Supporting Information for

Preparation of 3-azoindoles and 3-hydrazonoindolin-2-imines as well as their applications as NNO pincer ligands for boron

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General Information

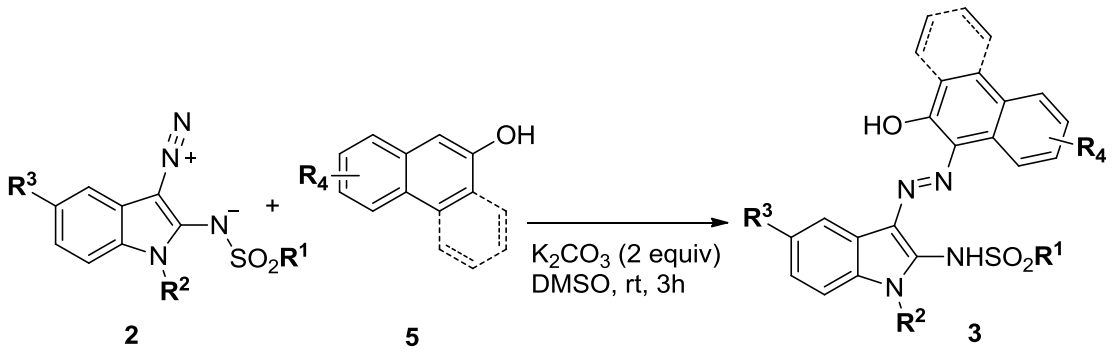
NMR spectra were recorded on 400MHz, 500MHz, or 600MHz spectrometer. The chemical shifts for ^{1}H NMR spectra were reported relative to internal TMS (0 ppm) in $CDCl_3$ or $(CD_3)_2SO$. The following abbreviations were used to describe peak patterns when appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants(*J* values) were reported in Hertz (Hz). ^{13}C NMR spectra were recorded on 100MHz, 125MHz, or 150MHz spectrometerand the chemical shifts were referenced to the central line of the triplet of $CDCl_3$(77.27 ppm) or the center line of the heptet of $(CD_3)_2SO$ (40.0 ppm). Infrared spectra were obtained on BRUKERVECTOR 22 spectrometer. Absorption spectra were obtained on SHIMAZU UV-Visible (UV-2450) spectrophotometer. High-resolution mass spectra (HRMS) data wererecorded onanMatrix-Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) mass spectrometer and Agilent Technologies 6224 TOF LC/MS apparatus (ESI). Melting points were recorded on a SGW X-4.

Compounds **2** were prepared according to the published methods.[1,2]Compounds**5**and **6** were purchased from chemical companies.

References

1. Y. P. Xing, G. R. Sheng, J. Wang, P. Lu, and Y.G. Wang, Org. Lett. 2014, 16, 1244−1247.
2. G. R. Sheng, K. Huang, Z. H. Chi, H. L. Ding, Y. P. Xing, P. Lu, and Y. G. Wang, Org. Lett., 2014, 16,5096–5099

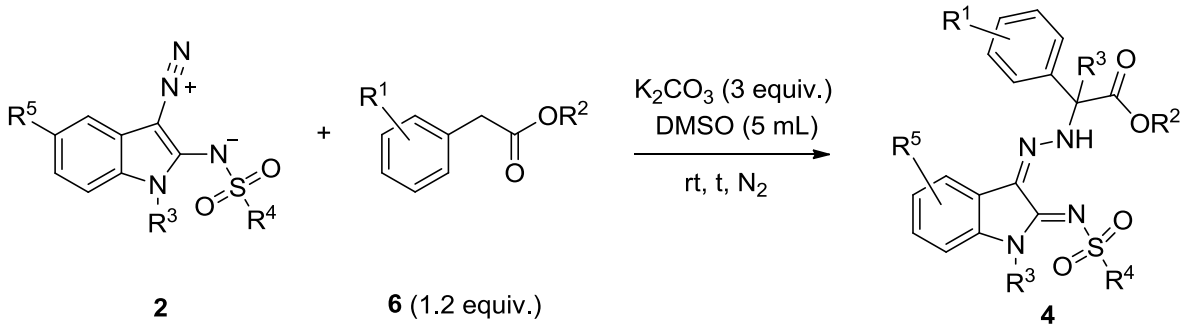
General Procedure for the Synthesis of 3



2 5 3

To a stirred suspension of**2**(0.25 mmol), K_2CO_3(69 mg) in DMSO (5 mL) was added **5**(0.275 mmol) at room temperature. Then the reaction mixture was stirred for 3h. After the reaction completed,the mixture was washed with diluted HCl, extracted with DCM, dried over anhydrousNa_2SO_4, then filtered and concentrated. The residue was purified by column chromatography over silica gel with hexane/DCMas the eluent to give **3**.

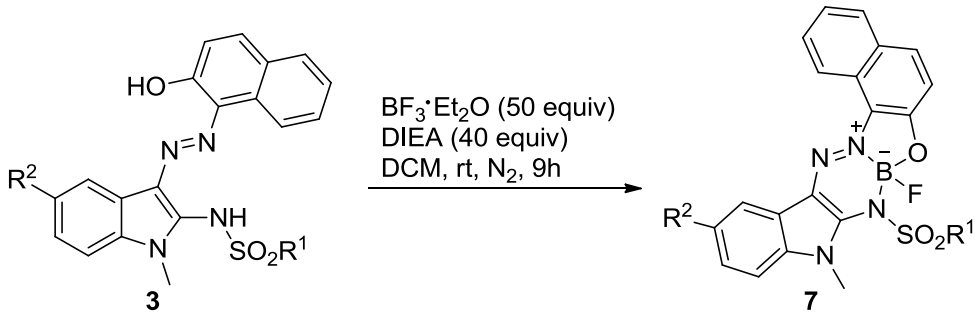
General Procedure for the Synthesis of 4



2 **6** (1.2 equiv.) 4

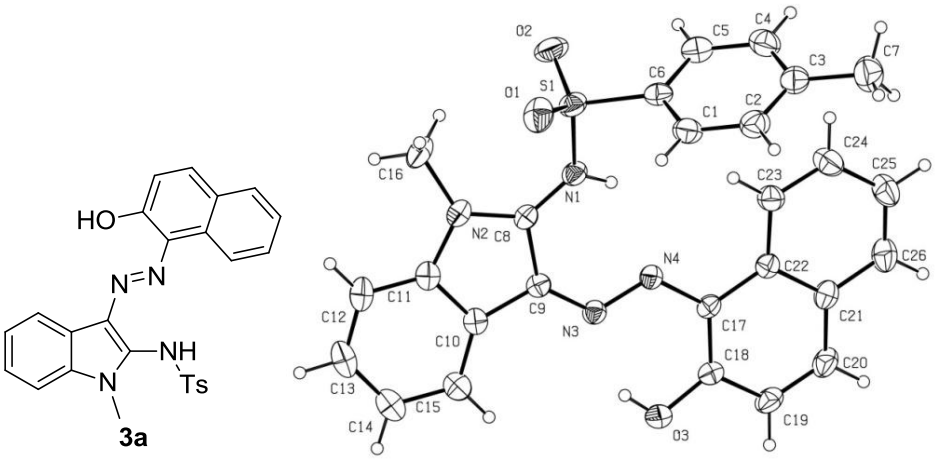
To a stirred solution of **2**(0.25 mmol), K_2CO_3 (104 mg) in DMSO (5 mL) at N_2 was added**6**via syringe at room temperature. After the reaction completed (checked by TLC), the mixture was washed with diluted HCl, extracted with DCM, dried over anhydrous Na_2SO_4, then filtered and concentrated. The residue was purified by column chromatography over silica gel with hexane/EtOAc as the eluent to give compound **4**.

General Procedure for the Synthesis of 7



To a stirred solution of **3**(0.25 mmol) in DCM (5mL) under N_2 atmosphere was addedBF_3 Ɛt_2O (1.6 ml) and DIEA (1.4 mL)via syringe at room temperature.The reaction mixture was stirred for about 9h at room temperature. After the reaction completed, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel with hexane/DCMas the eluent to give **7**.

The ORTEP diagram and Crystal Parametersof3a



Bond precision: C-C = 0.0039 A Wavelength=0.71073

Cell: a=8.2558(6) b=10.1328(7) c=13.9082(11)
alpha=77.492(6) beta=79.130(6) gamma=85.572(6)
Temperature: 293 K

	Calculated	Reported
Volume	1114.69(15)	1114.69(14)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C26 H22 N4 O3 S	C26 H22 N4 O3 S
Sum formula	C26 H22 N4 O3 S	C26 H22 N4 O3 S
Mr	470.54	470.54
Dx,g cm-3	1.402	1.402
Z	2	2
Mu (mm-1)	0.183	0.183
F000	492.0	492.0
F000'	492.44	
h,k,lmax	9,12,16	9,12,16
Nref	4069	4054
Tmin,Tmax	0.957,0.968	0.770,1.000
Tmin'	0.955	

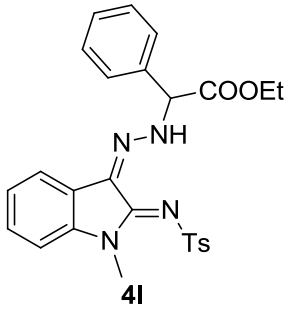
Correction method= MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.350

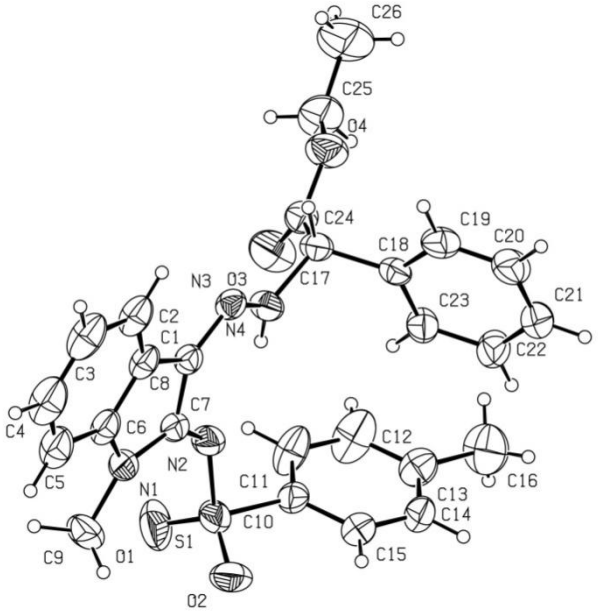
R(reflections)= 0.0505(2928) wR2(reflections)= 0.1446(4054)

S = 1.031 Npar= 310

The ORTEP diagram and Crystal Parametersof4l



4l



Bond precision: C-C = 0.0048 A Wavelength=0.71073

Cell:	**a=33.094(3)**	**b=9.7382(7)**	**c=15.8855(11)**
	alpha=90	**beta=96.540(7)**	**gamma=90**
Temperature:	**293 K**		

	Calculated	Reported
Volume	5086.2(7)	5086.3(7)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C26 H26 N4 O4 S	C26 H26 N4 O4 S
Sum formula	C26 H26 N4 O4 S	C26 H26 N4 O4 S
Mr	490.57	490.57
Dx,g cm-3	1.281	1.281
Z	8	8
Mu (mm-1)	0.166	0.166
F000	2064.0	2064.0
F000'	2065.85	
h,k,lmax	39,11,19	39,11,19
Nref	4666	4653
Tmin,Tmax	0.951,0.963	0.965,1.000
Tmin'	0.951	

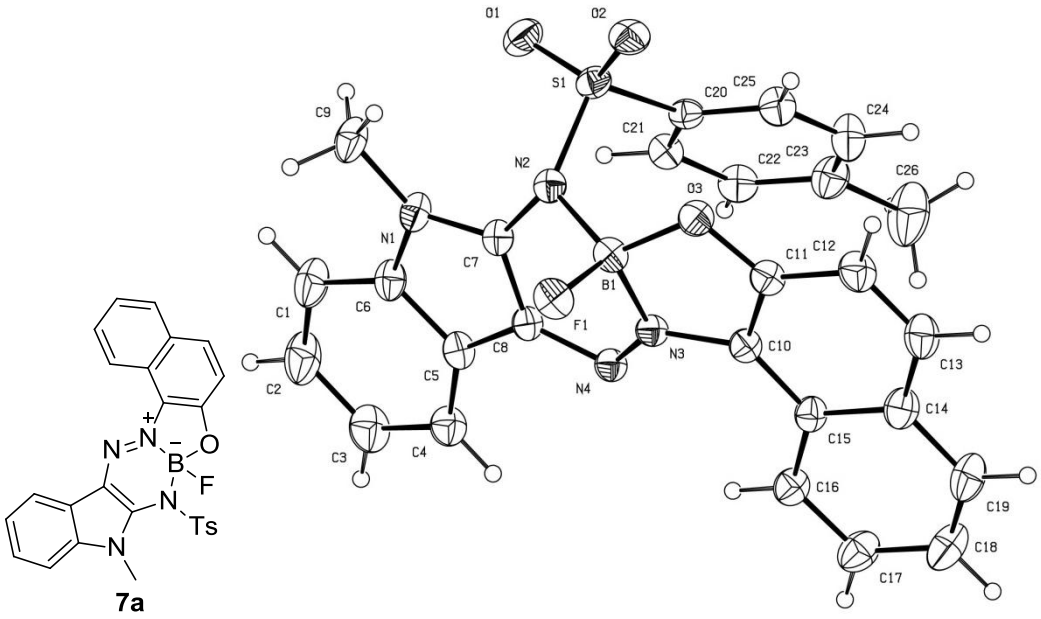
Correction method= MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.350

R(reflections)= 0.0531(2775) wR2(reflections)= 0.1563(4653)

S = 1.020 Npar= 319

The ORTEP diagram and Crystal Parametersof7a



Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=11.8786(8) b=14.6539(7) c=14.7921(10)
alpha=90 beta=112.989(8) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2370.3(3)	2370.3(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H20 B F N4 O3 S	C26 H20 B F N4 O3 S
Sum formula	C26 H20 B F N4 O3 S	C26 H20 B F N4 O3 S
Mr	498.33	498.33
Dx,g cm-3	1.396	1.396
Z	4	4
Mu (mm-1)	0.182	0.182
F000	1032.0	1032.0
F000'	1032.95	
h,k,lmax	14,17,17	14,17,17
Nref	4332	4317
Tmin,Tmax	0.926,0.943	0.888,1.000
Tmin'	0.926	

Correction method= # Reported T Limits: Tmin=0.888 Tmax=1.000
AbsCorr = MULTI-SCAN

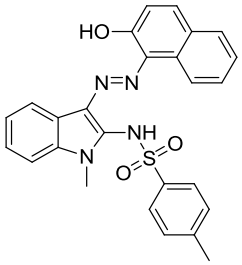
Data completeness= 0.997 Theta(max)= 25.340

R(reflections)= 0.0399(3352) wR2(reflections)= 0.1057(4317)

S = 1.017 Npar= 327

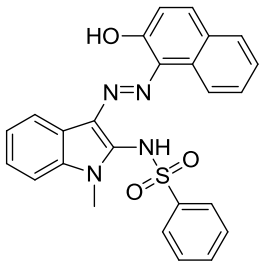
Characterization Data for Products

(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(**3a**)



Blacksolid (115 mg, 98%); m.p. 174.9-175.8^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.67 (b, 1H), 11.22 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.69 - 7.67 (m, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.40 - 7.36 (m, 1H), 7.27 - 7.20 (m, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.95 - 6.91 (m, 2H), 4.02 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ146.8, 144.0, 141.0, 139.7, 123.0, 128.7, 128.5, 128.1, 127.4, 127.2, 127.1, 126.7, 126.5, 125.0, 124.2, 123.7, 121.2, 120.4, 120.0, 118.8, 118.3, 110.4, 33.5, 21.7; IR (KBr) v 3451, 3167, 3058, 1591, 1556, 1471, 1372, 1284, 1144, 1085, 805 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{23}N_4O_3S]^+$:471.149; found:471.149.

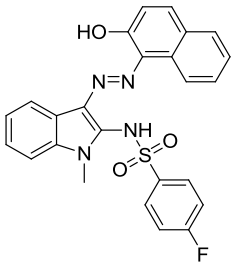
(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl)benzenesulfonamide(**3b**)



Reddish-brownsolid (116 mg, 99%); m.p. 184.3-185.1^{o}C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 13.05 (s, 1H), 11.46 (b, 1H), 8.64 (d,*J* = 8.4 Hz, 1H), 8.41 - 8.39 (m, 1H), 7.91 - 7.86 (m, 2H), 7.74 - 7.72 (m, 2H), 7.68 (t,*J* = 7.6 Hz, 1H), 7.61 - 7.60 (m, 1H), 7.48 - 7.42 (m, 6H), 7.17 (d, *J* = 8.8 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 149.7, 140.2, 135.6, 134.9, 133.6, 132.4, 131.9, 129.7, 129.2, 128.8, 128.6, 128.1, 127.6, 127.3, 125.2, 124.4, 124.0, 121.9, 121.8, 120.1, 117.5, 111.6,

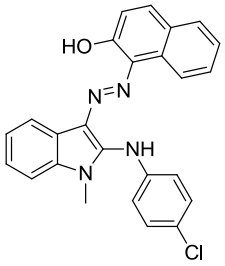
30.4; IR (KBr) v 3452, 3179, 3058, 1592, 1553, 1467, 1371, 1297, 1156, 1086, 796 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{21}N_4O_3S]^+$:457.133; found:457.133.

(E)-4-Fluoro-N-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl) benzenesulfonamide(3c)



Blacksolid (117 mg, 99%); m.p. 173.3-174.1°C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.80 (s, 1H), 11.51 (b, 1H), 8.65(d, *J* = 8.0 Hz, 1H), 8.40 - 8.38 (m, 1H), 7.91 - 7.86 (m, 2H), 7.78 - 7.75 (m, 2H), 7.70 - 7.63 (m, 2H), 7.48 - 7.43 (m, 3H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ165.1 (d, $^1J_{CF}$ = 250 Hz), 149.4, 136.5, 135.7, 134.9, 132.4, 131.8, 130.5 (d, $^3J_{CF}$ = 9 Hz), 129.1(d, $^4J_{CF}$ = 3 Hz), 128.8, 128.6, 128.1, 127.5, 125.3, 124.5, 124.1, 121.9, 121.8, 119.9, 117.5, 116.8 (d, $^2J_{CF}$ = 24 Hz), 111.6, 30.5; IR (KBr) v 3452, 3188, 3070, 1624, 1555, 1467, 1371, 1286, 1147, 1085, 795 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{20}FN_4O_3S]^+$:475.124; found:475.123.

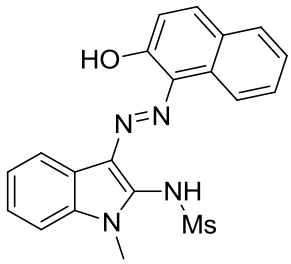
(E)-4-Chloro-N-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl) benzenesulfonamide(3d)



Blacksolid (116 mg,95%); m.p. 173.2-174.5°C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.70 (s, 1H), 11.57 (b, 1H), 8.64 (d, *J* = 7.2 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H),7.91 - 7.86 (m, 2H), 7.69 - 7.63 (m, 4H), 7.48 - 7.42 (m,5H), 7.16 (d, *J* = 8.8 Hz, 1H), 3.74(s,

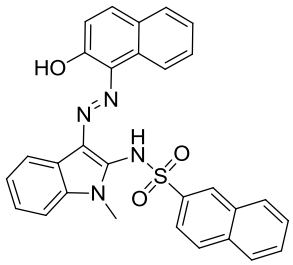
3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 149.3, 138.8, 135.7, 134.7, 132.4, 131.9, 129.7, 129.2, 128.7, 128.6, 128.1, 127.5, 125.3, 124.4, 124.1, 121.9, 121.8, 119.9, 117.5, 111.6, 30.5; IR (KBr) v 3436, 3185, 3057, 1578, 1470, 1375, 1305, 1147, 1087, 1002, 798 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{20}ClN_4O_3S]^+$:491.094; found:491.094.

(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl)methane sulfonamide(3e)



Orangepowder (93 mg, 94%); m.p. 165.0-166.2^{o}C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 13.22 (b, 1H), 11.67 (b, 1H), 8.89 (d, *J* = 7.2 Hz, 1H), 8.36 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.73 - 7.69 (m, 1H), 7.58 (d, *J* = 3.2 Hz, 1H), 7.50 - 7.43 (m, 3H), 7.29 (d,*J* = 8.8 Hz, 1H), 3.87 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 148.9, 138.2, 136.9, 131.4, 130.5, 128.9, 128.9, 128.1, 127.1, 125.8, 124.5, 124.1, 122.3, 121.2, 119.6, 118.6, 111.5, 42.6, 31.2; IR (KBr) v 3452, 3264, 3022, 1576, 1546, 1469, 1371, 1324, 1157, 982, 817 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{20}H_{19}N_4O_3S]^+$:395.117; found:395.118.

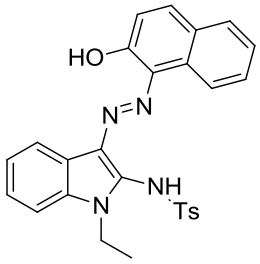
(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl)naphthalene-2-sulfonamide(3f)



Reddish-brownpowder (124 mg, 98%); m.p. 160.1-161.3^{o}C; ^{1}H NMR (400 MHz,

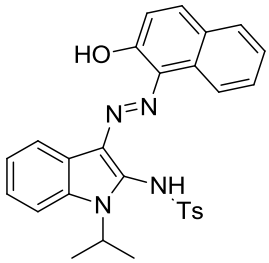
$(CD_3)_2SO$) δ 12.87 (s, 1H), 11.49 (b, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.40 (s, 1H), 8.37 - 8.35 (m, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.72 - 7.59 (m, 4H), 7.46 - 7.41 (m, 5H), 6.91 (d,*J* = 8.4 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 149.3, 137.2, 135.6, 134.9, 134.7, 132.2, 132.1, 131.8, 129.7, 129.6, 129.1, 128.6, 128.5, 128.5, 127.9, 127.7, 127.7, 125.1, 124.3, 124.0, 122.6, 121.9, 121.7, 119.9, 117.5, 111.6, 30.4; IR (KBr) v 3451, 3265, 3057, 1577, 1467, 1375, 1296, 1129, 1072, 1004, 797 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{29}H_{23}N_4O_3S]^+$:507.149; found:507.149.

(E)-N-(1-Ethyl-3-((2-hydroxynaphthalen-1-yl)diazenyl)-1H-indol-2-yl)-4-methylbenzenesulfonamide(3g)



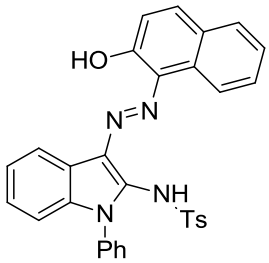
Blacksolid (120 mg, 99%); m.p. 156.3-157.5^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.31 (b, 1H), 11.32 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.70 - 7.66 (m, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.38 - 7.34 (m, 1H), 7.26 - 7.12 (m, 6H), 7.04 - 6.95 (m, 2H), 4.61 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.52 (t, *J* = 7.2 Hz,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.0, 139.5, 139.4, 129.9, 129.2, 128.7, 128.5, 127.8, 127.7, 127.2, 127.1, 126.6, 125.5, 124.0, 123.7, 121.4, 121.0, 119.9, 119.0, 118.5, 110.8, 40.7, 21.7, 13.6; IR (KBr) v 3452, 3057, 2973, 1576, 1547, 1465, 1358, 1283, 1146, 1084, 816, 739 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{27}H_{25}N_4O_3S]^+$:485.164; found:485.164.

(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1-isopropyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3h)



Blackpowder (116 mg, 93%); m.p. 153.3-154.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.55 (s, 1H), 10.09 (b, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.92 - 7.90 (m, 1H), 7.75 - 7.73 (m, 1H), 7.65 - 7.59 (m, 4H), 7.39 - 7.34 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.54 (m, 1H), 1.96 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 144.6, 137.1, 136.0, 135.2, 130.6, 129.6, 129.2, 128.6, 128.5, 127.7, 127.3, 126.1, 125.8, 125.6, 124.2, 123.3, 121.3, 120.4, 120.3, 119.8, 113.7, 49.1, 21.4, 20.9; IR (neat) v 3200, 3056, 2978, 1746, 1574, 1538, 1463, 1374, 1280, 1146, 1086, 910 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{28}H_{27}N_4O_3S]^+$:499.180; found:499.180.

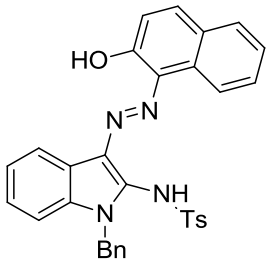
(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1-phenyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3i)



Blackpowder (125 mg,94%); m.p. 169.3-170.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (b, 1H), 11.74 (s, 1H), 7.86 - 7.84 (m,1H), 7.71 (d,*J* = 8.0 Hz, 1H), 7.63 (d,*J* = 8.4 Hz, 2H), 7.58 - 7.53 (m, 4H), 7.47 - 7.45 (m, 2H), 7.37 (d,*J* = 8.4 Hz, 1H), 7.30 - 7.22 (m, 3H), 7.16 (d, *J* = 9.2 Hz, 1H), 7.11 - 7.06 (m, 3H), 6.74 - 6.72 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 143.7, 141.5, 139.4, 135.7, 129.8, 129.7, 129.6, 129.4, 128.7, 128.6, 128.5, 127.6, 127.3, 127.0, 126.9, 126.3, 124.3, 123.9, 122.0, 120.4, 120.0, 119.2, 119.1, 111.6, 21.6; IR (neat) v 3203, 3061, 2920, 1573, 1548, 1499, 1377, 1302, 1150, 1087, 909, 734 cm^{-1}; MALDI-TOF-MS

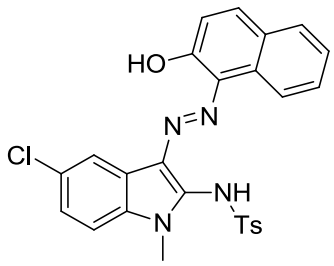
(DHB)calcd for $[C_{31}H_{25}N_4O_3S]^+$:533.164; found:533.164.

(E)-N-(1-Benzyl-3-((2-hydroxynaphthalen-1-yl)diazenyl)-1H-indol-2-yl)-4-methyl benzenesulfonamide(3j)



Redpowder (134 mg, 98%); m.p. 174.9-175.8^{o}C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.54 (s, 1H), 11.40 (b, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H),7.93 - 7.89 (m, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.55 - 7.45 (m,4H), 7.38-7.25 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 149.2, 144.2, 137.3, 136.3, 134.7, 134.2, 132.7, 132.2, 129.8, 129.6, 129.1, 128.7, 128.5, 128.1, 128.0, 128.0, 127.4, 127.2, 125.1, 124.5, 123.9, 122.1, 121.7, 120.1, 117.7, 112.2, 46.4, 20.8; IR (KBr) v 3452, 3060, 2920, 1571, 1464, 1349, 1296, 1167, 1087, 1051, 811 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{32}H_{27}N_4O_3S]^+$:547.180; found:547.180.

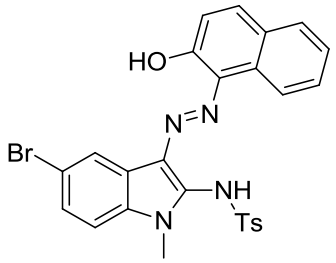
(E)-N-(5-Chloro-3-((2-hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl) -4-methylbenzenesulfonamide(3k)



Graypowder (120 mg,95%); m.p. 183.2-184.5^{o}C; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 12.55 (s, 1H), 11.34 (b, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.32 (s, 1H), 7.92 (t, *J* = 8.5 Hz, 2H), 7.69 - 7.67 (m,2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.47 - 7.44 (m, 2H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 149.3, 144.3, 136.4, 135.4, 133.8, 132.8, 132.1, 129.9, 129.4, 128.8,

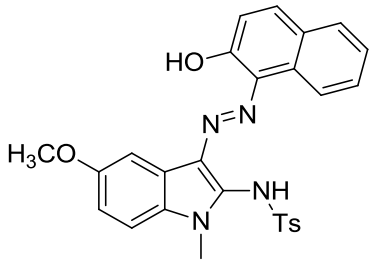
128.6, 128.1, 127.4, 127.0, 124.8, 124.5, 121.3, 120.9, 120.2, 118.1, 113.5, 30.6, 20.9; IR (KBr) v 3452, 3066, 2923, 1580, 1469, 1359, 1285, 1145, 1122, 1085, 926, 805 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{22}ClN_4O_3S]^+$:505.110; found:505.109.

(E)-N-(5-Bromo-3-((2-hydroxynaphthalen-1-yl)diazenyl)-1-methyl-1H-indol-2-yl) -4-methylbenzenesulfonamide(3l)



Nut-brownpowder (125 mg, 91%); m.p. 185.6-186.5^oC; ^1H NMR (500 MHz, $(CD_3)_2SO$) δ 12.53 (s, 1H), 11.35 (b, 1H), 8.51 - 8.48 (m, 2H), 7.92 (t, *J* = 8.0 Hz, 2H), 7.68 - 7.62 (m,2H), 7.56 (dd, *J* = 8.5,1.5 Hz, 1H), 7.51 - 7.46 (m, 3H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 149.3, 144.3, 136.4, 135.3, 134.1, 132.8, 132.1, 129.9, 129.4, 128.9, 128.6, 128.1, 127.3, 127.3, 126.8, 124.5, 124.0, 121.3, 120.2, 118.7, 116.1, 113.8, 30.5, 20.9; IR (KBr) v 3451, 3155, 3060, 1578, 1467, 1358, 1284, 1143, 1120, 1085, 922, 804 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{22}BrN_4O_3S]^+$:549.059; found:549.060.

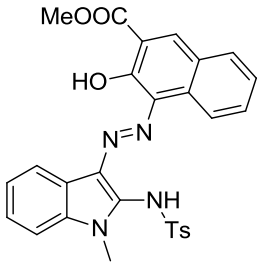
(E)-N-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-5-methoxy-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3m)



Reddish brownpowder (123 mg, 98%); m.p. 183.5-184.2^oC; ^1H NMR (500 MHz, $(CD_3)_2SO$) δ 12.66 (s, 1H), 11.21 (b, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.86 (m,

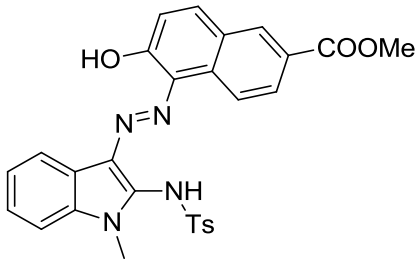
3H),7.65 (t, *J* = 7.5 Hz, 1H), 7.55 - 7.52 (m,3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.0Hz, 2H), 7.05 (dd, *J* = 8.5,2.0 Hz, 1H), 3.90 (s, 3H), 3.67 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 157.0, 149.2, 144.2, 136.7, 134.4, 132.1, 132.0, 130.2, 129.9, 129.3, 128.8, 128.5, 127.9, 127.7, 127.3, 124.4, 121.5, 120.1, 117.7, 114.2, 112.6, 104.0, 55.7, 30.4, 21.0; IR (KBr) v 3437, 2924, 2853,1578, 1488, 1368, 1282, 1140, 1122, 1084, 936, 805 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{27}H_{25}N_4O_4S]^+$:501.159; found:501.159.

(E)-Methyl3-hydroxy-4-((1-methyl-2-(4-methylphenylsulfonamido)-1H-indol-3-yl)diazenyl)-2-naphthoate (3n)



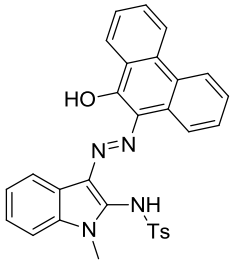
Redsolid (120 mg, 91%); m.p. 203.0-204.4^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.17 (s, 1H), 9.69 (s, 1H), 9.13 (d, *J* = 8.4 Hz, 1H), 8.08 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 2H),7.72 - 7.68 (m, 2H), 7.54 - 7.51 (m, 1H), 7.35 - 7.31 (m, 4H), 7.22 - 7.20 (m, 1H), 7.07 (d, *J* = 7.8 Hz, 1H),4.03 (s, 3H),4.00 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ170.0, 148.2, 145.5, 145.5, 143.4, 141.8, 140.9, 130.2, 129.6, 129.3, 128.0, 127.9, 127.7, 127.7, 127.6, 124.6, 124.0, 123.8, 123.3, 123.1, 118.6, 113.0, 109.9,52.8, 33.3, 21.8; IR (KBr) v 2950, 2925, 2849, 1685, 1576, 1546, 1462, 1438, 1384, 1308, 1209, 1145, 1108, 1085 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{28}H_{25}N_4O_5S]^+$:529.154; found:529.154.

(E)-Methyl 6-hydroxy-5-((1-methyl-2-(4-methylphenylsulfonamido)-1H-indol-3-yl)diazenyl)-2-naphthoate (3o)



Redsolid (111 mg, 84%); m.p. 177.3-178.5^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.58 (b, 1H), 11.39 (s, 1H), 8.36 (d, *J* = 1.2 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.40 - 7.37 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.73 (b, 1H),4.02 (s, 3H),3.97 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ167.1, 148.5, 144.6, 143.8, 139.6, 131.7, 130.2, 128.5, 128.4, 128.4, 127.6, 127.4, 127.0, 126.5, 125.2, 124.3, 121.0, 118.9, 118.2, 110.5, 52.4, 33.6, 21.7; IR (KBr) v 2949, 2923, 2852, 1717, 1625, 1575, 1466, 1436, 1384, 1285, 1203, 1145, 1109, 1085 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{28}H_{25}N_4O_5S]^+$:529.154; found:529.154.

