Supplementary Information

Controlling the regioselectivity of the ring opening of spiro-epoxyoxindole for efficient synthesis of C(3)–N(1′)-bisindole and C(3)–N(1′)-diindolylmethane

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[b]Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India.

[c]Dept. of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Manauli PO 140306, Punjab, India.

#S.M. & S.R contributed equally to this work.

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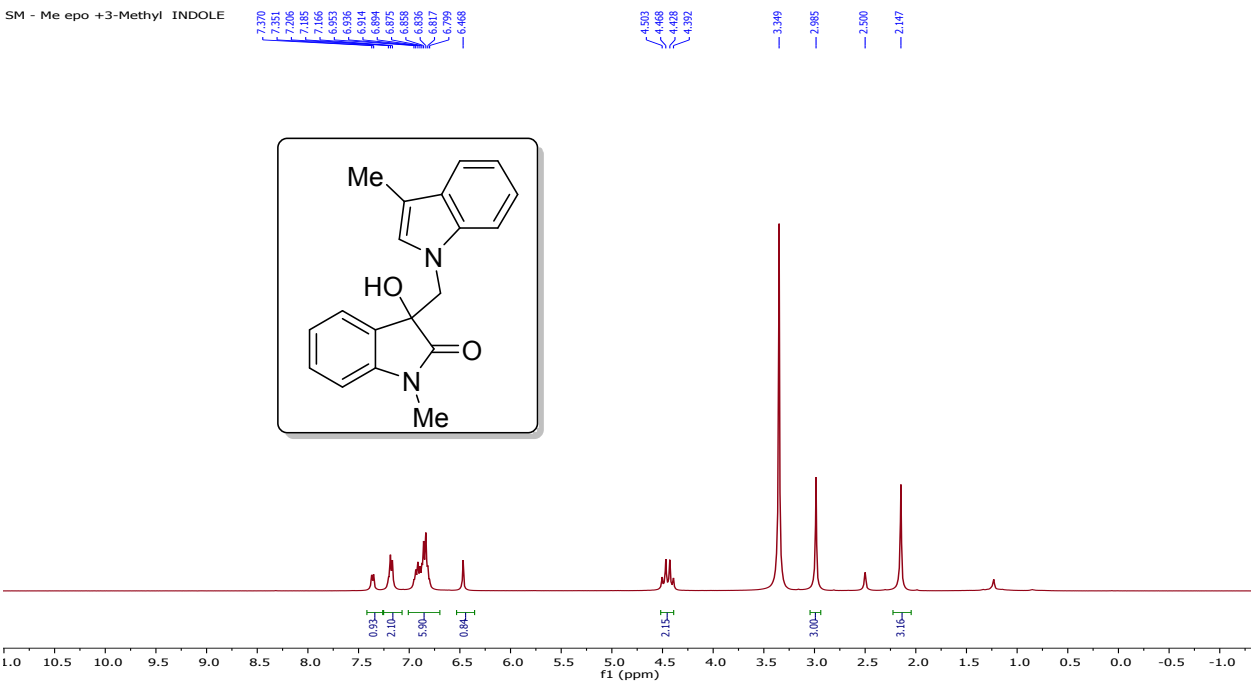
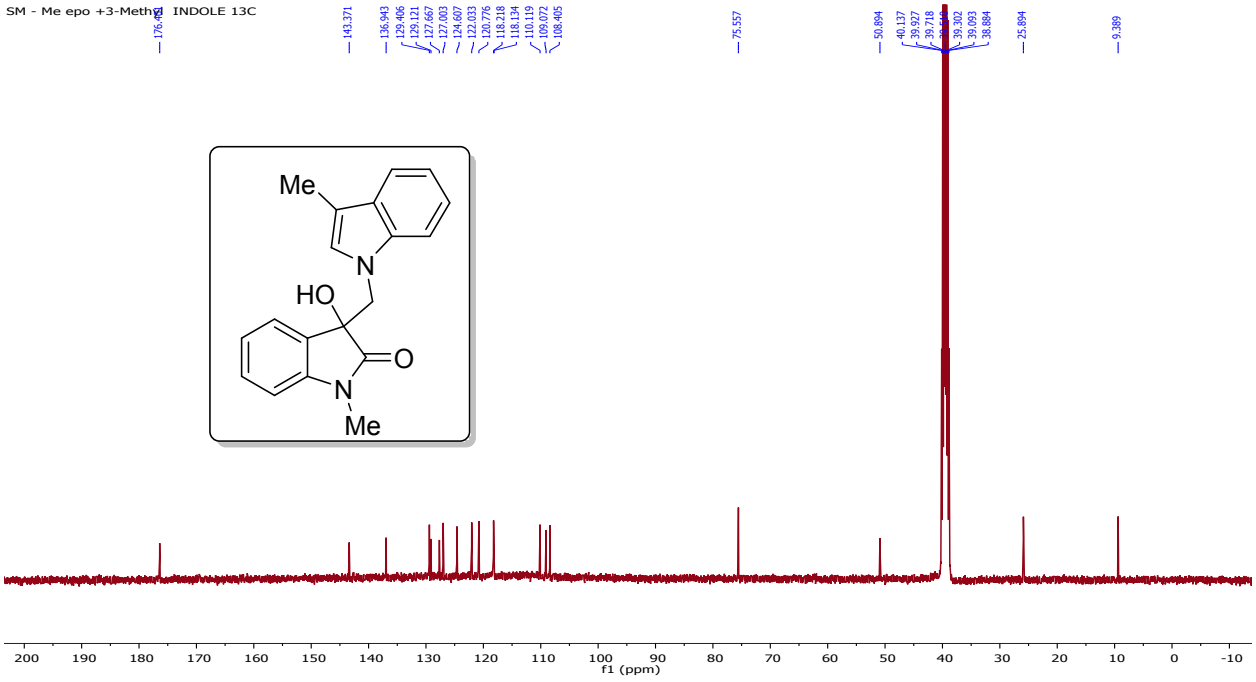
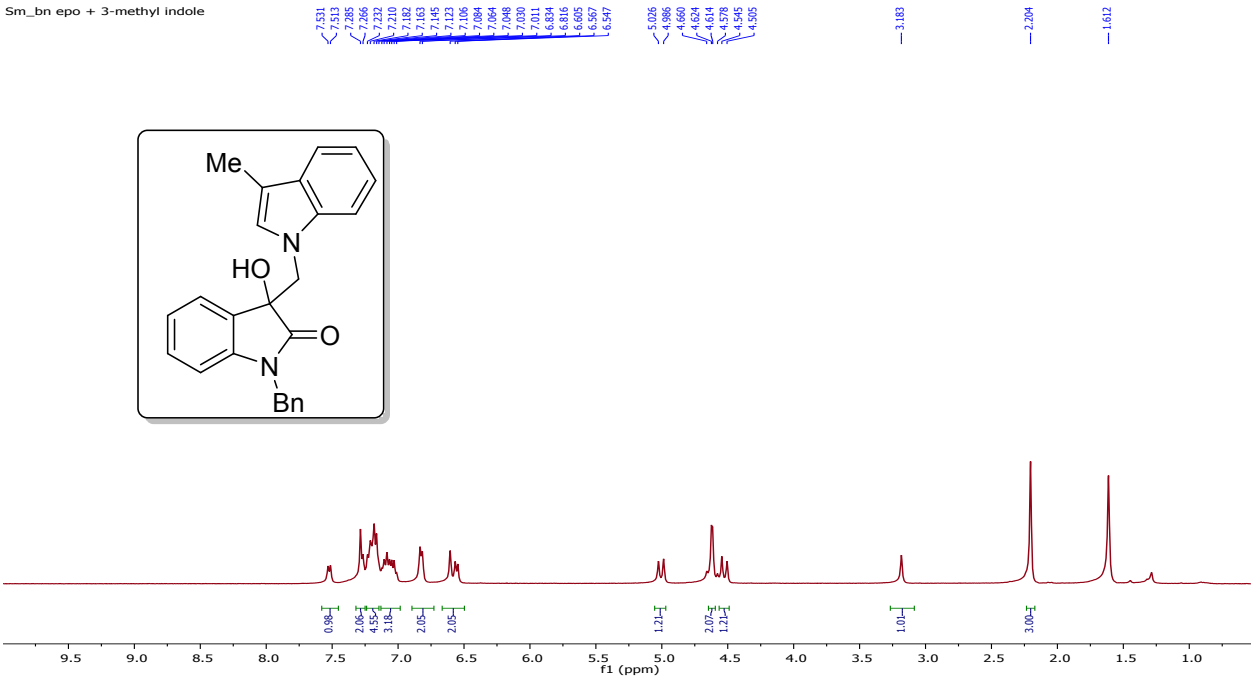


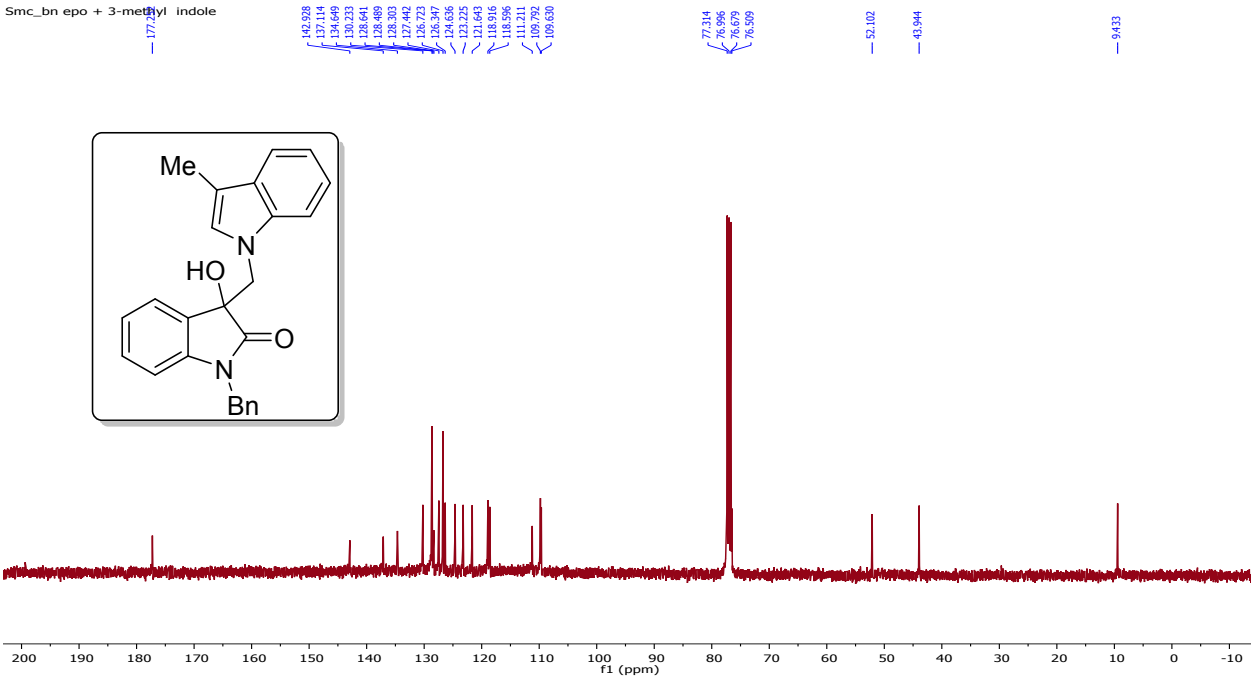
^{1}H NMR Spectrum of Compound **4a** (400MHz, DMSO-d_6).



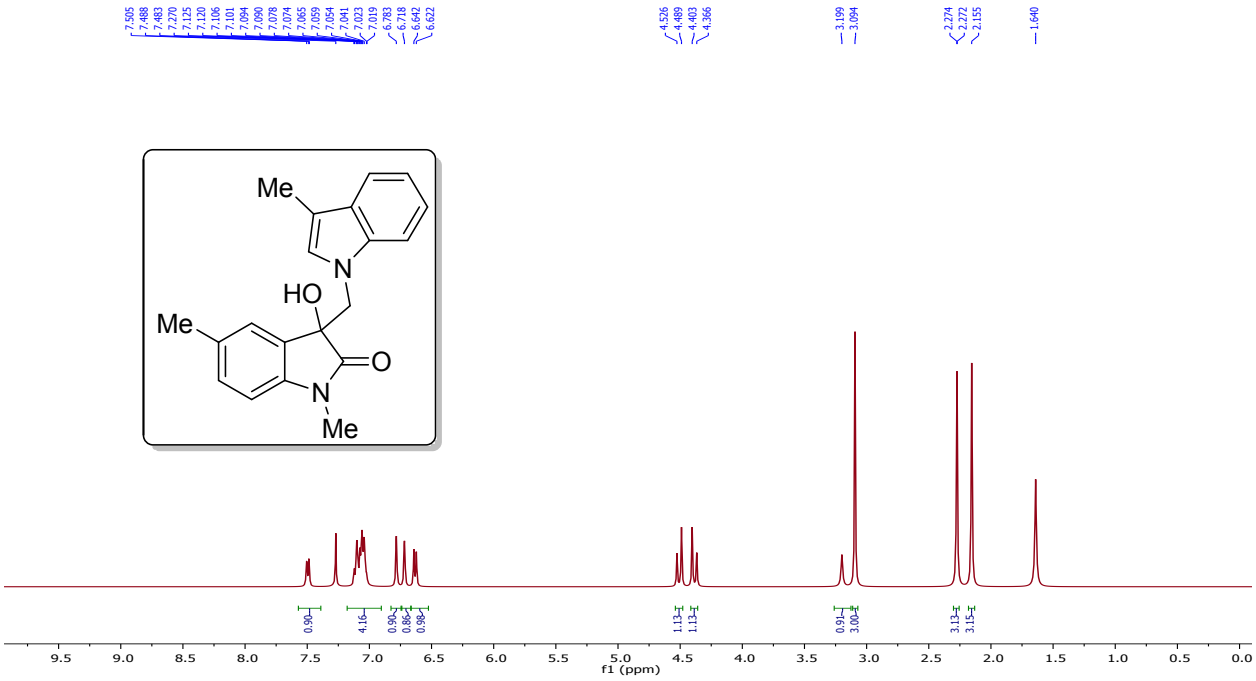
^{13}C NMR Spectrum of Compound **4a** (100MHz, DMSO-d_6)



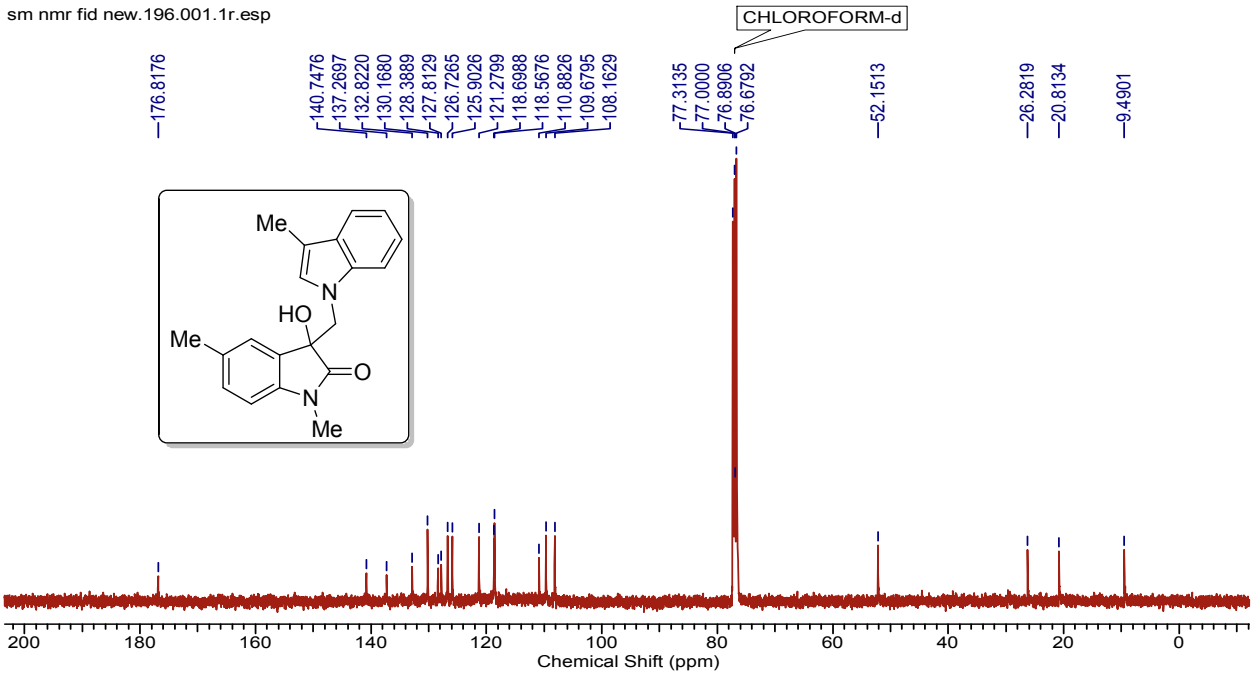
^{1}H NMR Spectrum of Compound **4b** (400MHz, $CDCl_3$).



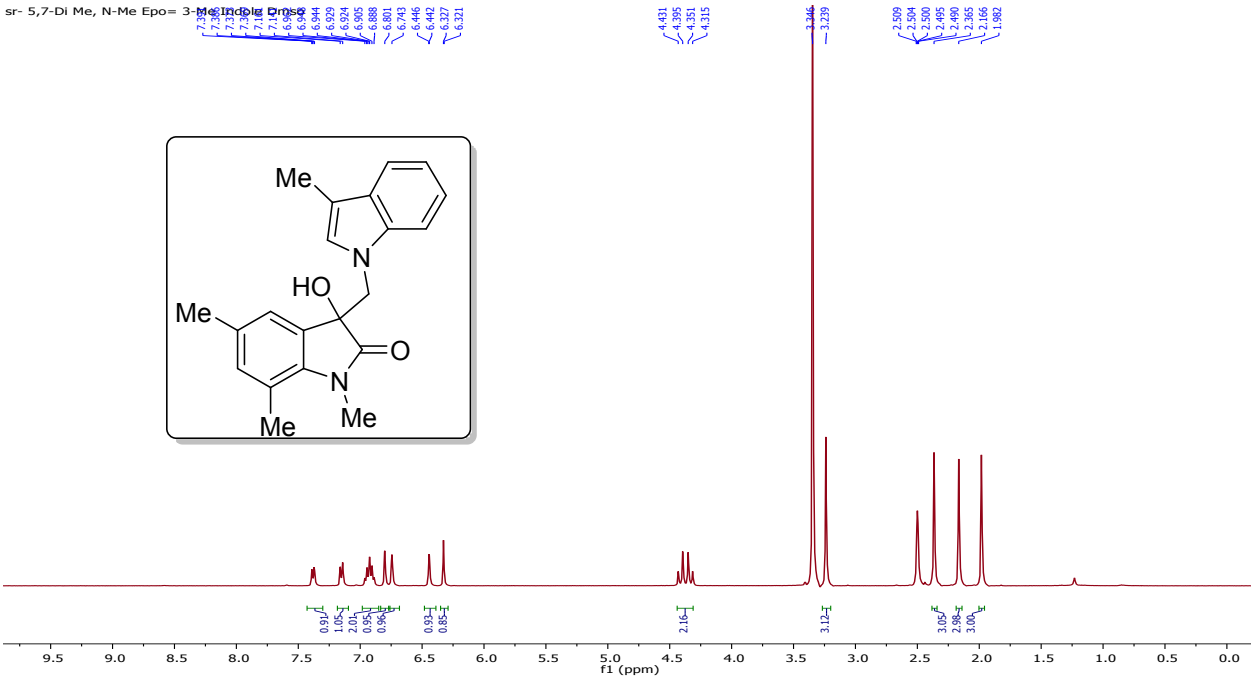
^{13}C NMR Spectrum of Compound **4b** (100MHz, $CDCl_3$).



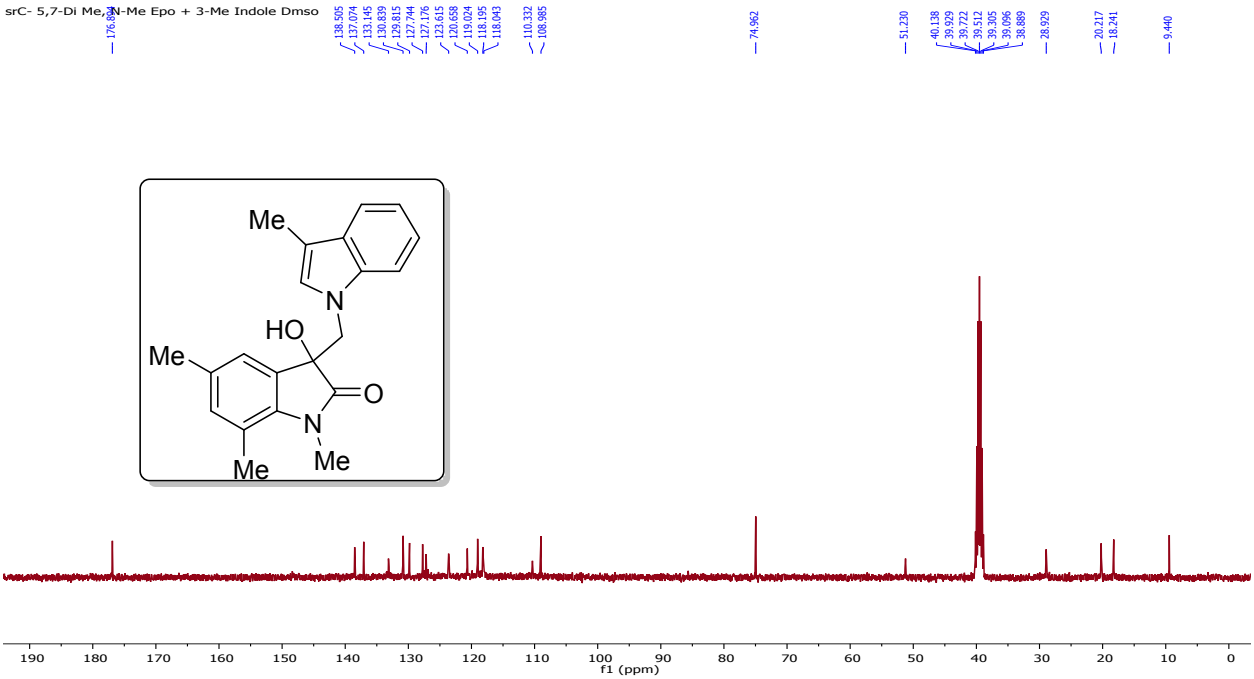
^{1}H NMR Spectrum of Compound **4c** (400MHz, $CDCl_3$).



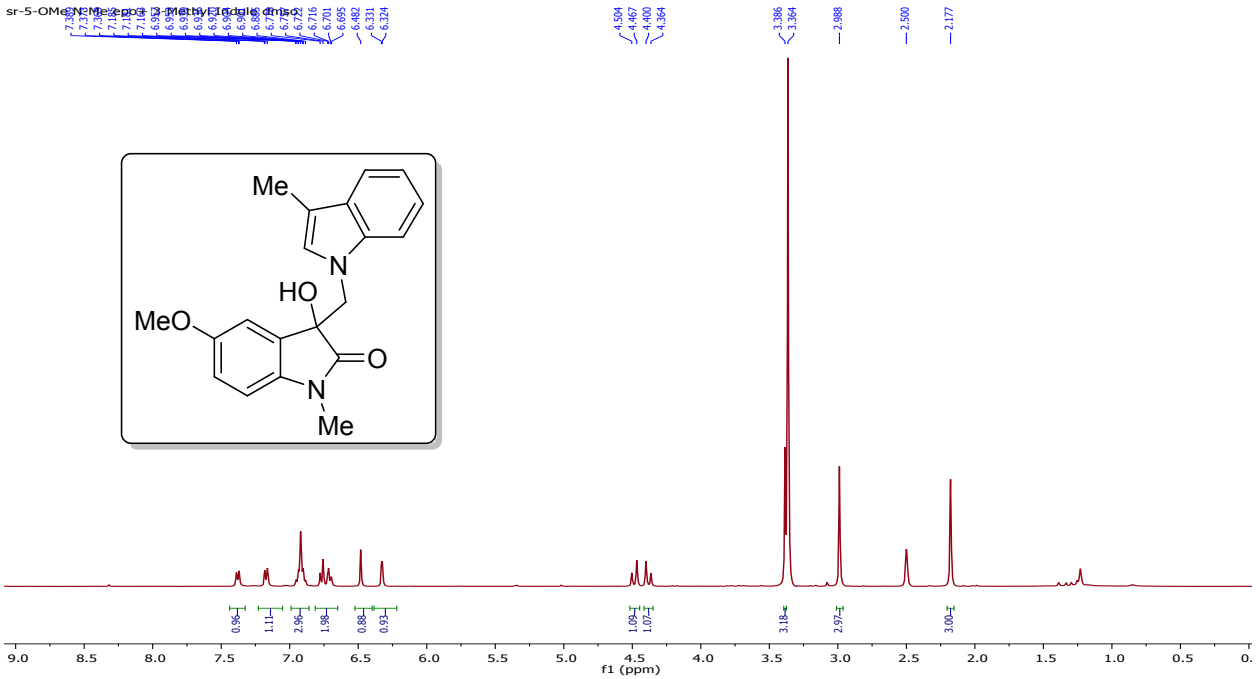
^{13}C NMR Spectrum of Compound **4c** (100MHz, $CDCl_3$).



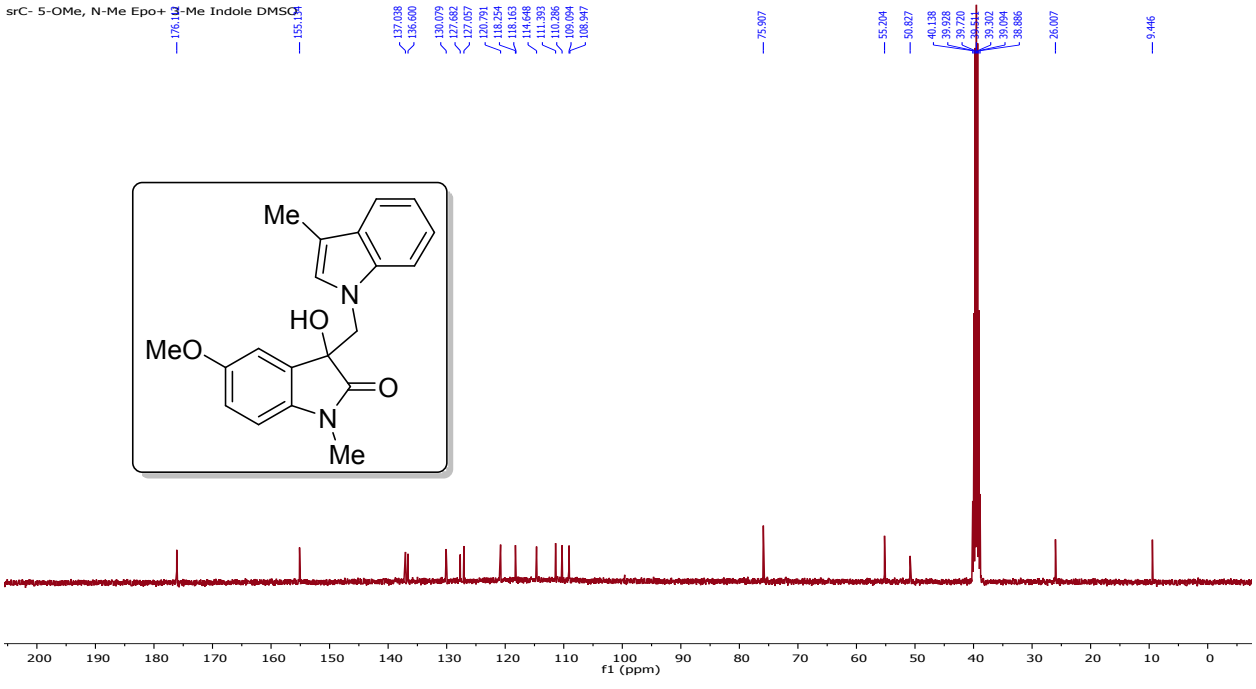
^{1}H NMR Spectrum of Compound **4d** (400MHz, DMSO-d_6).



^{13}C NMR Spectrum of Compound **4d** (100MHz, DMSO-d_6).



^{1}H NMR Spectrum of Compound **4e** (400MHz, DMSO-d_6).



