Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Ambient temperature synthesis of β,β′-fused nickel(II) pyrrolo[1,2-a]pyrazinoporphyrins *via* a DBSA-Catalyzed Pictet-Spengler approach

Dileep Kumar Singh and Mahendra Nath*

Department of Chemistry, University of Delhi, Delhi 110 007, India

Contents:

1. ^{1}H and ^{13}C NMR Spectra of synthesized products:

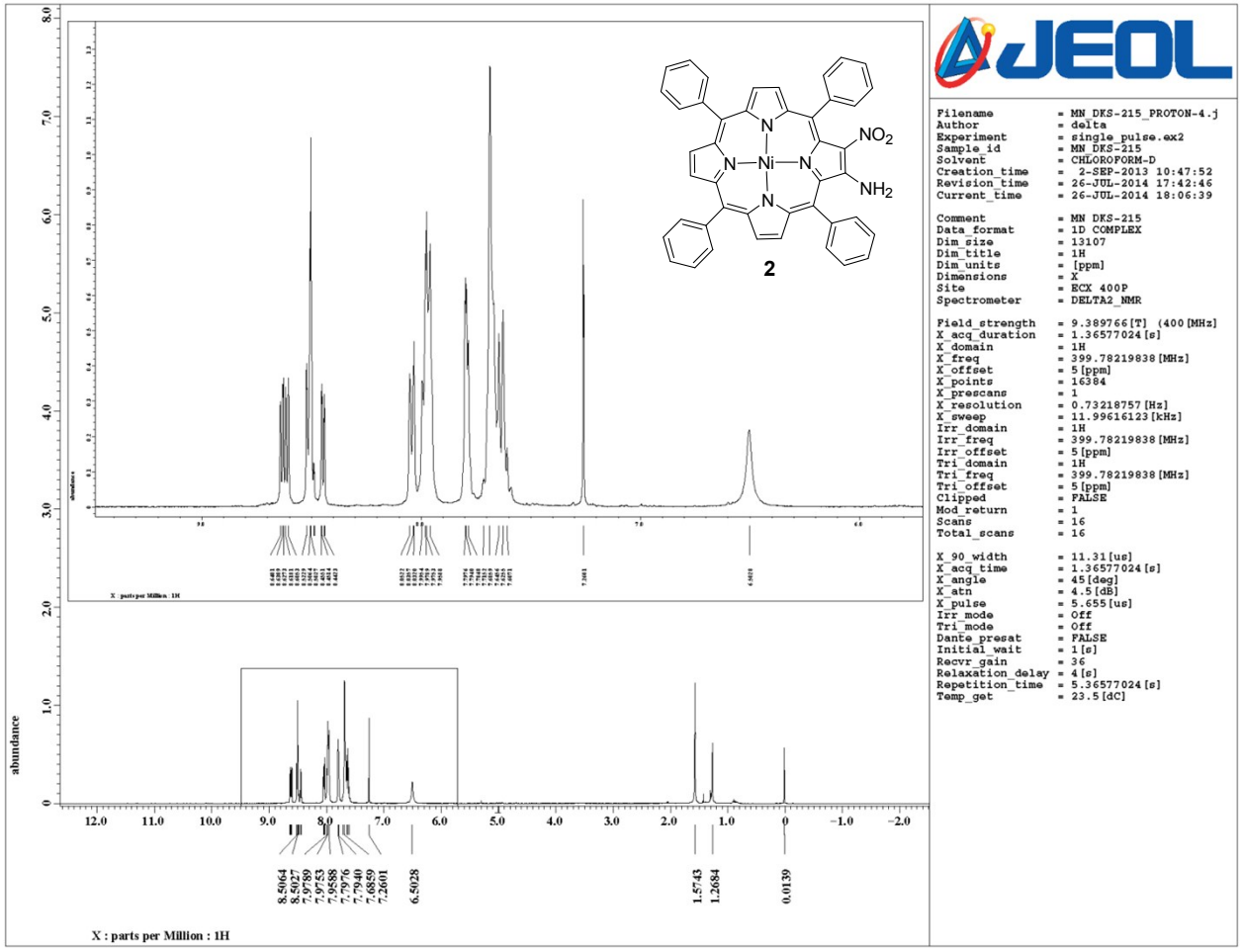

Fig. 1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

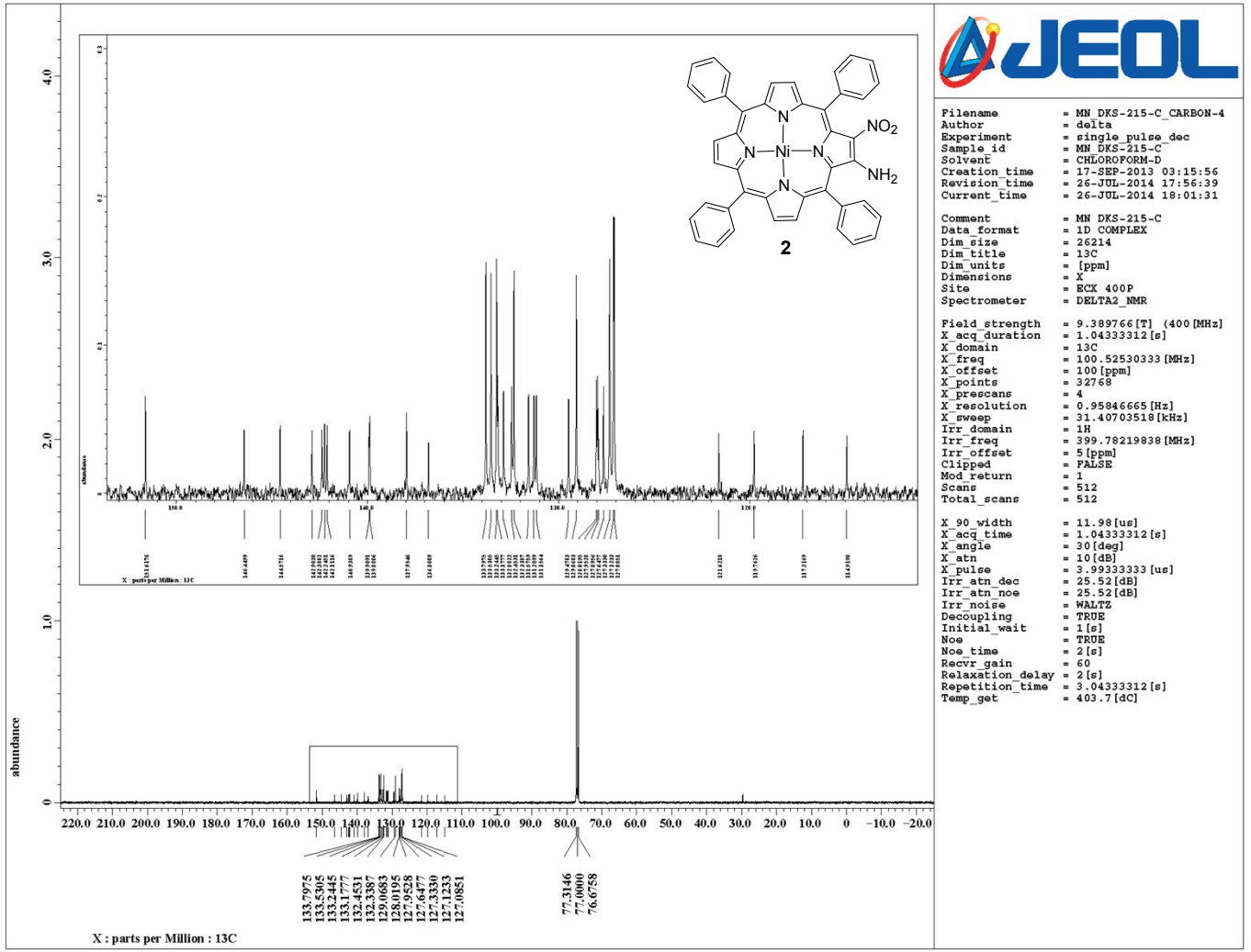

Fig. 2. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

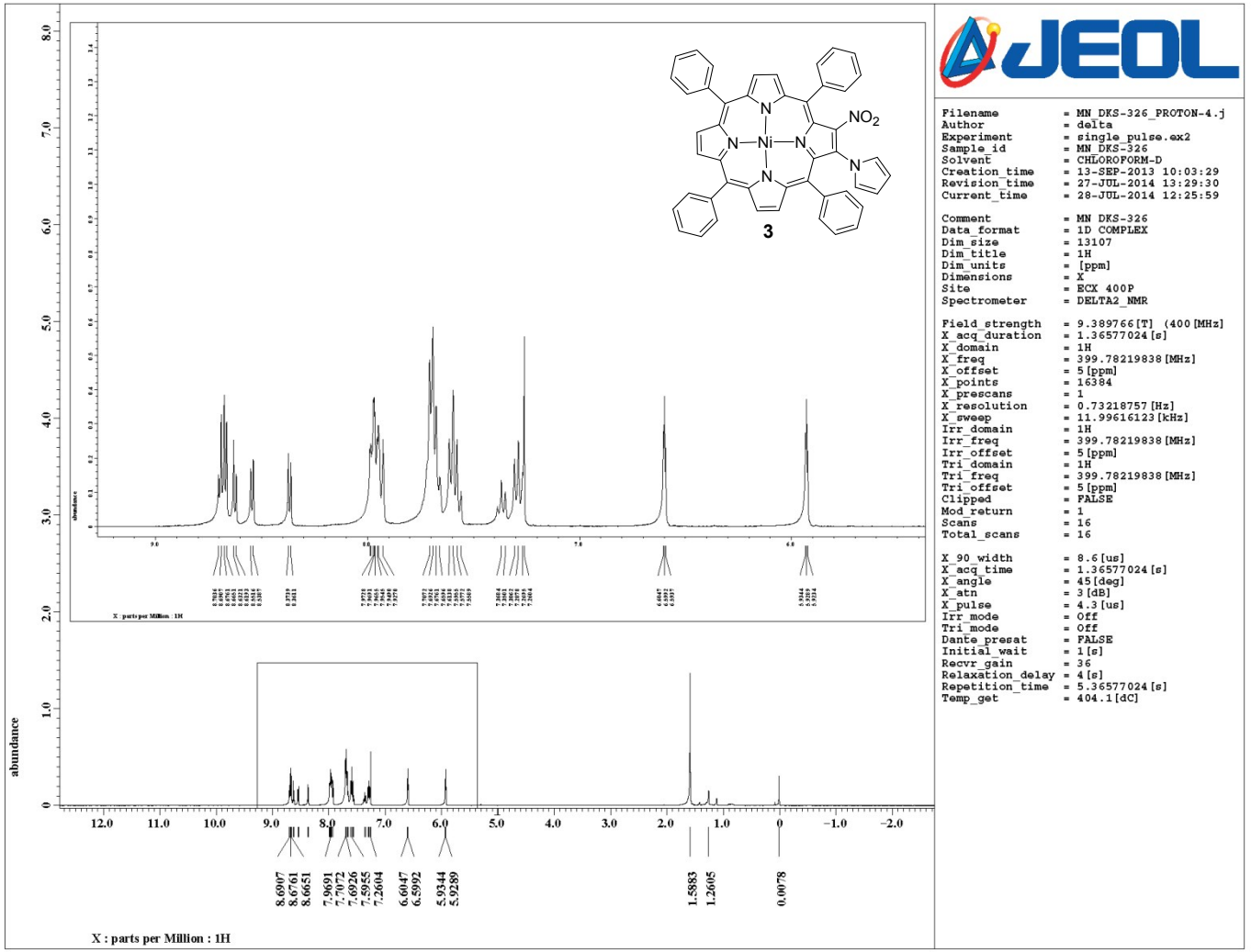

Fig. 3. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

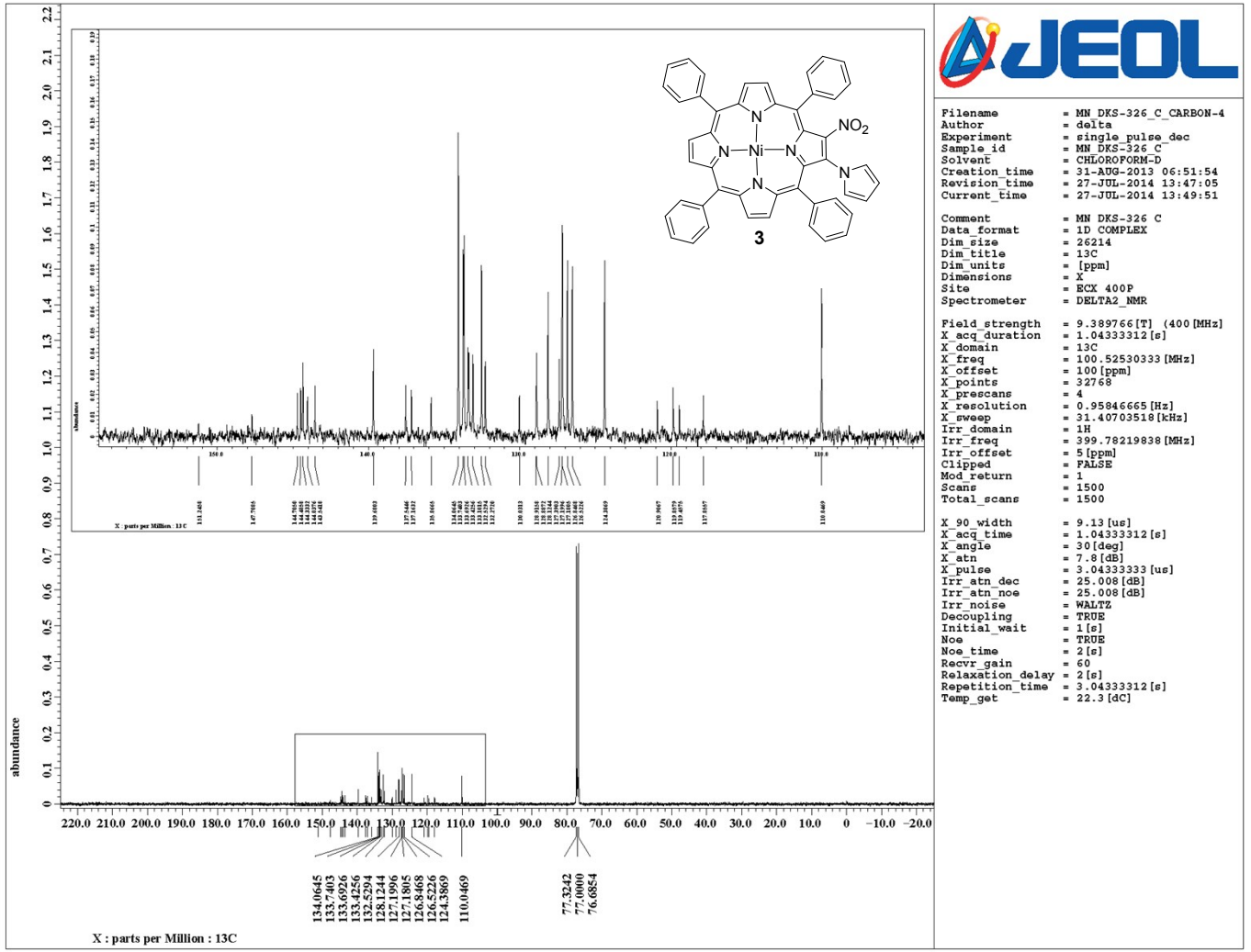

Fig. 4. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