(E)-N-(3-((10-Hydroxyphenanthren-9-yl)diazenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3p)

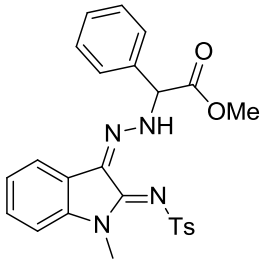


Red-brownsolid (84 mg,64%); m.p. 169.0-170.2^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.21 (s, 1H), 11.32 (b, 1H), 8.52 (t, *J* = 7.8 Hz, 2H), 8.41 – 8.40 (m, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.67 - 7.61 (m, 2H), 7.47 - 7.39 (m, 3H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.25 - 7.24 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H),7.03 (d, *J* = 7.8 Hz, 2H), 4.00 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ148.9, 144.3, 140.6, 139.2, 138.7, 130.9, 129.7, 128.6, 127.7, 127.3, 127.2, 127.0, 126.9, 126.0, 124.8, 124.5, 124.1, 123.7, 123.2, 122.7, 120.5, 120.0, 119.6, 119.2, 110.5, 32.6, 21.5; IR (neat) v

2917, 2842, 1586, 1459, 1426, 1373, 1334, 1281, 1215, 1146, 1102, 1081 cm^{-1}; HRMS (ESI)calcd for $[C_{30}H_{23}N_4O_3S]^-$:519.1496; found:519.1511.

methyl

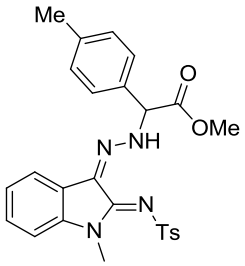
2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4a)



A yellow powder (86 mg, 72%); m.p. 126.8-127.7°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.46 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.23 -7.14 (m,5H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 2H), 5.34 (d, *J* = 7.0 Hz, 1H), 3.96 (s, 3H), 3.67 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 148.5, 142.7, 141.7, 141.2, 135.1, 129.6, 129.2, 128.8, 127.8, 127.7, 127.3, 126.7, 123.9, 123.2, 118.6, 109.8, 68.9, 52.9, 33.1, 21.8ppm;IR (neat) v 2952, 1747, 1574, 1538, 1494, 1464, 1375, 1284, 1146, 1087, 1005, 911, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{25}N_4O_4S]^+$:477.159; found:477.159.

methyl

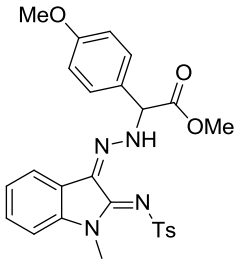
2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-(p-tolyl)acetate (4b)



A yellow powder (76 mg, 62%); m.p. 126.8-127.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.44 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.32 -

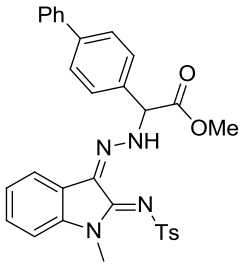
7.28 (m, 1H), 7.24 (d,*J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.30 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.66 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.5, 142.7, 141.7, 141.2, 138.7, 132.2, 129.8, 129.5, 127.6, 127.6, 127.2, 126.7, 123.9, 123.2, 118.5, 109.8, 68.7, 52.8, 33.1, 21.8, 21.5ppm;IR (neat) v 2953, 2924, 1746, 1581, 1538, 1493, 1464, 1375, 1283, 1146, 1086, 1005, 748, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_4S]^+$:491.175; found:491.175.

2-(4-methoxyphenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4c)



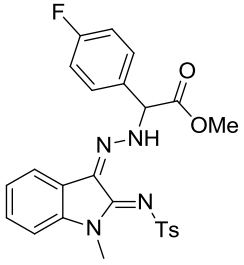
A yellow powder (72 mg, 57%); m.p. 126.8-127.5^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.32 - 7.28 (m, 1H), 7.23 (d,*J* = 8.0 Hz, 2H), 7.15 (td, *J* = 7.6 Hz, 0.4Hz,1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 5.28 (d, *J* = 6.8 Hz, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 3.67 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 160.0, 148.5, 142.7, 141.6, 141.2, 129.5, 128.6, 127.6, 127.6, 127.0, 126.6, 123.9, 123.2, 118.5, 114.5, 109.8, 68.3, 55.5, 52.8, 33.1, 21.7ppm;IR (neat) v 2954, 2923, 1746, 1578, 1538, 1463, 1374, 1281, 1251, 1146, 1083, 1033, 910, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_5S]^+$:507.170; found:507.170.

methyl 2-([1,1'-biphenyl]-4-yl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4d)



A yellow powder (102 mg, 74%); m.p. 165.9-166.3^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 3H), 7.48 - 7.45 (m, 2H), 7.42 (m, 3H), 7.31 (td, *J* = 7.2 Hz, 0.4Hz,1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 - 7.14 (m,1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.39 (d, *J* = 7.2 Hz, 1H), 3.97 (s, 3H), 3.70 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 148.5, 142.8, 141.8, 141.7, 141.2, 140.5, 134.1, 129.6, 129.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.3, 126.7, 124.0, 123.2, 118.6, 109.8, 68.6, 52.9, 33.2, 21.7ppm;IR (neat) v 2953, 2923, 1744, 1581, 1534, 1464, 1373, 1283, 1145, 1084, 1043, 1004 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{31}H_{29}N_4O_4S]^+$:553.190; found:553.190.

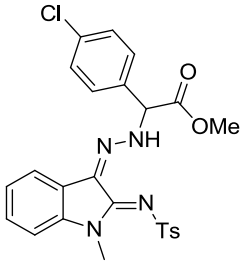
methyl 2-(4-fluorophenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4e)



A yellow foamedsolid (100 mg, 81%); m.p. 60.8-61.7^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.55 (dd, *J* = 7.6 Hz, 0.4Hz,1H), 7.32 (td, *J* = 7.6 Hz,1.2Hz, 1H), 7.23(d, *J* = 8.0 Hz, 2H), 7.15 (td, *J* = 7.6 Hz, 0.8Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.94 - 6.84 (m, 4H), 5.31 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.69 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 162.9 (d,$^{1}J_{CF}$ =250 Hz), 148.5, 142.9, 141.5 (d, $^{3}J_{CF}$ =8 Hz), 130.9(d,$^{4}J_{CF}$ =3 Hz), 129.5,

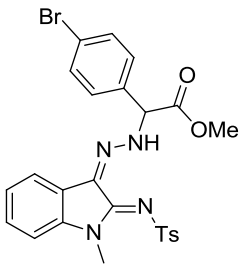
129.2, 129.1, 128.1, 127.9, 126.6, 124.0, 123.0, 118.6, 116.1 (d, $^{2}J_{CF}$ = 22 Hz), 109.8, 67.9, 53.0, 33.1, 21.7ppm;IR (neat) v 2954, 2920, 1747, 1583, 1538, 1510, 1464, 1375, 1283, 1224, 1146, 1086, 1045, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}FN_4O_4S]^+$:495.150; found:495.150.

methyl 2-(4-chlorophenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4f)



A yellow powder (105 mg, 82%); m.p. 131.5-132.6^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.41 (d, *J* = 6.8 Hz, 1H), 7.90 (d,*J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.32 (td, *J* = 8.0 Hz,1.2Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 3H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.30 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.68 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 148.5, 143.0, 141.9, 141.1, 134.9, 133.6, 129.5, 129.3, 128.7, 128.3, 127.9, 126.6, 124.0, 123.0, 118.7, 109.9, 68.0, 53.0, 33.1, 21.8ppm;IR (neat) v 2950, 2925, 1746, 1584, 1538, 1491, 1464, 1376, 1283, 1146, 1086, 1015, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}ClN_4O_4S]^+$:511.120; found:511.120.

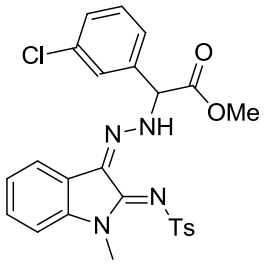
methyl 2-(4-bromophenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4g)



A yellow powder (115 mg, 83%); m.p. 139.2-140.4°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.41 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.33 - 7.30 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 - 7.14 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.29 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.68 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 148.5, 143.0, 141.9, 141.1, 134.1, 132.3, 129.5, 128.9, 128.4, 128.0, 126.7, 124.0, 123.0, 123.0, 118.7, 109.9, 68.1, 53.0, 33.2, 21.9ppm;IR (neat) v 3021, 2953, 1747, 1584, 1538, 1464, 1374, 1284, 1146, 1086, 1011, 749 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}BrN_4O_4S]^+$:555.070; found:555.070.

methyl

2-(3-chlorophenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4h)

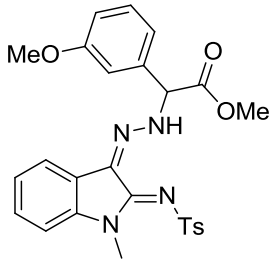


A yellow foamedsolid (121 mg, 95%); m.p. 57.8-58.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.34 - 7.27 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18 - 7.11 (m, 2H), 7.07 - 7.04 (m, 2H), 6.81 (d,*J* = 8.0 Hz,1H), 5.31 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.69 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 148.5, 142.8, 141.9, 141.0, 137.3, 135.0, 130.4, 129.6, 129.1, 128.3, 127.9, 127.6, 126.5, 125.4, 124.0, 123.0, 118.7, 109.8, 77.5, 77.3, 77.0, 68.2, 53.0, 33.1, 21.8ppm;IR (neat) v 2953, 1747, 1583, 1538, 1491, 1464, 1375, 1284, 1224, 1146, 1086, 1045, 1005, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}ClN_4O_4S]^+$:511.120; found:511.120.

methyl

2-(3-methoxyphenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydr

azinyl)acetate(4i)

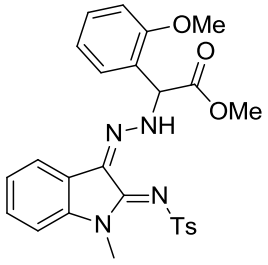


A yellow foamed solid (103 mg, 81%); m.p. 48.9-49.6^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.30 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.20 - 7.14 (m, 3H), 7.11 - 7.03 (m, 2H), 6.84 - 6.81 (m, 1H), 6.65 – 6.64 (m, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 5.31 (d, *J* = 6.8 Hz, 1H), 3.96 (s, 3H), 3.73 (s, 3H), 3.67 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.1, 148.5, 142.7, 141.7, 141.0, 136.5, 130.2, 129.5, 127.8, 127.7, 126.5, 123.9, 123.2, 119.3, 118.6, 114.5, 113.2, 109.8, 68.8, 55.5, 52.9, 33.1, 21.8ppm;IR (neat) v 2954, 2926, 1747, 1574, 1538, 1463, 1375, 1282, 1145, 1085, 1044, 1005, 900, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_5S]^+$:507.170; found:507.170.

methyl

2-(2-methoxyphenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydr

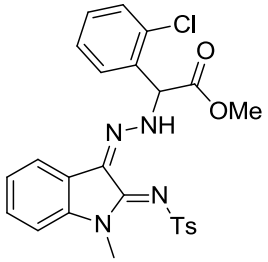
azinyl)acetate(4j)



A yellow powder (46 mg, 36%); m.p. 116.0-117.1^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.37 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.31 - 7.27 (m, 2H), 7.22(d, *J* = 8.0 Hz, 2H), 7.15 (td,*J* = 7.6 Hz, 0.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz,1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.74 - 6.73 (m, 2H), 5.68 (d, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 3.62 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 156.9, 148.8, 142.5, 141.5, 141.3, 130.2, 129.6, 128.7, 127.4, 127.1, 126.6,

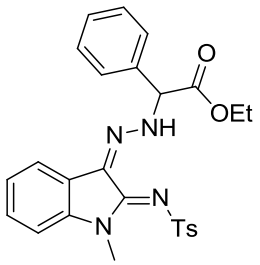
123.9, 123.8, 123.4, 121.0, 118.5, 111.3, 109.7, 64.1, 55.7, 52.8, 33.3, 21.8ppm;IR (neat) v 2951, 2840, 1746, 1580, 1537, 1464, 1374, 1282, 1144, 1086, 1045, 911, 804 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_5S]^+$:507.170; found:507.170.

methyl 2-(2-chlorophenyl)-2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4k)



A yellow powder (105 mg, 82%); m.p. 134.3-135.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.34 - 7.27 (m, 3H), 7.25 - 7.21 (m, 2H), 7.16 (td,*J* = 7.6 Hz, 0.8 Hz, 1H), 7.05 - 7.01 (m, 2H), 6.75 - 6.73 (m, 1H), 5.76 (d, *J* = 6.8 Hz, 1H), 3.96 (s, 3H), 3.69 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 148.6, 142.7, 141.8, 141.2, 14.0, 133.7, 130.2, 130.1, 129.6, 129.1, 128.0, 127.8, 127.4, 126.8, 123.9, 123.1, 118.7, 109.8, 66.1, 53.0, 33.2, 21.8ppm;IR (neat) v 2947, 1748, 1582, 1537, 1465, 1374, 1283, 1145, 1105, 1086, 1044, 1005, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}ClN_4O_4S]^+$:511.120; found:511.120.

(Z)-4-methyl-N-((Z)-1-methyl-3-(2-(2-oxo-1-phenylbutyl)hydrazono)indolin-2-ylidene)benzenesulfonamide(4l)

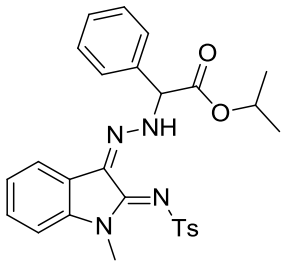


A yellowsolid (93 mg, 76%); m.p. 129.7-130.8°C; ^{1}H NMR (500 MHz, $CDCl_3$)

δ11.45 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.31 - 7.26 (m, 2H), 7.22-7.14 (m,5H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 2H), 5.31 (d, *J* = 7.0 Hz, 1H), 4.20 - 4.08 (m, 2H), 3.95 (s, 3H), 2.41 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 148.5, 142.6, 141.7, 141.2, 135.2, 129.6, 129.1, 128.7, 127.7, 127.6, 127.3, 126.6, 123.9, 123.2, 118.5, 109.8, 69.0, 62.0, 33.1, 21.8, 14.3ppm;IR (neat) v 2925, 1740, 1581, 1537, 1465, 1373, 1296, 1146, 1086, 1003, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_3S]^+$:491.175; found:491.175.

isopropyl

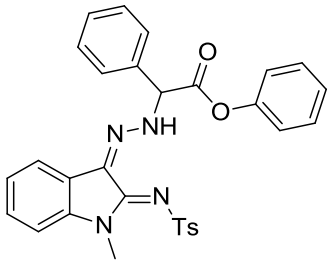
2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate (4m)



A yellow foamedsolid (69 mg, 55%); m.p. 45.5-46.4^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.55 (dd, *J* = 7.2, 0.4 Hz, 1H), 7.32 - 7.28 (m, 2H), 7.21-7.14 (m,5H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 5.28 (d, *J* = 6.8 Hz, 1H), 5.05 - 4.95 (m, 1H), 3.96 (s, 3H), 2.41 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 148.5, 142.6, 141.6, 141.2, 135.3, 129.6, 129.0, 128.7, 127.6, 127.6, 127.3, 126.6, 123.9, 123.3, 118.5, 109.8, 69.7, 69.1, 33.1, 21.9, 21.8, 21.6ppm;IR (neat) v 2926, 1738, 1574, 1538, 1464, 1375, 1284, 1146, 1086, 1004, 803 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{27}H_{29}N_4O_4S]^+$:505.190; found:505.190.

phenyl

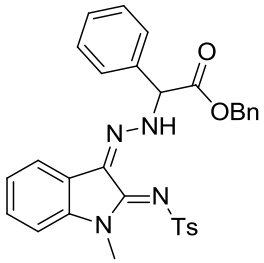
2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4n)



A yellow foamedsolid (118 mg, 88%); m.p. 67.9-68.7^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.37 - 7.29 (m, 4H), 7.25 -7.22 (m,3H), 7.19 - 7.15 (m,1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.06 - 7.02 (m, 3H), 6.96 - 6.93 (m, 2H), 5.55 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 150.5, 148.5, 142.7, 141.8, 141.0, 134.7, 129.7, 129.6, 129.3, 129.1, 128.2, 127.9, 127.4, 126.6, 126.5, 124.0, 123.1, 121.3, 118.6, 109.9, 69.0, 33.1, 21.8ppm;IR (neat) v 2925, 1762, 1583, 1538, 1491, 1464, 1375, 1284, 1191, 1146, 1086, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{30}H_{27}N_4O_4S]^+$:539.175; found:539.175.

benzyl

2-((Z)-2-((Z)-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4o)

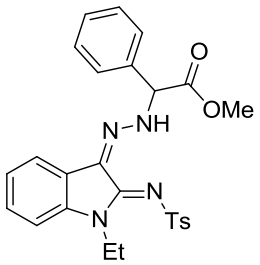


A yellow powder (117 mg, 85%); m.p. 118.5-119.7^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.32 - 7.26 (m, 5H), 7.20 -7.17 (m,2H), 7.16 - 7.10 (m,5H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 2H), 5.38 (d, *J* = 7.2 Hz, 1H), 5.17 - 5.09 (m, 2H), 3.95 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 148.5, 142.6, 141.7, 141.1, 135.5, 134.8, 129.5, 129.1, 128.8, 128.6, 128.2, 127.9, 127.7, 127.3, 126.6, 123.9, 123.1, 118.6, 109.8, 69.0, 67.4, 33.1, 21.8ppm;IR (neat) v 2956, 2925, 1744, 1581, 1538,

1495, 1464, 1375, 1284, 1146, 1086, 1004, 788 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{31}H_{29}N_4O_4S]^+$:553.190; found:553.188.

methyl

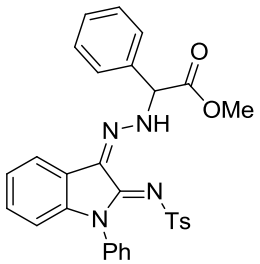
2-((Z)-2-((Z)-1-ethyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate (4p)



A yellow powder (120 mg, 98%); m.p. 113.9-114.7°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.32 - 7.26 (m, 2H), 7.23 - 7.13(m, 5H), 7.07 (d, *J* = 8.0 Hz,1H), 6.90 (d, *J* = 7.2 Hz,2H), 5.33 (d, *J* = 7.2 Hz, 1H), 4.61 - 4.51 (m, 2H), 3.69 (s, 3H), 2.41 (s, 3H), 1.54 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 146.9, 142.7, 141.2, 140.5, 135.1, 129.6, 129.1, 128.8, 127.8, 127.7, 127.3, 126.6, 123.8, 123.6, 118.6, 110.2, 69.1, 52.9, 40.4, 21.8, 13.4ppm;IR (neat) v 2977, 2952, 1747, 1574, 1537, 1463, 1373, 1283, 1197, 1147, 1086, 1010, 821 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_4S]^+$:491.175; found:491.175.

methyl

2-phenyl-2-((Z)-2-((Z)-1-phenyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)acetate(4q)

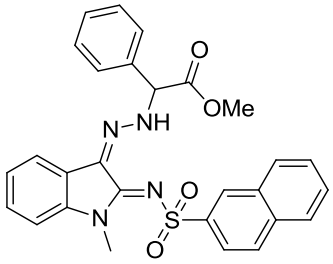


A yellow powder (129 mg, 96%); m.p. 116.5-117.4°C; ^{1}H NMR (400 MHz, $CDCl_3$)

δ11.62 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.62 - 7.55 (m, 6H), 7.31 - 7.27 (m, 1H), 7.21 - 7.12 (m, 6H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.54 - 6.52 (m, 1H),5.39 (d, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 147.5, 143.4, 142.3, 141.5, 135.8, 135.1, 130.1, 129.8, 129.5, 129.4, 129.2, 128.9, 127.7, 127.6, 127.3, 126.5, 124.0, 122.7, 118.4, 111.1, 69.1, 52.9, 21.8ppm;IR (neat) v 2953, 2925, 1746, 1574, 1531, 1496, 1455, 1374, 1299, 1149, 1088, 809, 749 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{30}H_{27}N_4O_4S]^+$:539.175; found:539.175.

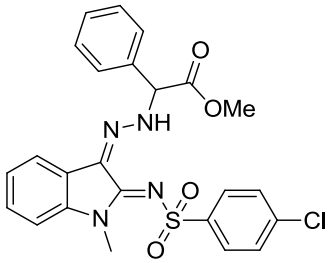
methyl

2-((Z)-2-((Z)-1-methyl-2-((naphthalen-2-ylsulfonyl)imino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4r)



A yellow solid (115 mg, 90%); m.p. 139.2-140.4^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (d, *J* = 6.8 Hz, 1H), 8.87 (d, *J* = 1.2 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.67 - 7.59 (m, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 (td, *J* = 7.2, 0.8 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.01 - 6.96 (m, 1H), 6.73 - 6.67 (m, 4H), 5.26 (d, *J* = 7.2 Hz, 1H), 4.00 (s, 3H), 3.53 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 148.5, 141.6, 140.9, 134.9, 134.7, 132.4, 129.7, 129.4, 128.9, 128.8, 128.6, 128.2, 127.7, 127.6, 127.5, 127.2, 127.0, 124.0, 123.2, 122.8, 118.6, 109.9, 68.9, 52.8, 33.1ppm;IR (neat) v 3051, 2950, 1742, 1574, 1534, 1492, 1462, 1377, 1294, 1144, 1045, 905, 793 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{28}H_{25}N_4O_4S]^+$:513.159; found:513.159.

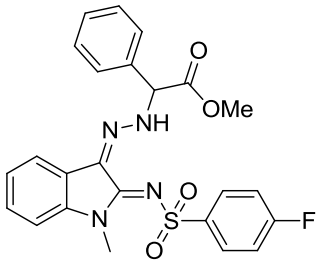
methyl2-((Z)-2-((Z)-2-(((4-chlorophenyl)sulfonyl)imino)-1-methylindolin-3-ylidene)hydrazinyl)-2-phenylacetate(4s)



A yellow powder (114 mg, 92%); m.p. 129.6-131.7°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.37 - 7.30 (m, 4H), 7.27 - 7.23 (m, 3H), 7.19 - 7.15 (m,1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.6 Hz,1H), 5.34 (d, *J* = 6.8 Hz, 1H), 3.95 (s, 3H), 3.70 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 148.5, 142.4, 141.6, 138.5, 134.8, 129.3, 129.2, 129.2, 128.1, 127.8, 127.7, 127.3, 124.1, 123.1, 118.7, 109.9, 68.6, 52.9, 33.1ppm;IR (neat) v 2953, 2925, 1746, 1581, 1538, 1464, 1378, 1302, 1148, 1087, 1005, 799 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{24}H_{22}ClN_4O_4S]^+$:497.105; found:497.105.

methyl

2-((Z)-2-((Z)-2-(((4-fluorophenyl)sulfonyl)imino)-1-methylindolin-3-ylidene)hydrazinyl)-2-phenylacetate(4t)

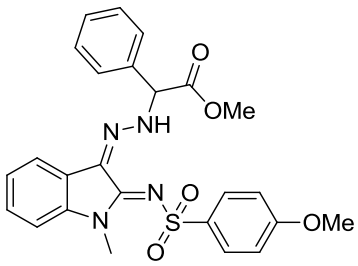


A yellow powder (109 mg, 91%); m.p. 113.4-114.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (d, *J* = 6.8 Hz, 1H), 8.03 - 7.99 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.34 - 7.29 (m, 2H), 7.25 - 7.22 (m, 2H), 7.16 (t,*J* = 7.6 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 3H), 6.97 (d, *J* = 7.2 Hz,2H), 5.34 (d, *J* = 6.8 Hz, 1H), 3.95 (s, 3H), 3.69 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 164.9 (d, $^{1}J_{CF}$ =250 Hz), 148.4, 141.6, 140.0(d, $^{4}J_{CF}$ =3 Hz), 135.0, 129.3, 129.3, 129.2(d, $^{3}J_{CF}$ =11 Hz), 127.8, 127.7, 127.3, 124.1, 123.1, 118.6, 116.0 (d, $^{2}J_{CF}$ =22 Hz), 109.9, 68.6, 52.9, 33.1ppm;IR (neat) v 2956, 2924, 2854, 1745, 1580, 1531, 1463, 1377, 1260, 1086, 1029, 800 cm^{-1}; MALDI-TOF-MS

(DHB)calcd for $[C_{24}H_{22}FN_4O_4S]^+$:481.134; found:481.134.

methyl

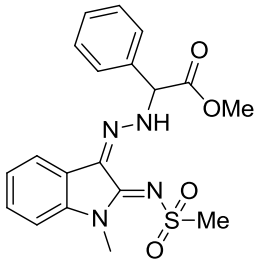
2-((Z)-2-((Z)-2-(((4-methoxyphenyl)sulfonyl)imino)-1-methylindolin-3-ylidene)hydrazinyl)-2-phenylacetate(4u)



A yellow powder (96 mg, 78%); m.p. 122.4-123.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.32 - 7.26 (m, 2H), 7.22 - 7.14 (m, 3H), 7.04 (d,*J* = 8.0 Hz, 1H), 6.95 (d, *J* = 7.2 Hz,2H), 6.90 (d, *J* = 8.8 Hz,2H), 5.34 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.68 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 162.6, 148.4, 141.7, 136.0, 135.0, 129.2, 128.9, 128.7, 127.8, 127.7, 127.3, 123.9, 123.1, 118.6, 114.1, 109.8, 68.8, 55.8, 52.9, 33.1ppm;IR (neat) v 2953, 2837, 1746, 1581, 1538, 1496, 1464, 1375, 1287, 1144, 808 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{25}N_4O_5S]^+$:493.154; found:493.154.

methyl

2-((Z)-2-((Z)-1-methyl-2-((methylsulfonyl)imino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4v)

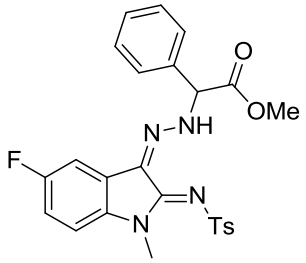


A yellow solid (71 mg, 71%); m.p. 143.9-144.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (d, *J* = 6.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41 - 7.38 (m, 5H), 7.29 - 7.25 (m,

1H), 7.12 (td,*J* = 7.6, 0.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz,1H), 5.50 (d, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 148.5, 141.6, 136.6, 129.4, 129.2, 127.9, 127.7, 127.5, 123.9, 123.0, 118.6, 109.7, 67.5, 53.2, 44.5, 32.9ppm;IR (neat) v 2953, 2923, 2852, 1737, 1582, 1538, 1459, 1375, 1280, 1107, 807 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{19}H_{21}N_4O_4S]^+$:401.128; found:401.128.

methyl

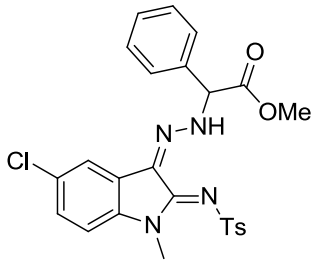
2-((Z)-2-((Z)-5-fluoro-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4w)



A yellow powder (104 mg, 84%); m.p. 116.8-117.5^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.26 - 7.23 (m, 3H), 7.21 - 7.17 (m, 2H), 7.01 - 6.94 (m, 2H), 6.91 (d, *J* = 7.6 Hz,2H), 5.32 (d, *J* = 6.8 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 160.3 (d, $^1J_{CF}$ =240 Hz), 148.8(d, $^5J_{CF}$ =0.8 Hz), 142.8, 141.0, 137.6(d, $^4J_{CF}$ =1.4 Hz), 134.9, 129.6, 129.2, 128.9, 127.3, 127.0(d, $^4J_{CF}$ =3.5 Hz), 126.7, 124.6(d, $^3J_{CF}$ =9.7 Hz), 114.2 (d, $^2J_{CF}$ =24.7 Hz), 110.7(d, $^3J_{CF}$ =8.7 Hz), 105.7 (d, $^2J_{CF}$ =25.8 Hz), 69.0, 52.9, 33.3, 21.8ppm;IR (neat) v 3029, 2955, 1747, 1583, 1538, 1480, 1363, 1281, 1146, 1086, 803 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}FN_4O_4S]^+$:495.150; found:495.150.

methyl

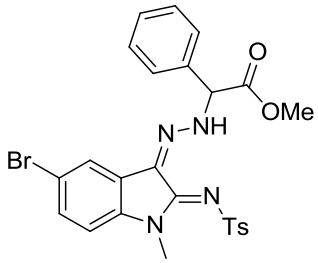
2-((Z)-2-((Z)-5-chloro-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4x)



A yellow powder (96 mg, 75%); m.p. 119.4-120.7°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.26 - 7.23 (m, 3H), 7.21 - 7.17 (m, 2H), 6.96 (d, *J* = 8.4 Hz,1H), 6.92 - 6.90 (m, 2H), 5.32 (d, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.5, 142.9, 140.9, 140.0, 134.8, 129.7, 129.6, 129.2, 129.0, 127.3, 127.3, 126.7, 126.5, 124.6, 118.6, 110.8, 69.0, 53.0, 33.3, 21.8ppm;IR (neat) v 3030, 2953, 1747, 1583, 1538, 1455, 1361, 1284, 1147, 1087, 919, 805 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}ClN_4O_4S]^+$:511.120; found:511.120.

methyl

2-((Z)-2-((Z)-5-bromo-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4y)

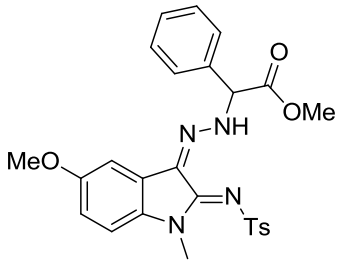


A yellow powder (108 mg, 78%); m.p. 114.9-115.7°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.32 - 7.28 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.21 - 7.17 (m, 2H), 6.93 - 6.89 (m, 3H), 5.32 (d, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.3, 142.9, 140.9, 140.4, 134.8, 130.1, 129.6, 129.2, 129.0, 127.3, 126.7, 126.4, 125.0, 121.5, 117.1, 111.3, 69.0, 53.0, 33.3, 21.9 ppm;IR (neat) v 2953, 1747, 1575, 1538, 1455, 1360, 1284, 1146, 1087, 916, 804

cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{24}BrN_4O_4S]^+$:555.070; found:555.070.

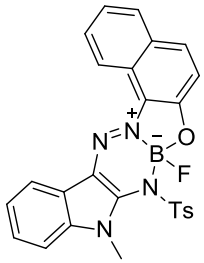
methyl

2-((Z)-2-((Z)-5-methoxy-1-methyl-2-(tosylimino)indolin-3-ylidene)hydrazinyl)-2-phenylacetate(4z)



A orange foamed solid (123 mg, 89%); m.p. 58.7-59.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.30 - 7.26 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.95 - 6.90 (m, 3H), 6.85 (dd, *J* = 8.8Hz,2.0Hz, 1H), 5.33 (d, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.67 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 157.1, 148.5, 142.6, 141.2, 135.7, 135.1, 129.5, 129.2, 128.8, 127.9, 127.3, 126.6, 124.2, 114.3, 110.6, 103.4, 68.9, 56.1, 52.9, 33.2, 21.8ppm;IR (neat) v 2953, 1747, 1583, 1538, 1486, 1367, 1285, 1145, 1086, 911, 791 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{27}N_4O_5S]^+$:507.170; found:507.170.

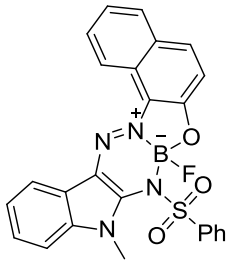
8-Fluoro-10-methyl-9-tosyl-9,10-dihydro-8H-naphtho[1'',2'':4',5'][1,3,2]oxazaborolo[3',2':2,3][1,2,4,3]triazaborinino[5,6-b]indol-16-ium-8-uide(7a)



Blacksolid (118 mg,95%); m.p. 208.6-209.8°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.12 - 8.10 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.62 - 7.58 (m, 1H), 7.54 - 7.46 (m, 3H), 7.44 - 7.40 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H),

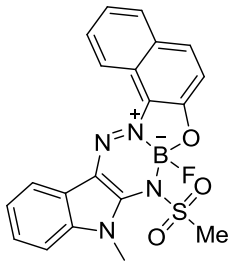
7.10 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.11 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 143.8, 138.2, 135.4, 134.1, 133.3, 129.3, 129.2, 129.2, 128.6, 126.3, 126.1, 125.3, 124.7, 123.8, 122.6, 122.1, 119.4, 116.3, 111.8, 34.7, 20.8; IR (neat) v 3062, 2925, 1568, 1515, 1463, 1371, 1240, 1169, 1089, 933 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{21}BFN_4O_3S]^+$:499.141; found:499.156.

8-Fluoro-10-methyl-9-(phenylsulfonyl)-9,10-dihydro-8H-naphtho[1'',2'':4',5'][1,3,2]oxazaborolo[3',2':2,3][1,2,4,3]triazaborinino[5,6-b]indol-16-ium-8-uide(7b)



Deep-bluesolid (113 mg,93%); m.p. 184.5-185.8^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.61 - 7.57 (m, 1H), 7.54 - 7.46 (m, 3H), 7.43 - 7.39 (m, 1H), 7.29 - 7.27 (m, 2H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.80 - 6.71 (m, 3H), 4.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 159.7, 138.4, 138.3, 134.0, 133.4, 132.4, 130.8, 129.4, 129.2, 128.6, 128.3, 126.3, 126.2, 125.4, 124.7, 123.7, 122.5, 122.0, 119.3, 116.0, 111.8, 34.9; IR (neat) v 3055, 2950, 1626, 1568, 1516, 1463, 1373, 1284, 1171, 1086, 935 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{25}H_{19}BFN_4O_3S]^+$:485.125; found:485.125.

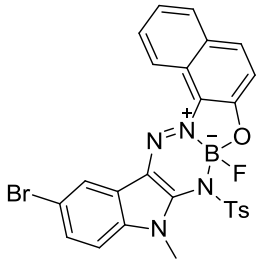
8-Fluoro-10-methyl-9-(methylsulfonyl)-9,10-dihydro-8H-naphtho[1'',2'':4',5'][1,3,2]oxazaborolo[3',2':2,3][1,2,4,3]triazaborinino[5,6-b]indol-16-ium-8-uide (7c)



Deep-bluesolid (97 mg, 92%); m.p. 157.4-158.8^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

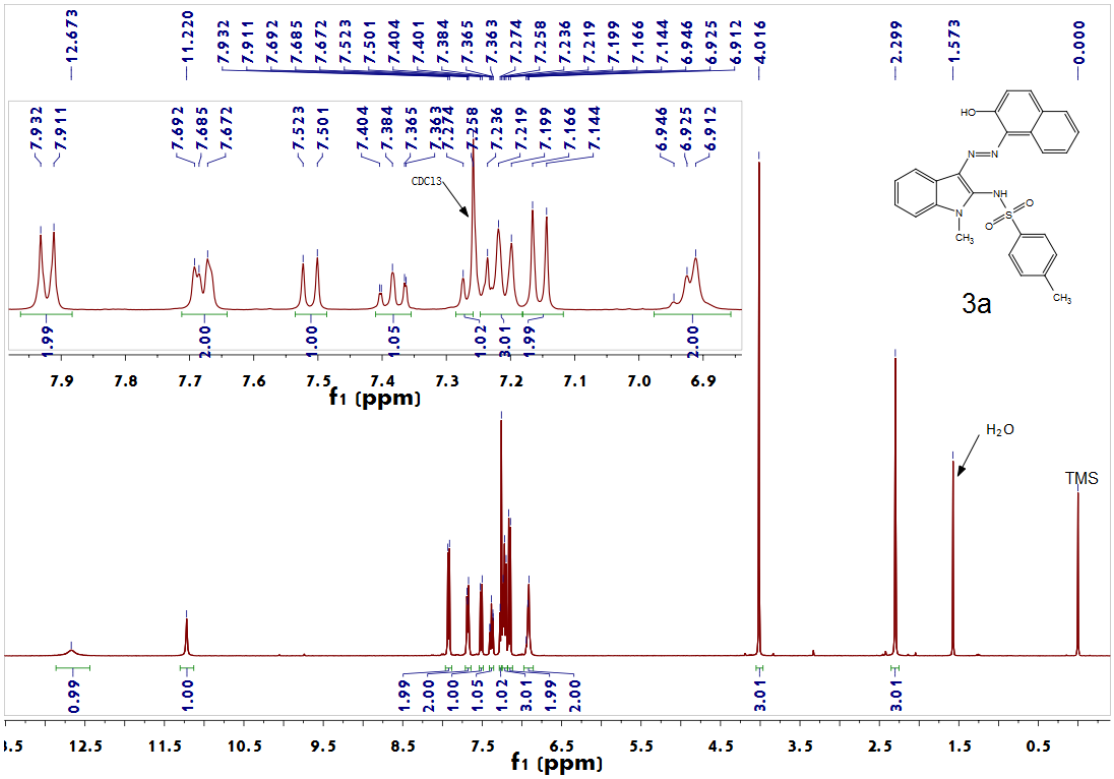
9.03 (d, *J* = 8.4 Hz, 1H), 8.12 - 8.10 (m, 1H), 7.86 (t, *J* = 9.6 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.51 - 7.39 (m, 5H), 3.96 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.3, 134.0, 133.9, 130.8, 129.9, 129.7, 129.4, 126.4, 125.7, 124.9, 124.1, 122.9, 122.1, 119.2, 116.0, 111.7, 42.6, 35.2; IR (neat) v 3054, 2926, 1626, 1569, 1520, 1464, 1370, 1284, 1239, 1166, 1069, 915 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{20}H_{17}BFN_4O_3S]^+$:423.110; found:423.110.

