

Supporting Information

Palladium-Catalyzed C-7 Alkenylation of Indolines Using Molecular Oxygen as the Sole Oxidant

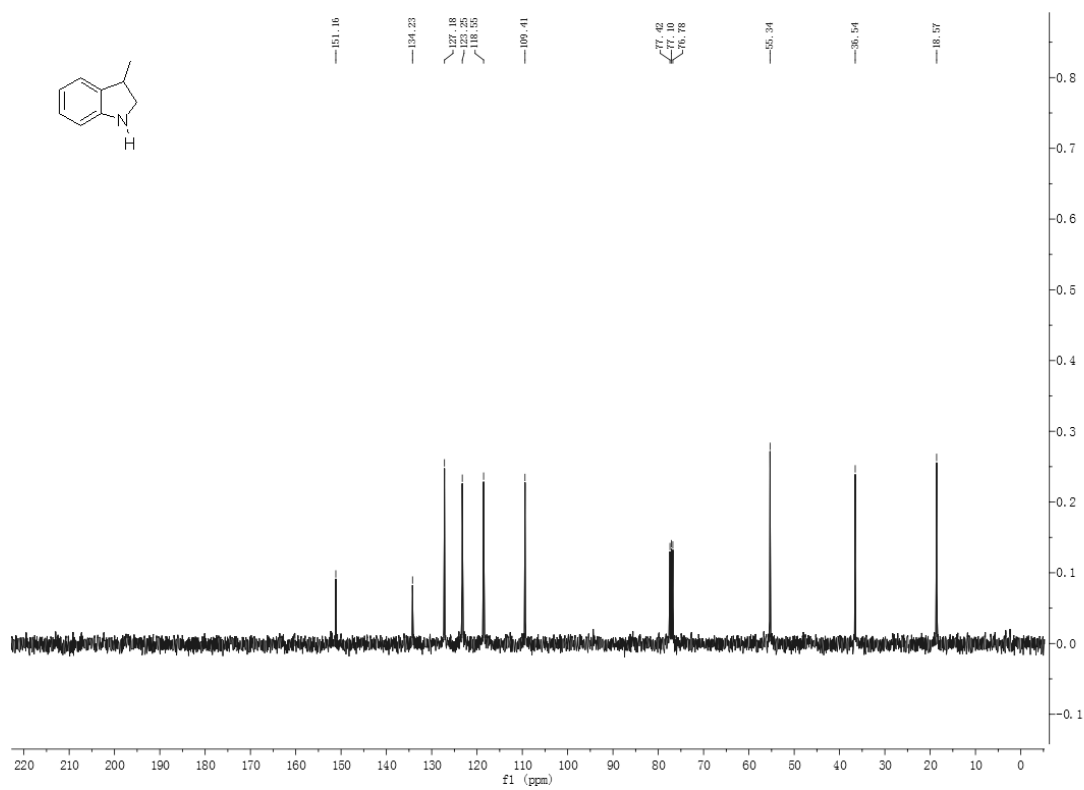
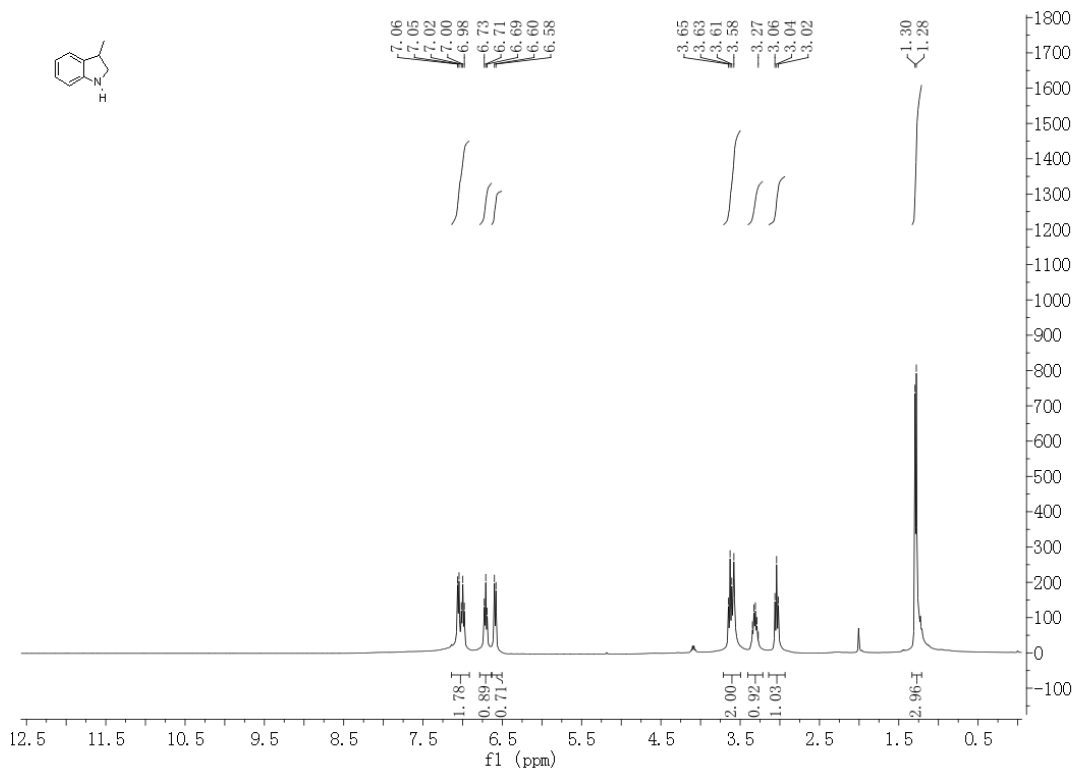
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Yong-Qiang Wang*

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of Education, Department of Chemistry & Materials Science, Northwest University,
Xi'an 710069, P. R. China
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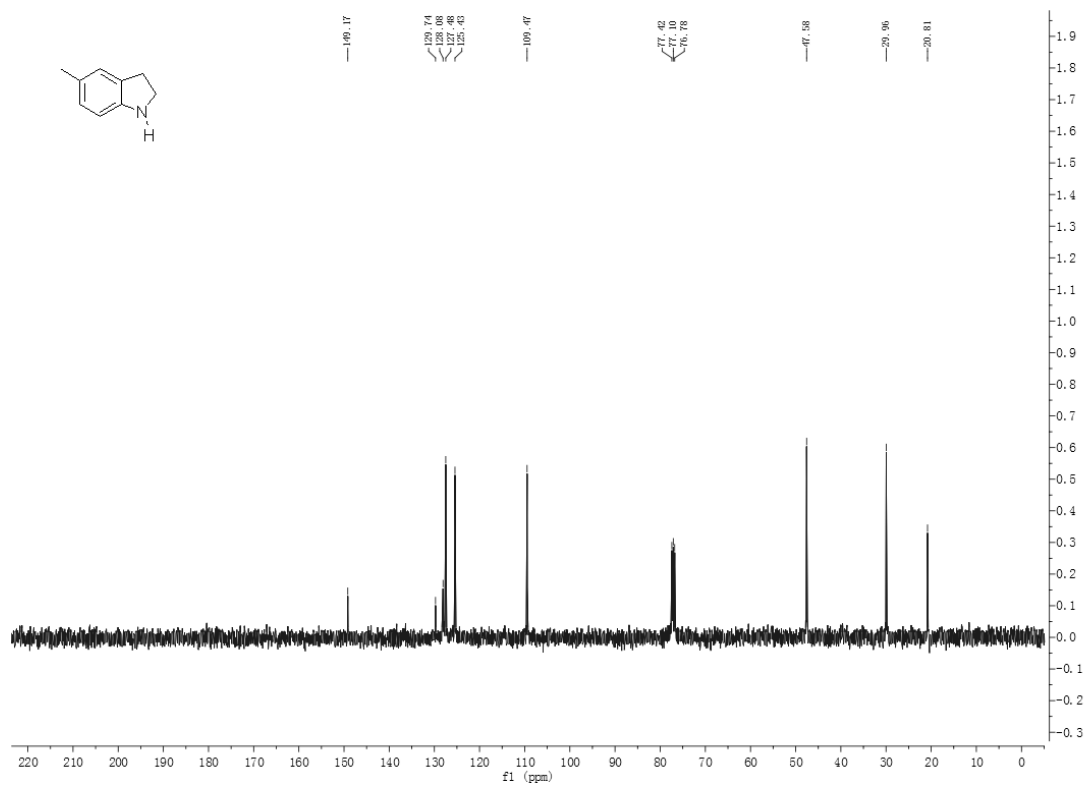
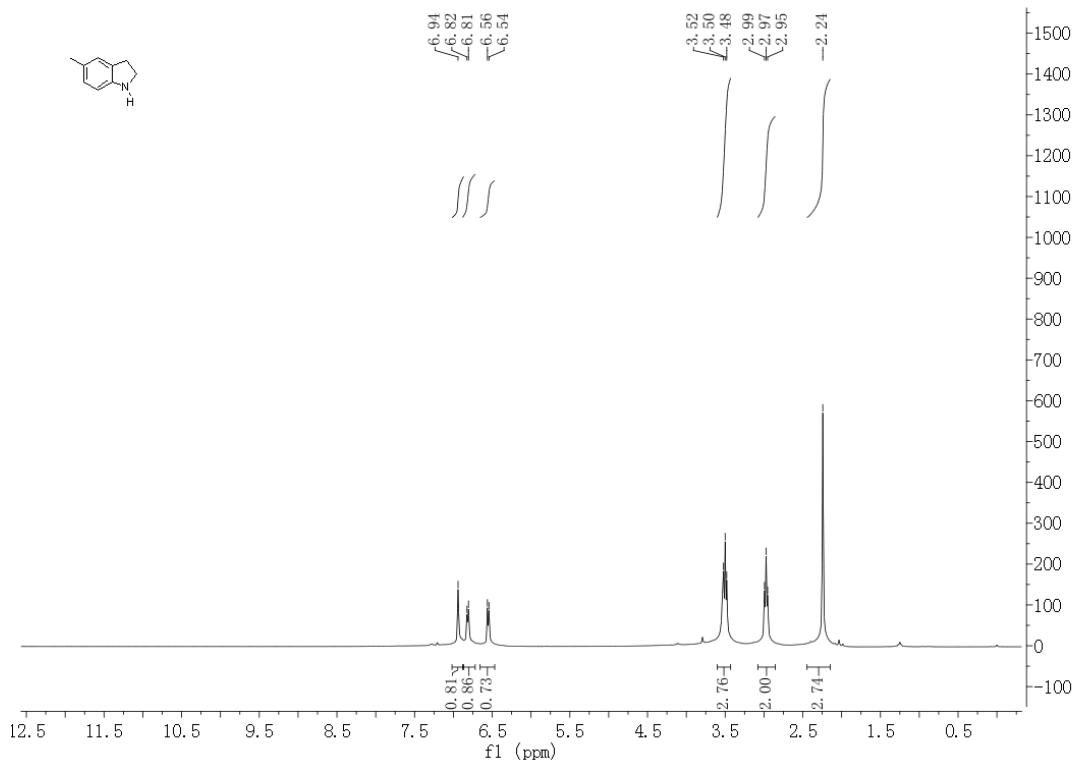
1: Copies of ^1H NMR and ^{13}C NMR spectra	S2—S47
2: X-Ray structure of 3da and 3dk	S48—S56

1: Copies of 1H NMR and 13C NMR spectra

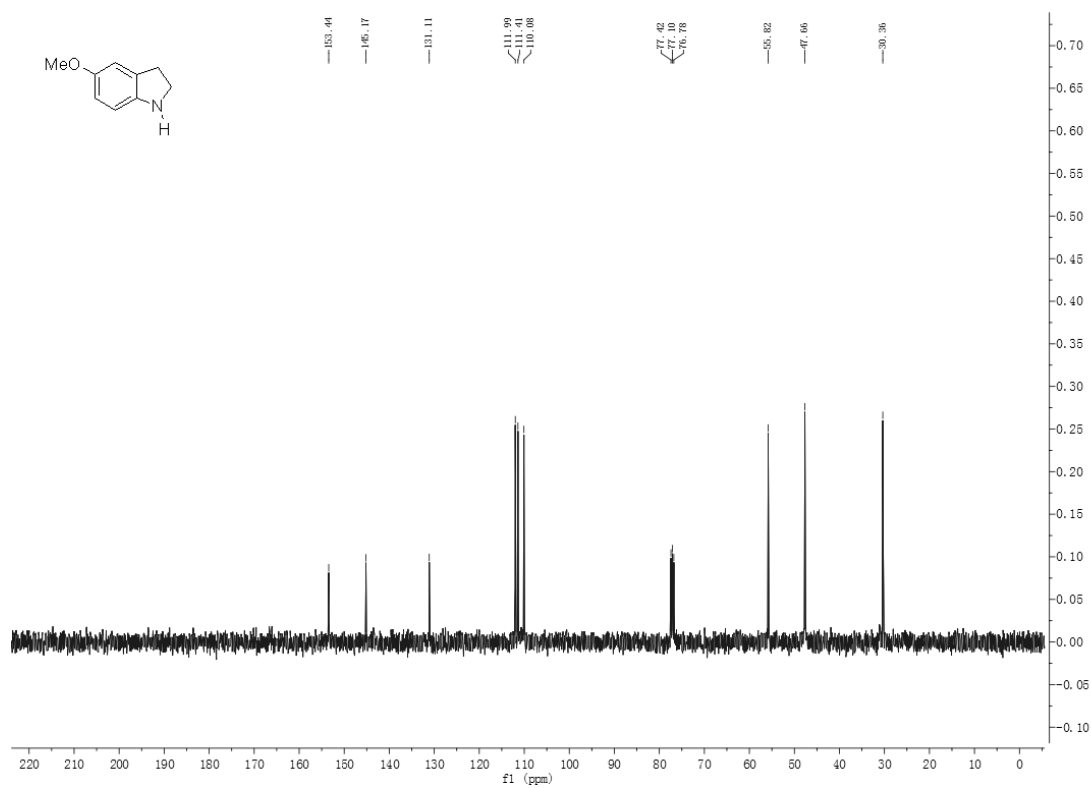
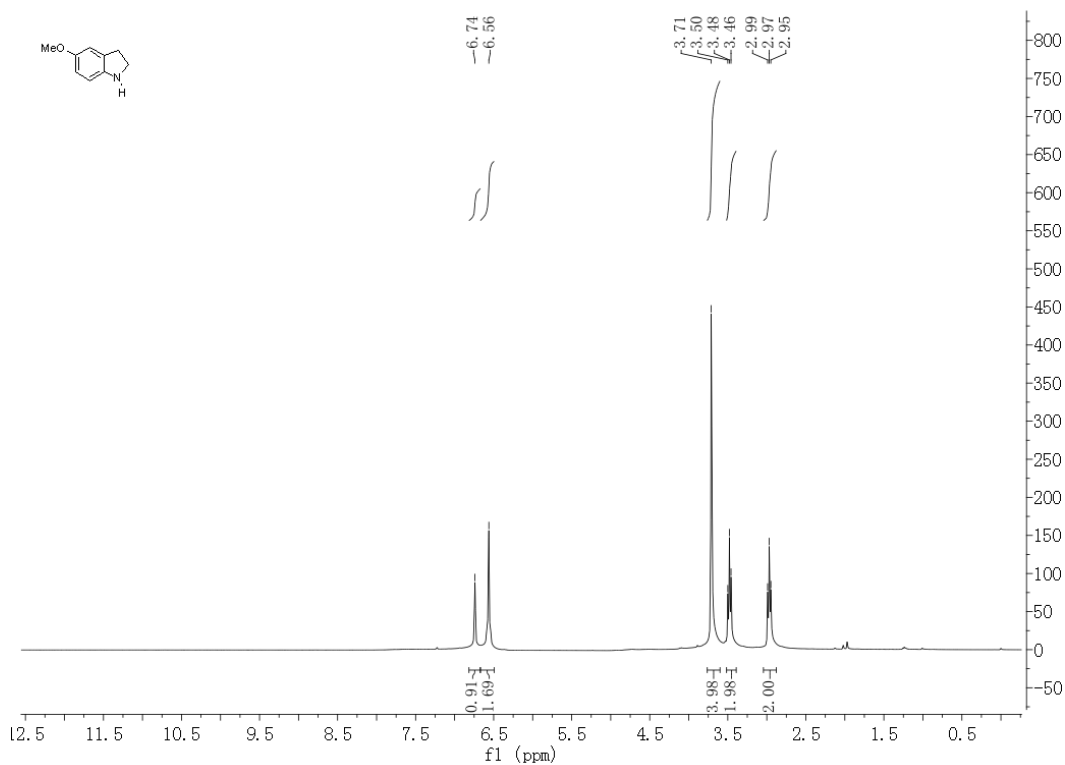
3-Methylindoline



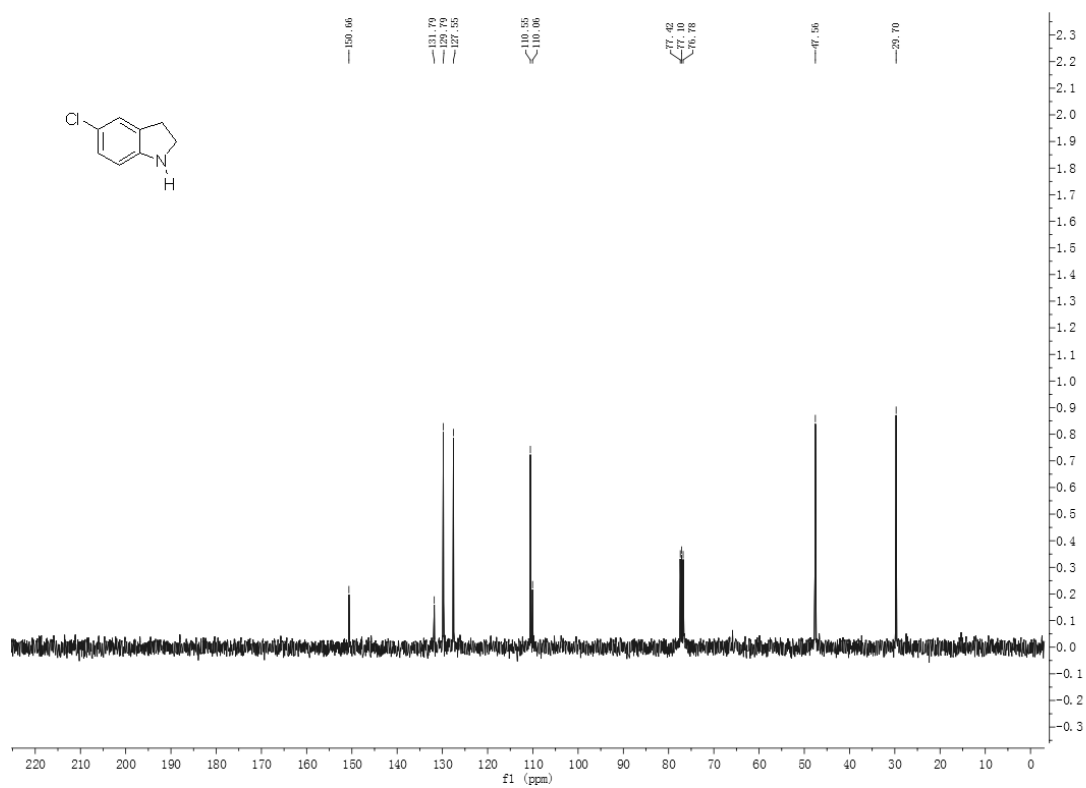
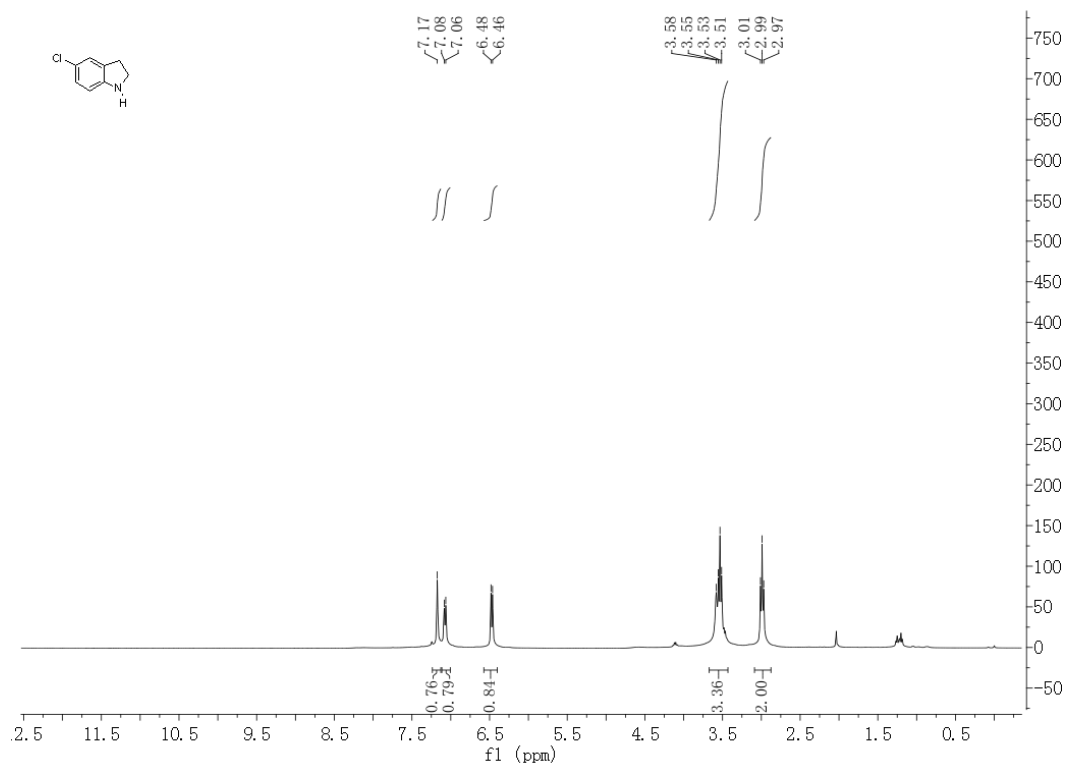
5-Methylindoline



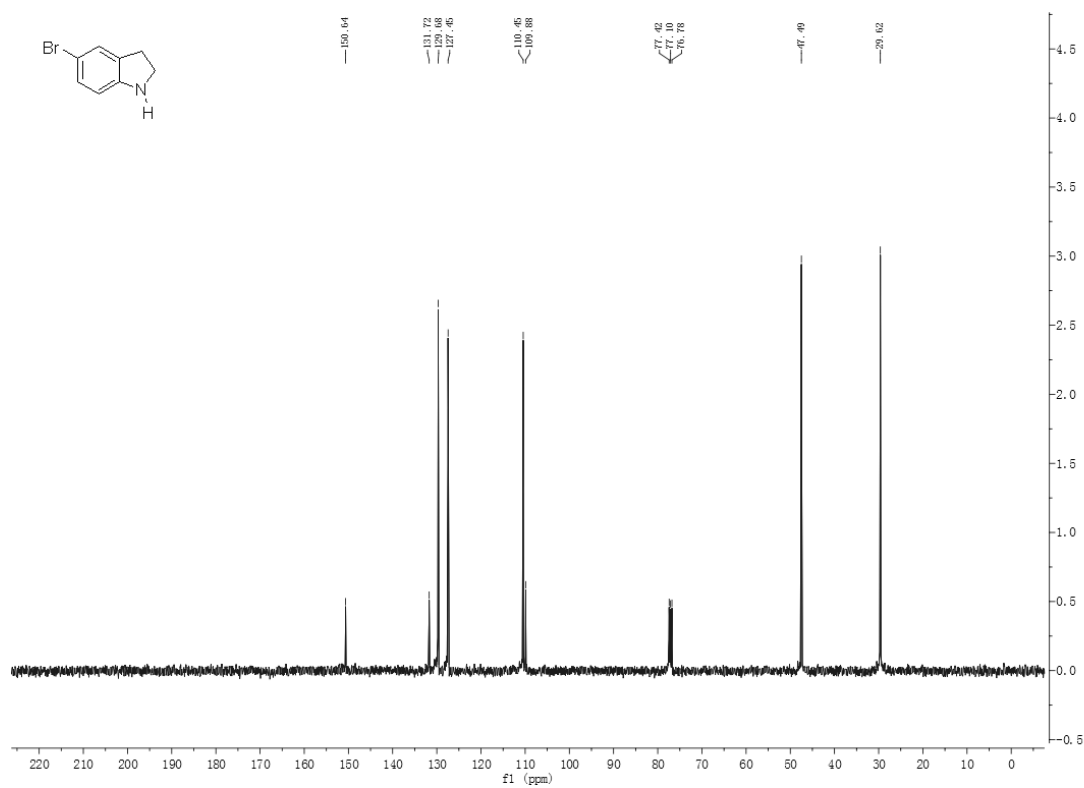
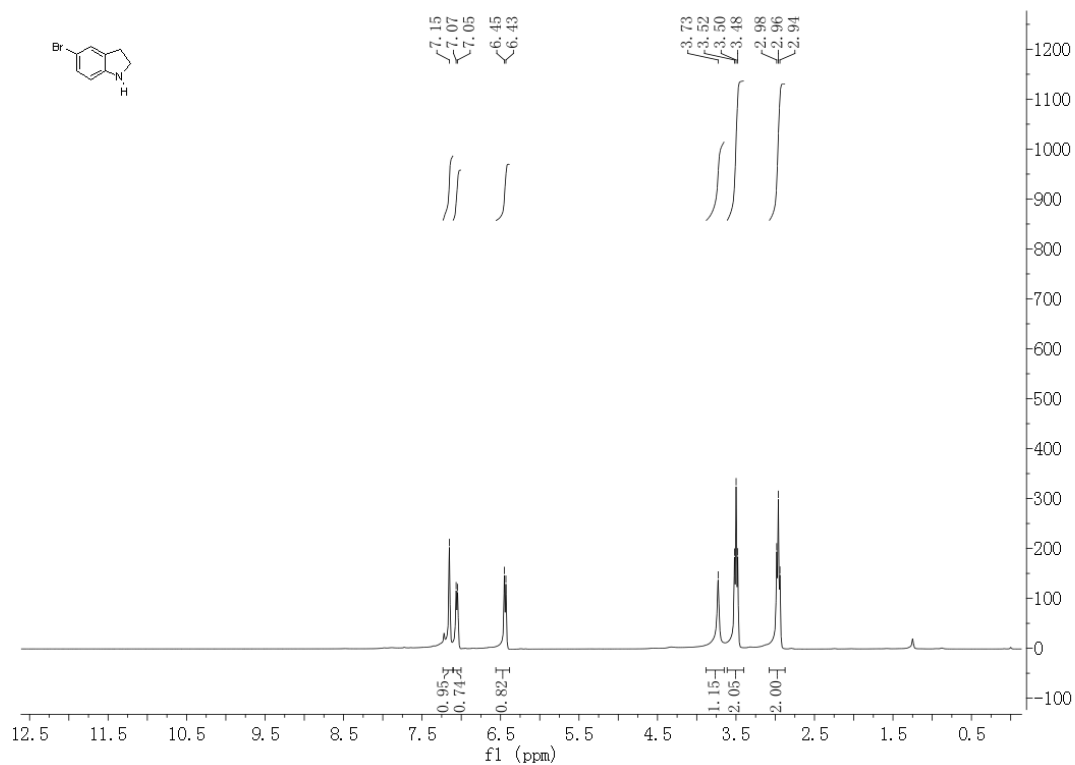
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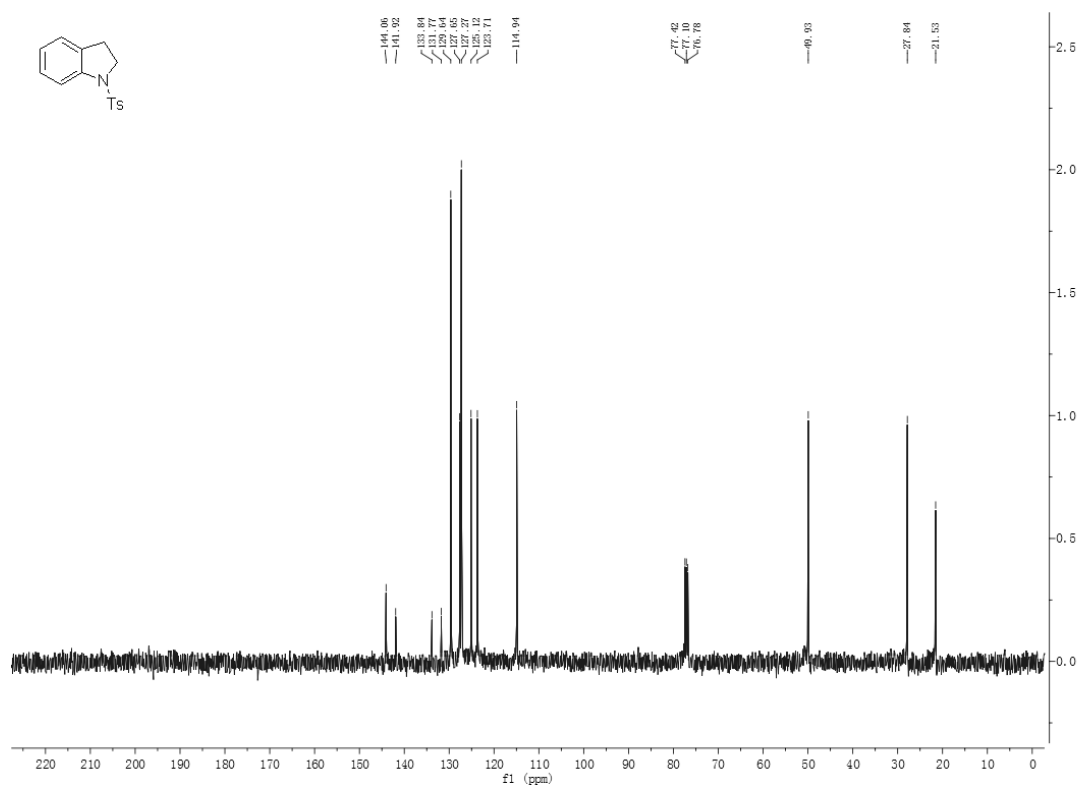
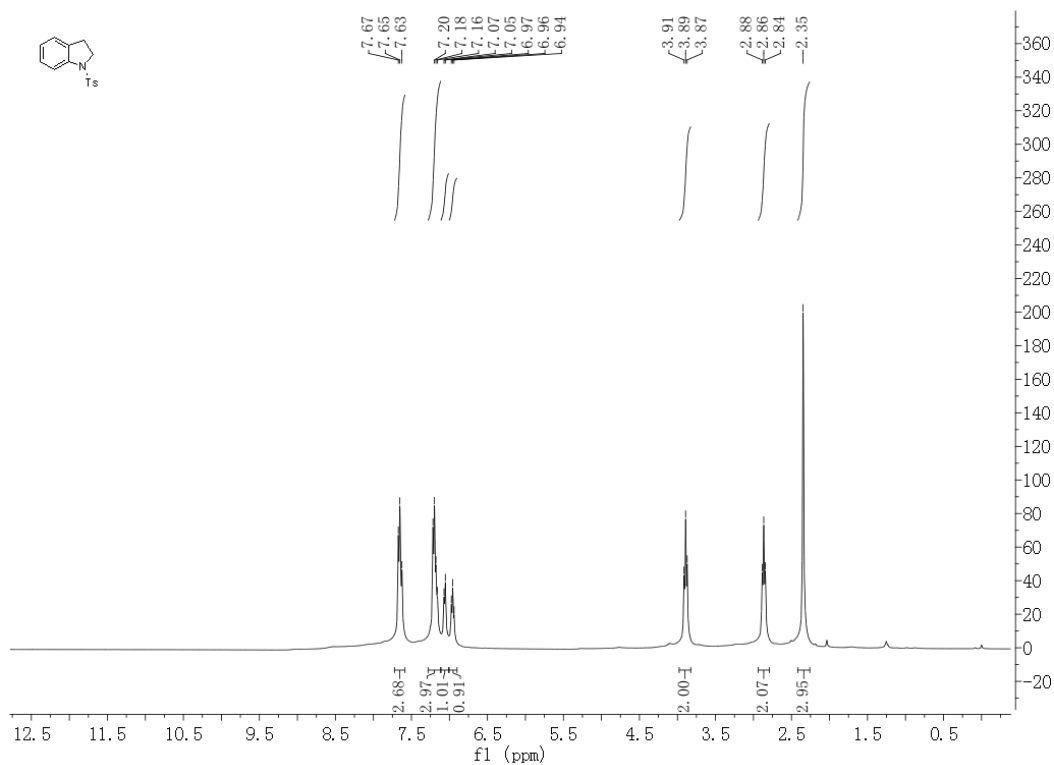
5-Chloroindoline



