Supporting Information for

Copper-Catalyzed Construction of (*Z*)-Benzo[*cd*]indoles: Stereoselective Intramolecular *trans*-Addition and S_N-Ar Reaction

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1. General

Unless stated otherwise, reactions were conducted in dried glassware. Commercially available reagents and solvents were used as received. 300-400 Mesh silica gel was used for flash column chromatography. Visualization on TLC was achieved by the use of UV light (254 nm). 400 MHz and 100 MHz were used for the record of ^{1}H NMR and ^{13}C NMR spectra. Chemical shifts (δ ppm) were reported in parts per million referring to either the internal standard of TMS or the residue of the deuterated solvents. Splitting pattern was described as follows: s for singlet, d for doublet, t for triplet, q for quartet, and m for multiplet. Coupling constants were reported in Hz. The high-resolution mass spectrum (HRMS) was performed on Waters Xevo G2-S QTof mass spectrometer. The crystal of **2f** was measured on Agilent Gemini E and the solvent system for crystal growth is dichloromethane and petroleum ether. PE is petroleum ether, and EA is ethyl acetate.

2. The details information of the crystal of 2f

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 20180329-1

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Bond precision:   C-C = 0.0045 A          Wavelength=0.71073

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Temperature:      296 K

                 Calculated                Reported
Volume           2156.0(2)                 2156.0(2)
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Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C25 H18 Cl N O3 S         C25 H18 Cl N O3 S
Sum formula      C25 H18 Cl N O3 S         C25 H18 Cl N O3 S
Mr               447.91                    447.95
Dx,g cm-3        1.380                     1.380
Z                4                         4
Mu (mm-1)        0.302                     0.302
F000             928.0                     929.6
F000'            929.46
h,k,lmax         14,28,13                  13,28,13
Nref             5978                      5032
Tmin,Tmax                                  0.730,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.730 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.842           Theta(max)= 29.460

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                                                 0.1573( 5032)
S = 1.038                Npar= 281
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C17 Check
PLAT334_ALERT_2_C Small <C-C> Benzene Dist.   C24      -C29      .      1.37 Ang.
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PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     3.637 Check
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Alert level G

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PLAT431_ALERT_2_G Short Inter HL..A Contact  C120     ..O30      .      3.12 Ang.
                                      -1+x,3/2-y,-1/2+z  =      4_475 Check
PLAT769_ALERT_4_G CIF Embedded explicitly supplied scattering data     Please Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600       914 Note
PLAT960_ALERT_3_G Number of Intensities with I  <   - 2*sig(I) ...        11 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         2 Info
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PLAT983_ALERT_1_G The  S-f"=    0.1244 Deviates from  IT-Value =       0.1234 Check
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  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  7 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 11 ALERT level G = General information/check it is not something unexpected

  8 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
  2 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/05/2022; check.def file version of 17/05/2022

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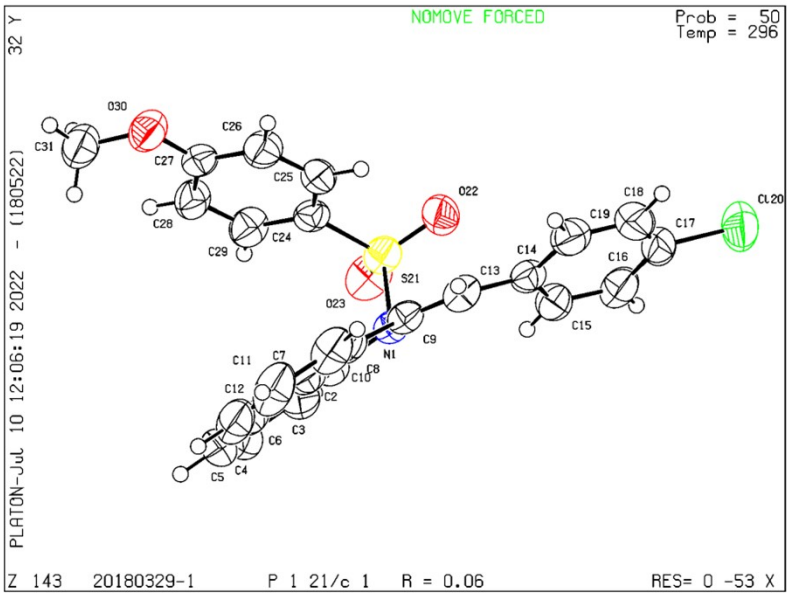

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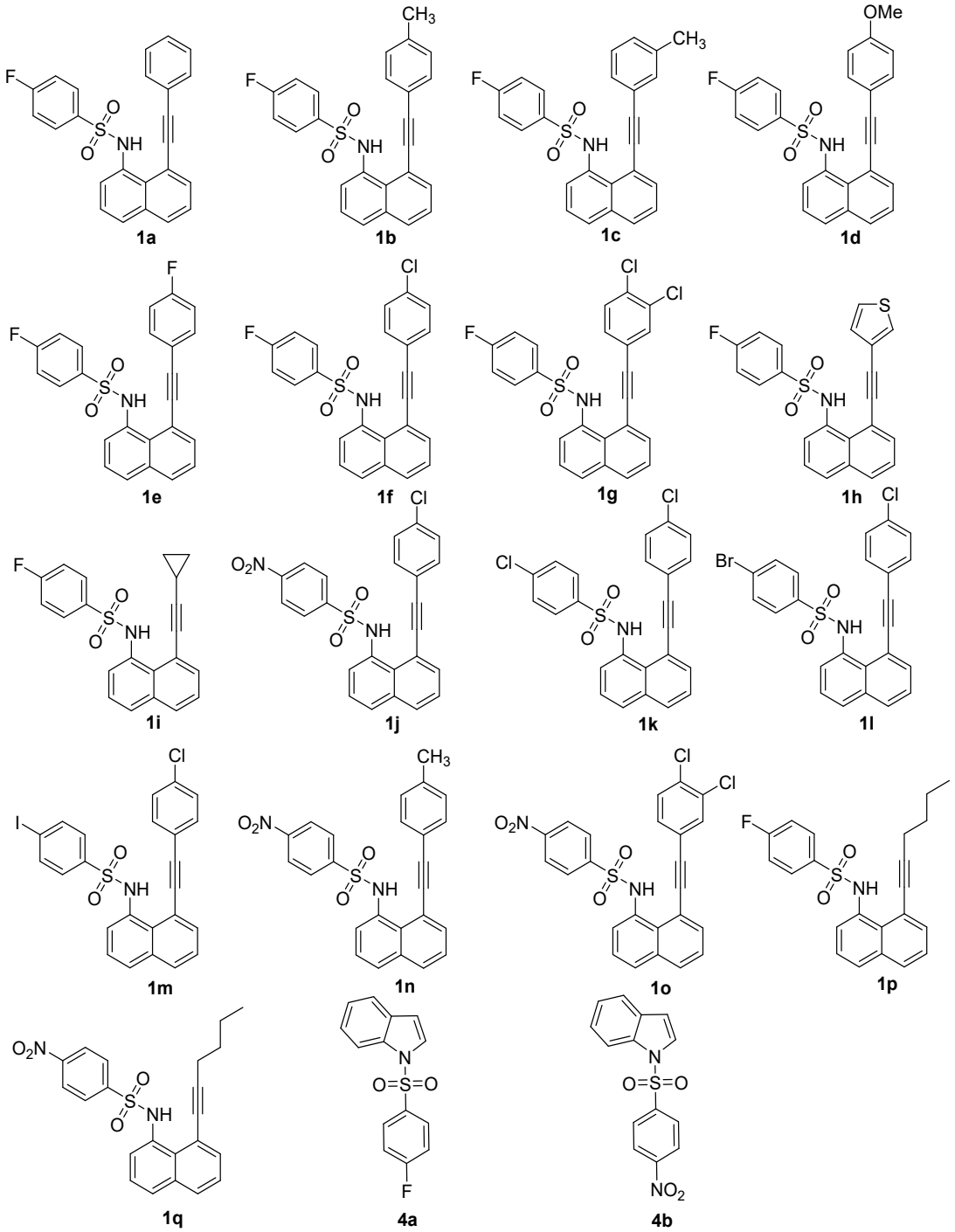
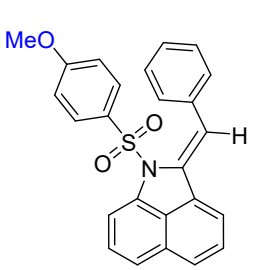


4. Structures of 2a-2o and 5



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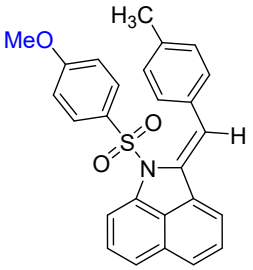

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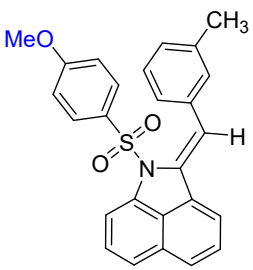

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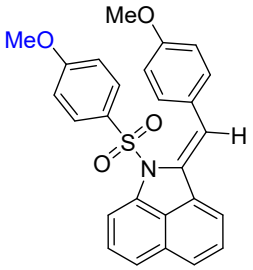

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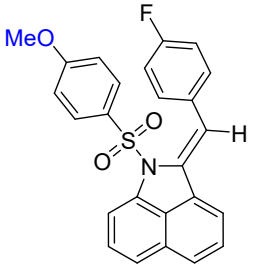

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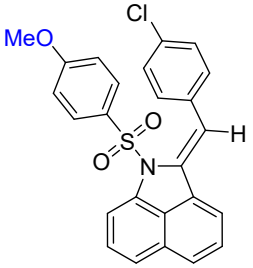

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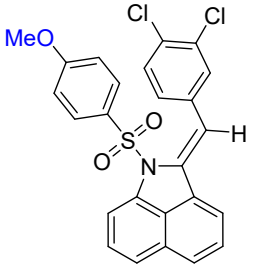

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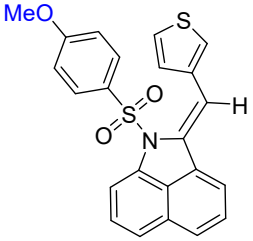

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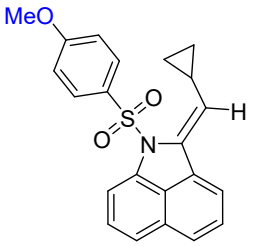

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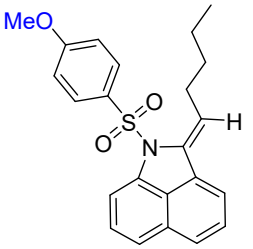

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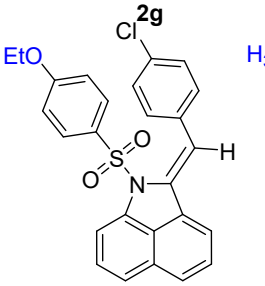

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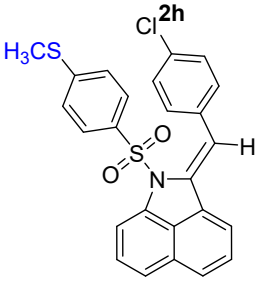

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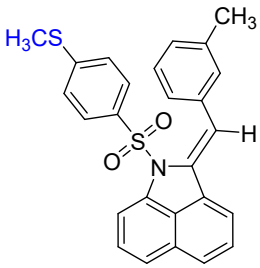

