

Supporting Information

Metal-free access of bulky *N*, *N'*-diarylcarbodiimides and their reduction: Bulky *N*, *N'*-diarylformamidines†

Thota Peddaraao, Ashim Baishya, Milan Kr. Barman, Ajay Kumar and Sharanappa Nembenna*

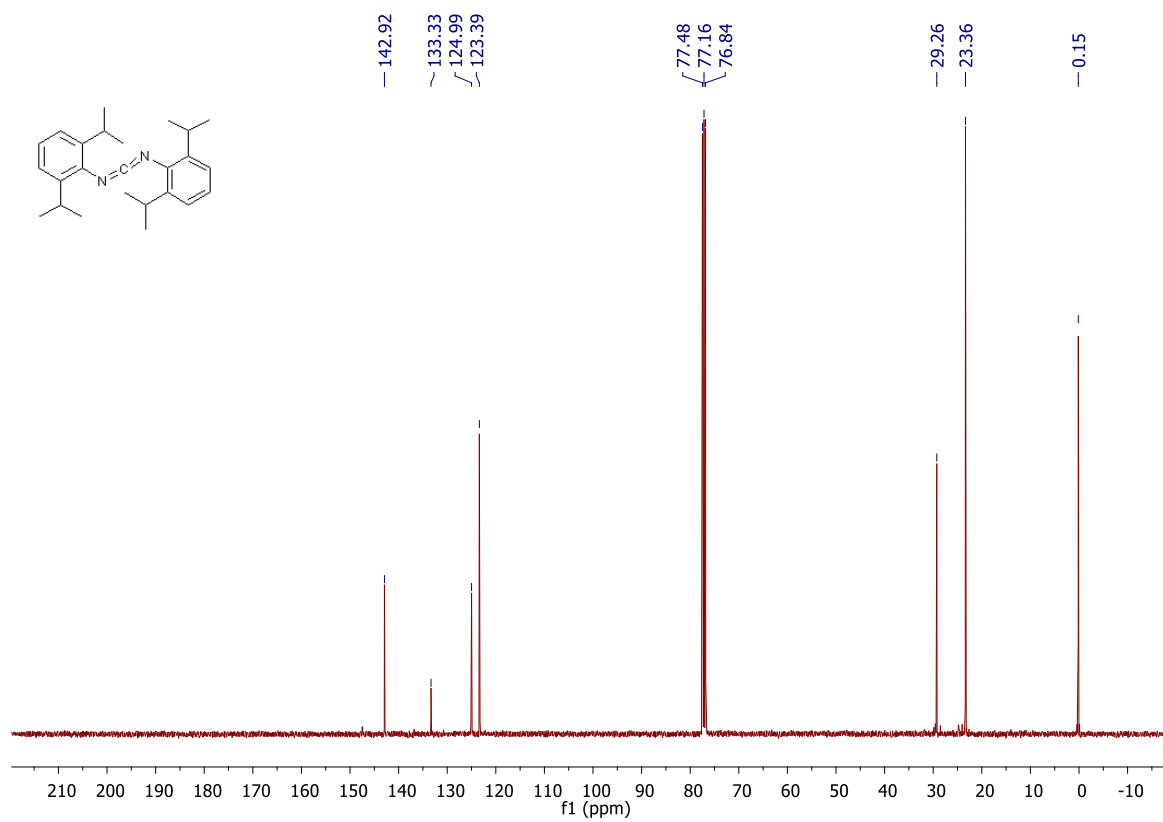
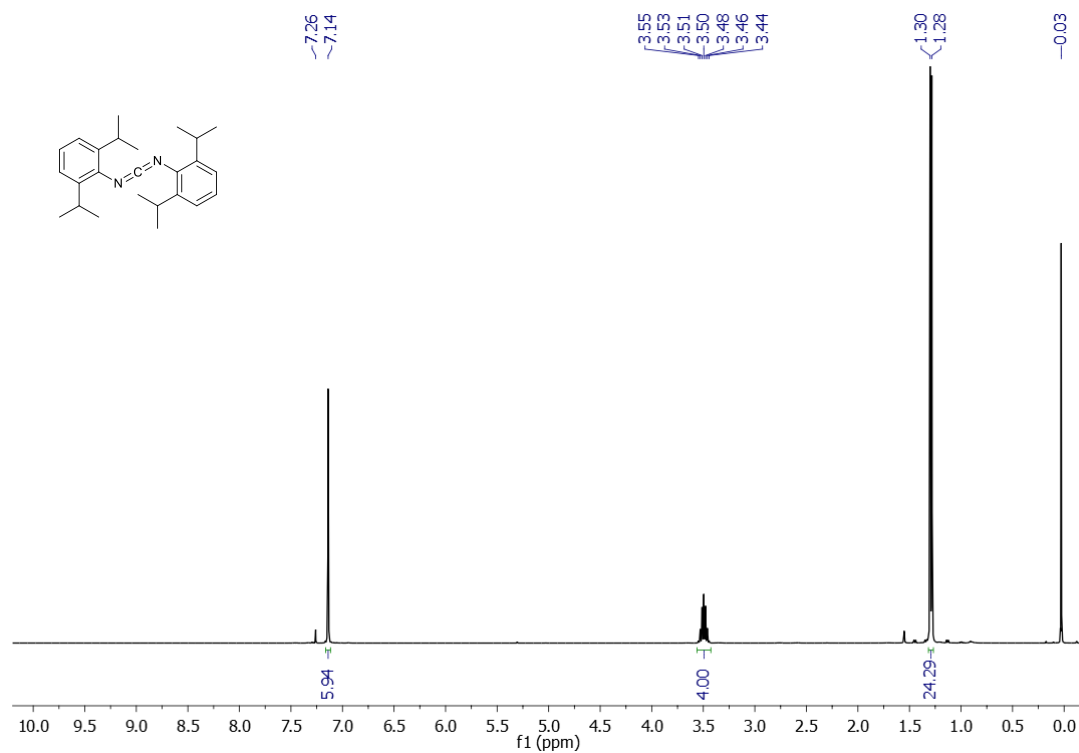
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Corresponding Author: Sharanappa Nembenna

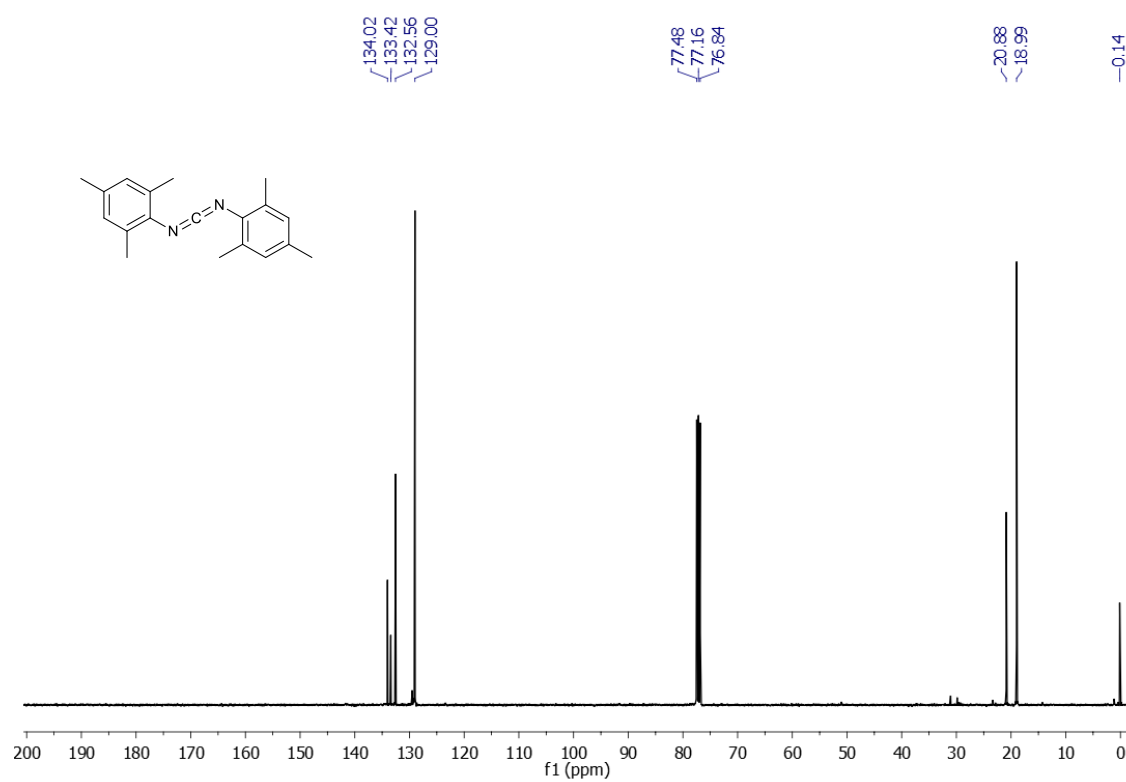
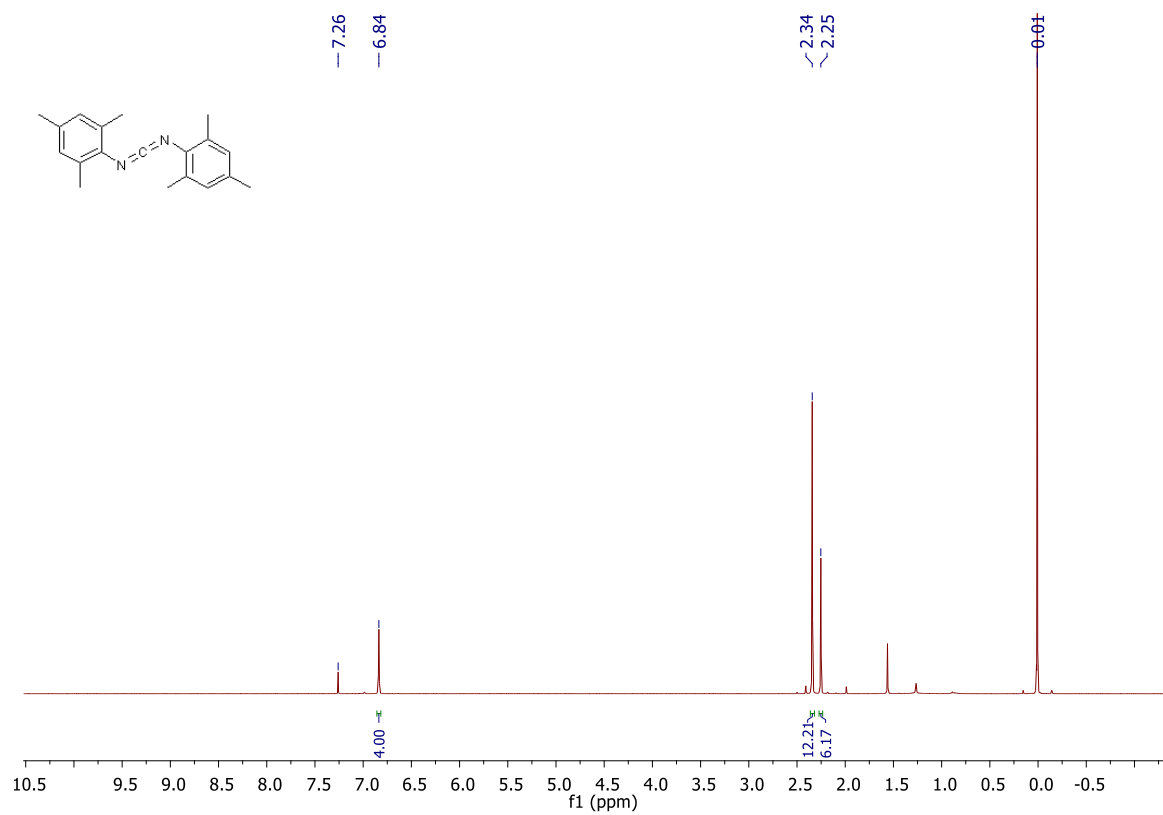
Fax: +91-674-2302436; Tel.: +91-674-2304126

Email: snembenna@niser.ac.in

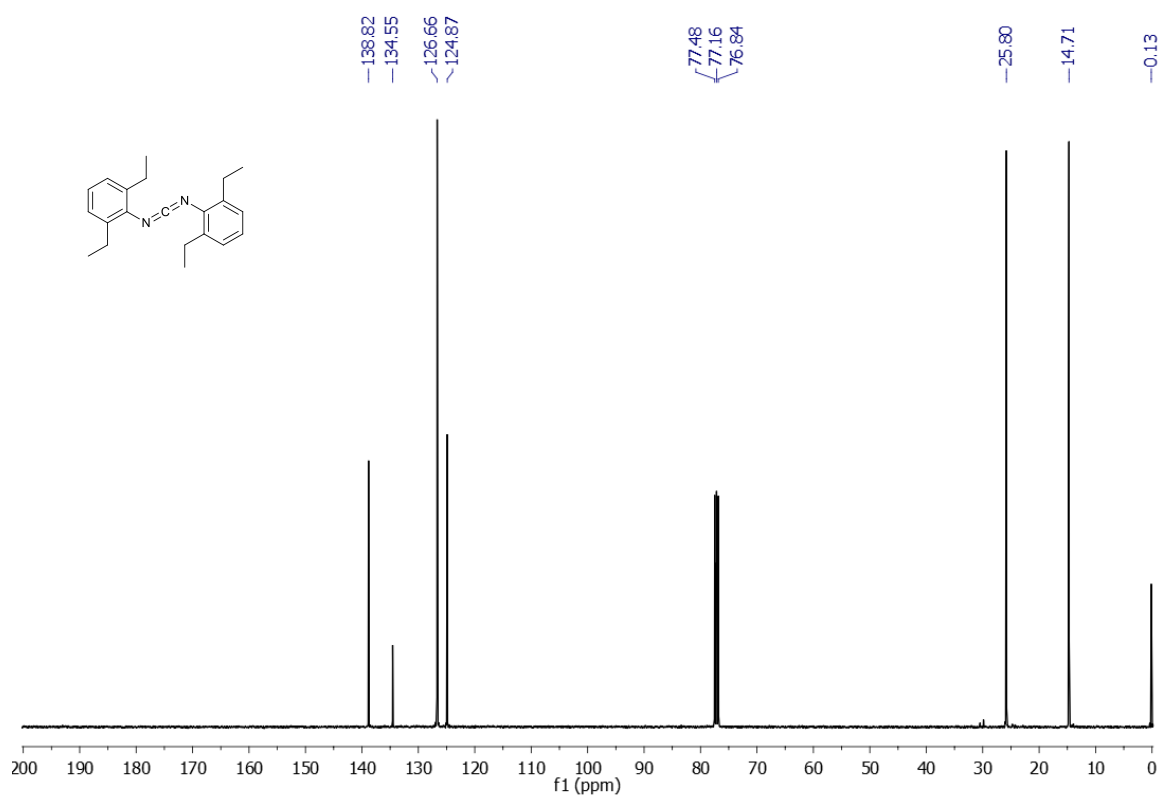
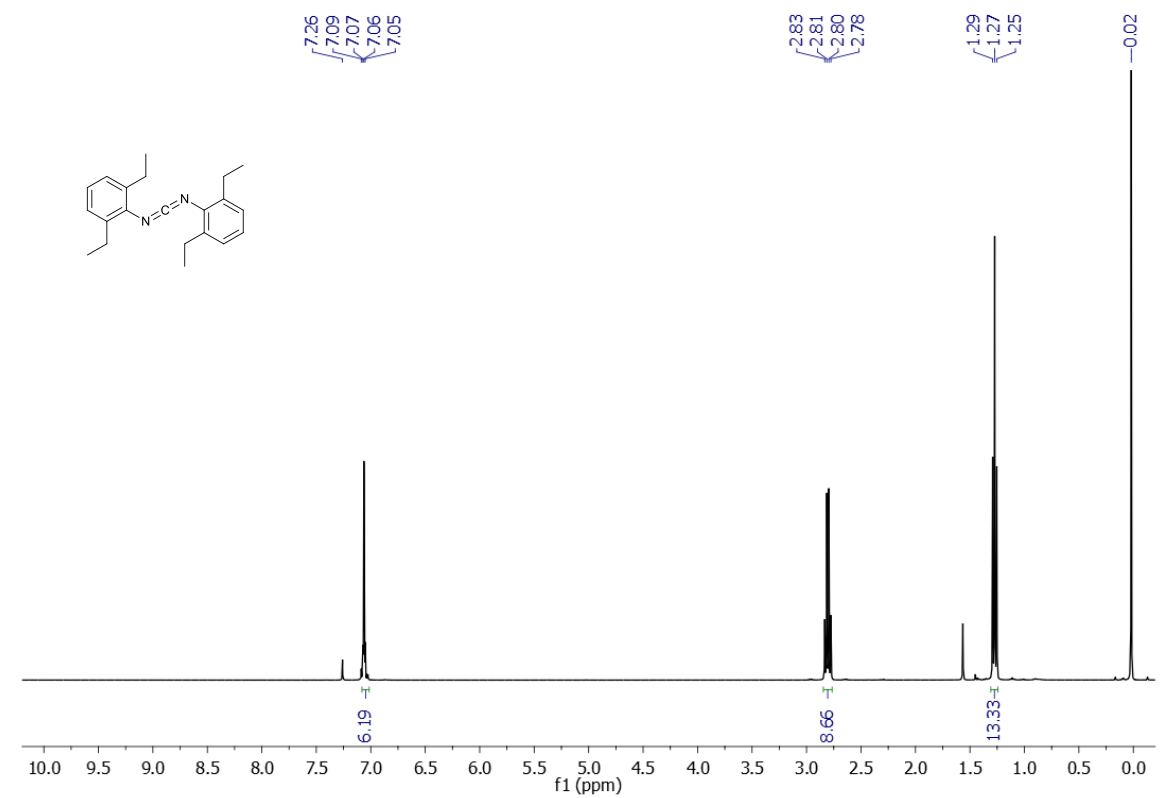
^1H & ^{13}C NMR spectra for 1, 3-Bis (2, 6-di-isopropyl-phenyl) carbodiimide (**1a**)