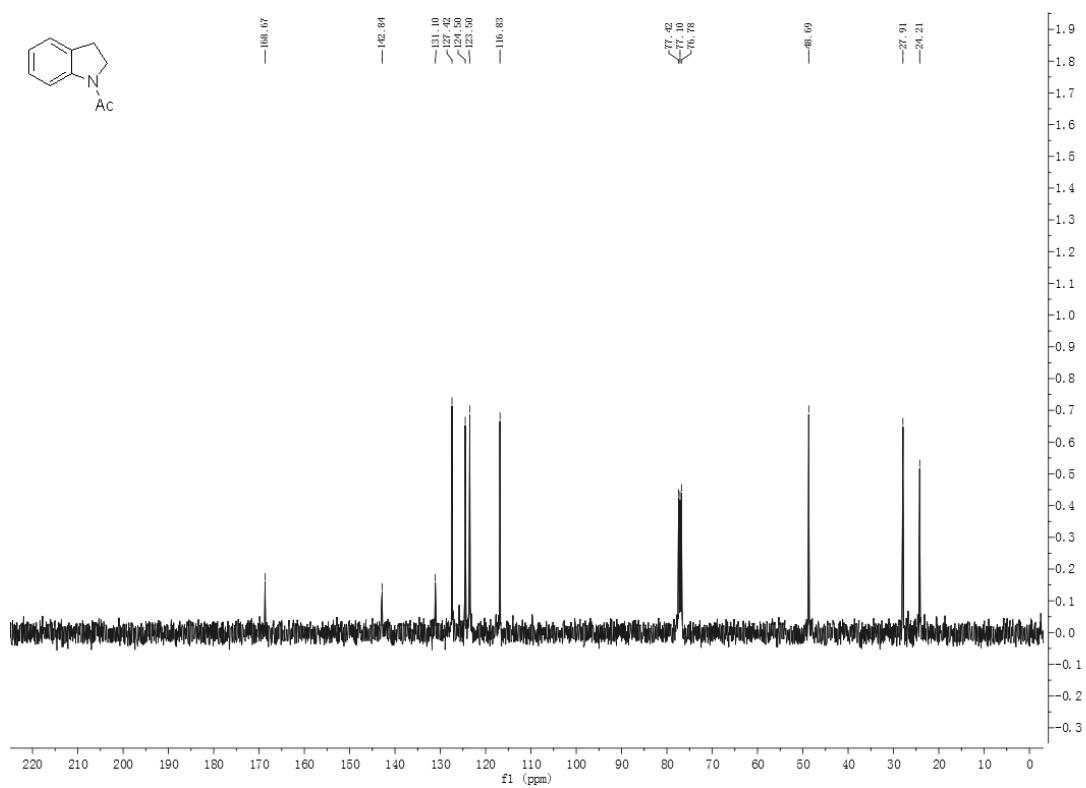
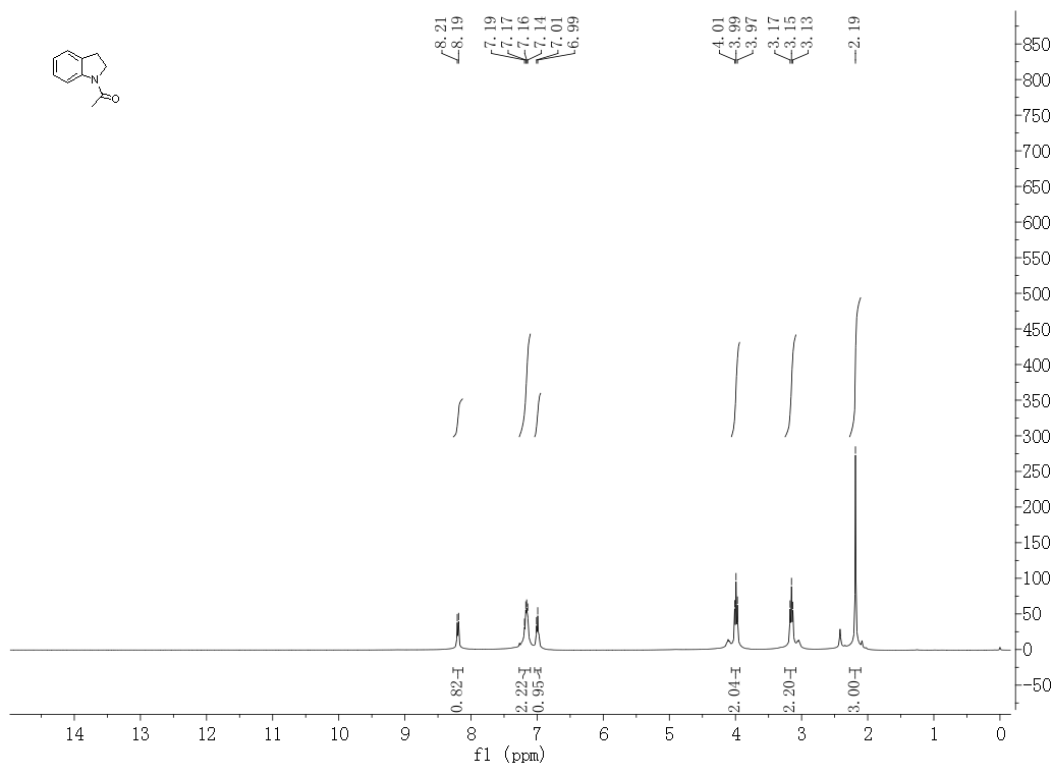
5-Bromoindoline



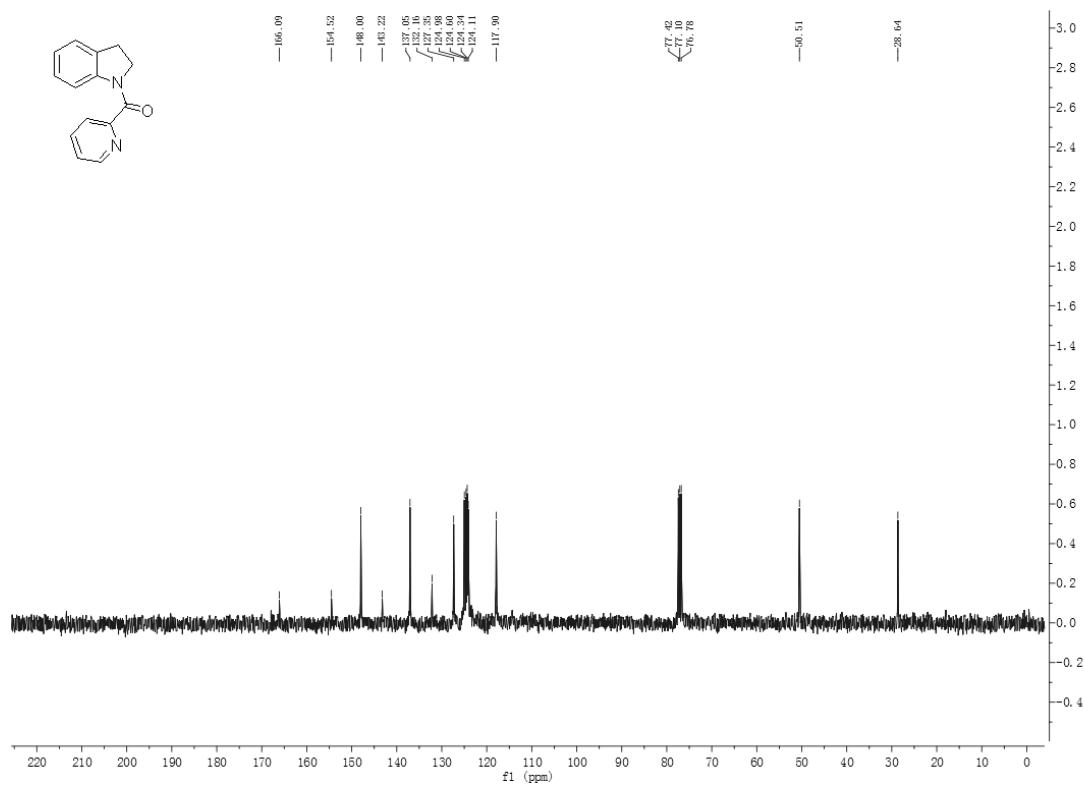
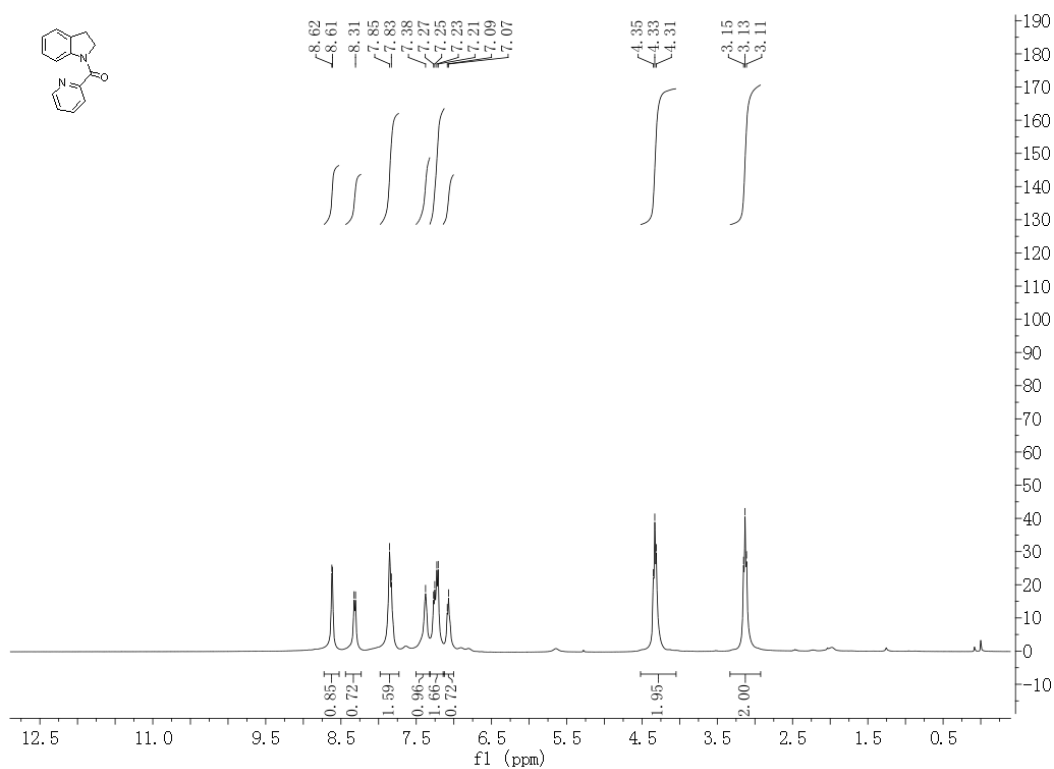
1-Tosylindoline (1a)



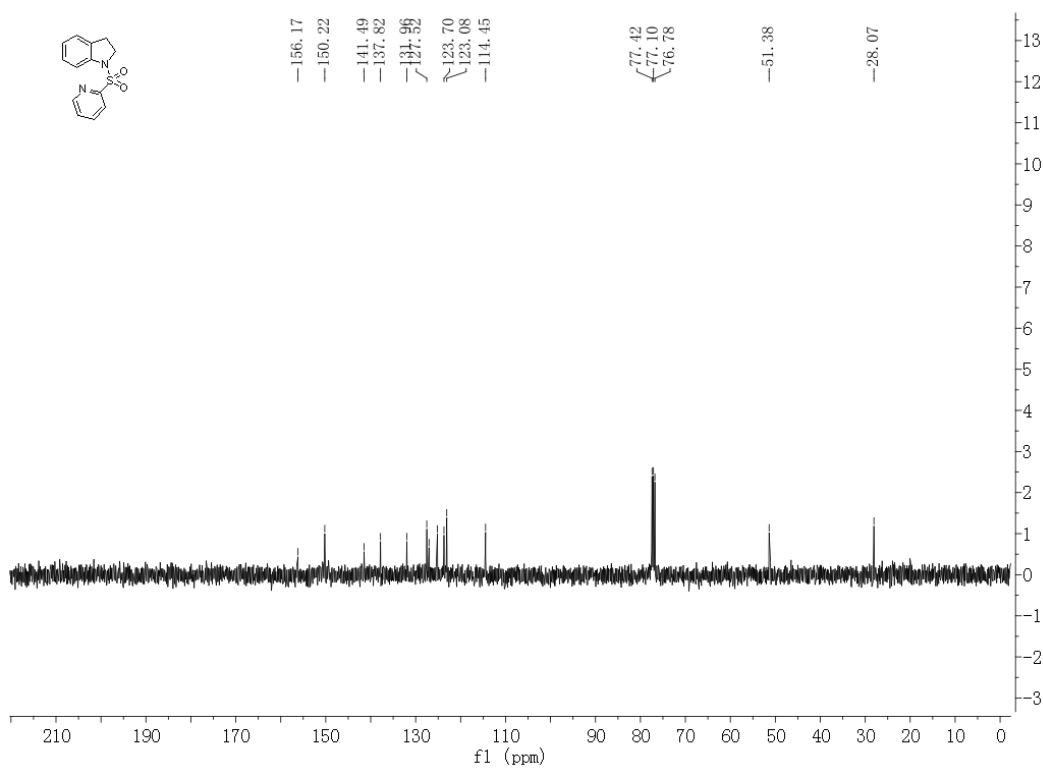
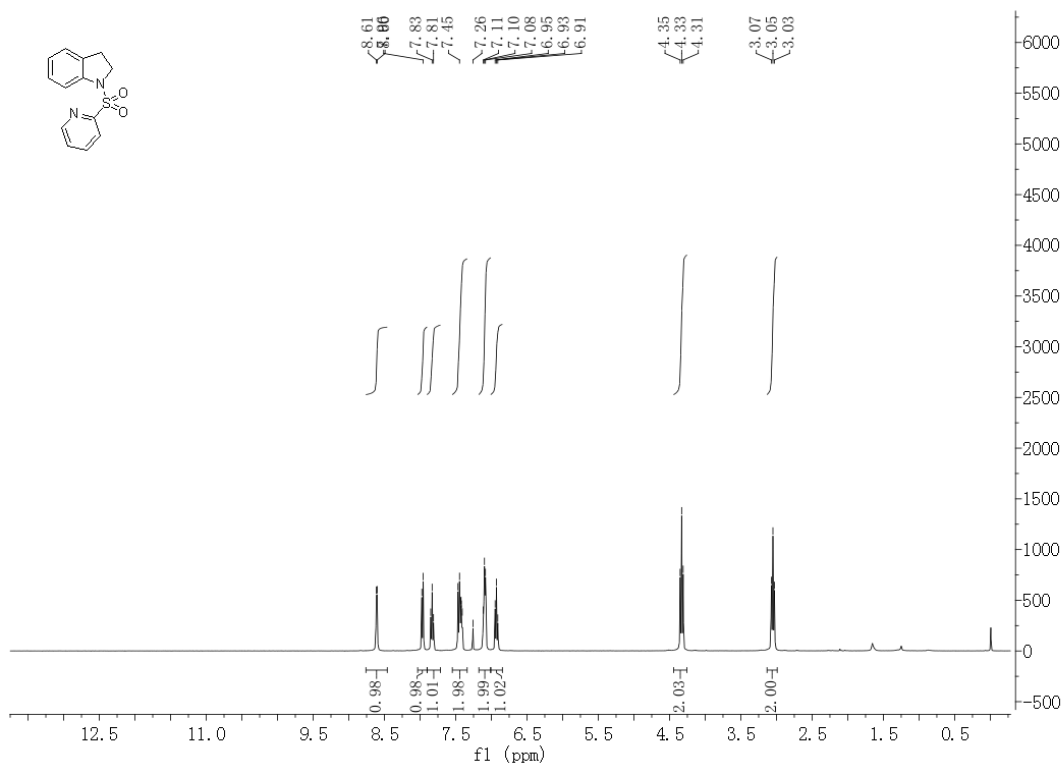
1-(Indolin-1-yl)ethanone (1b)



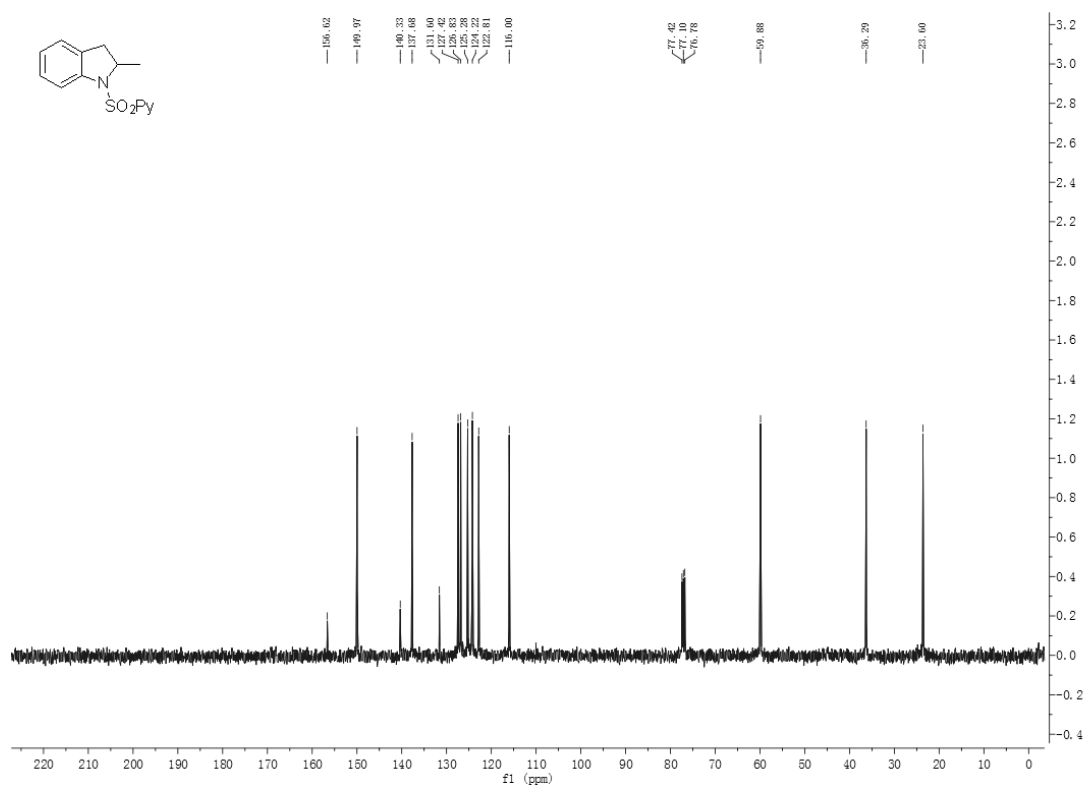
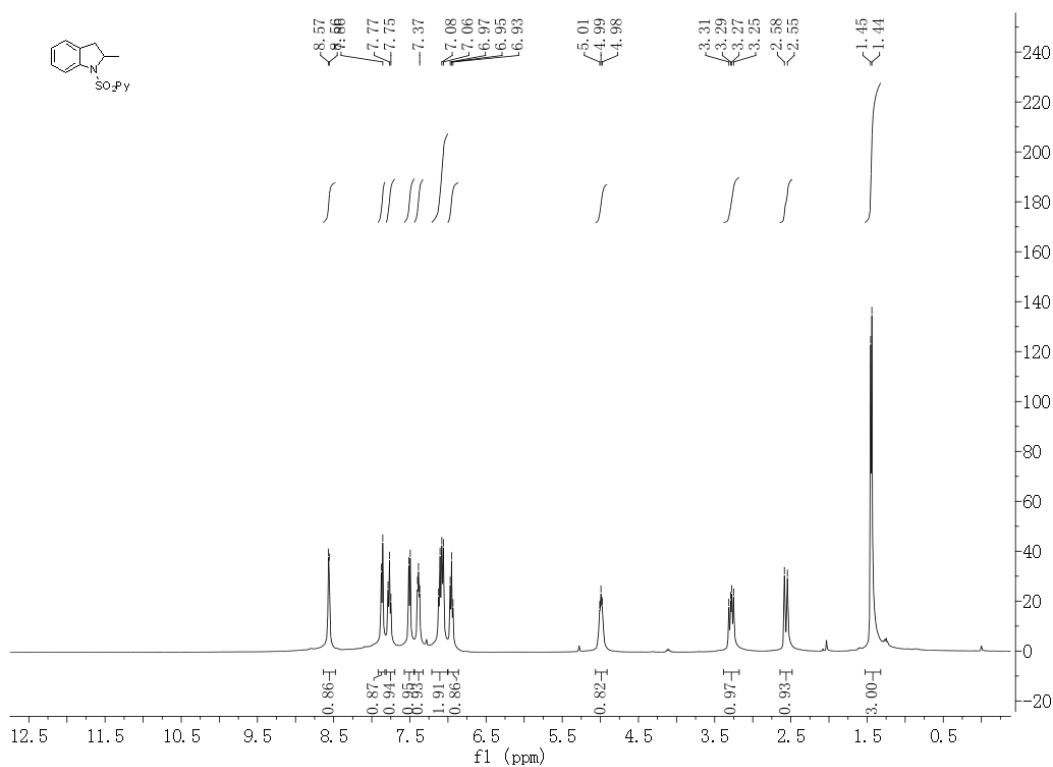
N-(2-Pyridyl) carbonyl indoline (1c)



