

Supporting Information

Phosphine-Catalyzed Regiospecific (3+2) Cyclization of 3-Nitroindoles with Allene Esters

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School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou, 221116, China

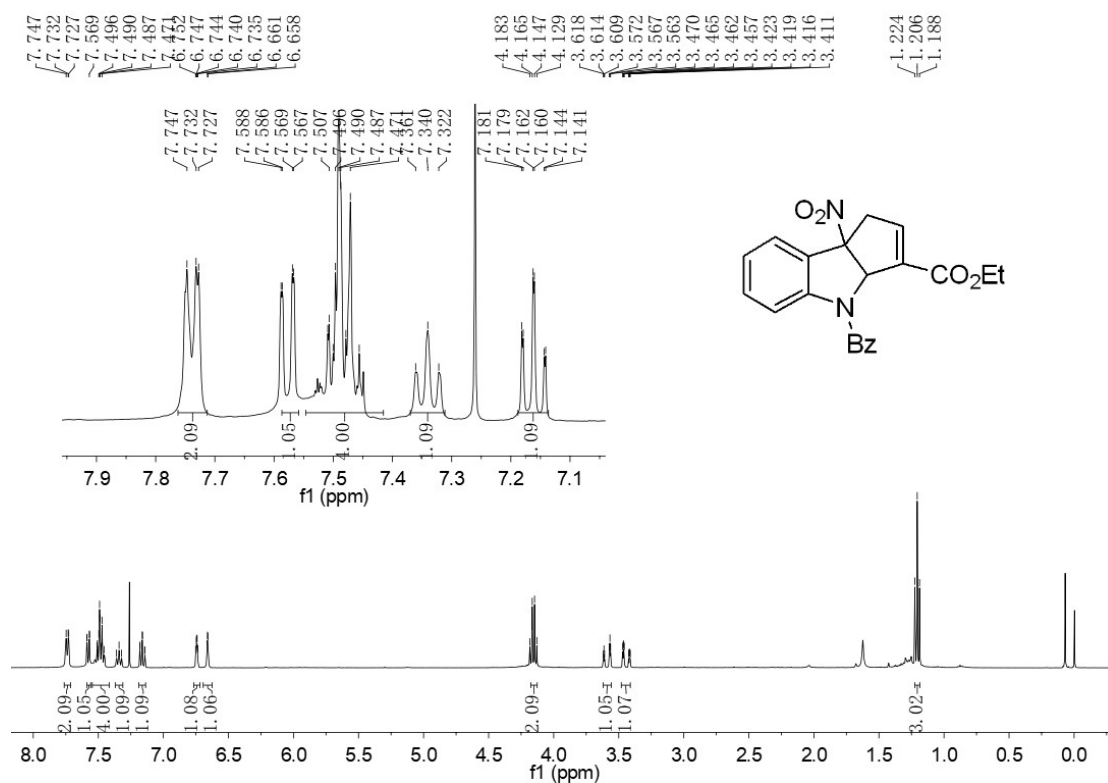
Contents:

- 1. NMR spectra of products 3 (S2-S23)**
- 2. X-ray single crystal data for compound 3aa (S24-S25)**
- 3. HPLC copies of product 3aa (S26)**

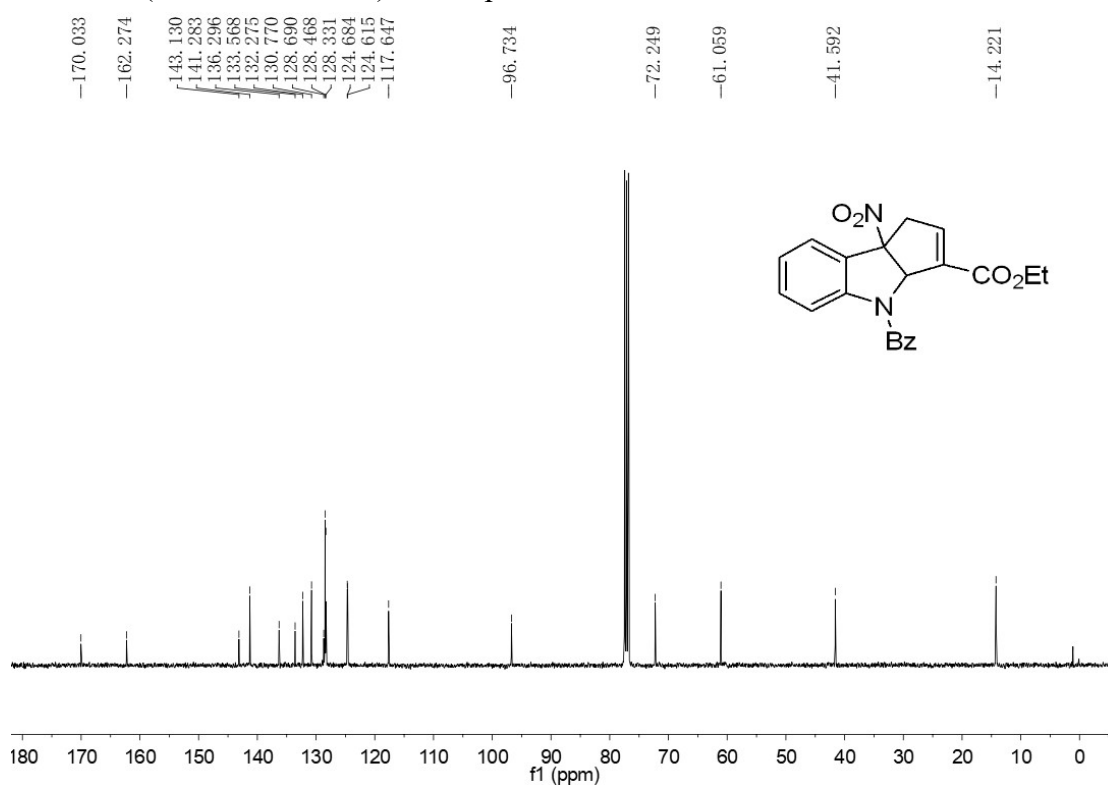
1. NMR spectra of products 3

NMR spectra of products 3

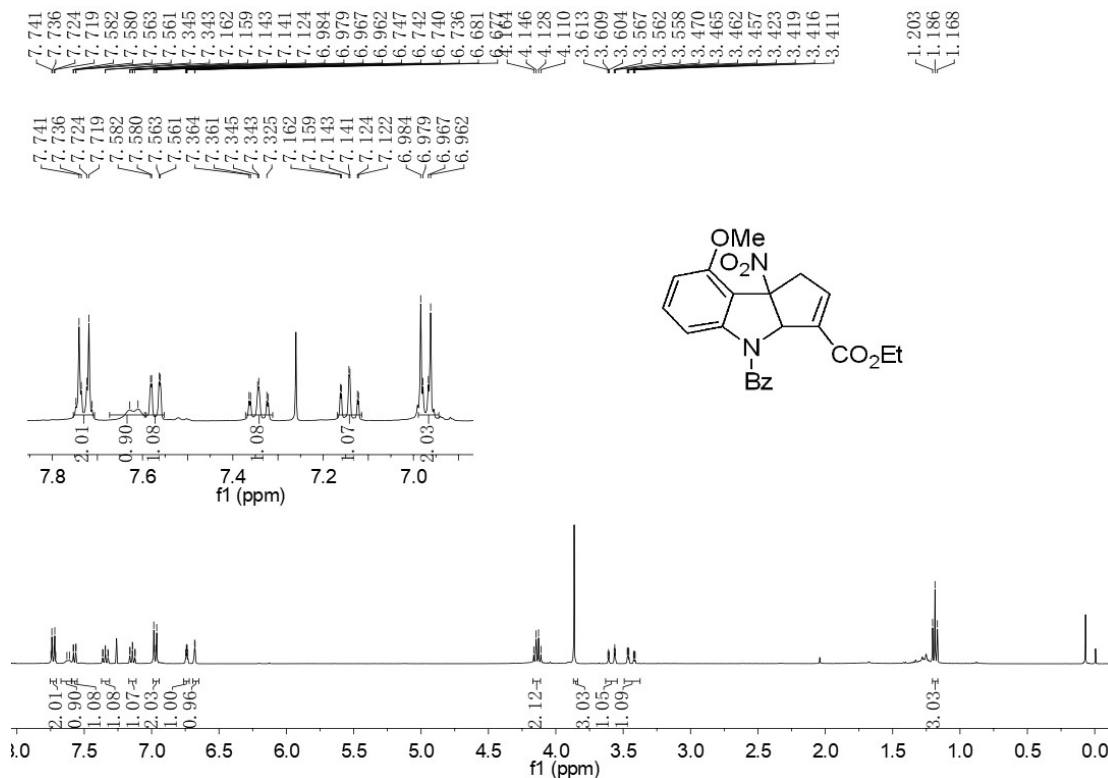
^1H NMR (400 MHz, CDCl_3) of compound **3aa**



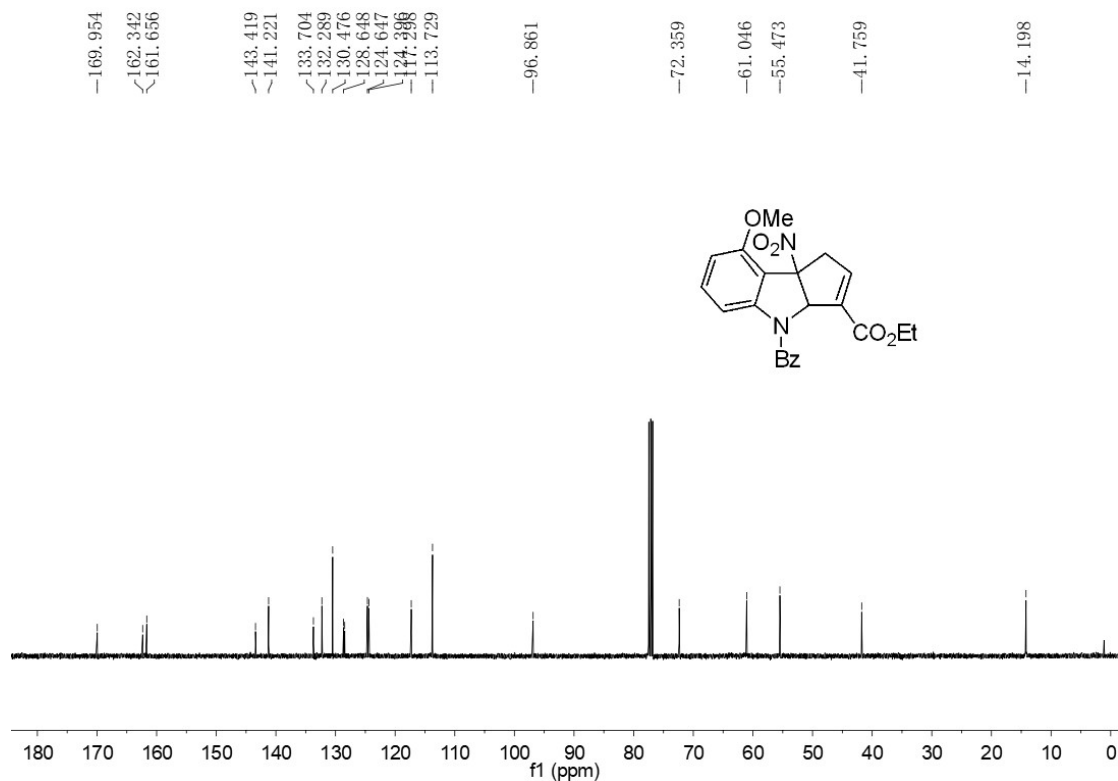
^{13}C NMR (100 MHz, CDCl_3) of compound **3aa**



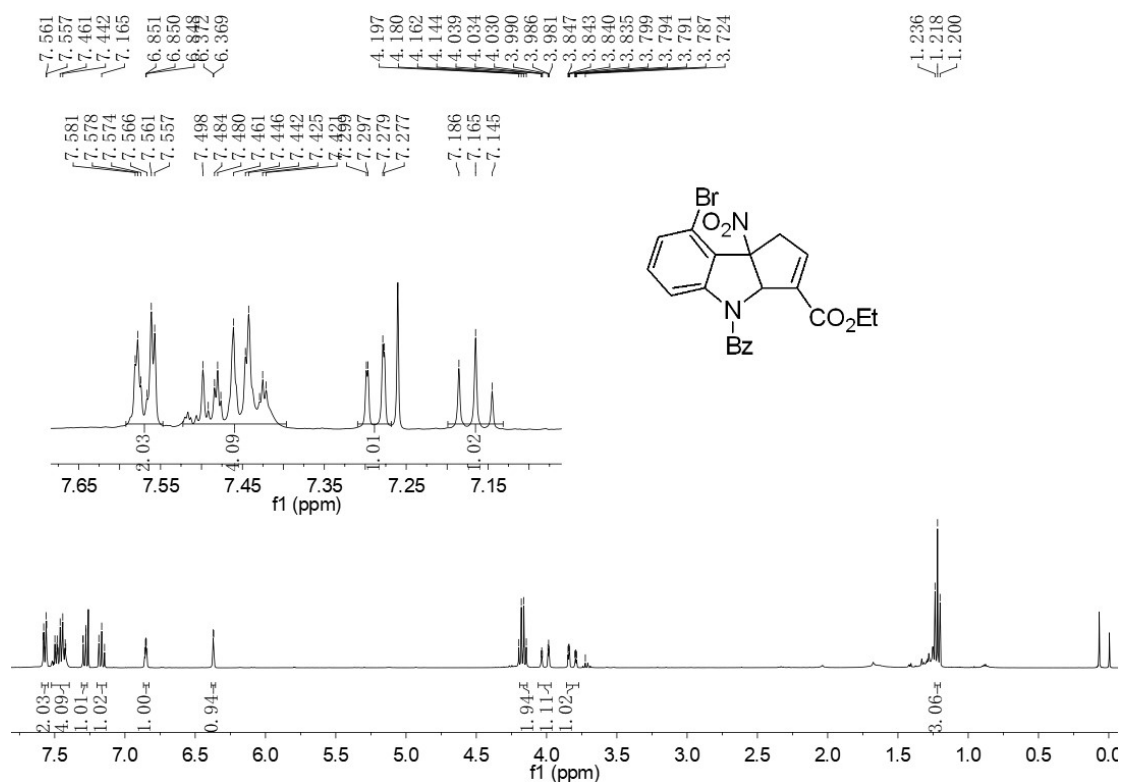
^1H NMR (400 MHz, CDCl_3) of compound **3ba**



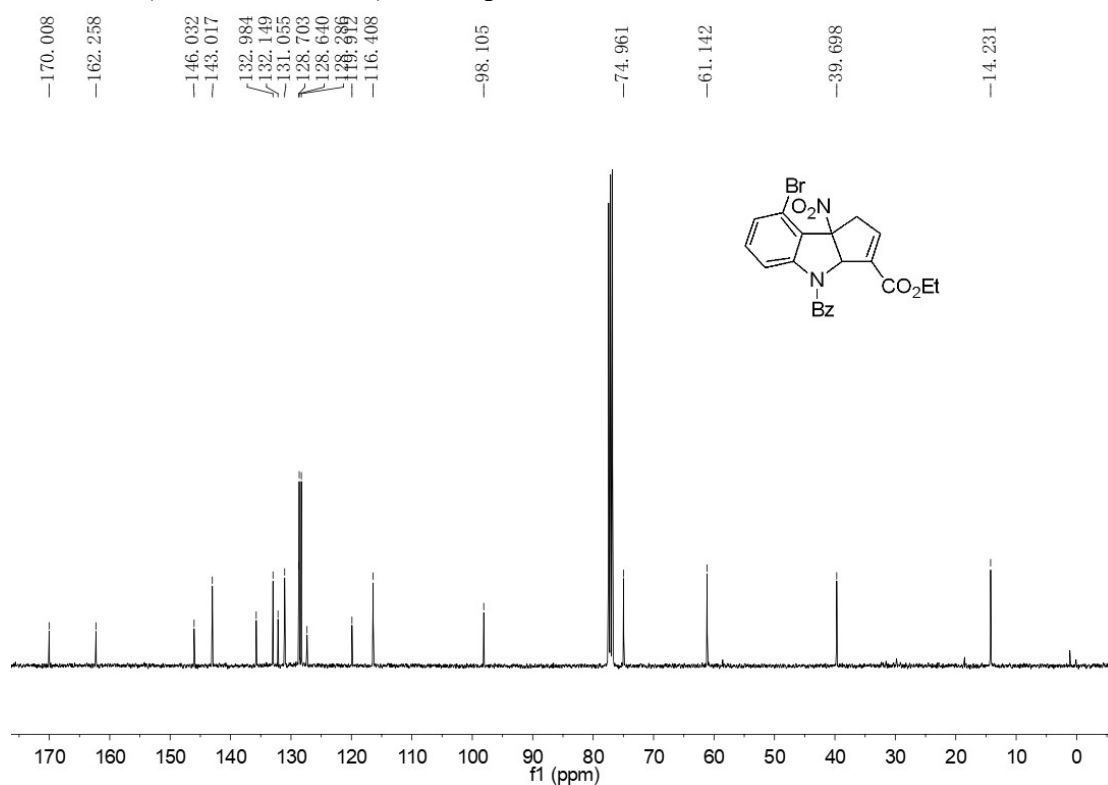
^{13}C NMR (100 MHz, CDCl_3) of compound **3ba**



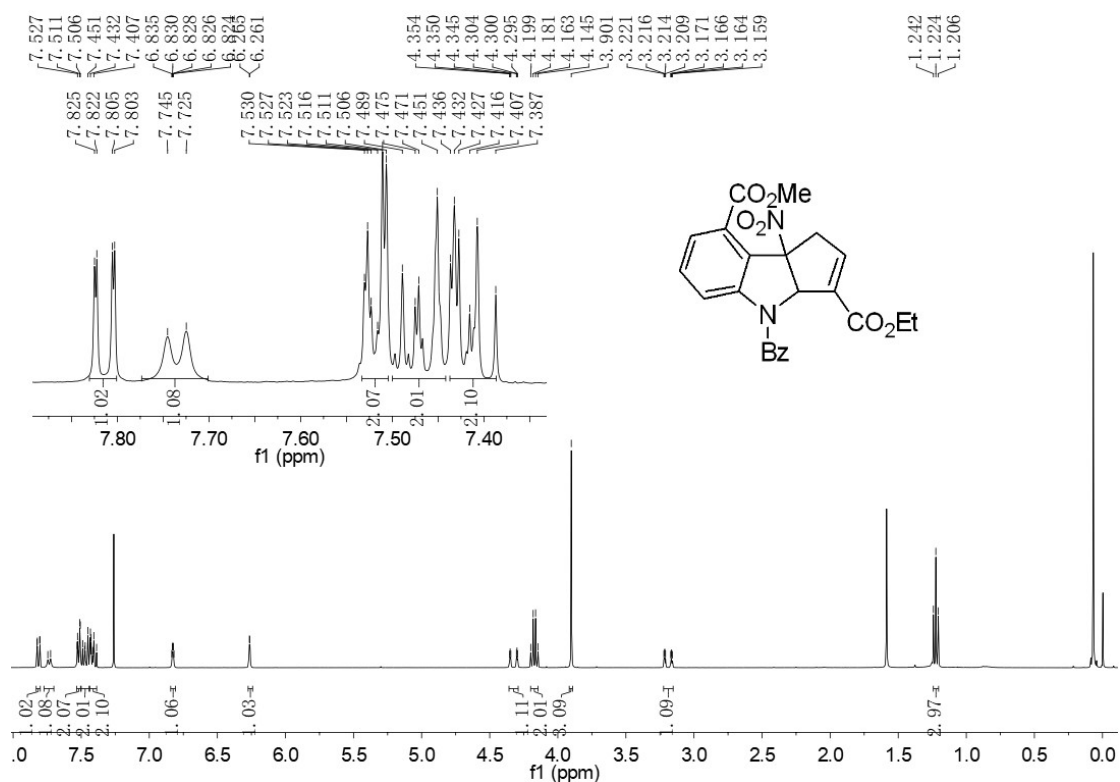
^1H NMR (400 MHz, CDCl_3) of compound **3ca**



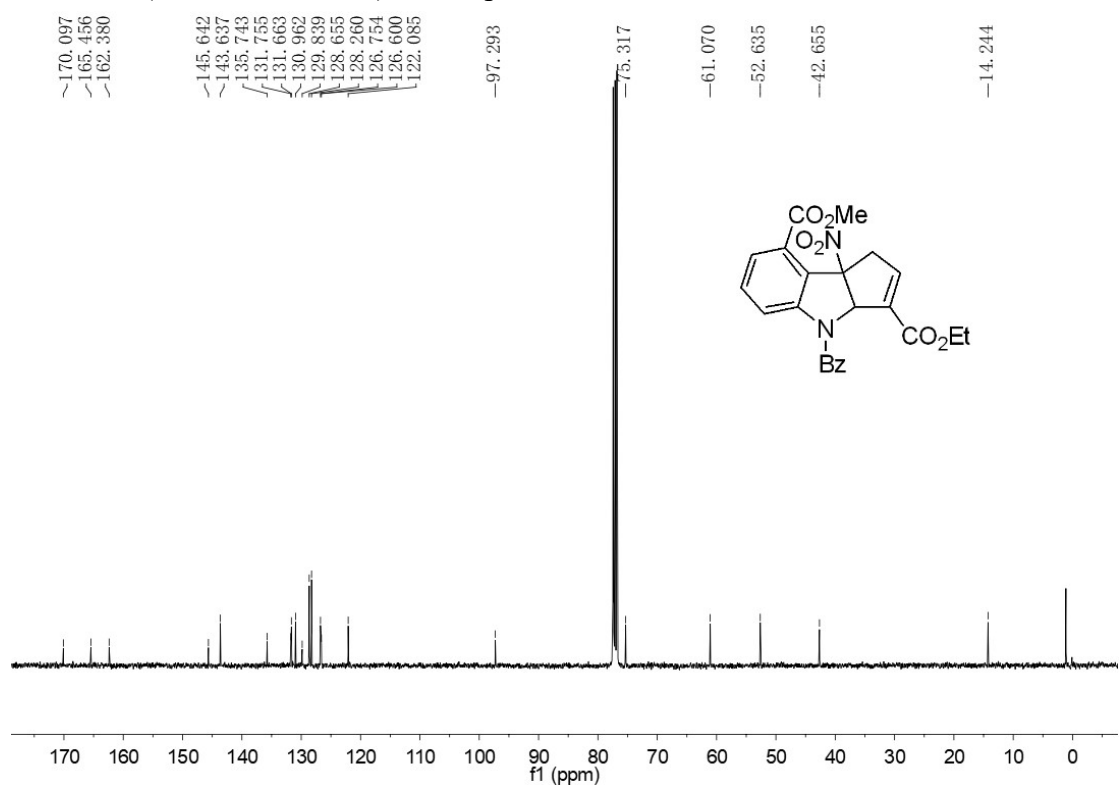
^{13}C NMR (100 MHz, CDCl_3) of compound **3ca**



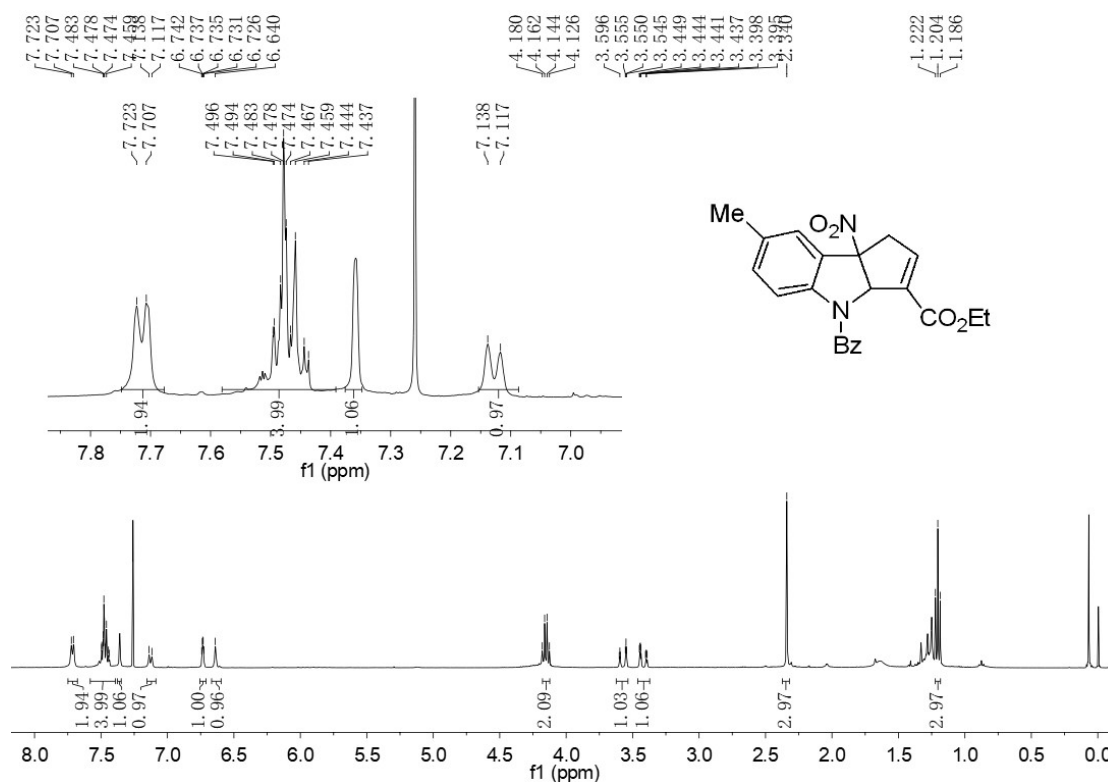
^1H NMR (400 MHz, CDCl_3) of compound **3da**



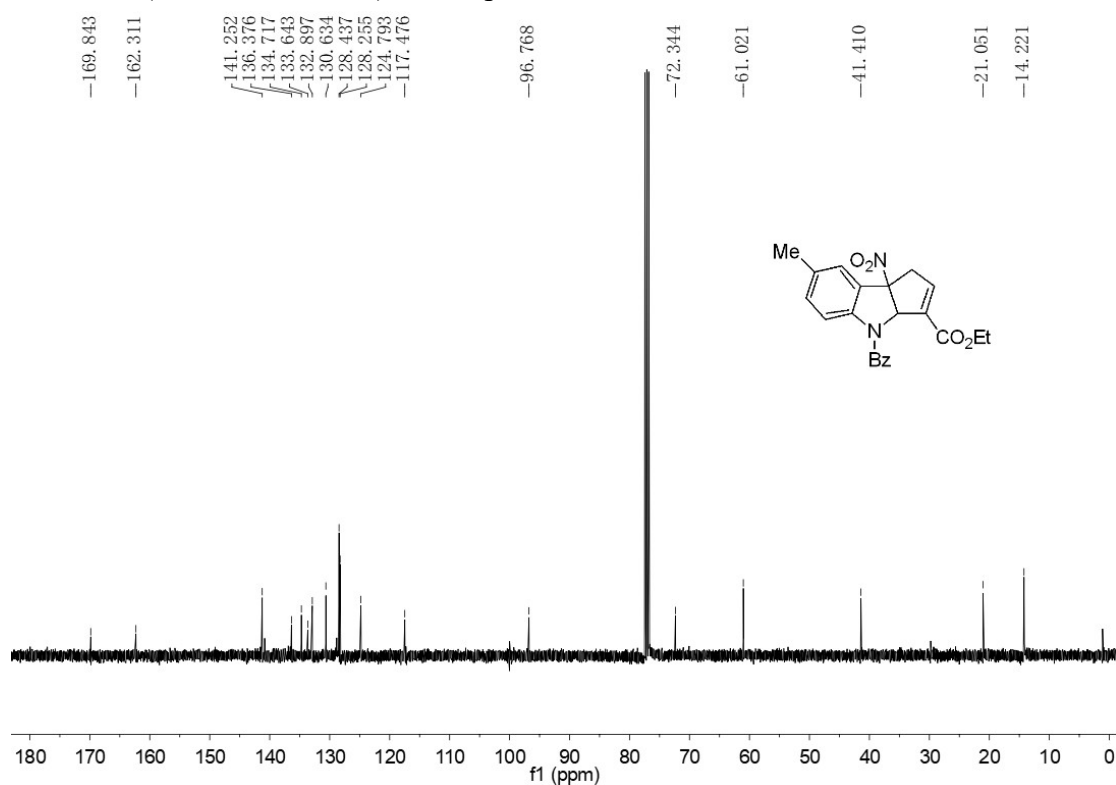
^{13}C NMR (100 MHz, CDCl_3) of compound **3da**



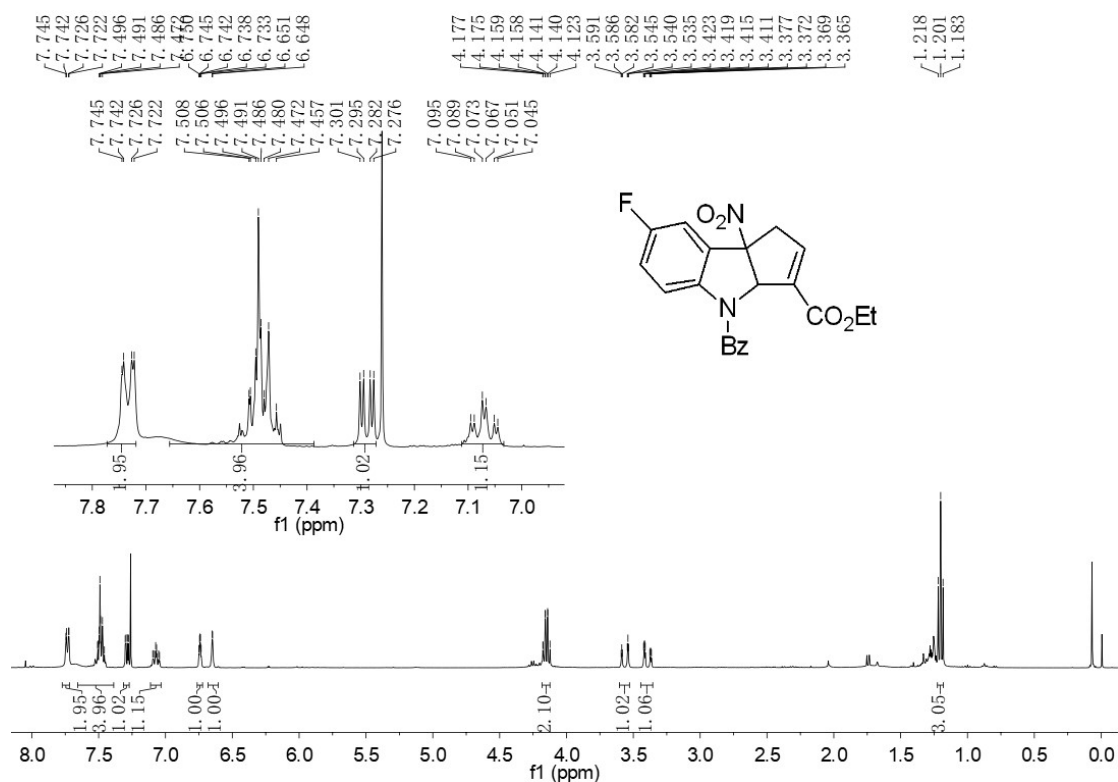
^1H NMR (400 MHz, CDCl_3) of compound **3ea**



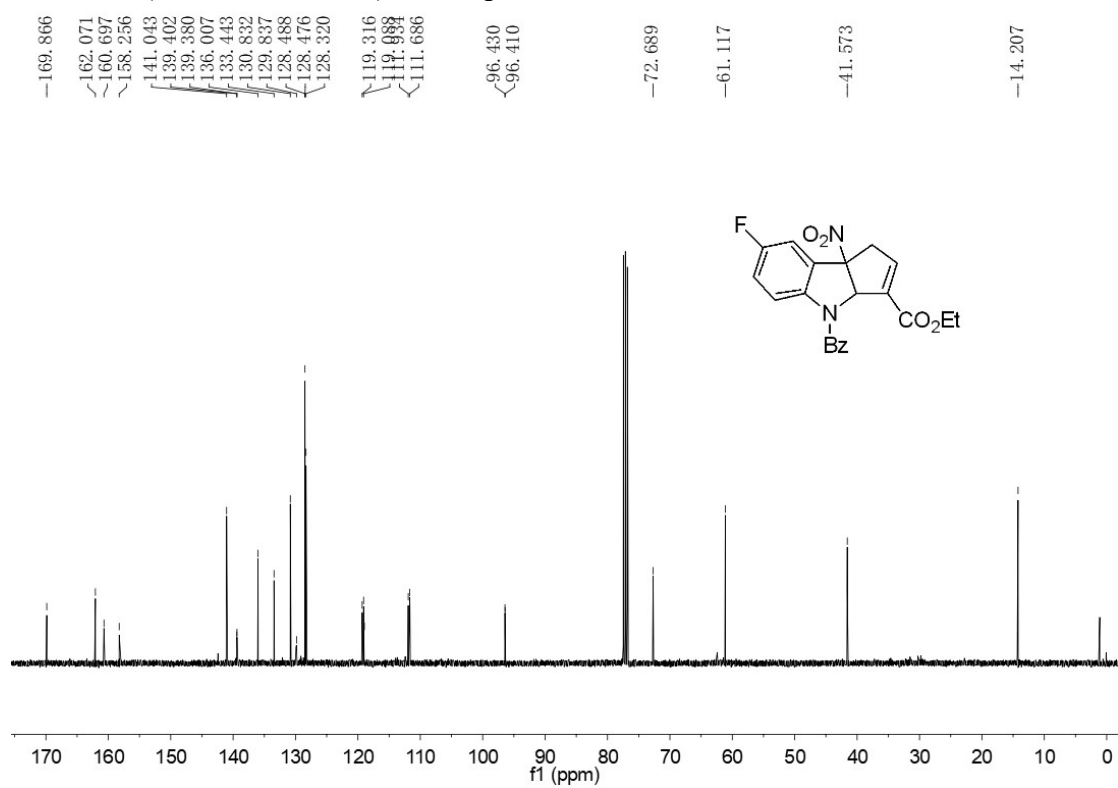
^{13}C NMR (100 MHz, CDCl_3) of compound **3ea**



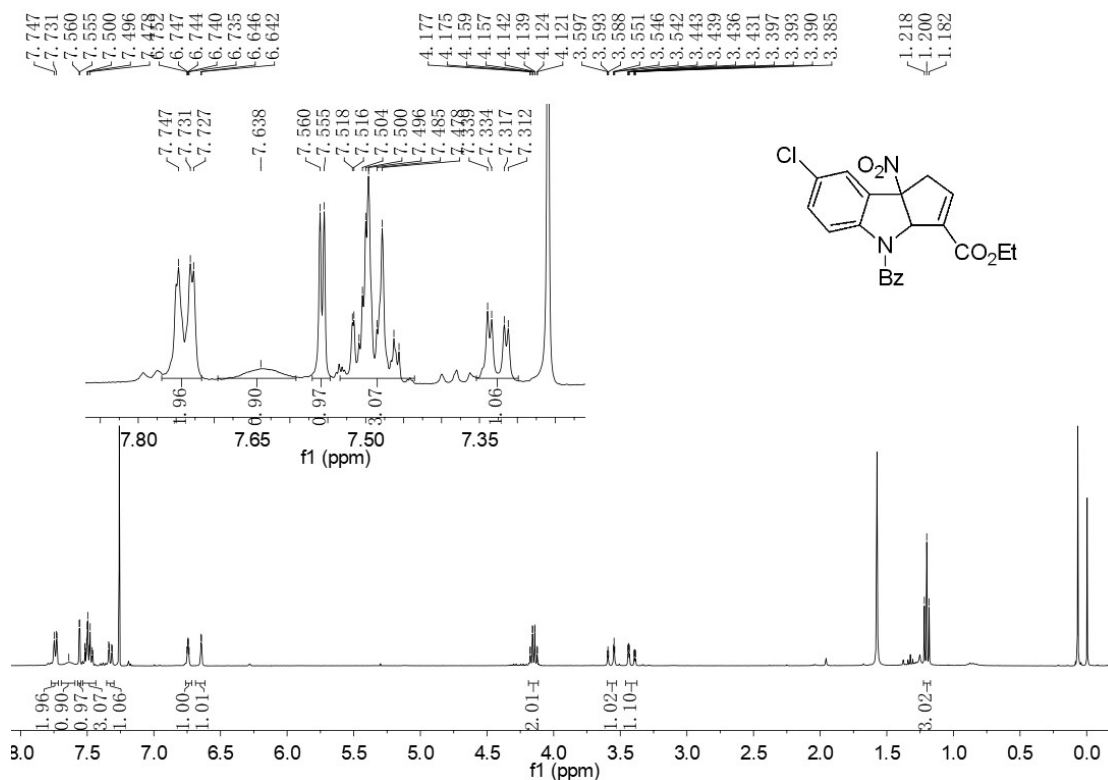
¹H NMR (400 MHz, CDCl₃) of compound **3fa**



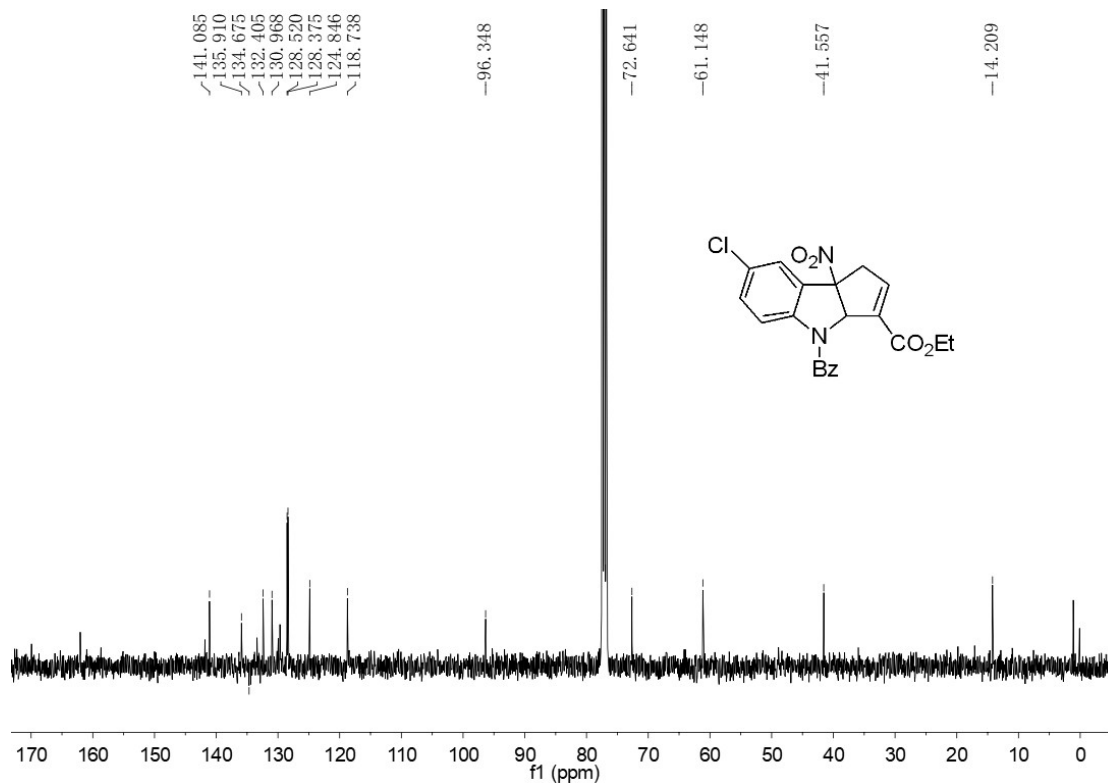
¹³C NMR (100 MHz, CDCl₃) of compound **3fa**



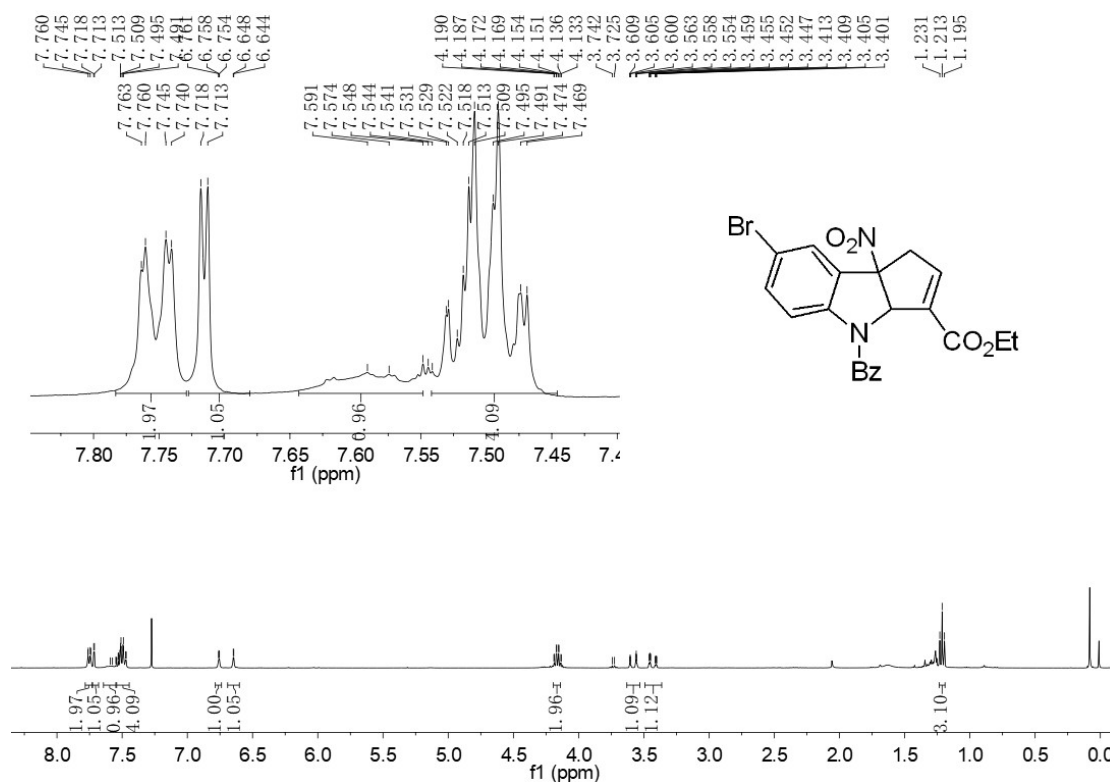
^1H NMR (400 MHz, CDCl_3) of compound **3ga**



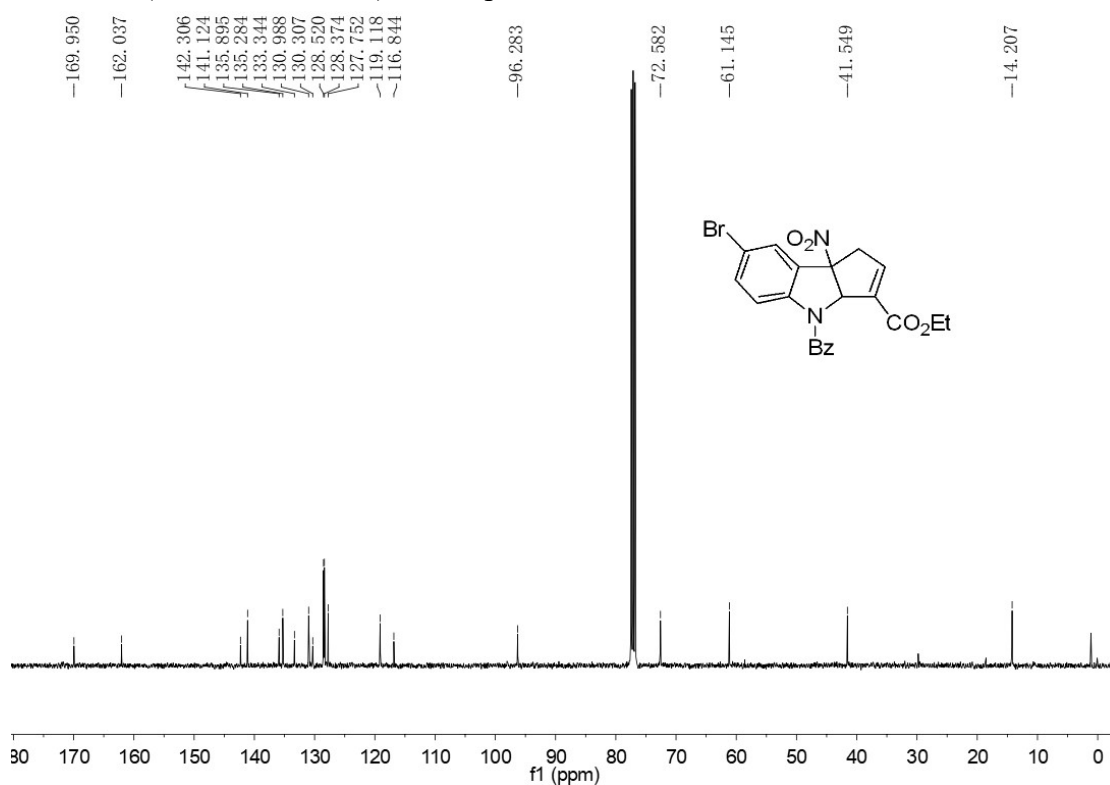
^{13}C NMR (100 MHz, CDCl_3) of compound **3ga**



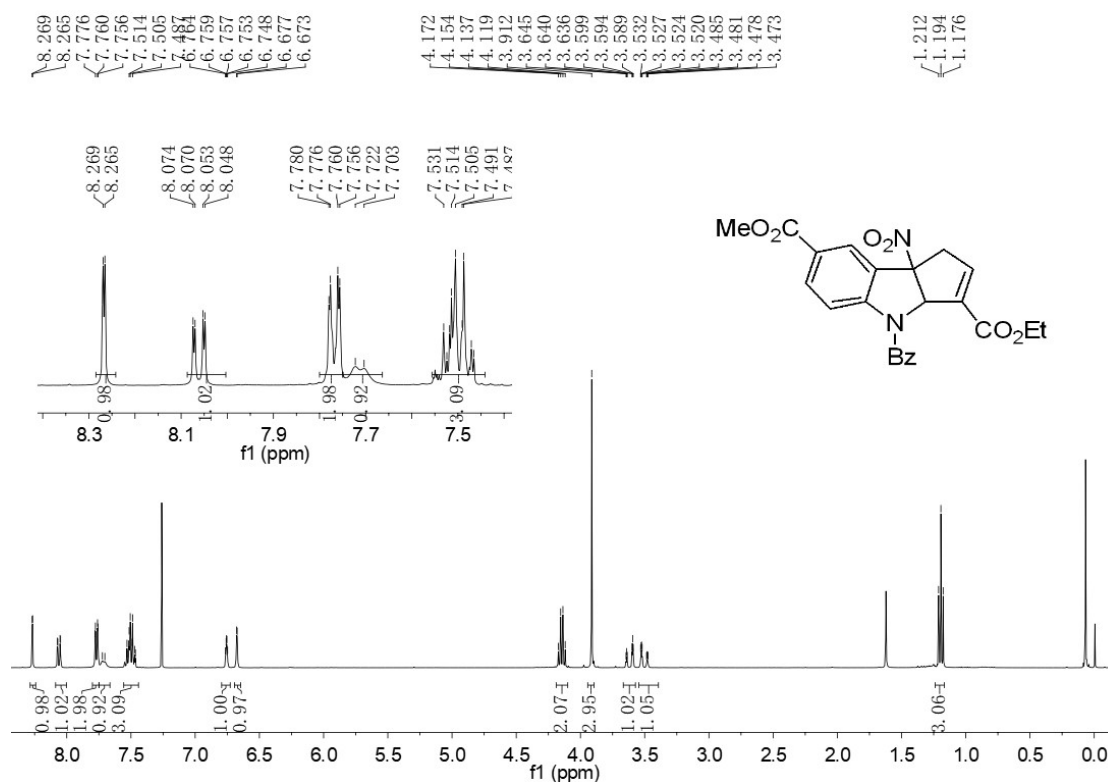
^1H NMR (400 MHz, CDCl_3) of compound **3ha**



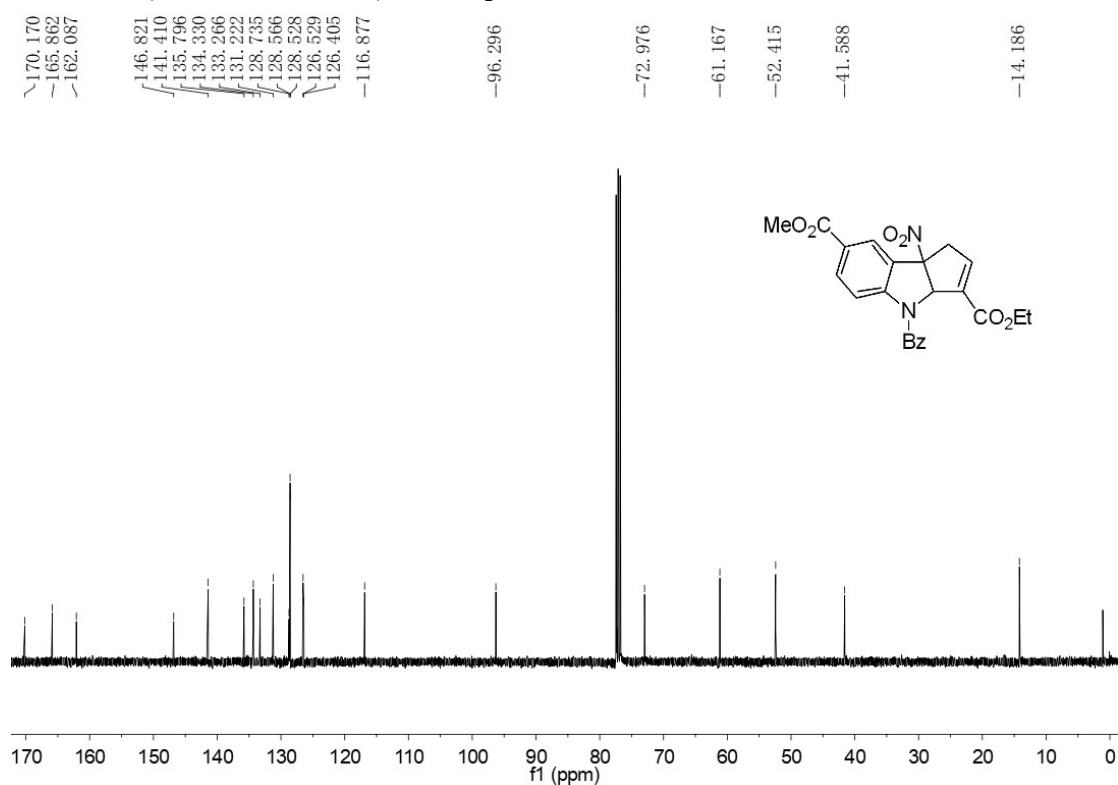
^{13}C NMR (100 MHz, CDCl_3) of compound **3ha**



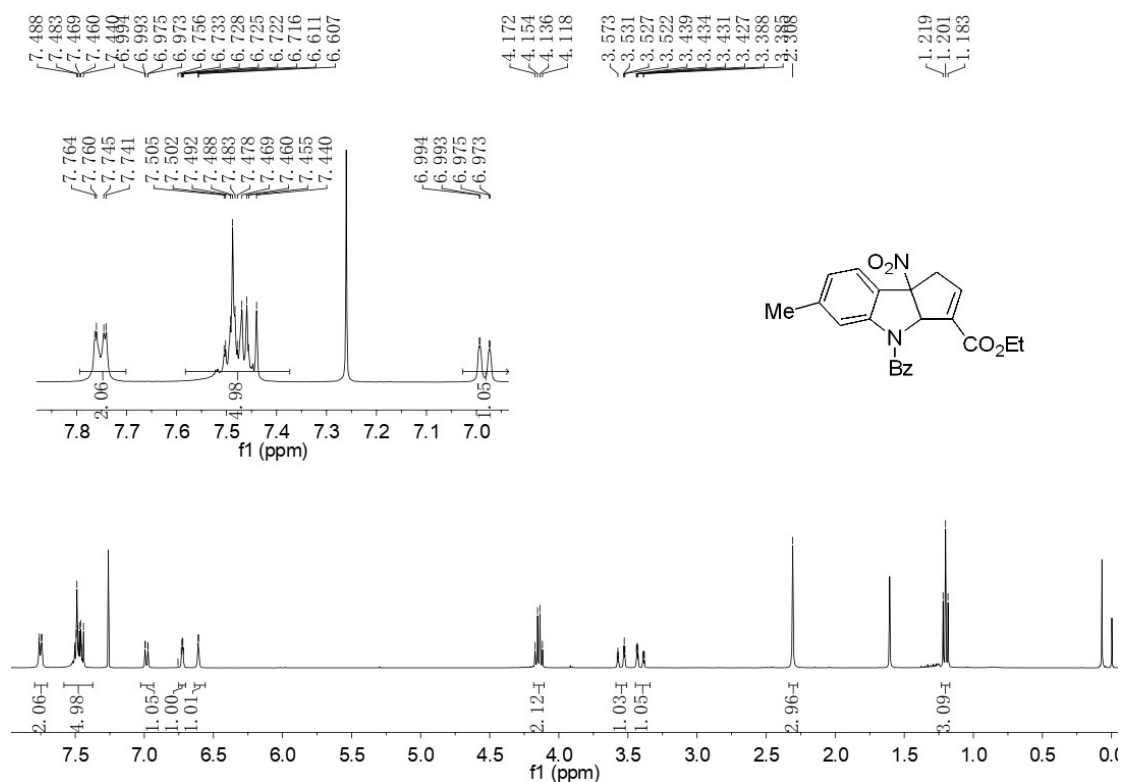
^1H NMR (400 MHz, CDCl_3) of compound **3ia**



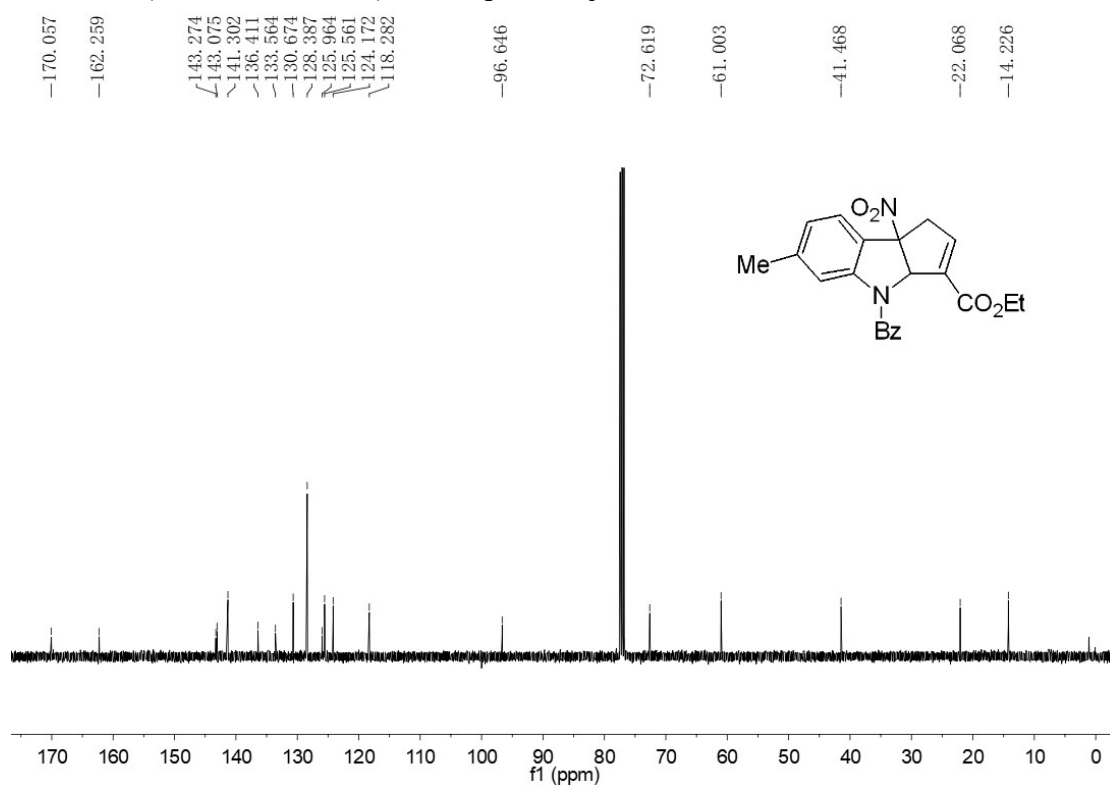
^{13}C NMR (100 MHz, CDCl_3) of compound **3ia**



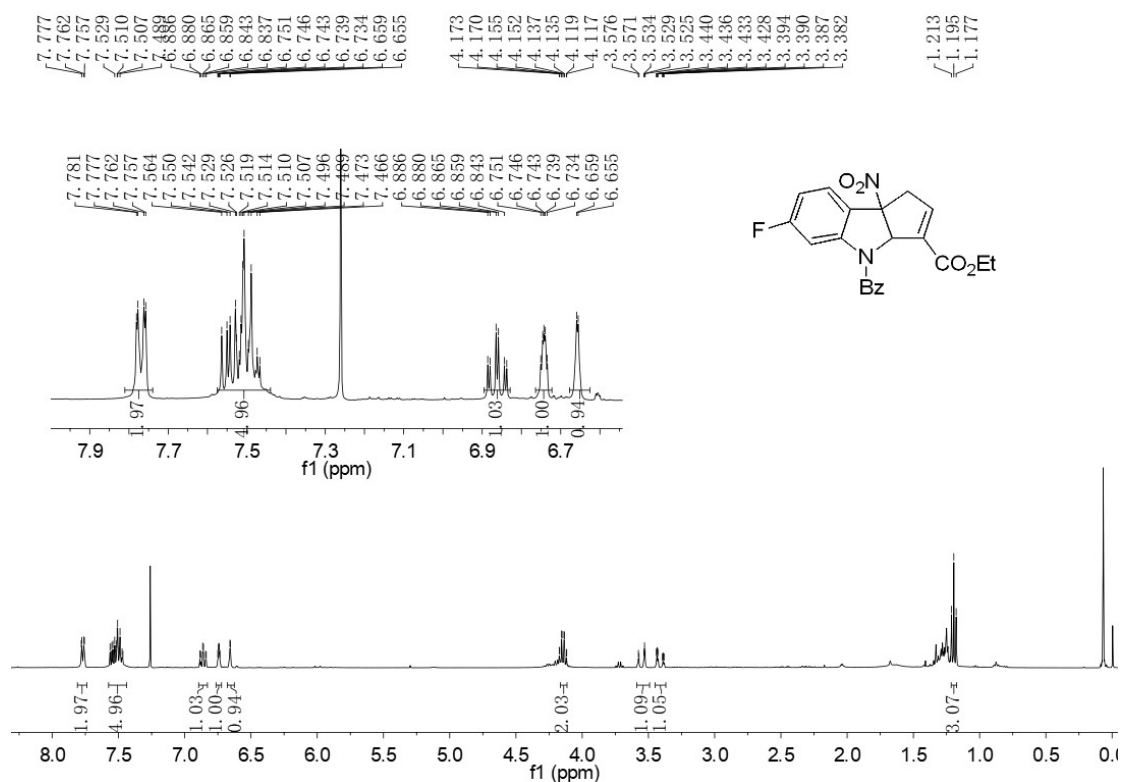
¹H NMR (400 MHz, CDCl₃) of compound **3ja**



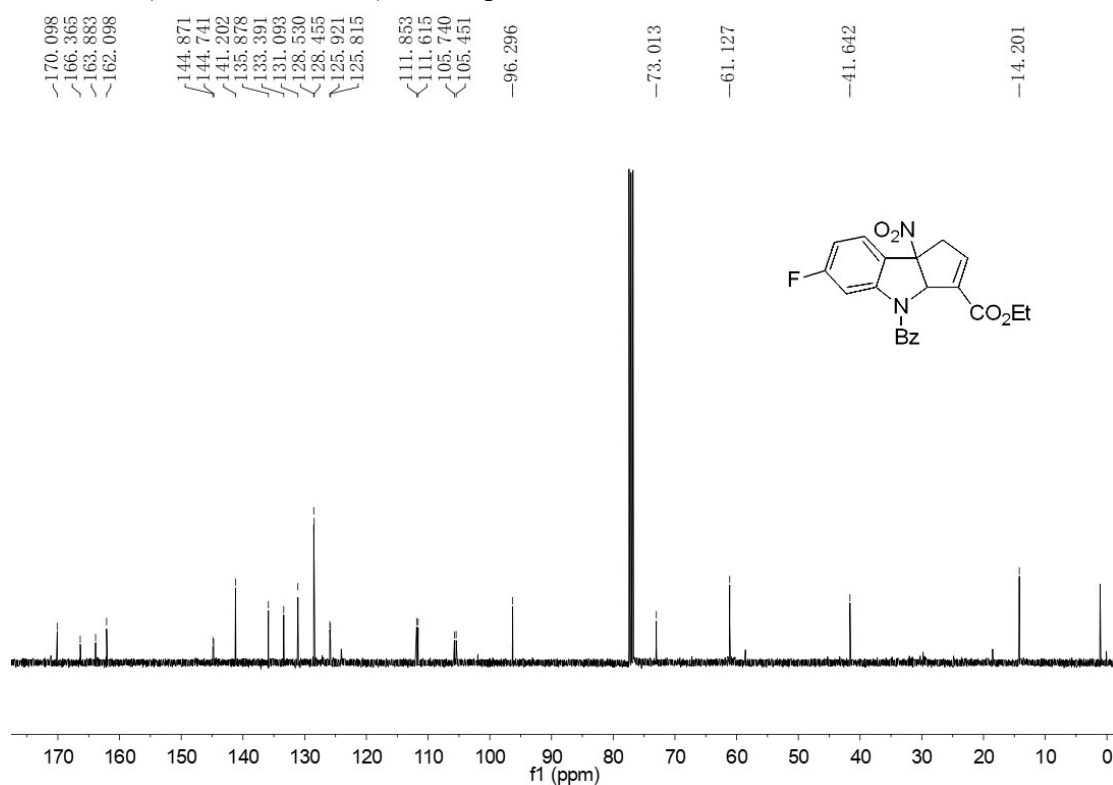
¹³C NMR (100 MHz, CDCl₃) of compound **3ja**



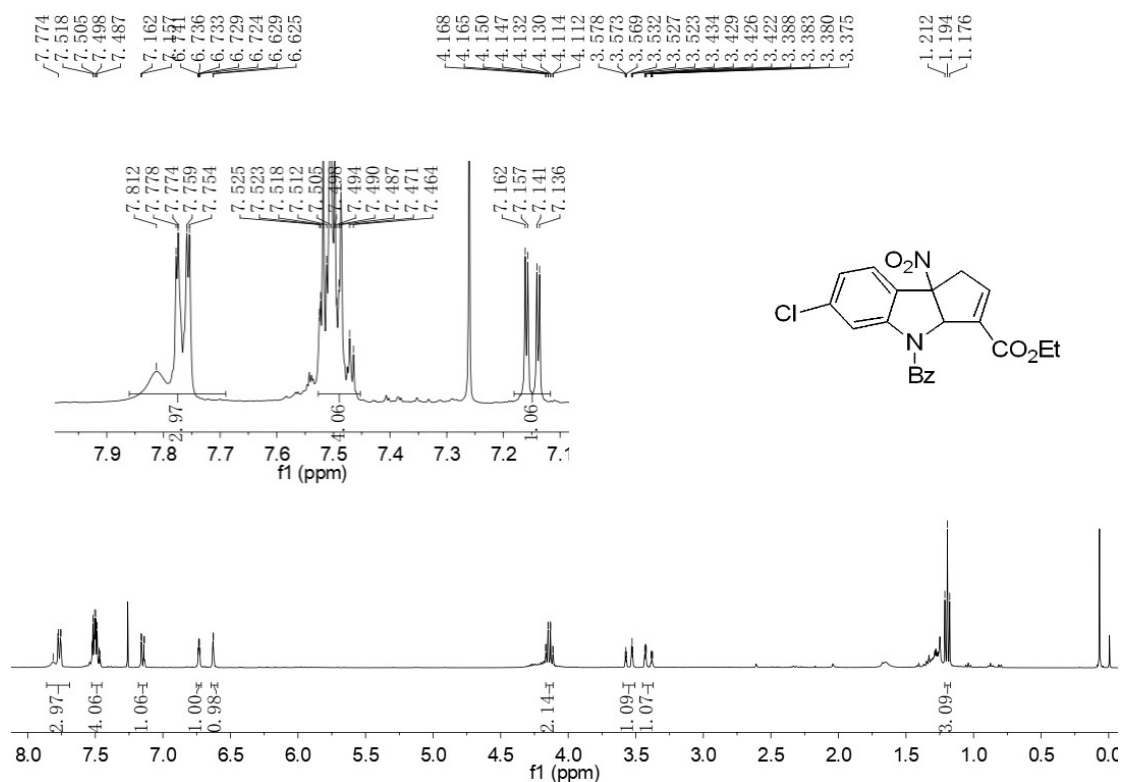
^1H NMR (400 MHz, CDCl_3) of compound **3ka**



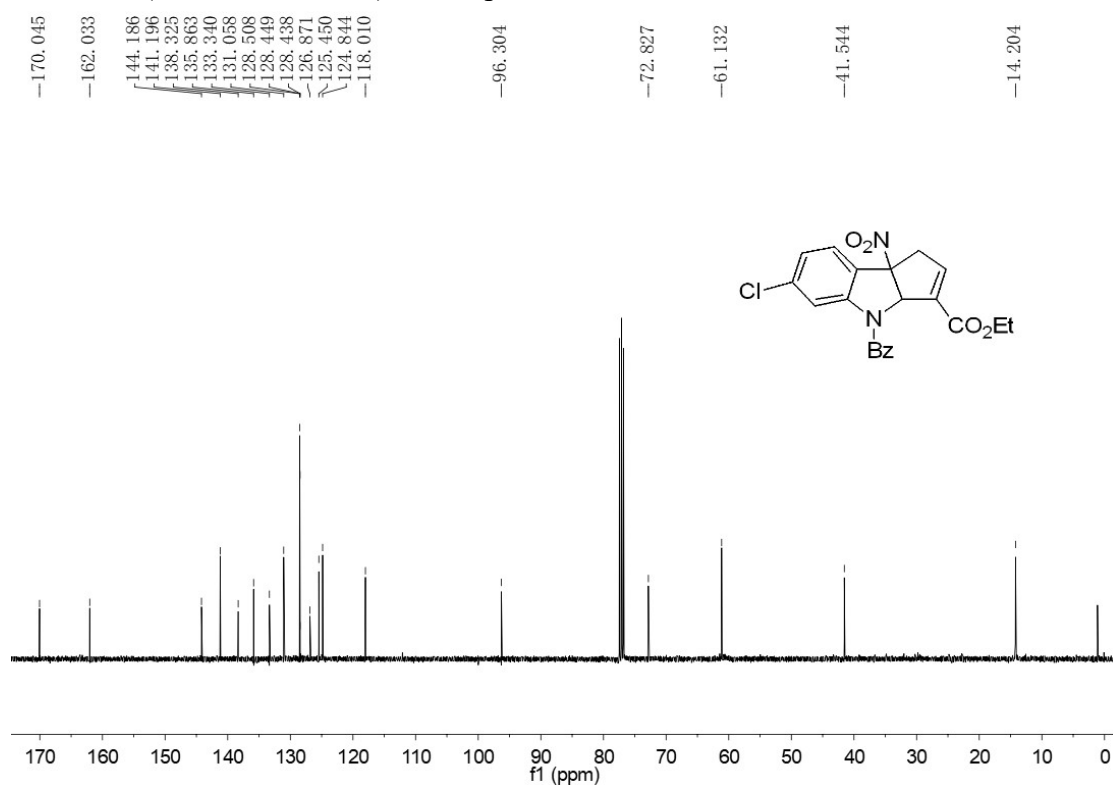
^{13}C NMR (100 MHz, CDCl_3) of compound **3ka**



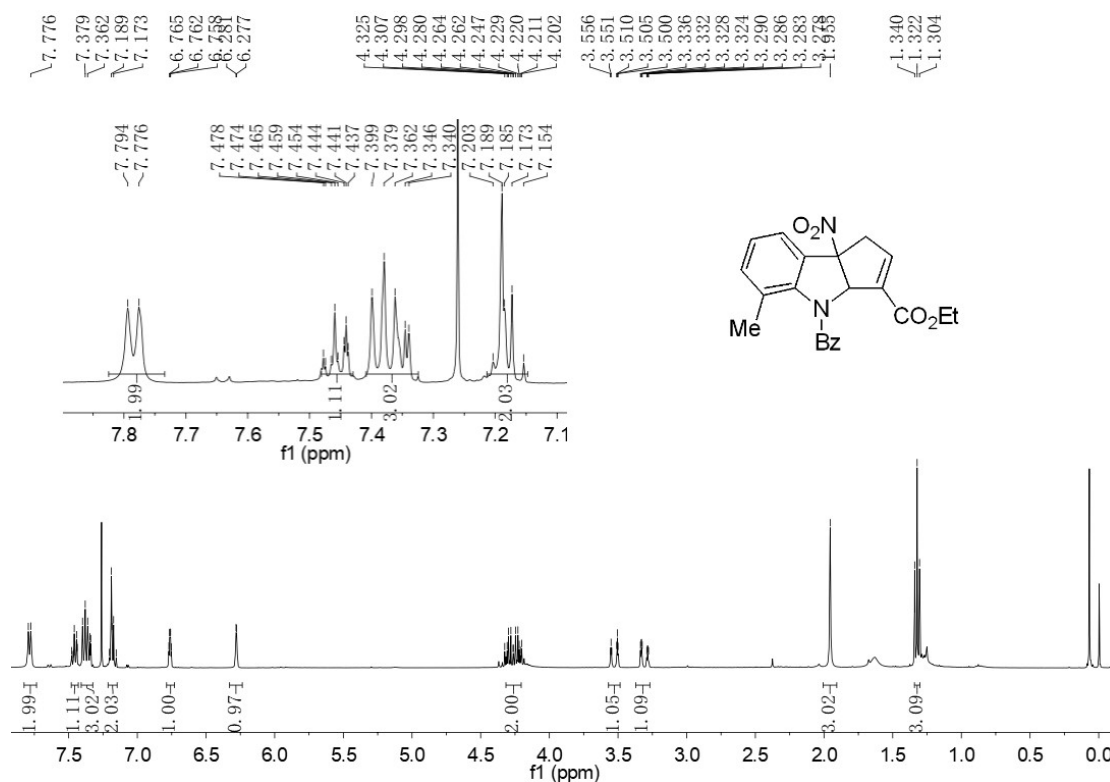
^1H NMR (400 MHz, CDCl_3) of compound **3la**



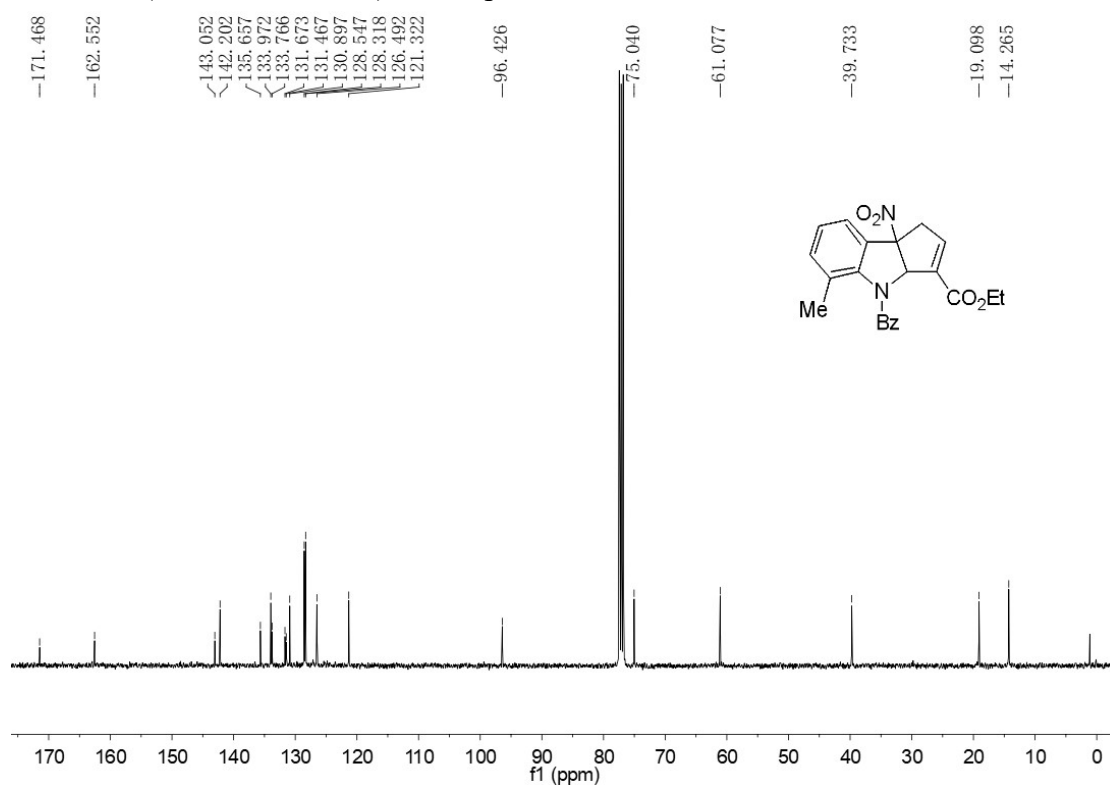
^{13}C NMR (100 MHz, CDCl_3) of compound **3la**



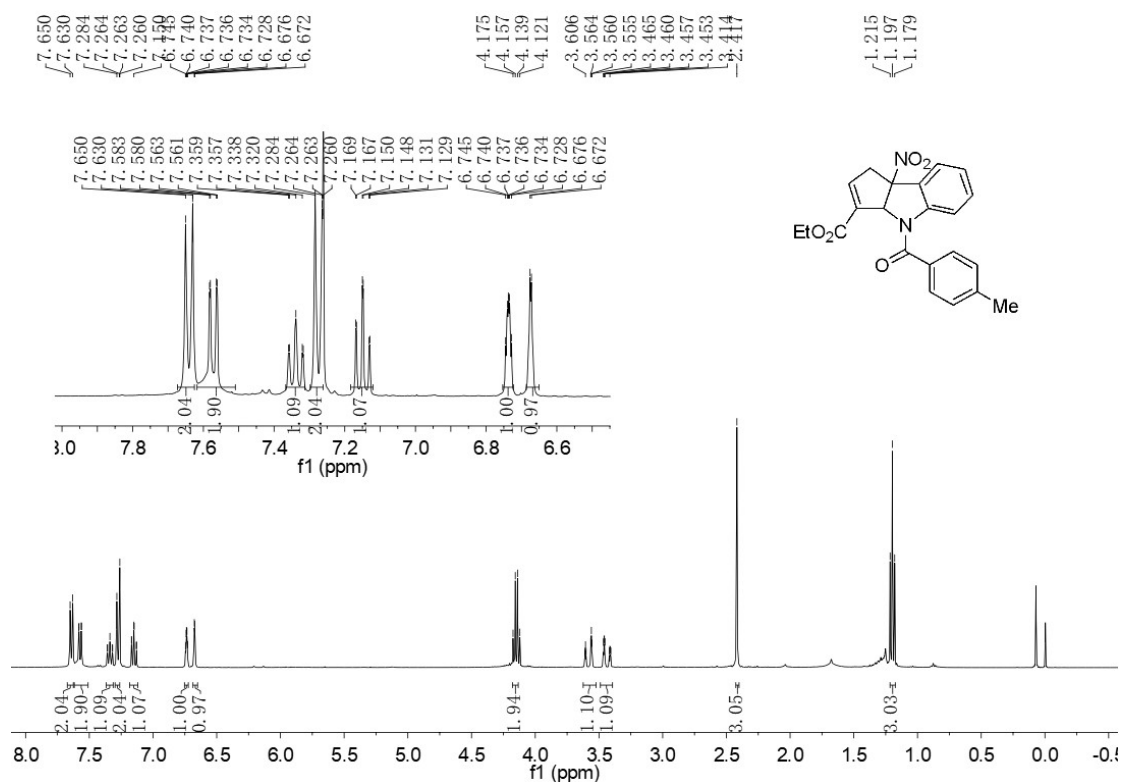
^1H NMR (400 MHz, CDCl_3) of compound **3ma**



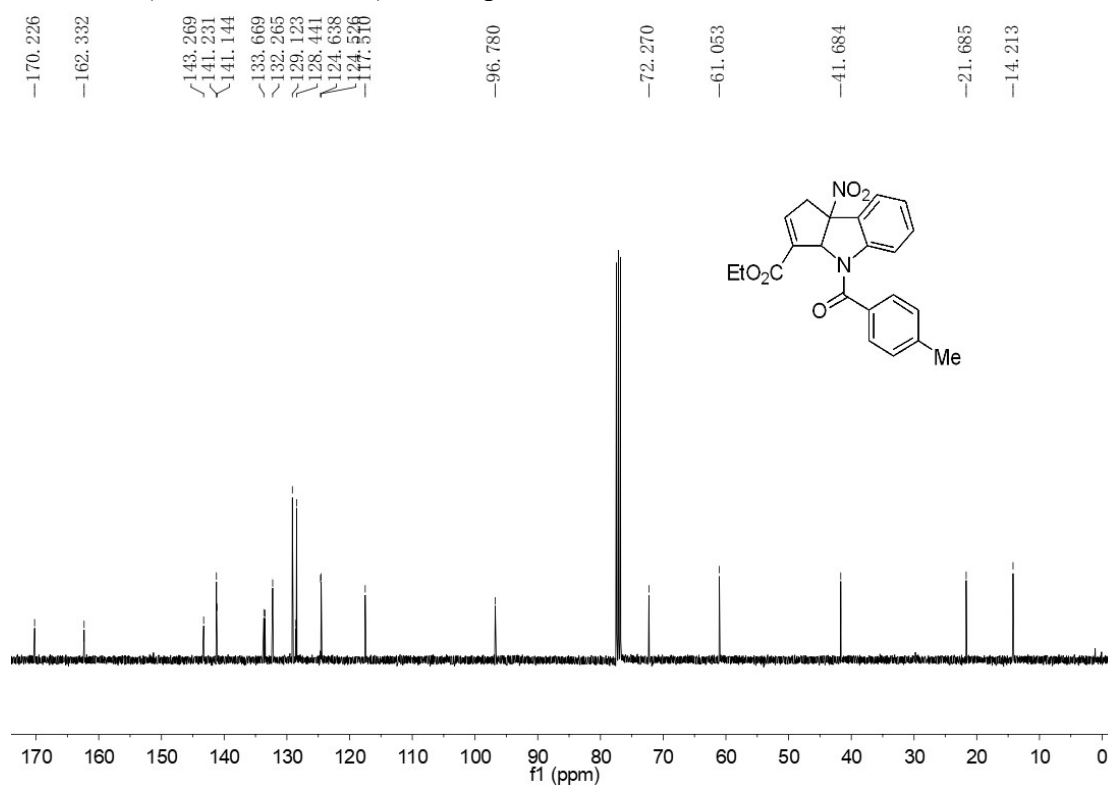
^{13}C NMR (100 MHz, CDCl_3) of compound **3ma**



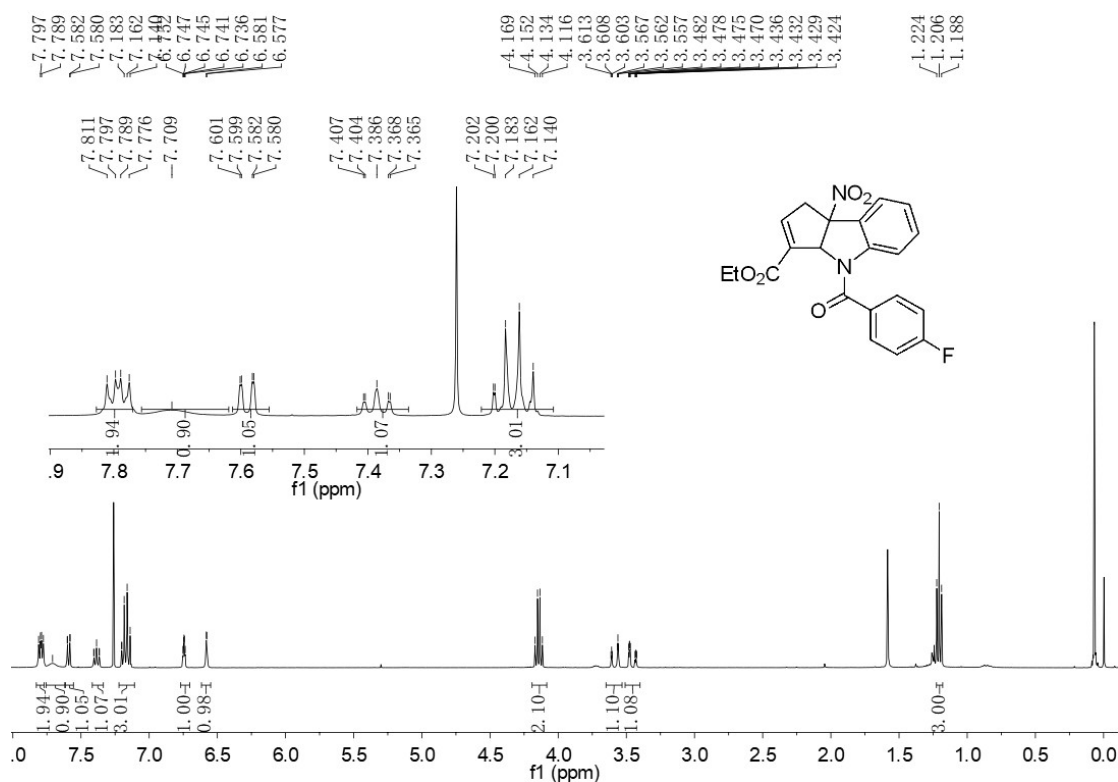
^1H NMR (400 MHz, CDCl_3) of compound **3na**



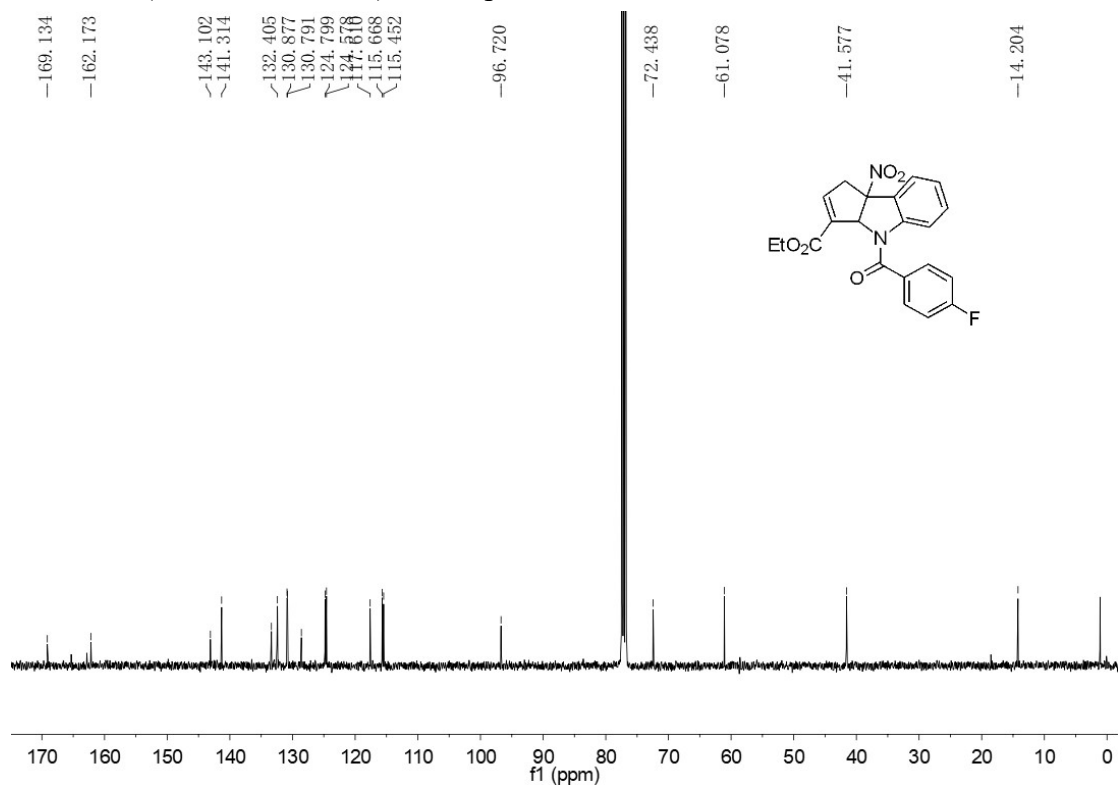
^{13}C NMR (100 MHz, CDCl_3) of compound **3na**



^1H NMR (400 MHz, CDCl_3) of compound **30a**



^{13}C NMR (100 MHz, CDCl_3) of compound **30a**



Chemical structure of compound 10: CCOC(=O)c1ccc2c(c1)c(c3ccccc3n2C(=O)c4ccc(C(F)(F)F)cc4)[C@@H]5C=CC=C[N+](=O)[O-]5

¹H NMR spectrum (CDCl₃):

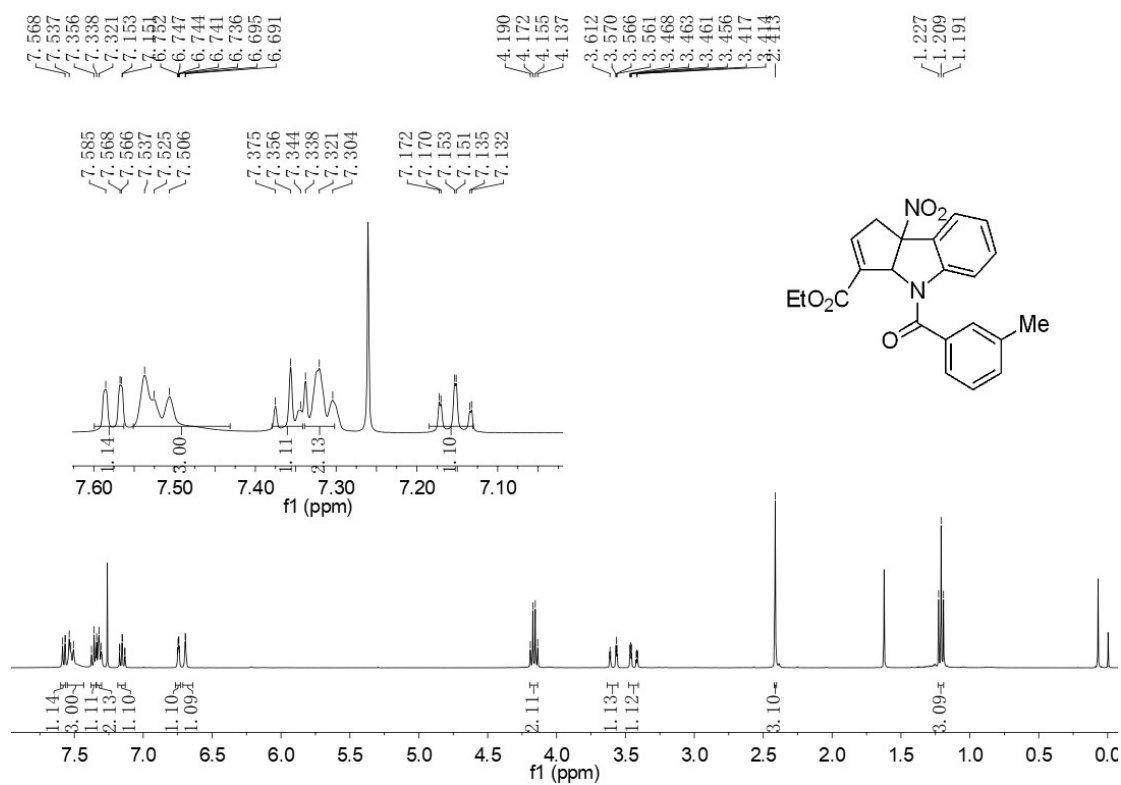
- Chemical shift range: 0.0 to 8.1 ppm.
- Integration values (from left to right): 2.10, 3.00, 1.10, 1.07, 1.05, 1.09, 1.03, 1.94, 1.09, 1.10, 3.06.
- Peak labels (from left to right): 7.909, 7.756, 7.736, 7.598, 7.214, 7.213, 6.745, 6.742, 6.737, 6.493, 7.928, 7.909, 7.756, 7.736, 7.619, 7.617, 7.599, 7.598, 7.440, 7.421, 7.401, 7.233, 7.231, 7.214, 7.212, 7.195, 7.193, 4.171, 4.153, 4.135, 4.117, 3.601, 3.597, 3.592, 3.555, 3.550, 3.490, 3.486, 3.483, 3.483, 3.478, 3.444, 3.440, 3.437, 3.432, 1.228, 1.210, 1.193.

Chemical structure of the compound is shown above the spectrum. The structure is a 1,2,3,4-tetrahydronaphthalene derivative with a nitro group (NO₂) at position 1, an ethyl ester group (EtO₂C) at position 2, and a 4-(trifluoromethyl)benzoyl group attached to the nitrogen atom.

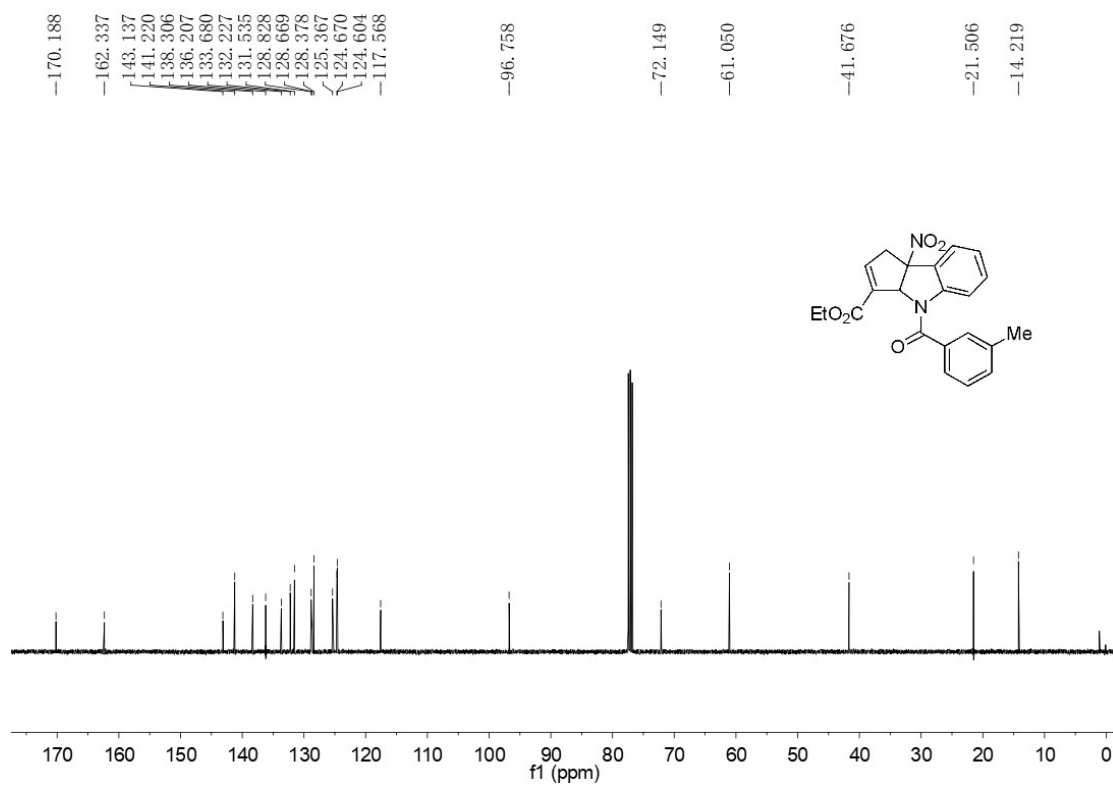
Peak values (ppm):

- 168.741
- 162.057
- 142.823
- 141.492
- 139.724
- 128.908
- 125.457
- 125.422
- 125.171
- 124.558
- 117.596
- 96.642
- 77.0
- 72.415
- 61.118
- 41.461
- 14.201

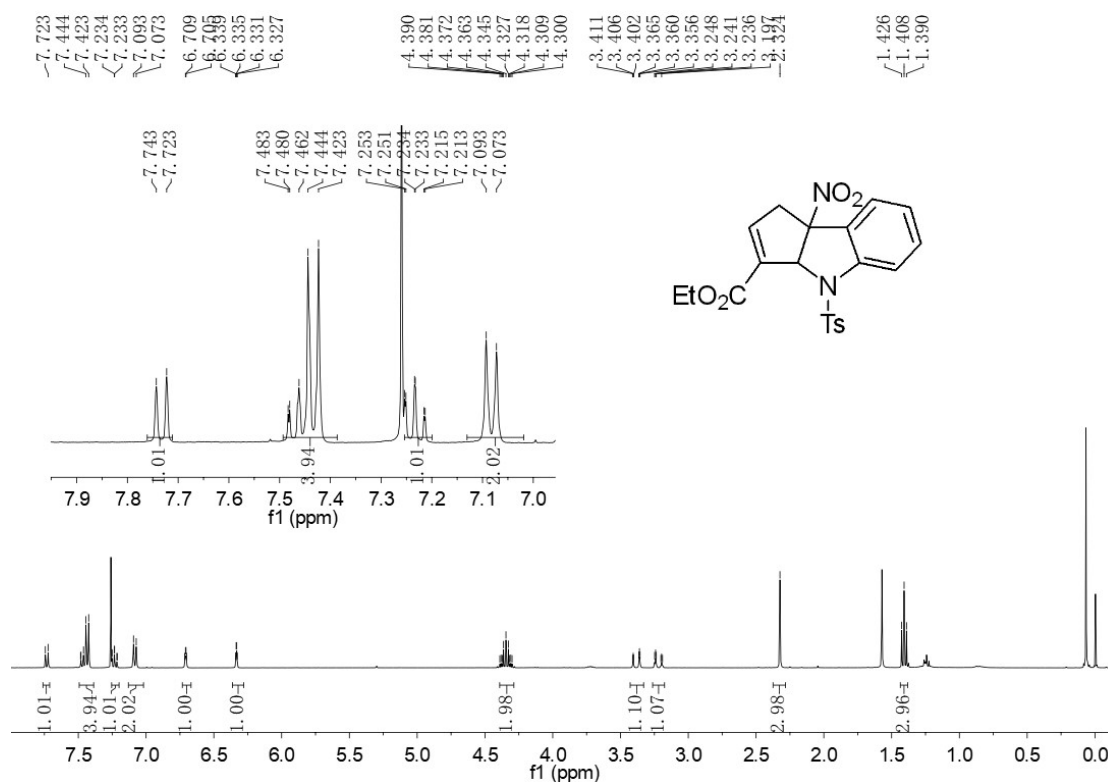
^1H NMR (400 MHz, CDCl_3) of compound **3qa**



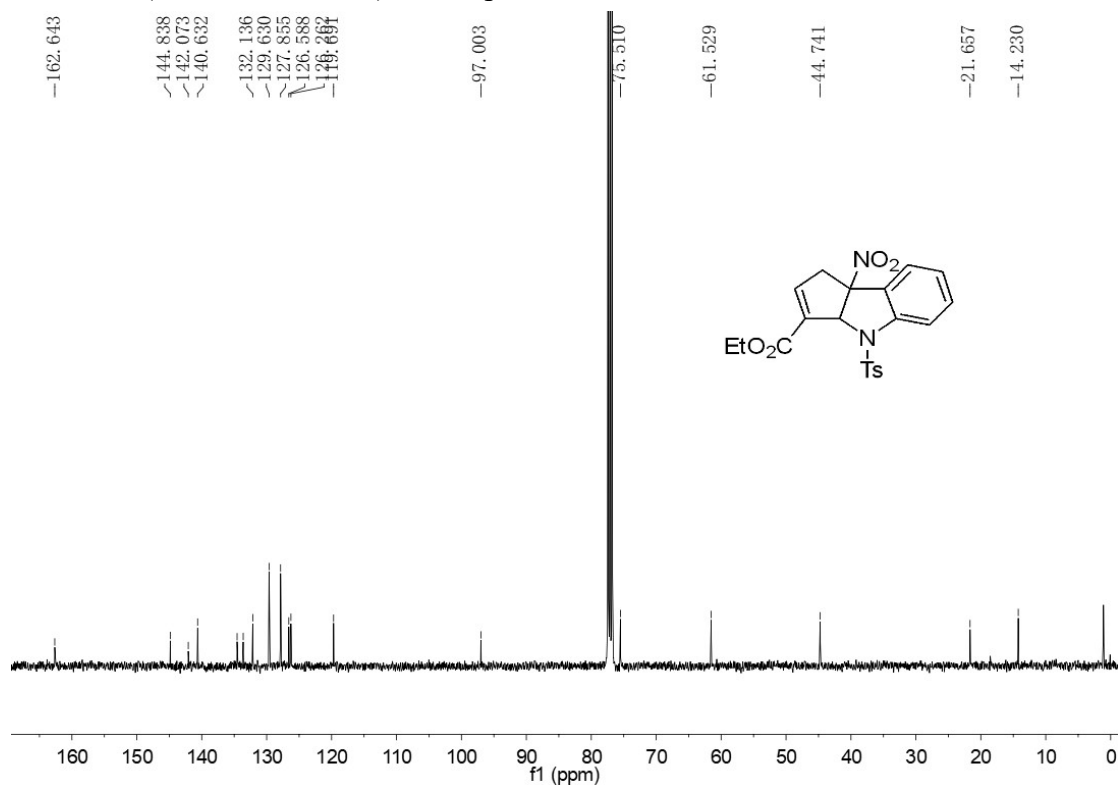
^{13}C NMR (100 MHz, CDCl_3) of compound **3qa**



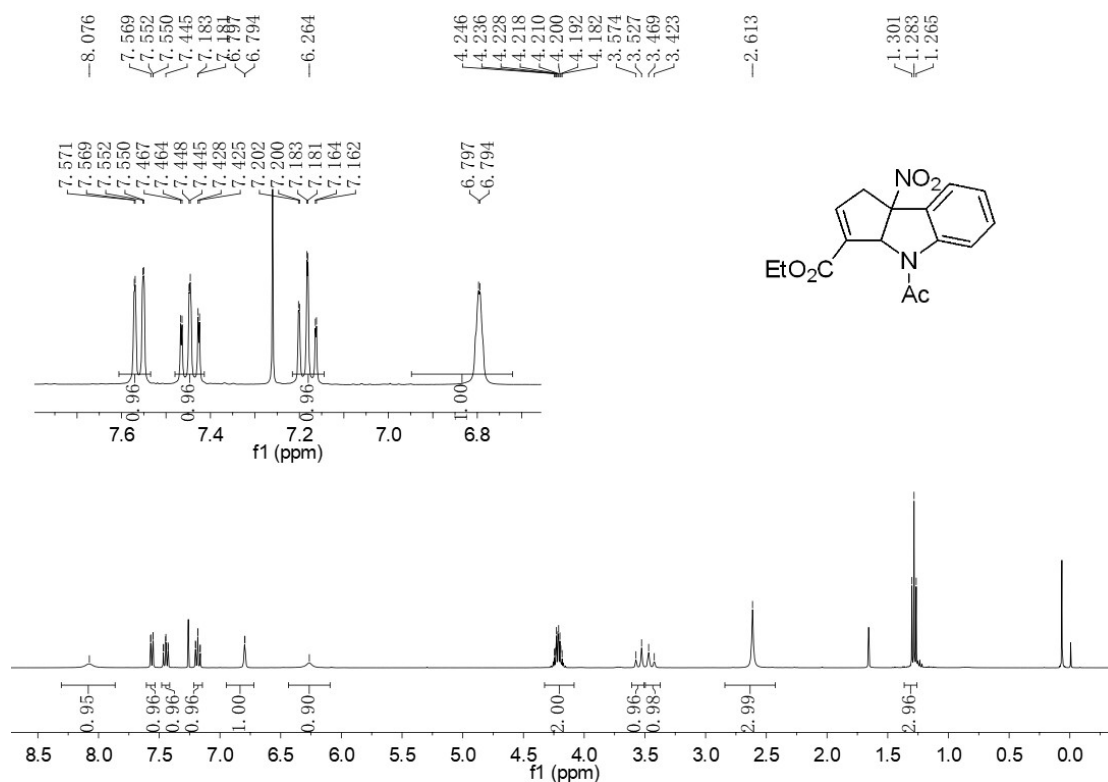
^1H NMR (400 MHz, CDCl_3) of compound **3ra**



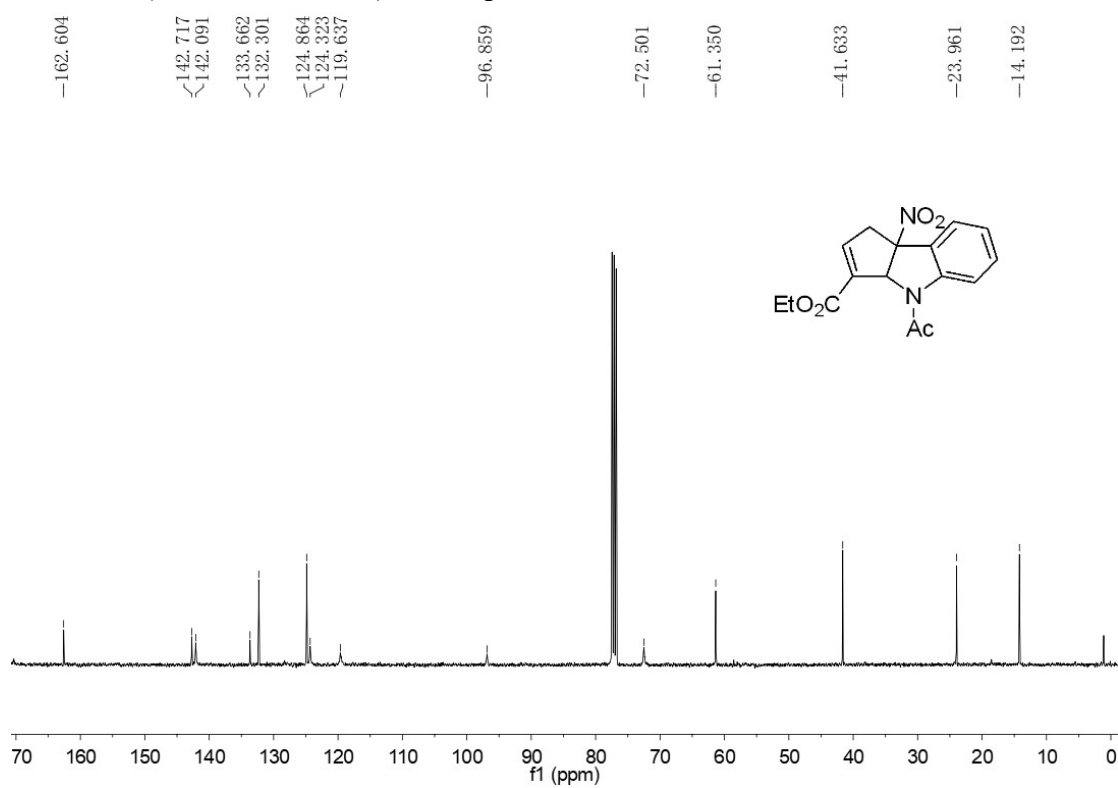
^{13}C NMR (100 MHz, CDCl_3) of compound **3ra**



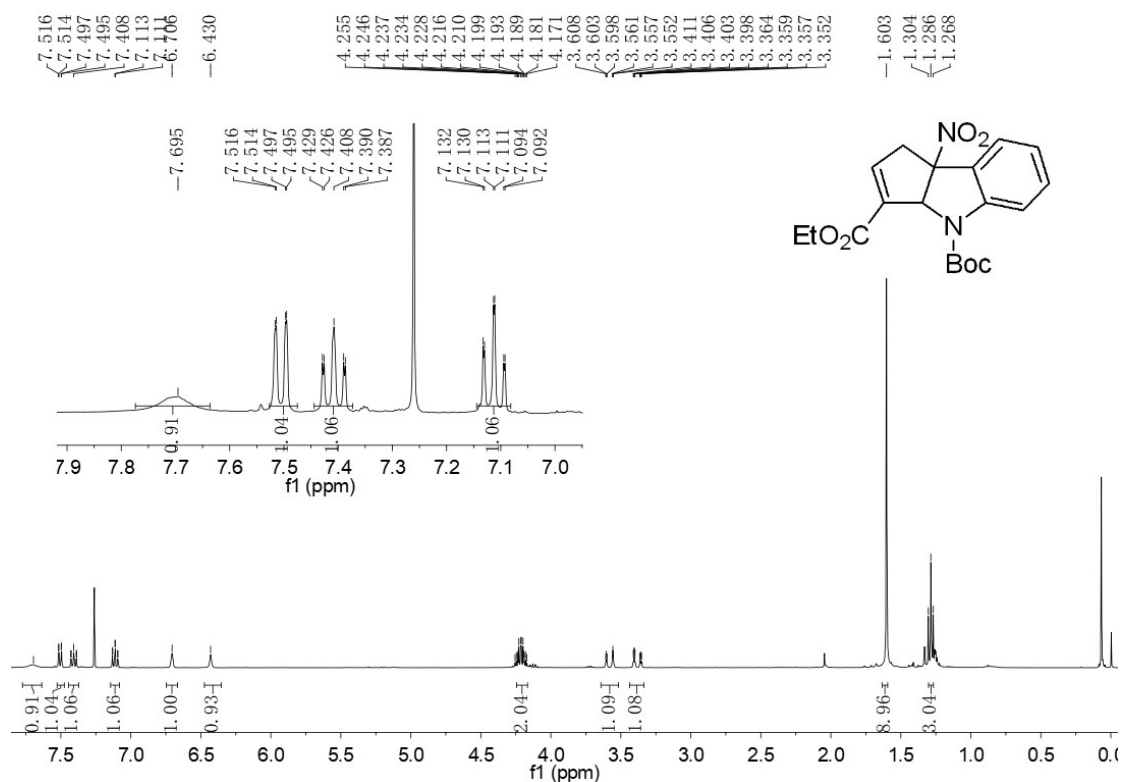
^1H NMR (400 MHz, CDCl_3) of compound **3sa**



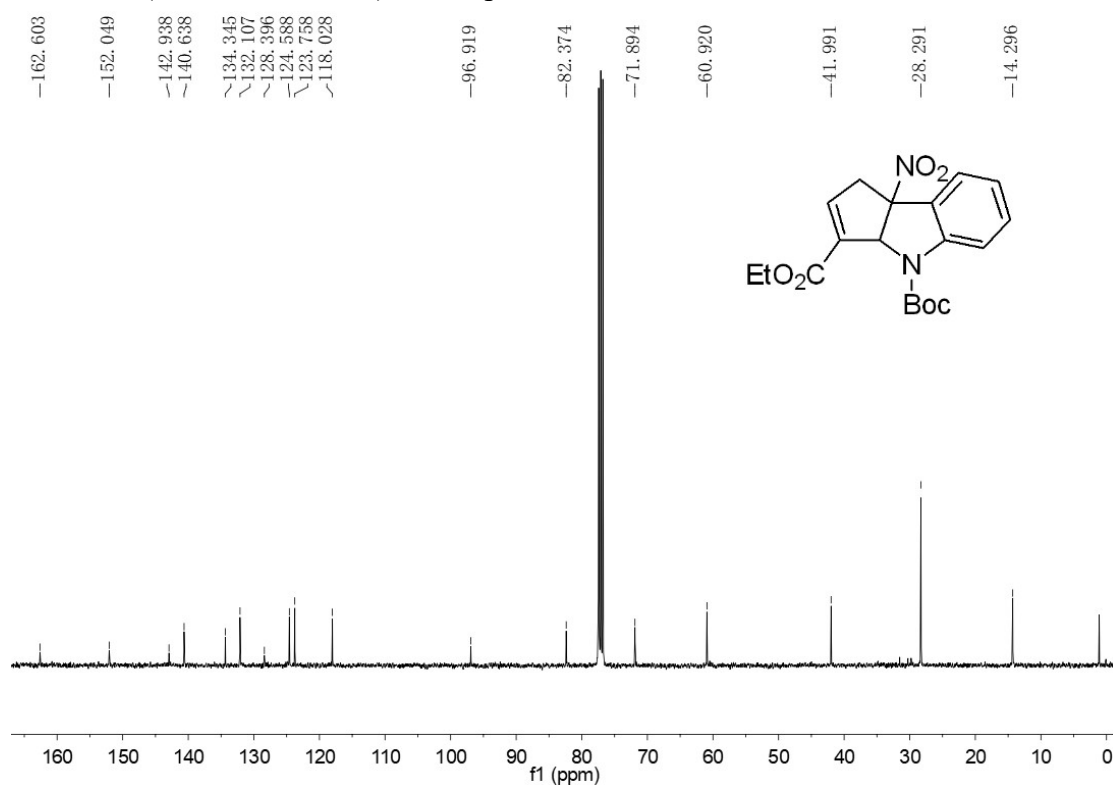
^{13}C NMR (100 MHz, CDCl_3) of compound **3sa**



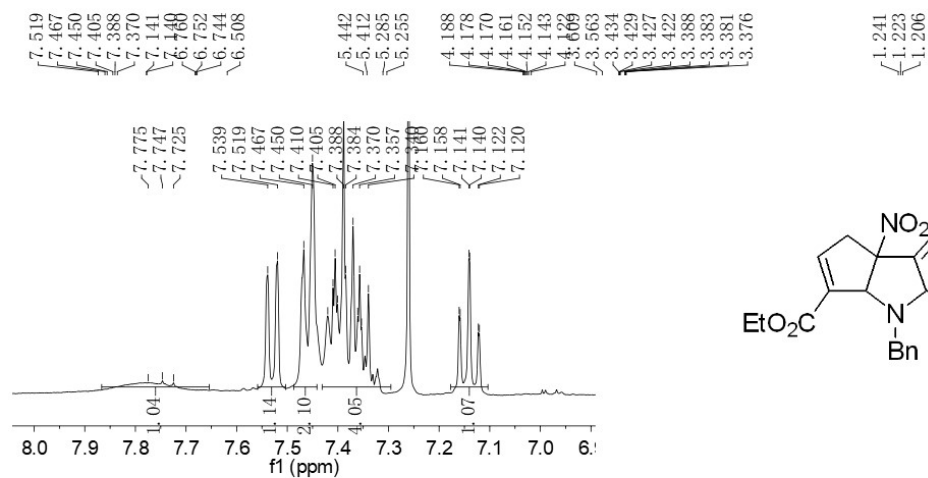
¹H NMR (400 MHz, CDCl₃) of compound **3ta**



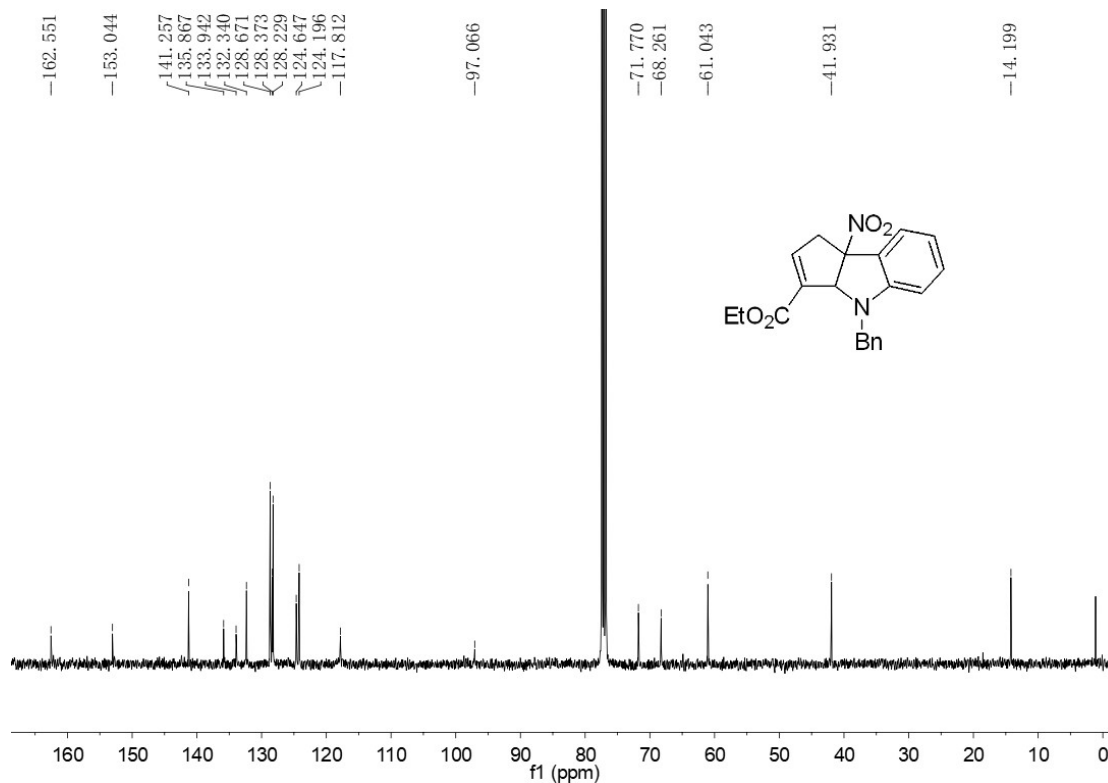
¹³C NMR (100 MHz, CDCl₃) of compound **3ta**



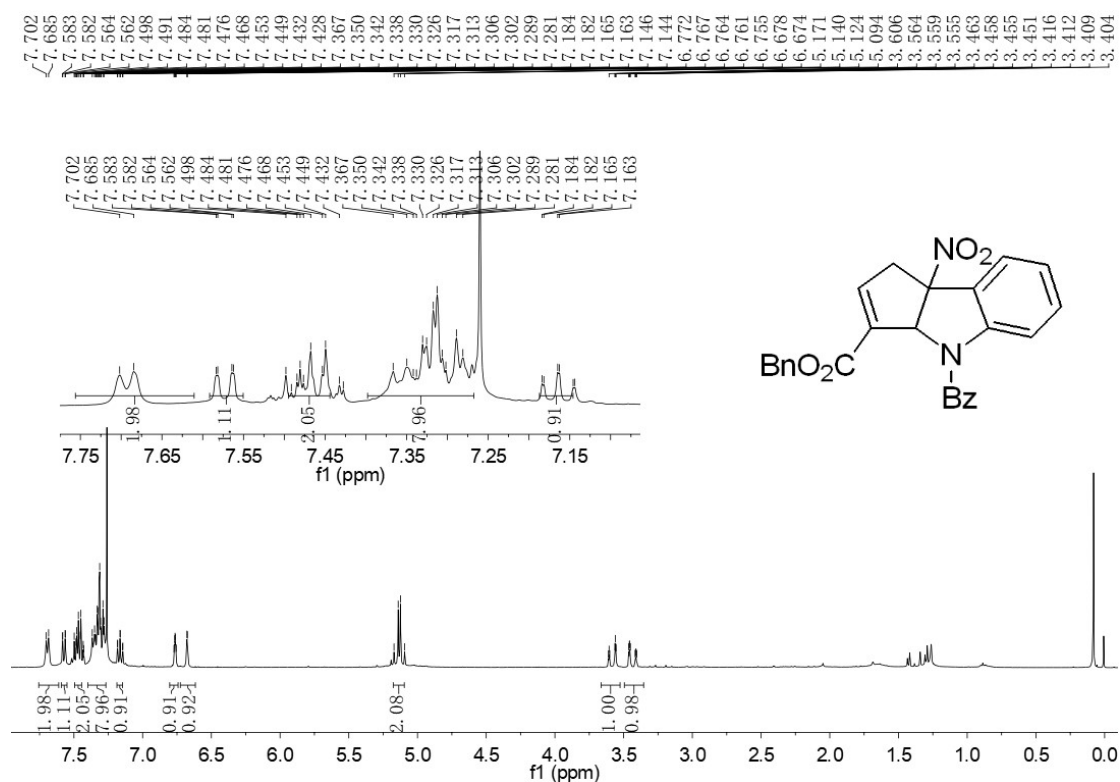
^1H NMR (400 MHz, CDCl_3) of compound **3ua**



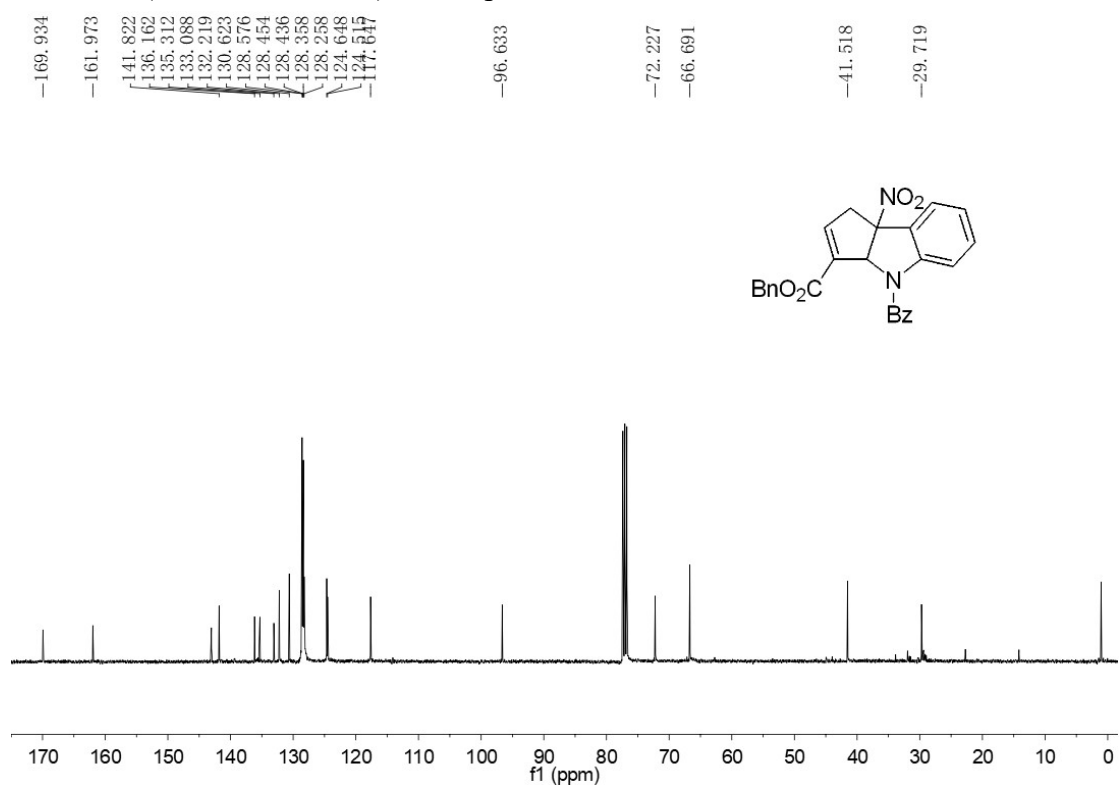
^{13}C NMR (100 MHz, CDCl_3) of compound **3ua**



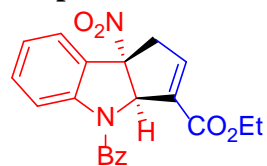
¹H NMR (400 MHz, CDCl₃) of compound **3ab**



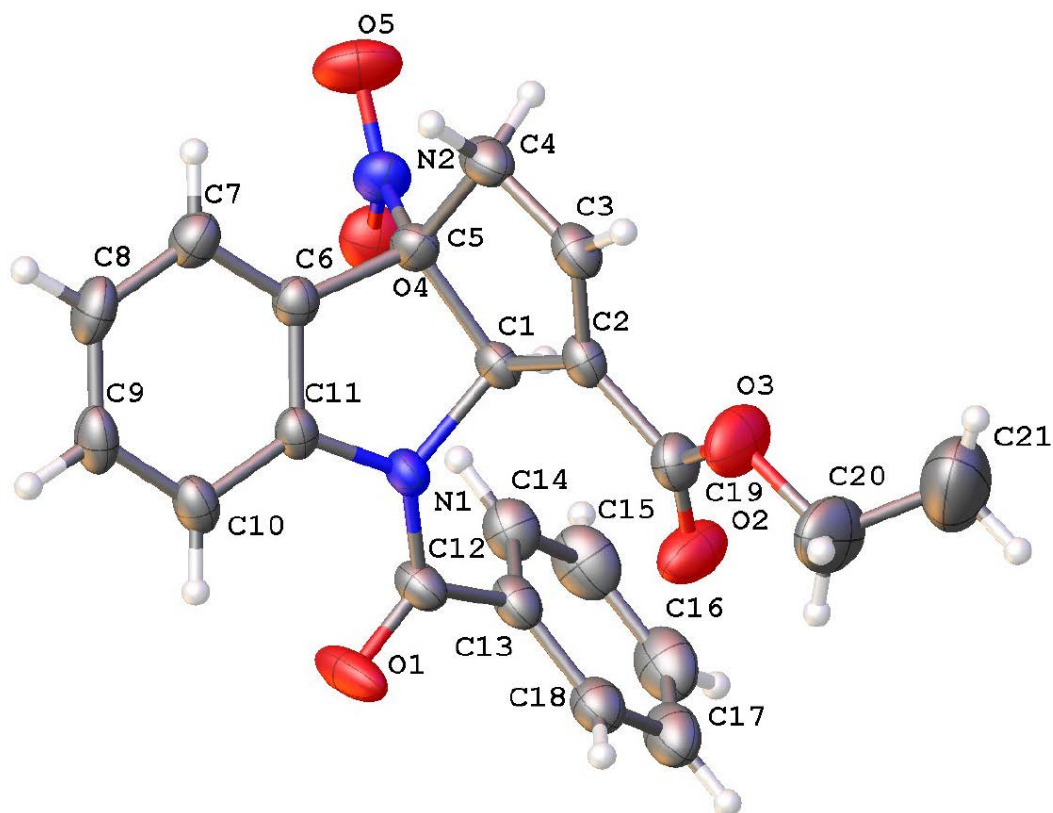
¹³C NMR (100 MHz, CDCl₃) of compound **3ab**



2. X-ray single crystal data for compound 3aa



(relative configuration)
3aa



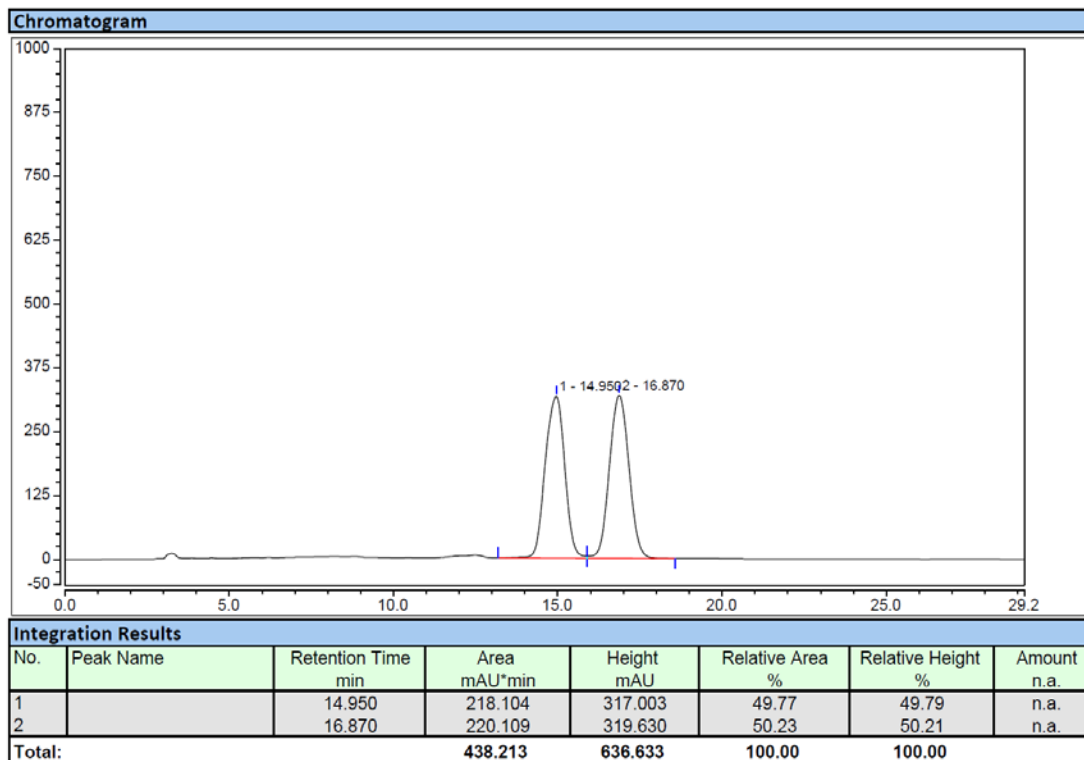
The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C ₂₁ H ₁₈ N ₂ O ₅	
Formula weight	378.37	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /c 1	
Unit cell dimensions	a = 15.7507(18) Å	α = 90°.
	b = 9.3997(11) Å	β = 93.560(2)°.
	c = 12.8142(15) Å	γ = 90°.
Volume	1893.5(4) Å ³	
Z	4	
Density (calculated)	1.327 Mg/m ³	
Absorption coefficient	0.096 mm ⁻¹	

F(000)	792
Crystal size	0.5 x 0.2 x 0.2 mm ³
Theta range for data collection	2.525 to 28.074°.
Index ranges	-19<= <i>h</i> <=20, -10<= <i>k</i> <=12, -16<= <i>l</i> <=16
Reflections collected	11052
Independent reflections	4370 [R(int) = 0.0255]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6661
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4370 / 19 / 254
Goodness-of-fit on F ²	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0715, wR2 = 0.2062
R indices (all data)	R1 = 0.1139, wR2 = 0.2455
Extinction coefficient	n/a
Largest diff. peak and hole	0.827 and -0.469 e.Å ⁻³

3. HPLC copies of product 3aa

Racemic:



Enantioselective:

