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Unprecedented amidation of 'transient' aryl thioaldehydes by *N,N*-dimethylformamide under basic conditions

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S1. NMR spectral data for compounds in Table 2 (4a–4i)

Table 2; entry 1

***N*,*N*-Dimethylbenzothioamide (4a)**, Yellow solid, mp 69-71 ^{o}C.[1] IR (KBr, ν cm^{-1}): 1525.6, 1386.7, 1272.9, 1134.1, 989.4, 759.9. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.12 (s, 3H, NCH_3), 3.56 (s, 3H, NCH_3), 7.28-7.31 (m, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 42.8, 43.8, 125,3, 127.9, 128.1, 143.0, 200.6.

Table 2; entry 2

4-Methoxy-*N*,*N*-dimethylbenzothioamide (4b), Pale yellow liquid. IR (Nujol, ν cm^{-1}): 1525.3, 1394.4, 1277.6, 1141.8, 1086.8, 989.4, 823.3. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.22 (s, 3H, NCH_3), 3.58 (s, 3H, NCH_3), 3.92 (s, 3H, OCH_3), 6.86-6.88 (m, 2H, ArH), 7.27-7.32 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 43.5, 44.2, 56.4, 111.2, 126.8, 131.1, 156.2, 199.4.

Table 2; entry 3

***N*,*N*-Dimethyl-4-nitrobenzothioamide (4c)**, Yellow solid, mp 142-144 ^{o}C.[2] IR (KBr, ν cm^{-1}): 1525.6, 1382.7, 1273.9, 1134.5, 989.4, 752.9. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.18 (s, 3H, NCH_3), 3.61 (s, 3H, NCH_3), 7.46 (d, J = 8.7 Hz, 2H, ArH), 8.22 (d, J = 9.0 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 42.9, 43.9, 123.8, 126.5, 147.2, 148.8, 197.8.

Table 2; entry 4

4-Chloro-*N*,*N*-dimethylbenzothioamide (4d), Yellow solid, mp 80-82 ^{o}C.[3] IR (KBr, ν cm^{-1}): 1525.6, 1394.4, 1280.6, 1141.8, 1087.8, 989.4, 829.3. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.15 (s, 3H, NCH_3), 3.57 (s, 3H, NCH_3), 7.22-7.32 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 43.3, 44.1, 127.3, 128.6, 134.6, 141.7, 200.0.

Table 2; entry 5

3-Chloro-*N*,*N*-dimethylbenzothioamide (4e), Pale yellow liquid. IR (Nujol, ν cm^{-1}): 1525.6, 1394.4, 1280.6, 1141.8, 1087.8, 989.4, 829.3. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.17 (s, 3H, NCH_3), 3.59 (s, 3H, NCH_3), 7.15-7.19 (m, 1H, ArH), 7.27-7.30 (m, 3H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 43.1, 44.1, 123.7, 125.8, 128.5, 129.7, 134.2, 144.7, 199.1.

Table 2; entry 6

2-Chloro-*N*,*N*-dimethylbenzothioamide (4f), Pale yellow liquid. IR (Nujol, ν cm^{-1}): 1525.6, 1394.4, 1280.6, 1141.8, 1087.8, 989.4, 829.3. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.11 (s, 3H,

NCH_3), 3.61 (s, 3H, NCH_3), 7.26-7.35 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 42.3, 42.8, 127.3, 127.7, 128.1, 129.3, 129.6, 142.0, 196.8.

Table 2; entry 7

4-Bromo-*N*,*N*-dimethylbenzothioamide (4g), Yellow solid, mp 120-122 ^oC.[3] IR (KBr, *v* cm^{-1}): 1525.6, 1394.4, 1280.6, 1141.8, 1087.8, 989.4, 829.3. ^1H NMR (300 MHz, $CDCl_3$), δ: 3.18 (s, 3H, NCH_3), 3.59 (s, 3H, NCH_3), 7.17-7.21 (m, 2H, ArH), 7.47-7.53 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 43.2, 44.1, 122.7, 127.4, 131.5, 142.0, 199.8.

Table 2; entry 8

3-Iodo-*N*,*N*-dimethylbenzothioamide (4h), Pale yellow liquid. IR (Nujol, *v* cm^{-1}): 1521.7, 1394.4, 1294.1, 1137.9, 997.1, 759.9, 698.2. ^1H NMR (300 MHz, $CDCl_3$), δ: 3.15 (s, 3H, NCH_3), 3.56 (s, 3H, NCH_3), 7.06-7.11 (m, 1H, ArH), 7.23-7.27 (m, 2H, ArH), 7.64-7.66 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 43.1, 44.1, 94.0, 124.8, 130.0, 134.3, 137.5, 145.0, 198.9.

Table 2; entry 9

***N*,*N*-Dimethylnaphthalene-1-carbothioamide (4i)**, Pale yellow liquid. IR (Nujol, *v* cm^{-1}): 1525.6, 1384.2, 1274.0, 1144.1, 983.2, 759.7. ^1H NMR (300 MHz, $CDCl_3$), δ: 2.94 (s, 3H, NCH_3), 3.69 (s, 3H, NCH_3), 7.34-7.37 (m, 1H, ArH), 7.42-7.51 (m, 3H, ArH), 7.69-7.72 (m, 1H, ArH), 7.77-7.84 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 42.4, 43.3, 122.8, 124.3, 125.2, 126.1, 126.9, 127.7, 128.1, 128.2, 133.3, 140.8, 199.5.

References:

1. C. Johnr, *J. Org.Chem.,* 1982, **47**, 4645.
2. B. Denis, *Synth. Commun.*, 1990, **20**, 3085.
3. A. O. Joseph, *Synthesis*, 1983, **9**, 730.

