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

Supporting Information

Fluorinated Alcohol-Mediated [4+3] Cycloaddition Reaction of Indolyl Alcohols with Cyclopentadiene

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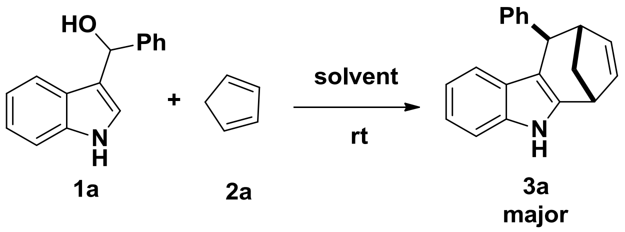
1. General Information

Chemical reagents were purchased from commercial companies. All solvents were dried according to standard procedures. All reactions were performed in pressure tube and monitored by TLC with silica gel-coated plates with 0.2 mm silica gel-coated HSGF 254 plates. And products were purified by column chromatography on silica gel (200-300 mesh) eluting with a gradient (petroleum ether / ethyl acetate).

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), and multiplet (m). Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.00, triplet). IR spectra of liquids were recorded as thin films and solids as KBr pellets on a Thermo Scientific Nicolet IR 200 FT-IR spectrometer. HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer. Melting point of solids were obtained with a GLO X-5 series micro melting point apparatus and were uncorrected.

2. Experimental Procedures

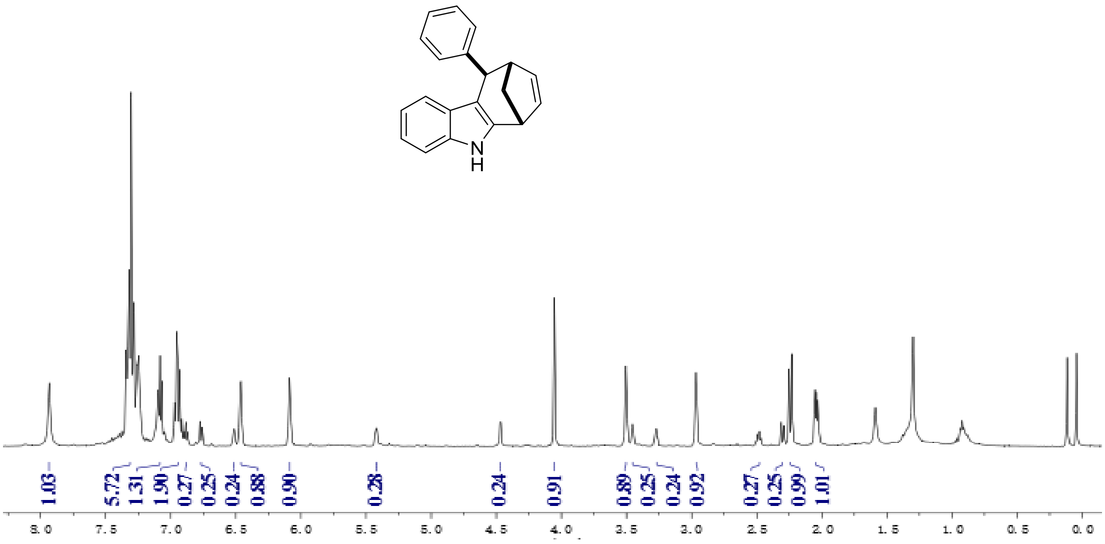
General Procedure for Synthesis of cyclohepta[b]indoles

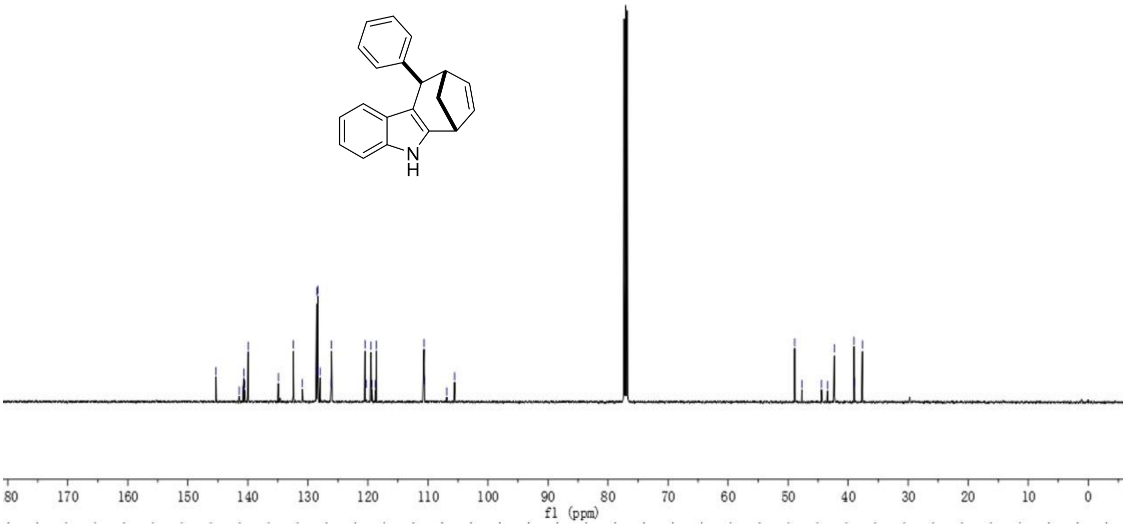


To a 25 mL pressure tube equipped with a magnetic stirrer bar were added HFIP (2 mL), indoly-3-methanol **1a** (0.1 mmol) and cyclopentadiene **2a** (0.5 mmol). The mixture was then stirred at room temperature. Reaction was monitored by TLC with silica gel-coated plates. The solvent was removed *in vacuo*. The residue was then purified by column chromatography on silica gel to afford the desired product **3a**.

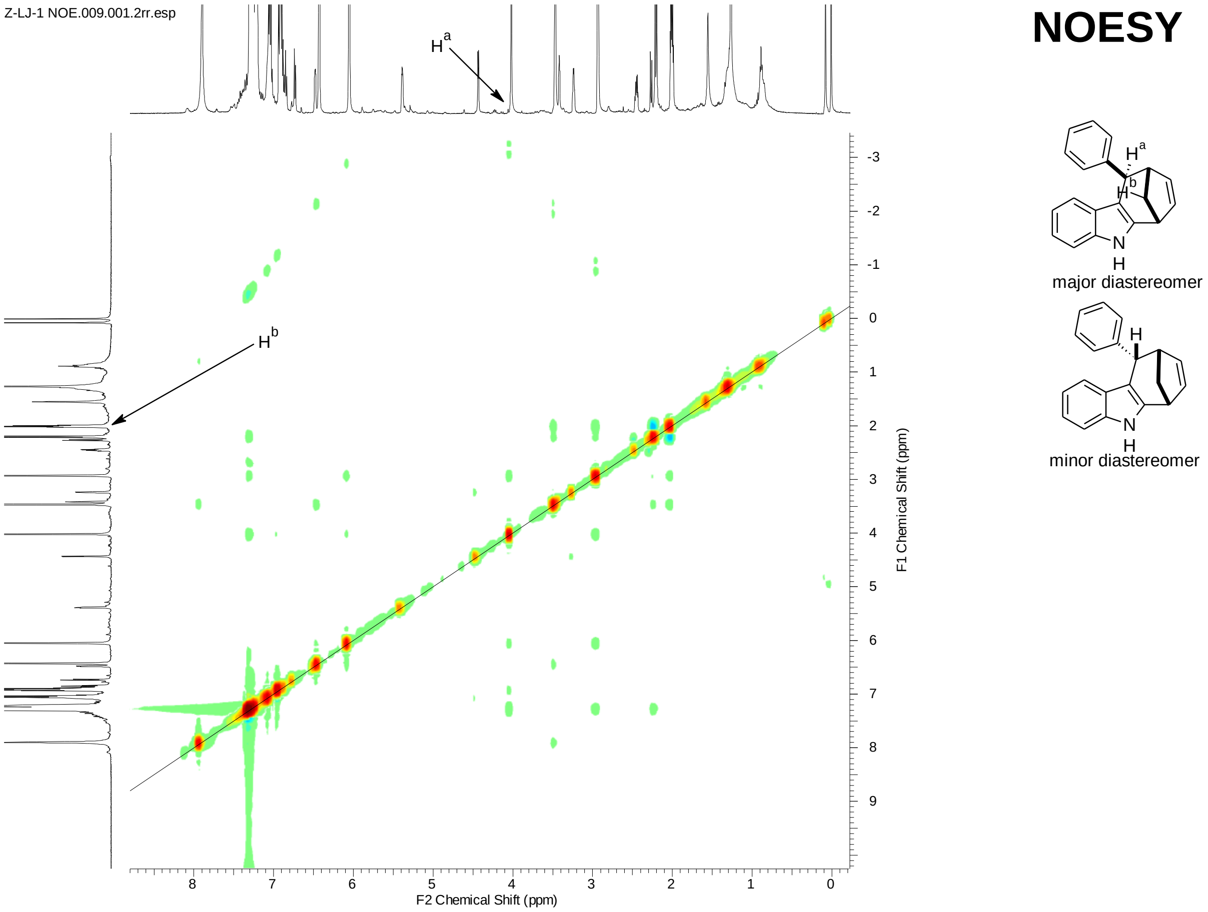
3. ^{1}H and ^{13}C-NMR Spectra

10-phenyl-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3a)

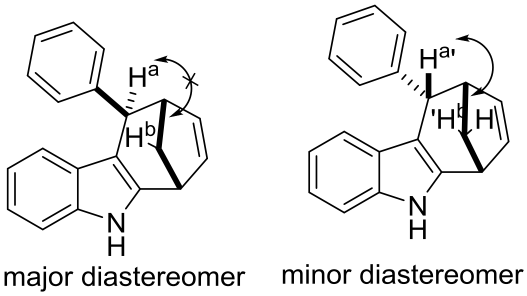




10-phenyl-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3a)

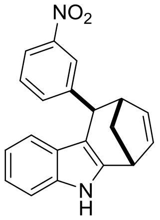


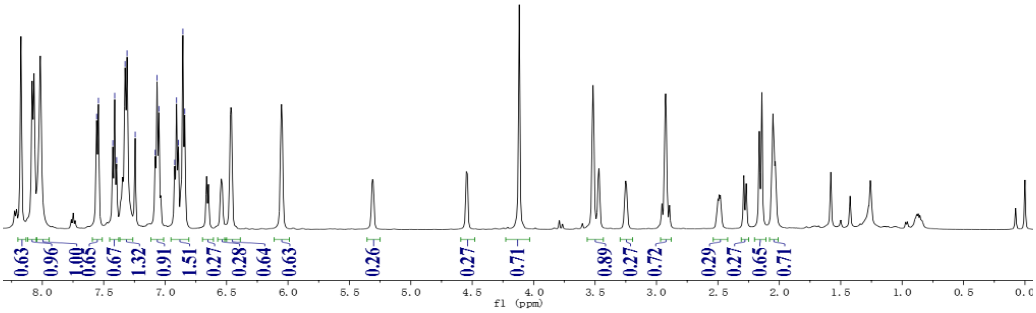
The relative configuration determination of the major diastereomer of product 3a

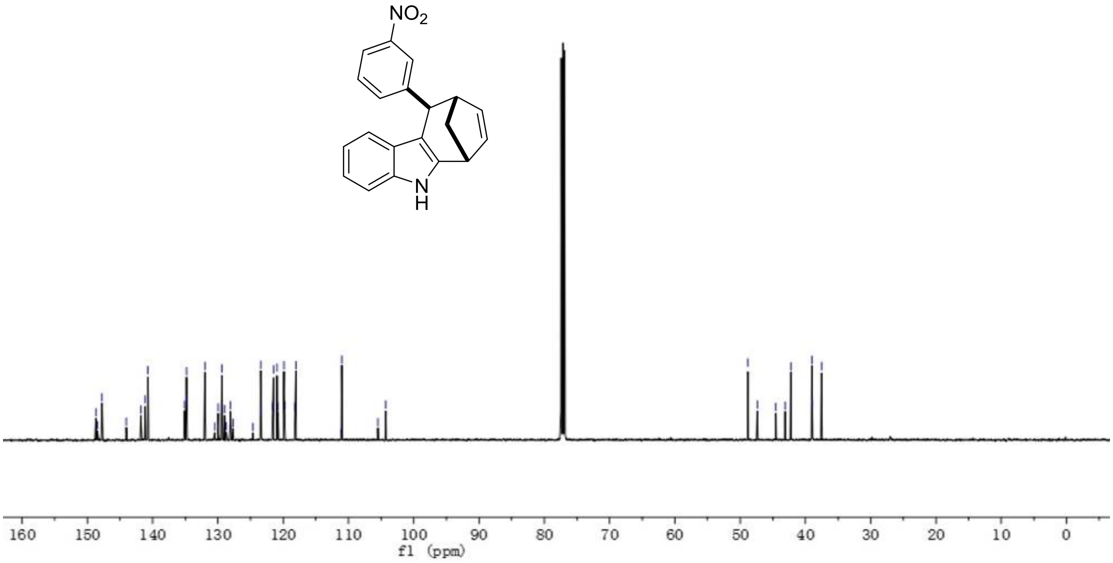


The relative configuration of the major diastereomer of 3a could be unambiguously determined by NOESY. The signals of H^a and H^b were selected for determination of relative configurations. No cross peak (NOESY signals) was observed between H^a and H^b in the major diastereomer of **3a**. In contrast, strong NOESY signal could be found between H^a and H^b in the minor diastereomer of **3b**. Hence, the relative configuration of the major diastereomer of 3a depicted above could be determined.

