

Supporting Information for
Catalytic Asymmetric [4+1] Cyclization of Benzofuran-Derived
Azadienes with 3-Chlorooxindoles

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

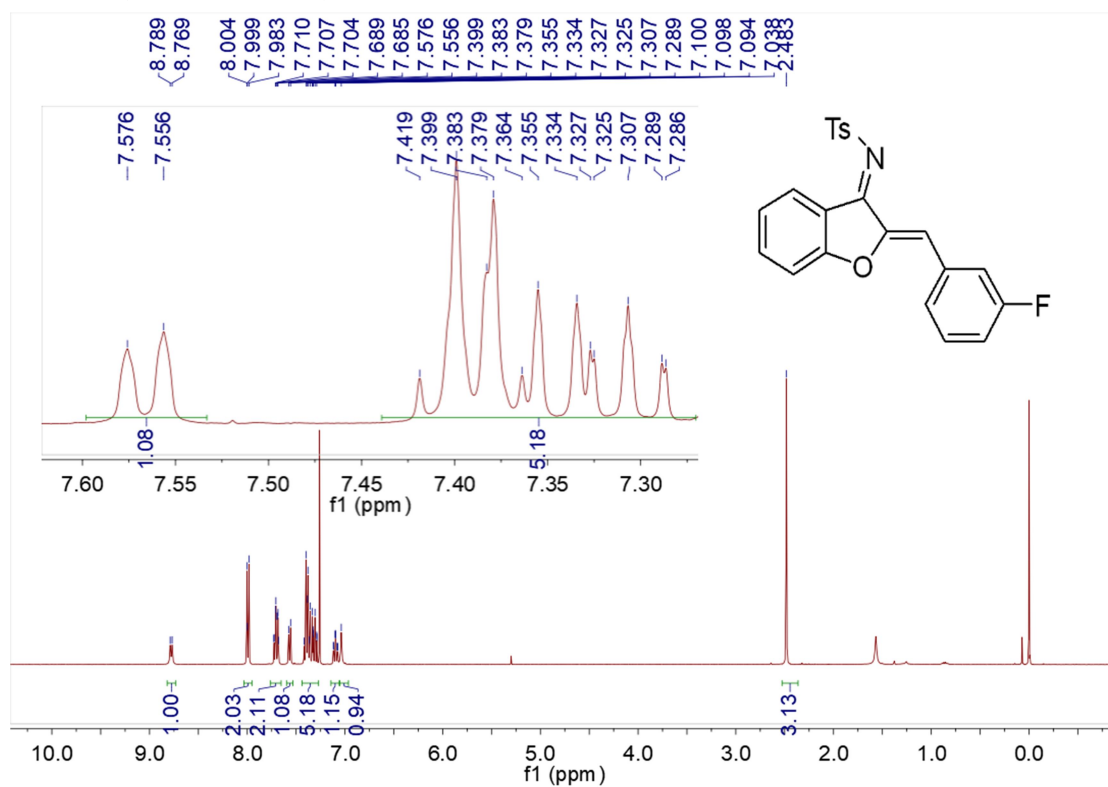
E-mail: fshi@jsnu.edu.cn

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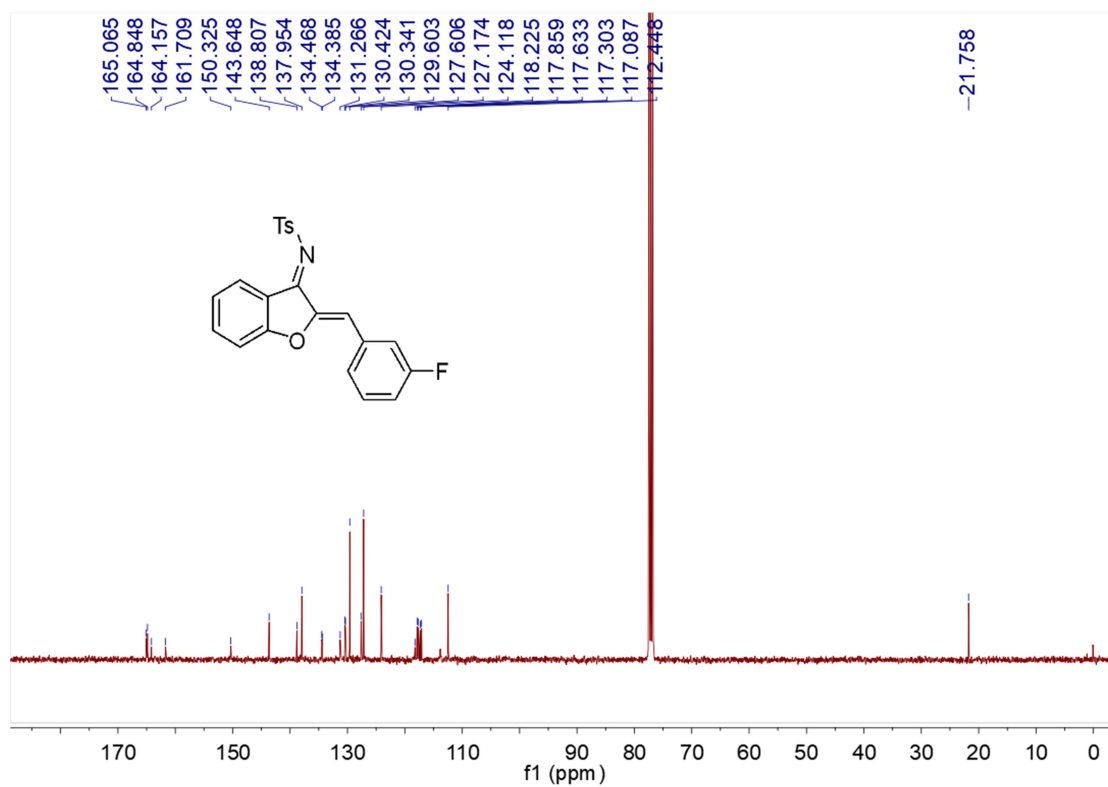
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- 2. NMR spectra of products 3 (S8-S27)**
- 3. HPLC spectra of products 3 (S28-S47)**
- 4. X-ray single-crystal data for product 3ae (S48-S49)**

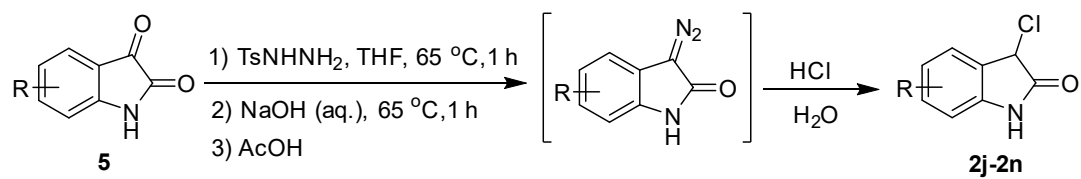
1. NMR spectra of substrates 1c and 2j-2n

¹H NMR (400 MHz, CDCl₃) of substrate 1c

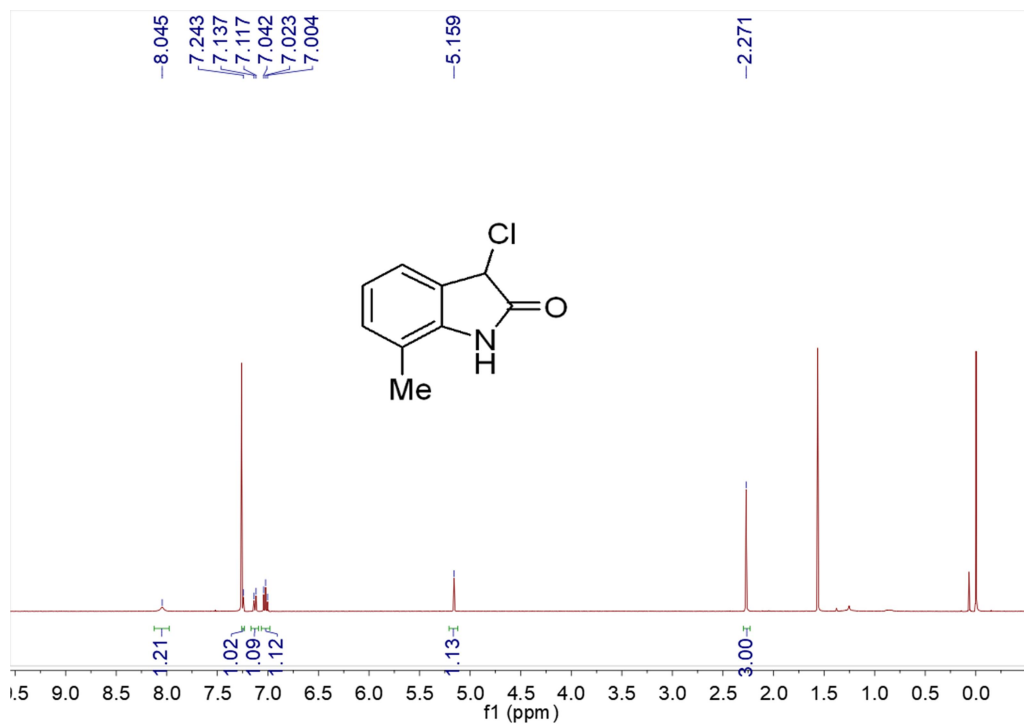


¹³C NMR (100 MHz, CDCl₃) of substrate 1c

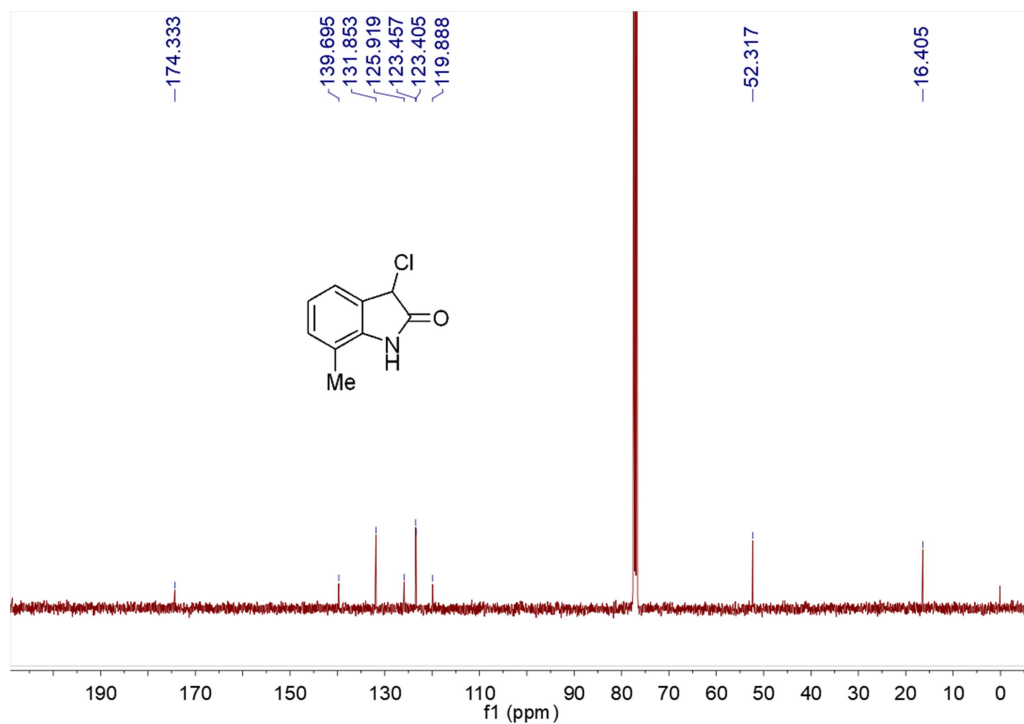




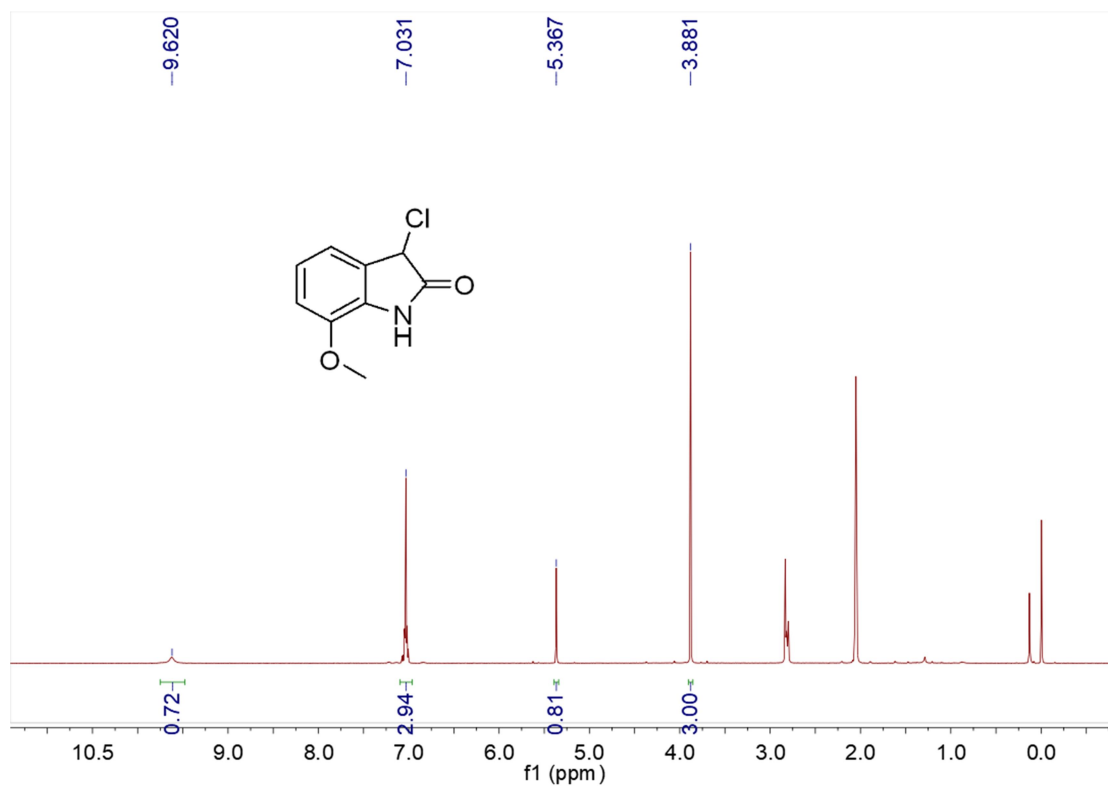
^1H NMR (400 MHz, CDCl_3) of substrate **2j**



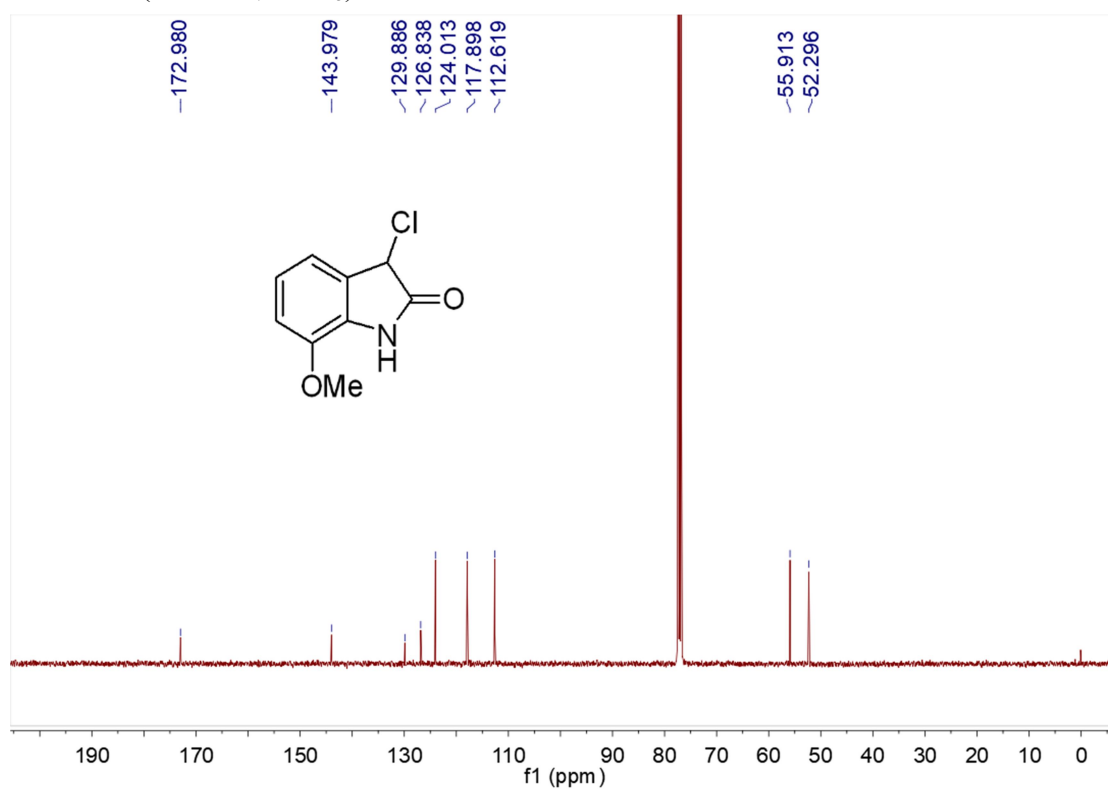
^{13}C NMR (100 MHz, CDCl_3) of substrate **2j**



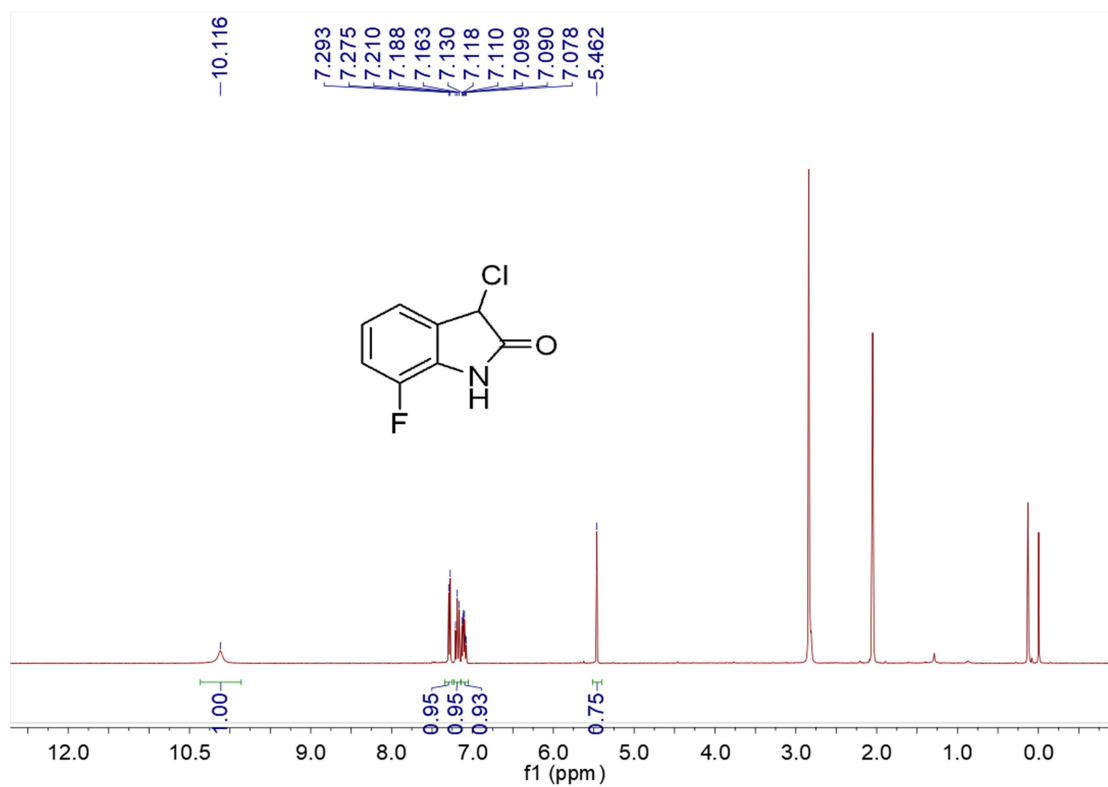
^1H NMR (400 MHz, Acetone- d_6) of substrate **2k**



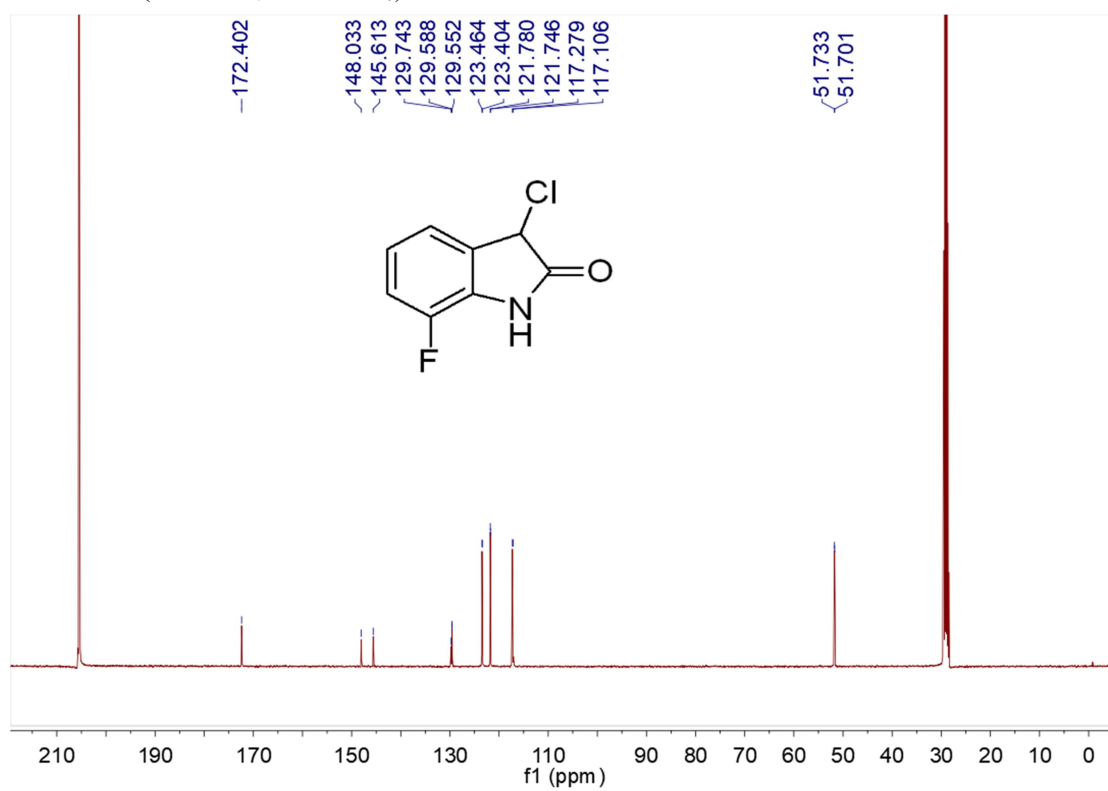
^{13}C NMR (100 MHz, CDCl_3) of substrate **2k**



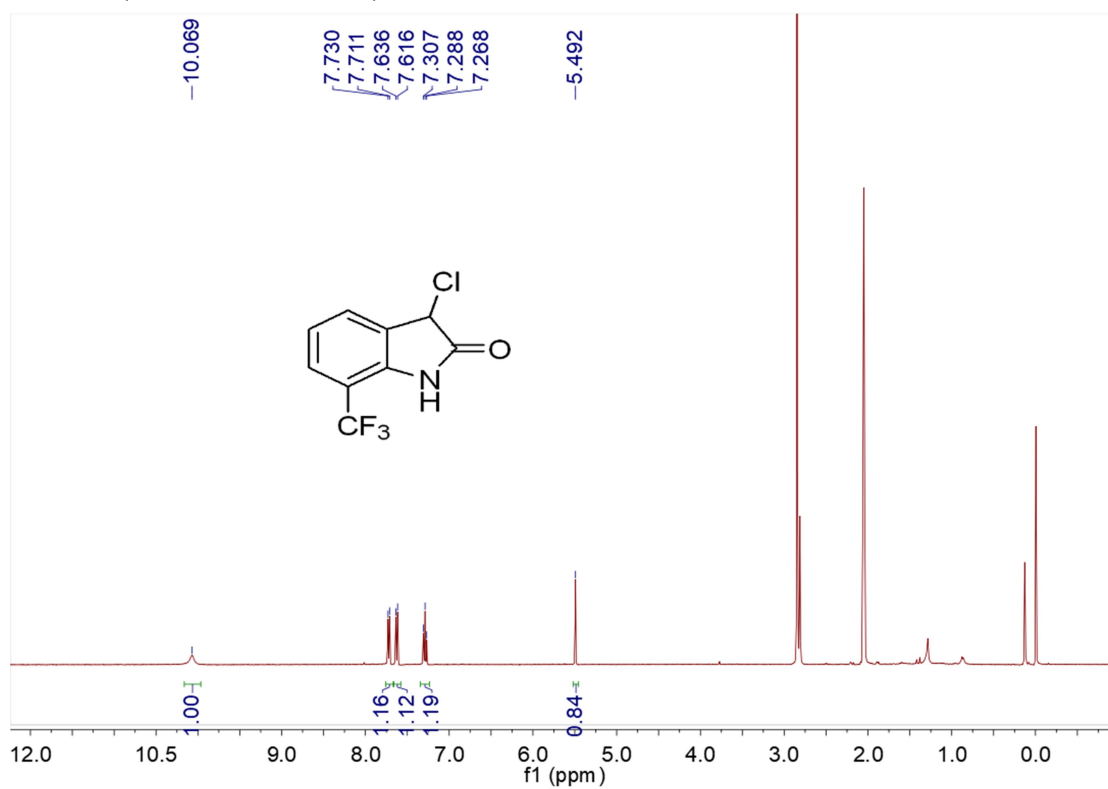
^1H NMR (400 MHz, Acetone- d_6) of substrate **2I**



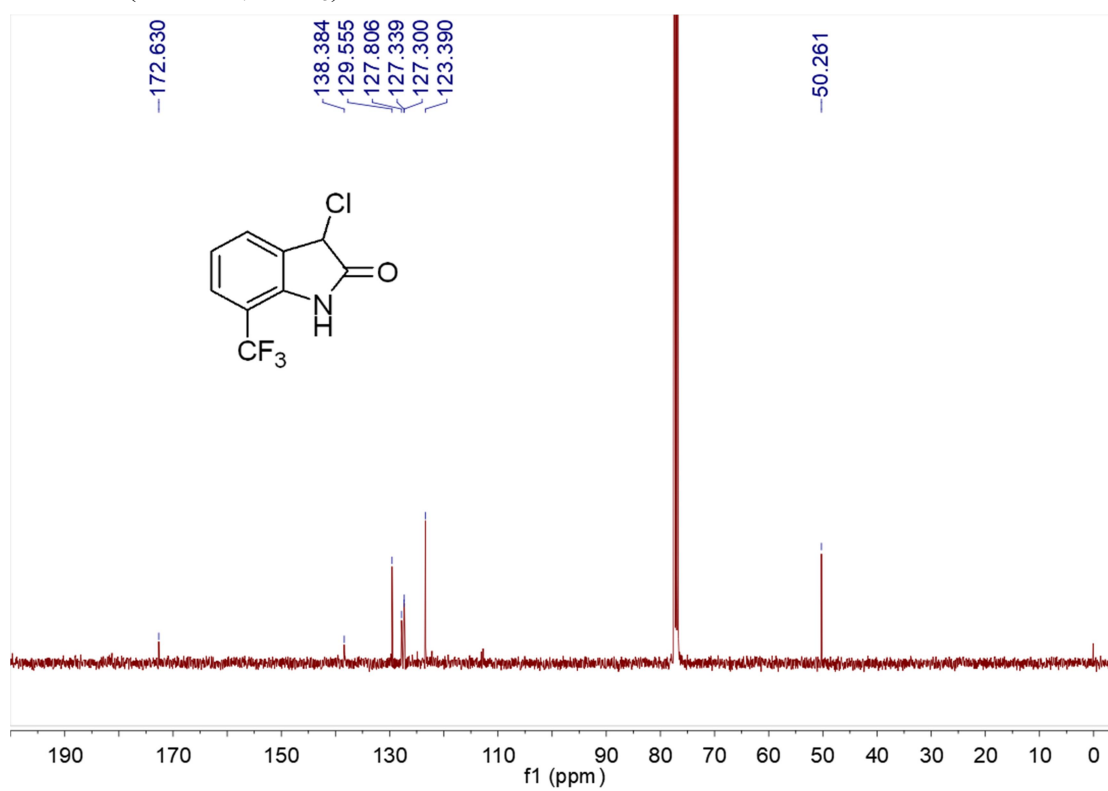
^{13}C NMR (100 MHz, Acetone- d_6) of substrate **2I**



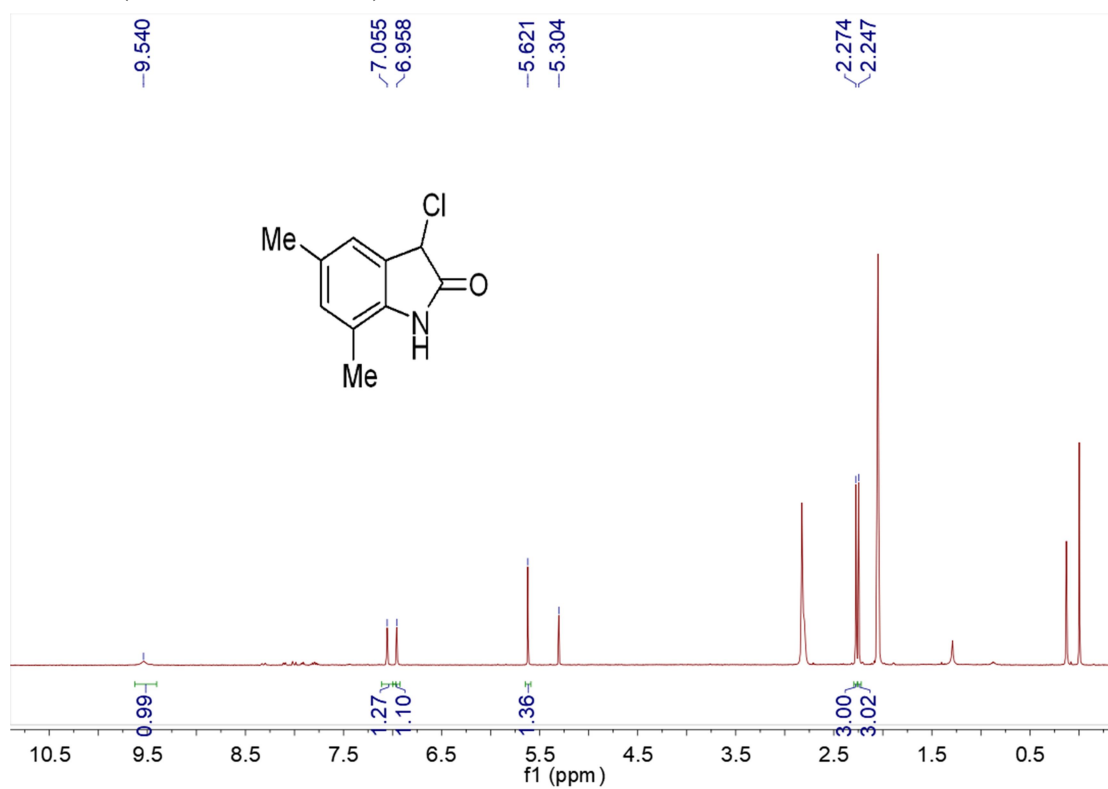
^1H NMR (400 MHz, Acetone- d_6) of substrate **2m**