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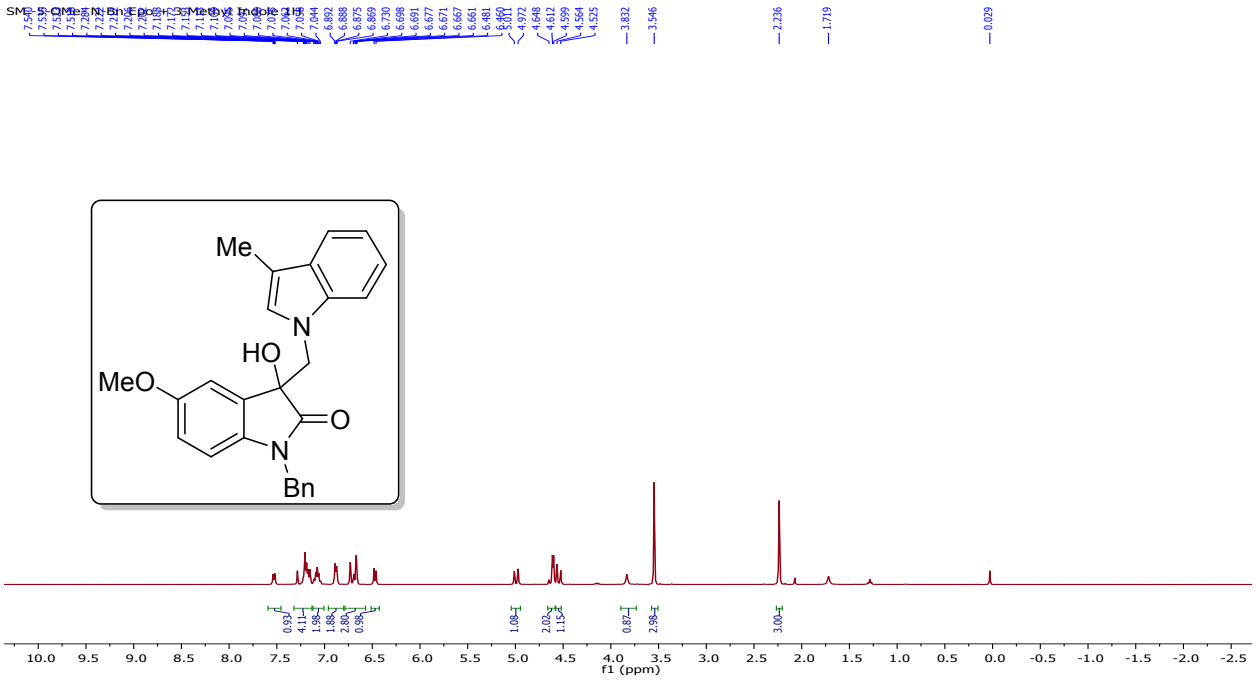
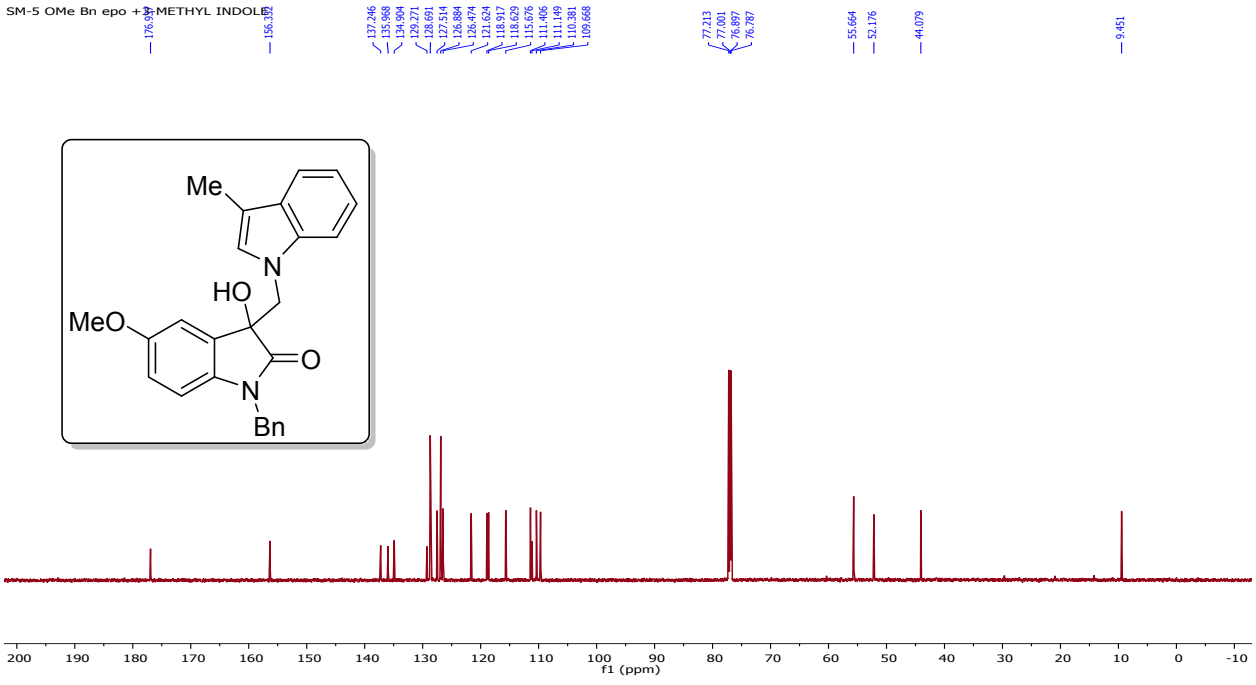
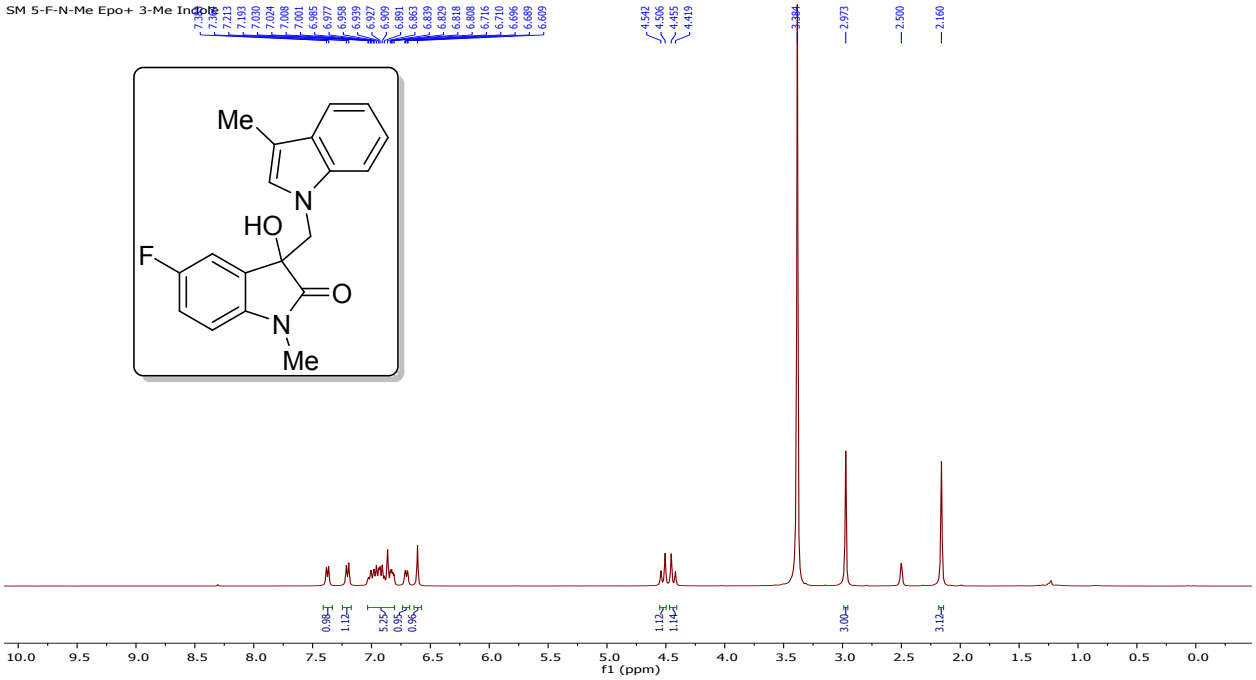


^{1}H NMR Spectrum of Compound **4f** (400MHz, $CDCl_3$).



^{13}C NMR Spectrum of Compound **4f** (100MHz, $CDCl_3$).



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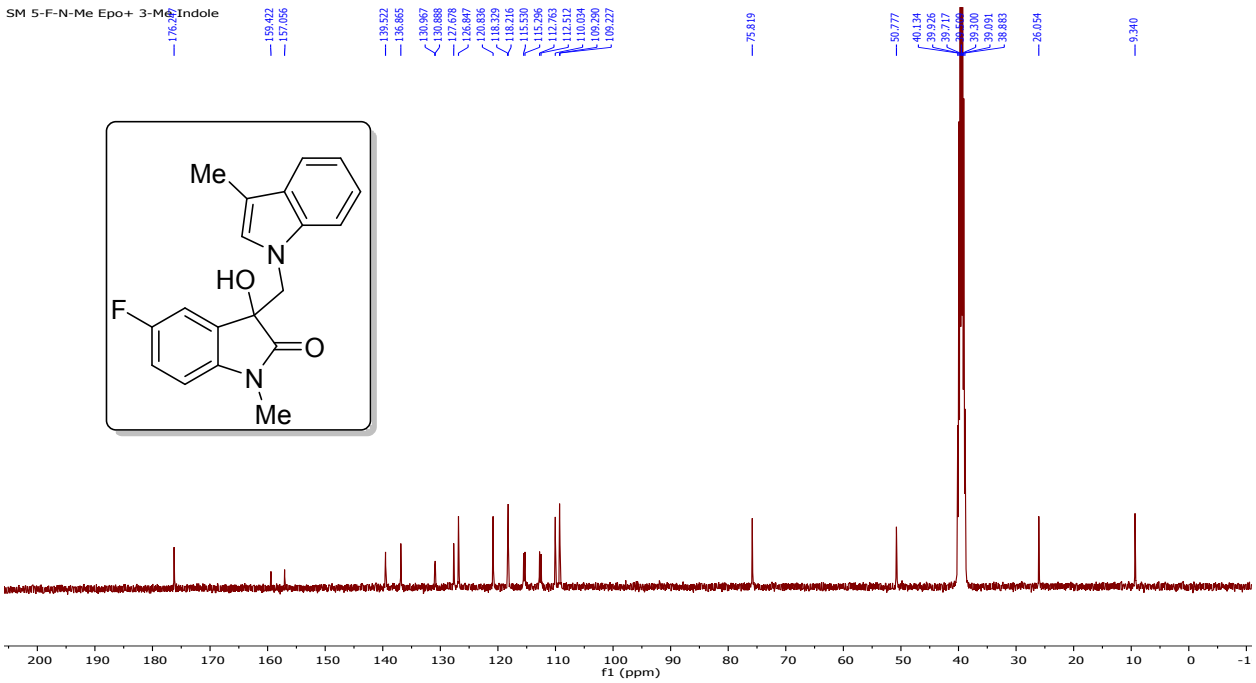
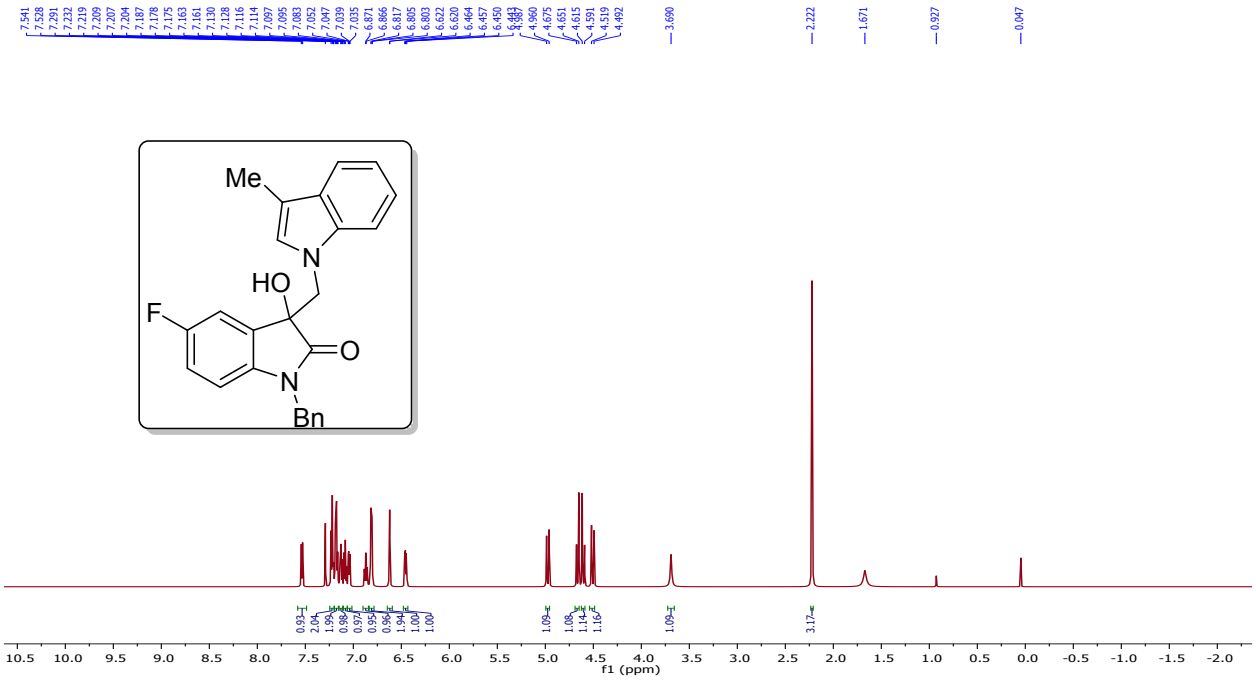
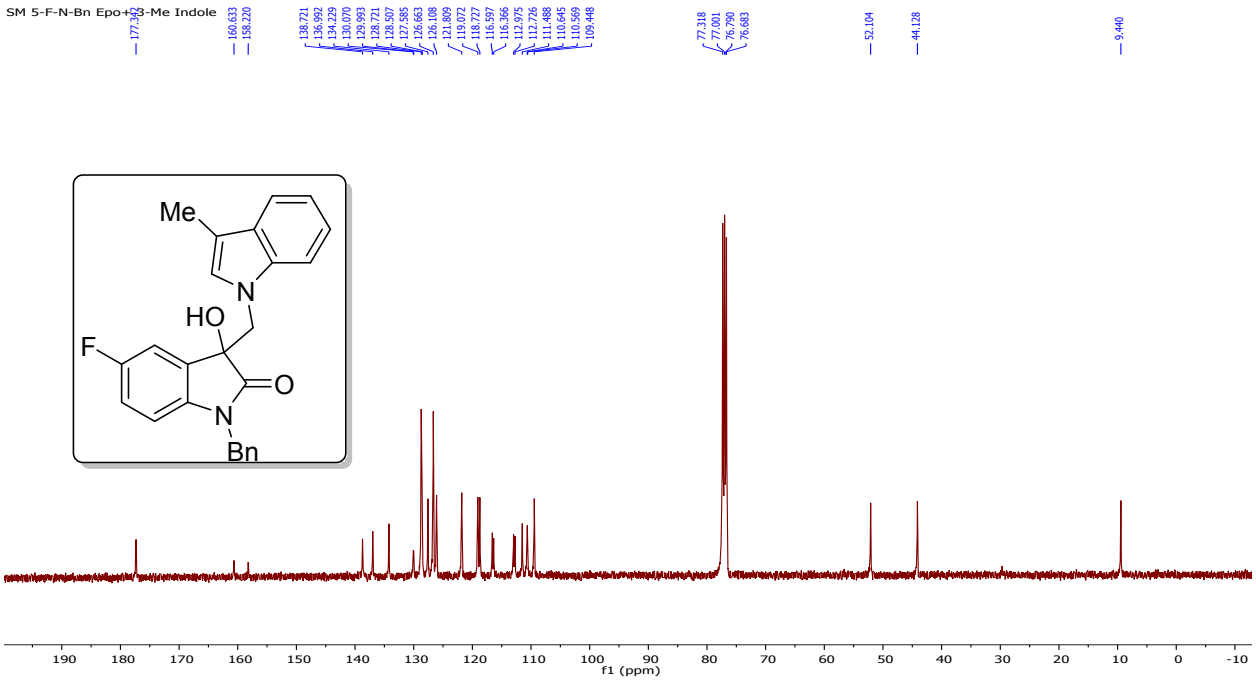


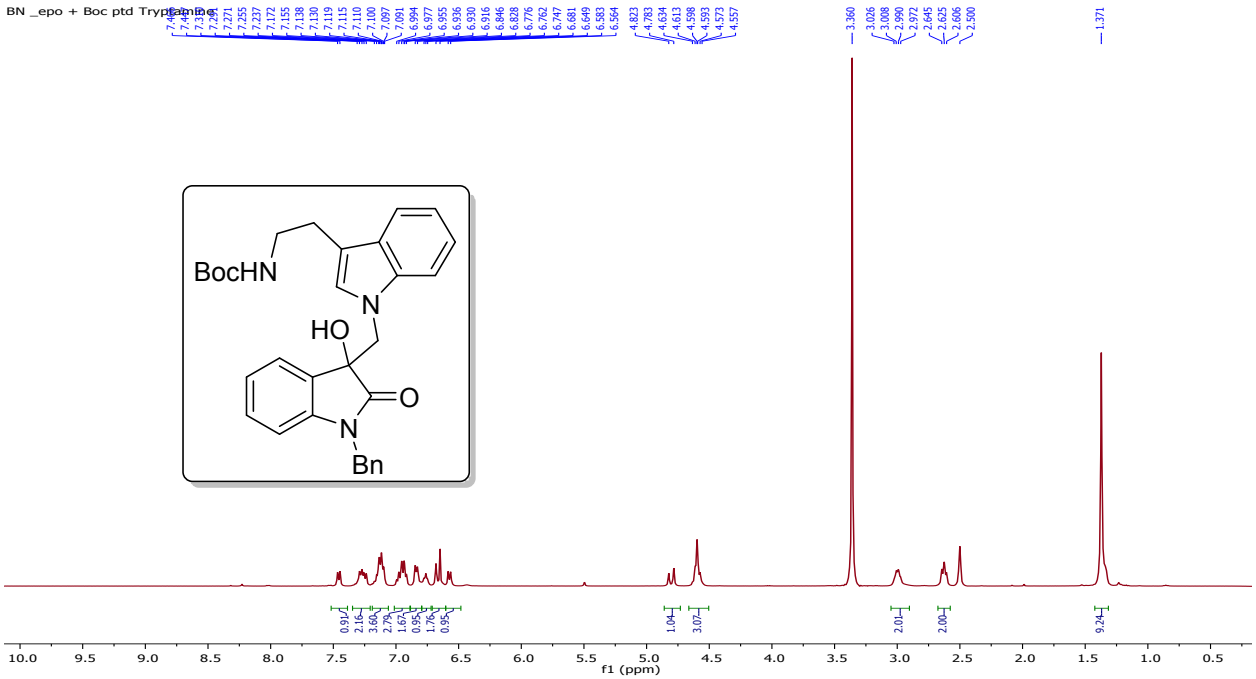
^{13}C NMR Spectrum of Compound **4g** (100MHz, DMSO-d_6).



^{1}H NMR Spectrum of Compound **4h** (600MHz, $CDCl_3$).



^{13}C NMR Spectrum of Compound **4h** (100 MHz, $CDCl_3$).



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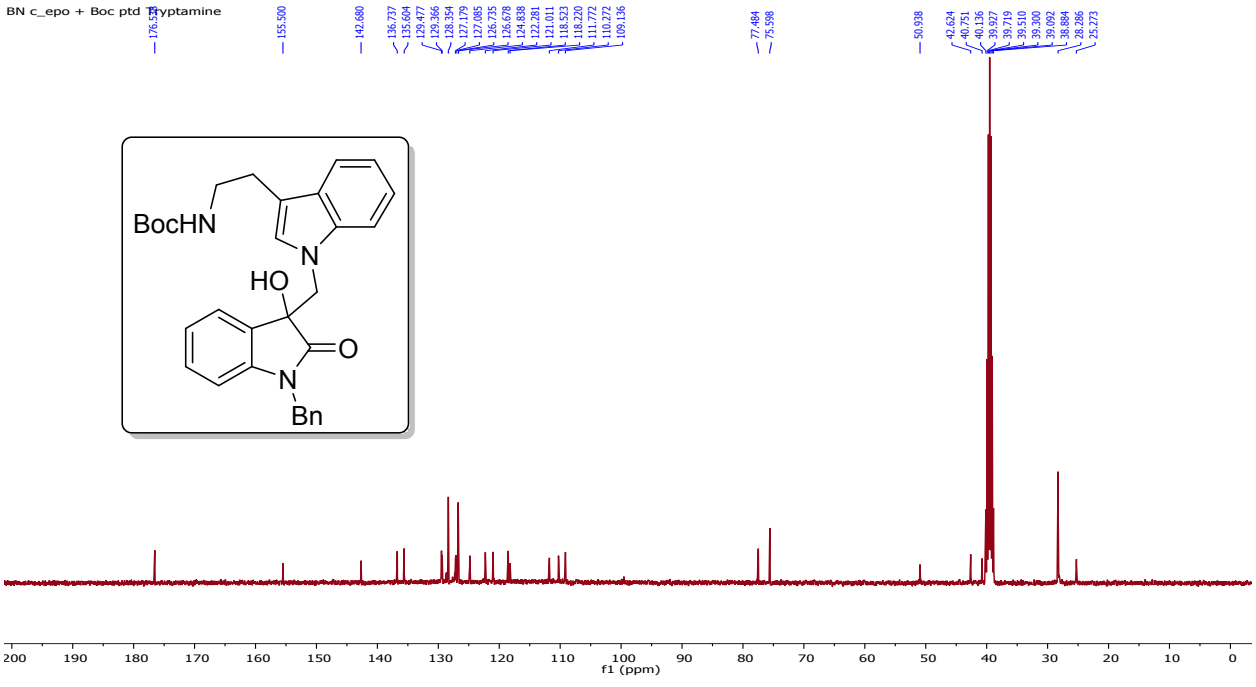
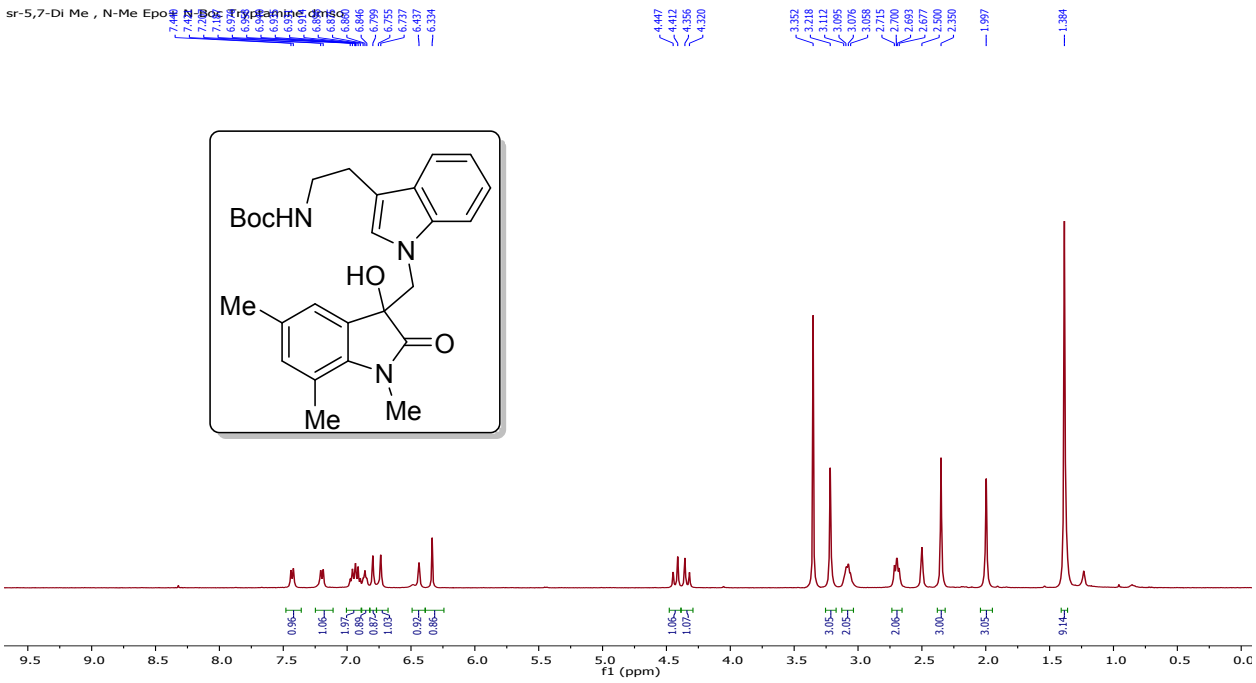
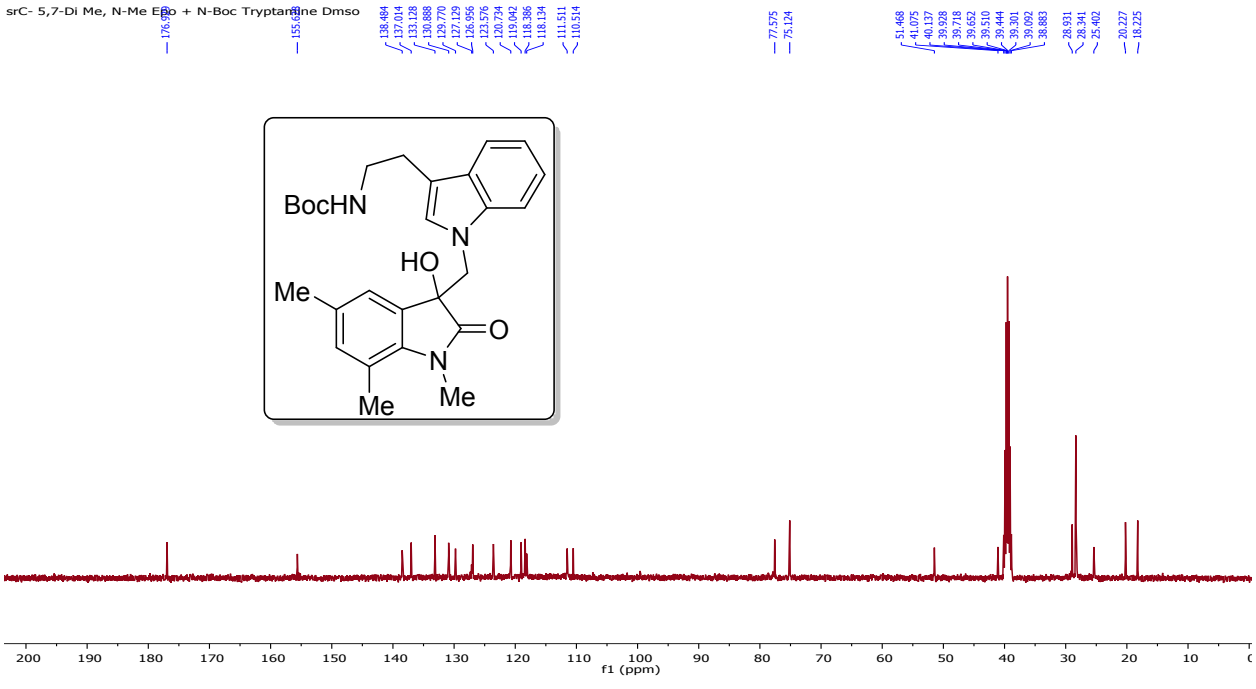


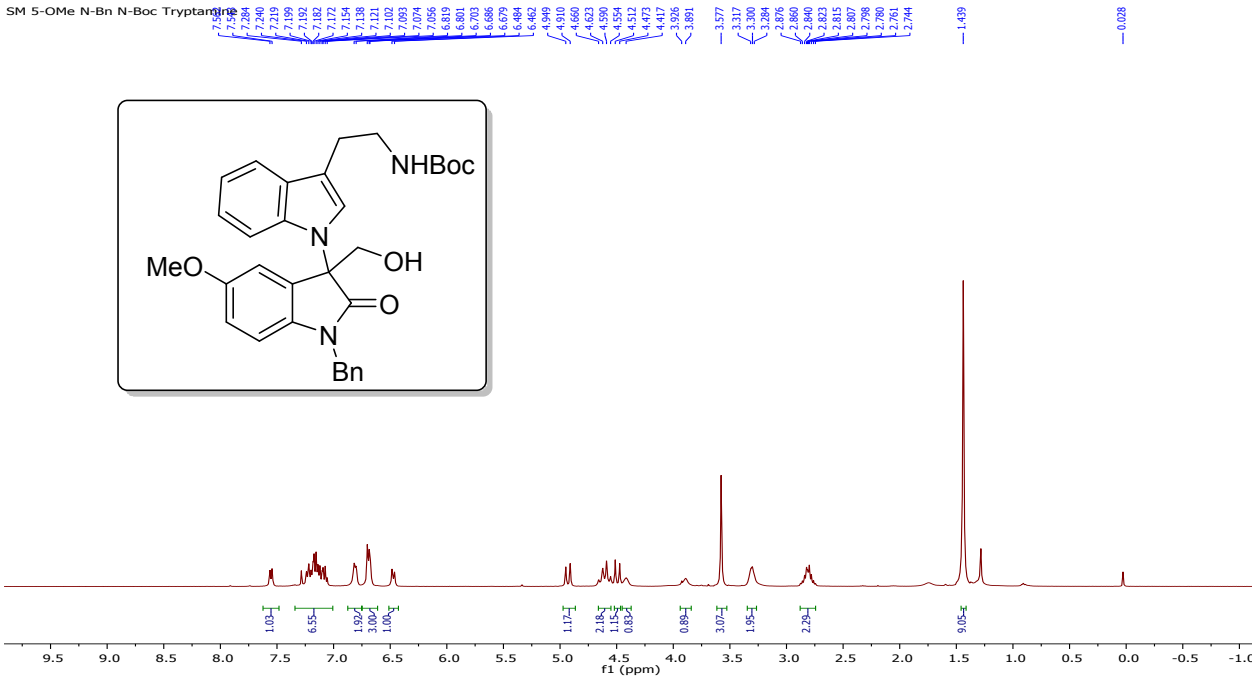
^{13}C NMR Spectrum of Compound **4i** (100MHz, DMSO-d_6).



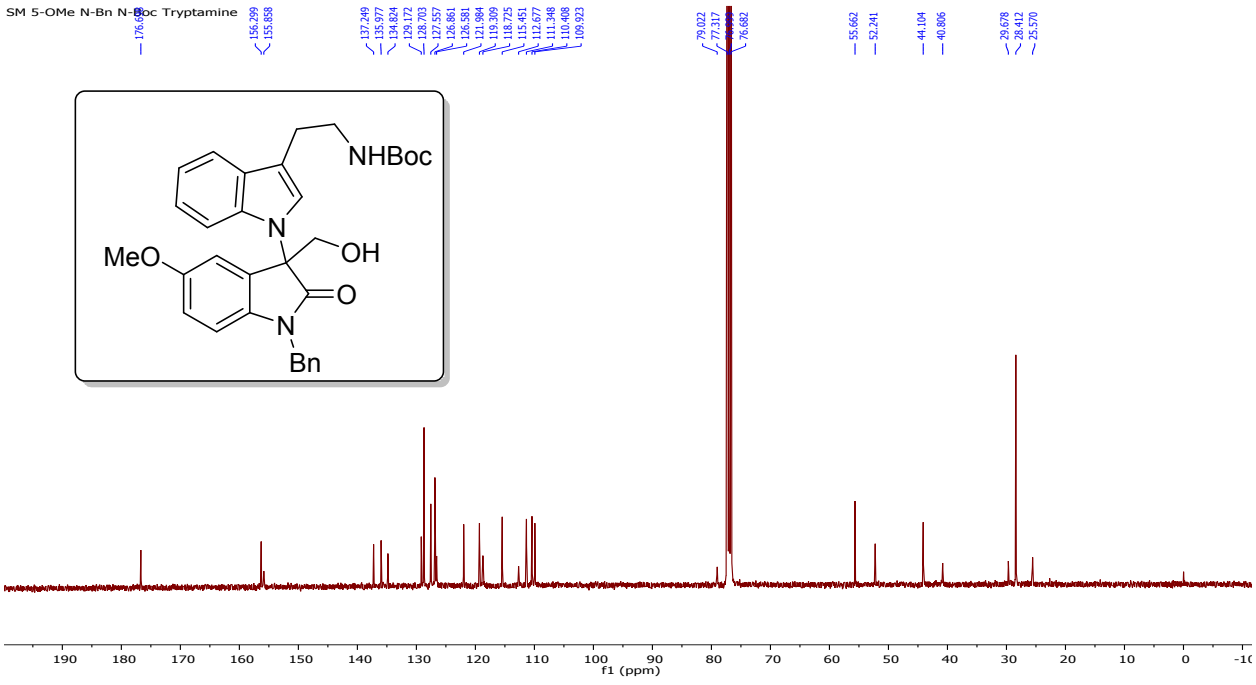
^{1}H NMR Spectrum of Compound **4j** (400MHz, DMSO-d_6).