10-(3-nitrophenyl)-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3b)







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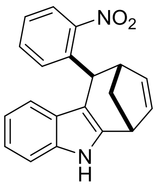
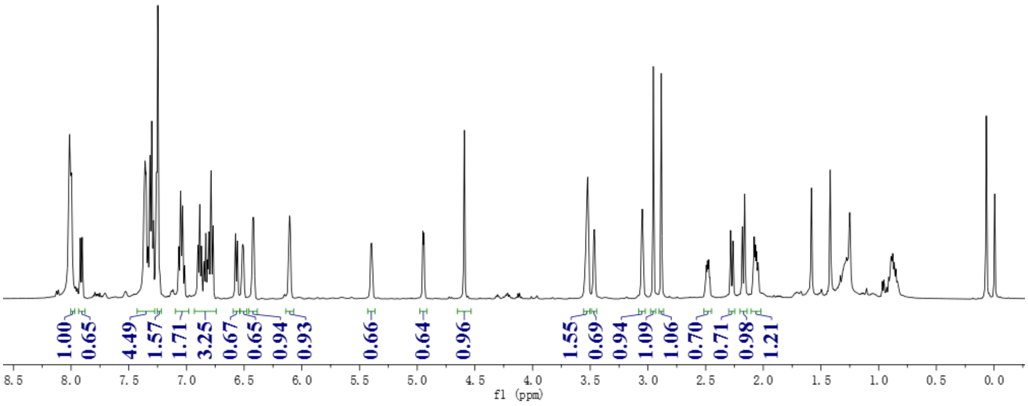
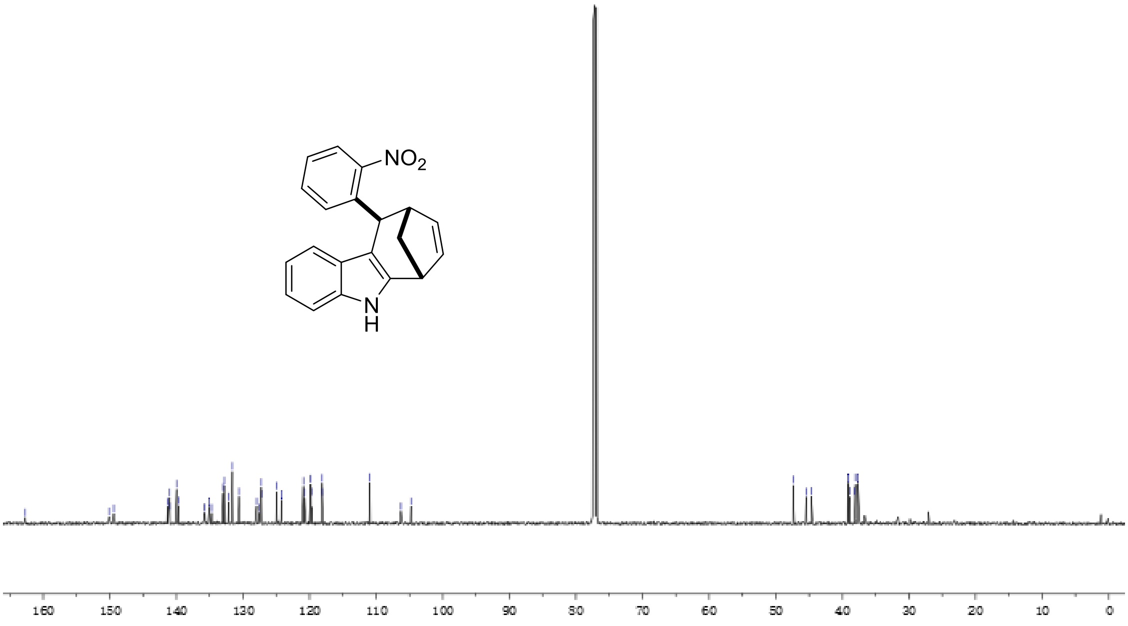
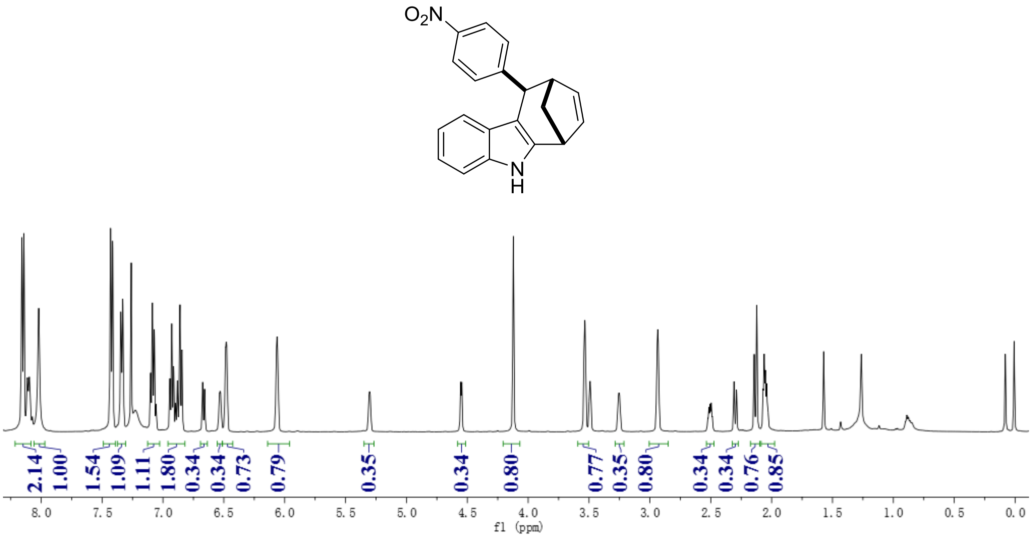
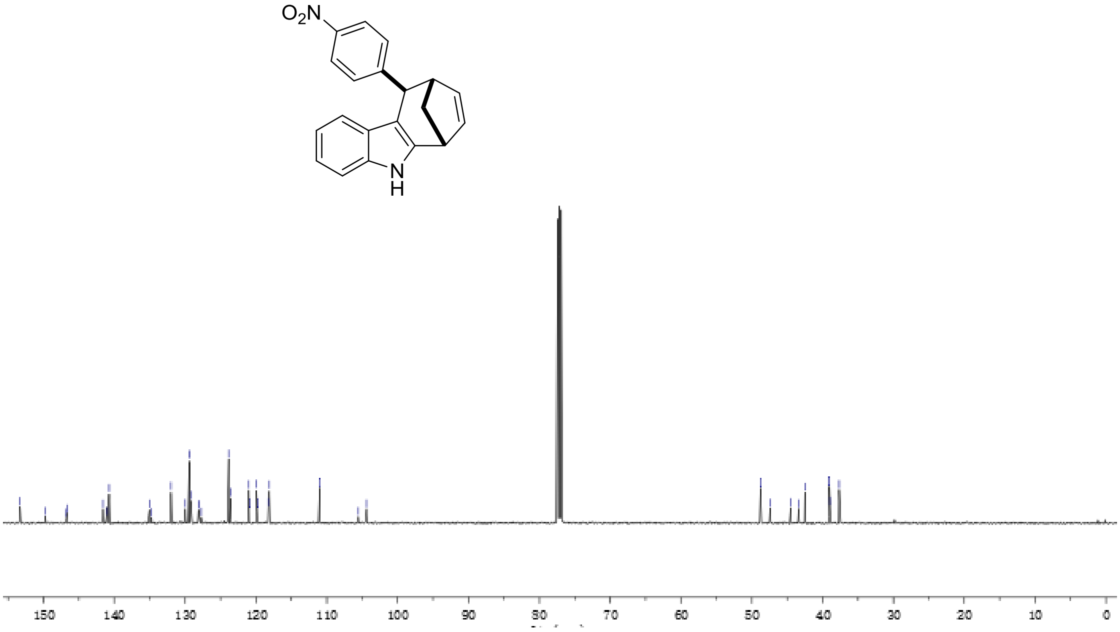






10-(4-nitrophenyl)-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3d)