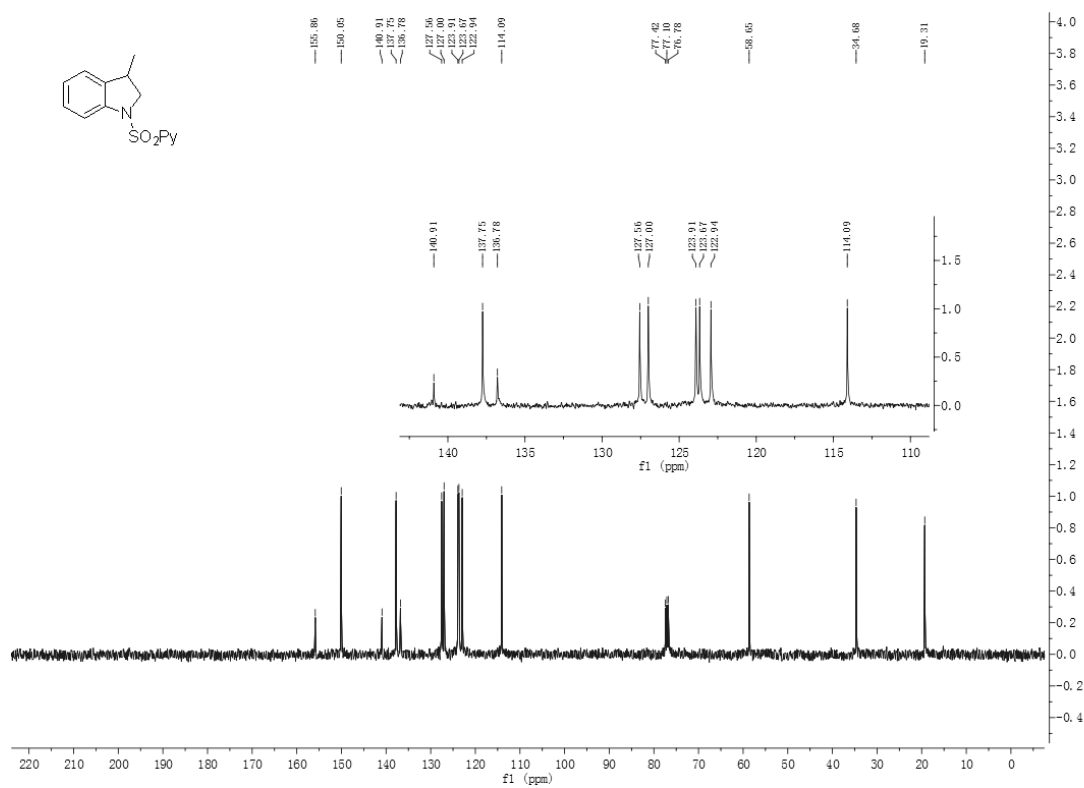
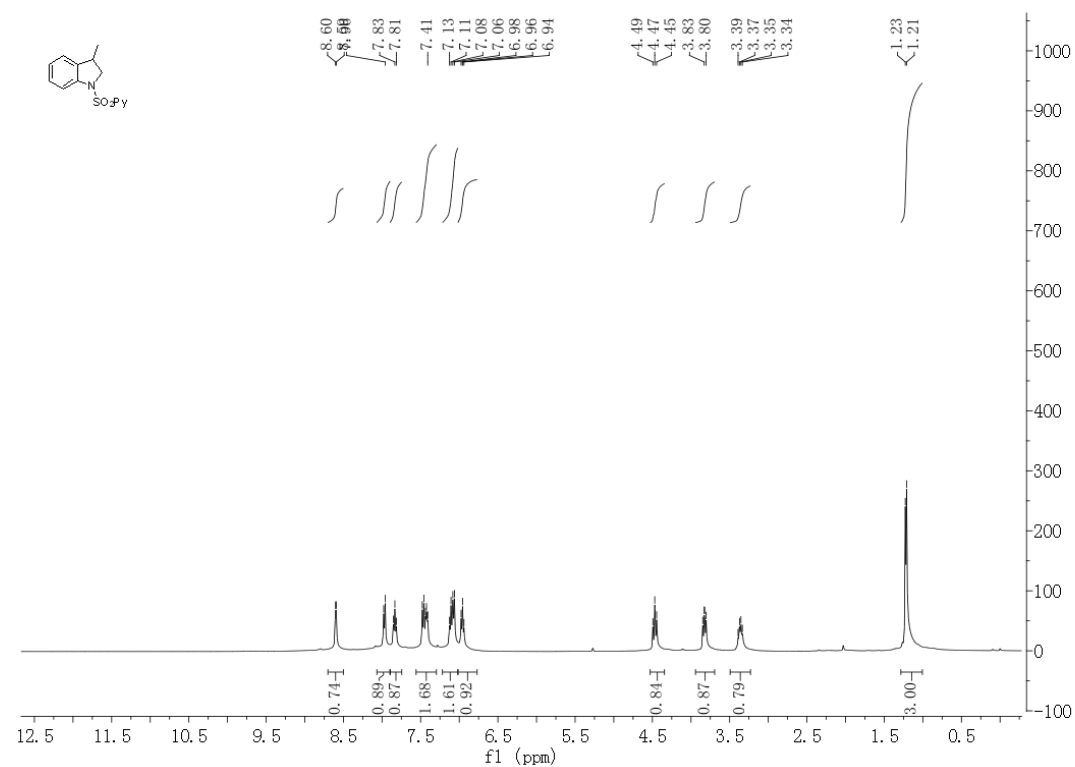
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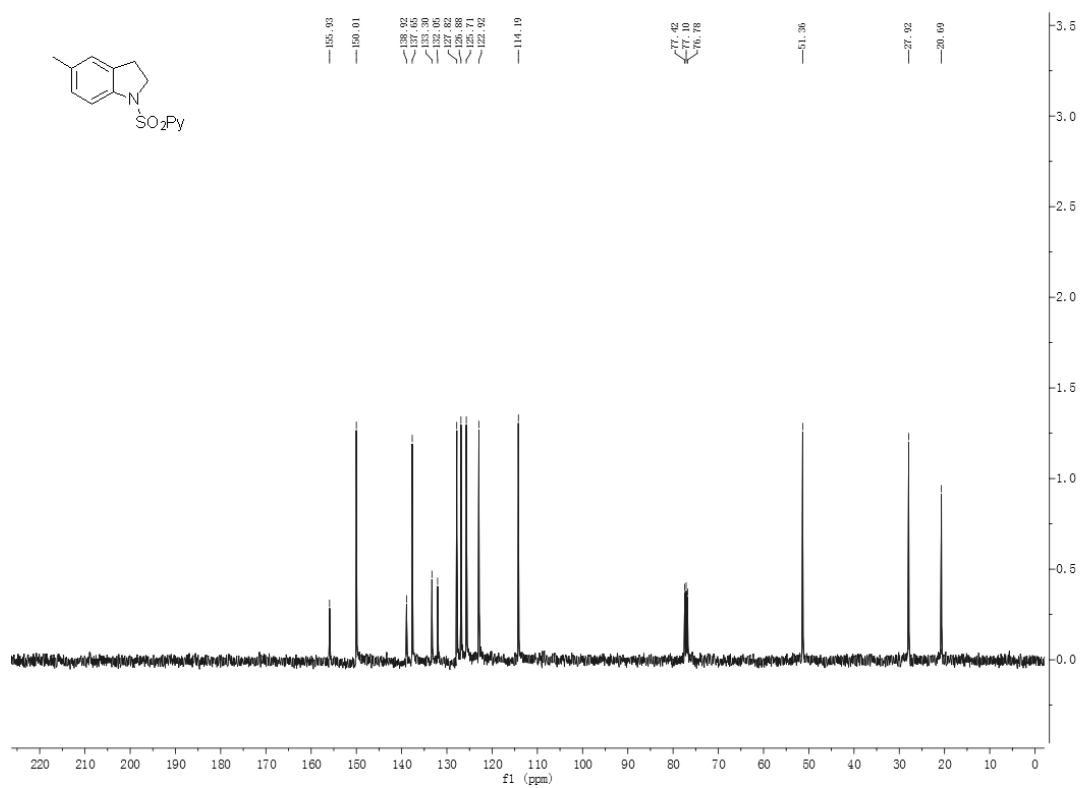
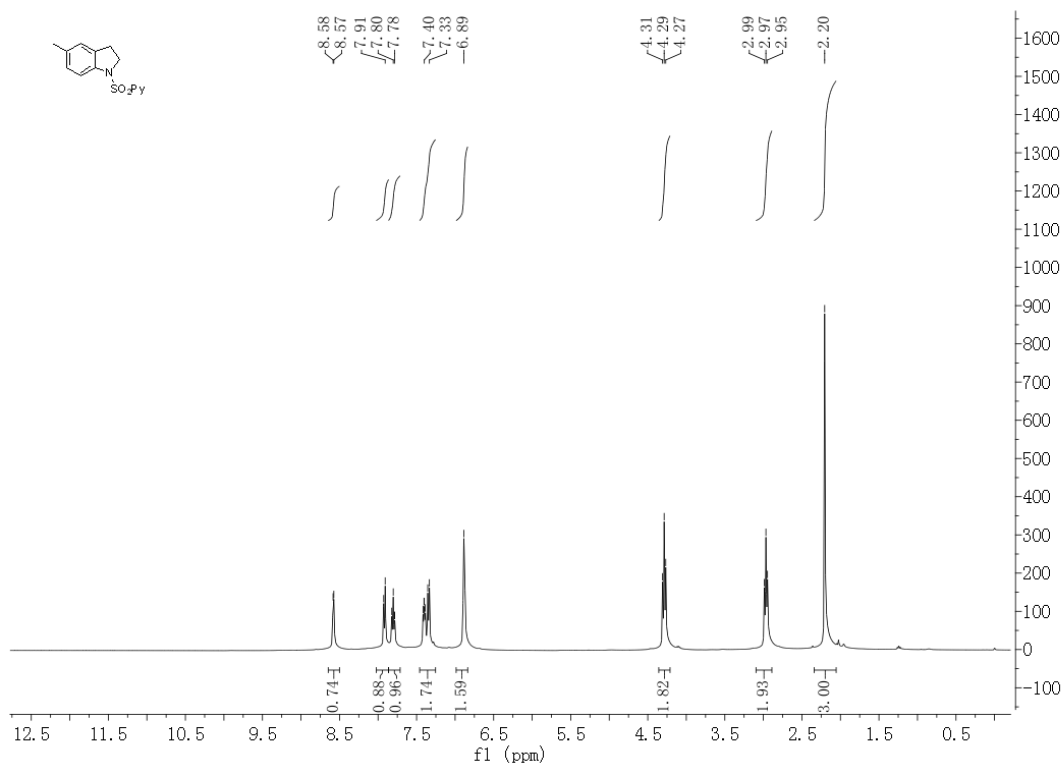
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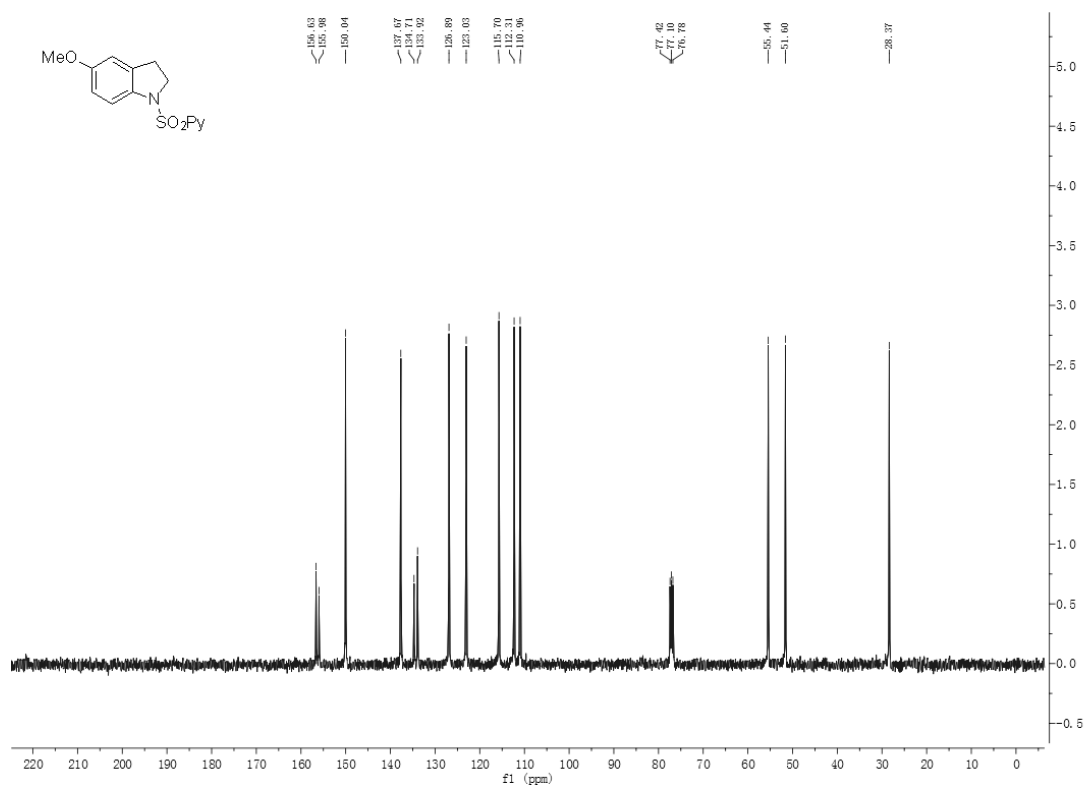
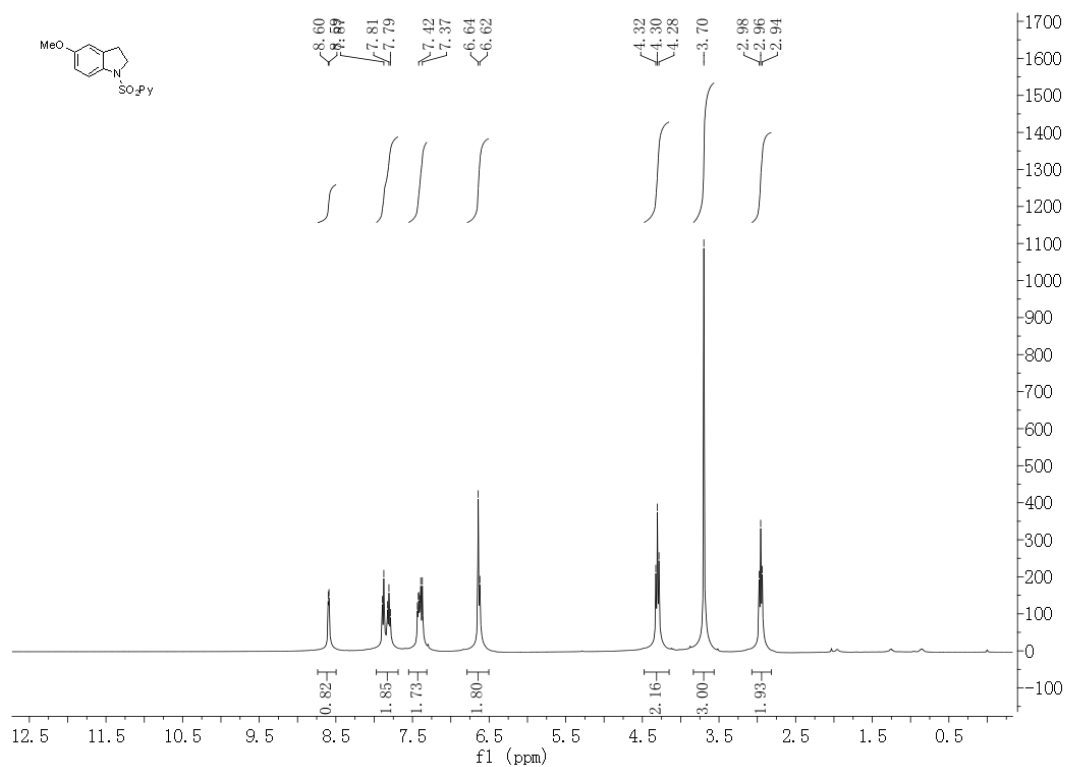
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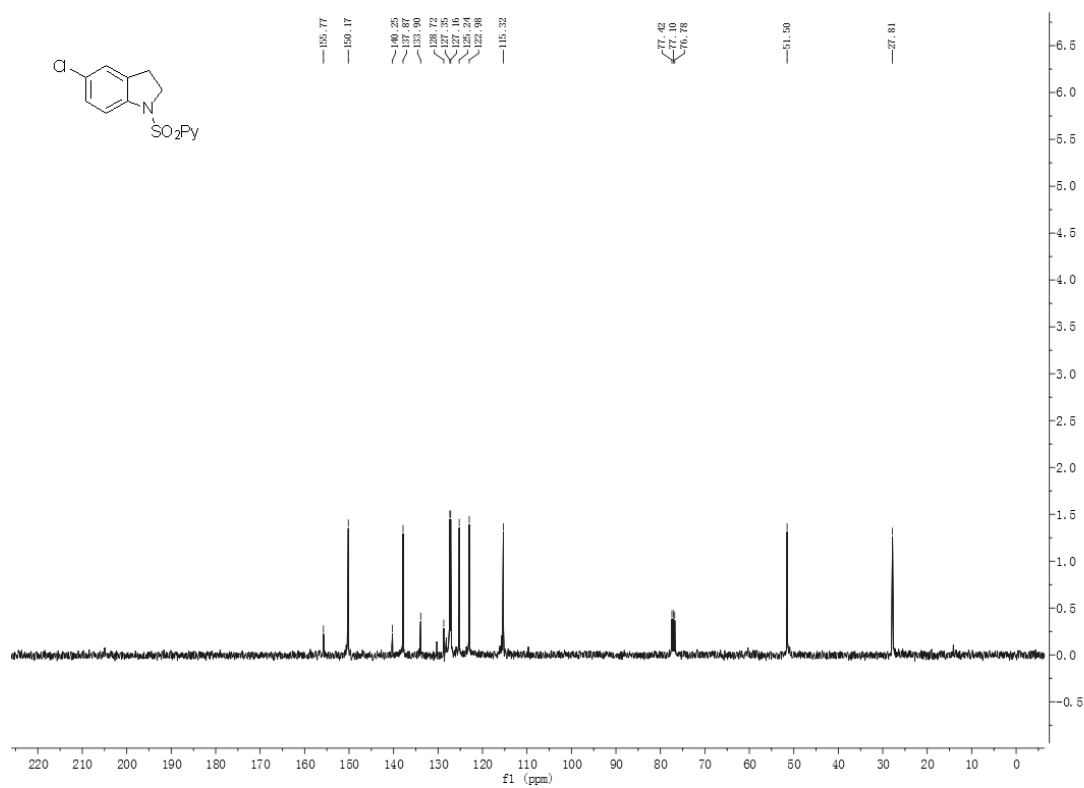
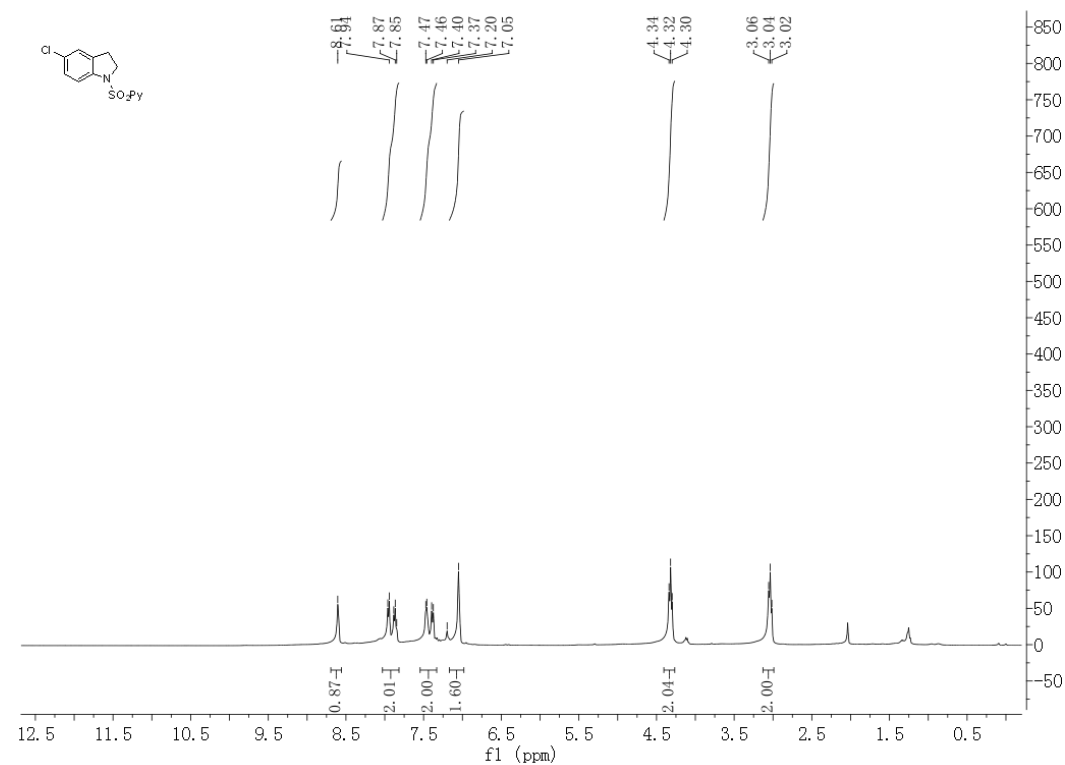
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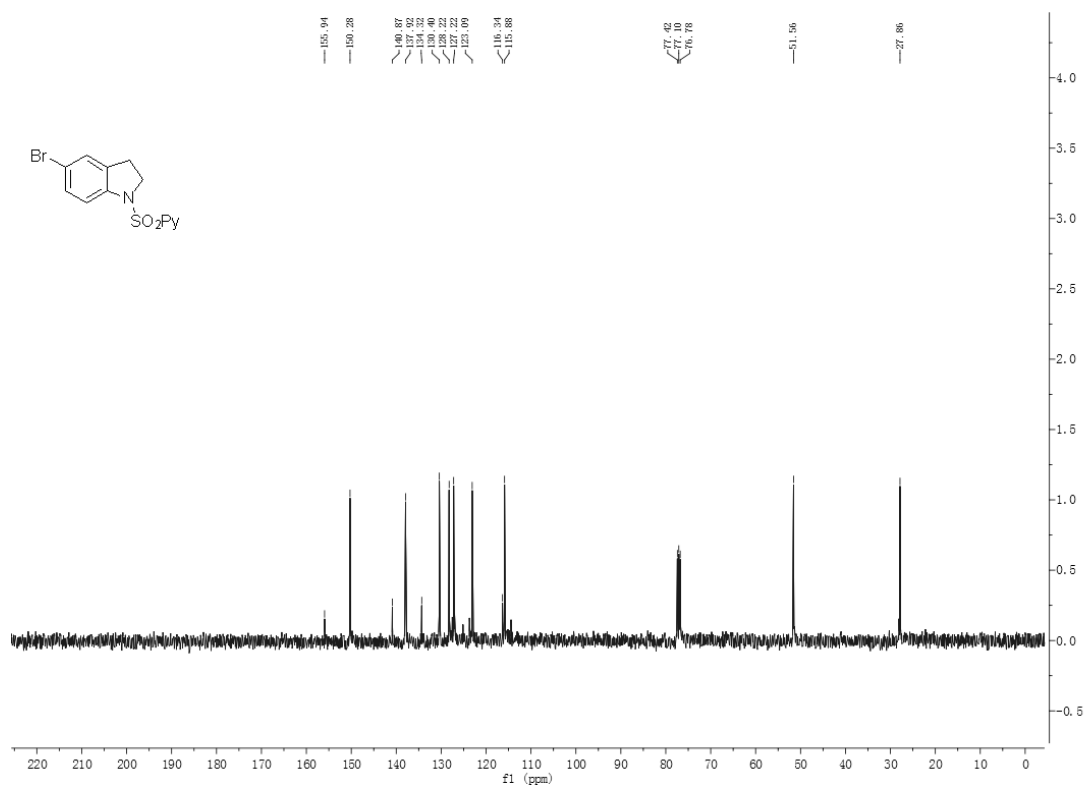
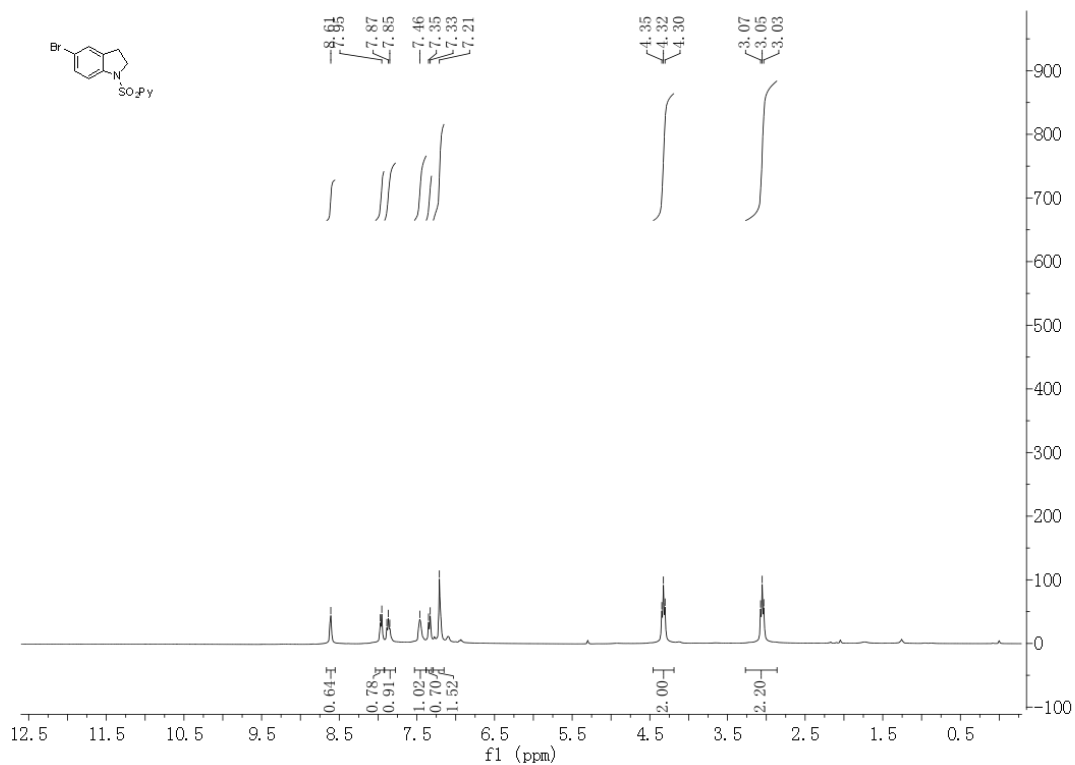
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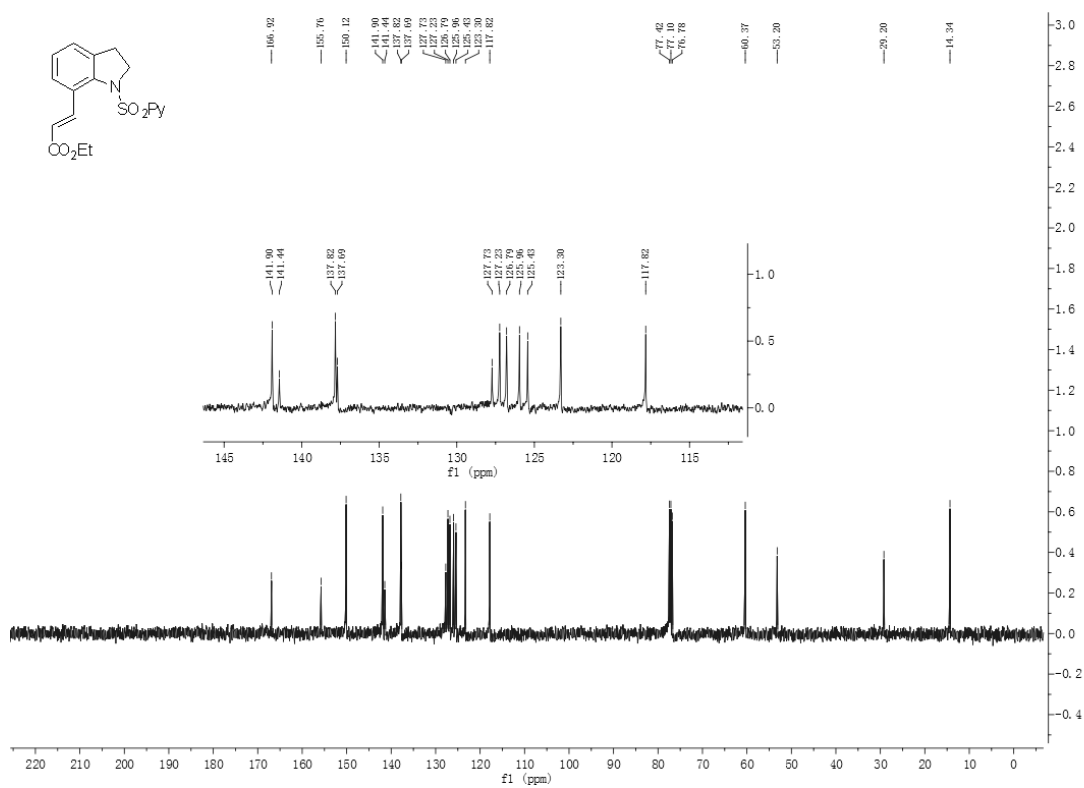
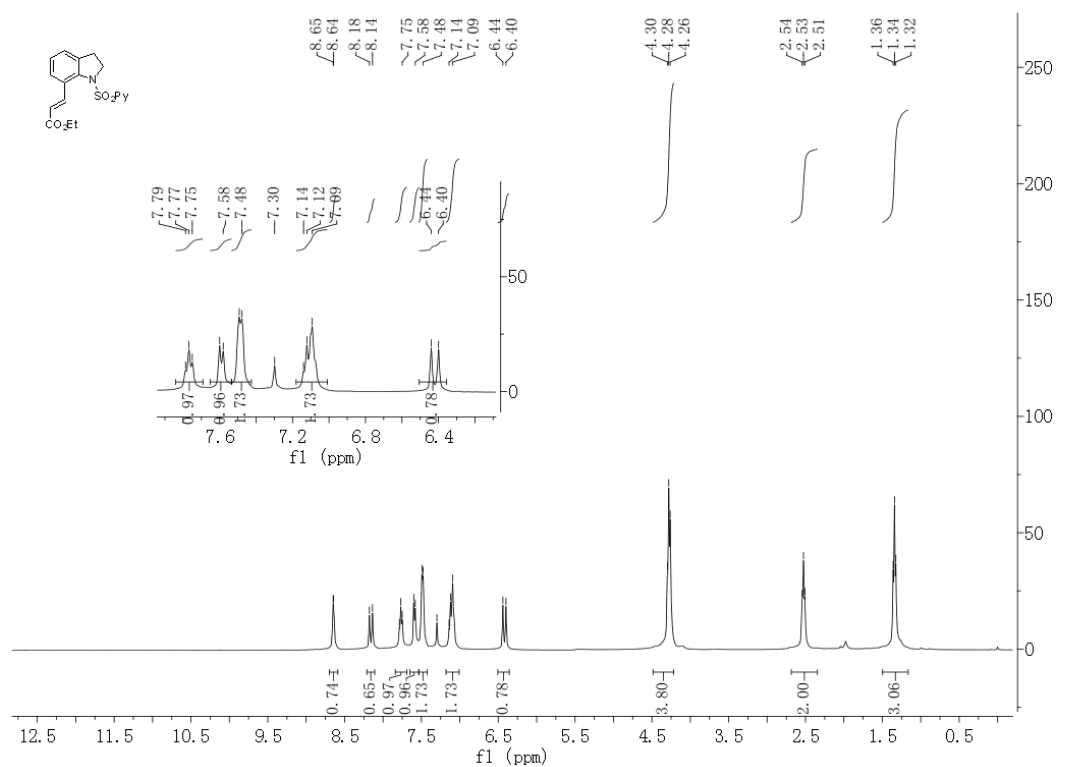
5-Chloro-1-(pyridin-2-ylsulfonyl)indoline



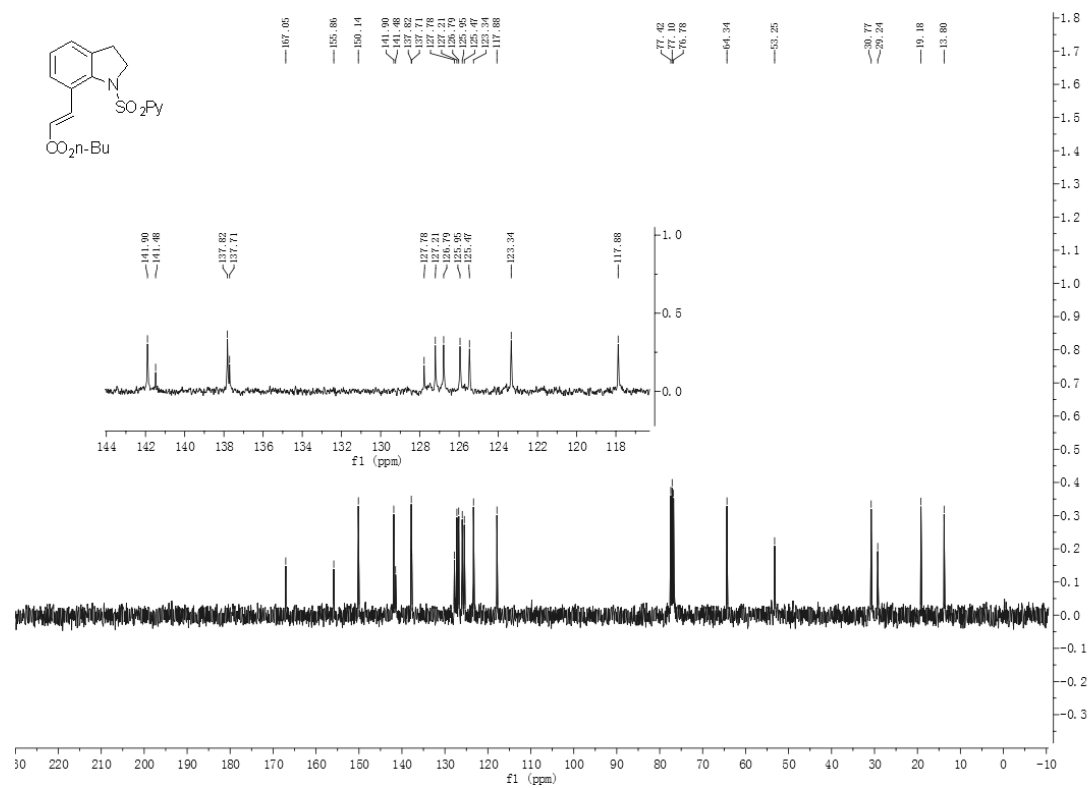
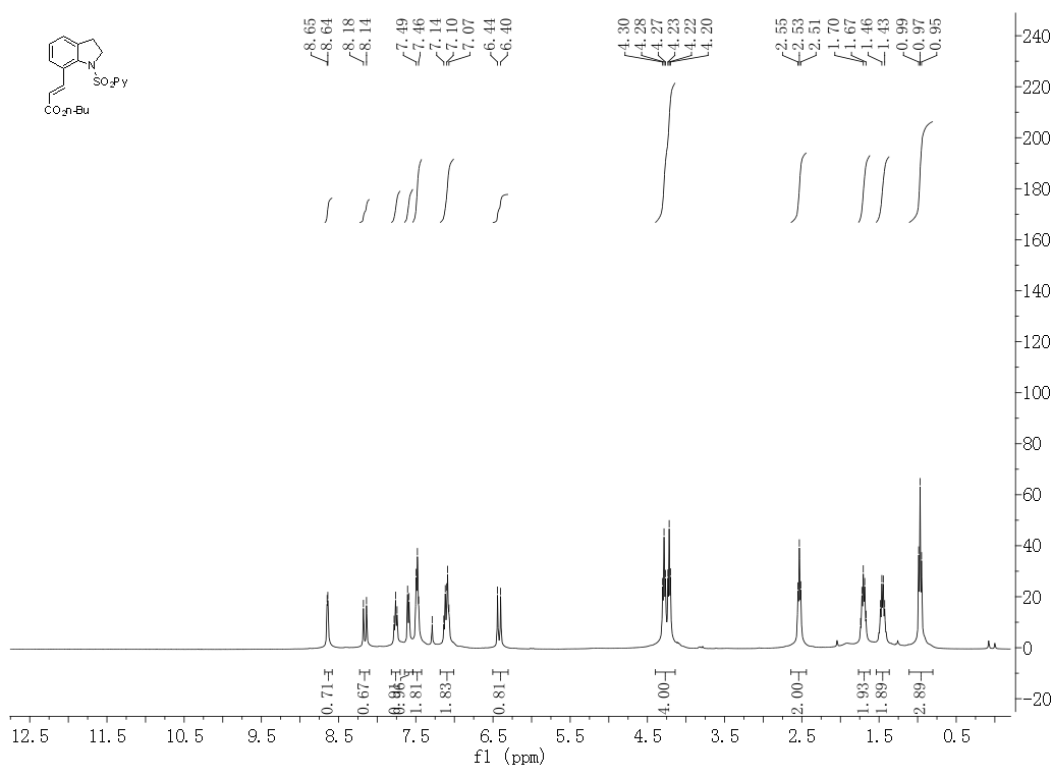
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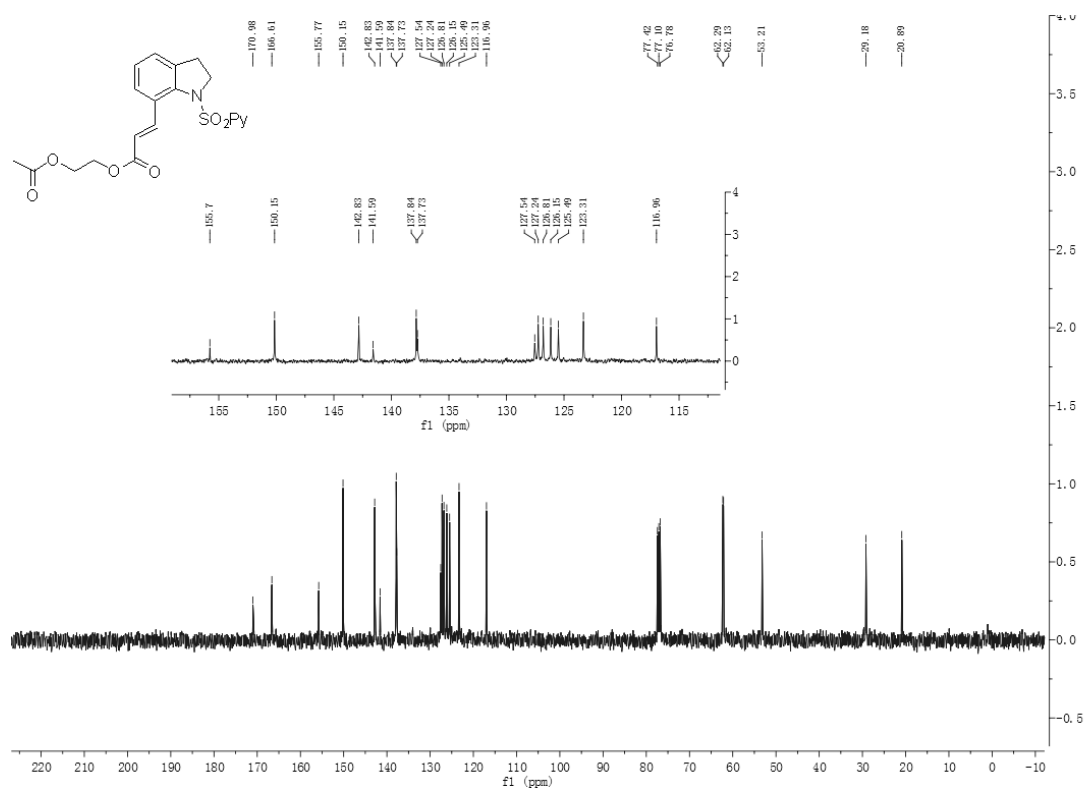
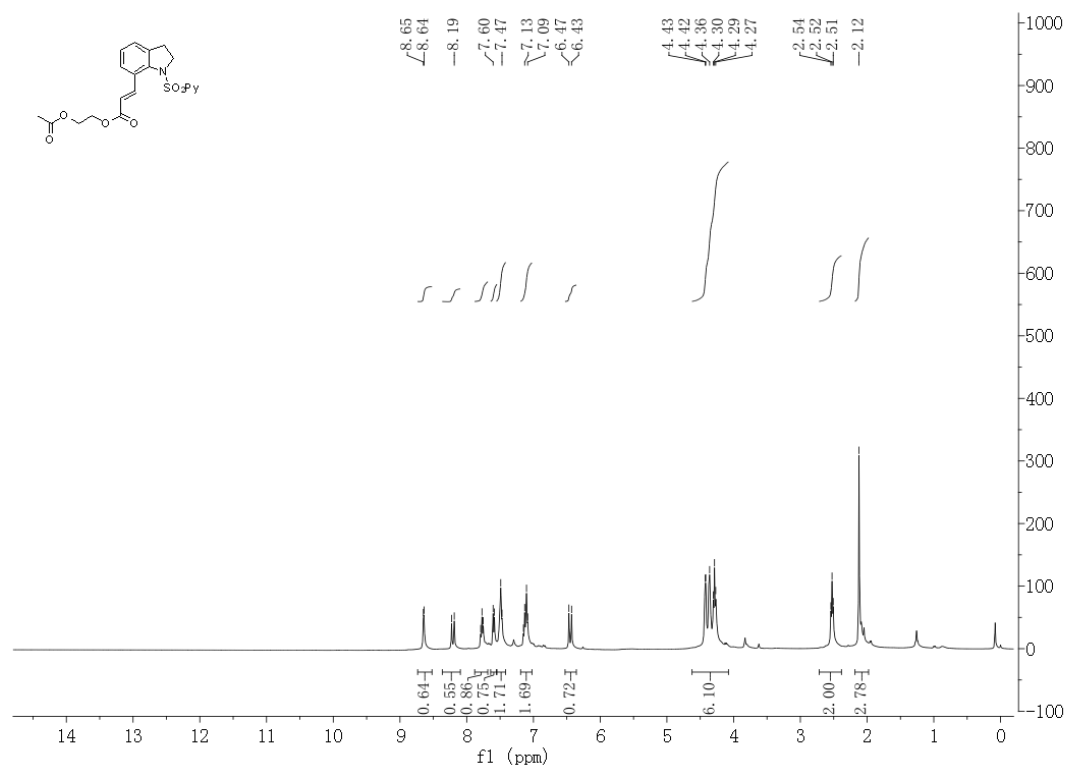
(E)-Ethyl 3-(1-(pyridin-2-ylsulfonyl)indolin-7-yl)acrylate (3da)



