Electronic Supplementary Information

A New Strategy for the Synthesis of Diverse Benzo[a]carbazoles *via* Divergent Catalytic Michael Reaction

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Crystallographic Data

X-ray diffraction experiments on **9b** and **9d** were carried out at 100 (2) K on a Bruker APEX II CCD diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Intensities were integrated[1] andabsorption corrections were based on equivalent reflections using SADABS.[2] Structures **9b** and **9d** were solved using Superflip [3,4] and refined against F^2 in SHELXL[5,6] using Olex2.[7] All of the non-hydrogen atoms were refined anisotropically. While all of the hydrogen atoms were located geometrically and refined using a riding model, apart from the NH$_2$ protons which were located in the difference map and refined with isotropic displacement parameters. The dataset from the crystal of **9b** was found to be twinned and was treated as a two component twin and refined against an hklf5 file. In the case of **9d** the molecule displayed disorder, the occupancies of the fragments was determined by refining them against a free variable with the sum of the two sites set to equal 1, the occupancies were then fixed at the refined values restraints were applied to maintain sensible geometries and thermal parameters. Crystal structure and refinement data are given in Table S1. Crystallographic data for compounds **9b** and **9d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1547596-1547597. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Reference

1   Bruker, SAINT+ Integration Engine, Data Reduction Software, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 2007.

2   Bruker, SADABS, Bruker AXS area detector scaling and absorption correction, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 2001.

3   L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786-790.

4   L. Palatinus, S. J. Prathapa and S. van Smaalen, *J. Appl. Crystallogr.*, 2012, **45**, 575-580.

5   G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.,* 2008, **64**, 112-122.

6   G. M. Sheldrick, *Acta Crystallogr.*, C, 2015, **71**, 3-8.

7   O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H.Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

Table S1. Crystal data and structure refinement for **9b** and **9d**.

Identification code	**9b**	**9d**
Empirical formula	$C_{24}H_{18}N_4O_2$	$C_{23}H_{16}N_4O_2$
Formula weight	394.42	380.40
Temperature/K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	8.7409(5)	8.3973(8)
b/Å	9.6037(6)	8.5161(9)
c/Å	12.1665(7)	14.1035(13)
α/°	72.299(4)	97.848(6)
β/°	87.366(4)	104.222(6)
γ/°	72.955(5)	108.609(6)
Volume/Å^3	929.19(10)	900.83(16)
Z	2	2
ρ_{calc}g/cm^3	1.410	1.402
μ/mm^{-1}	0.093	0.093
F(000)	412.0	396.0
Crystal size/mm^3	0.379 × 0.245 × 0.189	0.371 × 0.285 × 0.21
Radiation	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	3.518 to 52.738	3.064 to 56.204
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $0 \leq l \leq 15$	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-17 \leq l \leq 18$
Reflections collected	3785	16596
R_{int} / R_{sigma}	0.0713 / 0.0604	0.0470 /0.0480
Data/restraints/parameters	3785/0/285	4340/275/345
Goodness-of-fit on F^2	1.050	1.023
Final R indexes [I>=2σ (I)]	$R_1 = 0.0525$, $wR_2 = 0.1019$	$R_1 = 0.0495$, $wR_2 = 0.1160$
Final R indexes [all data]	$R_1 = 0.0807$, $wR_2 = 0.1168$	$R_1 = 0.0780$, $wR_2 = 0.1334$
Largest diff. peak/hole / e Å^{-3}	0.21/-0.27	0.29/-0.27

^{1}H and ^{13}C NMR Spectral Data
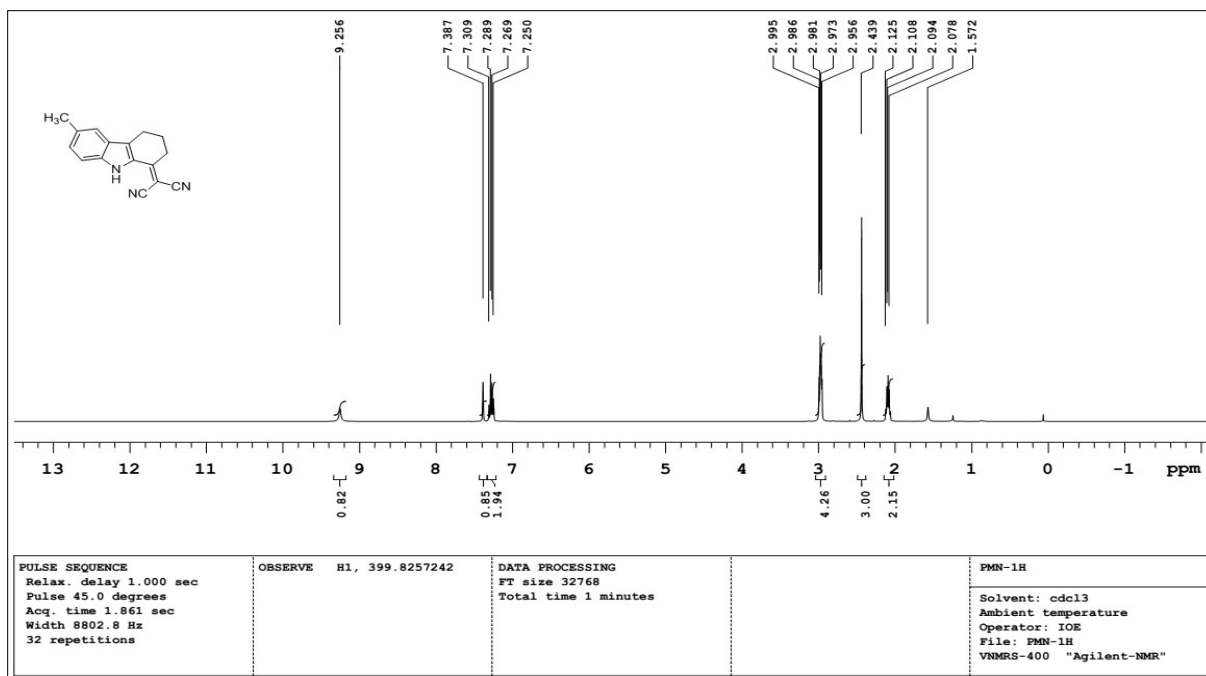
Fig. S1. ^{1}H NMR spectrum of 1-(dicyanomethylene)-6-methyl-2,3,4,9-tetrahydrocarbazole **(4a)**
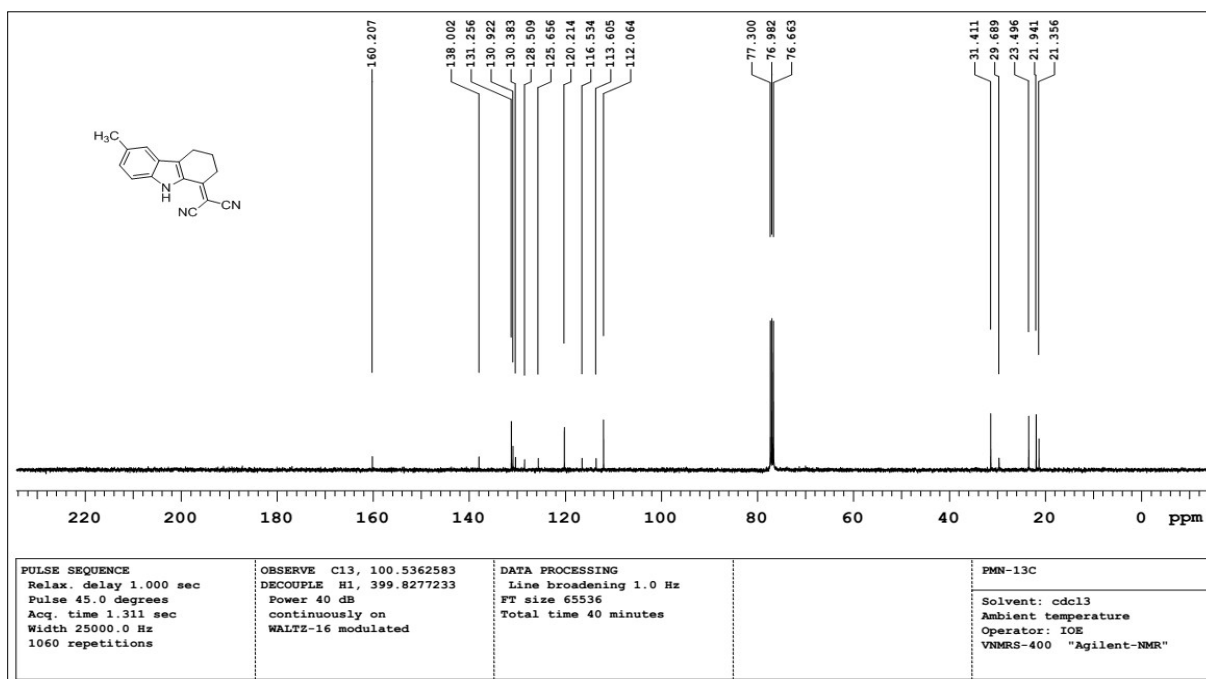
Fig. S2. ^{13}C NMR spectrum of 1-(dicyanomethylene)-6-methyl-2,3,4,9-tetrahydrocarbazole **(4a)**
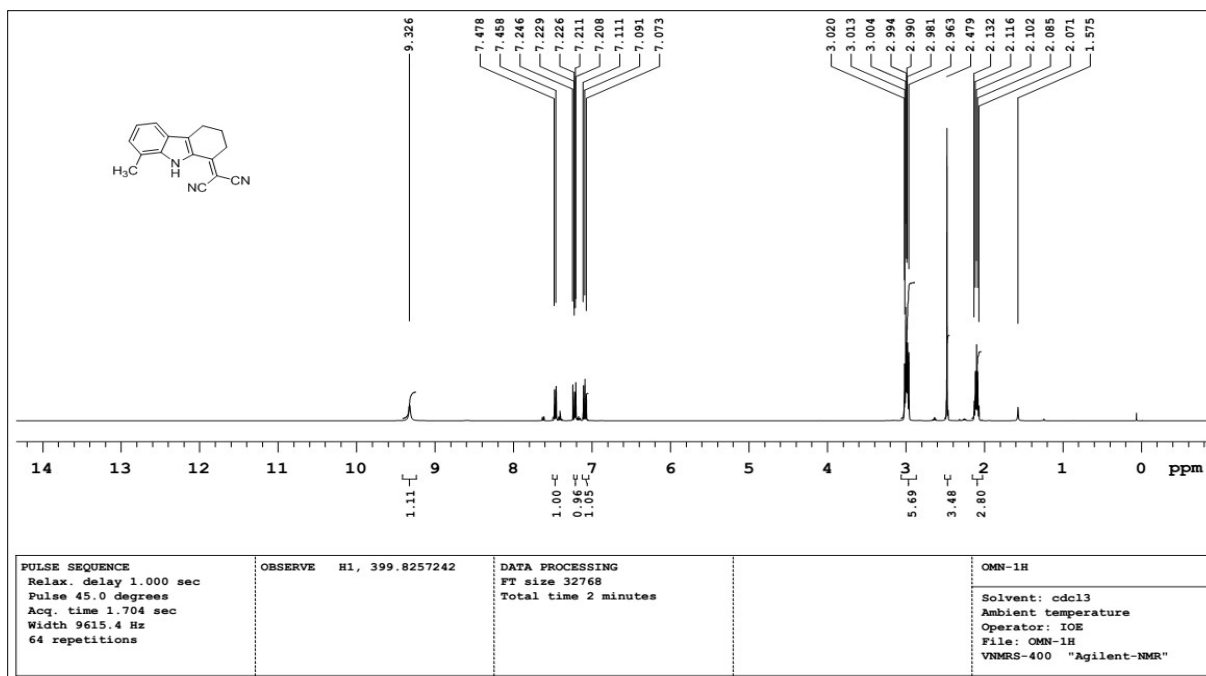
Fig. S3. ^{1}H NMR spectrum of 1-(dicyanomethylene)-8-methyl-2,3,4,9-tetrahydrocarbazole **(4b)**
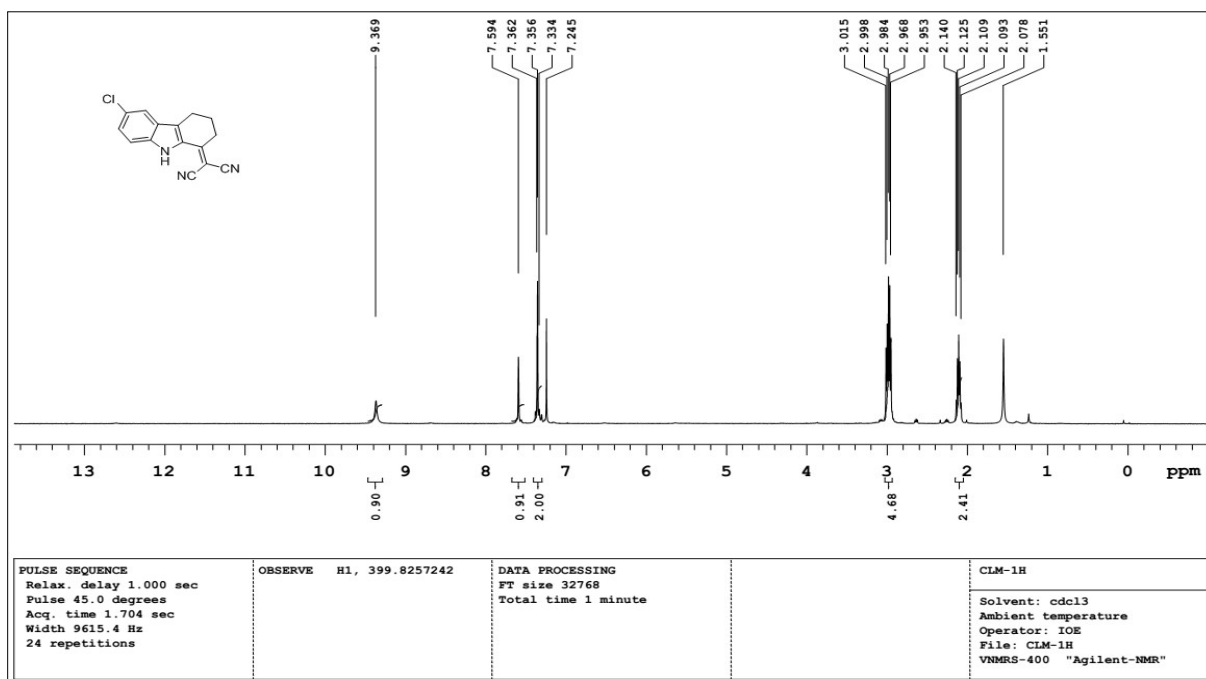

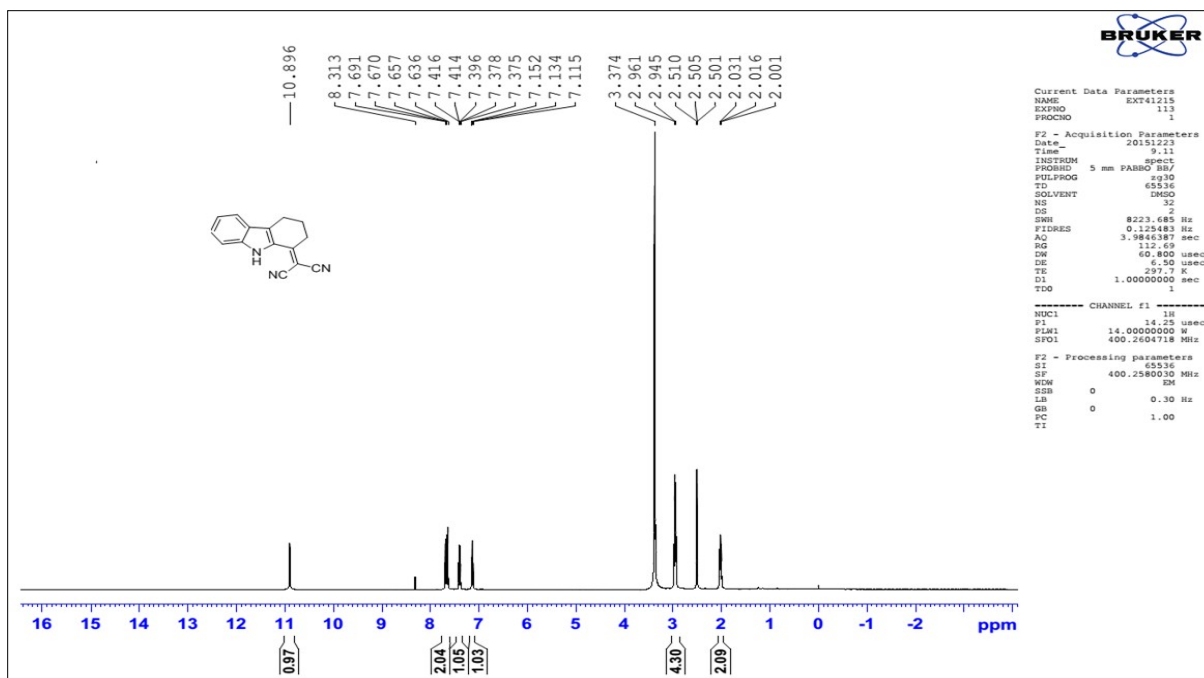**Fig. S4.** ^{1}H NMR spectrum of 1-(dicyanomethylene)-6-chloro-2,3,4,9-tetrahydrocarbazole **(4c)**