13-Bromo-8-fluoro-10-methyl-9-tosyl-9,10-dihydro-8H-naphtho[1'',2'':4',5'][1,3,2]oxazaborolo[3',2':2,3][1,2,4,3]triazaborinino[5,6-b]indol-16-ium-8-uide(7d)



Blacksolid (127 mg, 88%); m.p. 213.4-214.5^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.65 - 7.59 (m, 2H), 7.46 - 7.42 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.09 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 144.0, 136.7, 135.3, 134.3, 129.8, 129.6, 129.4, 129.2, 128.9, 128.7, 126.1, 125.6, 123.8, 123.5, 122.6, 122.0, 118.0, 116.4, 113.2, 34.8, 20.8; IR (neat) v 3060, 2947, 1569, 1505, 1462, 1367, 1285, 1170, 1091, 1038 cm^{-1}; MALDI-TOF-MS (DHB)calcd for $[C_{26}H_{20}BBrFN_4O_3S]^+$:577.051; found:577.021.

The 1H and 13C NMR Spectra of compound 3a-p, 4a-z, 7a-d


12.673
11.220
7.932
7.911
7.692
7.685
7.672
7.523
7.501
7.404
7.401
7.384
7.365
7.363
7.274
7.258
7.236
7.219
7.199
7.166
7.144
6.946
6.925
6.912
4.016
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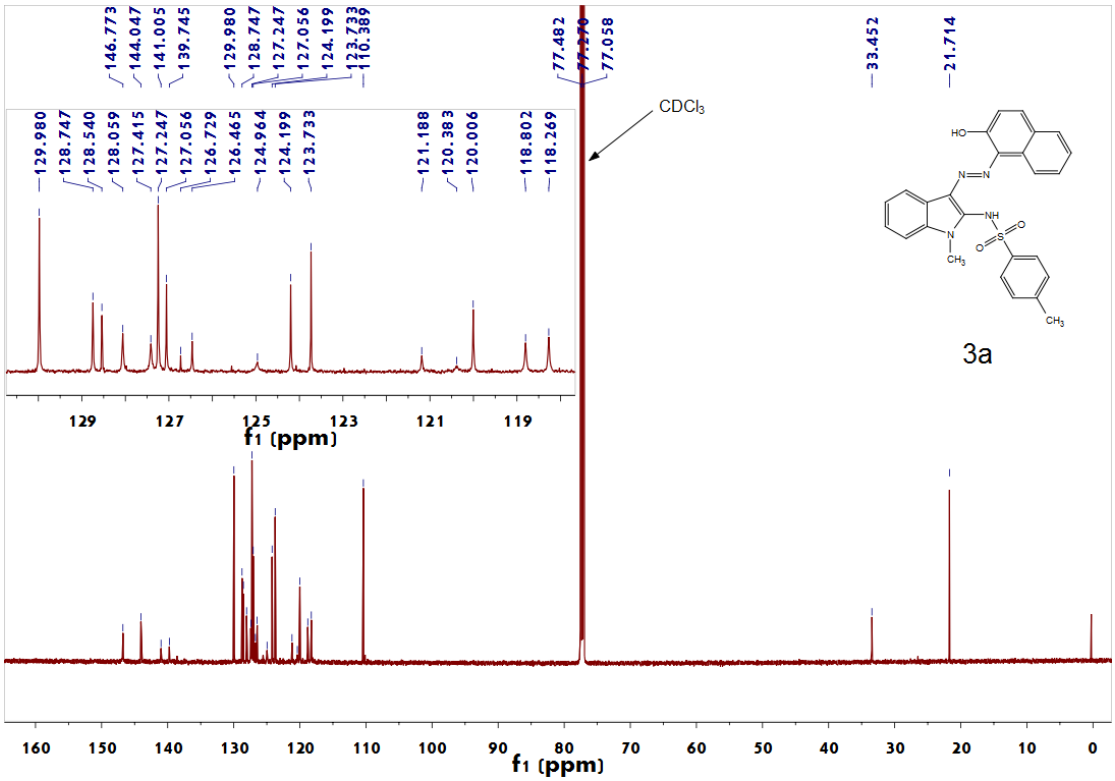
0.000
CDCl3
H2O
TMS
3a
f1 (ppm)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127.056
124.199
123.733
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77.482
77.270
77.058
33.452
21.714
129.980
128.747
128.540
128.059
127.415
127.247
127.056
126.729
126.465
124.964
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123.733
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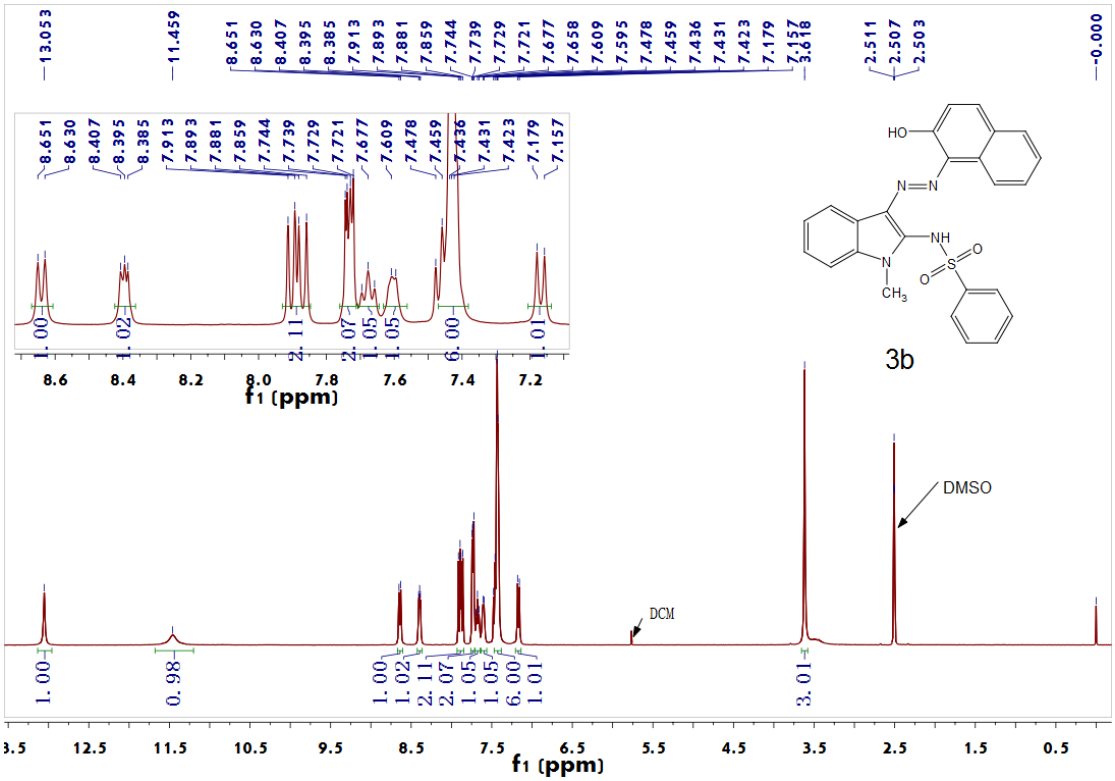
120.383
120.006
118.802
118.269
CDCl3
3a
f1 (ppm)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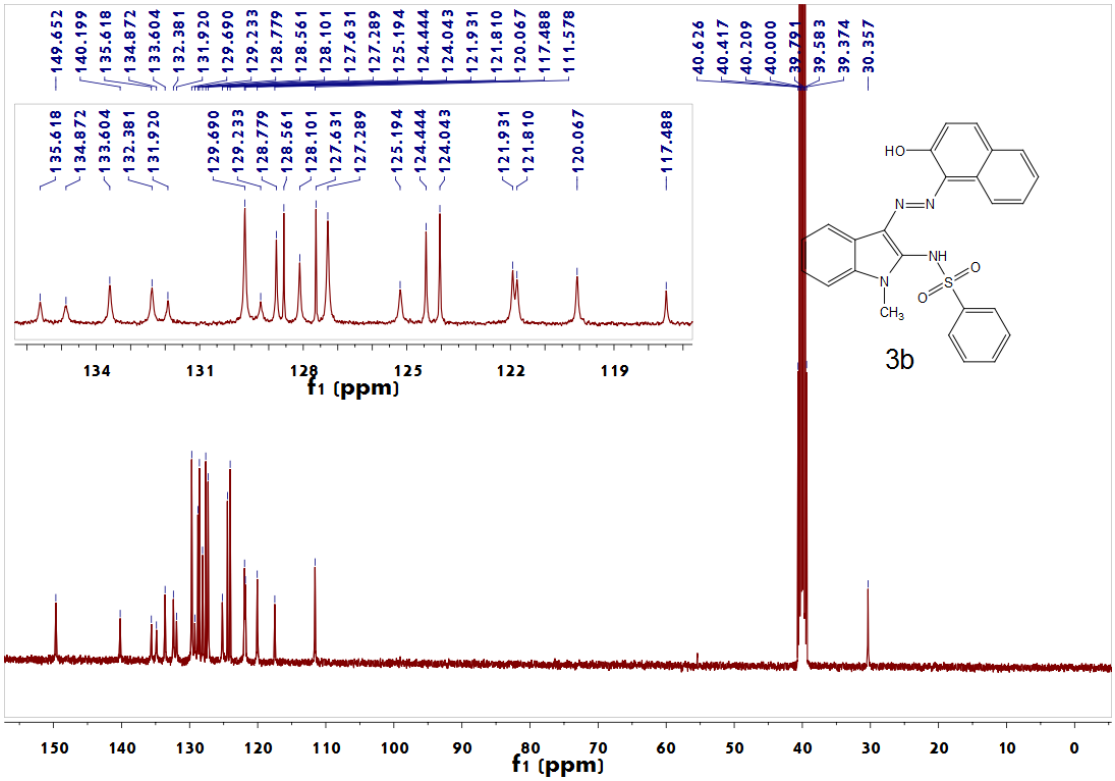
7.744
7.739
7.729
7.721
7.677
7.658
7.609
7.595
7.478
7.459
7.436
7.431
7.423
7.179
7.157
3.618
2.511
2.507
2.503
0.000
HO
N=N
NH
N
CH3
O
S
3b
DMSO
DCM
1.00
0.98
1.00
1.02
2.11
2.07
1.05
1.05
6.00
1.01
3.01
f1 (ppm)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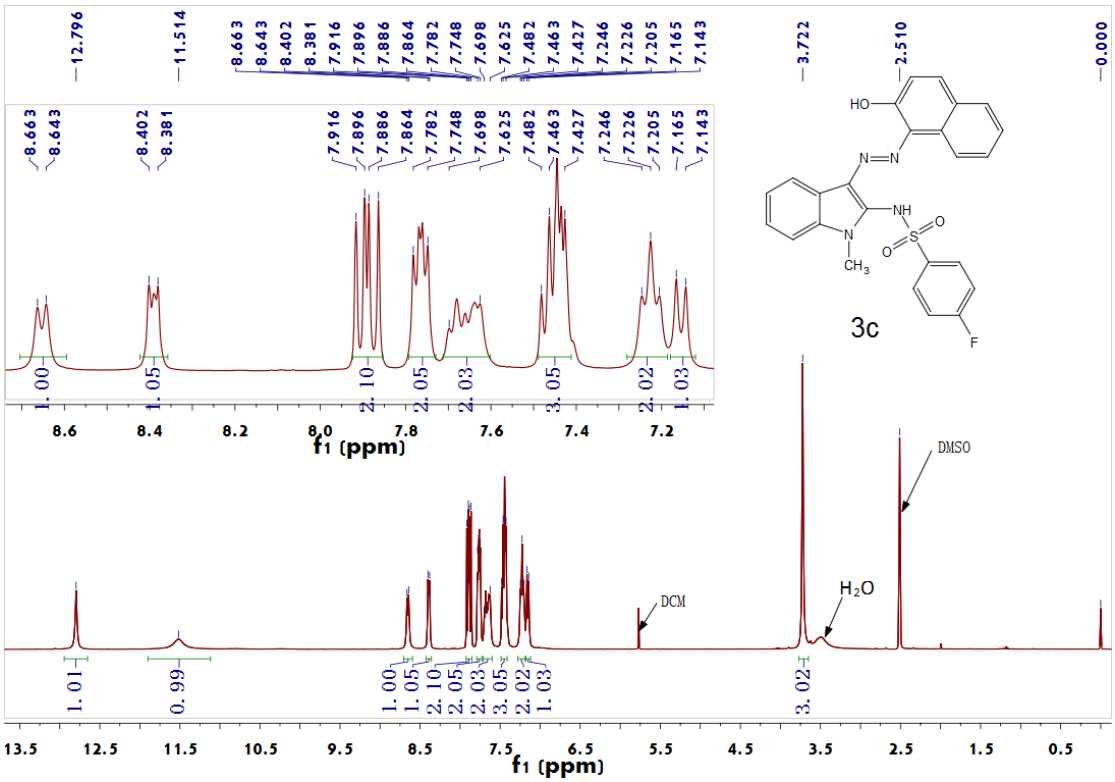
127.631
127.289
125.194
124.444
124.043
121.931
121.810
120.067
117.488
111.578
40.626
40.417
40.209
40.000
39.791
39.583
39.374
30.357
HO
N=N
NH
N
CH3
O
S
3b
f1 (ppm)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7.782
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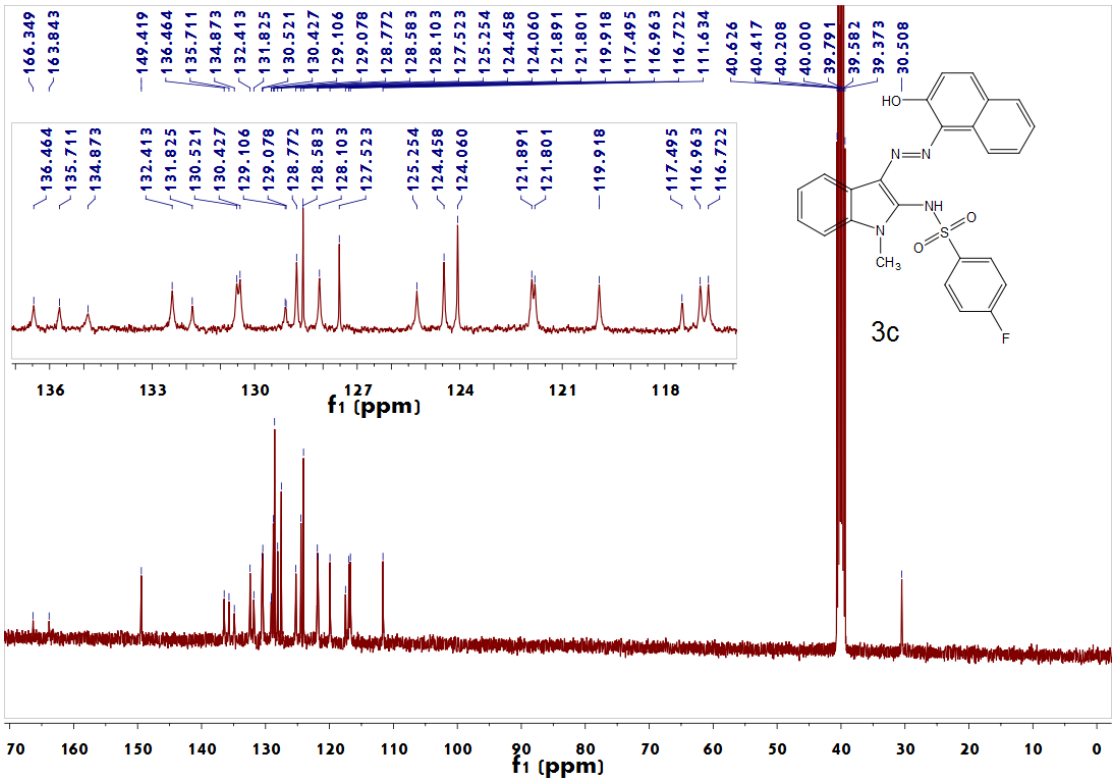
7.698
7.625
7.482
7.463
7.427
7.246
7.226
7.205
7.165
7.143
3.722
2.510
0.000
HO
N=N
NH
N
CH3
O
S
O
F
3c
1.00
1.05
2.10
2.05
2.03
3.05
2.02
1.03
f1 (ppm)
DMSO
DCM
H2O
1.01
0.99
1.00
1.05
2.10
2.05
2.03
3.05
2.02
1.03
3.02
f1 (ppm)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131.825
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130.427
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129.078
128.772
128.583
128.103
127.523
125.254
124.458
124.060
121.891
121.801
119.918
117.495
116.963
116.722
111.634
40.626
40.417
40.208
40.000
39.791
39.582
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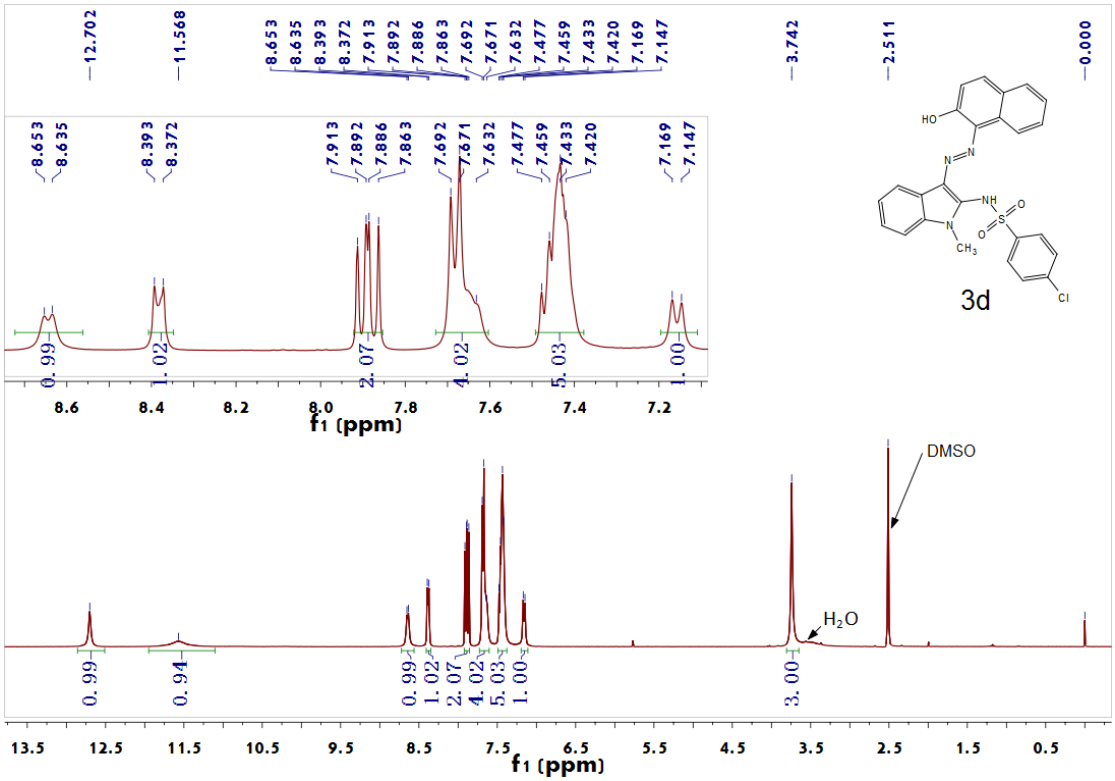
HO
N=N
NH
N
CH3
O
S
O
F
3c
f1 (ppm)
f1 (ppm)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7.892
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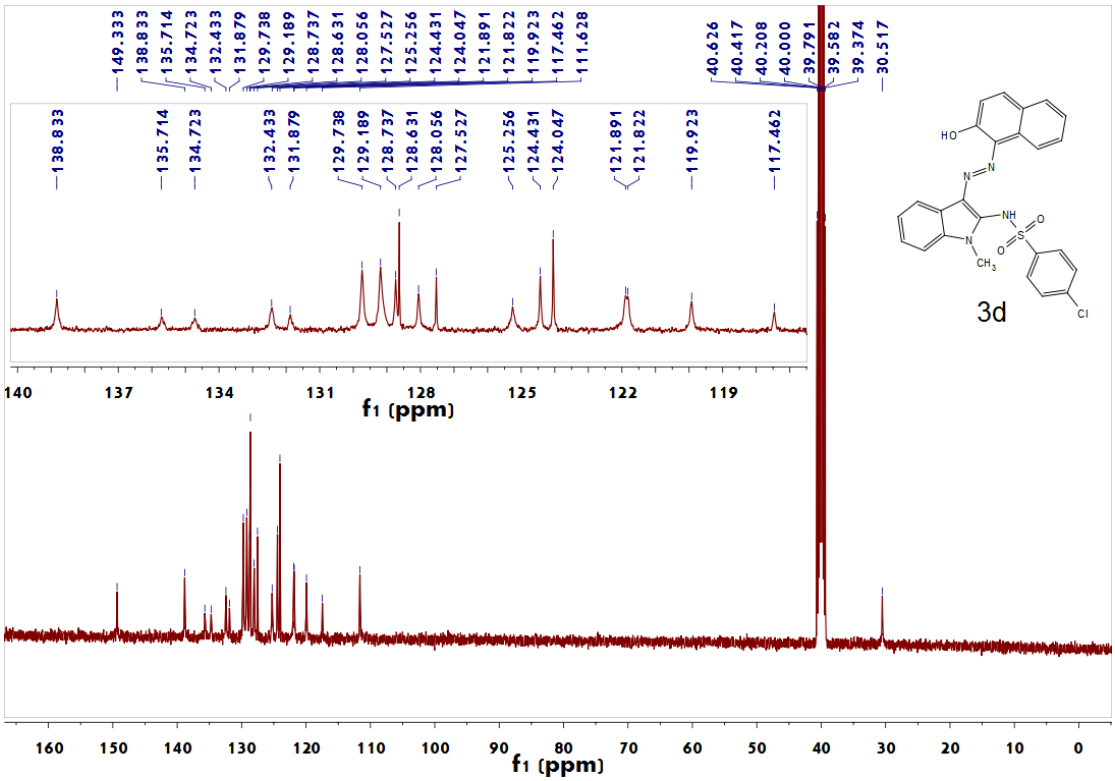
7.863
7.692
7.671
7.632
7.477
7.459
7.433
7.420
7.169
7.147
3.742
2.511
0.000
HO
N=N
NH
S
O
O
N
CH3
Cl
3d
DMSO
H2O
0.99
1.02
2.07
4.02
5.03
1.00
0.94
3.00
f1 (ppm)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132.433
131.879
129.738
129.189
128.737
128.631
128.056
127.527
125.256
124.431
124.047
121.891
121.822
119.923
117.462
111.628
40.626
40.417
40.208
40.000
39.791
39.582
39.374
30.517
HO
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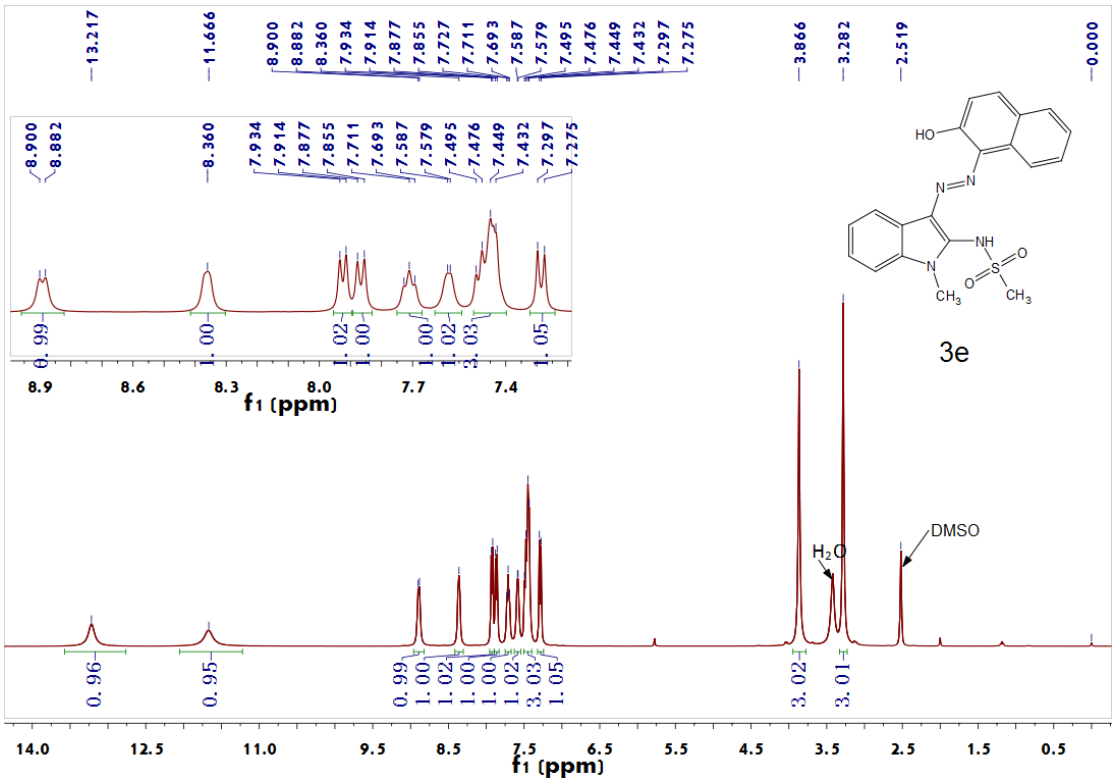
S
O
O
N
CH3
Cl
3d
f1 (ppm)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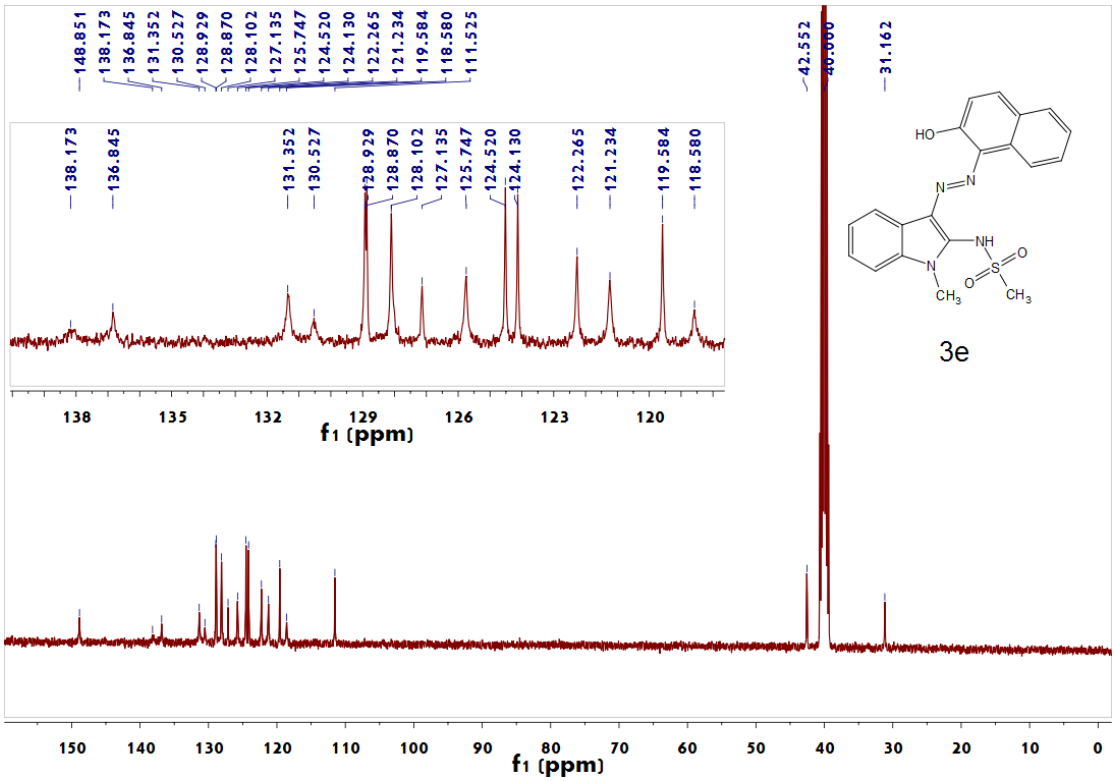
8.900
8.882
8.360
7.934
7.914
7.877
7.855
7.727
7.711
7.693
7.587
7.579
7.495
7.476
7.449
7.432
7.297
7.275
3.866
3.282
2.519
0.000
HO
N=N
NH
N
CH3
O
S
O
O
CH3
3e
f1 (ppm)
H2O
DMSO
0.96
0.95
0.99
1.00
1.02
1.00
1.00
1.02
3.03
1.05
3.02
3.01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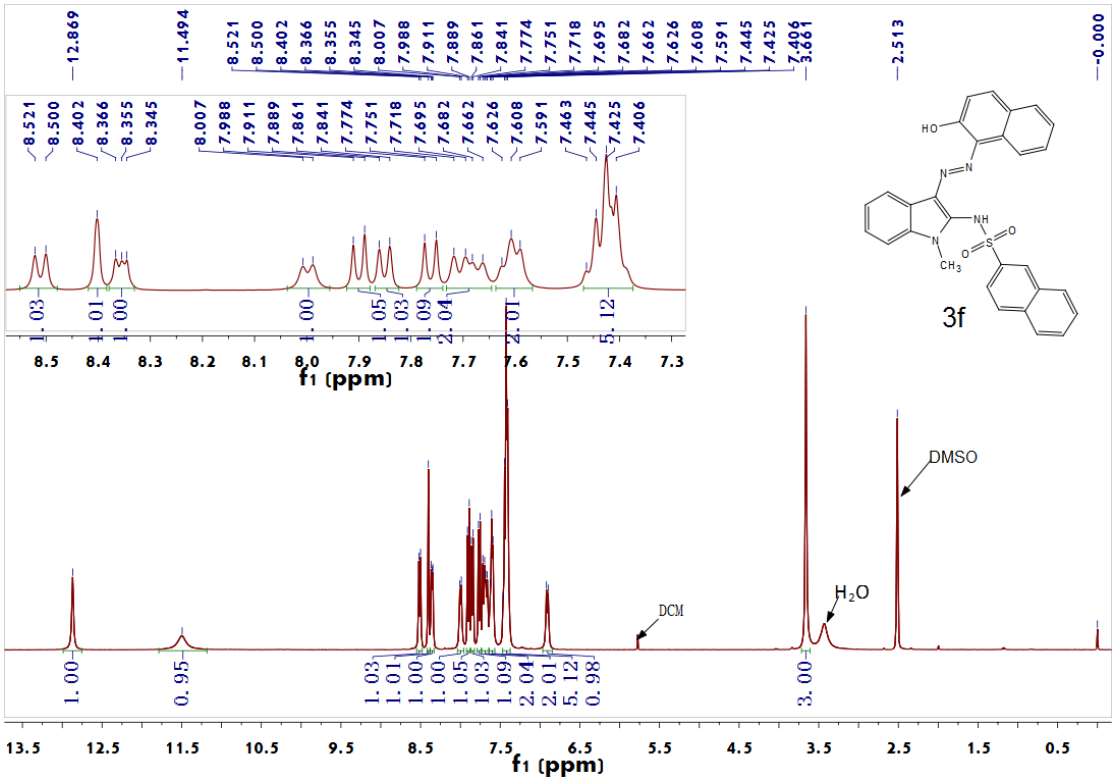
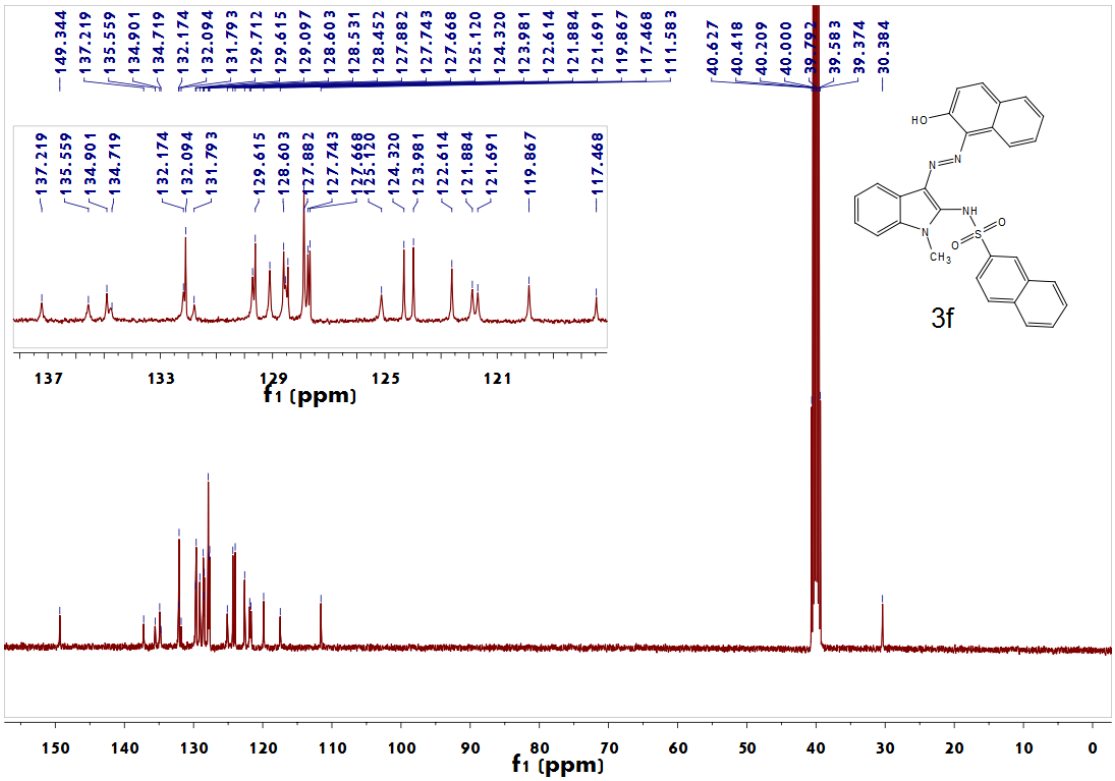
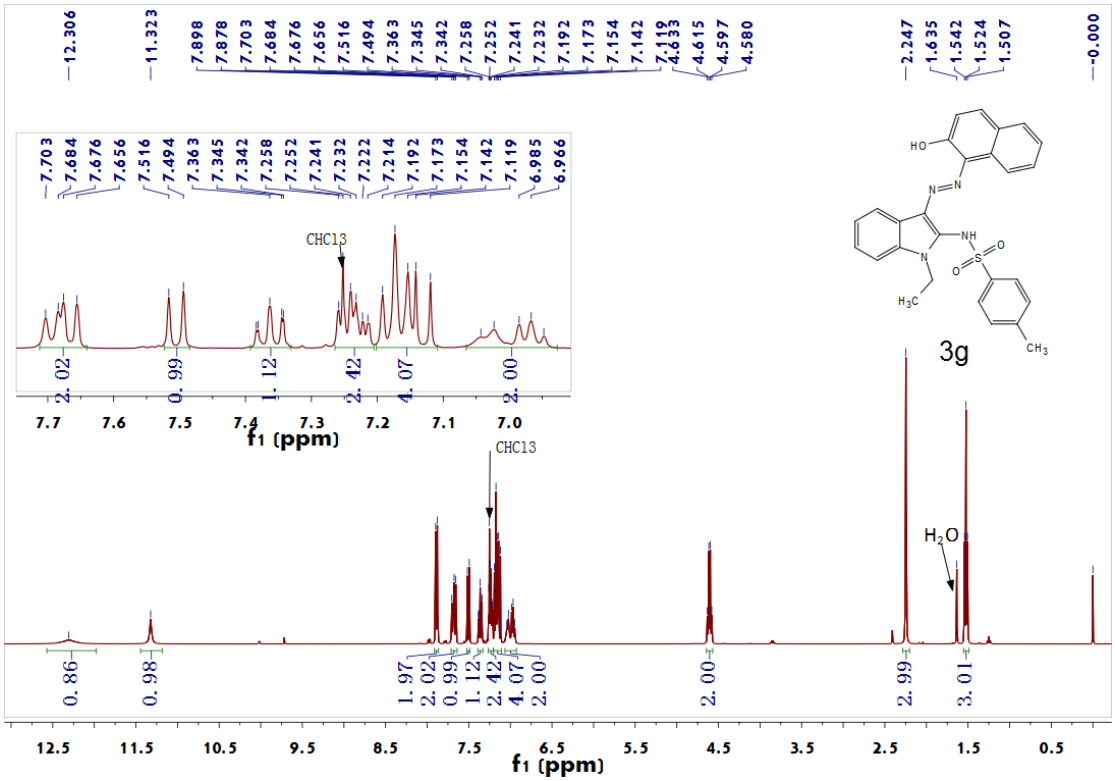
131.352
130.527
128.929
128.870
128.102
127.135
125.747
124.520
124.130
122.265
121.234
119.584
118.580
111.525
42.552
40.000
31.162
HO
N=N
NH
N
CH3
O
S
O
O
CH3
3e
f1 (ppm)


