Supporting Information

Inverse Electron-Demand Aza-Diels-Alder Reaction of *α,β*-Unsaturated Thioesters with in Situ Generated 1,2-Diaza-1,3-dienes for the Synthesis of 1,3,4-Thiadiazines

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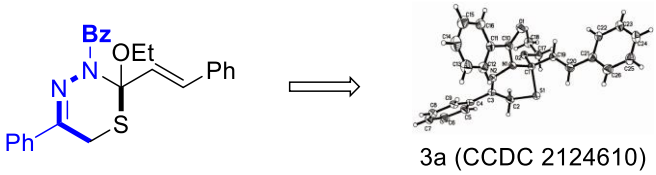
Table of Contents

1. X-ray crystal structure of 3a

Single crystals of compound **3a** were prepared through dissolving the sample in mixture solvent of EtOH/DCM (4/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on an 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

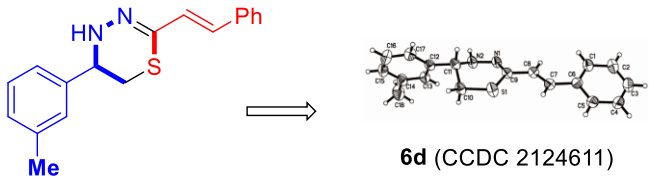


ORTEP of **3a** (at the 50% probability level)

Identification code	**3a**
Empirical formula	$C_{26}H_{24}N_2O_2S$
Formula weight	428.53
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.6215(5)
b/Å	10.5485(4)
c/Å	22.2134(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2254.51(17)
Z	4
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	1.469
F(000)	904.0
Crystal size/mm^3	0.15 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.96 to 143.6
Index ranges	$-10 \le h \le 11$, $-10 \le k \le 12$, $-26 \le l \le 18$
Reflections collected	9085
Independent reflections	4111 [R_{int} = 0.0381, R_{sigma} = 0.0498]
Data/restraints/parameters	4111/2/276
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0560, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27
Flack parameter	0.059(15)

2. X-ray crystal structure of 6d

Single crystals of compound **6d** were prepared through dissolving the sample in mixture solvent of EtOH/DCM (5/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on an 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.



ORTEP of **6d** (at the 50% probability level)

Identification code	202111331
Empirical formula	$C_{18}H_{18}N_2S$
Formula weight	294.40
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.1341(6)
b/Å	9.8354(4)
c/Å	12.1767(8)
α/°	90
β/°	93.123(5)
γ/°	90
Volume/Å^3	1570.63(15)
Z	4
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	1.769
F(000)	624.0
Crystal size/mm^3	0.15 × 0.1 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.246 to 134.15
Index ranges	-15 ≤ h ≤ 15, -10 ≤ k ≤ 11, -10 ≤ l ≤ 14
Reflections collected	5661
Independent reflections	2807 [R_{int} = 0.0251, R_{sigma} = 0.0342]
Data/restraints/parameters	2807/0/195
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1375
Final R indexes [all data]	R_1 = 0.0628, wR_2 = 0.1526
Largest diff. peak/hole / e Å^{-3}	0.22/-0.27

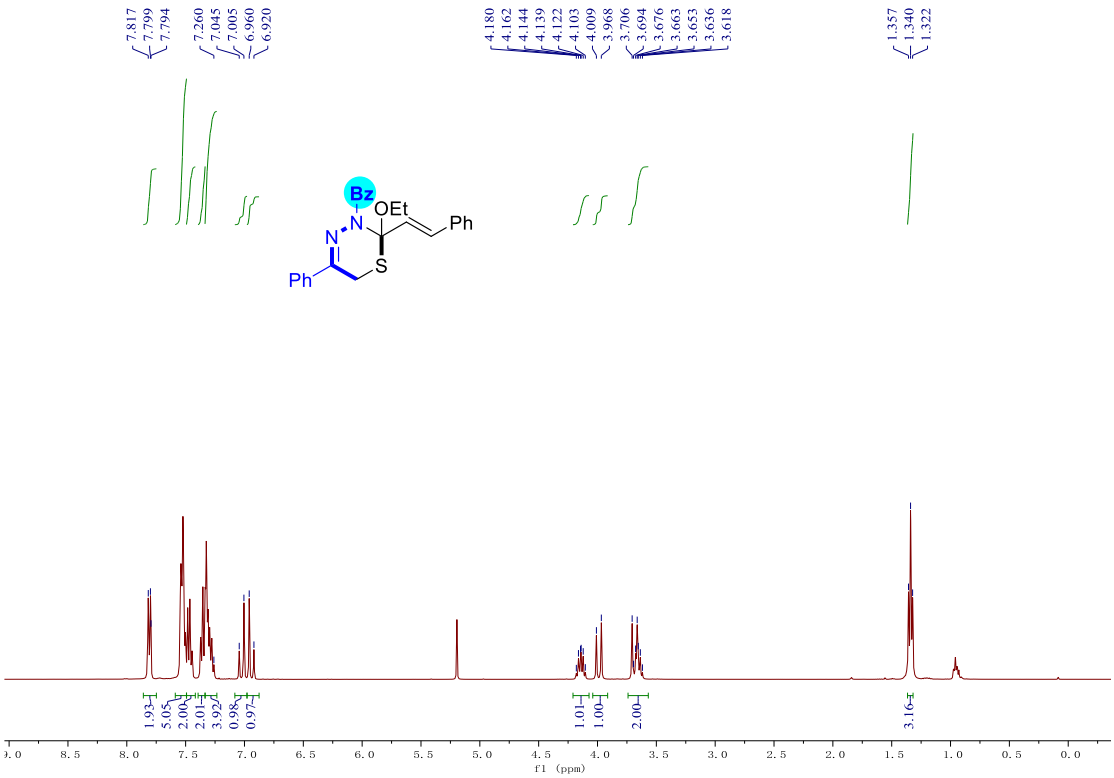
1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K; Puschmann, H. *J. Appl. Cryst.*, **2009**, *42*, 339-341.

2. Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.

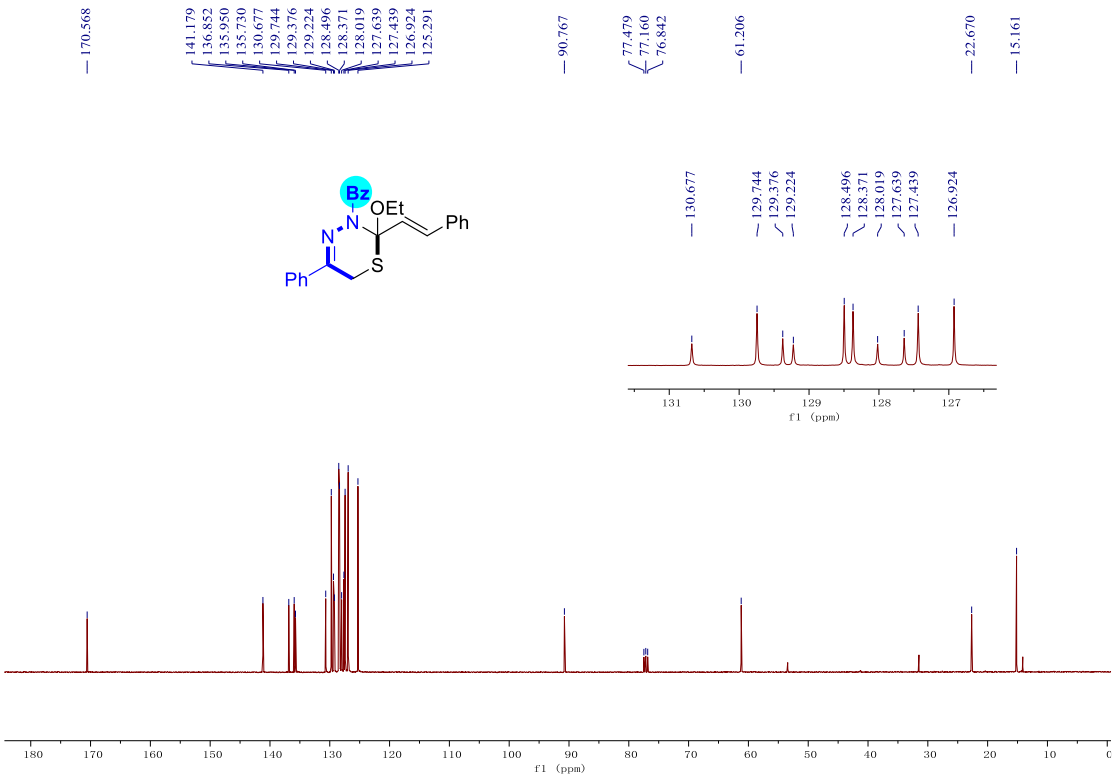
3. Sheldrick, G. M. *Acta Cryst.* **2015,** *C71***,** 3-8.

3. ^{1}H, ^{13}C NMR for compounds 3, 5, and 6

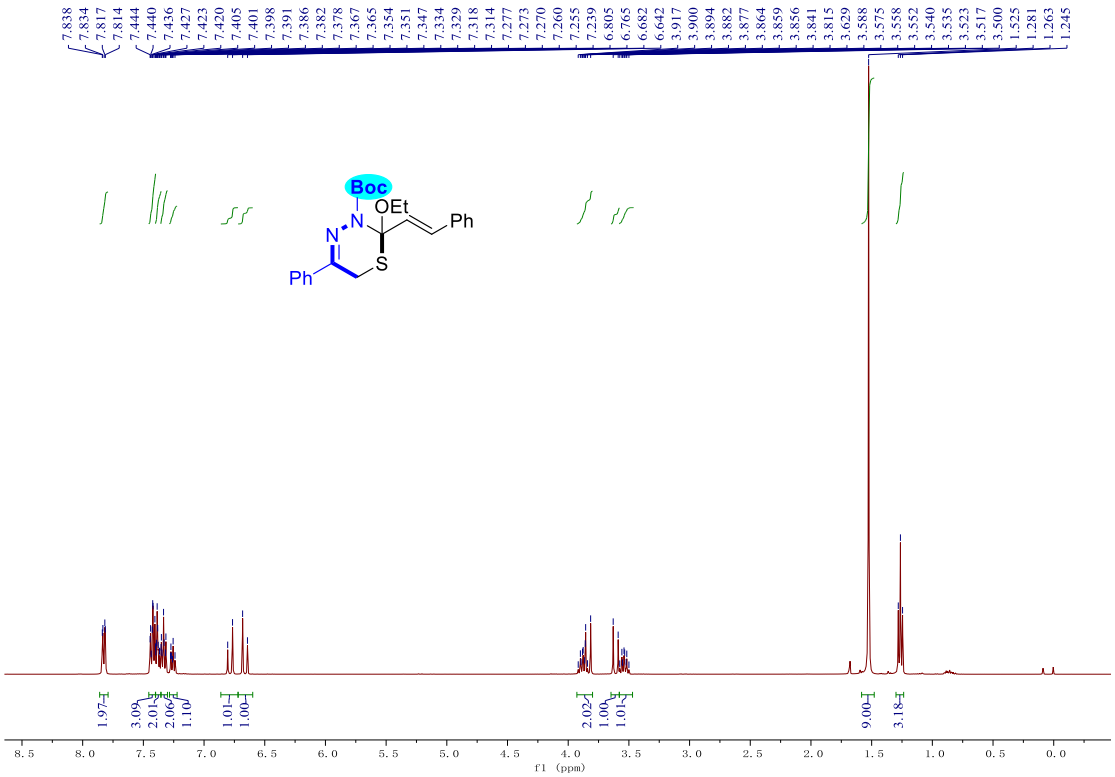
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



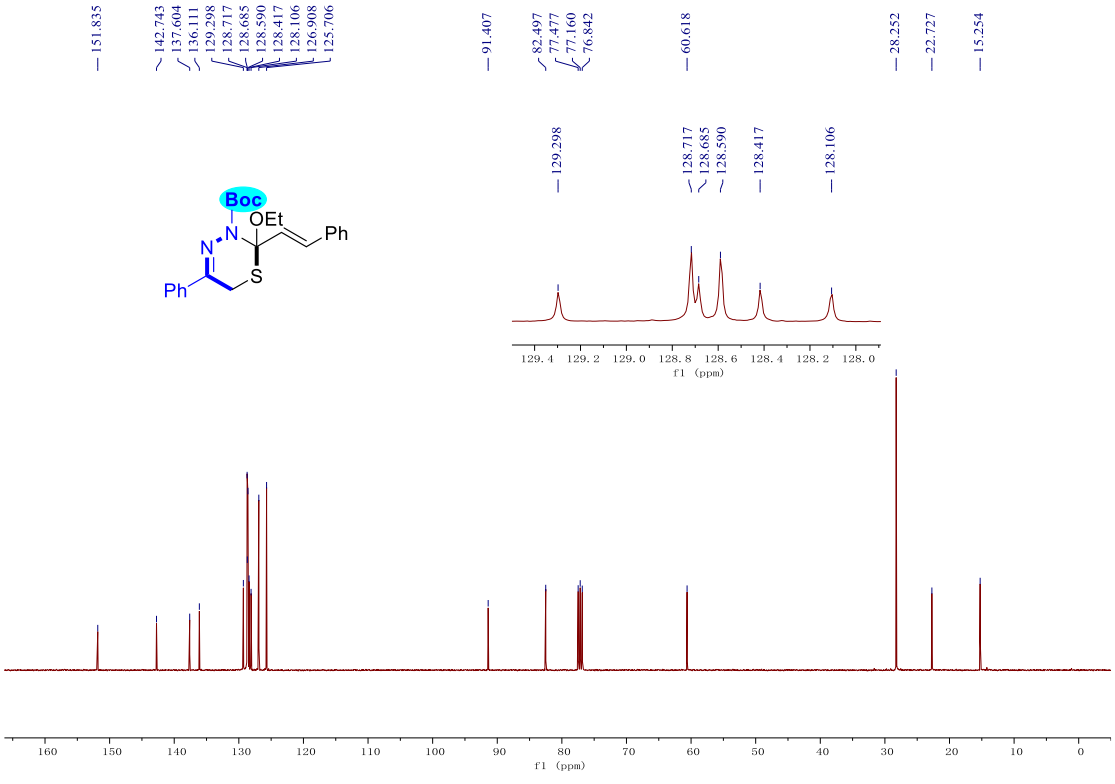
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3a**



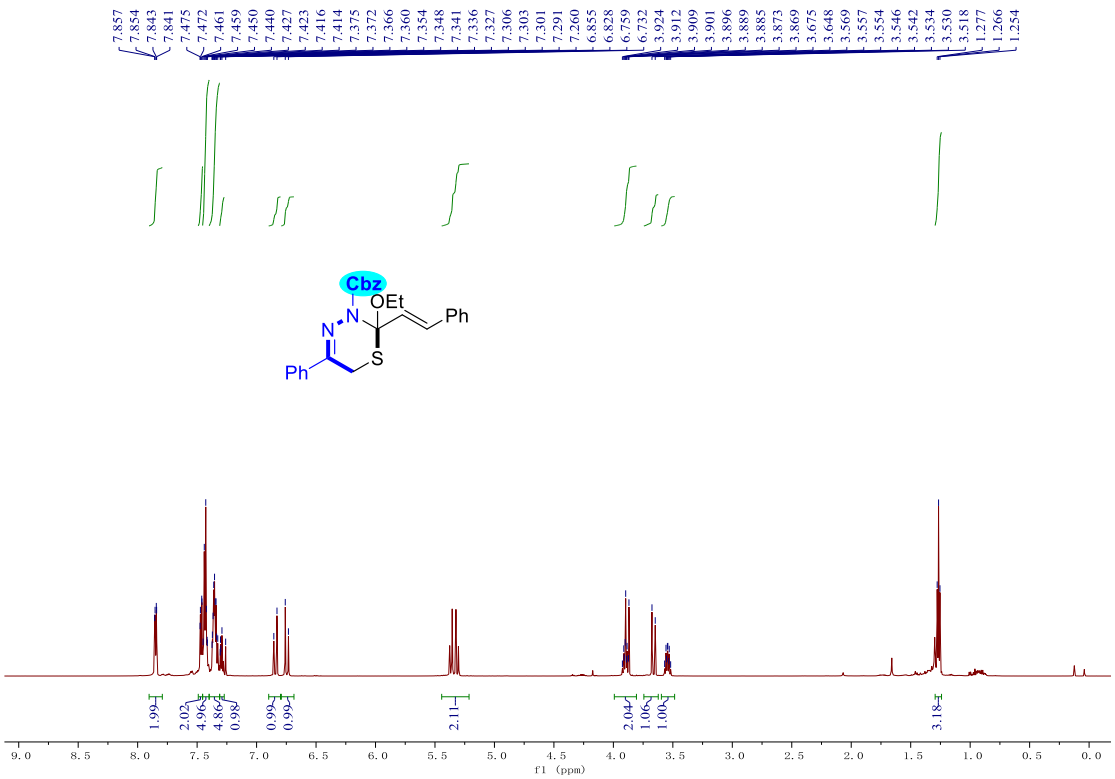
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



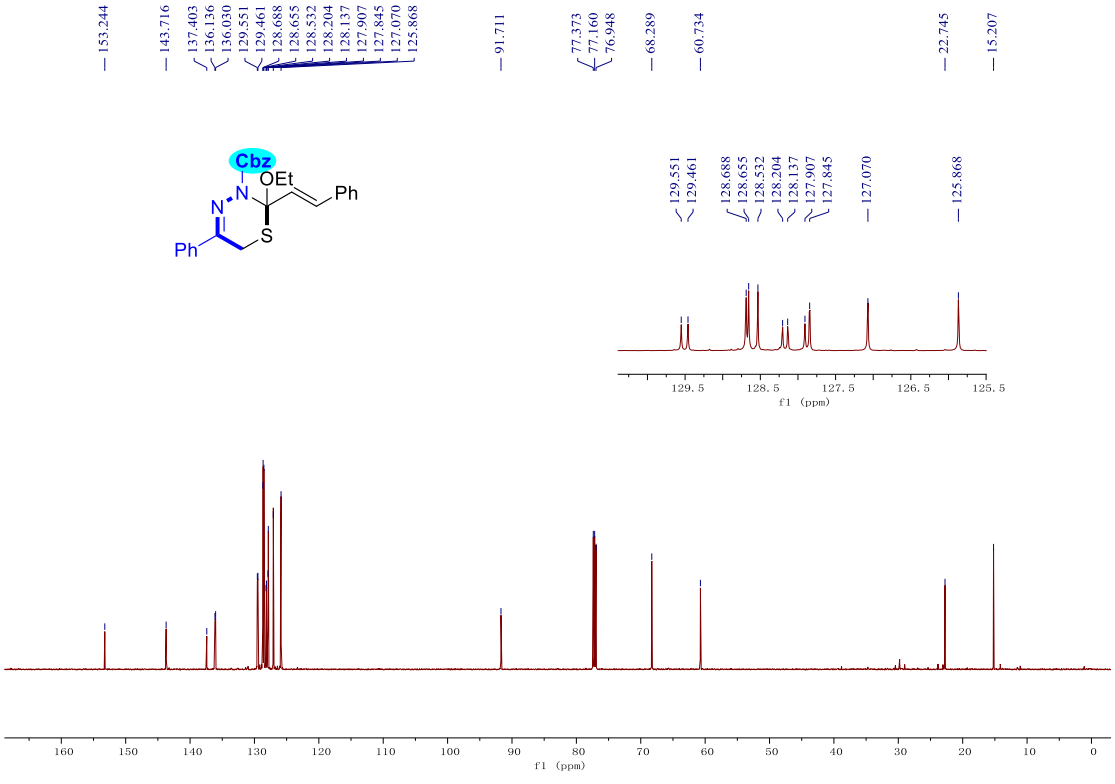
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3b**



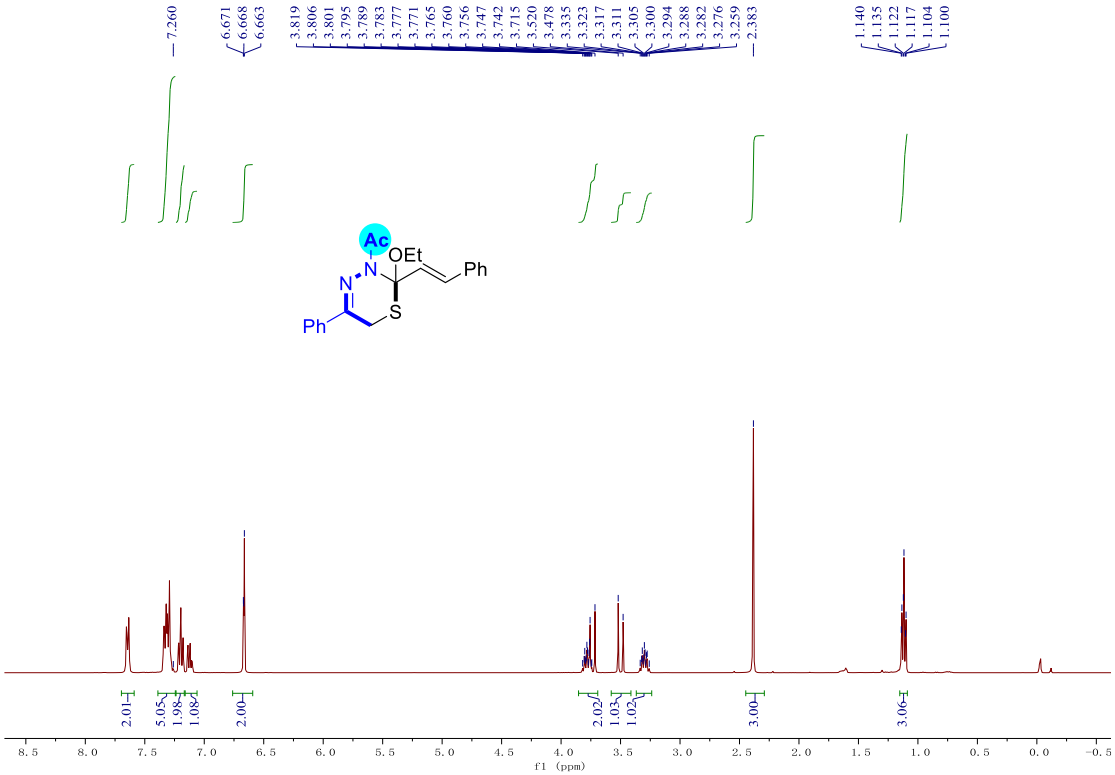
^{1}H NMR (600 MHz, $CDCl_3$) of **3c**



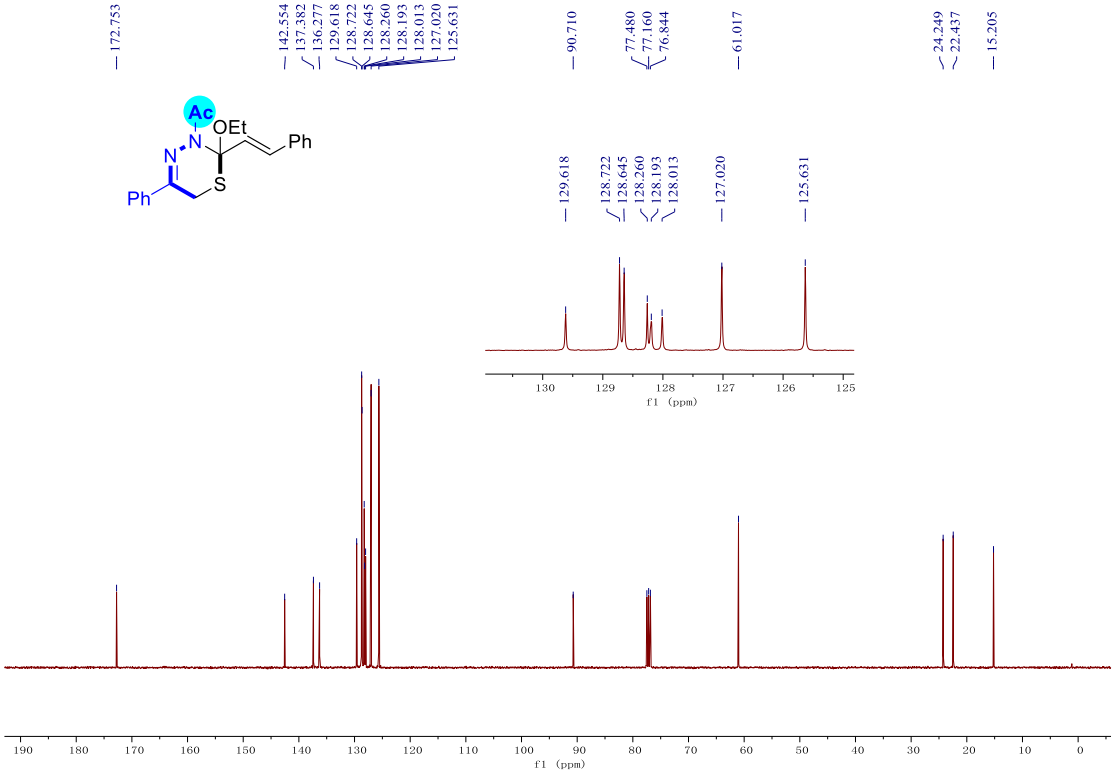
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **3c**