Fig. S5. ^{1}H NMR spectrum of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **(4d)**
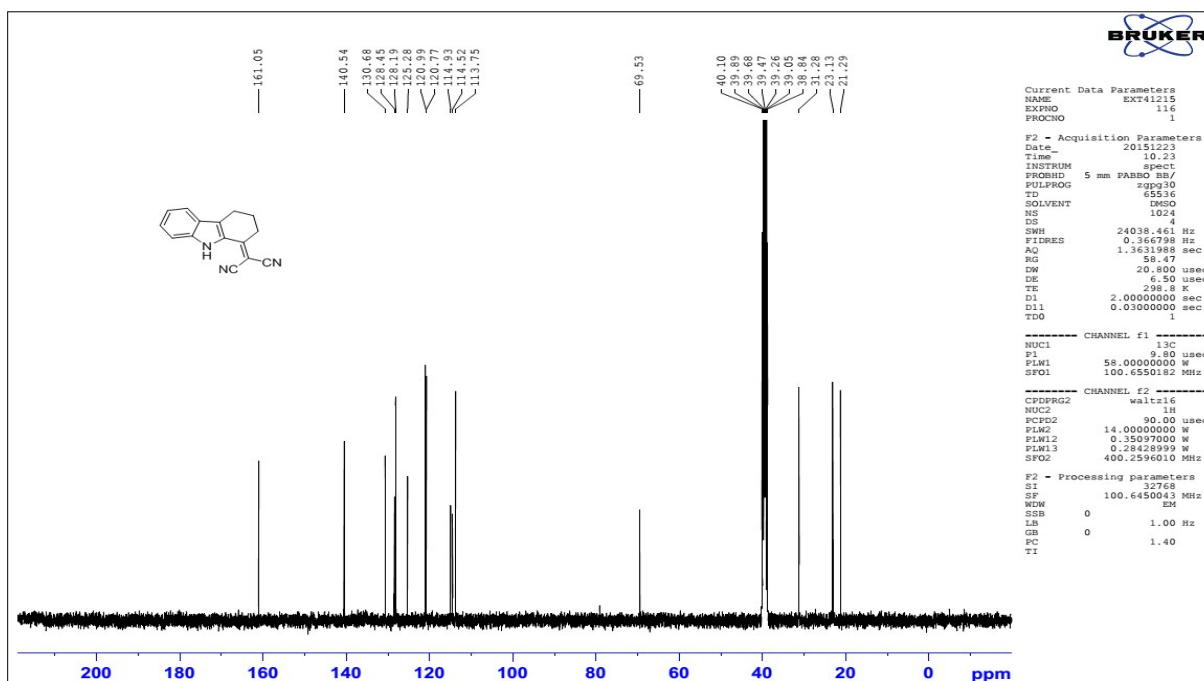
Fig. S6. ^{13}C NMR spectrum of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **(4d)**
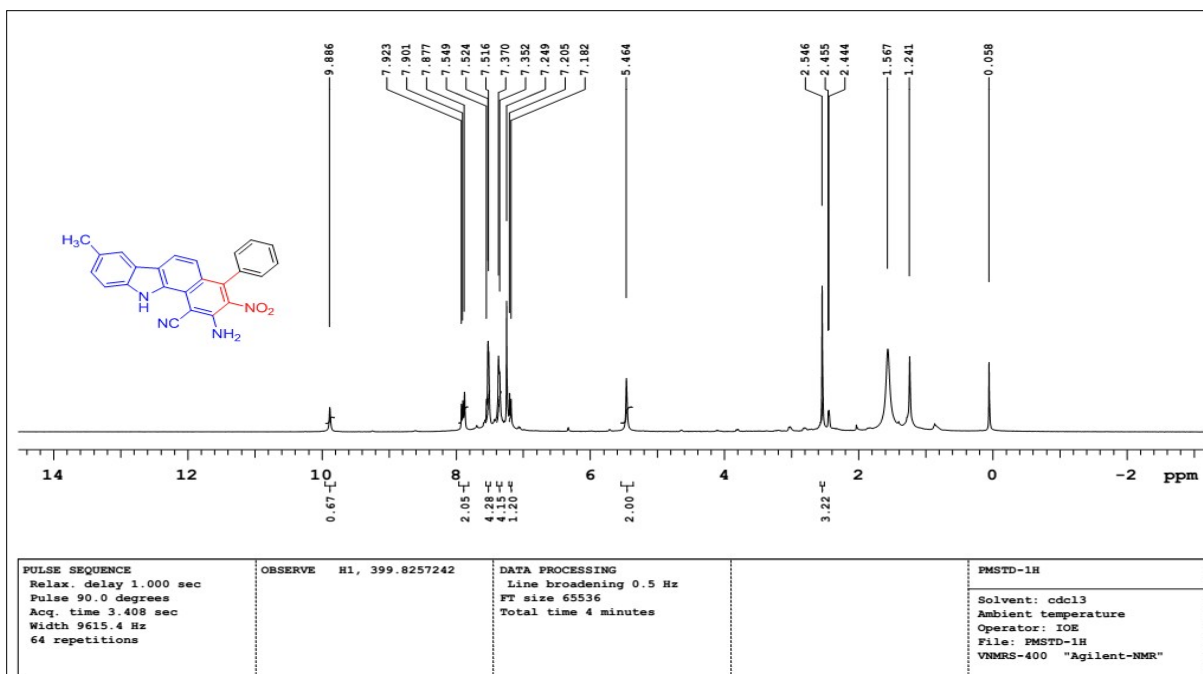
Fig. S7. ¹H NMR spectrum of 2-amino-8-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8a)**
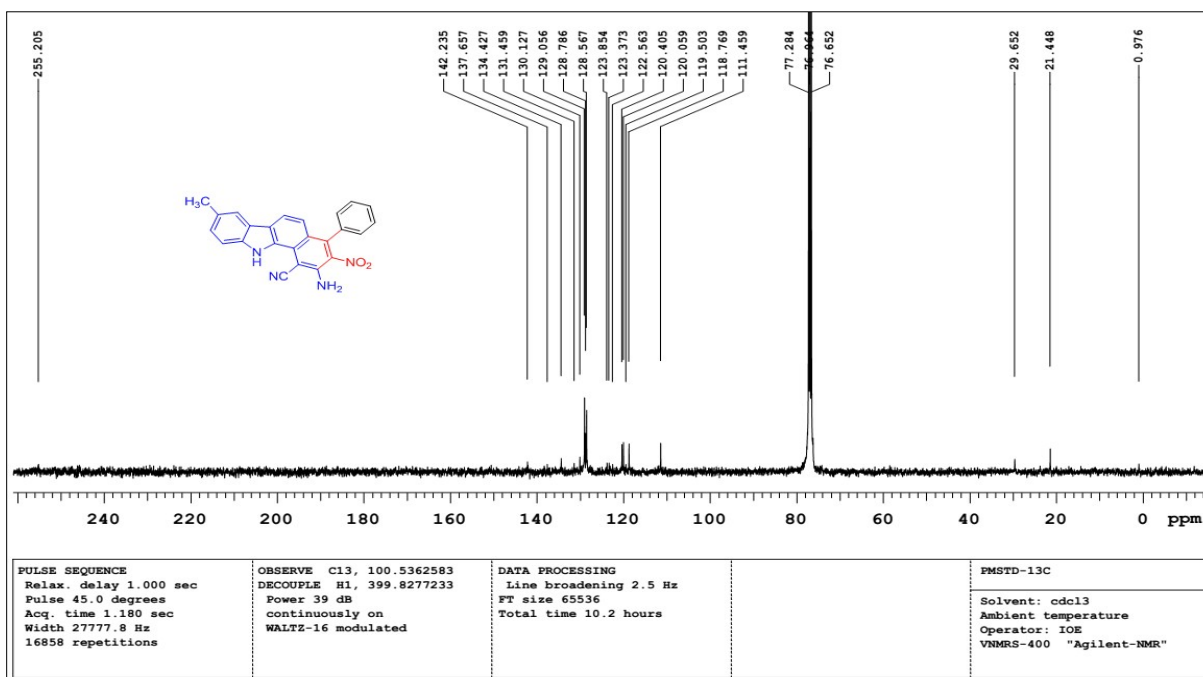
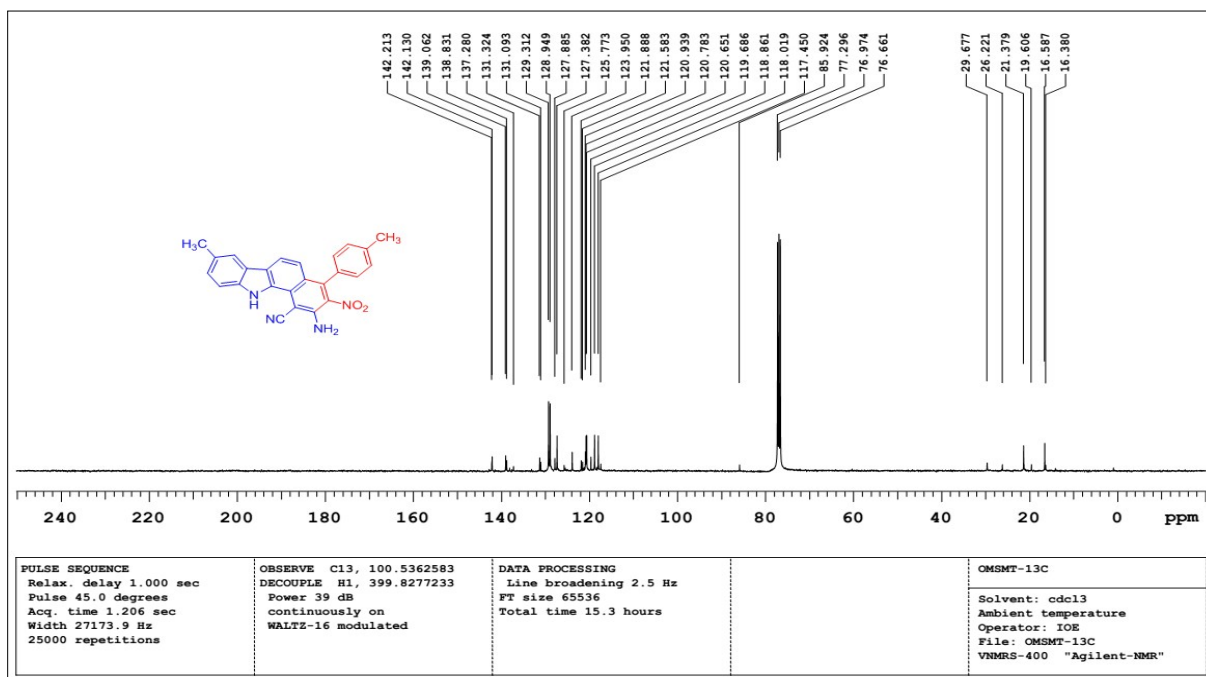**Fig. S8.** ¹³C NMR spectrum of 2-amino-8-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8a)**

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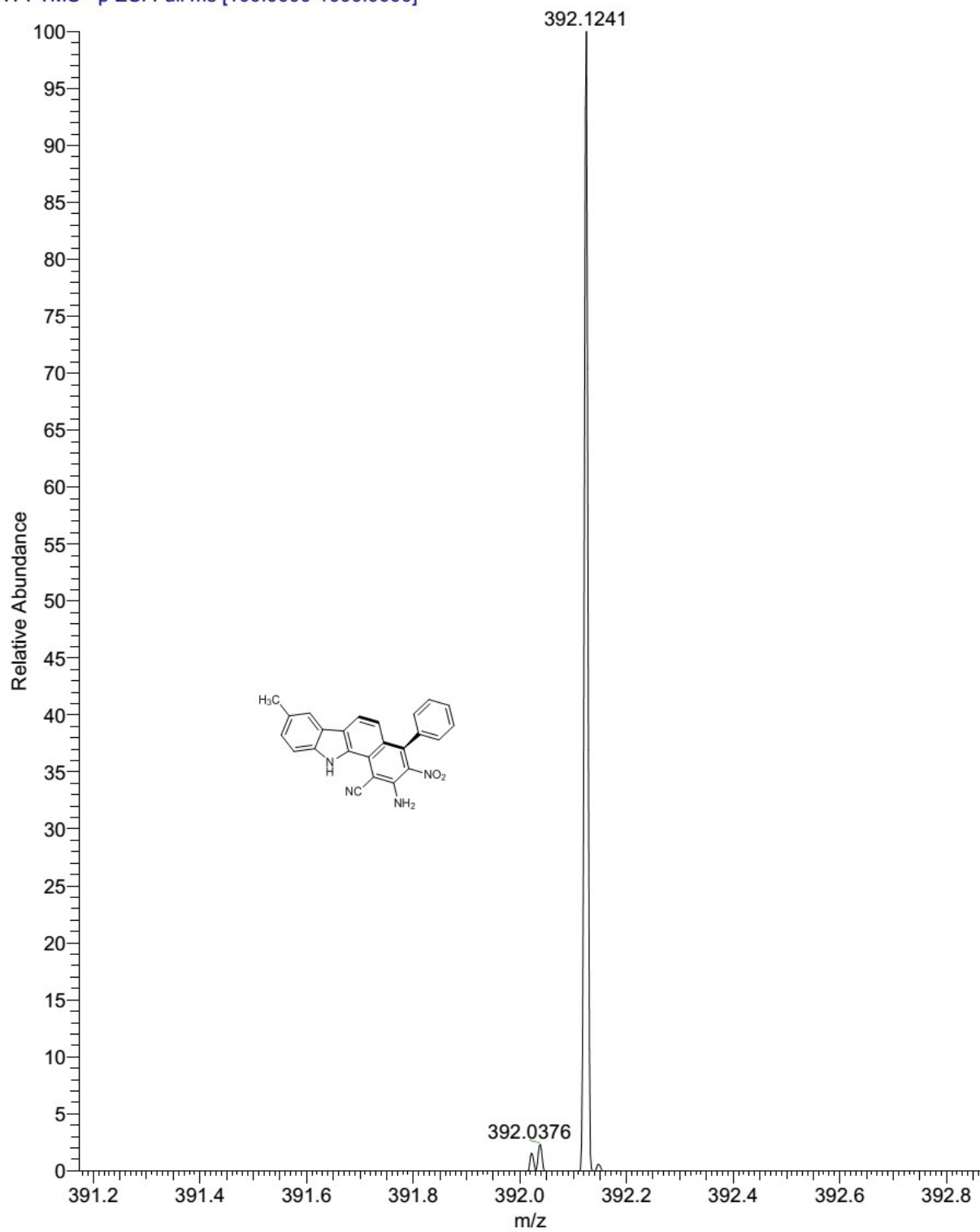
Fig. S9. HRMS spectrum of 2-amino-8-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8a)**
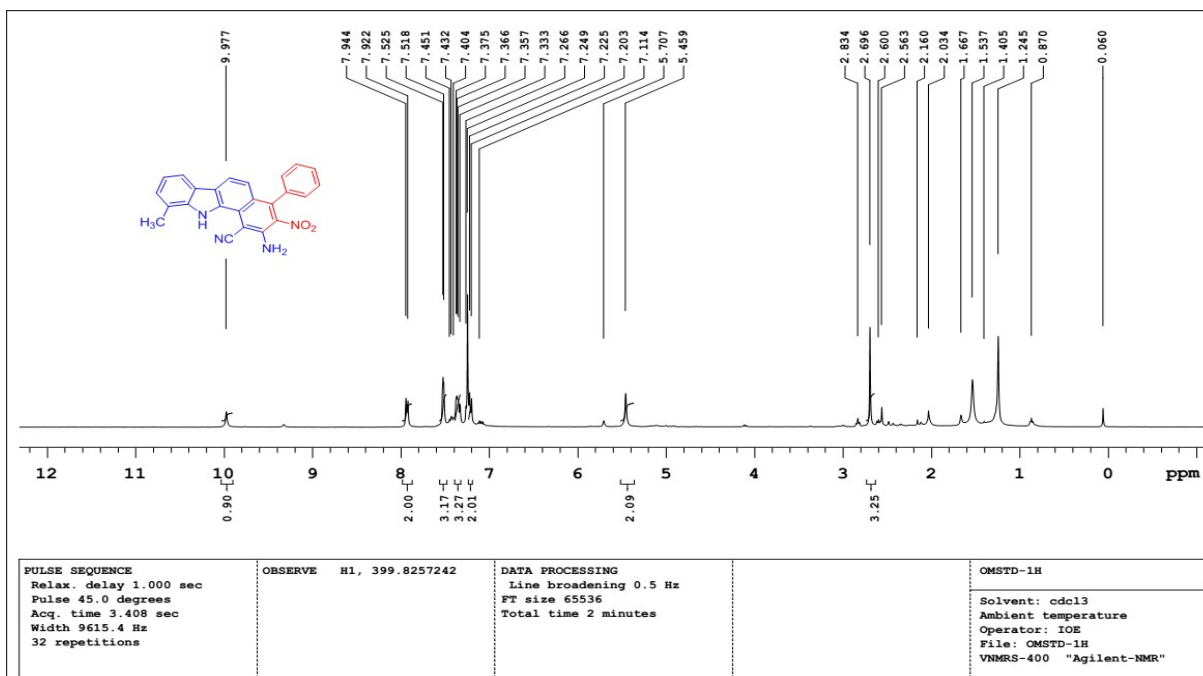
Fig. S10. ^{1}H NMR spectrum of 2-amino-10-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8b)**
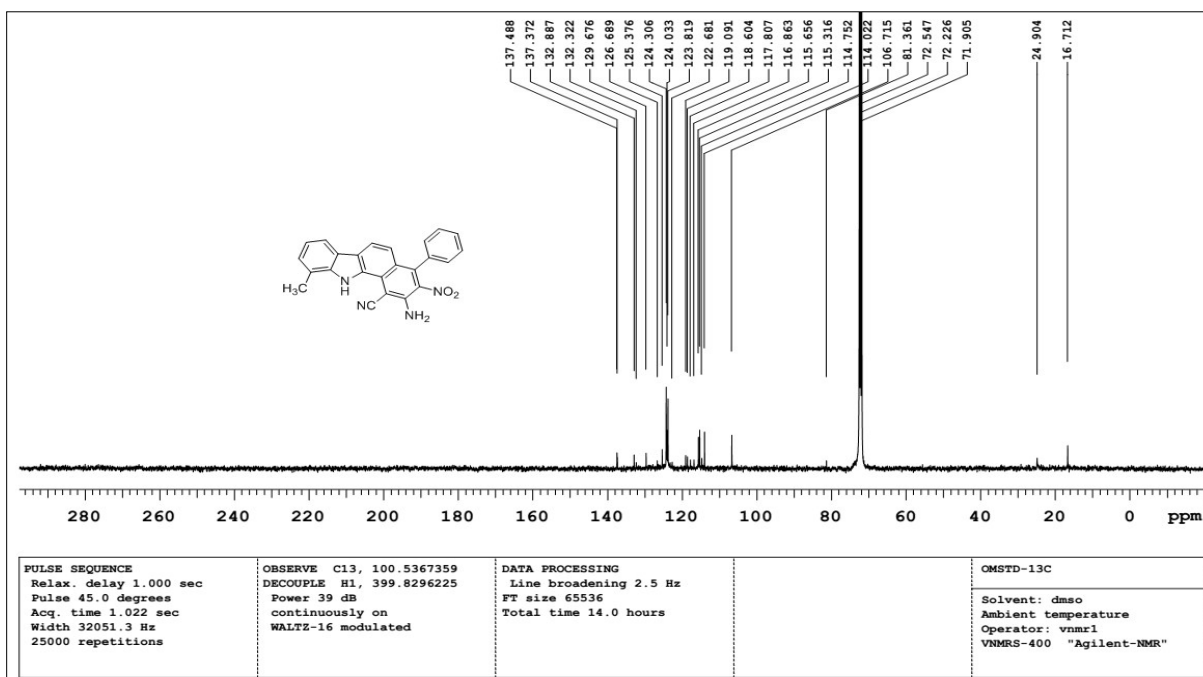
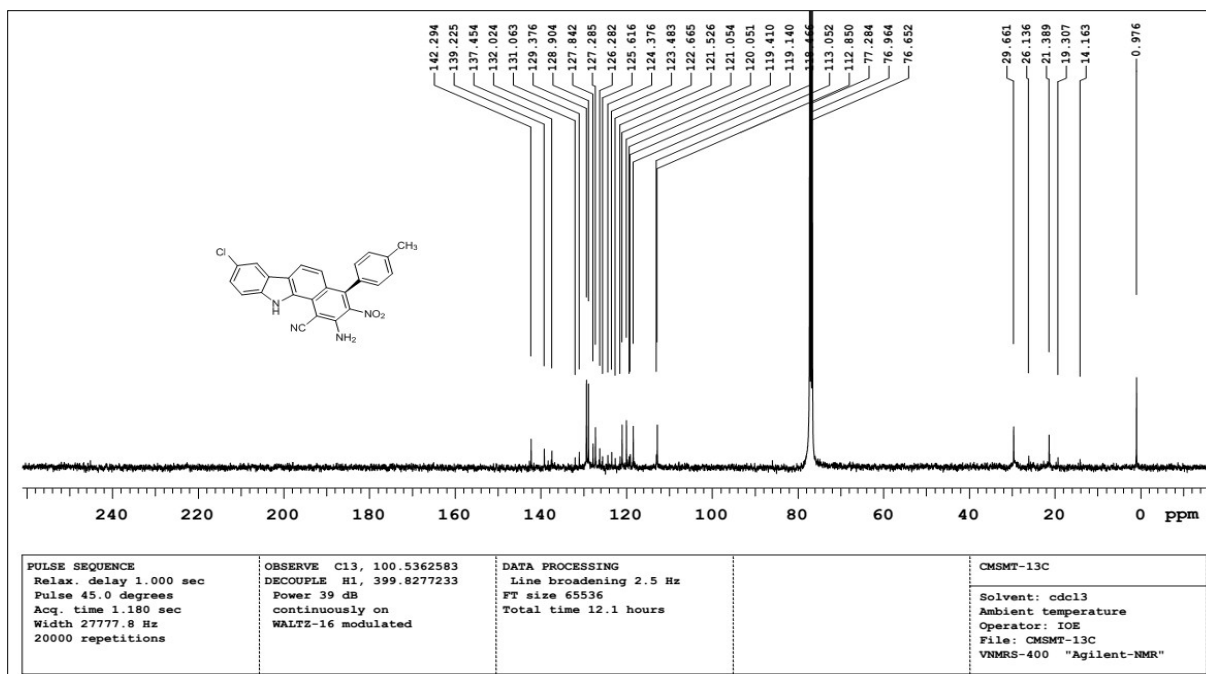**Fig. S11.** ^{13}C NMR spectrum of 2-amino-10-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8b)**

