Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Ring-opening hydrolysis of spiro-epoxyoxindoles using reusable sulfonic acid functionalized nitrogen rich carbon catalyst

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X-ray Crystallography

The crystallographic data and refinement for **2a**, **2b**, **2c**, **2e** and **2g** are provided in **Table S1**. Crystal of suitable size was selected from the mother liquor and immersed in paratone oil and then mounted for data collection. Single crystal X-ray data was collected using a Bruker D8 QUEST (PHOTON) diffractometer. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were obtained from International Tables for X-ray Crystallography. The data integration and reduction were processed using SAINTPLUS software.[S1] An empirical absorption correction was applied to the collected reflections with SADABS using XPREP.[S2] The structure was solved by the direct method using SHELXTL[S3] and was refined on F^2 by a full-matrix least-squares technique using the SHELXL-2014[S4] program package. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms

attached to the organic moiety were stereochemically fixed. CCDC numbers 1961234-1961238 corresponds to all the compounds reported in this manuscript and this data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Table S1. Crystal Data and Refinement Parameters for **2a**, **2b**, **2c**, **2e**, and **2g**.

Identification code	**2a**	**2b**	**2c**	**2e**	**2g**
Chemical formula	$C_{128}H_{120}N_8O_{24}$	$C_{10}H_{11}NO_3$	$C_{12}H_{13}NO_3$	$C_{17}H_{17}NO_4$	$ClC_{16}H_{14}NO_3$
Formula weight (g/mol)	2154.31	193.20	219.23	299.31	303.73
Crystal Color	Colorless	Colorless	Colorless	Light Yellow	Colorless
Crystal Size (mm)	0.44 x 0.08 x 0.05	0.29 x 0.24 x 0.22	0.33 x 0.12 x 0.04	0.60 x 0.40 x 0.10	0.36 x 0.07 x 0.06
Temperature (K)	301(2)	122(2)	150(2)	305(2)	301(2)
Crystal System	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space Group	P 2_1 2_1 2_1	P 2_1/n	P 2_1 2_1 2_1	P c	F d d 2
a(Å)	5.1638(3)	8.3175(11)	5.8505(12)	8.4593(5)	62.210(8)
b(Å)	19.3060(12)	10.2481(16)	11.594(2)	5.8691(4)	17.713(2)
c(Å)	27.209(2)	10.9658(17)	16.205(3)	30.718(2)	5.2259(7)
α(°)	90	90	90	90	90
β(°)	90	98.059(5)	90	97.420(2)	90
γ(°)	90	90	90	90	90
Z	1	4	4	4	16
V(Å^3)	2712.5(3)	925.5(2)	1099.2(4)	1512.33(18)	5758.6(13)
Density (Mg/m^3)	1.319	1.387	1.325	1.315	1.401
μ(mm^{-1})	0.092	0.103	0.096	0.094	0.274
F(000)	1136	408	464	632	194
Reflections Collected	20795	11988	5494	22546	18150
Independent Reflections	6671	2254	1934	5901	9343
R_{int}	0.1001	0.0426	0.0510	0.0409	0.0835
Number of parameters	369	160	175	469	194
GOF on F^2	0.994	1.135	1.114	1.043	1.009
Final R_1/wR_2 (I ≥2σ(I)	0.0621/0.1019	0.0604/0.1858	0.0767/0.1348	0.0511/0.1309	0.0635/0.1328
Weighted R_1/wR_2 (all data)	0.2041/0.1476	0.0725/0.1953	0.0888/0.1387	0.0661/0.1430	0.1448/0.1730
CCDC number	1961235	1961236	1961234	1961237	1961238

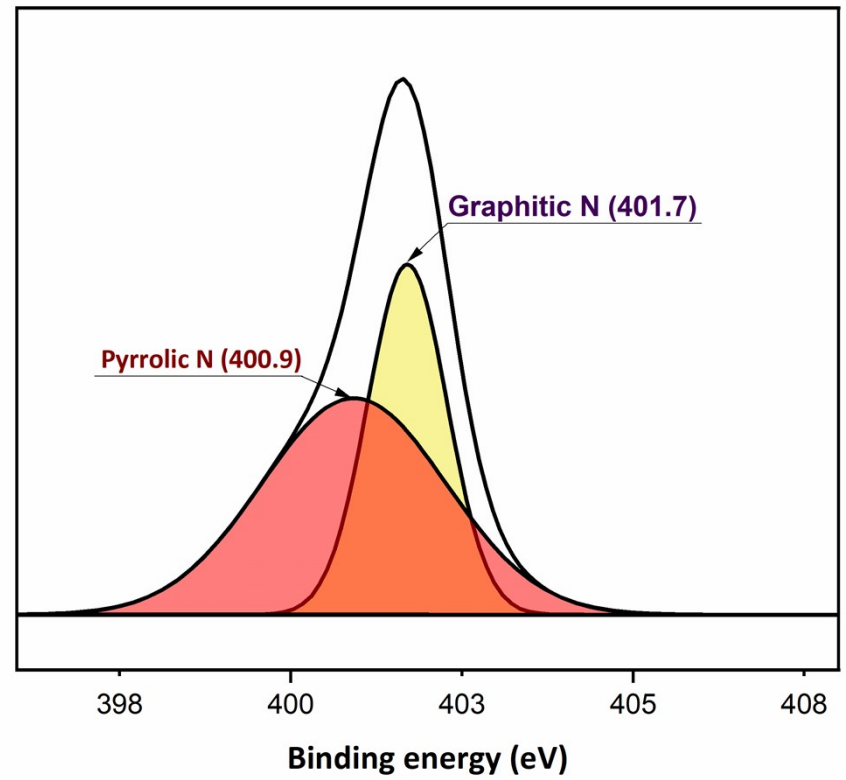


Figure S1. XPS Deconvoluted Spectrum of N 1S.

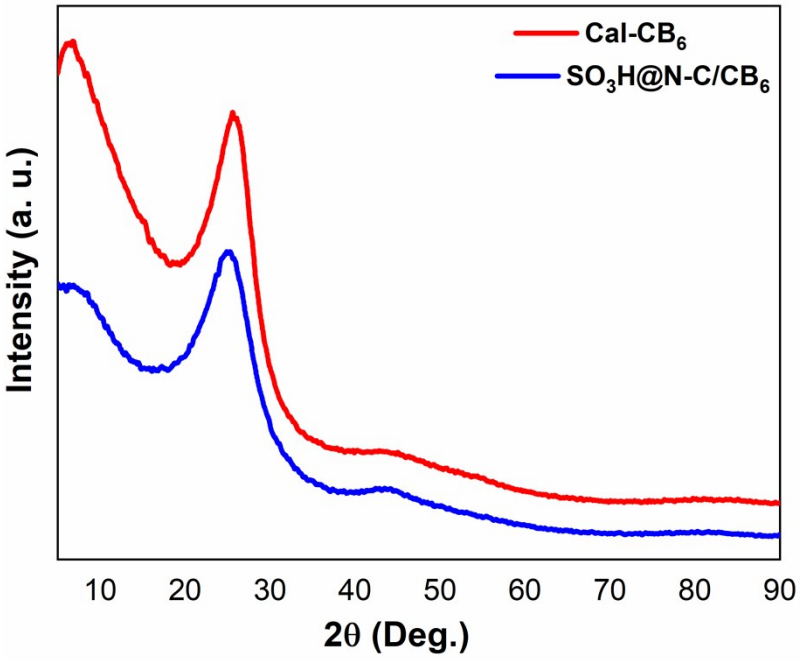


Figure S2. Powder XRD pattern of Cal-CB_6 and SO_3H@N-C/CB_6.

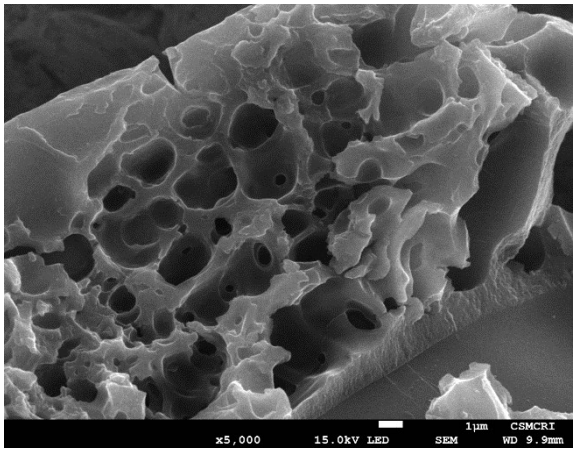
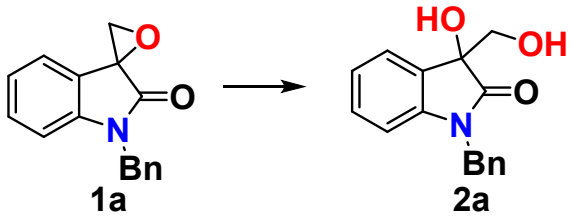
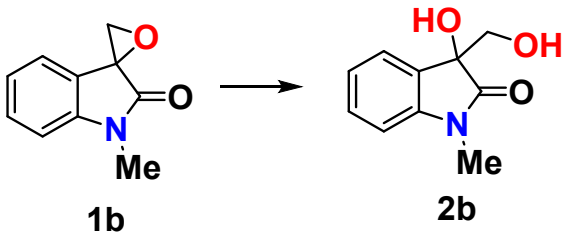


Figure S3. SEM image of SO_3H@N-C/CB_6.

