Supporting Information

Transition Metal-free Efficient Synthesis of Bis(indolyl)propynes (BIPs)

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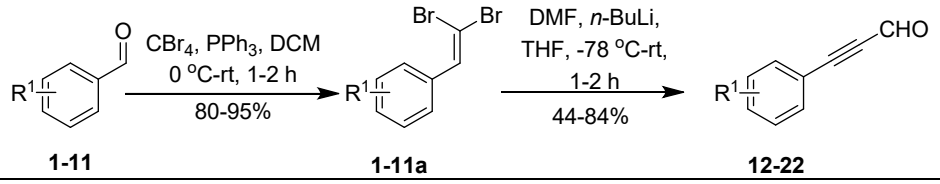
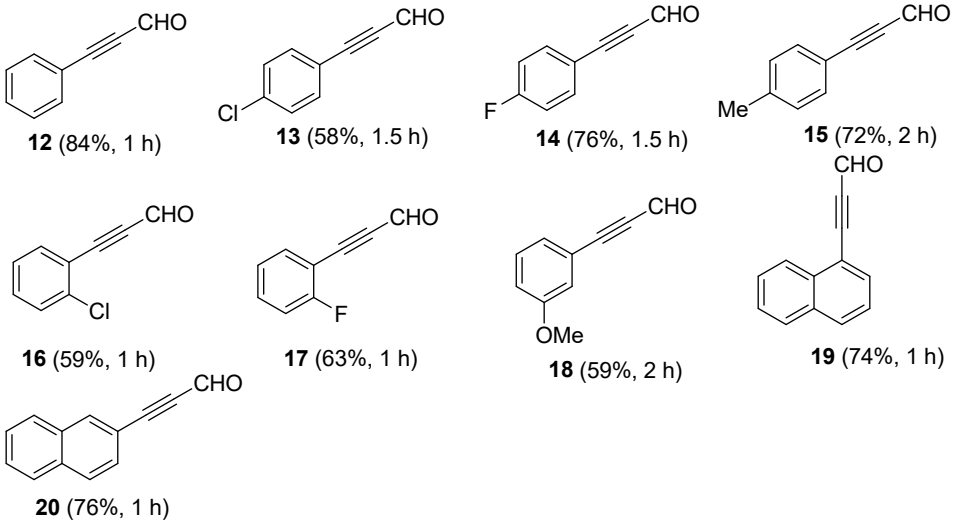
Experimental Section:

1. **Synthesis of α,β-unsaturated aromatic acetylenic aldehydes:**



1-11 **1-11a** **12-22**



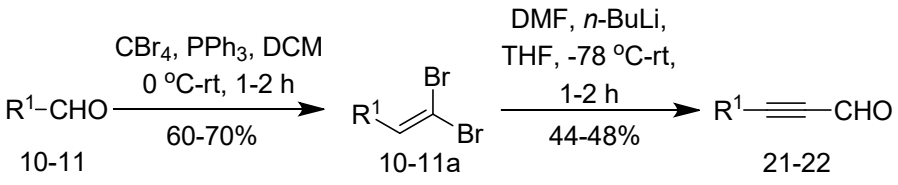
12 (84%, 1 h) **13** (58%, 1.5 h) **14** (76%, 1.5 h) **15** (72%, 2 h)

16 (59%, 1 h) **17** (63%, 1 h) **18** (59%, 2 h) **19** (74%, 1 h)

20 (76%, 1 h)

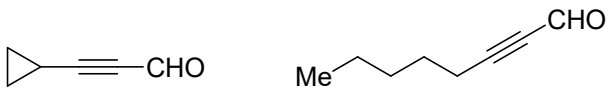
Scheme S1. Synthesis of α,β-unsaturated aromatic acetylenic aldehydes

Synthesis of α,β-unsaturated aliphatic acetylenic aldehydes:



10-11 10-11a 21-22

R^1 = cyclopropyl, hexyl



21 (44%, 1.5 h) **22** (48%, 2 h)

Scheme S2. Synthesis of α,β-unsaturated aliphatic acetylenic aldehydes:

General Procedure for the Synthesis of the intermediate *gem*-dibromolefins 1a:

Under an atmosphere of argon, a solution of triphenylphosphine (3 eq., 0.141 mol) and tetrabromomethane (1.5 eq., 0.071 mol) in anhydrous DCM was stirred at 0 °C for 30 minutes. The aldehyde (**1**, 1.0 eq., 0.047 mol) was added over a period of five minutes and the mixture as stirred at 0 °C for one hour. After addition of water, the layers were separated, and the aqueous layer was extracted with DCM (3 x 100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with 100% hexane as the eluent to afford the intermediate *gem*-dibromolefins **1a** with 95% yield.

Procedure for the synthesis of α,β-unsaturated acetylenic aldehydes 12:

Under an atmosphere of argon, n-BuLi (14.4 mL, 1.2 eq., 1.6 M in *n*-hexane) was added over a period of 30 minutes via syringe pump to a solution of *gem*-dibromoolefine (**1a**, 5.0 g, 1.0 eq.) in anhydrous THF at −78 °C, and the mixture was stirred at −40 °C for 15 minutes. After addition of DMF (3 mL, 2.0 eq.) in one lot, the mixture was allowed to warm to room temperature and stirred for one hour. The mixture was added to a stirring solution of KH_2PO_4 (aq.)/diethyl ether (1:1). After five minutes, the layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure and the crude product was subjected to column chromatography (hexane/EtOAc, 99:1, v/v) to obtain 3-phenylpropiolaldehyde (**12**) in 84% yield.

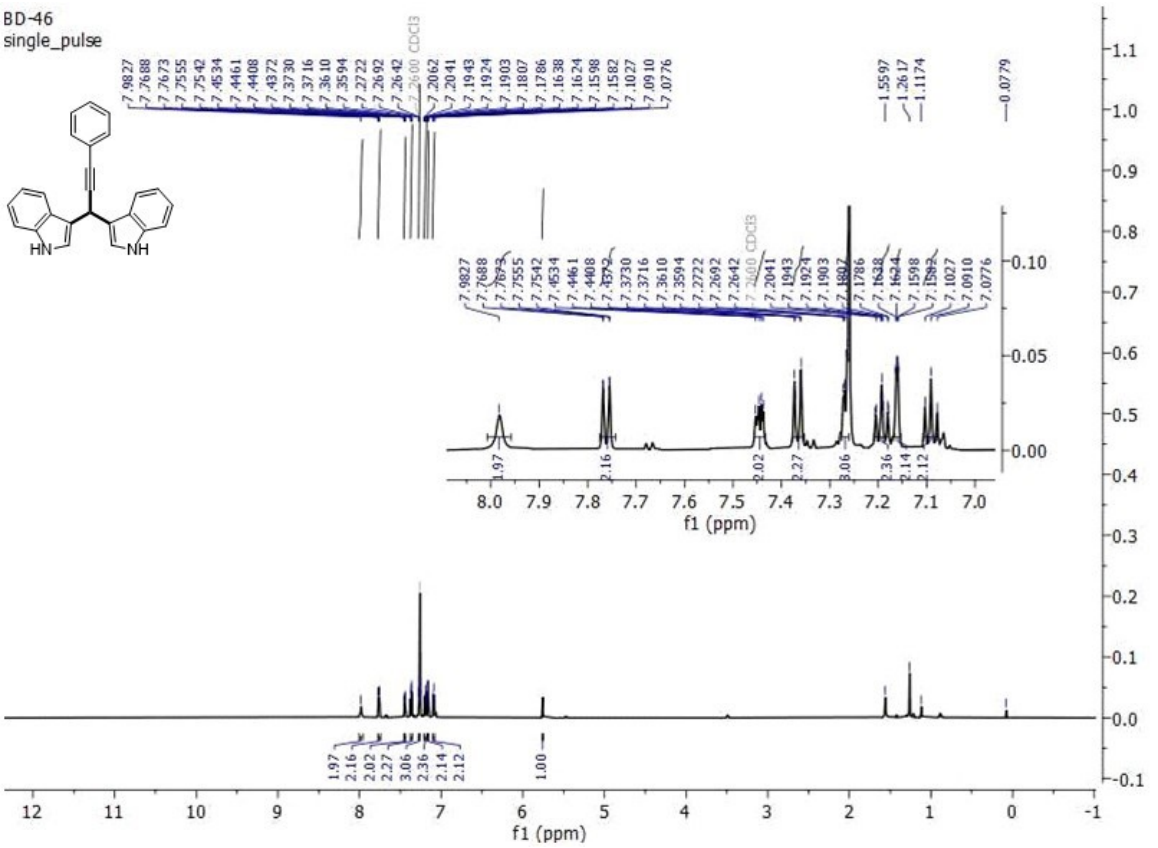


Fig. S1. ^{1}H-NMR spectrum of **12a** in $CDCl_3$.

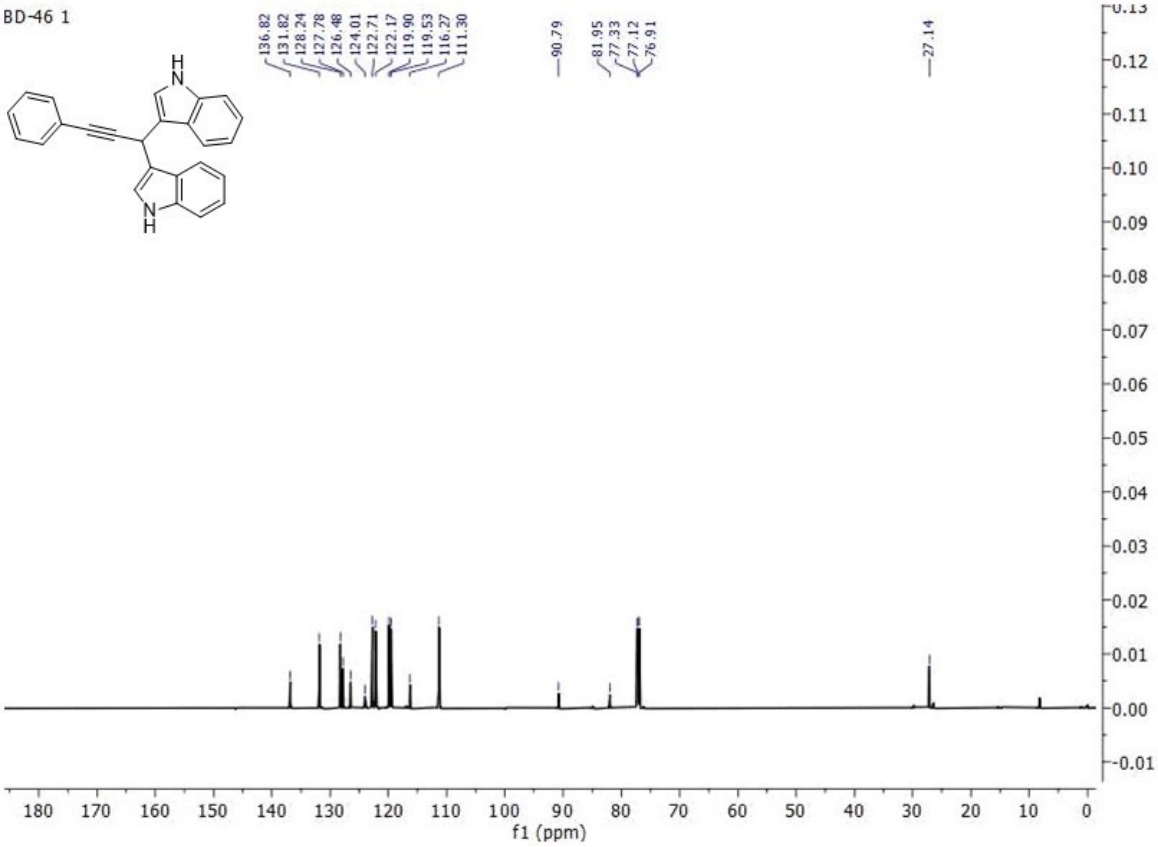


Figure S2 ^{13}C-NMR spectrum of **12a** in $CDCl_3$.

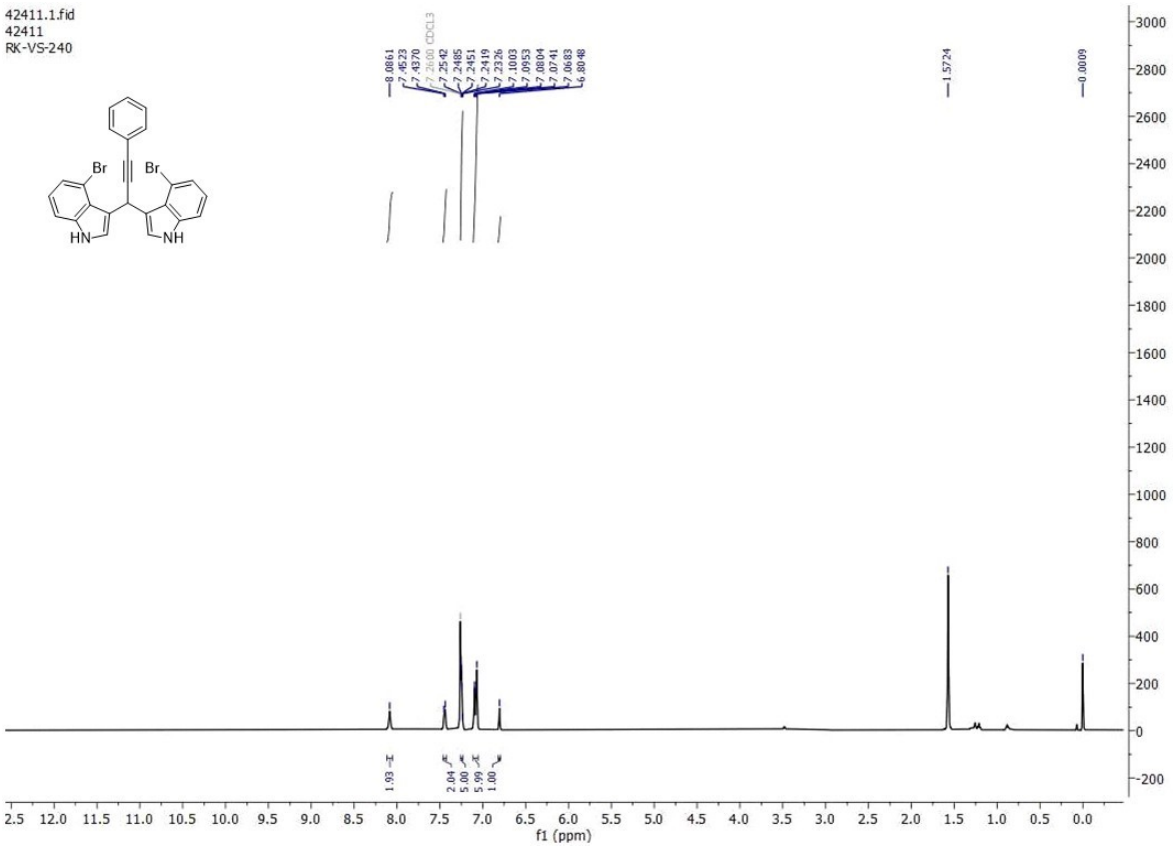


Figure S3 ^{1}H-NMR spectrum of **12b** in $CDCl_3$.

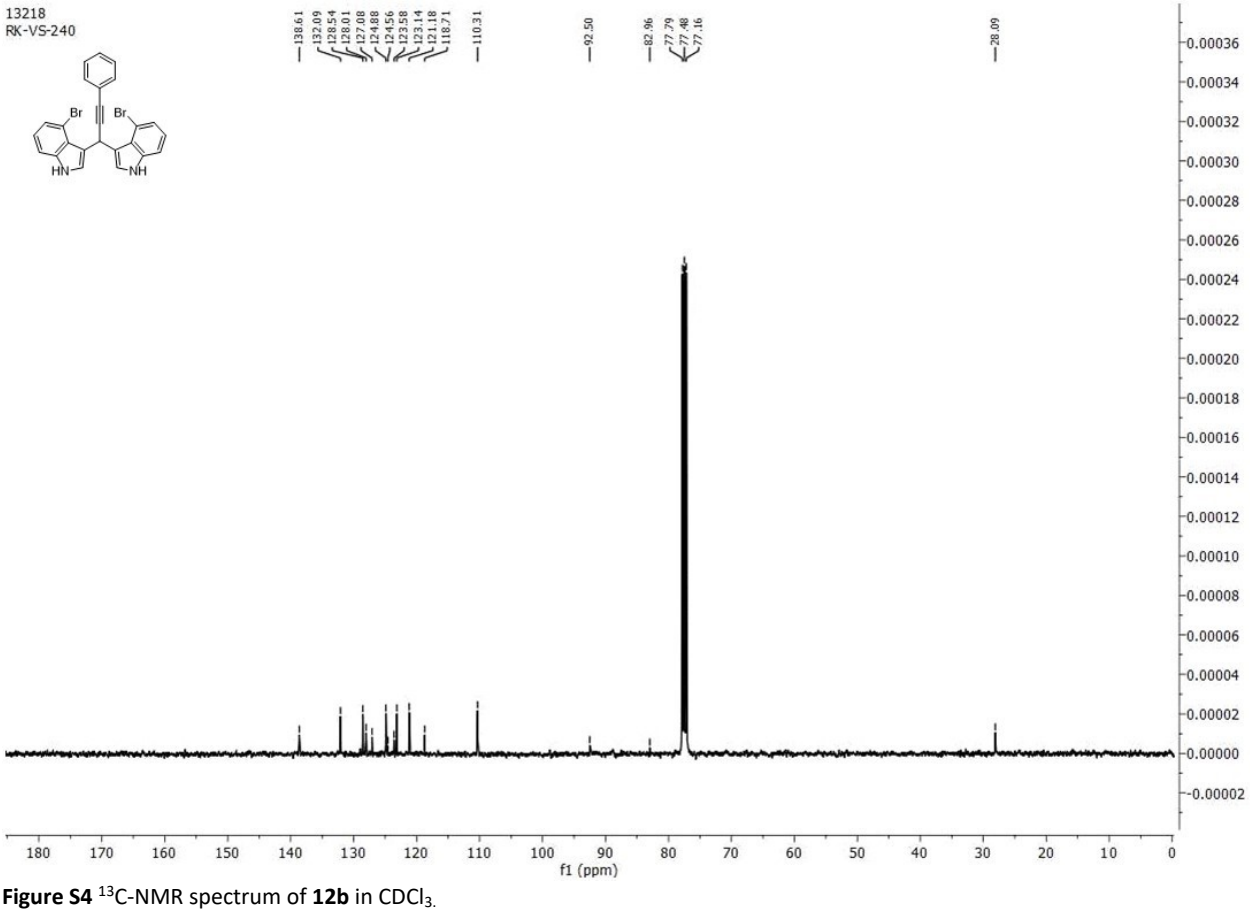


Figure S4 ^{13}C-NMR spectrum of **12b** in $CDCl_3$.

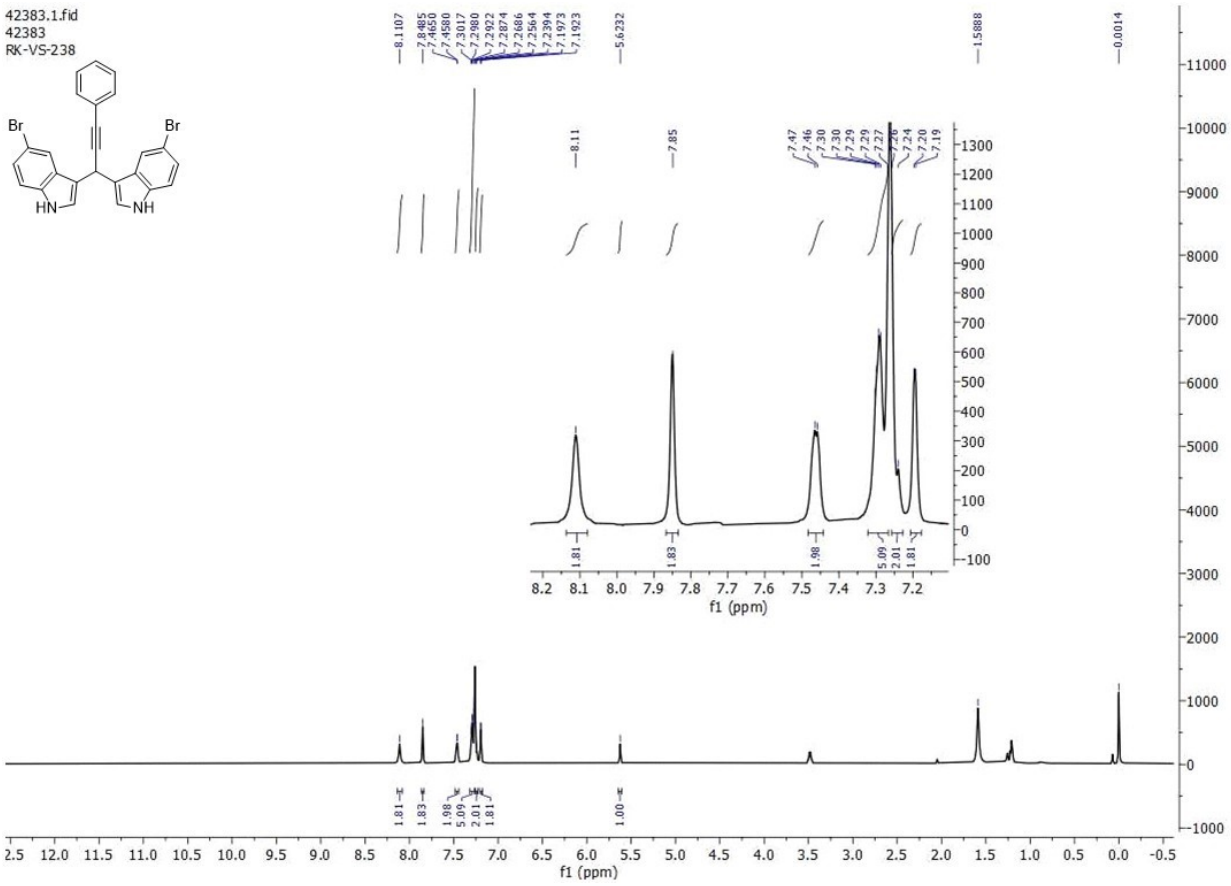


Figure.S5 ^{1}H-NMR spectrum of **12c** in $CDCl_3$.

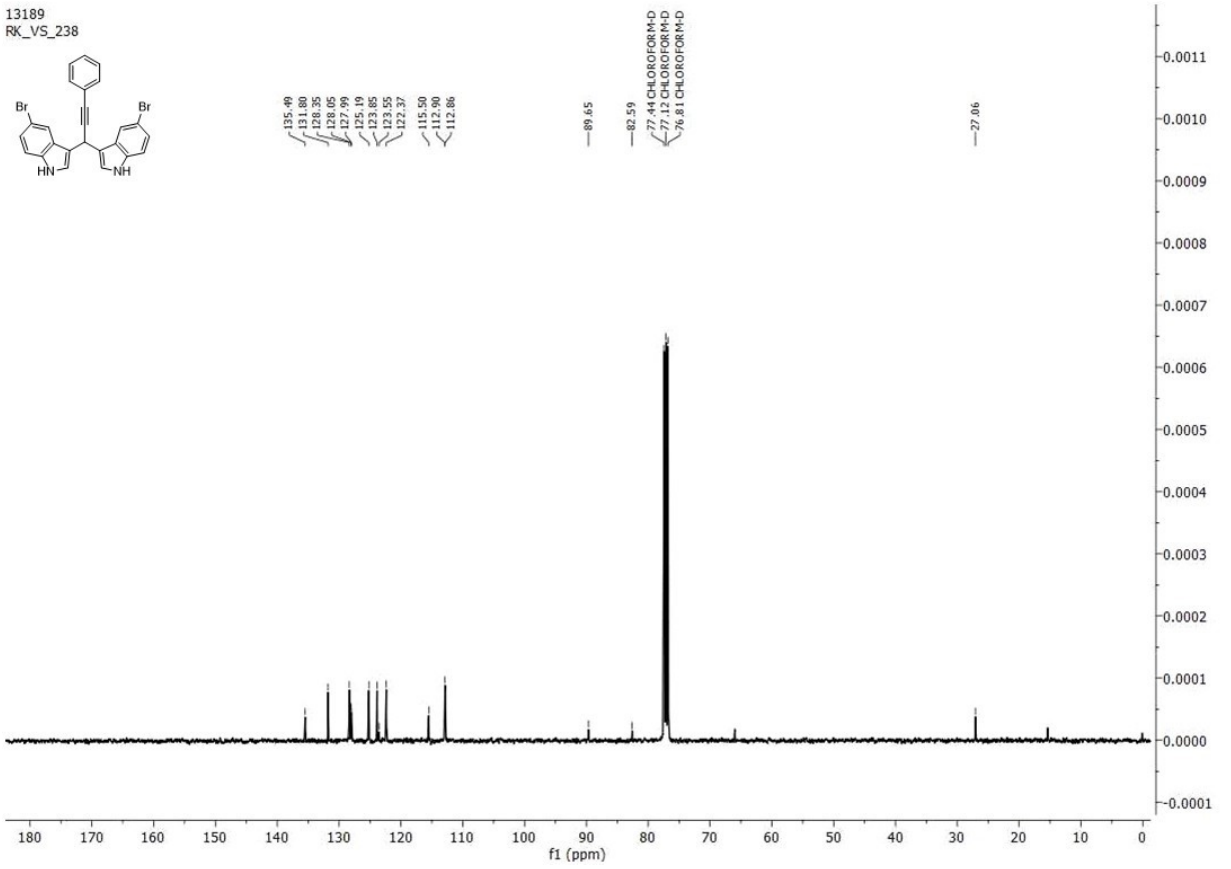


Figure.S6 ^{13}C-NMR spectrum of **12c** in $CDCl_3$.

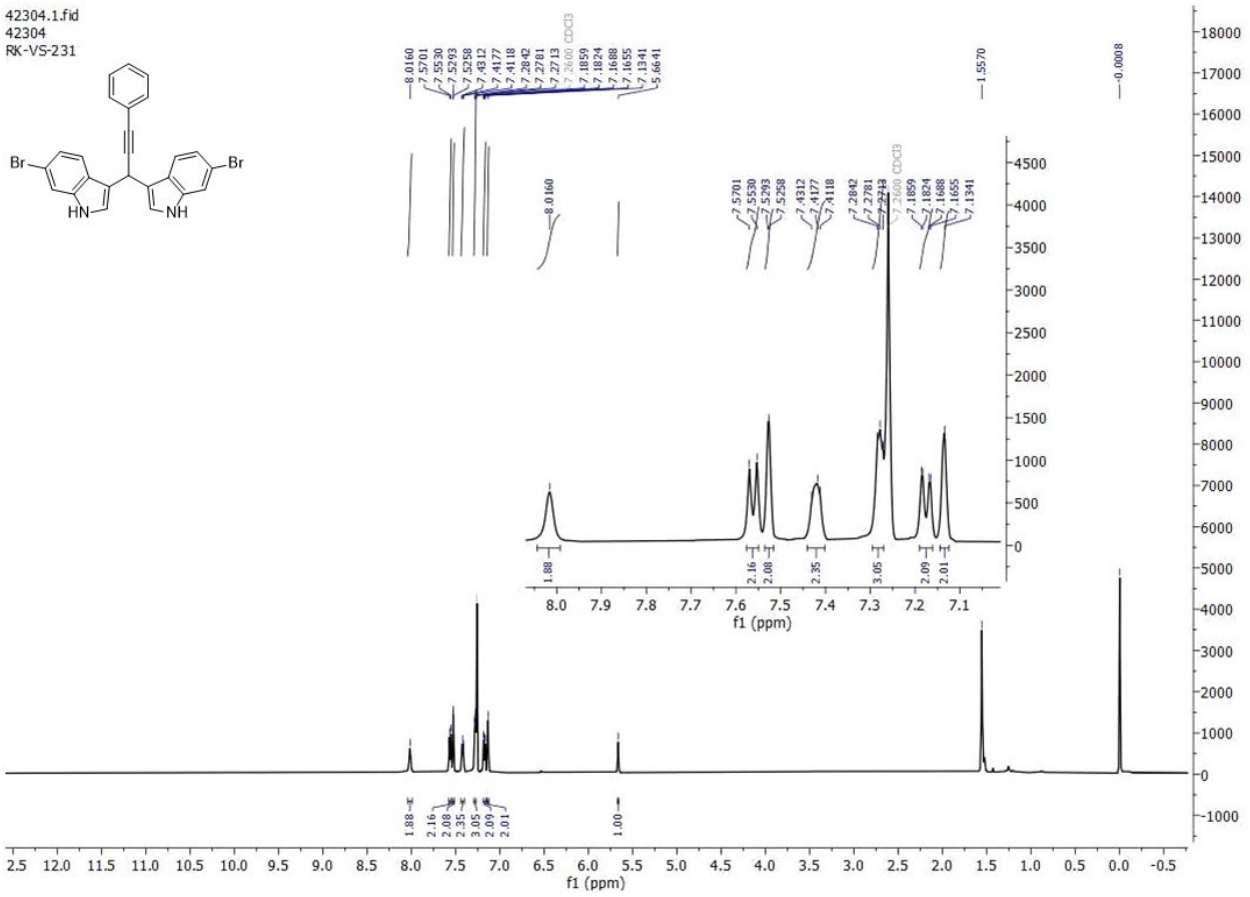


Figure.S7. ^{1}H-NMR spectrum of **12d** in $CDCl_3$.

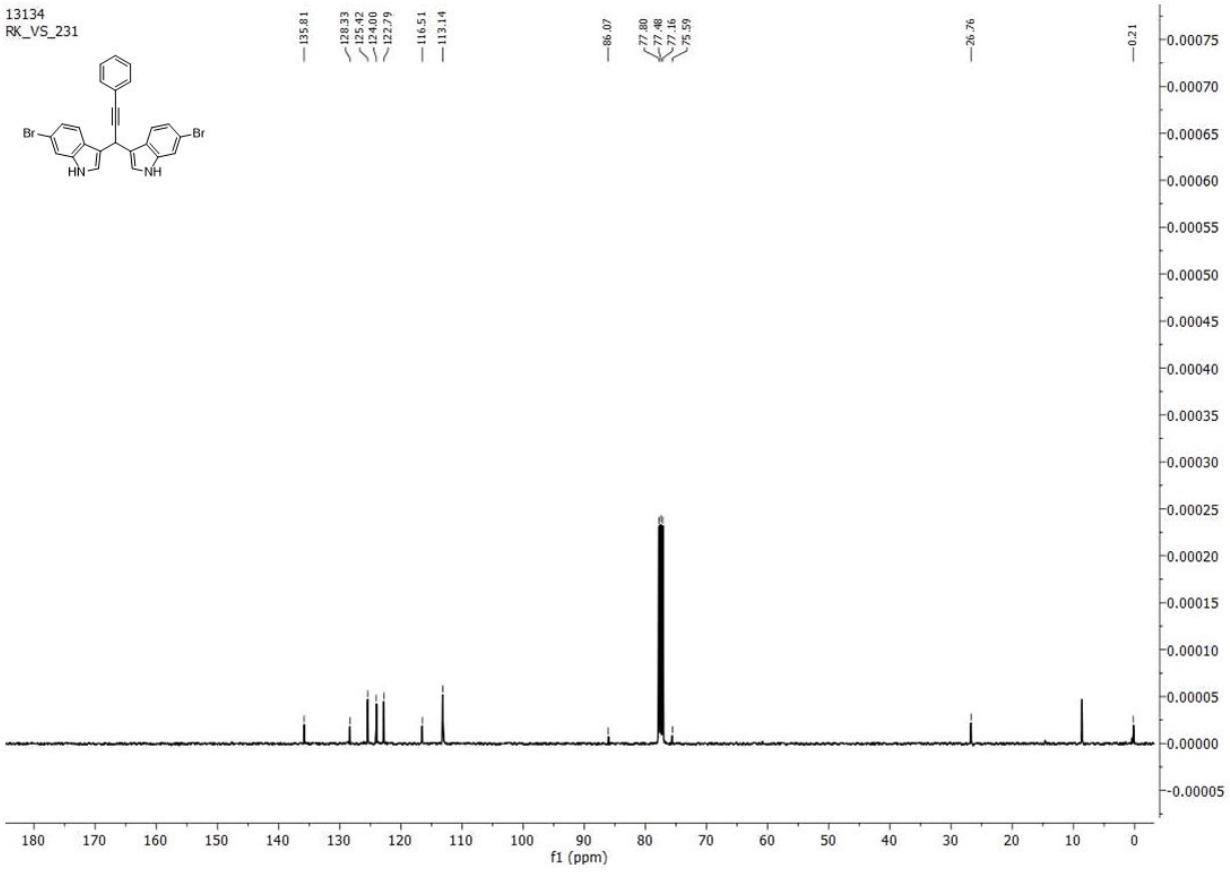


Figure.S8 ^{13}C-NMR spectrum of **12d** in $CDCl_3$.

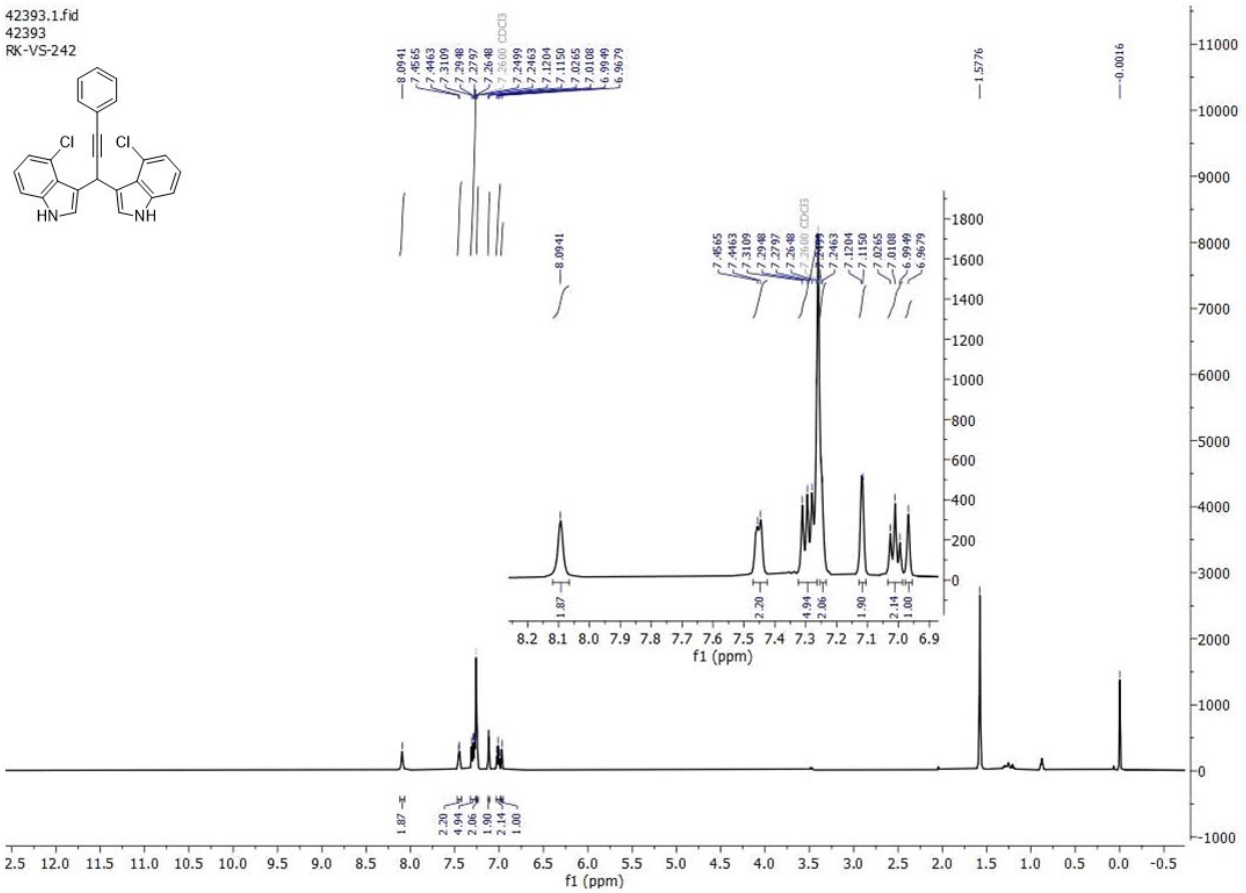


Figure S9 ^{1}H-NMR spectrum of **12e** in $CDCl_3$.

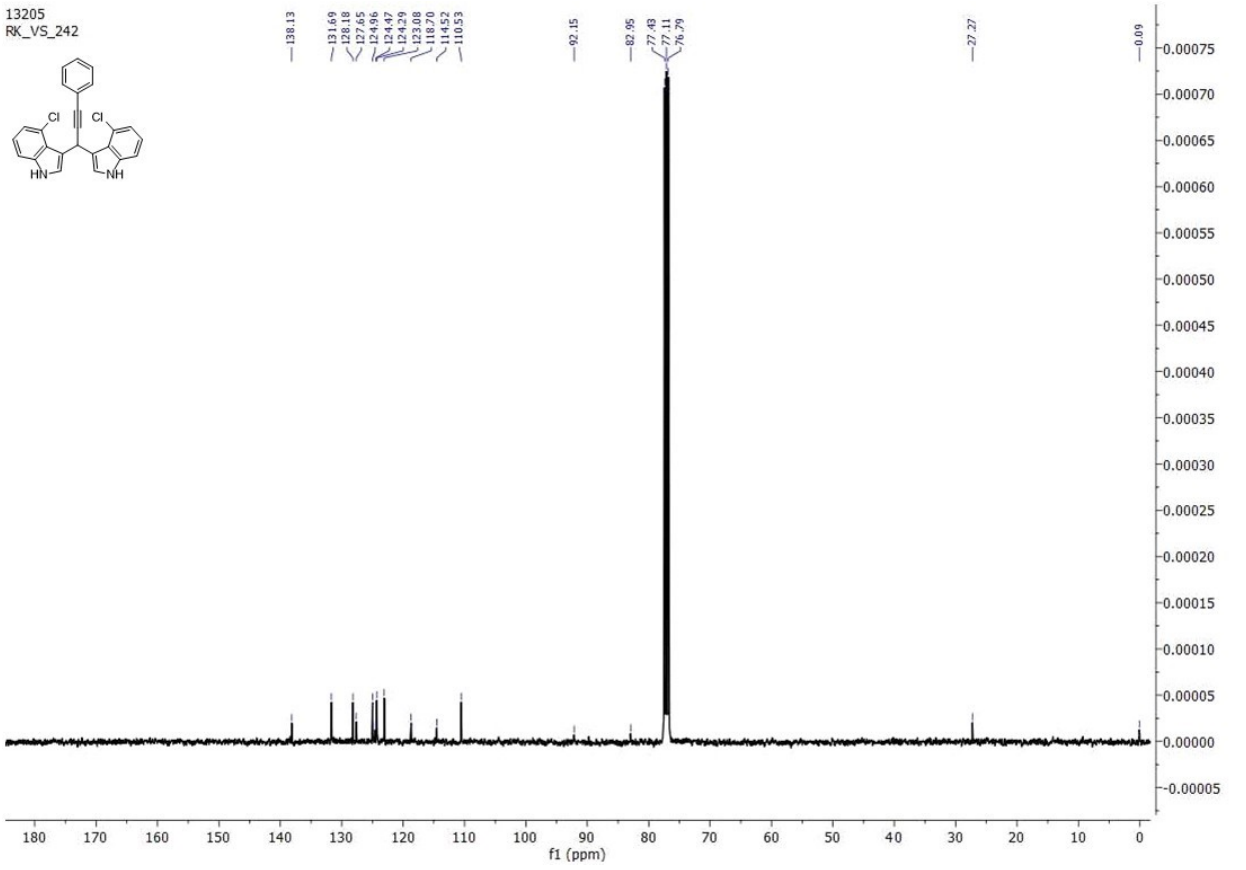


Figure S10 ^{13}C-NMR of spectrum **12e** in $CDCl_3$.