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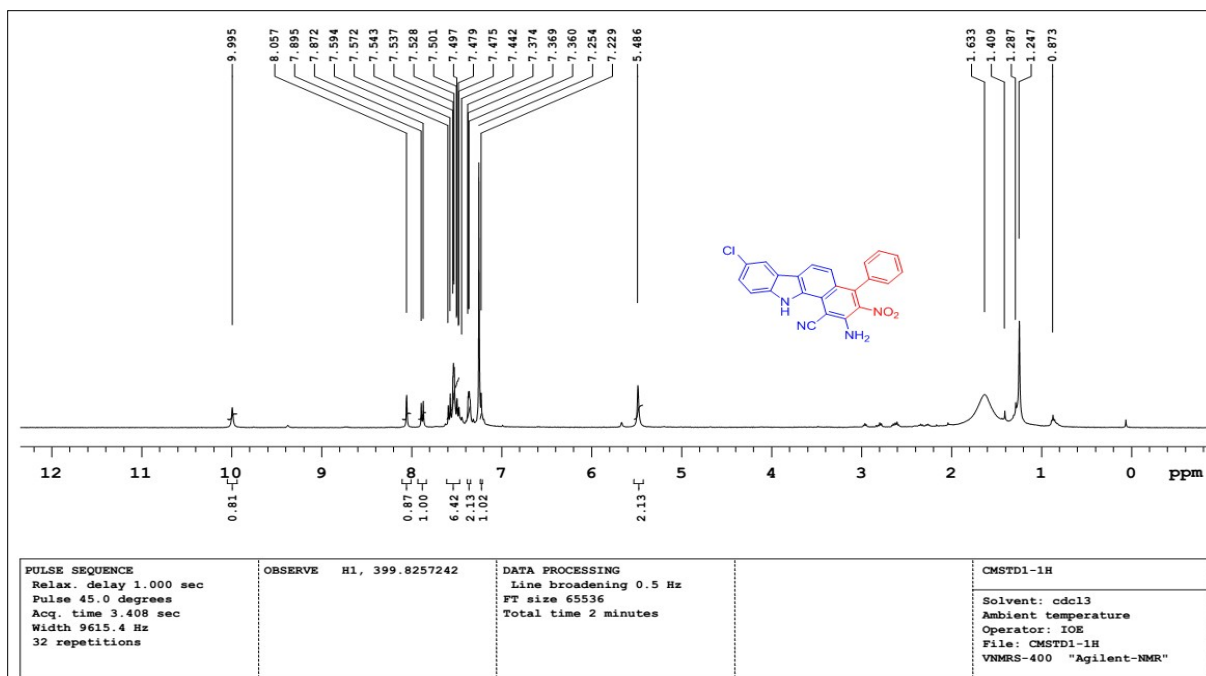
Fig. S12. ^{1}H NMR spectrum of 2-amino-8-chloro-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8c)**
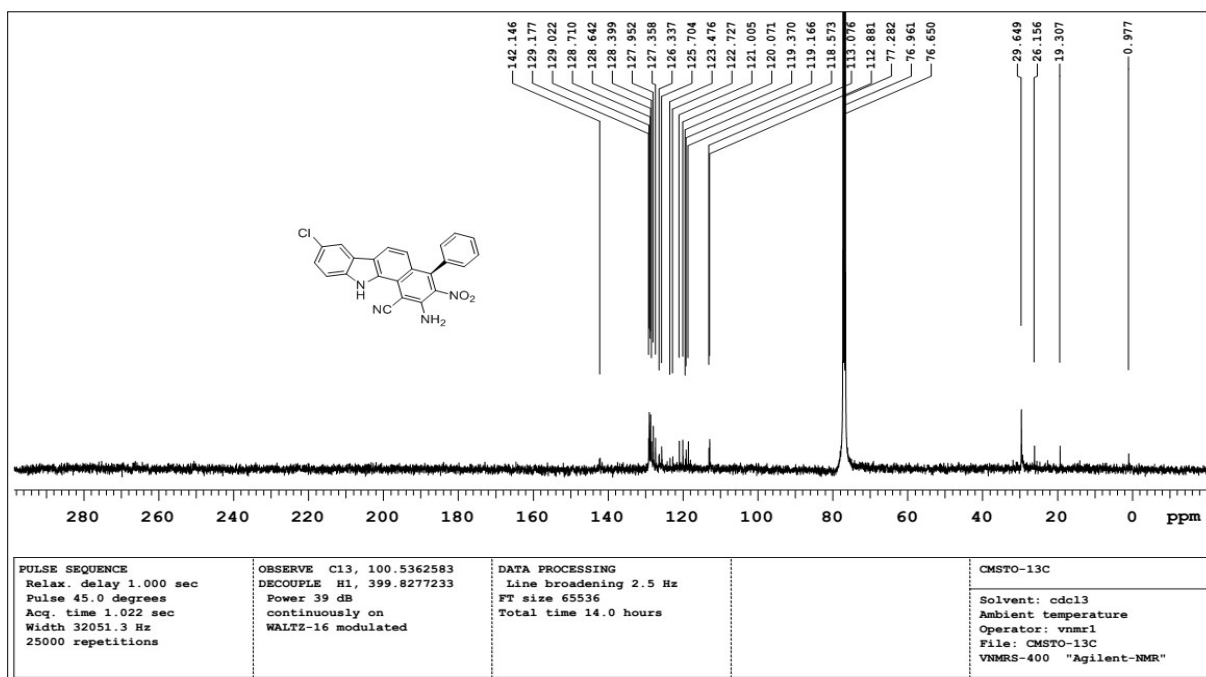
Fig. S13. ^{13}C NMR spectrum of 2-amino-8-chloro-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8c)**
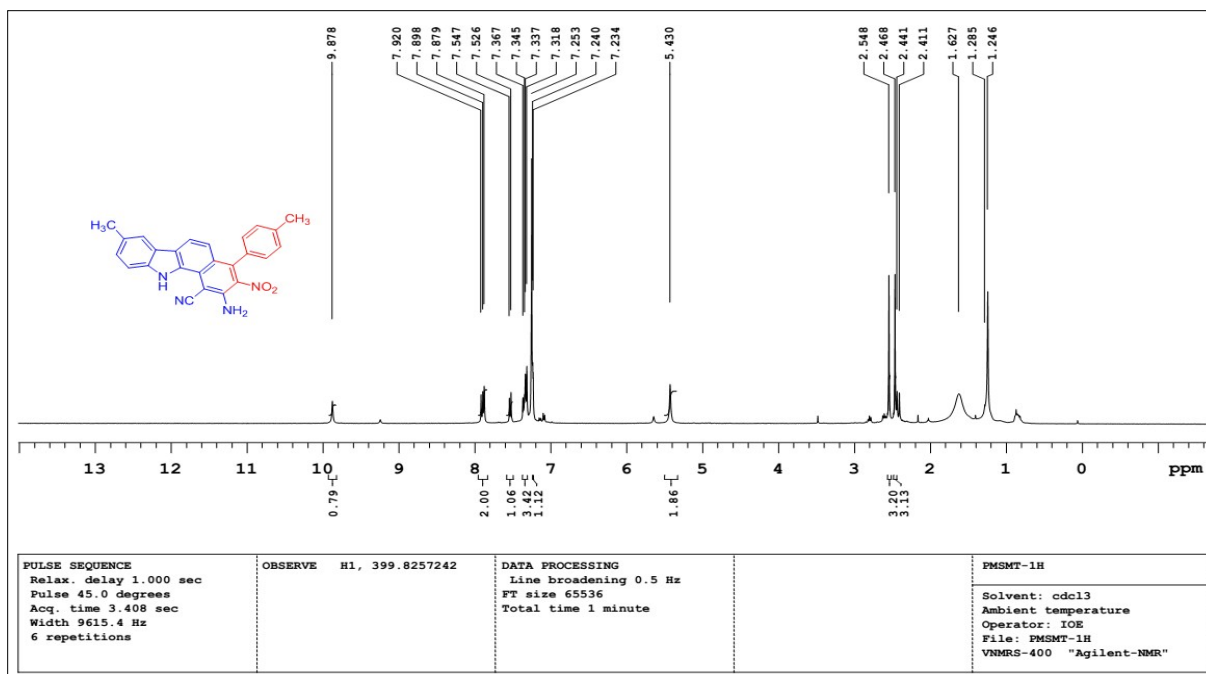
Fig. S14. ^{1}H NMR spectrum of 2-amino-8-methyl-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8e)**
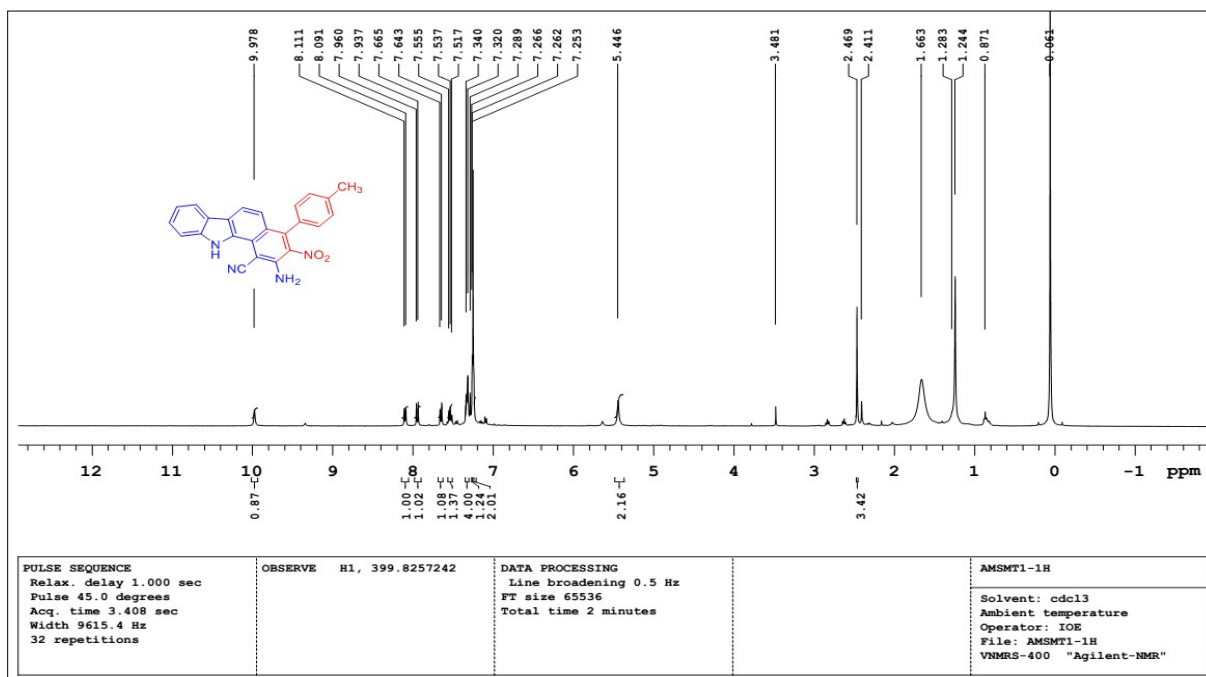

