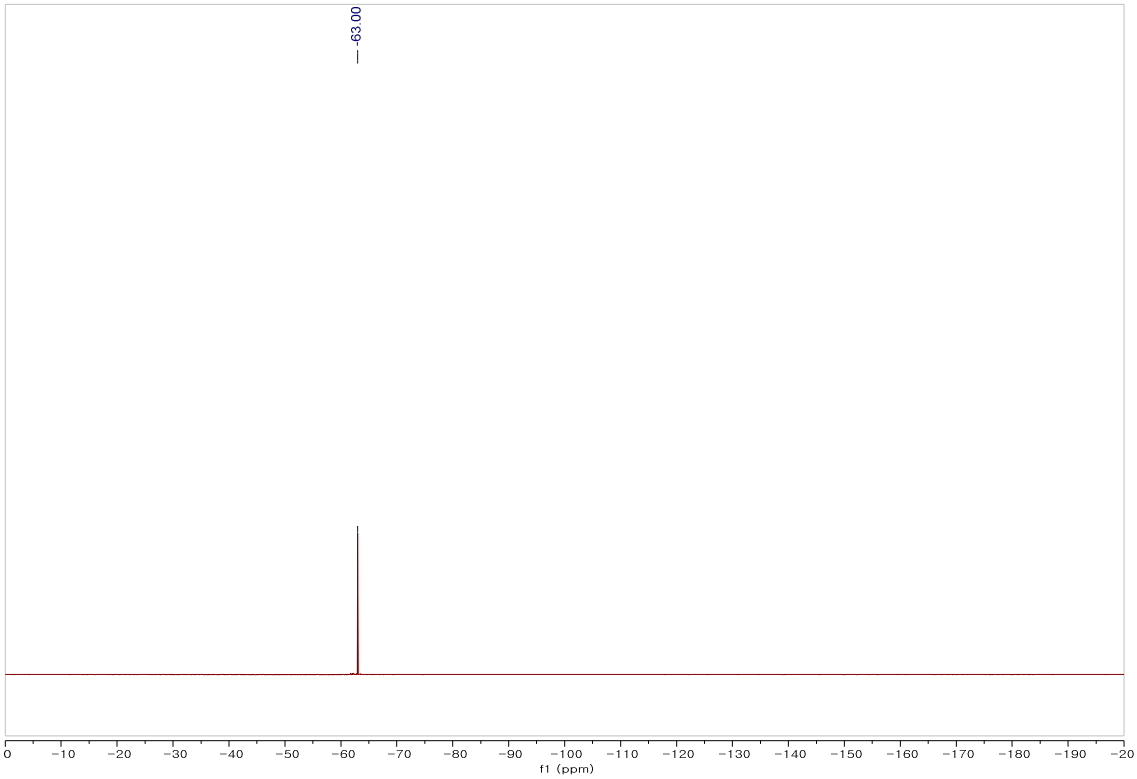




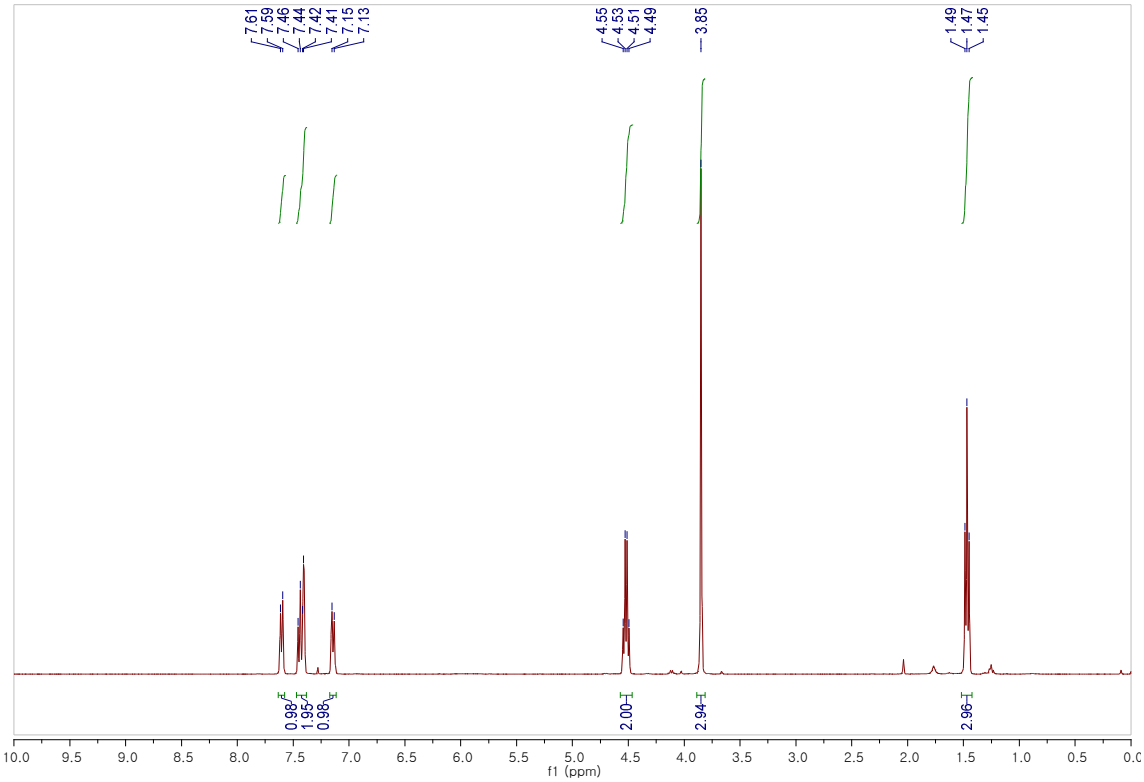
Ethyl 2-(4-(trifluoromethyl)phenyl)azocarboxylate (2i)

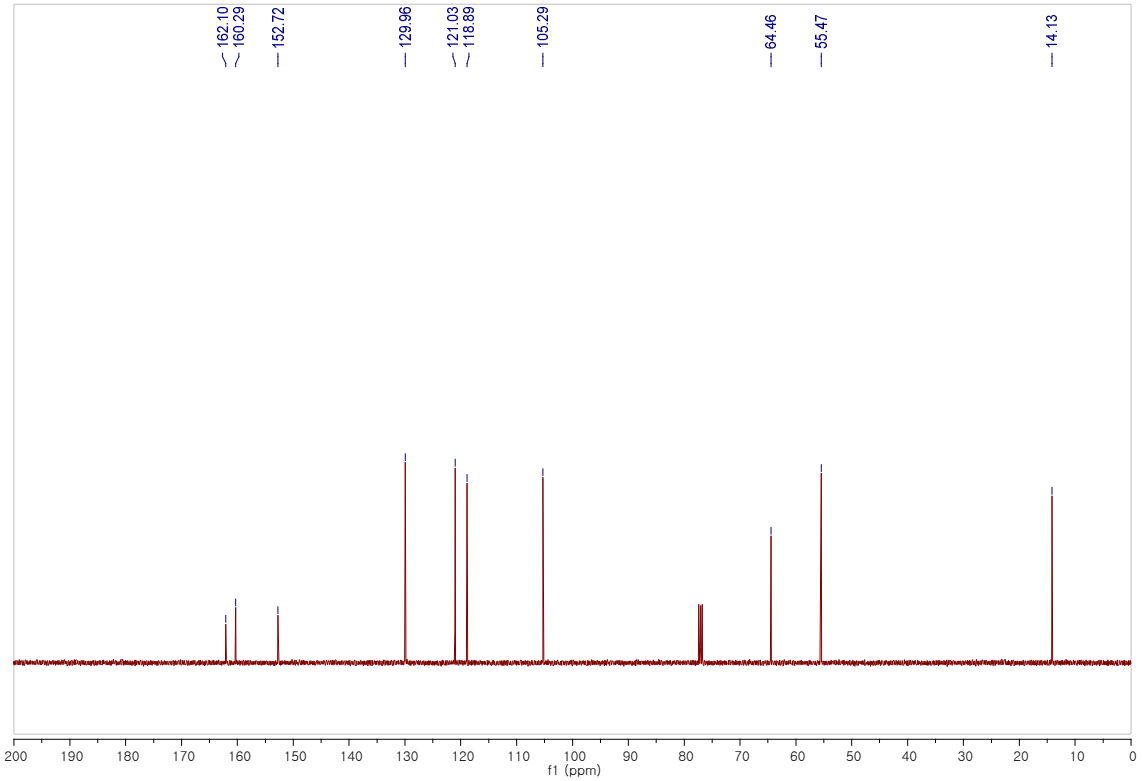




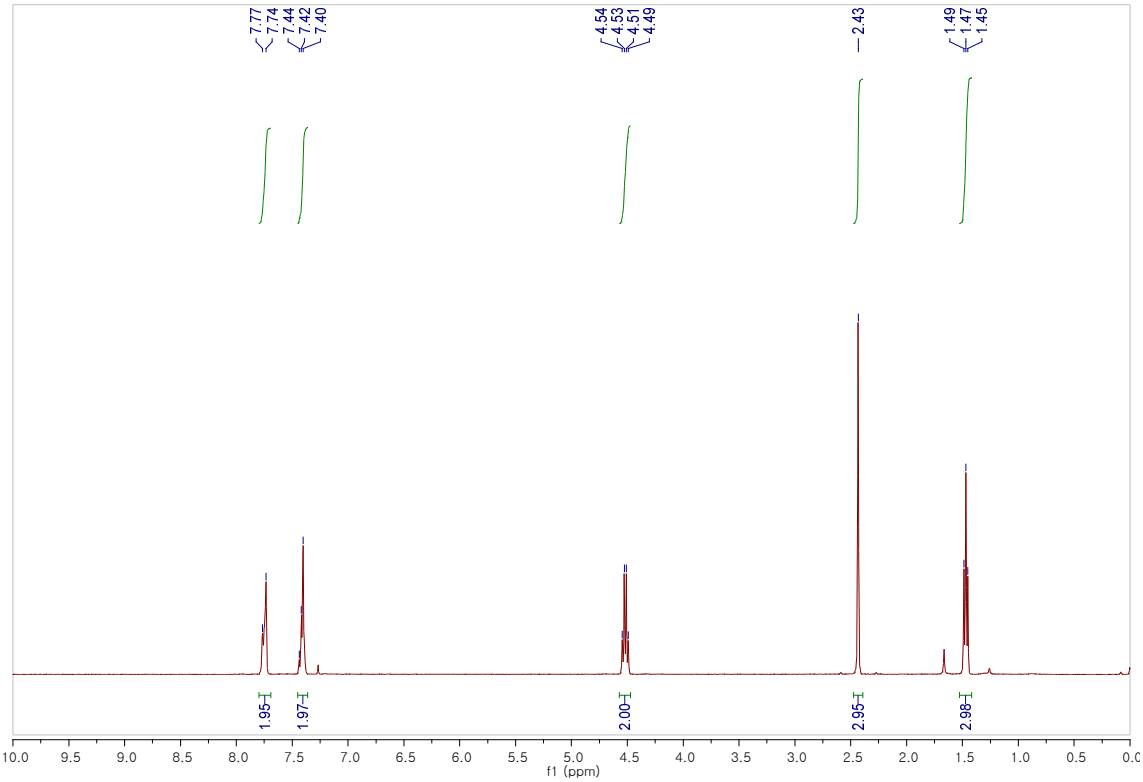

-63.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

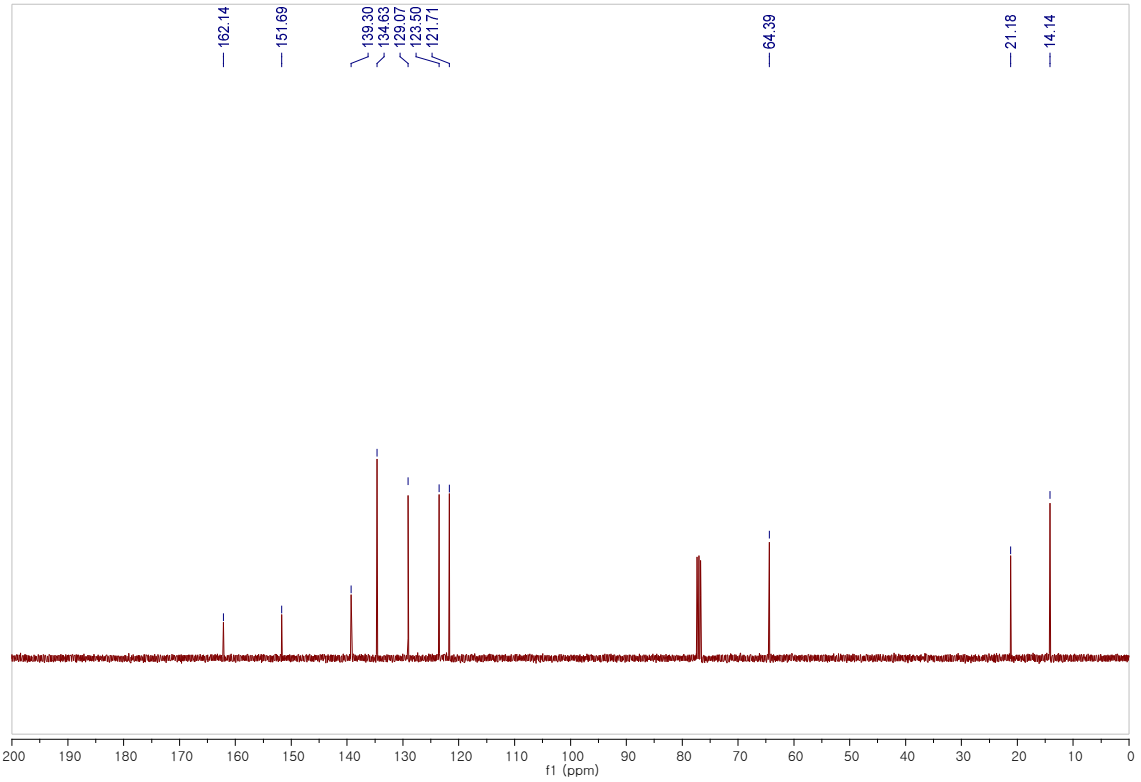
Ethyl 2-(3-methoxyphenyl)azocarboxylate (2j)



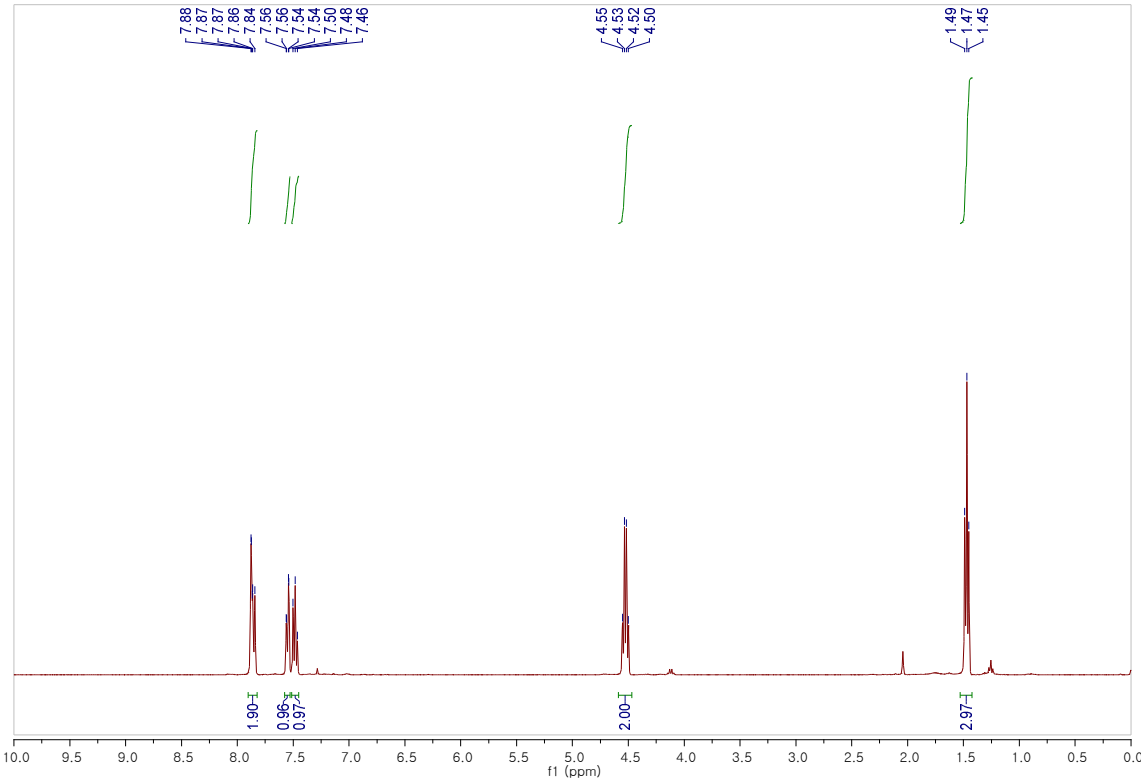


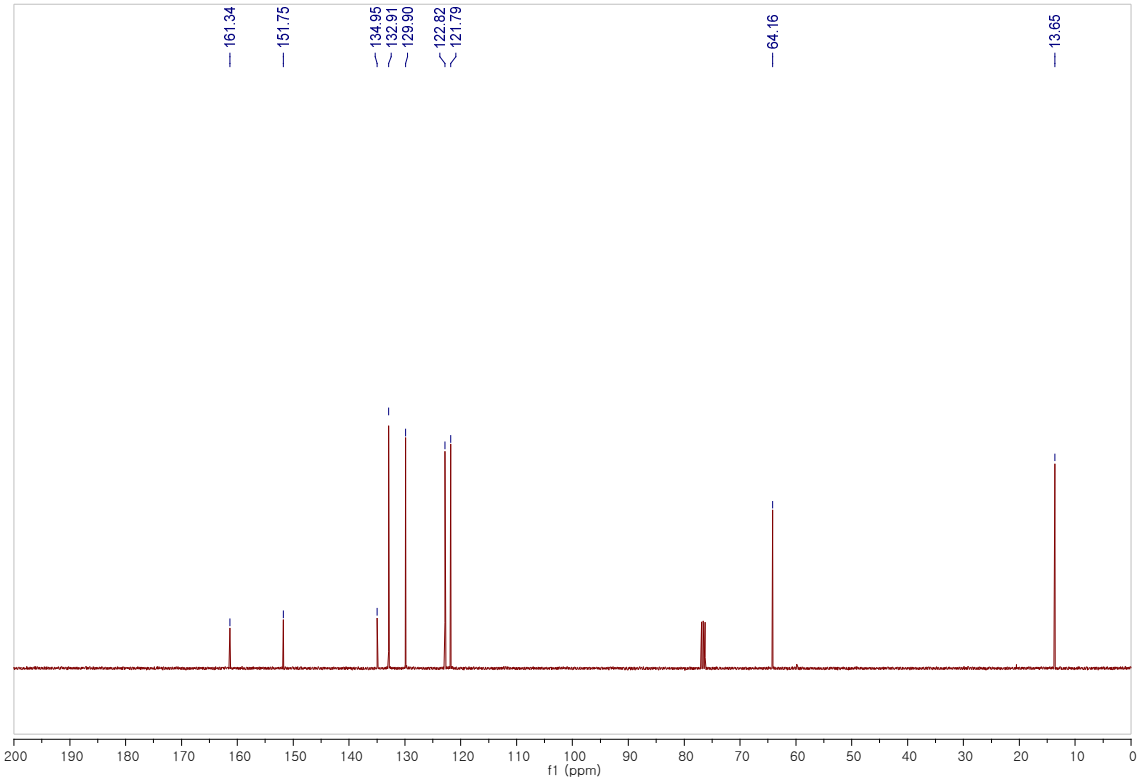
Ethyl 2-(3-methylphenyl)azocarboxylate (2k)