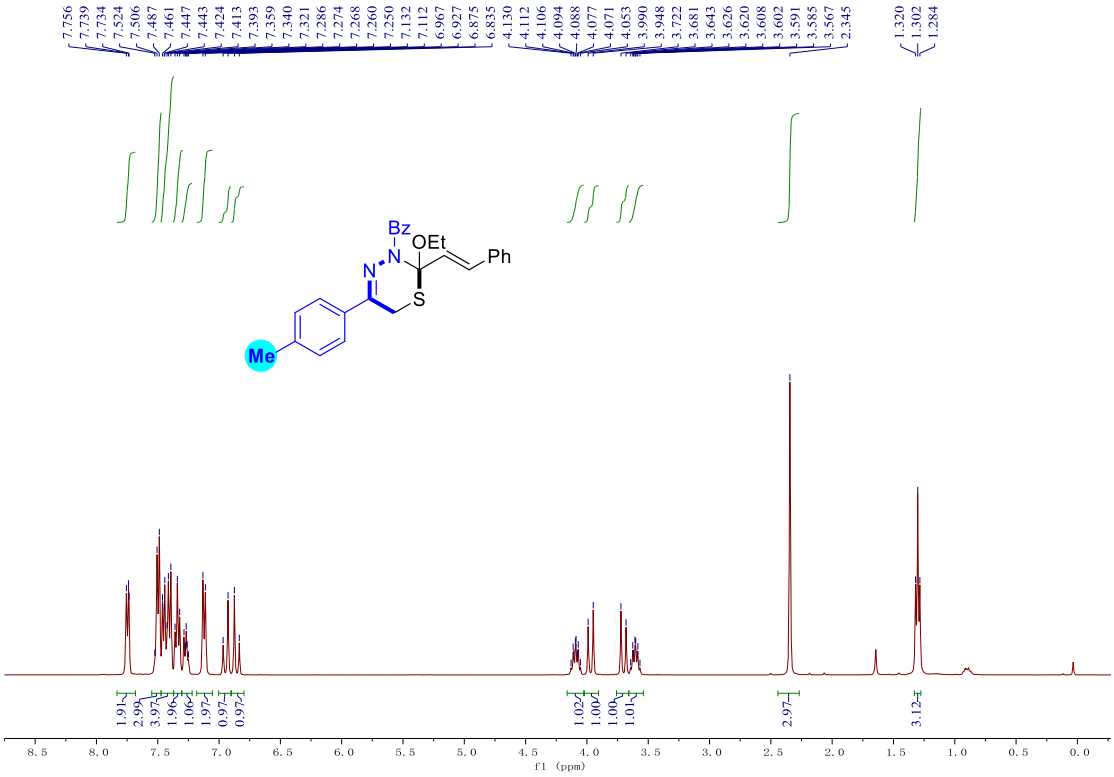
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



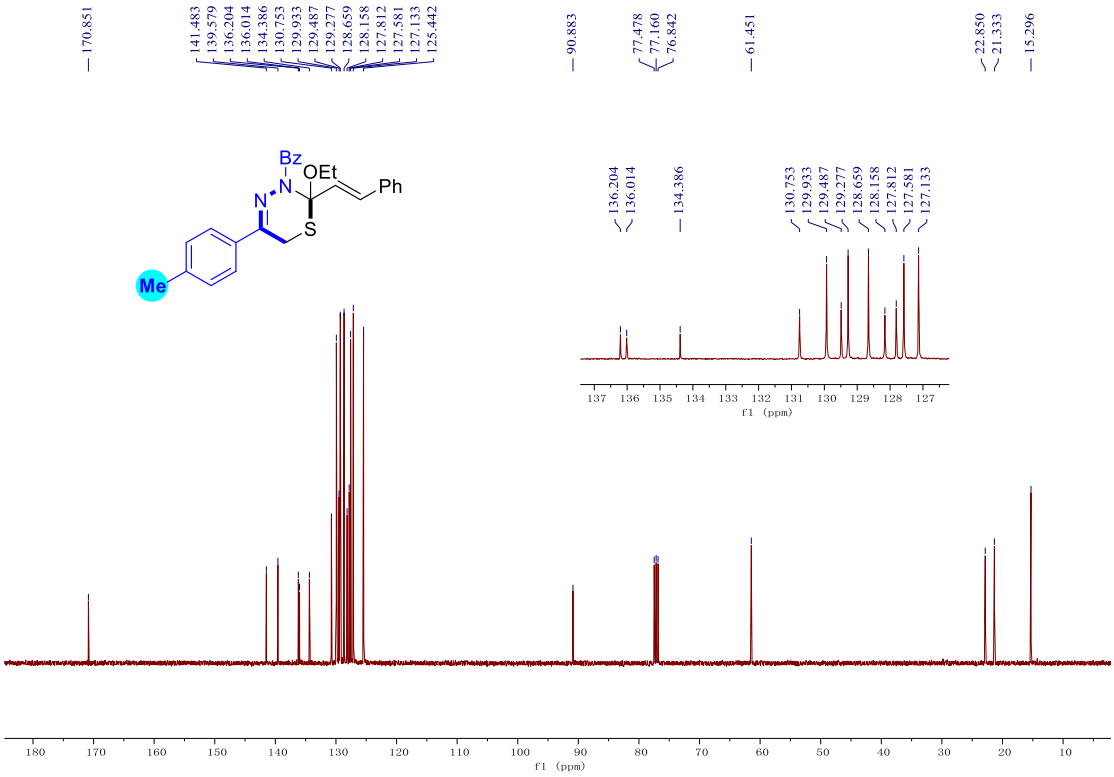
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3d**



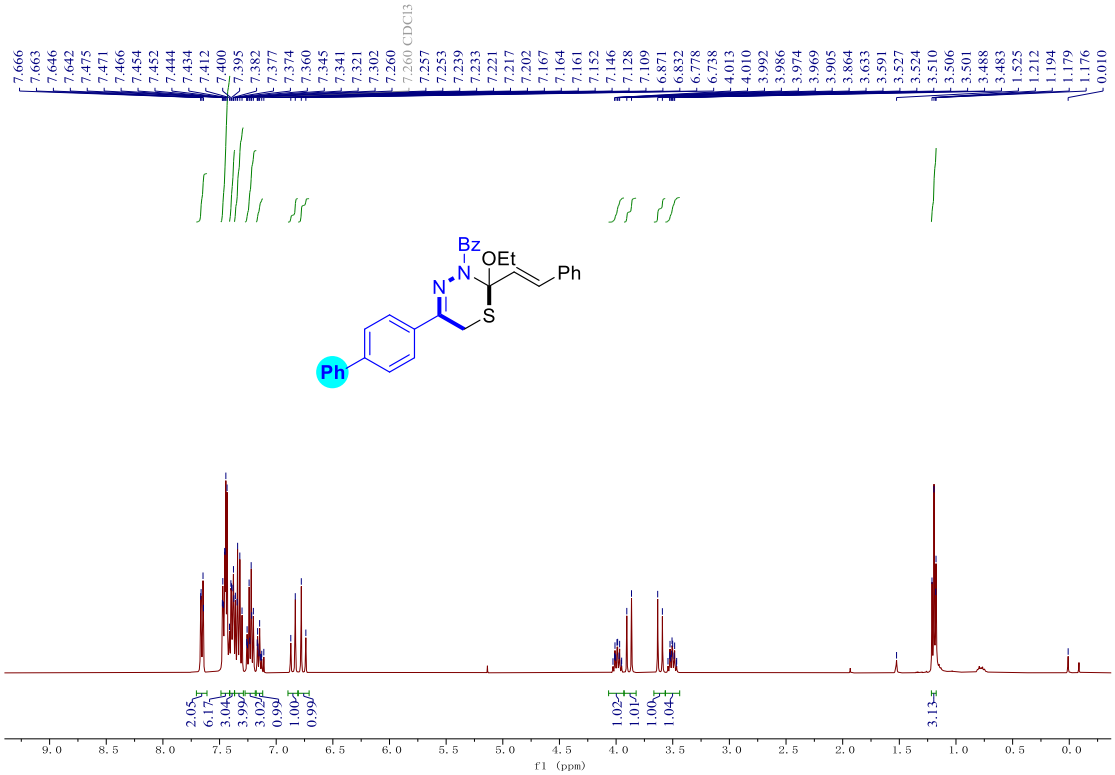
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



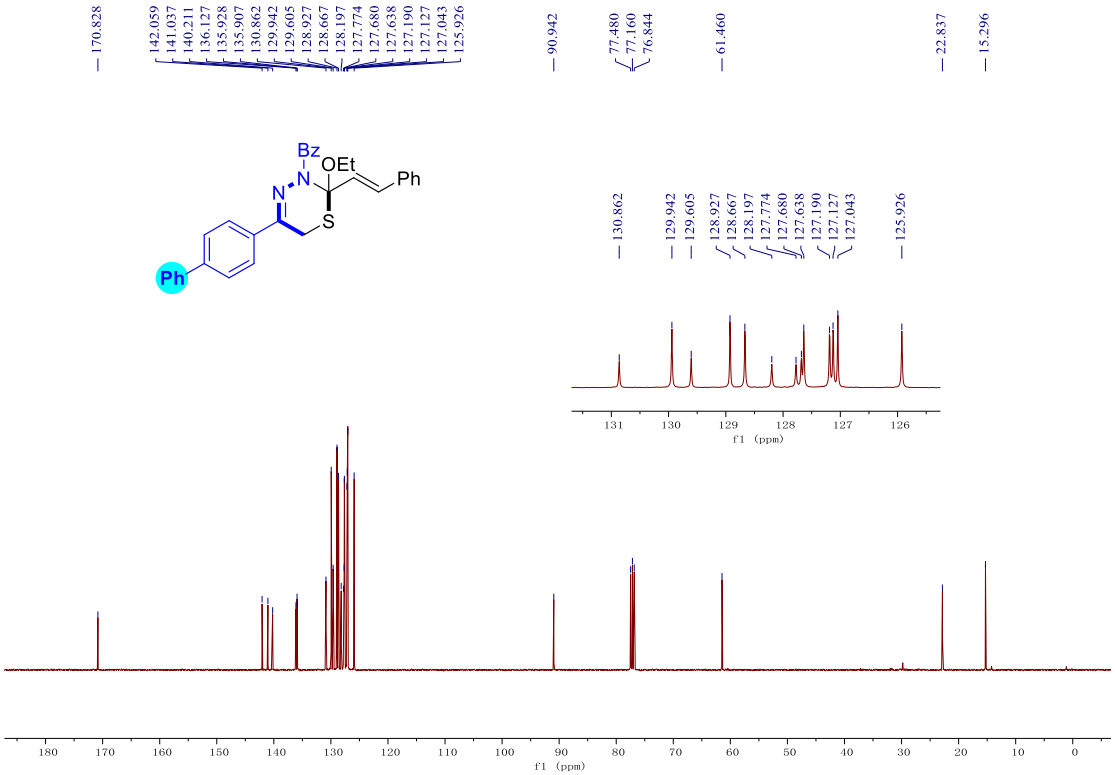
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3e**



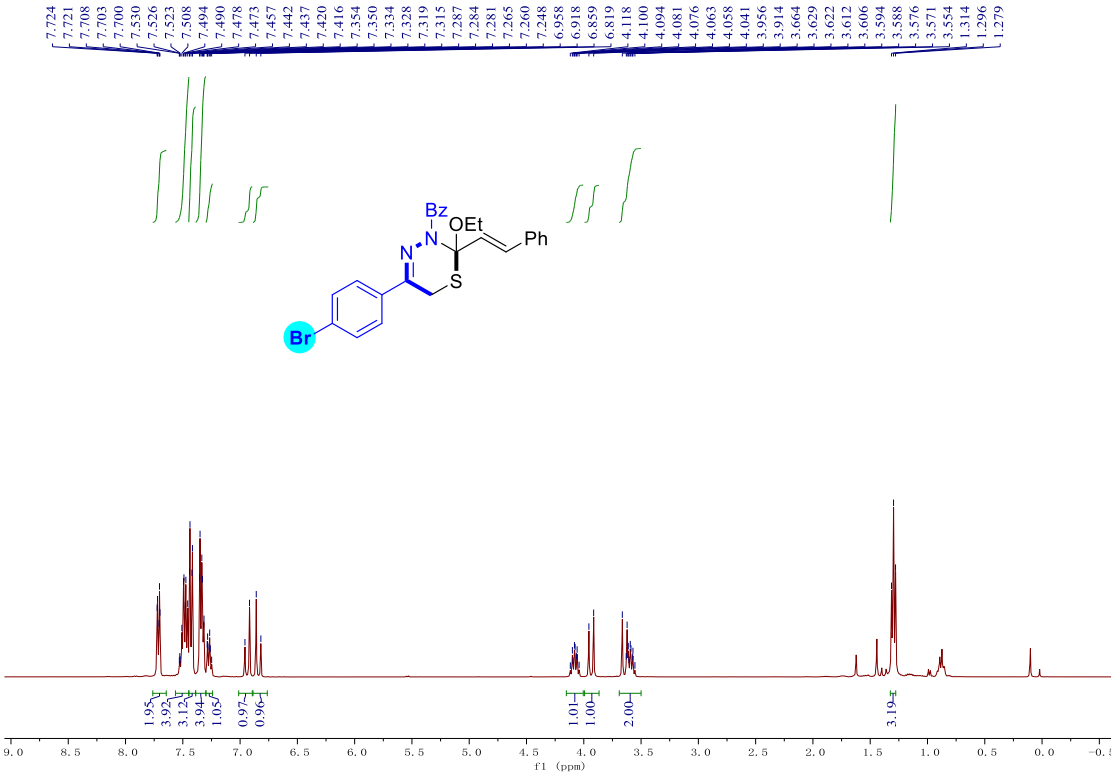
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



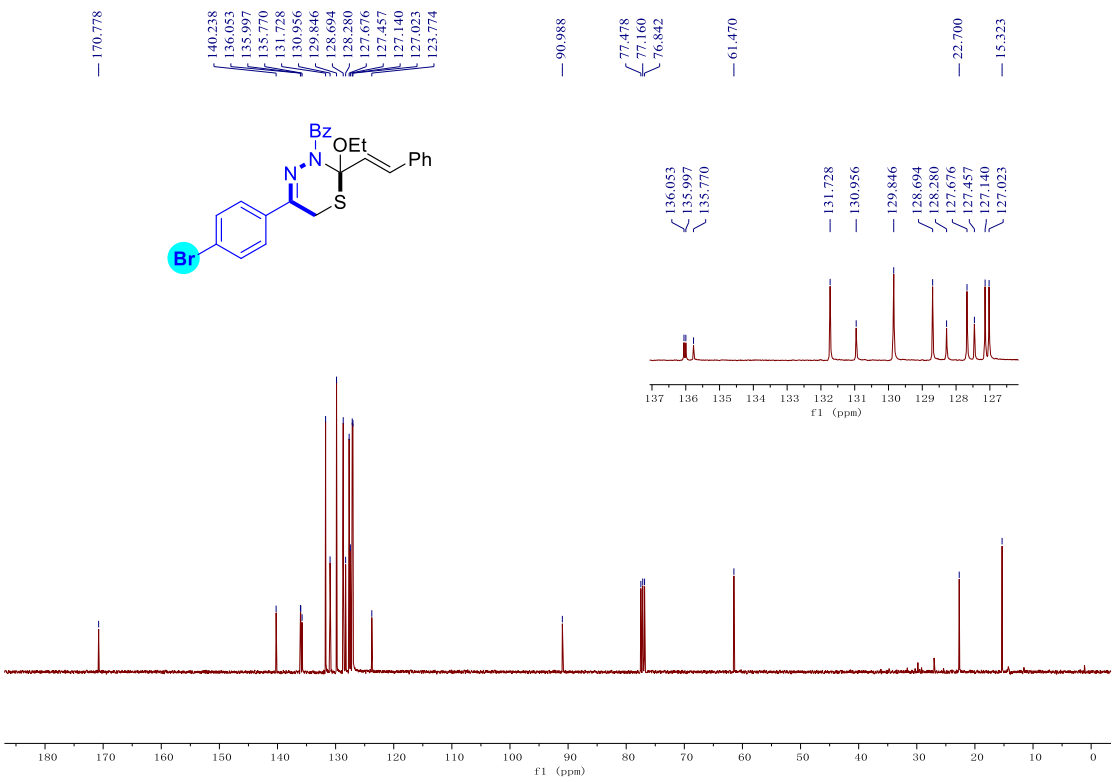
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3f**



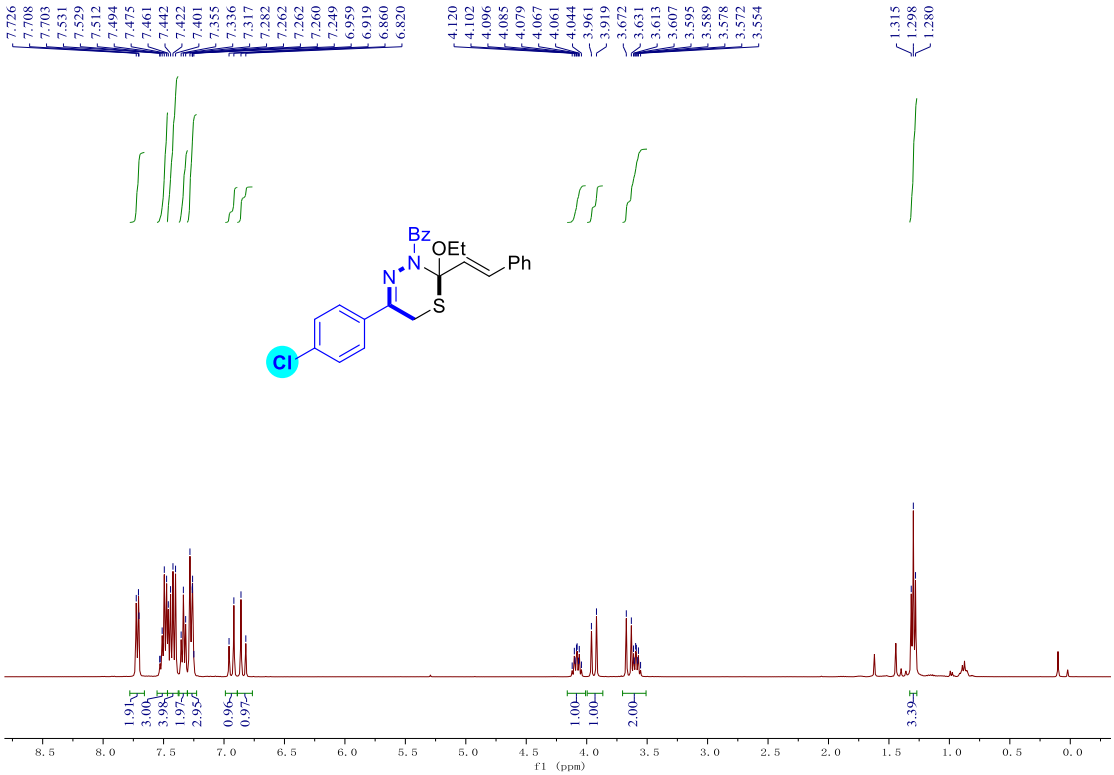
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



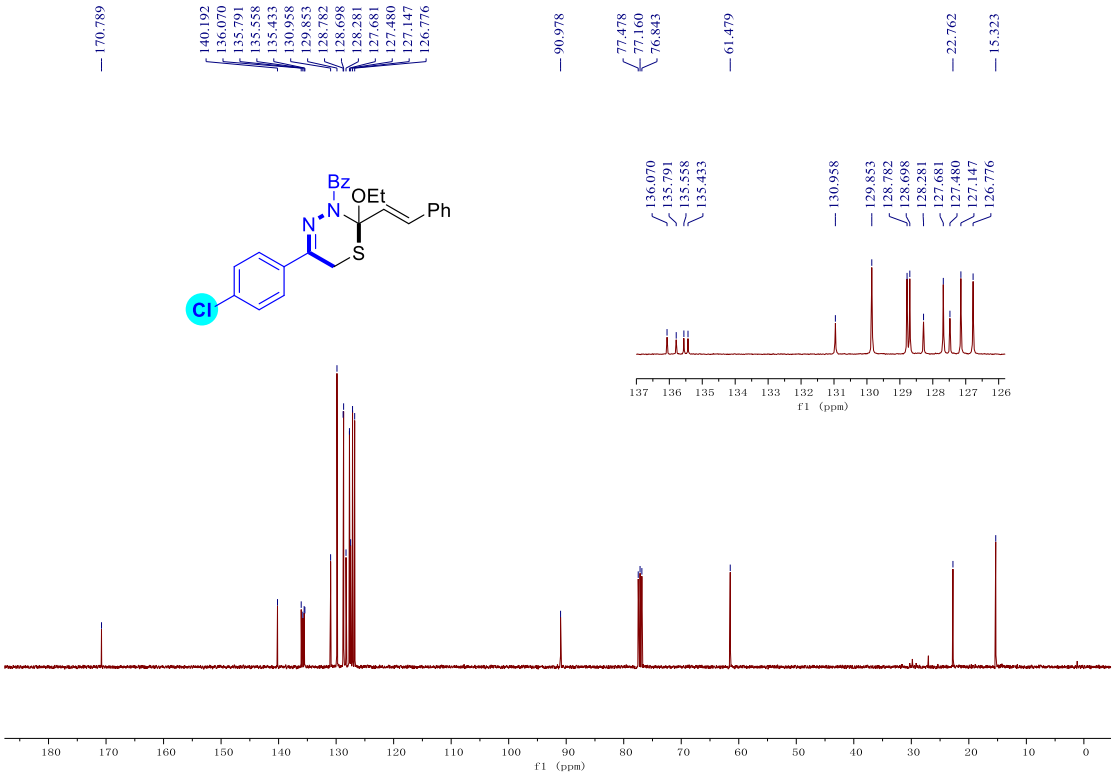
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3g**



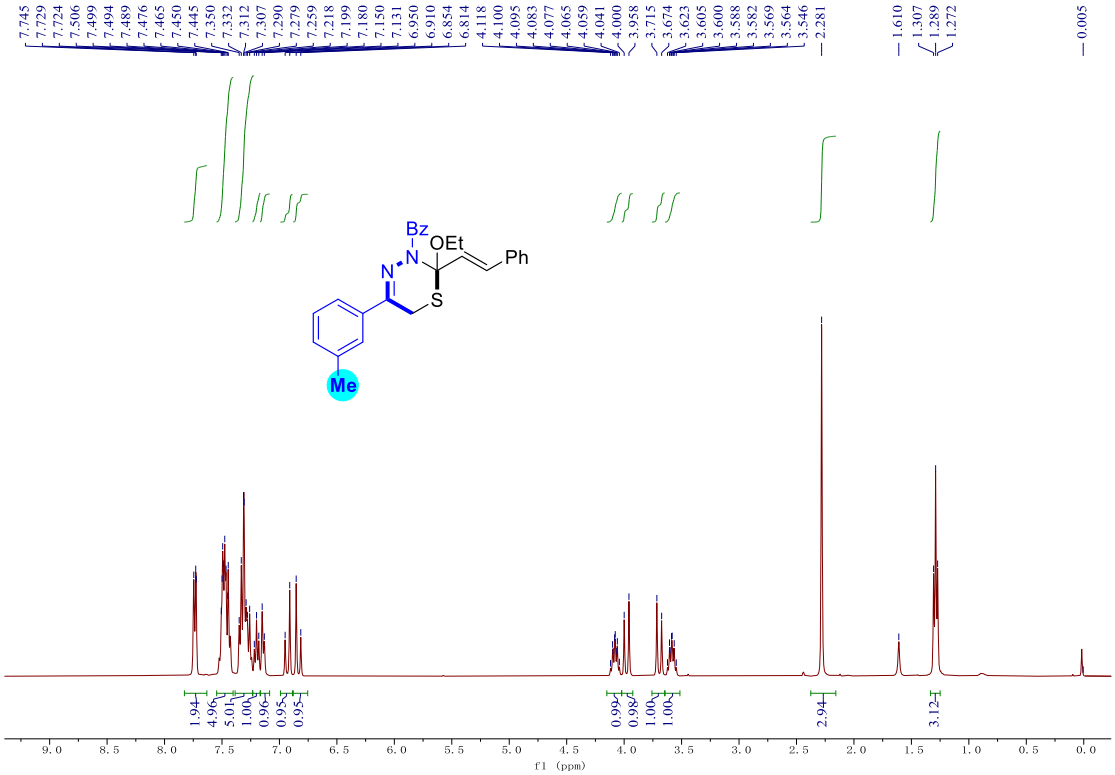
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