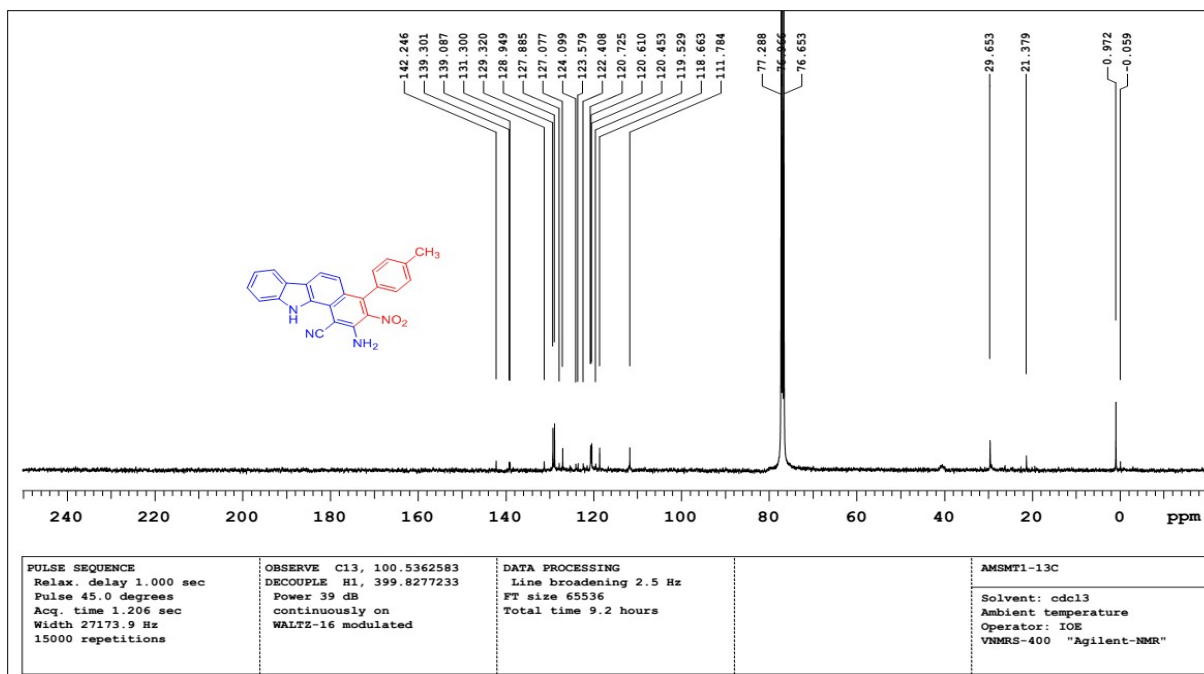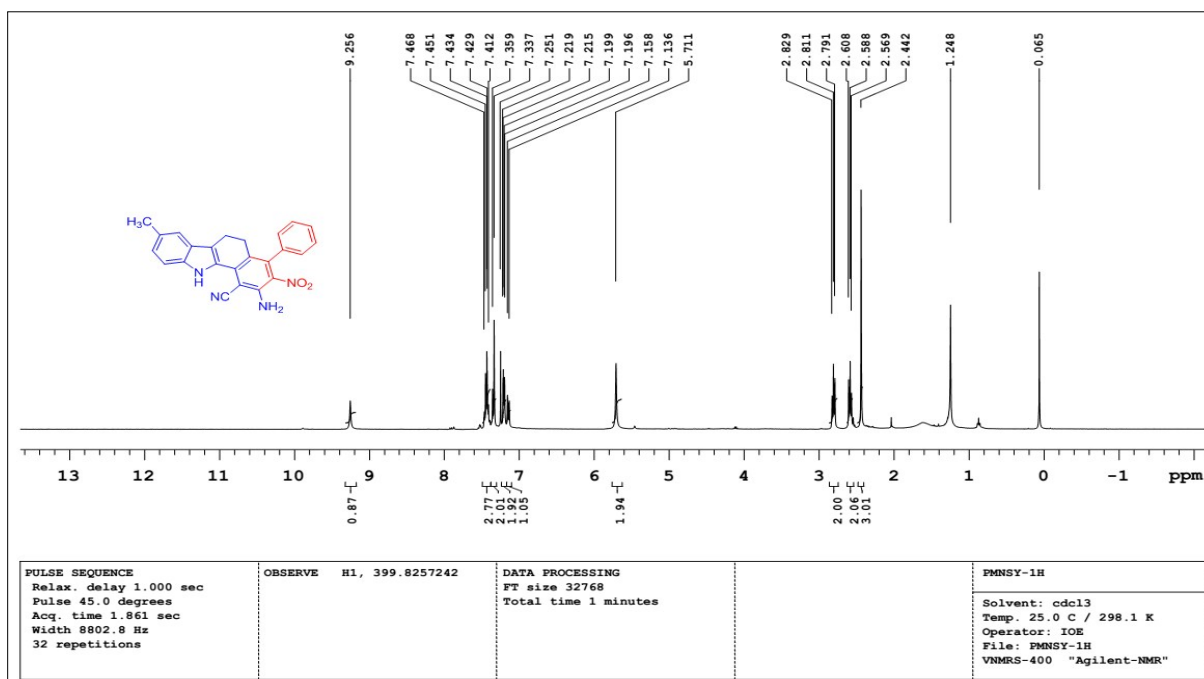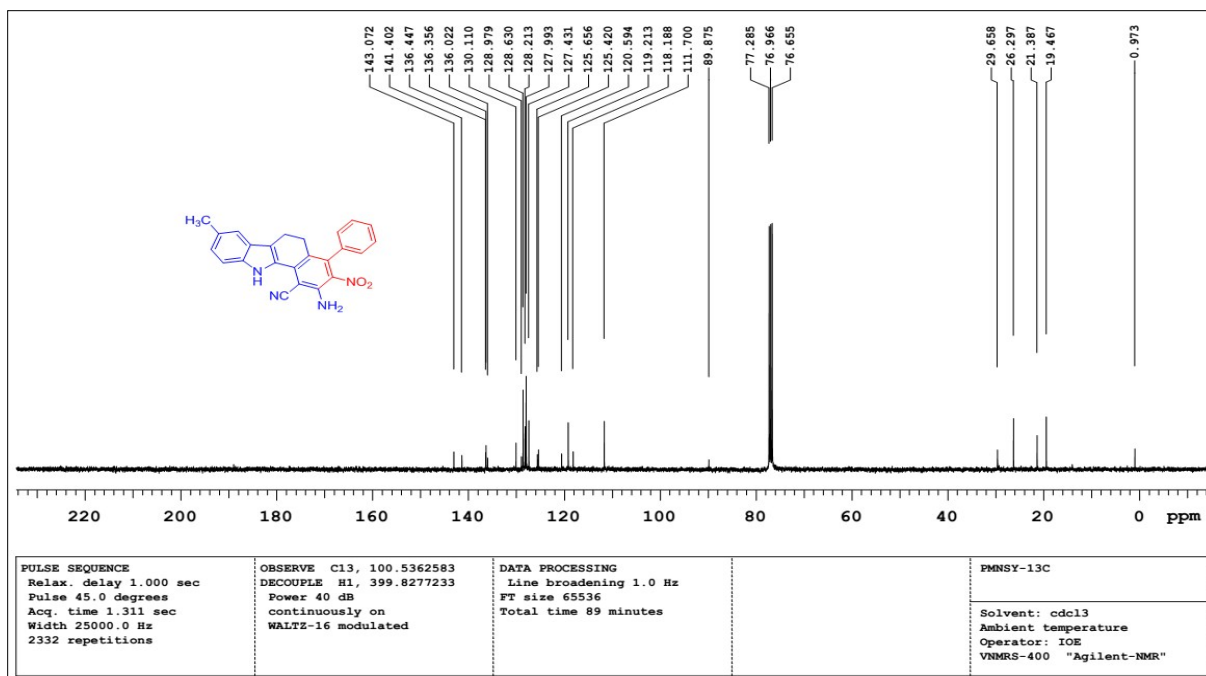**Fig. S15.** ^{13}C NMR spectrum of 2-amino-8-methyl-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8e)**
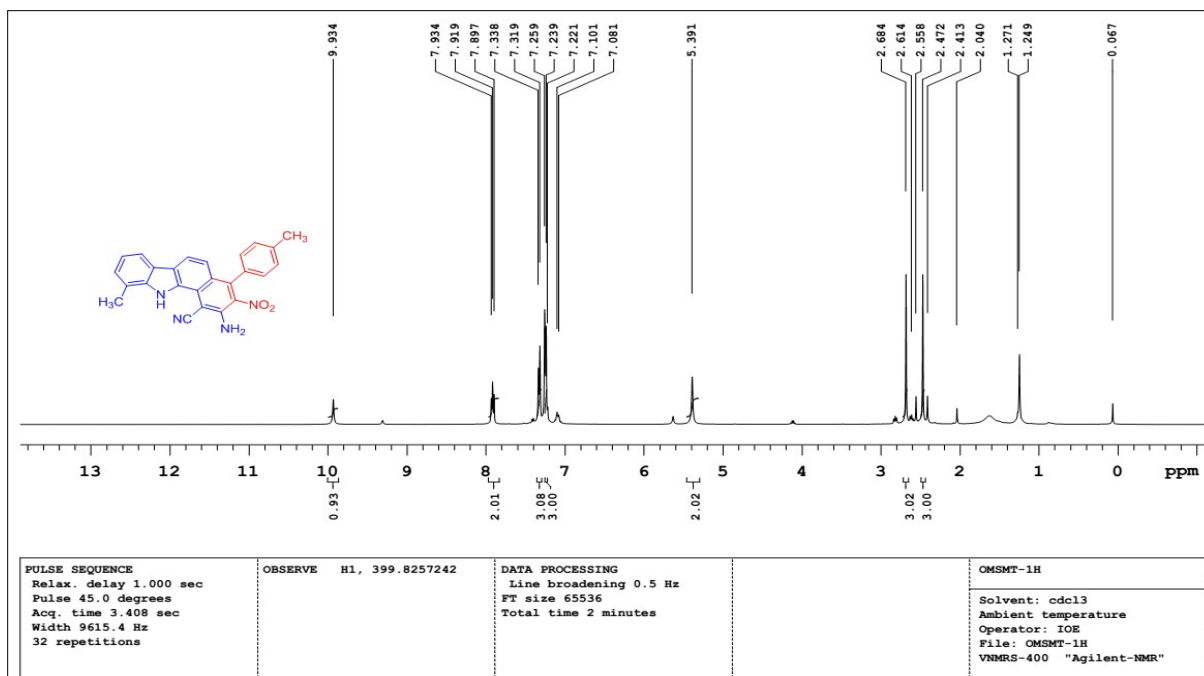
Fig. S16. [1] H NMR spectrum of 2-amino-10-methyl-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8f)**
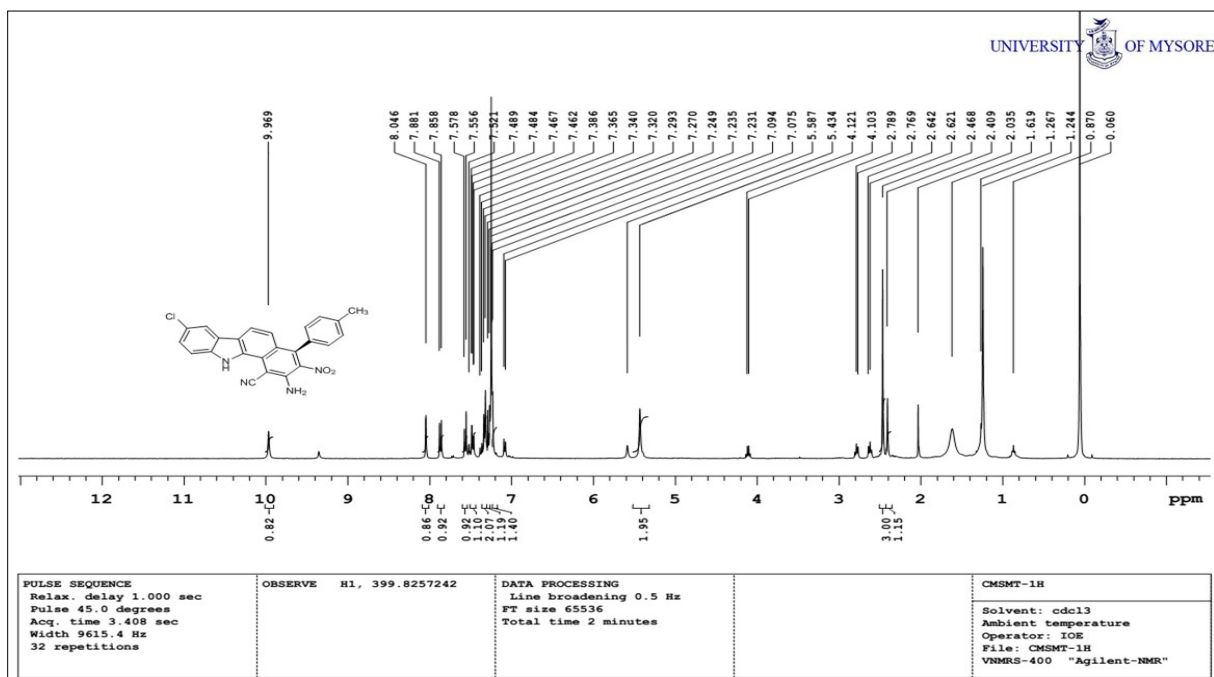
Fig. S17. [1] H NMR spectrum of 2-amino-8-chloro-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8g)**

Fig. S18. ^{13}C NMR spectrum of 2-amino-8-chloro-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8g)**

Fig. S19. ^{1}H NMR spectrum of 2-amino-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8h)**

Fig. S20. ^{13}C NMR spectrum of 2-amino-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile **(8h)**

Fig. S21. ^{1}H NMR spectrum of 2-amino-8-methyl-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9a)**

Fig. S22. ¹³C NMR spectrum of 2-amino-8-methyl-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9a)**

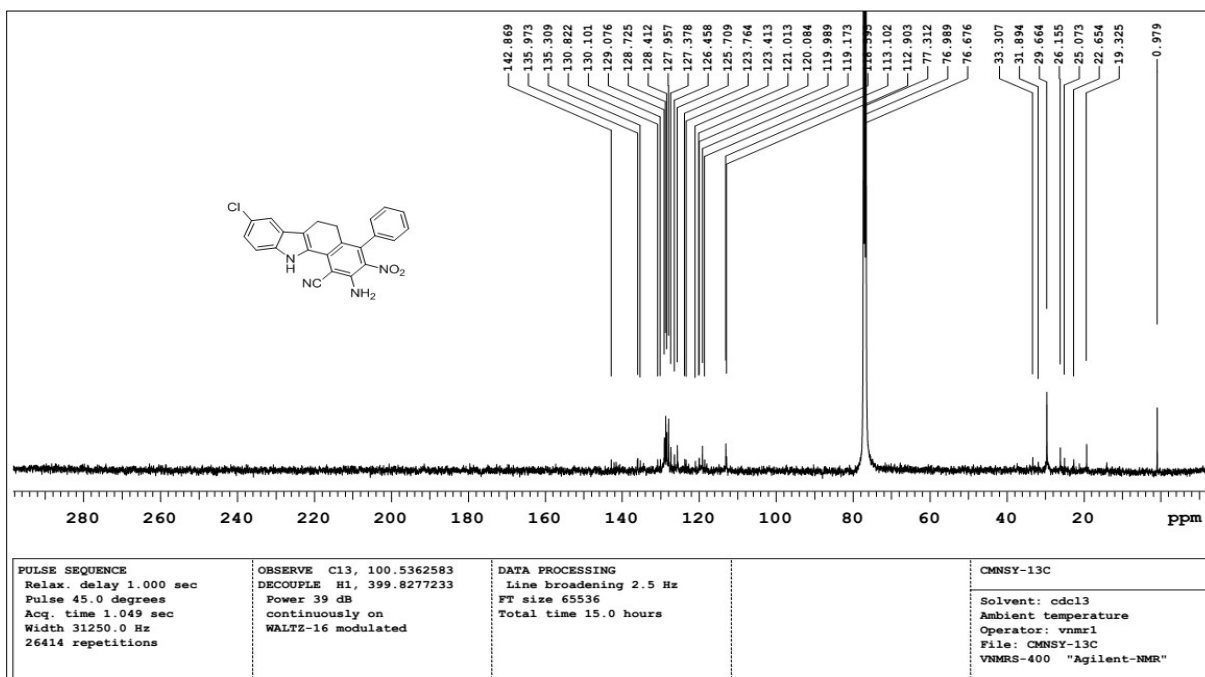6 #85-114 RT: 0.83-1.10 AV: 15 NL: 2.10E6
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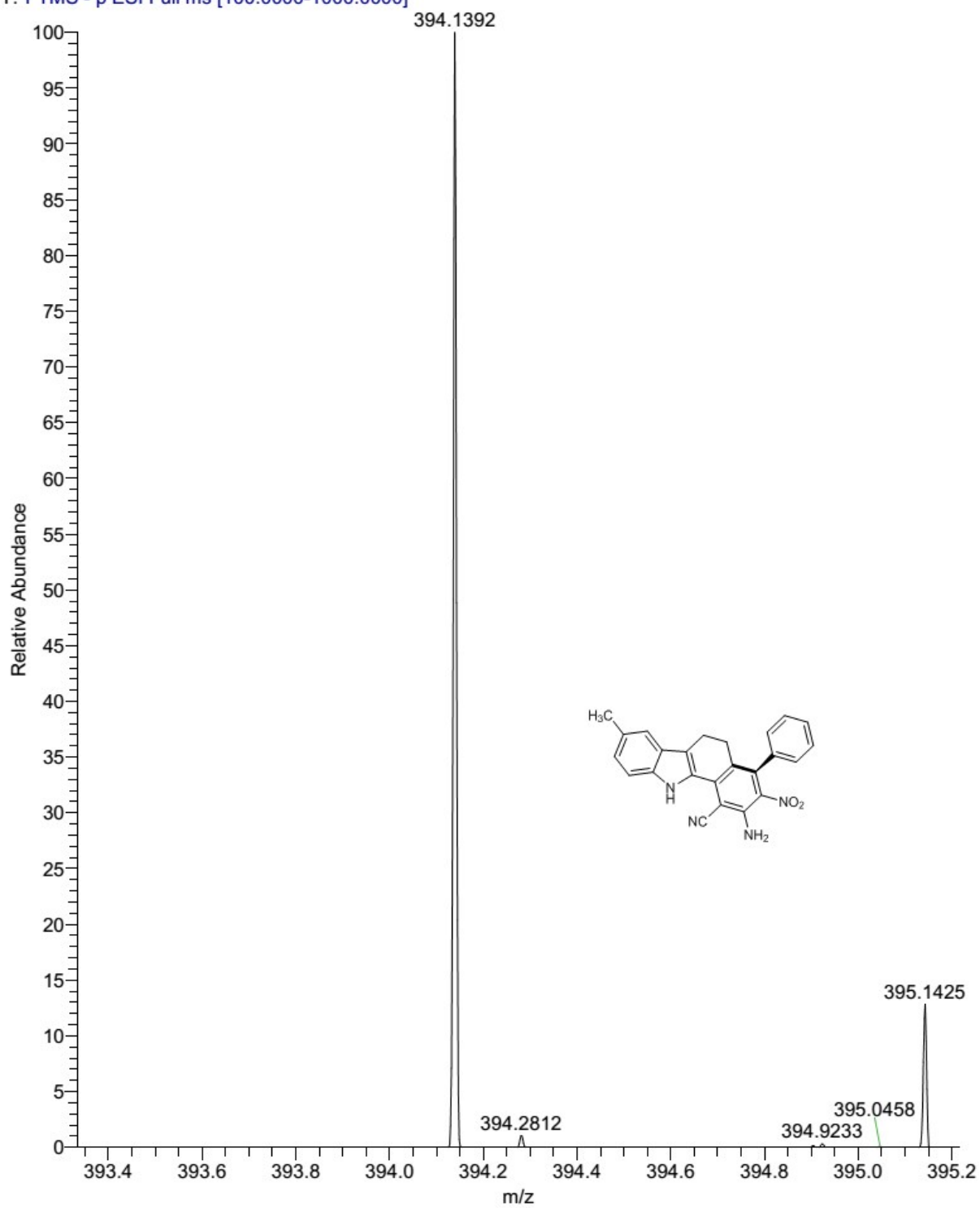
Fig. S23. HRM spectrum of 2-amino-8-methyl-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile
(9a)
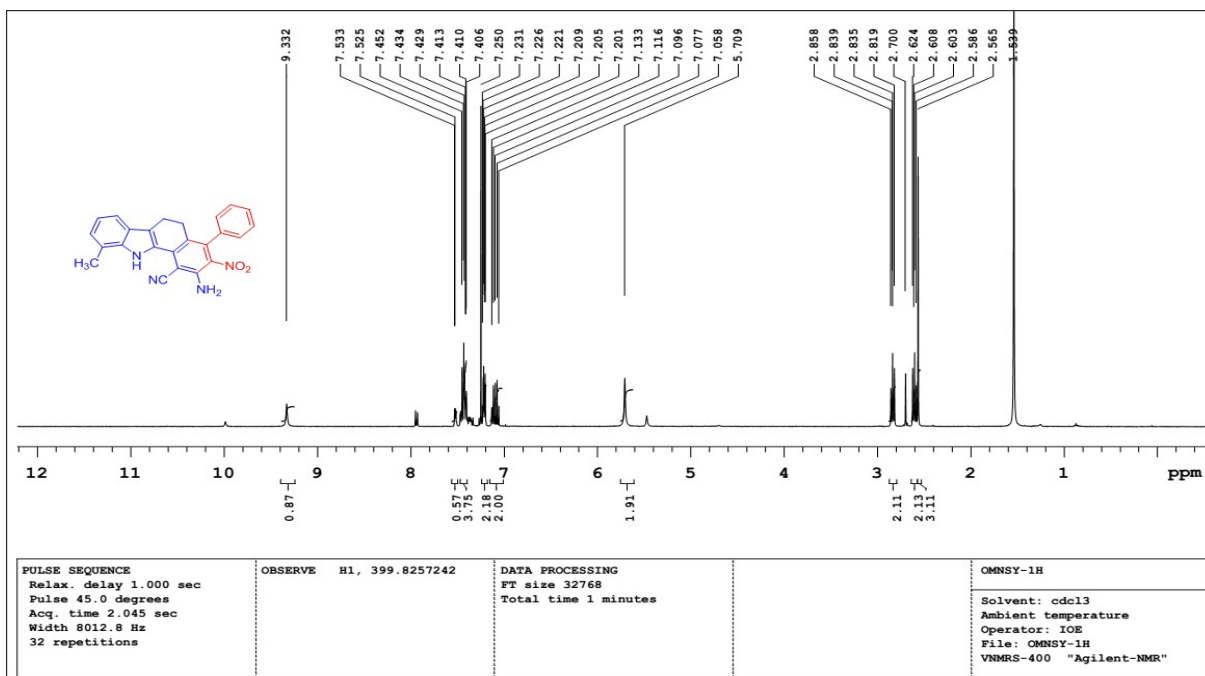
Fig. S24. ^{1}H NMR spectrum of 2-amino-10-methyl-3-nitro-4-phenyl-5,6-dihydro-11H-benzo[a]carbazol-1-carbonitrile **(9b)**