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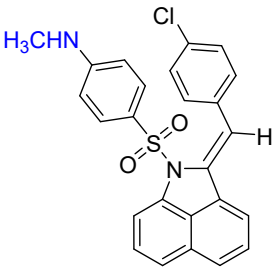

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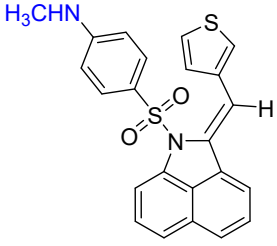

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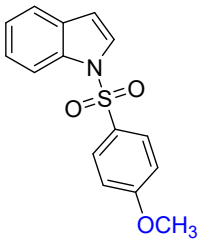
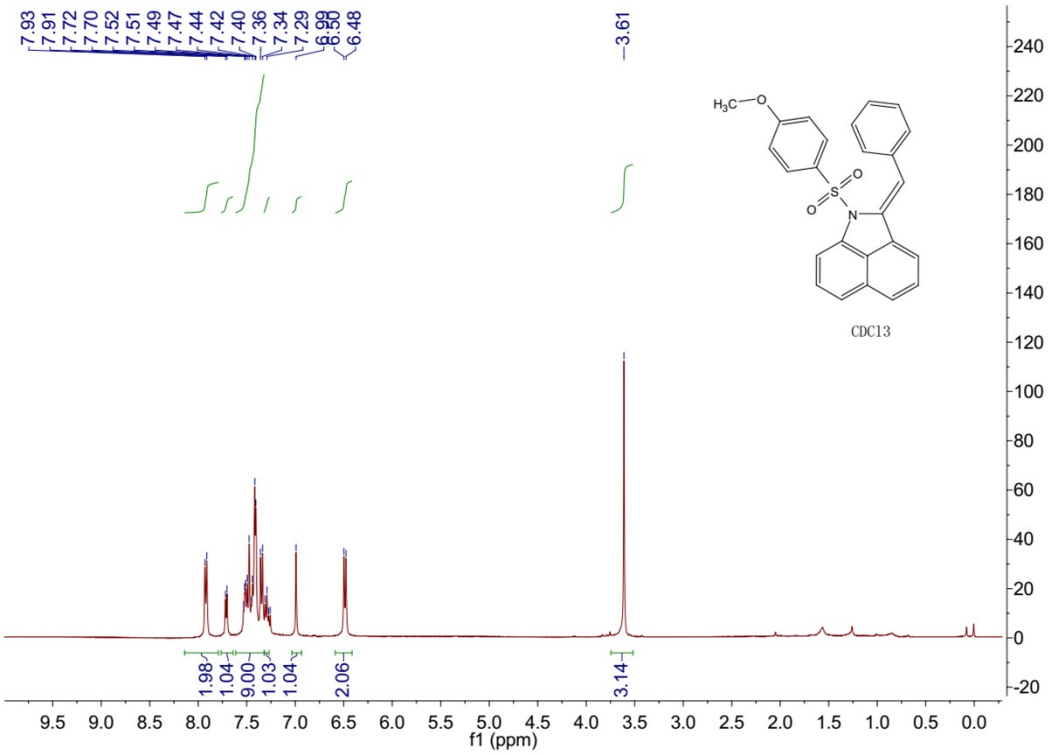


5

5. Copies of the Products ^{1}H NMR, ^{13}C NMR

Figure S1 ^{1}H-NMR spectrum of **2a**



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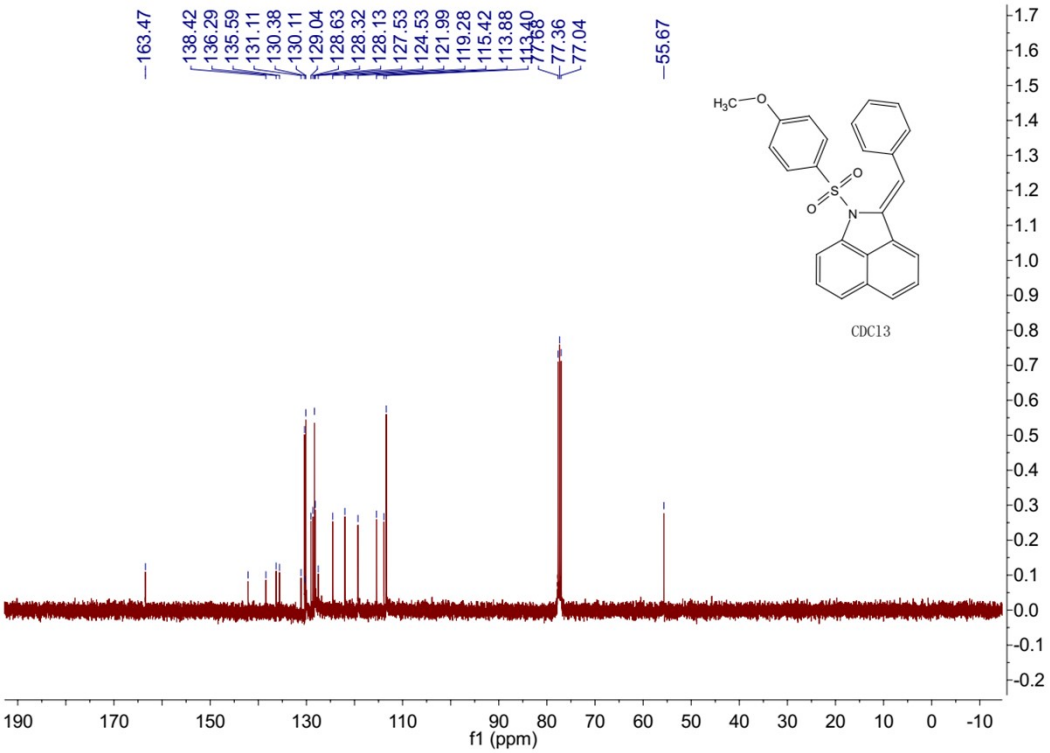

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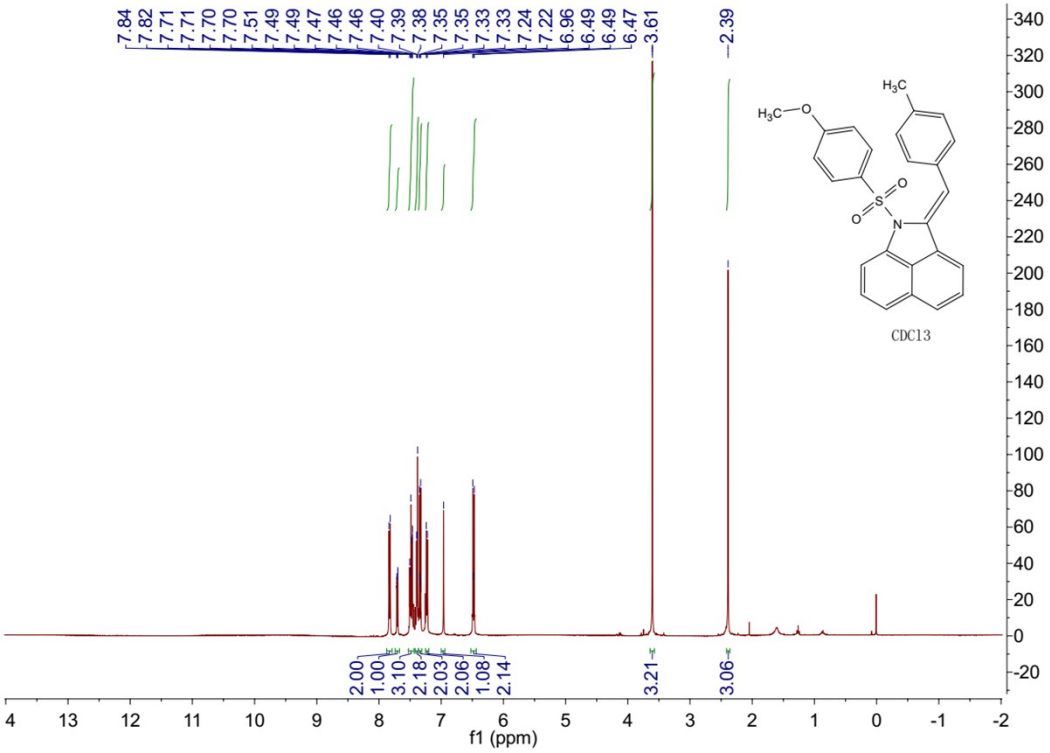

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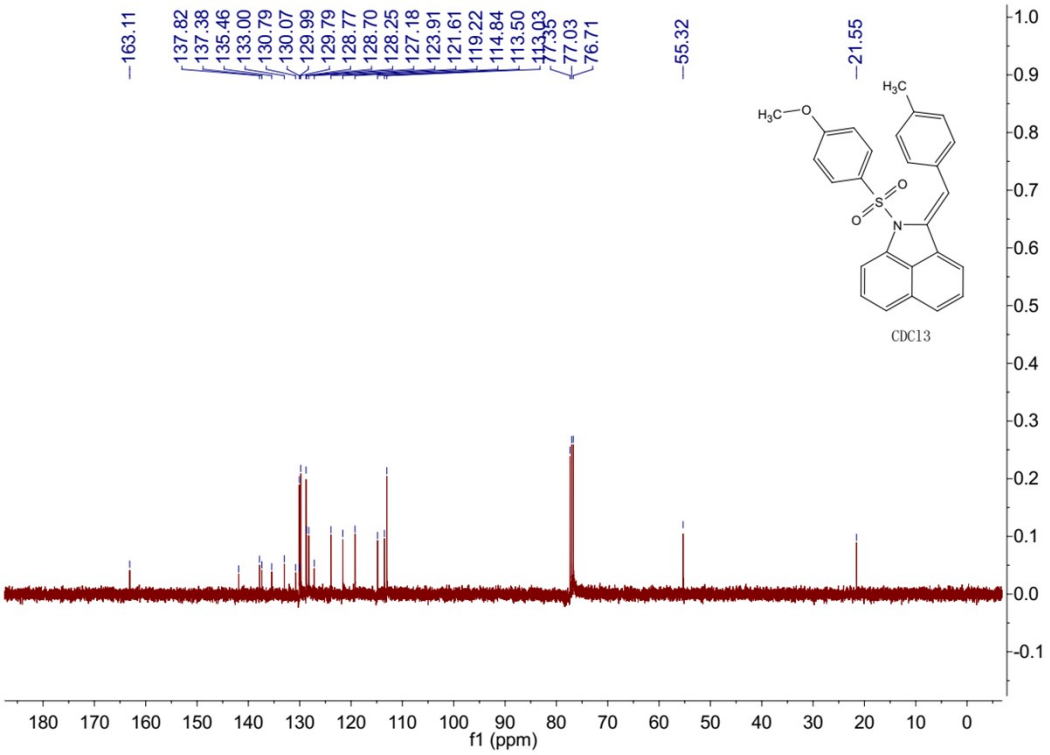