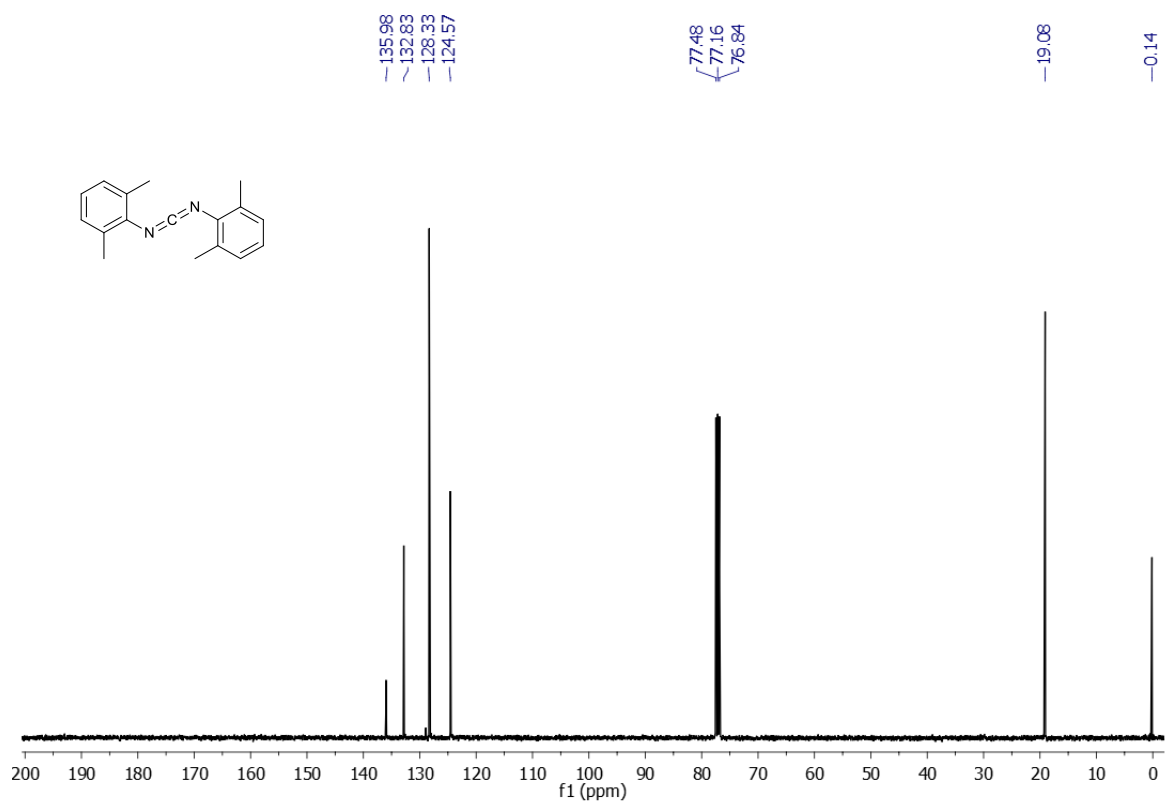
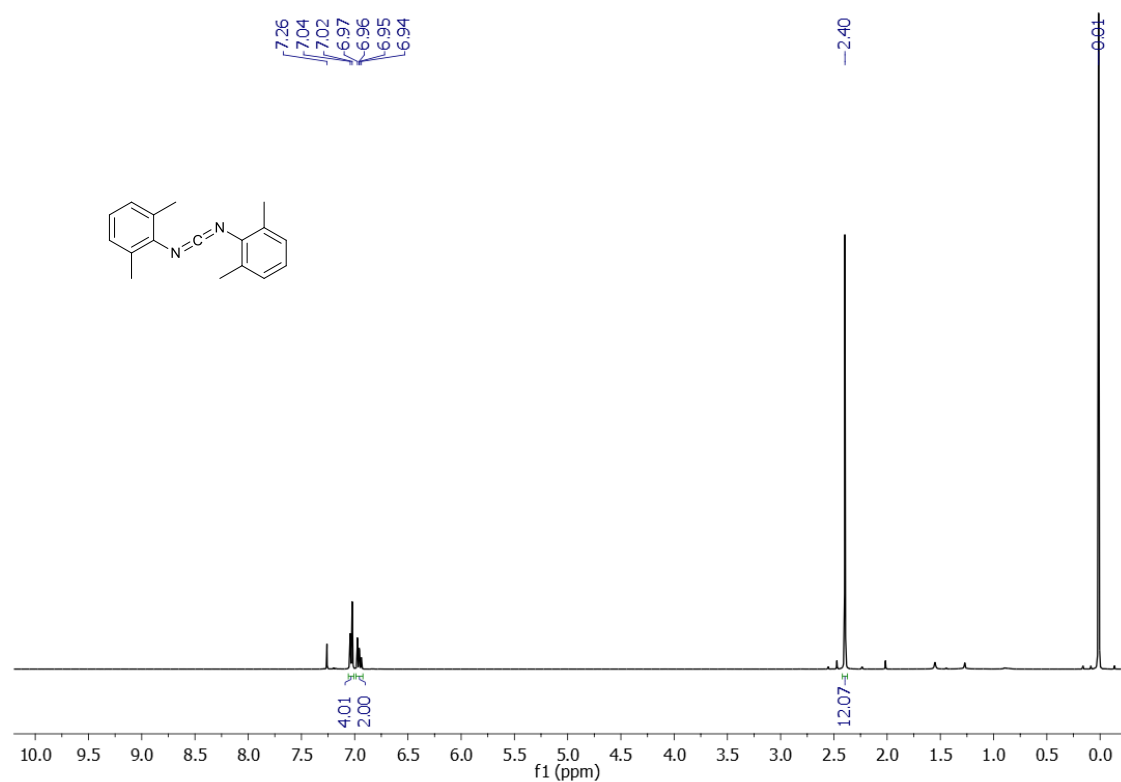
^1H & ^{13}C NMR spectra for 1, 3-Bis (2, 4, 6-trimethyl-phenyl) carbodiimide (**2a**)



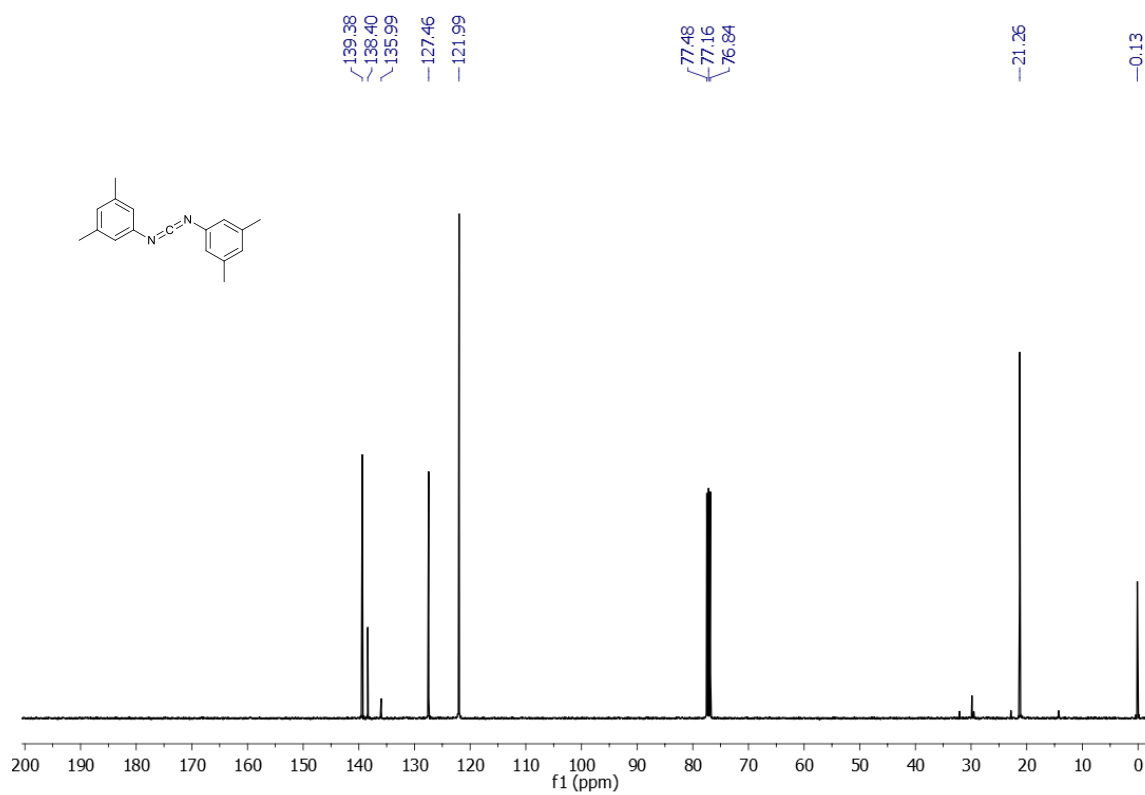
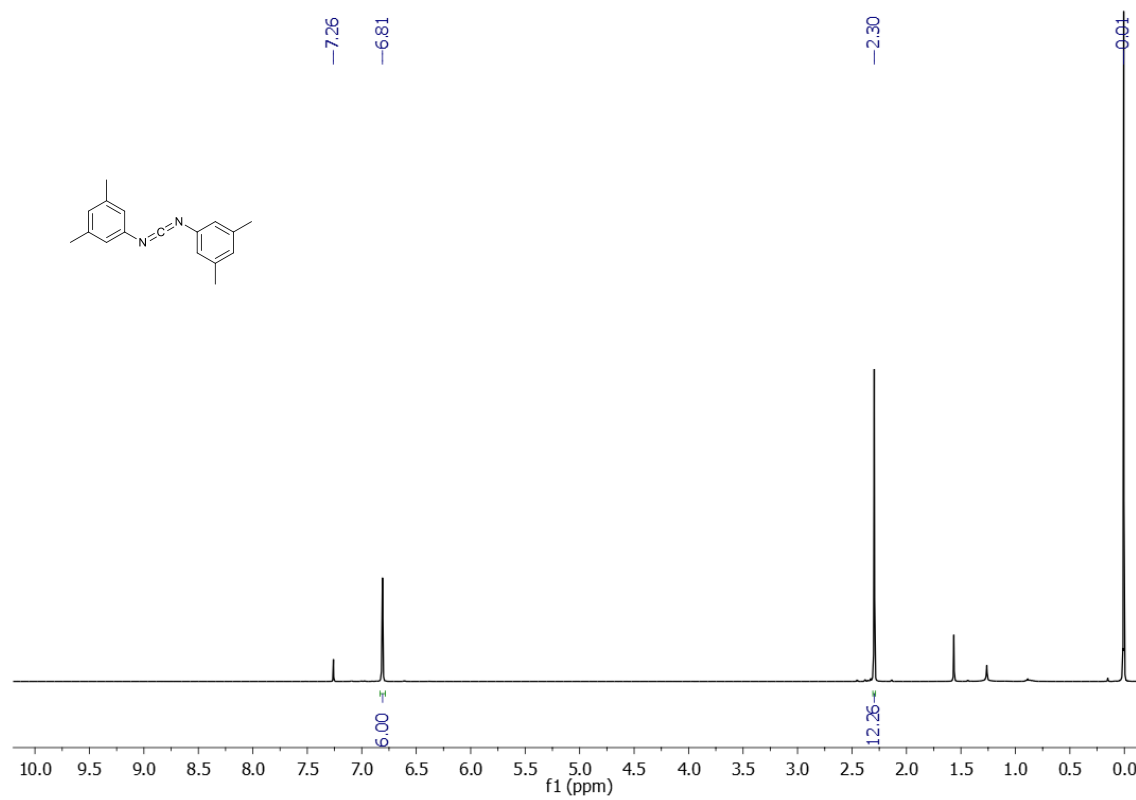
^1H & ^{13}C NMR spectra for 1, 3-Bis (2, 6-diethyl-phenyl) carbodiimide (**3a**)



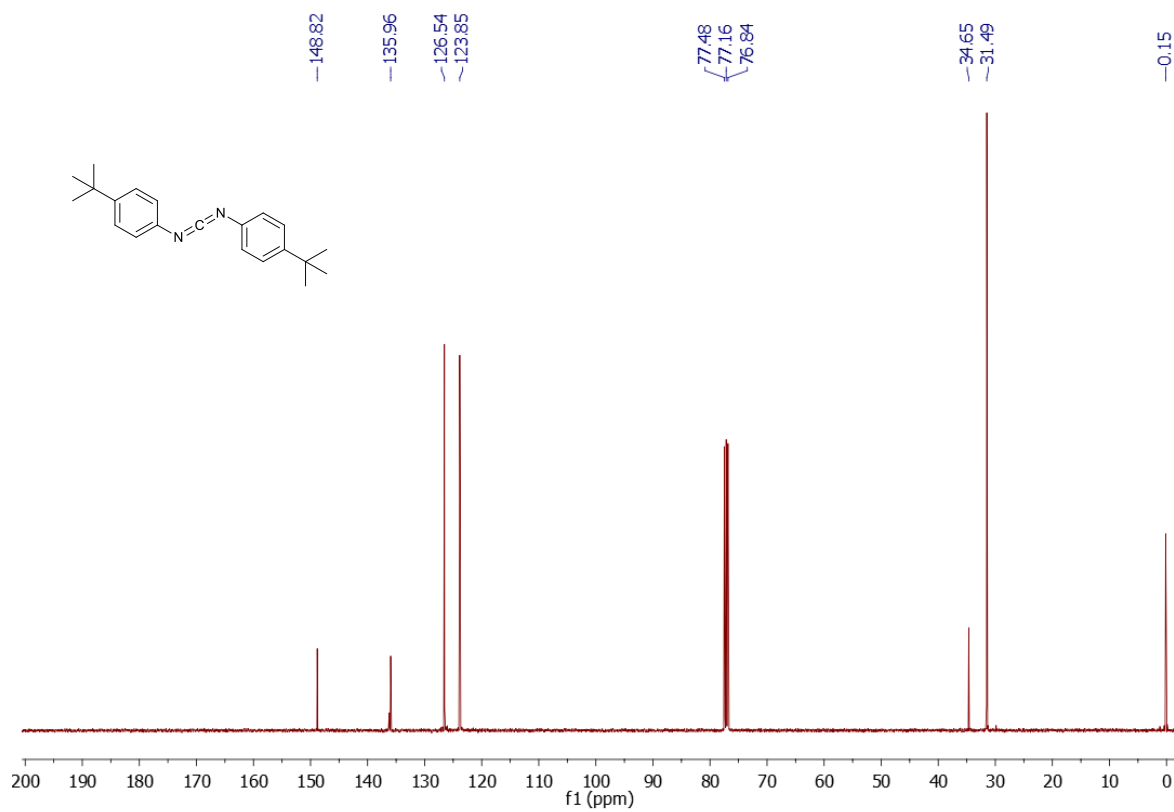
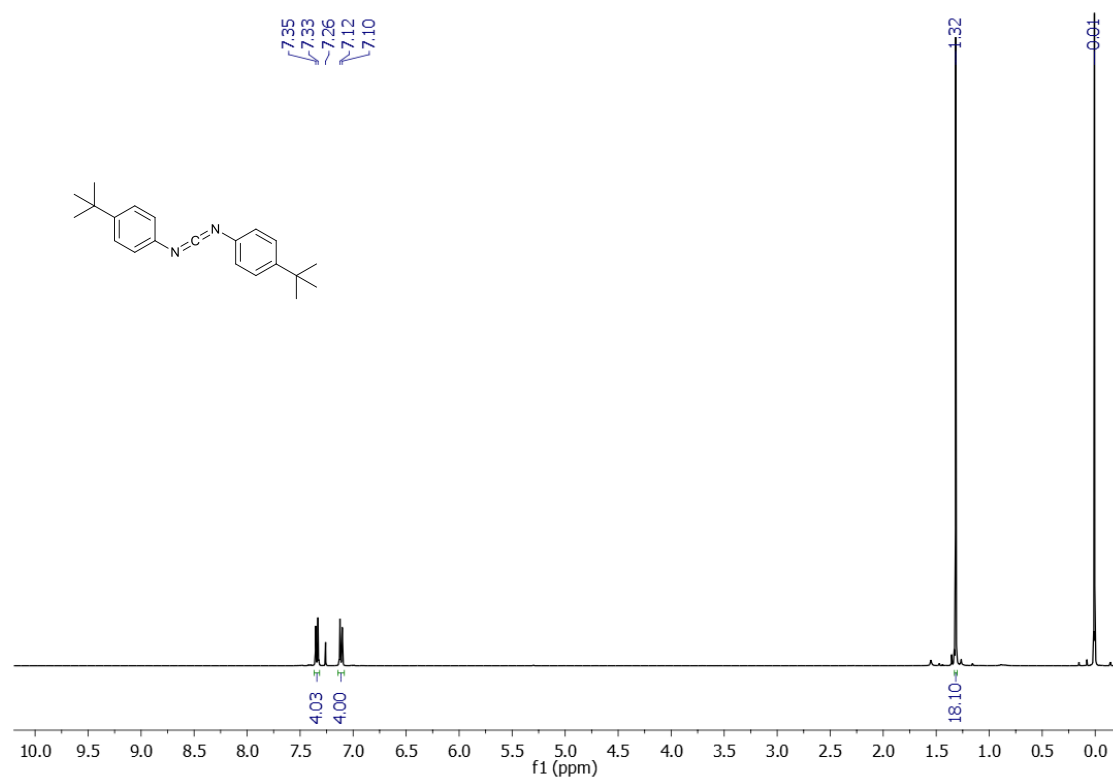
^1H & ^{13}C NMR spectra for 1, 3-Bis (2, 6-dimethyl-phenyl) carbodiimide (**4a**)