S2. X-ray analysis data and ortep diagram for compounds 4a & 4d

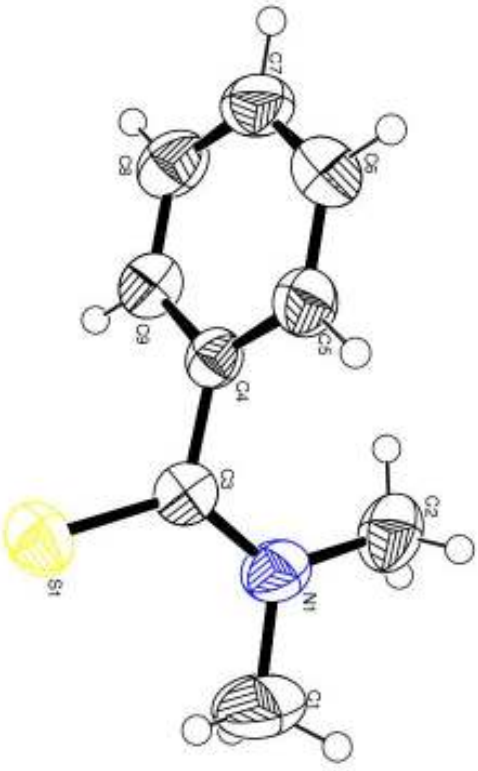
The crystal data of compound **4a** and **4d** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference numbers are 994136 and 994137 respectively. Software used for data collection is Mercury 3.3.

X-ray analysis data for compounds 4a (smk-164) and 4d (smk-170)

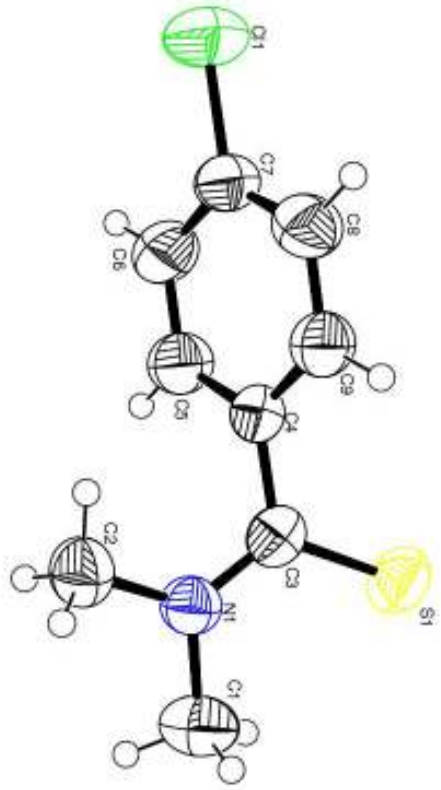
Identification code	4a (smk-164)	4d (smk-170)
Empirical formula	$C_9H_{11}NS$	$C_9H_{10}ClNS$
Formula weight	165.25	199.69
Temperature	296 K	296 K
Wave length	0.71073	0.71073
Bond precision(C-C)	0.0027 Å	0.0030 Å
Space group	P2 (1) /n	P2 (1)/c
Hall group	-P 2yn	-P 2ybc
Unit cell dimensions	a = 5.9271 (15) Å	a = 10.1194 (3) Å
	b = 12.790 (3) Å	b = 14.4115 (4) Å
	c = 12.361 (3) Å	c = 7.3247 (2) Å
	$\alpha = 90^o$	$\alpha = 90^o$
	$\beta = 100.163\ (13)^o$	$\beta = 106.198\ (2)^o$
	$\gamma = 90^o$	$\gamma = 90^o$
Volume (calculated)	922.4 (4) $Å^3$	1026.18 (5) $Å^3$
Density (calculated)	1.190 g/cm^3	1.293 g/cm^3
Z	4	4
Absorption coefficient (Mu)	0.287 mm^{-1}	0.522 mm^{-1}
F(000)	352.0	416.0
Index ranges (h, k, l max)	7, 15, 14	12, 17, 8
Nref (calculated)	1610	1808
Data completeness	98.9%	99.9%
Theta (max)	24.99^o	25.00^o
R(reflections)/wR2 (reflections)	0.0342 (1290)/0.0958 (1593)	0.0439 (1355)/0.1340 (1807)
S	1.005	1.049

Npar = Npar	103	112

Ortep diagrams for compounds 4a and 4d



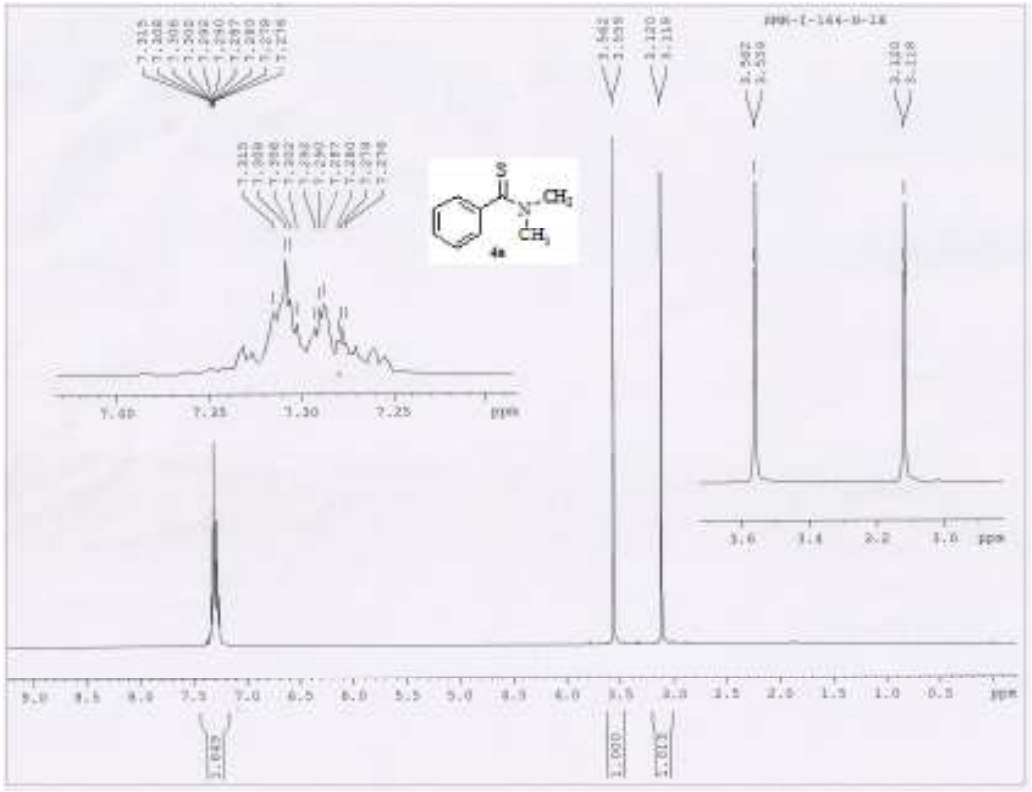
N,N-Dimethylbenzothioamide (4a)



4-Chloro-*N*,*N*-dimethylbenzothioamide (4d)

S3. Scanned copies of 1H & 13C spectra for compounds Table 2; entries 1-9 (4a – 4i).

