SUPPORTING INFORMATION

Selective *Ortho*-Bromination of Substituted Benzaldoximes using Pd-Catalyzed C-H Activation: application to the Synthesis of Substituted 2-Bromobenzaldehydes.

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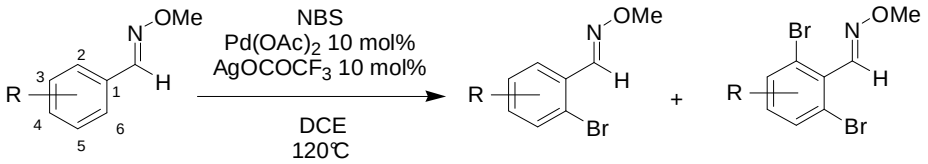
1. General.

All commercially available compounds were used as received without further purification. Silica gel 0.06-0.2 mm, 60 Å was used for all column chromatography. All microwave reactions were performed in a Biotage Initiator microwave oven using sealed Biotage microwave vials (0.5-2 mL, 2-5 mL or 10-20 mL). Temperatures were measured with an IR-sensor and reaction times given as hold times. NMR spectra were recorded in chloroform-*d* at 400 or 500 MHz for ^{1}H NMR spectra and 100 MHz or 125 MHz for ^{13}C NMR spectra. Chemical shifts were reported in ppm and multiplicities were described as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants '*J*' were reported in Hz. Data for ^{13}C NMR were reported in terms of chemical shift. IR spectra were recorded on KBr discs. Melting points were determined on a Kofler melting point apparatus. High resolution mass spectral (EI-HRMS) data were performed at 70 eV. The configuration of (*E*)-benzaldehyde *O*-methyloxime **1a** was determined from NOE experiment data realized on pure isolated product. The configuration of (*E*)-2-bromo-5-nitrobenzaldehyde *O*-methyloxime **7b** was obtained from RX crystallography data. For all others compounds, the configuration of diastereoisomers was determined by comparison between ^{1}H NMR shifts of references and undetermined compound. All diastereoisomers ratios were determined from ^{1}H NMR of mixture before purification on silica gel.

2. Influence of AcOH on the bromination reaction

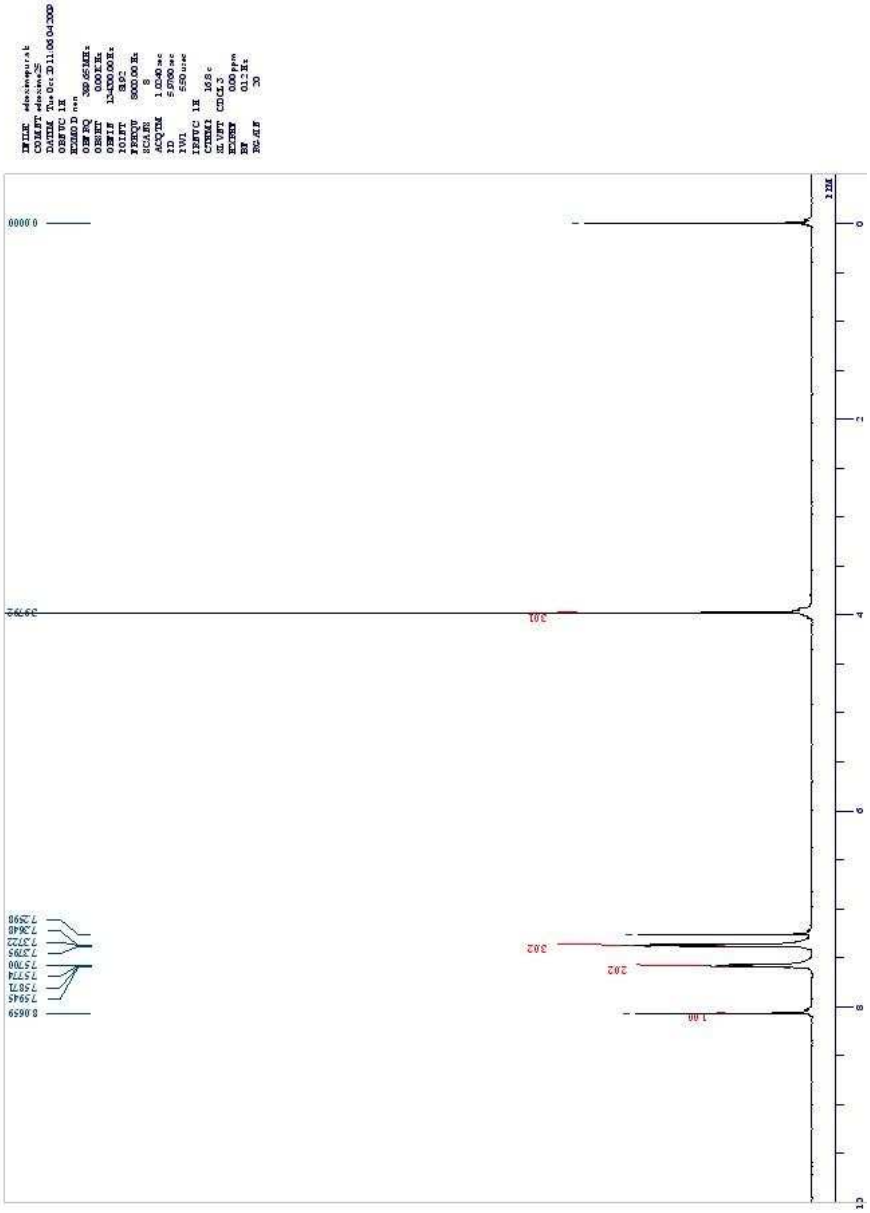


6a, 7a, 9a, 10a

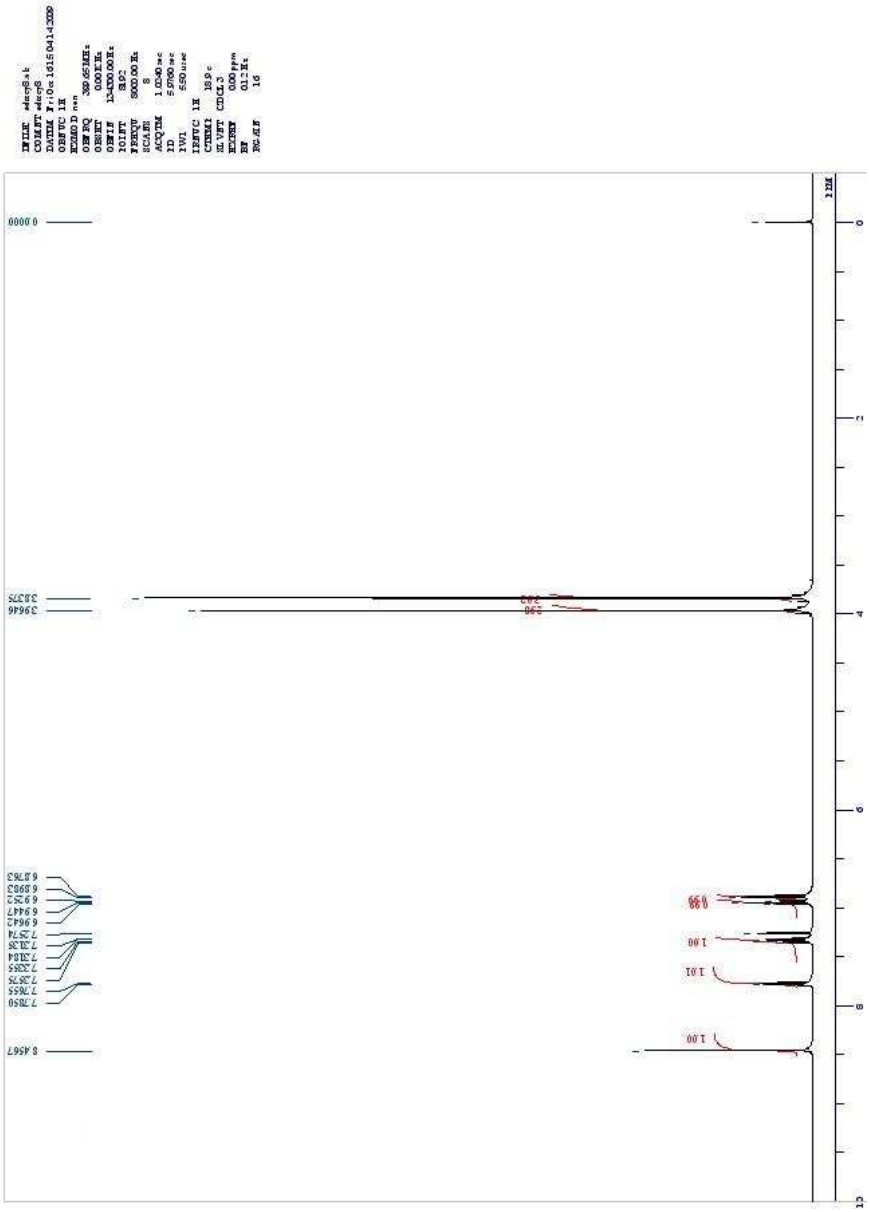
Substituent	Starting material	NBS eq.	AcOH eq.	Reaction time	% Br	% diBr
3-Cl	**6a**	1	0	2h30	47	-
		1	1		67	15
3-NO_2	**7a**	2	0	24h	53	-
		2	1		38	-
3-F	**9a**	2	0	2h30	47	49
			1		25	75
4-CF_3	**10a**	2	0	2h30	50	-
			1	2h30	63	6
			1	24h	63	20

3. ^{1}H NMR Spectra of substituted benzaldehyde O-methyloximes 1a-14a

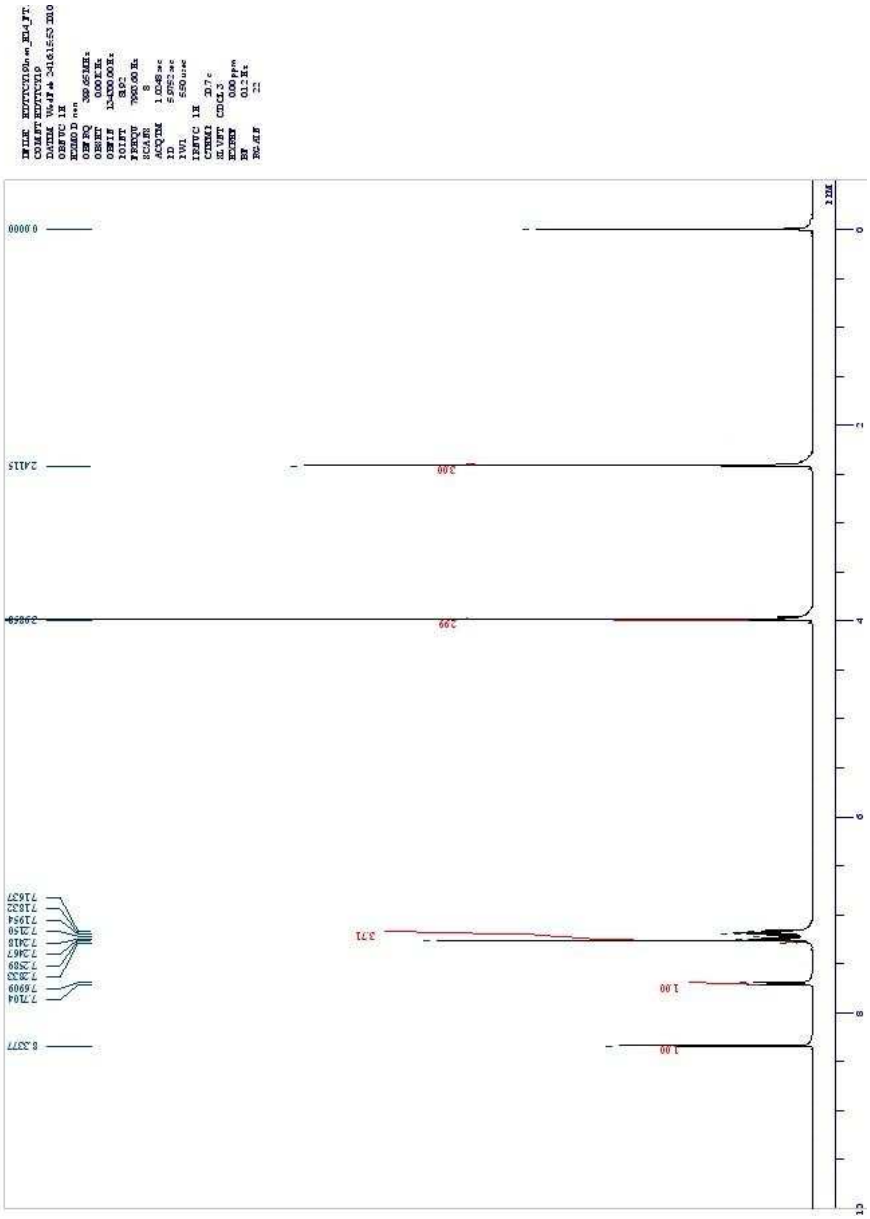
(*E*)-Benzaldehyde *O*-methyloxime 1a



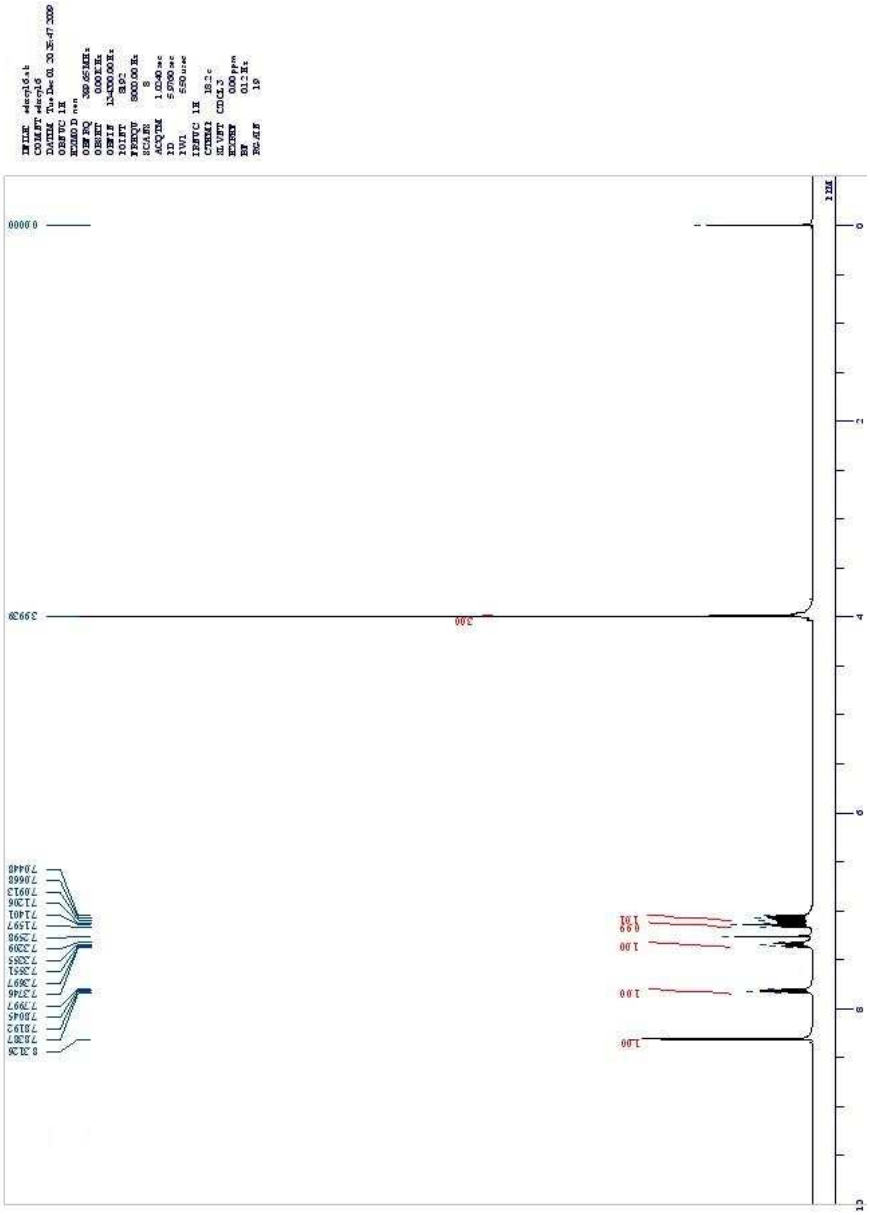
(*E*)-2-Methoxybenzaldehyde *O*-methyloxime 2a



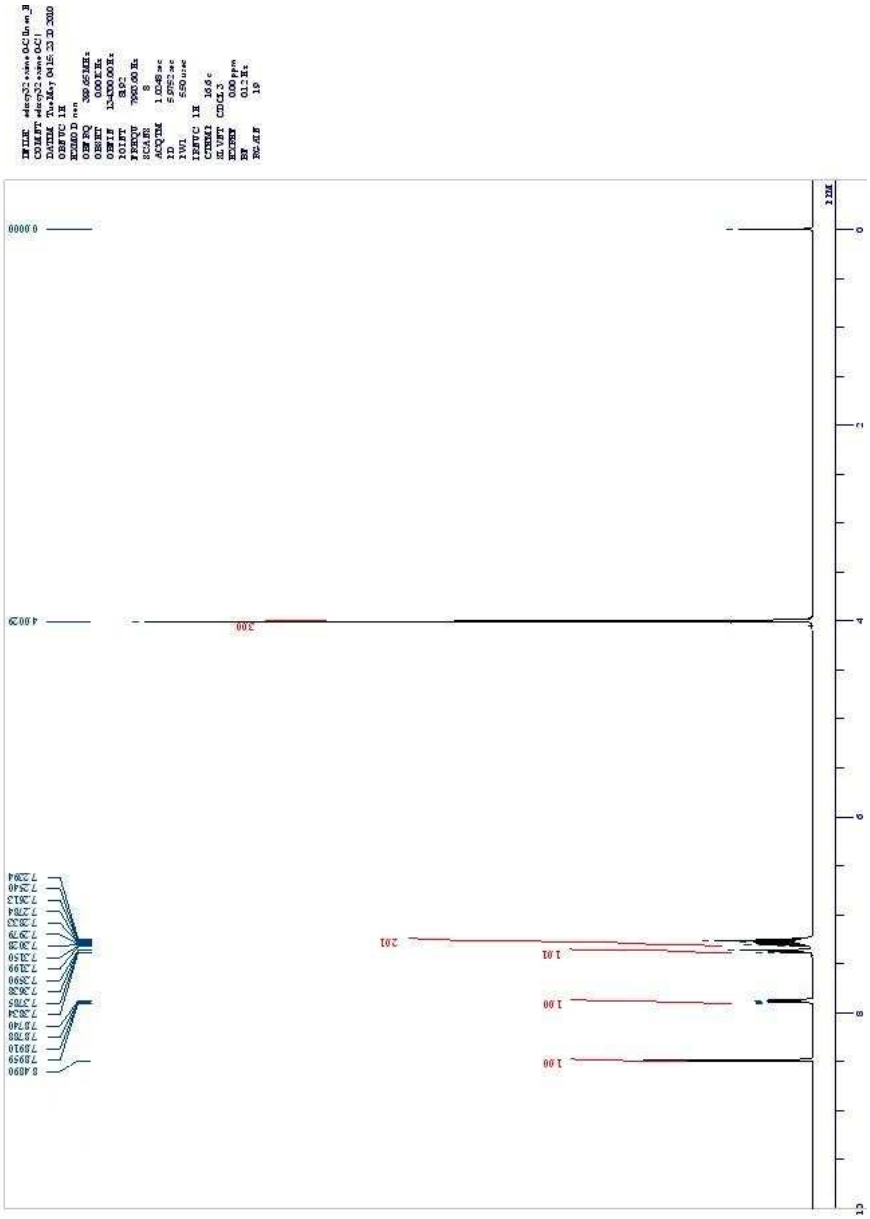
(*E*)-2-Methylbenzaldehyde *O*-methyloxime 3a



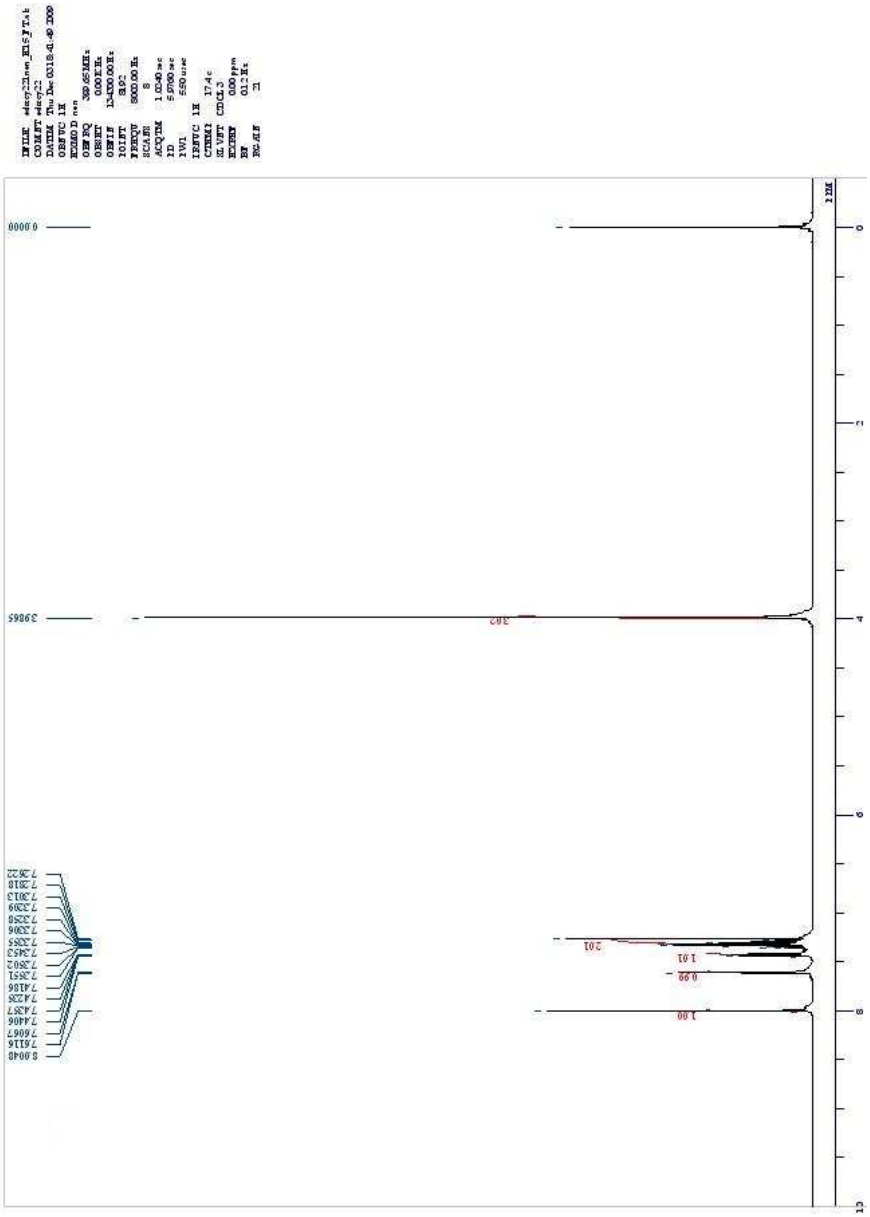
(*E*)-2-Fluorobenzaldehyde *O*-methyloxime 4a



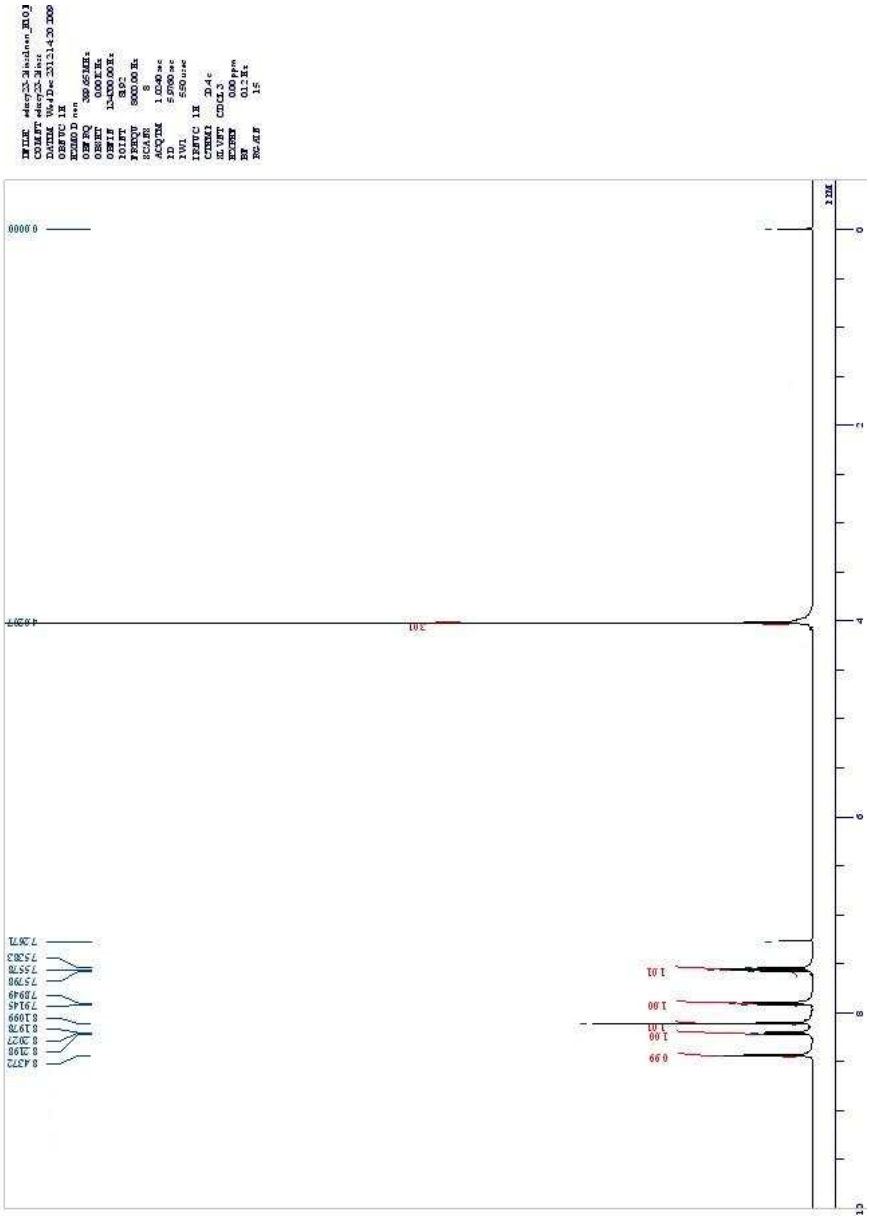
(*E*)-2-Chlorobenzaldehyde *O*-methyloxime 5a



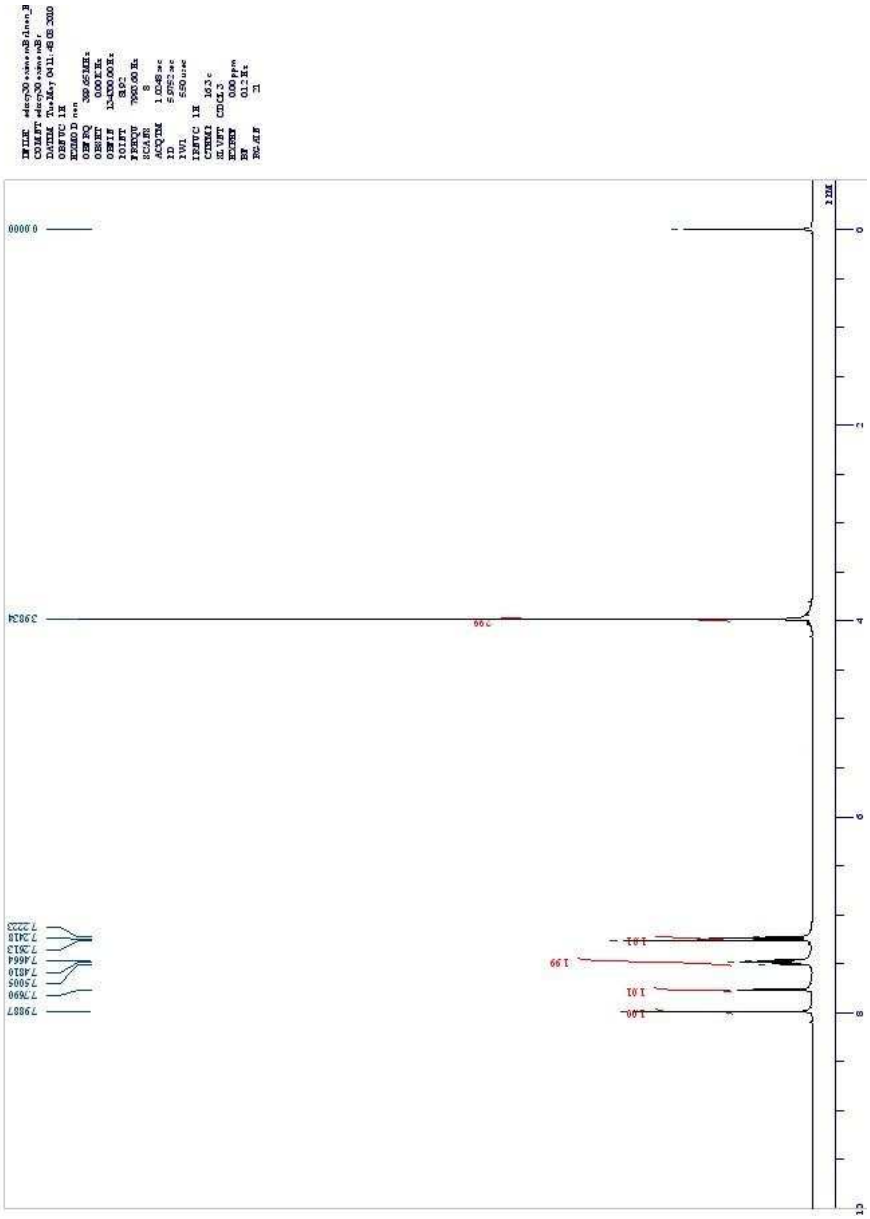
(*E*)-3-Chlorobenzaldehyde *O*-methyloxime 6a



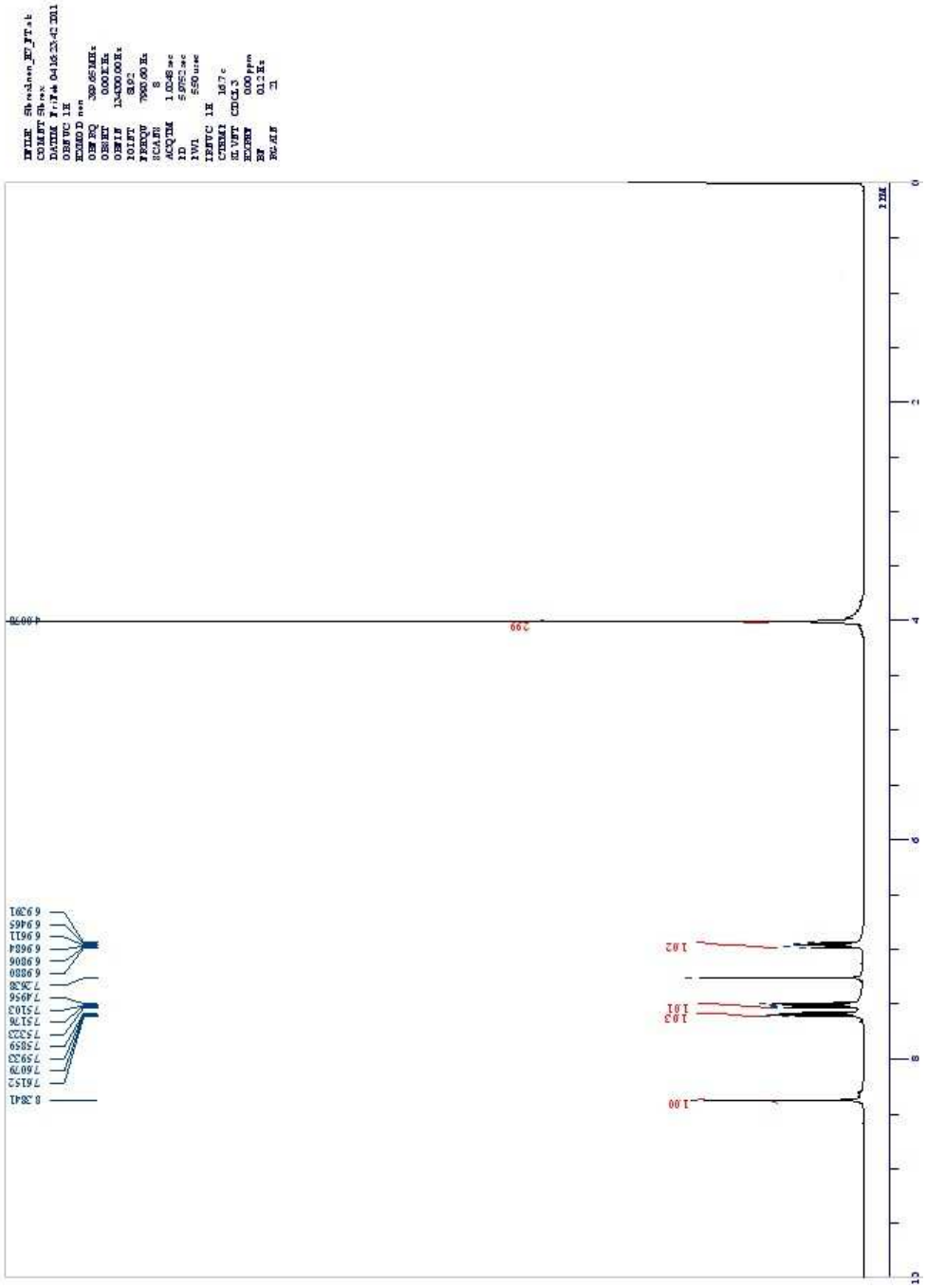
(*E*)-3-Nitrobenzaldehyde *O*-methyloxime 7a