Fig. S25. ^{13}C NMR spectrum of 2-amino-8-chloro-3-nitro-4-phenyl-5,6-dihydro-11H-benzo[a]carbazol-1-carbonitrile **(9c)**
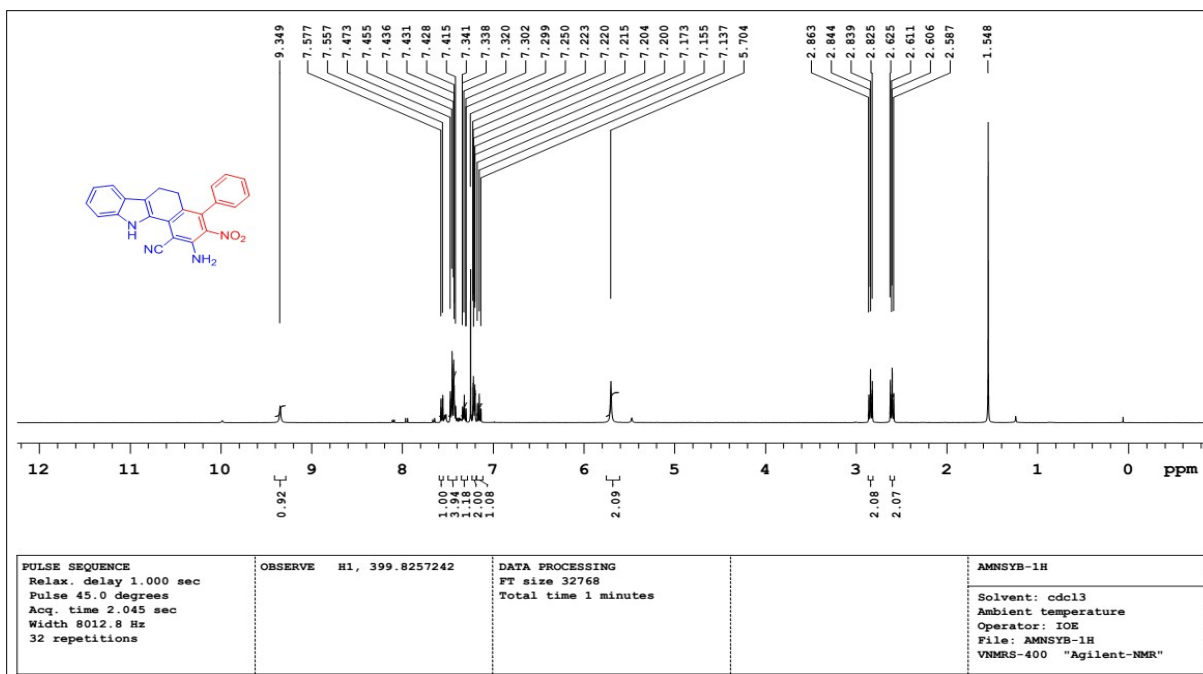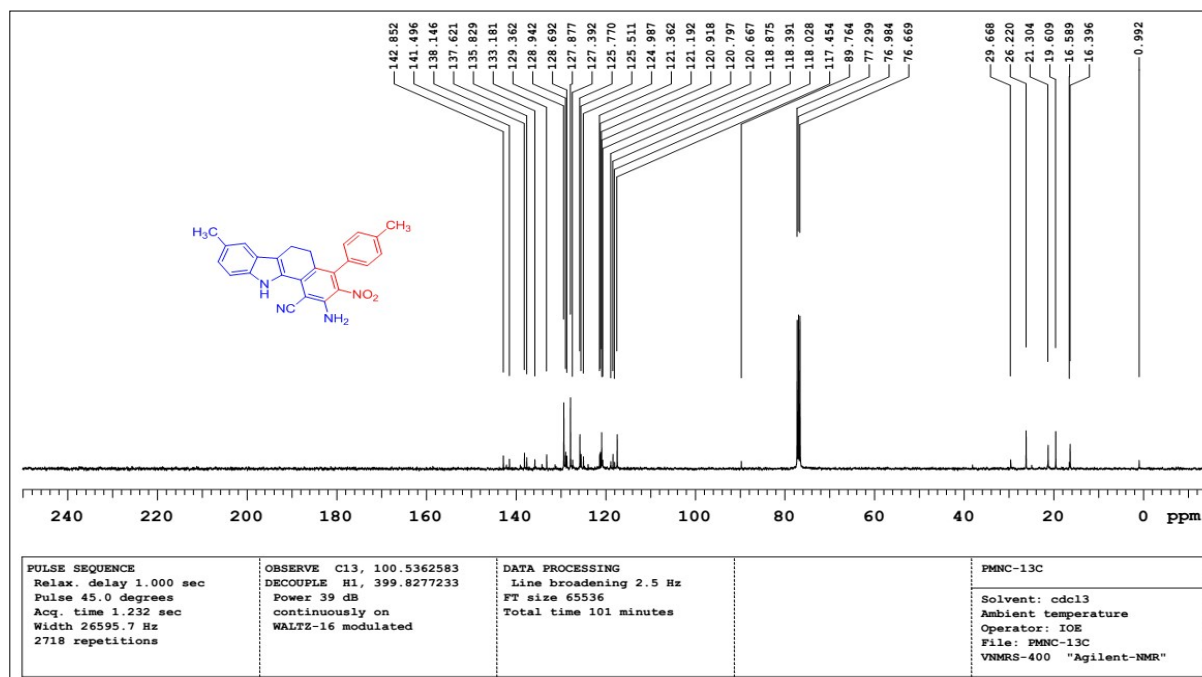
Fig. S26. ¹H NMR spectrum of 2-amino-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9d)**
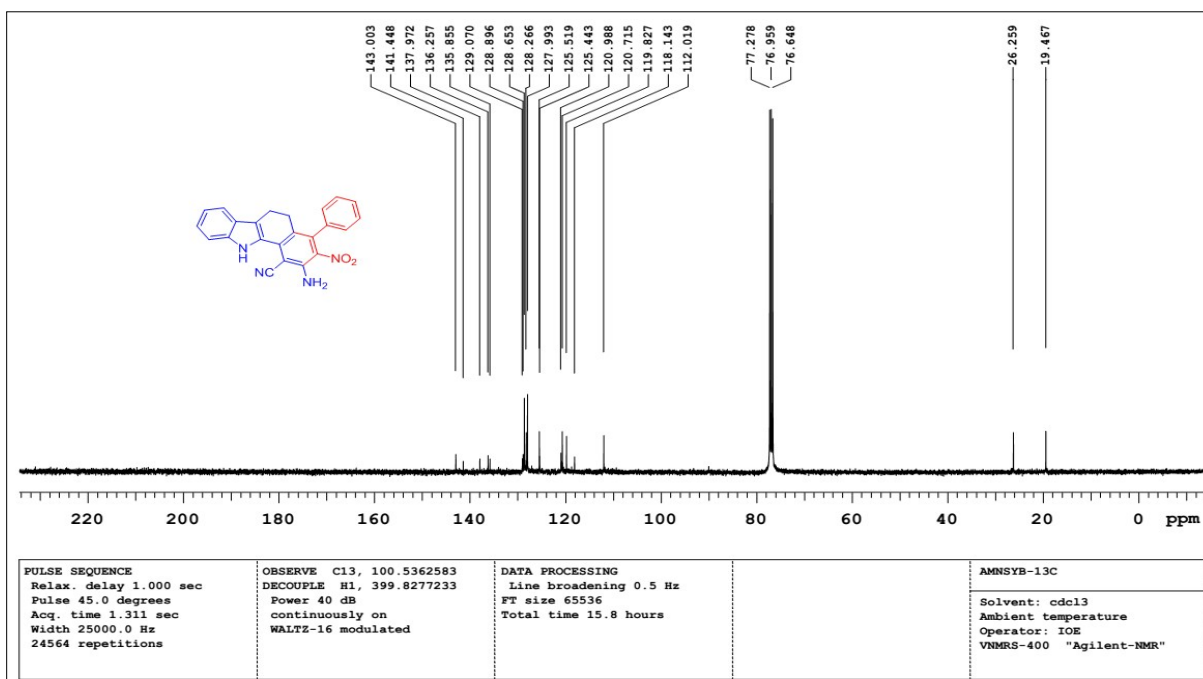
Fig. S27. ¹³C NMR spectrum of 2-amino-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9d)**
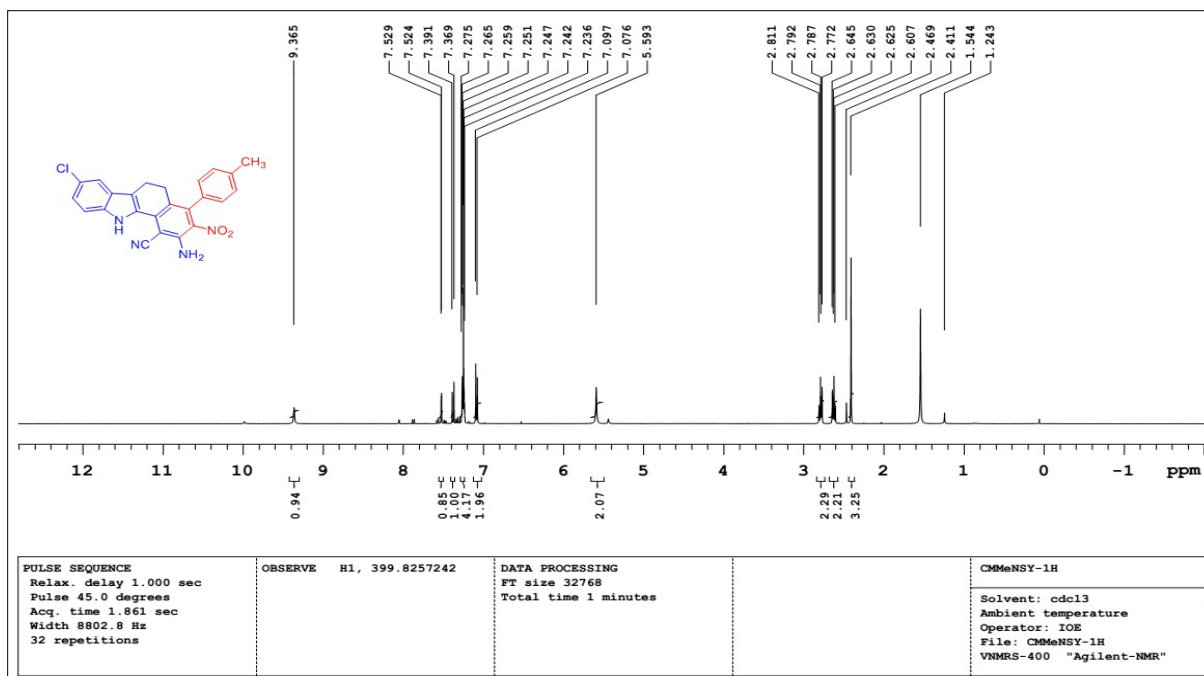
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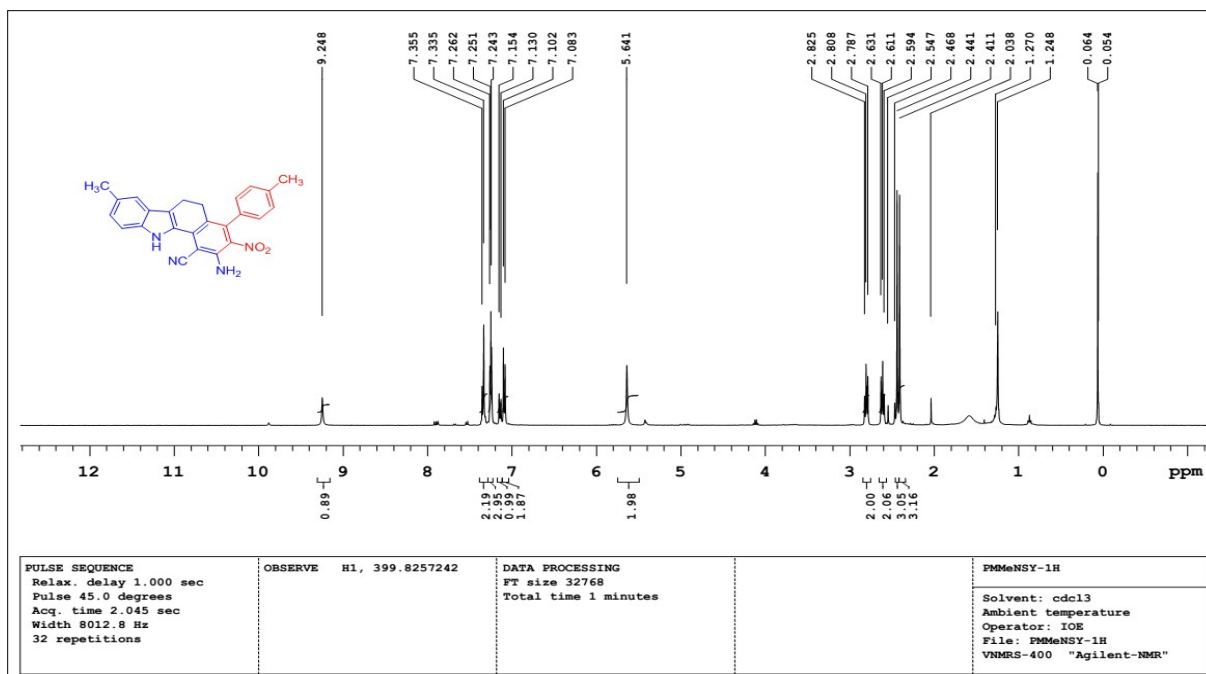
Fig. S28. ^{1}H NMR spectrum of 2-amino-8-methyl-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9e)**