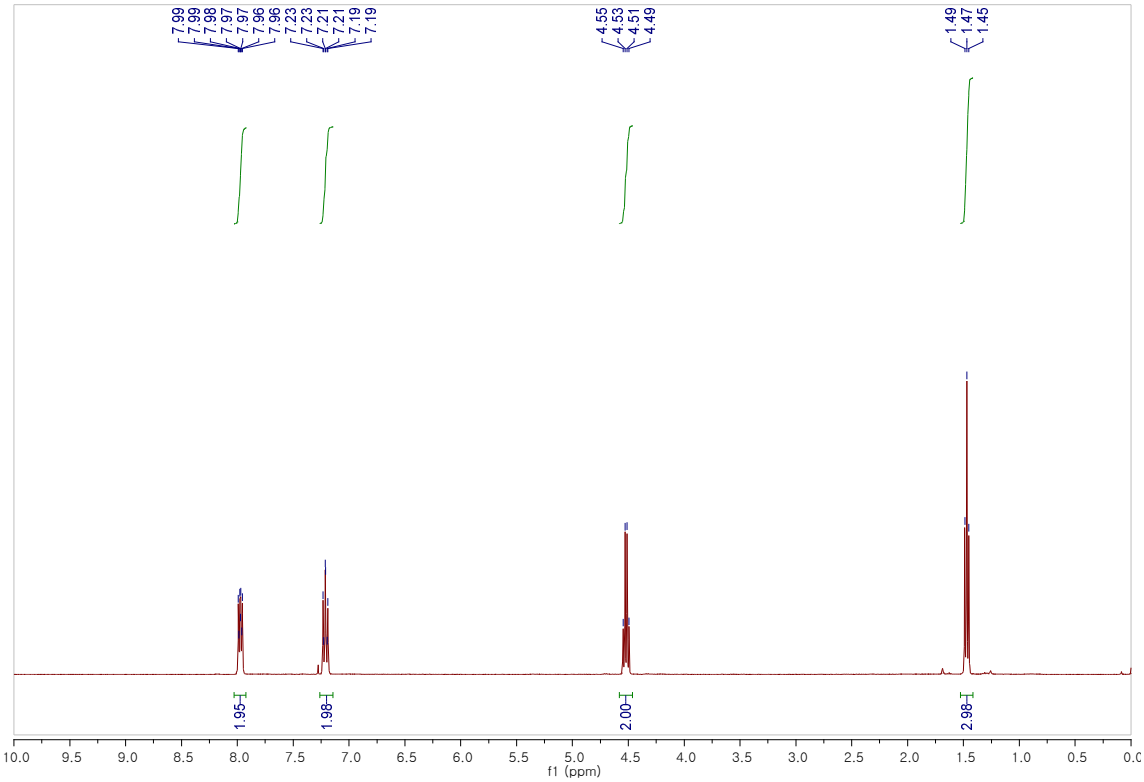


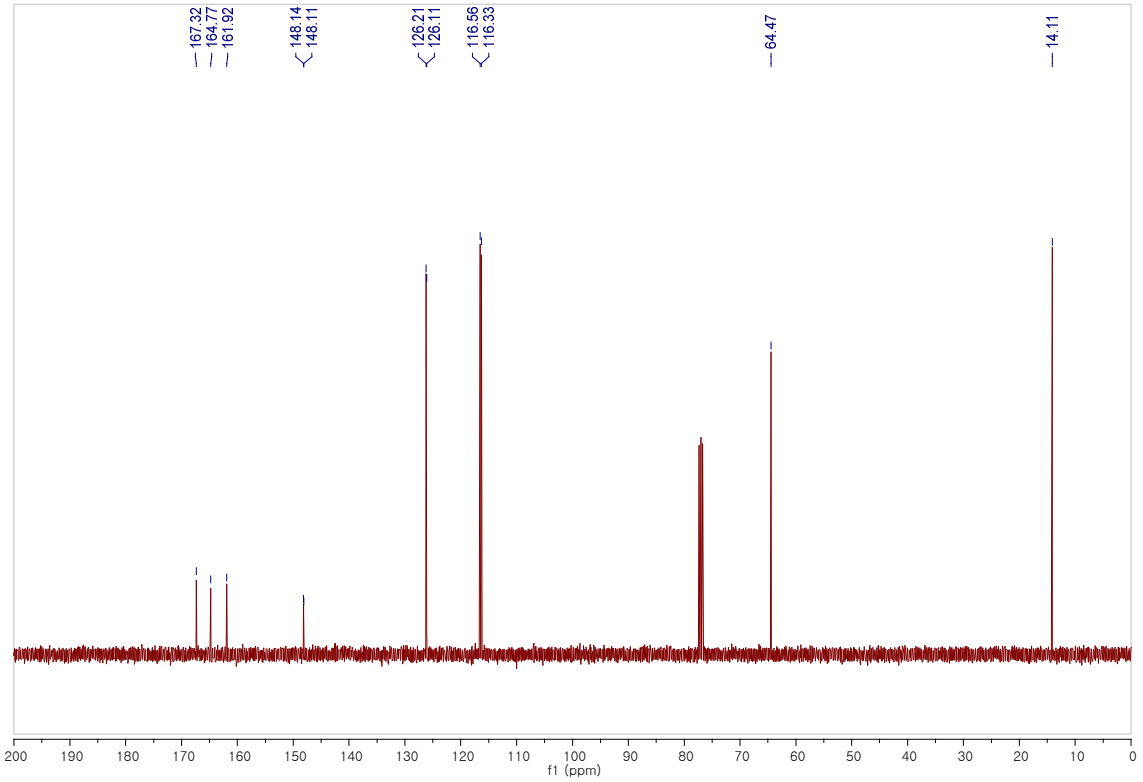
Ethyl 2-(3-chlorophenyl)azocarboxylate (2l)

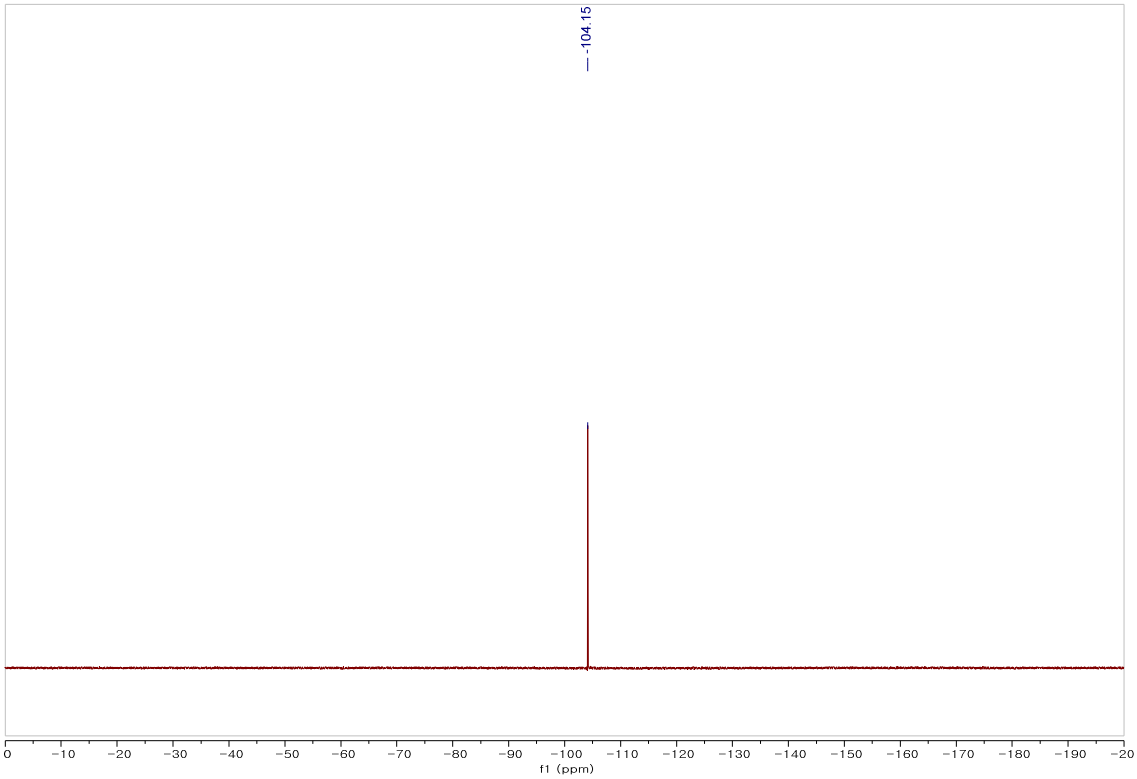




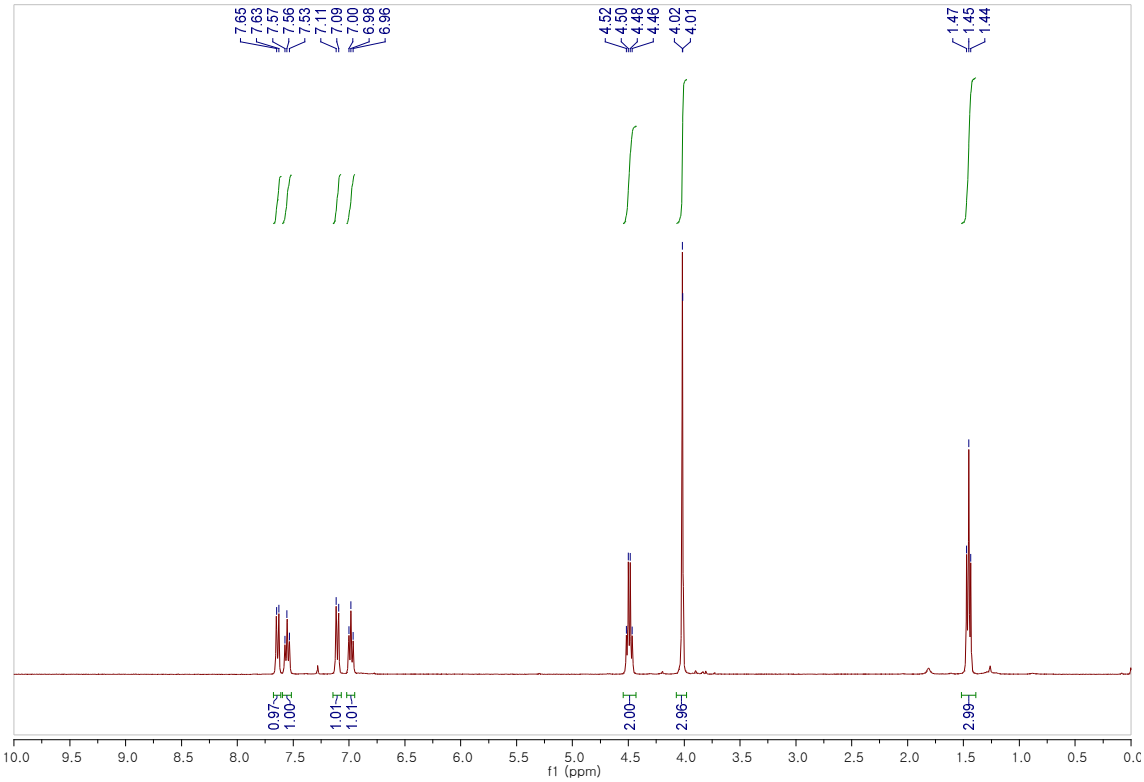
Ethyl 2-(3-fluorophenyl)azocarboxylate (2m)