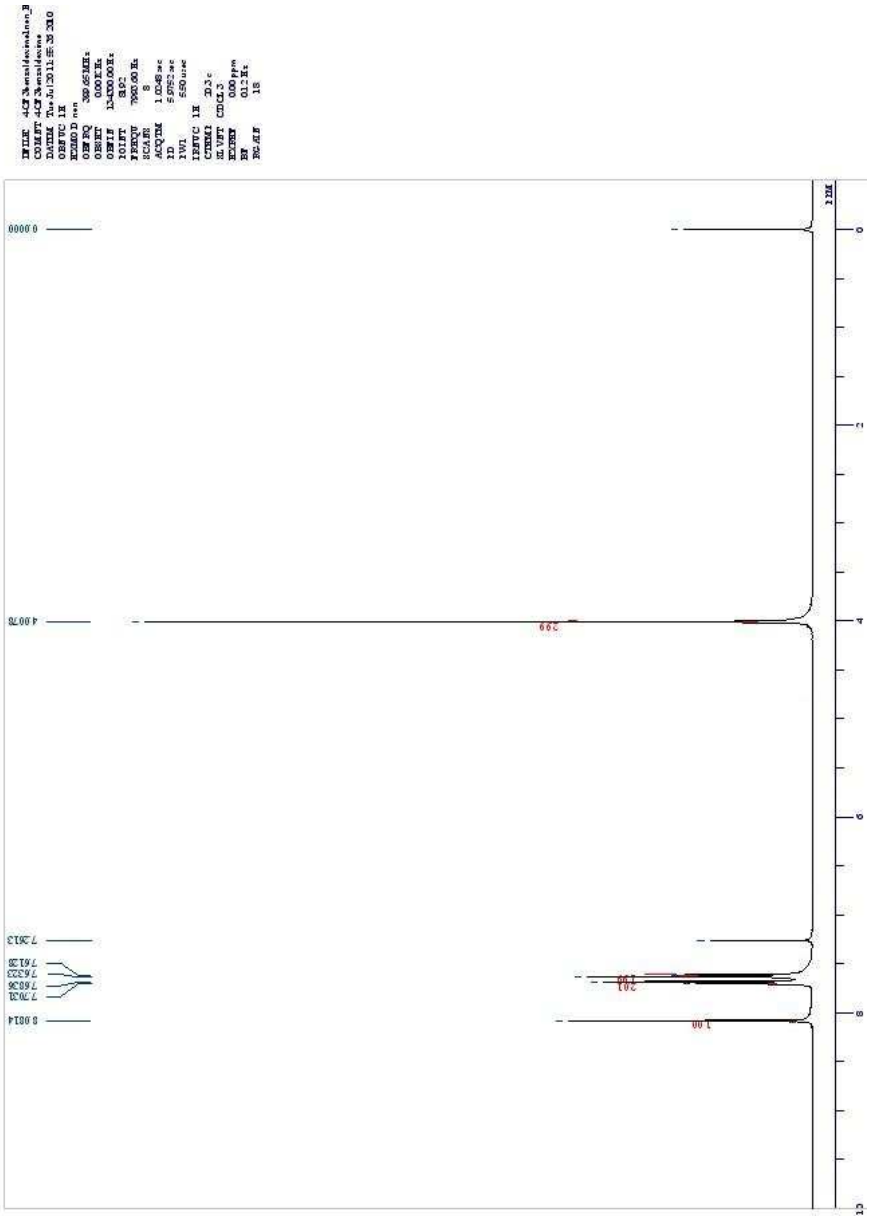
(*E*)-3-Bromobenzaldehyde *O*-methyloxime 8a



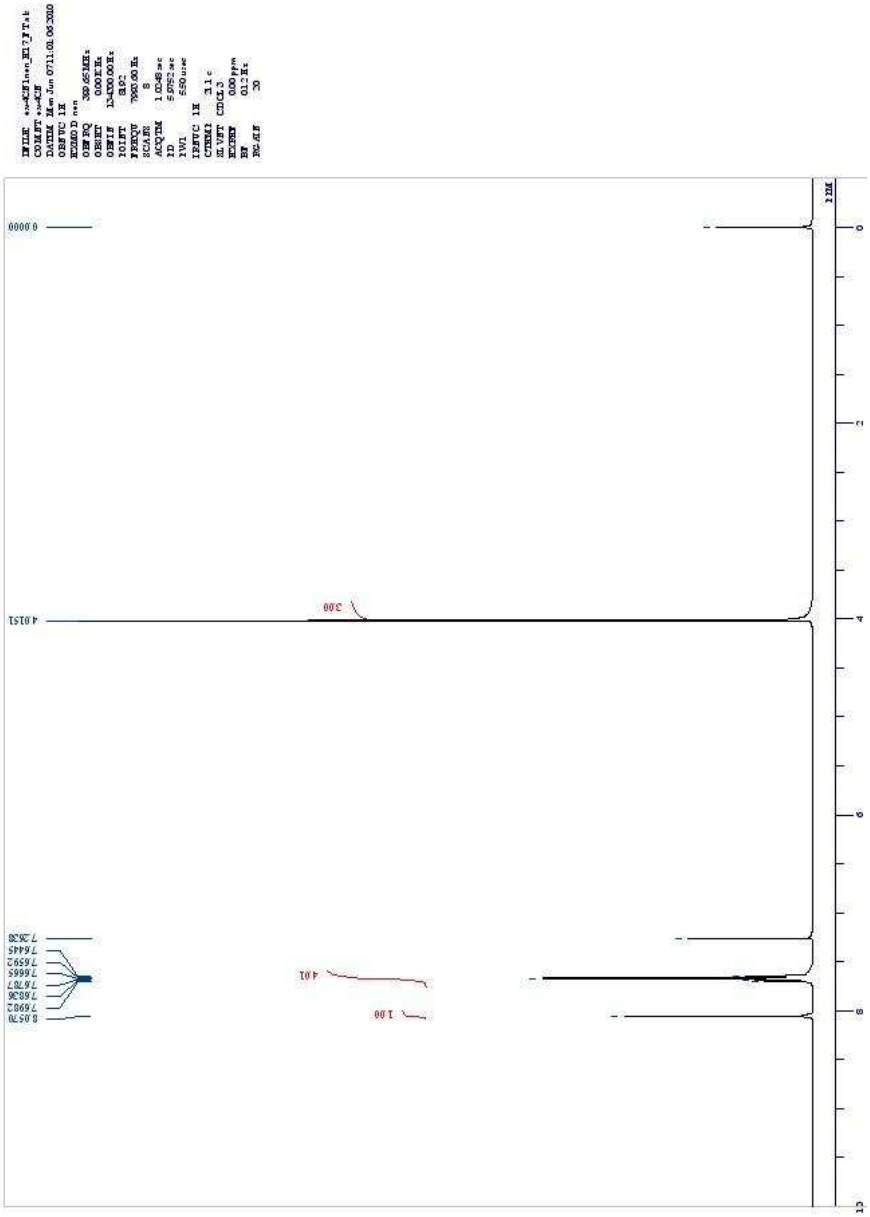
(*E*)-3-Fluorobenzaldehyde *O*-methyloxime 9a



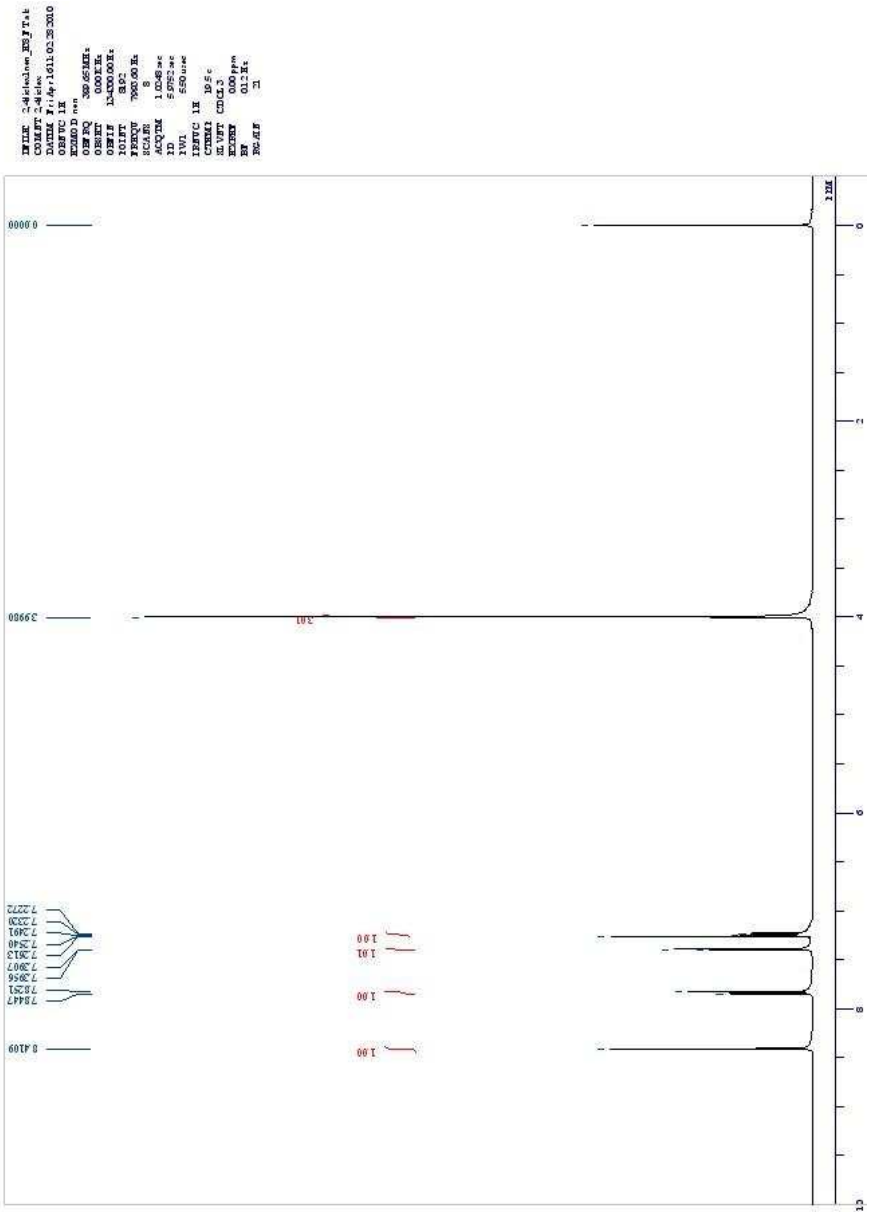
(*E*)-4-Trifluoromethylbenzaldehyde *O*-methyloxime 10a



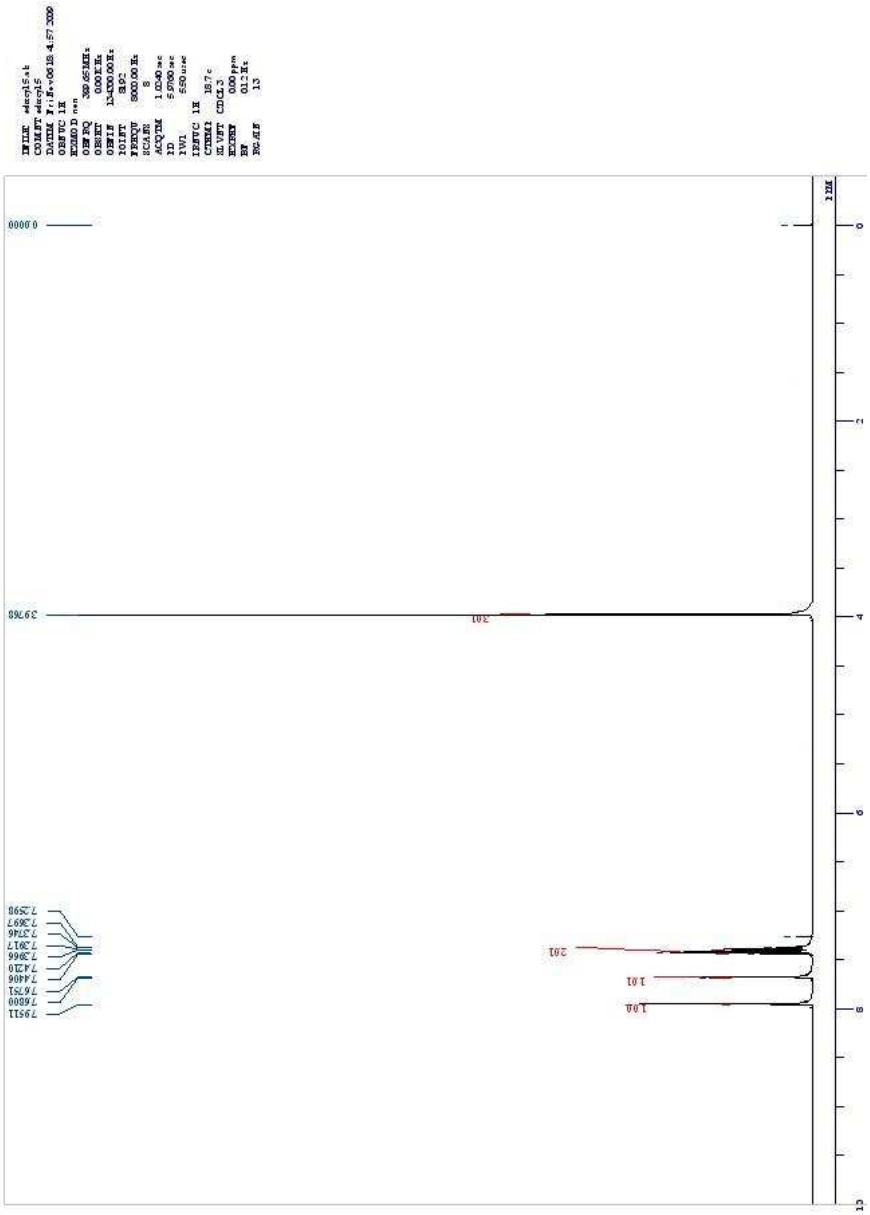
(*E*)-4-Cyanobenzaldehyde *O*-methyloxime 11a



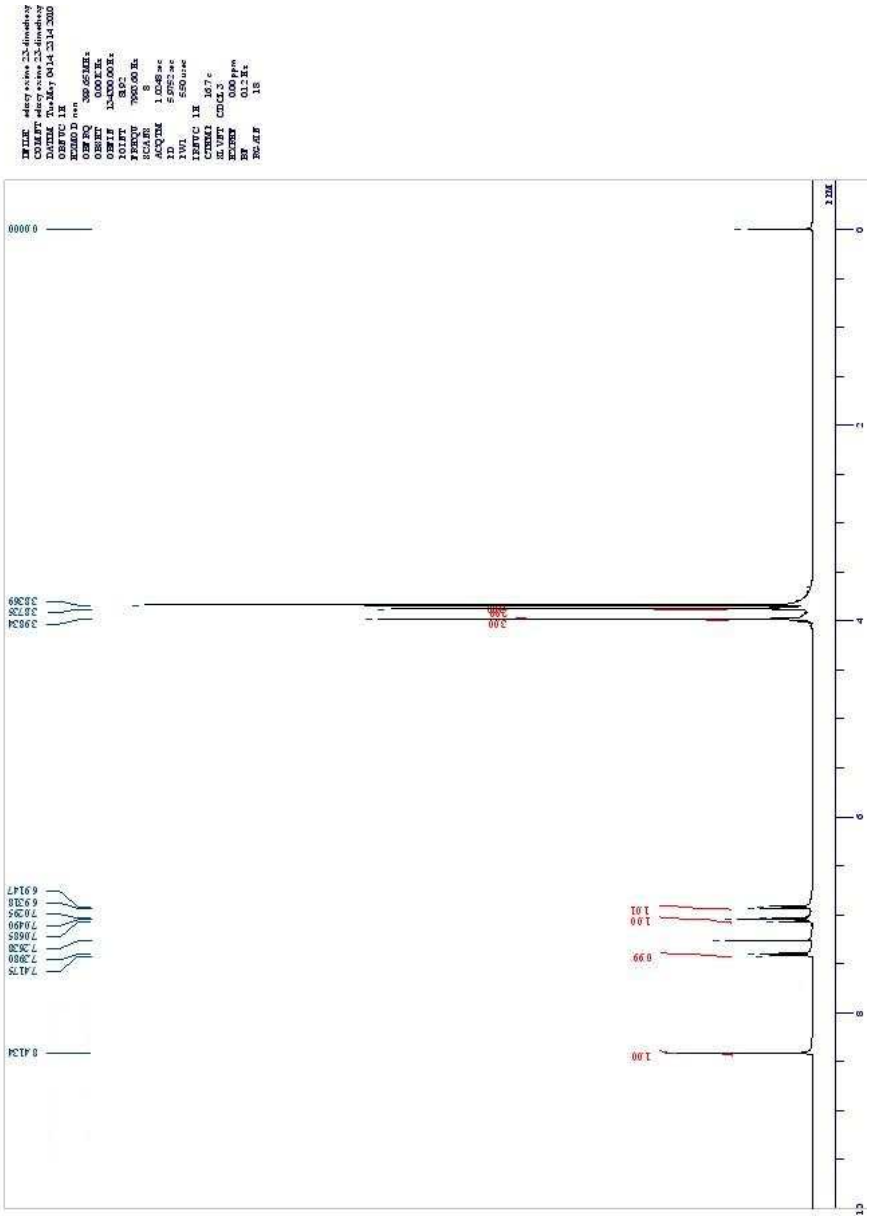
(*E*)-2,4-Dichlorobenzaldehyde *O*-methyloxime 12a



(*E*)-3,4-Dichlorobenzaldehyde *O*-methyloxime 13a

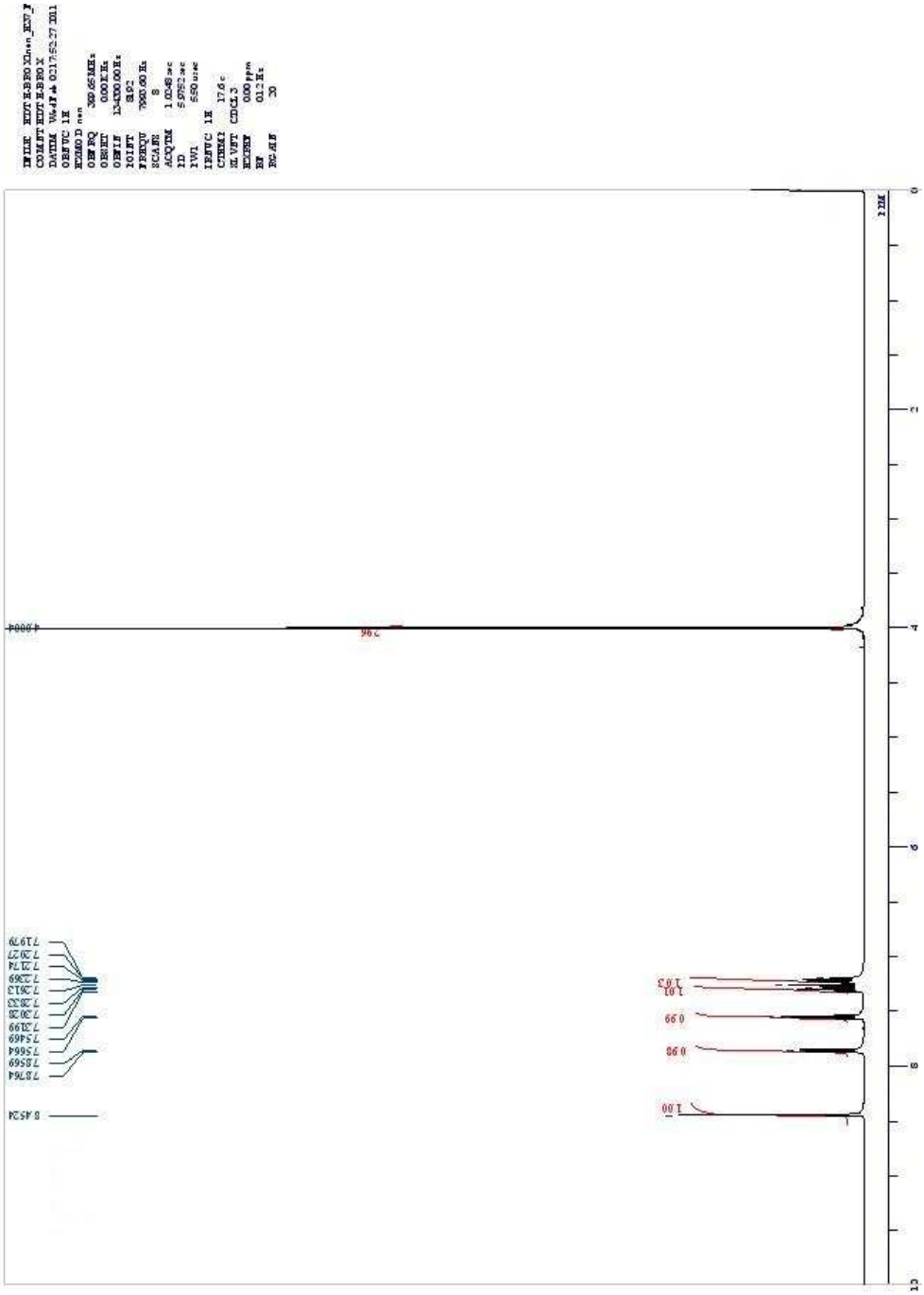


(*E*)-2,3-Dimethoxybenzaldehyde *O*-methyloxime 14a

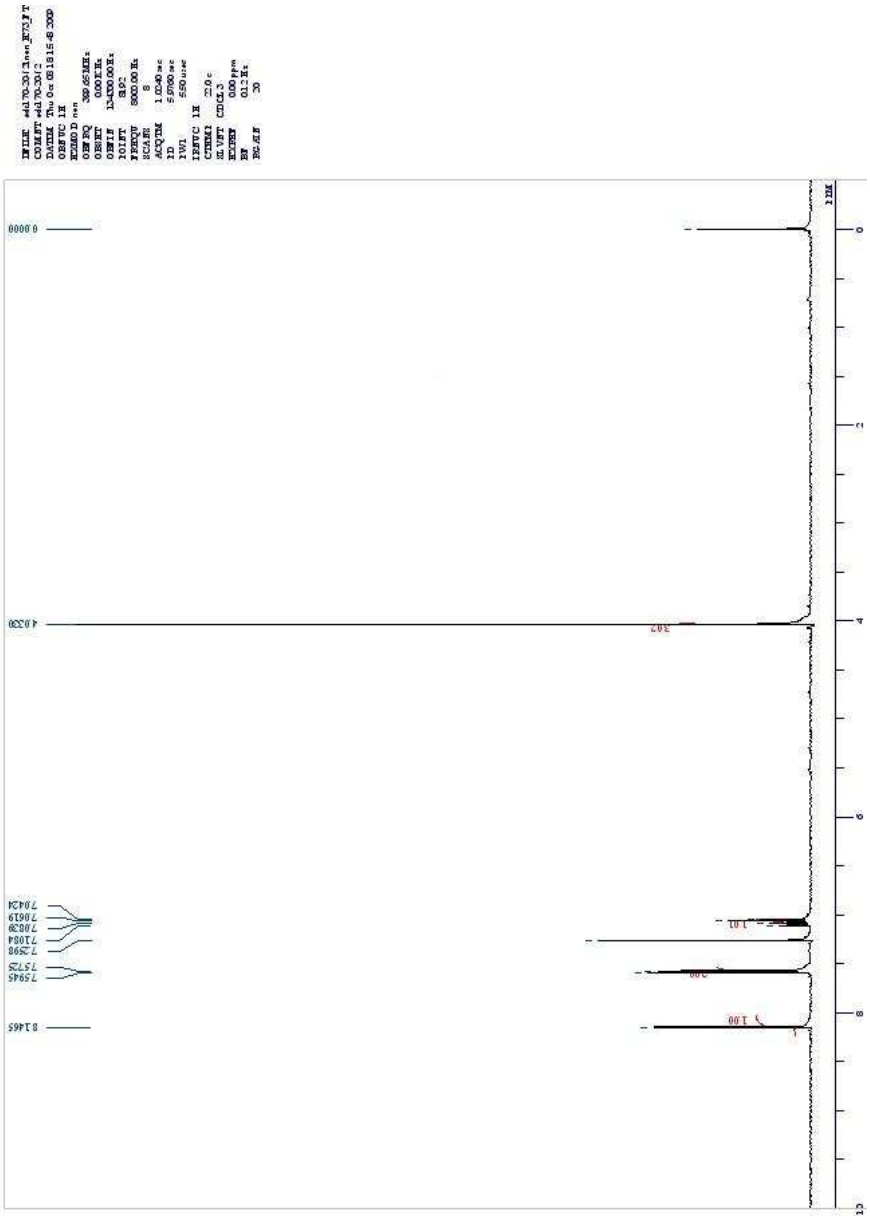


4. ^{1}H NMR of substituted 2-bromobenzaldehyde *O*-methyloximes 1b-14b

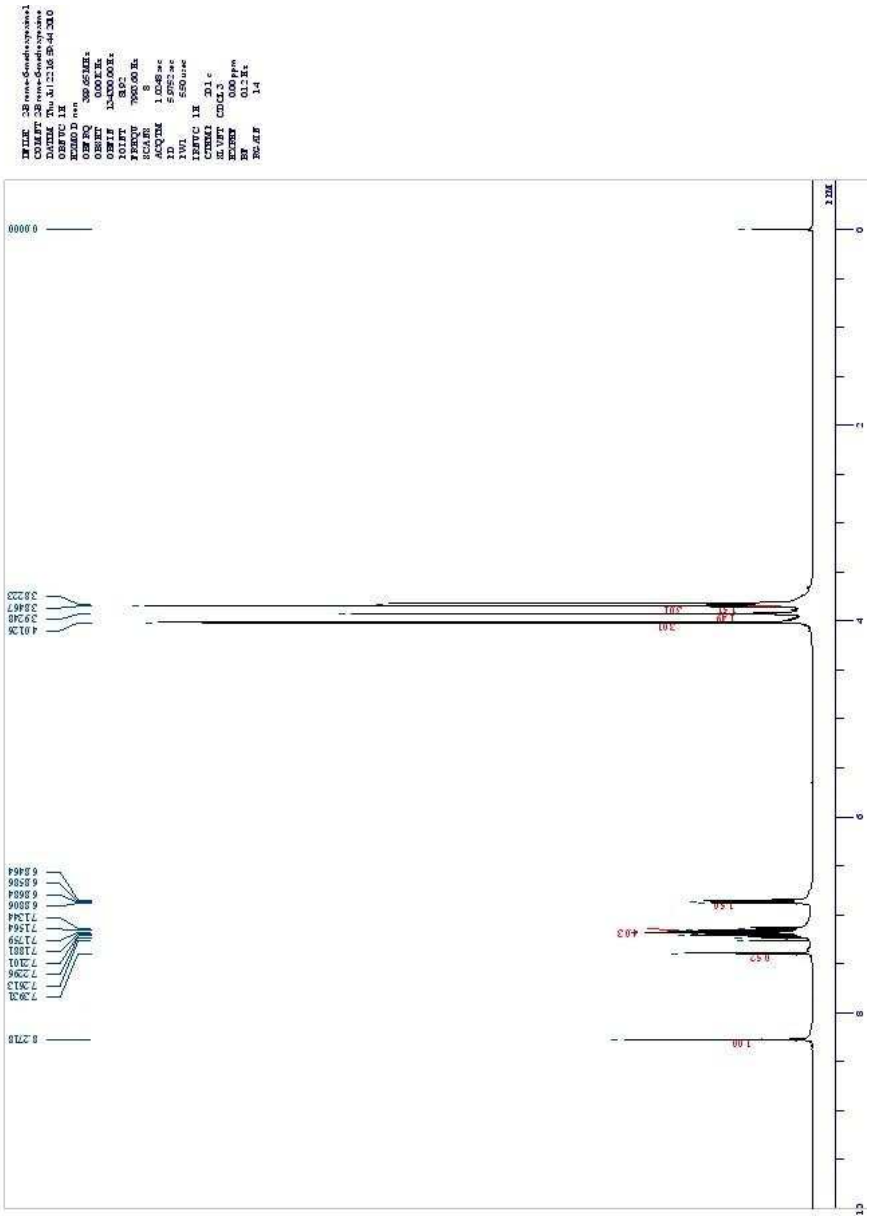
(*E*)-2-Bromobenzaldehyde *O*-methyloxime 1b



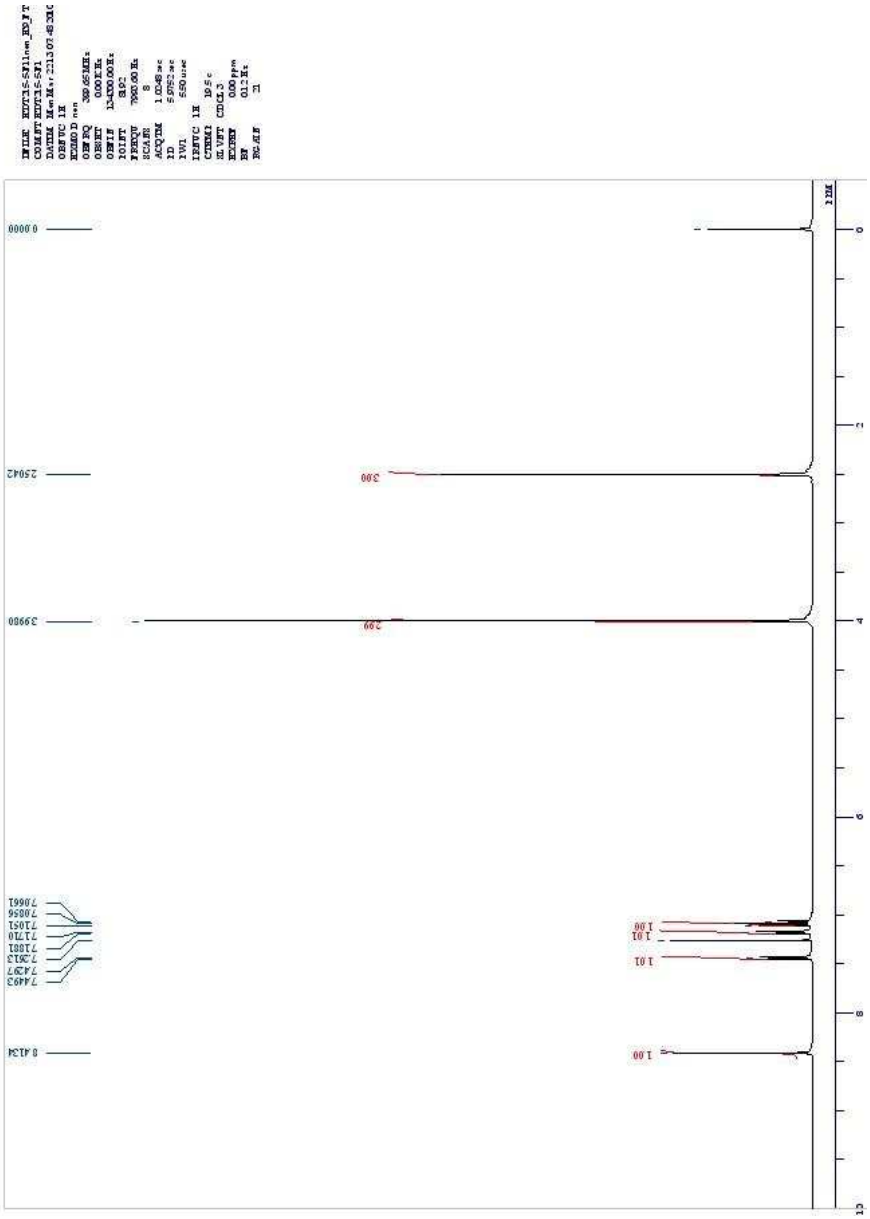
(*E*)-2,6-Dibromobenzaldehyde *O*-methyloxime 1c



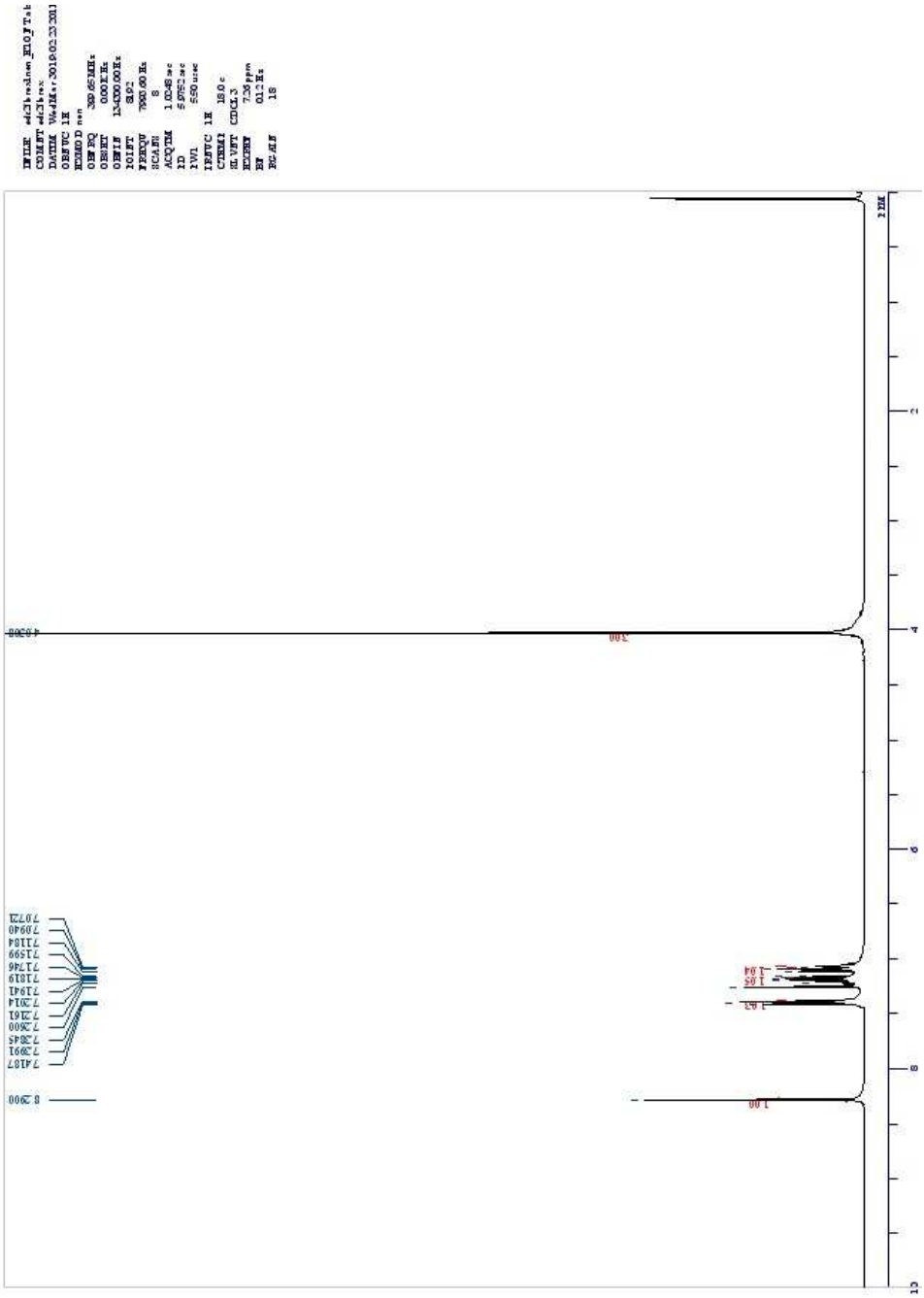
2-Bromo-6-methoxybenzaldehyde *O*-methyloxime 2b