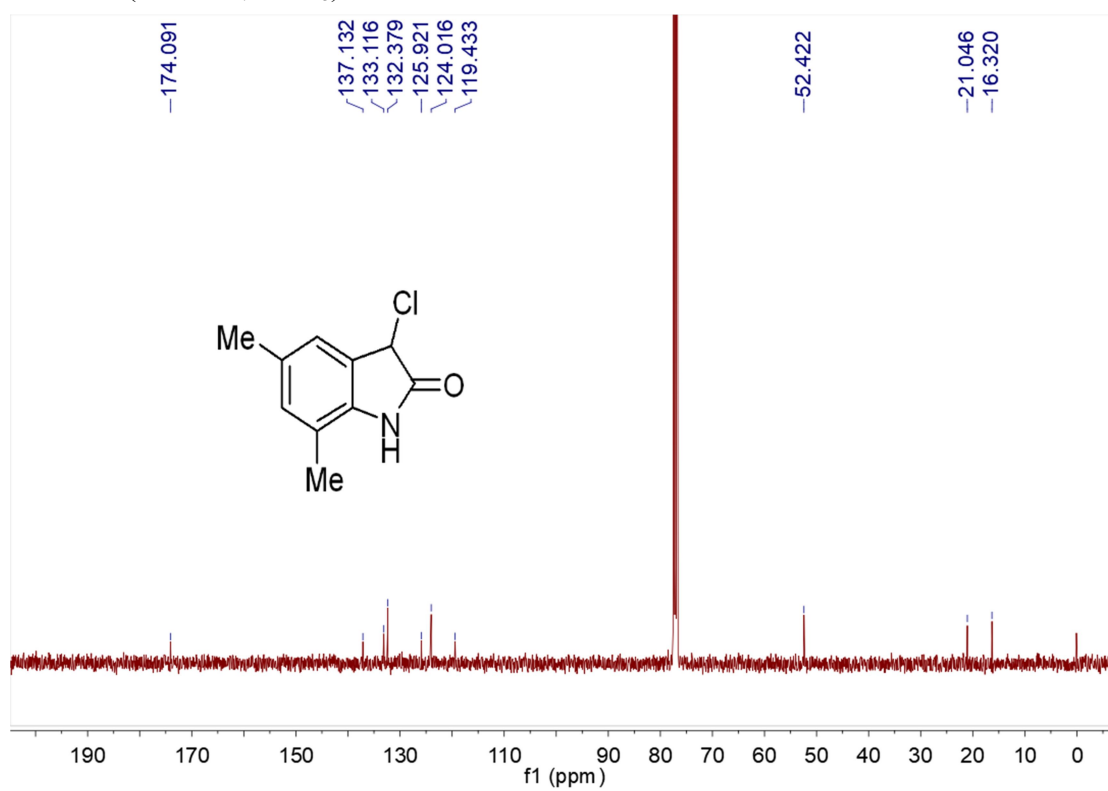
^{13}C NMR (100 MHz, CDCl_3) of substrate **2m**



^1H NMR (400 MHz, Acetone- d_6) of substrate **2n**

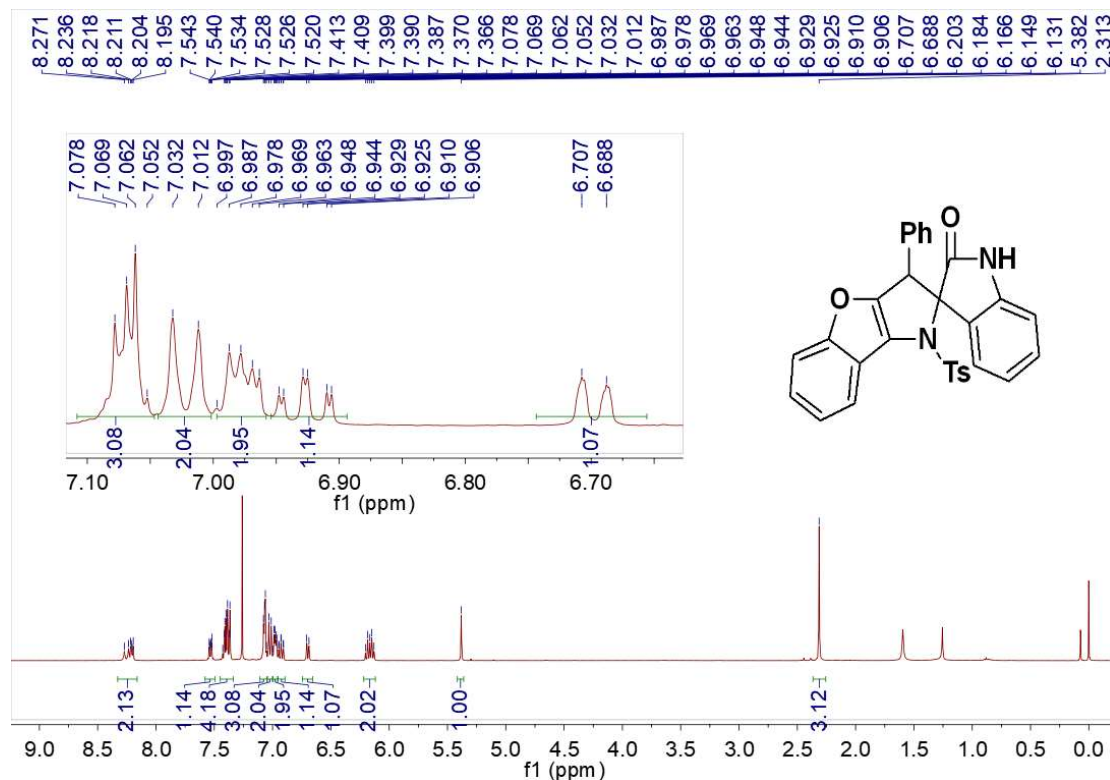


^{13}C NMR (100 MHz, CDCl_3) of substrate **2n**

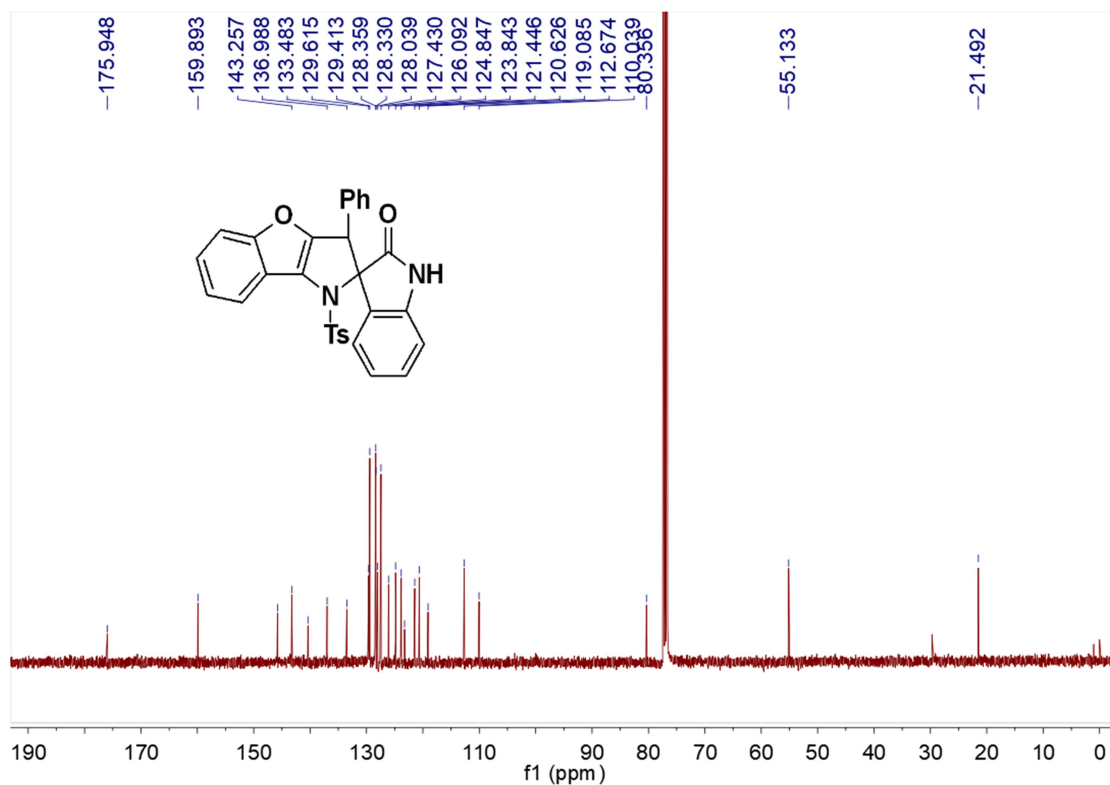


2. NMR spectra of products 3

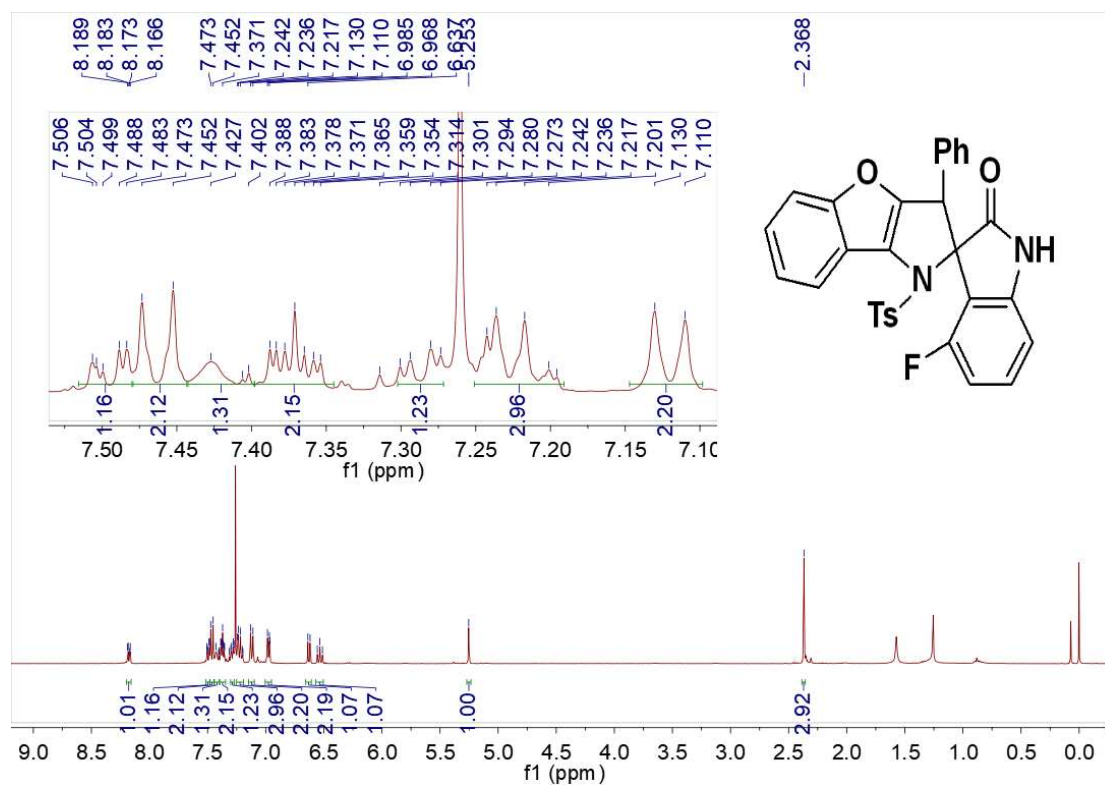
^1H NMR (400 MHz, CDCl_3) of compound **3aa**



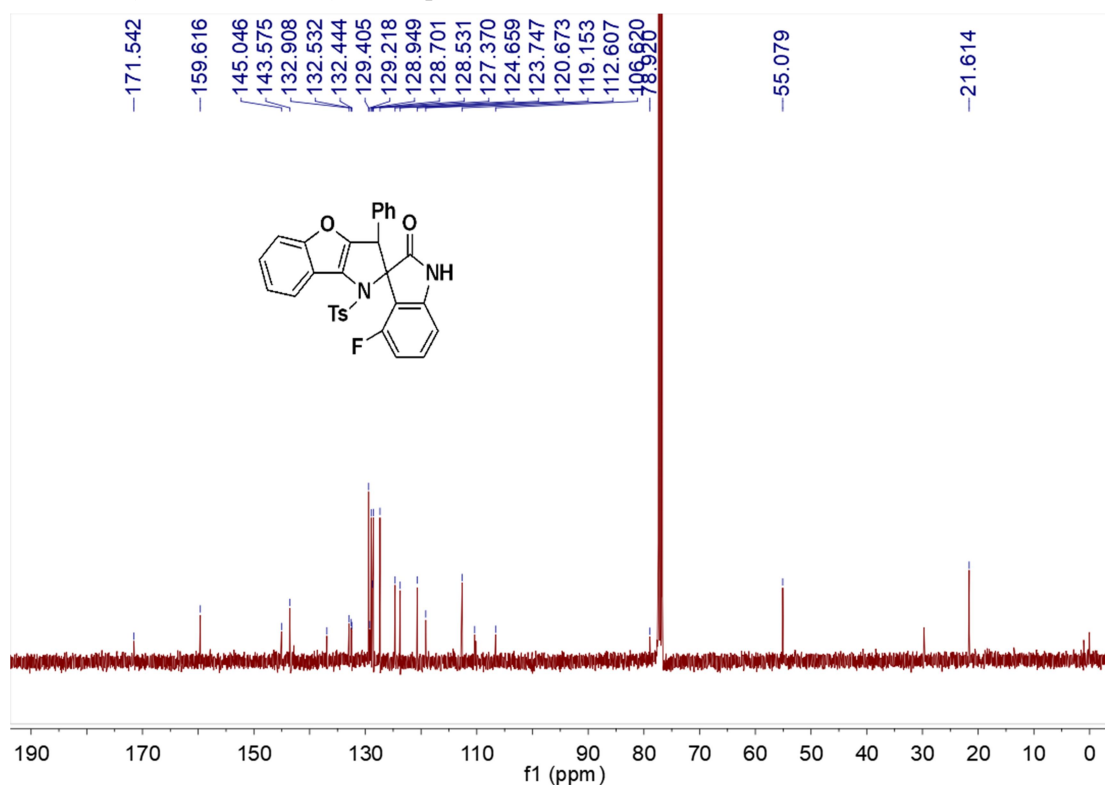
^{13}C NMR (100 MHz, CDCl_3) of compound **3aa**



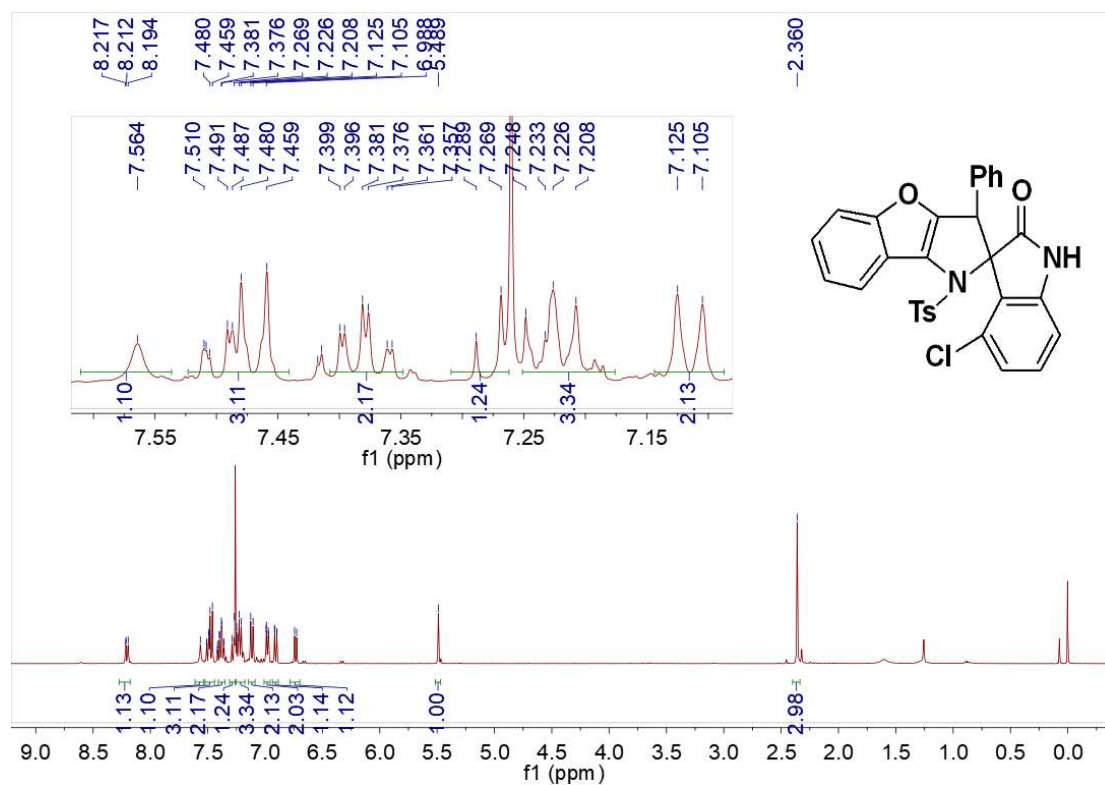
^1H NMR (400 MHz, CDCl_3) of compound **3ab**



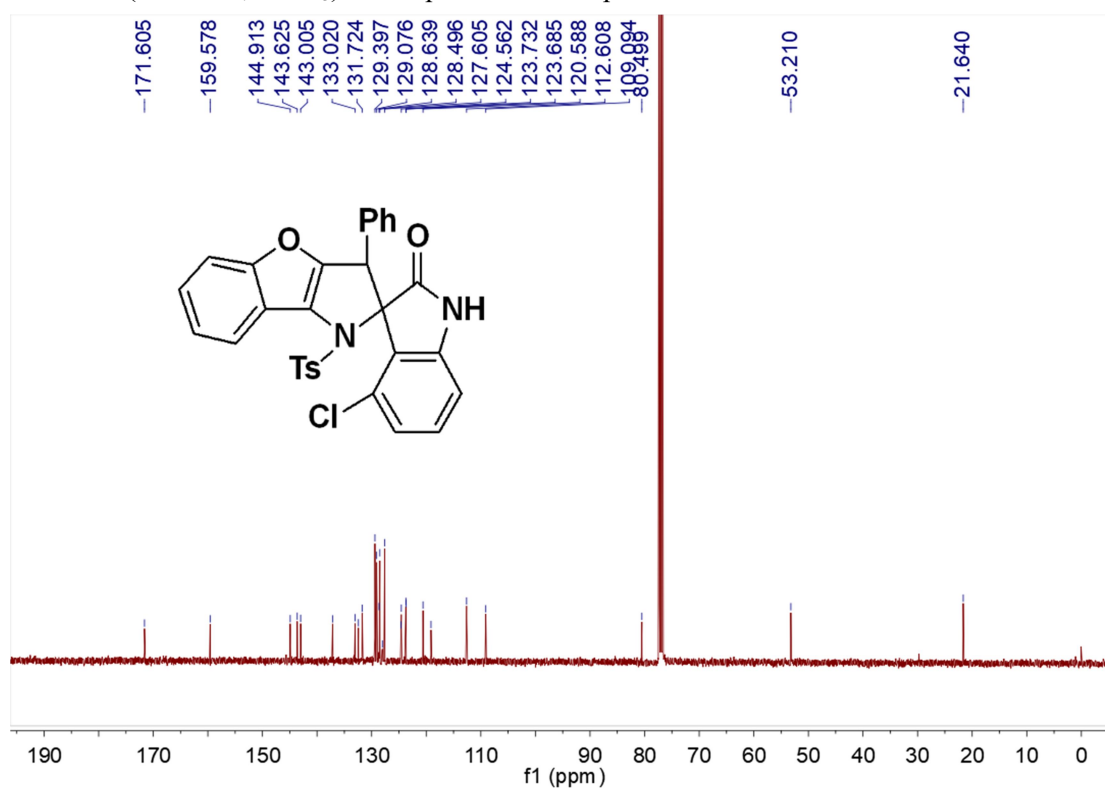
^{13}C NMR (100 MHz, CDCl_3) of compound **3ab**



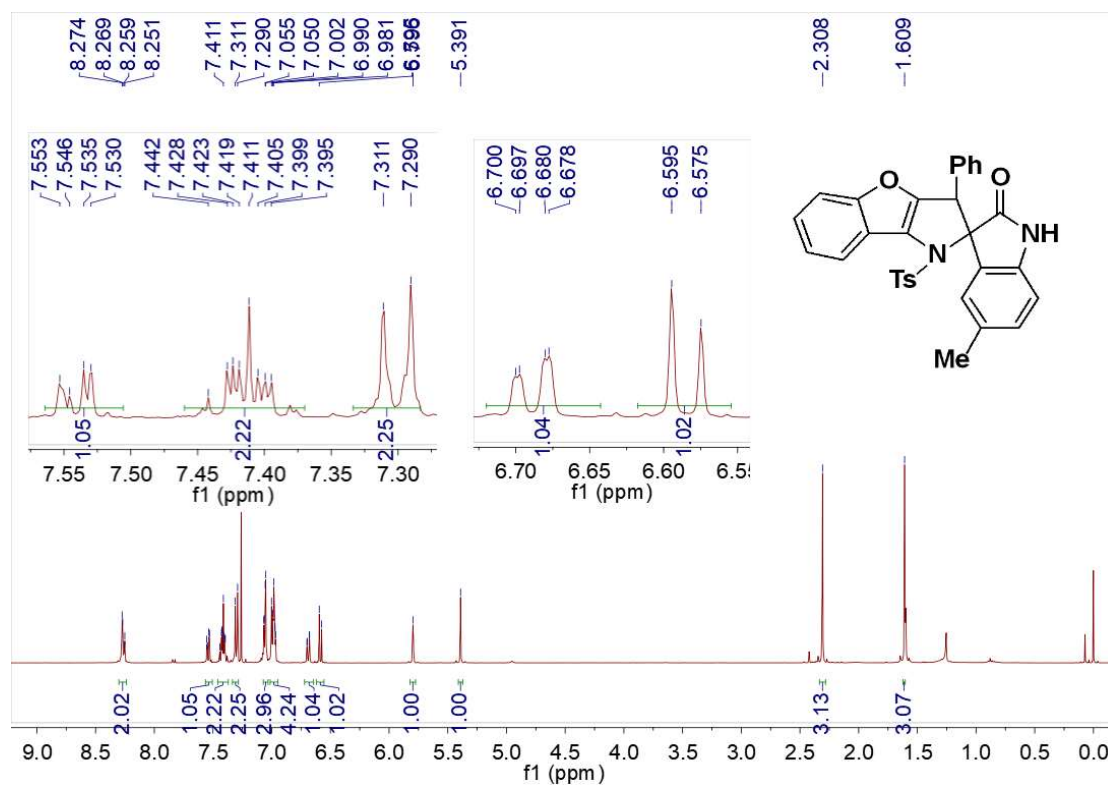
^1H NMR (400 MHz, CDCl_3) of compound **3ac**: inseparable diastereomers with 89:11 dr



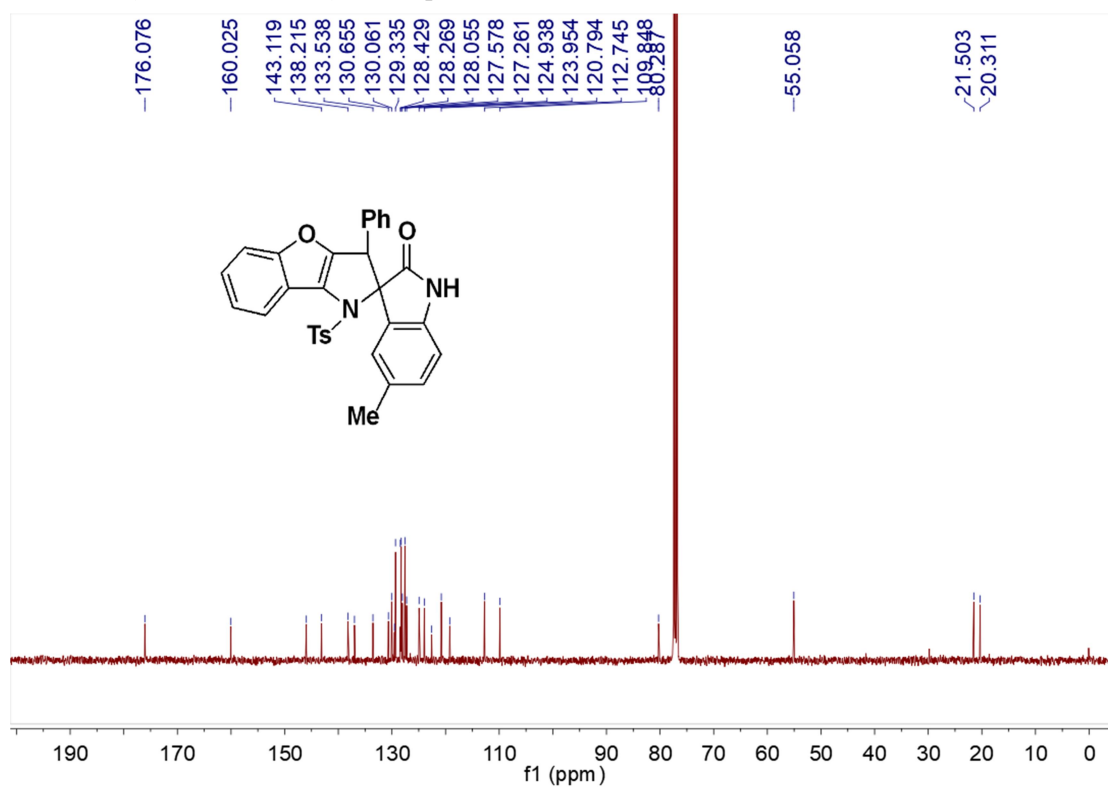
^{13}C NMR (100 MHz, CDCl_3) of compound **3ac**: inseparable diastereomers with 89:11 dr



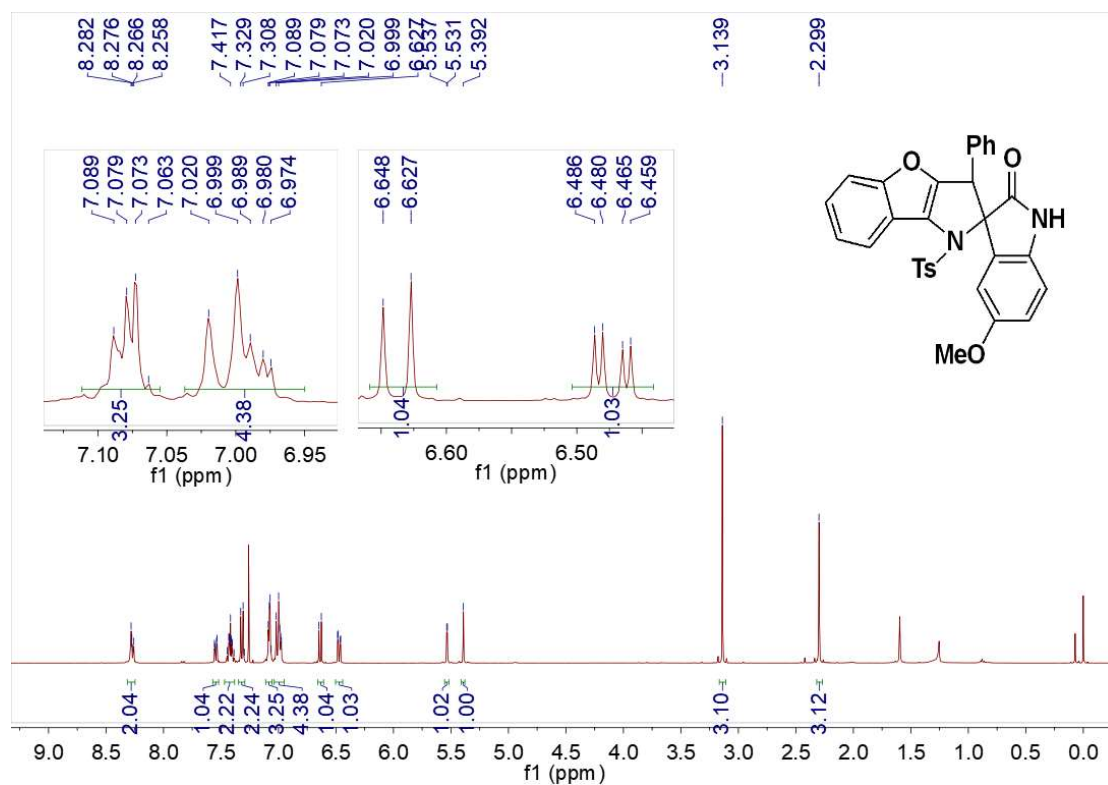
^1H NMR (400 MHz, CDCl_3) of compound **3ad**



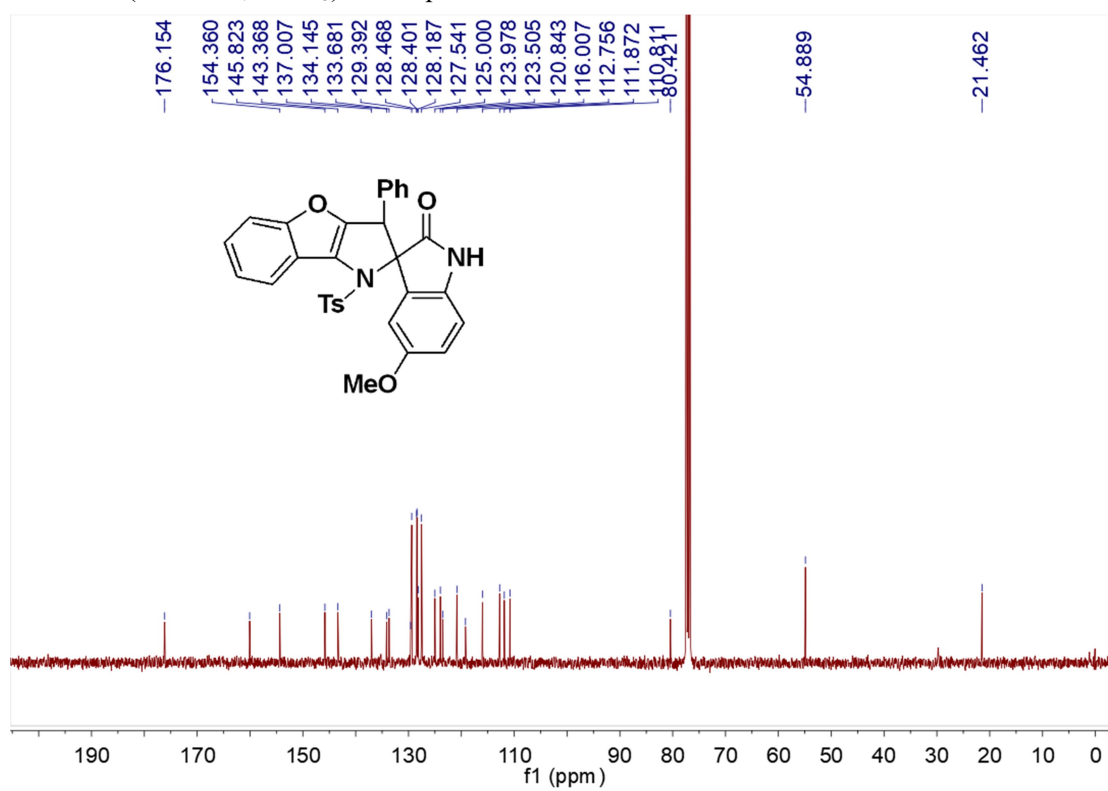
^{13}C NMR (100 MHz, CDCl_3) of compound **3ad**