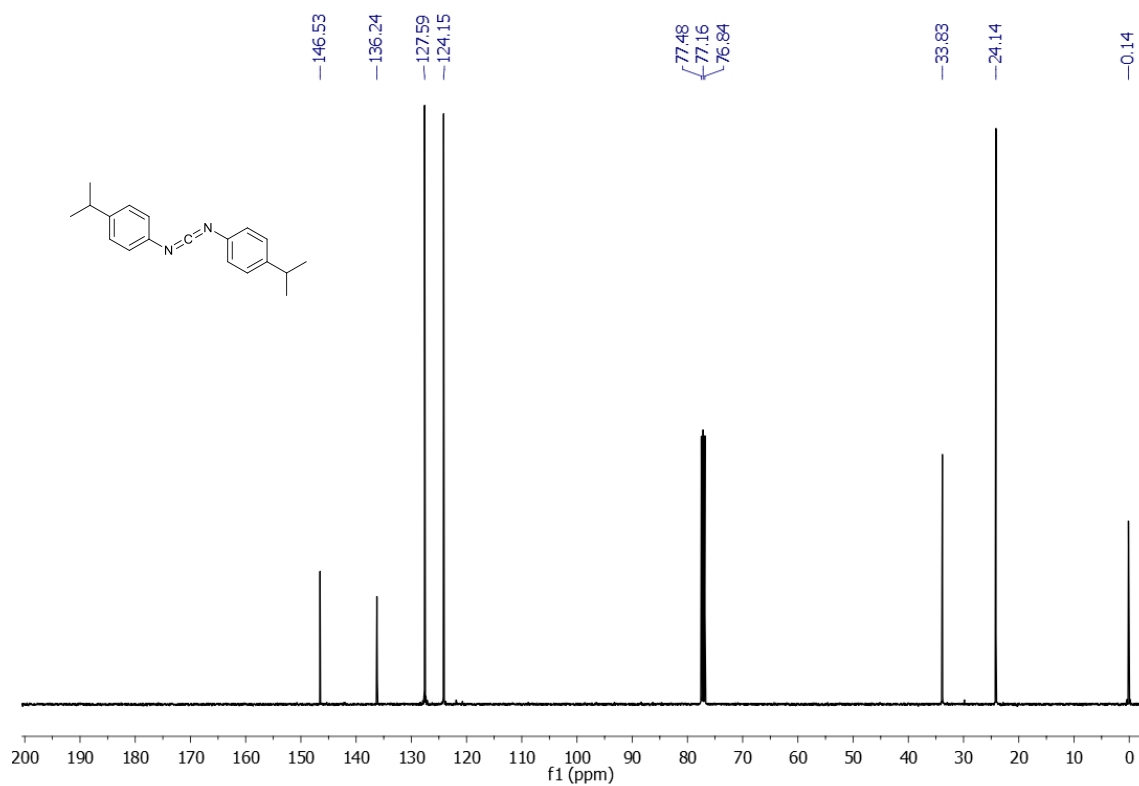
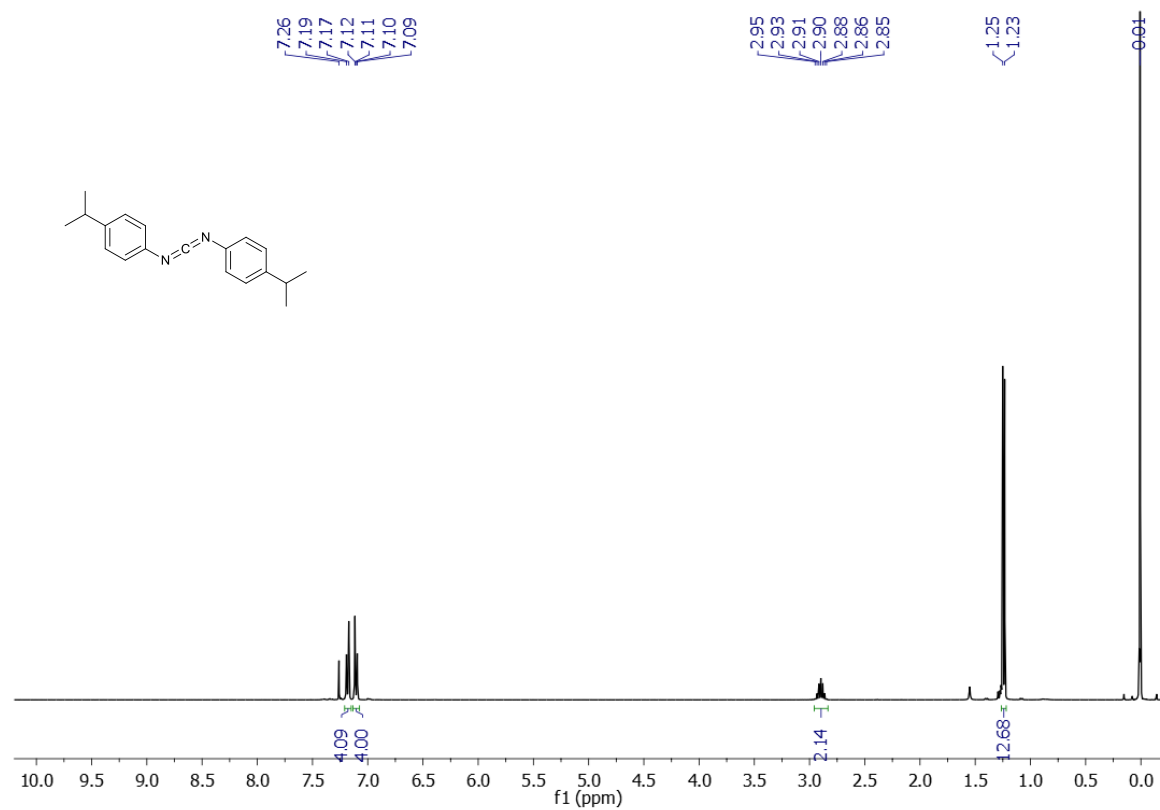
^1H & ^{13}C NMR spectra for 1, 3-Bis (3, 5-dimethyl-phenyl) carbodiimide (**5a**)



^1H & ^{13}C NMR spectra for 1, 3-Bis (p-tert-butyl-phenyl) carbodiimide (**6a**)

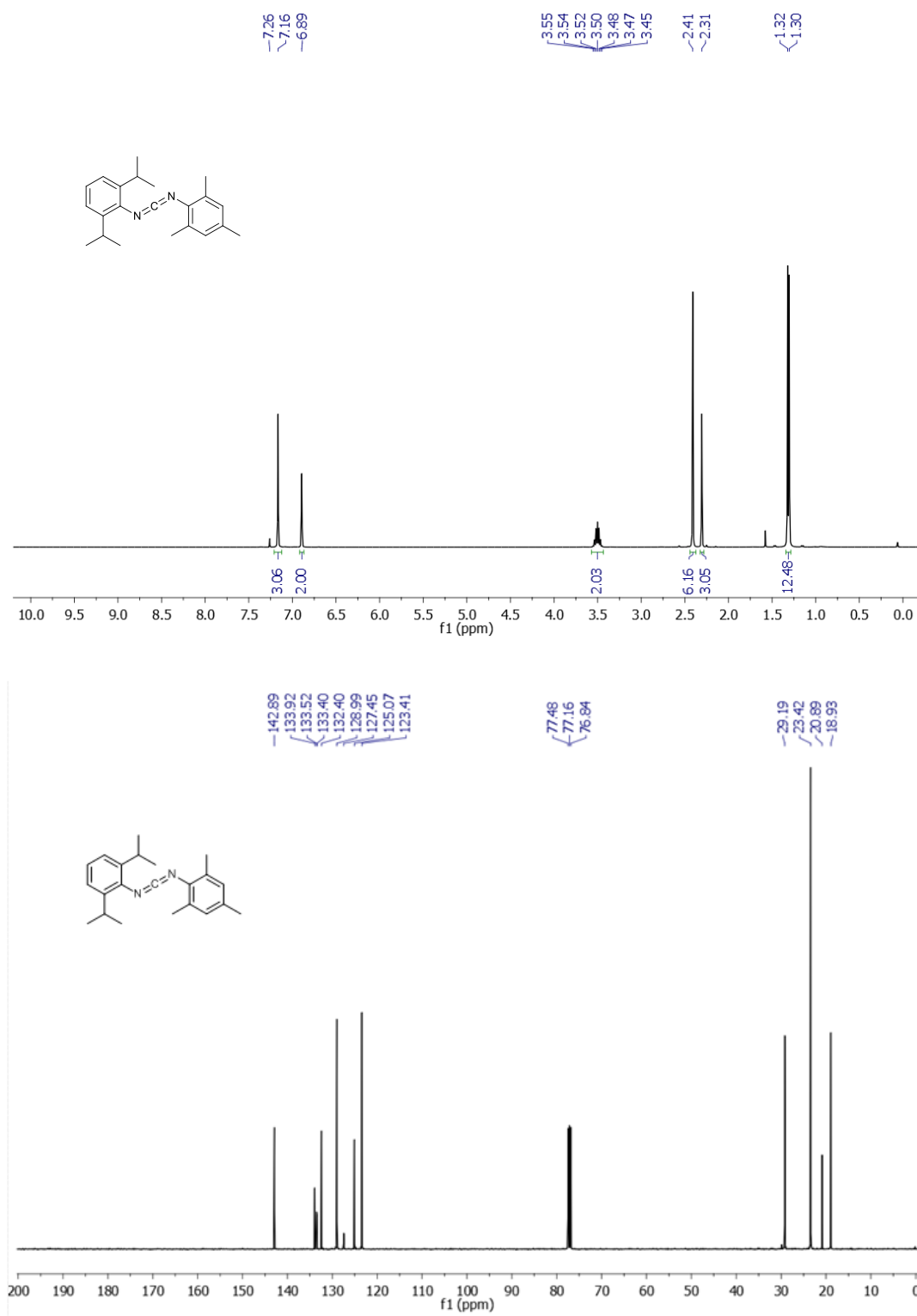


^1H & ^{13}C NMR spectra for 1, 3-Bis (p-isopropyl-phenyl) carbodiimide (**7a**)



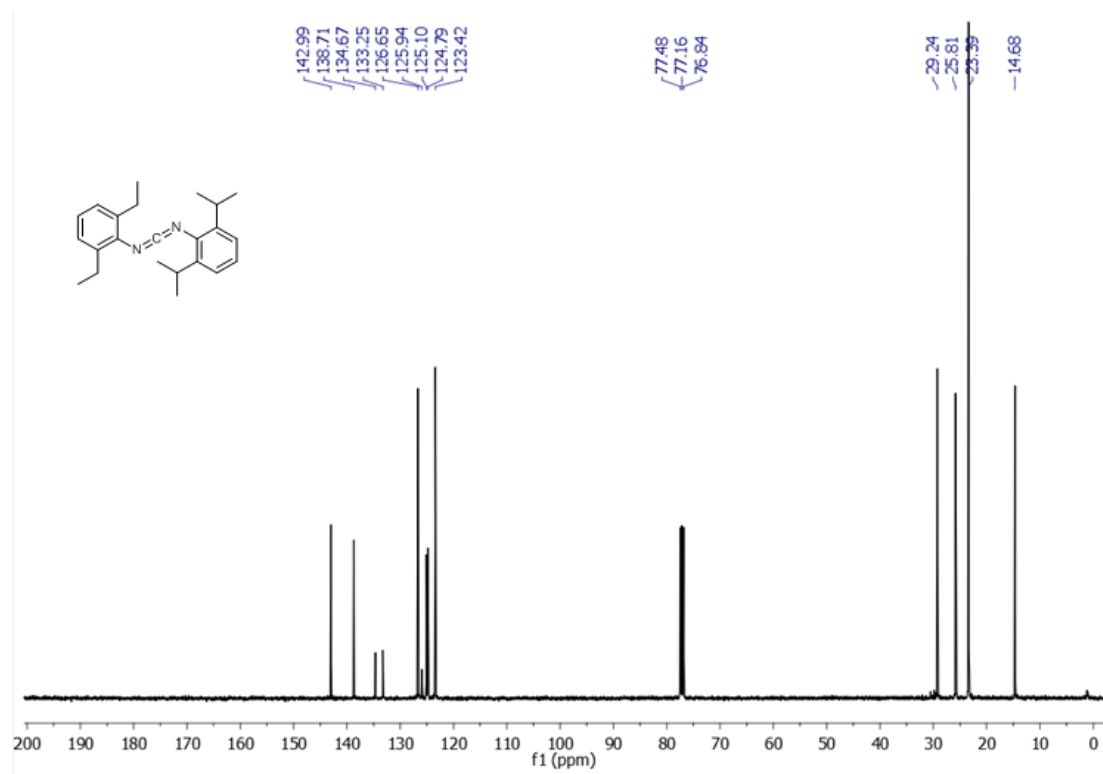
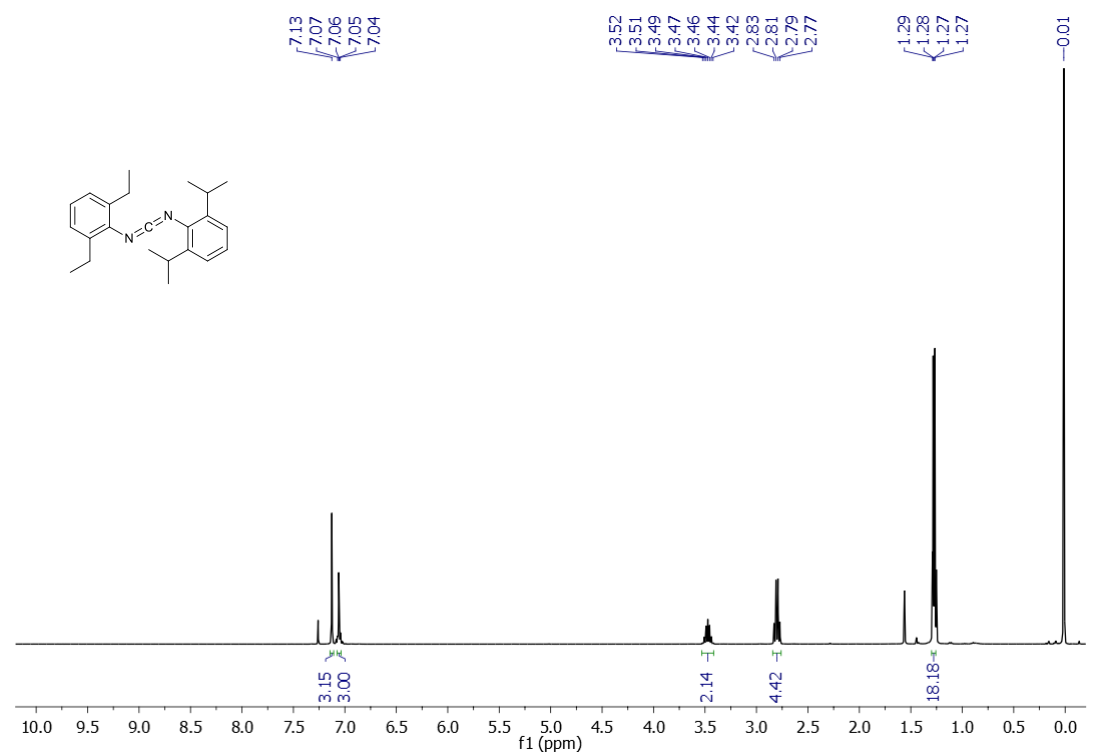
^1H & ^{13}C NMR spectra for (2, 6-di-isopropyl-phenyl) - (2, 4, 6-Tri-methyl-phenyl) carbodiimide

(8a)



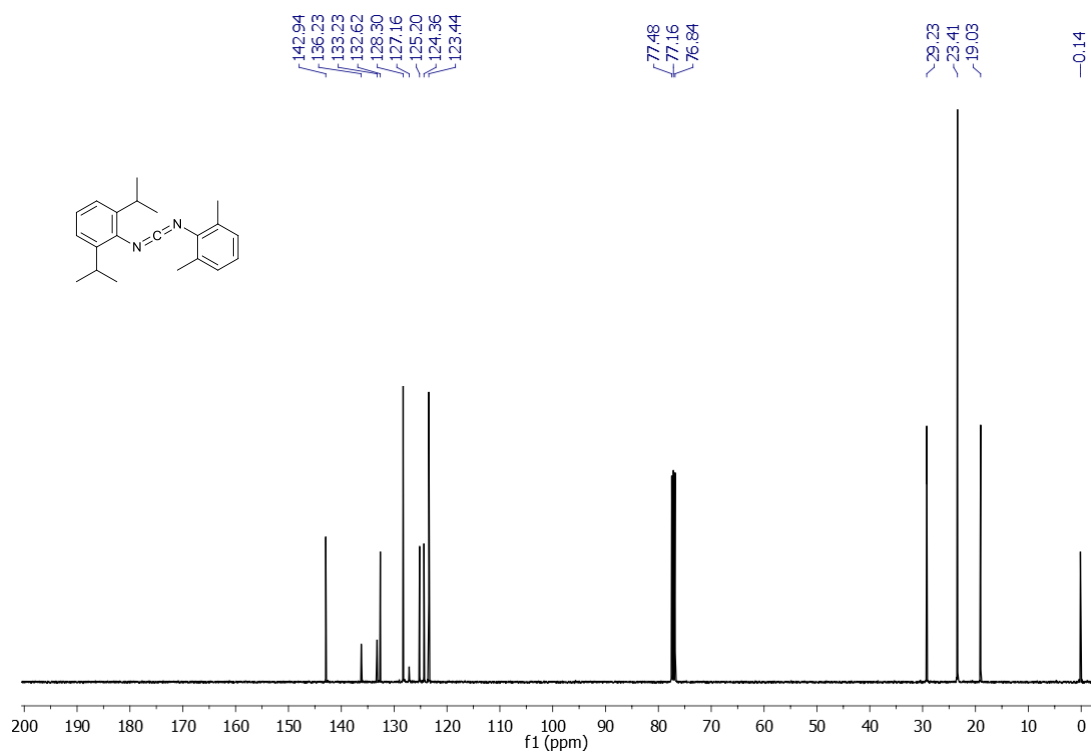
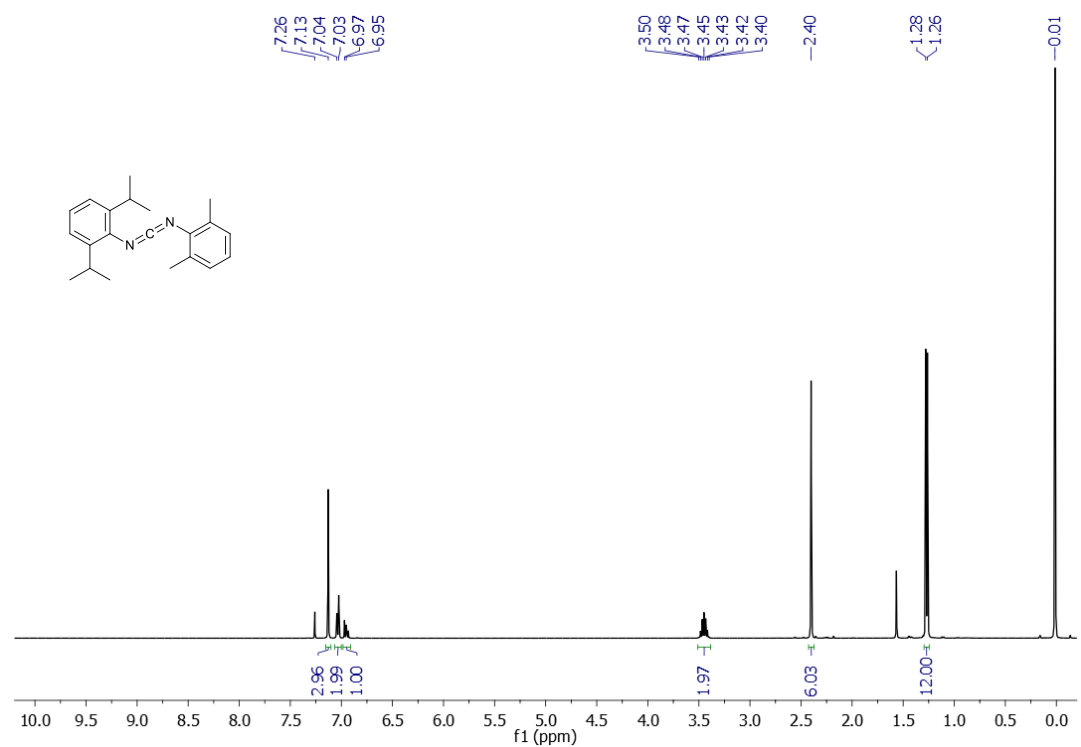
^1H & ^{13}C NMR spectra for (2, 6-Di-isopropyl-phenyl) - (2, 6-Di-ethyl-phenyl)-carbodiimide

(9a)