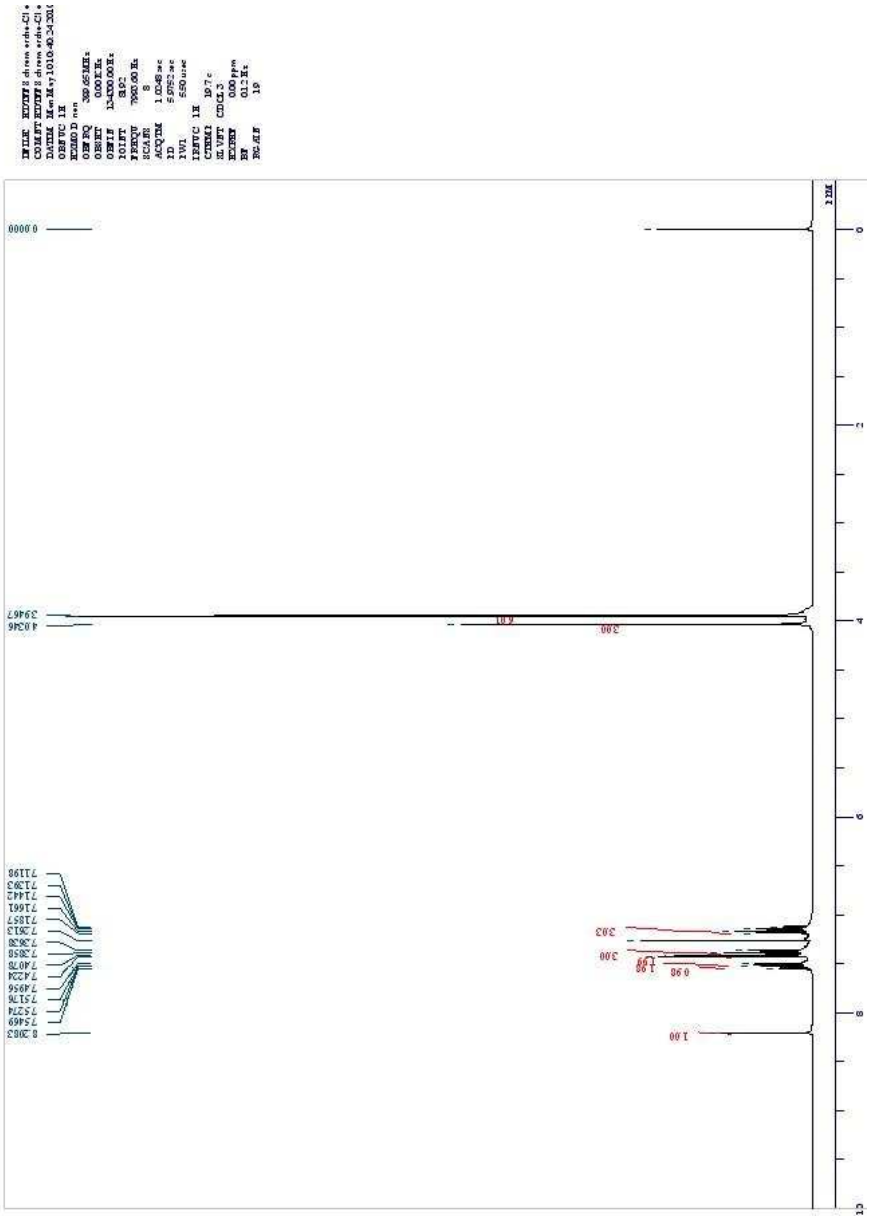
(*E*)-2-Bromo-6-methylbenzaldehyde *O*-methyloxime 3b



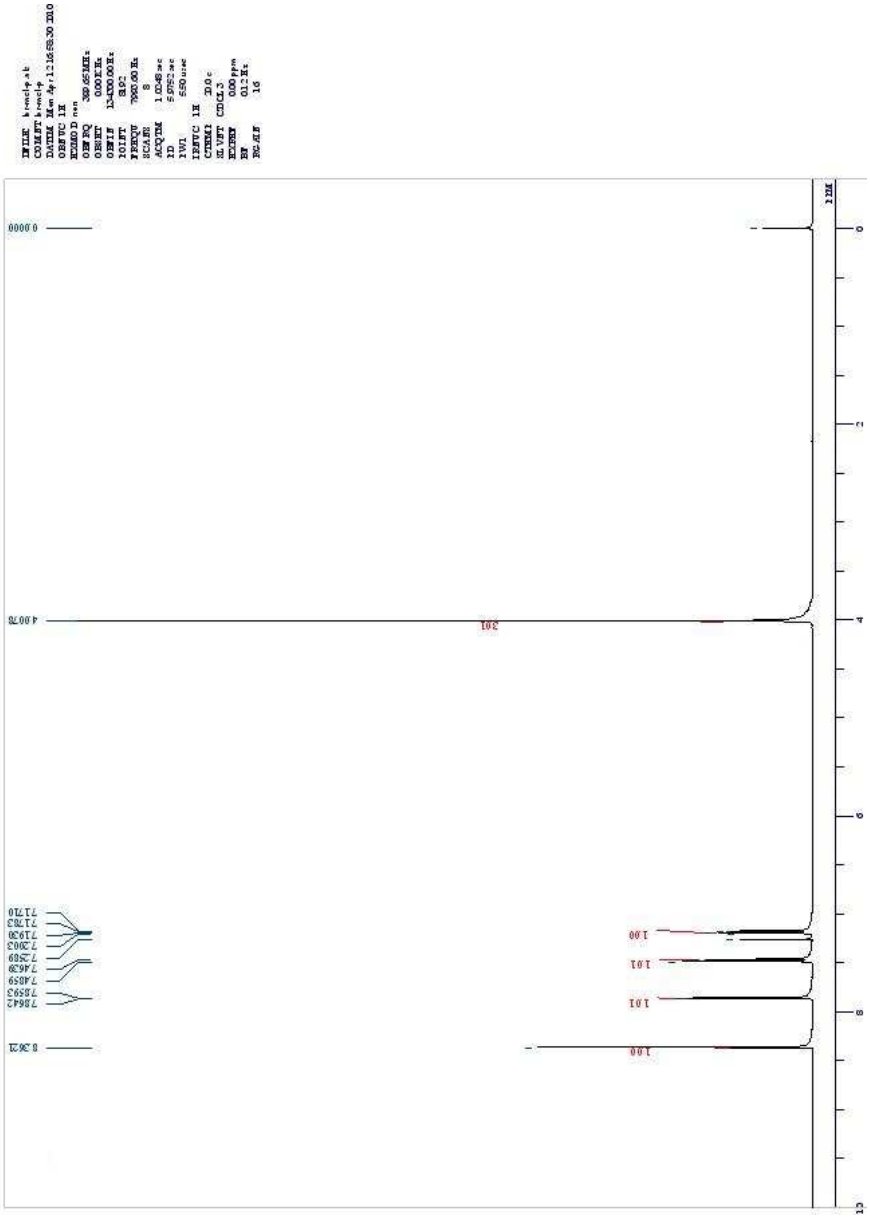
(*E*)-2-Bromo-6-fluorobenzaldehyde *O*-methyloxime 4b



2-Bromo-6-chlorobenzaldehyde *O*-methyloxime 5b



(*E*)-2-Bromo-5-chlorobenzaldehyde *O*-methyloxime 6b.



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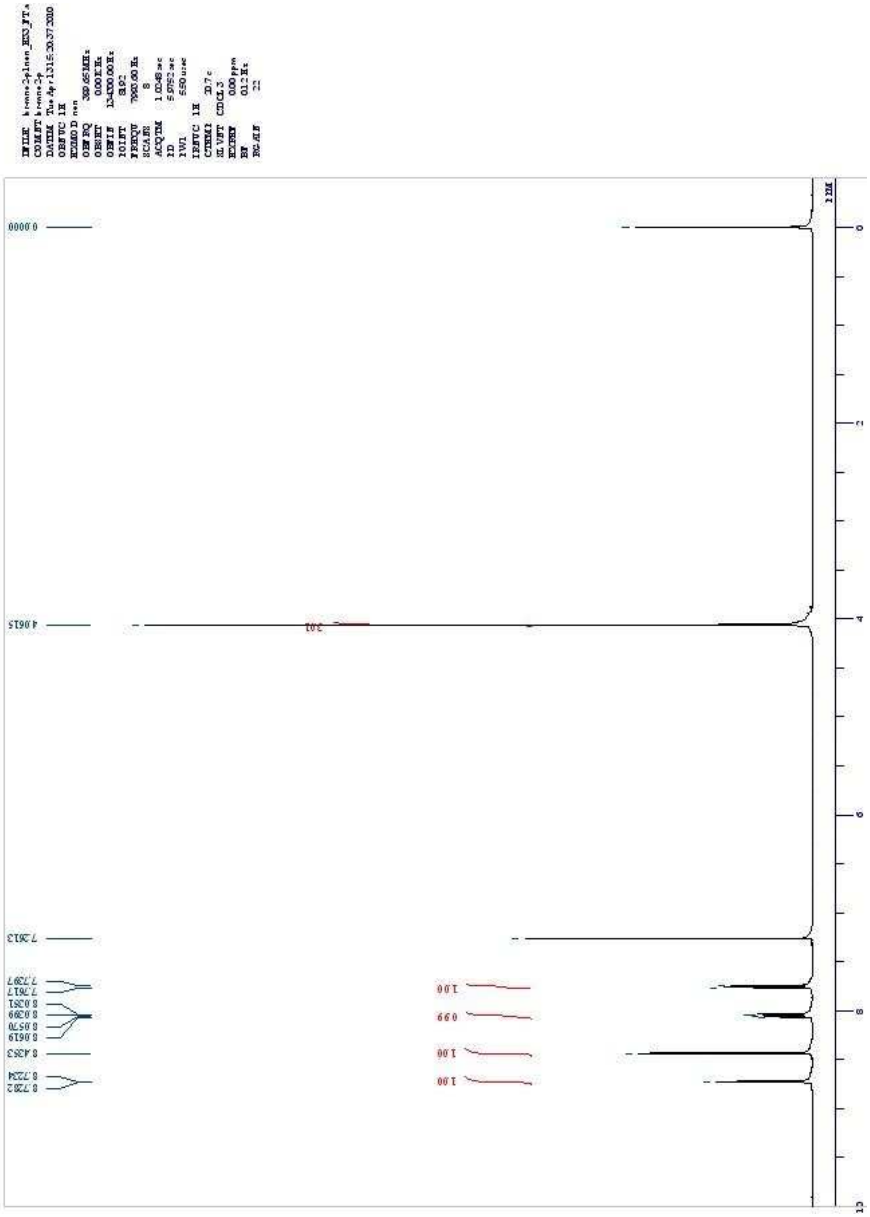
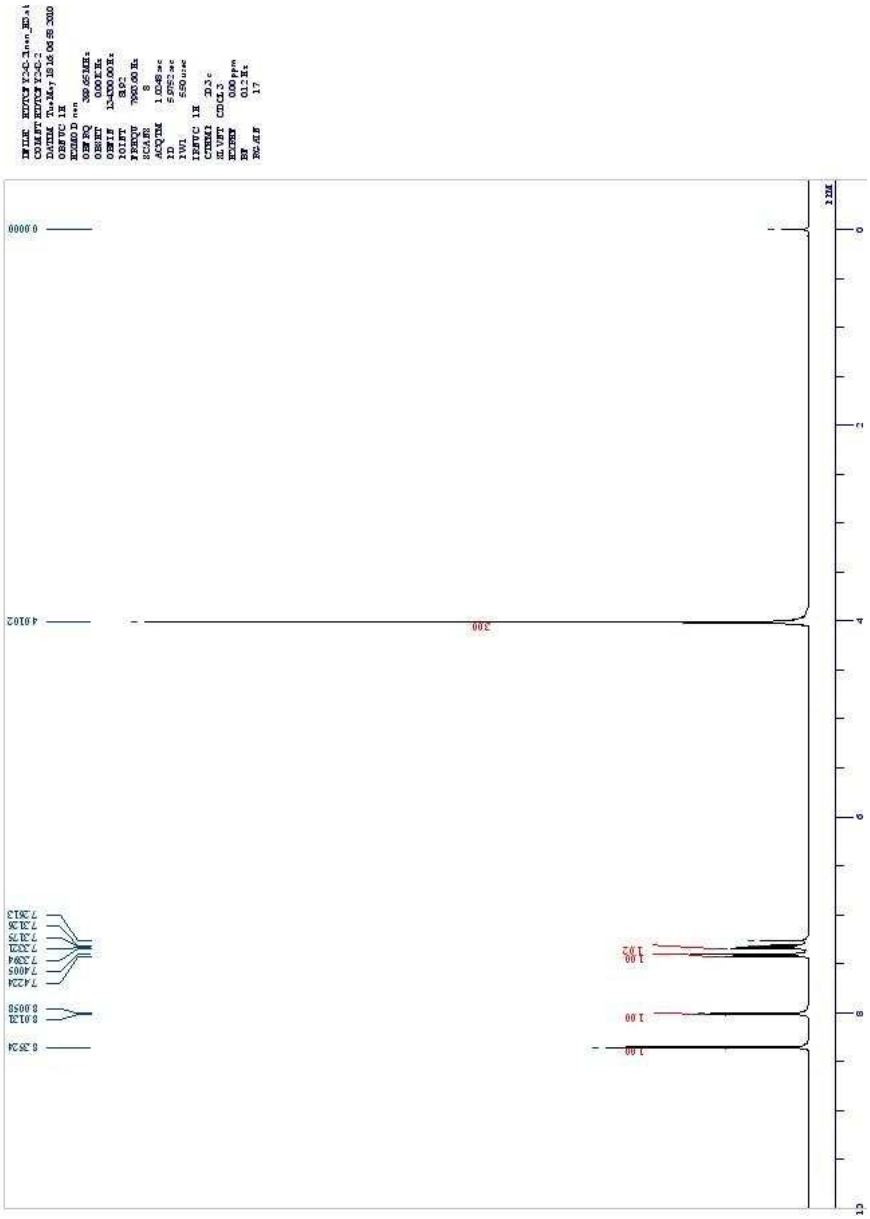
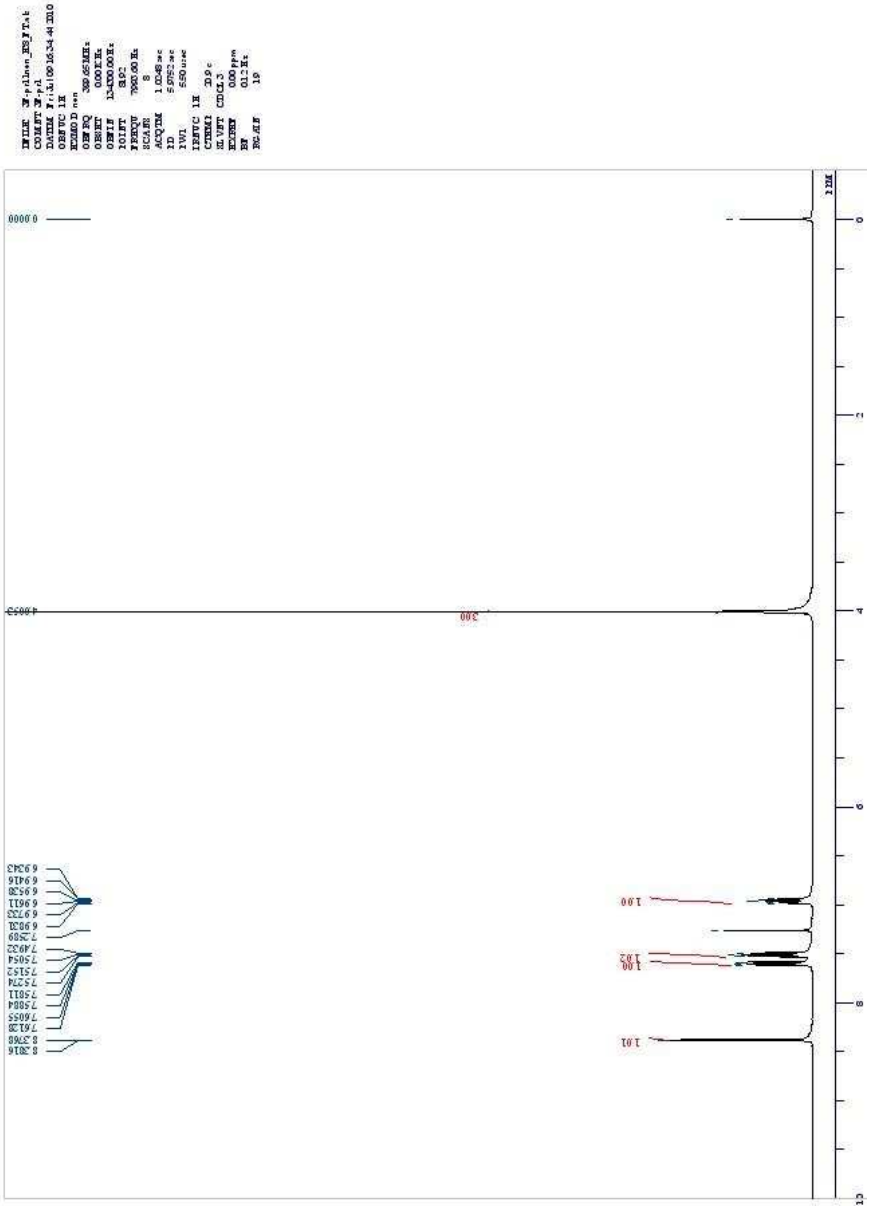


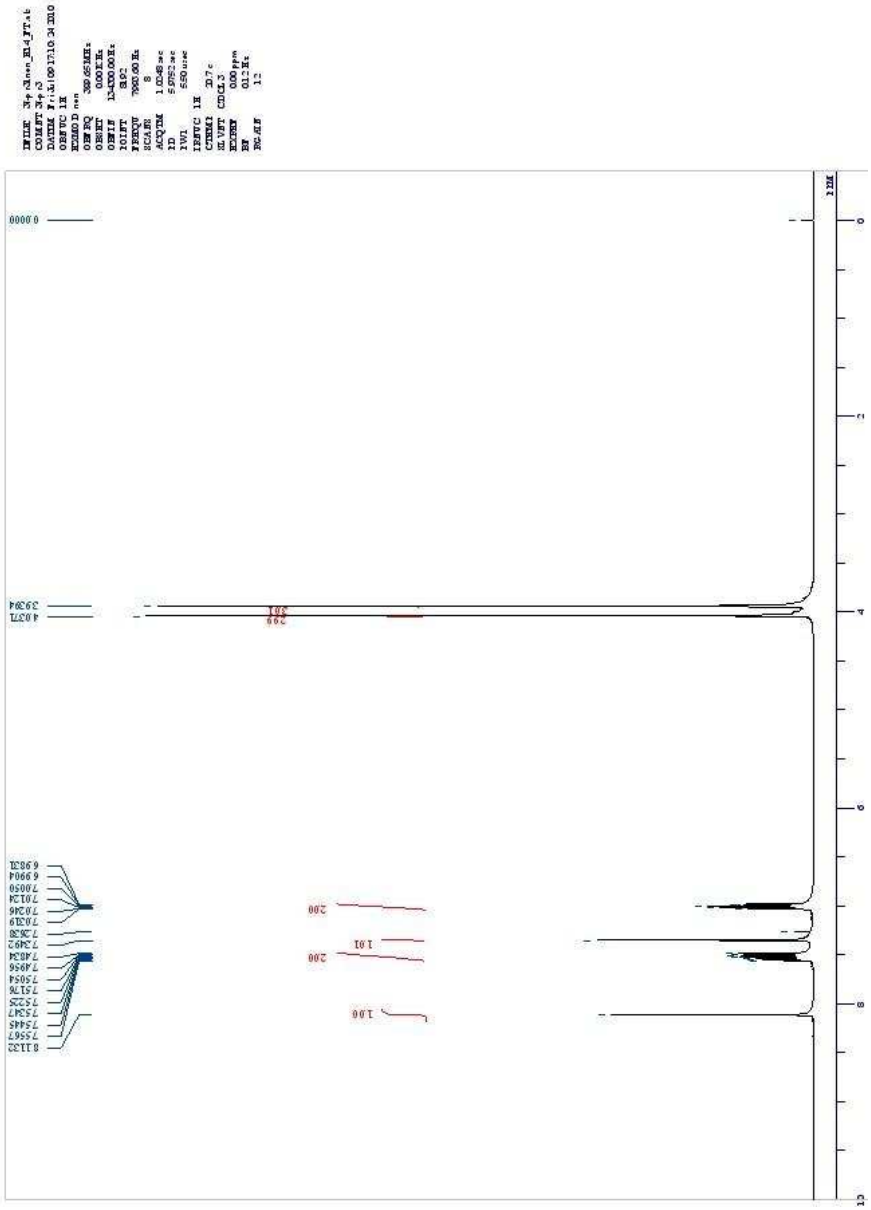
(*E*)-2,5-Dibromobenzaldehyde *O*-methyloxime 8b



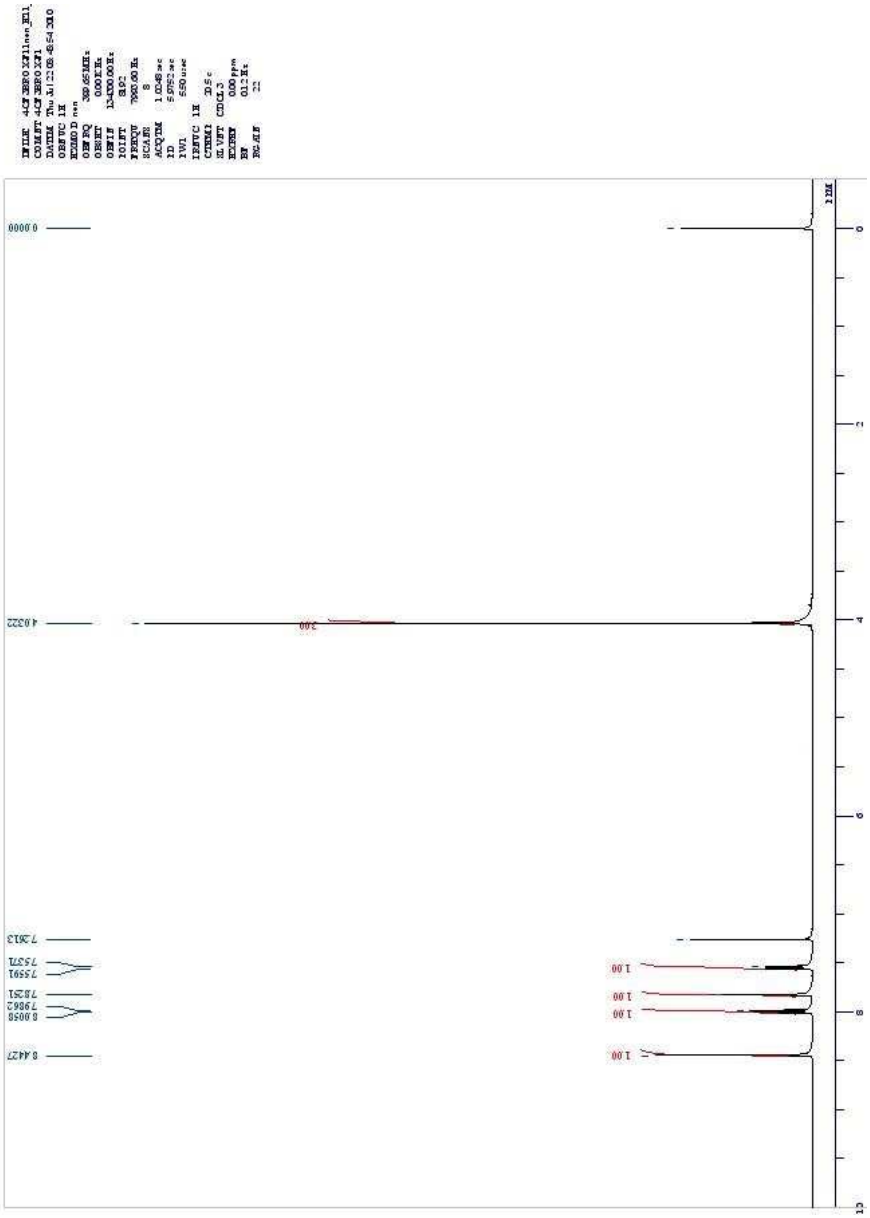
2-Bromo-5-fluorobenzaldehyde *O*-methyloxime 9b



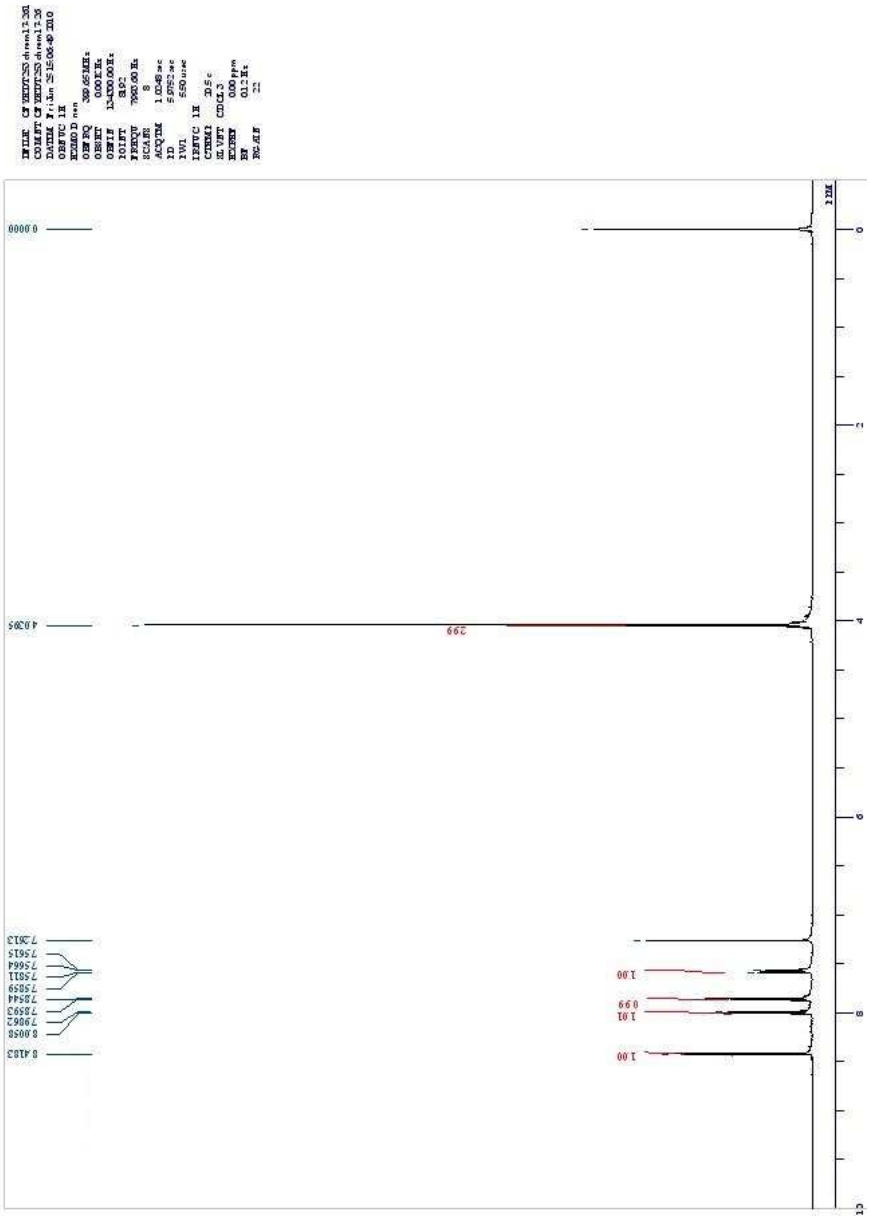
2,6-Dibromo-3-fluorobenzaldehyde *O*-methyloxime 9c



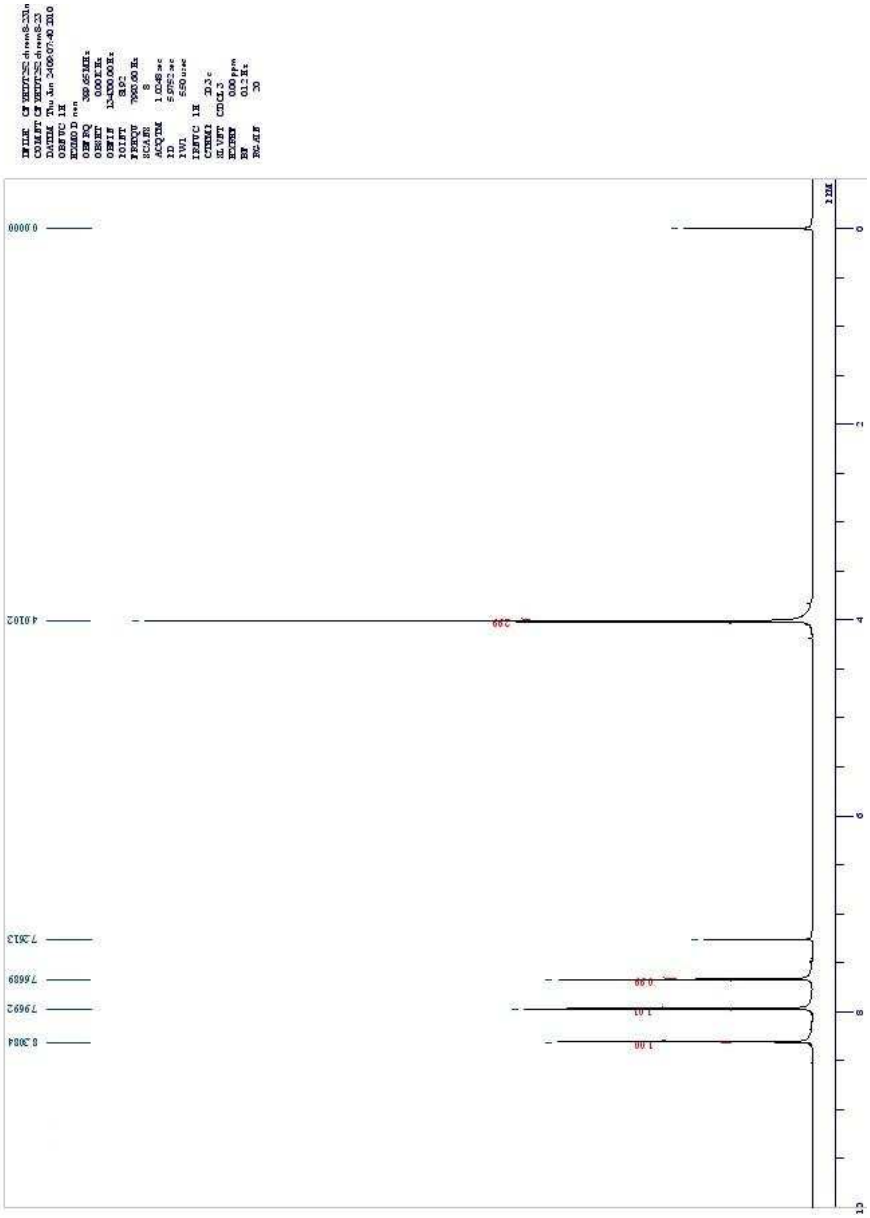
(*E*)-2-Bromo-4-trifluoromethylbenzaldehyde *O*-methyloxime 10b



(*E*)-2-Bromo-4-cyanobenzaldehyde *O*-methyloxime 11b

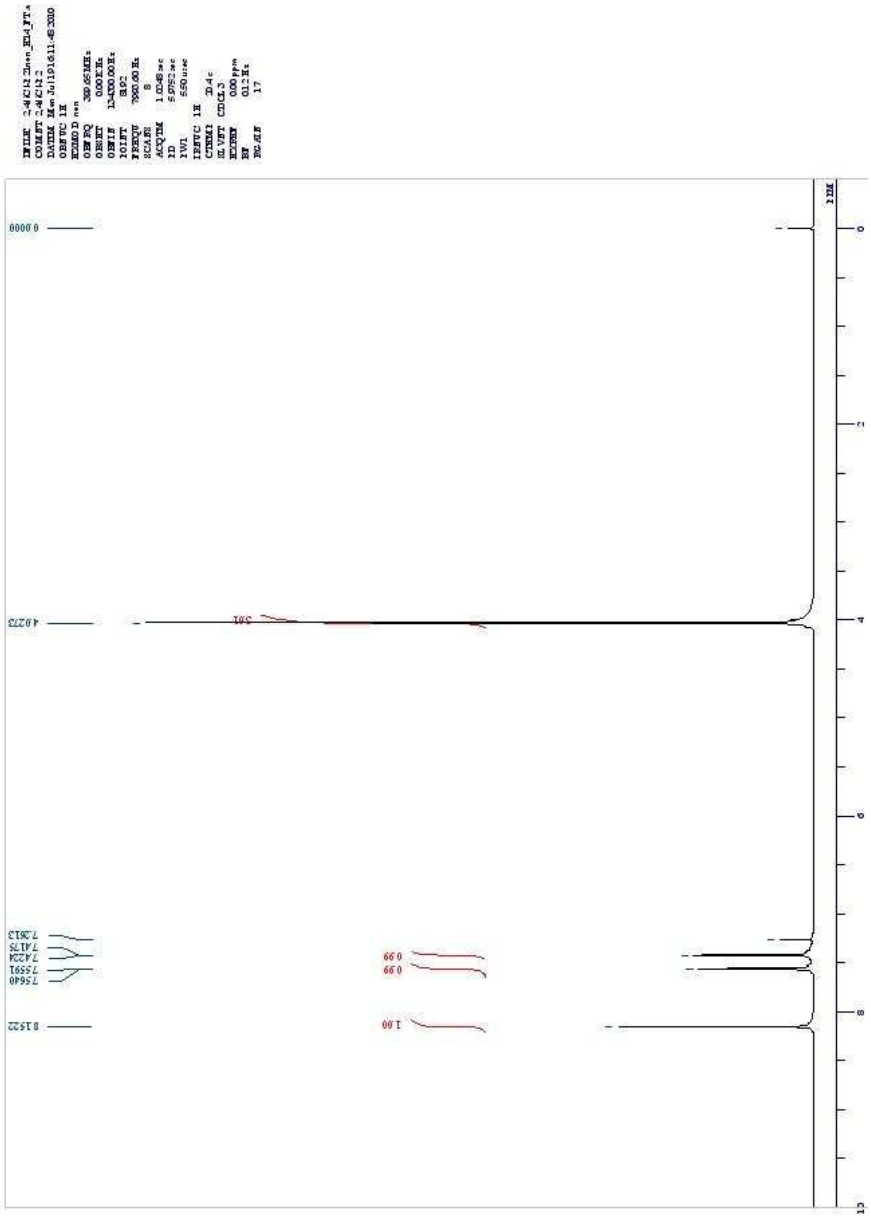


(*E*)-2-Bromo-4,5-dichlorobenzaldehyde *O*-methyloxime 12b



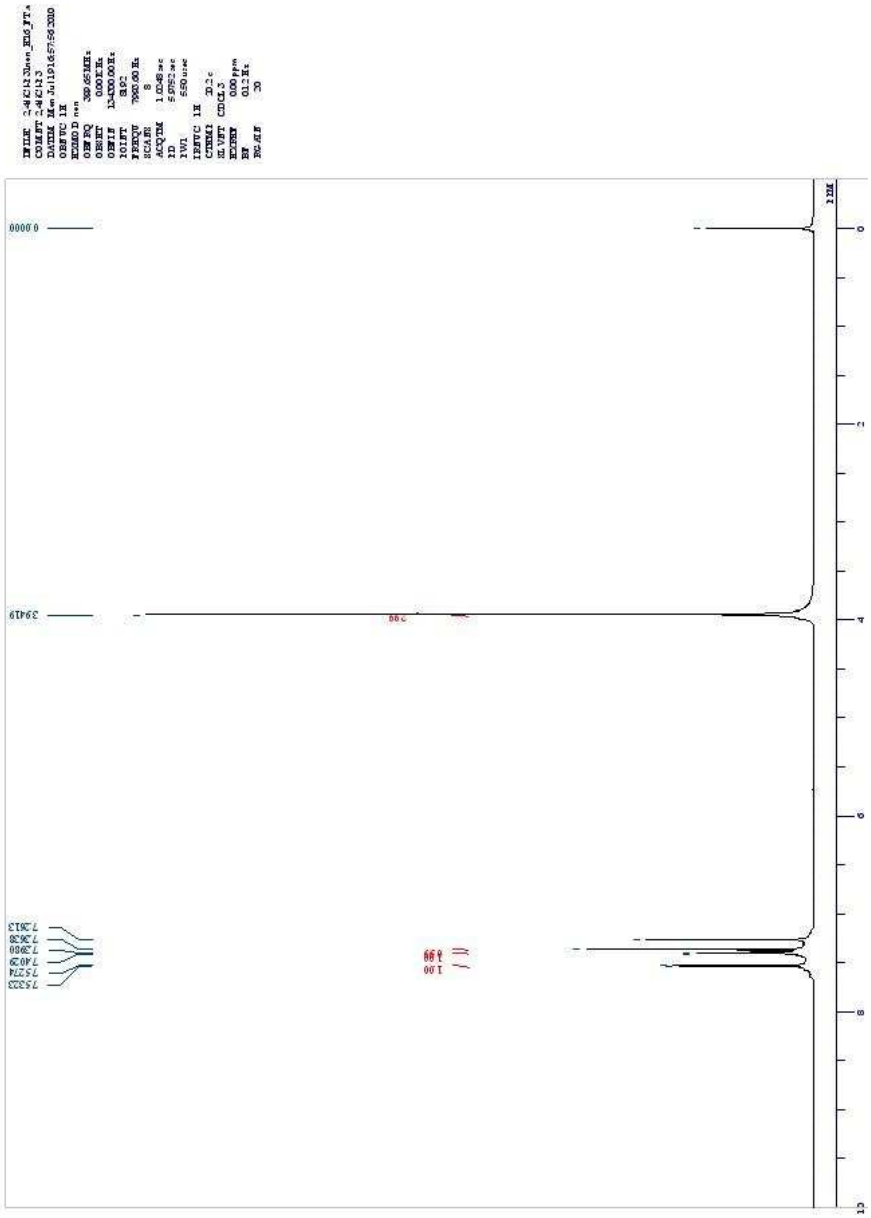
2-Bromo-4,6-dichlorobenzaldehyde *O*-methyloxime 13b