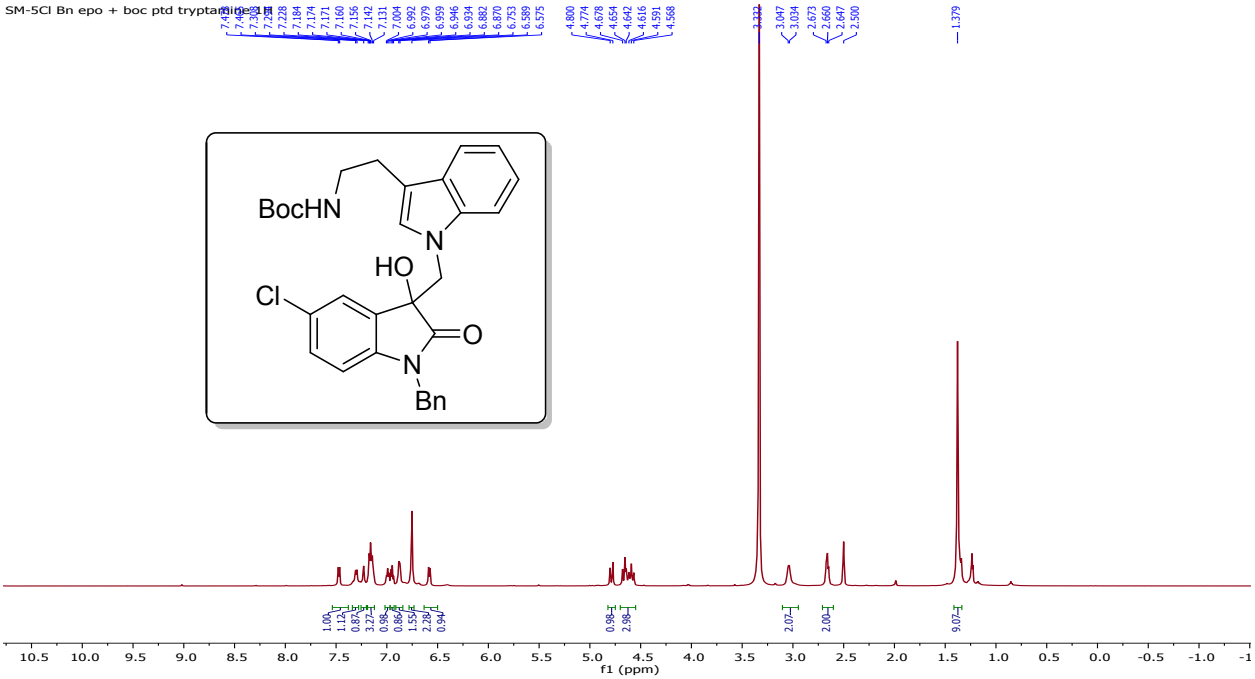
^{13}C NMR Spectrum of Compound **4j** (100MHz, DMSO-d_6).



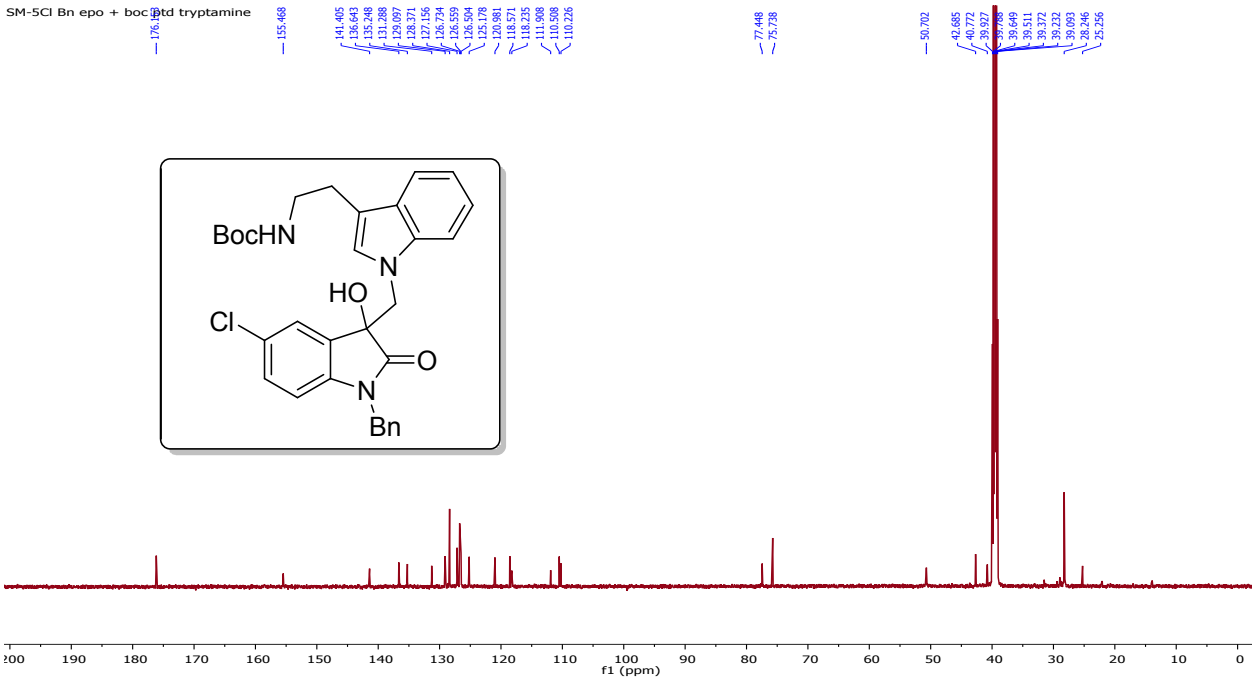
^{1}H NMR Spectrum of Compound **4k** (400MHz, $CDCl_3$).



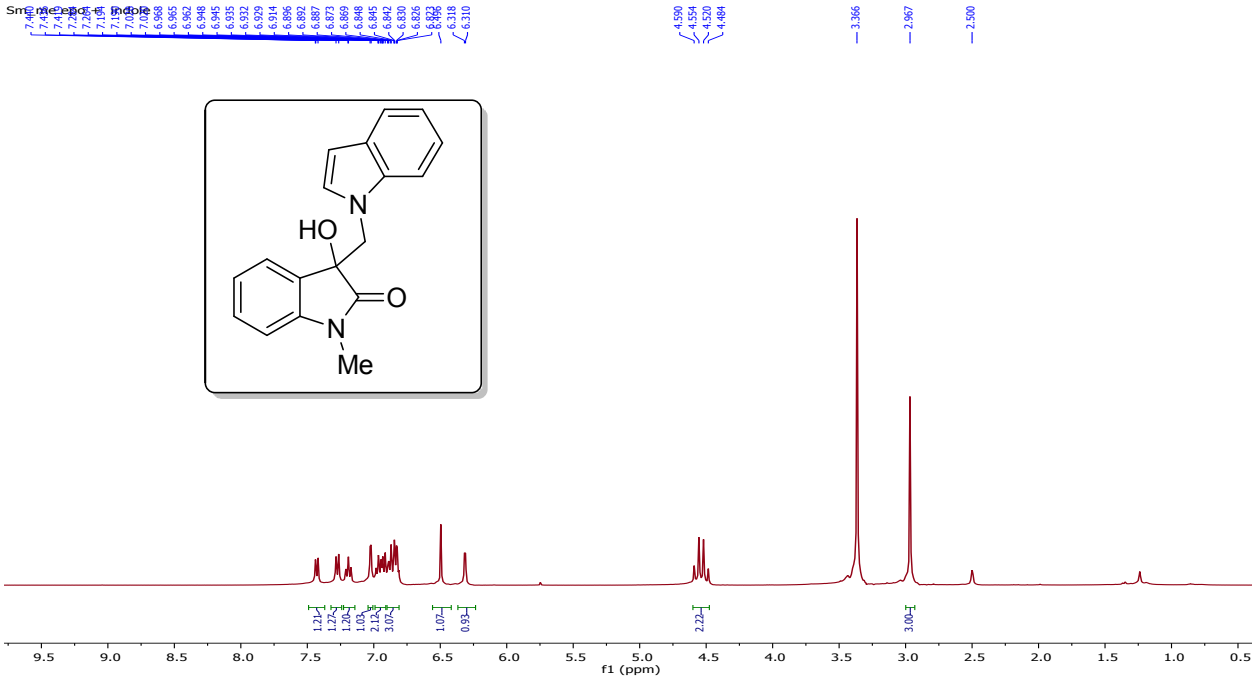
^{13}C NMR Spectrum of Compound **4k** (100MHz, $CDCl_3$).



^{1}H NMR Spectrum of Compound **4l** (600 MHz, DMSO-d_6).



^{13}C NMR Spectrum of Compound **4l** (150 MHz, DMSO-d_6).



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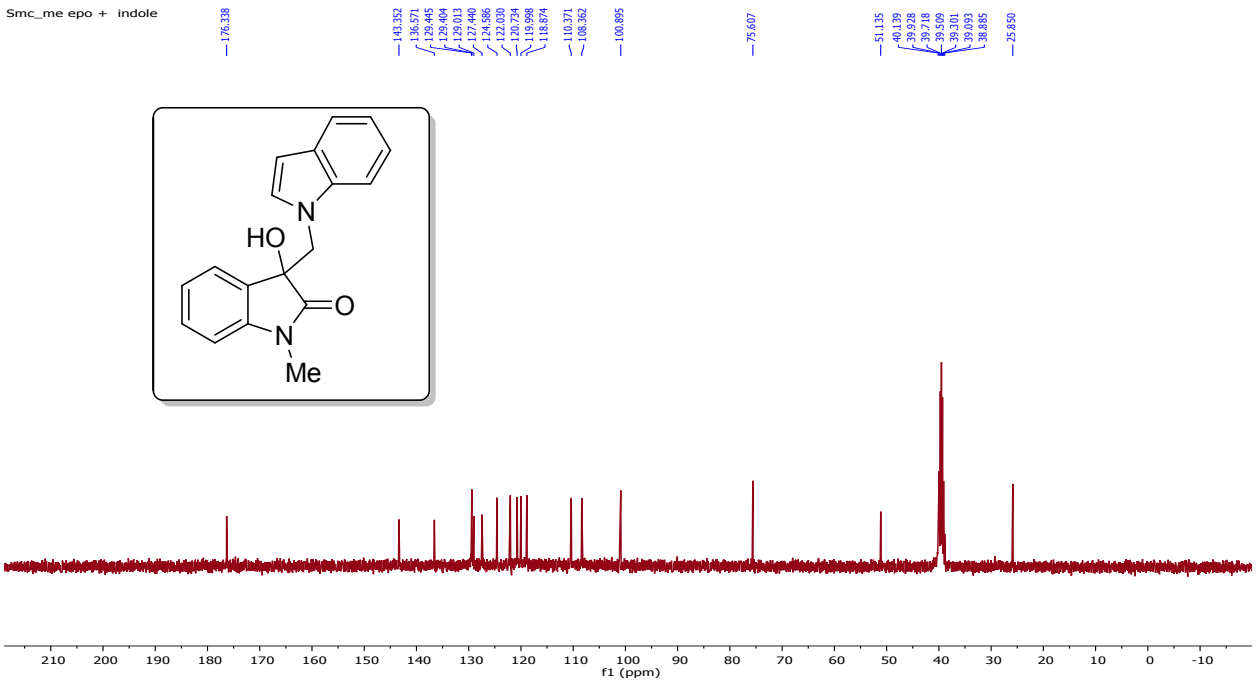
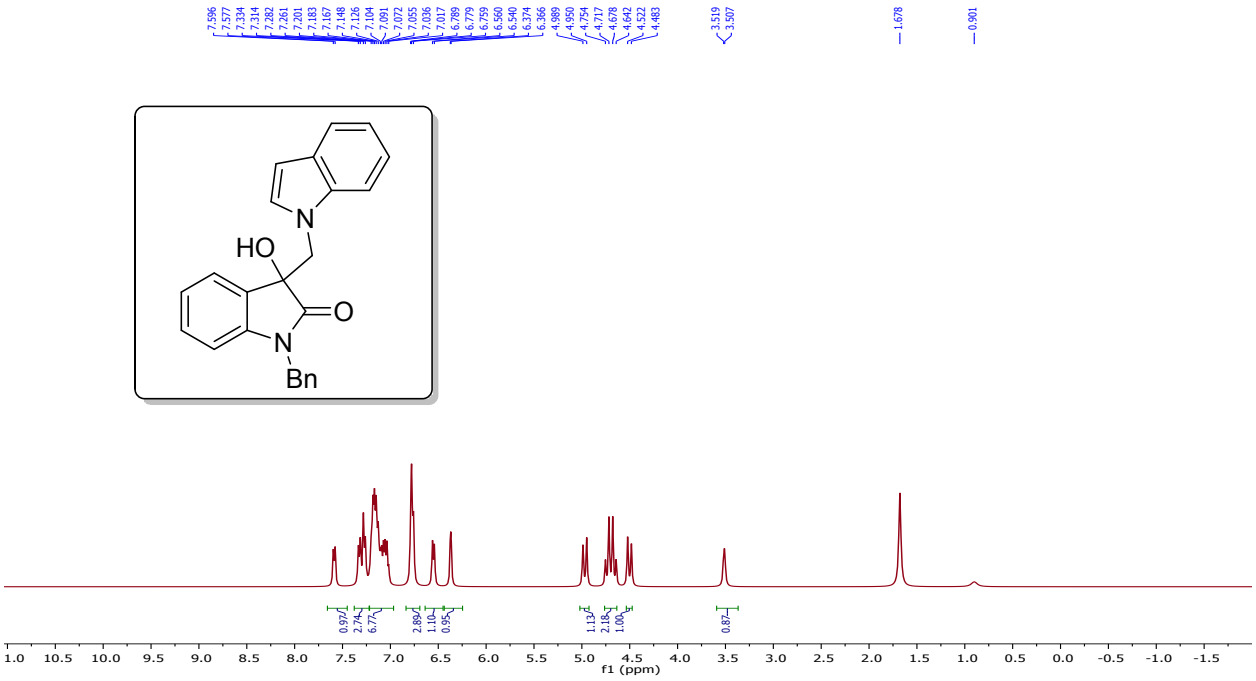
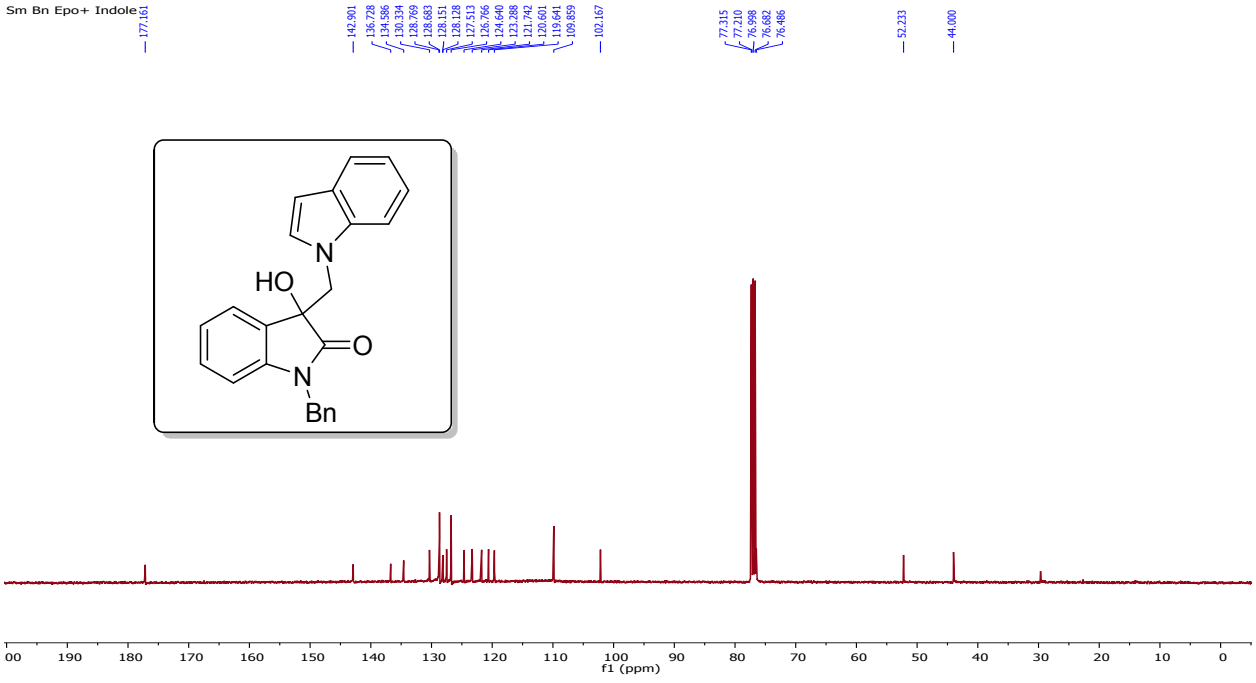


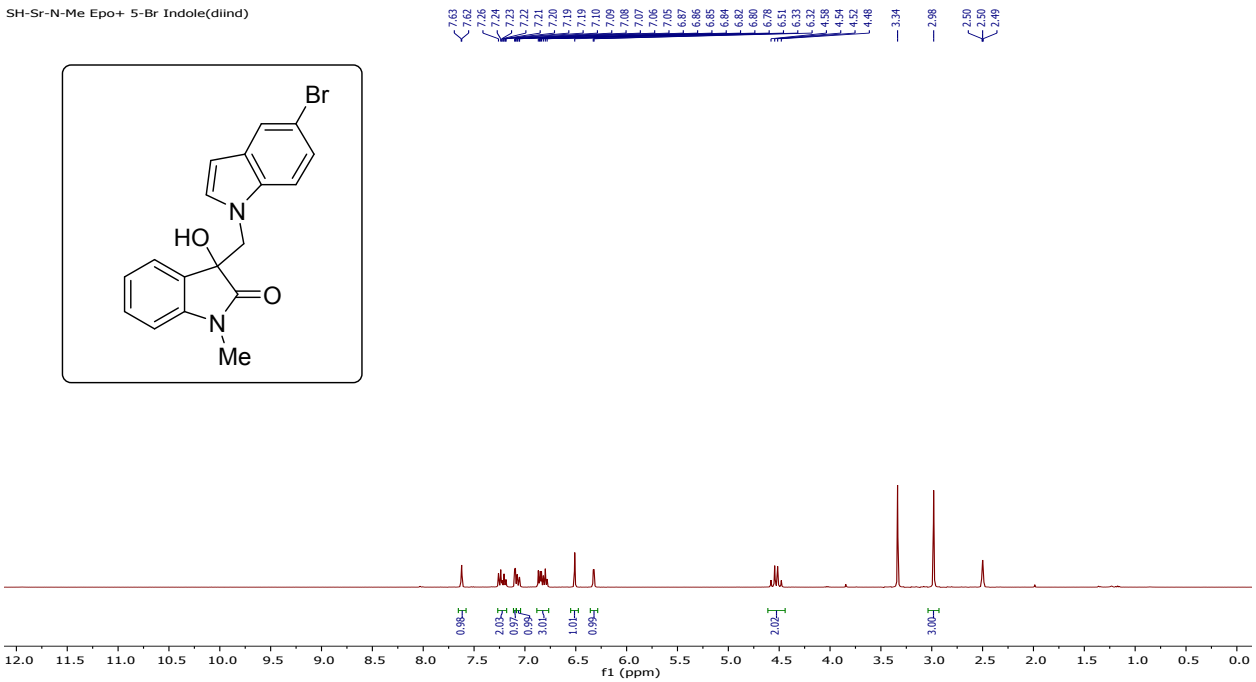
^{13}C NMR Spectrum of Compound **4m** (100 MHz, DMSO-d_6).



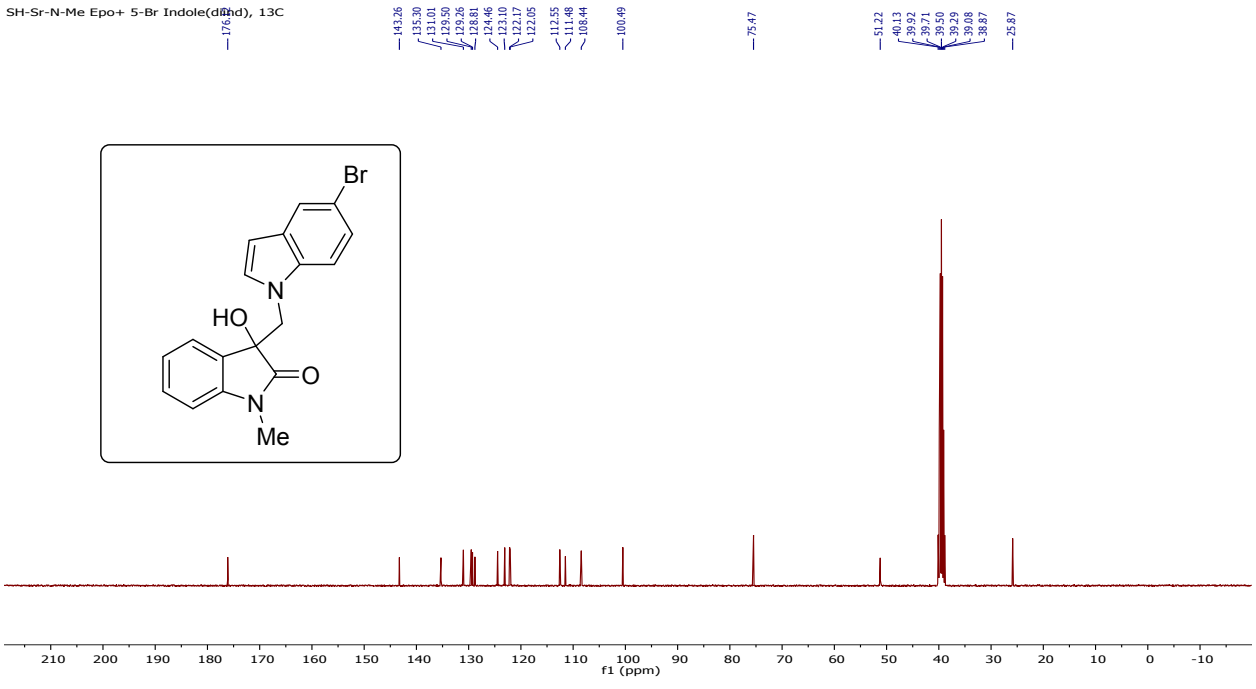
^{1}H NMR Spectrum of Compound **4n** (400 MHz, $CDCl_3$).



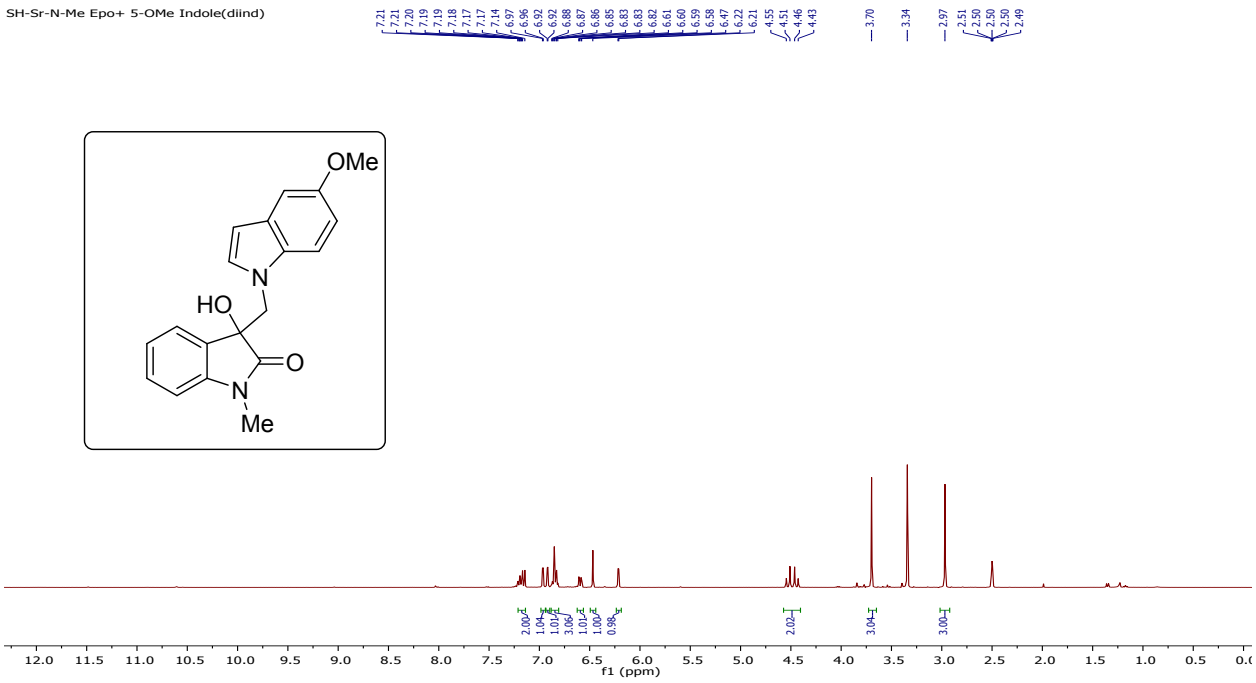
^{13}C NMR Spectrum of Compound **4n** (100 MHz, $CDCl_3$).



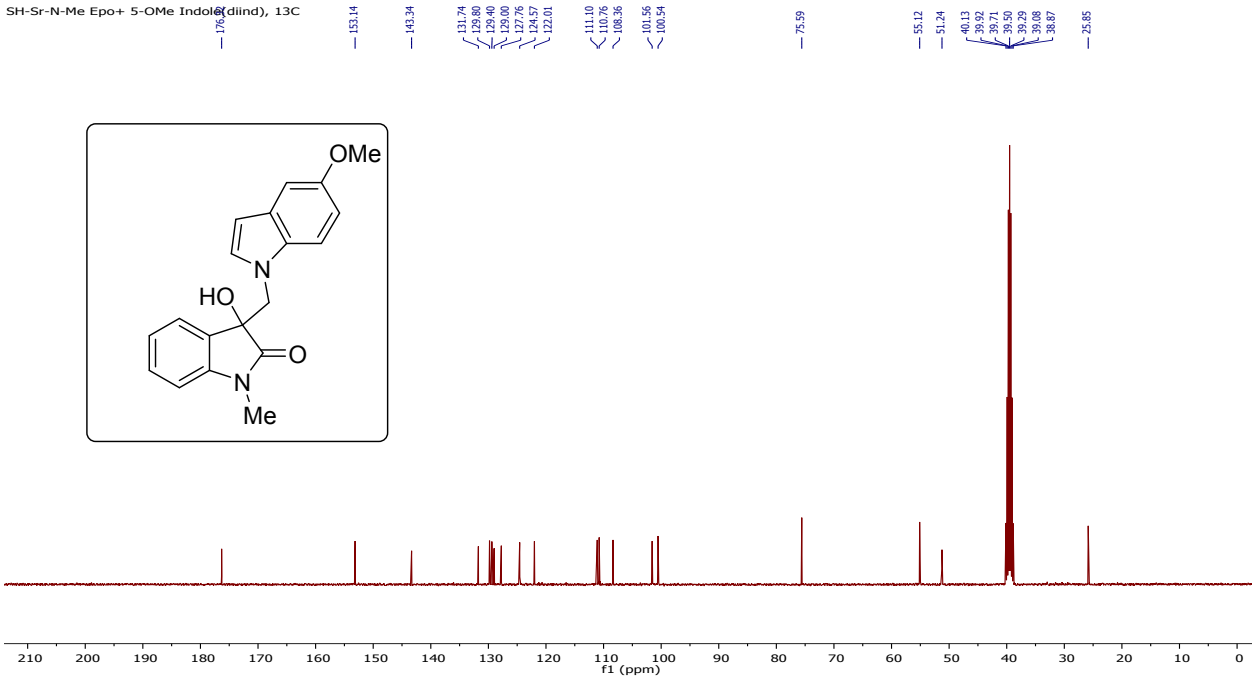
^{1}H NMR Spectrum of Compound **4o** (400 MHz, DMSO-d_6).



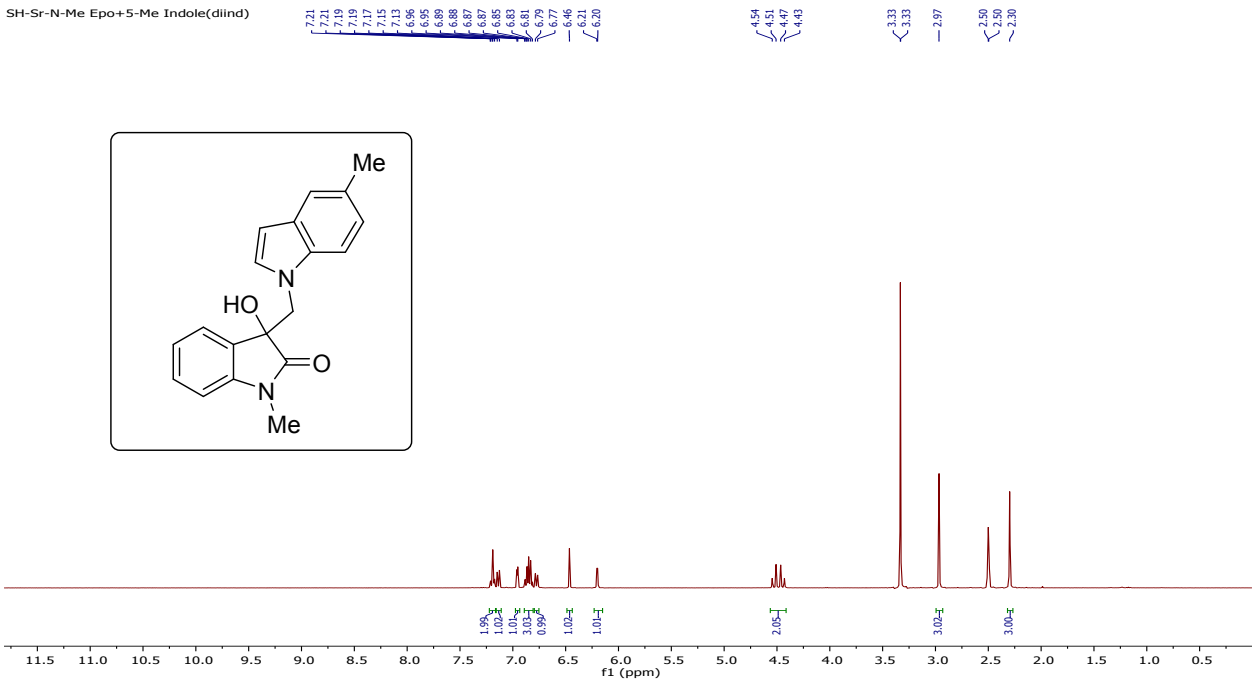
^{13}C NMR Spectrum of Compound **4o** (100 MHz, DMSO-d_6).



^{1}H NMR Spectrum of Compound **4p** (400 MHz, DMSO-d_6).



^{13}C NMR Spectrum of Compound **4p** (100 MHz, DMSO-d_6).