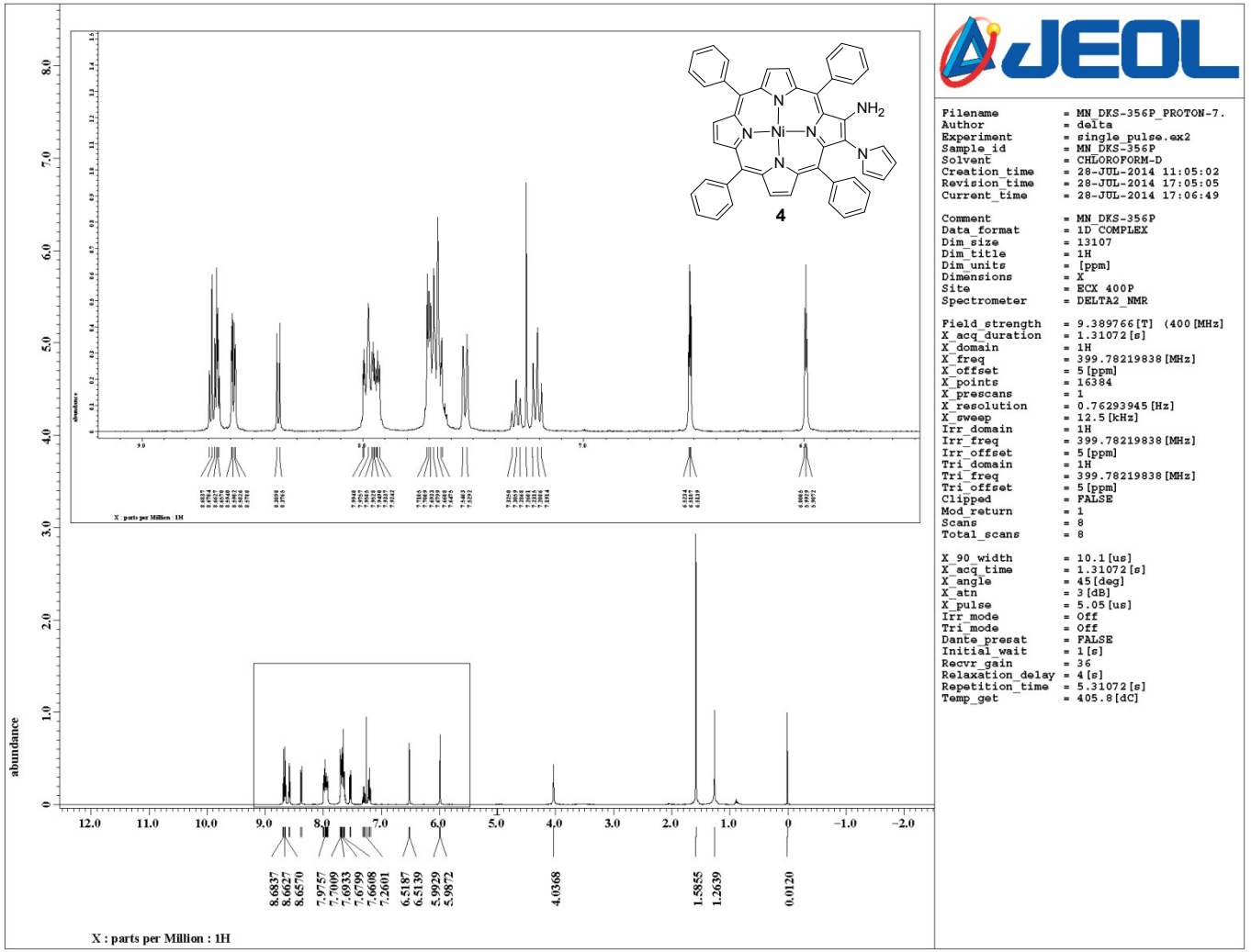

Fig. 5. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

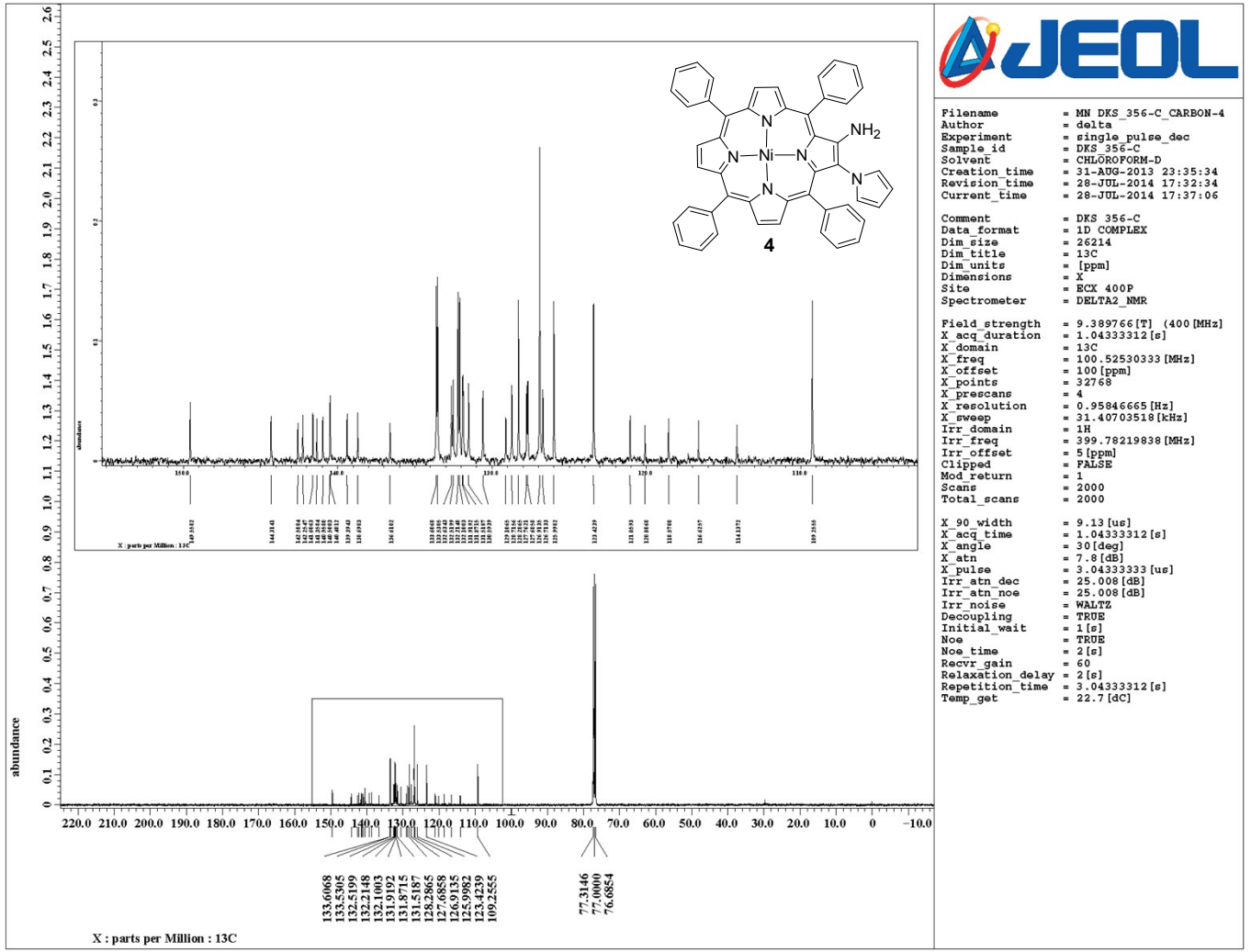

Fig. 6. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

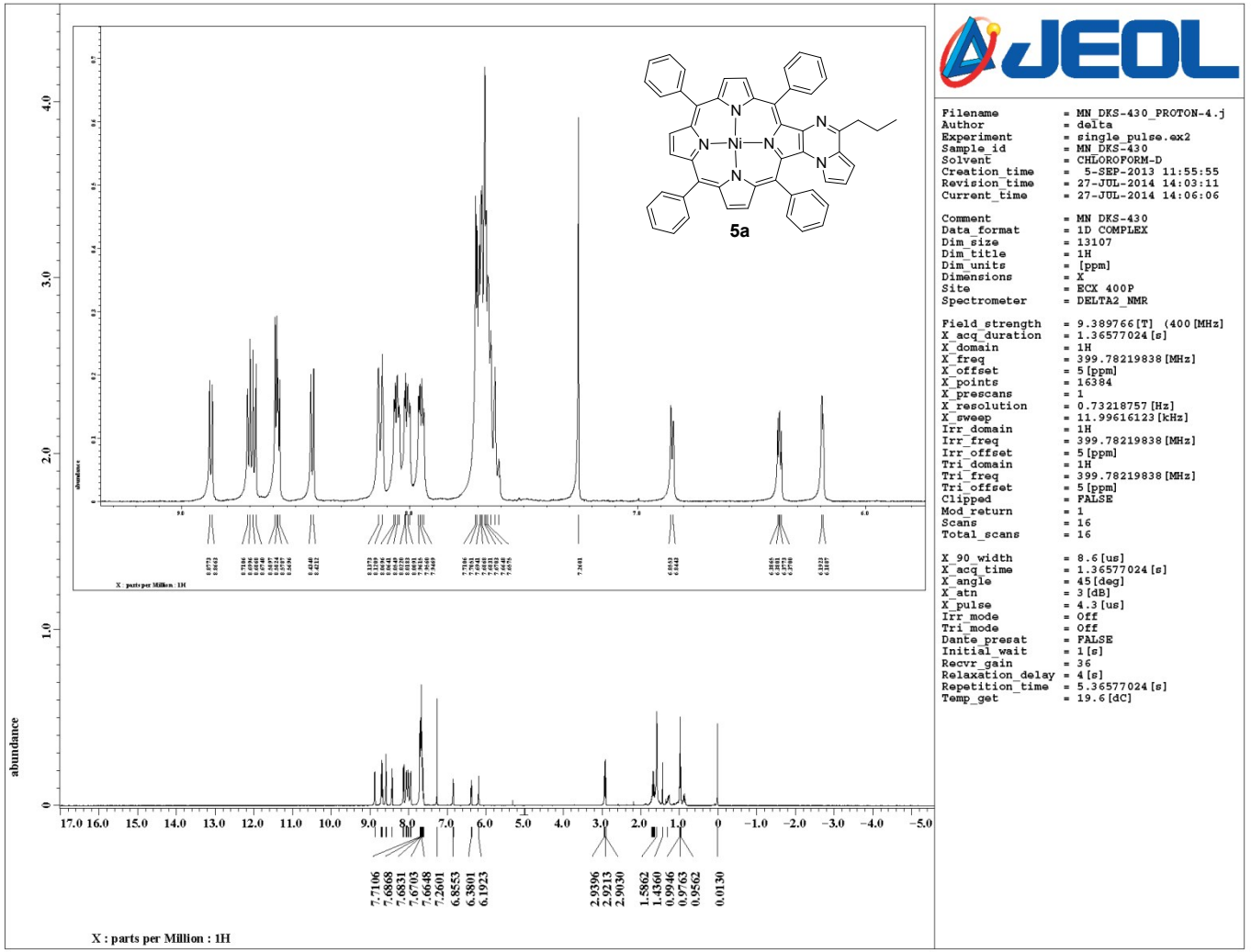

Fig. 7. ^{1}H NMR spectrum of compound **5a** in $CDCl_3$.

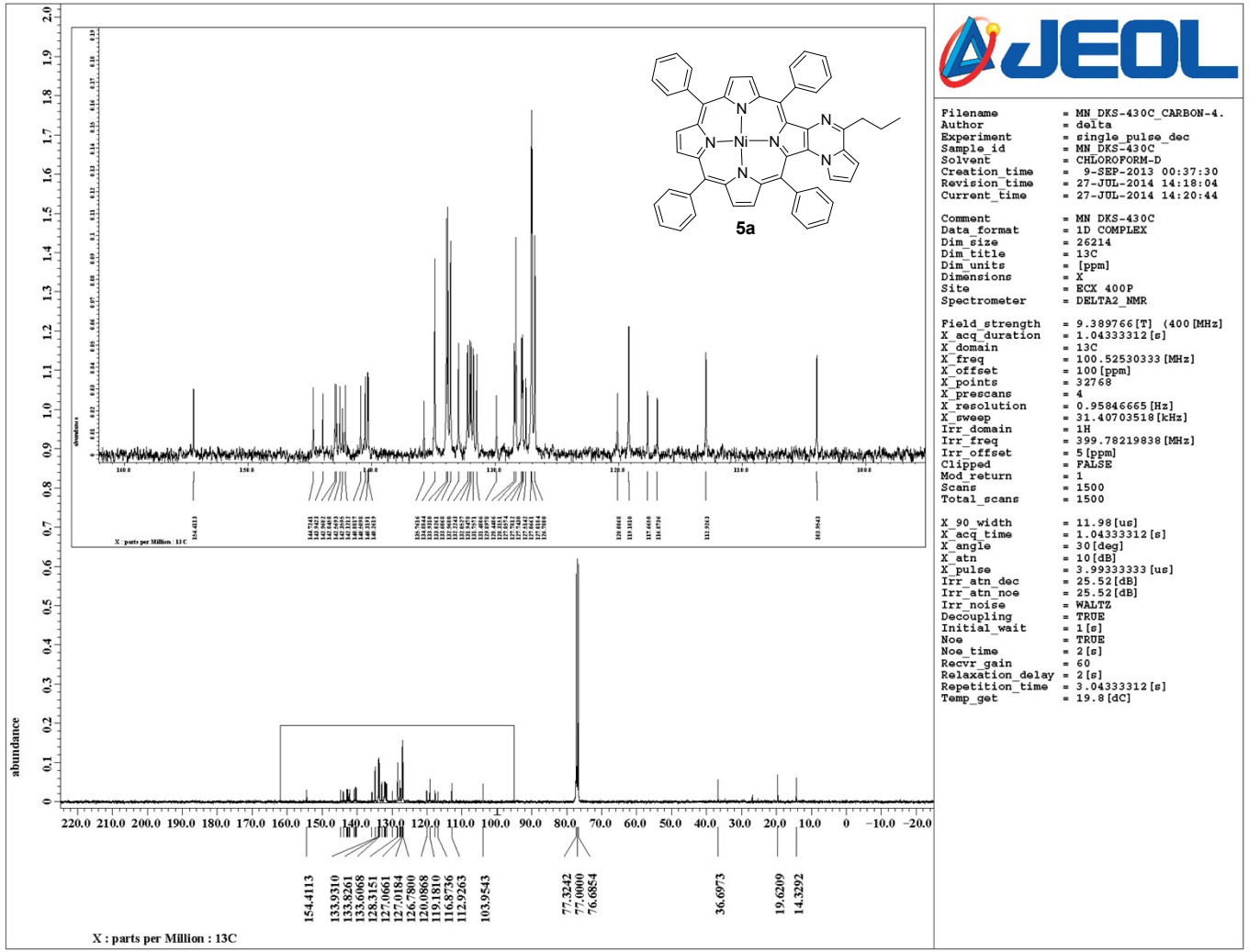

Fig. 8. ^{13}C NMR spectrum of compound **5a** in $CDCl_3$.

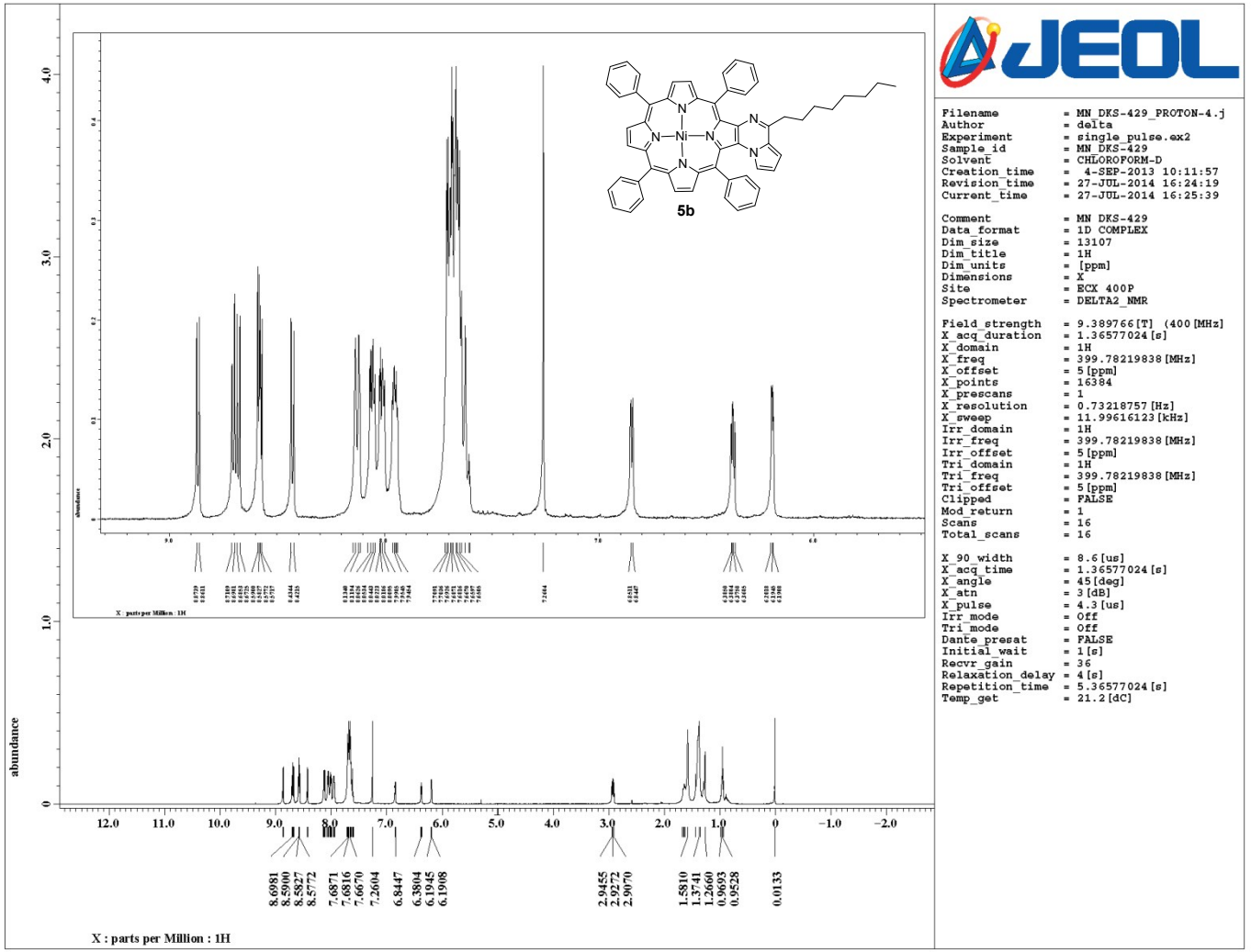

Fig. 9. ^{1}H NMR spectrum of compound **5b** in $CDCl_3$.

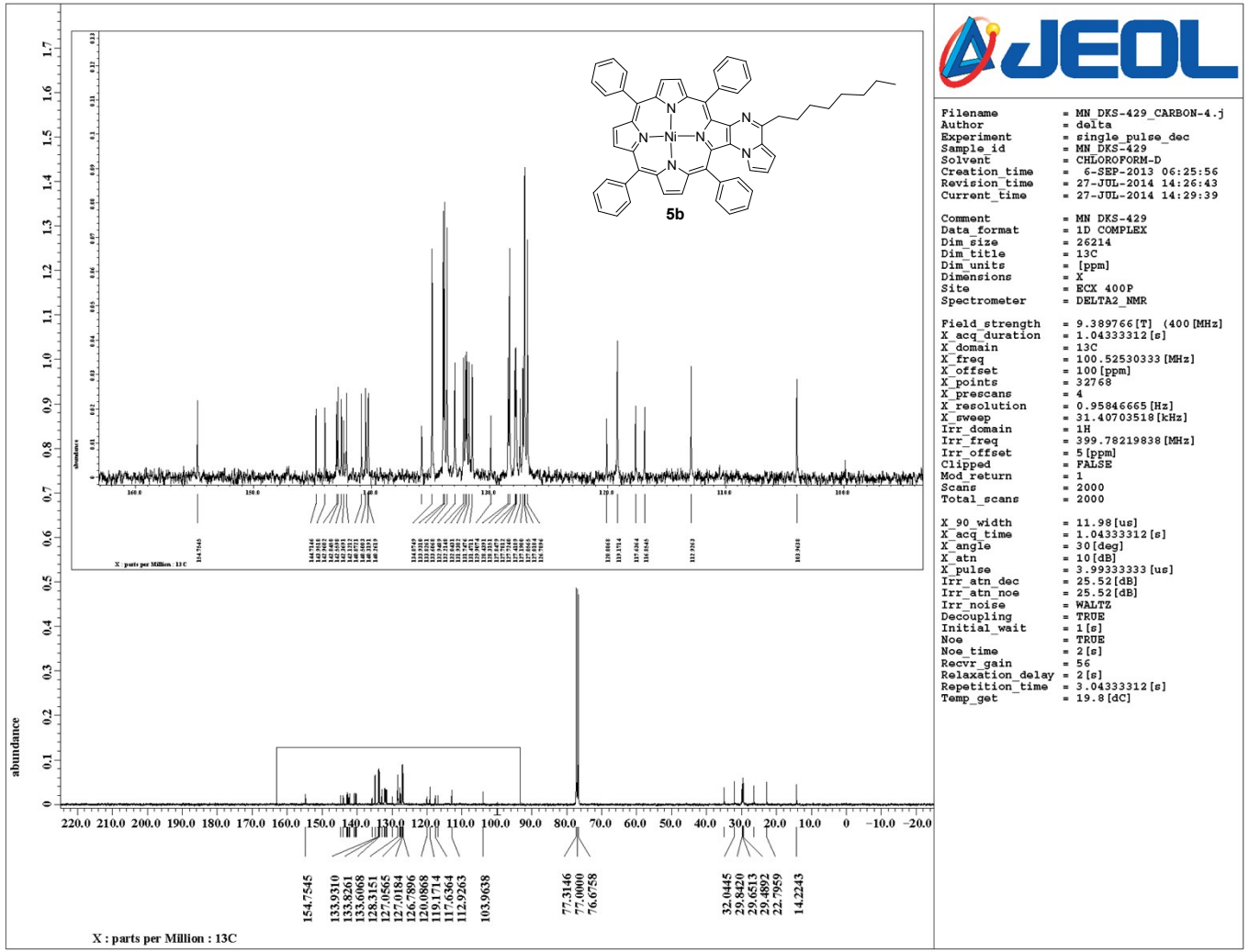

Fig. 10. ^{13}C NMR spectrum of compound **5b** in $CDCl_3$.

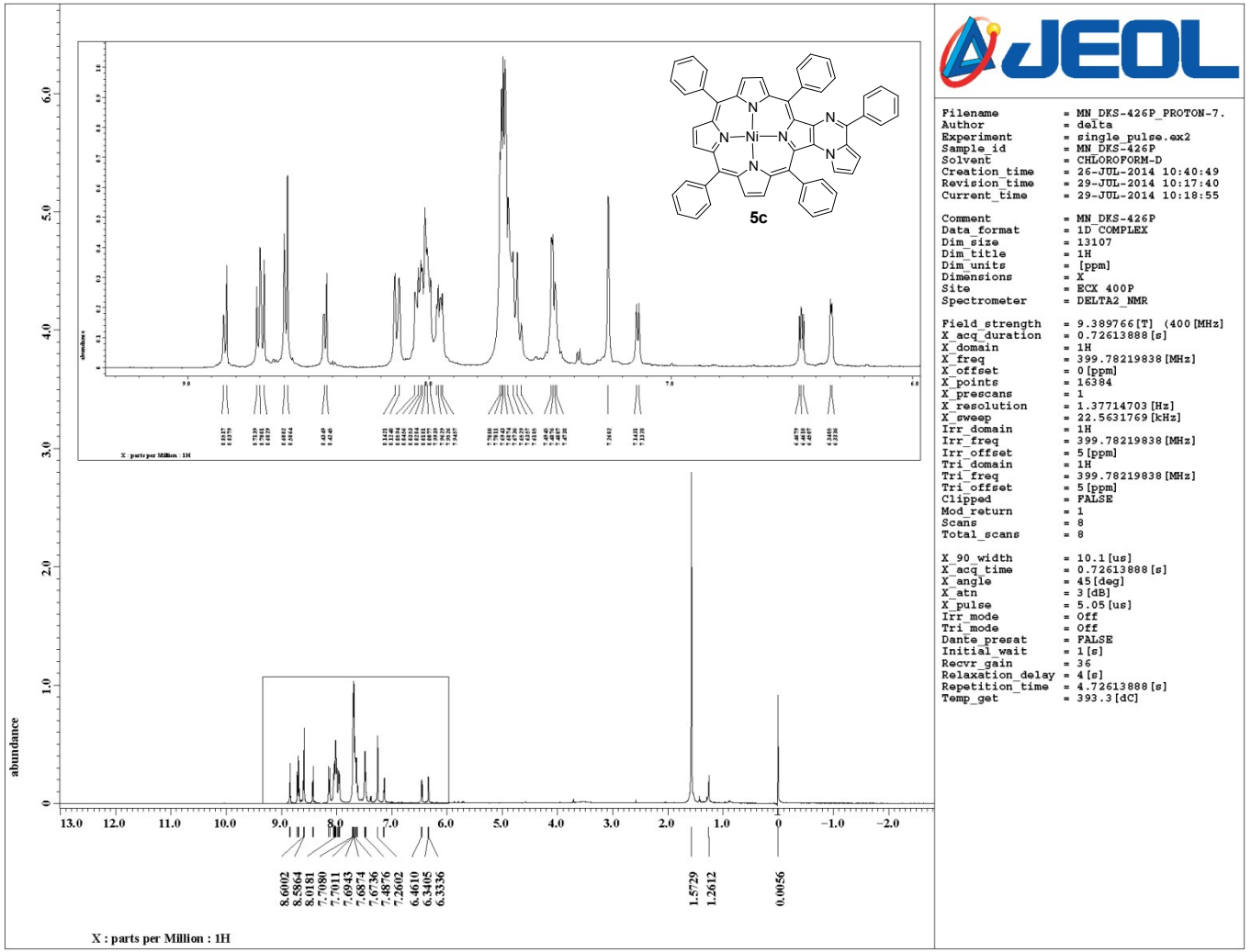

Fig.11. ^{1}H NMR spectrum of compound **5c** in $CDCl_3$.