Diastereoisomer (*E*)

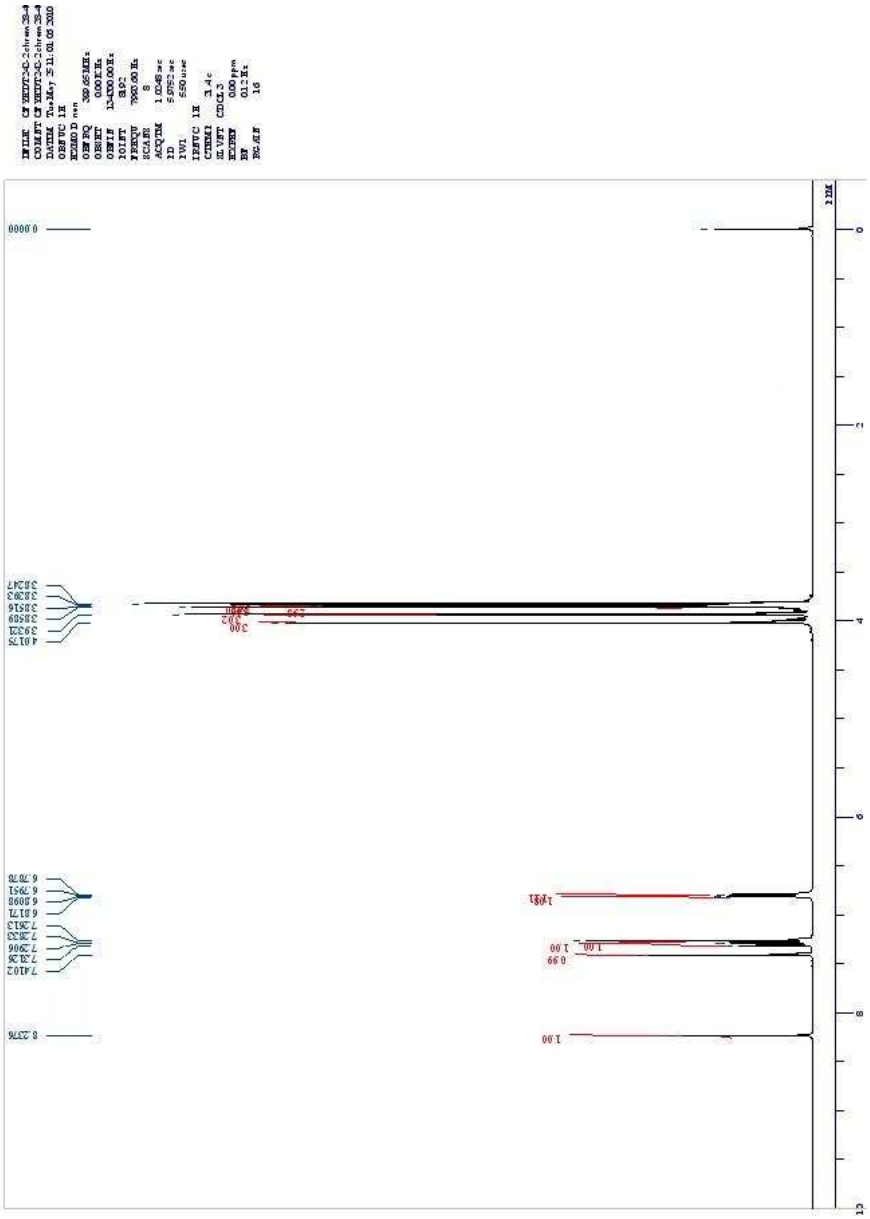


2-Bromo-4,6-dichlorobenzaldehyde *O*-methyloxime 13b

Diastereoisomer (*Z*)