Fig. S29. ^{13}C NMR spectrum of 2-amino-8-methyl-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9e)**
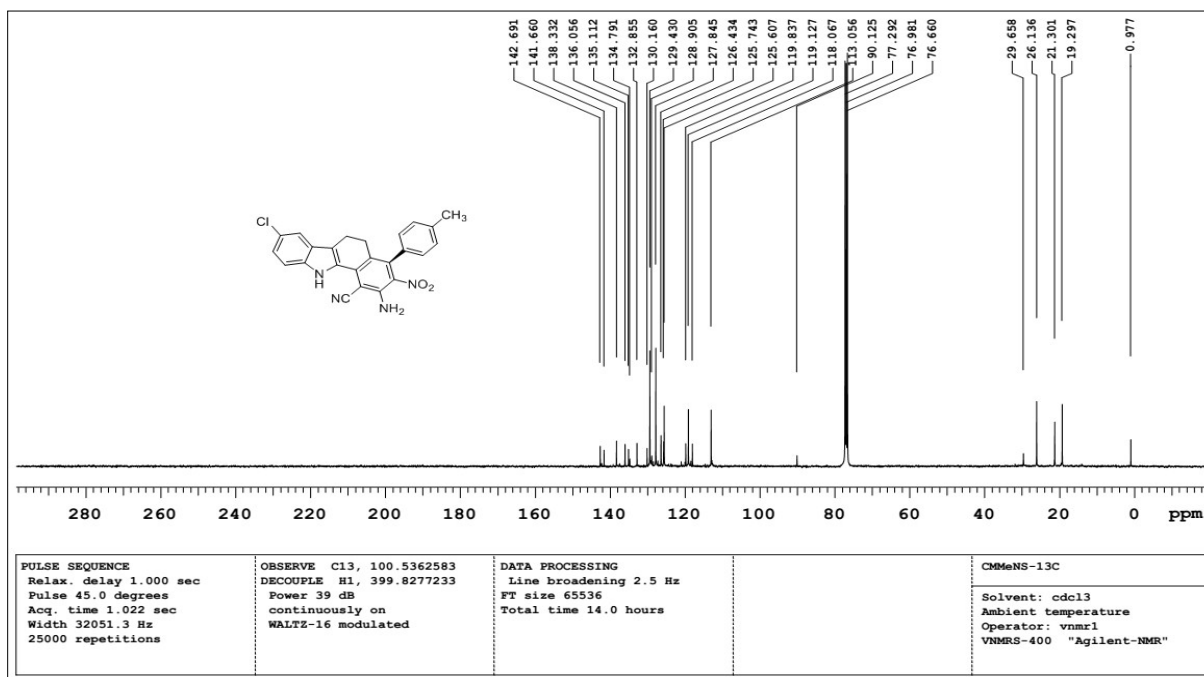
Fig. S30. ^{1}H NMR spectrum of 2-amino-8-chloro-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9g)**
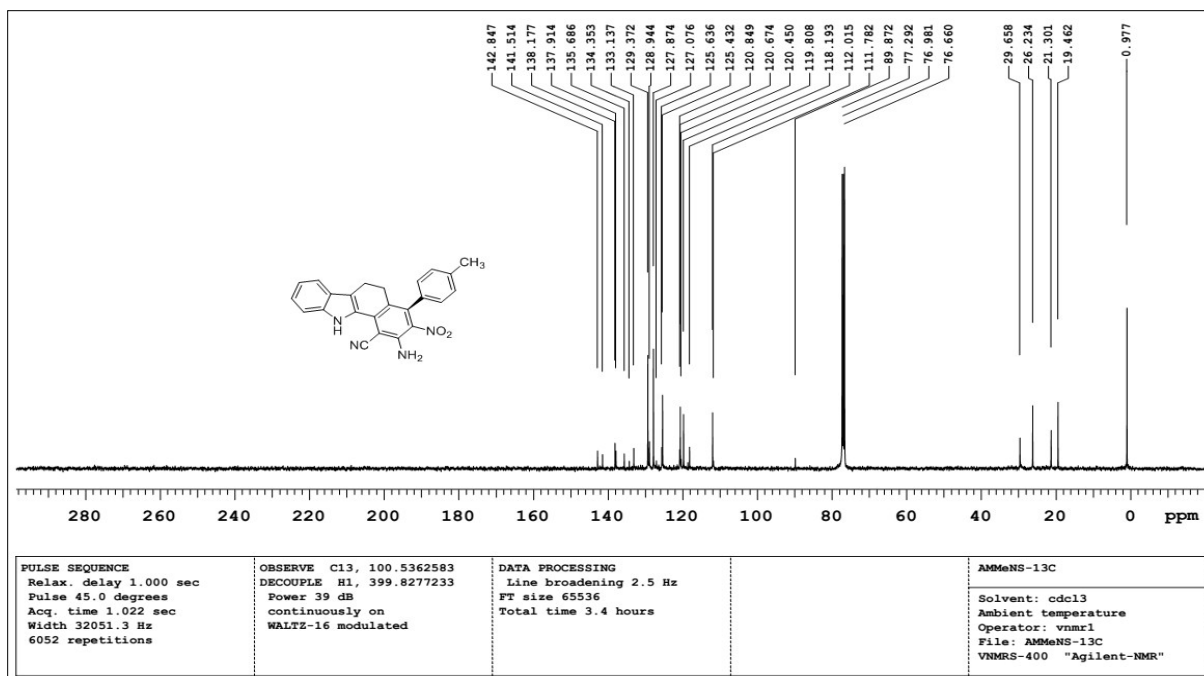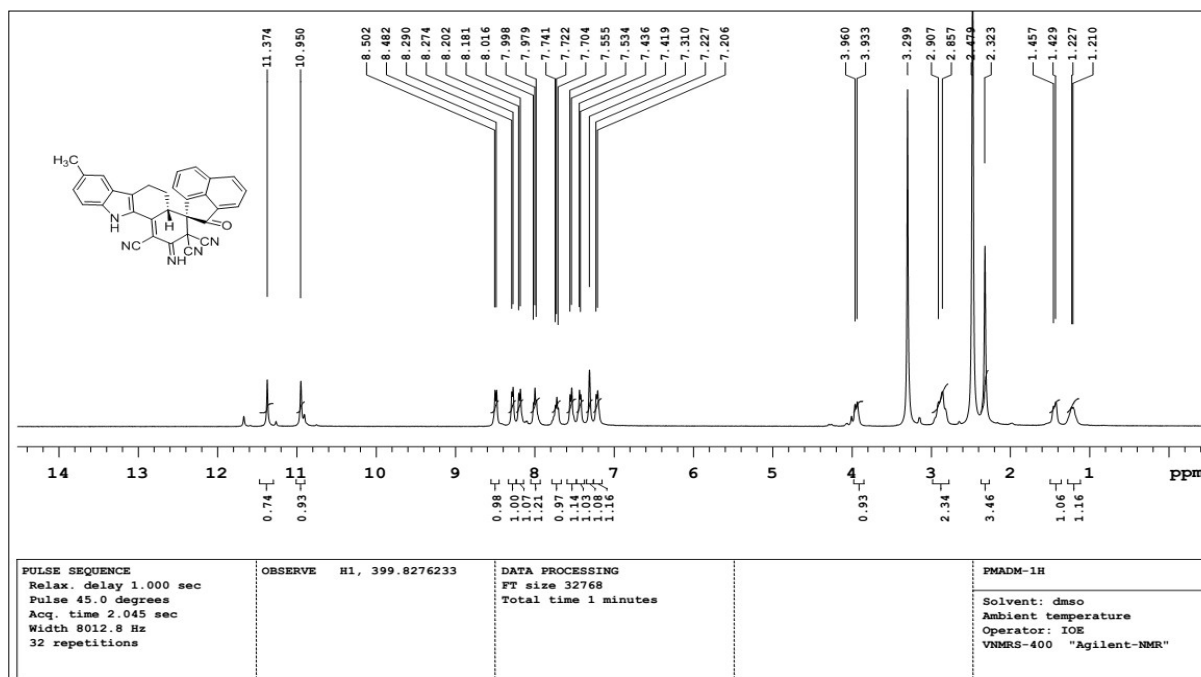

Fig. S31. ^{13}C NMR spectrum of 2-amino-8-chloro-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **(9g)**
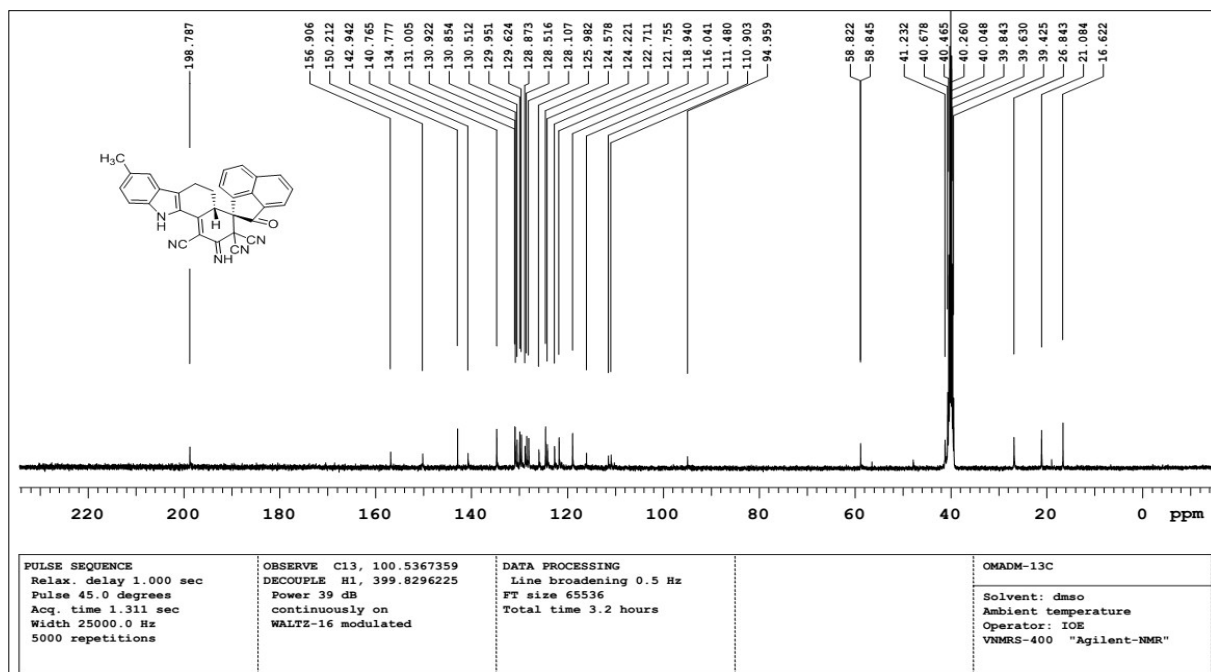
Fig. S32. ^{13}C NMR spectrum of 2-amino-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11H-benzo[a]carbazol-1-carbonitrile **(9h)**

g. S33. ^{1}H NMR spectrum of 2-imino-8-methyl-1'-oxo-5,6-dihydro-11H-spiro[acenaphthylene-8',4-benzo[a]carbazole]-1,3,3-tricarbonitrile **(11a)**
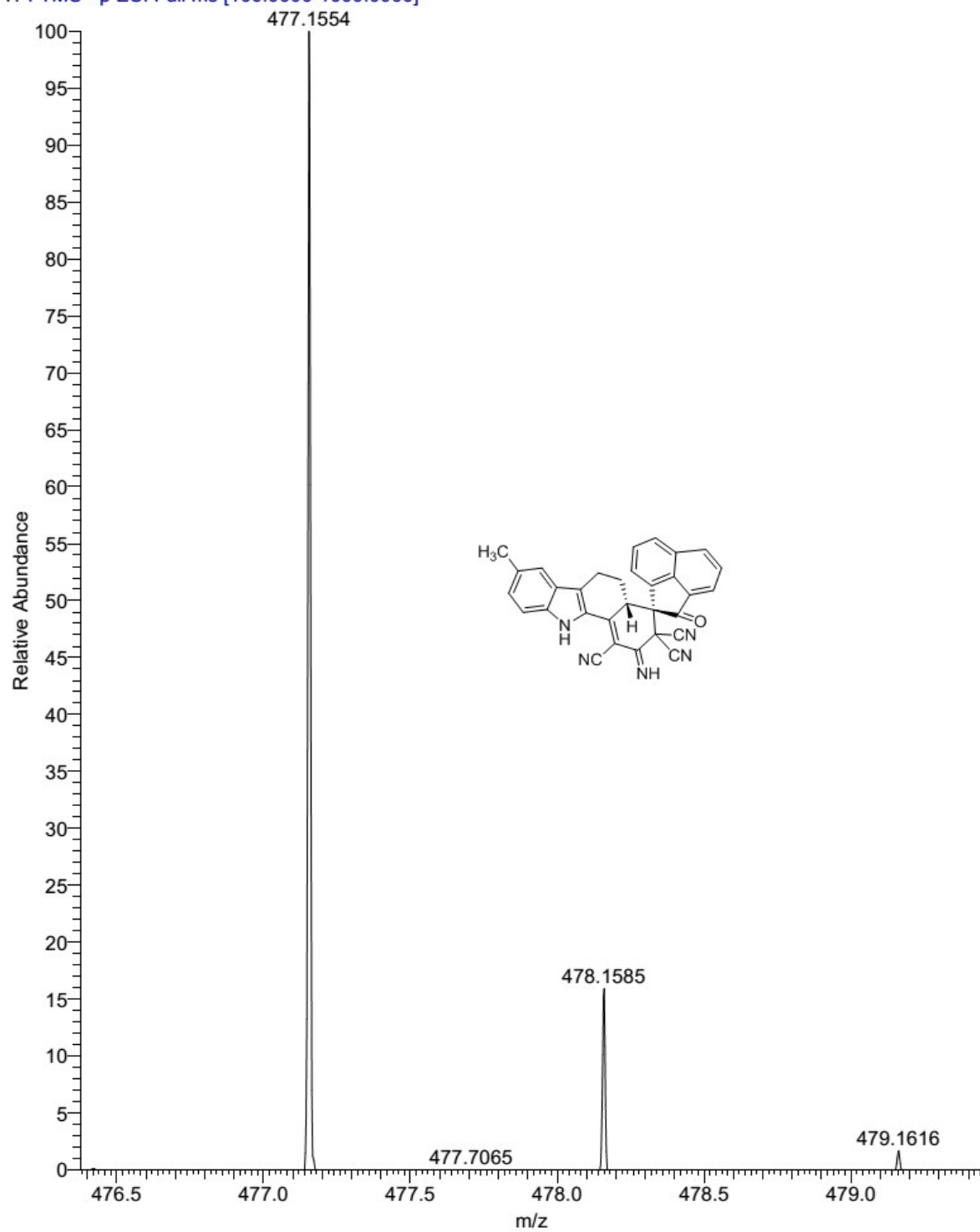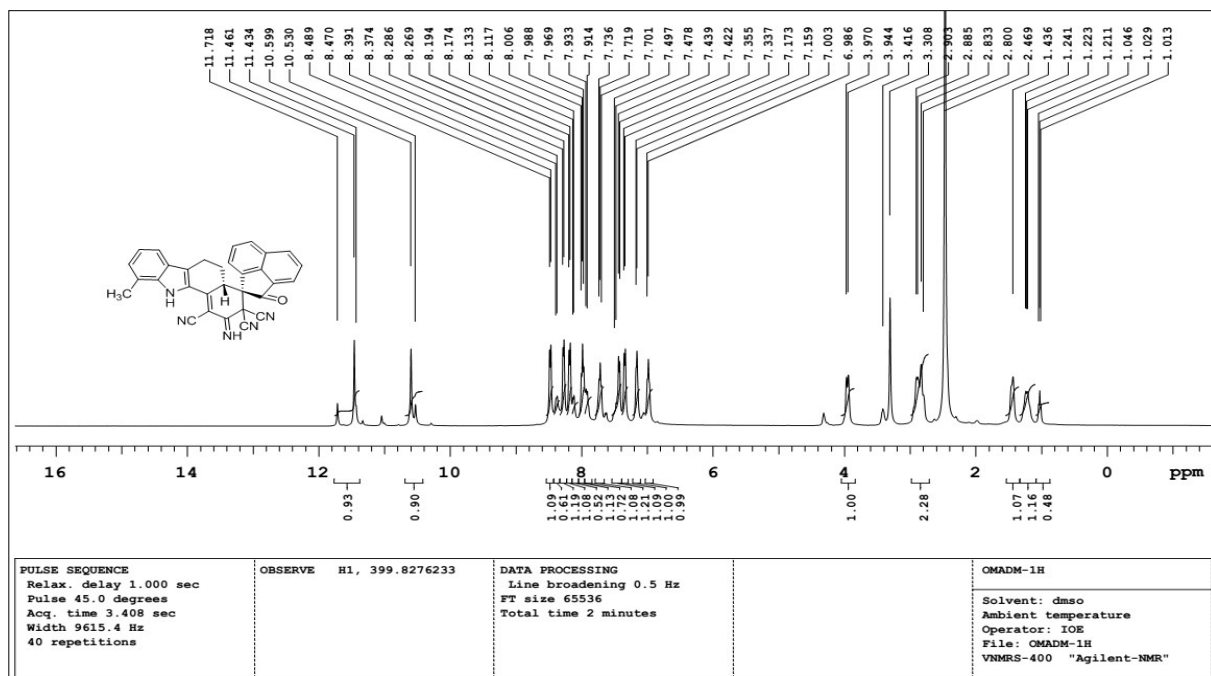
g. S34. ^{13}C NMR spectrum of 2-imino-8-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11a)**
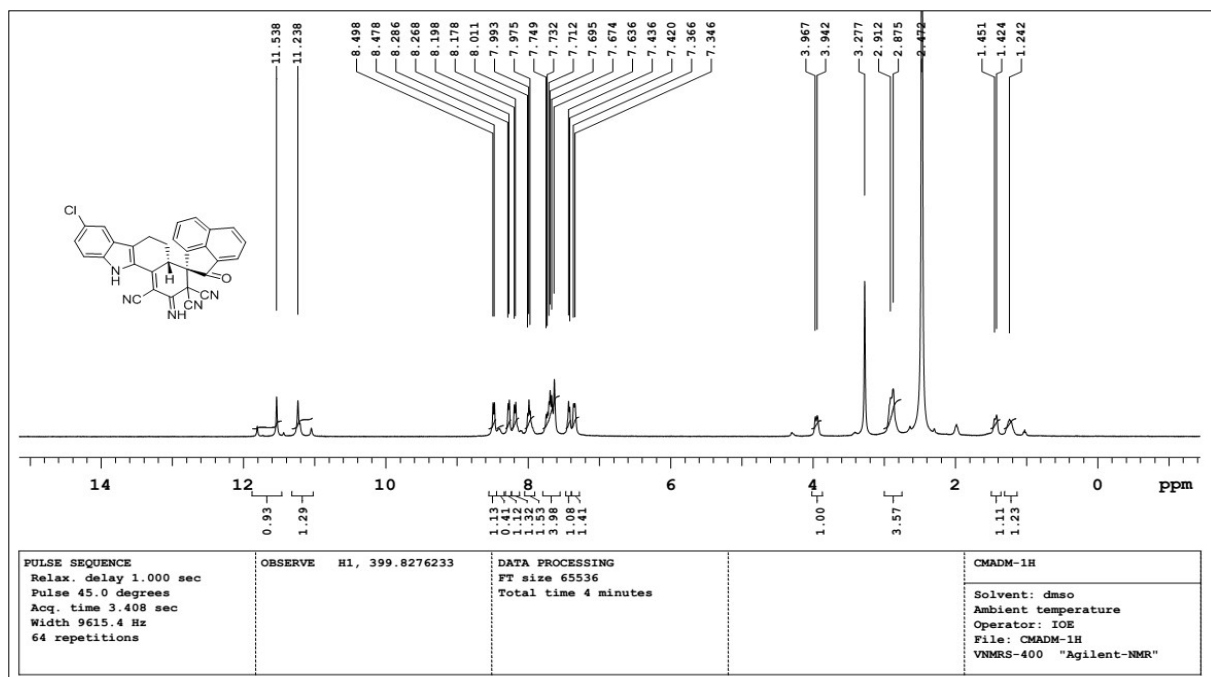
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Fig. S35. HRMS spectrum of 2-imino-8-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11a)**