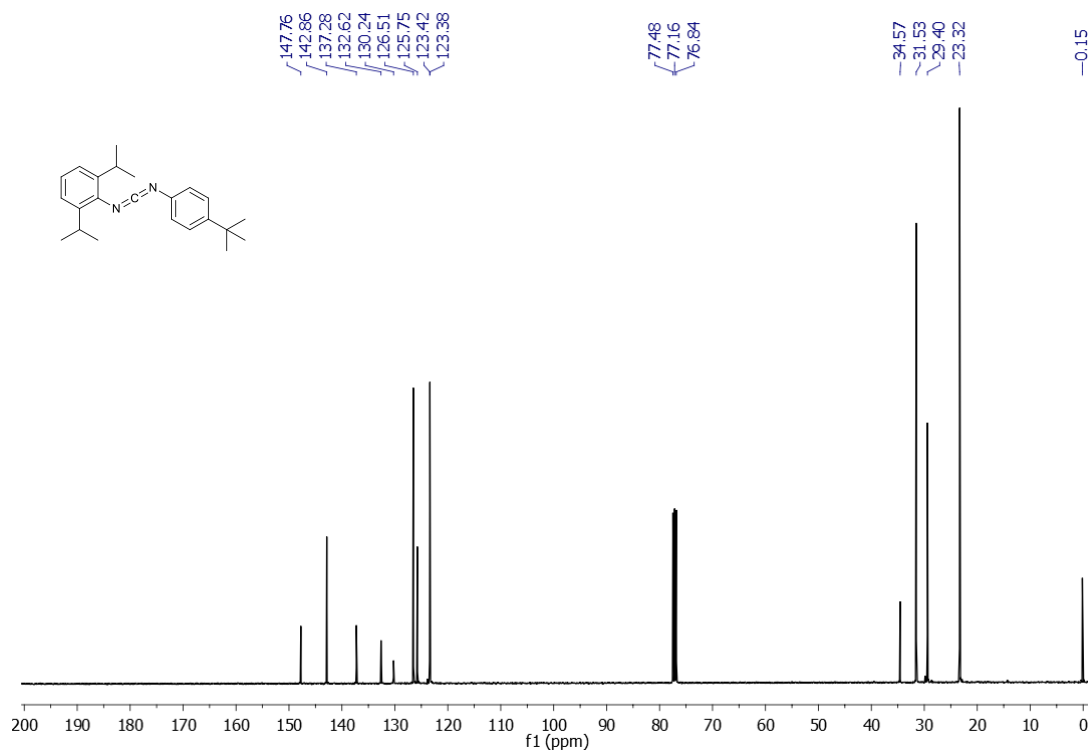
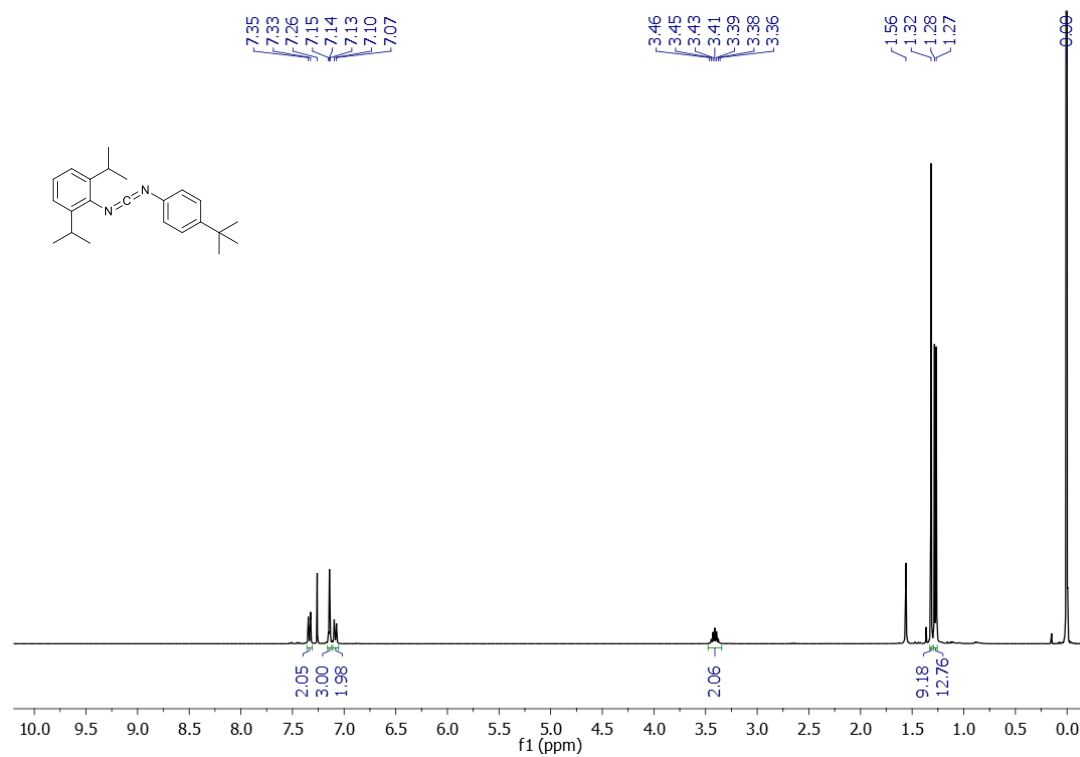


^1H & ^{13}C NMR spectra for (2, 6-Di-isopropyl-phenyl) - (2, 6-Di-methyl-phenyl) -carbodiimide

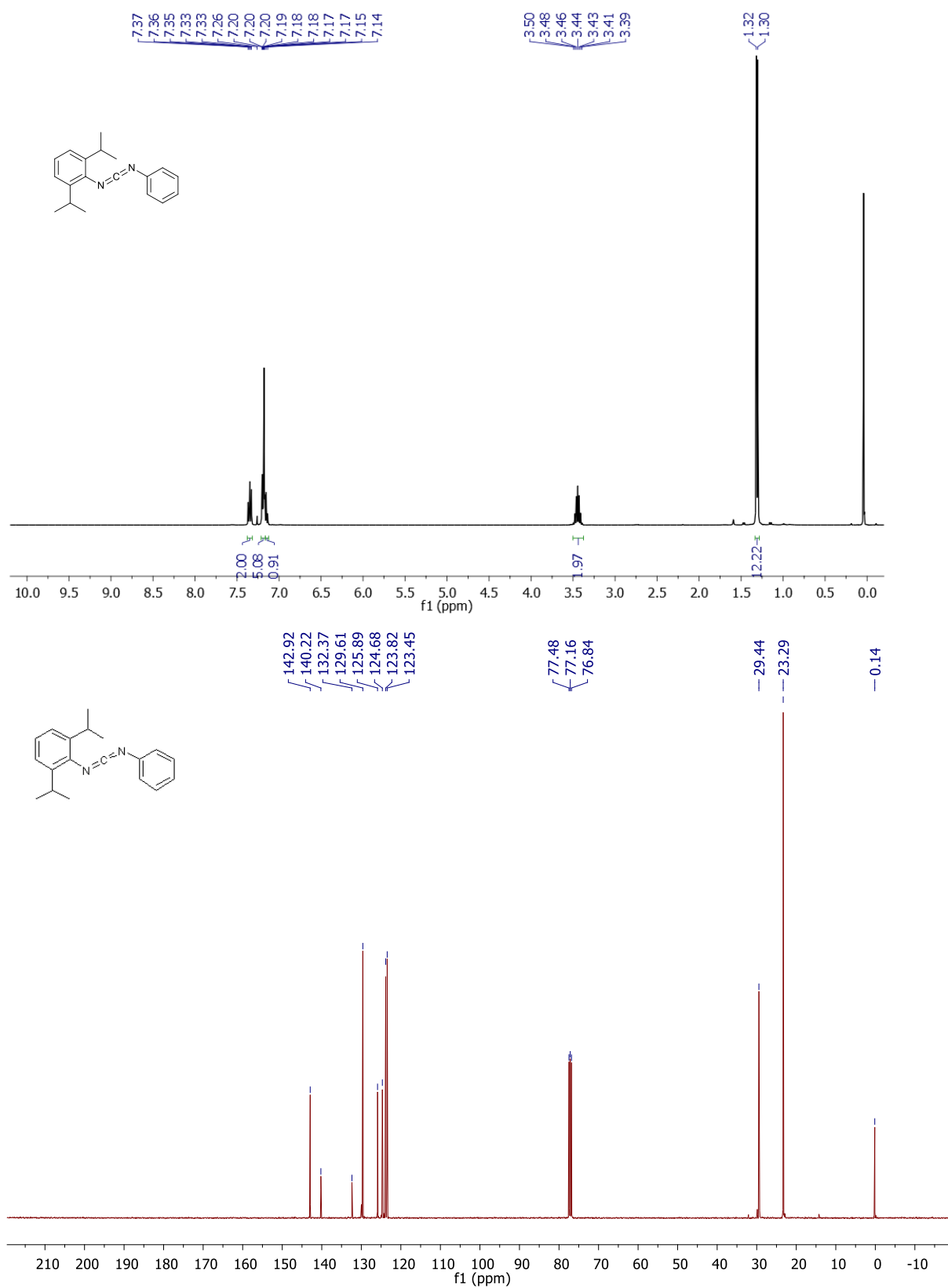
(10a)



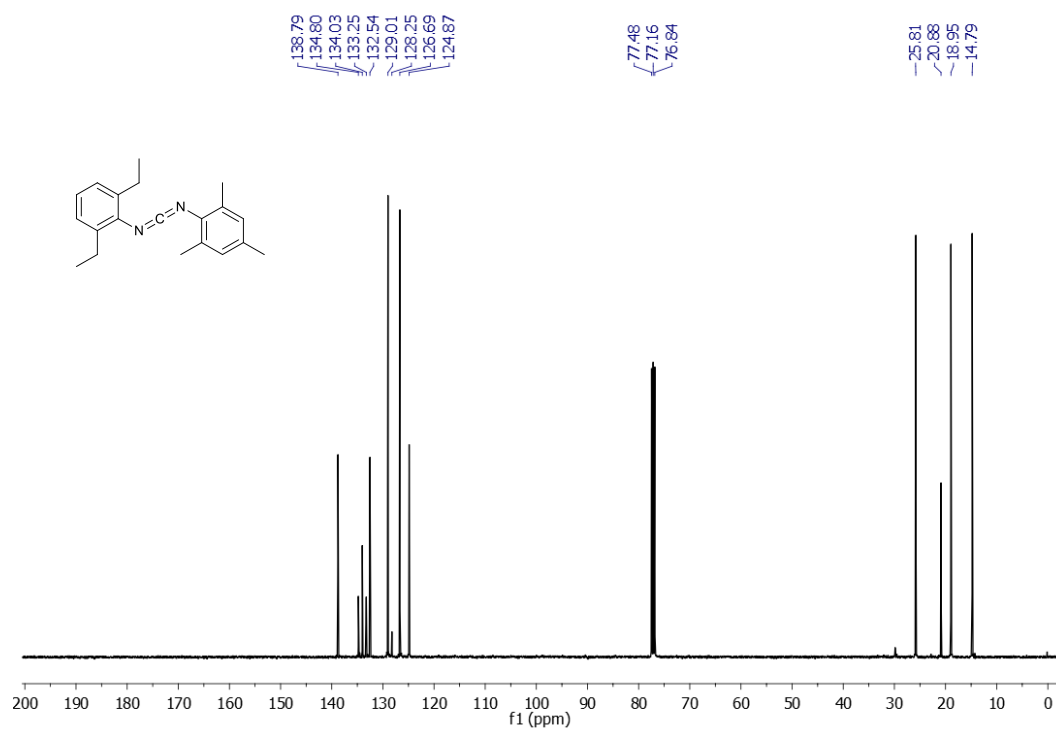
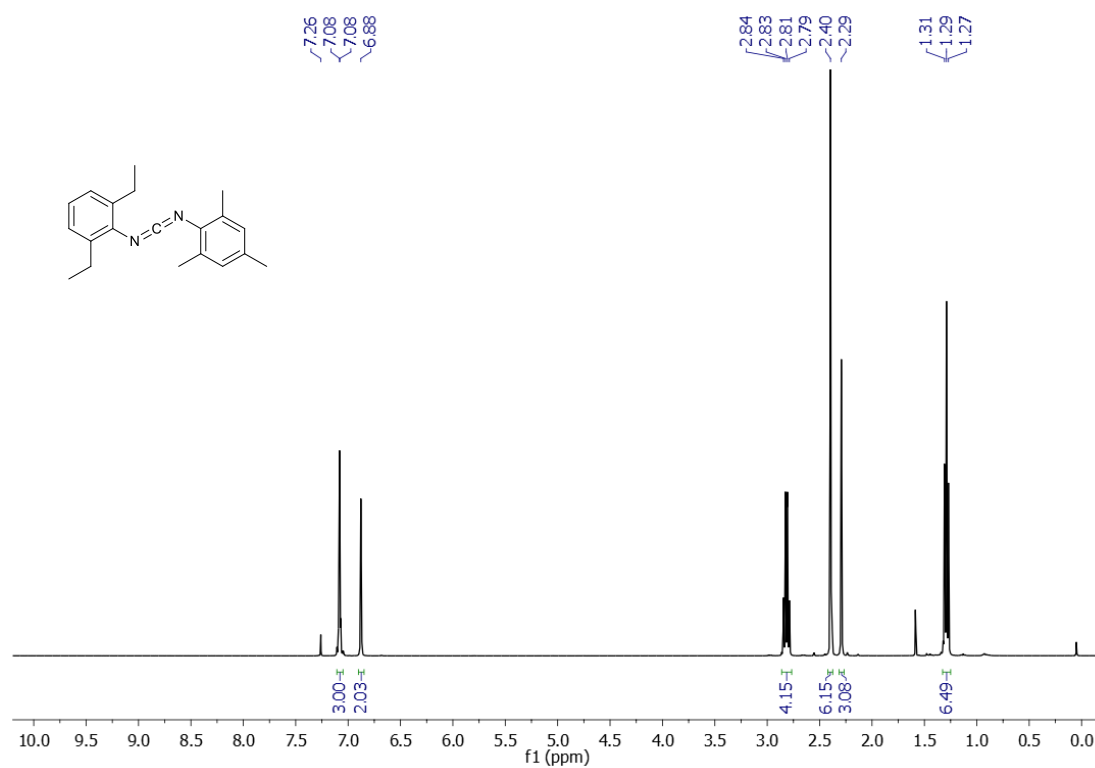
^1H & ^{13}C NMR spectra for (2, 6-Di-isopropyl-phenyl) - (p-tert-butyl-phenyl)-carbodiimide
(11a)



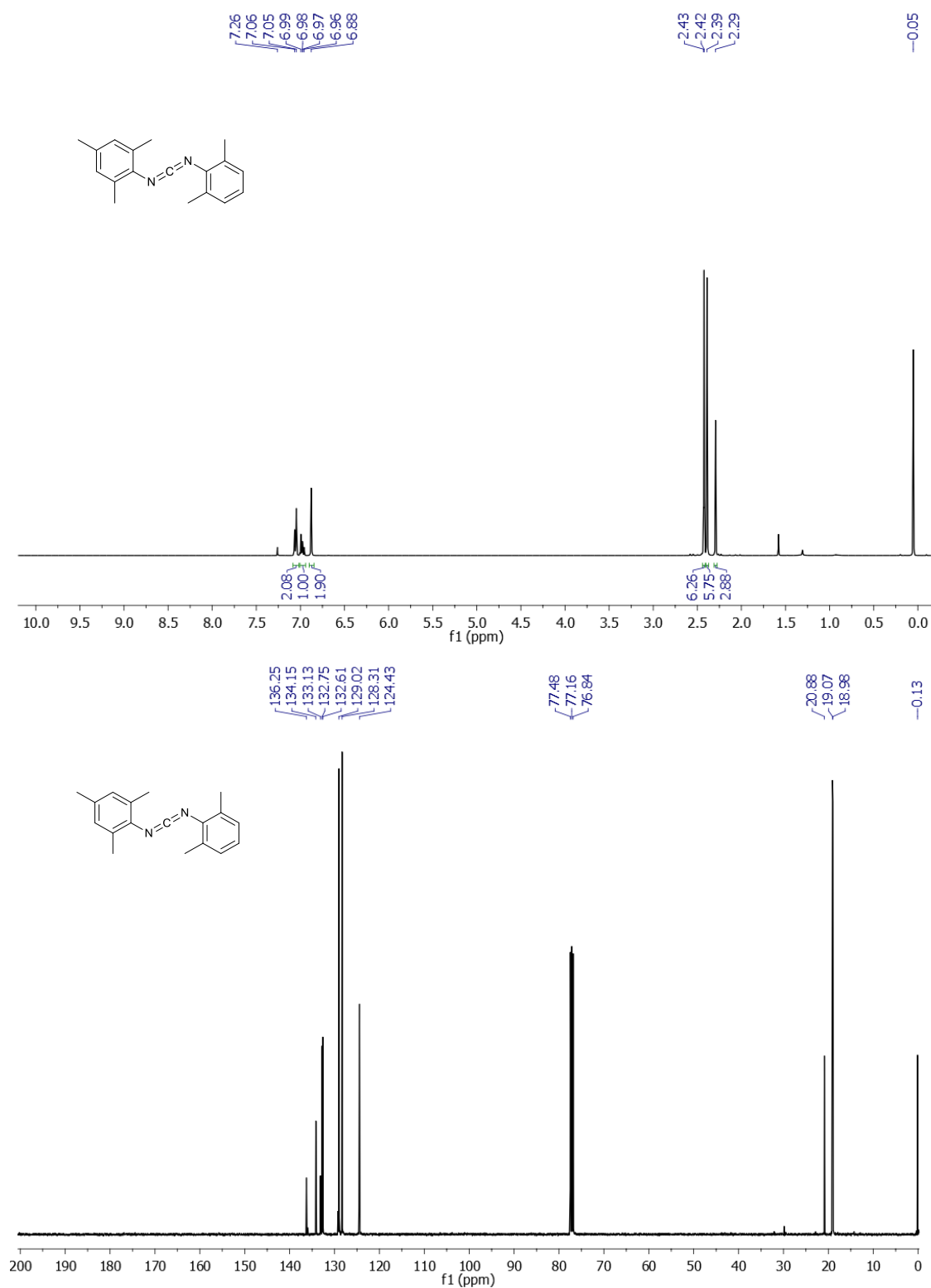
^1H and ^{13}C NMR spectra for (2, 6-Di-isopropyl-phenyl)-phenyl-carbodiimide (**12a**)



^1H and ^{13}C NMR spectra for (2, 4, 6-tri-methyl-phenyl) - (2, 6-Di-ethylphenyl) –carbodiimide
(13a)



^1H and ^{13}C NMR spectra for (2, 4, 6-tri-methyl-phenyl)-(2, 6-Di-methyl-phenyl)-carbodiimide
(14a)



^1H and ^{13}C NMR spectra for (2, 4, 6-tri-methyl-phenyl) - phenyl-carbodiimide (**15a**)