Table 2; entry 1



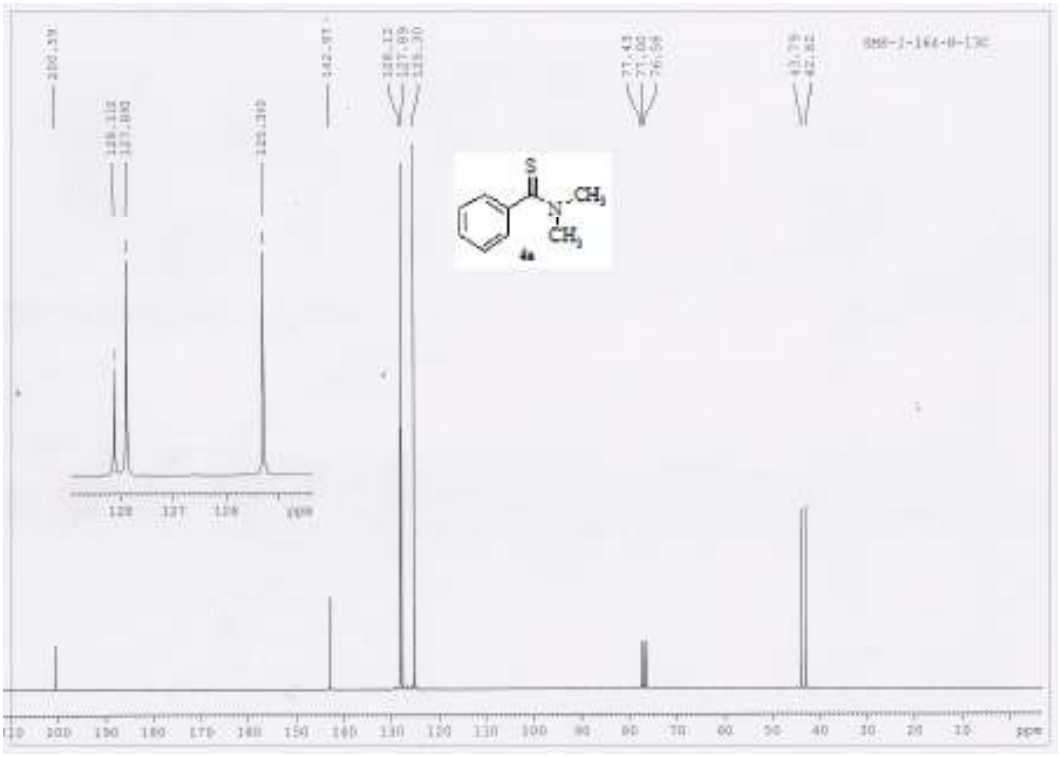
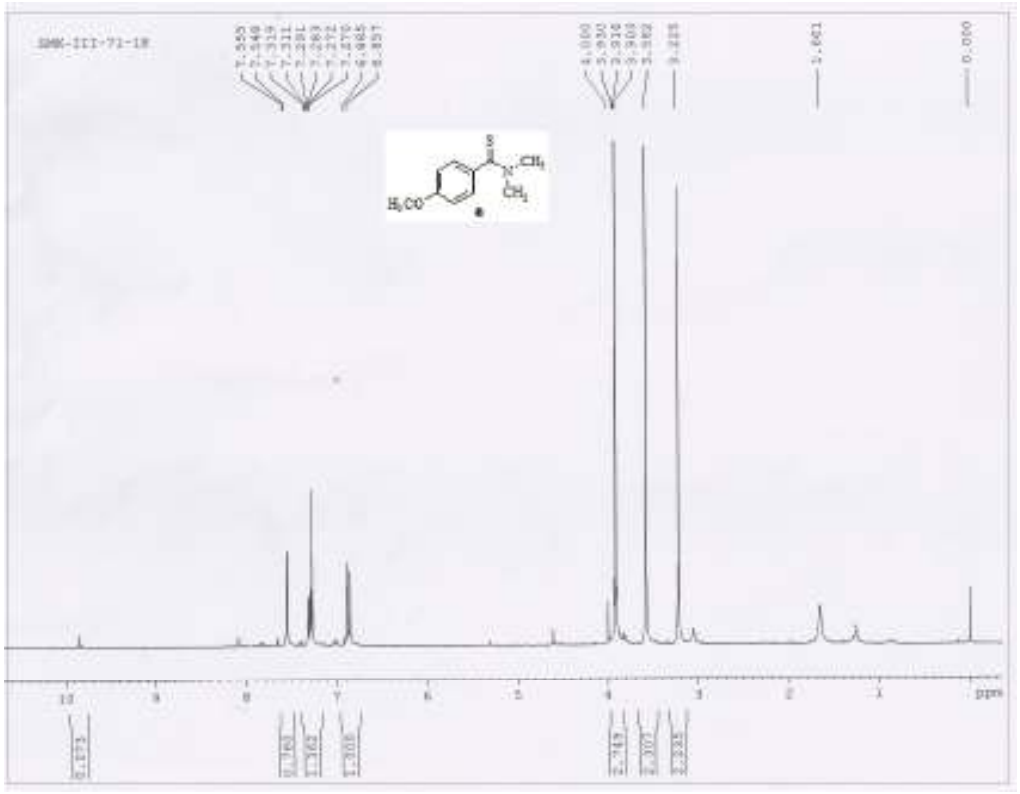
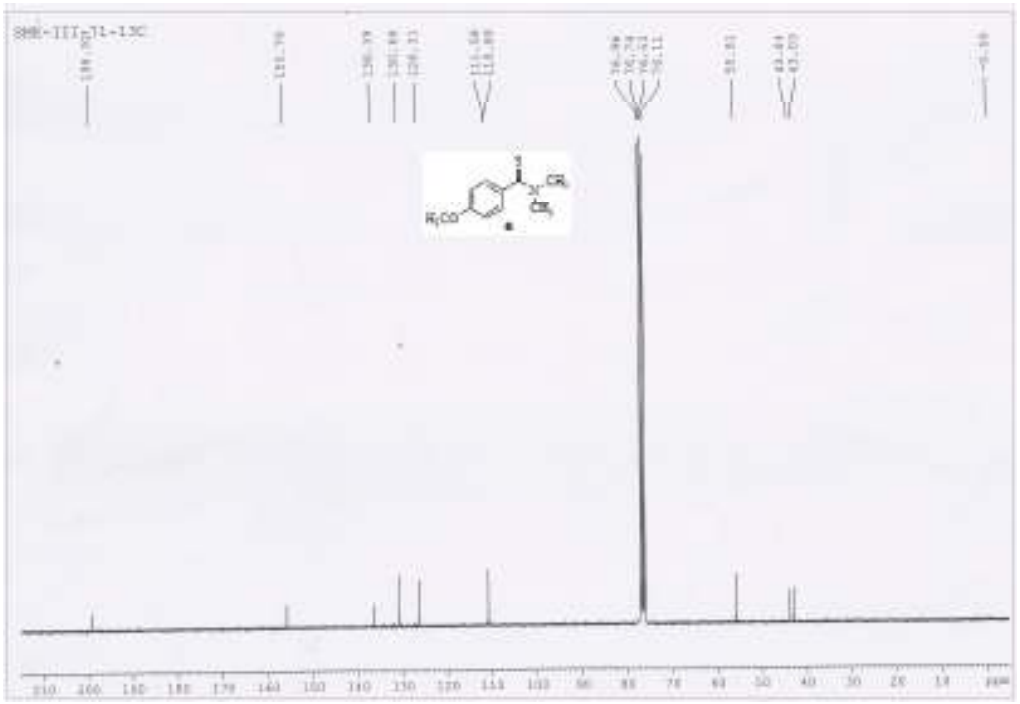