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g. S36. ^{1}H NMR spectrum of 2-imino-10-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11b)**

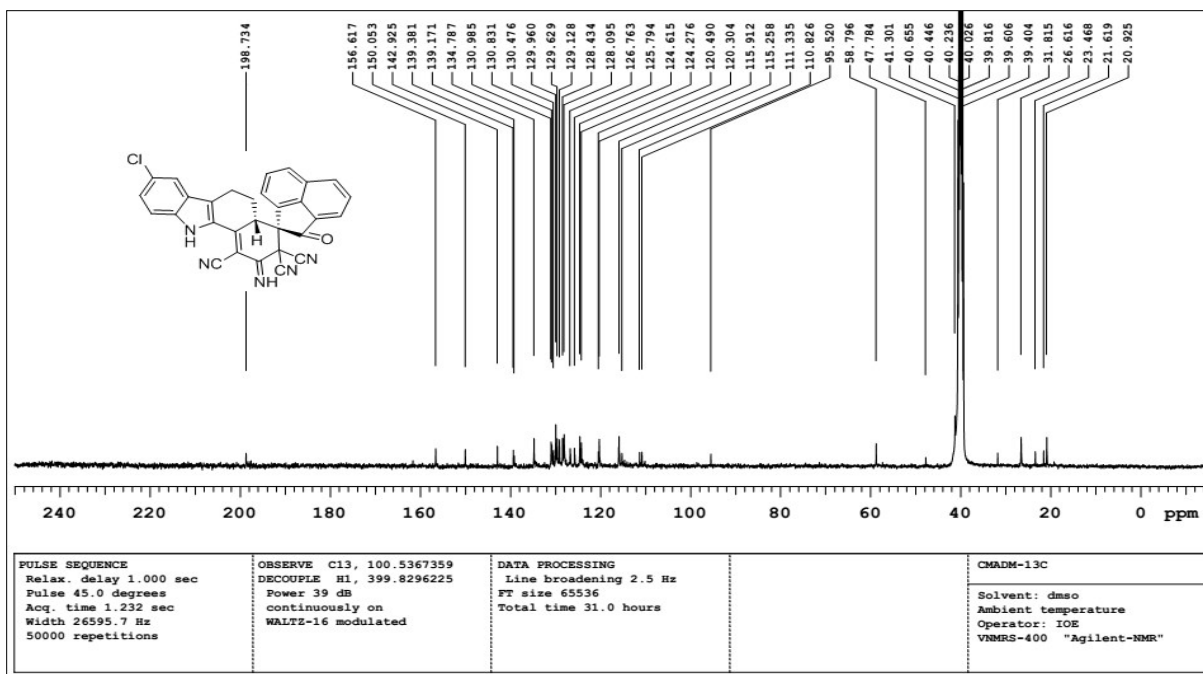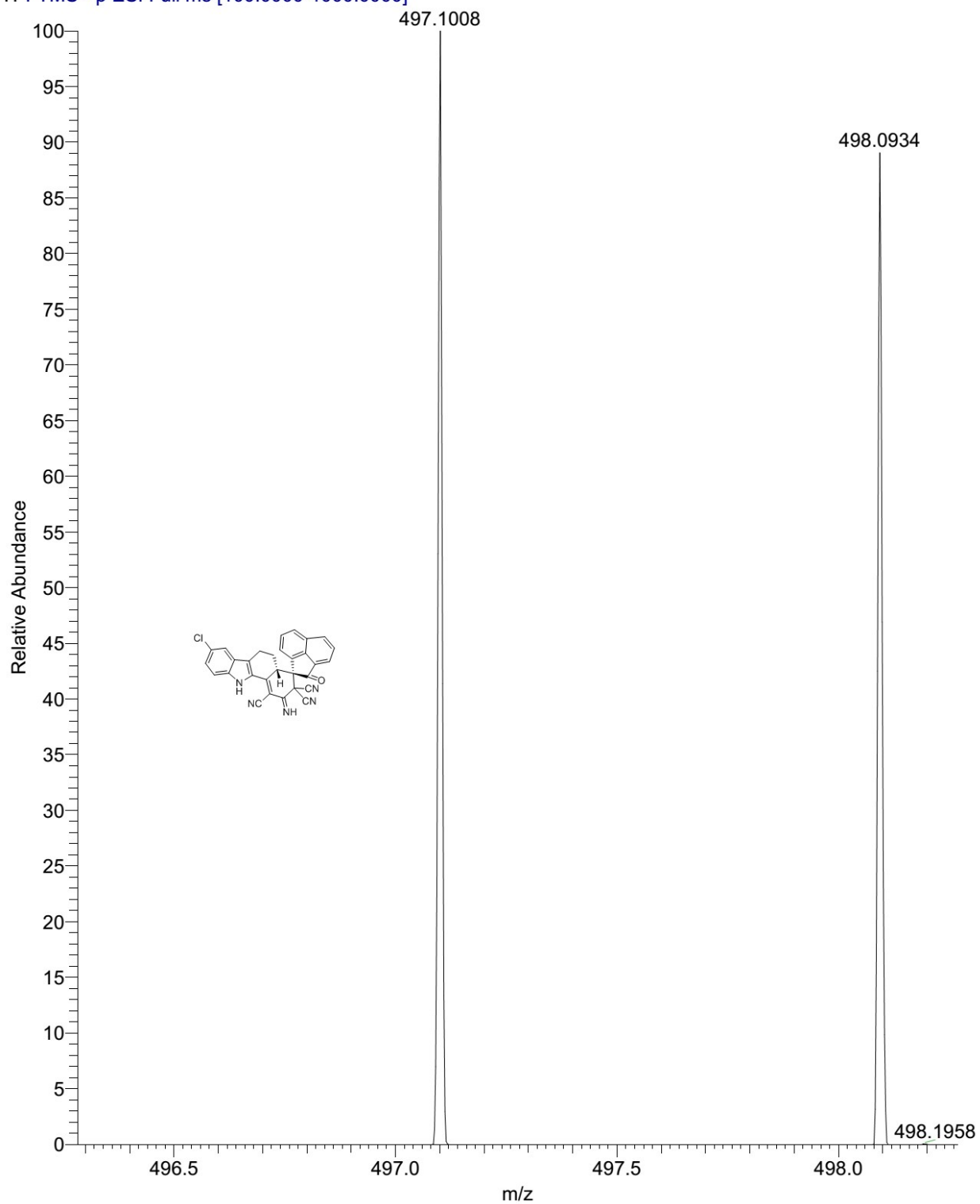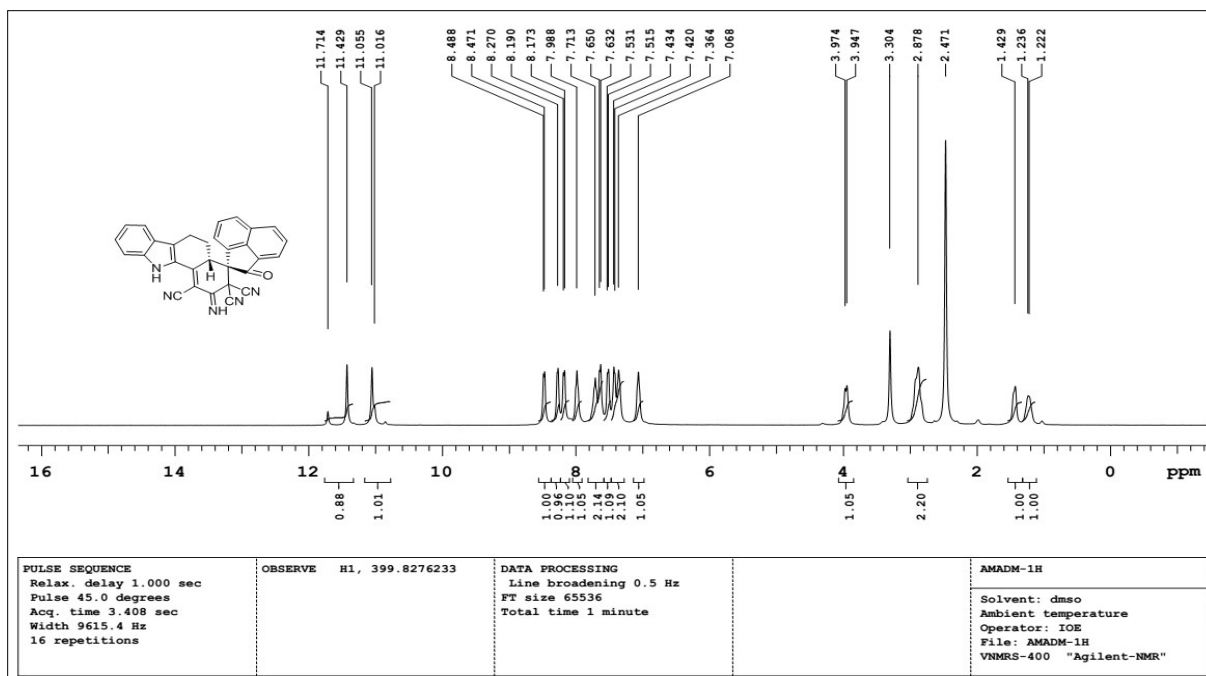**g. S37.** ^{1}H NMR spectrum of 2-imino-8-chloro-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11c)**

Fig. S38. ^{13}C NMR spectrum of 2-imino-8-chloro-1'-oxo-5,6-dihydro-11H-spiro[acenaphthylene-8',4-benzo[a]carbazole]-1,3,3-tricarbonitrile **(11c)**
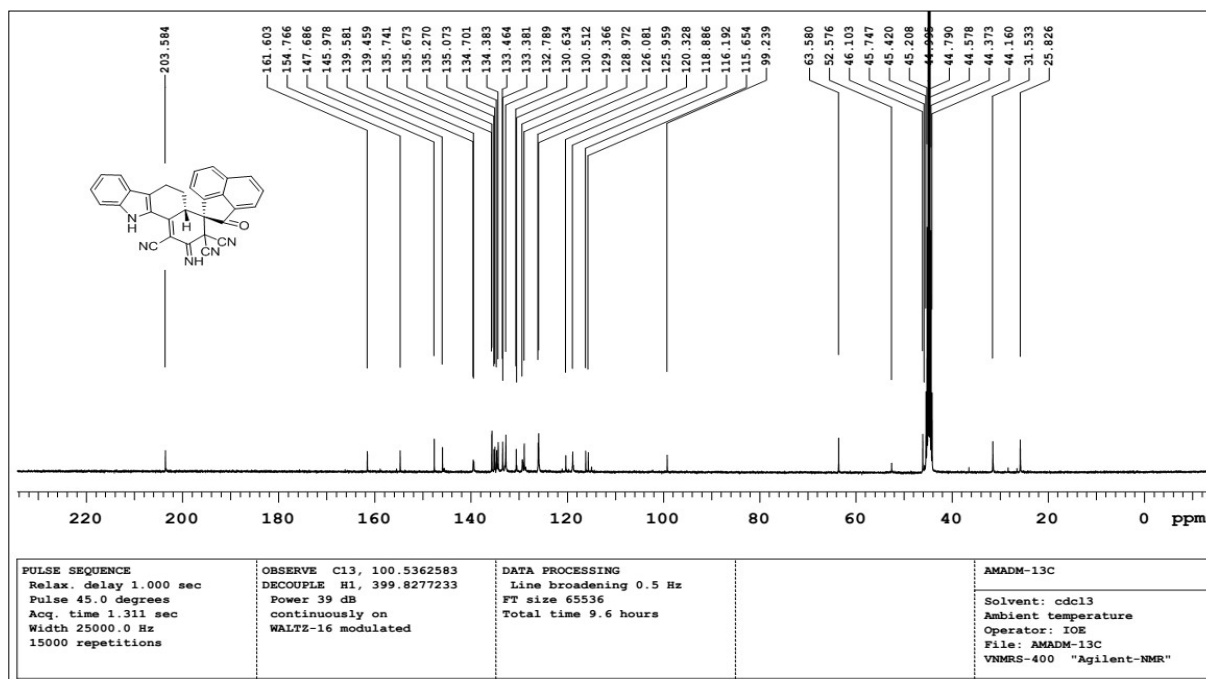
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Fig. S39. HRMS spectrum of 2-imino-8-chloro-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11c)**
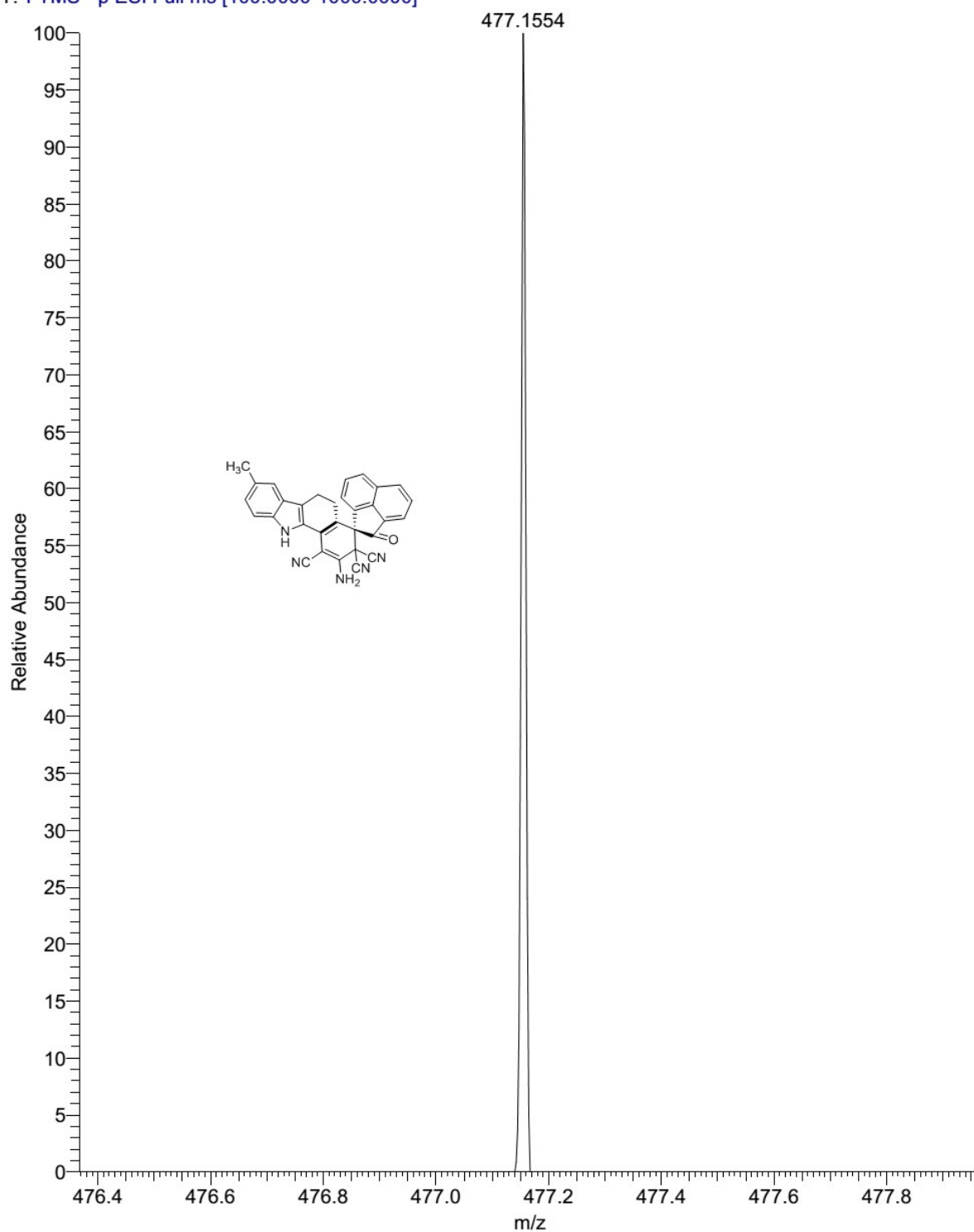
Fig. S40. ^{1}H NMR spectrum of 2-imino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11d)**
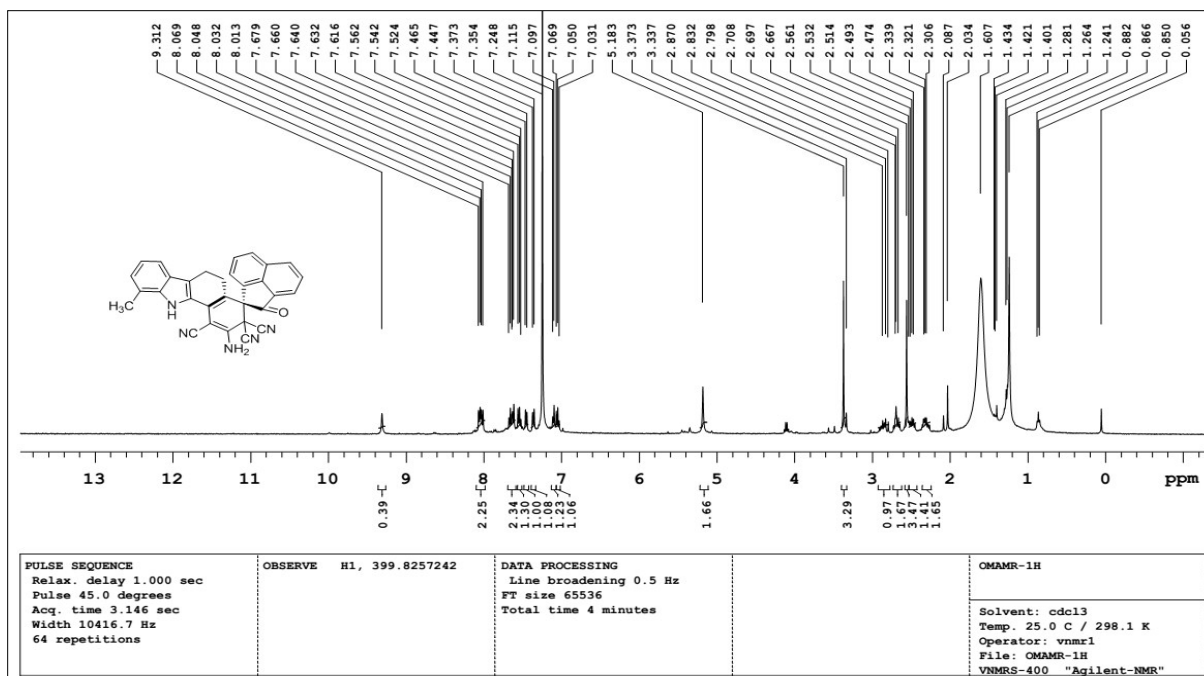