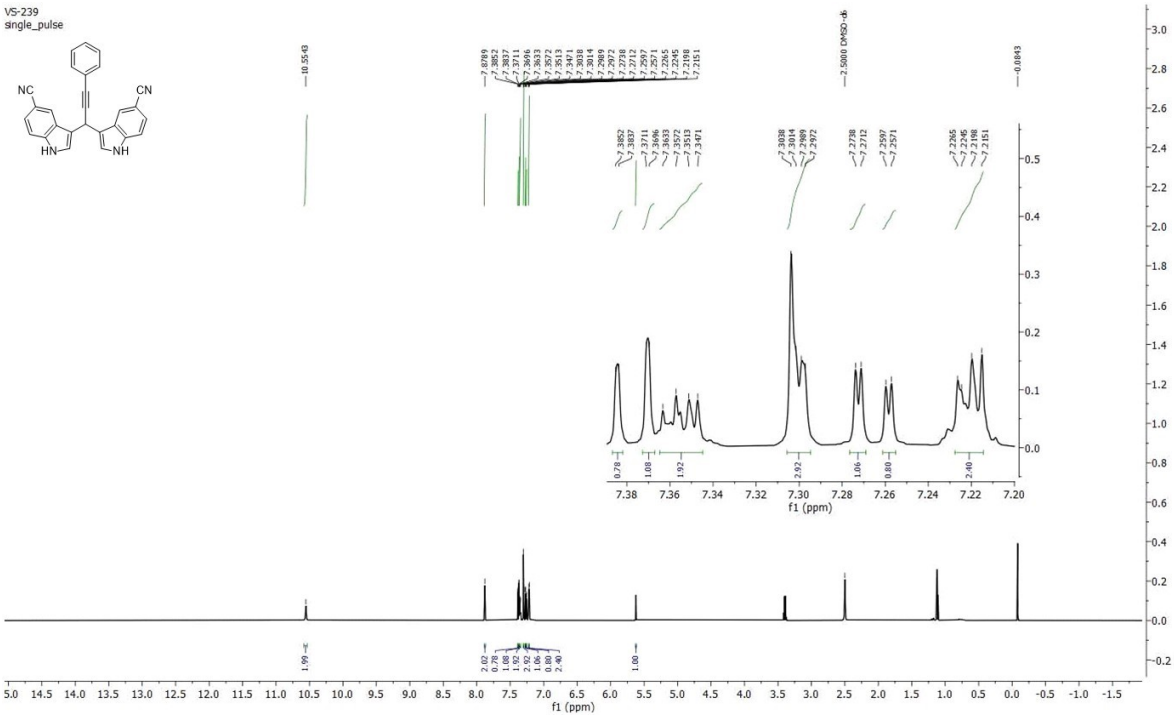


Figure S11 ^{1}H-NMR spectrum of **12f** in $CDCl_3$. ^{13}C-NMR Could not be recorded due to solubility problem.

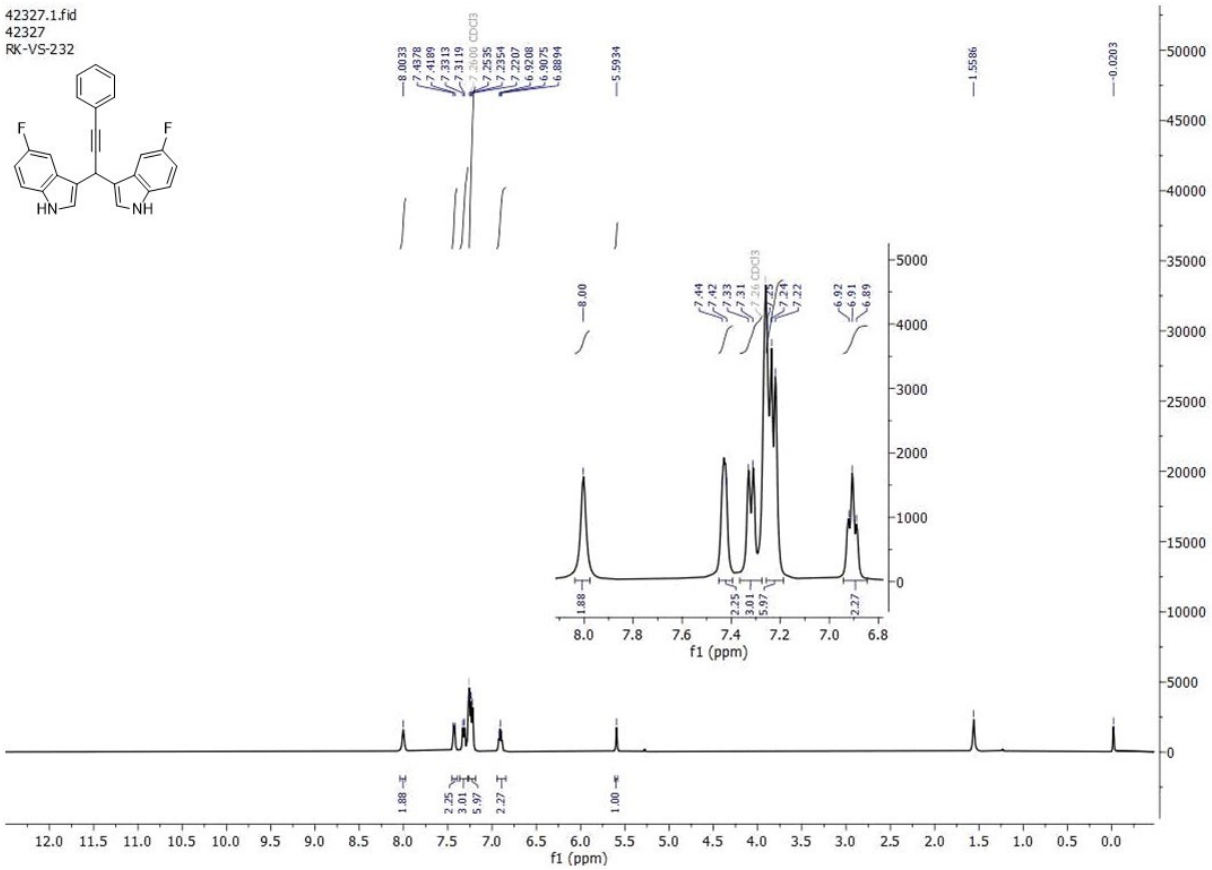


Figure S12 ^{1}H-NMR spectrum of **12h** in $CDCl_3$.

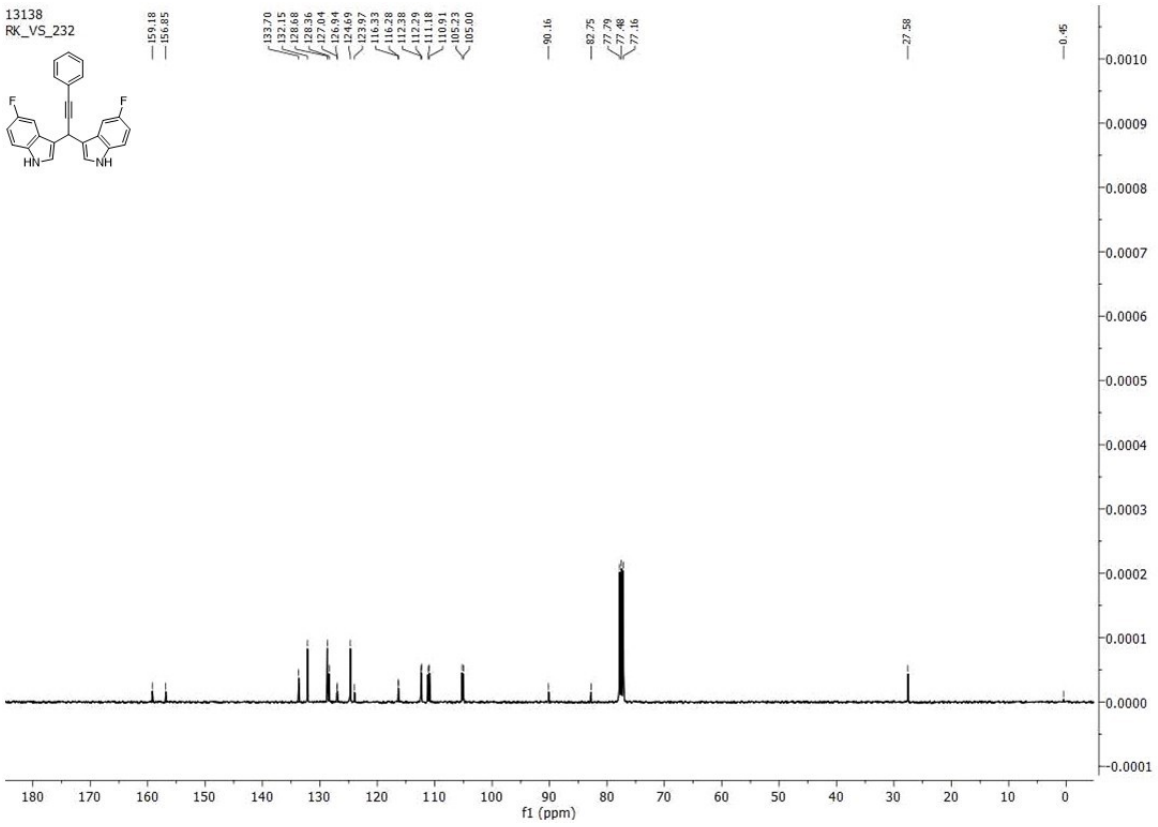


Fig ure S13 ^{13}C-NMR spectrum of **12h** in $CDCl_3$.

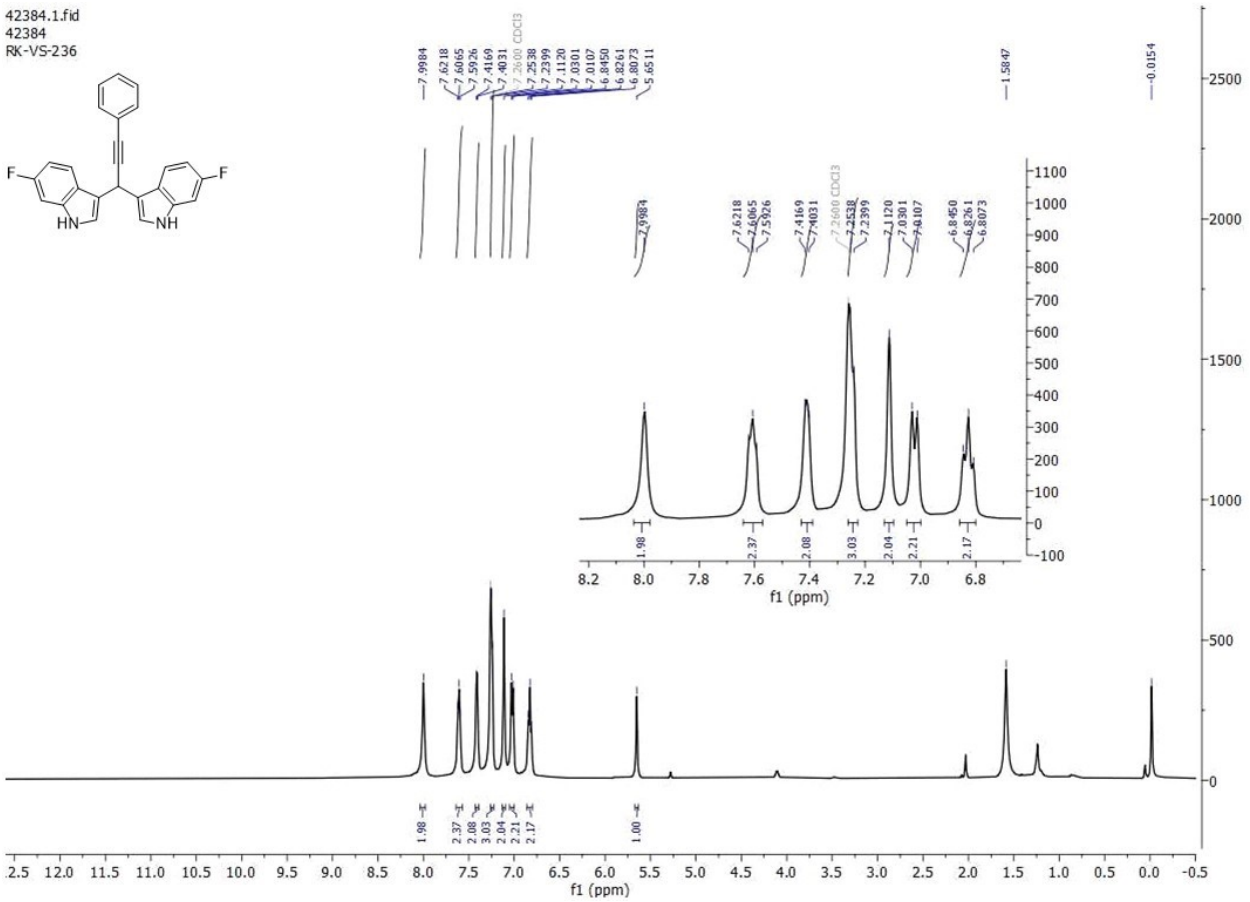


Figure S14 ^{1}H-NMR spectrum of **12i** in $CDCl_3$.

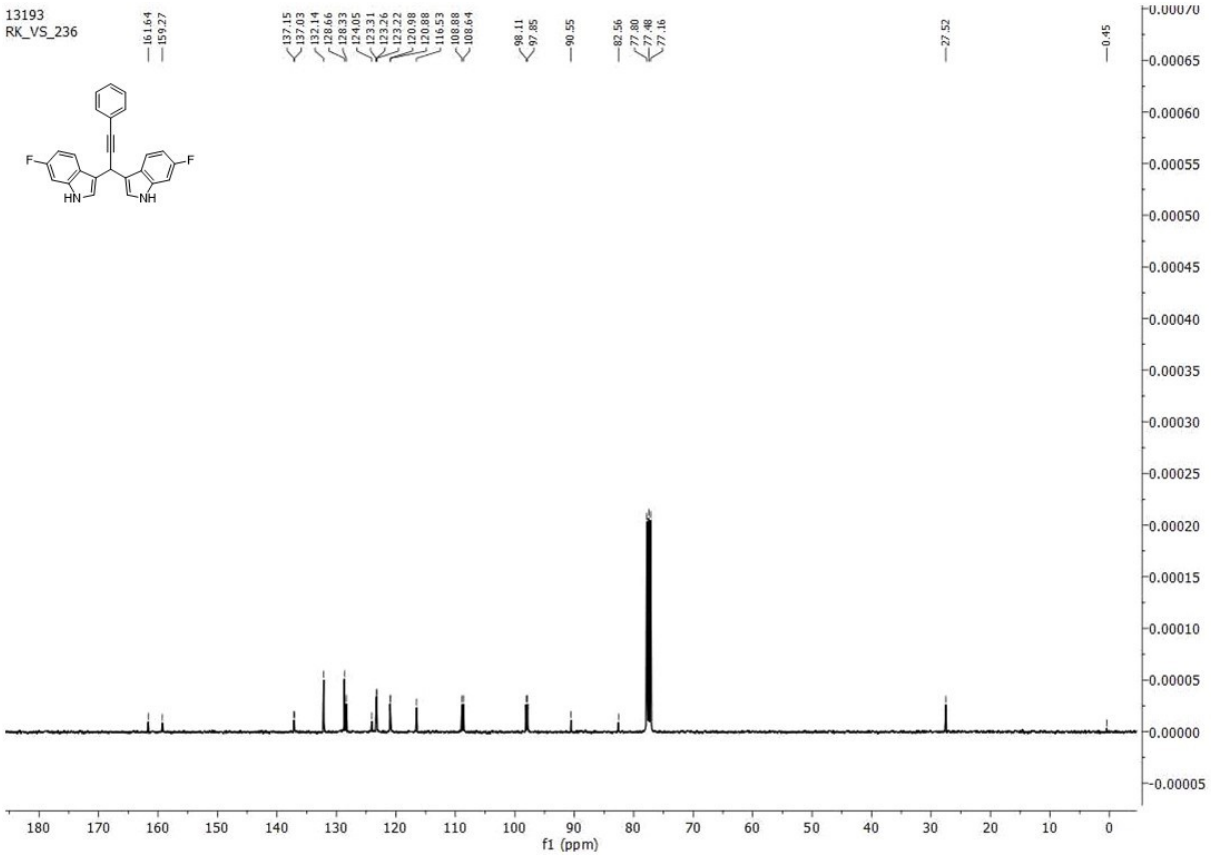


Figure S15 ^{13}C-NMR spectrum of **12i** in $CDCl_3$.

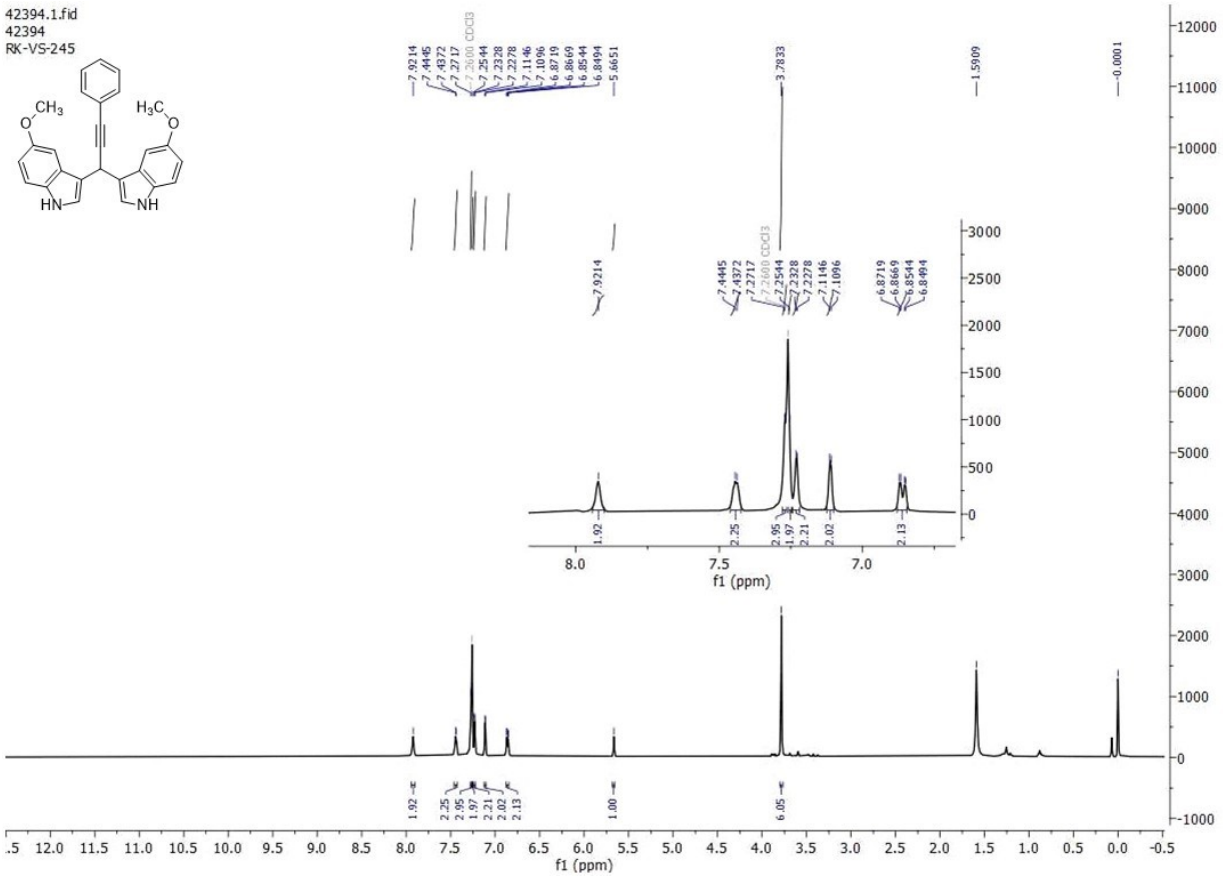


Figure S16 ^{1}H-NMR spectrum of **12j** in $CDCl_3$.

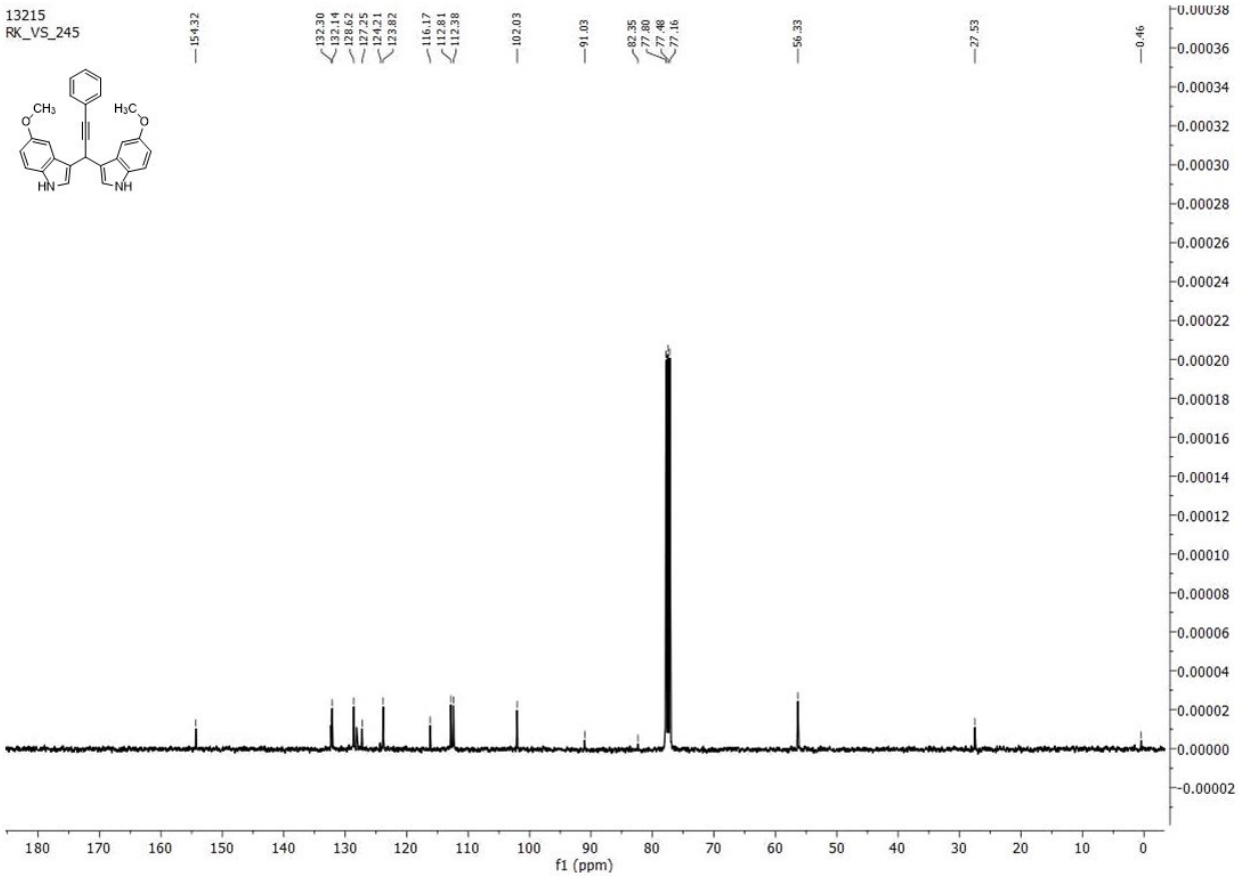


Figure S17 ^{13}C-NMR spectrum of **12j** in $CDCl_3$.

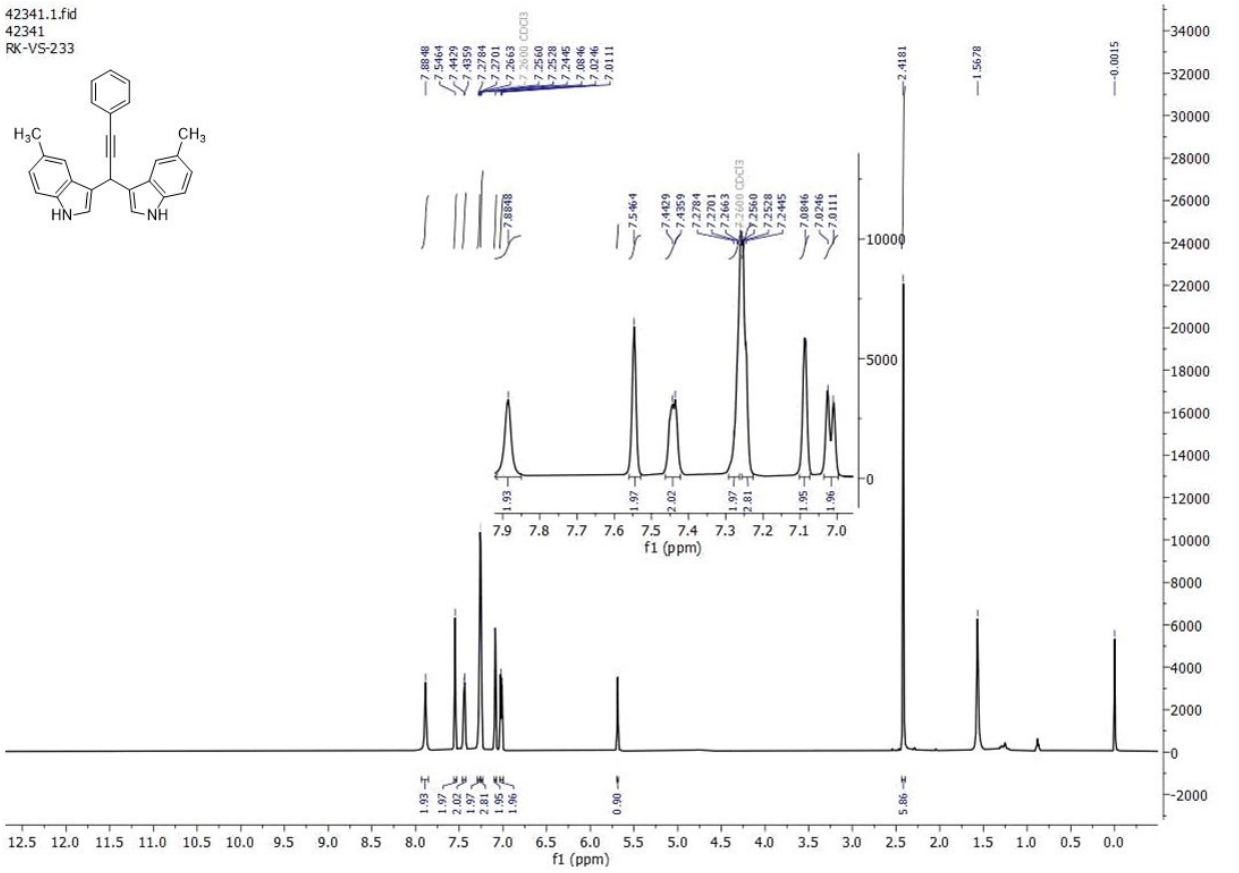


Figure S18 ^{1}H-NMR spectrum of **12k** in $CDCl_3$.

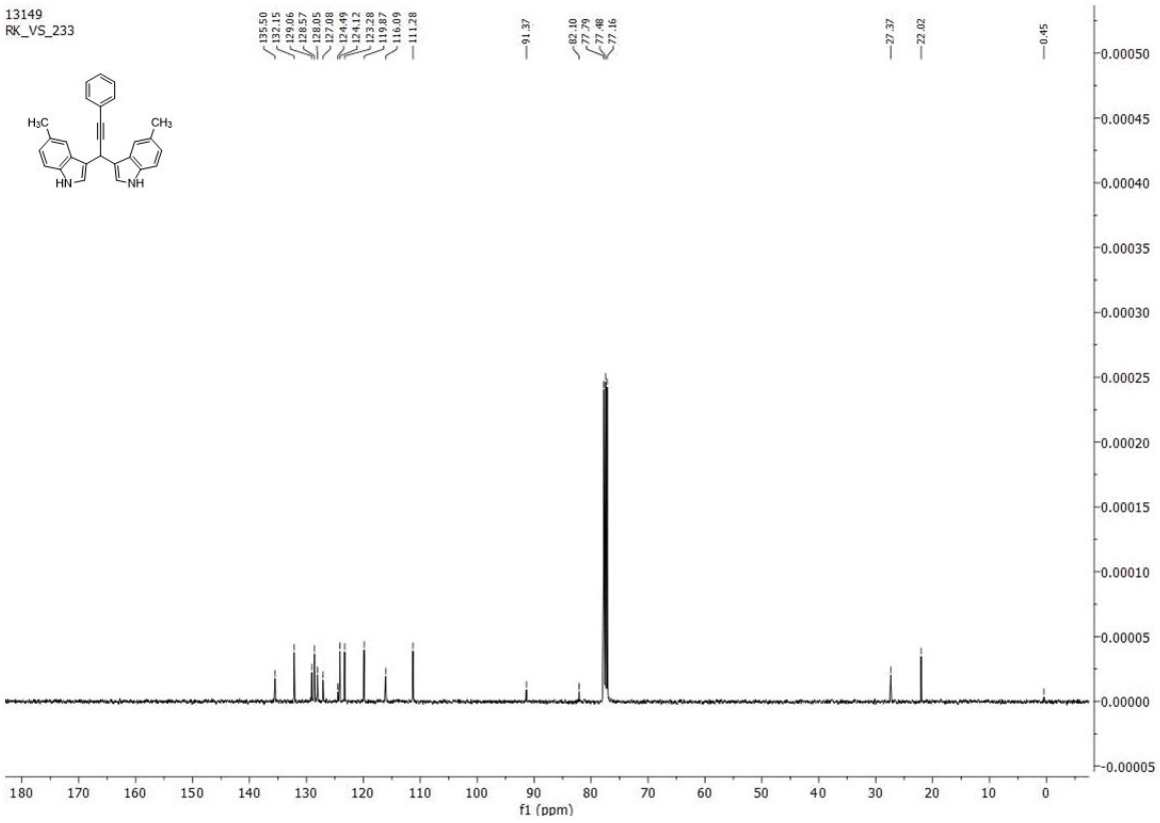


Figure S19 ^{1}H-NMR spectrum of **12k** in $CDCl_3$.

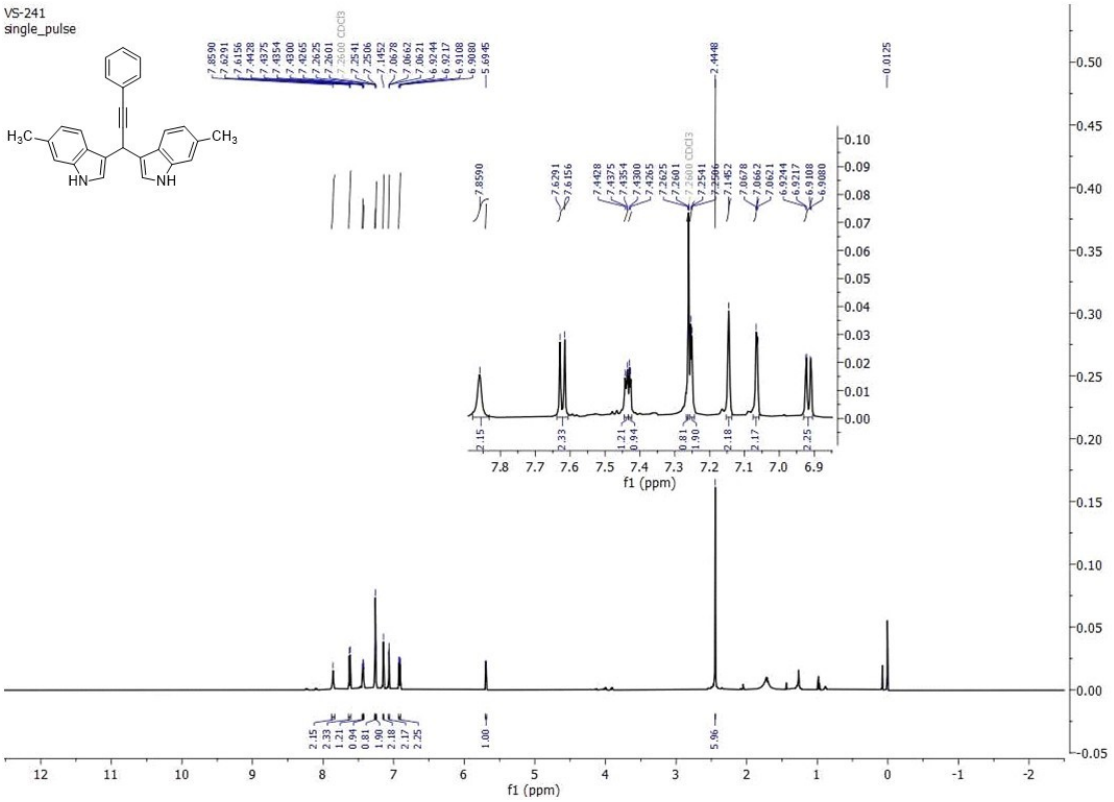


Figure S20 ^{1}H-NMR spectrum of **12l** in $CDCl_3$.

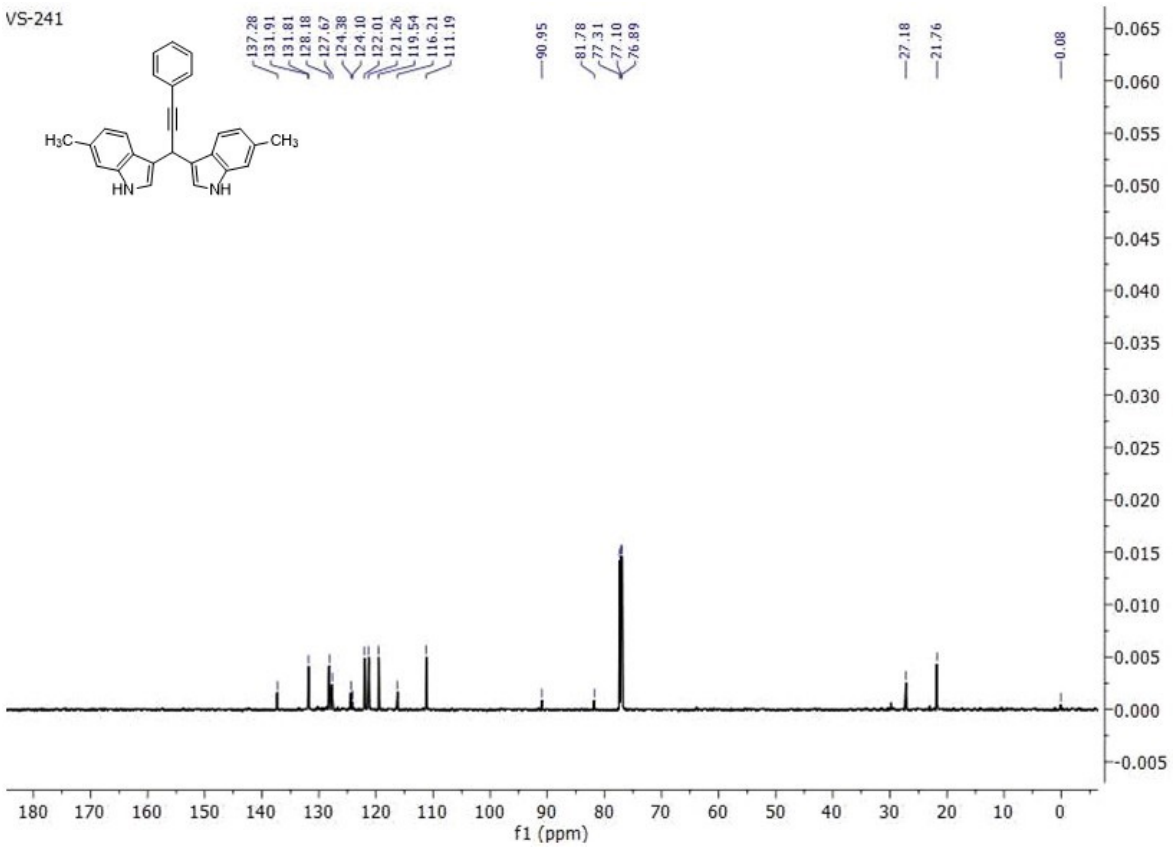


Figure S21 ^{13}C-NMR spectrum of **12l** in $CDCl_3$.

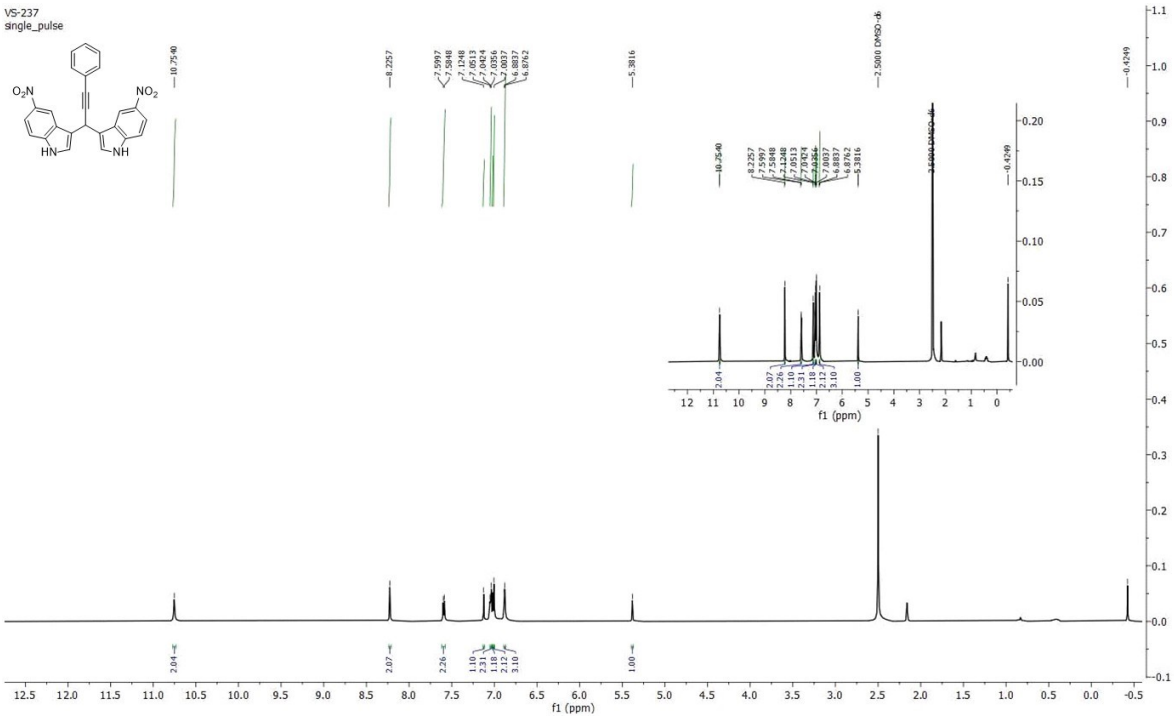


Figure S22 ^{1}H-NMR spectrum of **12n** in $CDCl_3$ ^{13}C-NMR Could not be recorded due to solubility problem.