3f
DMSO
H2O
DCM
f1 (ppm)


3f
f1 (ppm)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7.363
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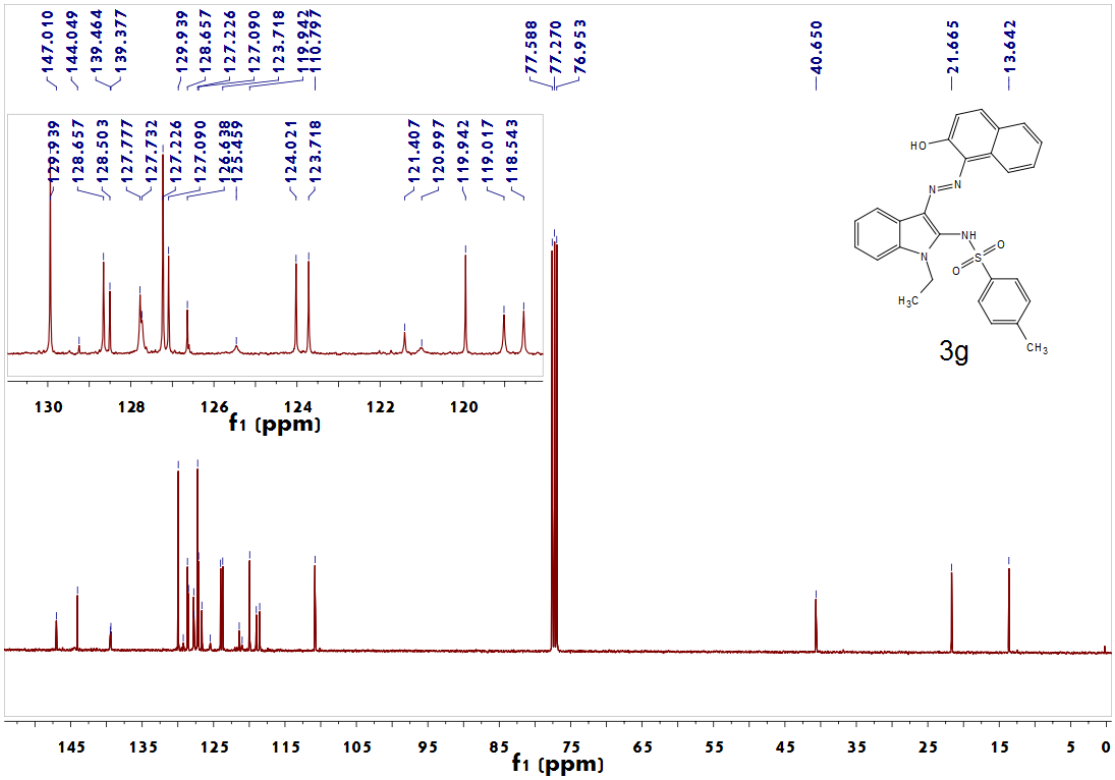
7.342
7.258
7.252
7.241
7.232
7.192
7.173
7.154
7.142
7.119
4.633
4.615
4.597
4.580
2.247
1.635
1.542
1.524
1.507
0.000
CHCl3
H2O
3g
f1 (ppm)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128.657
127.226
127.090
123.718
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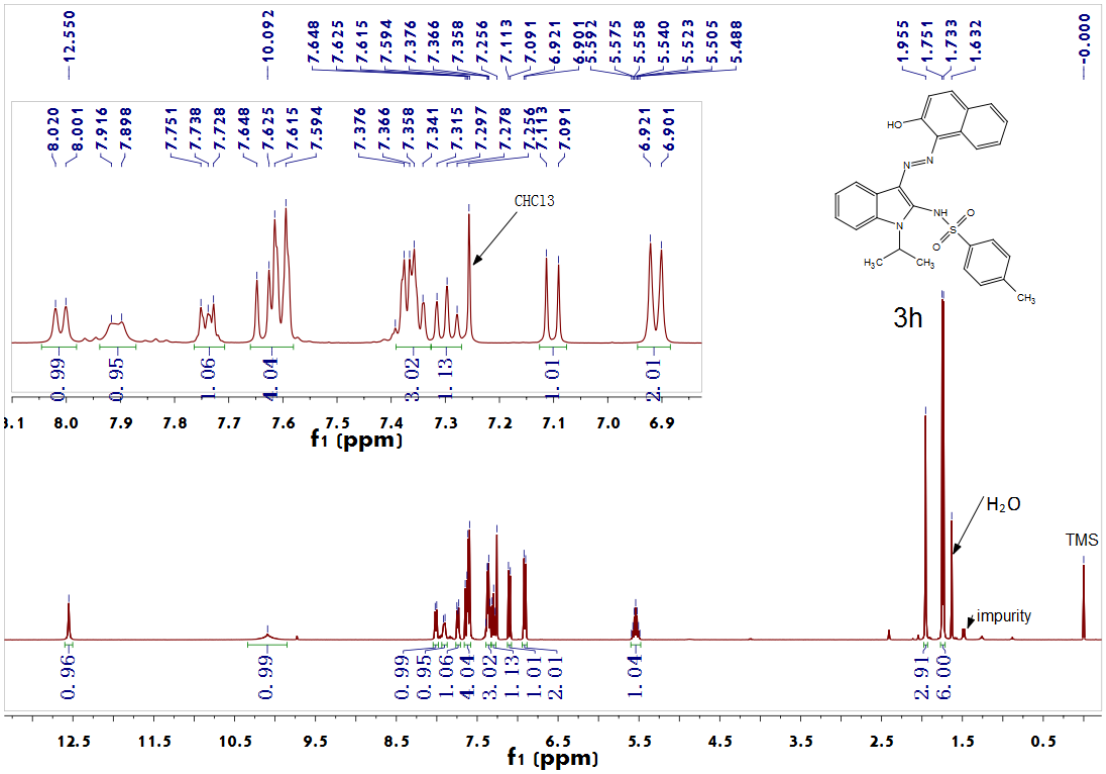
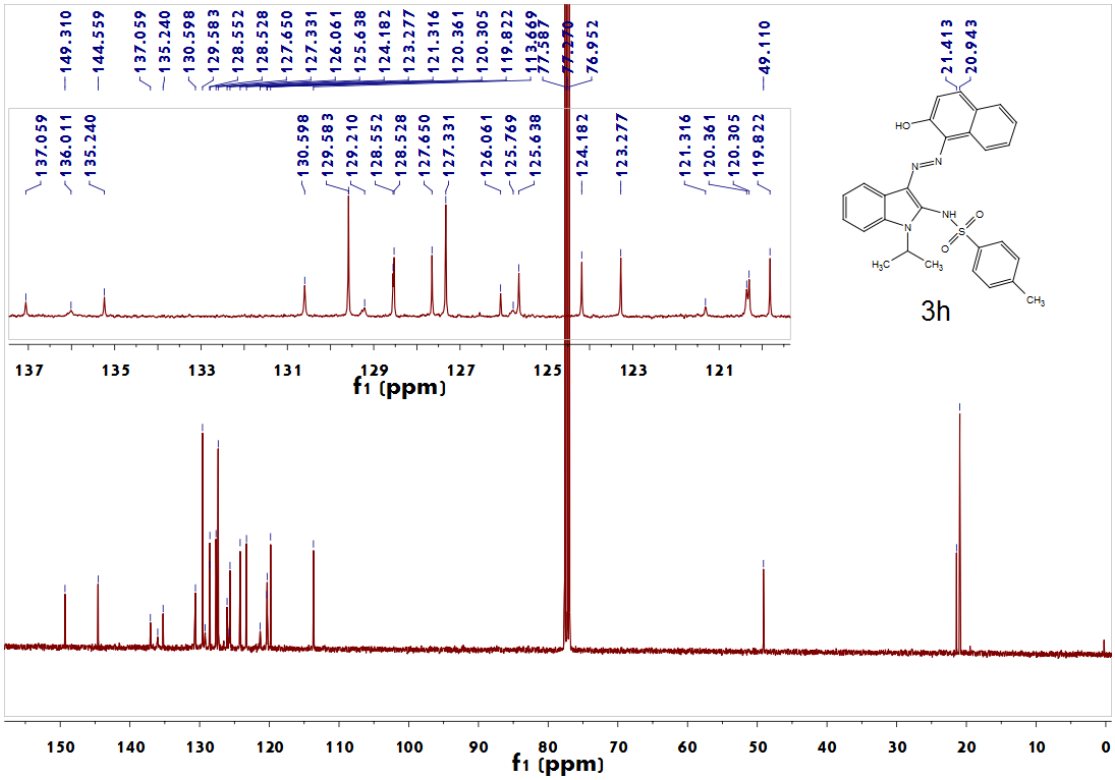
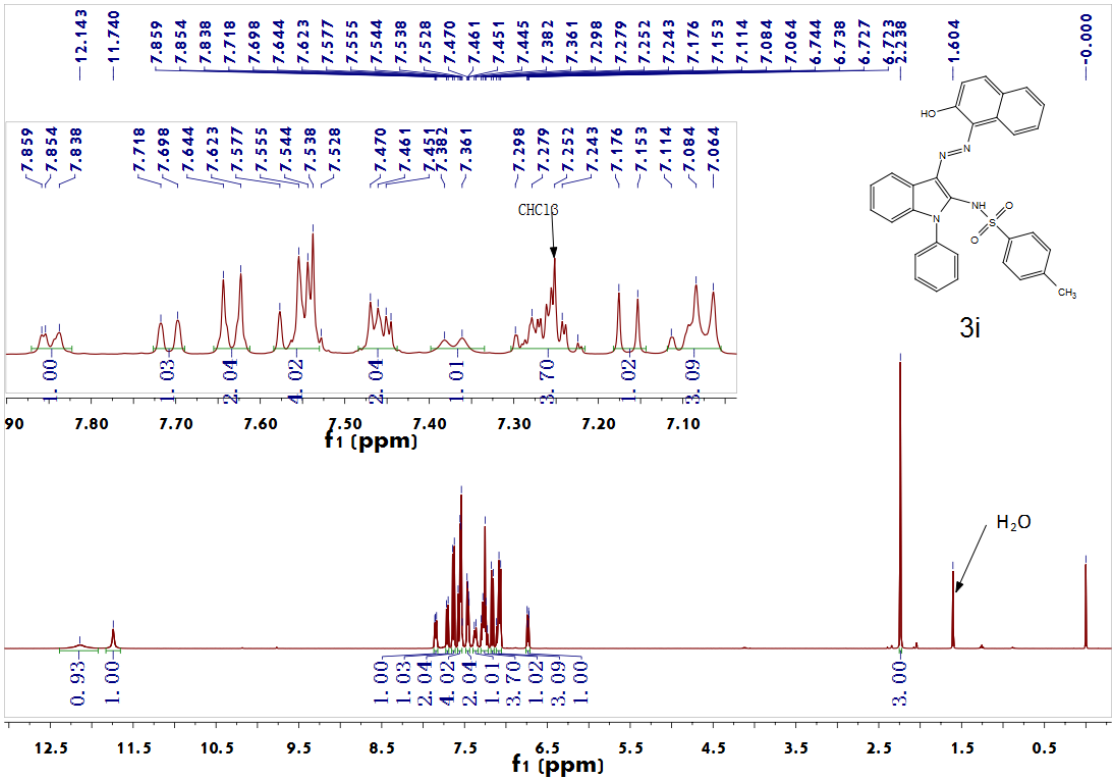
40.650
21.665
13.642
3g
f1 (ppm)


CHCl3
3h
H2O
TMS
impurity
f1 (ppm)


3h
f1 (ppm)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7.838
7.718
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7.577
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7.538
7.528
7.470
7.461
7.451
7.445
7.382
7.361
7.298
7.279
7.252
7.243
7.176
7.153
7.114
7.084
7.064
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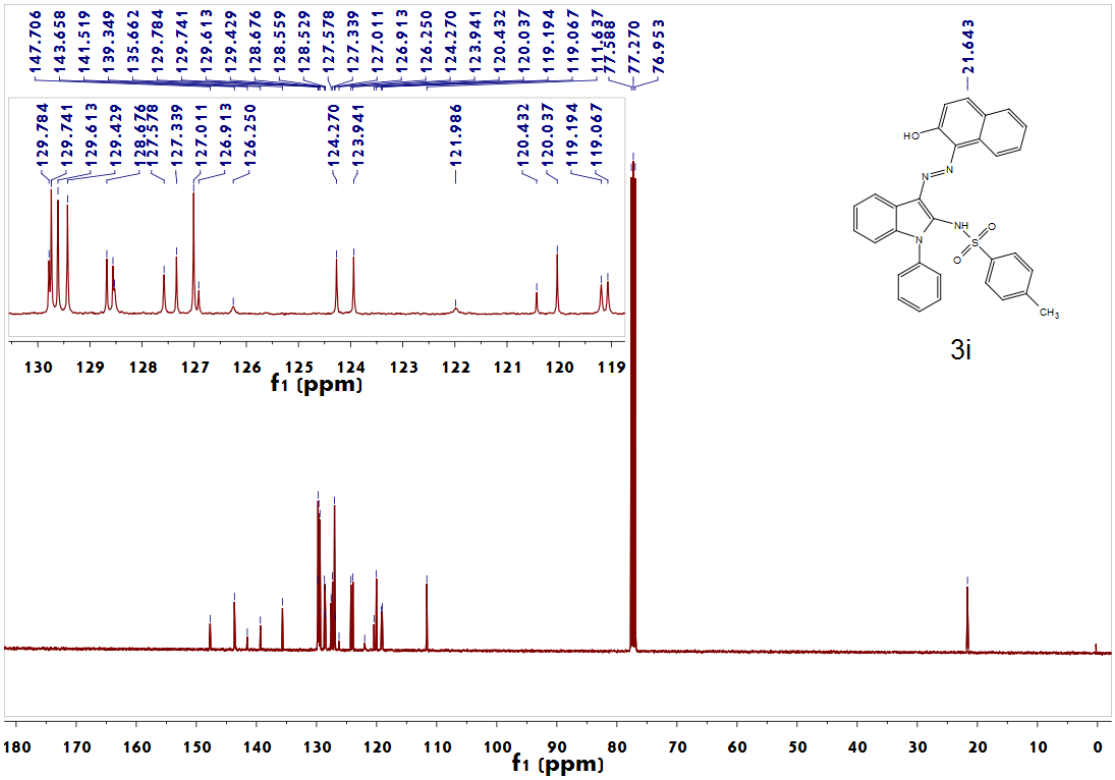
6.727
6.723
2.238
1.604
-0.000
CHCl3
3i
H2O
f1 (ppm)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127.339
127.011
126.913
126.250
124.270
123.941
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120.037
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119.067
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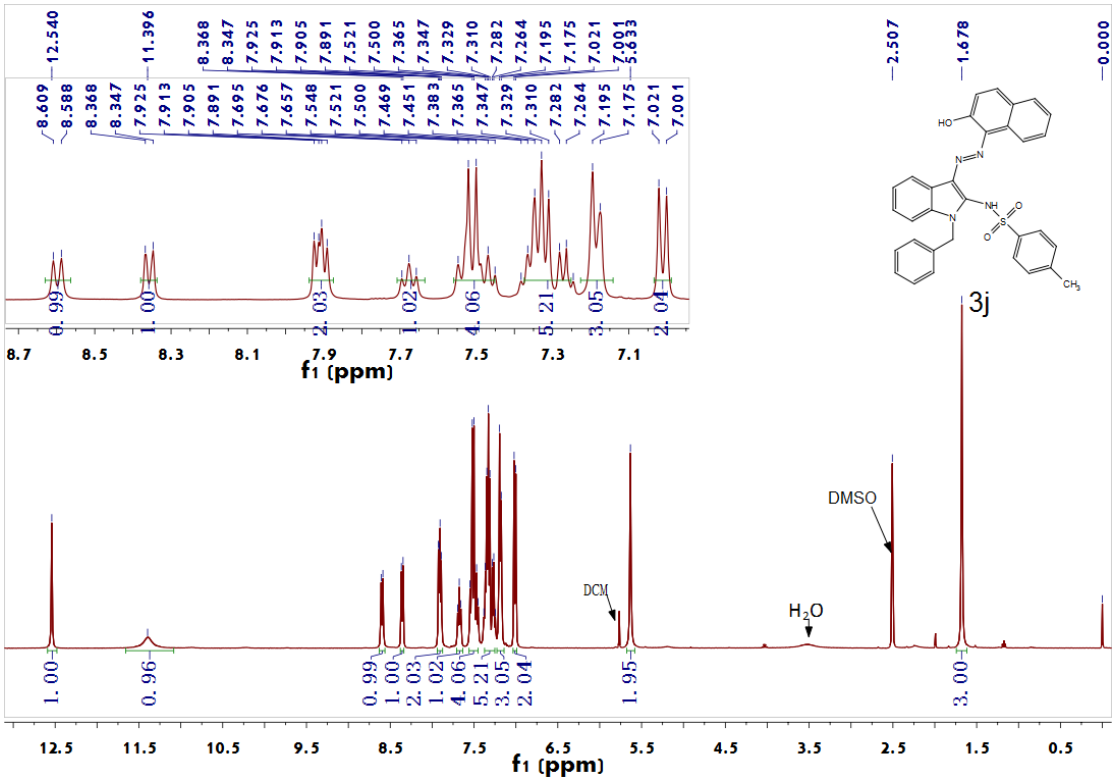
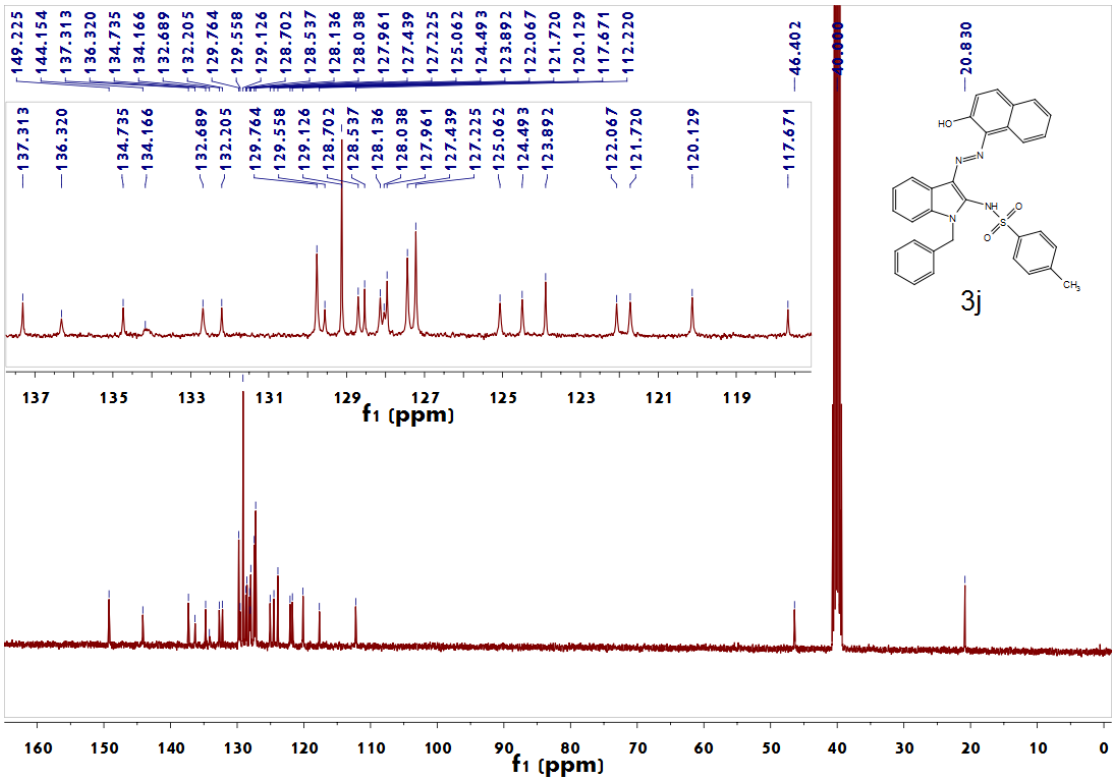
77.270
76.953
21.643
3i
f1 (ppm)


3j
DMSO
DCM
H_2O
f1 (ppm)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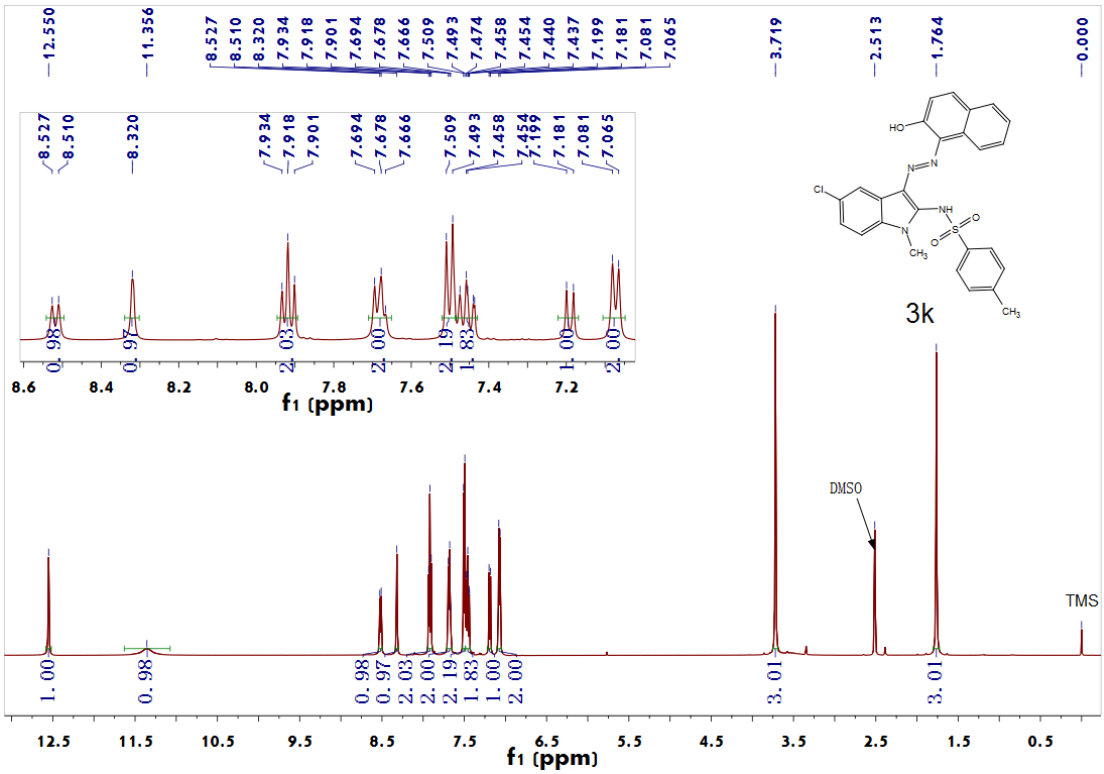
f1 (ppm)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7.901
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7.666
7.509
7.493
7.474
7.458
7.454
7.440
7.437
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7.081
7.065
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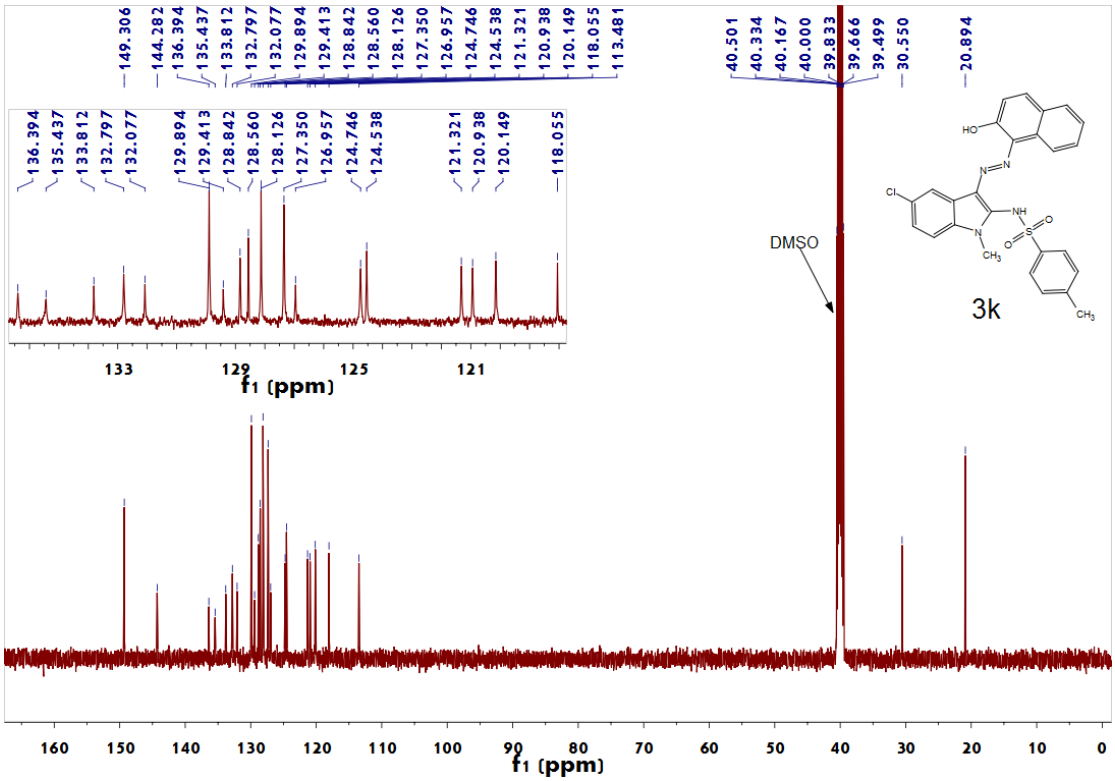
0.000
DMSO
TMS
3k
f1 (ppm)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124.538
121.321
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113.481
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40.000
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30.550
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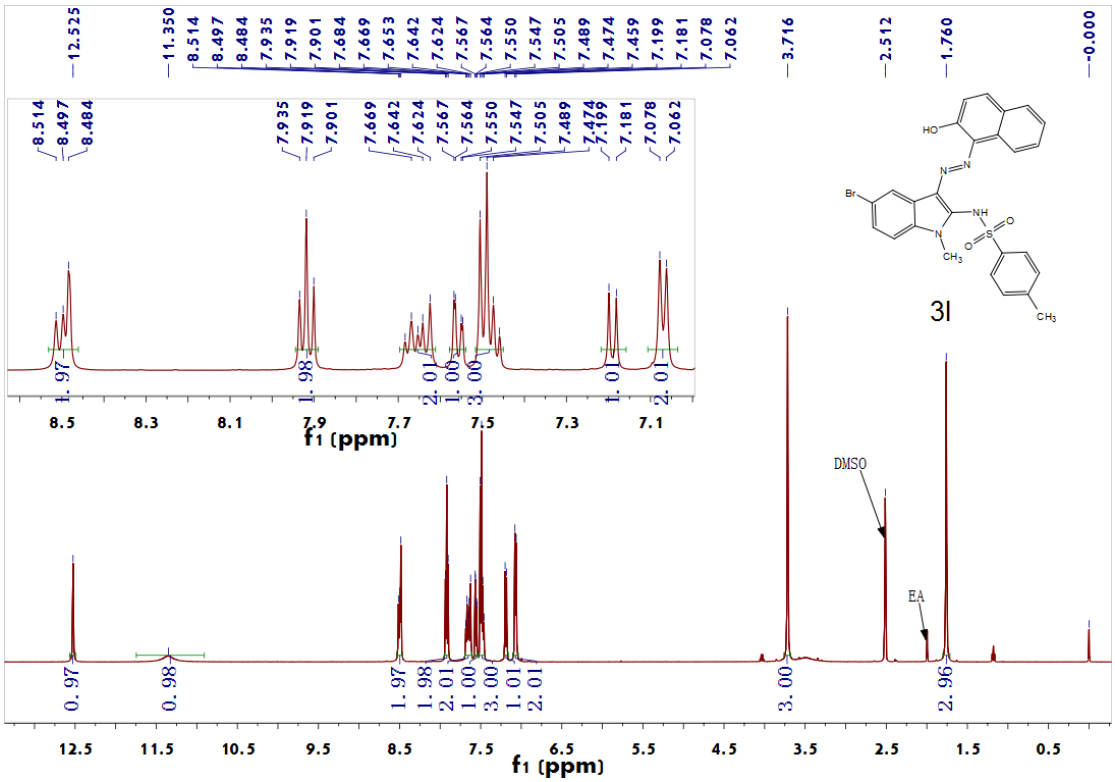
DMSO
3k
f1 (ppm)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7.547
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7.474
7.459
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7.062
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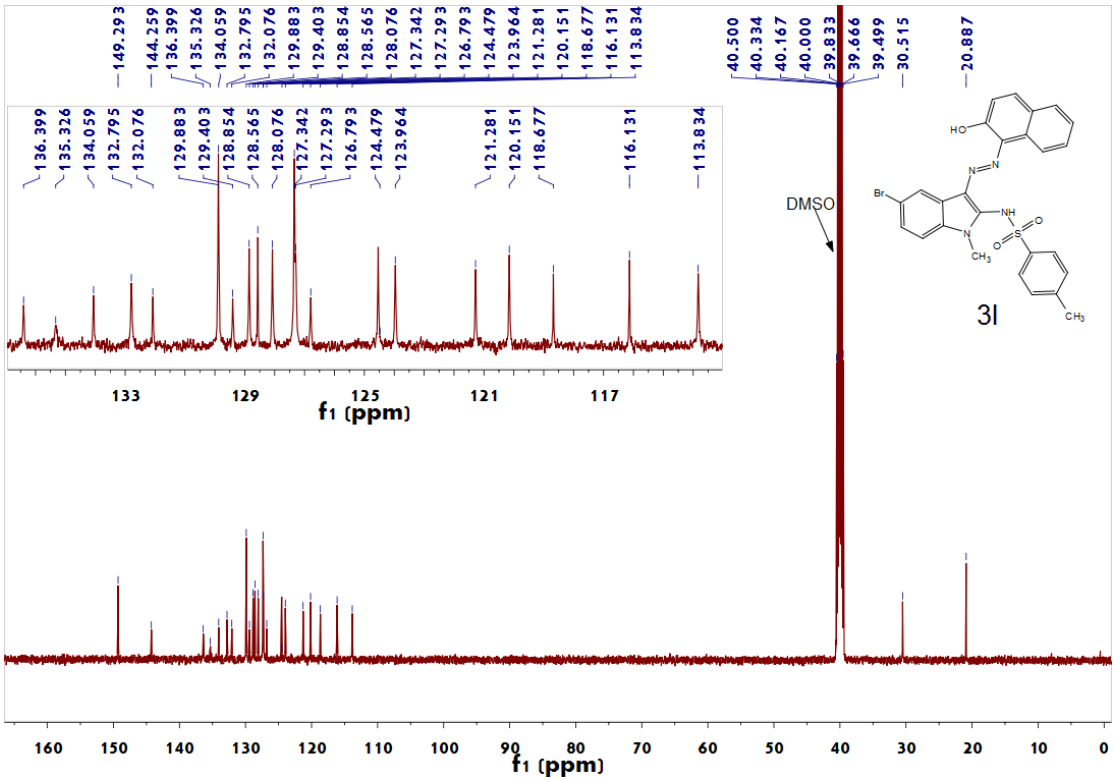
DMSO
EA
3l
f1 (ppm)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124.479
123.964
121.281
120.151
118.677
116.131
113.834
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40.167
40.000
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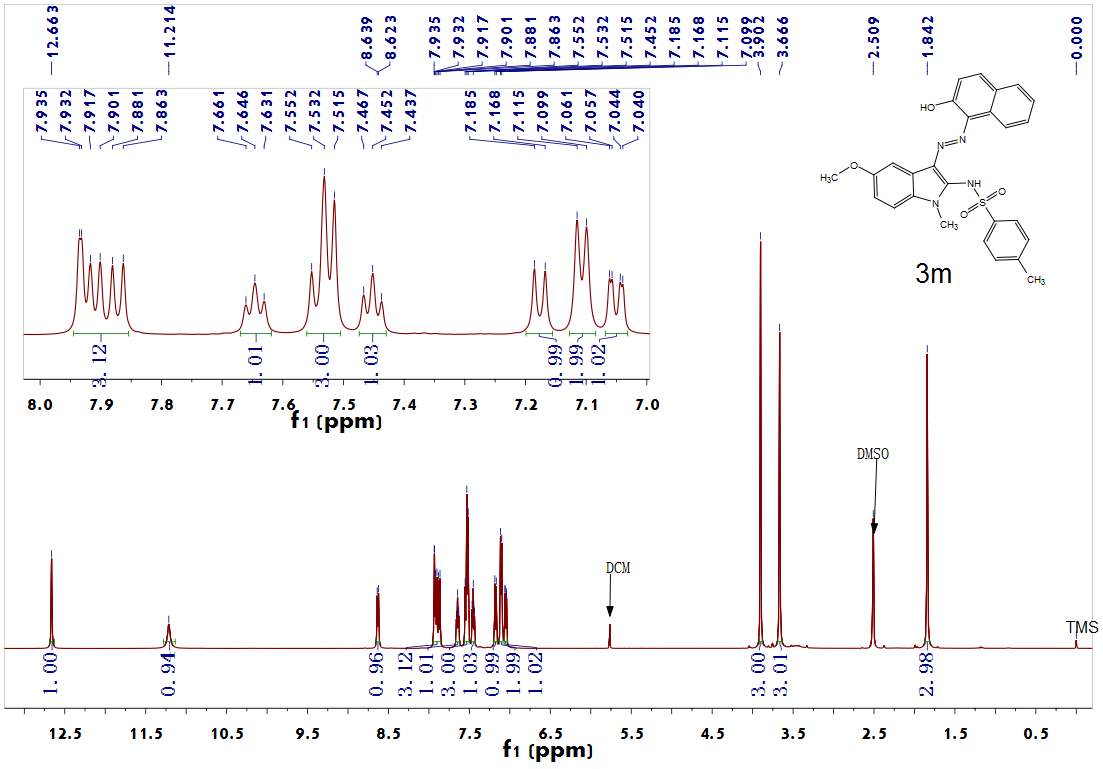
39.666
39.499
30.515
20.887
DMSO
3l
f1 (ppm)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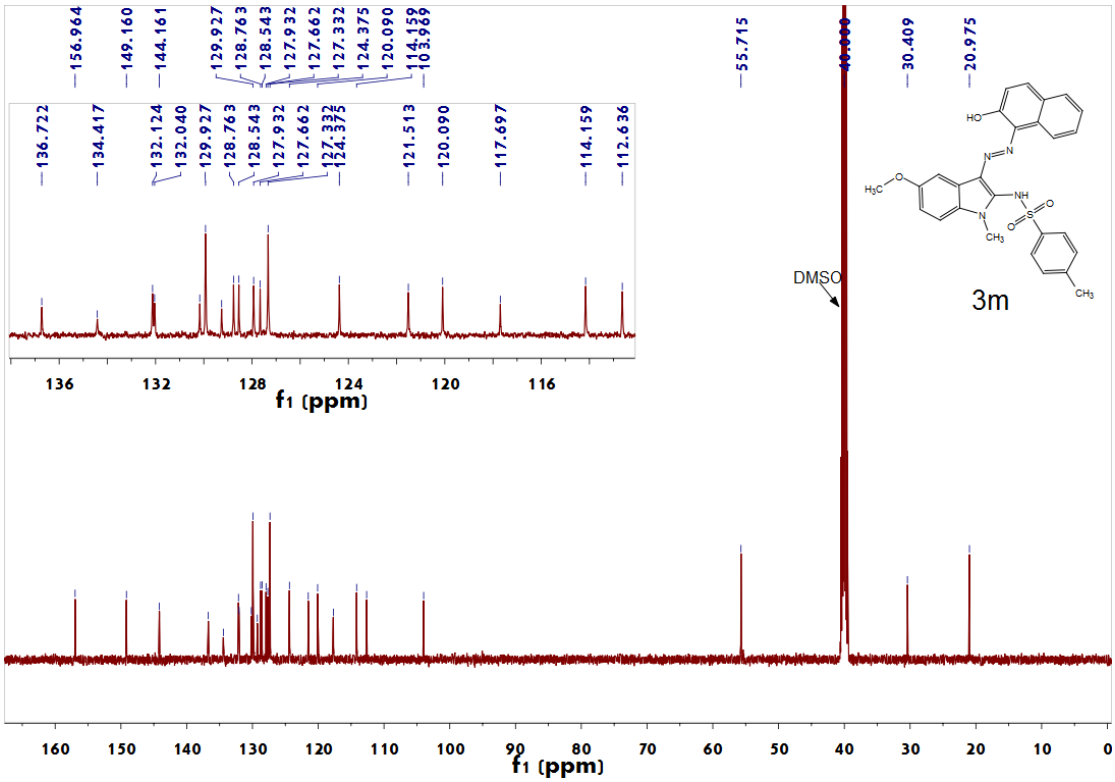
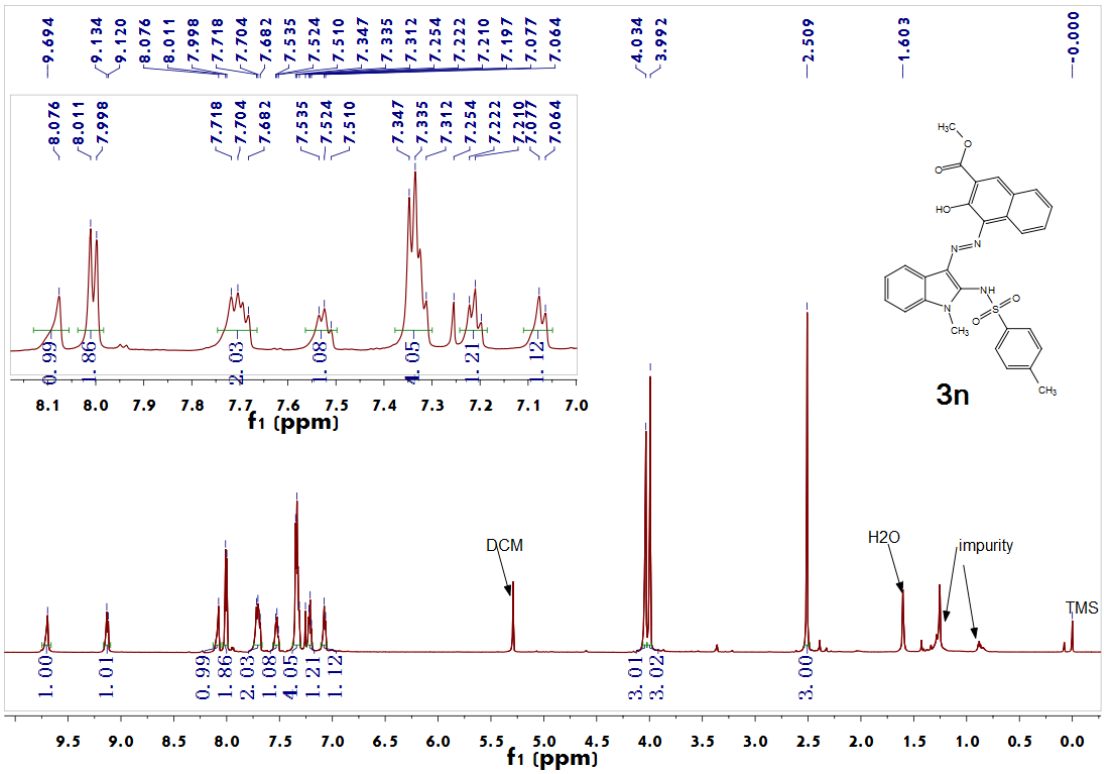
DMSO
DCM
TMS
f1 (ppm)