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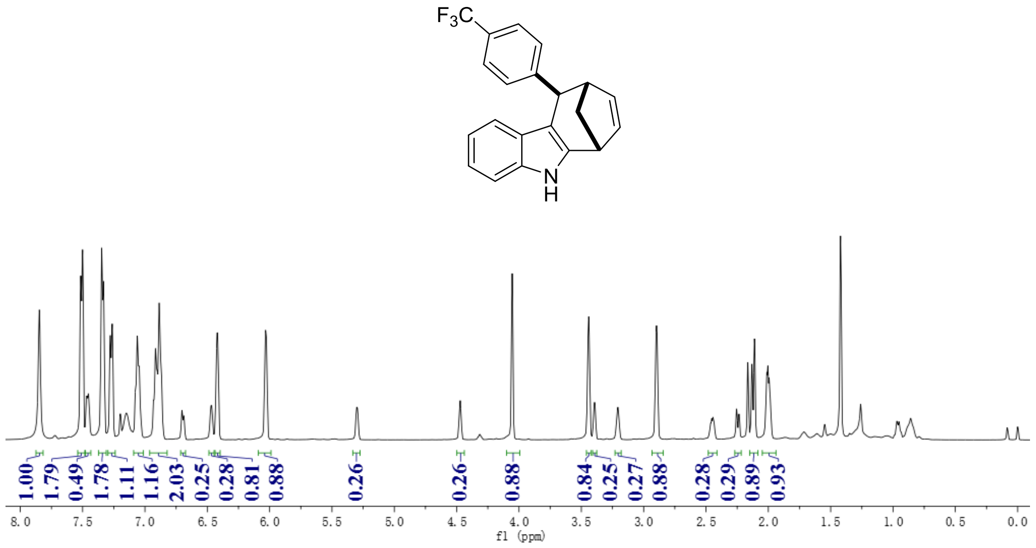
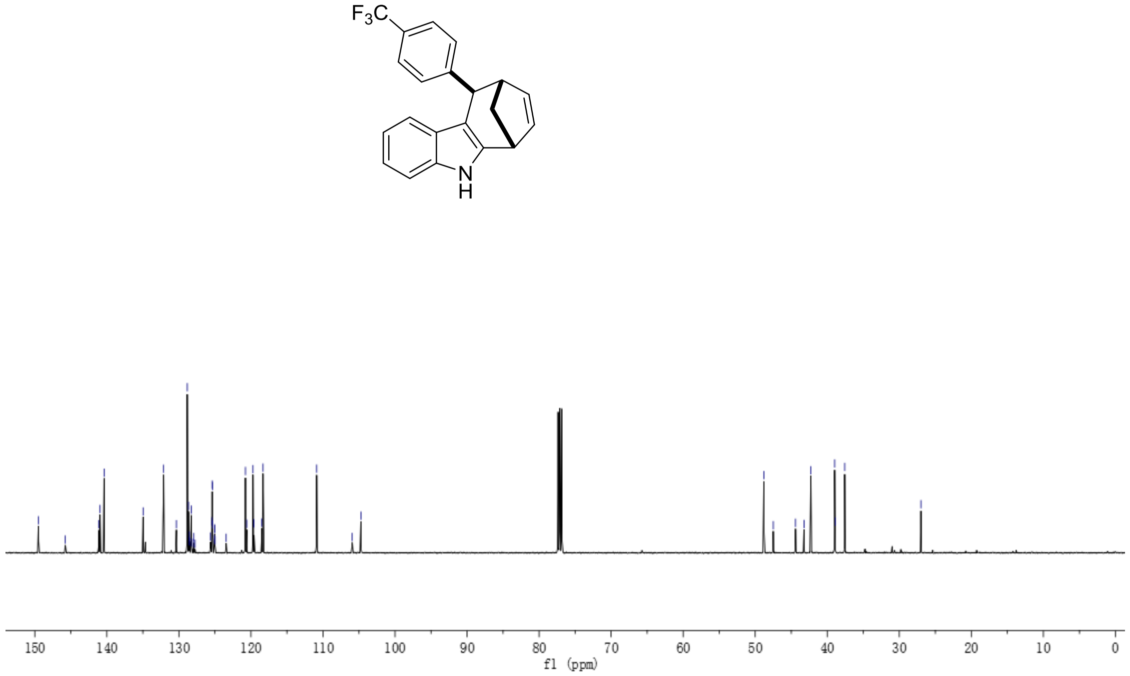
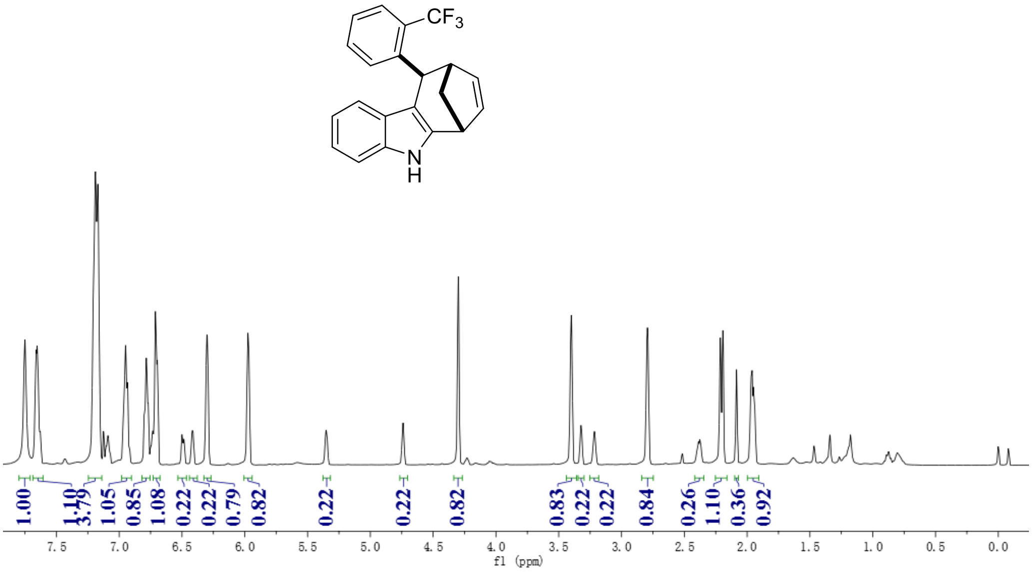
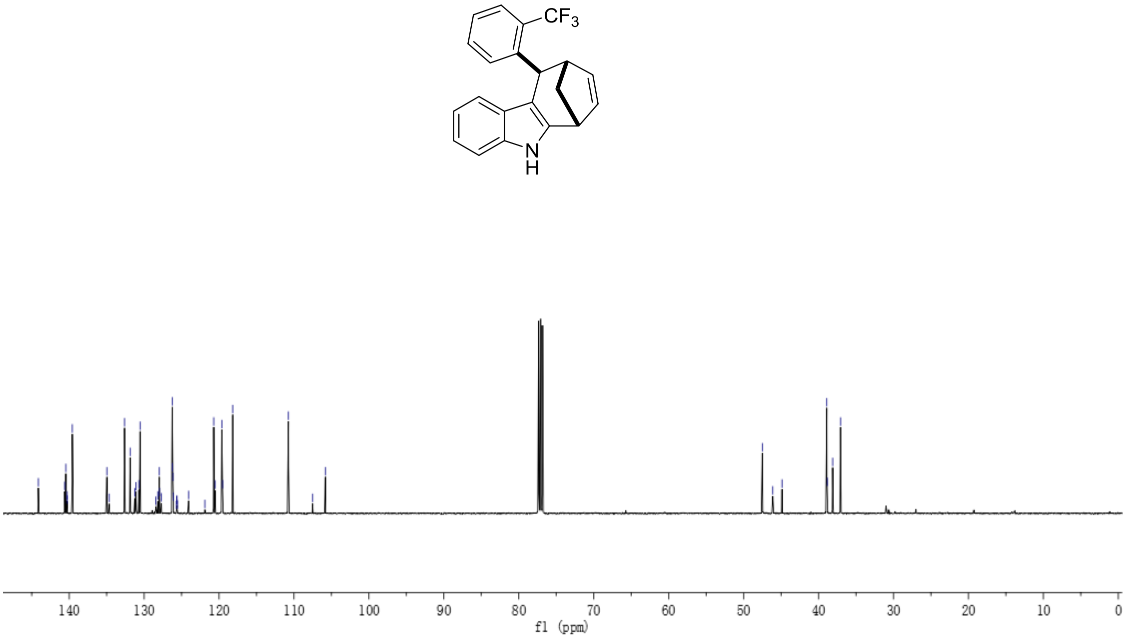




10-(2-(trifluoromethyl)phenyl)-5,6,9,10-tetrahydro-6,9-methanocyclohepta[b]indole (3f)





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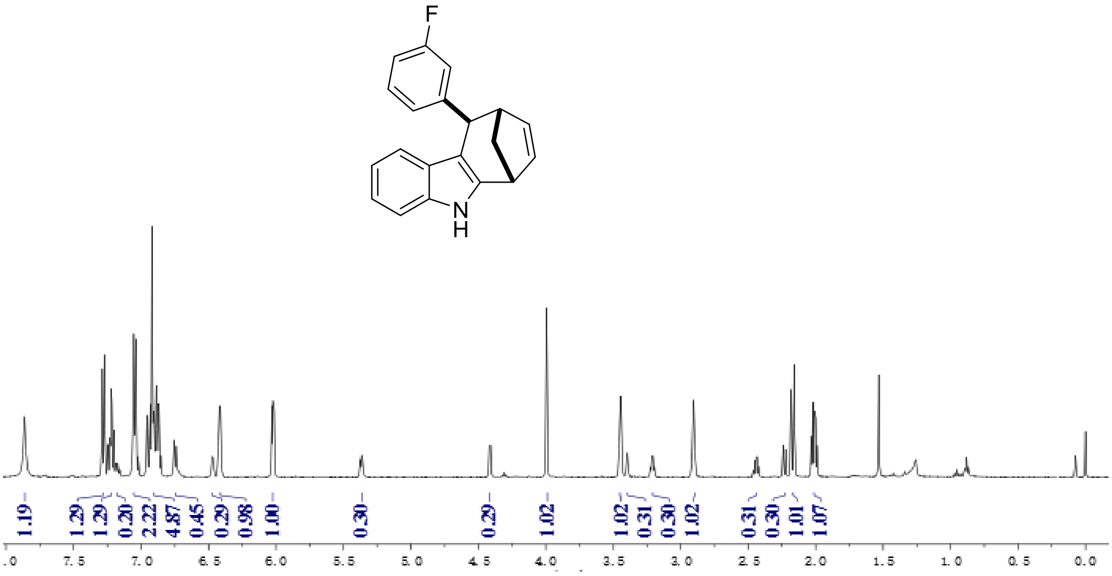

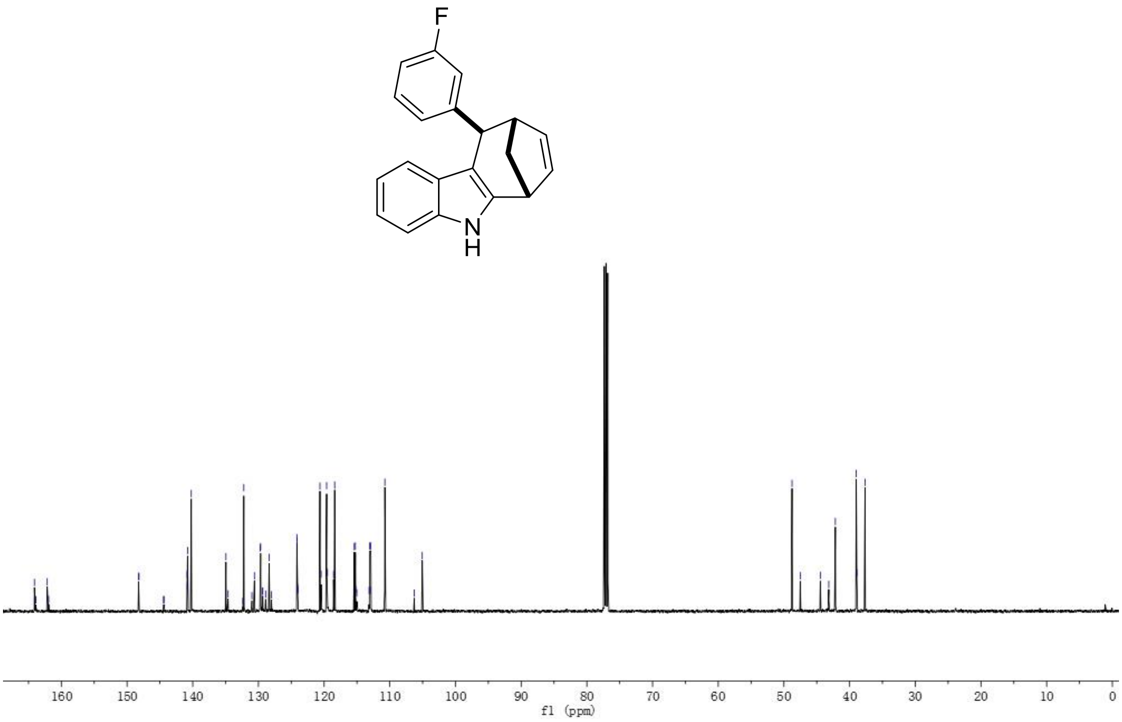

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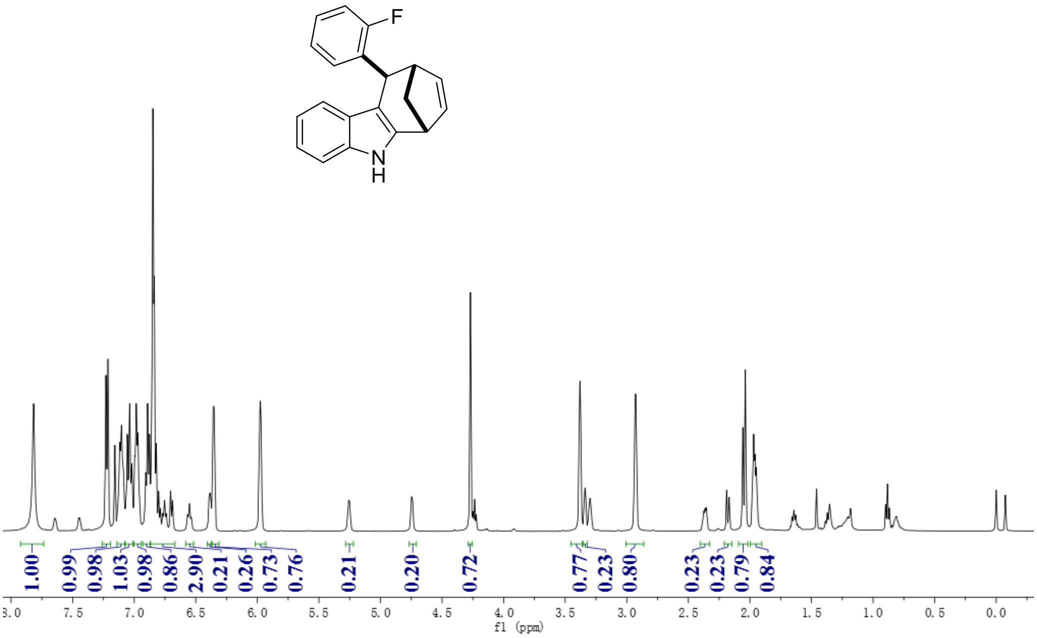
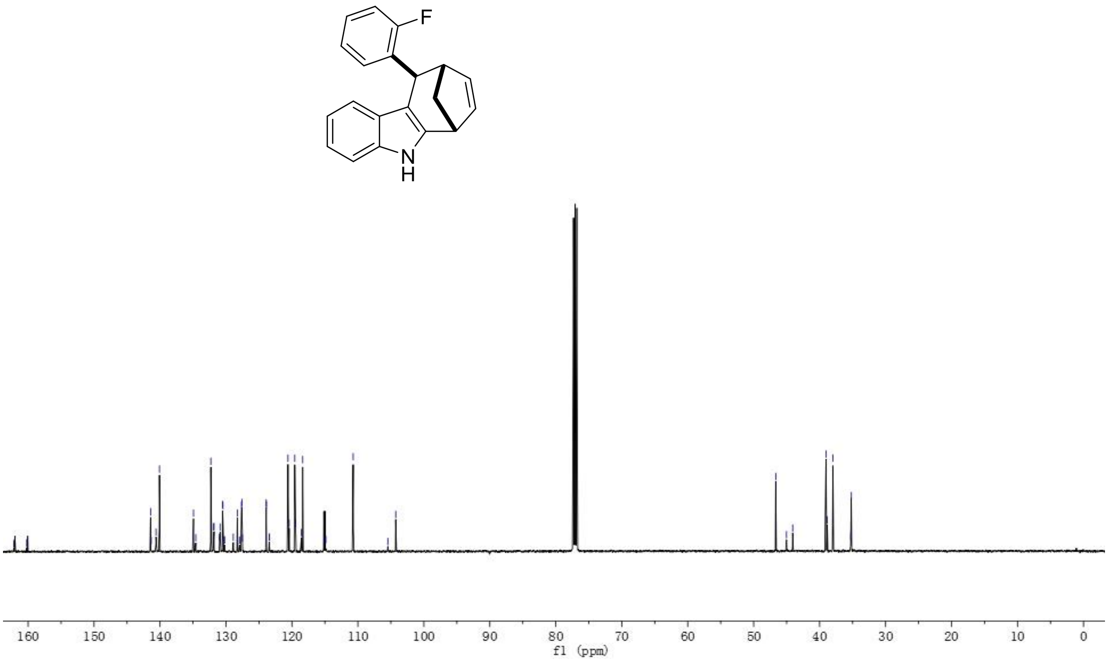
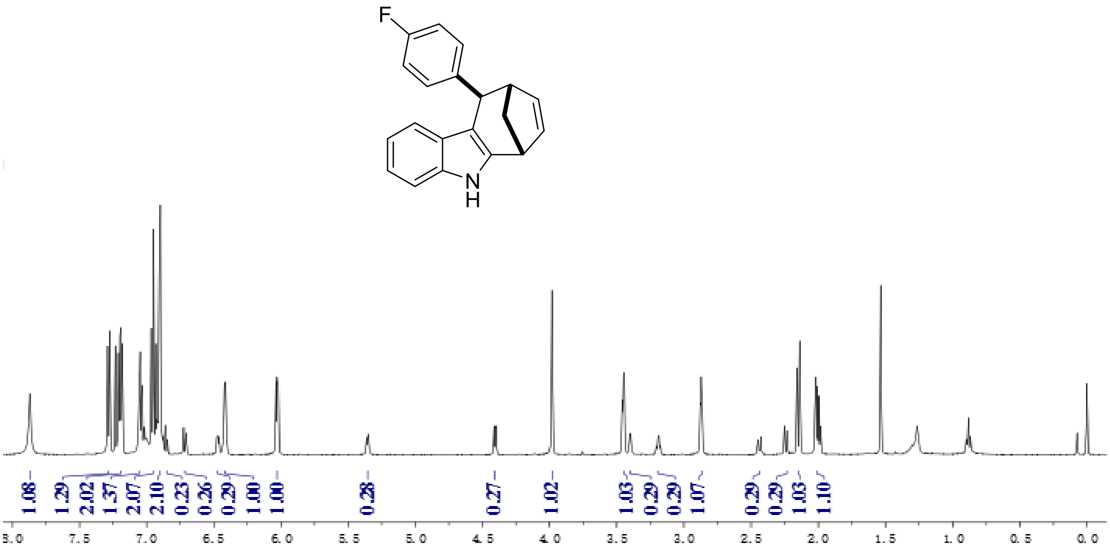
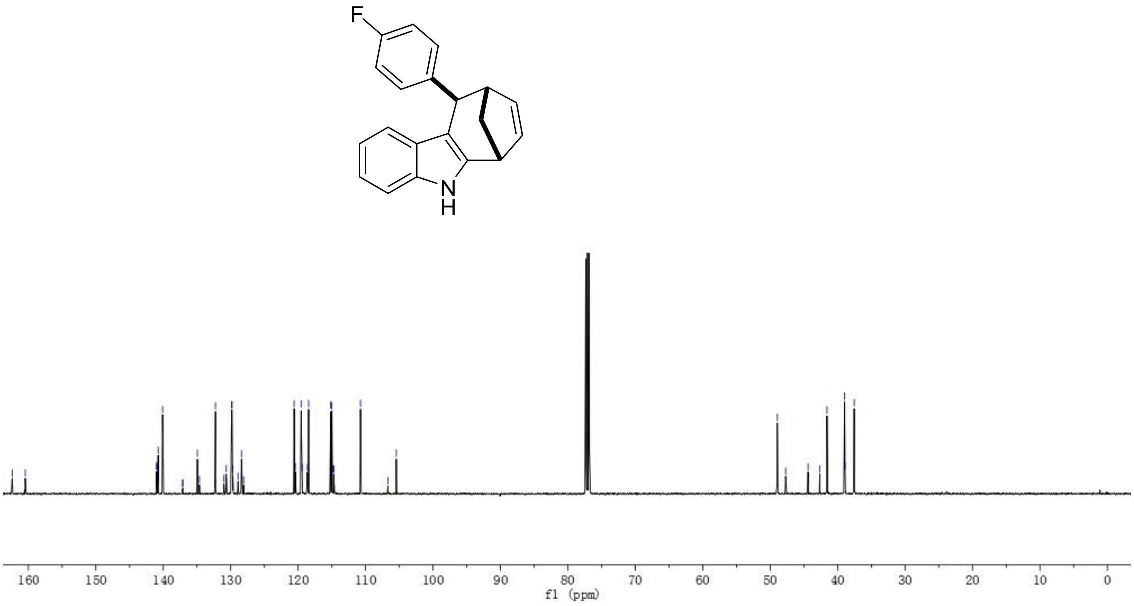




10-(4-fluorophenyl)-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3i)





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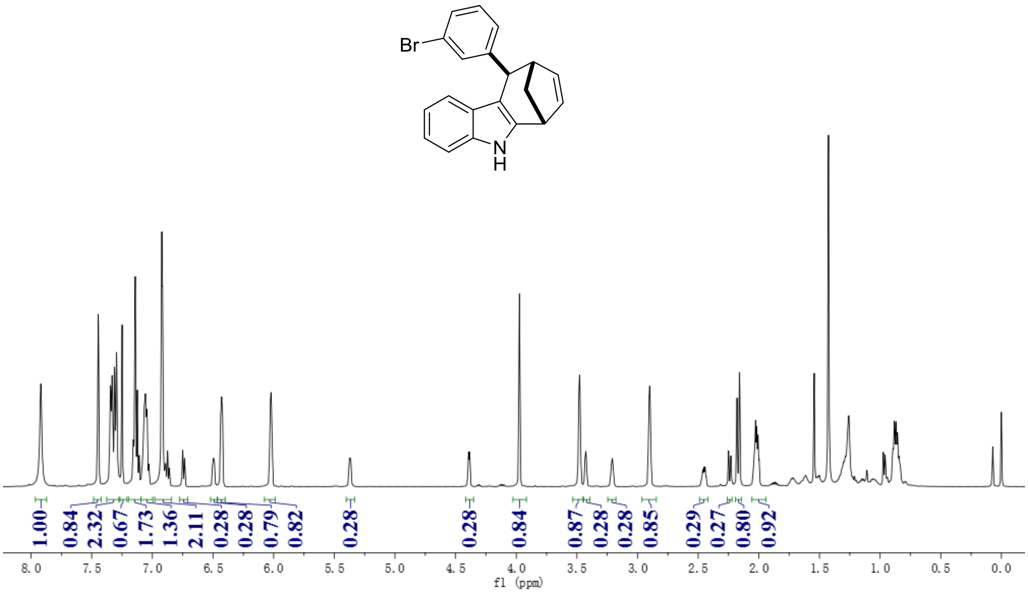
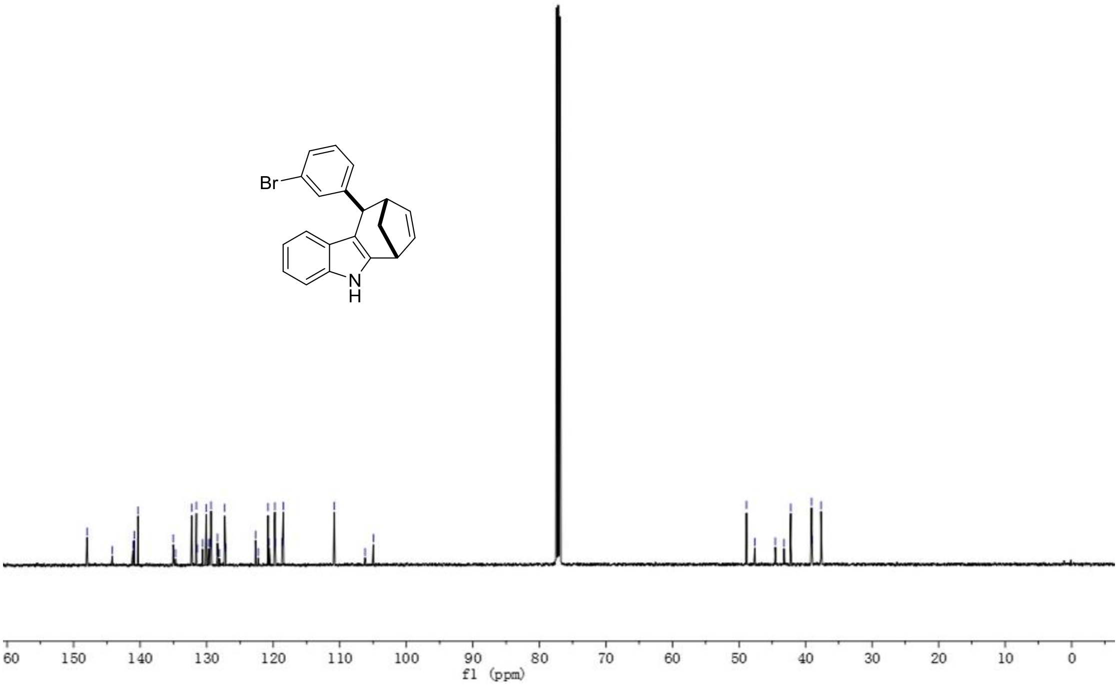
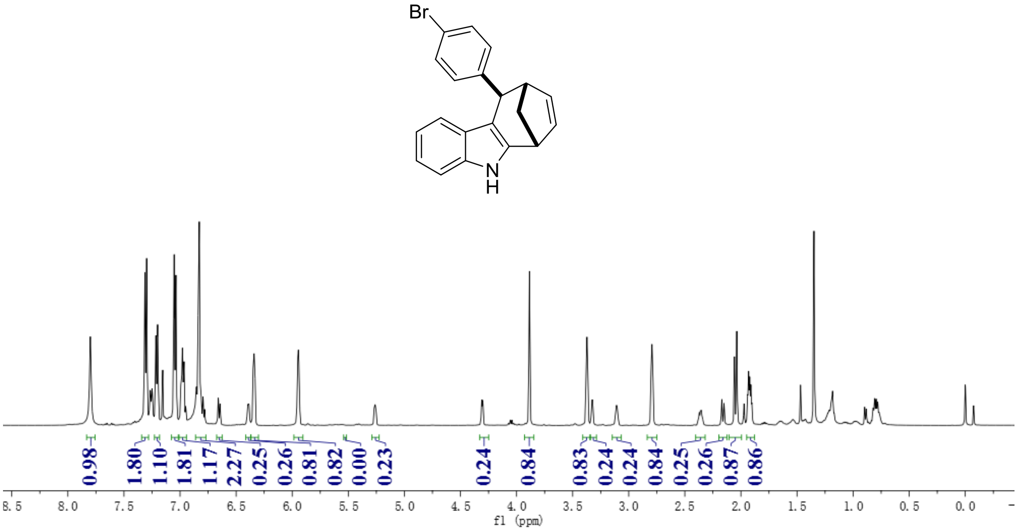
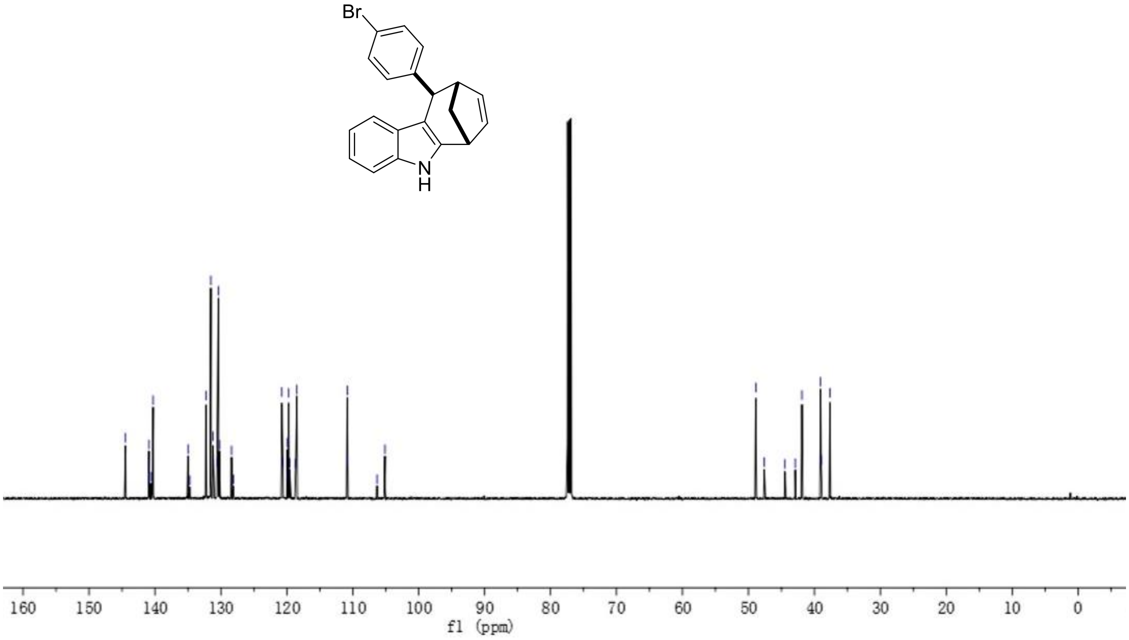




10-(4-bromophenyl)-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3k)





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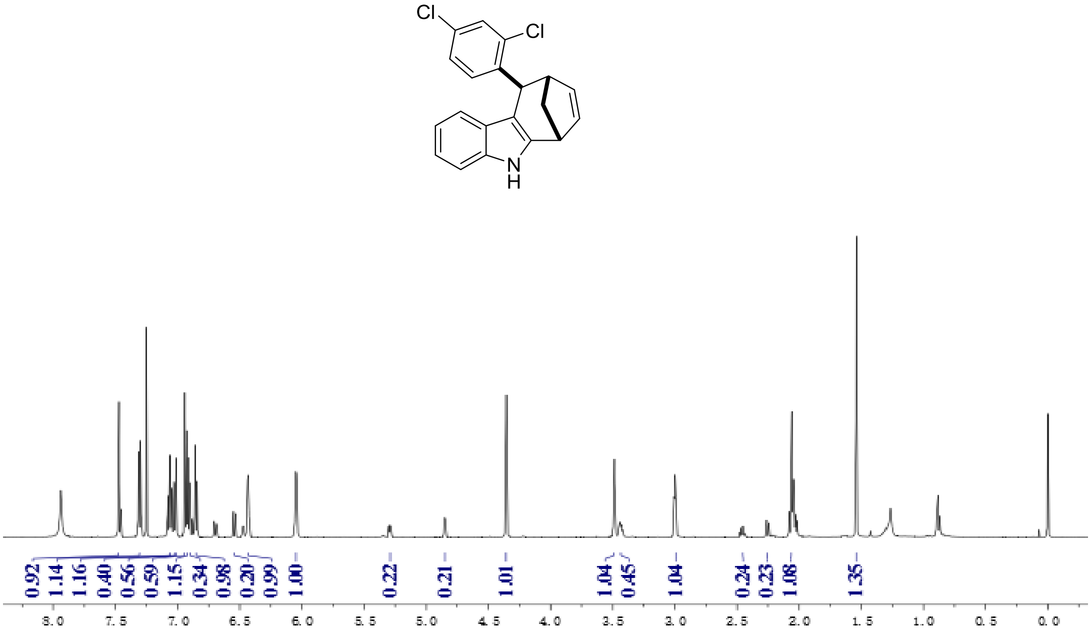

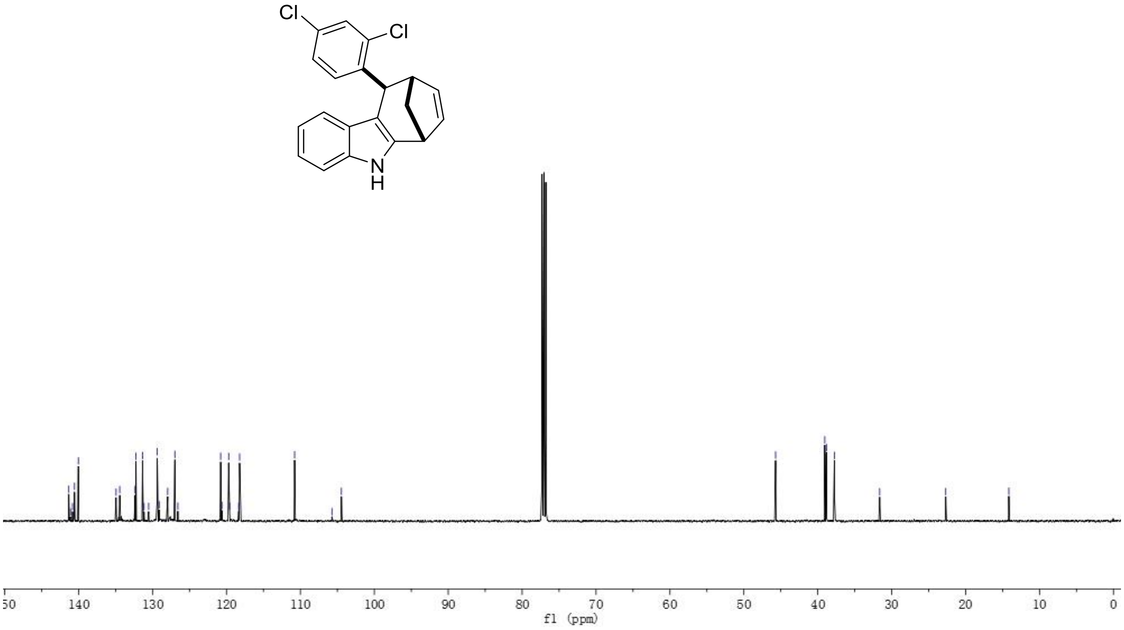

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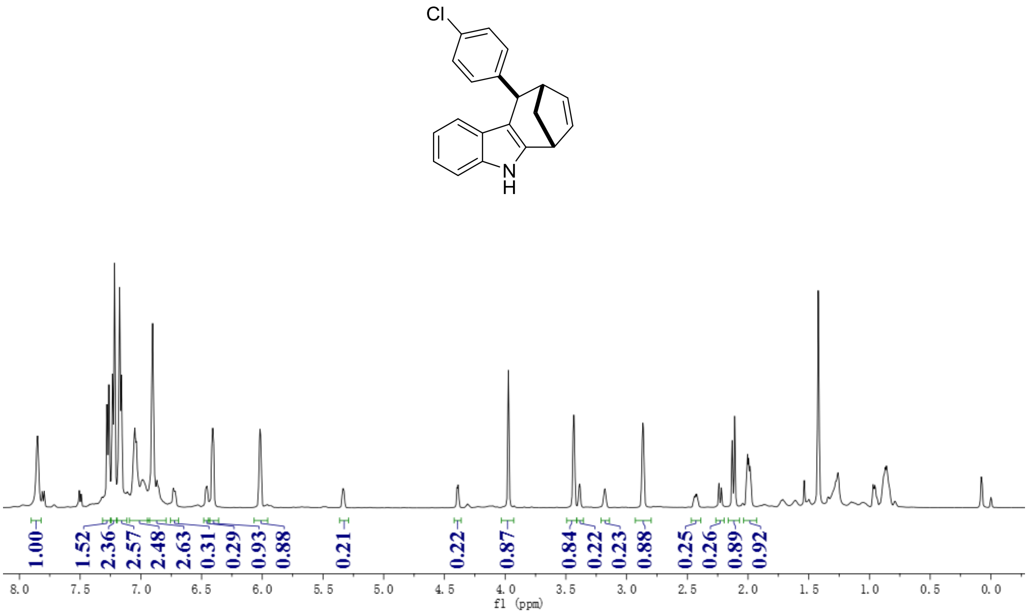

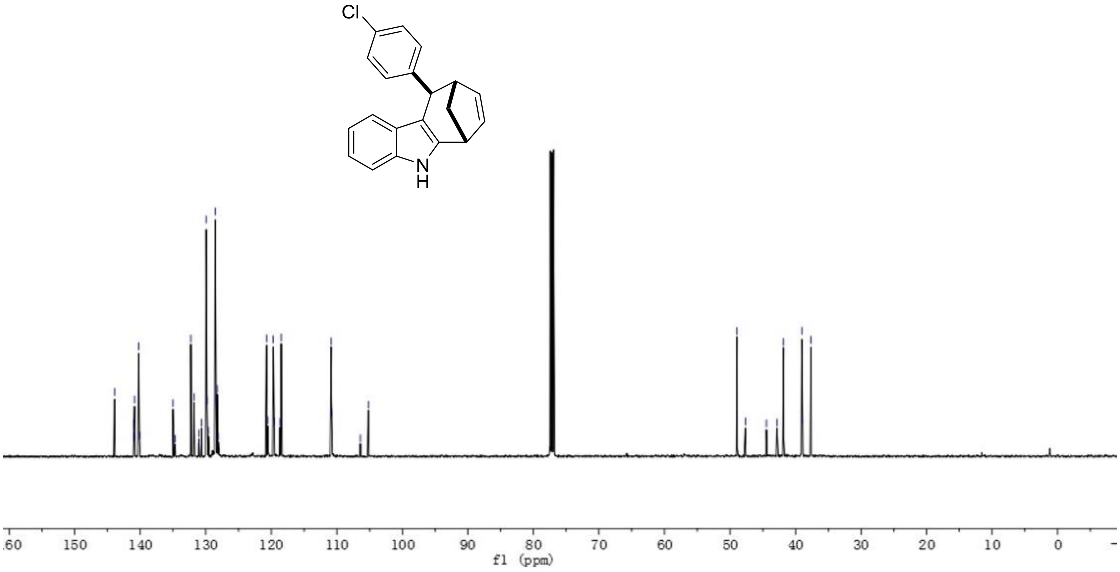

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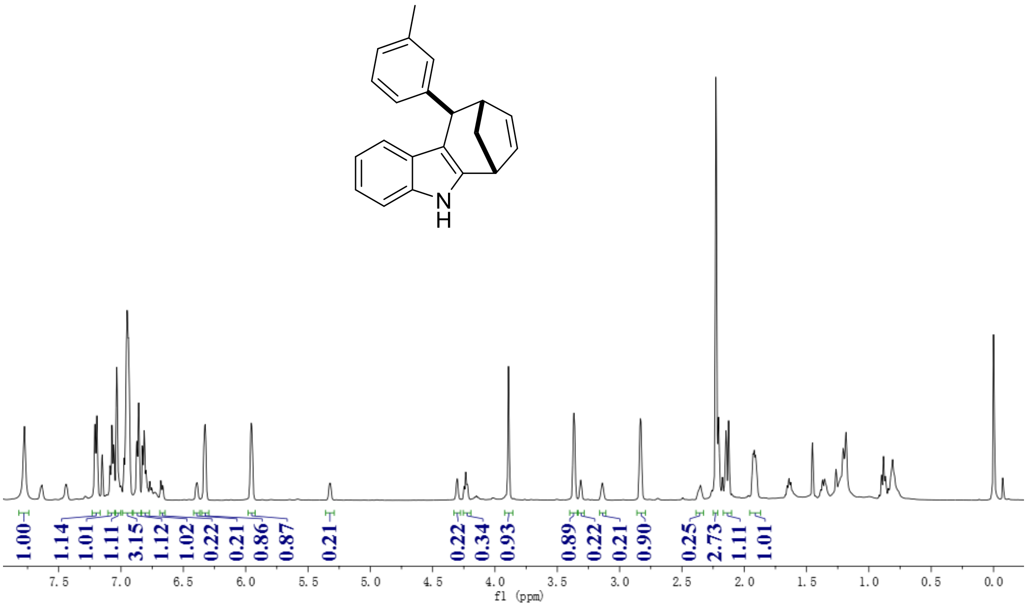
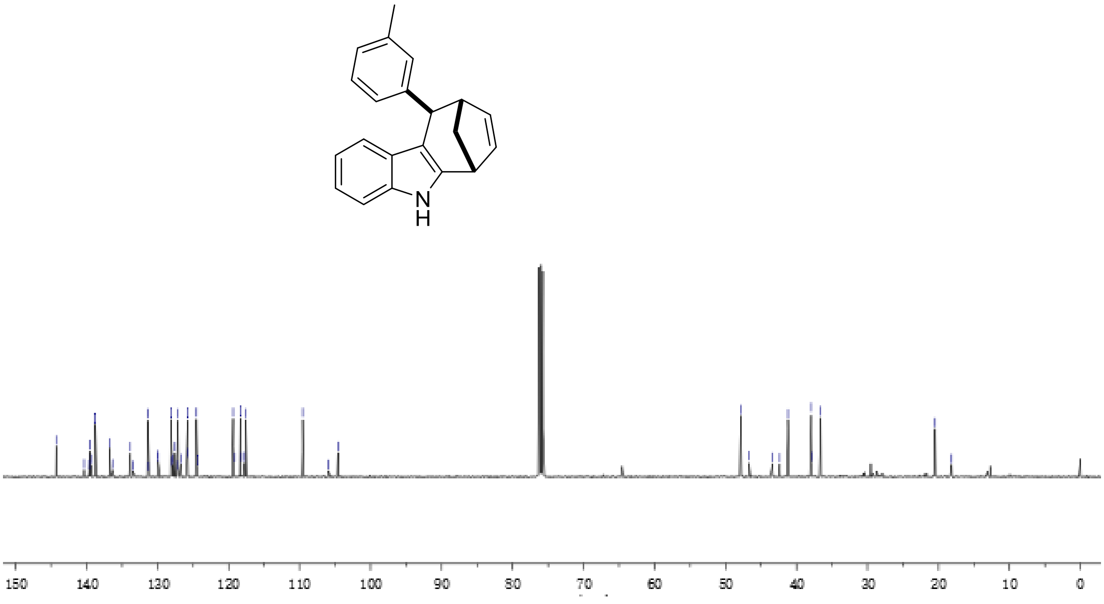
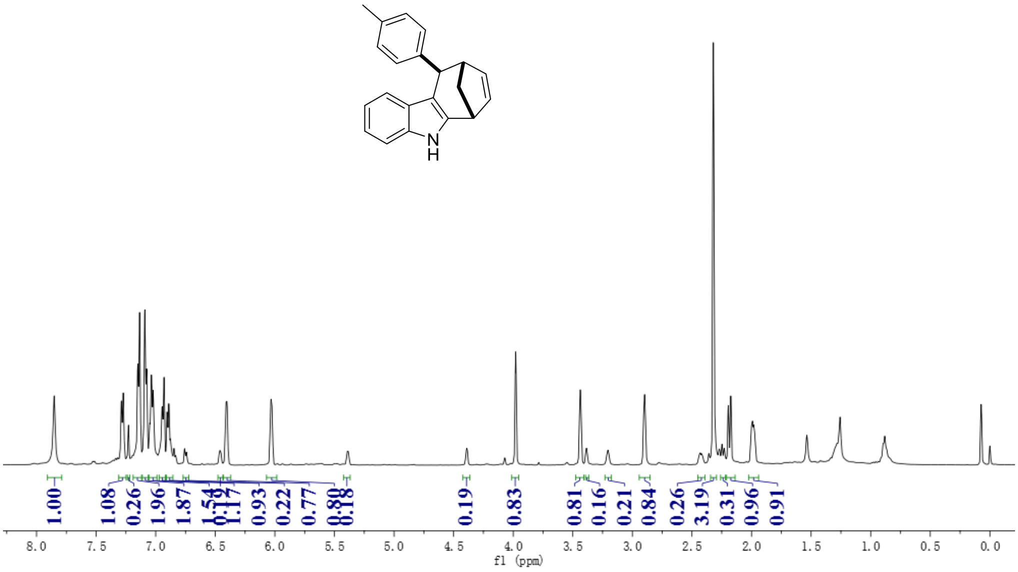
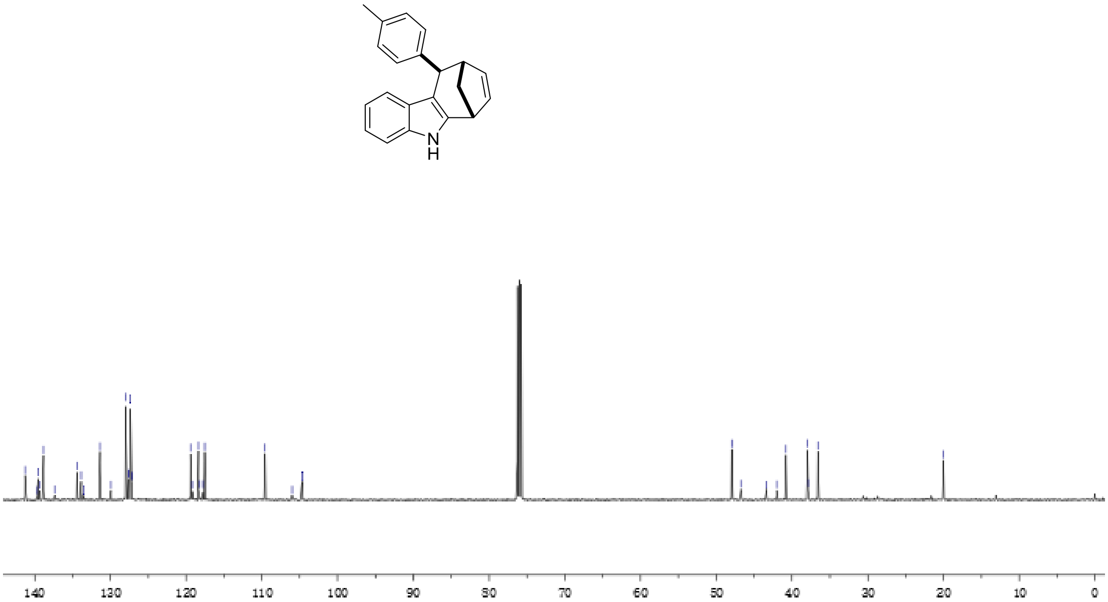




10-(p-tolyl)-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3o)





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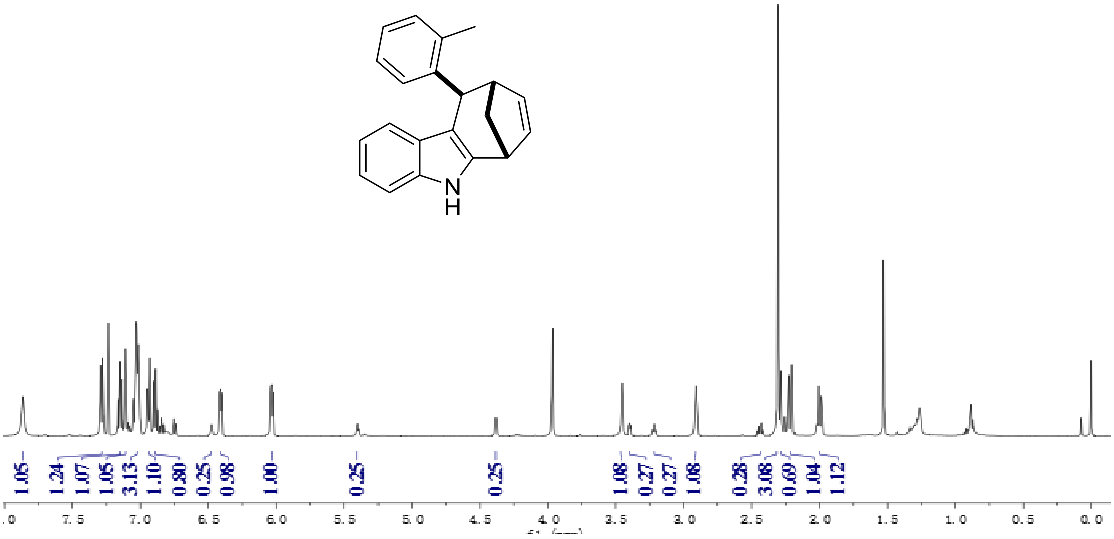

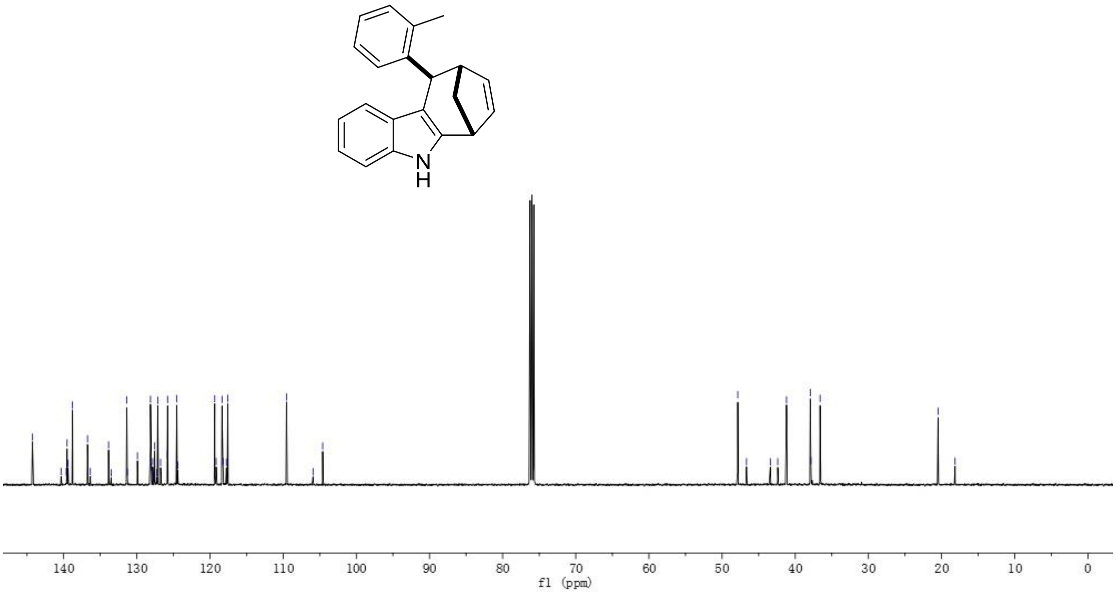

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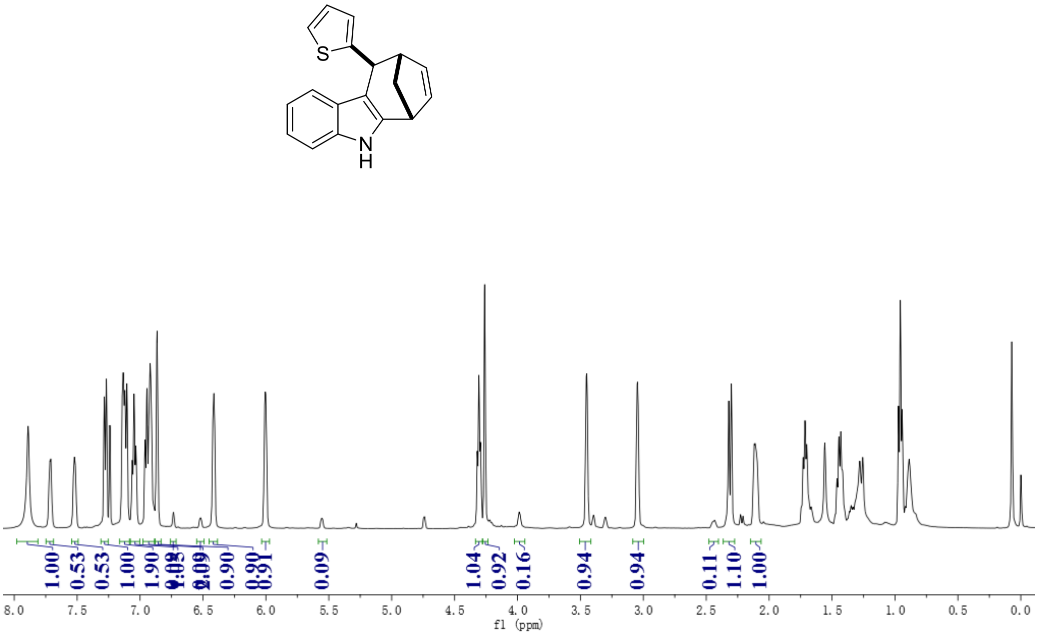

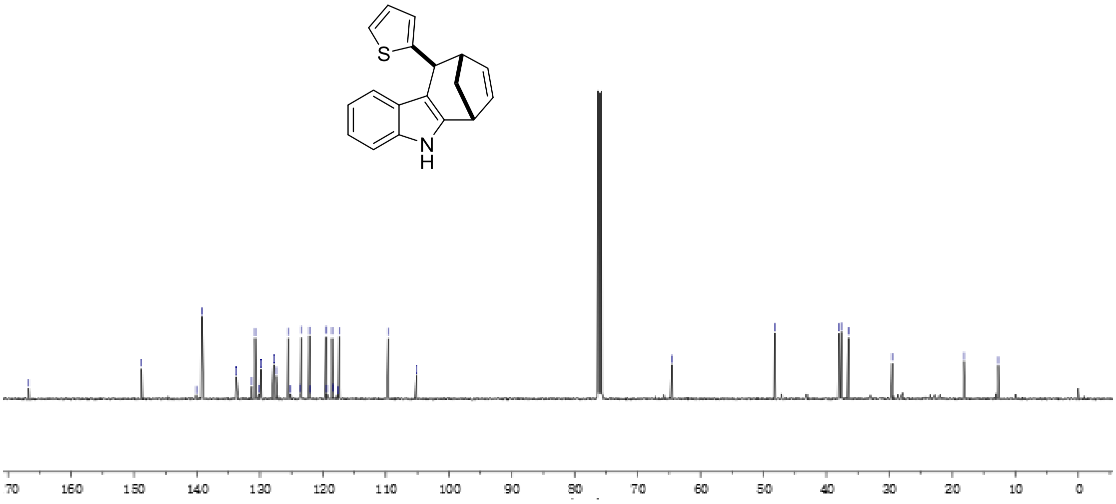

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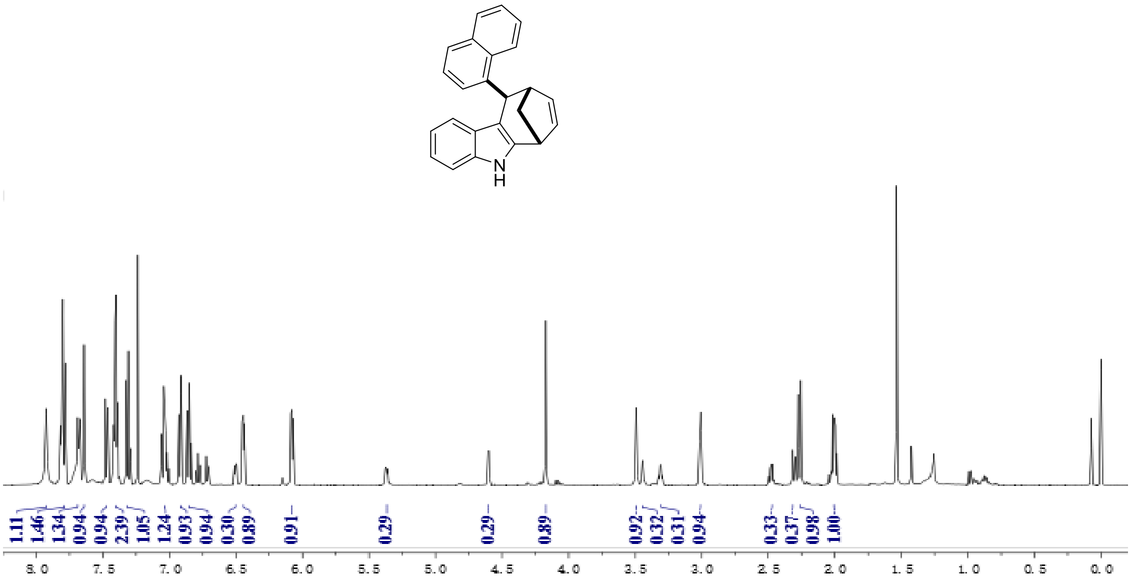
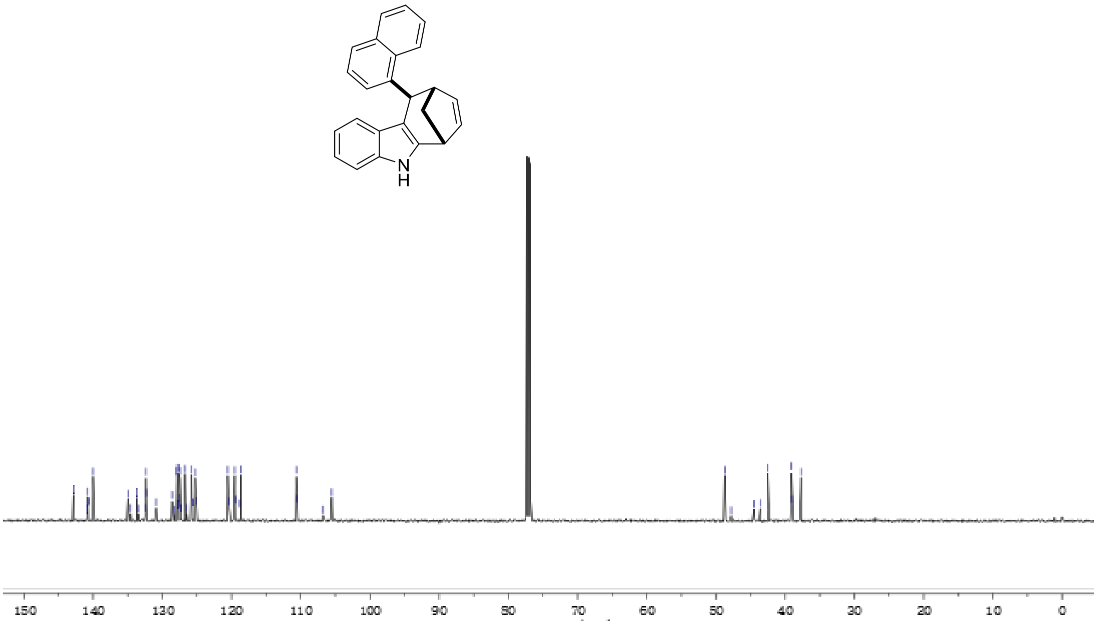
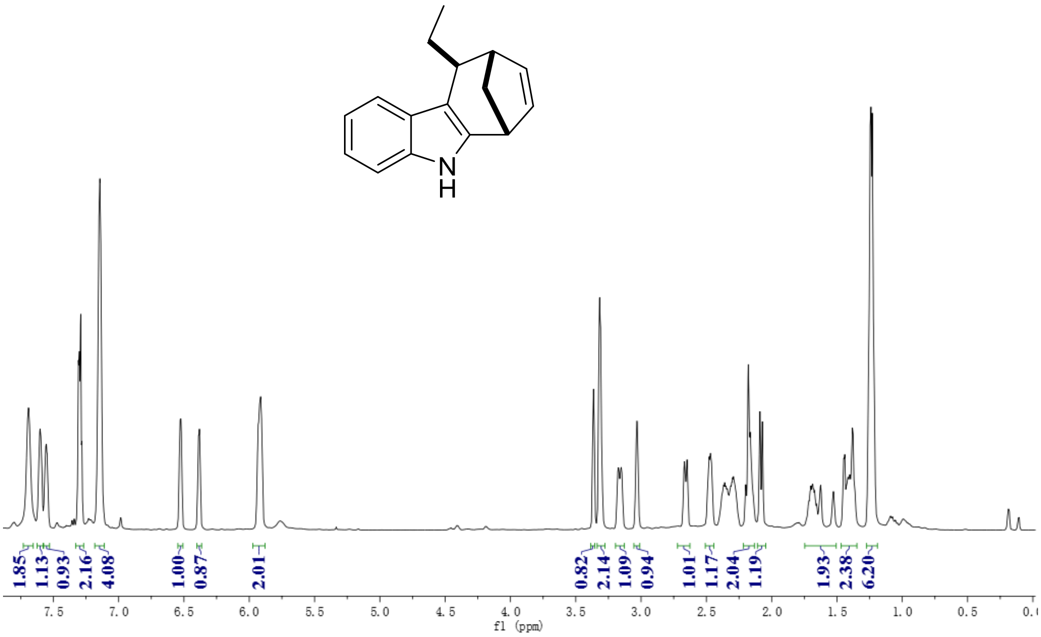
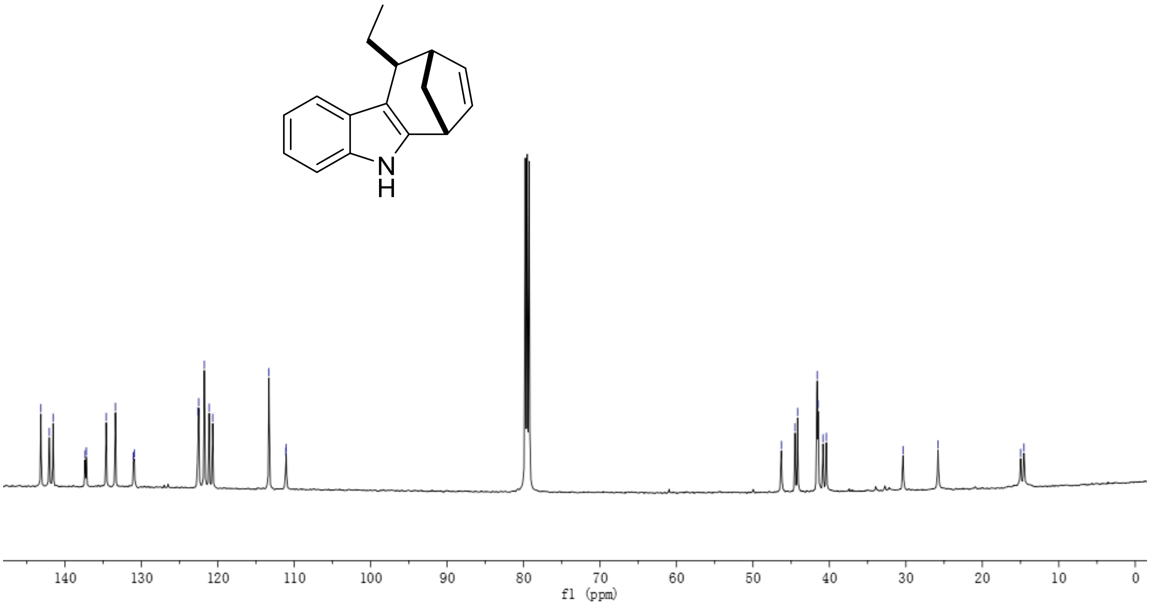




(6R,9S,10S)-10-ethyl-5,6,9,10-tetrahydro-6,9-methanocyclohepta[b]indole (3s)





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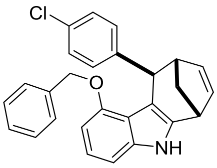
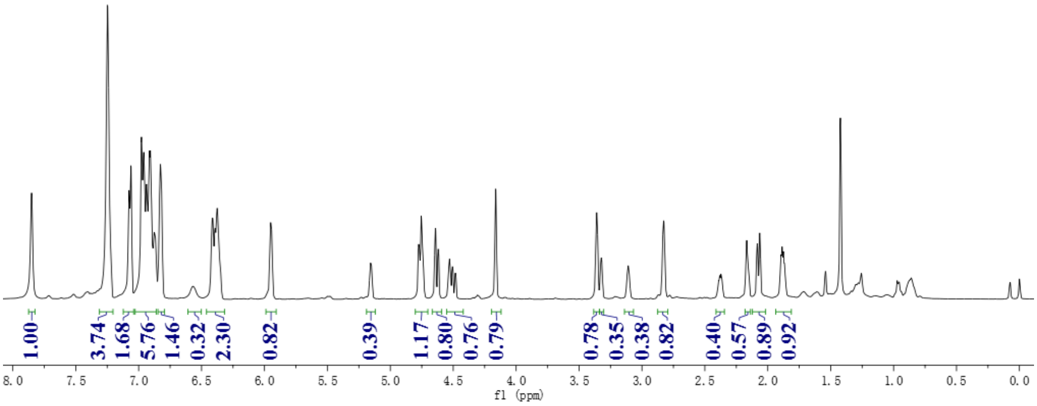
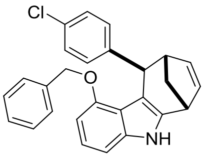
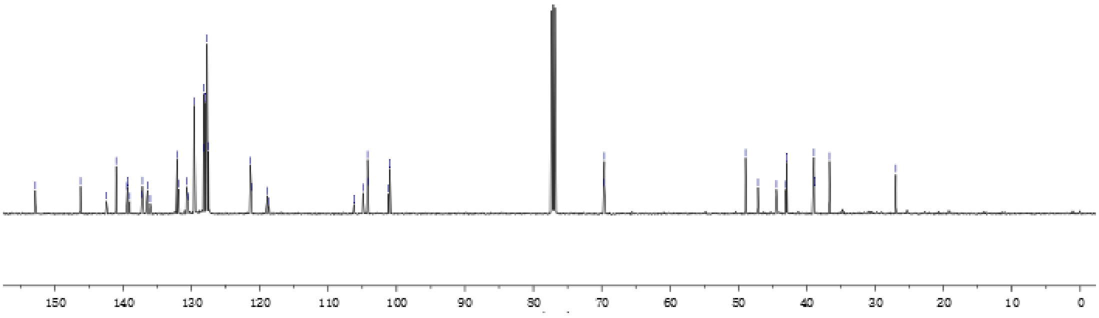
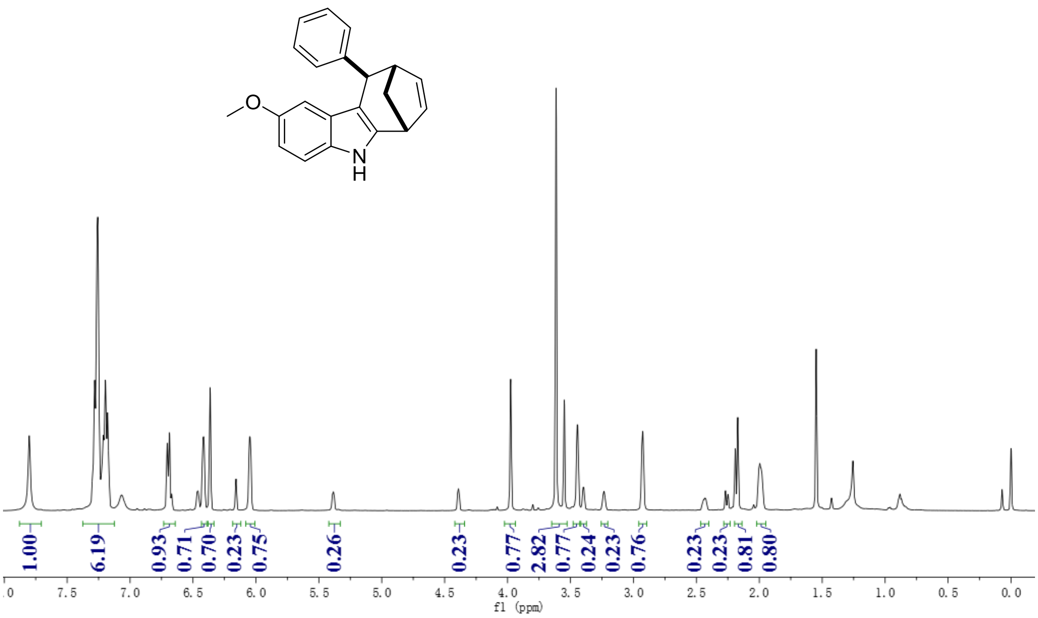


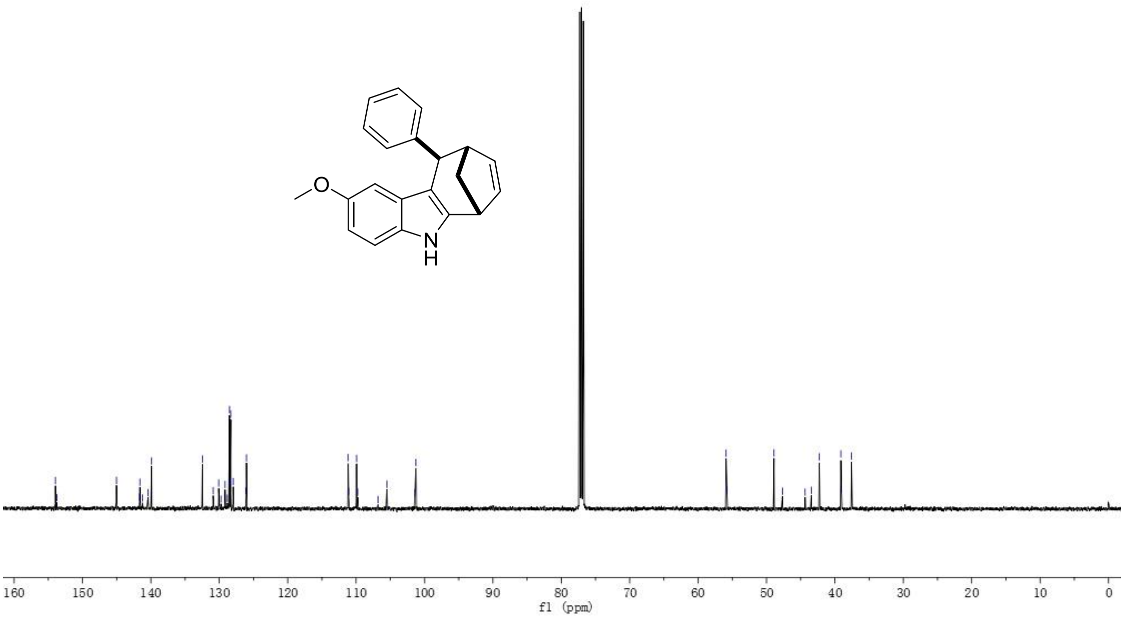




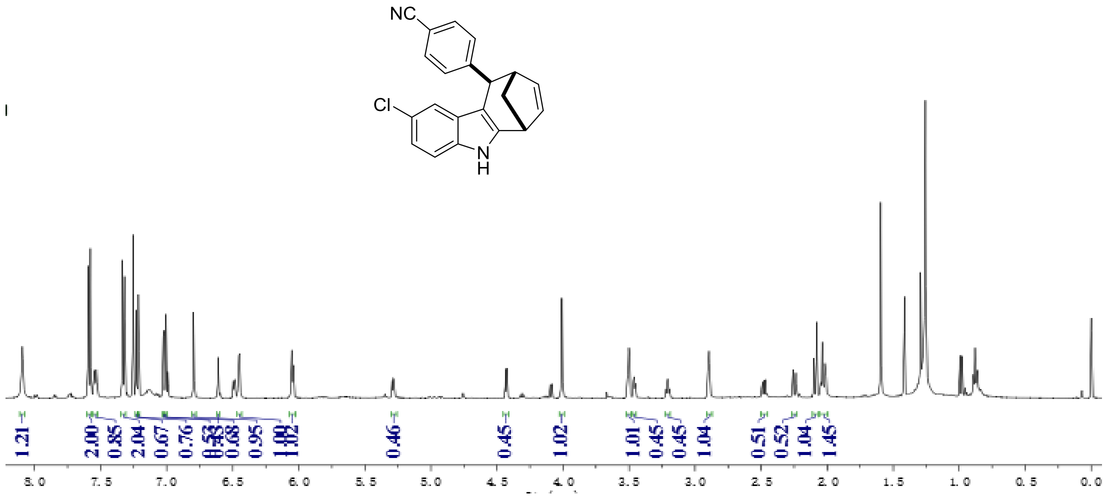


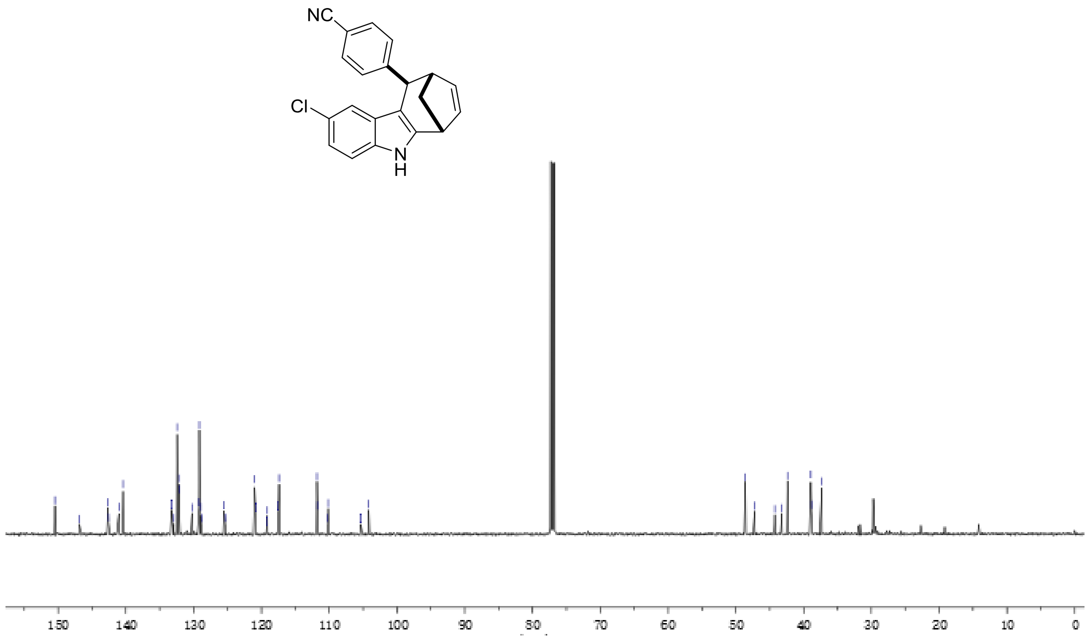
2-methoxy-10-phenyl-5, 6, 9, 10-tetrahydro-6, 9-methanocyclohepta[b]indole (3u)





4-(2-chloro-5,5a,6,9,10,10a-hexahydro-6,9-methanocyclohepta[b]indol-10-yl)benzonitrile (3v)





5-methyl-10-phenyl-5,6,9,10-tetrahydro-6,9-methanocyclohepta[b]indole (3w)