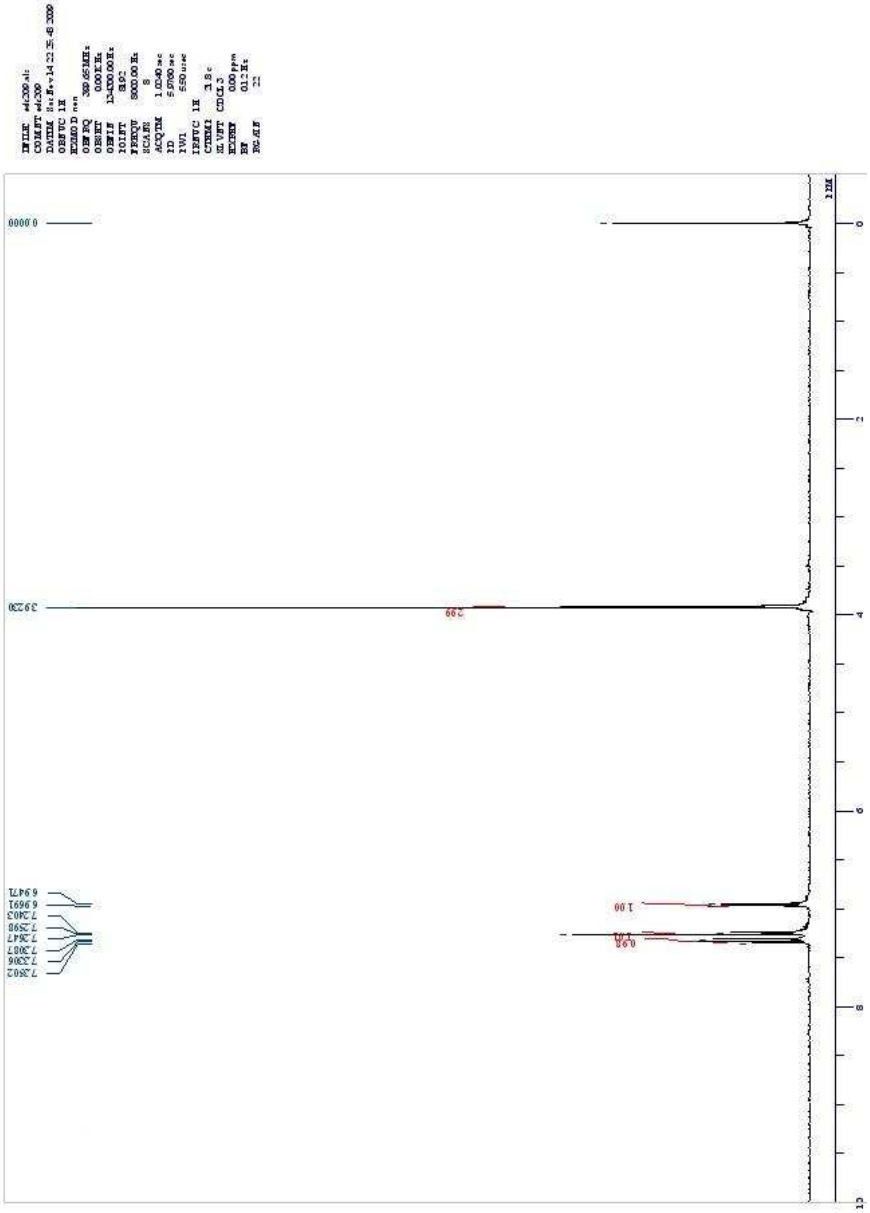


2-Bromo-5,6-dimethoxybenzaldehyde *O*-methyloxime 14b

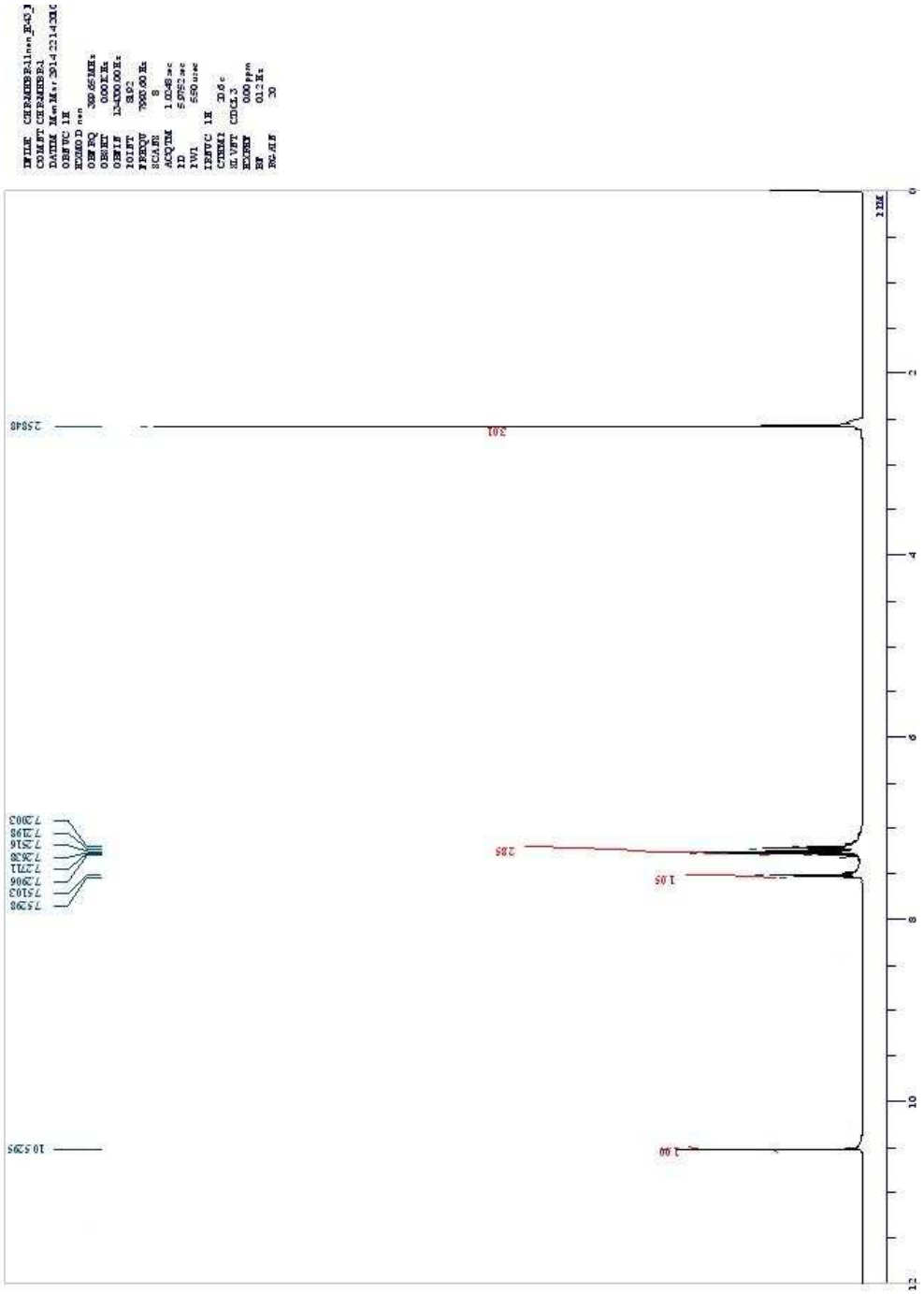


5 ^{1}H NMR of substituted 2-bromobenzaldehydes 2d-14d

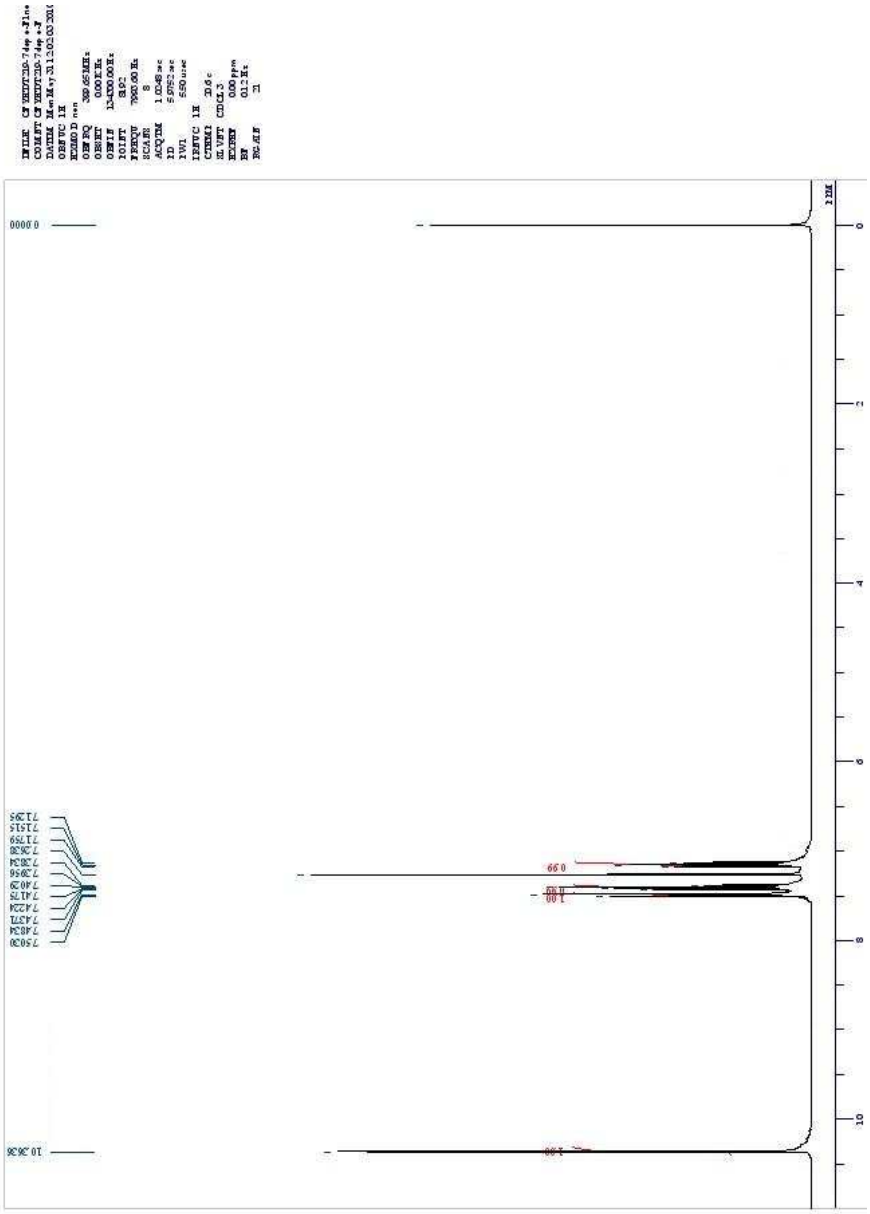
2-Bromo-6-methoxybenzaldehyde 2d



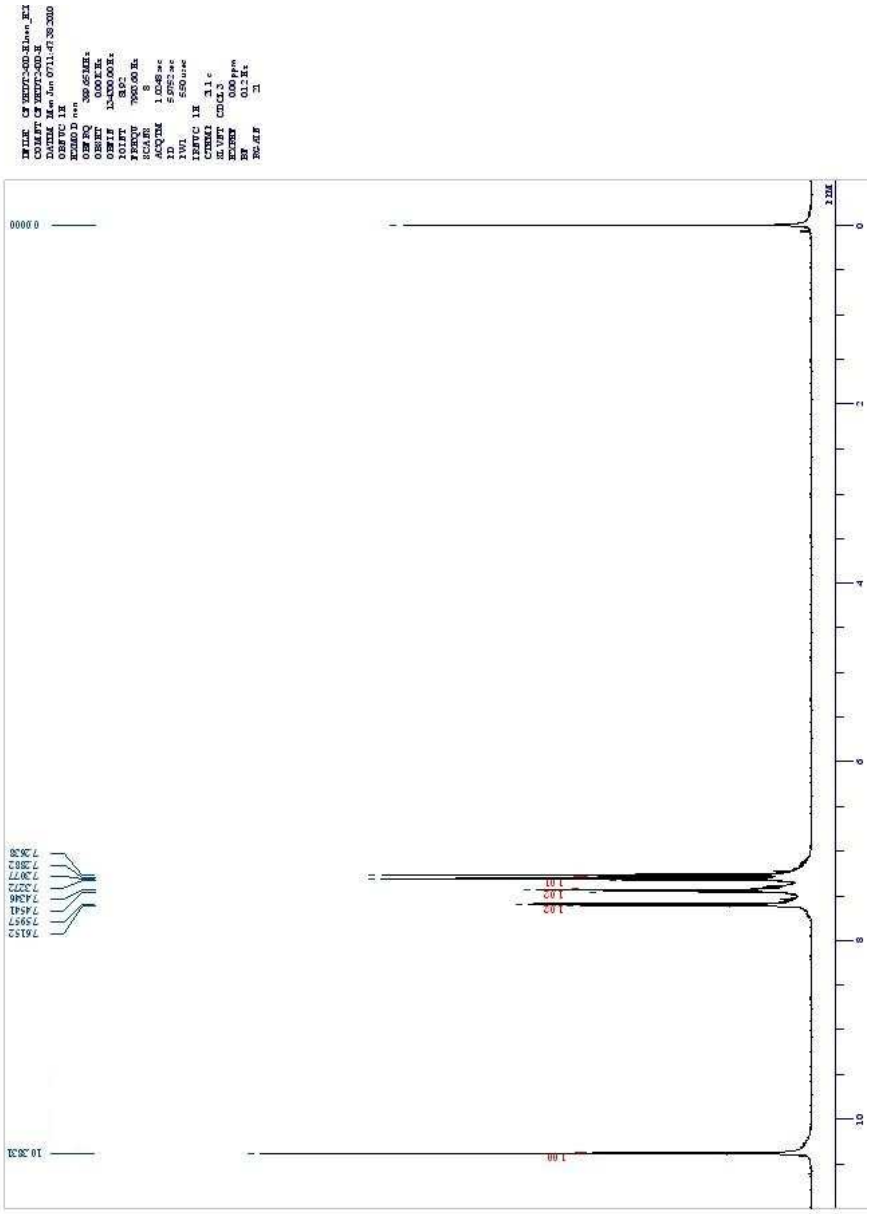
2-Bromo-6-methylbenzaldehyde 3d



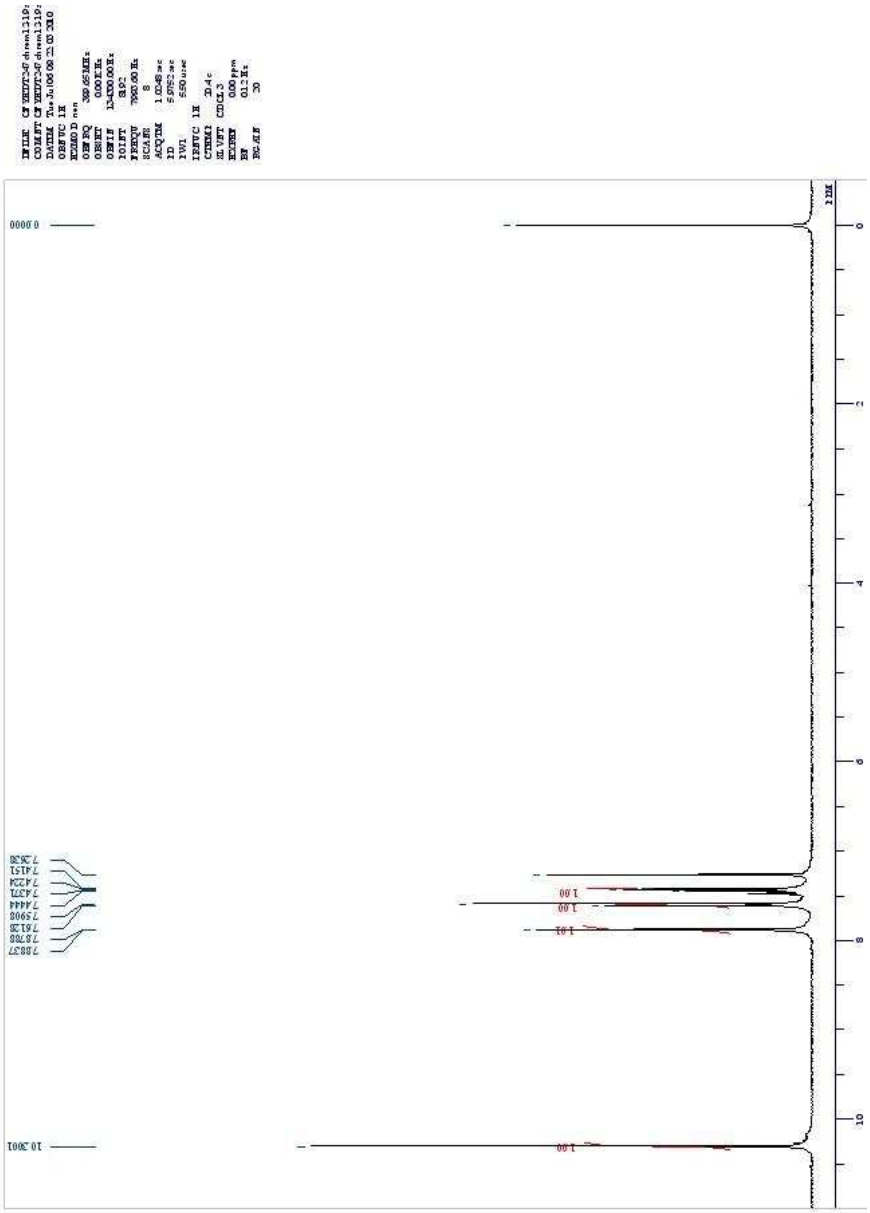
2-Bromo-6-fluorobenzaldehyde 4d



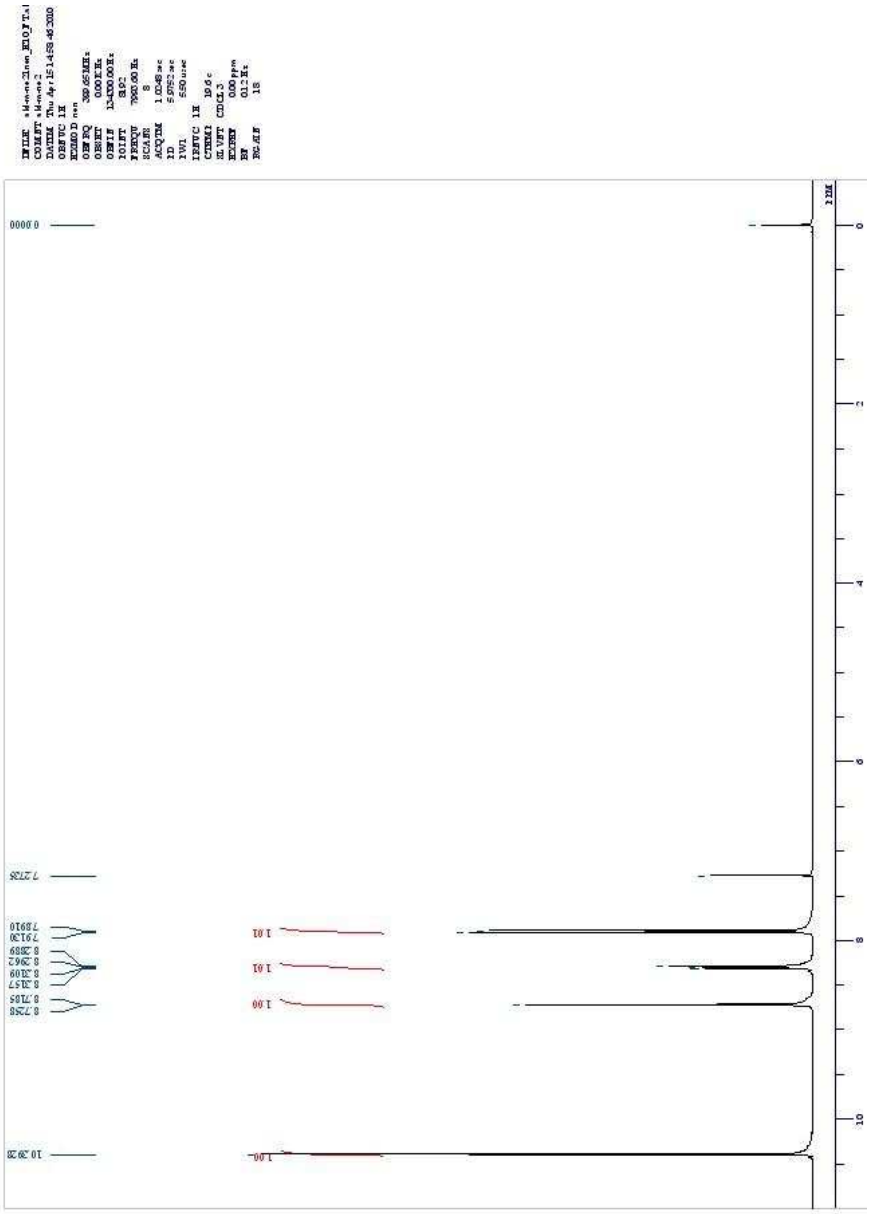
2-Bromo-6-chlorobenzaldehyde 5d



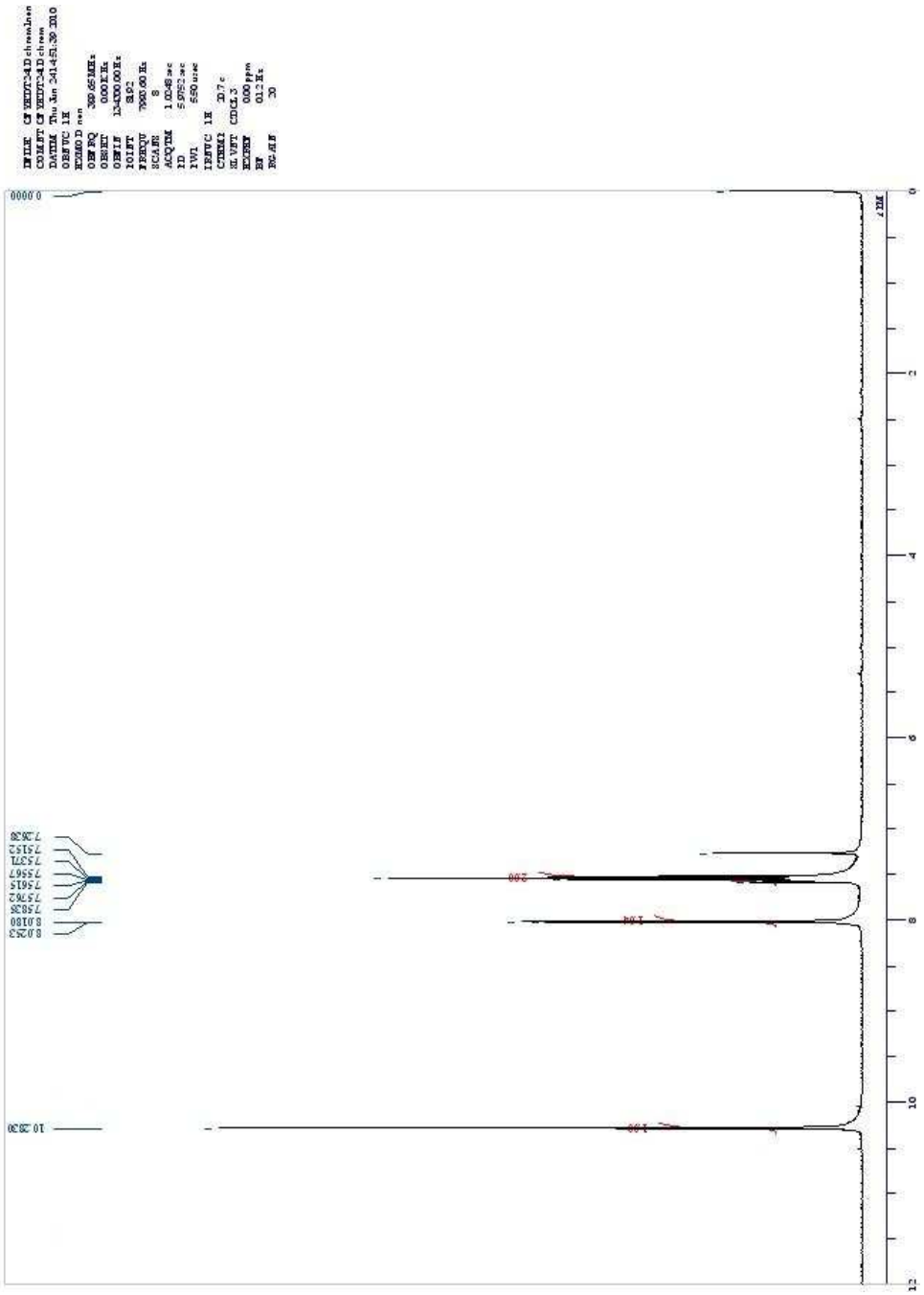
2-Bromo-5-chlorobenzaldehyde 6d



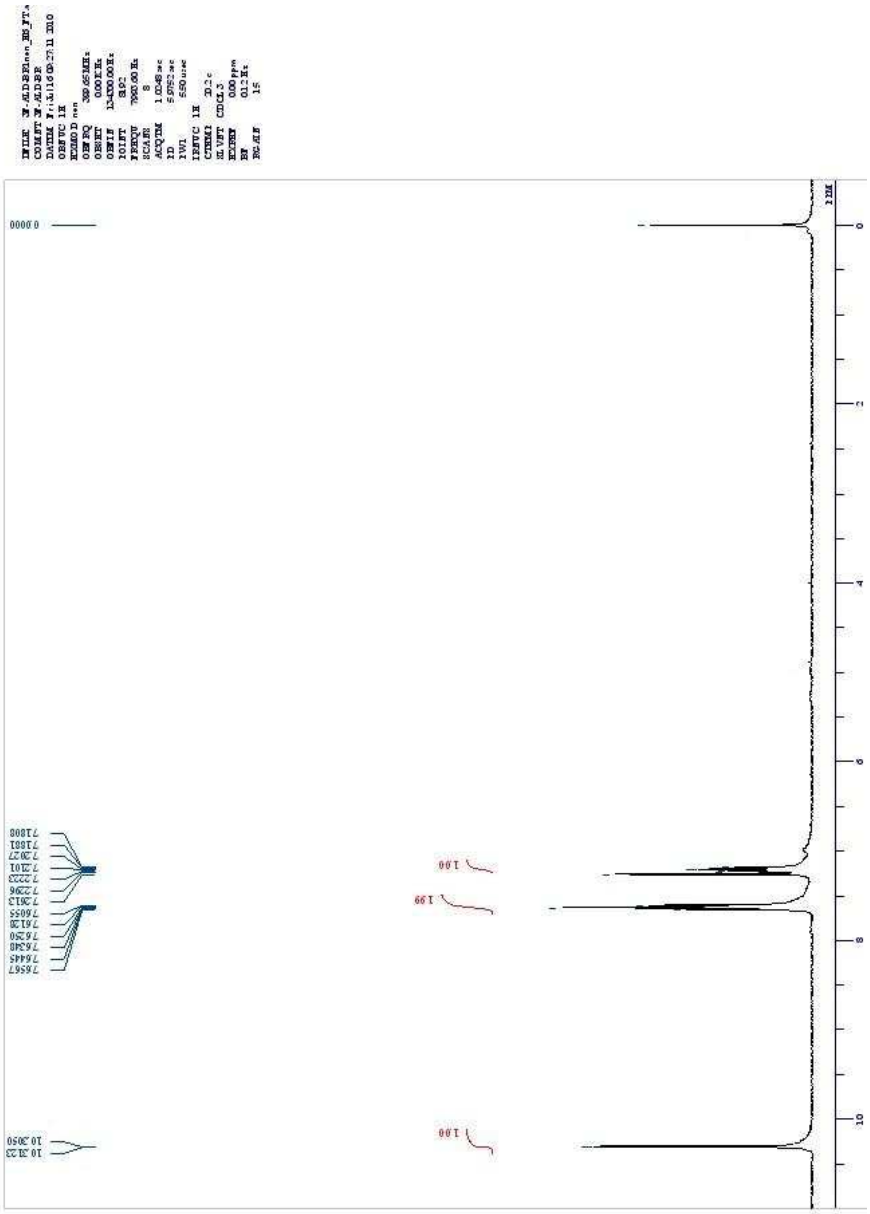
2-Bromo-5-nitrobenzaldehyde 7d



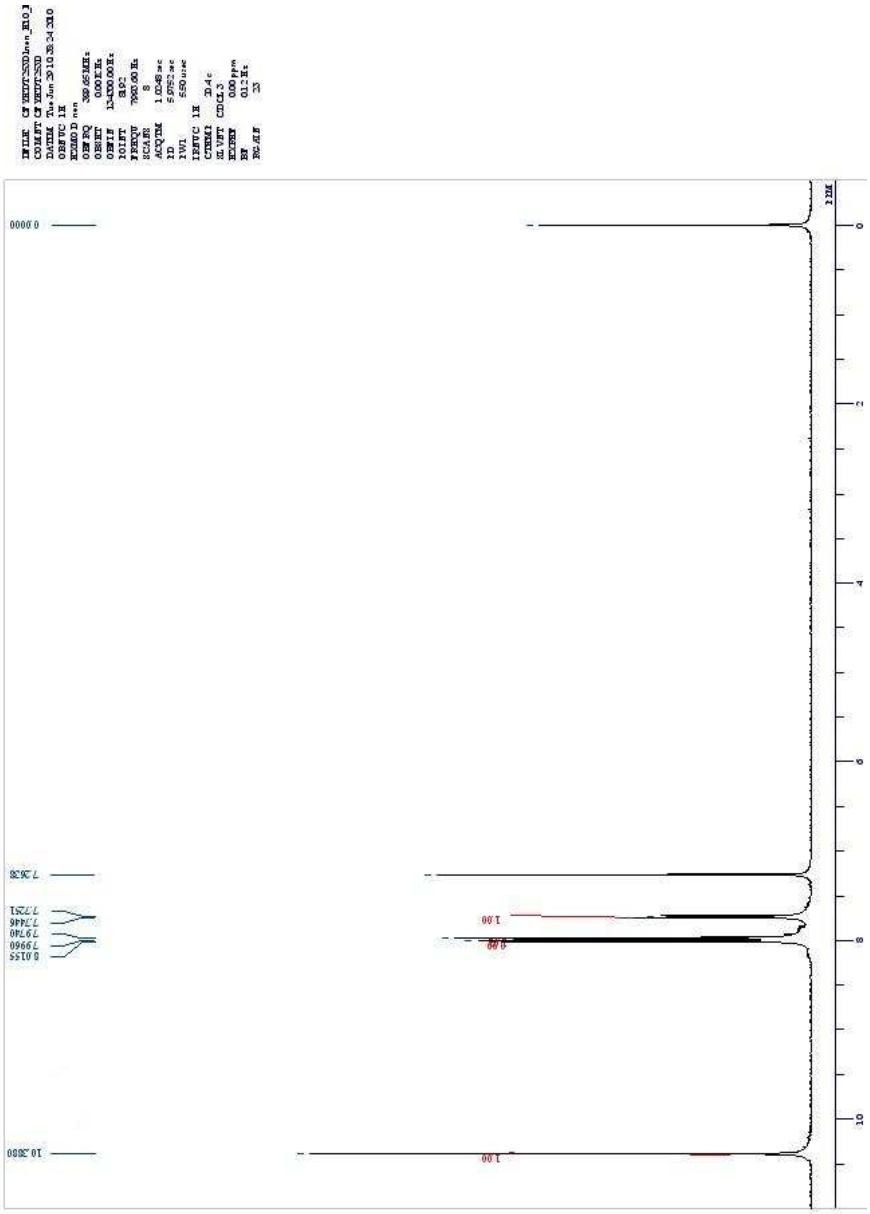
2,5-Dibromobenzaldehyde 8d



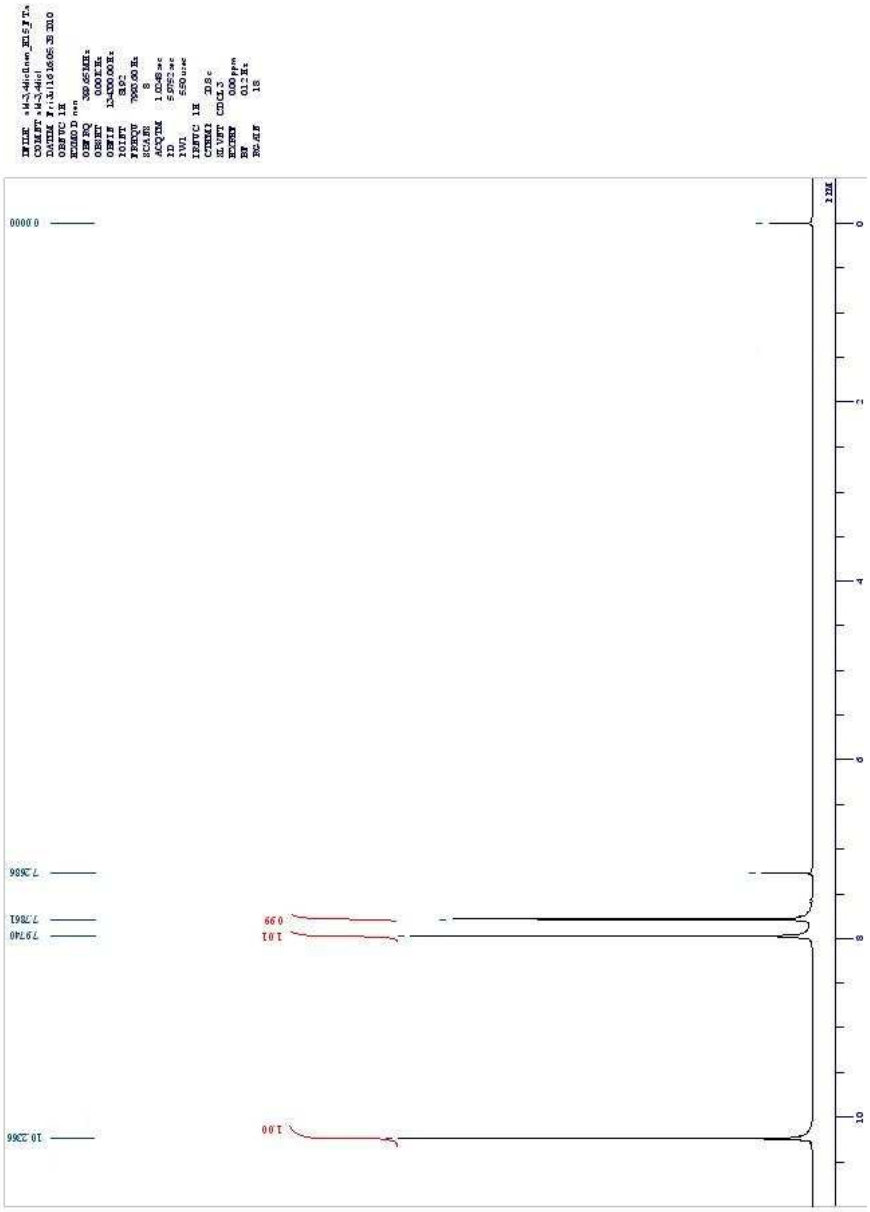
2-Bromo-5-fluorobenzaldehyde 9d



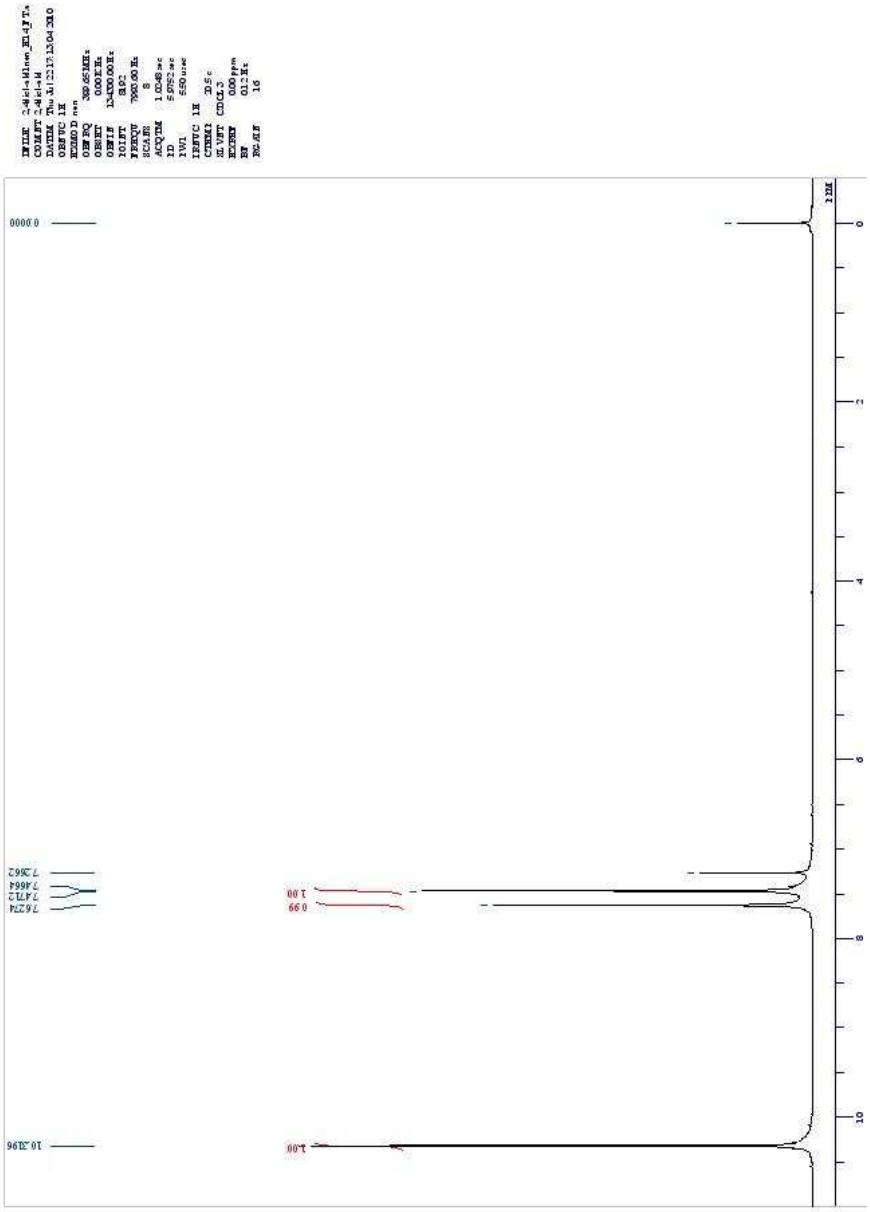
2-Bromo-4-cyanobenzaldehyde 11d



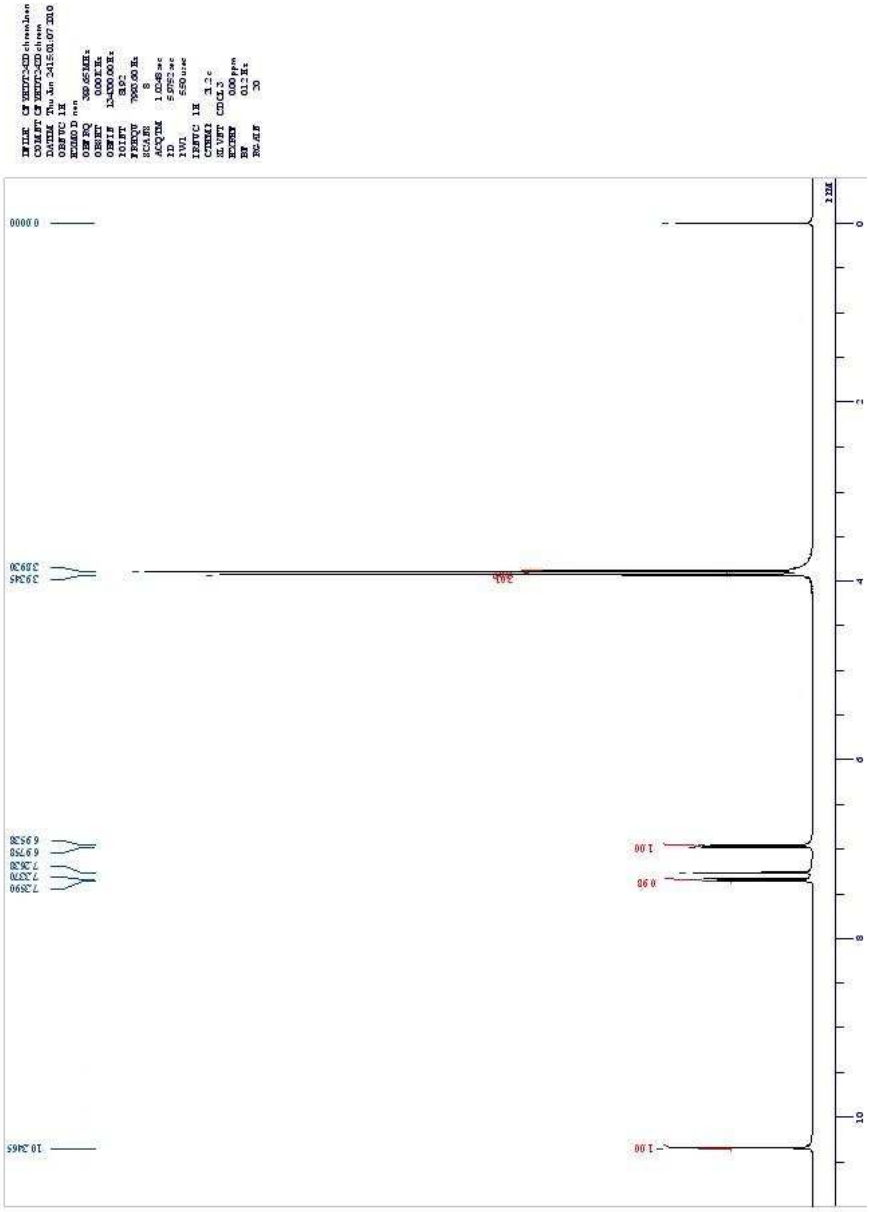
2-Bromo-4,5-dichlorobenzaldehyde 12d



2-Bromo-4,6-dichlorobenzaldehyde 13d

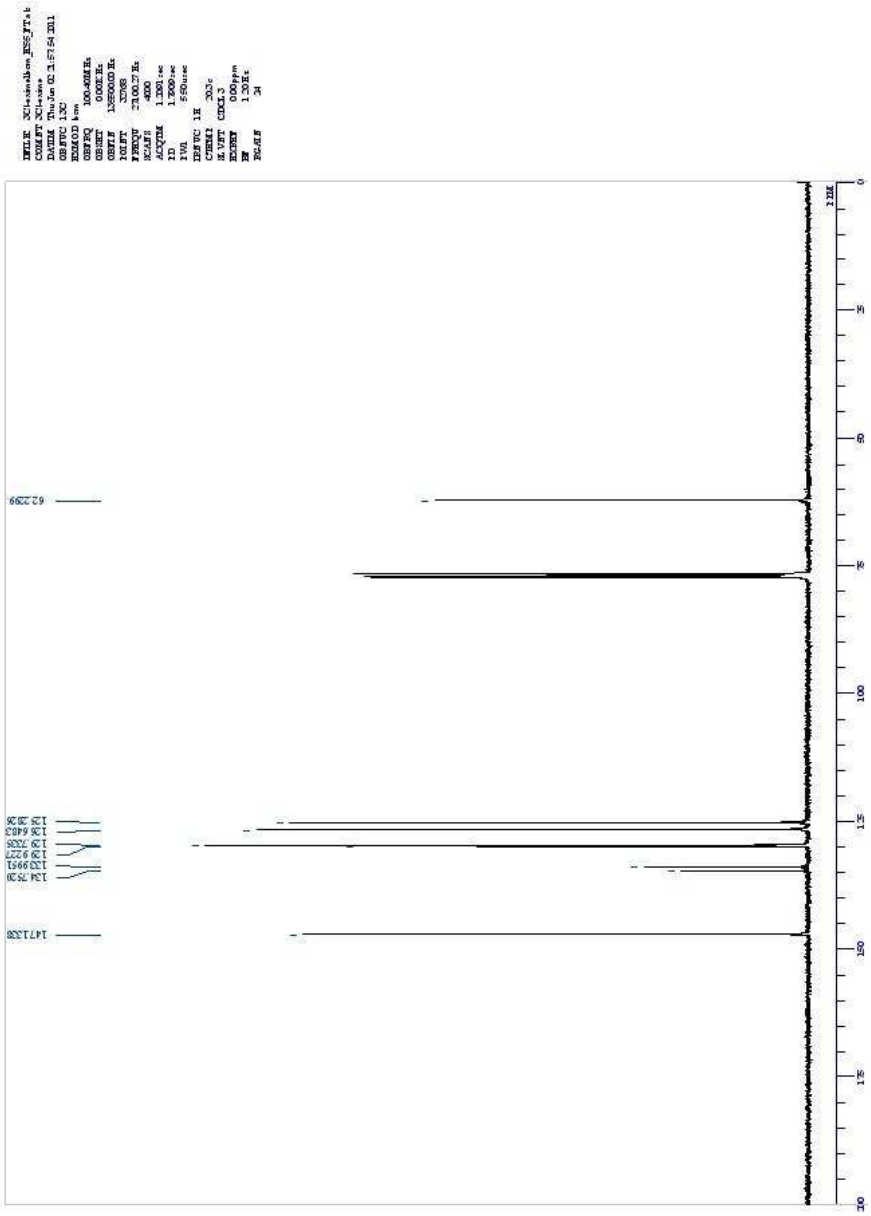


2-Bromo-5,6-dimethoxybenzaldehyde 14d

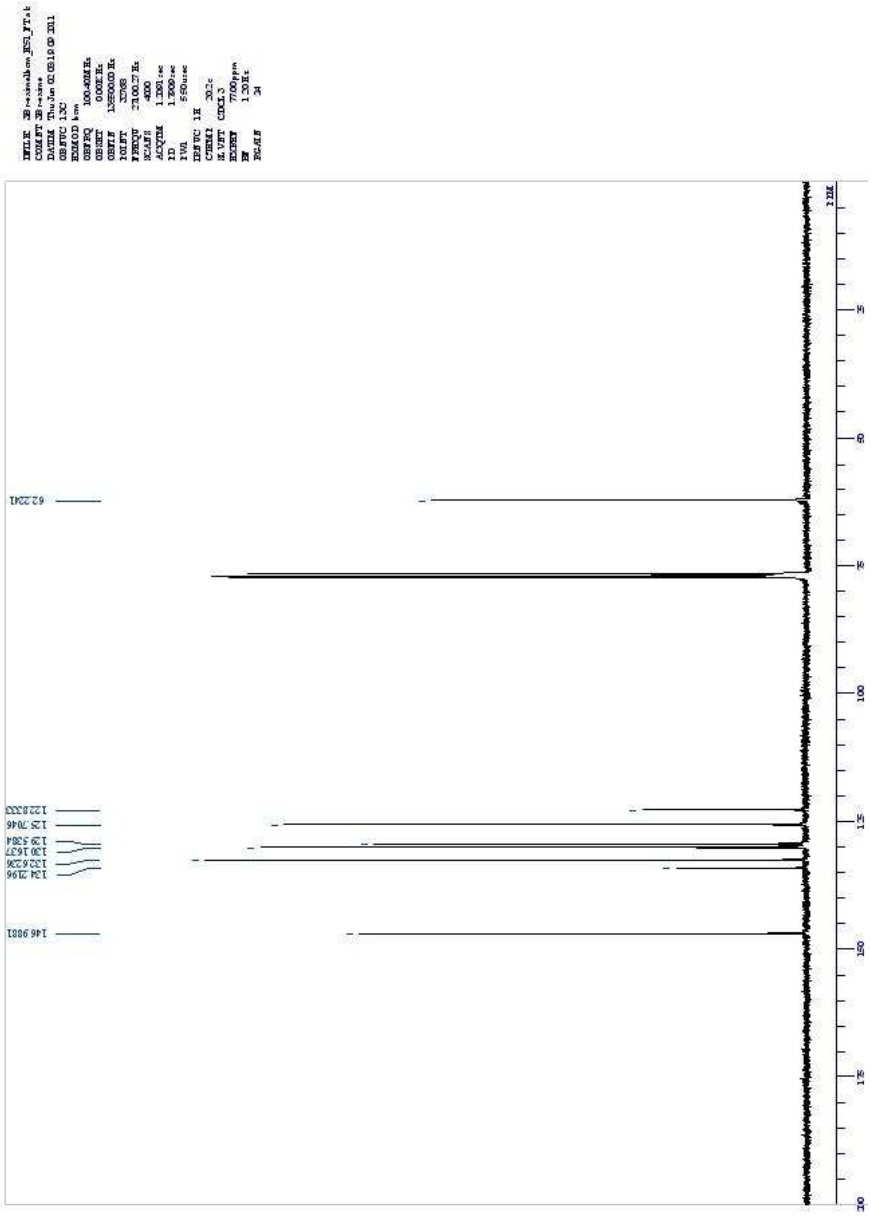


6 ^{13}C NMR data for substituted benzaldehyde O-methyloximes 6a, 8a, 9a, 11a-14a.

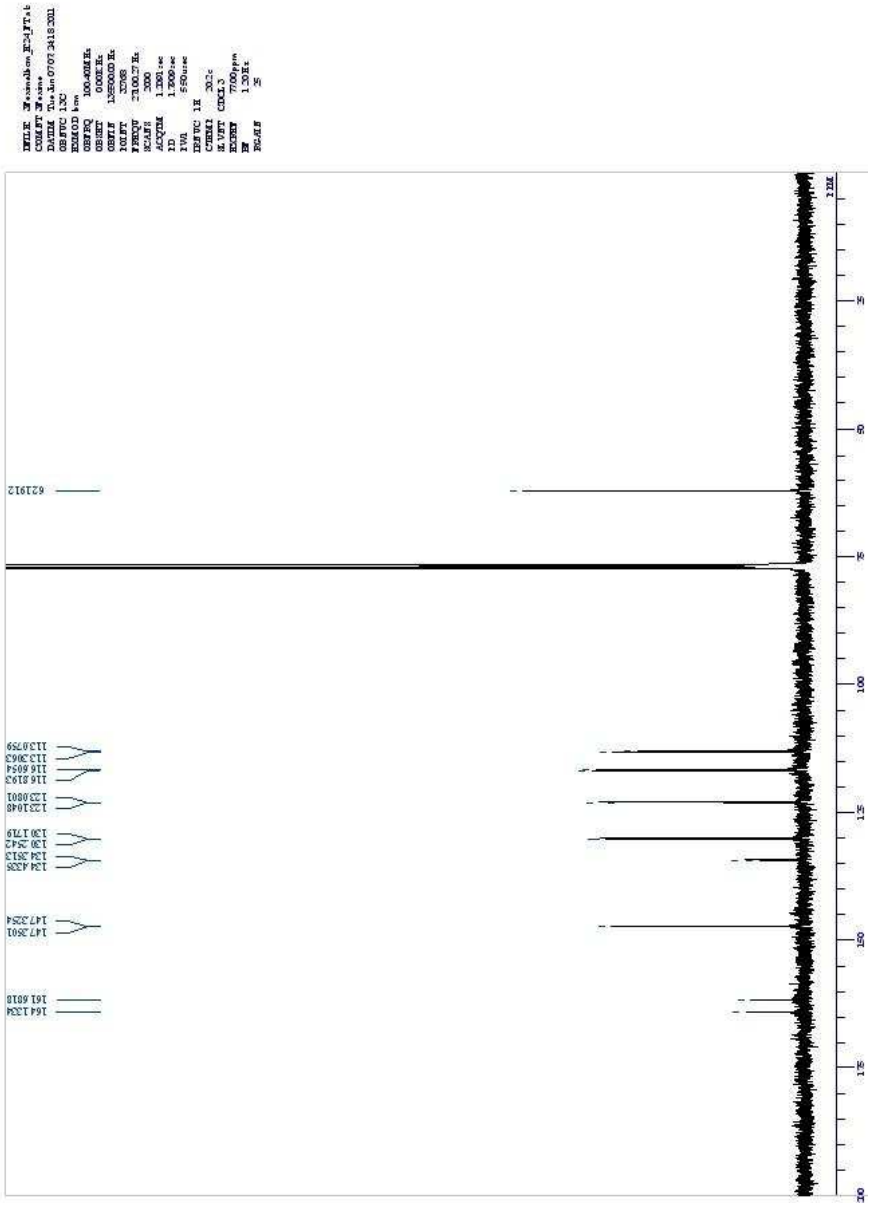
(*E*)-3-Chlorobenzaldehyde *O*-methyloxime 6a.



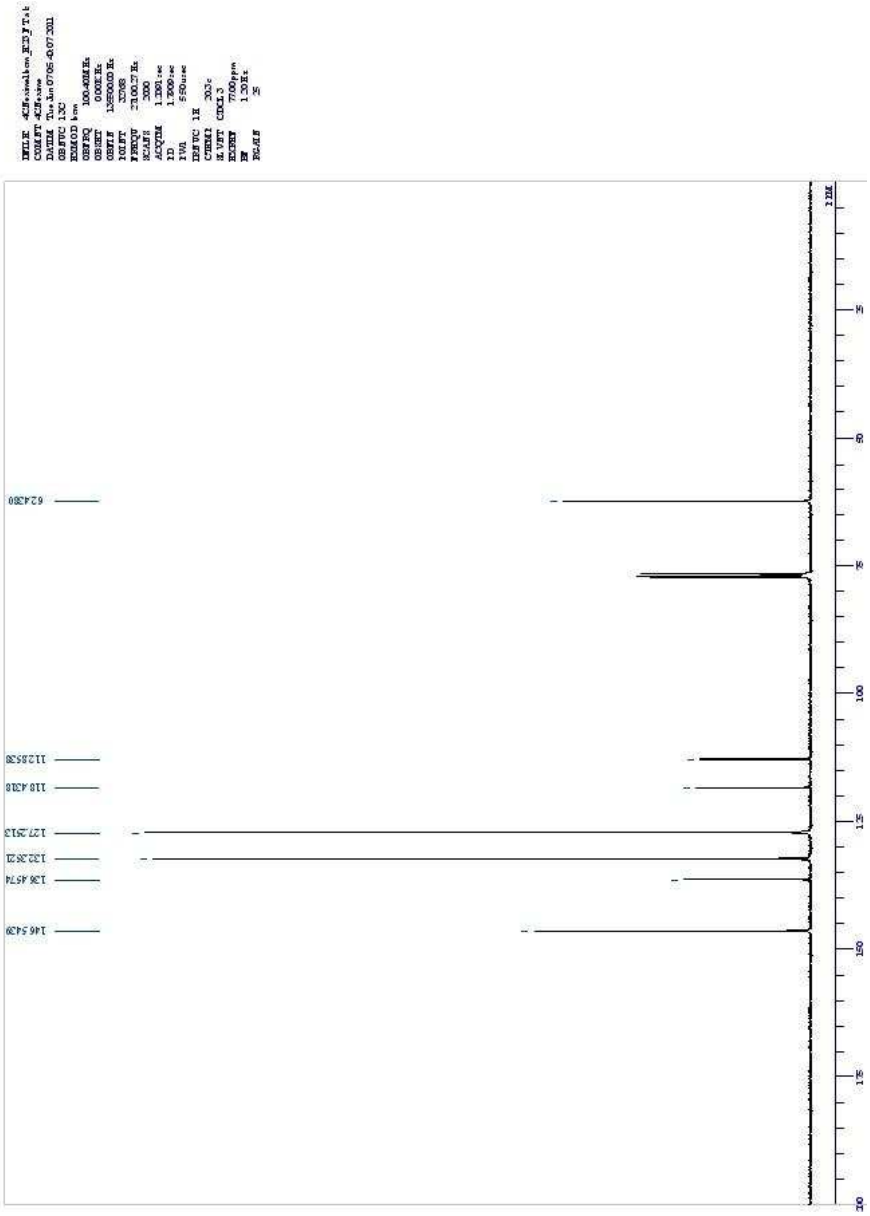
(*E*)-3-Bromobenzaldehyde *O*-methyloxime 8a.



***E*)-3-Fluorobenzaldehyde *O*-methyloxime 9a**.



(*E*)-4-Cyanobenzaldehyde *O*-methyloxime 11a.



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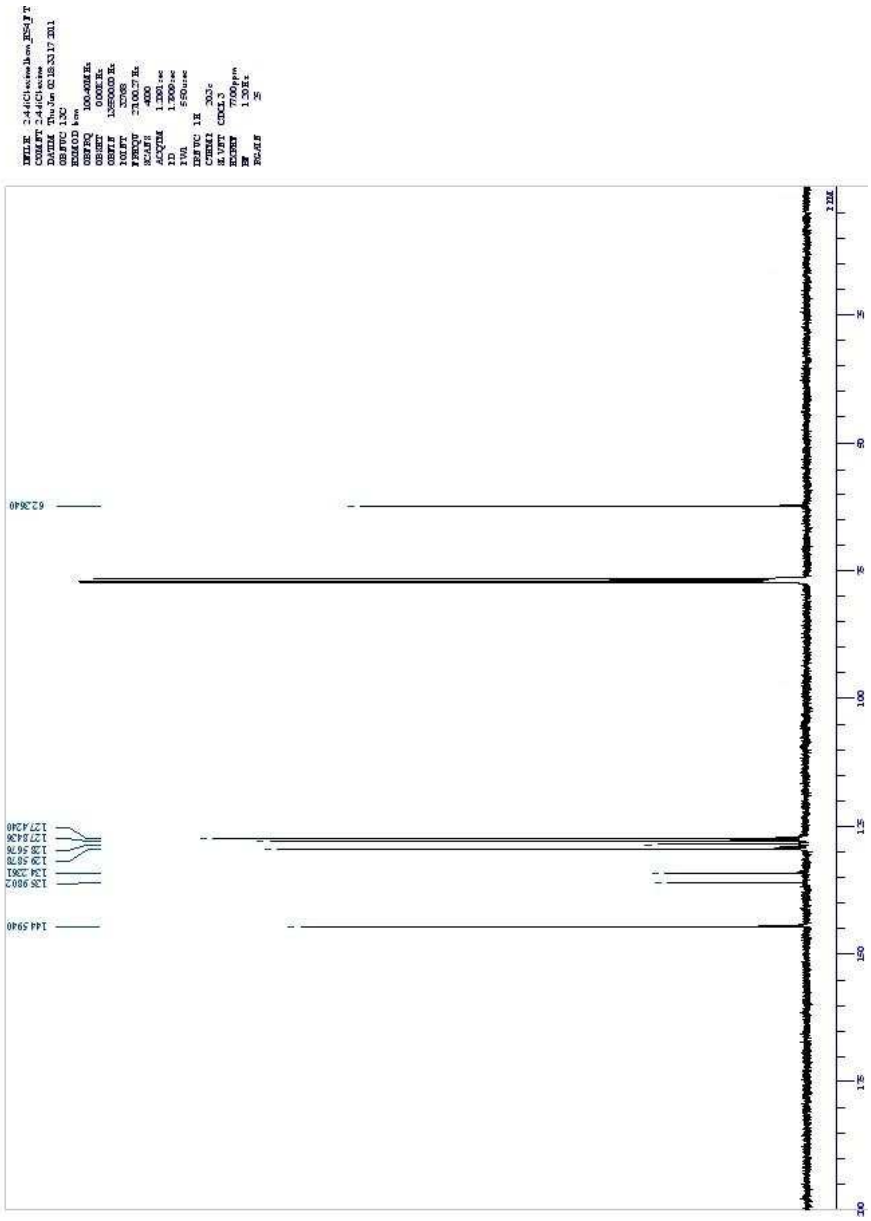

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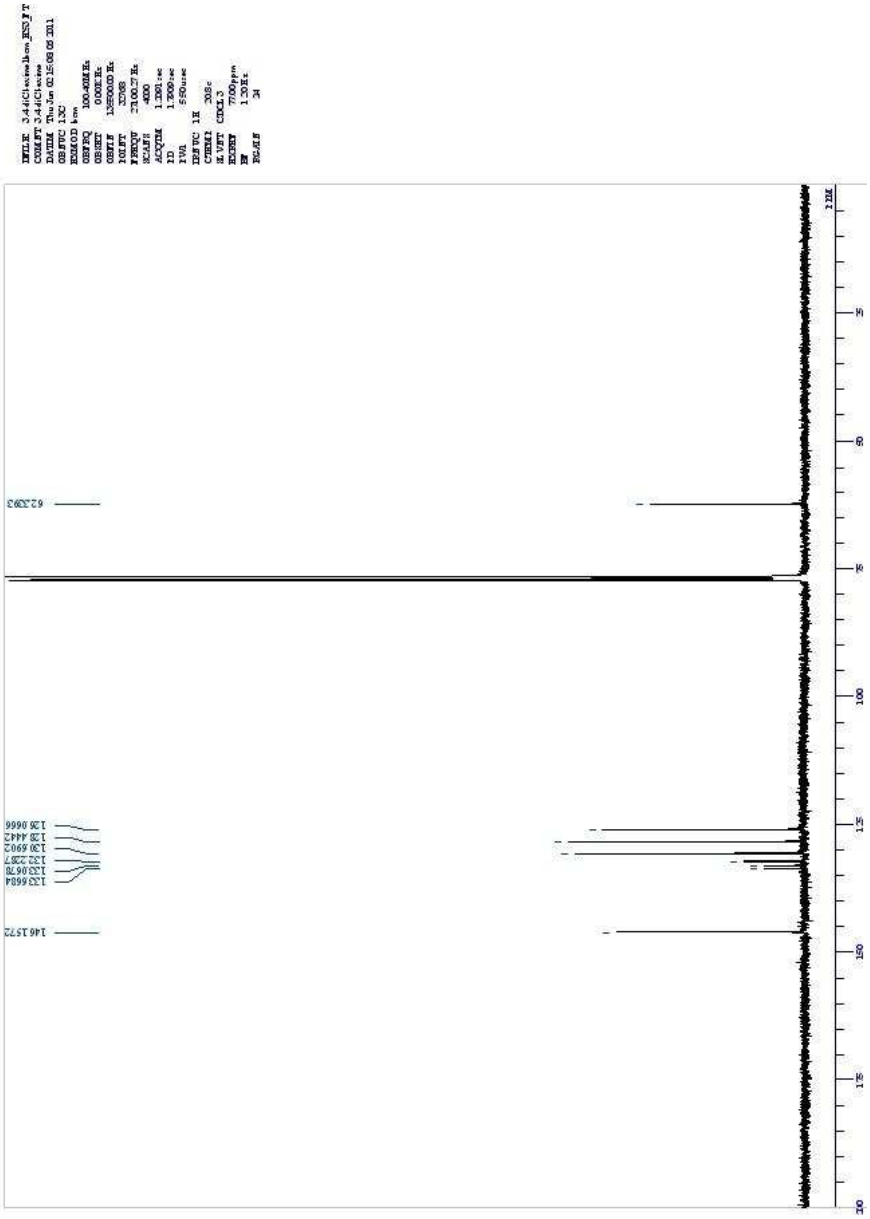
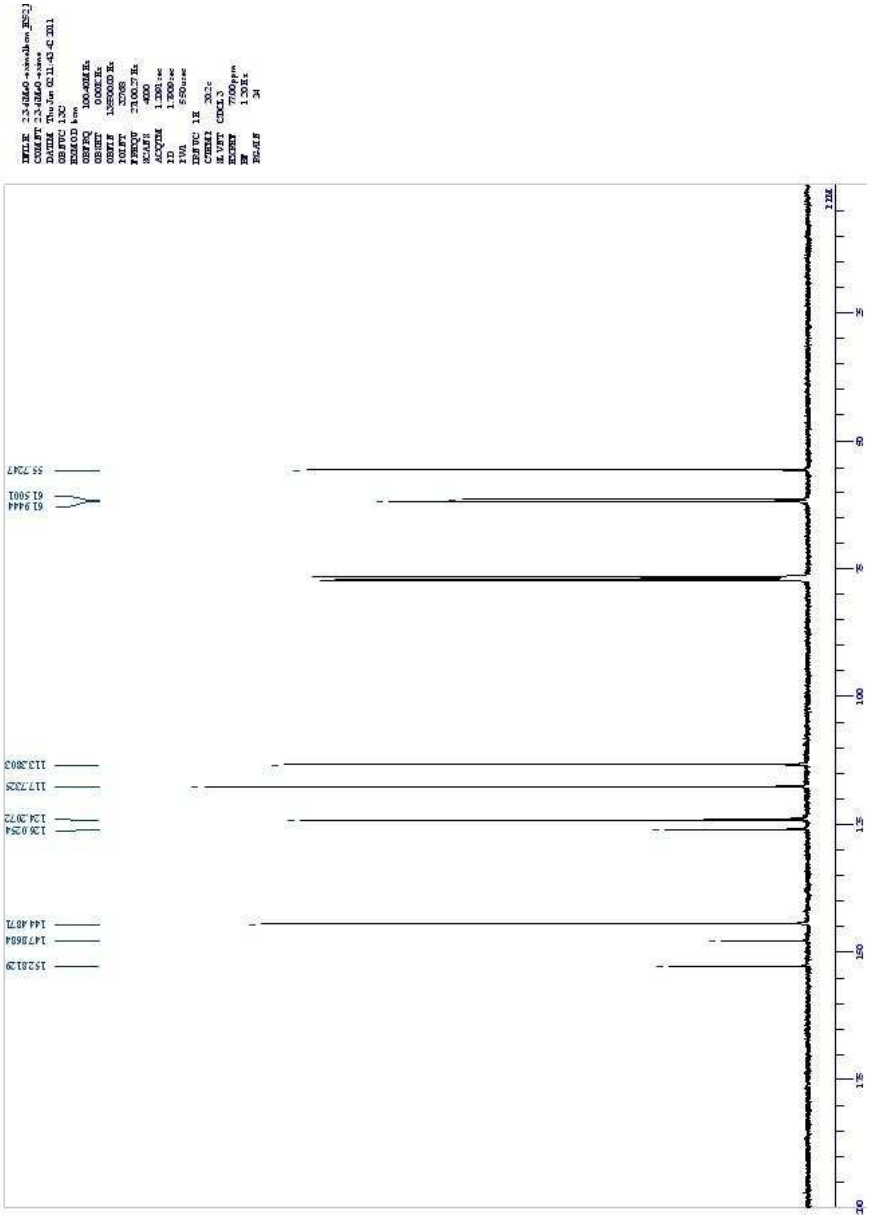
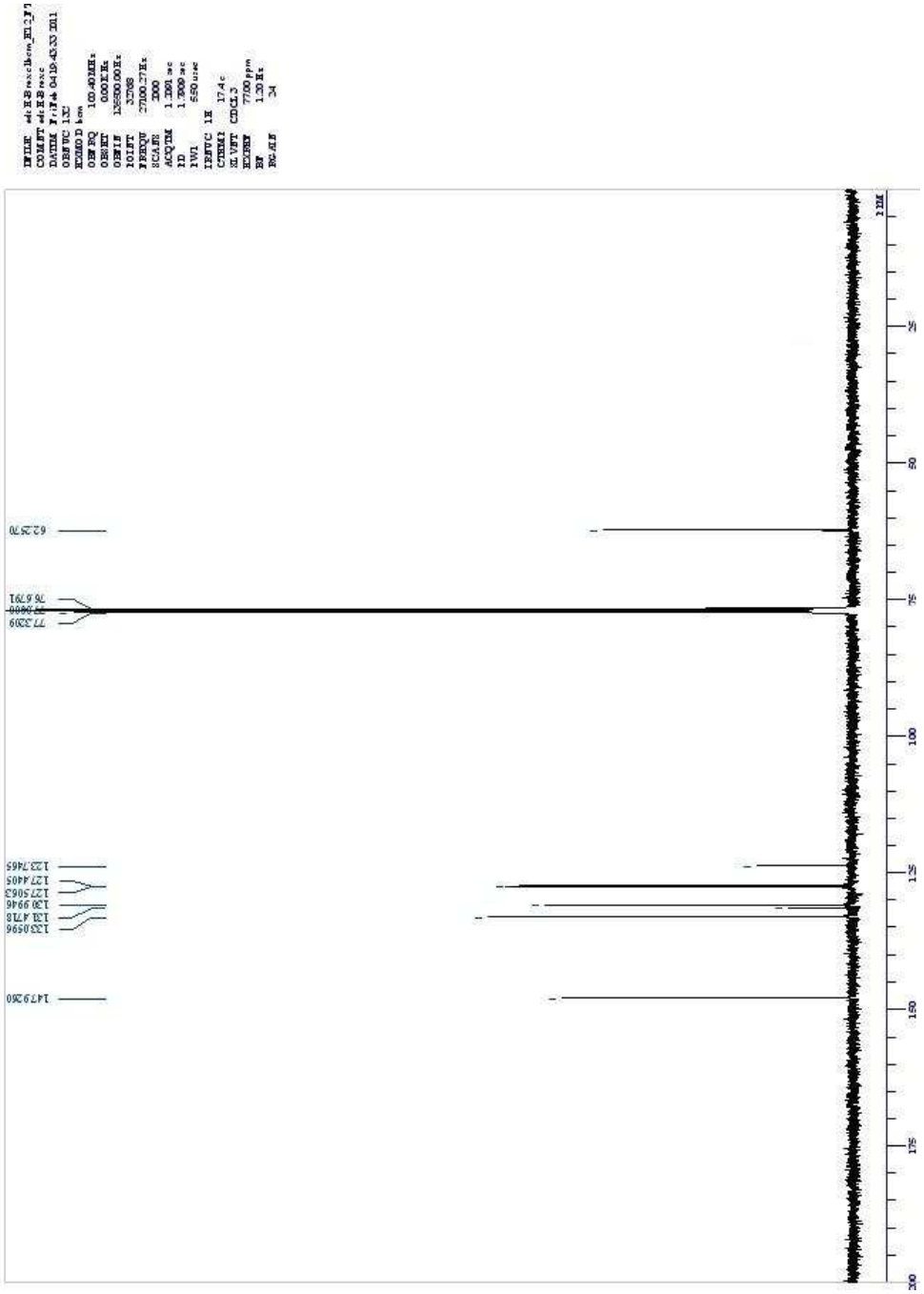


(*E*)-2,3-Dimethoxybenzaldehyde *O*-methyloxime 14a.