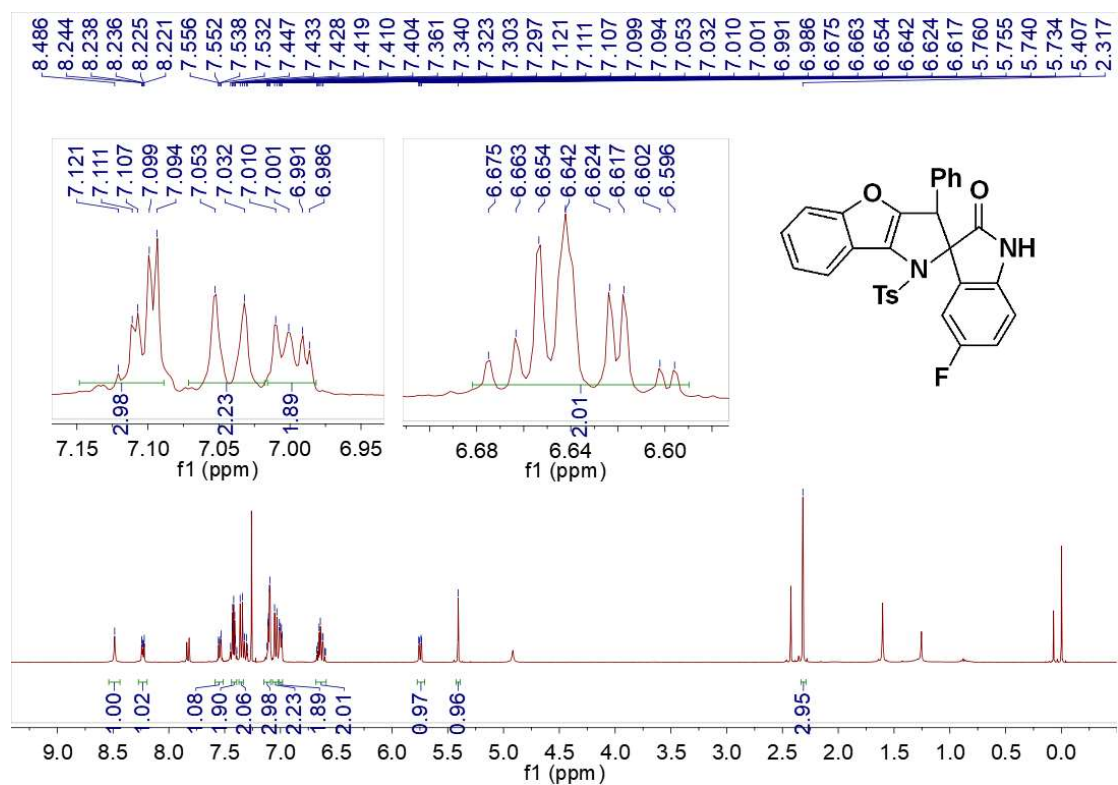
^1H NMR (400 MHz, CDCl_3) of compound **3ae**



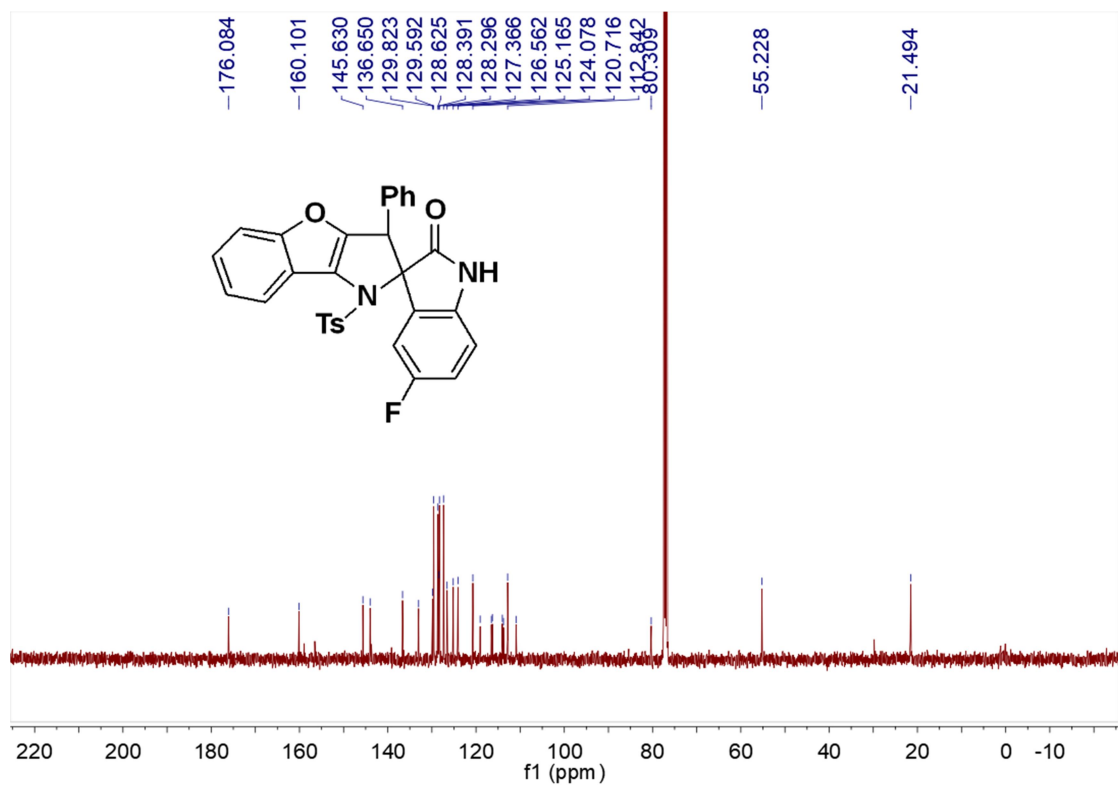
^{13}C NMR (100 MHz, CDCl_3) of compound **3ae**



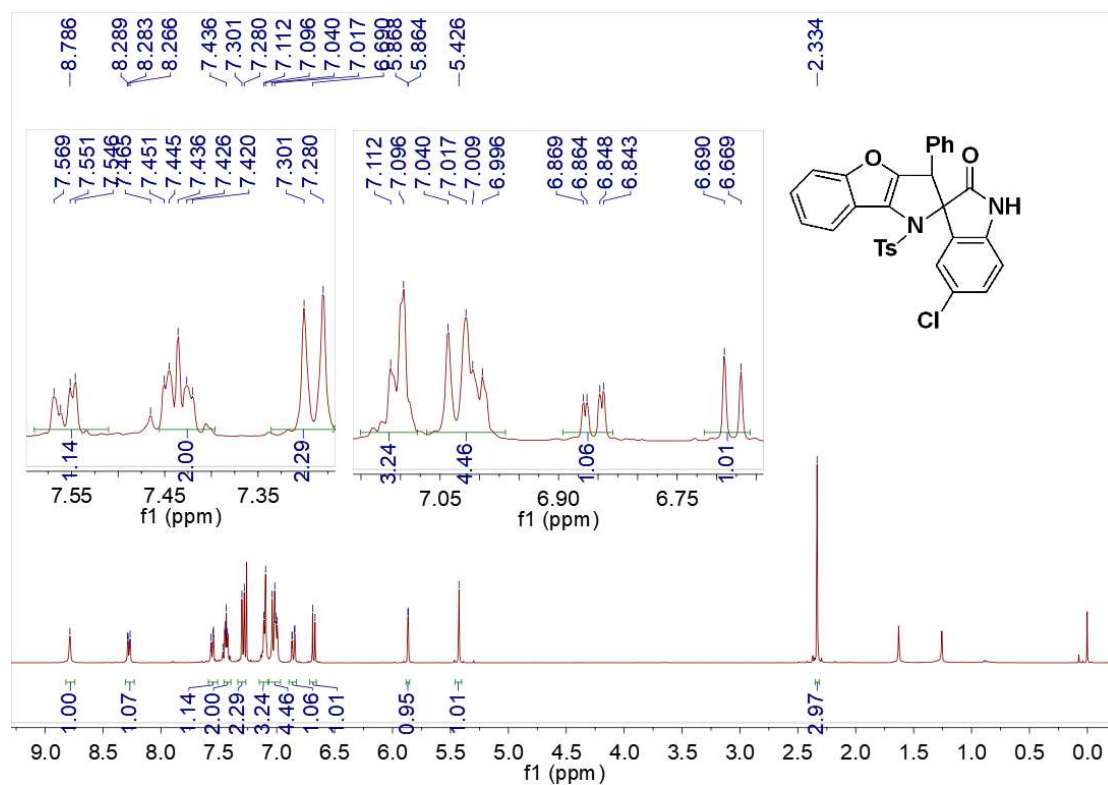
^1H NMR (400 MHz, CDCl_3) of compound **3af**



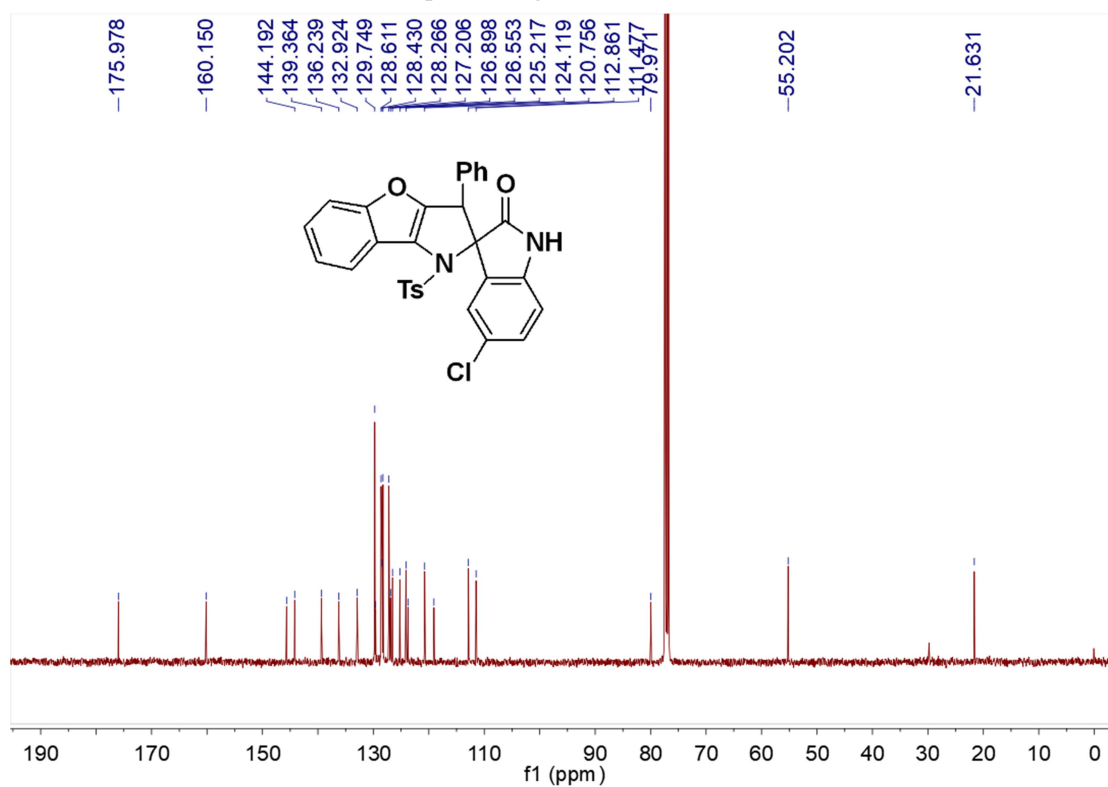
^{13}C NMR (100 MHz, CDCl_3) of compound **3af**



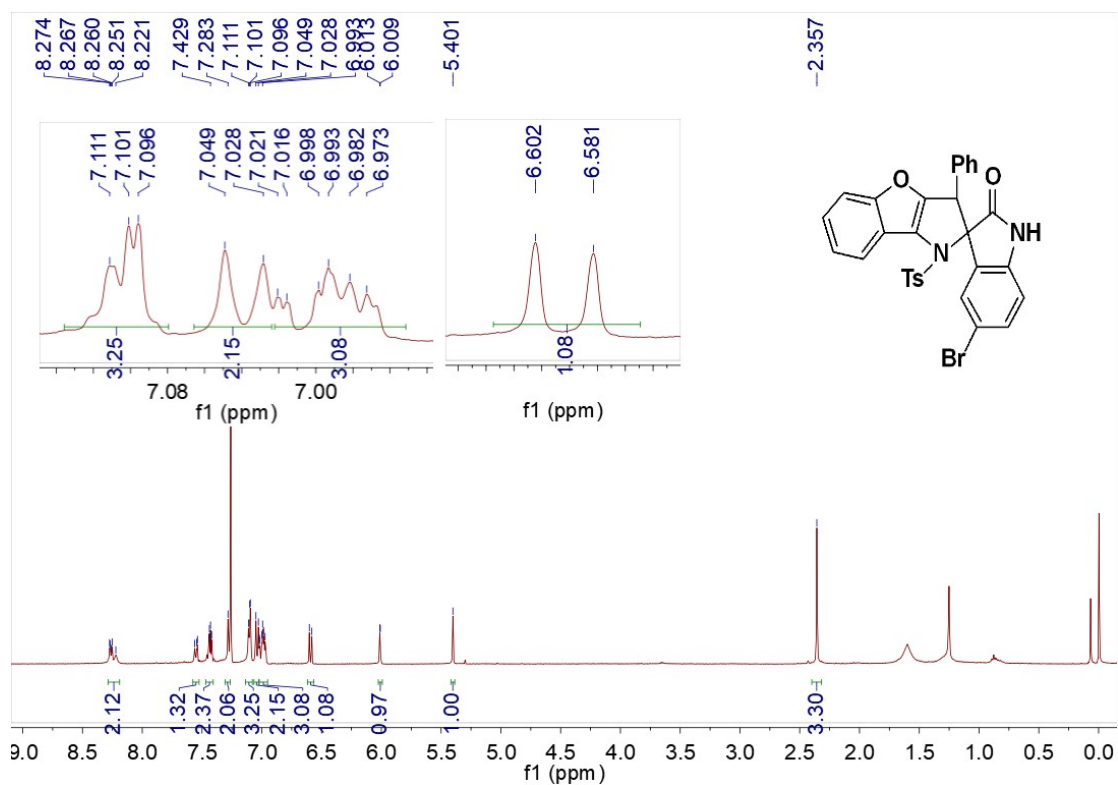
^1H NMR (400 MHz, CDCl_3) of compound **3ag**



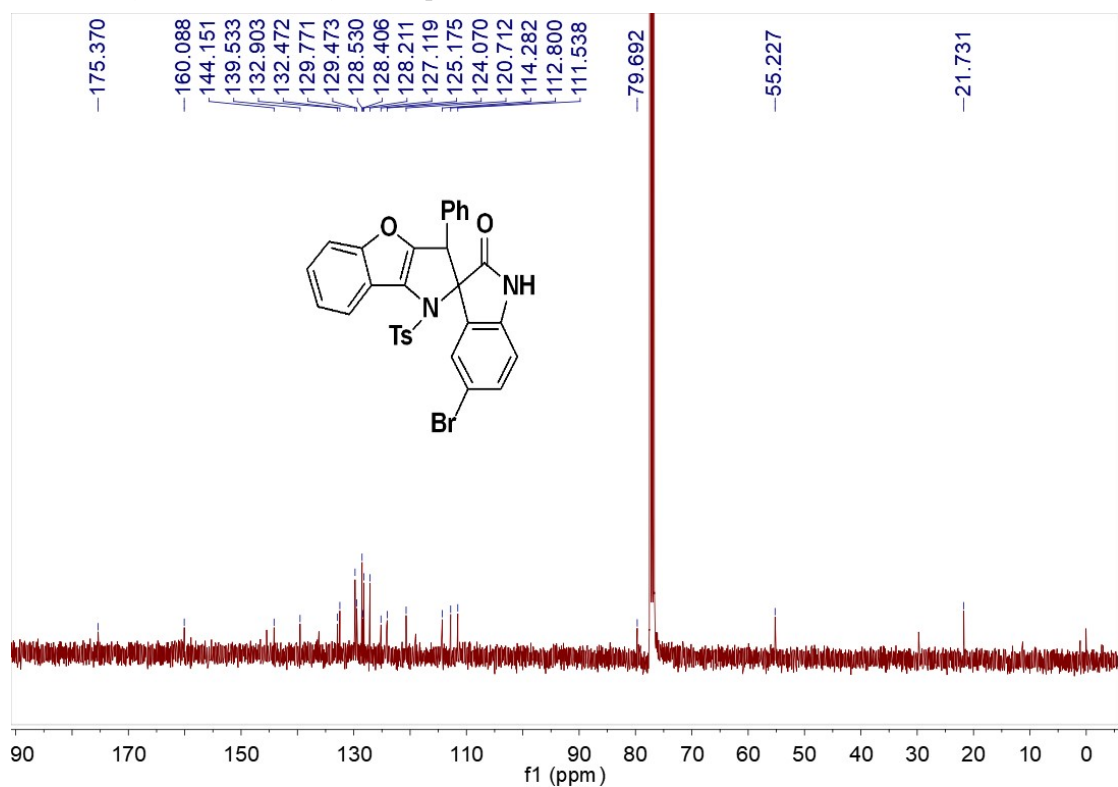
^{13}C NMR (100 MHz, CDCl_3) of compound **3ag**



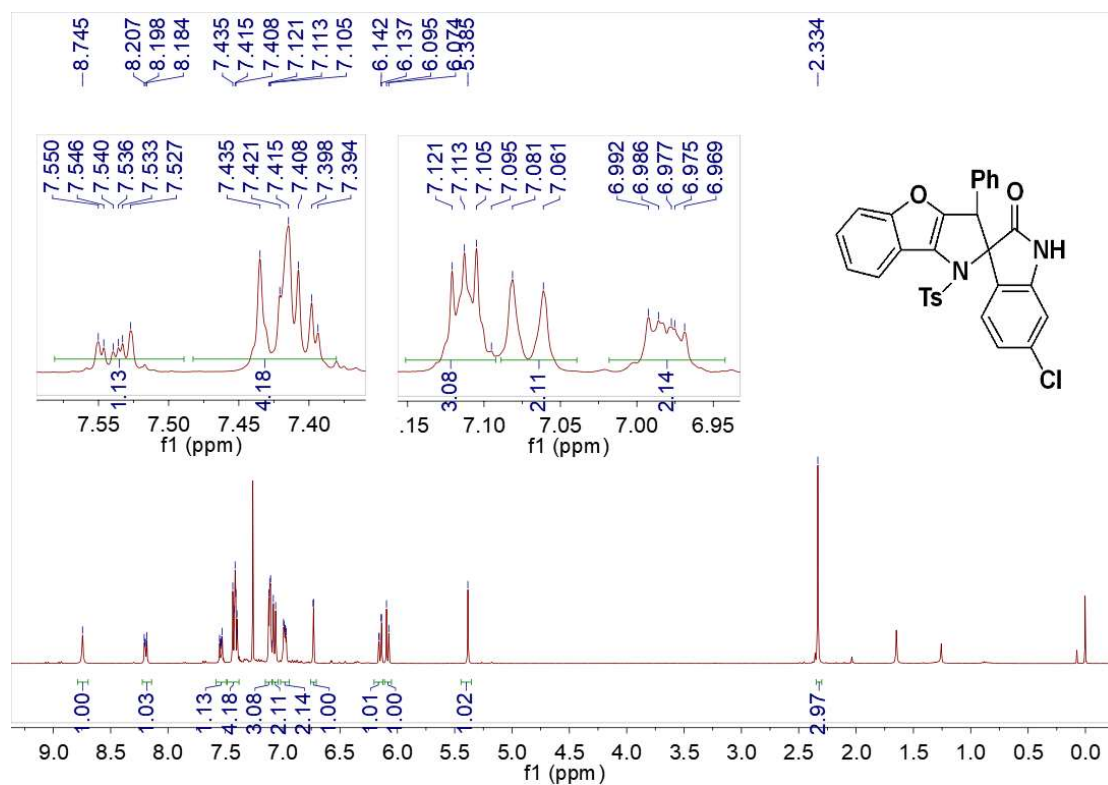
^1H NMR (400 MHz, CDCl_3) of compound **3ah**



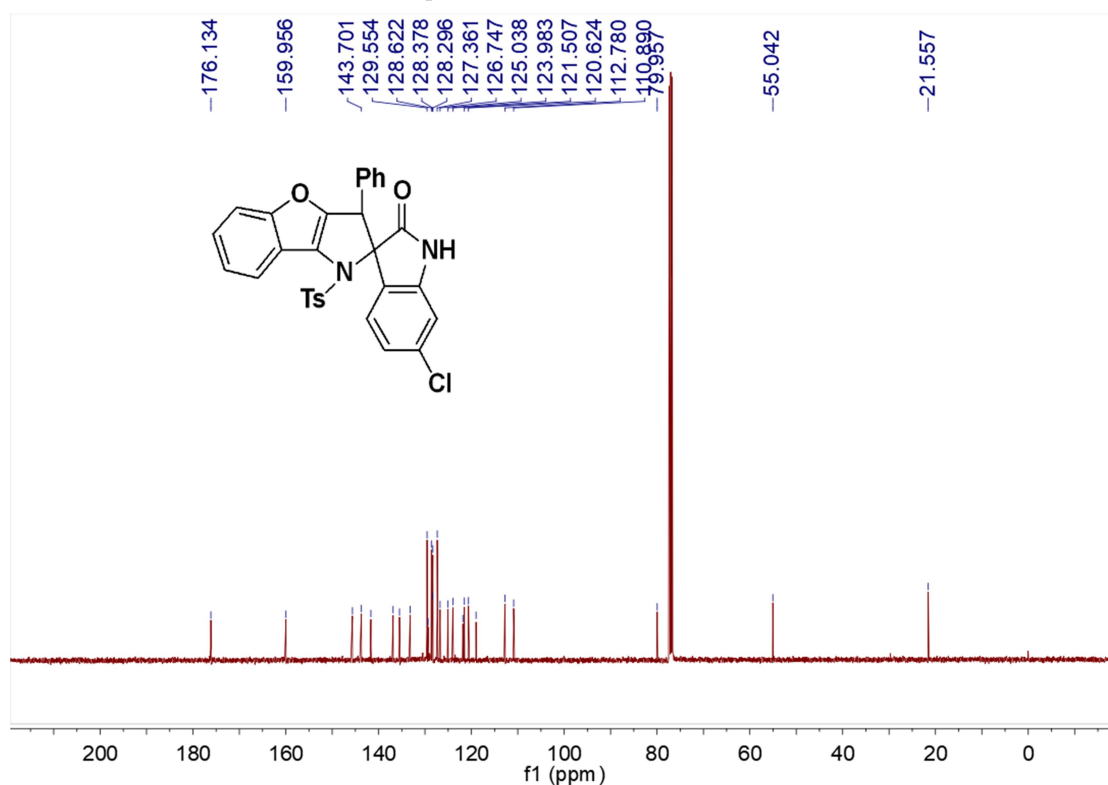
^{13}C NMR (100 MHz, CDCl_3) of compound **3ah**



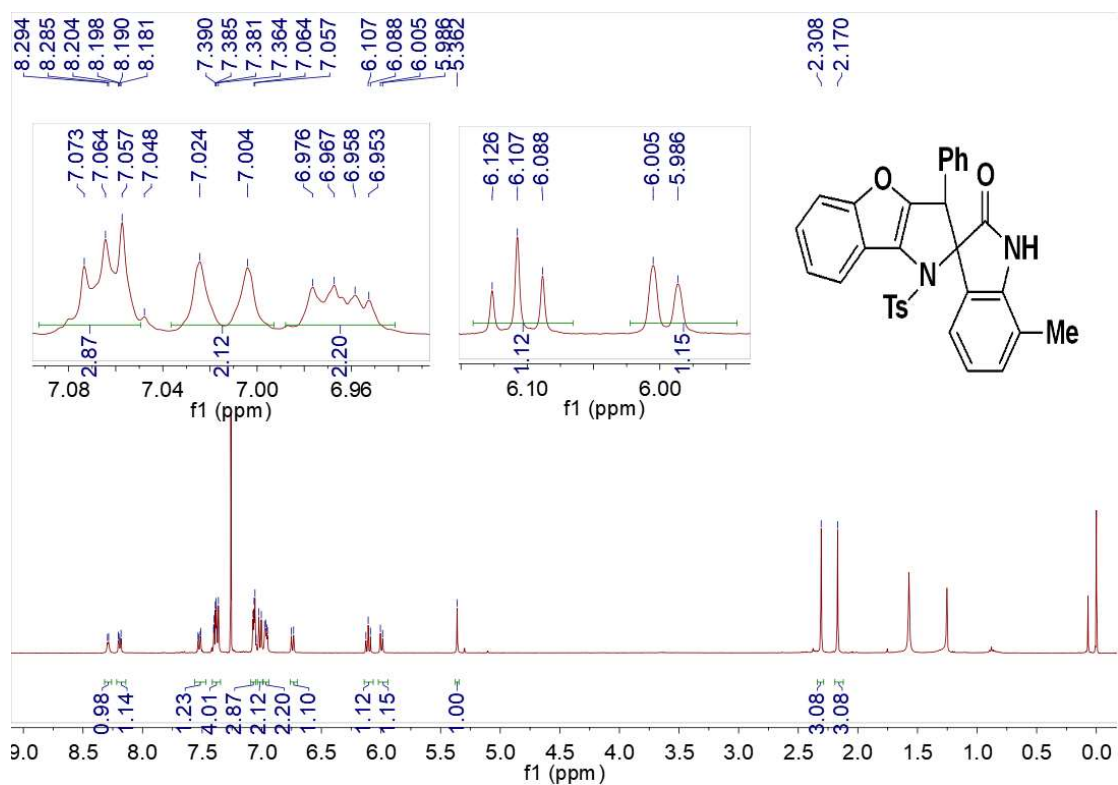
^1H NMR (400 MHz, CDCl_3) of compound **3ai**



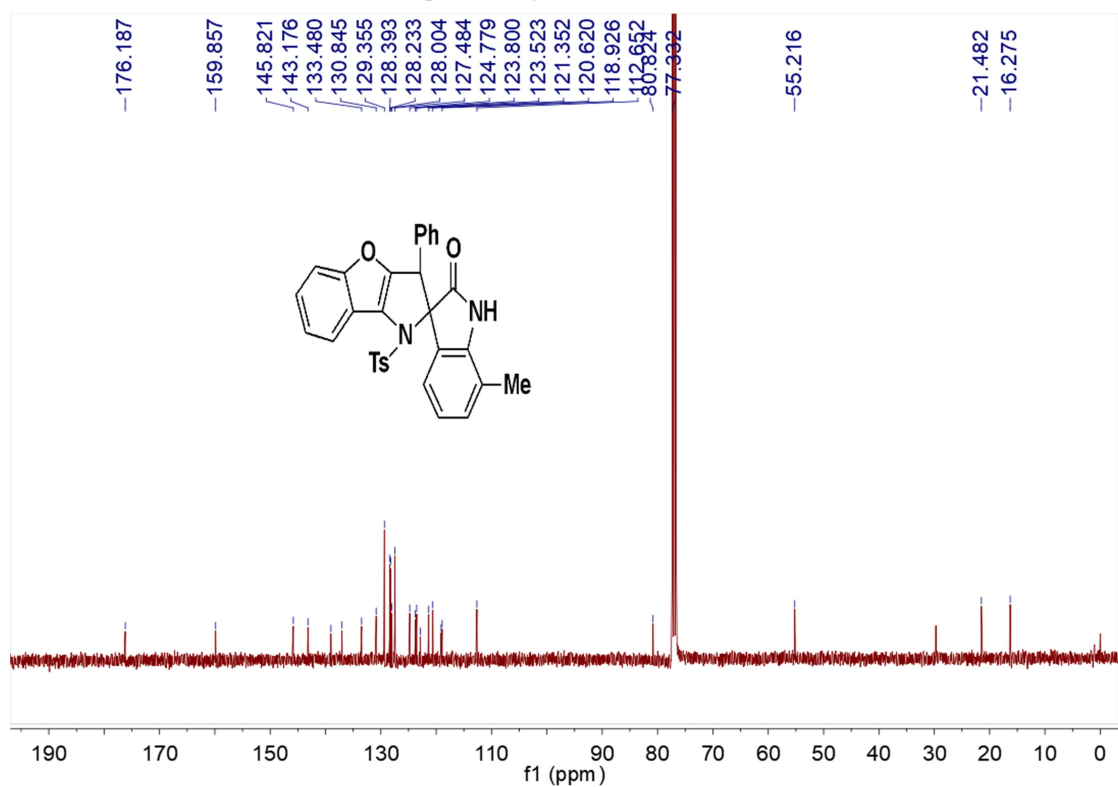
^{13}C NMR (100 MHz, CDCl_3) of compound **3ai**



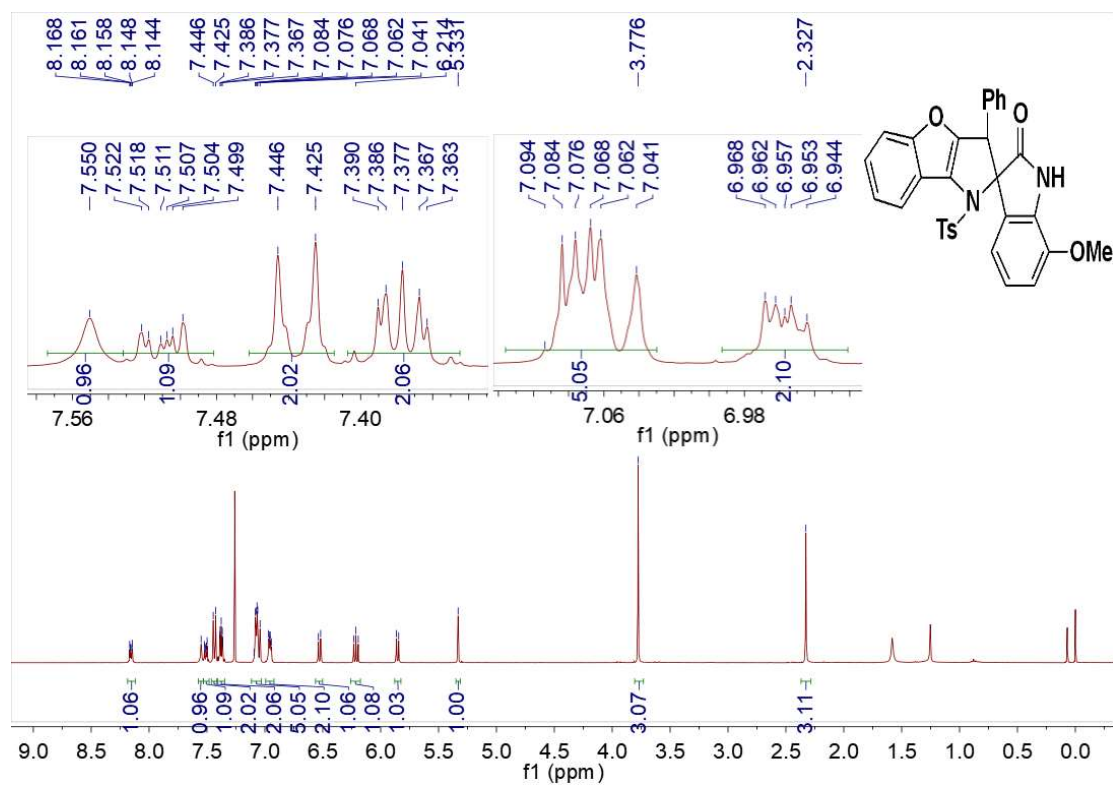
^1H NMR (400 MHz, CDCl_3) of compound **3aj**