3m
DMSO
f1 (ppm)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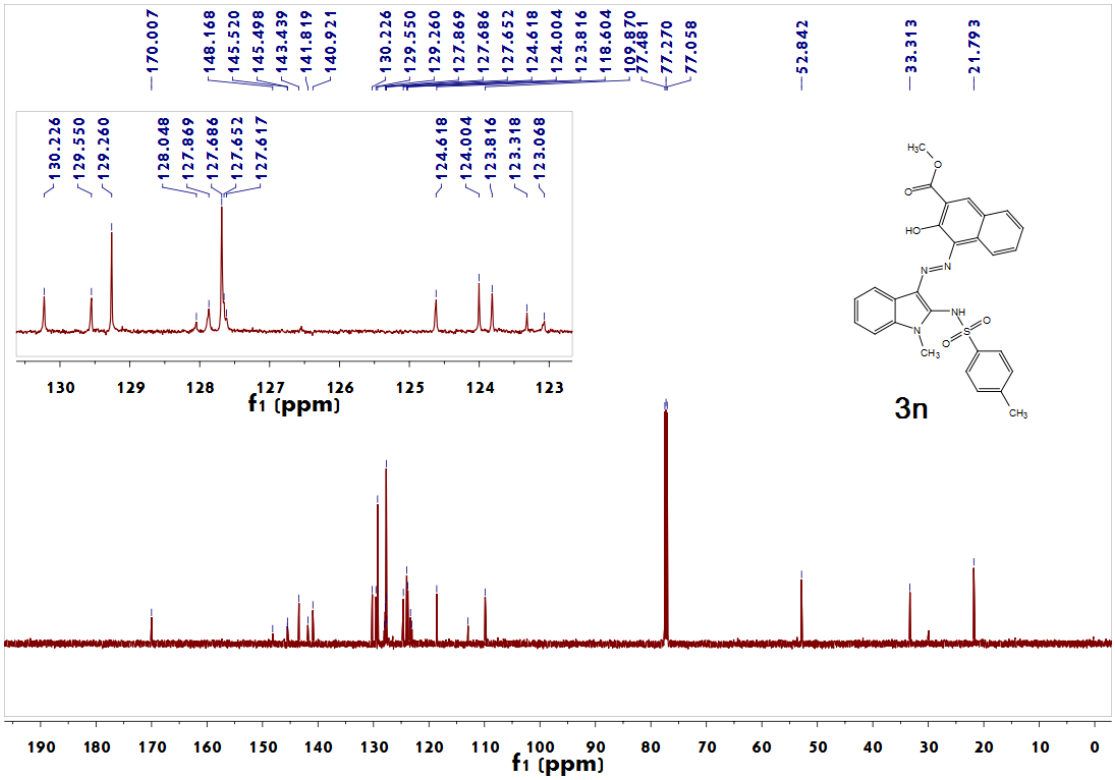
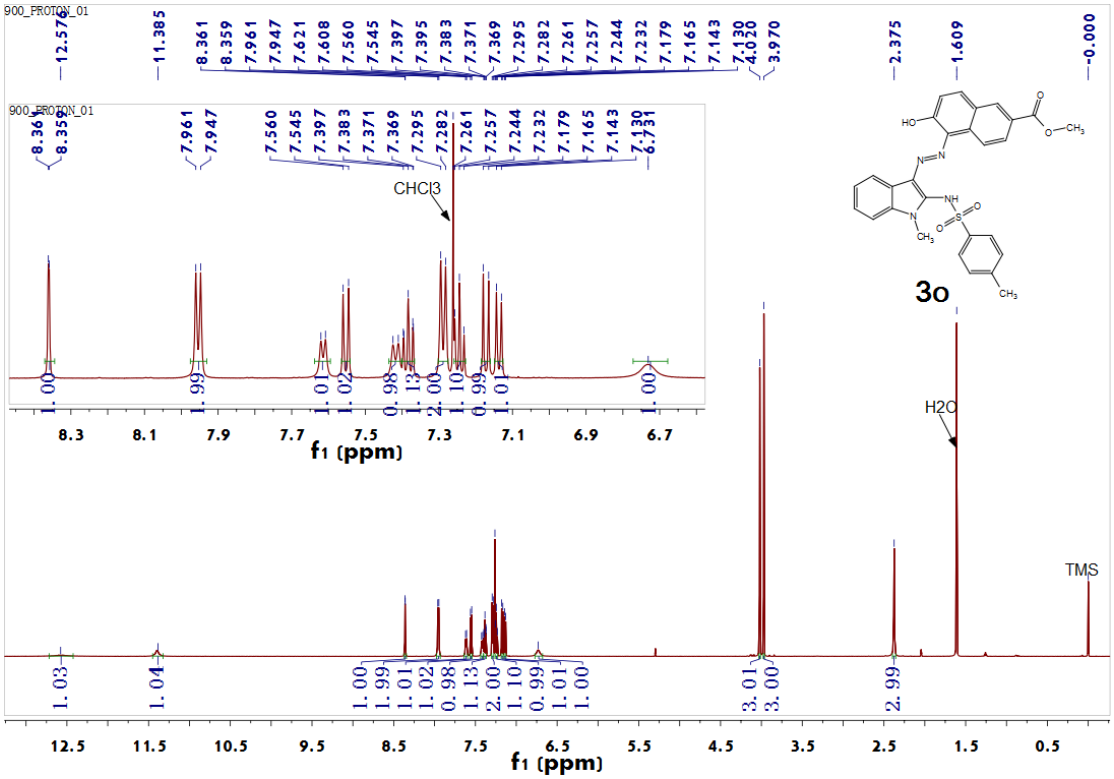
DCM
H2O
impurity
TMS
f1 (ppm)


3n
f1 (ppm)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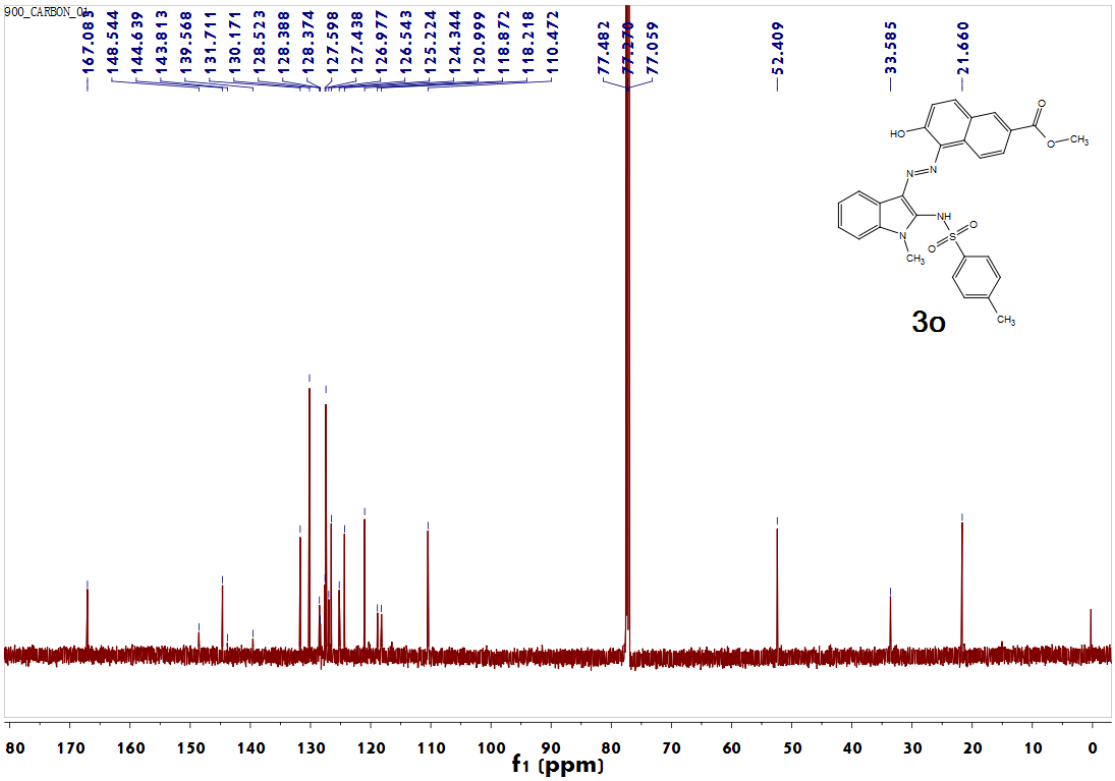
CHCl3
H2O
TMS
3o
f1 (ppm)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3o
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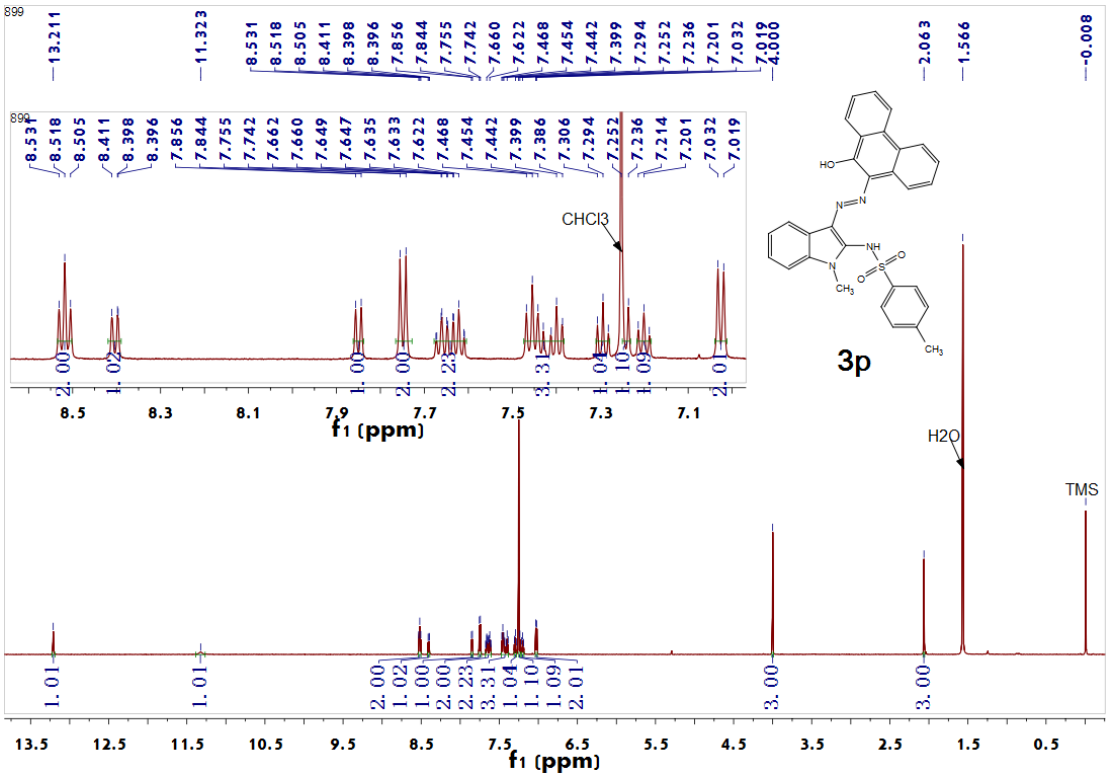
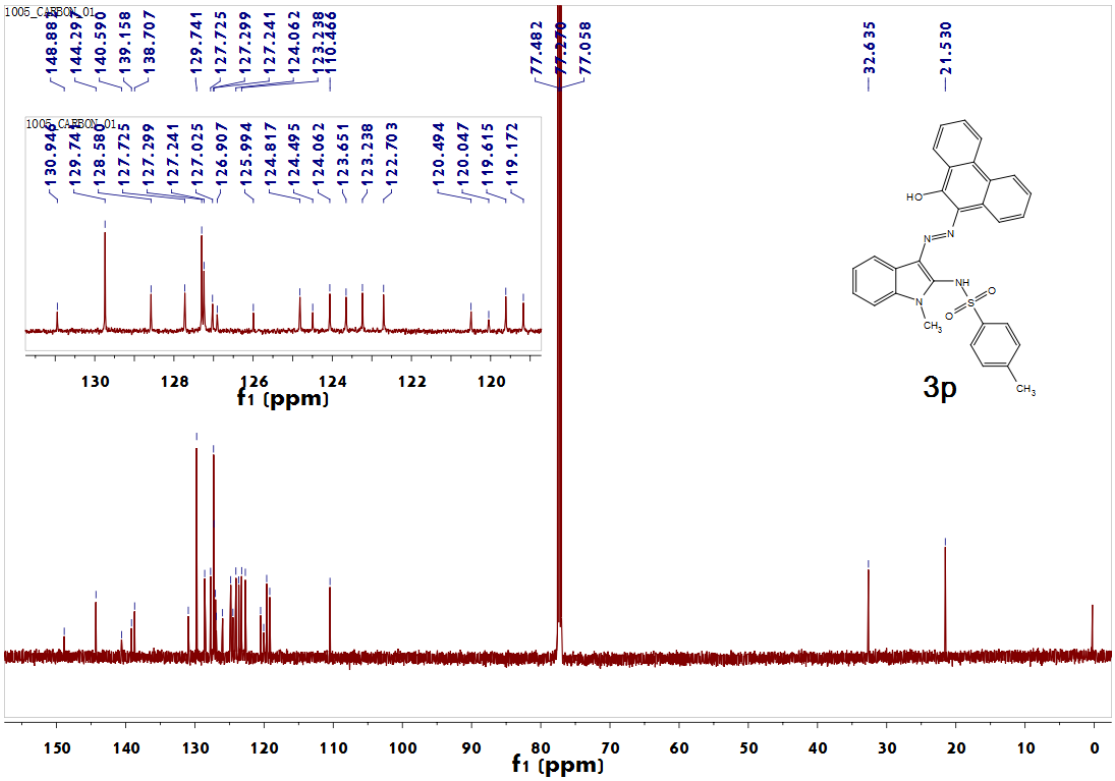
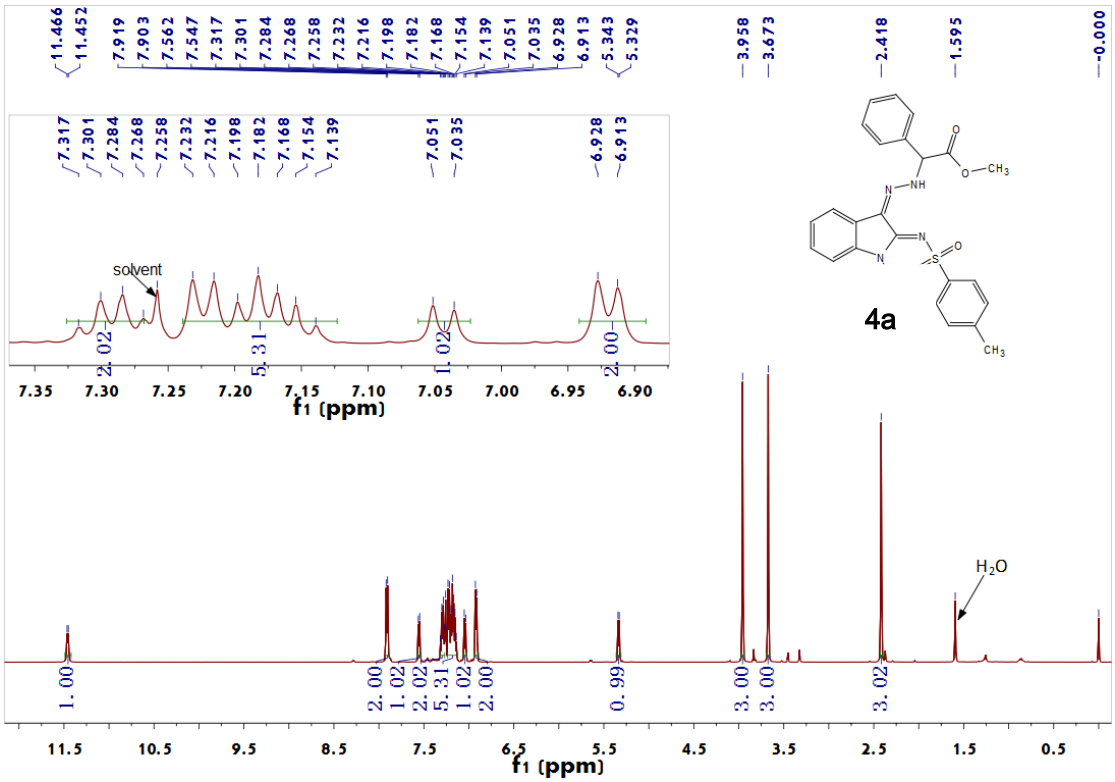

CHCl3
H2O
TMS
3p
f1 (ppm)


3p
f1 (ppm)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7.562
7.547
7.317
7.301
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7.232
7.216
7.198
7.182
7.168
7.154
7.139
7.051
7.035
6.928
6.913
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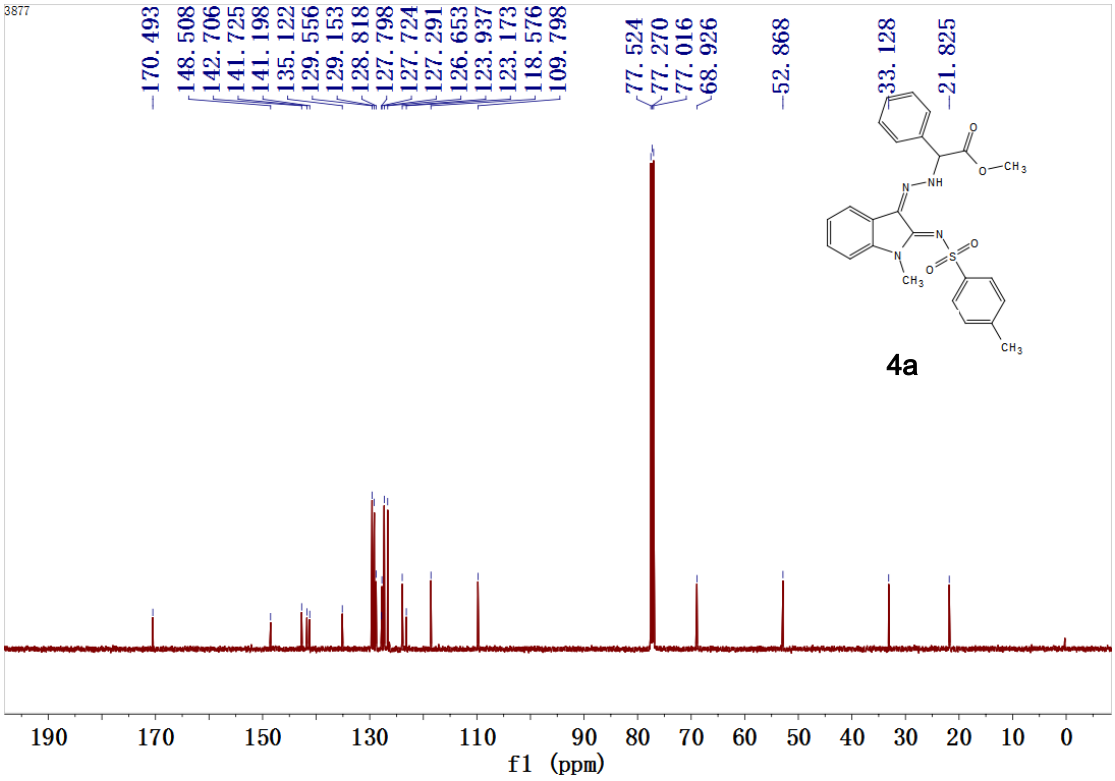
3.958
3.673
2.418
1.595
-0.000
solvent
4a
H2O
f1 (ppm)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126.653
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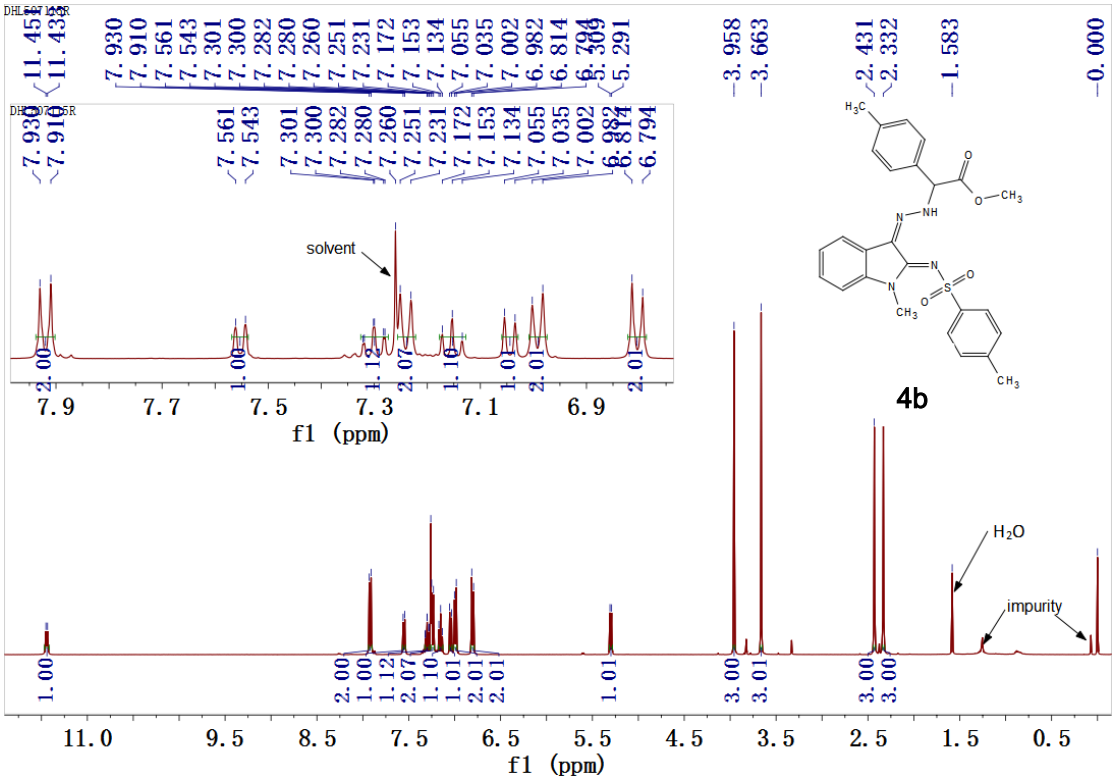
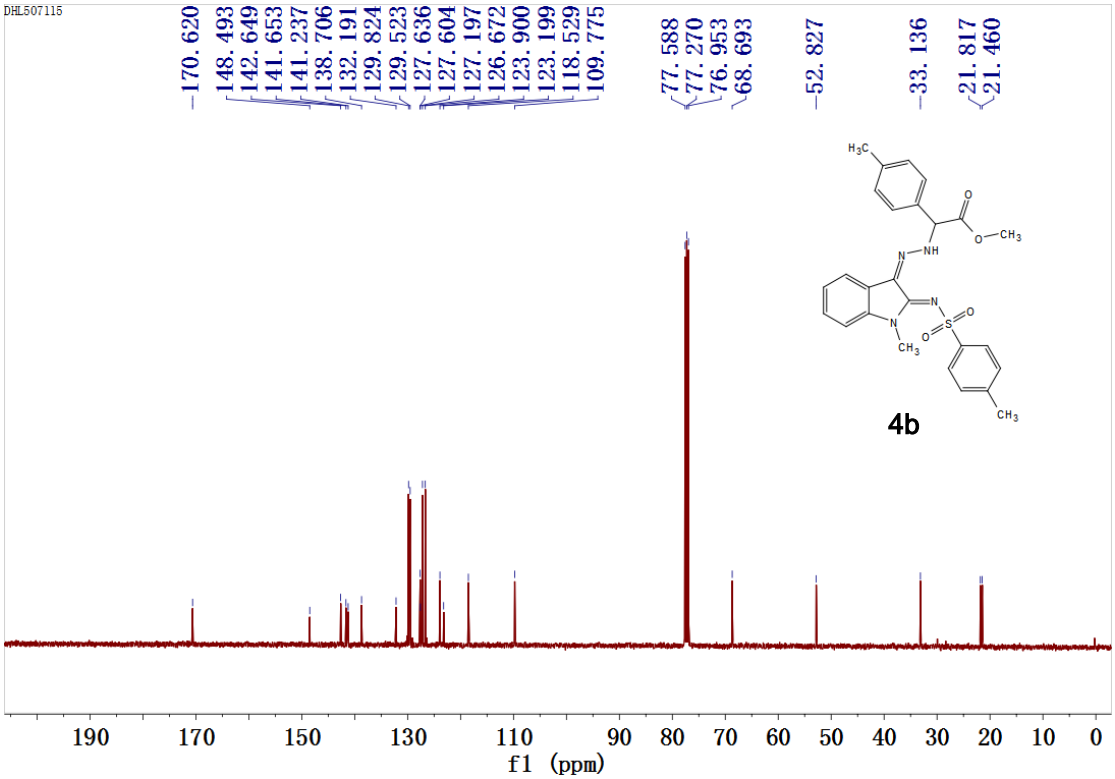
77.524
77.270
77.016
68.926
52.868
33.128
21.825
4a
f1 (ppm)