7. ^{13}C NMR of substituted 2-bromobenzaldehyde *O*-methyloximes 1b-14b

(*E*)-2-Bromobenzaldehyde *O*-methyloxime 1b



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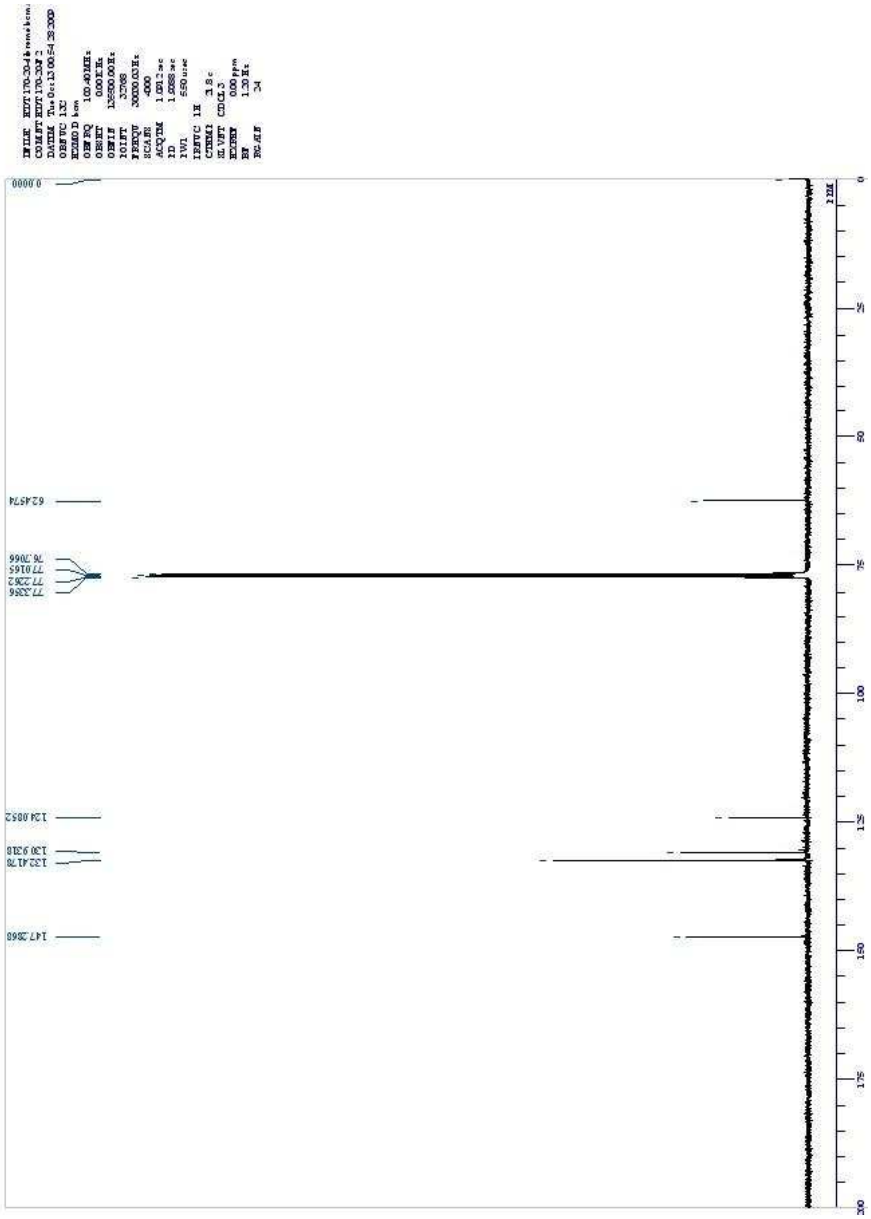
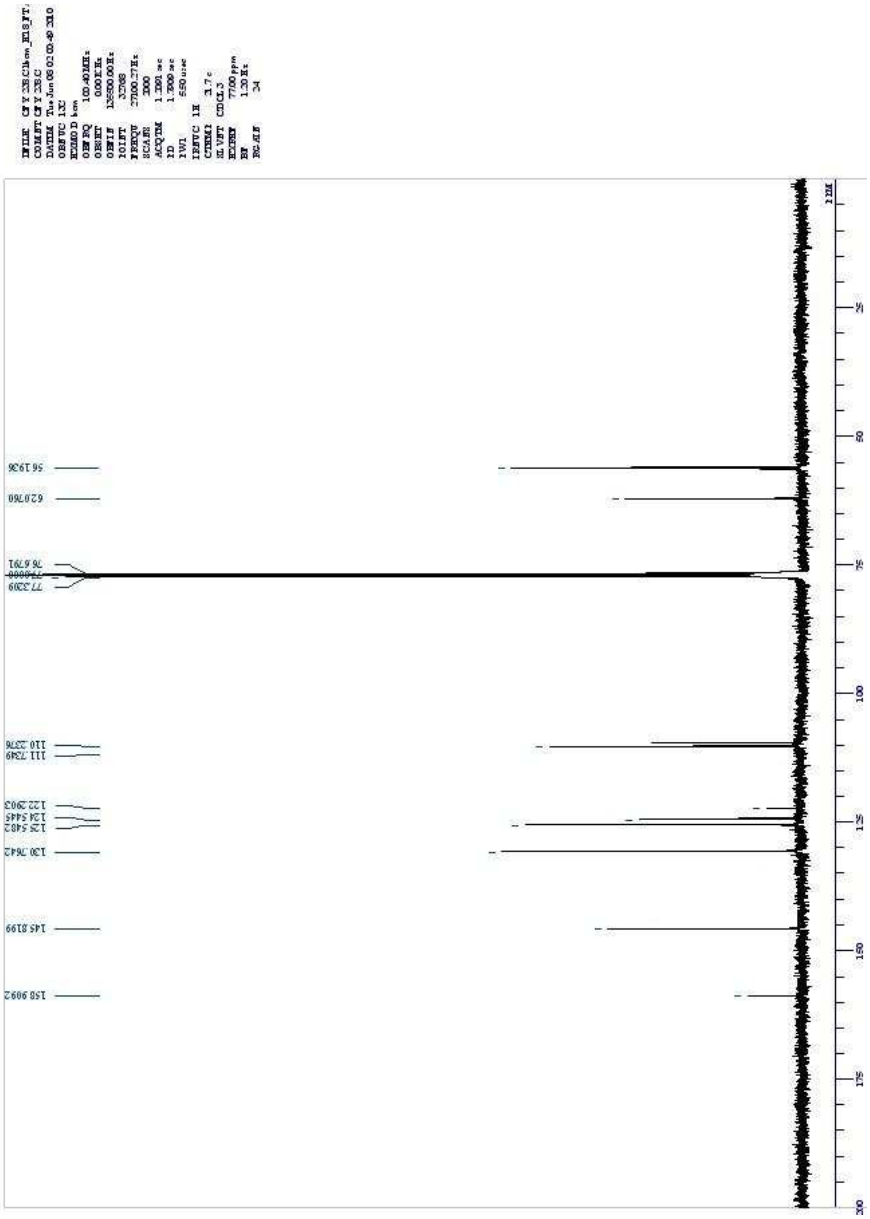


2-Bromo-6-methoxybenzaldehyde *O*-methyloxime 2b



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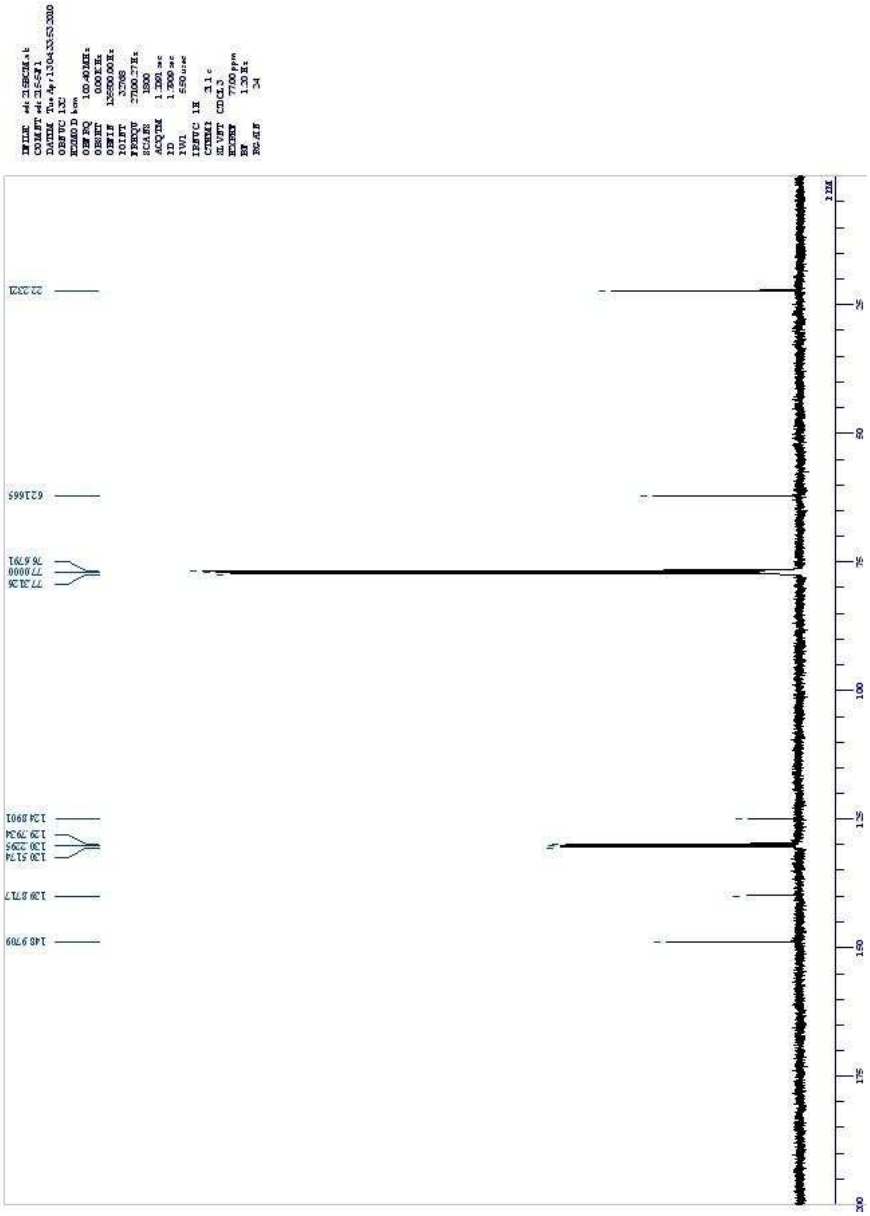
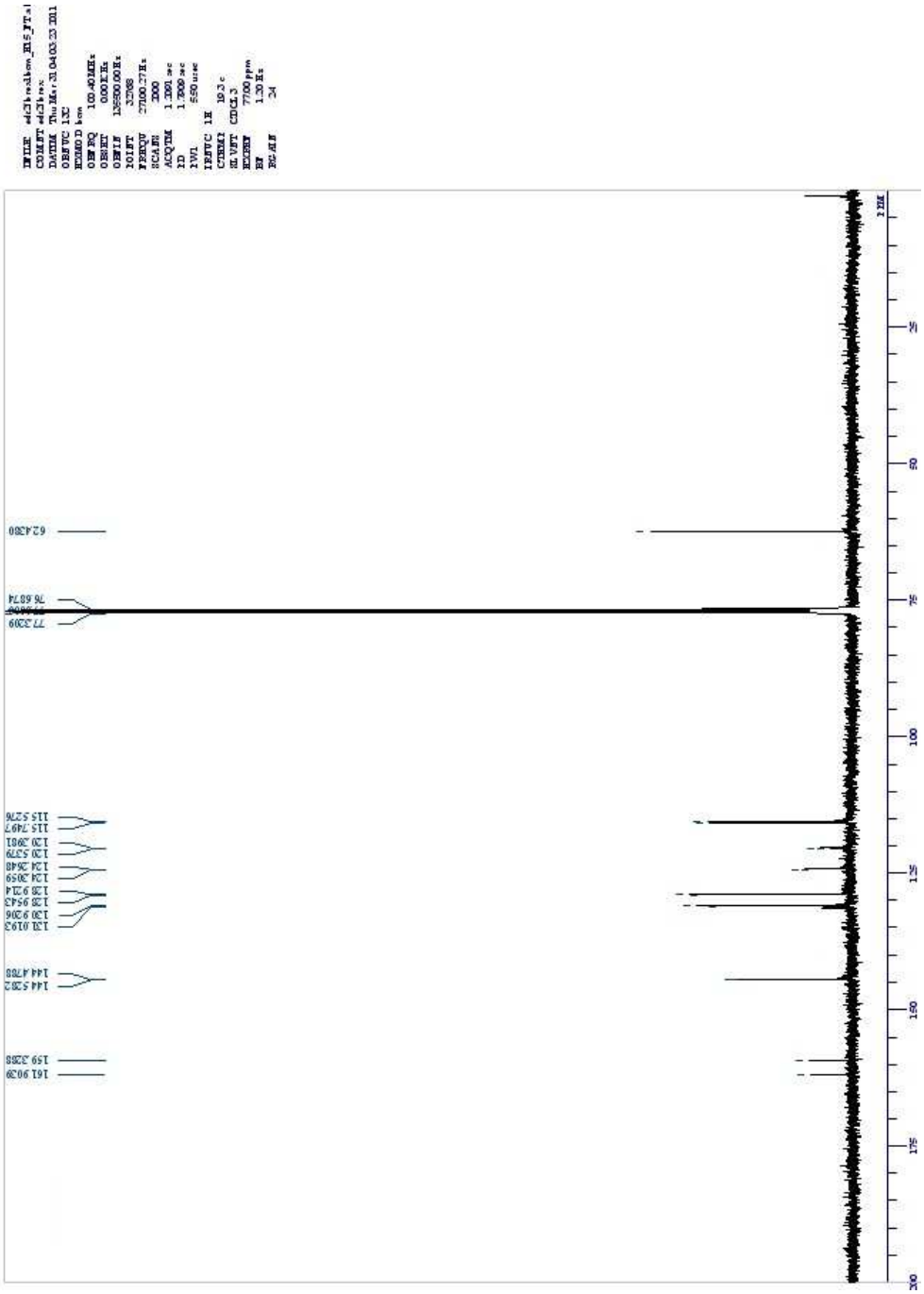
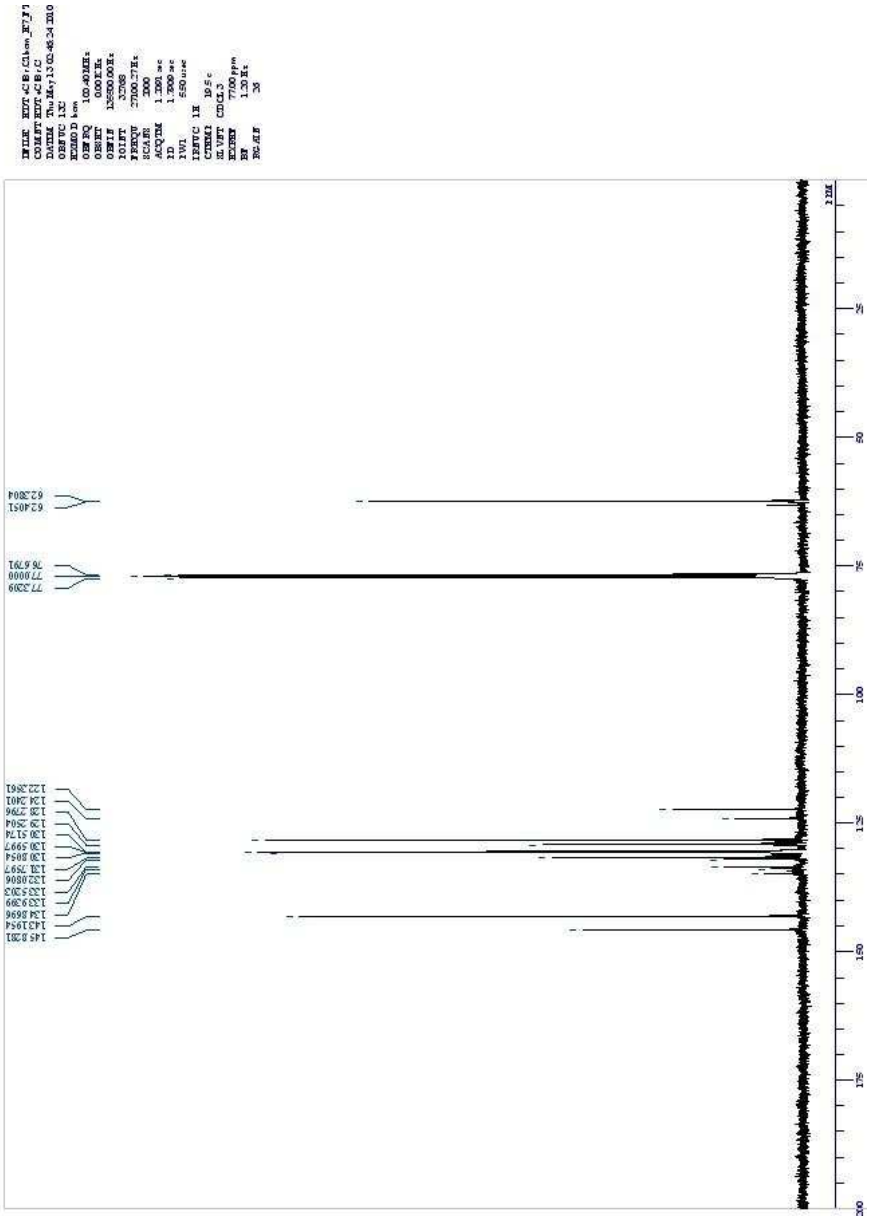


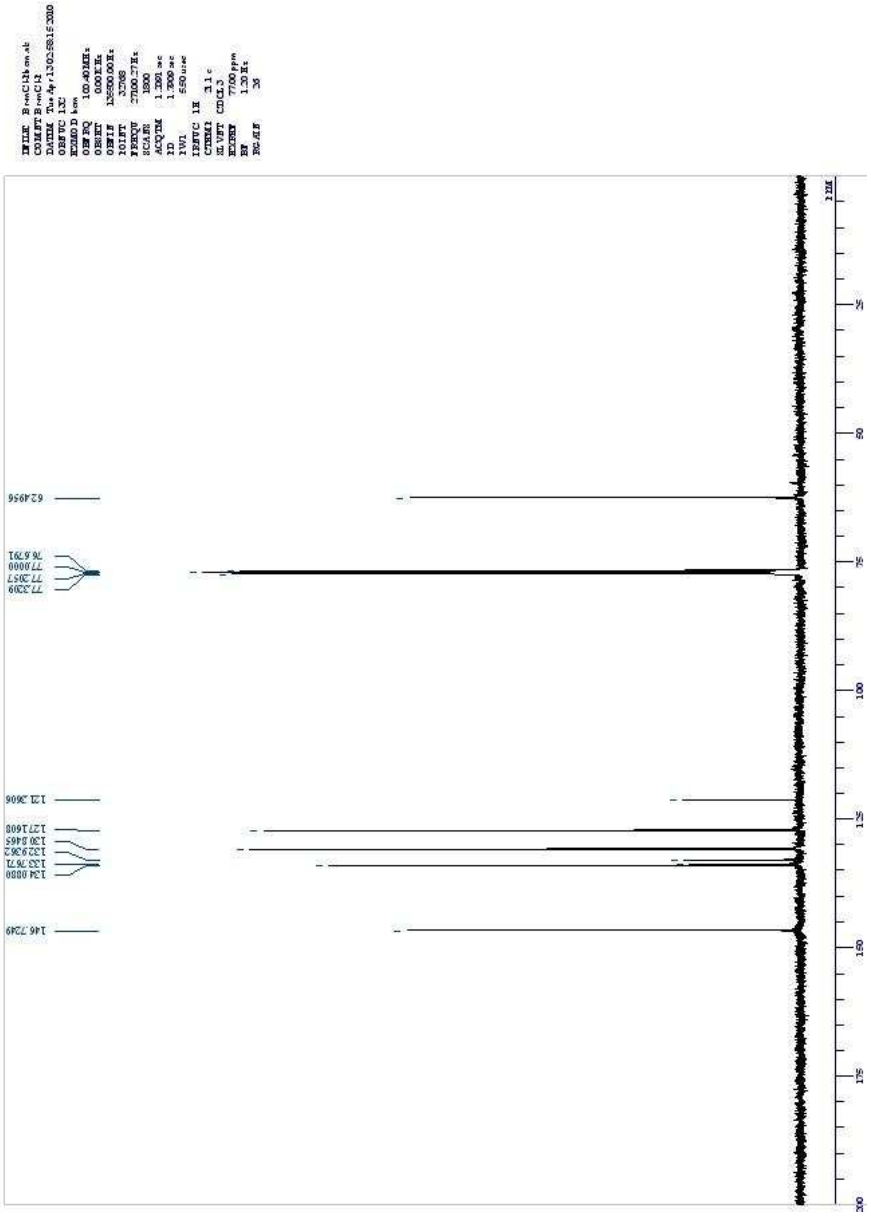
2-Bromo-6-fluorobenzaldehyde *O*-methyloxime 4b



2-Bromo-6-chlorobenzaldehyde *O*-methyloxime 5b



(*E*)-2-Bromo-5-chlorobenzaldehyde *O*-methyloxime 6b.



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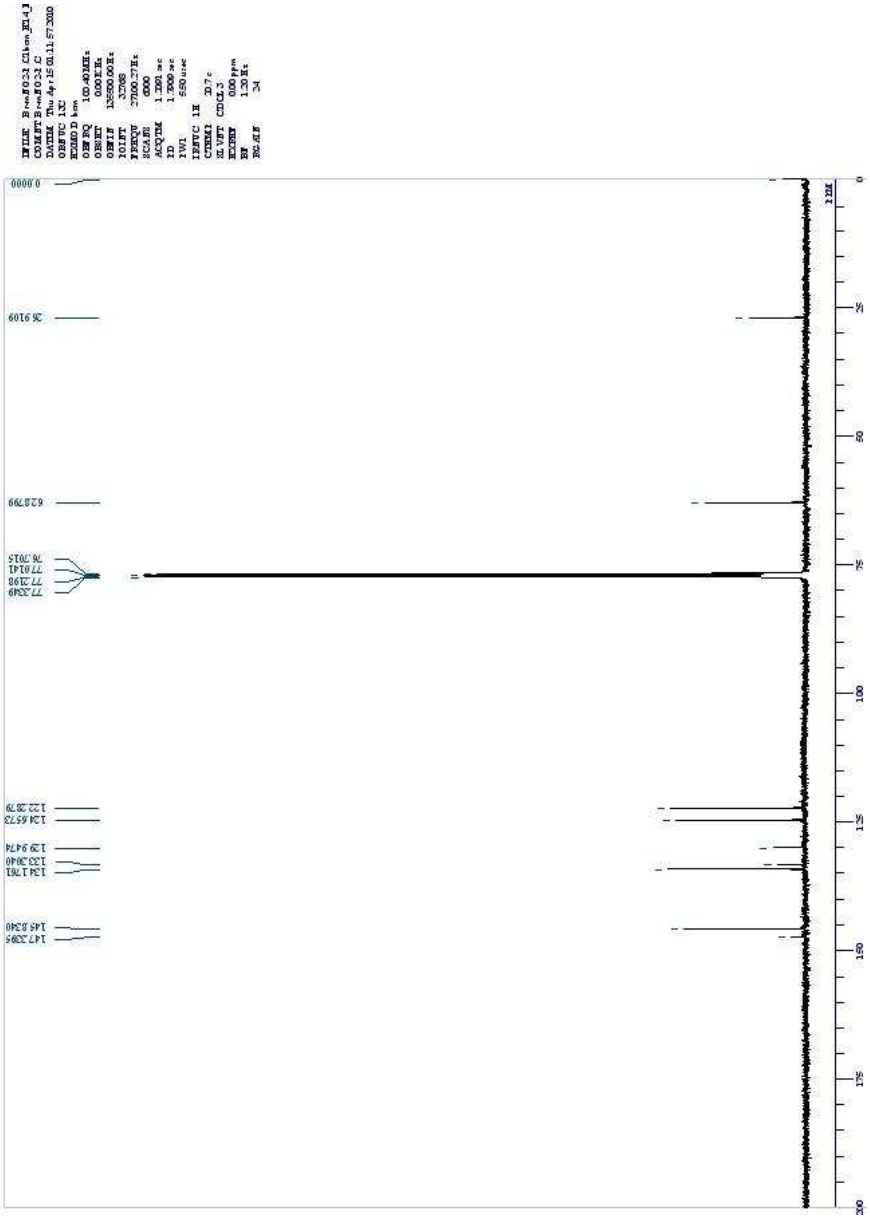
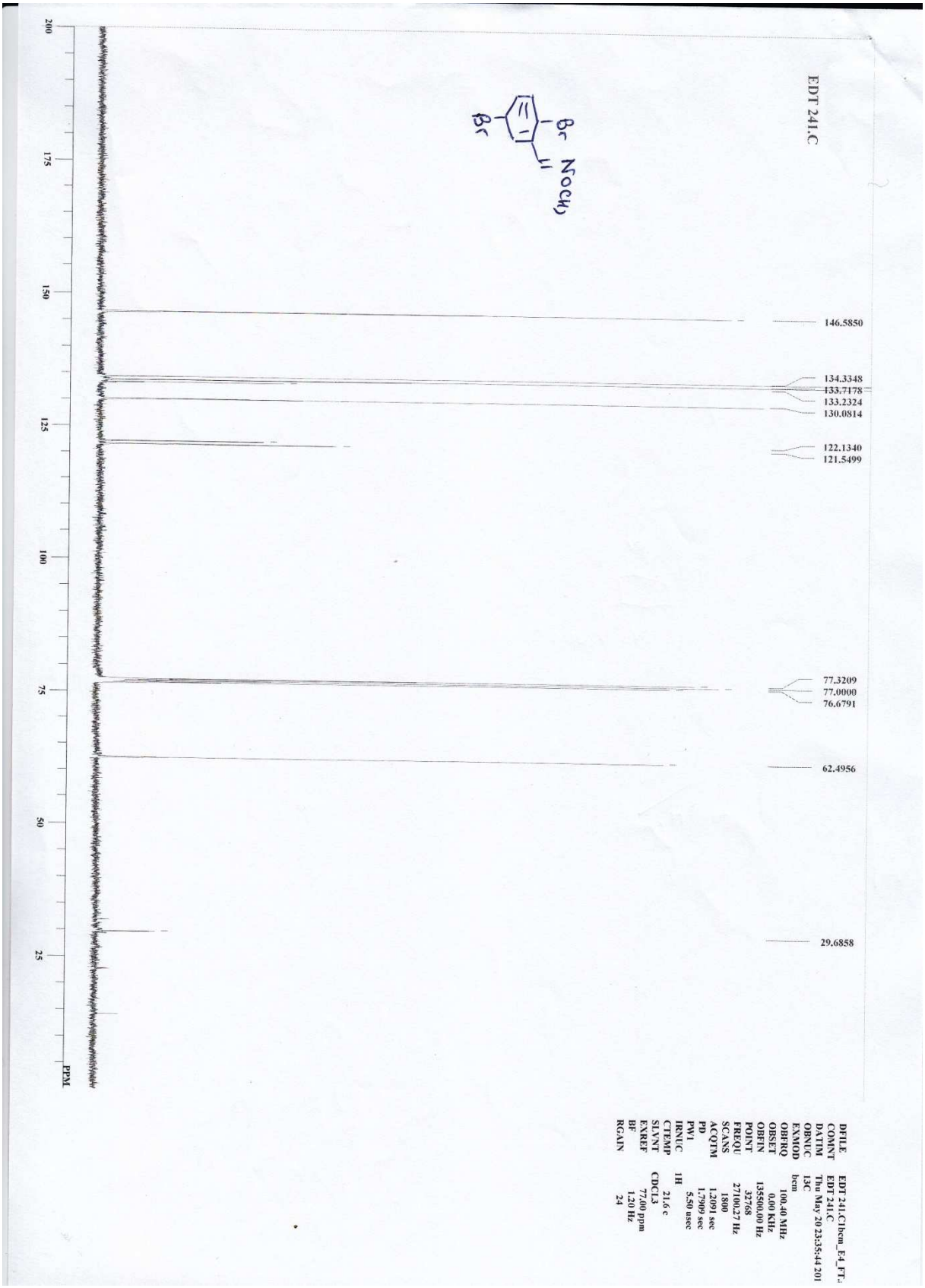
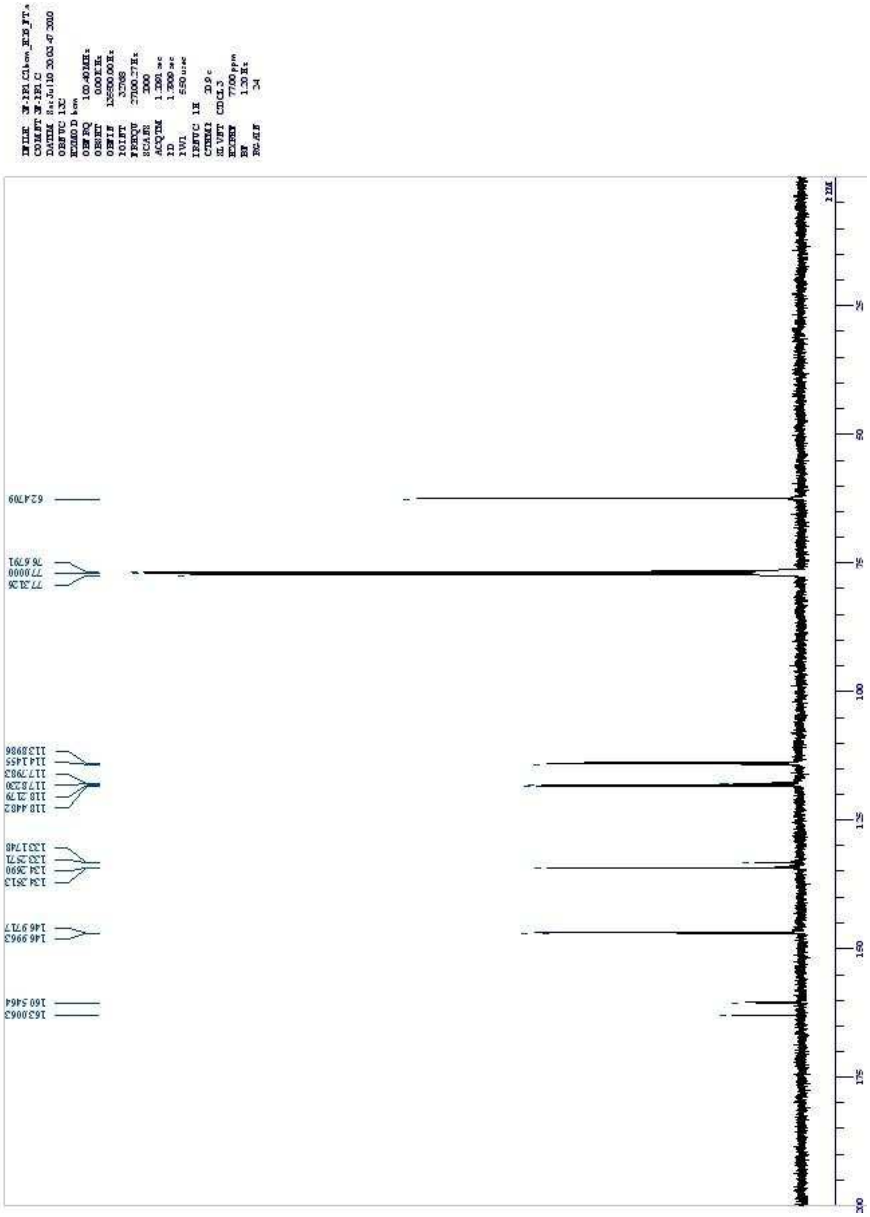