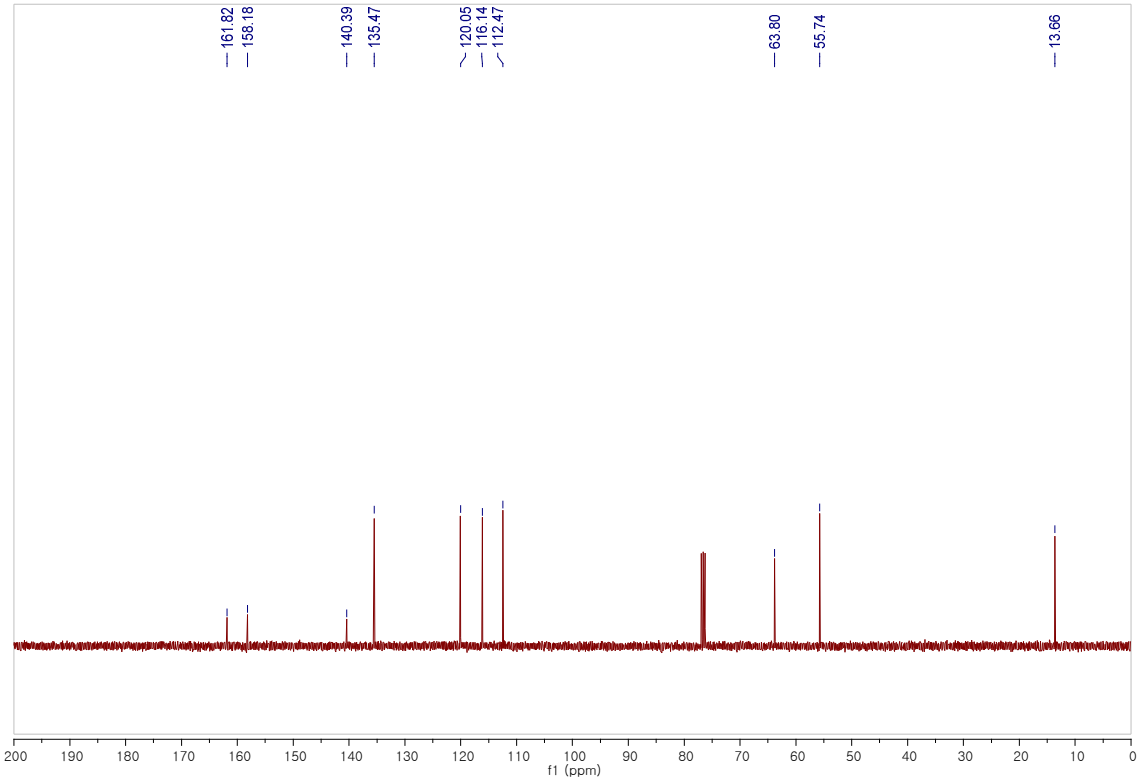




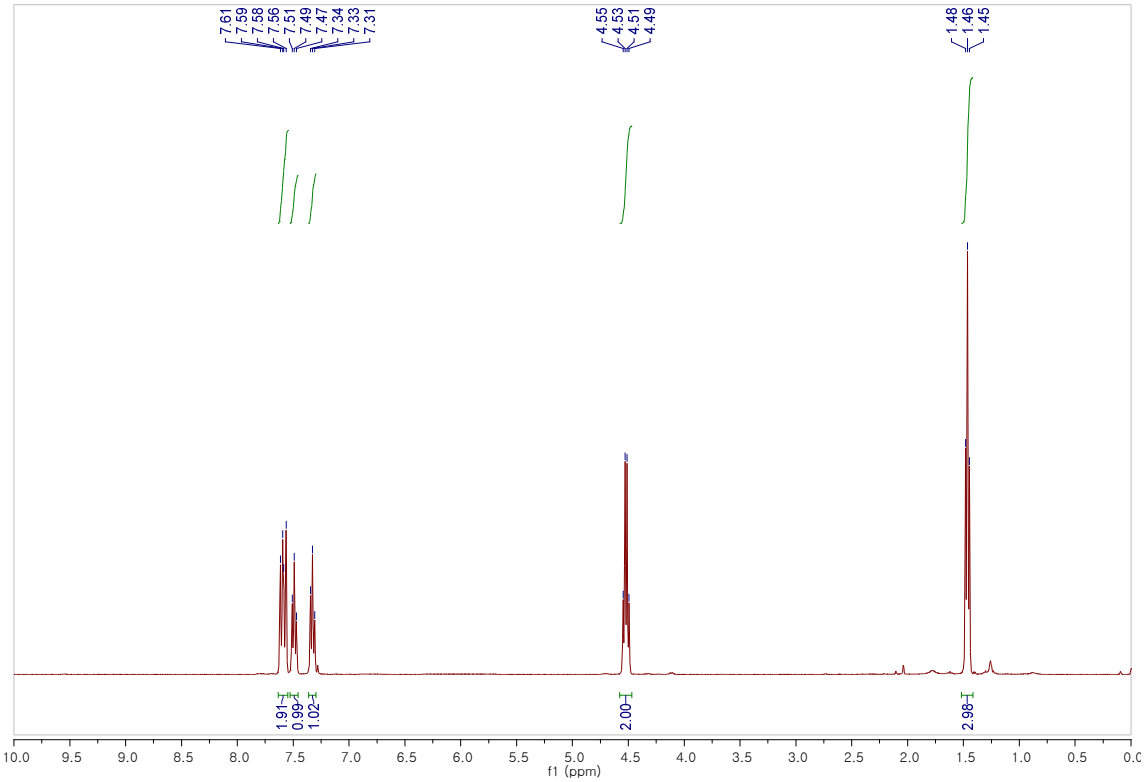

-104.15
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

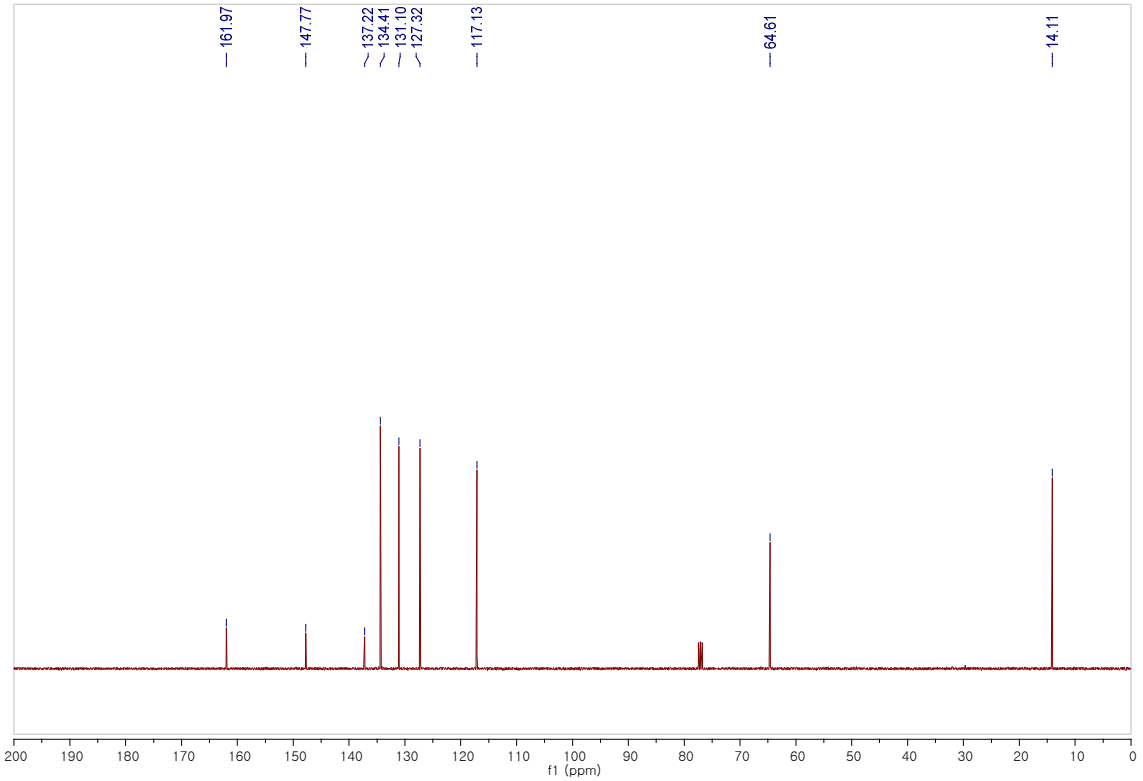
Ethyl 2-(2-methoxyphenyl)azocarboxylate (2n)



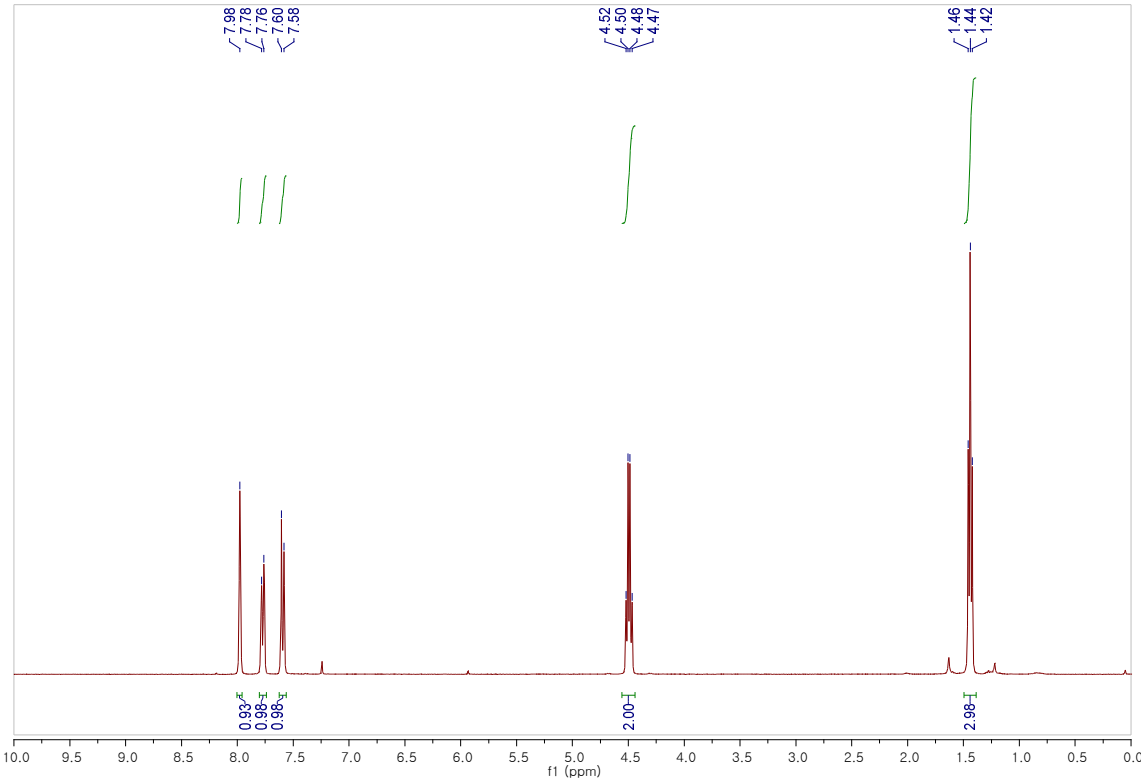


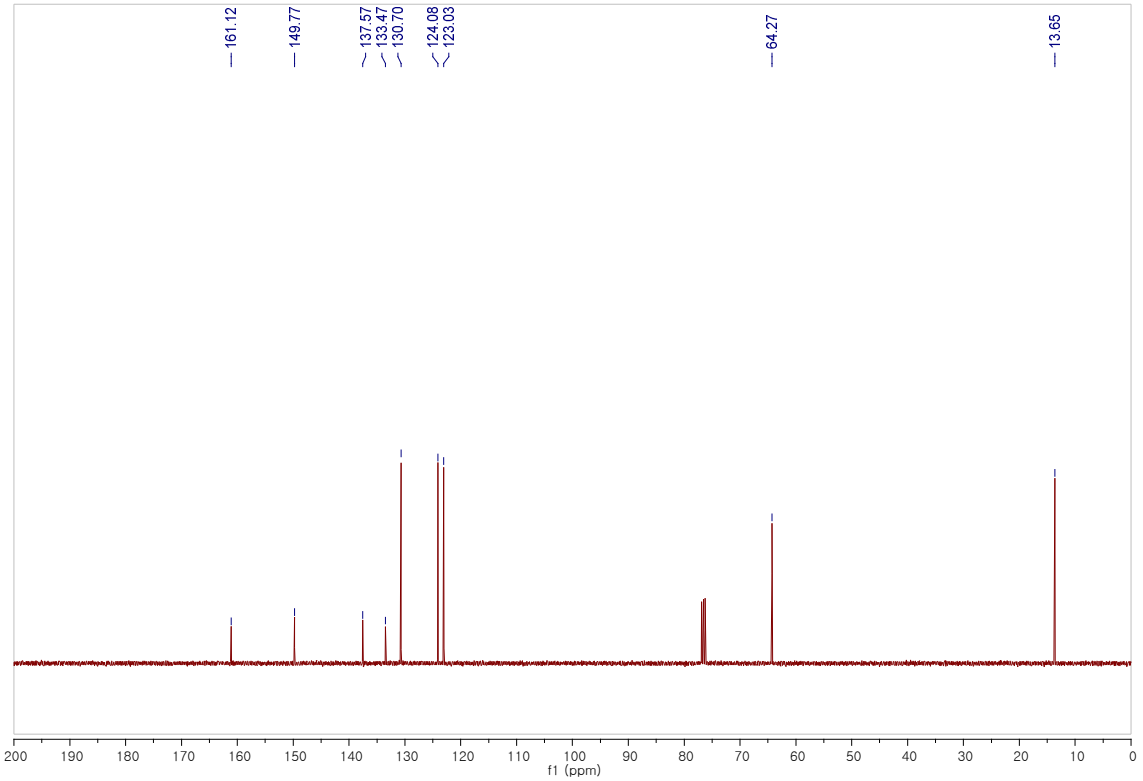
Ethyl 2-(2-chlorophenyl)azocarboxylate (2o)



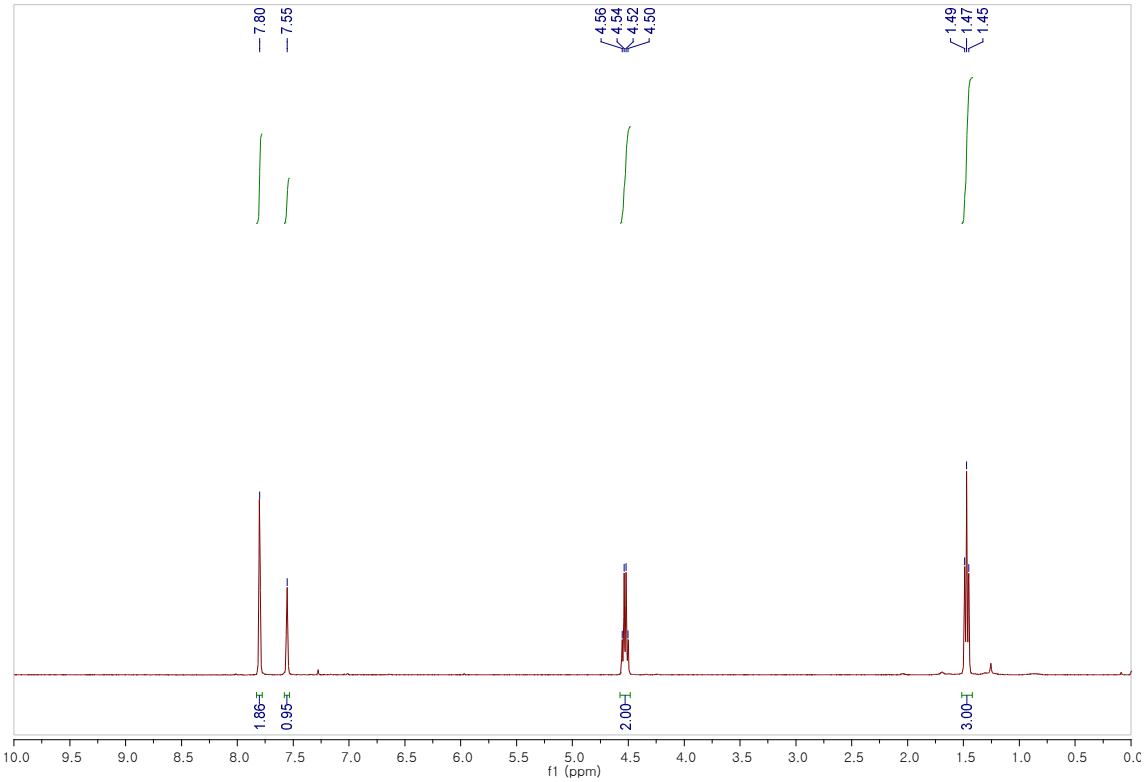


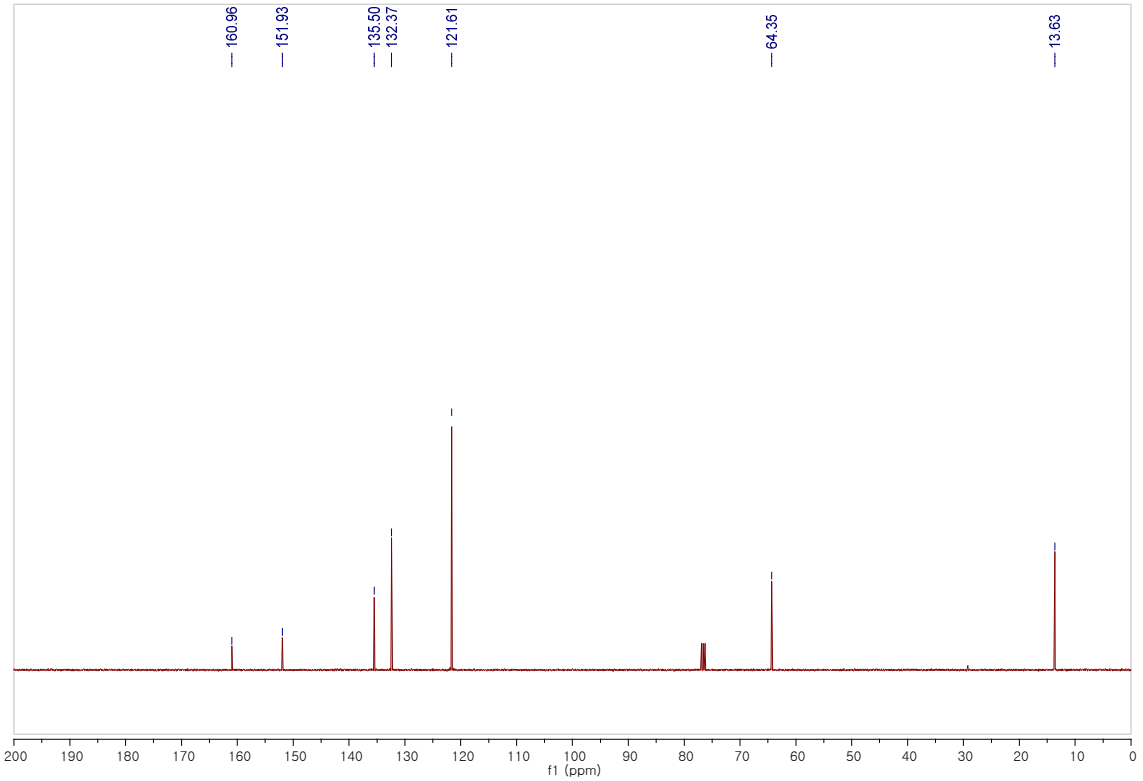
Ethyl 2-(3,4-dichlorophenyl)azocarboxylate (2p)