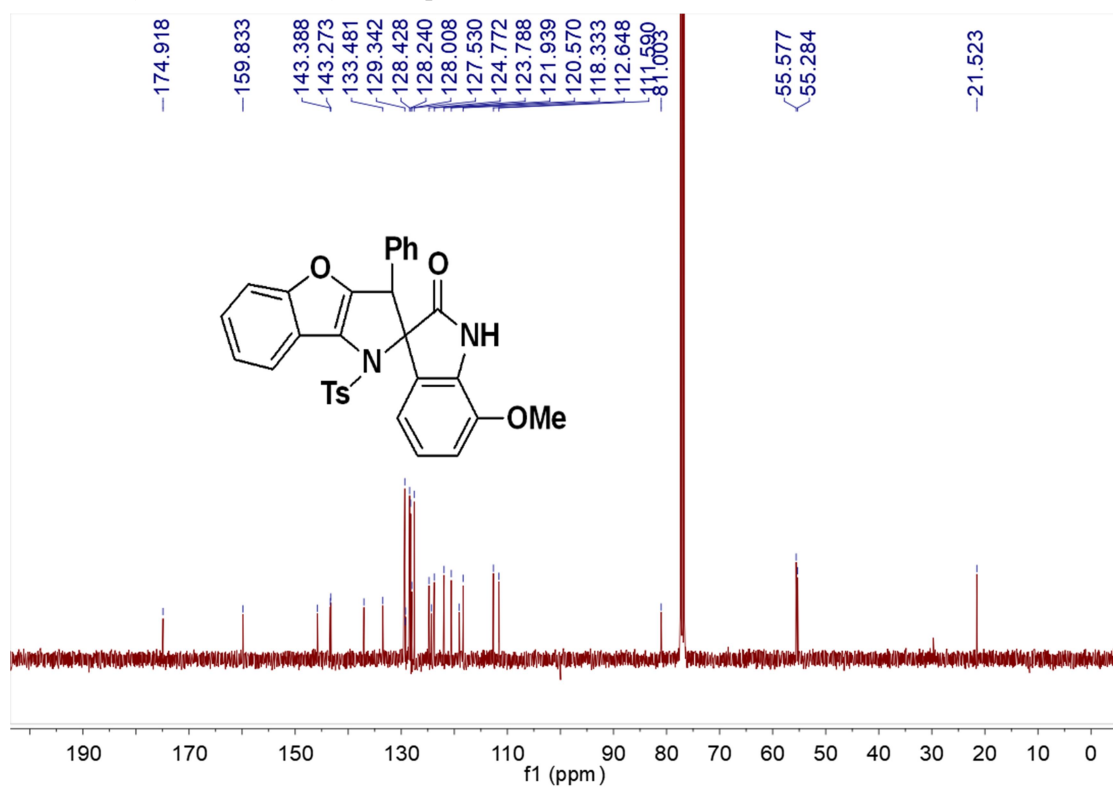
^{13}C NMR (100 MHz, CDCl_3) of compound **3aj**



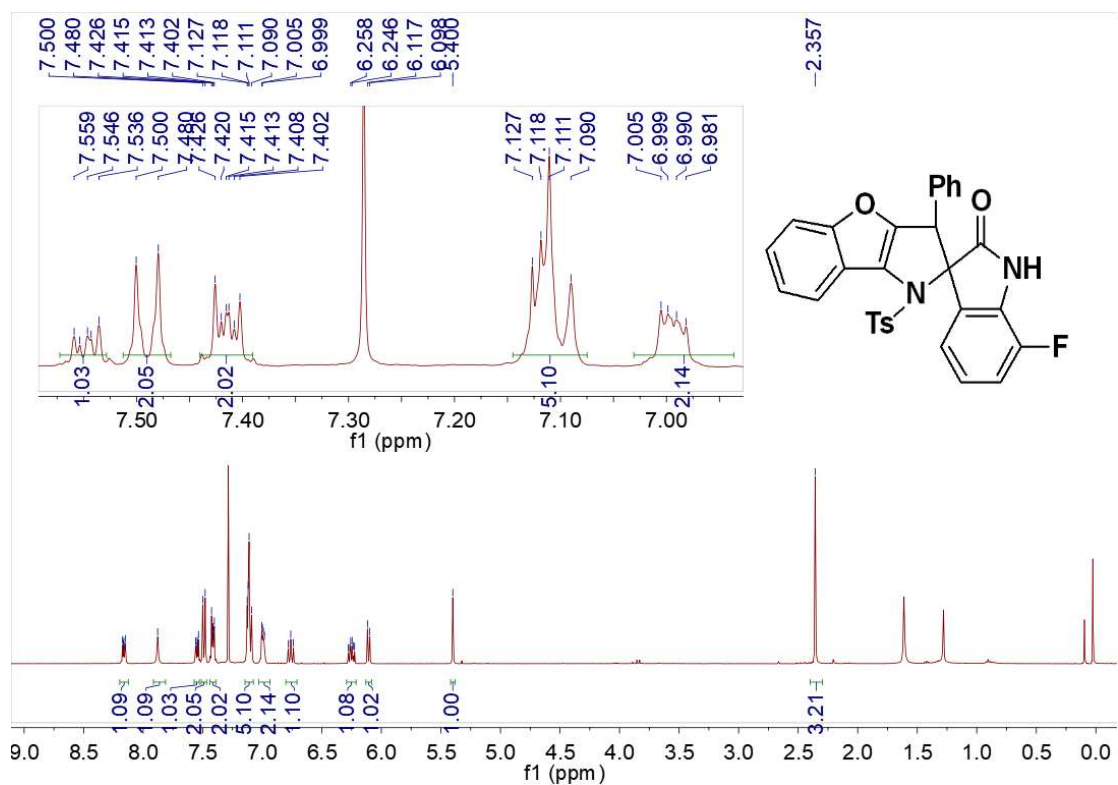
^1H NMR (400 MHz, CDCl_3) of compound **3ak**



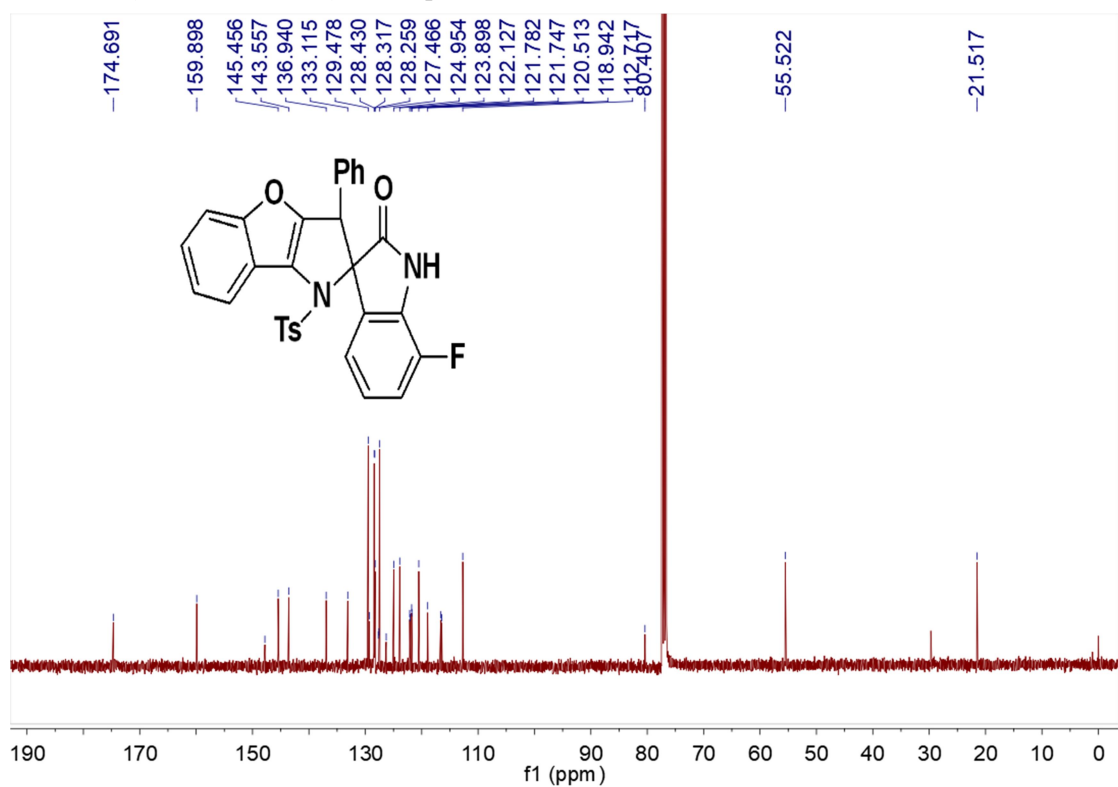
^{13}C NMR (100 MHz, CDCl_3) of compound **3ak**



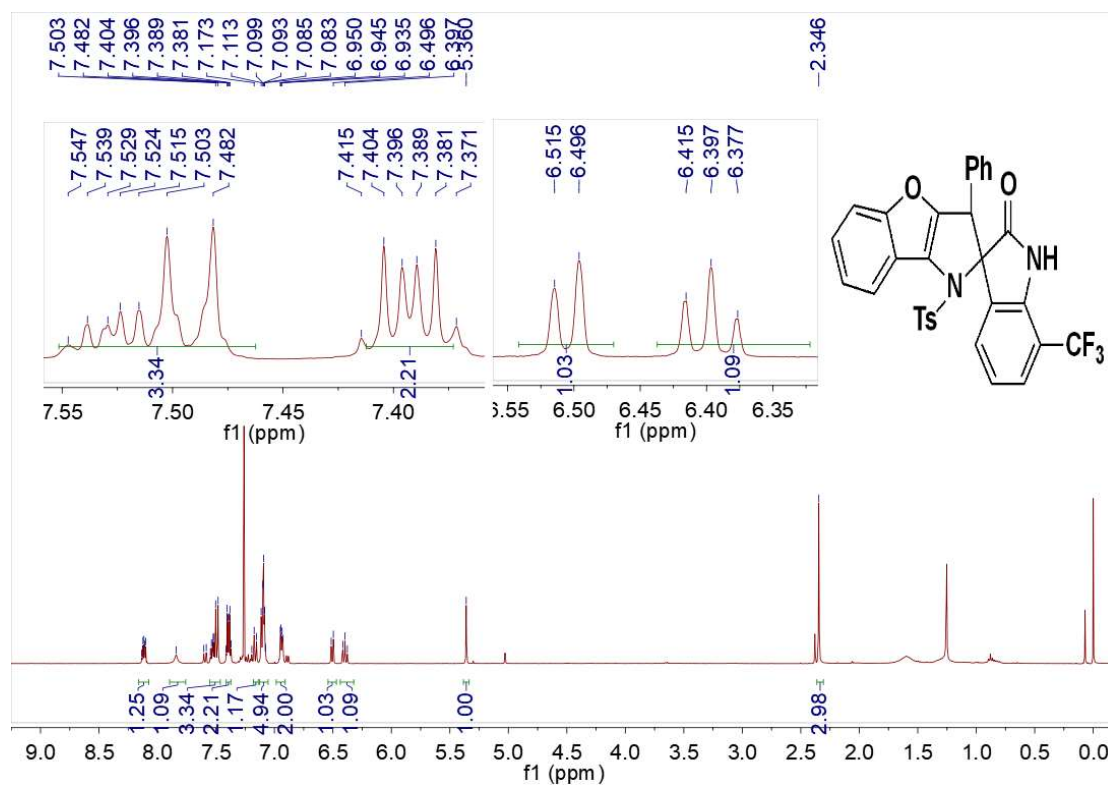
^1H NMR (400 MHz, CDCl_3) of compound **3al**



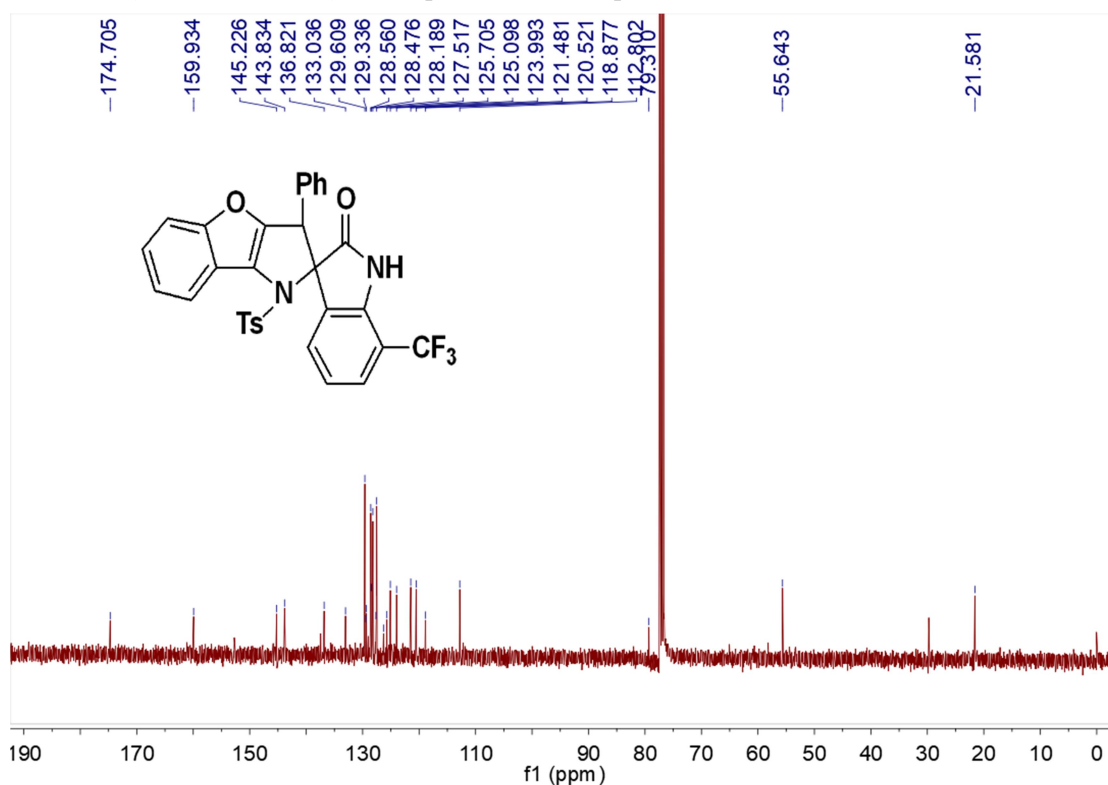
^{13}C NMR (100 MHz, CDCl_3) of compound **3al**



^1H NMR (400 MHz, CDCl_3) of compound **3am**: inseparable diastereomers with 83:17 dr



^{13}C NMR (100 MHz, CDCl_3) of compound **3am**: inseparable diastereomers with 83:17 dr



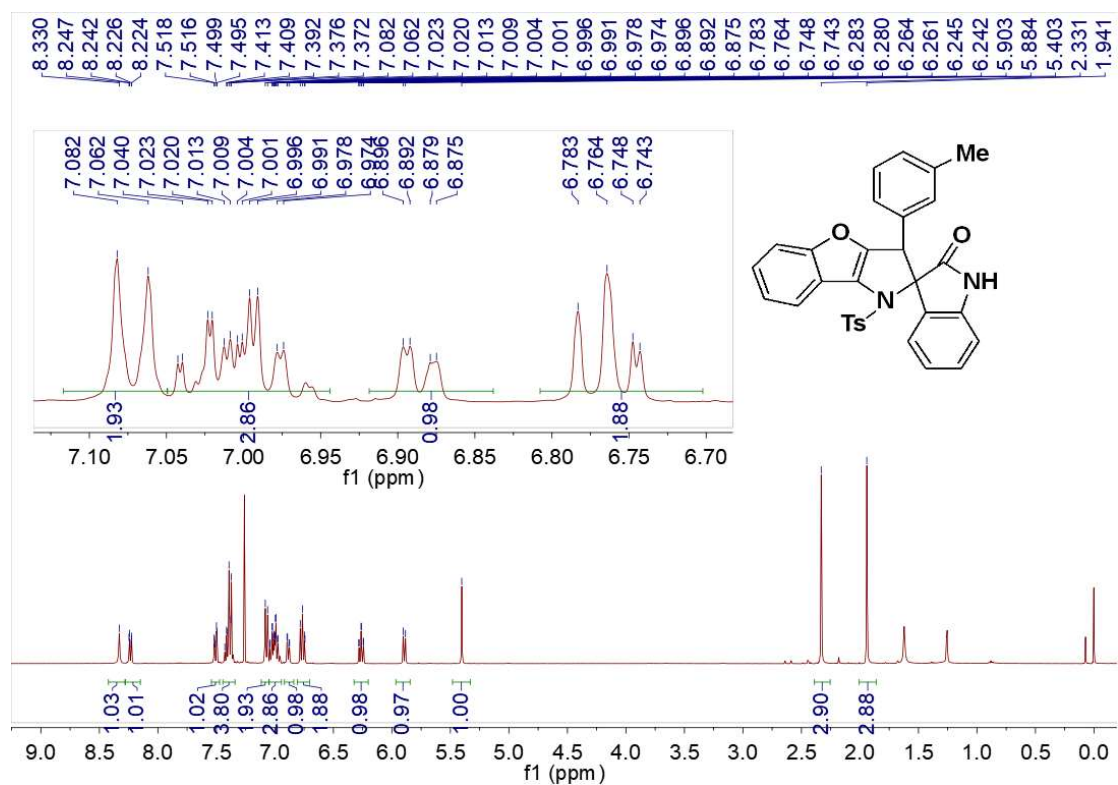
Chemical structure of compound 10: Cc1cc(C)c(C)c2c(c1)c3ccccc3c4c2c5ccccc5oc4n(C6=CC=CC=C6)C6=CC(=CC=C6)S(=O)(=O)C7=CC=CC=C7

¹H NMR spectrum (CDCl₃):

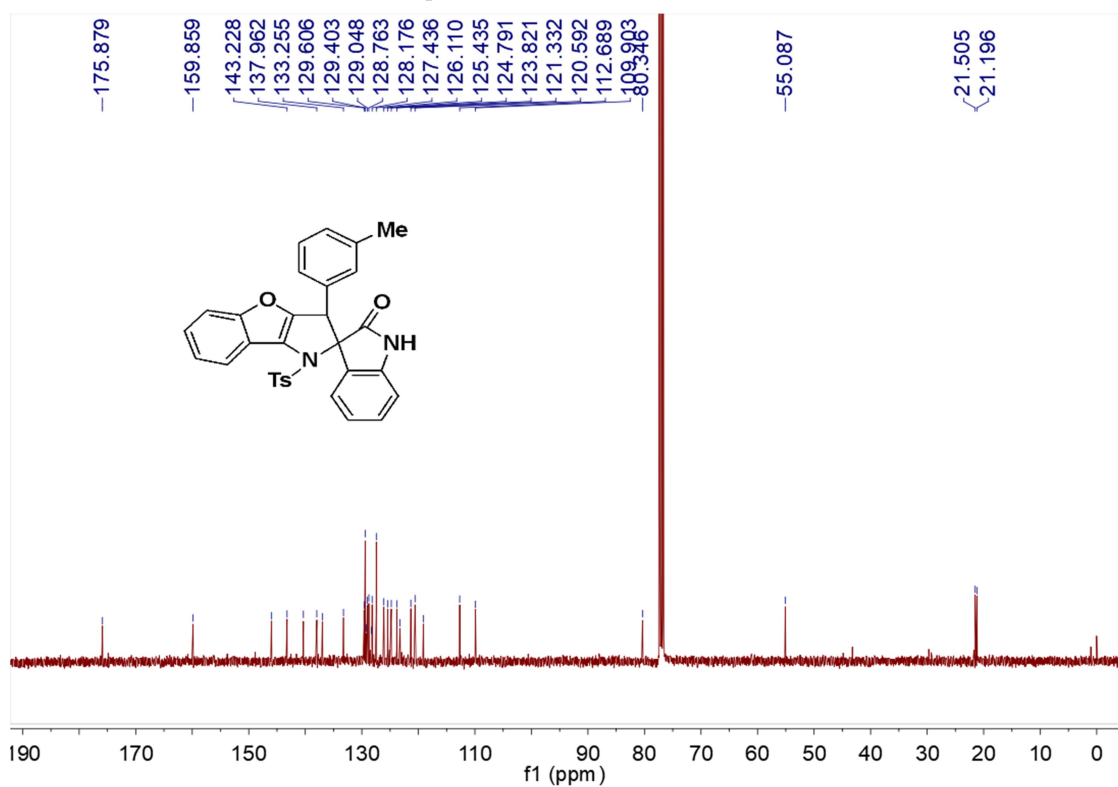
- Chemical shift range:** 0.0 – 8.6 ppm.
- Integration values:** 1.18, 1.17, 1.05, 2.13, 1.96, 0.96, 3.00, 3.35, 0.96, 1.00, 3.27, 2.94, 3.22.
- Peak assignments (ppm):**
 - 8.553, 8.269, 8.264, 8.253, 8.246
 - 7.407, 7.302, 7.281, 7.052, 7.047, 6.983, 6.513
 - 5.640, 5.384
 - 2.296, 2.146, 1.575
 - 7.549, 7.531, 7.526, 7.424, 7.419, 7.414, 7.407, 7.401, 7.394, 7.389, 7.281
 - 7.153, 7.134, 7.116, 7.075, 7.065, 7.060, 7.052, 7.047, 7.040, 6.989, 6.983, 6.971, 6.963

Chemical structure of compound 10 is shown above the spectrum. The structure is a spirocyclic compound consisting of a benzofuran ring system spiro-fused to a 2-methyl-4-(2-methyl-4-methylphenyl)-2-oxo-1,2,3,4-tetrahydroquinolin-3-ylidene system. The peaks are labeled with their chemical shifts in ppm: 176.415, 159.910, 145.944, 142.928, 136.891, 133.414, 131.397, 130.391, 129.189, 128.371, 128.097, 127.932, 127.541, 124.789, 124.495, 123.833, 120.699, 112.649, 80.685, 55.044, 21.412, 20.175, and 16.259.

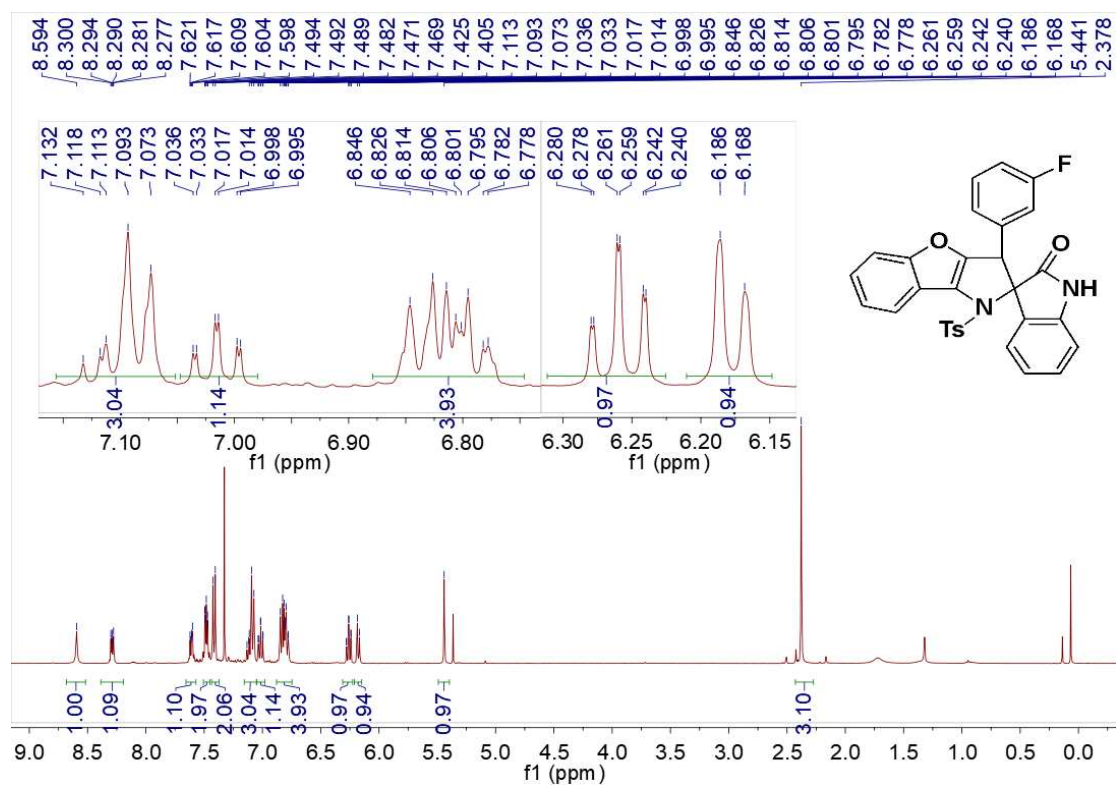
^1H NMR (400 MHz, CDCl_3) of compound **3ba**



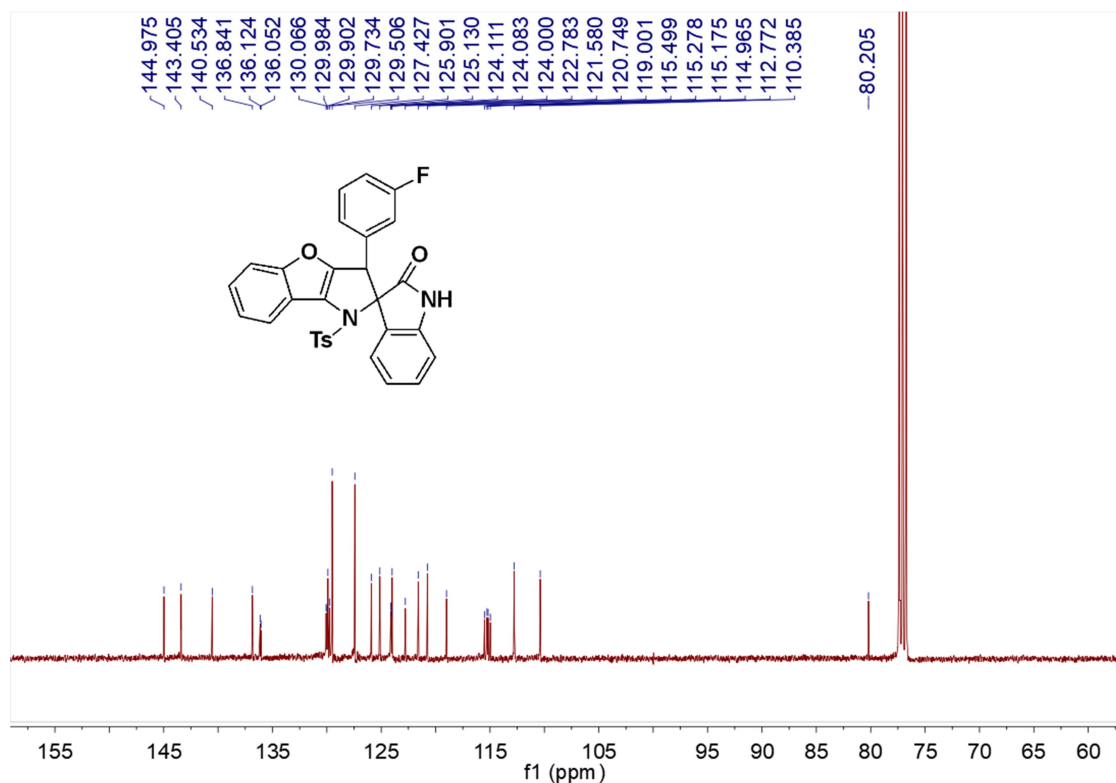
^{13}C NMR (100 MHz, CDCl_3) of compound **3ba**



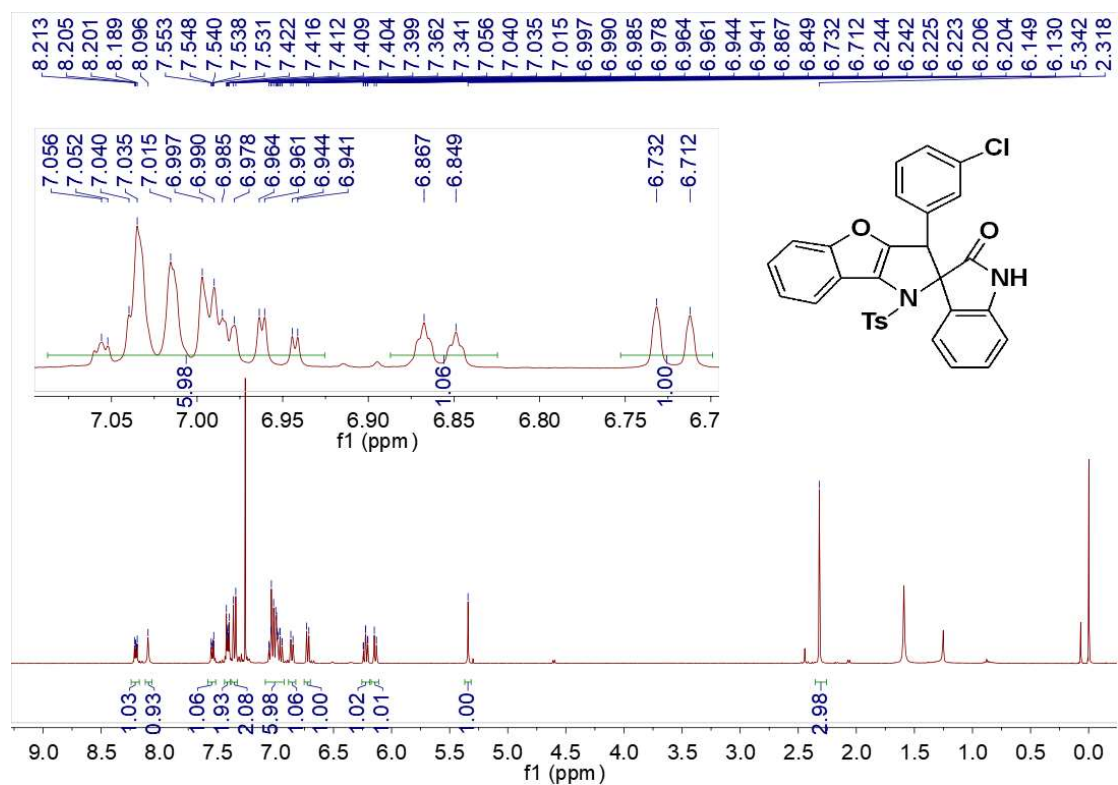
^1H NMR (400 MHz, CDCl_3) of compound **3ca**



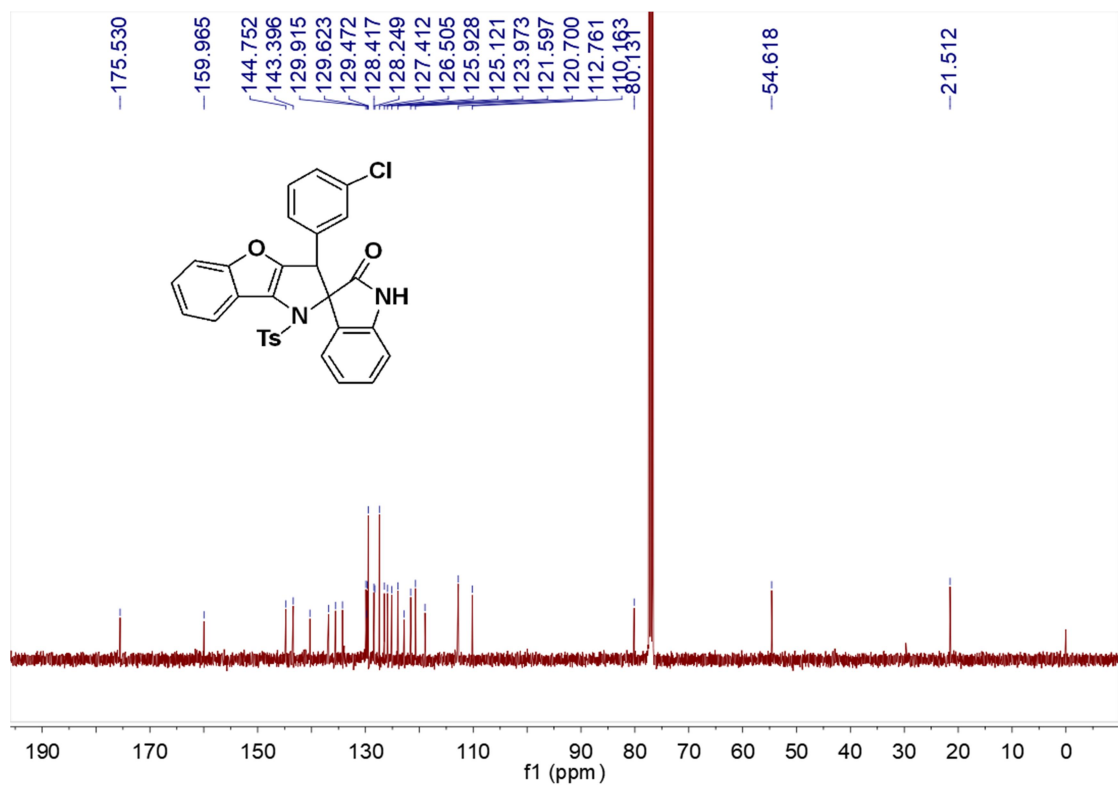
^{13}C NMR (100 MHz, CDCl_3) of compound **3ca**



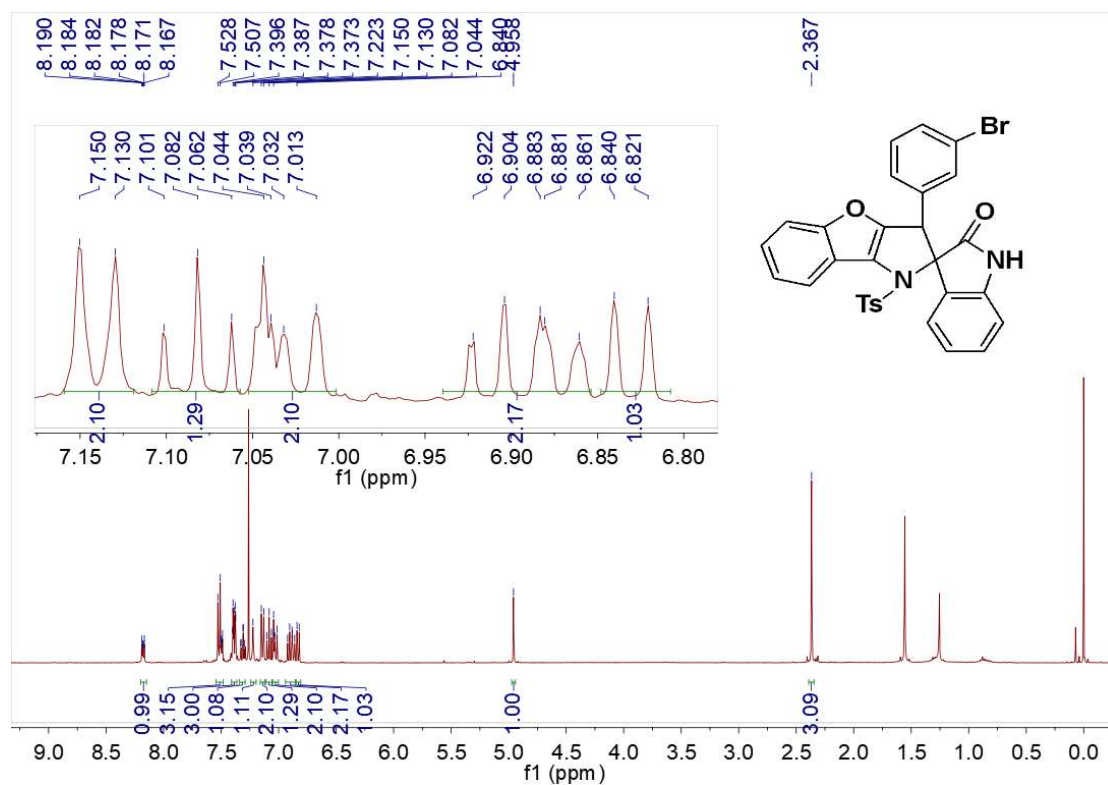
^1H NMR (400 MHz, CDCl_3) of compound **3da**: inseparable diastereomers with 91:9 dr



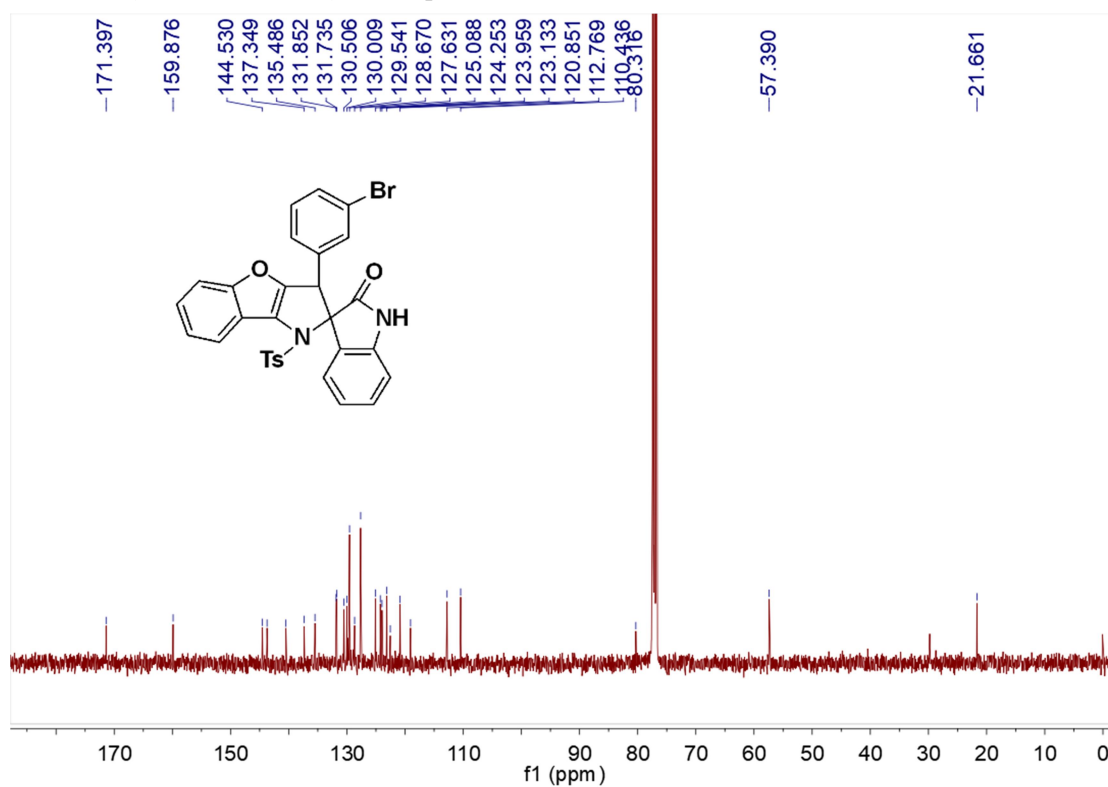
^{13}C NMR (100 MHz, CDCl_3) of compound **3da**: inseparable diastereomers with 91:9 dr



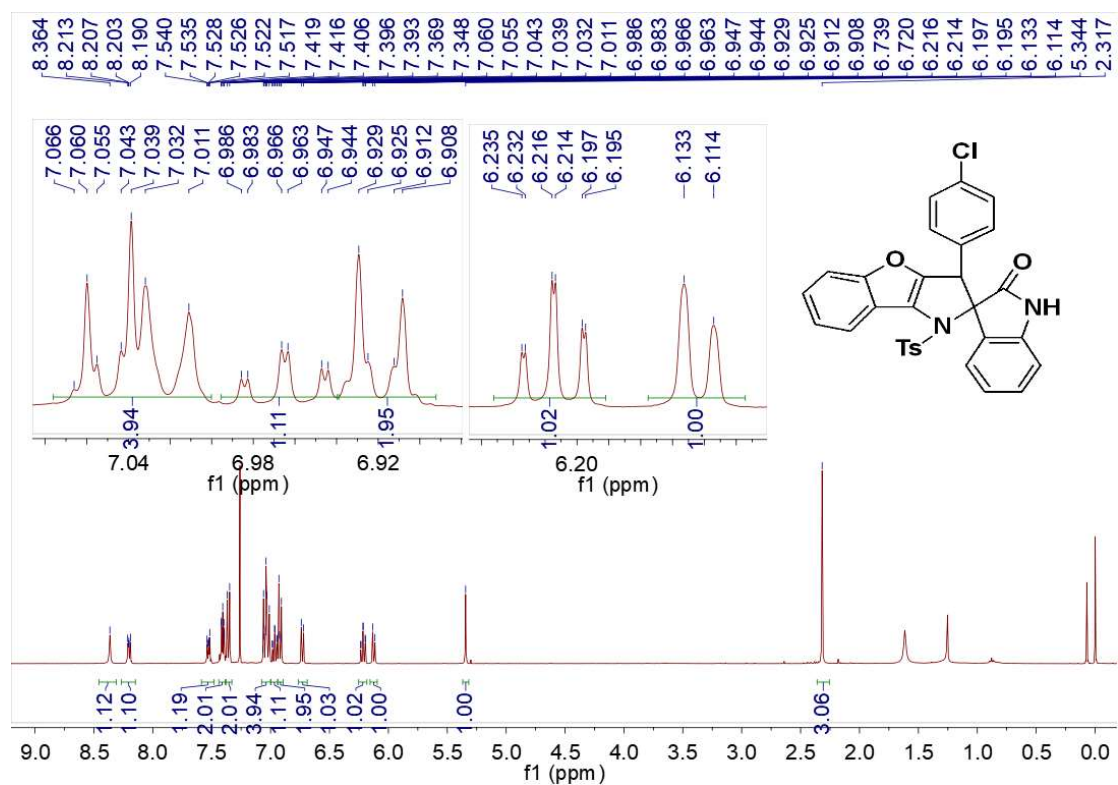
^1H NMR (400 MHz, CDCl_3) of compound **3ea**



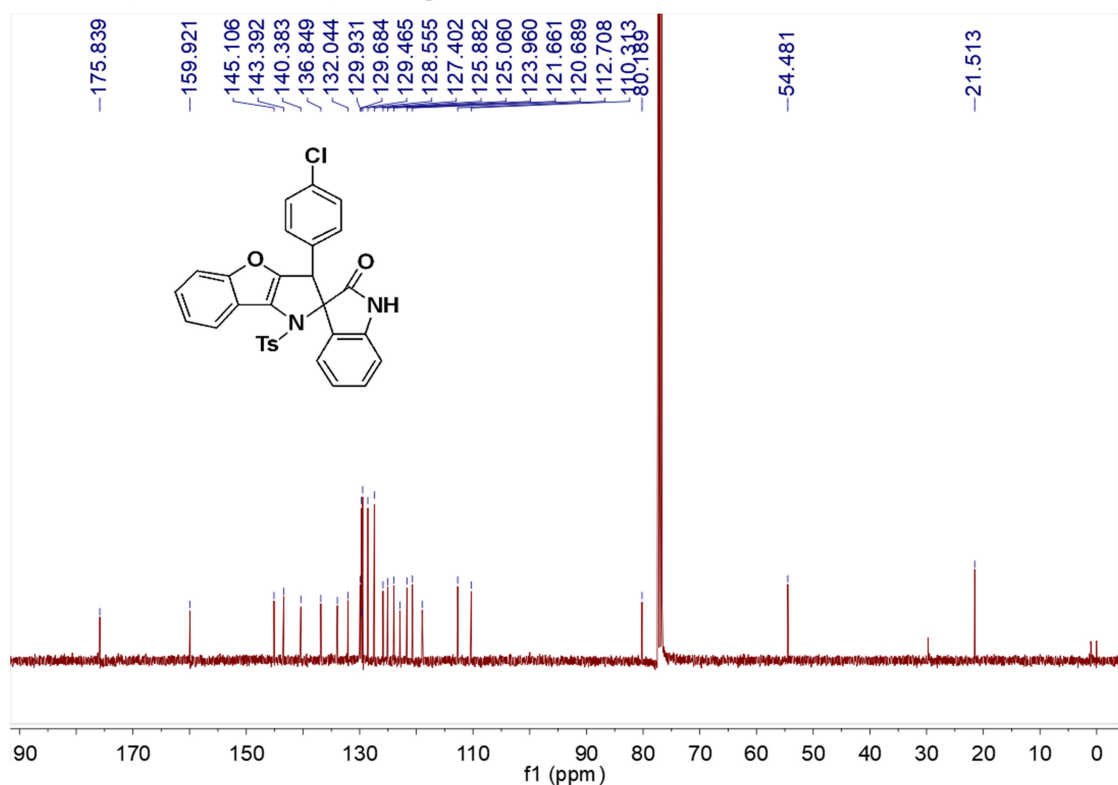
^{13}C NMR (100 MHz, CDCl_3) of compound **3ea**



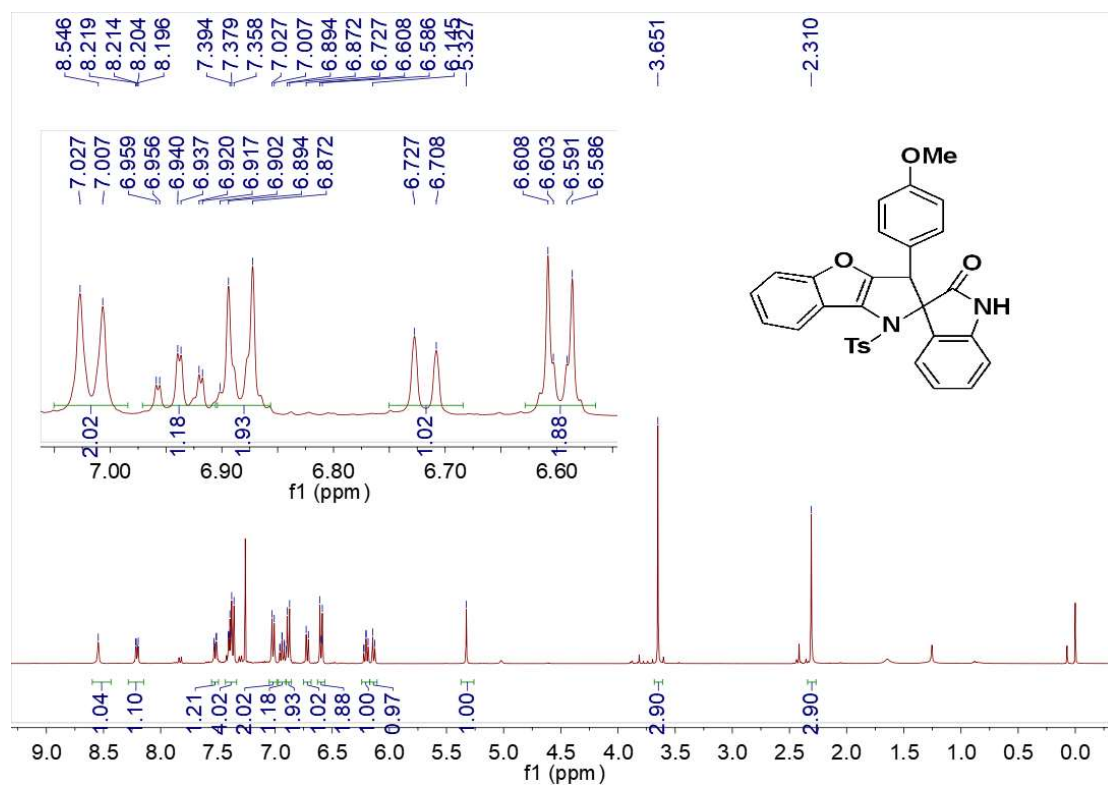
^1H NMR (400 MHz, CDCl_3) of compound **3fa**



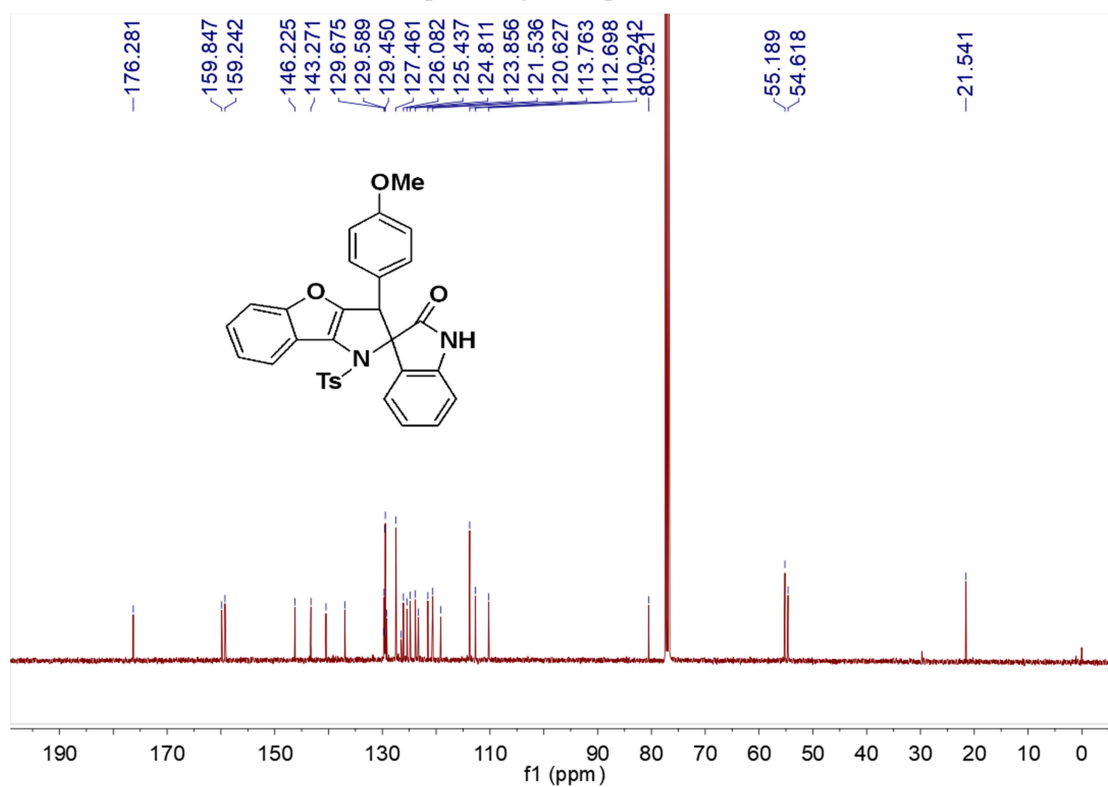
^{13}C NMR (100 MHz, CDCl_3) of compound **3fa**



^1H NMR (400 MHz, CDCl_3) of compound **3ga**: inseparable diastereomers with 91:9 dr

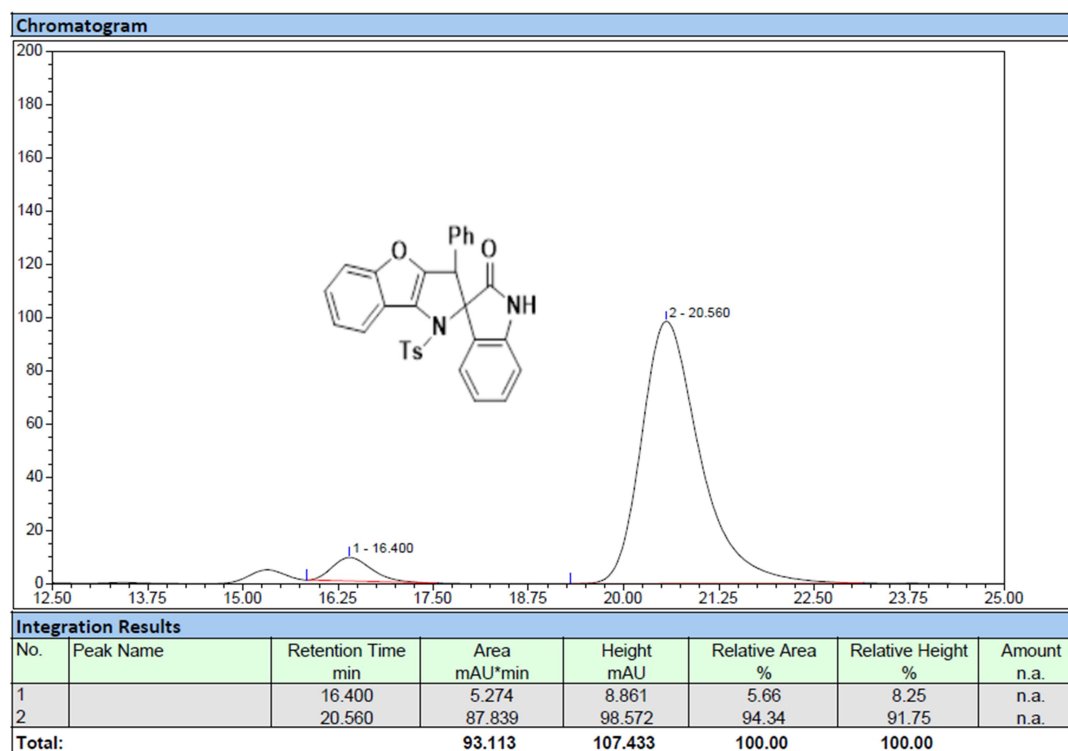
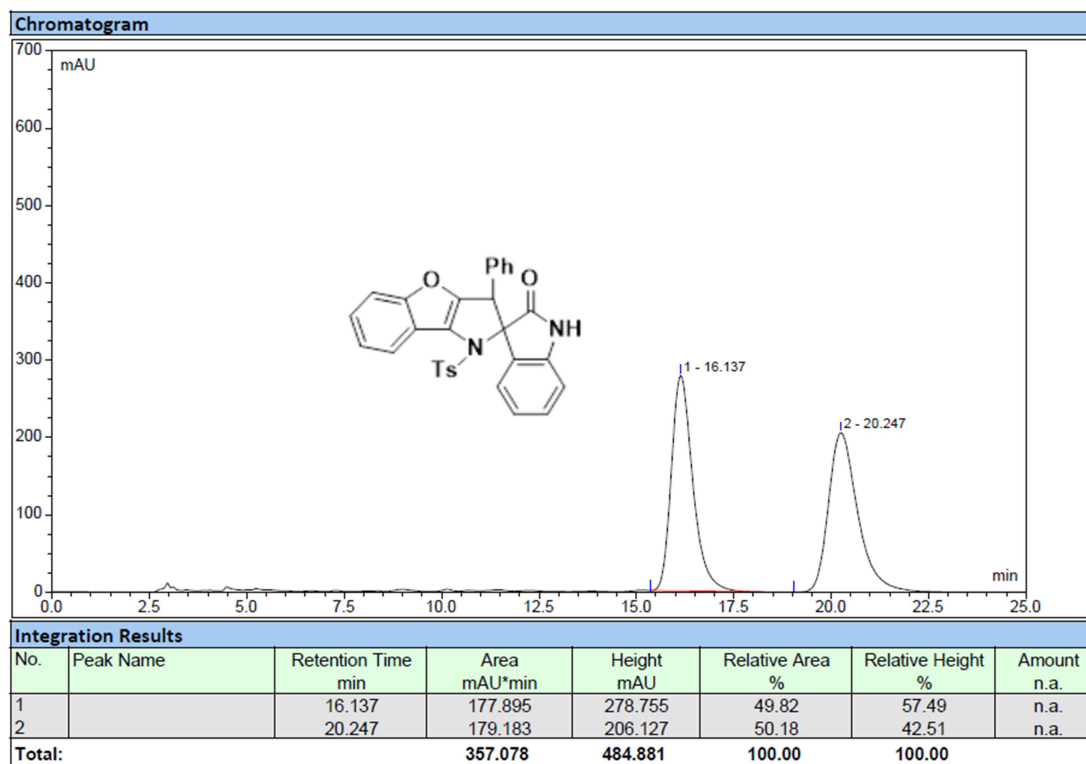


^{13}C NMR (100 MHz, CDCl_3) of compound **3ga**: inseparable diastereomers with 91:9 dr

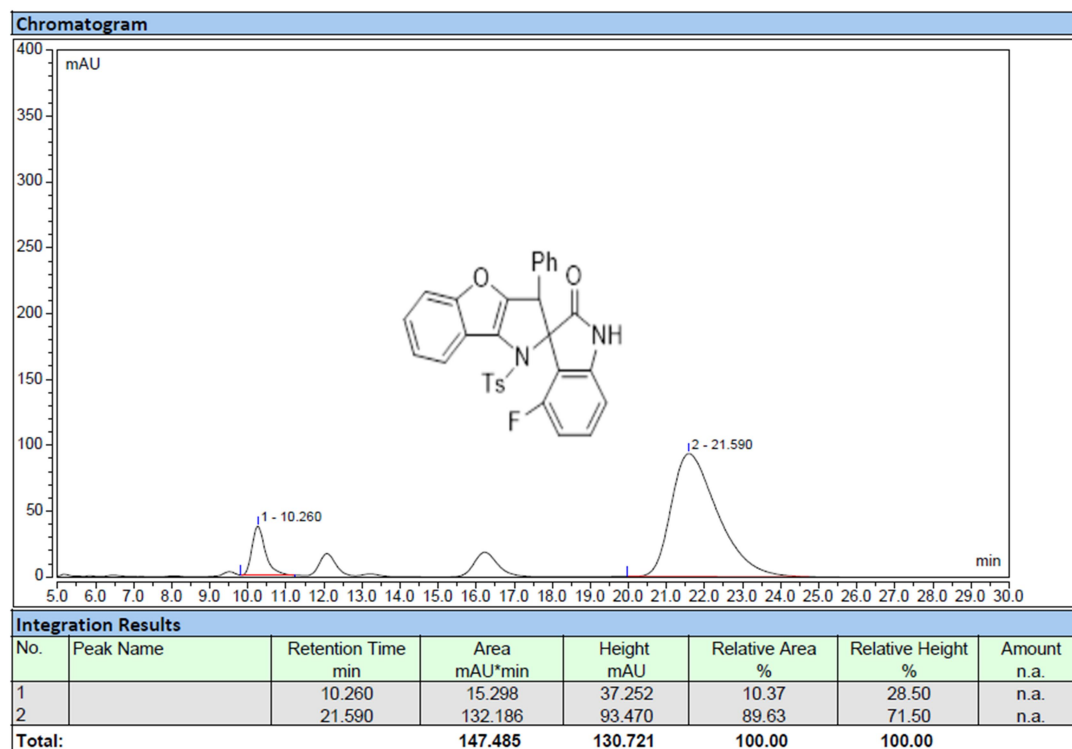
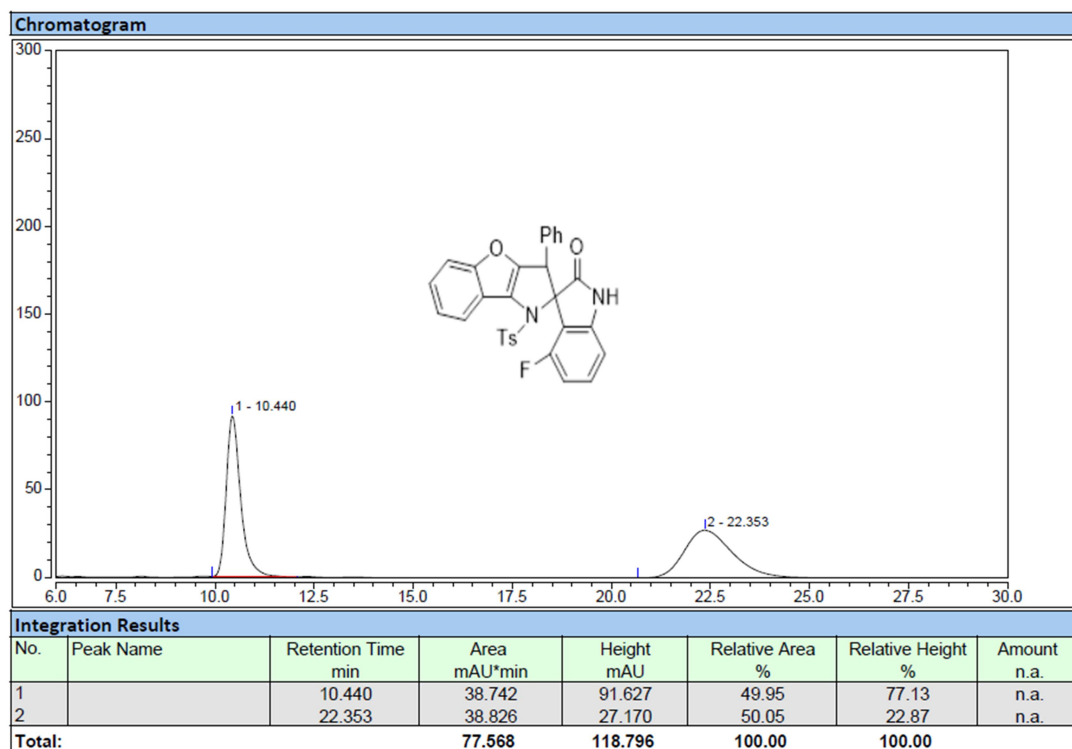