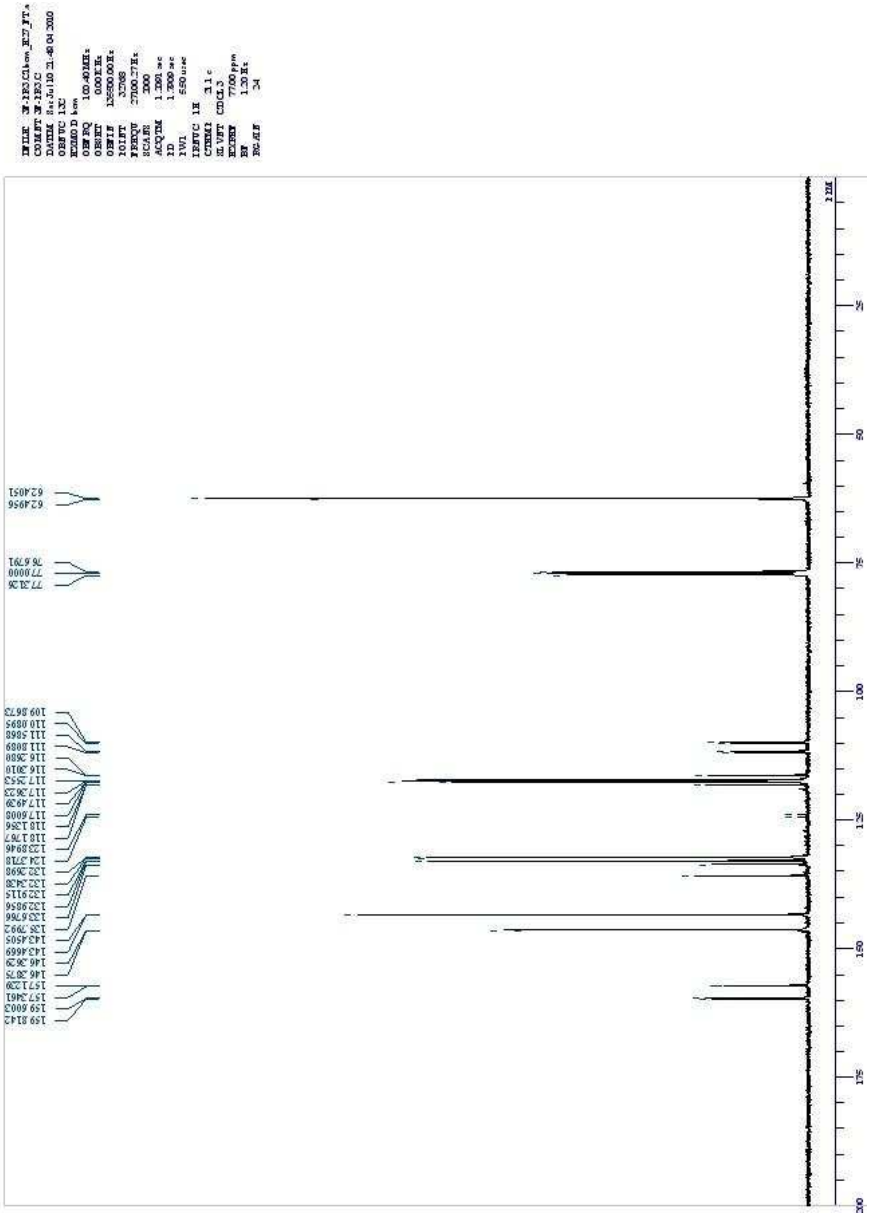
(*E*)-2,5-Dibromobenzaldehyde *O*-methyloxime 8b



2-Bromo-5-fluorobenzaldehyde *O*-methyloxime 9b



2,6-Dibromo-3-fluorobenzaldehyde *O*-methyloxime 9c



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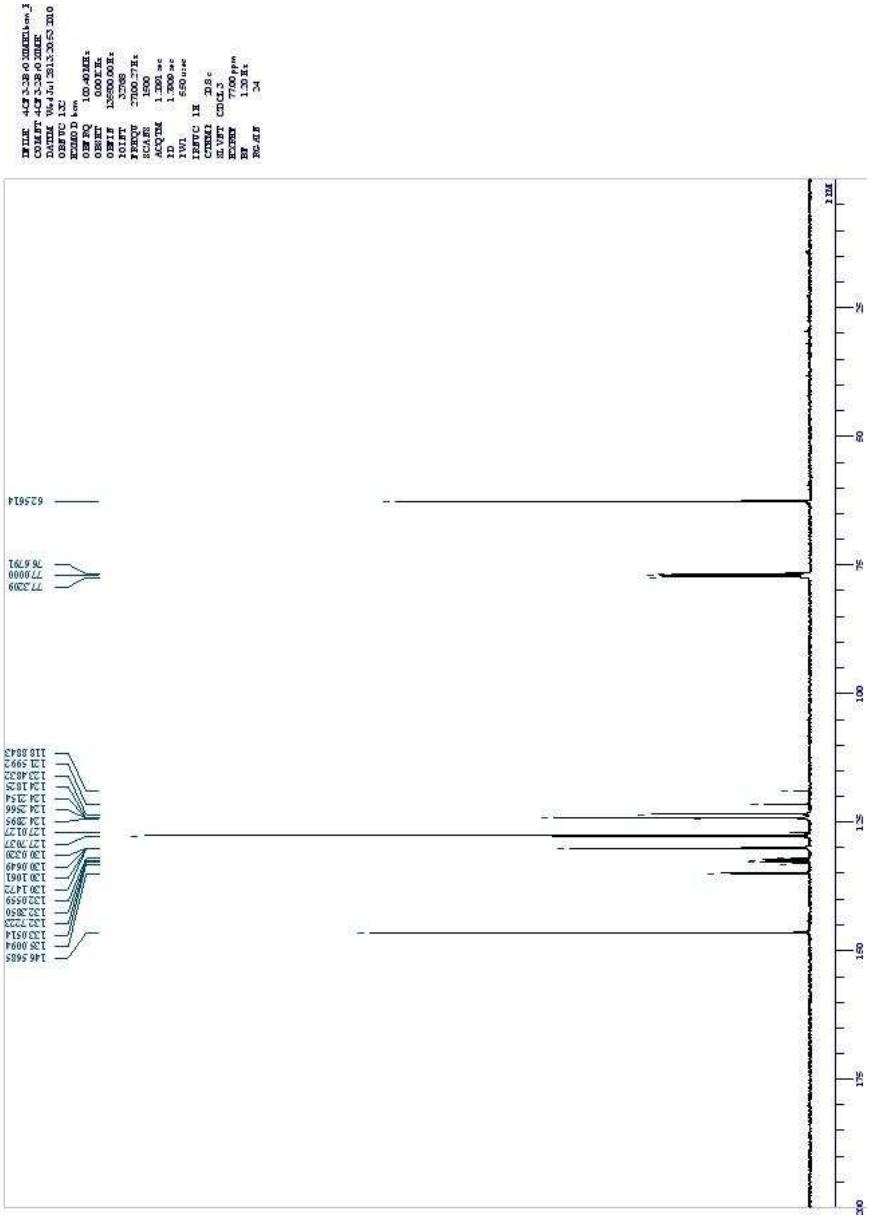

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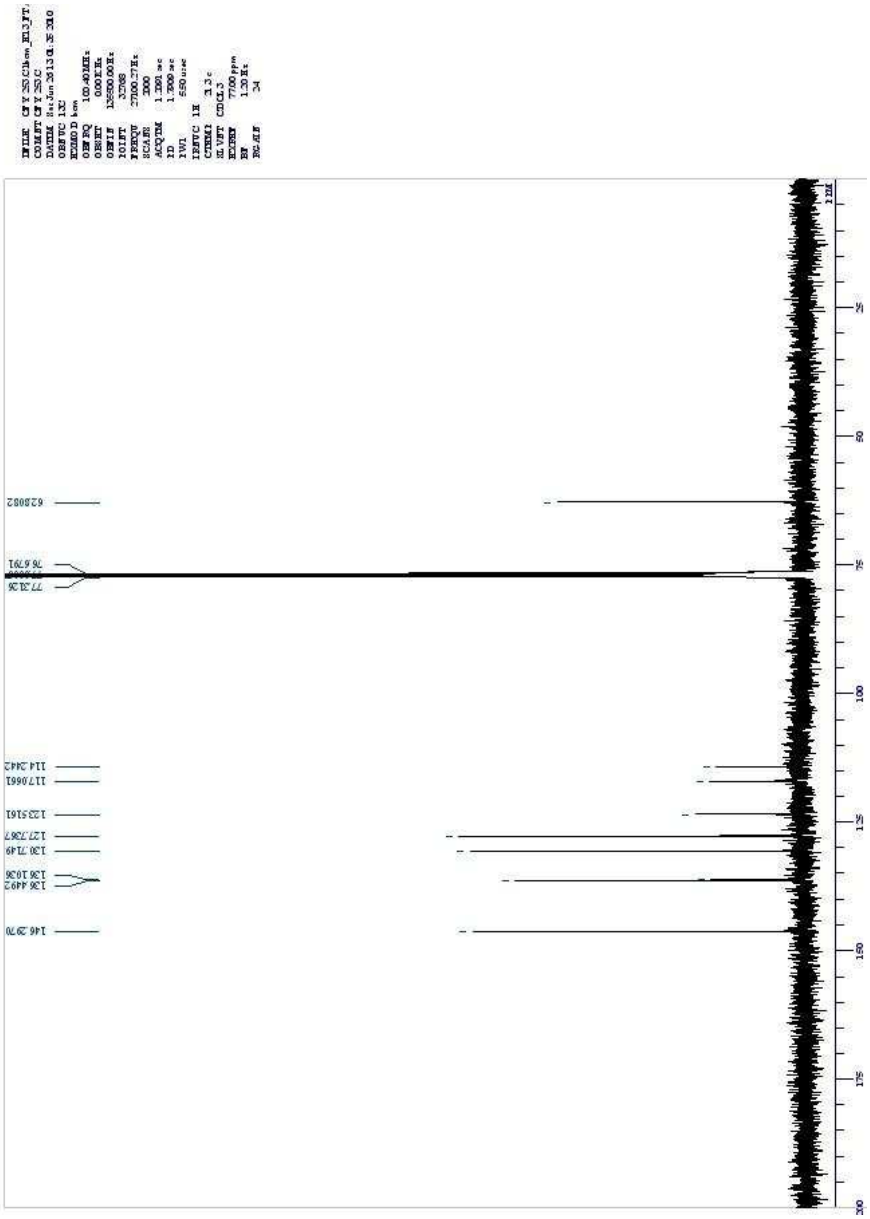

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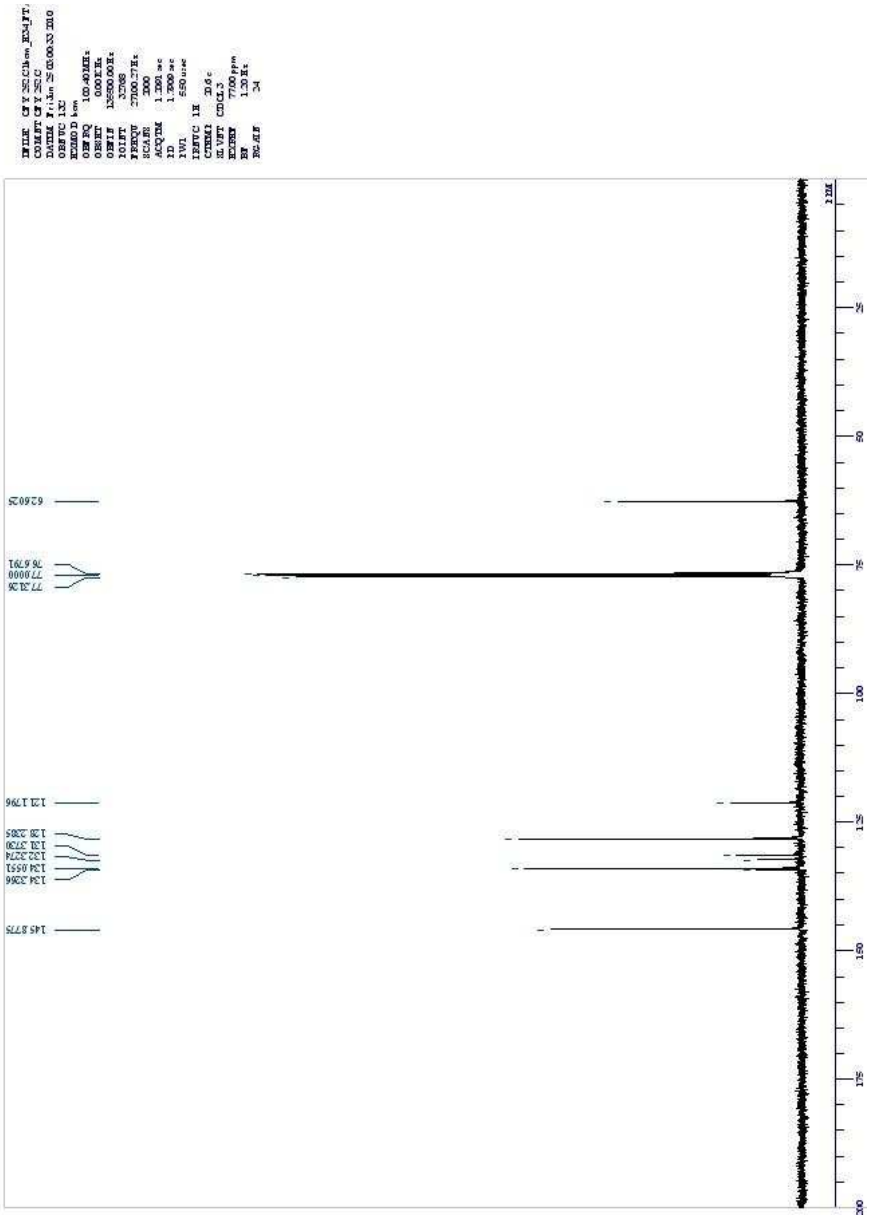
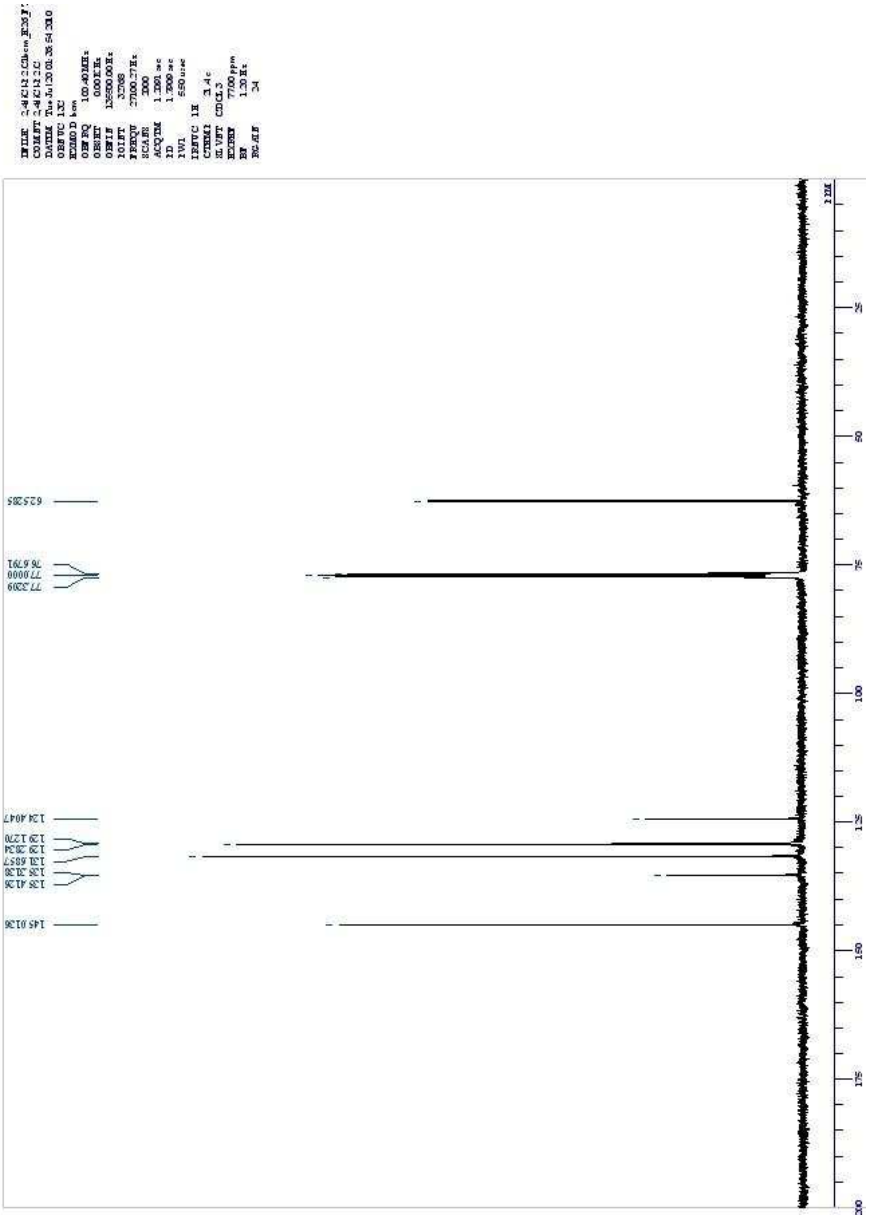


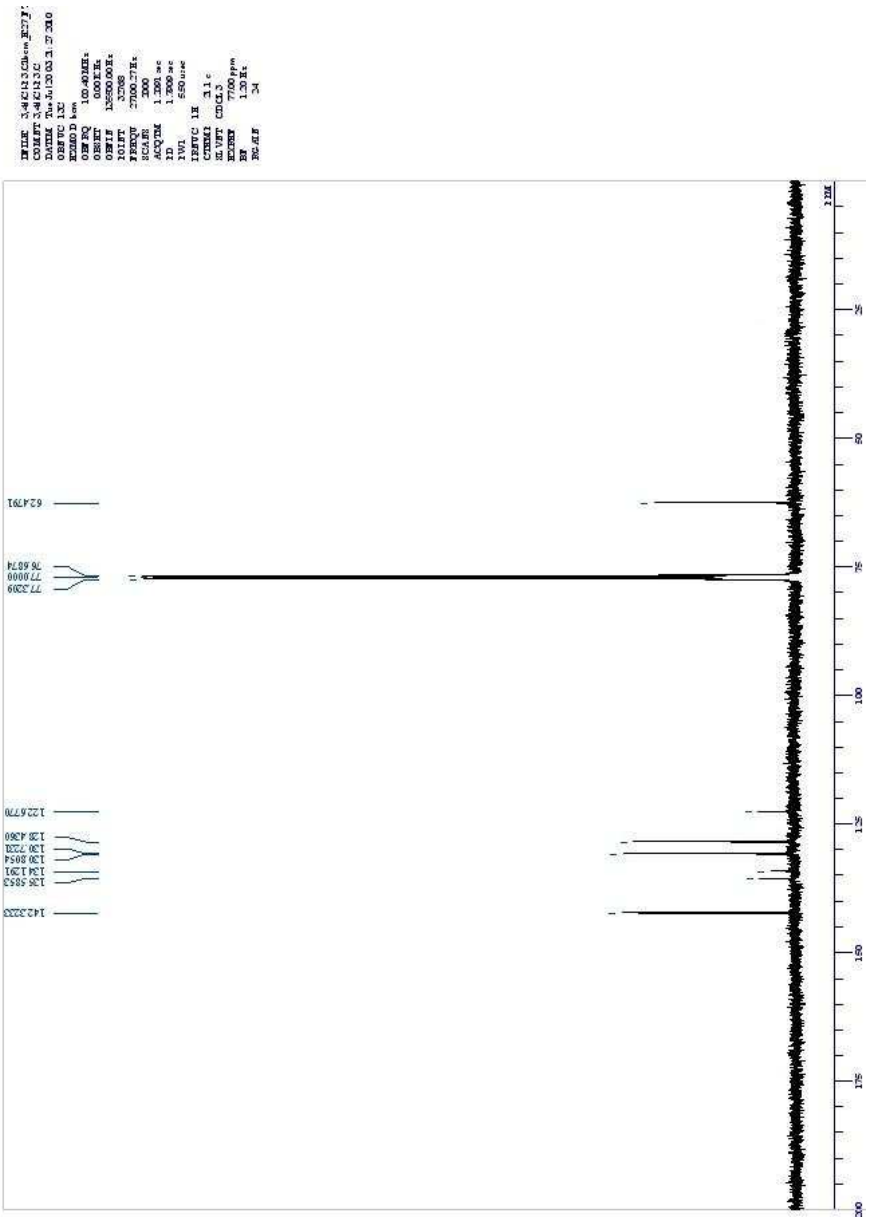
2-Bromo-4,6-dichlorobenzaldehyde *O*-methyloxime 13b

Diastereoisomer (*E*)

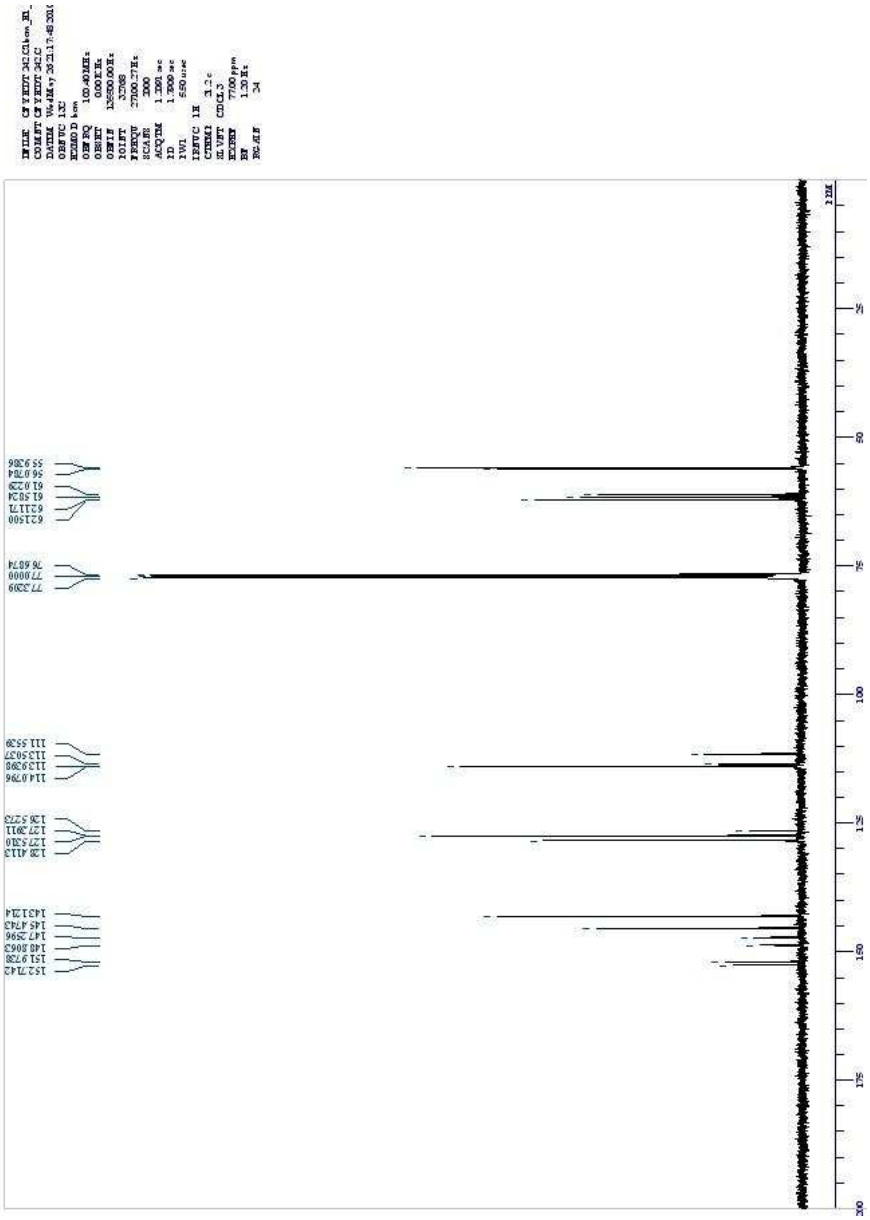


2-Bromo-4,6-dichlorobenzaldehyde *O*-methyloxime 13b

Diastereoisomer (*Z*)

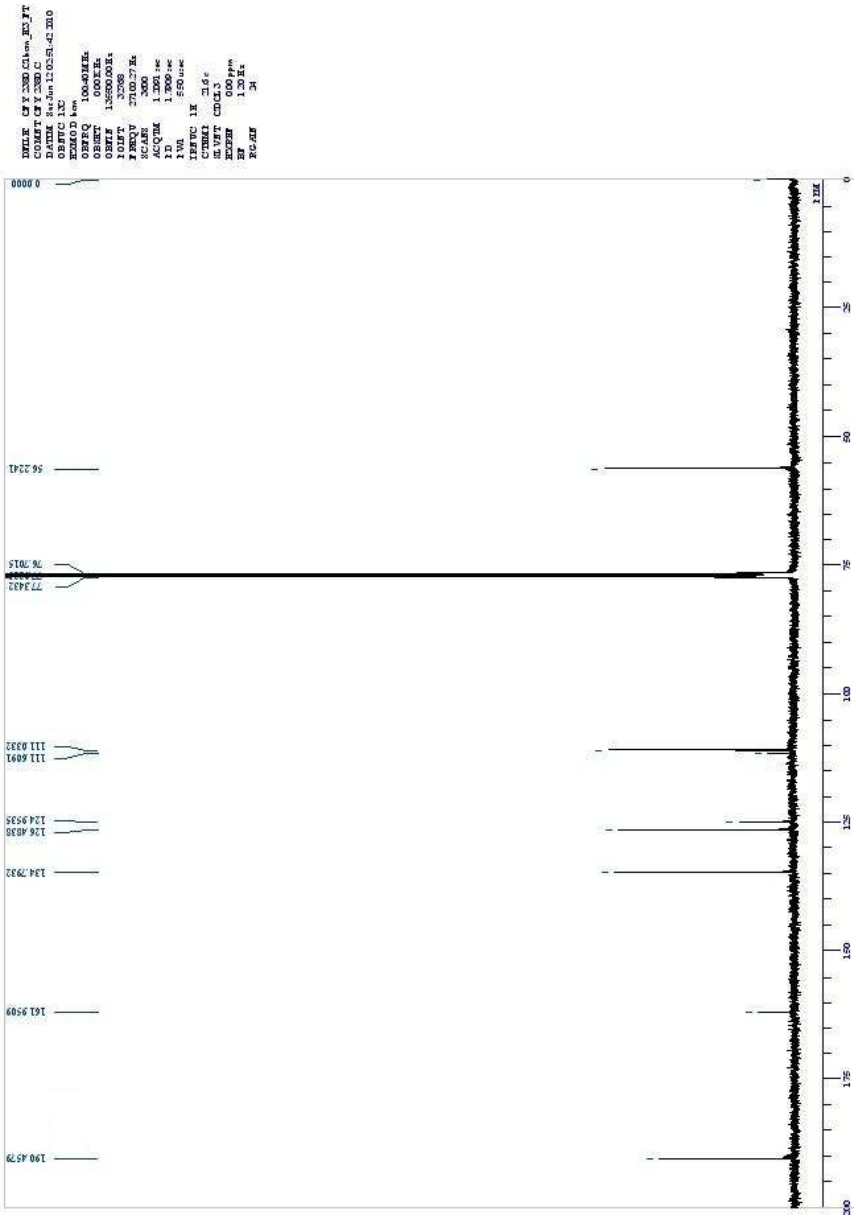


2-Bromo-5,6-dimethoxybenzaldehyde *O*-methyloxime 14b



8. ^{13}C NMR of substituted 2-bromobenzaldehydes 2d-14d

2-Bromo-6-methoxybenzaldehyde 2d



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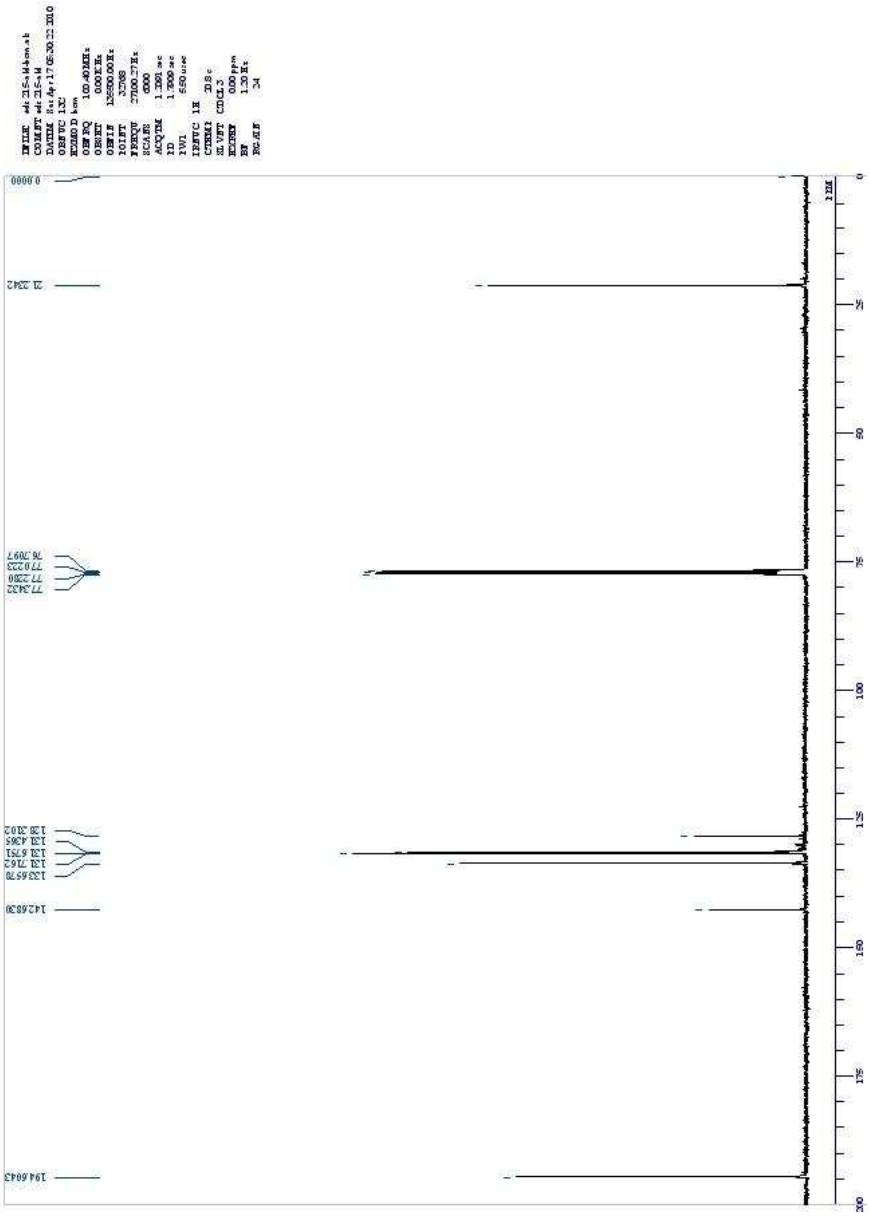

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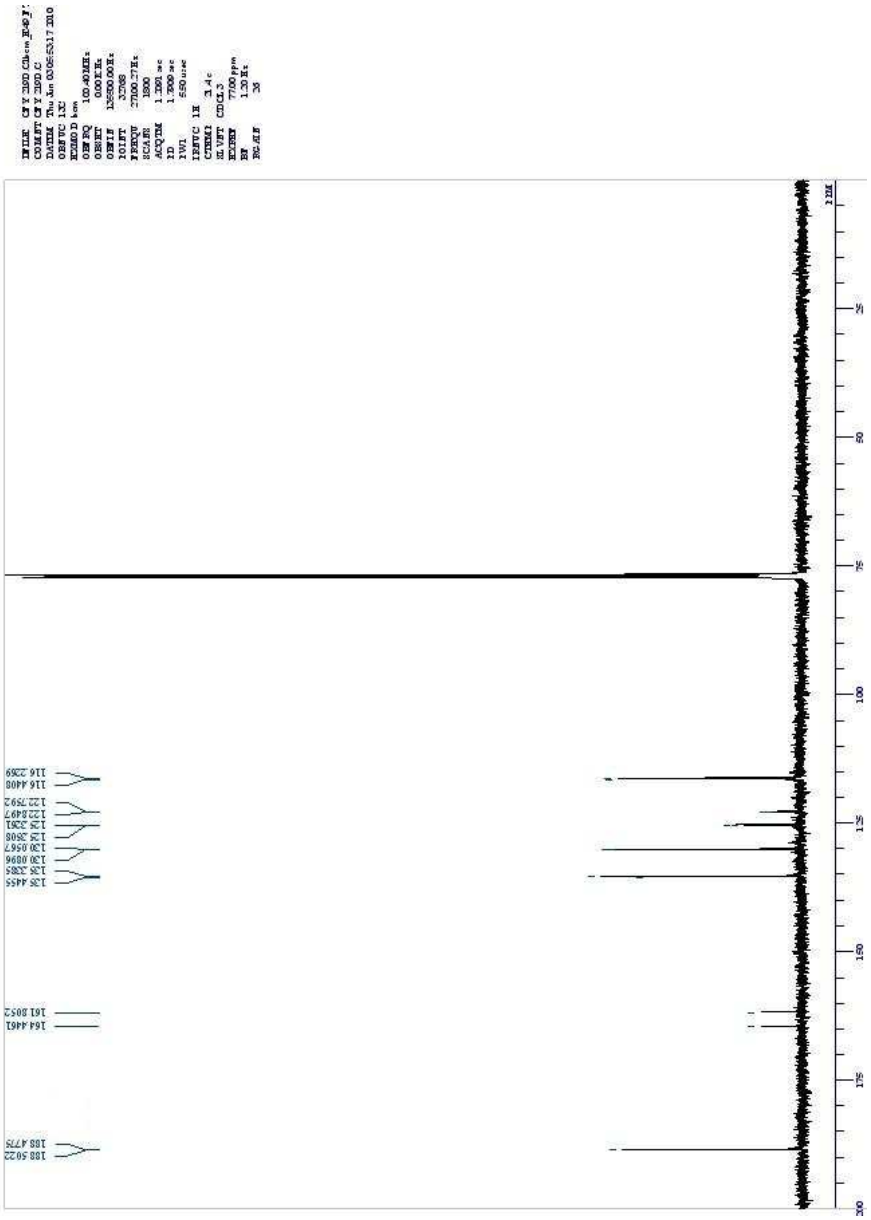
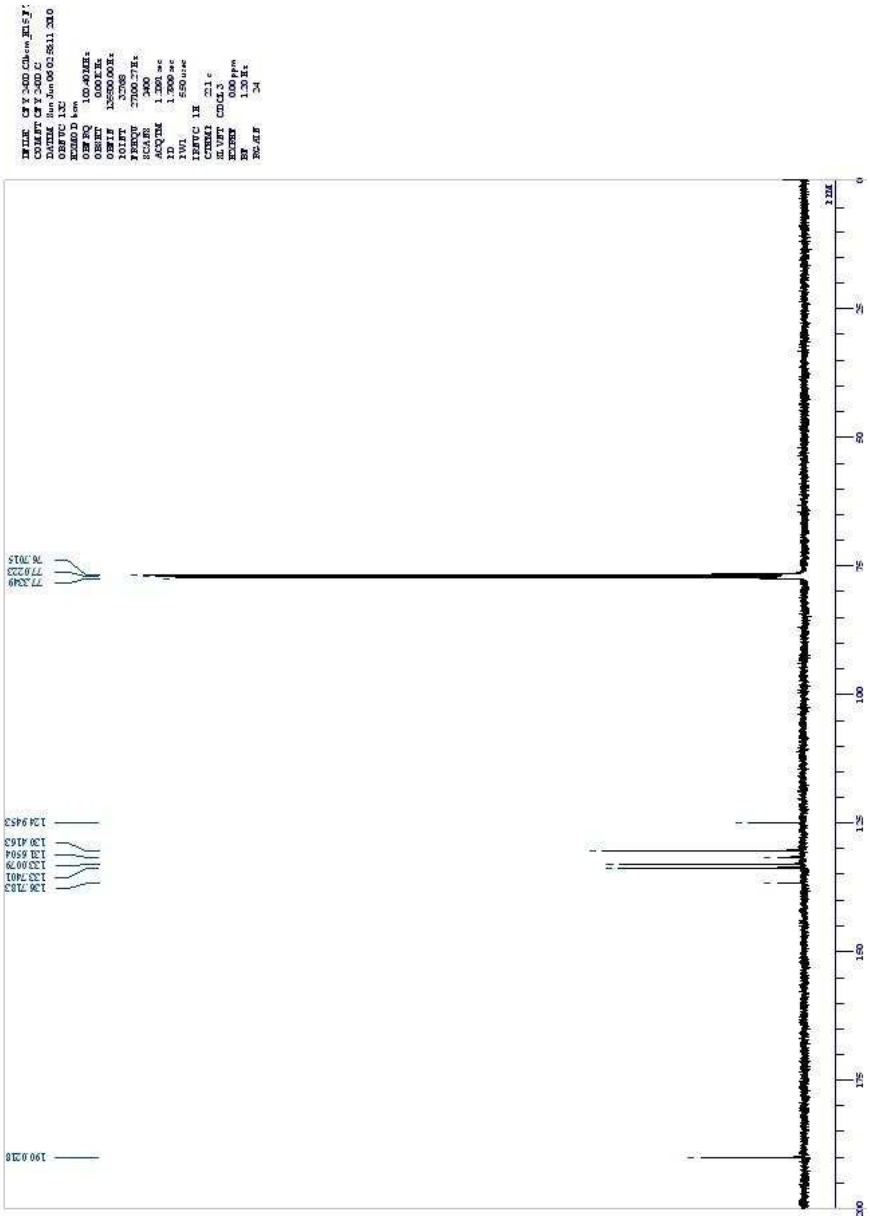