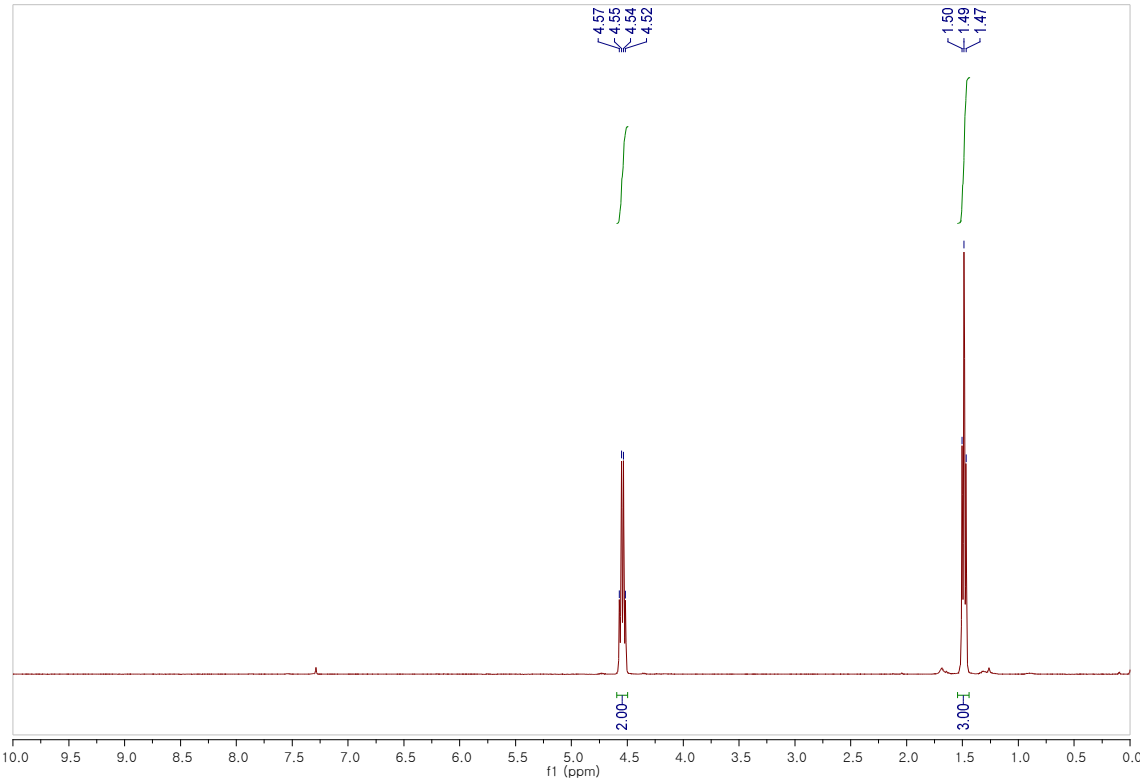


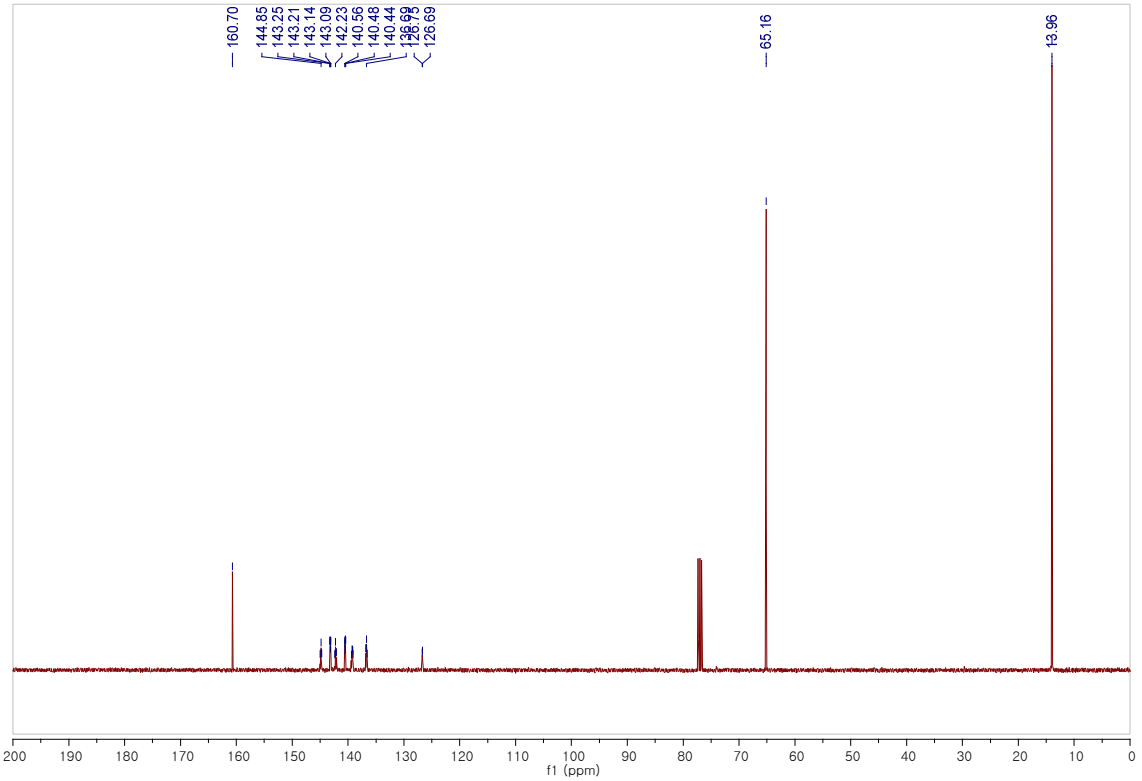
Ethyl 2-(3,5-dichlorophenyl)azocarboxylate (2q)

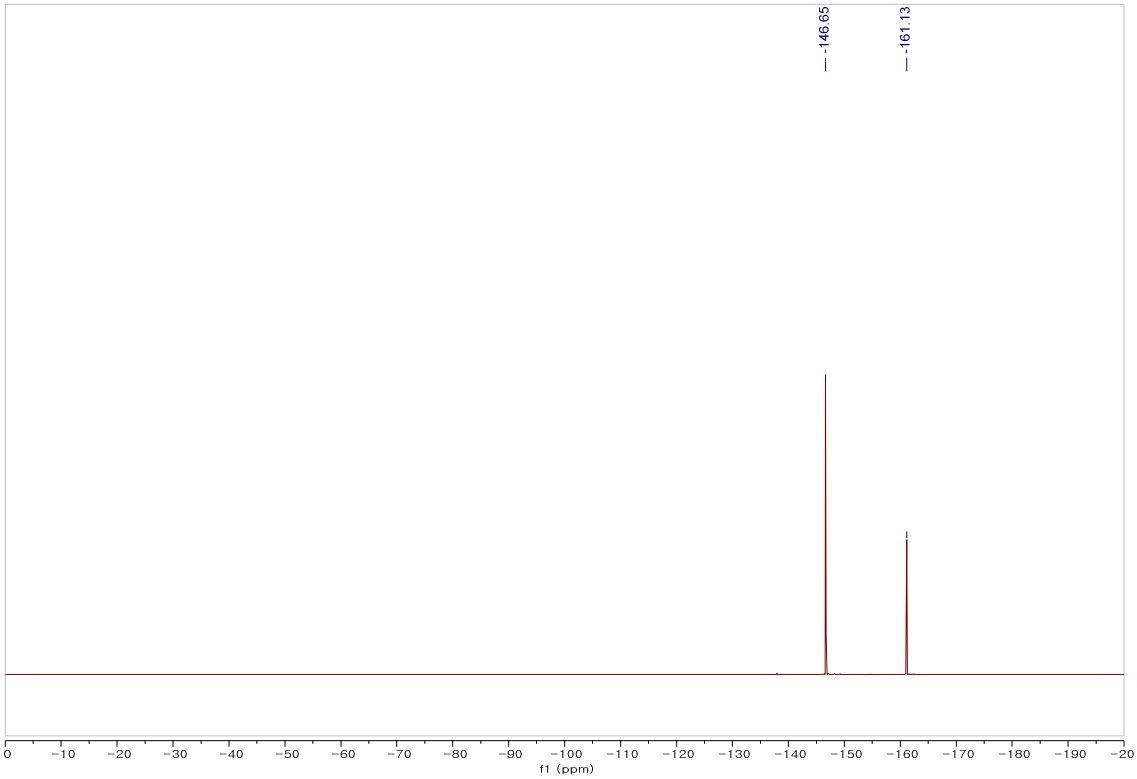




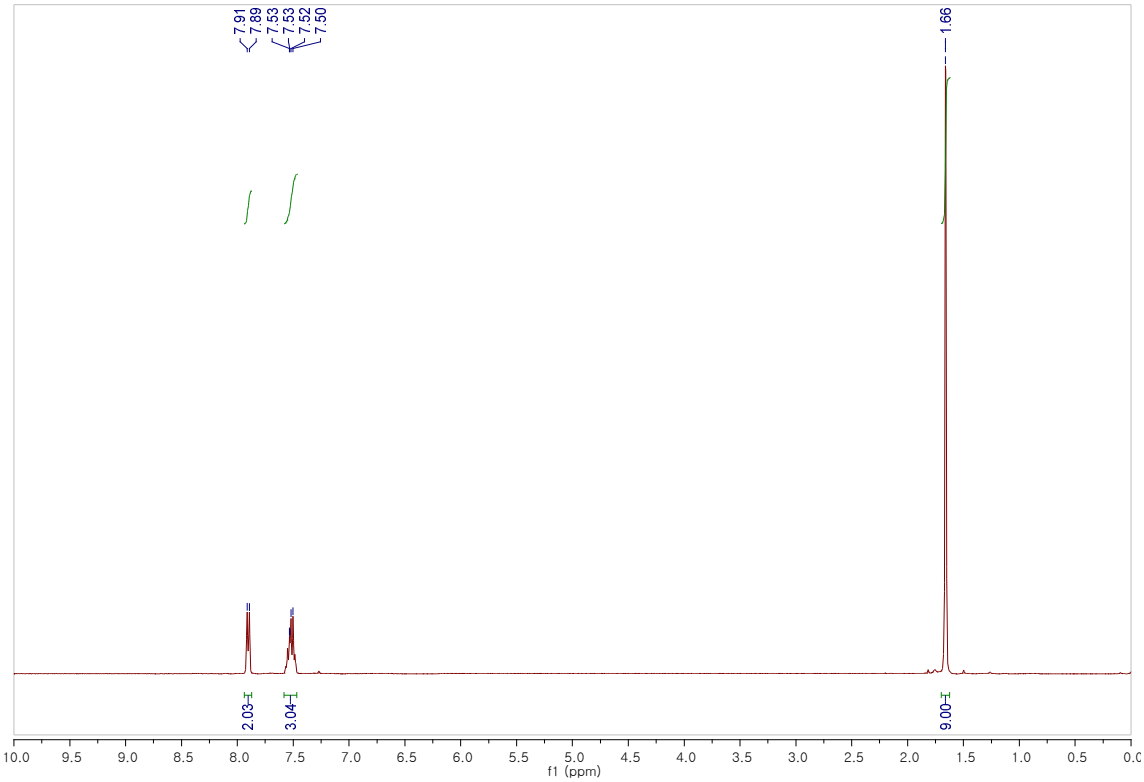
Ethyl 2-(2,3,4,5,6-pentafluorophenyl)azocarboxylate (2r)

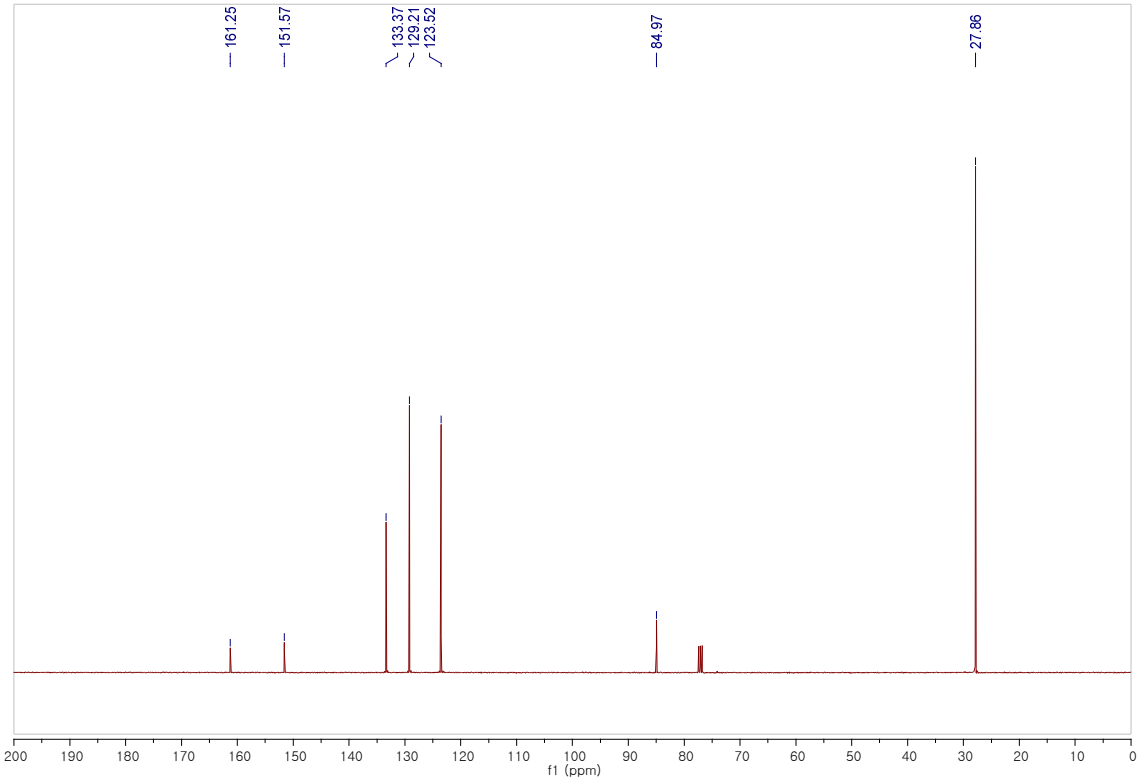




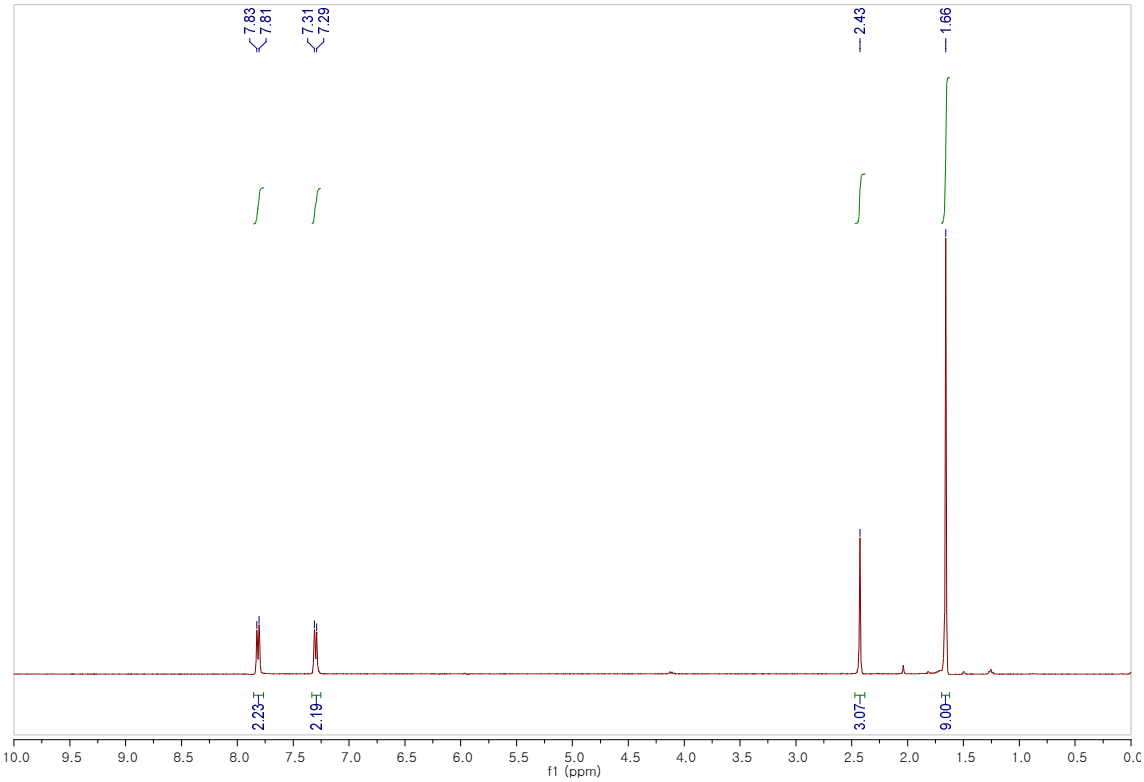

-146.65
-161.13
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

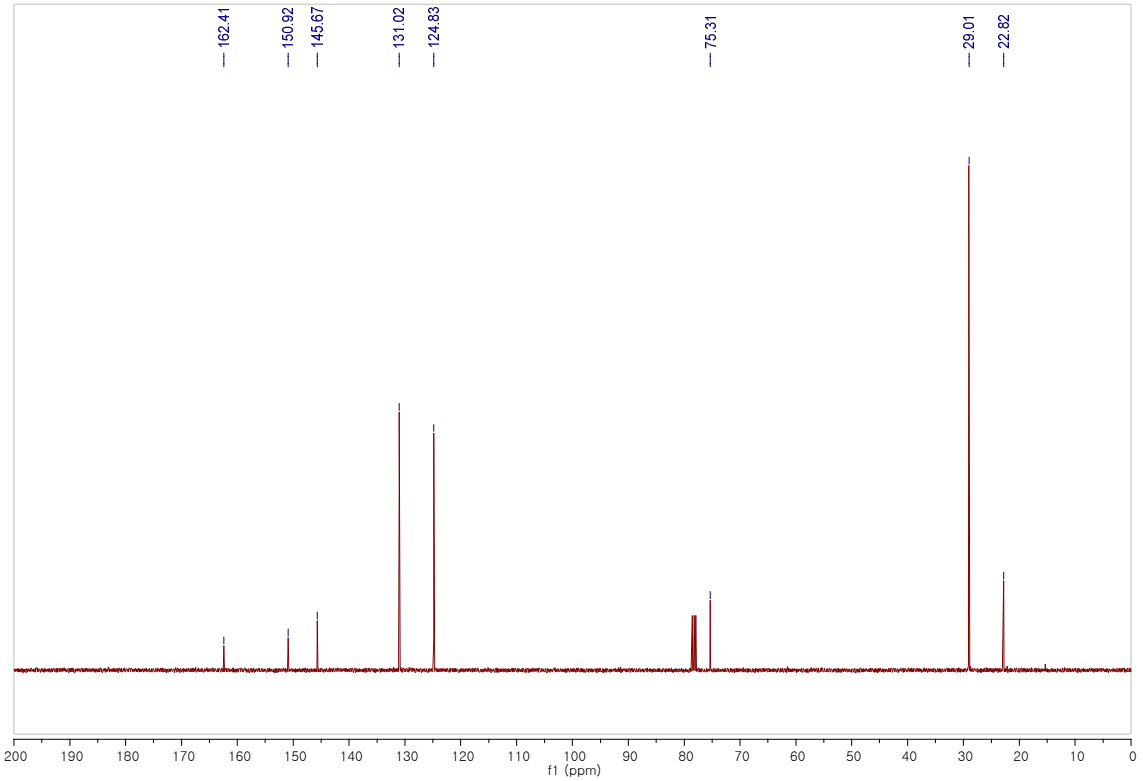
***tert*-Butyl 2-phenylazocarboxylate (2s)**