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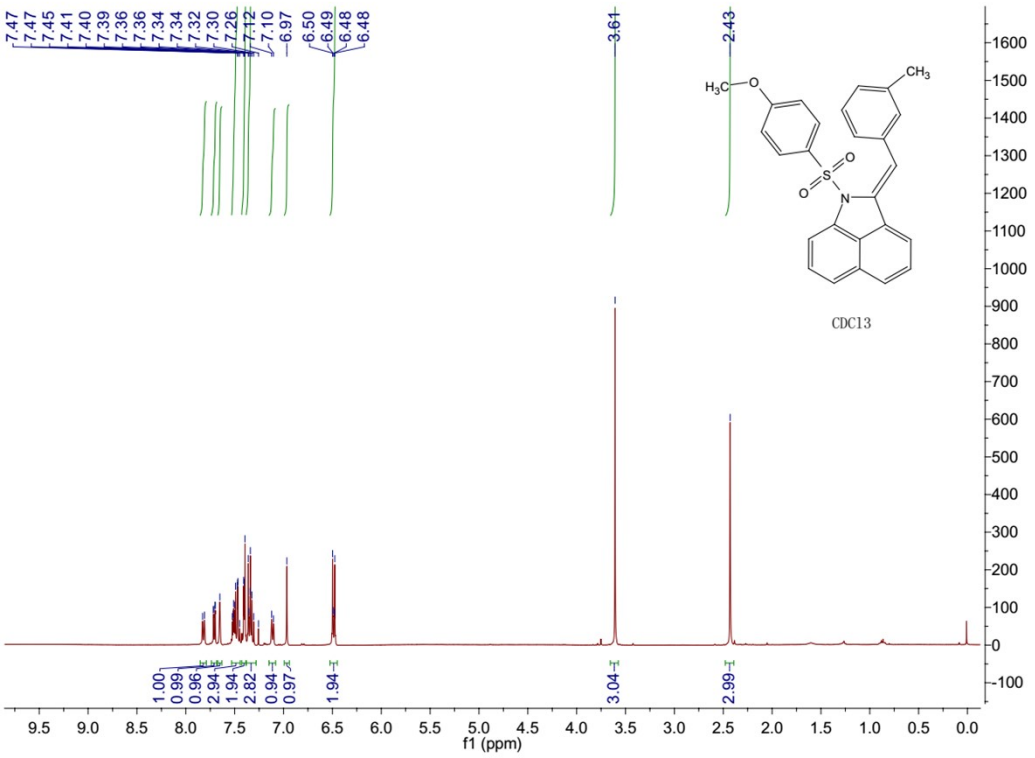

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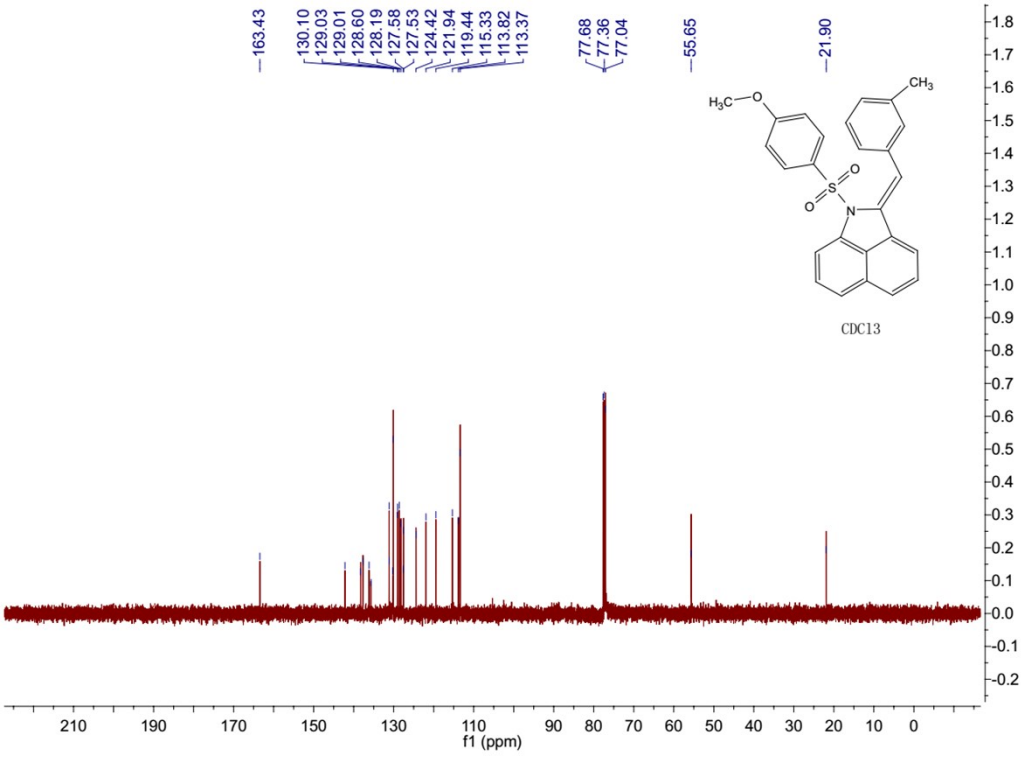

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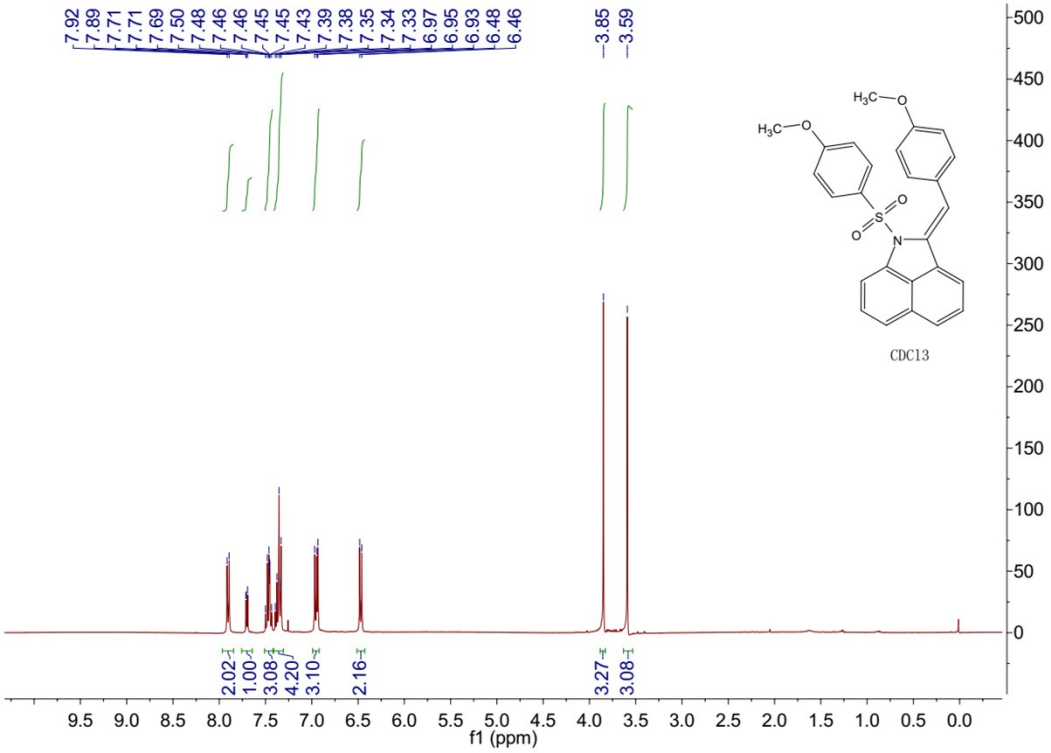

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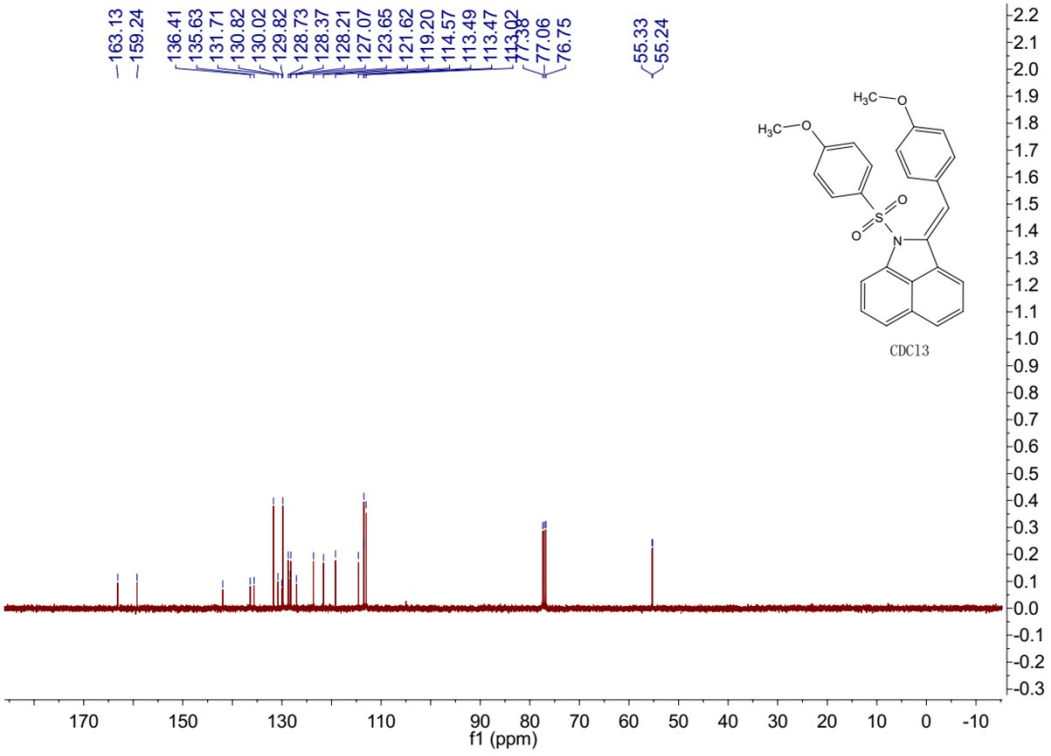

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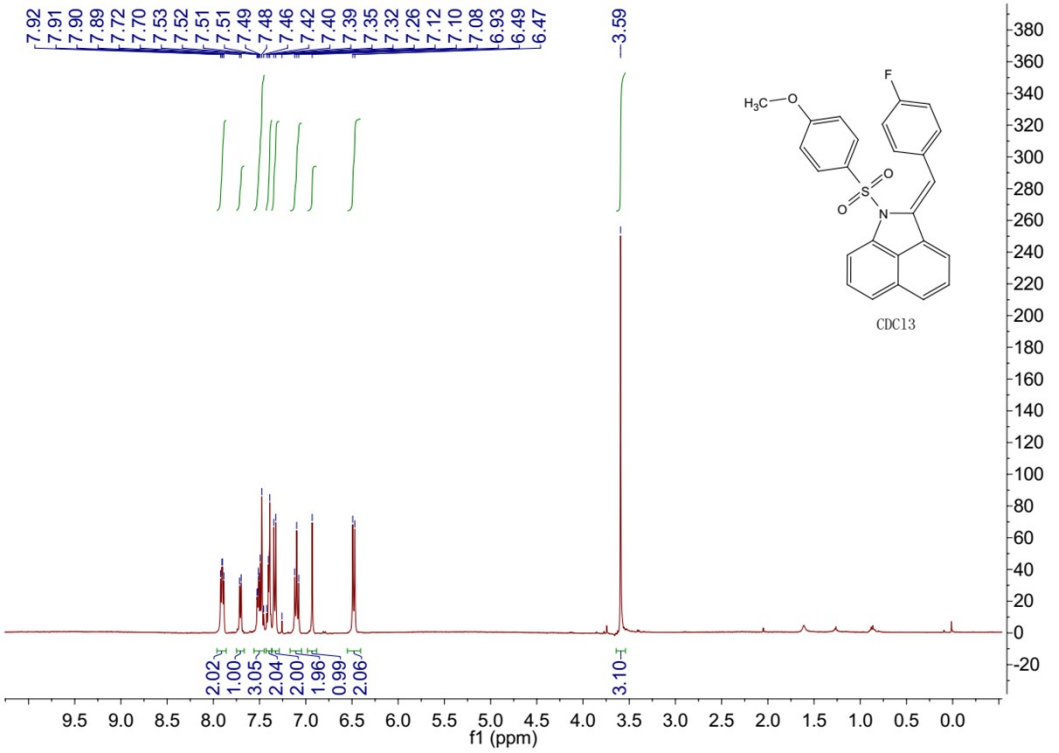