Table 2; entry 2





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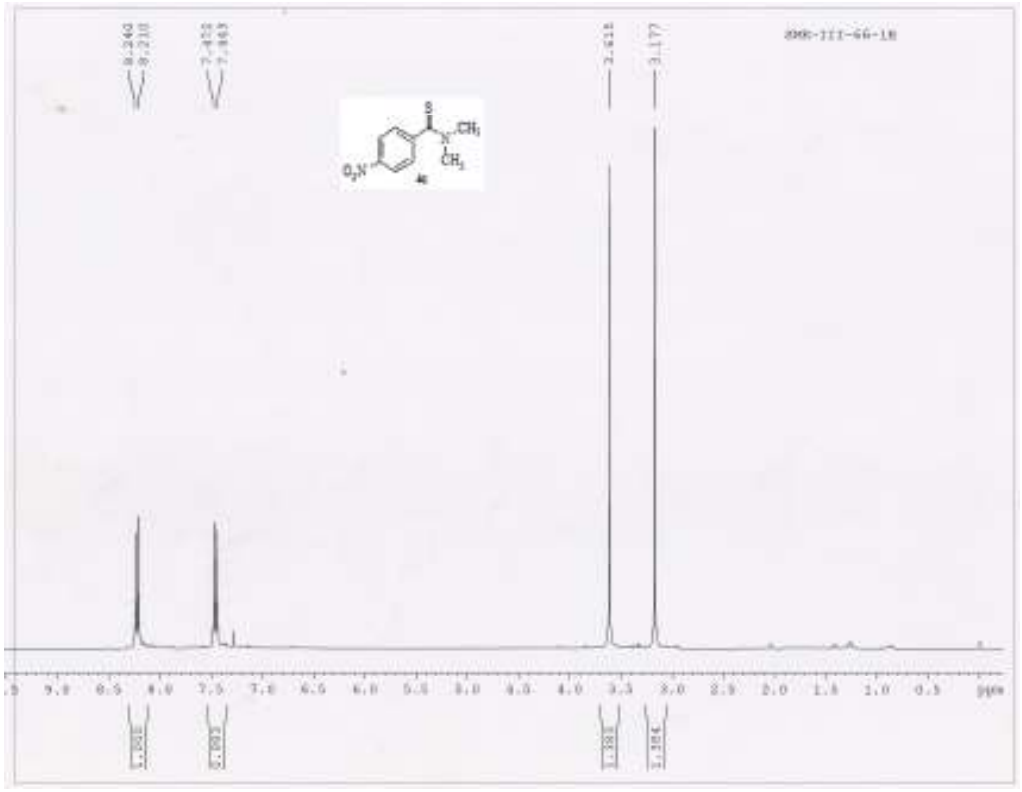