3. HPLC spectra of products 3

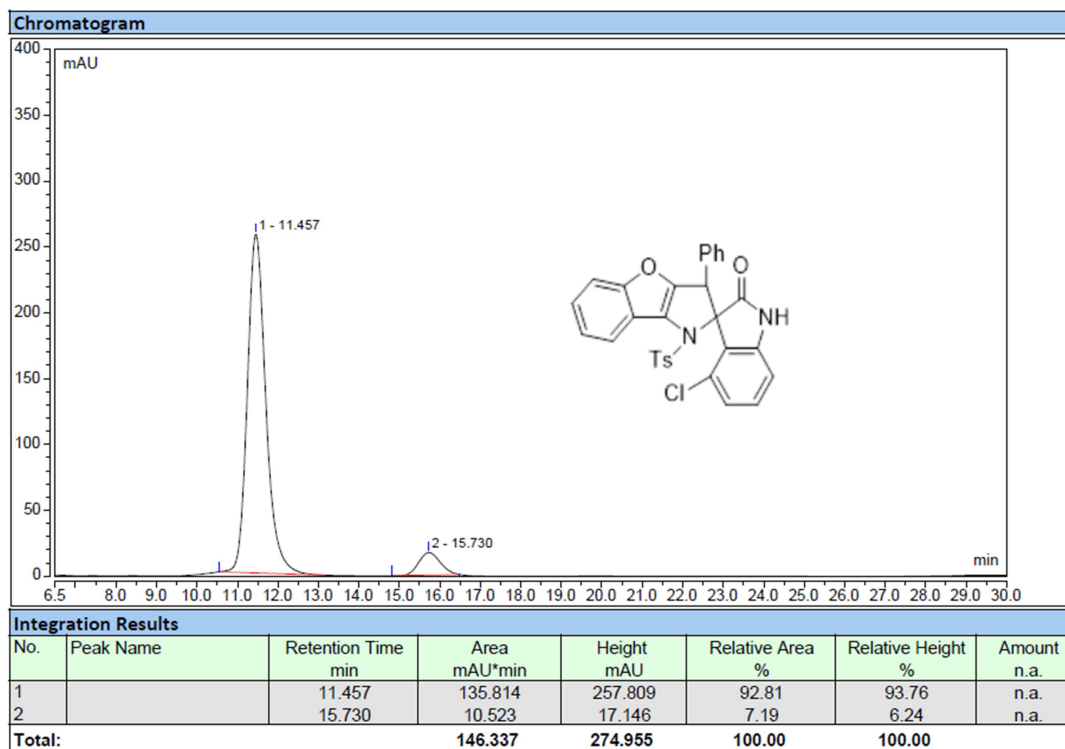
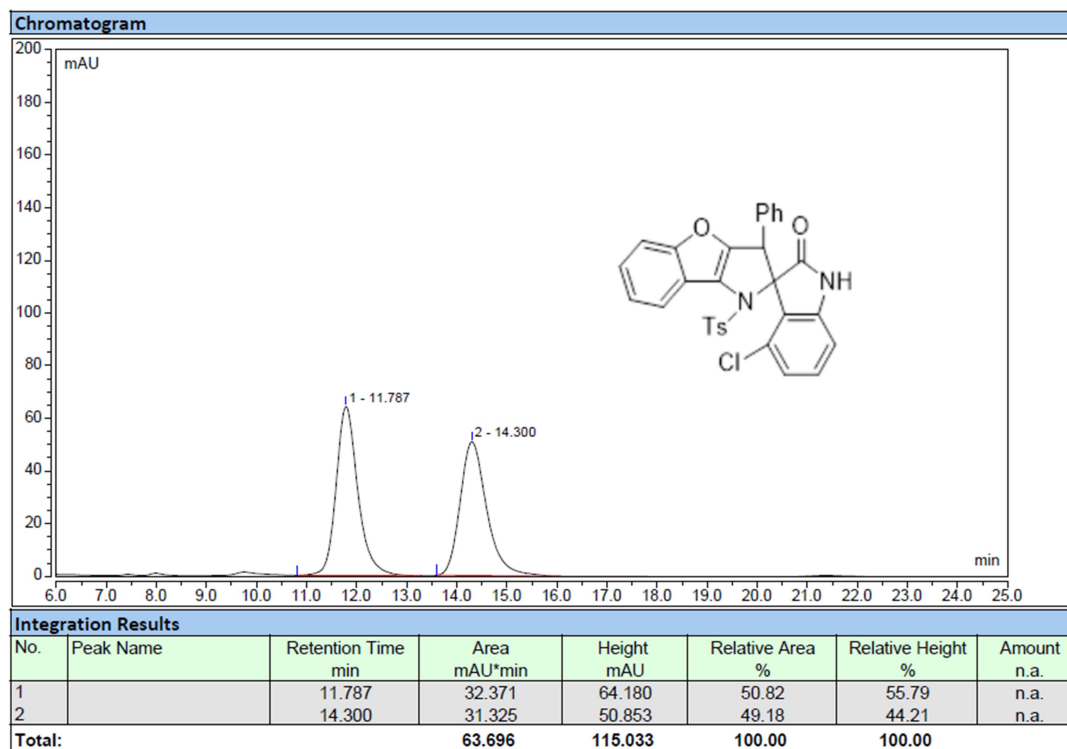
3aa



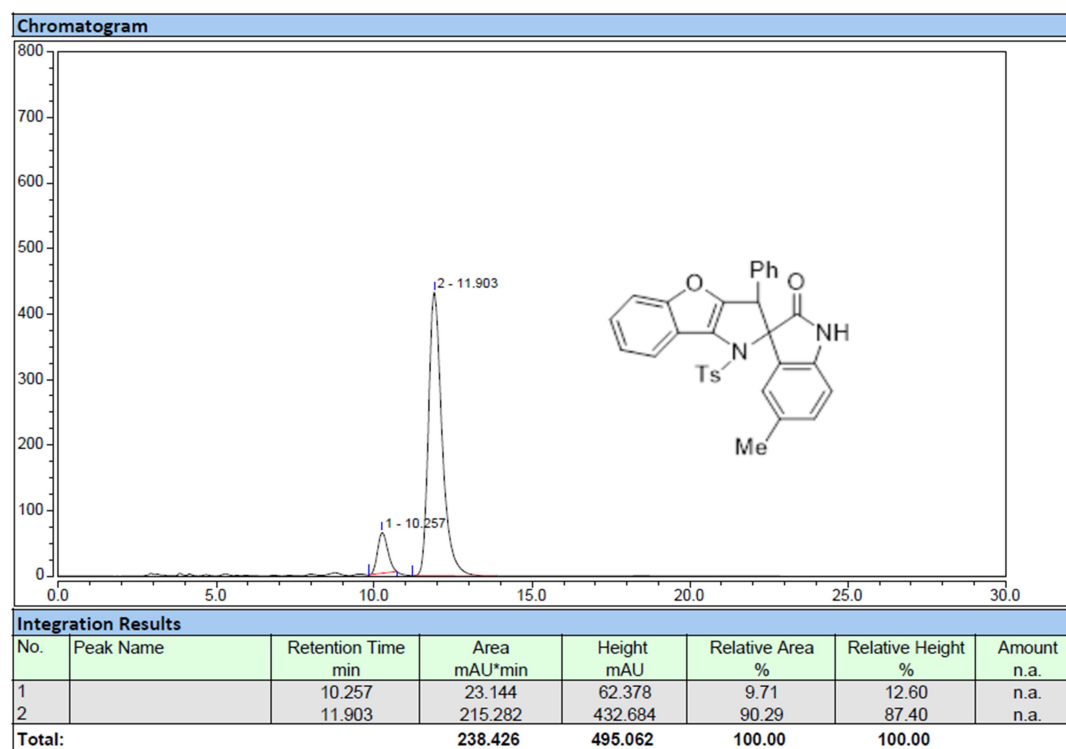
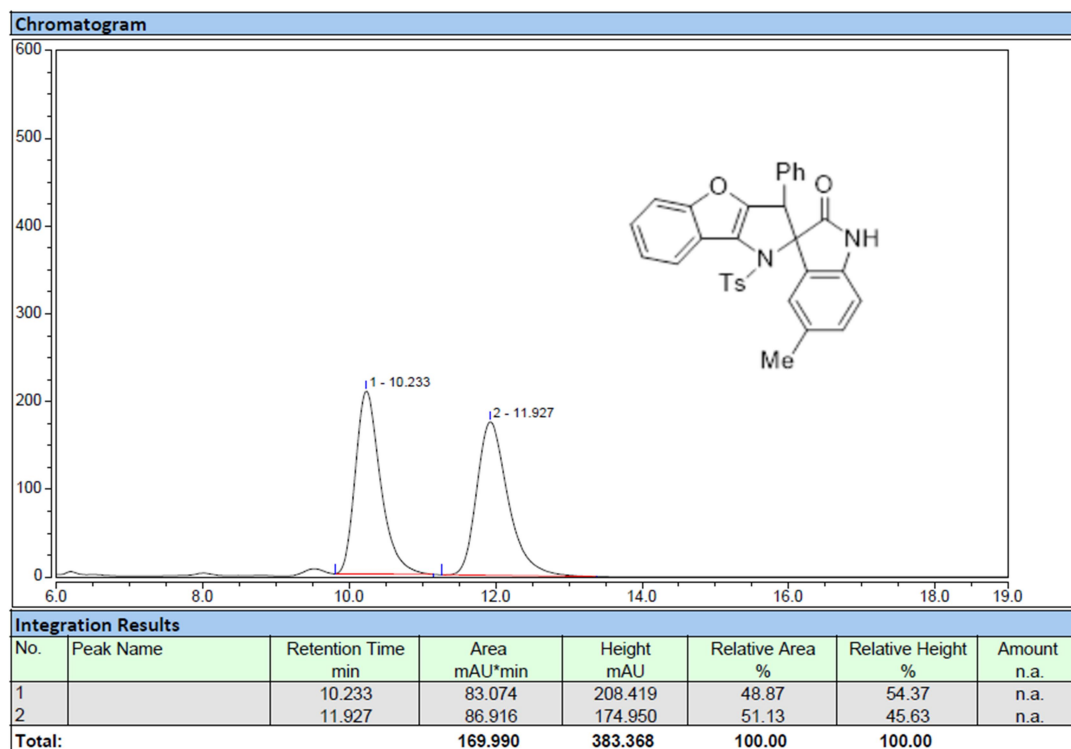
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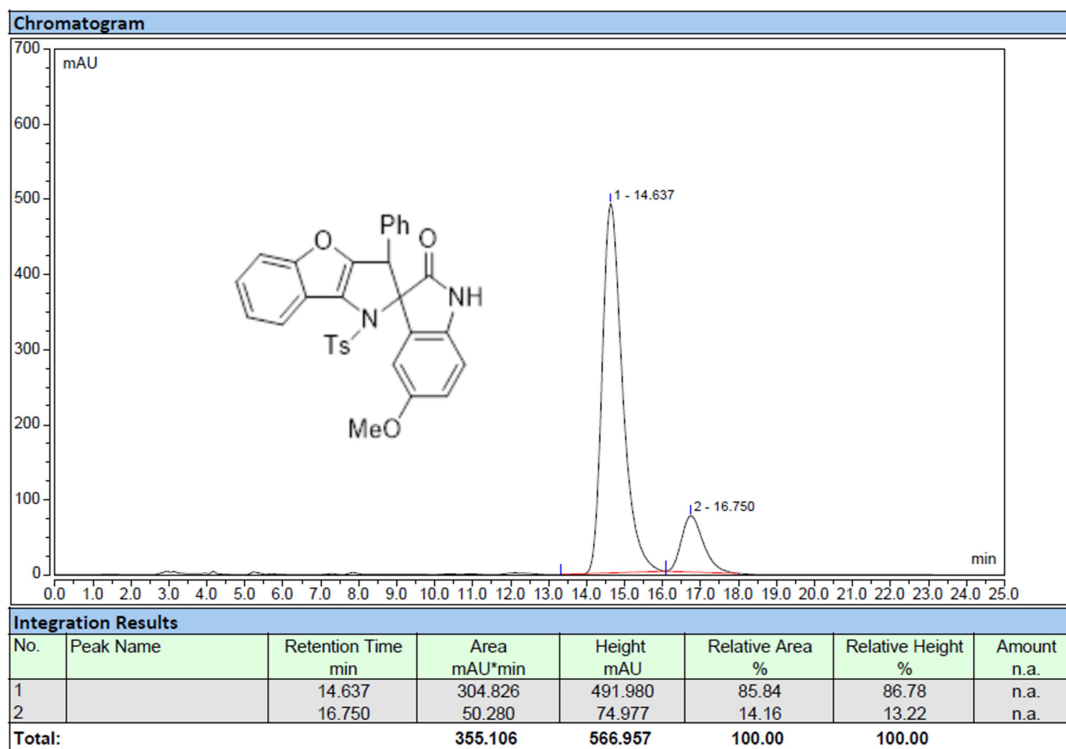
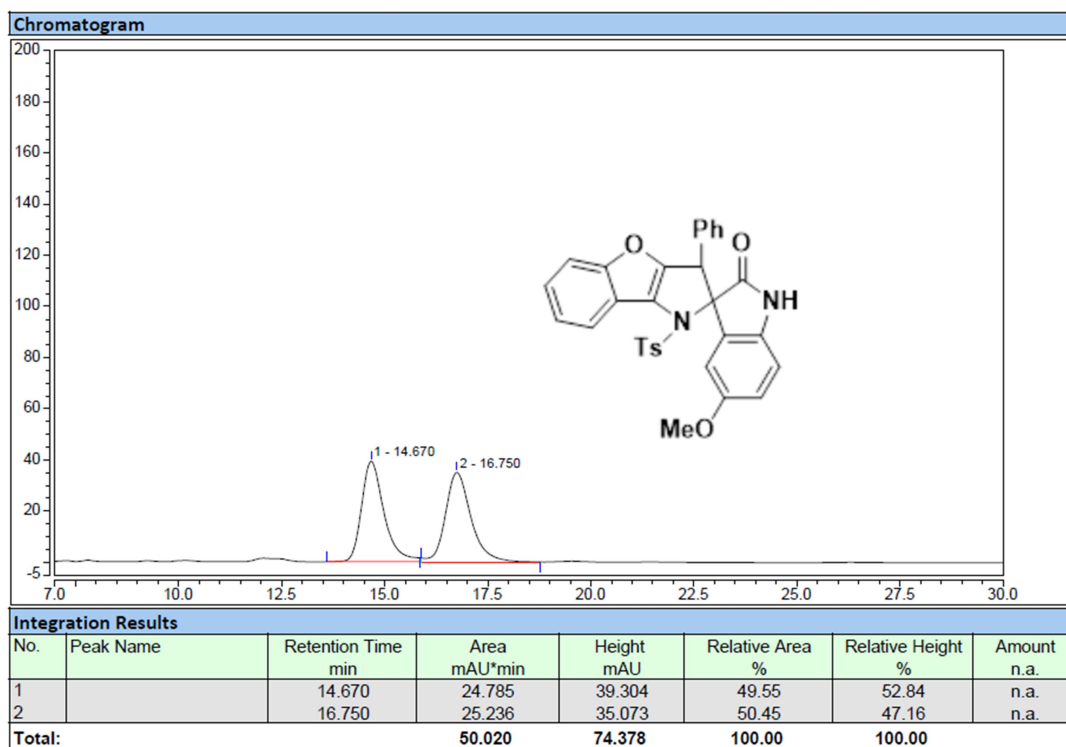
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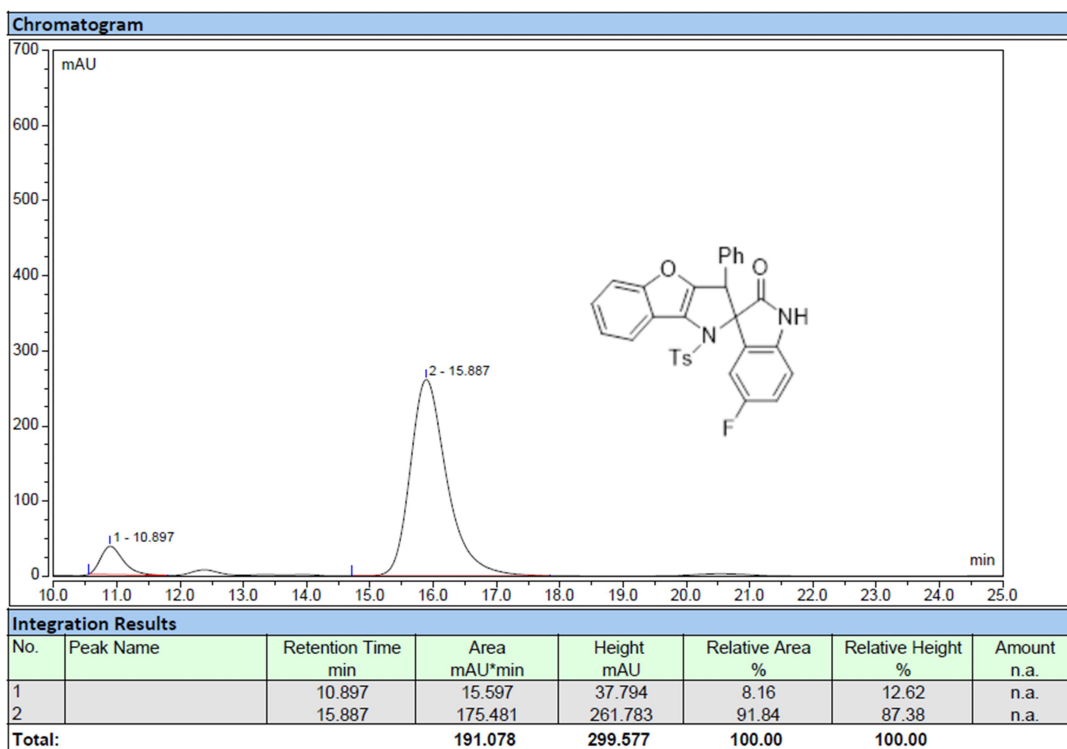
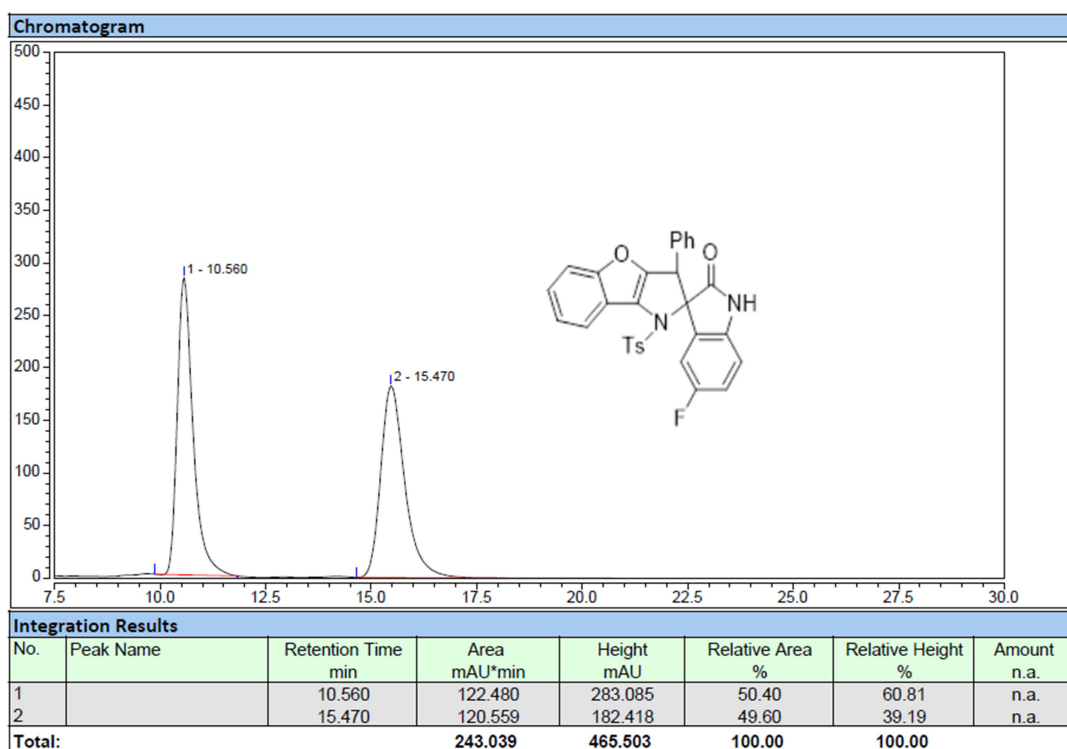
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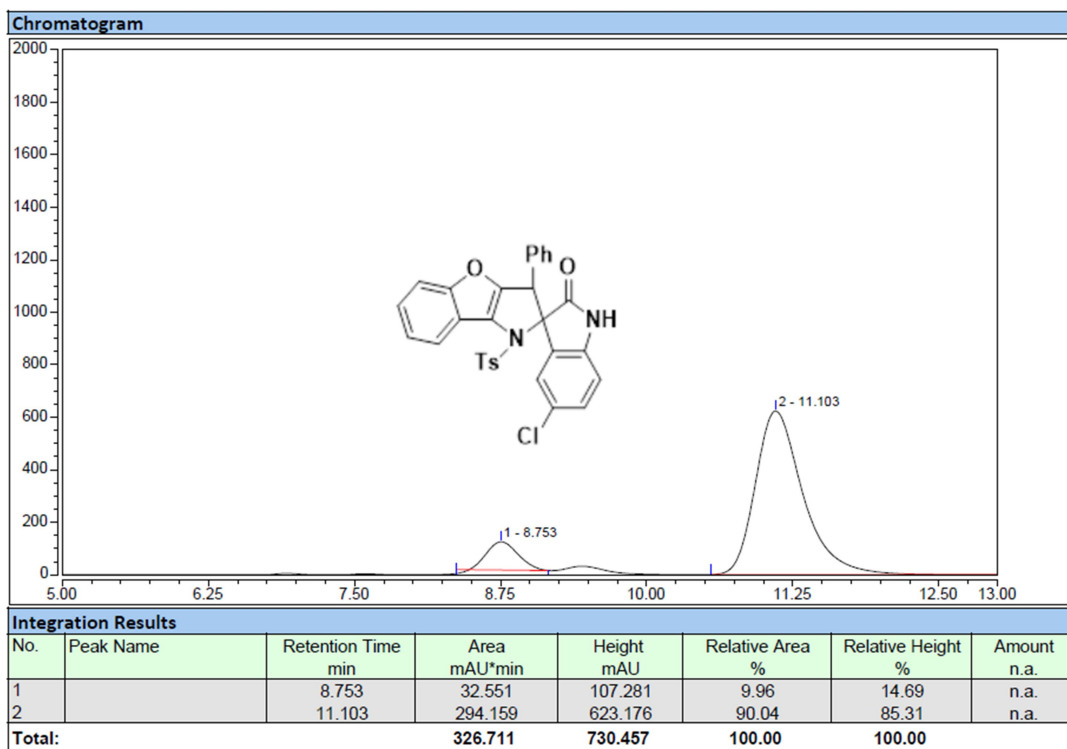
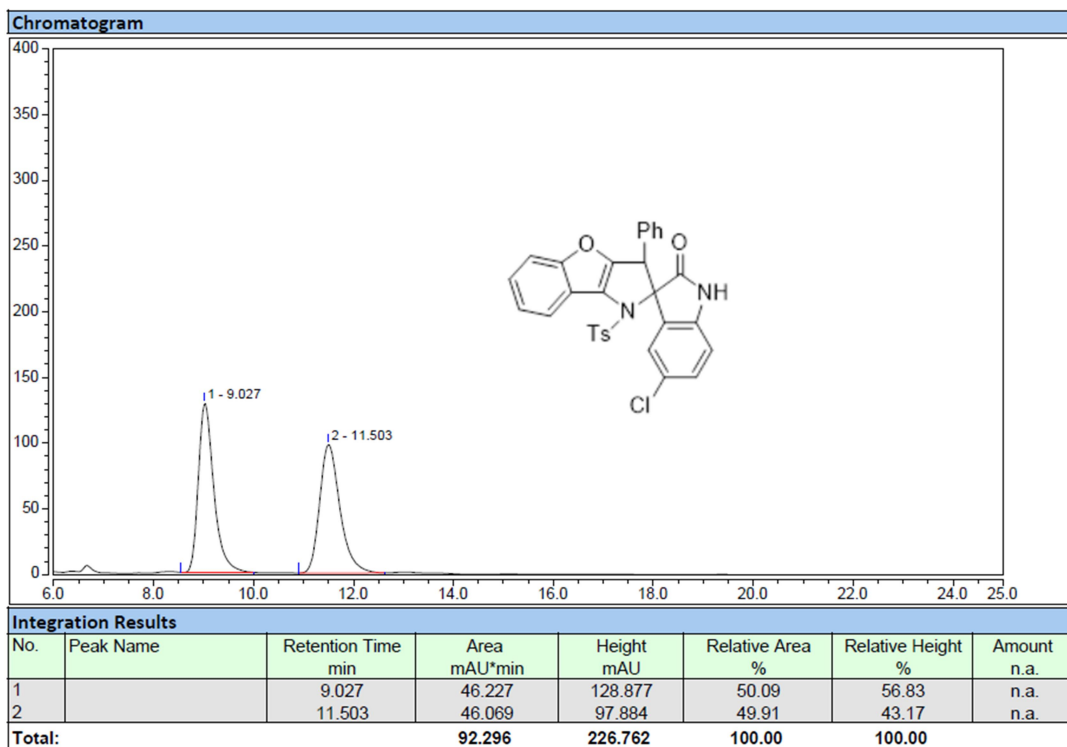
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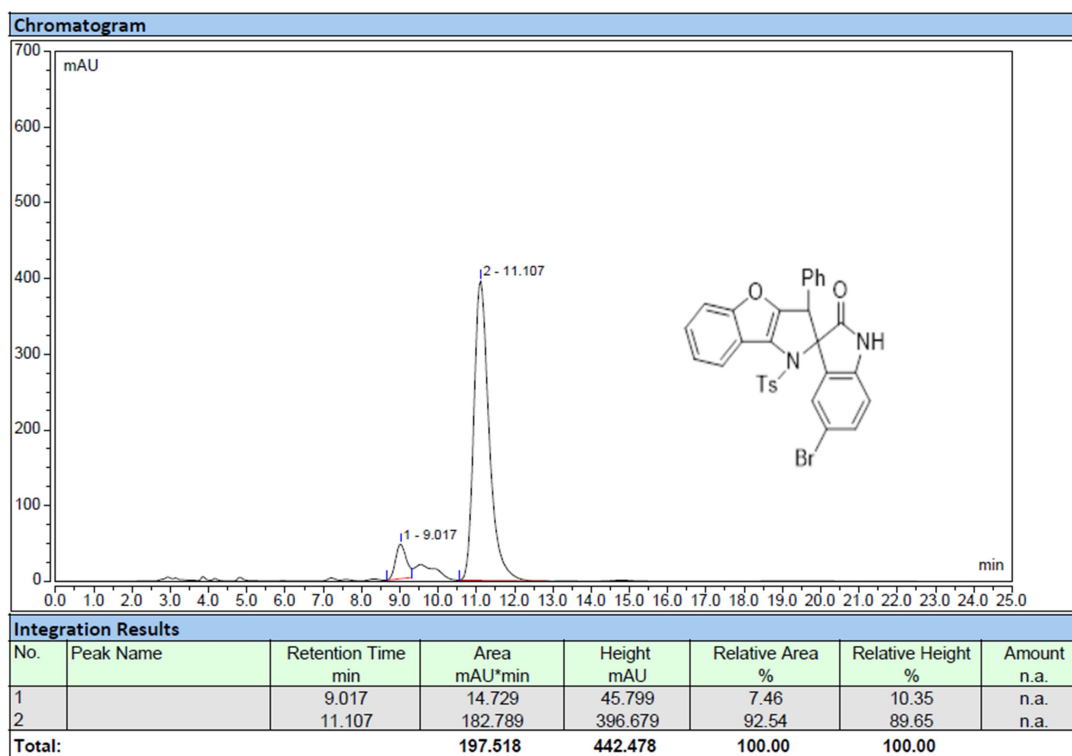
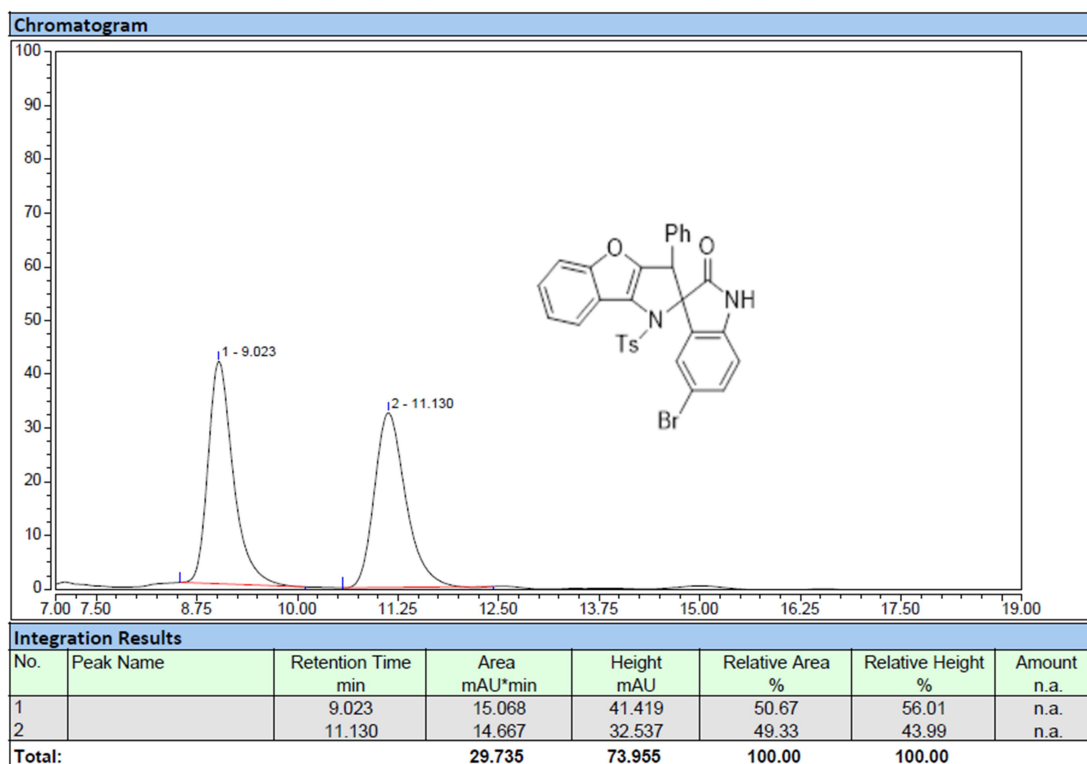
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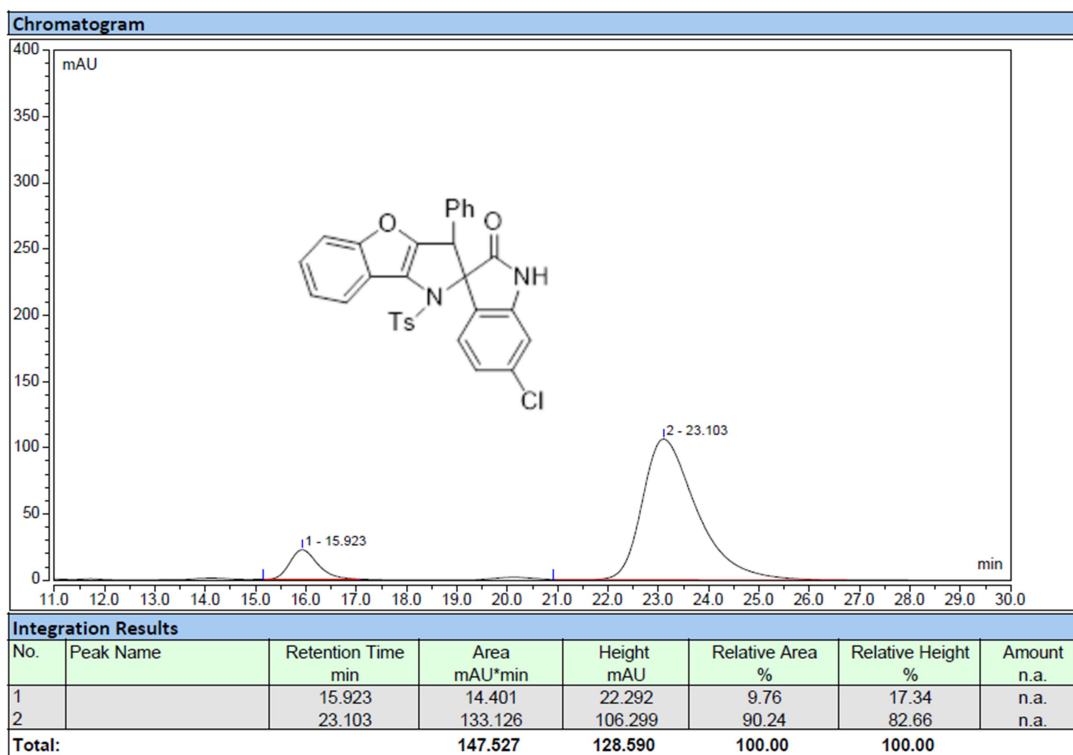
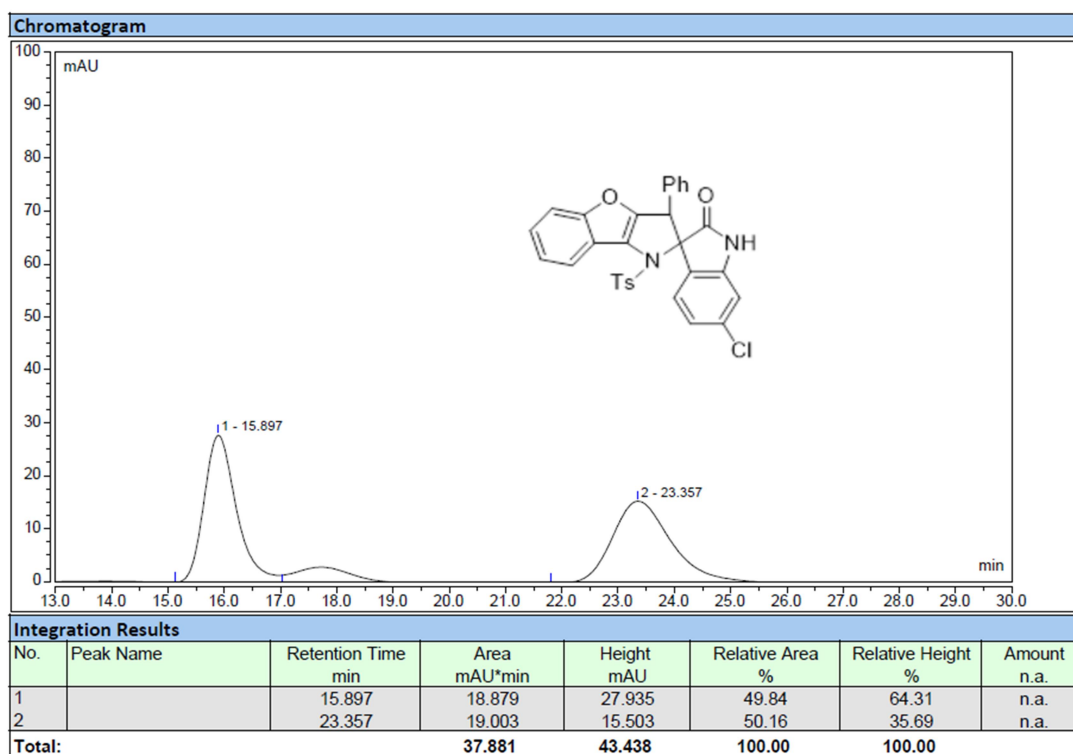
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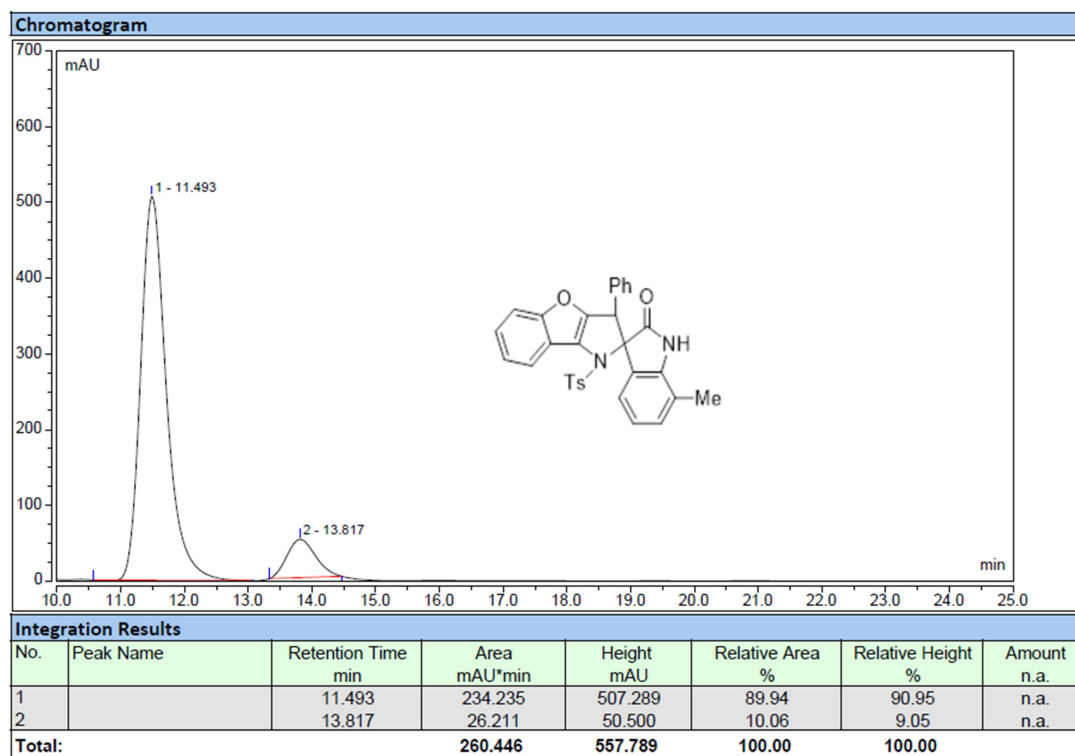
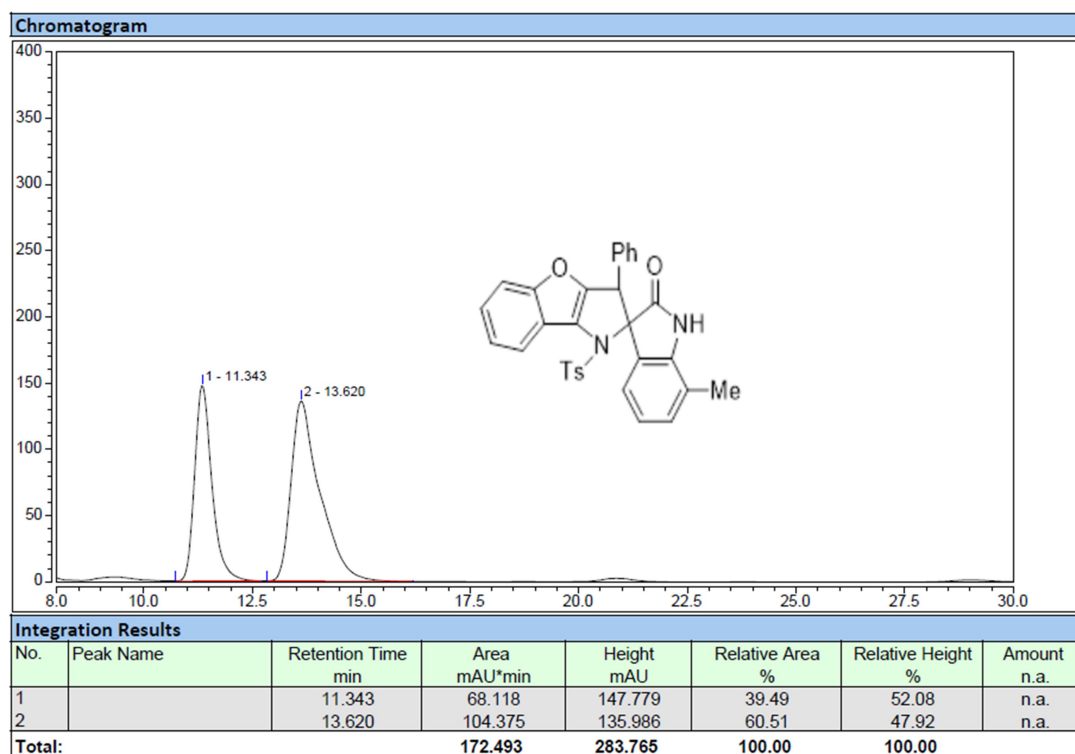
3ah