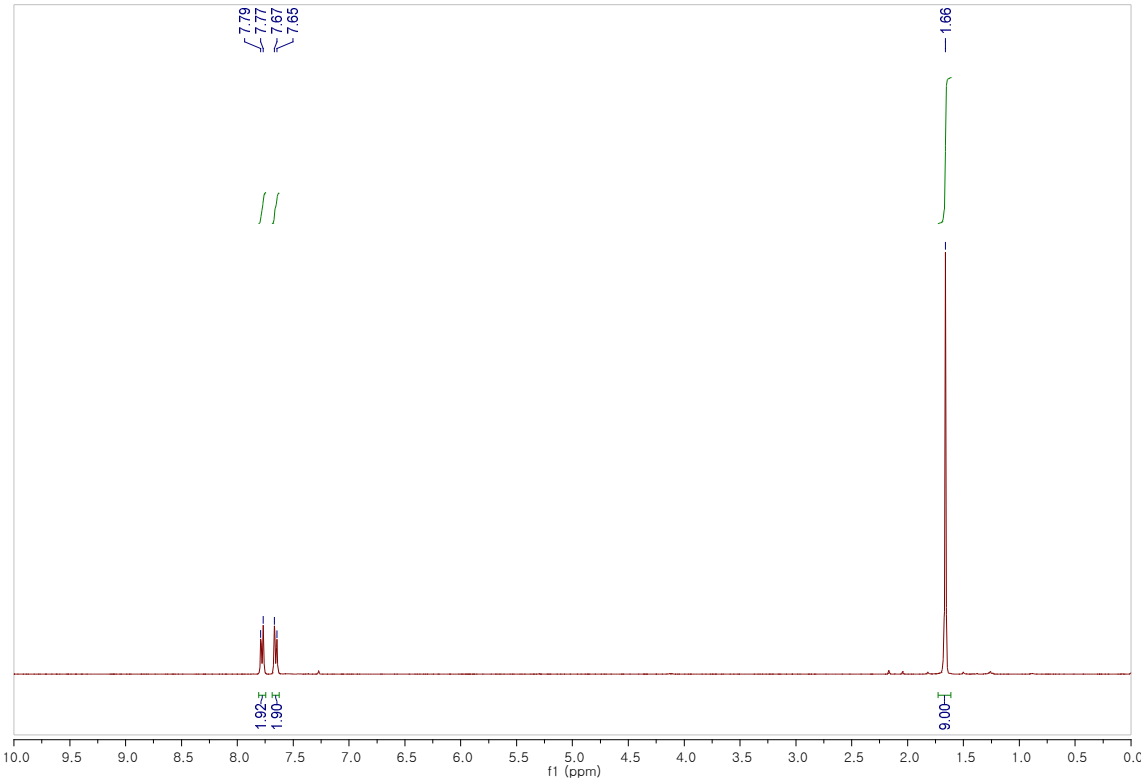


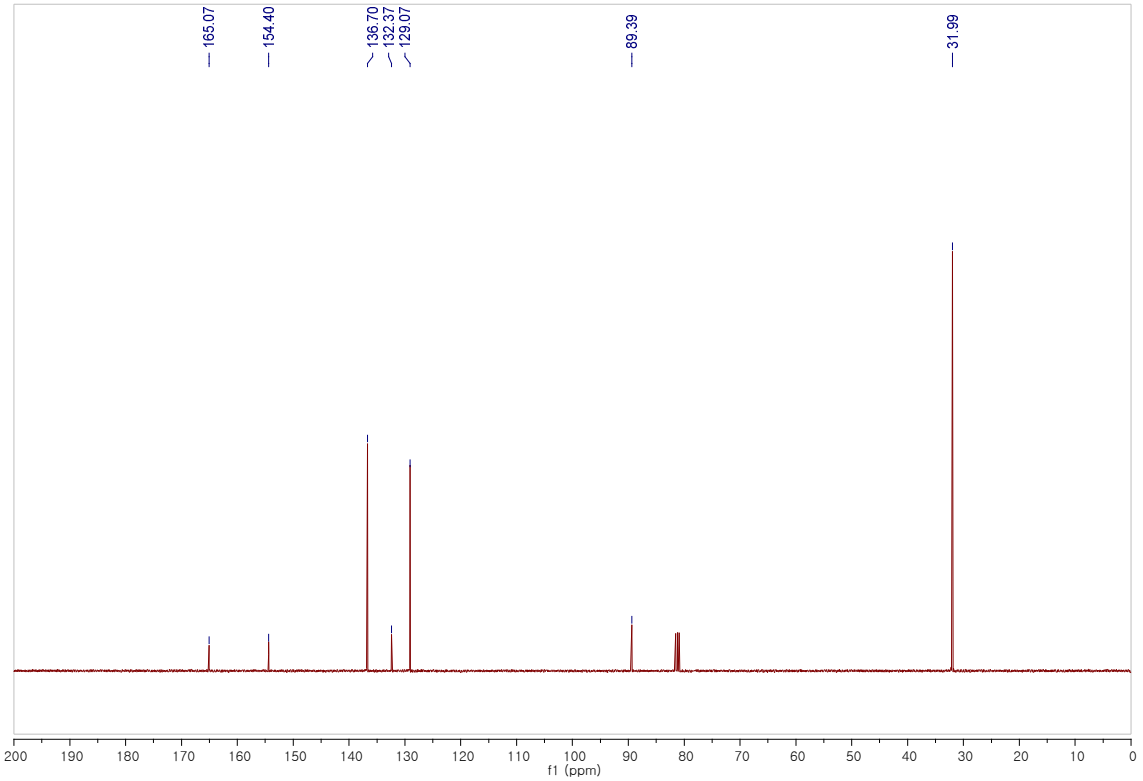
***tert*-Butyl 2-(4-methylphenyl)azocarboxylate (2t)**



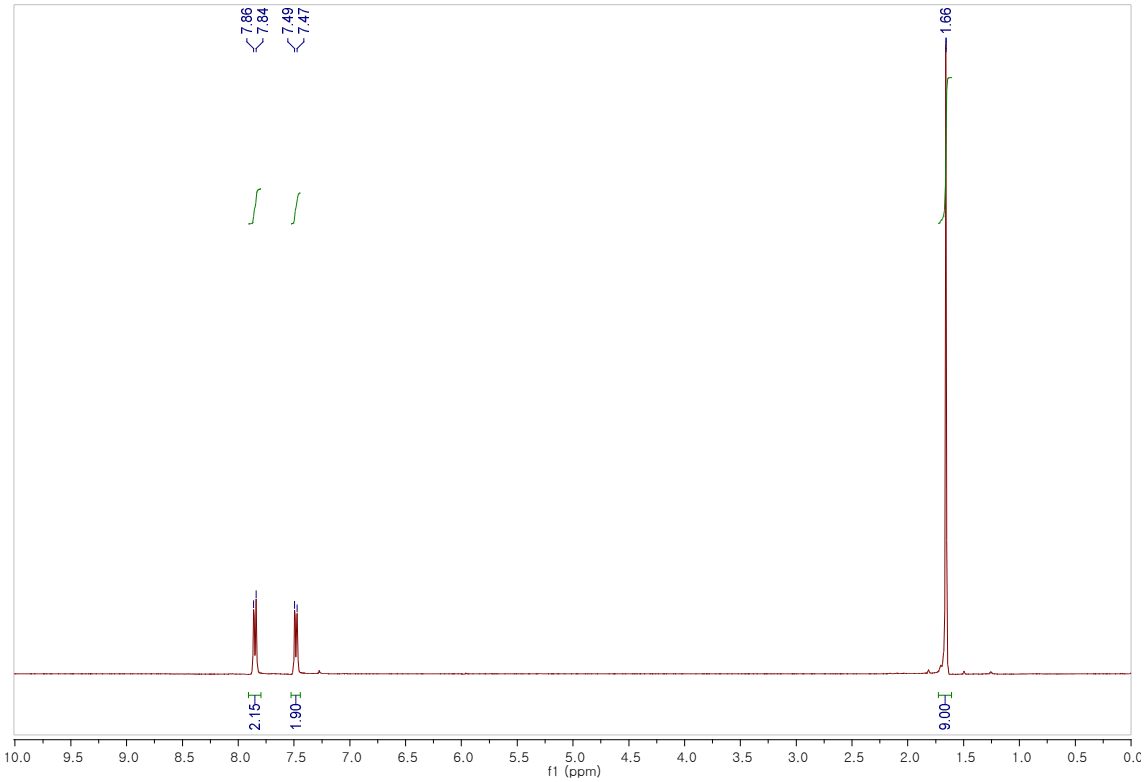


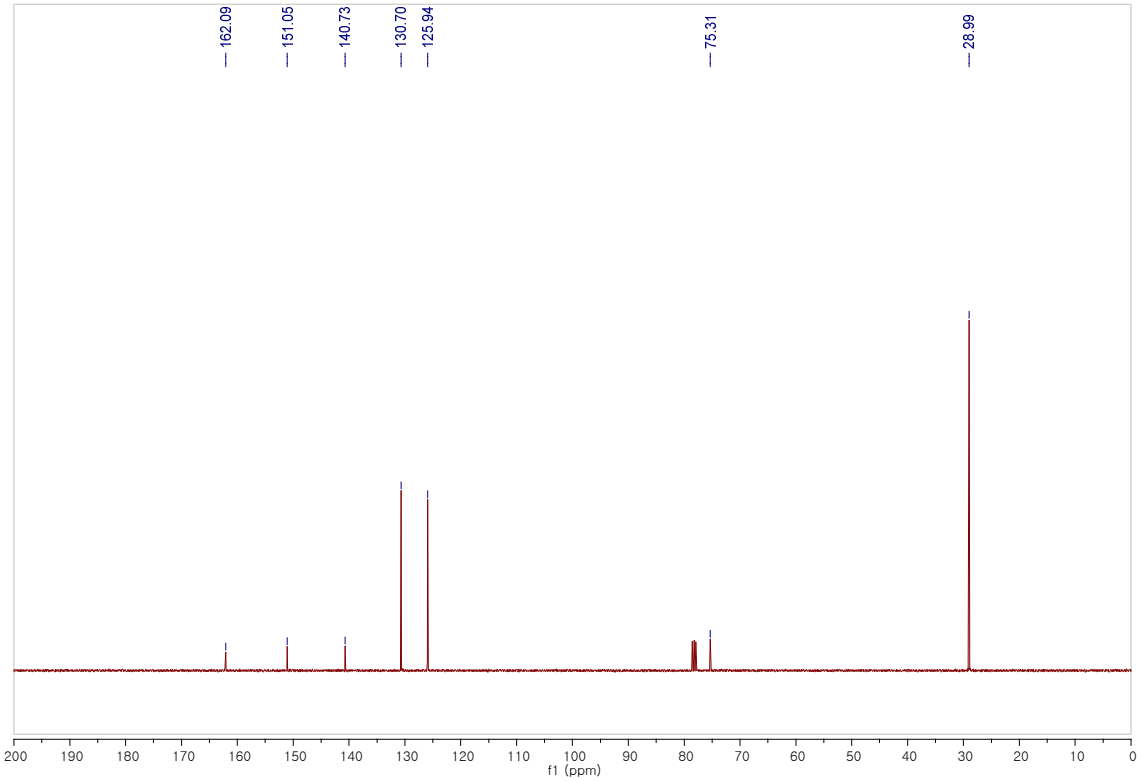
***tert*-Butyl 2-(4-bromophenyl)azocarboxylate (2u)**



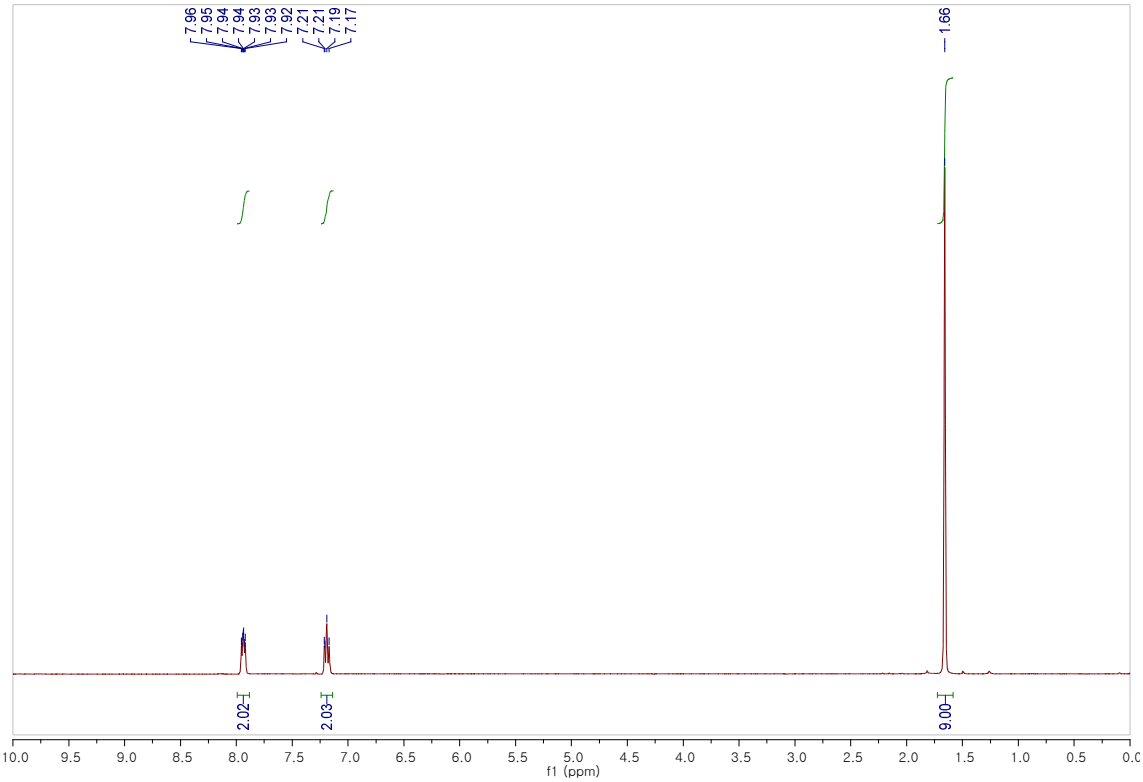


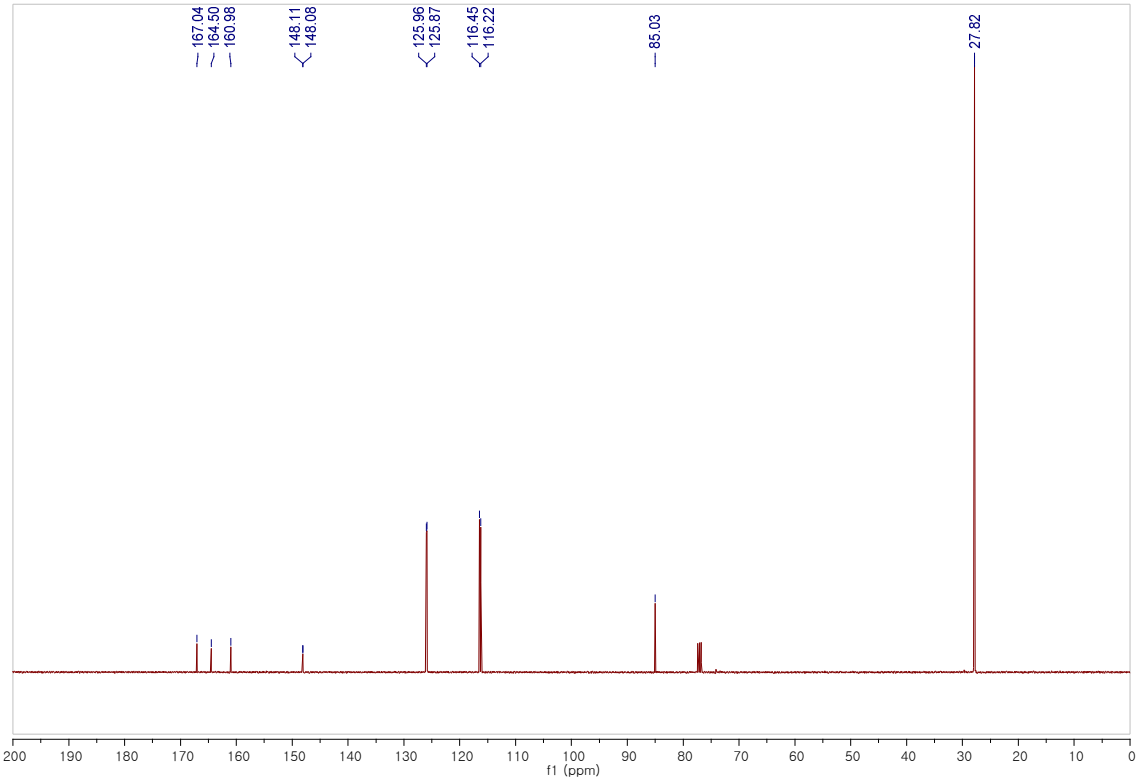
***tert*-Butyl 2-(4-chlorophenyl)azocarboxylate (2v)**