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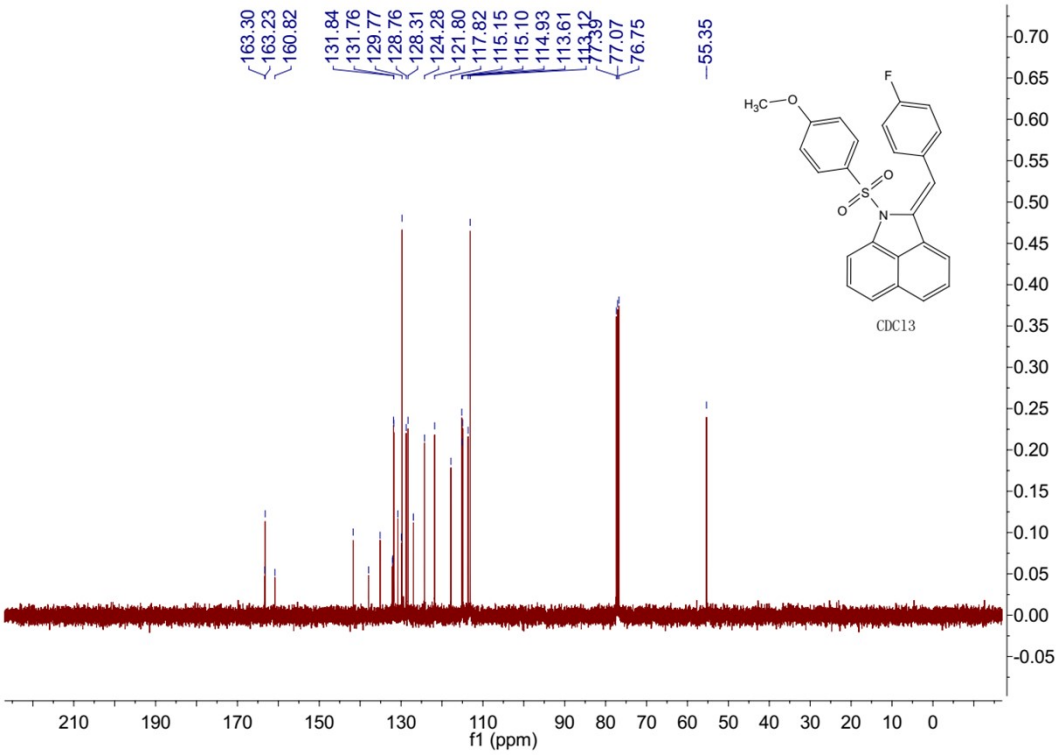

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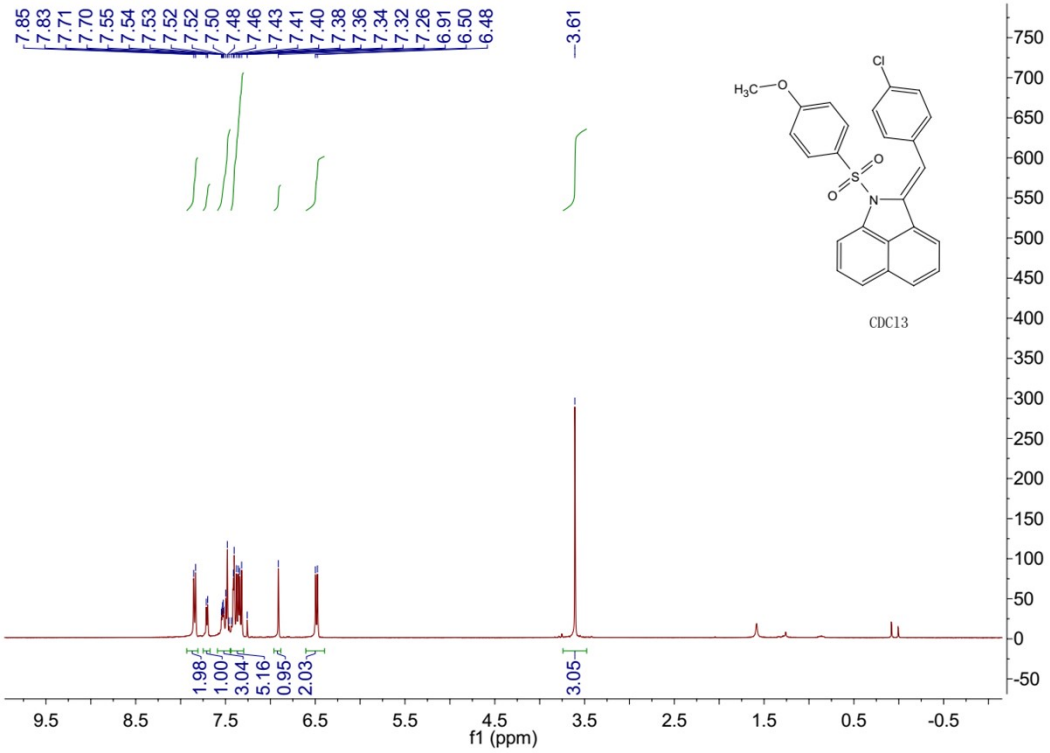

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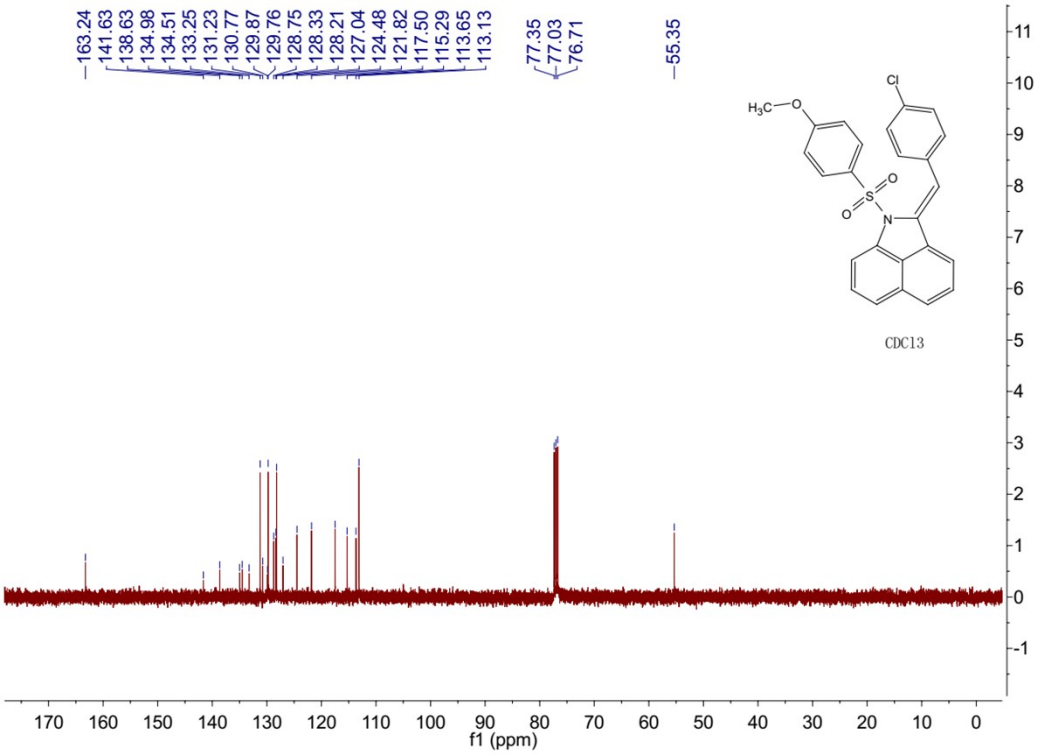

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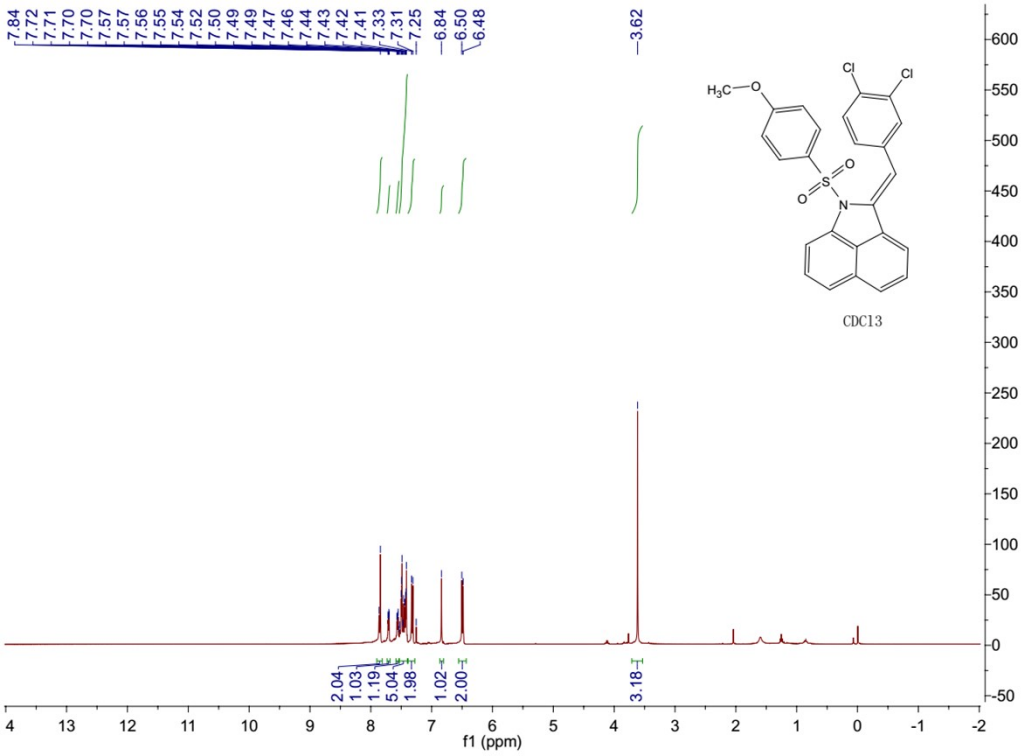

