Supporting Information

Impact of Aryl bulky group on One-pot Reaction of Aldehyde with Malononitrile and *N*-substituted 2-cyanoacetamide

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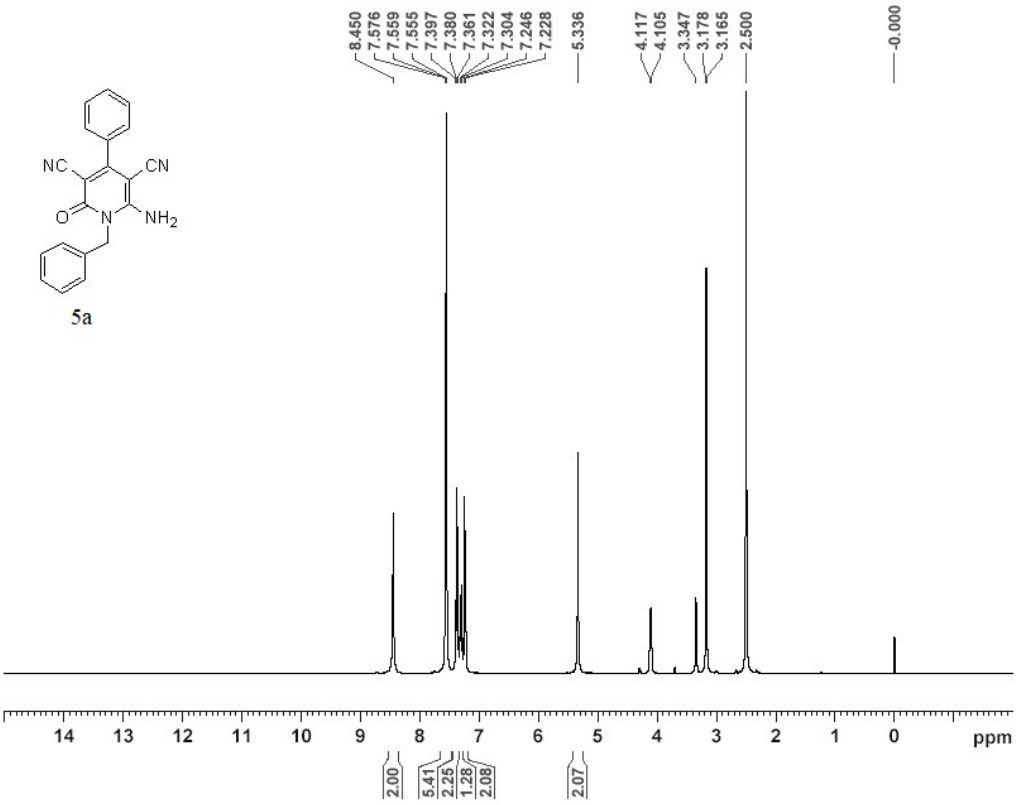
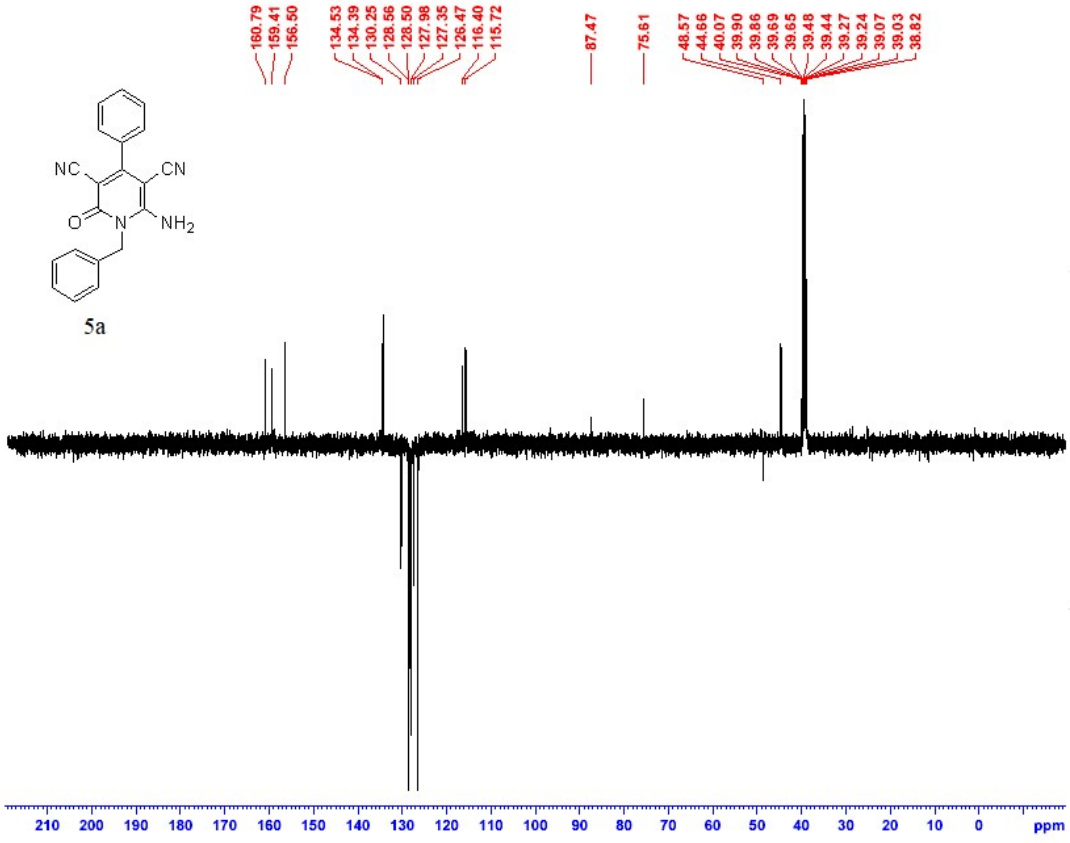
^{1}H-NMR (400 MHz, DMSO-d6, CD_3OD)



^{13}C{1H}-APT (100 MHz, DMSO-d6, CD_3OD)



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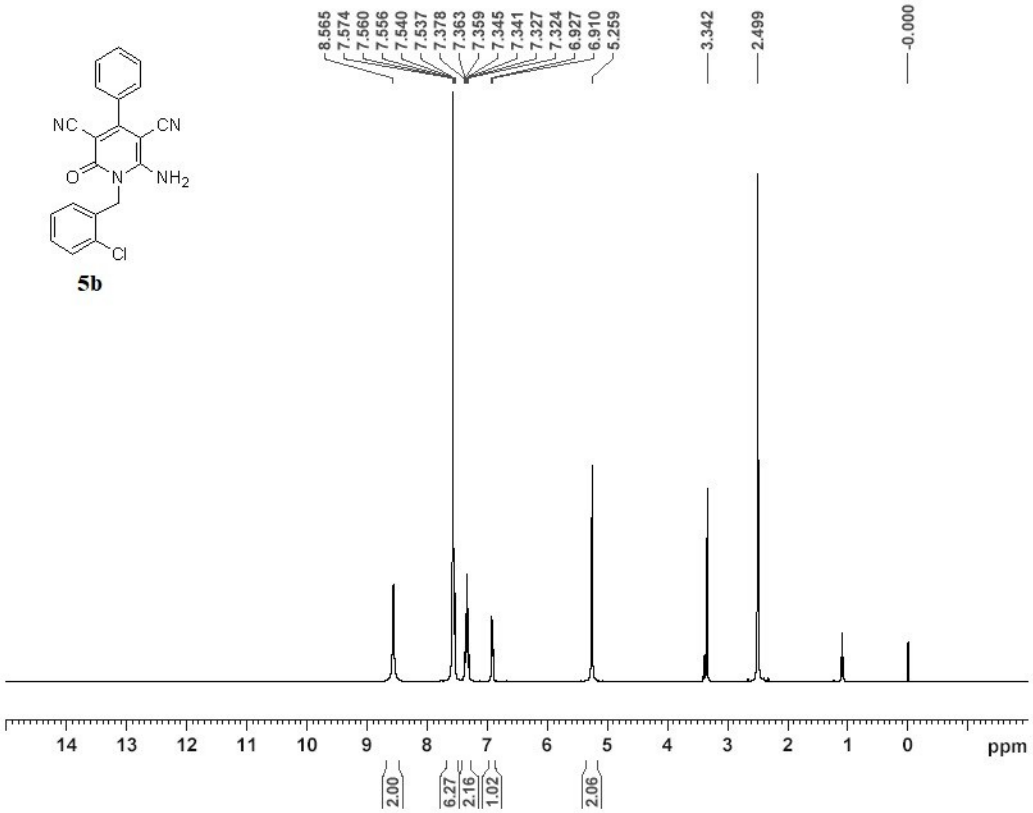

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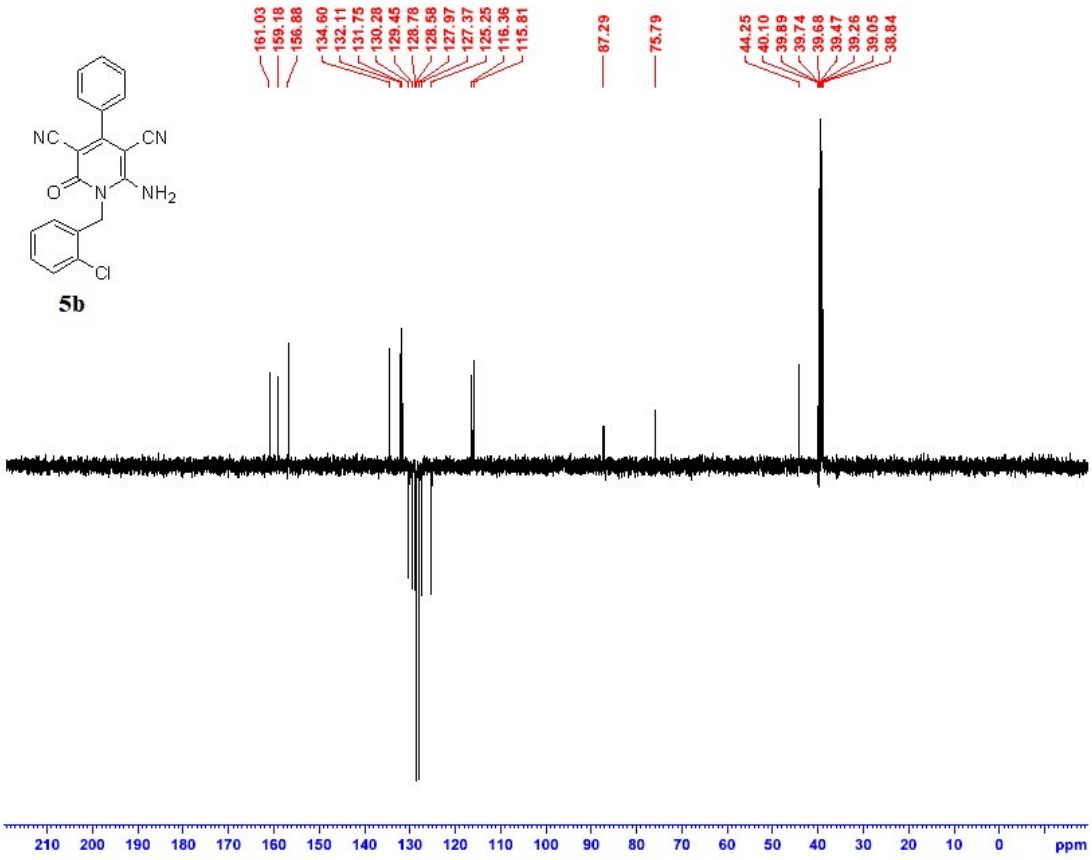

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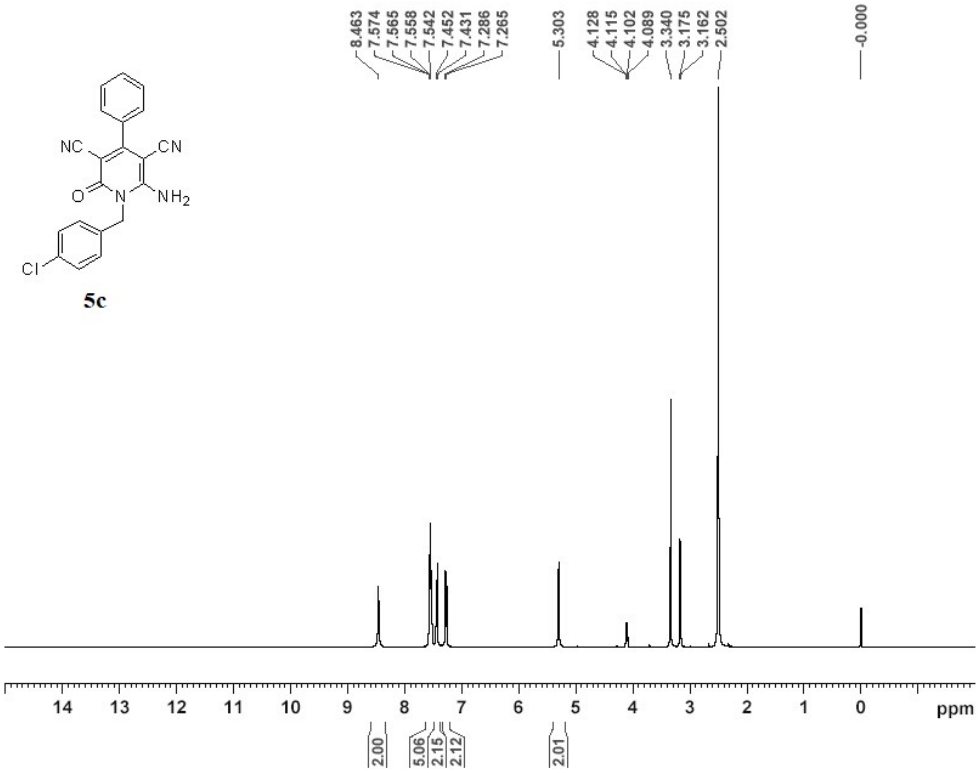

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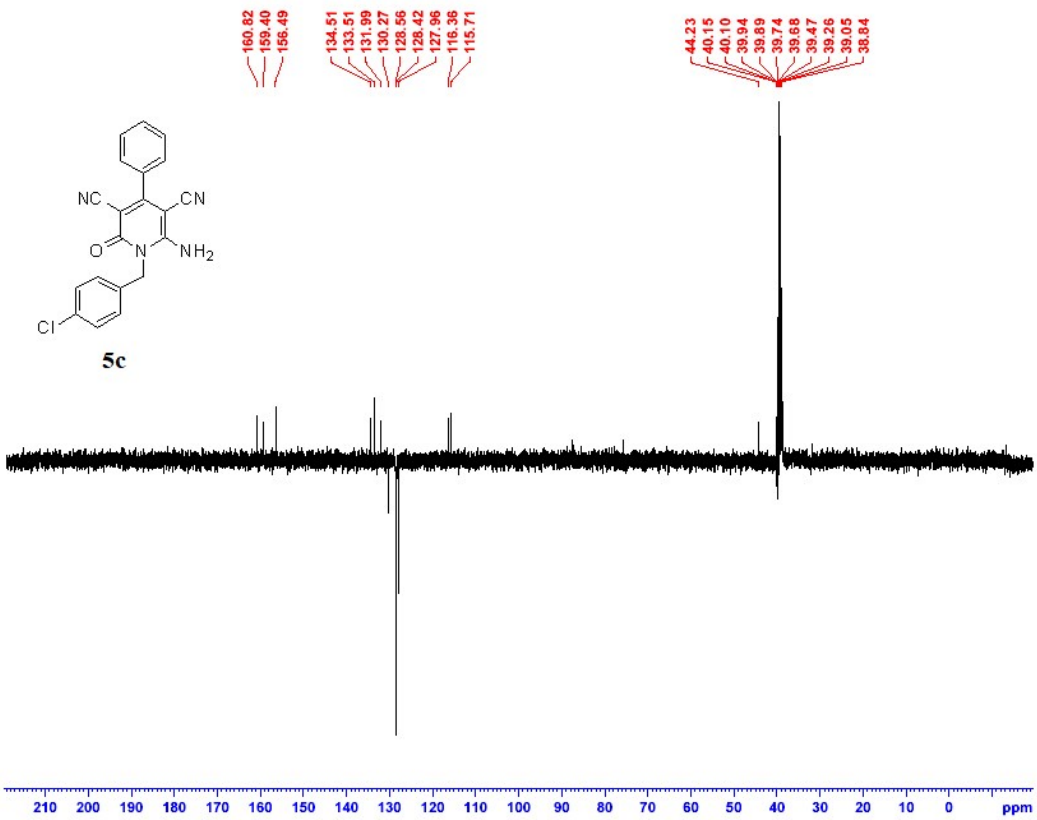

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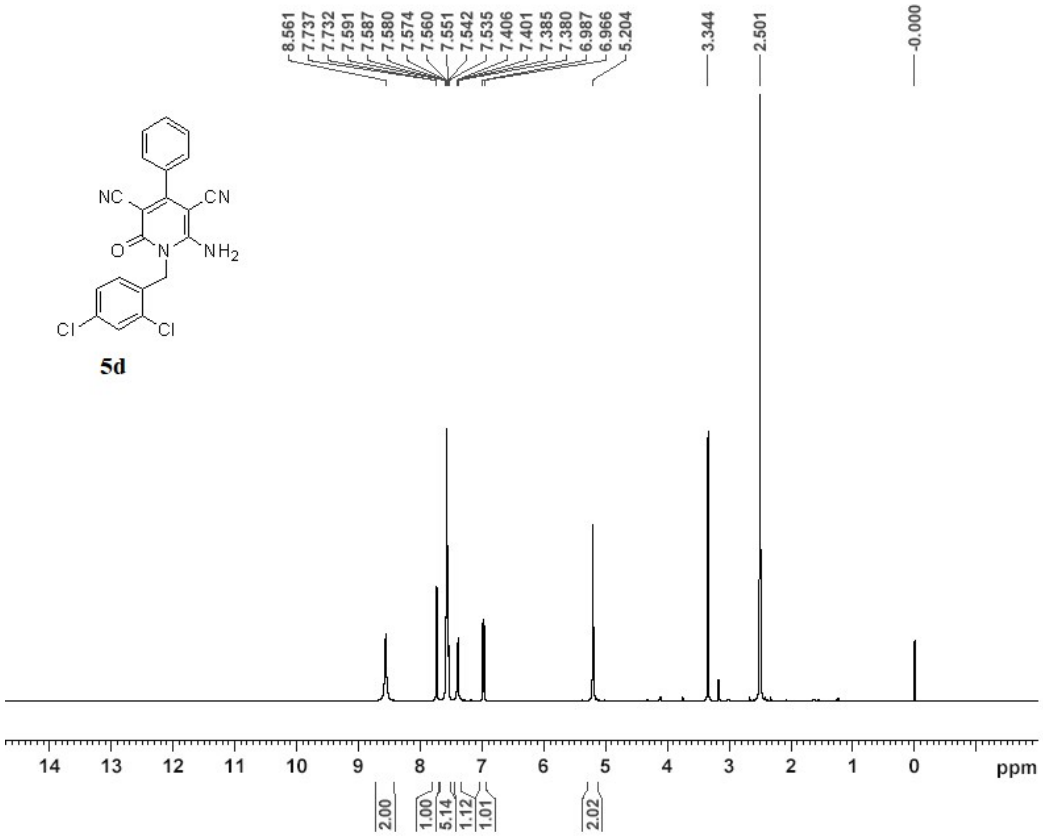