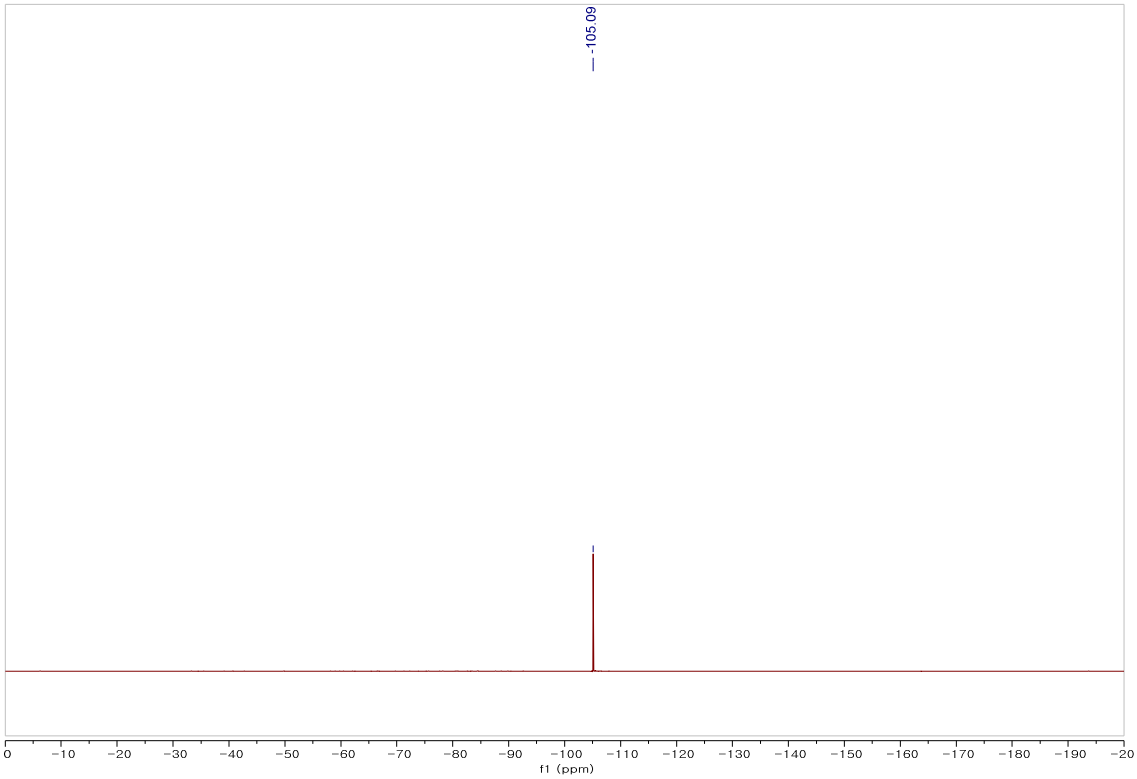




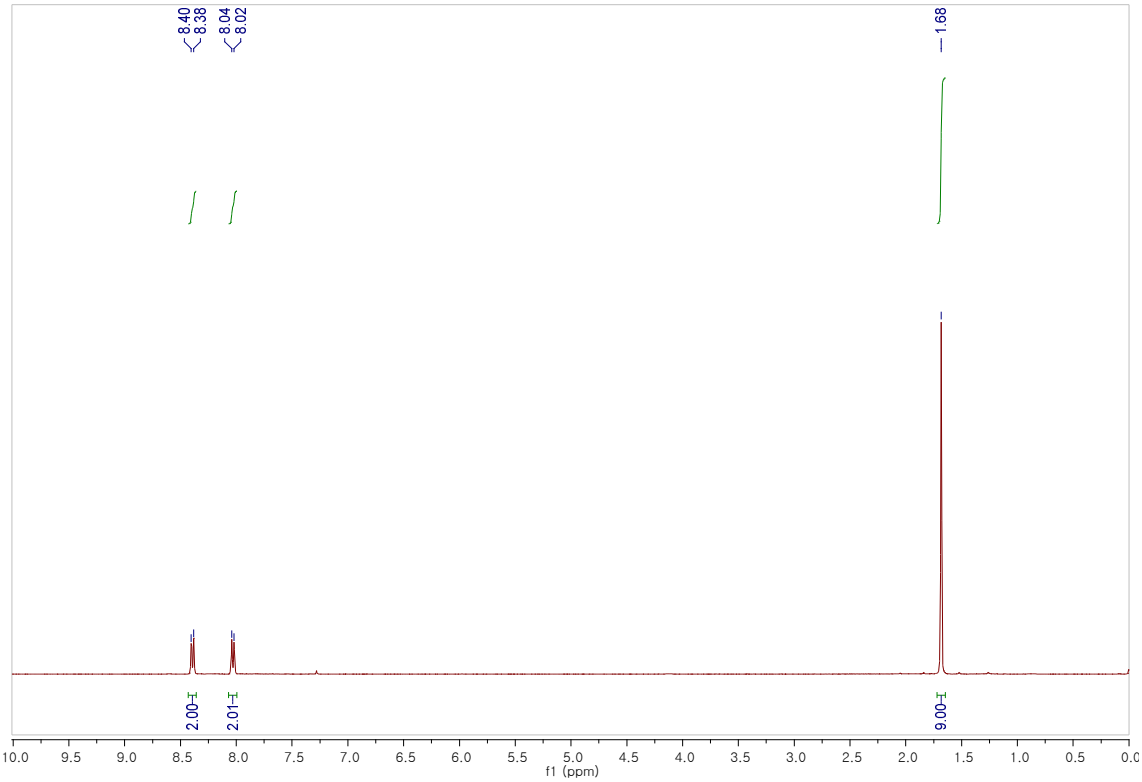
***tert*-Butyl 2-(4-fluorophenyl)azocarboxylate (2w)**

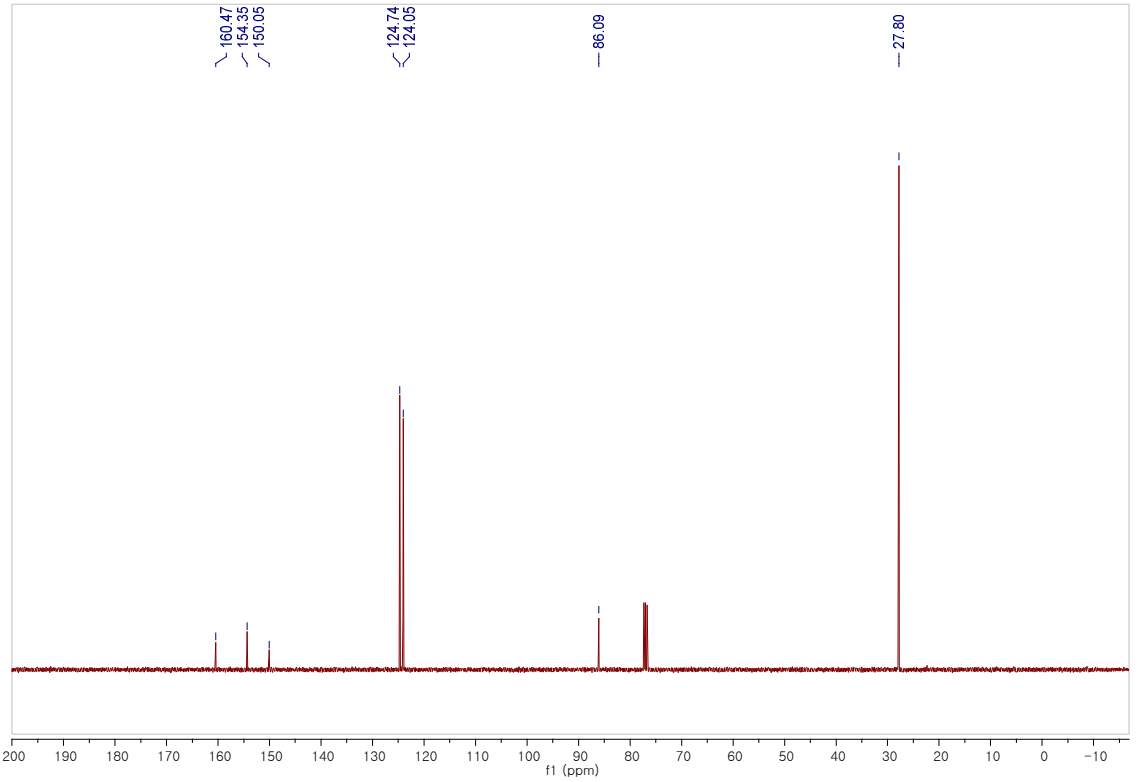




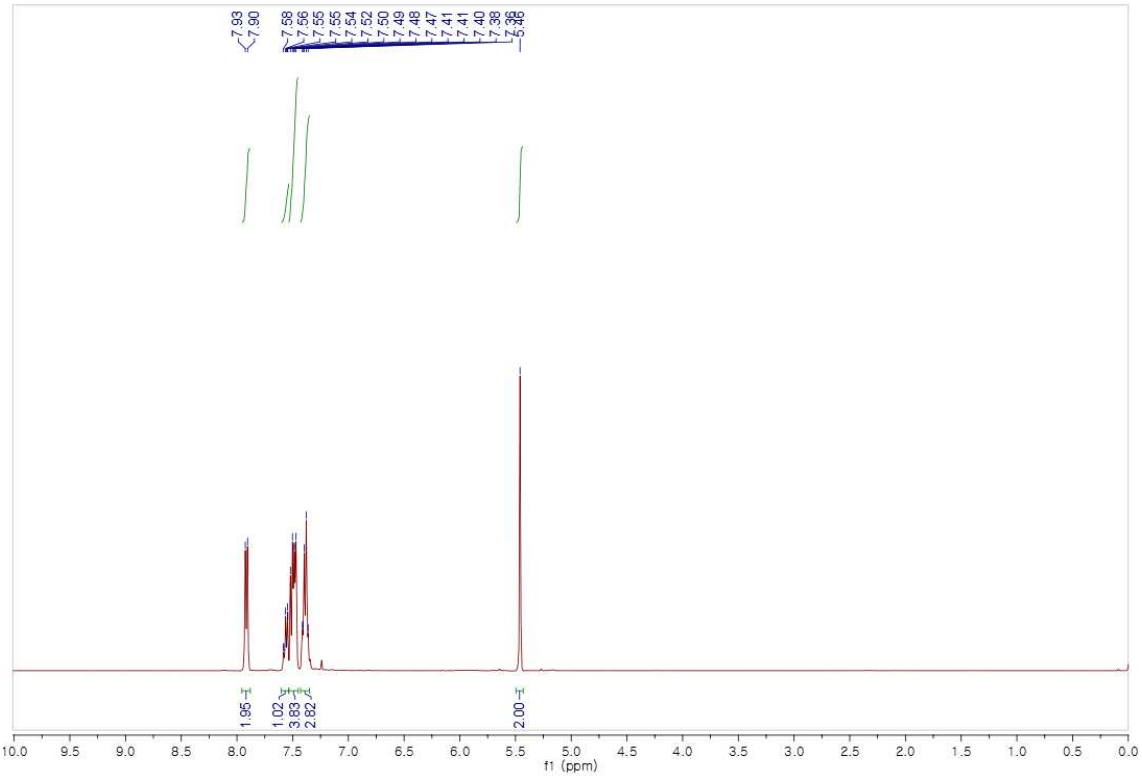

-105.09
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

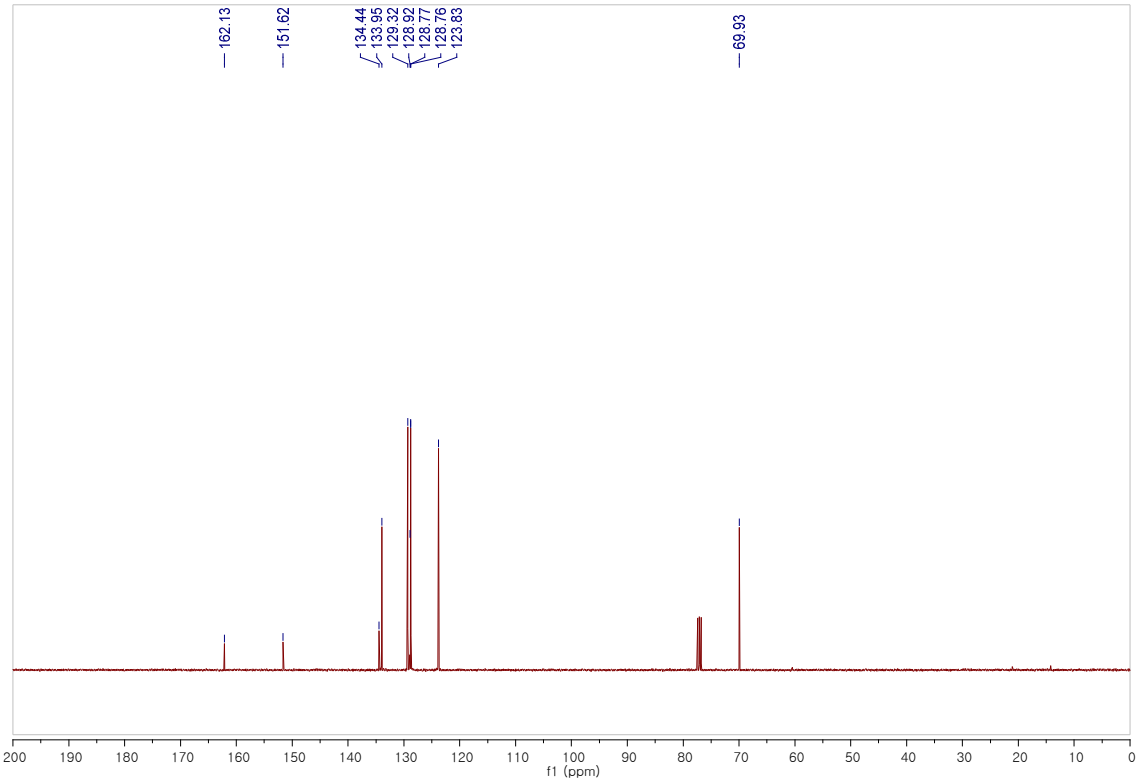
***tert*-Butyl 2-(4-nitrophenyl)azocarboxylate (2x)**