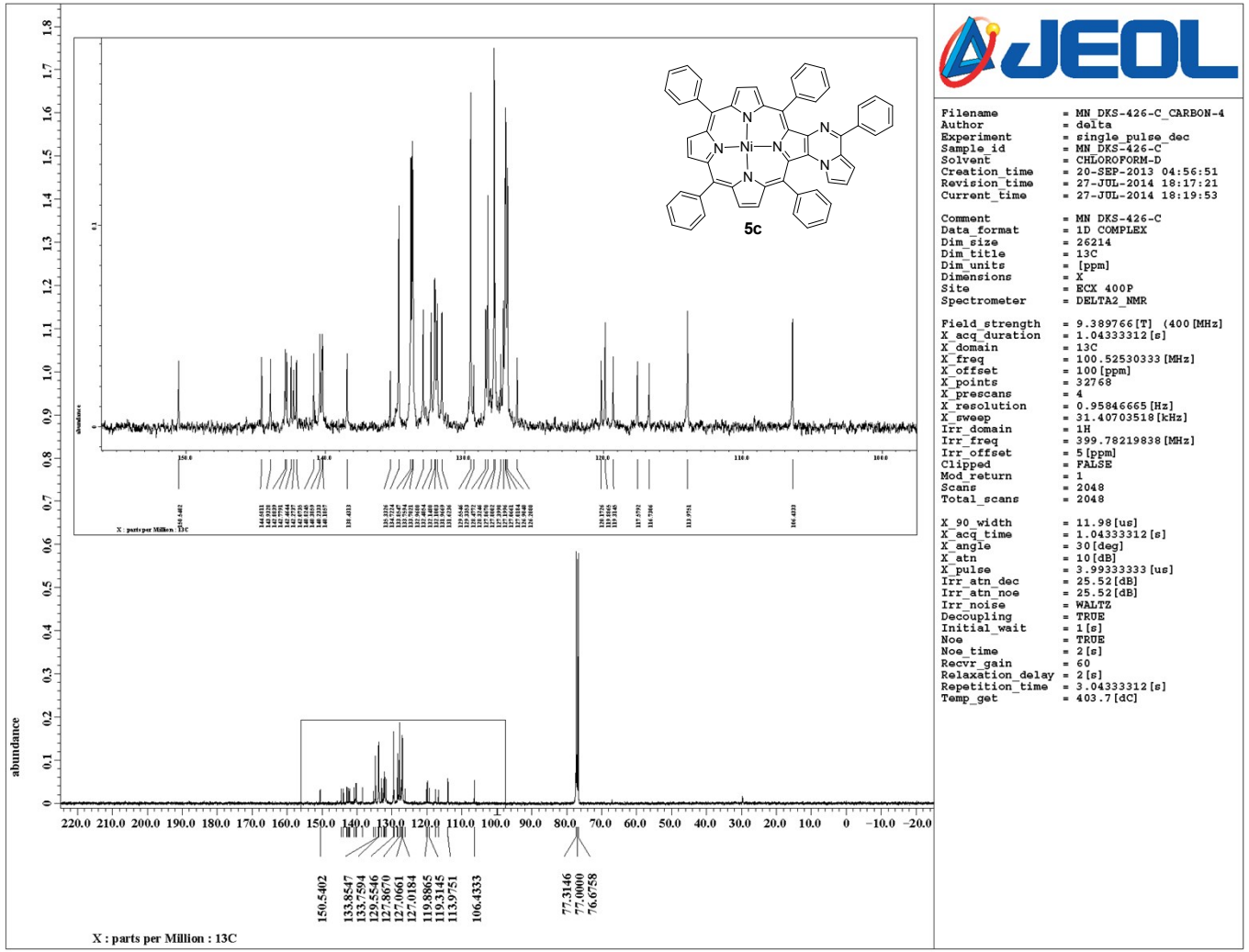

Fig. 12. ^{13}C NMR spectrum of compound **5c** in $CDCl_3$.

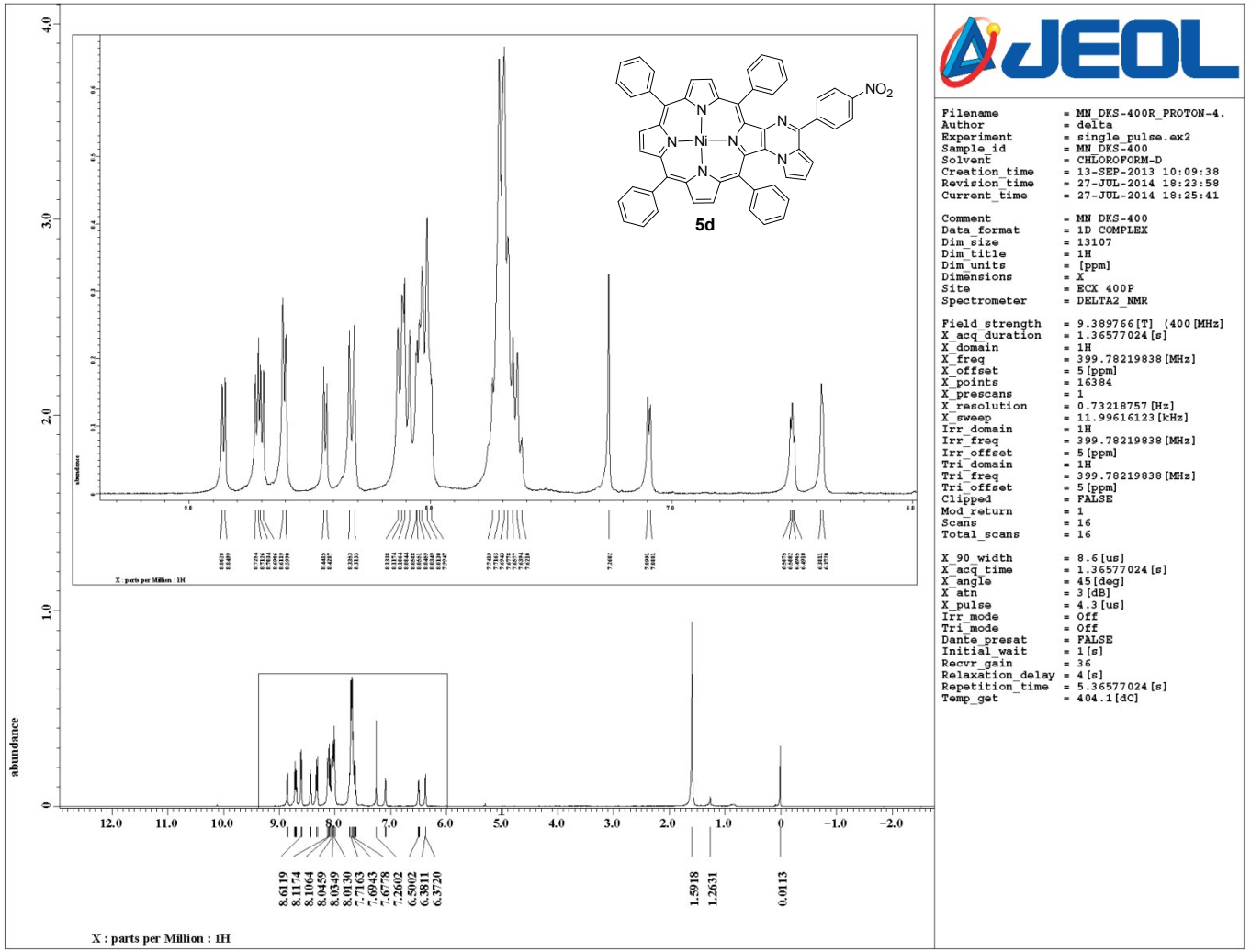

Fig. 13. ^{1}H NMR spectrum of compound **5d** in $CDCl_3$.

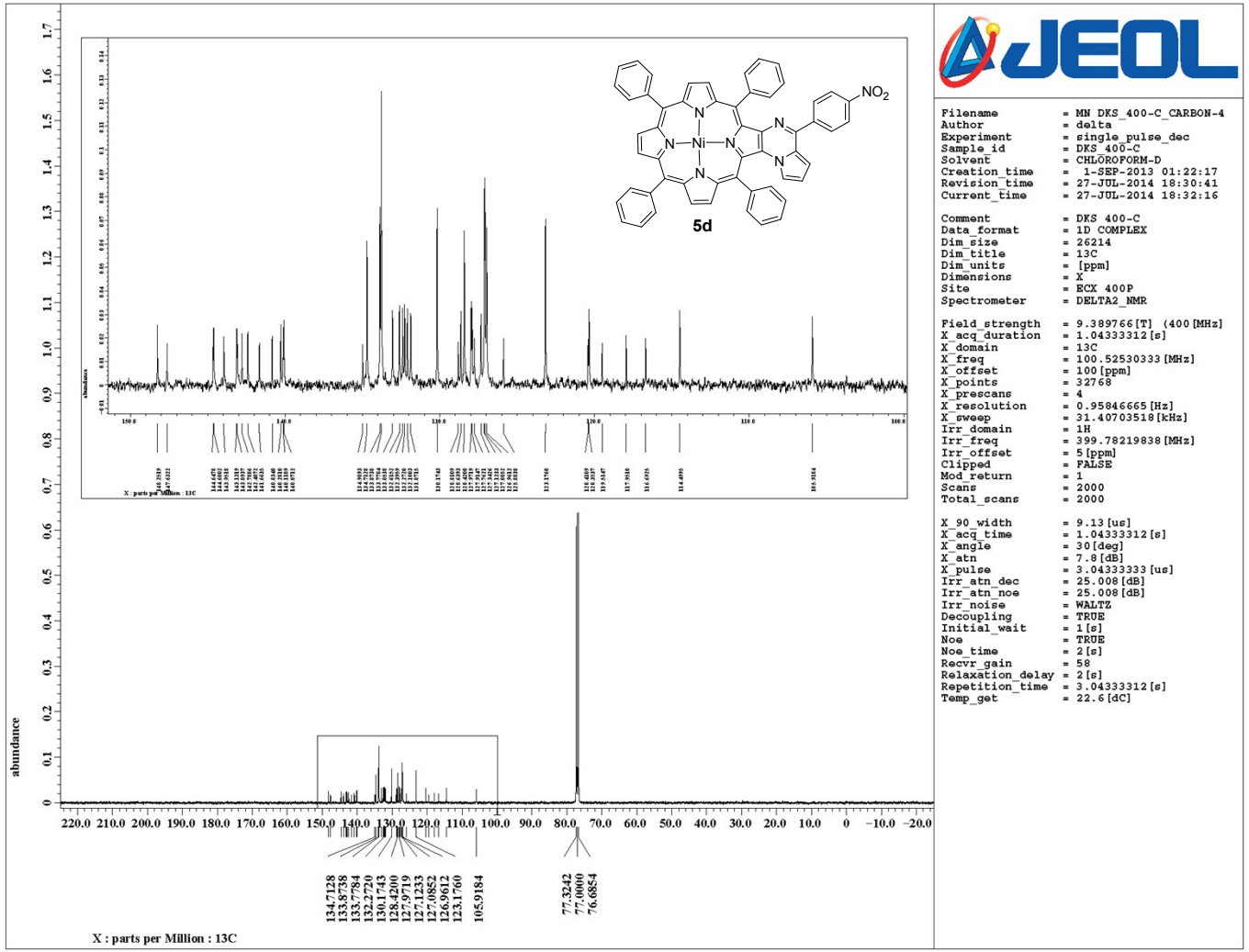

Fig. 14. ^{13}C NMR spectrum of compound **5d** in $CDCl_3$.

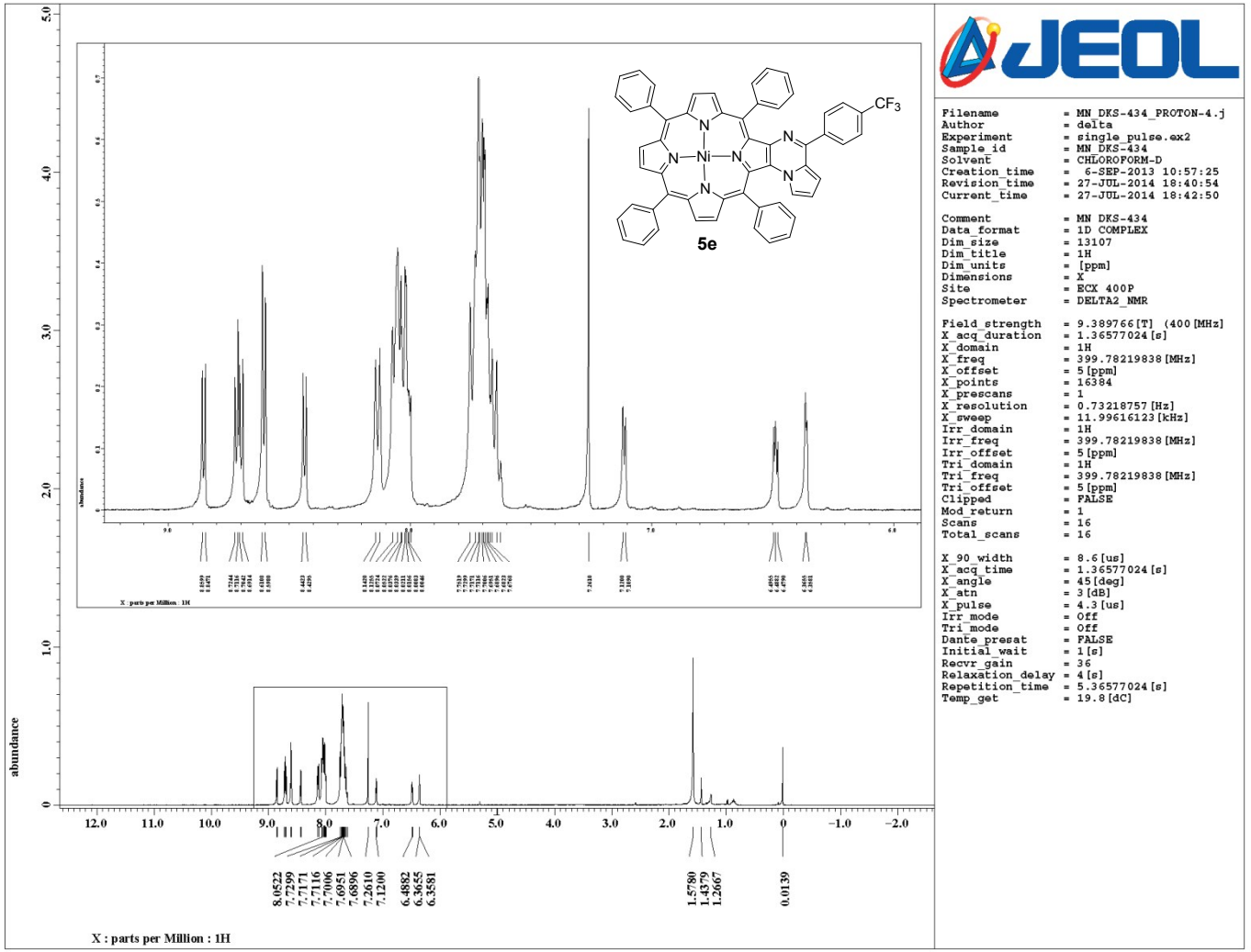

Fig. 15. ^{1}H NMR spectrum of compound **5e** in $CDCl_3$.

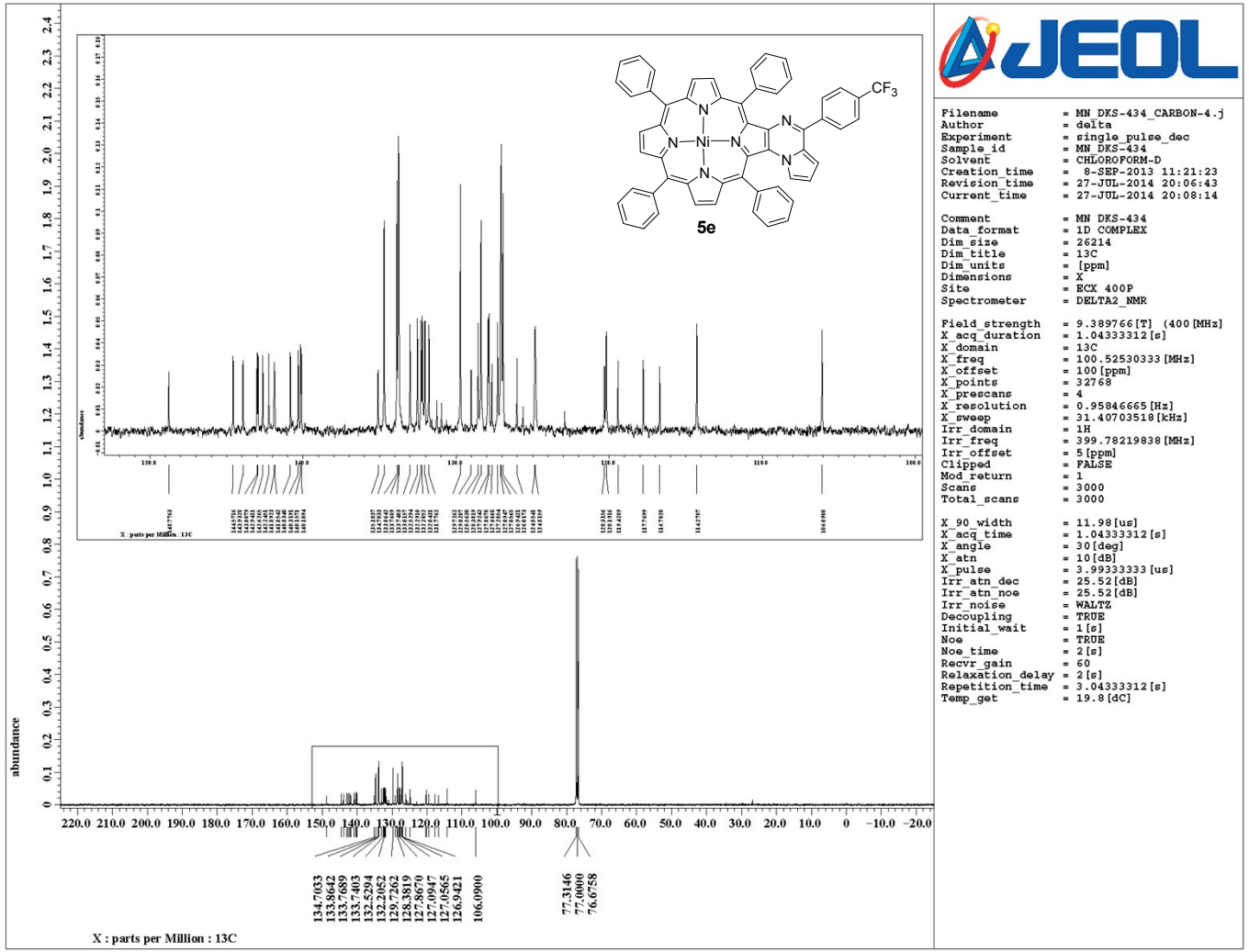

Fig. 16. ^{13}C NMR spectrum of compound **5e** in $CDCl_3$.

