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Electronic Supporting Information

Photoactivation of PMS over CuO-ZnO p-n heterojunction for selective C2 trimerization of indoles

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1. Physical measurements

All the characterizations and analysis were done by using the following analytical approaches to complete physical measurements. X-ray diffraction (XRD) of the samples was carried out in a Philips PANalytical Empyrean instrument, enabling low-angle measurement from 0-60° with a minimum step size (2θ) of 0.0001, and BRUKER AXS, D8 FOCUS instrument in the 2θ value range of 5-80°. The Infra-red (FTIR) spectra in the mid-IR range were recorded in a Frontier MIR-FIR from Perkin-Elmer having mid-IR range 400-4000 cm^{-1}. The IR spectra were recorded as KBr pellets. The UV-Vis experiments were carried out in Shimadzu, UV-2550 spectrophotometer. The Raman analyses were performed in an EZ Raman-N (Enwave Optronics) Raman spectrophotometer, having laser light of 150 mW, 785 nm incident wavelength through 100× (0.3 N.A.) objective lens. The X-ray photoelectron spectroscopy (XPS) analyses were measured with KRATOS (ESCA AXIS 165) spectrometer using Mg Kα (1253.6 eV) radiation as a source. The oven-dried samples (finely ground) were dusted on a graphite sheet (double stick) and mounted over the regular sample holder, before being transferred to an analysis chamber. The material was degassed overnight in a vacuum oven before recording the XPS. The binding energy values were corrected with reference to C 1s peak at 284.8 eV. The peaks were deconvoluted using Origin software (OriginPro 8.5). Mott Schottky (MS) analysis studies was performed in a CHI-600E meter from CH Instruments using the glassy carbon electrode (GCE) as a working electrode, Ag/AgCl as reference electrode and Pt wire as a counter electrode, respectively. Thermogravimetric analysis was recorded on a simultaneous TG-DTA thermo analyzer, Mettler Toledo, with a Pt crucible, Pt/Pt-Rh 13% thermocouples and flow rate of the controlling (air) of 20 mL/min. The H_2-TPR (Temperature Programmed Reduction) was performed by taking the same amount of catalyst within the temperature range of 100-600 °C with heating rate of 10 K/min using He gas and a flow rate of 80 mL/min. It was then flushed with H_2 gas with flow rate 80mL/min. Scanning electron microscopic (SEM) images were recorded with JEOL, JAPAN (Model: JSM 6390LV) with resolution: 3nm, magnification: 3,00,000X, applied voltage: 30 kV (max.). The transmission electron microscopic (TEM) images were recorded on a JEOL (JEM-2010) instrument equipped with a CCD camera (slow-scan) with a 200 kV accelerating voltage. Energy dispersive X-ray (EDX) analysis was performed with JEOL, model No: 7582 (Oxford make), resolution: 137 eV at 5.9 KeV; Minimum weight % = .01%, sample size: 10mm dia, 1mm thick(max), dry and moisture free. PL spectra were recorded in FL3C-KIT_2031C-4819-FL instrument. The photoelectrochemical measurements of the samples was carried out in a three-electrode working set up consisting of WE (Substrates), RE (Ag/AgCl) and CE (Pt wire), 1 M KOH and Potentiostat (Interface 1010E, Gamry). Thin Layer Chromatographic (TLC) plate (TLC Silica gel 60 F254) was used for monitoring the progress of the reaction. The reactions were monitored through TLC by comparing the retention factor (R_f) of the reactant molecule with the reaction mixture. The isolated % yields were calculated after isolation of desired product using the following equation: % yield = [mole of isolated product/mole of limiting reactant] × 100. ^{1}H NMR spectra are recorded on 400 spectrometers. ^{13}C NMR spectra were recorded on 101MHz.1H and ^{13}C nuclear magnetic resonance (NMR) analyses were done by DRX-400 Varian, Bruker AVANCE III HD 400 MHz spectrometers. Mass spectrum (MS) was recorded in a Q-T of Electron Spray Ionization Mass spectroscopy (ESI-MS) instrument (model HAB 273) in DMSO (HPLC-grade).

Electronic Supporting Information

1. Synthesis of CuO-ZnO catalyst

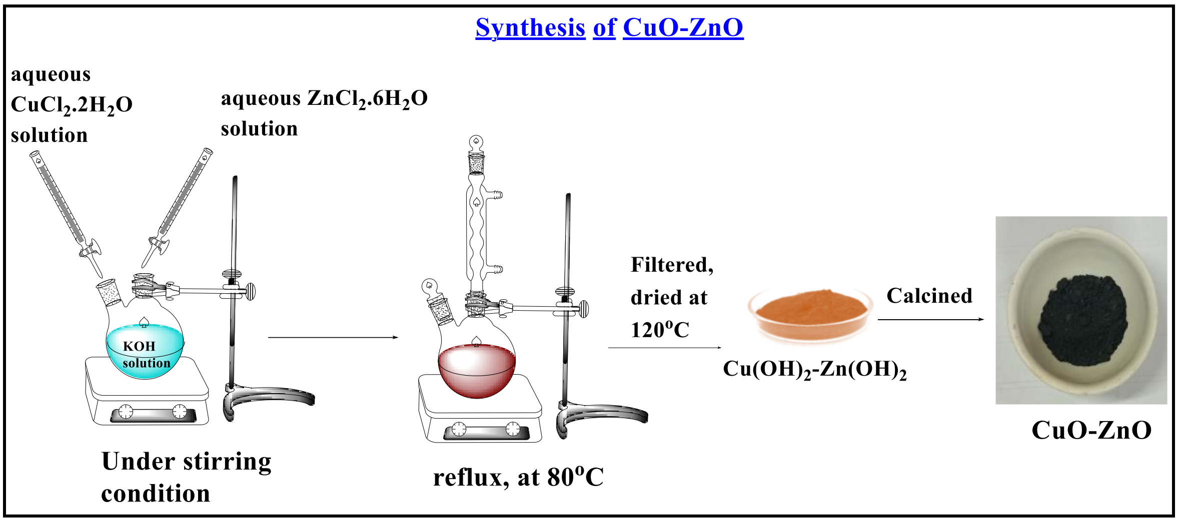


Fig. S1 Synthesis of CuO-ZnO catalyst

2. Characterisation of the neat metal oxides: CuO and ZnO

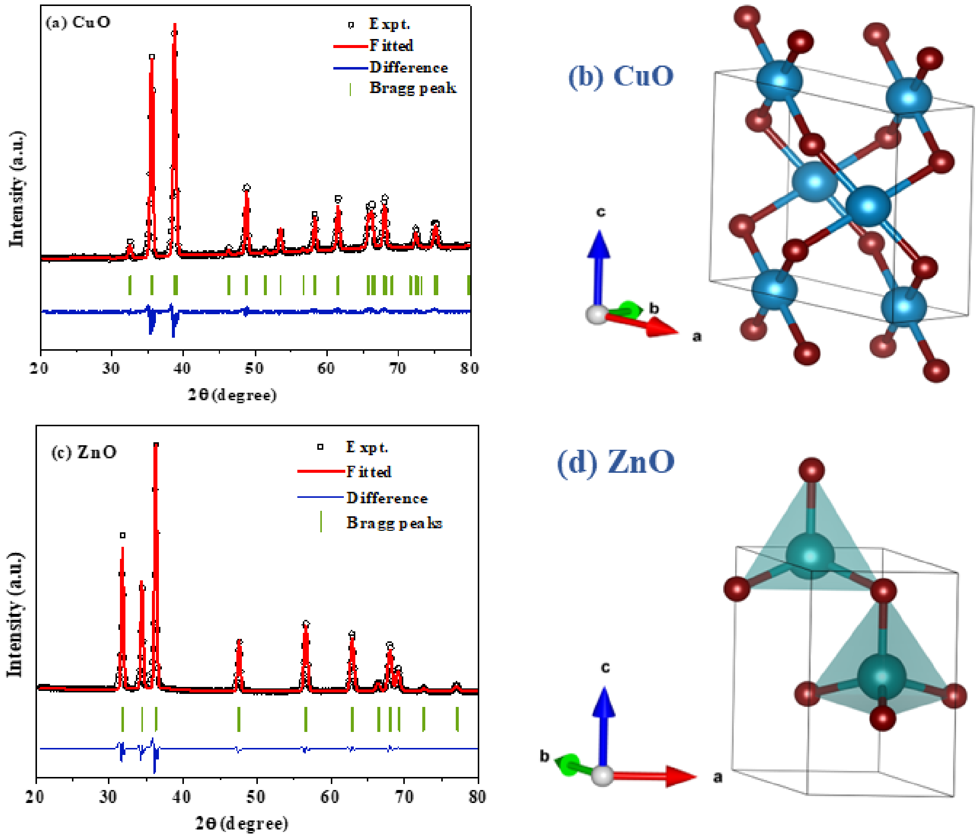


Fig. S2 Rietveld refinement and structural representation of (a, b) CuO and (c, d) ZnO.

3. PXRD analysis of CuO-ZnO catalyst synthesized in different ratios

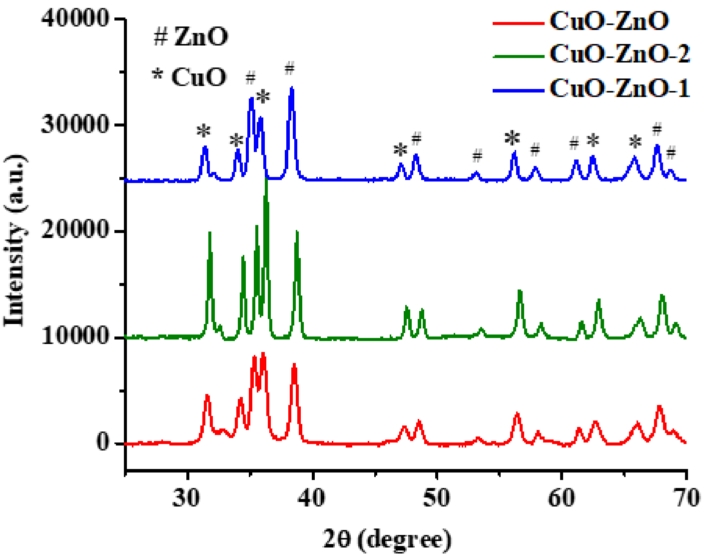


Fig. S3 PXRD analysis of CuO-ZnO catalysts with different copper percentage

4. XPS analysis of C

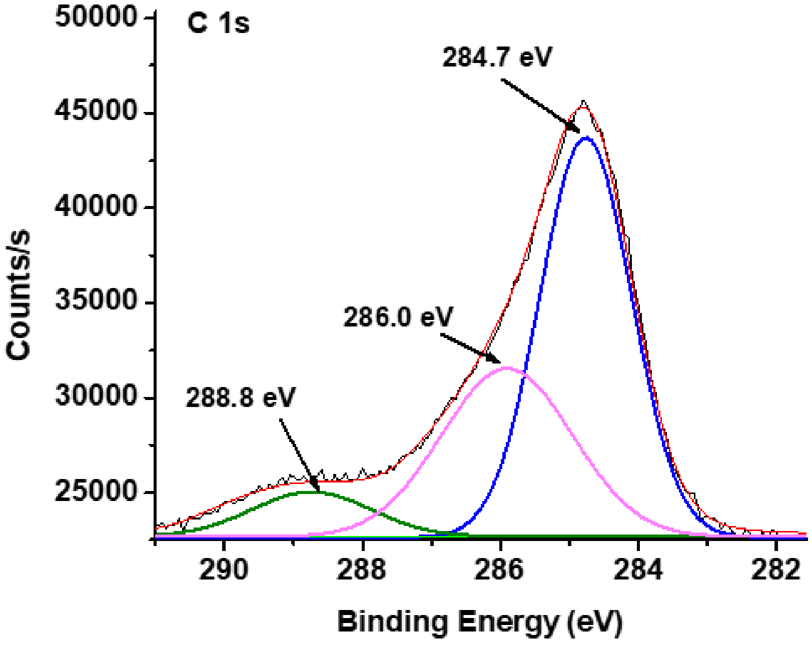


Fig. S4 XPS spectra of carbon

5. Morphological study of ZnO

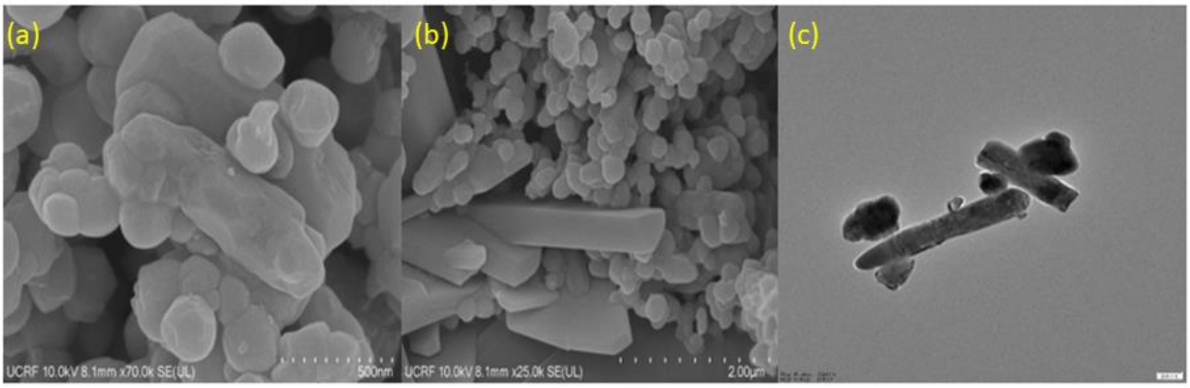
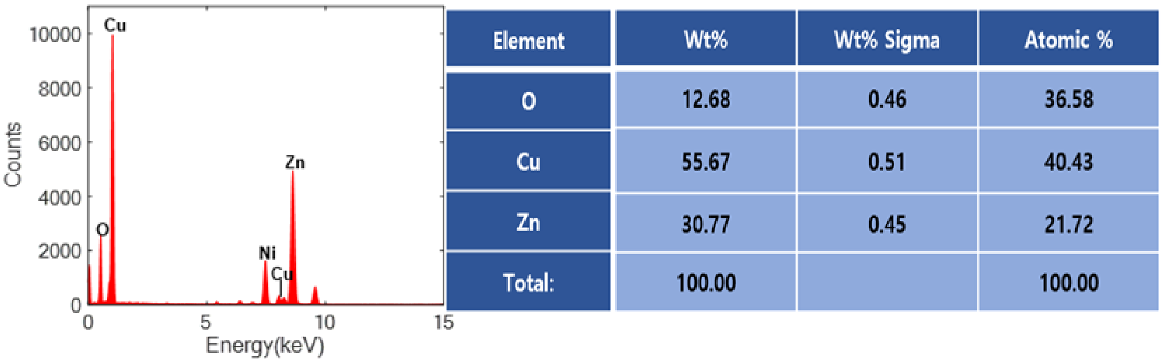


Fig. S5 SEM and TEM images of ZnO catalyst

6. EDX spectra of mixed CuO-ZnO catalyst



Element	Wt%	Wt% Sigma	Atomic %
O	12.68	0.46	36.58
Cu	55.67	0.51	40.43
Zn	30.77	0.45	21.72
Total:	100.00		100.00

Fig. S6 EDX spectra showing the presence of all the elements in the CuO-ZnO material and the elemental amounts are given in weight% (Ni is from Ni grid).

7. Comparison of catalytic activity of CuO, ZnO and CuO-ZnO catalysts

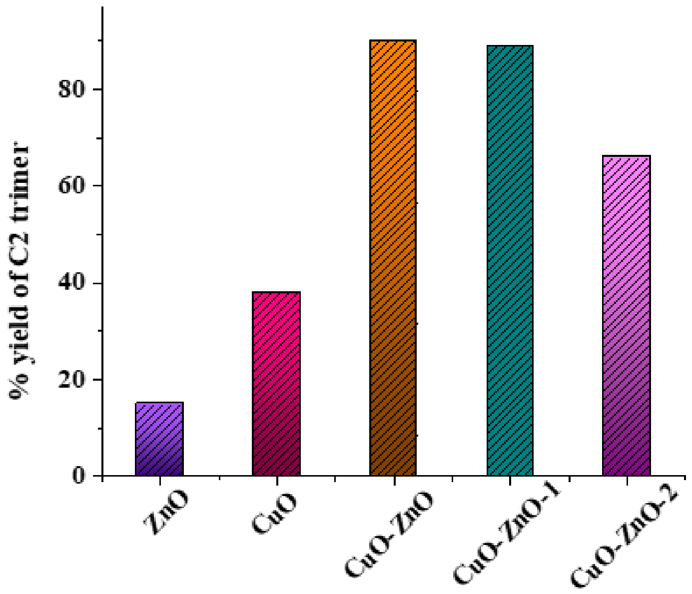


Fig. S7 Comparison of catalytic activities of the different synthesized catalysts.

8. Catalyst recyclability study

(a) Activity of CuO-ZnO catalyst in consecutive catalytic runs

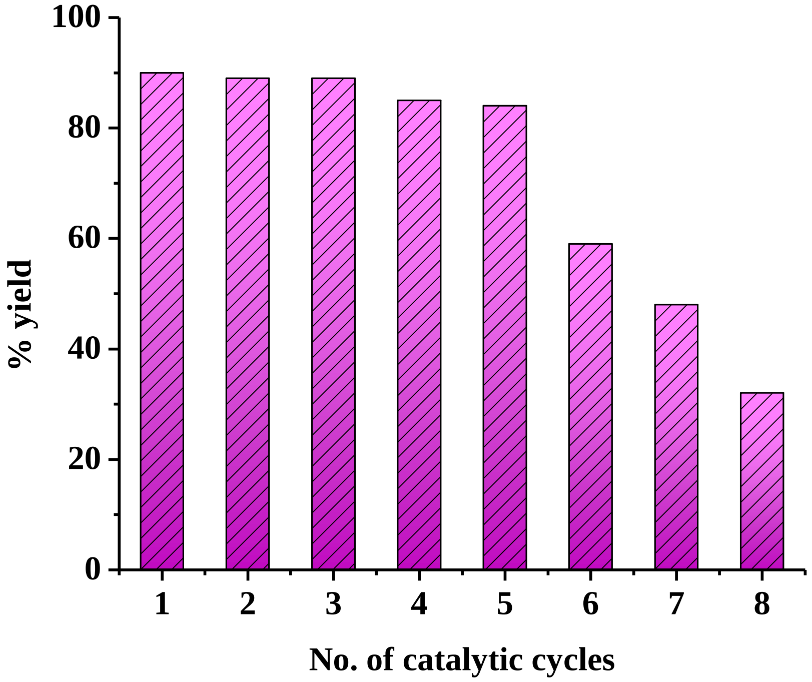


Fig. S8 Showing % yield of C2 trimer of indole in each consecutive run of CuO-ZnO catalyst.

(b) Characterization of the recycled catalyst

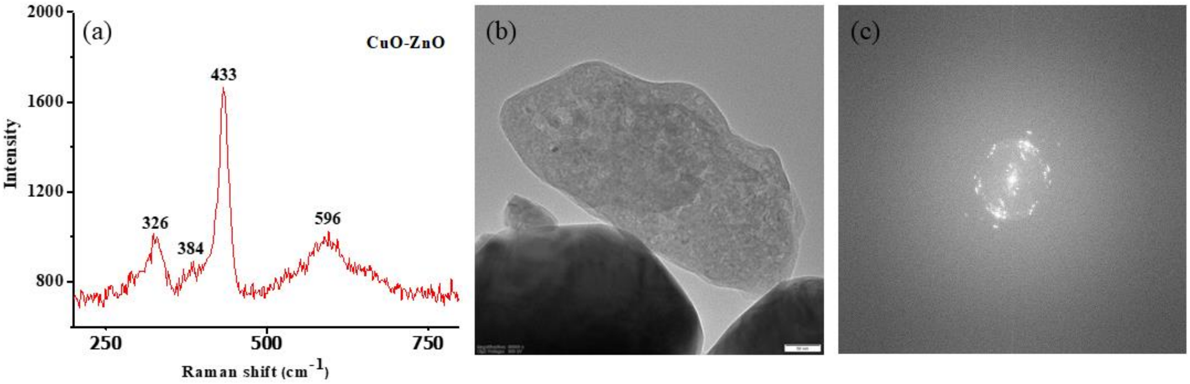
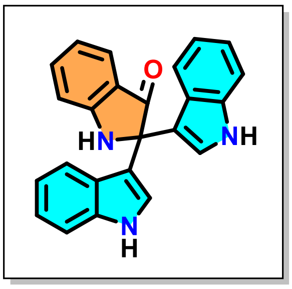


Fig. S9 (a) Raman spectra and (b) TEM image and (c) SAED pattern of the recycled catalyst.

9. Characterization of the compounds:

NMR Analysis: ^{1}H and ^{13}C NMR

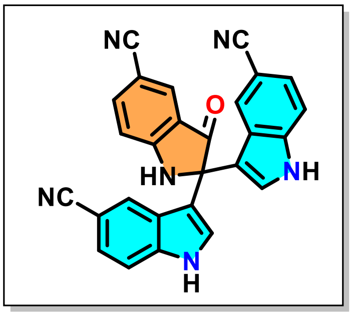
Compound 2a): [3,2':2',3''-terindolin]-3'-one[1]



^{1}H NMR (400 MHz, MeOD): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 4H), 7.12 – 7.00 (m, 4H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 7.1 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, MeOD): δ 205.2, 162.8, 139.2, 138.8, 127.2, 125.9, 125.4, 122.5, 121.7, 119.8, 118.9, 115.3, 113.3, 112.4, 69.9.