2-Bromo-6-chlorobenzaldehyde 5d



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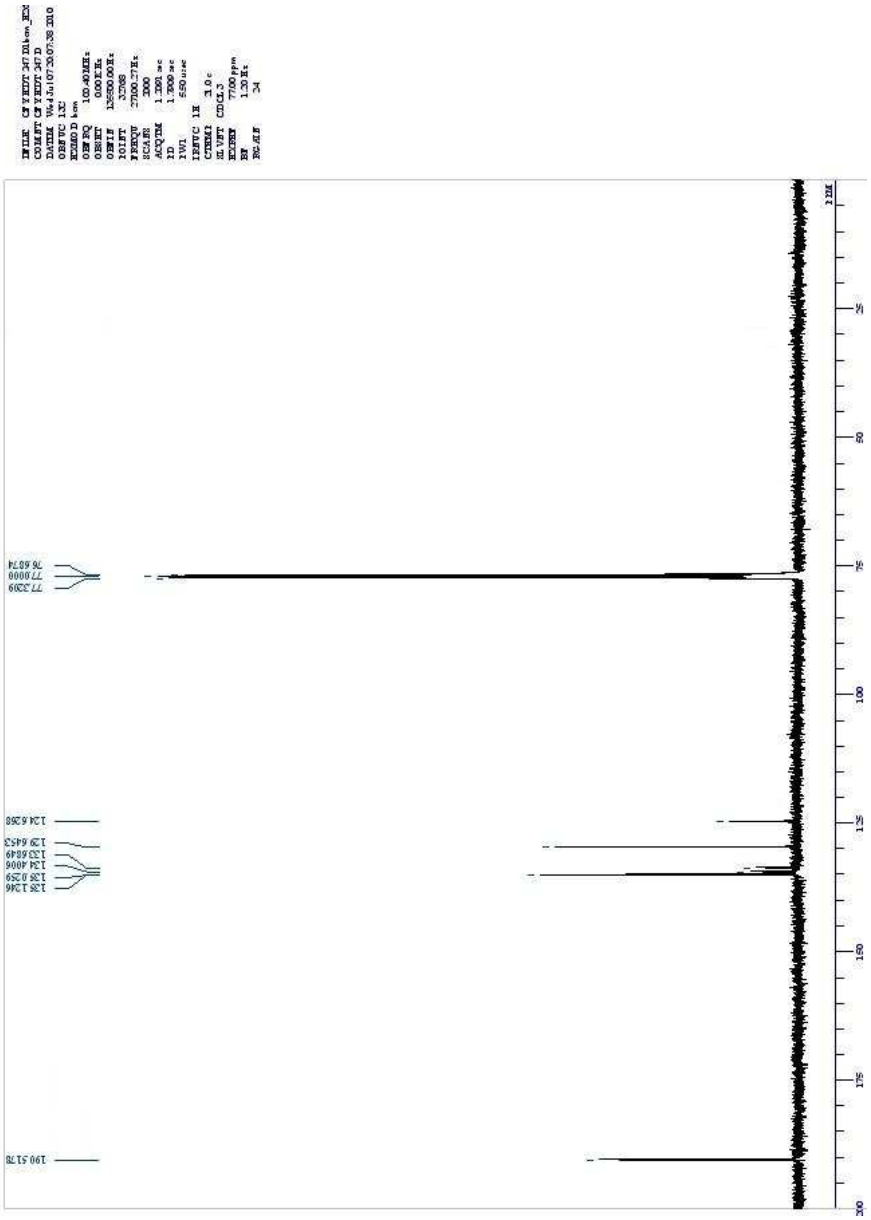

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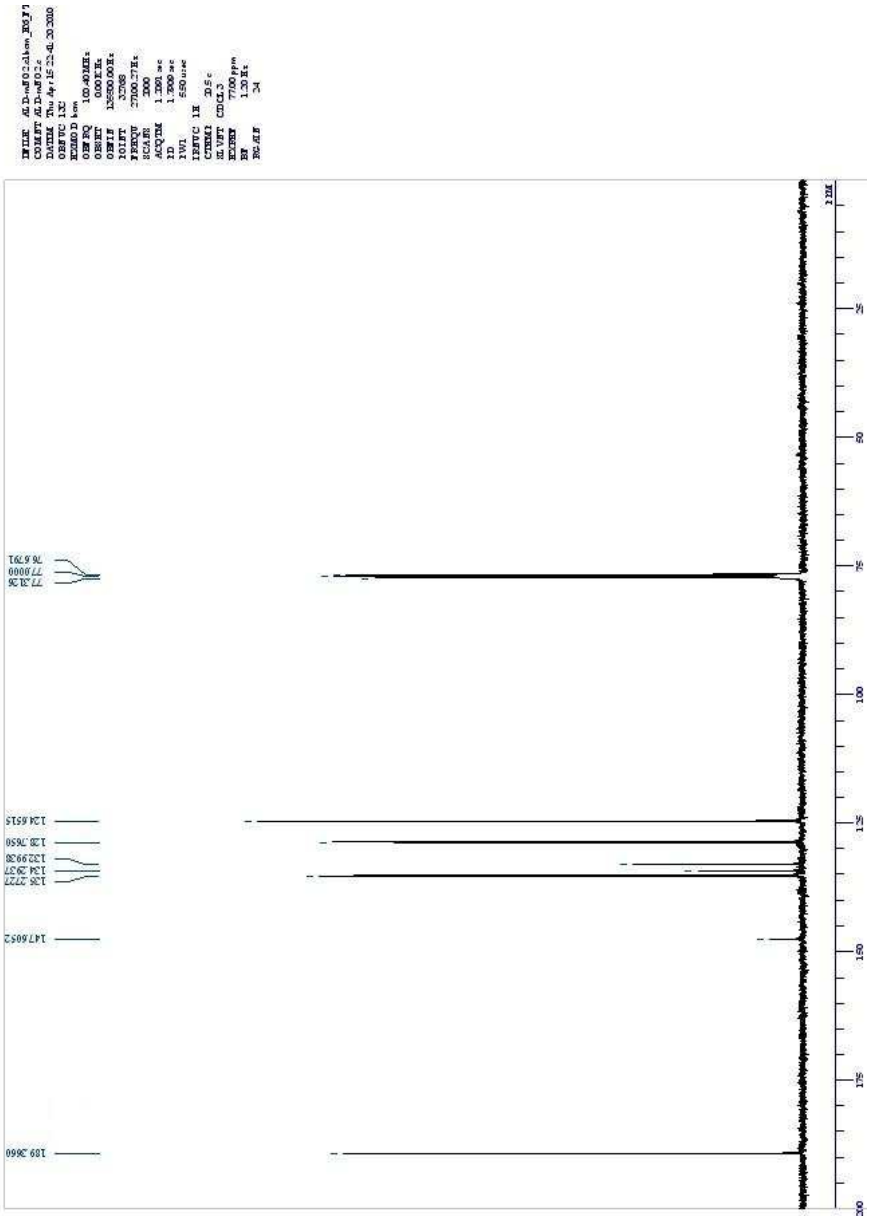

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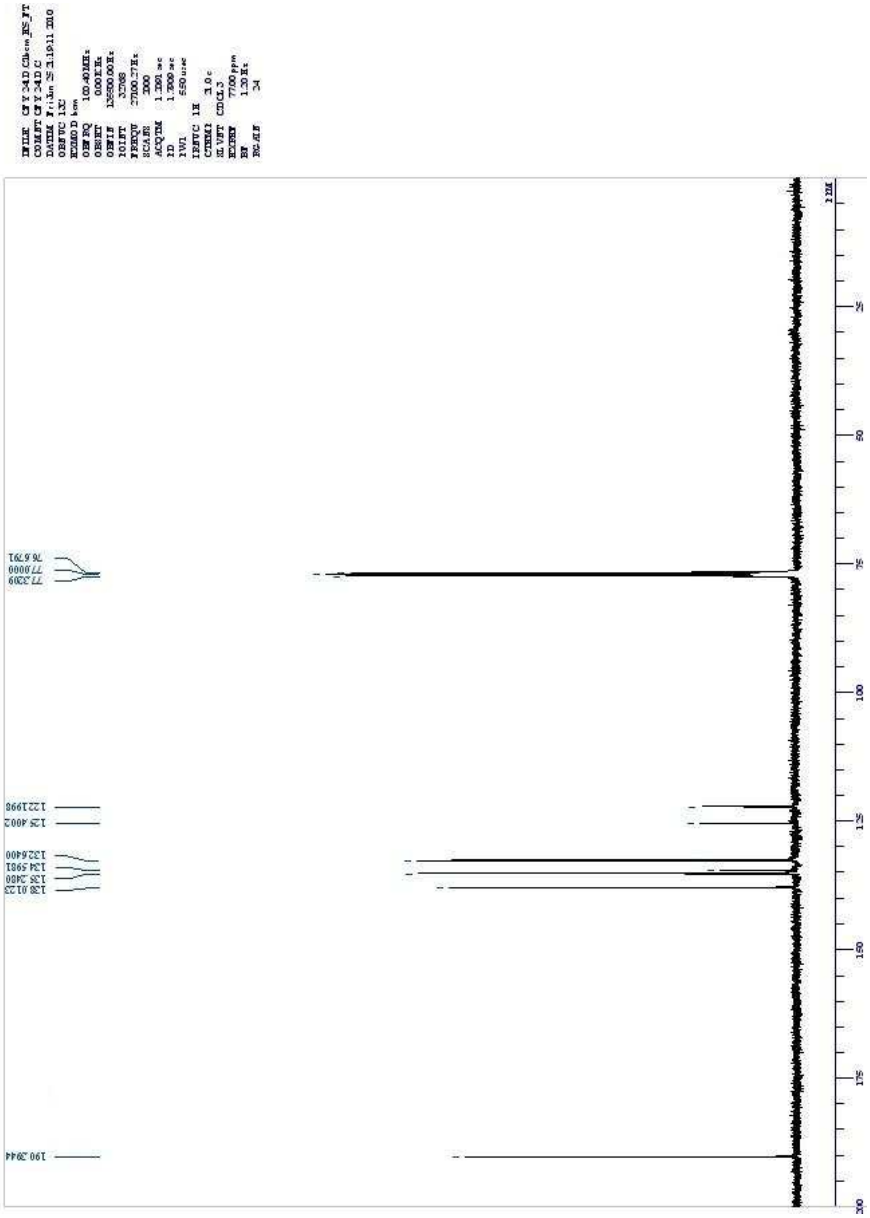

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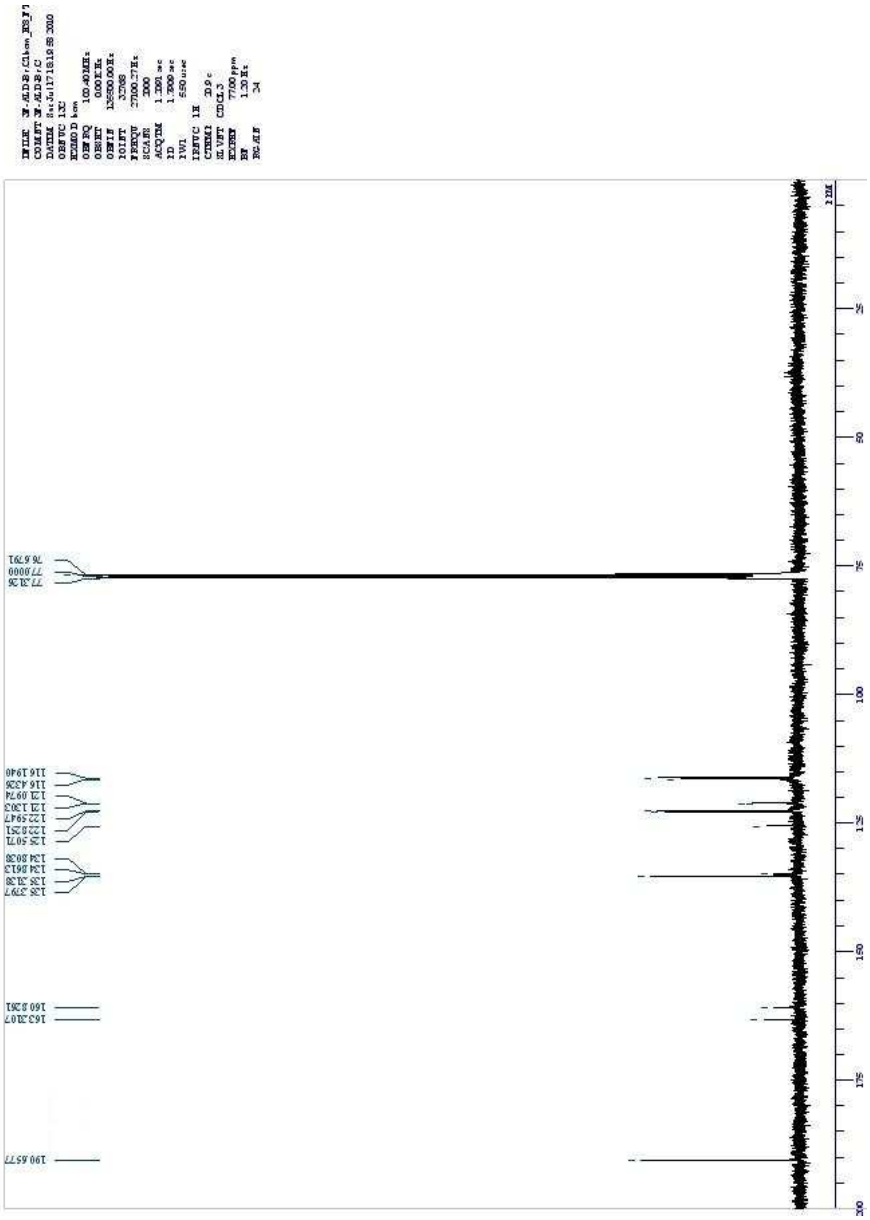
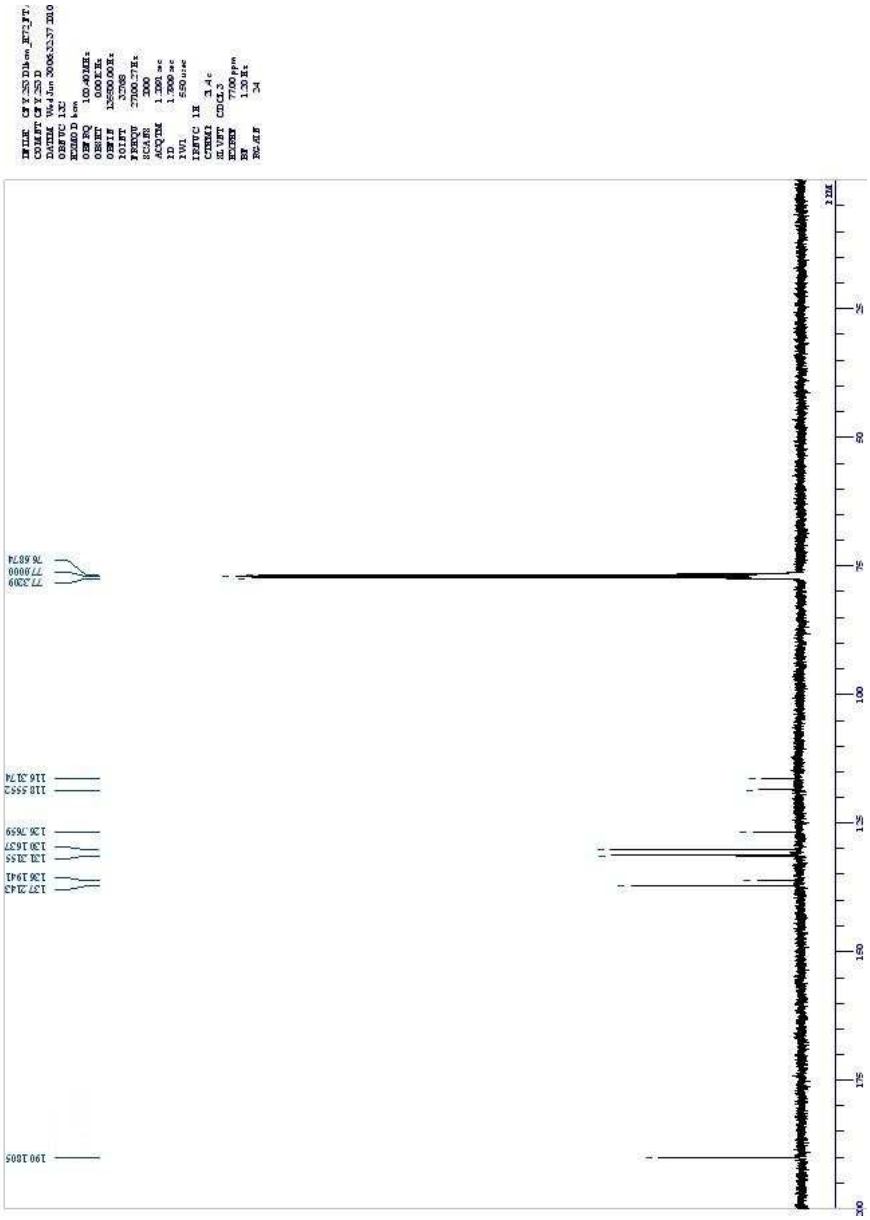
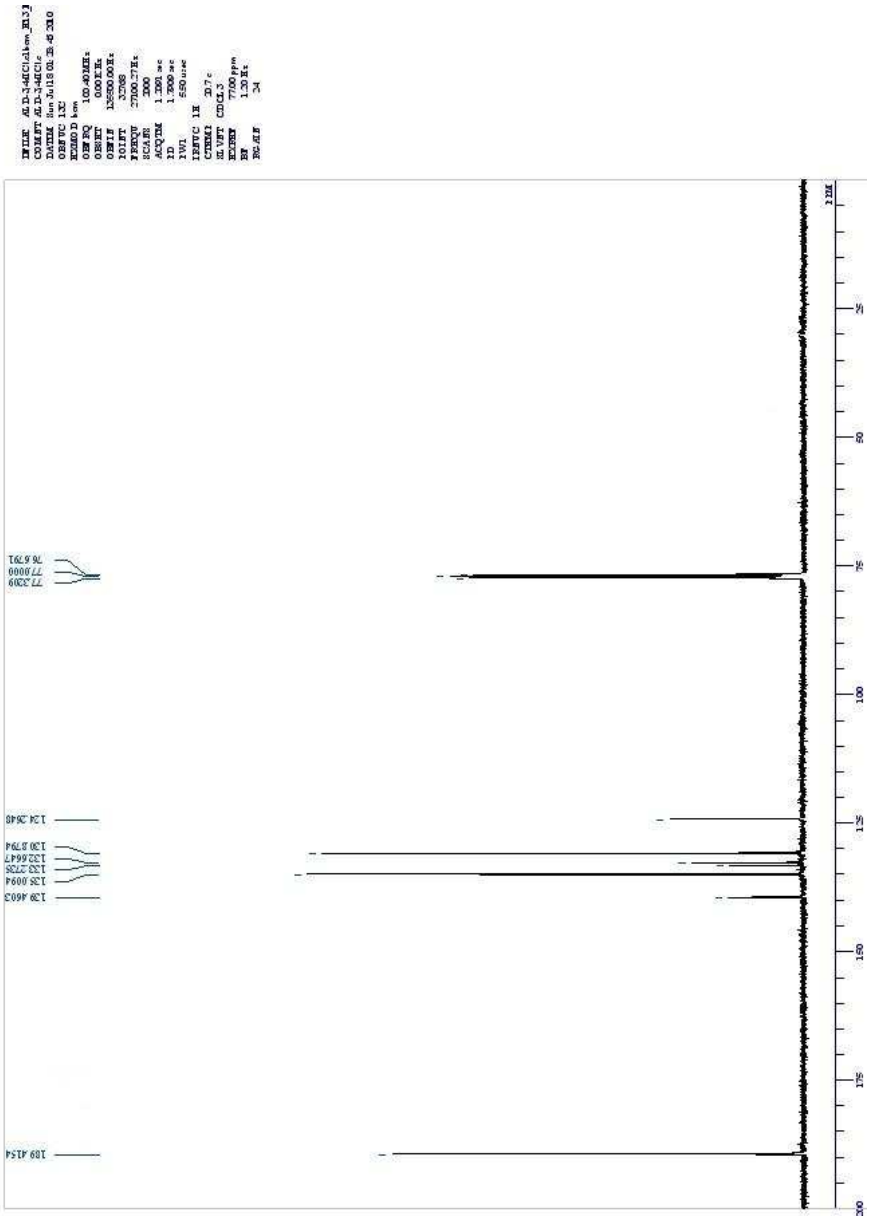


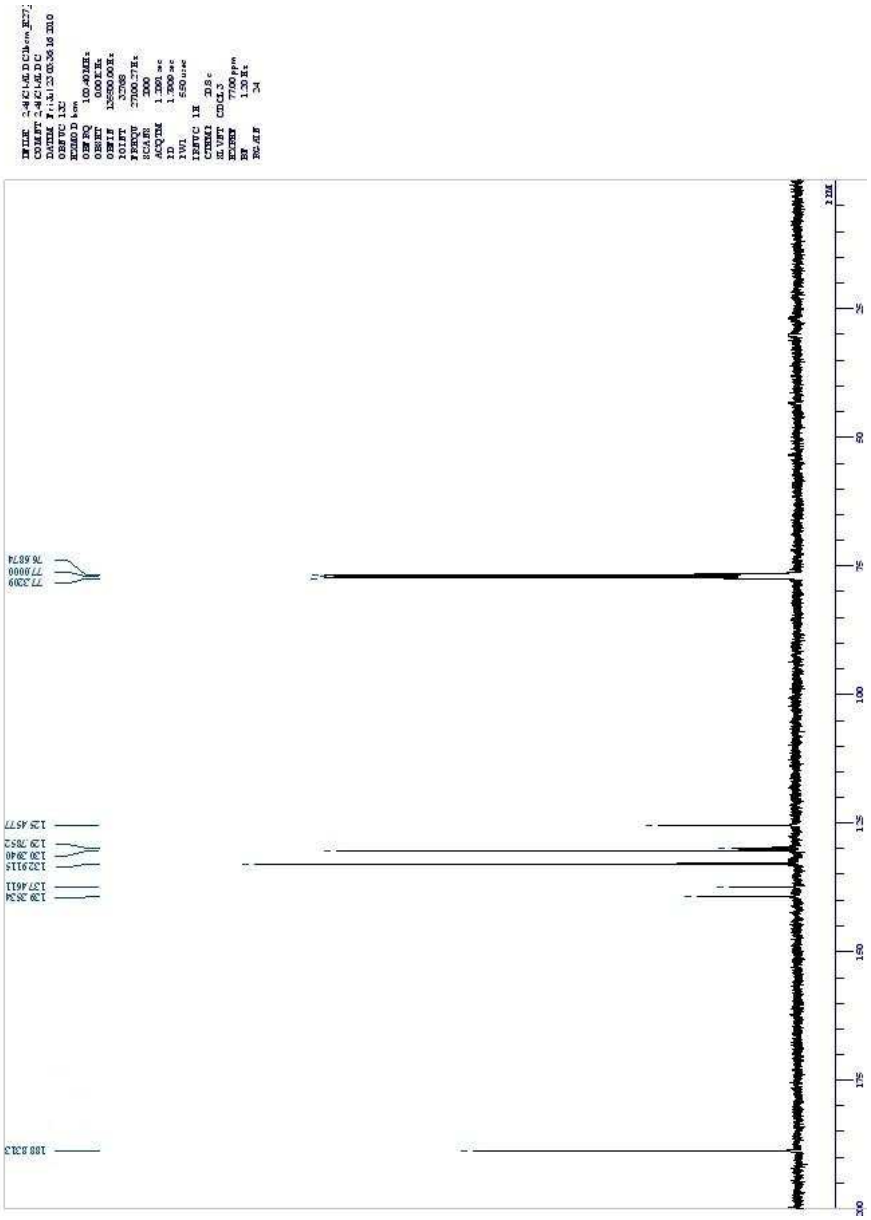
2-Bromo-4-cyanobenzaldehyde 11d



2-Bromo-4,5-dichlorobenzaldehyde 12d



2-Bromo-4,6-dichlorobenzaldehyde 13d



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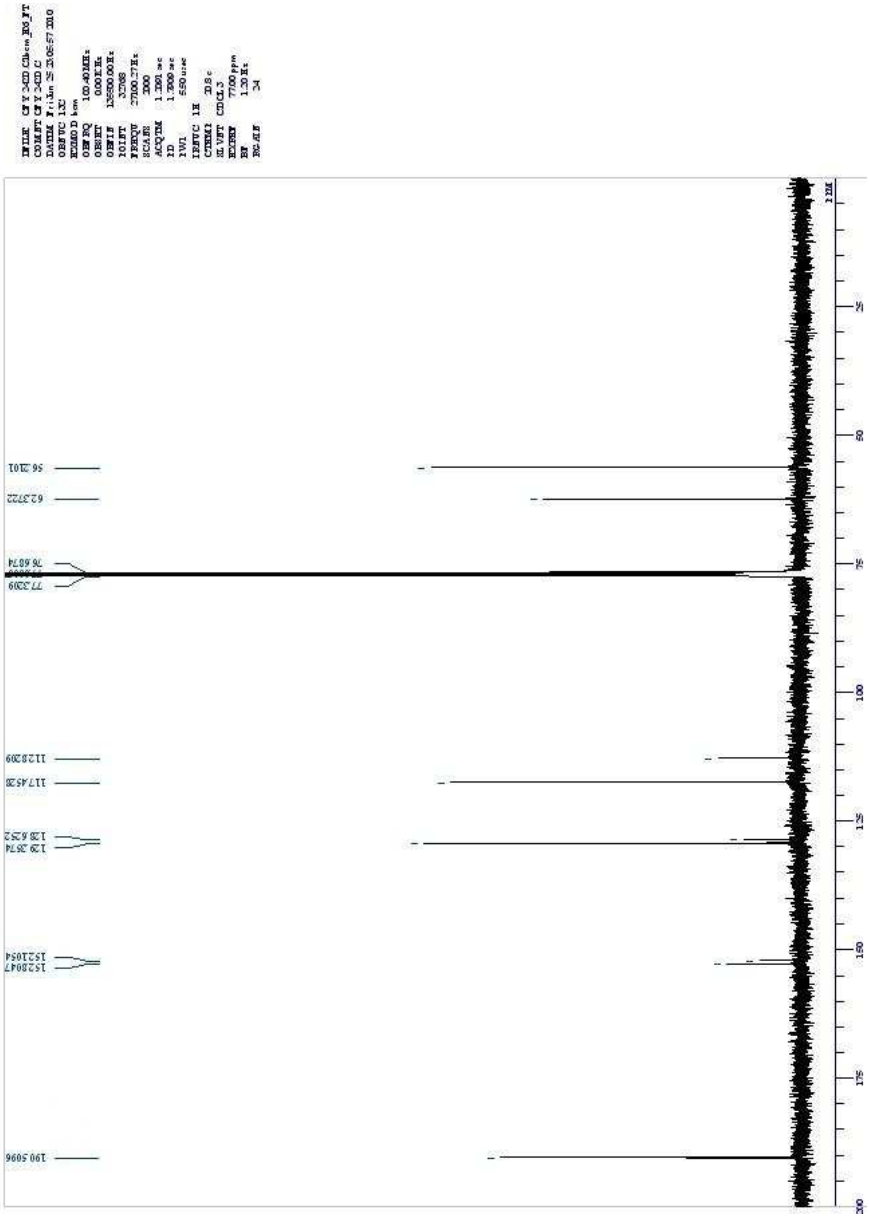
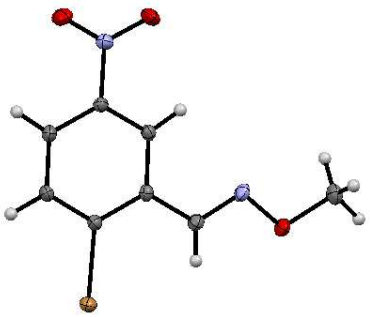


9. RX (ORTEP) and crystallographic data of (*E*)-2-Bromo-5-nitrobenzaldehyde *O*-methyloxime 7b



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O2 O 0.61821(14) 0.89723(6) 0.97418(5) 0.02401(17) Uani 1 1 d . . .
C8 C 0.81473(16) 0.98929(7) 0.64647(6) 0.01627(17) Uani 1 1 d . . .
N9 N 0.82455(14) 0.91069(6) 0.62333(5) 0.01678(15) Uani 1 1 d . . .
O3 O 0.89177(13) 0.90749(5) 0.54750(5) 0.01992(15) Uani 1 1 d . . .
C10 C 0.88901(19) 0.81976(8) 0.52212(7) 0.0215(2) Uani 1 1 d . . .
H1 H 0.649(2) 1.0468(10) 0.9377(9) 0.018(4) Uiso 1 1 d . . .
H2 H 0.758(3) 0.7985(12) 0.5190(12) 0.030(5) Uiso 1 1 d . . .
H3 H 0.834(2) 1.0319(11) 0.6124(10) 0.024(4) Uiso 1 1 d . . .
H4 H 0.954(3) 0.8209(10) 0.4714(10) 0.032(5) Uiso 1 1 d . . .
H5 H 0.696(2) 1.1652(10) 0.8533(10) 0.019(4) Uiso 1 1 d . . .
H6 H 0.740(2) 0.8818(10) 0.7639(9) 0.015(4) Uiso 1 1 d . . .
H7 H 0.961(2) 0.7851(10) 0.5577(9) 0.023(4) Uiso 1 1 d . . .

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Br1 0.02355(5) 0.01406(5) 0.01610(5) 0.00278(3) -0.00122(4) -0.00310(3)
C1 0.0148(4) 0.0117(3) 0.0148(4) -0.0017(3) -0.0013(3) 0.0009(3)
C3 0.0148(4) 0.0121(3) 0.0134(4) 0.0003(3) -0.0011(3) -0.0011(3)
C6 0.0148(4) 0.0119(4) 0.0139(4) 0.0009(3) -0.0023(3) 0.0001(3)
C5 0.0181(4) 0.0138(4) 0.0129(4) -0.0015(3) -0.0010(3) -0.0005(3)
C2 0.0124(3) 0.0143(4) 0.0134(4) -0.0019(3) -0.0005(3) -0.0003(3)
C4 0.0194(4) 0.0112(4) 0.0141(4) -0.0018(3) -0.0012(3) -0.0001(3)
N7 0.0201(4) 0.0138(3) 0.0172(4) 0.0022(3) -0.0013(3) 0.0002(3)

O1 0.0507(6) 0.0121(3) 0.0231(4) 0.0007(3) 0.0025(4) 0.0005(4)
O2 0.0340(5) 0.0221(4) 0.0159(4) 0.0035(3) 0.0050(3) 0.0013(3)
C8 0.0191(4) 0.0162(4) 0.0135(4) -0.0011(3) 0.0011(3) -0.0015(3)
N9 0.0197(4) 0.0200(4) 0.0107(3) -0.0012(3) 0.0010(3) -0.0004(3)
O3 0.0289(4) 0.0185(4) 0.0123(3) -0.0023(3) 0.0042(3) -0.0009(3)
C10 0.0265(5) 0.0190(5) 0.0191(5) -0.0057(4) 0.0003(4) 0.0010(4)

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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C1 C6 1.3786(15) . ?
C1 C2 1.4023(14) . ?
C1 H6 0.909(15) . ?
C3 C4 1.3913(15) . ?
C3 C2 1.4041(14) . ?
C6 C5 1.3866(14) . ?
C6 N7 1.4696(13) . ?
C5 C4 1.3888(15) . ?
C5 H1 0.964(16) . ?
C2 C8 1.4627(15) . ?
C4 H5 0.973(16) . ?
N7 O2 1.2241(13) . ?
N7 O1 1.2255(12) . ?
C8 N9 1.2852(14) . ?
C8 H3 0.896(17) . ?
N9 O3 1.3940(12) . ?
O3 C10 1.4301(14) . ?
C10 H2 0.962(18) . ?
C10 H4 0.987(18) . ?
C10 H7 0.957(16) . ?

loop_
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_geom_angle_atom_site_label_2
_geom_angle_atom_site_label_3
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_geom_angle_site_symmetry_3
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C6 C1 C2 119.41(9) . . ?
C6 C1 H6 117.1(10) . . ?

C2 C1 H6 123.5(10) . . ?
C4 C3 C2 121.73(9) . . ?
C4 C3 Br1 117.05(7) . . ?
C2 C3 Br1 121.21(8) . . ?
C1 C6 C5 123.13(9) . . ?
C1 C6 N7 118.37(9) . . ?
C5 C6 N7 118.51(9) . . ?
C6 C5 C4 117.86(10) . . ?
C6 C5 H1 119.9(9) . . ?
C4 C5 H1 122.3(9) . . ?
C1 C2 C3 117.77(9) . . ?
C1 C2 C8 119.77(9) . . ?
C3 C2 C8 122.41(9) . . ?
C5 C4 C3 120.07(9) . . ?
C5 C4 H5 118.6(10) . . ?
C3 C4 H5 121.3(10) . . ?
O2 N7 O1 123.61(10) . . ?
O2 N7 C6 118.62(9) . . ?
O1 N7 C6 117.77(9) . . ?
N9 C8 C2 119.12(10) . . ?
N9 C8 H3 119.1(11) . . ?
C2 C8 H3 121.6(11) . . ?
C8 N9 O3 110.20(9) . . ?
N9 O3 C10 108.63(9) . . ?
O3 C10 H2 110.9(11) . . ?
O3 C10 H4 104.5(10) . . ?
H2 C10 H4 112.4(16) . . ?
O3 C10 H7 109.2(10) . . ?
H2 C10 H7 109.3(15) . . ?
H4 C10 H7 110.4(14) . . ?

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