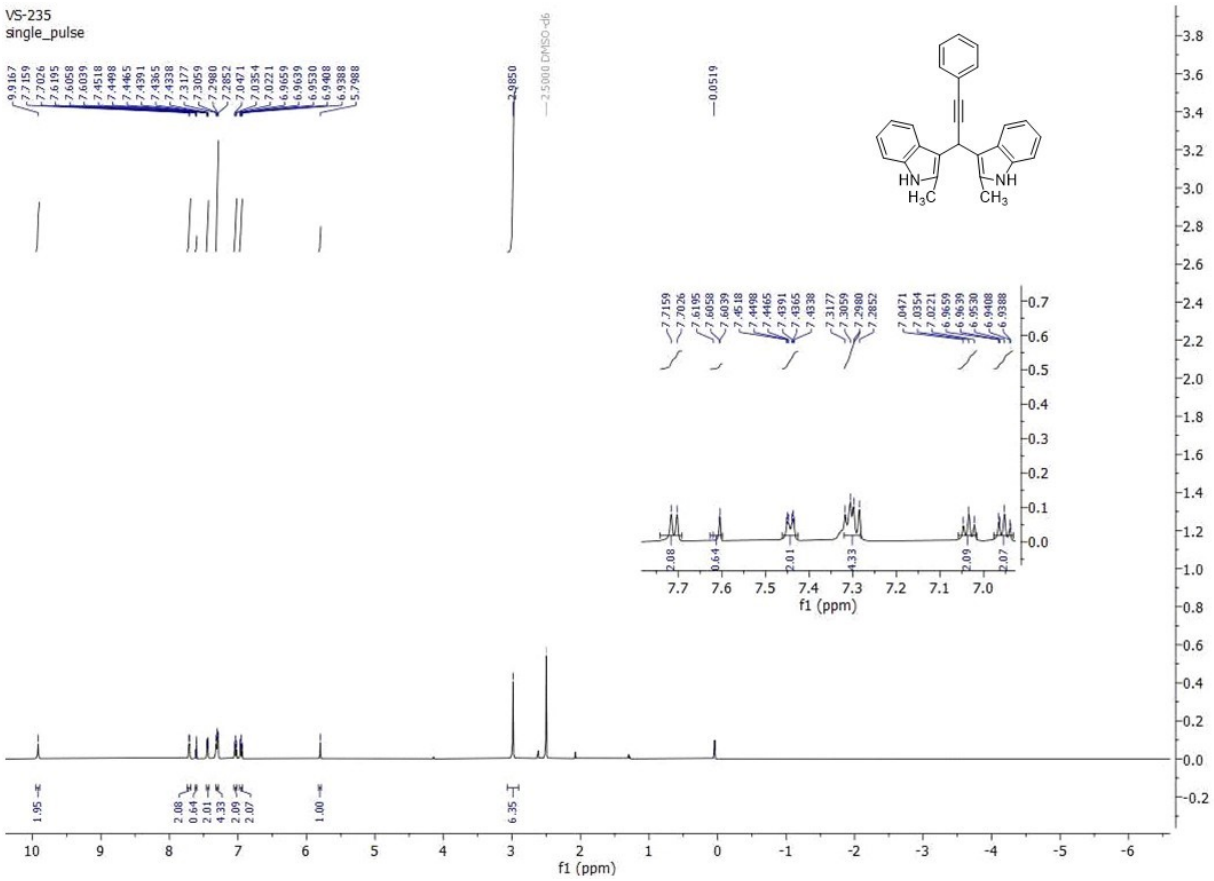


Figure S23 ^{1}H-NMR spectrum of **12o** in $CDCl_3$ + DMSO-d_6

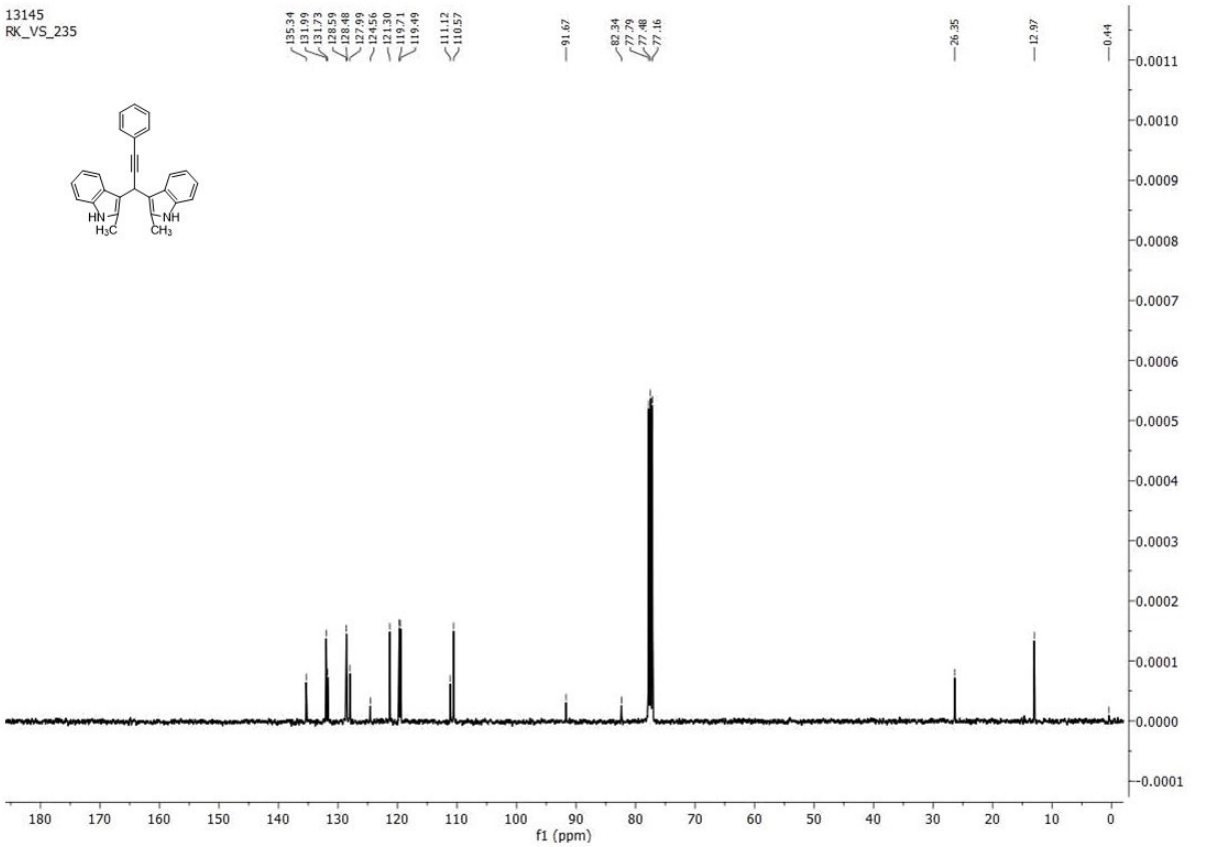


Figure S24 ^{13}C-NMR spectrum of **12o** in $CDCl_3$.

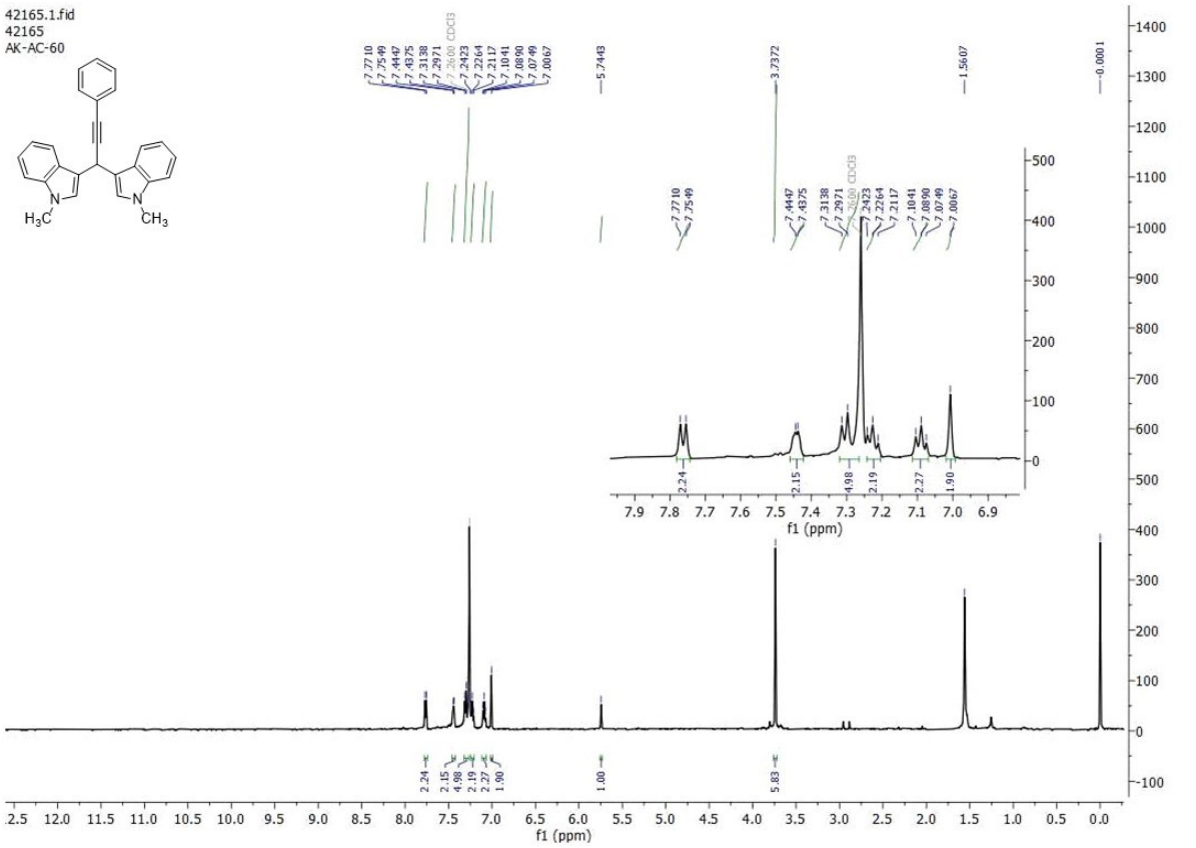


Figure S25 ^{1}H-NMR spectrum of **12p** in $CDCl_3$.

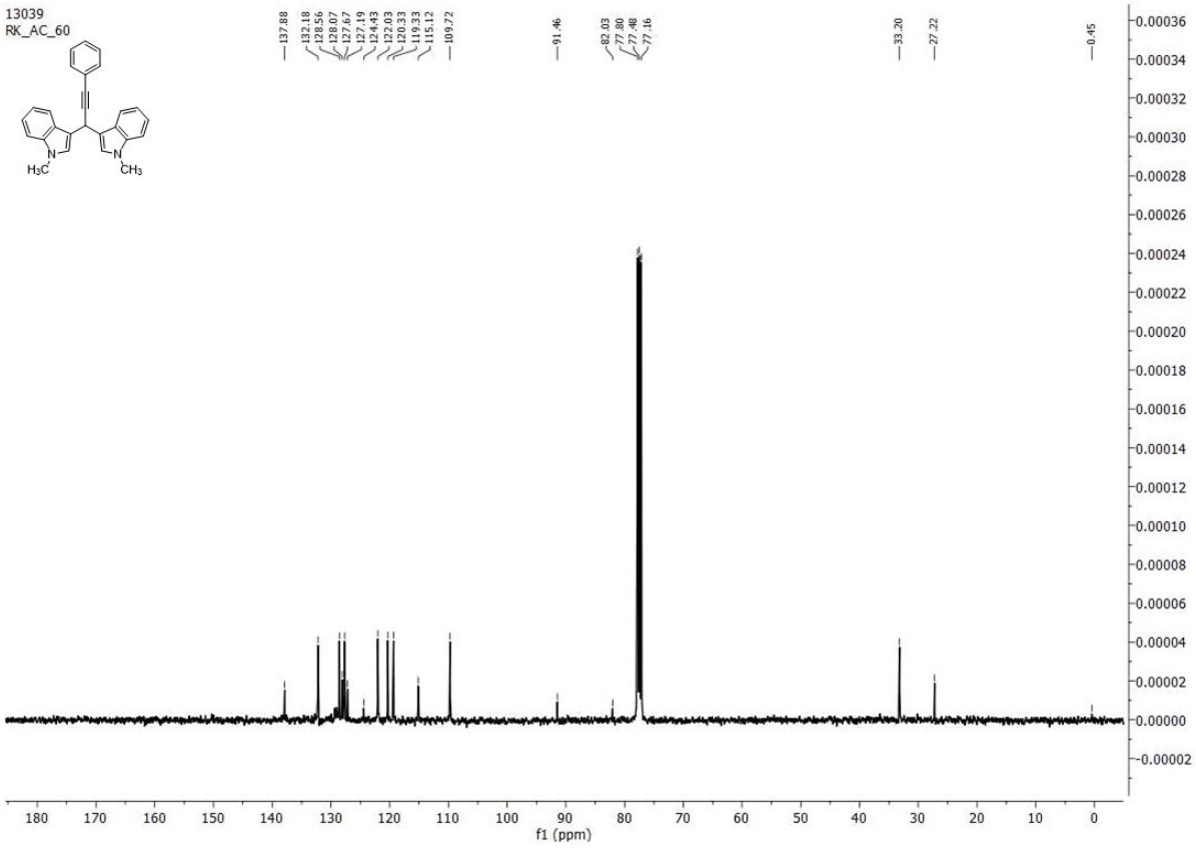


Figure S26 ^{13}C-NMR of spectrum **12p** in $CDCl_3$.

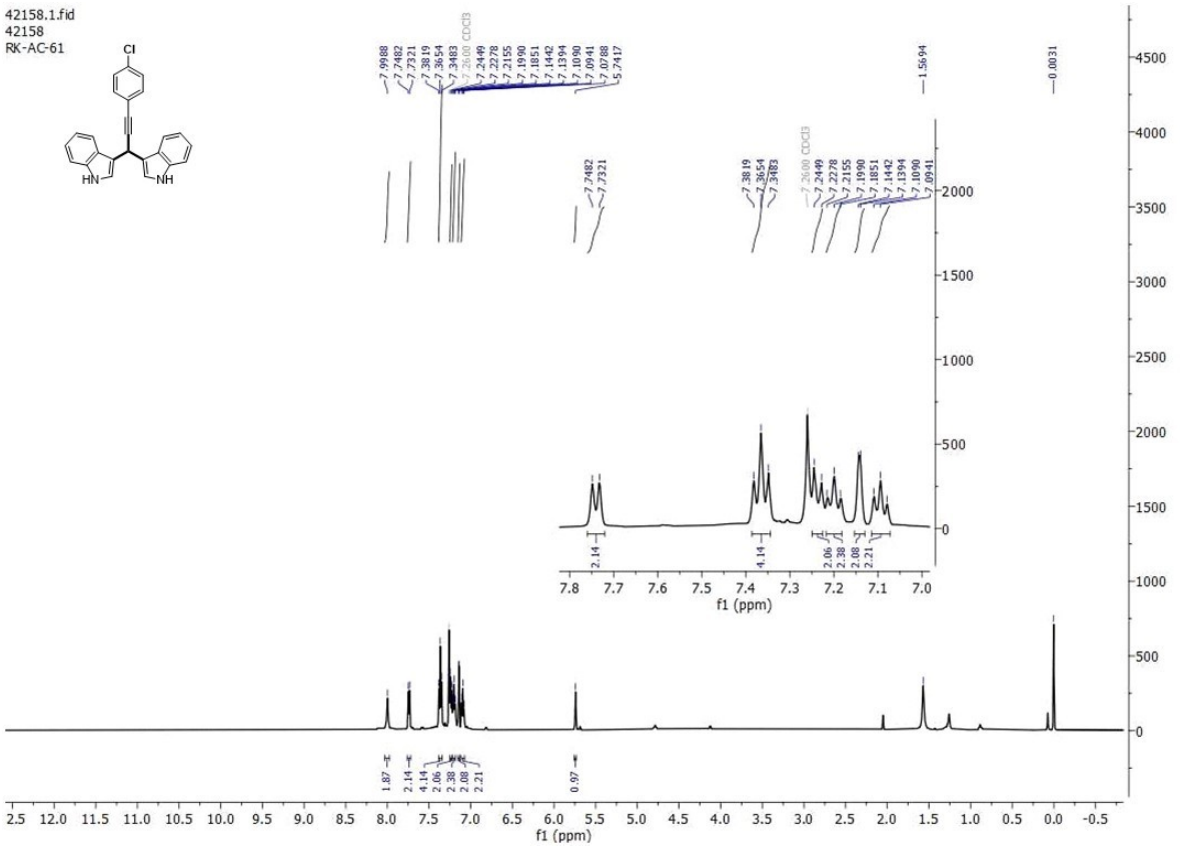


Figure S27 ^{1}H-NMR spectrum of **13a** in $CDCl_3$.

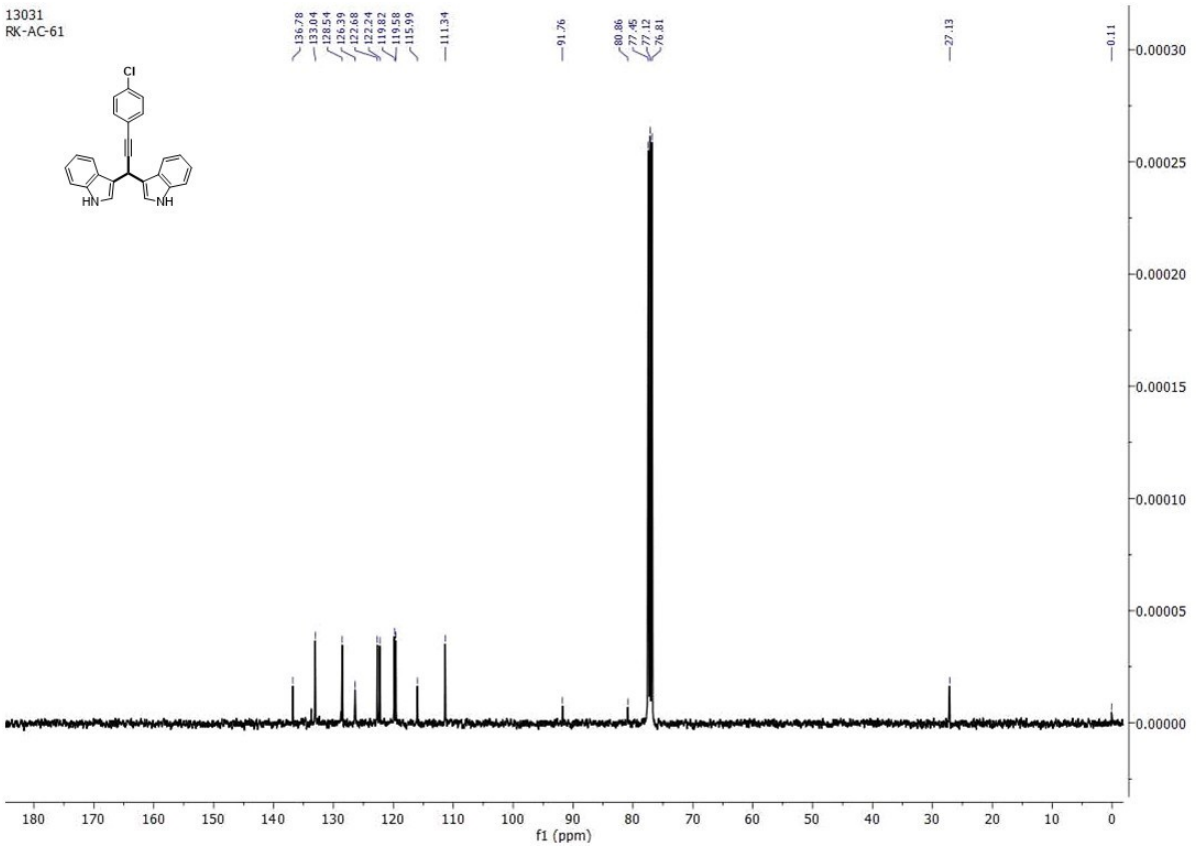


Figure S28 ^{13}C-NMR spectrum of **13a** in $CDCl_3$.

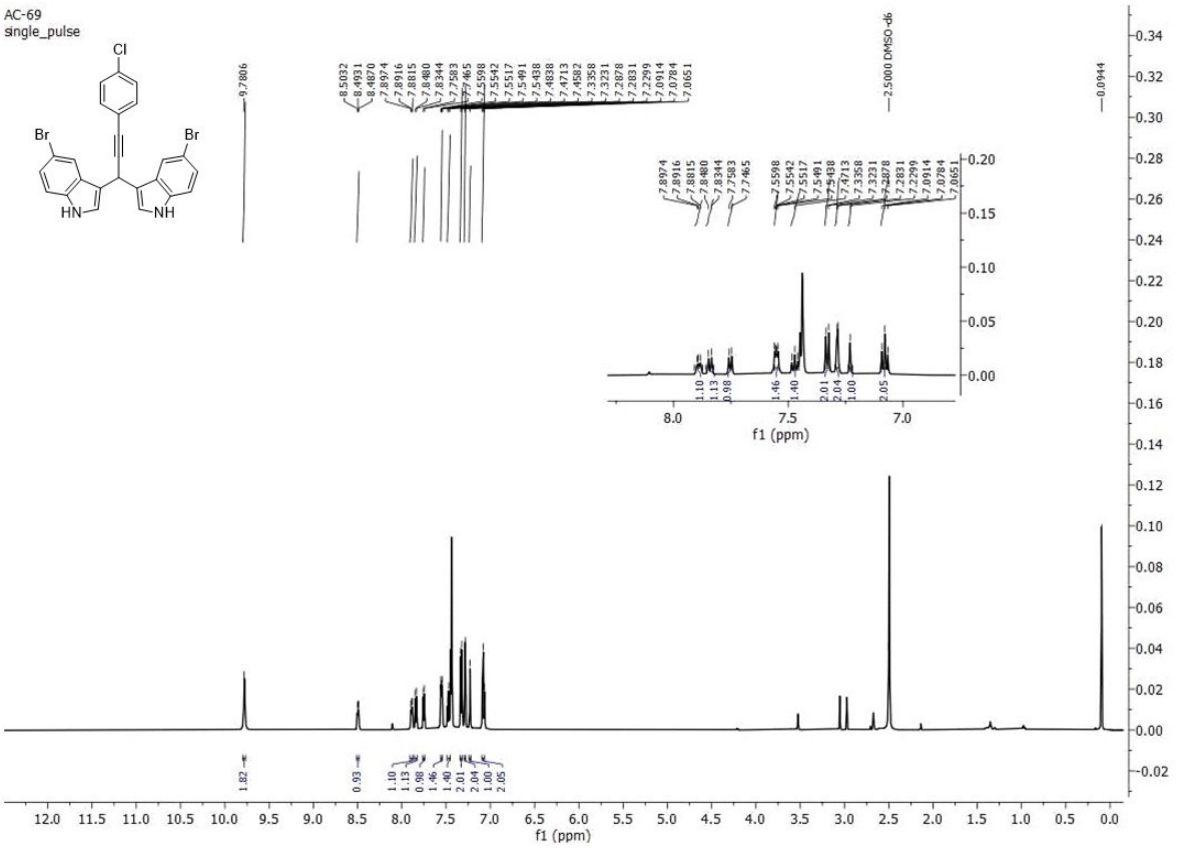


Figure S29 ^{1}H-NMR spectrum of **13c** in $CDCl_3$ + DMSO-d_6.

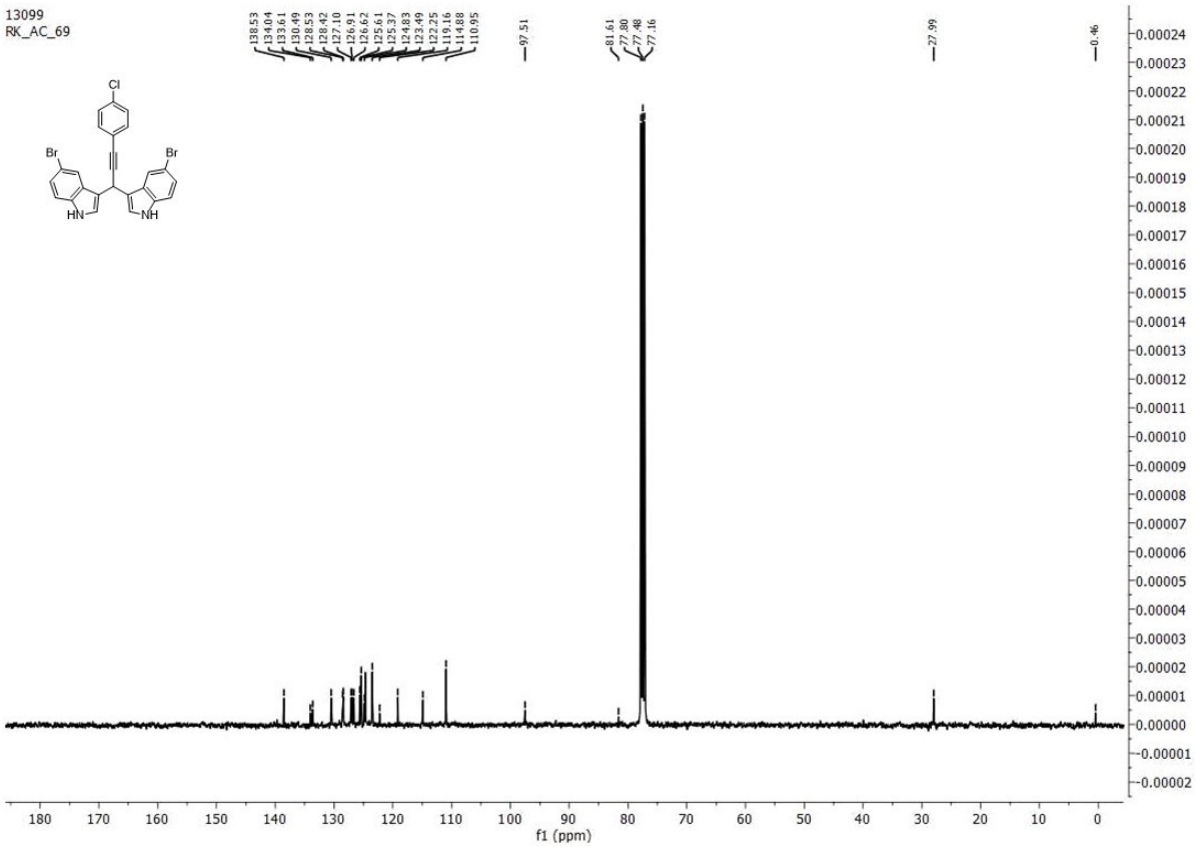


Figure S30 ^{13}C-NMR spectrum of **13c** in $CDCl_3$.

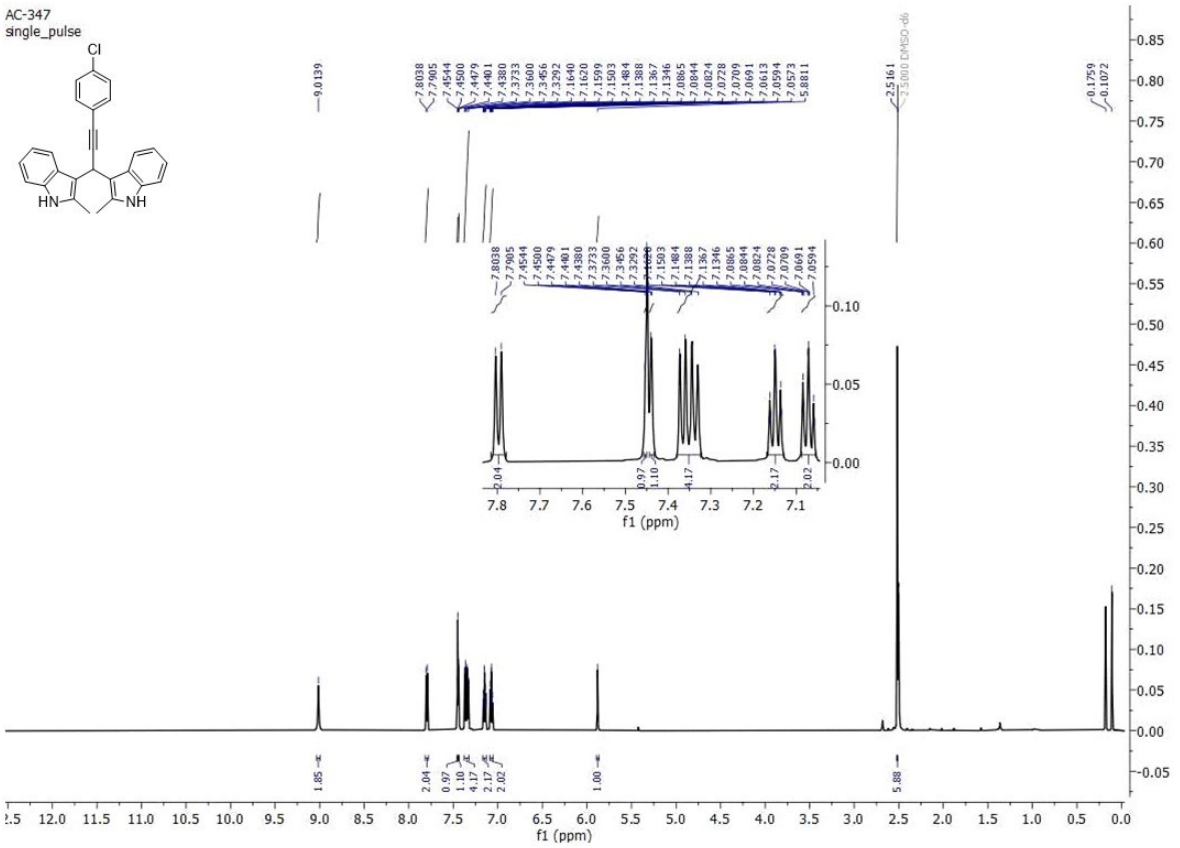


Figure S31 ^{1}H-NMR spectrum of **13o** in $CDCl_3$ + DMSO-d_6.

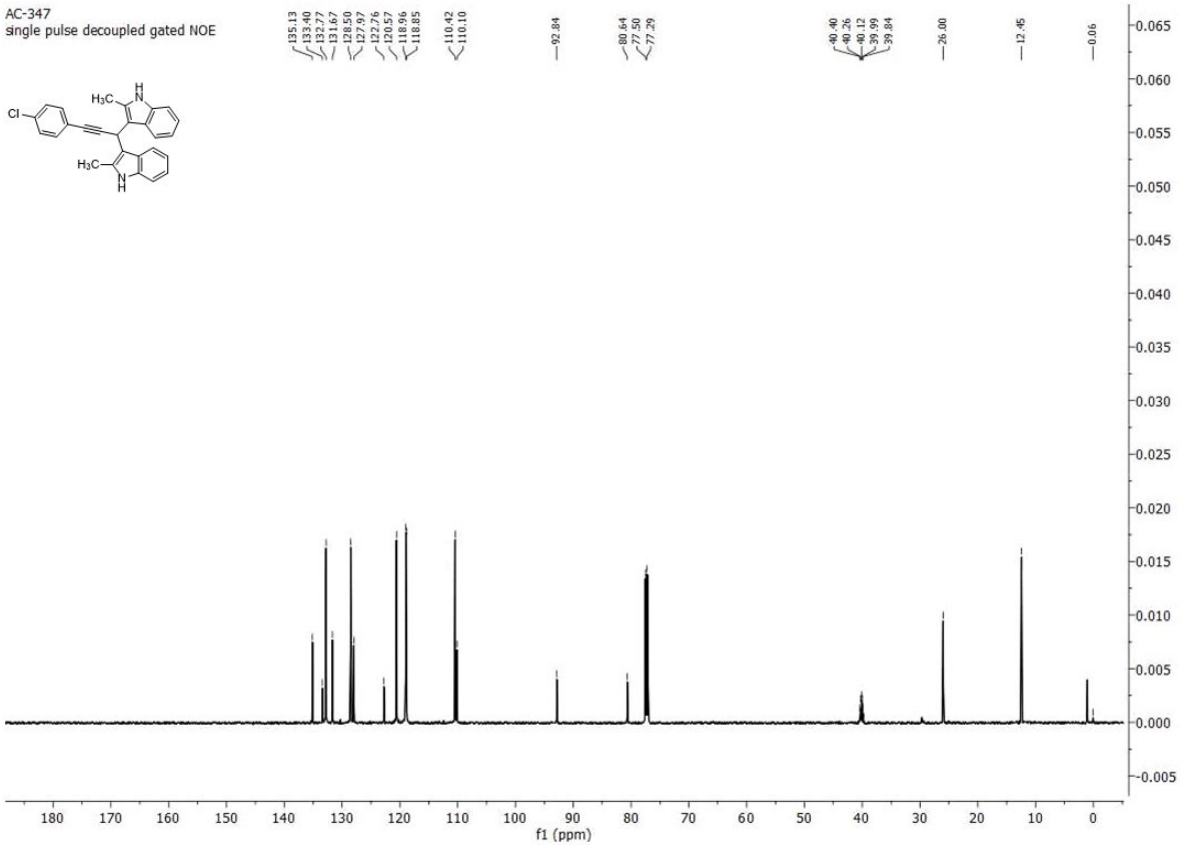


Figure S32 ^{13}C-NMR spectrum of **13o** in $CDCl_3$ + DMSO-d_6.

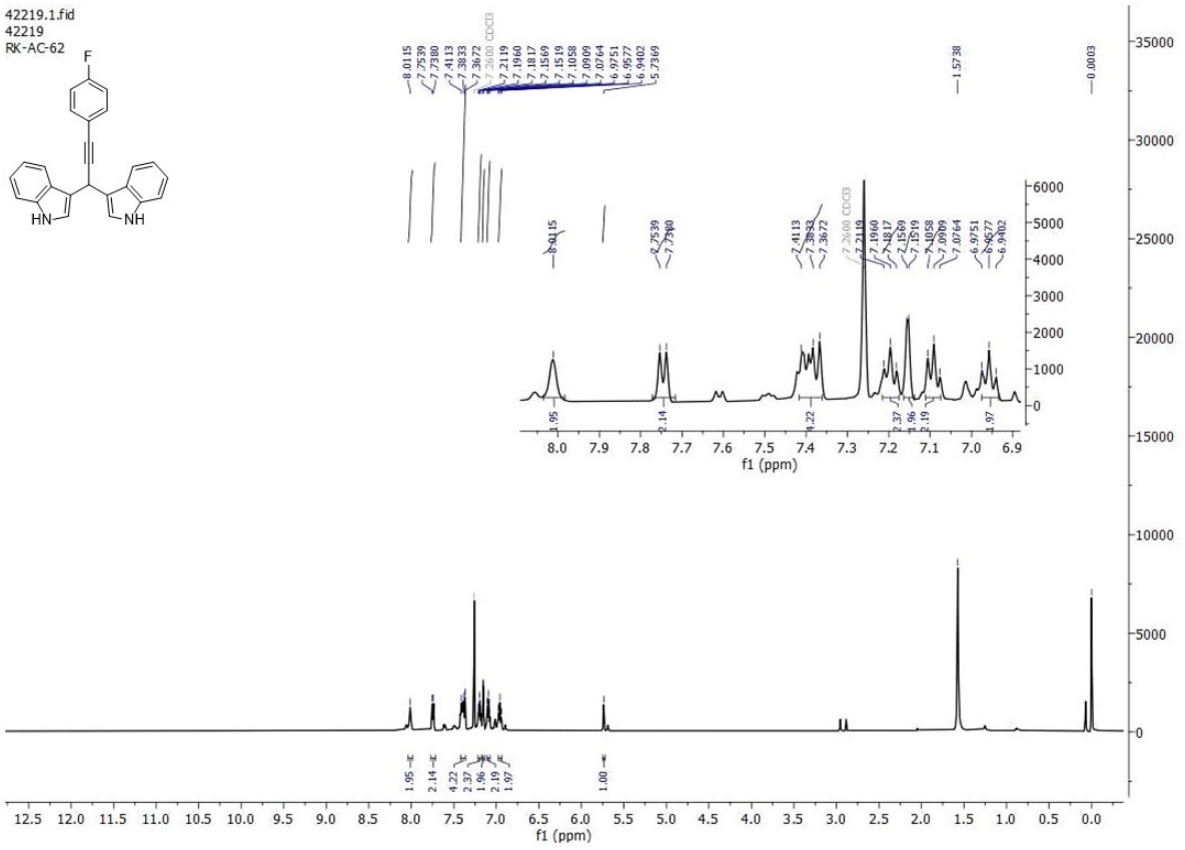


Figure.S33 ^{1}H-NMR spectrum **14a** in $CDCl_3$.

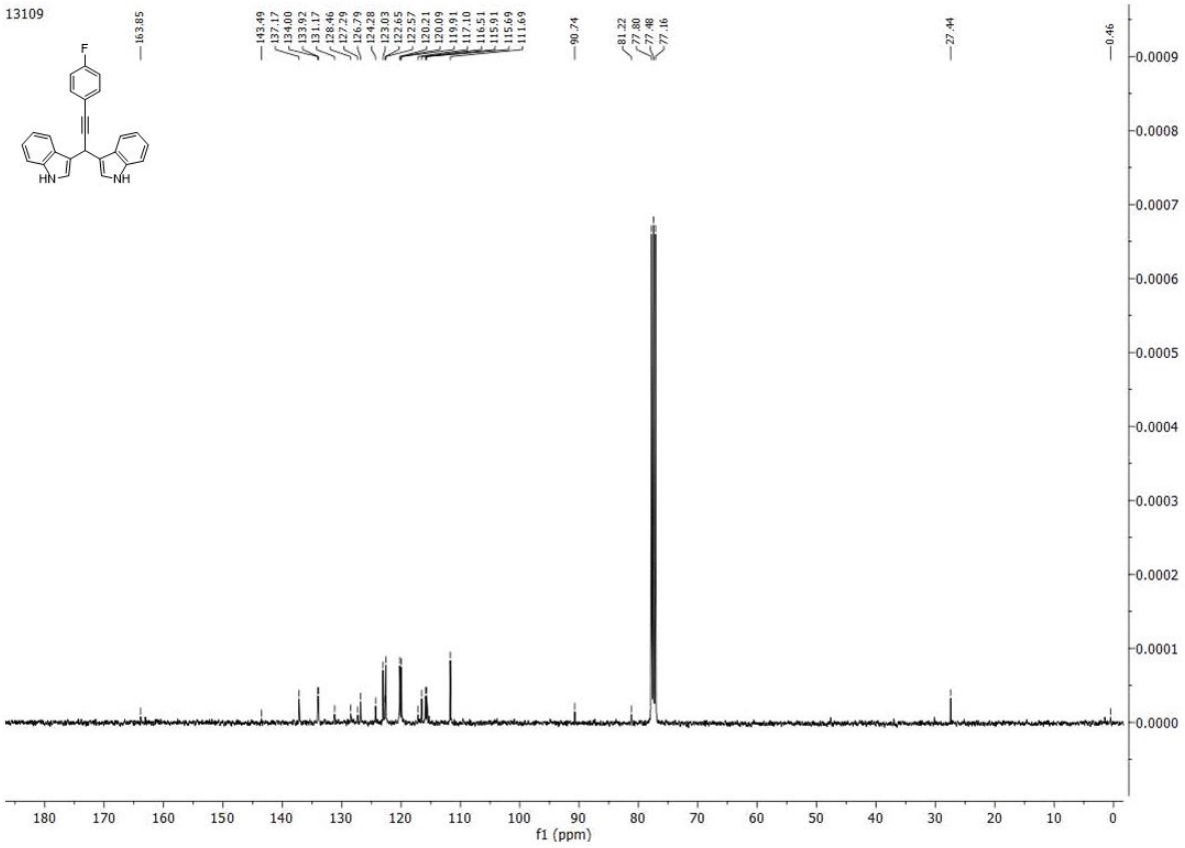


Figure.S34 ^{13}C-NMR spectrum of **14a** in $CDCl_3$.

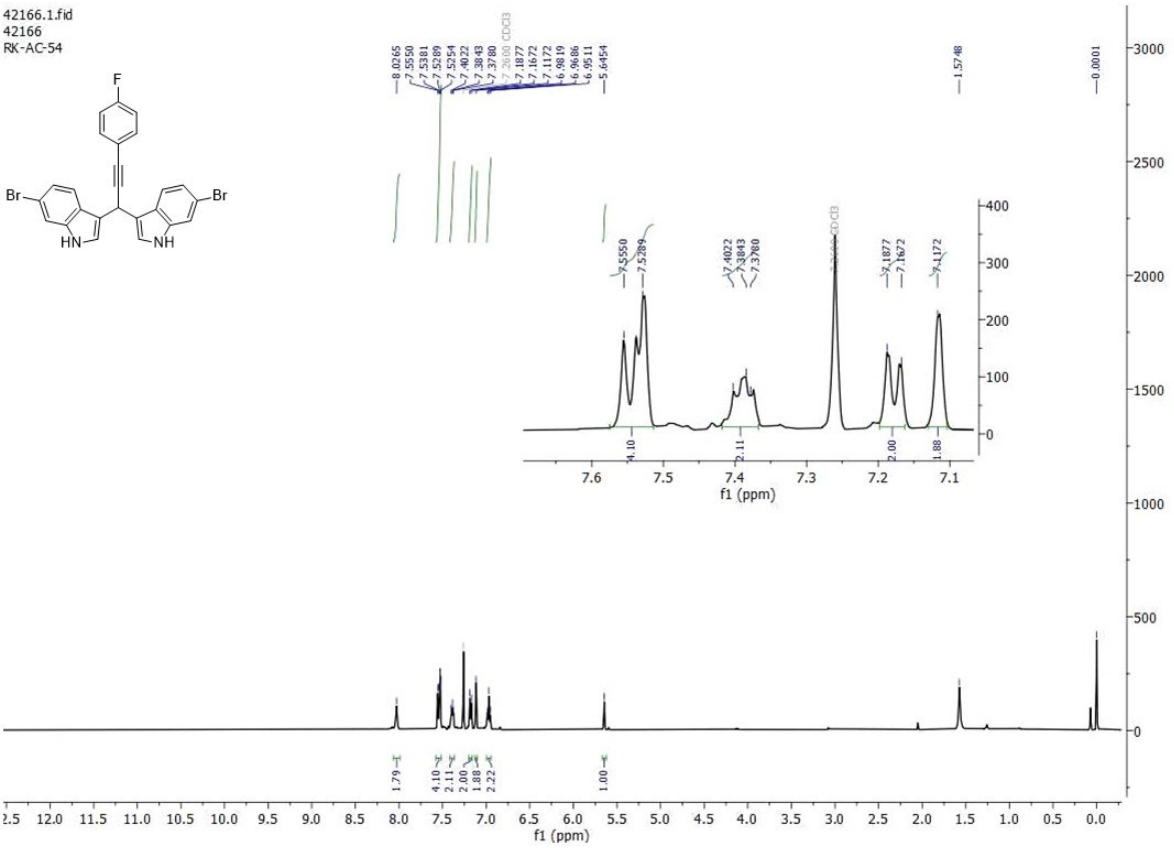


Figure.S35 ^{1}H-NMR spectrum of **14d** in $CDCl_3$.

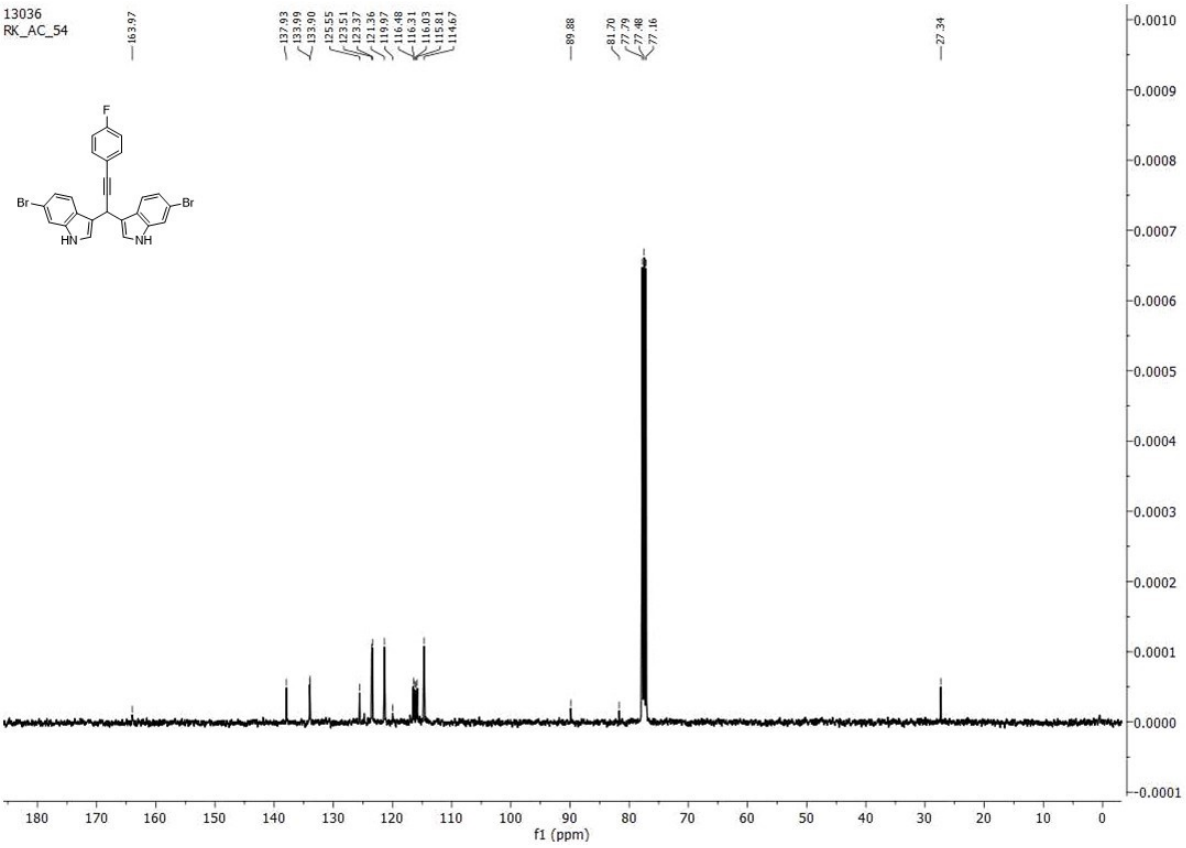


Figure.S36 ^{13}C-NMR spectrum of **14d** in $CDCl_3$.

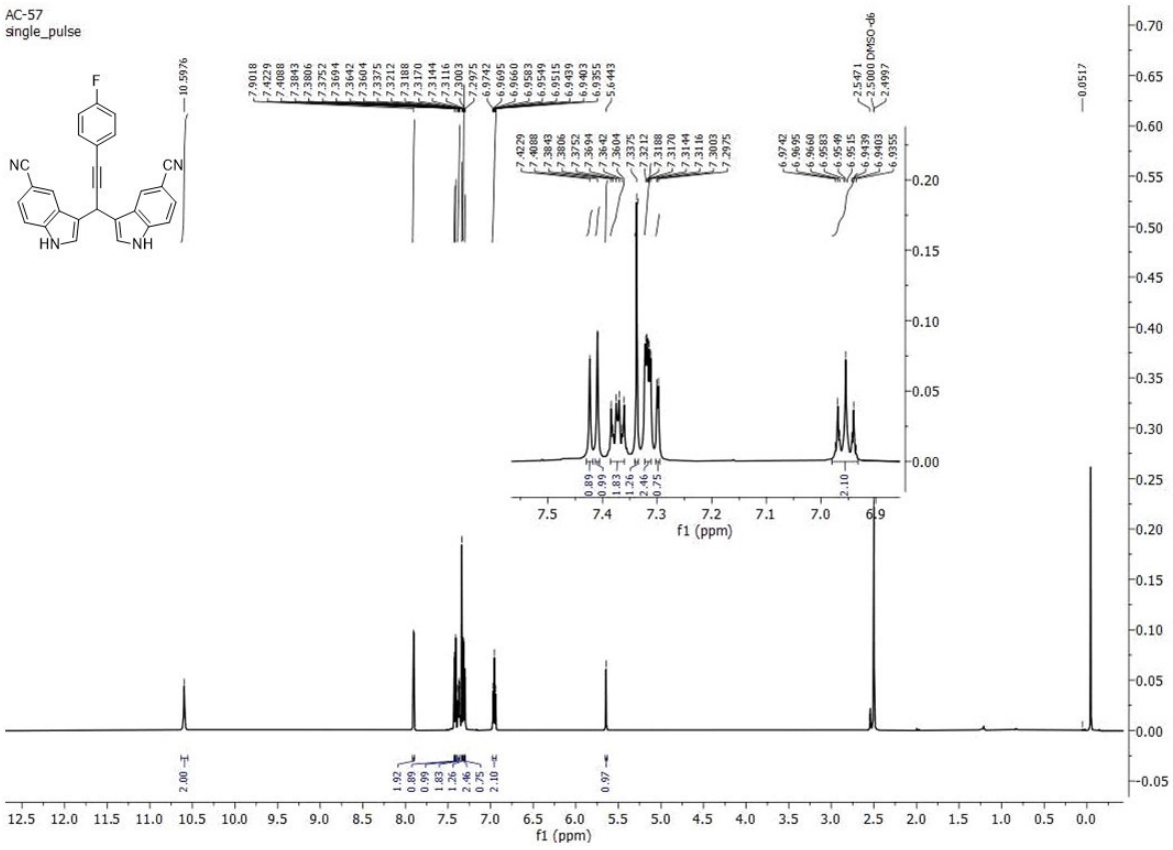


Figure.S37 ^{1}H-NMR spectrum of **14f** in $CDCl_3$ + DMSO-d_6.

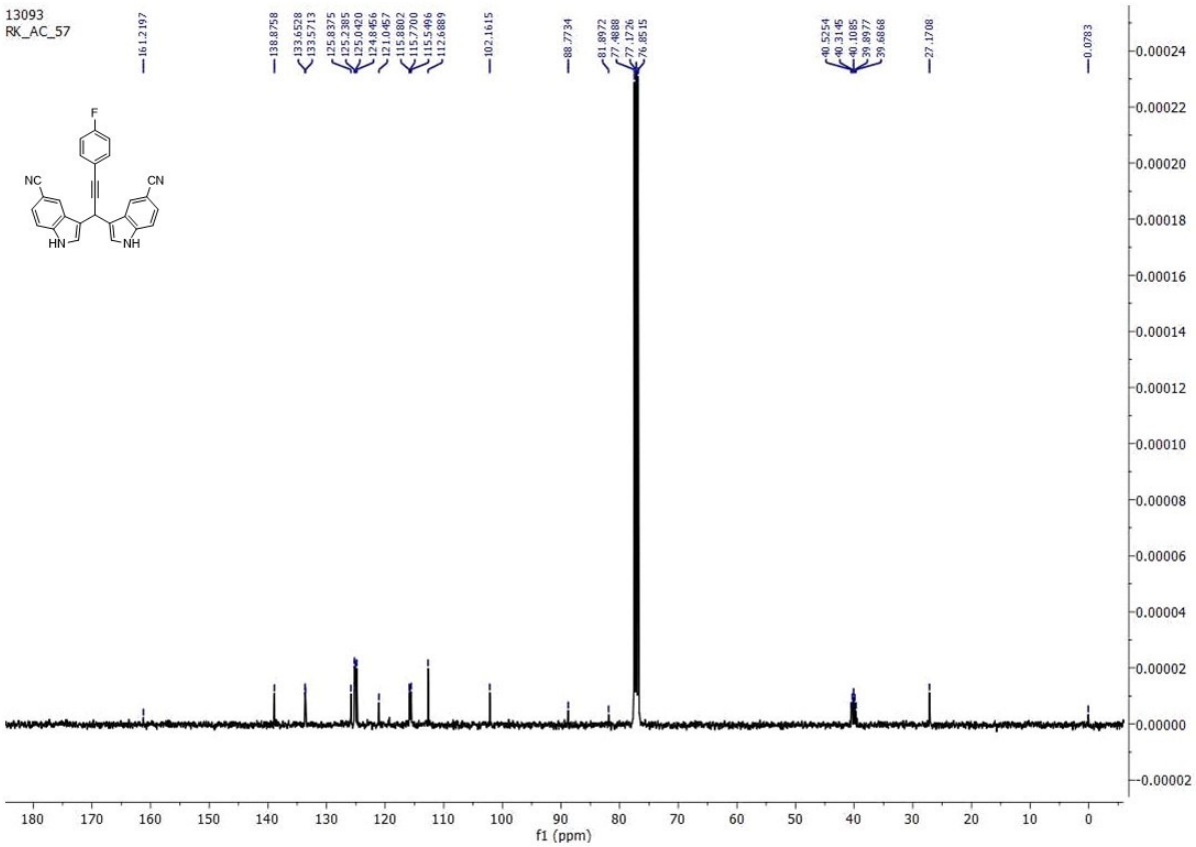


Figure.S38 ^{13}C-NMR spectrum of **14f** in $CDCl_3$ + DMSO-d_6.

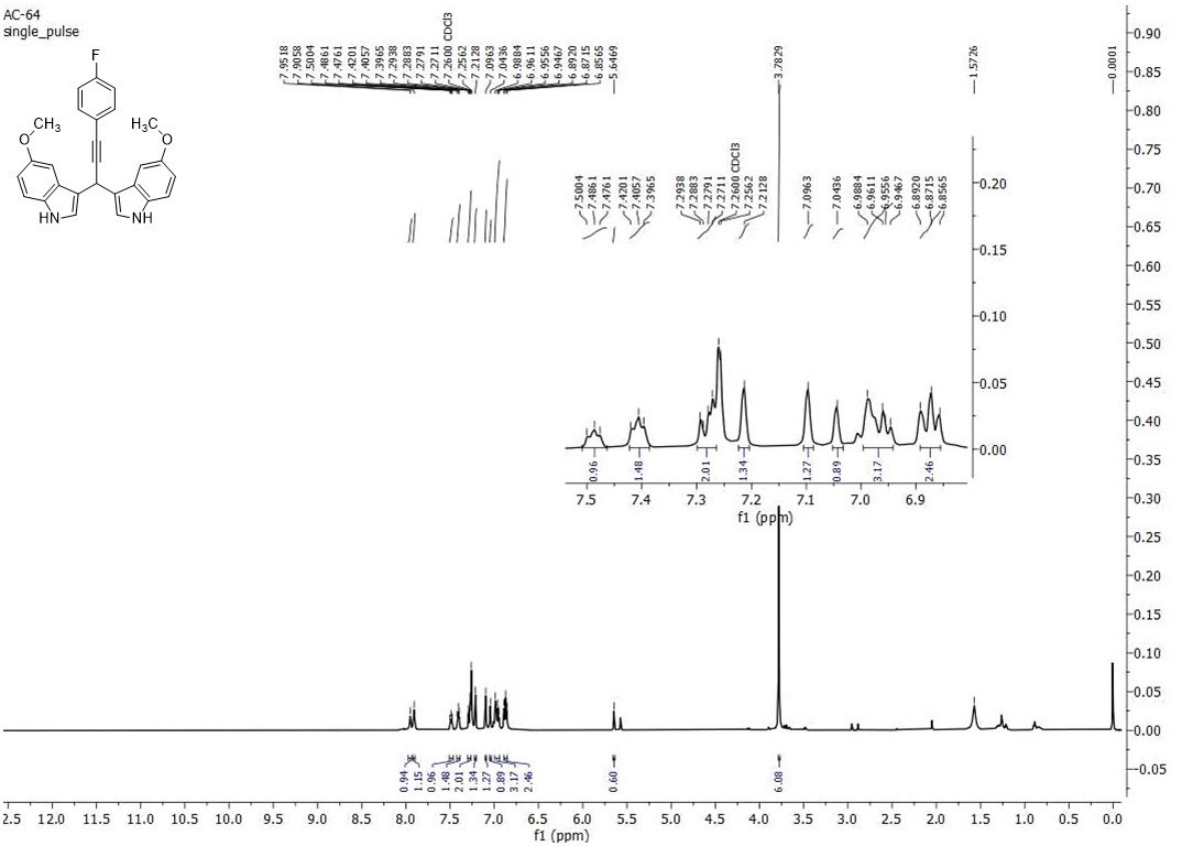


Figure S39 ^{1}H-NMR spectrum of **14j** in $CDCl_3$.

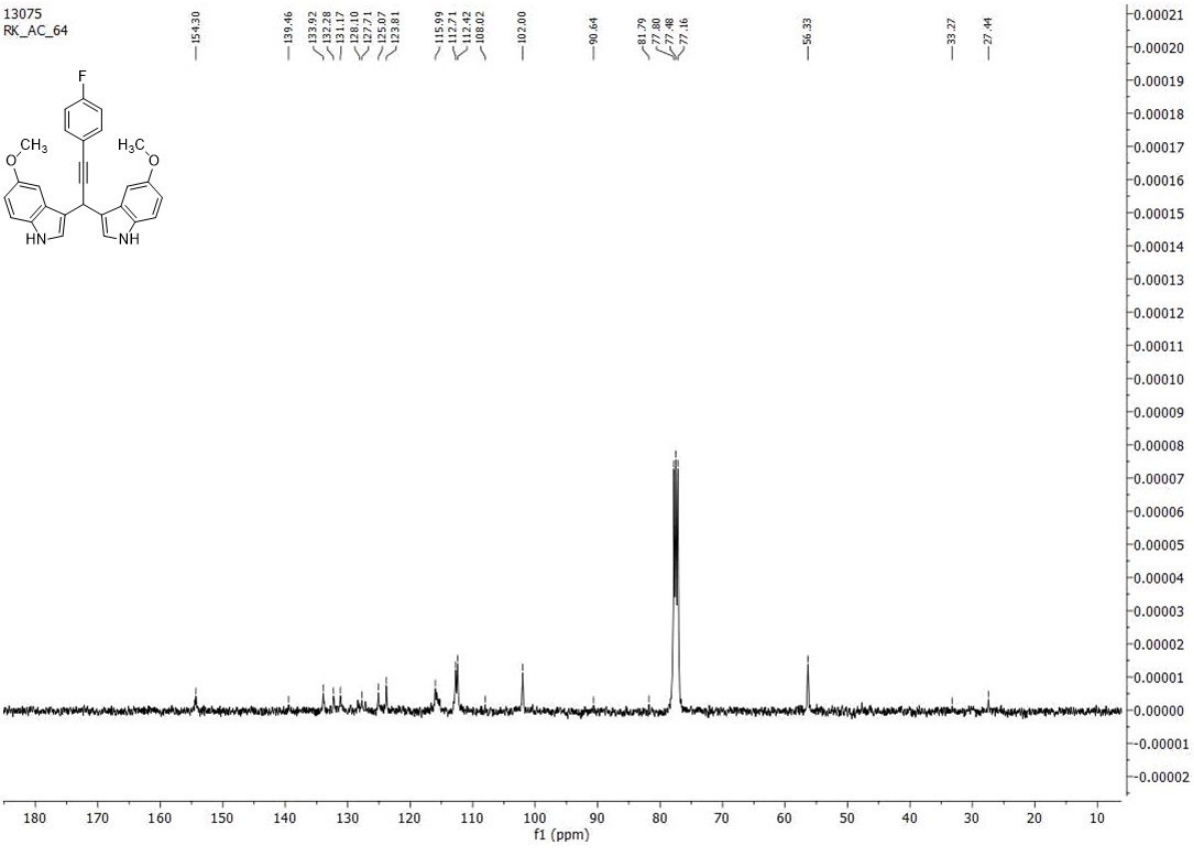


Figure.S40 ^{13}C-NMR spectrum of **14j** in $CDCl_3$.

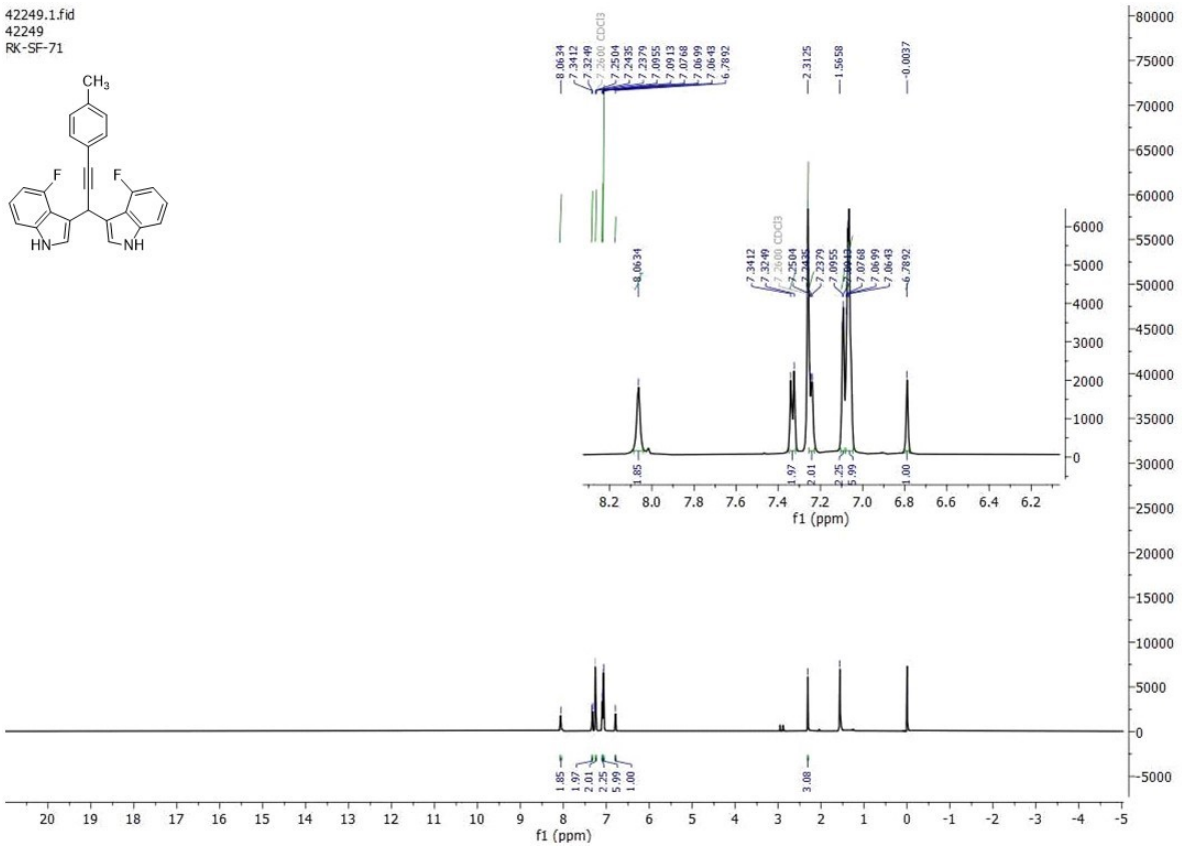


Figure.S41 ^{1}H-NMR spectrum of **15g** in $CDCl_3$.

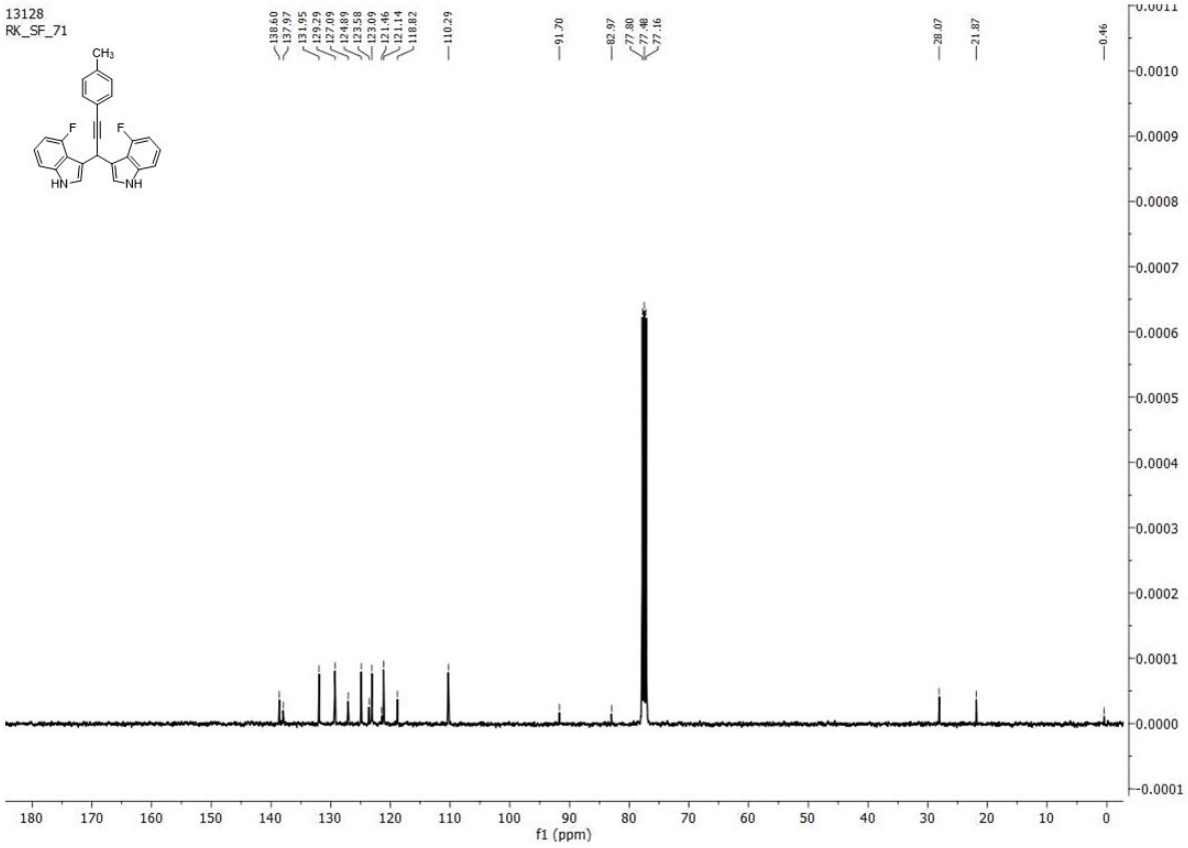


Figure.S42 ^{13}C-NMR spectrum of **15g** in $CDCl_3$.

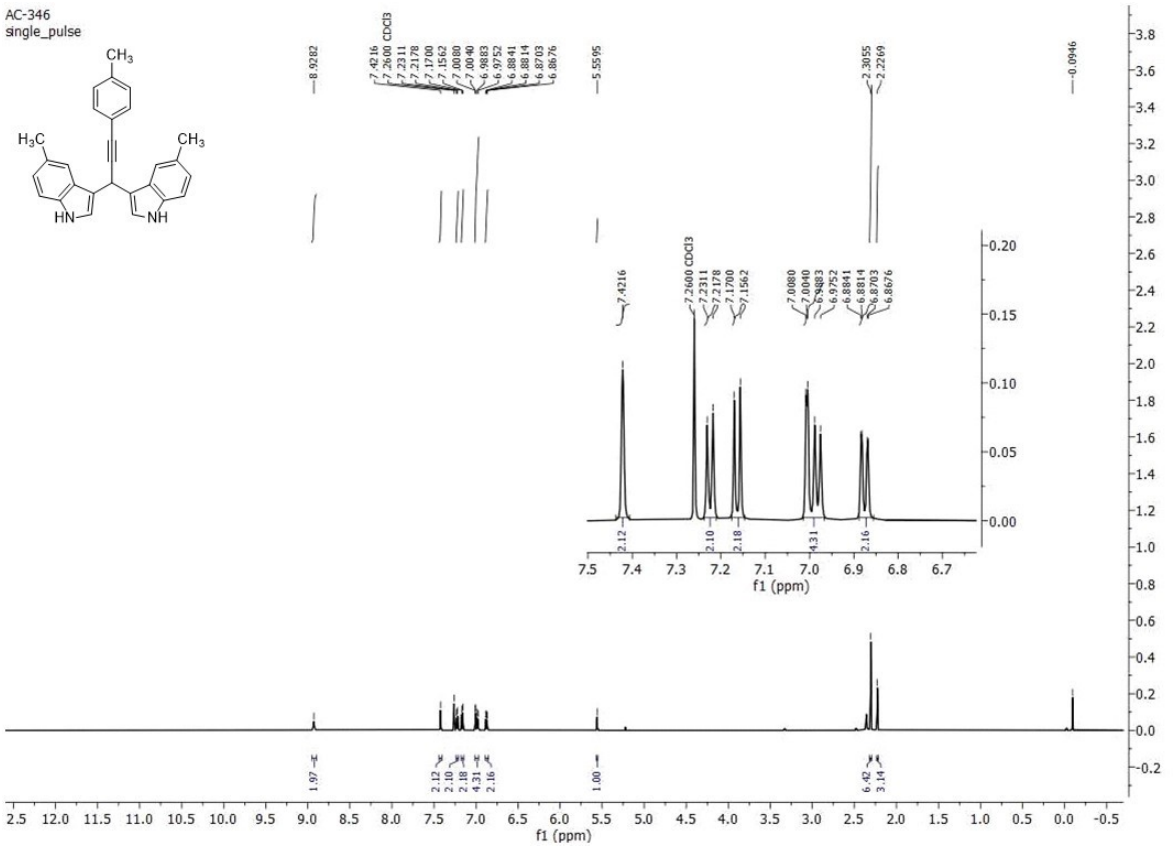


Figure.S43 ^{1}H-NMR spectrum of **15k** in $CDCl_3$.

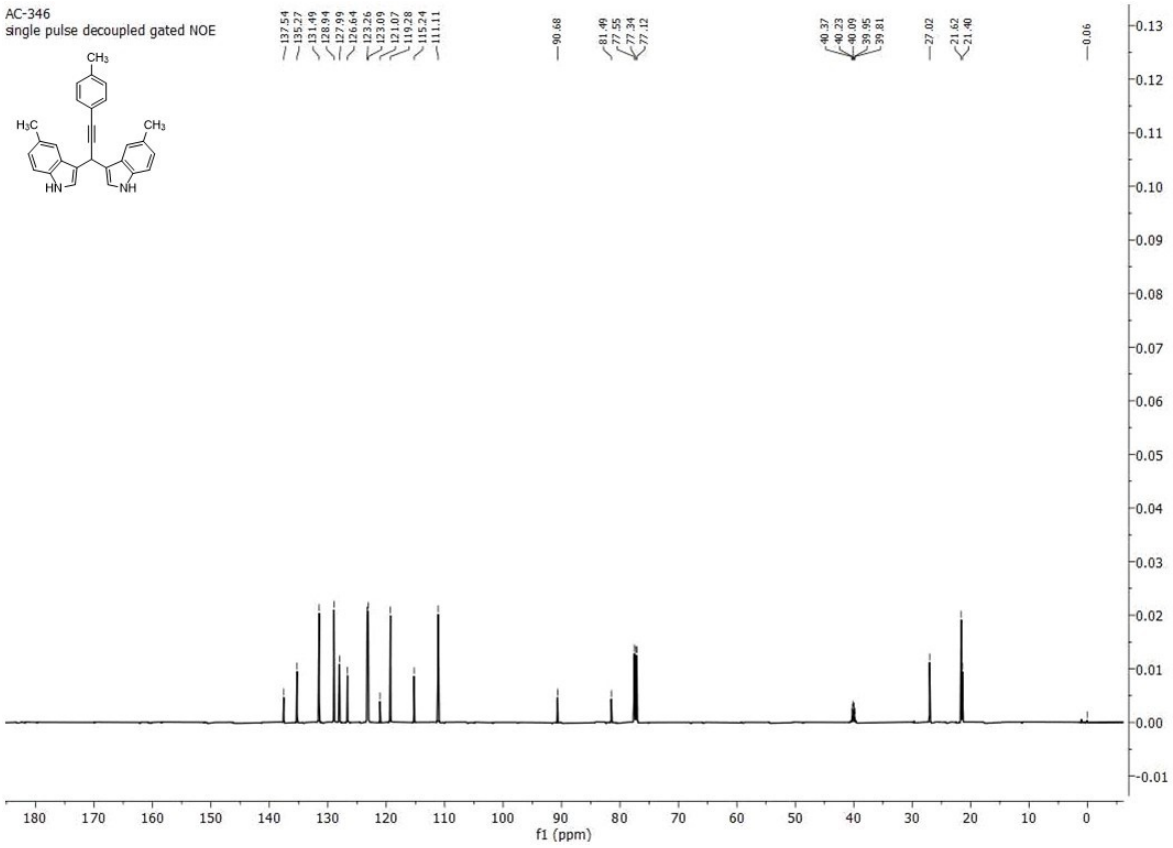


Figure.S44 ^{13}C-NMR spectrum of **15k** in $CDCl_3$ + DMSO-d_6.

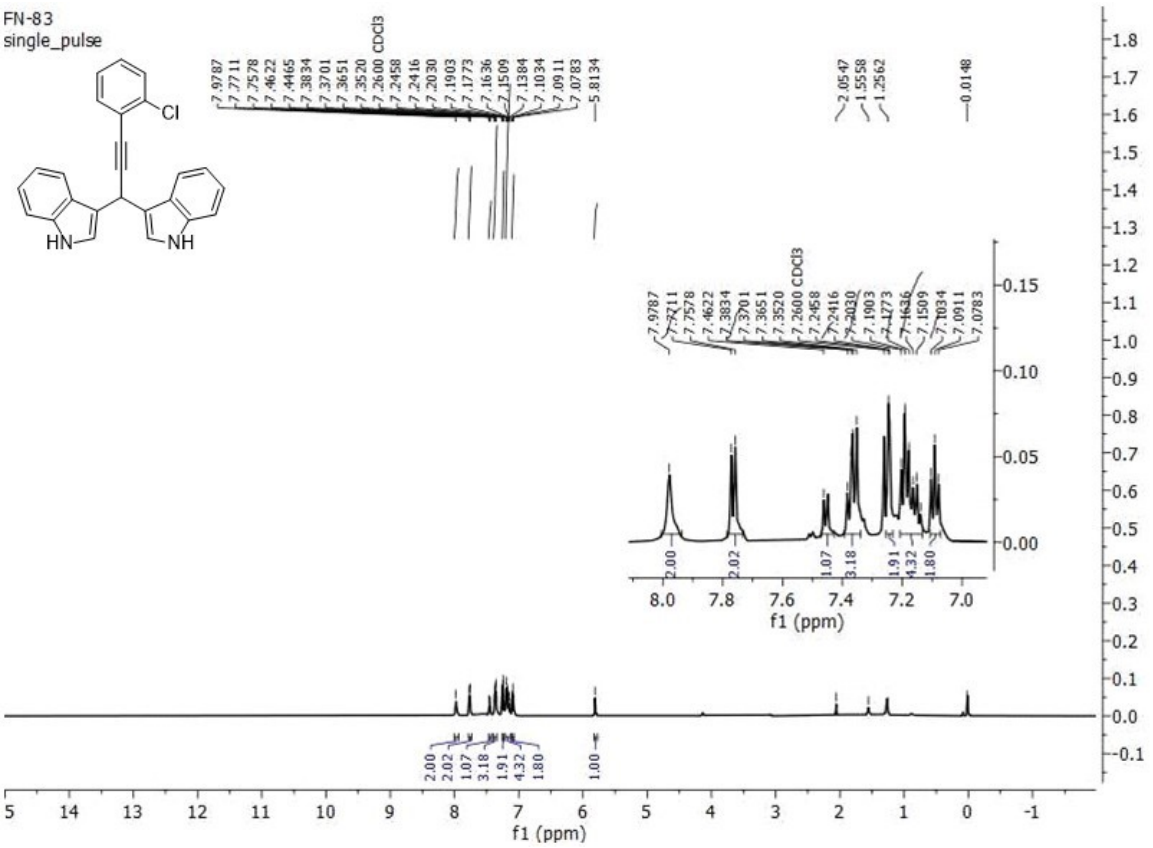


Figure.S45 ^{1}H-NMR spectrum of **16a** in $CDCl_3$.

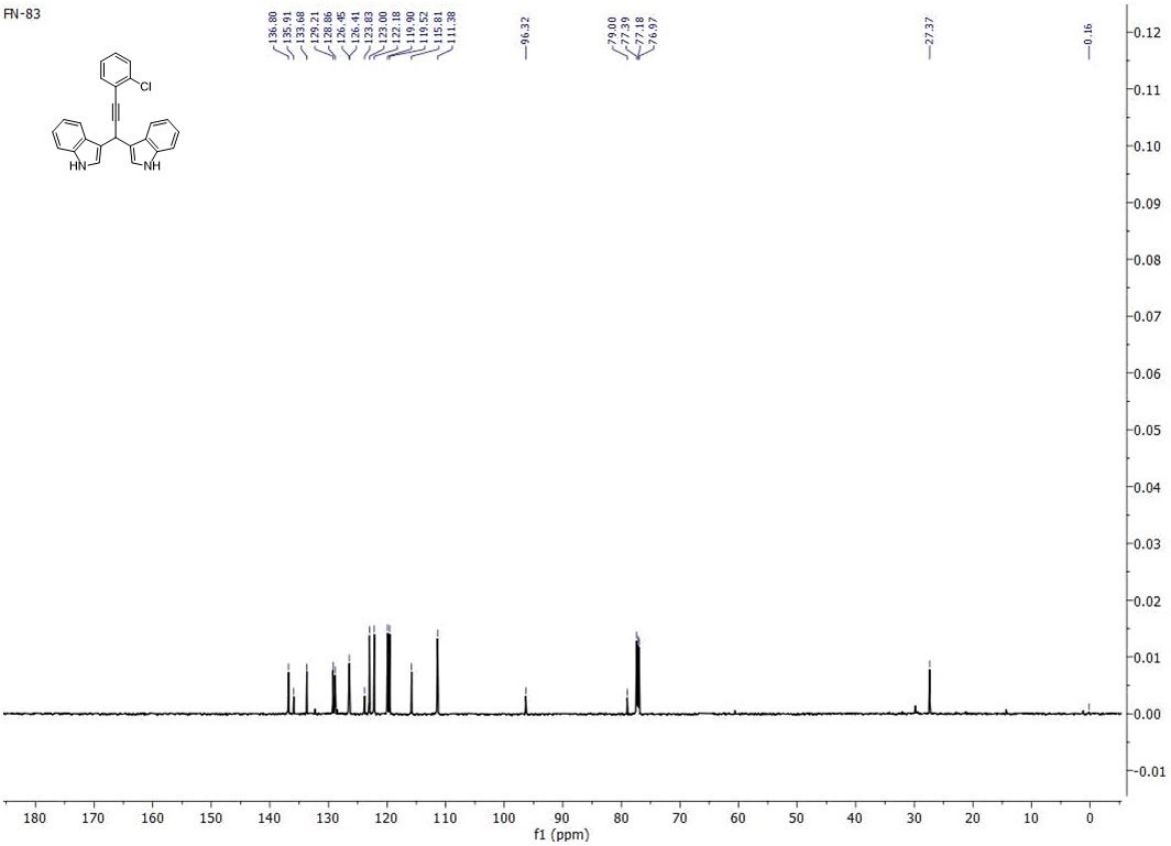


Figure.S46 ^{13}C-NMR spectrum of **16a** in $CDCl_3$.

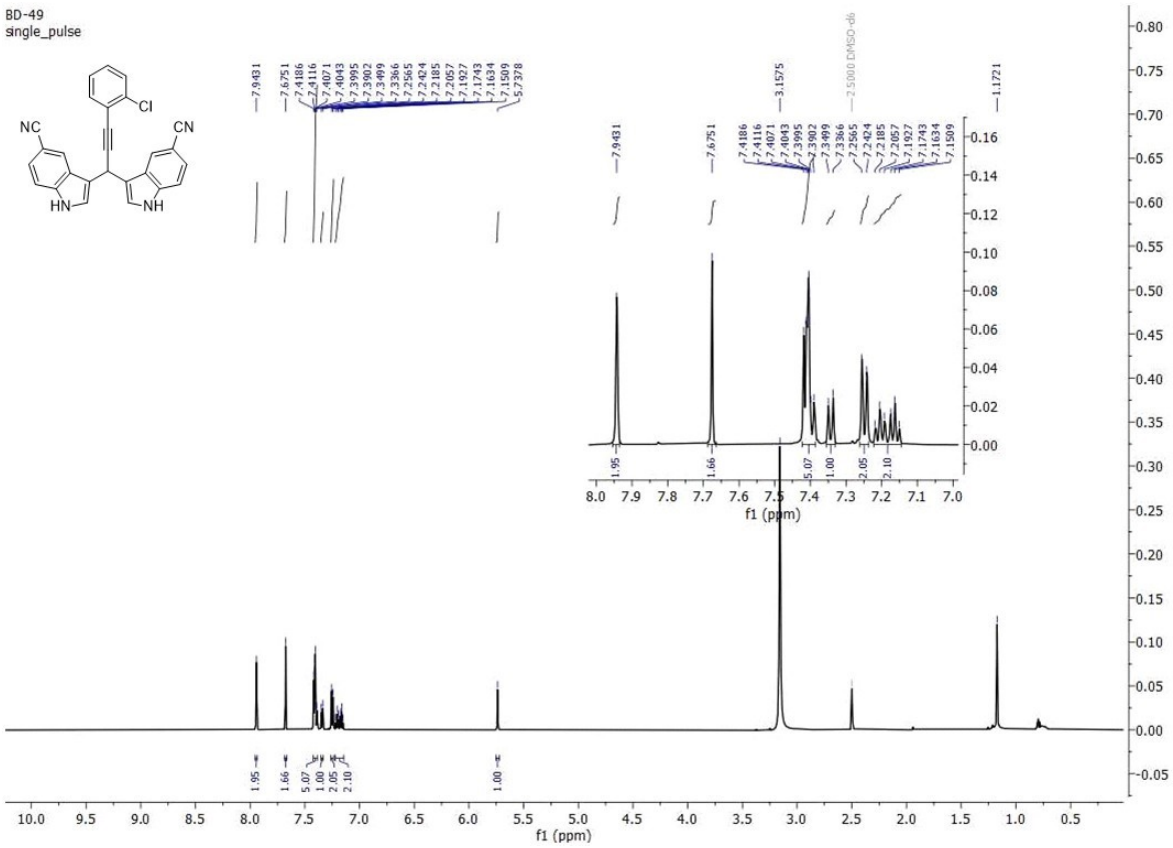


Figure.S47 ^{1}H-NMR spectrum of **16f** in $CDCl_3$ + DMSO-d_6.

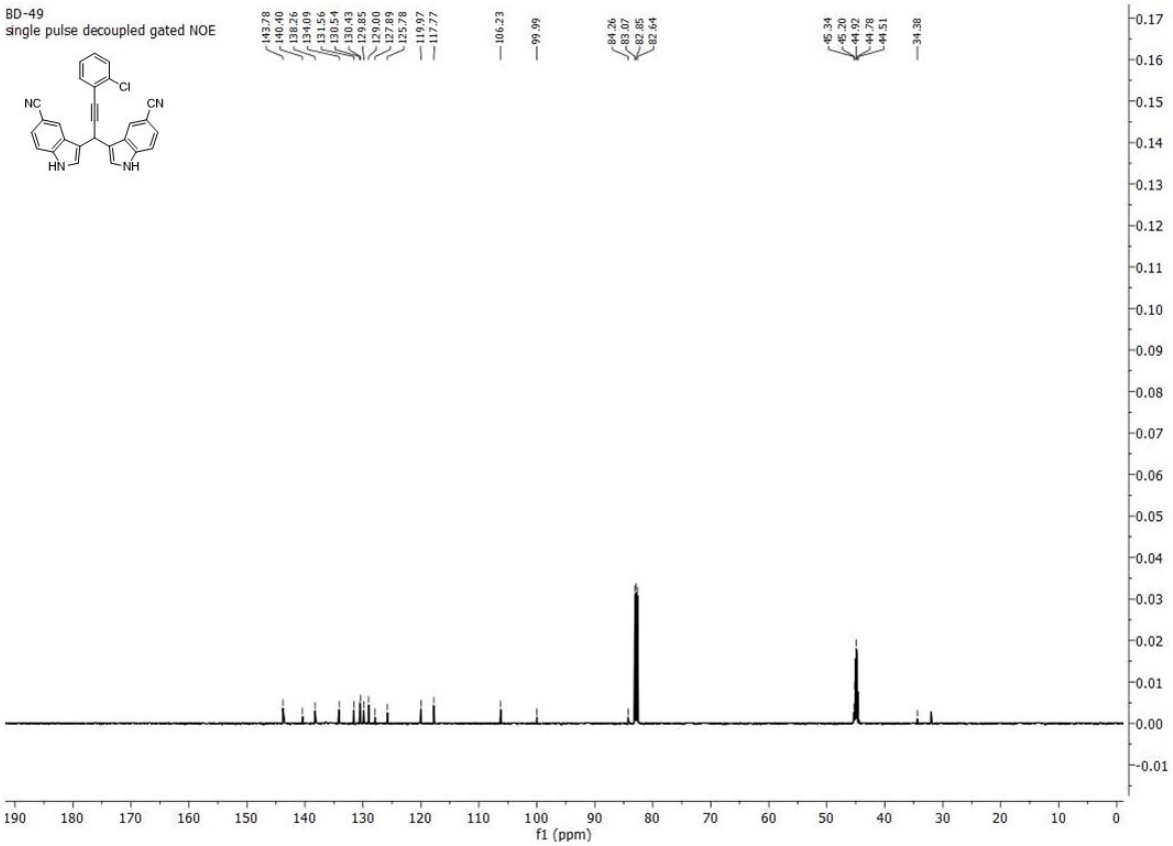


Figure.S48 ^{13}C-NMR spectrum of **16f** in $CDCl_3$ + DMSO-d_6.

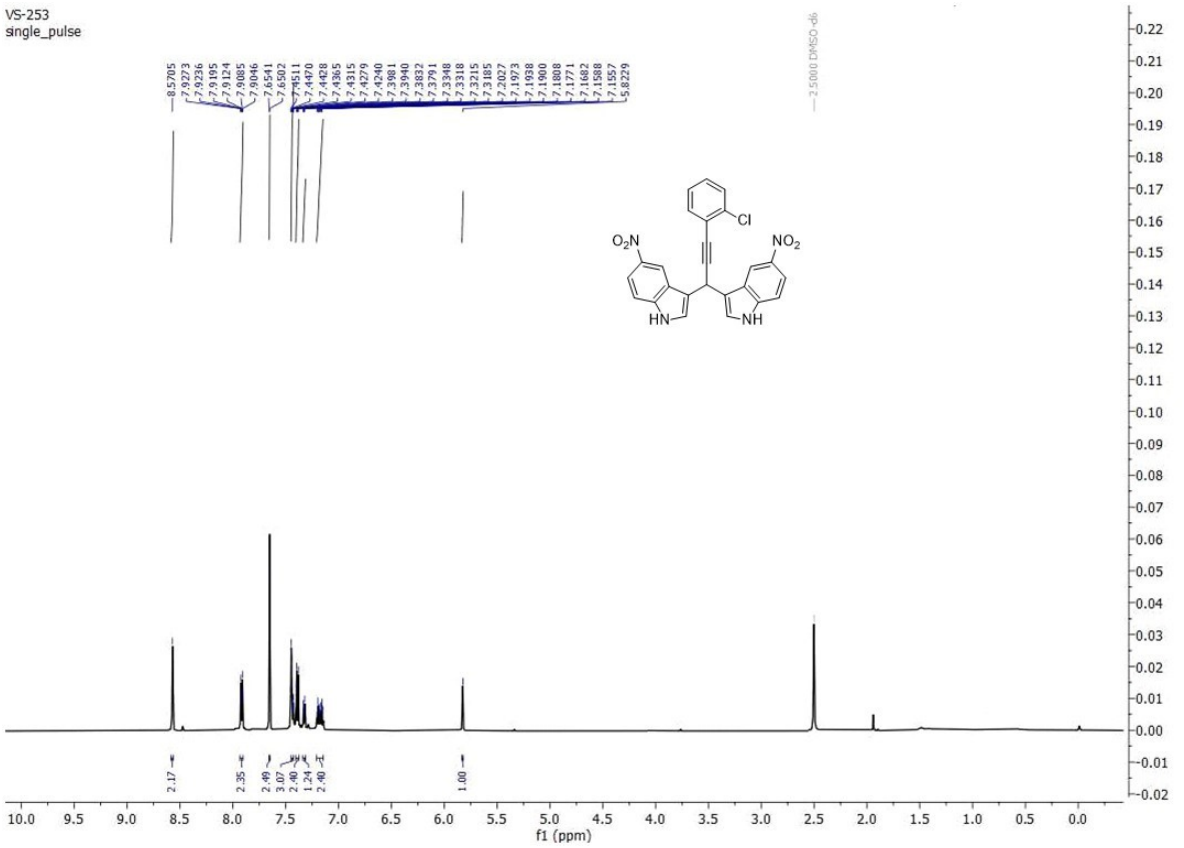


Figure S49 ^{1}H-NMR spectrum of **16n** $CDCl_3$ + DMSO-d_6.

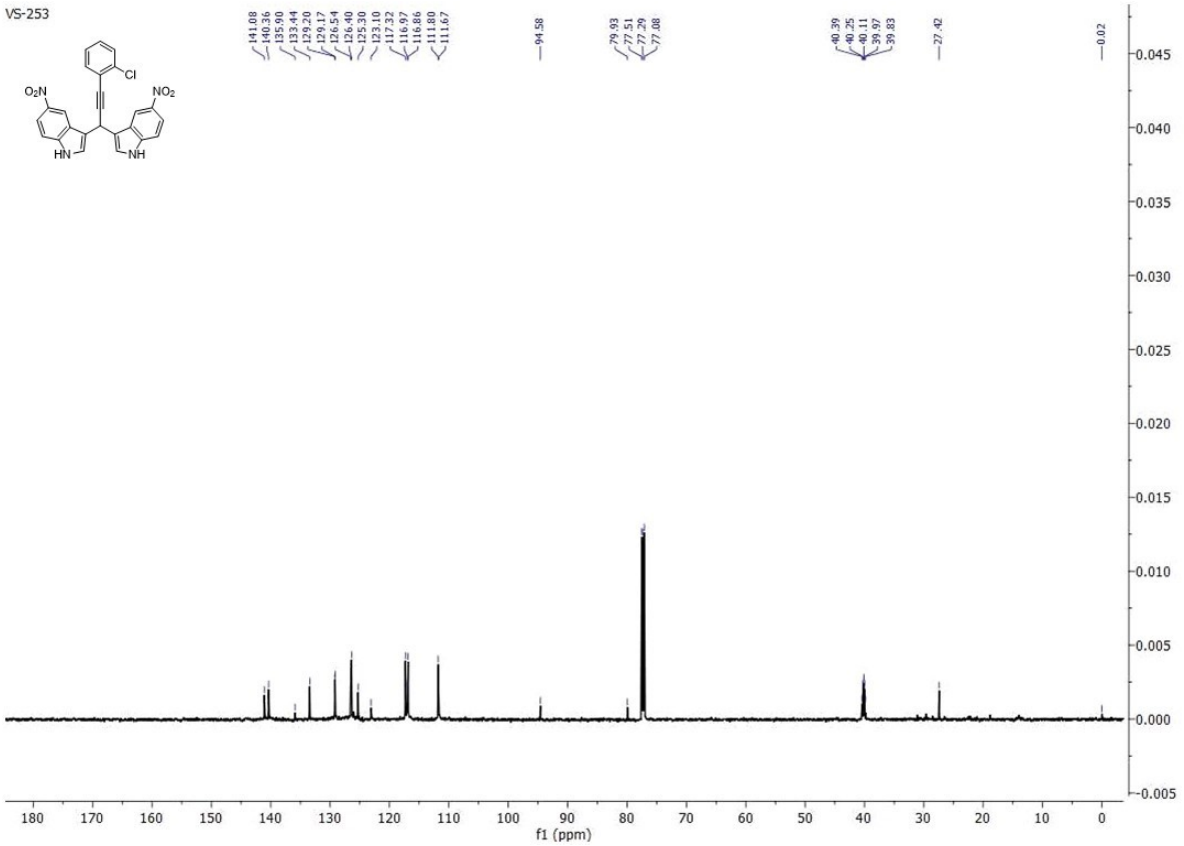


Figure S50 ^{13}C-NMR spectrum of **16n** $CDCl_3$ + DMSO-d_6.

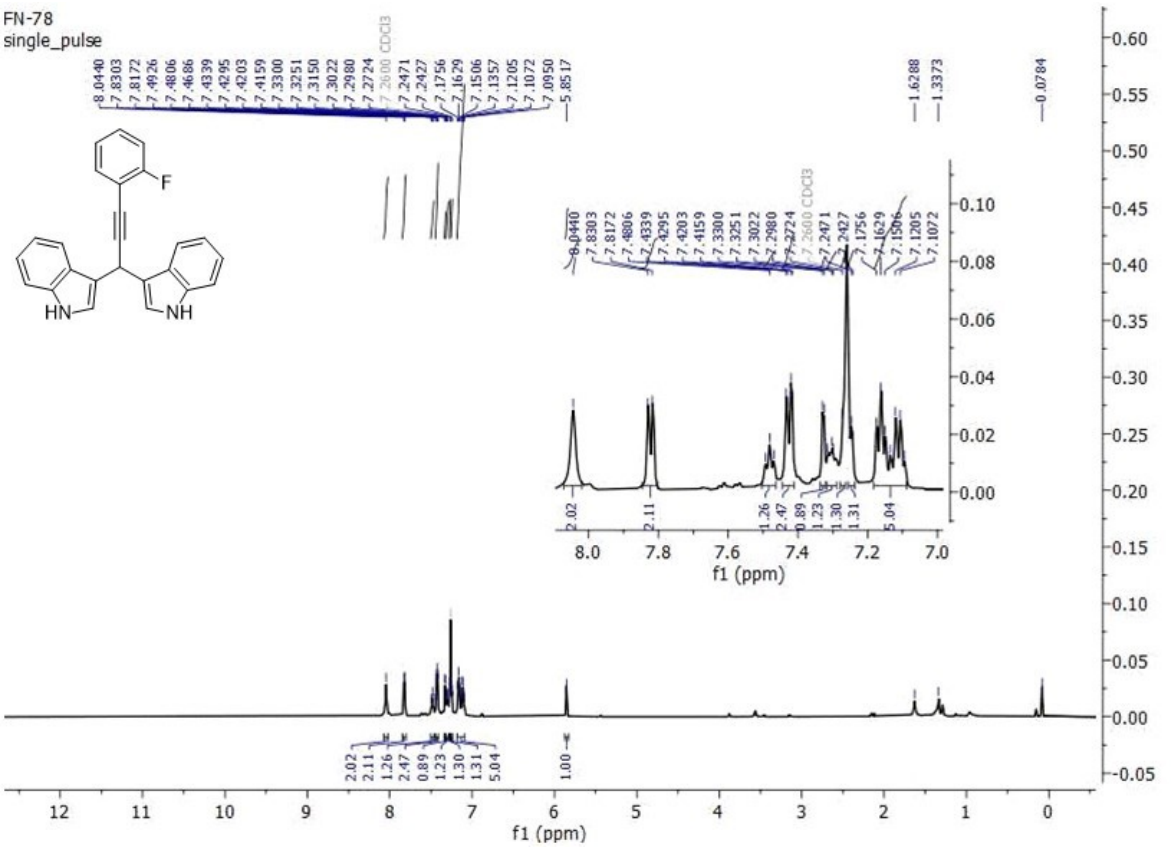


Figure S51 ^{1}H-NMR spectrum of **17a** in $CDCl_3$.

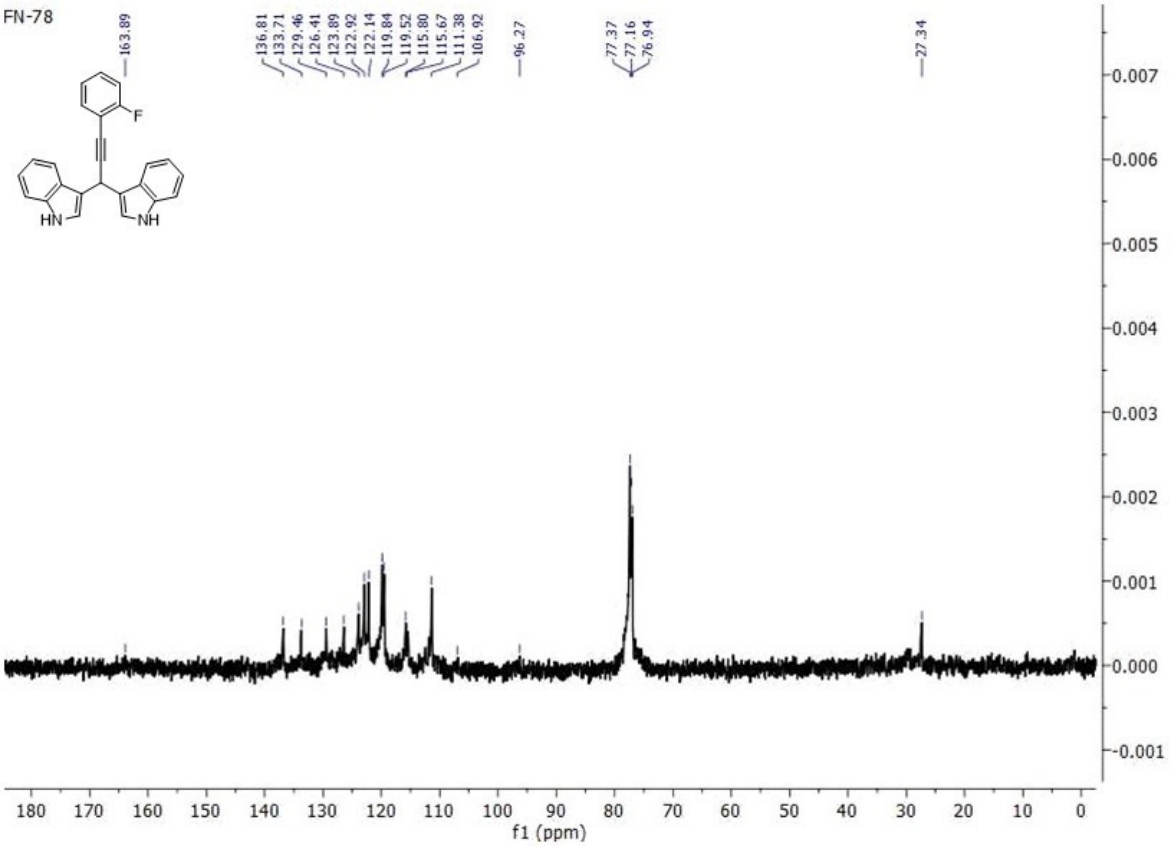


Figure S52 ^{13}C-NMR spectrum **of 17a** in $CDCl_3$.

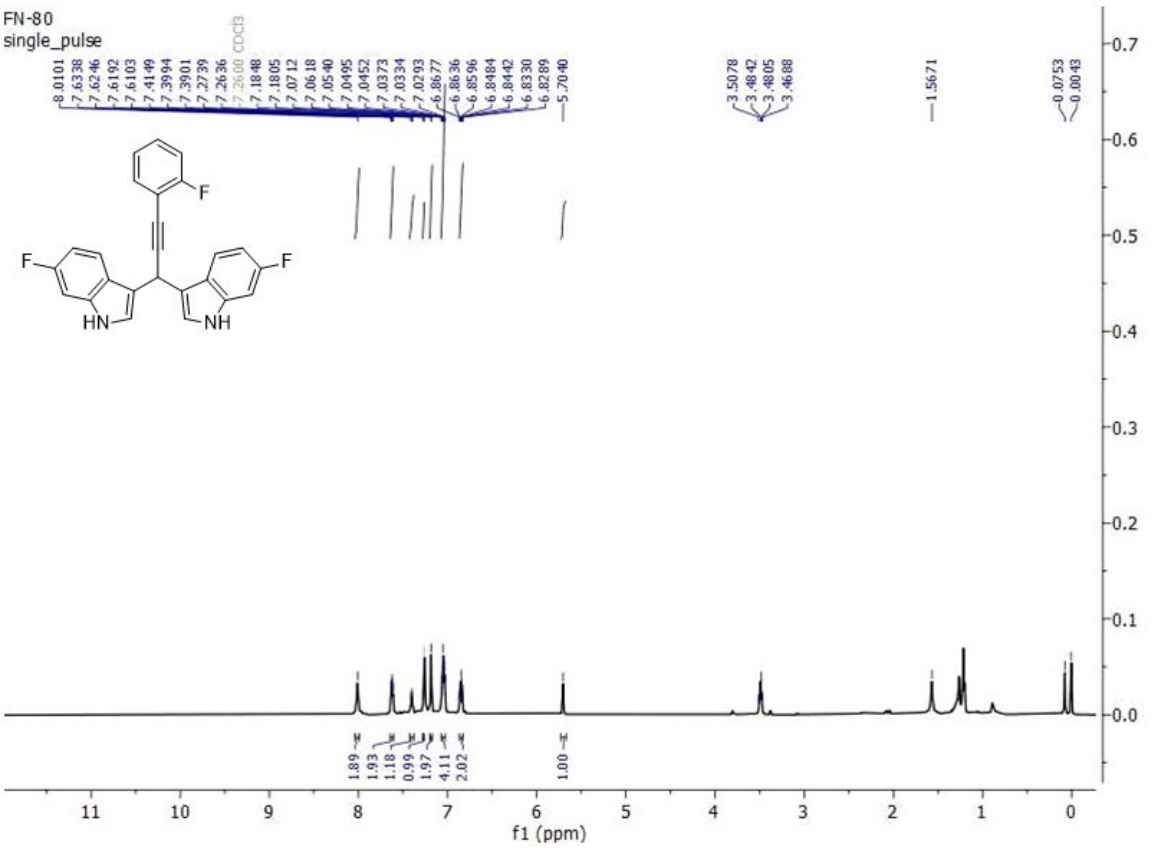


Figure S53 ^{1}H-NMR spectrum of **17i** in $CDCl_3$.

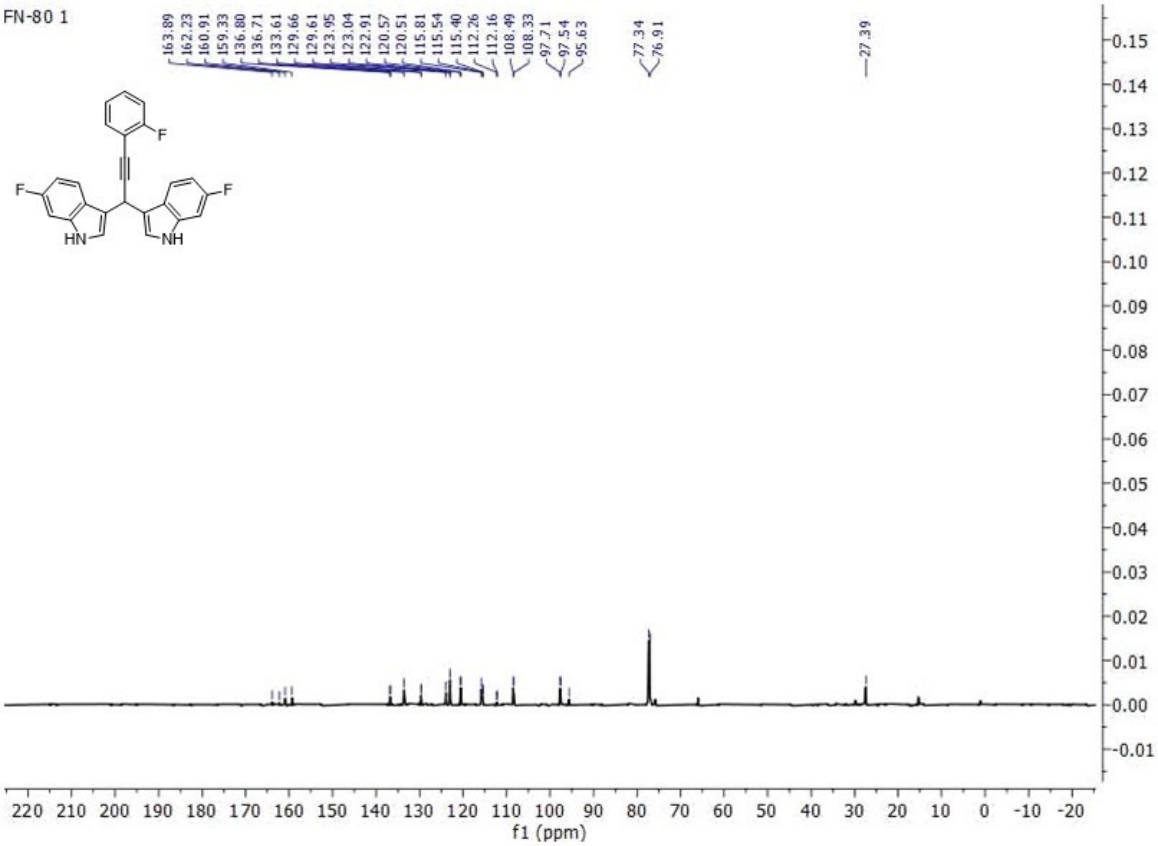


Figure S54 ^{13}C-NMR spectrum of **17i** in $CDCl_3$.

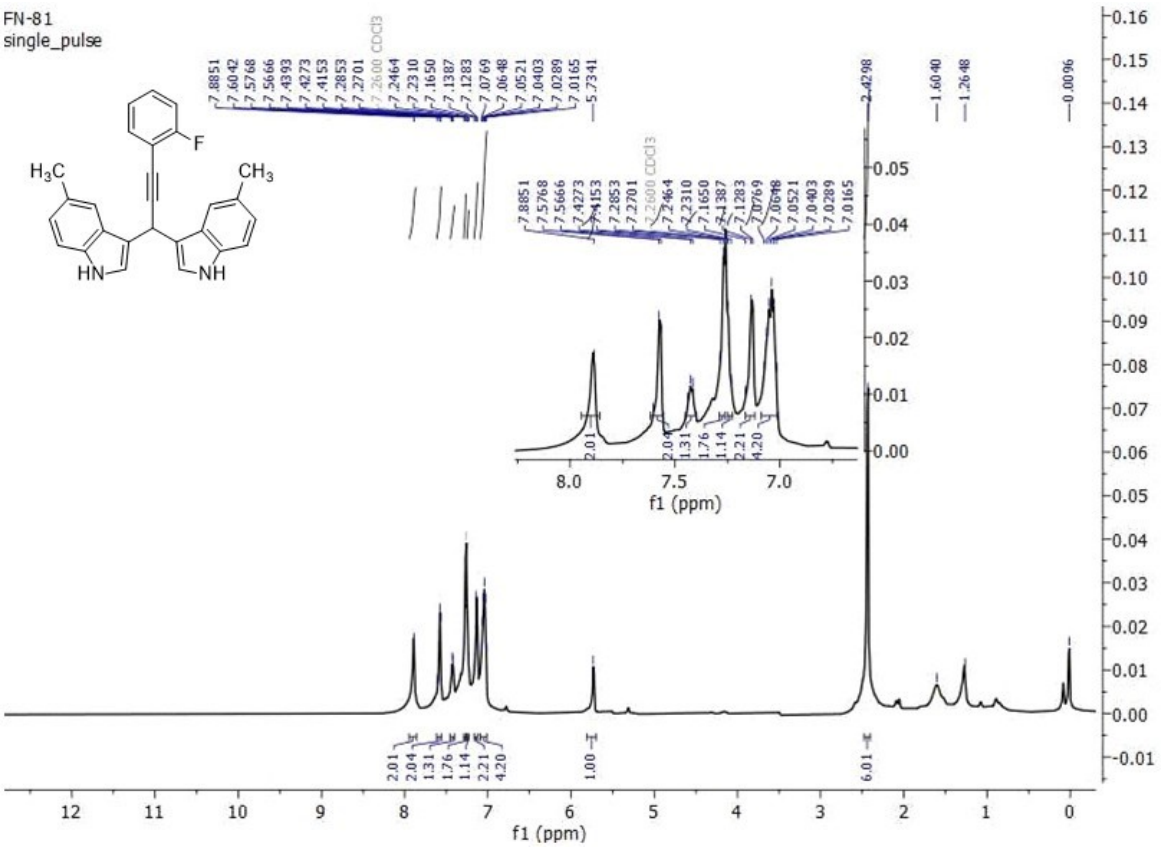


Figure S55 ^{1}H-NMR spectrum of **17k** in $CDCl_3$.

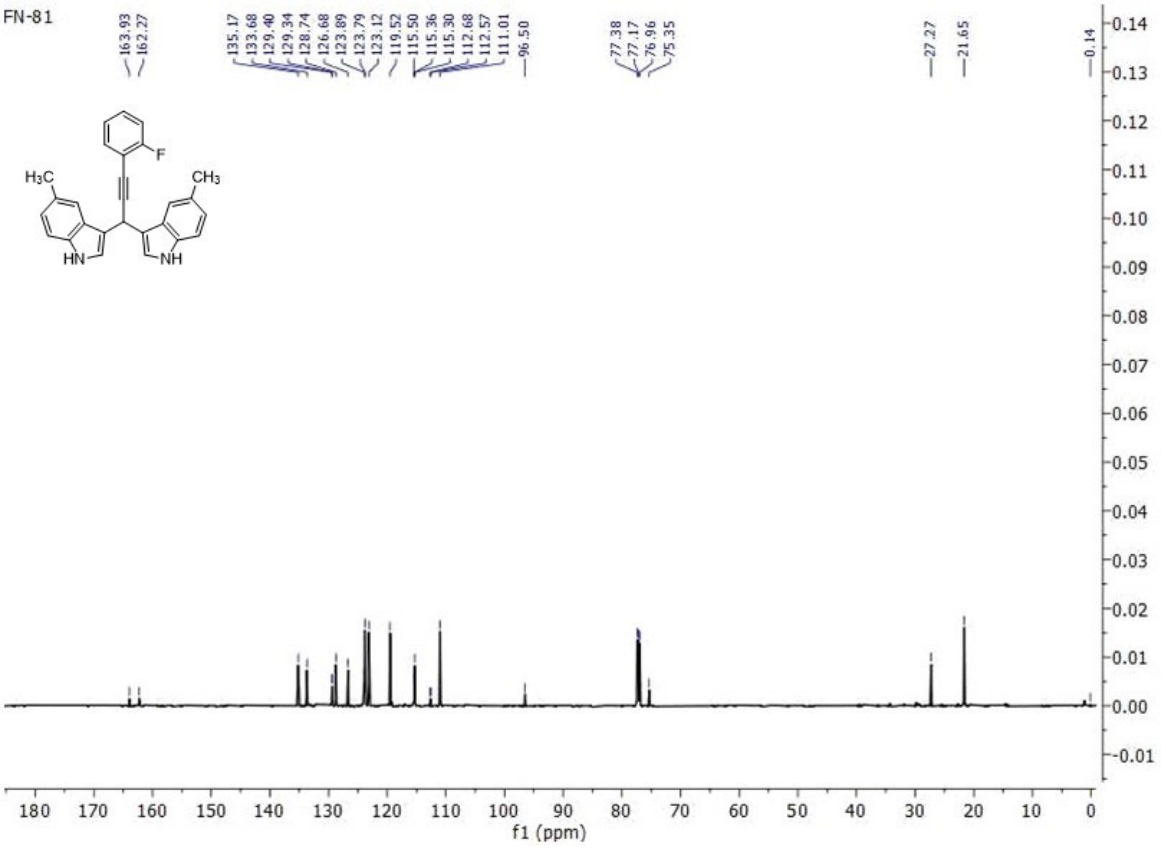


Figure S56^{13}C-NMR spectrum of **17k** in $CDCl_3$.

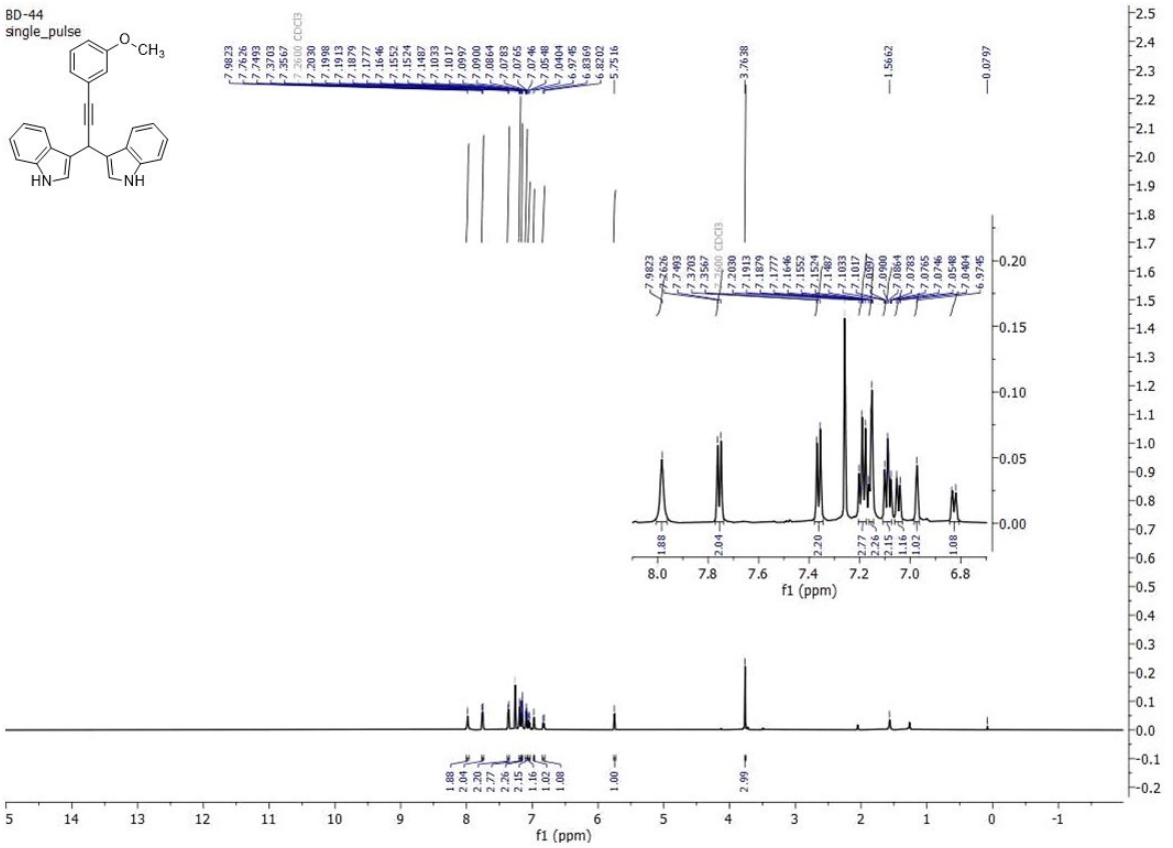


Figure S57 ^{1}H-NMR spectrum of **18a** in $CDCl_3$.

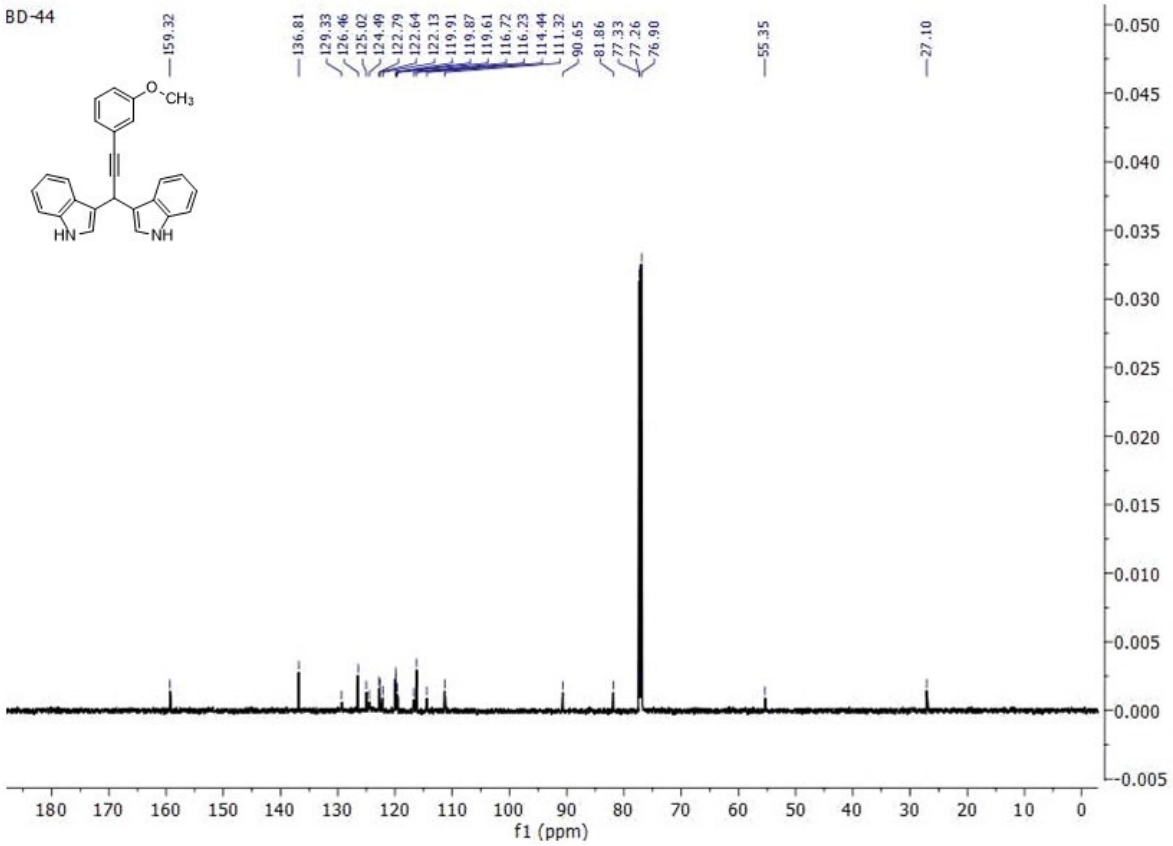


Figure S58 ^{13}C-NMR spectrum of **18a** in $CDCl_3$.

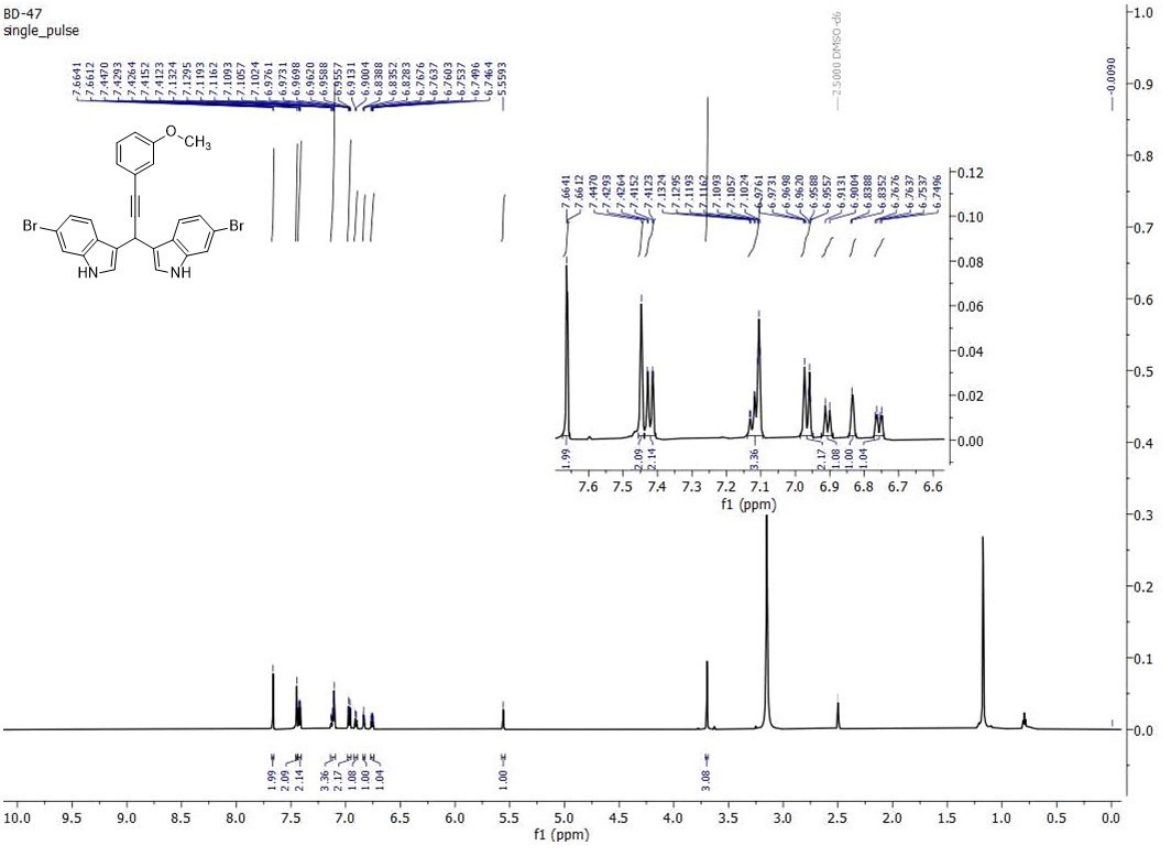


Figure S59 ^{1}H-NMR spectrum of **18d** in $CDCl_3$.

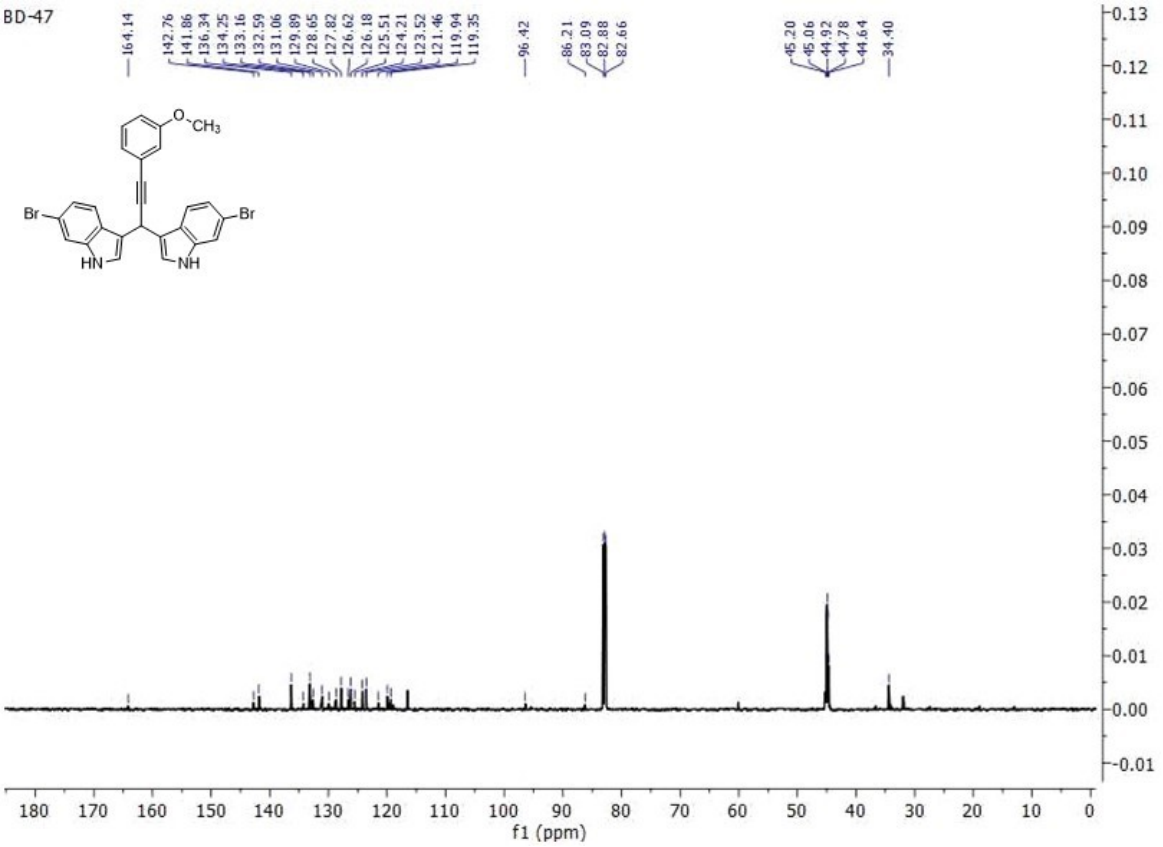


Figure S60 ^{13}C-NMR spectrum of **18d** in $CDCl_3$.

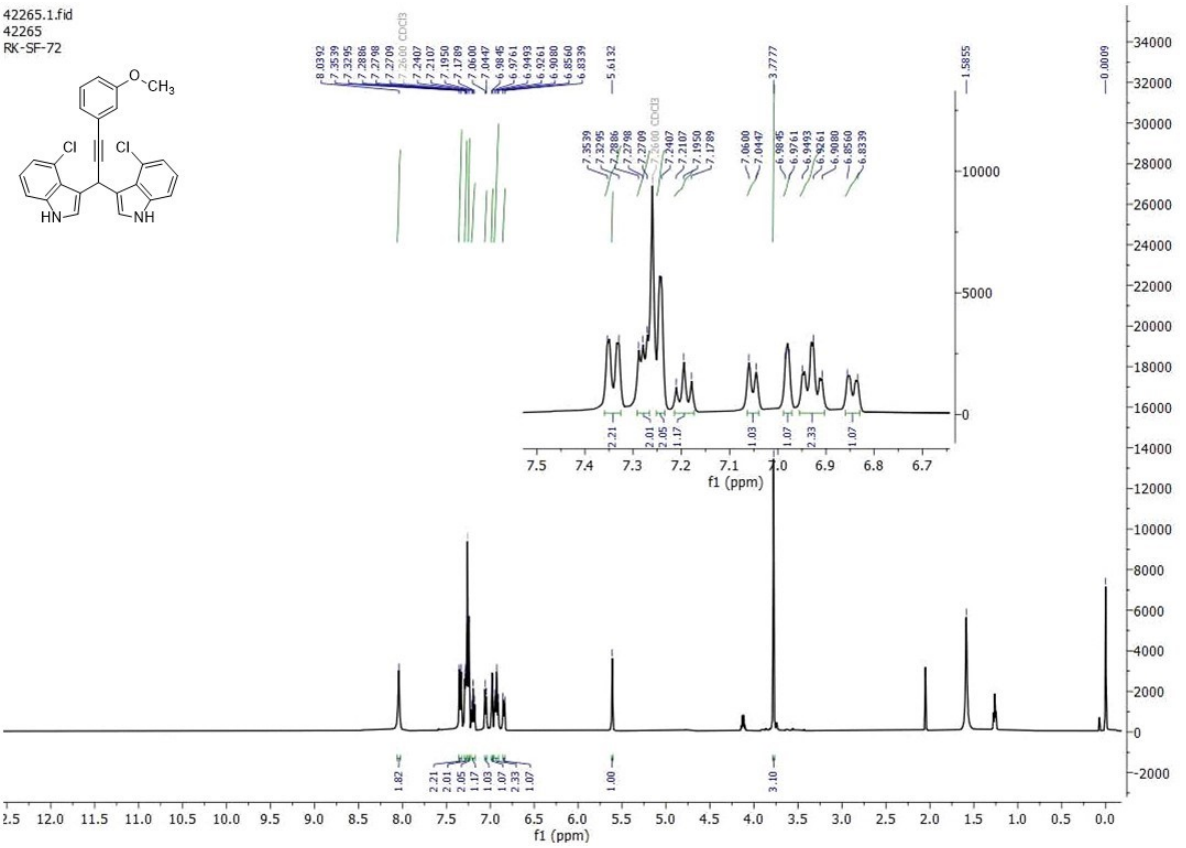


Figure S61 ^{1}H-NMR spectrum of **18e** in $CDCl_3$.

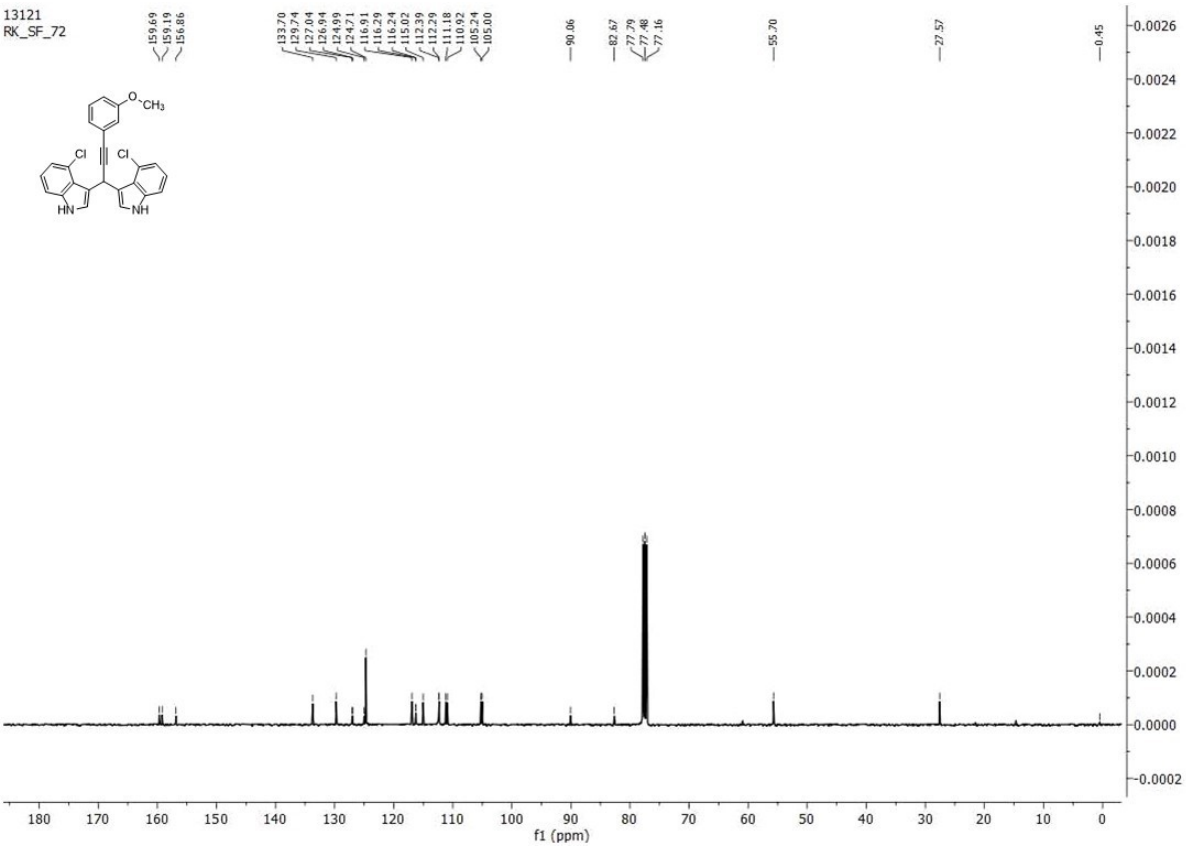


Figure S62 ^{13}C-NMR spectrum of **18e** in $CDCl_3$.

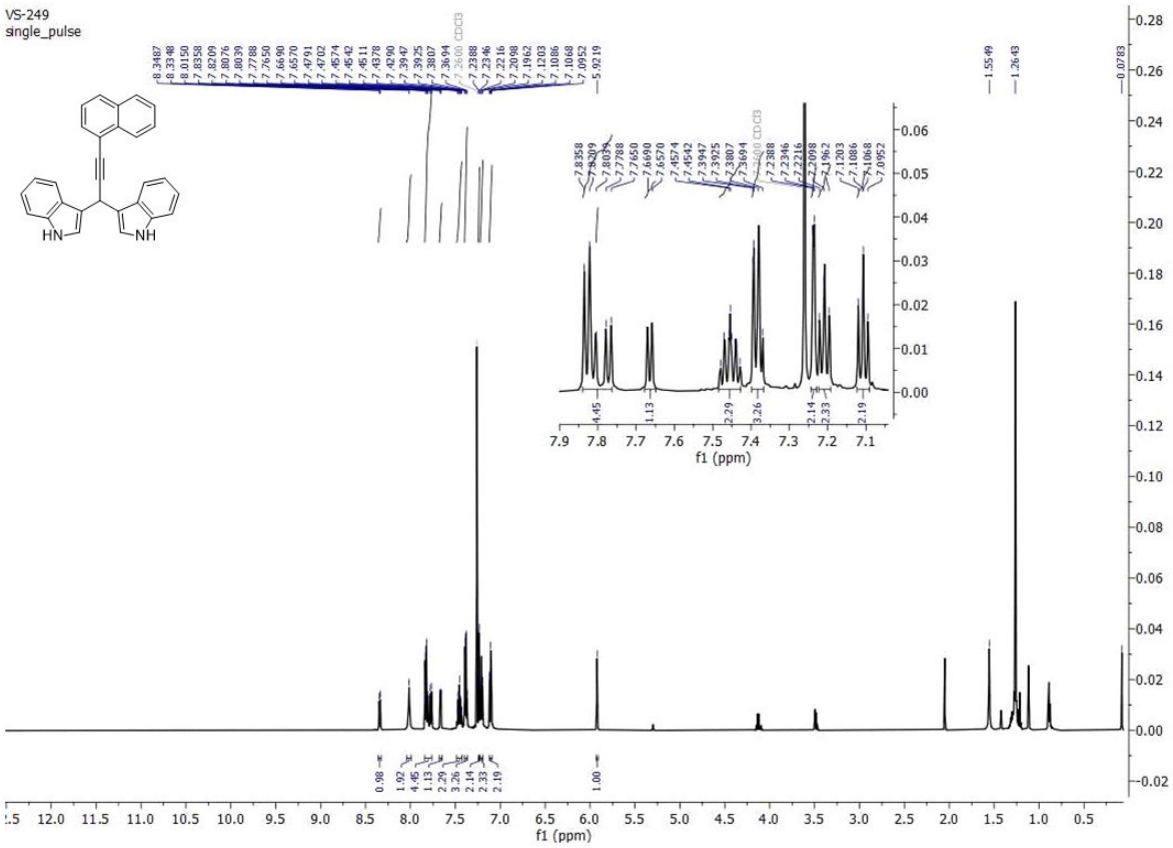


Figure S63 ^{1}H-NMR spectrum of **19a** in $CDCl_3$.

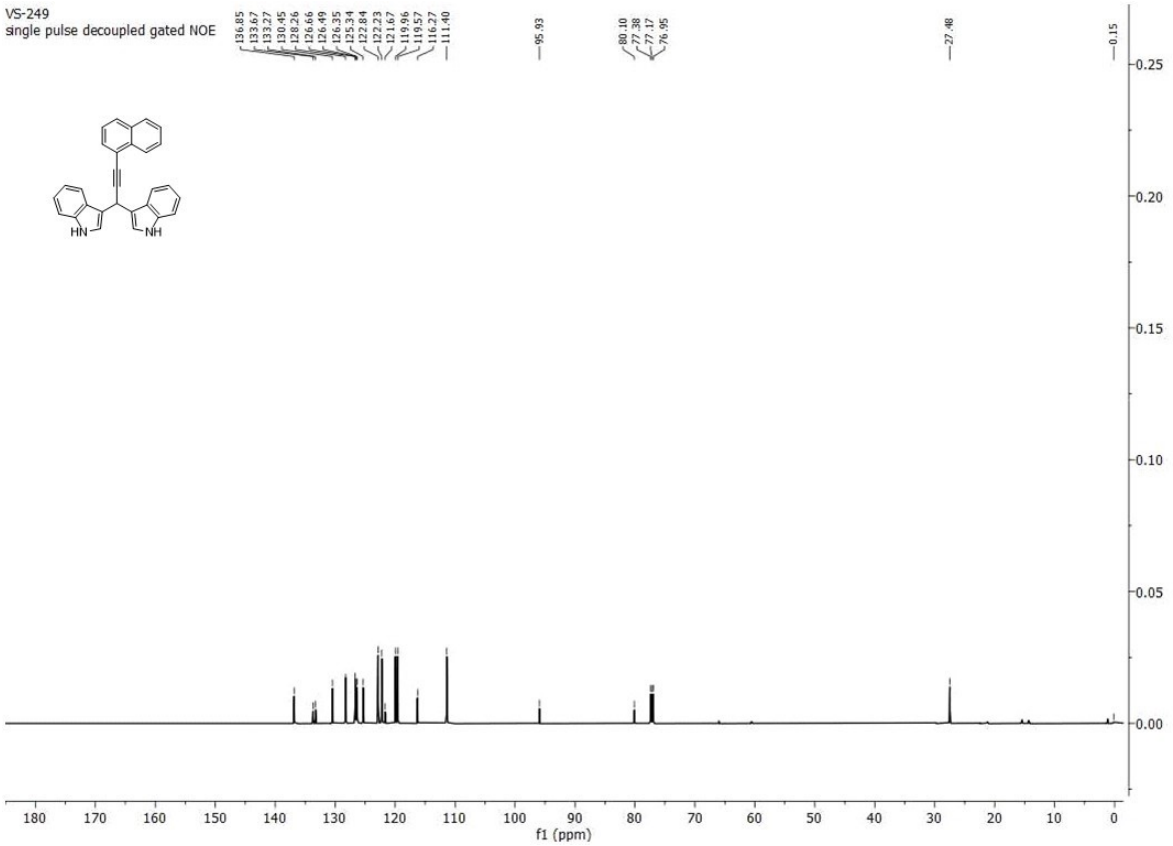


Figure S64 ^{13}C-NMR spectrum of **19a** spectrum in $CDCl_3$.

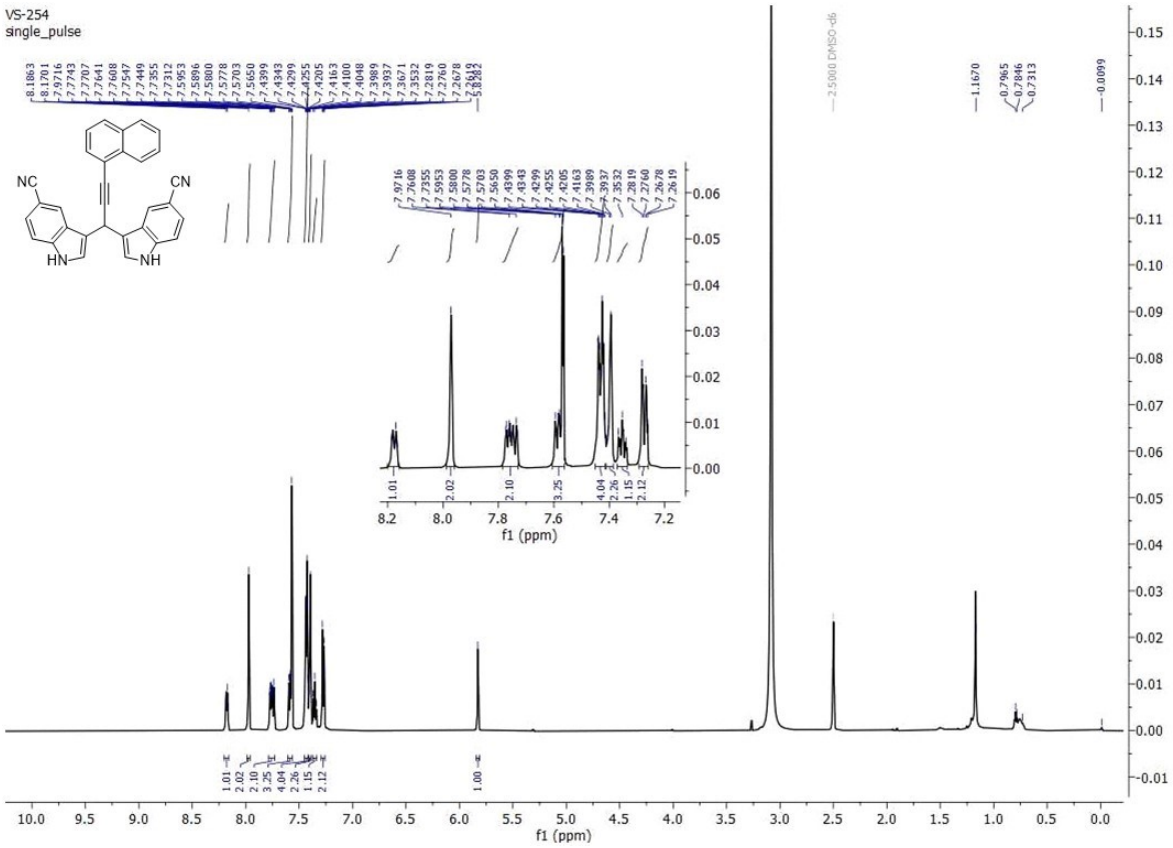


Figure S65 ^{1}H-NMR spectrum of **19f** in $CDCl_3$ + DMSO-d_6.

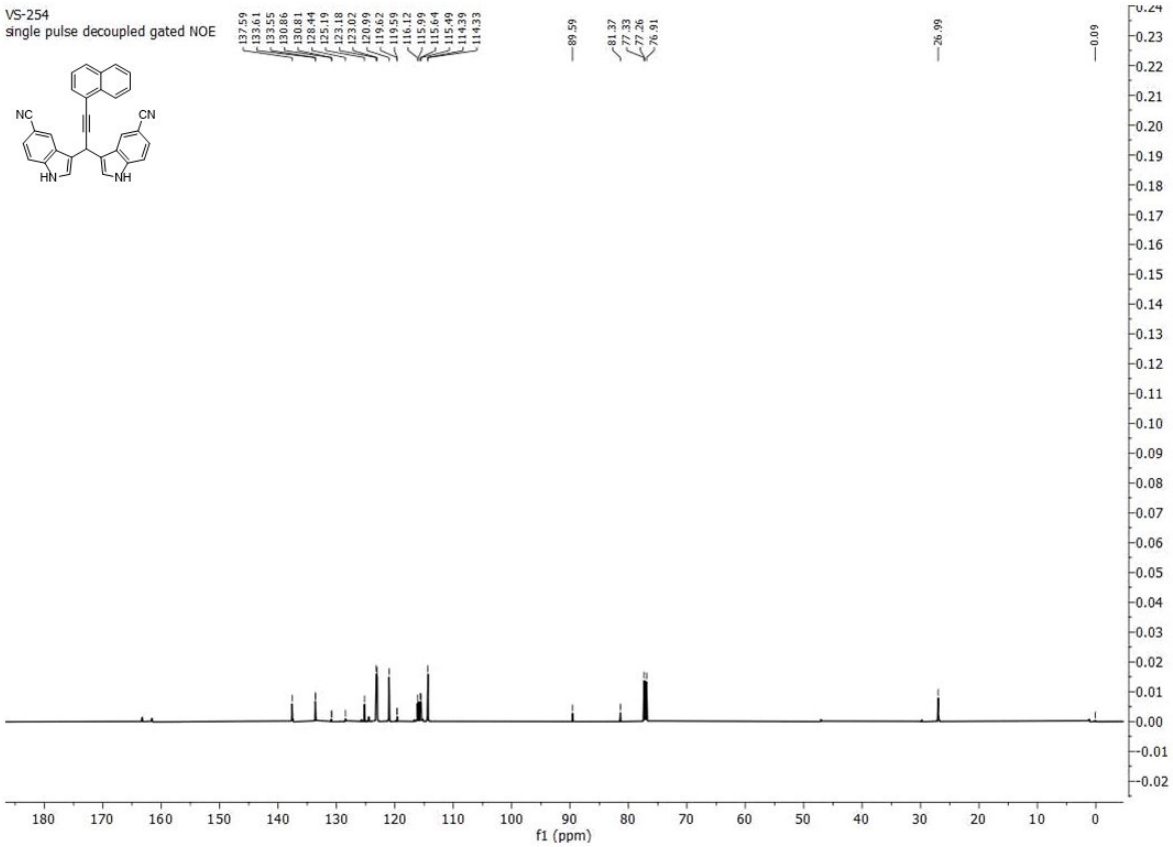


Figure S66 ^{13}C-NMR spectrum of **19f** in $CDCl_3$.

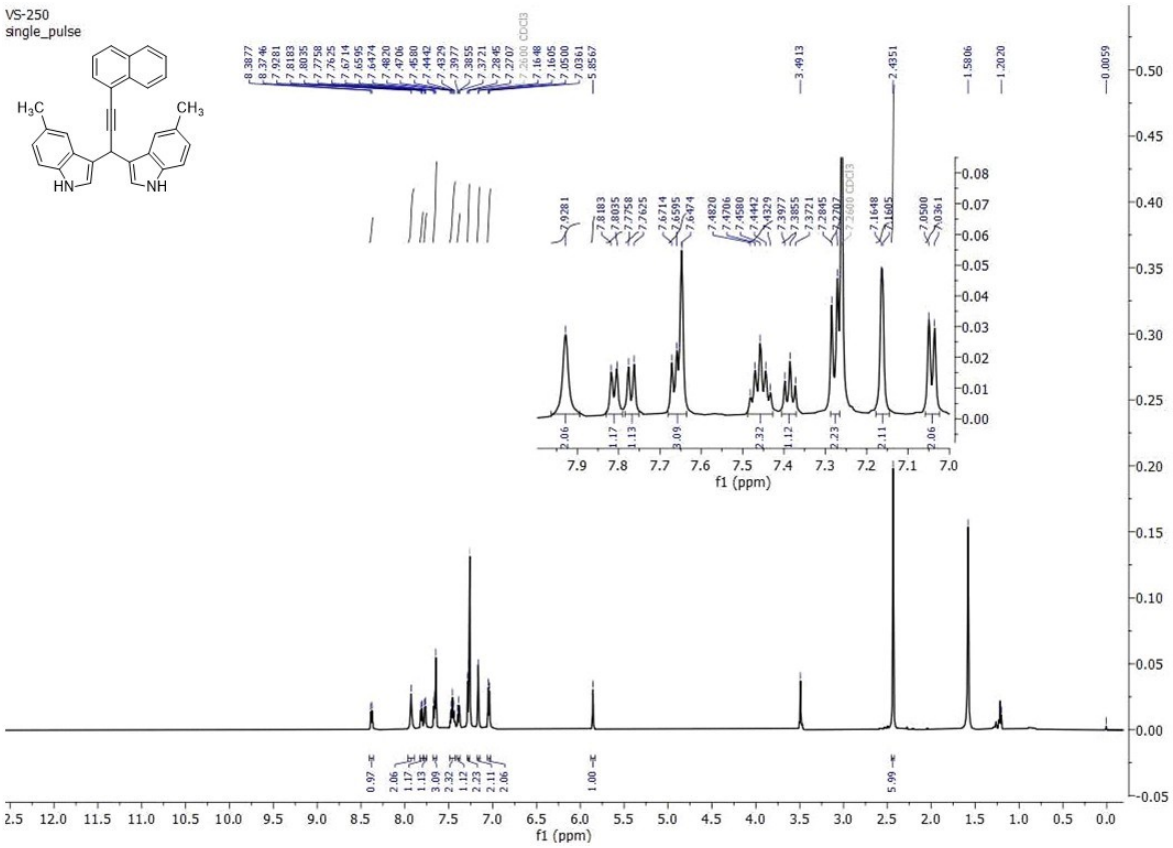


Figure S67 ^{1}H-NMR spectrum of **19k** in $CDCl_3$.

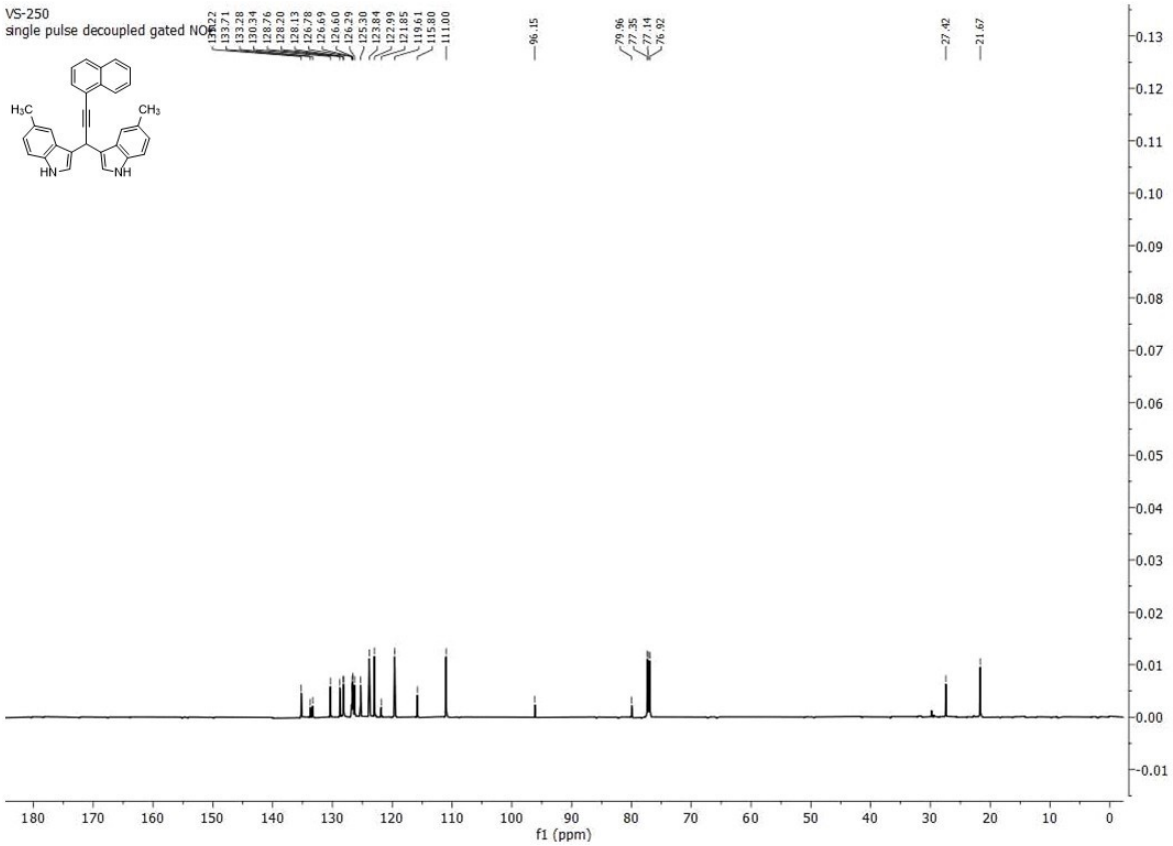


Figure S68 ^{13}C-NMR spectrum of **19k** in $CDCl_3$.

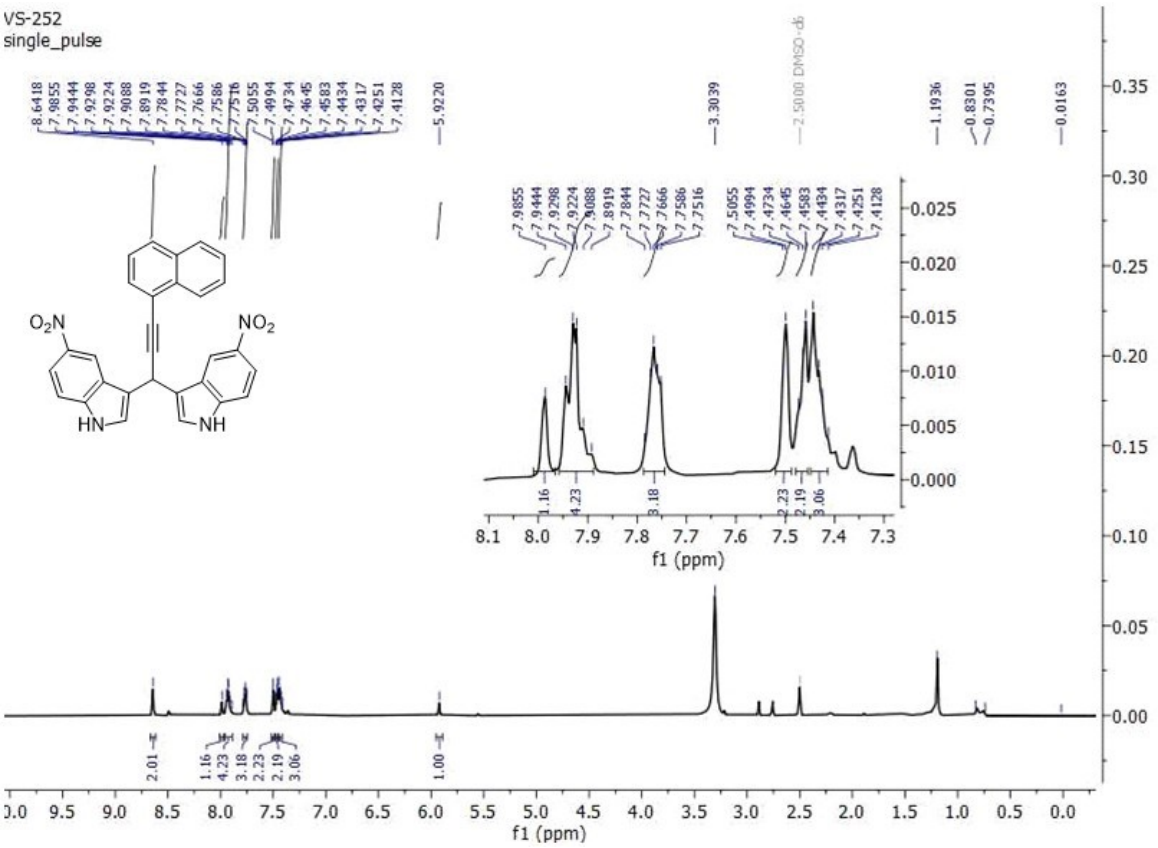


Figure S69 ^{1}H-NMR spectrum of **19n** in $CDCl_3$ + DMSO-d_6.

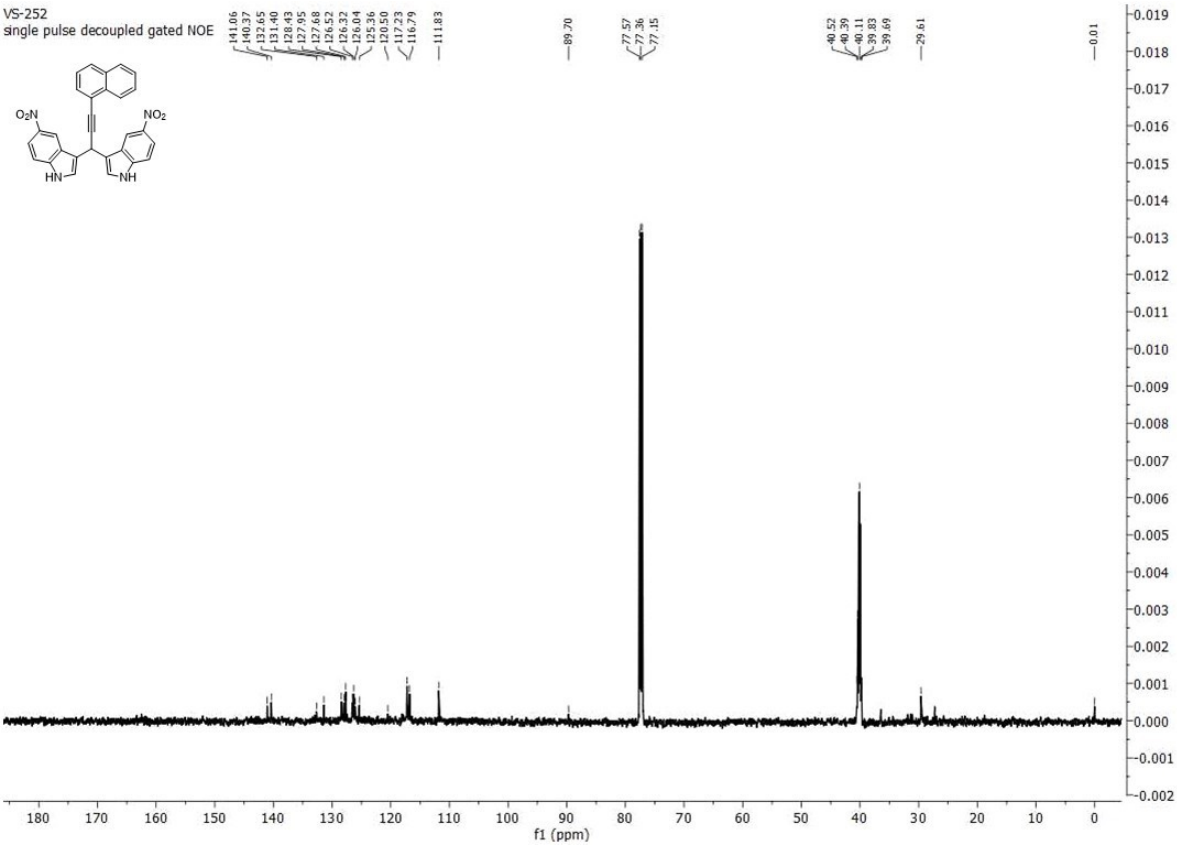


Figure S70 ^{13}C-NMR spectrum of **19n** in $CDCl_3$ + DMSO-d_6.

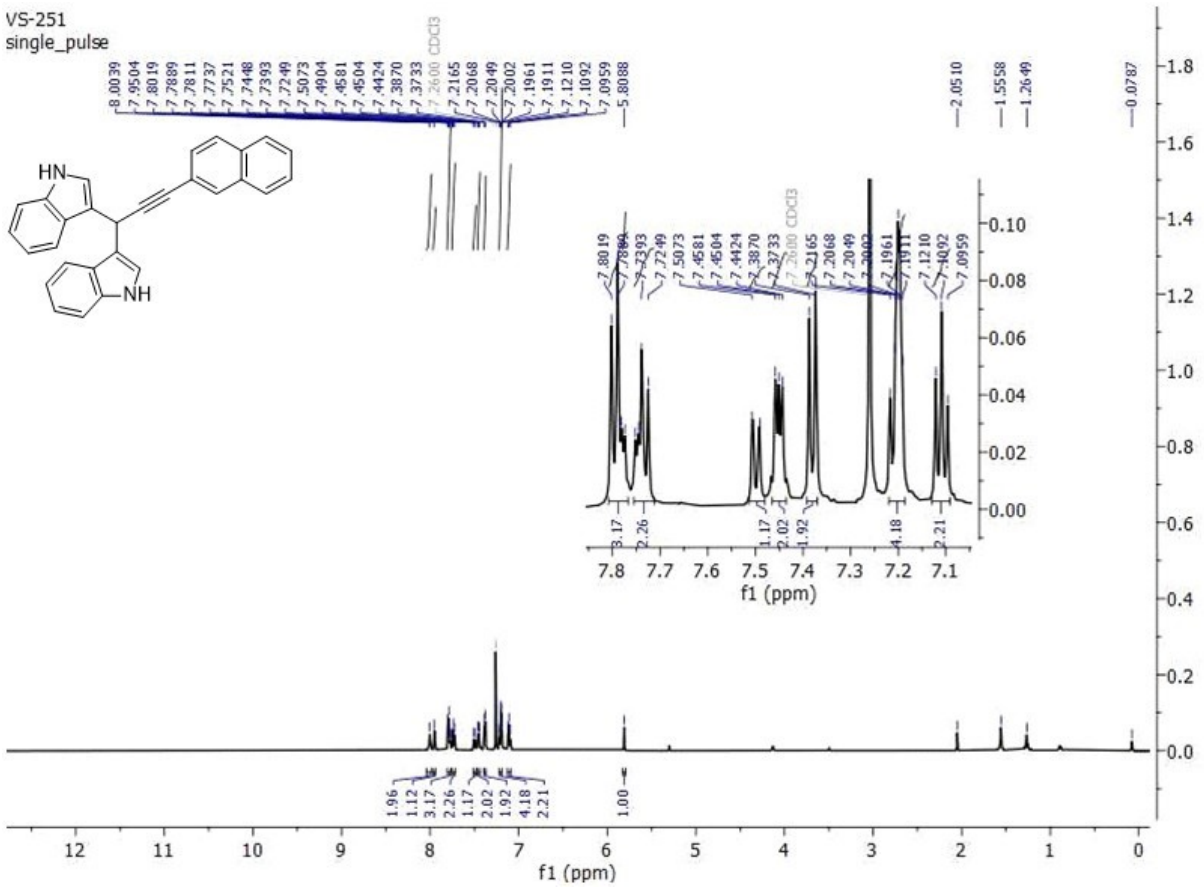


Figure S71 ^{1}H-NMR spectrum of **20a** in $CDCl_3$.

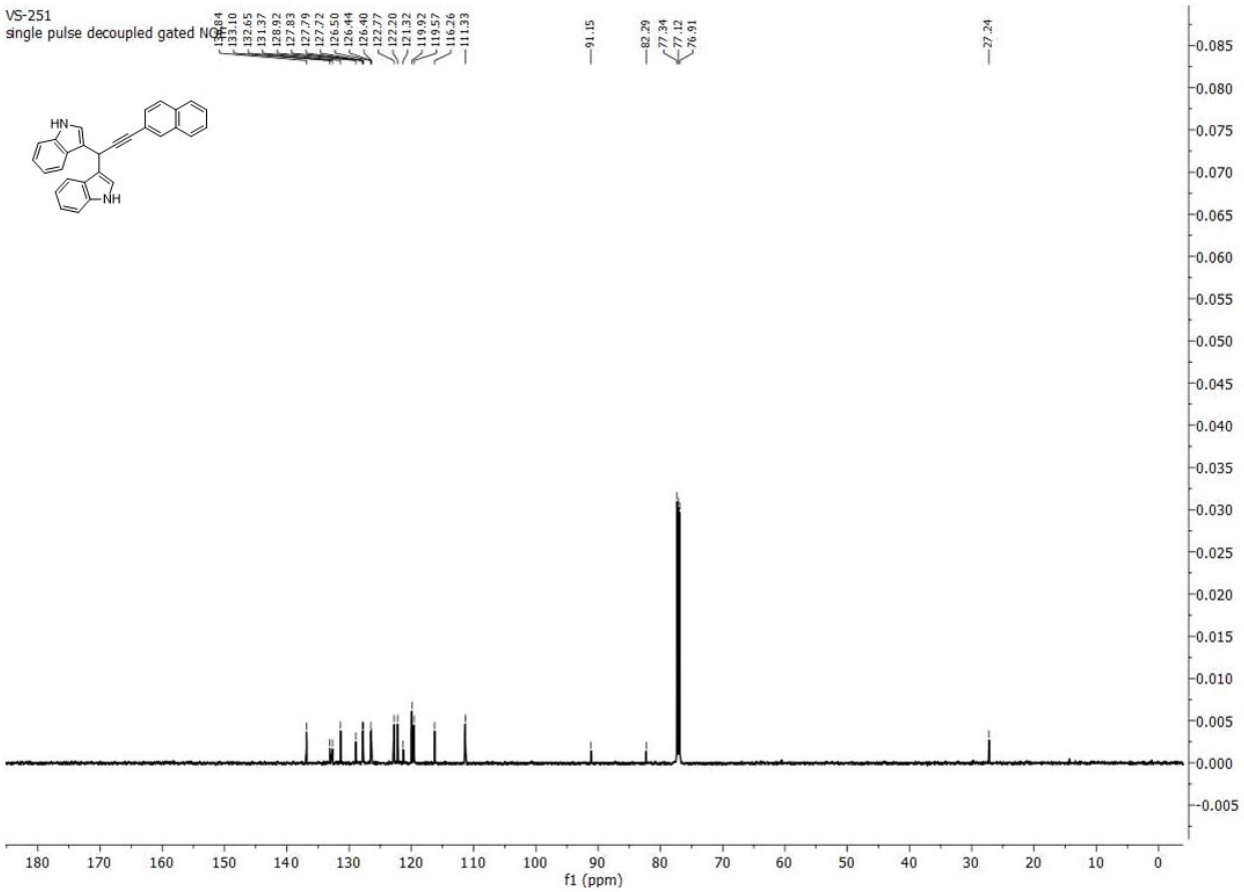


Figure S72 ^{13}C-NMR spectrum of **20a** in $CDCl_3$.

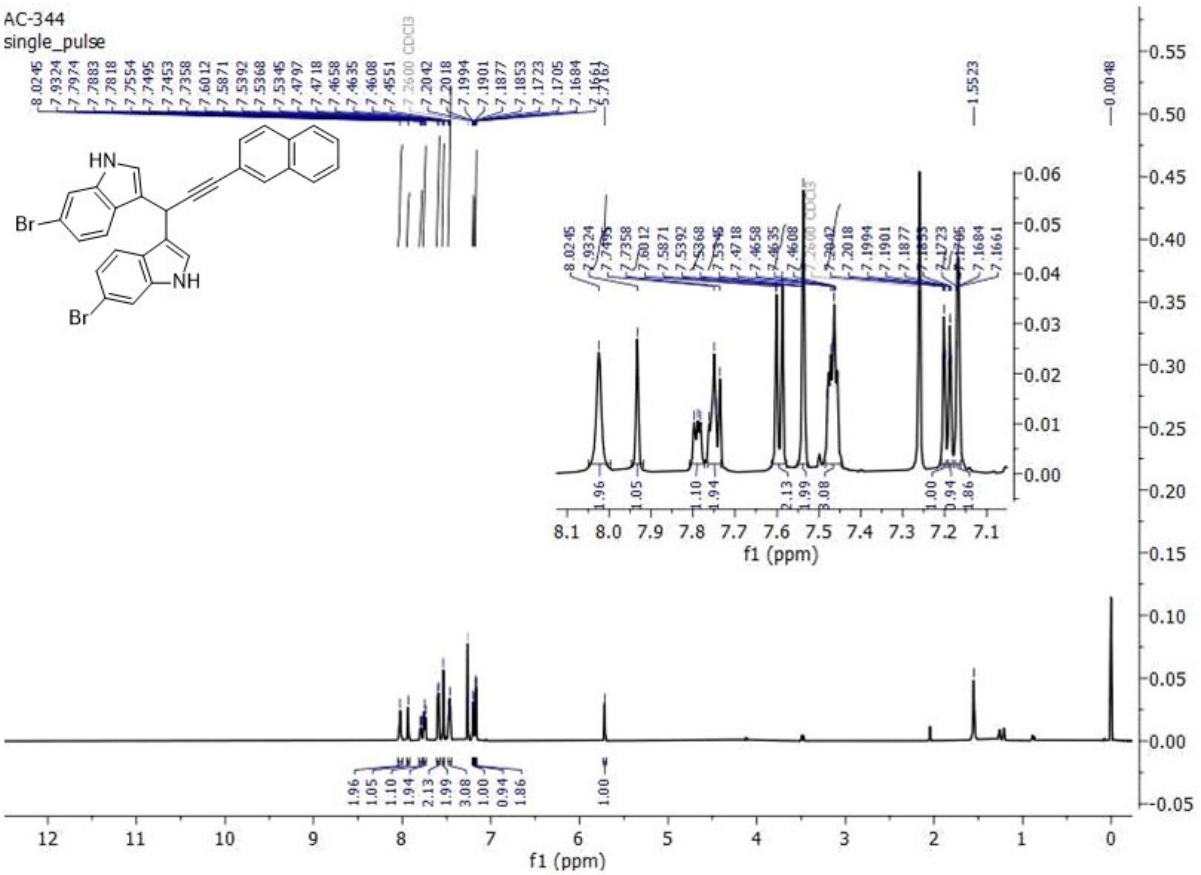


Figure S73 ^{1}H-NMR spectrum of **20d** in $CDCl_3$.

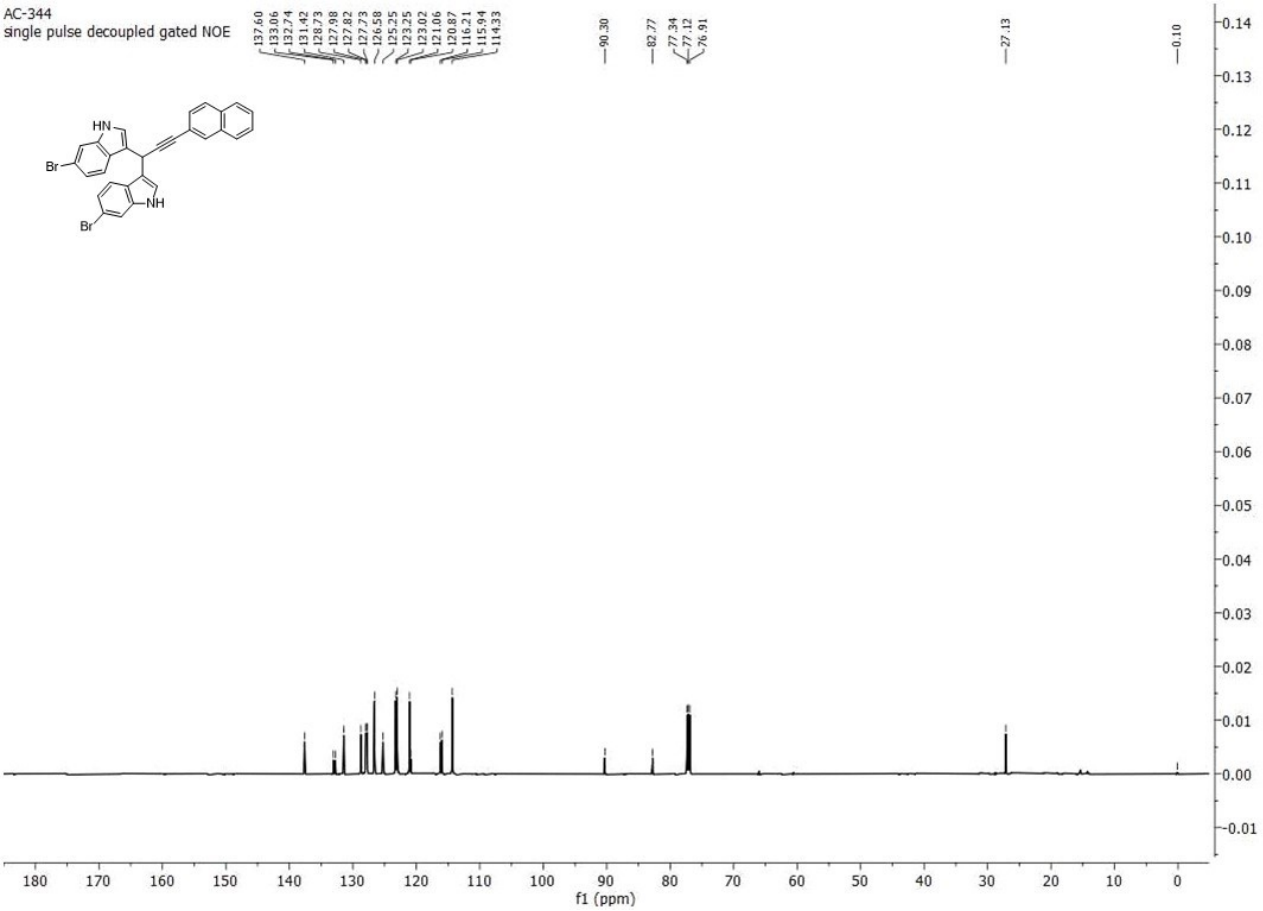


Figure S74 ^{13}C-NMR spectrum of **20d** in $CDCl_3$.

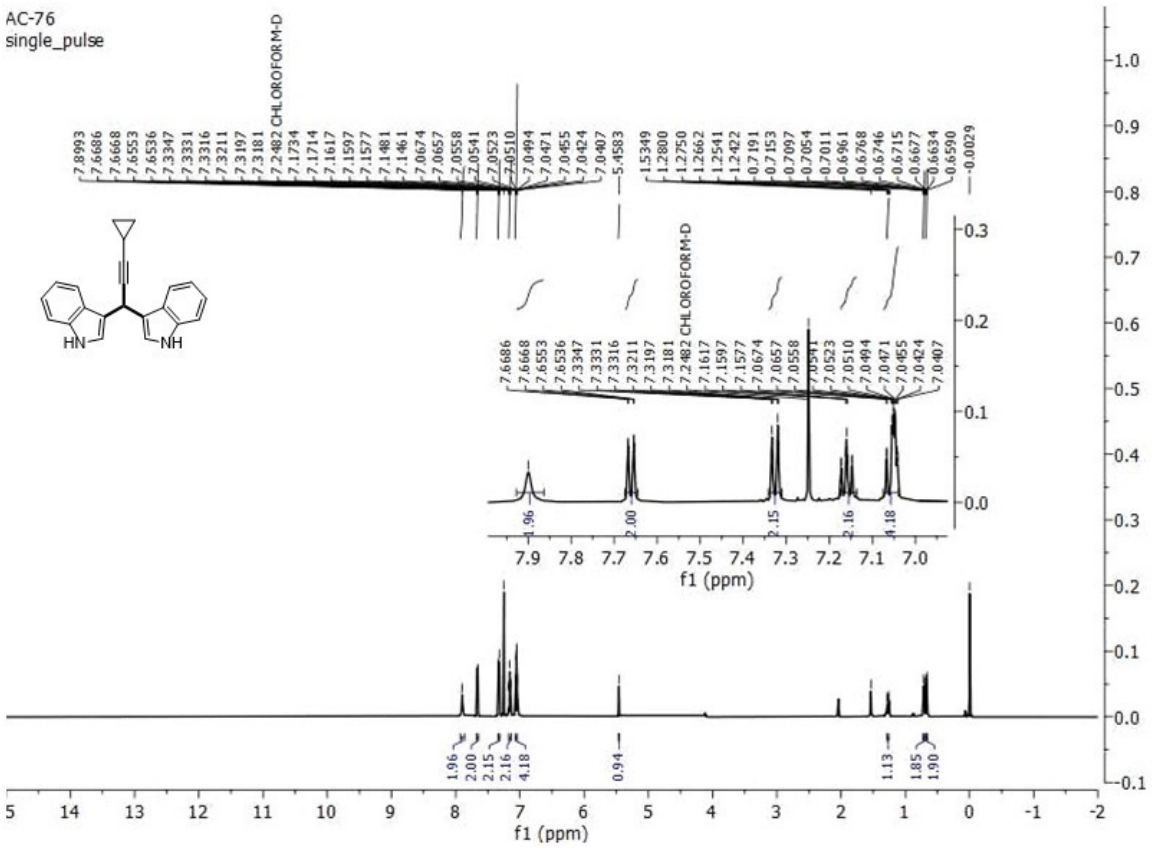


Figure S75 ^{1}H-NMR spectrum of **21a** in $CDCl_3$.

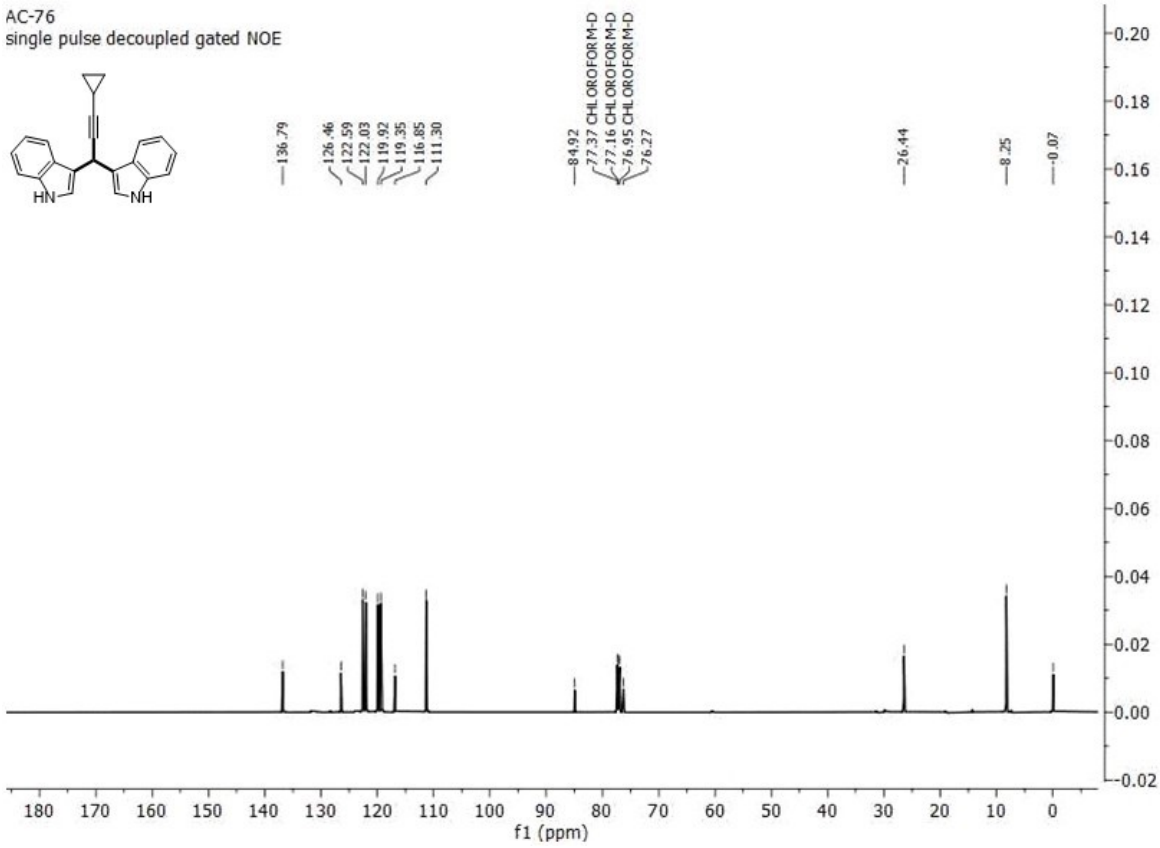


Figure S76 ^{13}C-NMR spectrum of **21a** in $CDCl_3$.

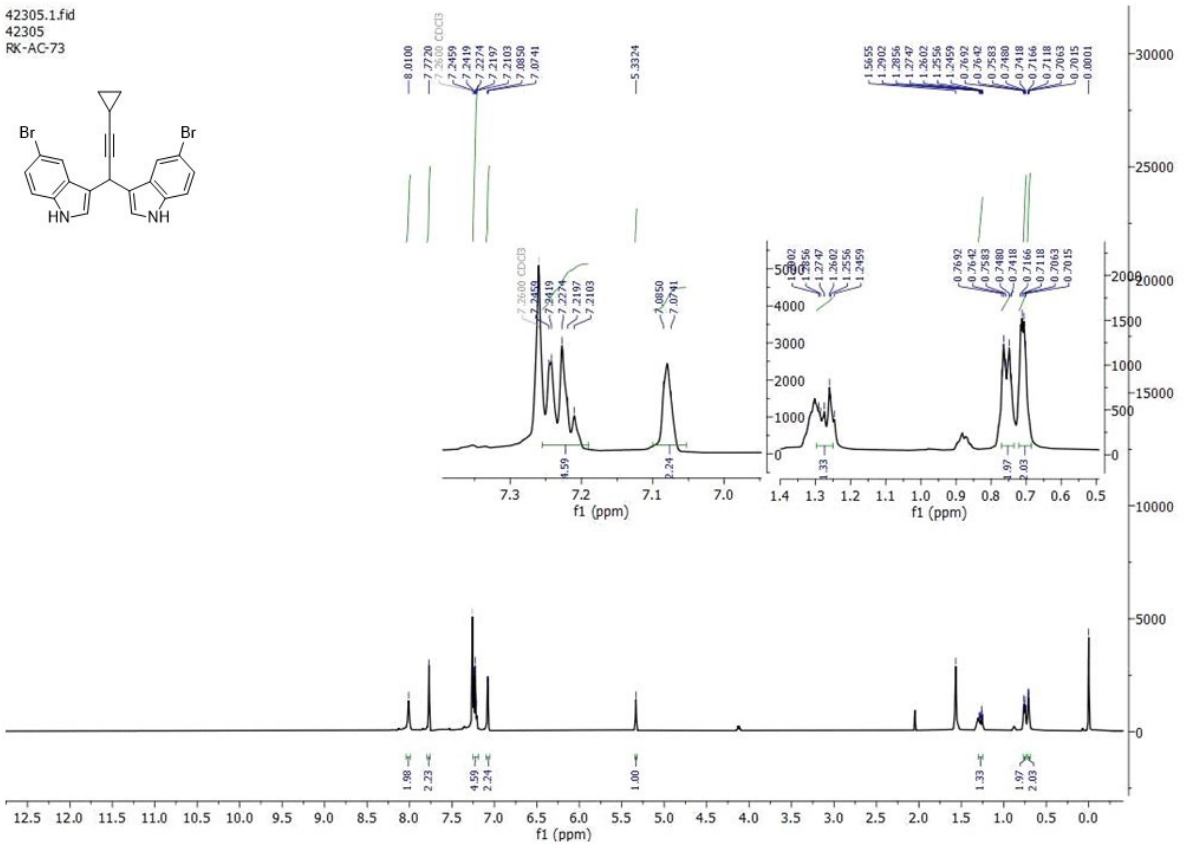


Figure S77 ^{1}H-NMR spectrum of **21c** in $CDCl_3$.

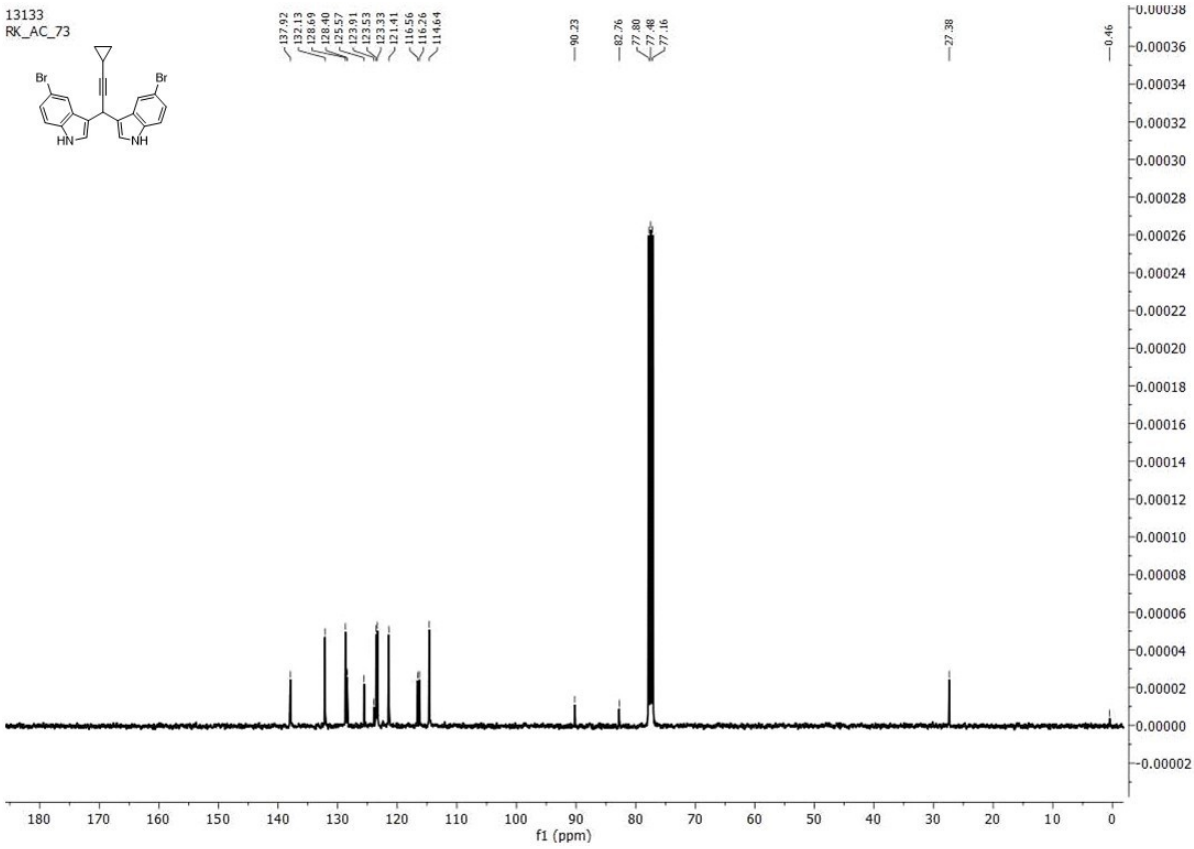


Figure S78 ^{13}C-NMR spectrum of **21c** in $CDCl_3$.

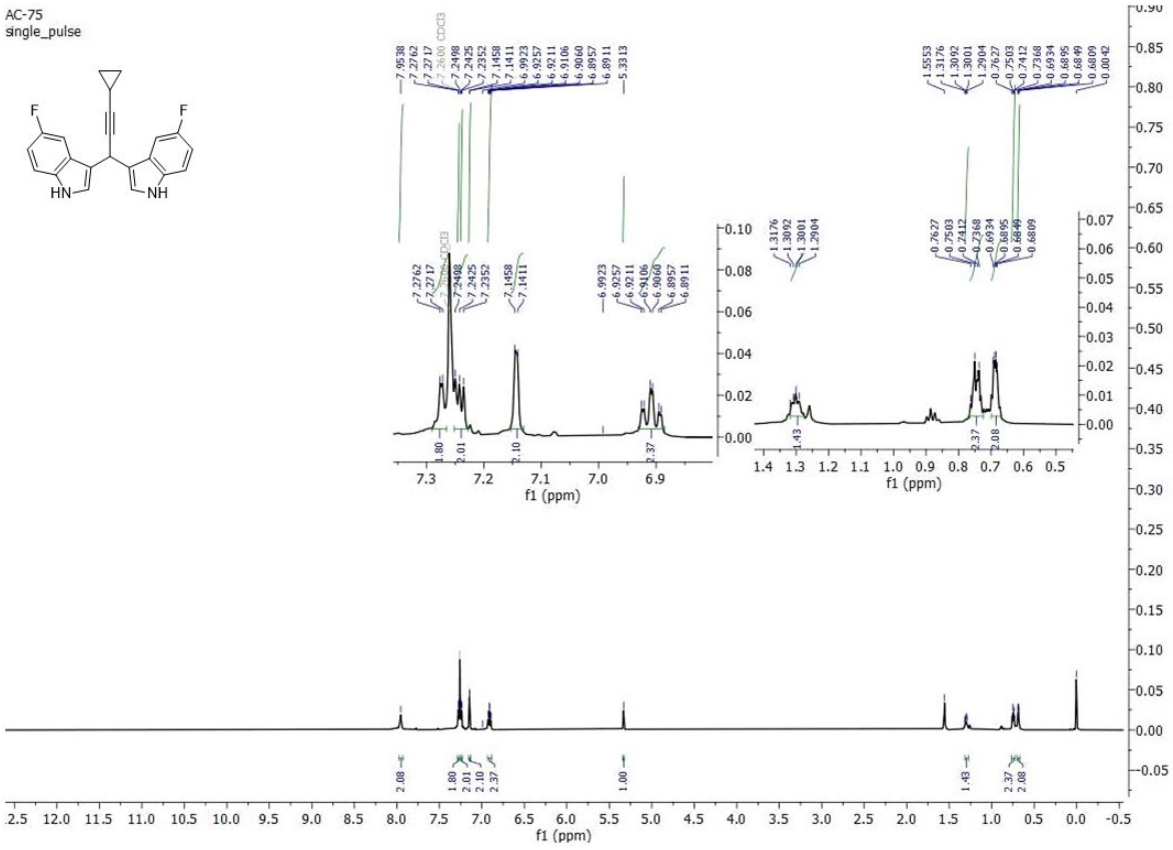


Figure S79 ^{1}H-NMR spectrum of **21h** in $CDCl_3$.

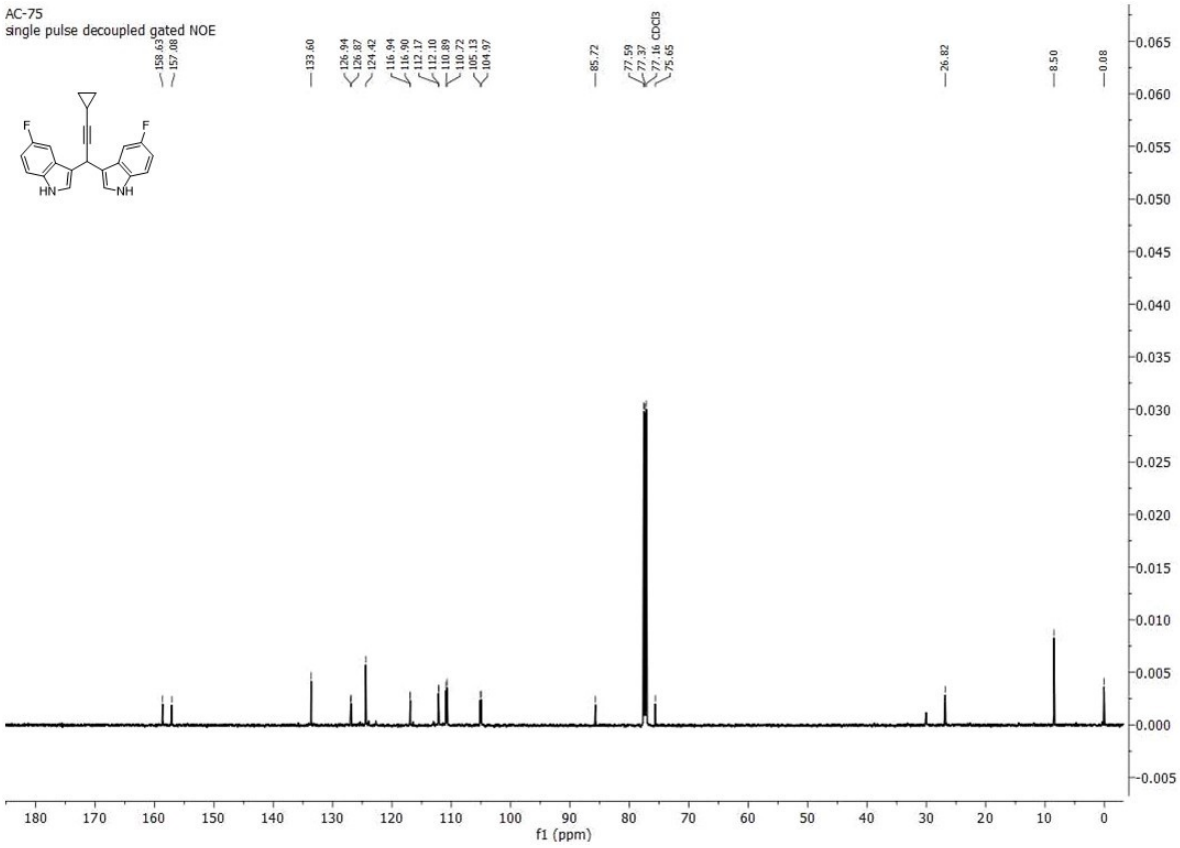


Figure S80 ^{13}C-NMR spectrum of **21h** in $CDCl_3$.

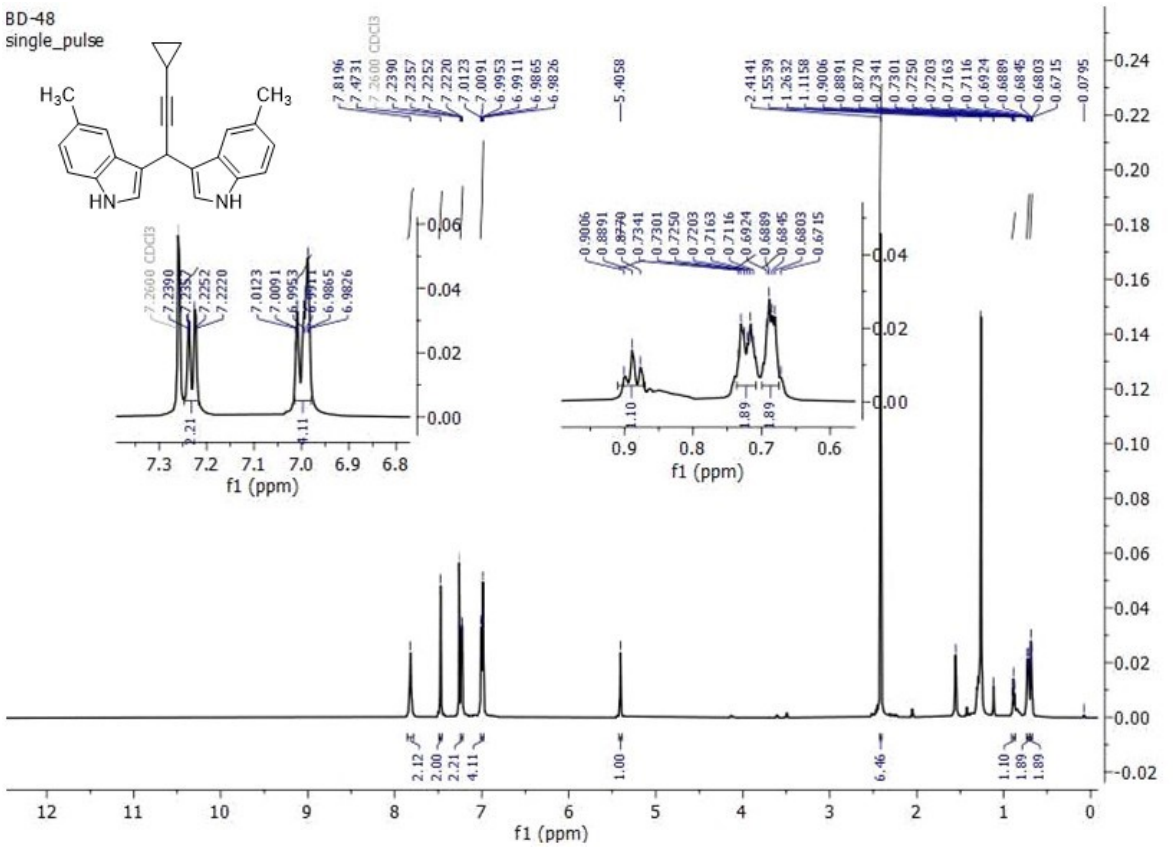


Figure S81 ^{1}H-NMR spectrum of **21k** in $CDCl_3$.

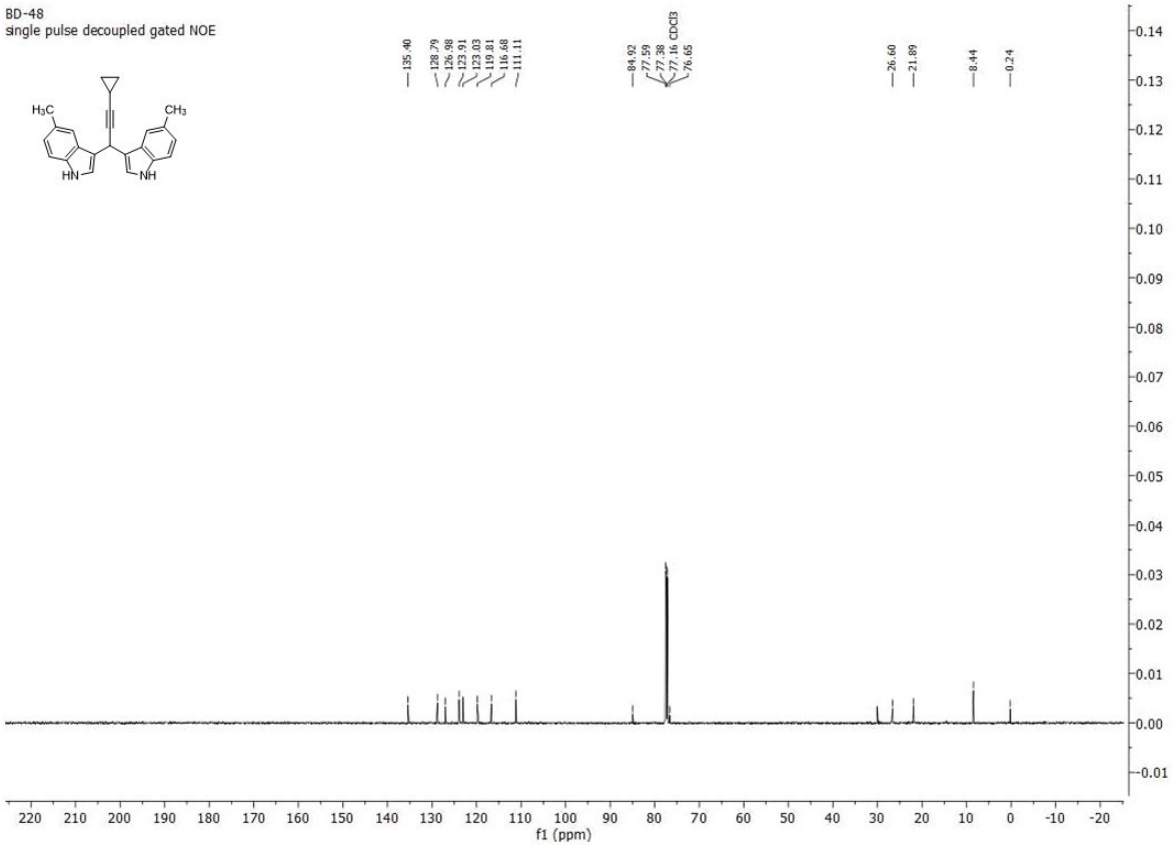


Figure S82 ^{13}C-NMR spectrum of **21k** in $CDCl_3$.

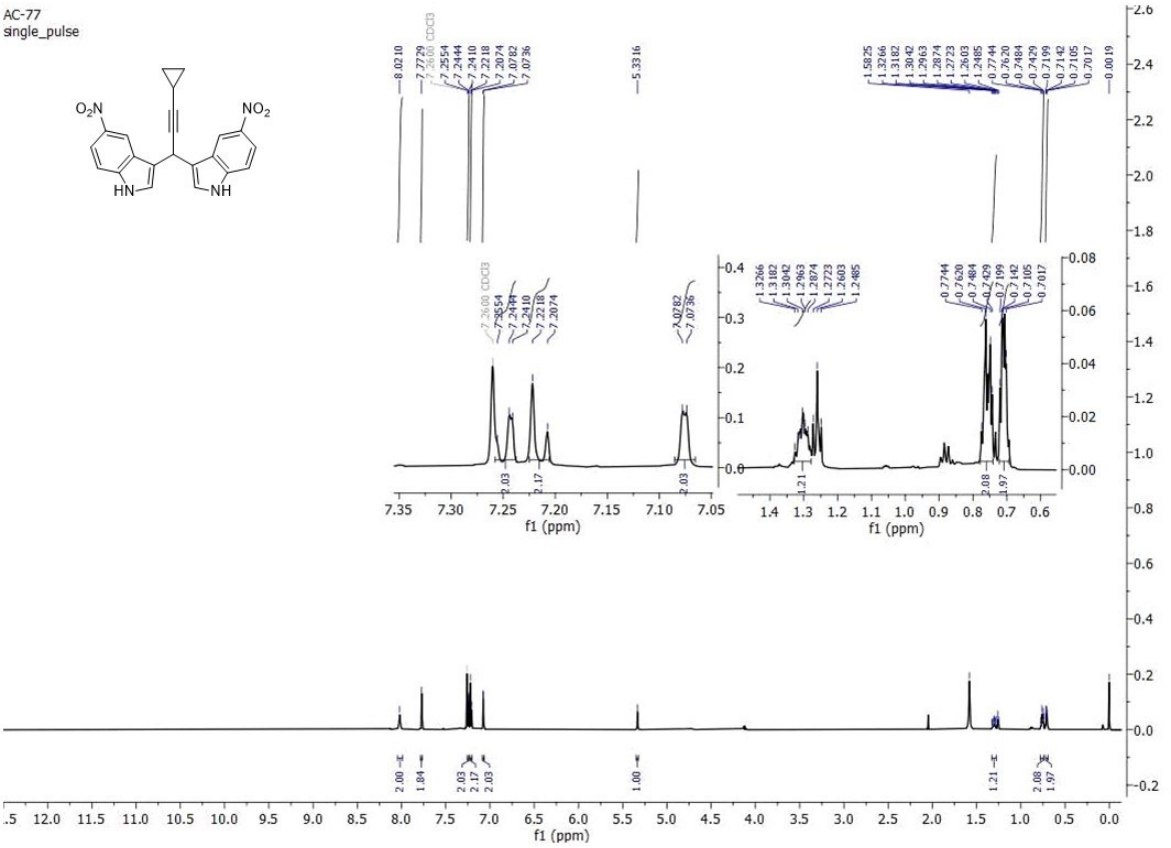


Figure S83 ^{1}H-NMR spectrum of **21n** in $CDCl_3$.

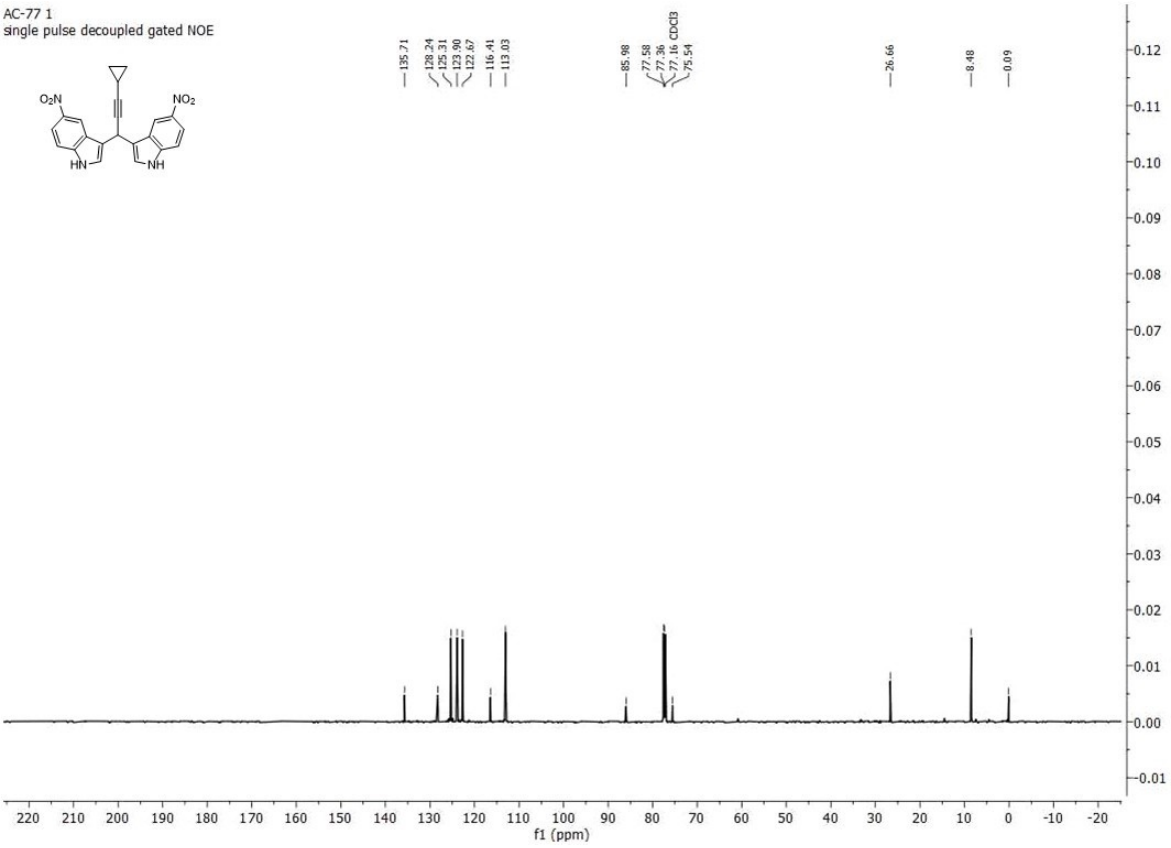


Figure S84 ^{13}C NMR spectrum of **21n** in $CDCl_3$.

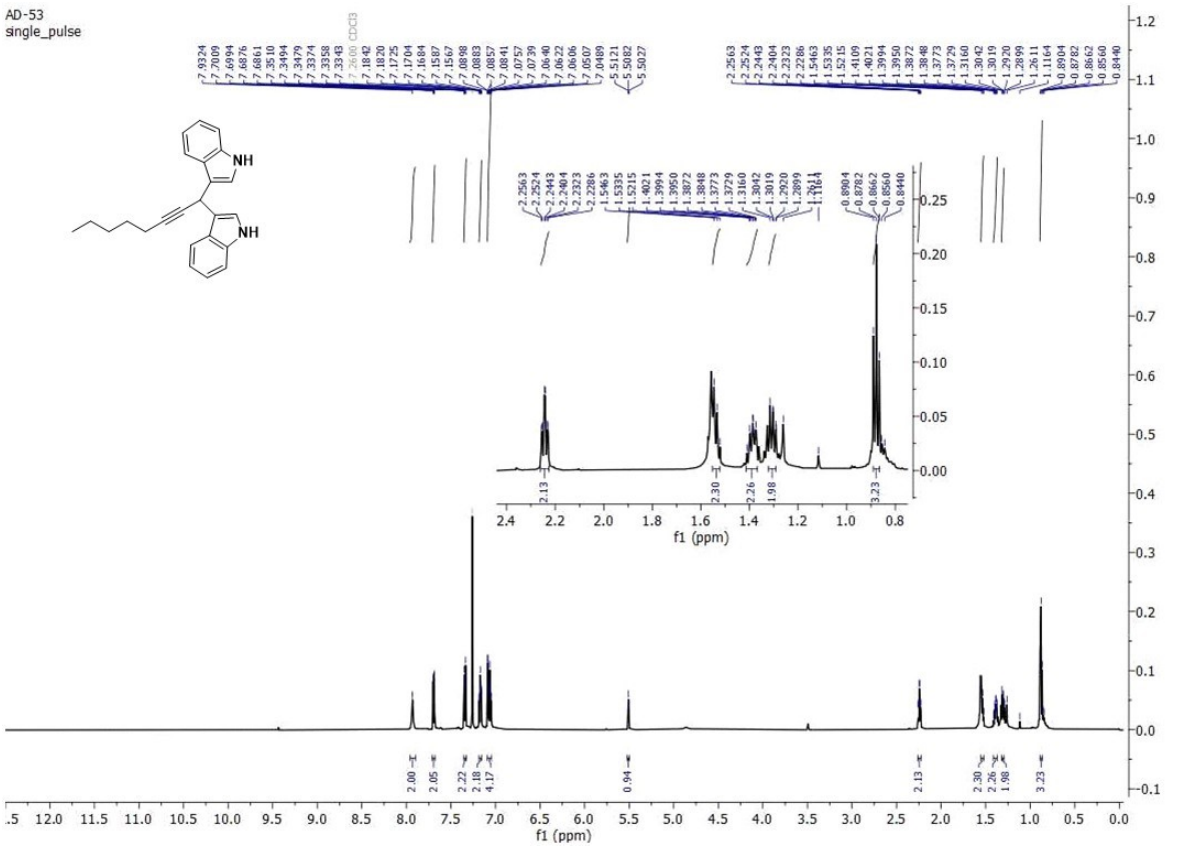


Figure S85 ^{1}H-NMR spectrum of **22a** in $CDCl_3$.

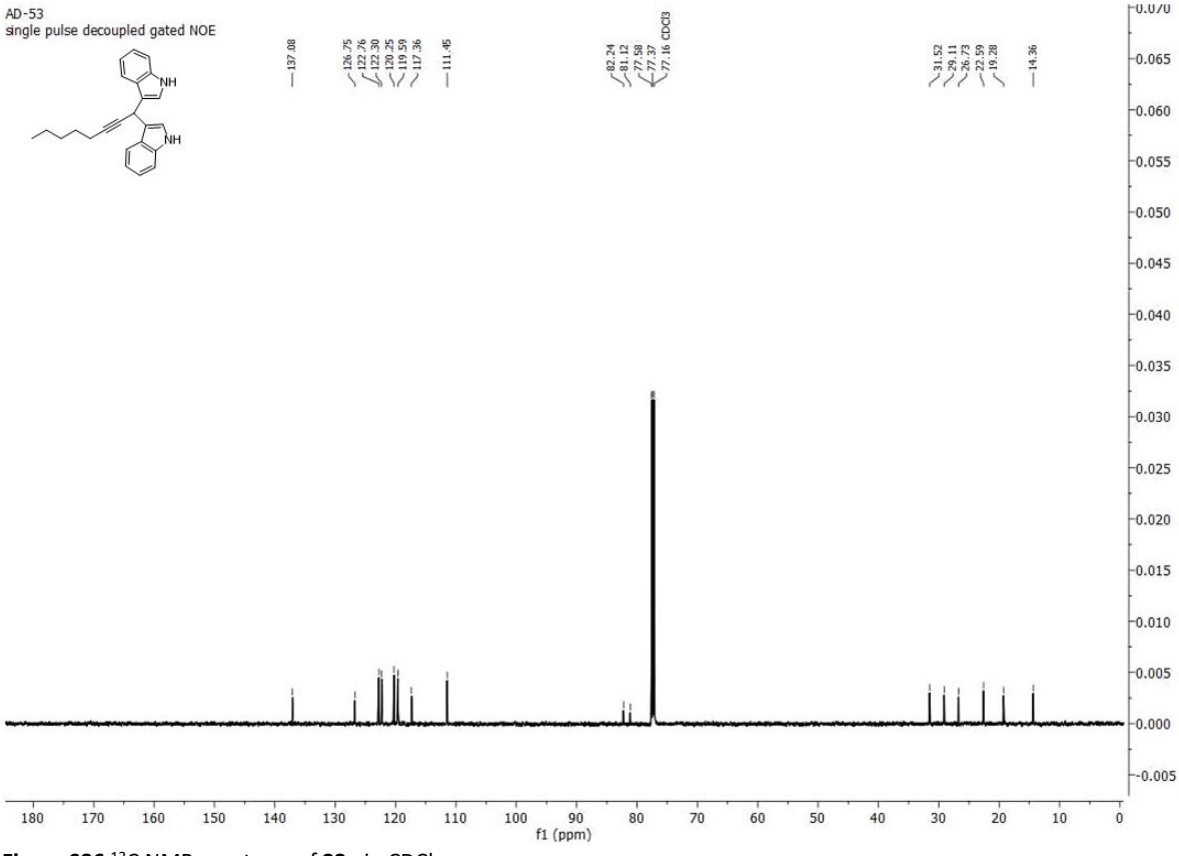


Figure S86 ^{13}C NMR spectrum of **22a** in $CDCl_3$.

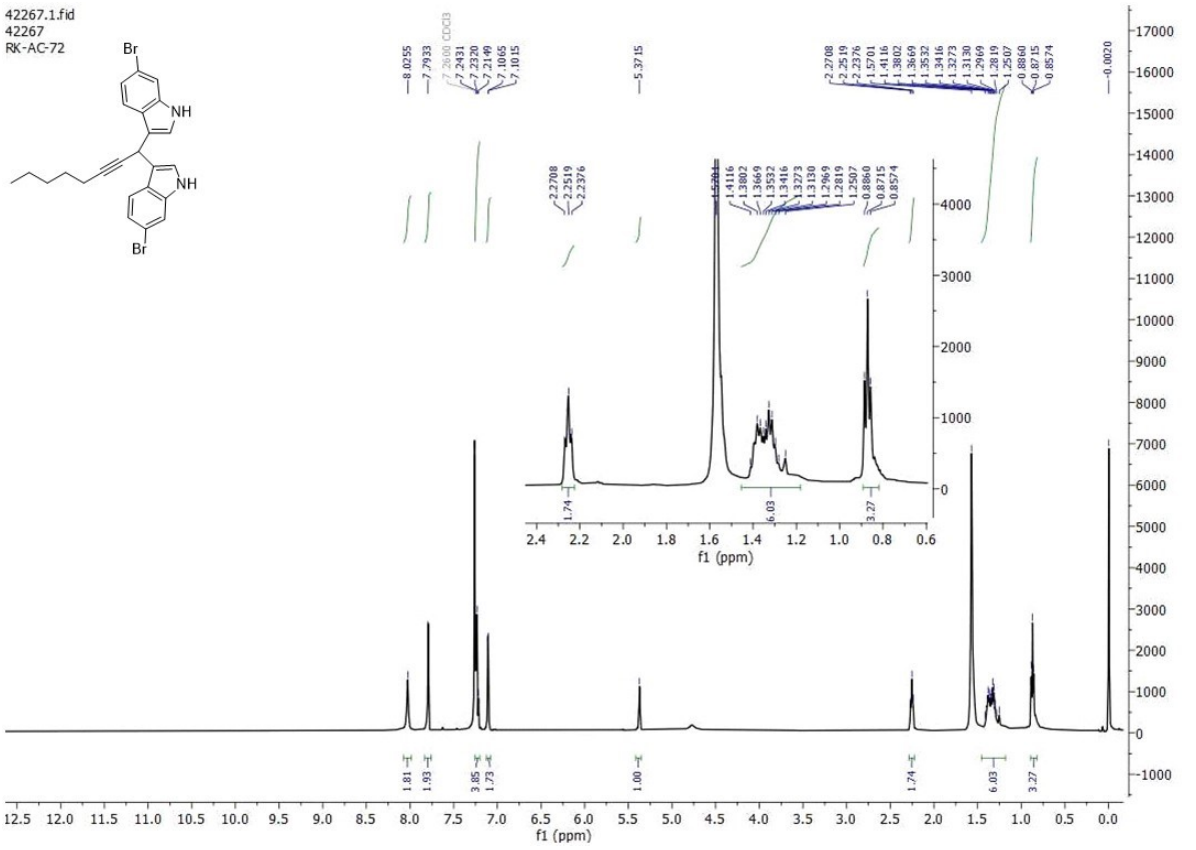


Figure S87 ^{1}H-NMR spectrum of **22c** in $CDCl_3$.

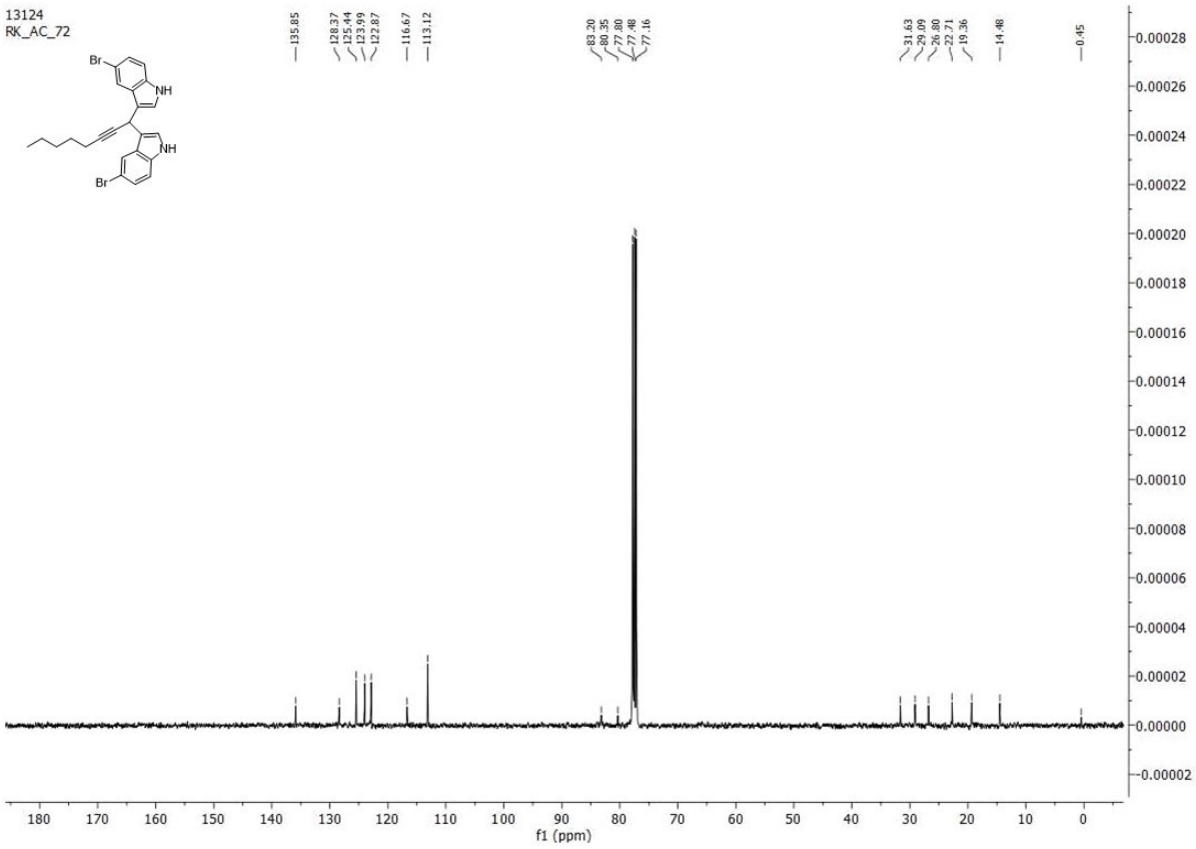


Figure S88 ^{13}C-NMR spectrum of **22c** in $CDCl_3$.

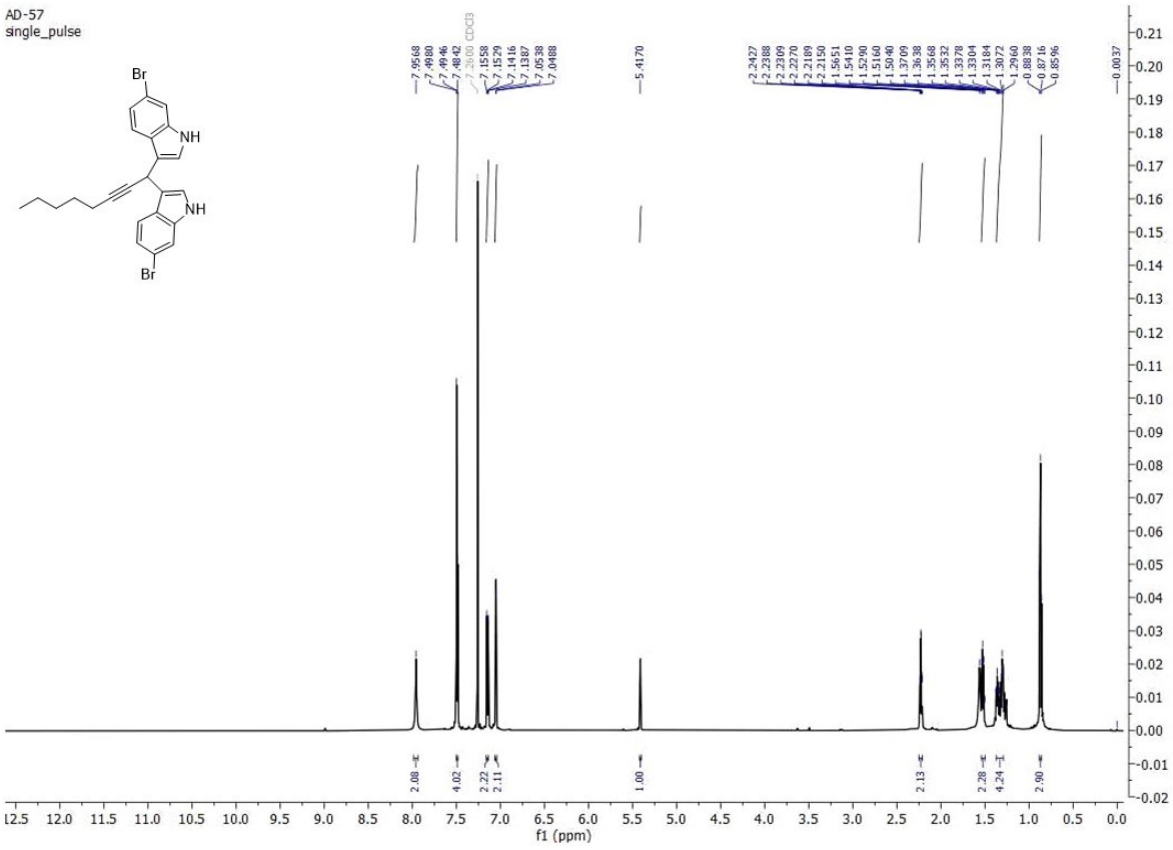


Figure S89 ^{1}H NMR spectrum of **22d** in $CDCl_3$.

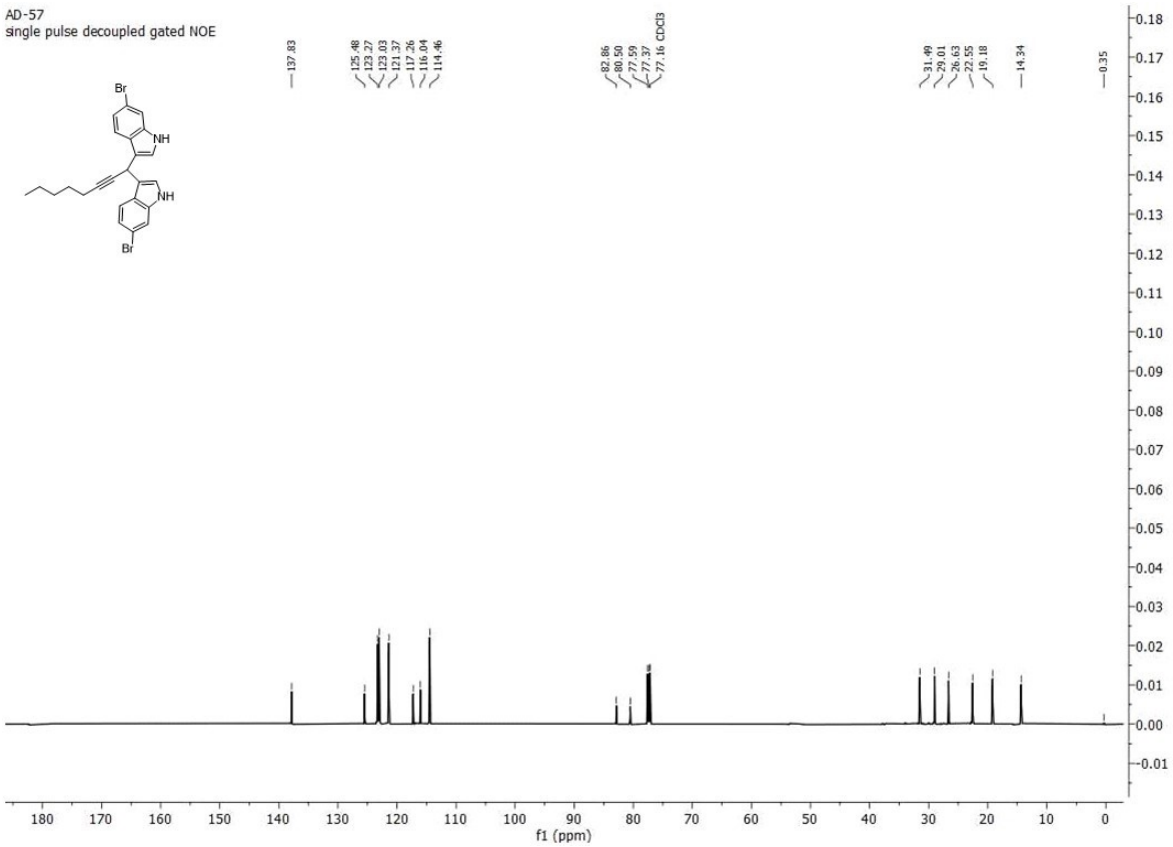


Figure S90 ^{13}C NMR spectrum of **22d** in $CDCl_3$.

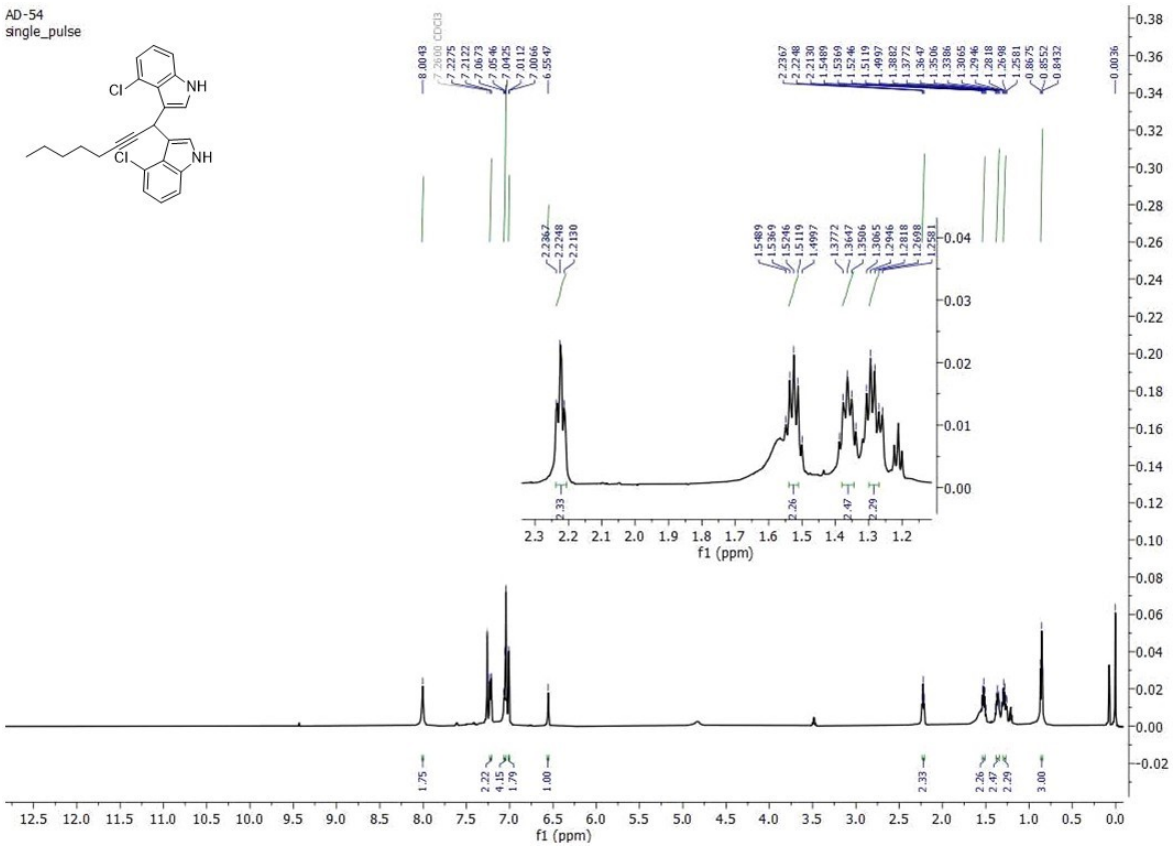


Figure S91 ^{1}H NMR spectrum of **22e** in $CDCl_3$.

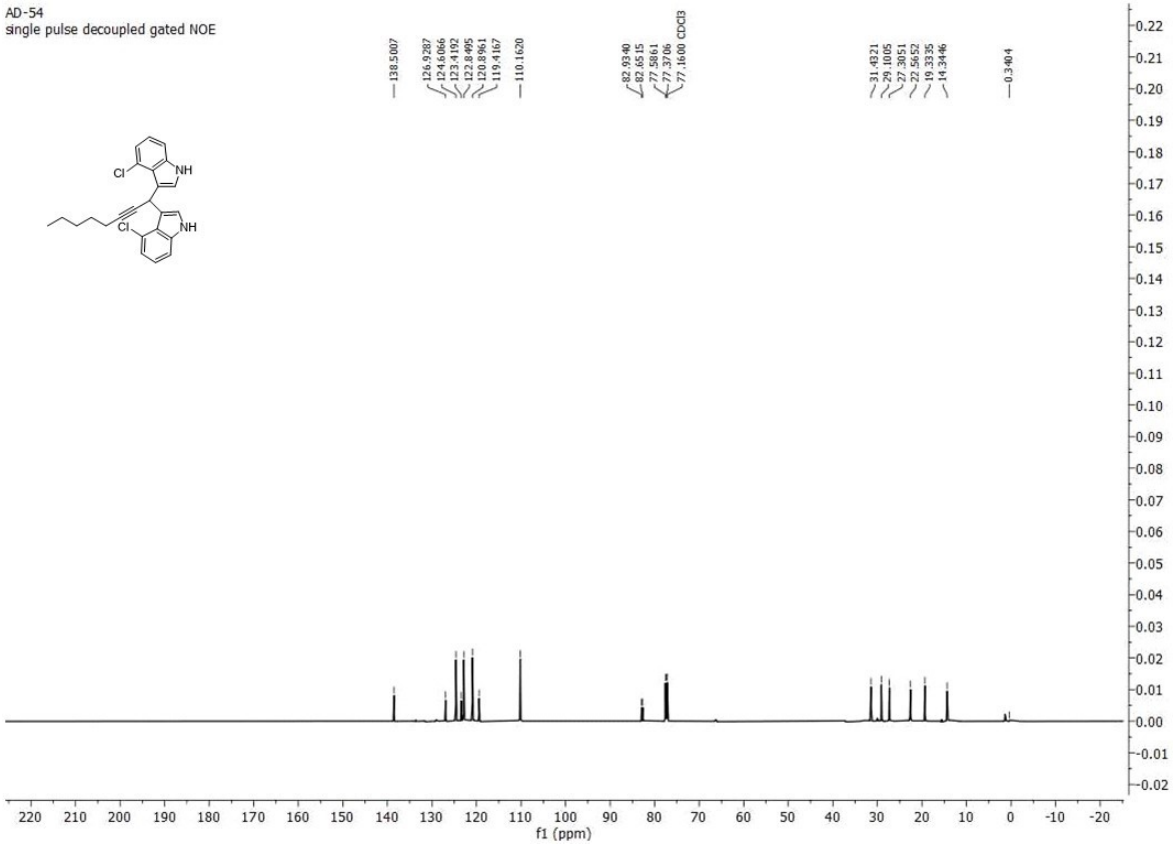


Figure S92 ^{13}C NMR spectrum of **22e** in $CDCl_3$.

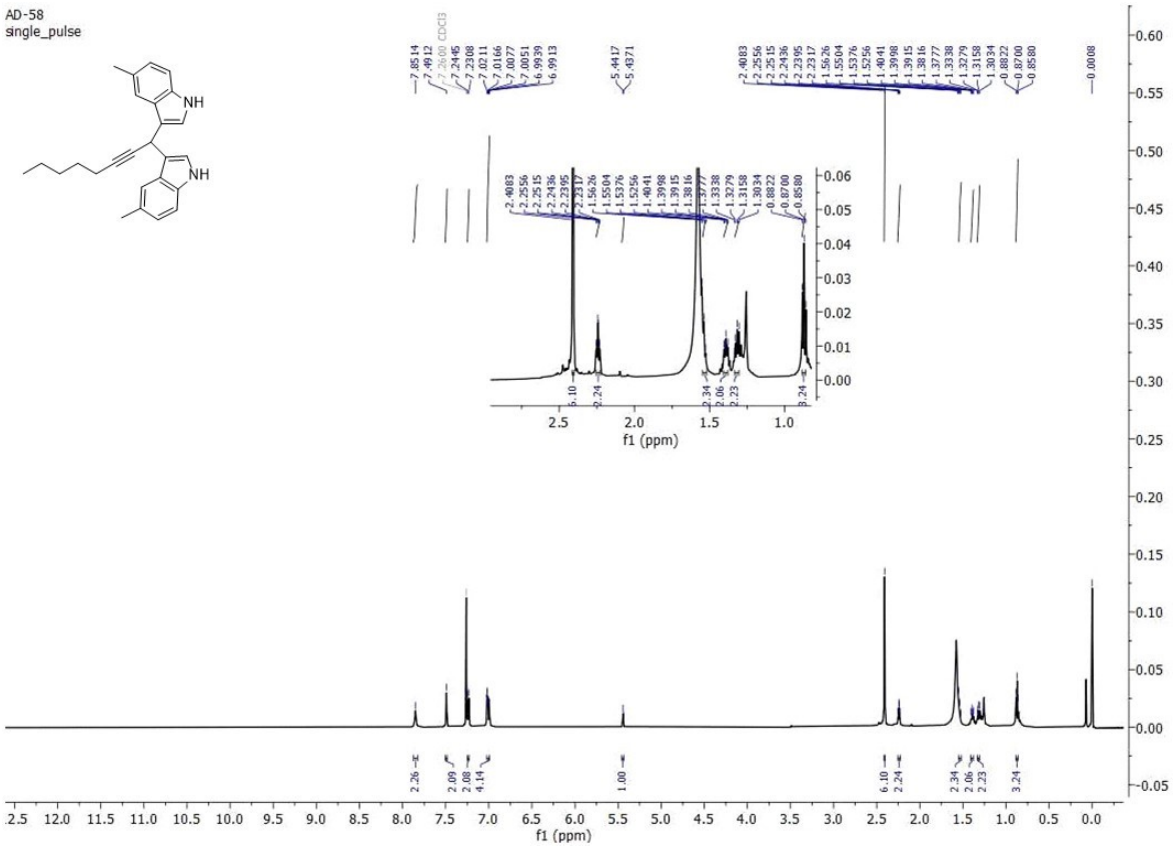


Figure S93 ^{1}H NMR spectrum of **22k** in $CDCl_3$. -

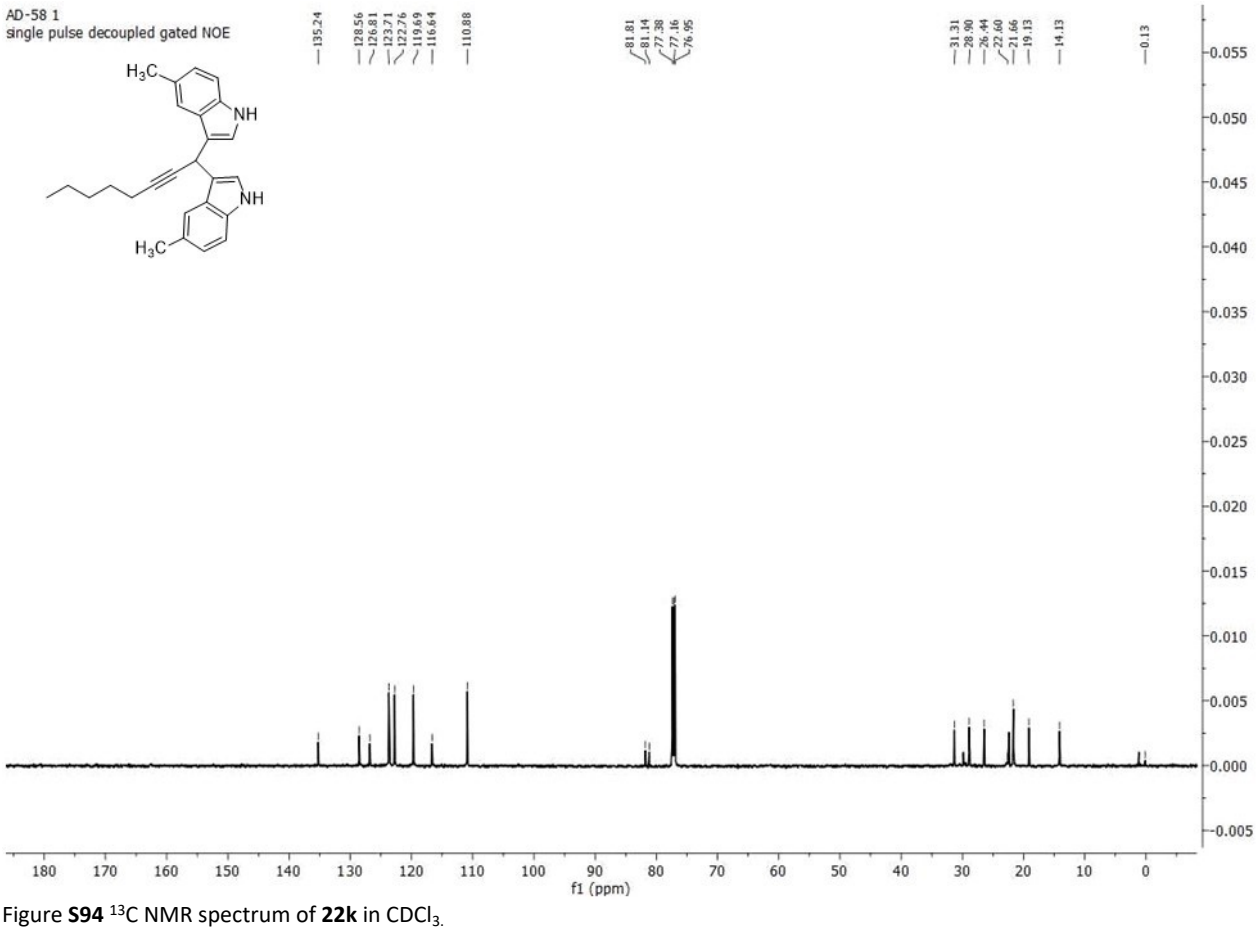


Figure **S94** ^{13}C NMR spectrum of **22k** in $CDCl_3$.

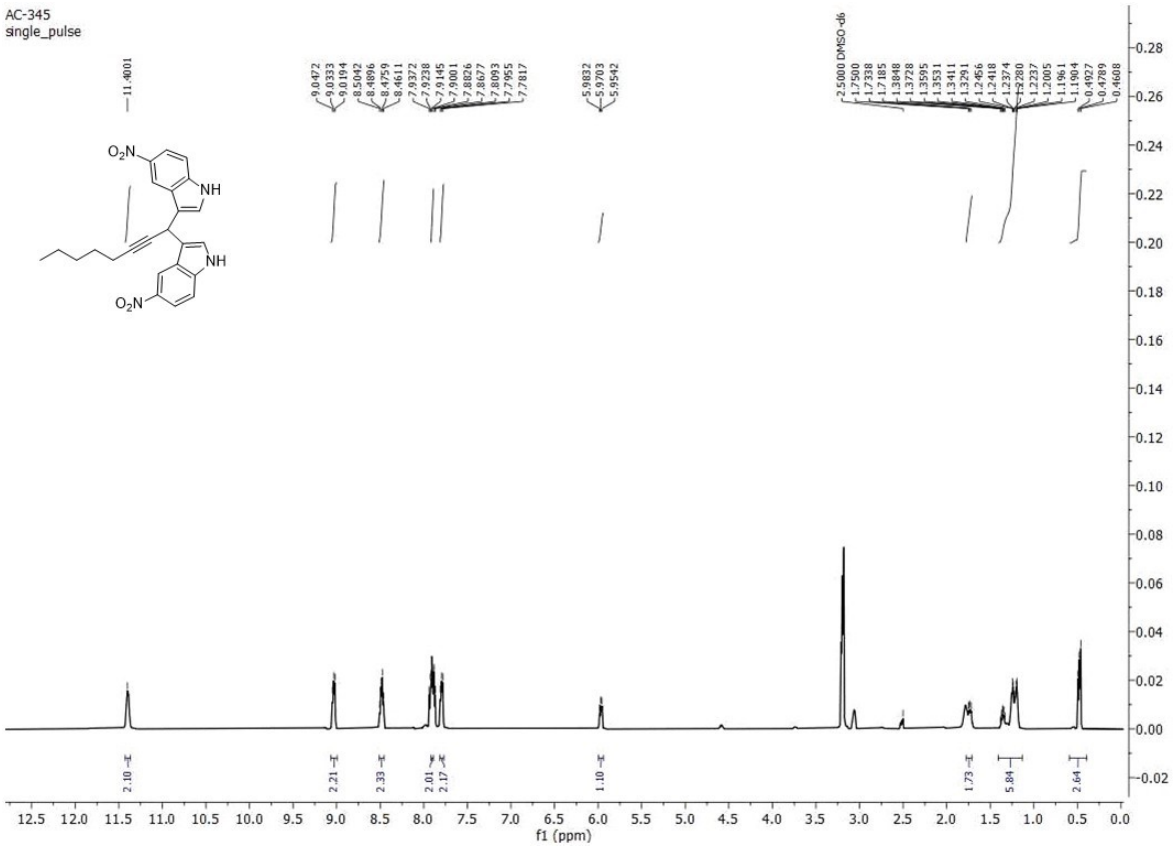


Figure S95 ^{1}H NMR spectrum of **22n** in $CDCl_3$ + DMSO-d_6

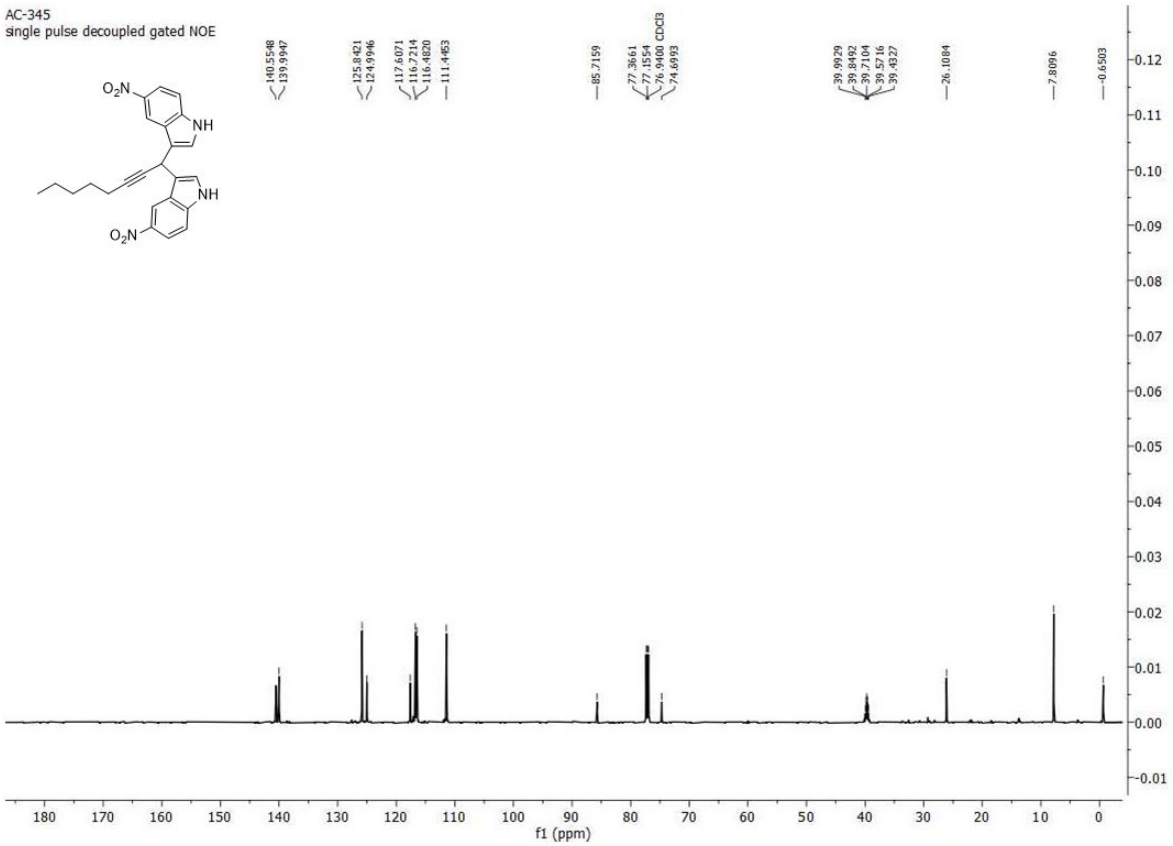


Figure S96 ^{13}C NMR spectrum of **22n** in $CDCl_3$ + DMSO-d_6.

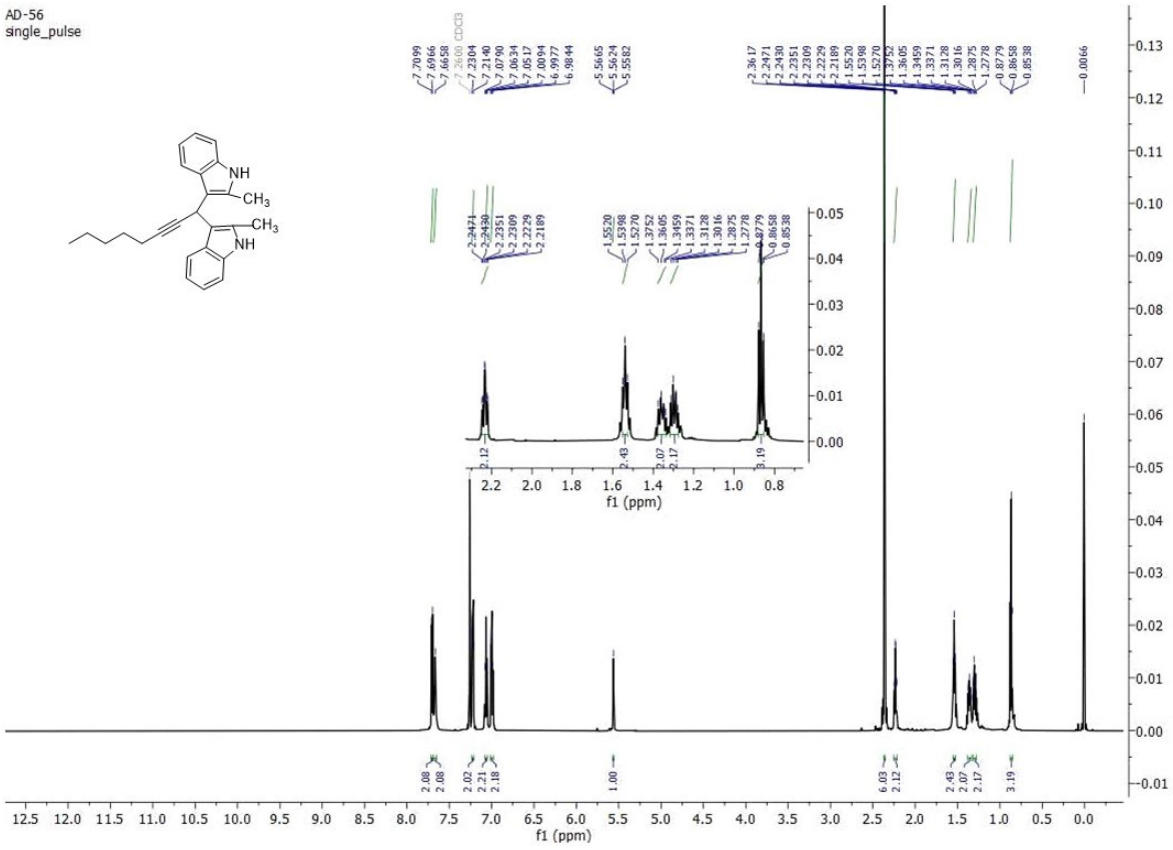


Figure S97 ^{1}H NMR spectrum of **22o** in $CDCl_3$.

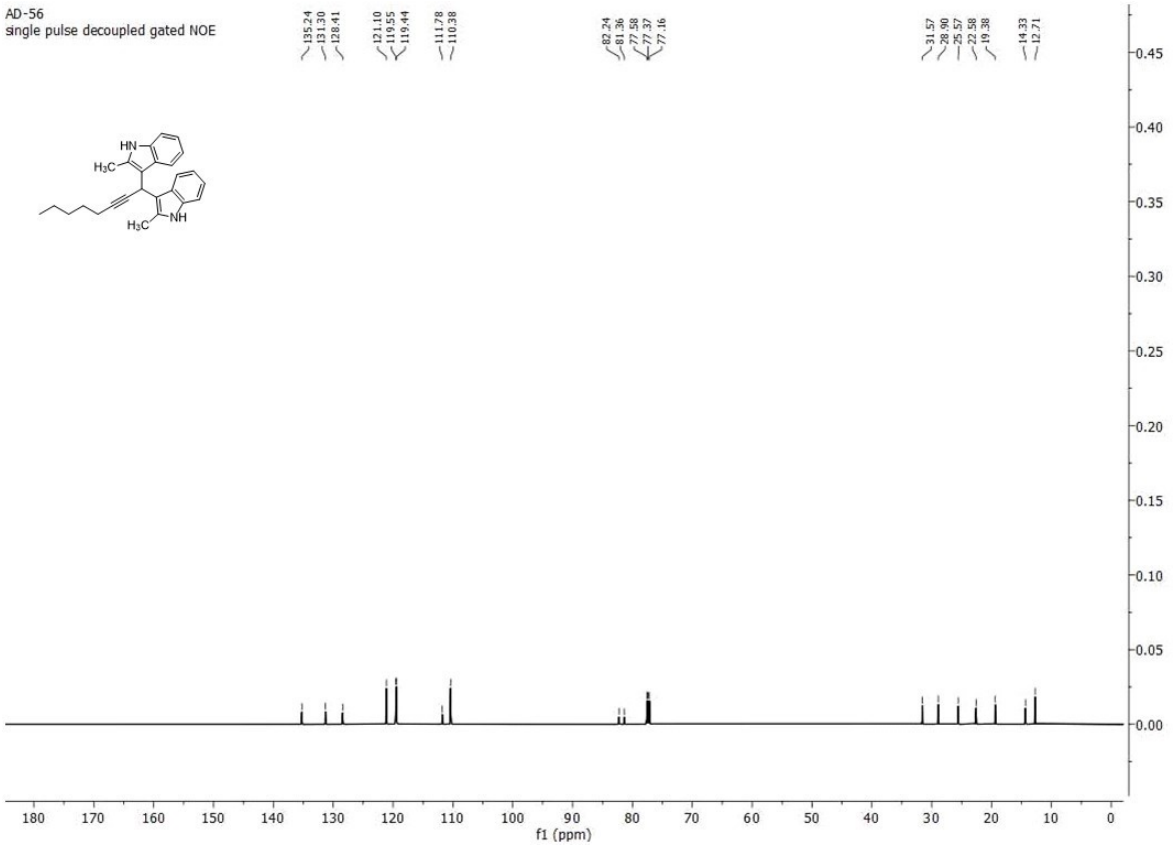


Figure S98 ^{13}C NMR spectrum of **22o** in $CDCl_3$.