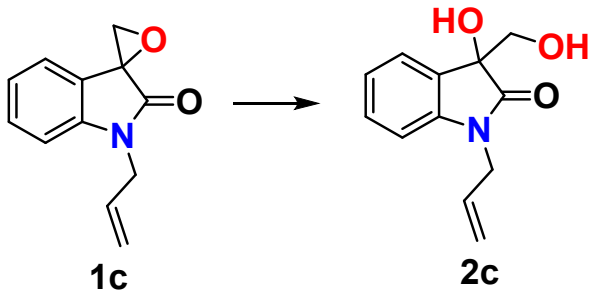
^{1}H & ^{13}C NMR analysis of hydrolysis products of spiro epoxyoxindoles



2a: ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.41 (d, J = 7.5 Hz, 1H), 7.28 – 7.20 (m, 5H), 7.17 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 4.91 (d, J = 15.9 Hz, 1H), 4.73 (d, J = 15.7 Hz, 1H), 3.89 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.98, 142.59, 135.26, 129.90, 128.90, 127.75, 127.19, 124.59, 123.46, 109.70, 76.23, 66.92, 43.78.

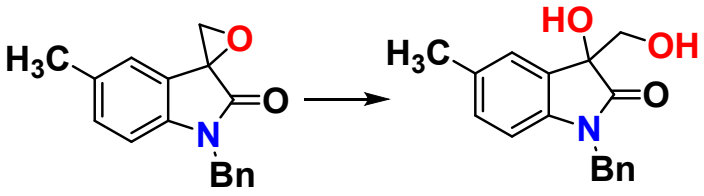


2b: ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.39 (d, J = 7.2 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.86 – 3.77 (m, 2H), 3.19 (s, 3H), 1.67 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.66, 143.66, 130.32, 127.57, 124.42, 123.52, 108.76, 75.42, 66.92, 26.29.



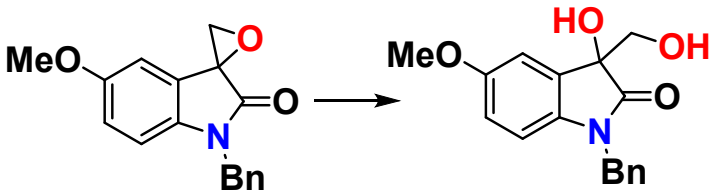
1c 2c

2c : ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 7.3 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.9 Hz, 1H), 5.80 (ddd, J = 21.6, 10.3, 5.3 Hz, 1H), 5.25 – 5.18 (m, 2H), 4.36 – 4.32 (m, 1H), 4.24 (dd, J = 16.5, 4.9 Hz, 1H), 3.89 – 3.79 (m, 2H), 3.17 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.49, 142.82, 130.90, 130.14, 127.72, 124.50, 123.45, 117.94, 109.64, 75.57, 67.02, 42.35.



1d 2d

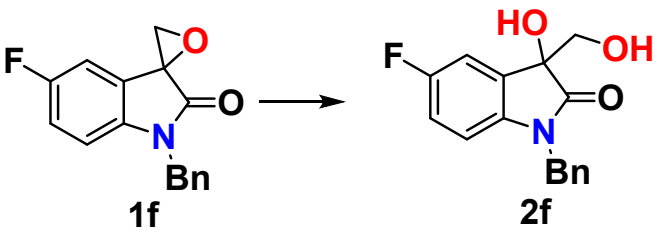
2d : ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.26 – 7.22 (m, 4H), 7.01 (d, J = 7.9 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 4.96 – 4.72 (m, 2H), 3.88 (dt, J = 21.2, 11.4 Hz, 2H), 3.16 – 3.00 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.78, 140.36, 135.31, 133.25, 130.44, 128.94, 127.82, 127.21, 125.25, 109.61, 75.59, 67.09, 43.79, 21.09.



1e 2e

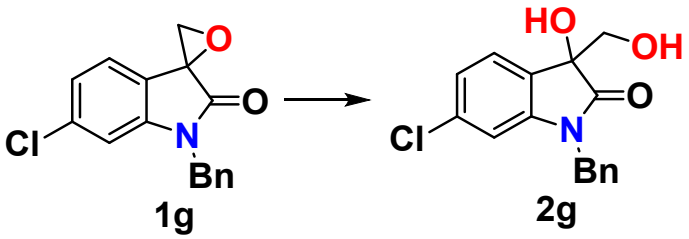
2e : ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.27 (d, J = 5.9 Hz, 4H), 7.02 (t, J = 2.0 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.62 (d, J = 8.6 Hz, 1H), 4.93 (d, J = 15.7 Hz, 1H), 4.80 (d, J = 15.7 Hz,

1H), 3.88 (d, J = 13.8 Hz, 2H), 3.76 (s, 3H), 2.90 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.04, 127.95, 127.28, 111.48, 110.52, 67.21, 55.97, 43.93.



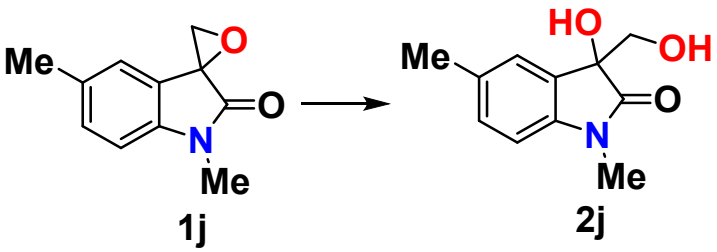
1f 2f

2f : ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.30 – 7.21 (m, 5H), 7.17 (dd, J = 7.9, 2.3 Hz, 1H), 6.88 (td, J = 8.6, 2.4 Hz, 1H), 6.60 (dd, J = 8.6, 4.0 Hz, 1H), 4.91 (d, J = 15.7 Hz, 1H), 4.78 (s, 1H), 4.75 (d, J = 15.6 Hz, 1H), 3.89 (s, 2H), 3.54 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.73, 160.45, 138.42, 134.87, 129.78, 129.73, 129.03, 127.97, 127.16, 116.36, 116.21, 112.98, 112.81, 110.53, 110.47, 76.22, 66.93, 43.97.



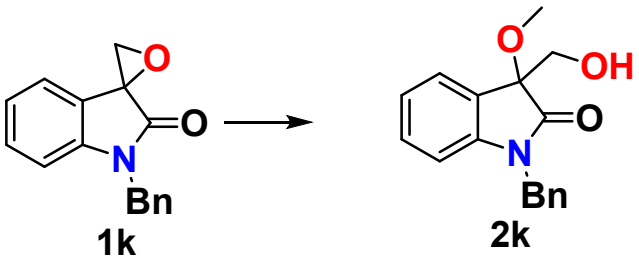
1g 2g

2g : ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.25 (d, J = 7.3 Hz, 3H), 7.05 (d, J = 8.3 Hz, 1H), 6.72 (s, 1H), 4.91 (s, 1H), 4.78 (d, J = 15.6 Hz, 1H), 3.85 (d, J = 3.3 Hz, 2H), 2.68 (s, 1H). ^{13}C NMR (151 MHz,$CDCl_3$) δ 129.14, 128.14, 127.17, 125.48, 123.45, 110.49, 66.87, 43.90.



1j 2j

2j : ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37 – 7.08 (m, 2H), 6.76 (d, J = 7.9 Hz, 1H), 4.43 (s, 1H), 3.85 (s, 2H), 3.19 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.61, 141.13, 133.11, 130.30, 127.75, 125.18, 108.40, 66.90, 26.24, 21.05.



2k : ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.39 (d, J = 7.2 Hz, 1H), 7.32 – 7.23 (m, 6H), 7.08 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 4.93 (s, 2H), 3.91 (q, J = 11.4 Hz, 2H), 3.13 (s, 3H), 2.69 (s, 1H). ^{13}C NMR (151 MHz,$CDCl_3$) δ 175.04, 143.45, 135.50, 130.25, 128.96, 127.85, 127.27, 125.20, 125.02, 123.27, 109.76, 82.74, 66.85, 53.49, 43.90.

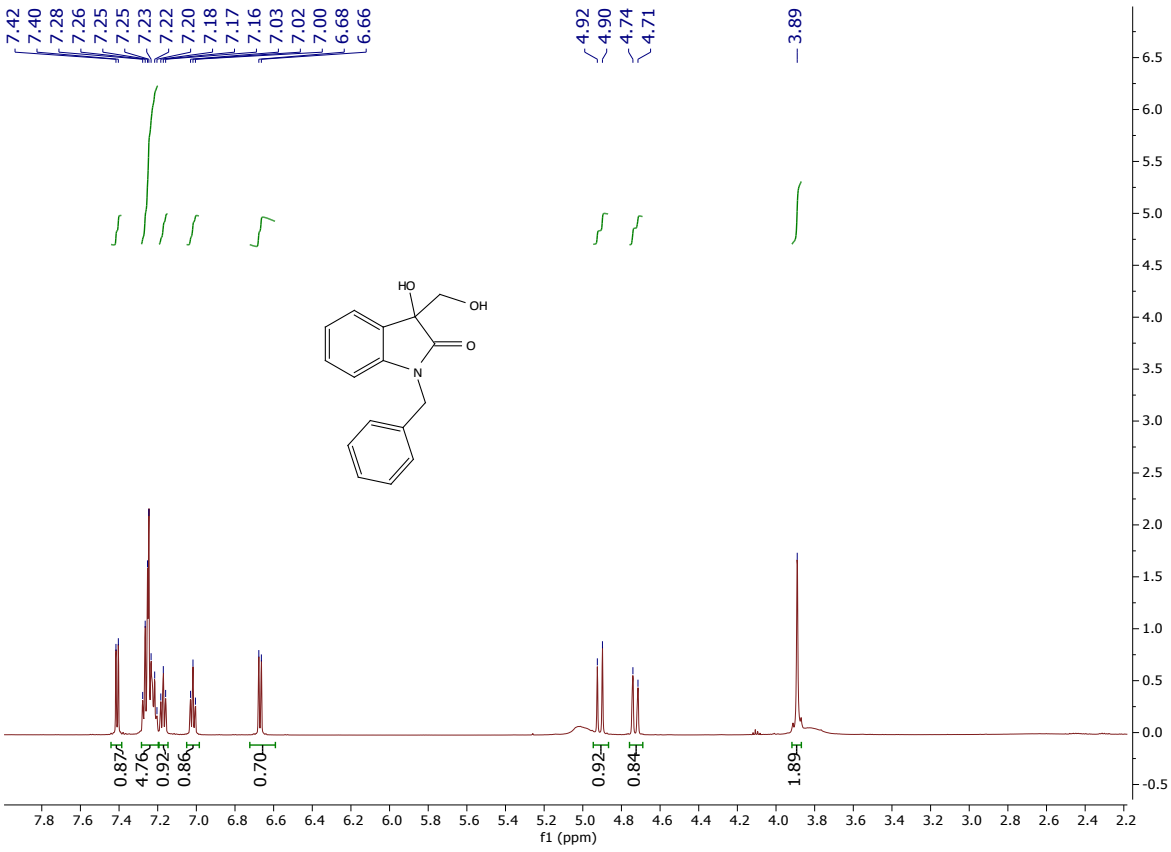


Figure S4. ^{1}H NMR of **2a**.

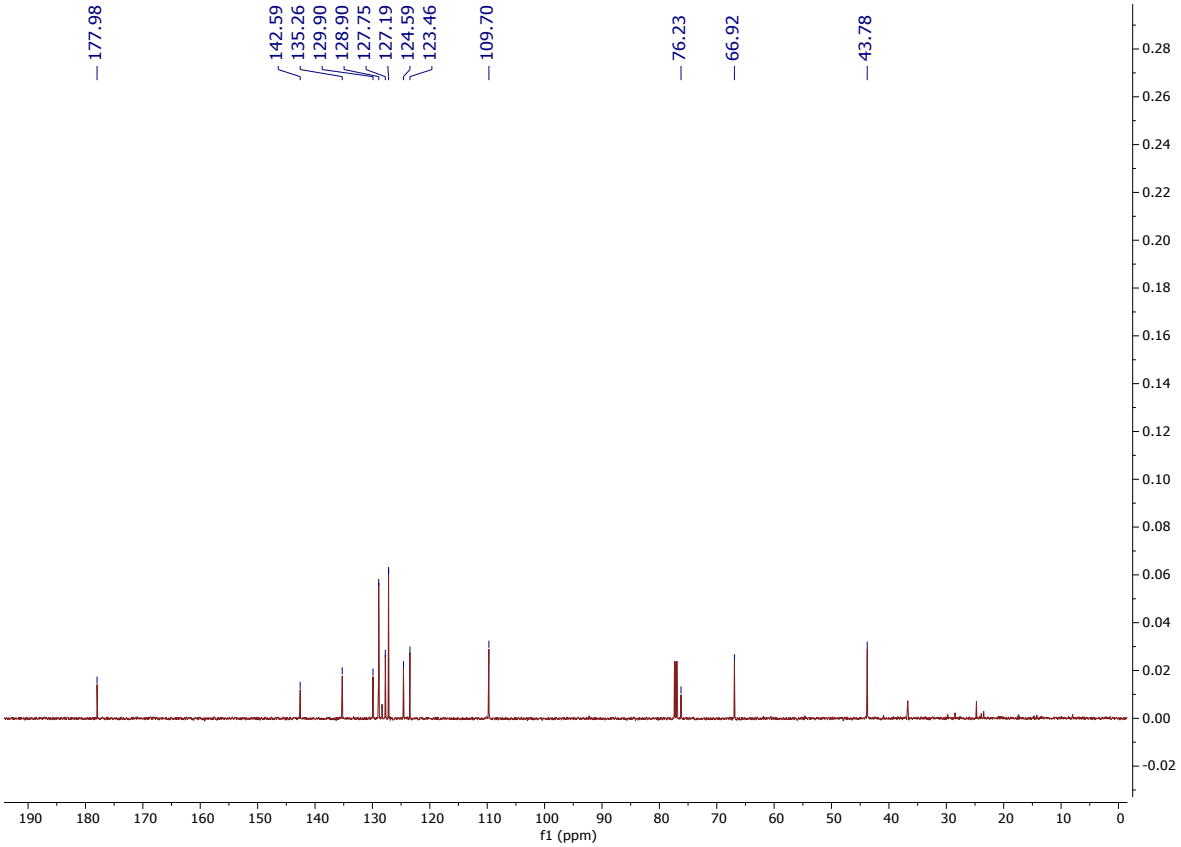


Figure S5. ^{13}C NMR of **2a**.

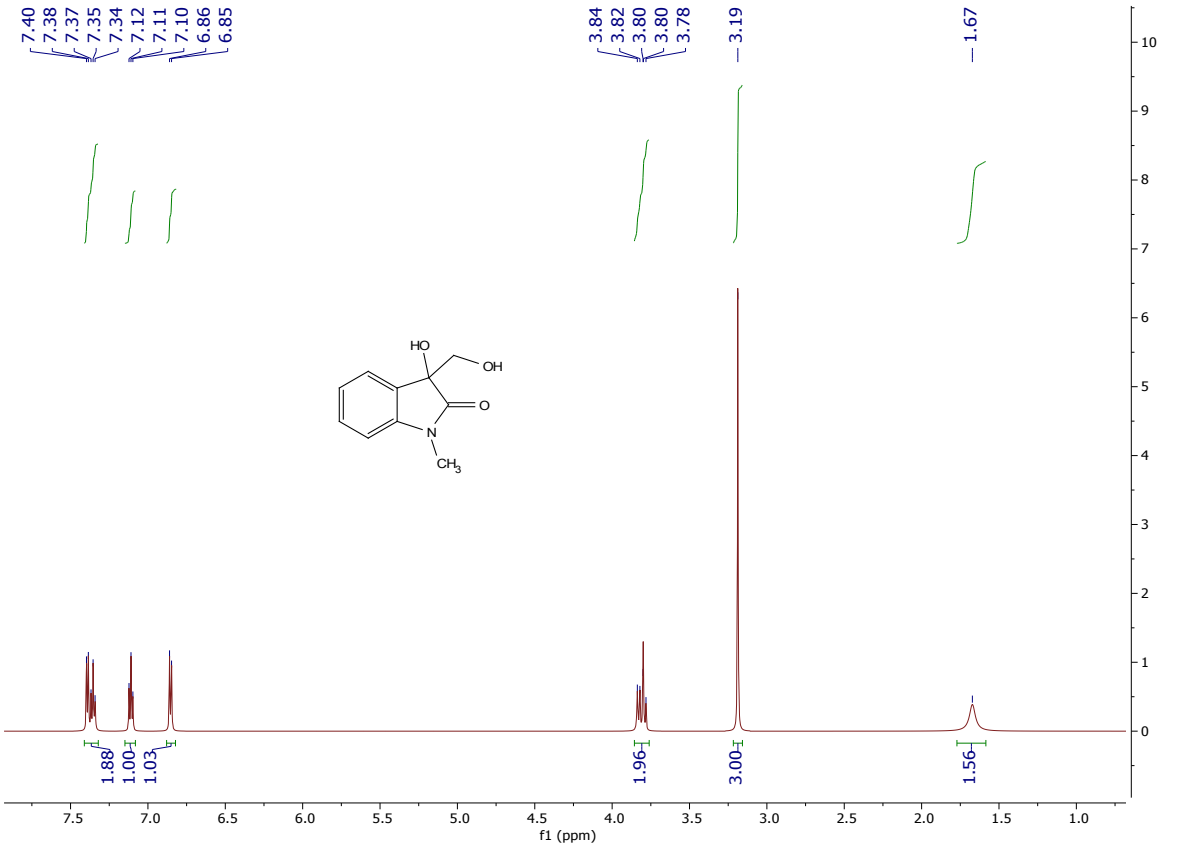


Figure S6. ^{1}H NMR of **2b**.

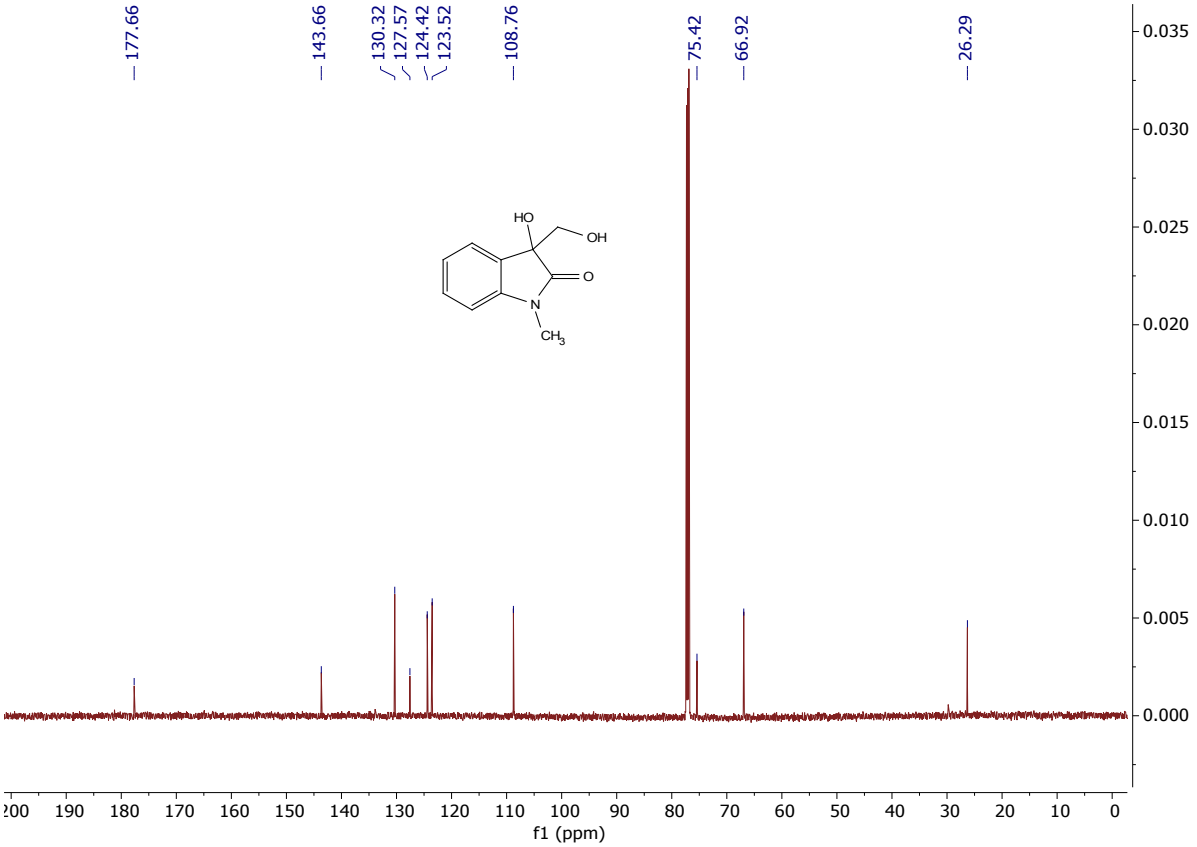


Figure S7. ^{13}C NMR of **2b**.

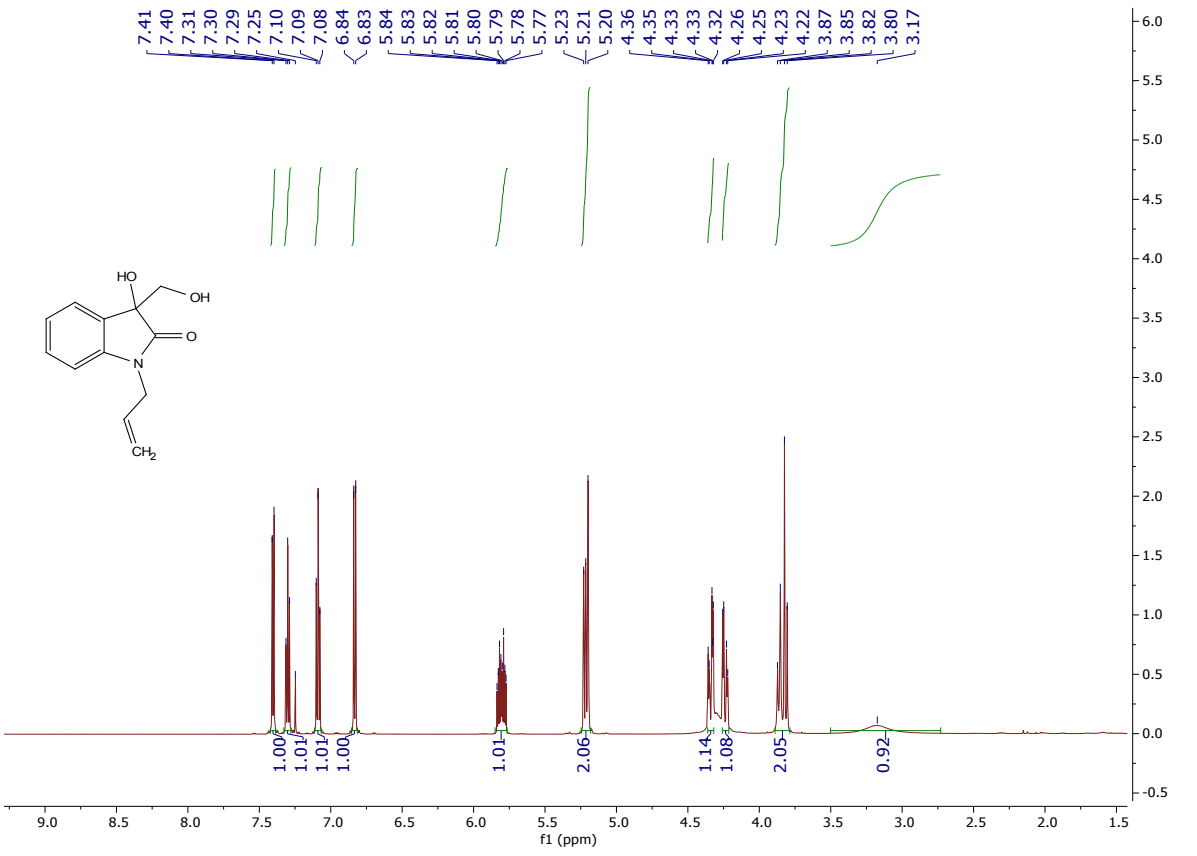


Figure S8. ^{1}H NMR of **2c**.

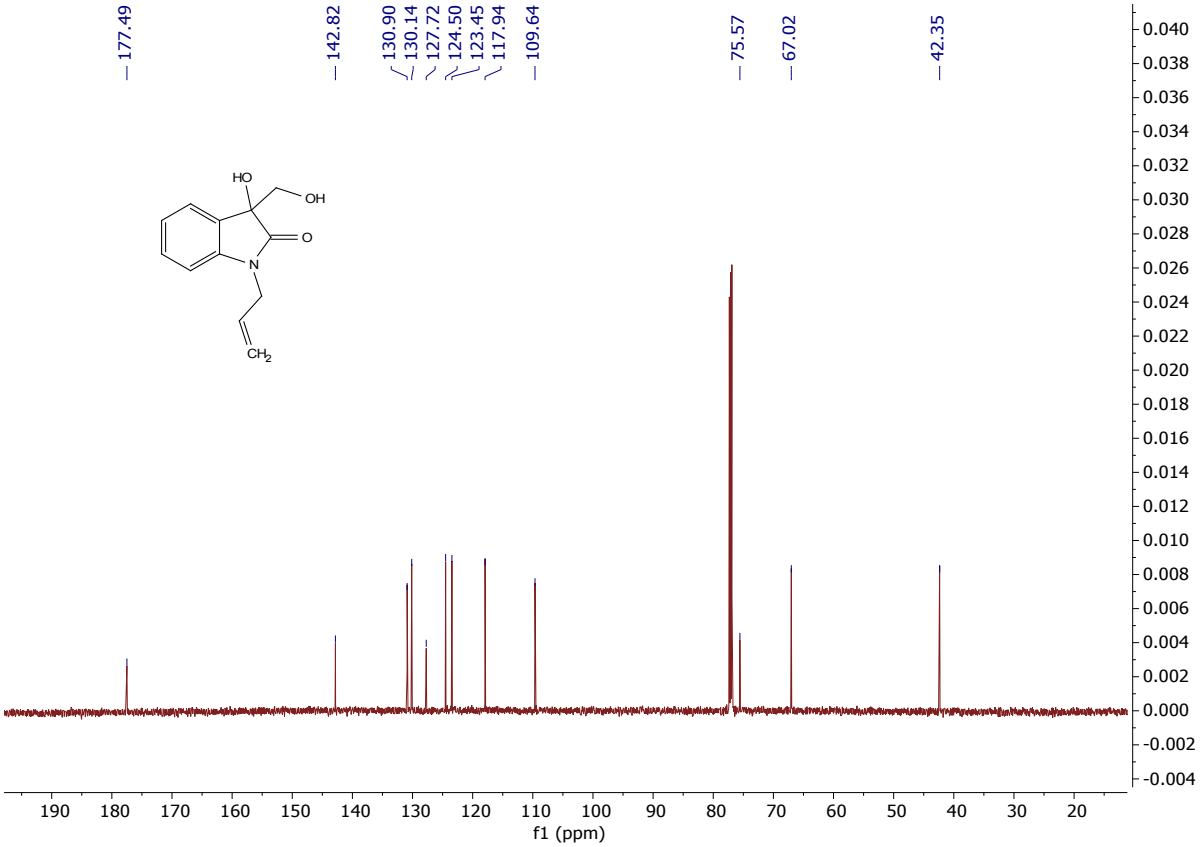


Figure S9. ^{13}C NMR of **2c**.

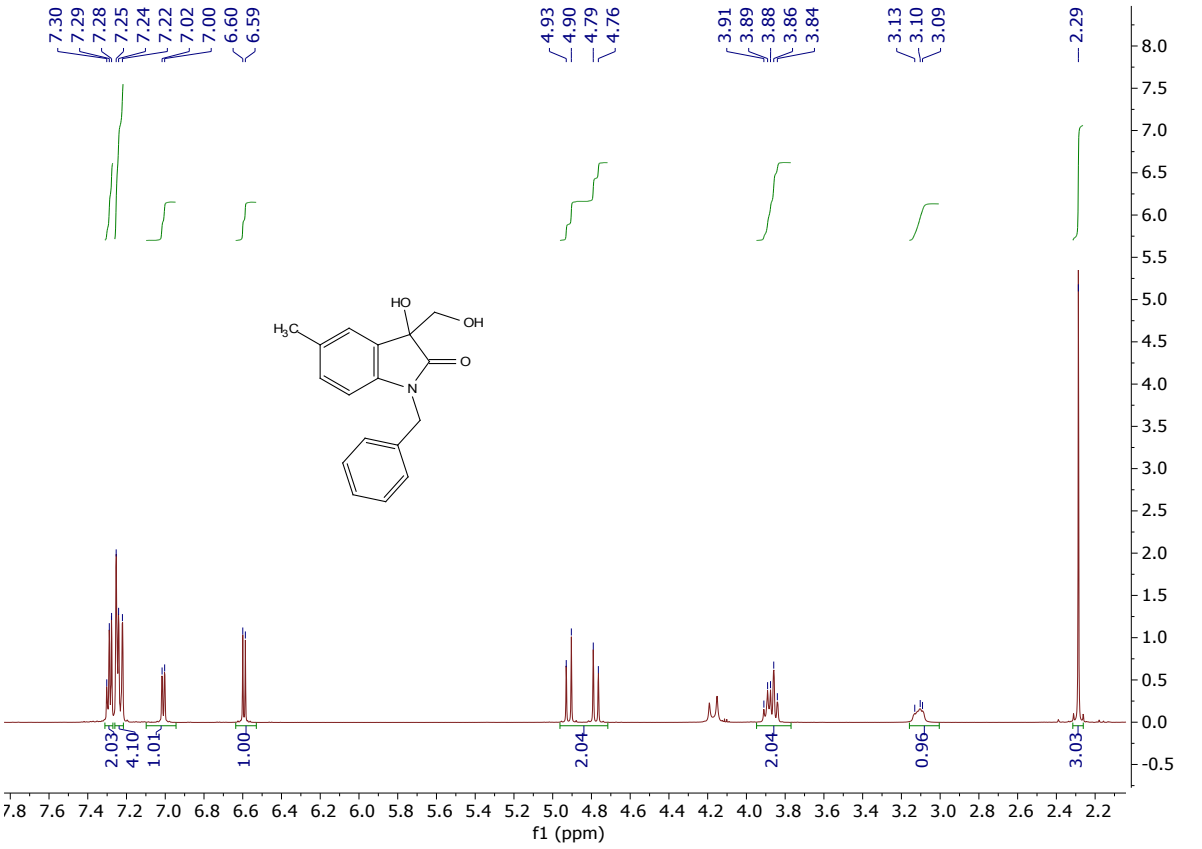


Figure S10. ^{1}H NMR of **2d**.

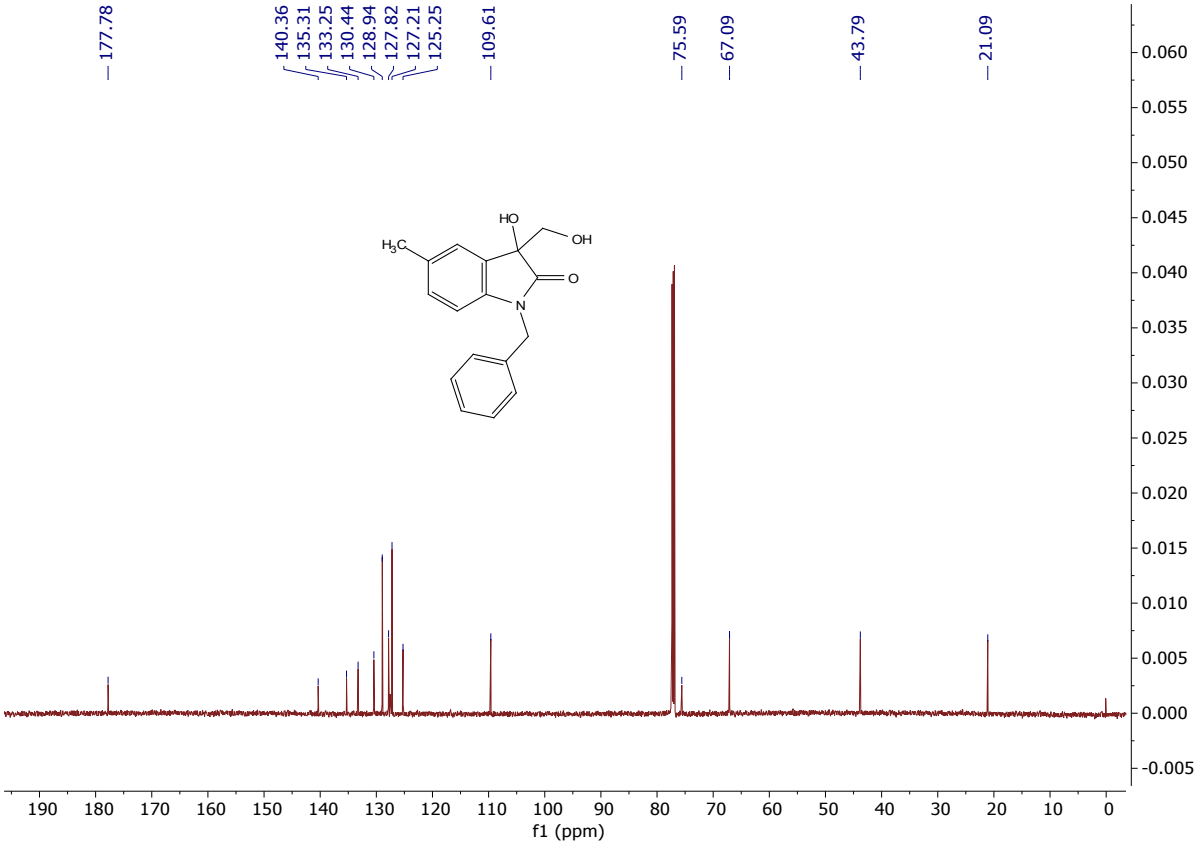


Figure S11. ^{13}C NMR of **2d**.

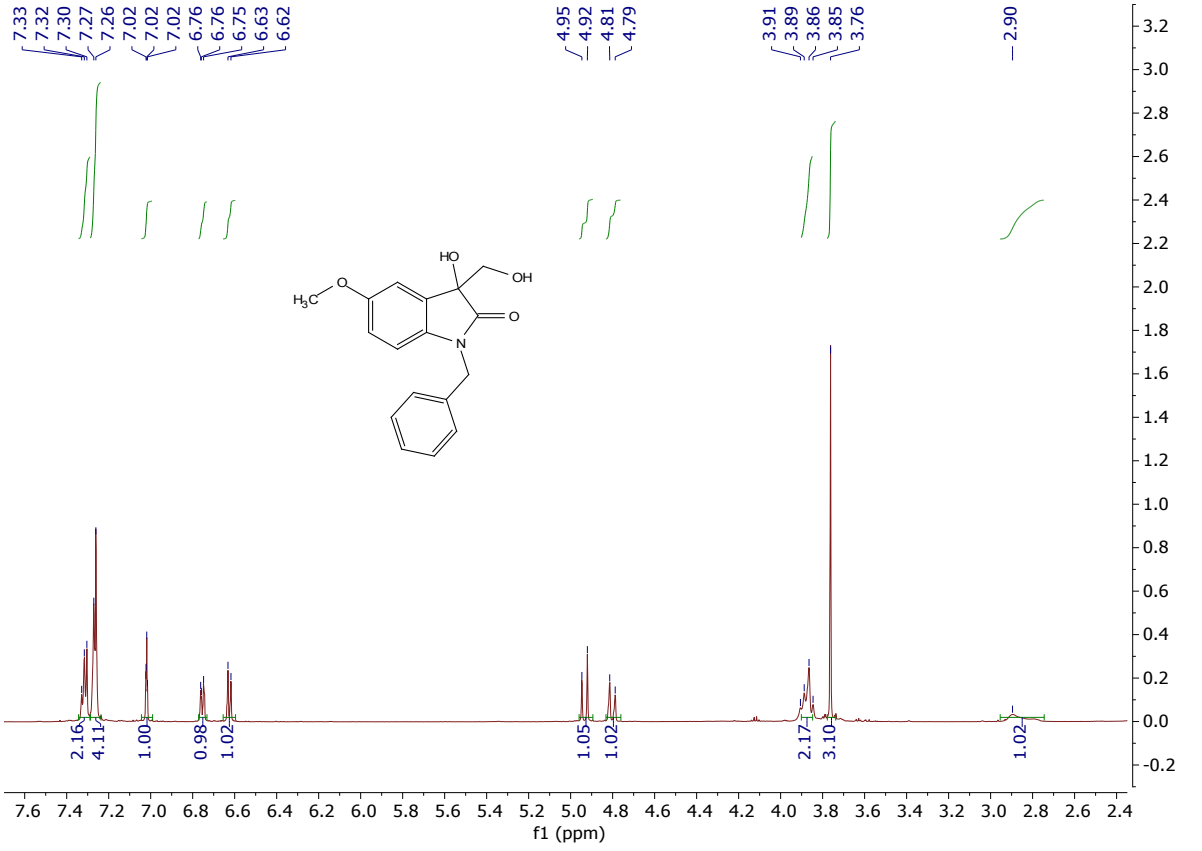


Figure S12. ^{1}H NMR of **2e**.

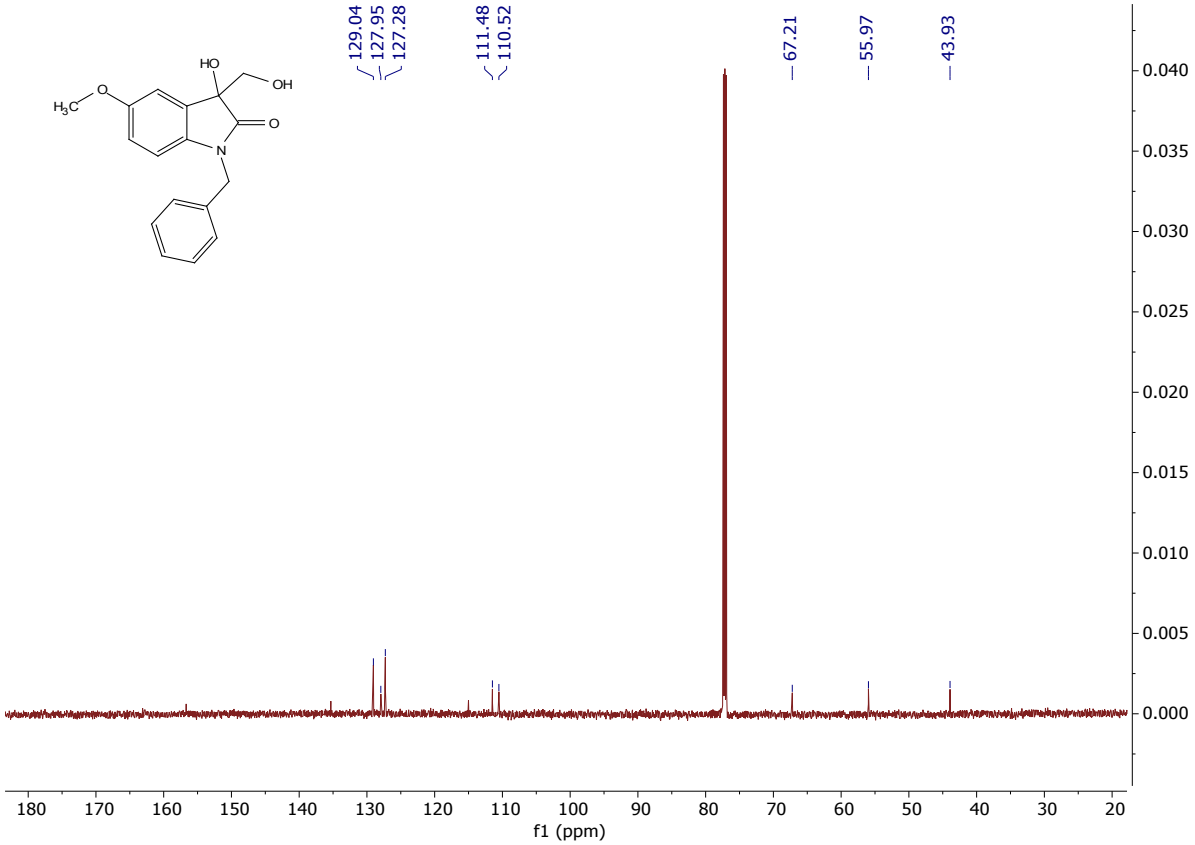


Figure S13. ^{13}C NMR of **2e**.

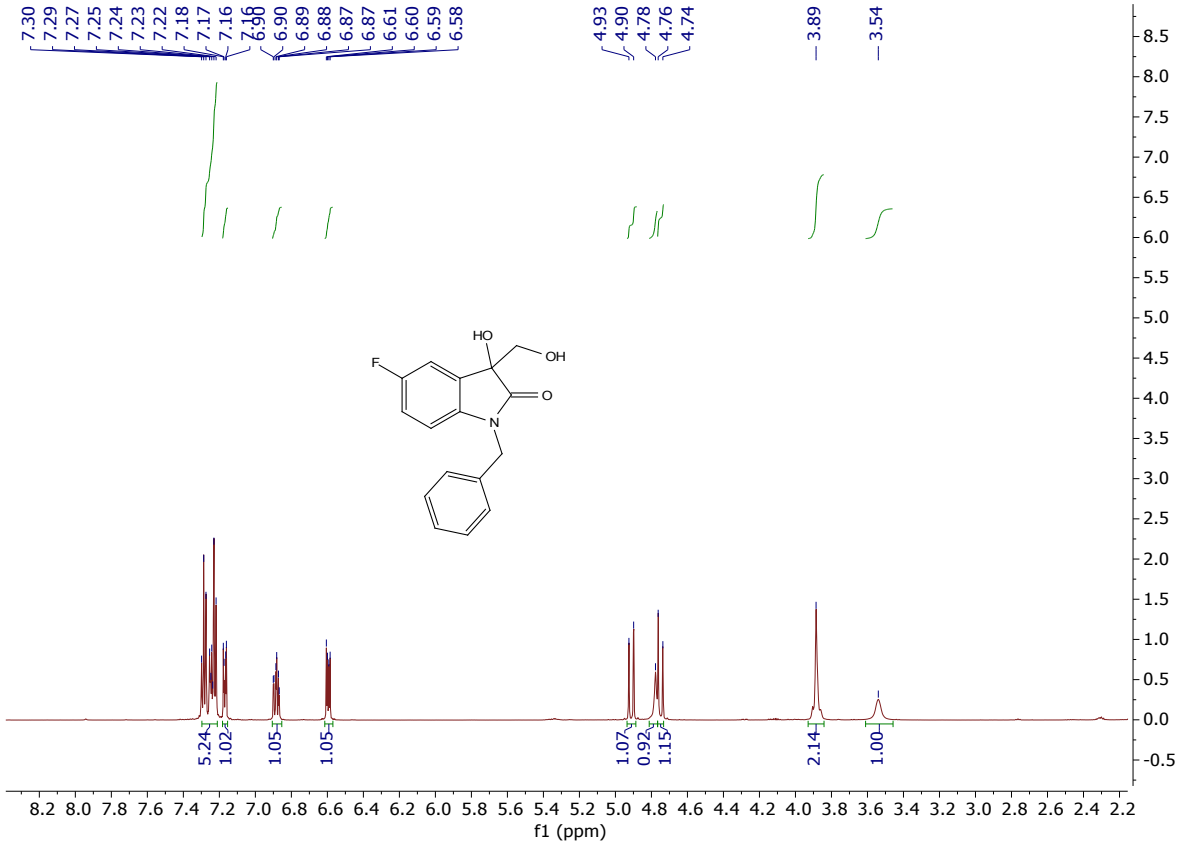


Figure S14. ^{1}H NMR of **2f**.

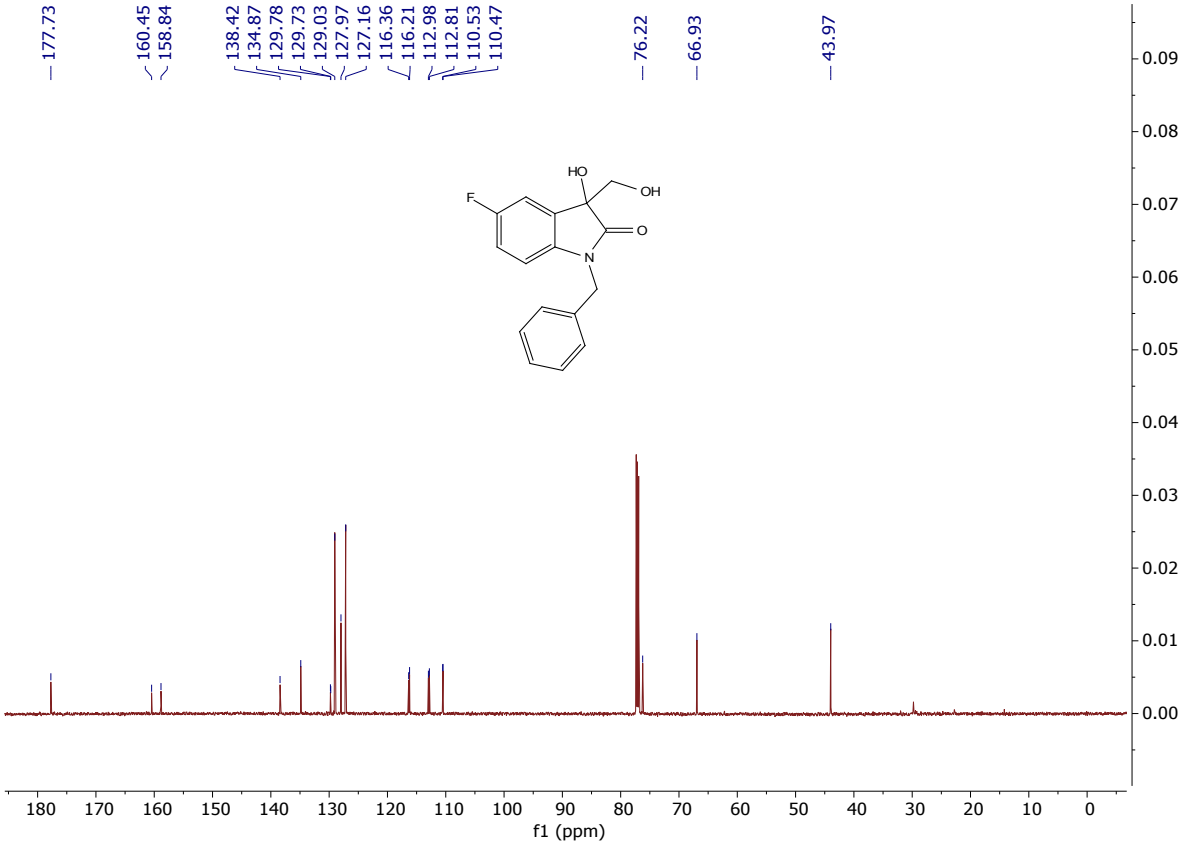


Figure S15. ^{13}C NMR of **2f**.

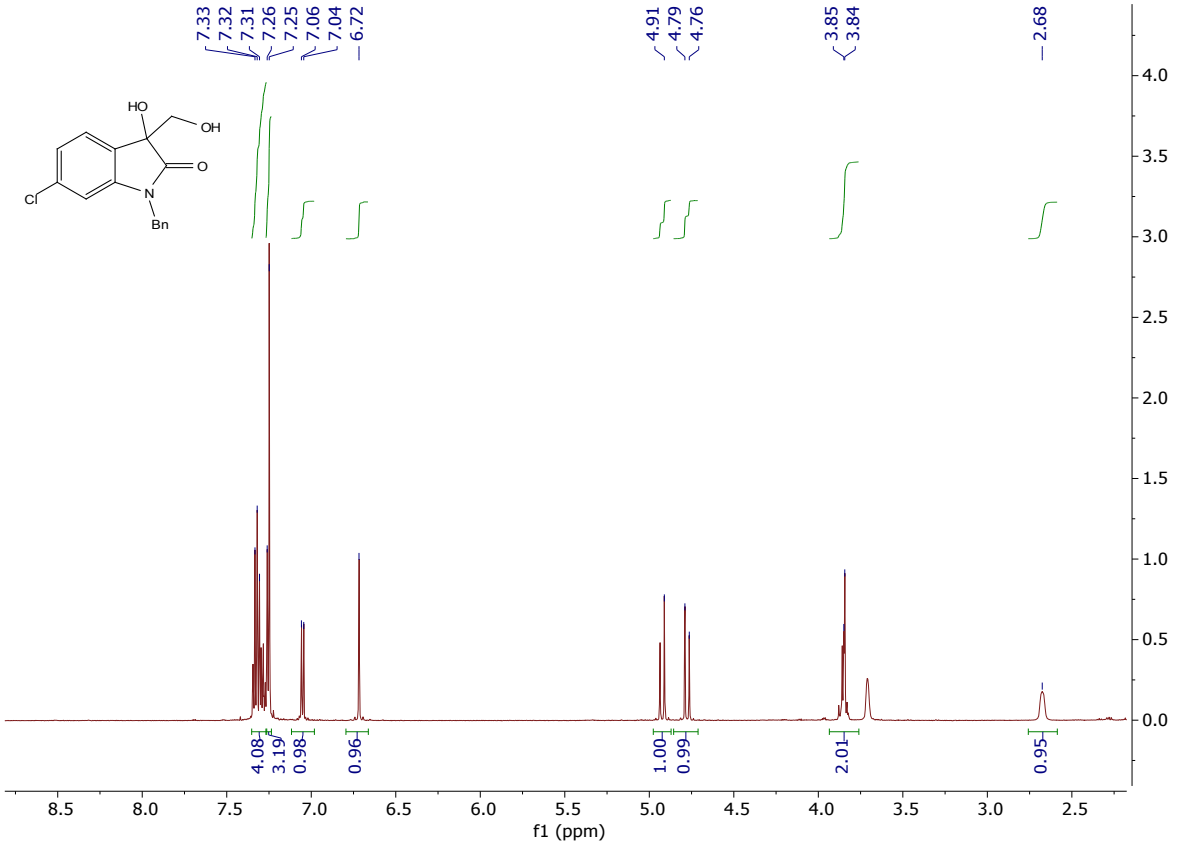


Figure S16. ^{1}H NMR of **2g**.

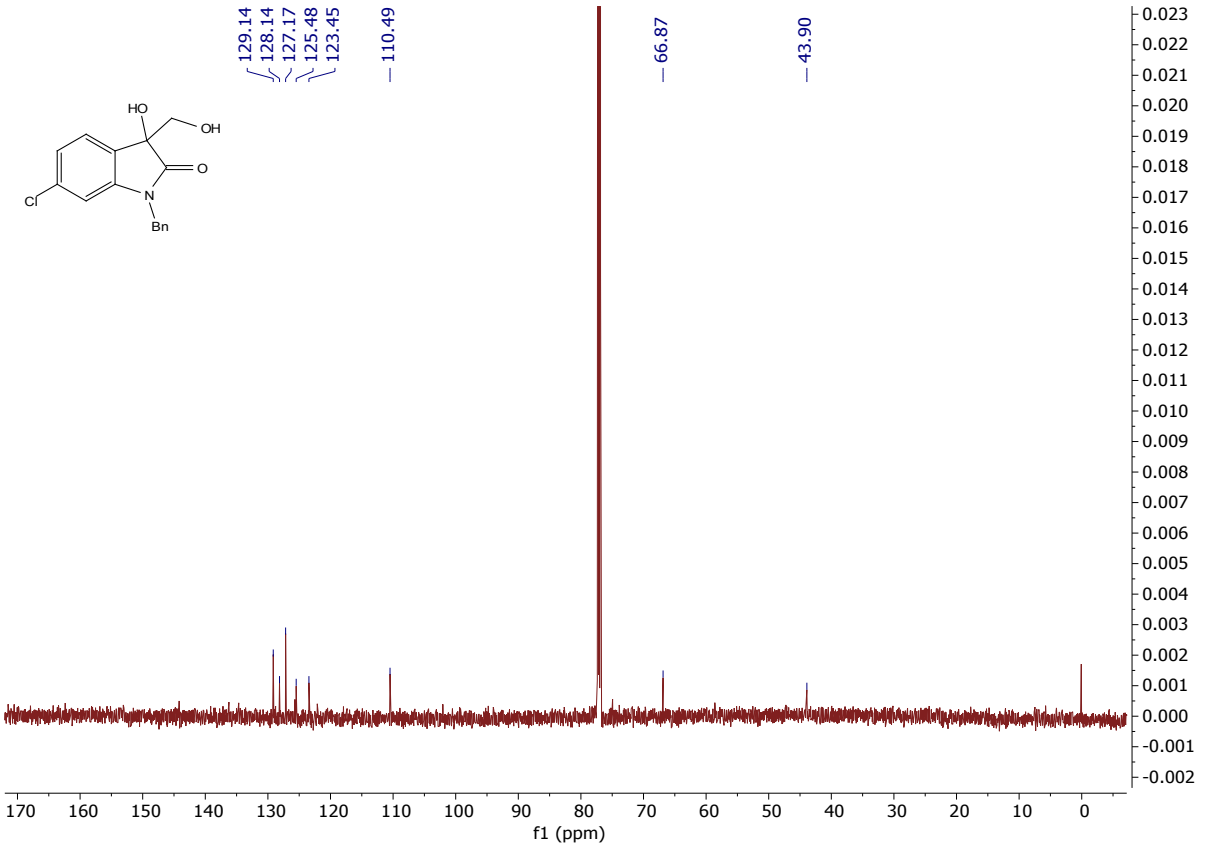


Figure S17. ^{13}C NMR of **2g**.

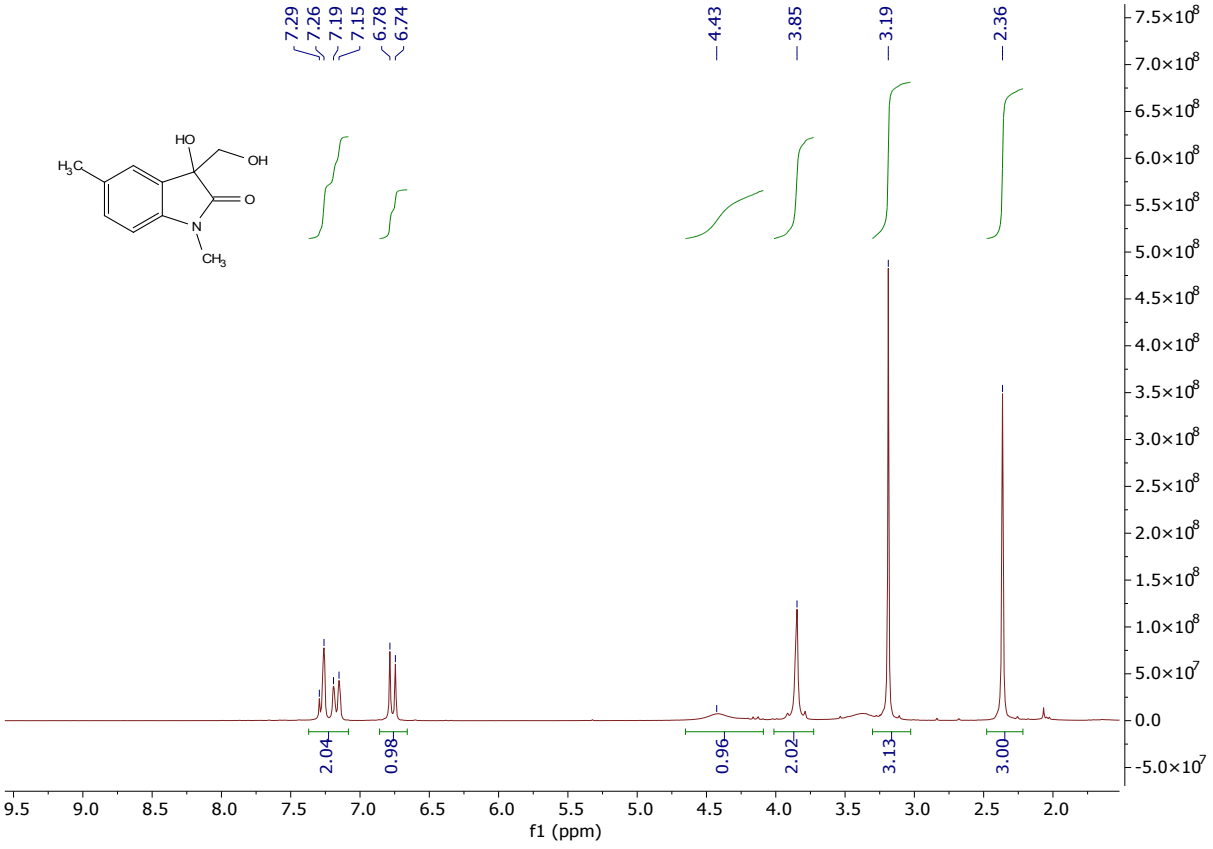


Figure S18. ^{1}H NMR of **2j**.

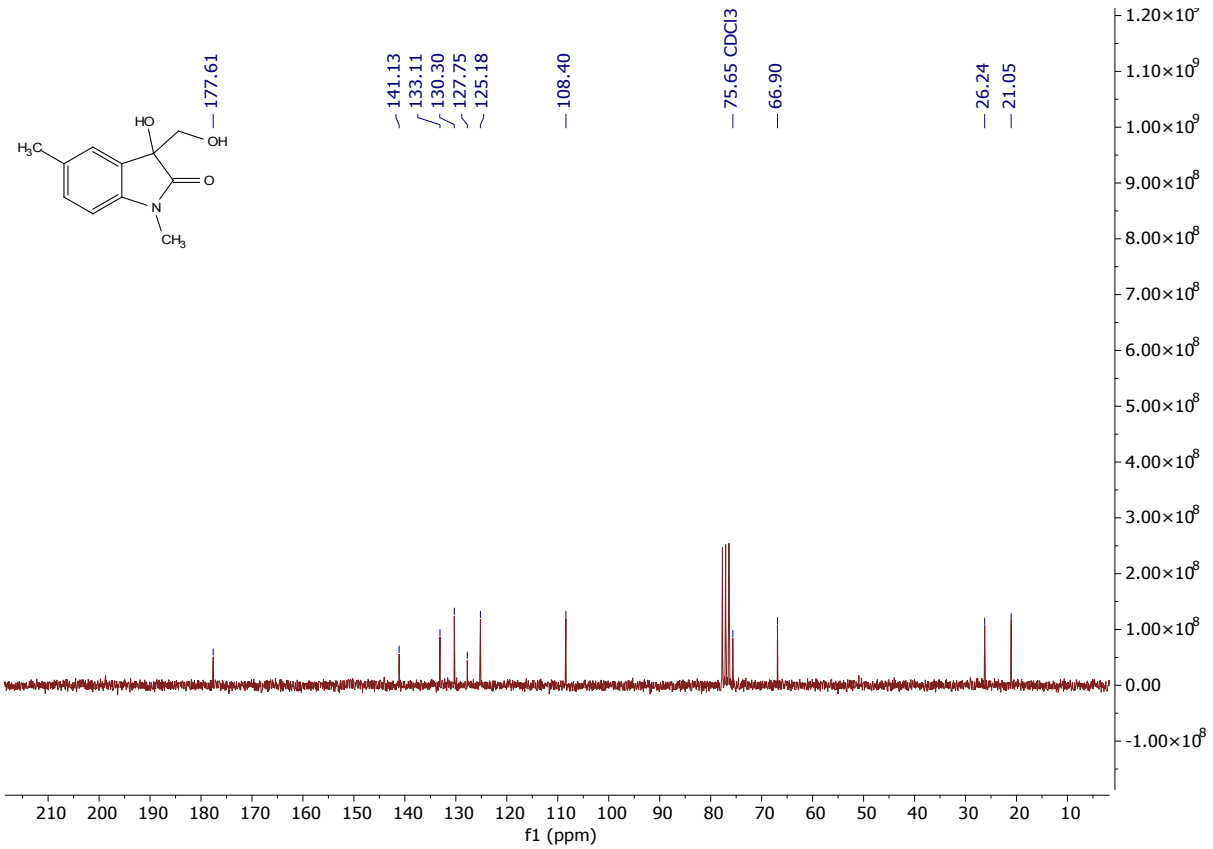


Figure S19. ^{13}C NMR of **2j**.

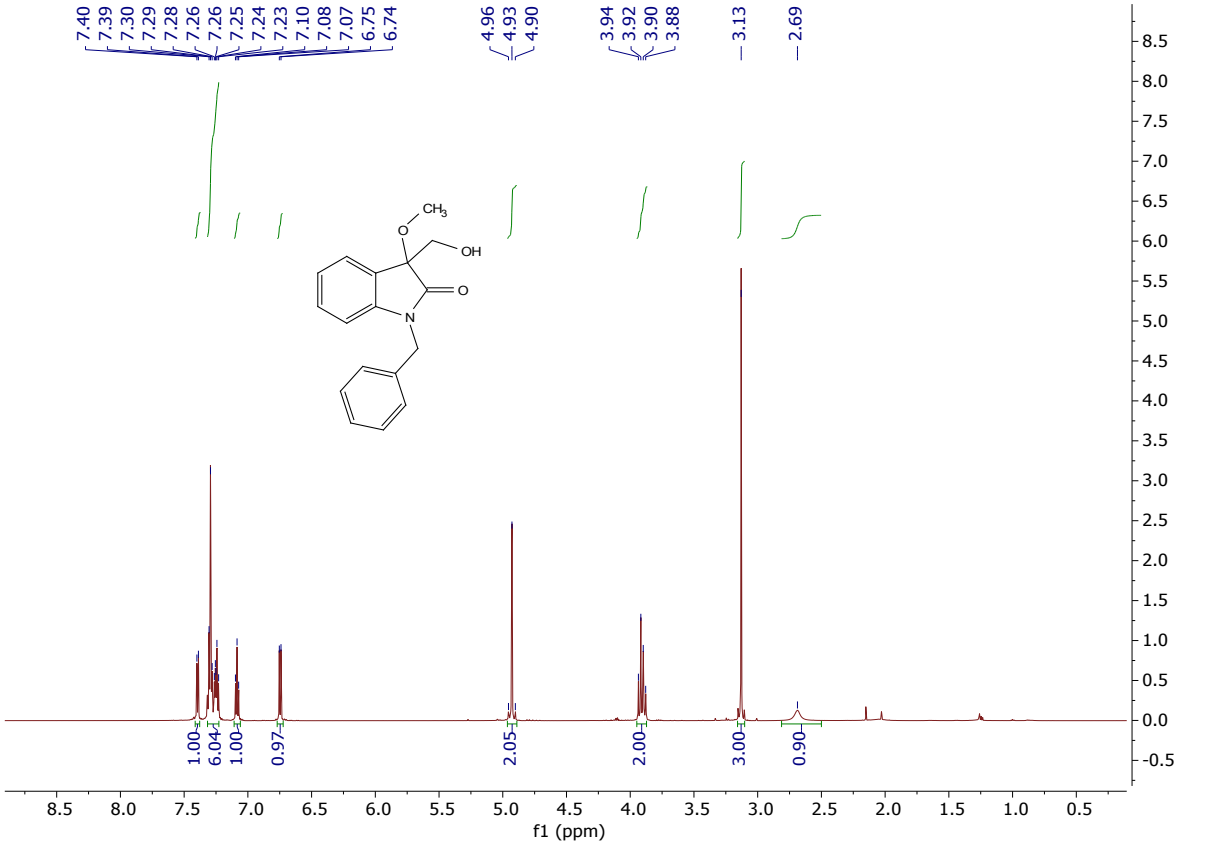


Figure S20. ^{1}H NMR of **2k**.

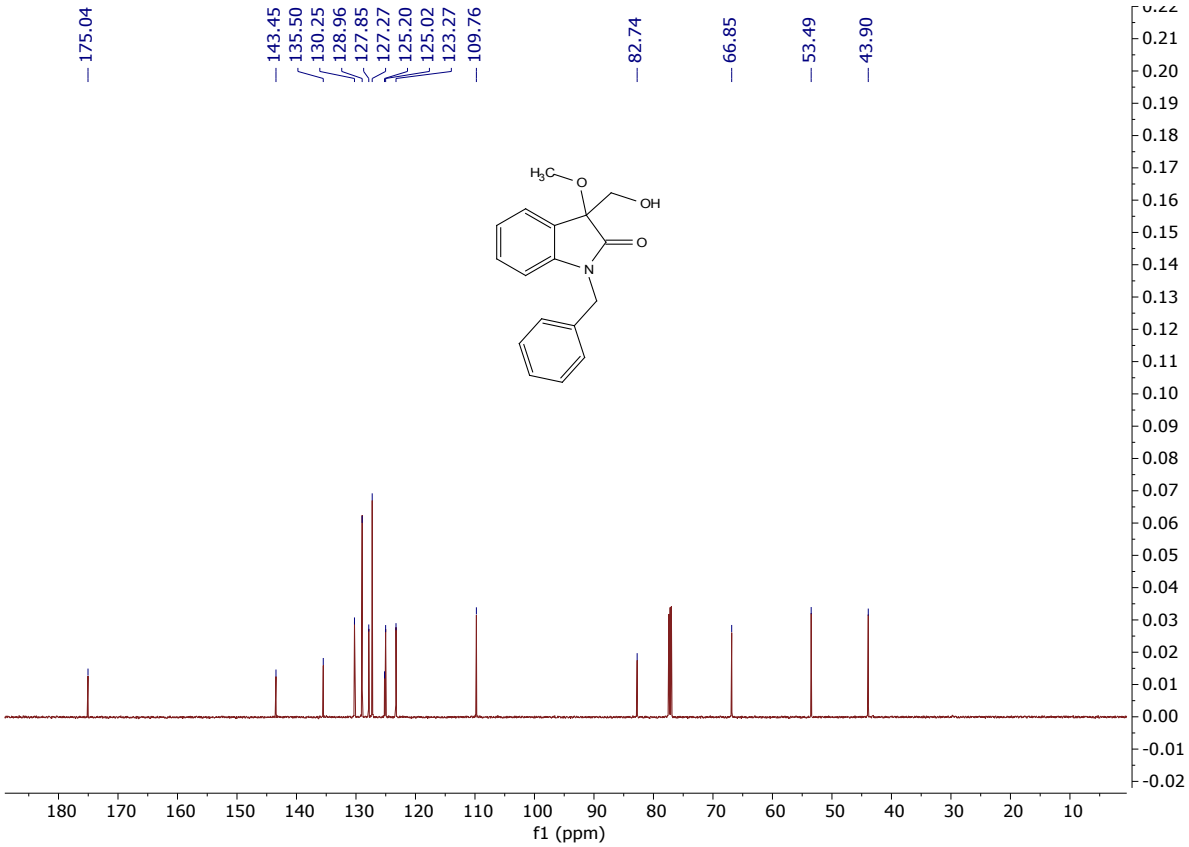


Figure S21. ^{13}C NMR of **2k**.

References:

S1. *SAINT+, 6.02 ed*, Bruker AXS, Madison, WI, 1999.

S2. *XPREP, 5.1 ed*, Siemens Industrial Automation Inc., Madison, WI, 1995.

S3. Sheldrick, G. M. *SHELXTL Reference Manual: Version 5.1*; Bruker AXS, Madison, WI, 1997.

S4. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3-8.