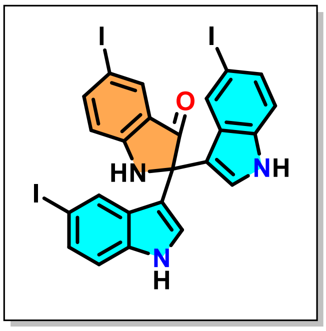
Compound 2b): 3'-oxo-[3,2':2',3''-terindoline]-5,5',5''-tricarbonitrile[2]



^{1}H NMR (400 MHz, MeOD): δ 7.96 (d, *J* = 1.2 Hz, 1H), 7.76 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.65 (s, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.39 (s, 2H), 7.34 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 1H).

^{13}C NMR (100 MHz, MeOD): δ 199.1, 161.6, 140.3, 139.3, 130.5, 126.1, 125.6, 125.2, 124.3, 120.2, 118.8, 117.7, 114.0, 112.7, 112.3, 101.6, 99.9, 67.9.

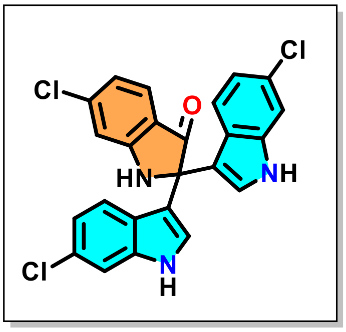
Compound 2c): 5,5',5''-triiodo-[3,2':2',3''-terindolin]-3'-one[3]



^{1}H NMR (400 MHz, MeOD): δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.76 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.67 (d, *J* = 1.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.33 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.09 (s, 1H), 6.85 (d, *J* = 8.7 Hz, 1H).

^{13}C NMR (150 MHz, MeOD): δ 202.3, 161.5, 147.1, 140.1, 137.9, 134.5, 132.3, 131.1, 130.5, 129.5, 126.1, 125.9, 125.2, 121.8, 120.1, 115.6, 114.7, 114.4, 83.2, 78.9, 69.6.

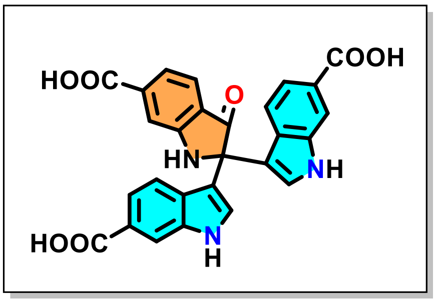
Compound 2d): 6,6',6''-trichloro-[3,2':2',3''-terindolin]-3'-one[3]



^{1}H NMR (500 MHz, MeOD): δ 7.52 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.11 (s, 2H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.85 (dd, *J* = 8.6, 1.9 Hz, 2H), 6.75 (dd, *J* = 8.3, 1.7 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 202.7, 162.7, 145.5, 139.2, 128.6, 127.3, 126.1, 125.6, 122.6, 120.5, 119.6, 118.0, 115.3, 112.7, 112.3, 69.9.

Compound 2e): 3'-oxo-1',3'-dihydro-1H,1''H-[3,2':2',3''-terindole]-6,6',6''-tricarboxylic acid

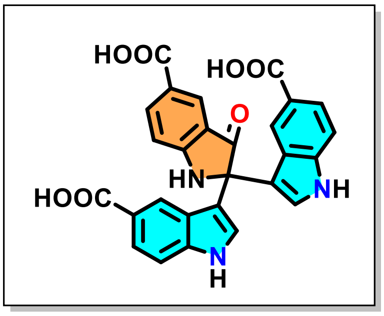


^{1}H NMR (400 MHz, MeOD): δ 8.11 (d, *J* = 0.8 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.43 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (s, 2H).

^{13}C NMR (100 MHz, MeOD): δ 203.8, 177.7, 171.2, 169.3, 162.1, 140.6, 138.1, 130.7, 128.9, 125.9, 124.7, 121.2, 121.1, 120.0, 119.8, 115.6, 115.2, 114.7, 69.9.

HRMS (ESI) m/z [M+H]$^+$ calculated for $C_{27}H_{18}N_3O_7$: 496.1139, found 496.1152.

Compound 2f): 3'-oxo-1',3'-dihydro-1H,1''H-[3,2':2',3''-terindole]-5,5',5''-tricarboxylic acid

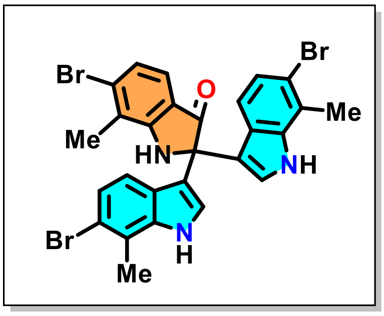


^{1}H NMR (400 MHz, MeOD): δ 8.31 (d, *J* = 1.4 Hz, 1H), 8.21 (d, *J* = 1.0 Hz, 2H), 8.17 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.79 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.25 (s, 2H), 7.02 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (100 MHz, MeOD): δ 202.8, 171.3, 169.6, 164.8, 141.6, 140.2, 129.3, 126.9, 126.5, 125.1, 124.3, 122.4, 121.1, 118.9, 116.3, 112.5, 112.3, 70.2.

HRMS (ESI) m/z [M+H]$^+$ calculated for $C_{27}H_{18}N_3O_7$: 496.1139, found 496.1147.

Compound 2g): 6,6',6''-tribromo-7,7',7''-trimethyl-1H,1''H-[3,2':2',3''-terindol]-3'(1'H)-one

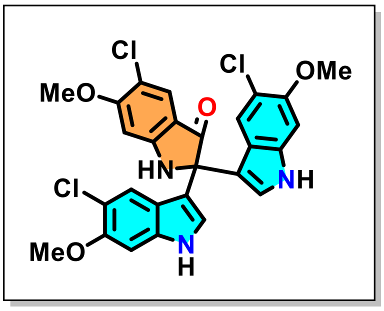


^{1}H NMR (400 MHz, MeOD): δ 7.30 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 3.8 Hz, 2H), 7.01 (d, *J* = 3.4 Hz, 1H), 2.52 (s, 6H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, MeOD): δ 203.9, 161.5, 138.7, 135.7, 126.8, 126.3, 125.9, 124.2, 124.0, 123.6, 122.53, 121.6, 120.7, 118.4, 118.3, 115.8, 70.3, 16.8, 16.2.

HRMS (ESI) m/z [M+H]$^+$ calculated for $C_{27}H_{21}Br_3N_3O$: 639.9229, found 639.9240.

Compound 2h): 5,5',5''-trichloro-6,6',6''-trimethoxy-1H,1''H-[3,2':2',3''-terindol]-3'(1'H)-one



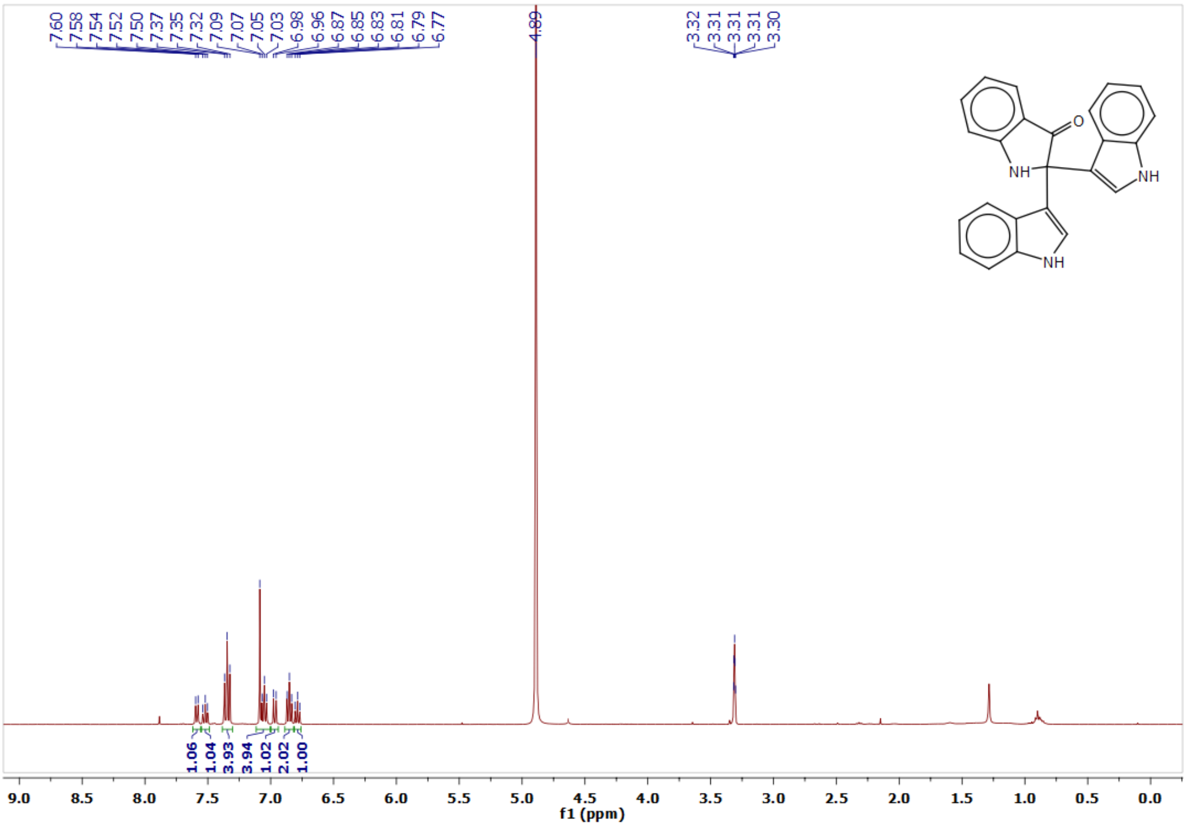
^{1}H NMR (400 MHz, MeOD): δ 7.53 (s, 1H), 7.31 (s, 2H), 7.03 (s, 2H), 6.94 (s, 2H), 6.50 (s, 1H), 3.83 (d, *J* = 38.3 Hz, 9H).