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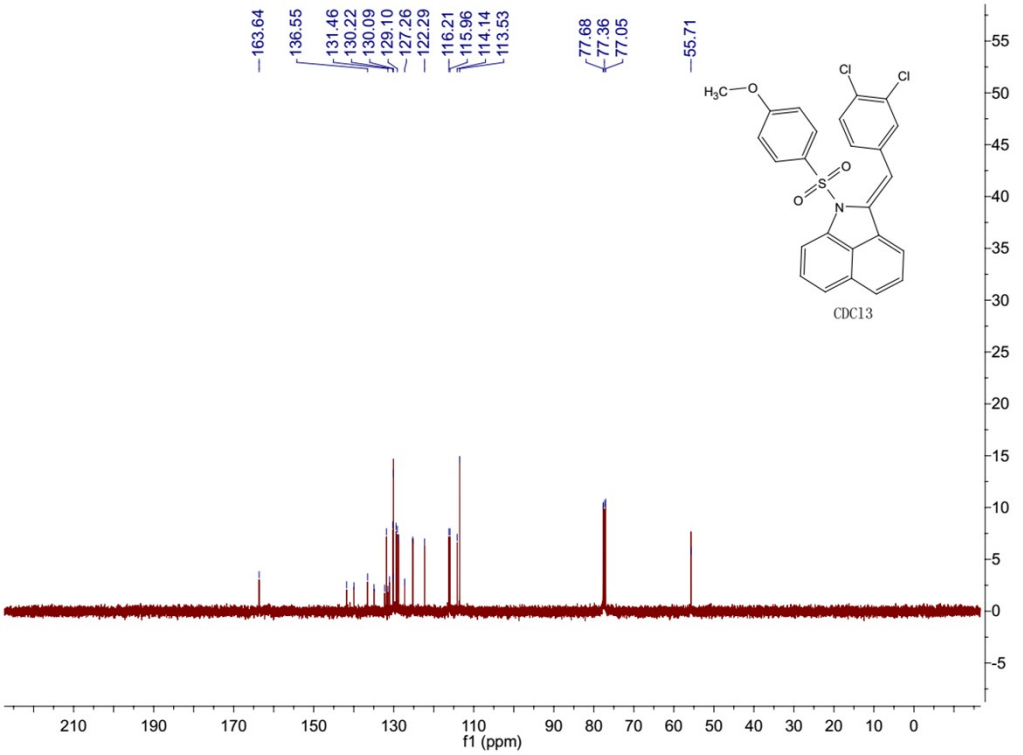

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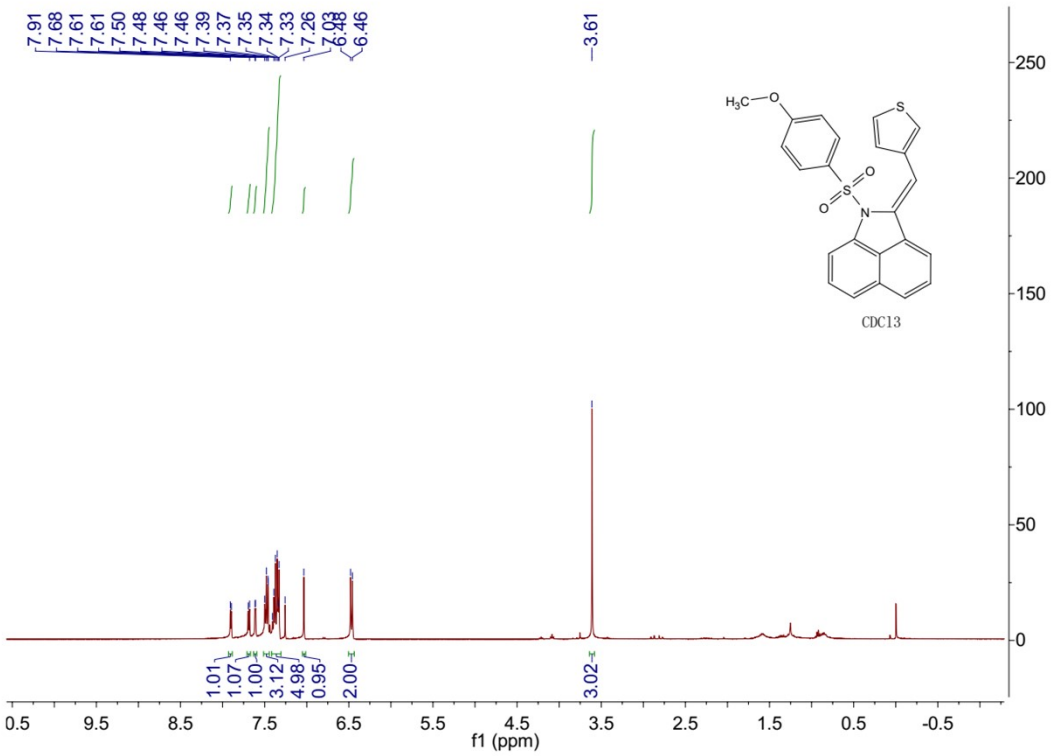

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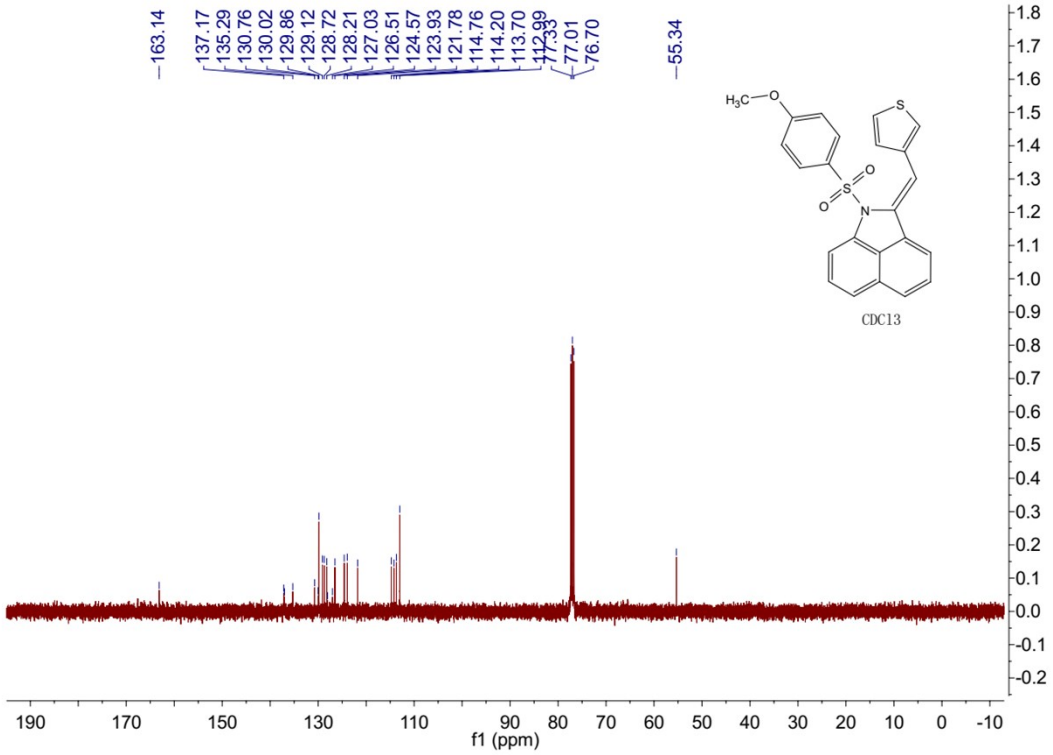

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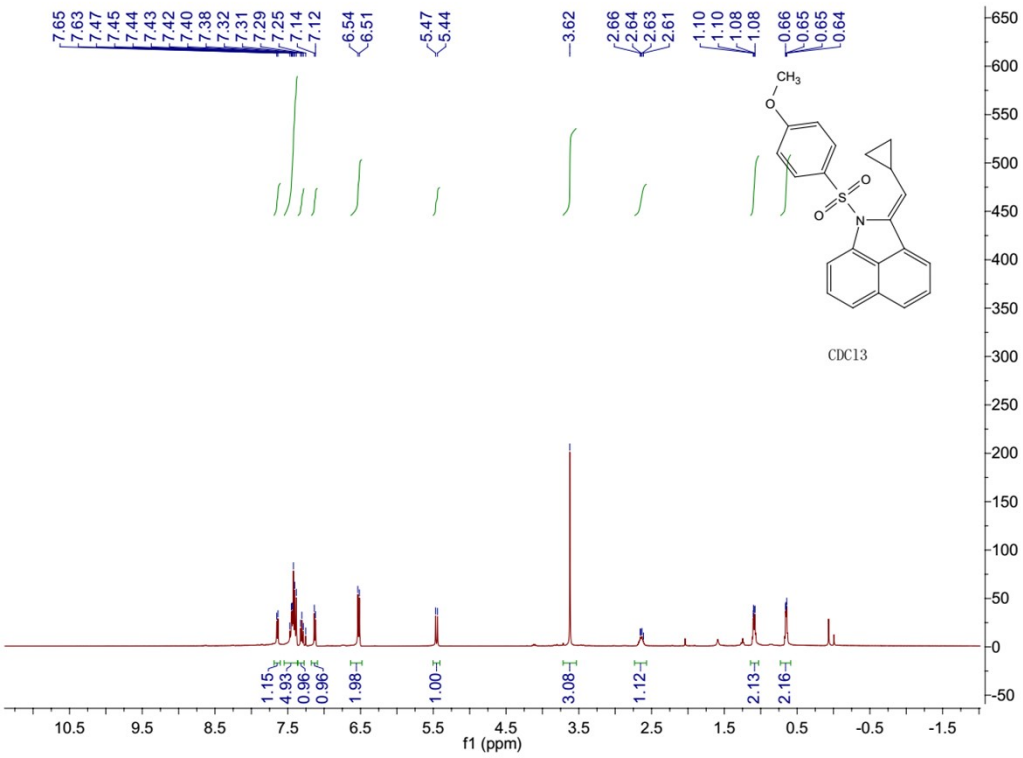

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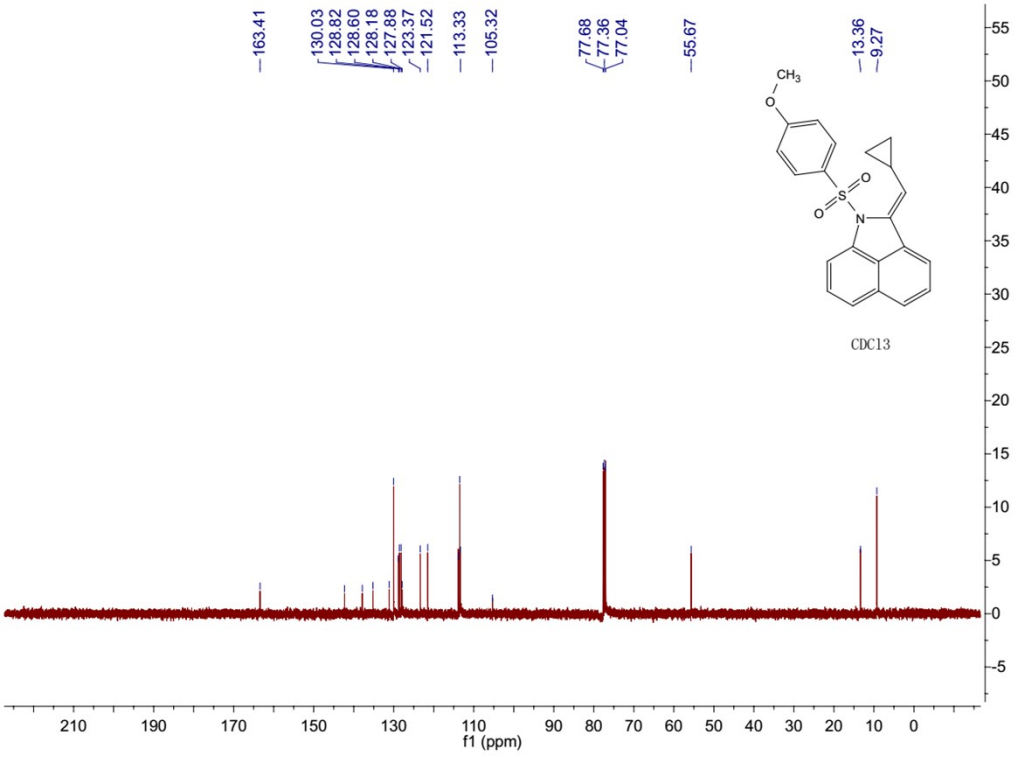