Fig. S41. ^{13}C NMR spectrum of 2-imino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **(11d)**
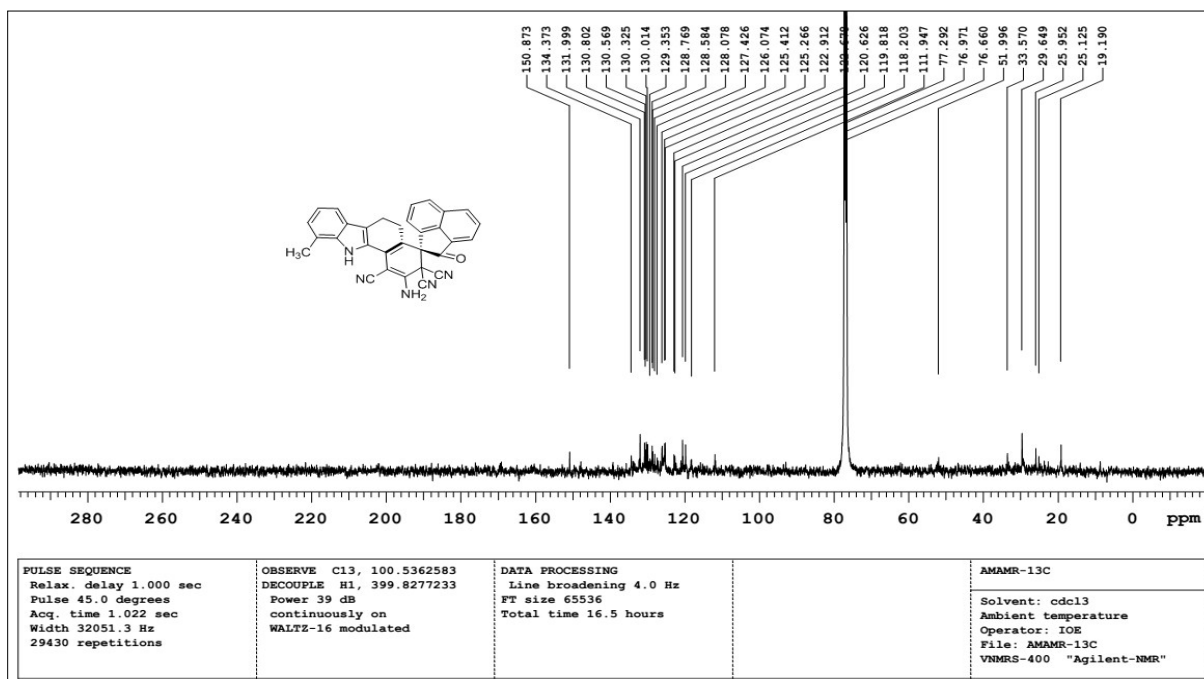
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Fig. S42. HRMS spectrum of 2-amino-8-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12a**)
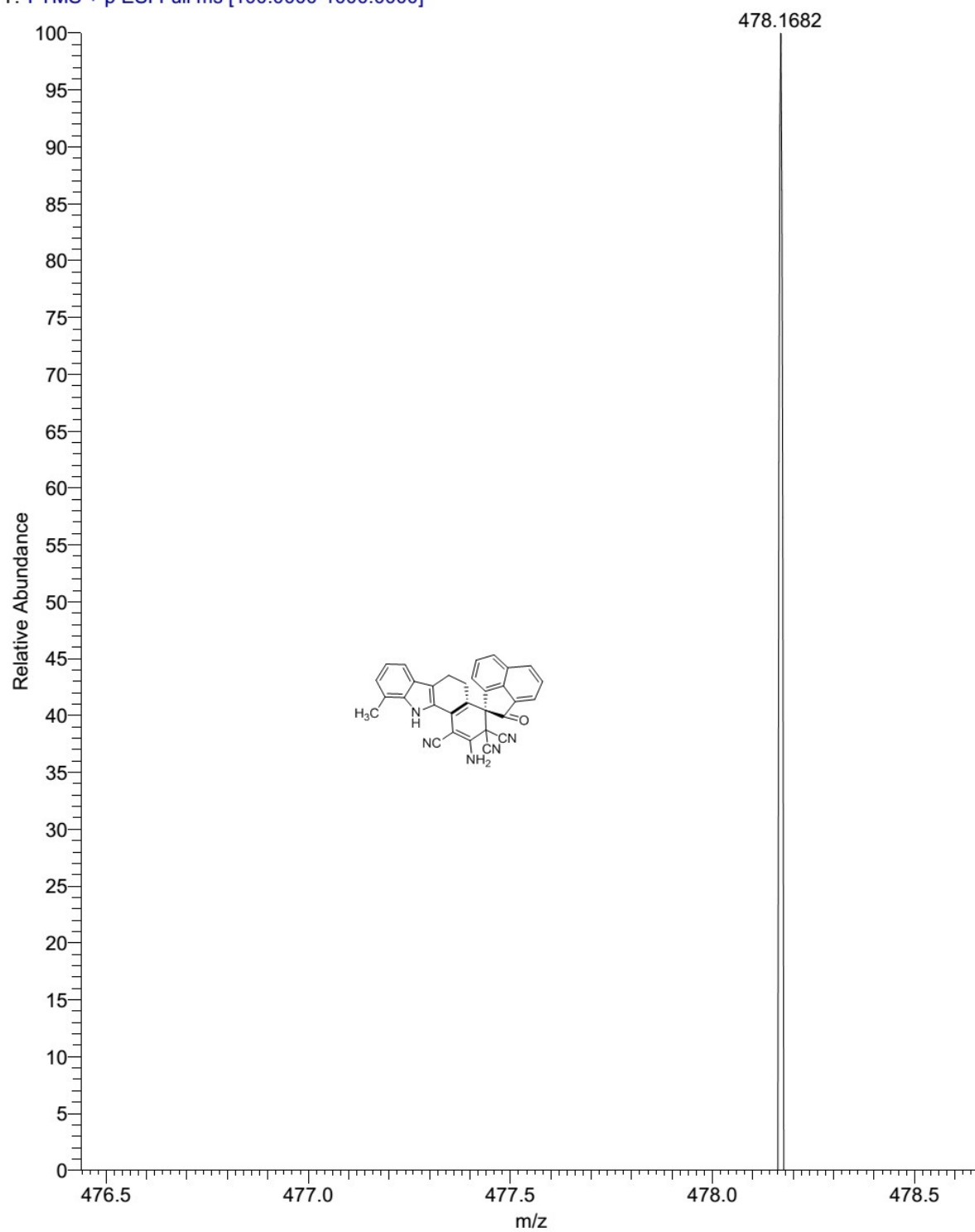
Fig. S43. ^{1}H NMR spectrum of 2-amino-10-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12b**)

Fig. S44. ^{13}C NMR spectrum of 2-amino-10-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12b**)
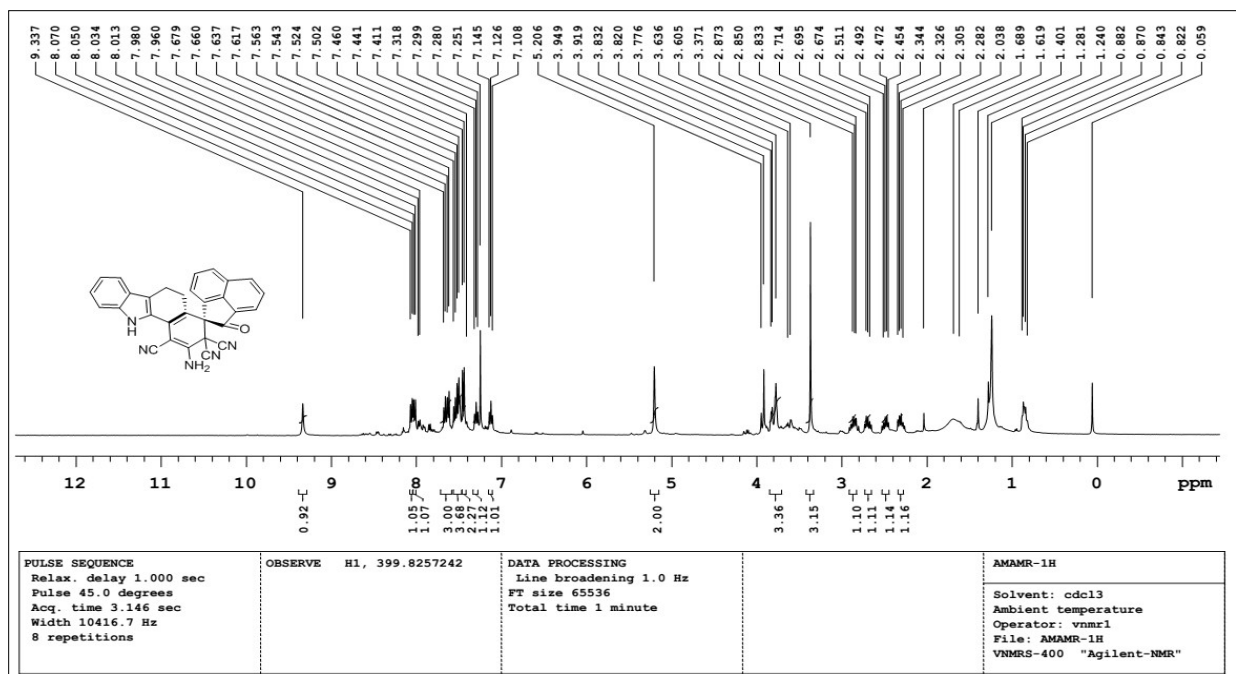
2 #167-191 RT: 1.59-1.82 AV: 13 NL: 1.34E4
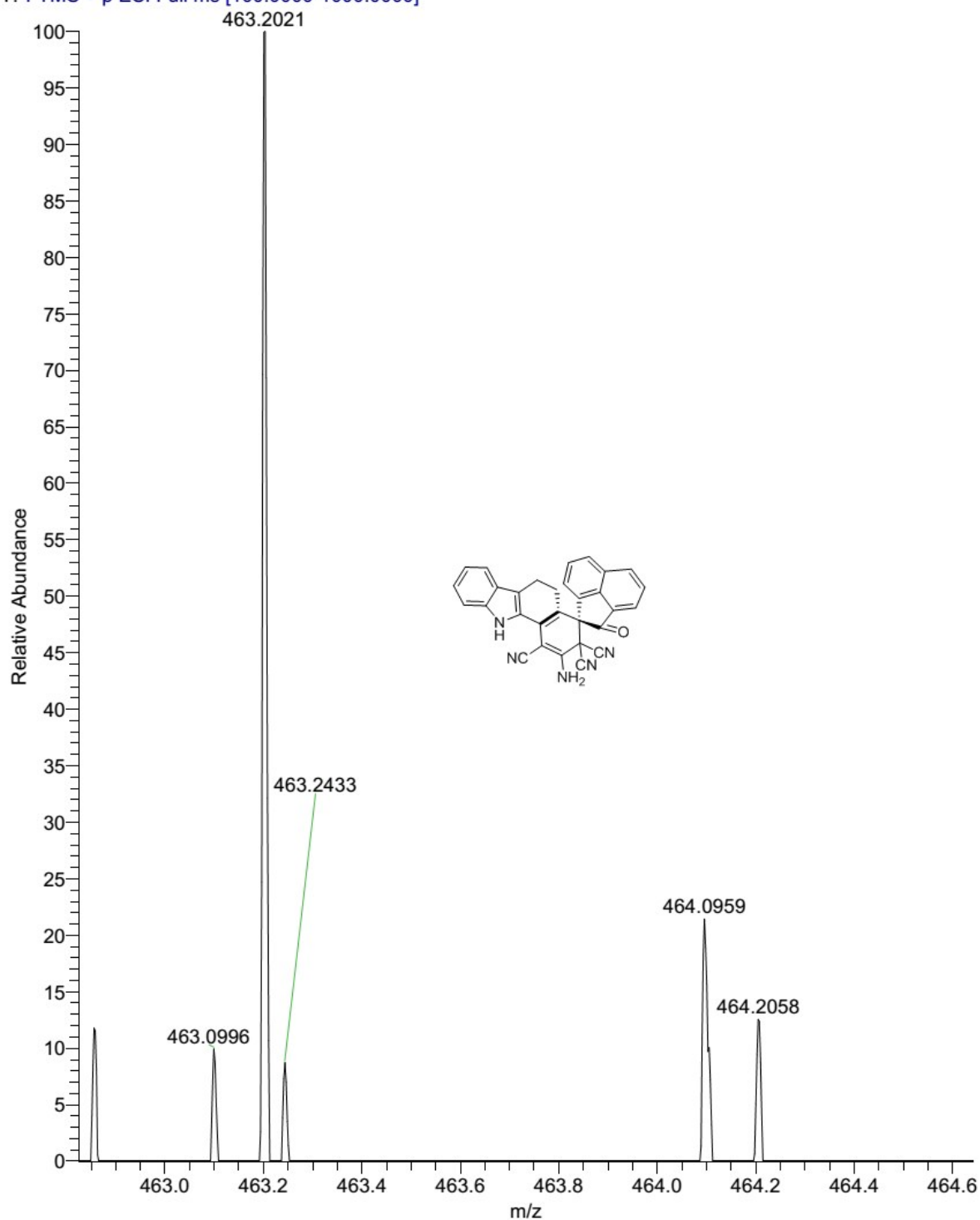T: FTMS + p ESI Full ms [100.0000-1000.0000]

Fig. S45. HRMS spectrum of 2-amino-10-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12b**)

Fig. S46. ^{1}H NMR spectrum of 2-amino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12d**)

Fig. S47. HRMS spectrum of 2-amino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12d**)