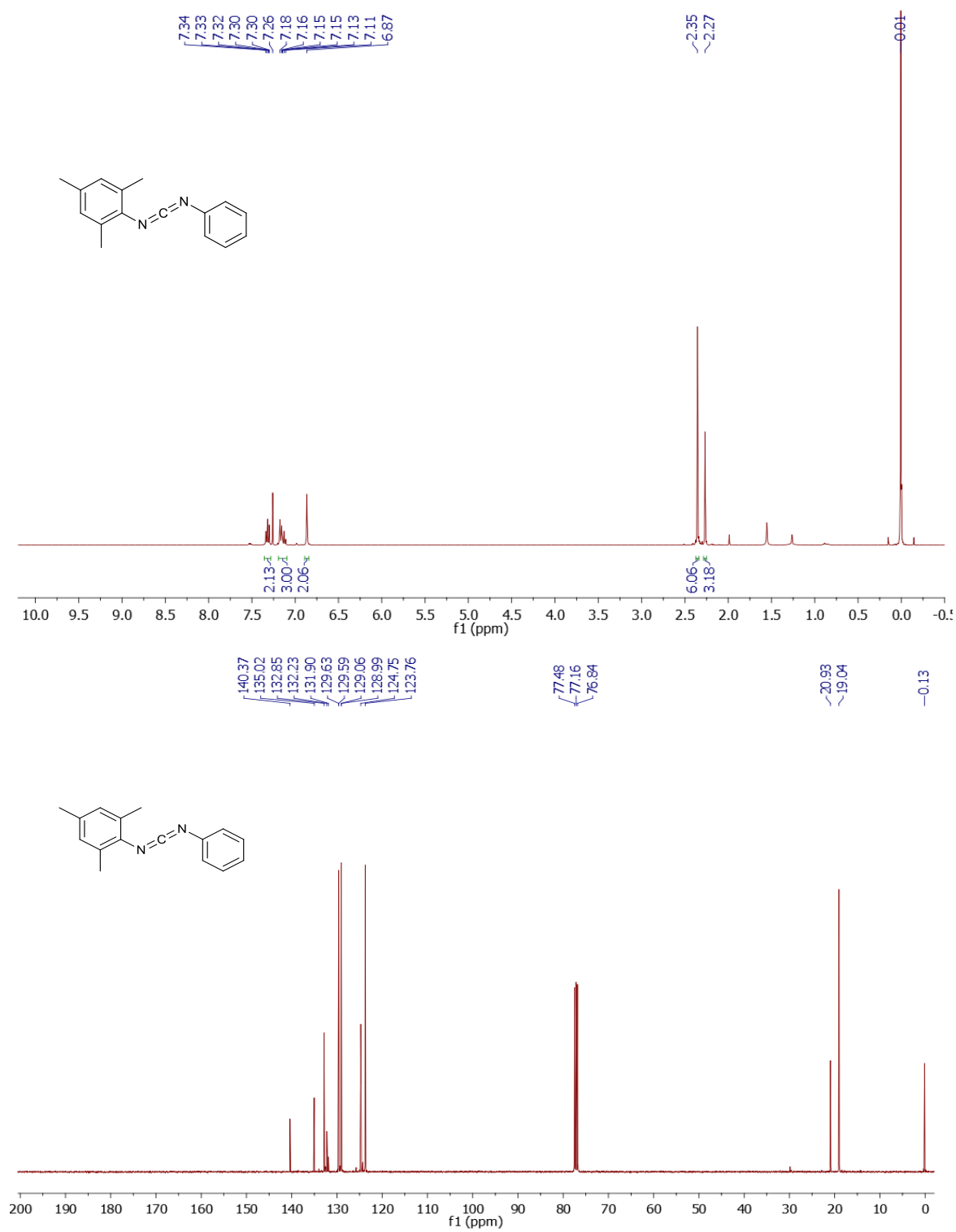
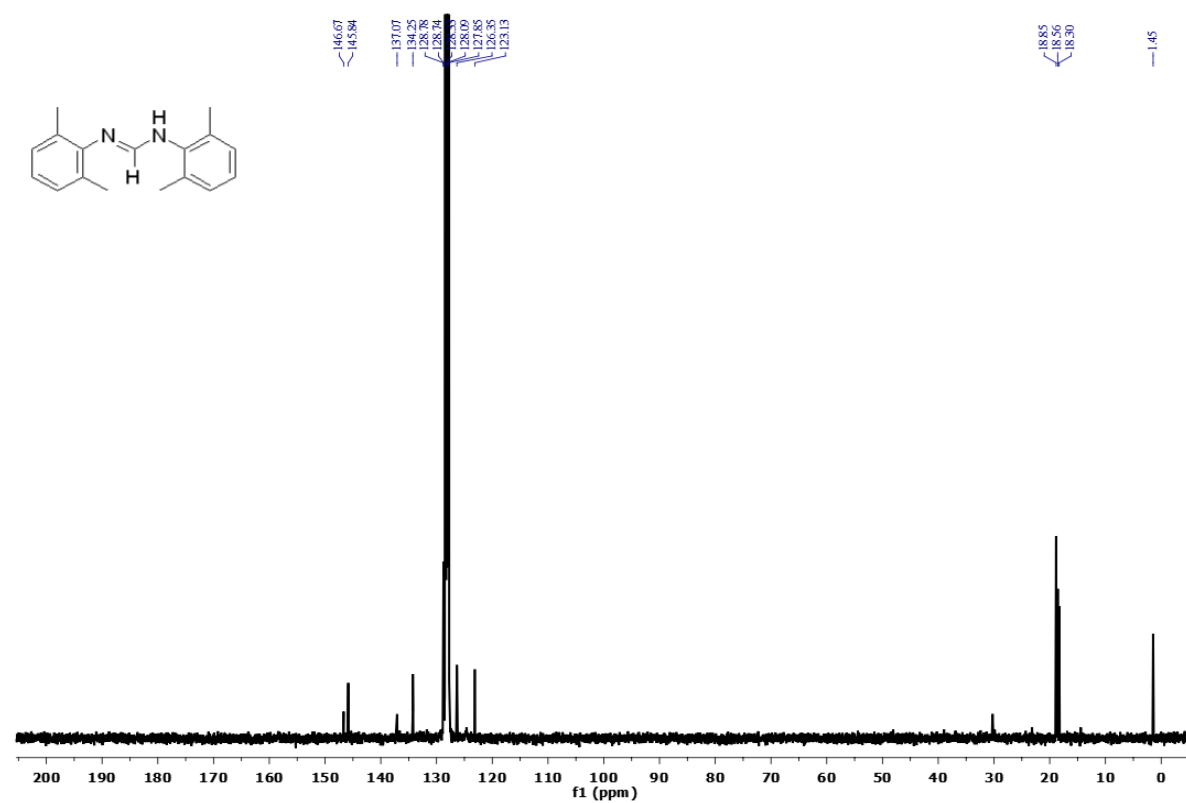
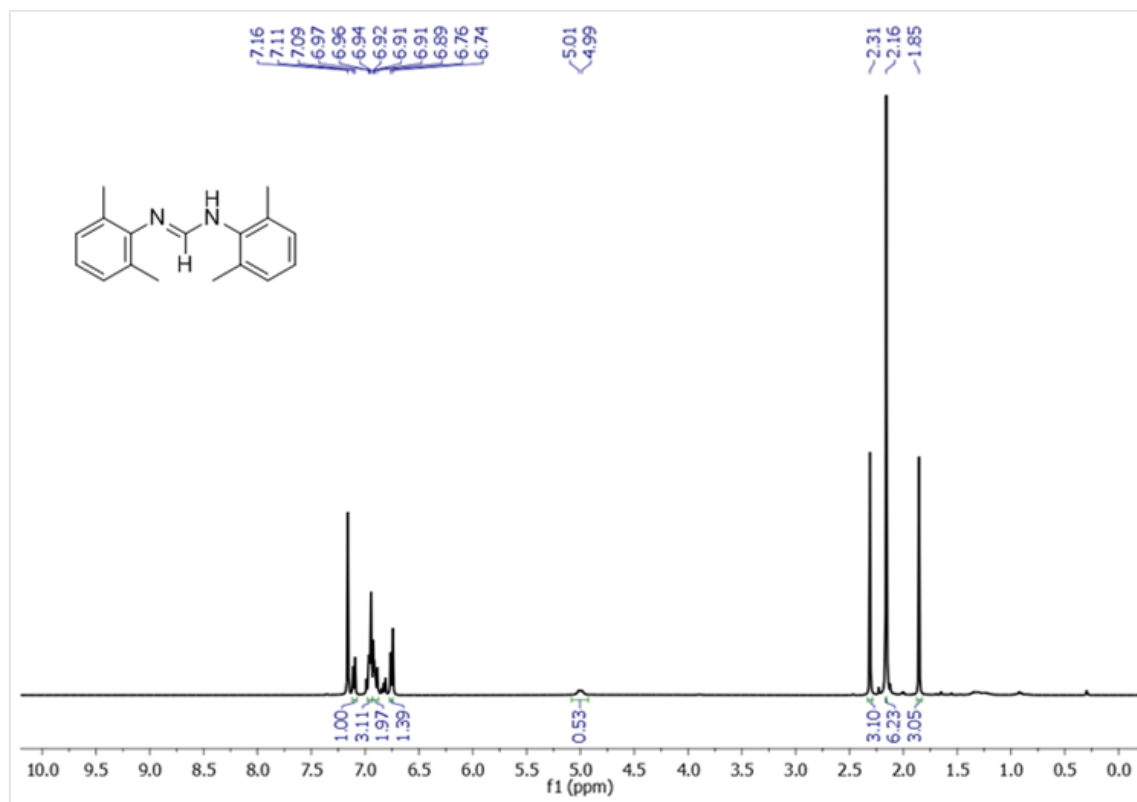


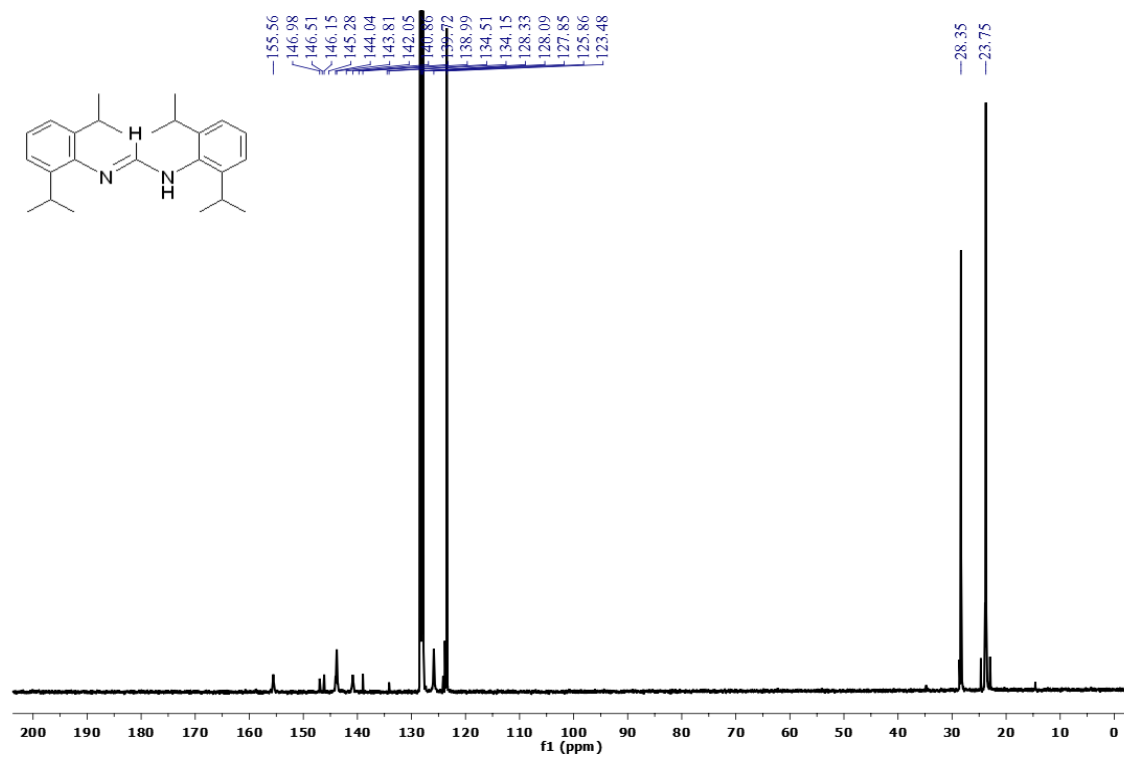
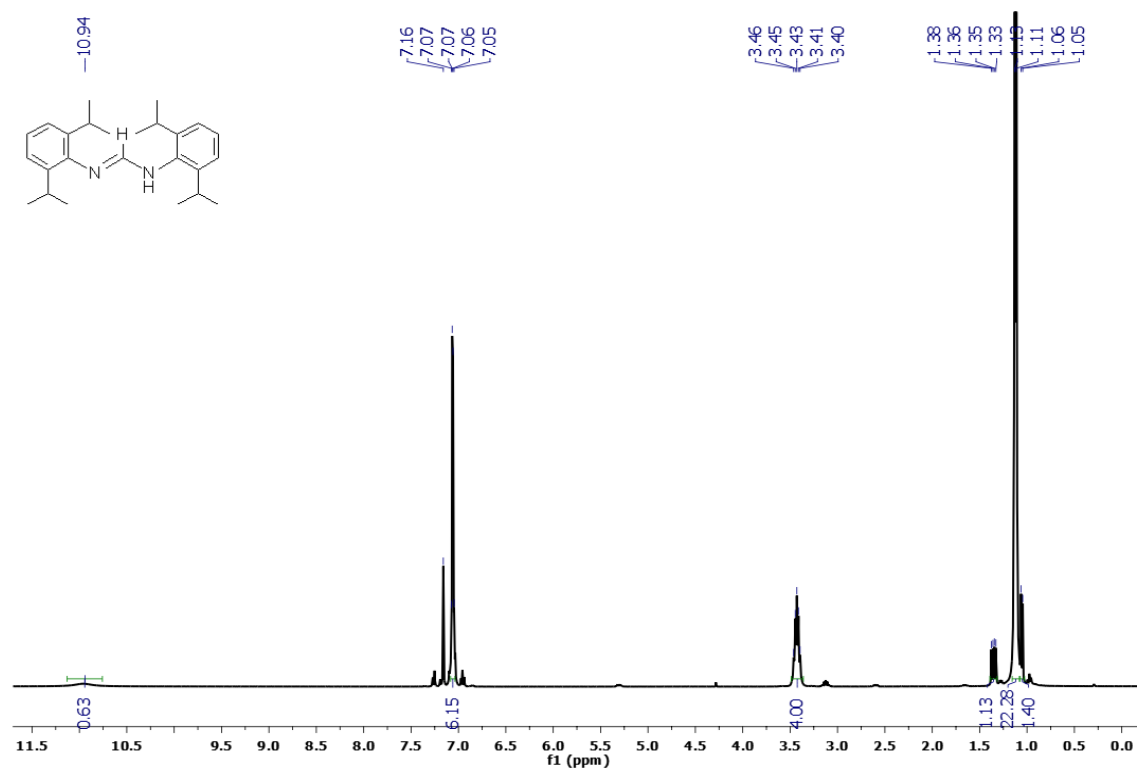
Table 1. Crystal data and structure refinement for sn_132_999

Identification code	shelx	
Empirical formula	C17 H18 N2	
Formula weight	250.33	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 21/ <i>c</i>	
Unit cell dimensions	<i>a</i> = 8.2782(2) Å	<i>a</i> = 90°.
	<i>b</i> = 7.7779(2) Å	<i>b</i> = 99.957(2)°.
	<i>c</i> = 23.1597(6) Å	<i>g</i> = 90°.
Volume	1468.72(6) Å ³	
<i>Z</i>	4	
Density (calculated)	1.132 Mg/m ³	
Absorption coefficient	0.067 mm ⁻¹	
<i>F</i> (000)	536	
Crystal size	0.220 x 0.180 x 0.150 mm ³	
Theta range for data collection	2.767 to 26.401°.	
Index ranges	-10 ≤ <i>h</i> ≤ 10, -9 ≤ <i>k</i> ≤ 9, -28 ≤ <i>l</i> ≤ 28	
Reflections collected	19269	
Independent reflections	3008 [<i>R</i> (int) = 0.0344]	
Completeness to theta = 26.000°	99.9 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	3008 / 0 / 176	
Goodness-of-fit on <i>F</i> ²	1.038	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0613, <i>wR</i> 2 = 0.1655	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0893, <i>wR</i> 2 = 0.1909	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.207 and -0.278 e.Å ⁻³	

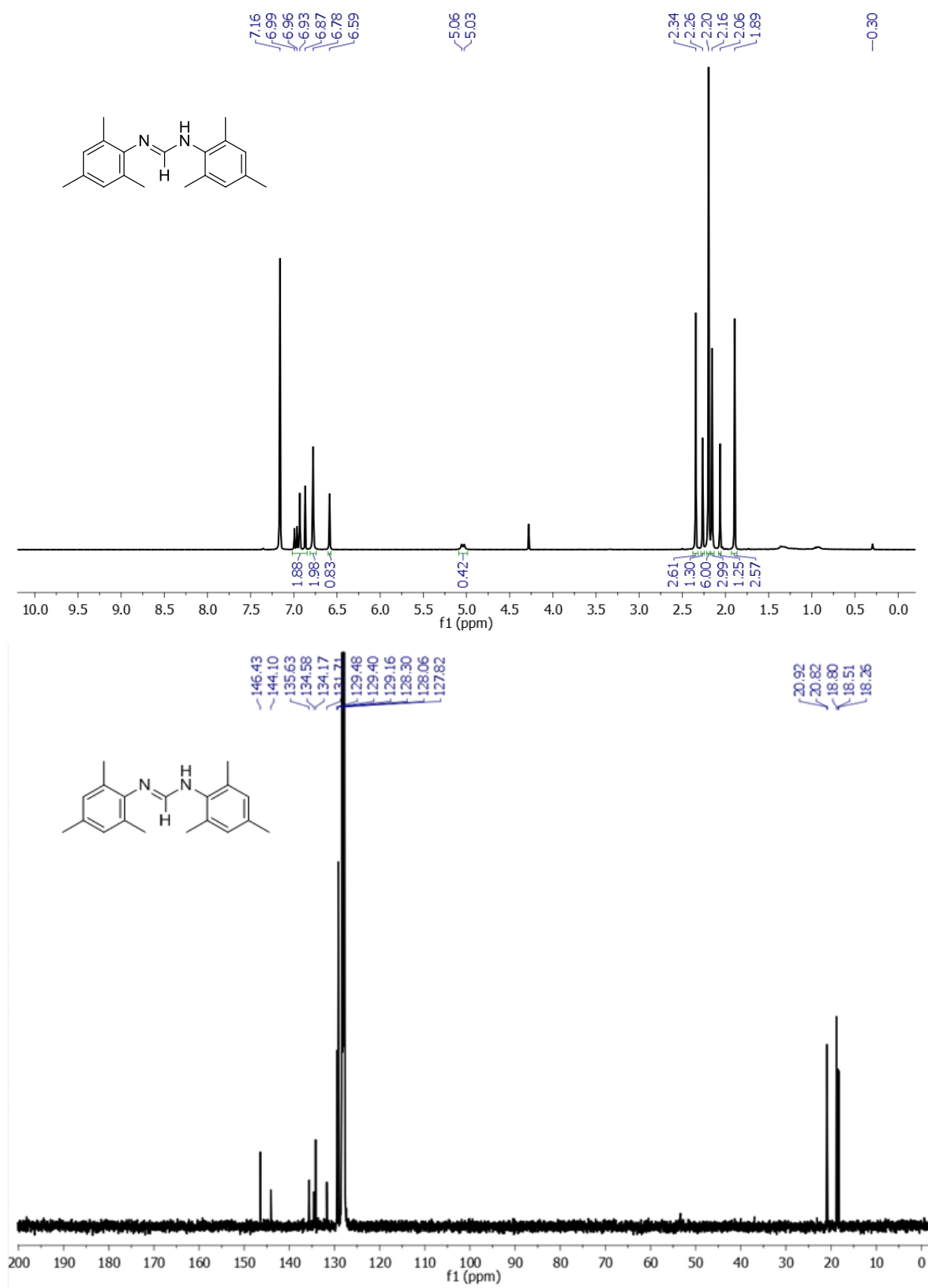
^1H & ^{13}C NMR spectra of N,N'-Bis(2,6-dimethylphenyl) formamidine (**1b**)



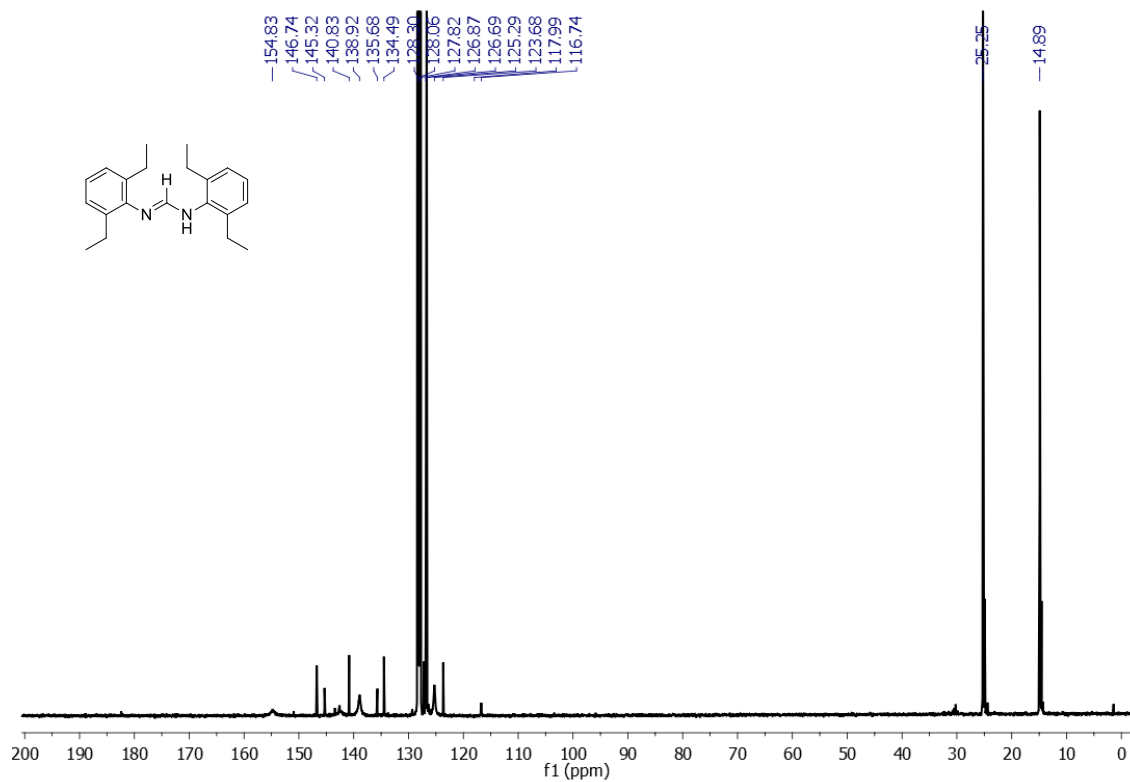
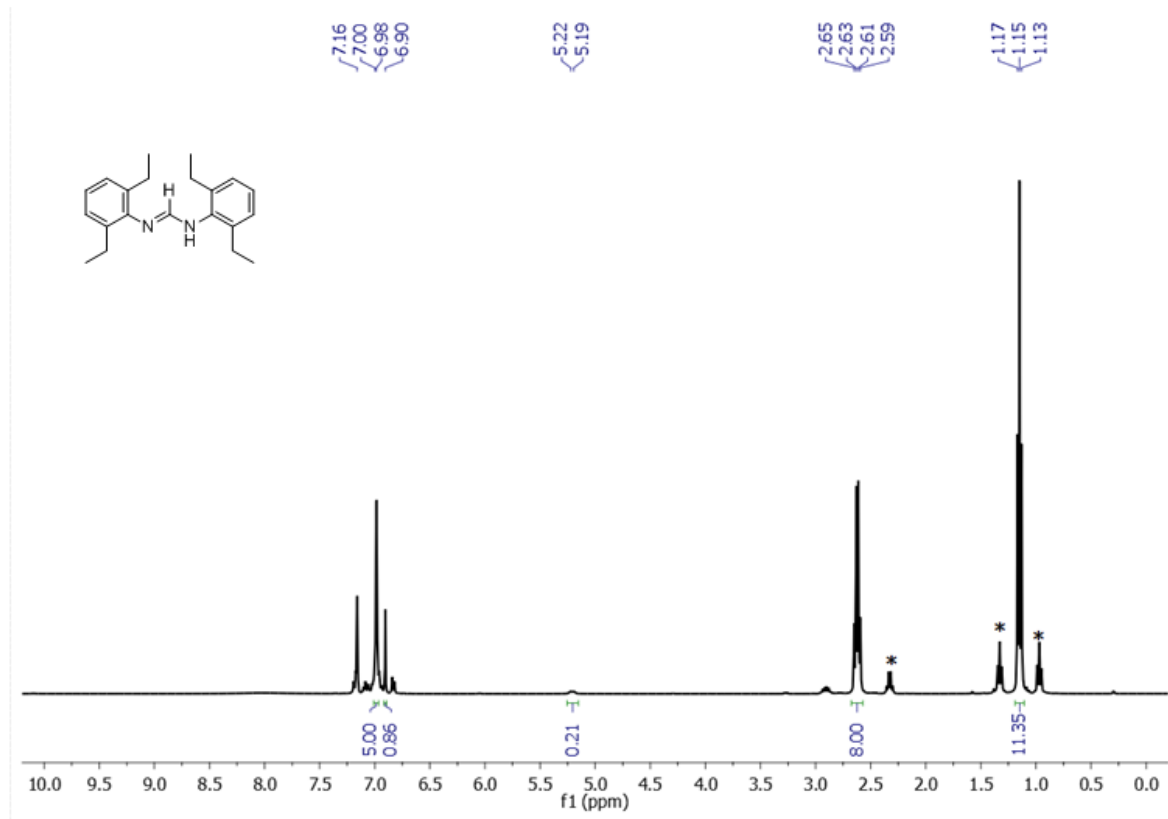
^1H & ^{13}C NMR spectra of N,N'-Bis(2,6-diisopropylphenyl)formamidine (2b)



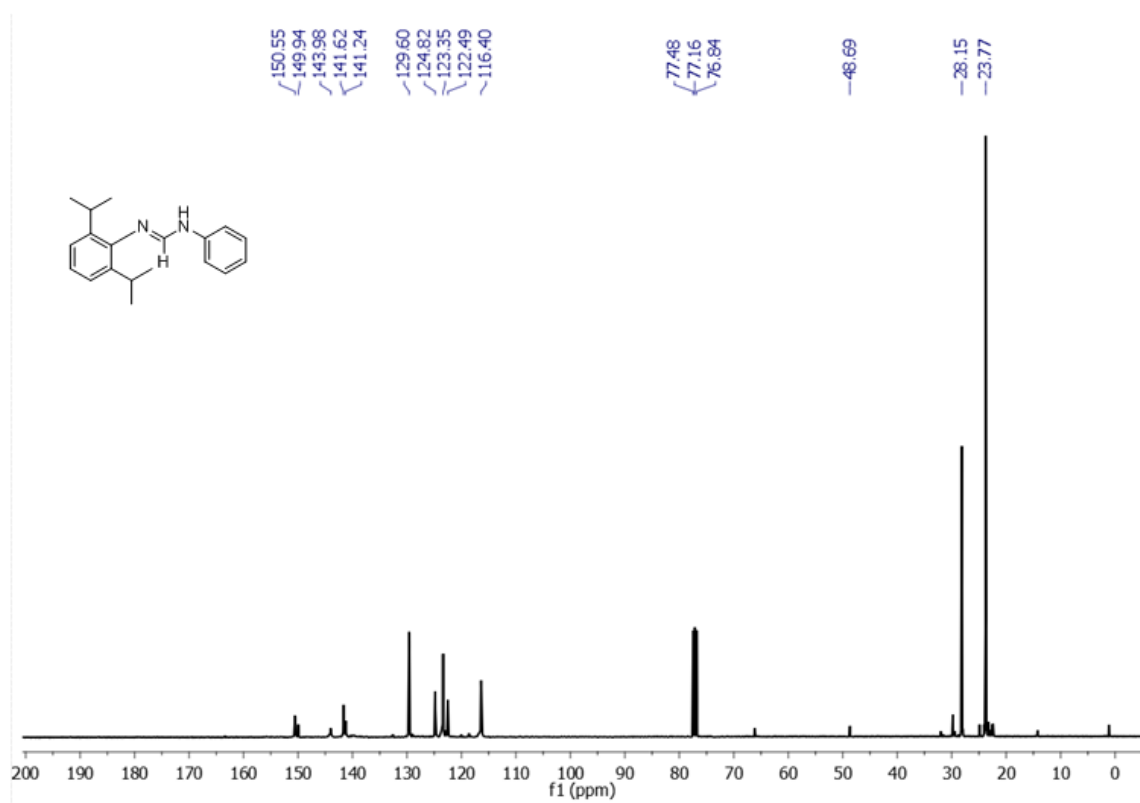
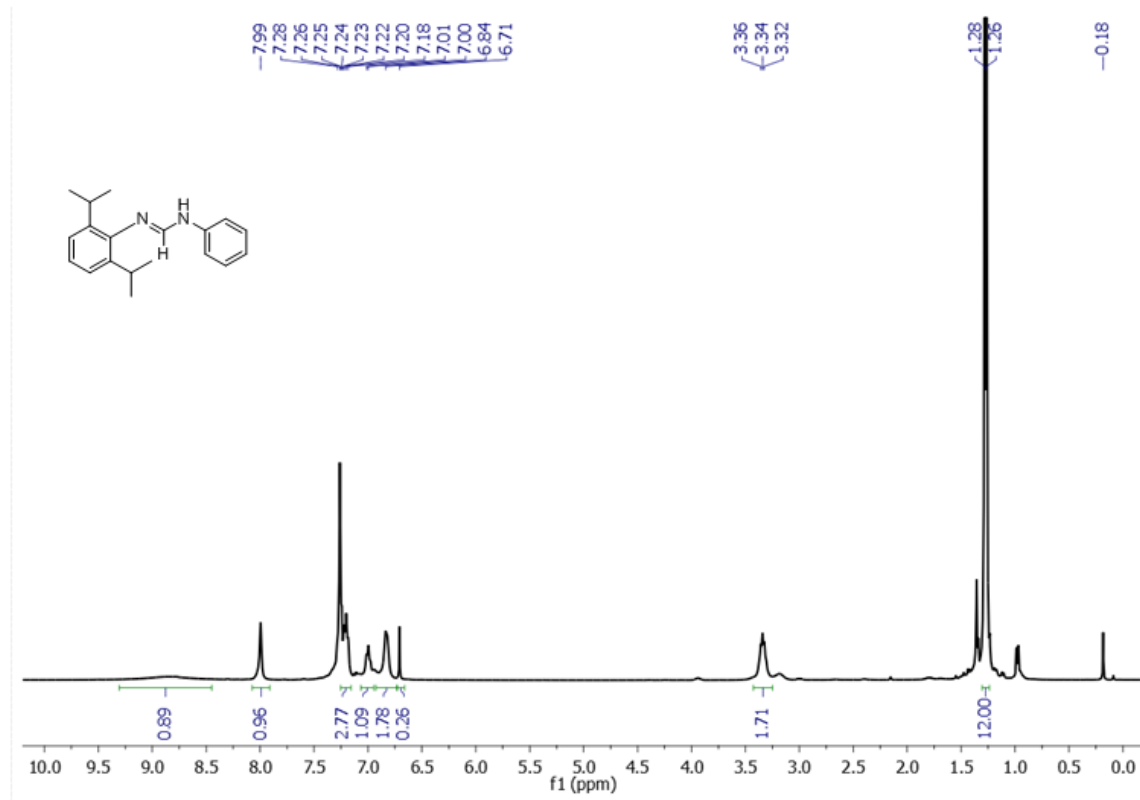
^1H & ^{13}C NMR spectra of N,N'-Dimesitylformamidine (**3b**)



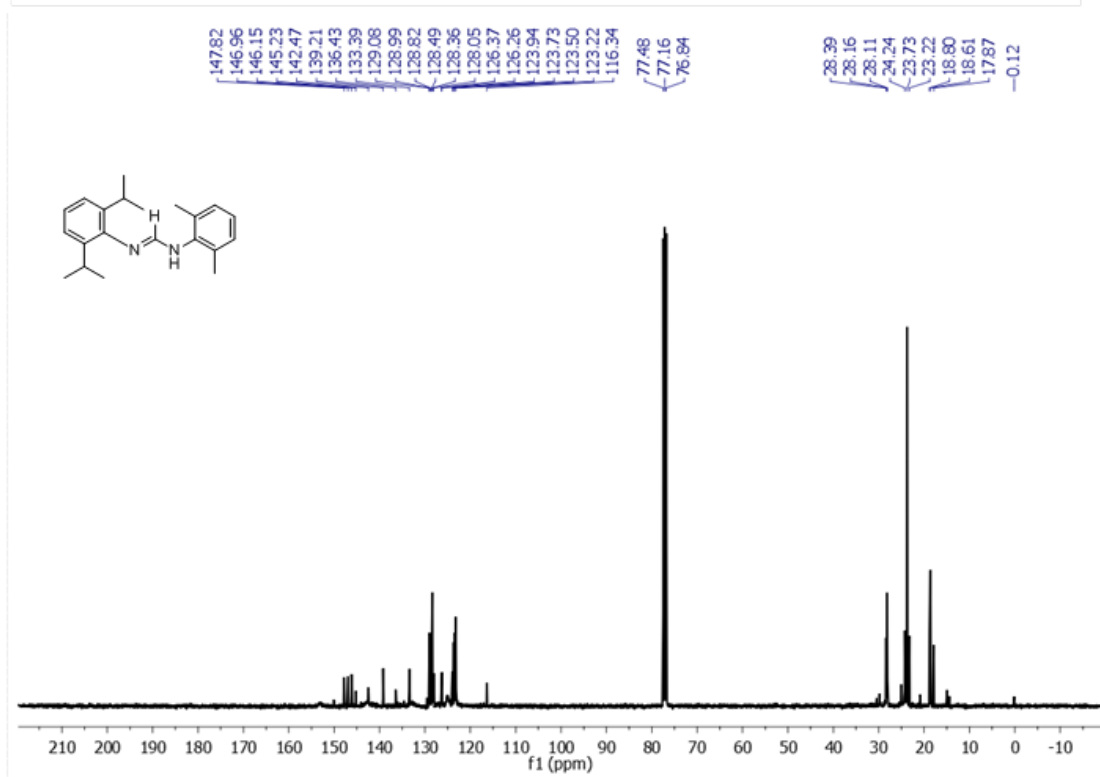
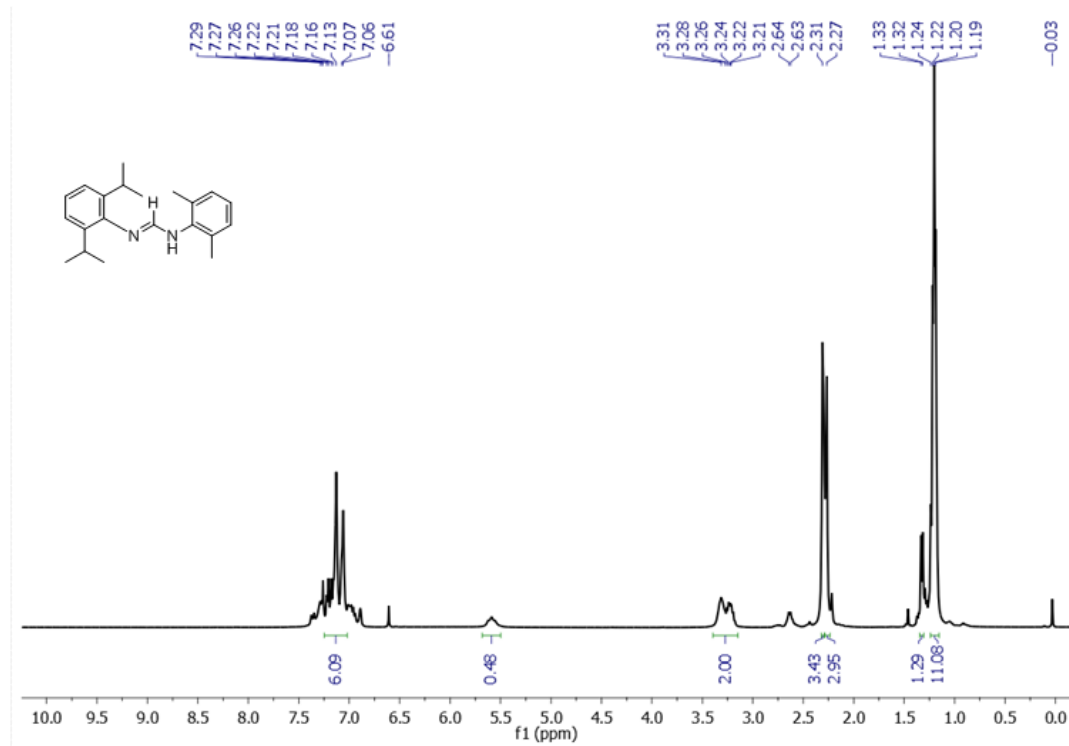
^1H & ^{13}C NMR spectra of N,N'-Bis (2,6-diethylphenyl)formamidine(**4b**)



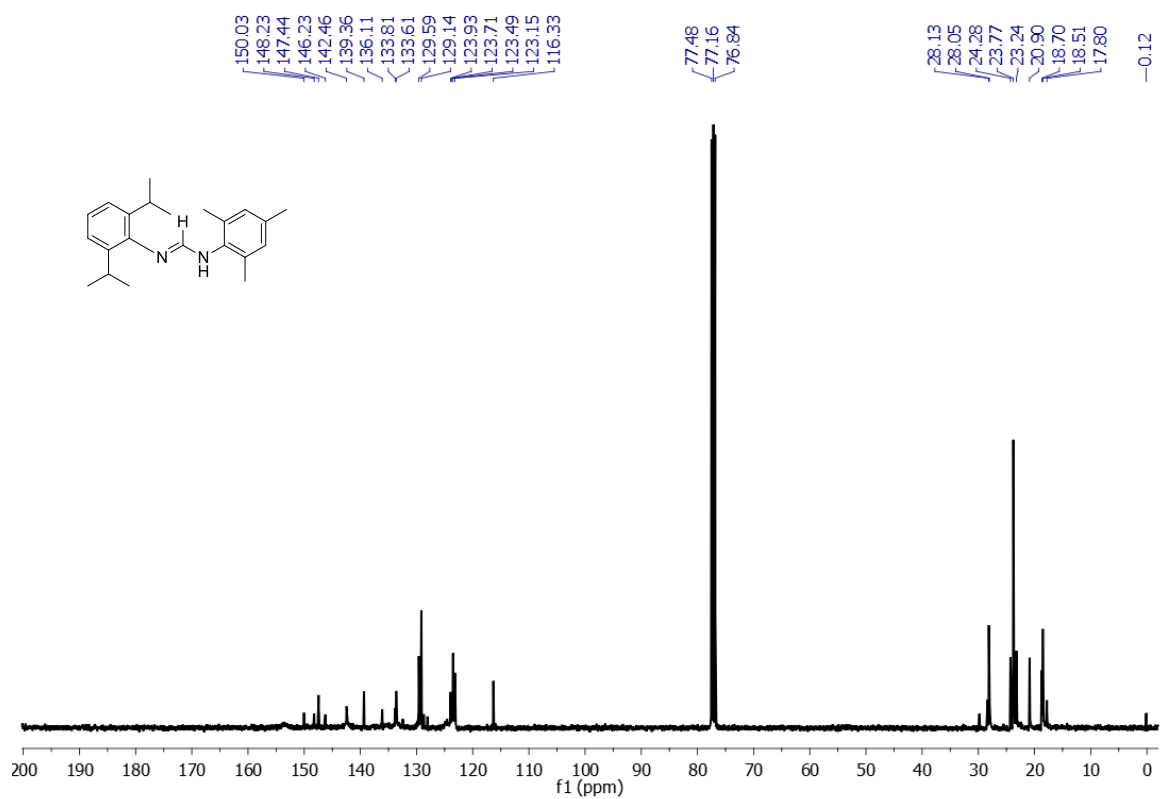
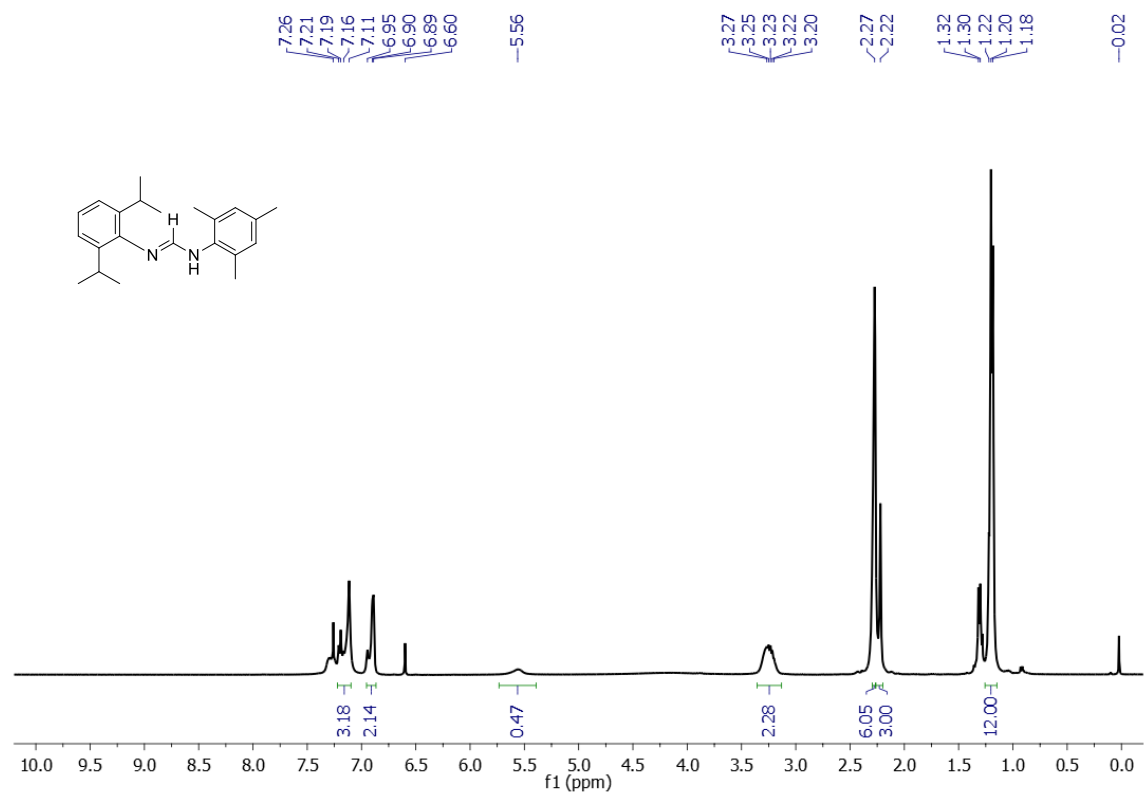
^1H & ^{13}C NMR spectra of N-(2, 6-diisopropylphenyl)-N'-phenyl formamidine(**5b**)



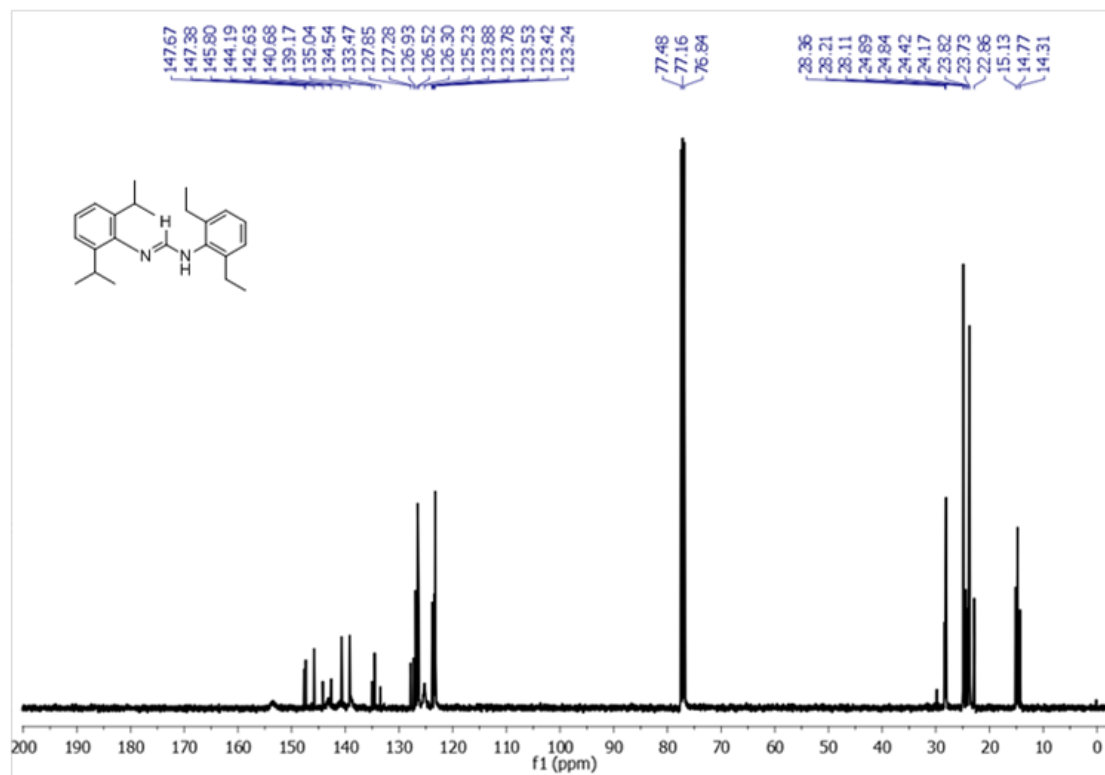
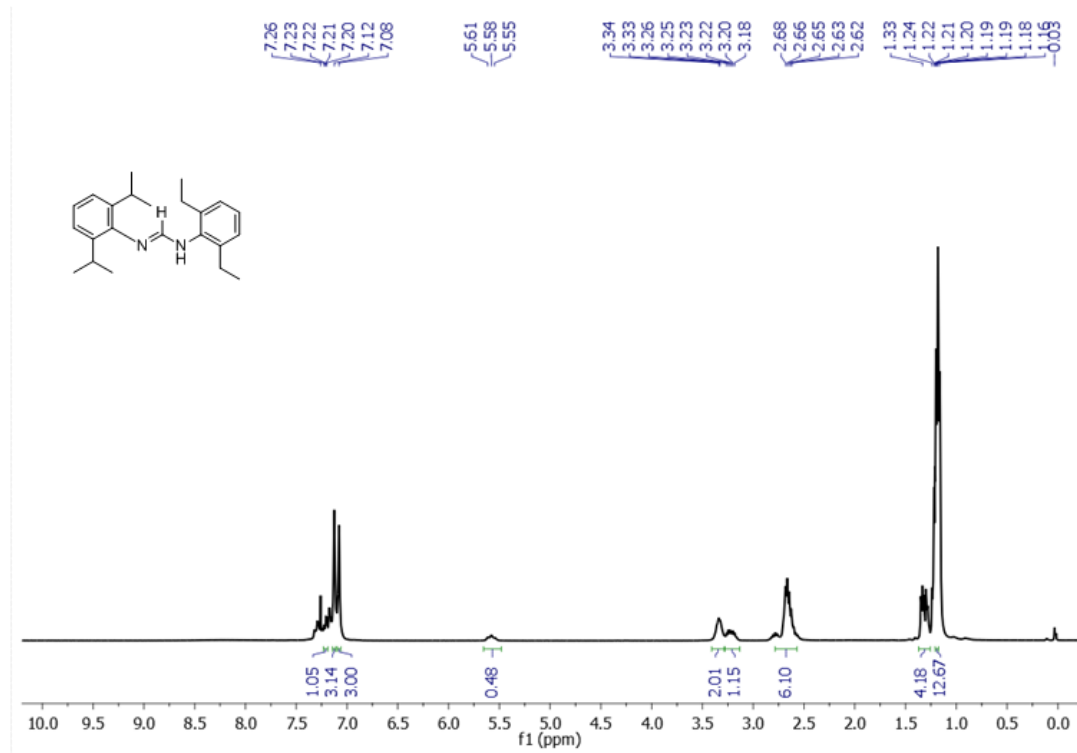
^1H & ^{13}C NMR spectra of N-(2,6-diisopropylphenyl)-N'-(2,6-dimethylphenyl) formamidine (**6b**)



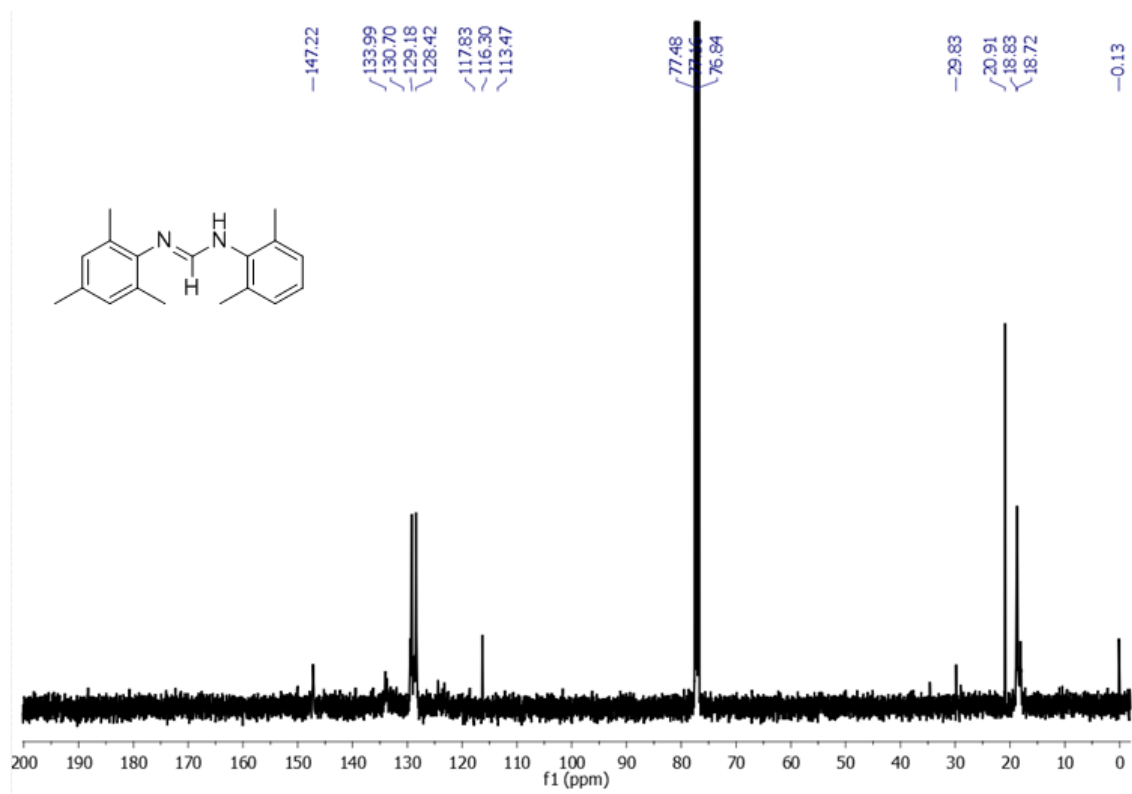
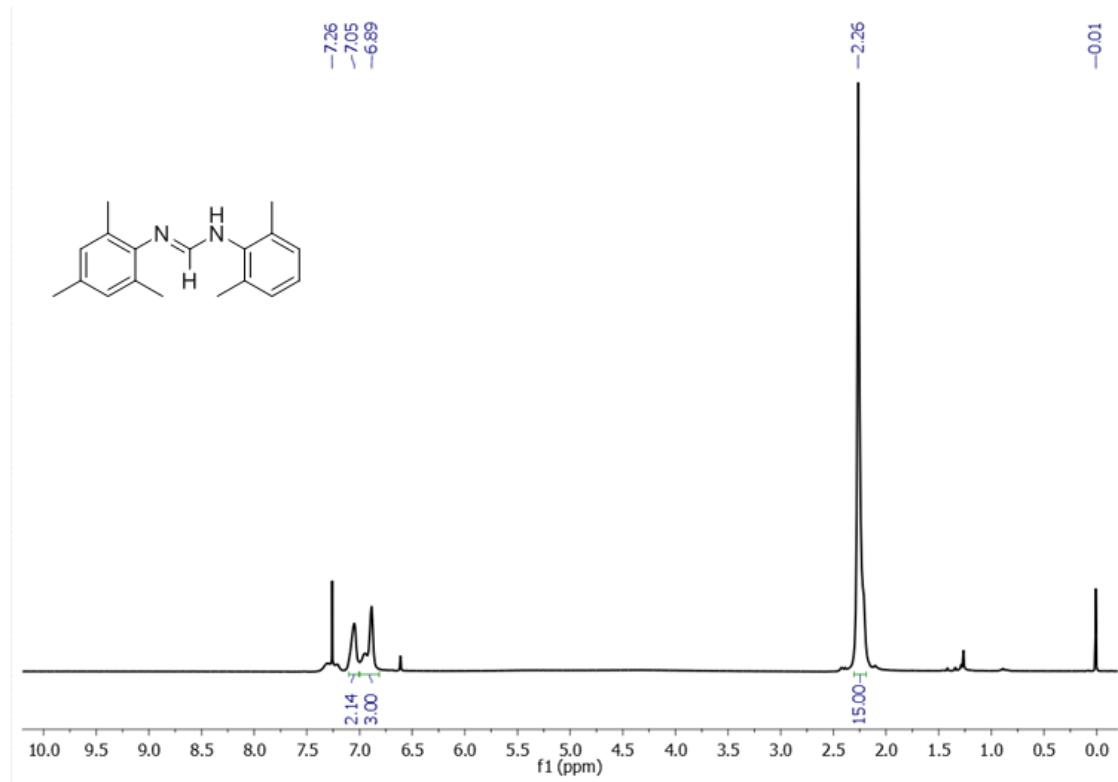
^1H & ^{13}C NMR spectra of N-(2, 6-diisopropylphenyl)-N'-mesityl formamidine(**7b**)



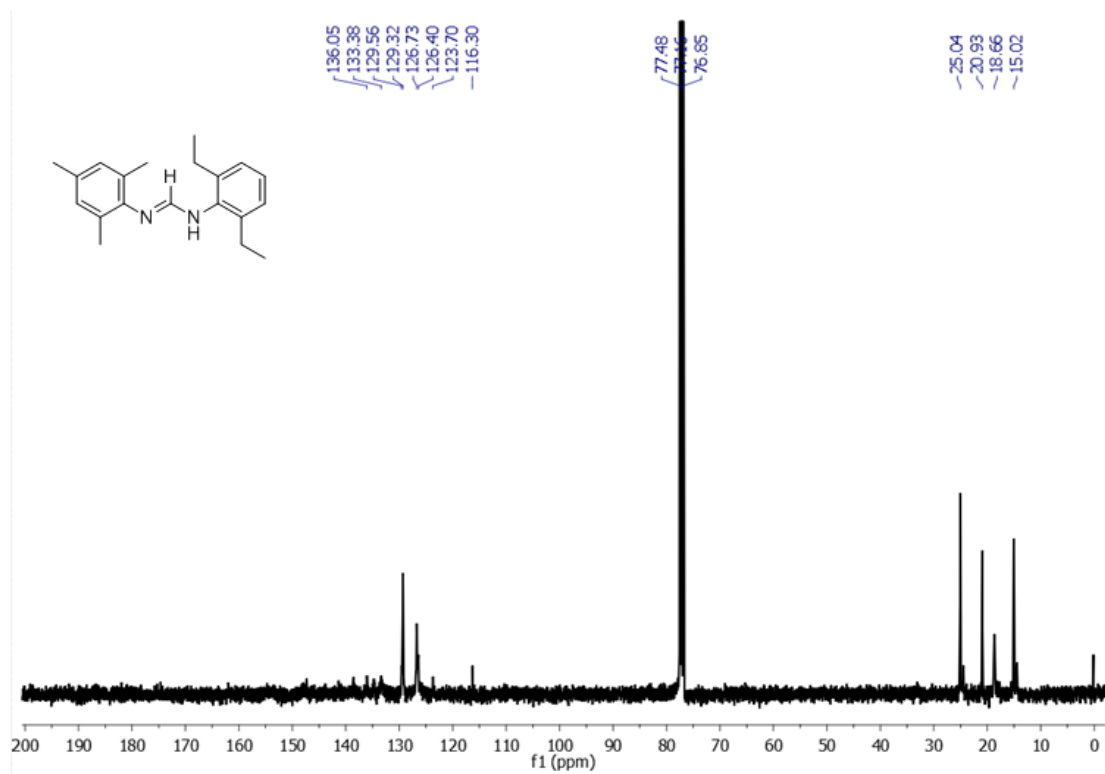
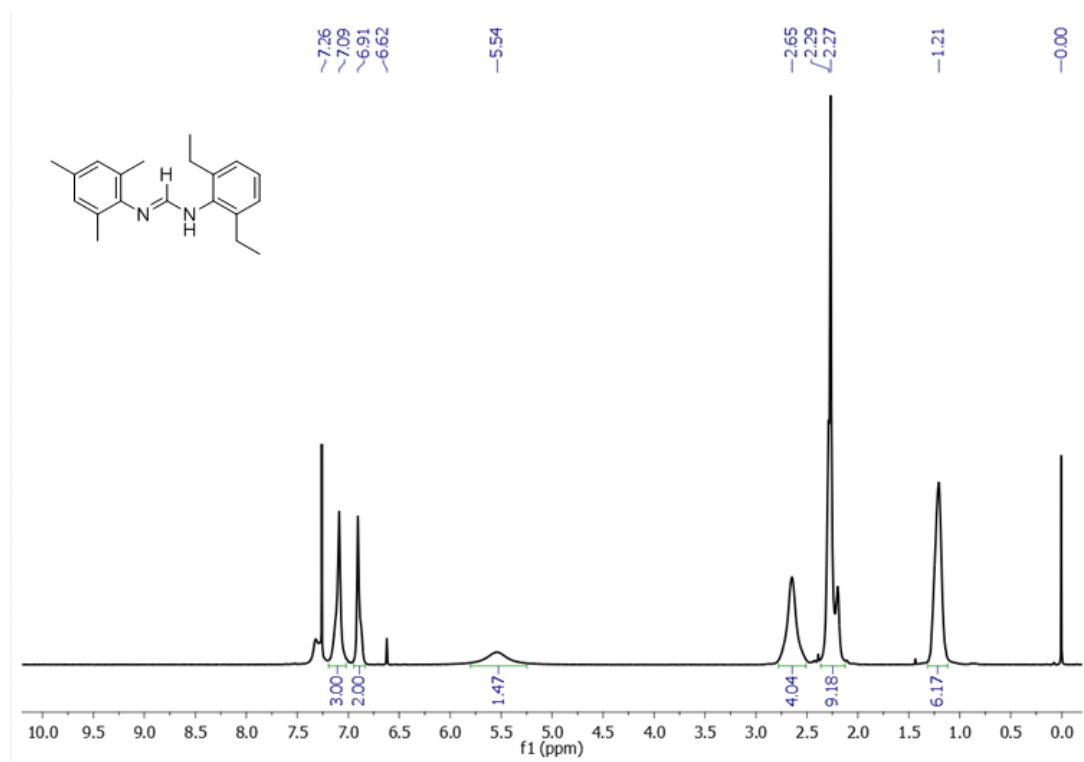
^1H & ^{13}C NMR spectra of N-(2,6-diisopropylphenyl)- N'-(2,6-diethylphenyl) formamidine **8b**



^1H & ^{13}C NMR spectra of N-mesityl -N'-(2, 6-dimethylphenyl)formamidine (**9b**)



^1H & ^{13}C NMR spectra of N-mesityl-N'-(2, 6-diethylphenyl)formamidinium (**10b**)



HPLC

Formamidines (FormHs) purities were determined by HPLC

HPLC conditions:

System: Agilent Technologies 1200 Series Quat Pump

Detector: Agilent DAD

Column: Agilent ZoRBAX GF-450 Eclipse XDB C-18, 6 μ m, 9.4 mm x 250mm

Mobile Phase: 70% Hexane/30% Isopropanol

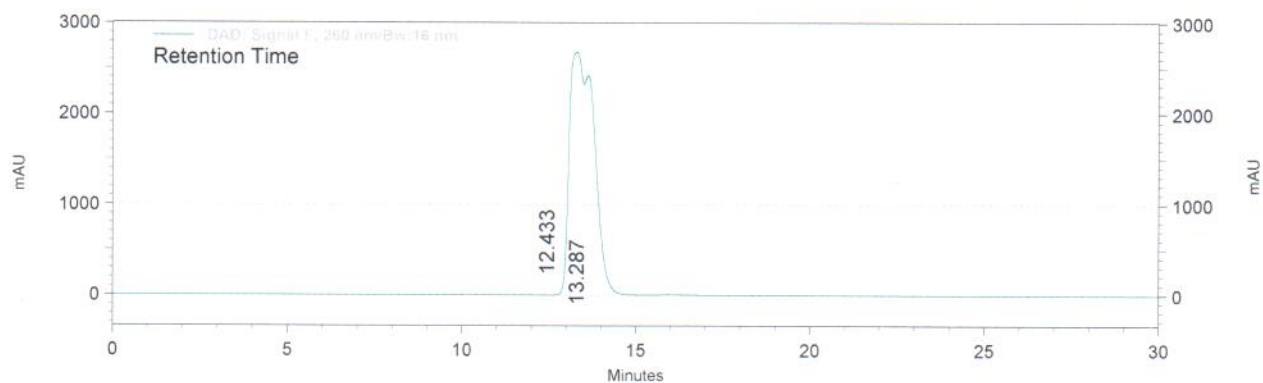
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Flow rate: 1mL/ min

Area % Report

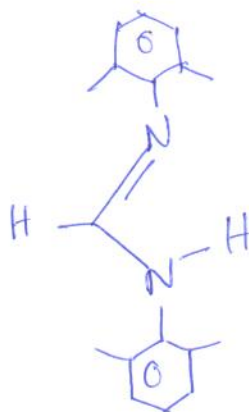
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(1b)



DAD: Signal F,
 260 nm/Bw: 16 nm
 Results

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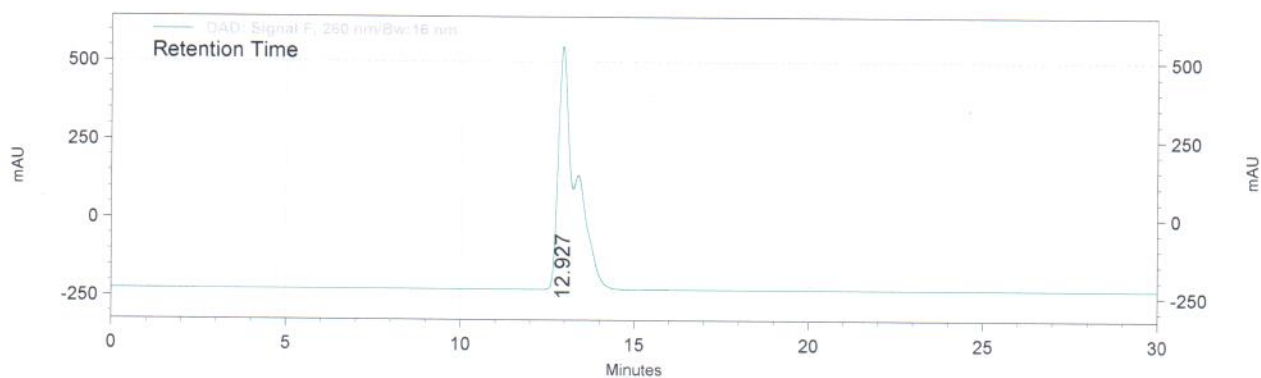


(1b)

Area % Report

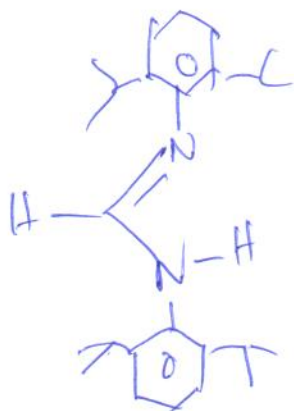
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(26)



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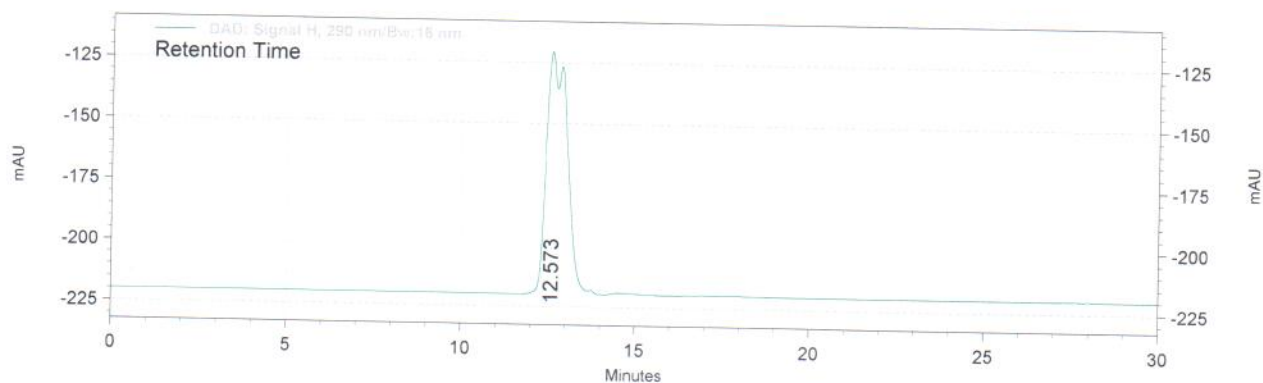
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Area % Report

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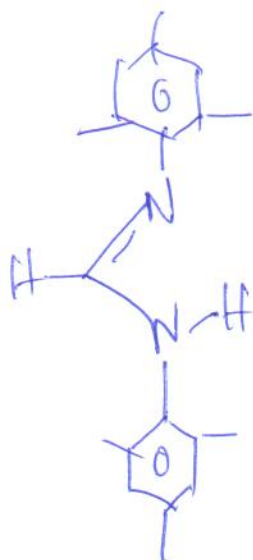
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(3b)



DAD: Signal H,
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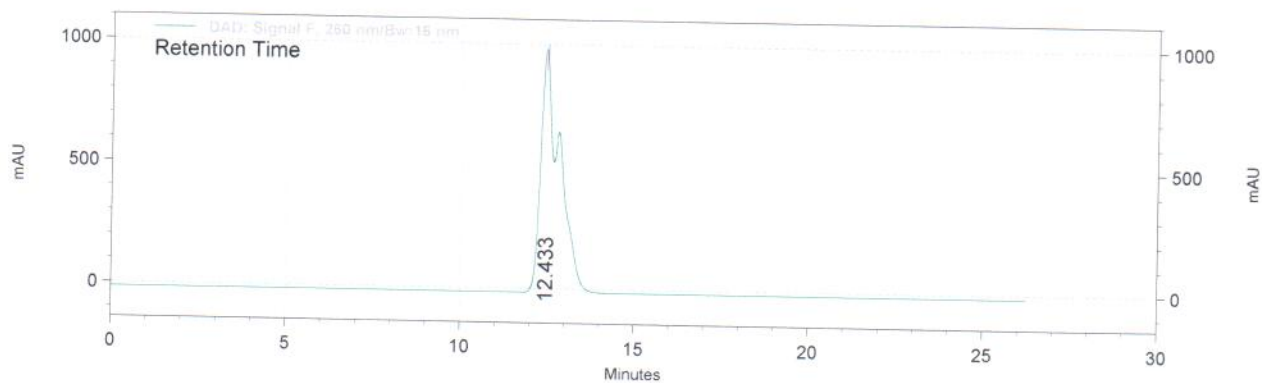
(3b)

Area % Report

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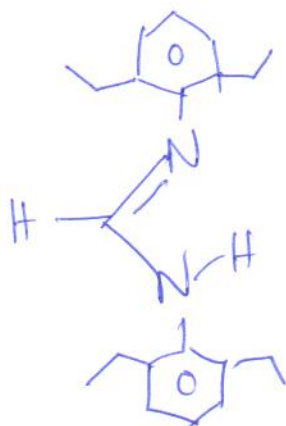
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(46)



DAD: Signal F,
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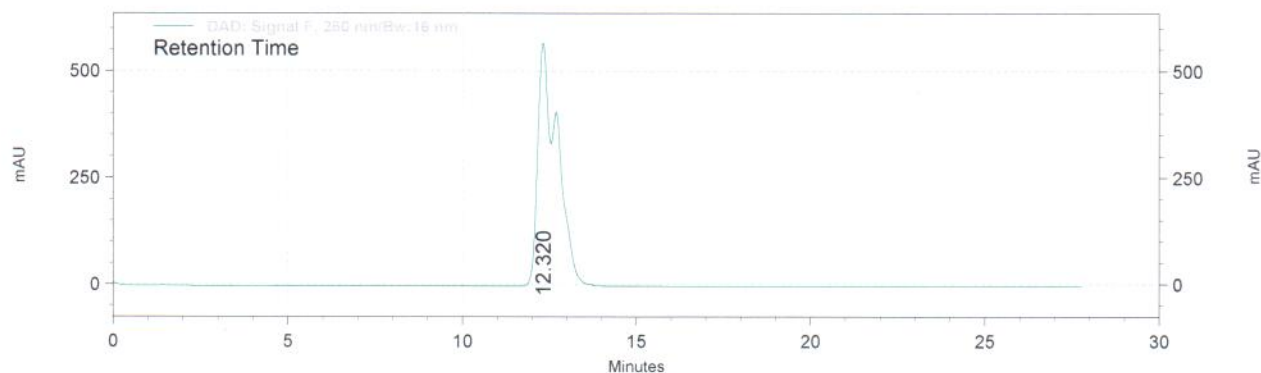


(46)

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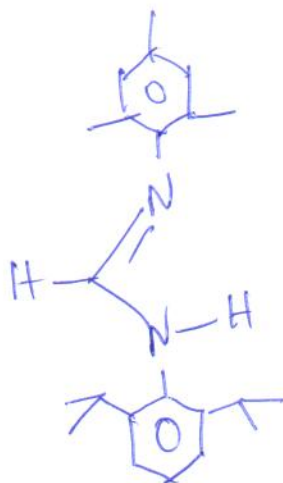
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(7b)



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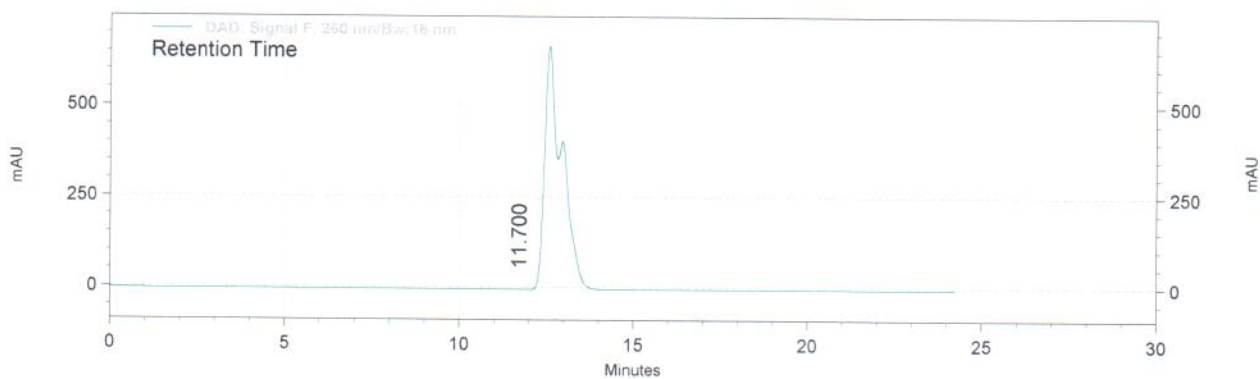


(7b)

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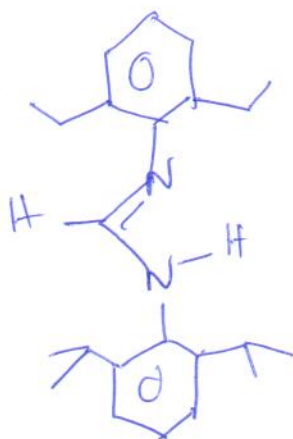
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(86)



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Results

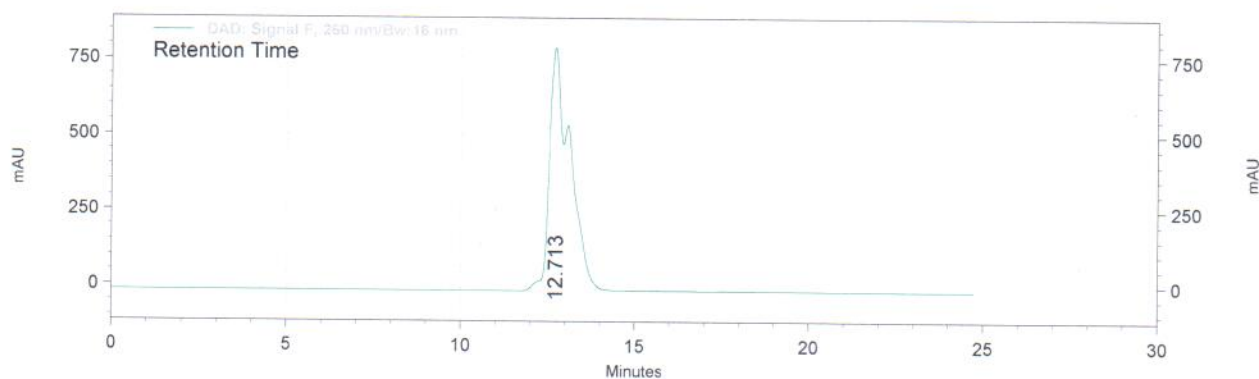
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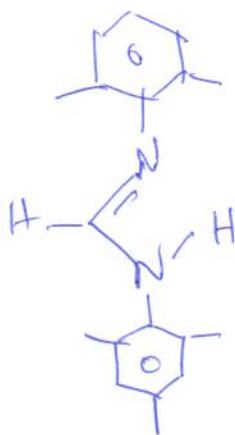
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95



**DAD: Signal F,
 260 nm/Bw:16 nm
 Results**

Retention Time	Area	Area %	Height	Height %
12.713	1965190	100.00	199377	100.00
Totals	1965190	100.00	199377	100.00



me (95)