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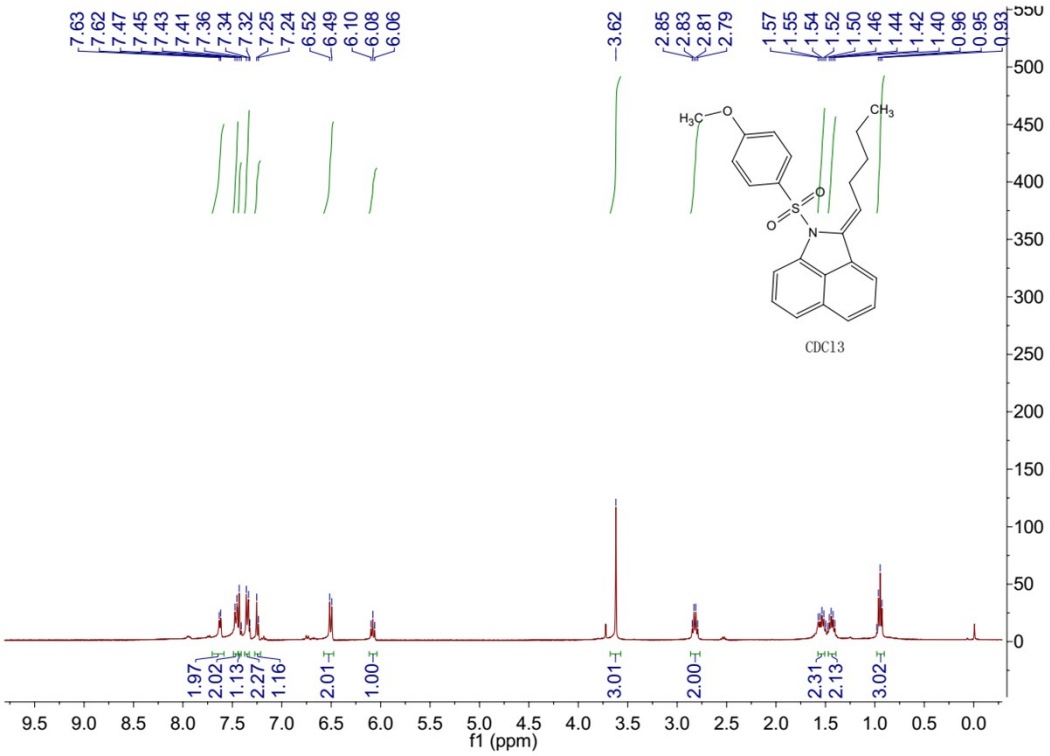

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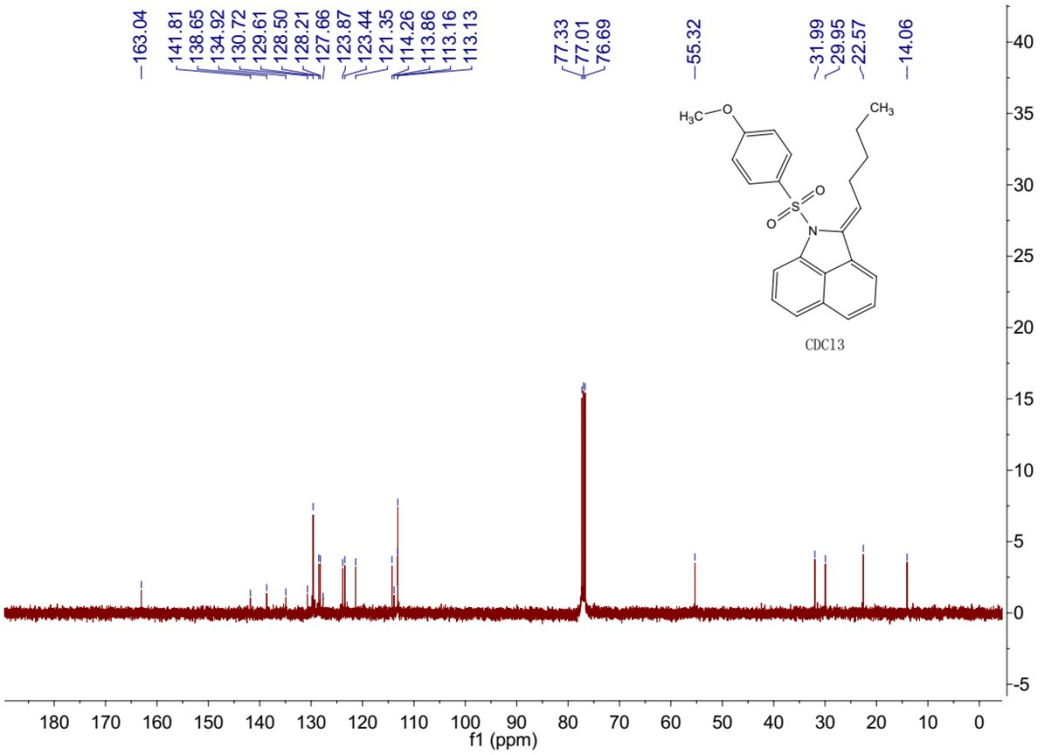

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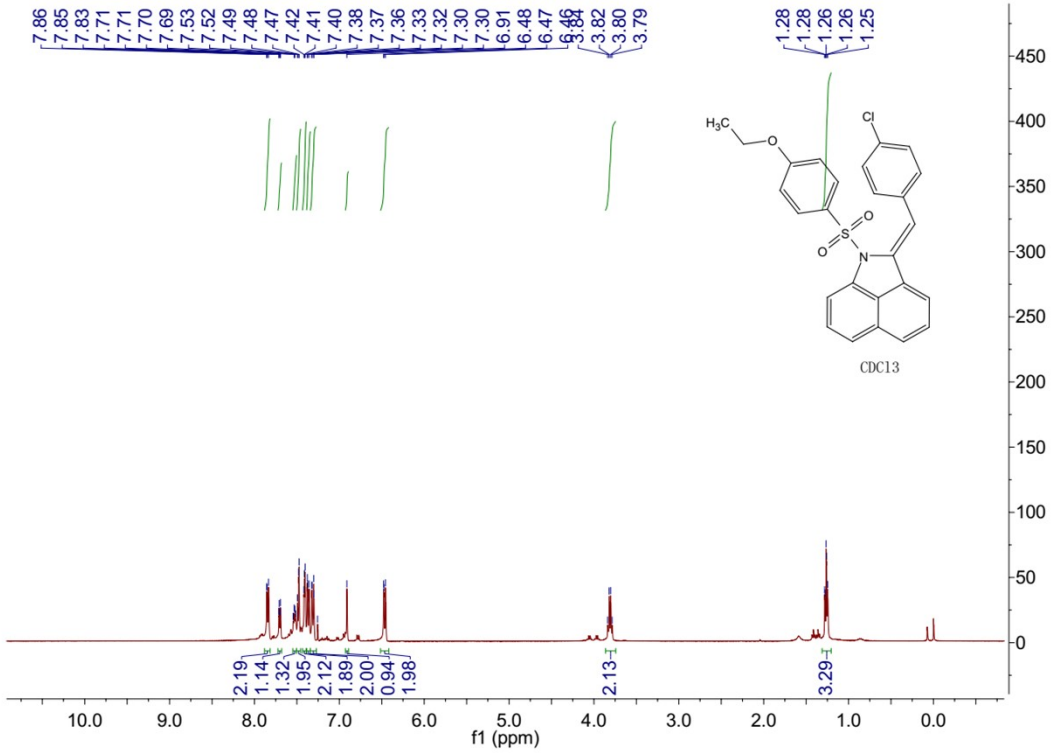

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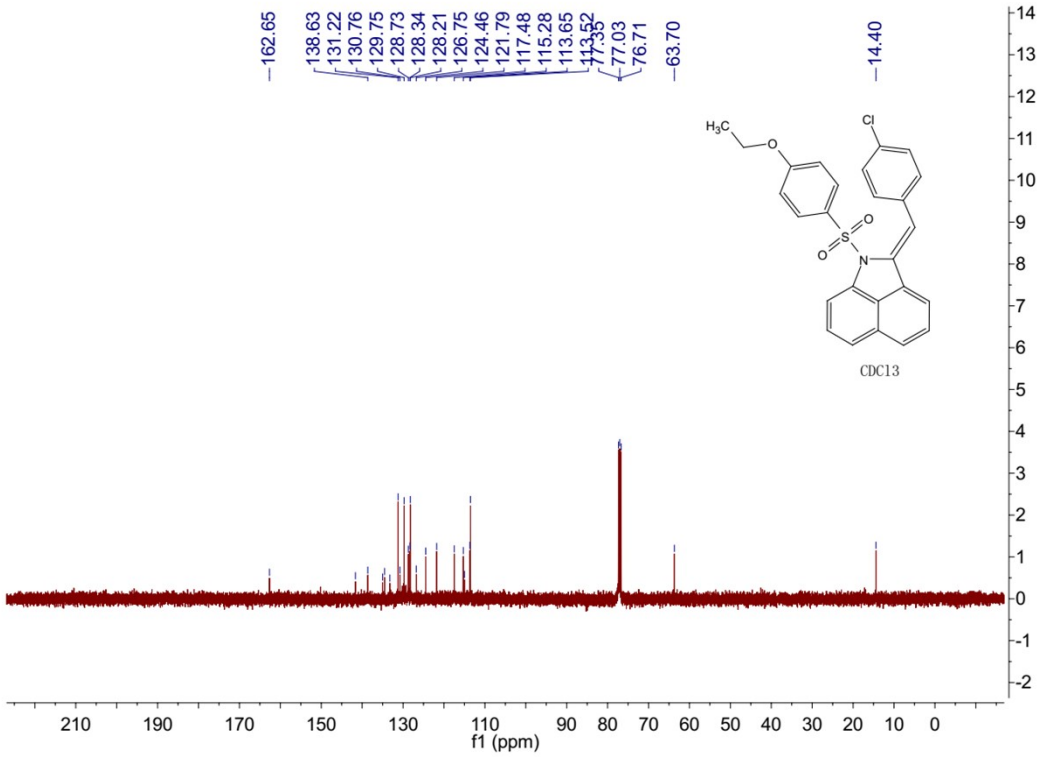