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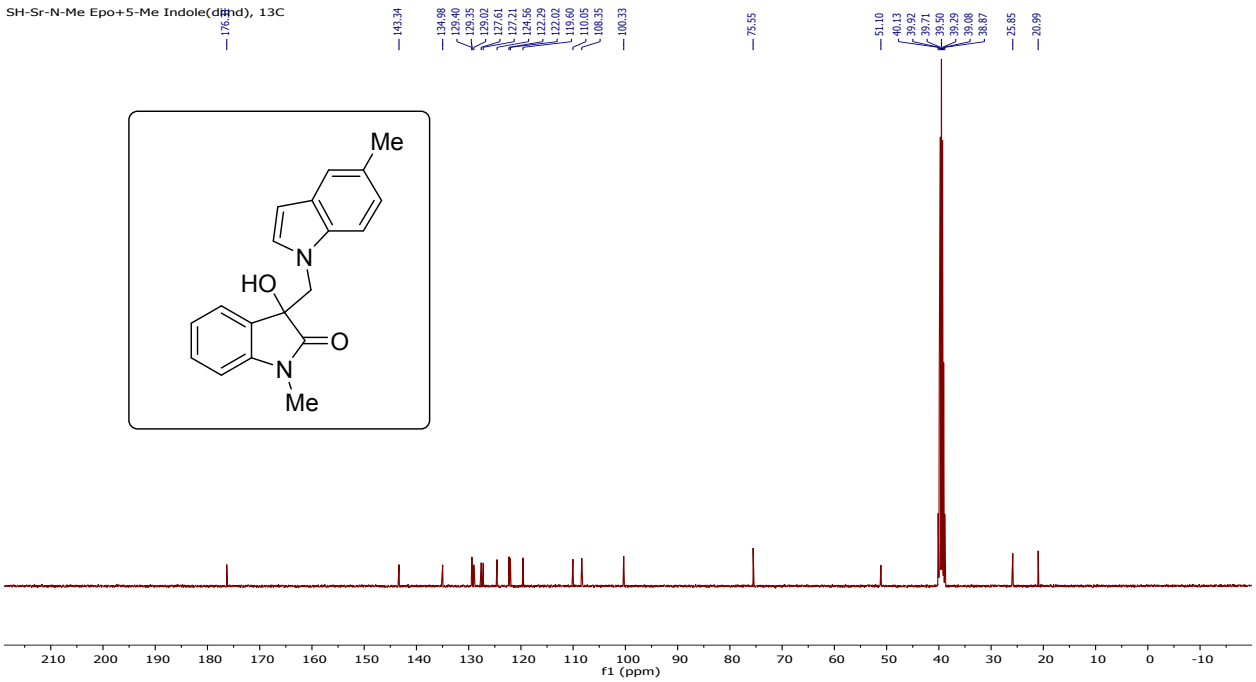
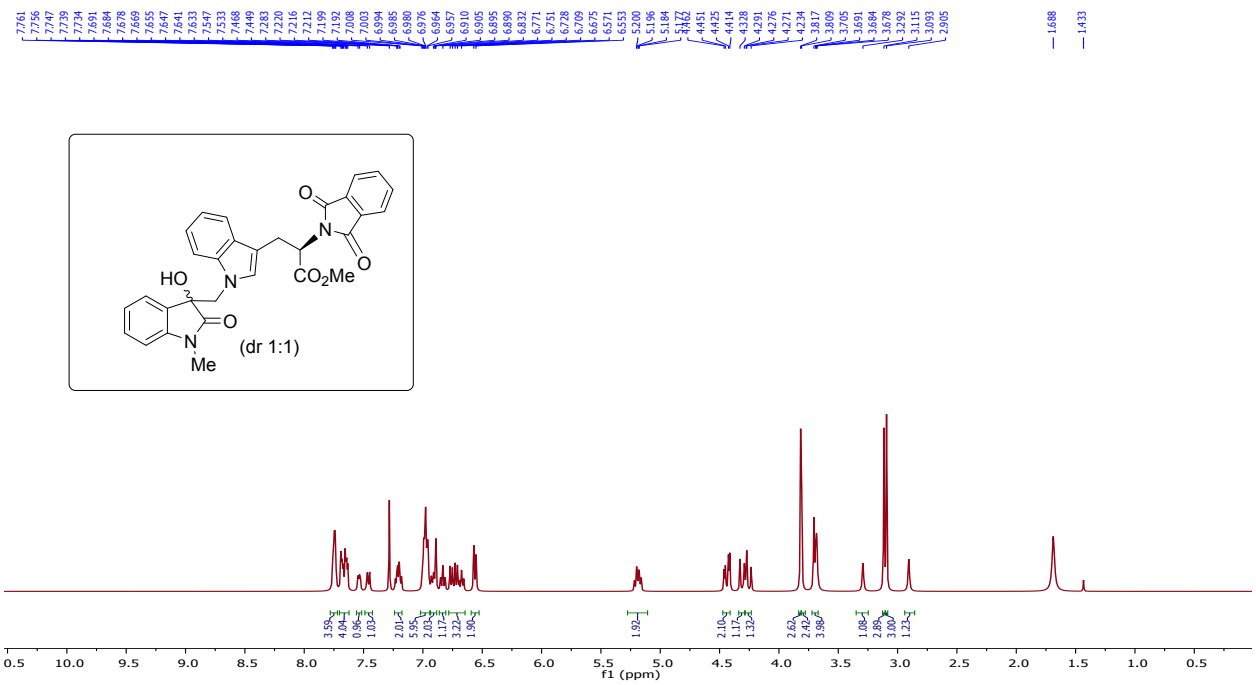
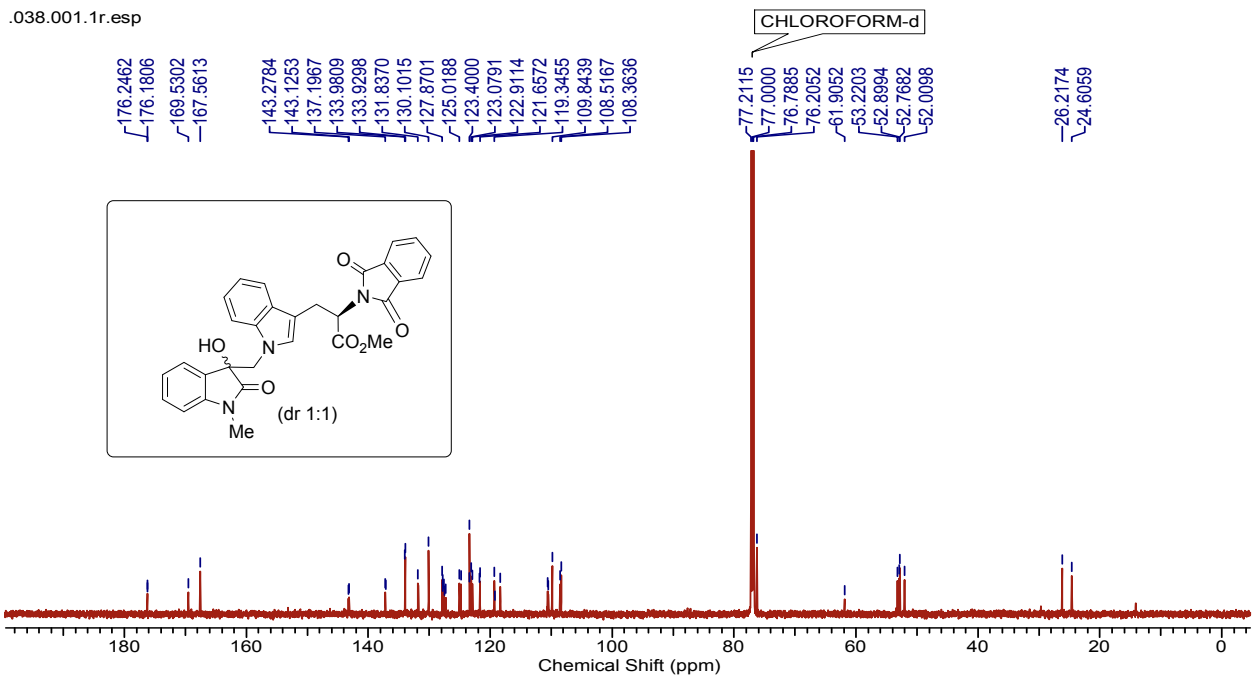


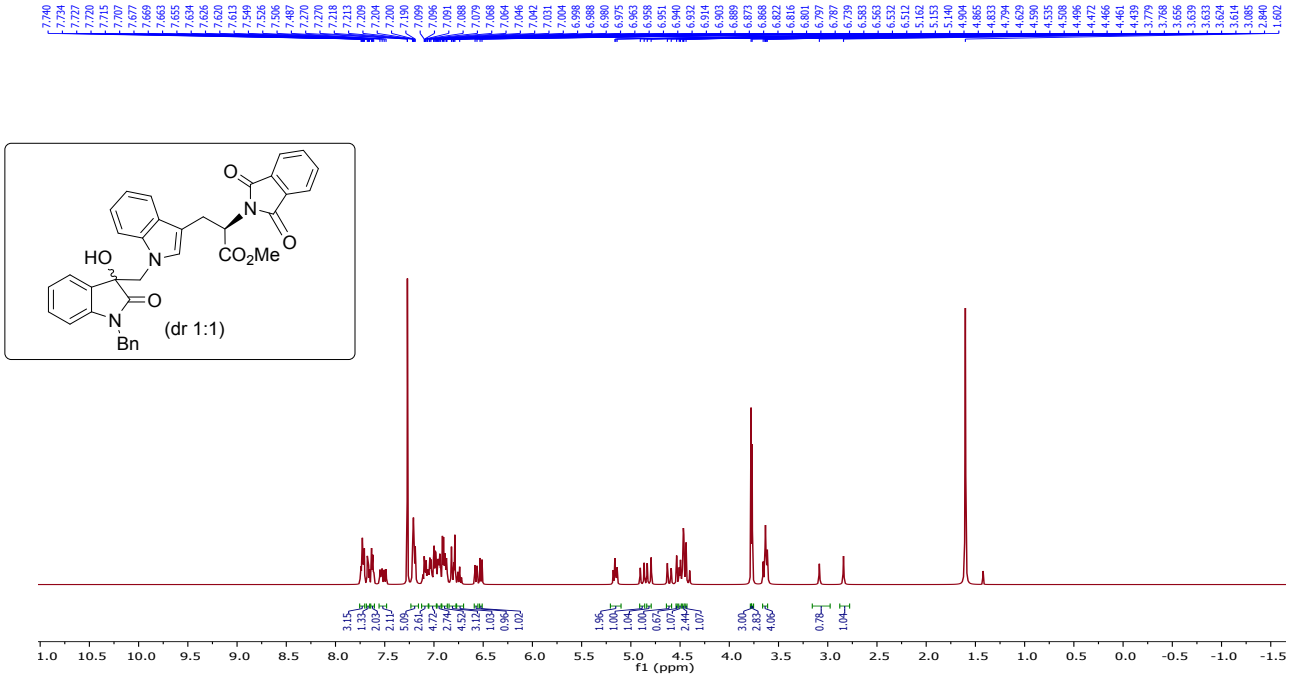
^{13}C NMR Spectrum of Compound **4q** (100 MHz, DMSO-d_6).



^{1}H NMR Spectrum of Compound **4r** (400 MHz, $CDCl_3$).



^{13}C NMR Spectrum of Compound **4r** (150 MHz, $CDCl_3$).



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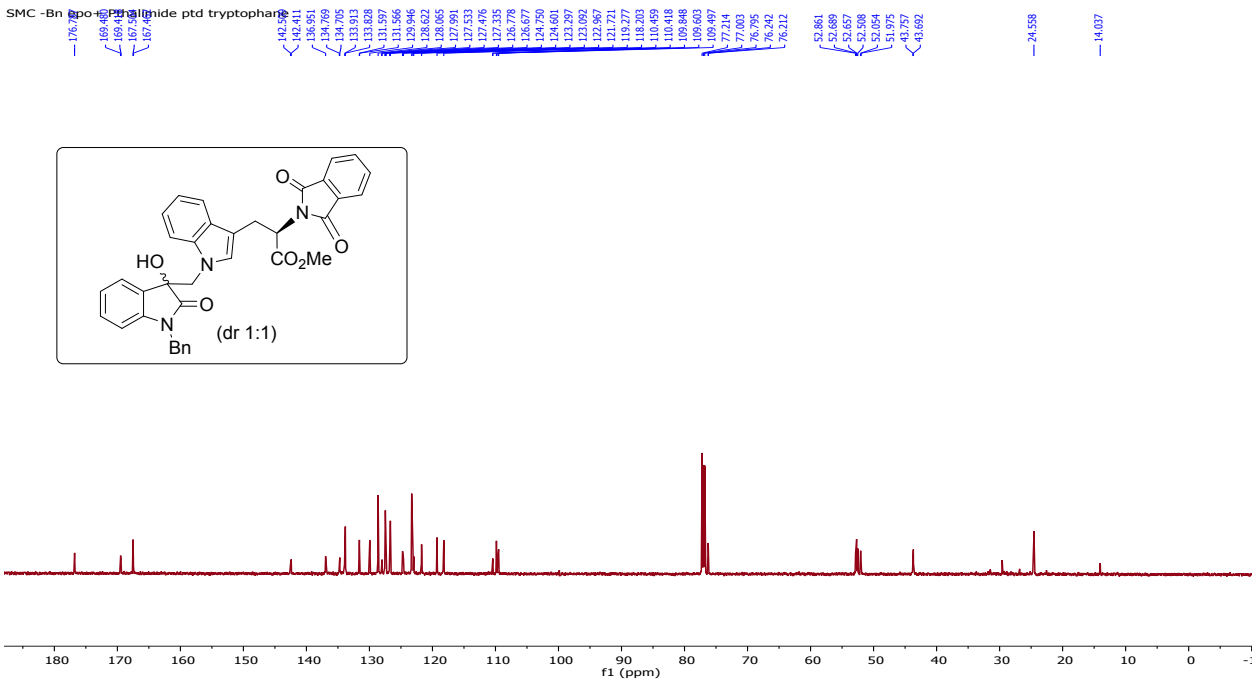
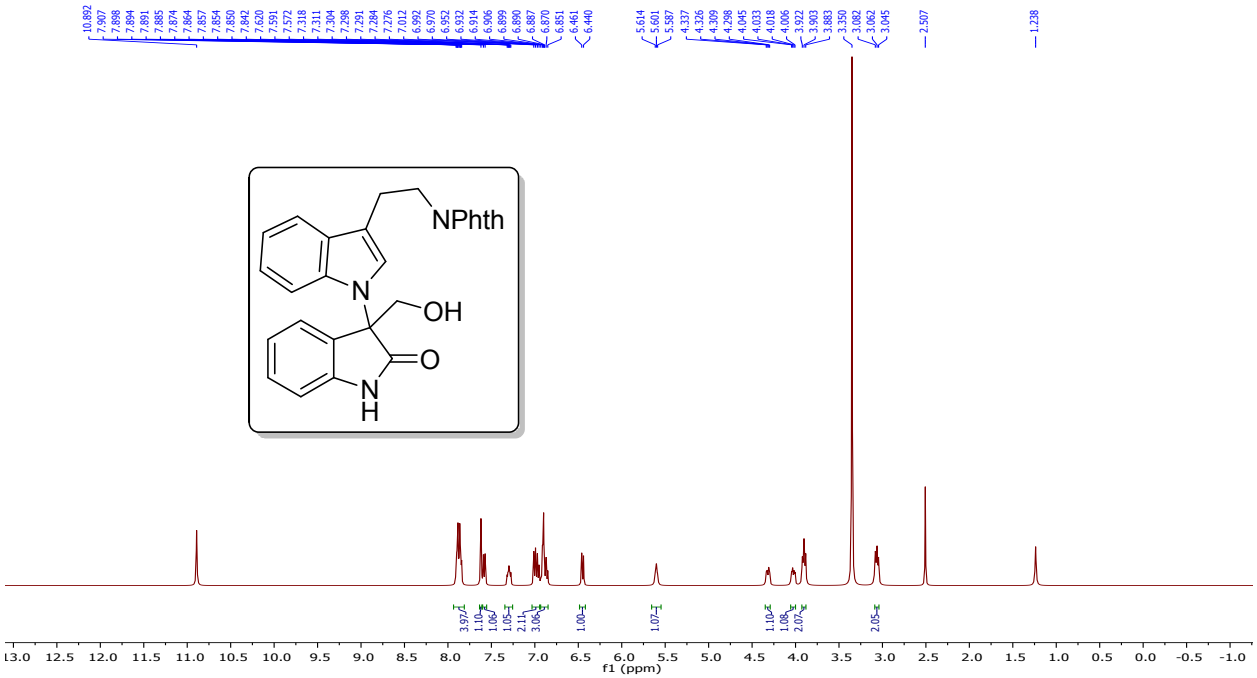
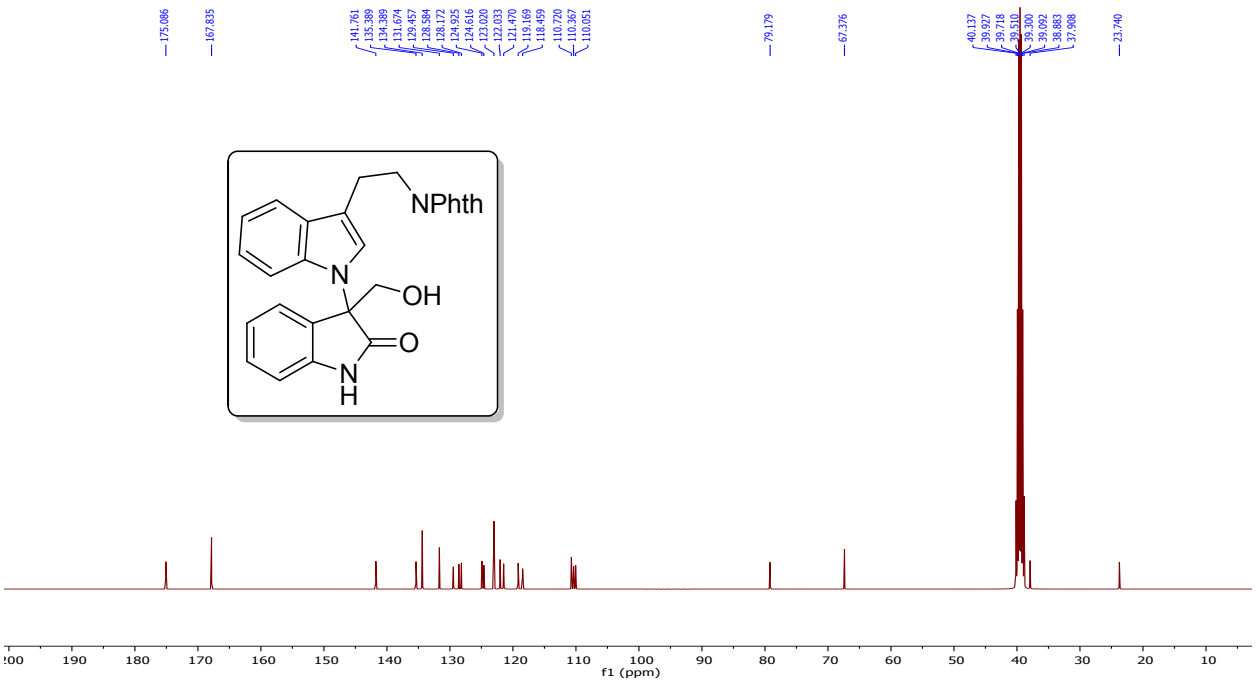


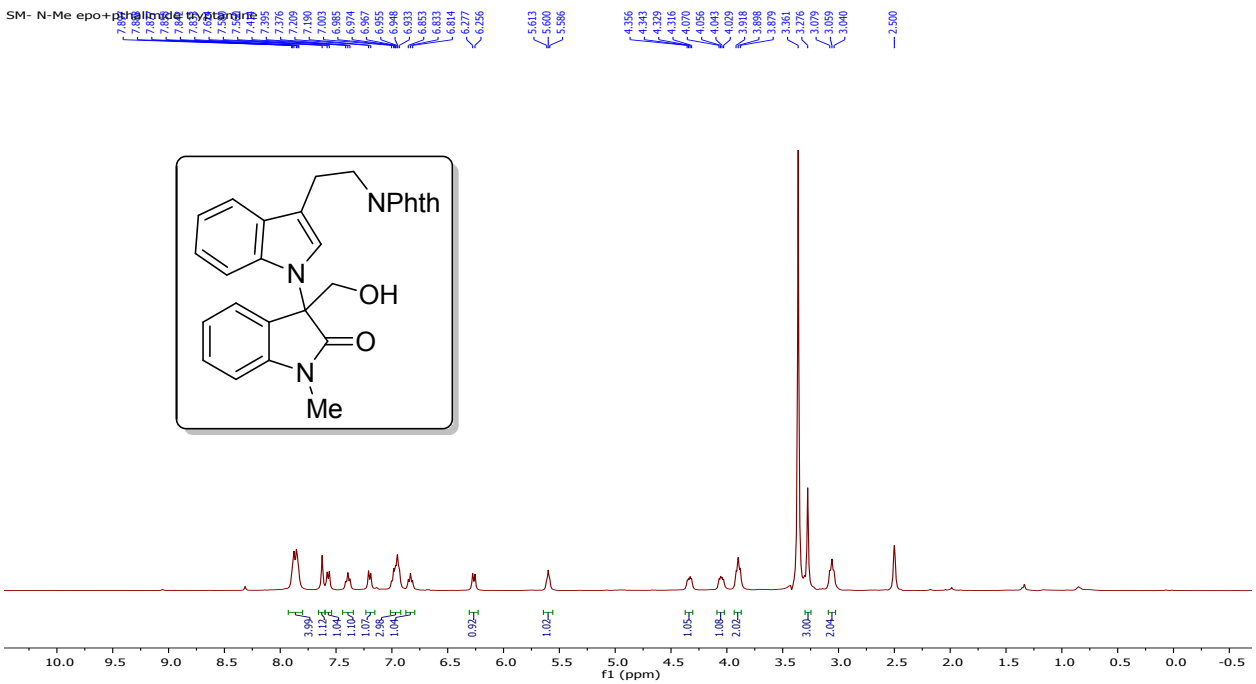
^{13}C NMR Spectrum of Compound **4s** (150 MHz, $CDCl_3$).



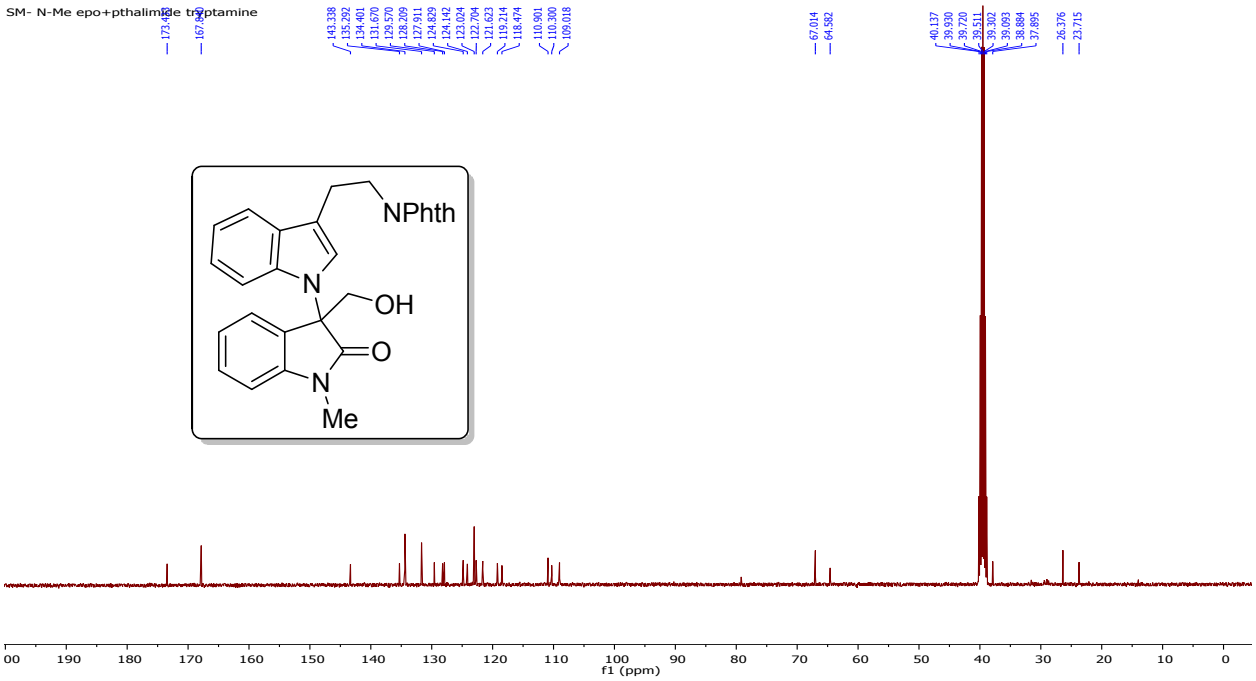
^{1}H NMR Spectrum of Compound **1a** (400MHz, DMSO-d_6)



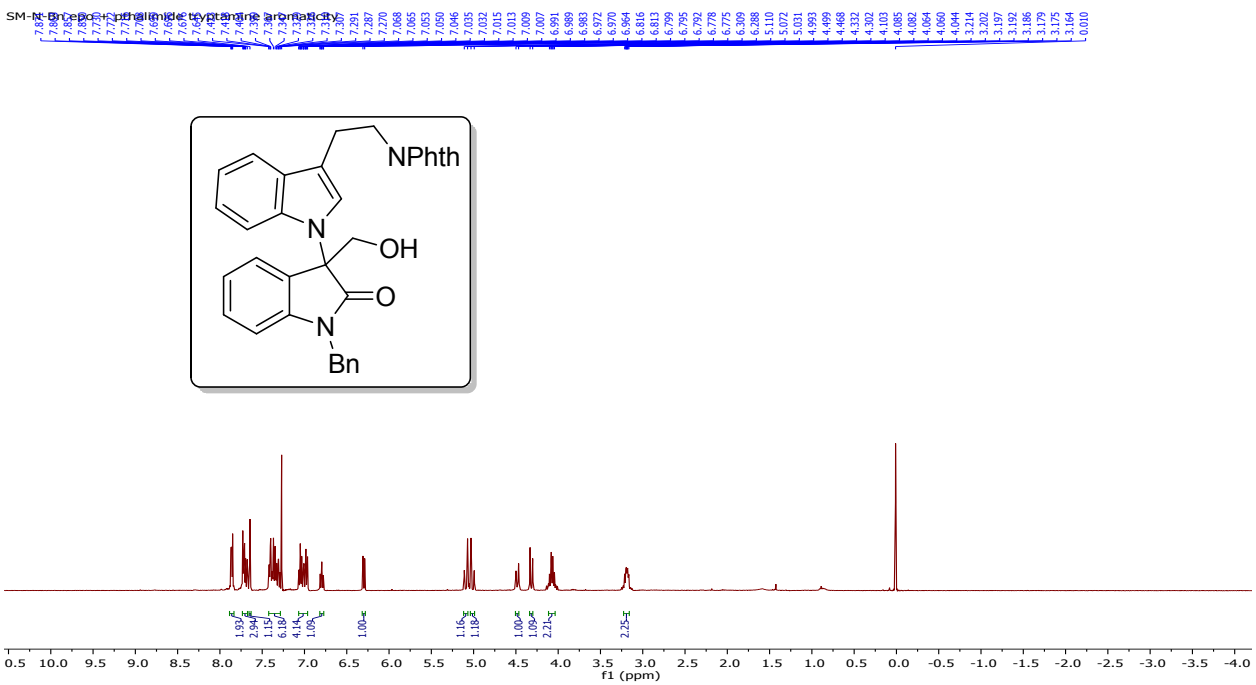
^{13}C NMR Spectrum of Compound **1a** (100MHz, DMSO-d_6).



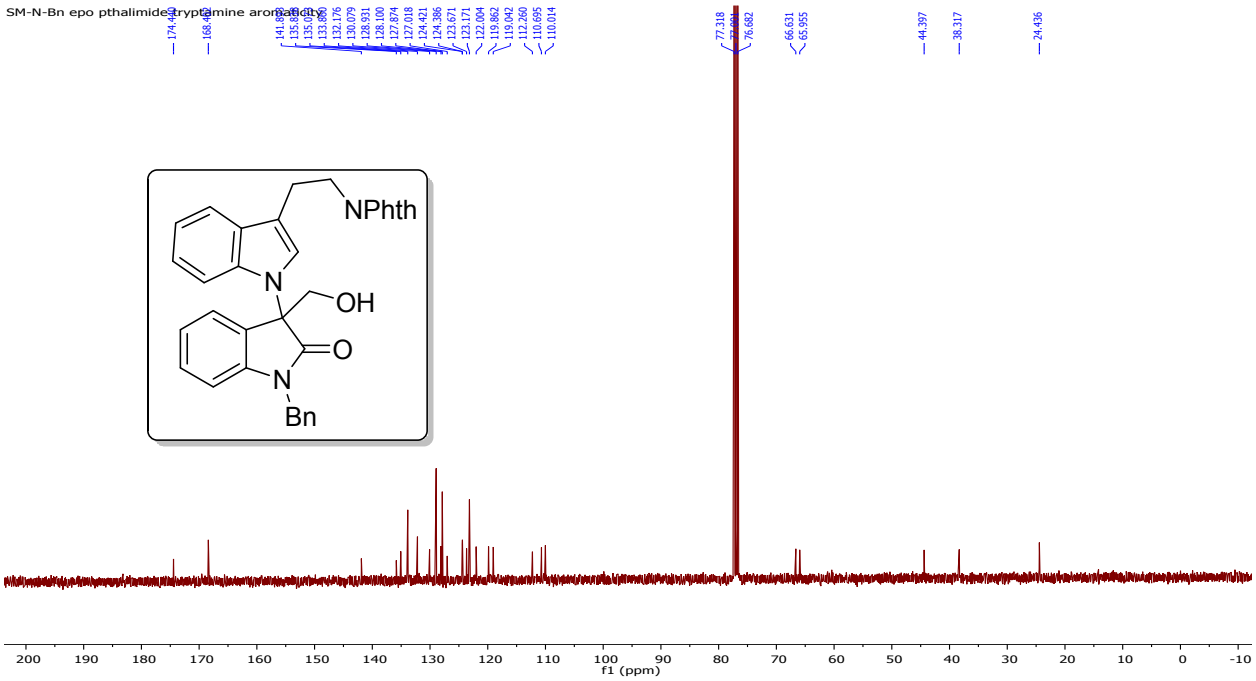
^{1}H NMR Spectrum of Compound **1b** (400MHz, DMSO-d_6)



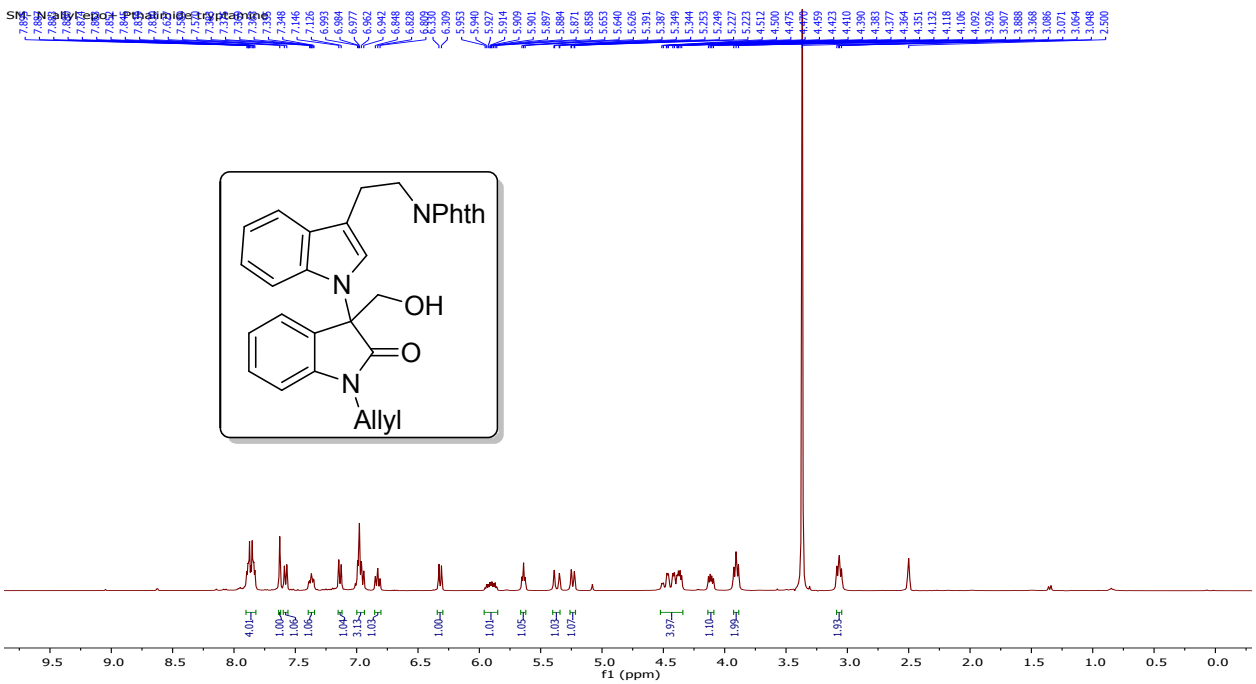
^{13}C NMR Spectrum of Compound **1b** (100MHz, DMSO-d_6)