solvent
4b
H2O
impurity
f1 (ppm)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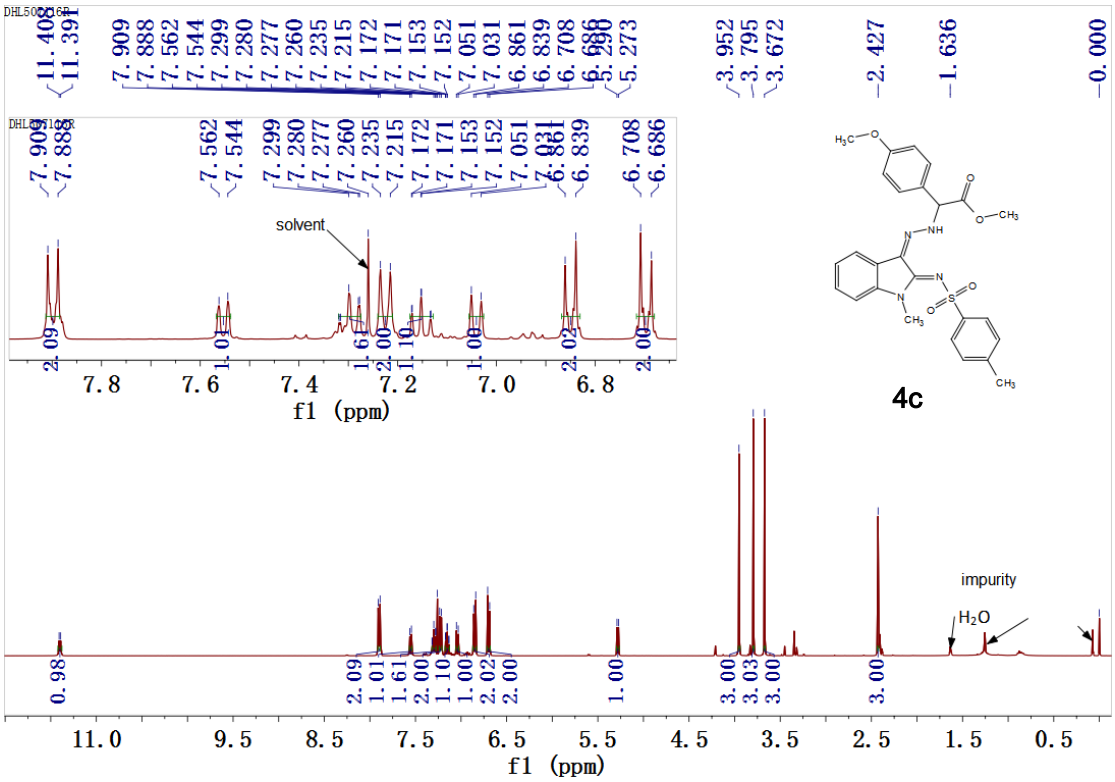
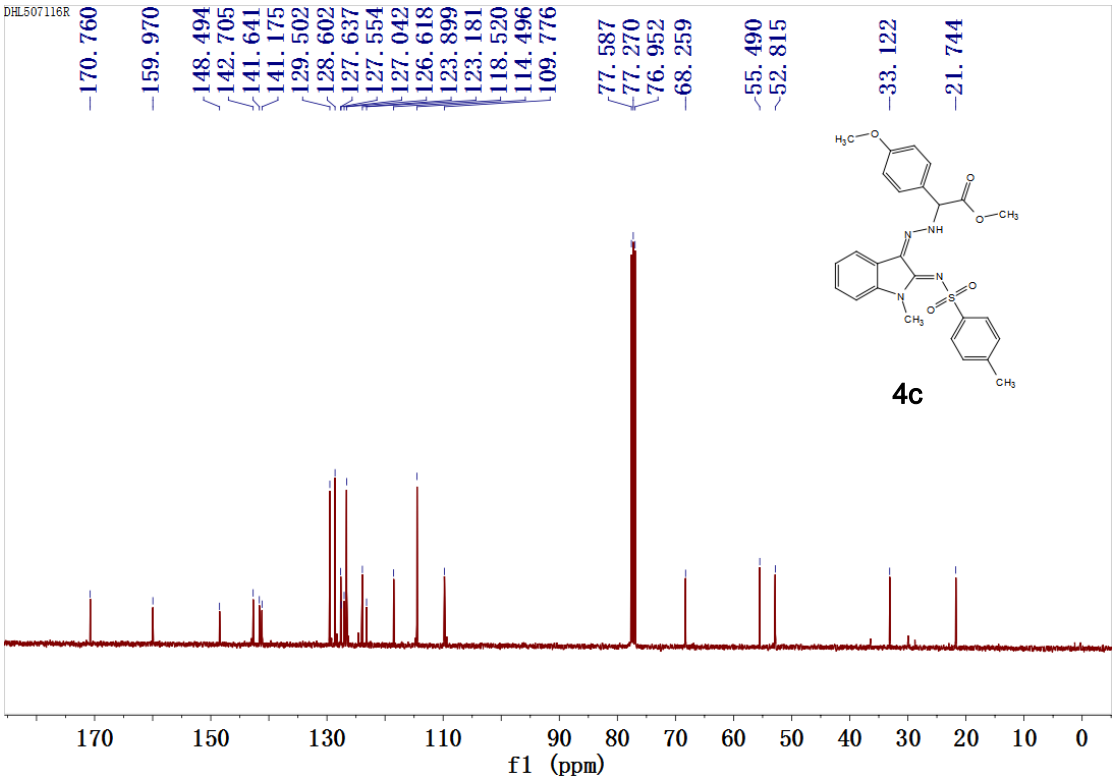
f1 (ppm)


solvent
4c
impurity
H2O
f1 (ppm)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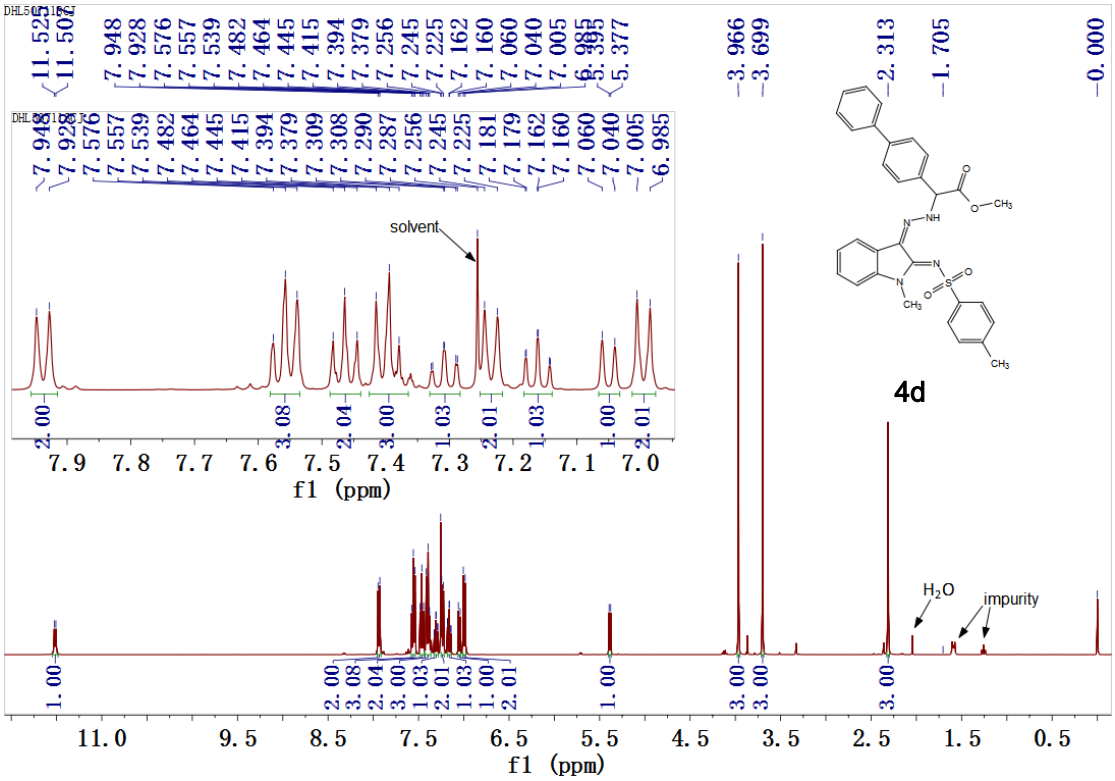
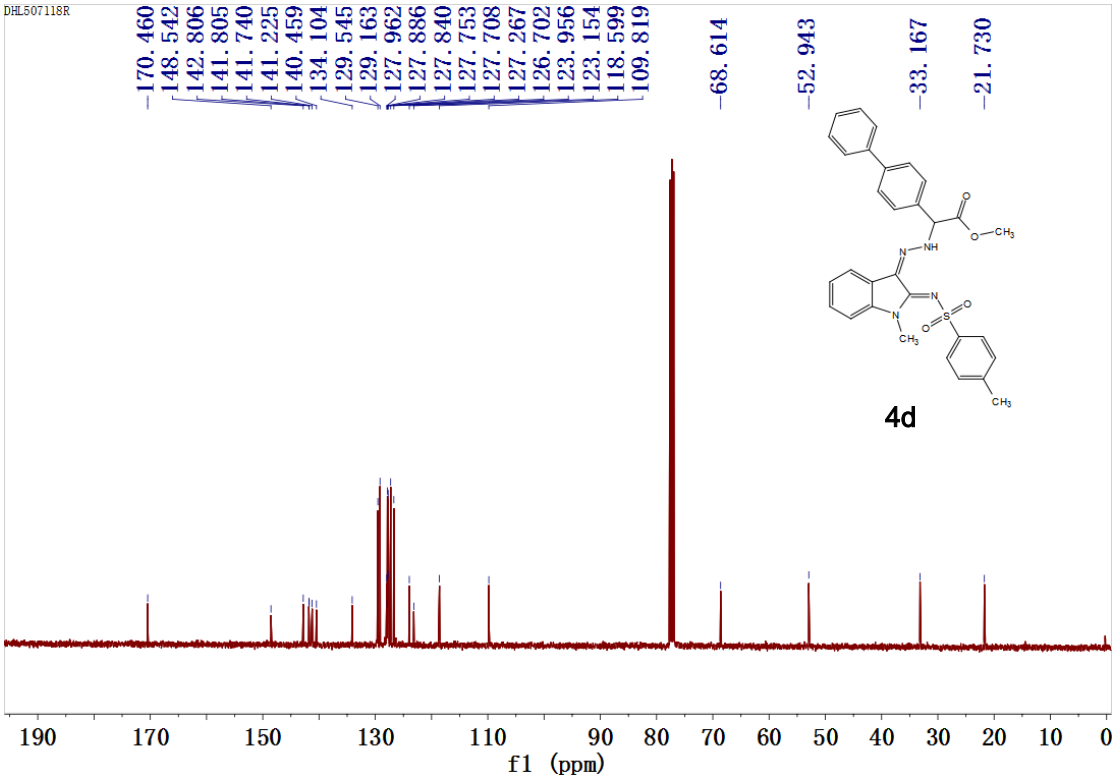
f1 (ppm)


solvent
4d
H2O
impurity
f1 (ppm)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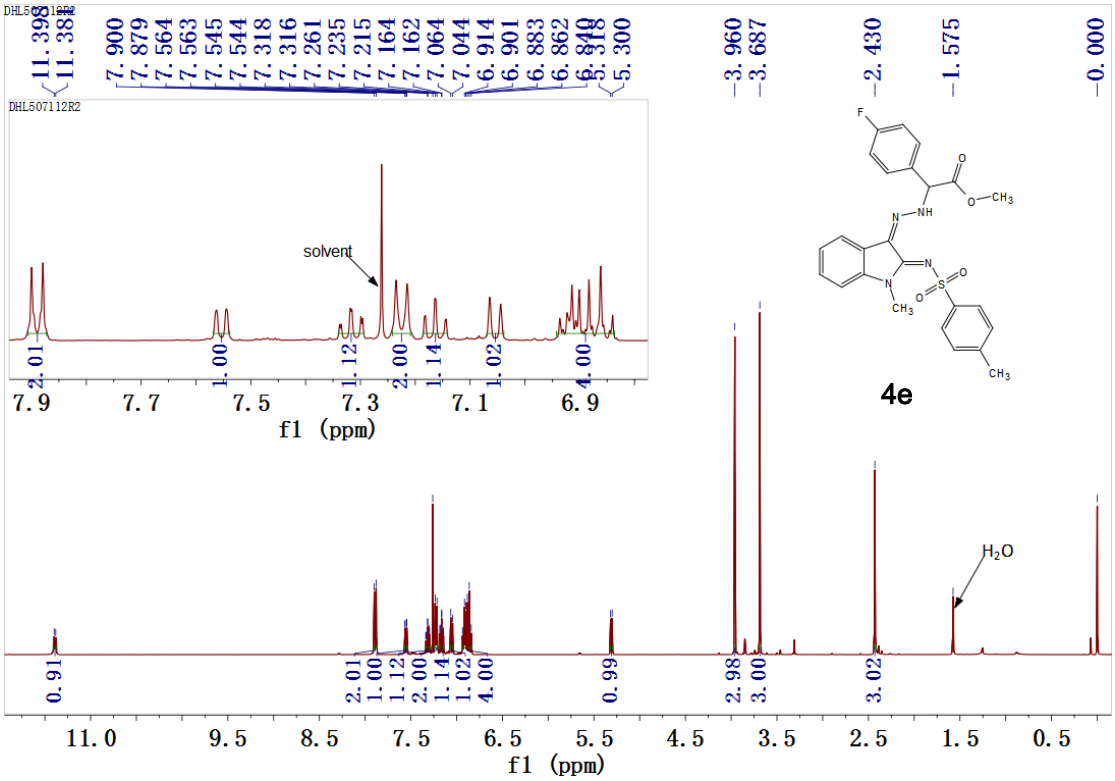
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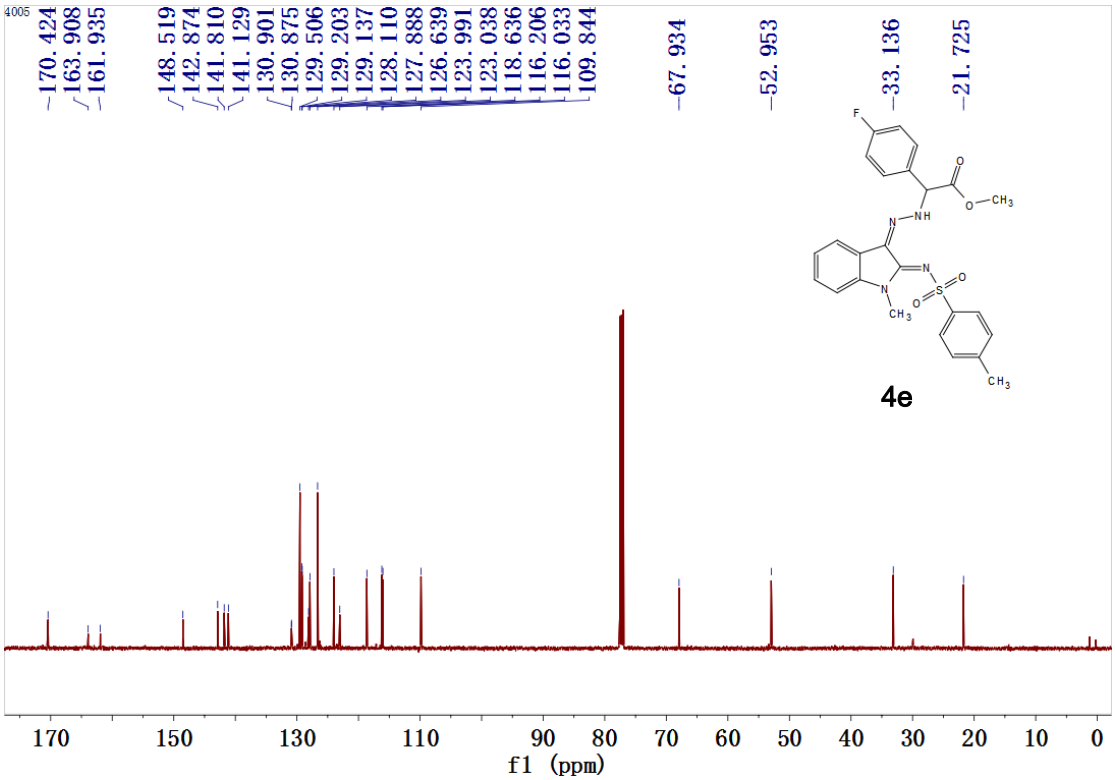
7.261
7.235
7.215
7.164
7.162
7.064
7.044
6.914
6.901
6.883
6.862
6.840
6.818
5.318
5.300
3.960
3.687
2.430
1.575
0.000
solvent
2.01
1.00
1.12
2.00
1.14
1.02
4.00
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
4e
H2O
0.91
2.01
1.00
1.12
2.00
1.14
1.02
4.00
0.99
2.98
3.00
3.02
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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148.519
142.874
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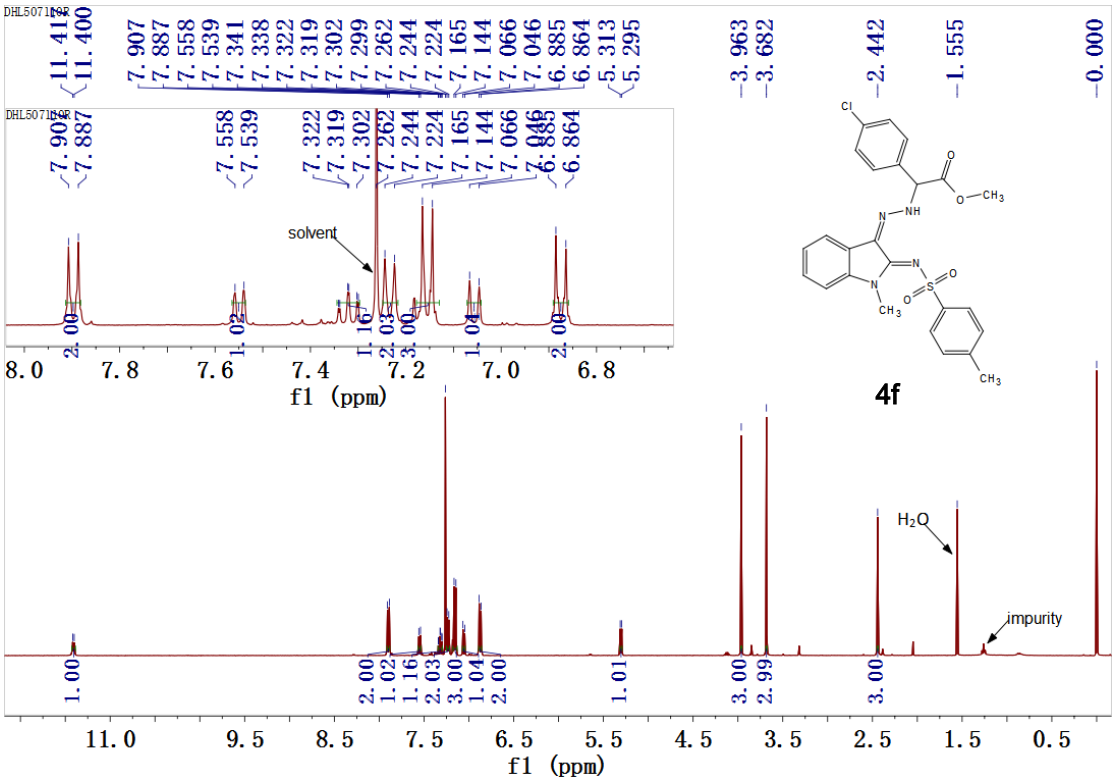
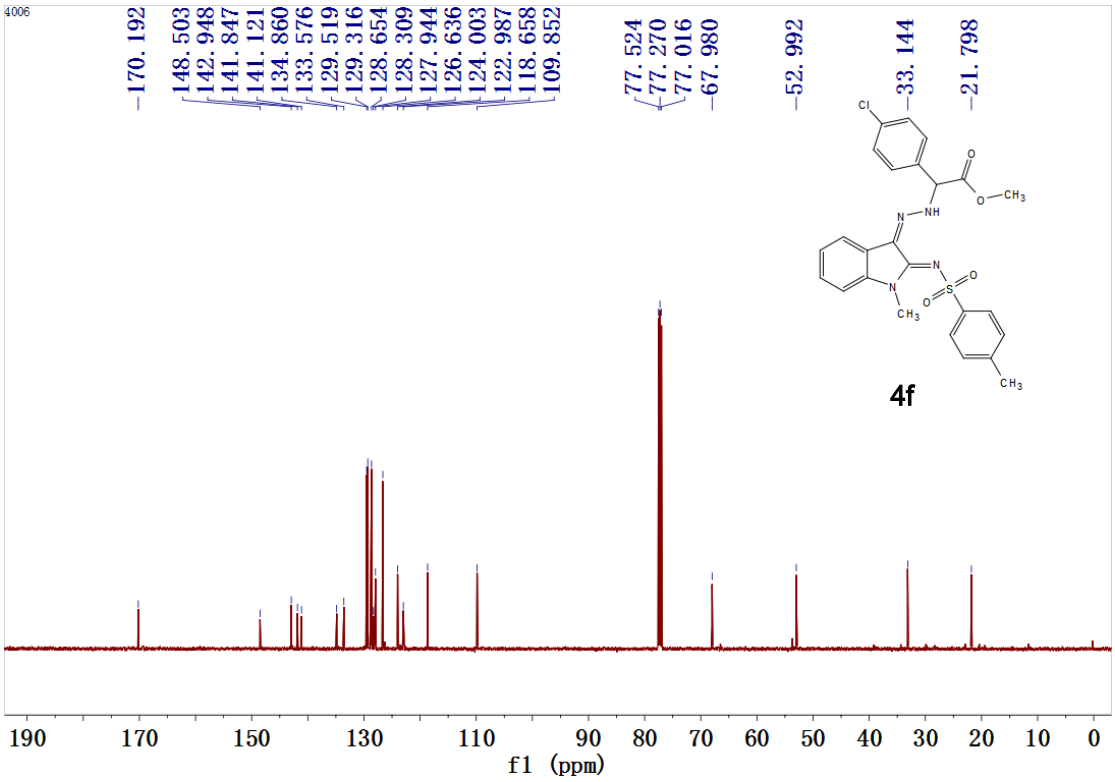
141.129
130.901
130.875
129.506
129.203
129.137
128.110
127.888
126.639
123.991
123.038
118.636
116.206
116.033
109.844
67.934
52.953
33.136
21.725
4e
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


solvent
4f
H2O
impurity
f1 (ppm)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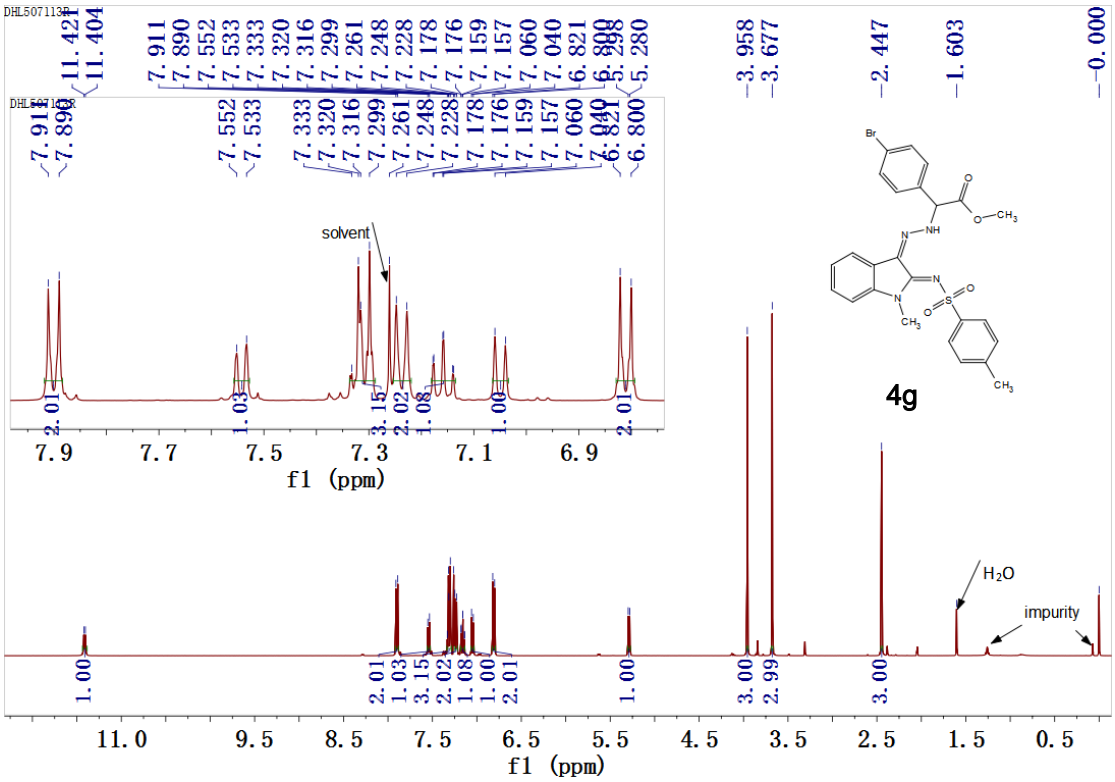
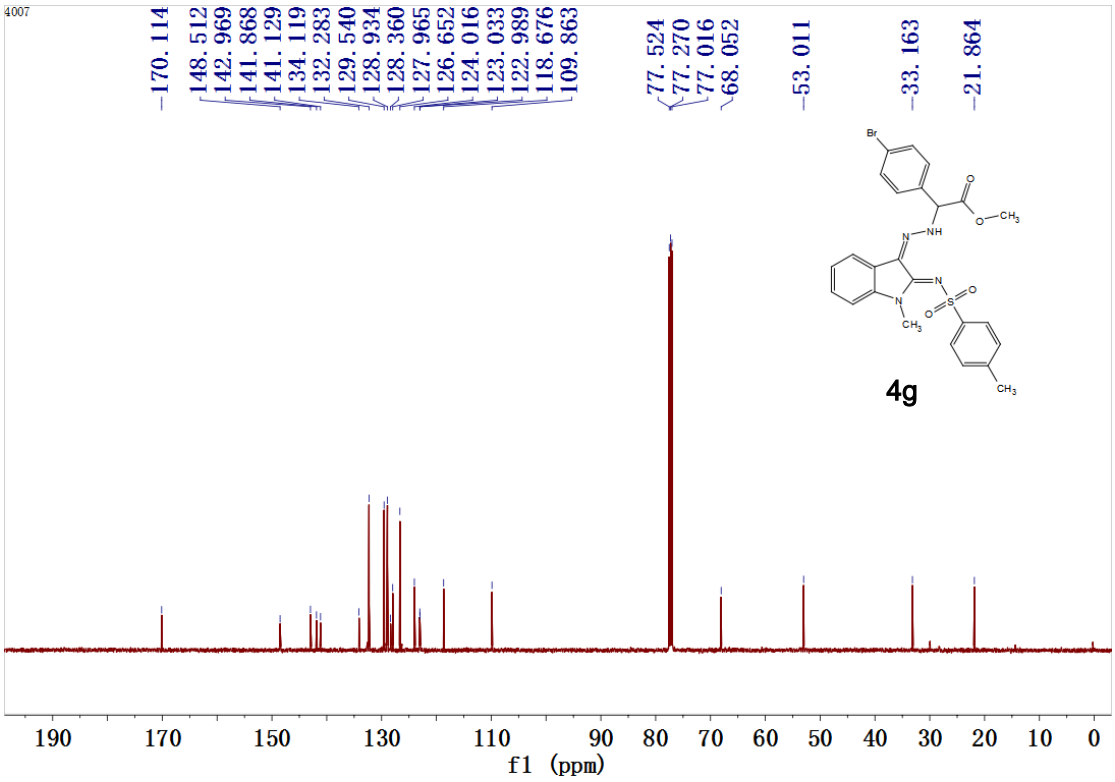
f1 (ppm)


solvent
4g
H2O
impurity
f1 (ppm)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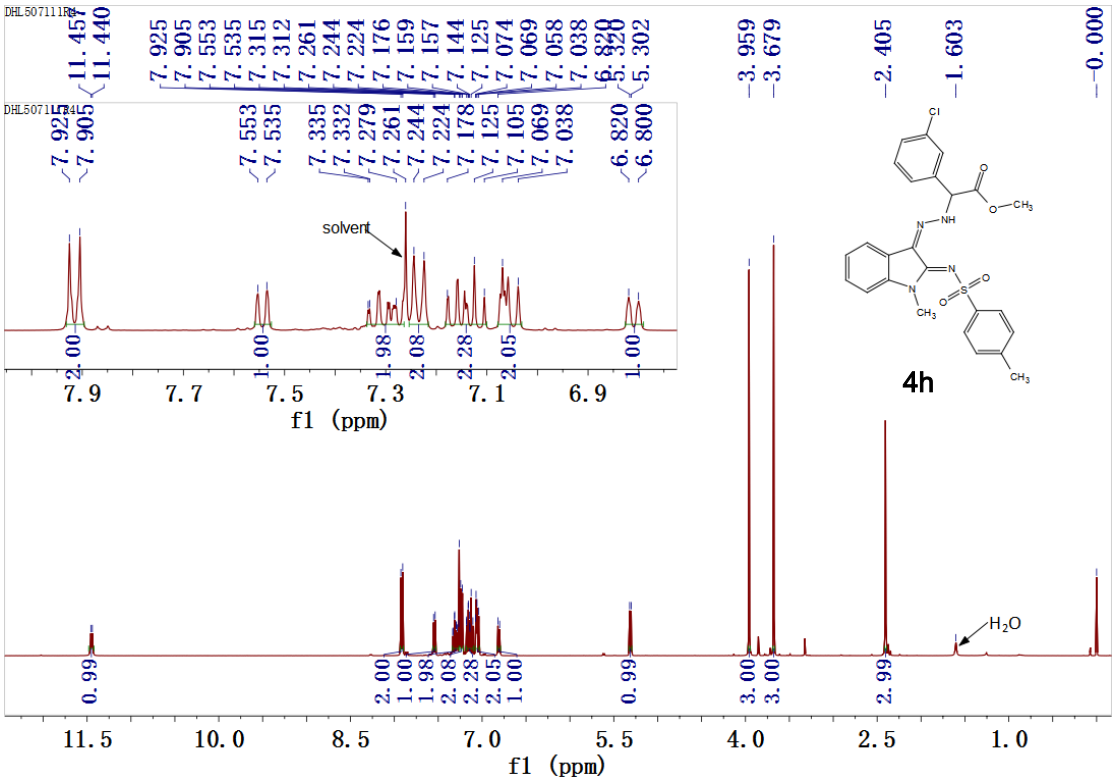
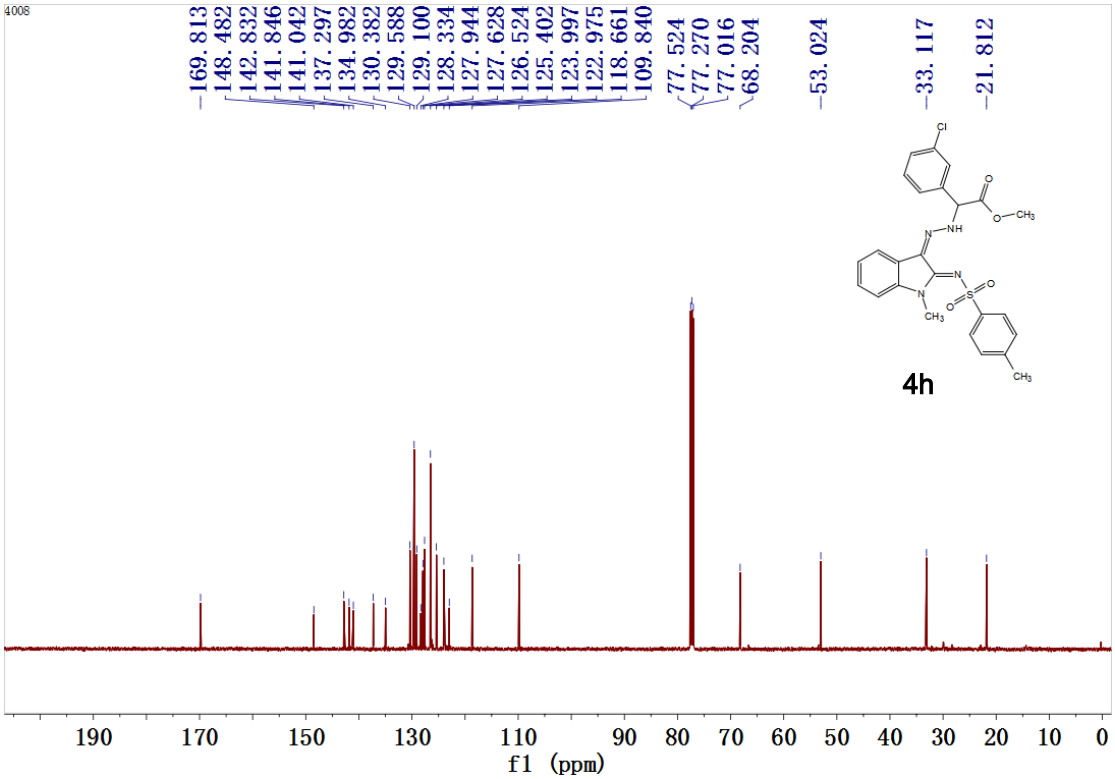
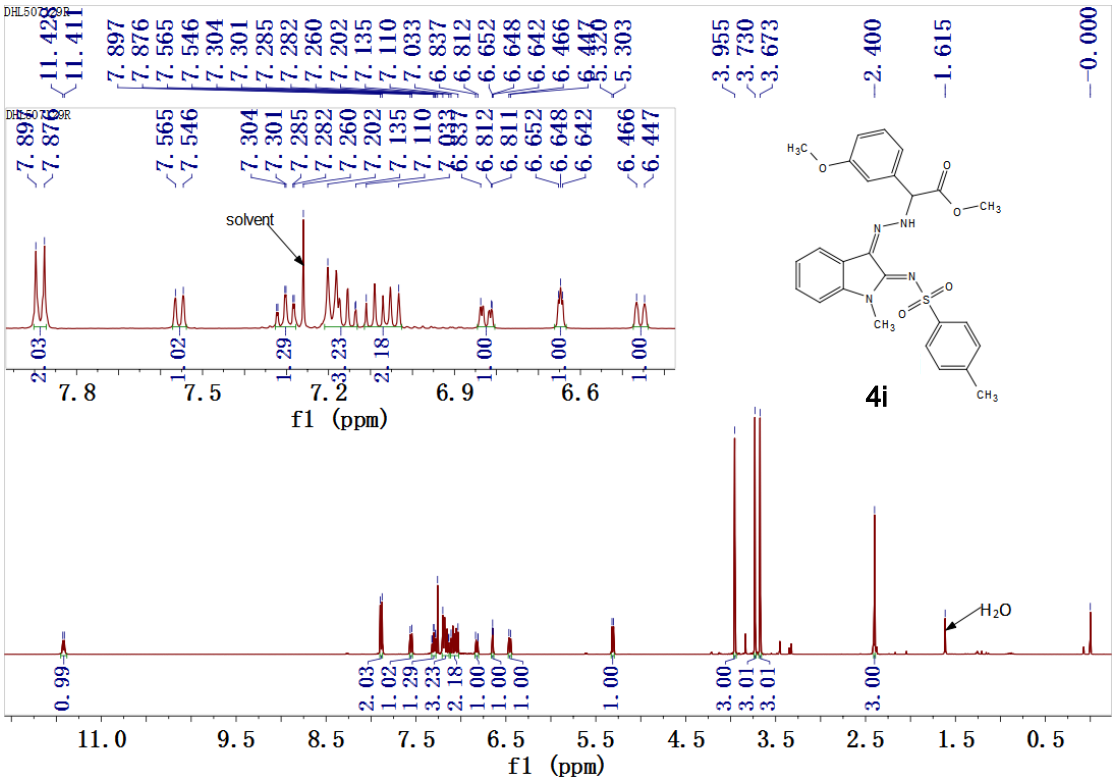
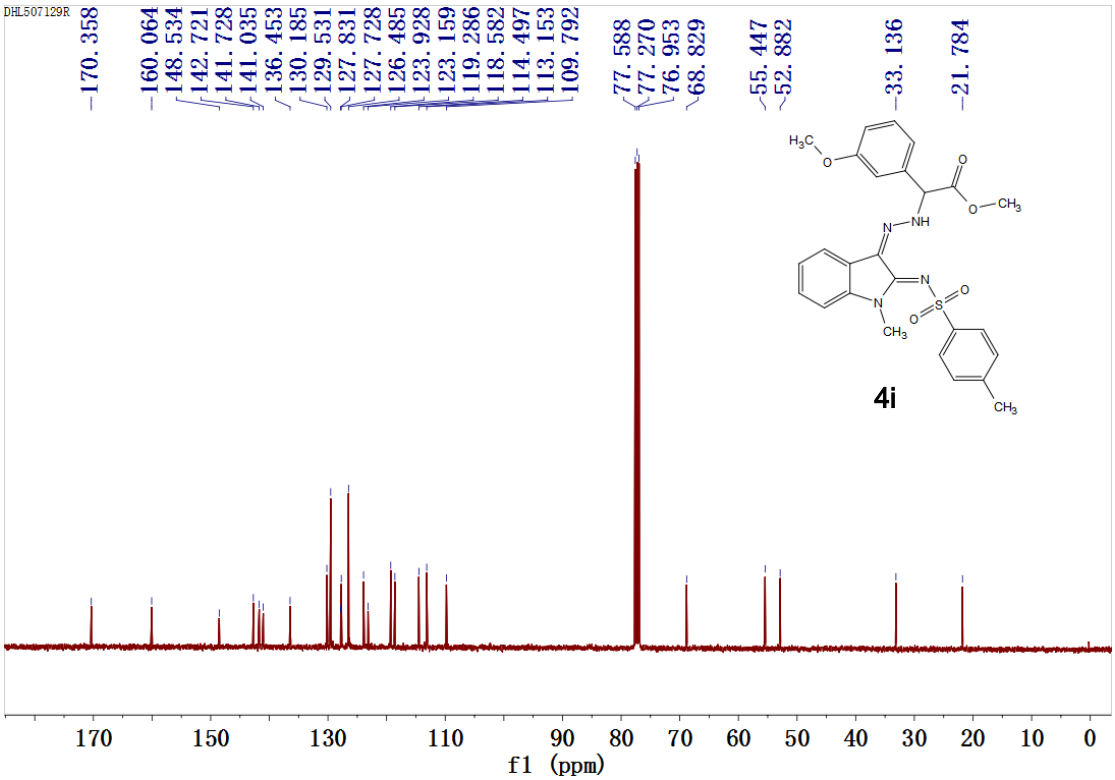
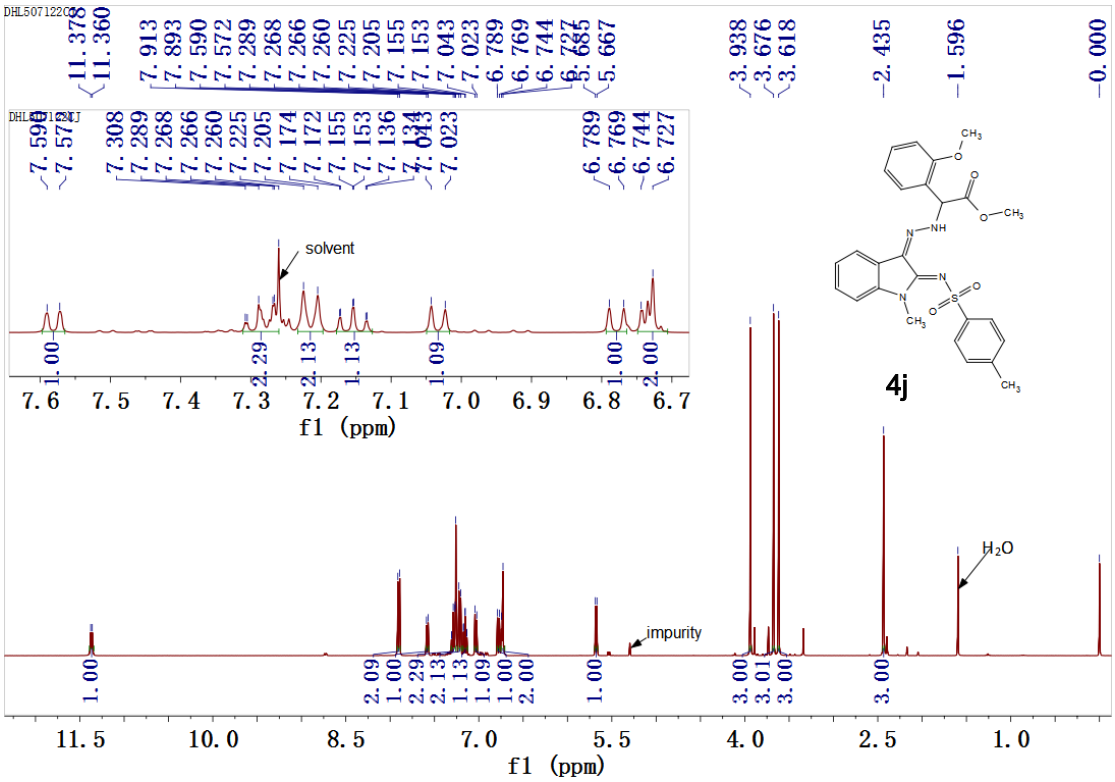
f1 (ppm)