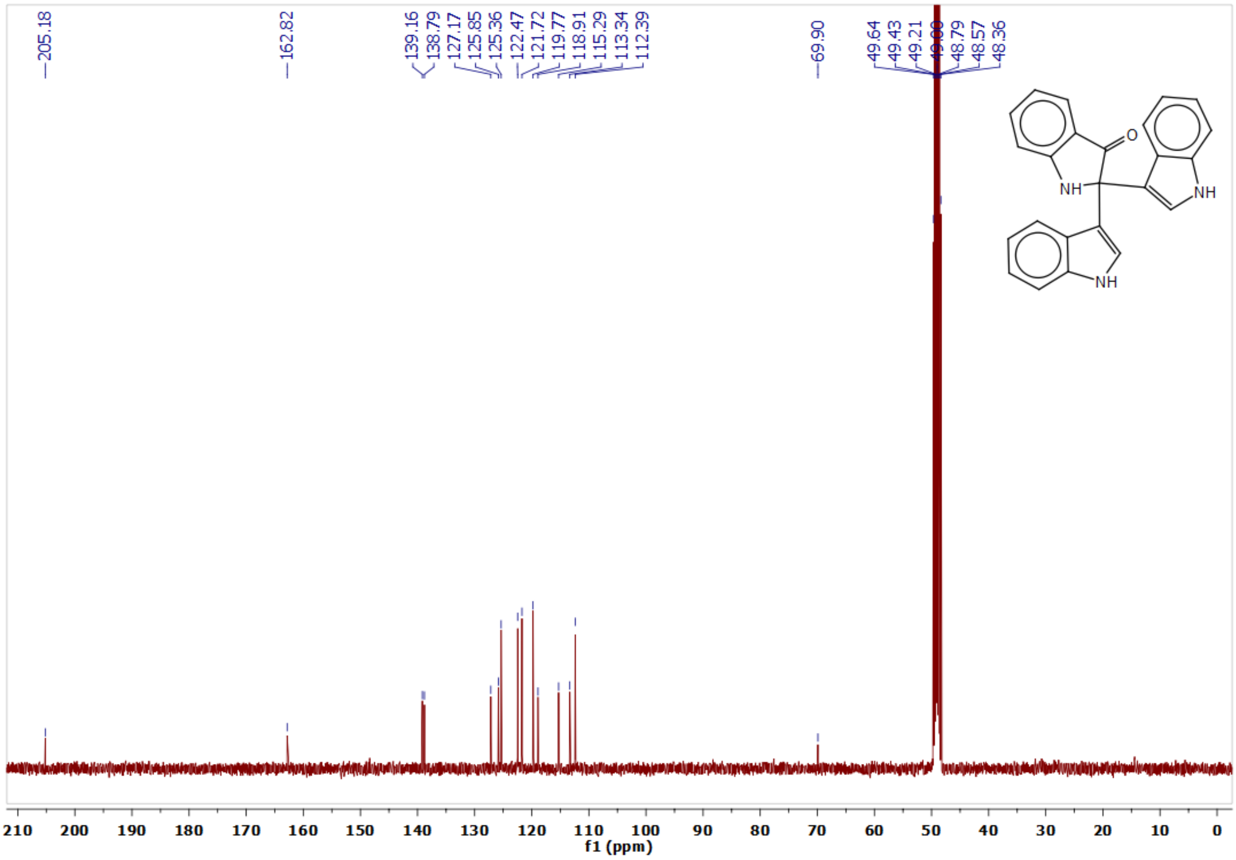
^{13}C NMR (125 MHz, MeOD): δ 201.2, 164.6, 163.2, 152.3, 137.8, 126.5, 124.8, 122.2, 121.3, 115.4, 114.9, 112.4, 96.2, 94.9, 70.1, 56.9, 56.7.

HRMS (ESI) m/z [M+H]$^+$ calculated for $C_{27}H_{21}Cl_3N_3O_4$: 556.0592, found 556.0598.

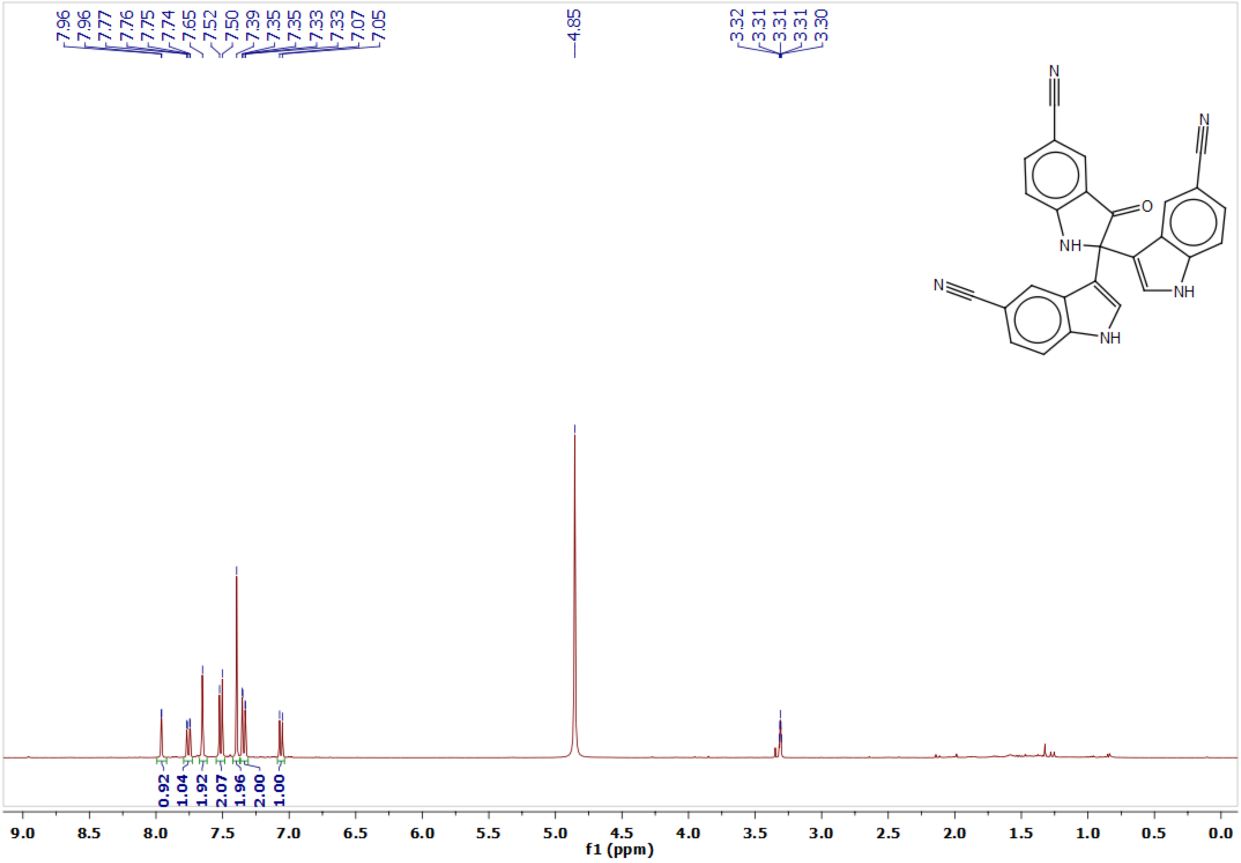
10. NMR Spectra of Isolated Compounds: ^{1}H & ^{13}C Spectra

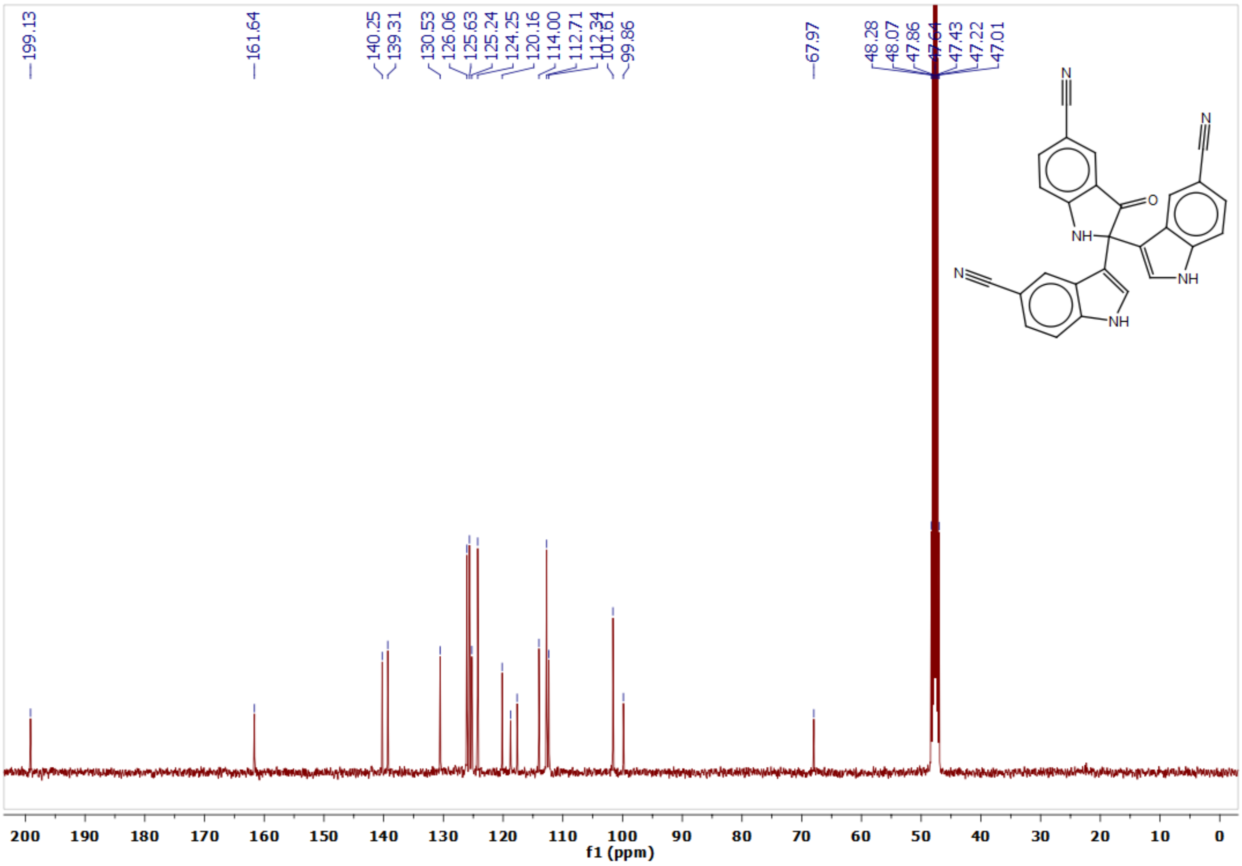
Compound 2a: [3,2':2',3''-terindolin]-3'-one