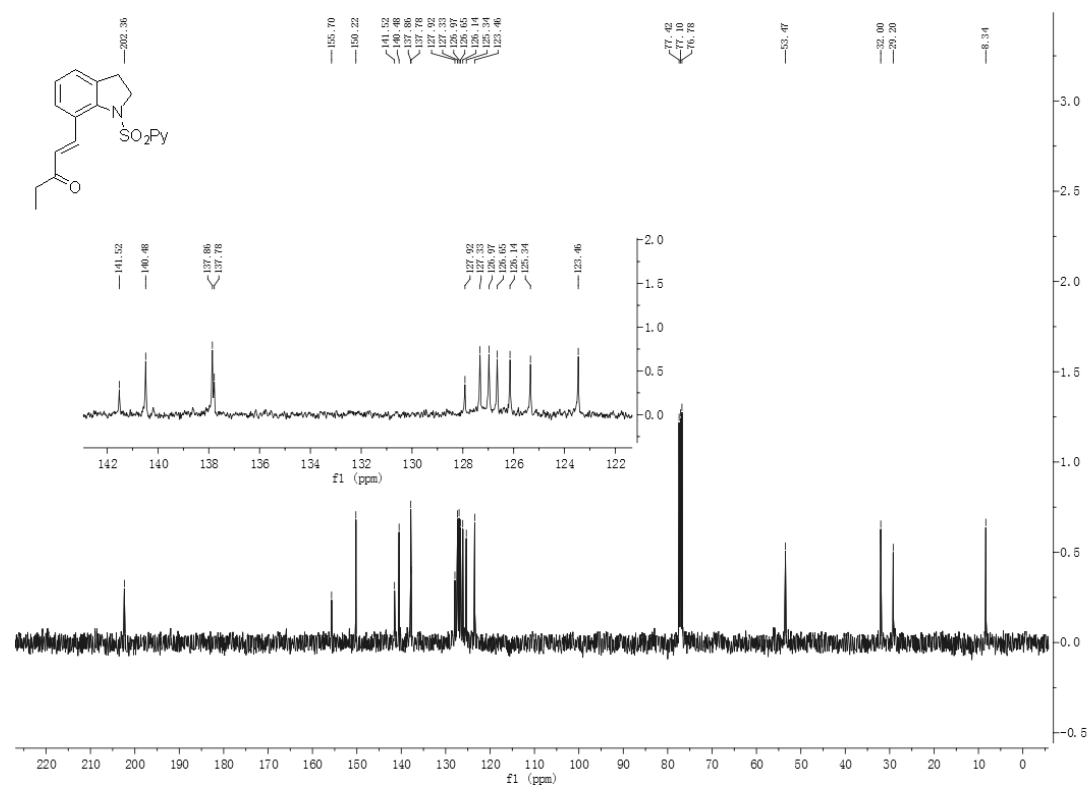
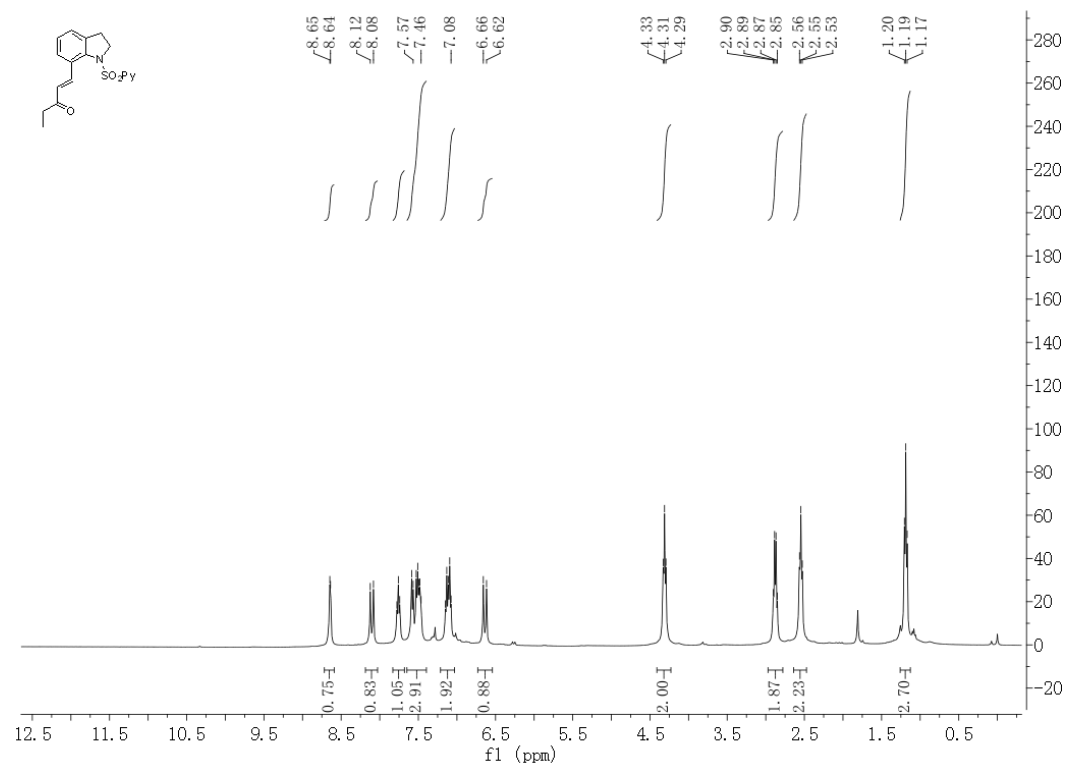
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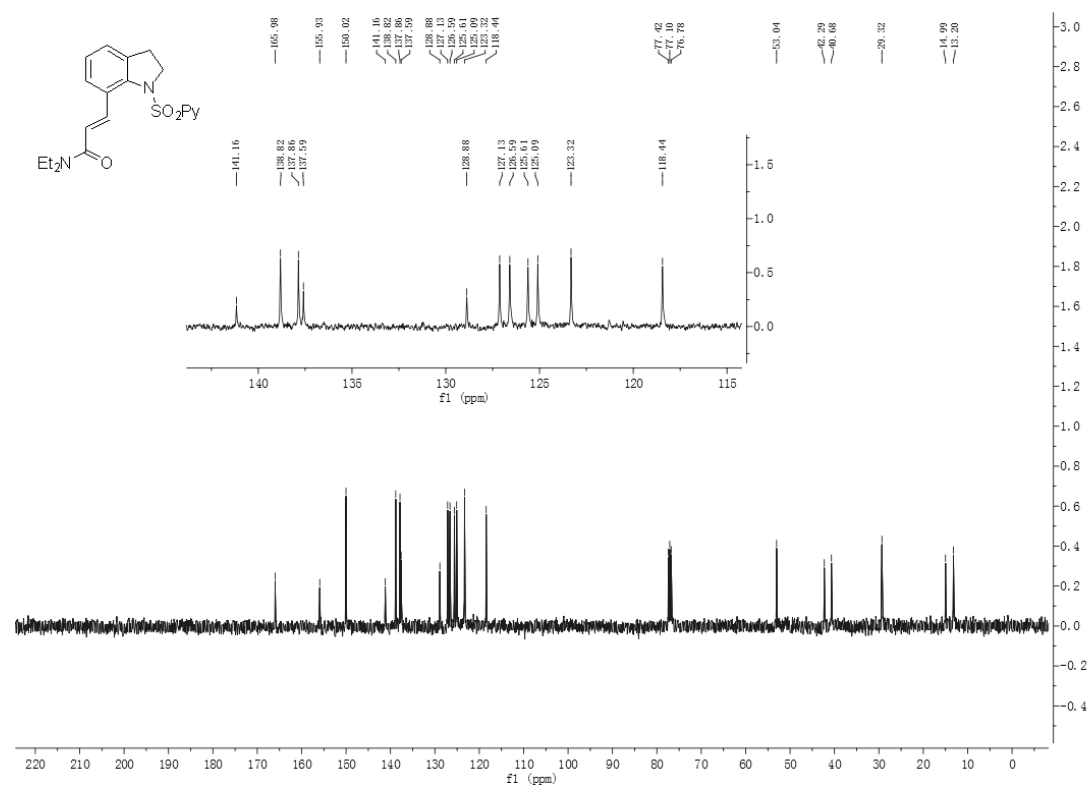
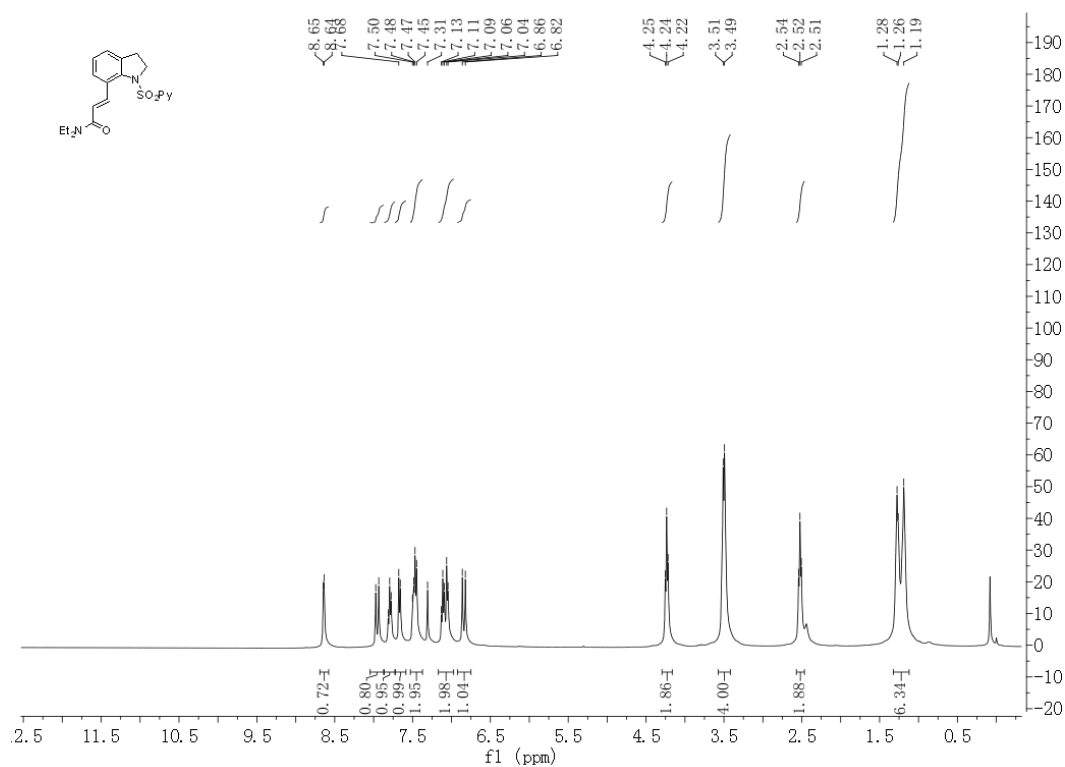
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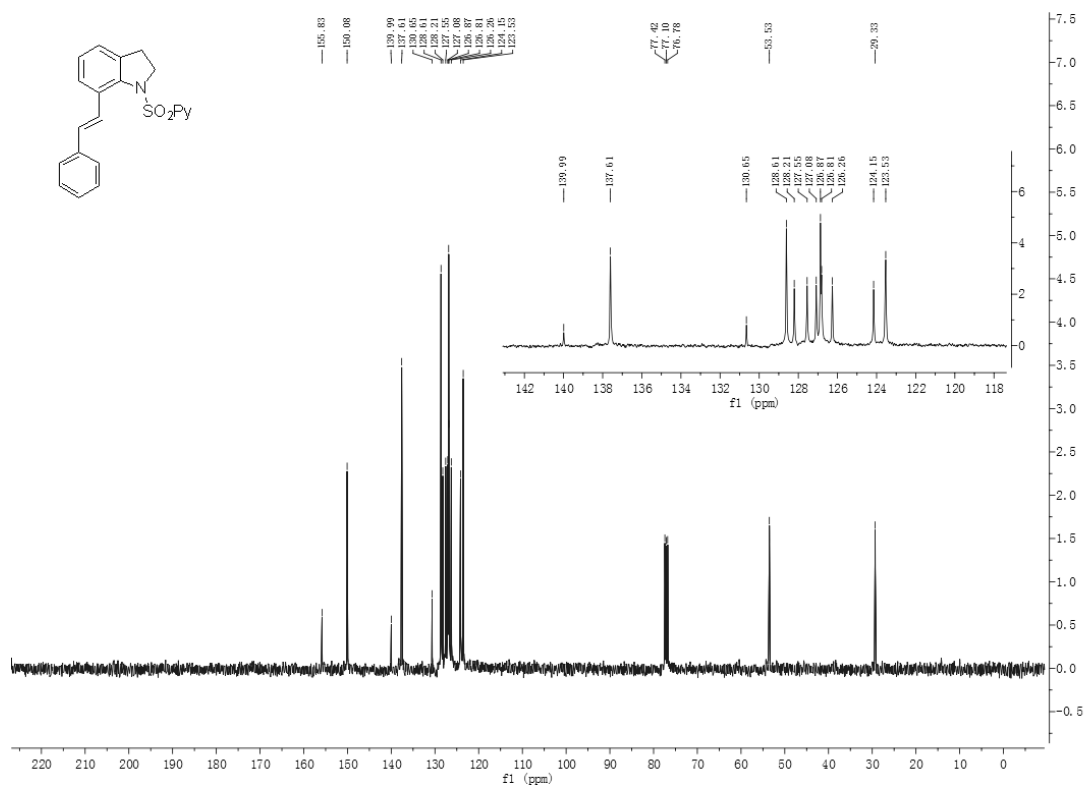
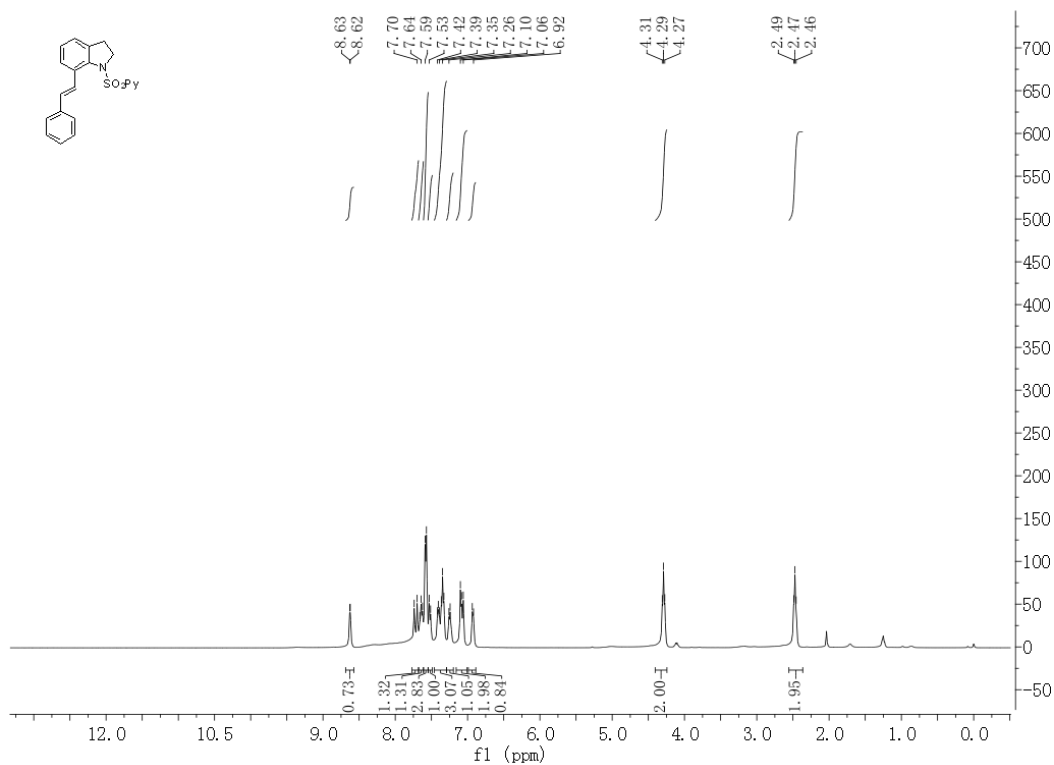
(E)-1-(1-(Pyridin-2-ylsulfonyl)indolin-7-yl)pent-1-en-3-one (3dd)



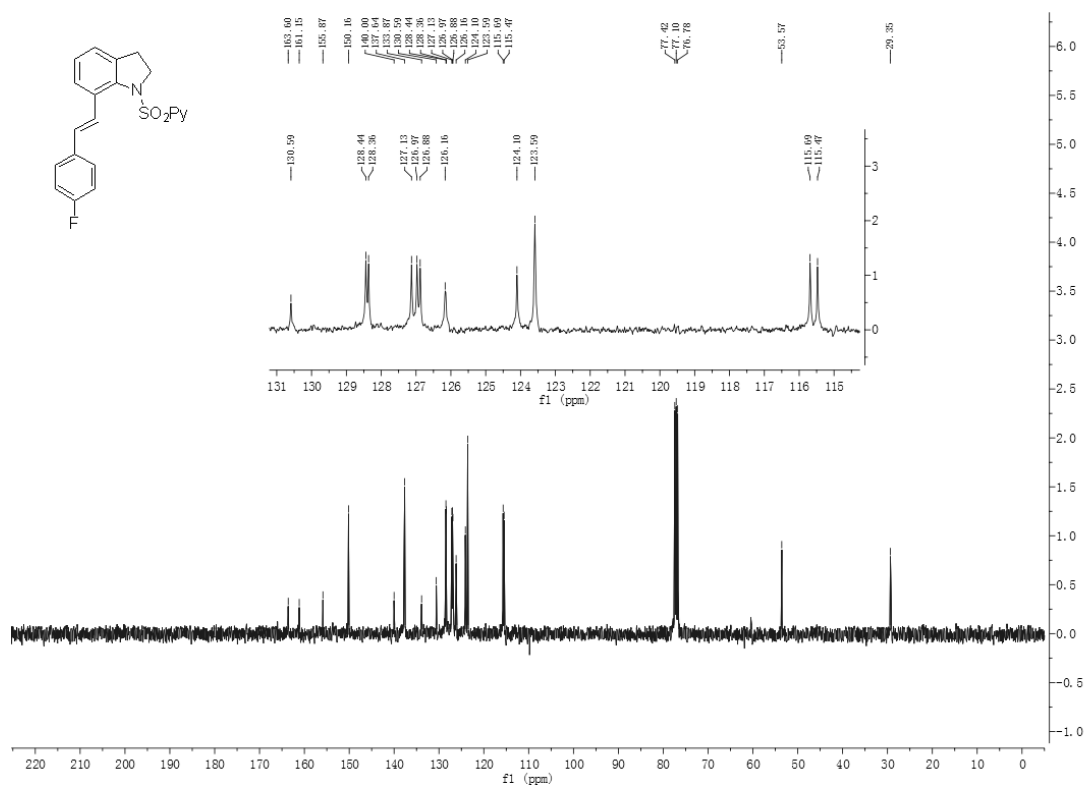
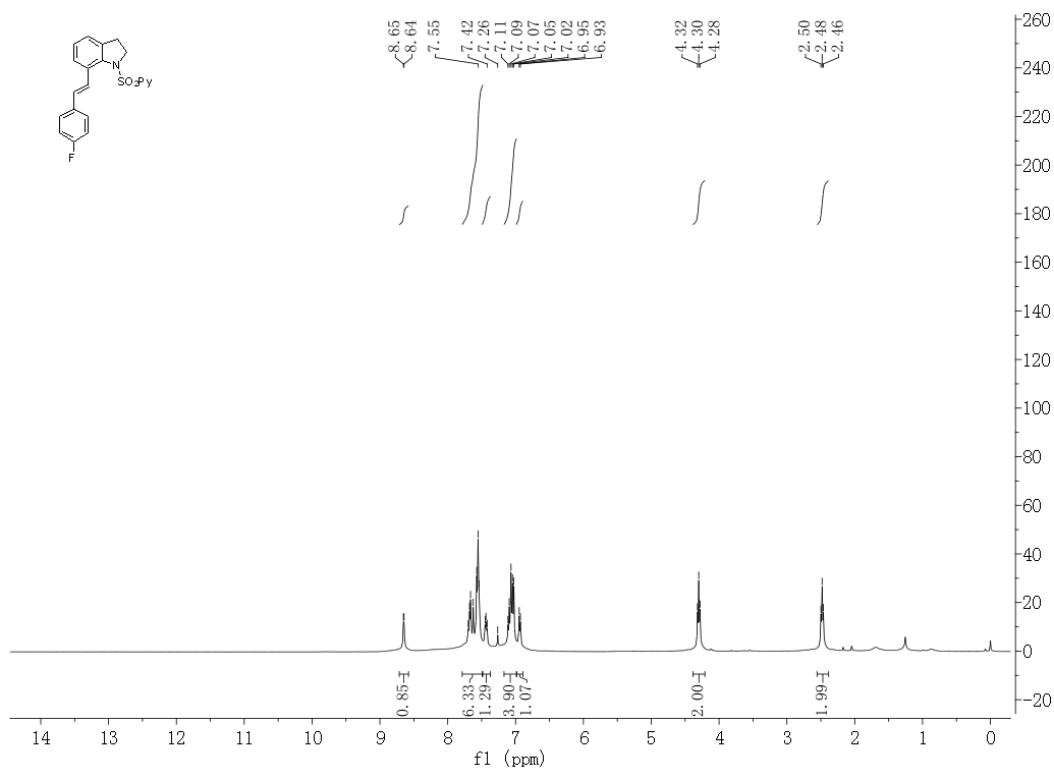
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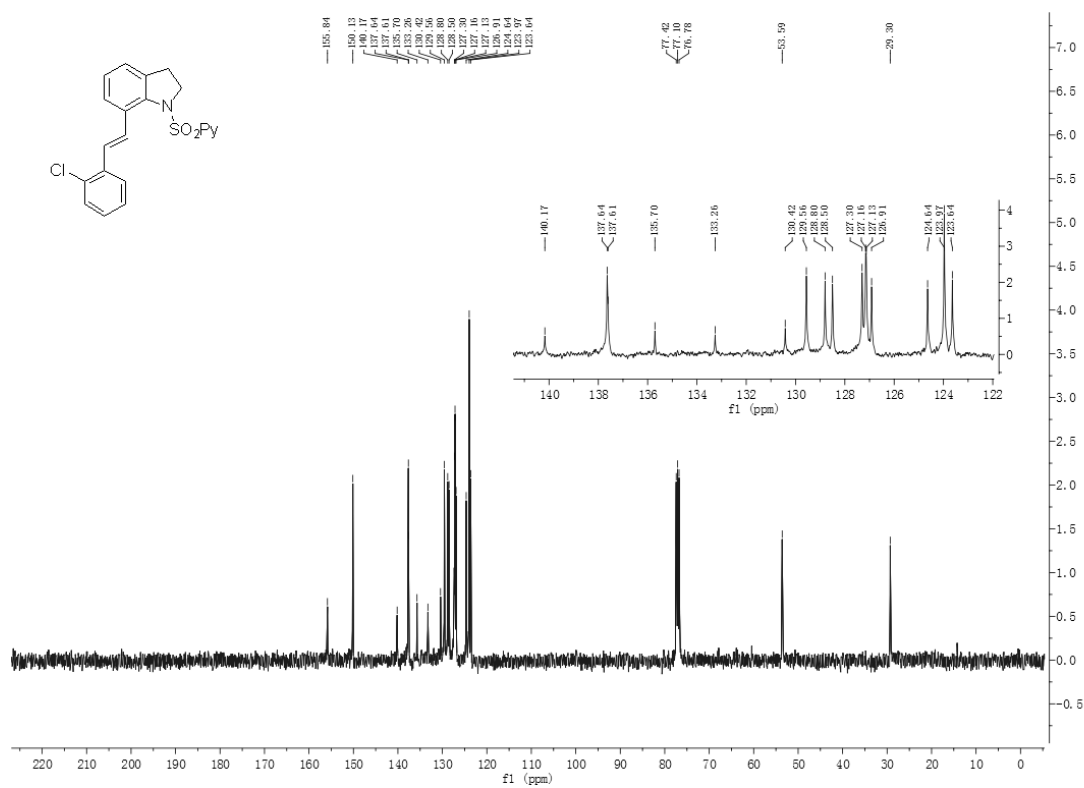
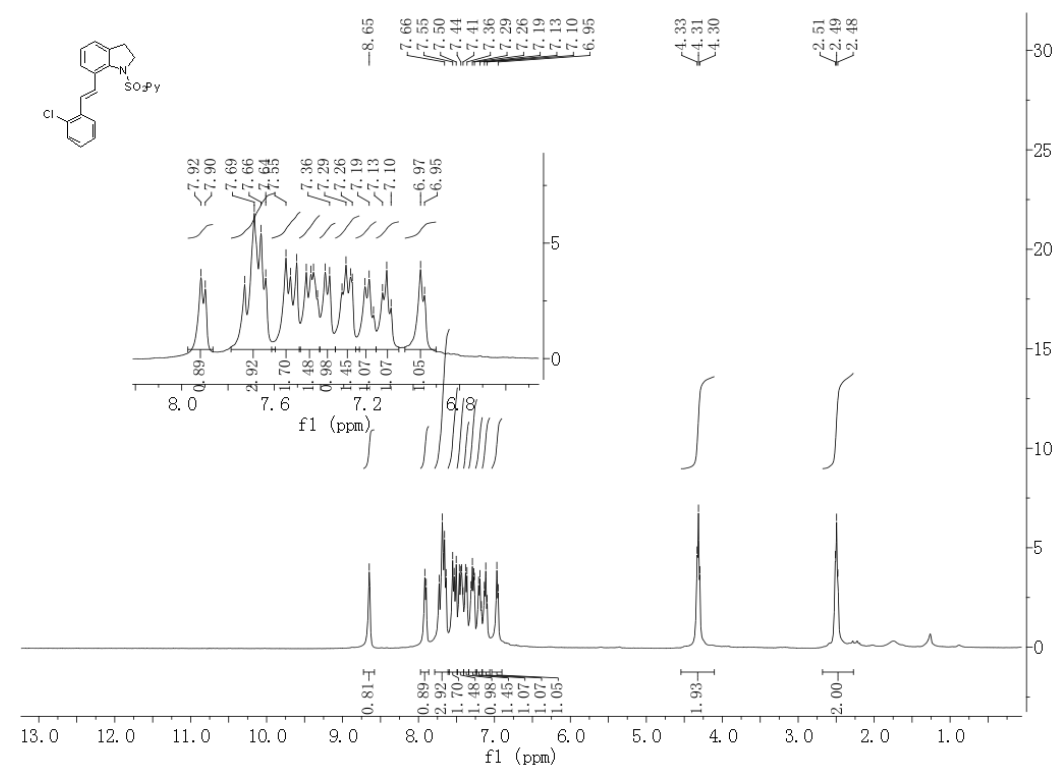
(E)-1-(Pyridin-2-ylsulfonyl)-7-styrylindoline (3df)



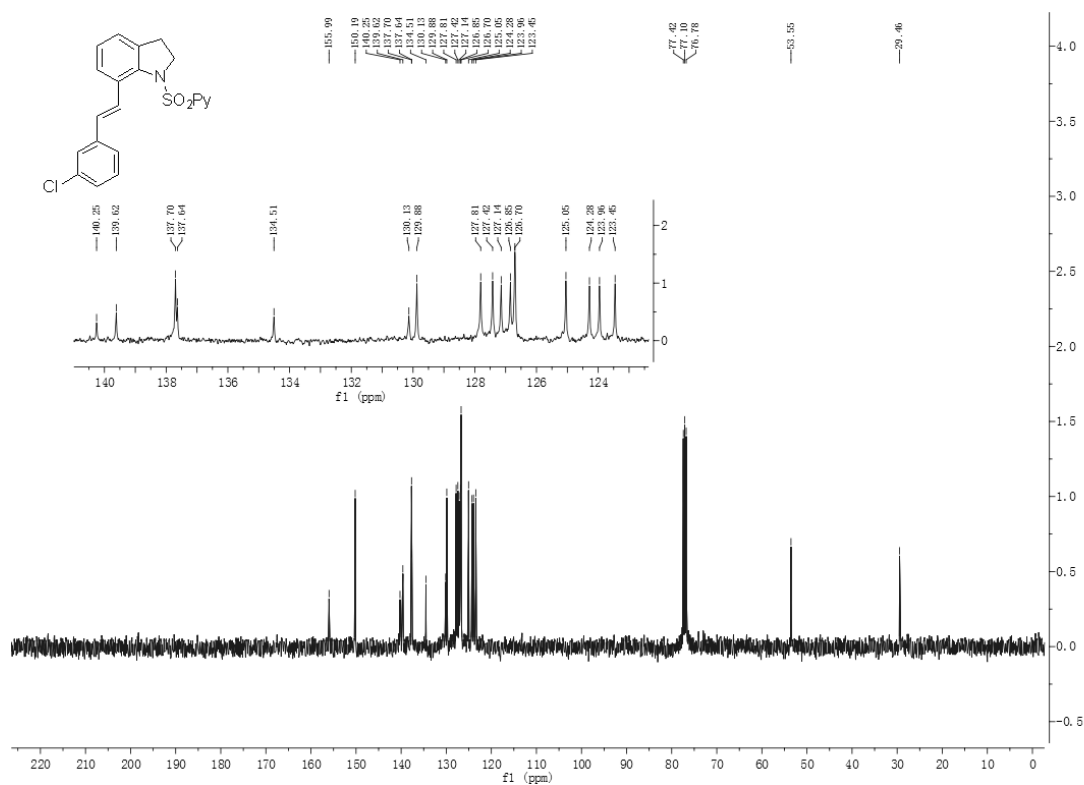
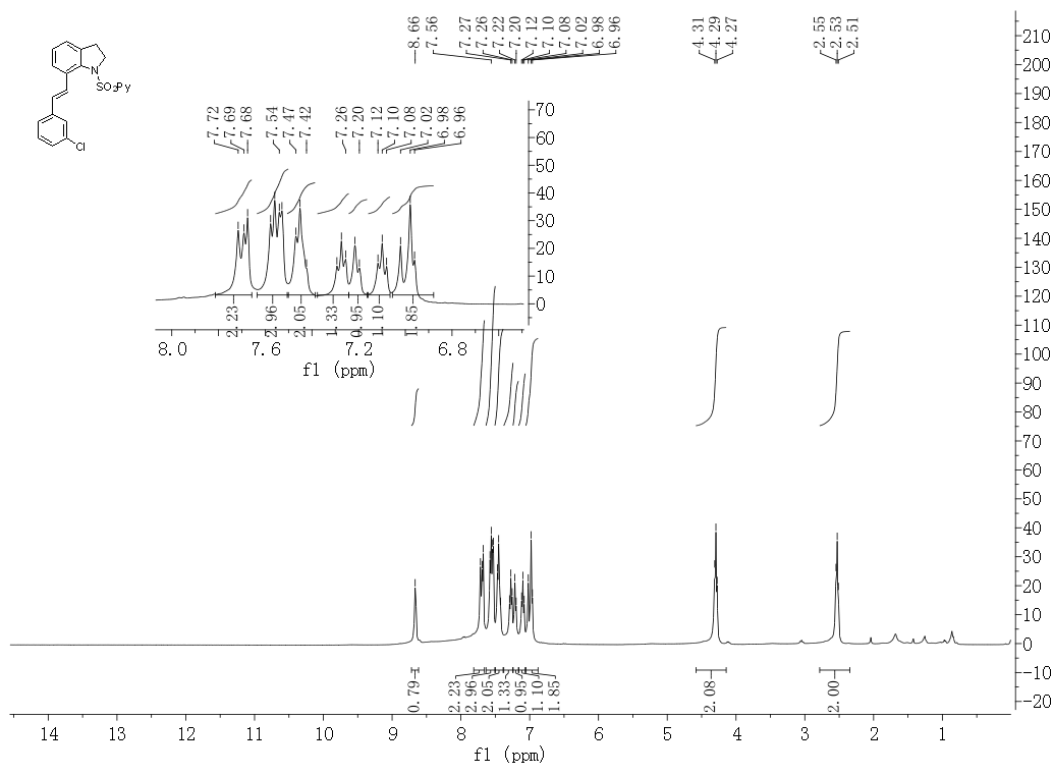
(E)-7-(4-Fluorostyryl)-1-(pyridin-2-ylsulfonyl)indoline (3dg)