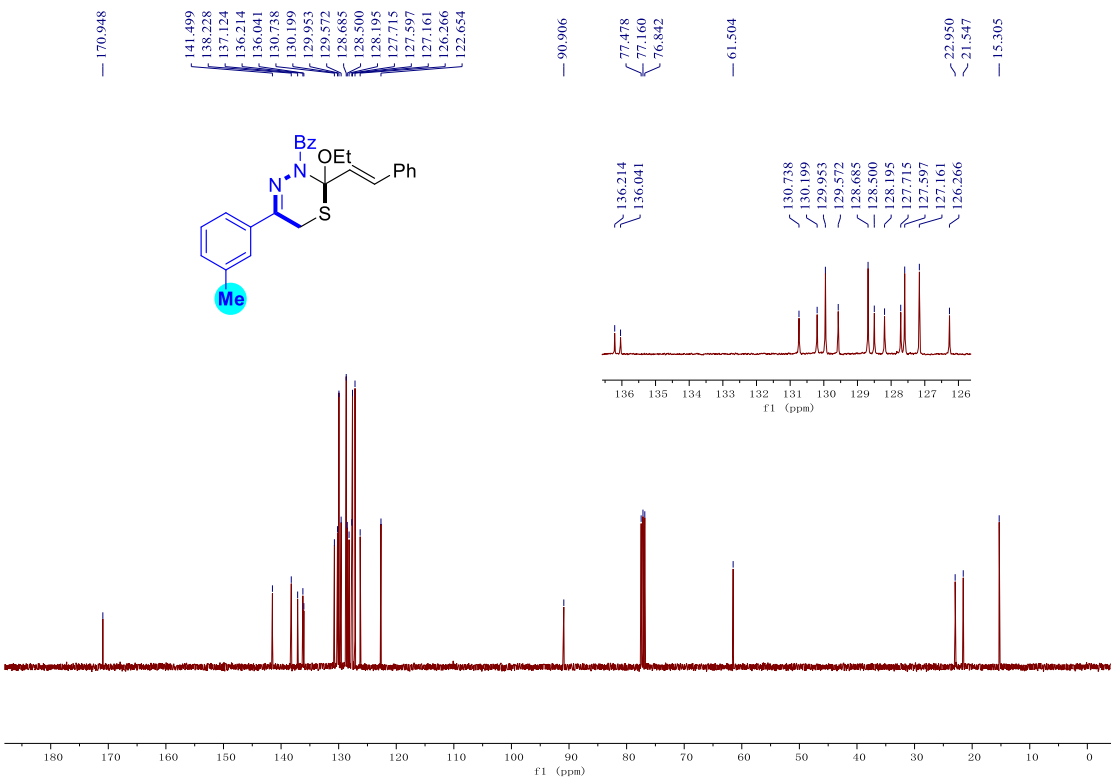
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3h**



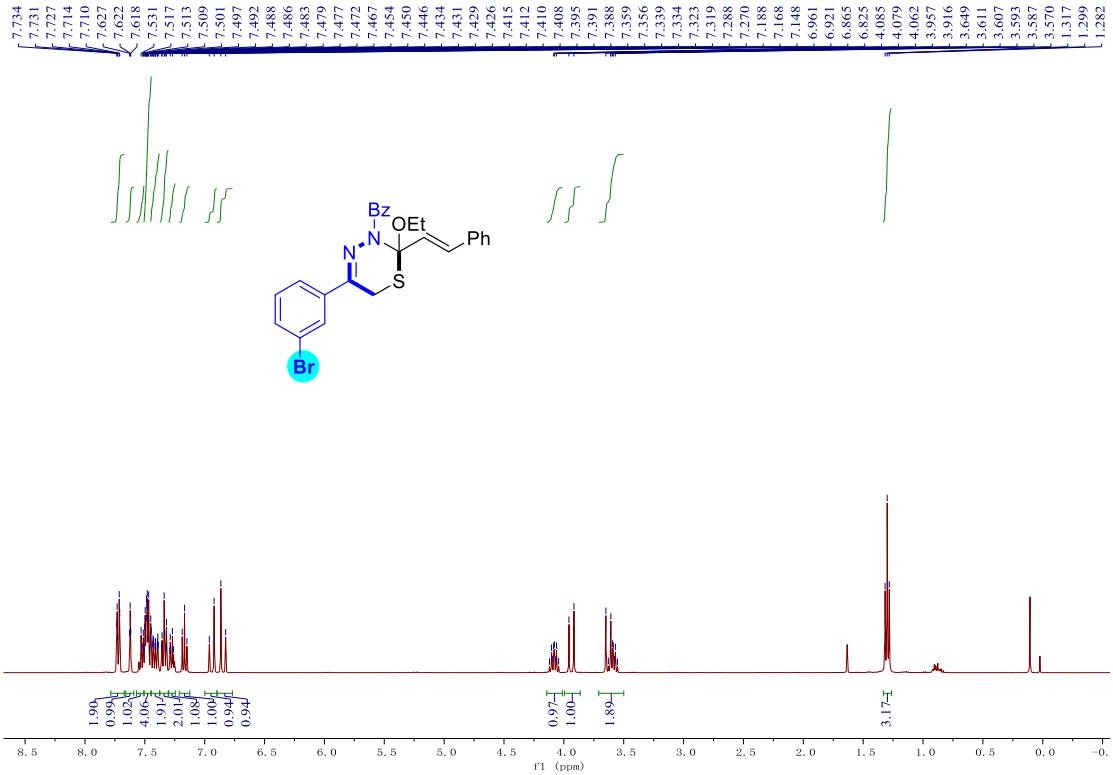
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



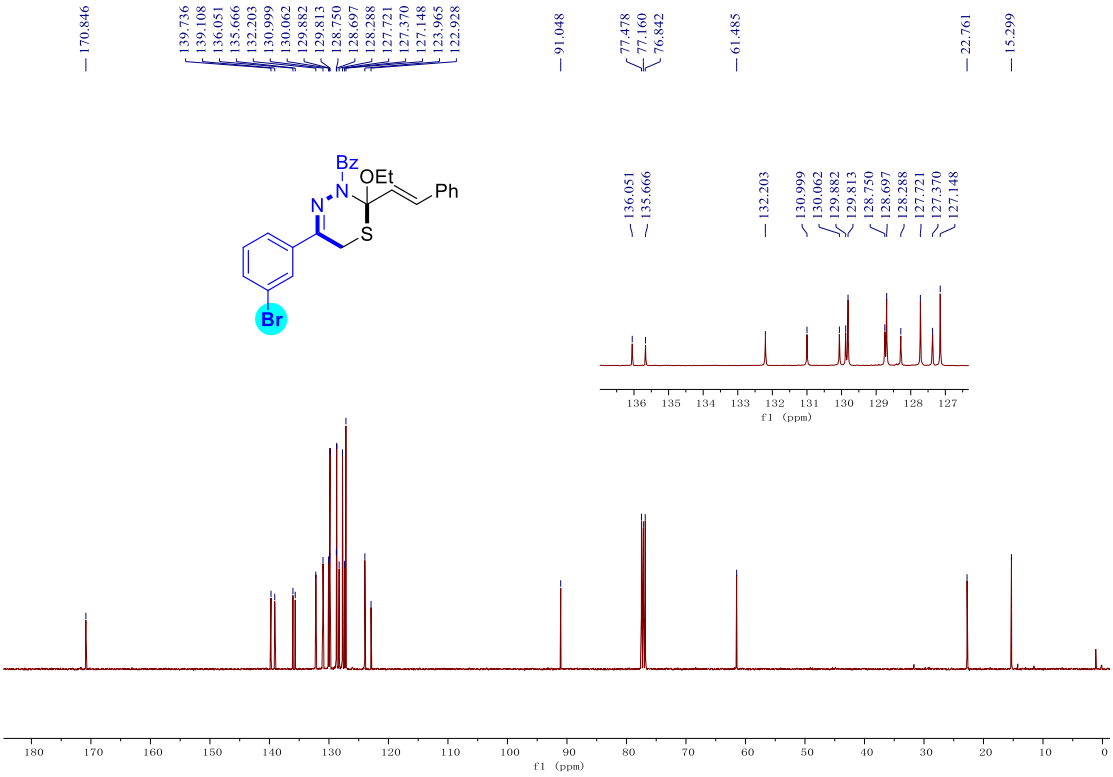
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3i**



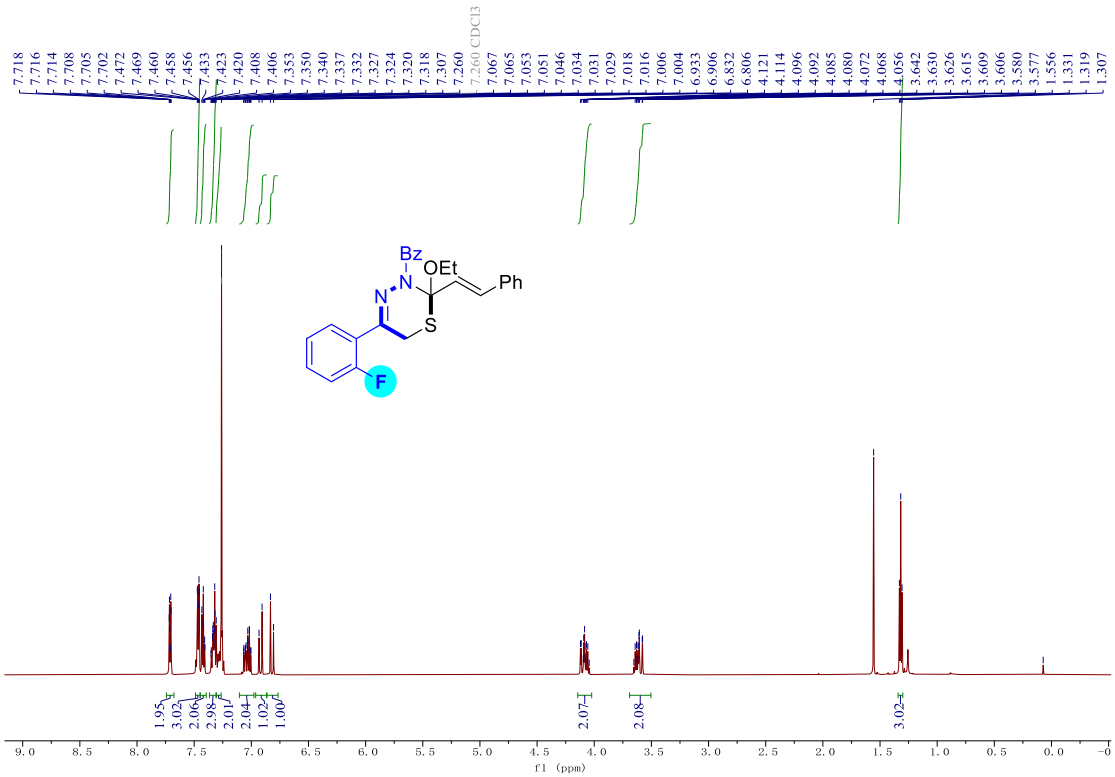
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



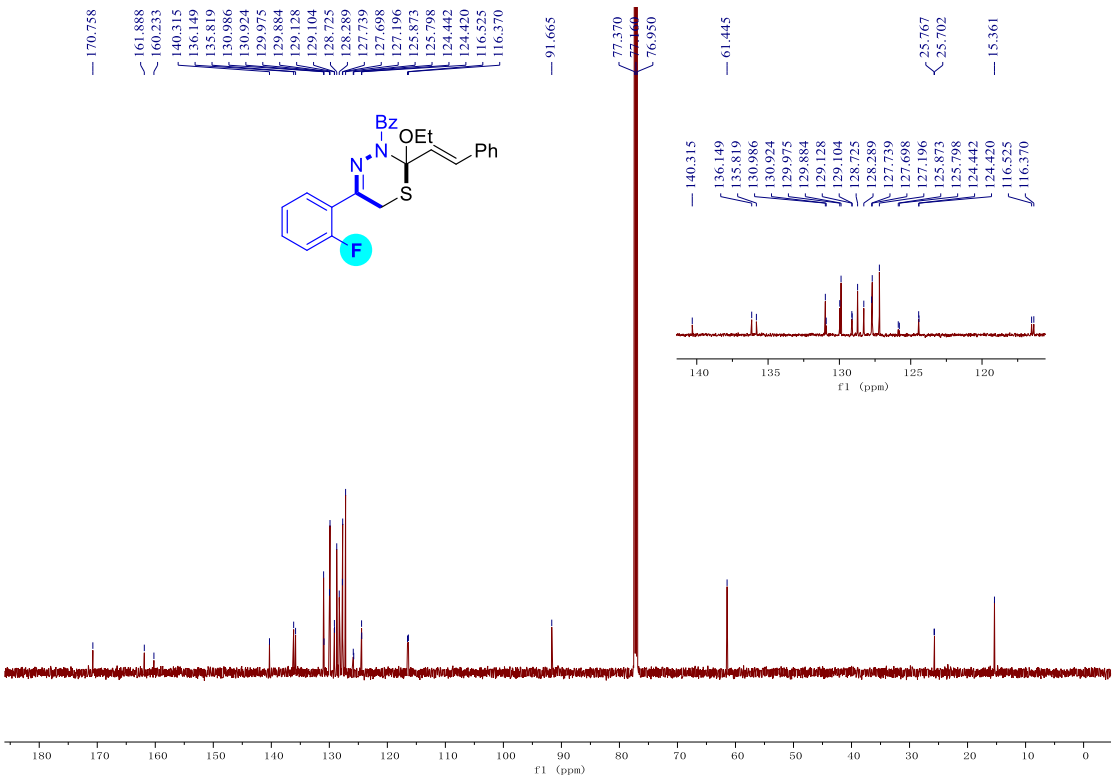
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3j**



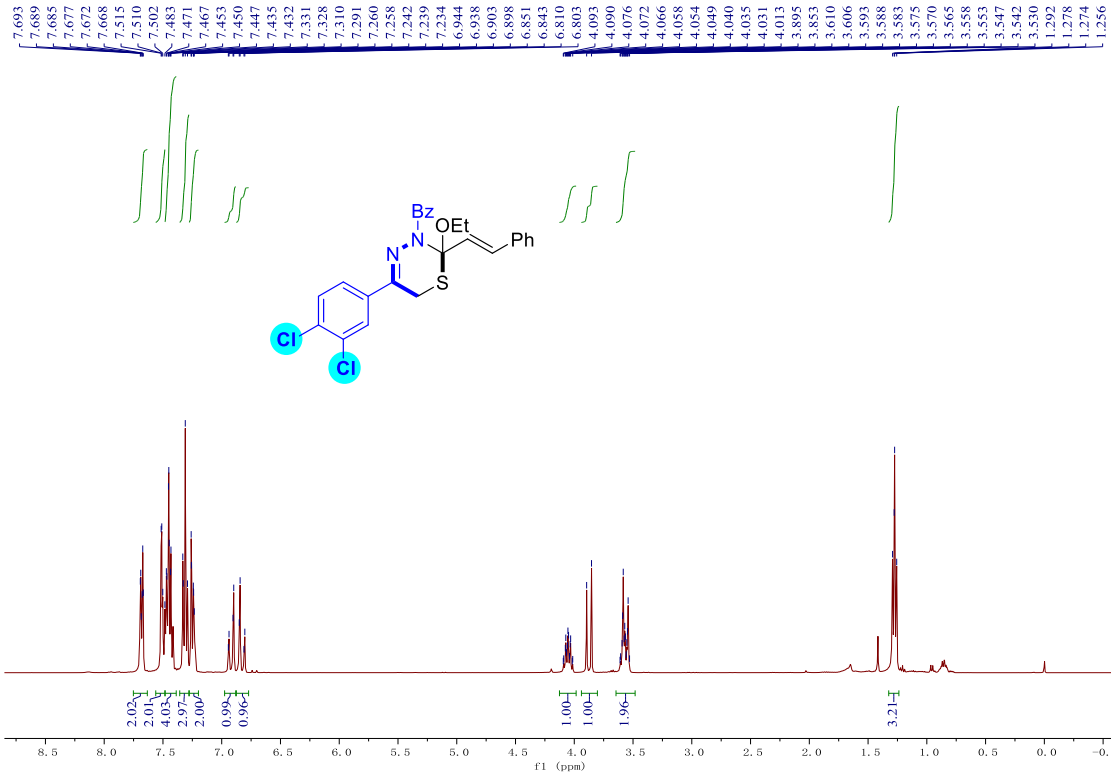
^{1}H NMR (600 MHz, $CDCl_3$) of **3k**



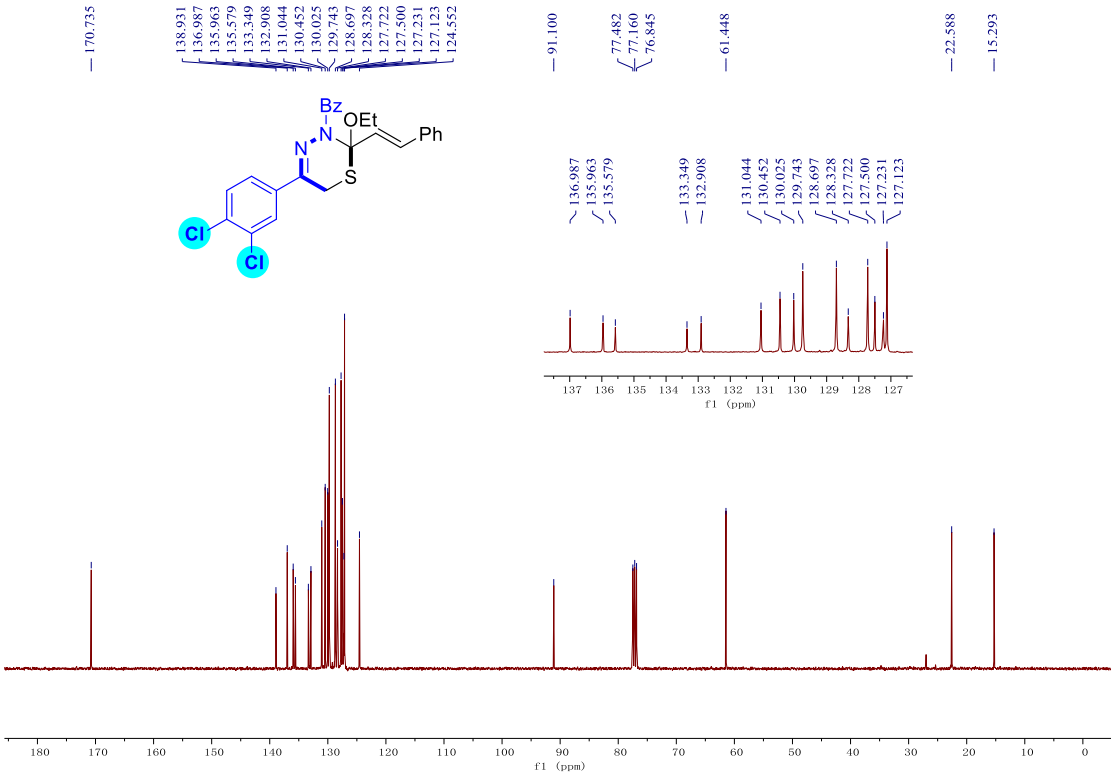
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **3k**



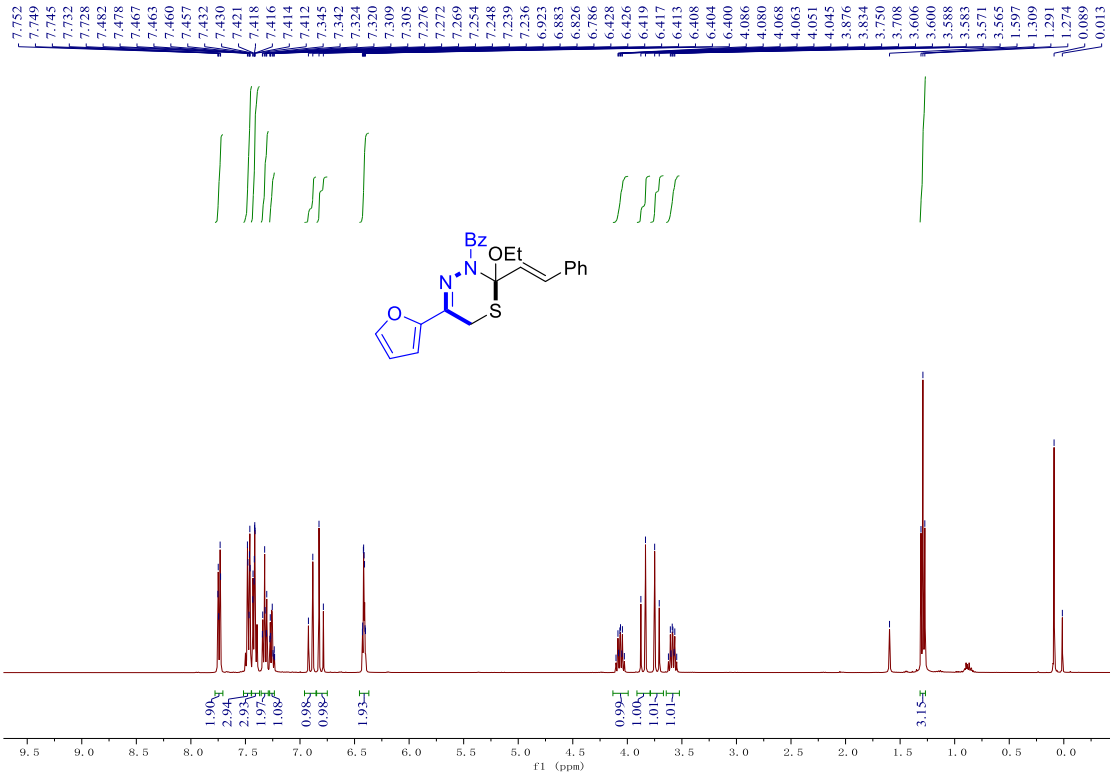
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



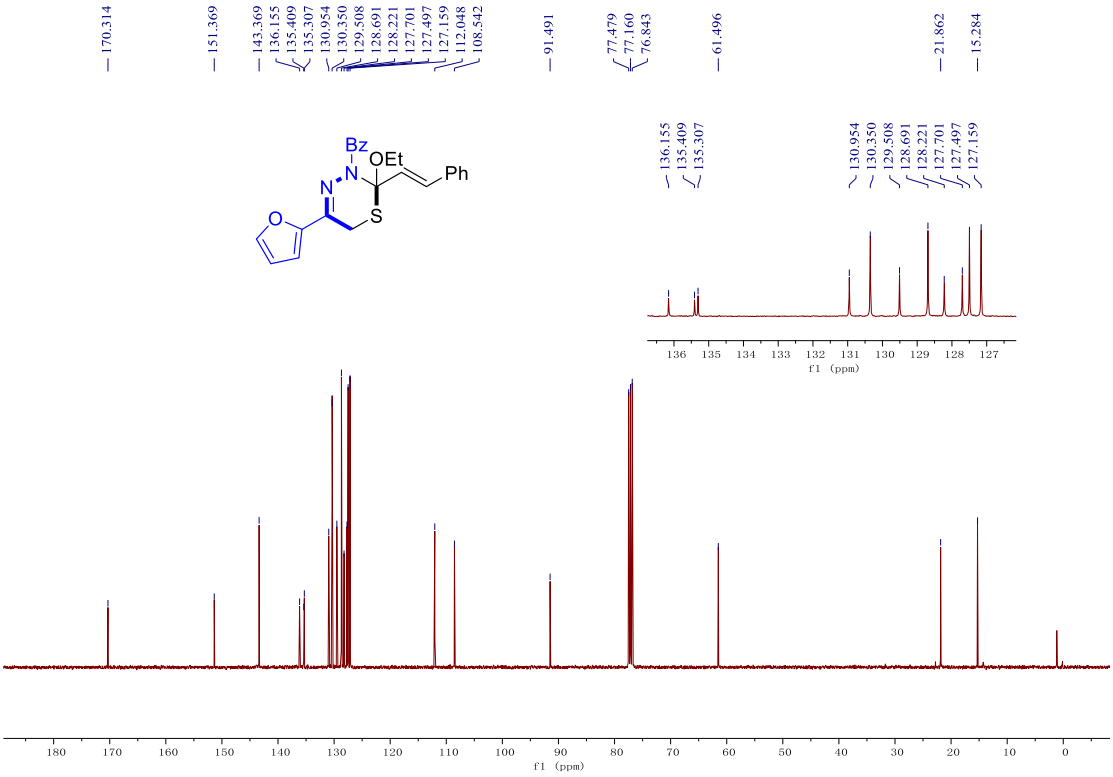
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3l**



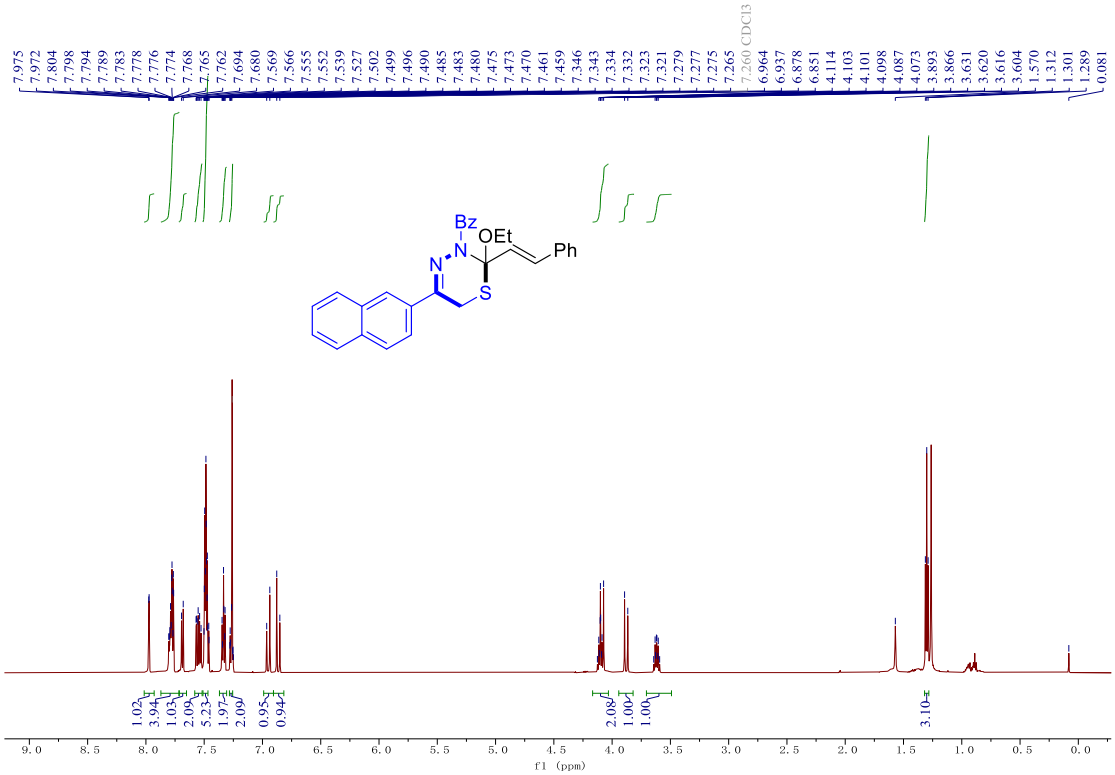
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



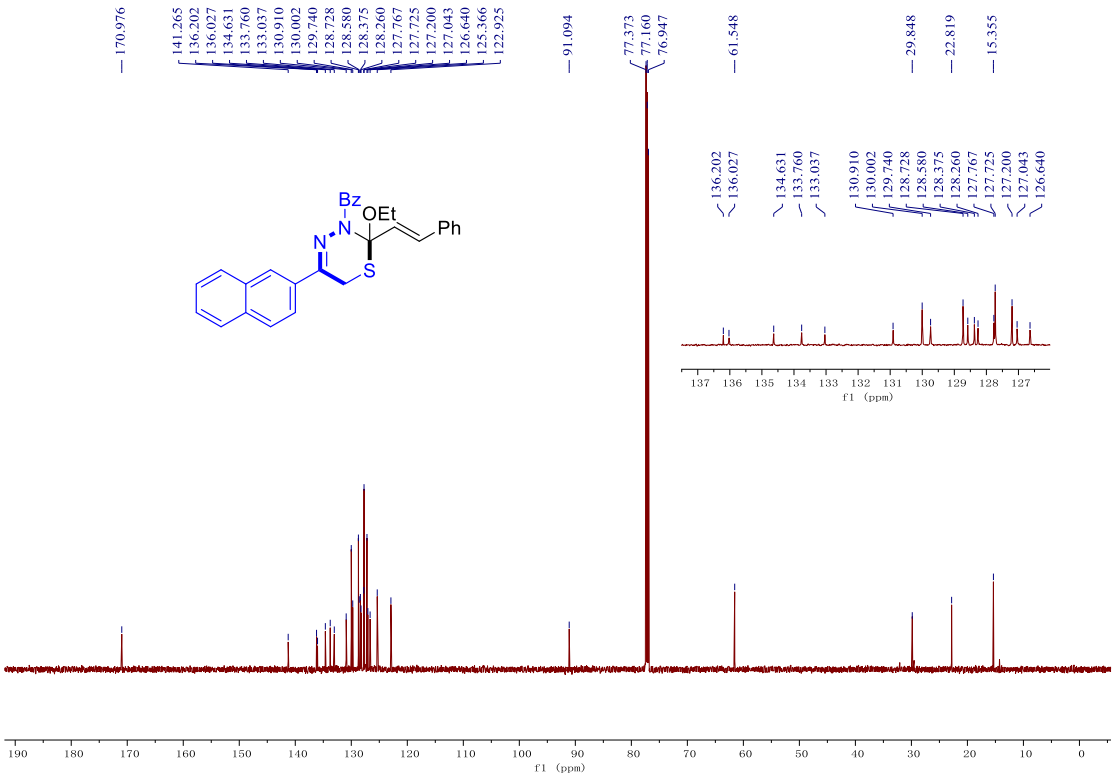
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3m**



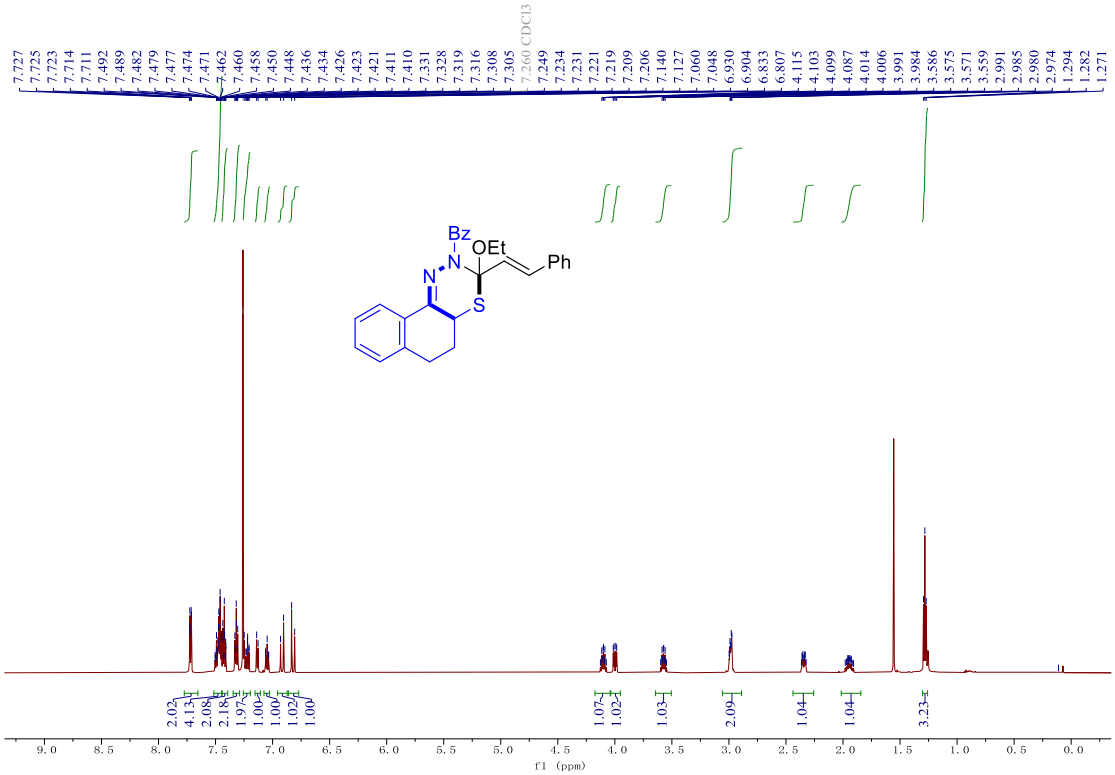
^{1}H NMR (600 MHz, $CDCl_3$) of **3n**



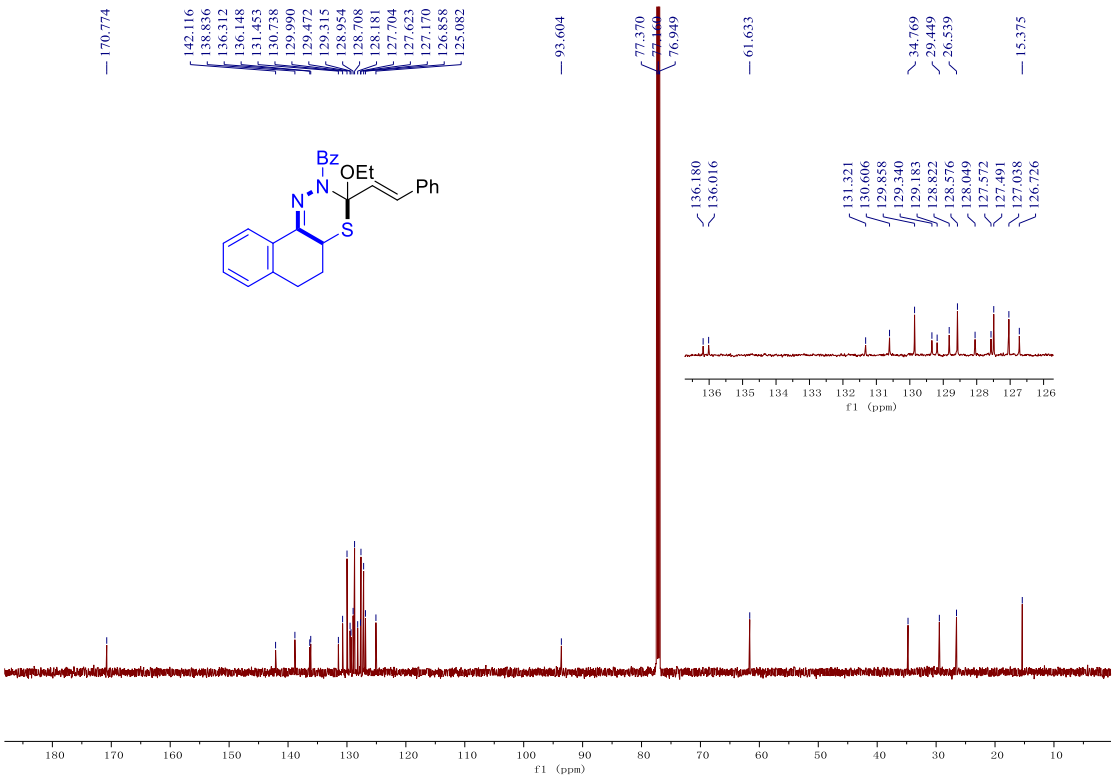
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **3n**



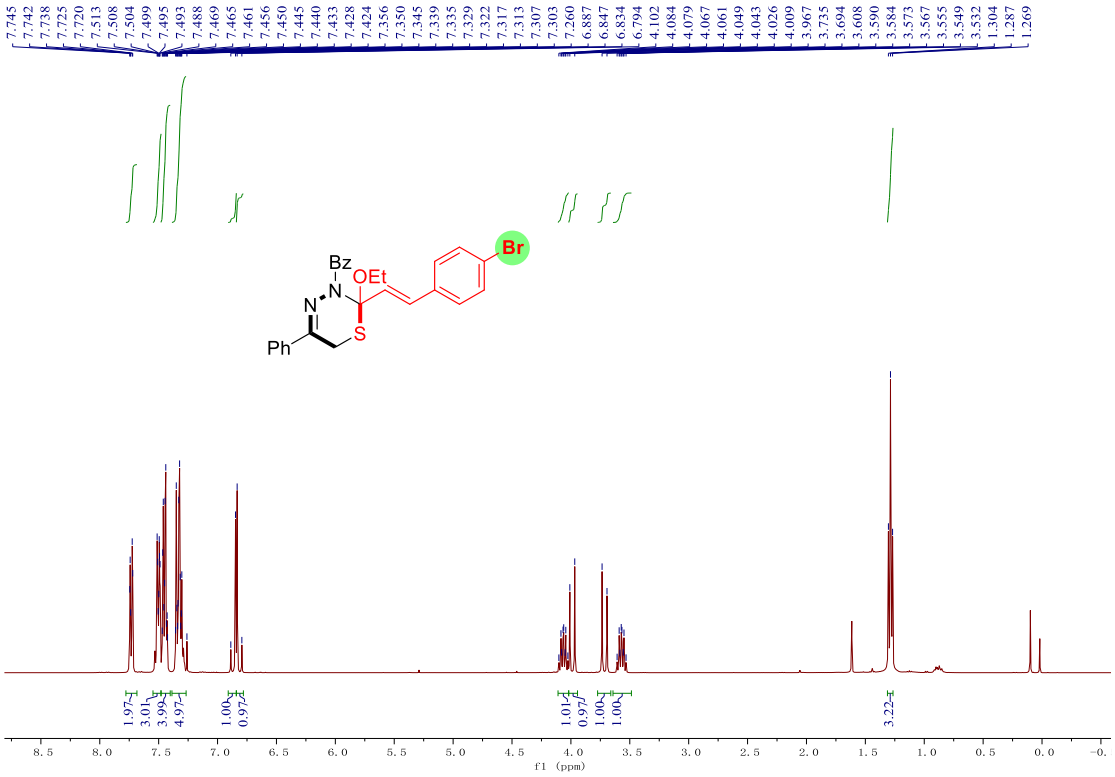
^{1}H NMR (600 MHz, $CDCl_3$) of **3o**



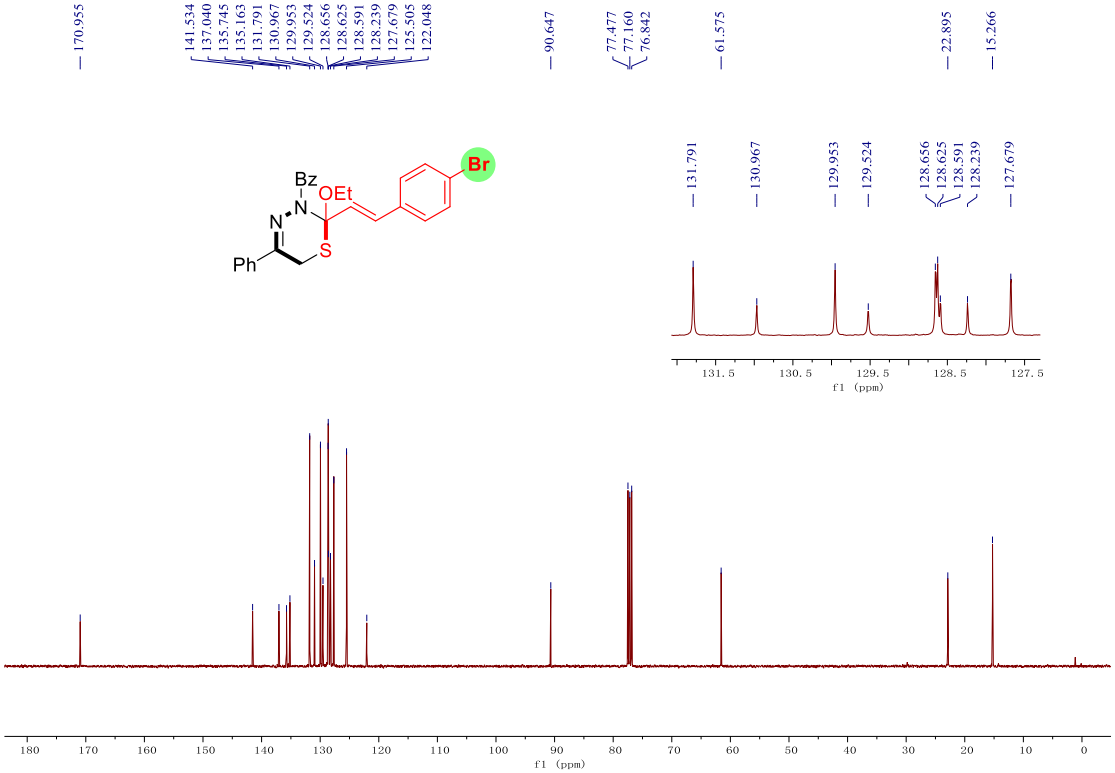
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **3o**



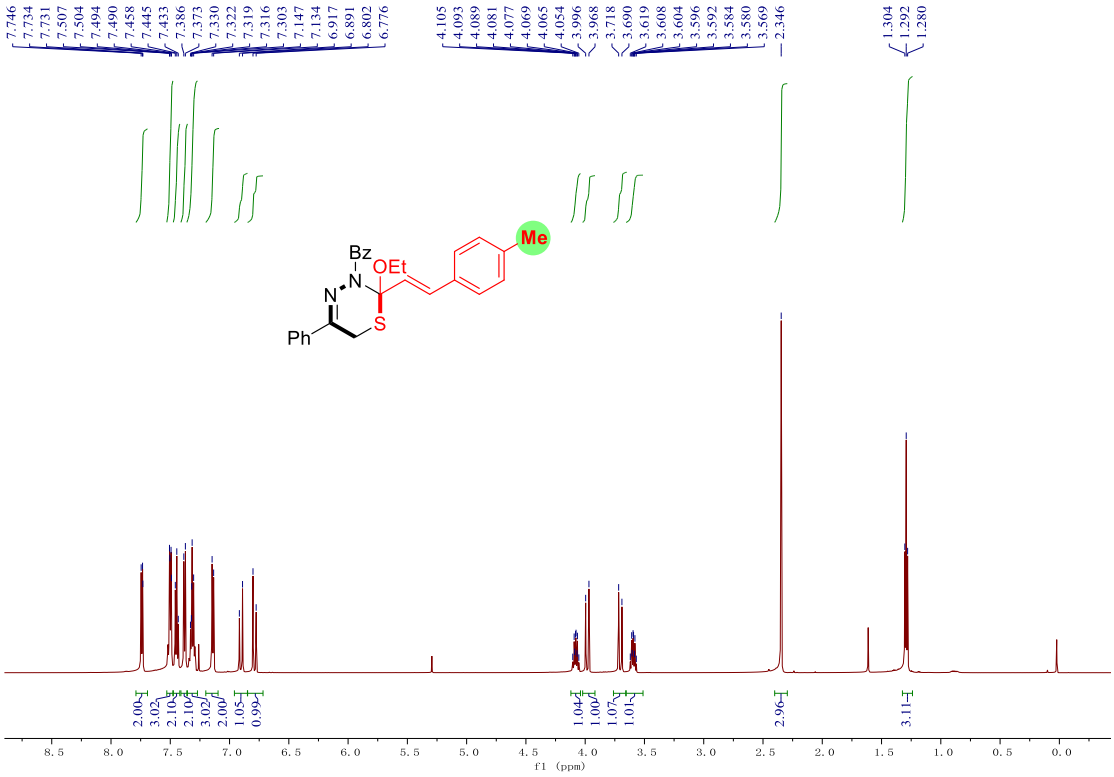
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



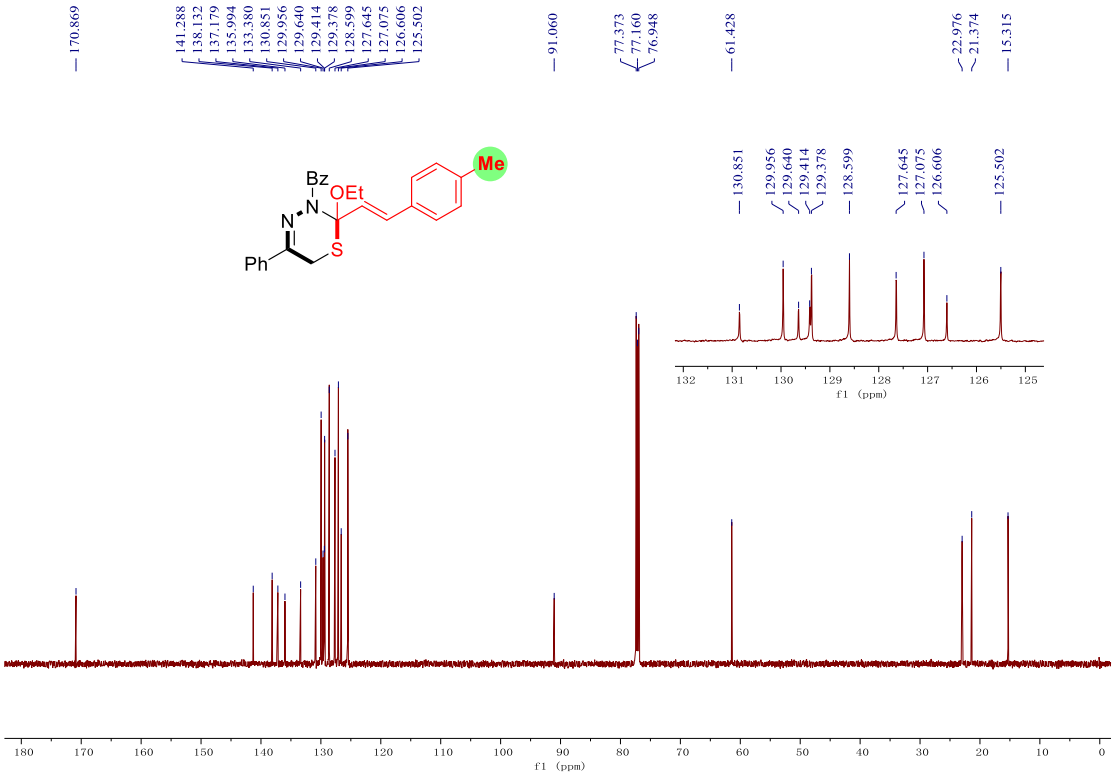
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3p**



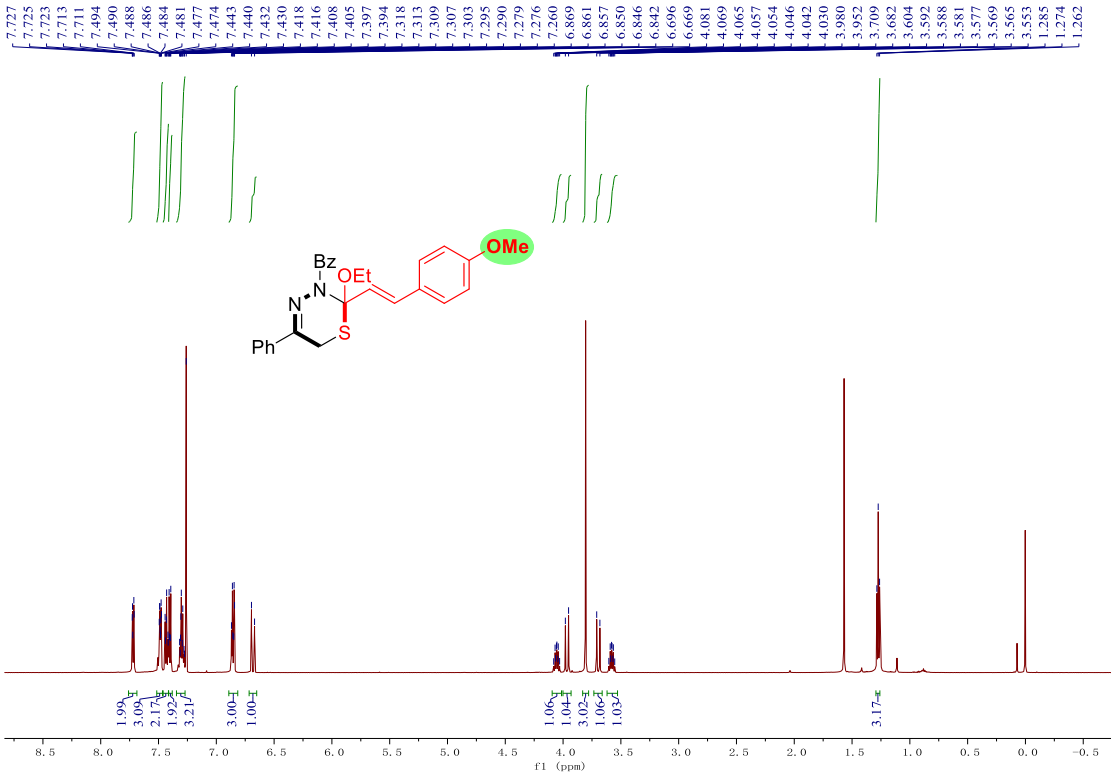
^{1}H NMR (600 MHz, $CDCl_3$) of **3q**



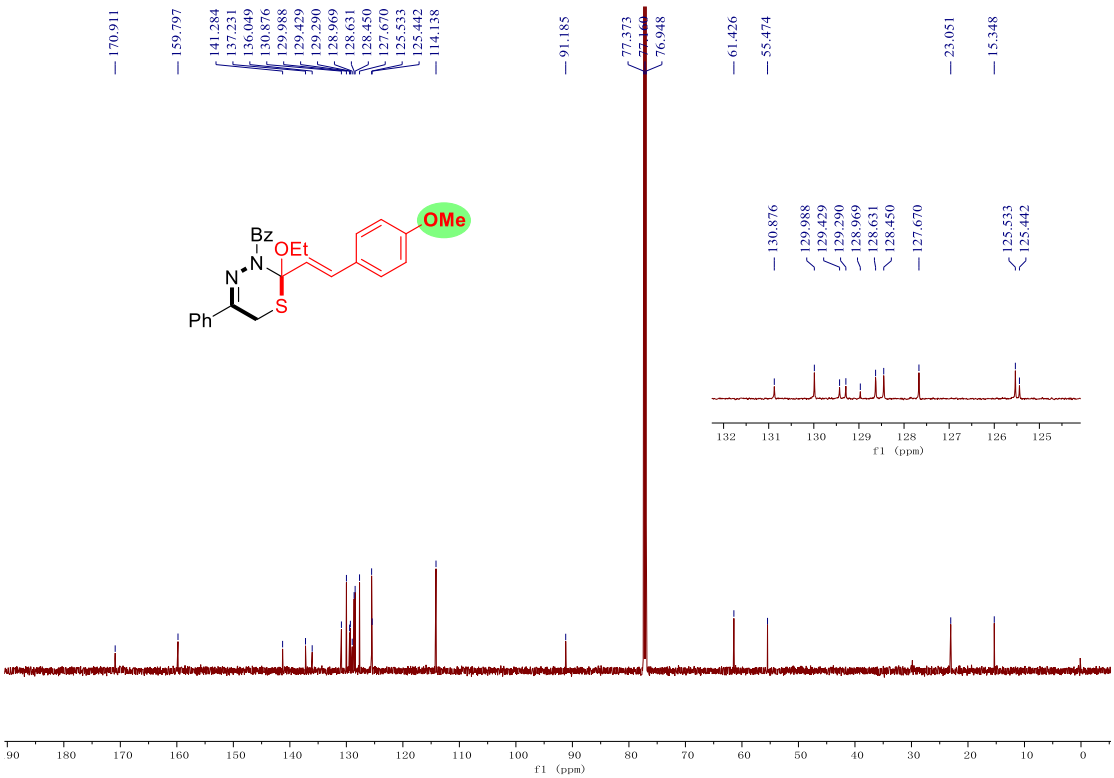
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **3q**



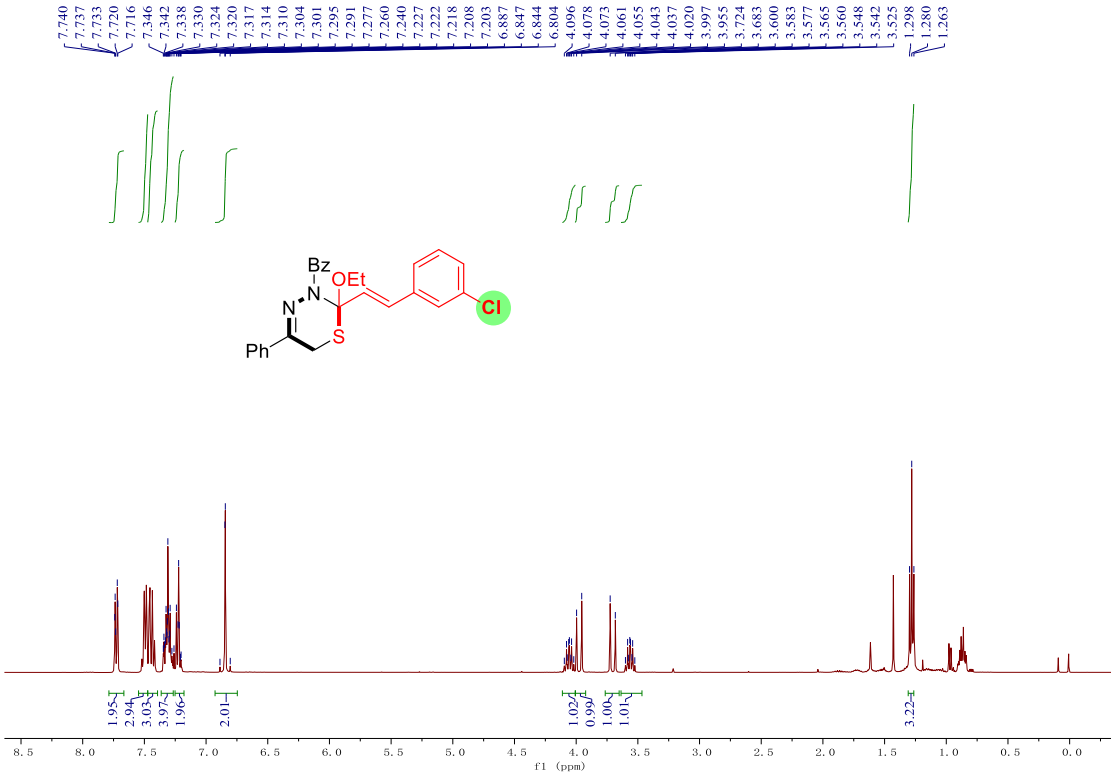
^{1}H NMR (600 MHz, $CDCl_3$) of **3r**



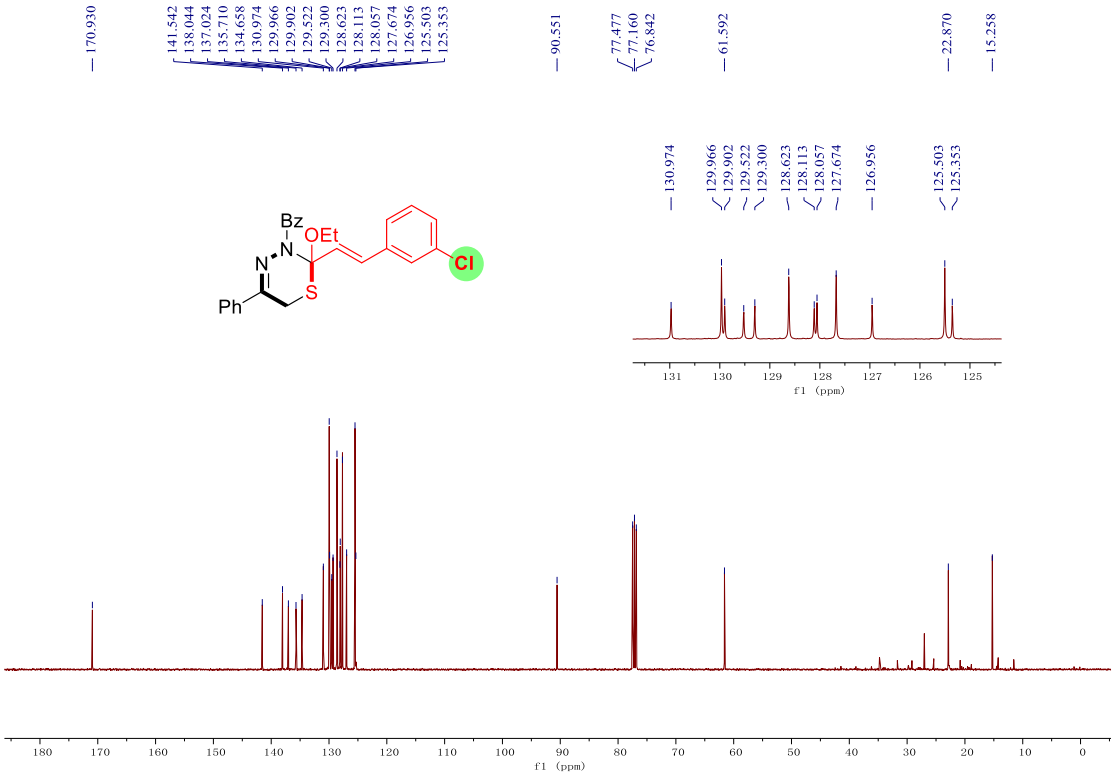
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **3r**



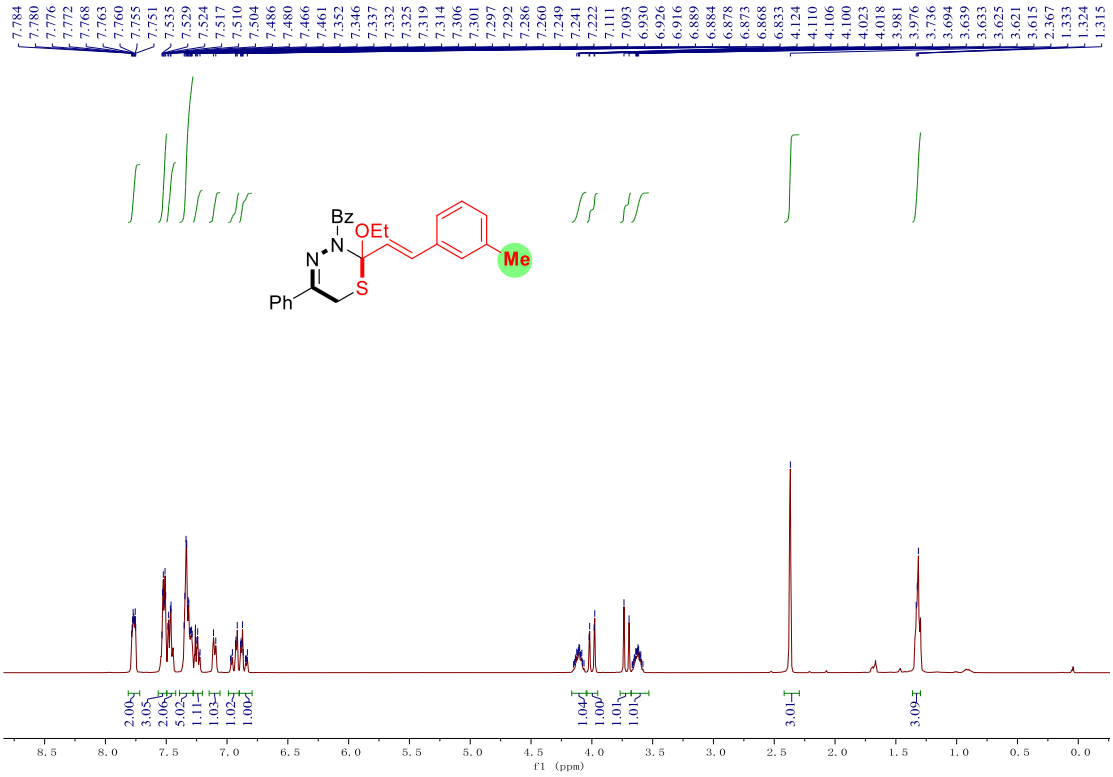
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



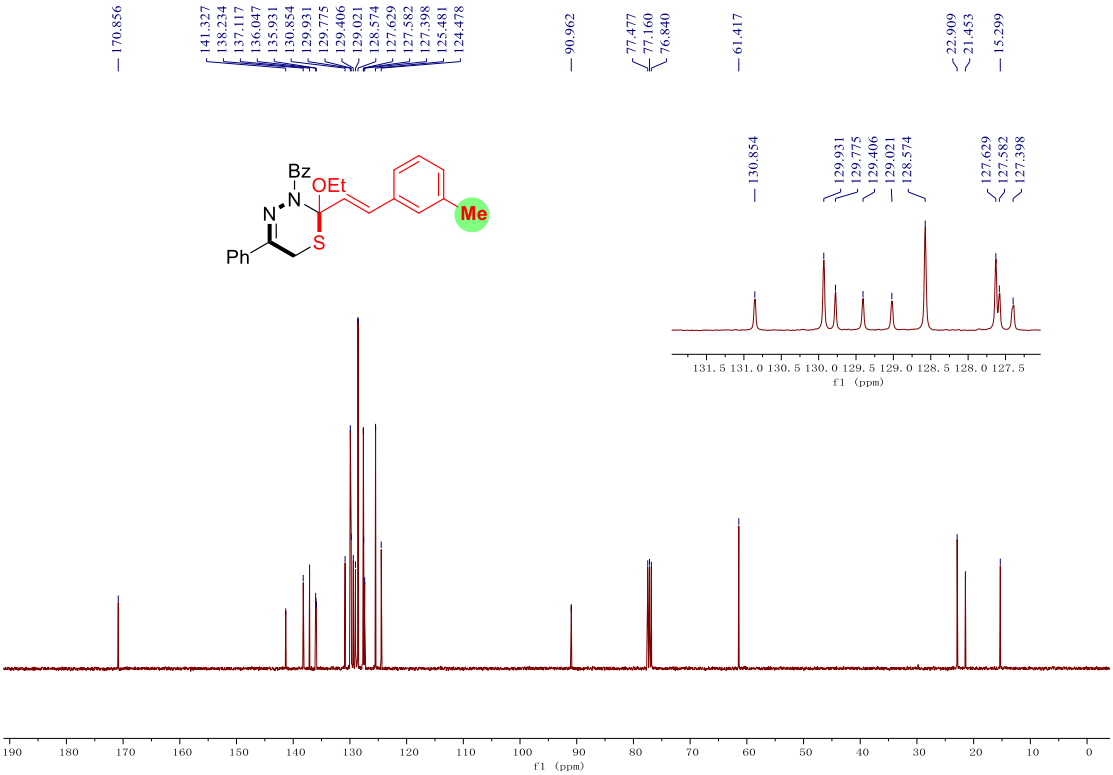
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3s**



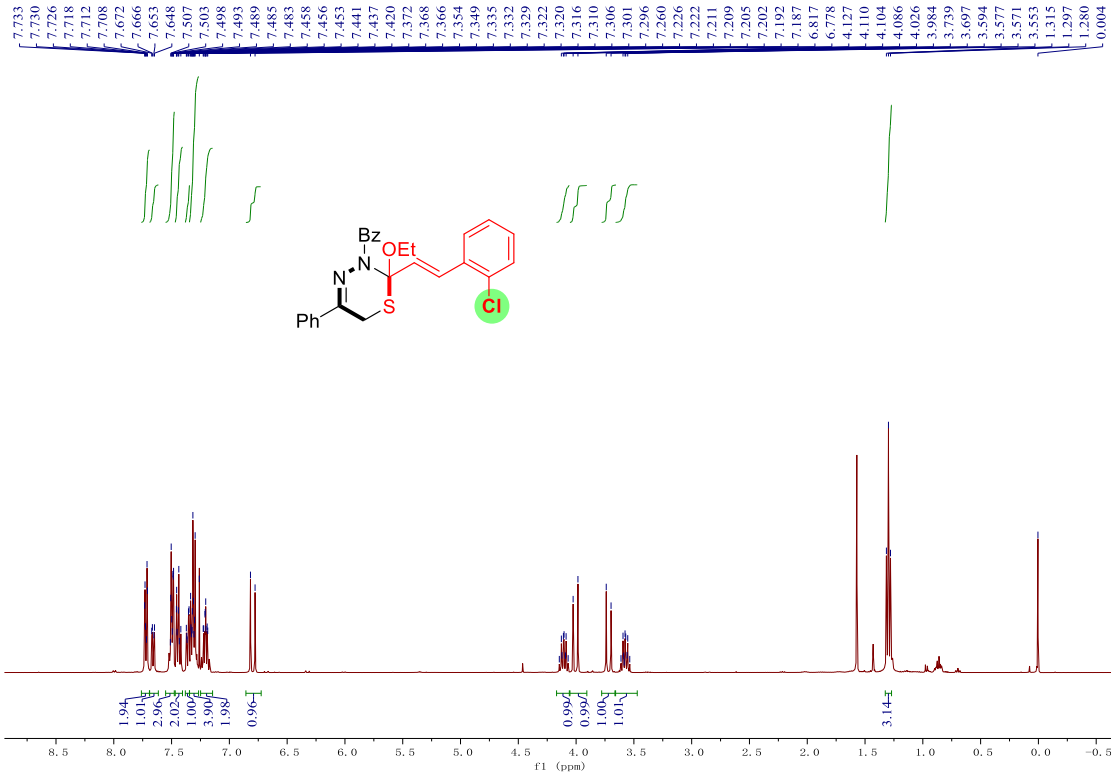
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



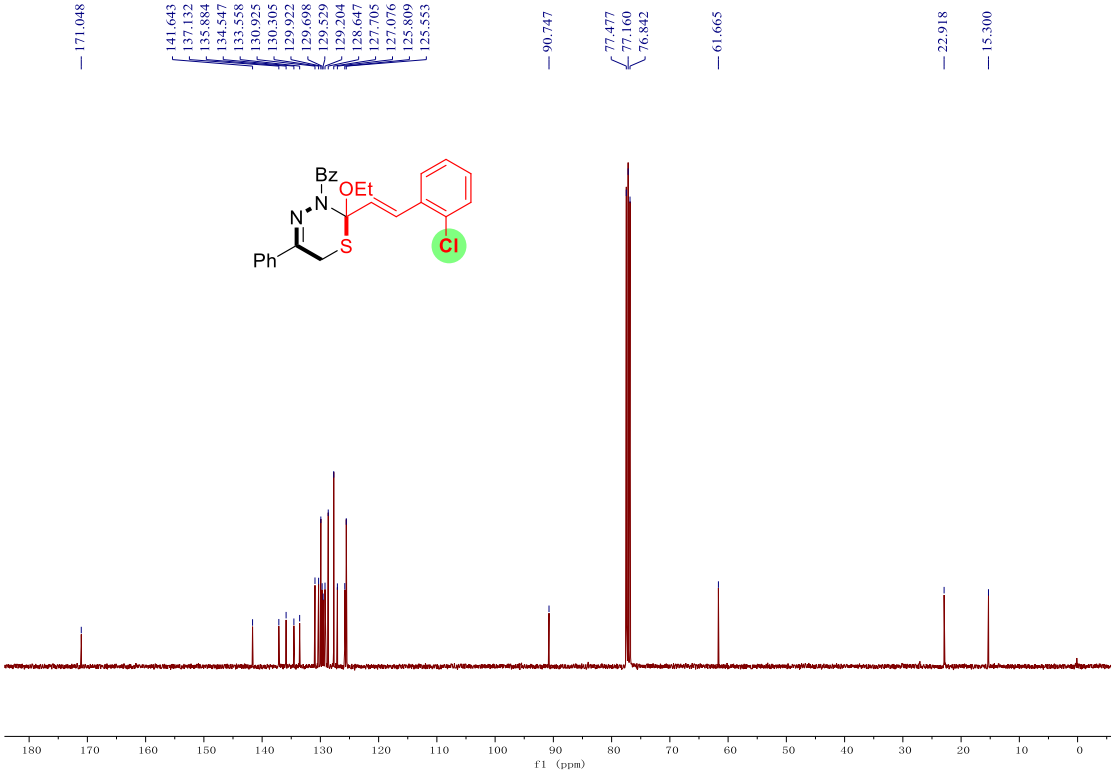
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3t**



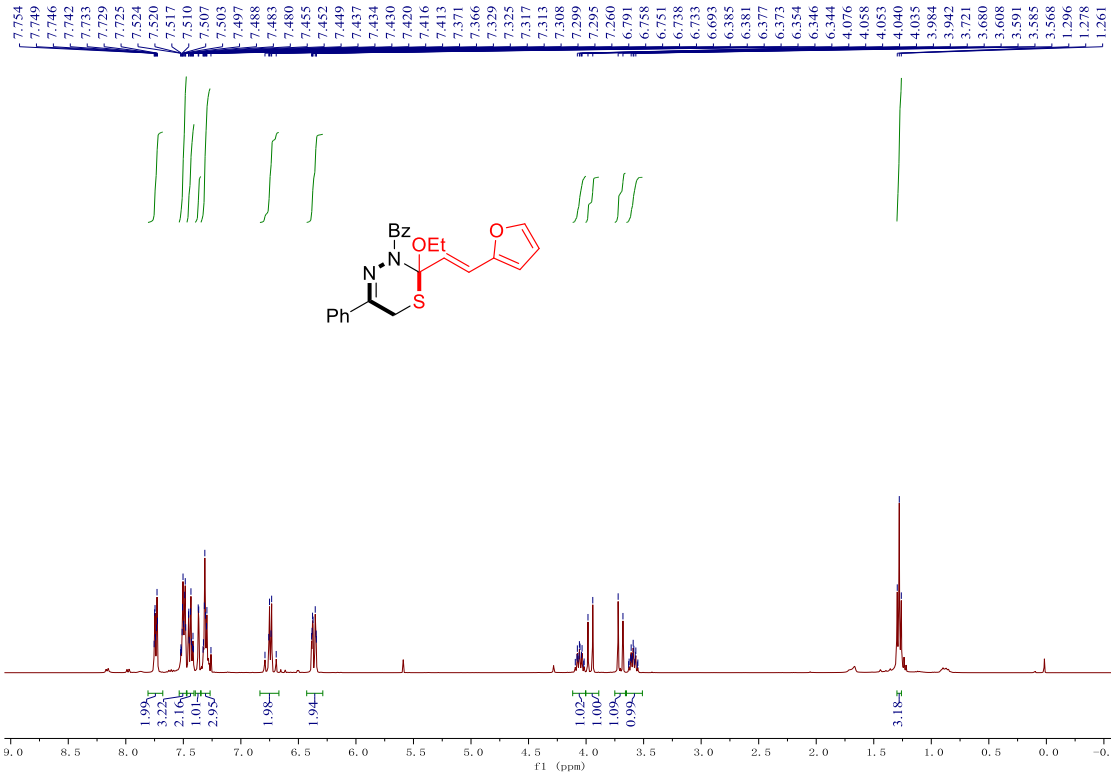
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



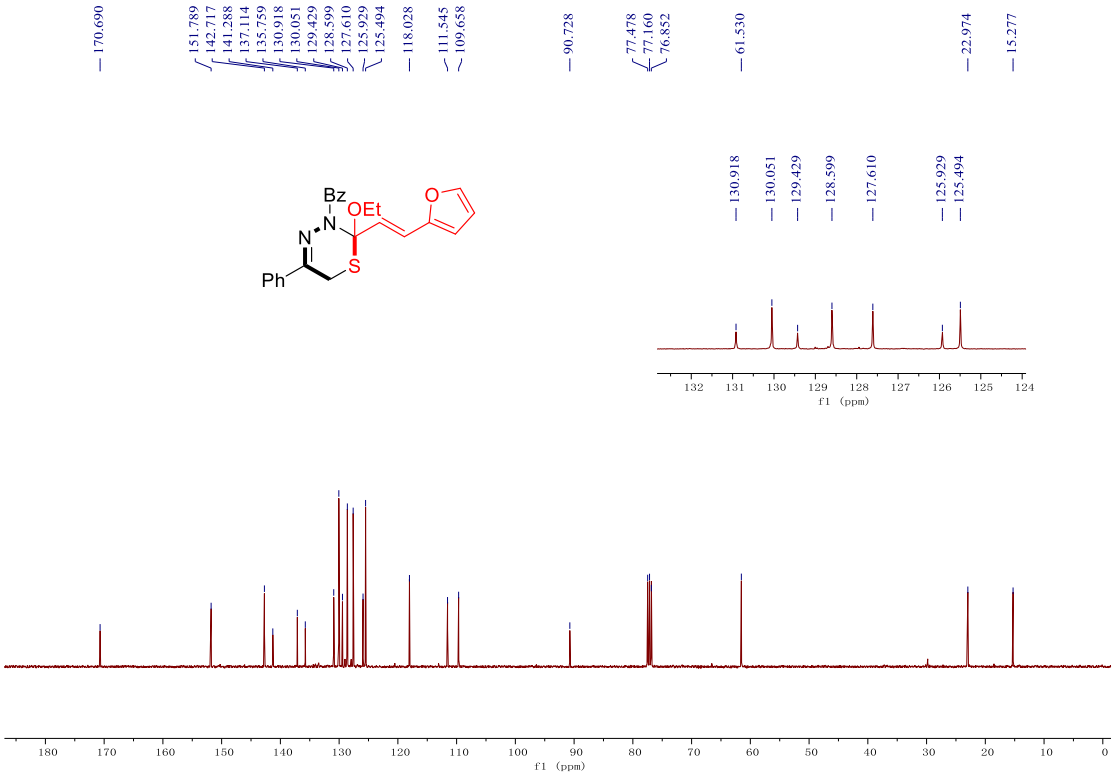
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3u**



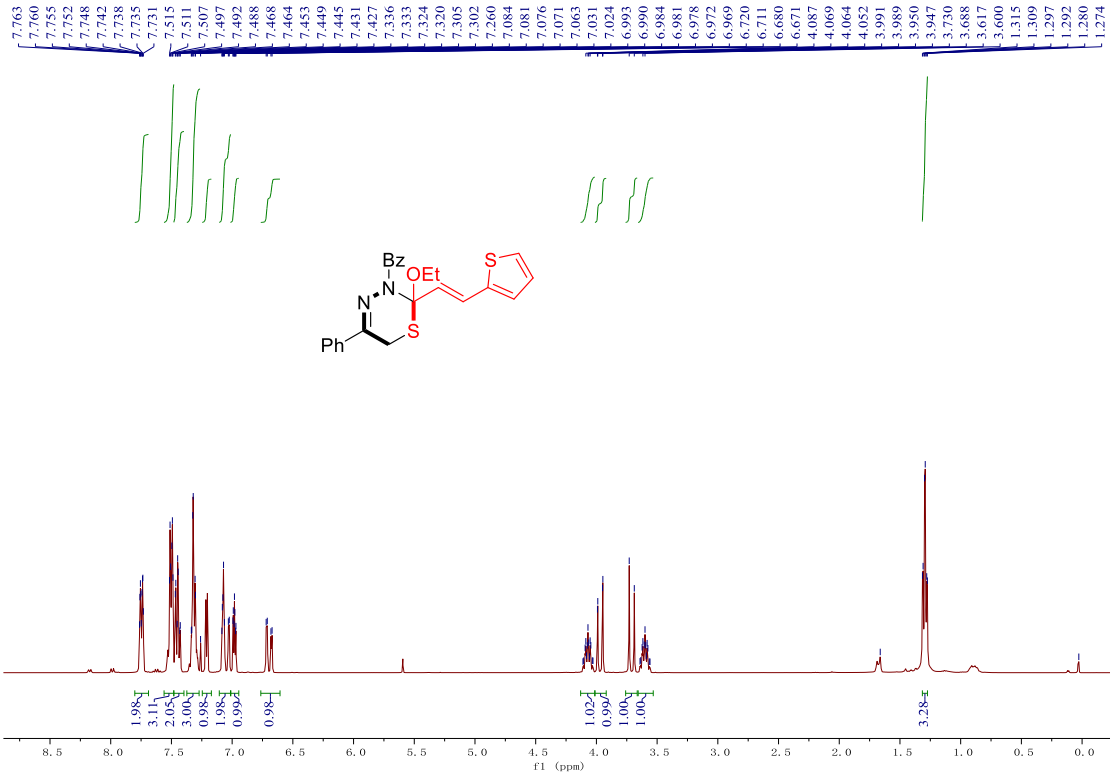
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



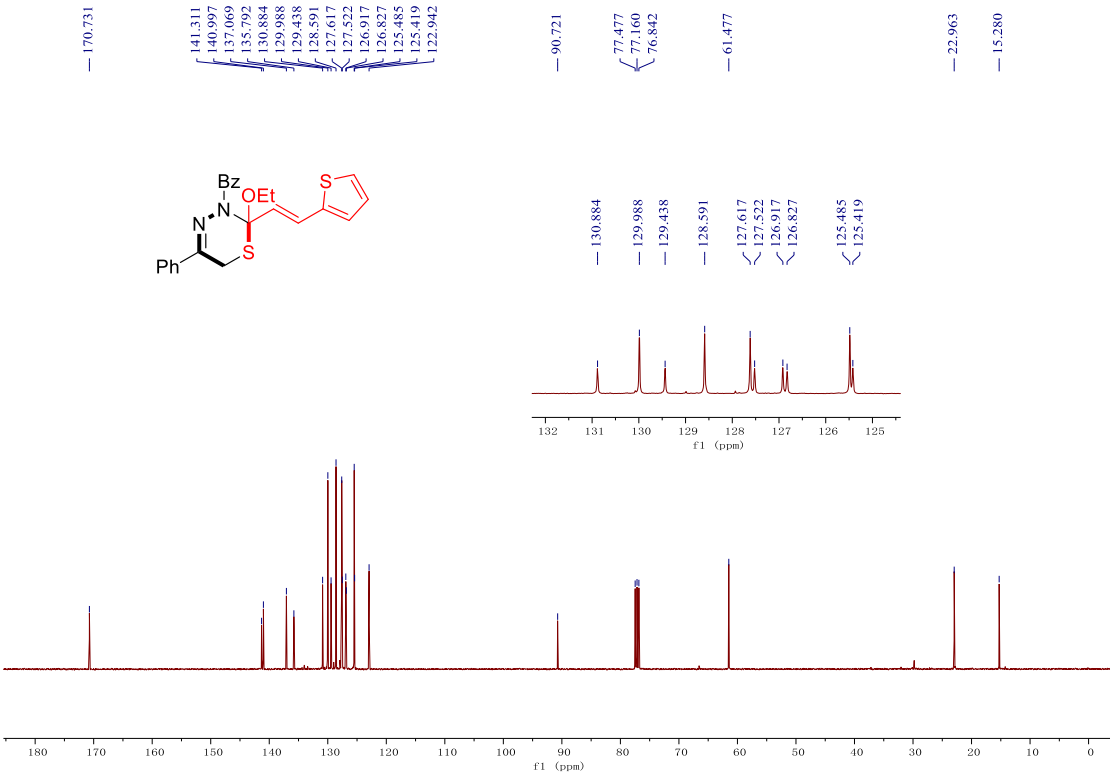
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3v**



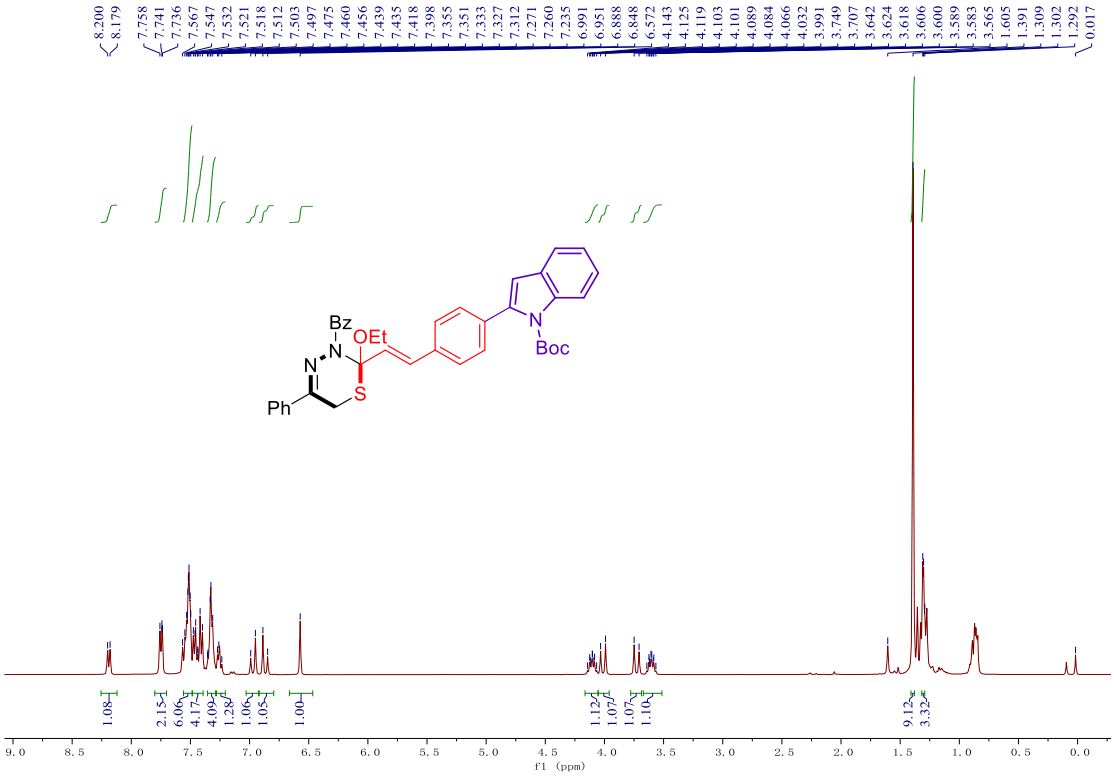
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



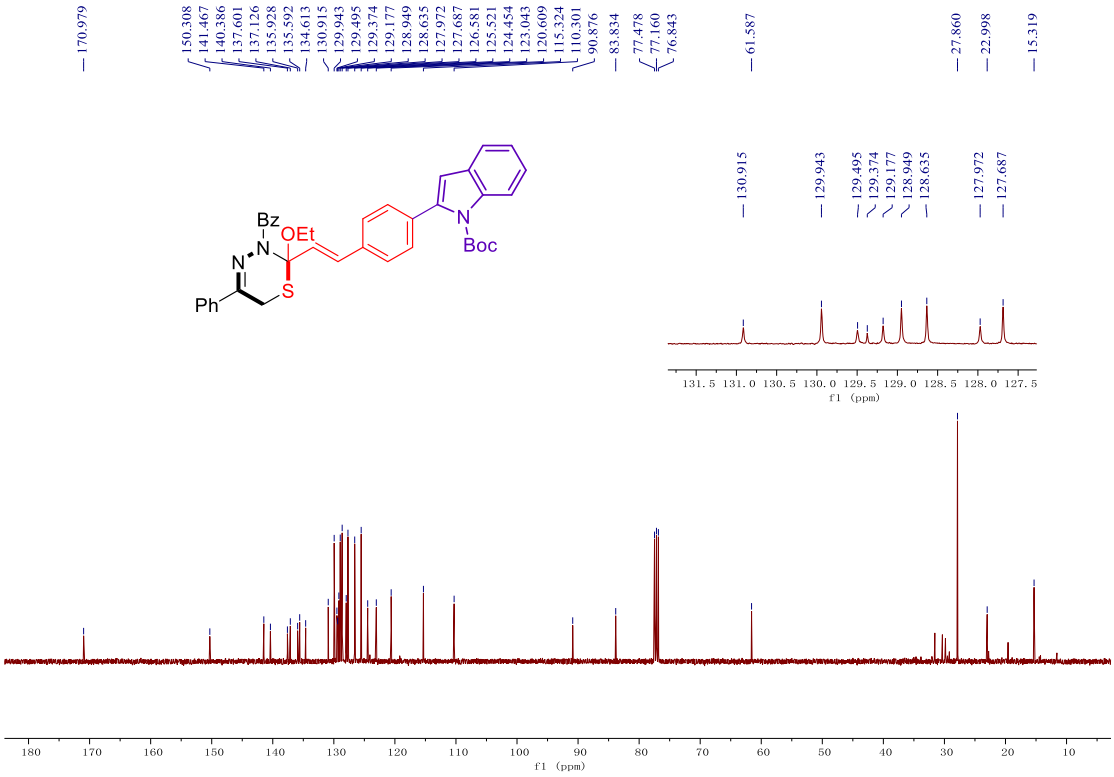
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3w**



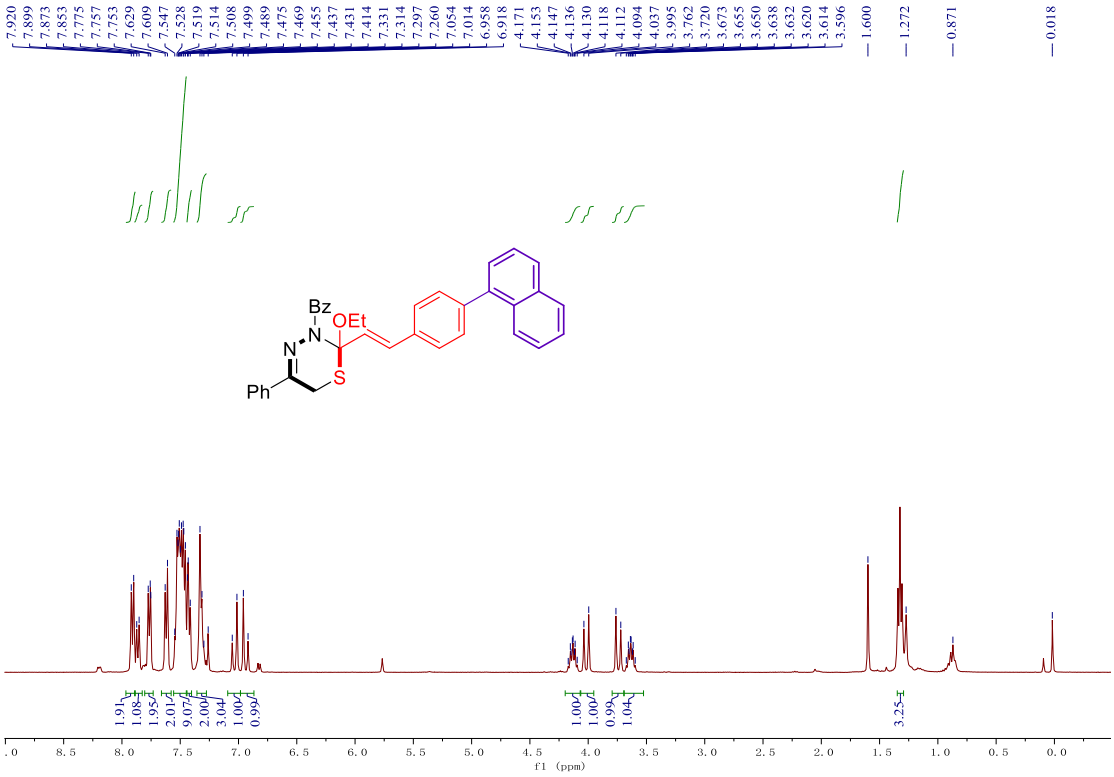
^{1}H NMR (400 MHz, $CDCl_3$) of **5a**



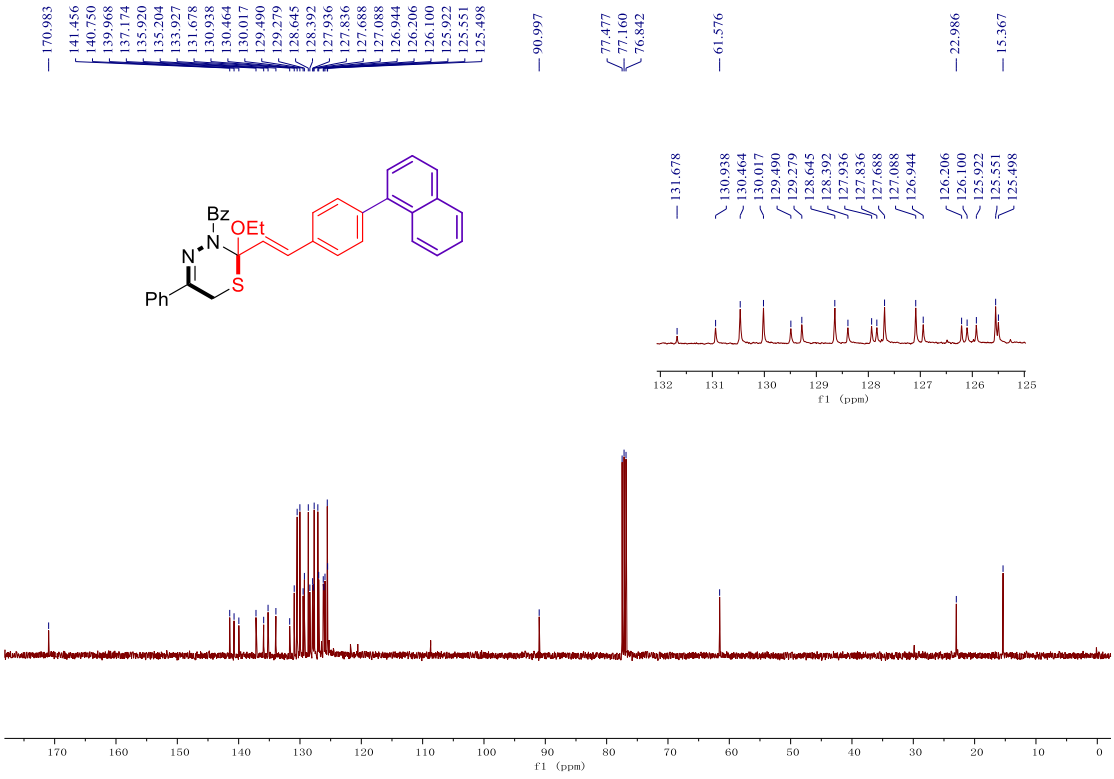
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **5a**



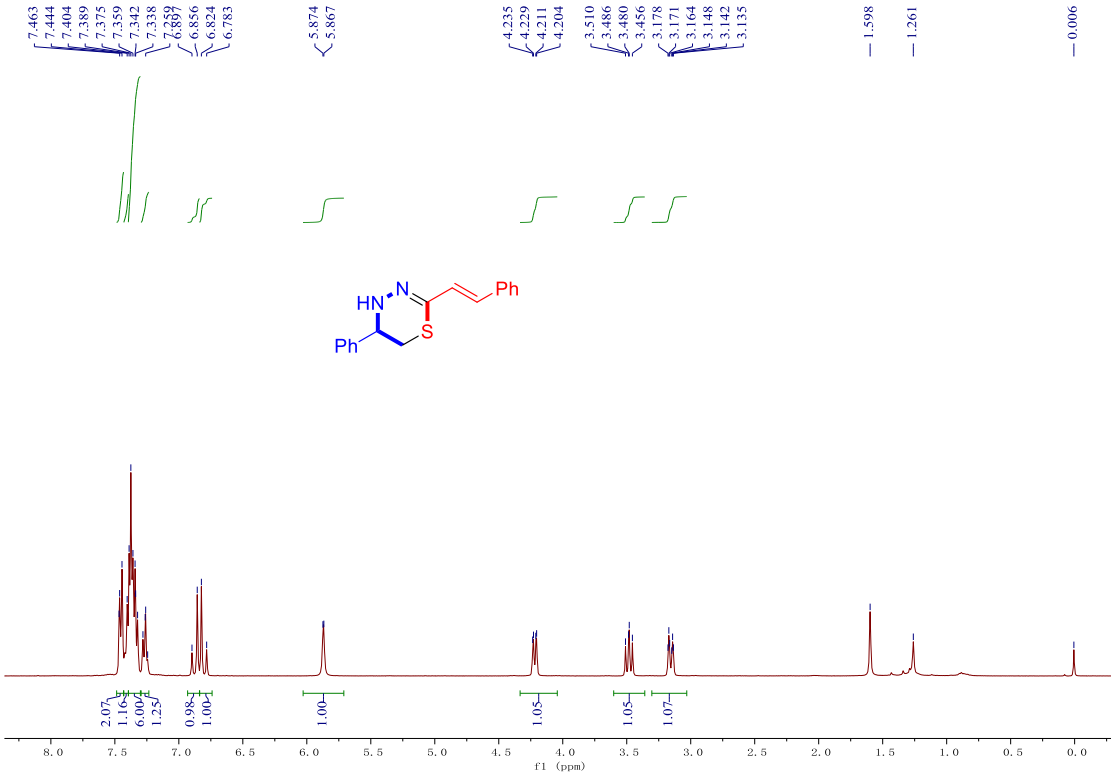
^{1}H NMR (400 MHz, $CDCl_3$) of **5b**



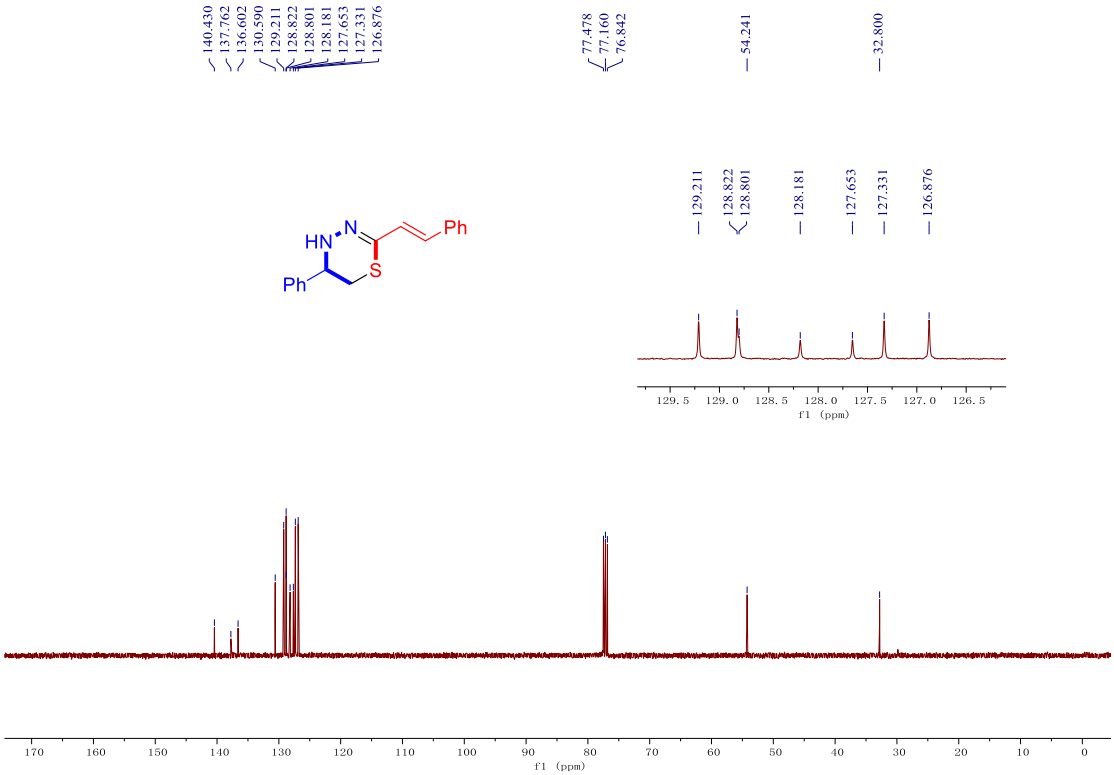
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **5b**



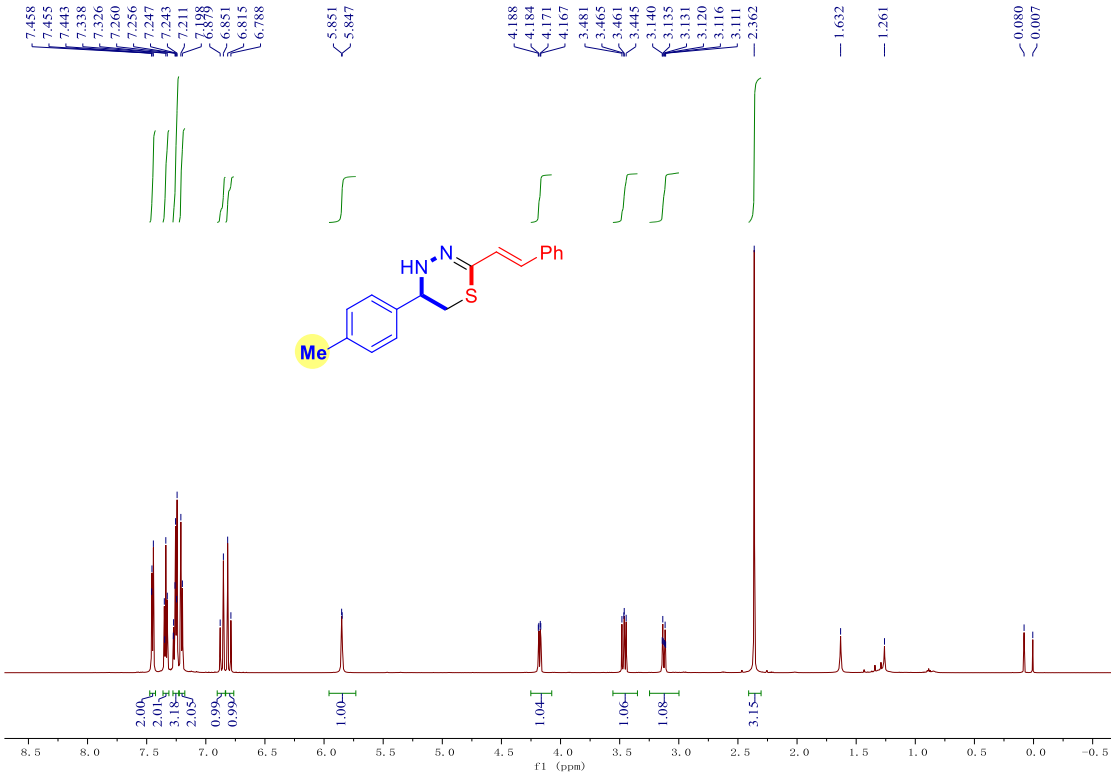
^{1}H NMR (400 MHz, $CDCl_3$) of **6a**



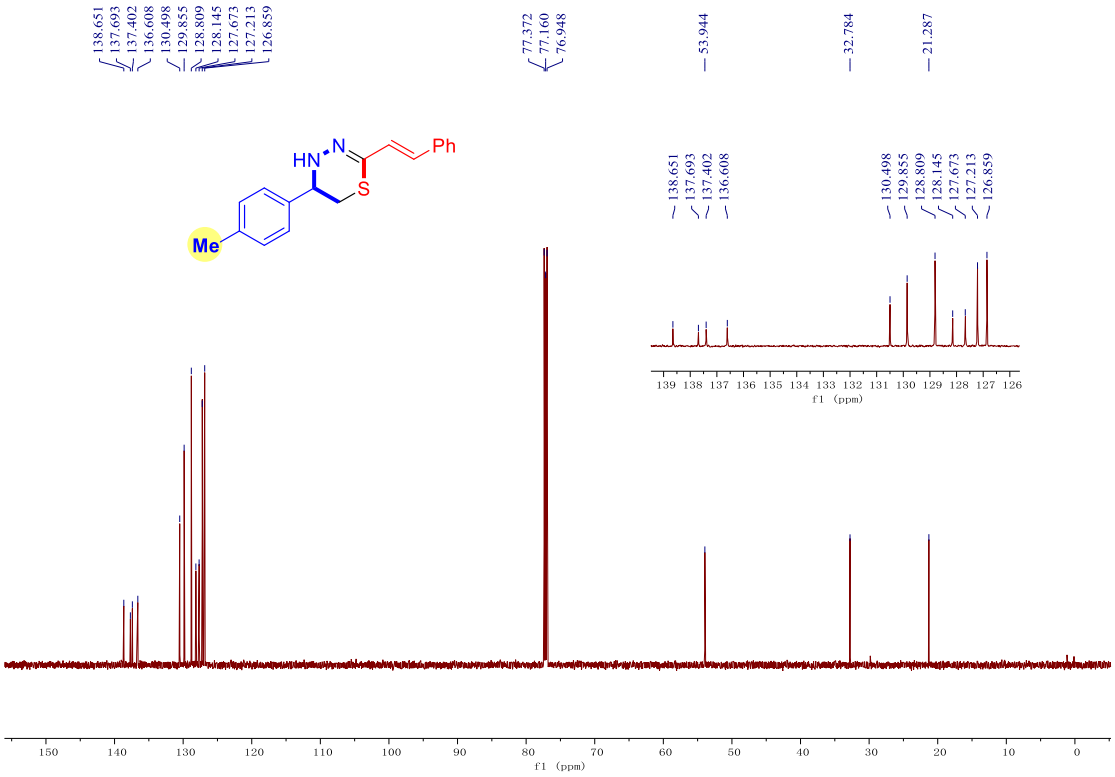
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **6a**



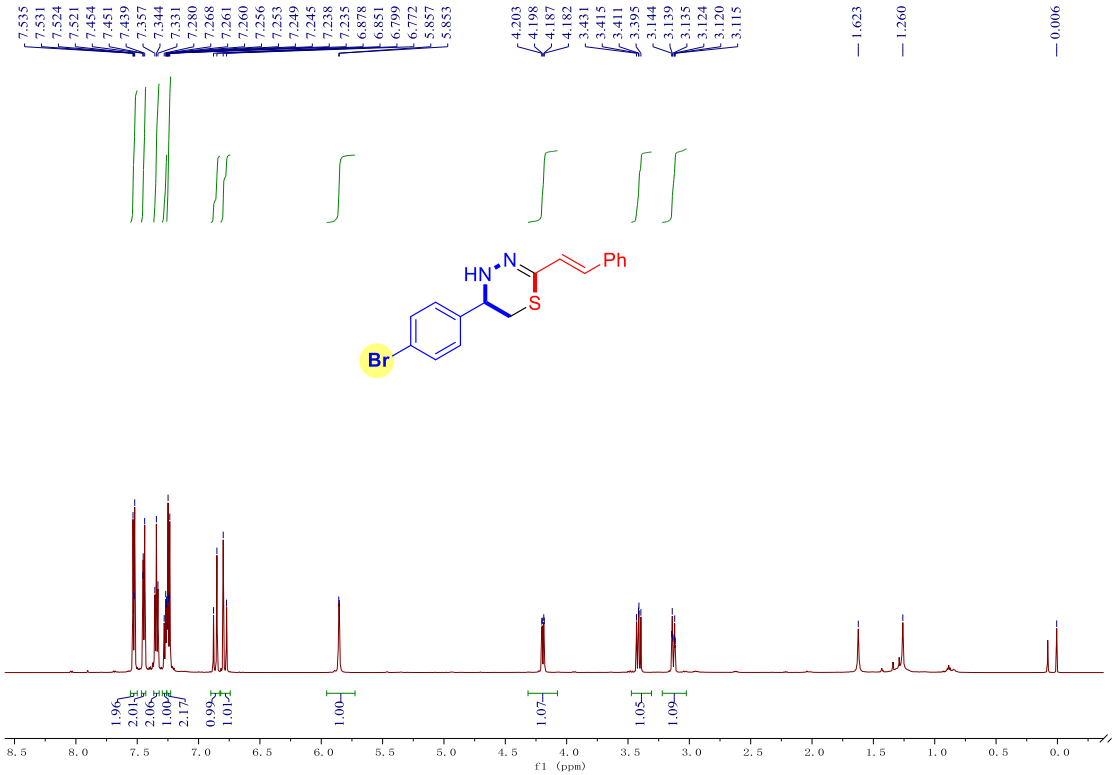
^{1}H NMR (600 MHz, $CDCl_3$) of **6b**



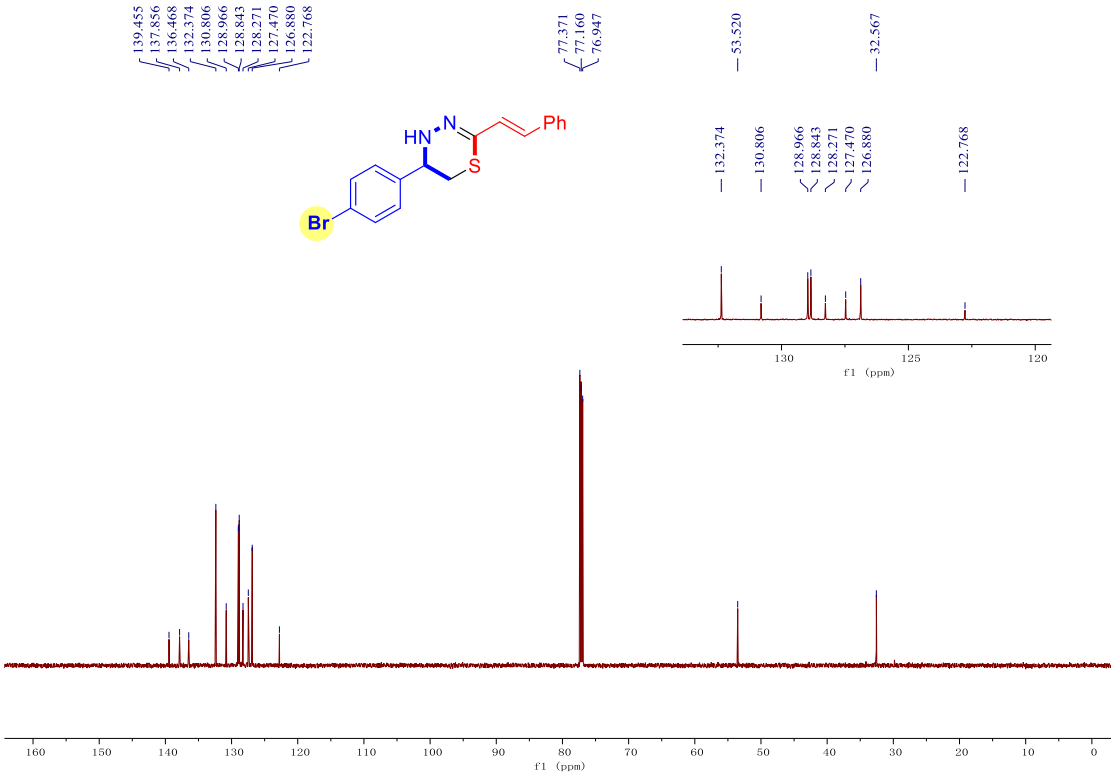
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **6b**



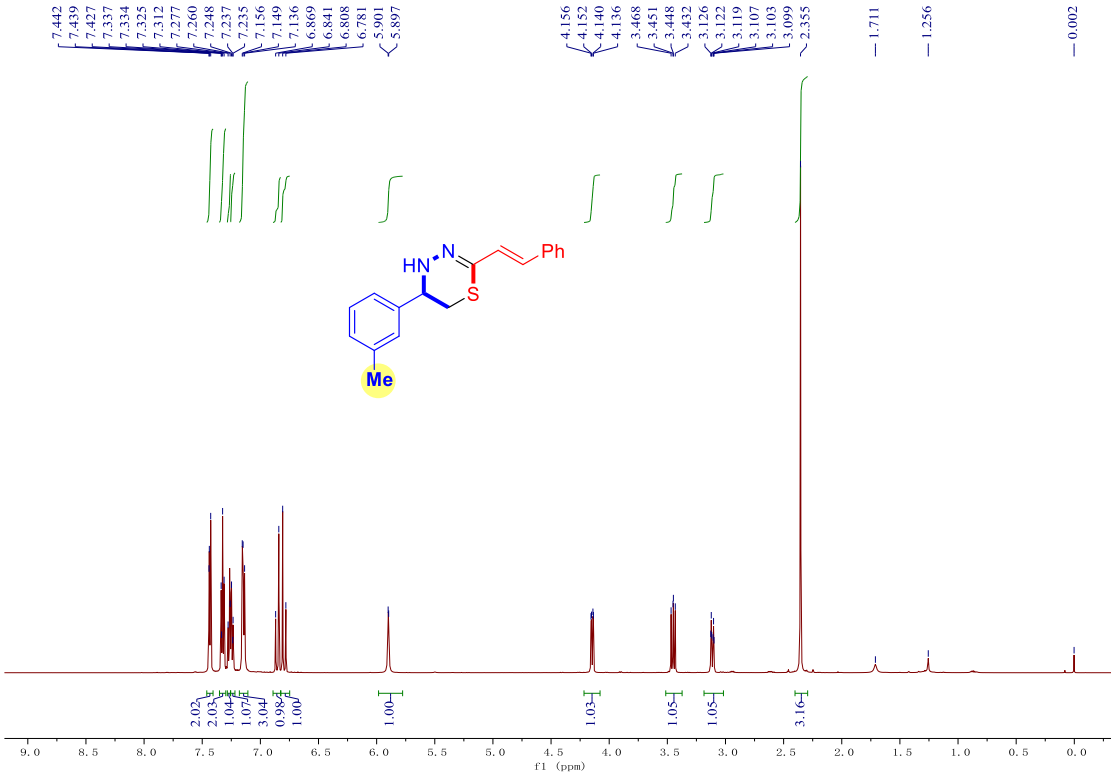
^{1}H NMR (600 MHz, $CDCl_3$) of **6c**



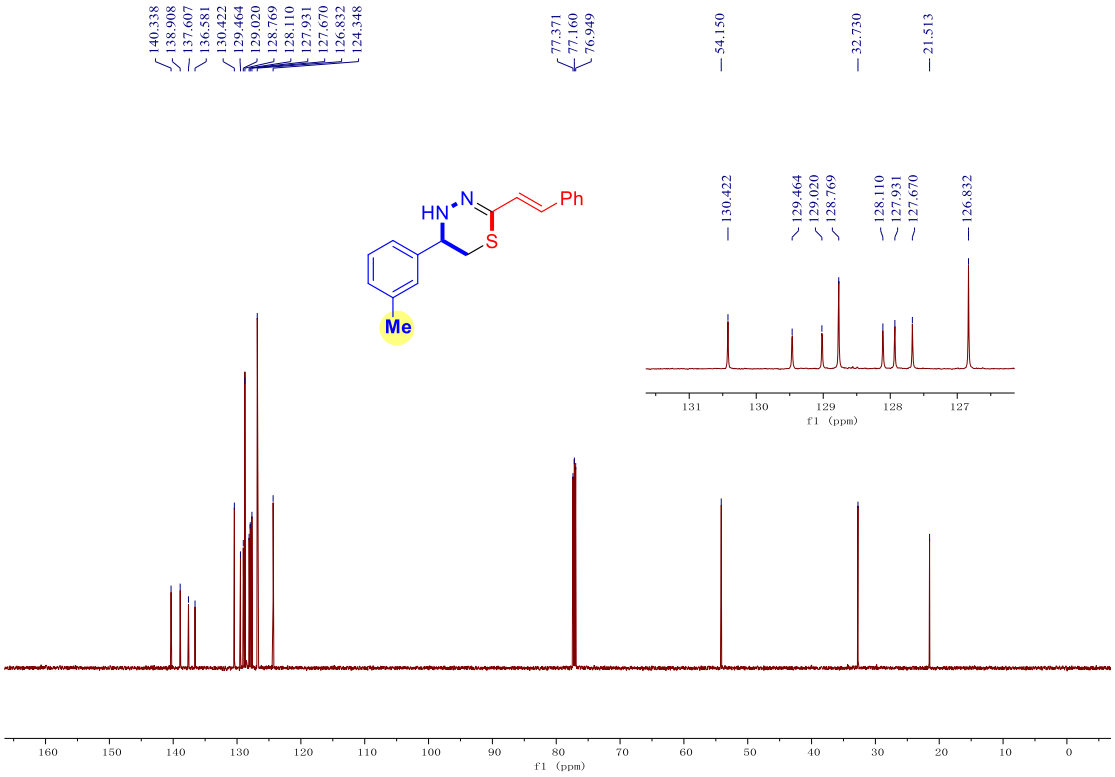
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **6c**



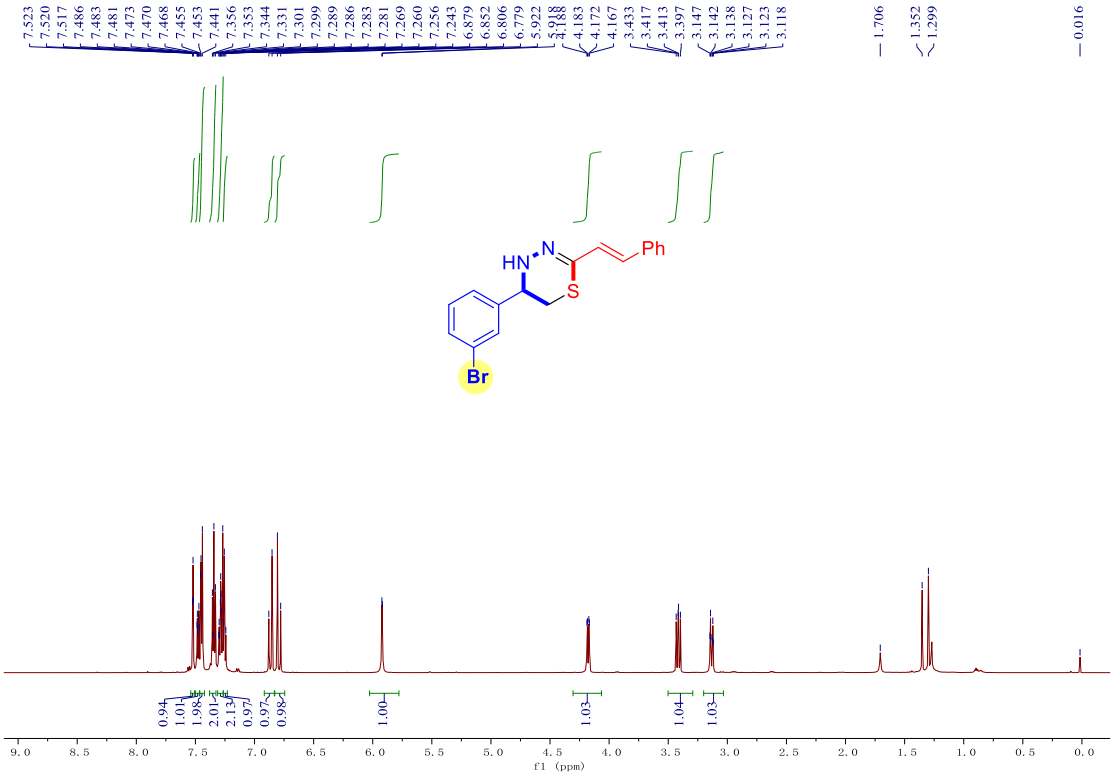
^{1}H NMR (600 MHz, $CDCl_3$) of **6d**



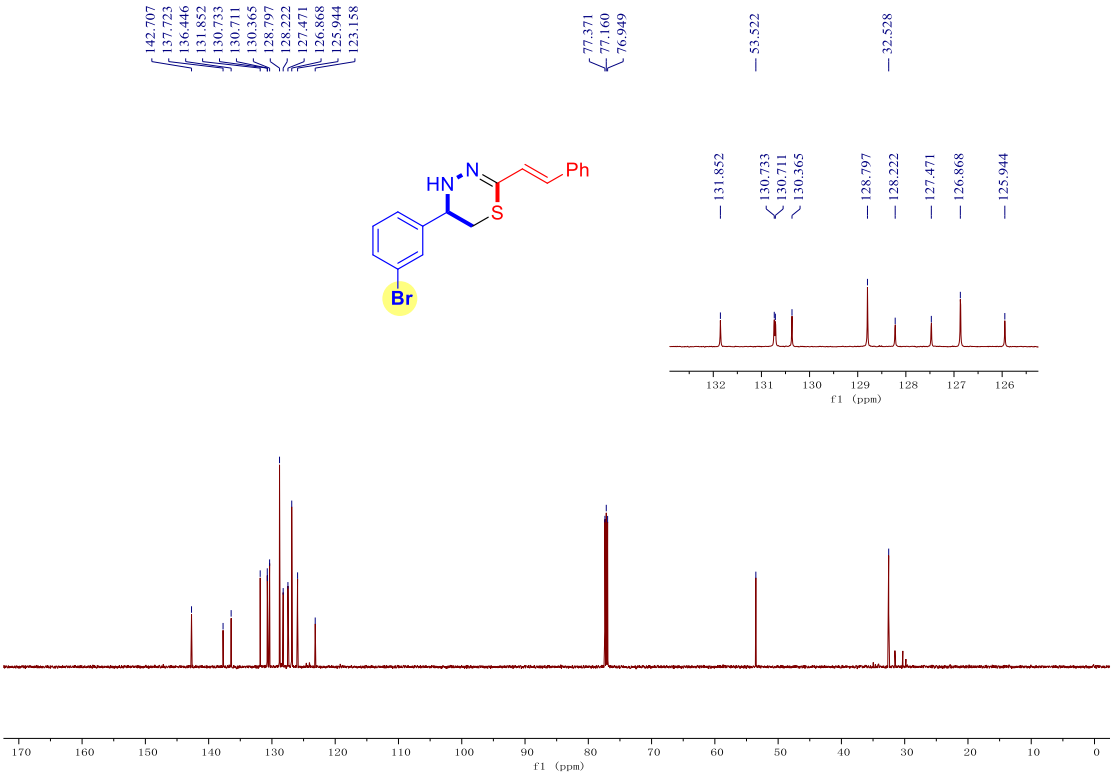
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **6d**



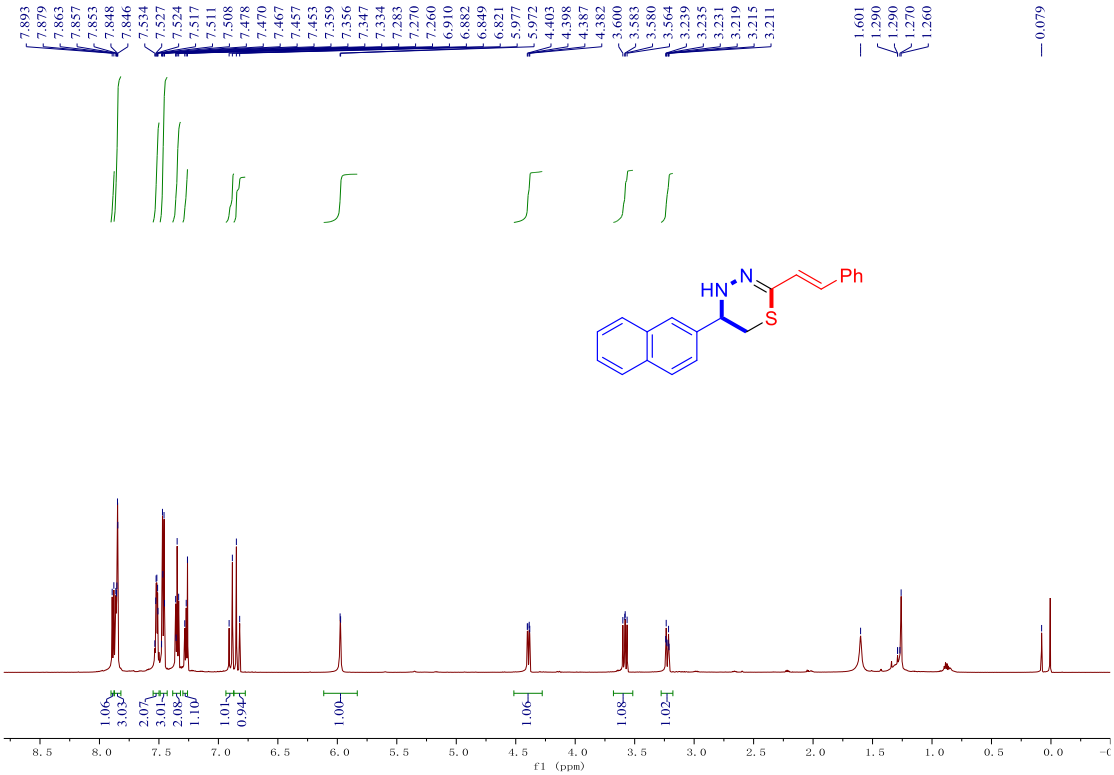
^{1}H NMR (600 MHz, $CDCl_3$) of **6e**



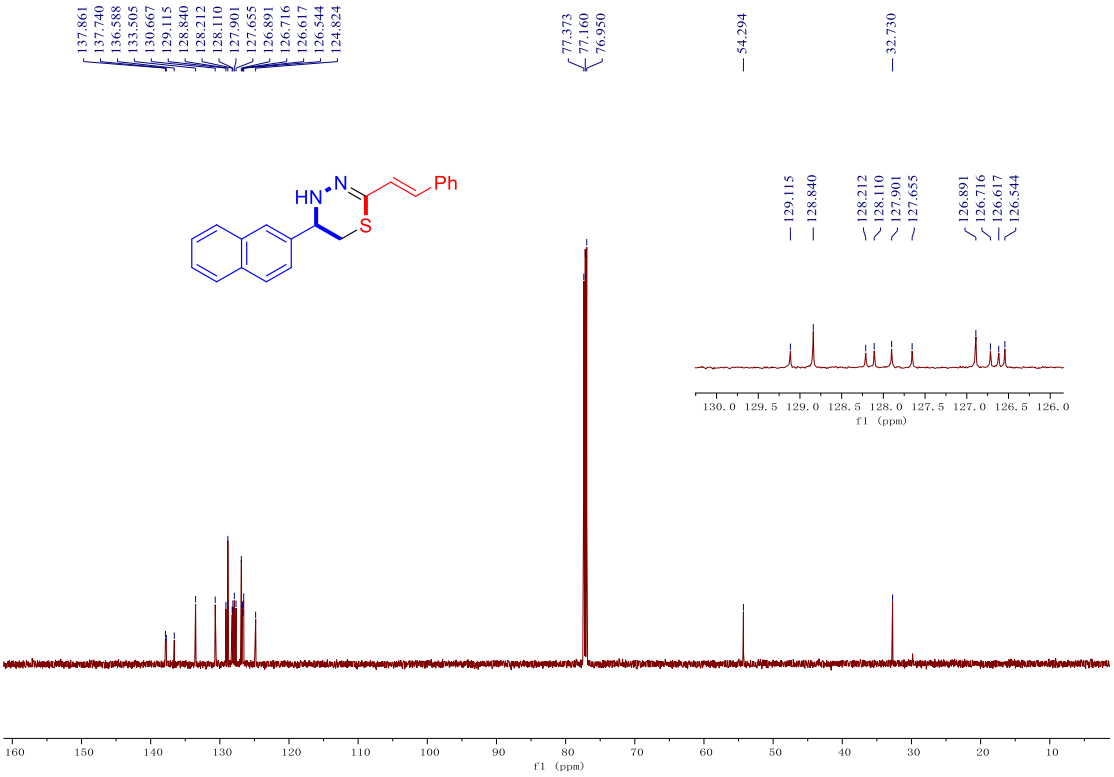
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **6e**



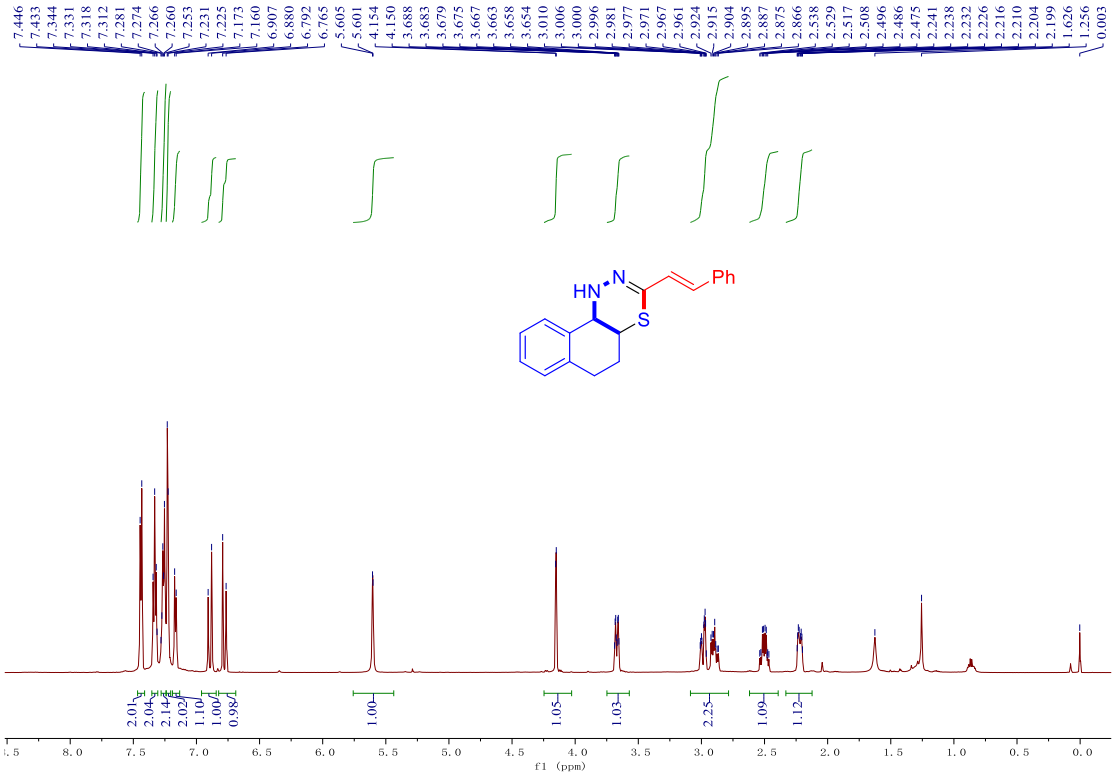
^{1}H NMR (600 MHz, $CDCl_3$) of **6f**



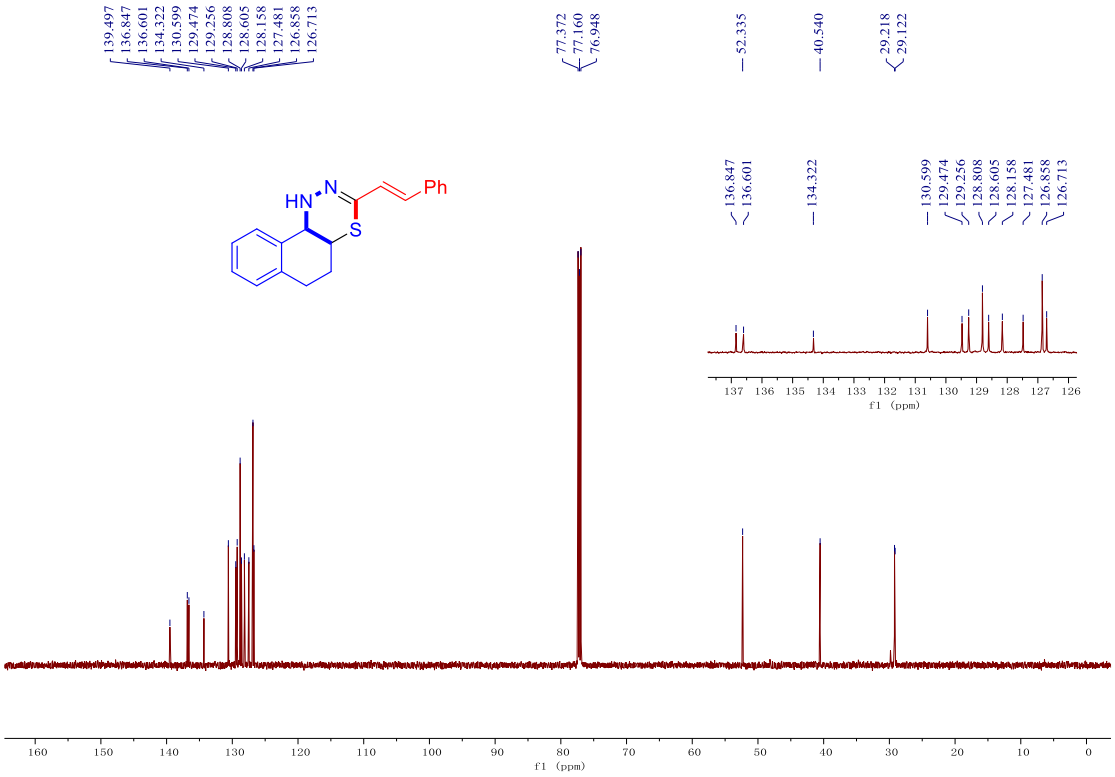
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **6f**



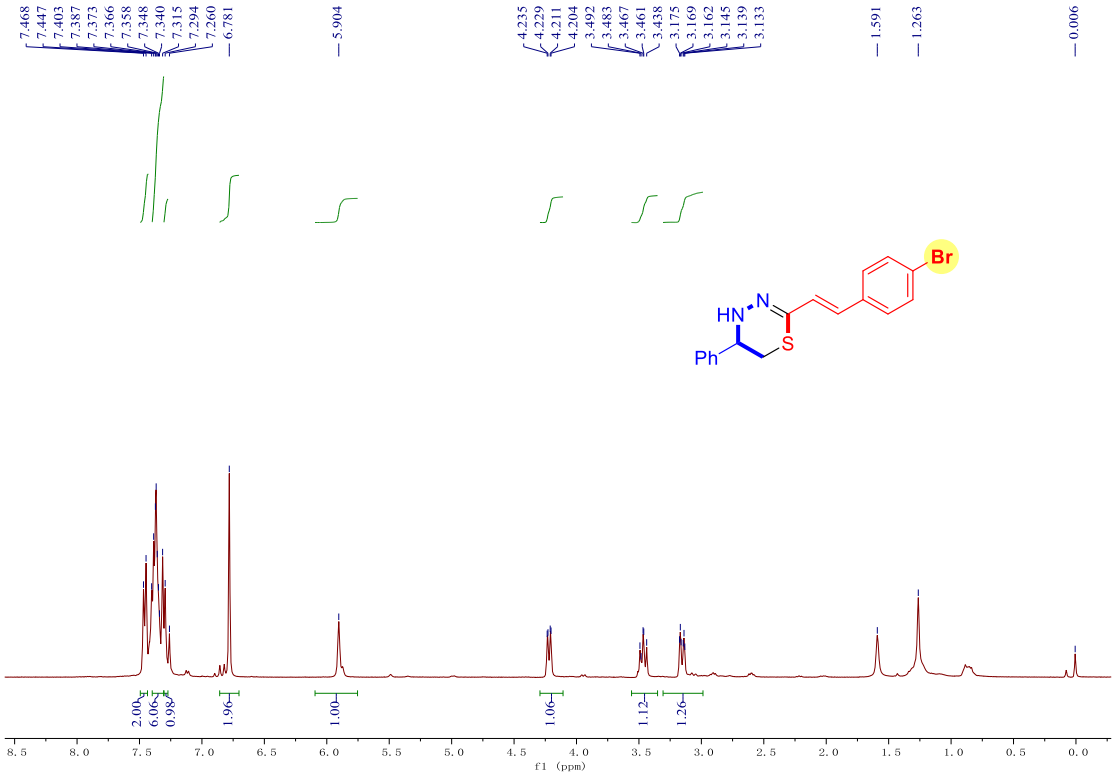
^{1}H NMR (600 MHz, $CDCl_3$) of **6g**



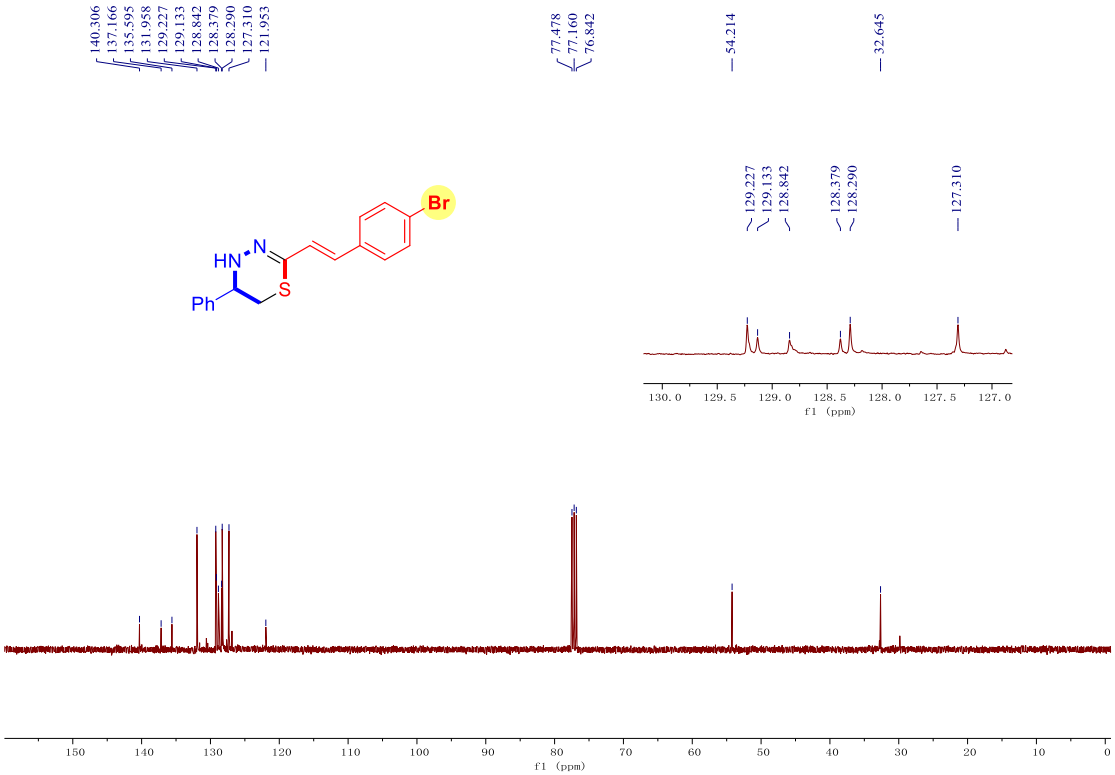
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of **6g**



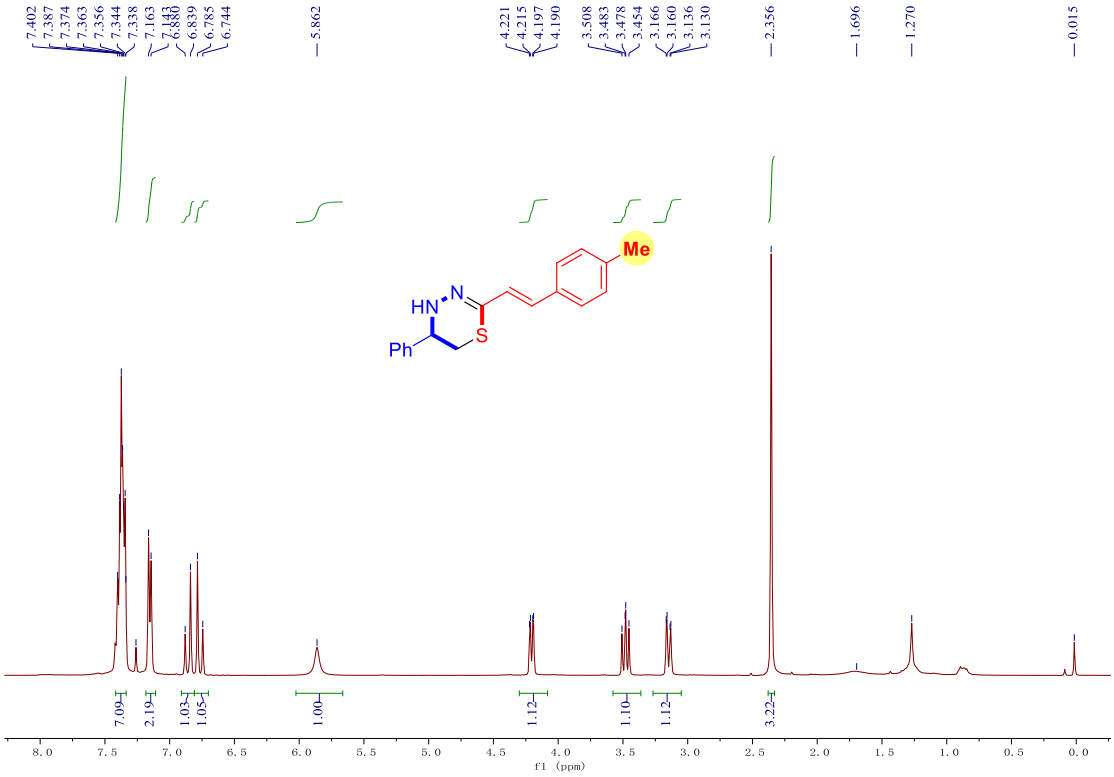
^{1}H NMR (400 MHz, $CDCl_3$) of **6h**



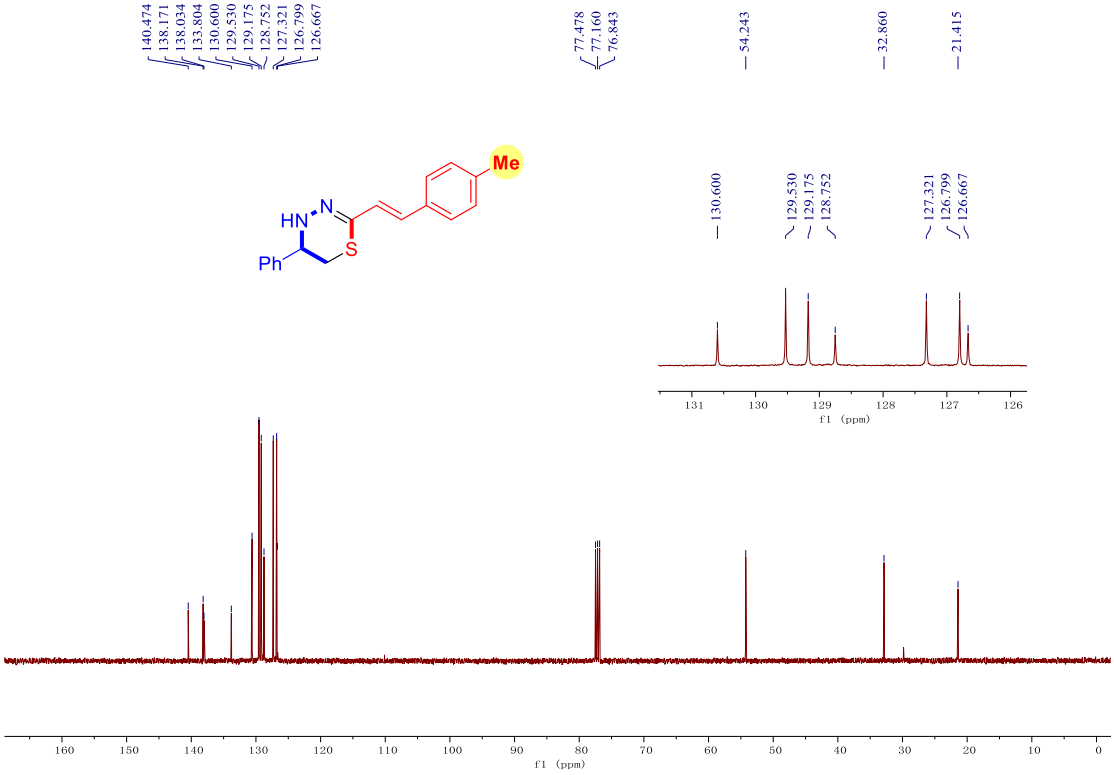
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **6h**



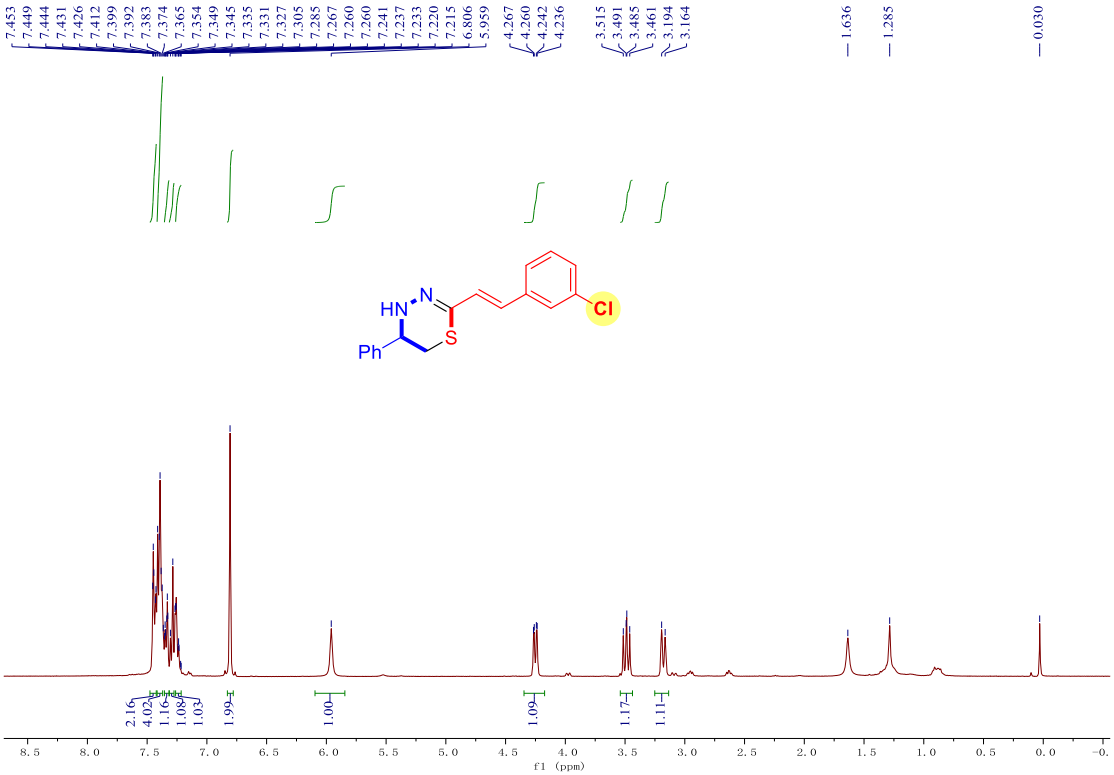
^{1}H NMR (400 MHz, $CDCl_3$) of **6i**



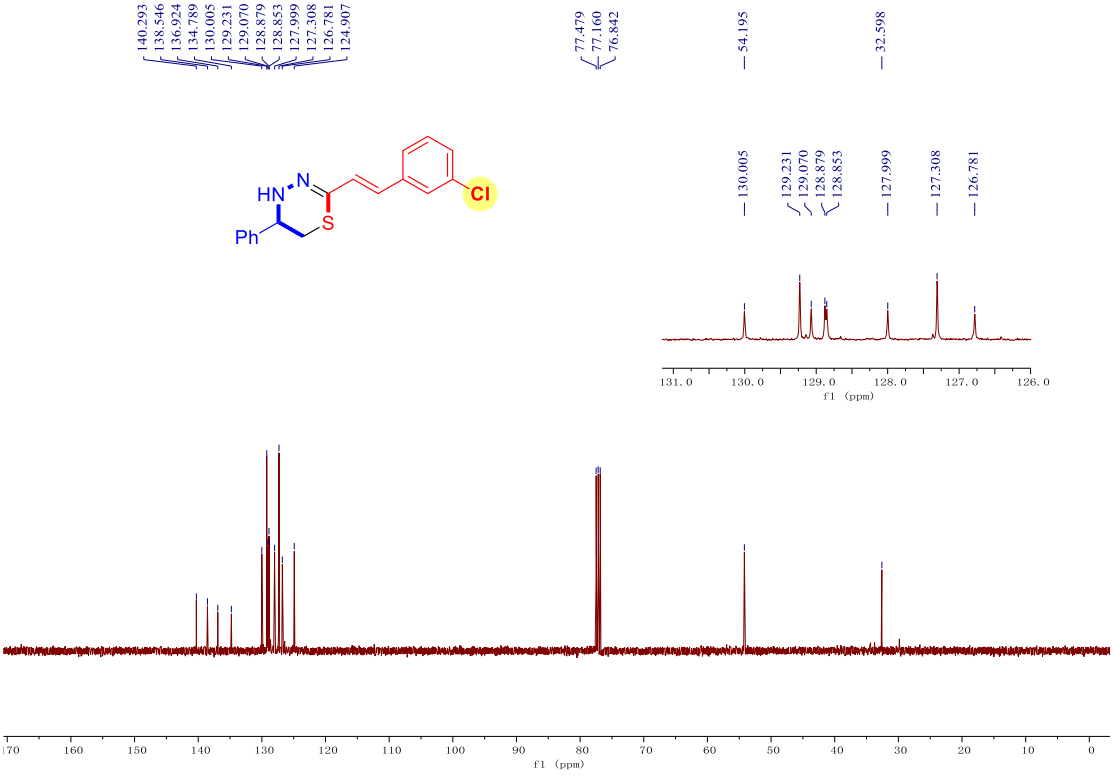
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **6i**



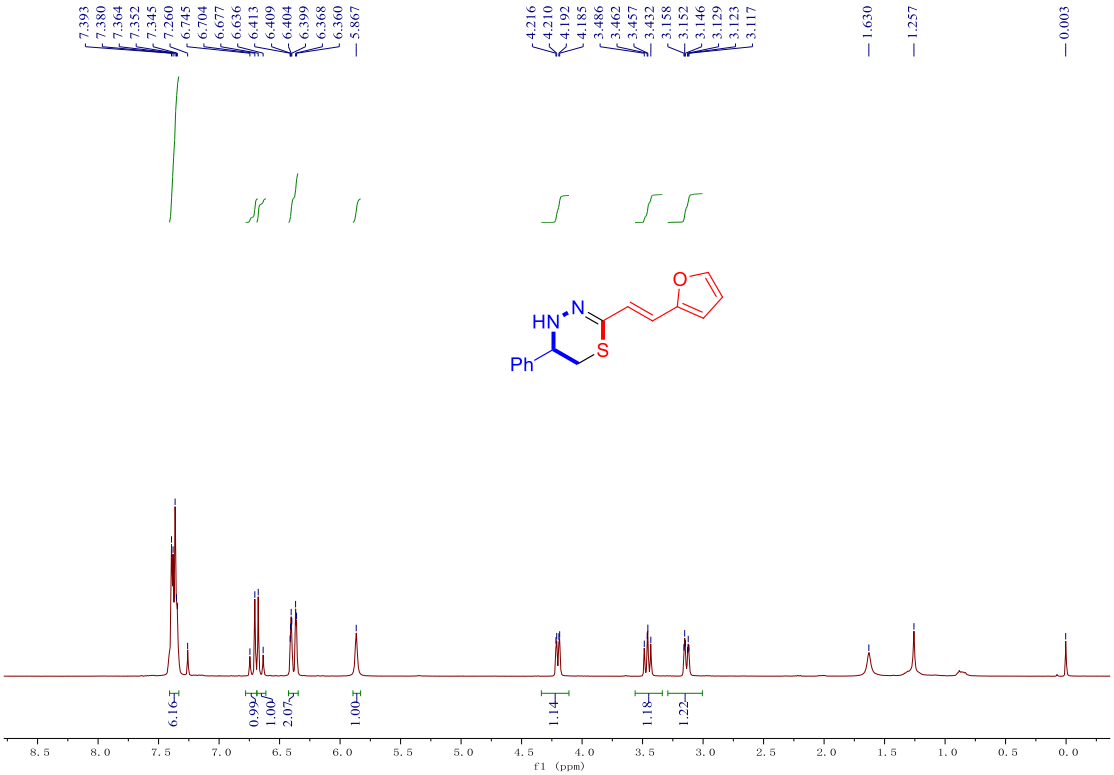
^{1}H NMR (400 MHz, $CDCl_3$) of **6j**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **6j**



^{1}H NMR (400 MHz, $CDCl_3$) of **6k**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **6k**