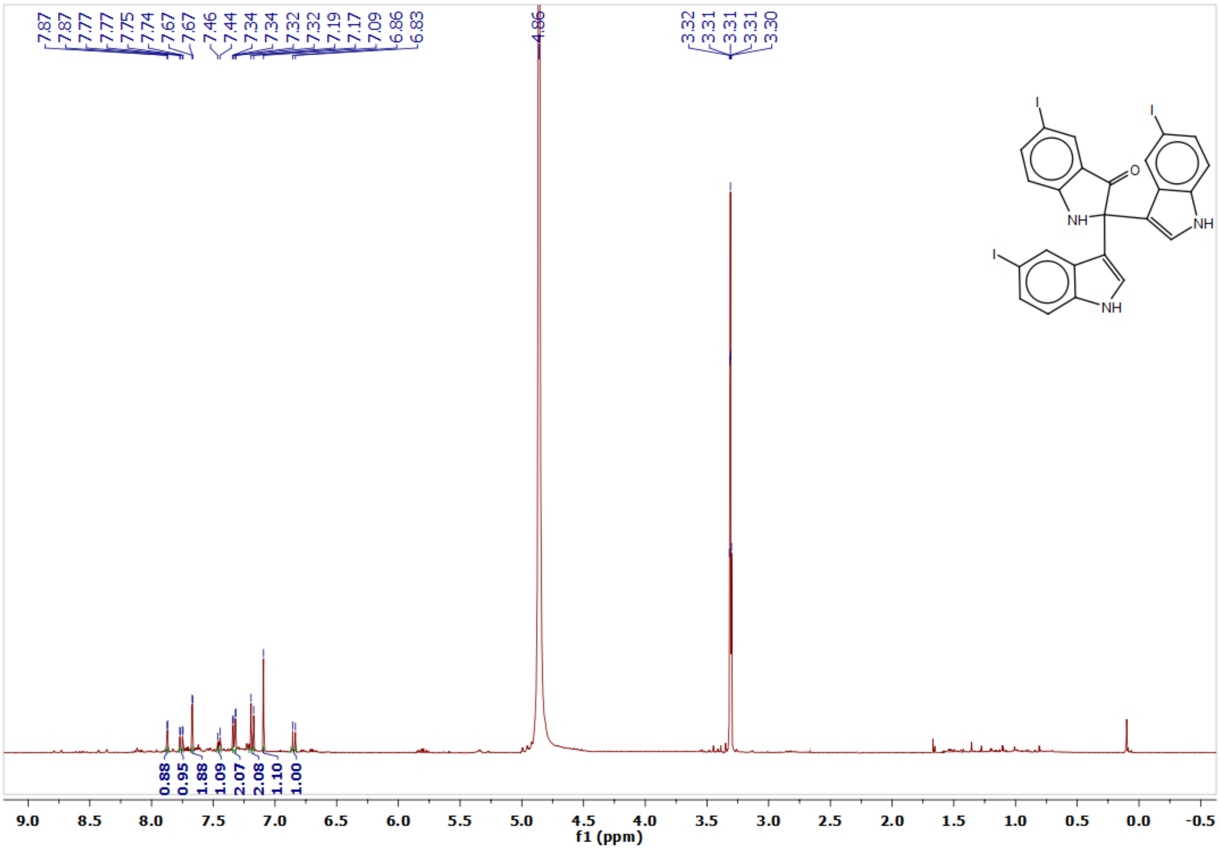


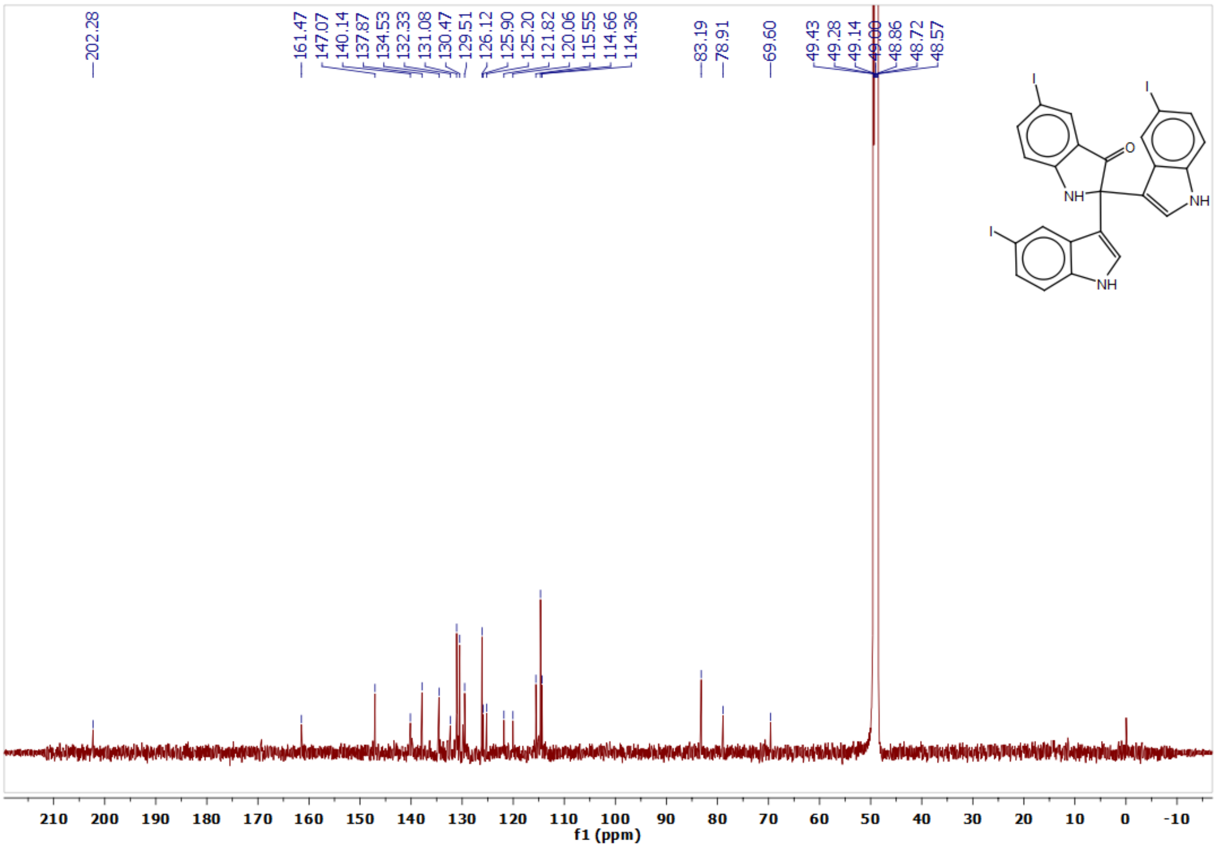
Compound 2b: 3'-oxo-[3,2':2',3''-terindoline]-5,5',5''-tricarbonitrile



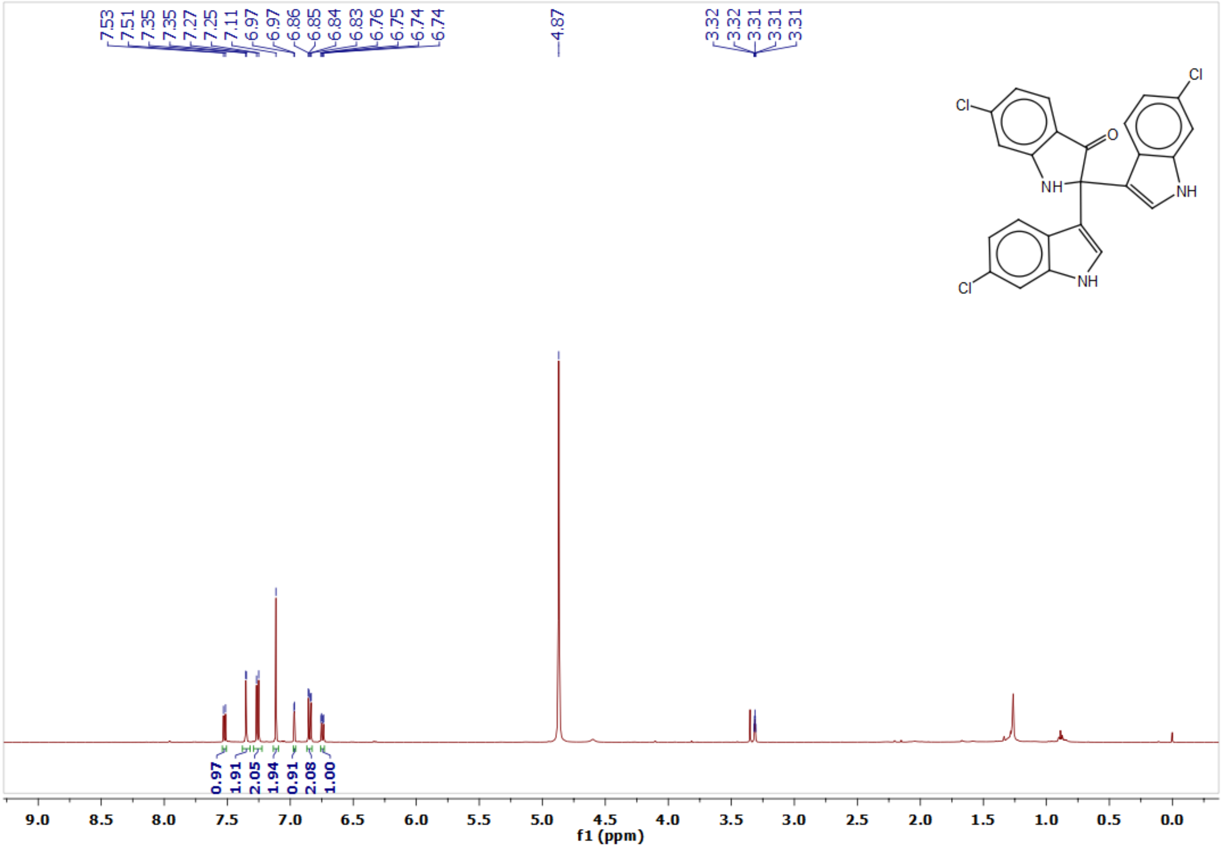


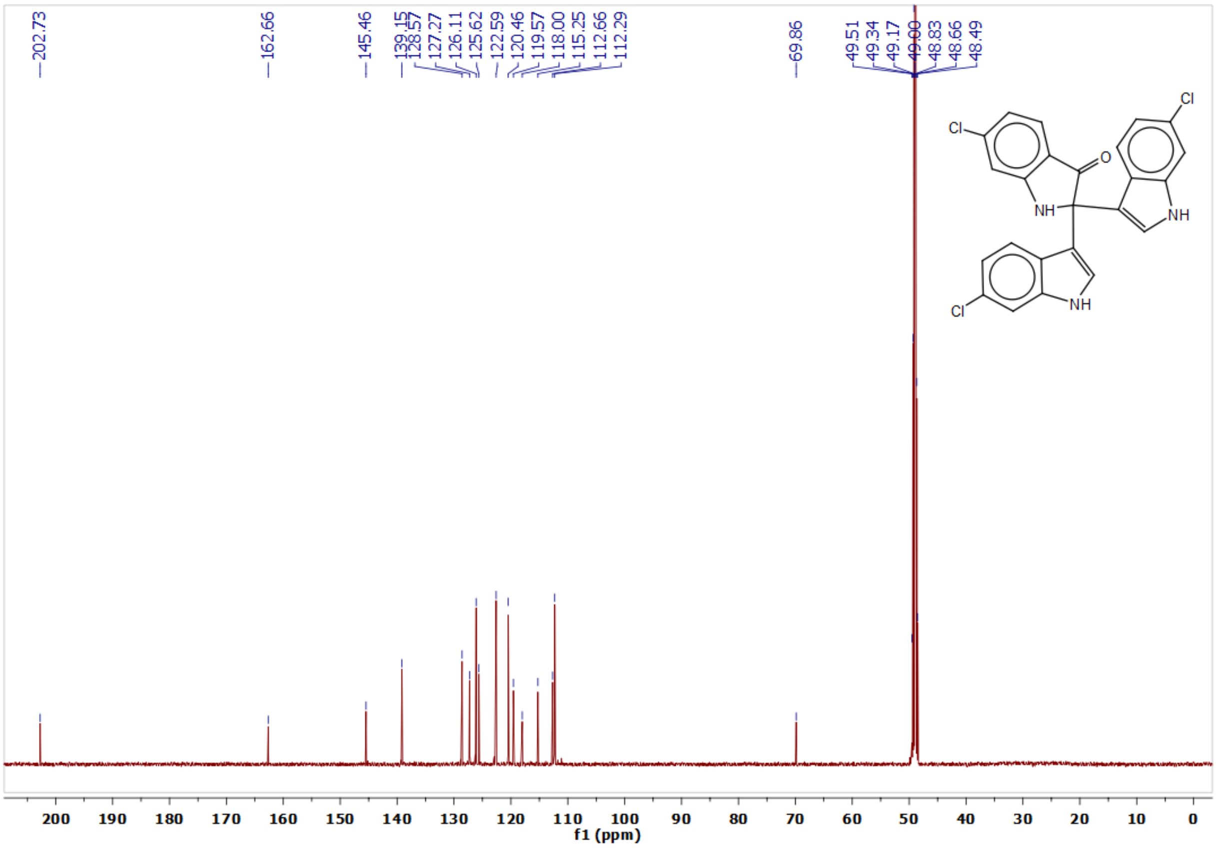
Compound 2c: 5,5',5''-triiodo-[3,2':2',3''-terindolin]-3'-one



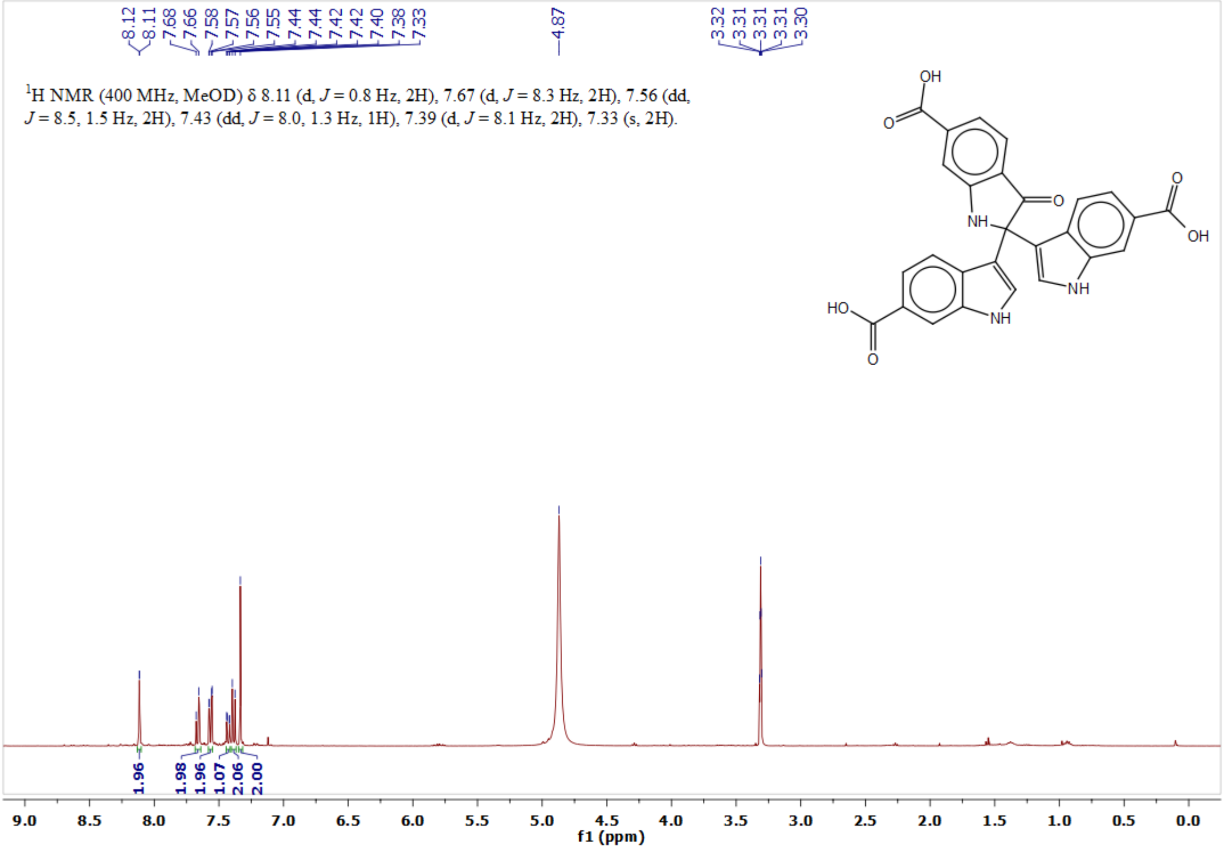


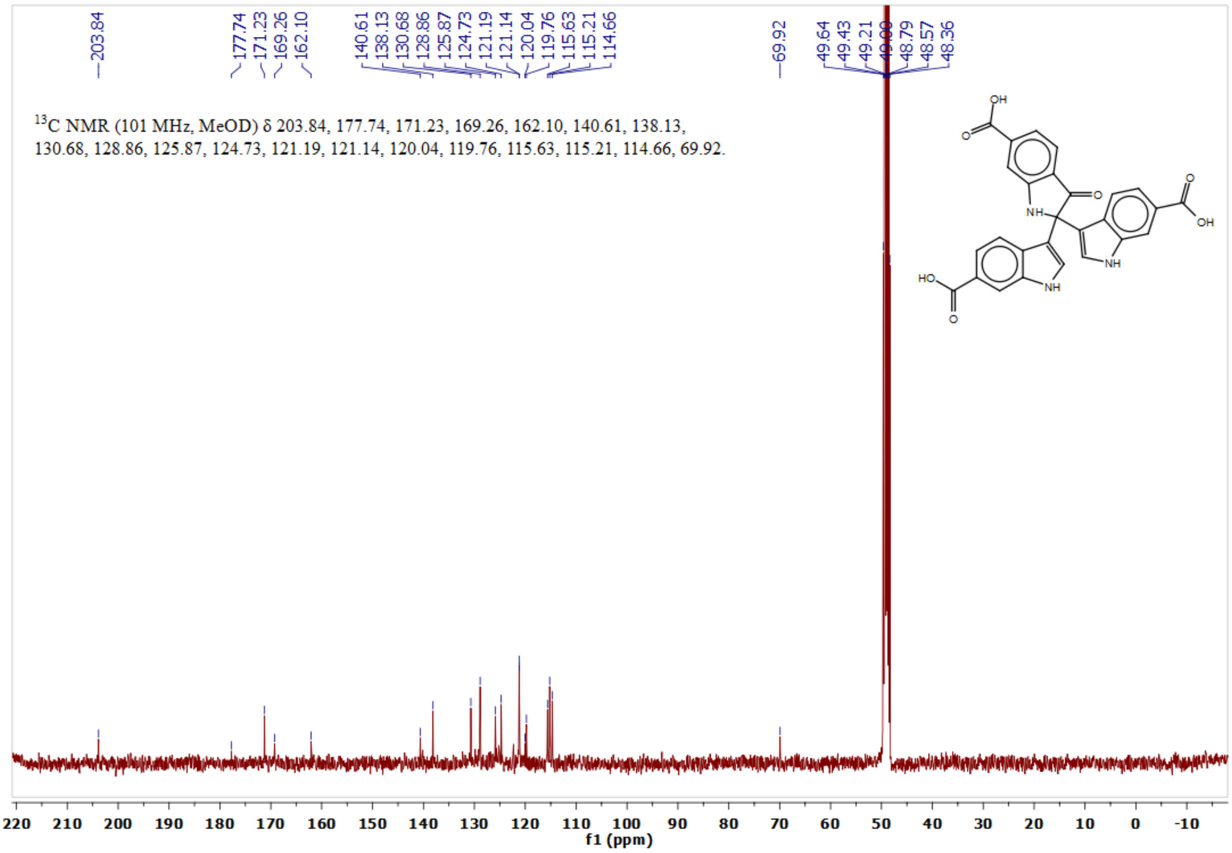
Compound 2d: 6,6',6''-trichloro-[3,2':2',3''-terindolin]-3'-one



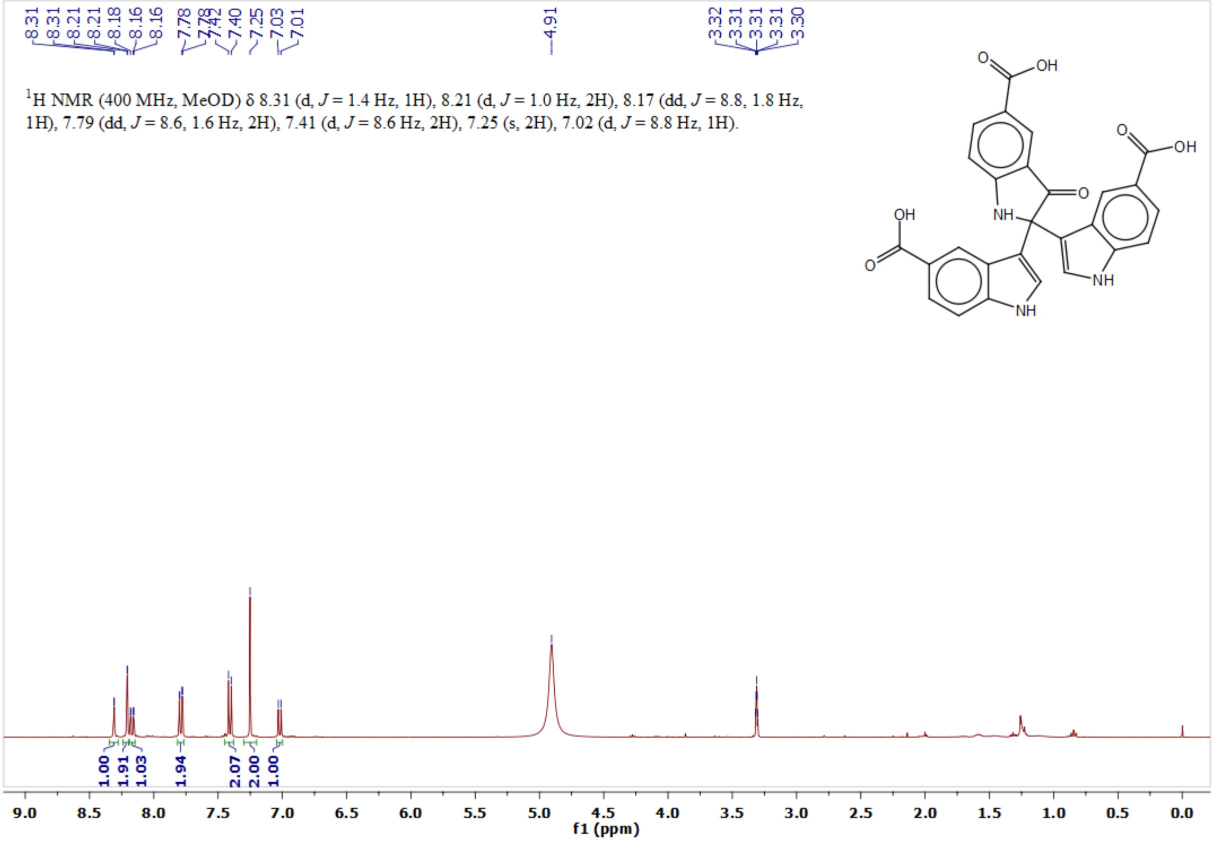


Compound 2e: 3'-oxo-1',3'-dihydro-1H,1''H-[3,2':2',3''-terindole]-6,6',6''-tricarboxylic acid

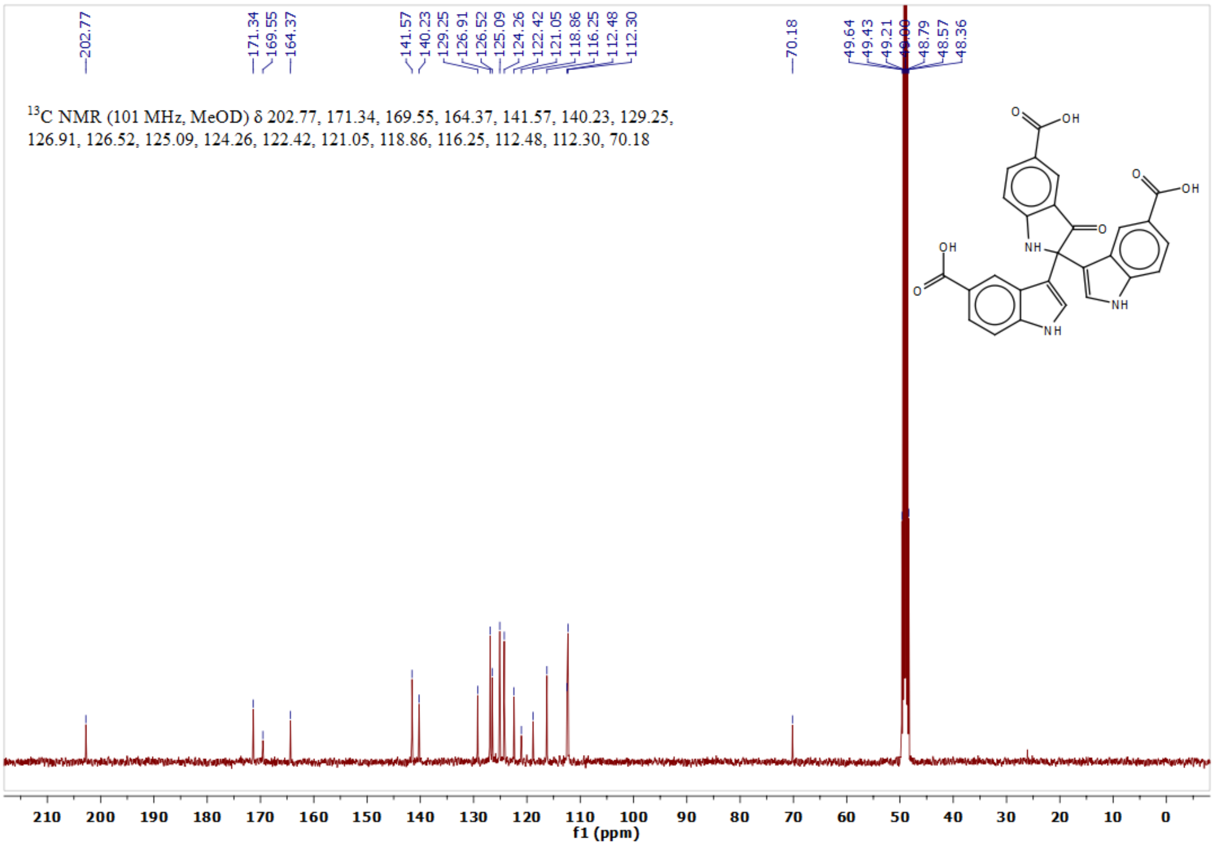

^{1}H NMR (400 MHz, MeOD) δ 8.11 (d, *J* = 0.8 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.43 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (s, 2H).


^{13}C NMR (101 MHz, MeOD) δ 203.84, 177.74, 171.23, 169.26, 162.10, 140.61, 138.13, 130.68, 128.86, 125.87, 124.73, 121.19, 121.14, 120.04, 119.76, 115.63, 115.21, 114.66, 69.92.

Compound 2f: 3'-oxo-1',3'-dihydro-1H,1''H-[3,2':2',3''-terindole]-5,5',5''-tricarboxylic acid

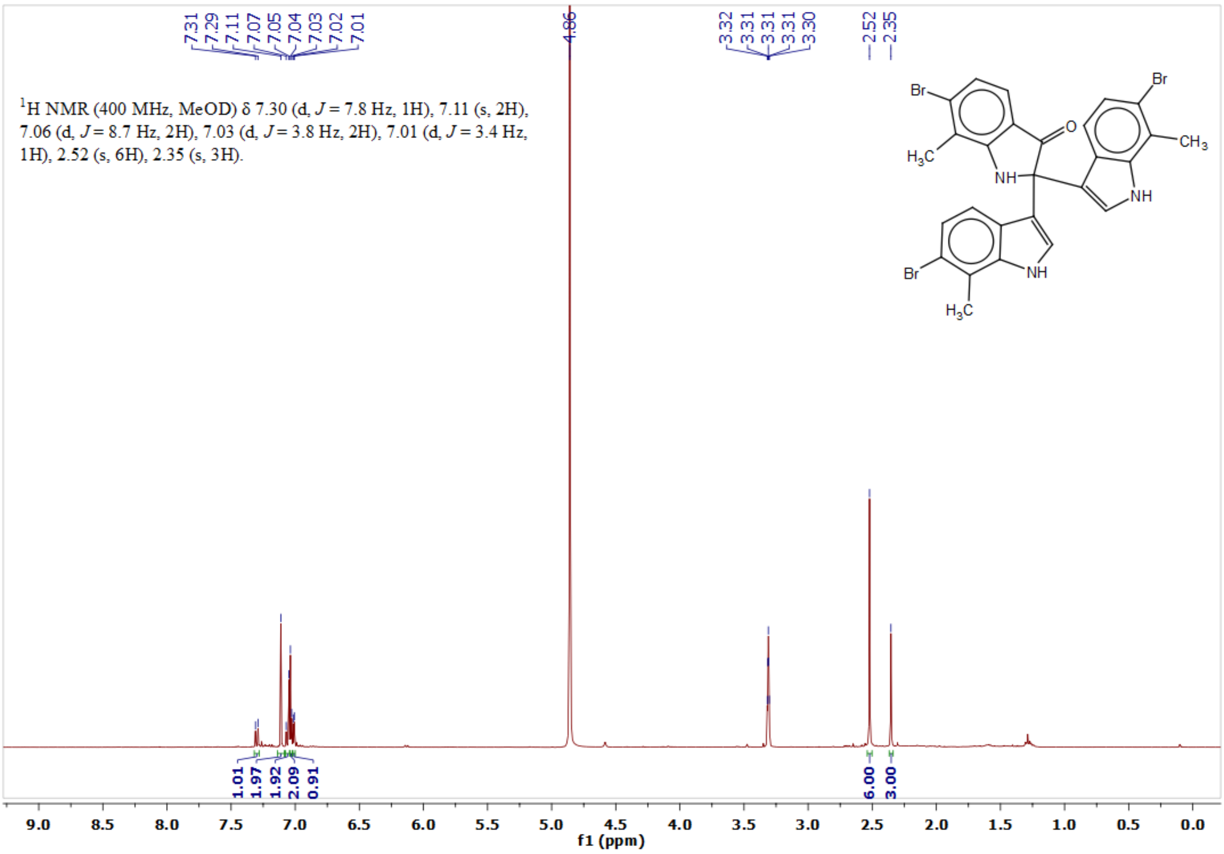


^{1}H NMR (400 MHz, MeOD) δ 8.31 (d, *J* = 1.4 Hz, 1H), 8.21 (d, *J* = 1.0 Hz, 2H), 8.17 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.79 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.25 (s, 2H), 7.02 (d, *J* = 8.8 Hz, 1H).

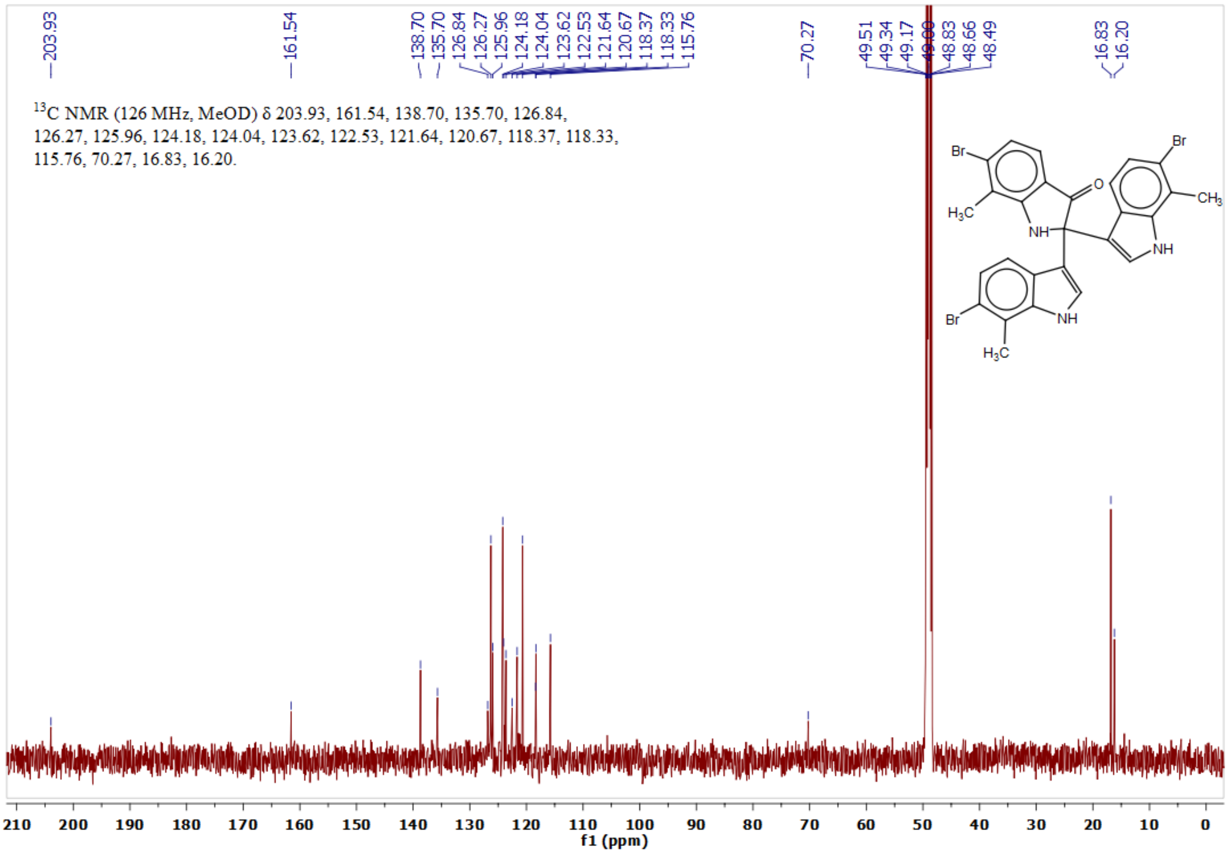


^{13}C NMR (101 MHz, MeOD) δ 202.77, 171.34, 169.55, 164.37, 141.57, 140.23, 129.25, 126.91, 126.52, 125.09, 124.26, 122.42, 121.05, 118.86, 116.25, 112.48, 112.30, 70.18

Compound 2g: 6,6'',6''-tribromo-7,7',7''-trimethyl-1H,1''H-[3,2':2',3''-terindol]-3'(1'H)-one

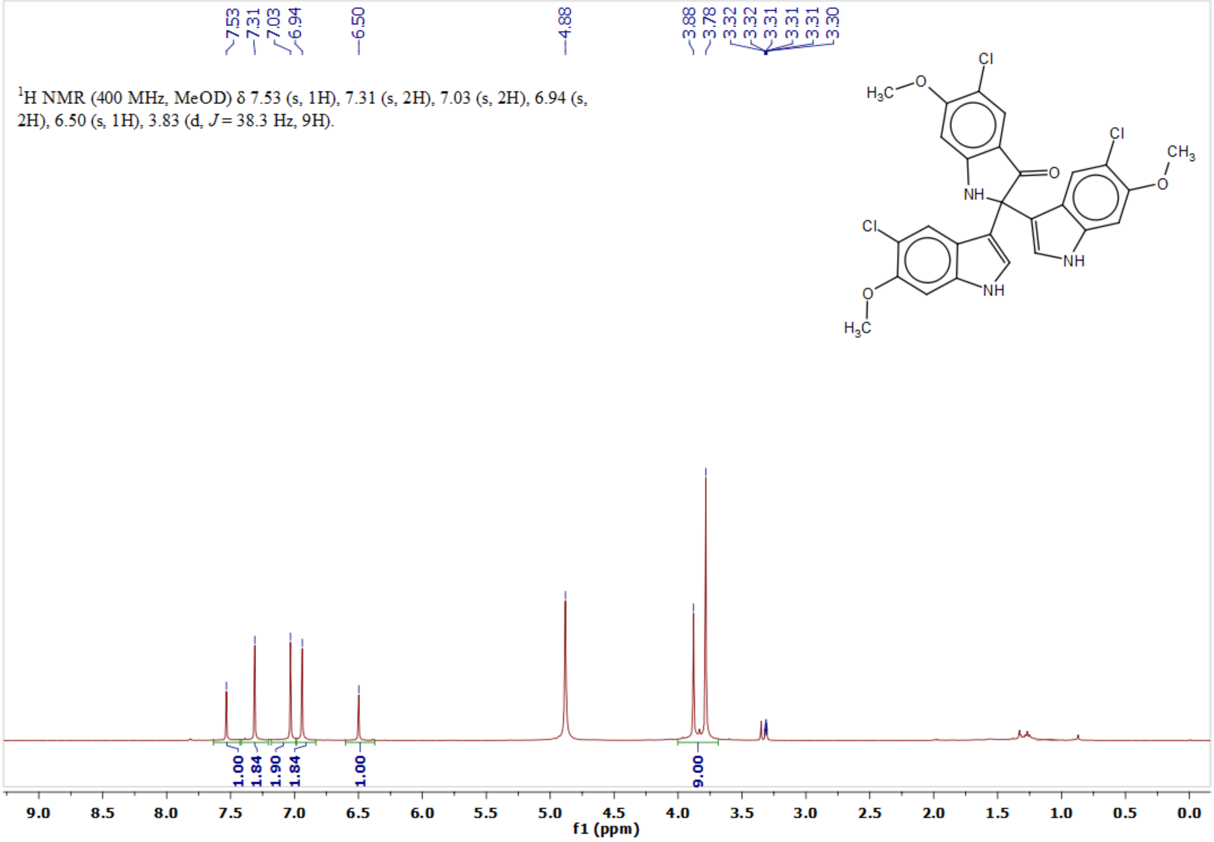


^{1}H NMR (400 MHz, MeOD) δ 7.30 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 3.8 Hz, 2H), 7.01 (d, *J* = 3.4 Hz, 1H), 2.52 (s, 6H), 2.35 (s, 3H).

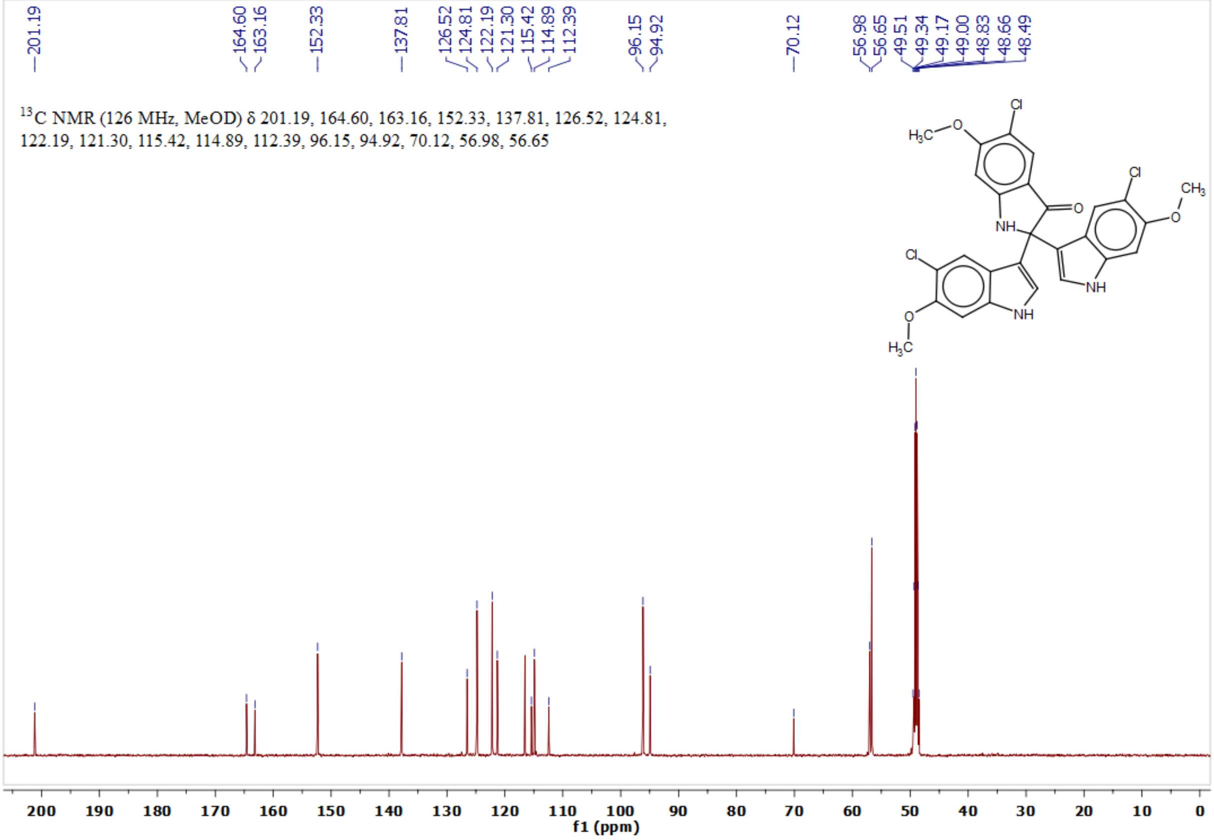


^{13}C NMR (126 MHz, MeOD) δ 203.93, 161.54, 138.70, 135.70, 126.84, 126.27, 125.96, 124.18, 124.04, 123.62, 122.53, 121.64, 120.67, 118.37, 118.33, 115.76, 70.27, 16.83, 16.20.

Compound 2h: 5,5',5''-trichloro-6,6',6''-trimethoxy-1H,1''H-[3,2':2',3''-terindol]-3'(1'H)-one



^{1}H NMR (400 MHz, MeOD) δ 7.53 (s, 1H), 7.31 (s, 2H), 7.03 (s, 2H), 6.94 (s, 2H), 6.50 (s, 1H), 3.83 (d, *J* = 38.3 Hz, 9H).



^{13}C NMR (126 MHz, MeOD) δ 201.19, 164.60, 163.16, 152.33, 137.81, 126.52, 124.81, 122.19, 121.30, 115.42, 114.89, 112.39, 96.15, 94.92, 70.12, 56.98, 56.65

11. **References**

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