^{1}H NMR Spectrum of Compound **1c** (400MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound **1c** (100MHz, $CDCl_3$)



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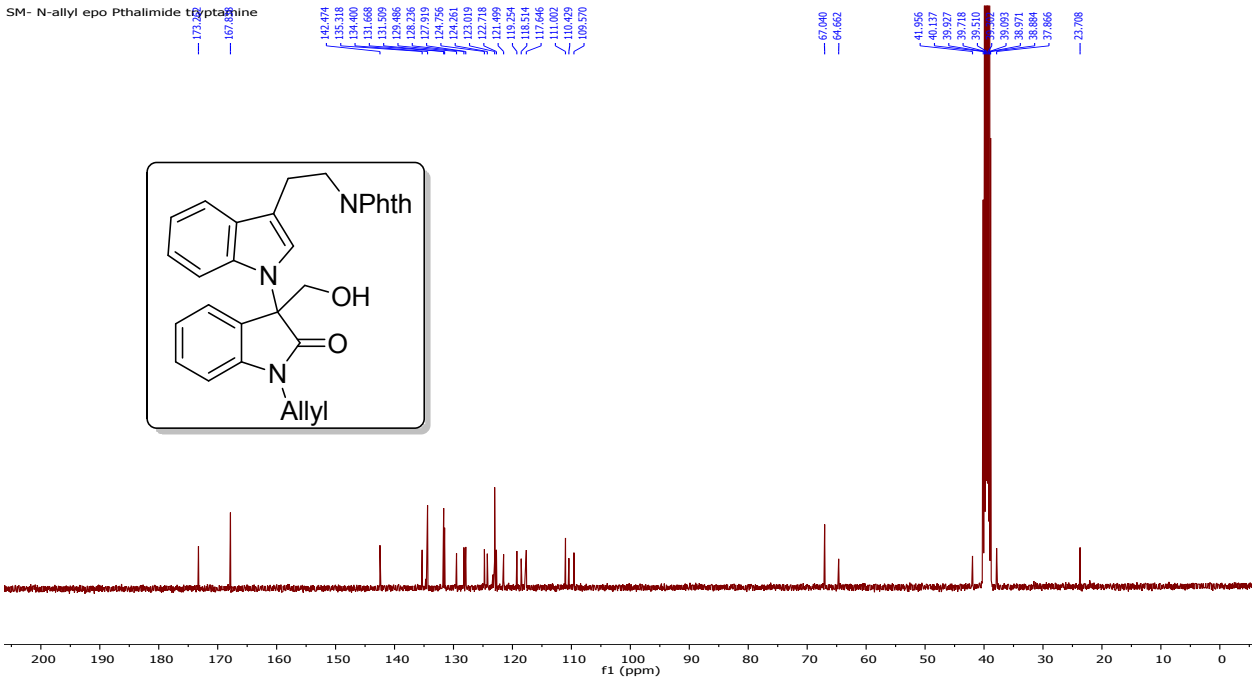
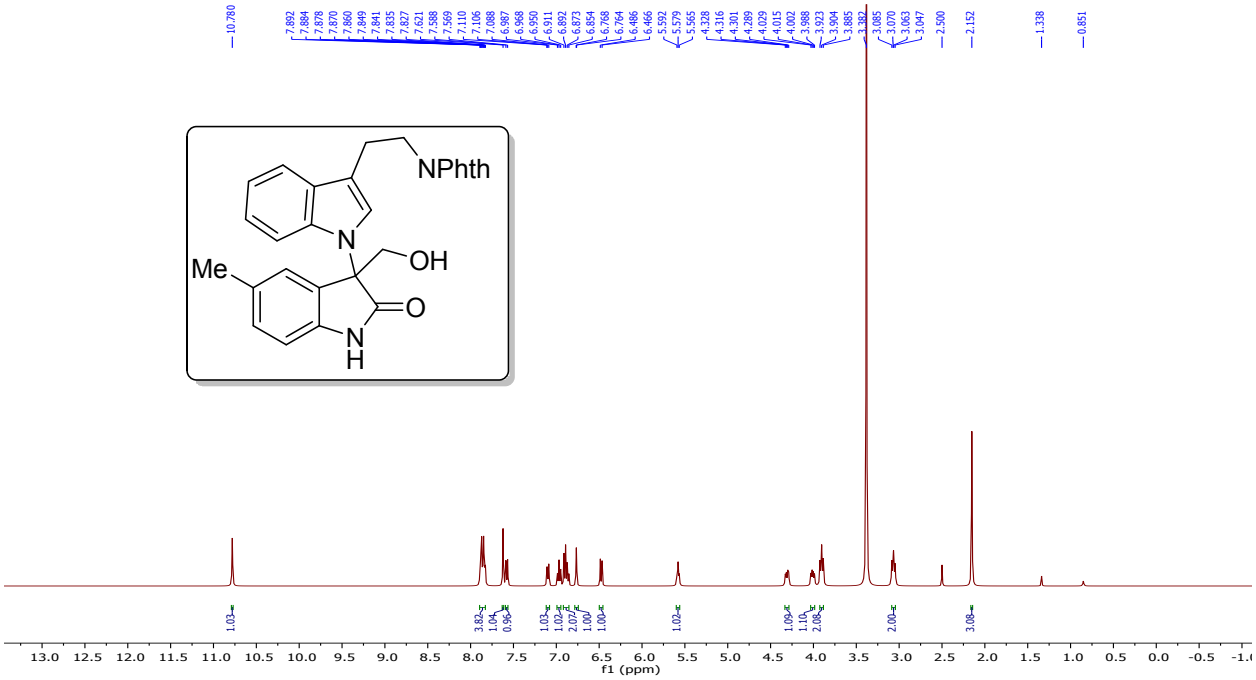
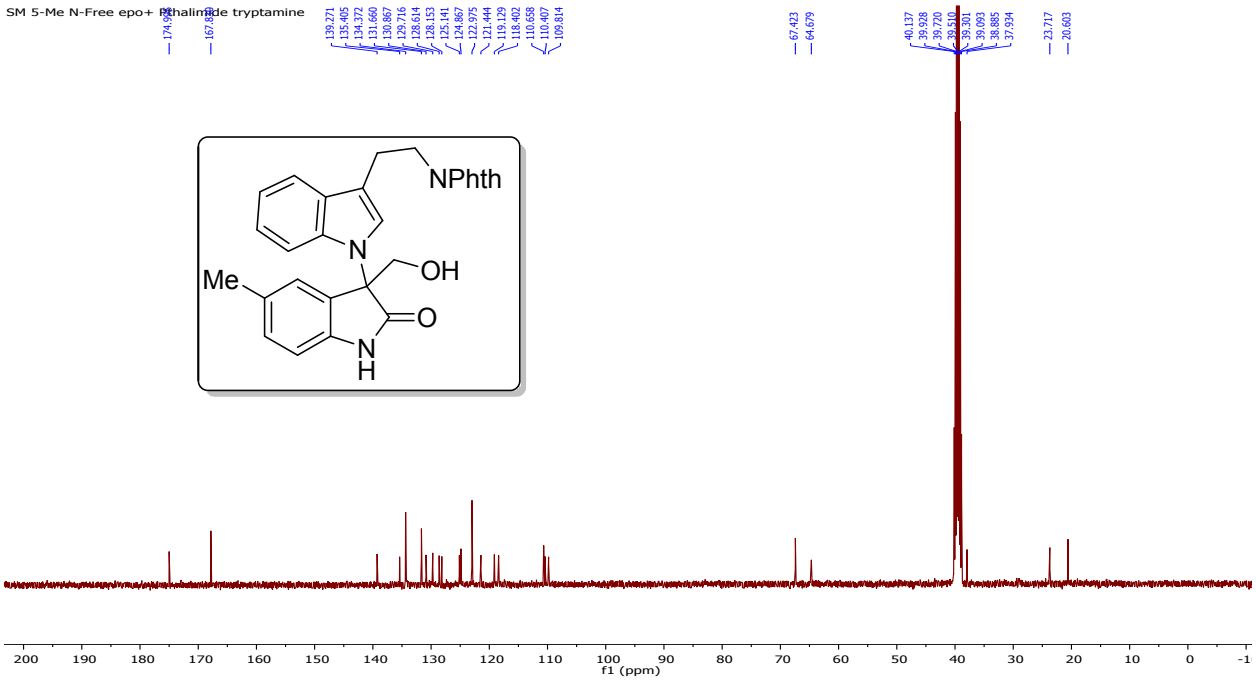


^{13}C NMR Spectrum of Compound **1d** (100MHz, DMSO-d_6).



^{1}H NMR Spectrum of Compound **1e** (400MHz, DMSO-d_6)



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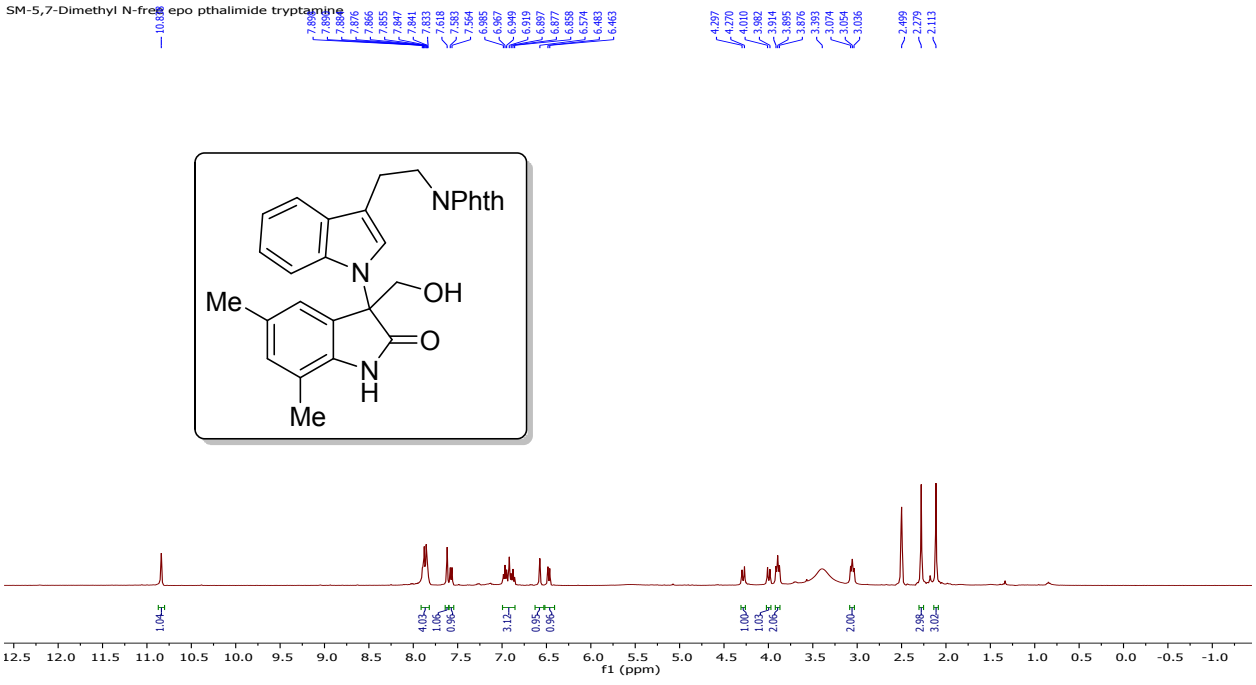
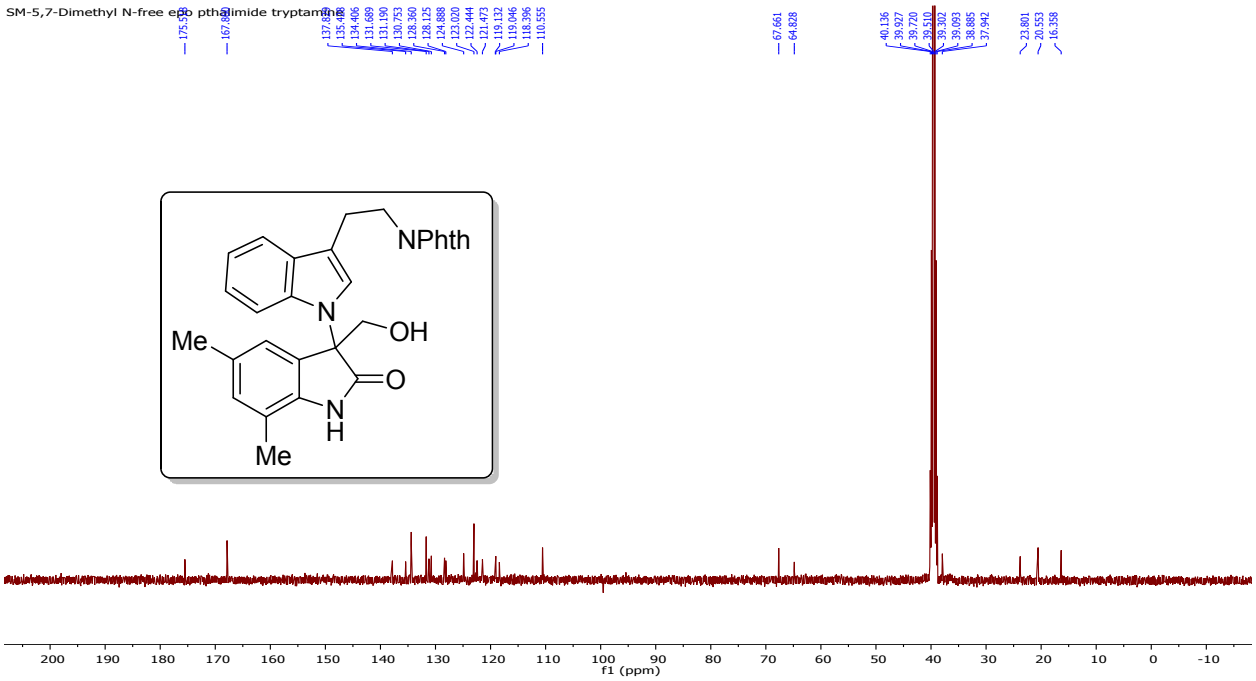
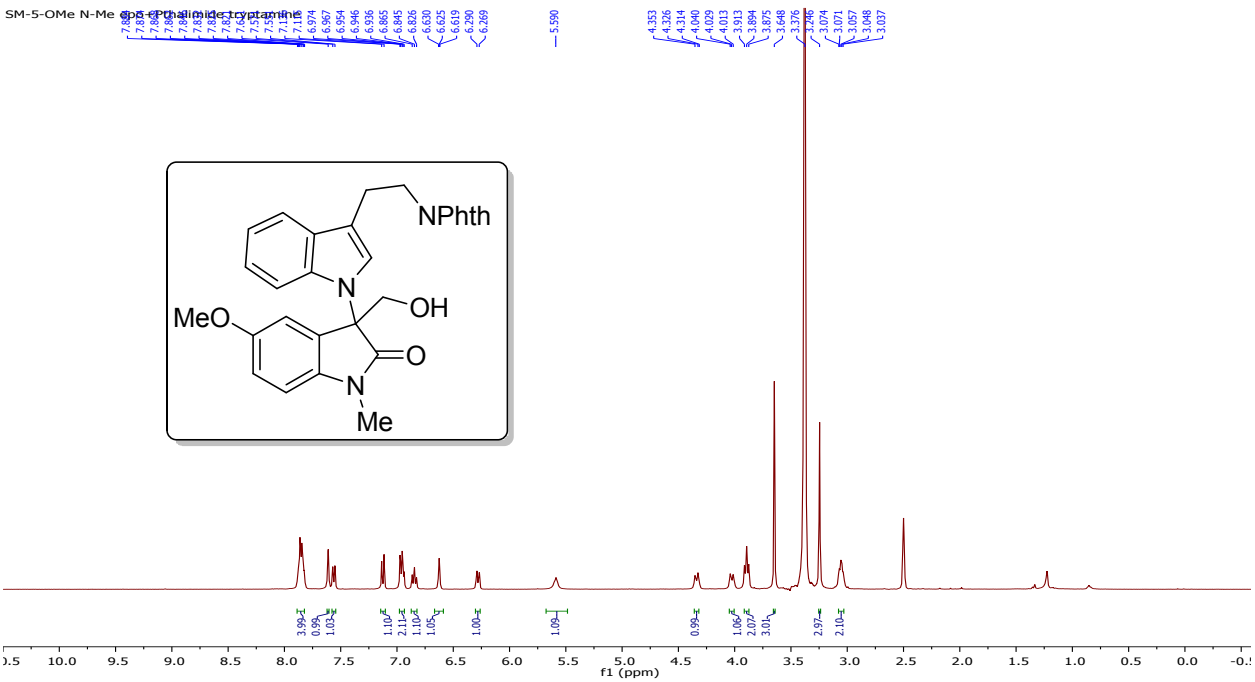


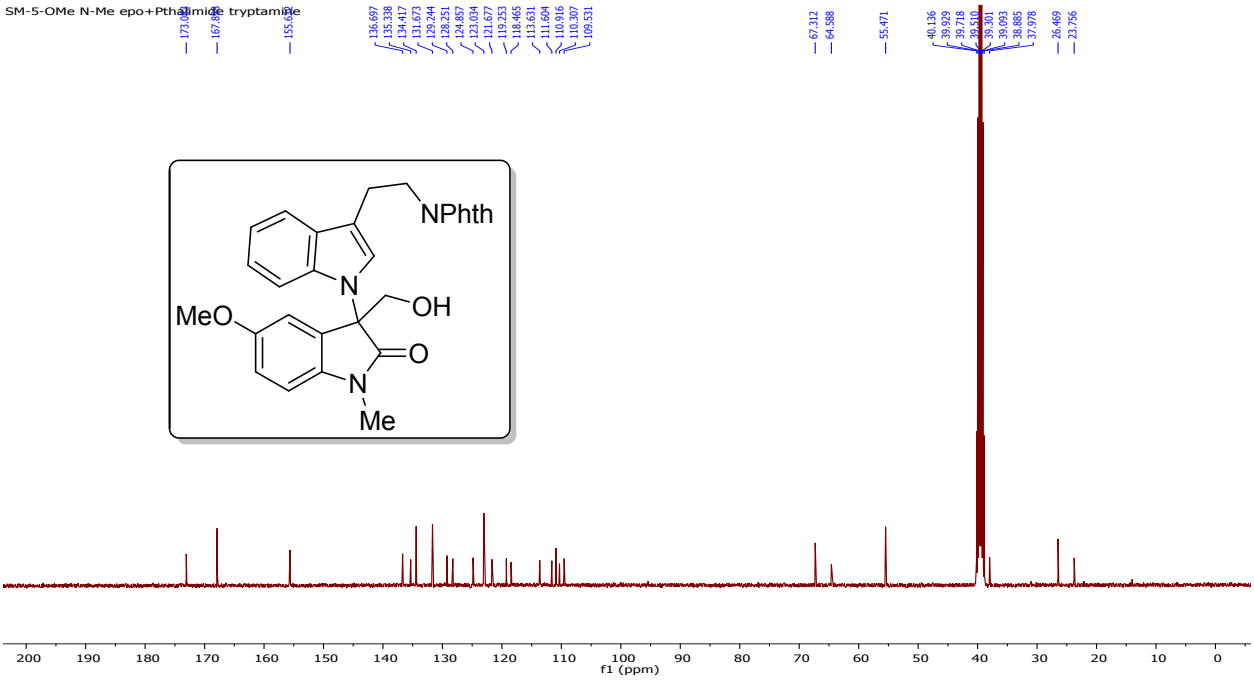
^{1}H NMR Spectrum of Compound **1f** (400MHz, DMSO-d_6)



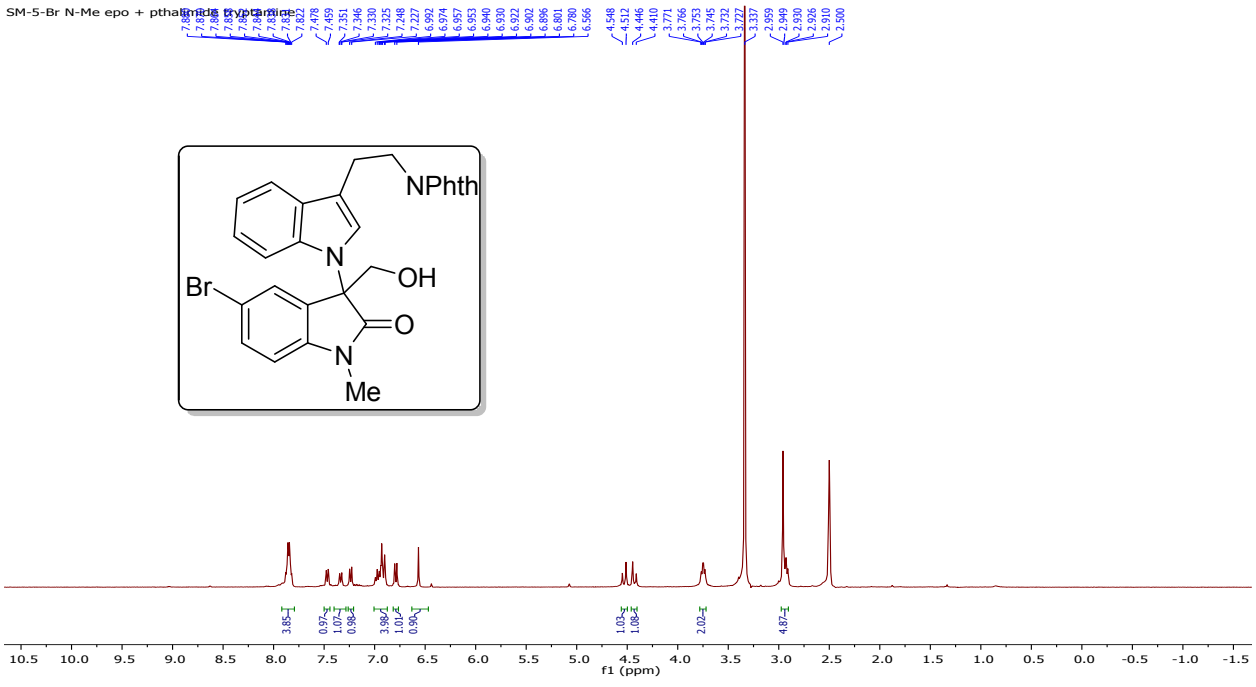
^{13}C NMR Spectrum of Compound **1f** (100MHz, DMSO-d_6).



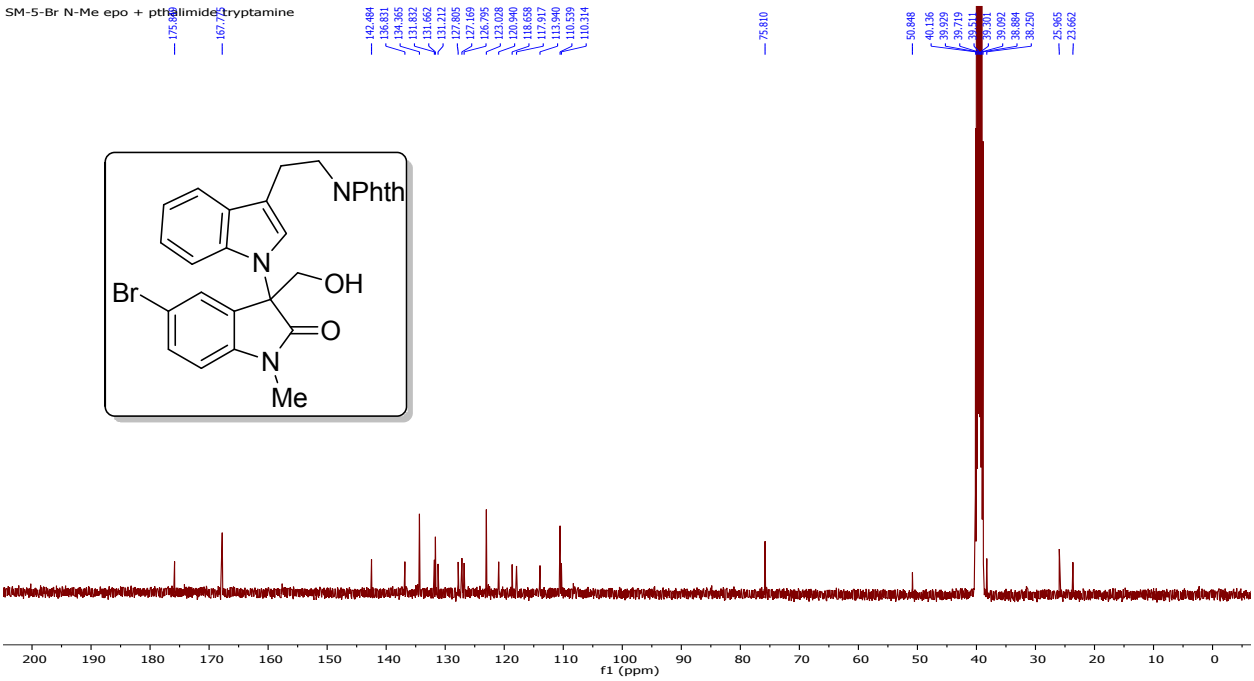
^{1}H NMR Spectrum of Compound **1g** (400MHz, DMSO-d_6)



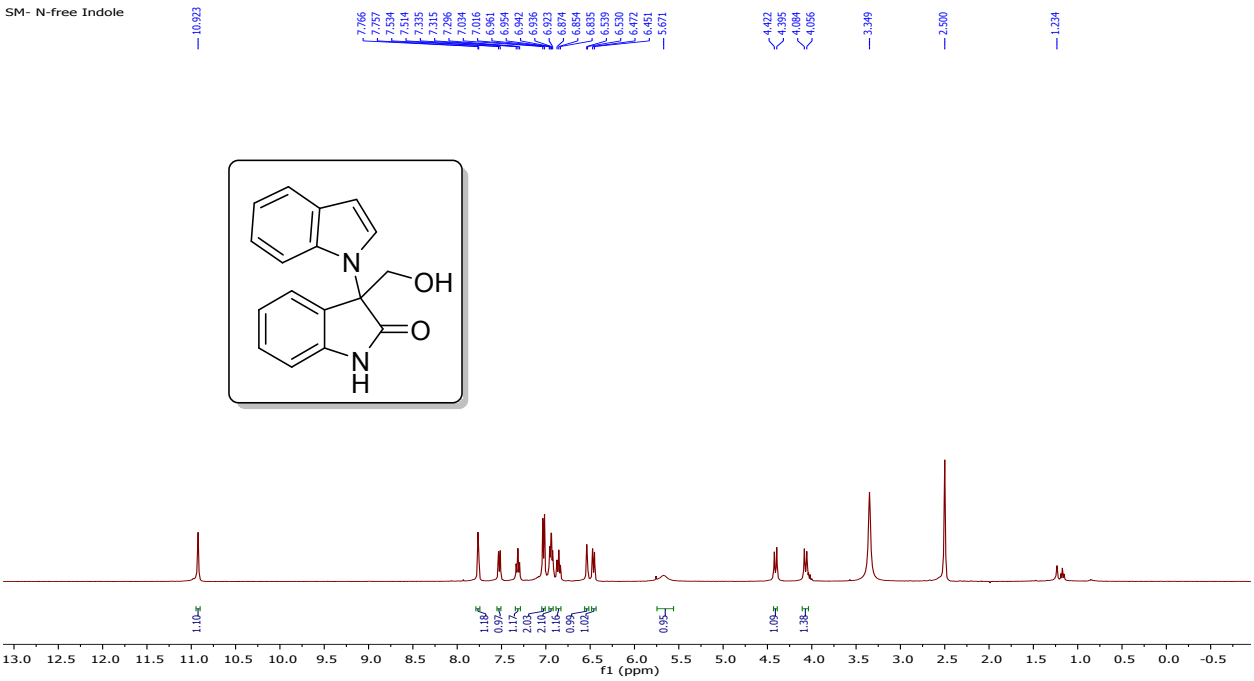
^{13}C NMR Spectrum of Compound **1g** (100MHz, DMSO-d_6).



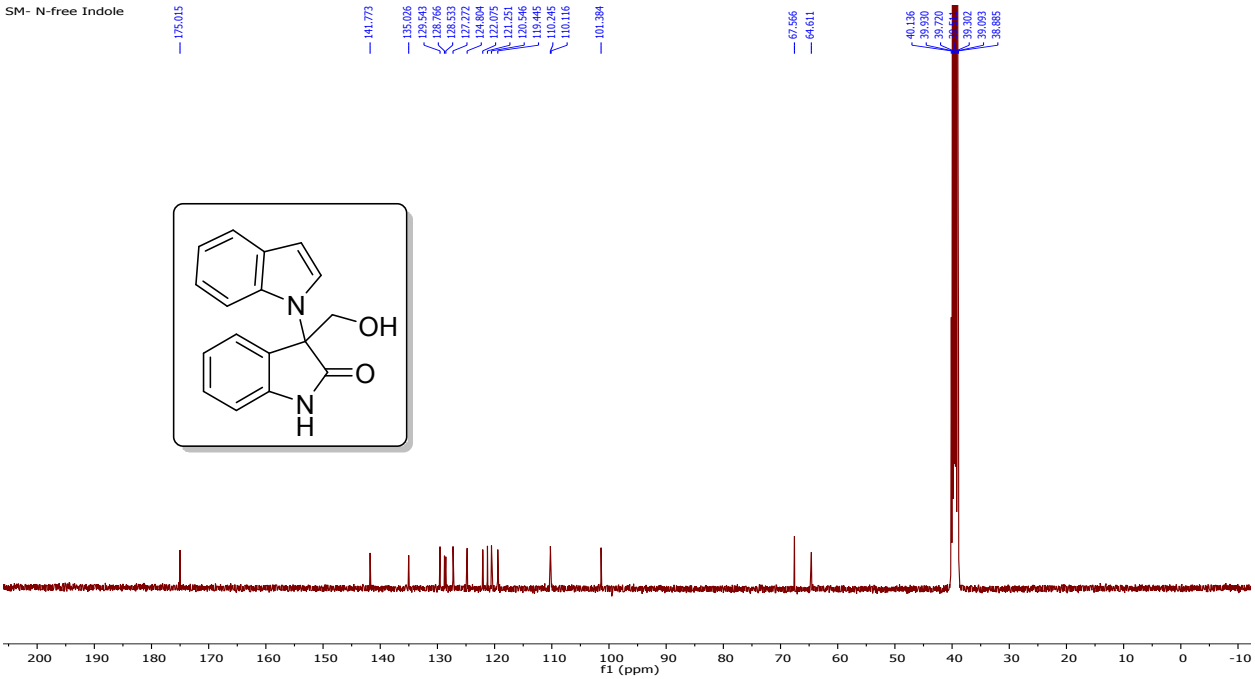
^{1}H NMR Spectrum of Compound **1h** (400MHz, DMSO-d_6)



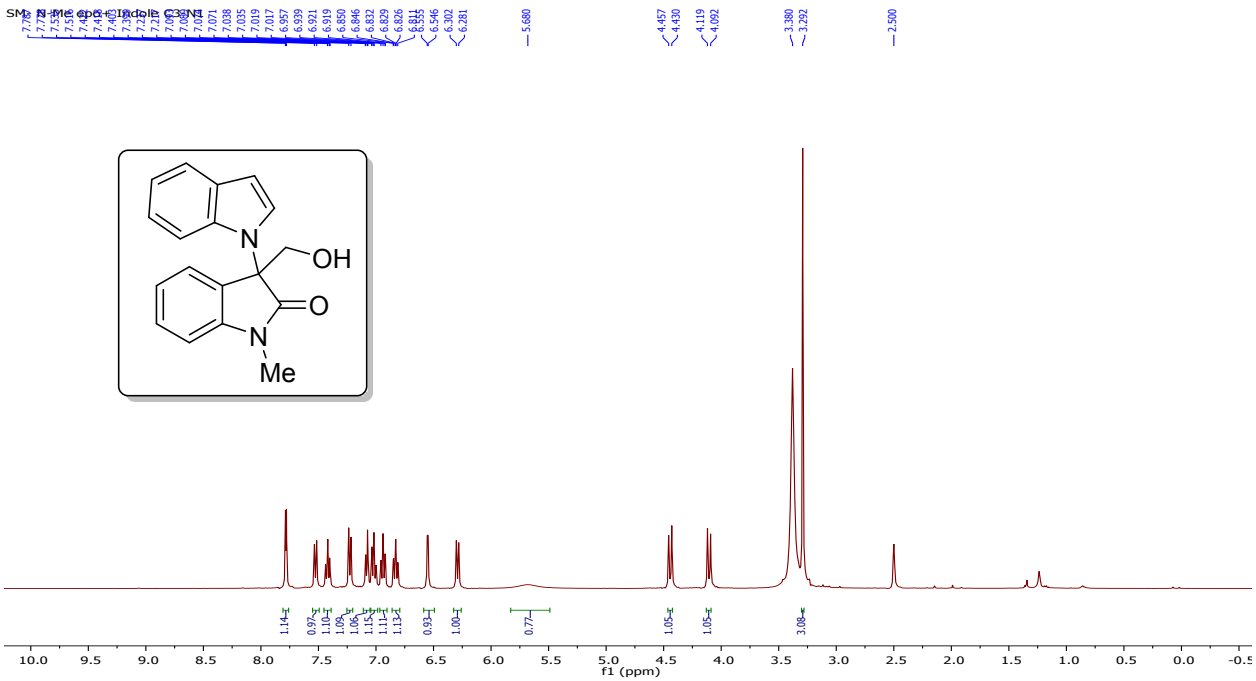
^{13}C NMR Spectrum of Compound **1h** (100MHz, DMSO-d_6).