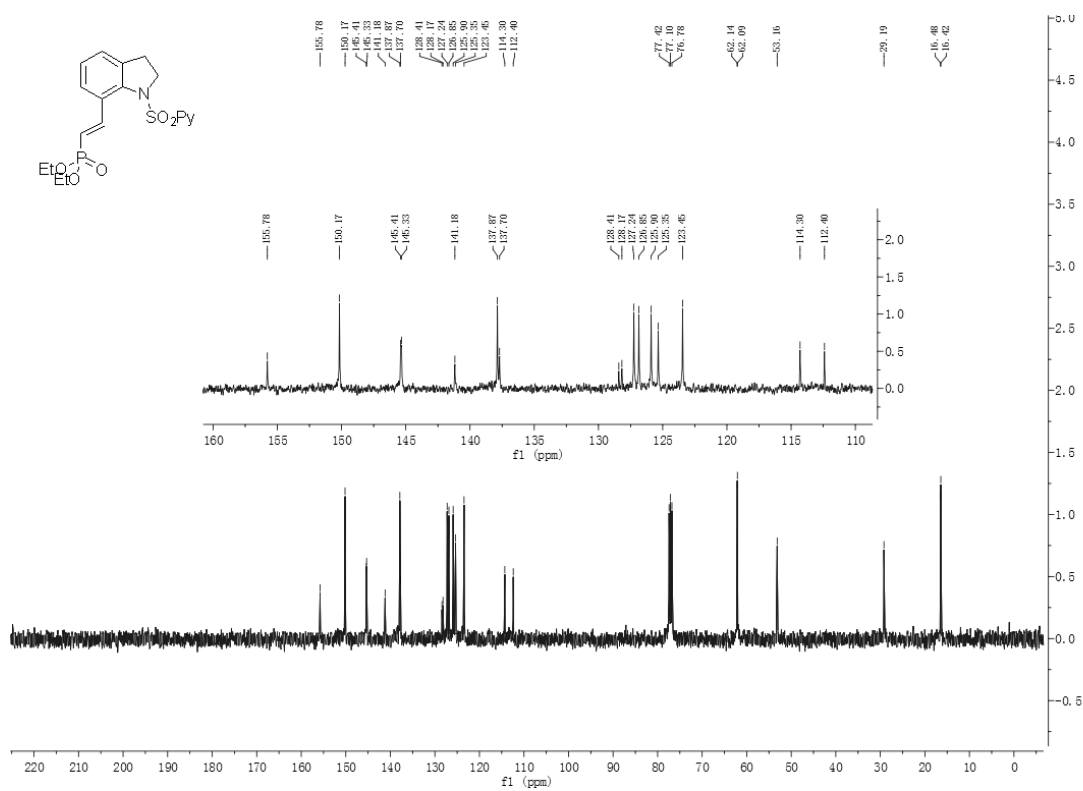
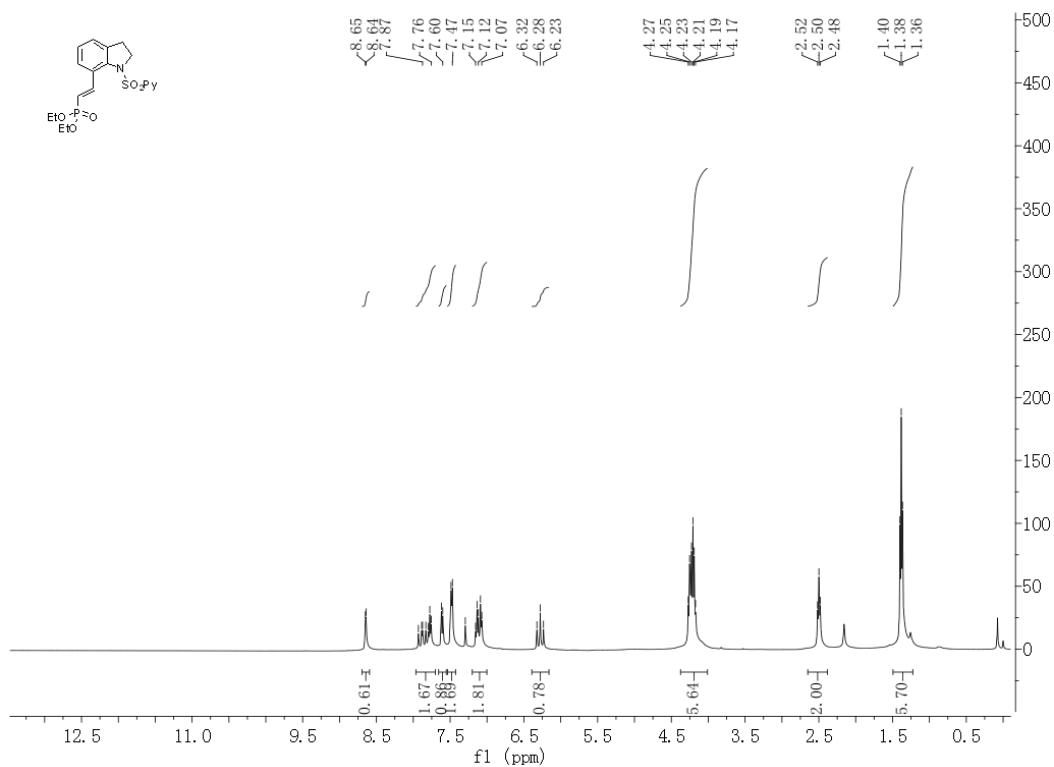
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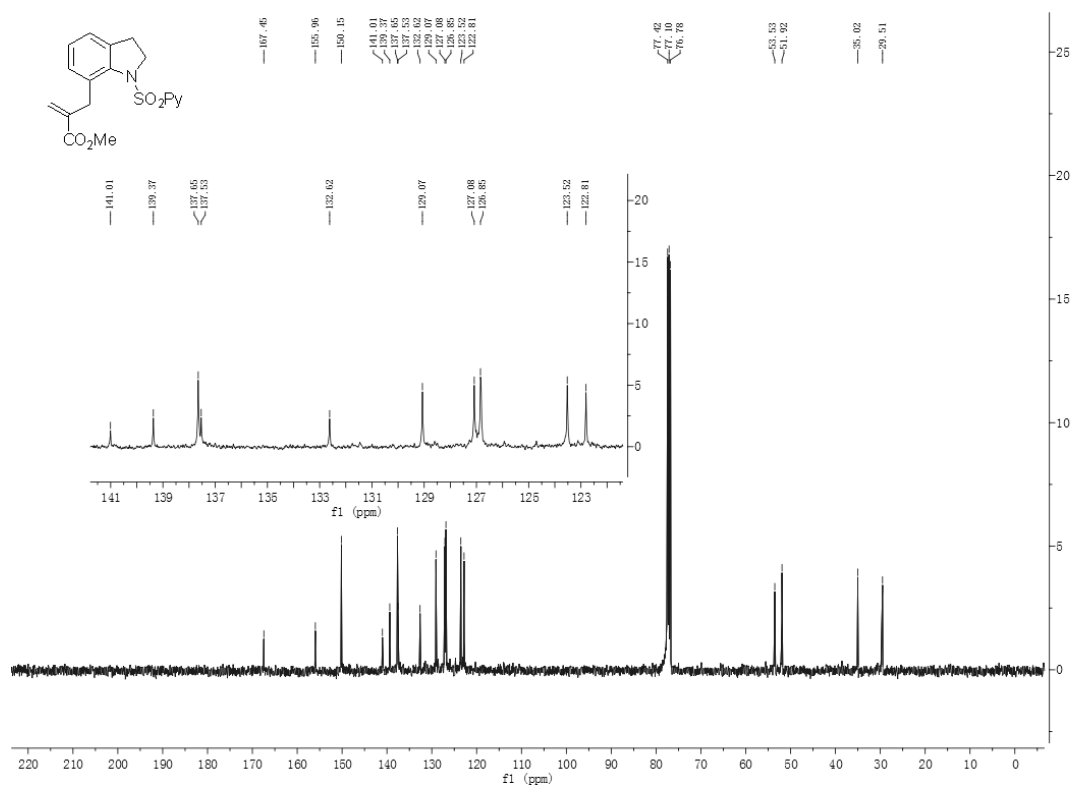
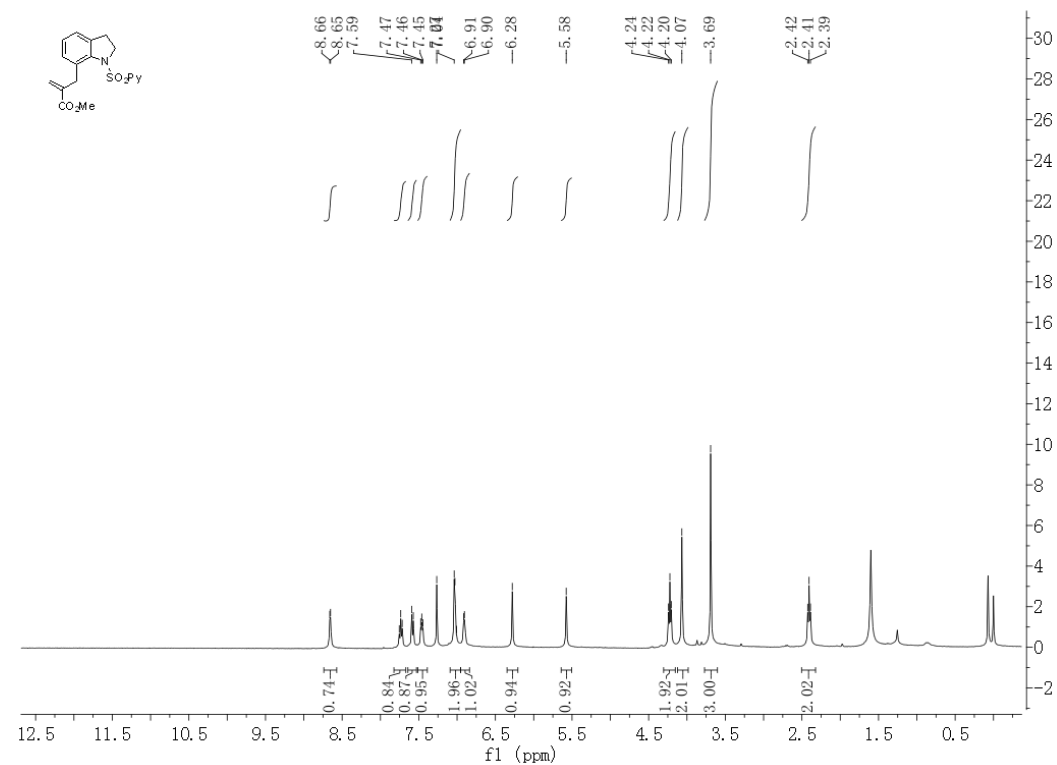
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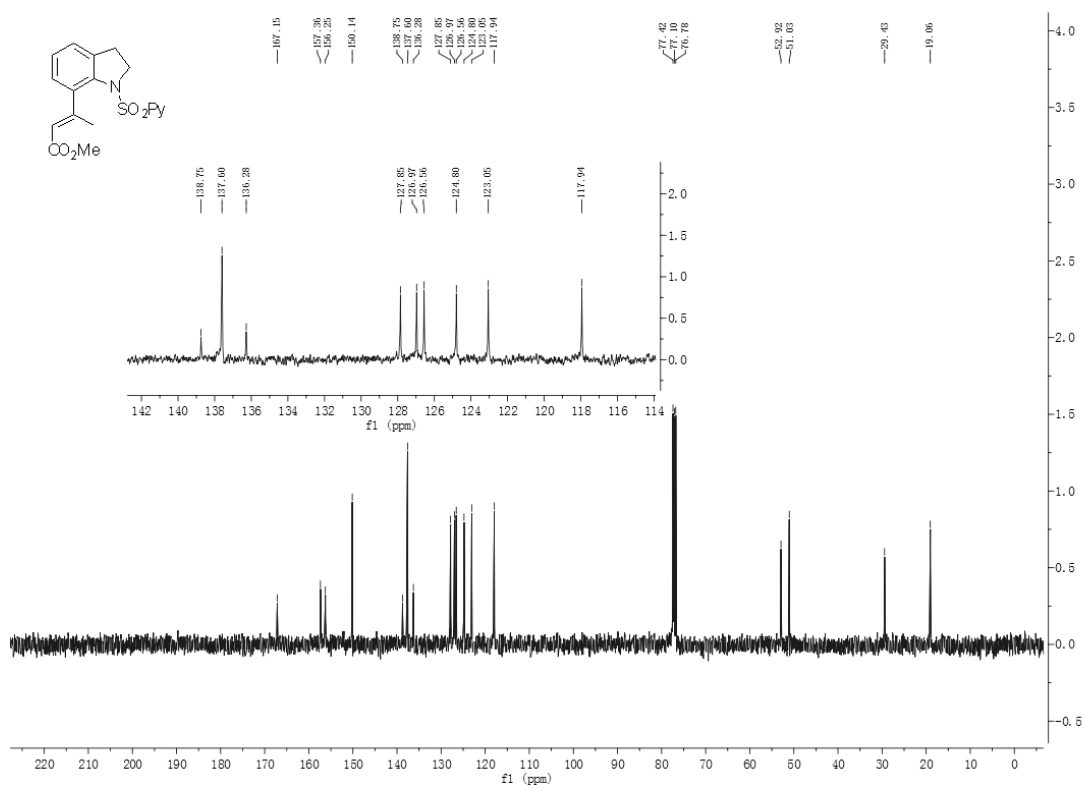
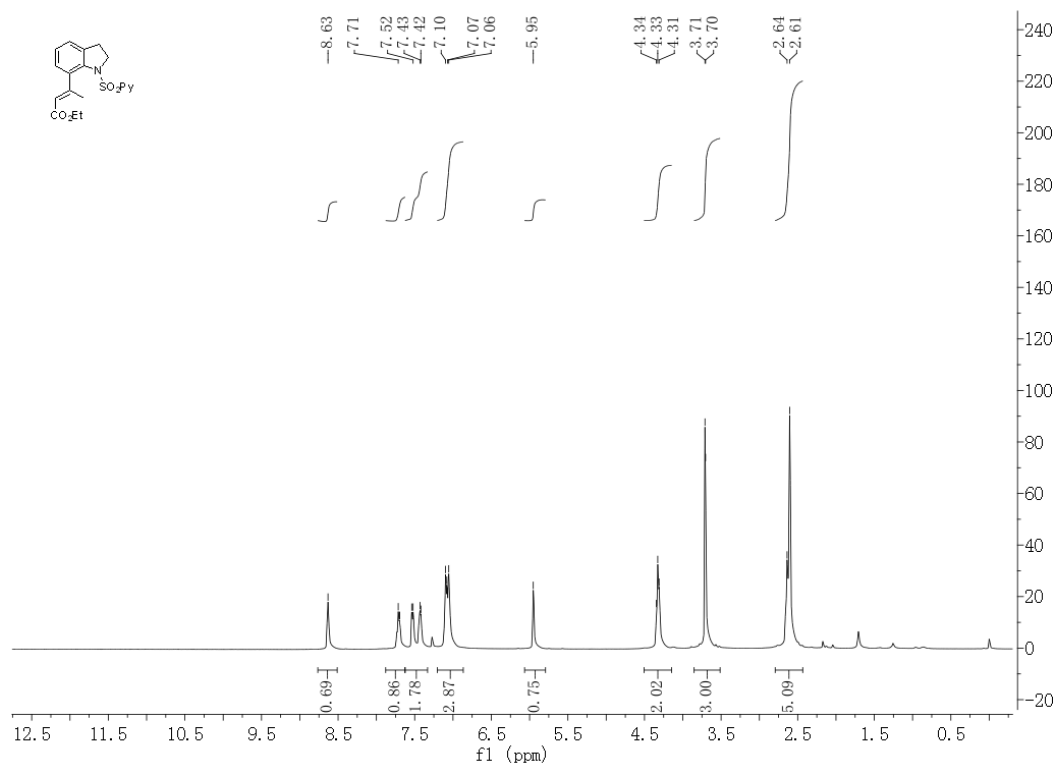
(E)-Diethyl2-(1-(pyridin-2-ylsulfonyl)indolin-7-yl)vinylphosphonate (3dj)