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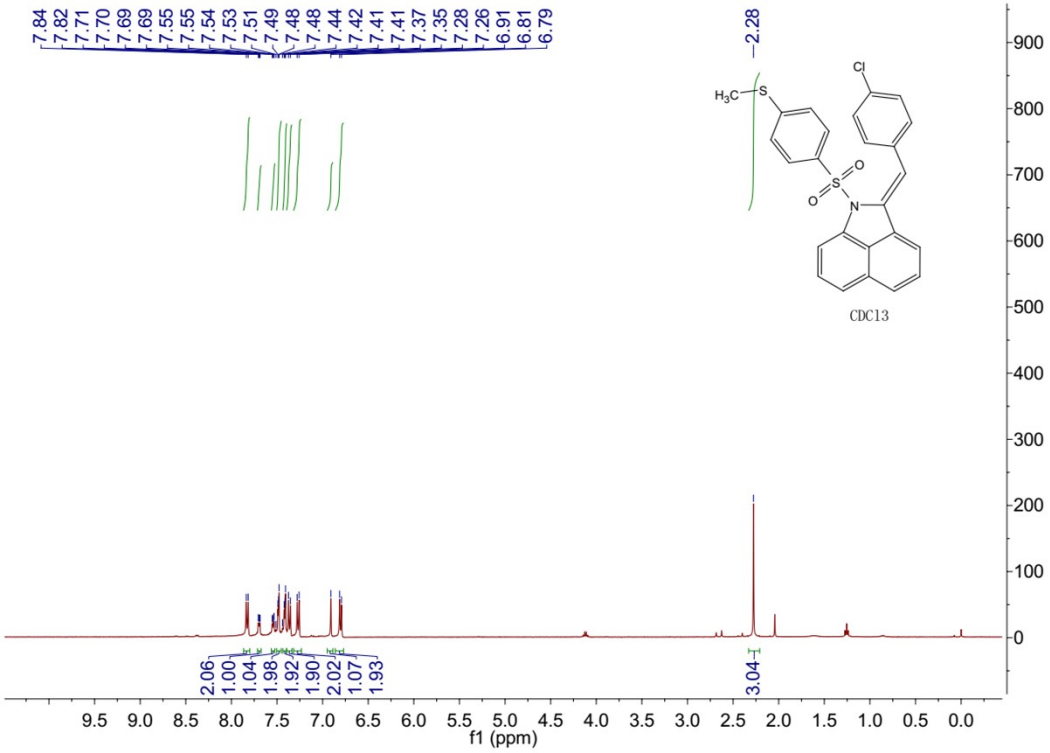