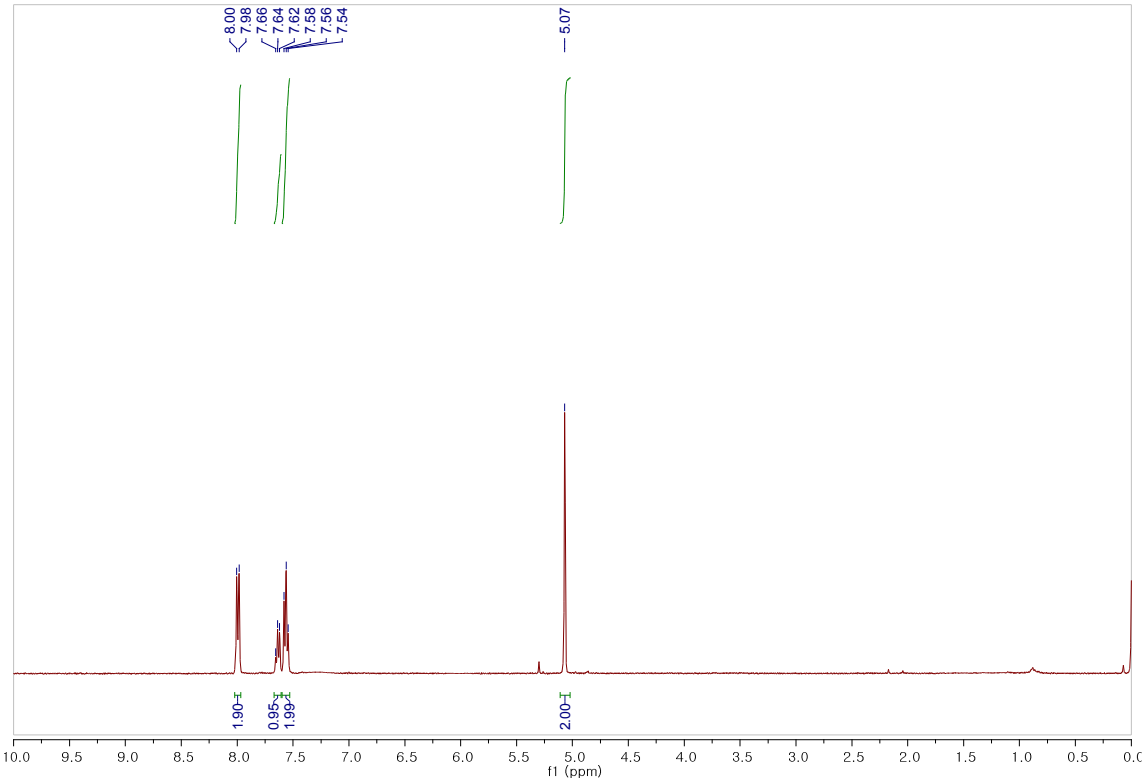


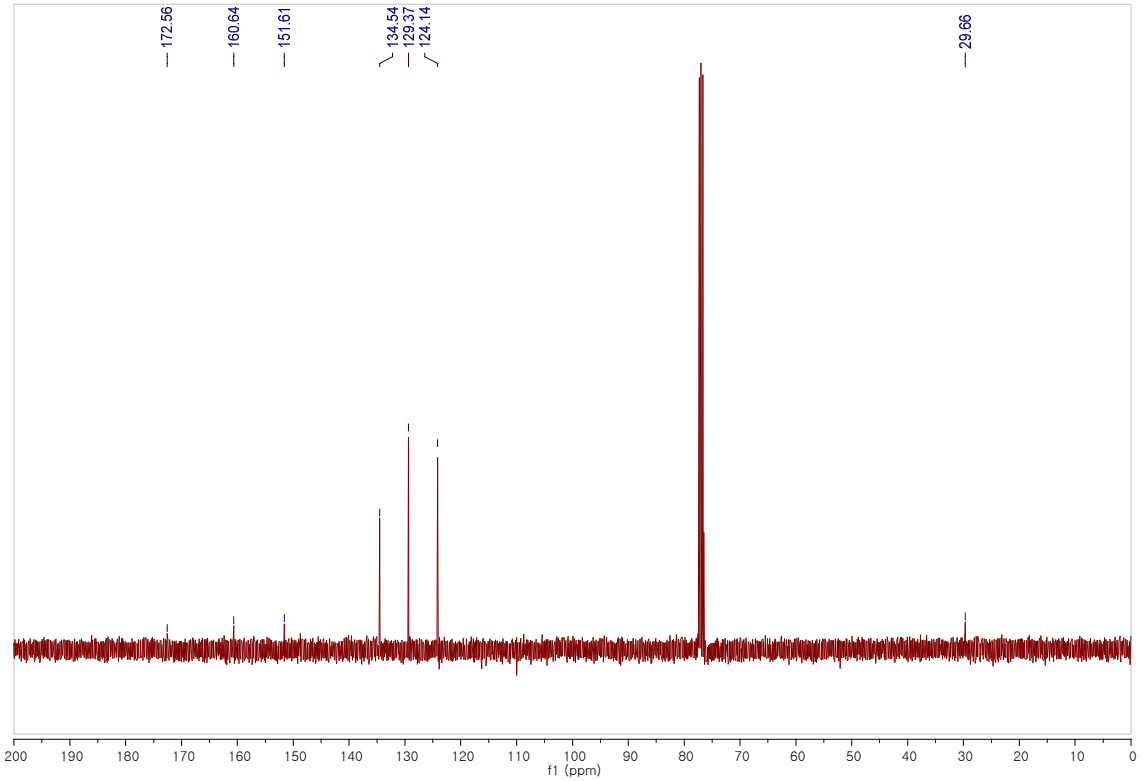
Benzyl 2-phenylazocarboxylate (2y)



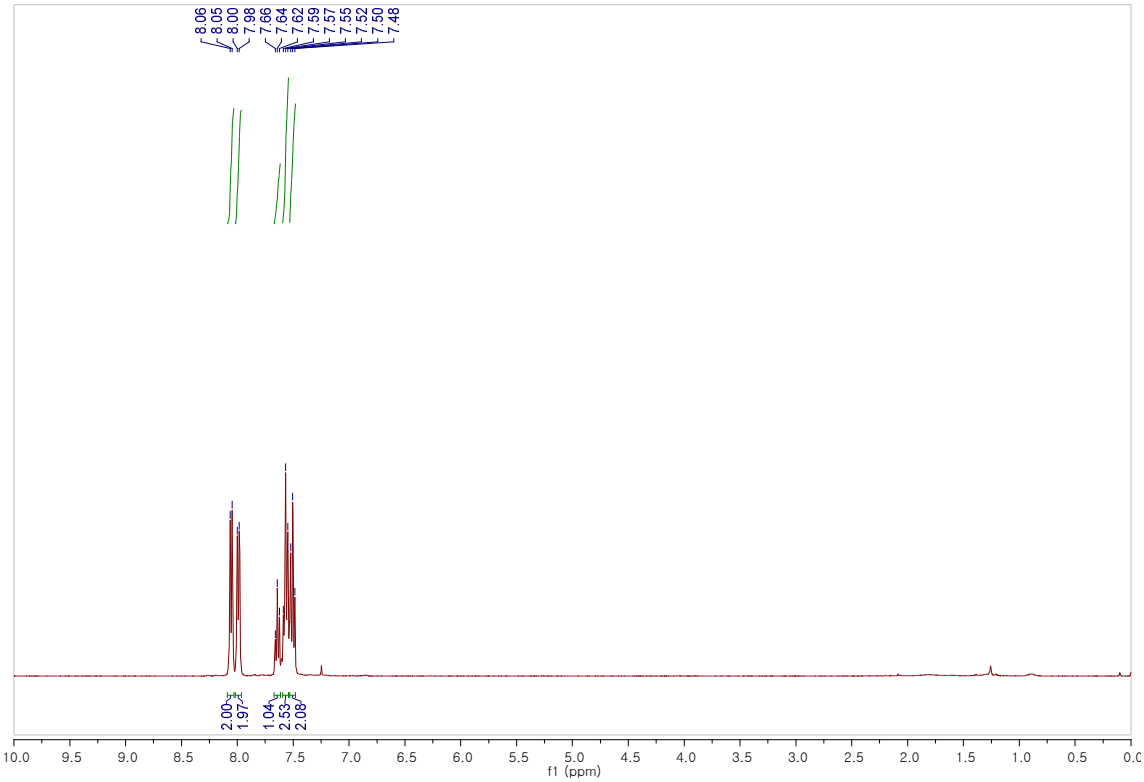


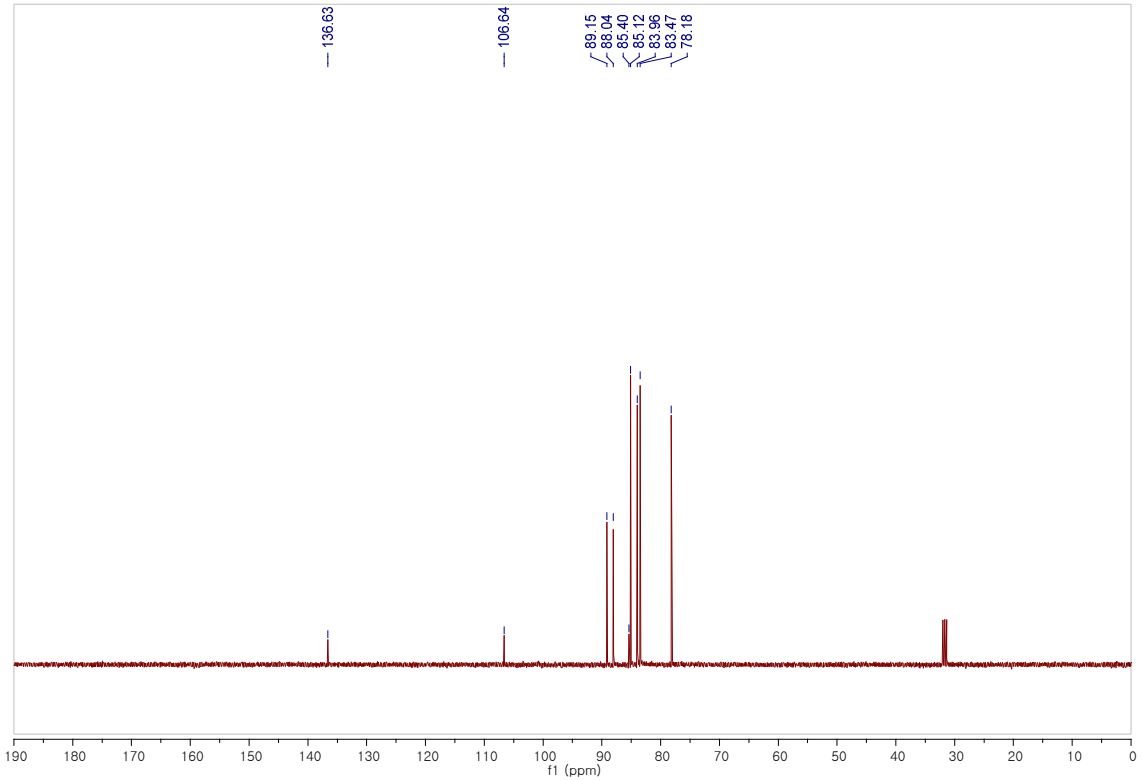
2,2,2,-Trichloroethyl 2-phenylazocarboxylate (2z)



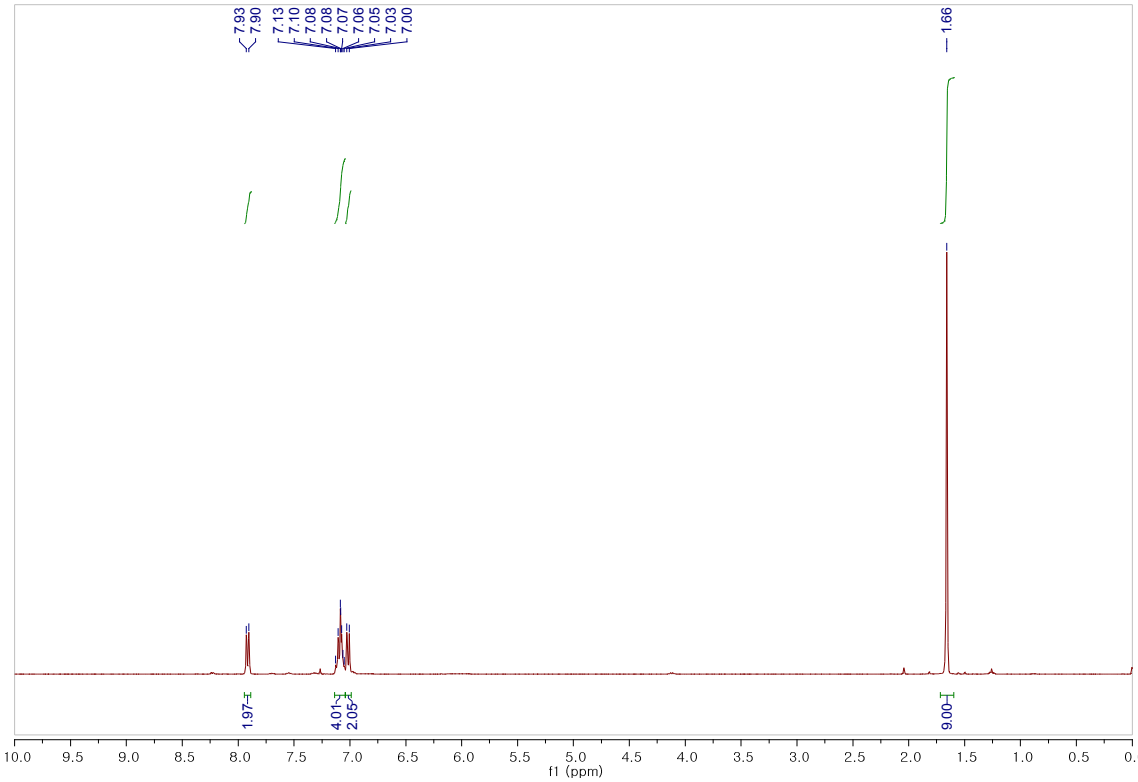


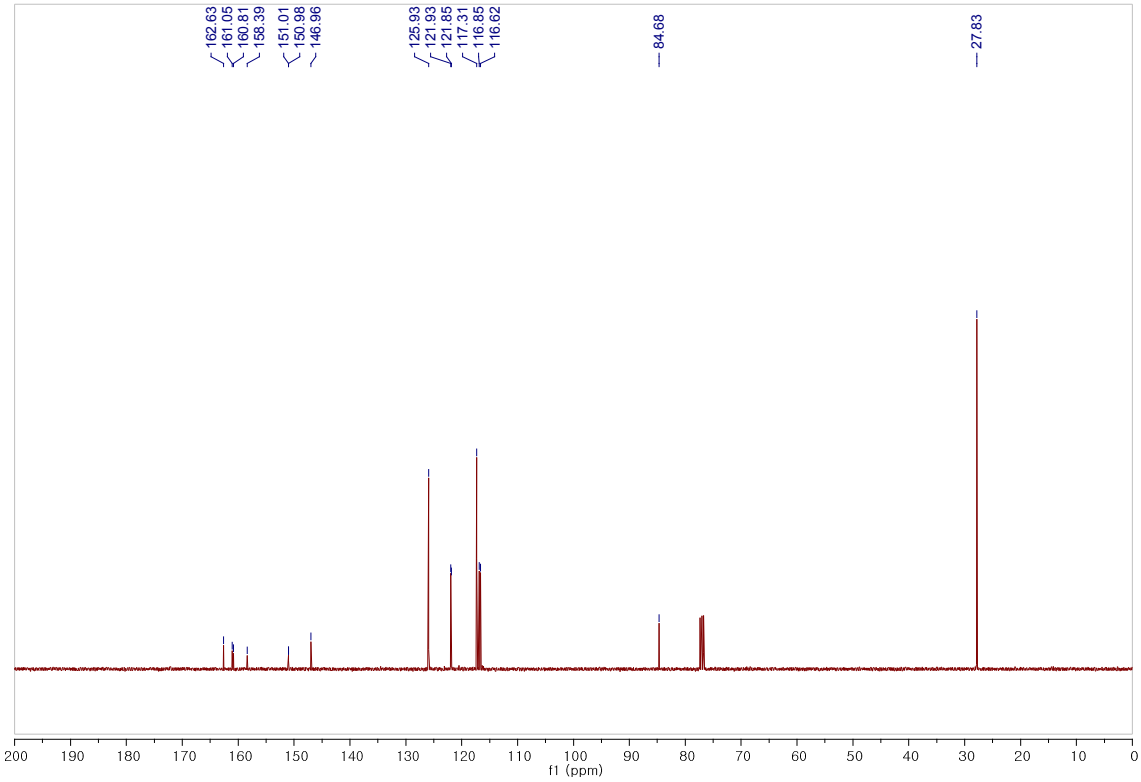
Benzoylazobenzene (2aa)

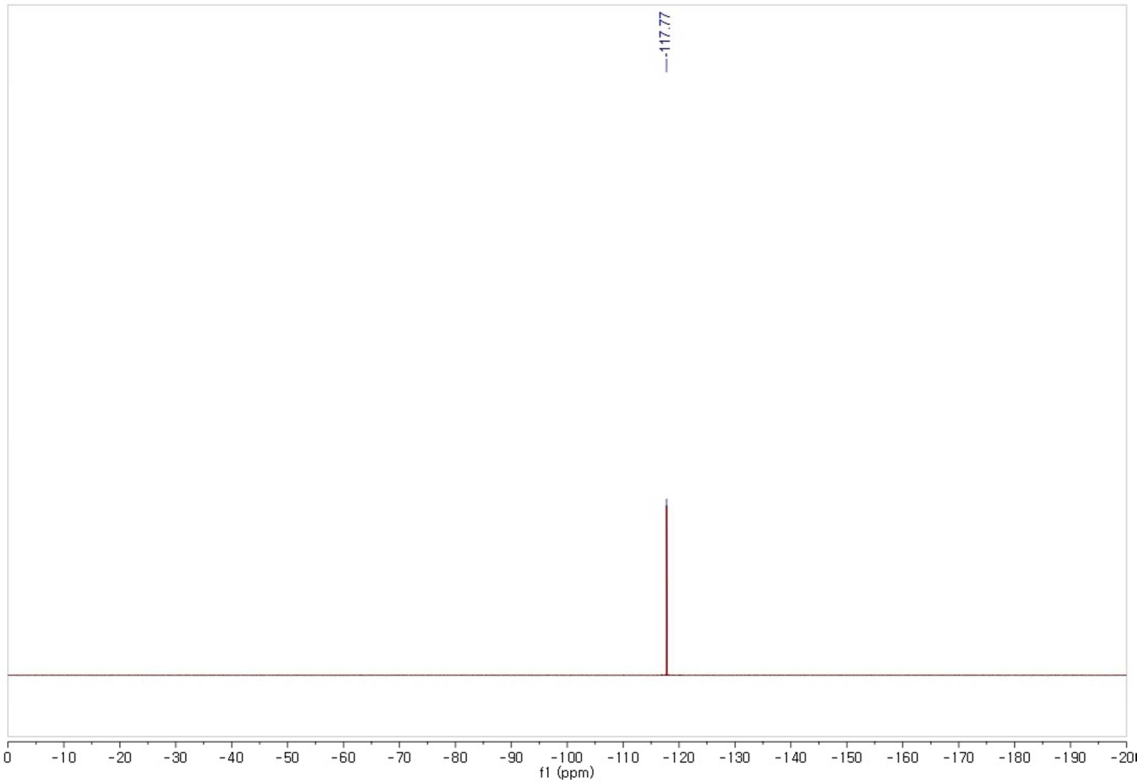




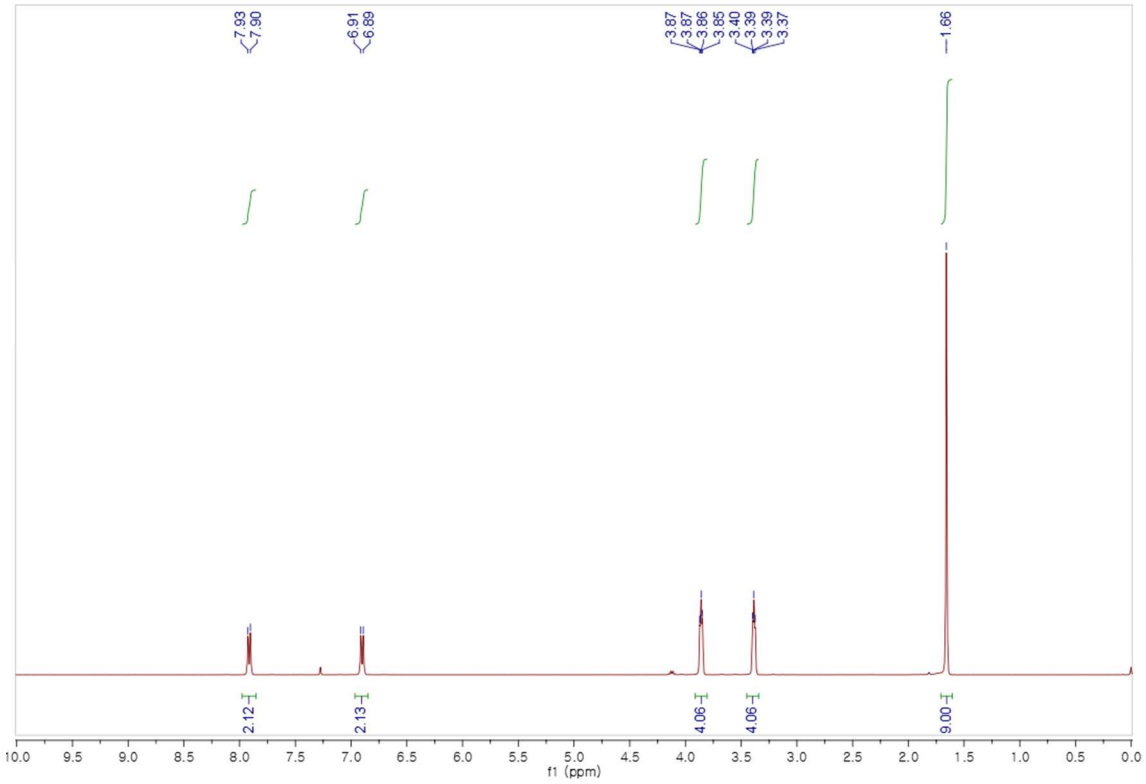
***tert*-Butyl 2-(4-(4'-fluorophenoxy)phenyl)azocarboxylate (3)**

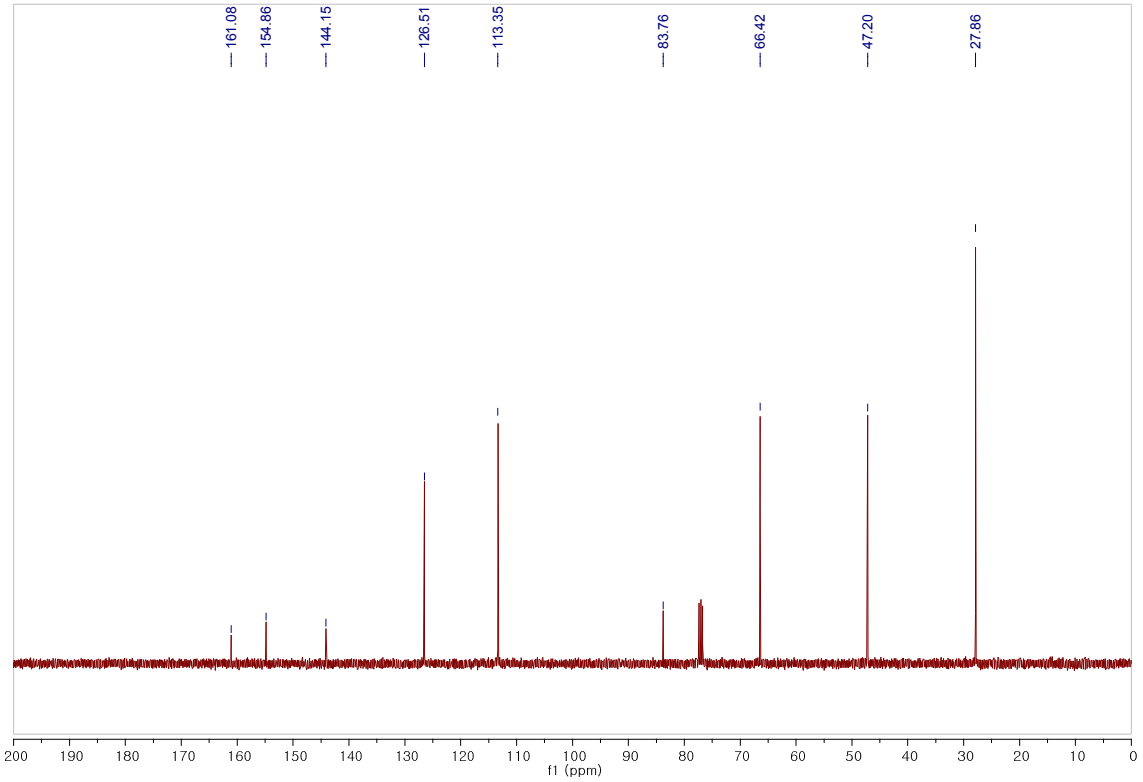




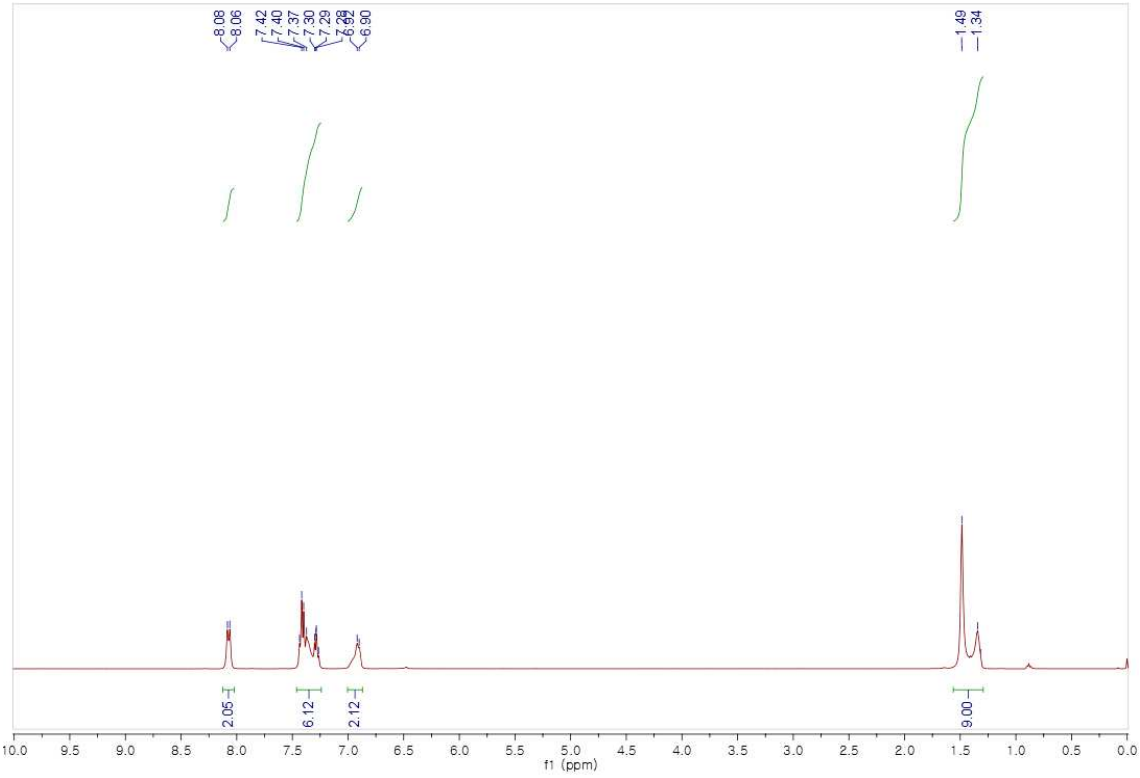

-117.77
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

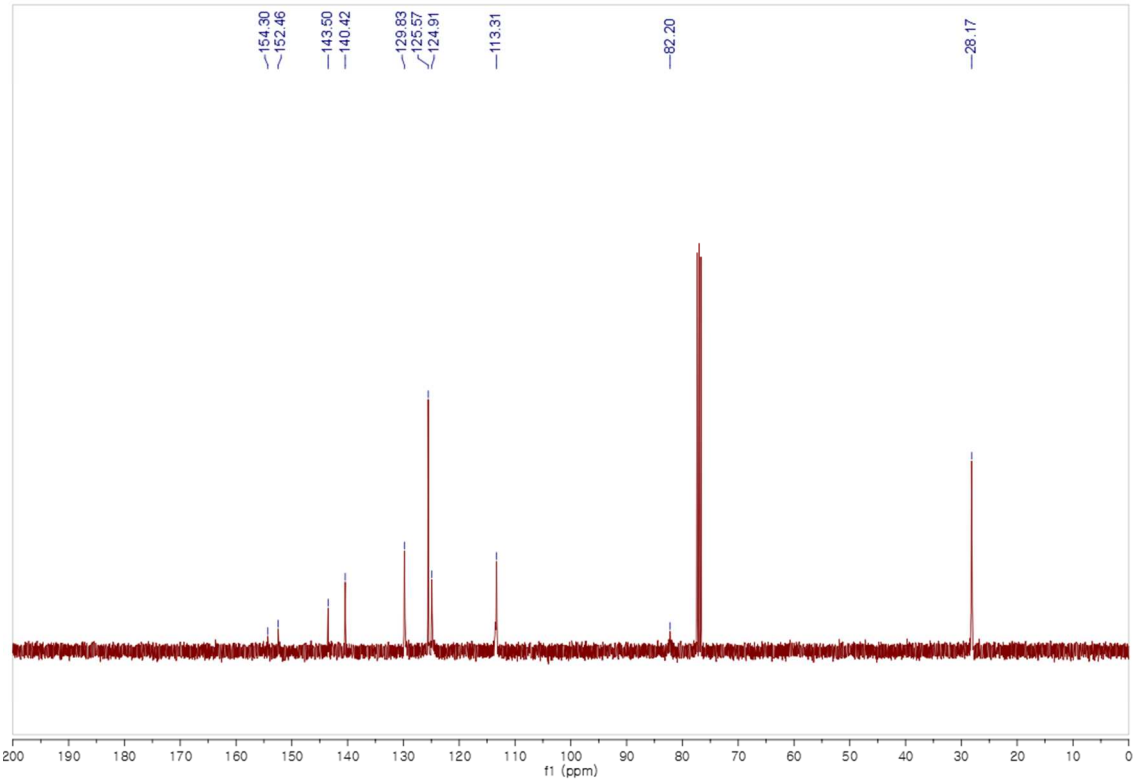
***tert*-Butyl 2-(*N*'-(4-Morpholin-4-yl-phenyl))azocarboxylate (4)**



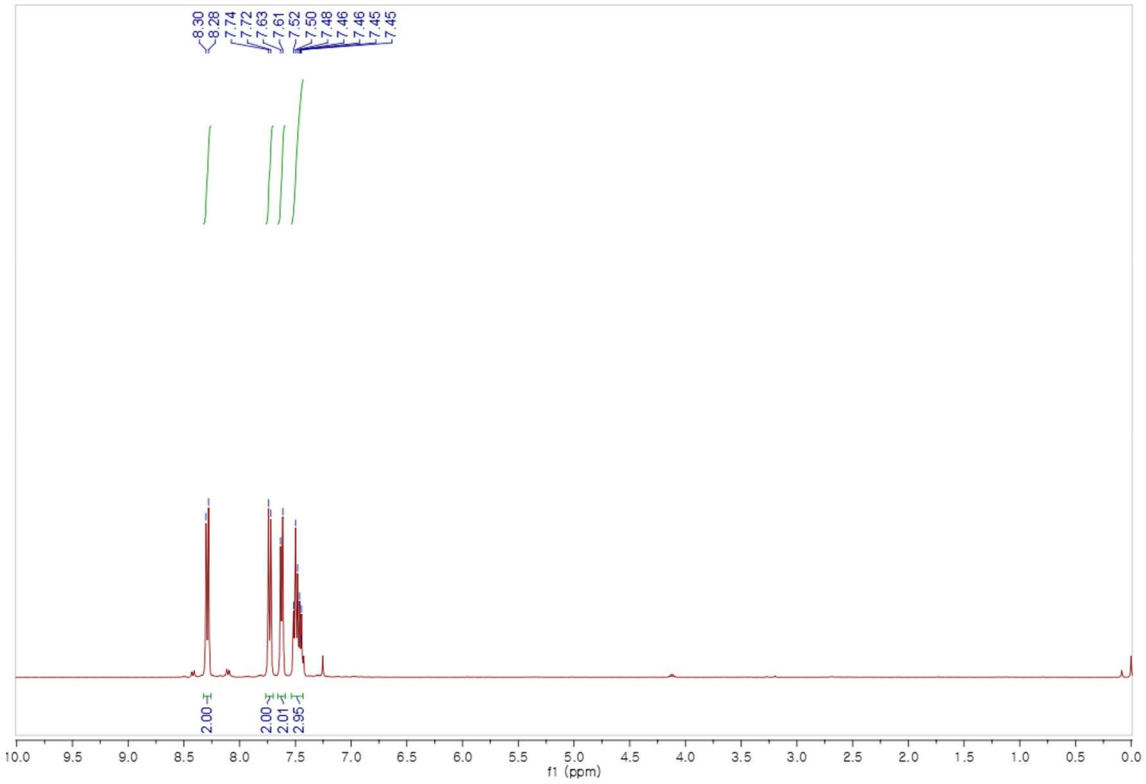


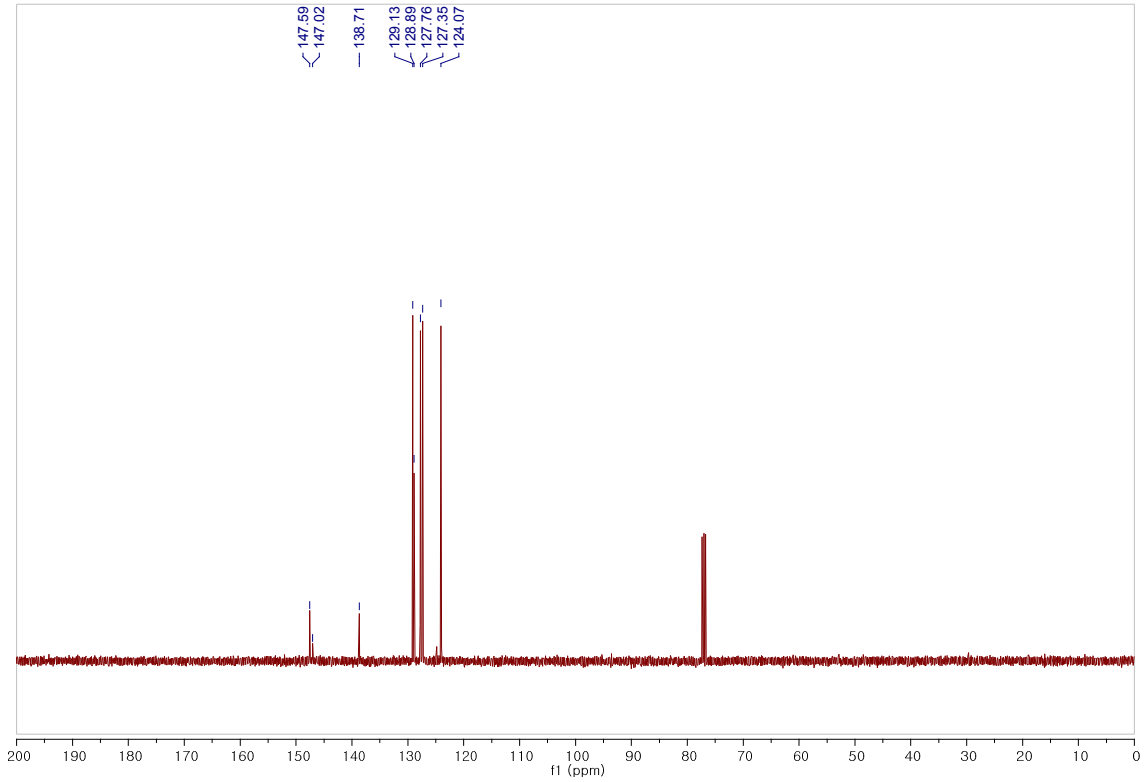
***tert*-Butyl 2-(4-nitrophenyl)-2-phenylhydrazinecarboxylate (5)**





1-Phenyl-4-nitrobenzene (6)





1-Iodo-4-nitrobenzene (7)