

Supplementary Information for

Hydrogen peroxide/dimethyl carbonate: a green system for epoxidation of *N*-alkylimines and *N*-sulfonylimines. One-pot synthesis of *N*-alkyloxaziridines from *N*-alkylamines and (hetero)aromatic aldehydes

Jamil Kraiem,^{a,b} Donia Ghedira,^b Thierry Ollevier^{a*}

a Département de chimie, Université Laval, 1045 avenue de la Médecine Québec, QC, G1V 0A6, Canada.

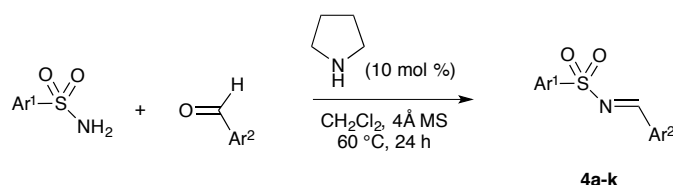
b Laboratoire de Développement Chimique, Galénique et Pharmacologique des Médicaments, Faculté de Pharmacie de Monastir, Université de Monastir, Rue Avicenne, 5000 Monastir, Tunisia.

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General methods

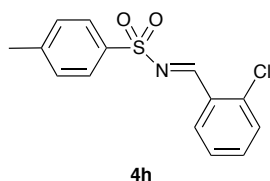
NMR spectra were acquired using CDCl_3 as solvent, running at 300 and 75 MHz for ^1H and ^{13}C respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CHCl_3 , 7.28 ppm and CH_2Cl_2 , 5.32 ppm, H_2O 1.61 ppm for ^1H NMR; CDCl_3 , 76.5 ppm for ^{13}C NMR). In all ^1H NMR spectra, multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constant values (in Hertz) and number of protons for each signal are also indicated. Melting points were determined on a Büchi SMP-20 capillary apparatus and are uncorrected. TLC was carried out on Merck 60F-254 precoated silica gel plates (0.25 mm). Dimethyl carbonate (Reagent plus®, 99%) and hydrogen peroxide (30 % wt in water) were purchased from Sigma-Aldrich. All starting materials purchased from commercial suppliers were used without further purification, except alkylamines and aromatic aldehydes which were distilled or recrystallized (solid reagents) before use. *N*-Sulfonylimines were prepared according to the eco-friendly procedure reported by Morales.¹

Synthesis of *N*-sulfonylimines



Typical procedure: 2-chlorobenzaldehyde (2.4 mmol), pyrrolidine (0.2 mmol) and molecular sieves 4 Å (2 g) were added to a solution of *p*-toluenesulfonamide (2 mmol) in dry dichloromethane (1 mL). The mixture was stirred in a sealed vial at 60 °C for 24 h. Then, the reaction was filtered through a short pad of silica gel, the solvent was evaporated under reduced pressure and the residue was recrystallized with ethyl acetate/petroleum ether (20:80) to yield pure *N*-(2-chlorobenzylidene)-*p*-toluenesulfonamide **4h** as a white solid; mp 131–132 °C; yield 89%; δ_{H} (CDCl_3) 2.43 (s, 1H, CH_3), 7.30–7.53 (m, 5H, CH-Ar), 7.89 (d,

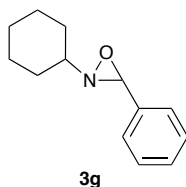
$J = 8.1$ Hz, 2H, CH–Ar), 8.13 (d, $J = 7.8$ Hz, 1H, CH–Ar); δ_{C} (CDCl_3) 21.17 (CH_3), 126.88, 127.77, 129.26, 129.39, 129.66, 129.98, 134.19, 135.16, 138.40, 144.37, 166.25 (CH=N).



Compounds **4a**,² **4b**,³ **4c**,⁴ **4d**,⁵ **4e**,⁶ **4f**,⁷ **4g**,⁶ **4h**,⁶ **4i**,⁶ **4j**,⁶ and **4k**⁸ were characterized by comparing their NMR spectra with literature data.

Synthesis of *N*-alkyloxaziridines

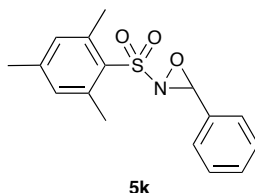
Typical procedure: To a solution of benzaldehyde (1 mmol) in DMC (1 mL) was added cyclohexylamine (1.5 mmol). The mixture was stirred for 10 min. An hydrogen peroxide solution (30 % wt, 5 mmol) was then added over a period of 5 min. The mixture was stirred at room temperature until disappearance of aldehyde (15 h, reaction monitored by TLC). The reaction mixture was then diluted with ethyl acetate (5 mL), washed with a solution of sodium sulfite (5 mL) and extracted with ethyl acetate (3 × 2 mL). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure to yield pure 2-cyclohexyl-3-phenyloxaziridine **3g**. Colorless oil; Yield 96%; δ_{H} (CDCl_3) 1.15–2.15 (m, 11H, cyclohexyl), 4.56 (s, 1H, O–CH–N, *trans* 91%), 5.31 (s, H, O–CH–N, *cis* 9%), 7.39–7.47 (m, 5H, Ar); δ_{C} (CDCl_3) *trans*-isomer: 24.08 (CH_2), 24.56 (CH_2), 25.77 (CH_2), 29.21 (CH_2), 31.60 (CH_2), 70.18 (CH–cyclohexyl), 79.84 (O–CH–N), 127.45 (CH–Ar), 128.49 (CH–Ar), 129.90 (CH–Ar), 135.26 (C–Ar); *cis*-isomer: 23.92 (CH_2), 23.98 (CH_2), 25.65 (CH_2), 28.15 (CH_2), 31.71 (CH_2), 59.25 (CH–cyclohexyl), 79.70 (O–CH–N), 127.95 (CH–Ar), 128.11 (CH–Ar), 129.36 (CH–Ar), 131.90 (C–Ar).



N-Alkyloxaziridines **3a**,⁹ **3b**,¹⁰ **3c**,¹⁰ **3d**,⁵ **3e**,¹¹ **3f**,¹⁰ **3g**,¹² **3h**,¹³ **3i**,¹⁴ **3j**,¹⁵ **3k**¹⁶ and **3l**¹⁷ were characterized by comparing their NMR spectra with literature data.

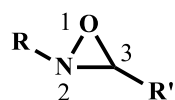
Synthesis of *N*-sulfonyloxaziridines

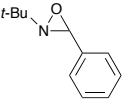
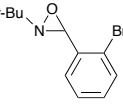
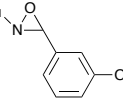
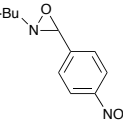
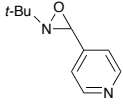
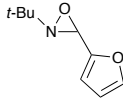
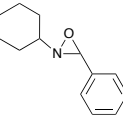
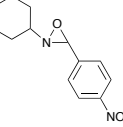
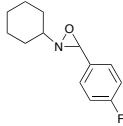
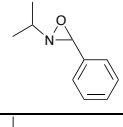
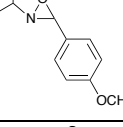
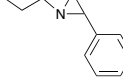
Typical procedure: To a solution of *N*-benzylidene-2,4,6-benzenesulfonamide **4k** (0.5 mmol) in DMC (1.5 mL) was added Na₂CO₃ (0.6 mmol) and Zn(OAc)₂·2H₂O (0.025 mmol). An hydrogen peroxide solution (30 % wt, 5 mmol) was then added over a period of 5 min. The mixture was stirred at room temperature until disappearance of the imine (14 h, TLC). The reaction mixture was then diluted with ethyl acetate (5 mL), washed with a solution of sodium sulfite (5 mL) and extracted with ethyl acetate (3 × 2 mL). The combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. The residue was filtered through a short pad of silica gel to yield pure 2-(2,4,6-trimethylbenzenesulfonyl)-3-phenyloxaziridine **5k** as white solid; mp 104–106 °C; yield 93%; δ_H (CDCl₃) 2.36 (s, 3H, CH₃), 2.78 (s, 6H, 2 CH₃), 5.52 (s, 1H, O–CH–N), 7.06 (s, 2H, CH–Ar), 7.43–7.50 (m, 5H, CH–Ar); δ_C (CDCl₃) 21.09 (CH₃), 23.06 (2 CH₃), 75.47 (O–CH–N), 128.20, 128.68, 129.74, 130.78, 131.18, 132.11, 141.94, 144.72.

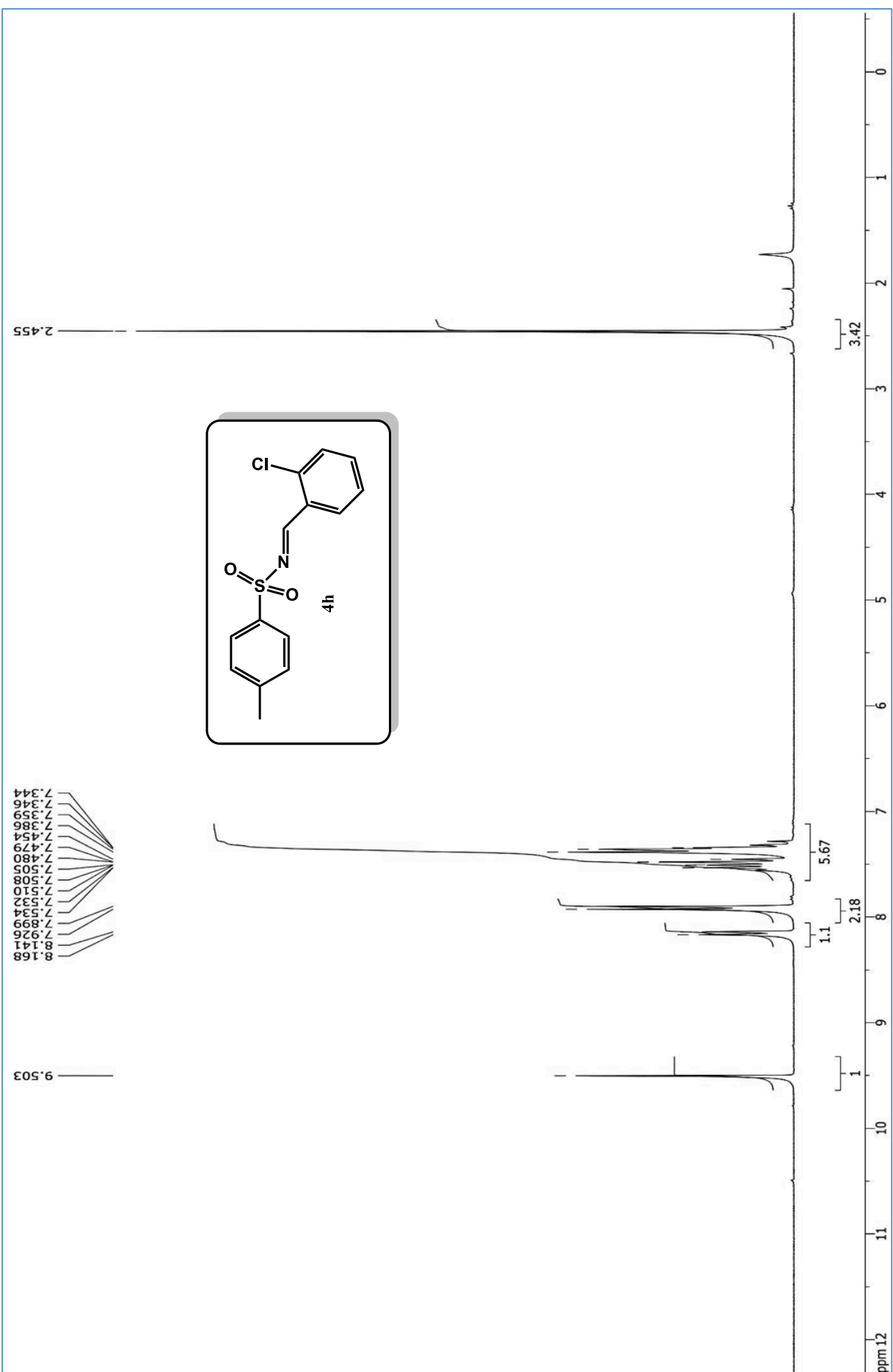


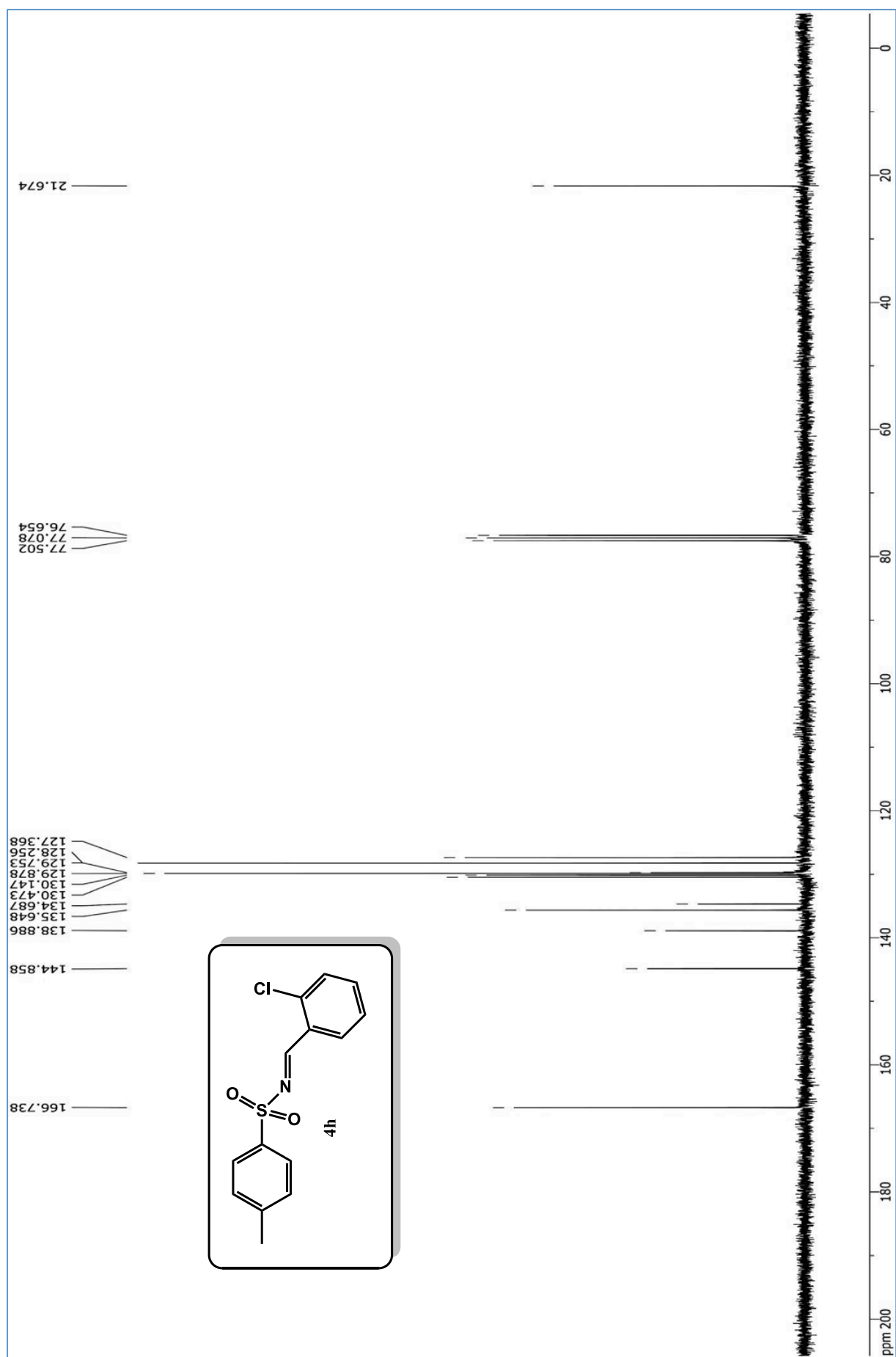
N-Sulfonyloxaziridines **5a**,¹⁸ **5b**,¹⁹ **5c**,²⁰ **5d**,¹⁸ **5e**,²¹ **5f**,²⁰ **5g**,²⁰ **5h**,²² **5i**,²⁰ **5j**,¹⁸ and **5k**²³ were characterized by comparing their NMR spectra with literature data.

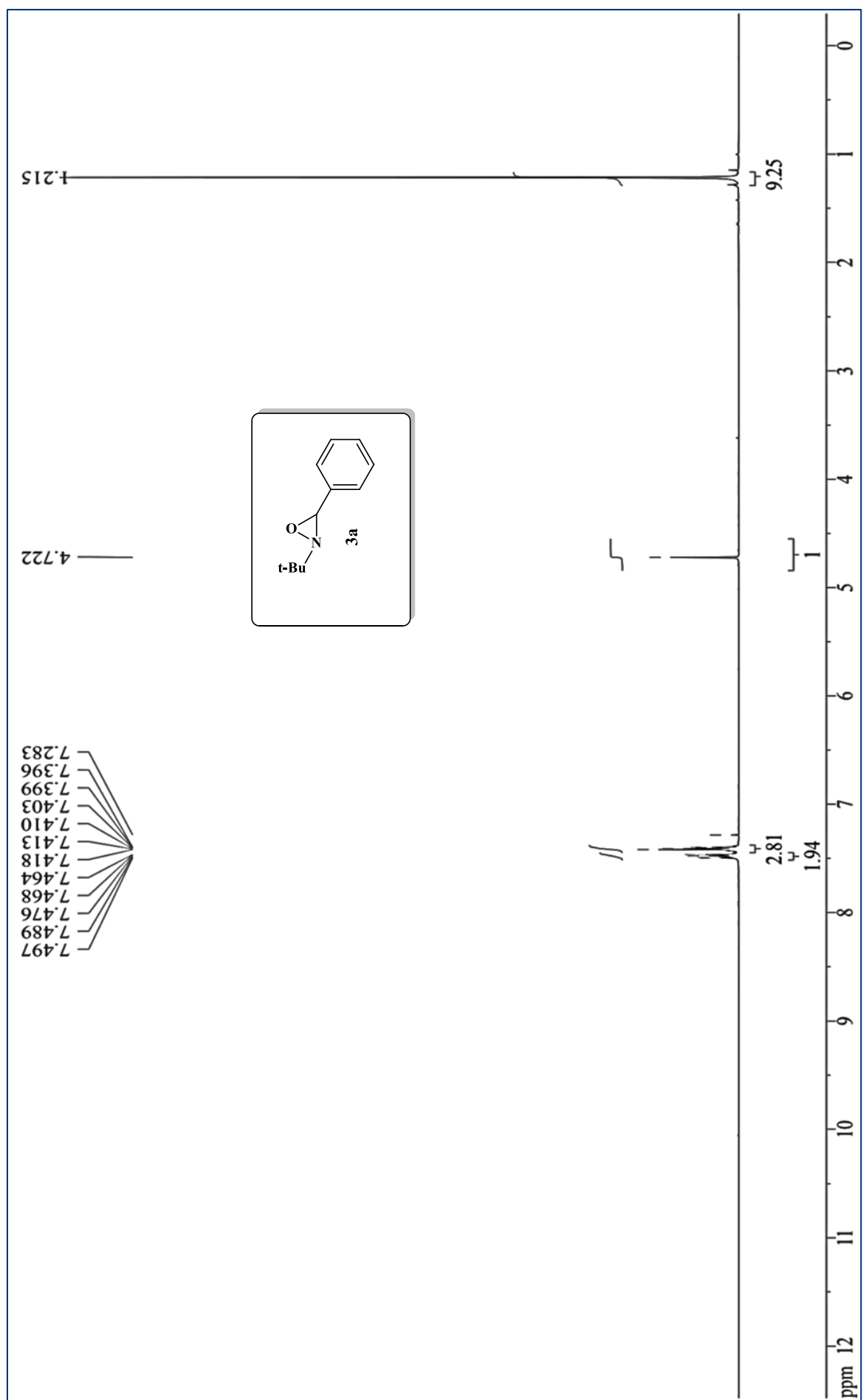
Table: Characteristic NMR chemical shifts of *cis* and *trans*-*N*-alkyloxaziridines.

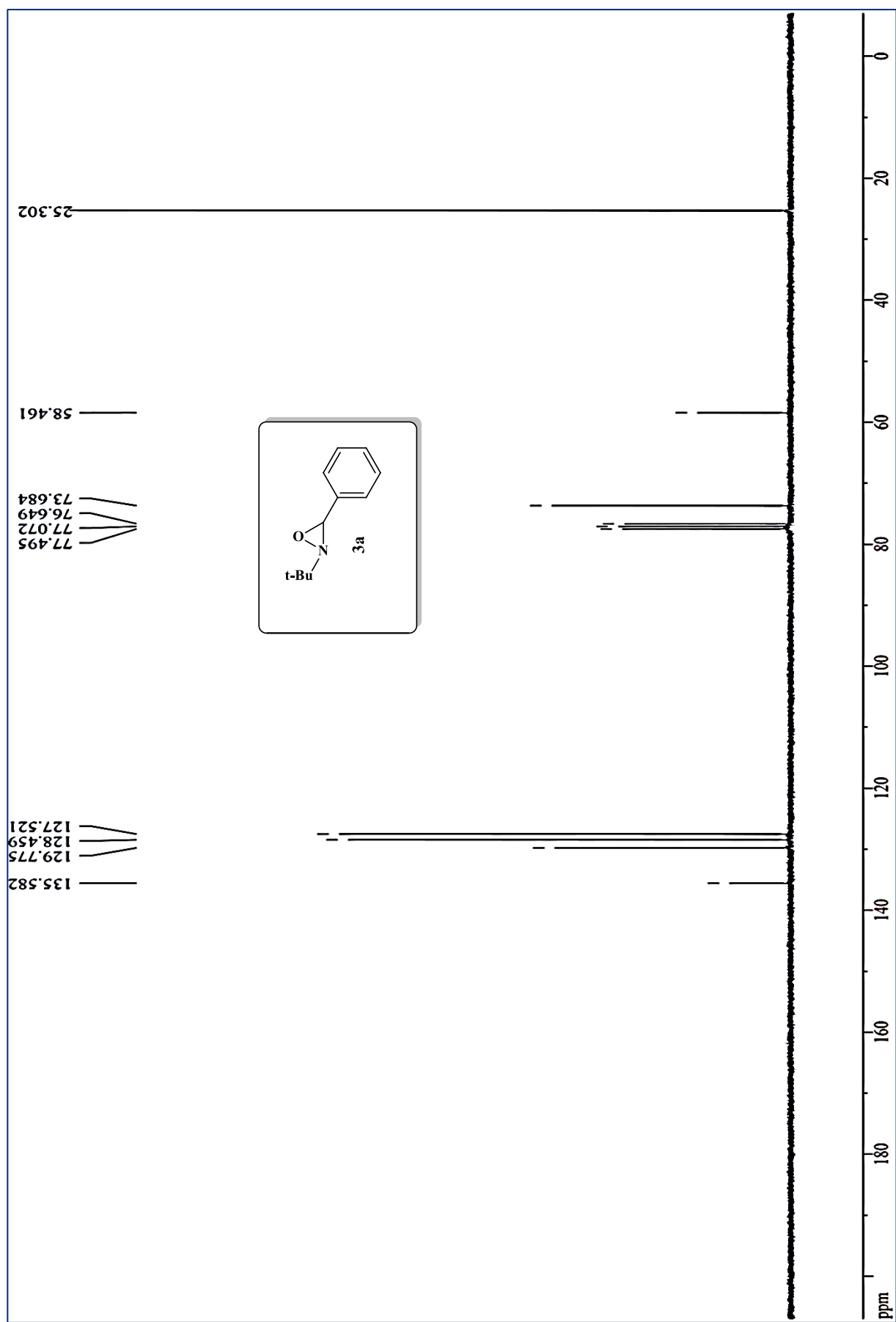


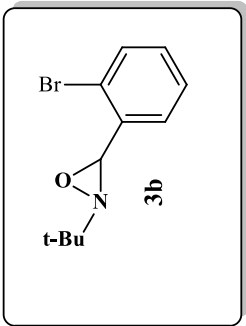
Oxaziridine	$\delta_{\text{H-3}}$ (ppm)		$\delta_{\text{C-3}}$ (ppm)		<i>Trans/Cis</i>
	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	
 3a	4.72	-	73.68	-	100:0
 3b	5.15	-	73.45	-	100:0
 3c	4.68	-	73.59	-	100:0
 3d	4.76	-	71.82	-	100:0
 3e	4.65	-	72.15	-	100:0
 3f	4.78	-	67.93	-	100:0
 3g	4.56	5.31	79.84	79.70	91:9
 3h	4.61	5.33	77.70	78.20	92:8
 3i	4.51	5.26	79.02	79.09	91:9
 3j	4.52	5.29	80.03	79.87	92:8
 3k	4.46	5.23	79.91	79.69	90:10
 3l	4.50	5.28	8.046	79.47	90:10

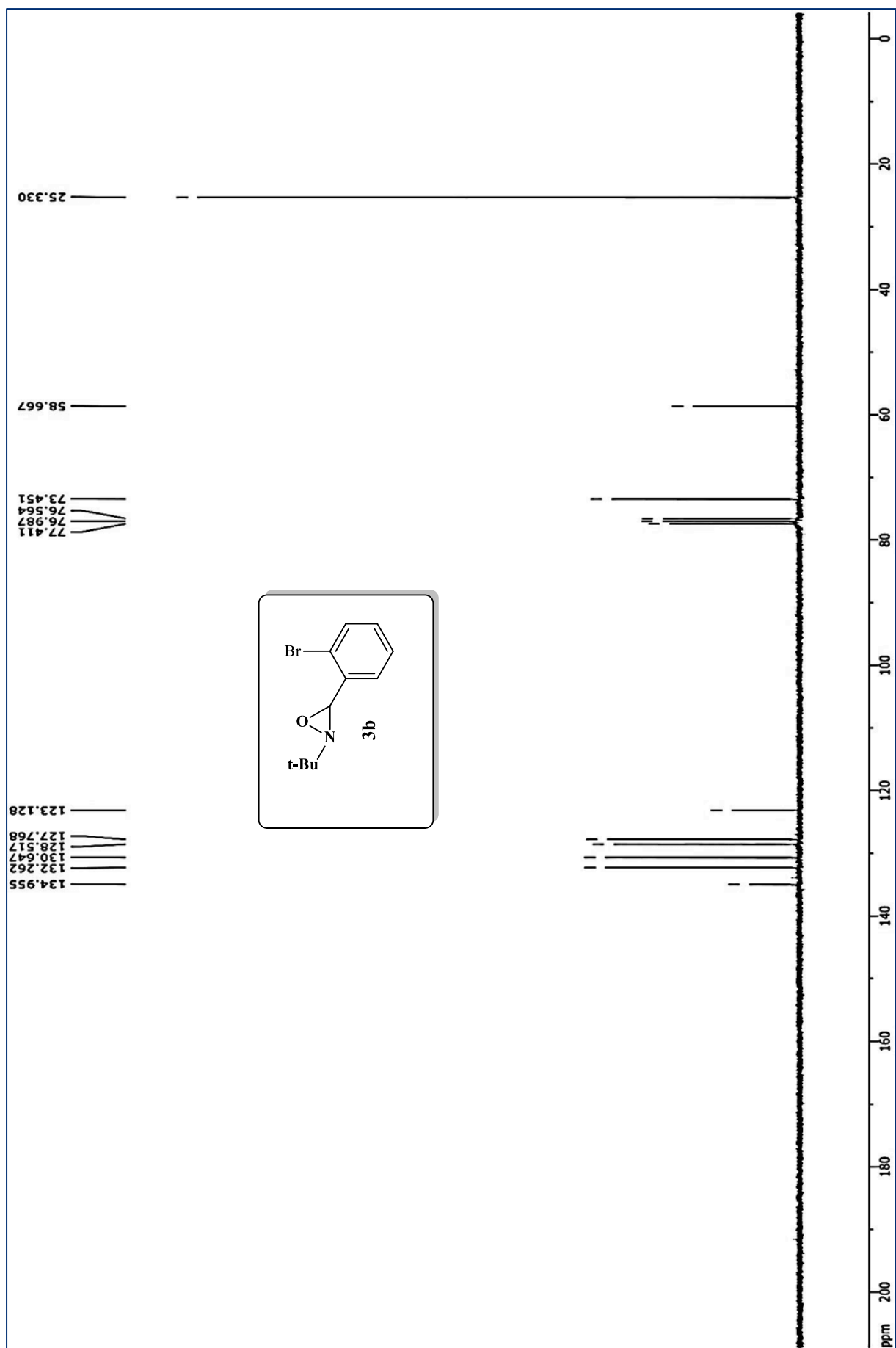


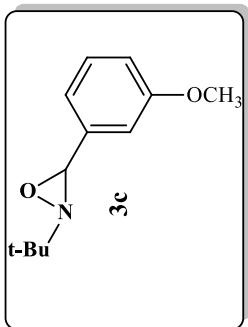


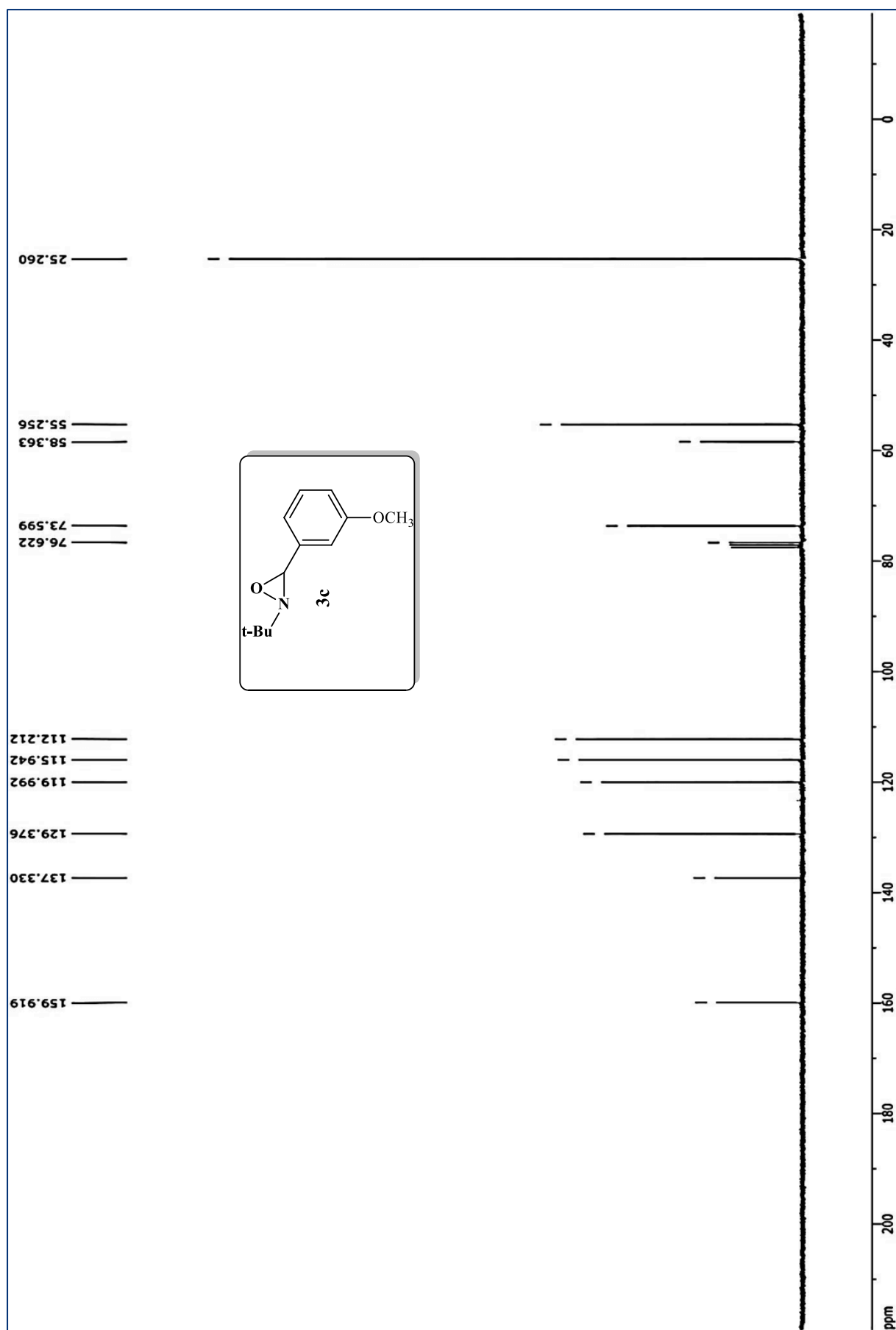


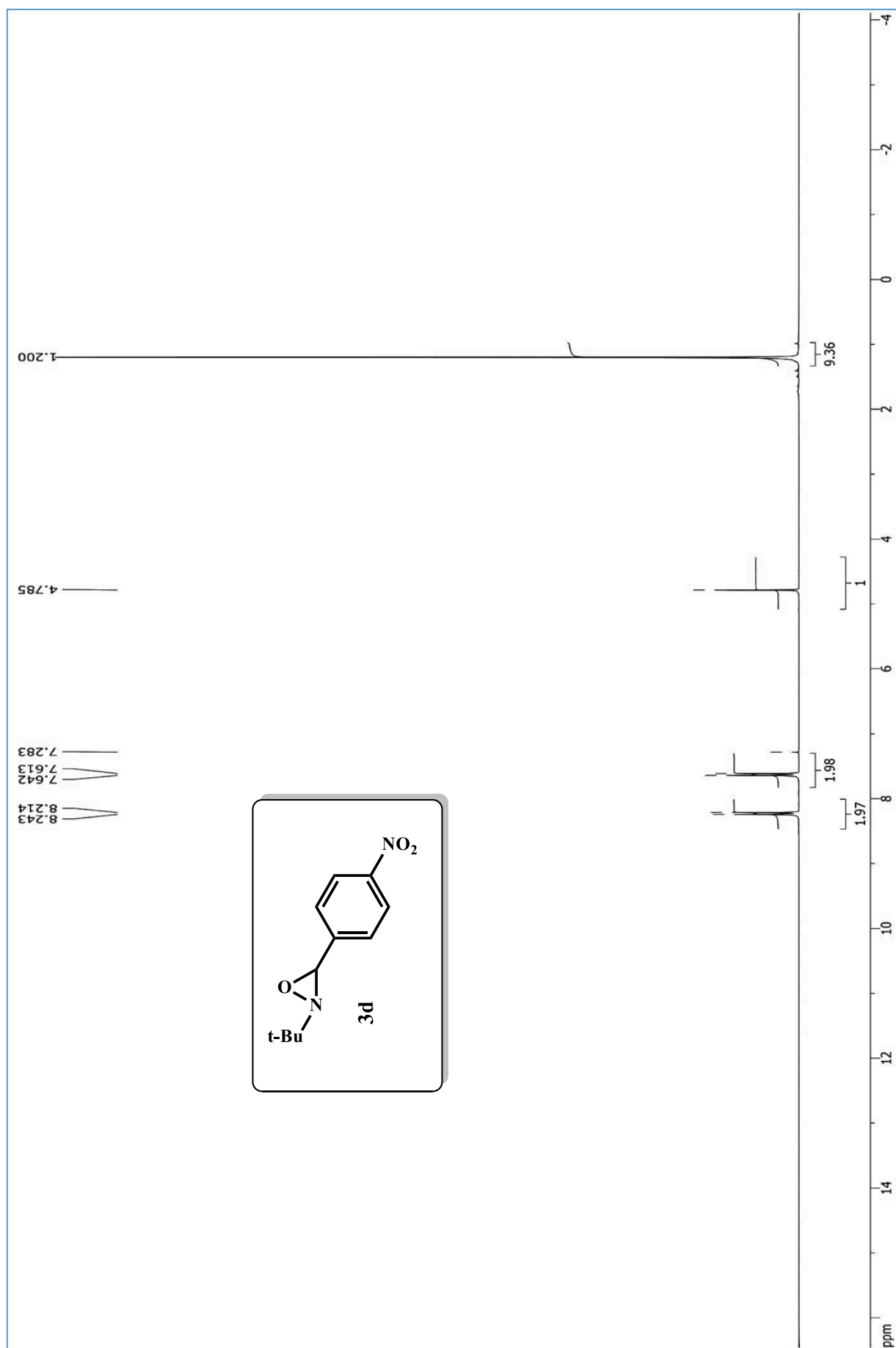


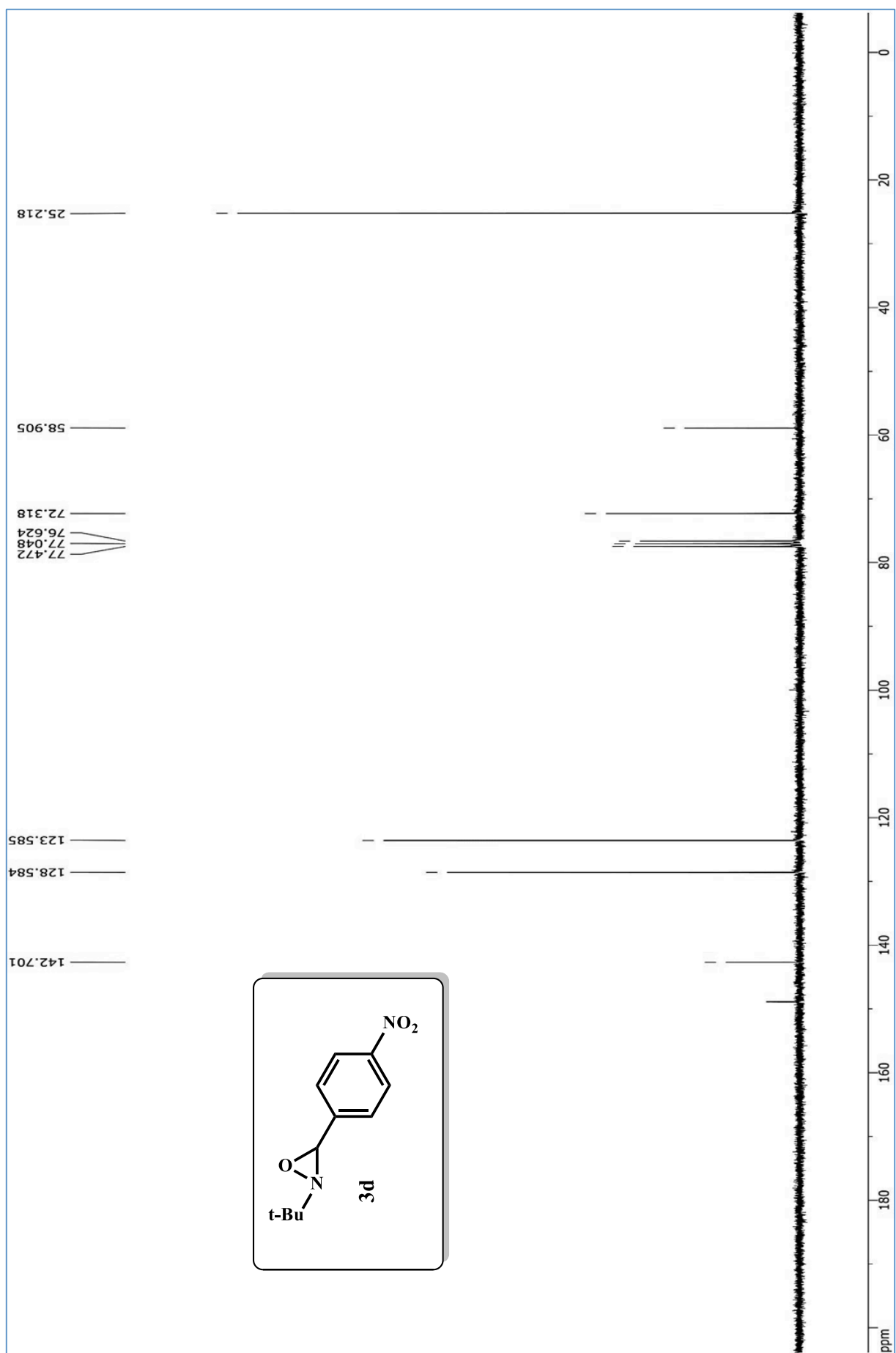


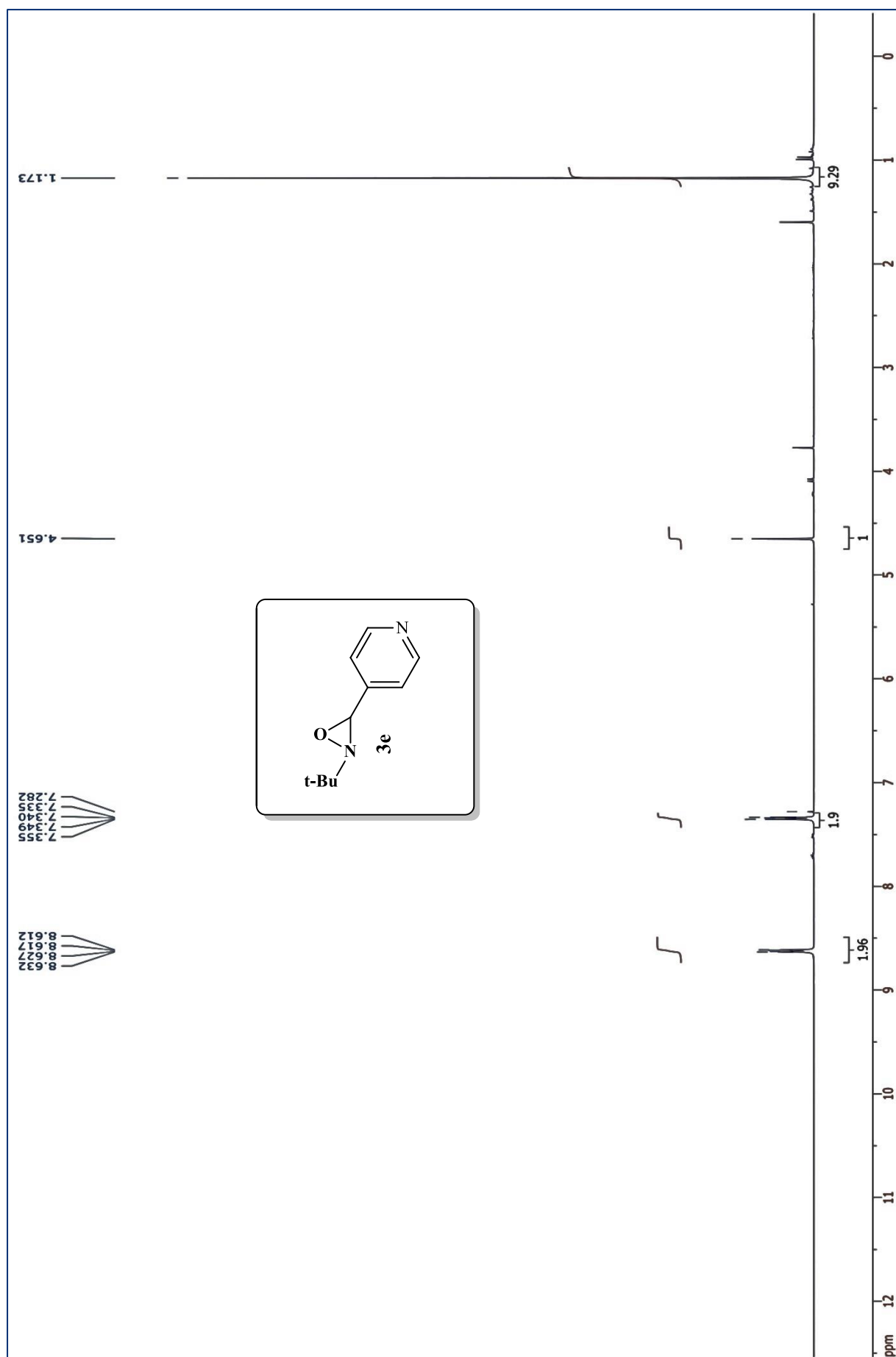


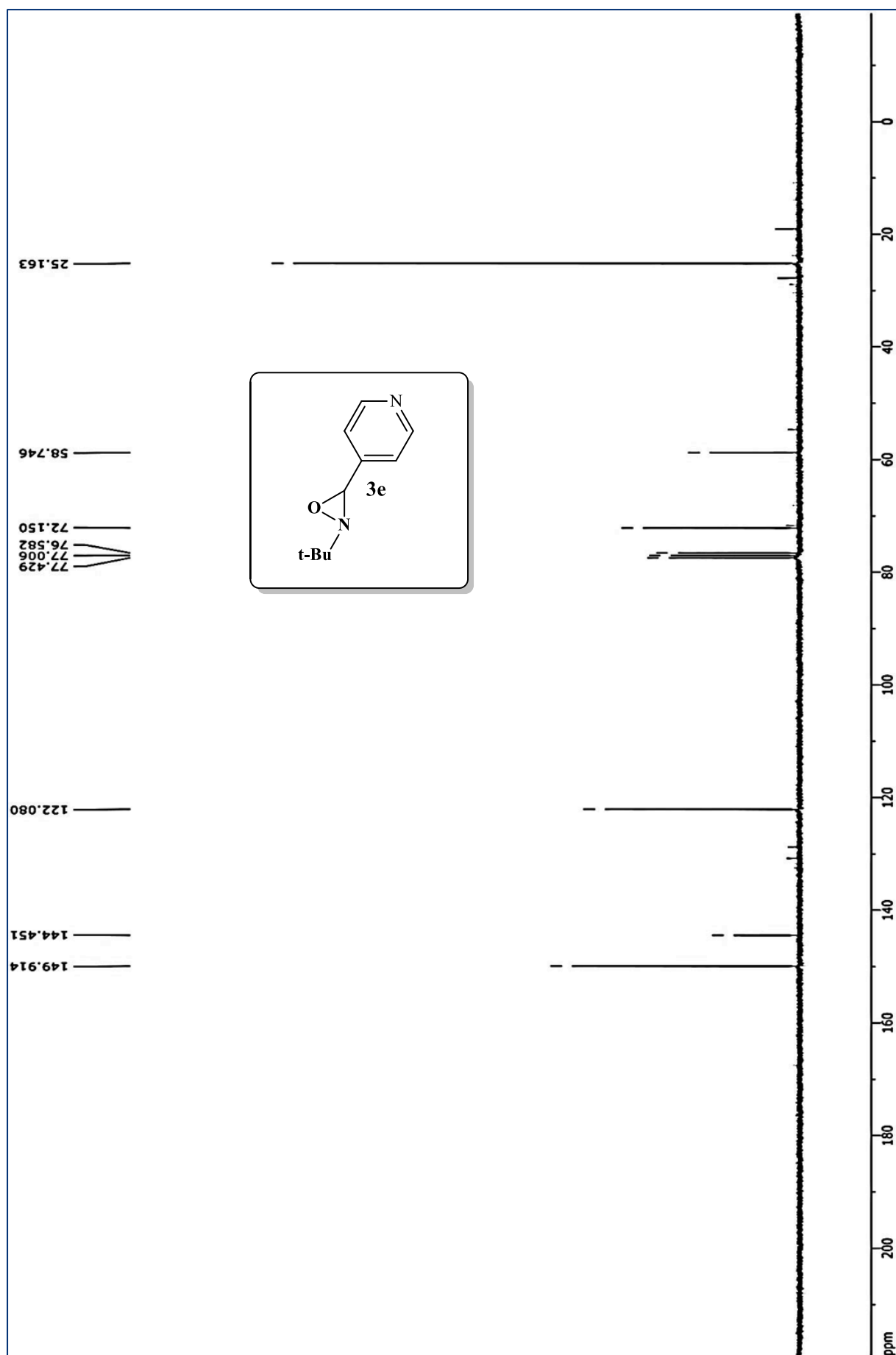


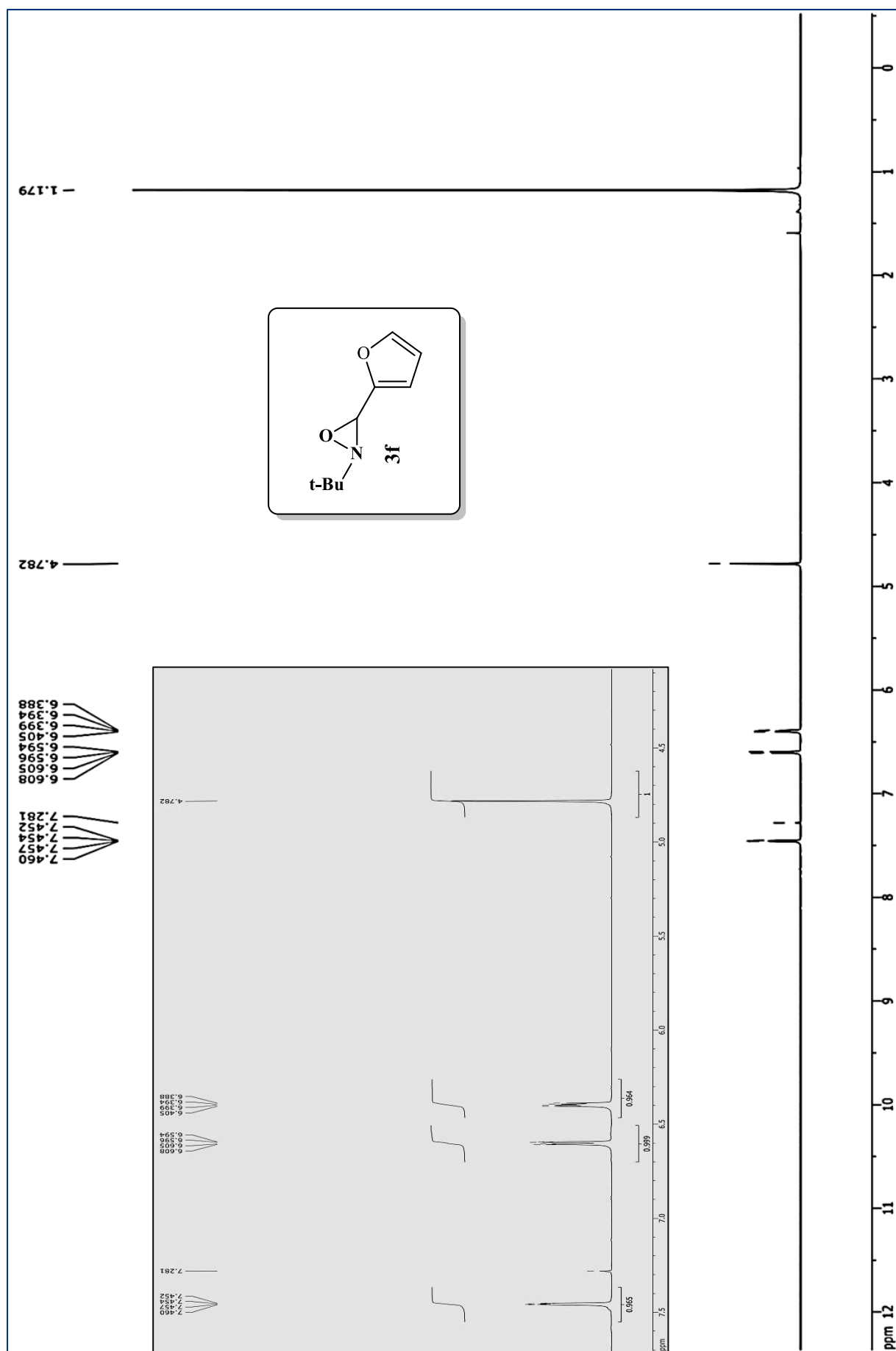


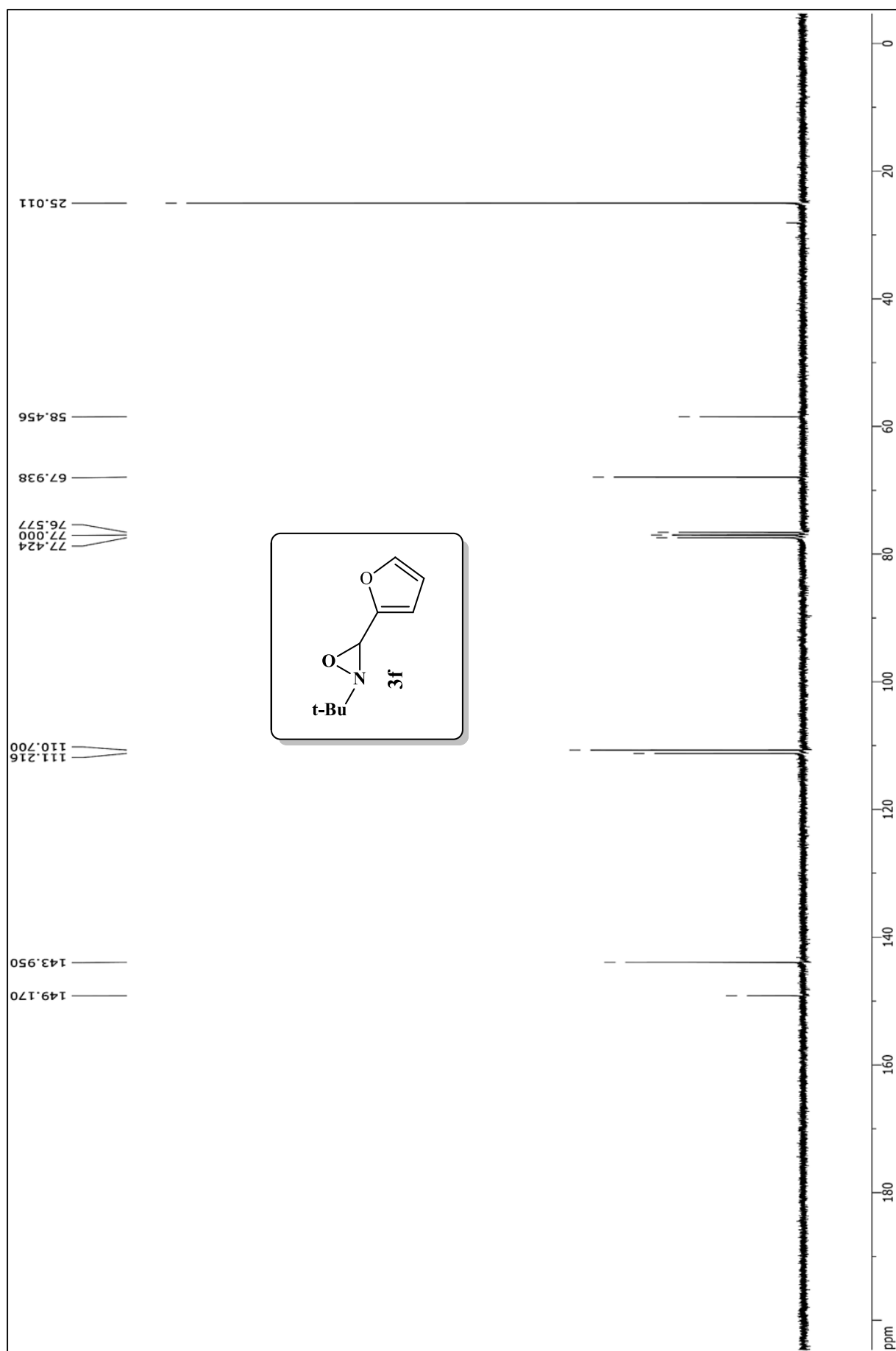


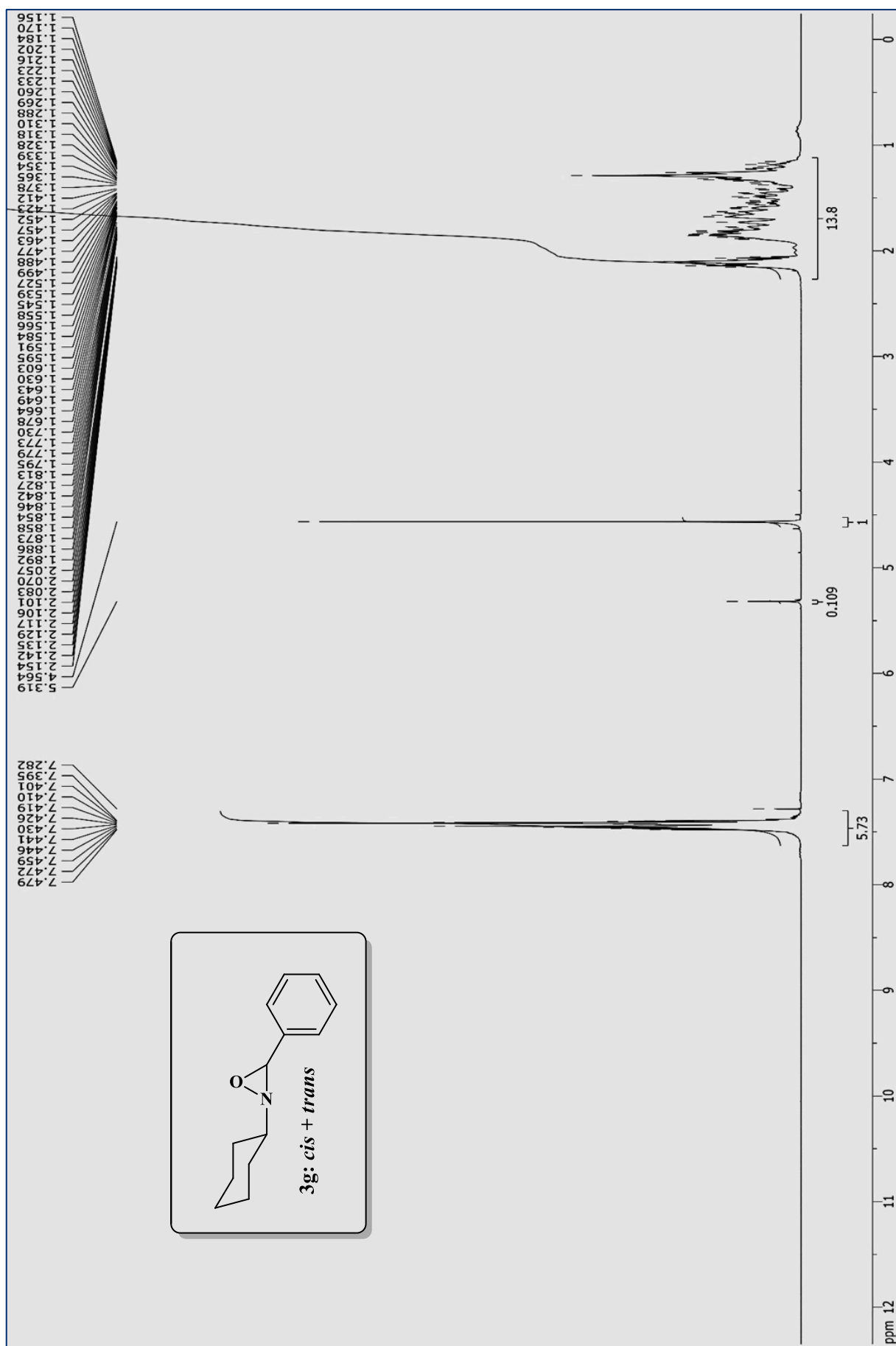


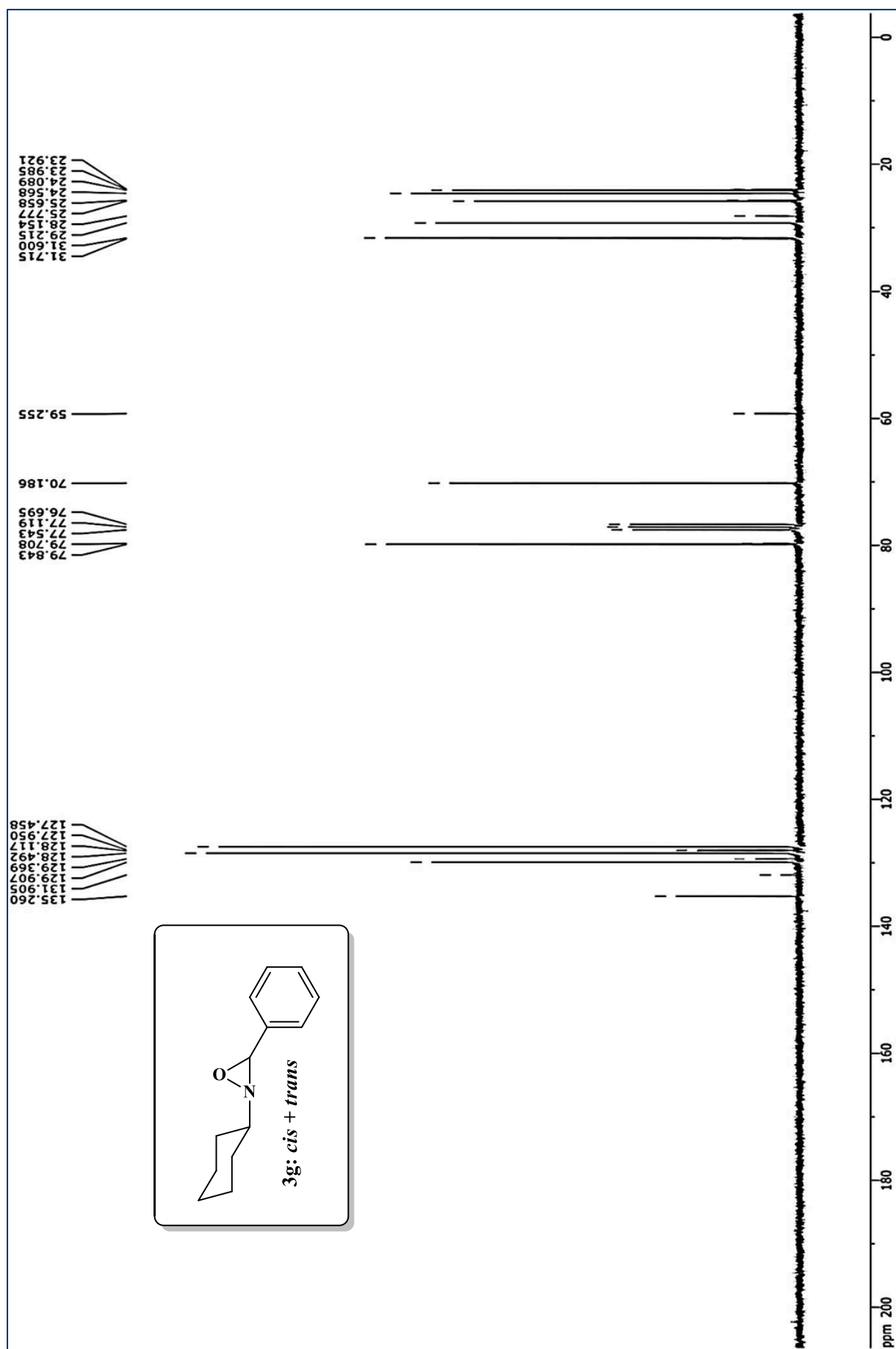


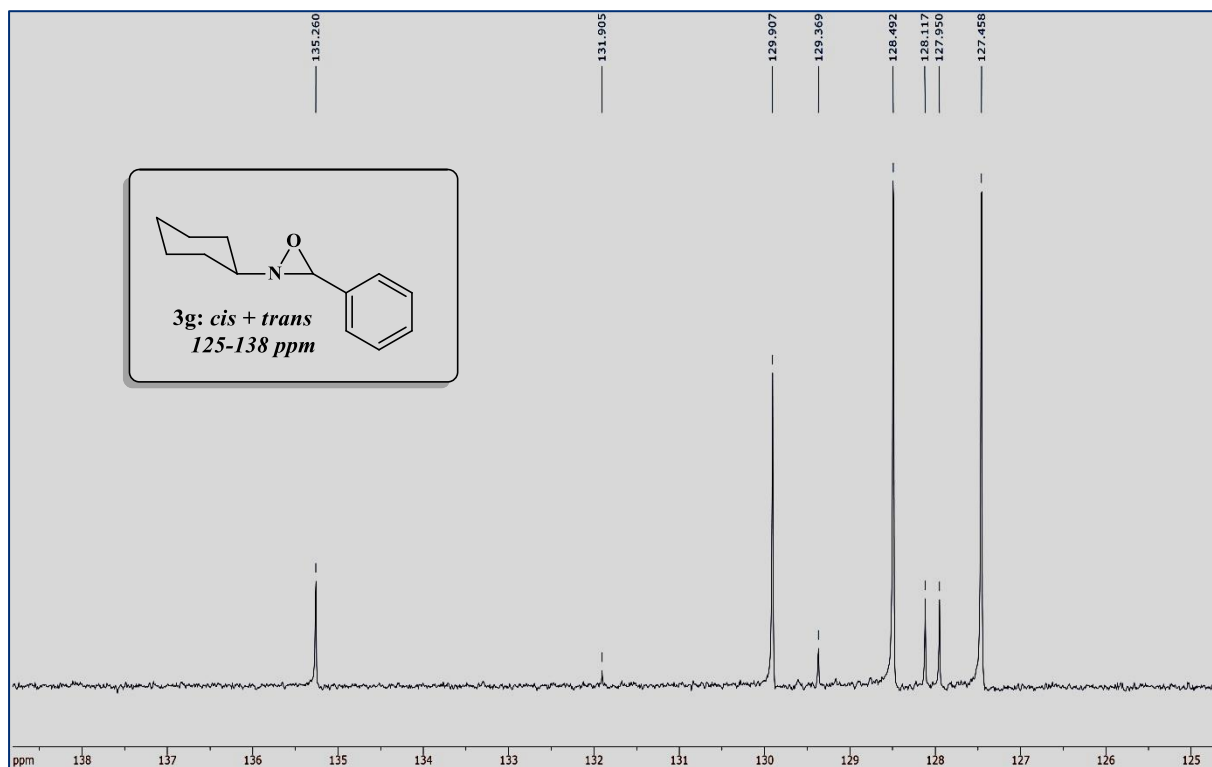
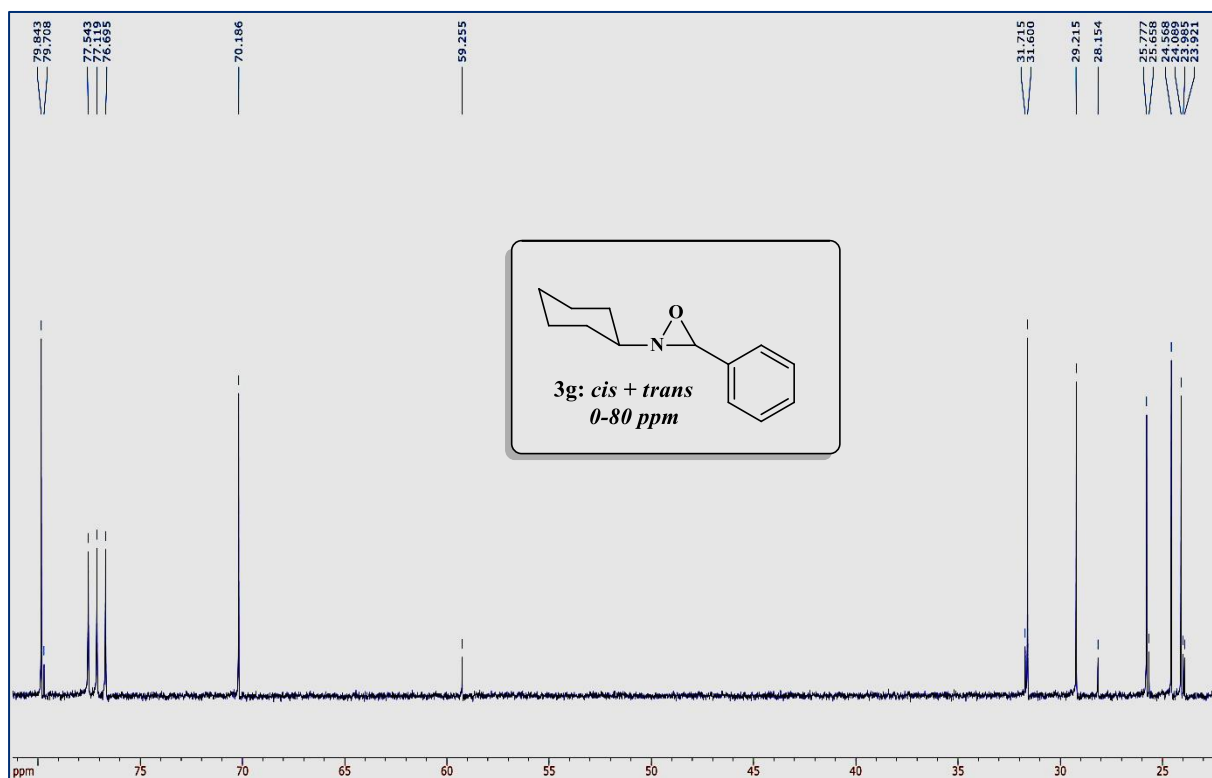


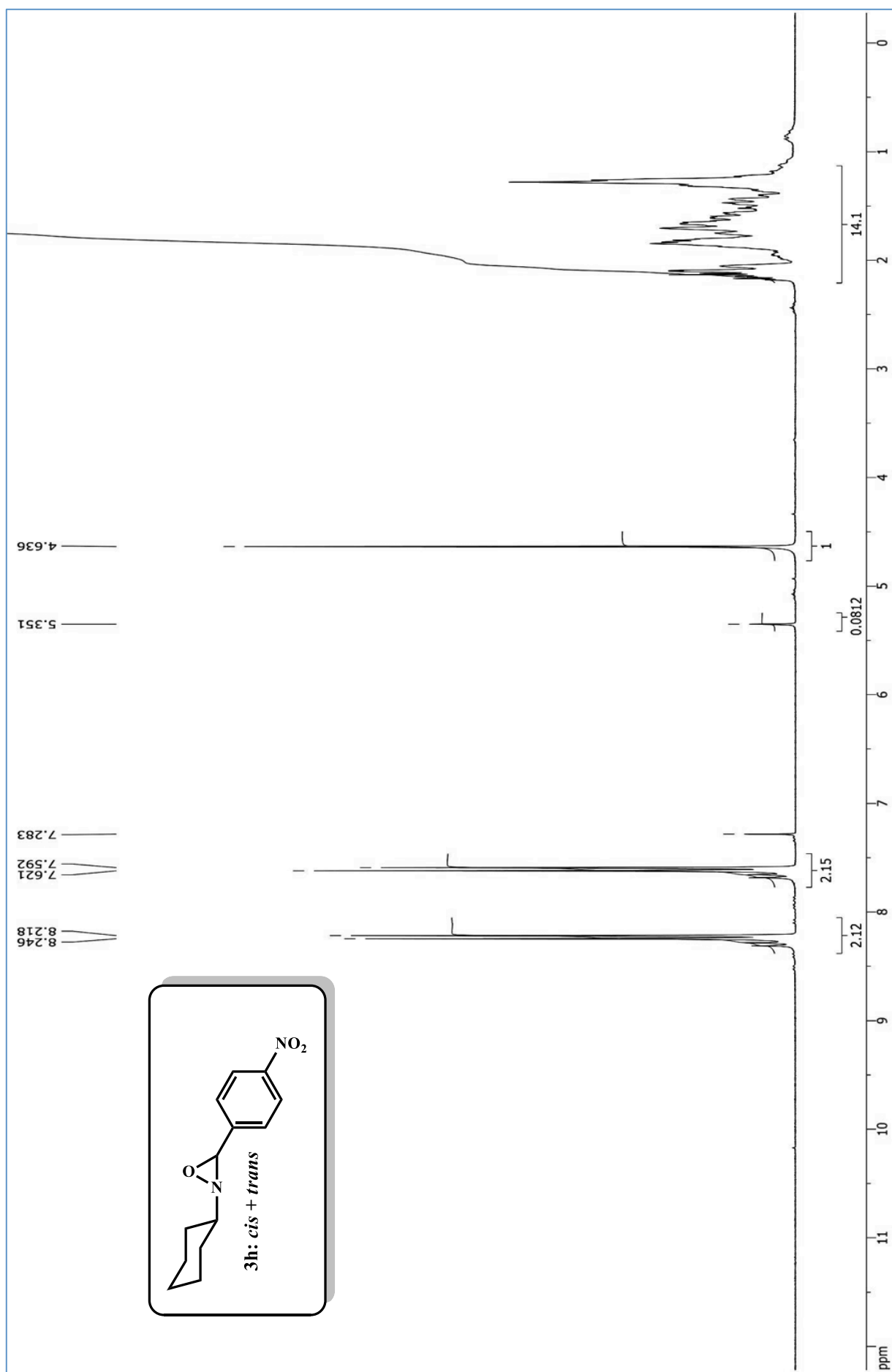


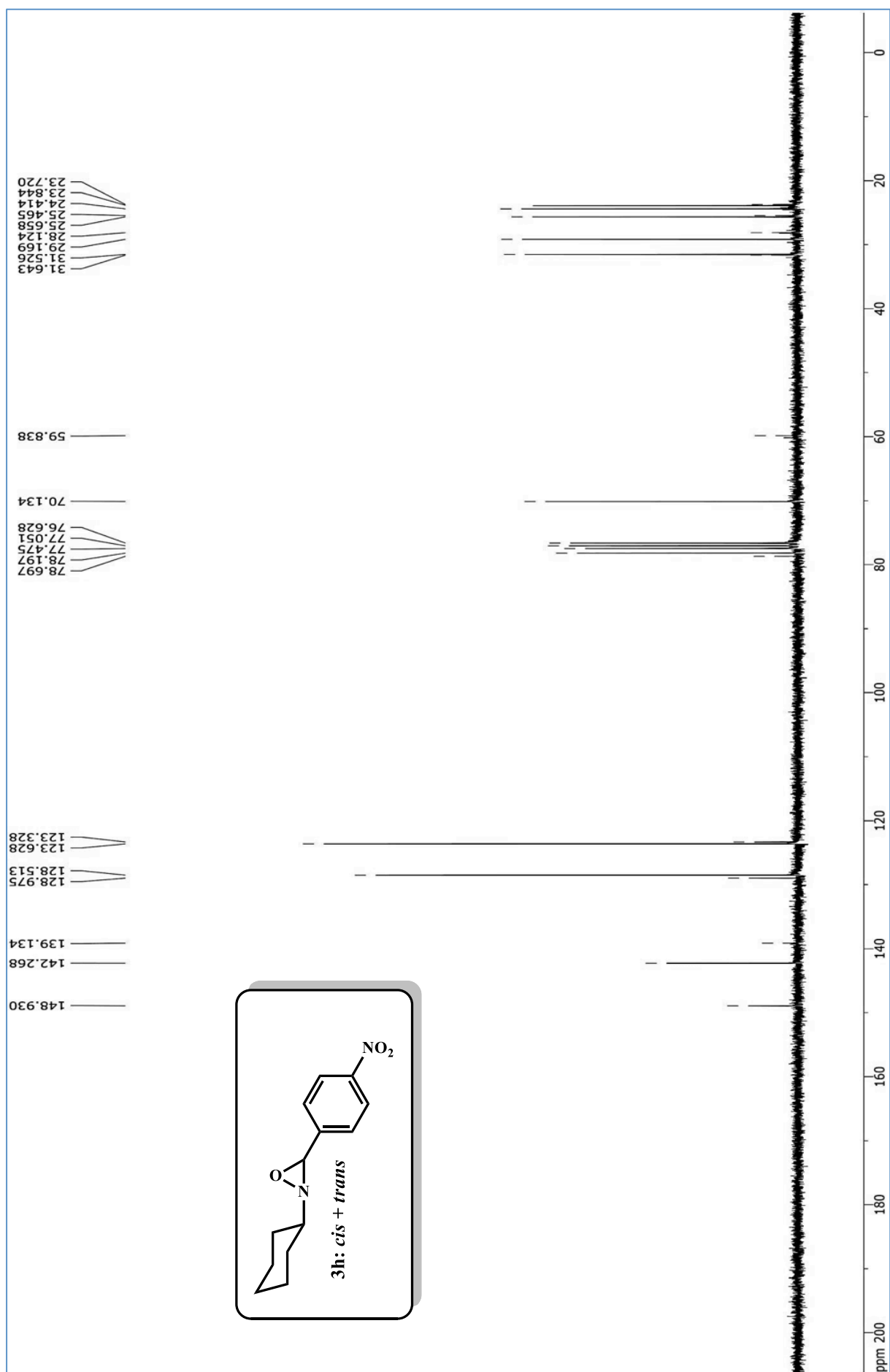


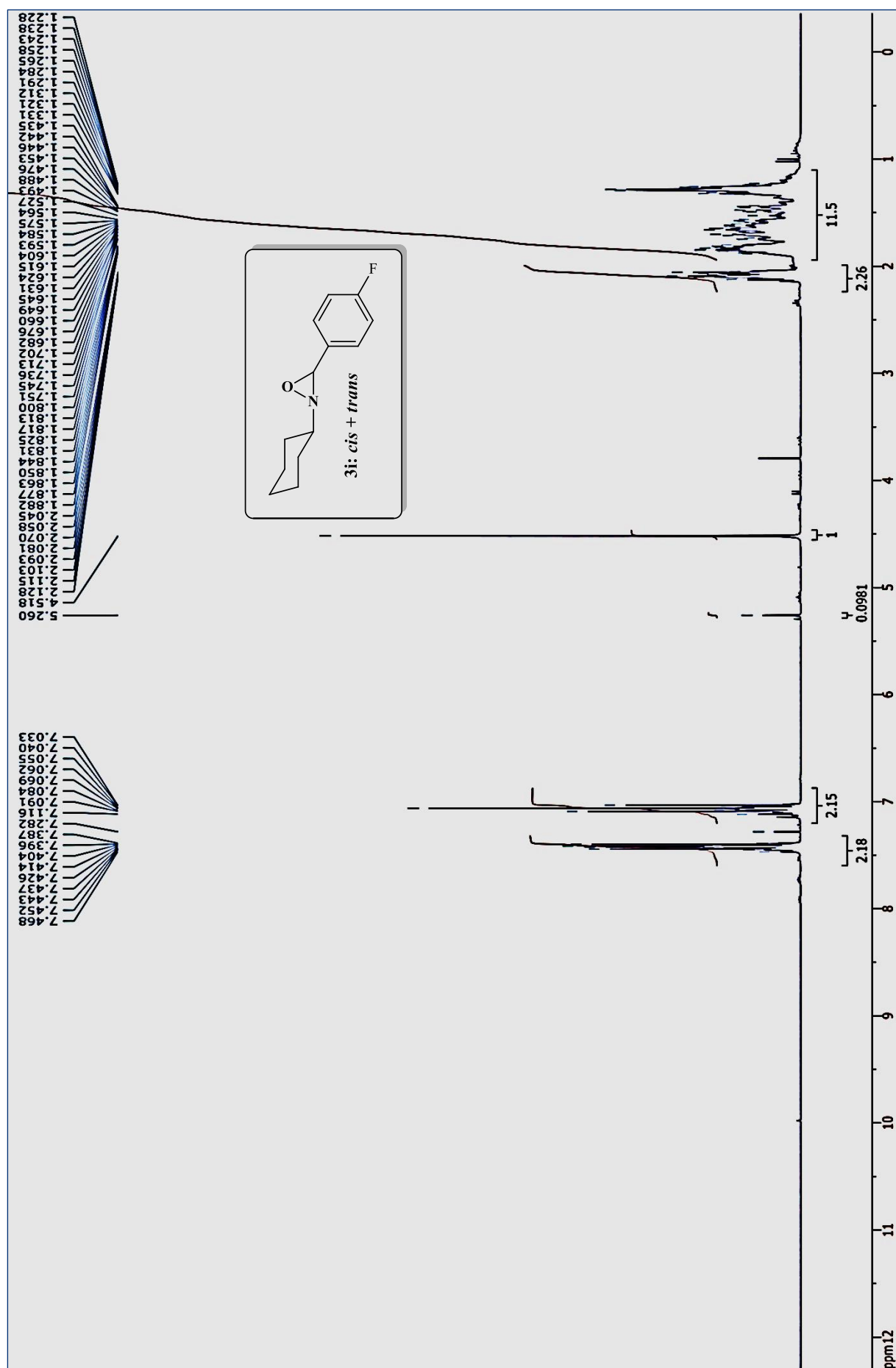


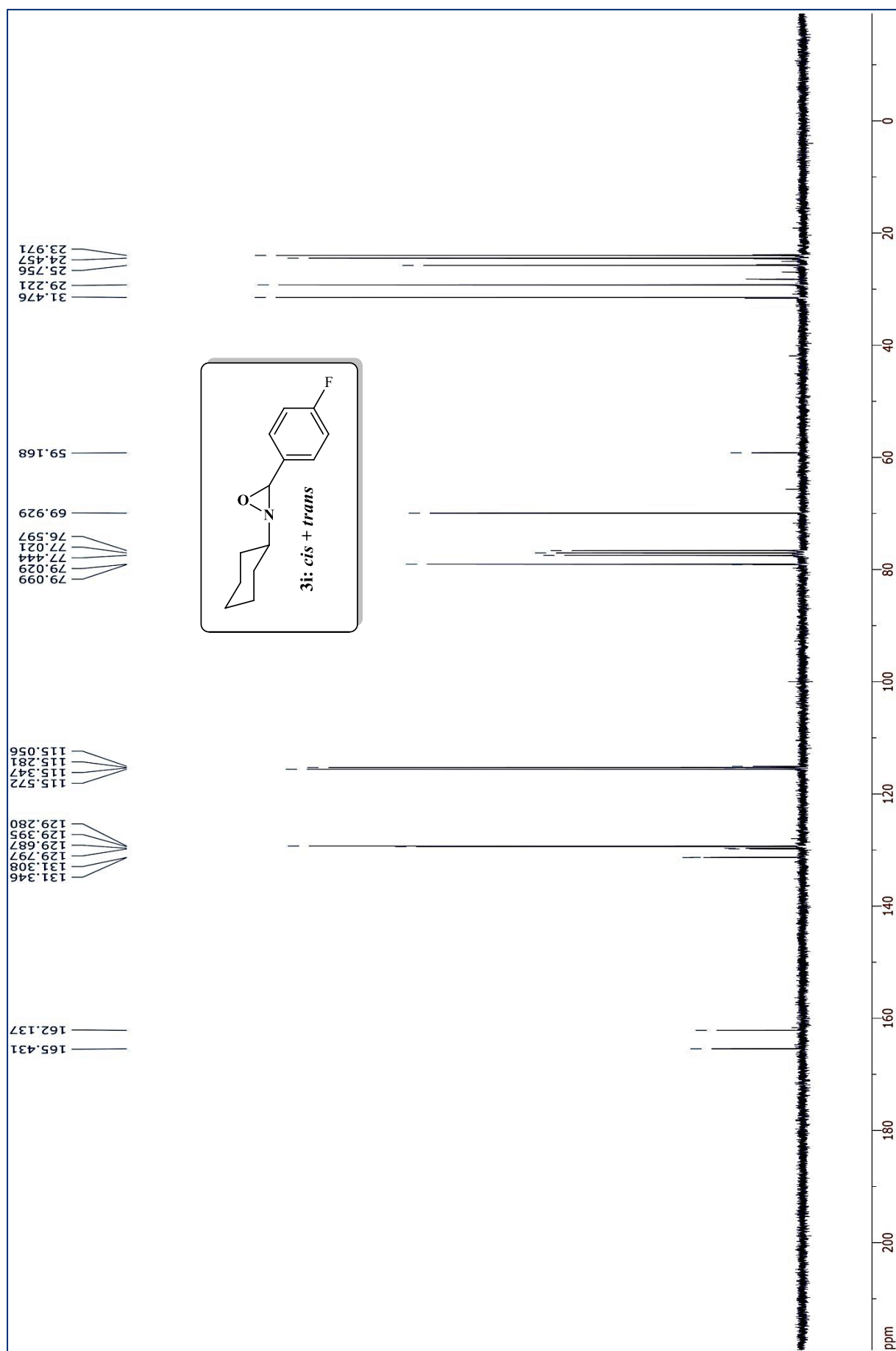


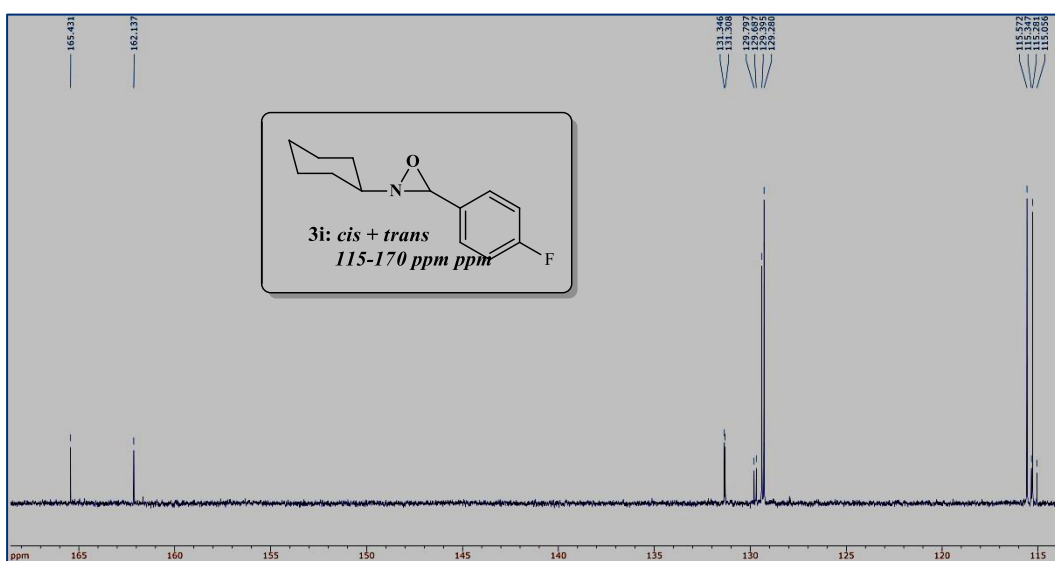
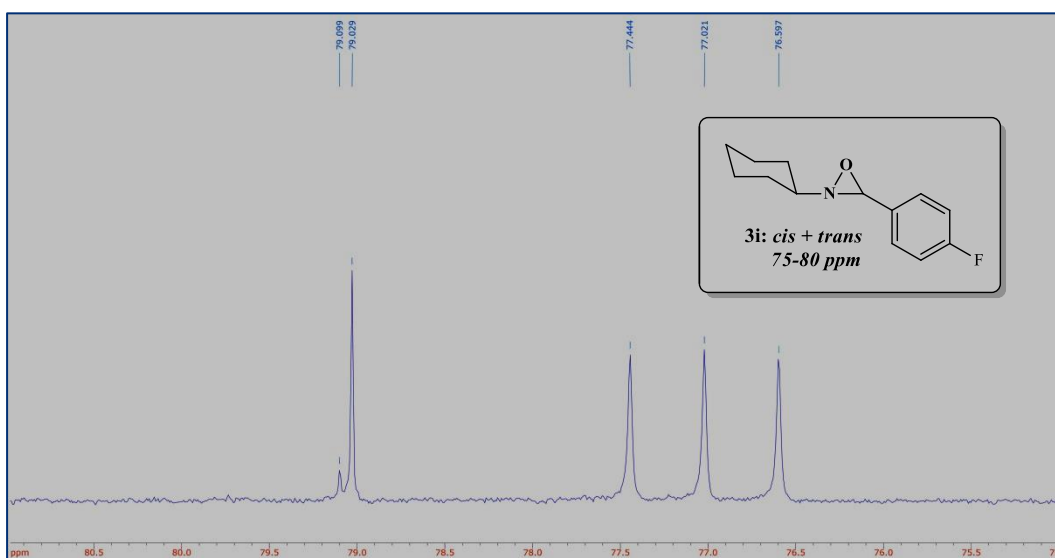
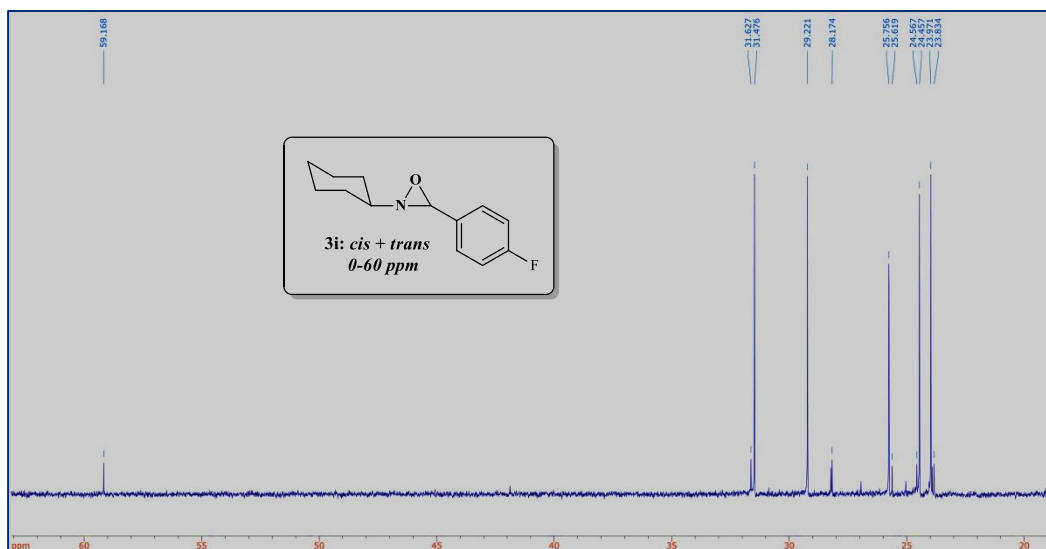


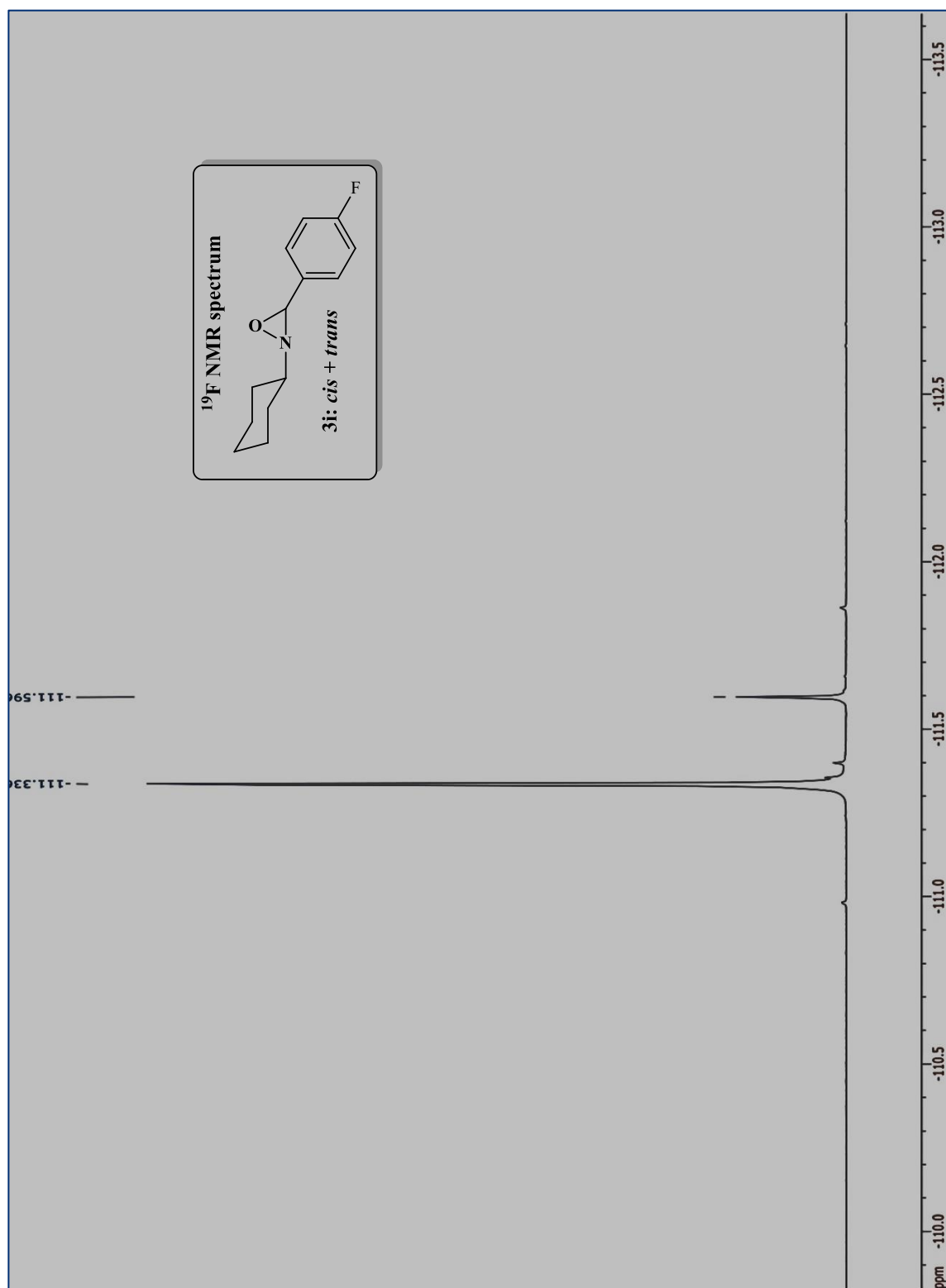


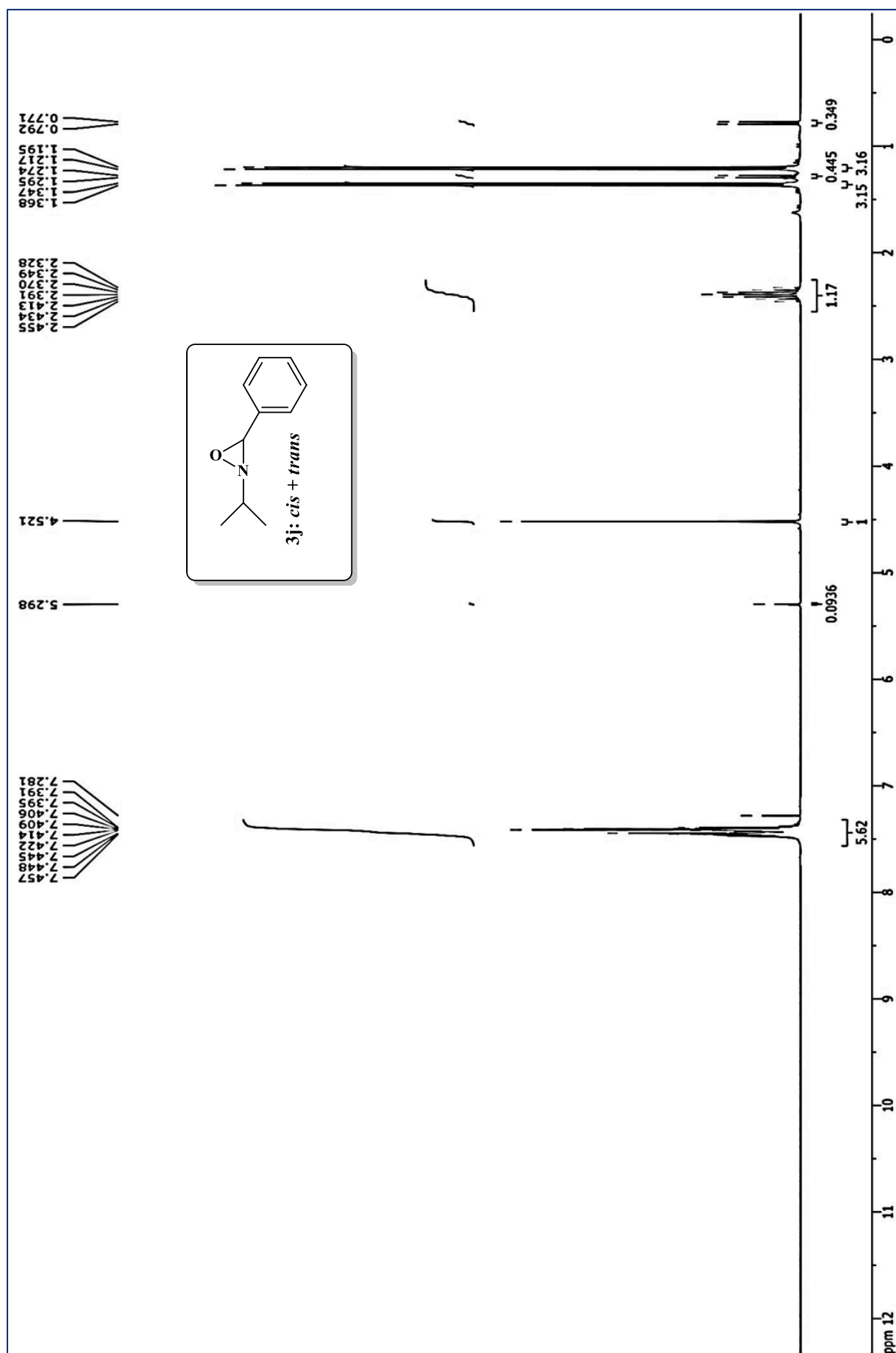


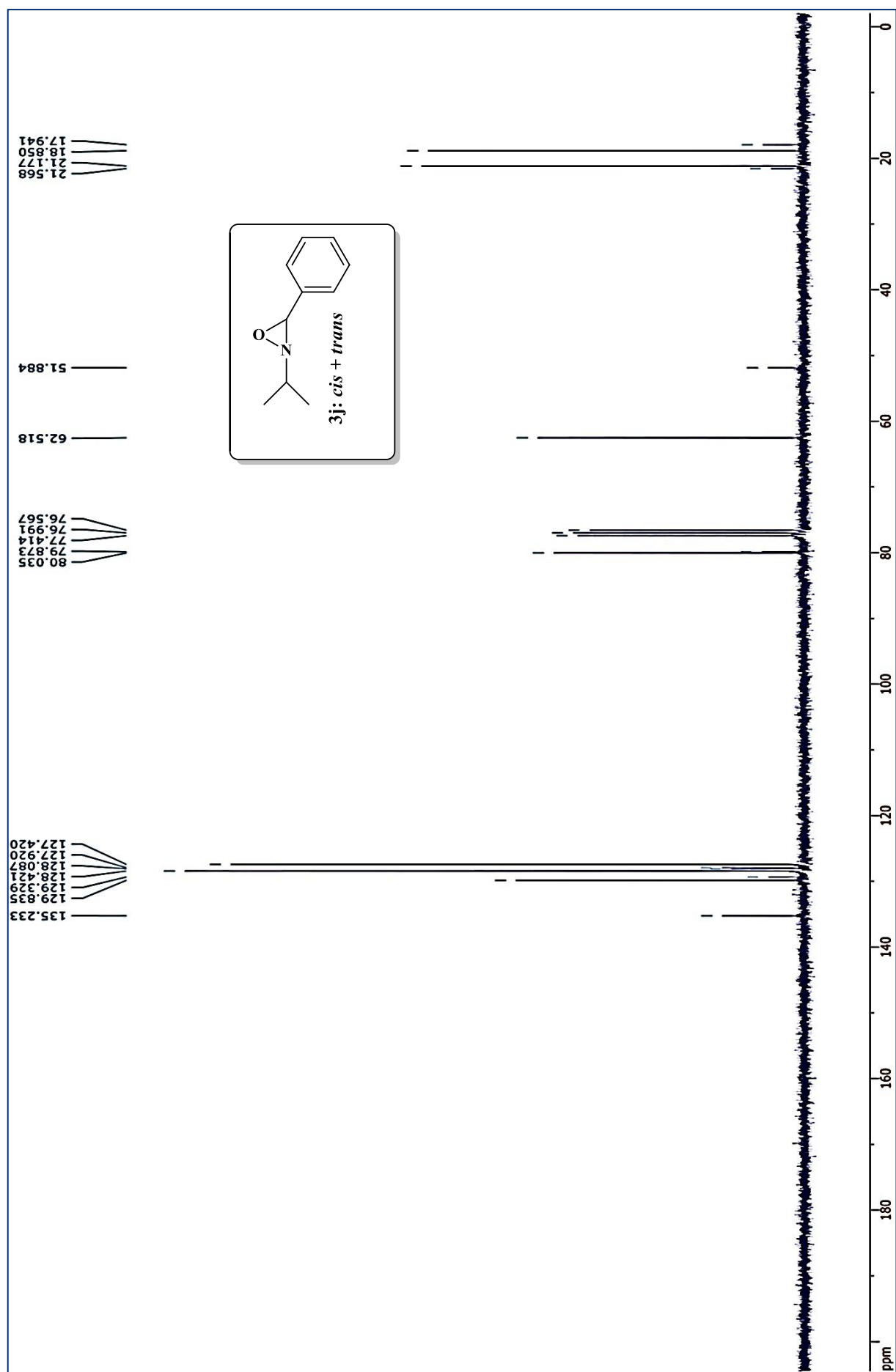


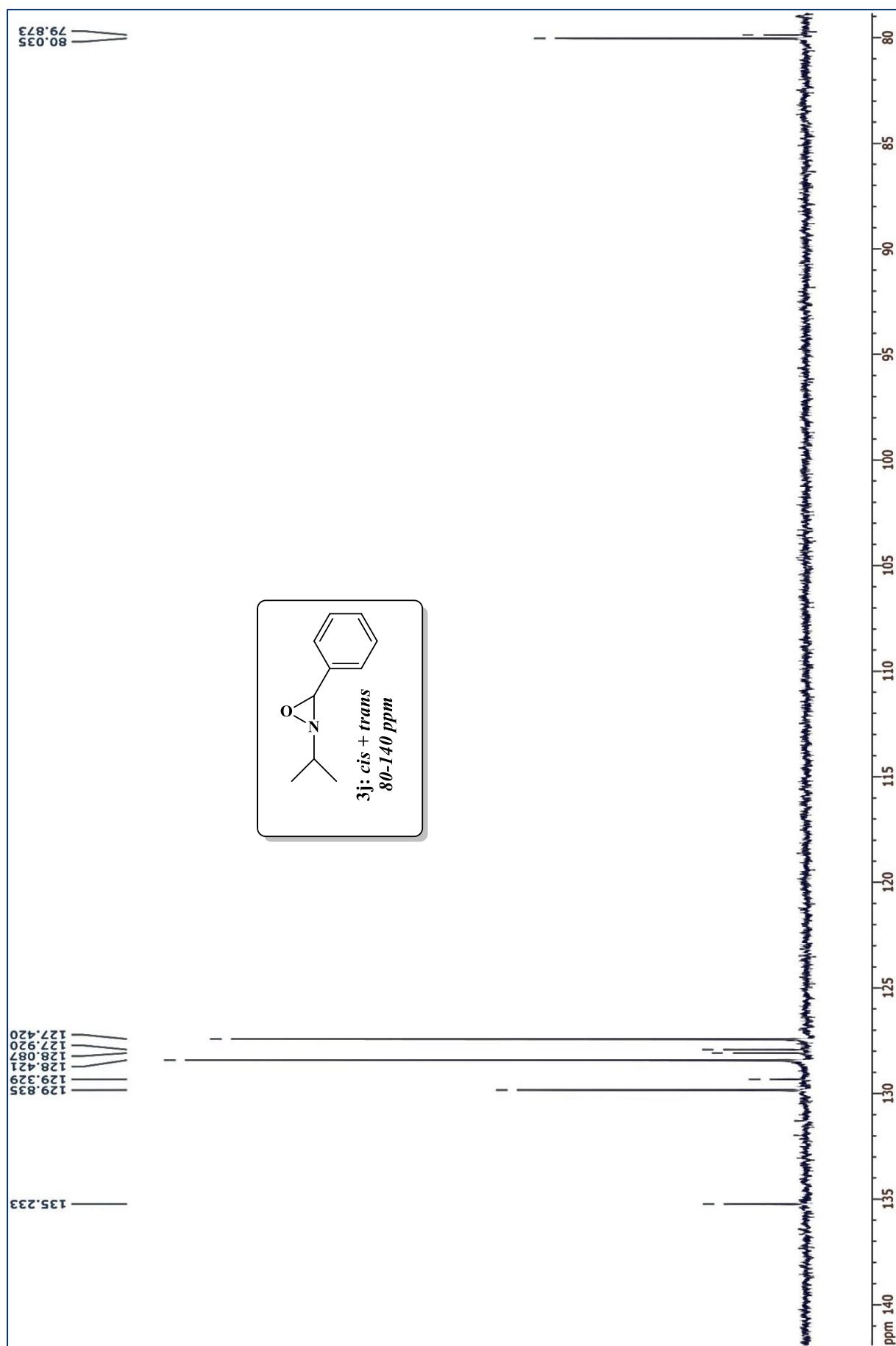


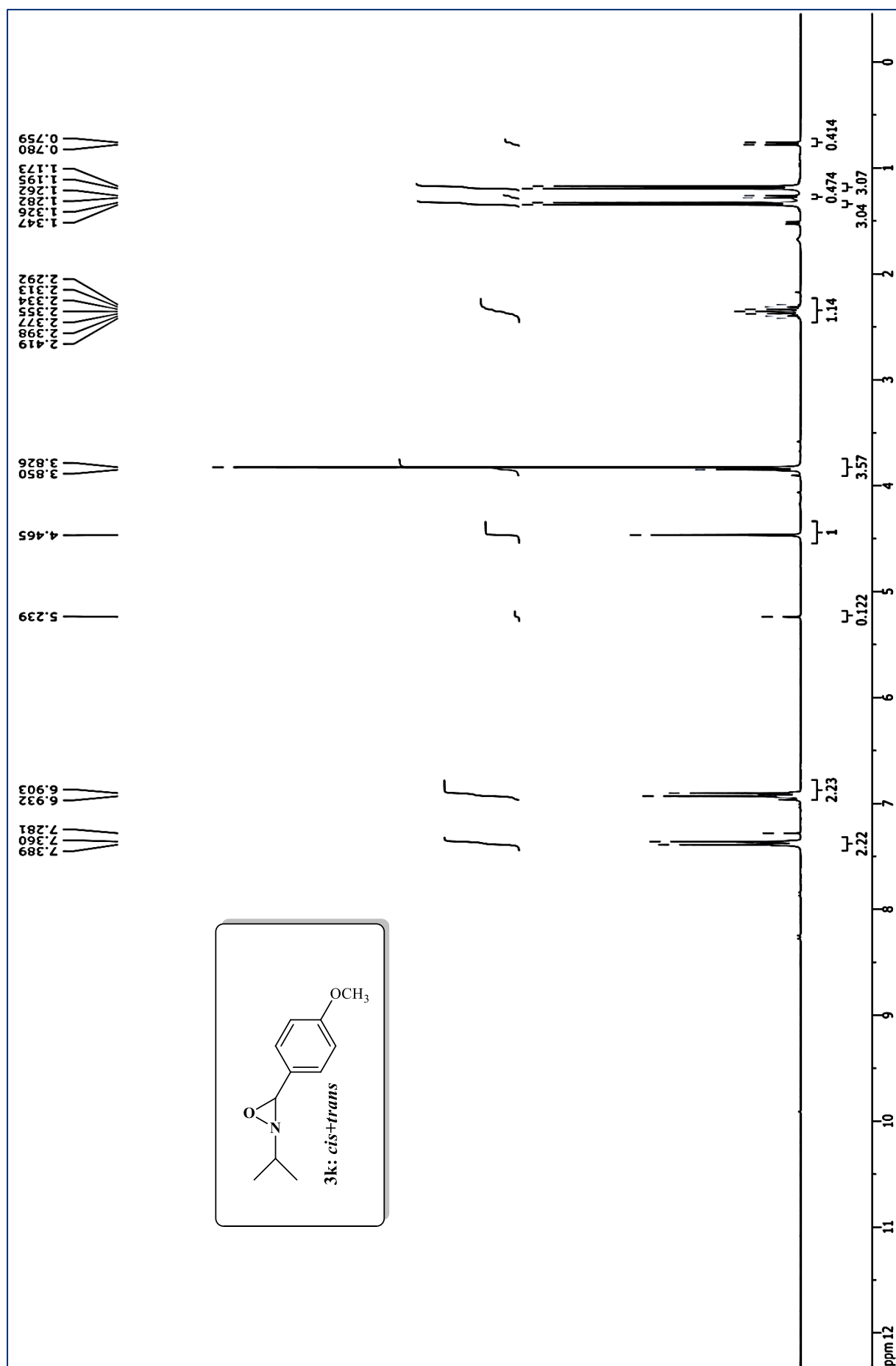


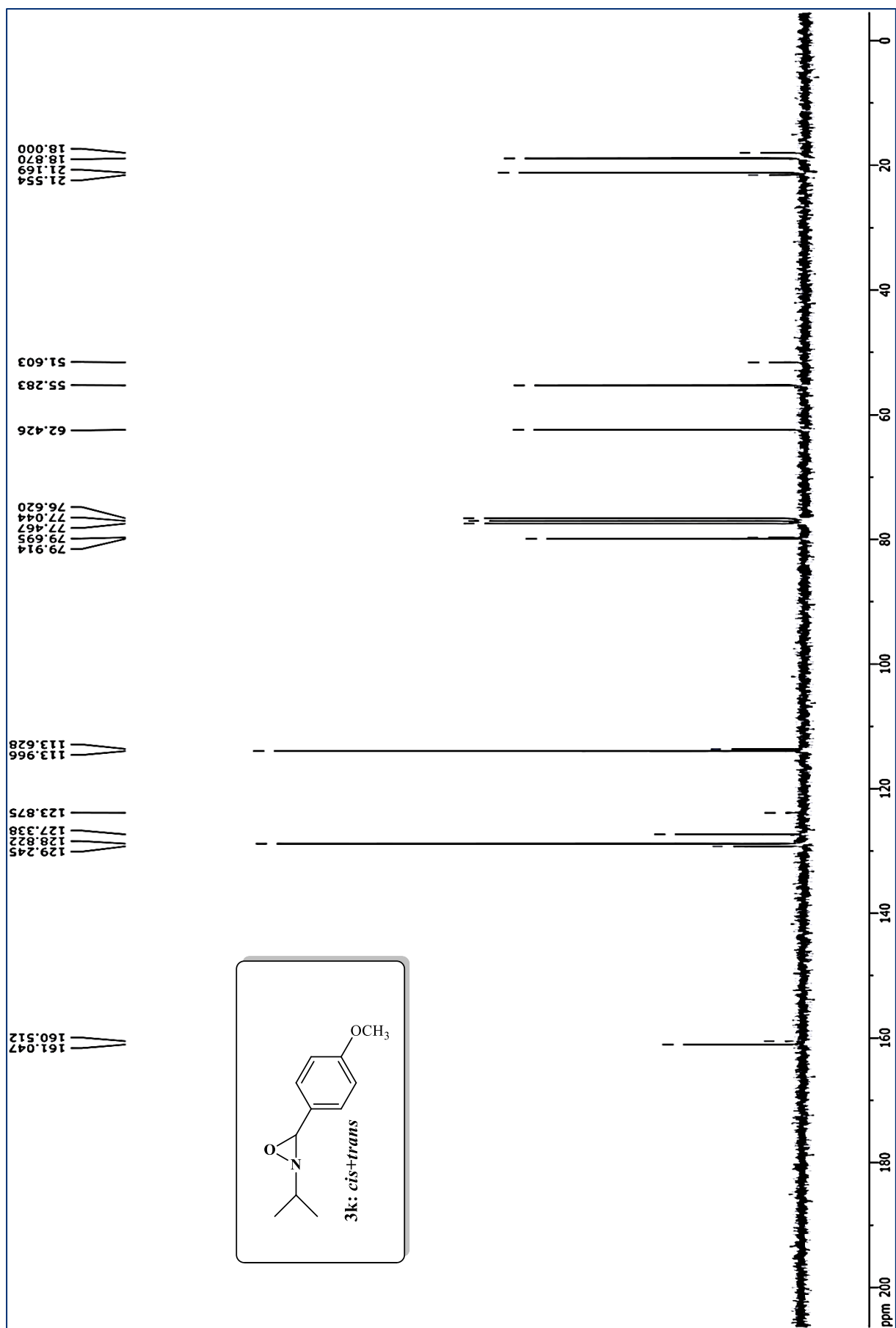


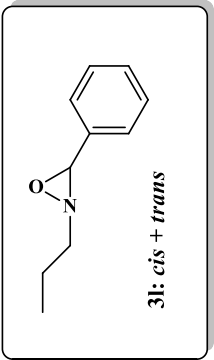


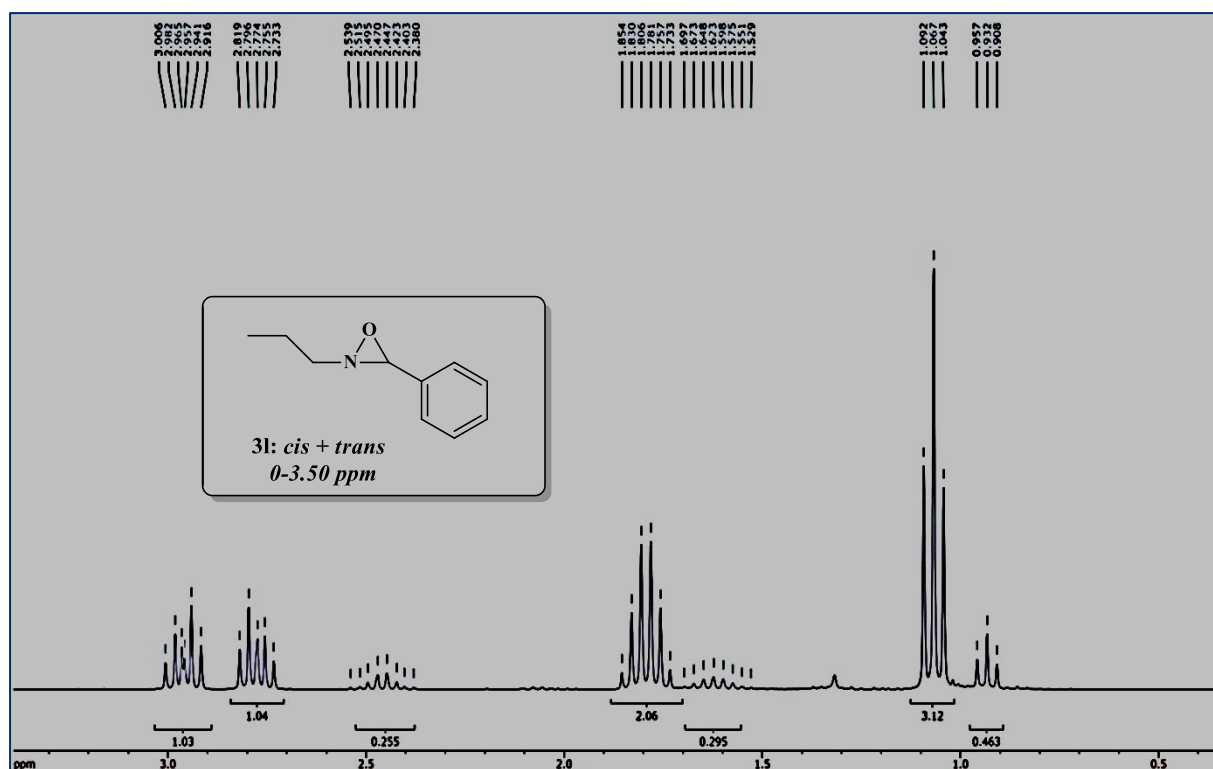


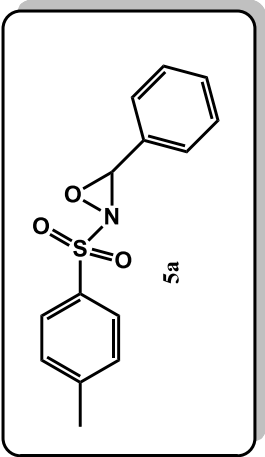


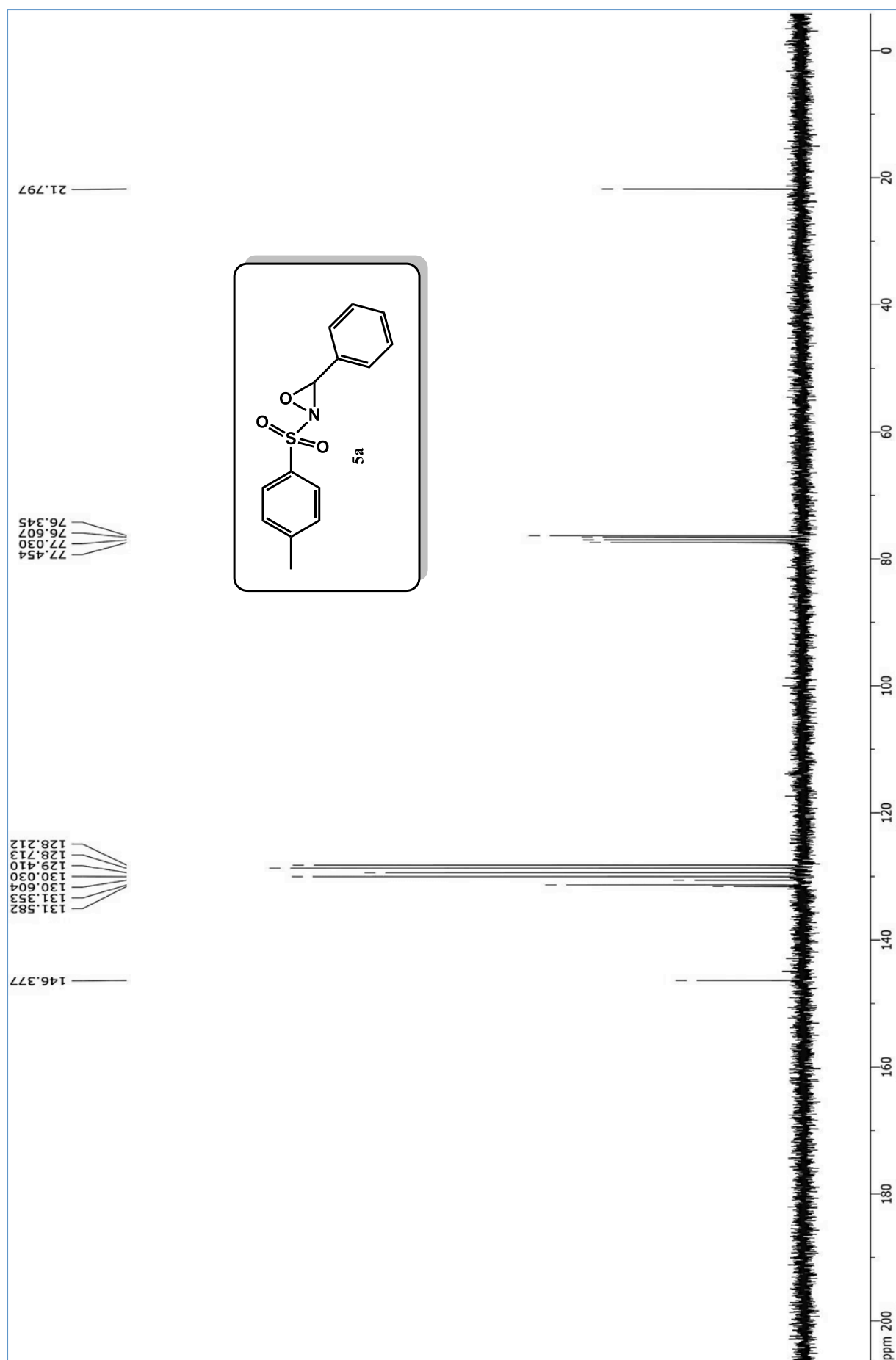


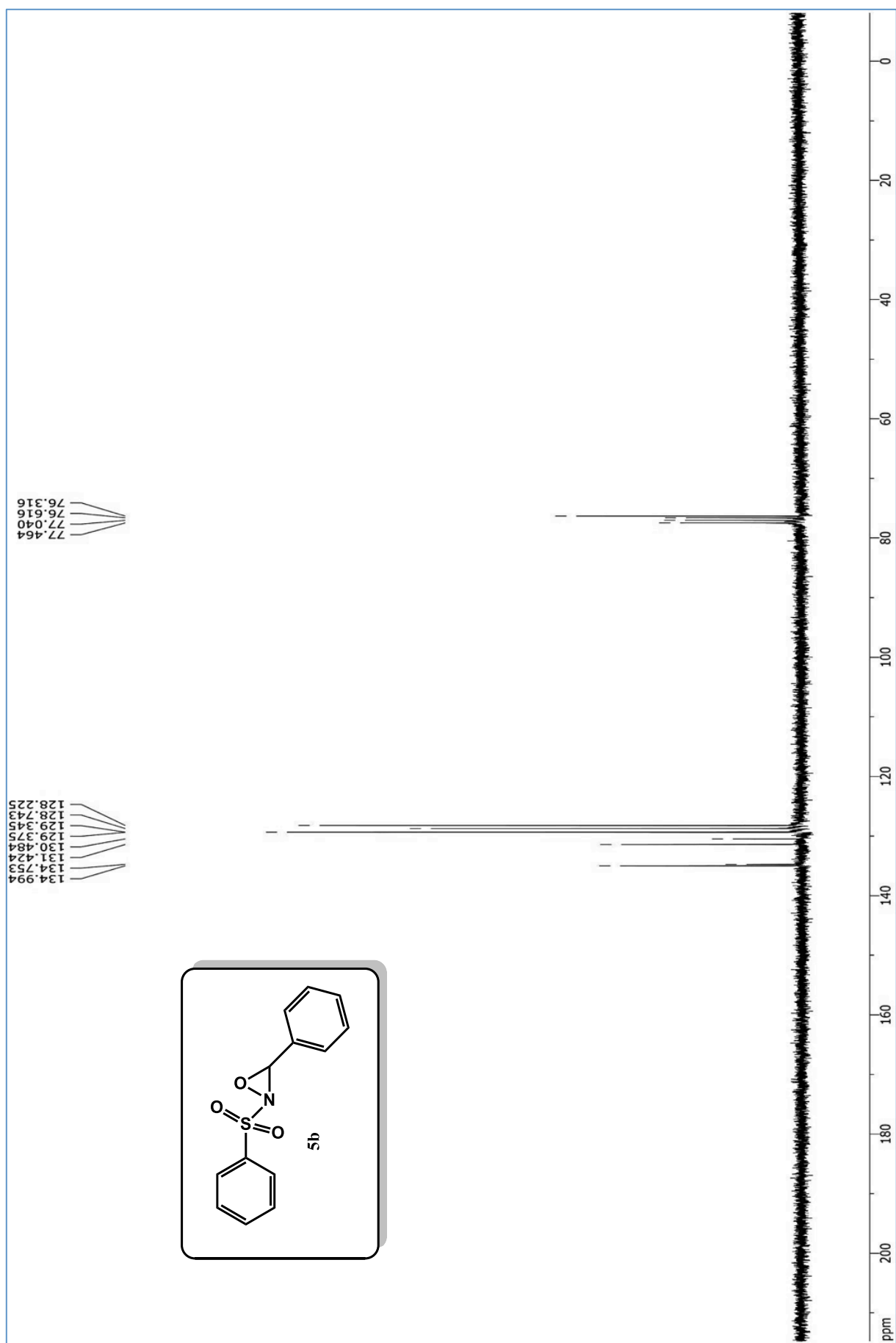


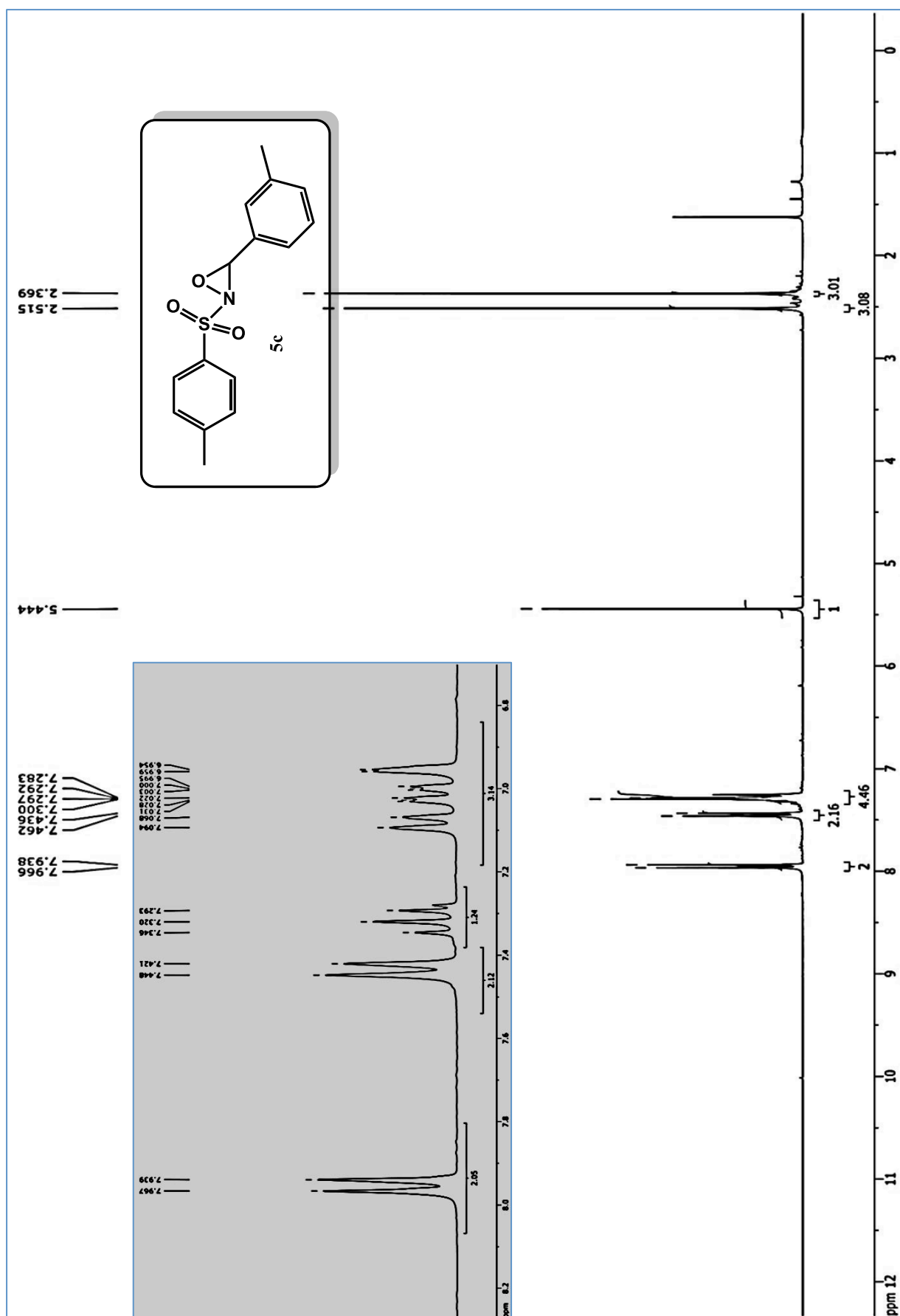


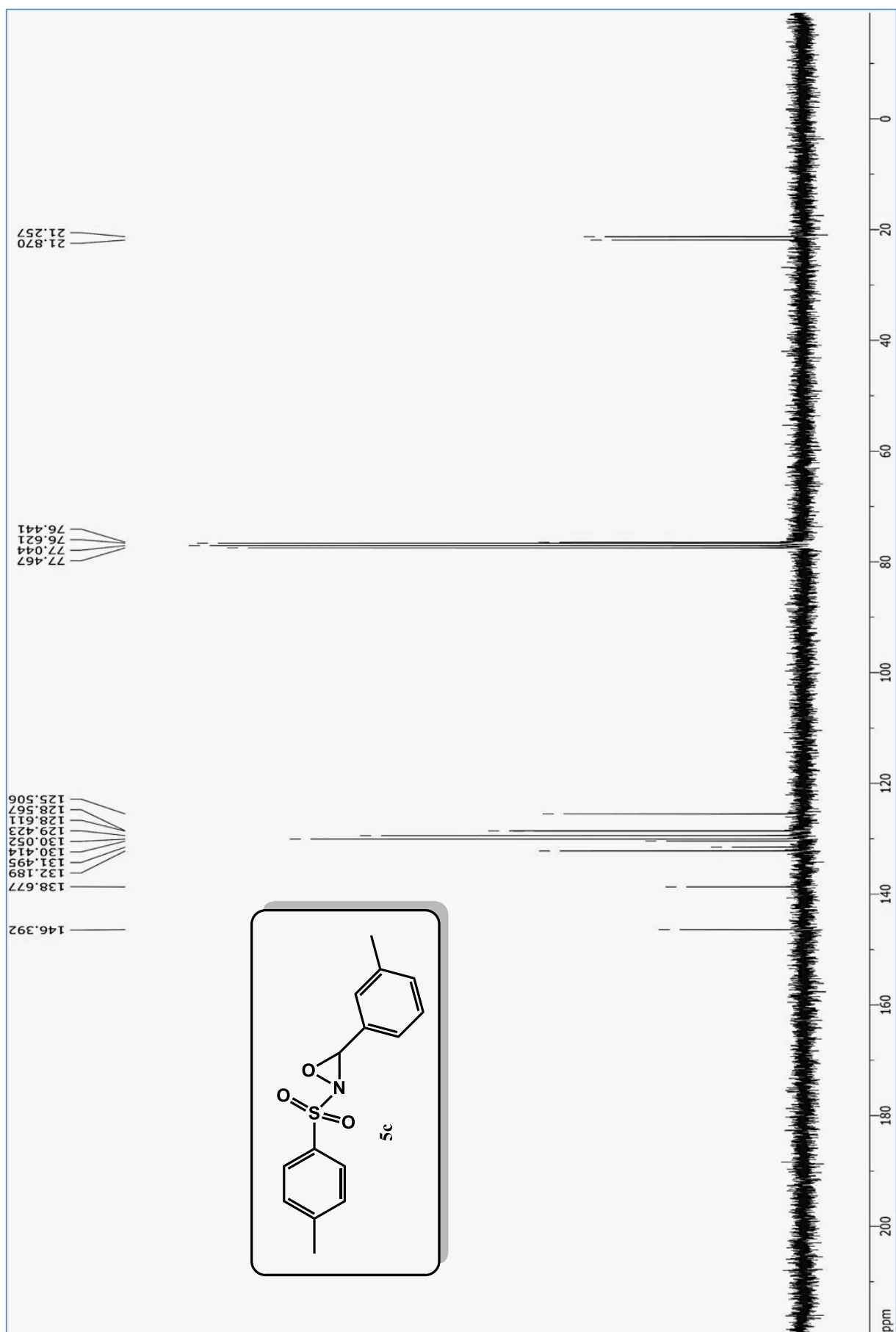


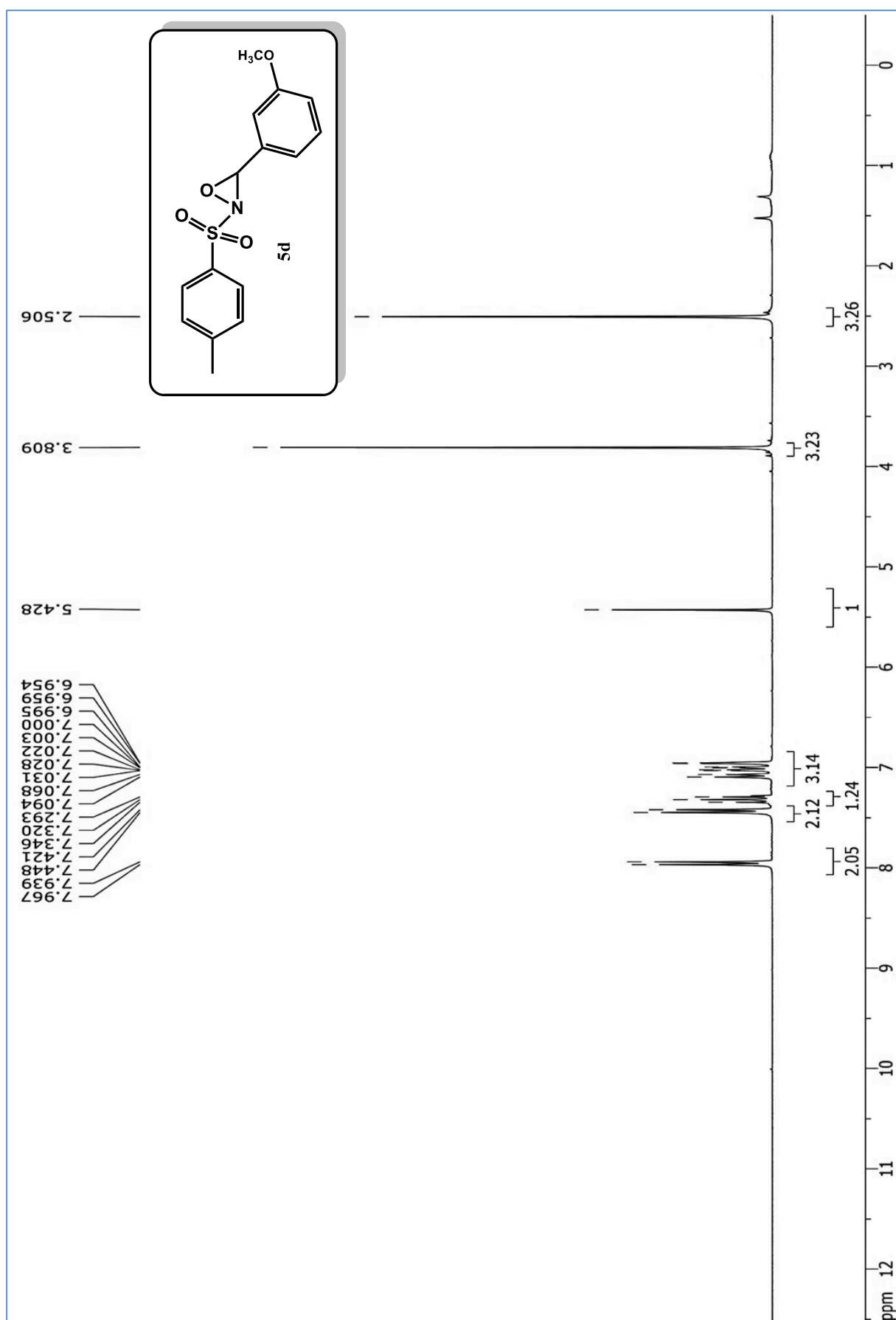


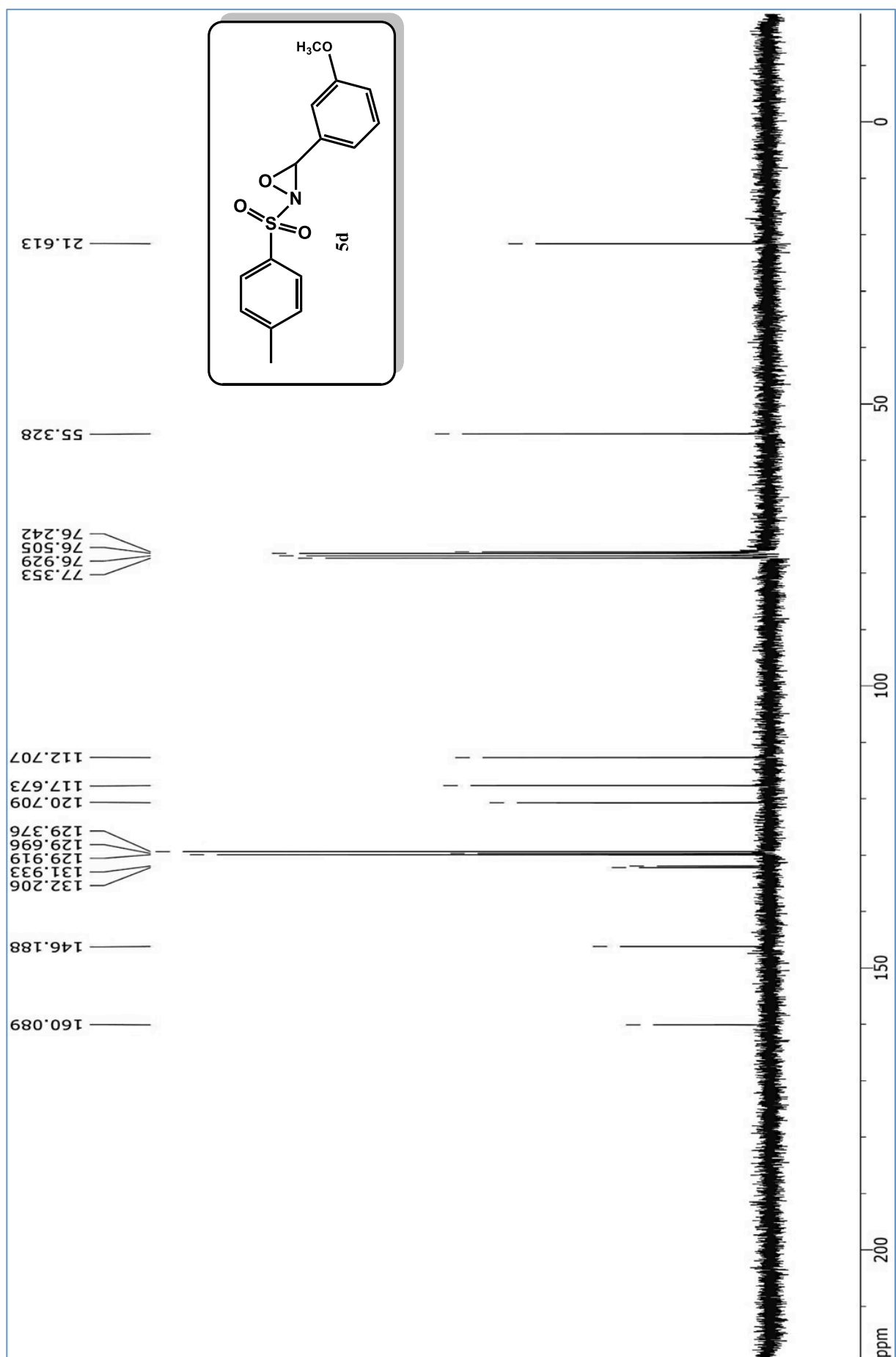


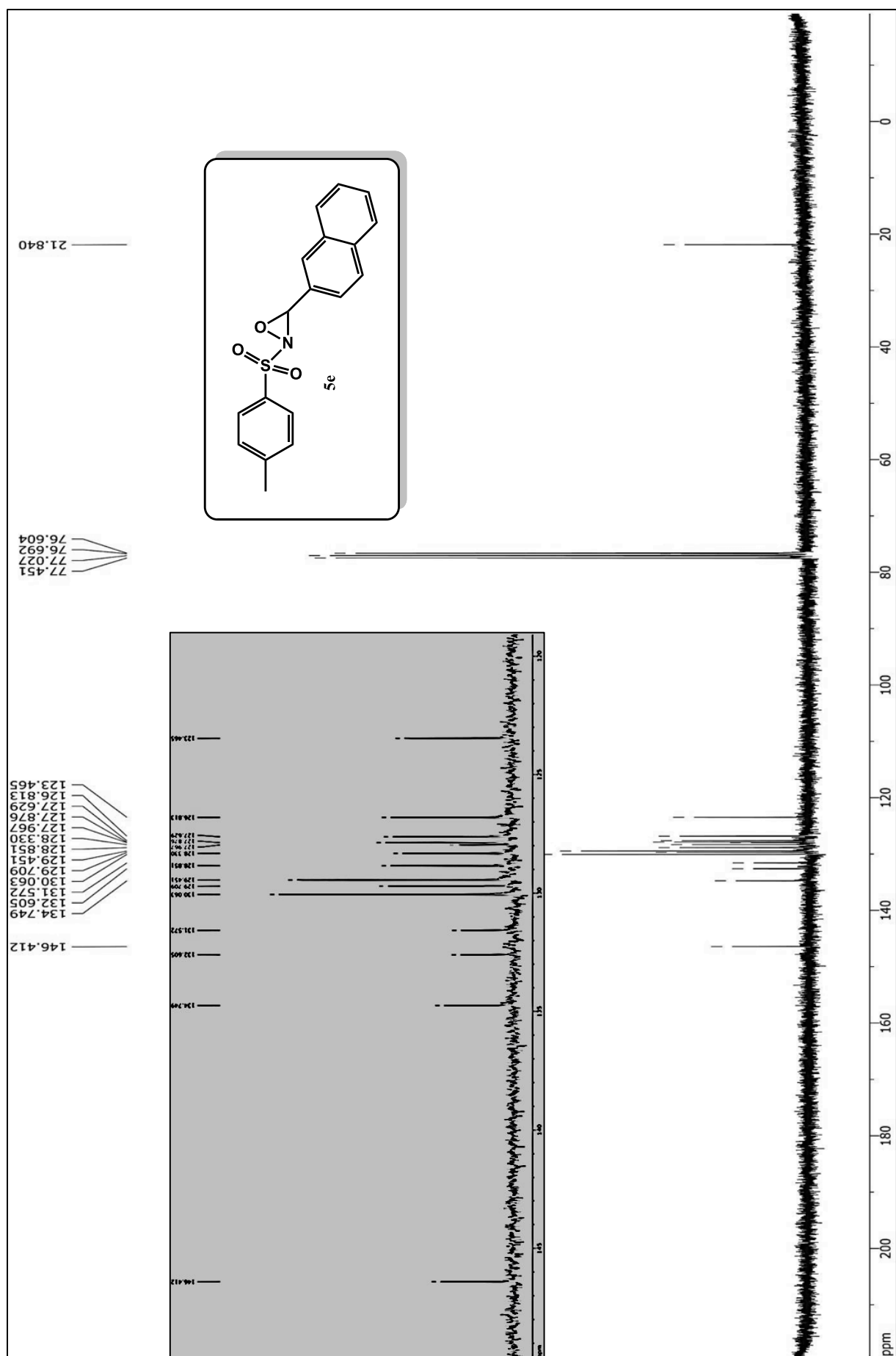


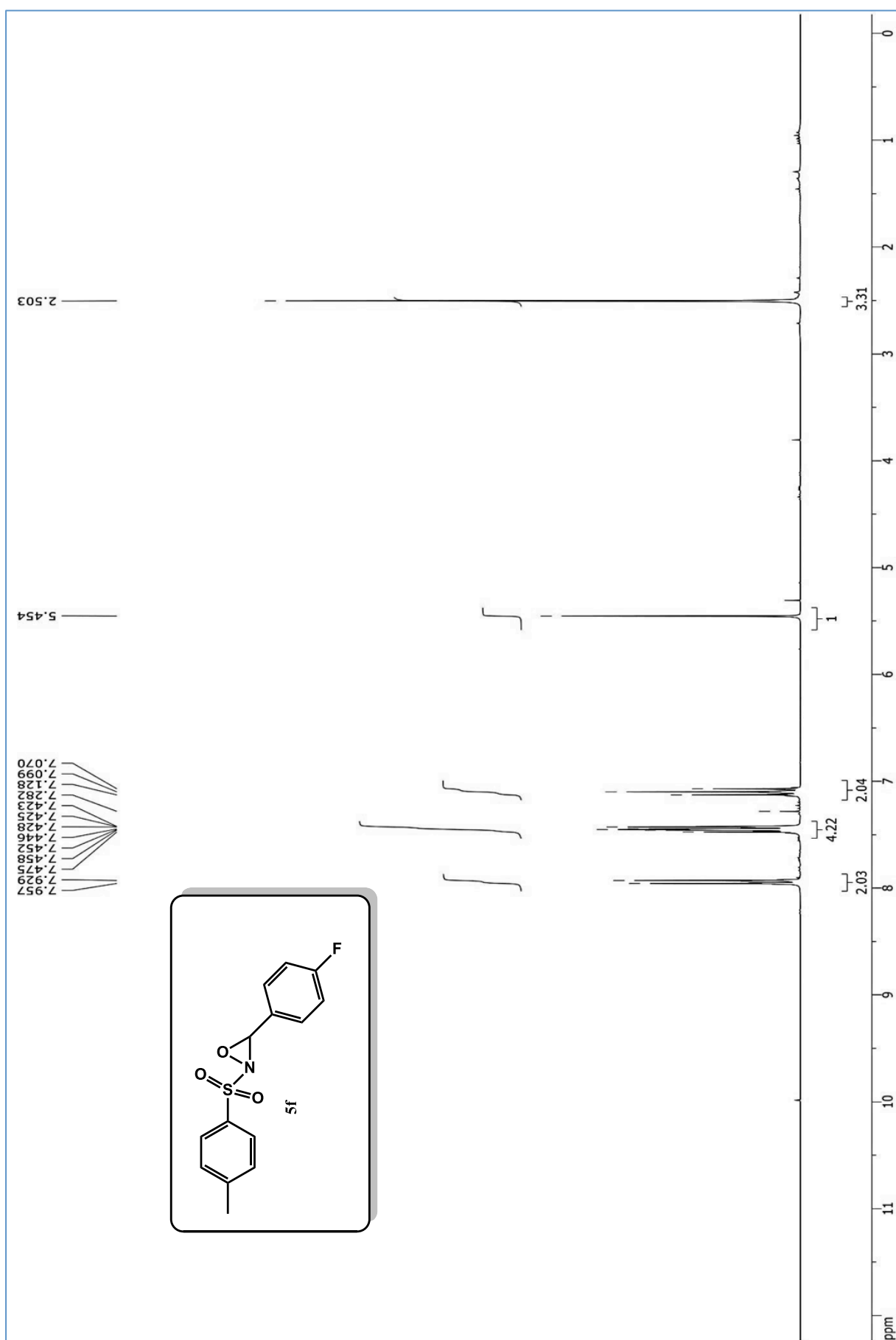


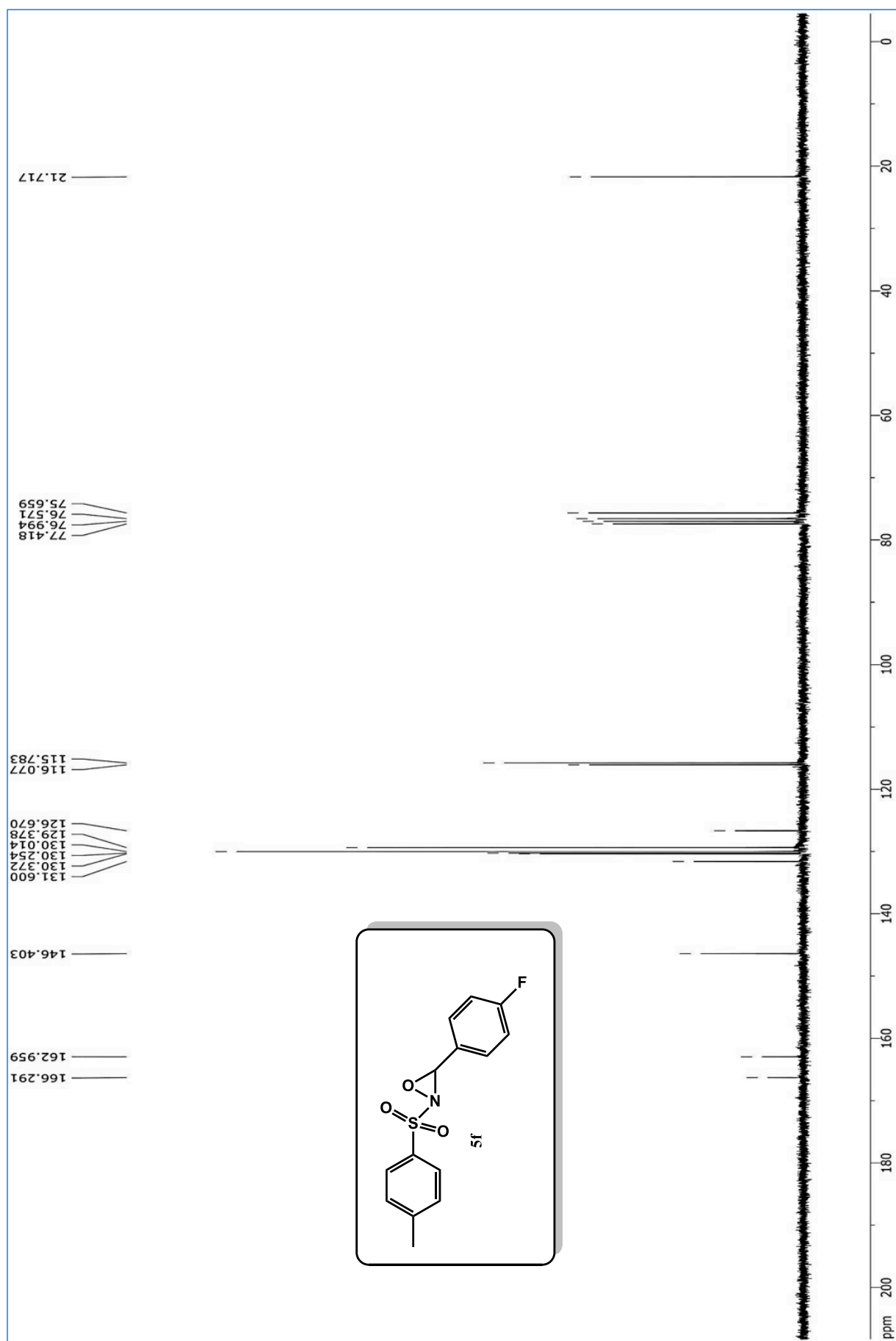


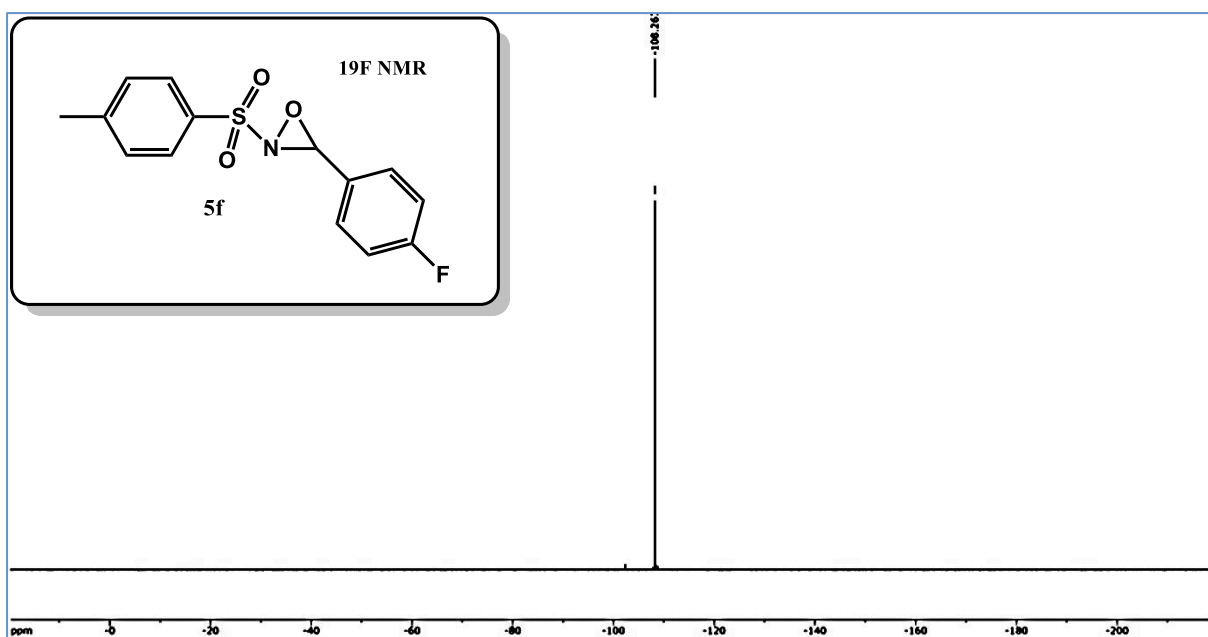


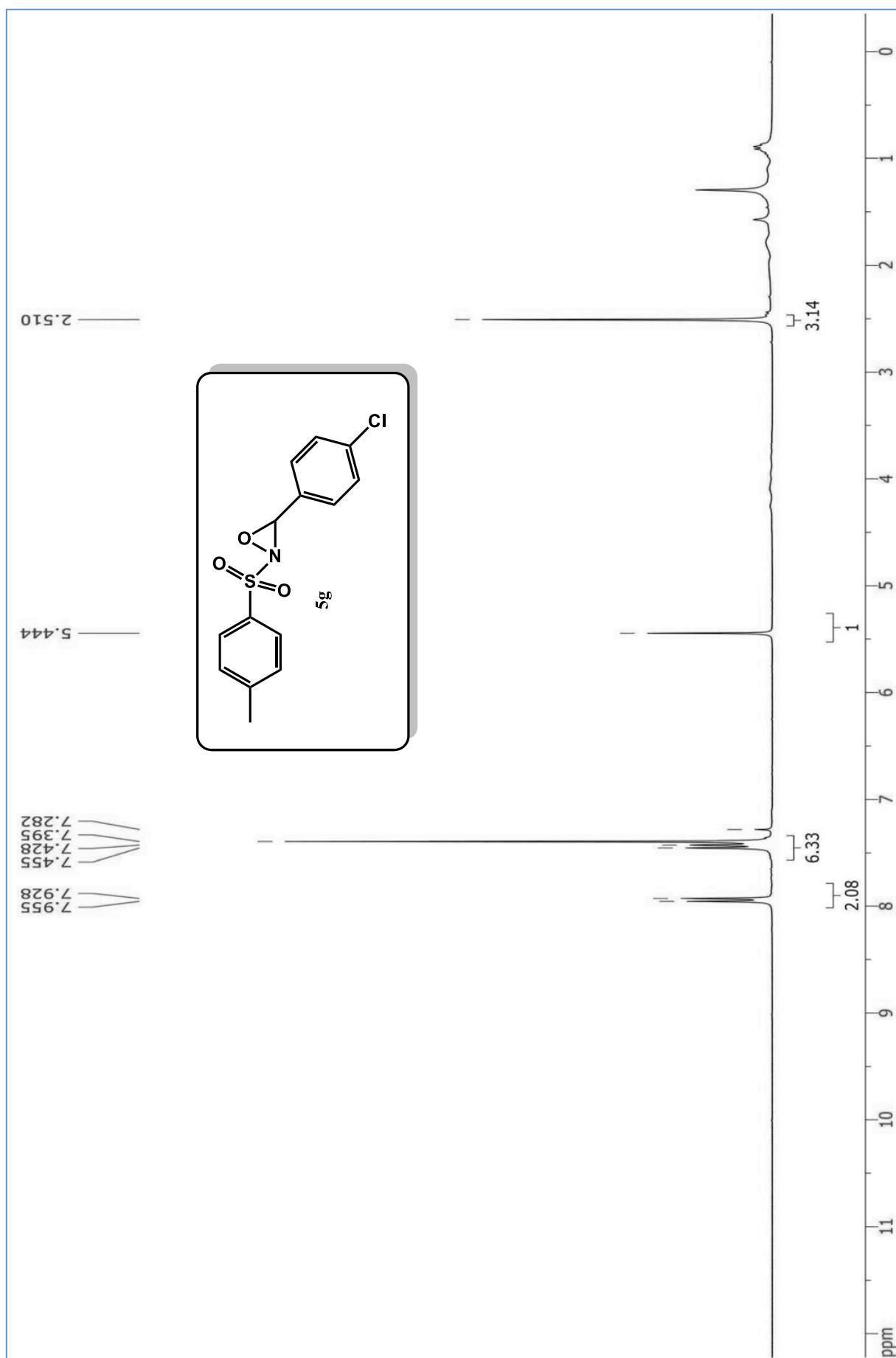


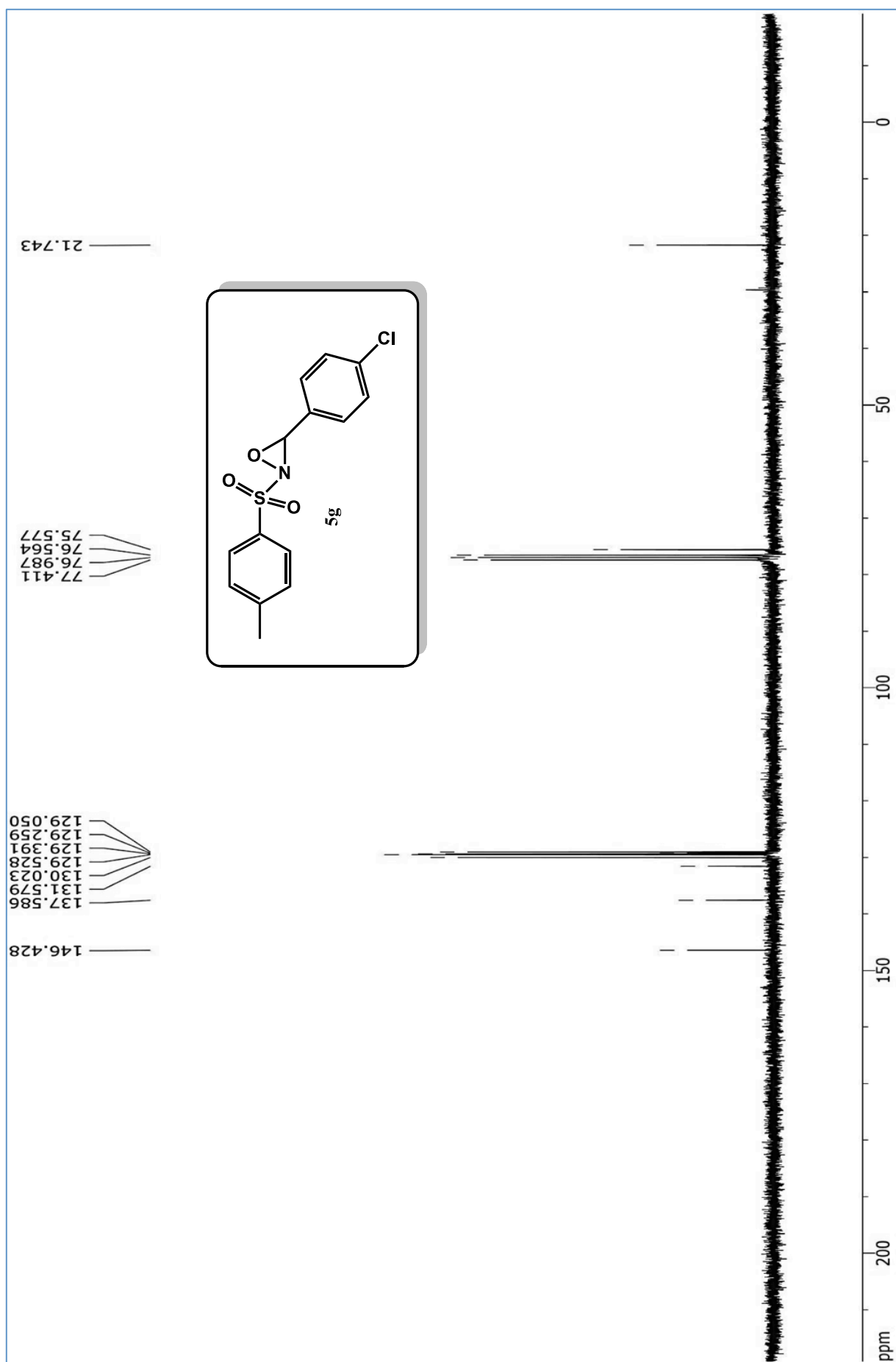


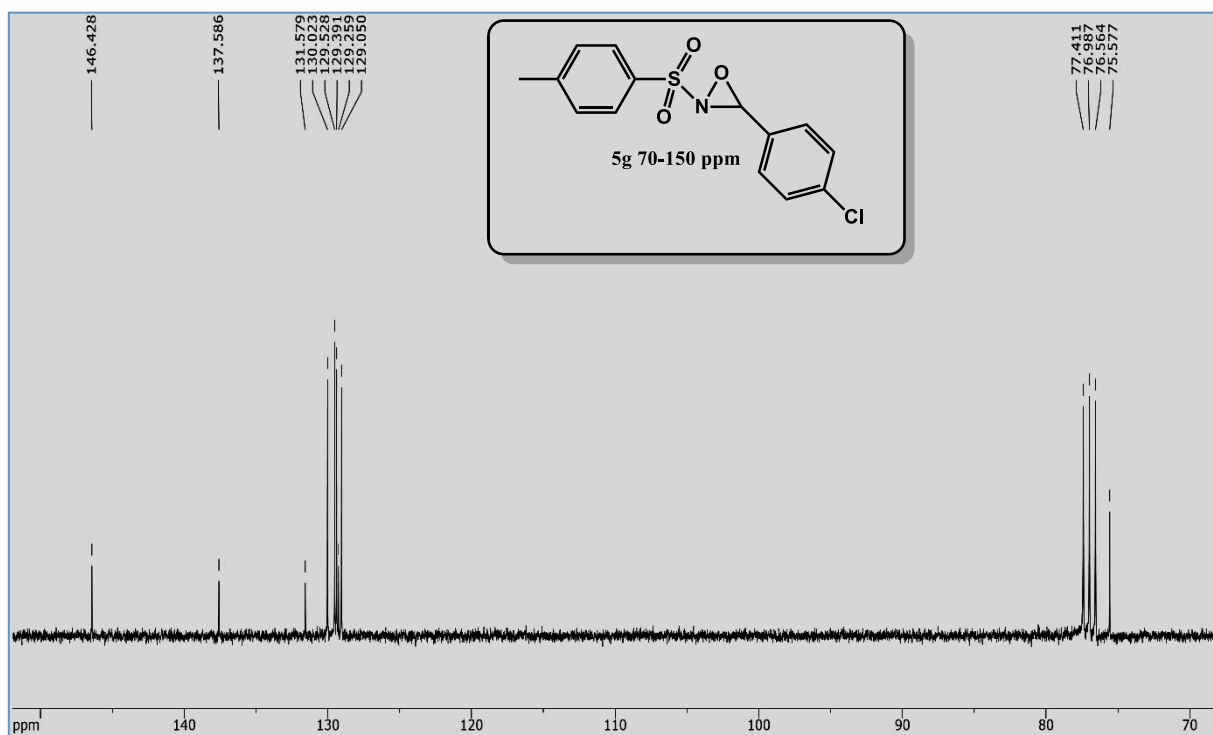


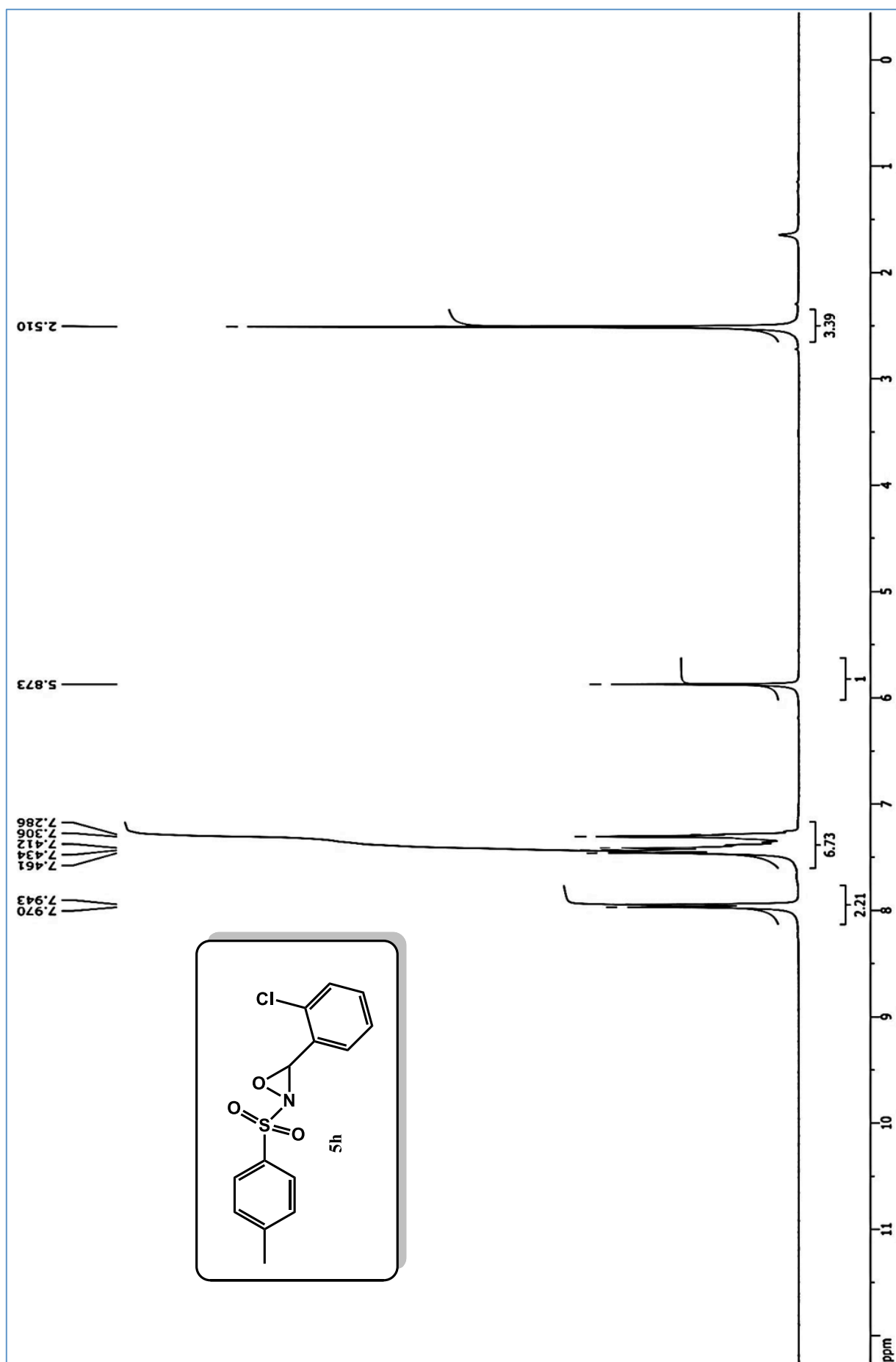


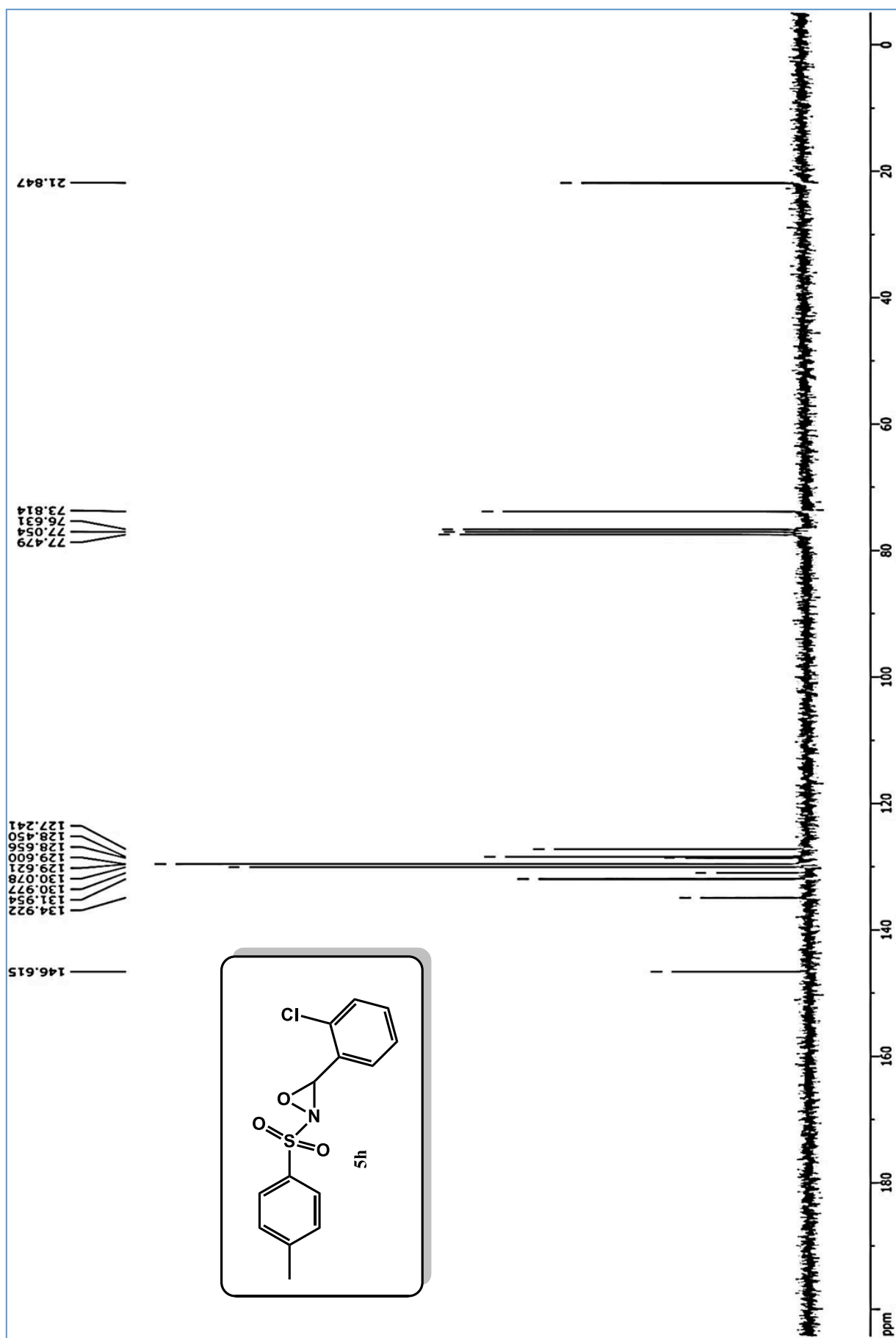


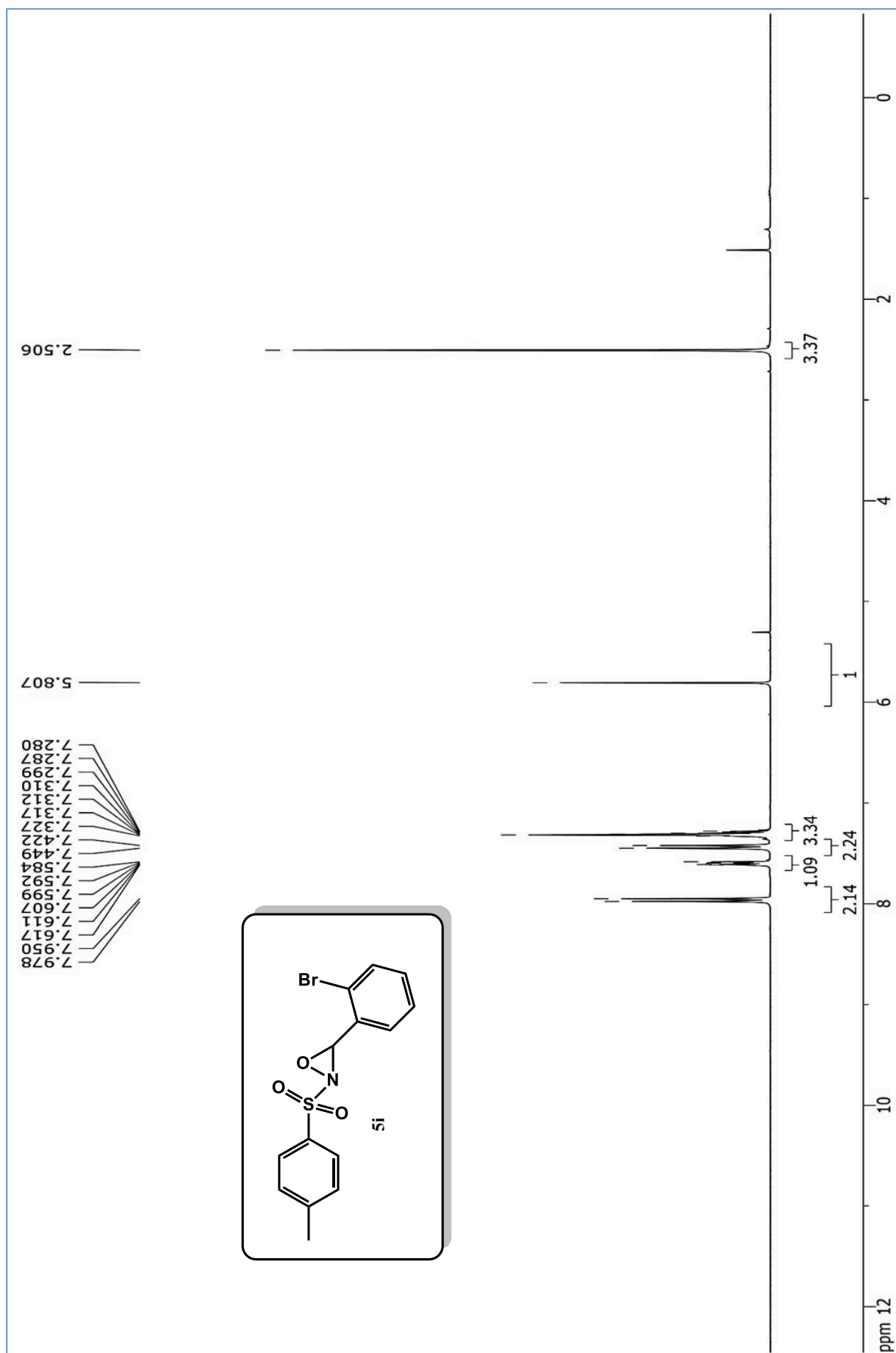


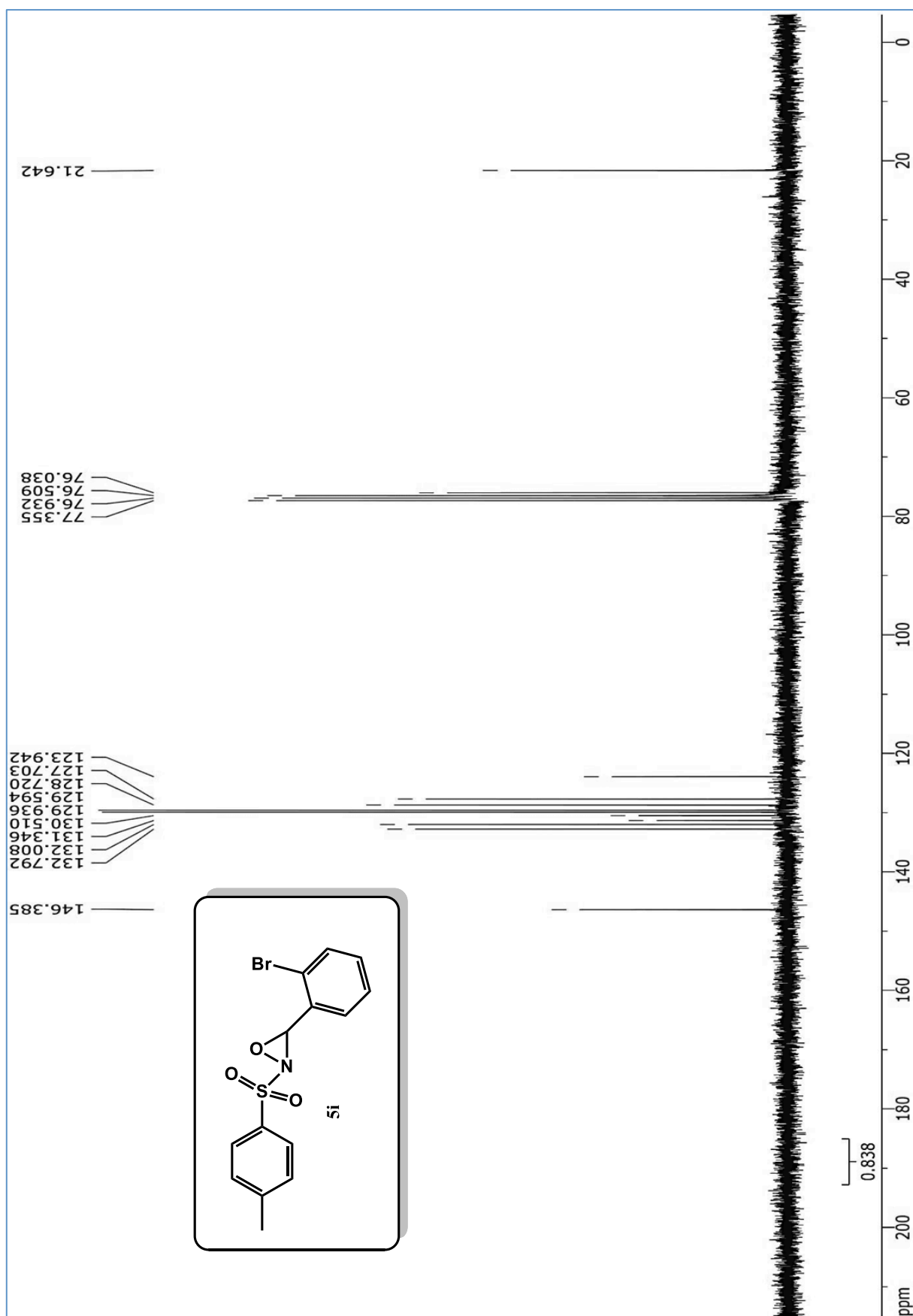


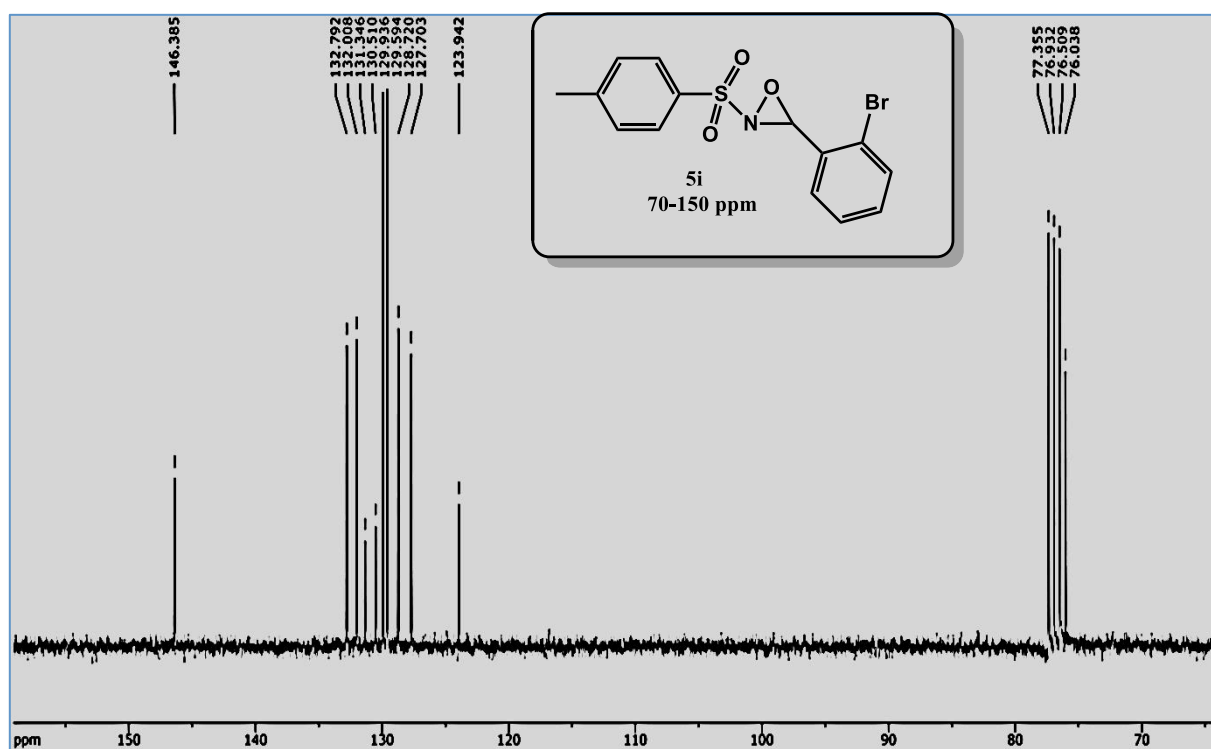


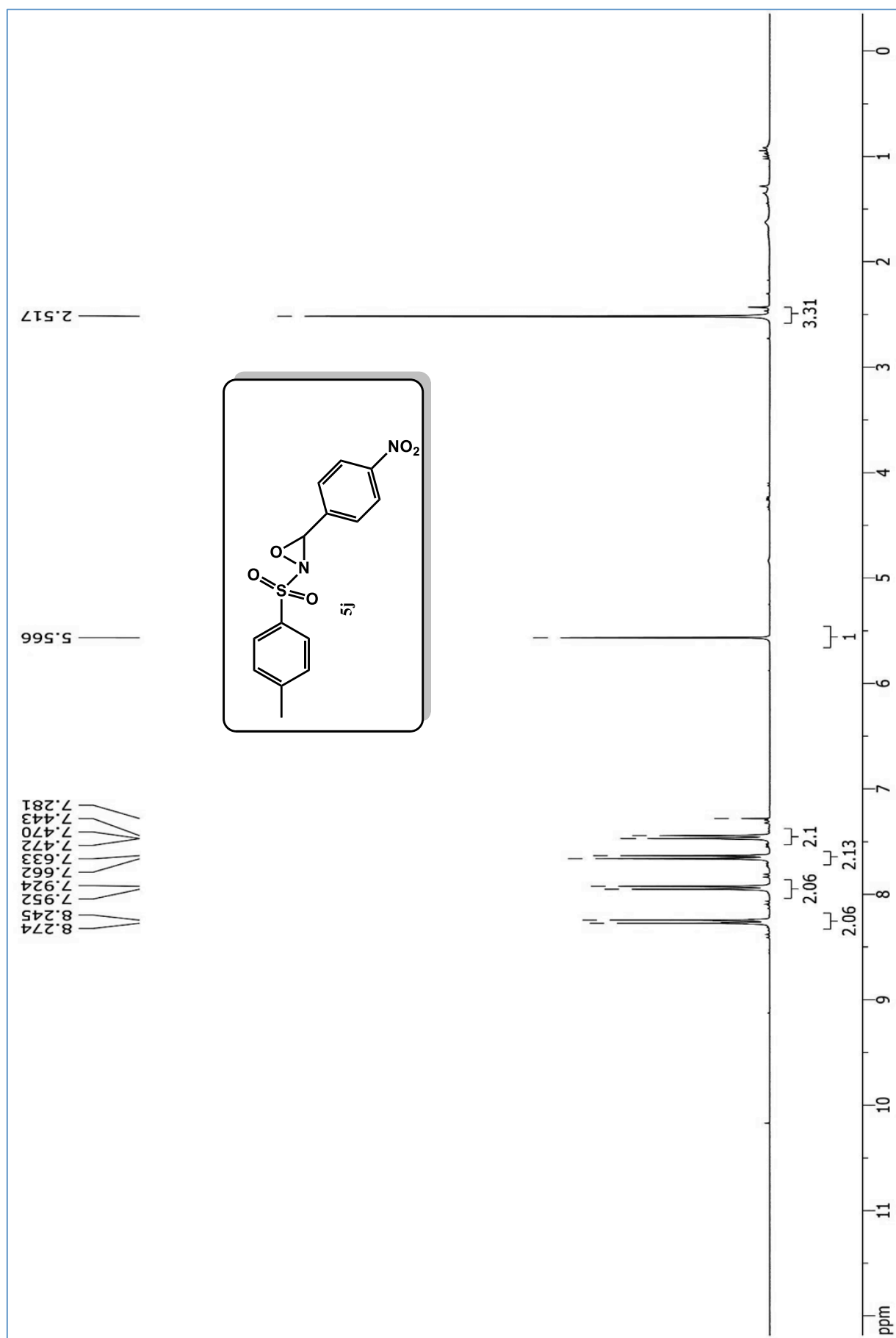


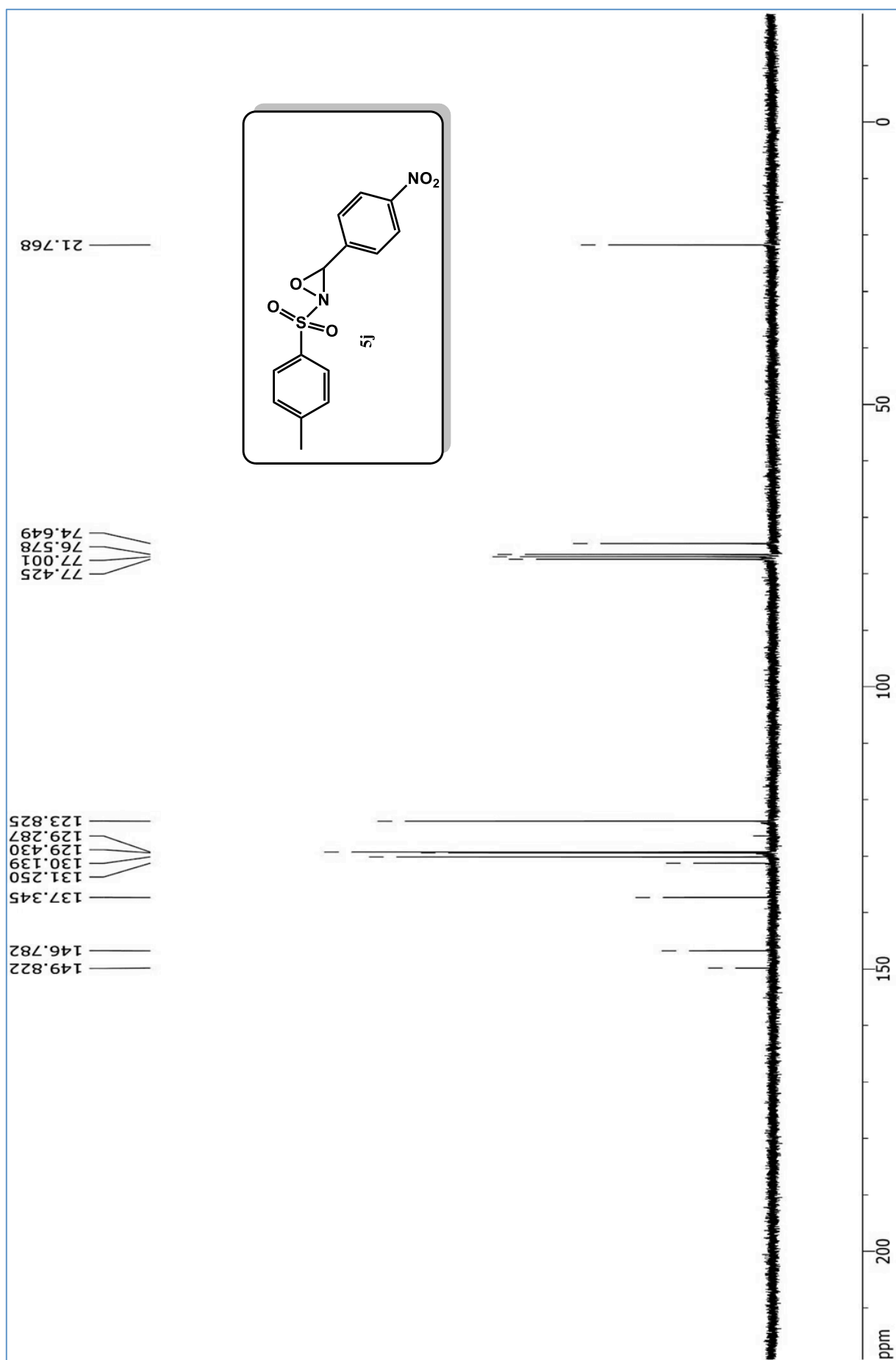


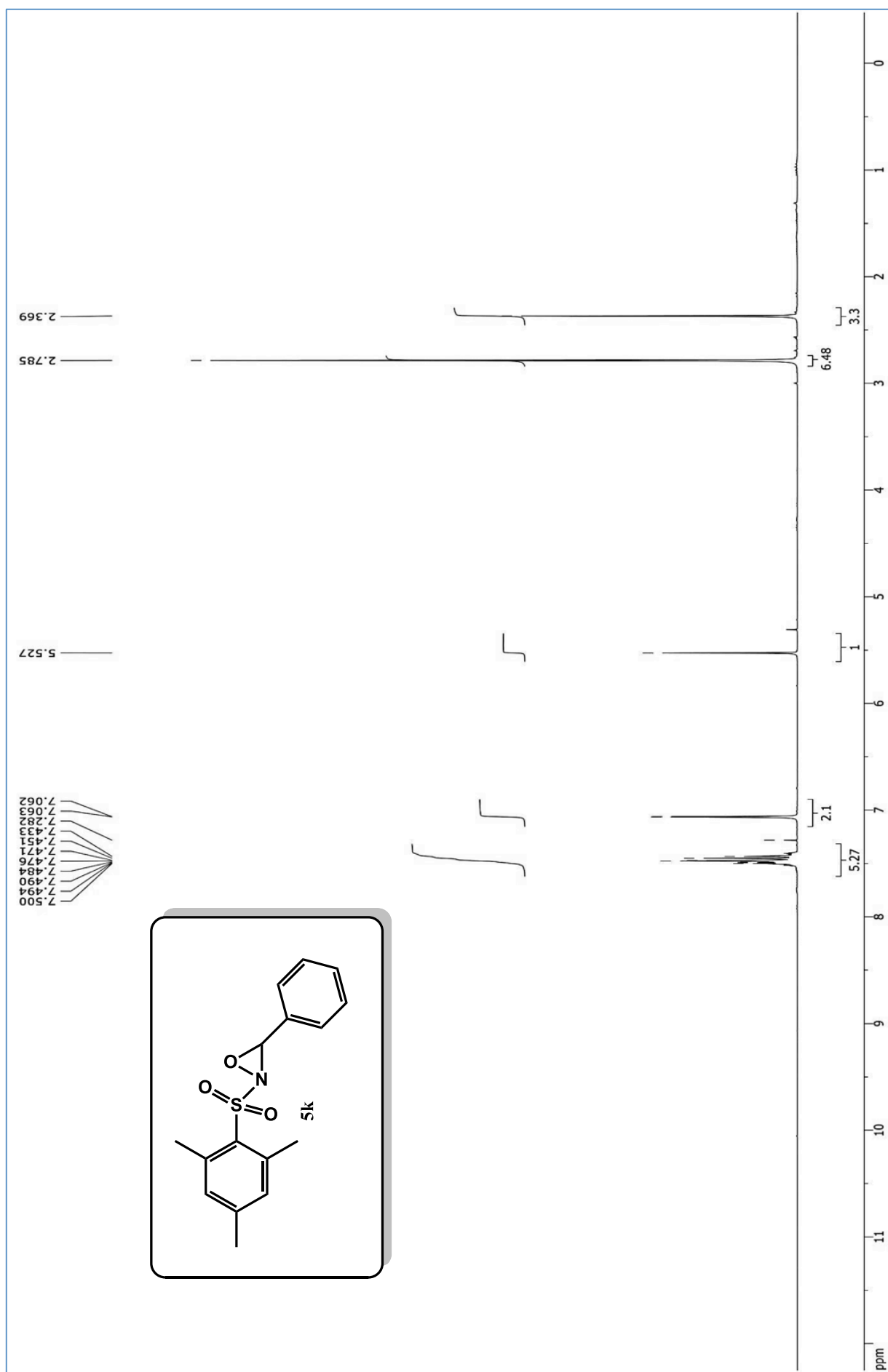


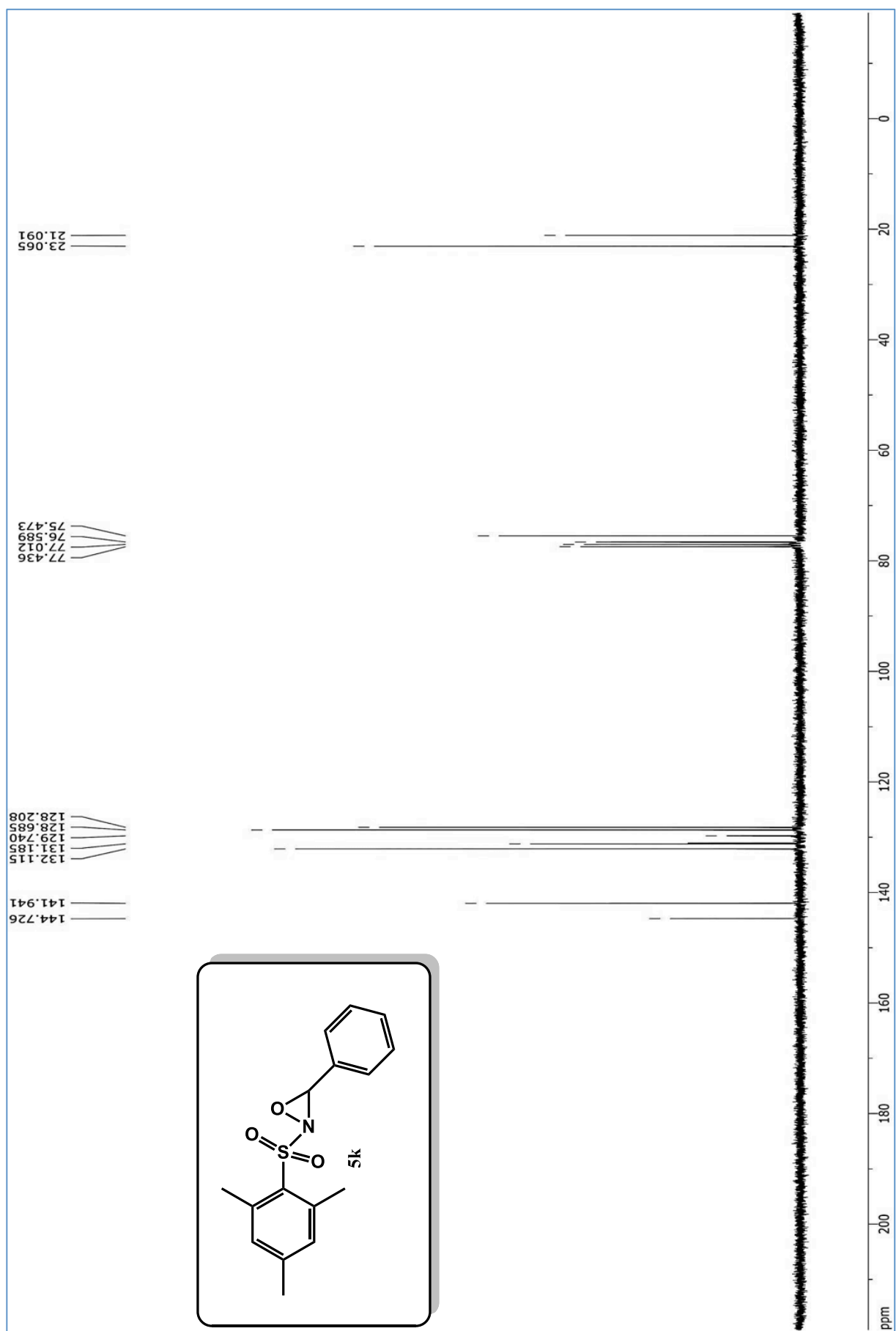












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