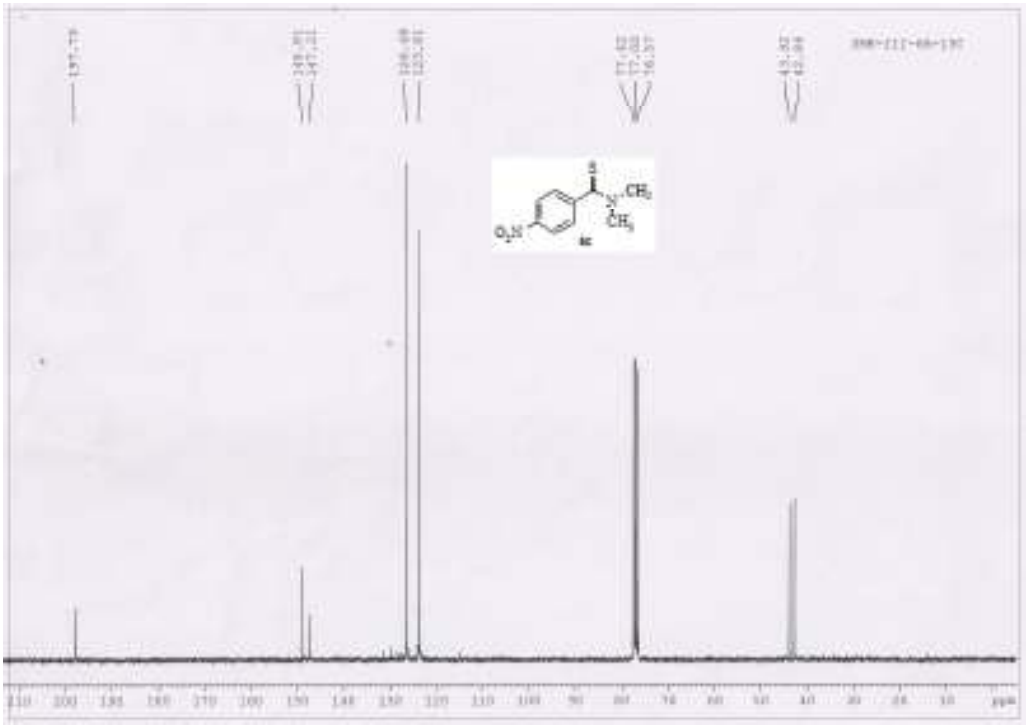

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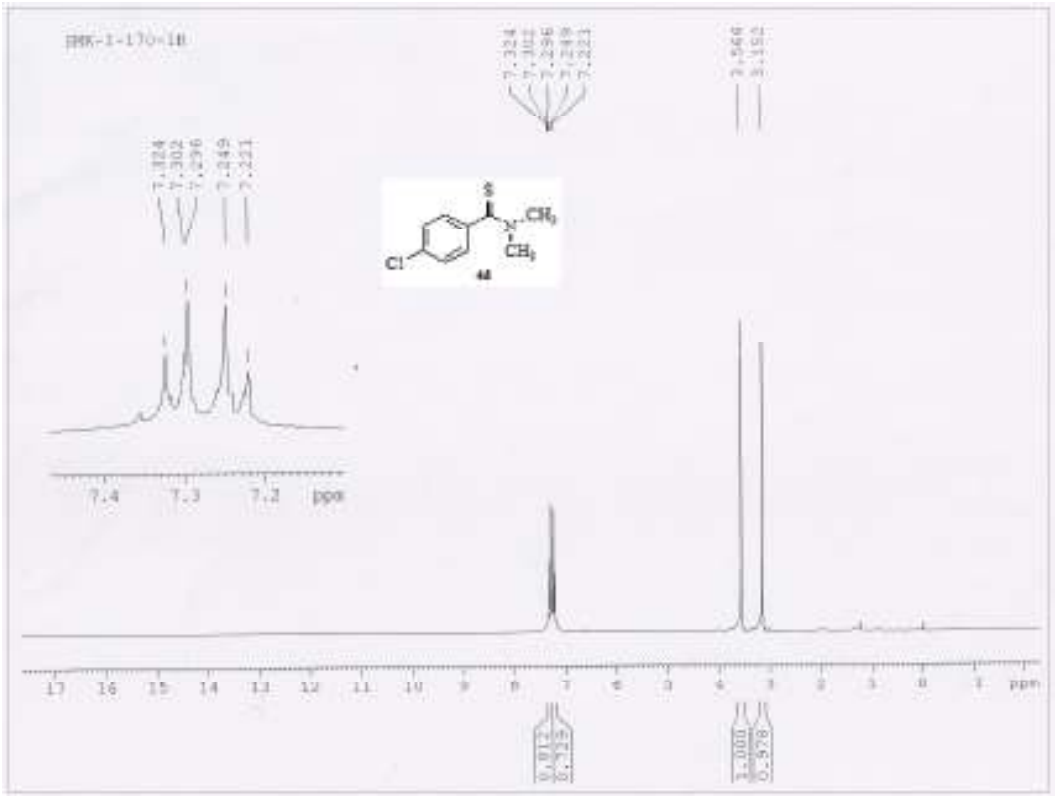

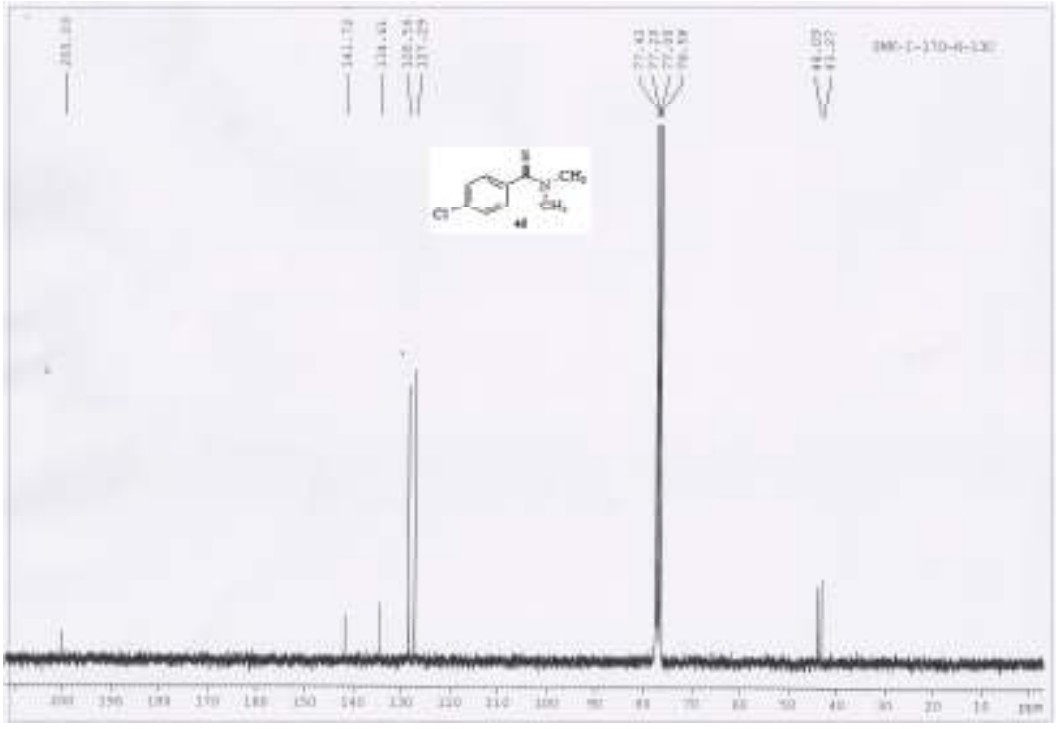

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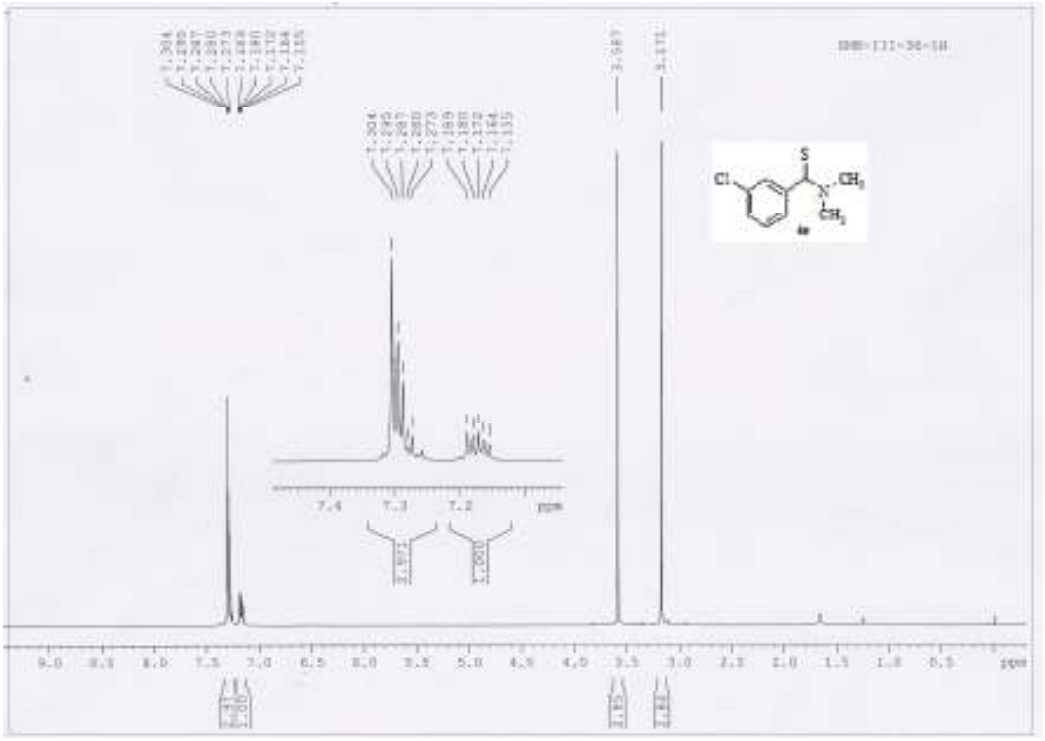

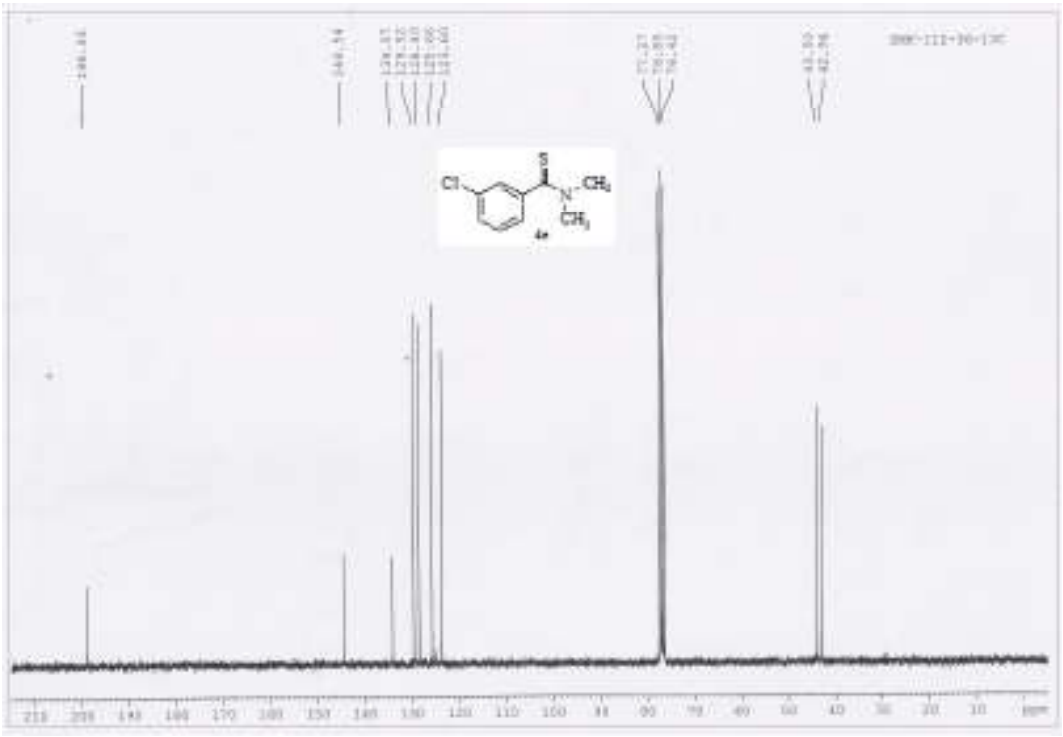

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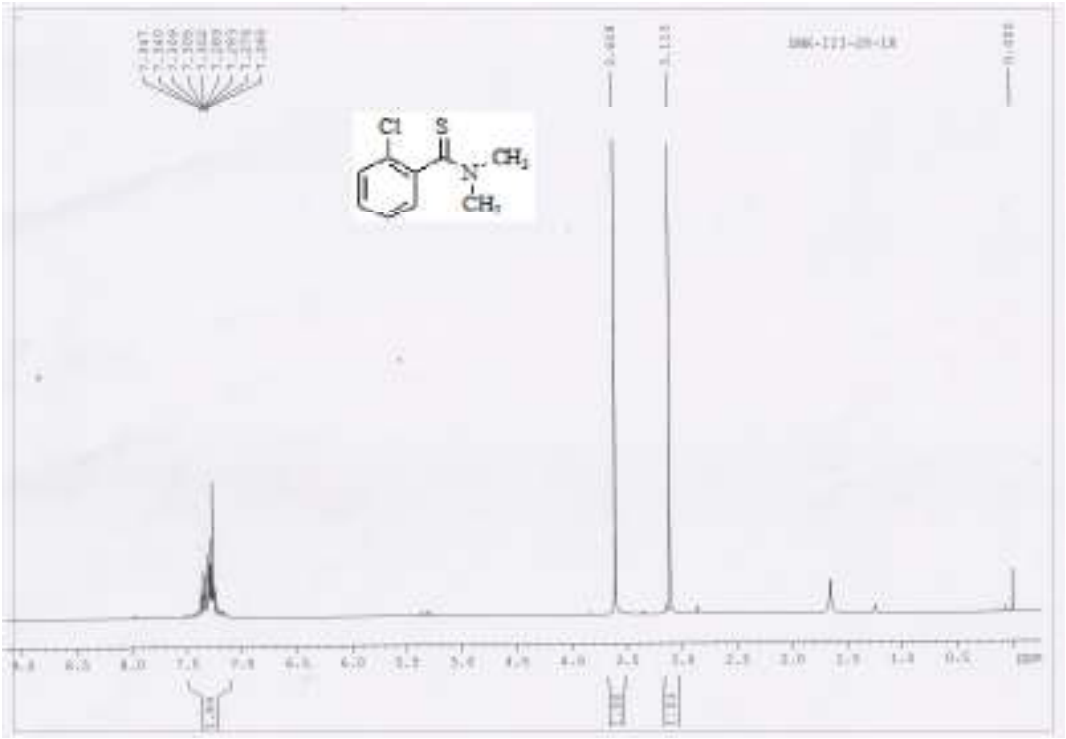

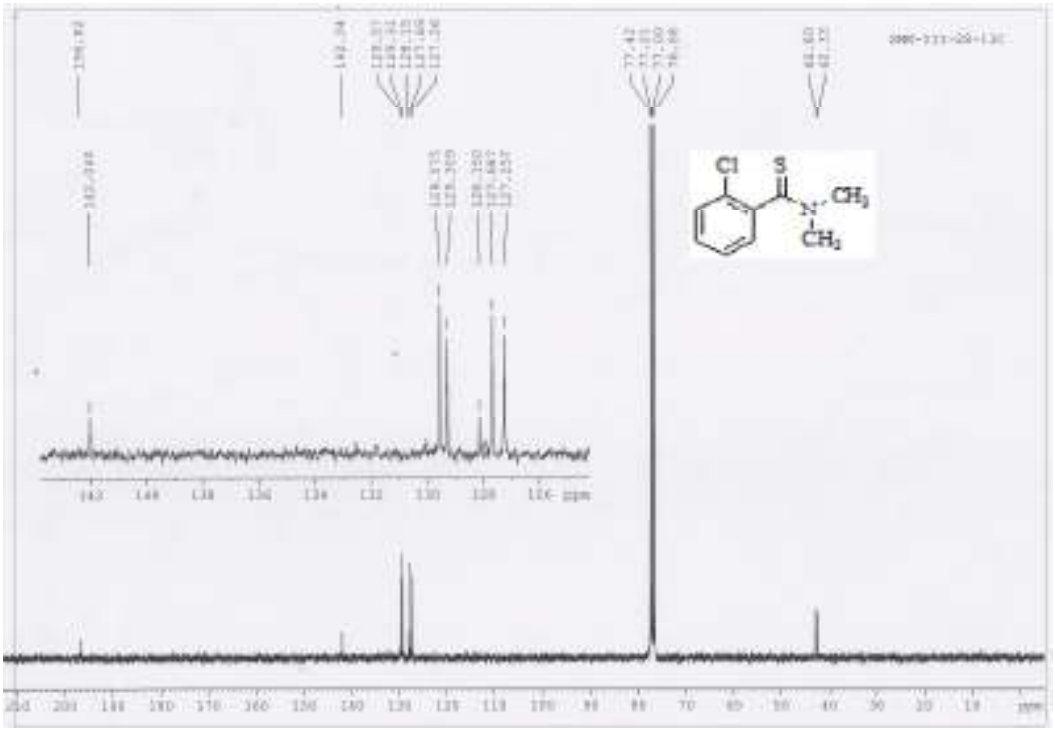

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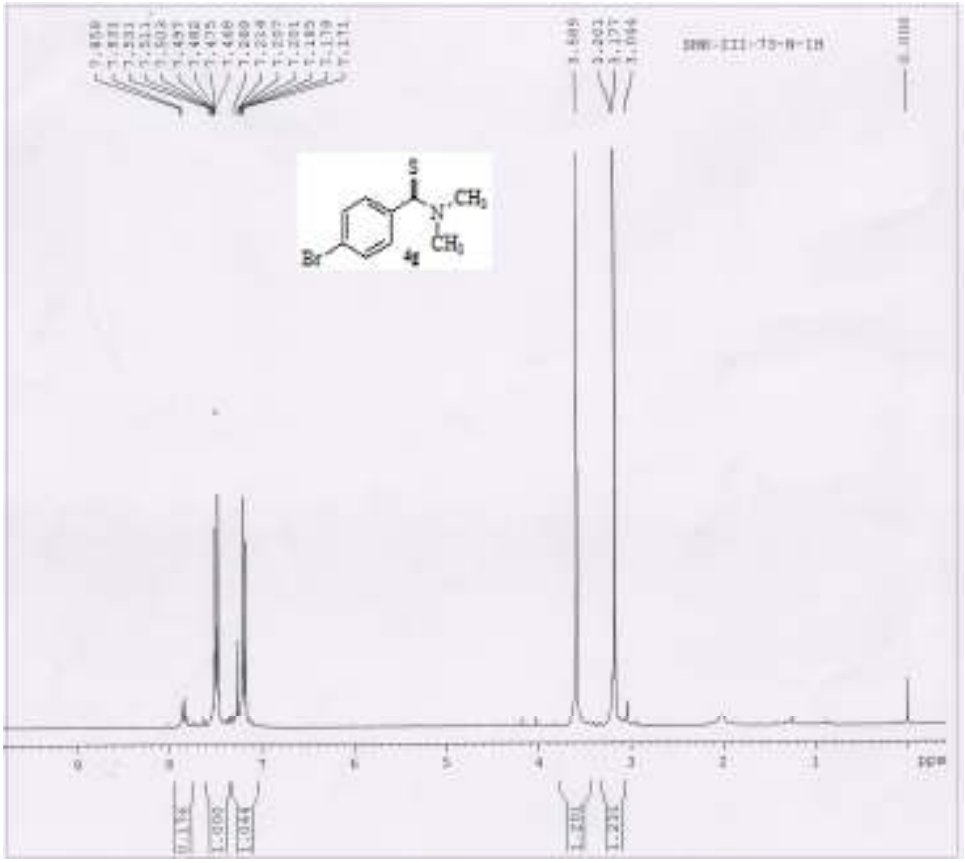

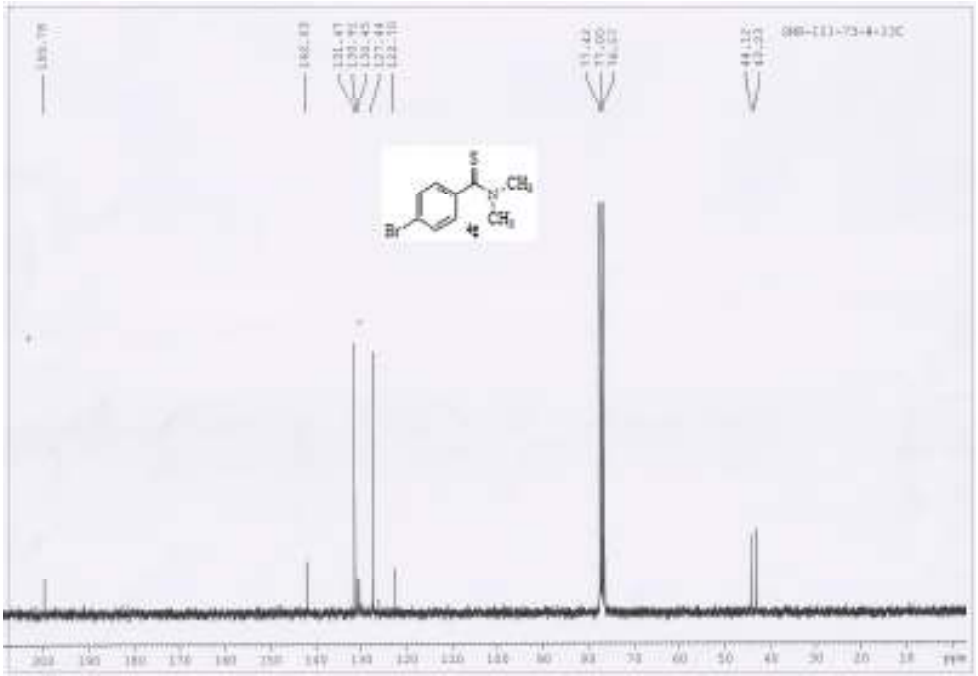

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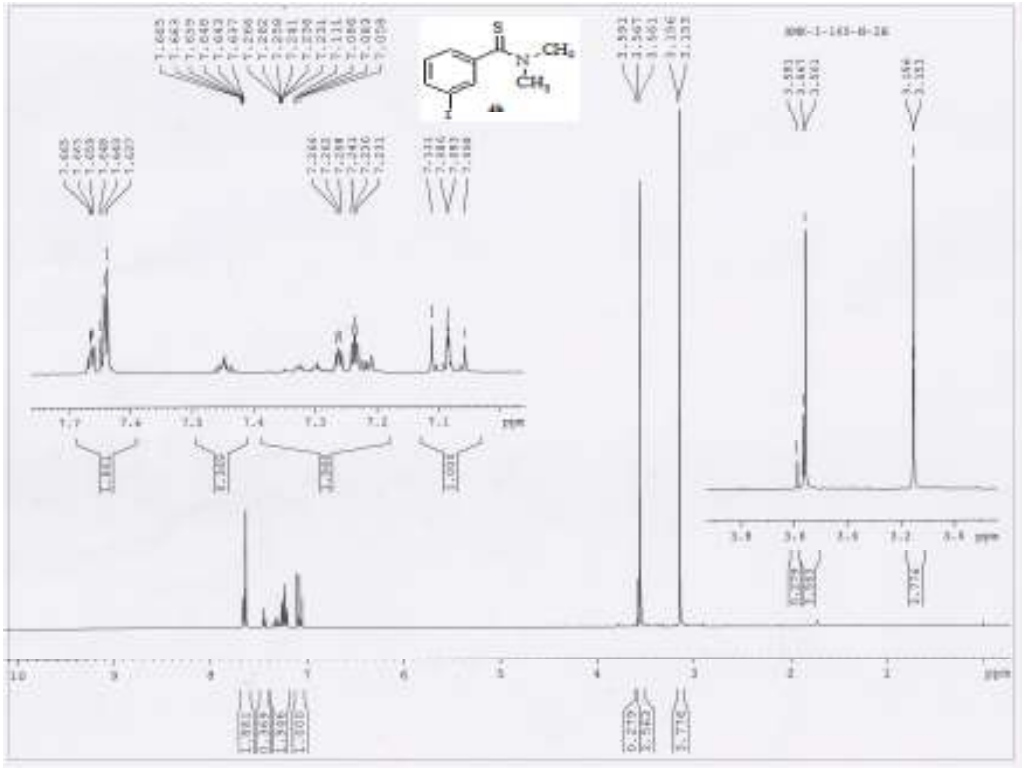

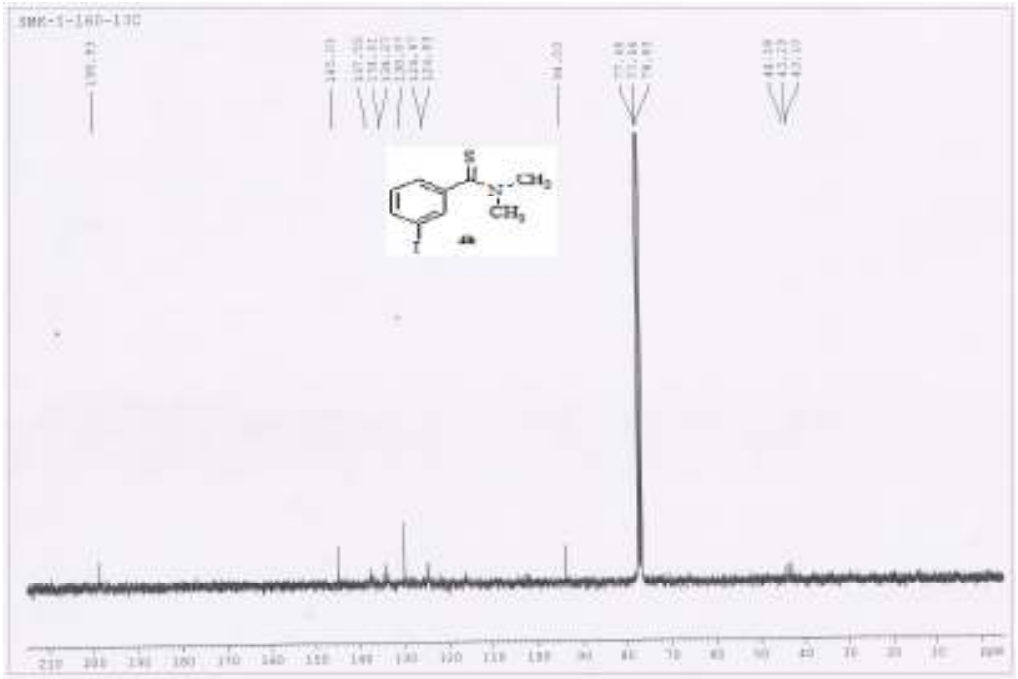

Table 2; entry 9