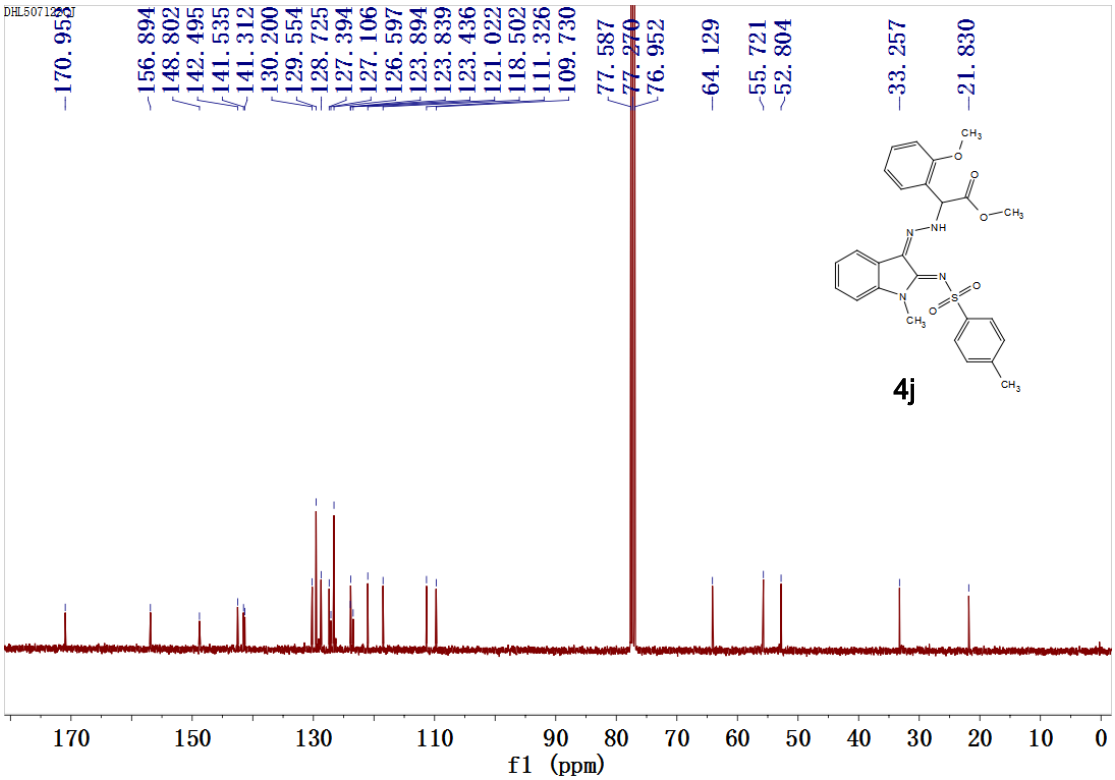

solvent
4h
H_2O
f1 (ppm)

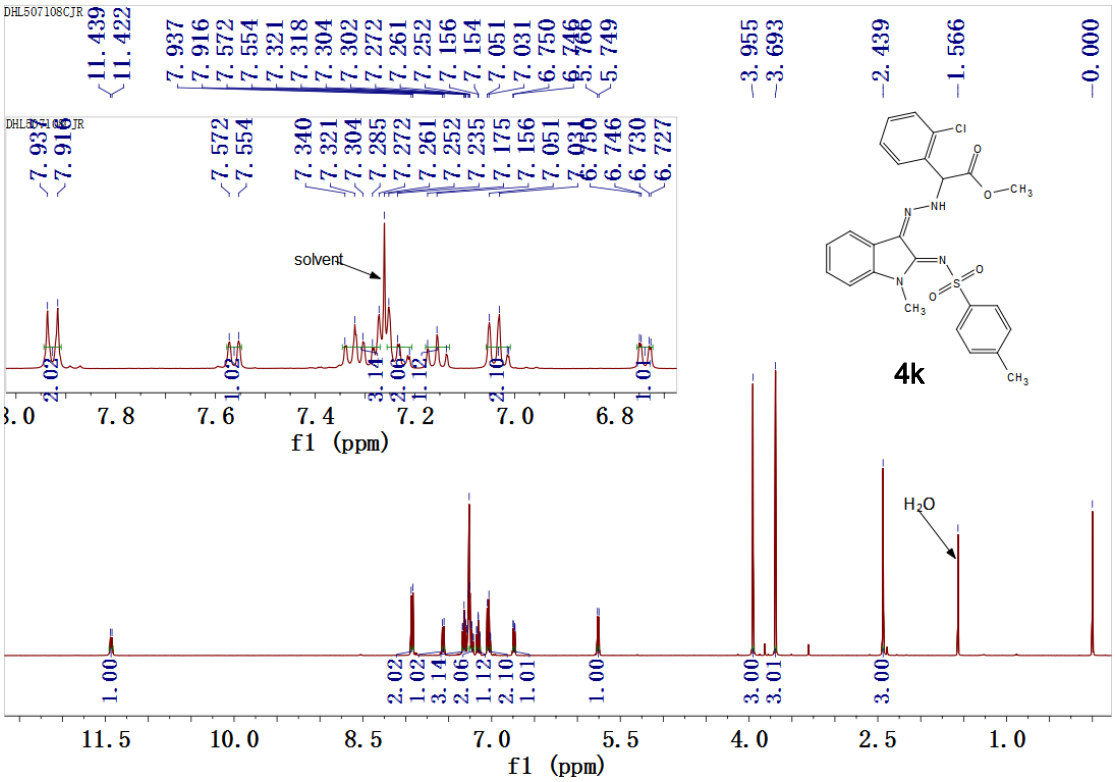

4h
f1 (ppm)

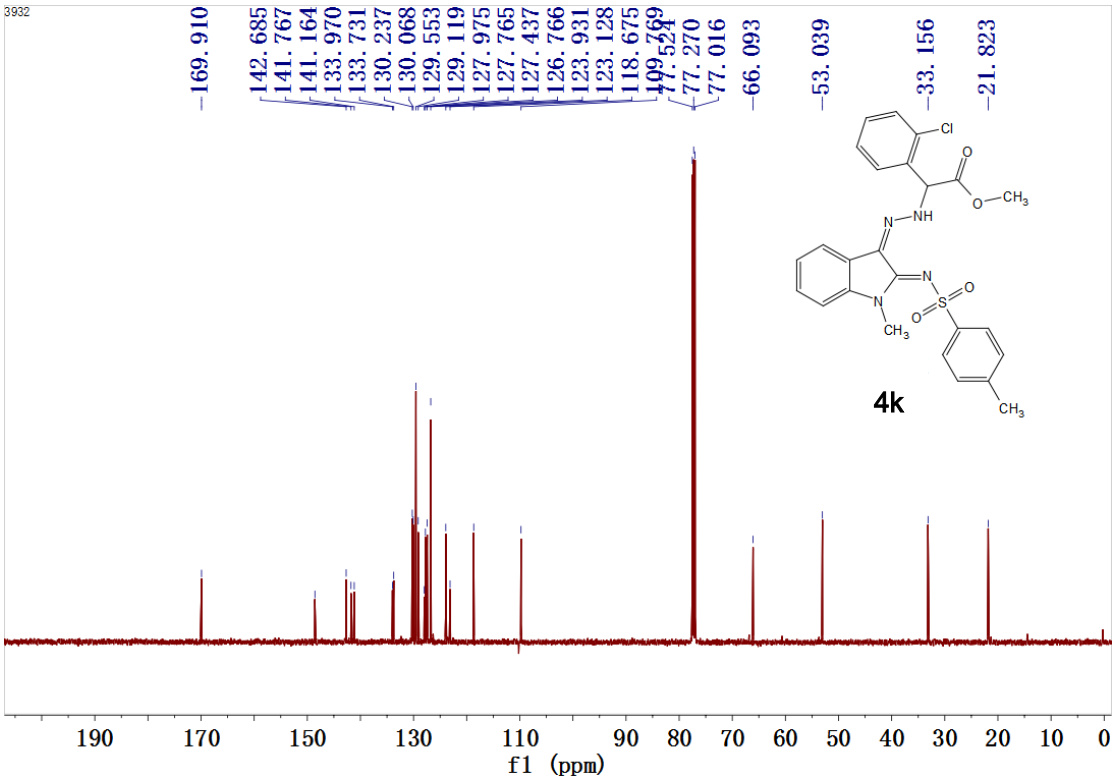

solvent
4i
H2O
f1 (ppm)

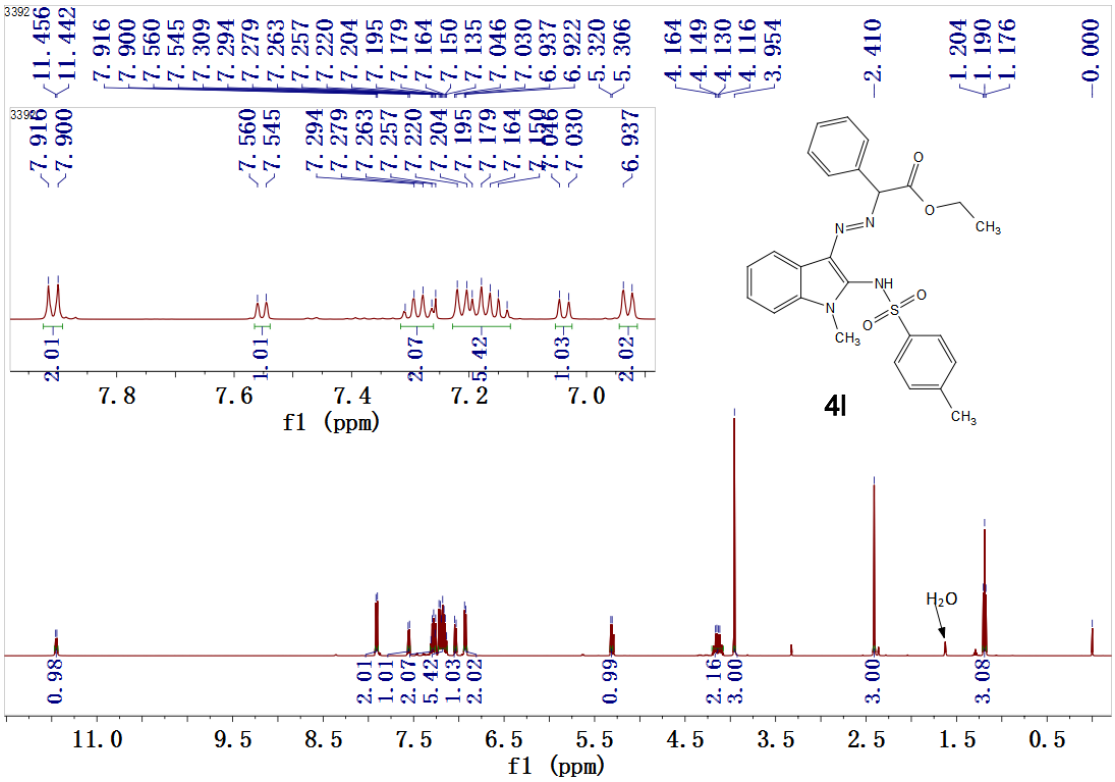

4i
f1 (ppm)


solvent
impurity
H2O
4j
f1 (ppm)


4j
f1 (ppm)


solvent
4k
H2O
f1 (ppm)


4k
f1 (ppm)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7.257
7.220
7.204
7.195
7.179
7.164
7.150
7.135
7.046
7.030
6.937
6.922
5.320
5.306
4.164
4.149
4.130
4.116
3.954
2.410
1.204
1.190
1.176
0.000
f1 (ppm)
4l
H2O
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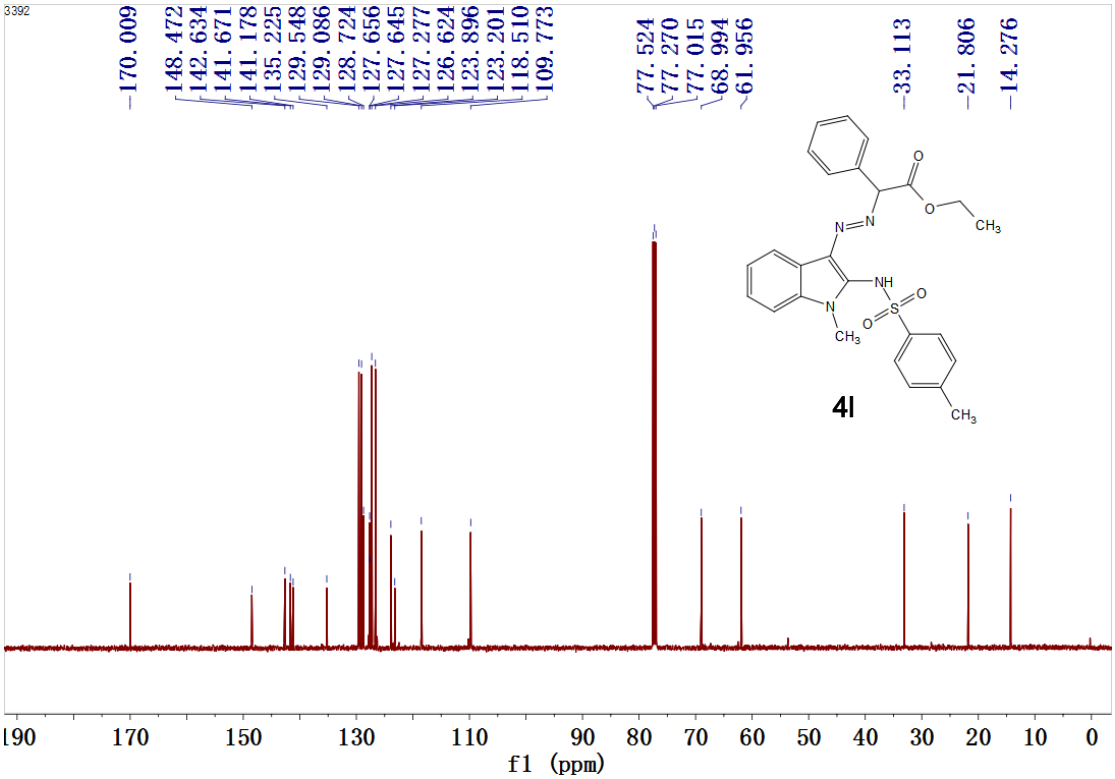
1.01
2.07
5.42
1.03
2.02
0.99
2.16
3.00
3.00
3.08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129.086
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127.656
127.645
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126.624
123.896
123.201
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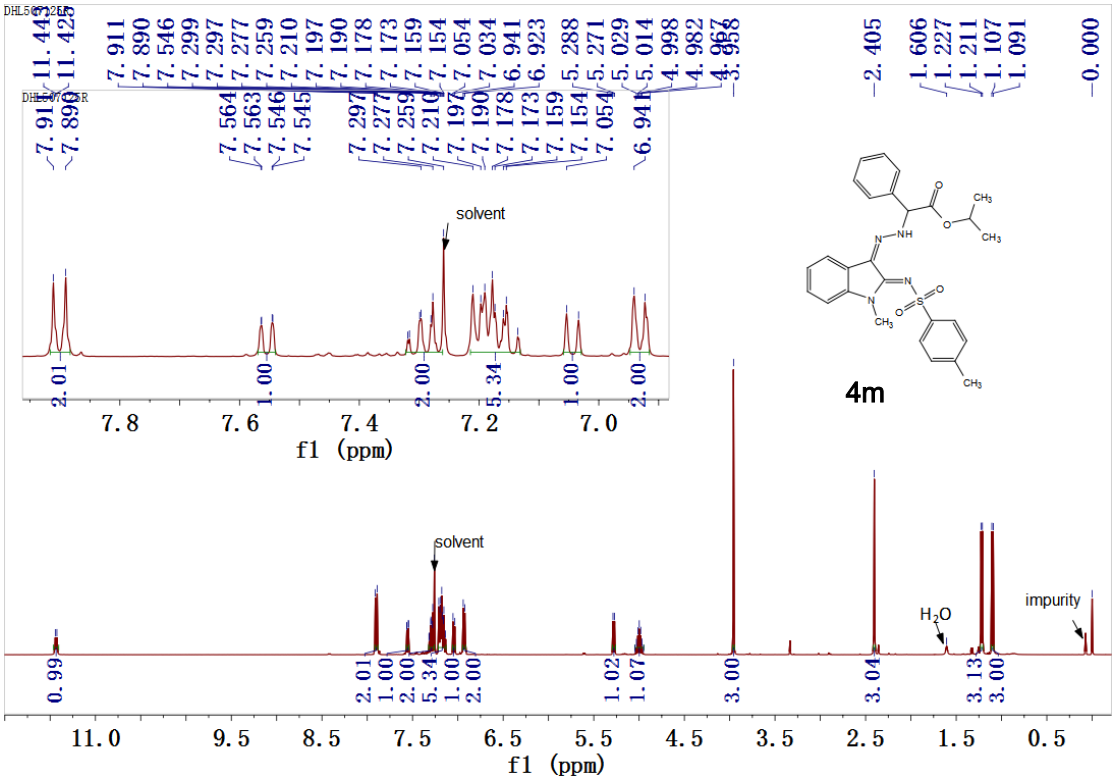
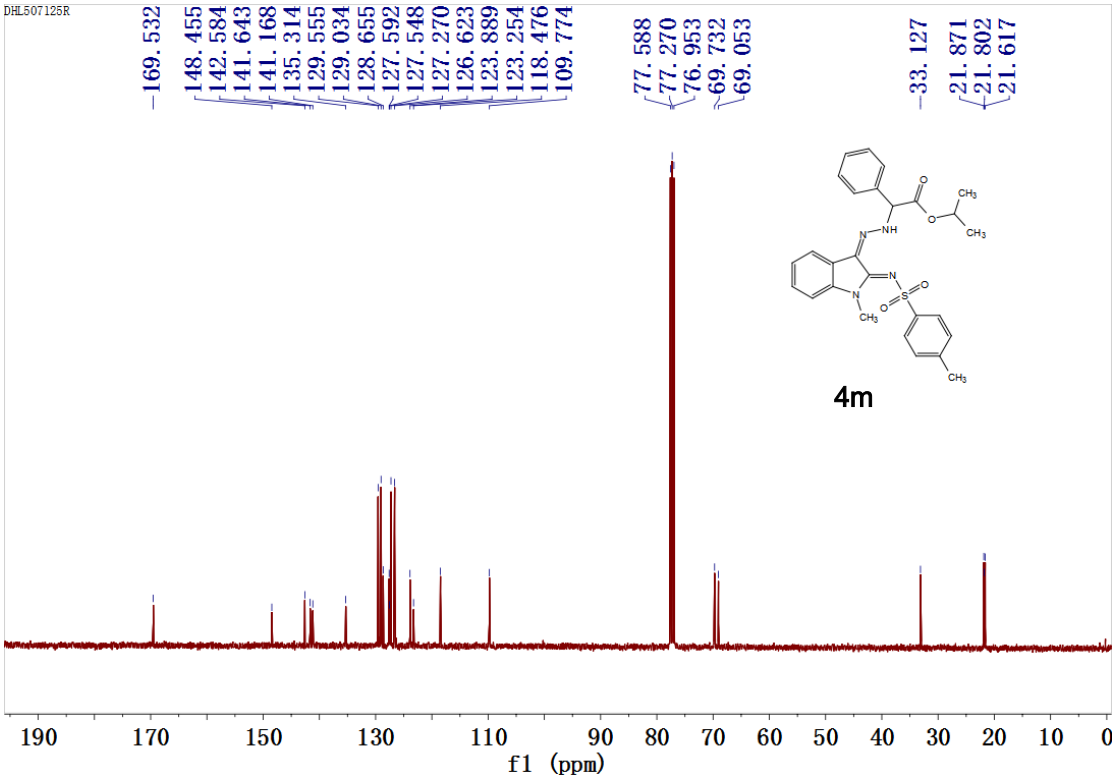
77.270
77.015
68.994
61.956
33.113
21.806
14.276
f1 (ppm)
4l


solvent
4m
solvent
H2O
impurity
f1 (ppm)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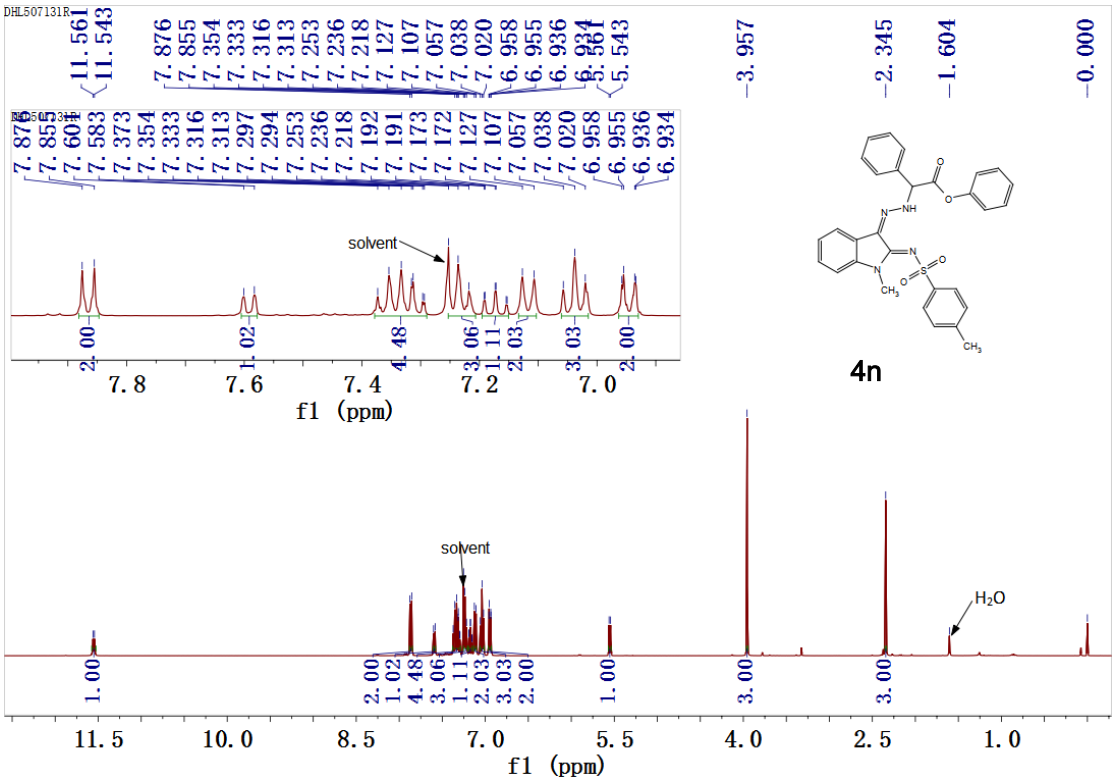
f1 (ppm)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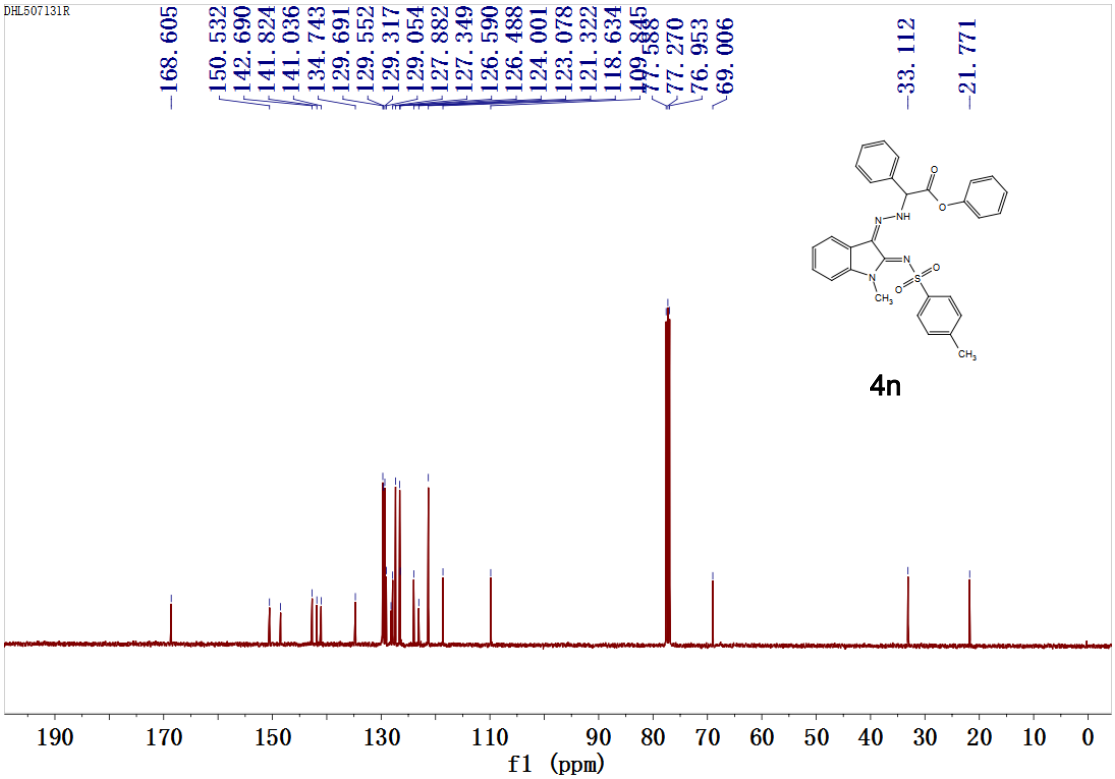
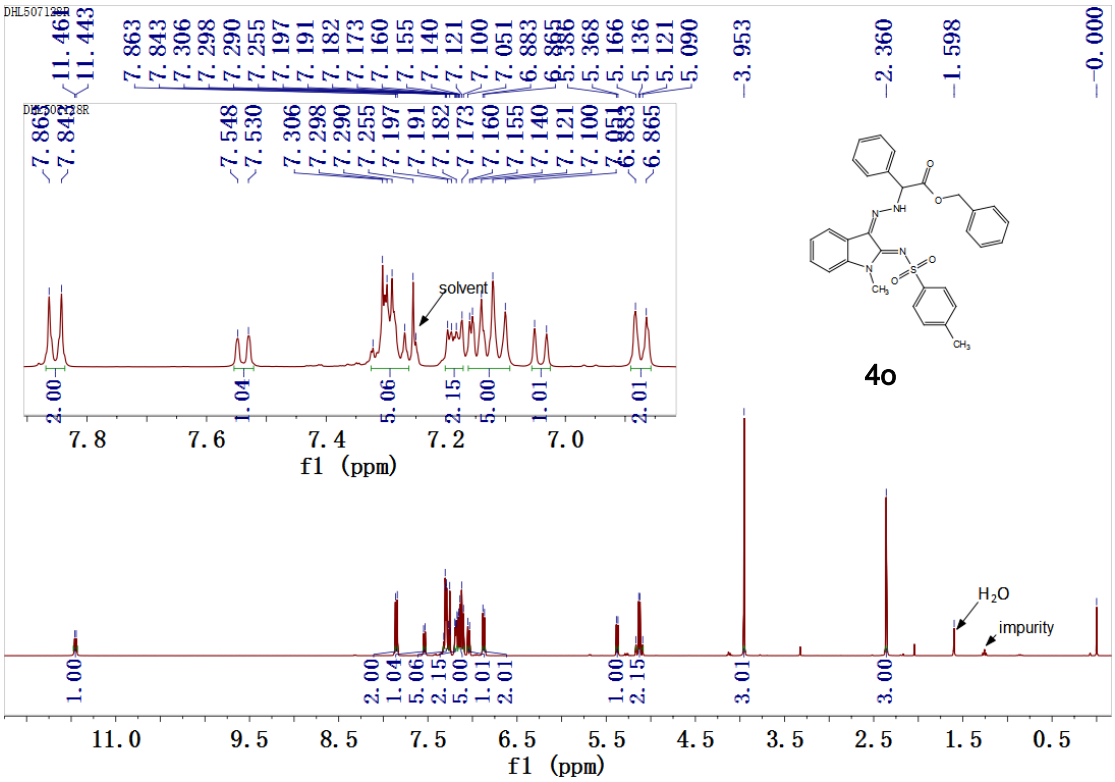
solvent
4n
solvent
H2O
f1 (ppm)