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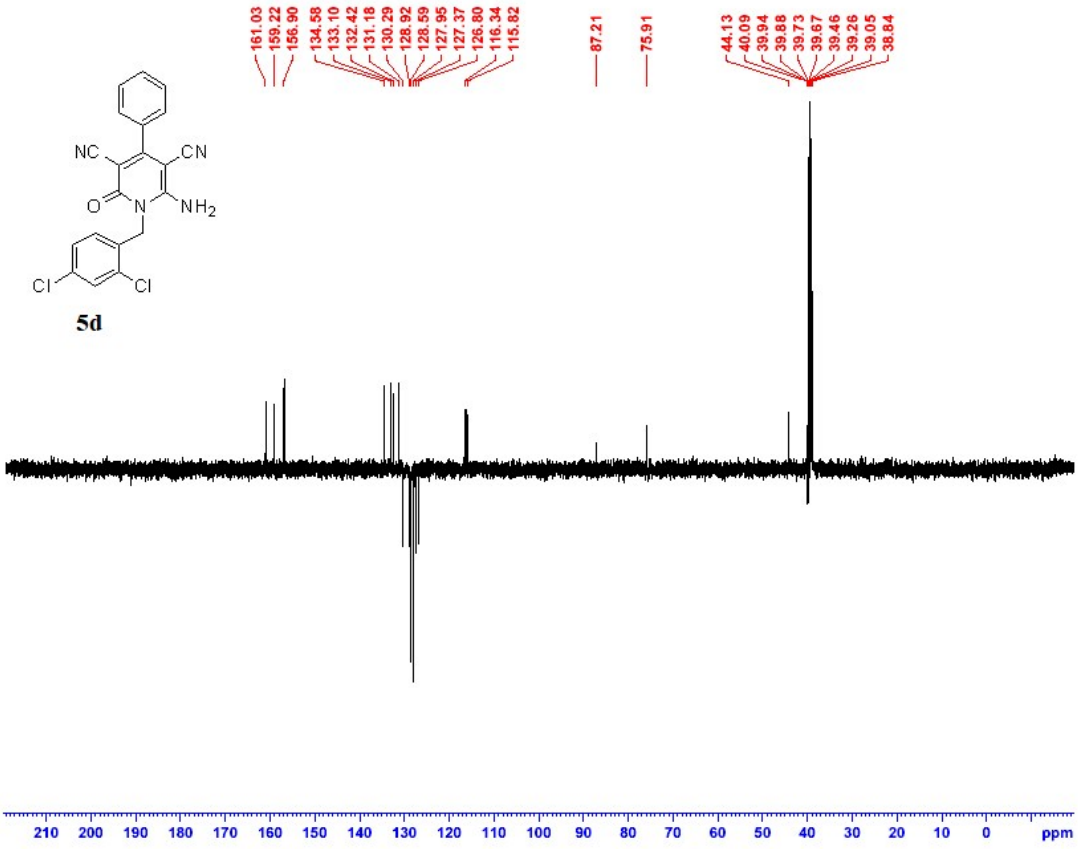

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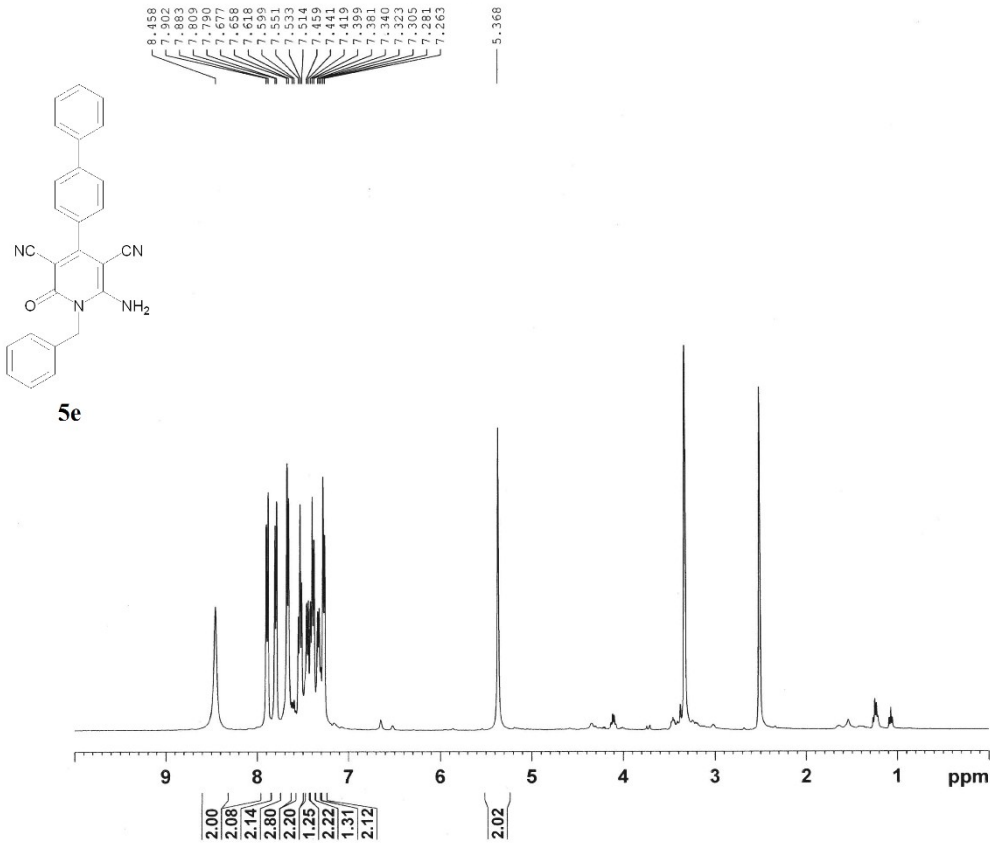

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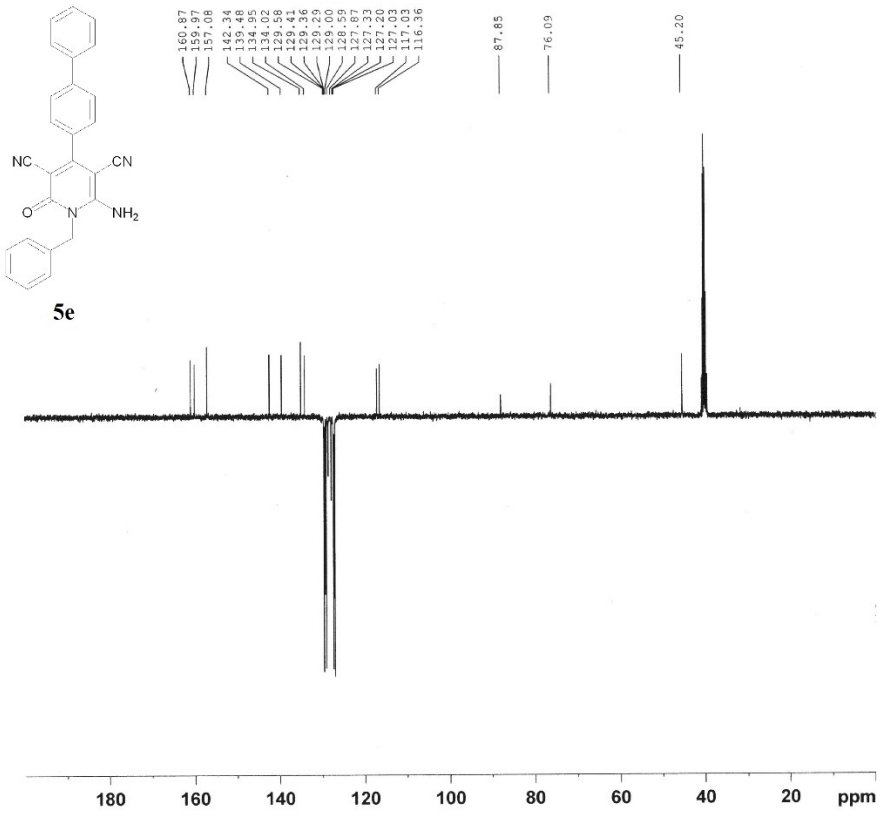

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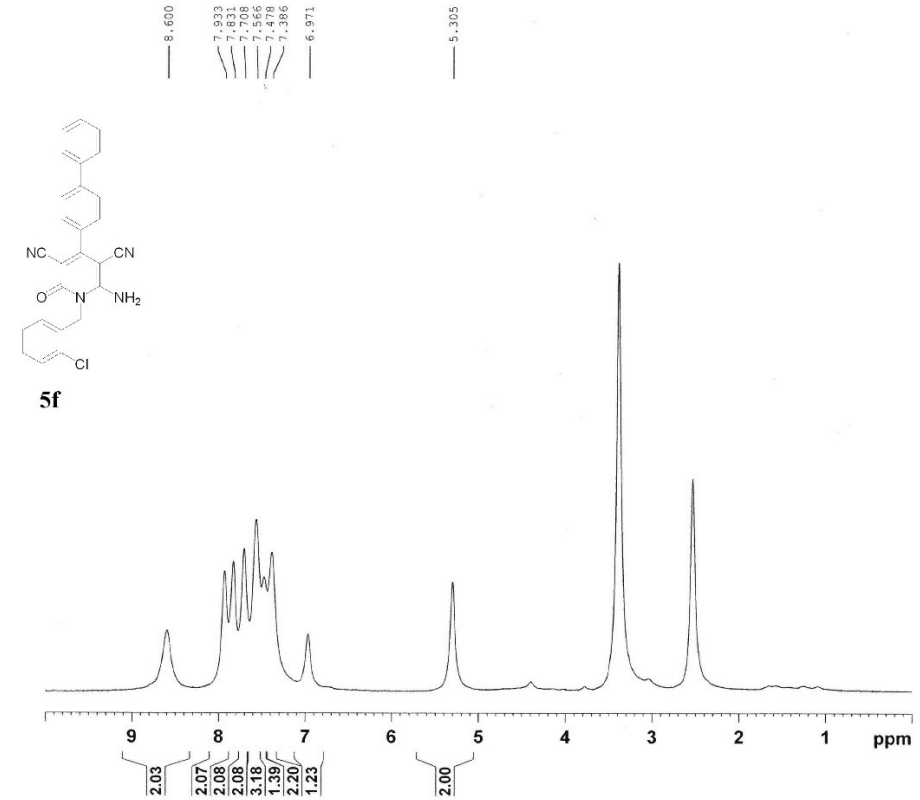

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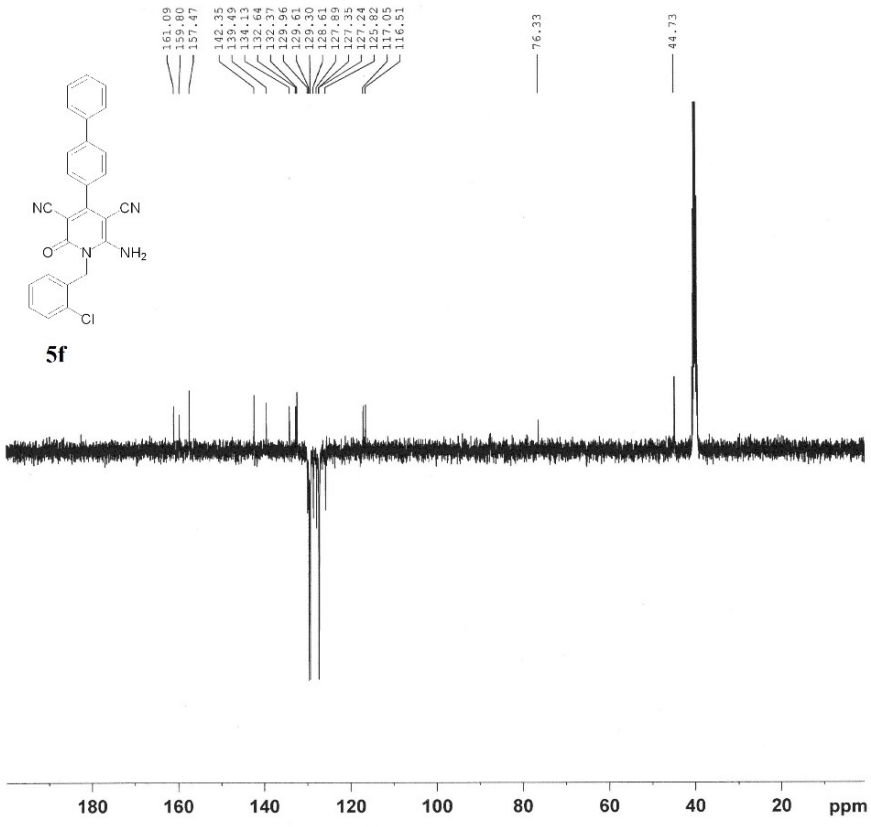

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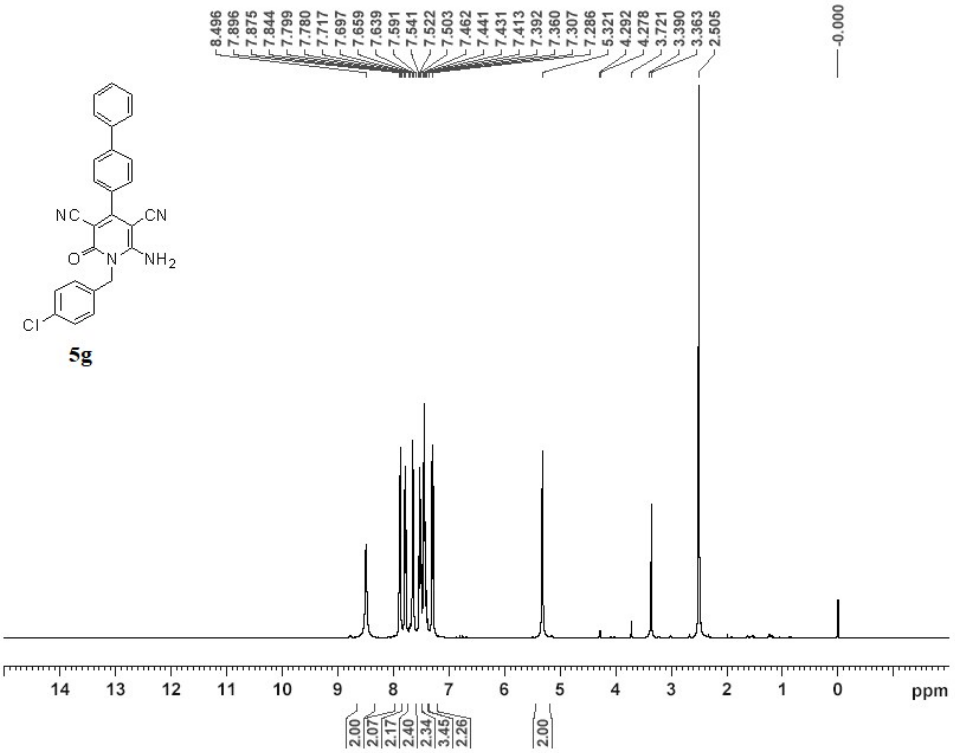

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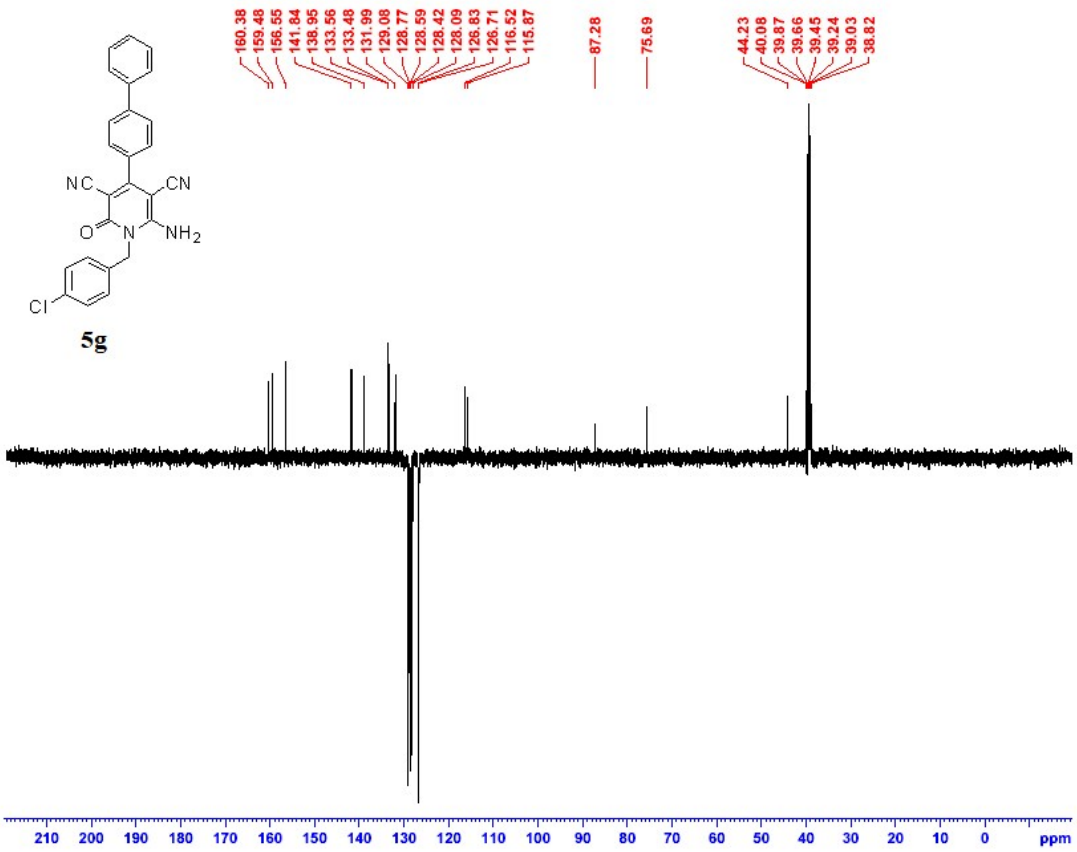