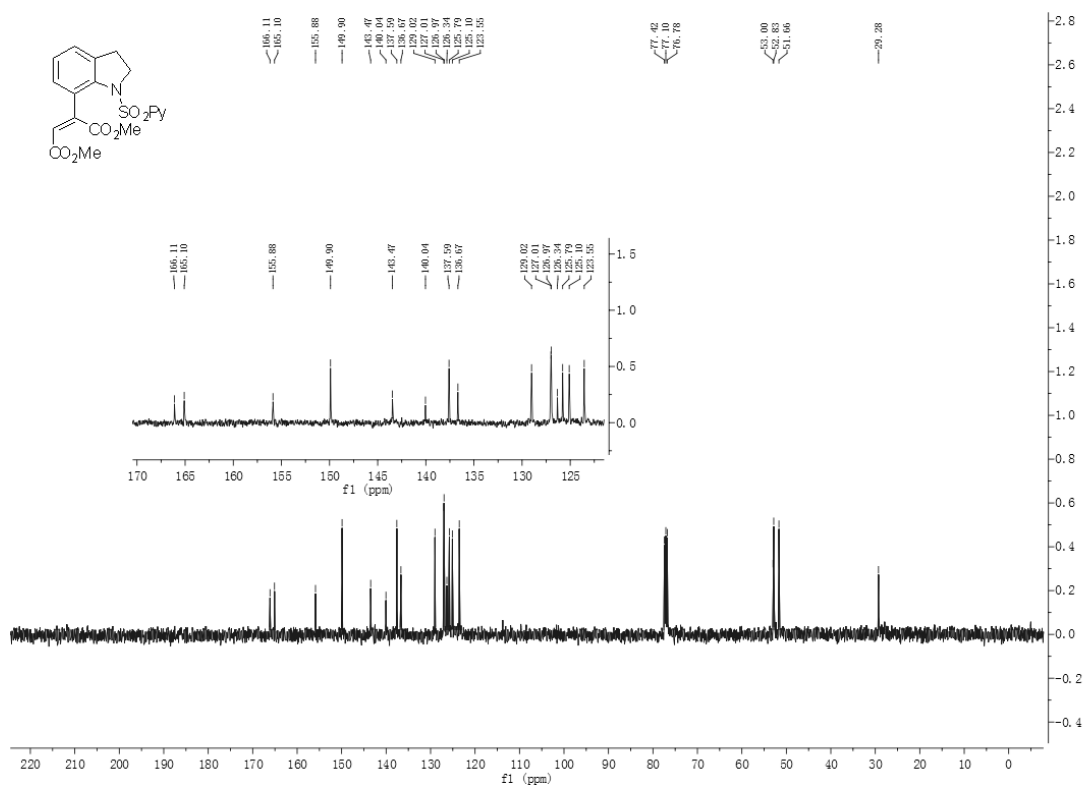
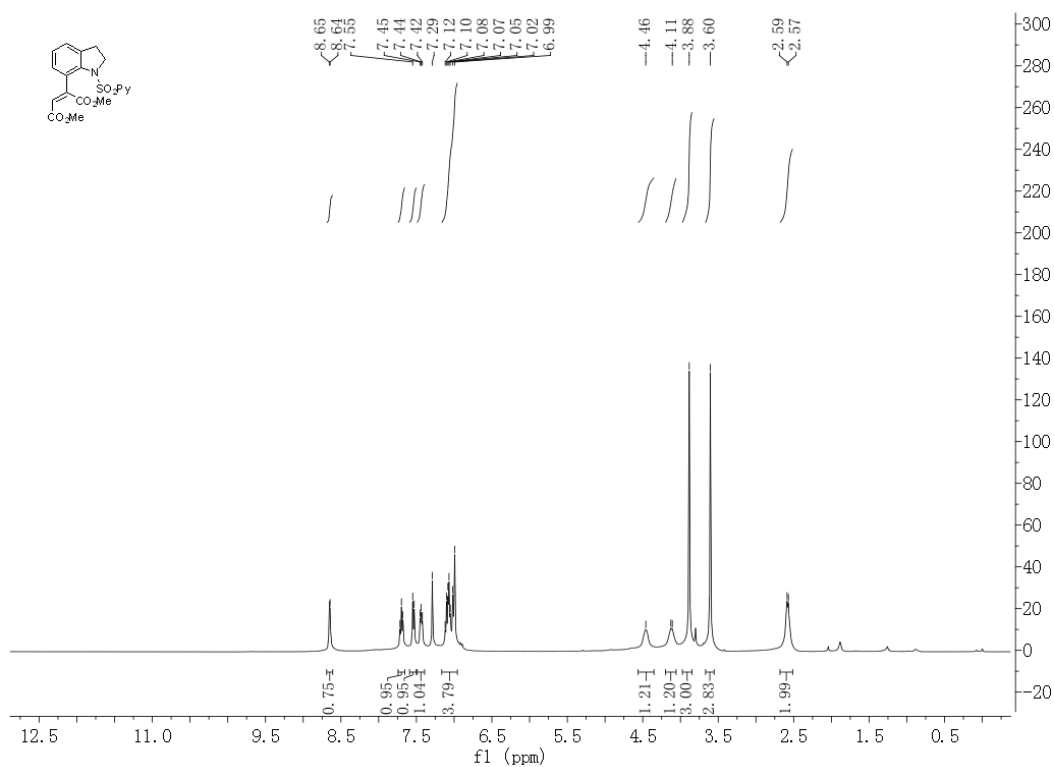
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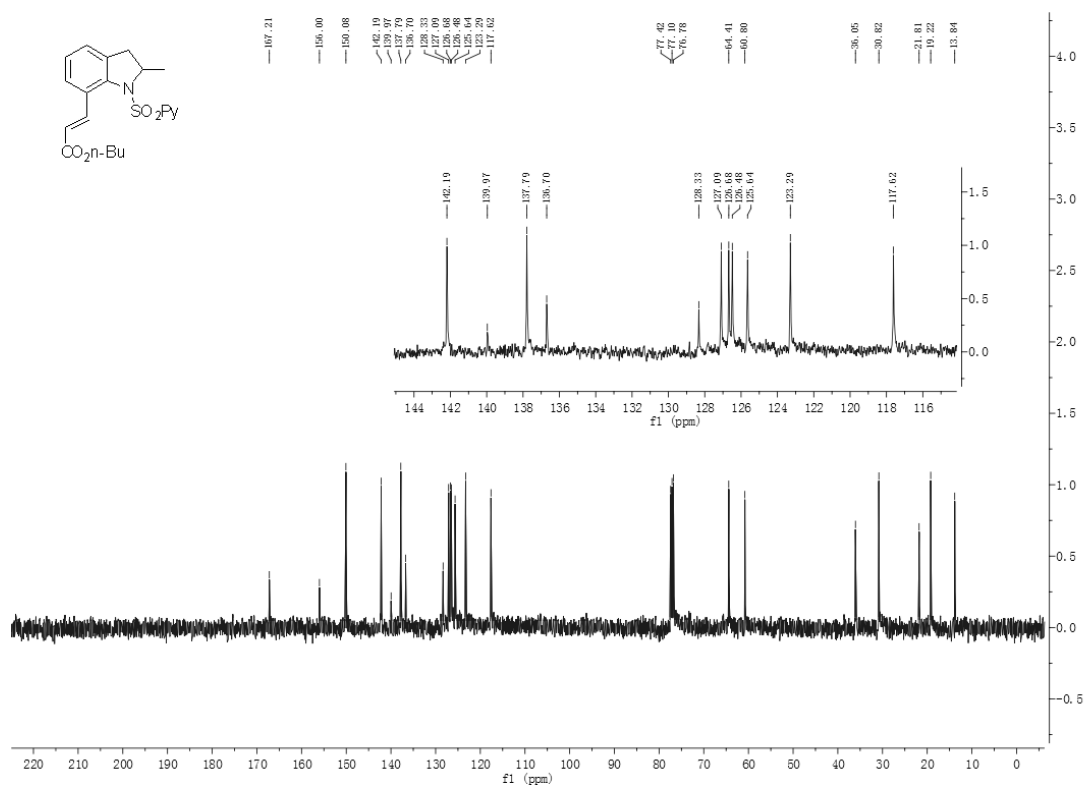
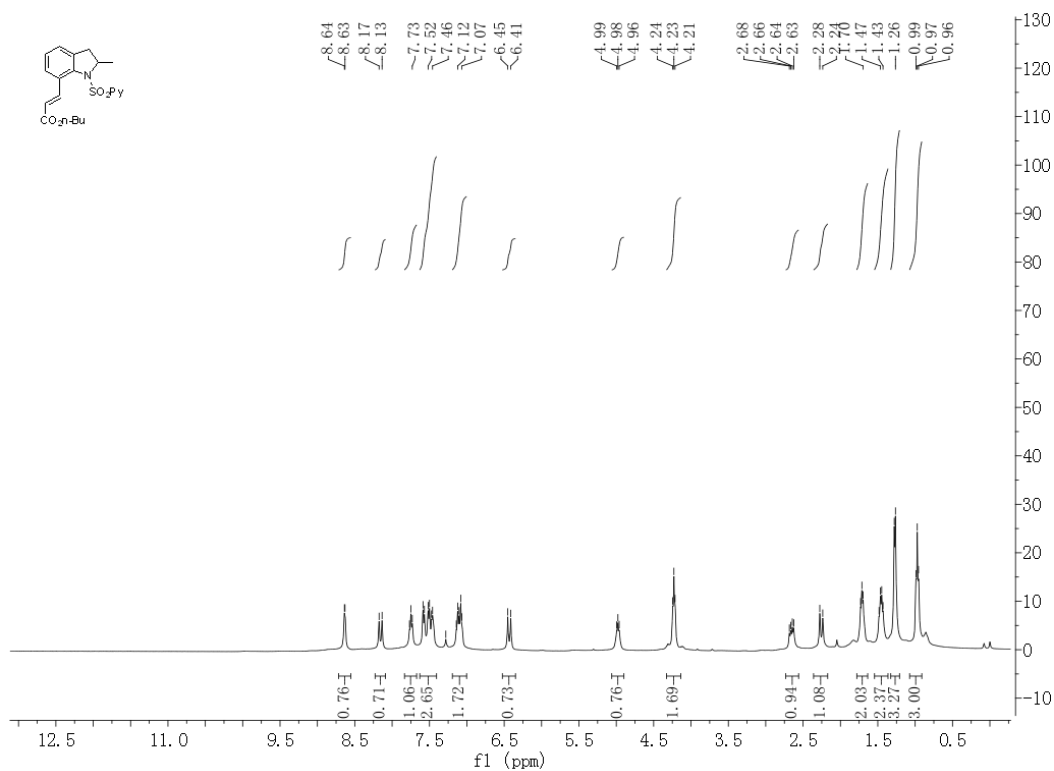
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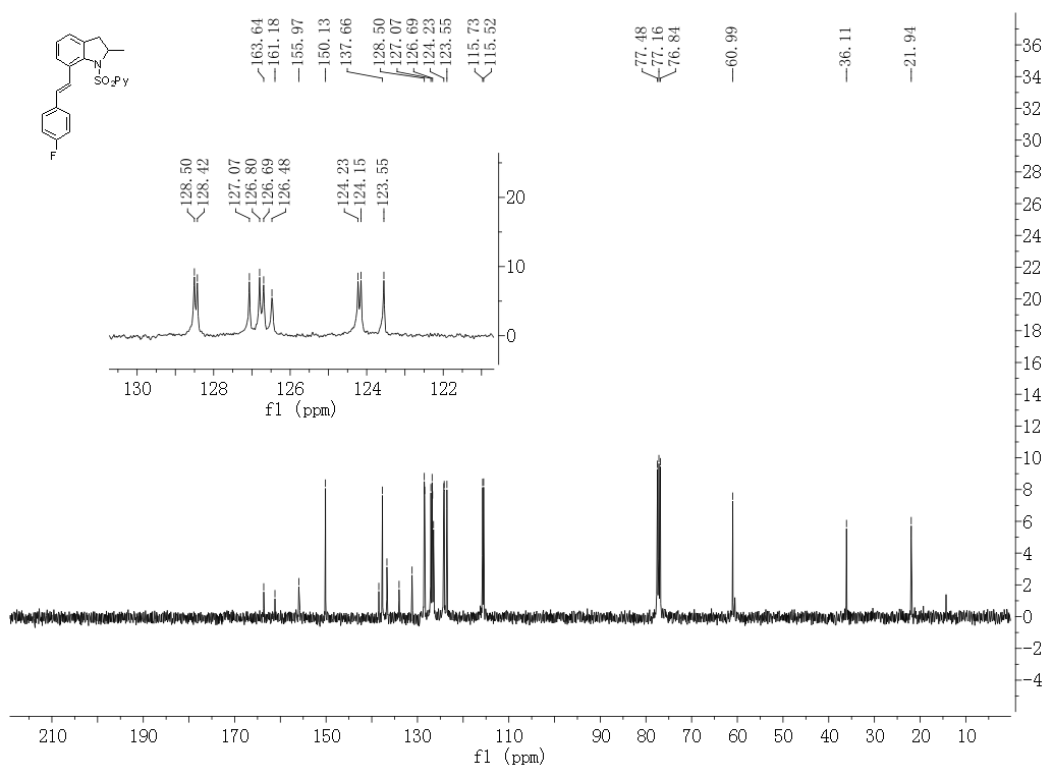
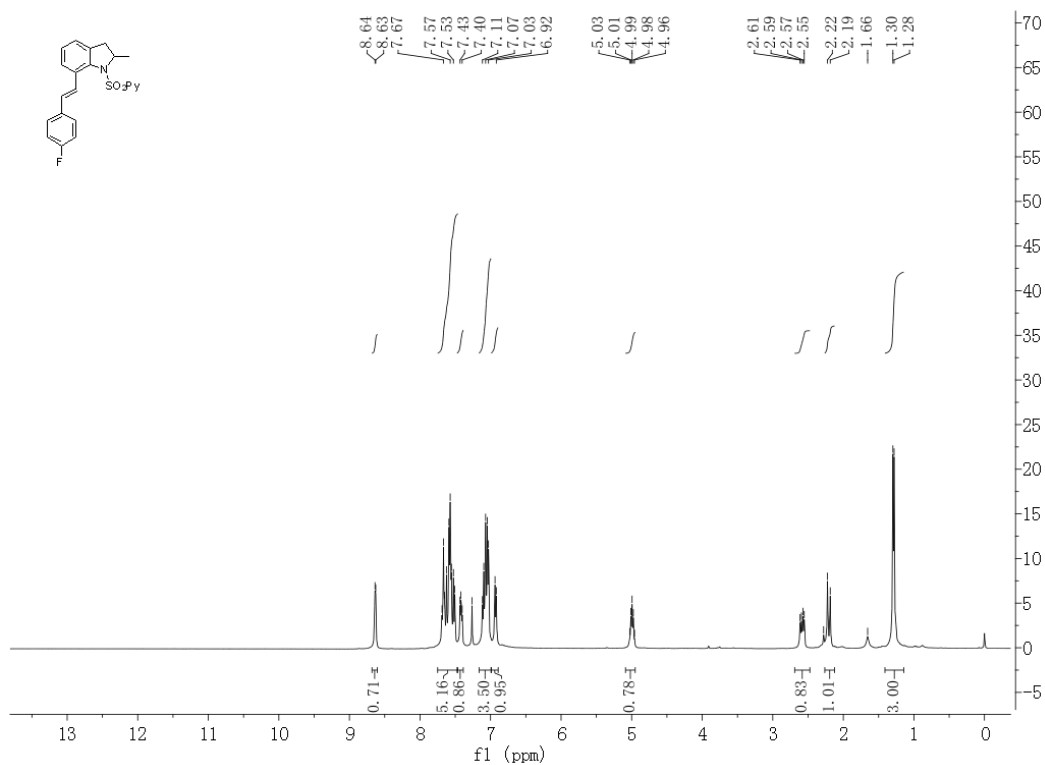
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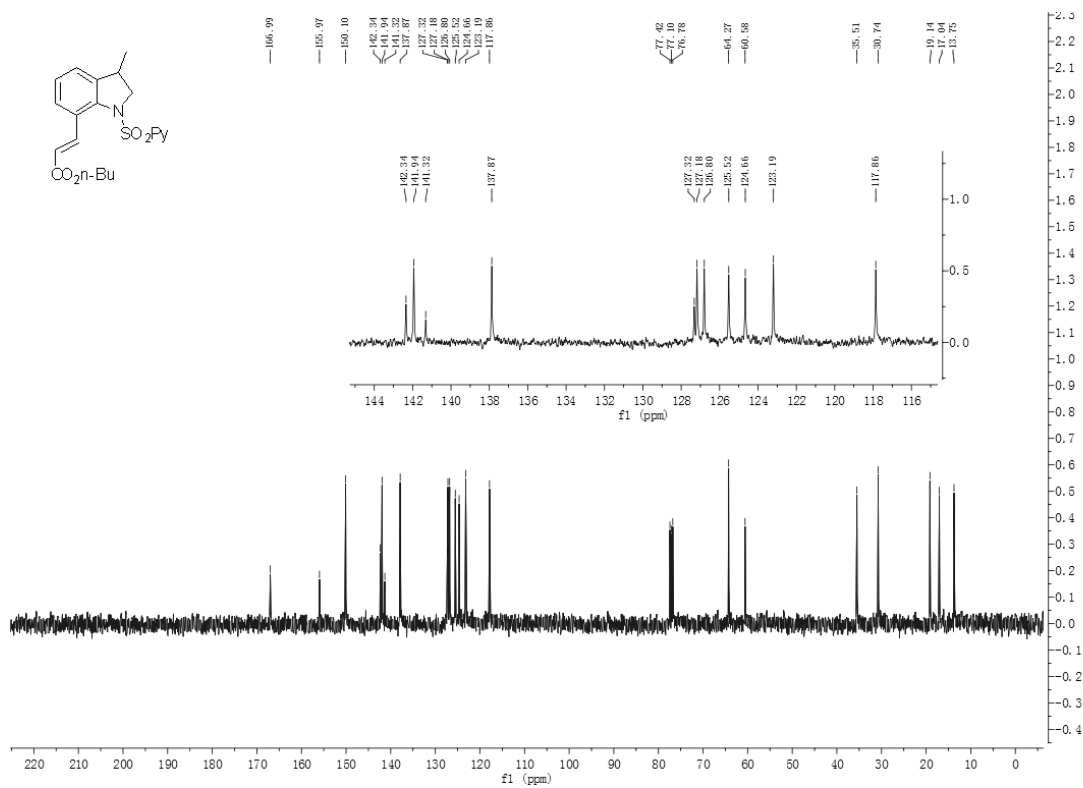
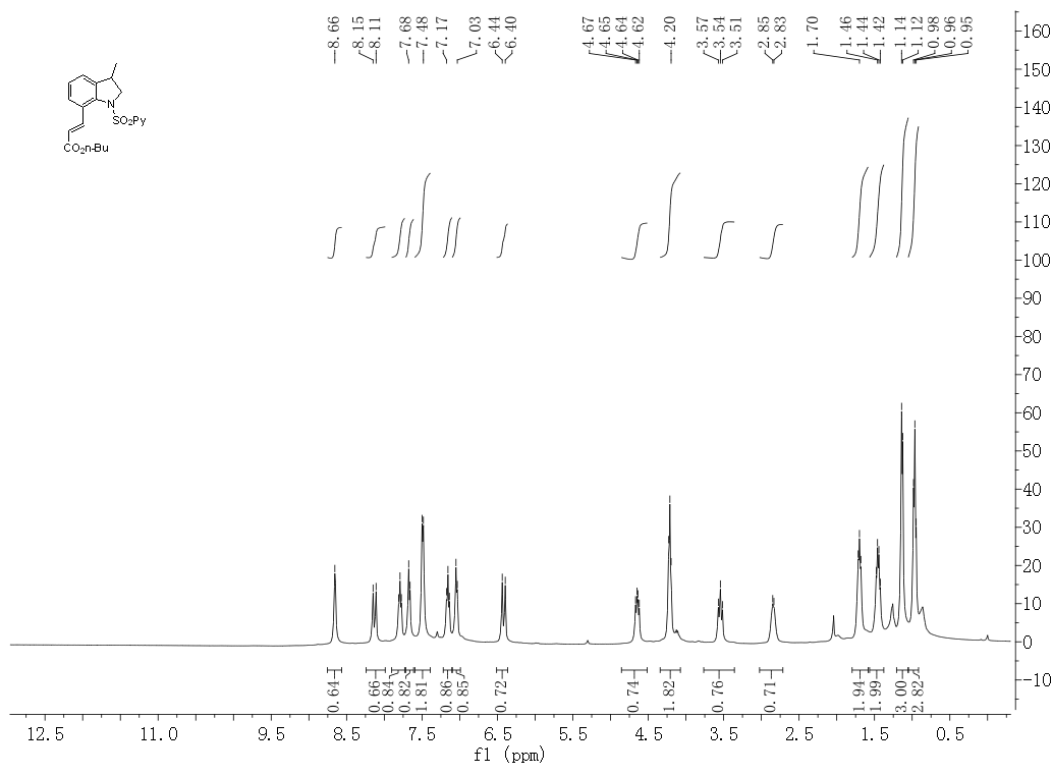
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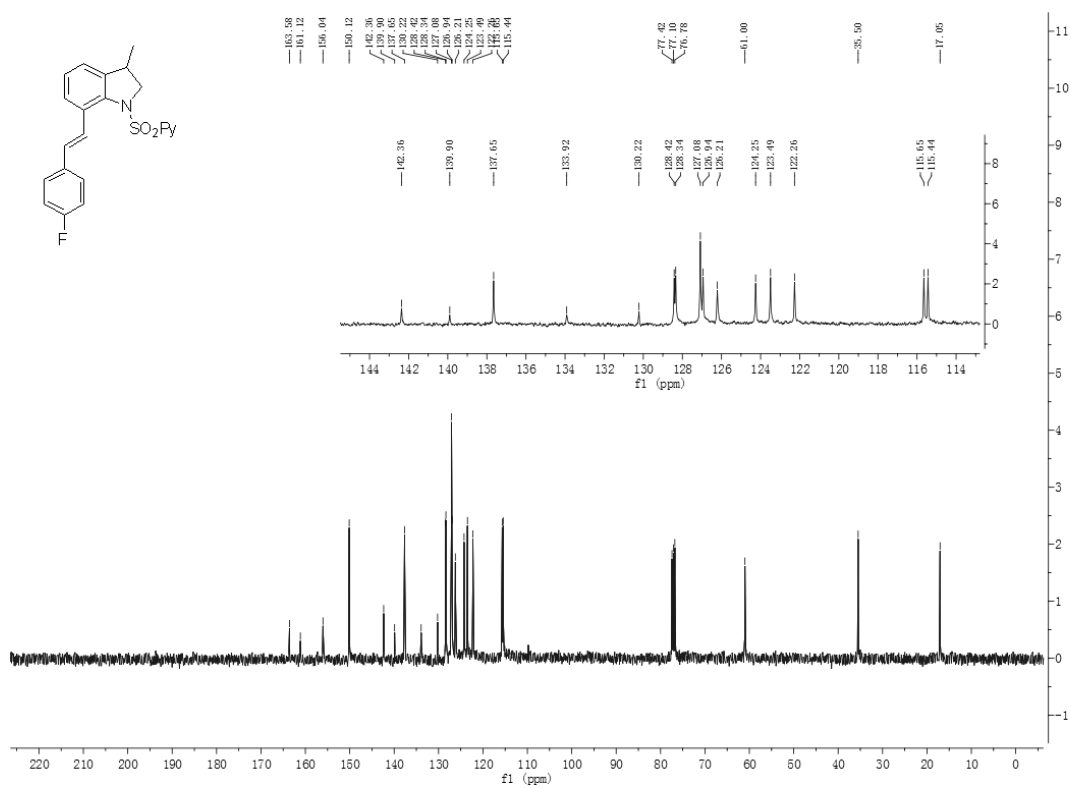
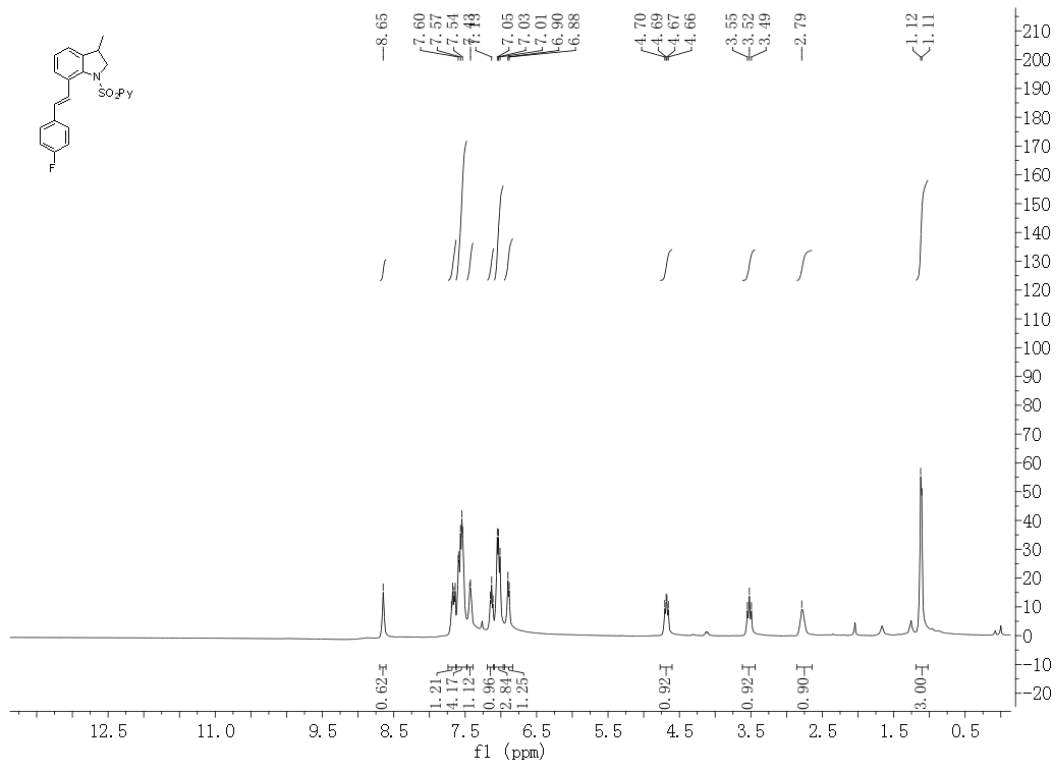
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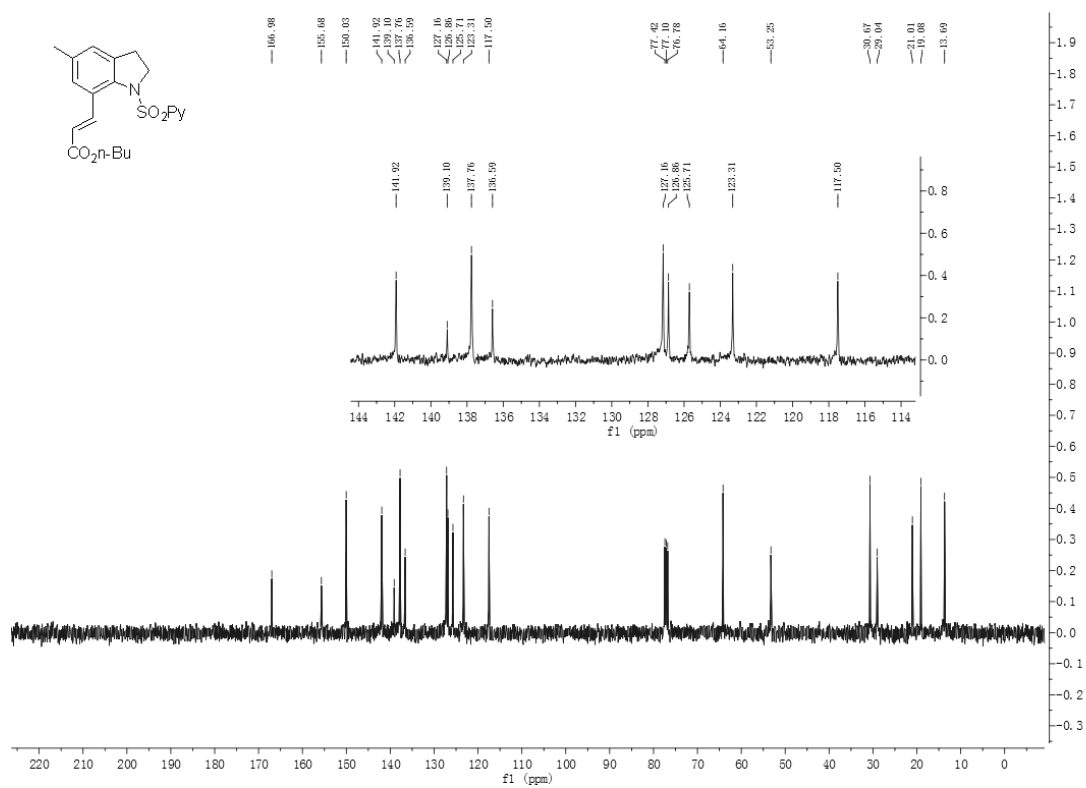
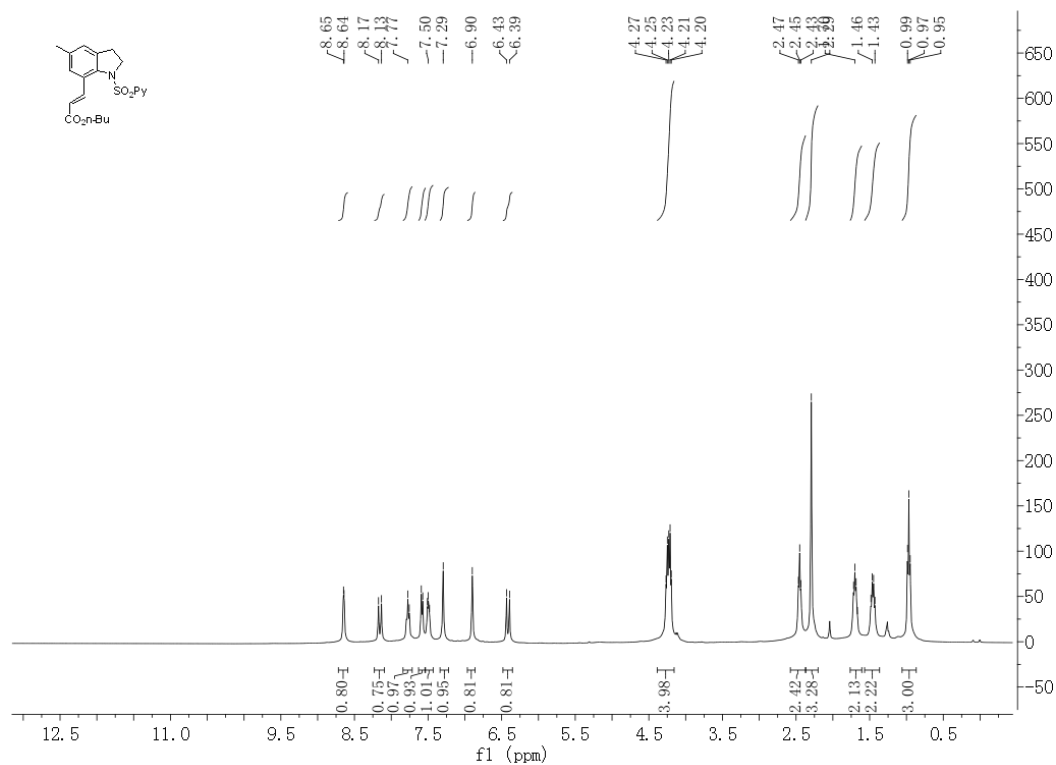
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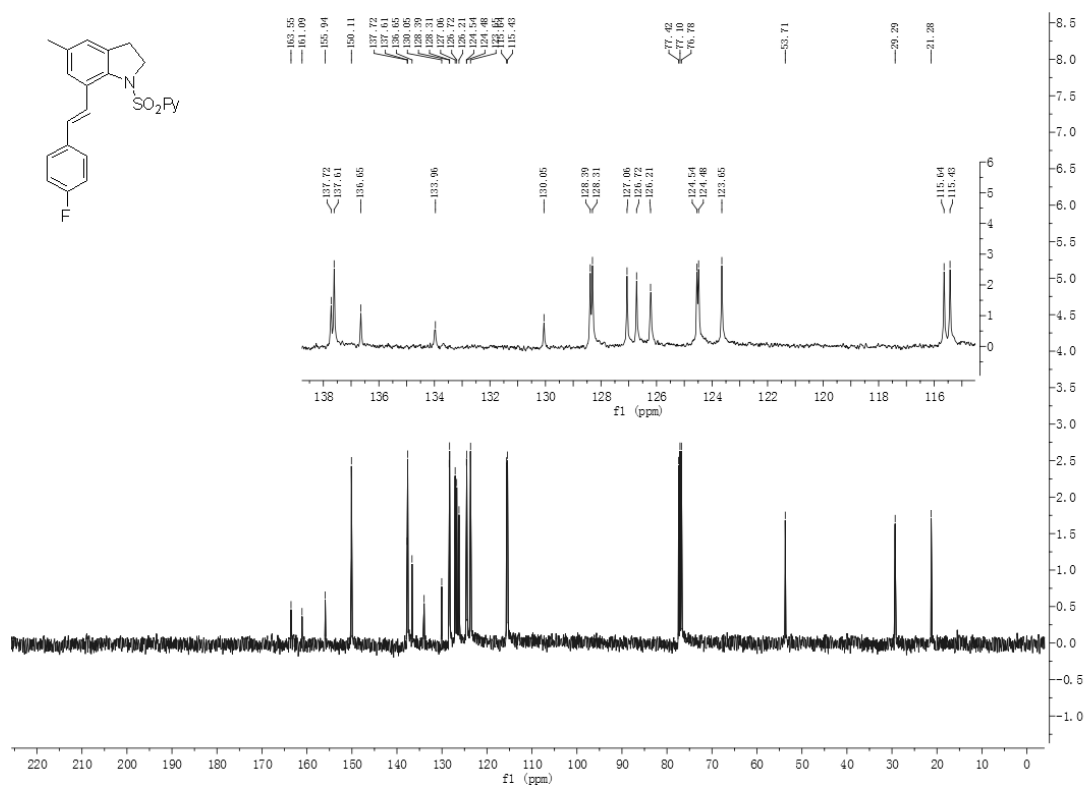
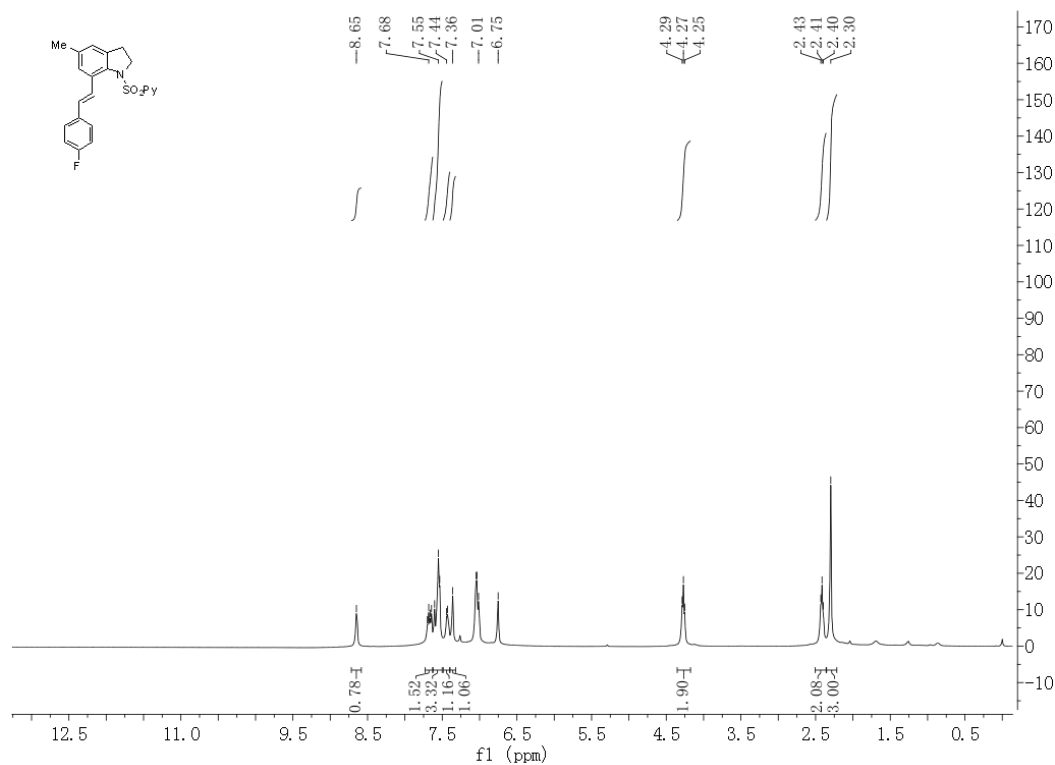
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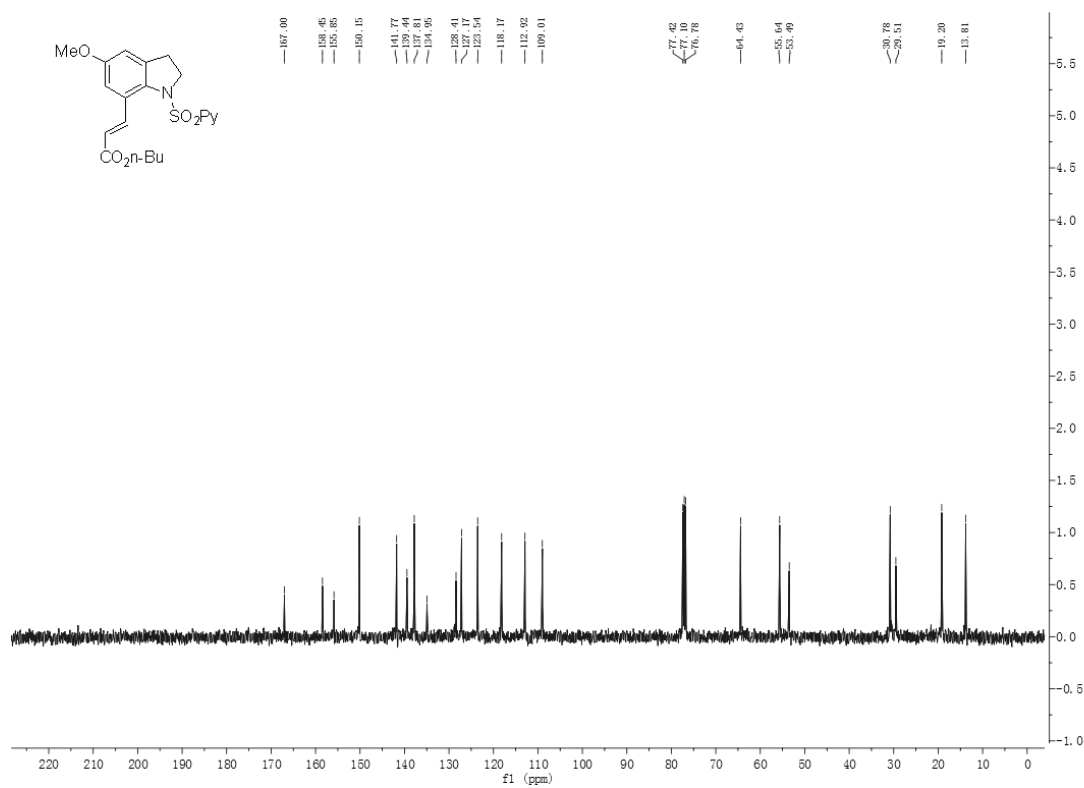
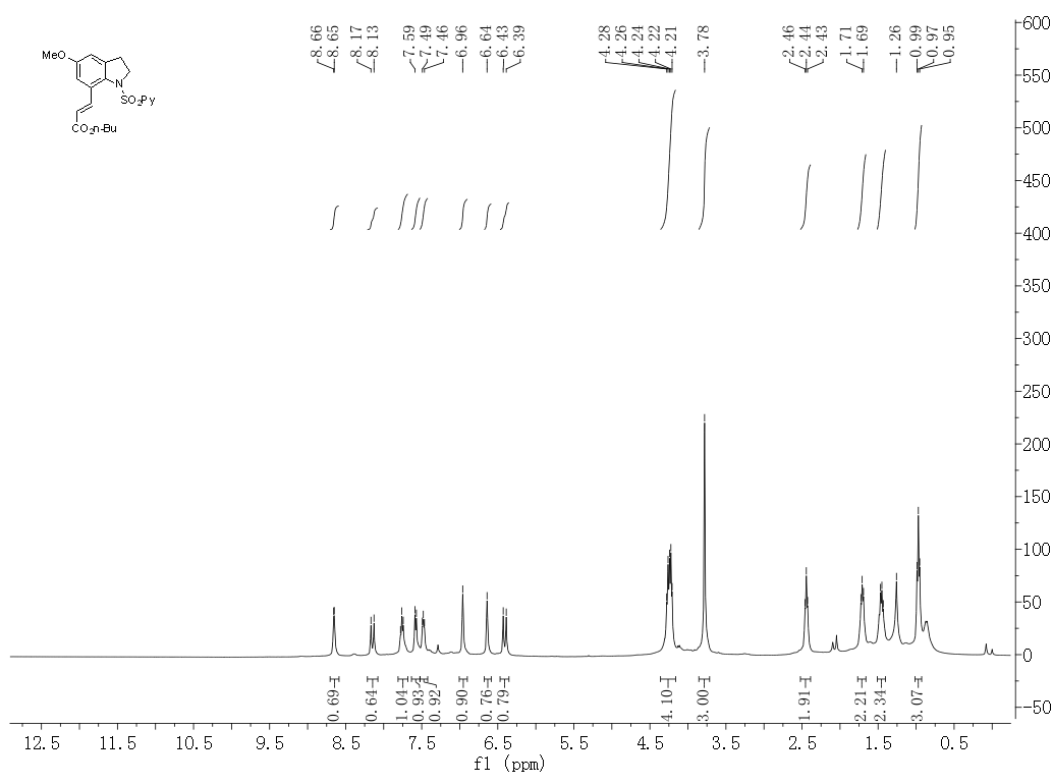
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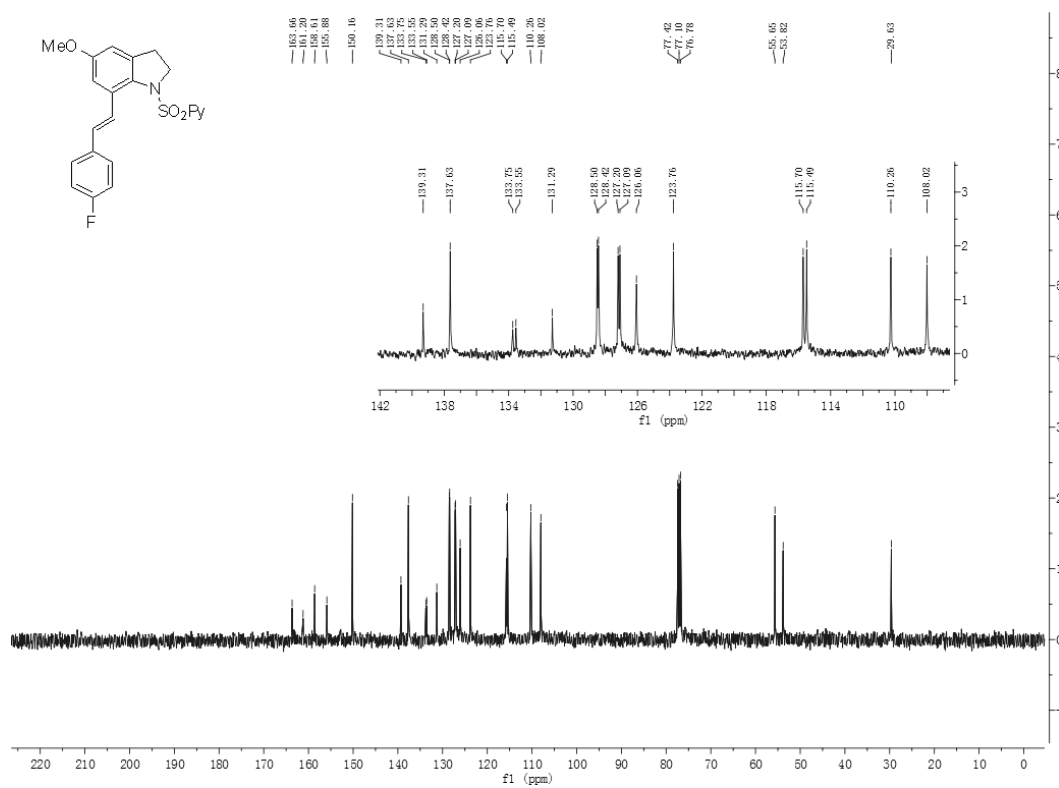
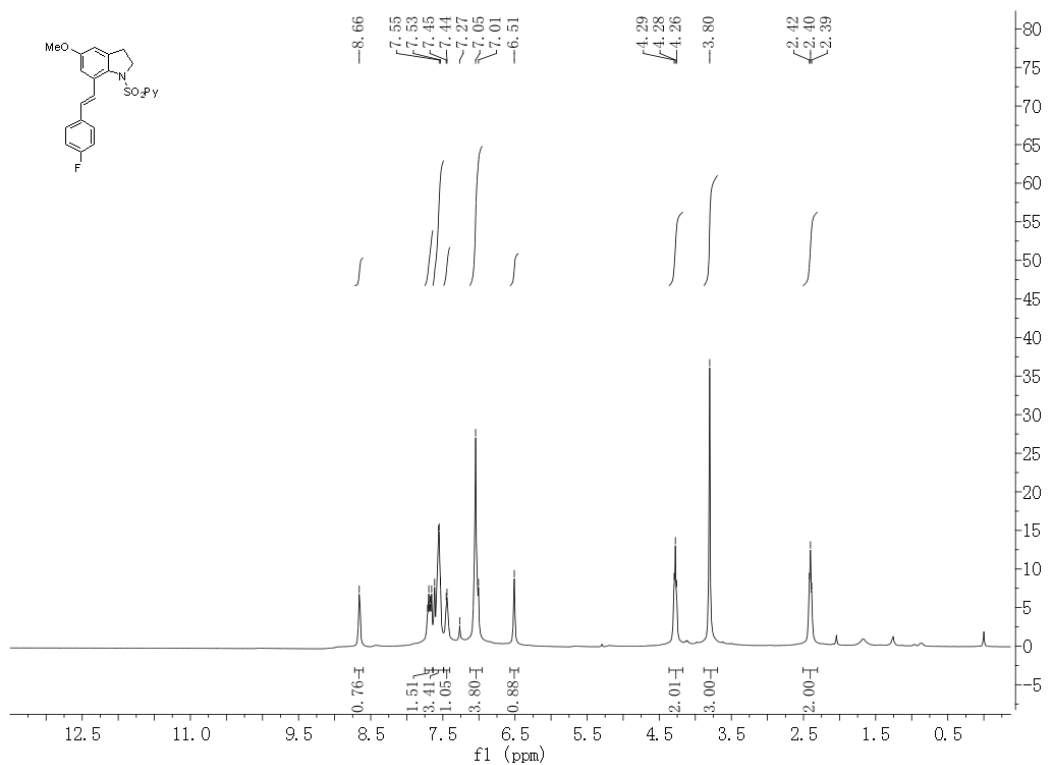
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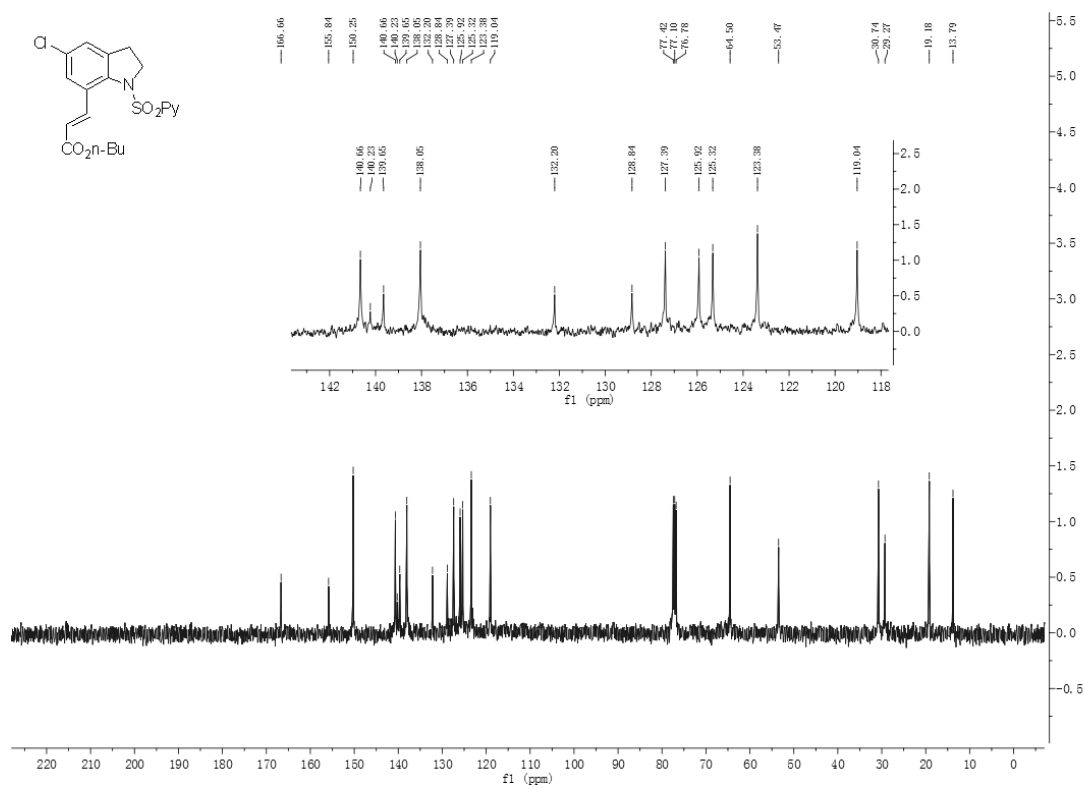
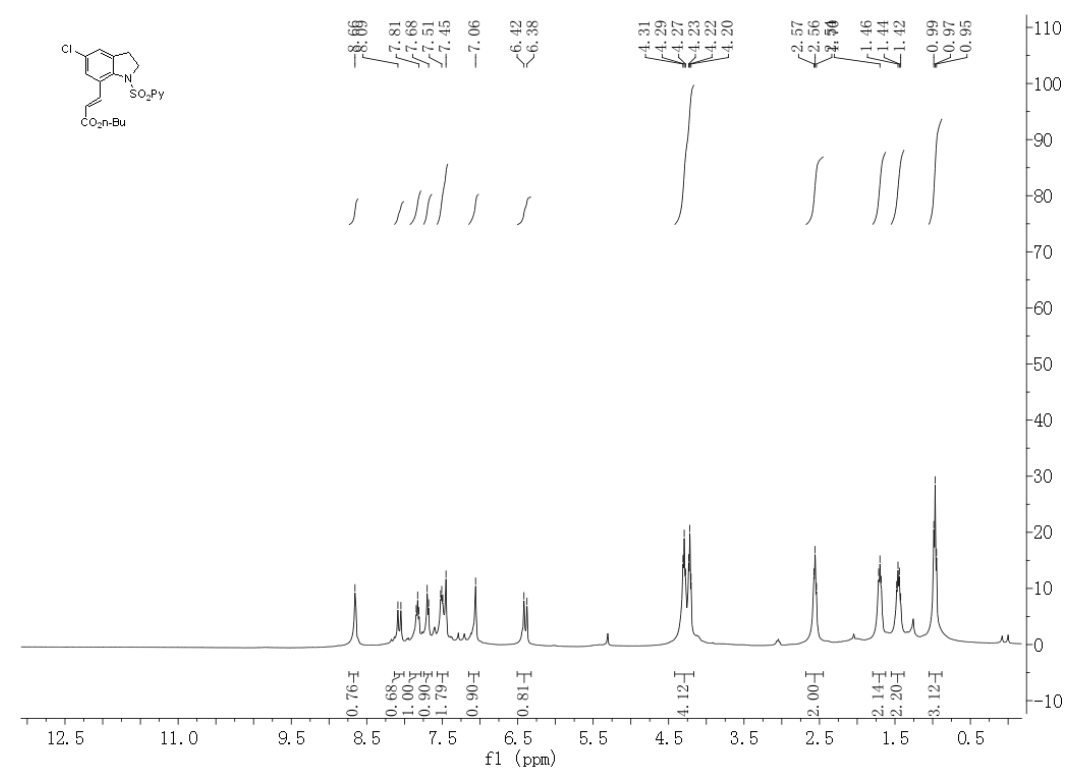
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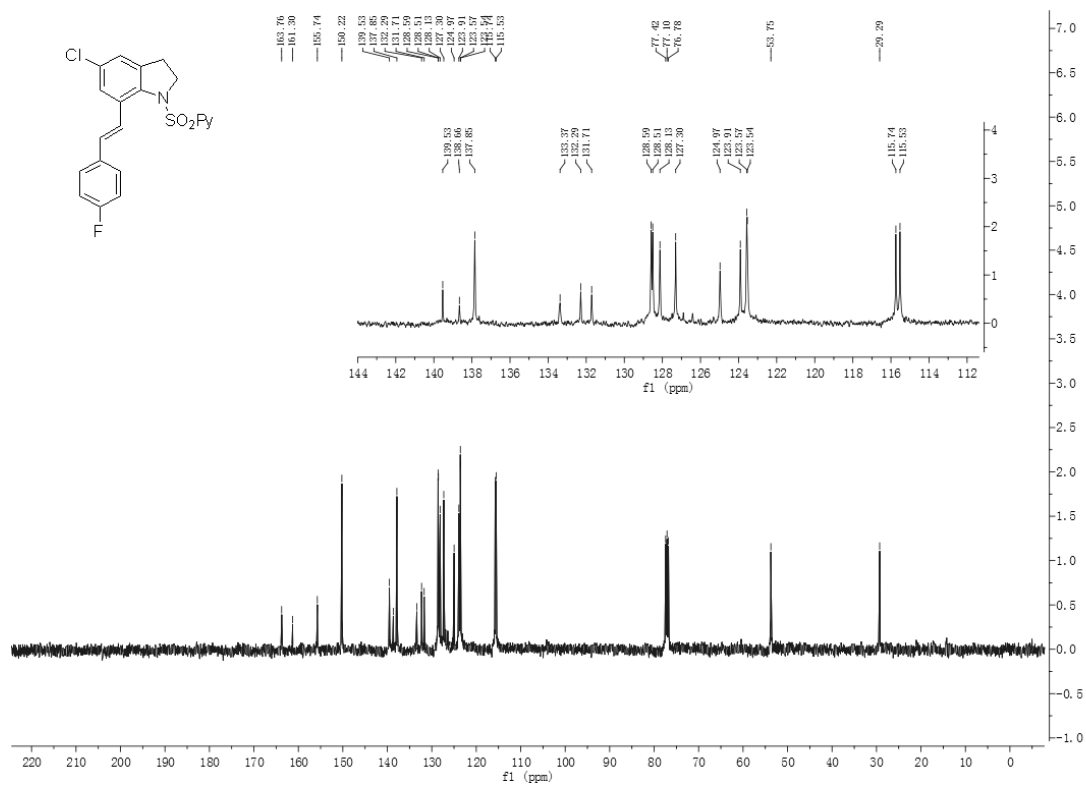
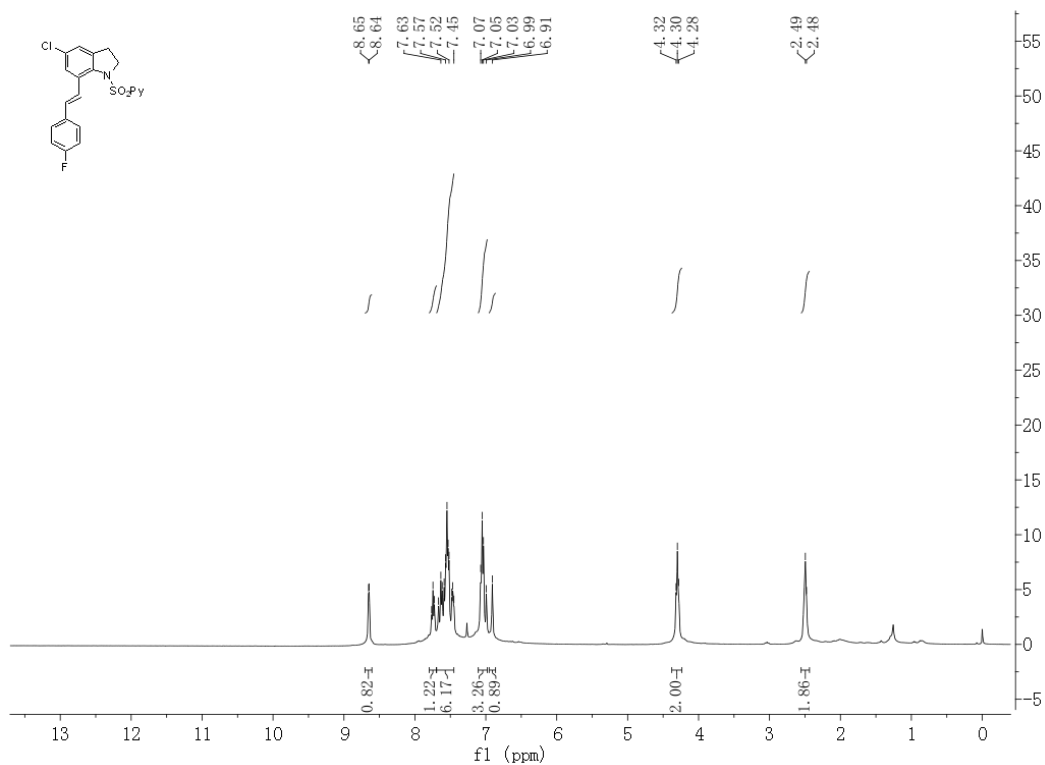
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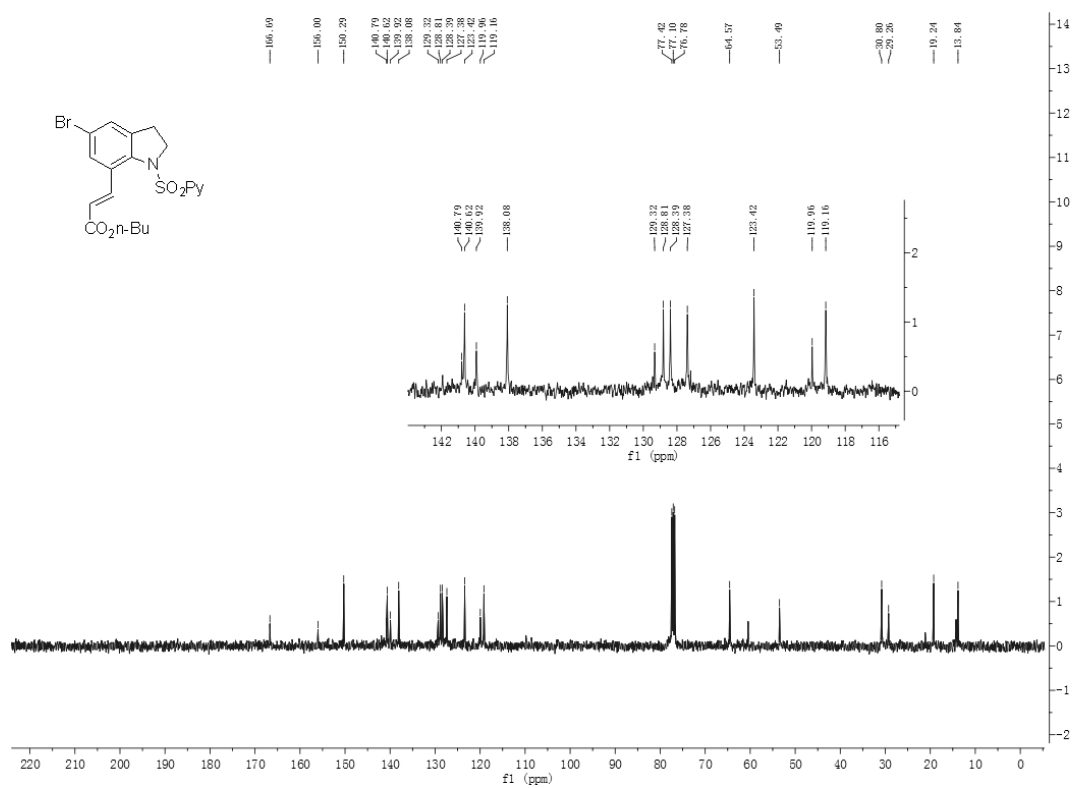
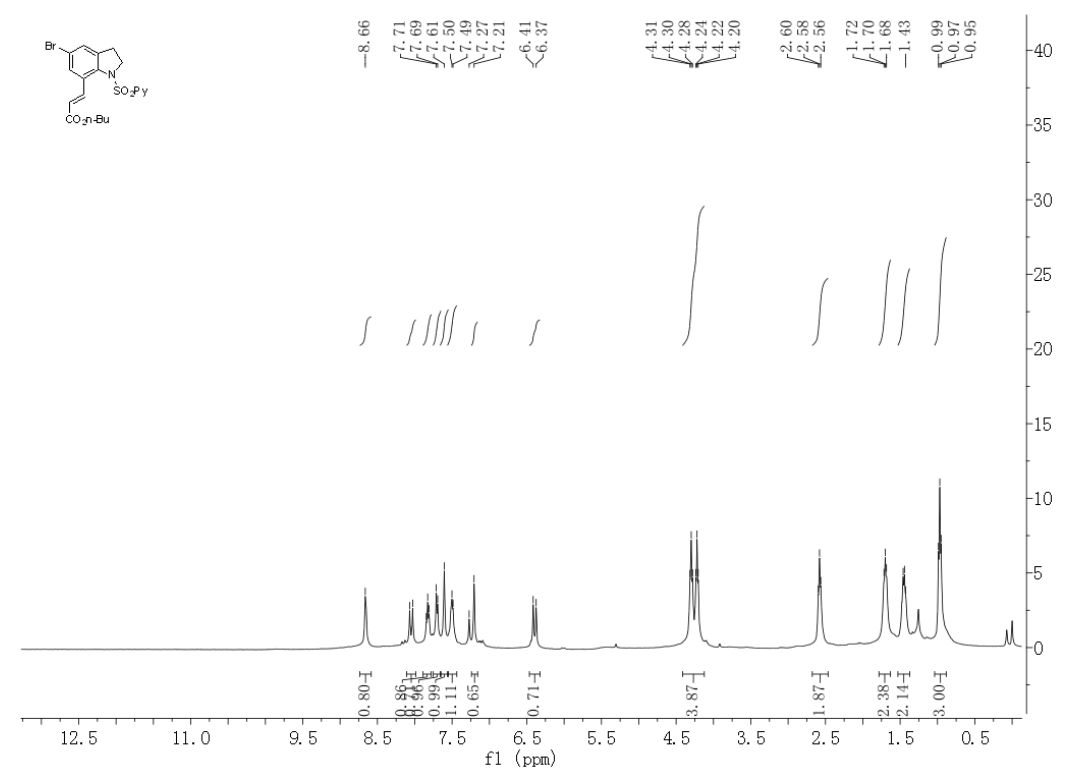
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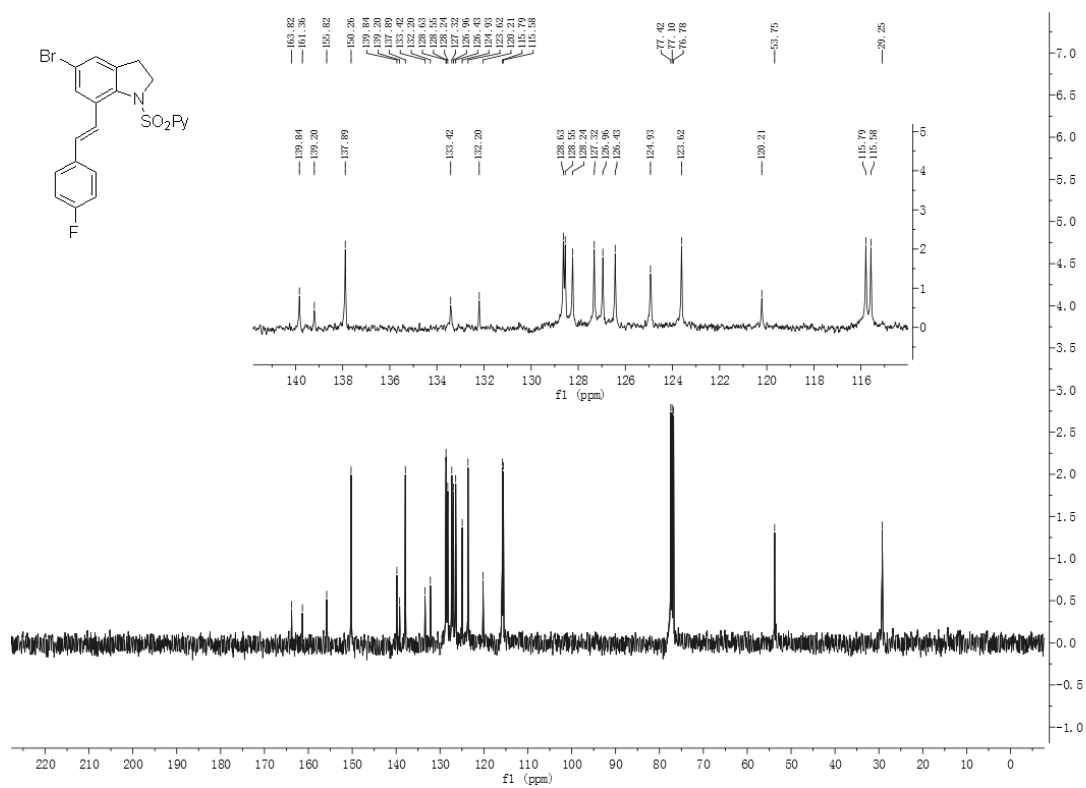
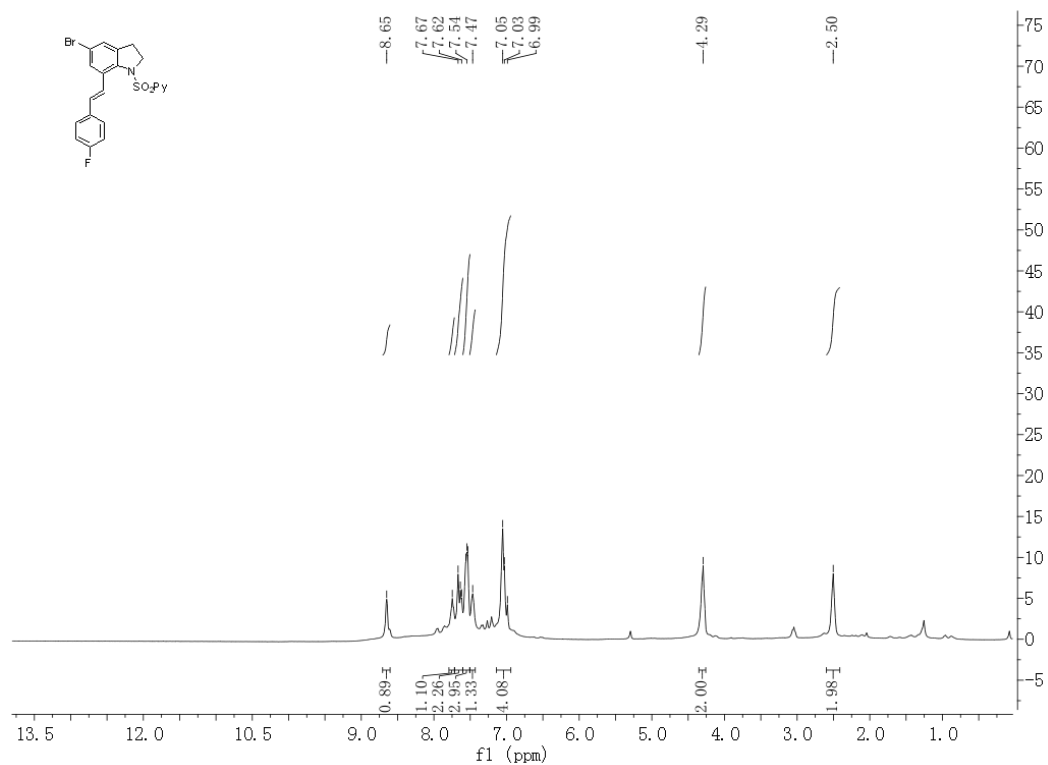
(E)-5-Chloro-7-(4-fluorostyryl)-1-(pyridin-2-ylsulfonyl) indoline (3ig)