Figure S24 ^{13}C-NMR spectrum of **2l**

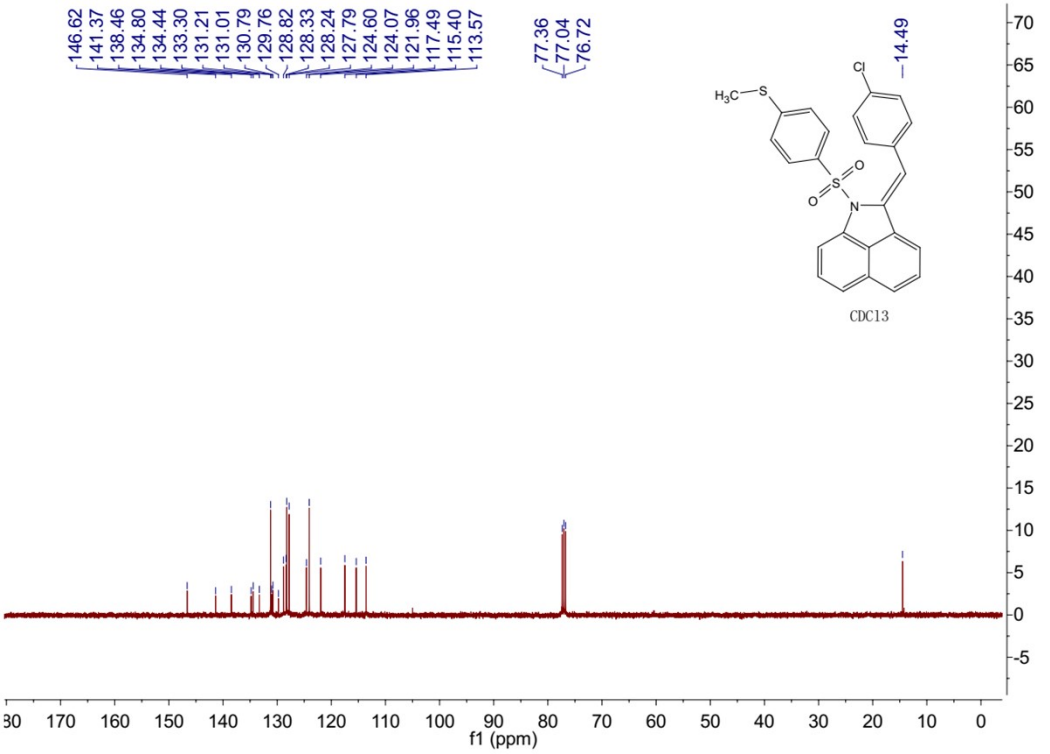

Figure S25 ^{1}H-NMR spectrum of **2m**

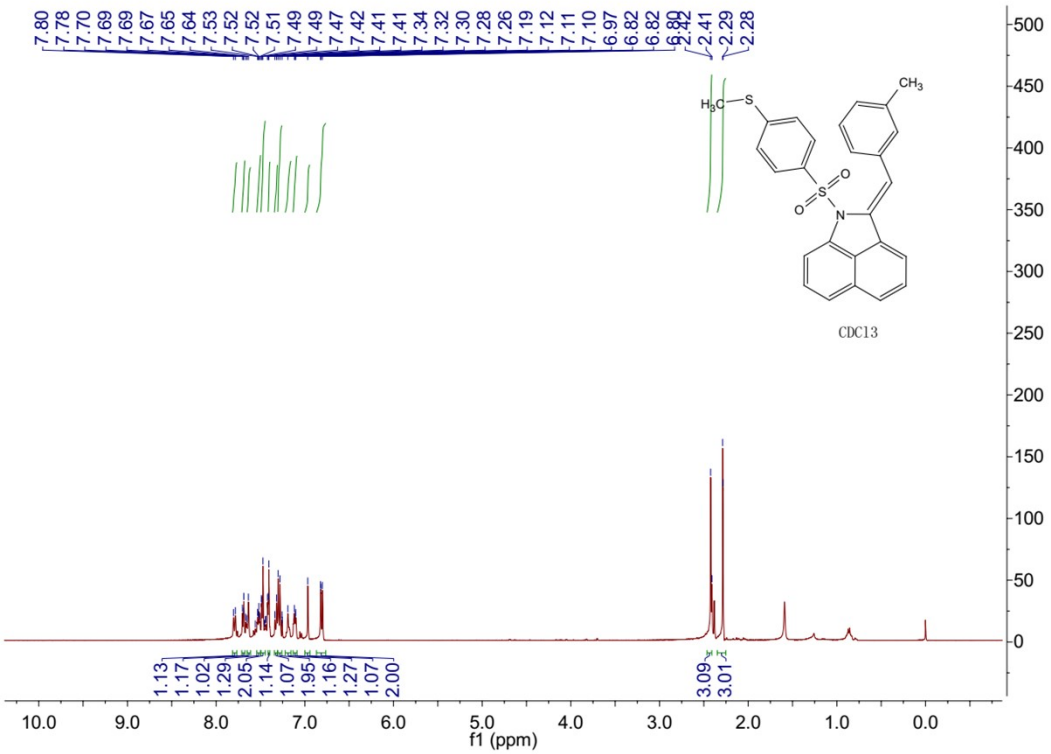

Figure S26 ^{13}C-NMR spectrum of **2m**

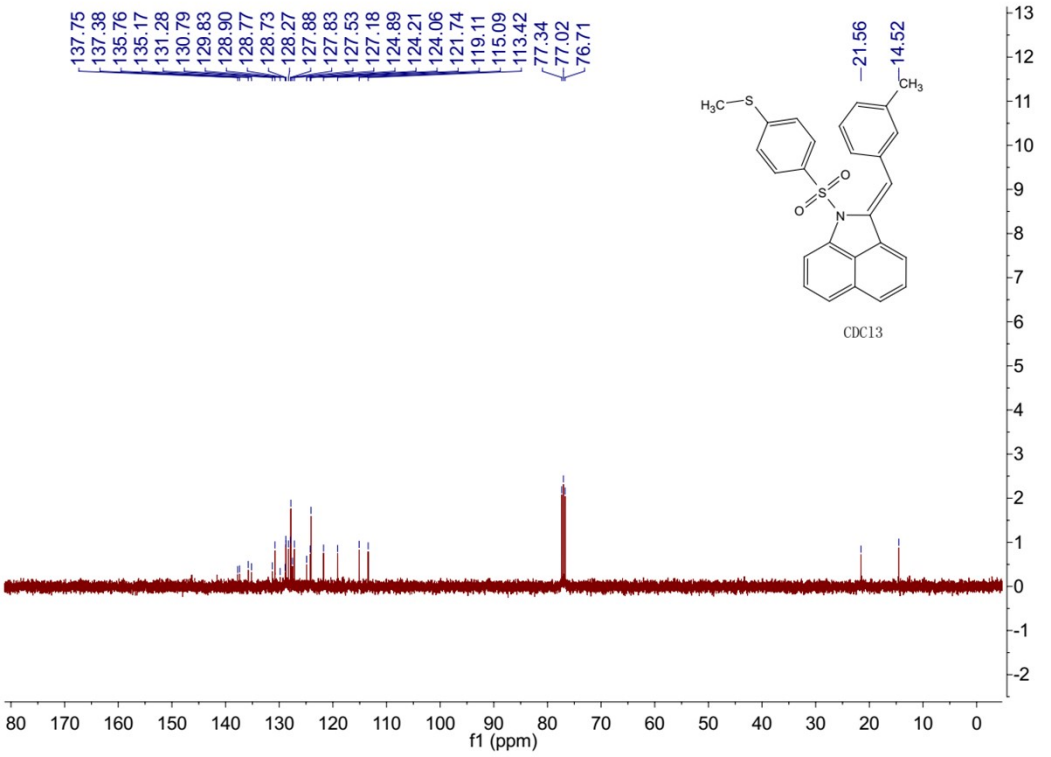

Figure S27 ^{1}H-NMR spectrum of **2n**

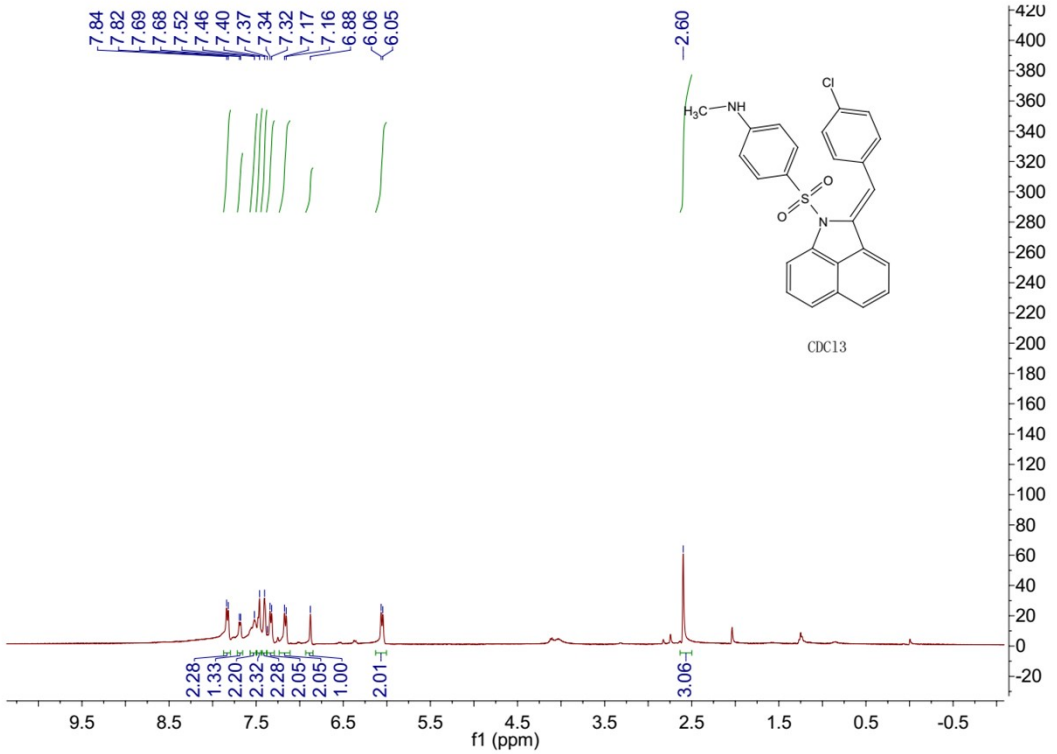

Figure S28 ^{13}C-NMR spectrum of **2n**

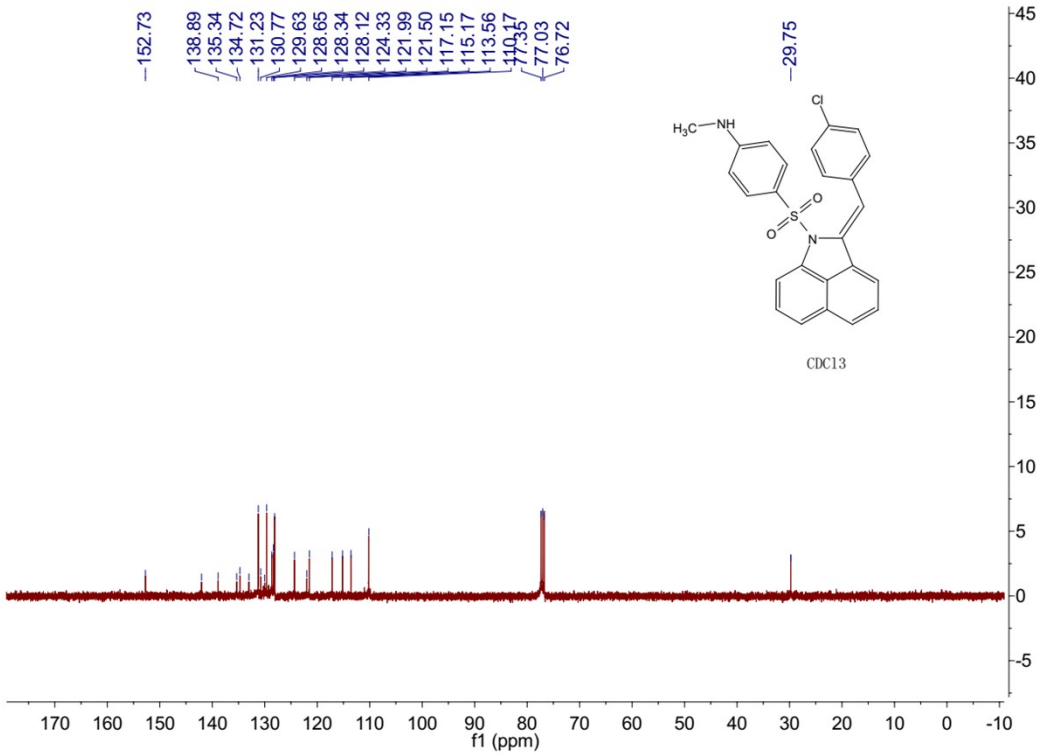

Figure S29 ^{1}H-NMR spectrum of **2o**

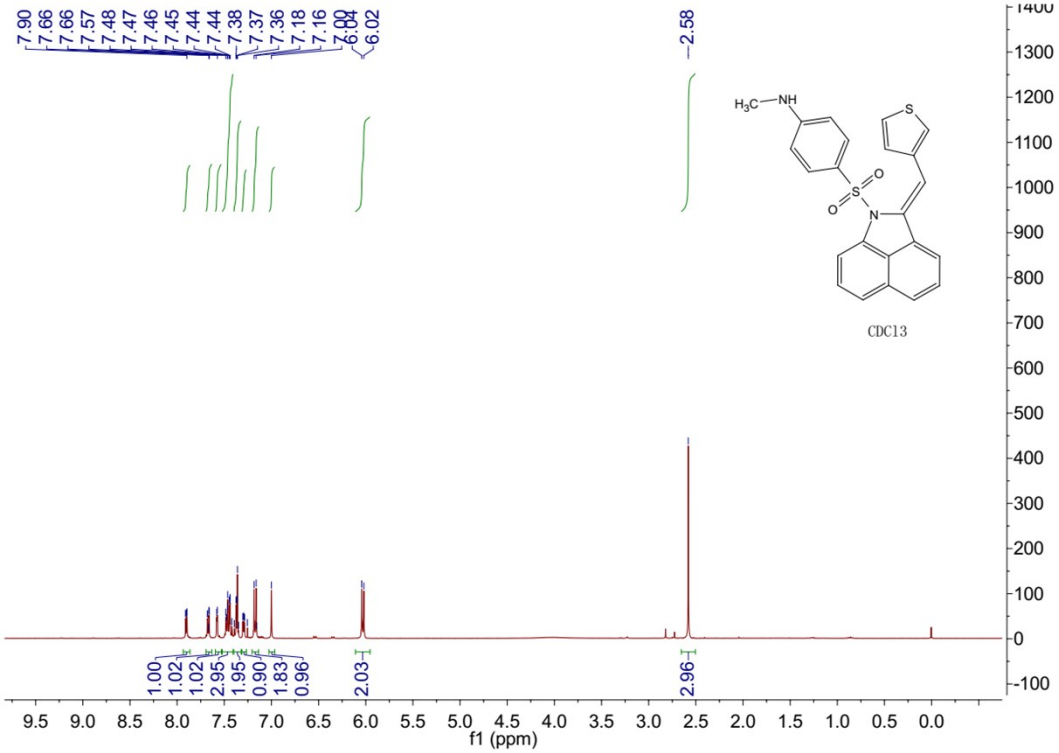

Figure S30 ^{13}C-NMR spectrum of **2o**

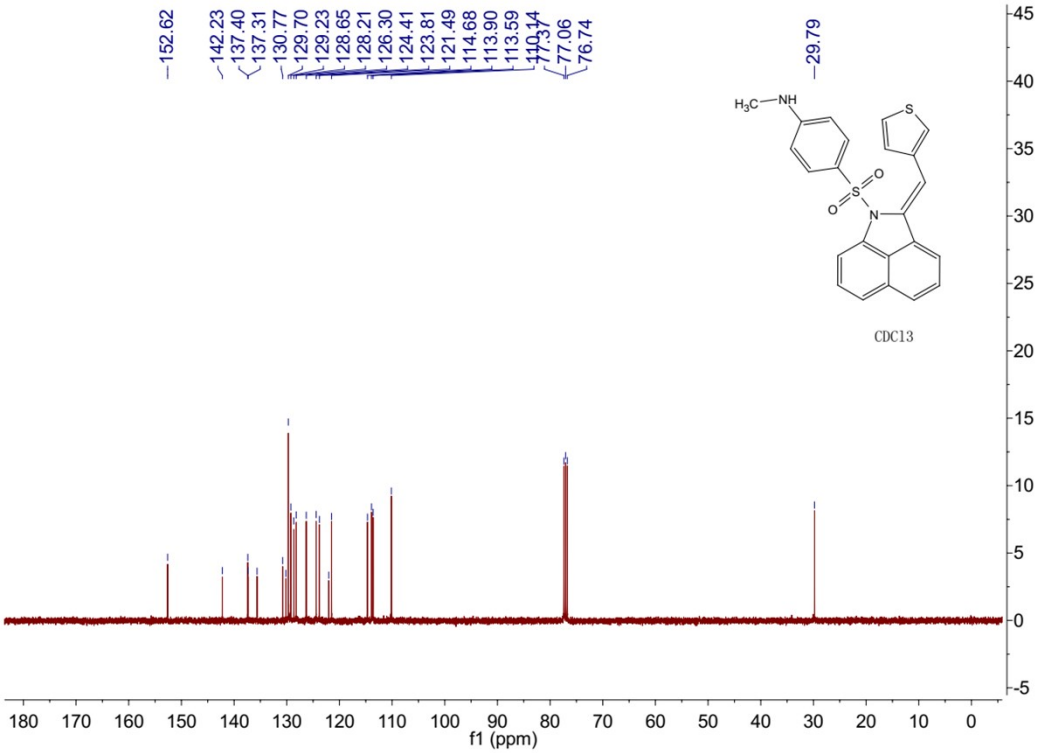

Figure S31 ^{1}H-NMR spectrum of **4**

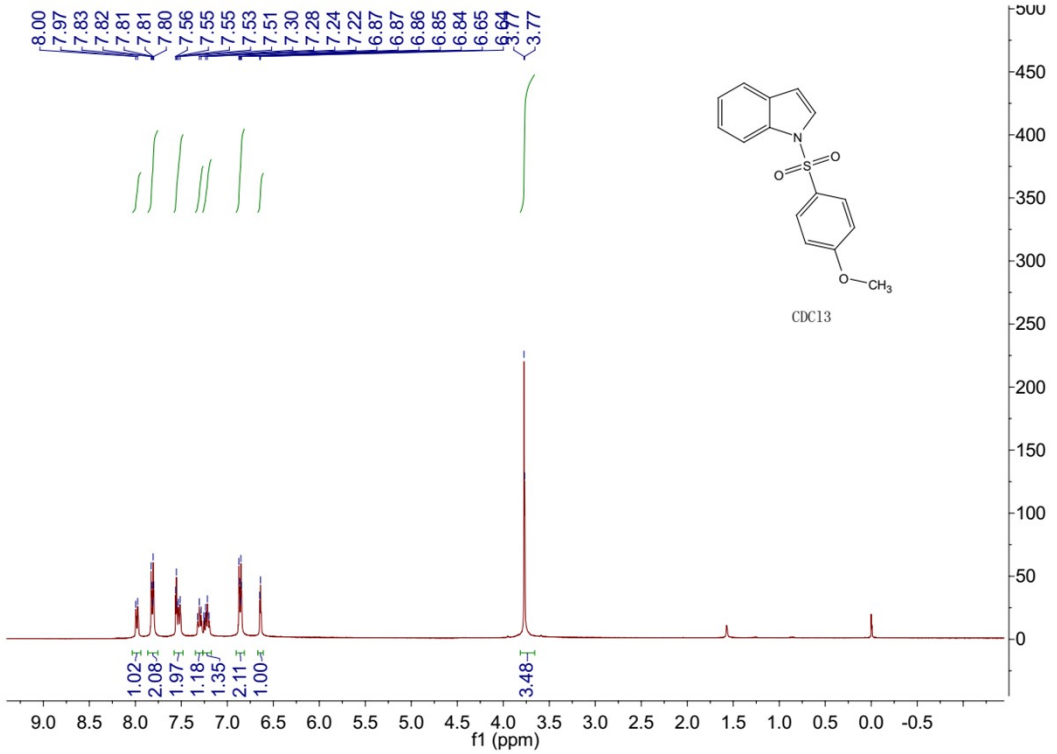

Figure S32 ^{13}C-NMR spectrum of **4**