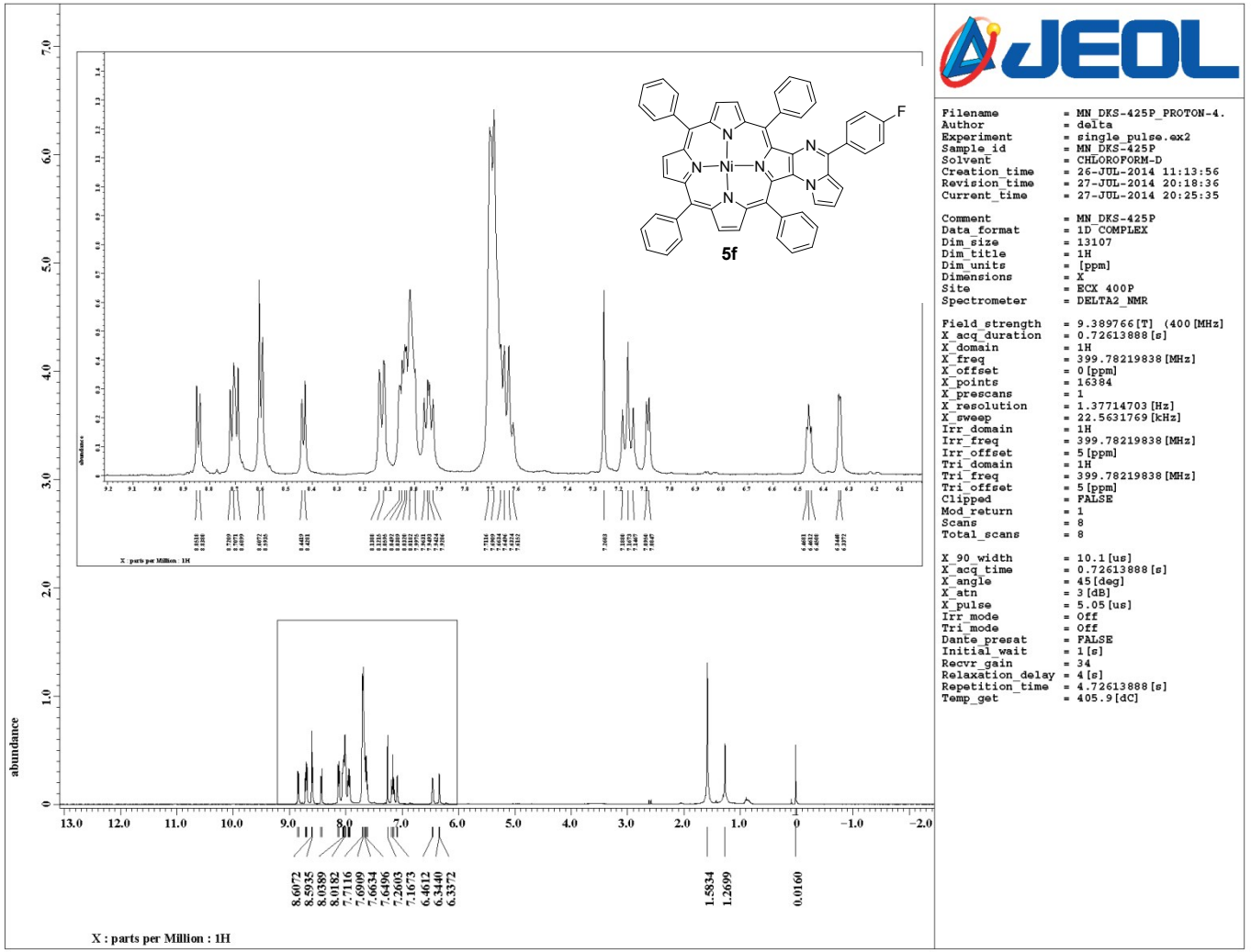

Fig. 17. ^{1}H NMR spectrum of compound **5f** in $CDCl_3$.

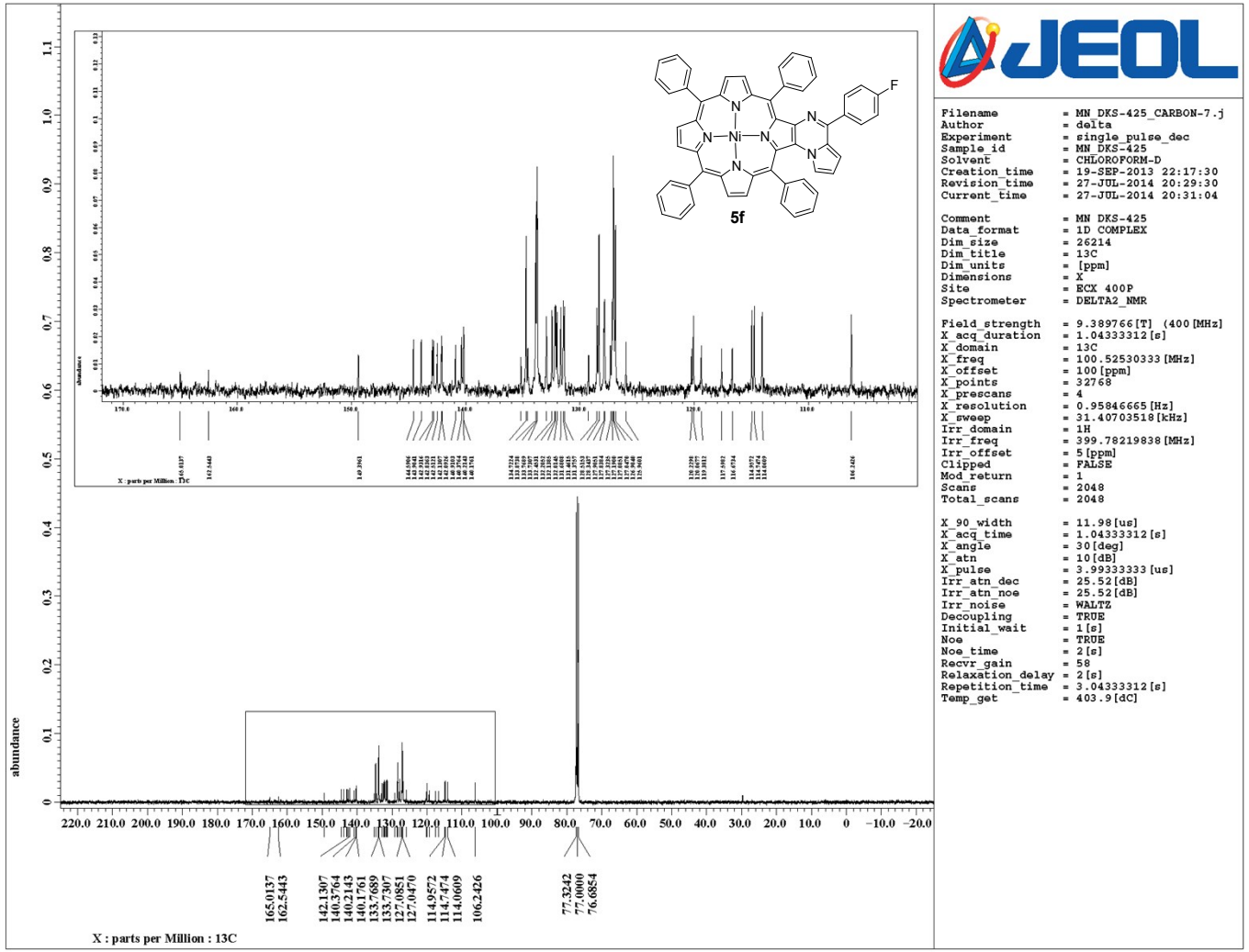

Fig. 18. ^{13}C NMR spectrum of compound **5f** in $CDCl_3$.

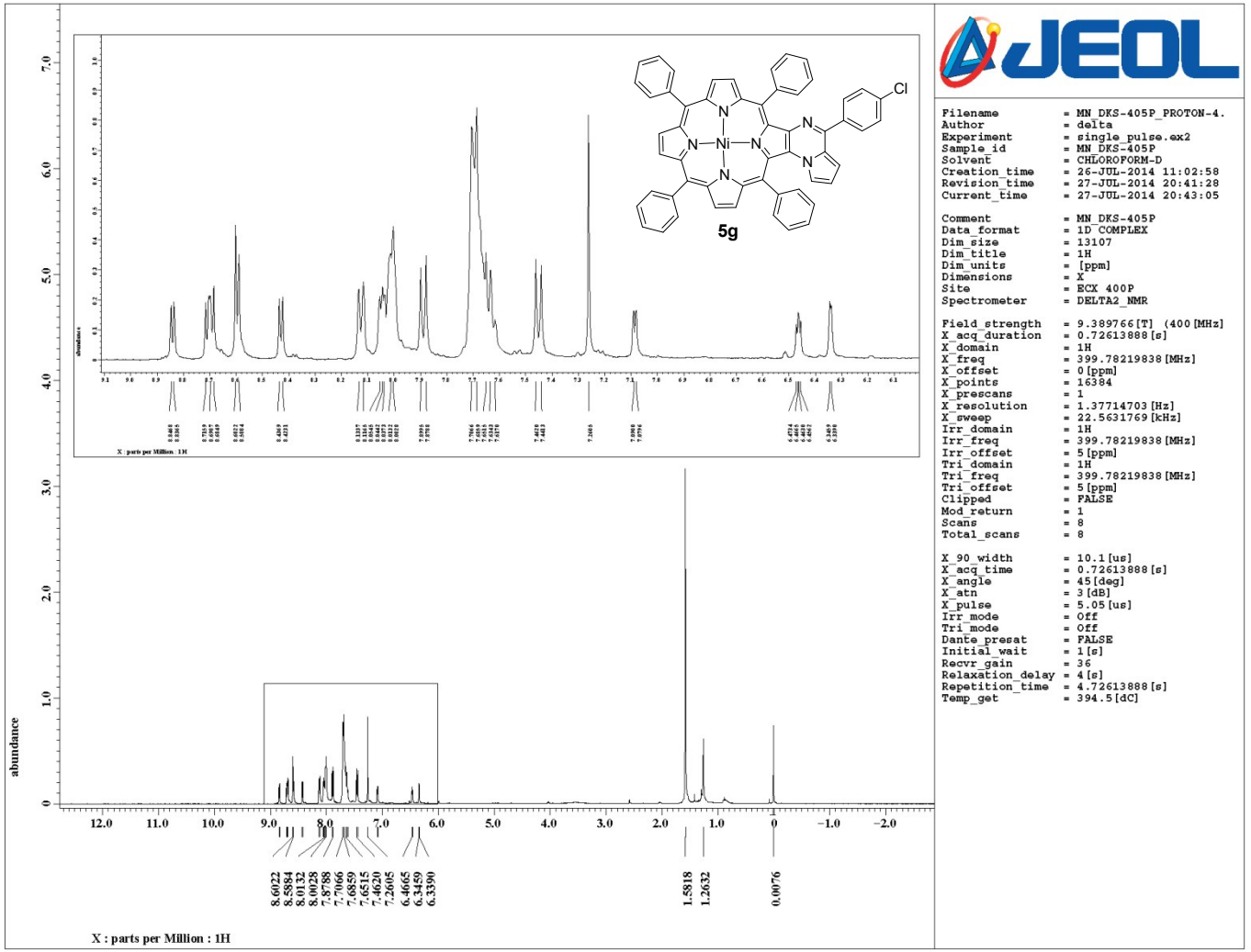

Fig. 19. ^{1}H NMR spectrum of compound **5g** in $CDCl_3$.

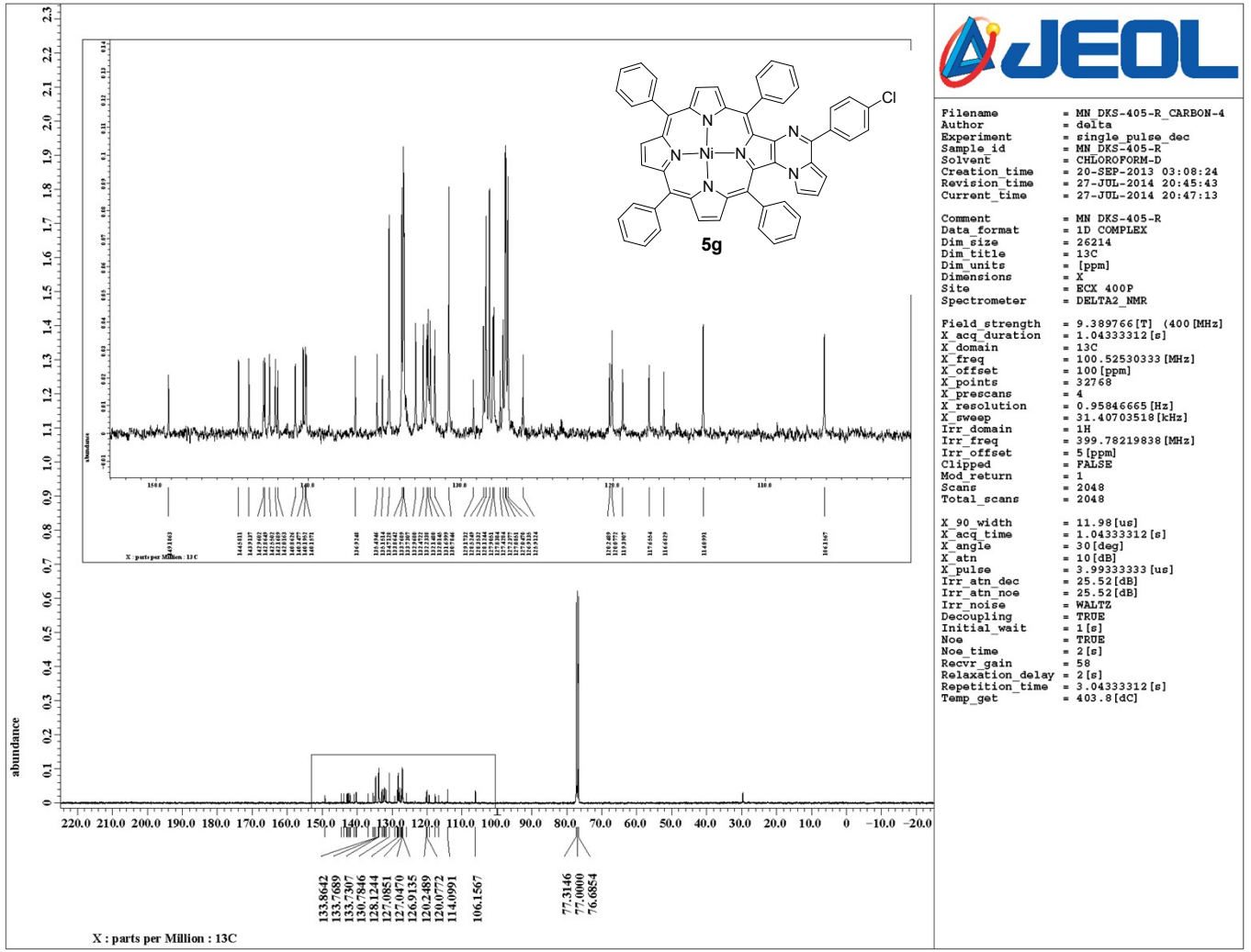

Fig. 20. ^{13}C NMR spectrum of compound **5g** in $CDCl_3$.

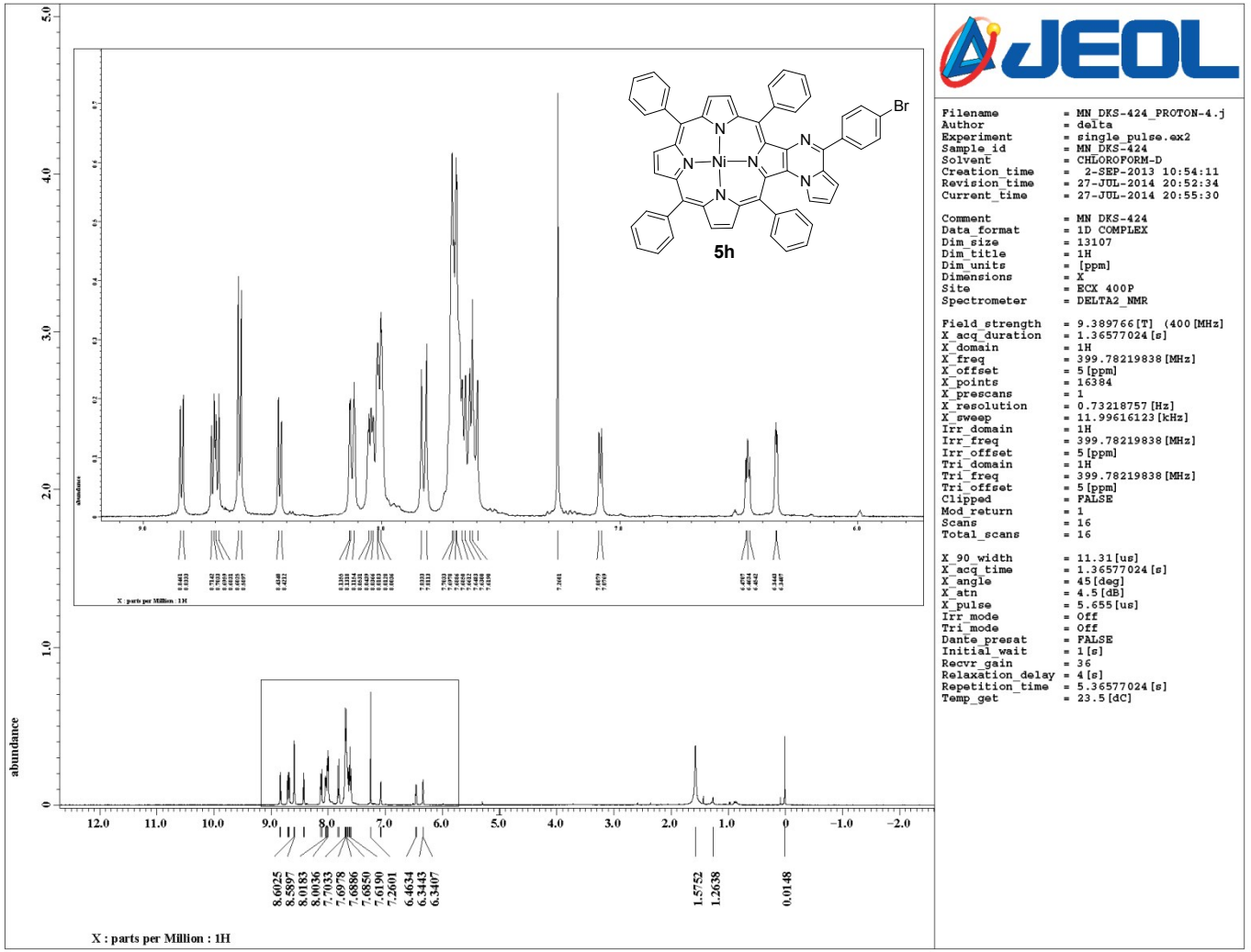

Fig. 21. ^{1}H NMR spectrum of compound **5h** in $CDCl_3$.

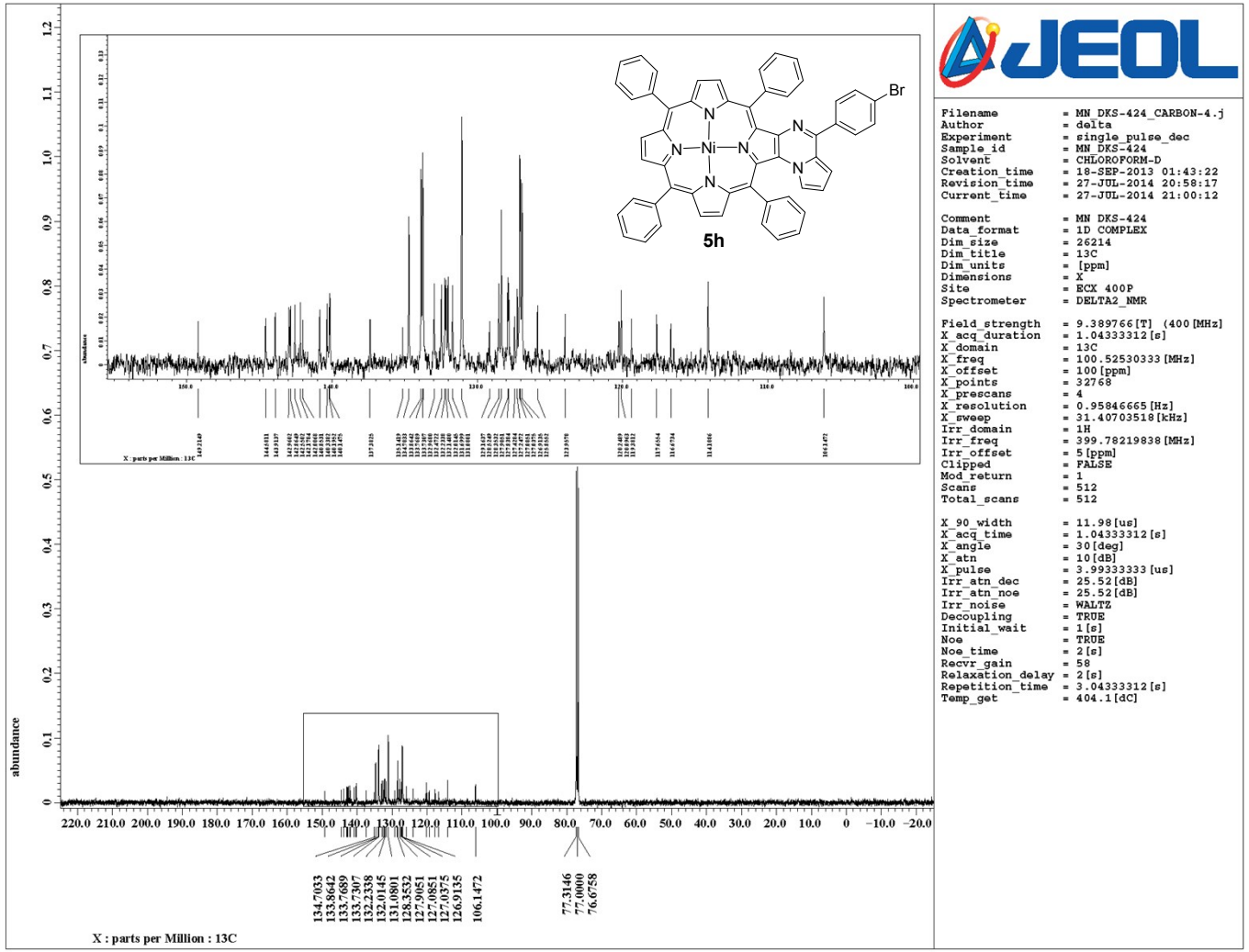

Fig. 22. ^{13}C NMR spectrum of compound **5h** in $CDCl_3$.

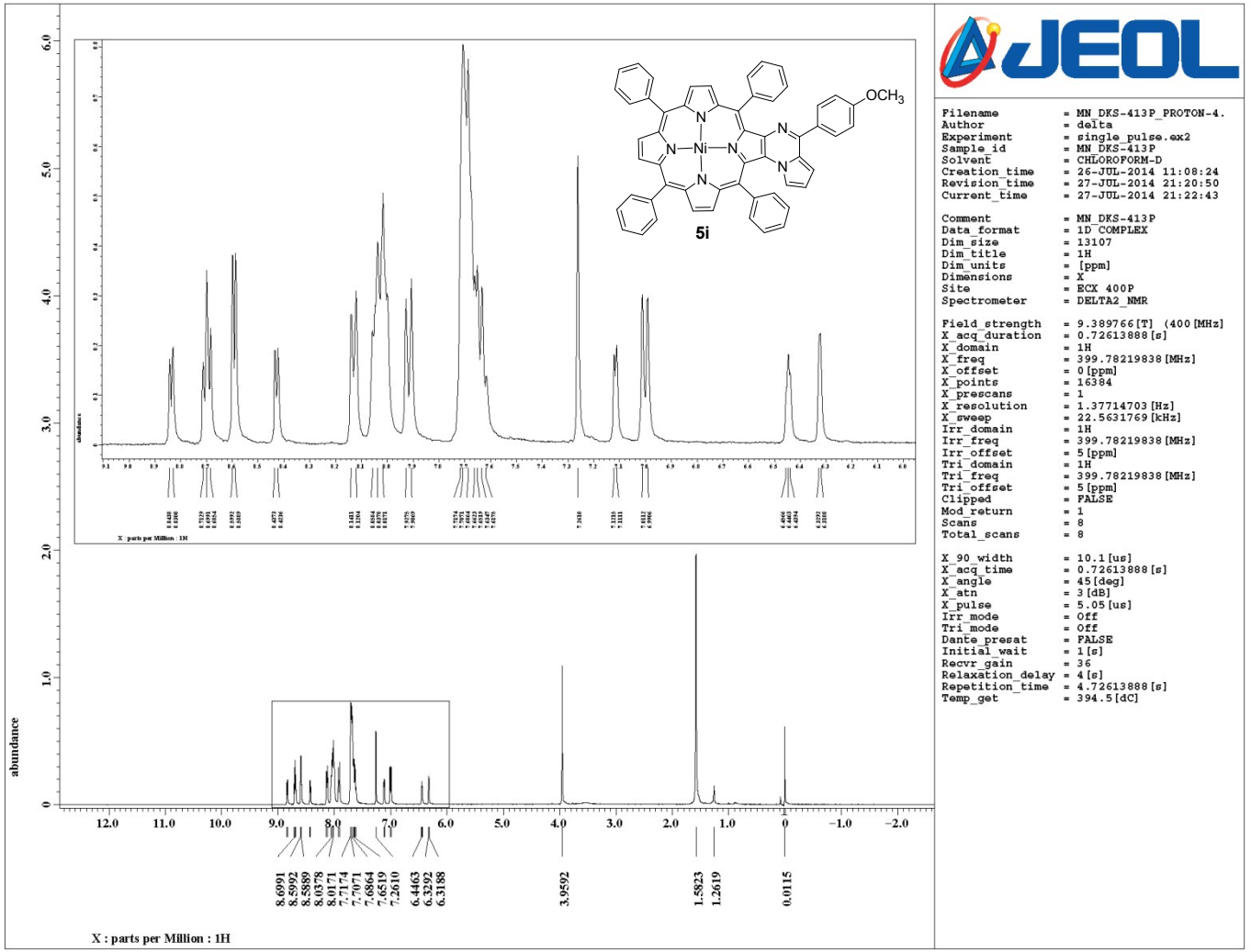

Fig. 23. ^{1}H NMR spectrum of compound **5i** in $CDCl_3$.

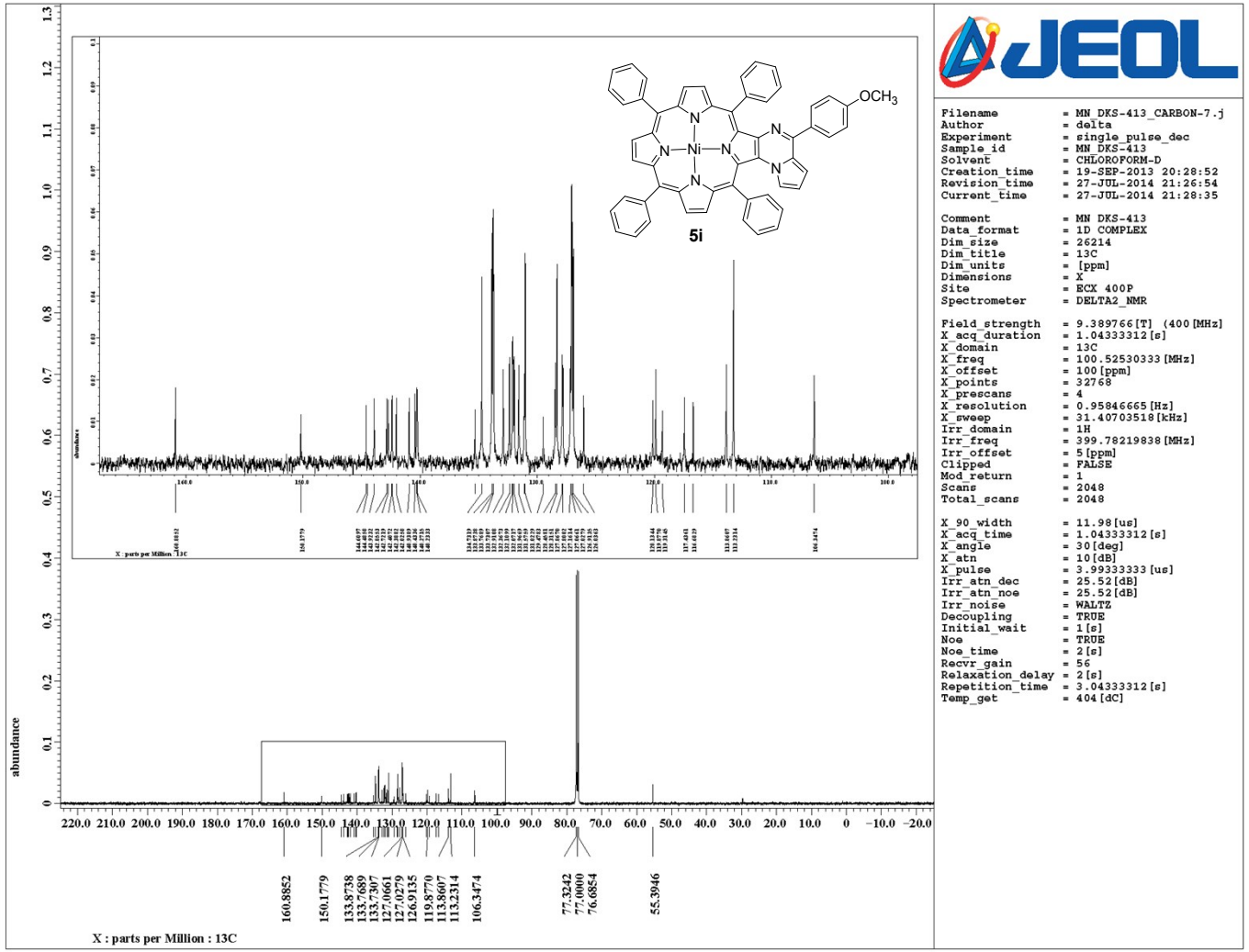

Fig. 24. ^{13}C NMR spectrum of compound **5i** in $CDCl_3$.

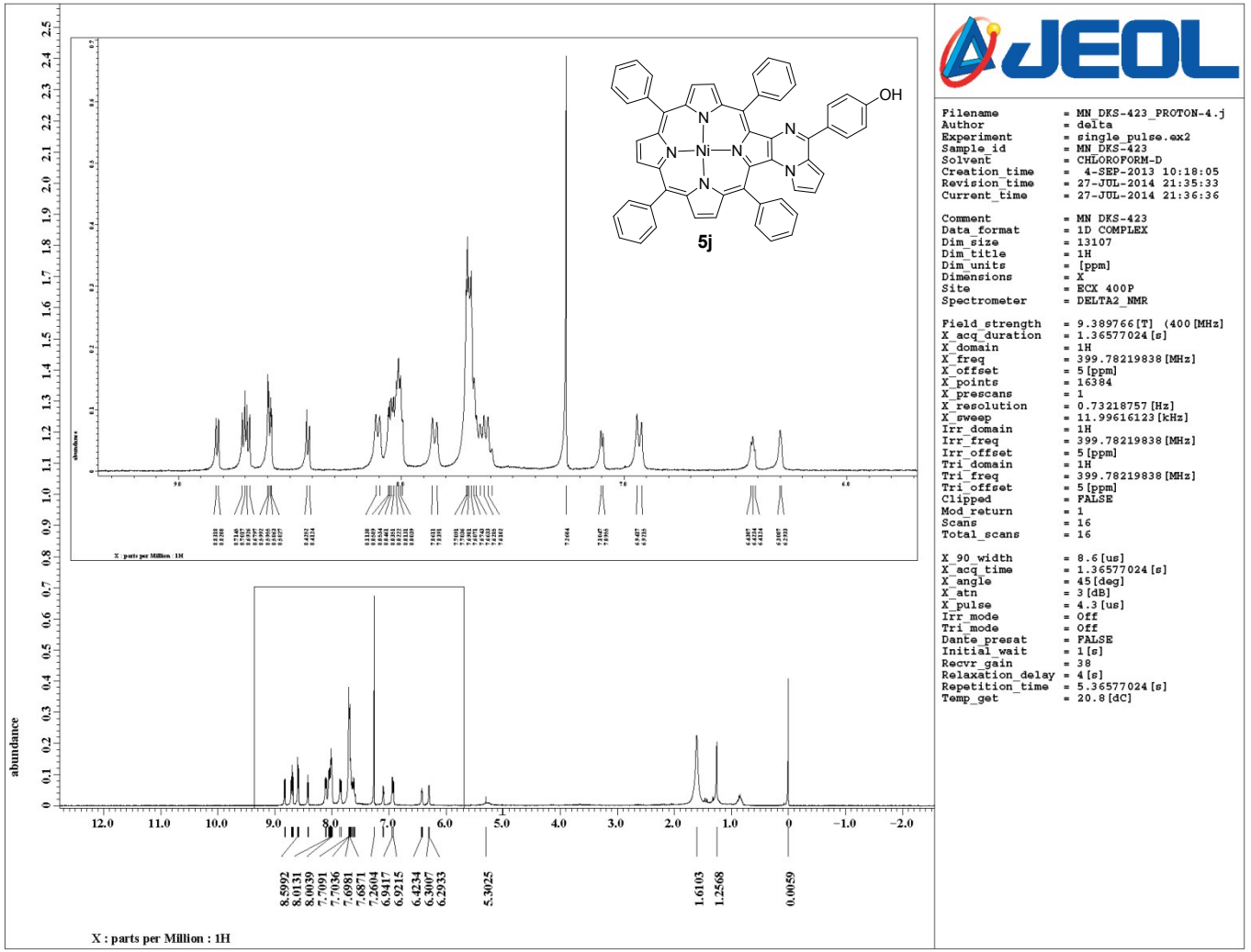

Fig. 25. ^{1}H NMR spectrum of compound **5j** in $CDCl_3$.

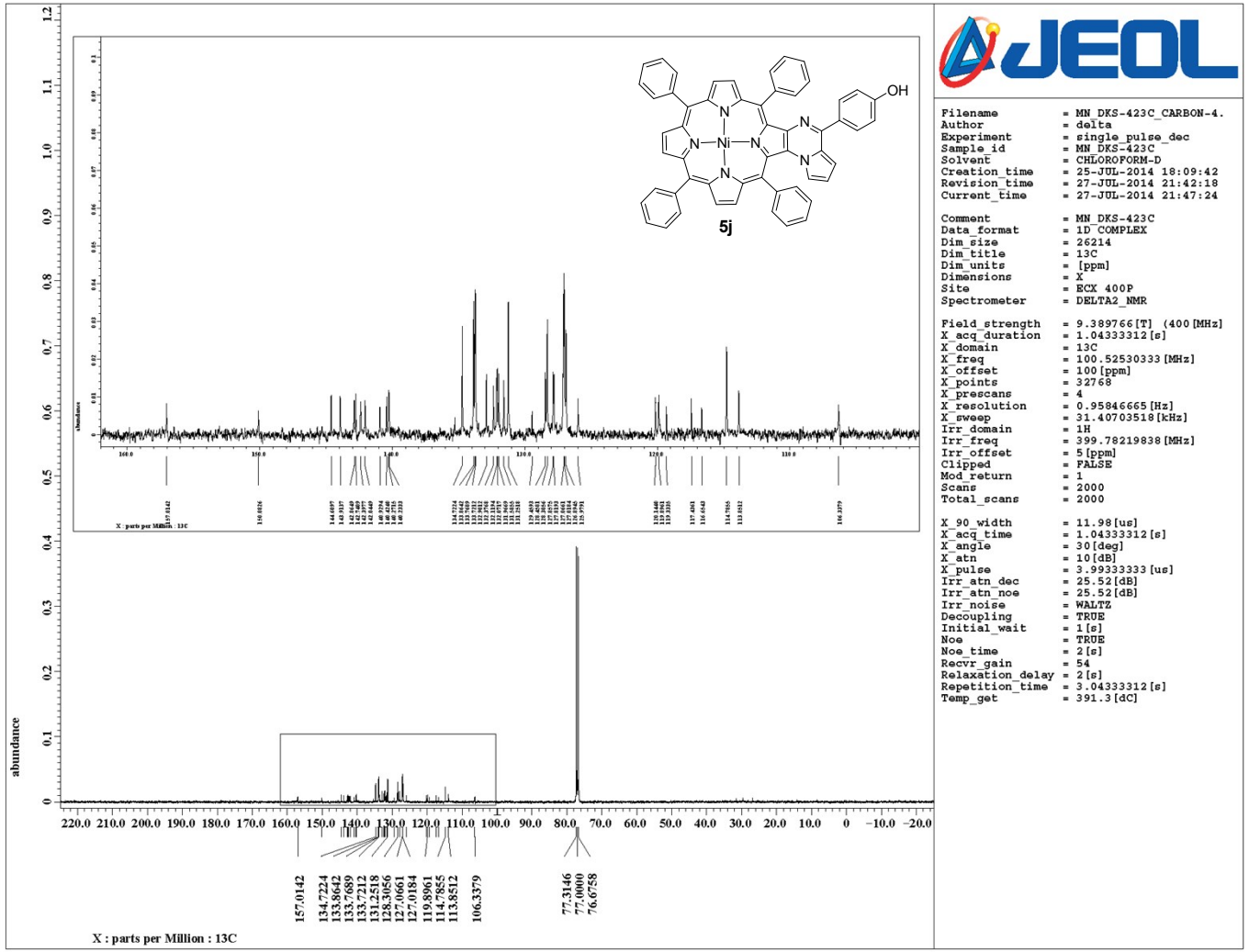

Fig. 26. ^{13}C NMR spectrum of compound **5j** in $CDCl_3$.

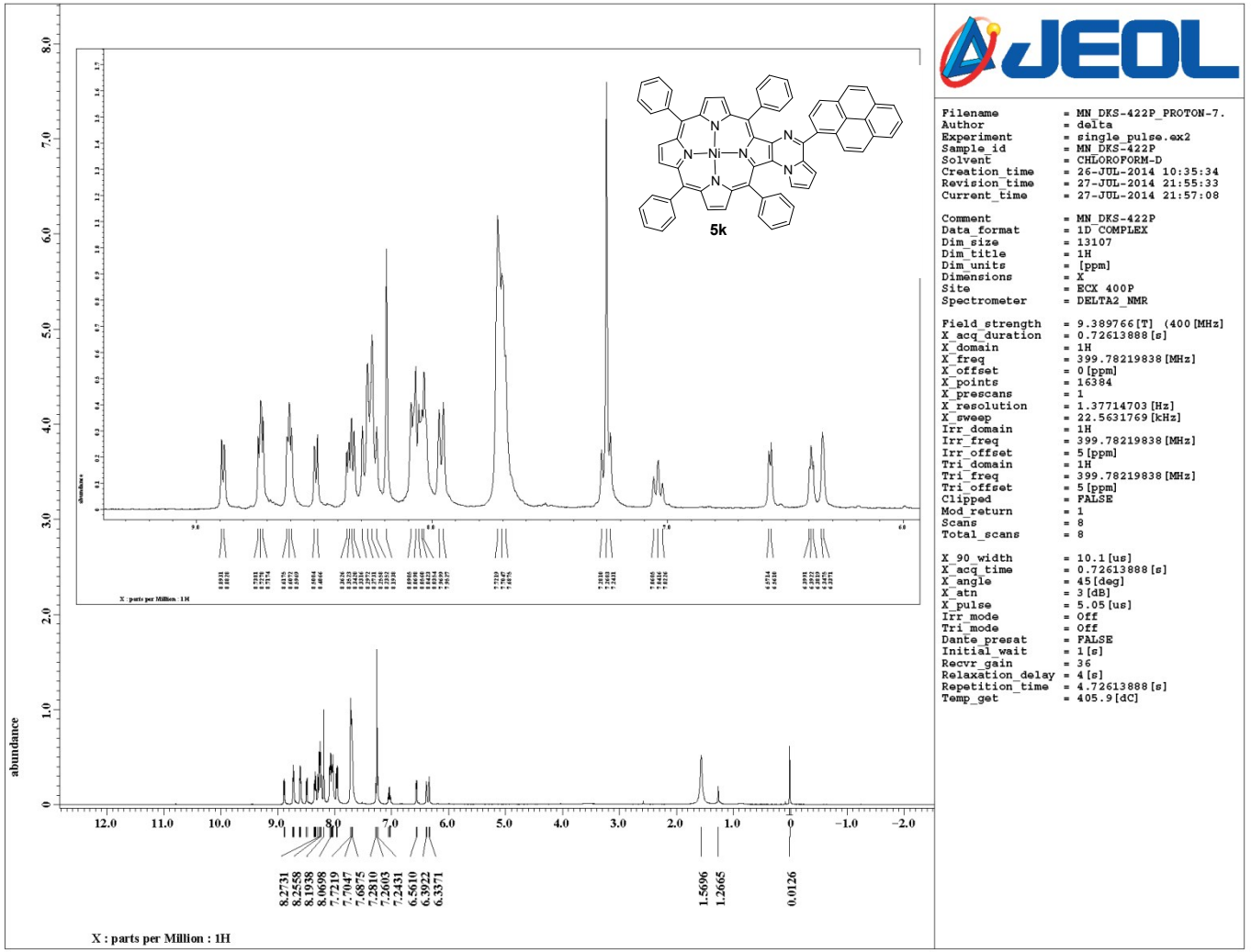

Fig.27. ^{1}H NMR spectrum of compound **5k** in $CDCl_3$.

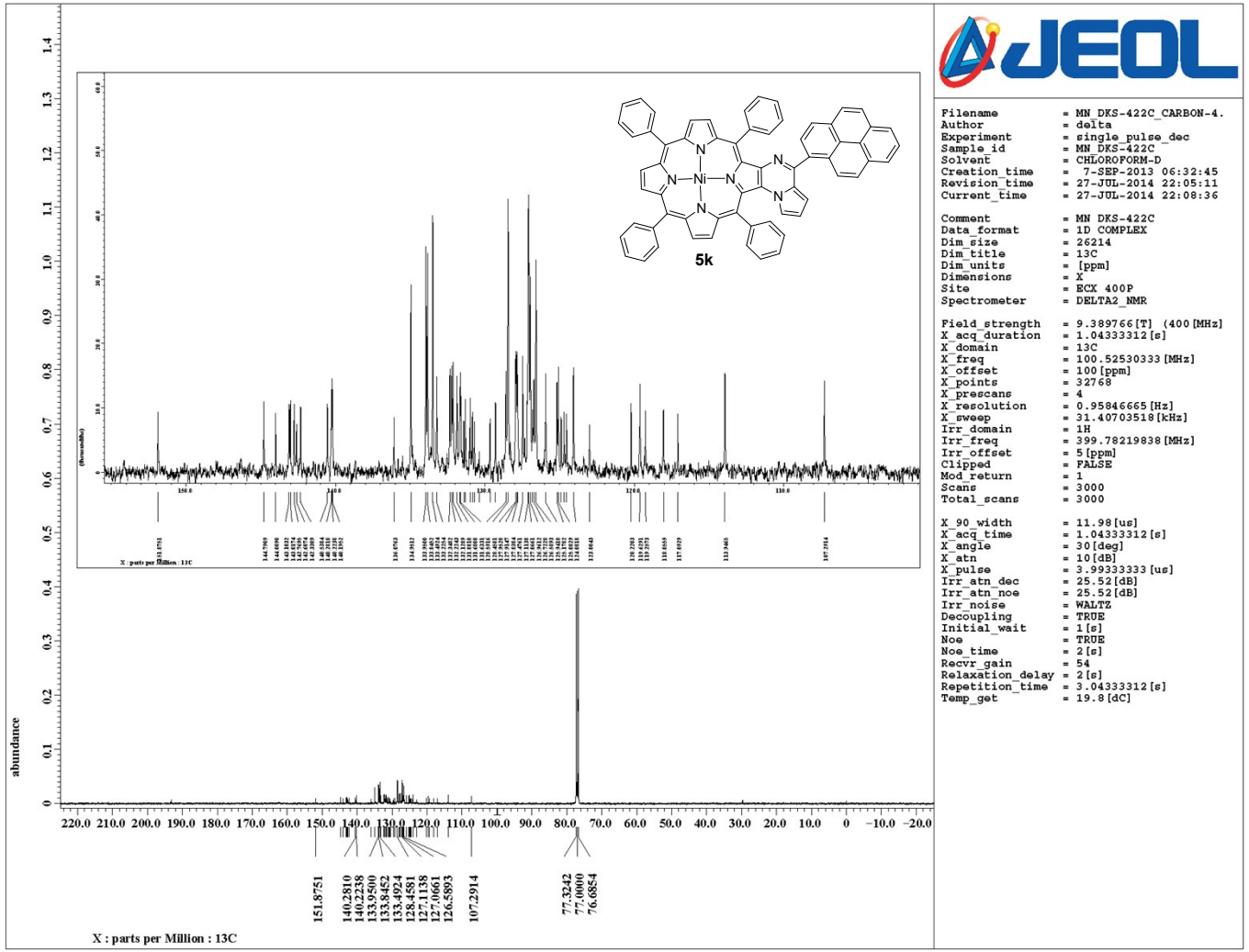

Fig. 28. ^{13}C NMR spectrum of compound **5k** in $CDCl_3$.

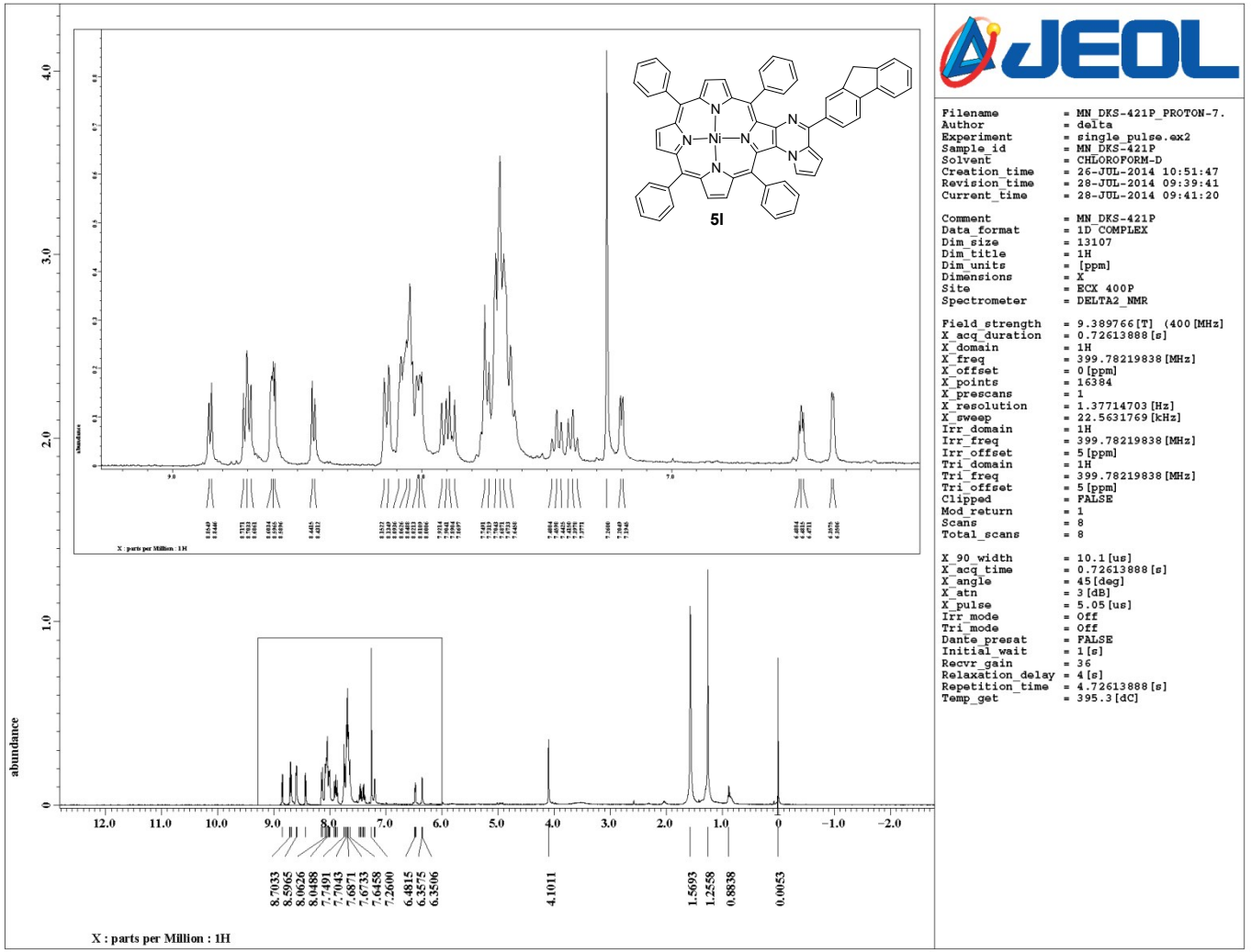

Fig. 29. ^{1}H NMR spectrum of compound **5l** in $CDCl_3$.

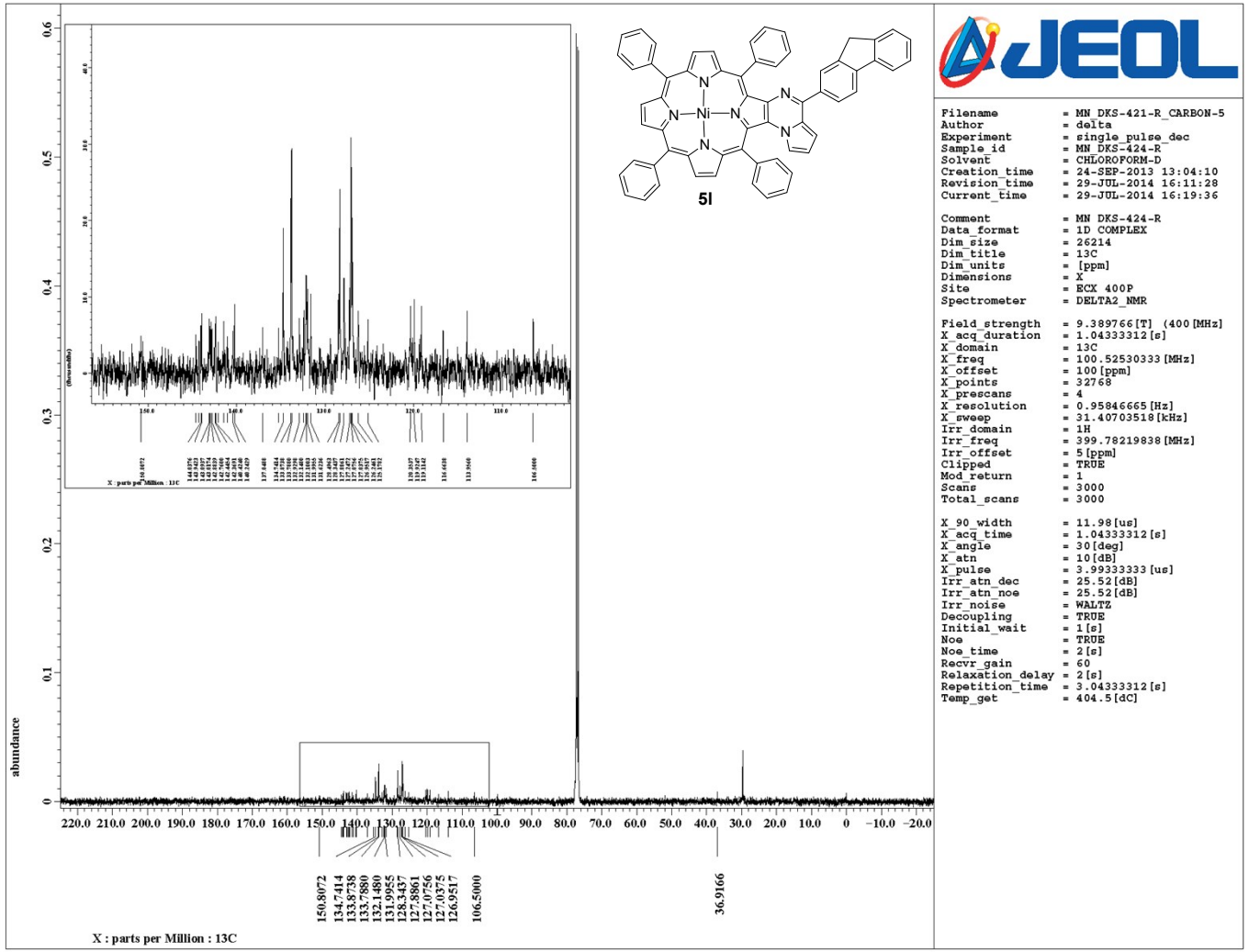

Fig. 30. ^{13}C NMR spectrum of compound **5l** in $CDCl_3$.

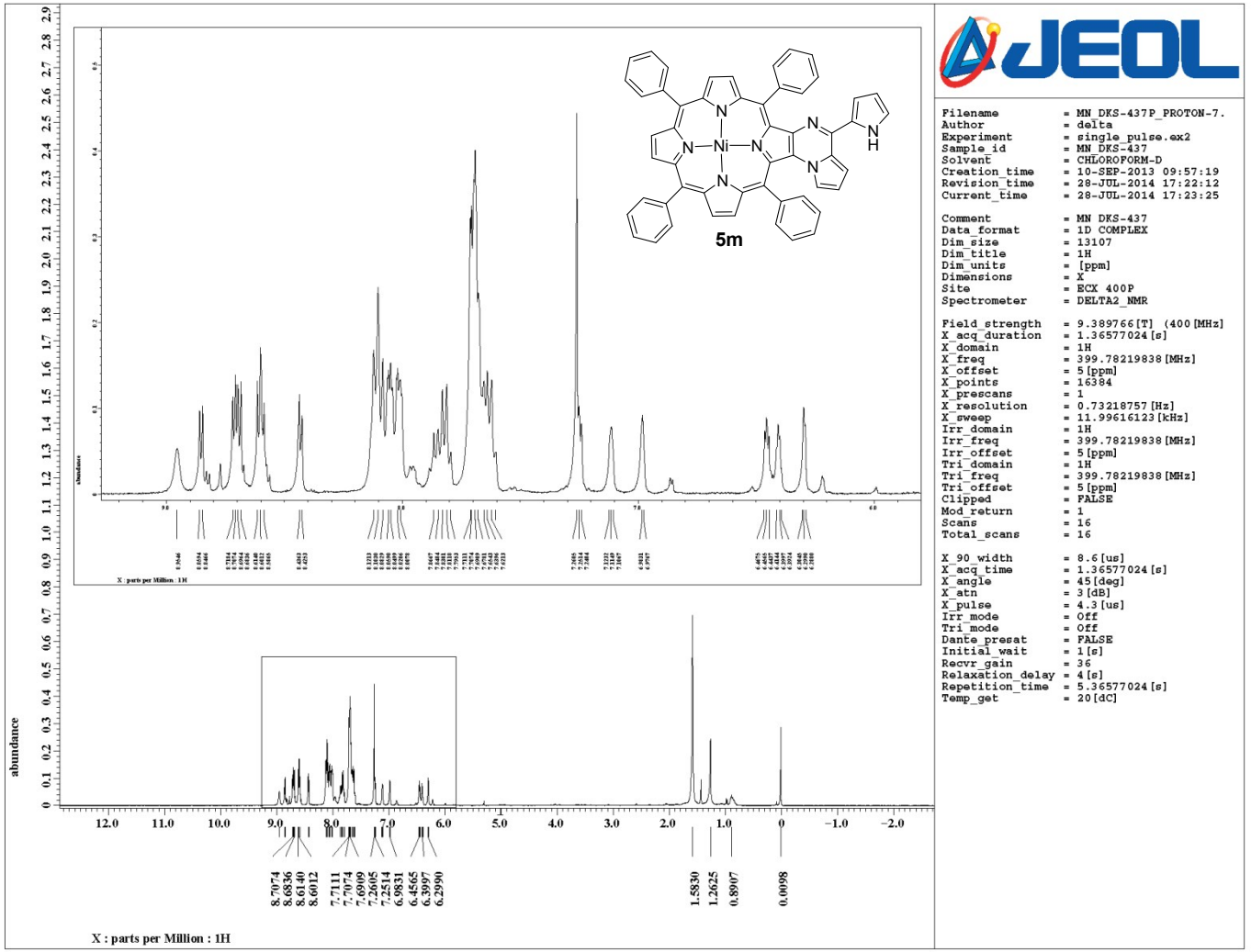

Fig. 31. ^{1}H NMR spectrum of compound **5m** in $CDCl_3$.

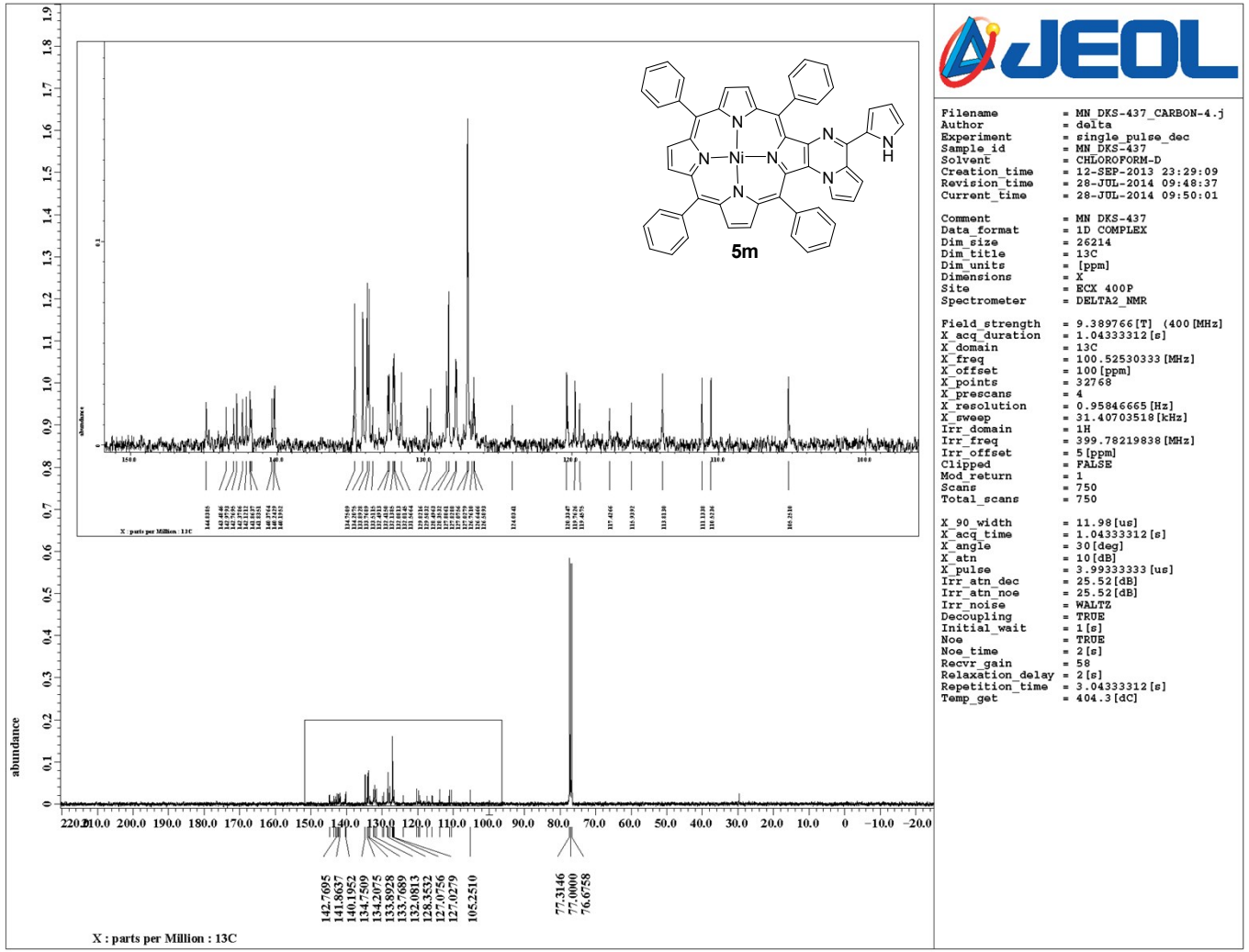

Fig. 32. ^{13}C NMR spectrum of compound **5m** in $CDCl_3$.

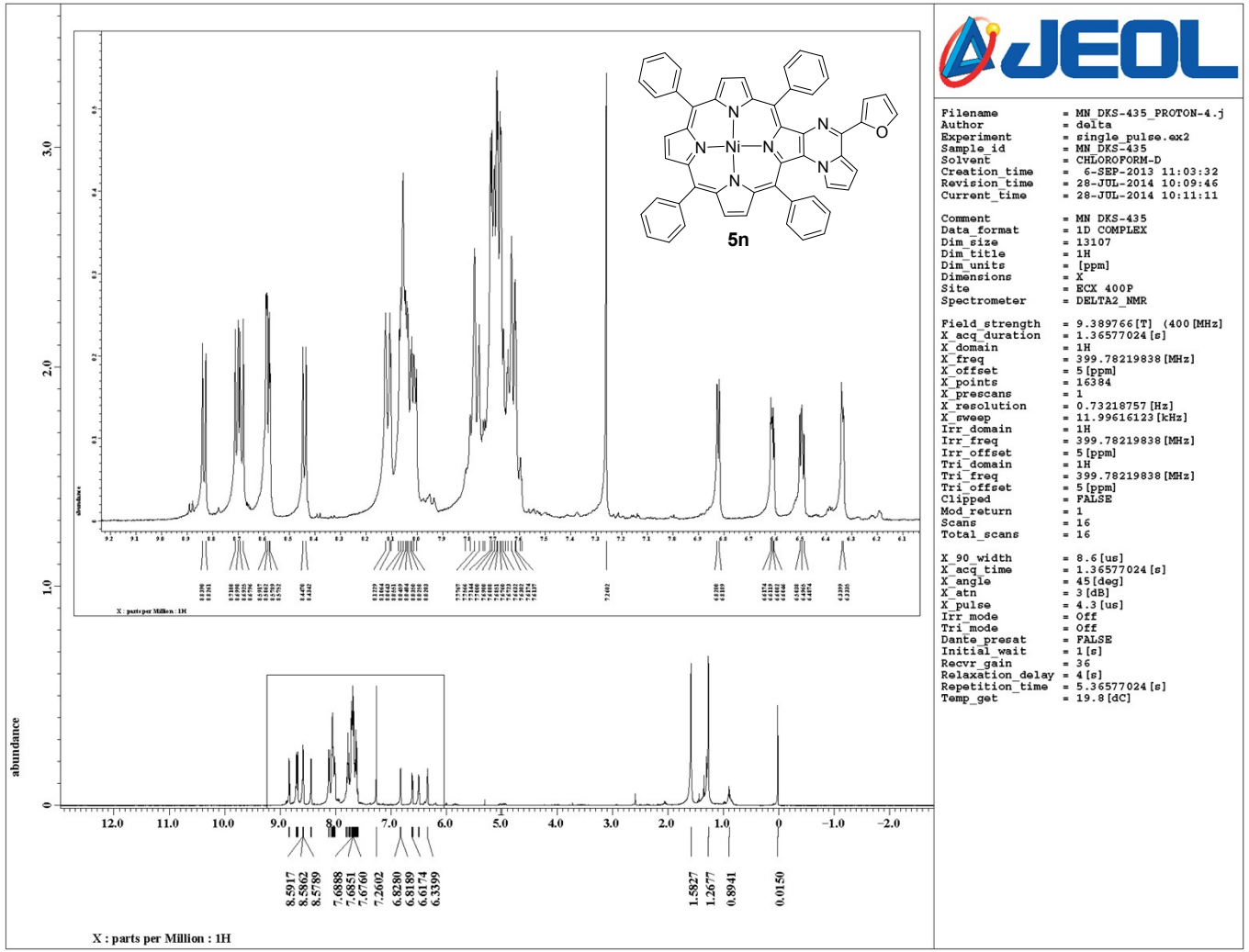

Fig. 33. ^{1}H NMR spectrum of compound **5n** in $CDCl_3$.

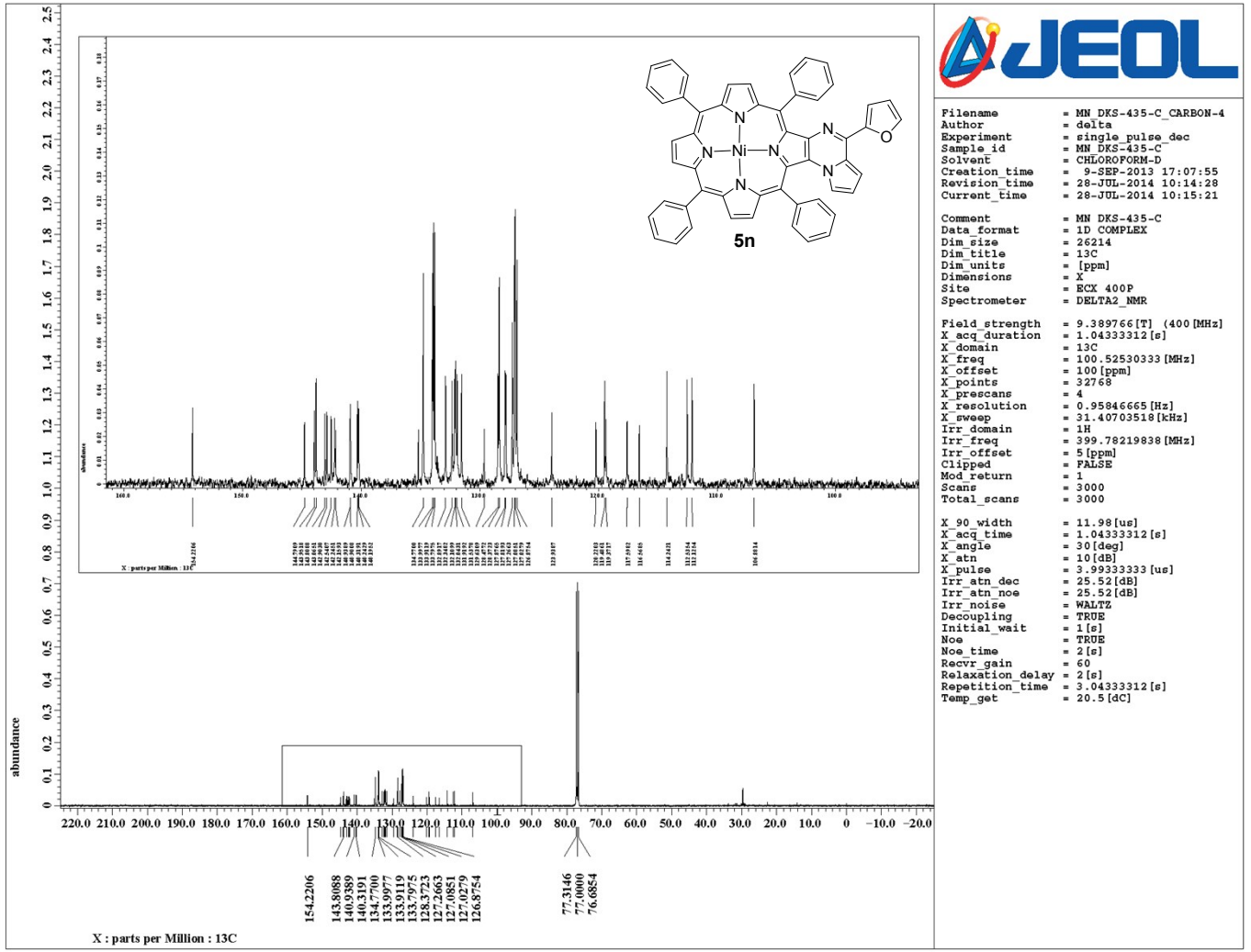

Fig. 34. ^{13}C NMR spectrum of compound **5n** in $CDCl_3$.

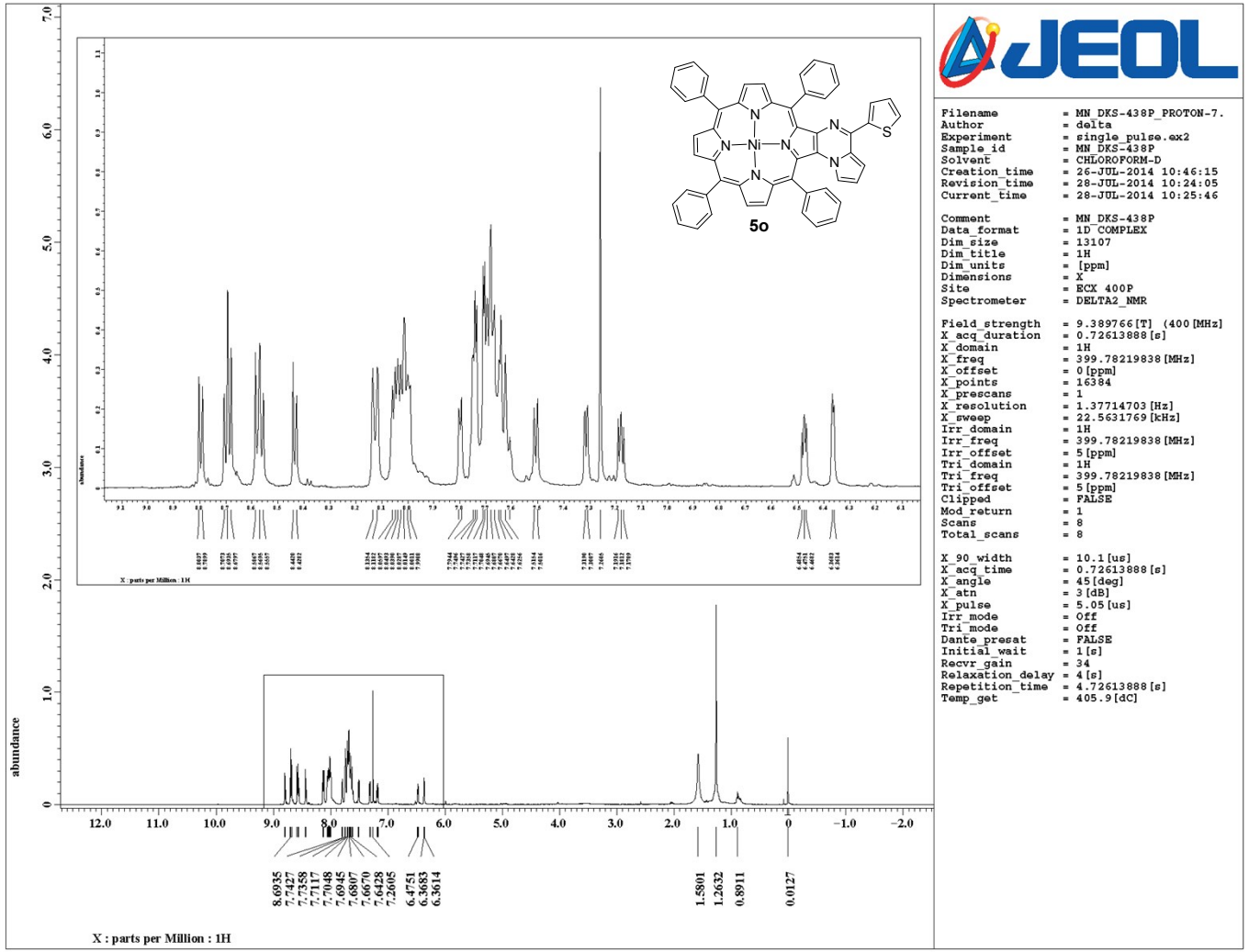

Fig. 35. ^{1}H NMR spectrum of compound **5o** in $CDCl_3$.

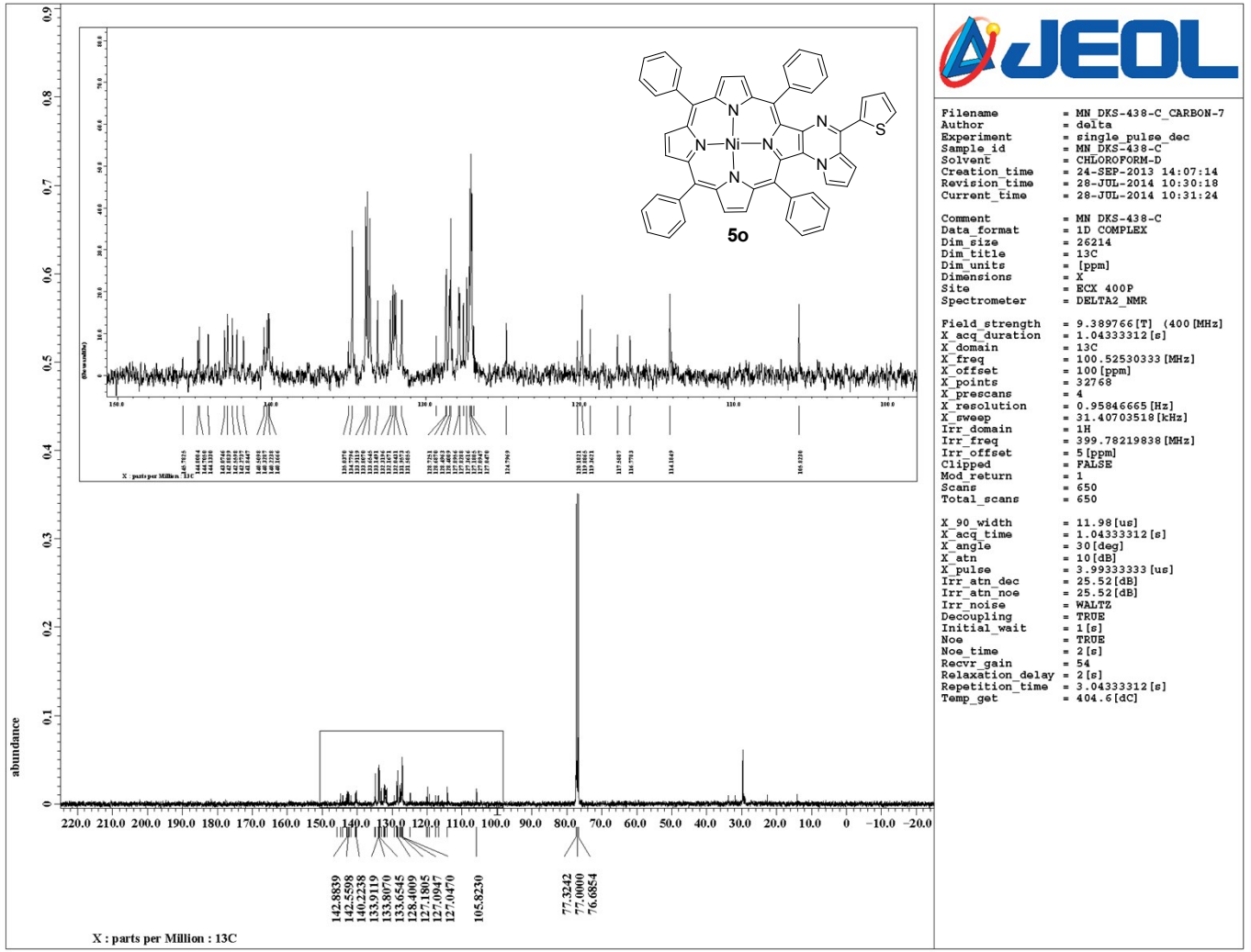

Fig. 36. ^{13}C NMR spectrum of compound **5o** in $CDCl_3$.

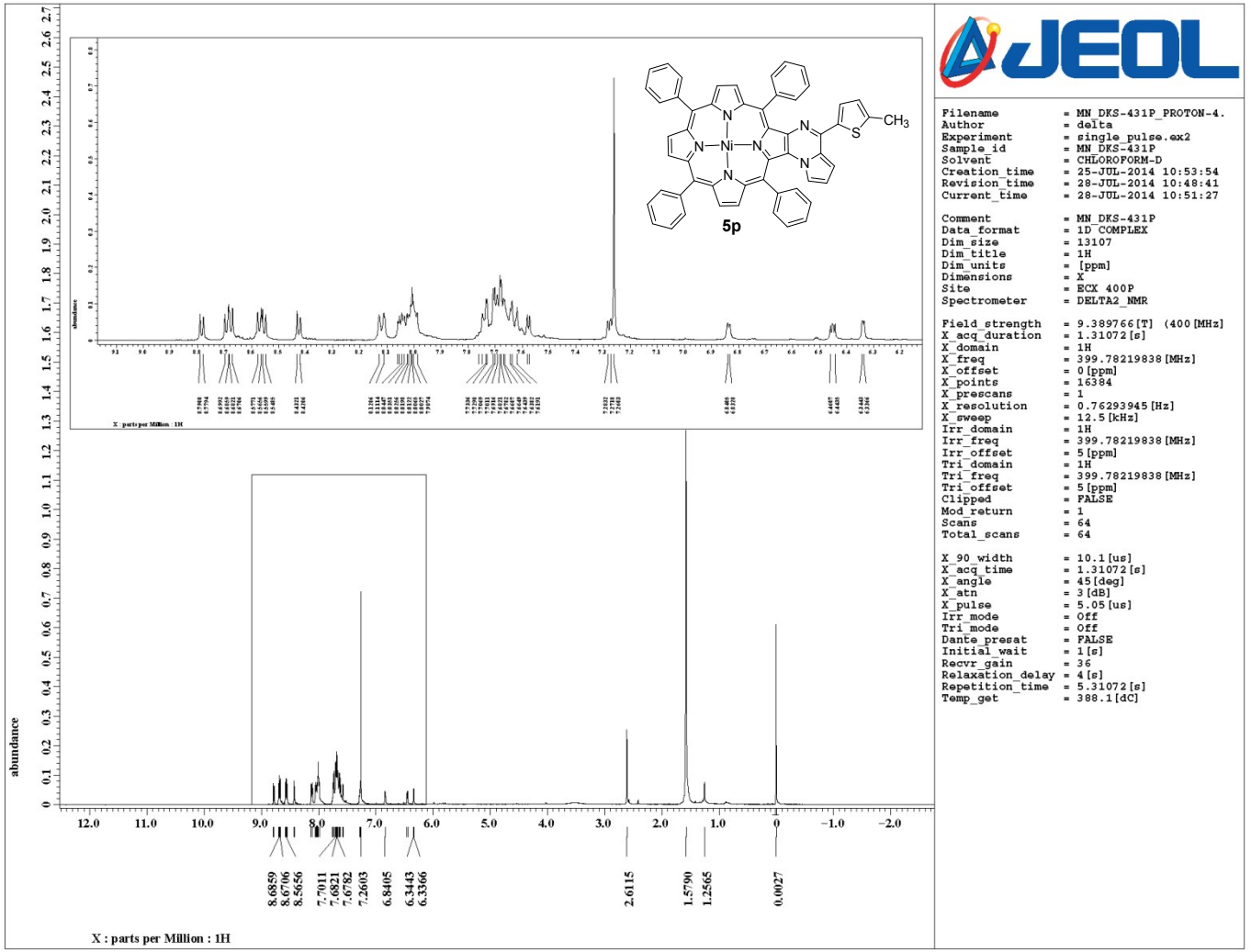

Fig. 37. ^{1}H NMR spectrum of compound **5p** in $CDCl_3$.

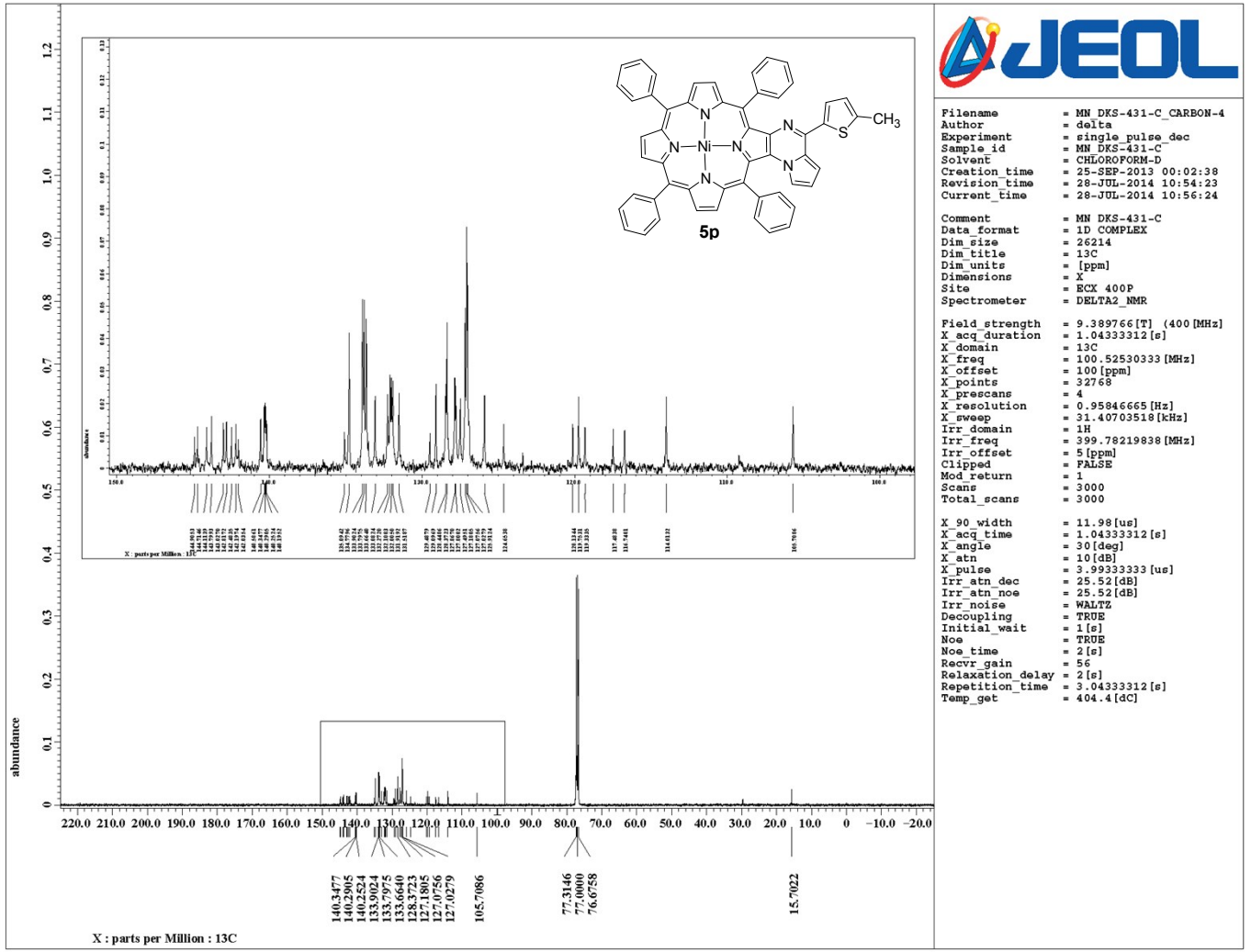

Fig. 38. ^{13}C NMR spectrum of compound **5p** in $CDCl_3$.

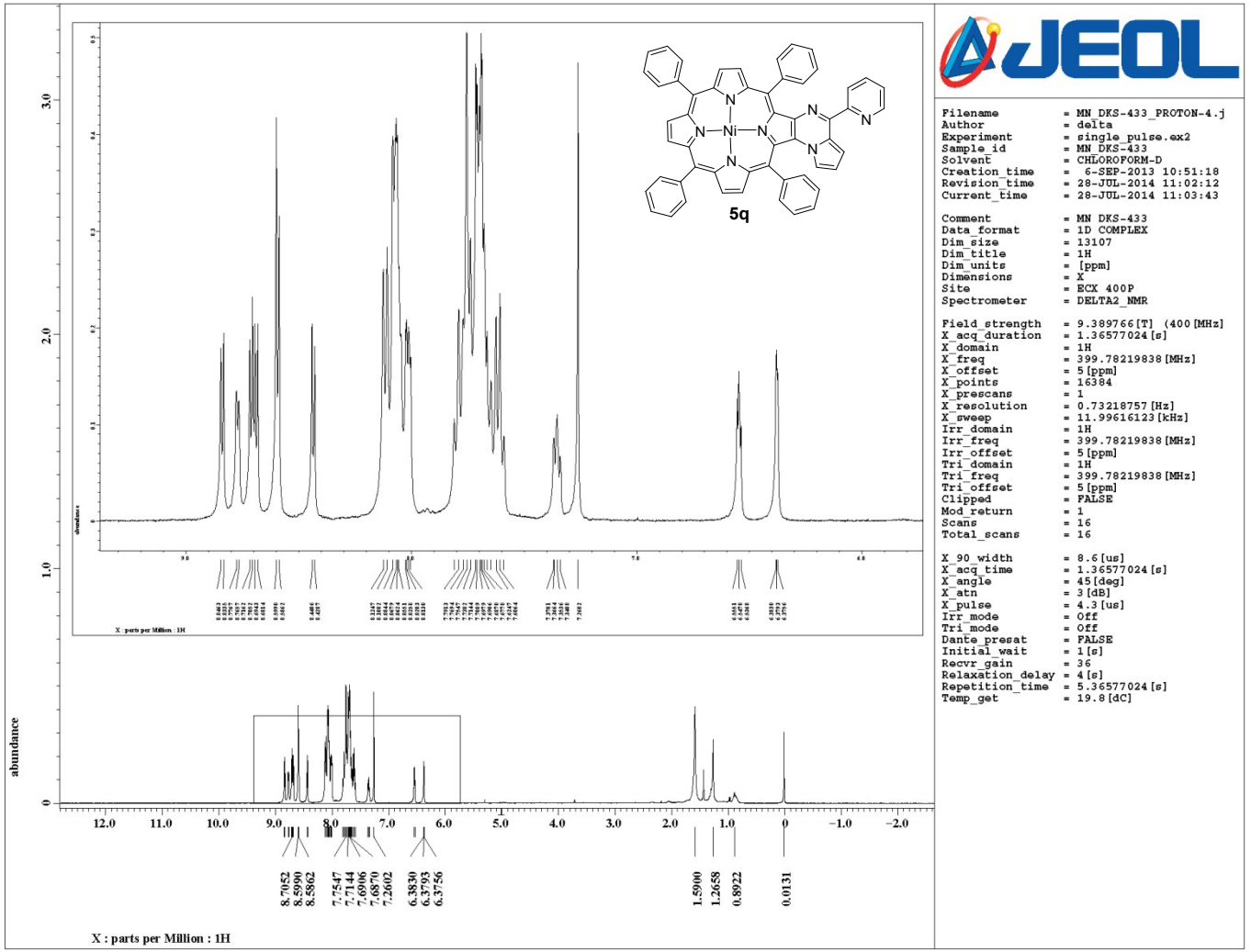

Fig. 39. ^{1}H NMR spectrum of compound **5q** in $CDCl_3$.

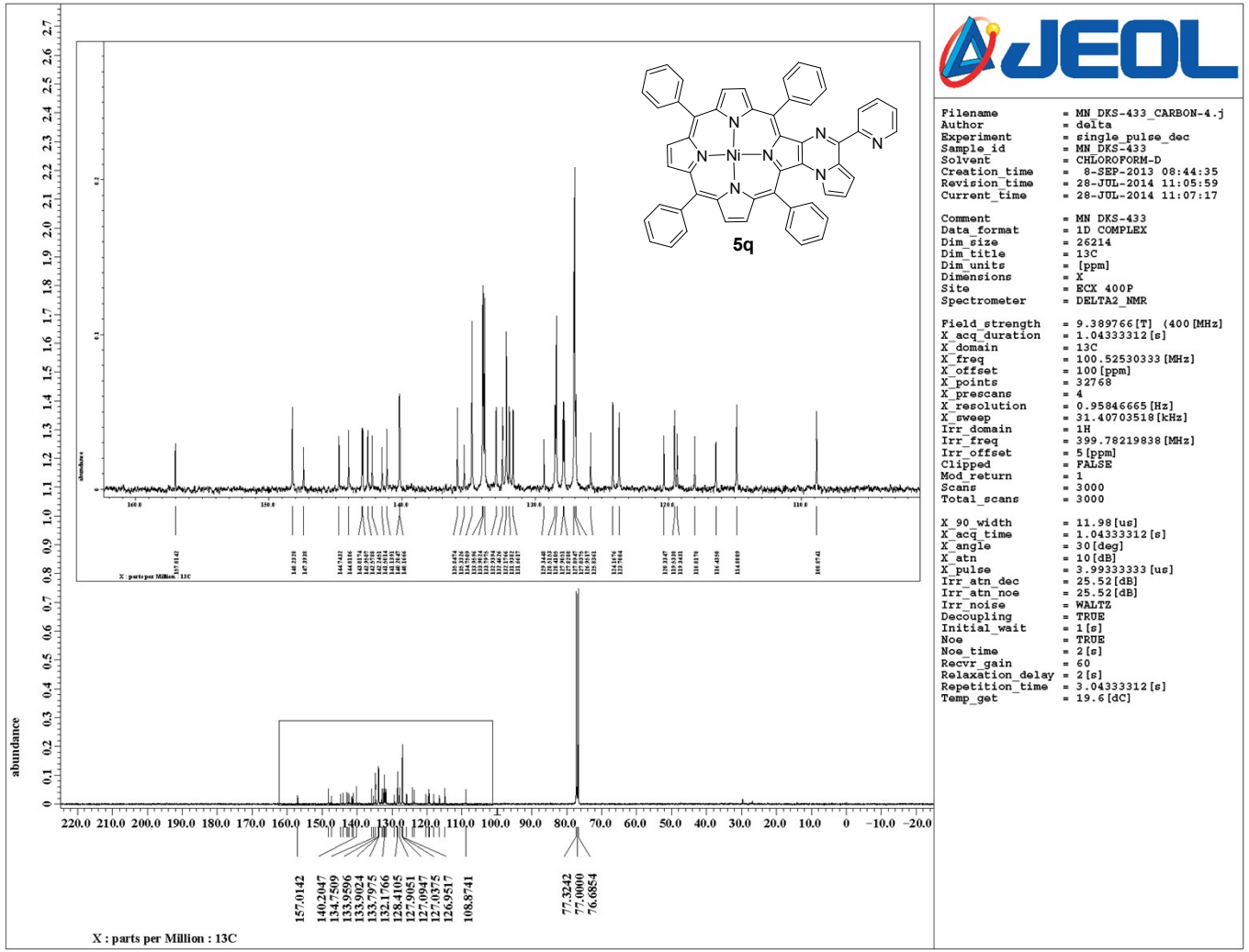

Fig. 40. ^{13}C NMR spectrum of compound **5q** in $CDCl_3$

2. Single crystal X-ray analysis of porphyrins 5o and 5p:

The intensity data of suitably sized crystals of **5o** and **5p** were collected on an Oxford Xcalibur S diffractometer (Sapphire-3 CCD detector, 4-circle κ goniometer, graphite monochromator, a single wavelength enhanced X-ray source with MoKα radiation (λ = 0.71073 Å), and ω scans) at 298(2) K.[1], Data collection, Pre-experiment, absorption corrections and data reduction were performed with the CrysAlisPro software suite.[2] The structures of nickel (II) *β,β′*-fused pyrrolo[1,2-a]pyrazinoporphyrins were solved by direct methods using SIR-92[3] and refined by full-matrix least-squares refinement techniques on F^2 using SHELXL97[4] program package. The hydrogen atoms were placed into the calculated positions and included in the last cycles of the refinement. Non-hydrogen atoms were refined anisotropically. All calculations were done using Wingx software package.[5]

REFERENCES

[1]. ENHANCE, Oxford Xcalibur Single Crystal Diffractometer, version 1.171.34.40; Oxford Diffraction Ltd: Oxford, U.K., 2006.

[2] CrysAlisPro, version 1.171.34.40; Oxford Diffraction Ltd: Oxford, U.K., 2006.

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; olidori, G.; Camalli, M.; *Appl. Crystallogr.* 1994, **27**, 435.

[4] Sheldrick, G. M.; Schneider T. R.; SHELXL-97 and SHELXS-97, program for refinement of crystal structures from diffraction data, University of Goettingen, Goettingen (Germany), *Methods Enzymol.* 1997, **277**, 319.

[5] Farrugia, L. J.; WinGX Version 1.80.05, An integrated system of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data; Department of Chemistry, University of Glasgow, 1997-2009.

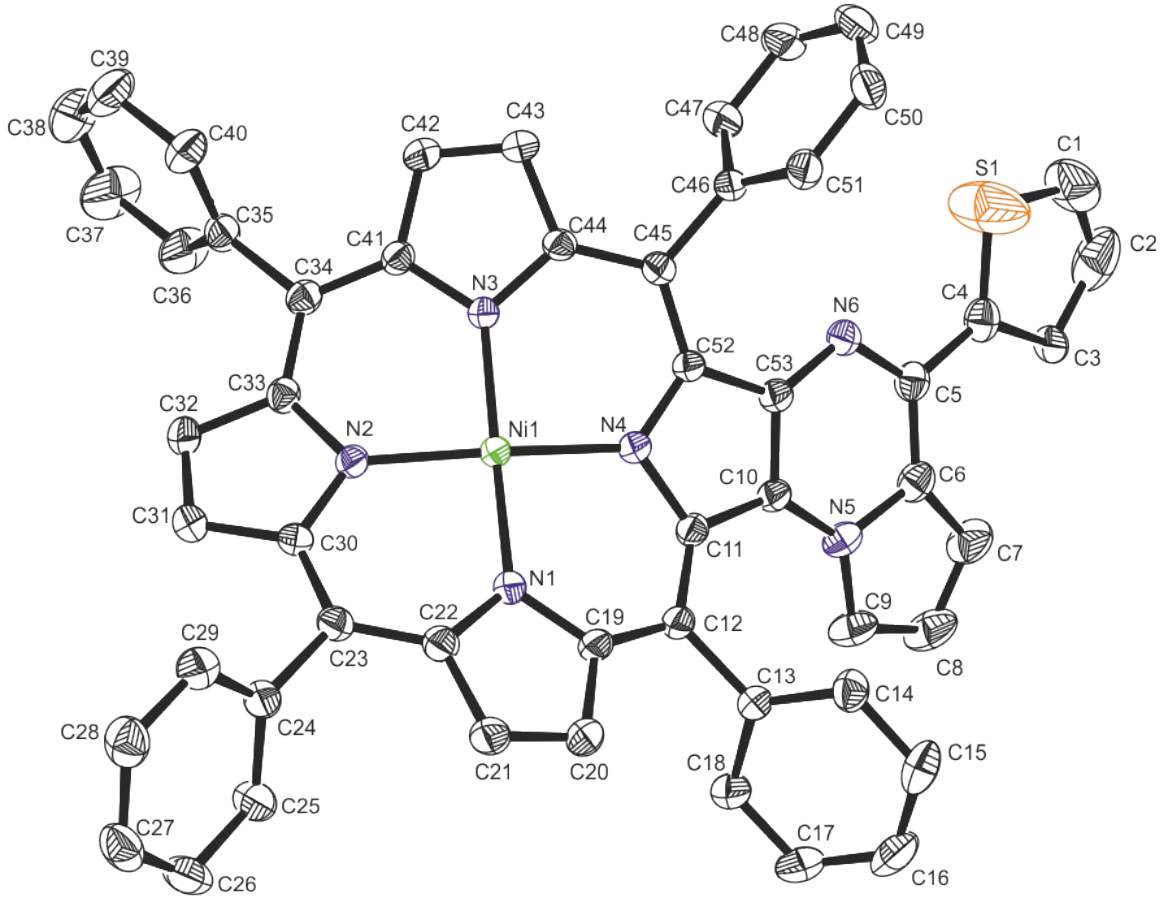

Figure 1. X-Ray crystal structure of **5o**. Thermal ellipsoids are shown at the 30% probability level and solvent molecules and all hydrogen atoms are omitted for clarity. Selected bond distances (Å)**:** Ni(1)-N(1) = 1.909(3), Ni(1)-N(2) = 1.923(3), Ni(1)-N(3) = 1.913(3), Ni(1)-N(4) = 1.941(3), N(1)-C(19) = 1.371(5), N(1)-C(22) = 1.385(5), N(2)-C(30) = 1.370(5), N(2)-C(33) = 1.384(5), N(3)-C(44) = 1.380(5), N(3)-C(41) = 1.383(5), N(4)-C(52) = 1.370(5), N(4)-C(11) = 1.405(5); Selected bond angles (deg): N(1)-Ni(01)-N(3) = 172.11(14), N(1)-Ni(01)-N(2) = 89.94(13), N(3)-Ni(01)-N(2) = 90.25(13), N(1)-Ni(01)-N(4) = 90.64(13), N(3)-Ni(01)-N(4) = 90.28(13), N(2)-Ni(01)-N(4) = 171.86(13).

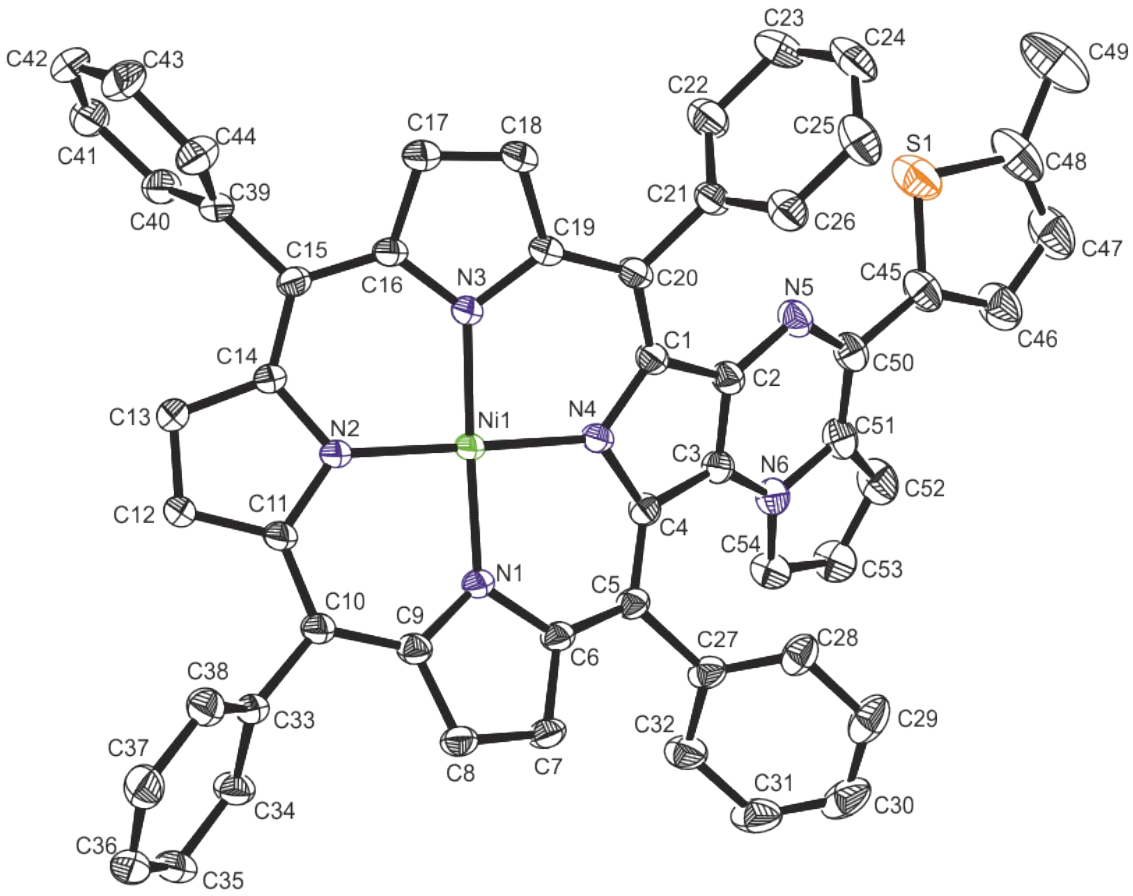

Figure 2. X-Ray crystal structure of **5p**. Thermal ellipsoids are shown at the 30% probability level and solvent molecules and all hydrogen atoms are omitted for clarity. Selected bond distances (Å)**:** Ni(1)-N(1) = 1.917(3), Ni(1)-N(2) = 1.919(3), Ni(1)-N(3) = 1.916(3), Ni(1)-N(4) = 1.937(3), N(1)-C(6) = 1.383(5), N(1)-C(9) = 1.387(5), N(2)-C(14) = 1.385(5), N(2)-C(11) = 1.387(5), N(3)-C(16) = 1.375(5), N(3)-C(19) = 1.388(5), N(4)-C(1) = 1.381(5), N(4)-C(4) = 1.401(5); Selected bond angles (deg): N(3)-Ni(1)-N(1) = 171.42(15), N(3)-Ni(1)-N(2) = 89.77(14), N(1)-Ni(1)-N(2) = 90.48(14), N(3)-Ni(1)-N(4) = 90.42(14), N(1)-Ni(1)-N(4) = 90.35(14), N(2)-Ni(1)-N(4) = 173.16(15).

Table 1. Crystallographic data and structure refinements for porphyrins **5o·CHCl$_3$**, and **5p·2CHCl$_3$**

Compound	**5o·CHCl$_3$**	**5p·2CHCl$_3$**
Formula	$C_{54}H_{33}Cl_3N_6NiS$	$C_{56}H_{36}Cl_6N_6NiS$
Fw	962.98	1096.38
Crystal system	Monoclinic	Triclinic
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Space group	*P* $2_1/n$ (No. 14)	*P*-1 (No. 2)
a (Å)	13.3636(13)	12.0020(9)
b (Å)	29.0621(18)	14.6553(10)
c (Å)	12.7286(11)	15.1609(13)
α (deg)	90	79.909(6)
β (deg)	116.573(12)	70.047(7)
γ (deg)	90	81.089(6)
Volume (Å^3)	4421.3(6)	2454.8(3)
Z	4	2
μ(Mo Kα) (mm^{-1})	0.714	0.811
θ range (deg)	3.05-26.37	3.01-26.37
F(000)	1976	1120
$\rho_{calcd.}$(g cm^{-3})	1.447	1.483
Completeness	0.999	0.998
Reflections collected	65192	34800
Independent reflections	9018	10014
R(int.)	0.0390	0.0321
Max. and min. transmission	1.0000 and 0.7674	0.8546 and 0.7929
R_1 [I>2σ (I)][a]	0.0776	0.0844
wR_2 [I>2σ (I)]	0.1907	0.2479
R_1 (all data)	0.0894	0.0964
wR_2 (all data)[b]	0.1978	0.2611
GooF on F^2 [c]	1.141	1.021
Largest diff. peak and hole (e.Å^{-3})	0.782 / -0.947	1.779 / -1.117
Solvent System	$CHCl_3$/MeOH	$CHCl_3$/MeOH
CCDC No.	980828	980827

[a]$R_1 = \sum(\|Fo\| - |Fc|)/\sum|Fo|$; [b]$_wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; [c]$S = \{\sum[w(F_o^2 - F_c^2)^2]/[(n - p)\}^{1/2}$