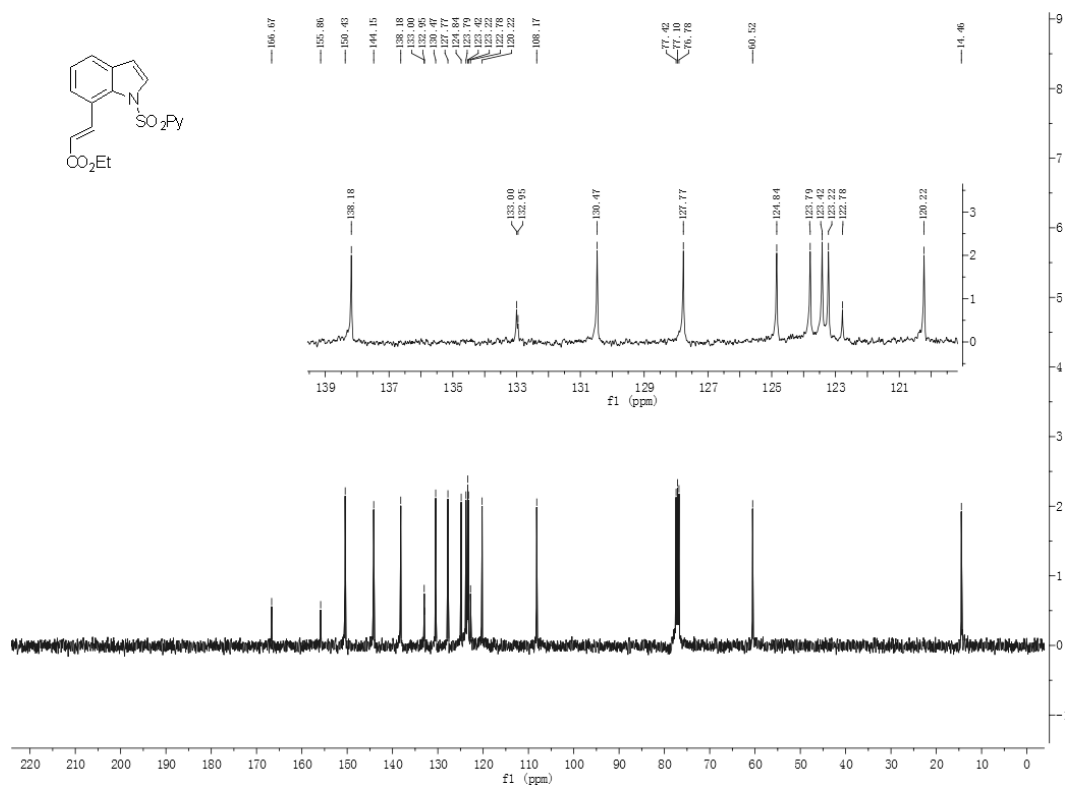
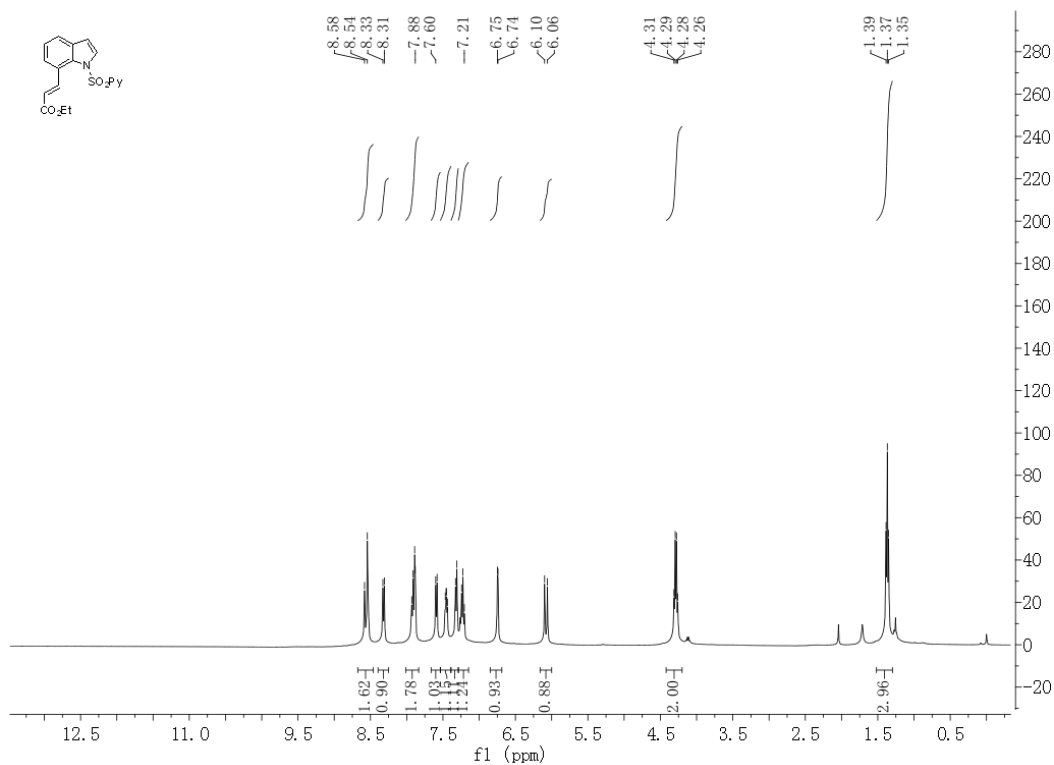
(E)-Butyl 3-(5-bromo-1-(pyridin-2-ylsulfonyl)indolin-7-yl)acrylate (3jb)



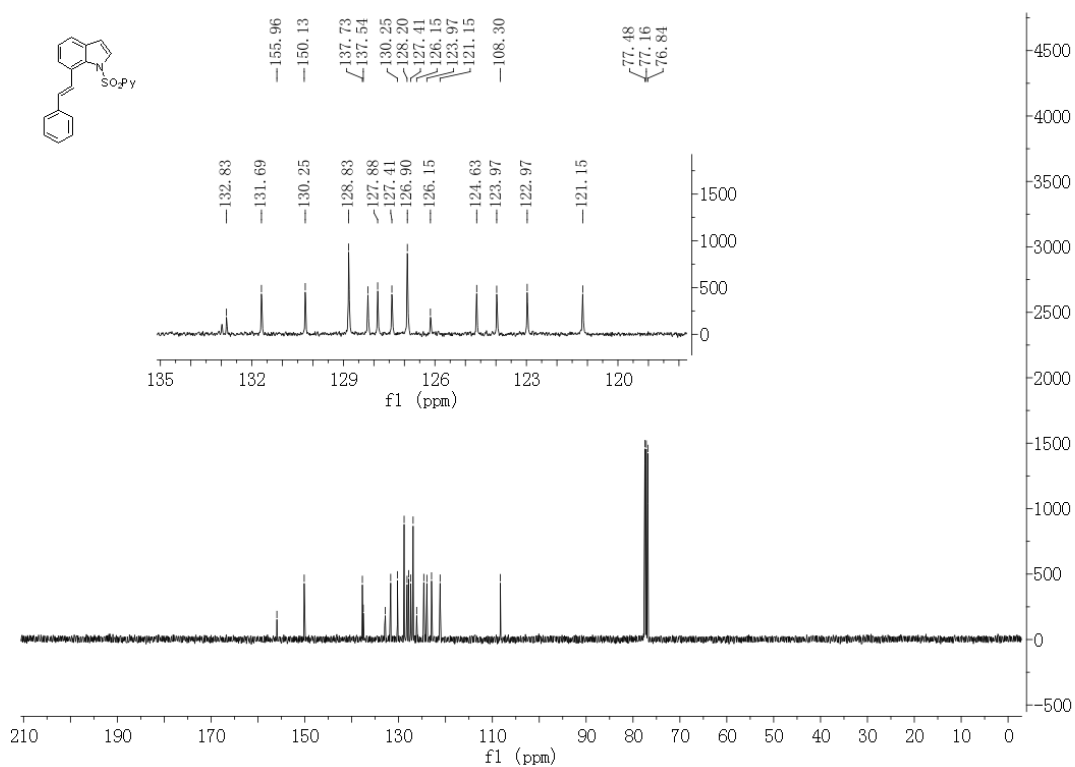
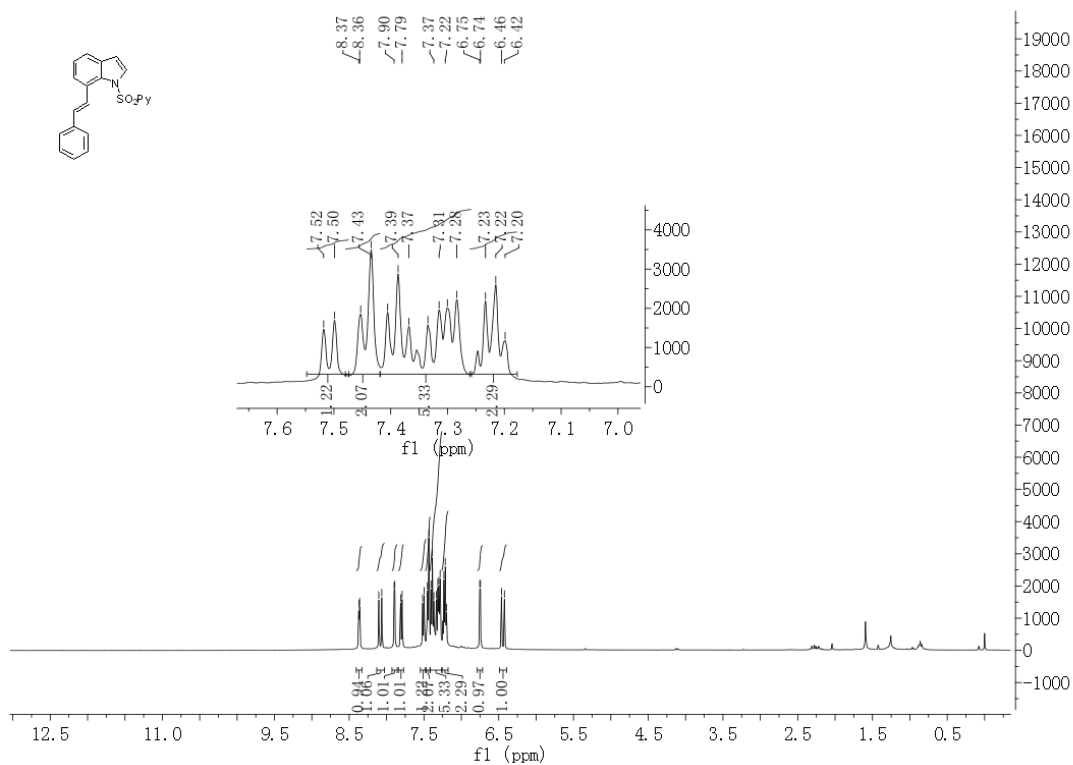
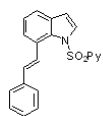
(E)-5-Bromo-7-(4-fluorostyryl)-1-(pyridin-2-ylsulfonyl)indoline (3jg)



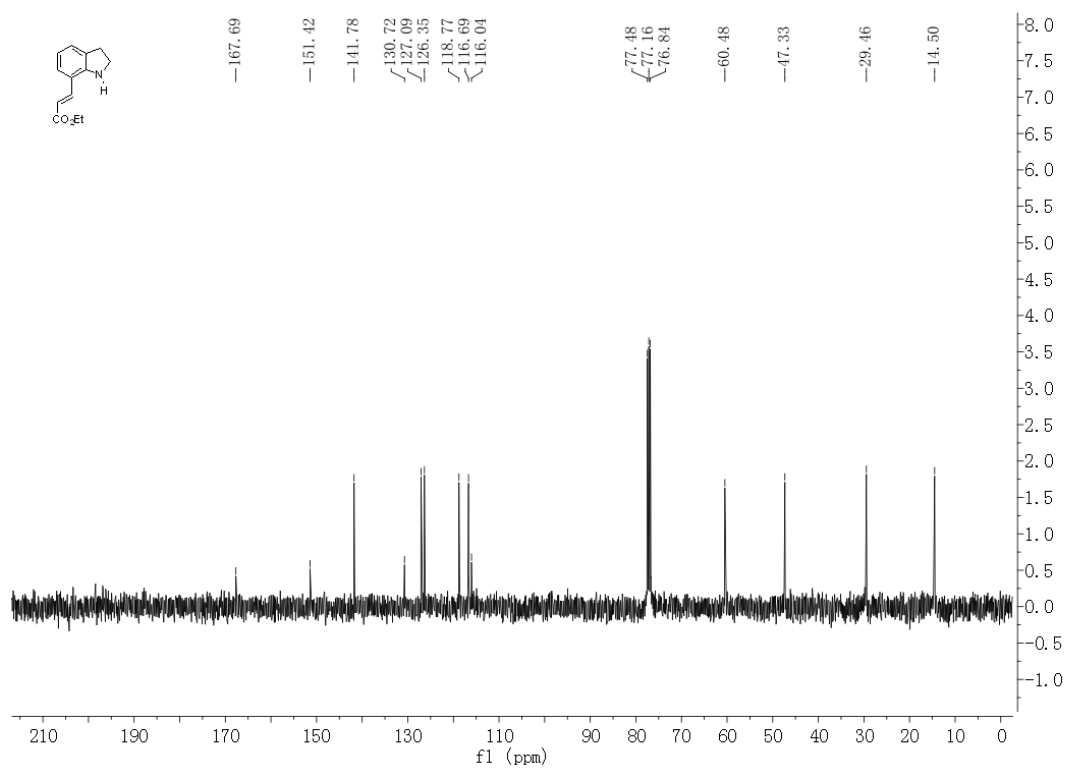
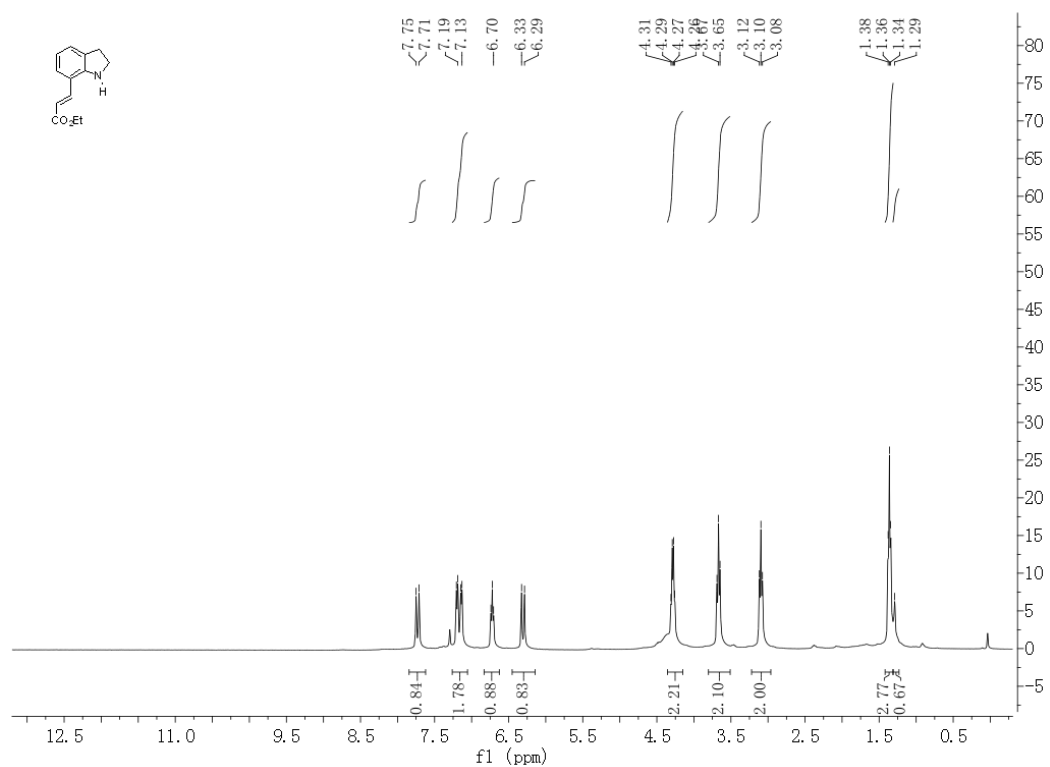
(E)-Ethyl 3-(1-(pyridin-2-ylsulfonyl)-1H-indol-7-yl)acrylate (4da)