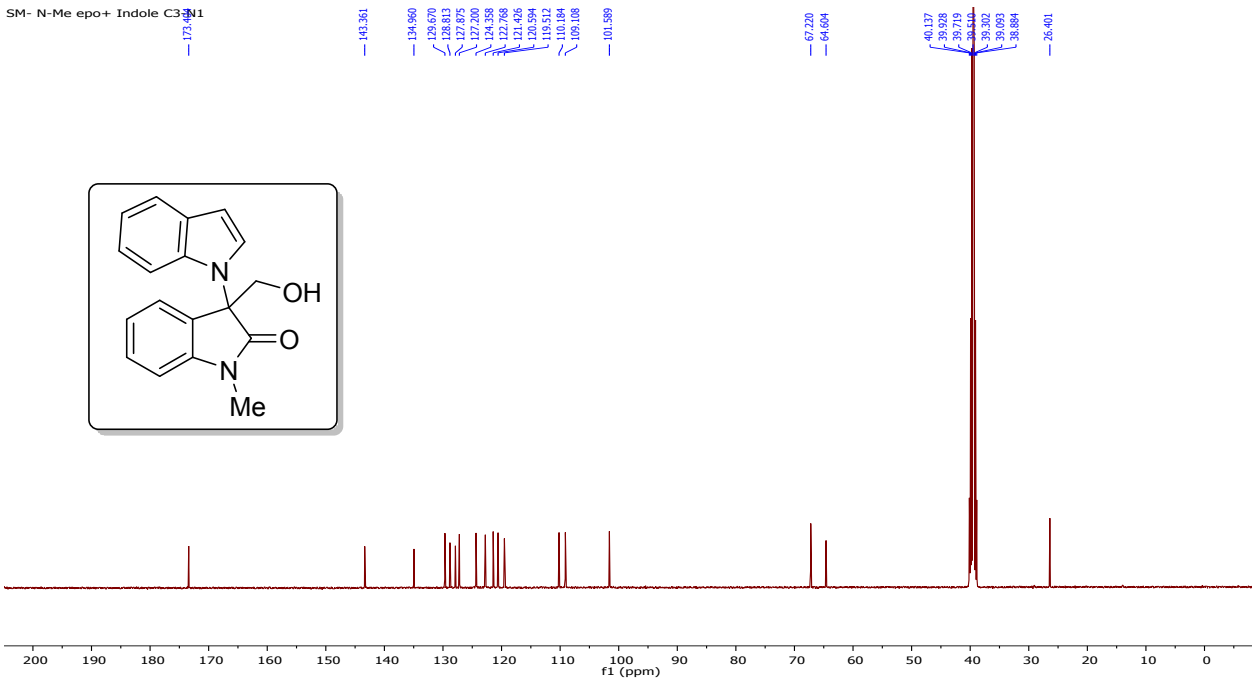
^{1}H NMR Spectrum of Compound **1i** (400MHz, DMSO-d_6)



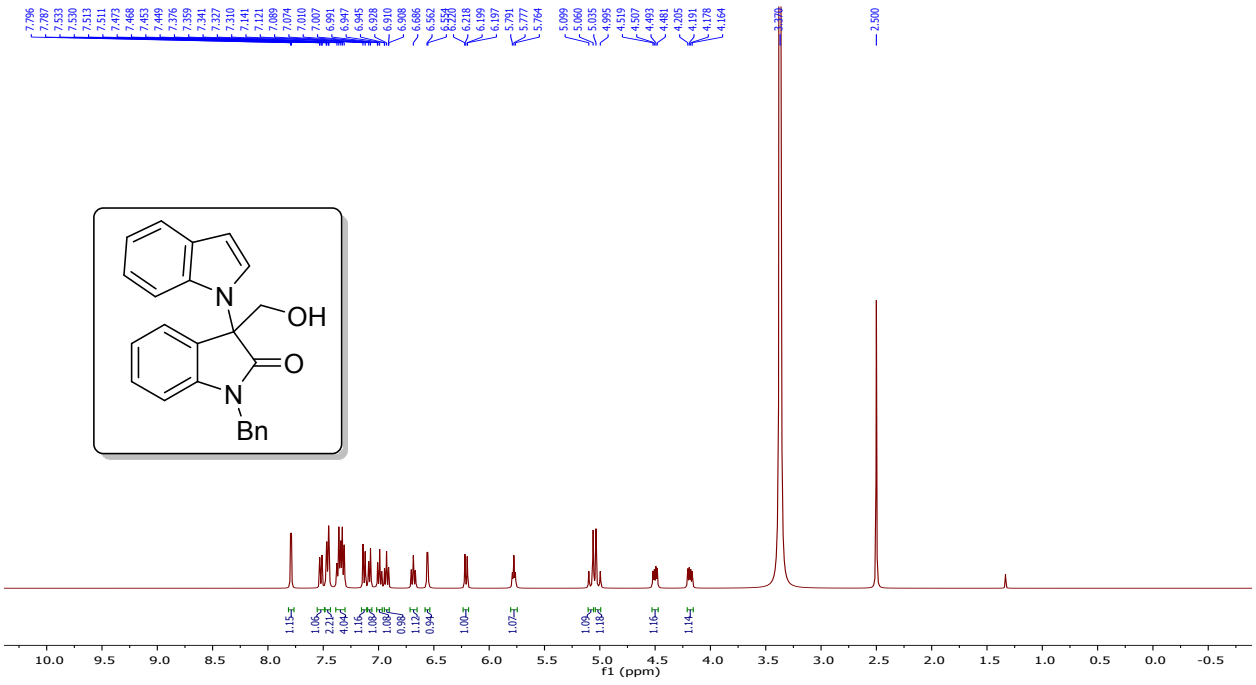
^{13}C NMR Spectrum of Compound **1i** (100MHz, DMSO-d_6).



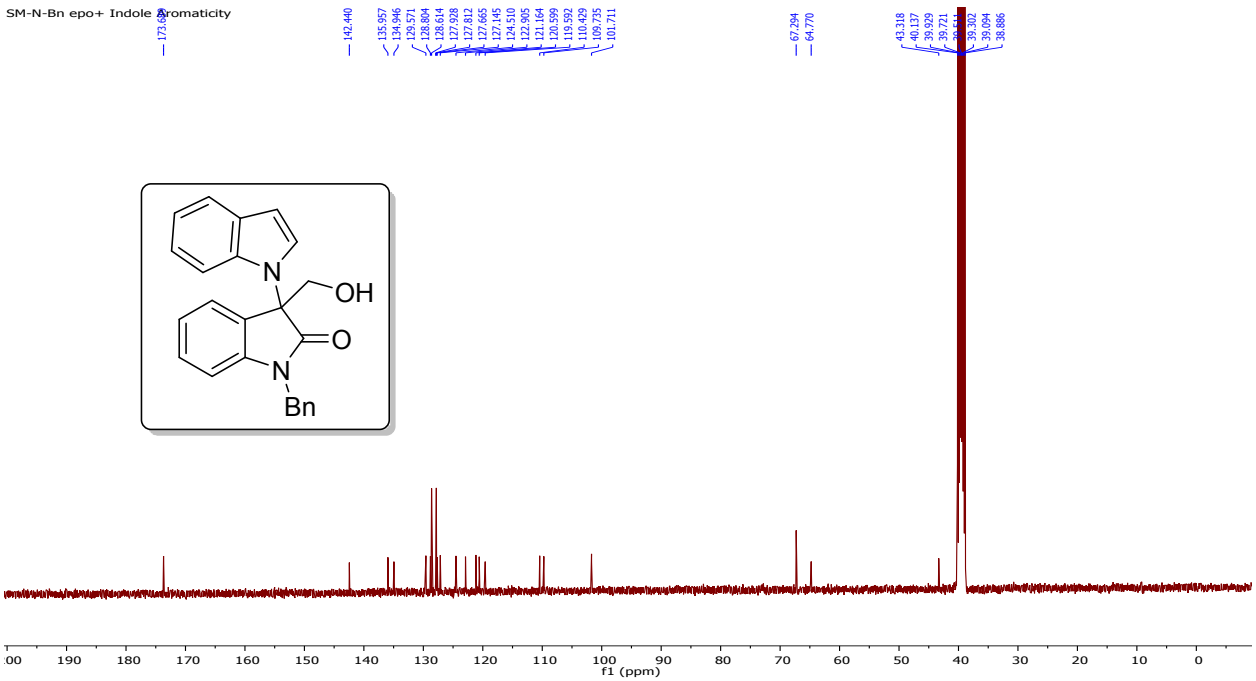
^{1}H NMR Spectrum of Compound **1j** (400MHz, DMSO-d_6)



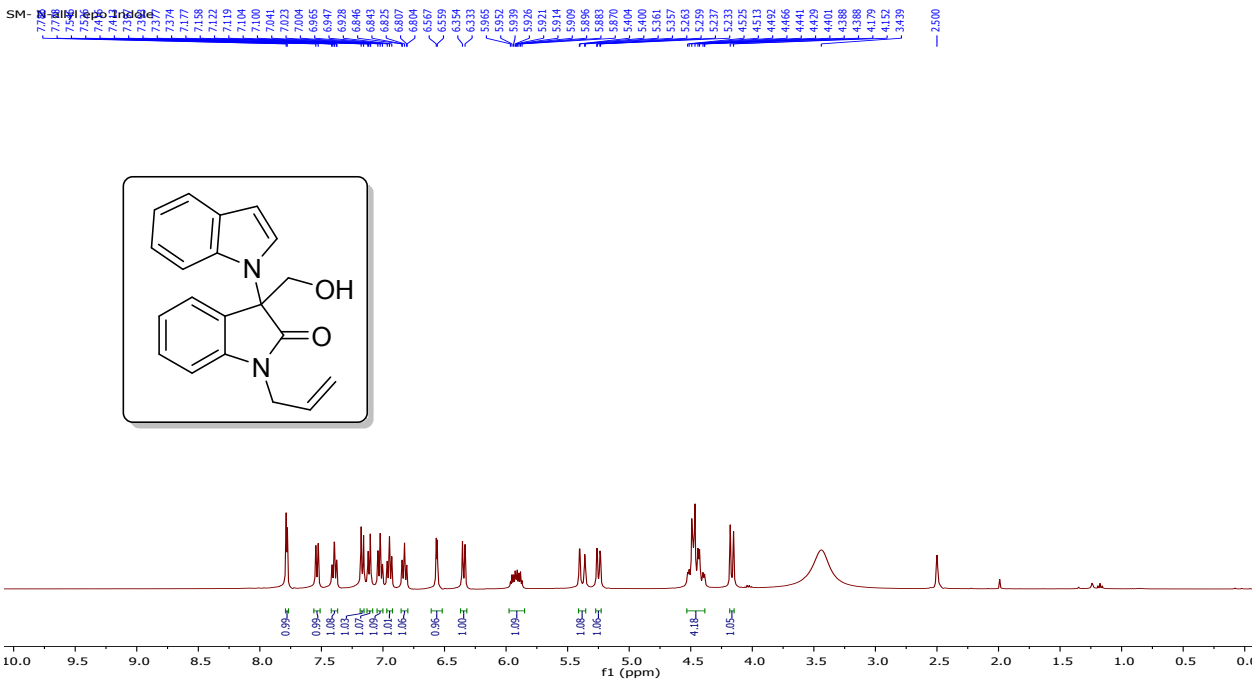
^{13}C NMR Spectrum of Compound **1j** (100MHz, DMSO-d_6)



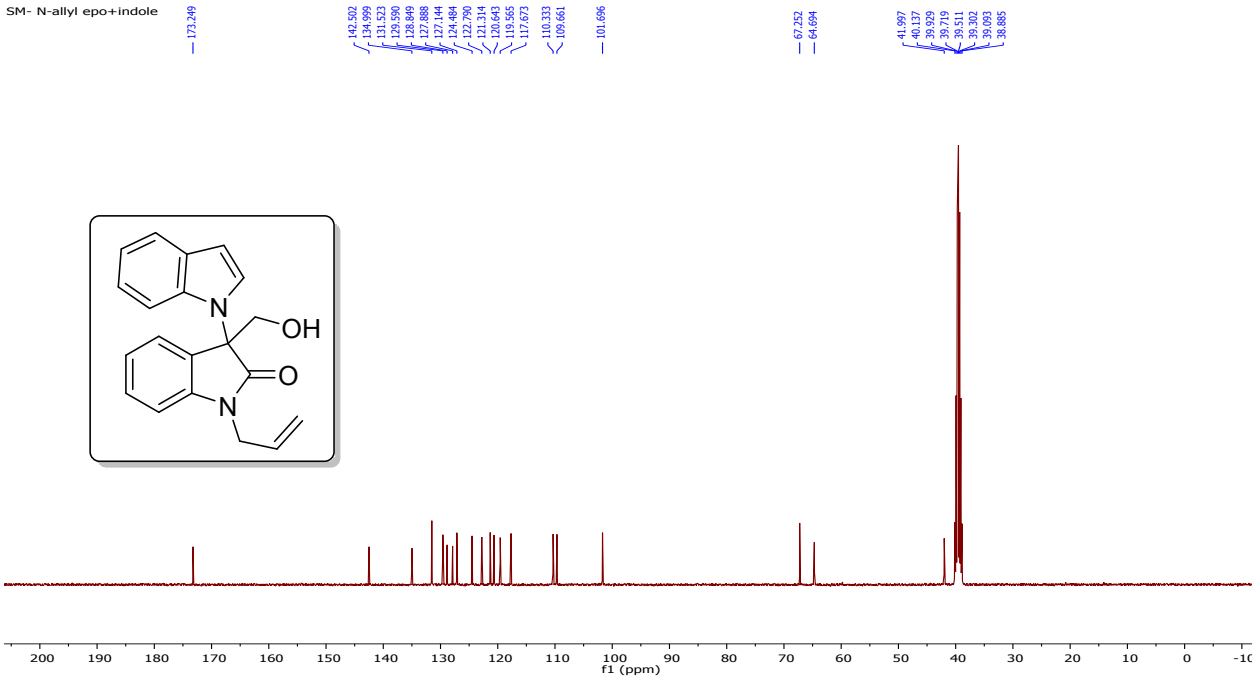
^{1}H NMR Spectrum of Compound **1k** (400MHz, DMSO-d_6)



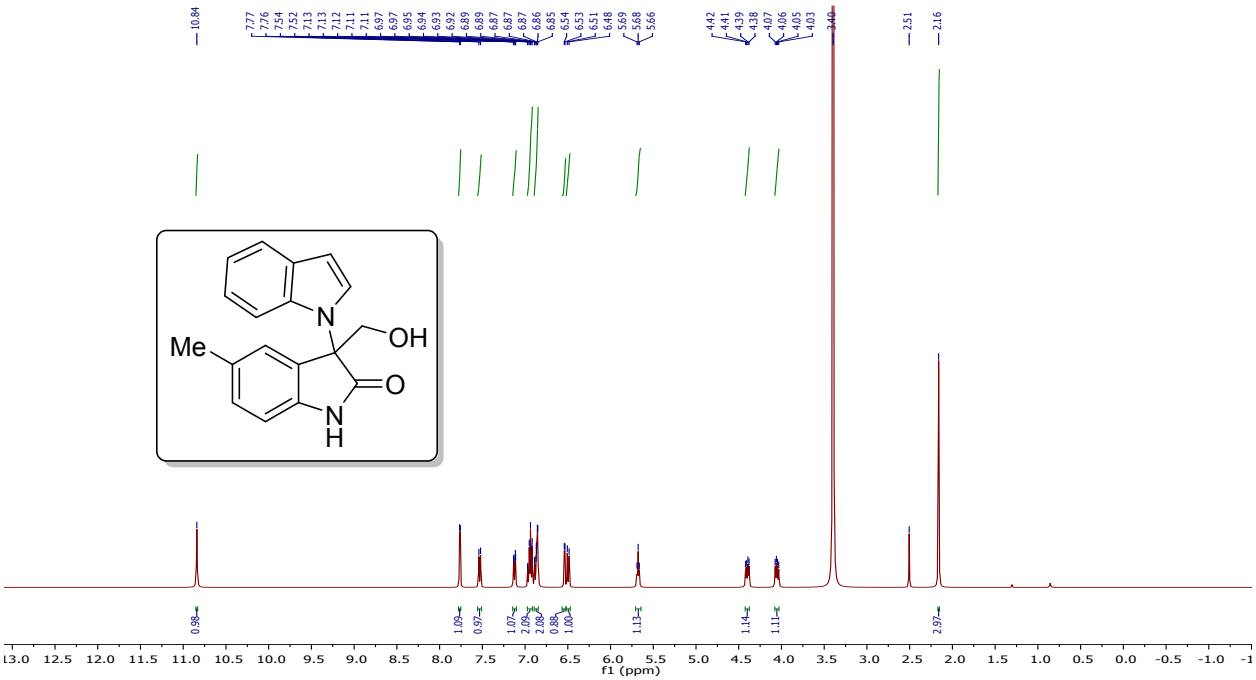
^{13}C NMR Spectrum of Compound **1k** (100MHz, DMSO-d_6).



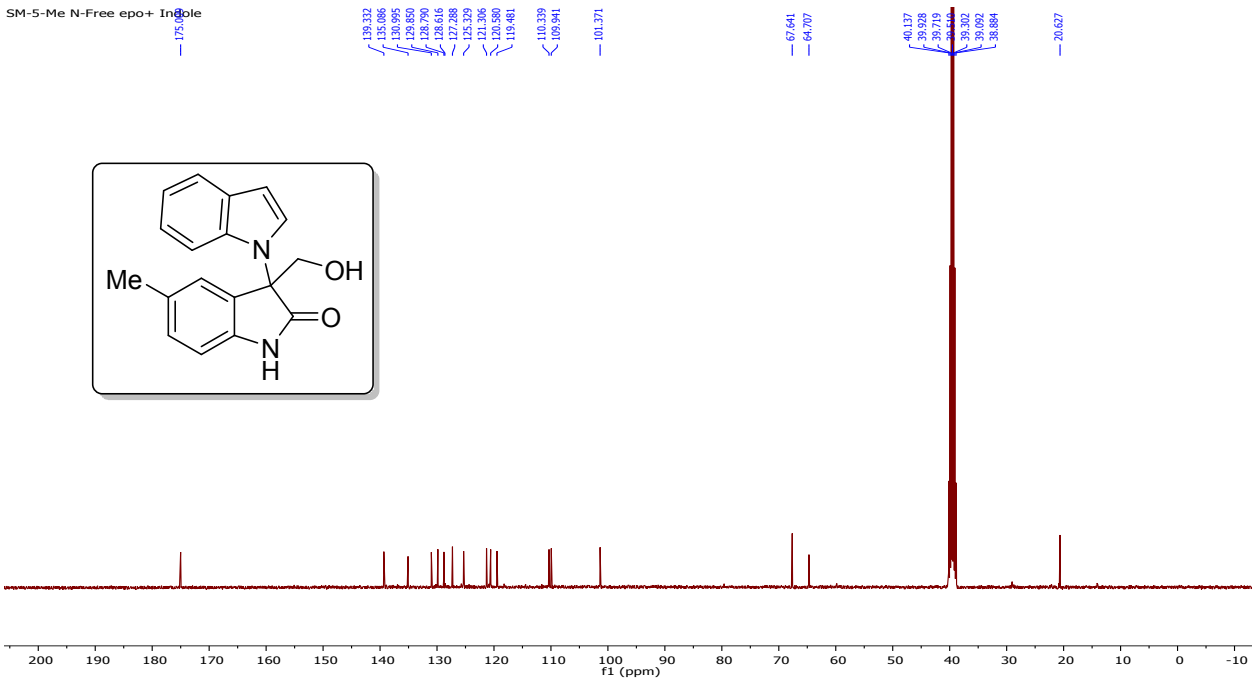
^{1}H NMR Spectrum of Compound **1l** (400MHz, DMSO-d_6)



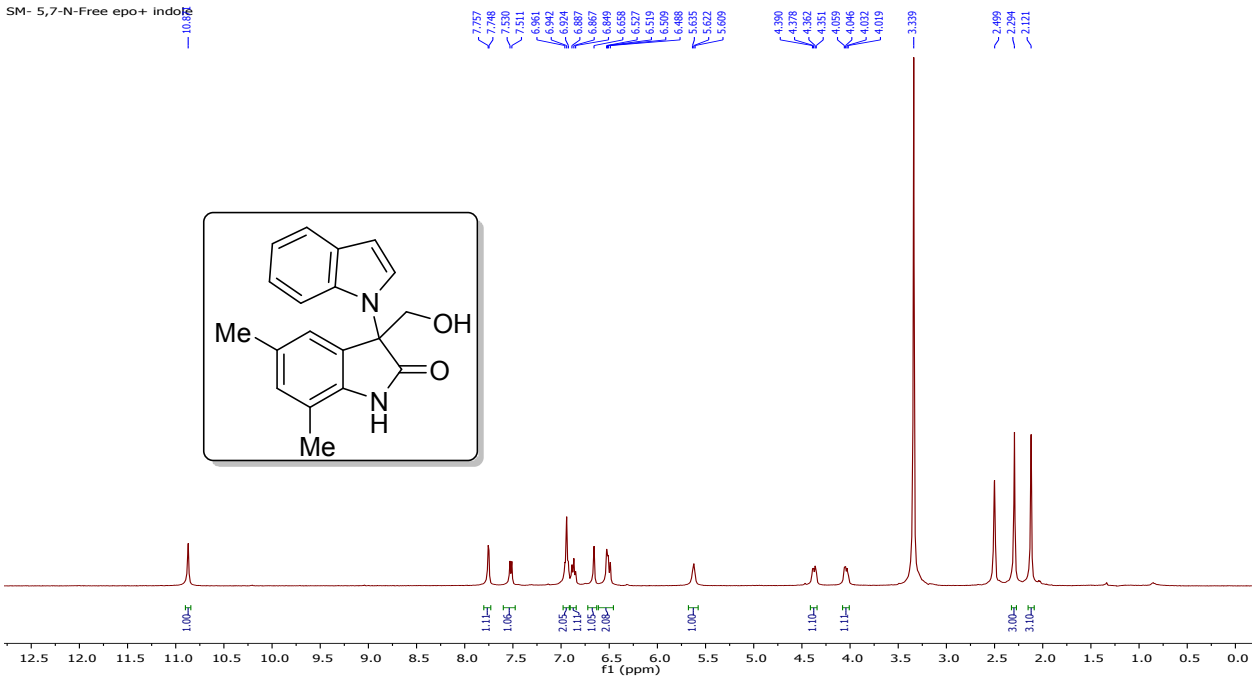
^{13}C NMR Spectrum of Compound **1l** (100MHz, DMSO-d_6).



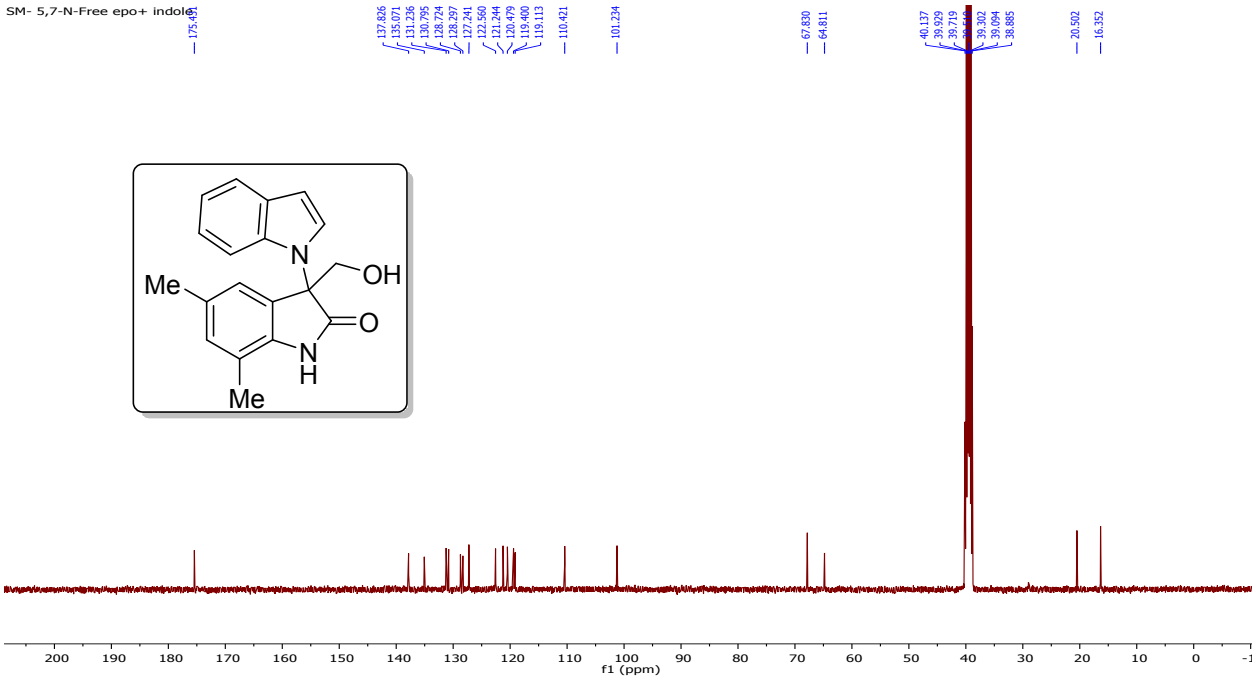
^{1}H NMR Spectrum of Compound **1m** (400MHz, DMSO-d_6)



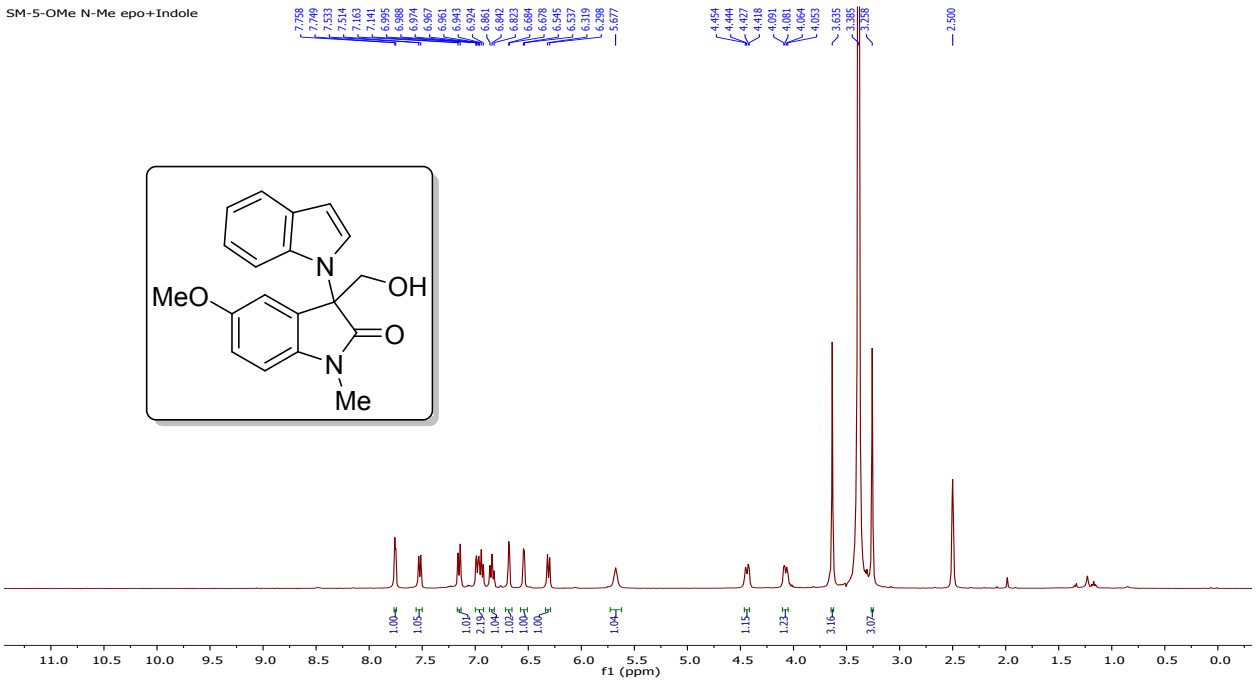
^{13}C NMR Spectrum of Compound **1m** (100MHz, DMSO-d_6).



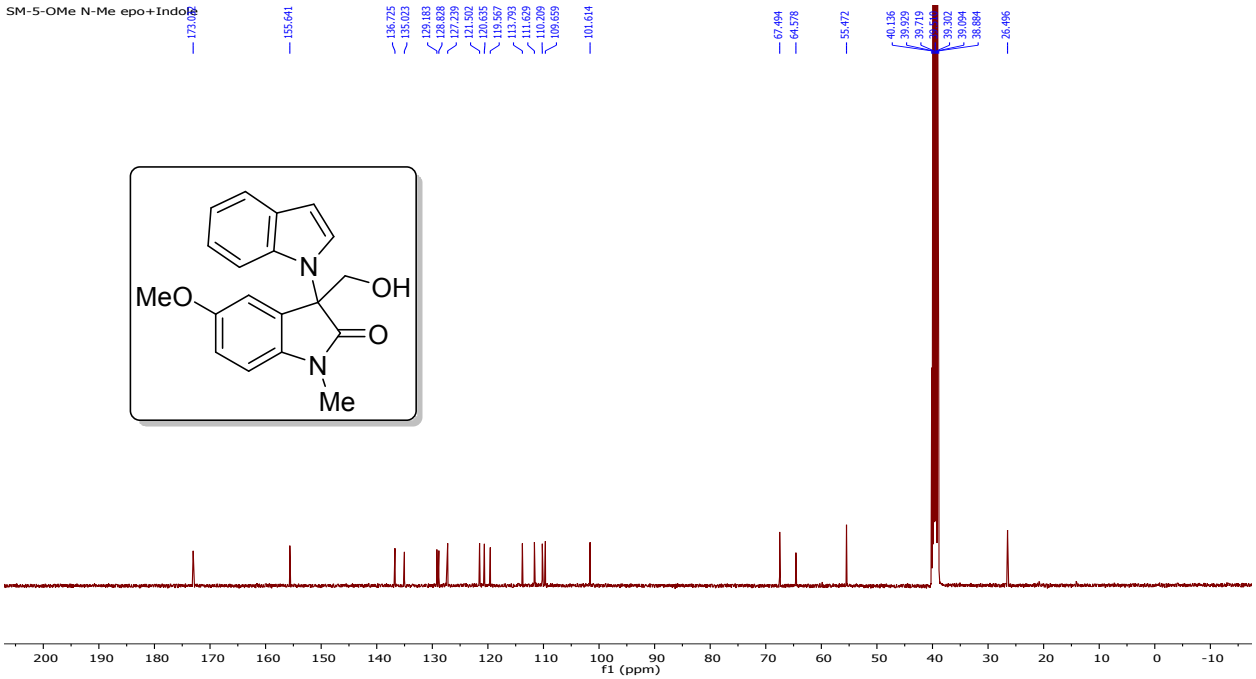
^{1}H NMR Spectrum of Compound **1n** (400MHz, DMSO-d_6)



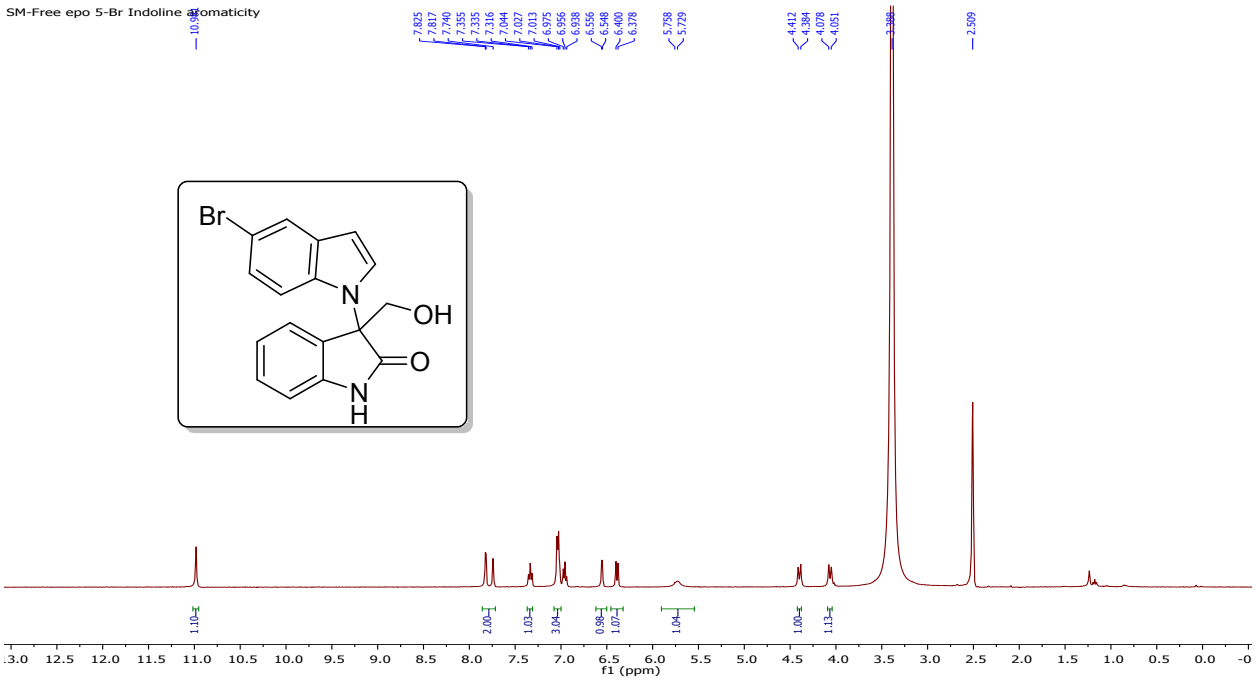
^{13}C NMR Spectrum of Compound **1n** (100MHz, DMSO-d_6).



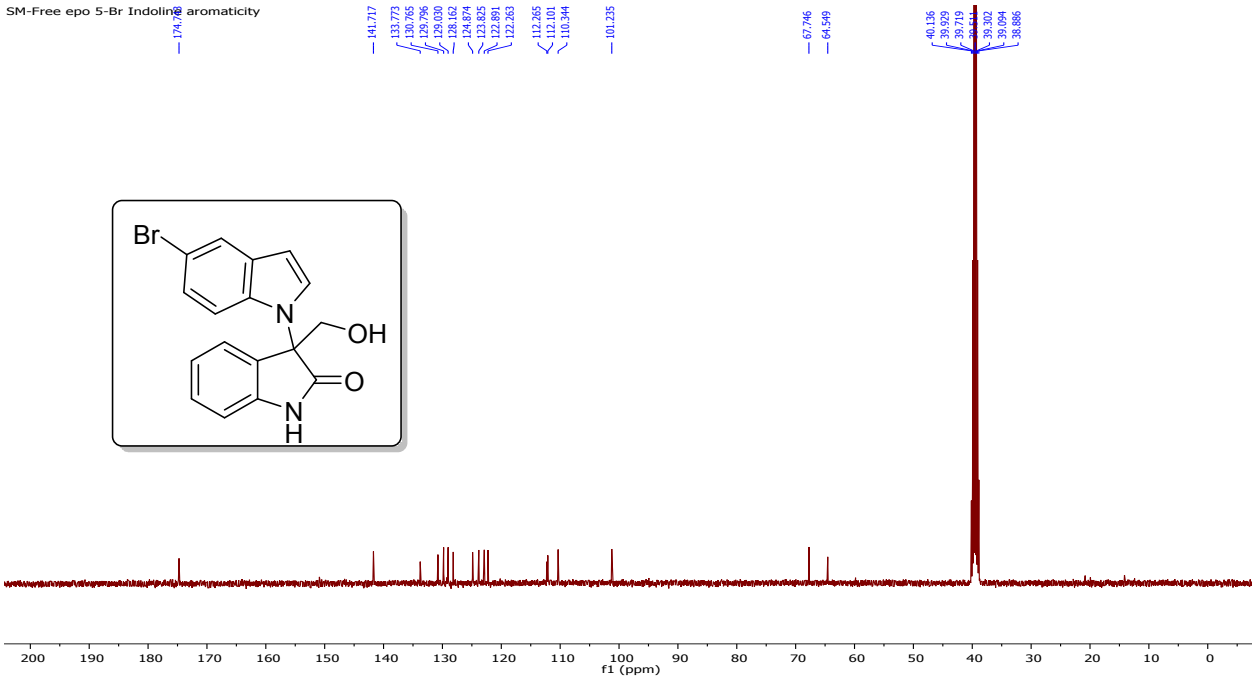
^{1}H NMR Spectrum of Compound **1o** (400MHz, DMSO-d_6)



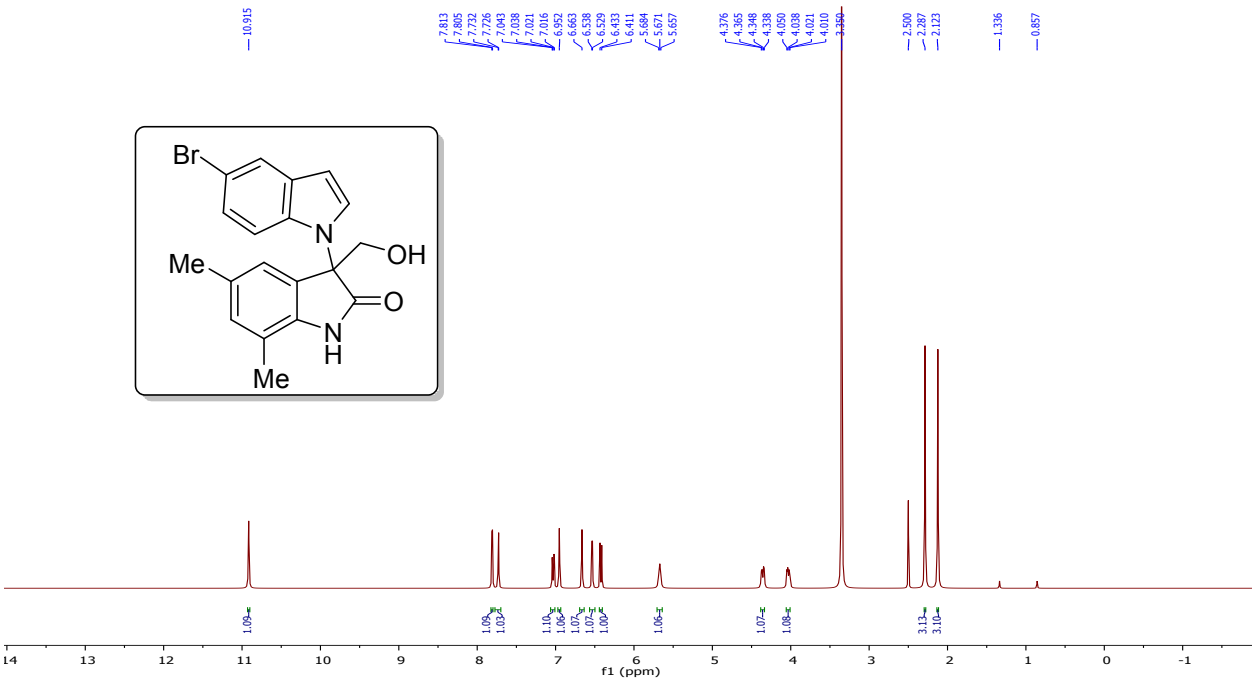
^{13}C NMR Spectrum of Compound **1o** (100MHz, DMSO-d_6).



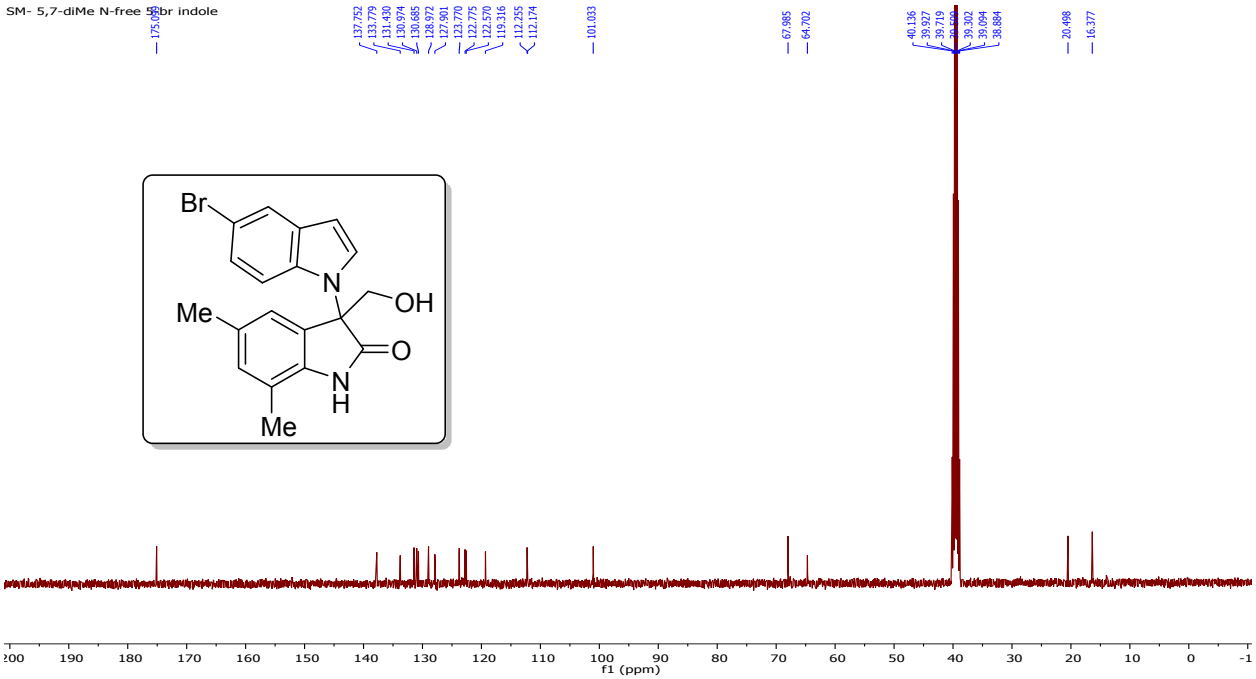
^{1}H NMR Spectrum of Compound **1p** (400MHz, DMSO-d_6)



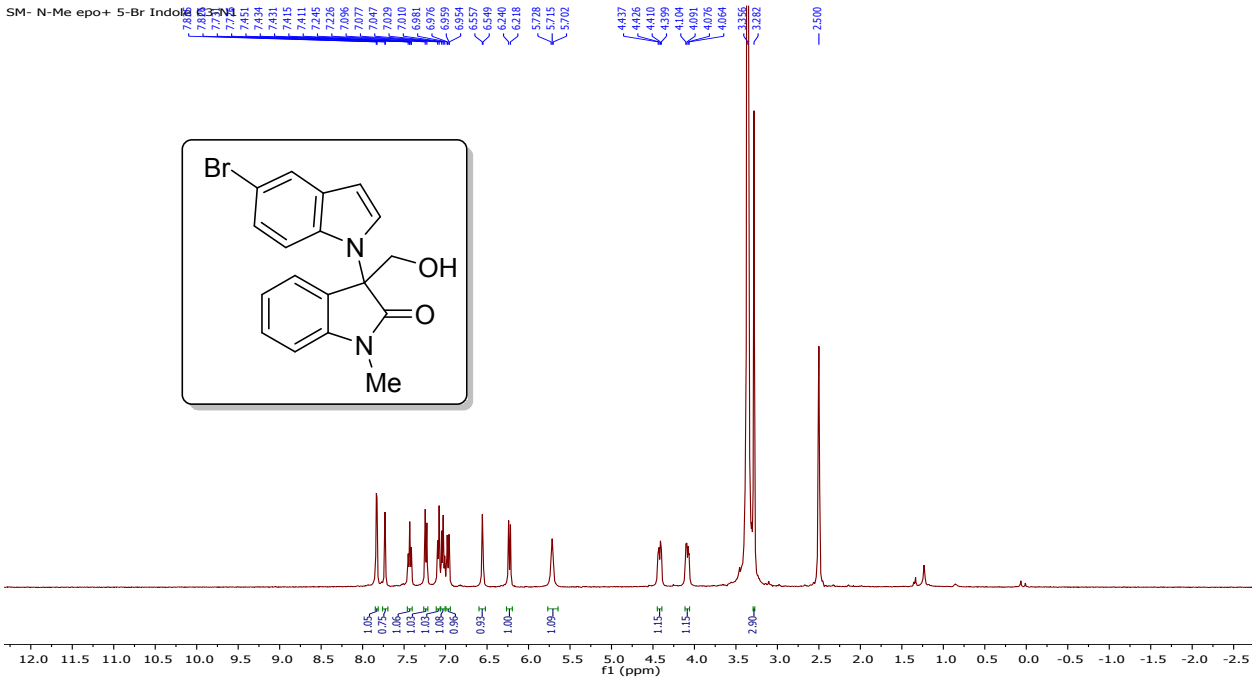
^{13}C NMR Spectrum of Compound **1p** (100MHz, DMSO-d_6).



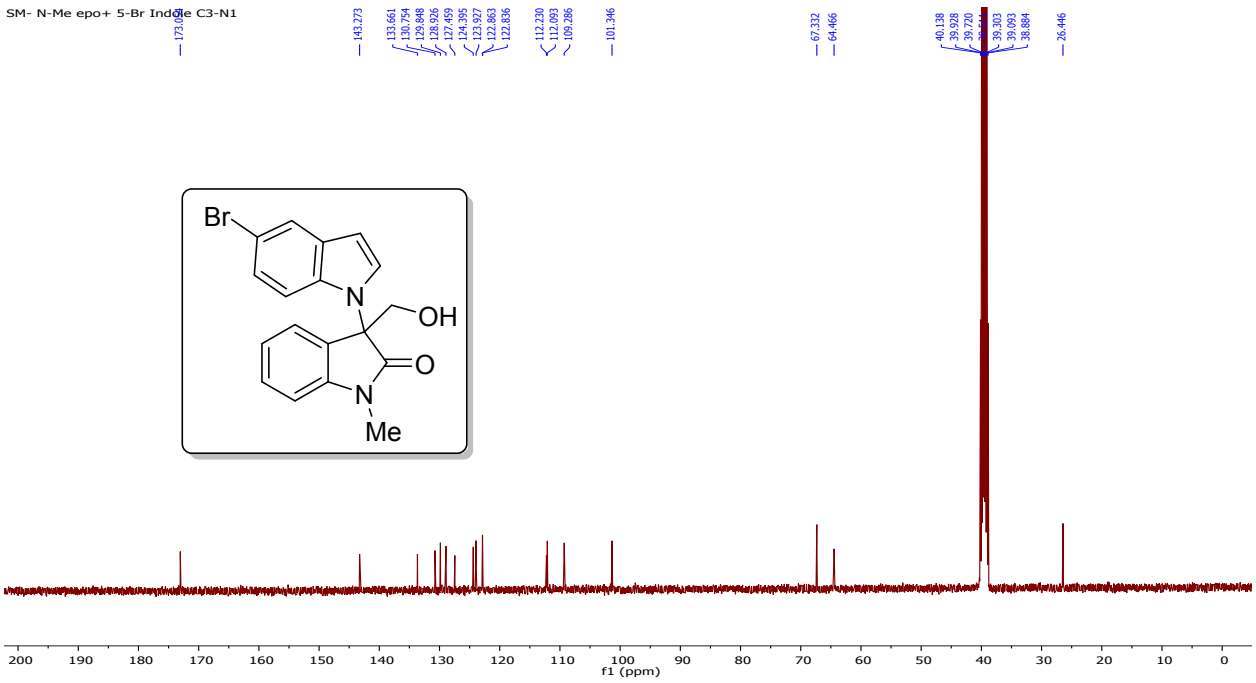
^{1}H NMR Spectrum of Compound **1q** (400MHz, DMSO-d_6)



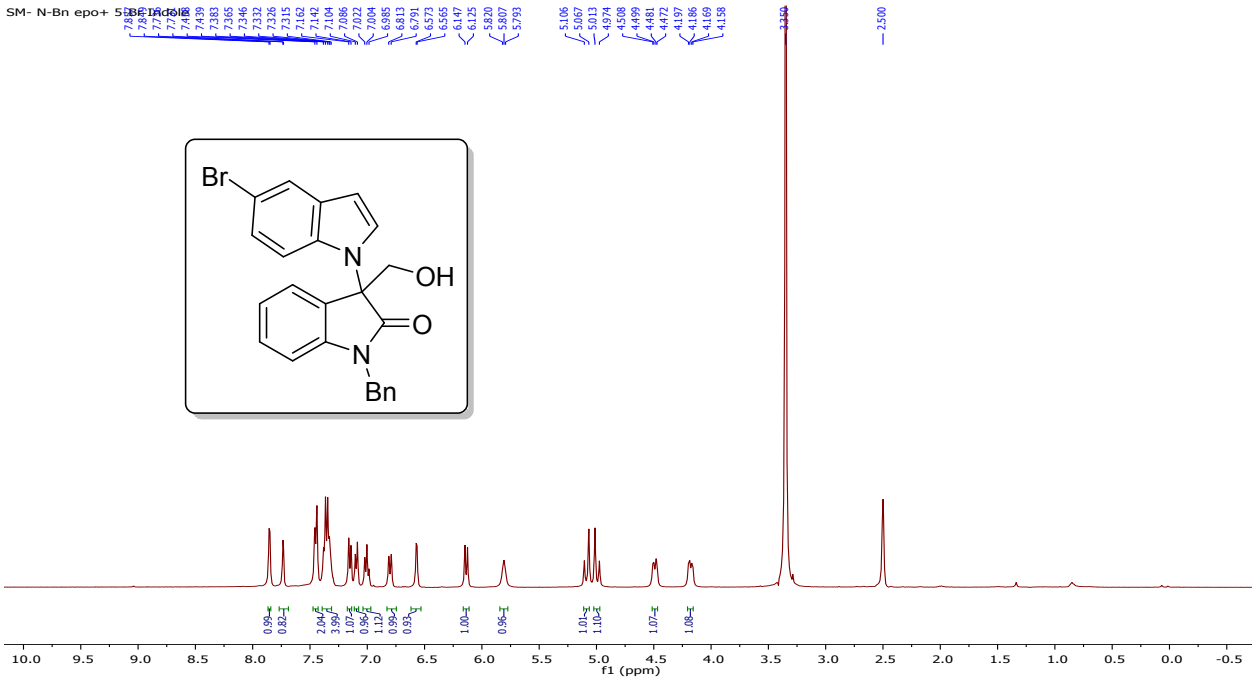
^{13}C NMR Spectrum of Compound **1q** (100MHz, DMSO-d_6).



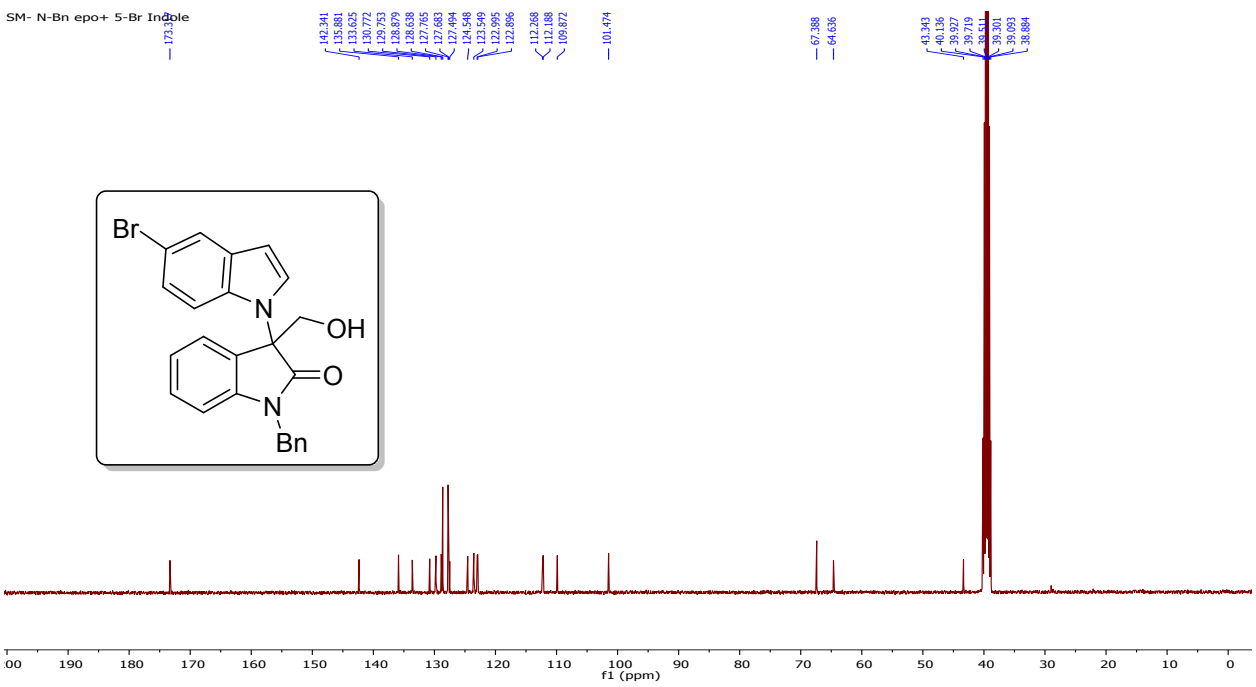
^{1}H NMR Spectrum of Compound **1r** (400MHz, DMSO-d_6)



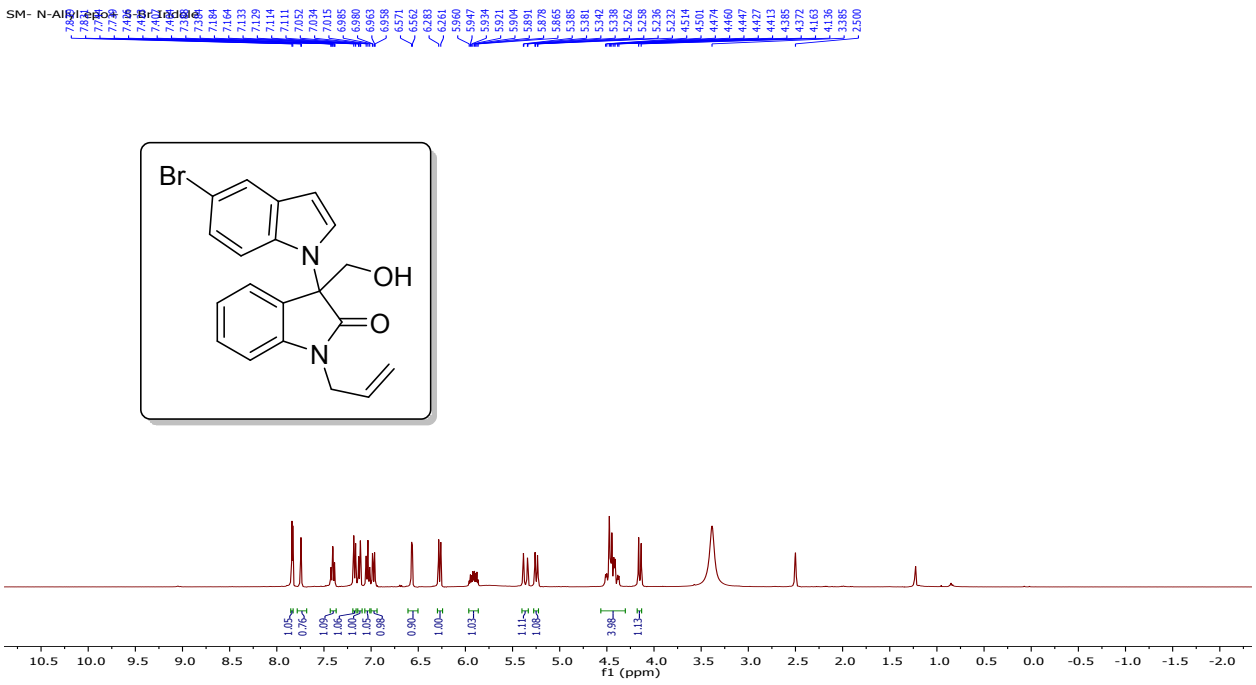
^{13}C NMR Spectrum of Compound **1r** (100MHz, DMSO-d_6).



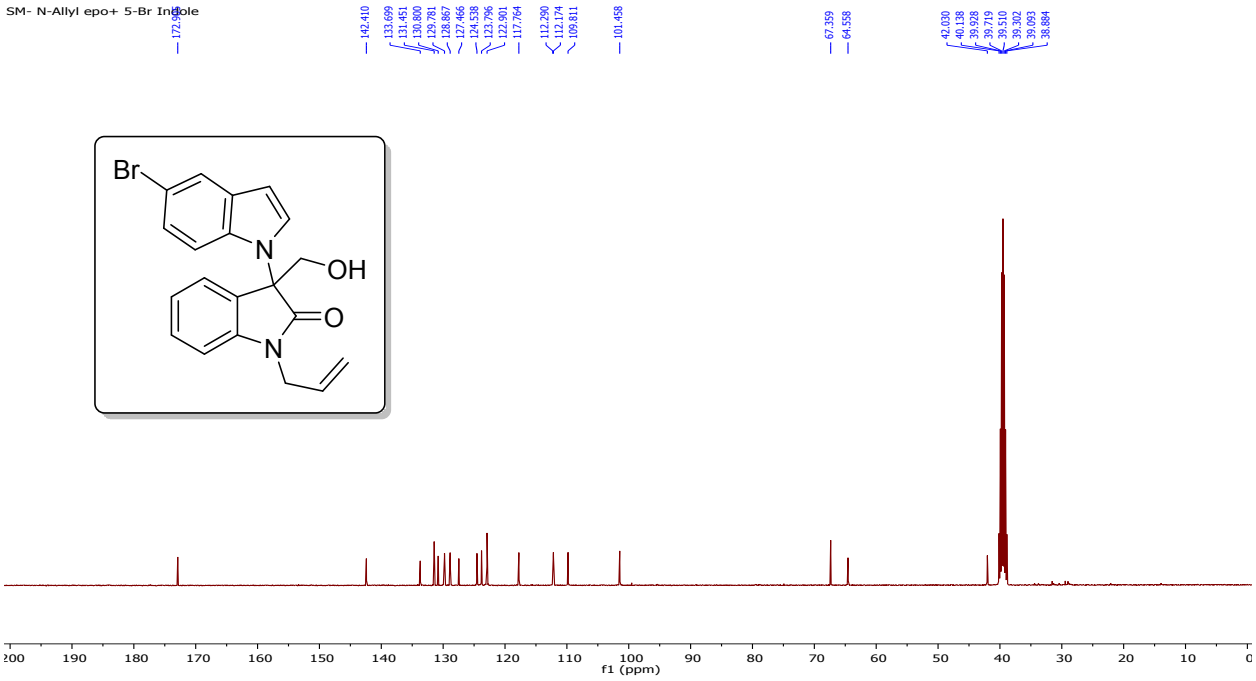
^{1}H NMR Spectrum of Compound **1s** (400MHz, DMSO-d_6)



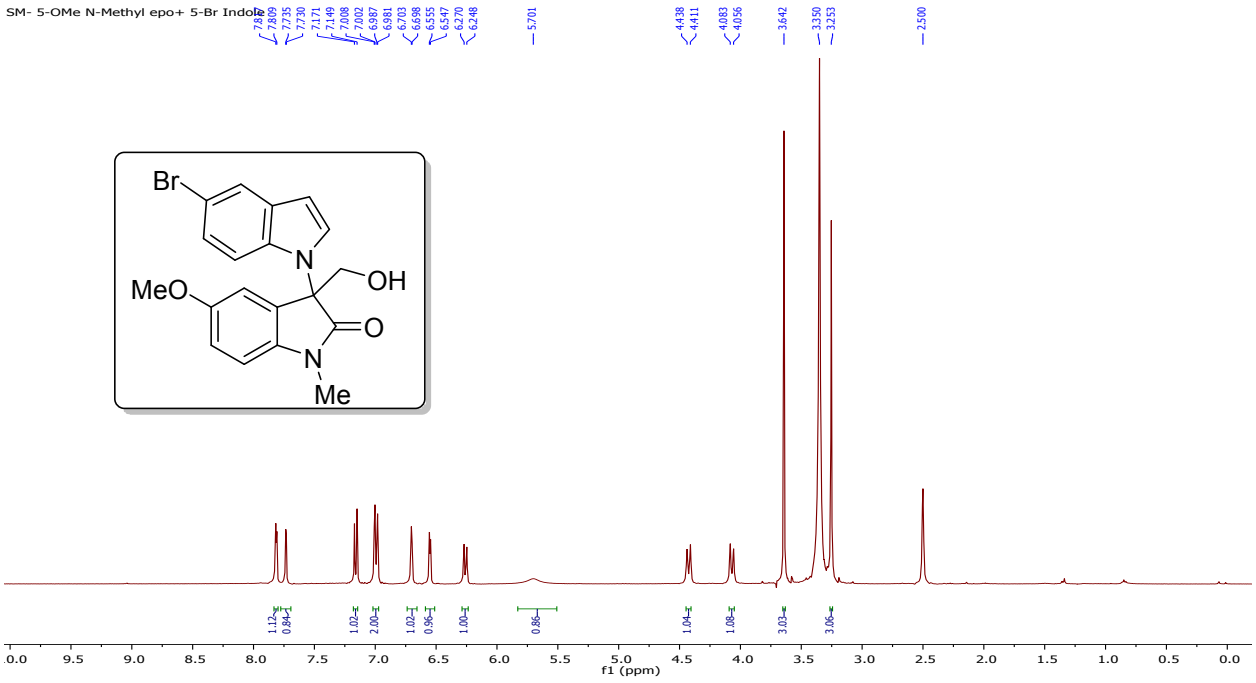
^{13}C NMR Spectrum of Compound **1s** (100MHz, DMSO-d_6).



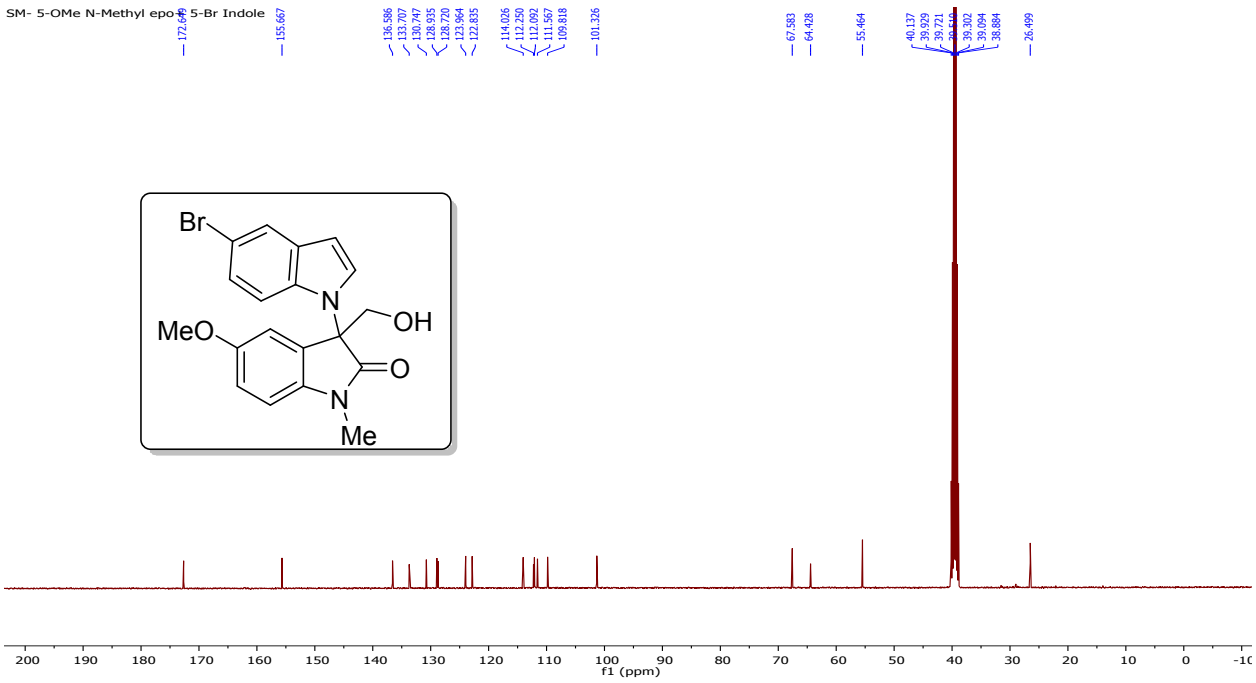
^{1}H NMR Spectrum of Compound **1t** (400MHz, DMSO-d_6)



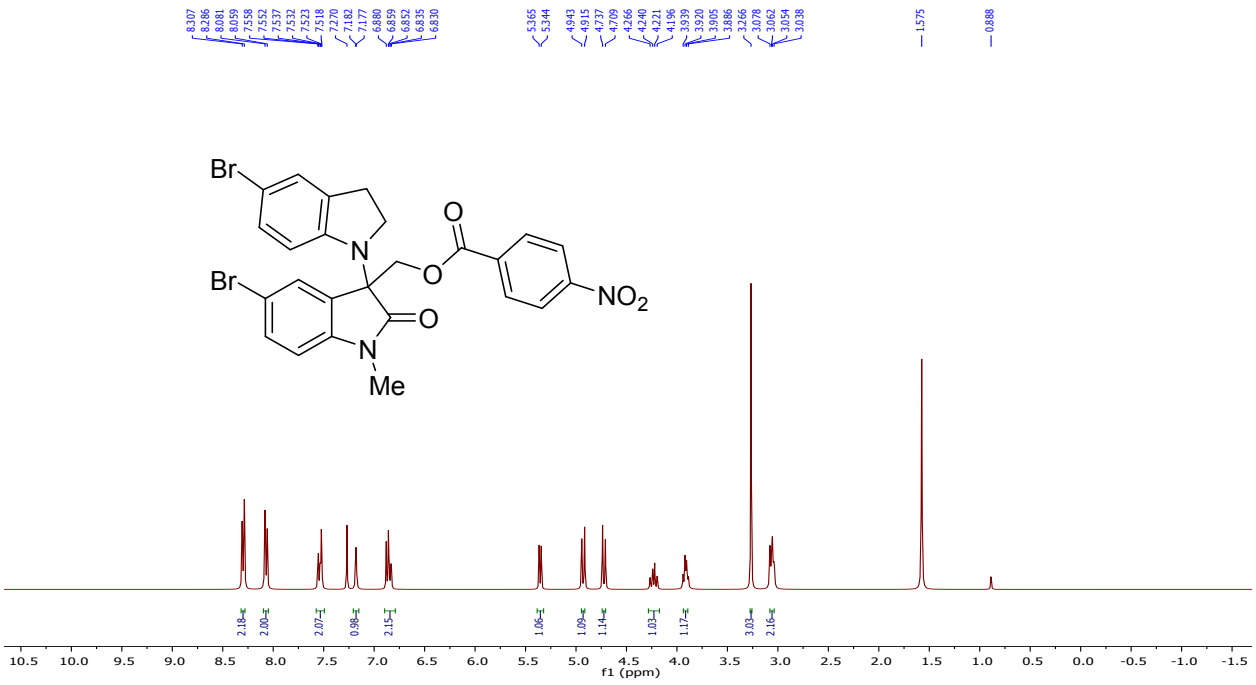
^{13}C NMR Spectrum of Compound **1t** (100MHz, DMSO-d_6).



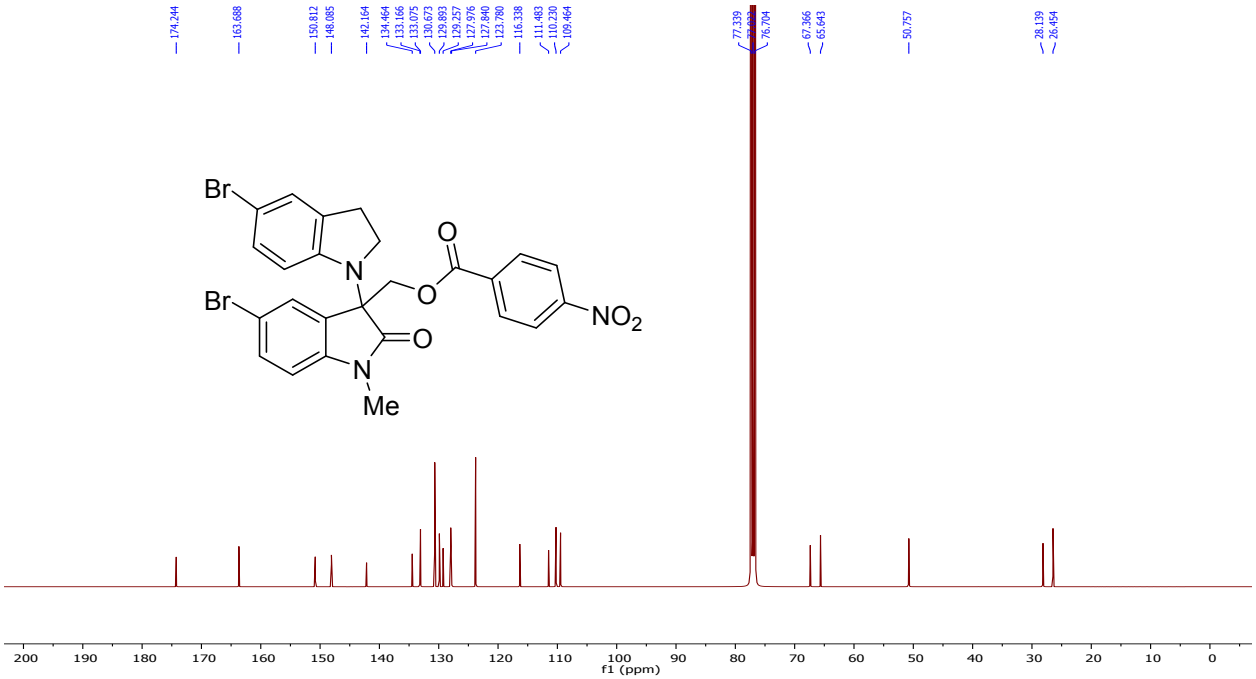
^{1}H NMR Spectrum of Compound **1u** (400MHz, DMSO-d_6)



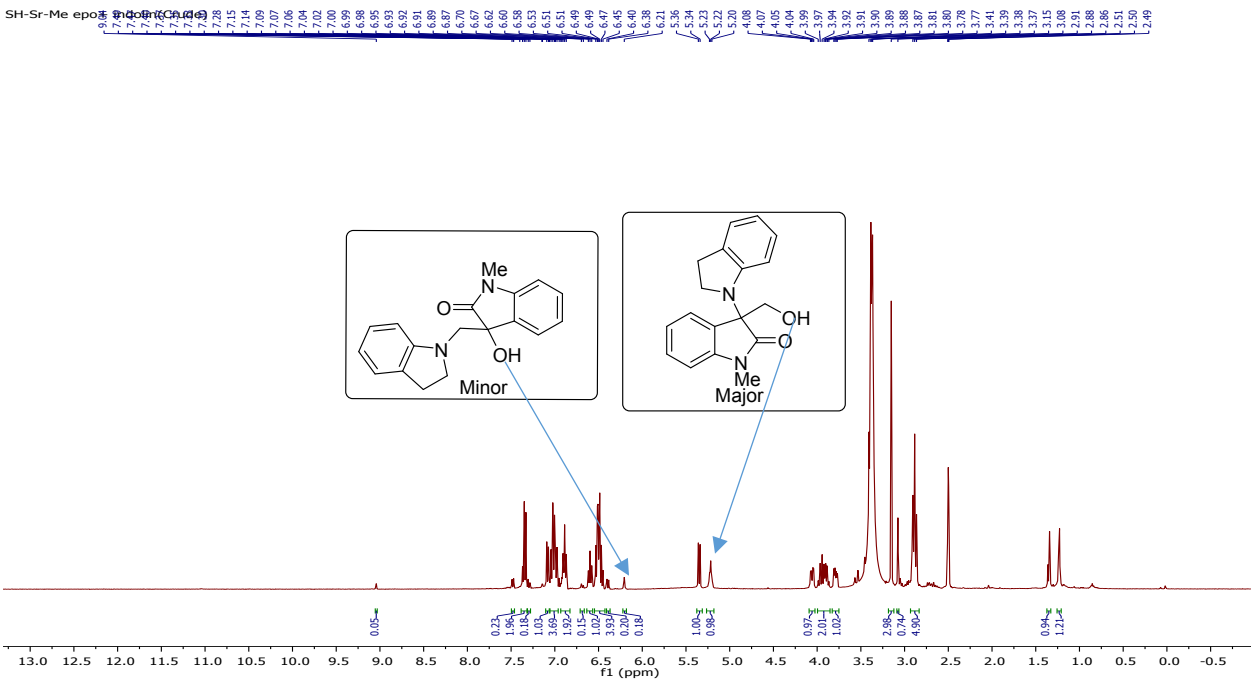
^{13}C NMR Spectrum of Compound **1u** (100MHz, DMSO-d_6).



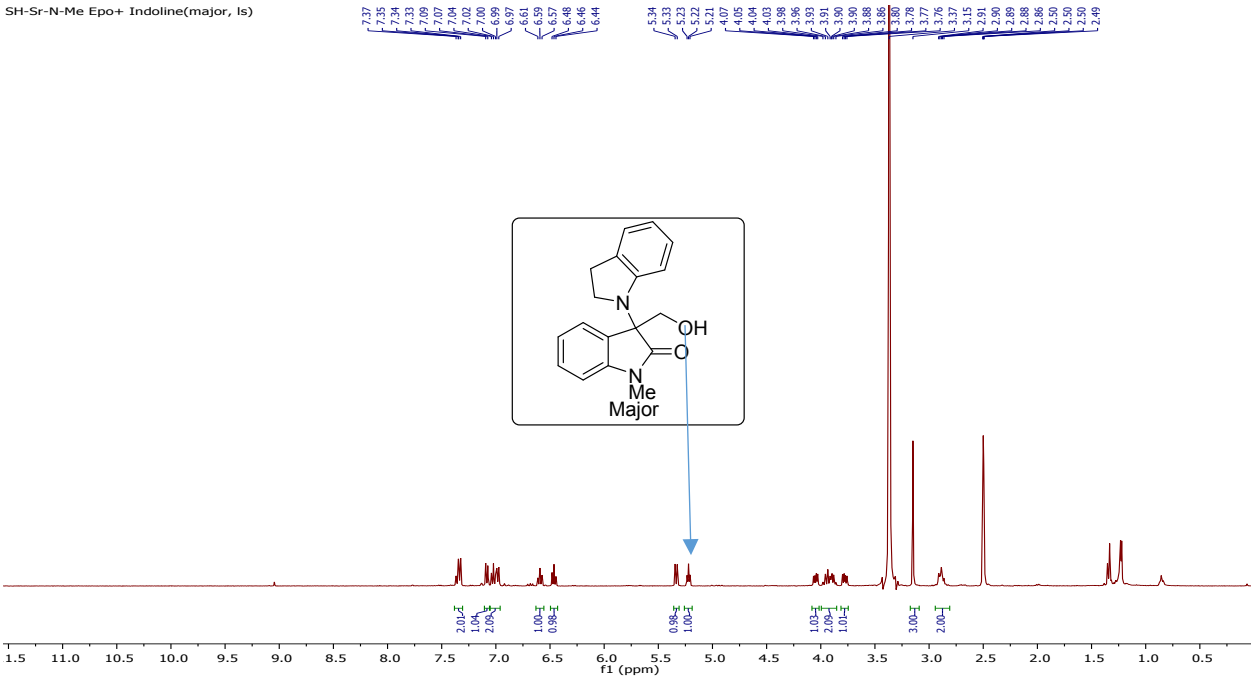
^{1}H NMR Spectrum of Compound **6** (400MHz, $CDCl_3$)



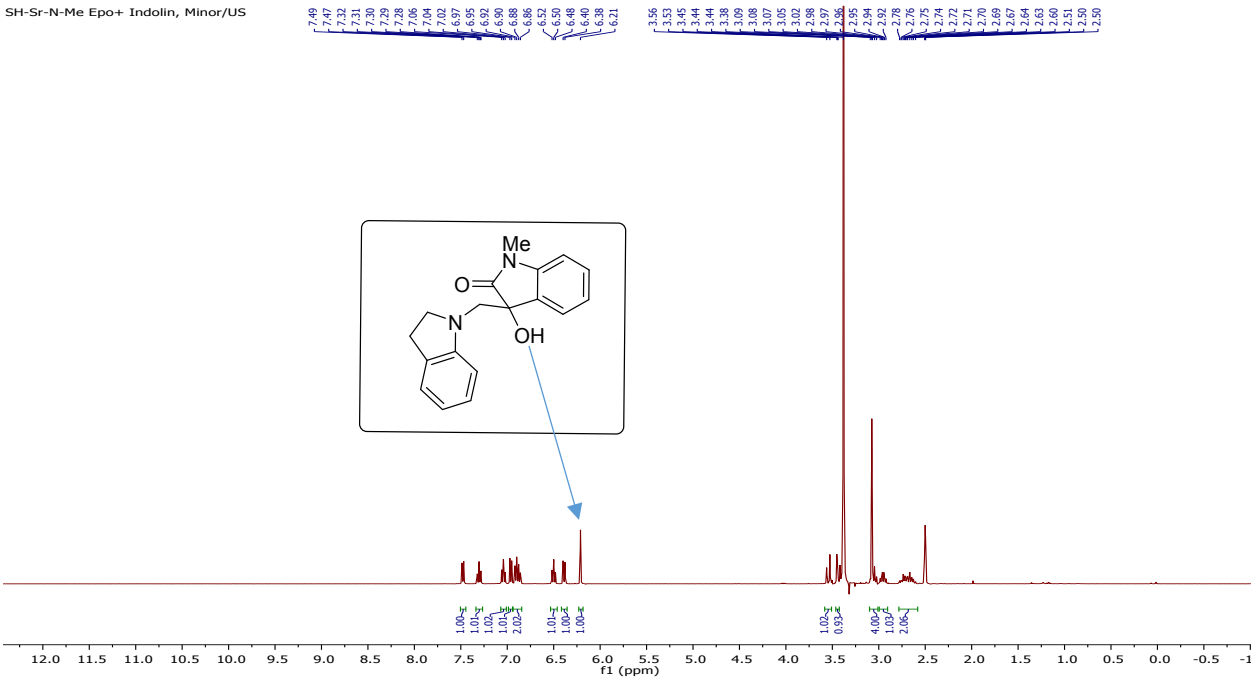
^{13}C NMR Spectrum of Compound **6** (100MHz, $CDCl_3$).



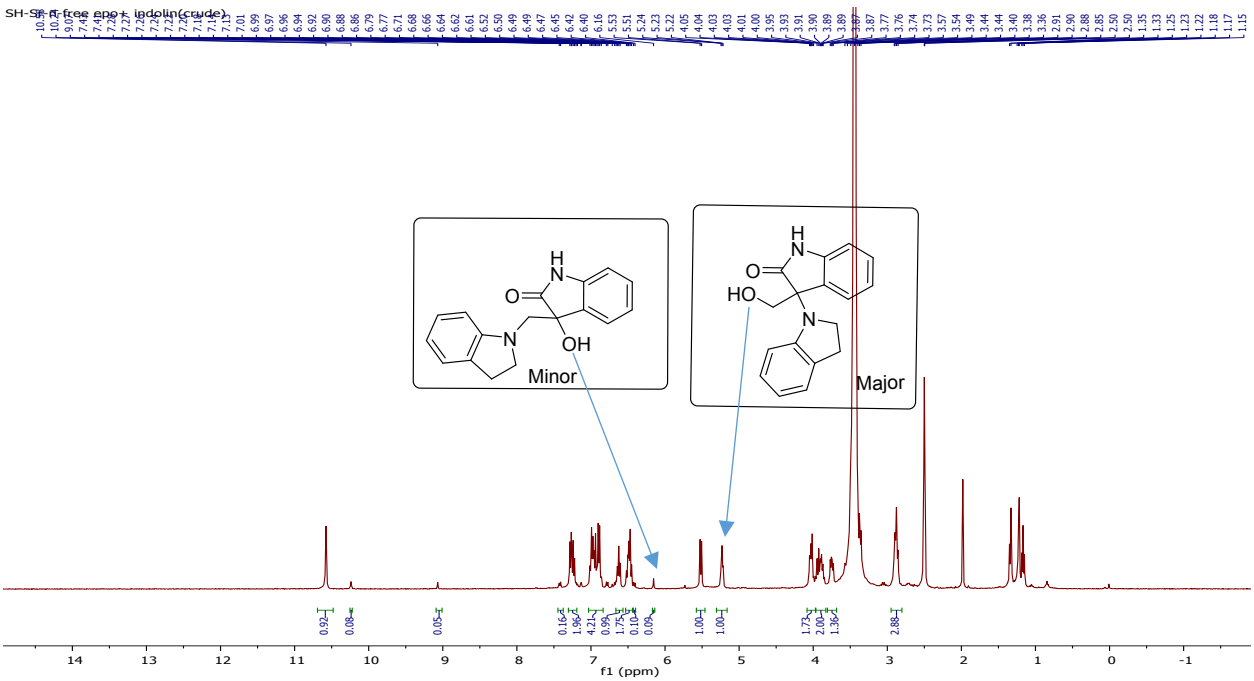
^{1}H NMR of the crude reaction mixture of *N*-Me epoxide **2a** + indoline **5b** (400 MHz, $(CD_3)_2SO$)



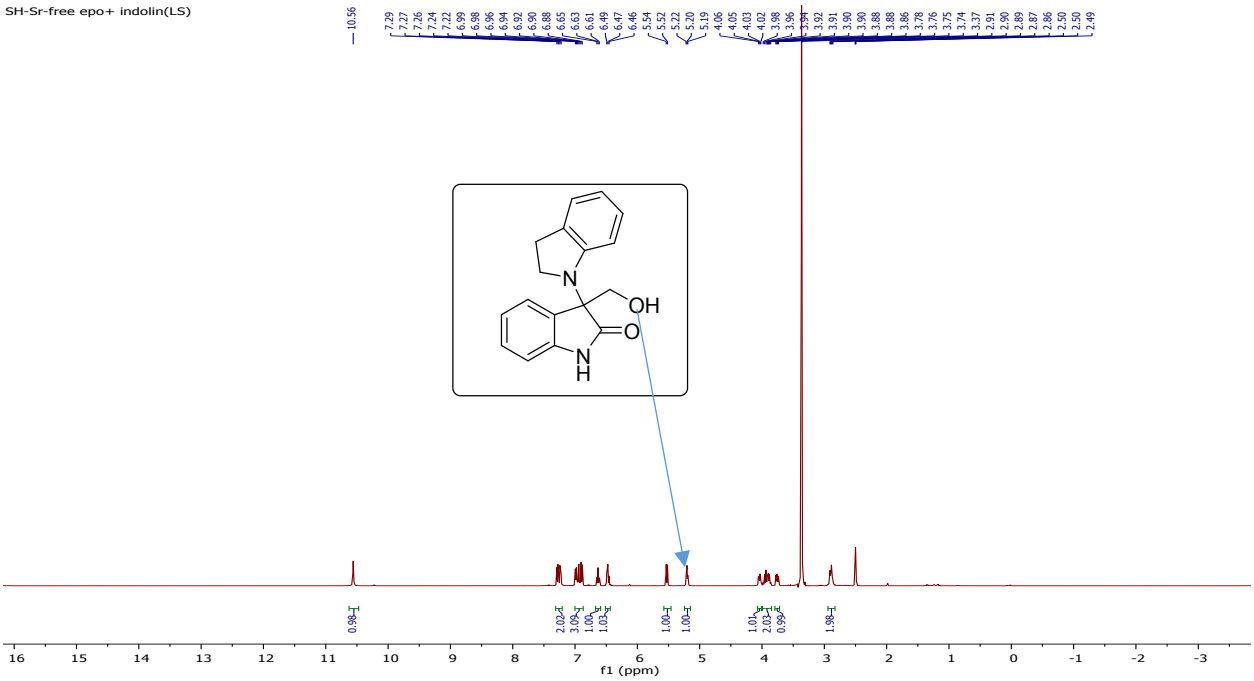
^{1}H NMR Spectrum of Compound **8** (400MHz, $(CD_3)_2SO$)



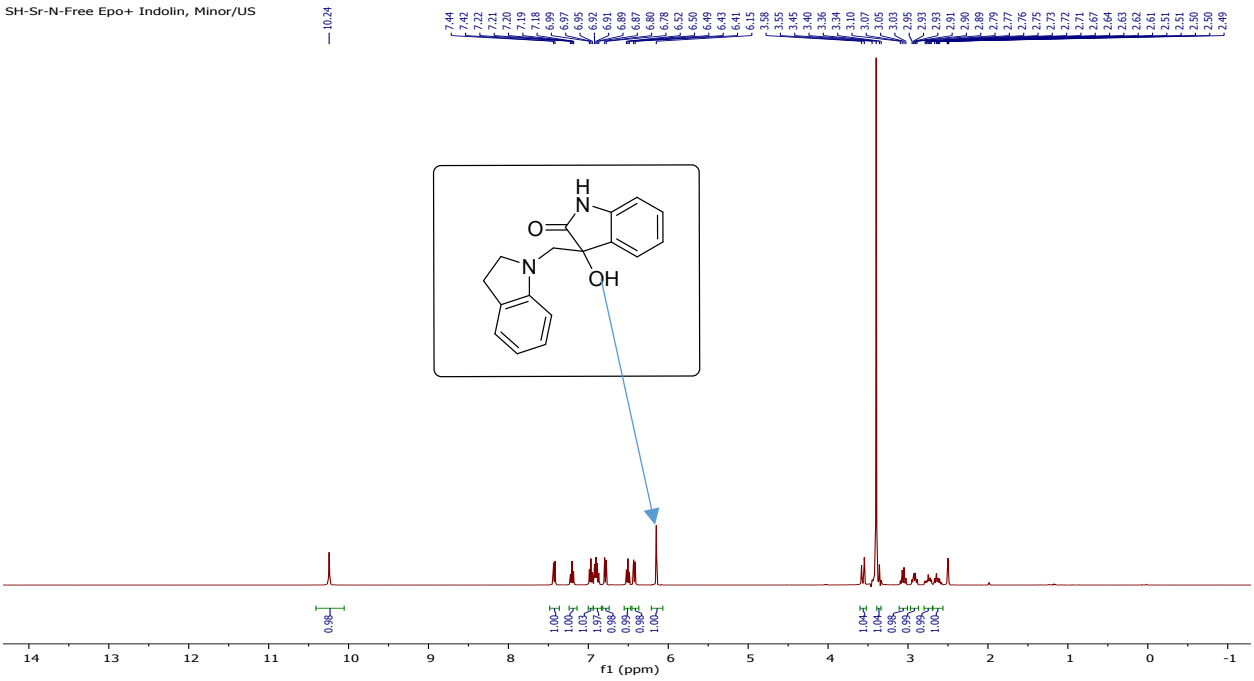
^{1}H NMR Spectrum of Compound **8′** (400MHz, $(CD_3)_2SO$)



^{1}H NMR of the crude reaction mixture of *N*-free epoxide **2k** + indoline **5b** (400 MHz, $(CD_3)_2SO$)



^{1}H NMR Spectrum of Compound **9** (400MHz, $(CD_3)_2SO$)



^{1}H NMR Spectrum of Compound **9′** (400MHz, $(CD_3)_2SO$)

Crystal Structure Determination

The single-crystal X-ray diffraction data of the compounds (**4i** and **6**) were collected on a Bruker D8 Venture system that uses graphite monochromated Mo Kα radiation (λ = 0.71073 A˚). The Structure were solved using ShelXT[1] and were refined using ShelXL[2] available within Olex2.[3] Non-hydrogen atoms were refined anisotropically and hydrogen atoms on C-atoms were fixed at calculated positions and refined using a riding model. The details of crystal data collection and refinement of the compounds are summarized in Table S1. CCDC (compound **1i**) 1887326 and (compound **6**)1887327 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge form The Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References

1. Sheldrick, G. M. *SHELXT – Integrated space-group and crystal-structure determination. Acta Cryst.* **2015**, *A71*, 3-8.

2. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.

3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2: A complete structure solution, refinement and analysis program*. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S1 Crystallographic data for the compounds

Empirical formula	$C_{31}H_{33}N_3O_4$	$C_{25}H_{19}Br_2N_3O_5$
CCDC number	1887326	1887327
FW	511.60	601.25
T, K	296.0(2)	296.0(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	9.899(2)	11.2334(8)
b, Å	11.547(3)	9.4327(6)
c, Å	13.186(3)	23.5205(18)
α, deg	111.235(17)	90
β, deg	91.111(16)	92.00(5)
γ, deg	102.013(16)	90
V, Å^3	1366.8(6)	2490.7(3)
Z, ρ, Mg m^{-3}	2, 1.243	4, 1.603
μ, mm^{-1}	0.083	3.296
F(000)	544.0	1200.0
Refln. collected	15844	29728
Ind. Reflen	4803	4386
Data/restn./param.	4803/0/347	4386/0/317

GOF on F^2	0.938	0.972
Final R indices [$I>2\sigma(I)$]	0.0645, 0.0898	0.0572, 0.1362
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
2Θ range for data collection/ deg	5.454 to 49.994	3.466 to 50
Index ranges	$-11 \le h \le 11$ $-13 \le k \le 13$ $-15 \le l \le 14$	$-13 \le h \le 13$ $-11 \le k \le 11$ $-27 \le l \le 26$
Largest diff. peak/hole / e Å^{-3}	0.15/-0.24	0.65/-0.69

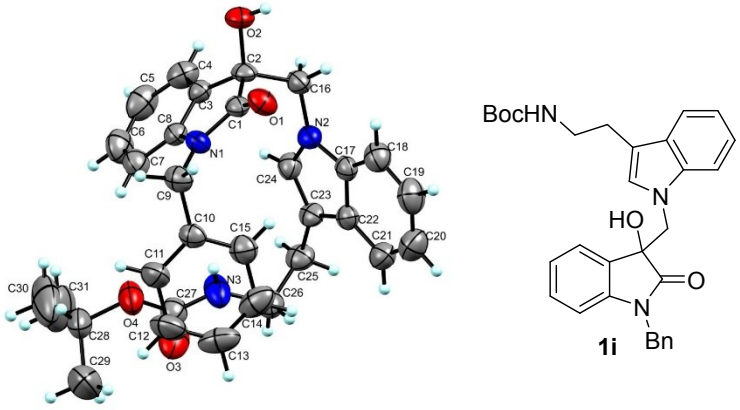


Figure 1. ORTEP diagram of compound **4i**

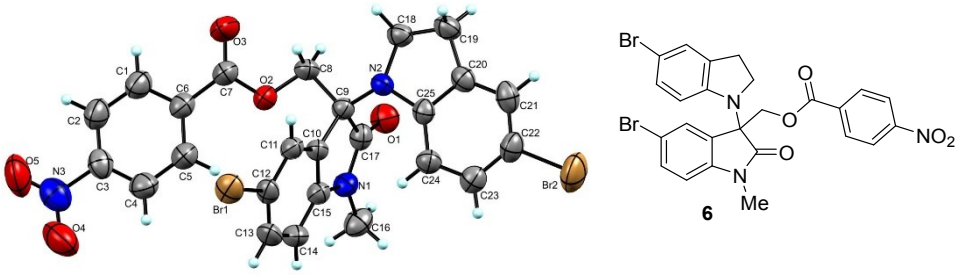


Figure 2. ORTEP diagram of compound **6**