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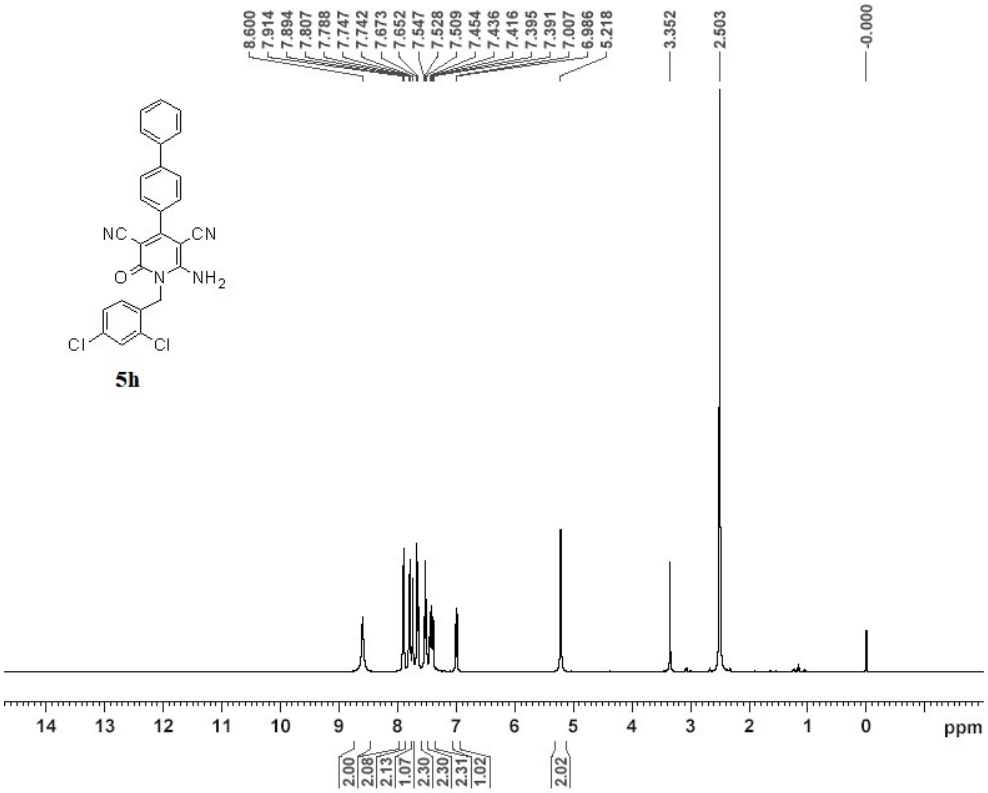

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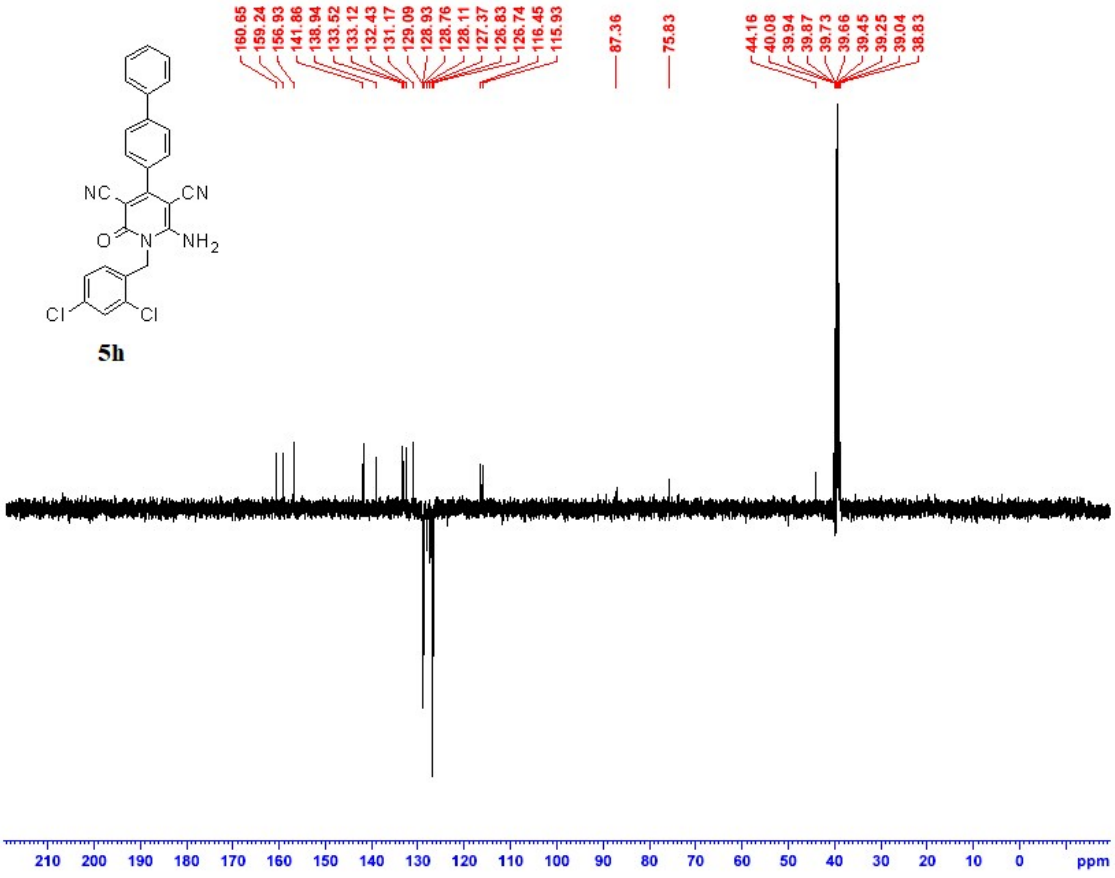

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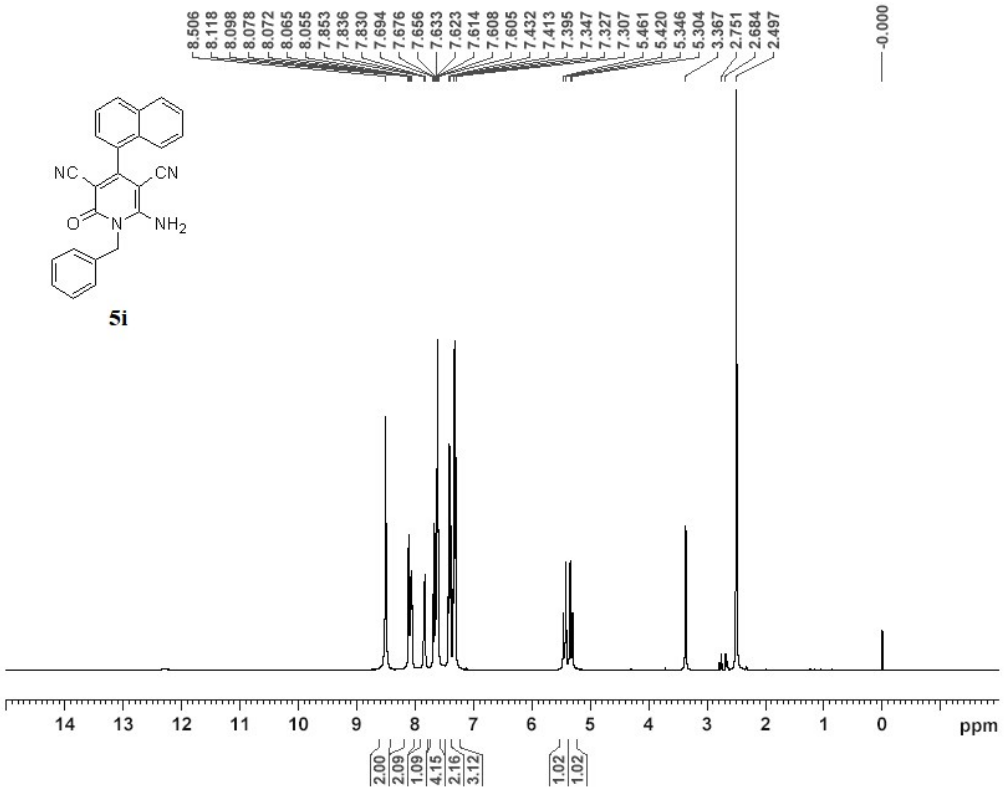

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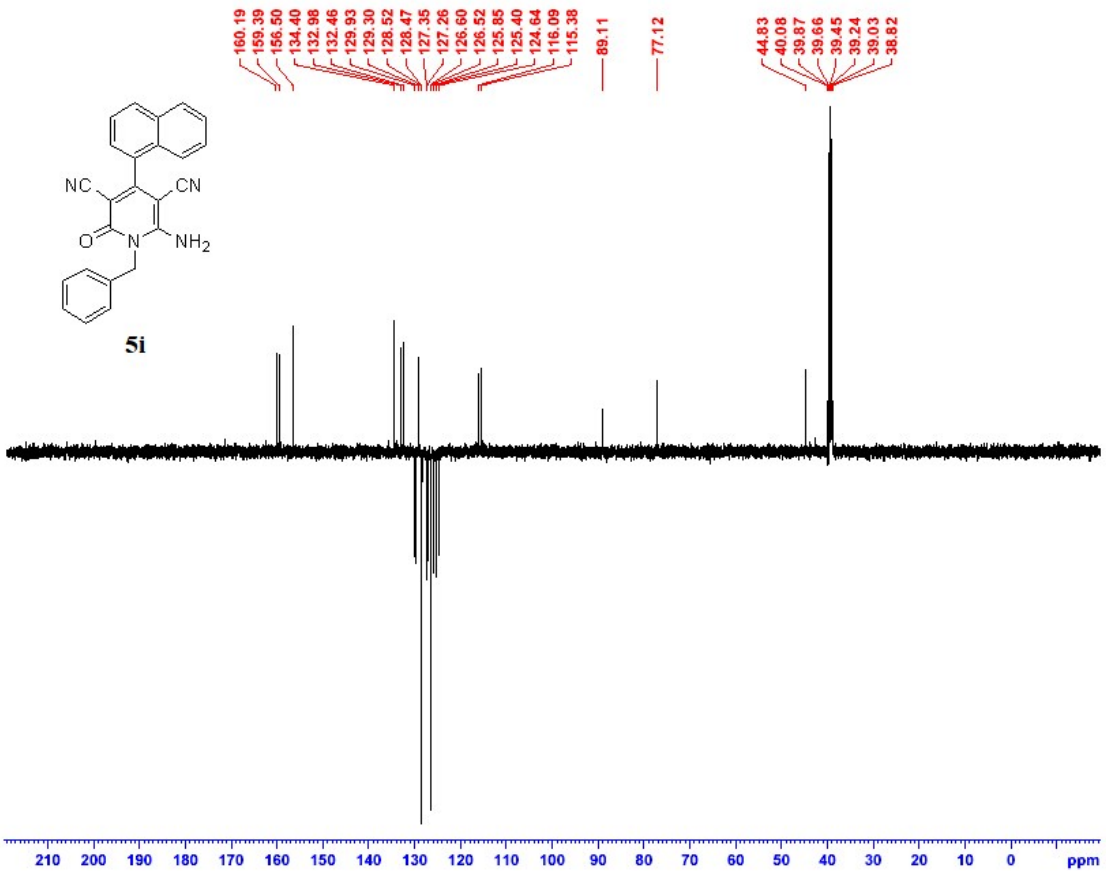

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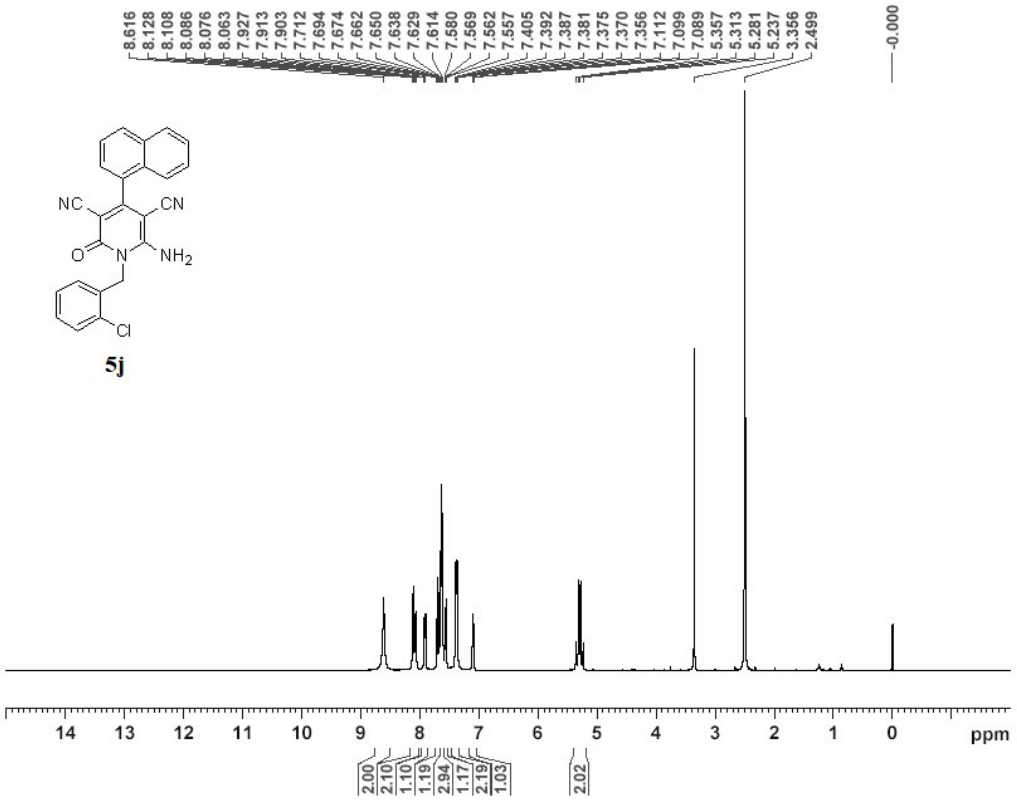

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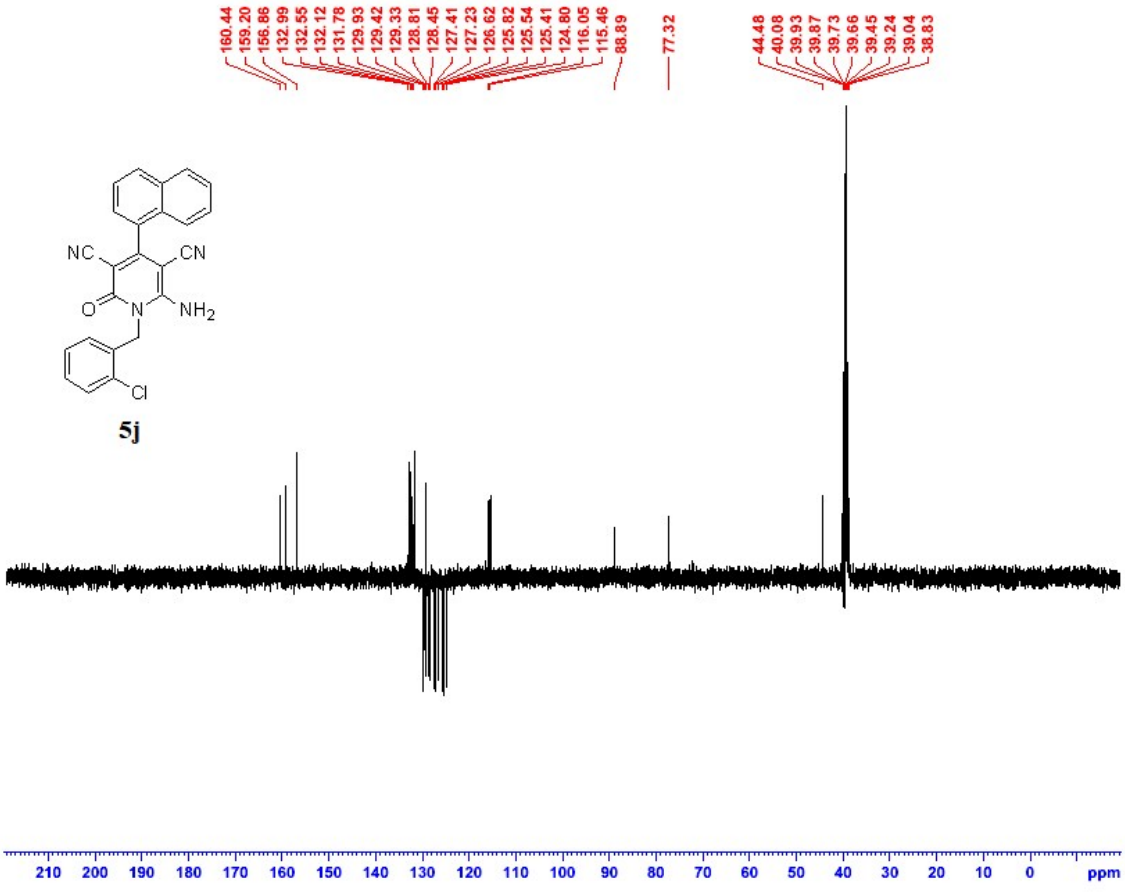

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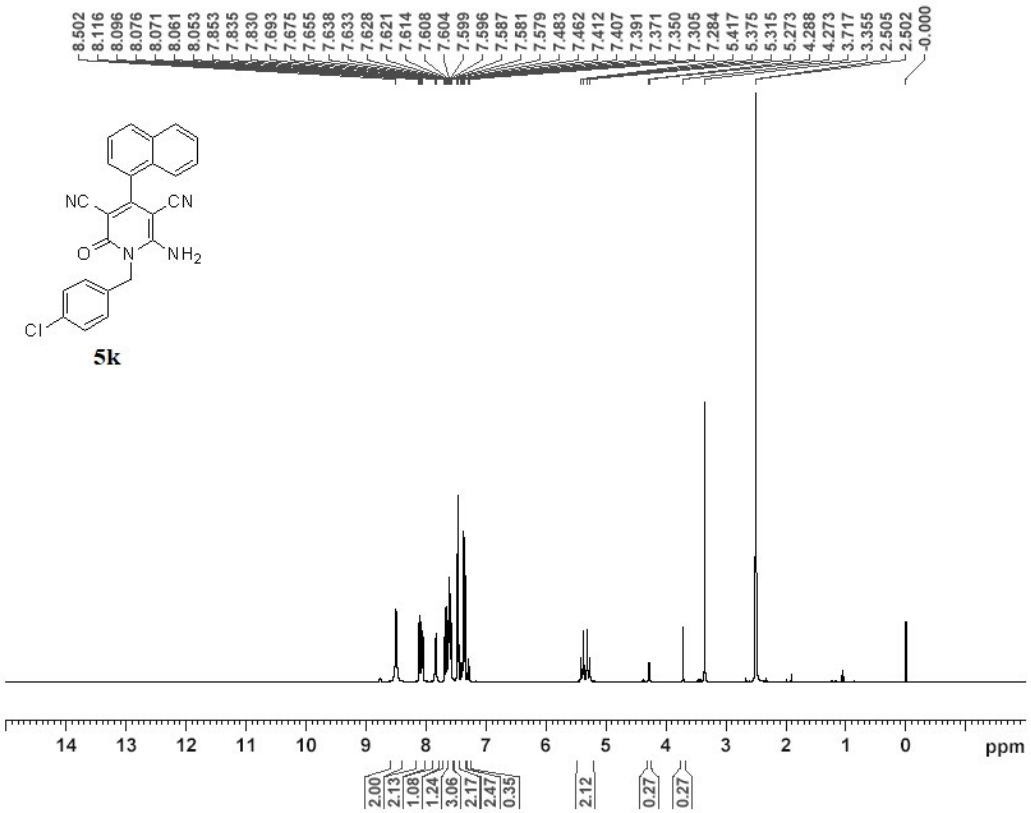