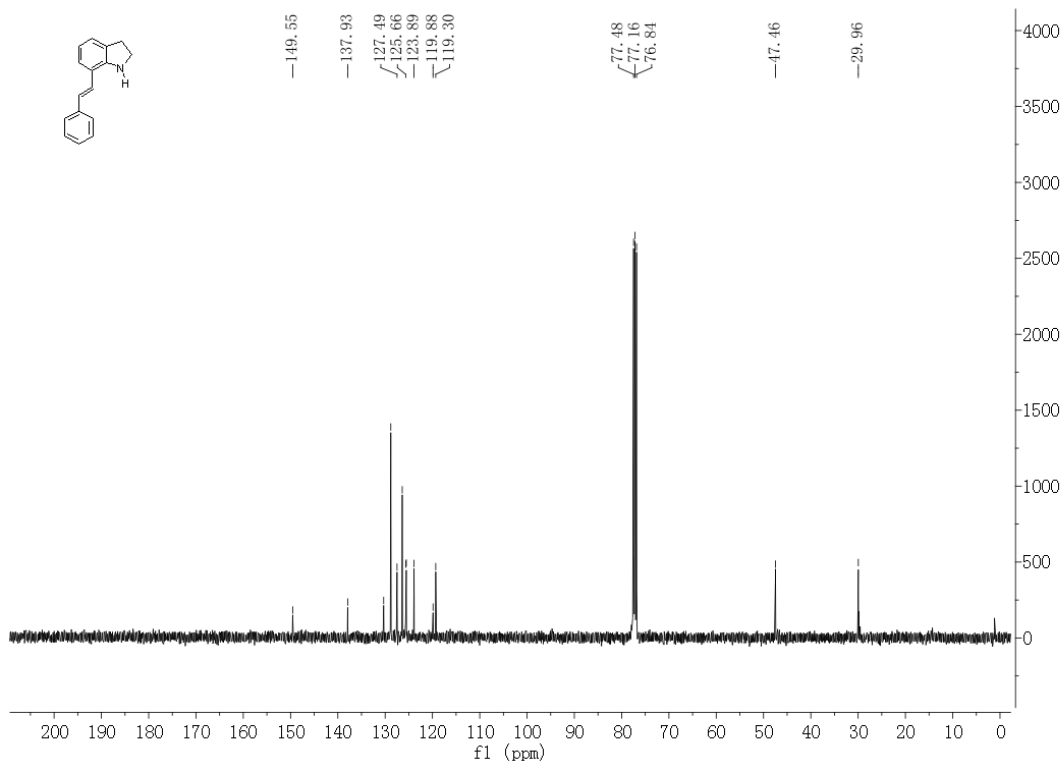
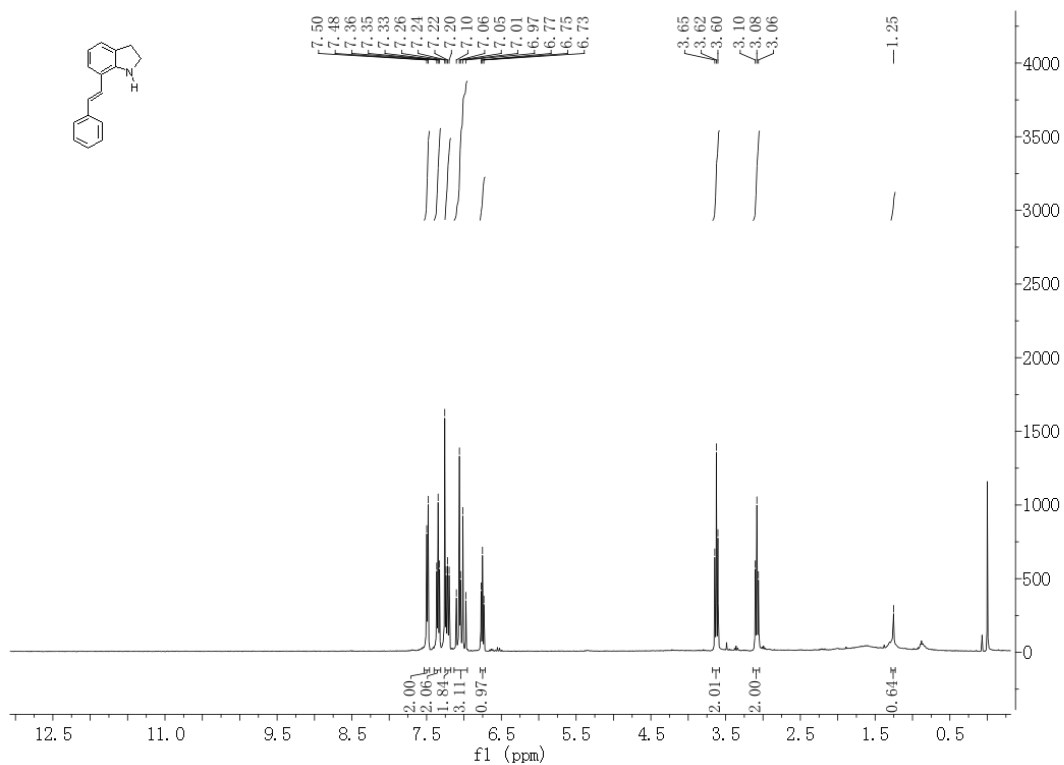
(E)-1-(Pyridin-2-ylsulfonyl)-7-styryl-1H-indole (4df)



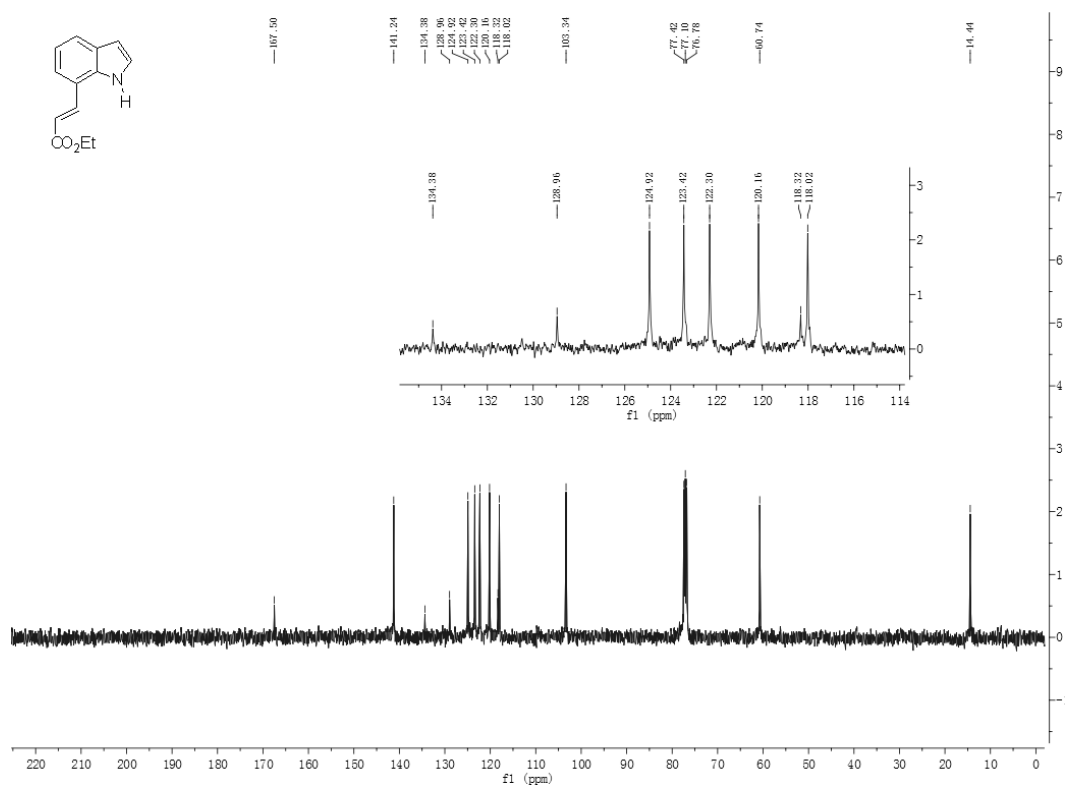
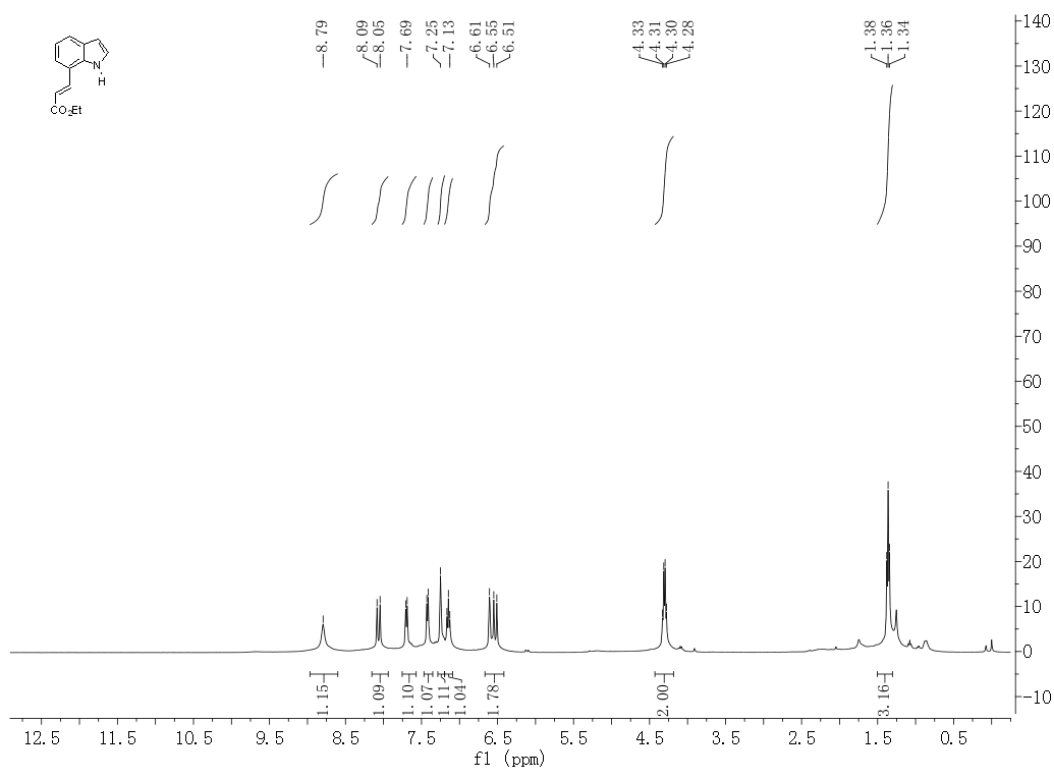
(E)-Ethyl 3-(indolin-7-yl)acrylate (5da)



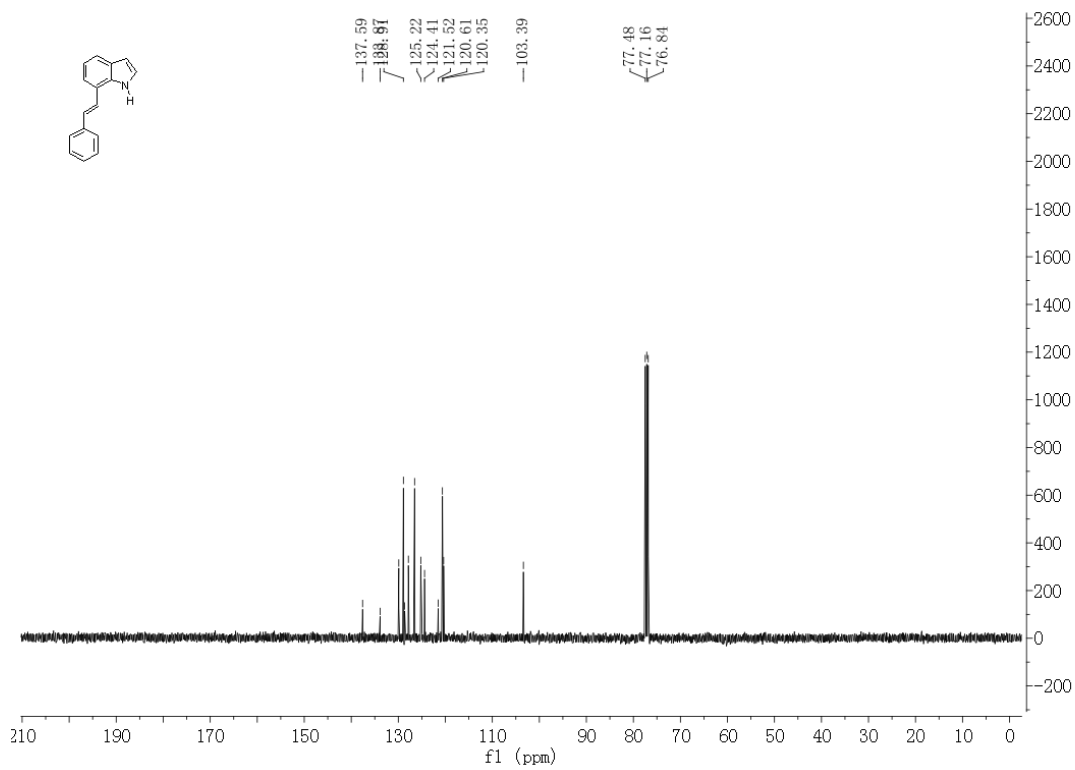
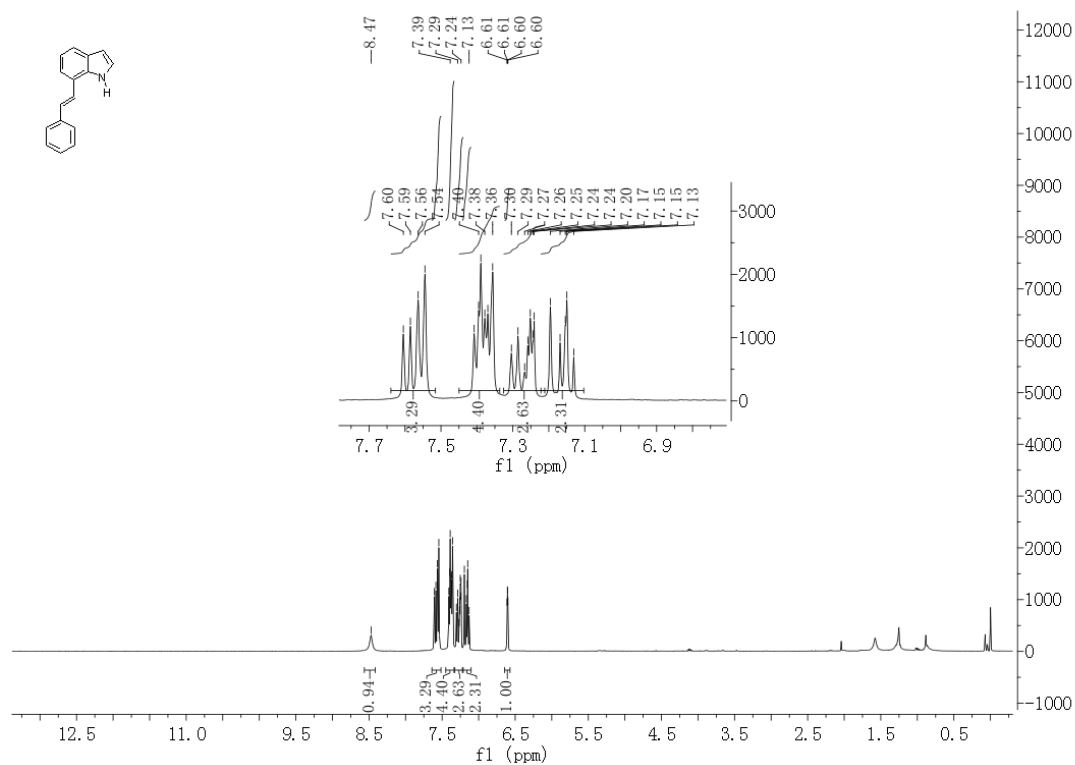
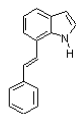
(E)-7-Styrylindoline (5df)



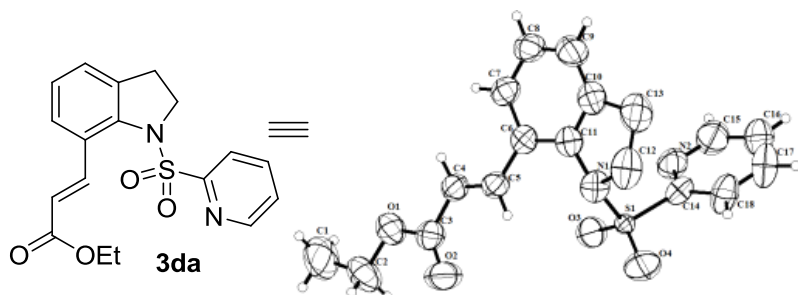
(E)-Ethyl 3-(1H-indol-7-yl)acrylate (6da)



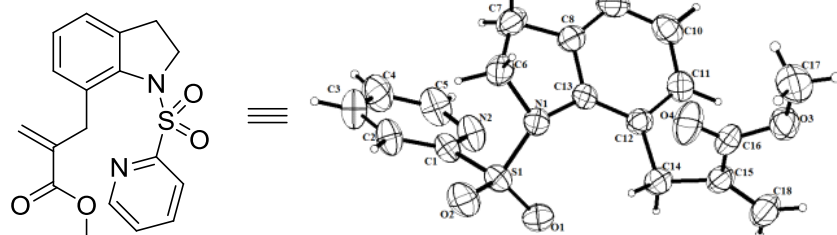
(E)-7-Styryl-1H-indole (6df)



2: X-Ray structure of 3da and 3dk



3da X-Ray



3dk X-Ray

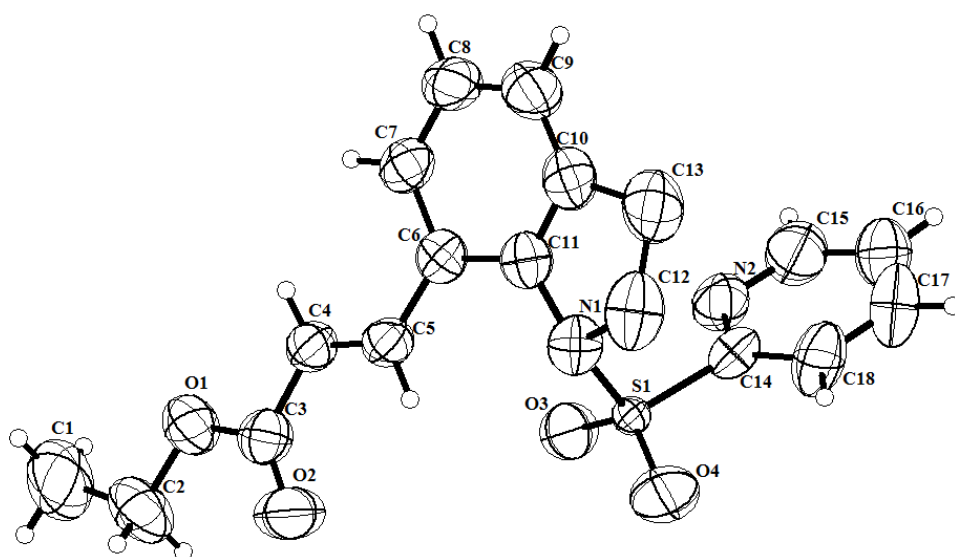


Table 1. Crystal data and structure refinement for 3da.

Identification code	3da
Empirical formula	C ₁₈ H ₁₈ N ₂ O ₄ S
Formula weight	358.40
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.8040(16) Å alpha = 90 deg. b = 10.9952(19) Å beta = 97.334(3) deg. c = 18.299(3) Å gamma = 90 deg.
Volume	1756.8(5) Å ³

Z, Calculated density	4, 1.355 Mg/m ³
Absorption coefficient	0.209 mm ⁻¹
F(000)	752
Crystal size	0.36 x 0.30 x 0.23 mm
Theta range for data collection	2.17 to 25.10 deg.
Limiting indices	-10<=h<=10, -9<=k<=13, -21<=l<=21
Reflections collected / unique	8577 / 3133 [R(int) = 0.0262]
Completeness to theta = 25.10	99.9 %
Absorption correction	Semi-empirical from equivalent
Max. and min. transmission	0.9532 and 0.9292
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3133 / 0 / 227
Goodness-of-fit on F ²	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0920
R indices (all data)	R1 = 0.0590, wR2 = 0.1040
Largest diff. peak and hole	0.156 and -0.220 e.A ⁻³

Table 2. Bond lengths [Å] and angles [deg] for **3da**.

S(1)-O(3)	1.4245(14)
S(1)-O(4)	1.4295(14)
S(1)-N(1)	1.6557(18)
S(1)-C(14)	1.785(2)
N(1)-C(11)	1.450(2)
N(1)-C(12)	1.510(3)
N(2)-C(14)	1.318(2)
N(2)-C(15)	1.338(3)
O(1)-C(3)	1.342(2)
O(1)-C(2)	1.447(3)
O(2)-C(3)	1.201(2)
C(1)-C(2)	1.480(4)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.458(3)
C(4)-C(5)	1.310(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.466(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.399(3)
C(6)-C(11)	1.402(3)
C(7)-C(8)	1.382(3)

C(7)-H(7)	0.9300
C(8)-C(9)	1.375(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.376(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.390(3)
C(10)-C(13)	1.505(3)
C(12)-C(13)	1.521(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(18)	1.370(3)
C(15)-C(16)	1.362(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.361(4)
C(16)-H(16)	0.9300
C(17)-C(18)	1.382(4)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
O(3)-S(1)-O(4)	120.21(10)
O(3)-S(1)-N(1)	107.54(9)
O(4)-S(1)-N(1)	105.47(9)
O(3)-S(1)-C(14)	108.50(9)
O(4)-S(1)-C(14)	107.15(10)
N(1)-S(1)-C(14)	107.33(9)
C(11)-N(1)-C(12)	104.16(17)
C(11)-N(1)-S(1)	121.05(12)
C(12)-N(1)-S(1)	115.47(14)
C(14)-N(2)-C(15)	116.0(2)
C(3)-O(1)-C(2)	116.89(18)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(1)	107.5(2)
O(1)-C(2)-H(2A)	110.2
C(1)-C(2)-H(2A)	110.2
O(1)-C(2)-H(2B)	110.2
C(1)-C(2)-H(2B)	110.2
H(2A)-C(2)-H(2B)	108.5

O(2)-C(3)-O(1)	123.1(2)
O(2)-C(3)-C(4)	125.4(2)
O(1)-C(3)-C(4)	111.52(18)
C(5)-C(4)-C(3)	121.66(19)
C(5)-C(4)-H(4)	119.2
C(3)-C(4)-H(4)	119.2
C(4)-C(5)-C(6)	126.94(18)
C(4)-C(5)-H(5)	116.5
C(6)-C(5)-H(5)	116.5
C(7)-C(6)-C(11)	116.03(18)
C(7)-C(6)-C(5)	121.29(18)
C(11)-C(6)-C(5)	122.58(18)
C(8)-C(7)-C(6)	121.9(2)
C(8)-C(7)-H(7)	119.1
C(6)-C(7)-H(7)	119.1
C(9)-C(8)-C(7)	120.5(2)
C(9)-C(8)-H(8)	119.8
C(7)-C(8)-H(8)	119.8
C(8)-C(9)-C(10)	119.5(2)
C(8)-C(9)-H(9)	120.2
C(10)-C(9)-H(9)	120.2
C(9)-C(10)-C(11)	119.9(2)
C(9)-C(10)-C(13)	130.7(2)
C(11)-C(10)-C(13)	109.3(2)
C(10)-C(11)-C(6)	121.92(19)
C(10)-C(11)-N(1)	111.06(18)
C(6)-C(11)-N(1)	126.65(18)
N(1)-C(12)-C(13)	105.34(18)
N(1)-C(12)-H(12A)	110.7
C(13)-C(12)-H(12A)	110.7
N(1)-C(12)-H(12B)	110.7
C(13)-C(12)-H(12B)	110.7
H(12A)-C(12)-H(12B)	108.8
C(10)-C(13)-C(12)	102.5(2)
C(10)-C(13)-H(13A)	111.3
C(12)-C(13)-H(13A)	111.3
C(10)-C(13)-H(13B)	111.3
C(12)-C(13)-H(13B)	111.3
H(13A)-C(13)-H(13B)	109.2
N(2)-C(14)-C(18)	124.6(2)
N(2)-C(14)-S(1)	114.97(15)
C(18)-C(14)-S(1)	120.43(17)
N(2)-C(15)-C(16)	124.2(2)
N(2)-C(15)-H(15)	117.9

C(16)-C(15)-H(15)	117.9
C(17)-C(16)-C(15)	118.3(3)
C(17)-C(16)-H(16)	120.9
C(15)-C(16)-H(16)	120.9
C(16)-C(17)-C(18)	119.3(2)
C(16)-C(17)-H(17)	120.4
C(18)-C(17)-H(17)	120.4
C(14)-C(18)-C(17)	117.6(2)
C(14)-C(18)-H(18)	121.2
C(17)-C(18)-H(18)	121.2

Symmetry transformations used to generate equivalent atoms:

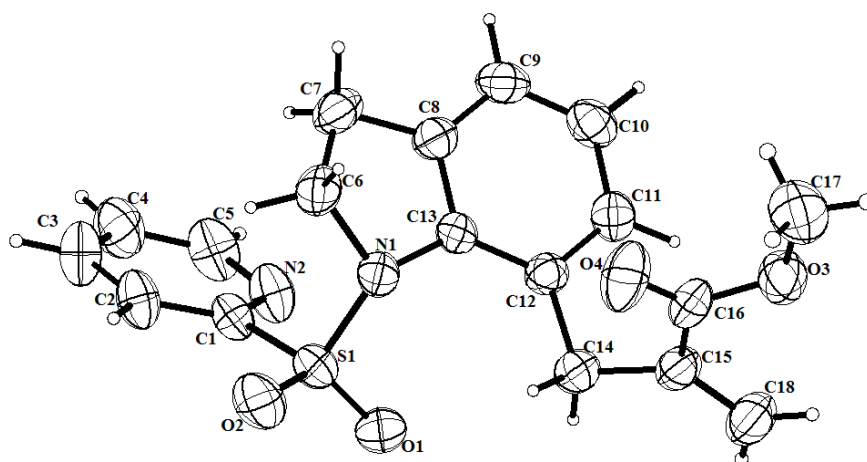


Table 3. Crystal data and structure refinement for 3dk.

Identification code	xb7209_0m
Empirical formula	C ₁₈ H ₁₈ N ₂ O ₄ S
Formula weight	358.40
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.0332(18) Å alpha = 90 deg. b = 10.971(2) Å beta = 90 deg. c = 17.316(3) Å gamma = 90 deg.
Volume	1716.0(6) Å ³
Z, Calculated density	4, 1.387 Mg/m ³
Absorption coefficient	0.214 mm ⁻¹
F(000)	752
Crystal size	0.37 x 0.31 x 0.25 mm
Theta range for data collection	2.20 to 25.09 deg.
Limiting indices	-8<=h<=10, -12<=k<=13, -20<=l<=13
Reflections collected / unique	8397 / 3057 [R(int) = 0.0443]
Completeness to theta = 25.09	100.0 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.9478 and 0.9259
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3057 / 0 / 227
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0736
R indices (all data)	R1 = 0.0343, wR2 = 0.0755
Absolute structure parameter	0.04(6)
Largest diff. peak and hole	0.197 and -0.204 e.A ⁻³

Table 4. Bond lengths [Å] and angles [deg] for 3dk.

S(1)-O(2)	1.4214(14)
S(1)-O(1)	1.4229(14)
S(1)-N(1)	1.6464(15)
S(1)-C(1)	1.7831(19)
N(1)-C(13)	1.448(2)
N(1)-C(6)	1.495(2)
N(2)-C(1)	1.321(2)
N(2)-C(5)	1.336(3)
O(3)-C(16)	1.335(2)
O(3)-C(17)	1.437(3)
O(4)-C(16)	1.195(2)
C(1)-C(2)	1.376(3)
C(2)-C(3)	1.381(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.363(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.369(3)
C(4)-H(4)	0.9300
C(5)-H(5)	0.9300
C(6)-C(7)	1.530(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.496(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.385(3)
C(8)-C(13)	1.388(2)
C(9)-C(10)	1.379(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.370(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.396(2)
C(11)-H(11)	0.9300
C(12)-C(13)	1.390(2)

C(12)-C(14)	1.512(2)
C(14)-C(15)	1.500(3)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(18)	1.320(3)
C(15)-C(16)	1.483(3)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9300
C(18)-H(18B)	0.9300

O(2)-S(1)-O(1)	119.72(9)
O(2)-S(1)-N(1)	106.33(9)
O(1)-S(1)-N(1)	107.88(8)
O(2)-S(1)-C(1)	106.57(9)
O(1)-S(1)-C(1)	109.65(9)
N(1)-S(1)-C(1)	105.86(8)
C(13)-N(1)-C(6)	105.22(13)
C(13)-N(1)-S(1)	121.31(11)
C(6)-N(1)-S(1)	114.62(12)
C(1)-N(2)-C(5)	116.60(18)
C(16)-O(3)-C(17)	116.10(17)
N(2)-C(1)-C(2)	124.56(18)
N(2)-C(1)-S(1)	114.58(14)
C(2)-C(1)-S(1)	120.70(15)
C(1)-C(2)-C(3)	117.2(2)
C(1)-C(2)-H(2)	121.4
C(3)-C(2)-H(2)	121.4
C(4)-C(3)-C(2)	119.5(2)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	118.7(2)
C(3)-C(4)-H(4)	120.7
C(5)-C(4)-H(4)	120.7
N(2)-C(5)-C(4)	123.4(2)
N(2)-C(5)-H(5)	118.3
C(4)-C(5)-H(5)	118.3
N(1)-C(6)-C(7)	105.15(15)
N(1)-C(6)-H(6A)	110.7
C(7)-C(6)-H(6A)	110.7
N(1)-C(6)-H(6B)	110.7
C(7)-C(6)-H(6B)	110.7
H(6A)-C(6)-H(6B)	108.8

C(8)-C(7)-C(6)	102.09(15)
C(8)-C(7)-H(7A)	111.4
C(6)-C(7)-H(7A)	111.4
C(8)-C(7)-H(7B)	111.4
C(6)-C(7)-H(7B)	111.4
H(7A)-C(7)-H(7B)	109.2
C(9)-C(8)-C(13)	119.67(17)
C(9)-C(8)-C(7)	130.03(17)
C(13)-C(8)-C(7)	110.18(16)
C(10)-C(9)-C(8)	118.57(17)
C(10)-C(9)-H(9)	120.7
C(8)-C(9)-H(9)	120.7
C(11)-C(10)-C(9)	121.02(18)
C(11)-C(10)-H(10)	119.5
C(9)-C(10)-H(10)	119.5
C(10)-C(11)-C(12)	122.25(18)
C(10)-C(11)-H(11)	118.9
C(12)-C(11)-H(11)	118.9
C(13)-C(12)-C(11)	115.73(16)
C(13)-C(12)-C(14)	123.89(15)
C(11)-C(12)-C(14)	120.10(16)
C(8)-C(13)-C(12)	122.68(16)
C(8)-C(13)-N(1)	110.10(15)
C(12)-C(13)-N(1)	126.76(15)
C(15)-C(14)-C(12)	111.43(15)
C(15)-C(14)-H(14A)	109.3
C(12)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14B)	109.3
C(12)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
C(18)-C(15)-C(16)	121.64(18)
C(18)-C(15)-C(14)	124.19(19)
C(16)-C(15)-C(14)	114.16(16)
O(4)-C(16)-O(3)	122.8(2)
O(4)-C(16)-C(15)	123.58(18)
O(3)-C(16)-C(15)	113.61(16)
O(3)-C(17)-H(17A)	109.5
O(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	120.0
C(15)-C(18)-H(18B)	120.0

H(18A)-C(18)-H(18B)

120.0

Symmetry transformations used to generate equivalent atoms: