

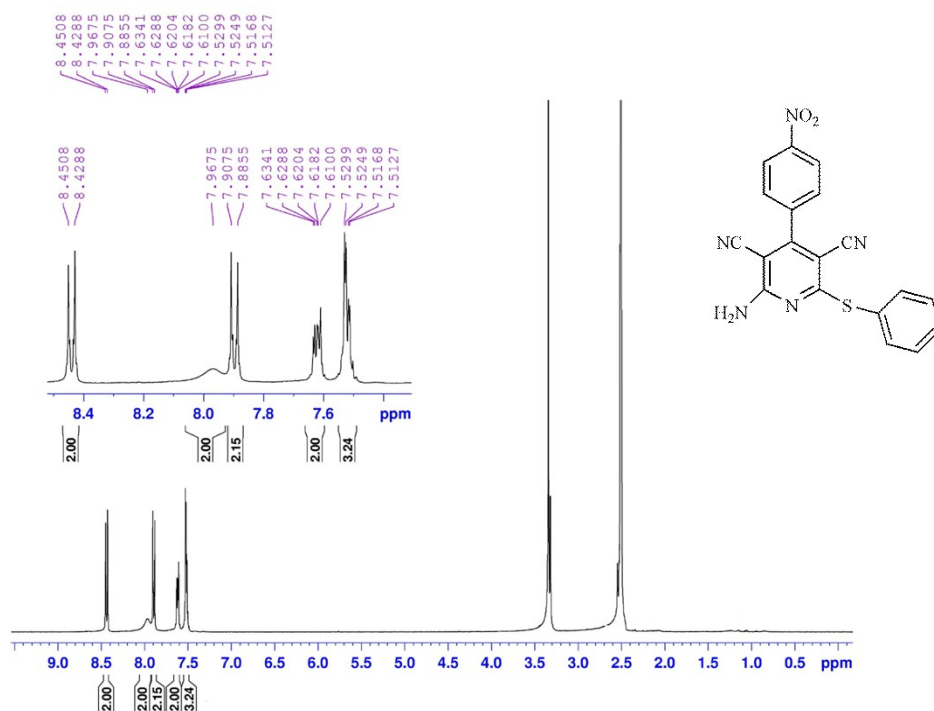
Supporting information

Propylphosphonium hydrogen carbonate ionic liquid supported on nano-silica as a reusable catalyst for the efficient multicomponent synthesis of fully substituted pyridines and *bis*-pyridines

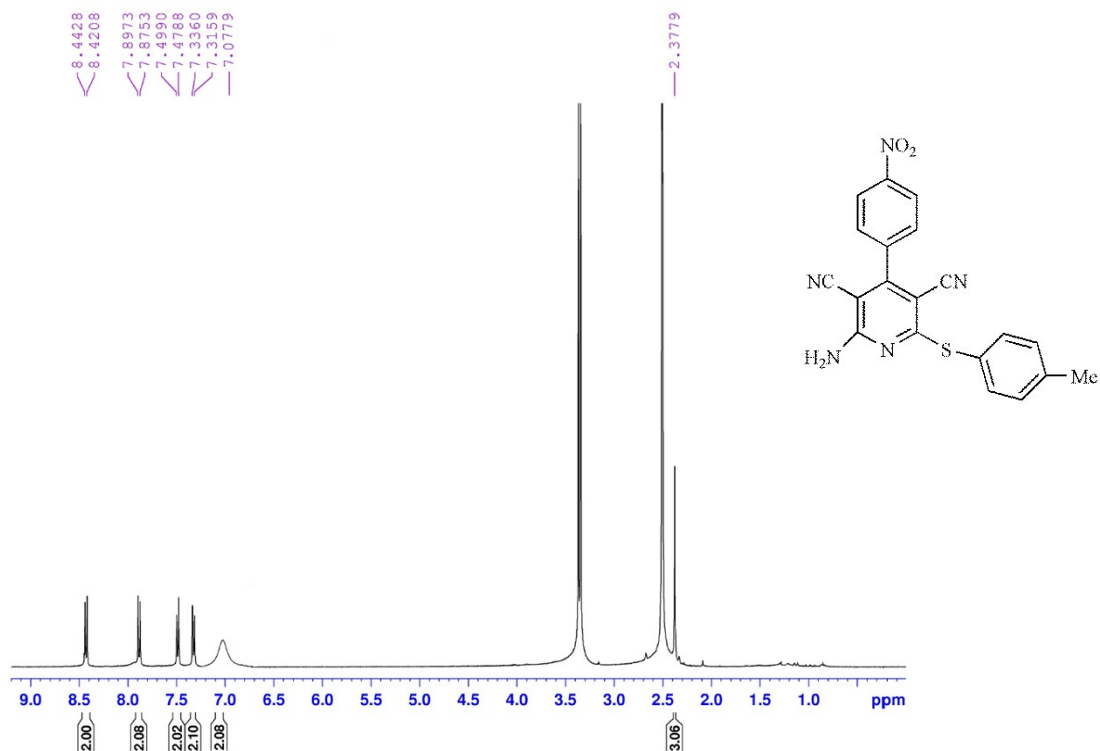
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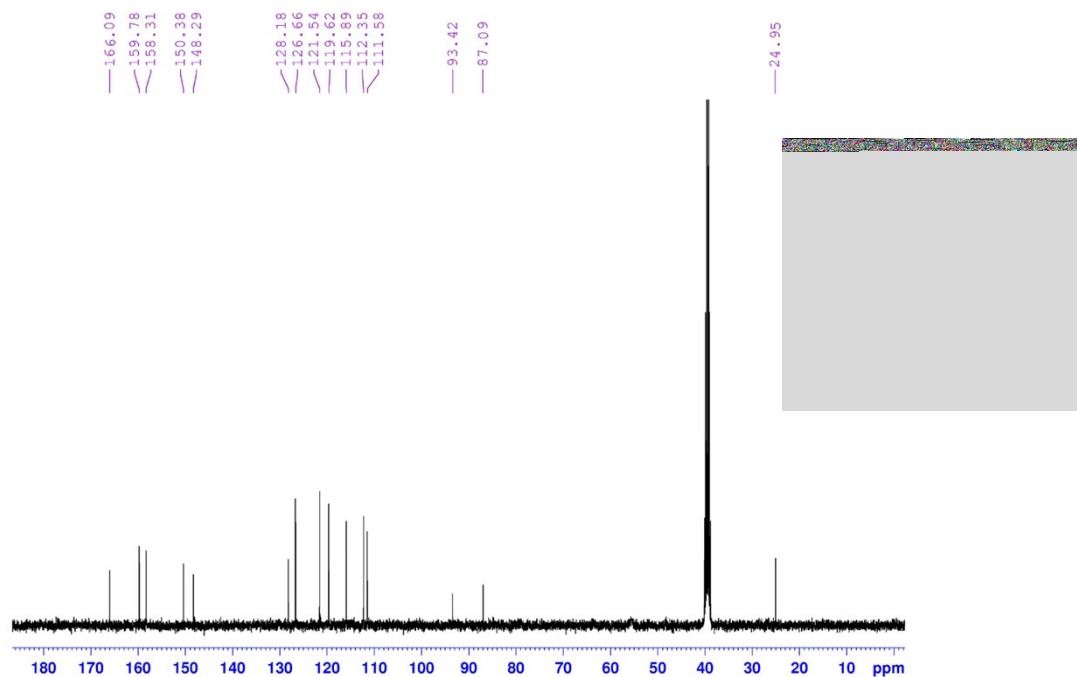
Spectroscopic data of products:
¹H NMR and ¹³C NMR spectra of the products



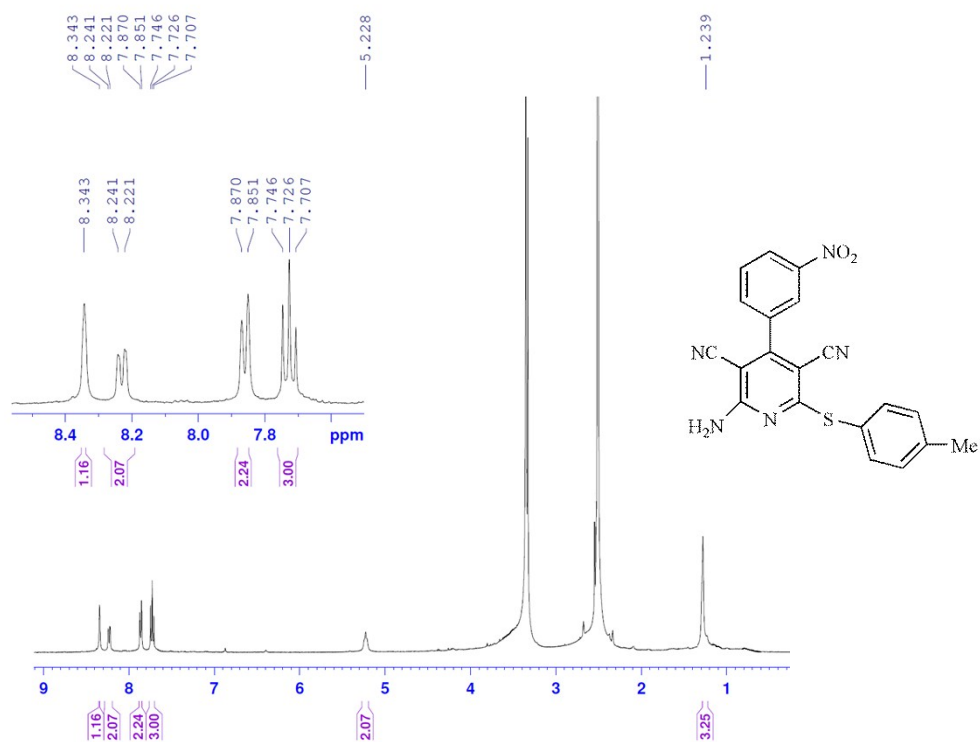
2-Amino-4-(4-nitrophenyl)-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3a); ¹H NMR (400 MHz, DMSO-*d*₆)



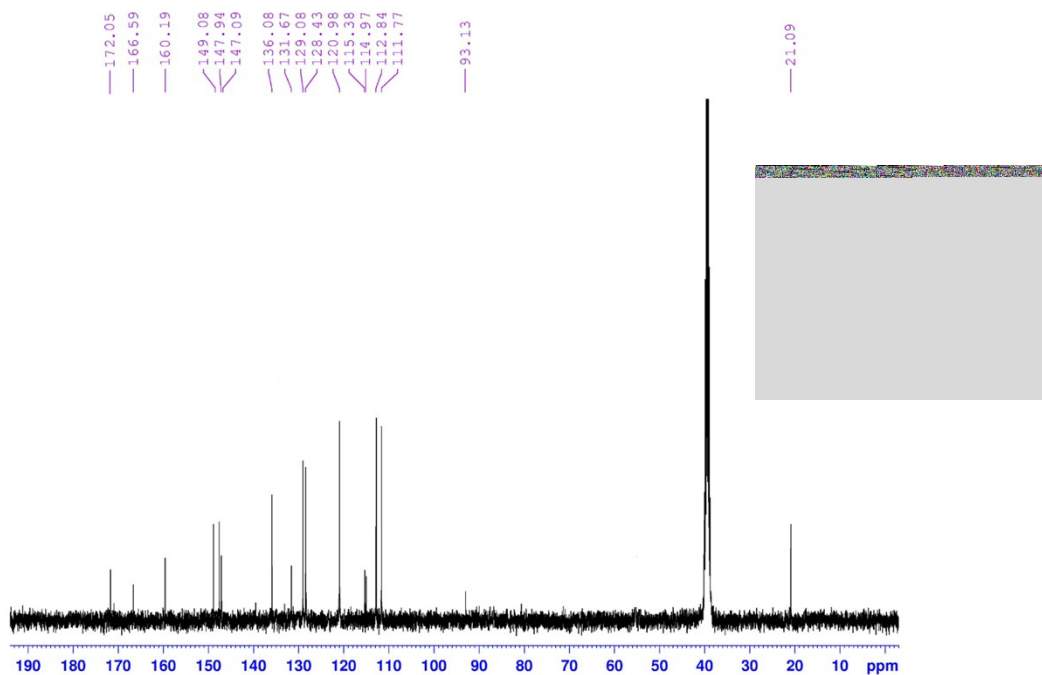
2-Amino-4-(4-nitrophenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3b); ¹H NMR (400 MHz, DMSO-*d*₆)



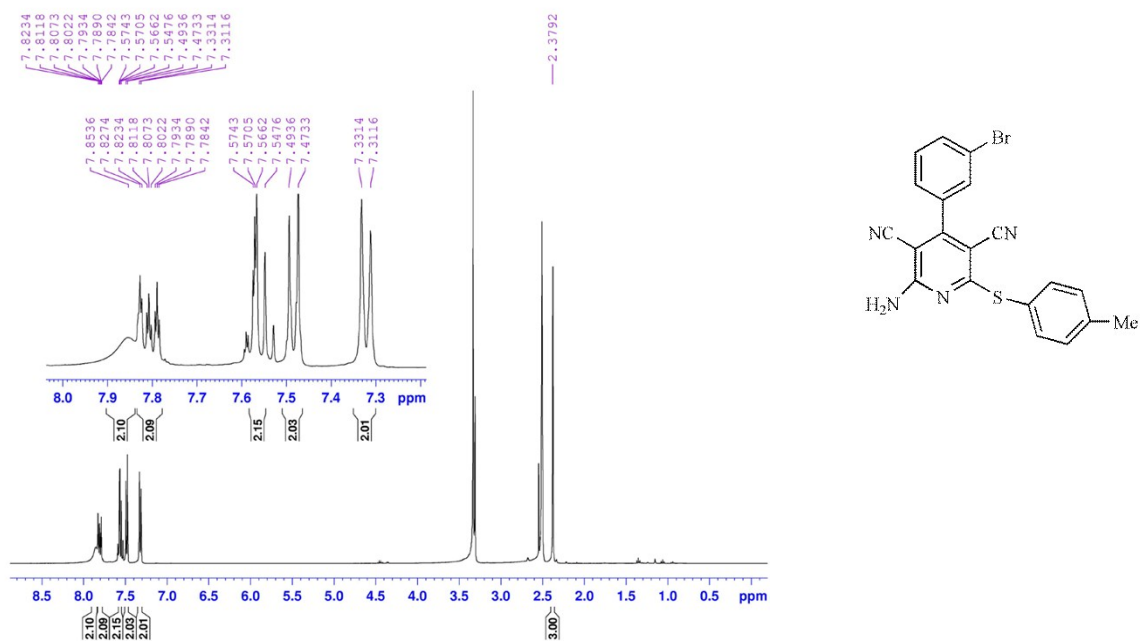
2-Amino-4-(4-nitrophenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3b); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



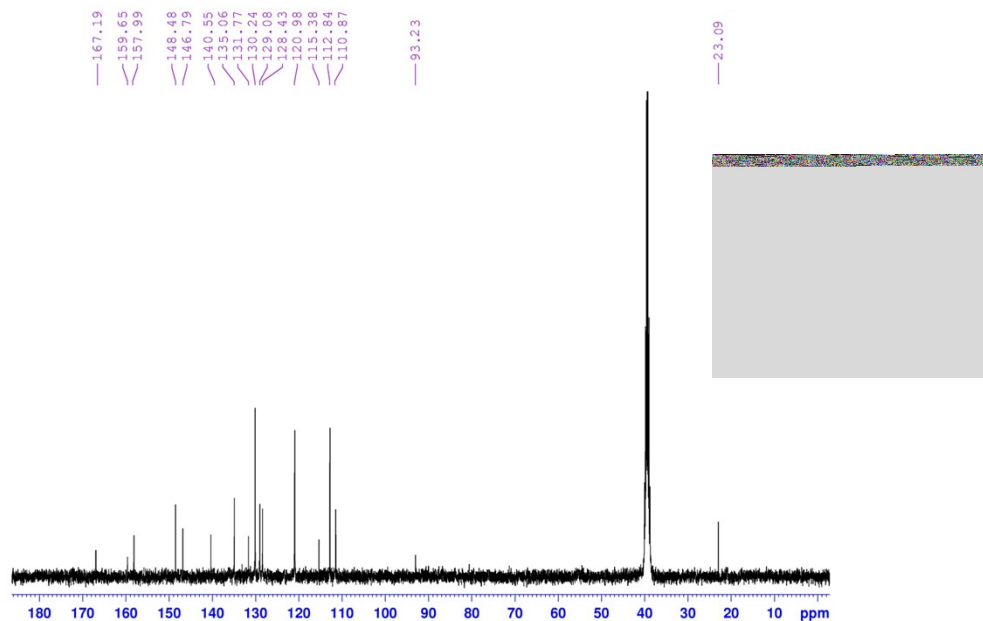
2-Amino-4-(3-nitrophenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3c); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



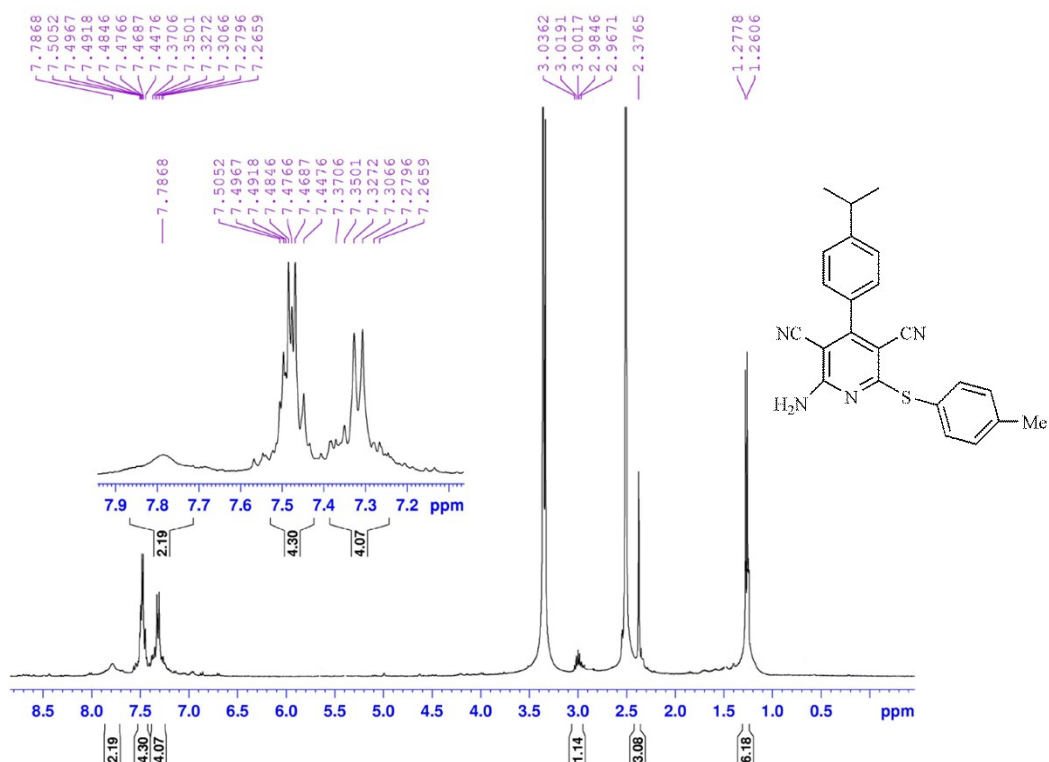
2-Amino-4-(3-nitrophenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3c); ¹³C NMR (100 MHz, DMSO-*d*₆)



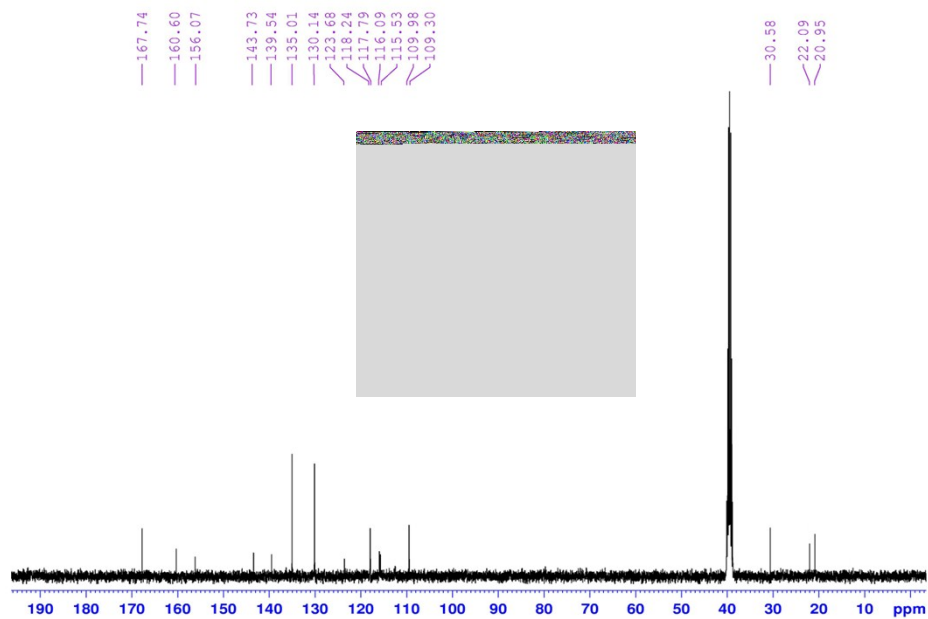
2-Amino-4-(3-bromophenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3d); ¹H NMR (400 MHz, DMSO-*d*₆)



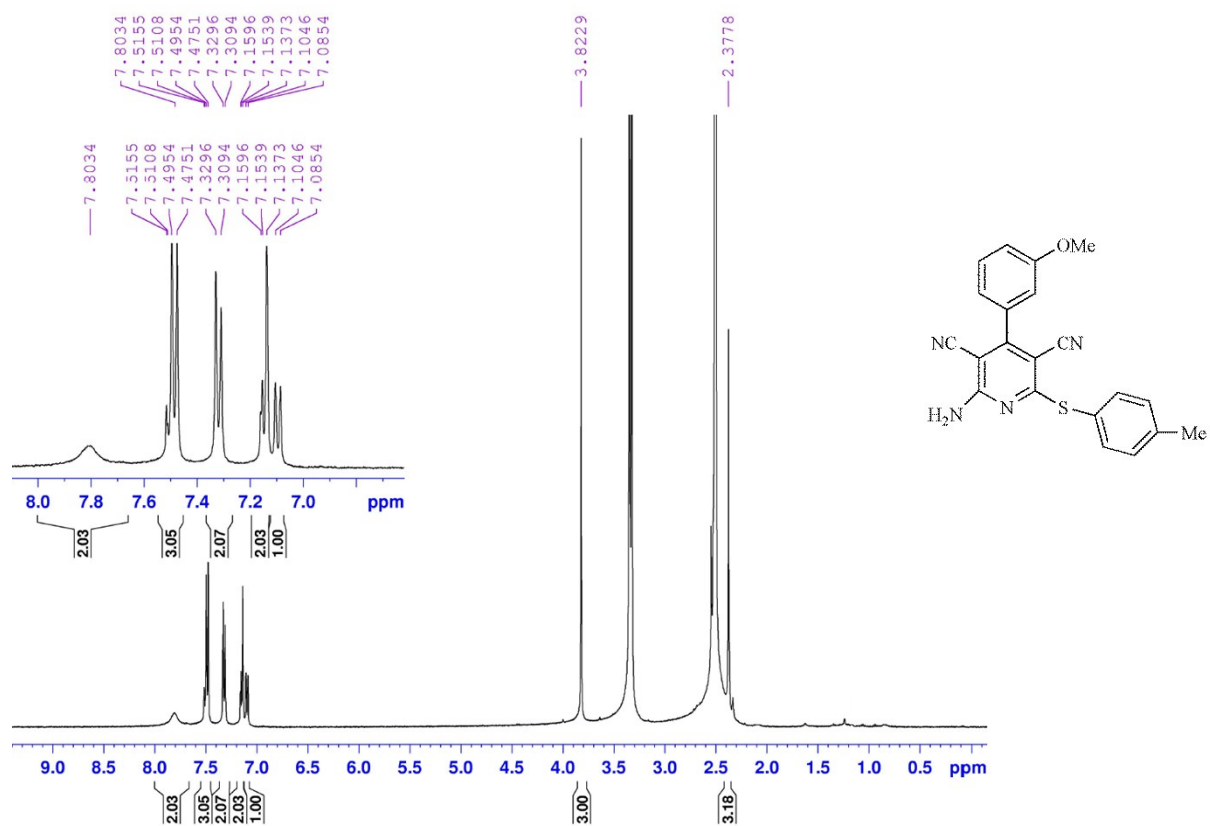
2-Amino-4-(3-bromophenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3d); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



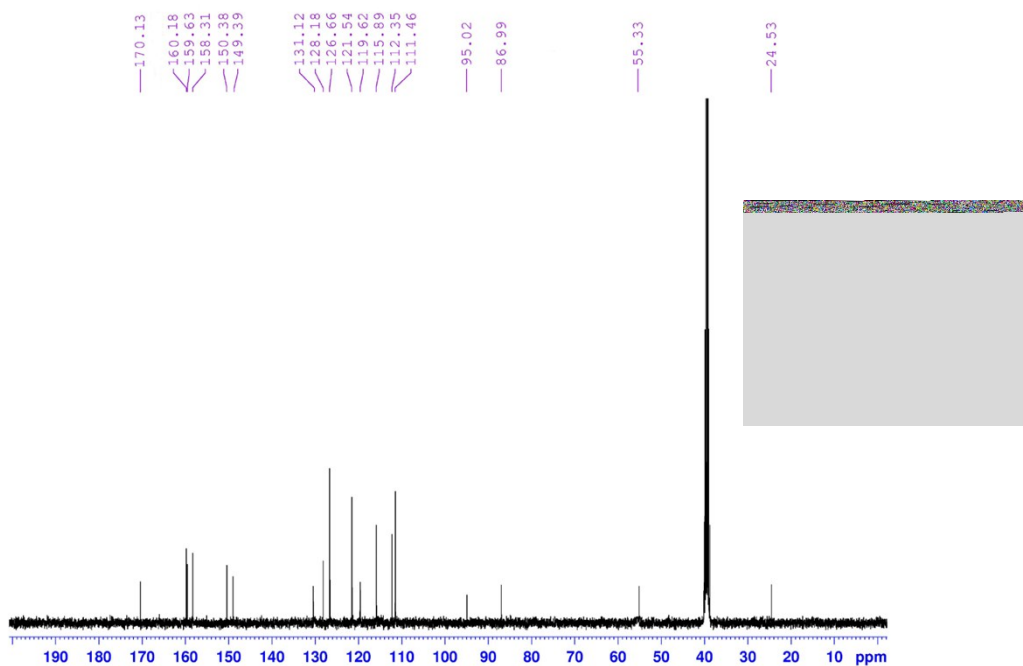
2-Amino-4-(4-isopropylphenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3e); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



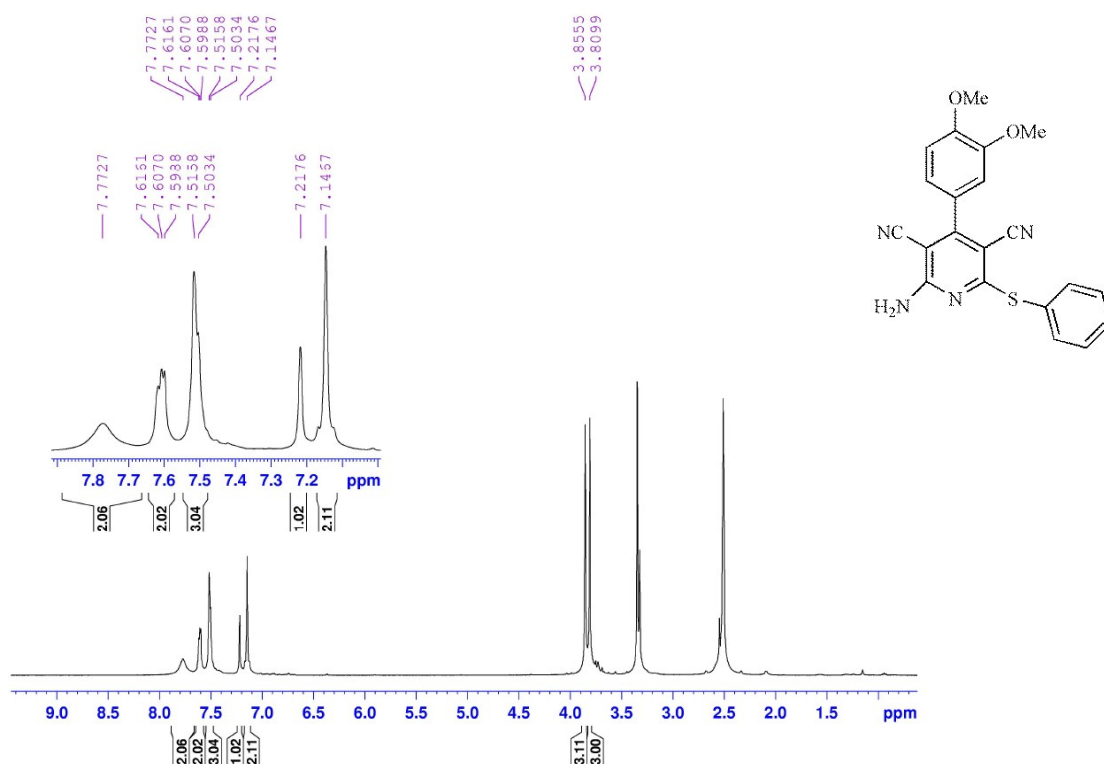
2-Amino-4-(4-isopropylphenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3e); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



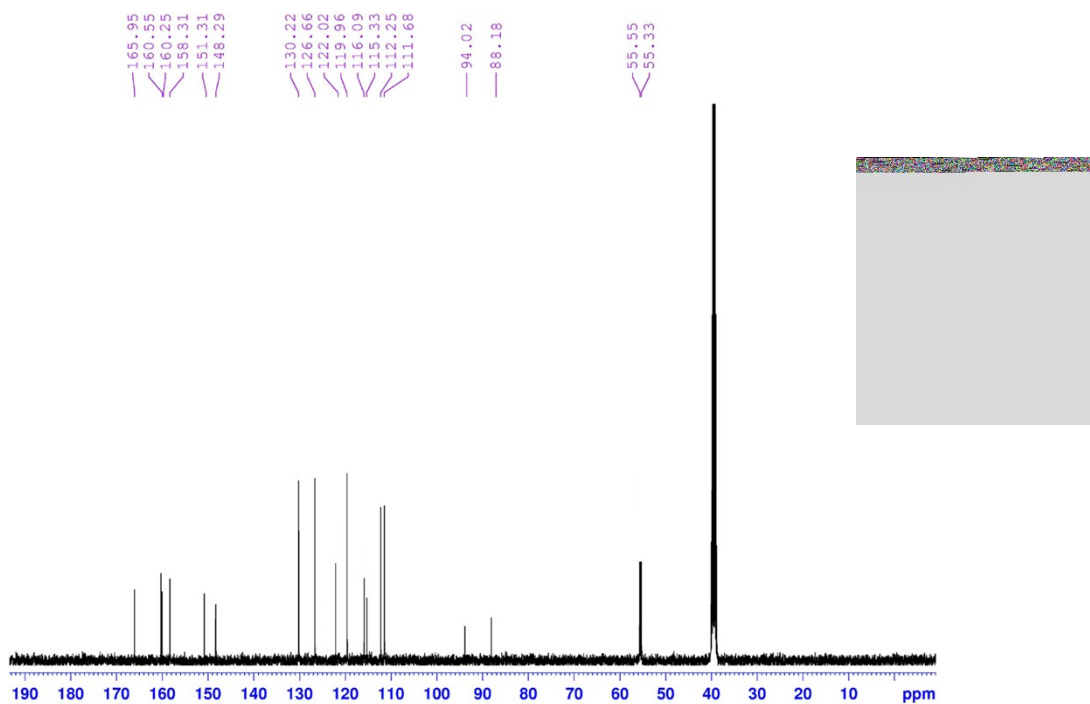
2-Amino-4-(3-methoxyphenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3f); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



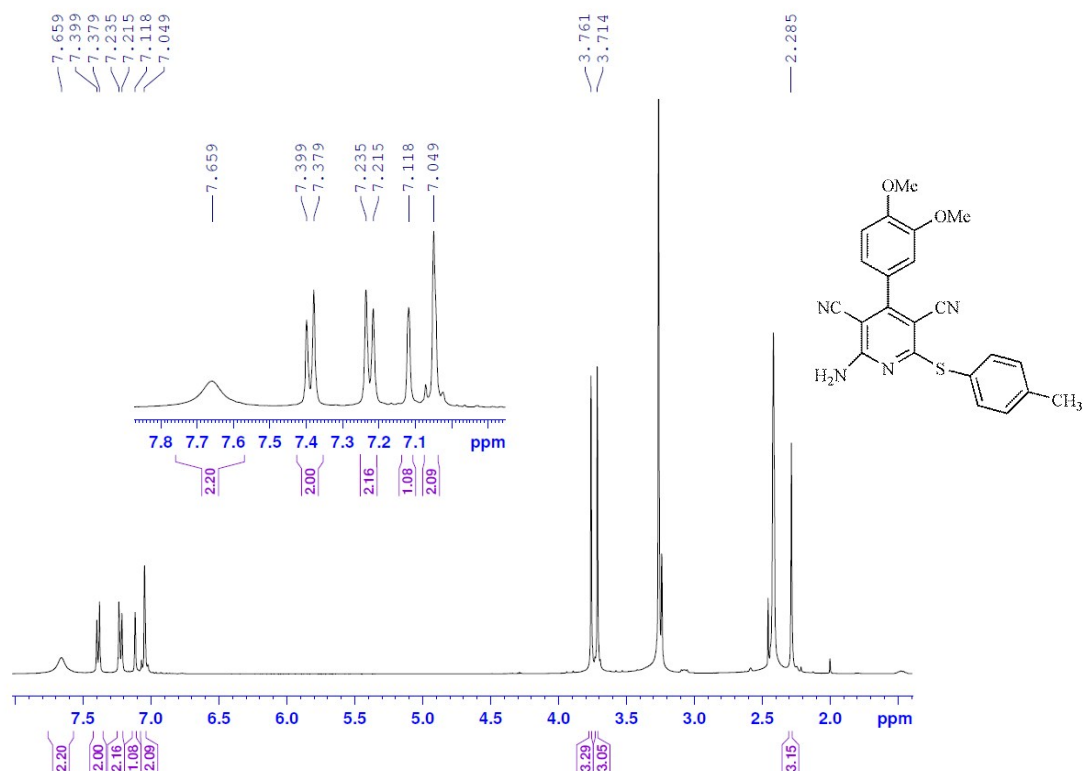
2-Amino-4-(3-methoxyphenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3f); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



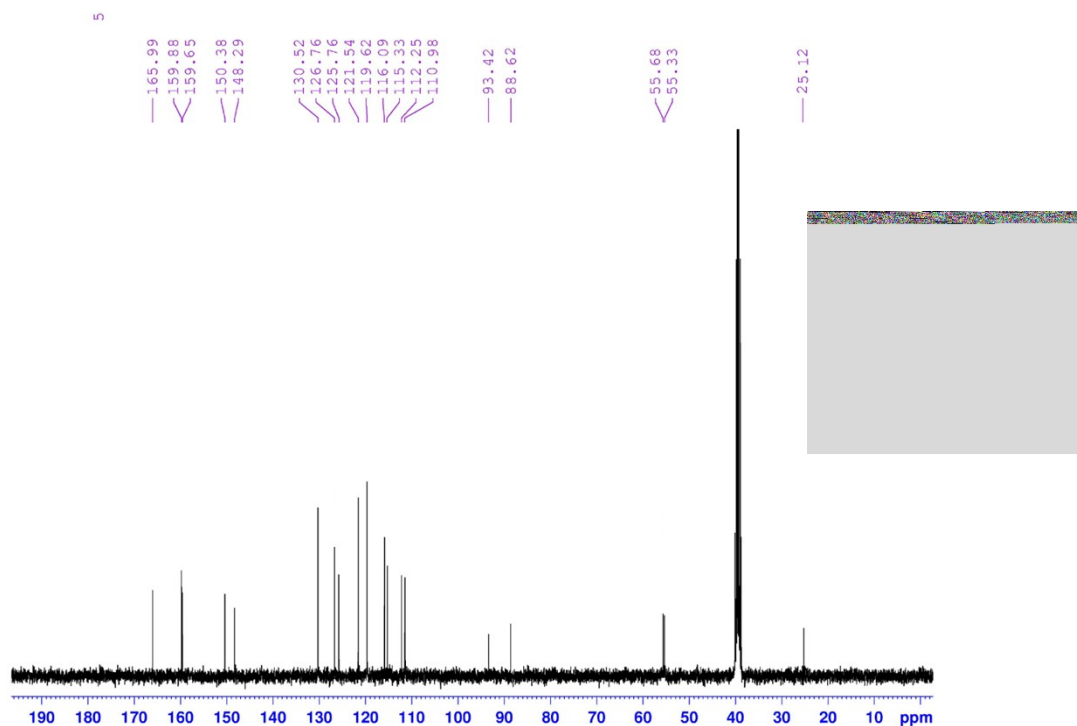
2-Amino-4-(3,4-dimethoxyphenyl)-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3g); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



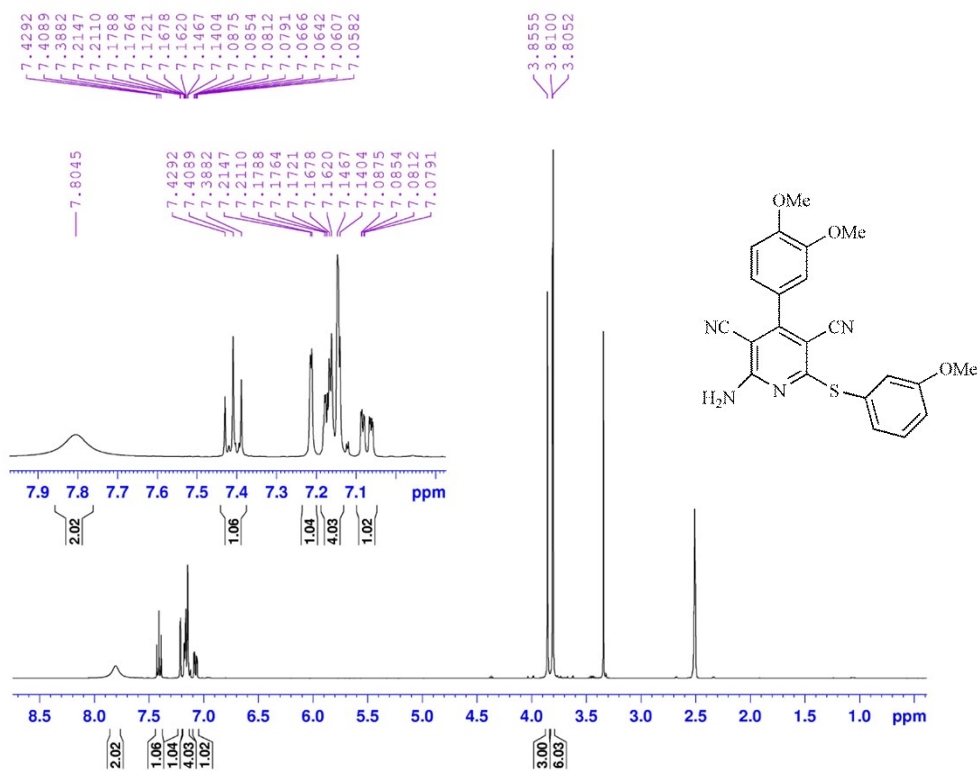
2-Amino-4-(3,4-dimethoxyphenyl)-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3g);
¹³C NMR (100 MHz, DMSO-*d*₆)



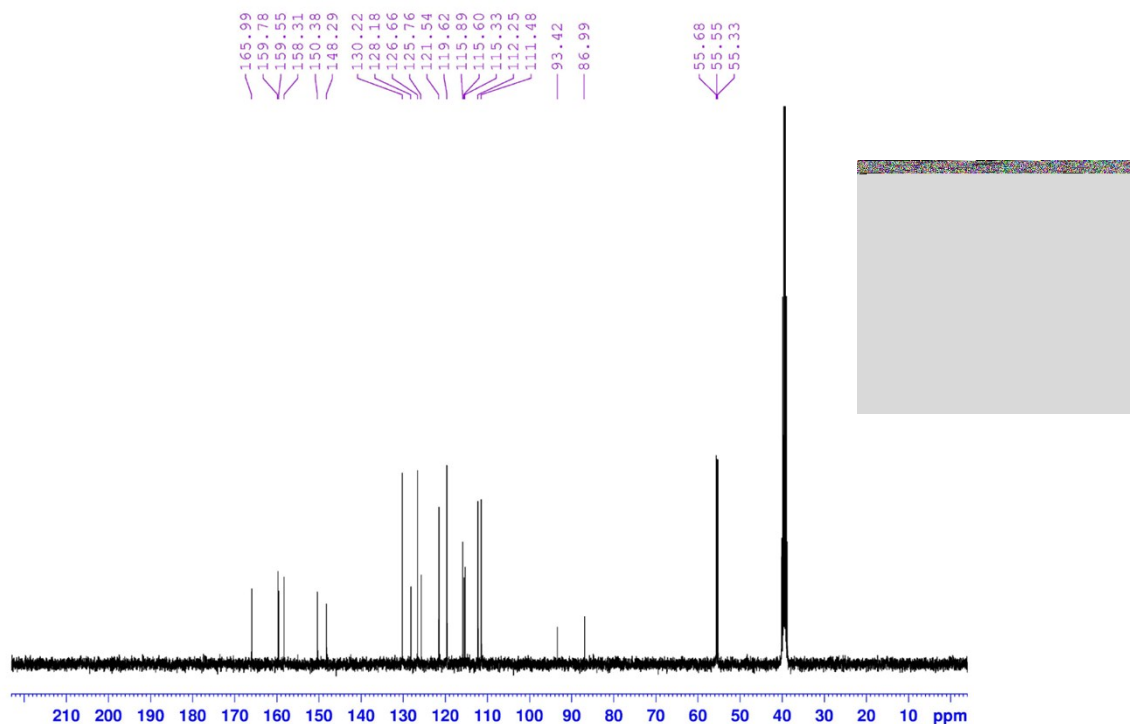
2-Amino-4-(3,4-dimethoxyphenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3h); ¹H NMR (400 MHz, DMSO-*d*₆)



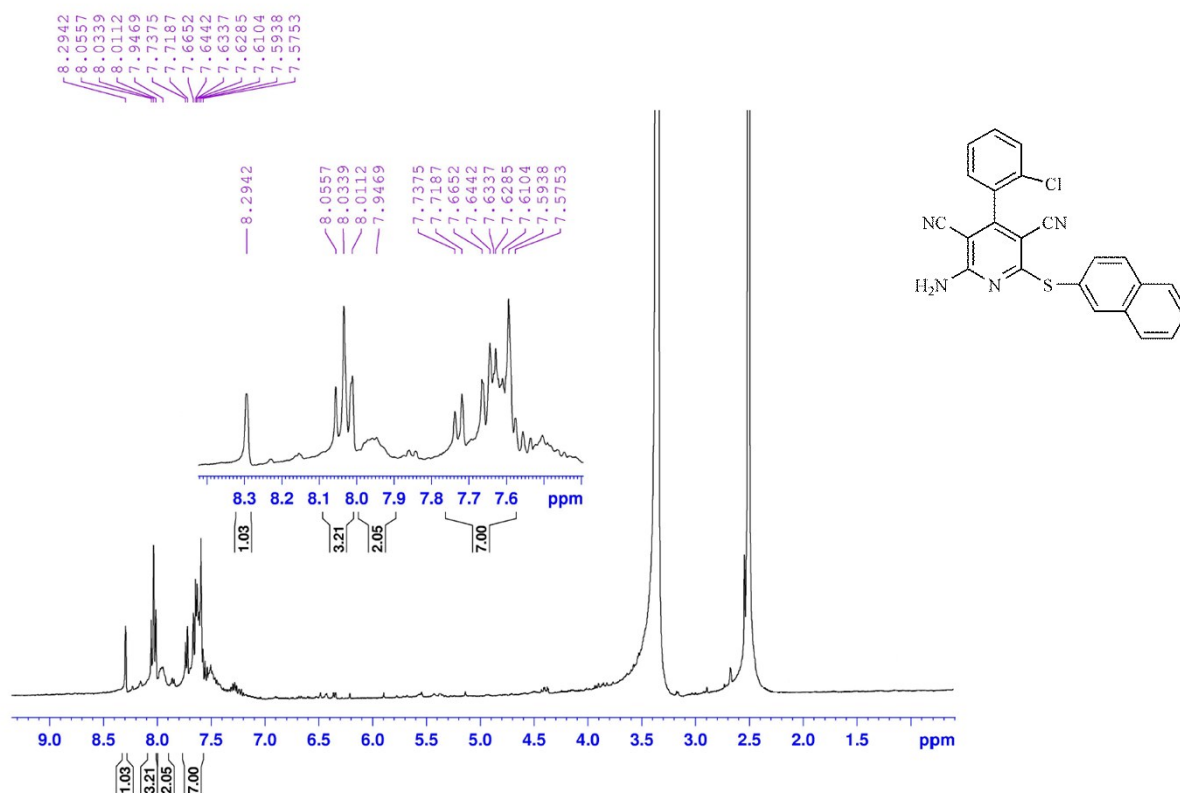
2-Amino-4-(3,4-dimethoxyphenyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3h); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



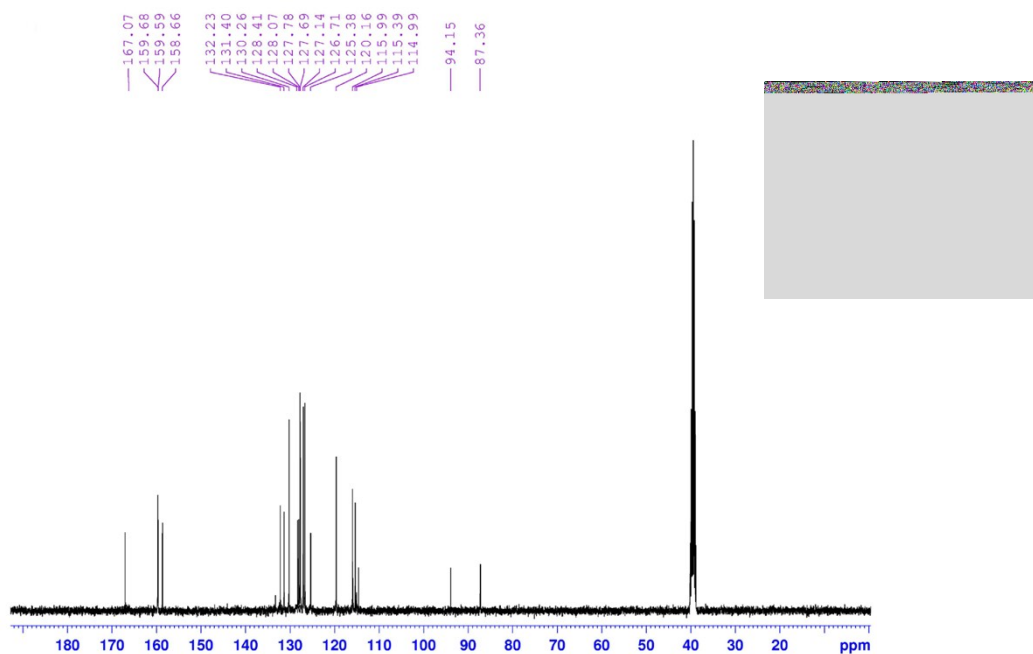
2-Amino-4-(3,4-dimethoxyphenyl)-6-(3-methoxyphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3i); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



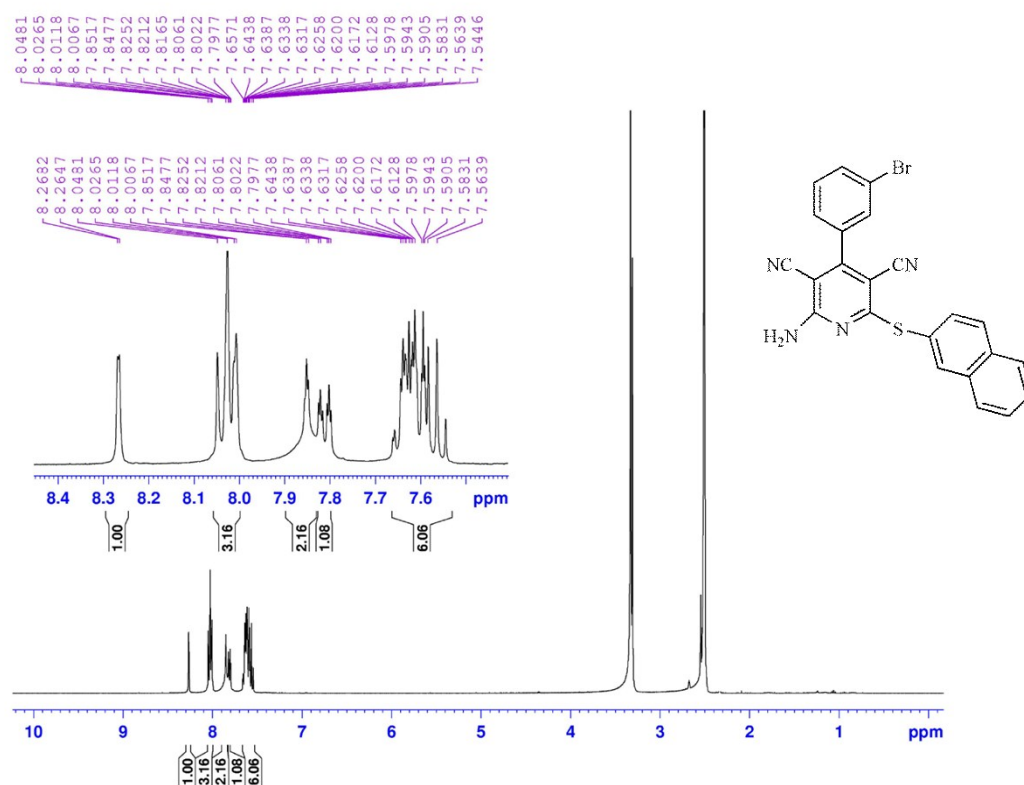
2-Amino-4-(3,4-dimethoxyphenyl)-6-(3-methoxyphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3i); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



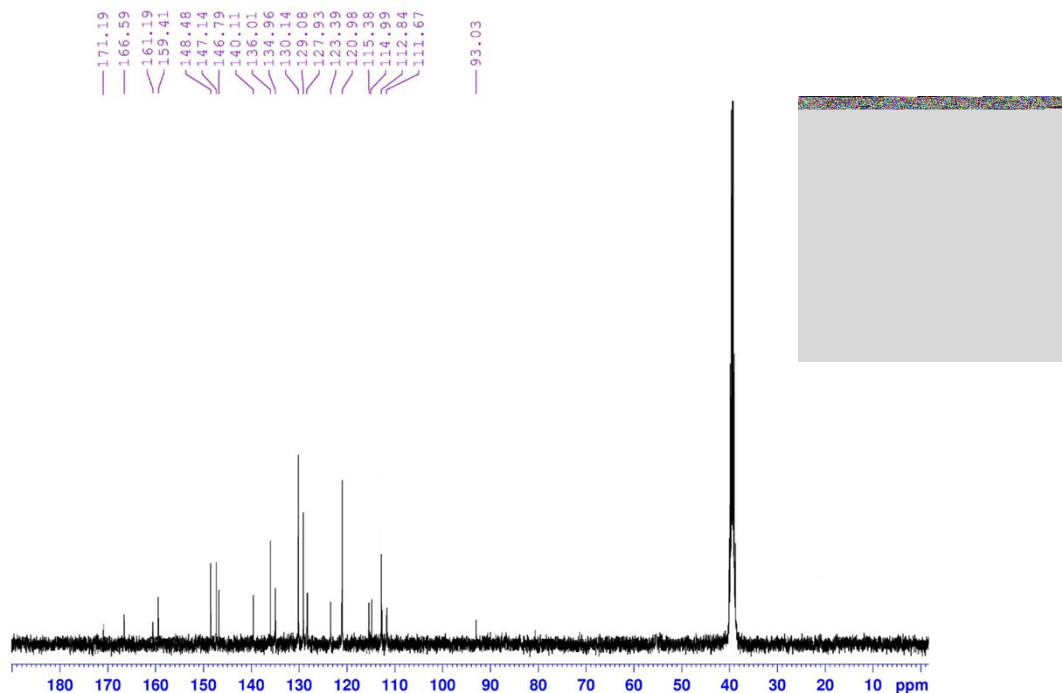
2-Amino-4-(2-chlorophenyl)-6-(β -naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3j); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



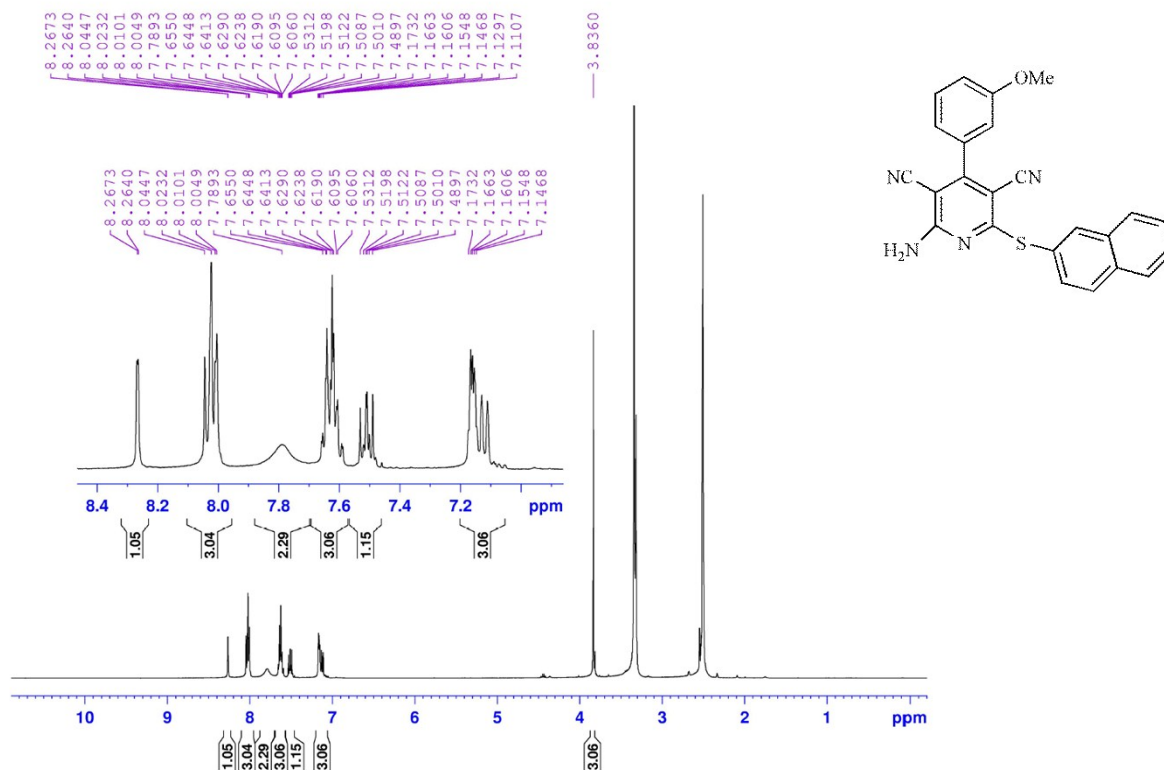
2-Amino-4-(2-chlorophenyl)-6-(β -naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3j); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$)



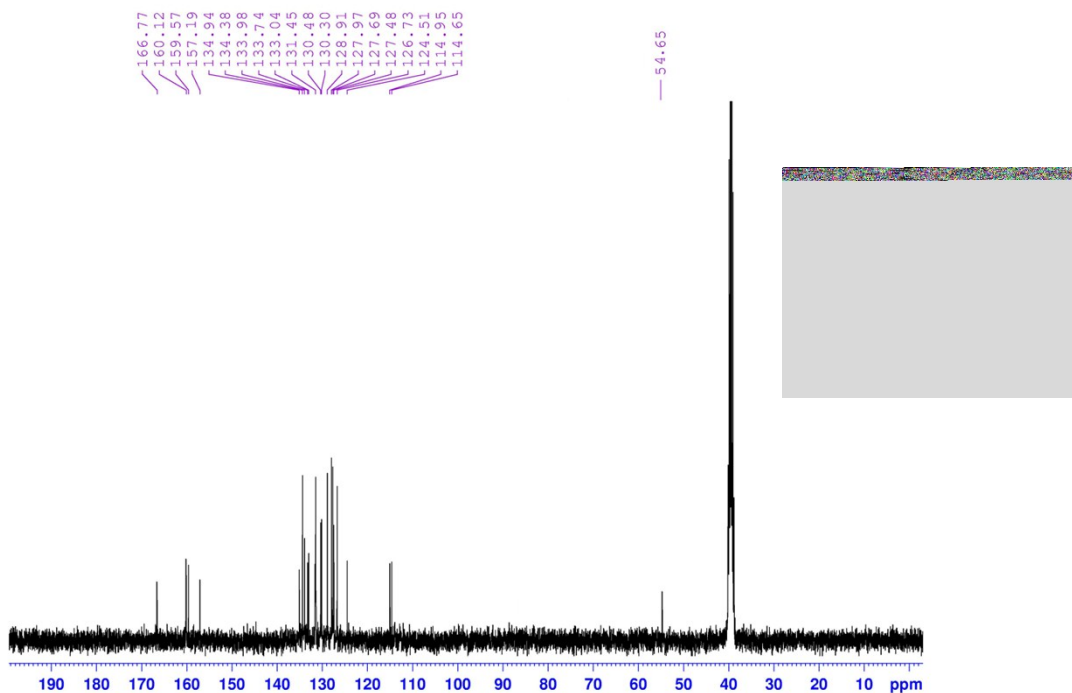
2-Amino-4-(3-bromophenyl)-6-(β -naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3k); ^1H NMR (400 MHz, $\text{DMSO-}d_6$)



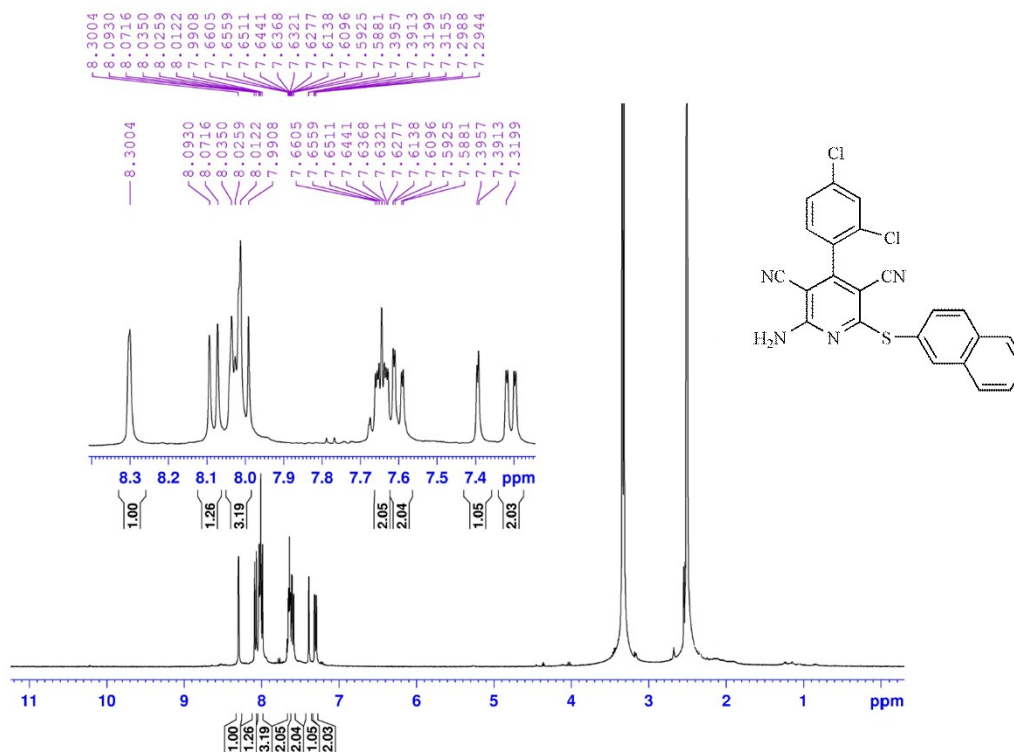
2-Amino-4-(3-bromophenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3k);
¹³C NMR (100 MHz, DMSO-*d*₆)



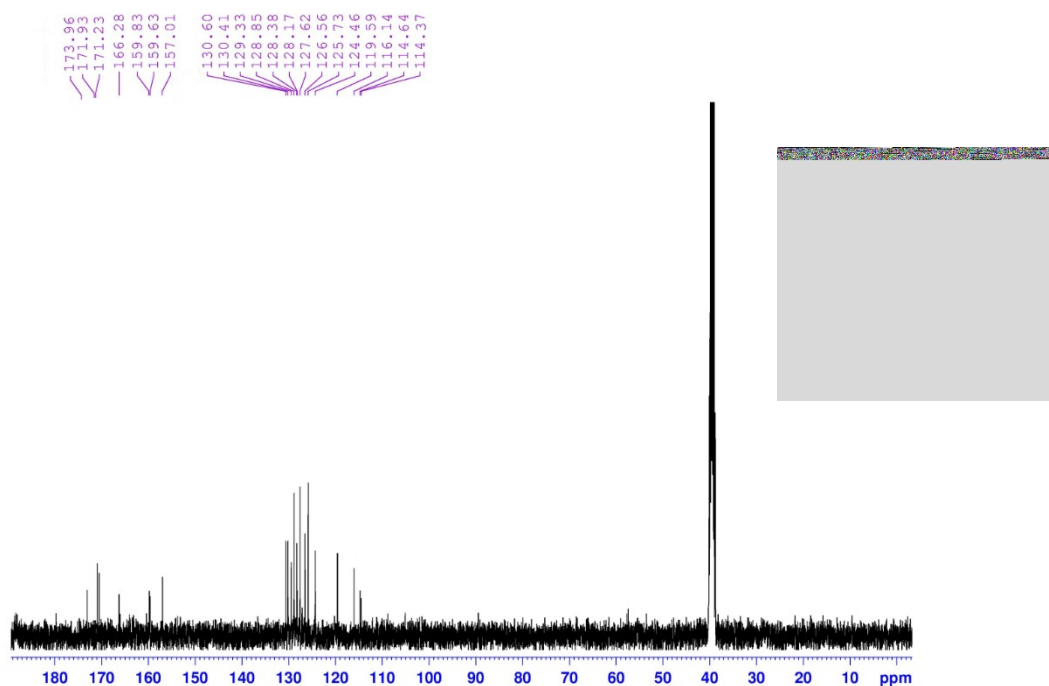
2-Amino-4-(3-methoxyphenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3l);
¹H NMR (400 MHz, DMSO-*d*₆)



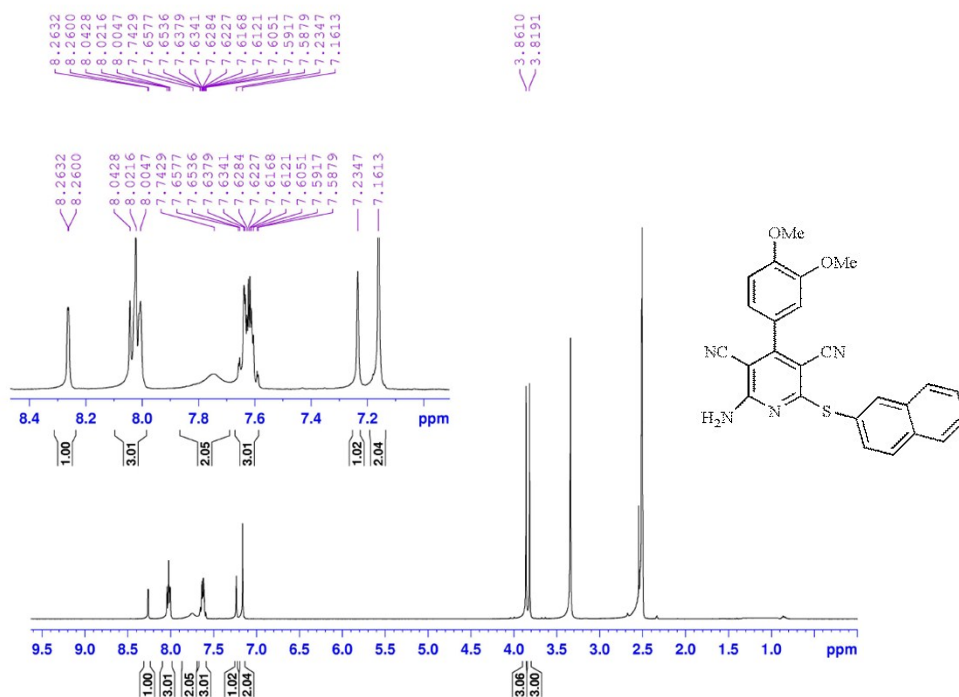
2-Amino-4-(3-methoxyphenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3l); ¹³C NMR (100 MHz, DMSO-*d*₆)



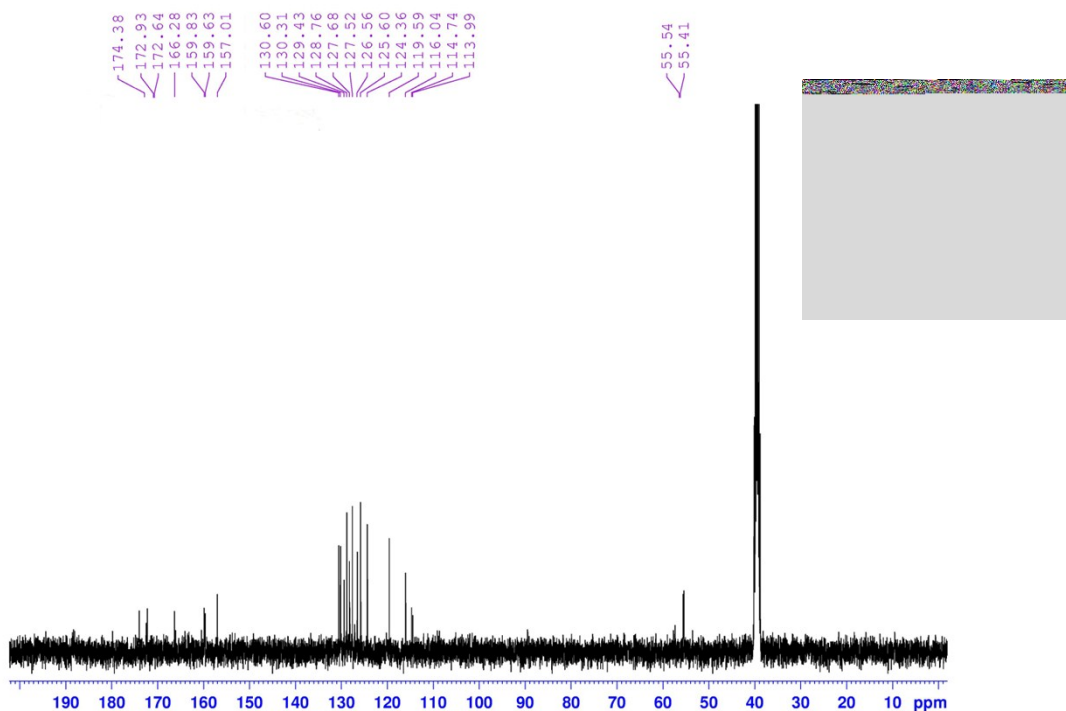
2-Amino-4-(2,4-dichlorophenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3m); ¹H NMR (400 MHz, DMSO-*d*₆)



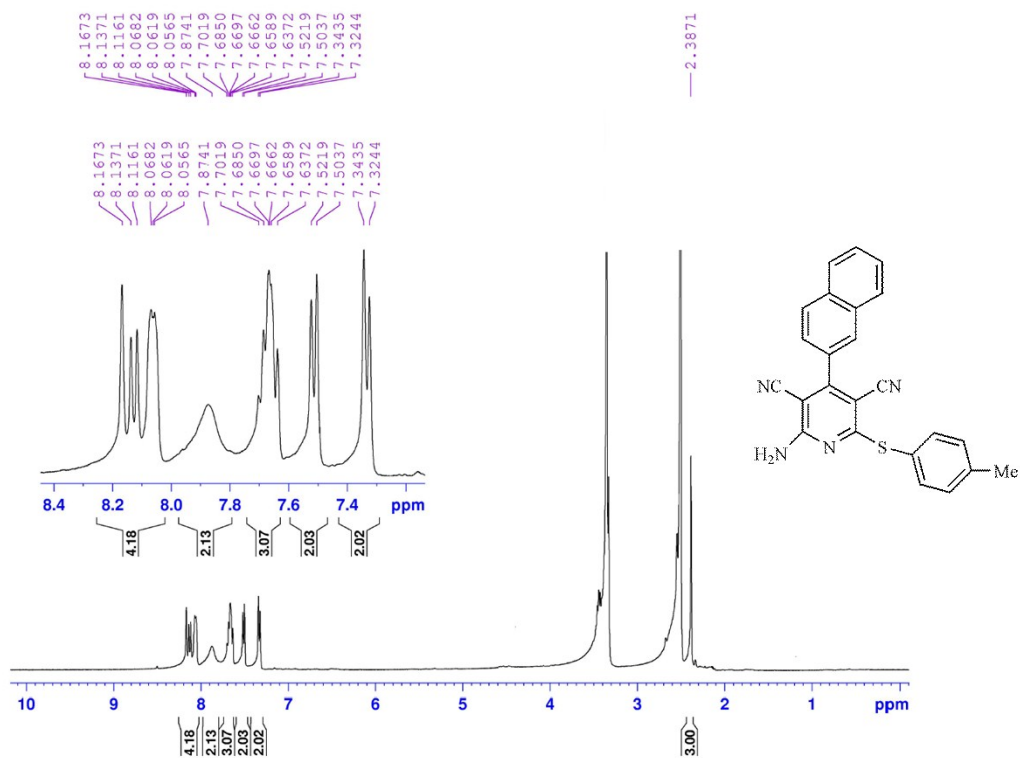
2-Amino-4-(2,4-dichlorophenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3m); ¹³C NMR (100 MHz, DMSO-*d*₆)



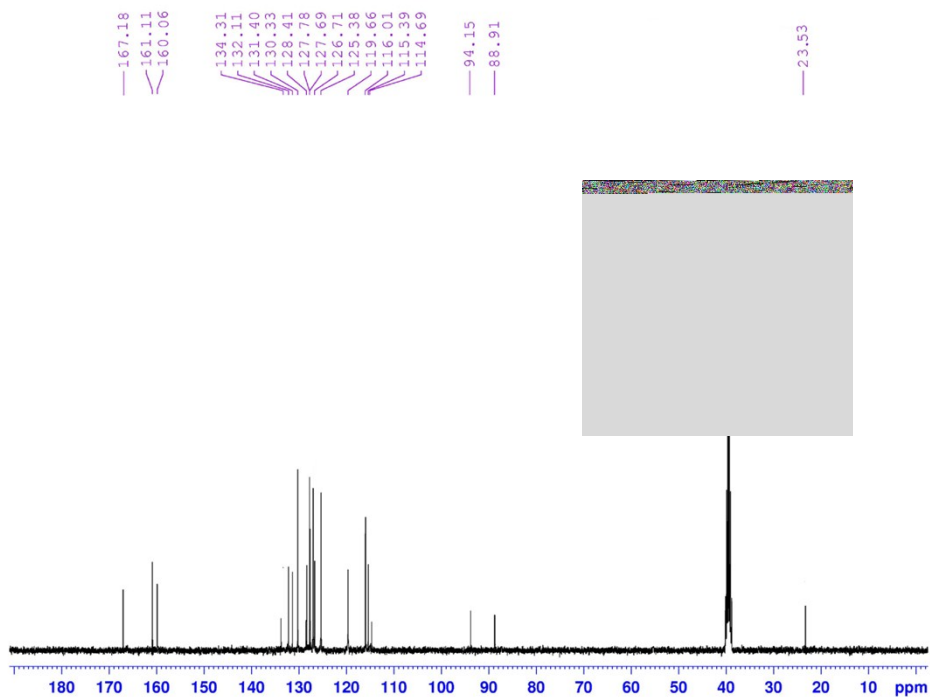
2-Amino-4-(3,4-dimethoxyphenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3n); ¹H NMR (400 MHz, DMSO-*d*₆)



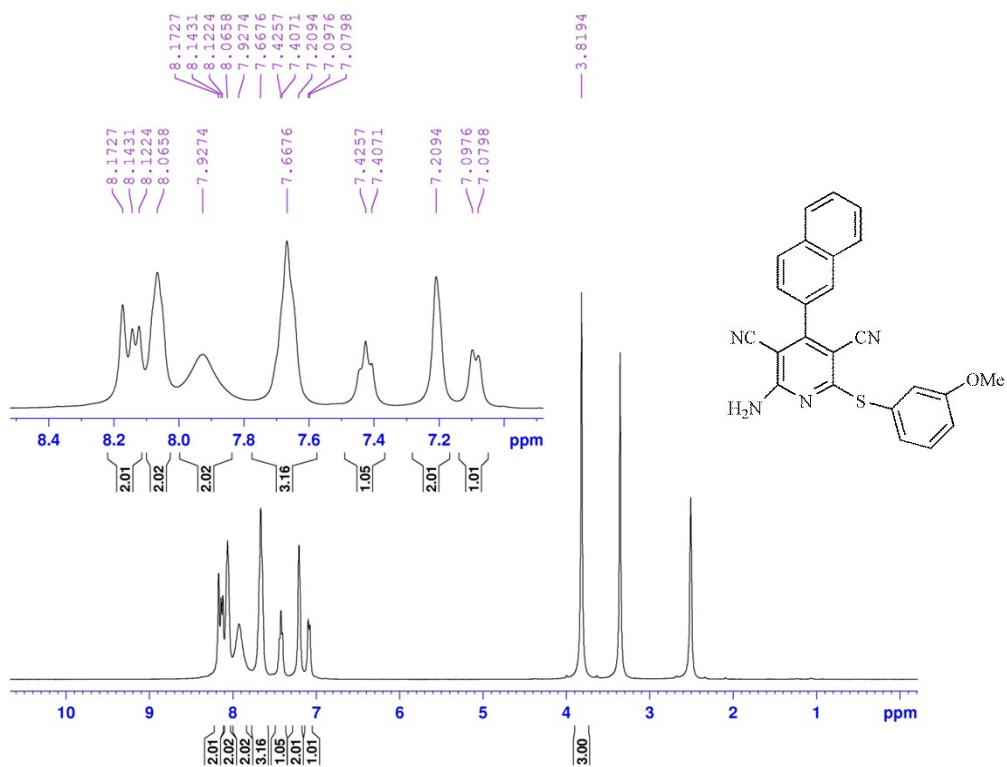
2-Amino-4-(3,4-dimethoxyphenyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3n); ¹³C NMR (100 MHz, DMSO-*d*₆)



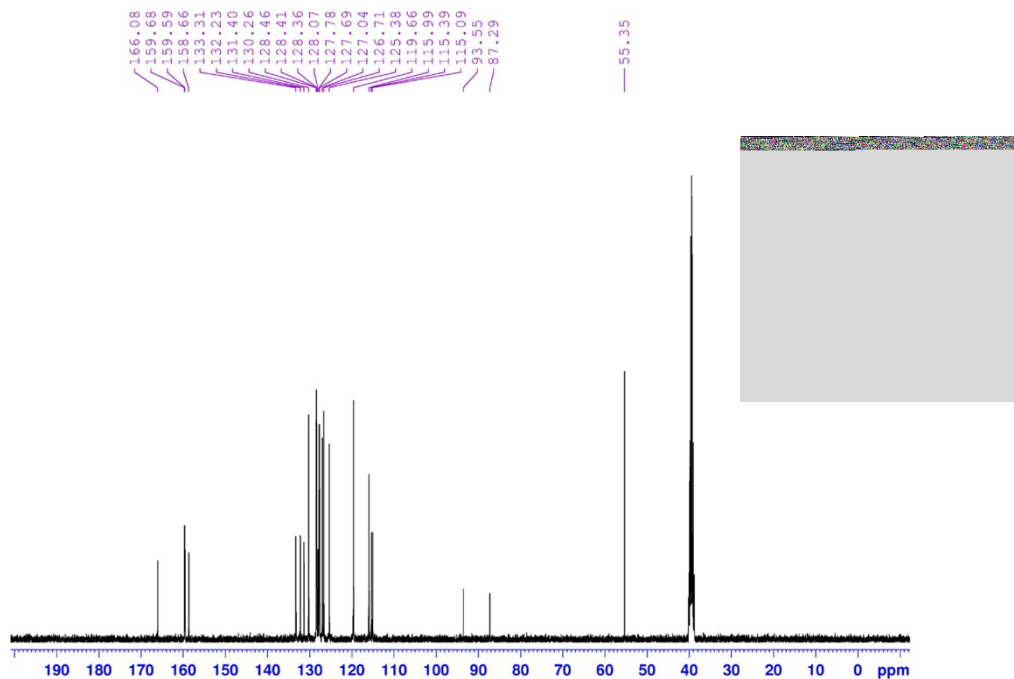
2-Amino-4-(β-naphthyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3o); ¹H NMR (400 MHz, DMSO-*d*₆)



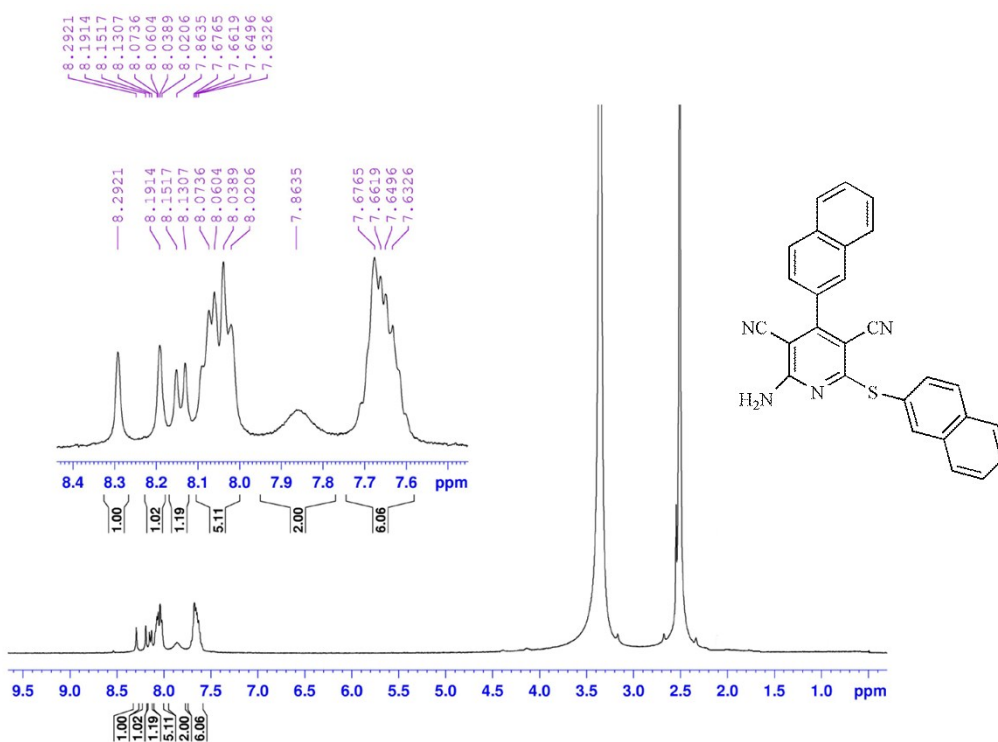
2-Amino-4-(β -naphthyl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3o);
 ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



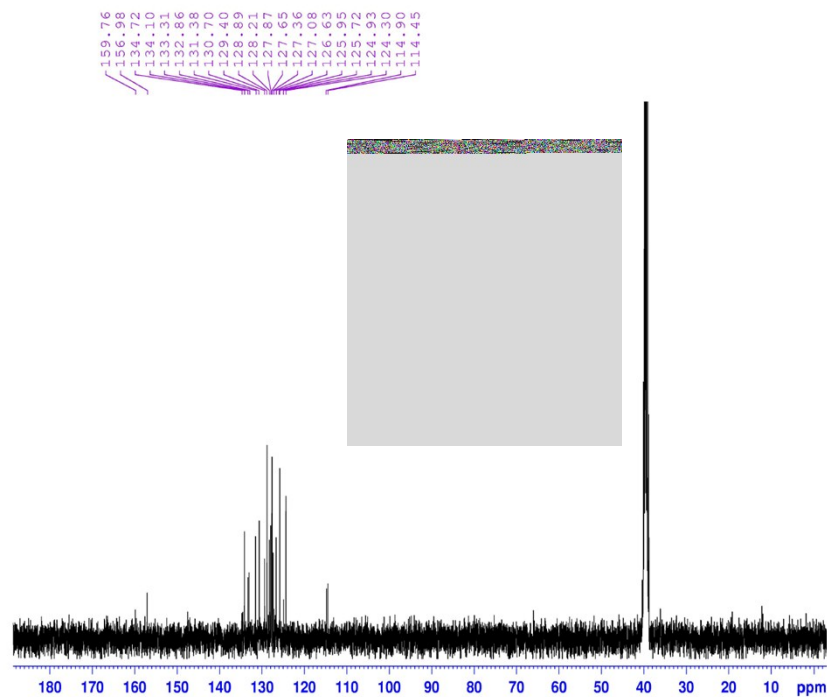
2-Amino-4-(β -naphthyl)-6-(3-methoxyphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3p);
 ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



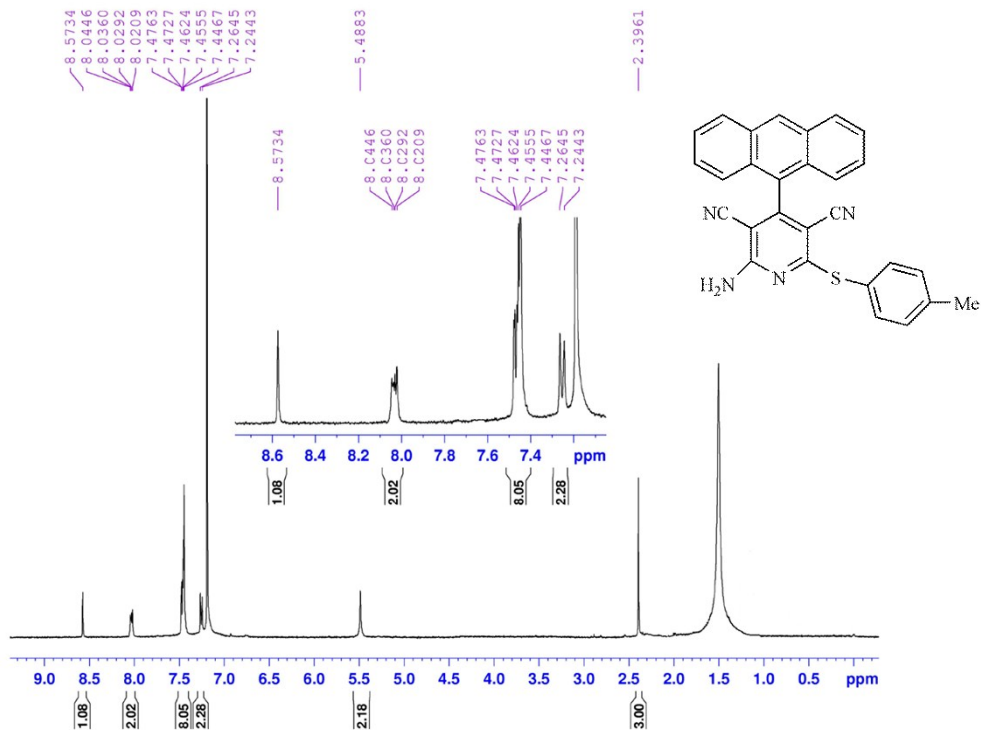
2-Amino-4-(β -naphthyl)-6-(3-methoxyphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3p); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$)



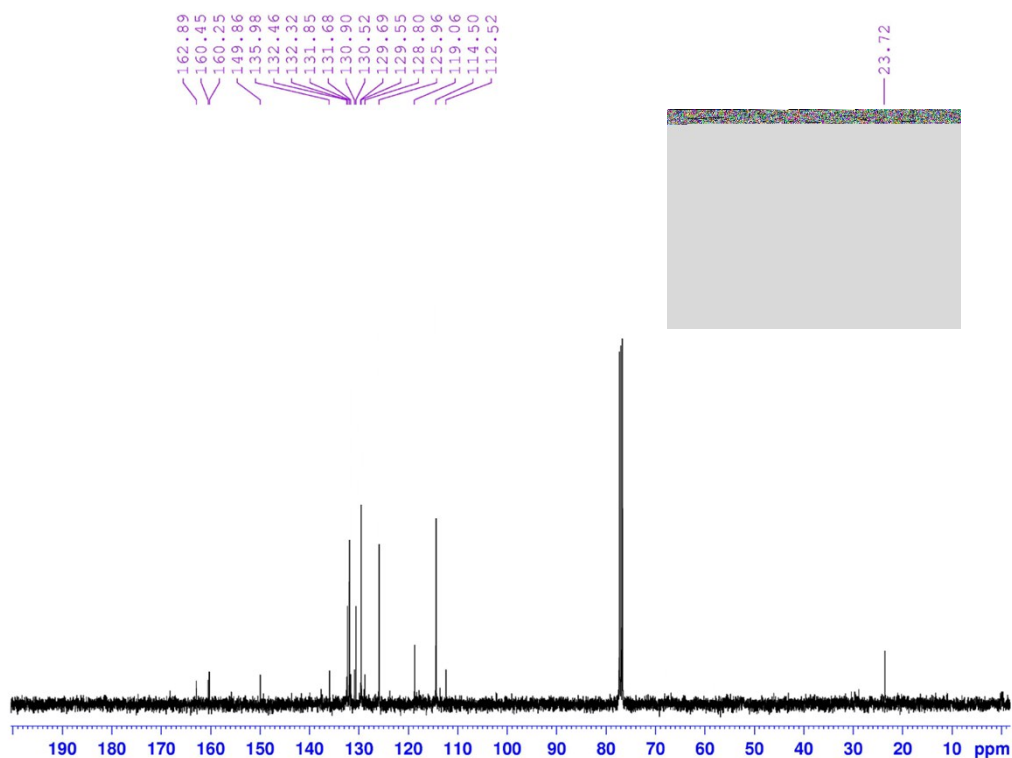
2-Amino-4-(β -naphthyl)-6-(β -naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3q); ^1H NMR (400 MHz, $\text{DMSO-}d_6$)



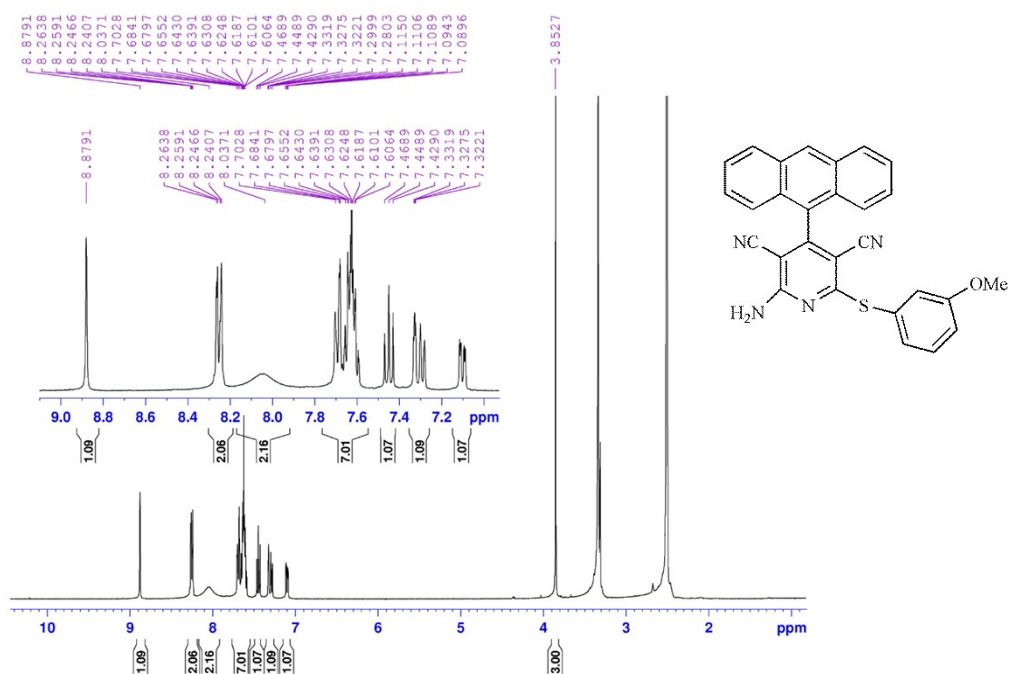
2-Amino-4-(β-naphthyl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3q); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



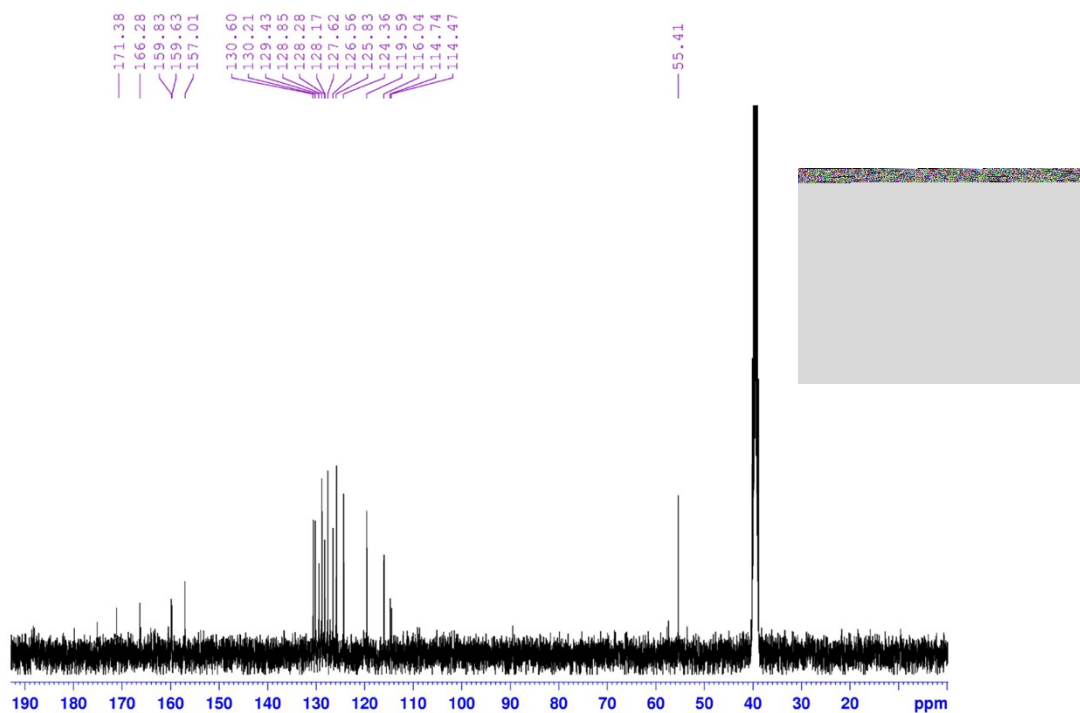
2-Amino-4-(Anthracen-9-yl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3r); ^1H NMR (400 MHz, CDCl_3)



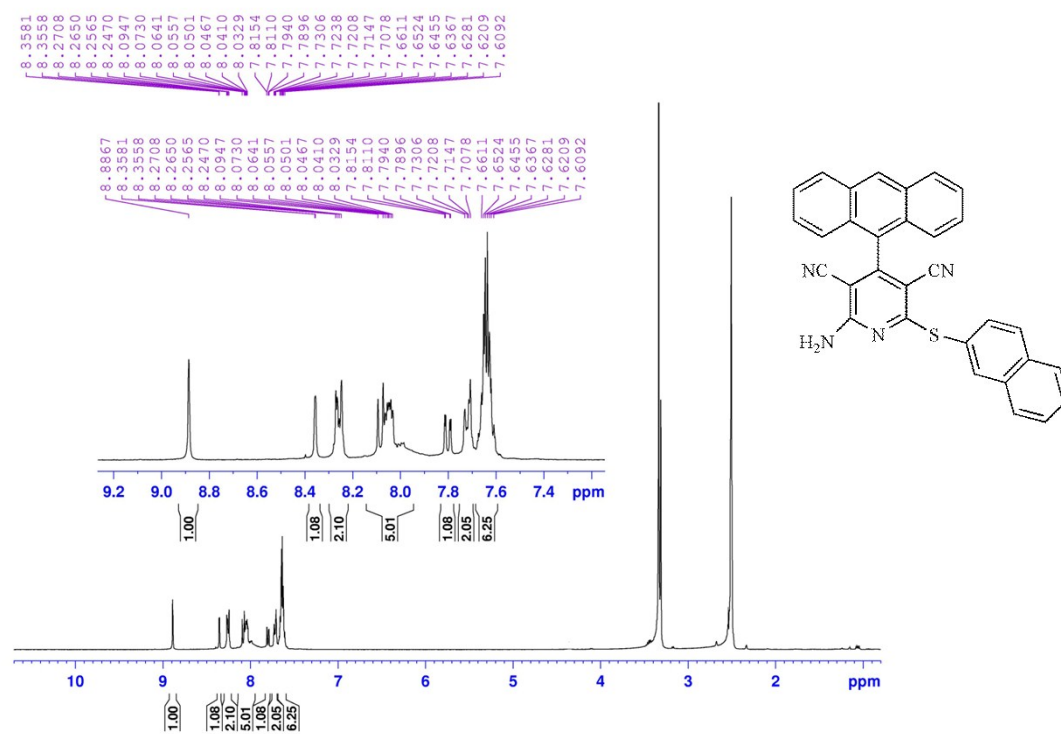
2-Amino-4-(Anthracen-9-yl)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3r); ^{13}C NMR (100 MHz, CDCl_3)



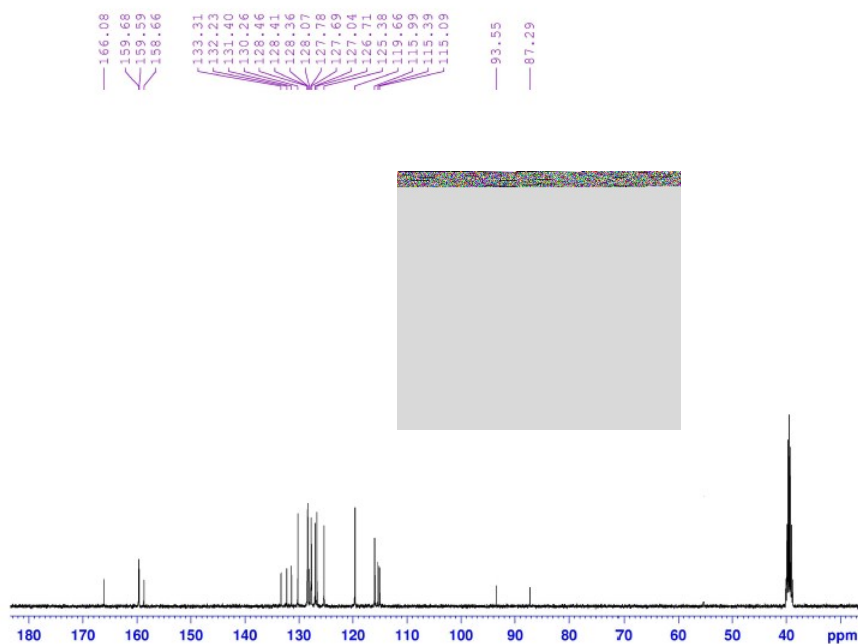
2-Amino-4-(Anthracen-9-yl)-6-(3-methoxyphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3s); ^1H NMR (400 MHz, $\text{DMSO}-d_6$)



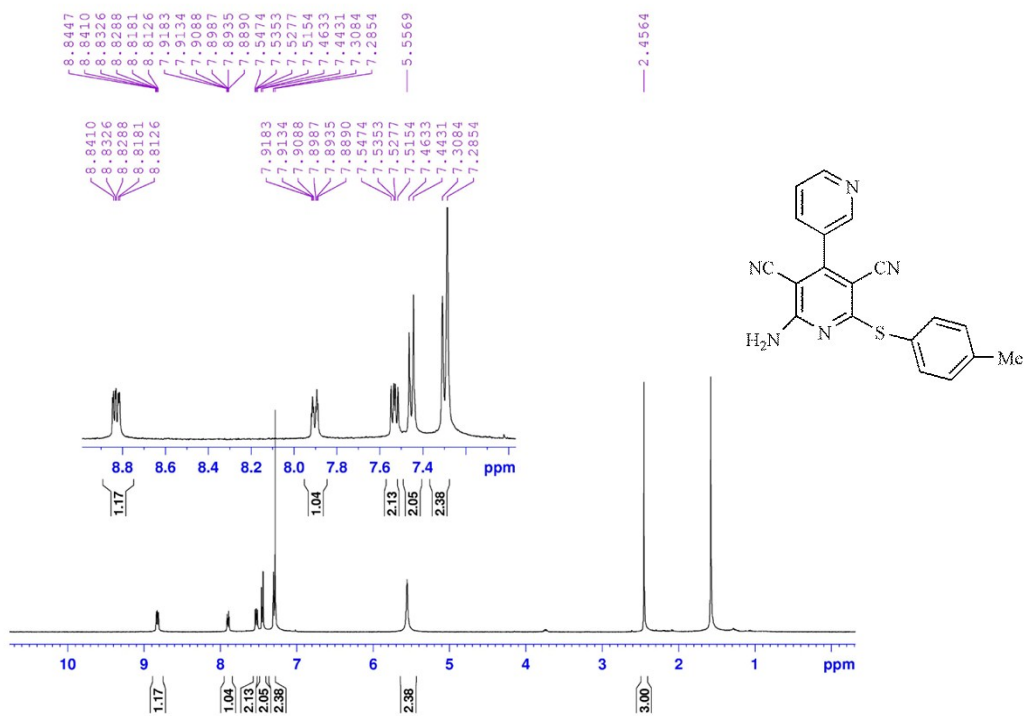
2-Amino-4-(Anthracen-9-yl)-6-(3-methoxyphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3s); ¹³C NMR (100 MHz, DMSO-*d*₆)



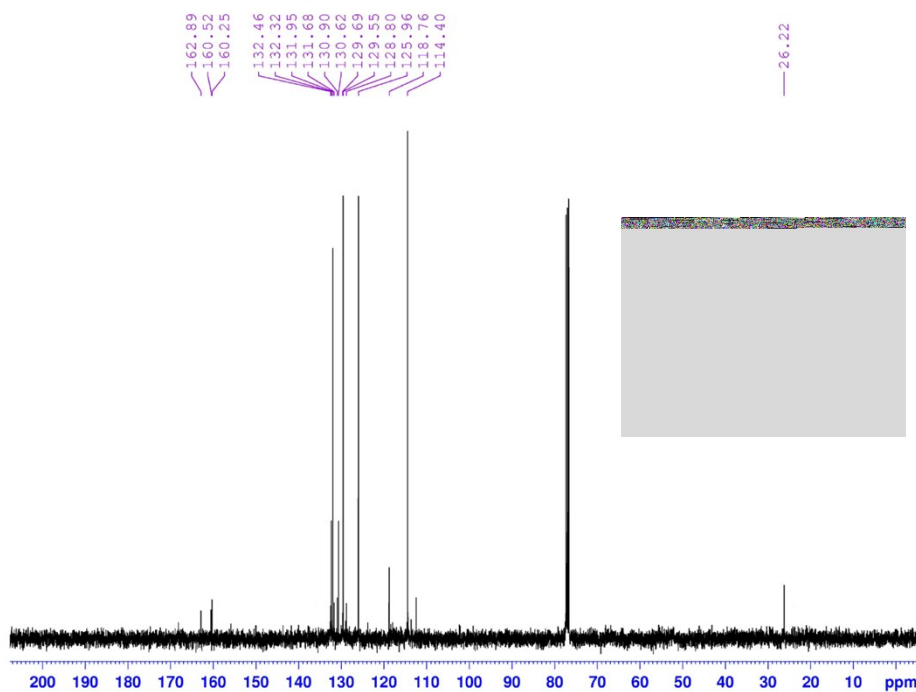
2-Amino-4-(Anthracen-9-yl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3t); ¹H NMR (400 MHz, DMSO-*d*₆)



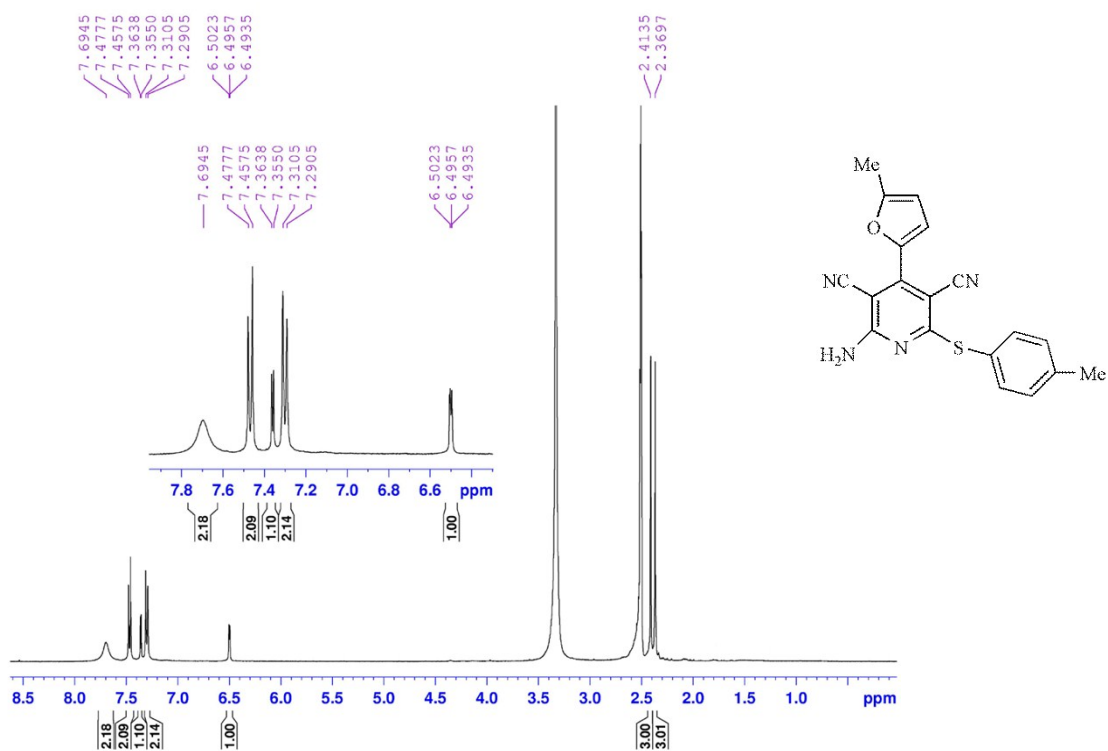
2-Amino-4-(Anthracen-9-yl)-6-(β-naphthylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3t); ¹³C NMR (100 MHz, DMSO-*d*₆)



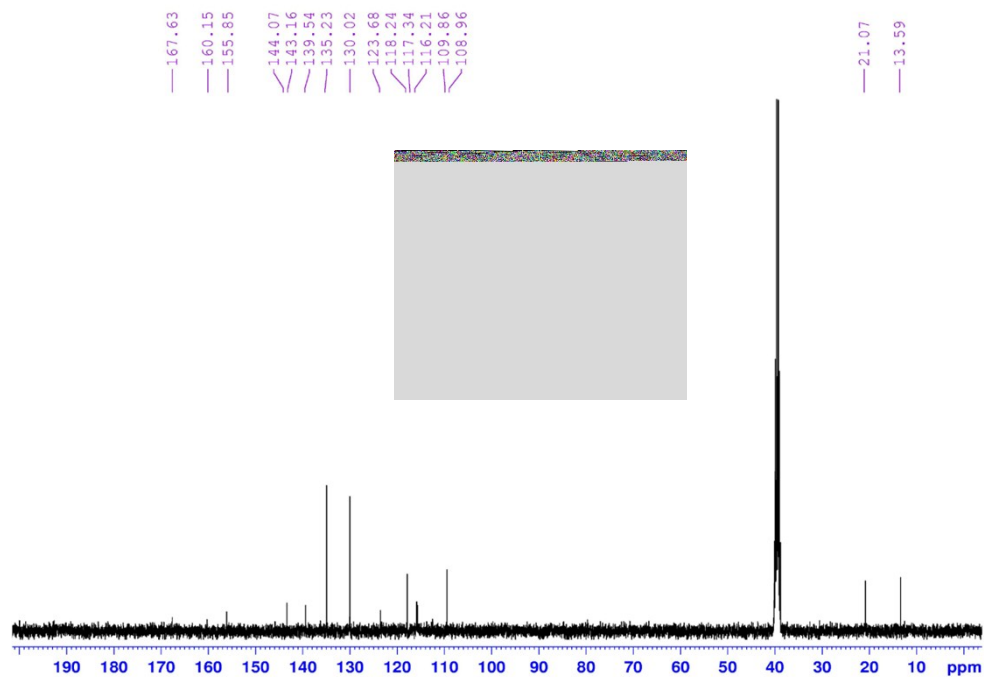
2-Amino-4-(3-pyridine)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3u); ¹H NMR (400 MHz, CDCl₃)



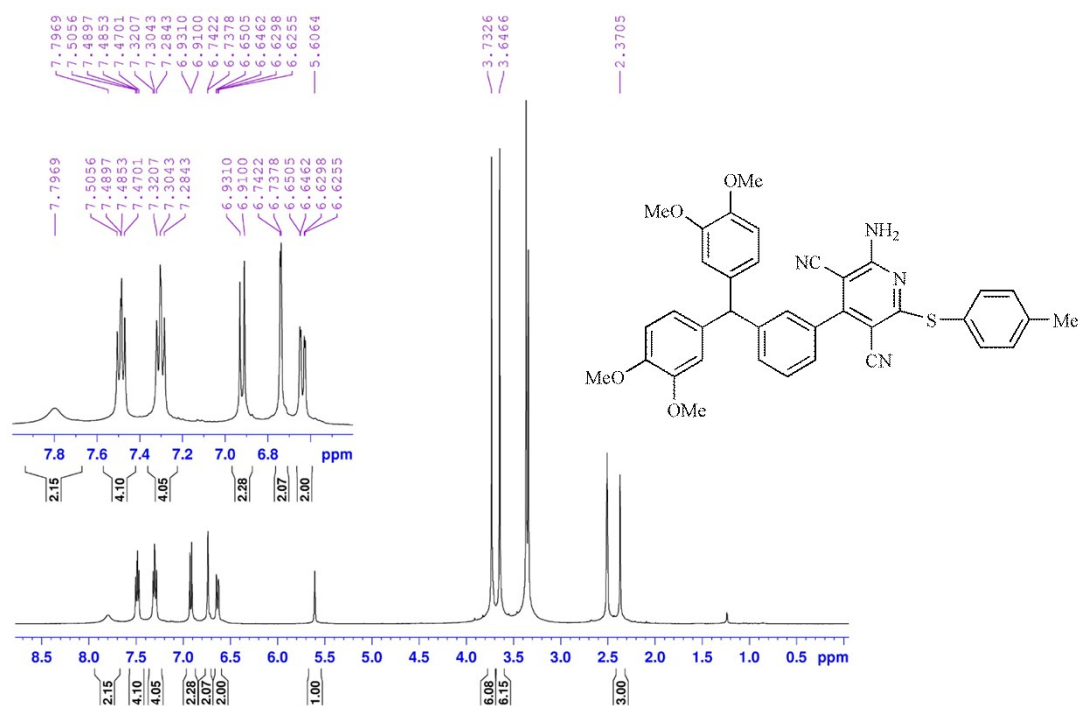
2-Amino-4-(3-pyridine)-6-(4-methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3u); ¹³C NMR (100 MHz, CDCl₃)



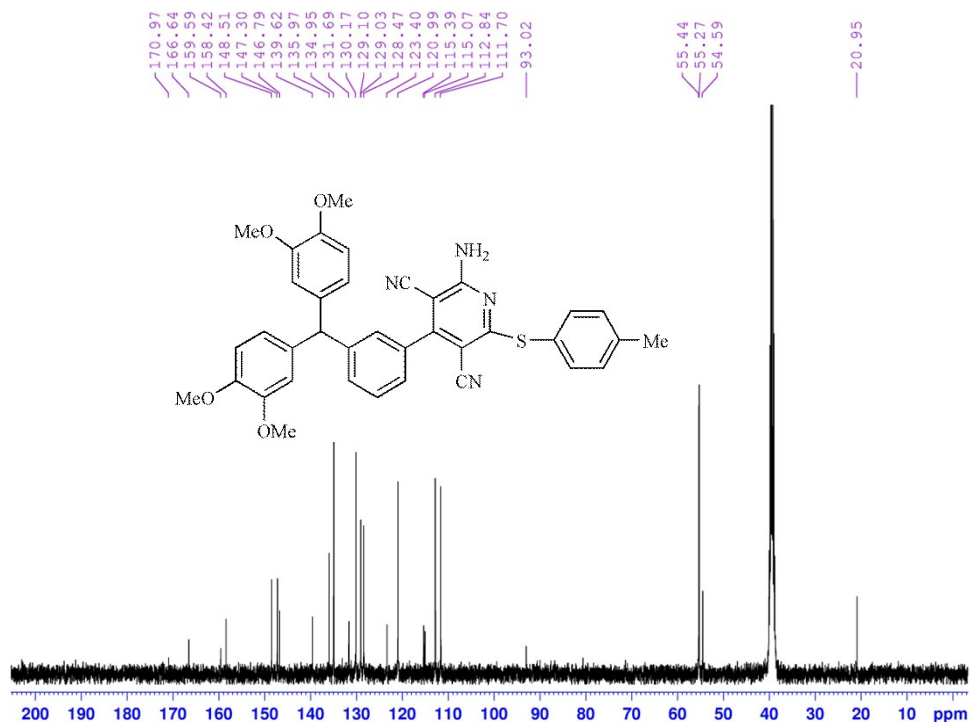
2-Amino-4-(5-methylfuryl)-6-(methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3v); ¹H NMR (400 MHz, DMSO-*d*₆)



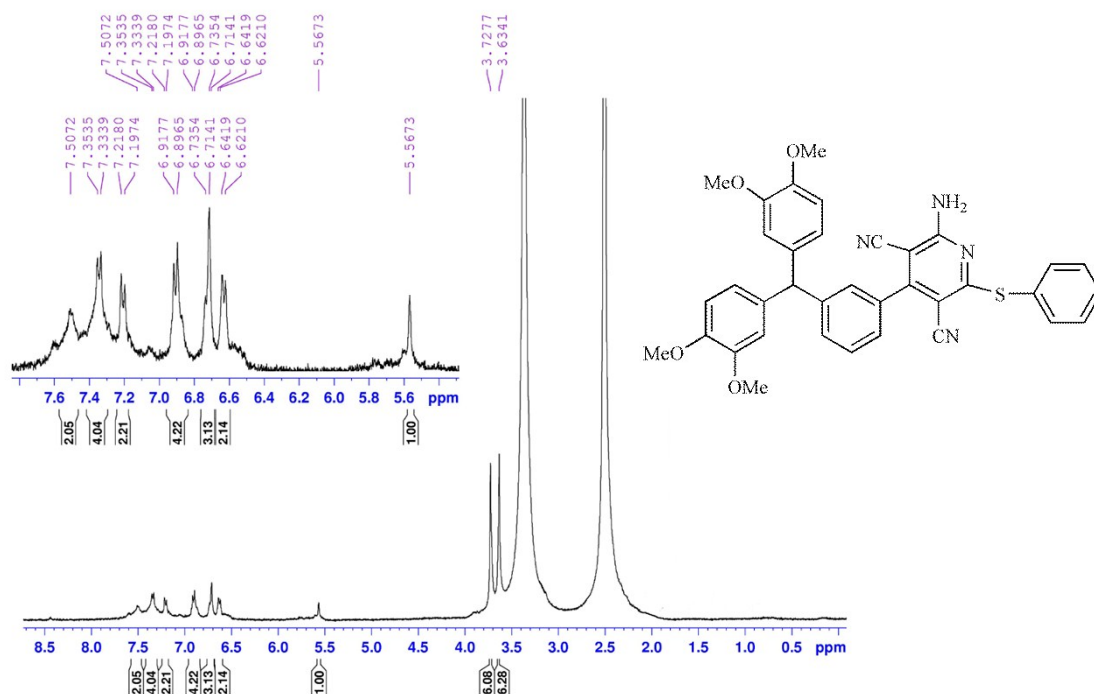
2-Amino-4-(5-methylfuryl)-6-(methylphenylsulfanyl)pyridine-3,5-dicarbonitrile (Table 2, 3v); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$)



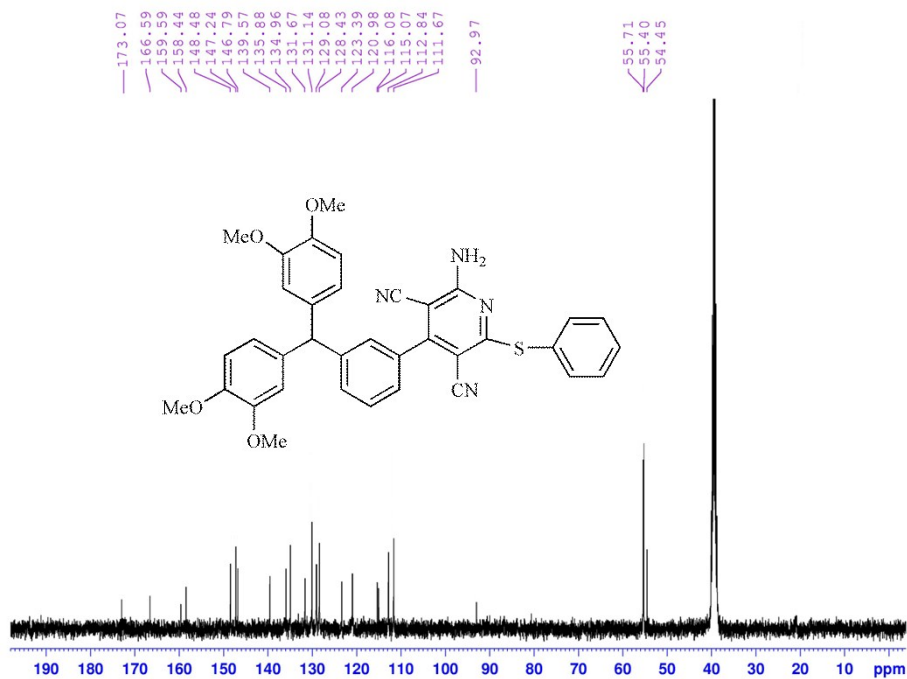
2-Amino-4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenyl)-6-(*p*-tolylthio)pyridine-3,5-dicarbonitrile (Table 2, 3w); ^1H NMR (400 MHz, $\text{DMSO-}d_6$)



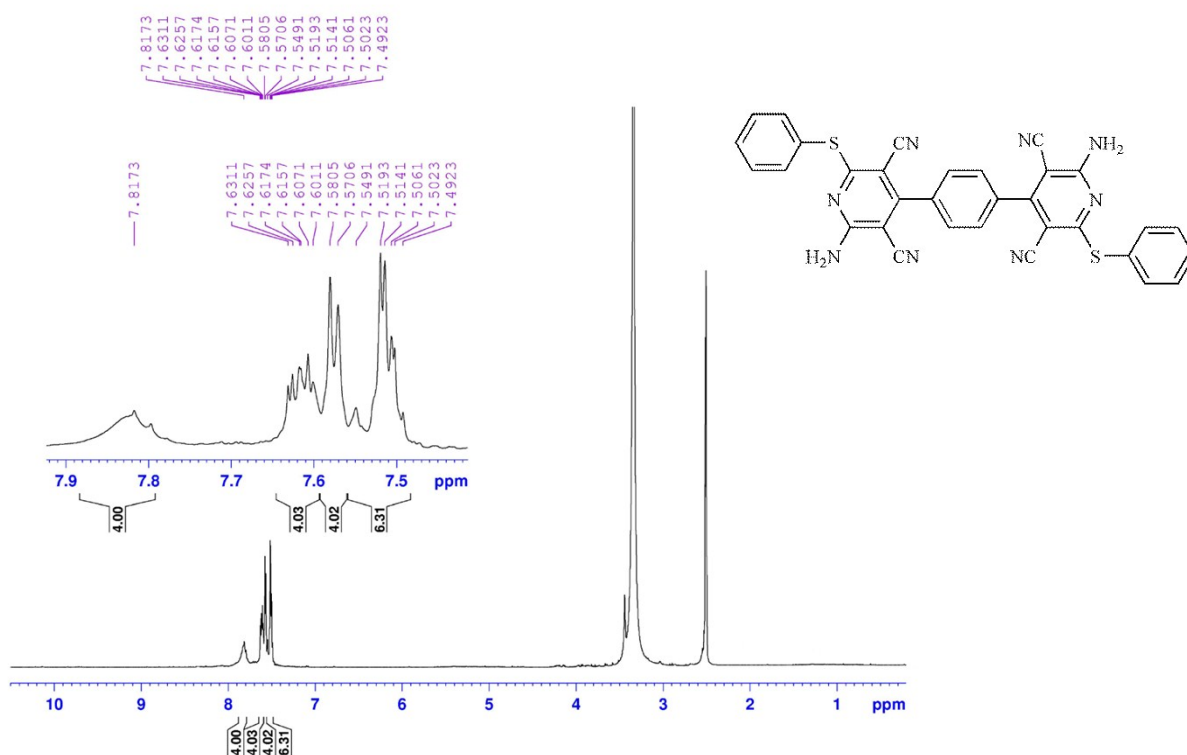
2-Amino-4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenyl)-6-(p-tolylthio)pyridine-3,5-dicarbonitrile (Table 2, 3w); ¹³C NMR (100 MHz, DMSO-d₆)



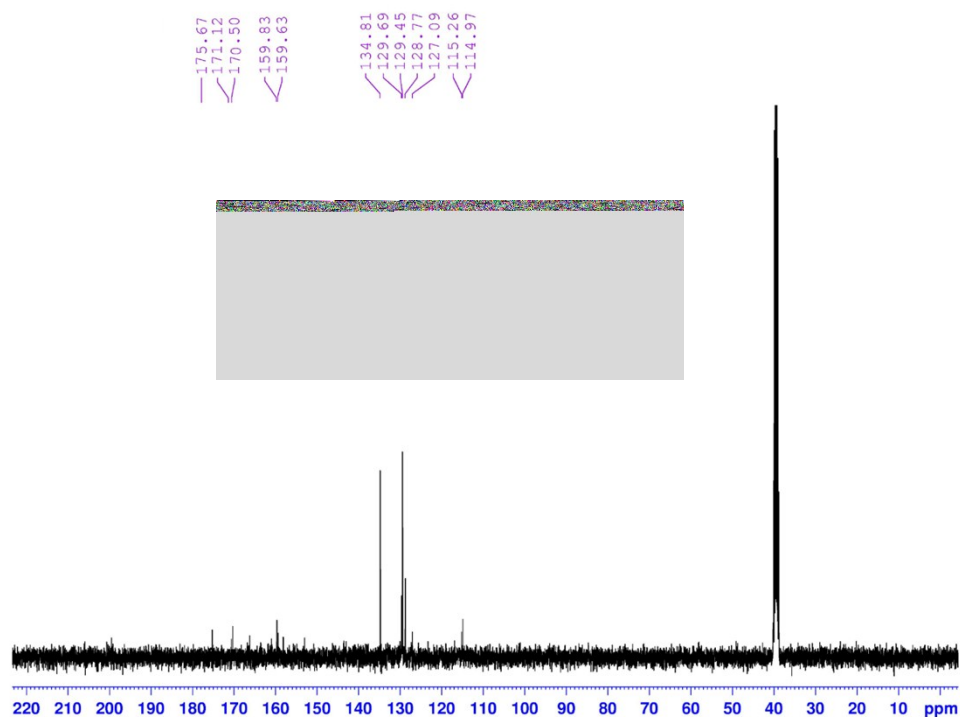
2-Amino-4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (Table 2, 3x); ¹H NMR (400 MHz, DMSO-d₆)



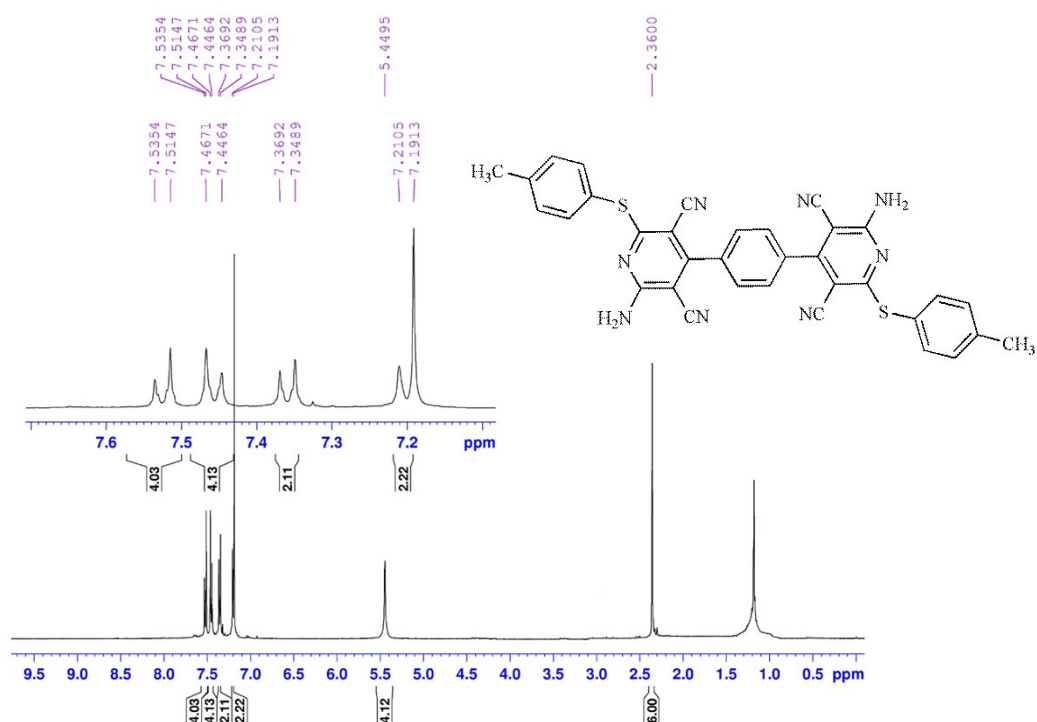
2-Amino-4-(3-(bis(3,4-dimethoxyphenyl)methyl)phenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (Table 2, 3x); ¹³C NMR (100 MHz, DMSO-*d*₆)



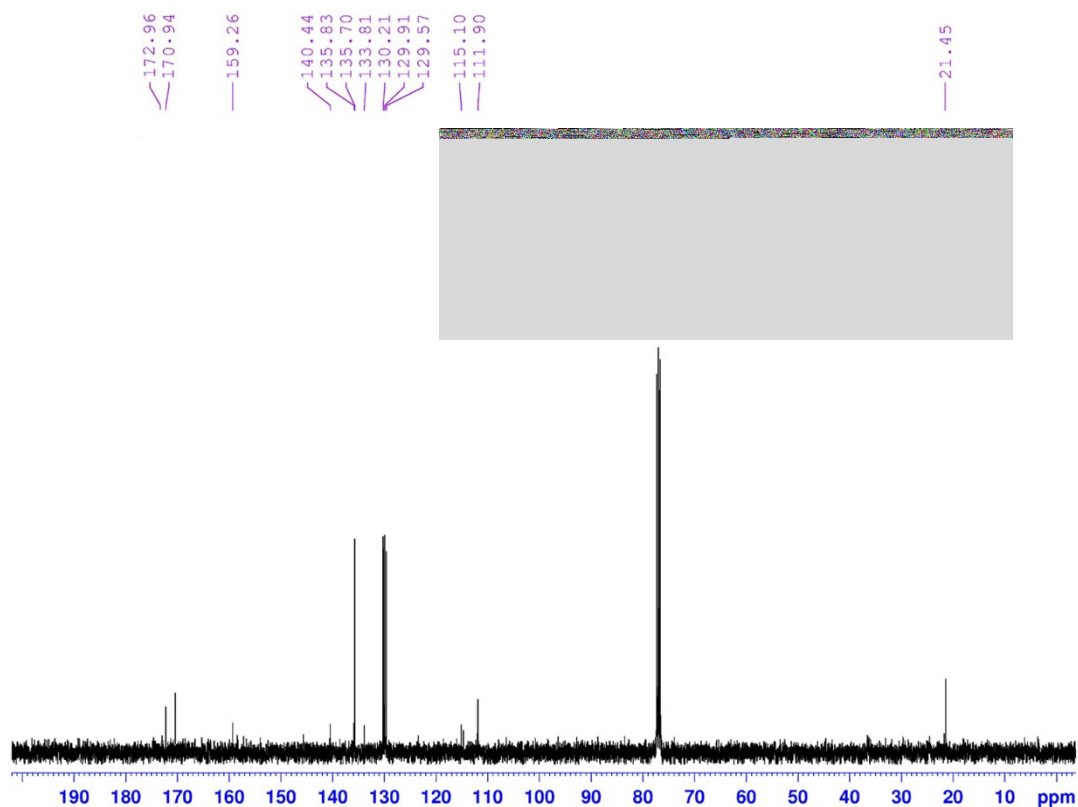
1,4-Bis(2-amino-6-(phenylsufanyl)-4-pyridyl)-3,5-dicarbonitrilebenzene (Scheme 3, 5a); ¹H NMR (400 MHz, DMSO-*d*₆)



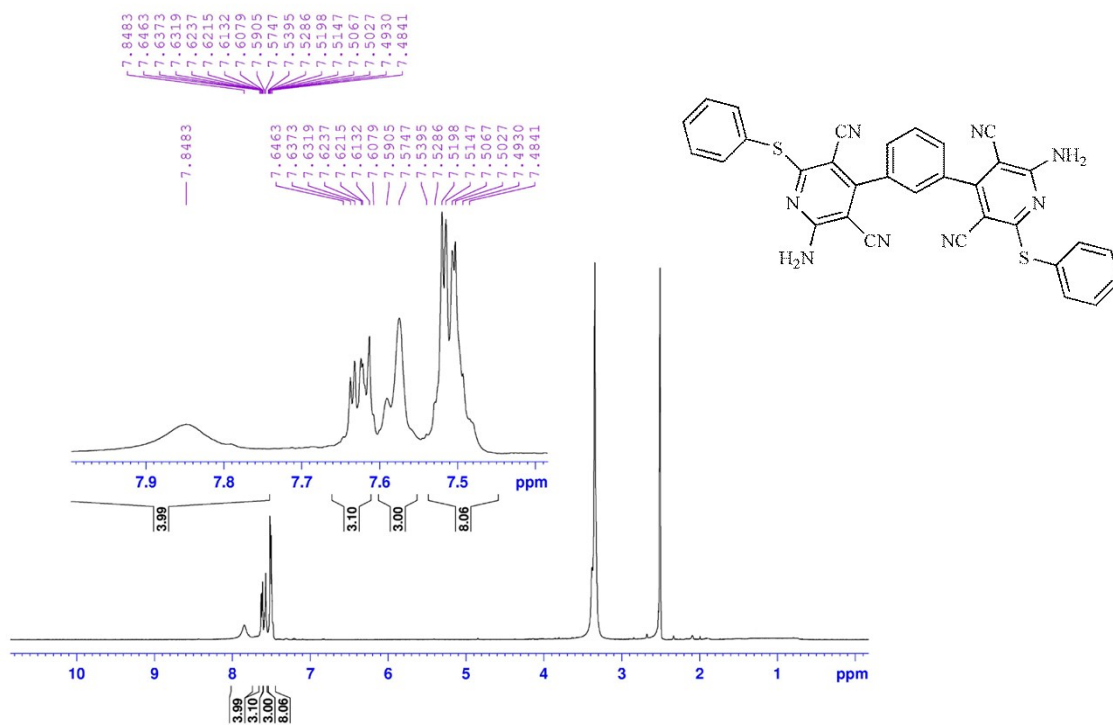
1,4-Bis(2-amino-6-(phenylsulfanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5a); ¹³C NMR (100 MHz, DMSO-*d*₆)



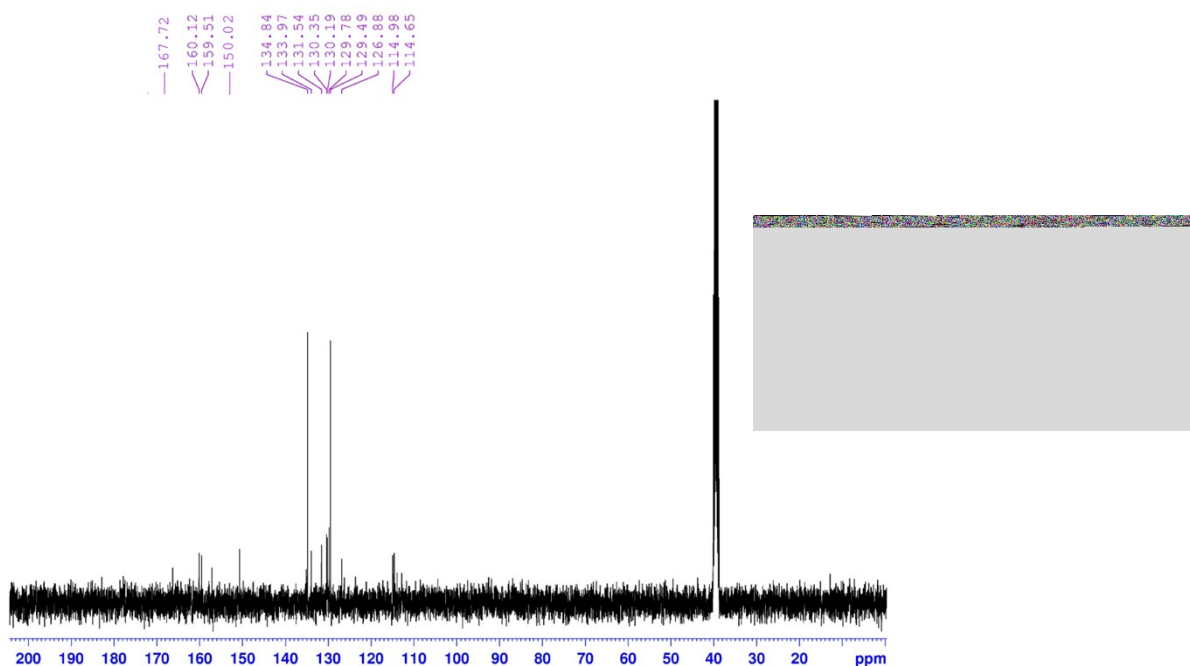
1,4-Bis(2-amino-6-(4-methylphenylsulfanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5b); ¹H NMR (400 MHz, CDCl₃)



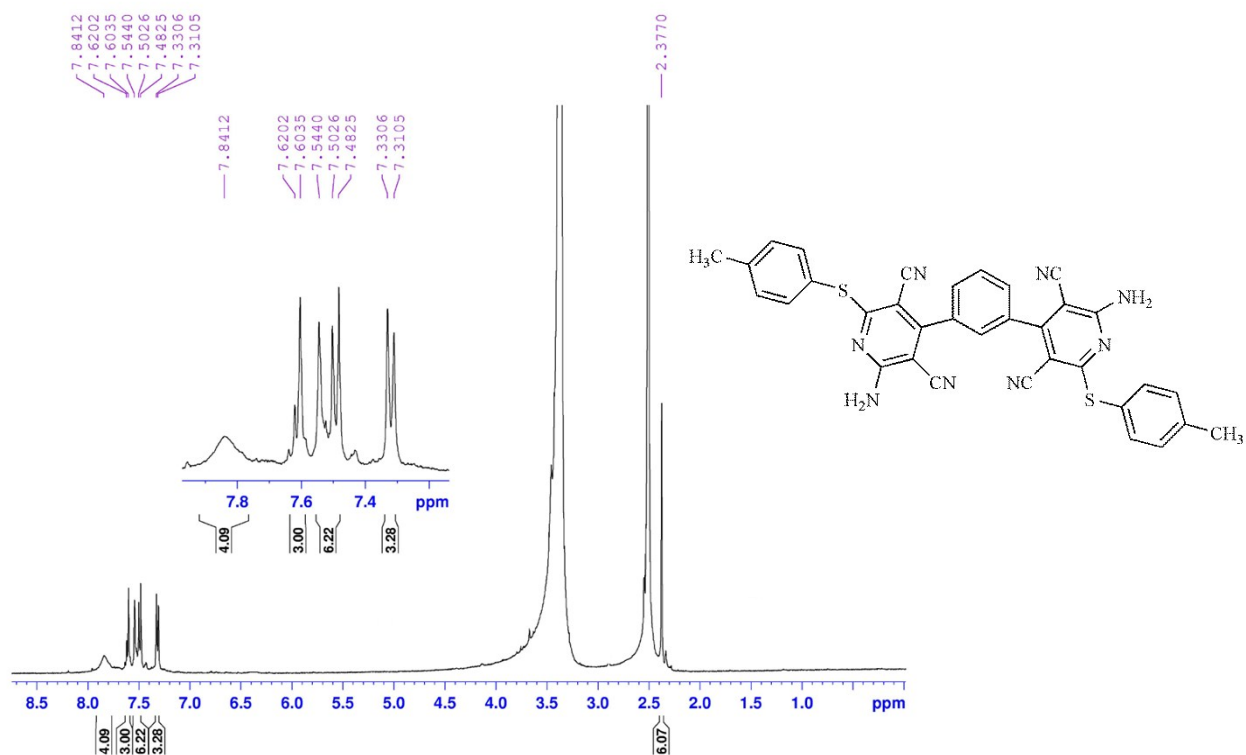
1,4-Bis(2-amino-6-(4-methylphenylsulfanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5b); ¹³C NMR (100 MHz, CDCl₃)



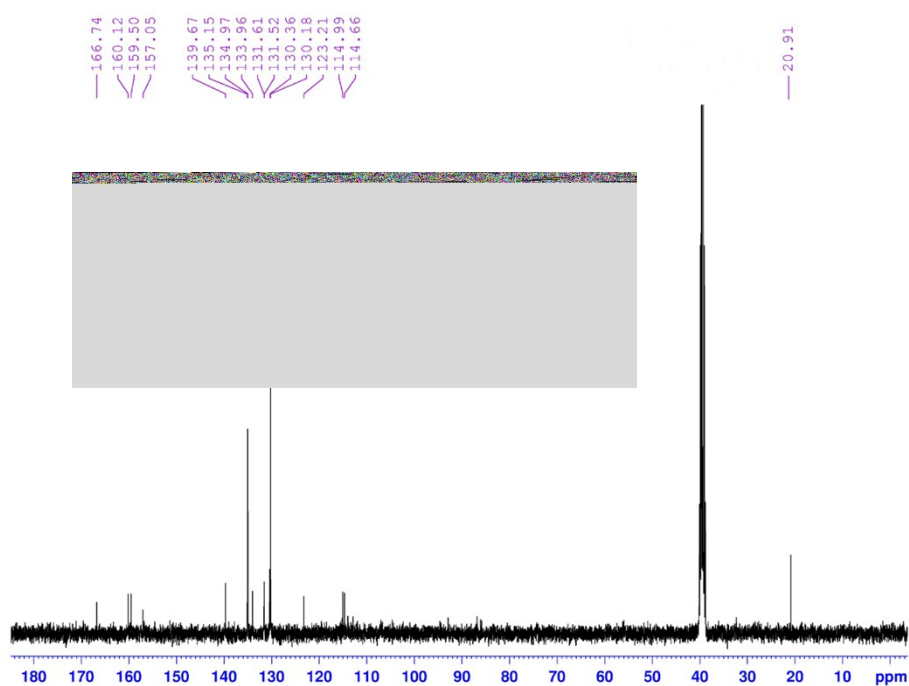
1,3-Bis(2-amino-6-(phenylsulfanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5c); ¹H NMR (400 MHz, DMSO-d₆)



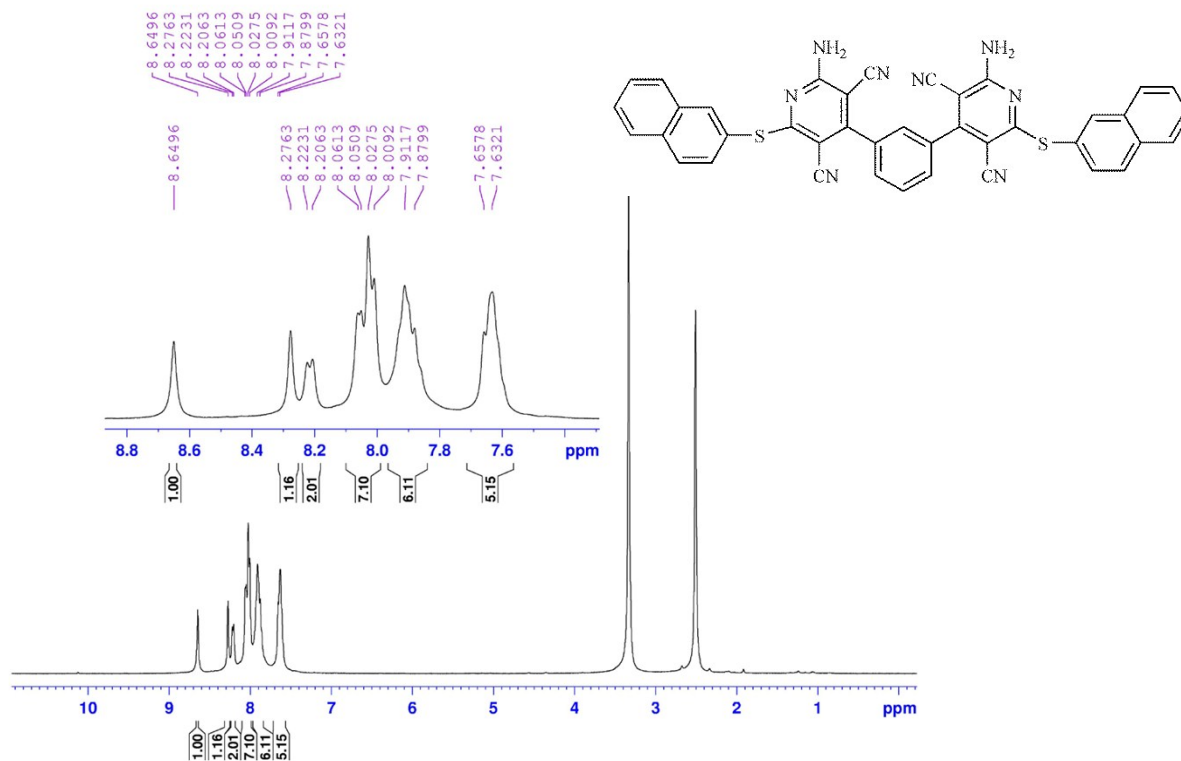
1,3-Bis(2-amino-6-(phenylsufanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5c); ¹³C NMR (100 MHz, DMSO-*d*₆)



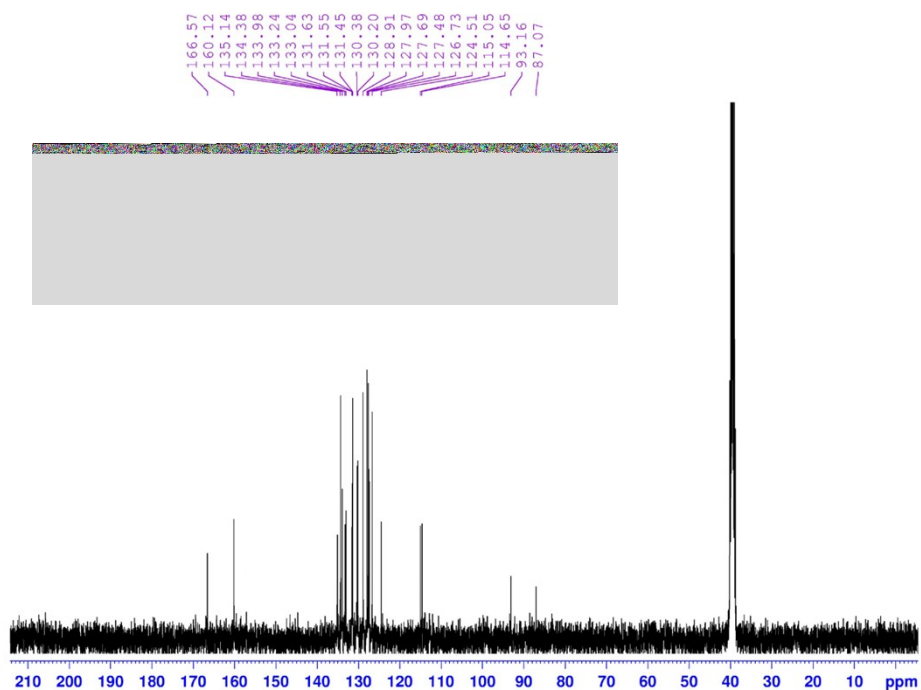
1,3-Bis(2-amino-6-(4-methylphenylsulfanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5d); ¹H NMR (400 MHz, DMSO-*d*₆)



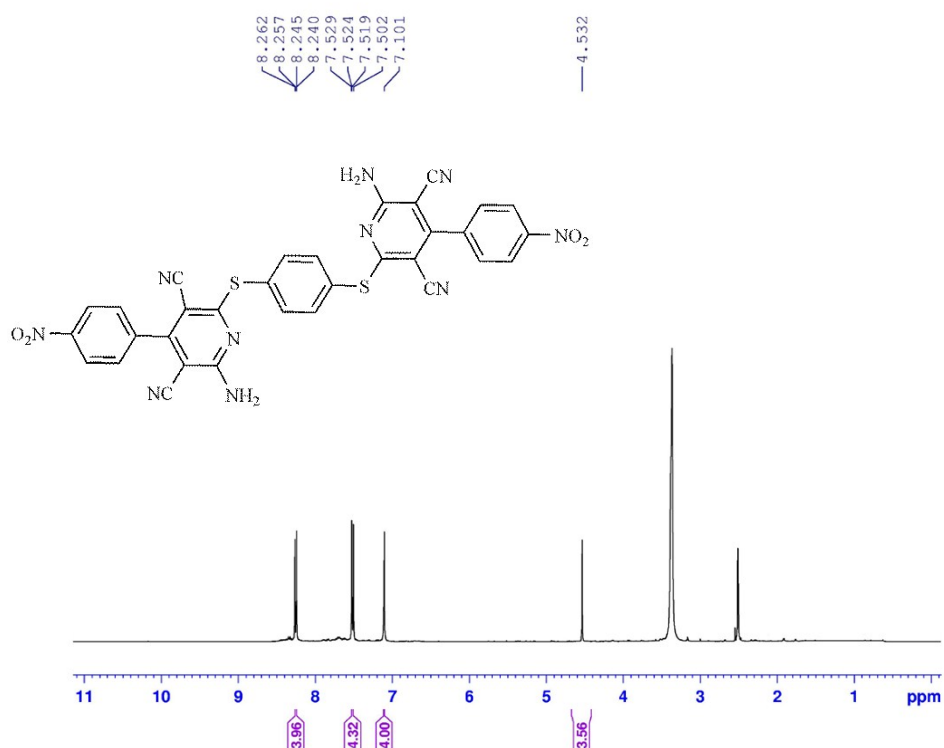
1,3-Bis(2-amino-6-(4-methylphenylsufanyl)-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5d); ¹³C NMR (400 MHz, DMSO-*d*₆)



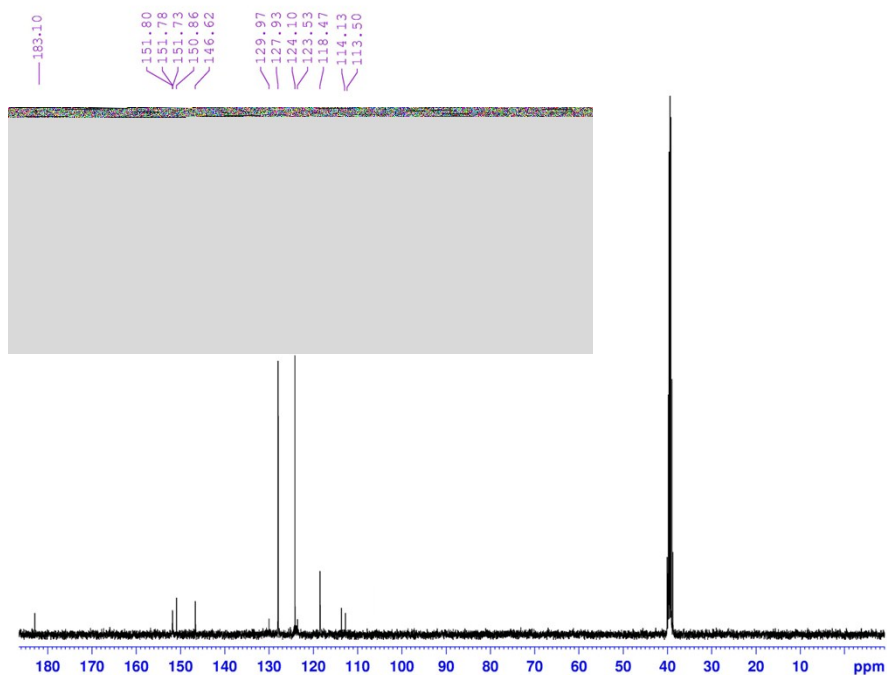
1,3-Bis(2-amino-6-β-naphthylsulfanyl-4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5e); ¹H NMR (400 MHz, DMSO-*d*₆)



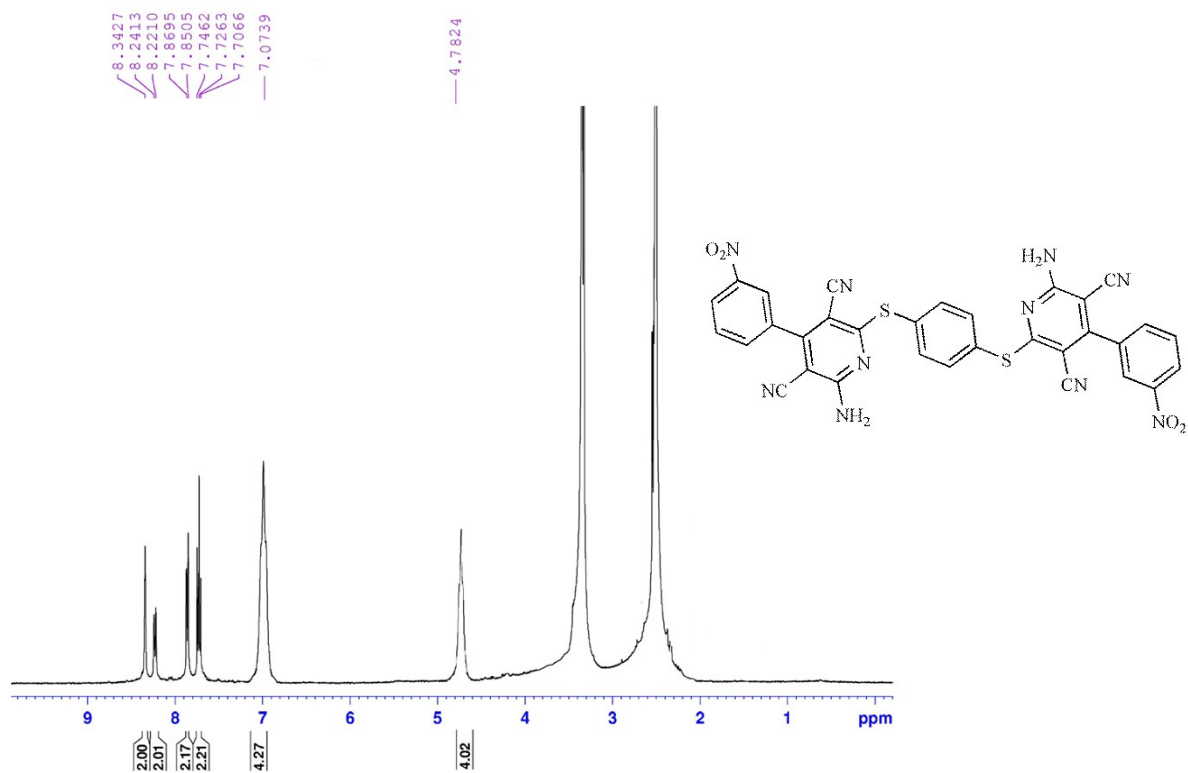
1,3-Bis(2-amino-6-β-naphthylsulfanyl -4-pyridyl-3,5-dicarbonitrile)benzene (Scheme 3, 5e); ¹³C NMR (100 MHz, DMSO-*d*₆)



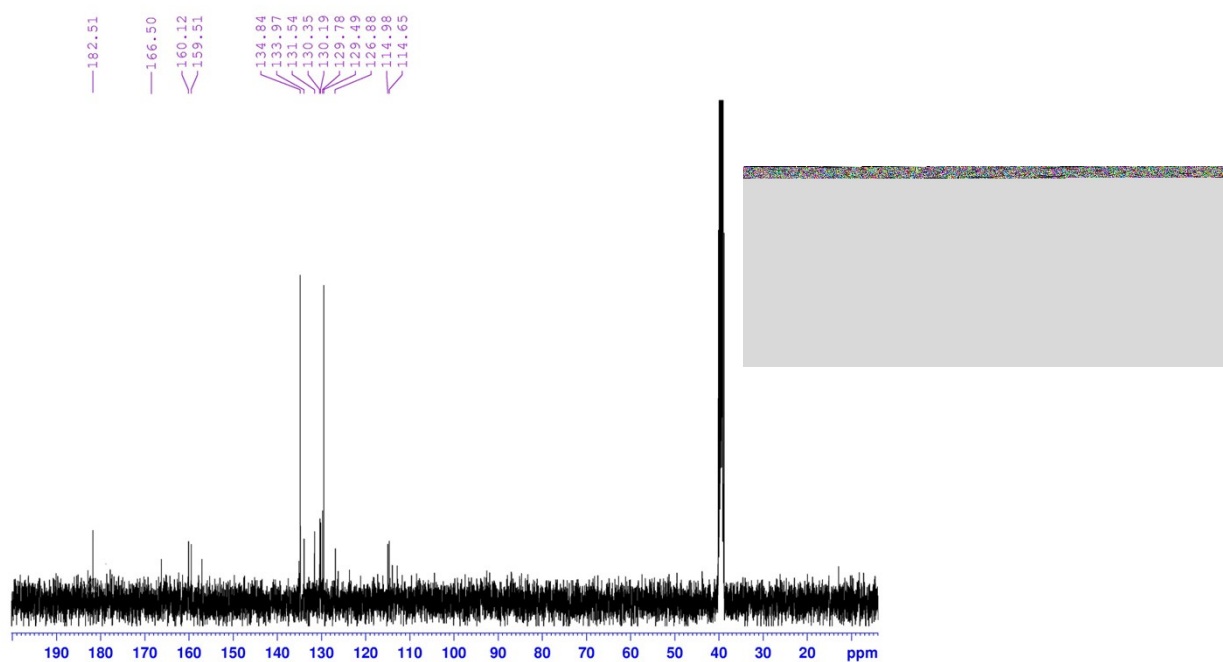
1,4-Bis(2-amino-4-(4-nitrophenyl)-3,5-dicyano-4-pyridyl) dithiophenol (Scheme 4, 7a); ¹H NMR (400 MHz, DMSO-*d*₆)



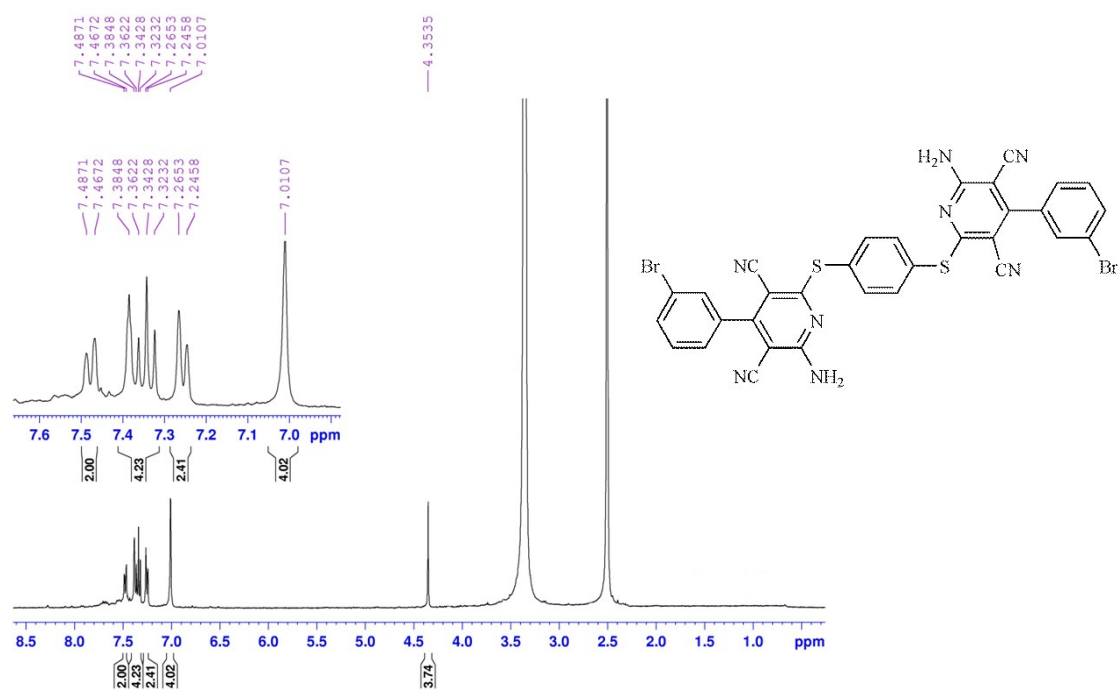
1,4-Bis(2-amino-4-(4-nitrophenyl-3,5-dicyano)-4-pyridyl)dithiophenol (Scheme 4, 7a); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$)



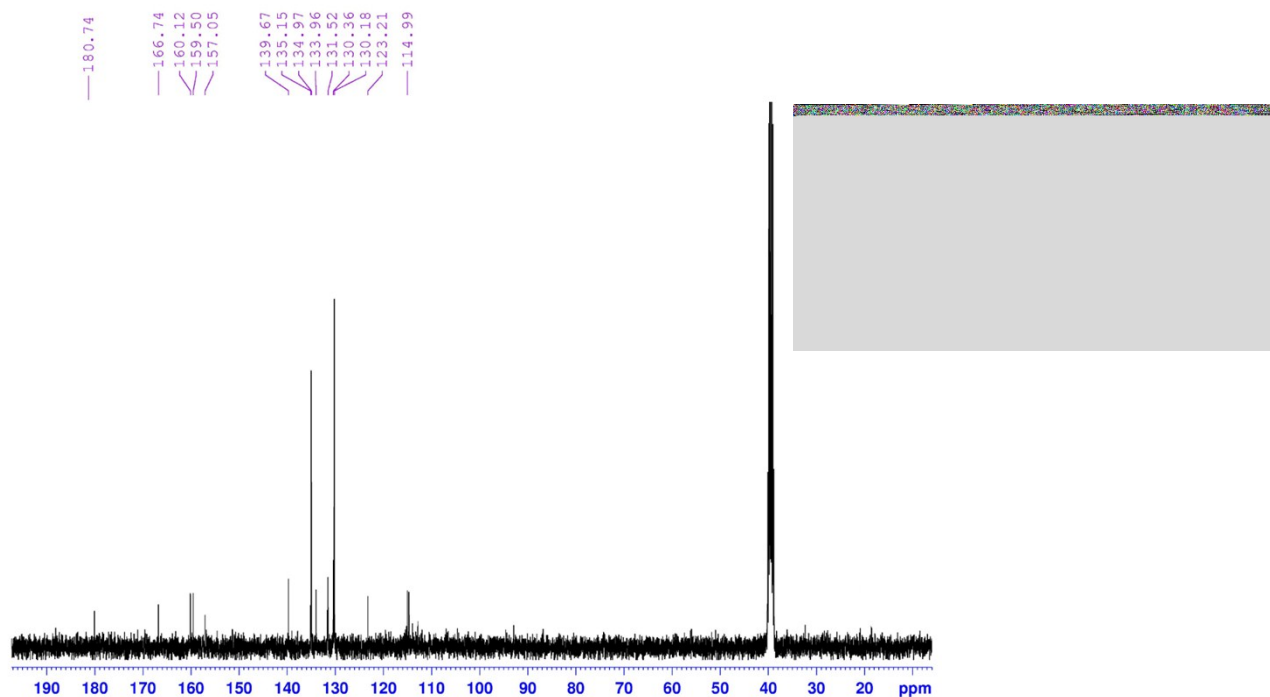
1,4-Bis(2-amino-4-(3-nitrophenyl)-3,5-dicyano-4-pyridyl)dithiophenol (Scheme 4, 7b); ^1H NMR (400 MHz, $\text{DMSO-}d_6$)



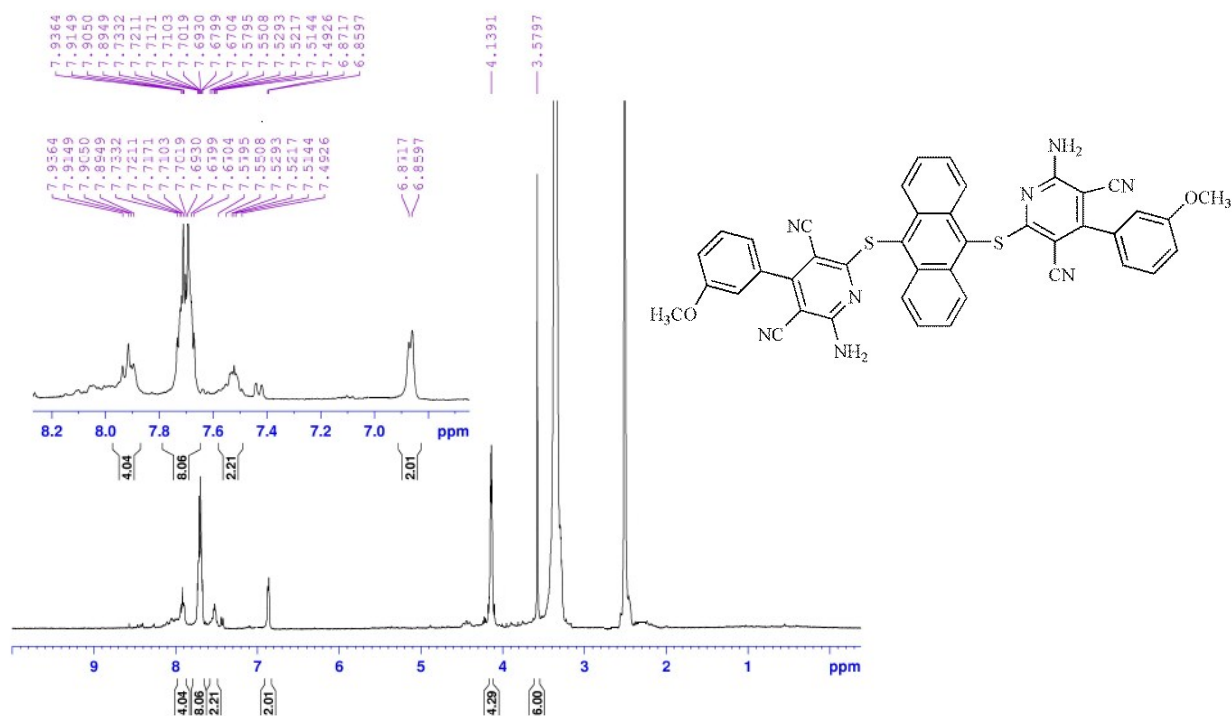
1,4-Bis(2-amino-4-(3-nitrobenzyl)-4-pyridyl)-3,5-dicarbonitriledithiophenol (Scheme 4, 7b); ¹³C NMR (100 MHz, DMSO-*d*₆)



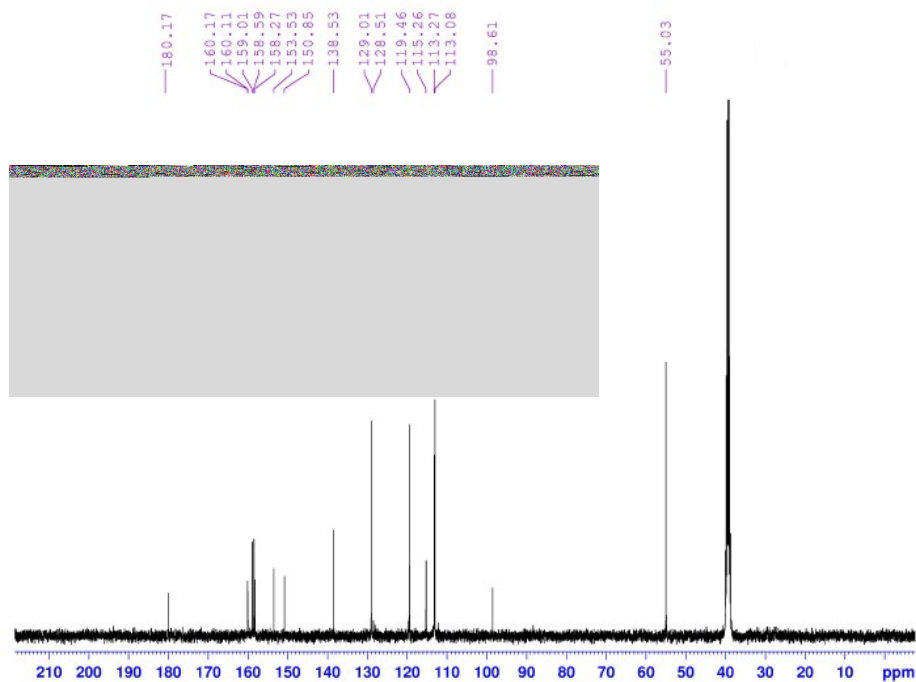
1,4-Bis(2-amino-4-(3-bromophenyl)-3,5-dicyano-4-pyridyl)dithiophenol (Scheme 4, 7c); ¹H NMR (400 MHz, DMSO-*d*₆)



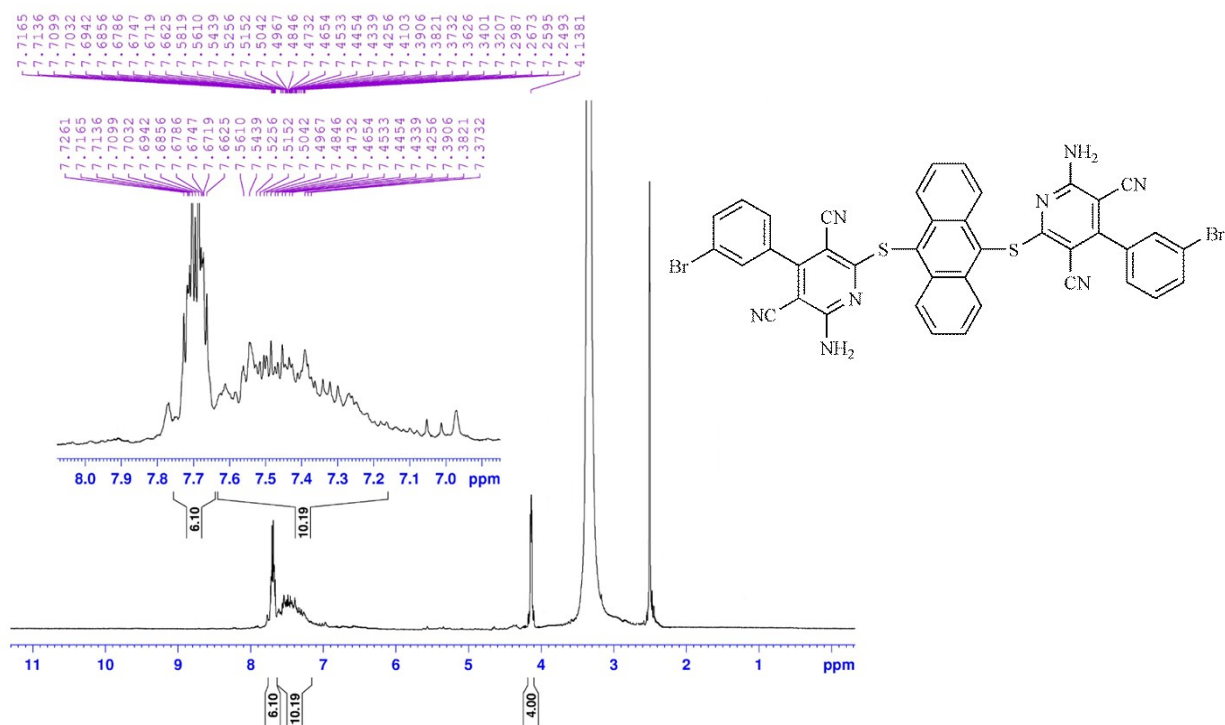
1,4-Bis(2-amino-4-(3-bromophenyl)-3,5-dicyano-4-pyridyl)dithiophenol (Scheme 4, 7c); ¹³C NMR (100 MHz, DMSO-*d*₆)



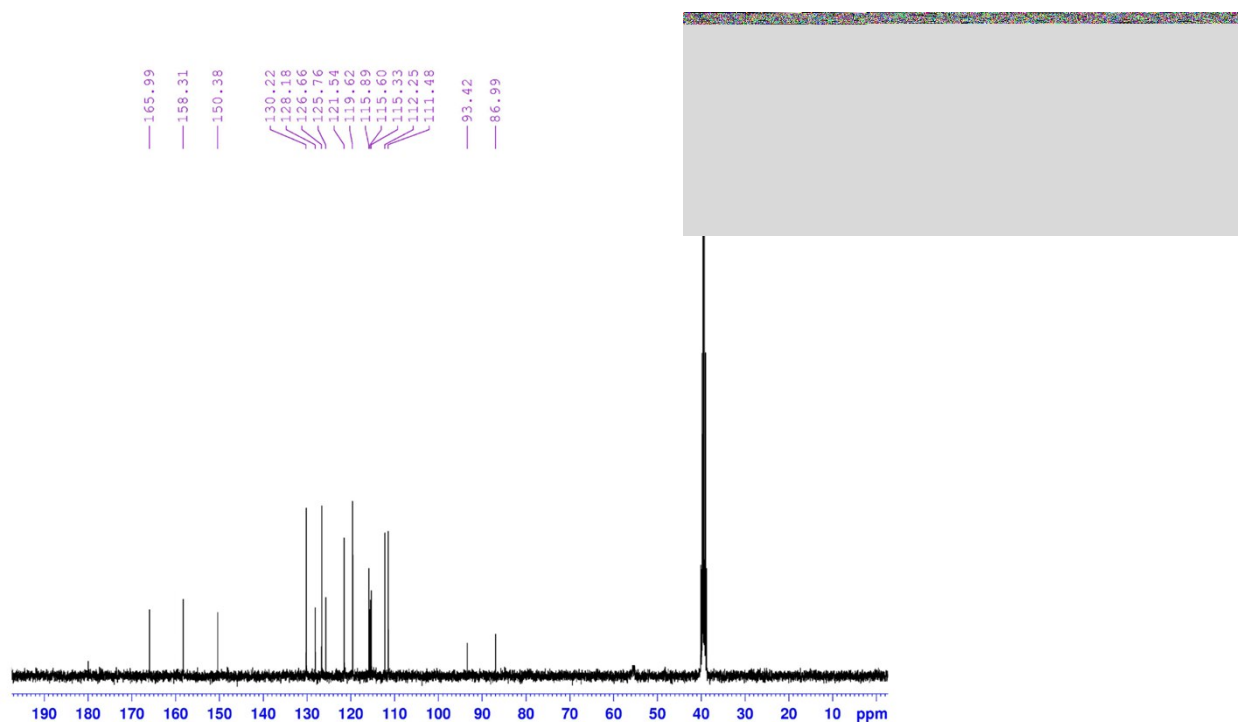
9,10-Bis(2-amino-4-(3-methoxybenzyl)-3,5-dicyano-4-pyridyl)anthracene dithiol (Scheme 4, 7d); ¹H NMR (400 MHz, DMSO-*d*₆)



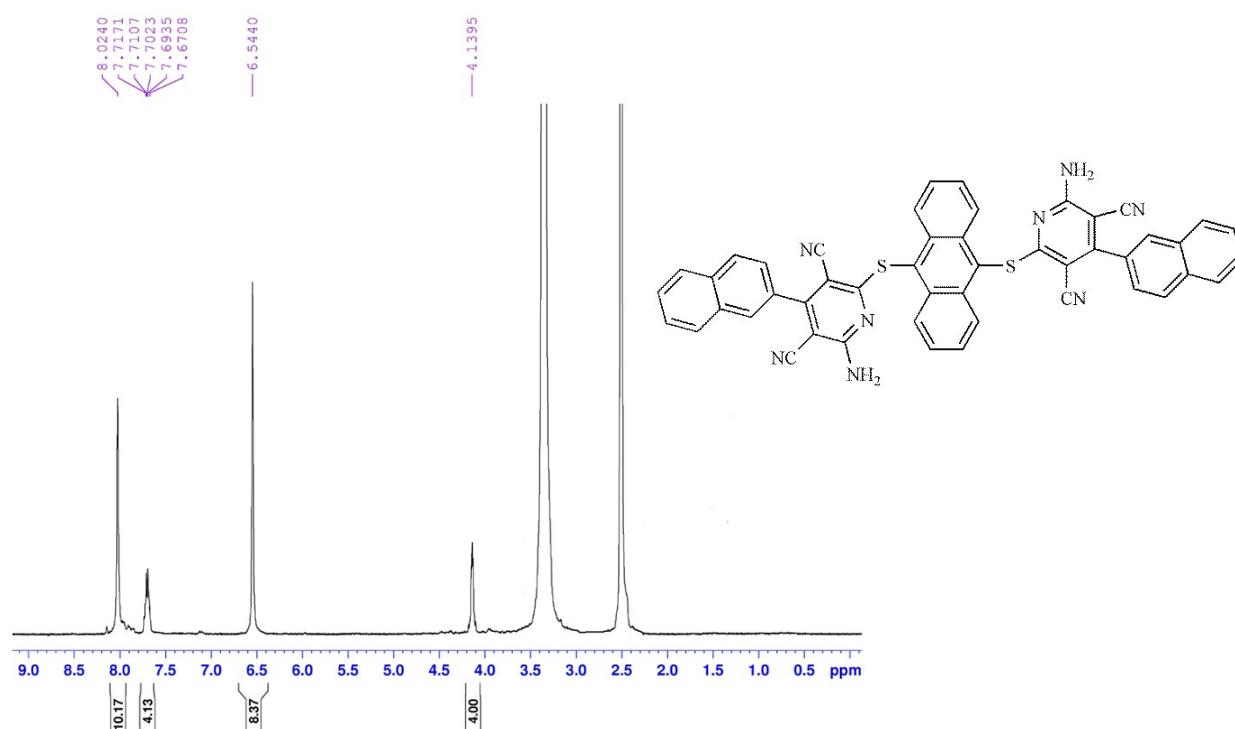
9,10-Bis(2-amino-4-(3-methoxybenzyl)-4-pyridyl)-3,5-dicarbonitrileanthracene dithiol (Scheme 3, 7d); ^{13}C NMR (100 MHz, DMSO- d_6)



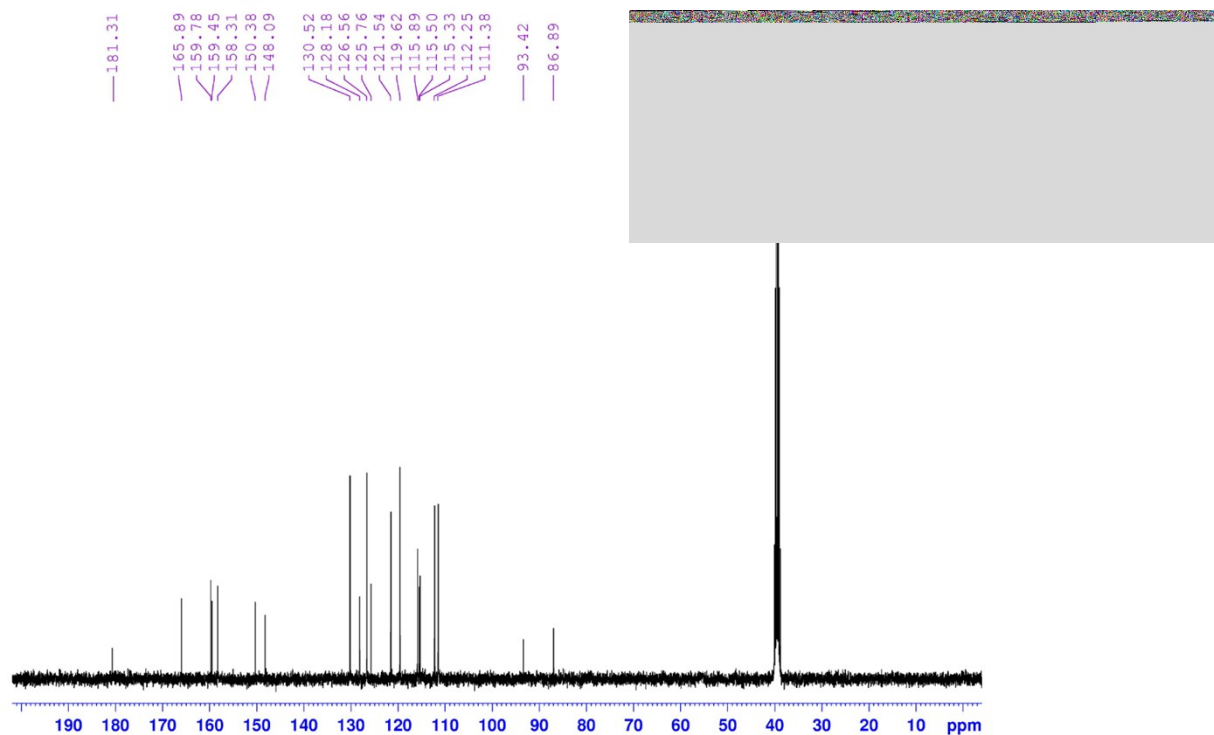
9,10-Bis(2-amino-4-(3-bromophenyl)-3,5-dicyano)-4-pyridylanthracene dithiol (Scheme 4, 7e); ^1H NMR (400 MHz, DMSO- d_6)



9,10-Bis(2-amino-4-(3-bromophenyl-3,5-dicyano)-4-pyridyl)anthracene dithiol (Scheme 4, 7e);
¹³C NMR (100 MHz, DMSO-*d*₆)



9,10-Bis(2-amino-4-(β-naphthyl-3,5-dicyano)-4-pyridyl)anthracene dithiol (Scheme 4, 7f); ¹H
NMR (400 MHz, DMSO-*d*₆)



9,10-Bis(2-amino-4-(β-naphthyl)-4-pyridyl-3,5-dicyano)-4-pyridylanthracene dithiol (Scheme 4, 7f); ¹³C NMR (100 MHz, DMSO-*d*₆)