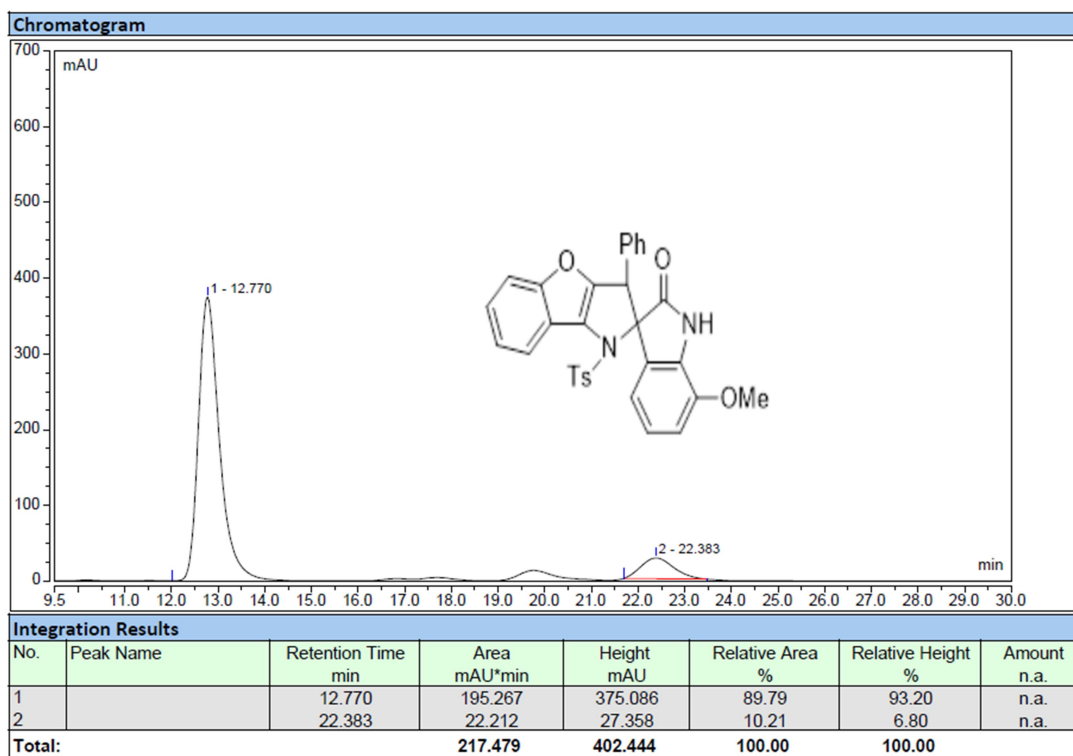
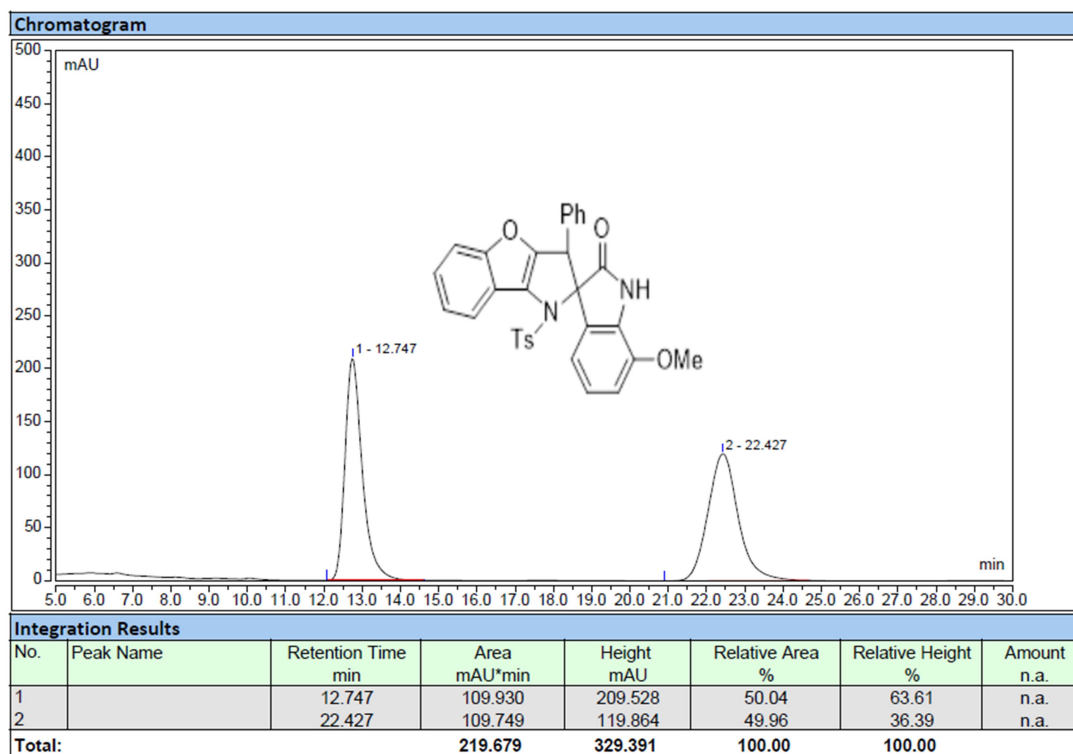
3ai



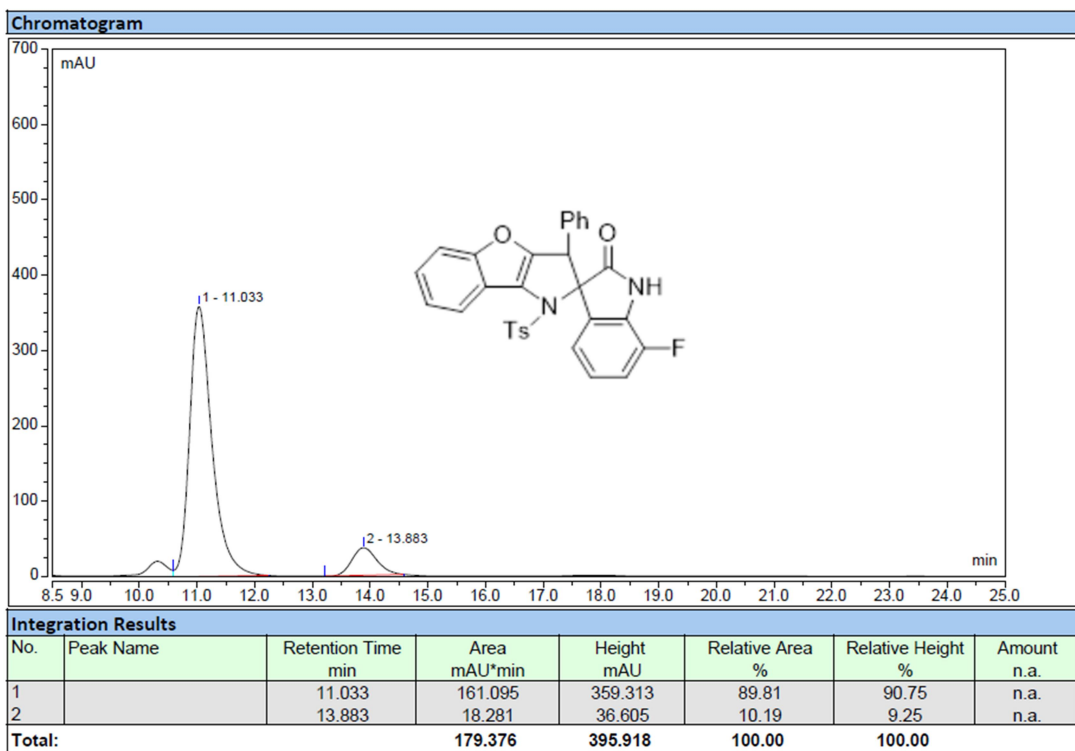
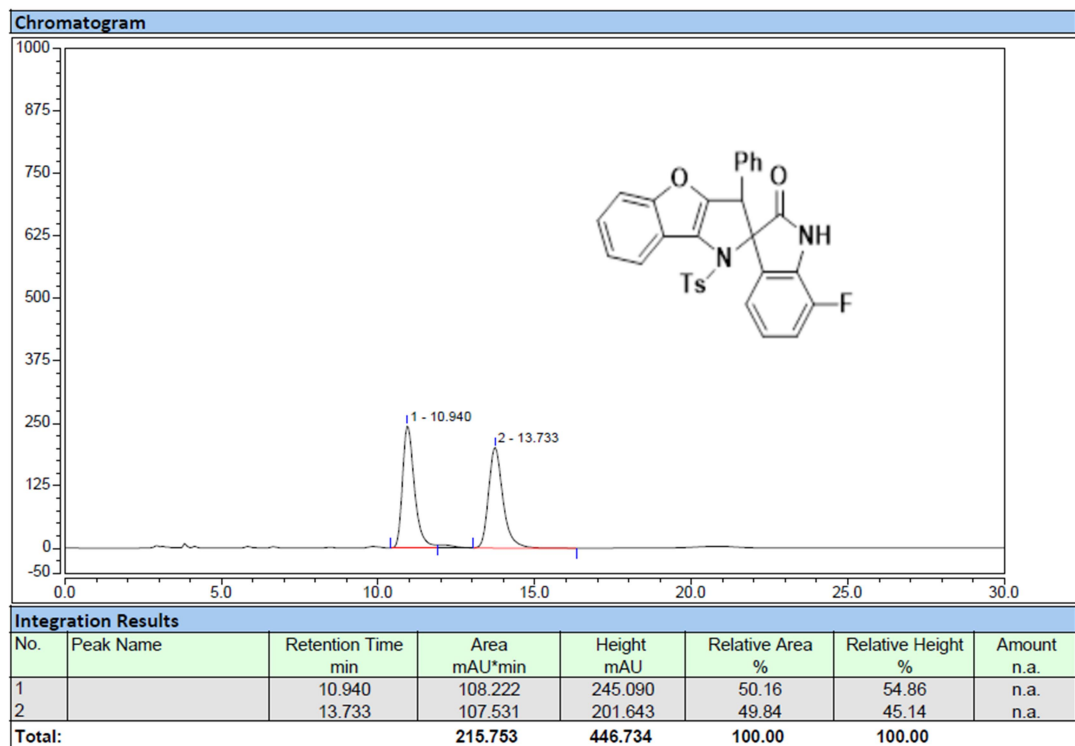
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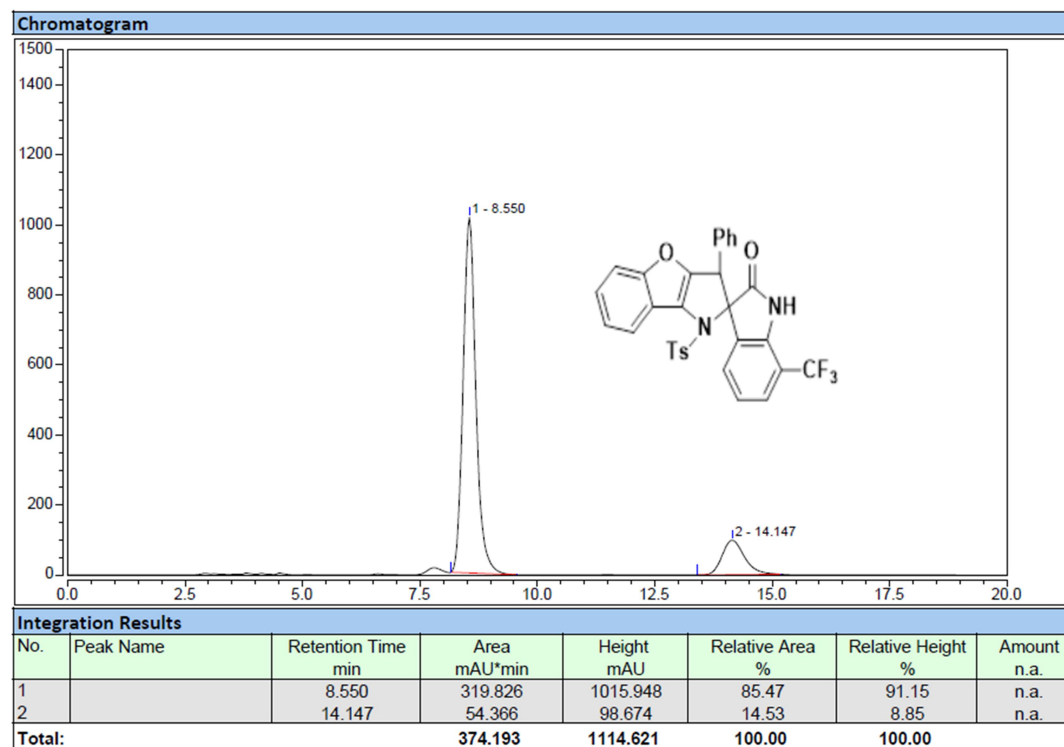
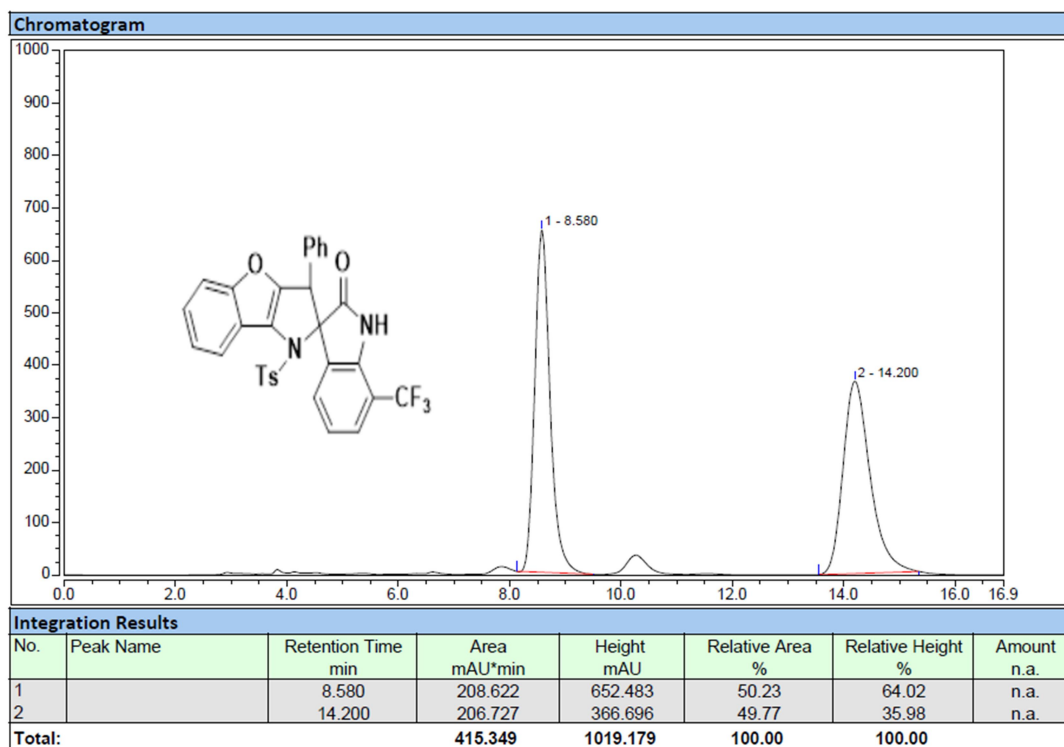
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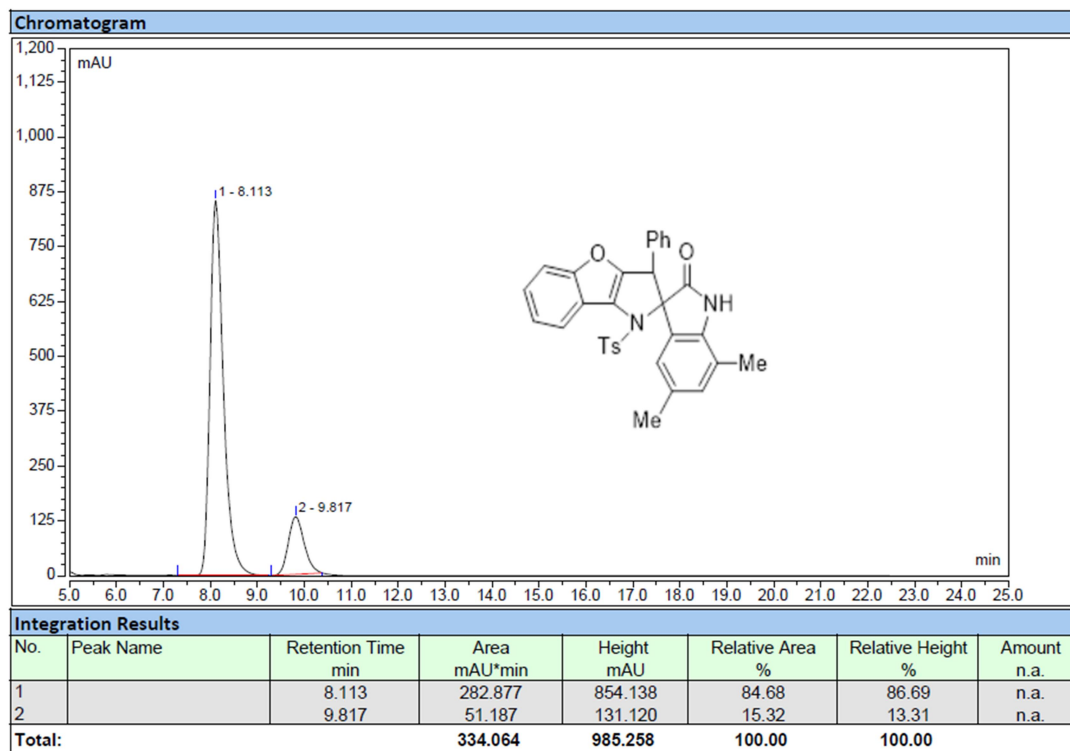
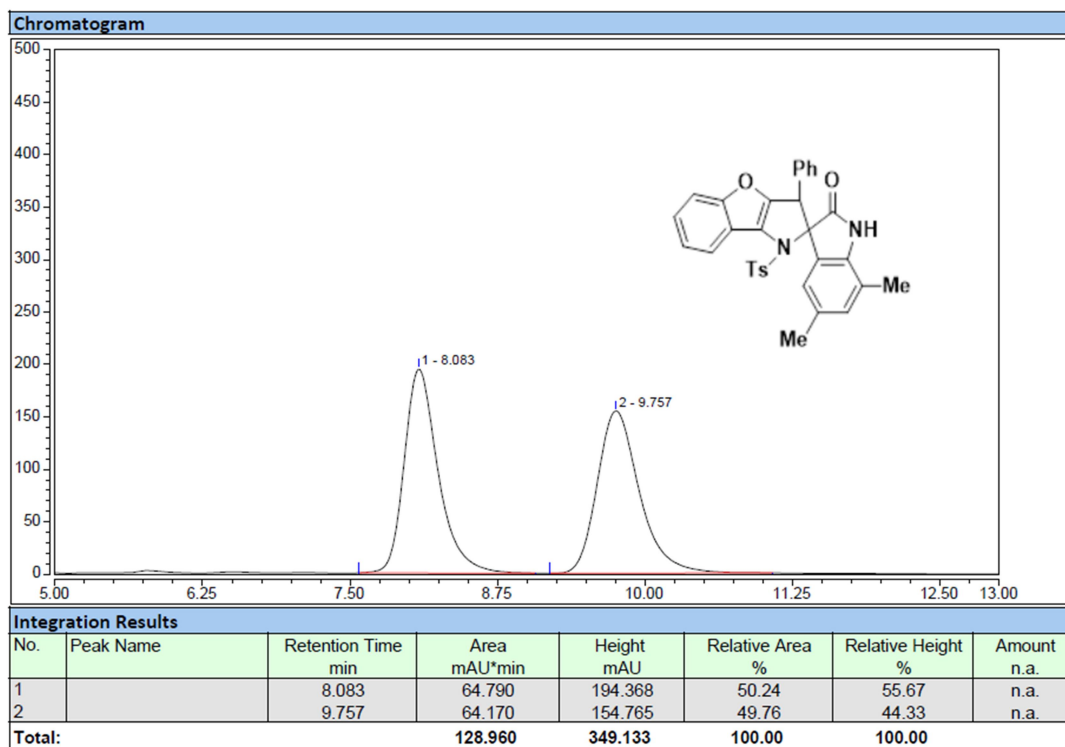
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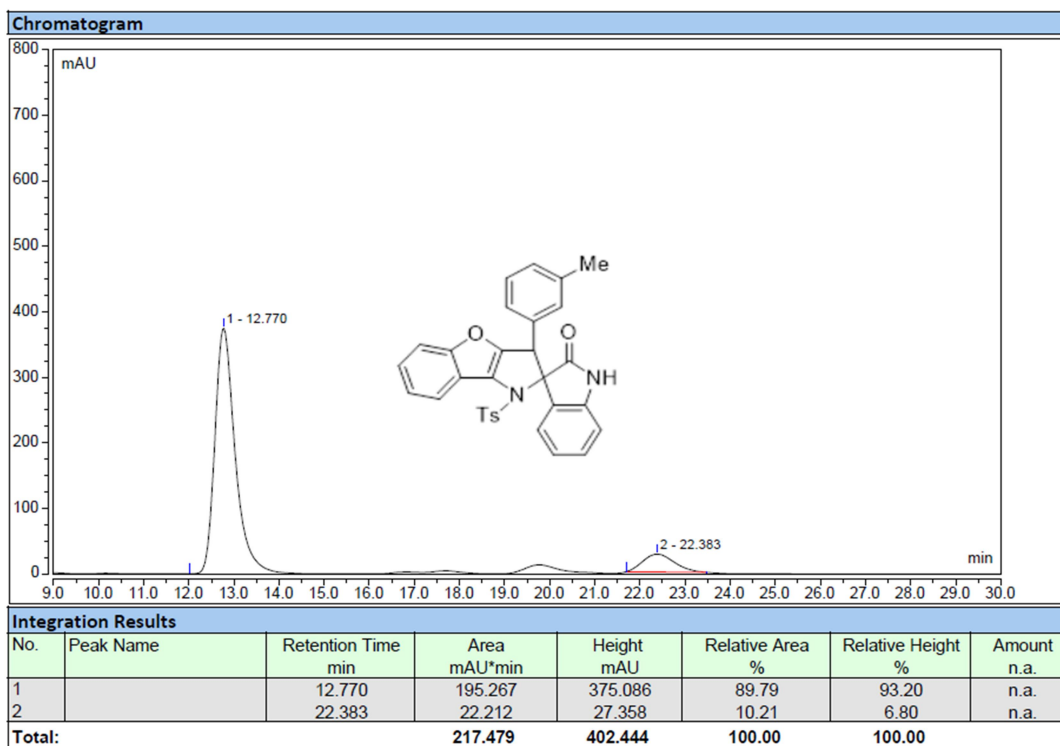
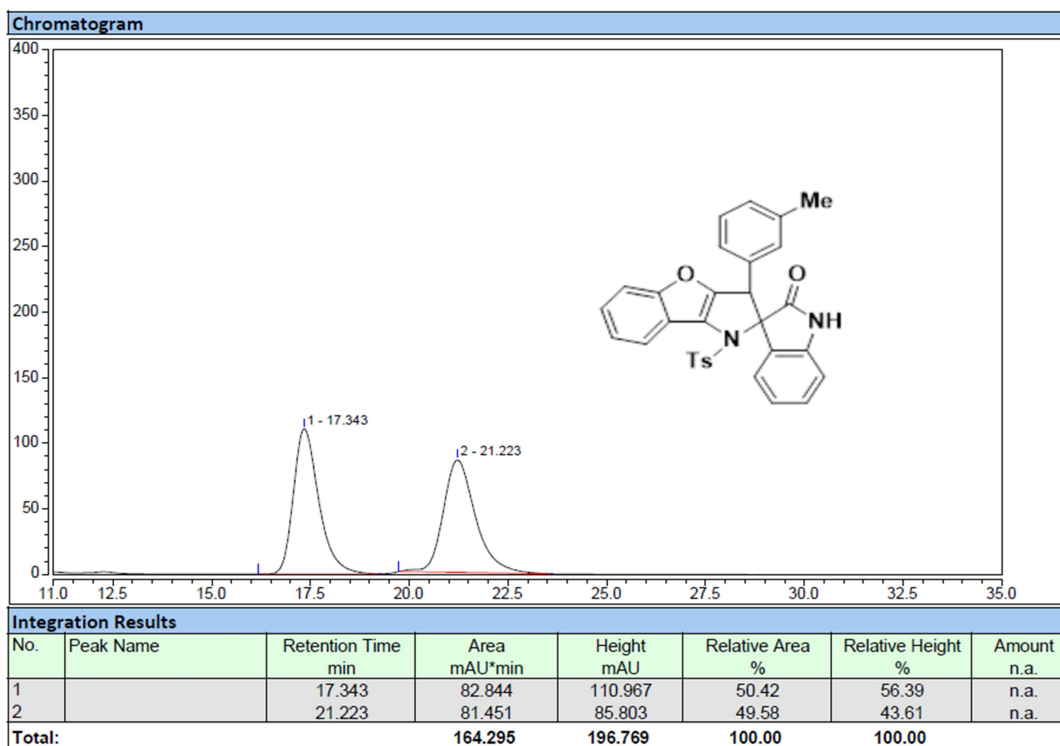
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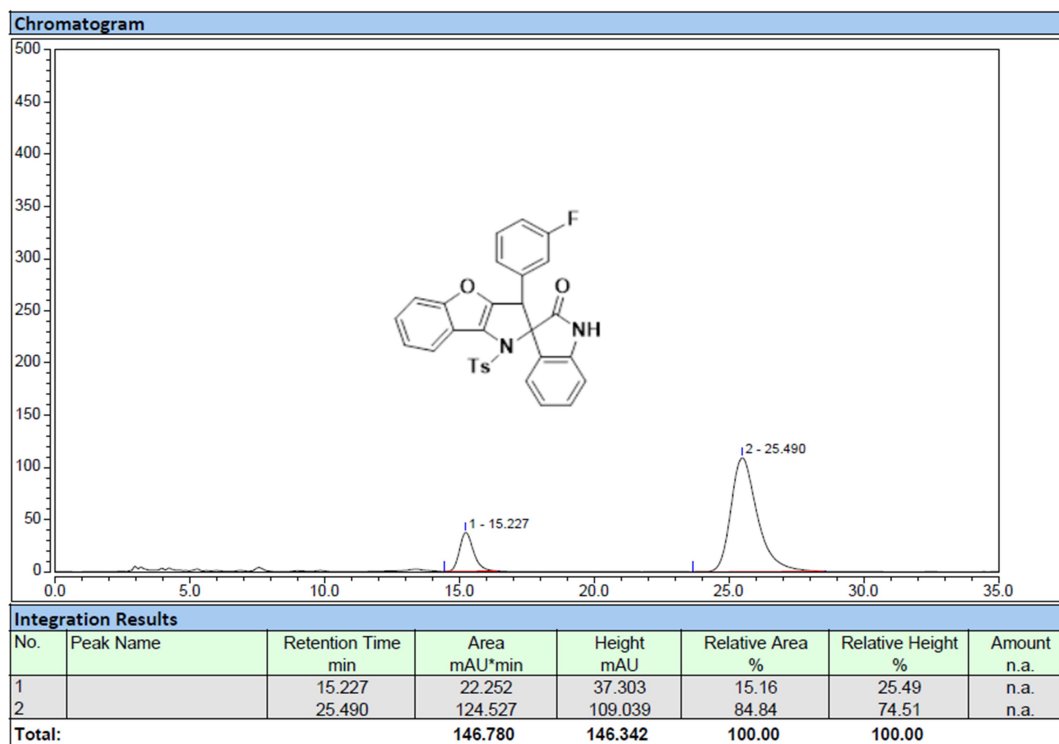
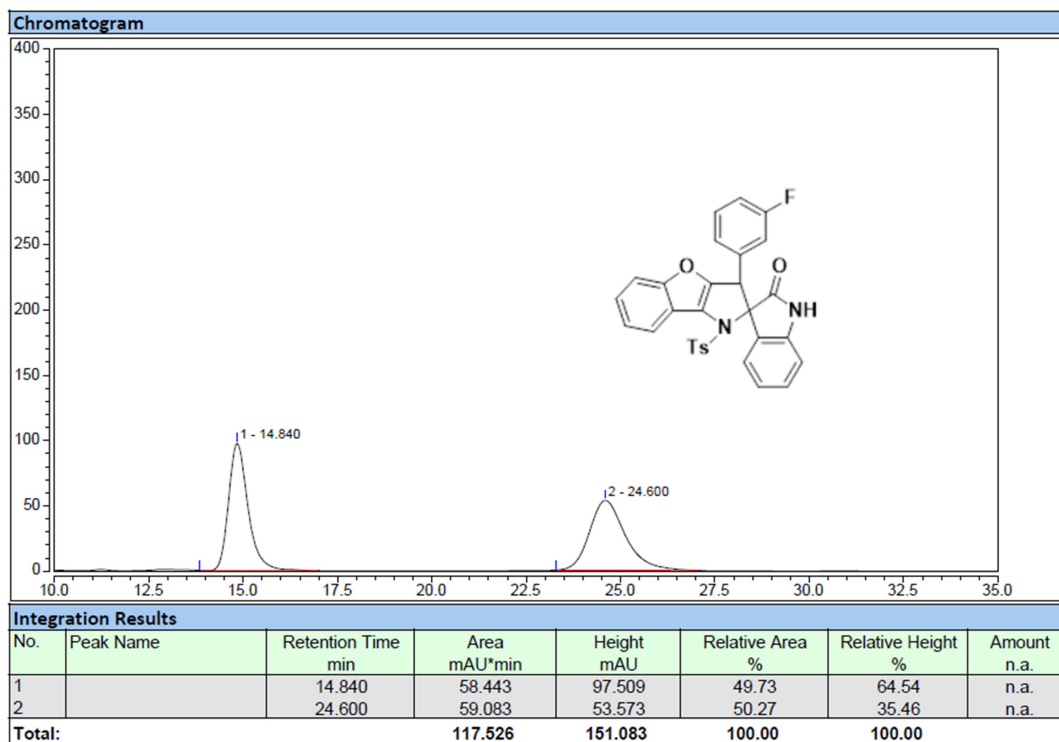
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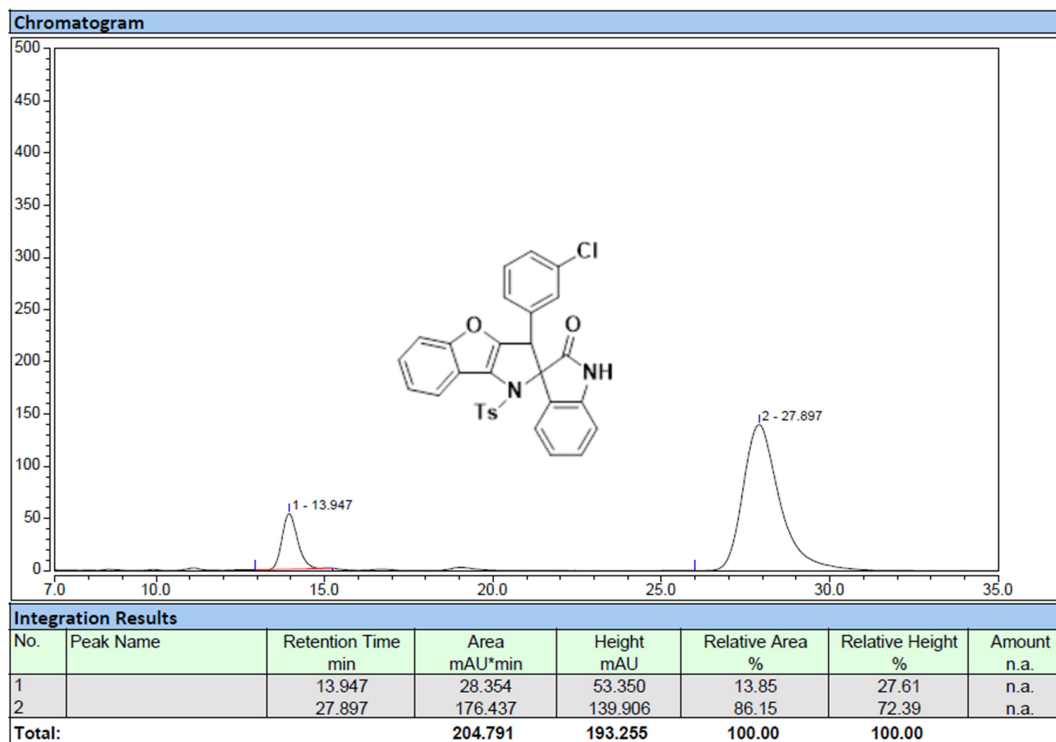
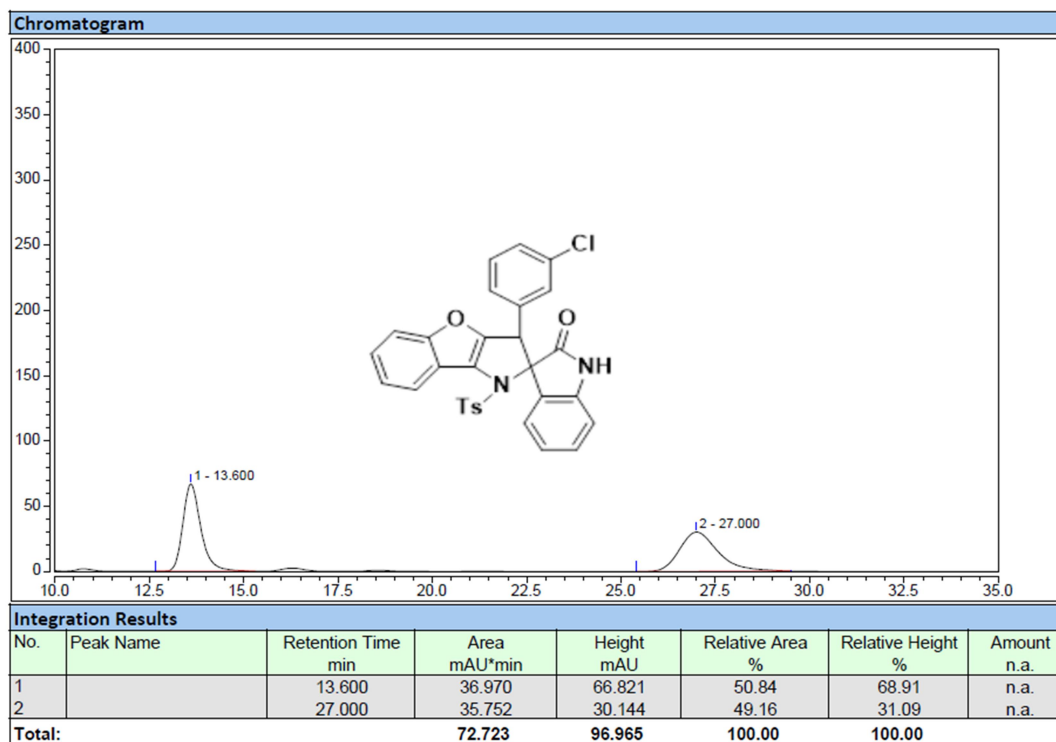
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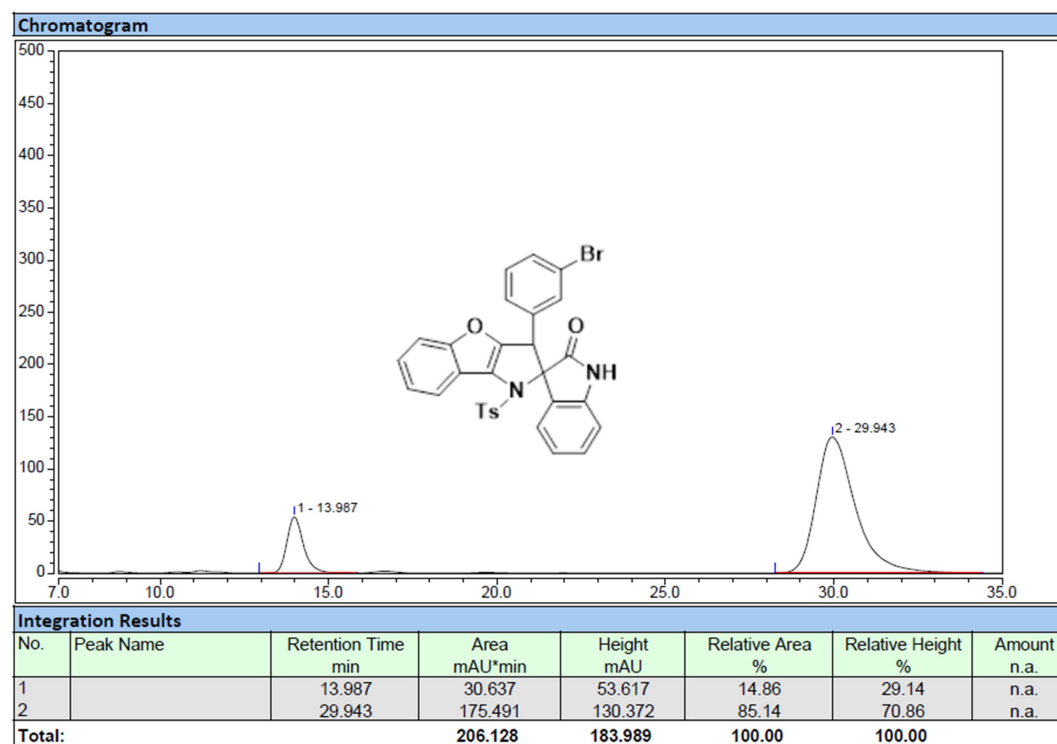
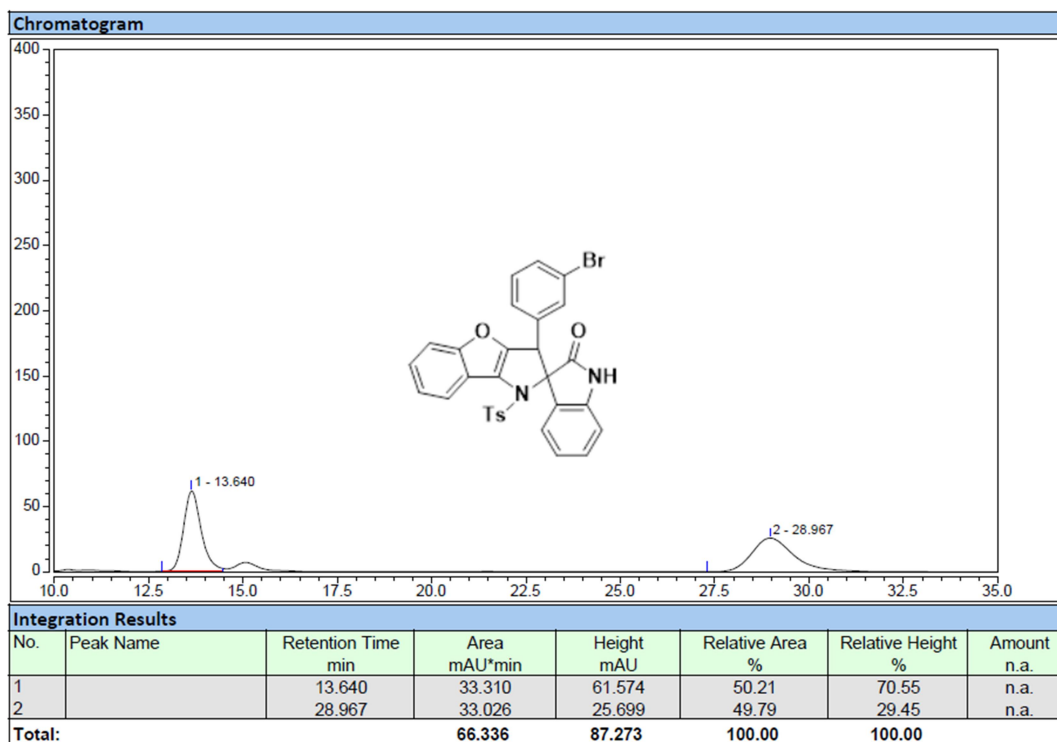
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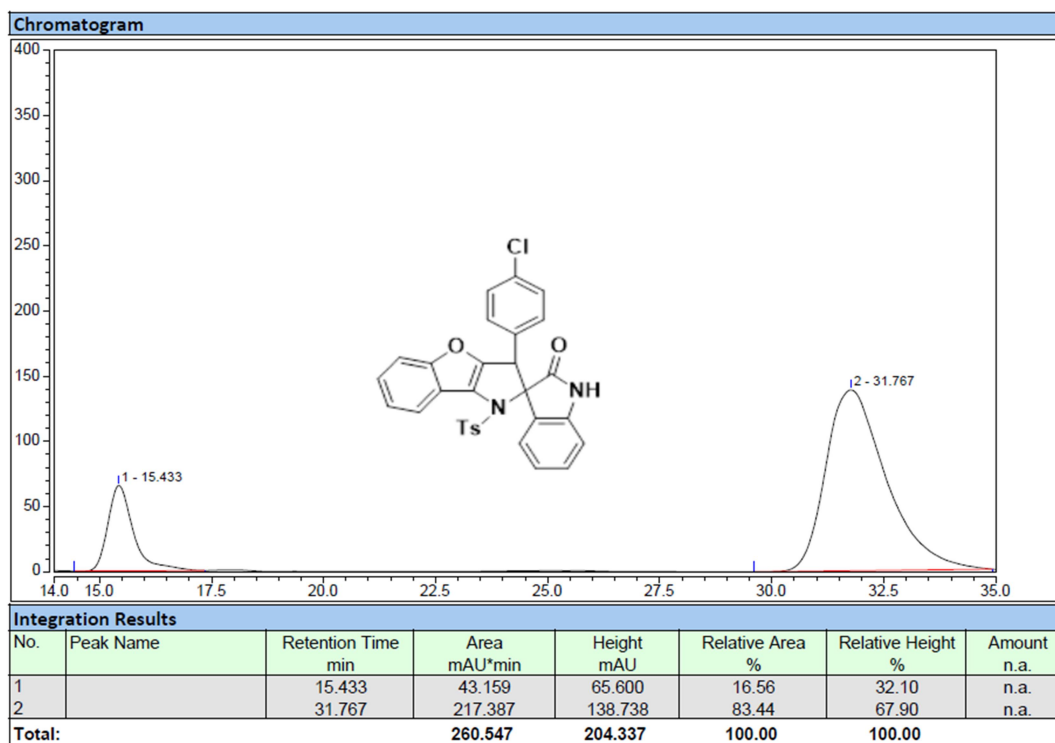
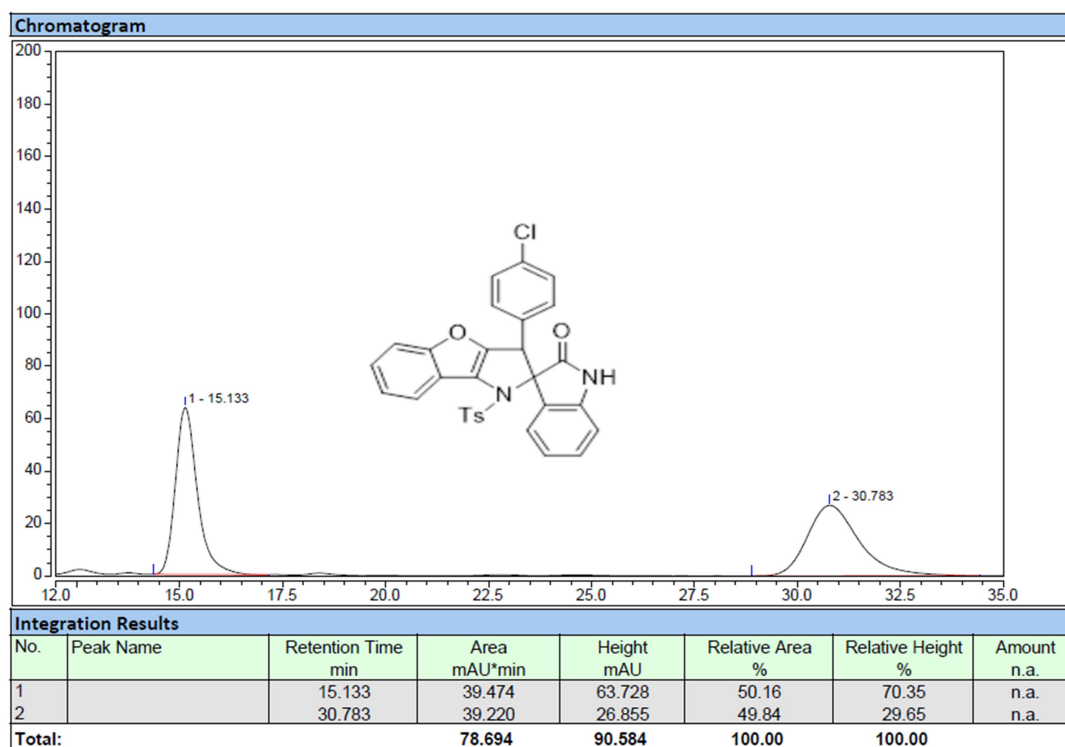
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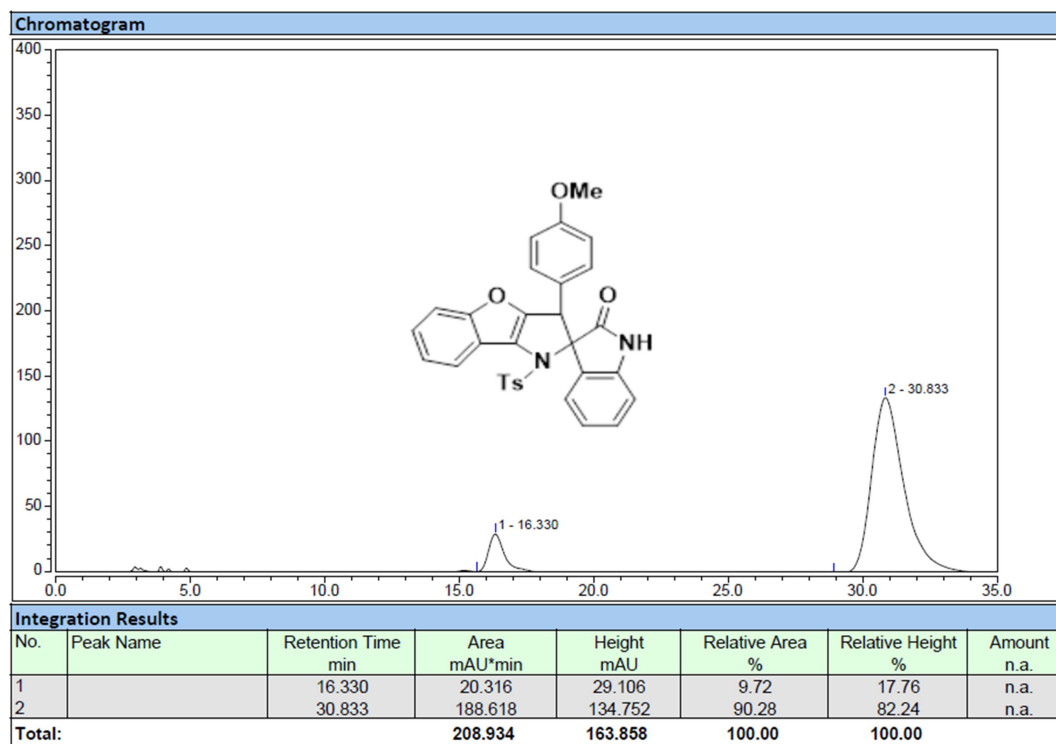
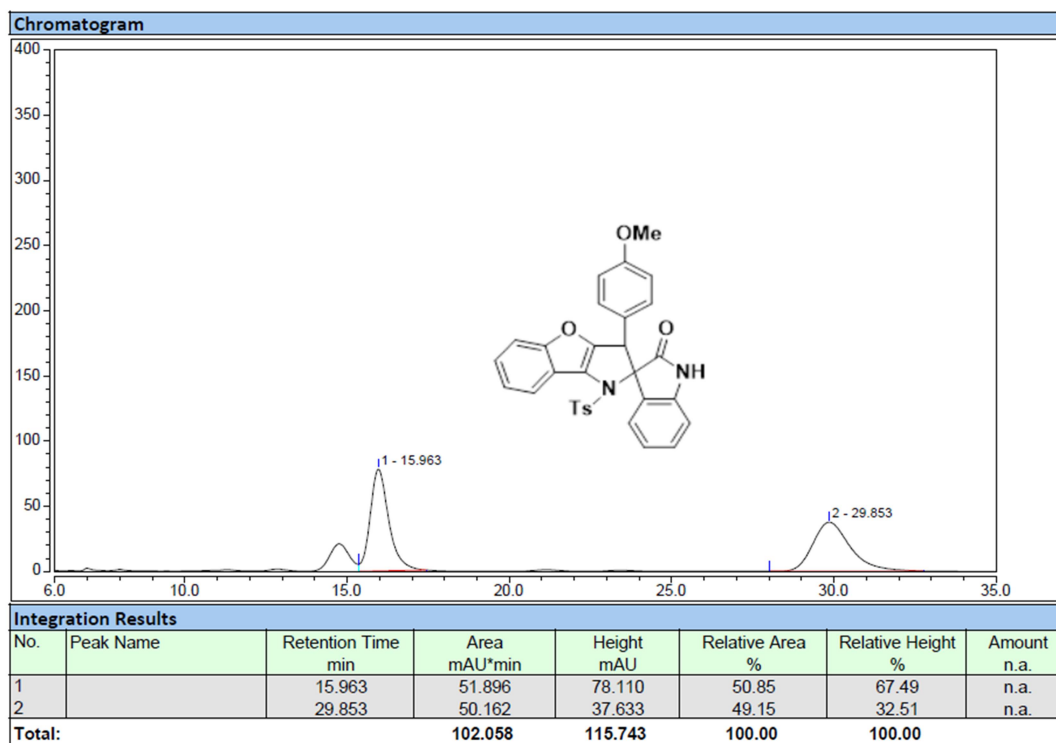
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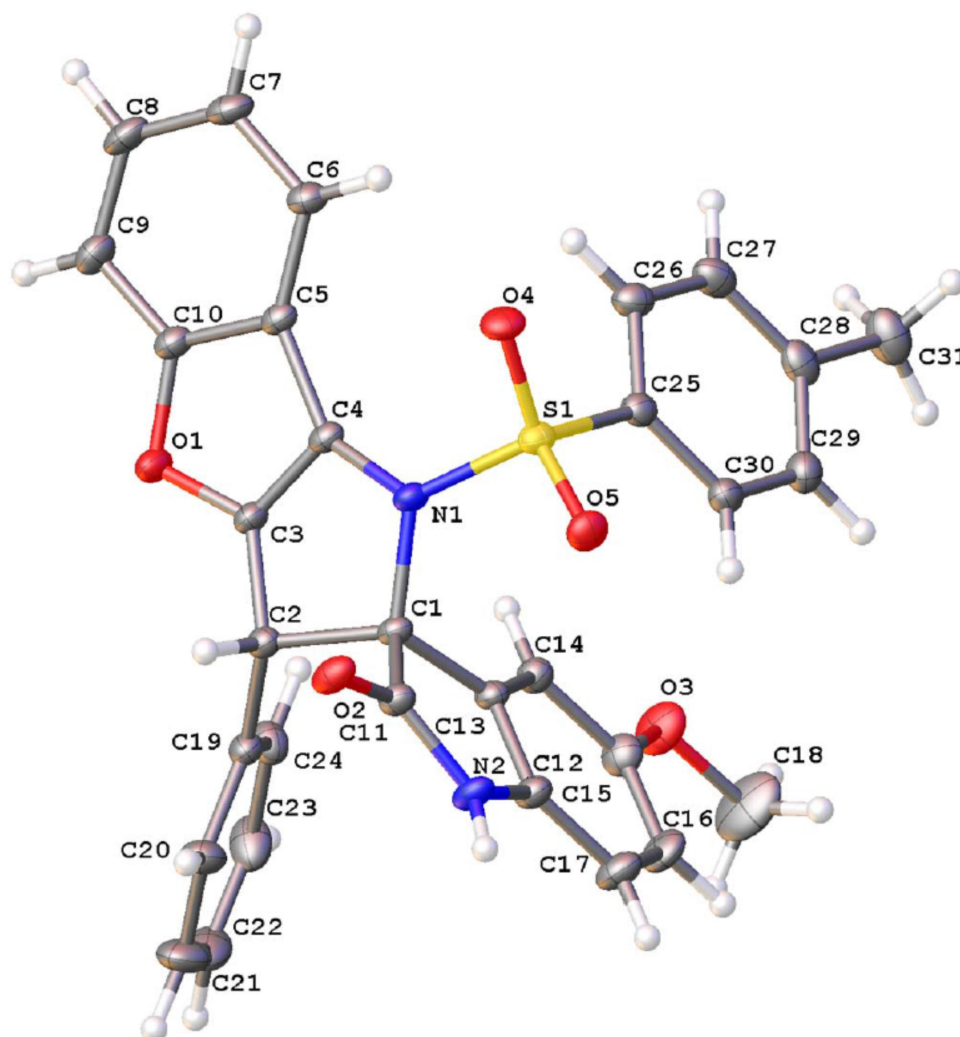
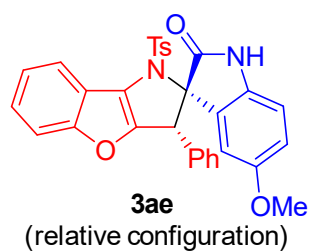
3fa



3ga



4. X-ray single-crystal data for product **3ae**



The single-crystal of **3ae** was grown from the mixed solution of dichloromethane and petrol ether (V/V = 1:4). The X-ray source used for the single crystal X-ray diffraction analysis of compound **3ae** was GaK α ($\lambda = 1.34139$), and the thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C ₃₁ H ₂₄ N ₂ O ₅ S
Formula weight	536.58
Temperature/K	170
Crystal system	triclinic
Space group	P-1
a/Å	9.8432(8)

b/Å	10.4209(9)
c/Å	14.3197(12)
$\alpha/^\circ$	83.441(5)
$\beta/^\circ$	74.668(4)
$\gamma/^\circ$	84.081(5)
Volume/Å ³	1403.2(2)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.270
μ/mm^{-1}	0.889
F(000)	560.0
Crystal size/mm ³	0.12 × 0.05 × 0.03
Radiation	GaK α (λ = 1.34139)
2 Θ range for data collection/ $^\circ$	10.988 to 110.568
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected	14431
Independent reflections	5288 [R_{int} = 0.0507, R_{sigma} = 0.0553]
Data/restraints/parameters	5288/0/354
Goodness-of-fit on F^2	1.025
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0439, wR_2 = 0.1074
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.1122
Largest diff. peak/hole / e Å ⁻³	0.30/-0.47