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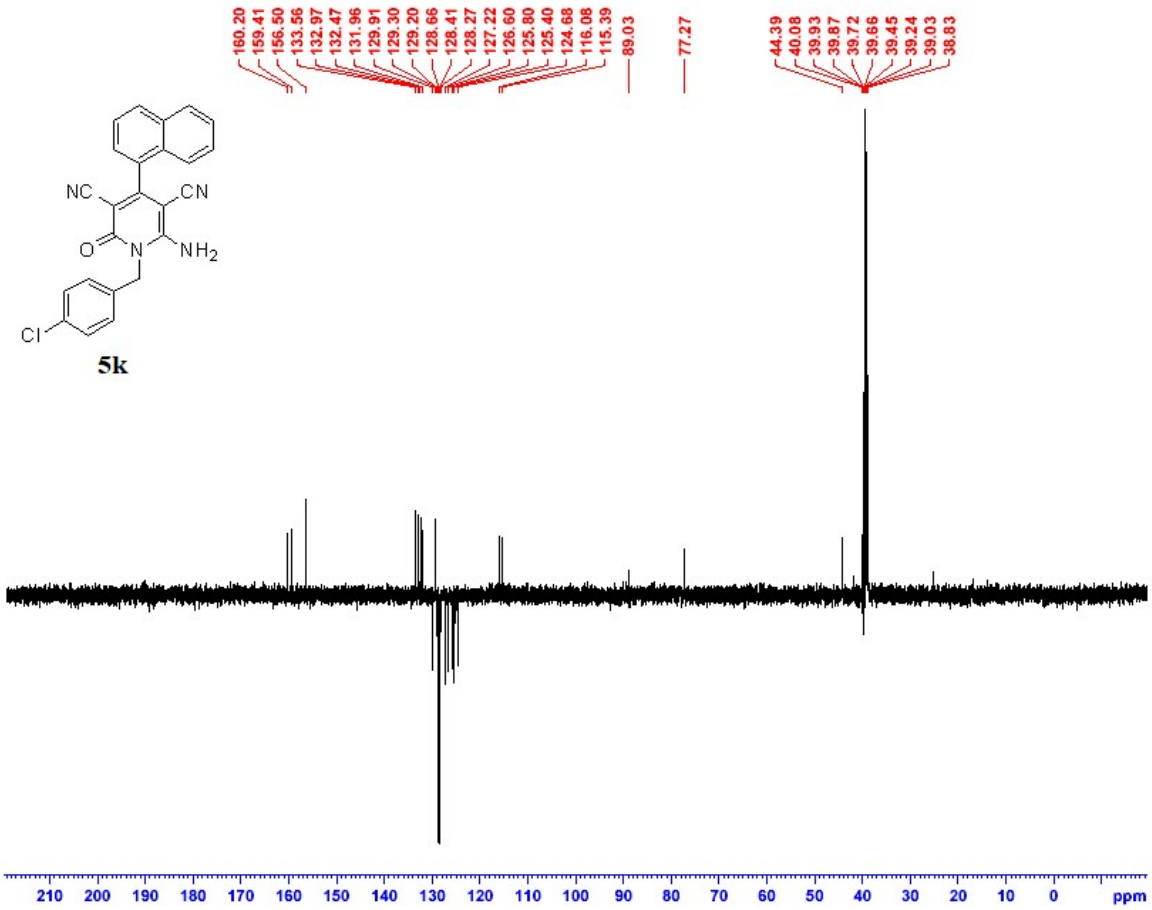
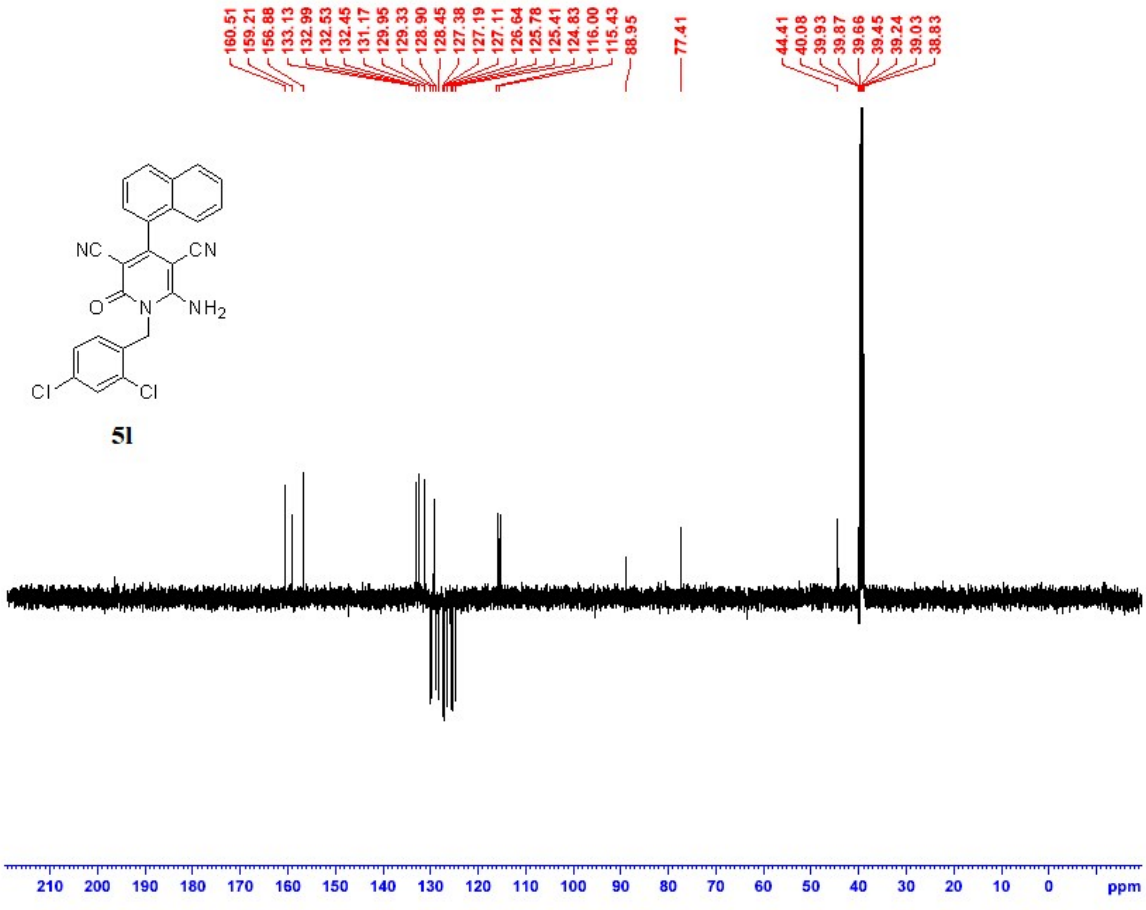


^{1}H-NMR (400 MHz, DMSO-d6)

^{13}C{1H}-APT (100 MHz, DMSO-d6)



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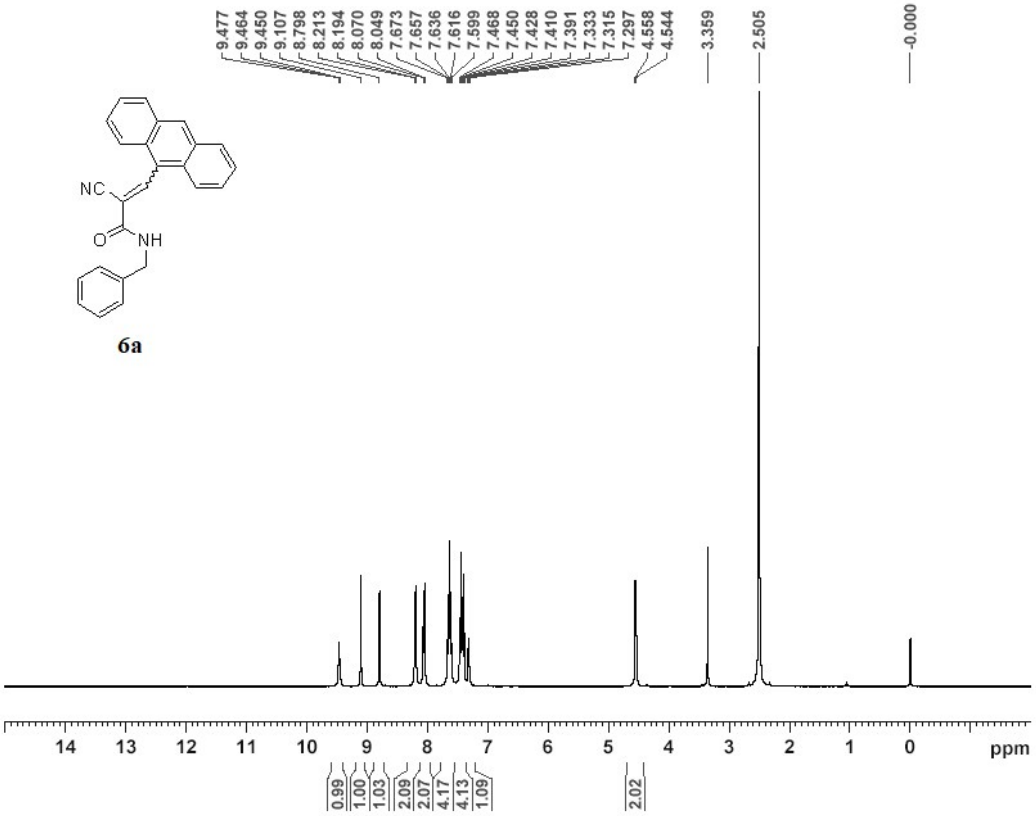

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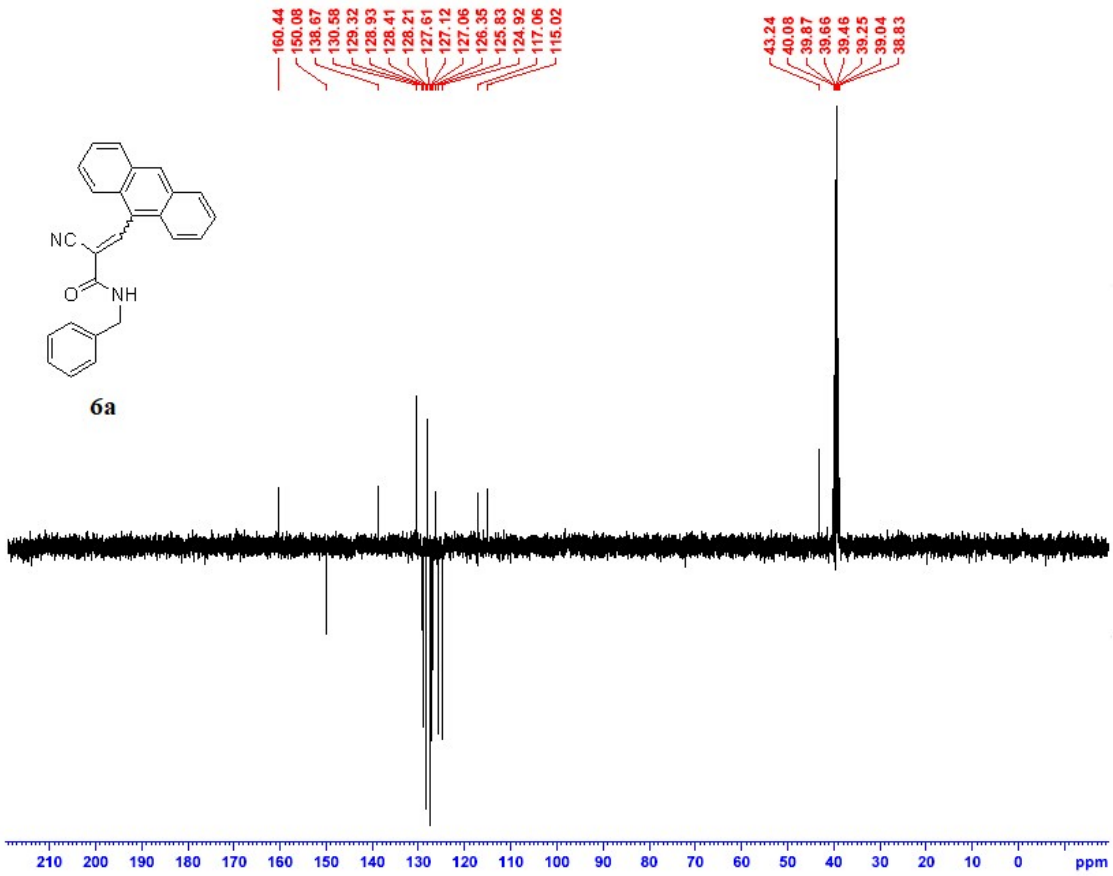

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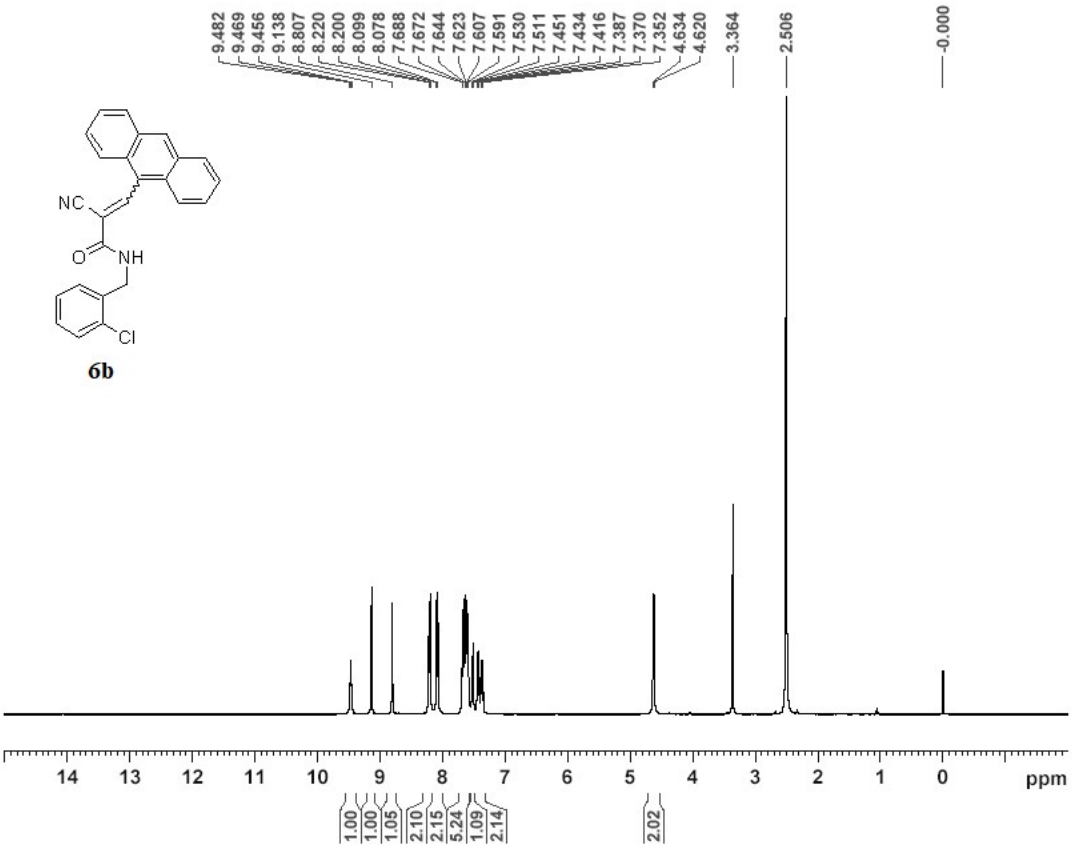
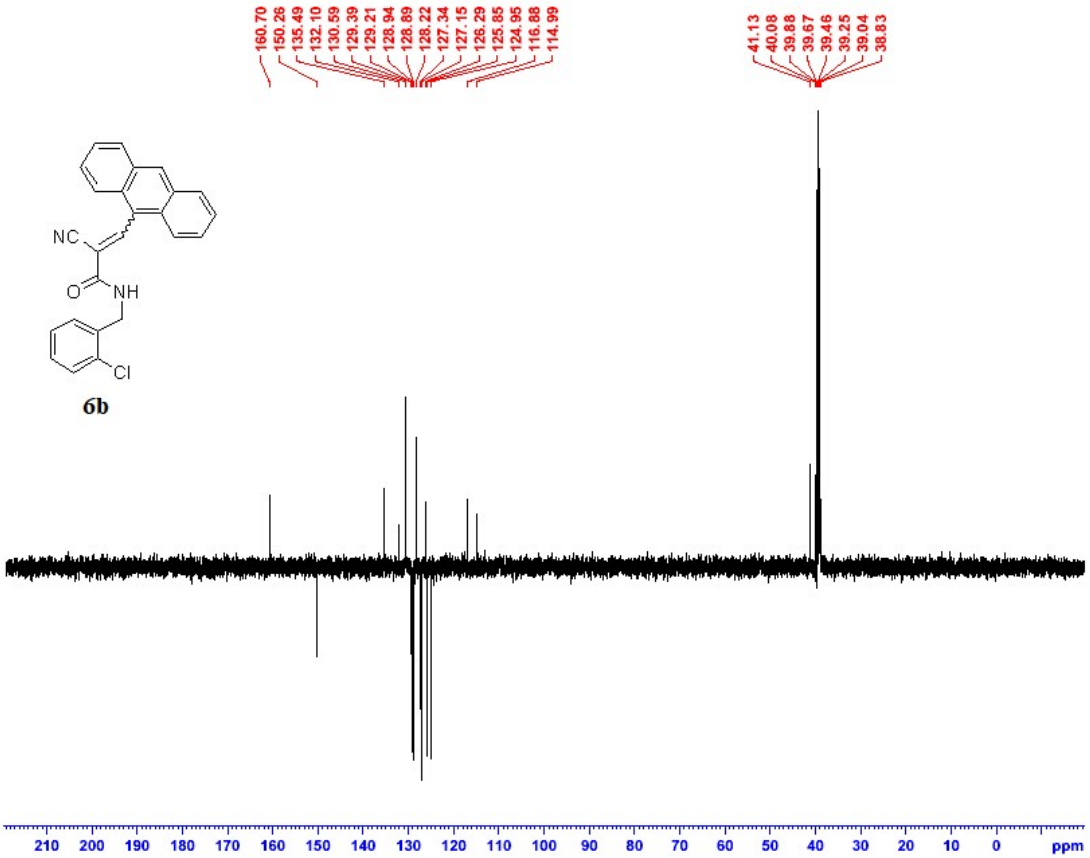


^{13}C{1H}-APT (100 MHz, DMSO-d6)



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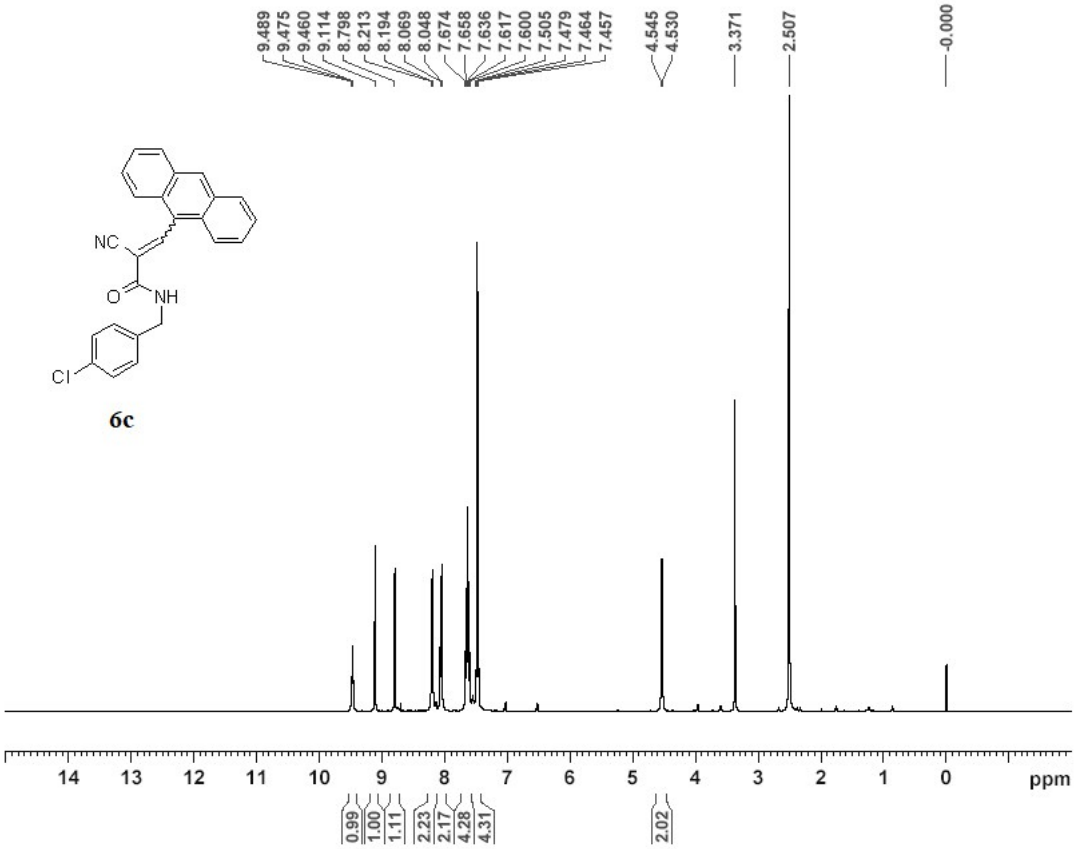

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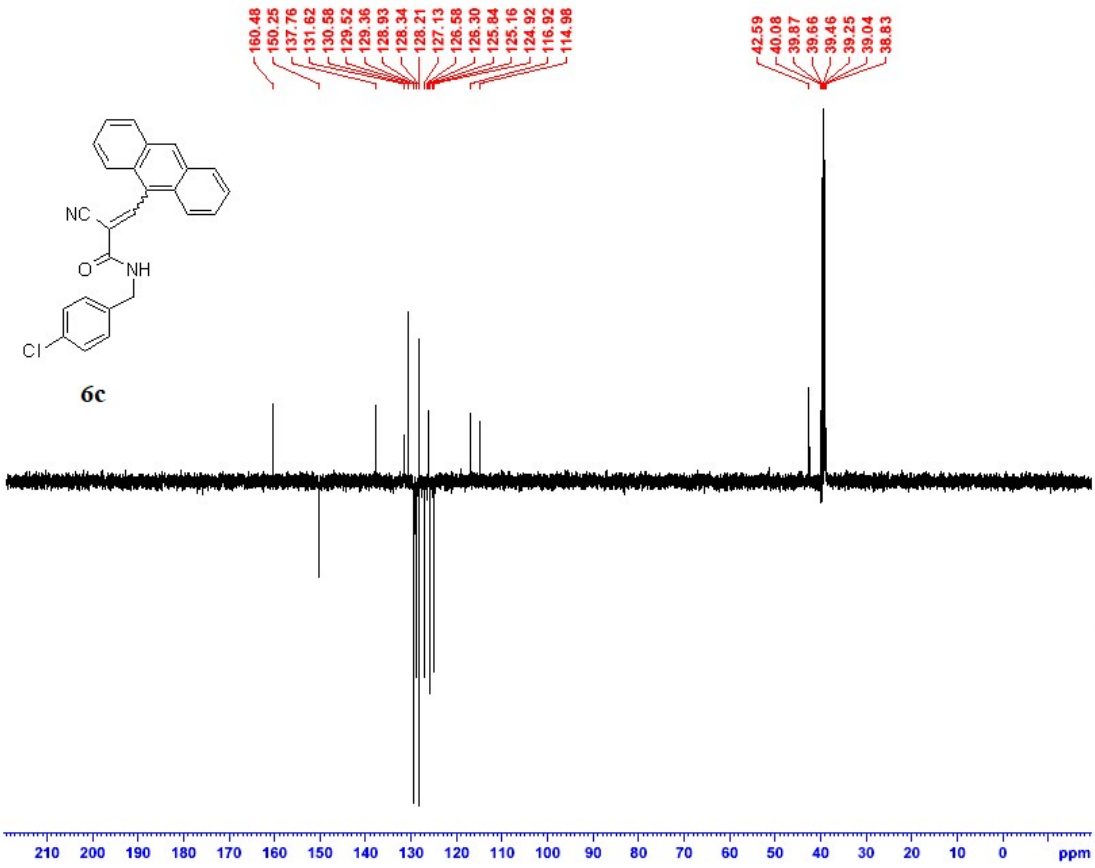

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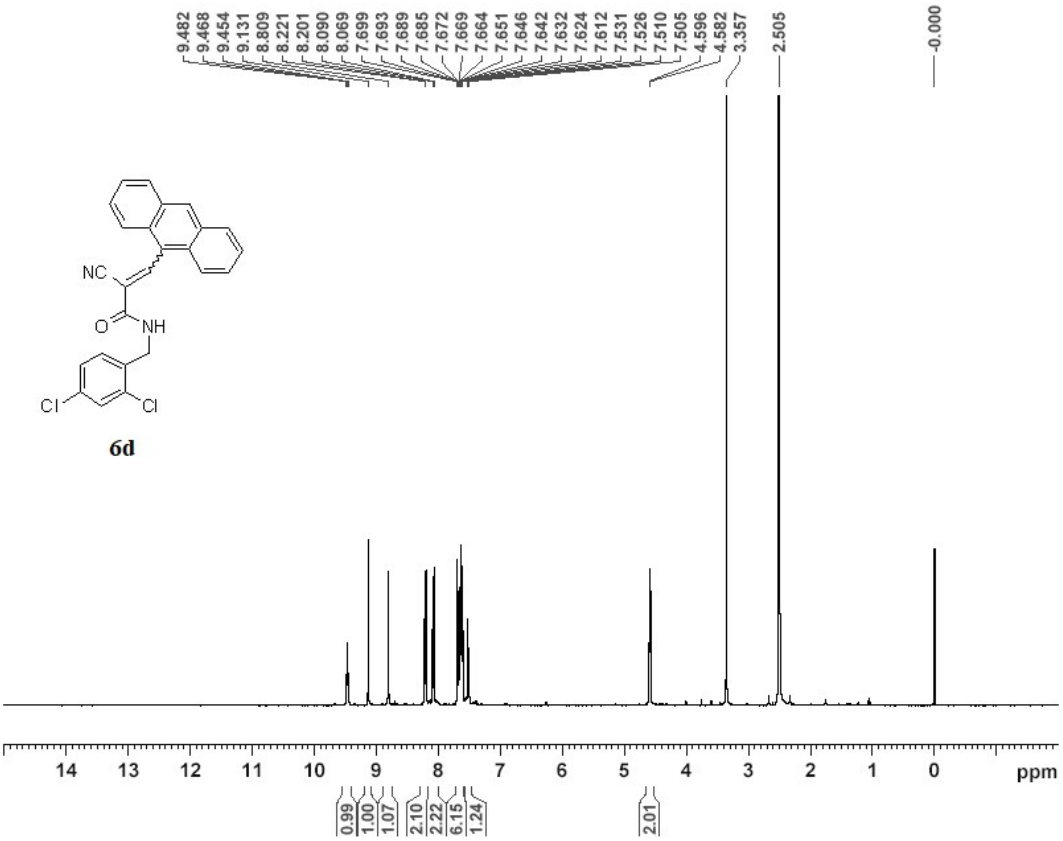

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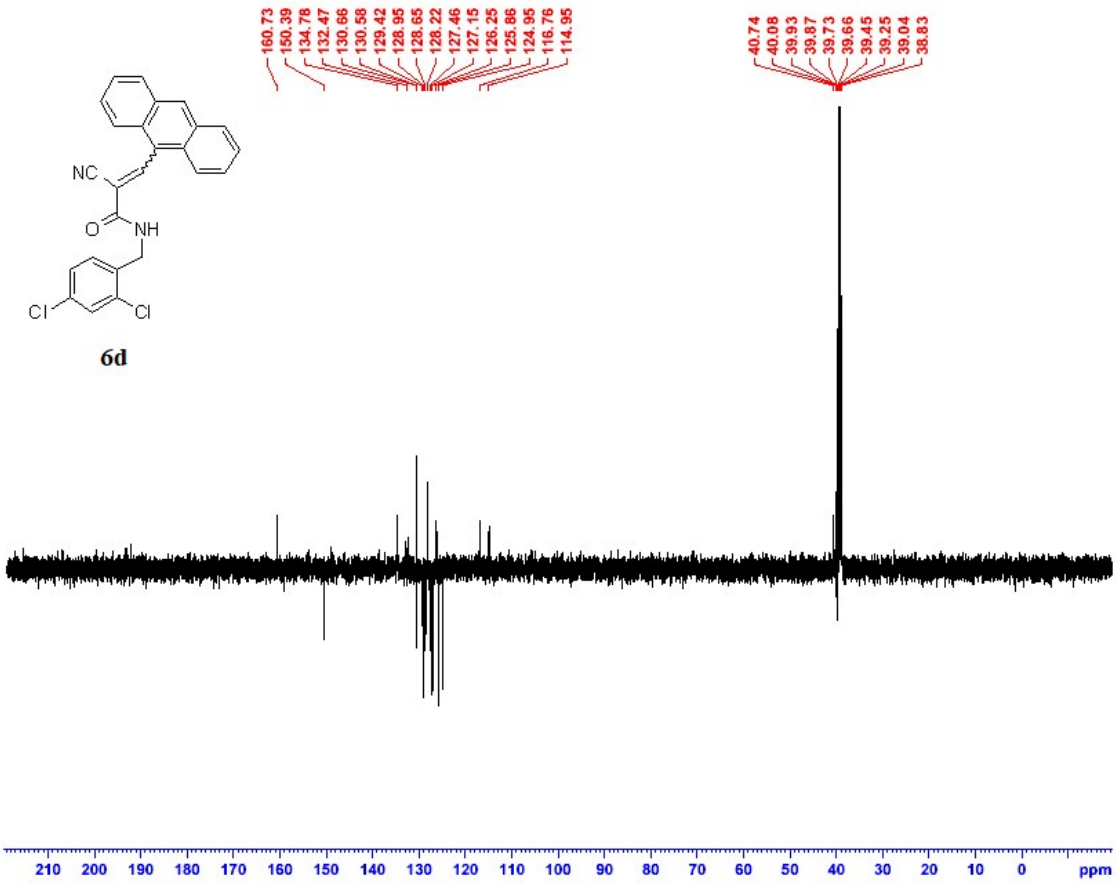

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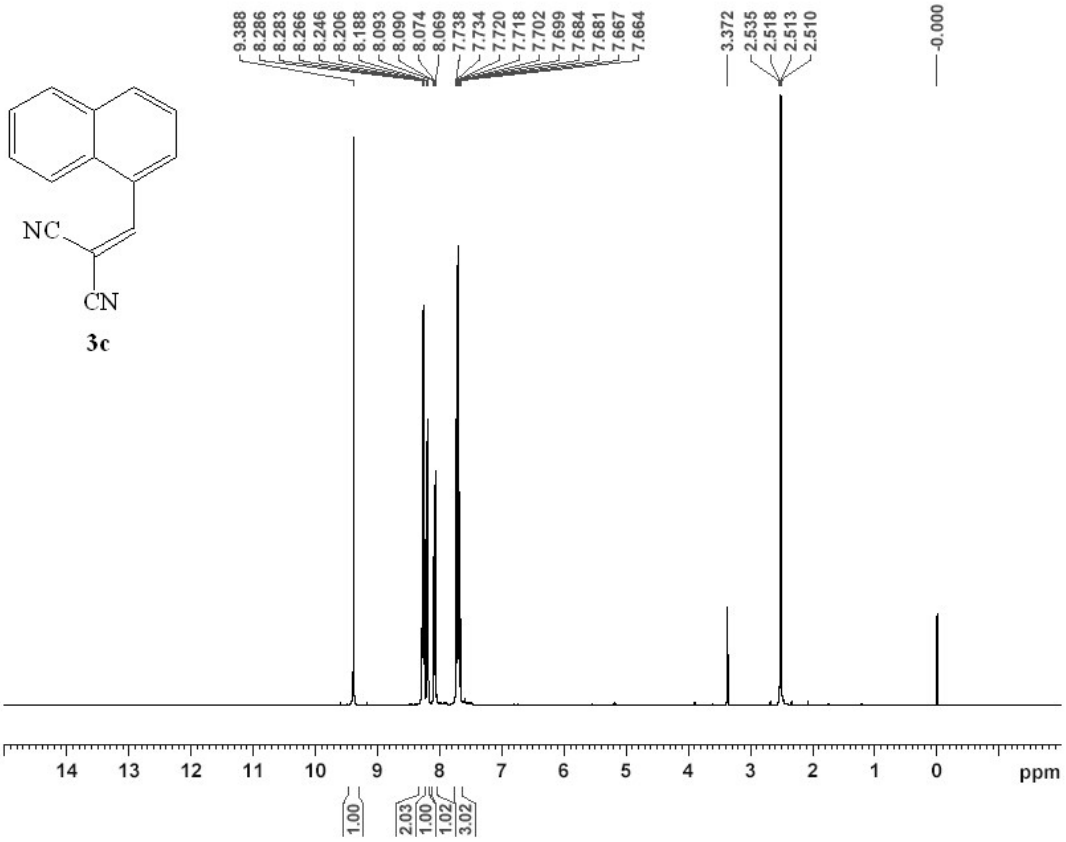

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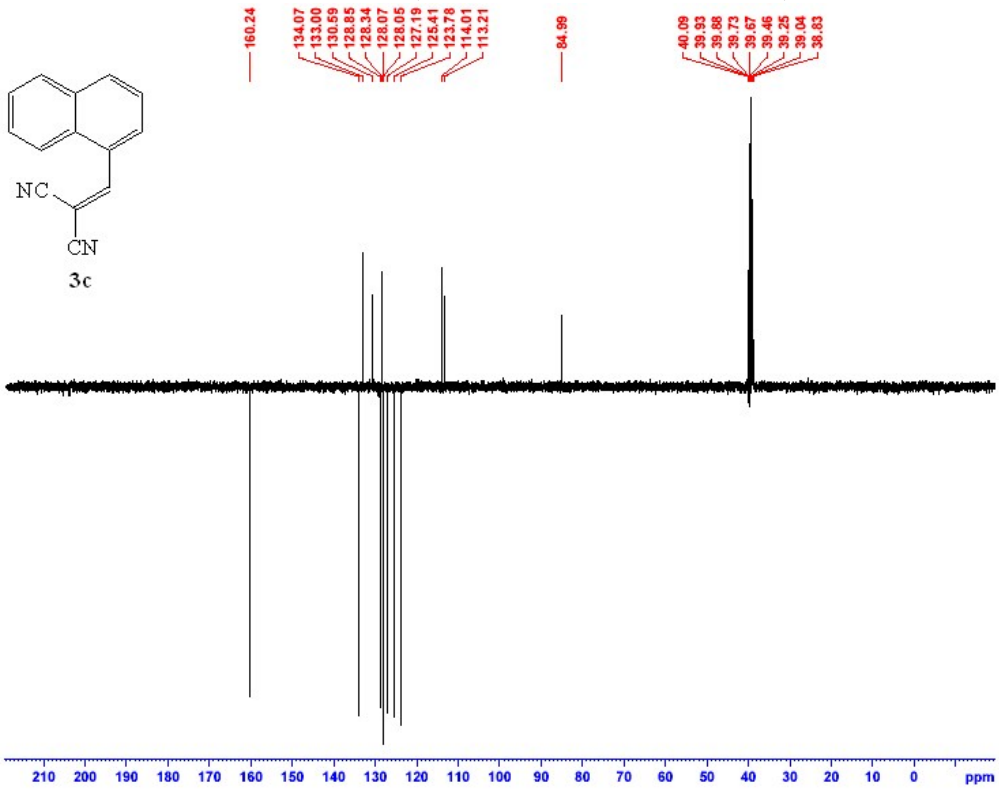

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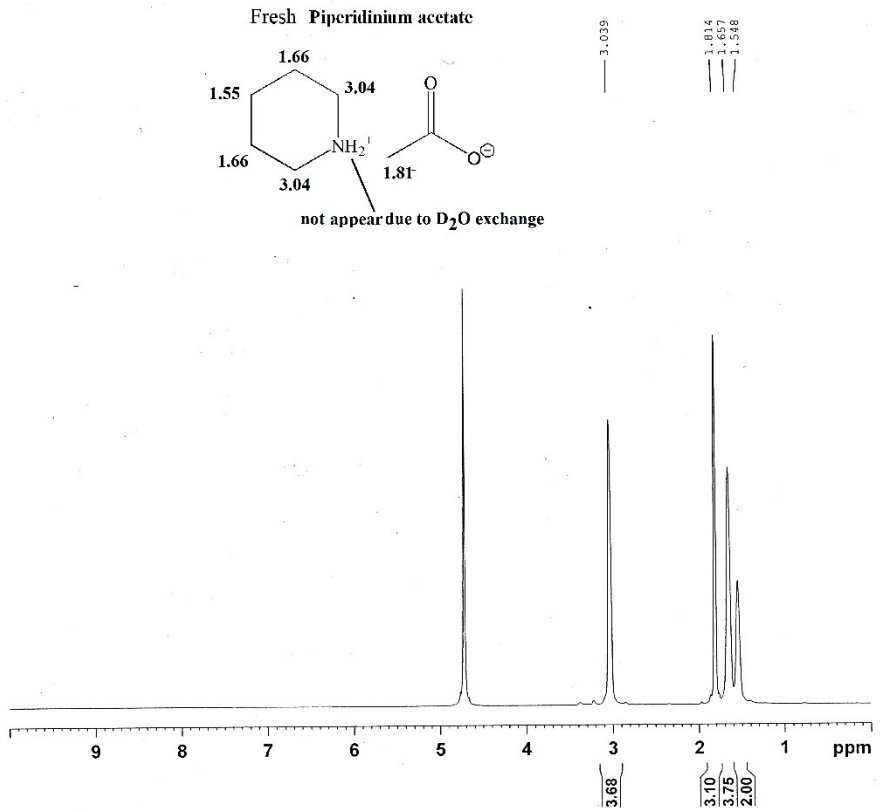

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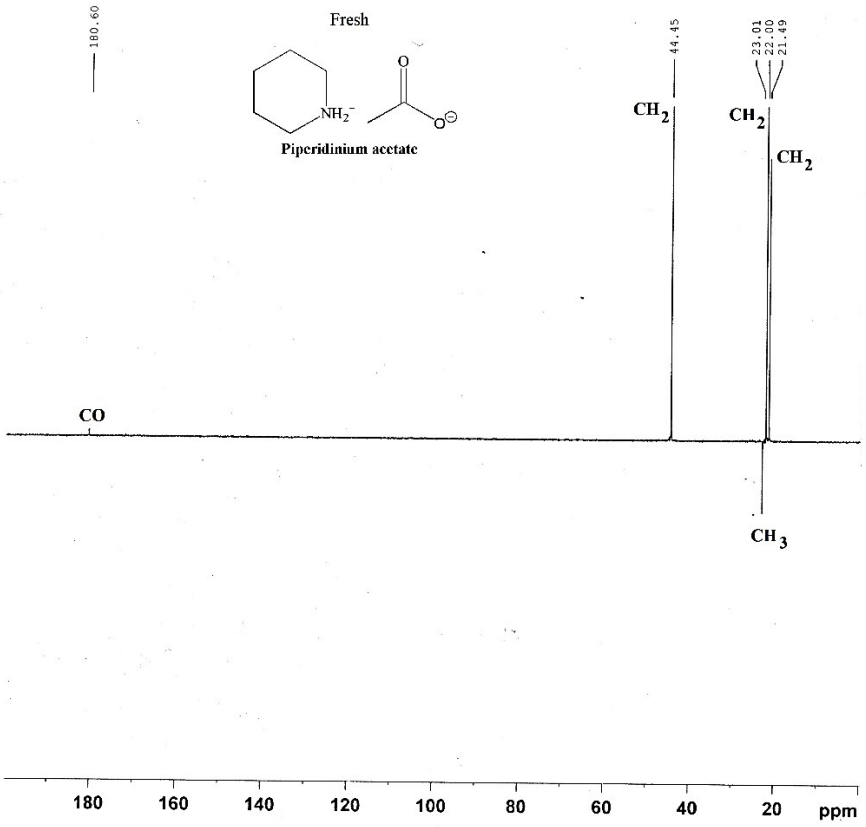

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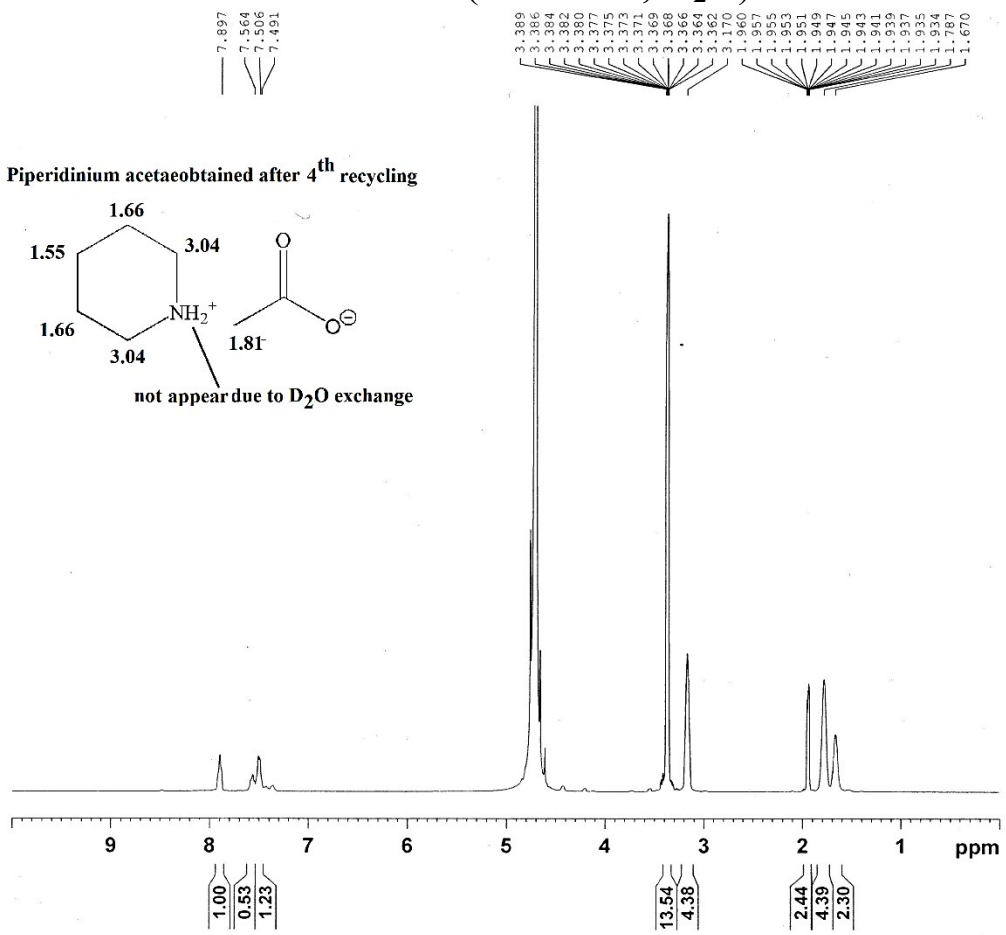

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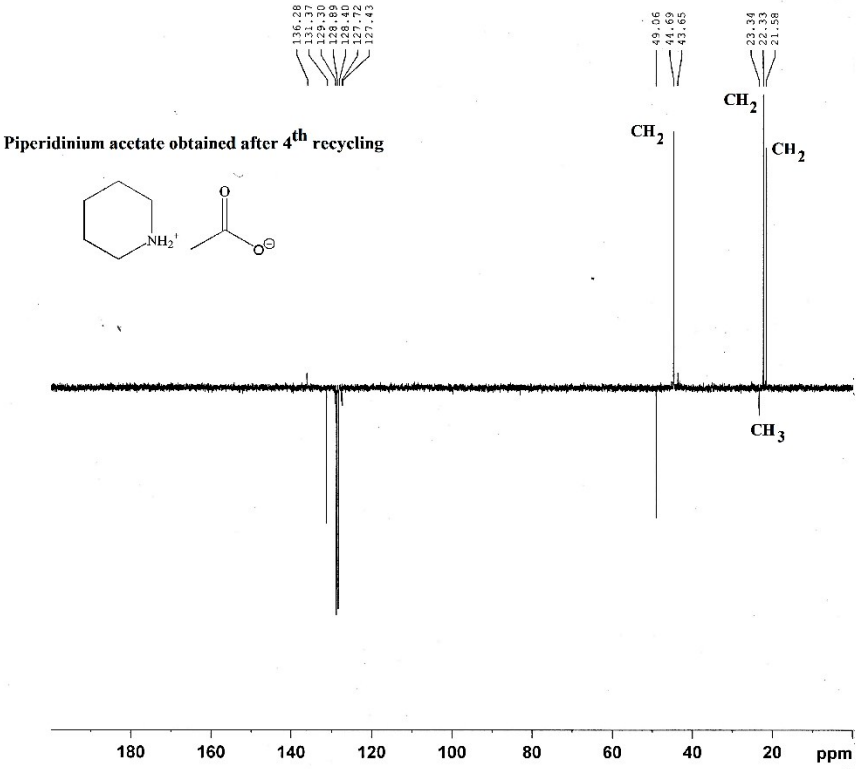
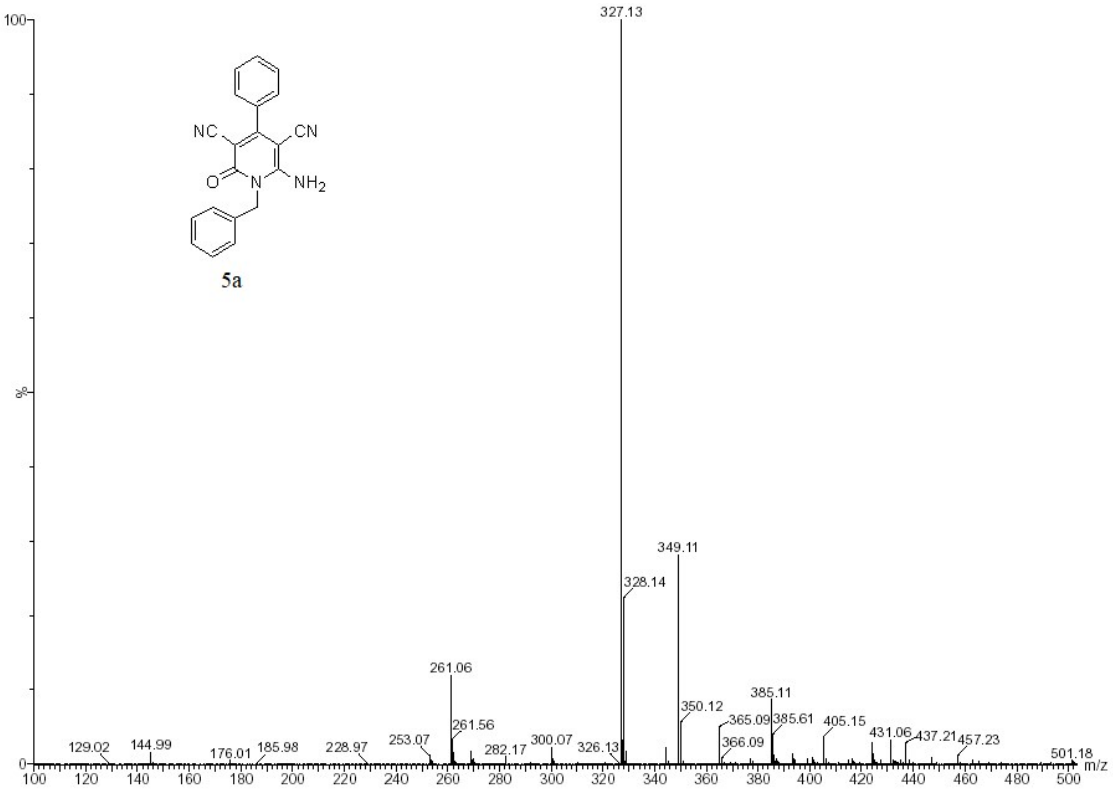
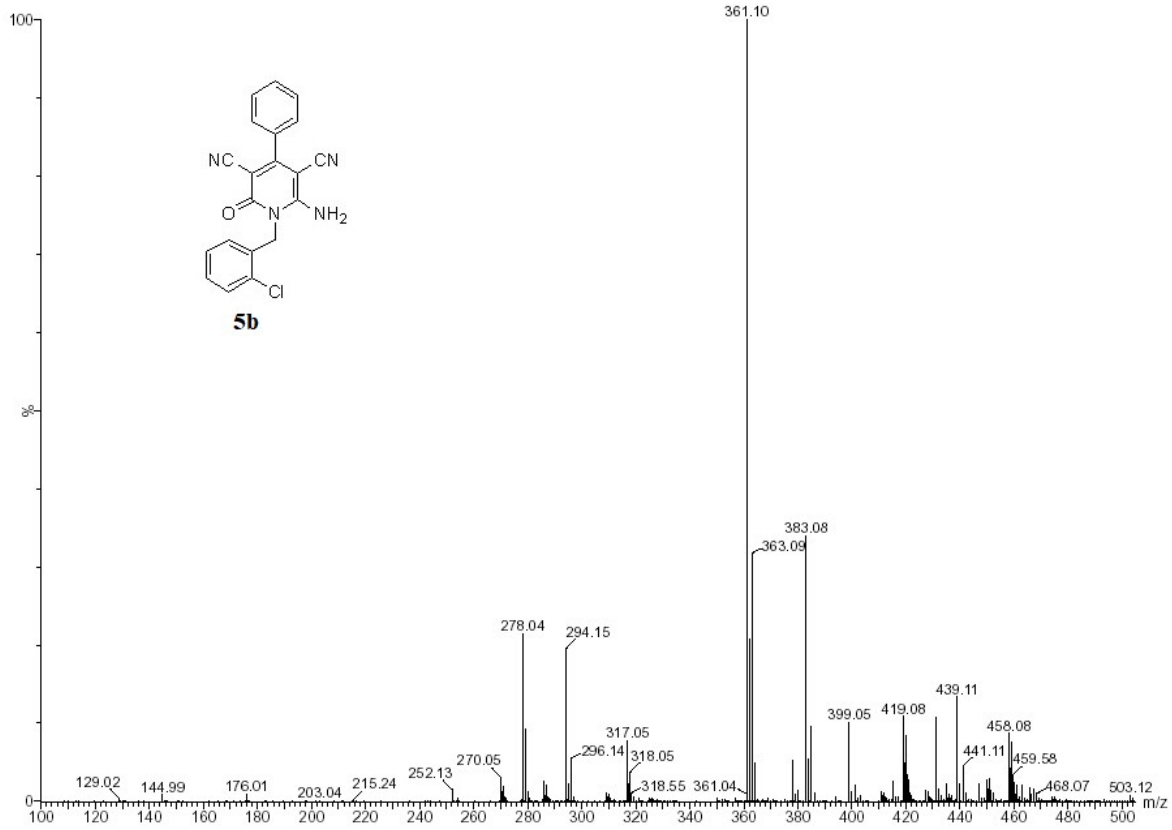


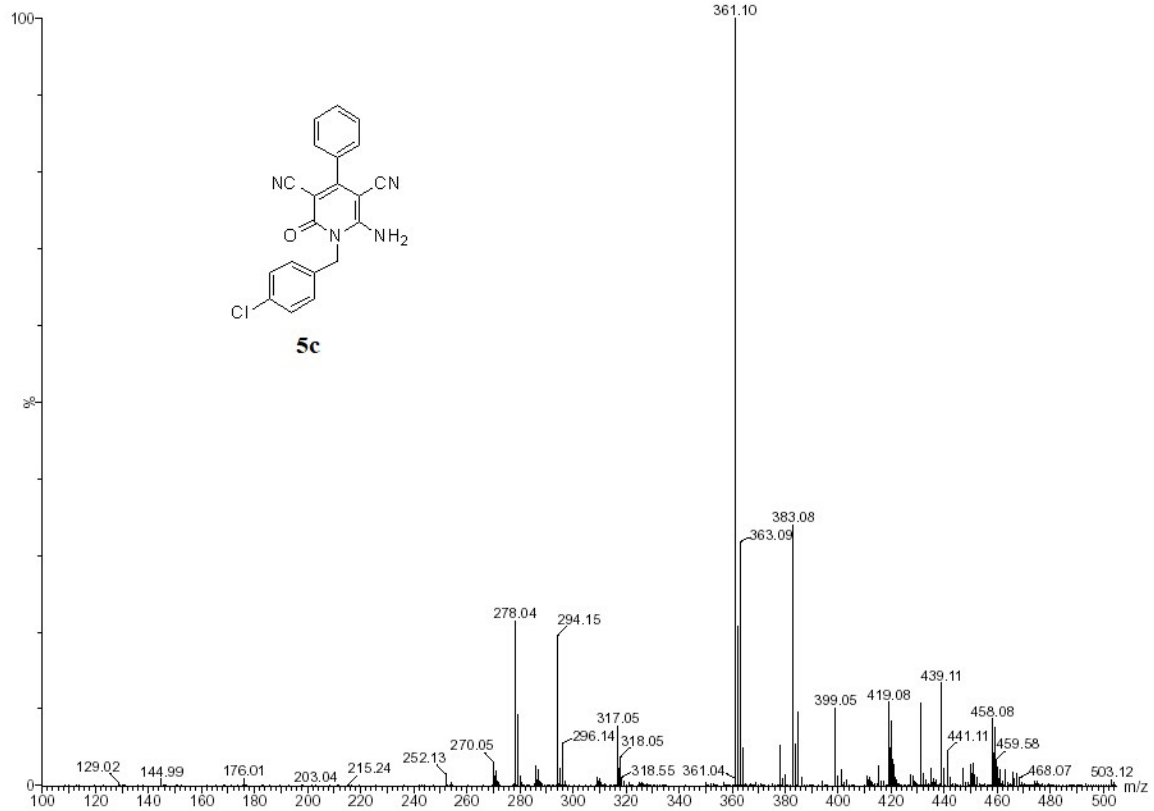
Mass spectrum of 5a



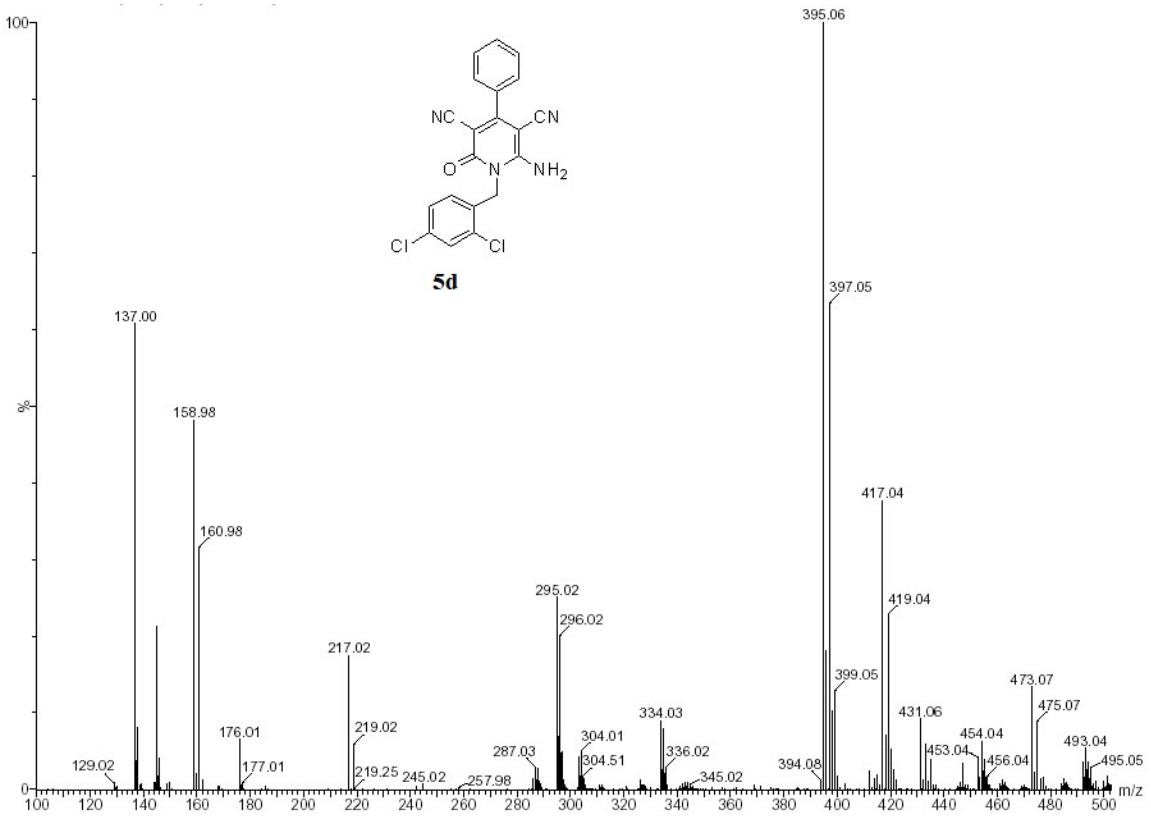
Mass spectrum of 5b



Mass spectrum of 5c

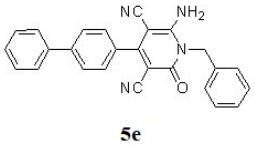


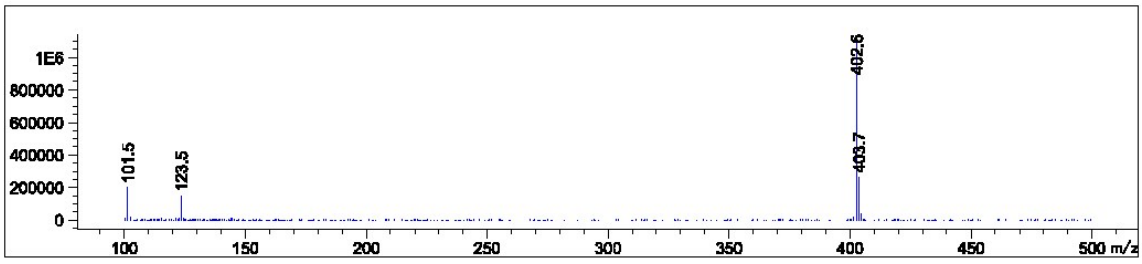
Mass spectrum of 5d



Mass spectrum of 5e

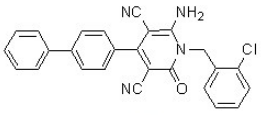
Retention Time (MS)	MS Area	Mol. Weight or Ion
5.595	8492896	403.70 I
		402.60 I
		123.50 I
		101.50 I



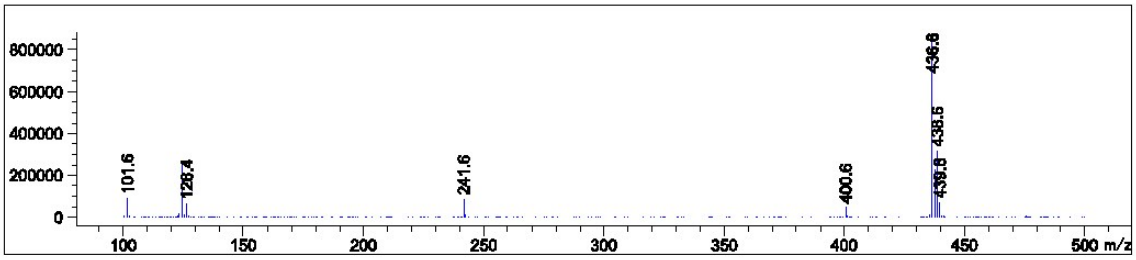


Mass spectrum of 5f

Retention Time (MS)	MS Area	Mol. Weight or Ion
5.752	8504891	438.60 I
		437.60 I
		436.60 I
		241.65 I
		124.40 I
		101.60 I

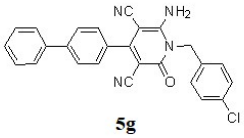


5f

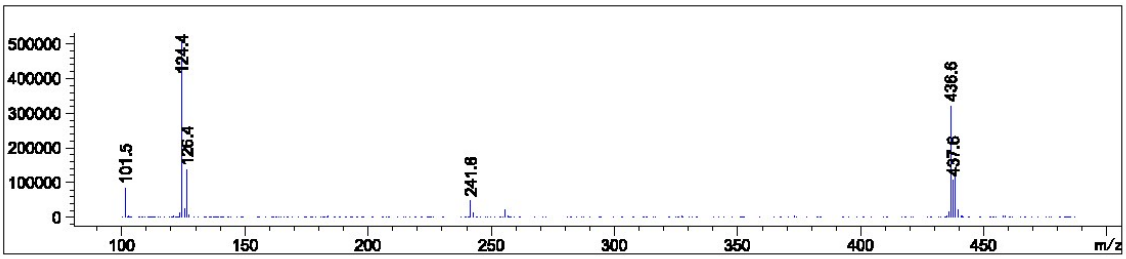


Mass spectrum of 5g

Retention Time (MS)	MS Area	Mol. Weight or Ion
5.826	5850985	438.60 I
		437.60 I
		436.60 I
		126.40 I
		124.40 I
		101.50 I

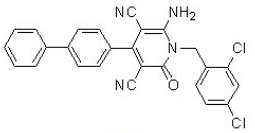


5g

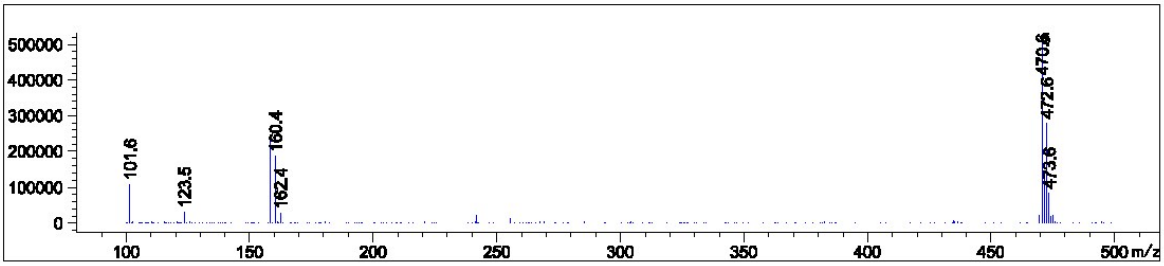


Mass spectrum of 5h

Retention Time (MS)	MS Area	Mol. Weight or Ion
5.989	5433183	473.65 I
		472.60 I
		471.65 I
		470.60 I
		160.35 I
		158.40 I
		101.60 I

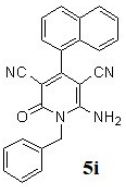


5h

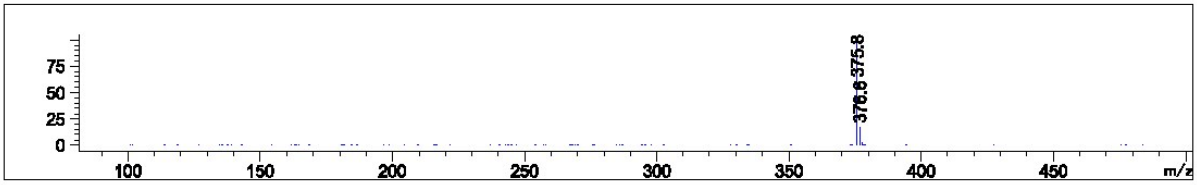


Mass spectrum of 5i

Retention Time (MS)	MS Area	Mol. Weight or Ion
5.192	1040582	376.65 I
		375.80 I

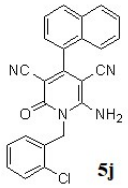


5i

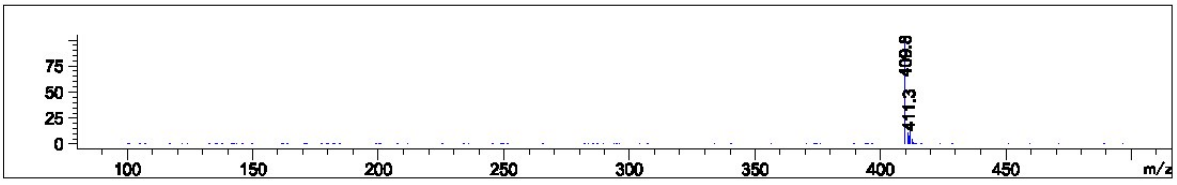


Mass spectrum of 5j

Retention Time (MS)	MS Area	Mol. Weight or Ion
5.372	973178	411.70 I
		410.95 I
		409.80 I

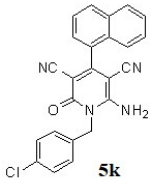


5j

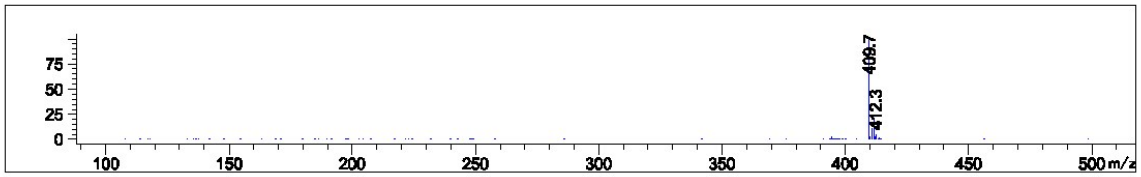


Mass spectrum of 5k

Retention Time (MS)	MS Area	Mol. Weight or Ion
5.456	1029597	411.70 I
		410.90 I
		409.70 I

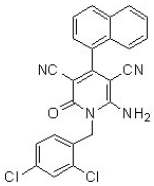


5k

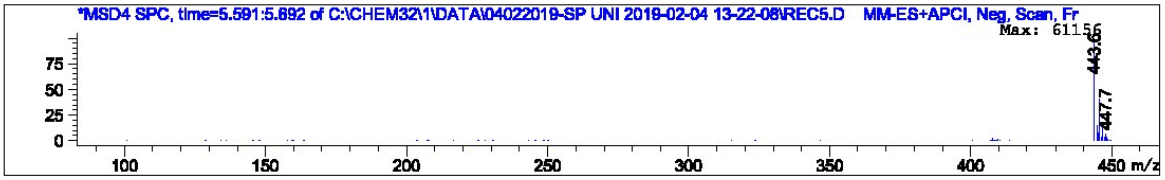


Mass spectrum of 5l

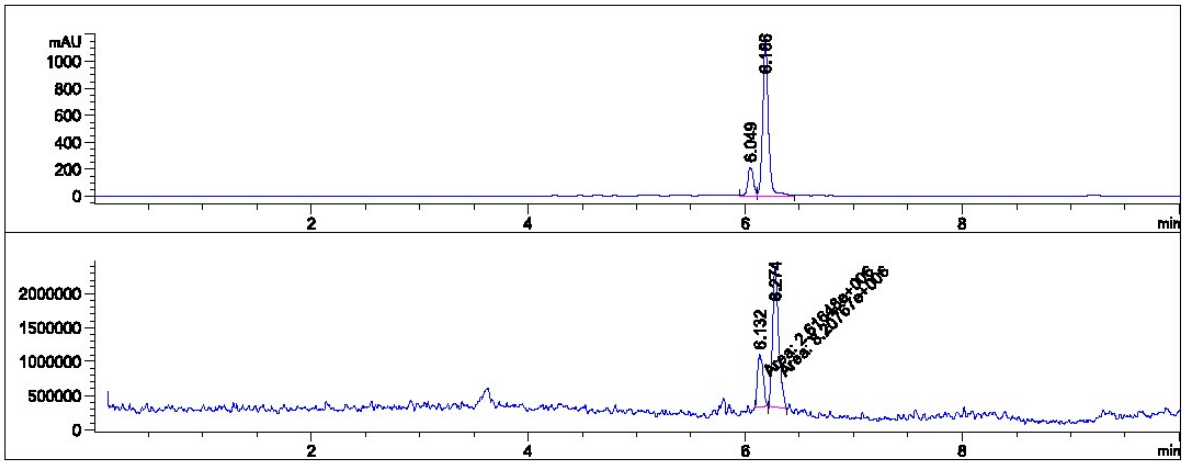
Retention Time (MS)	MS Area	Mol. Weight or Ion
5.637	1031967	446.70 I
		445.75 I
		444.75 I
		443.65 I



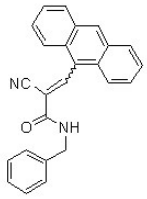
5l



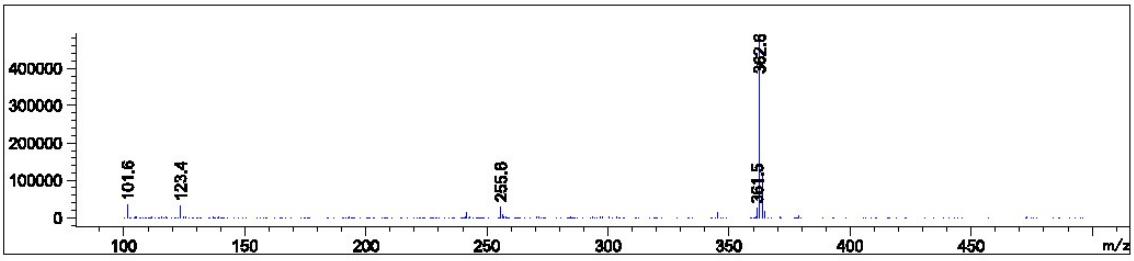
LCMS of 6a

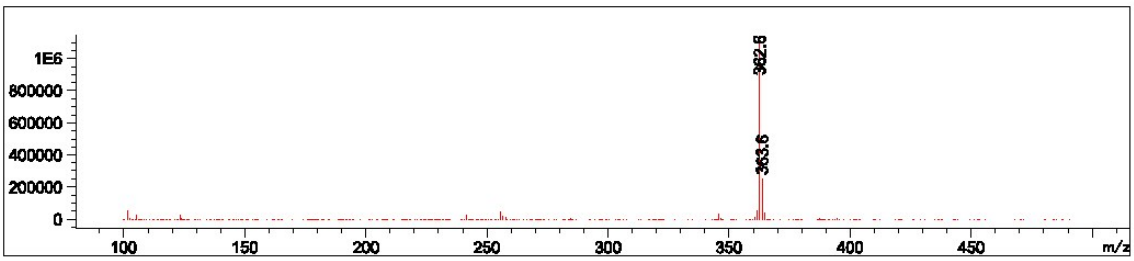


Retention Time (MS)	MS Area	Mol. Weight or Ion
6.132	2616479	363.60 I
		362.60 I
6.274	8207667	363.60 I
		362.60 I

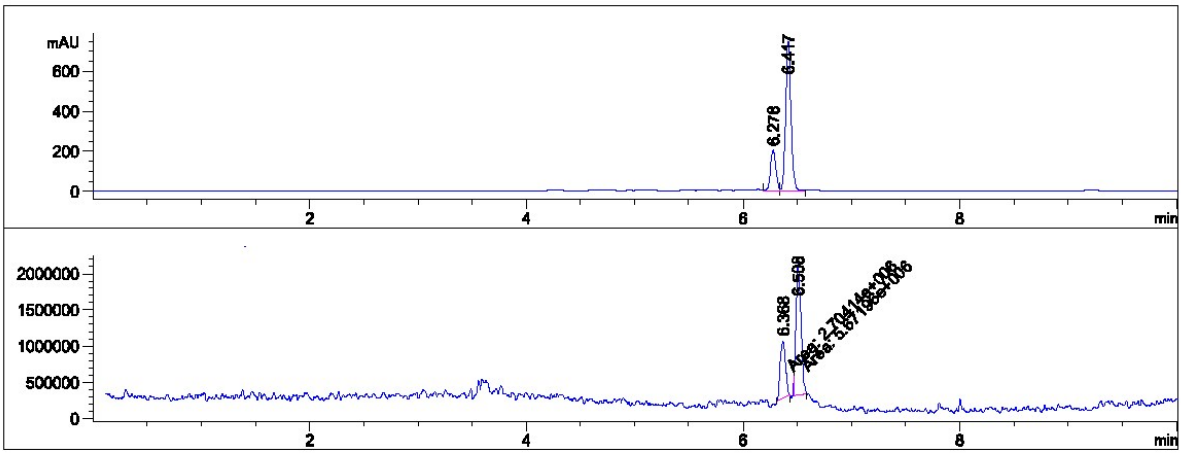


6a

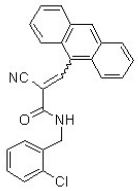




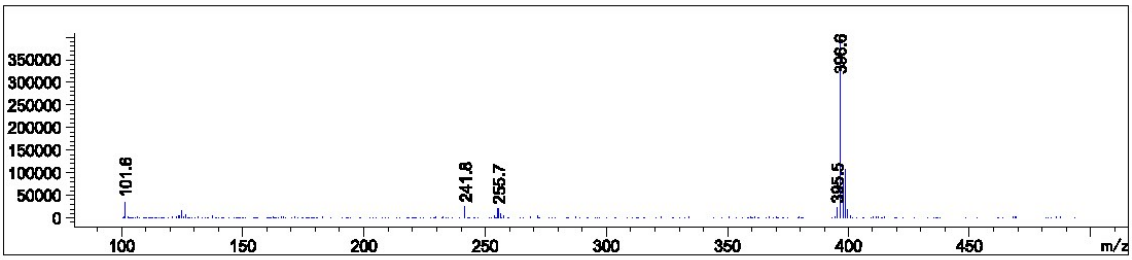
LCMS of 6b

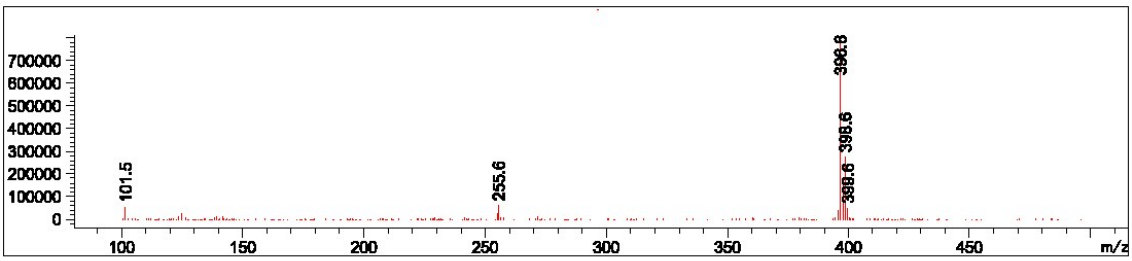


Retention Time (MS)	MS Area	Mol. Weight or Ion
6.368	2704141	398.60 I
		397.60 I
		396.65 I
6.508	5671964	398.60 I
		397.60 I
		396.60 I

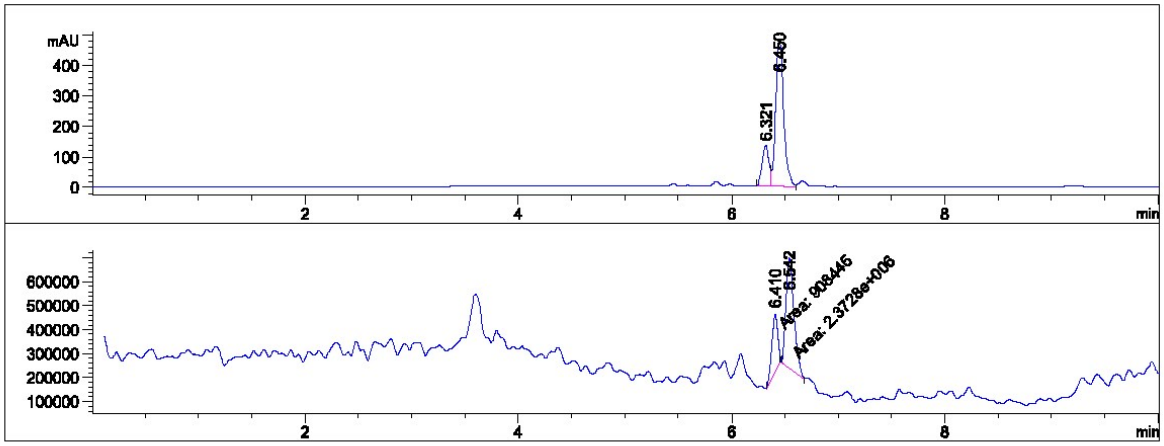


6b

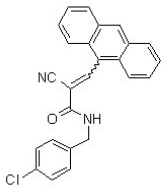




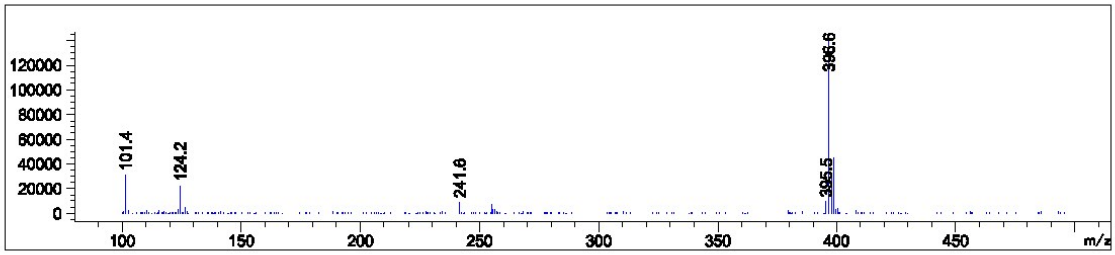
LCMS of 6c

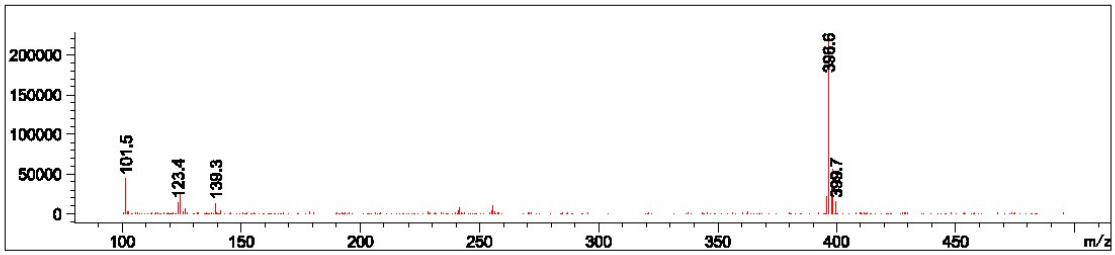


Retention Time (MS)	MS Area	Mol. Weight or Ion
6.410	908445	398.60 I
		397.60 I
		396.60 I
		124.20 I
		101.45 I
6.542	2372796	398.55 I
		397.65 I
		396.60 I
		124.40 I
		101.50 I

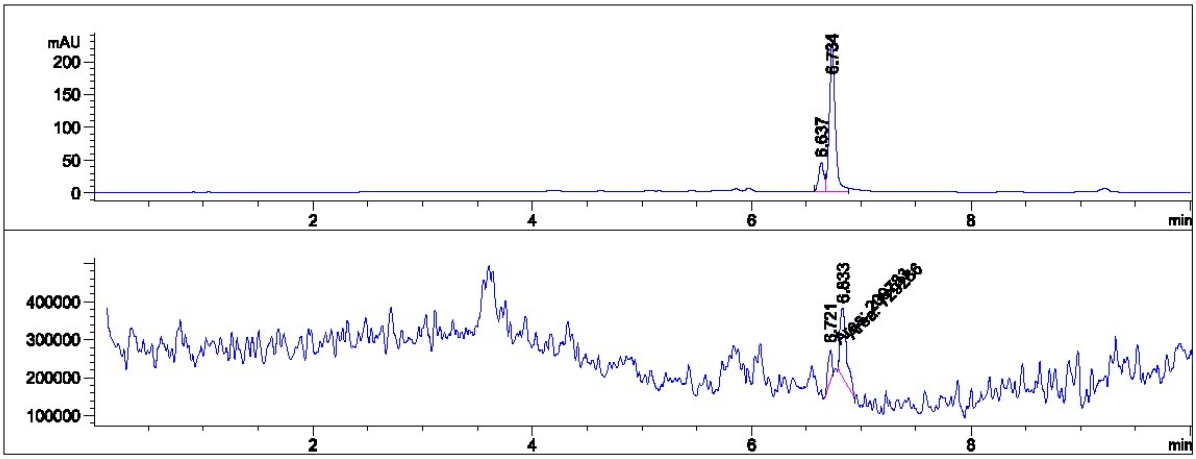


6c

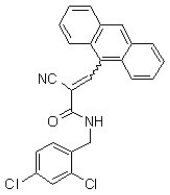




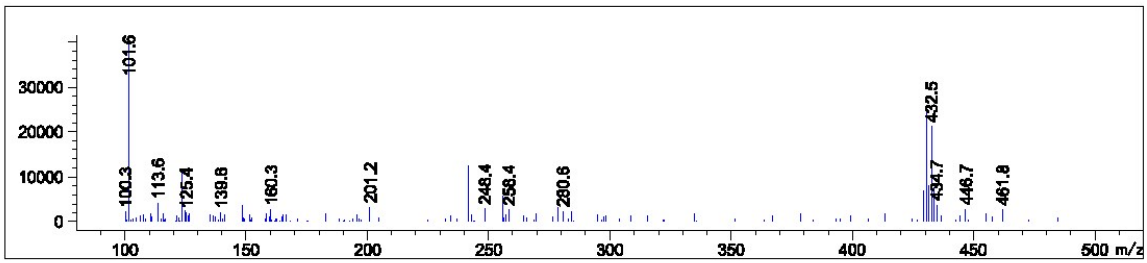
LCMS of 6d

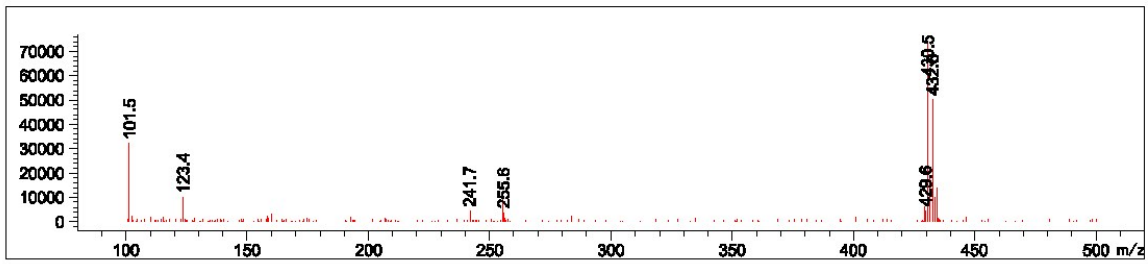


Retention Time (MS)	MS Area	Mol. Weight or Ion
6.721	209783	433.60 I
		432.50 I
		431.45 I
		430.55 I
		429.40 I
		255.60 I
		241.65 I
		123.60 I
		113.60 I
		101.55 I
6.833	729286	434.35 I
		433.60 I
		432.65 I
		431.50 I
		430.55 I
		255.35 I
		123.45 I
		101.50 I



6d





X-ray crystallography

Single crystal X-ray diffraction experimental

The crystal blocks of **5a** and **5i** were grown by the slow evaporation method using ethyl acetate as solvent. Single-crystal structural data of all of the compounds, **5a** and **5i,** were collected on a Bruker CMOS-based D8 Venture diffractometer equipped with a microfocus source with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Using Olex2,[1] the structures were solved with the olex2.solve[2] structure solution program using Charge Flipping and refined with the olex2.refine[2] refinement package using Gauss-Newton minimisation. The crystallographic information files (CIFs) are also deposited as CCDC 19222235 and 1922233 for compounds **5a** and **5i**, respectively, with the Cambridge Crystallographic Data Centre. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6-amino-1-benzyl-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (5a)

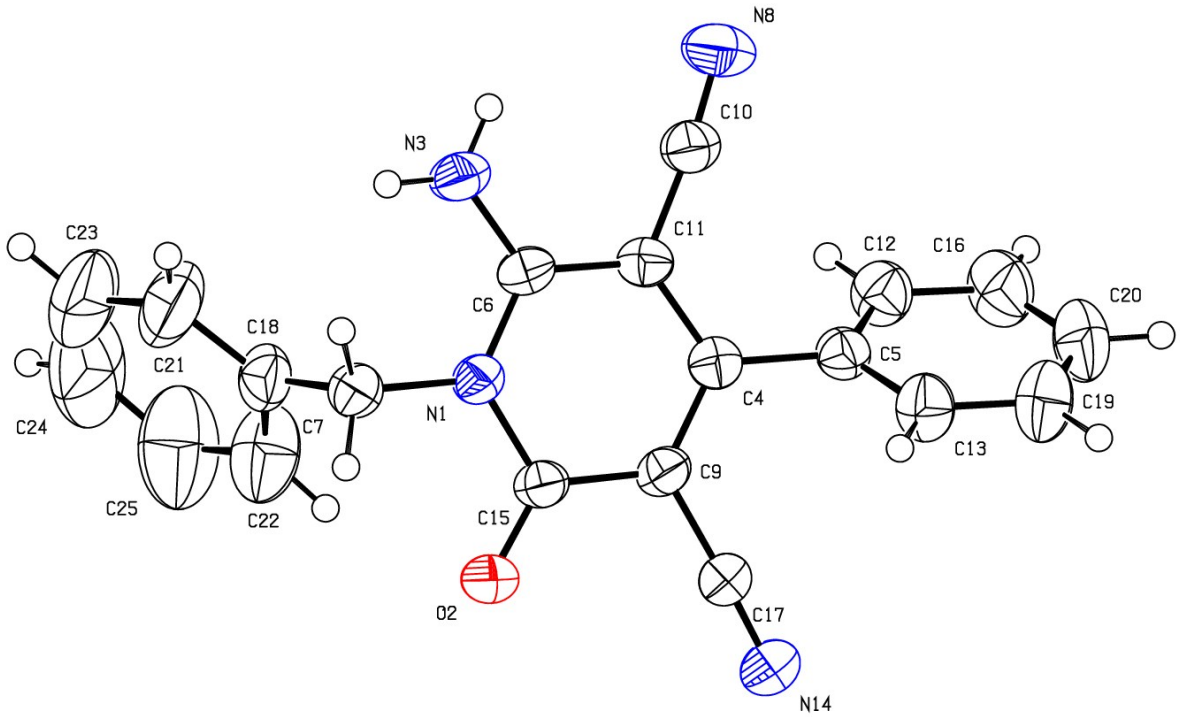


Figure S1 ORTEP view of compound **5a** with displacement ellipsoids drawn at 50%. H atoms are shown as small spheres of arbitrary radii.

Table S1 Crystal data and structure refinement for 5a.	
Identification code	5a
Empirical formula	$C_{20}H_{14}N_4O$
Formula weight	326.36
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5352(4)
b/Å	16.8113(8)
c/Å	11.9674(5)
α/°	90
β/°	112.7581(13)
γ/°	90
Volume/Å^3	1769.01(14)
Z	4
ρ_{calc}g/cm^3	1.2253
μ/mm^{-1}	0.079
F(000)	680.3
Crystal size/mm^3	9.5352 × 16.8113 × 11.9674
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 52.86
Index ranges	$-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-14 \leq l \leq 14$
Reflections collected	40629
Independent reflections	3615 [R_{int} = 0.0321, R_{sigma} = 0.0146]
Data/restraints/parameters	3615/0/226
Goodness-of-fit on F^2	2.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0700, wR_2 = 0.2503
Final R indexes [all data]	R_1 = 0.0767, wR_2 = 0.2551
Largest diff. peak/hole / e Å^{-3}	0.53/-0.39

6-amino-1-benzyl-4-(naphthalen-1-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5i)

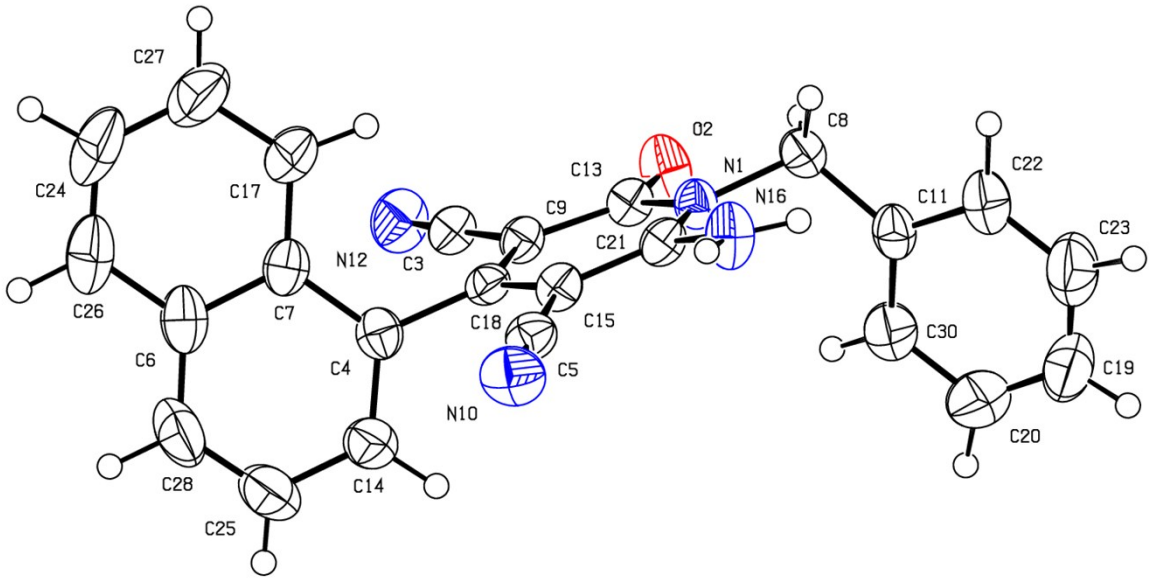


Figure S2 ORTEP view of compound **5i** with displacement ellipsoids drawn at 50%. H atoms are shown as small spheres of arbitrary radii.

Table S2 Crystal data and structure refinement for 5i.	
Identification code	5i
Empirical formula	$C_{24}H_{16}N_4O$
Formula weight	376.42
Temperature/K	273.15
Crystal system	orthorhombic
Space group	Aea2
a/Å	14.5818(13)
b/Å	28.597(2)
c/Å	9.1804(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3828.2(6)
Z	8
ρ_{calc}g/cm^3	1.3061
μ/mm^{-1}	0.083
F(000)	1568.6

Crystal size/mm^3	9.1804 × 28.597 × 14.5818
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.44 to 53.32
Index ranges	-18 ≤ h ≤ 18, -36 ≤ k ≤ 36, -11 ≤ l ≤ 11
Reflections collected	42627
Independent reflections	4033 [R_{int} = 0.0705, R_{sigma} = 0.0338]
Data/restraints/parameters	4033/1/117
Goodness-of-fit on F^2	2.703
Final R indexes [I>=2σ (I)]	R_1 = 0.0998, wR_2 = 0.3099
Final R indexes [all data]	R_1 = 0.1024, wR_2 = 0.3136
Largest diff. peak/hole / e Å^{-3}	0.70/-0.48
Flack parameter	-0(3)

REFERENCE:

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009,** *42* (2), 339-341.
2. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment - Olex2 dissected. *Acta Crystallographica Section A* **2015,** *71* (1), 59-75.