DHL507131R
4n
f1 (ppm)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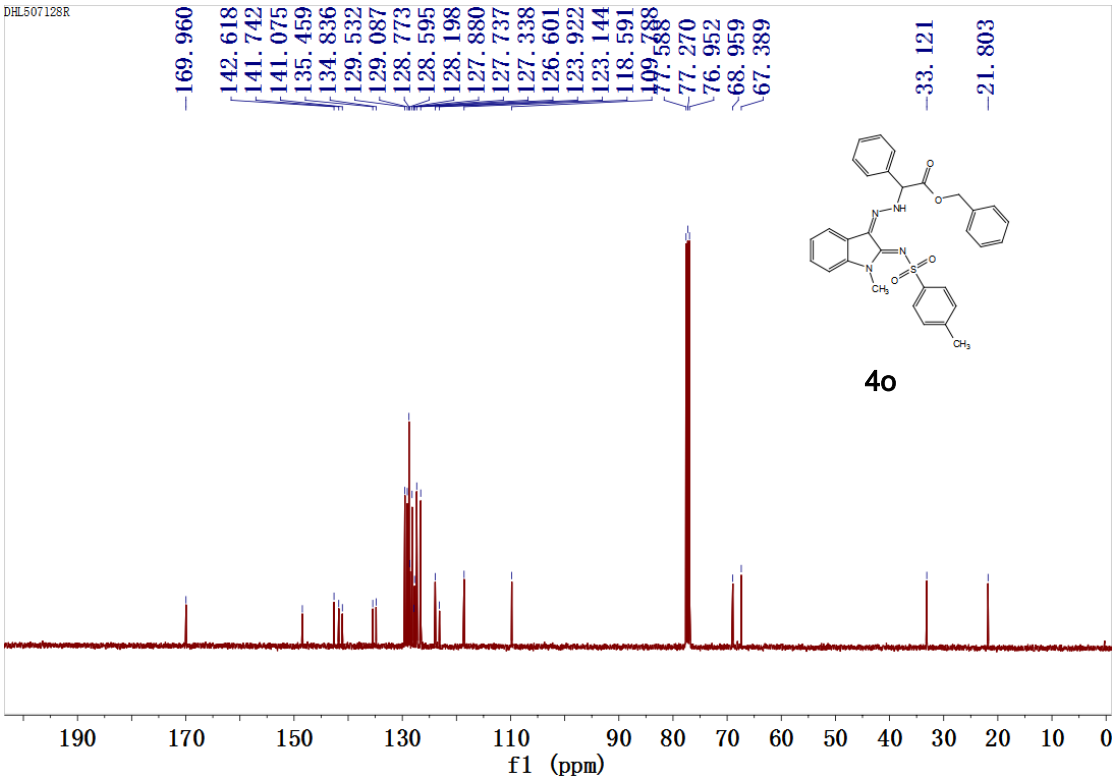
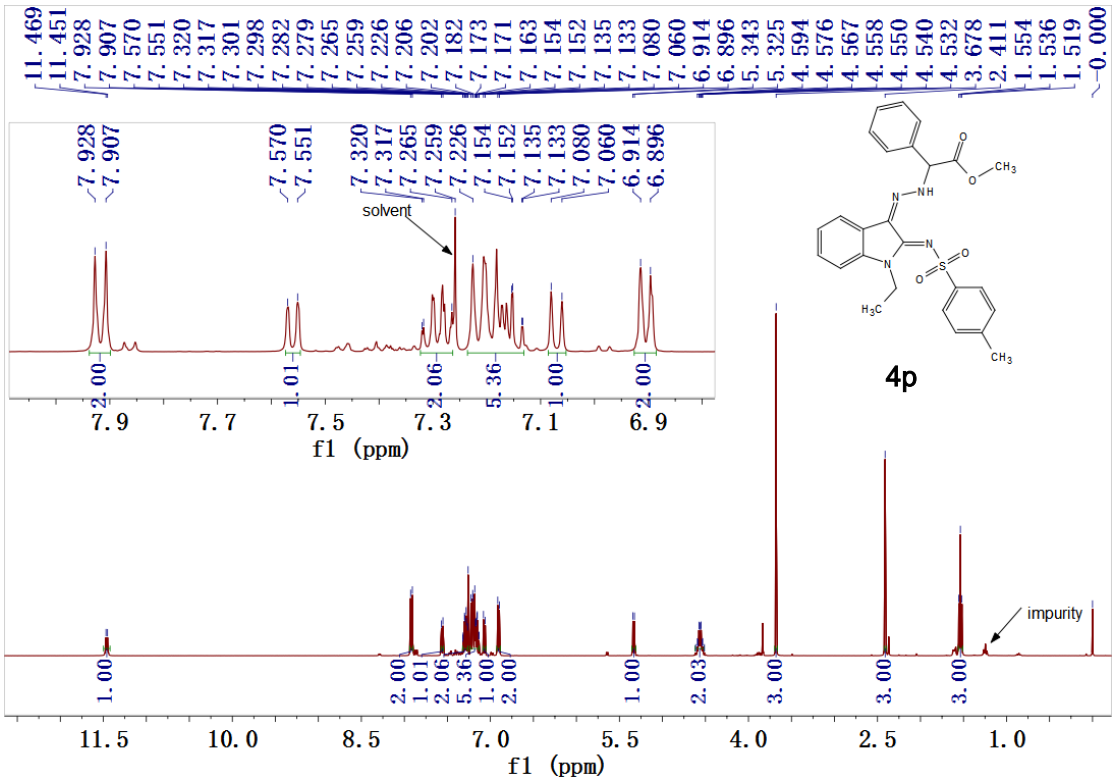
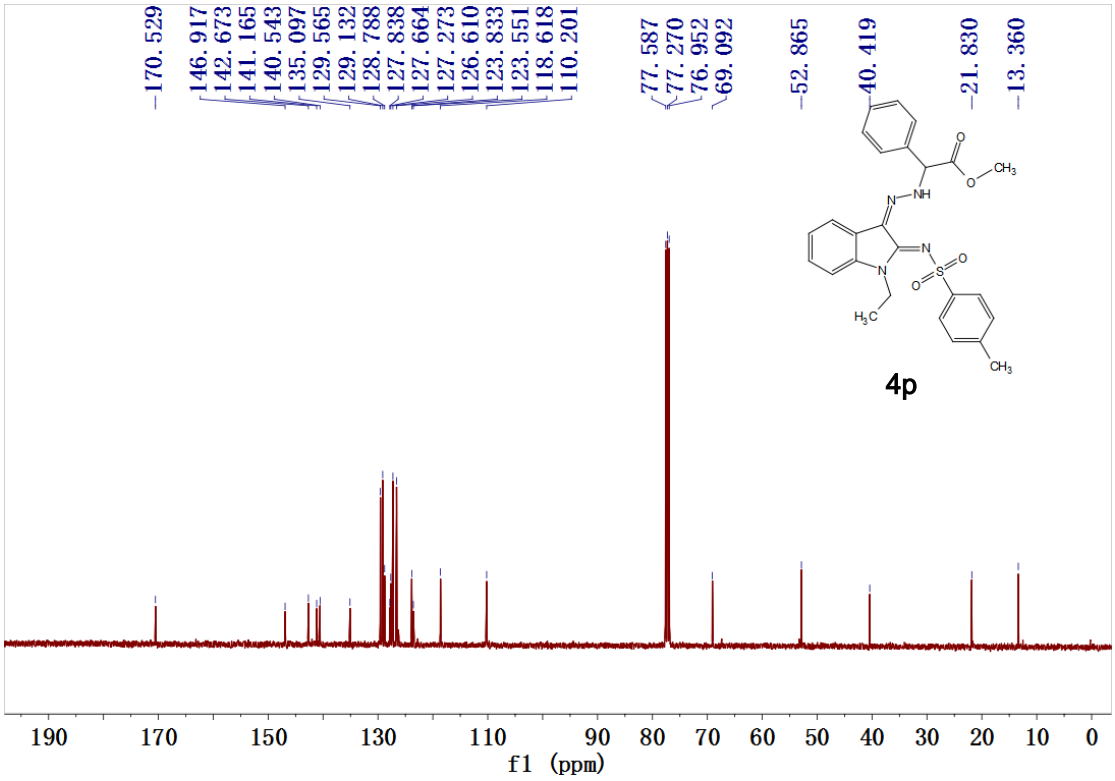
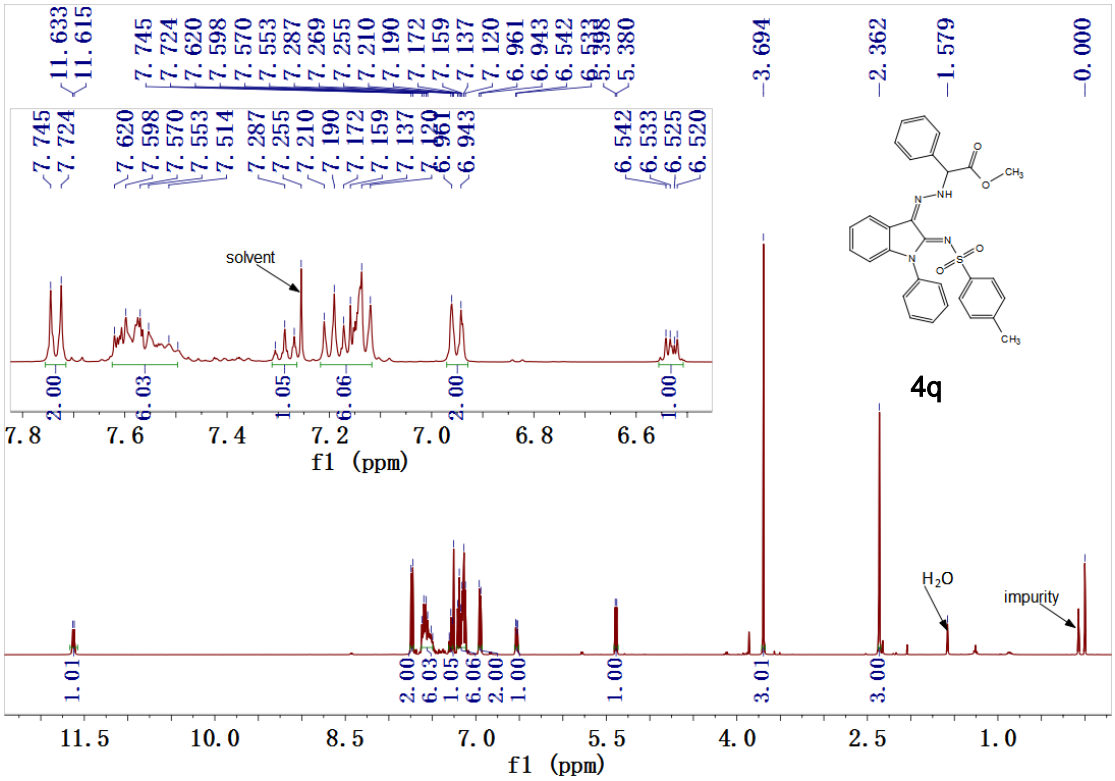
solvent
4o
H2O
impurity
f1 (ppm)


DHL507128R
4o
f1 (ppm)


solvent
impurity
4p
f1 (ppm)


4p
f1 (ppm)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7.269
7.255
7.210
7.190
7.172
7.159
7.137
7.120
6.961
6.943
6.542
6.533
6.525
6.520
5.380
3.694
2.362
1.579
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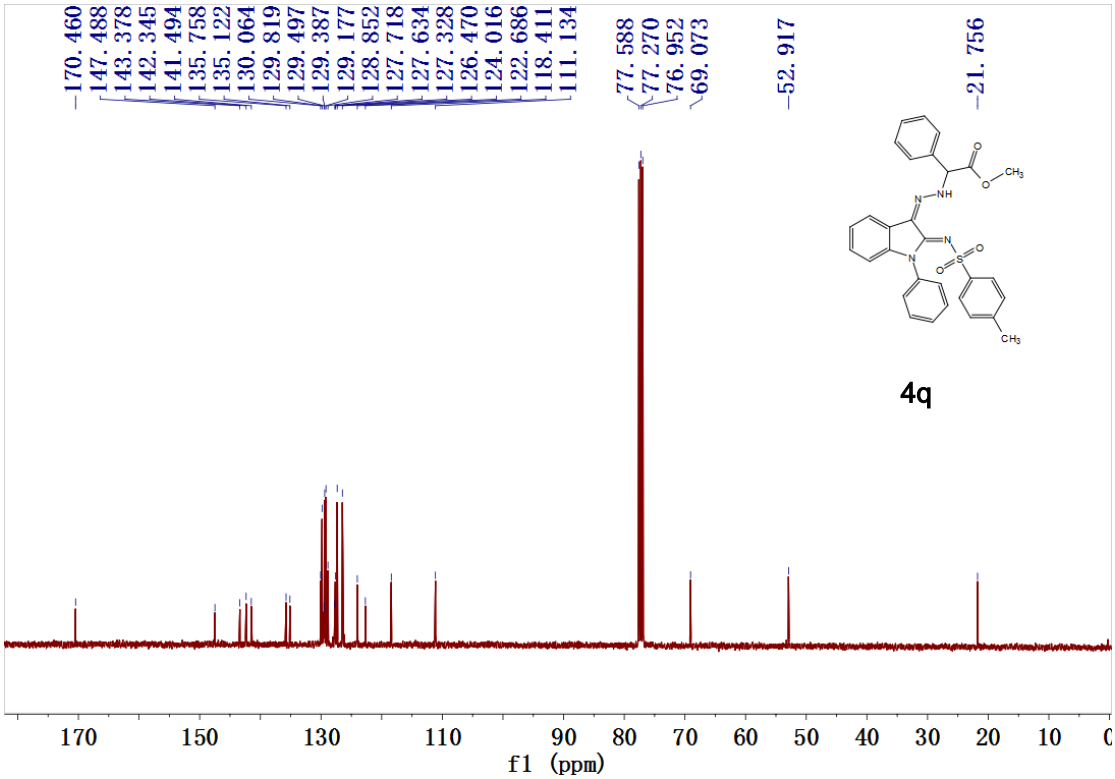
solvent
4q
H2O
impurity
f1 (ppm)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128.852
127.718
127.634
127.328
126.470
124.016
122.686
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111.134
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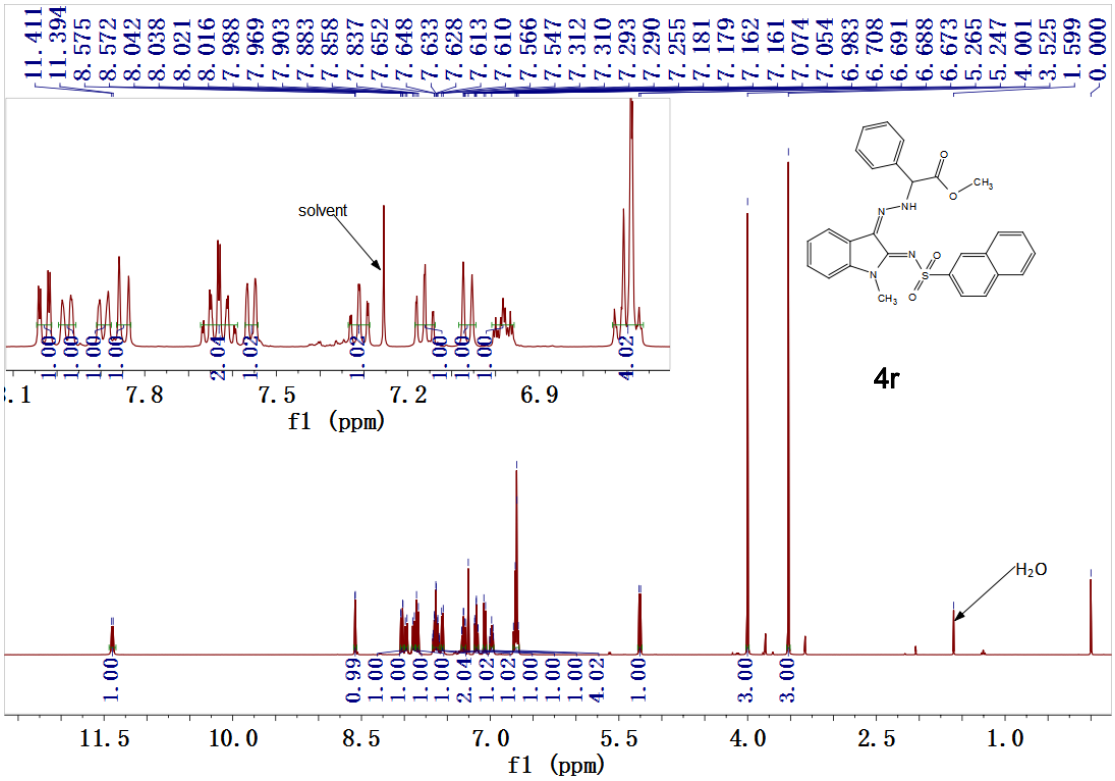
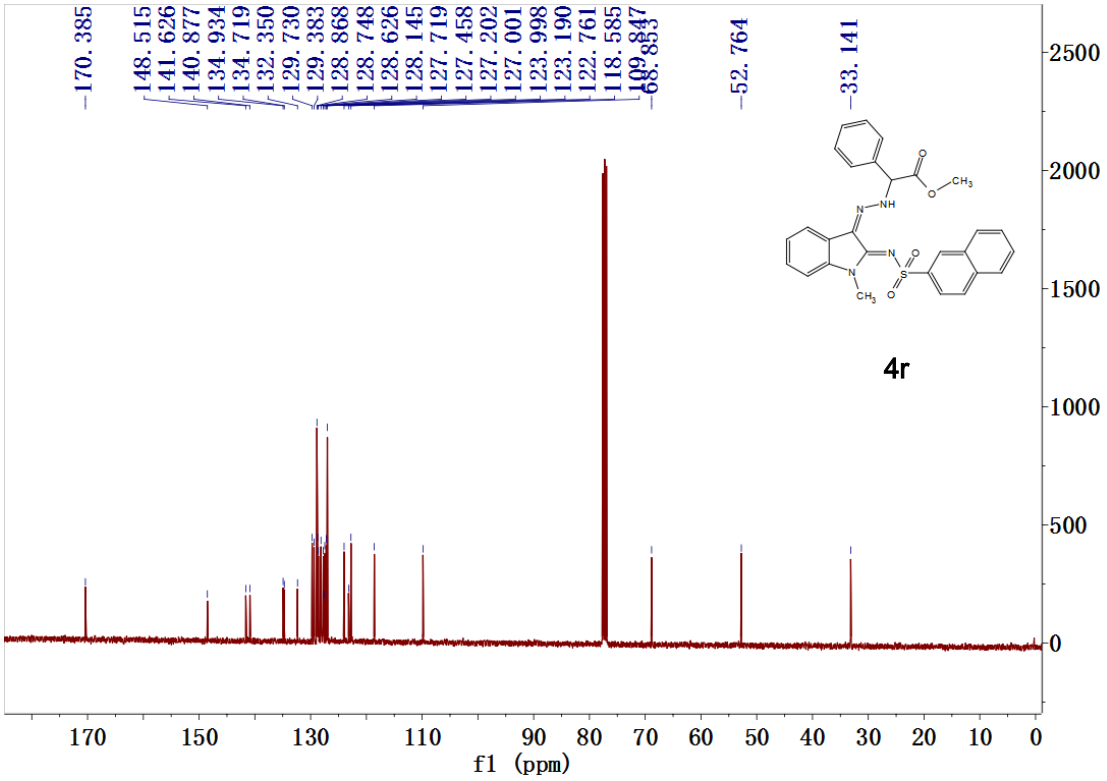
77.270
76.952
69.073
52.917
21.756
4q
f1 (ppm)


solvent
4r
H2O
f1 (ppm)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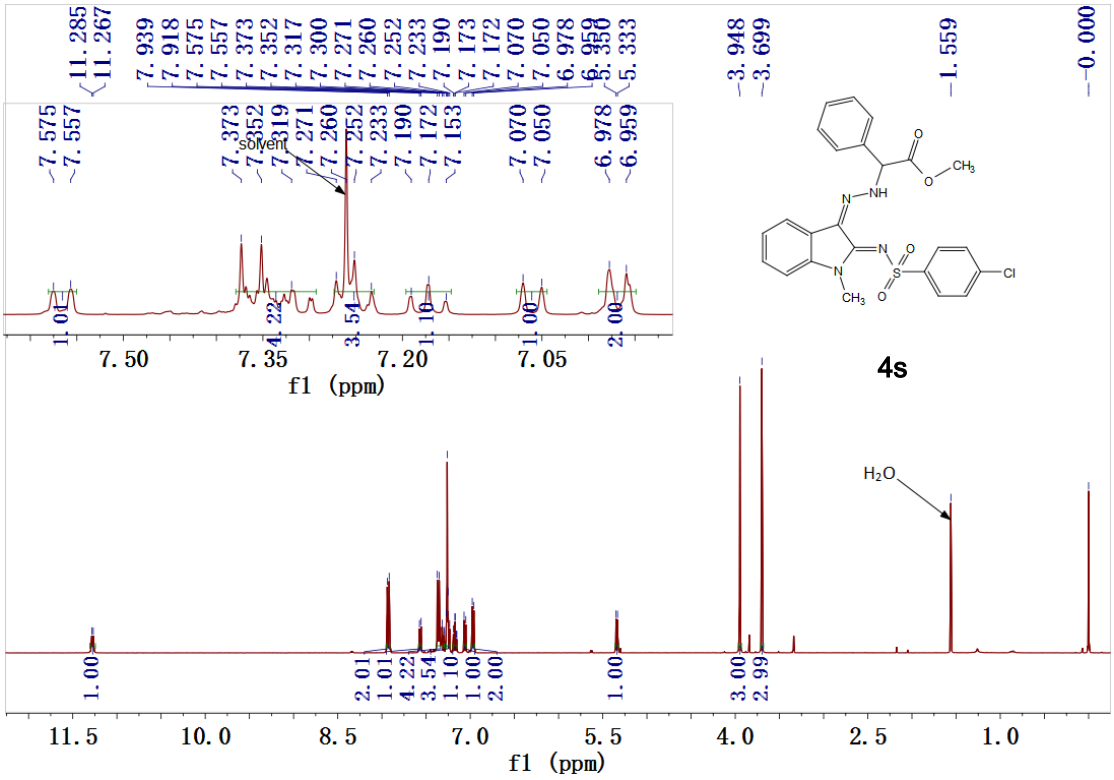
f1 (ppm)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7.300
7.271
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7.252
7.233
7.190
7.173
7.172
7.070
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5.333
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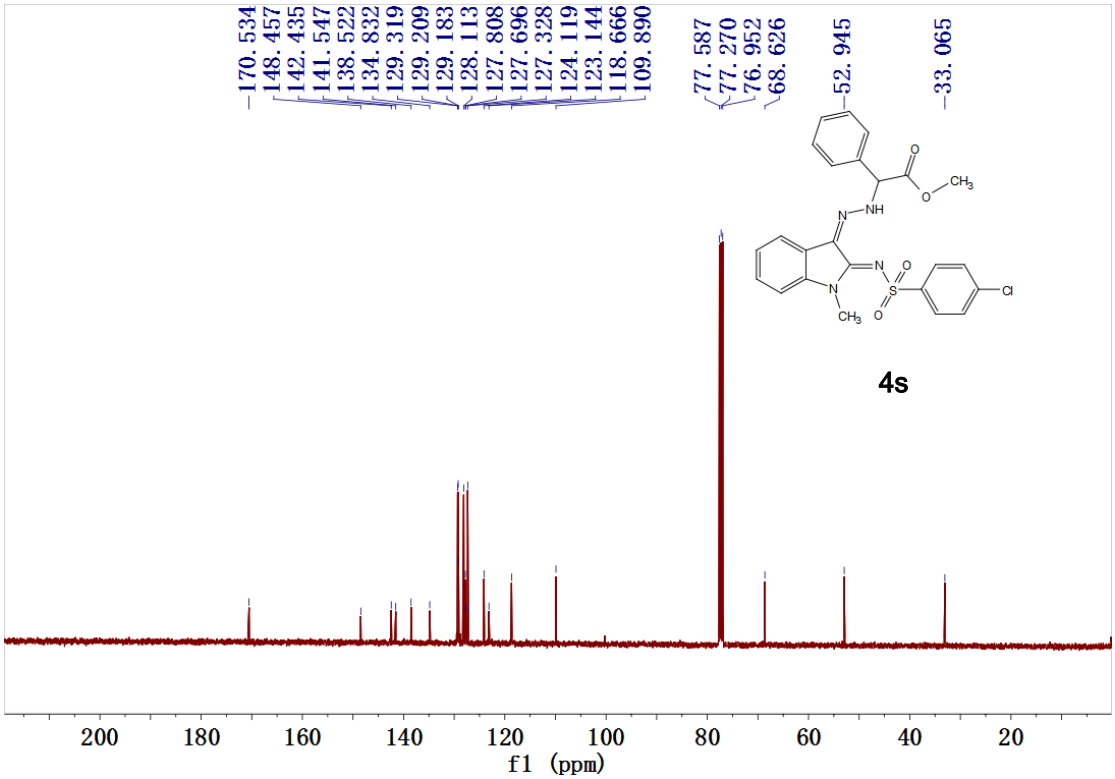
0.000
solvent
H2O
4s
f1 (ppm)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127.328
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77.270
76.952
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52.945
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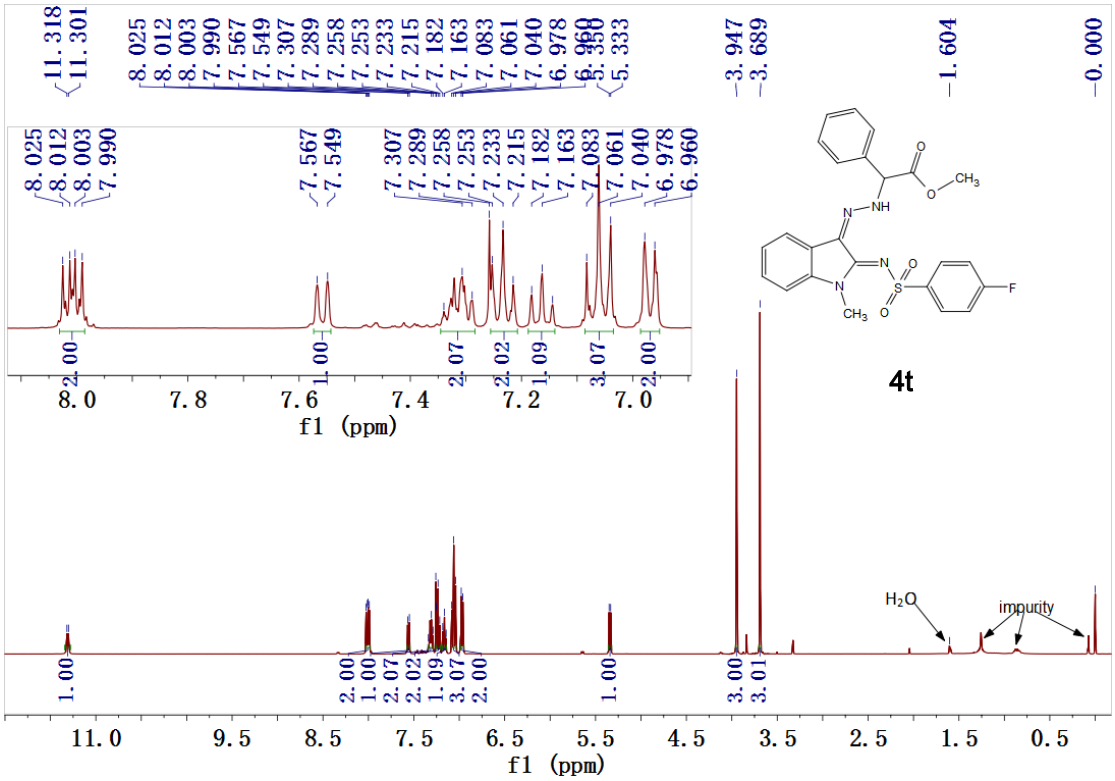
4s
f1 (ppm)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7.258
7.253
7.233
7.215
7.182
7.163
7.083
7.061
7.040
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5.333
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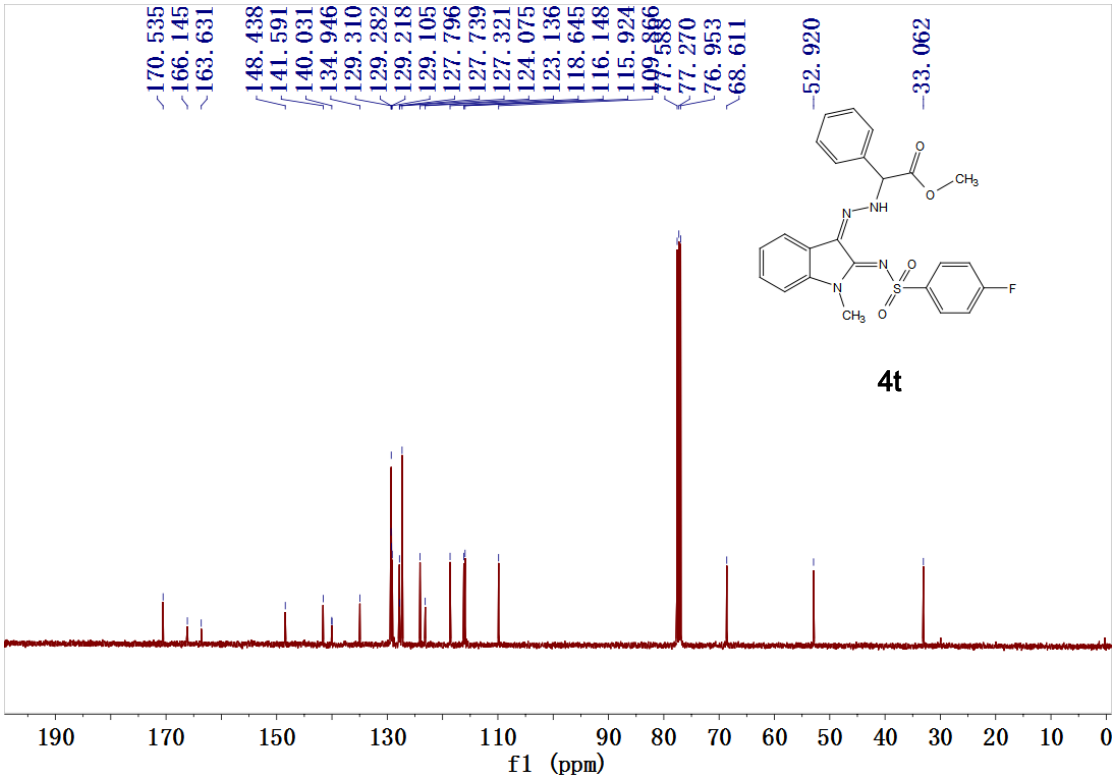
3.689
1.604
0.000
f1 (ppm)
4t
H2O
impurity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163.631
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129.310
129.282
129.218
129.105
127.796
127.739
127.321
124.075
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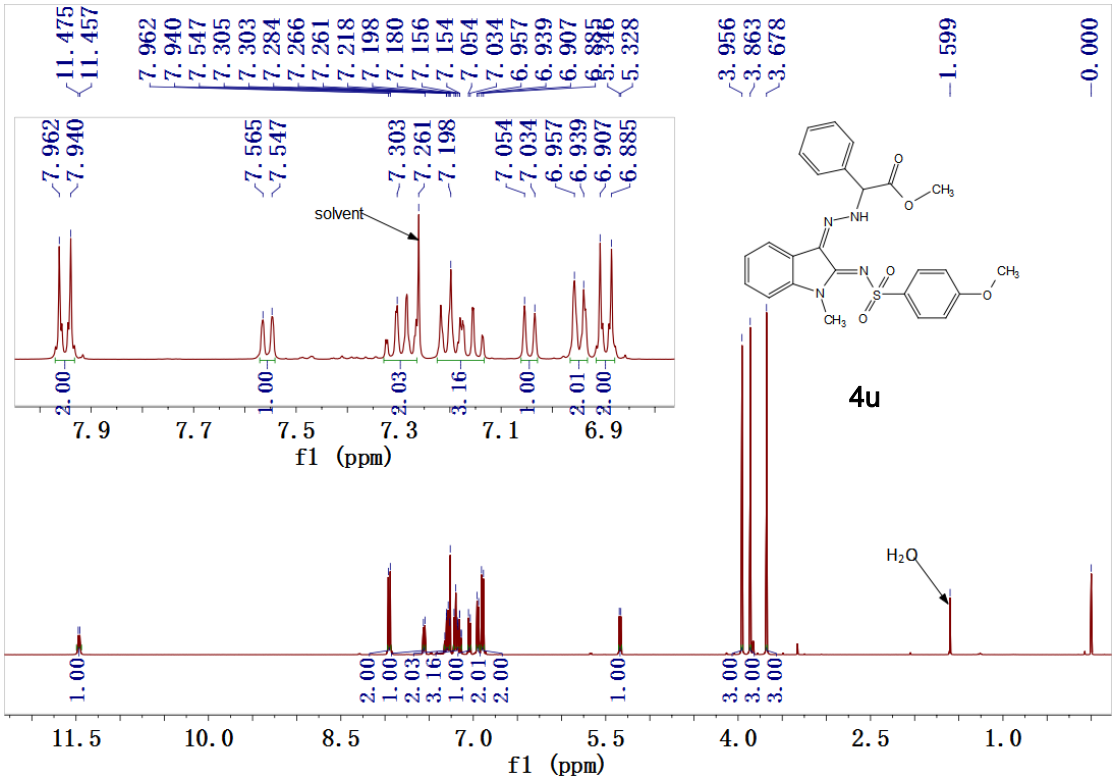
77.270
76.953
68.611
52.920
33.062
f1 (ppm)
4t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7.261
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7.180
7.156
7.154
7.054
7.034
6.957
6.939
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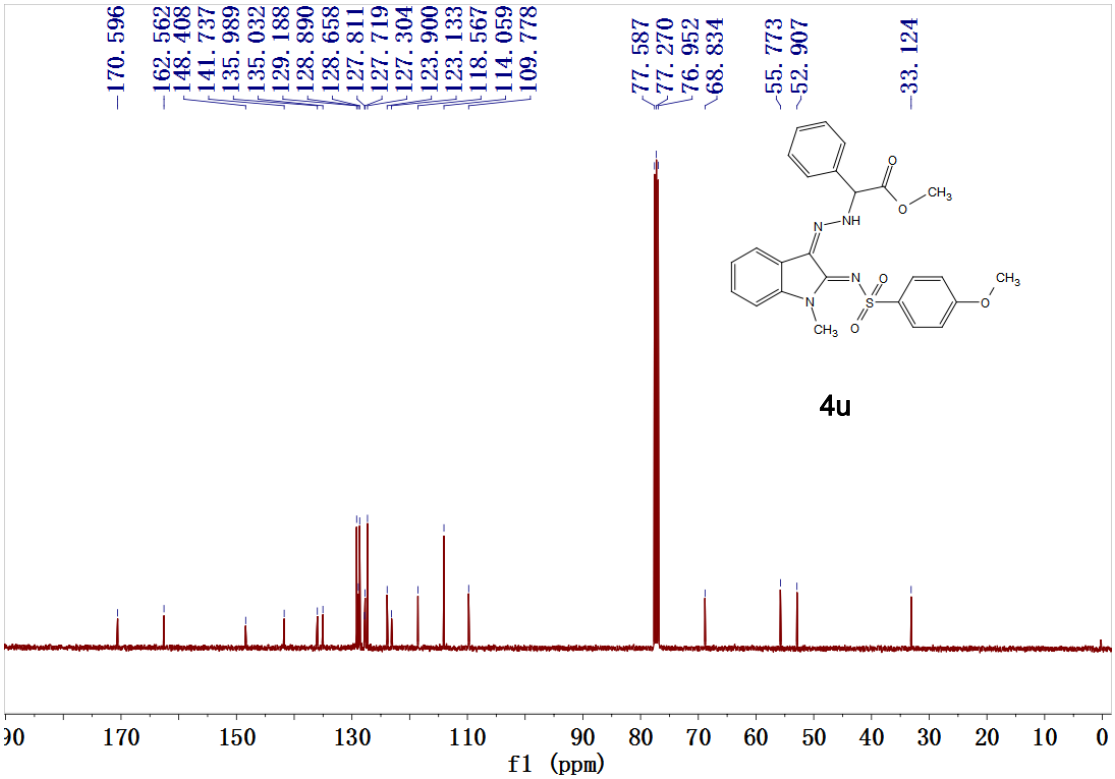
3.956
3.863
3.678
1.599
0.000
solvent
H2O
4u
f1 (ppm)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127.304
123.900
123.133
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68.834
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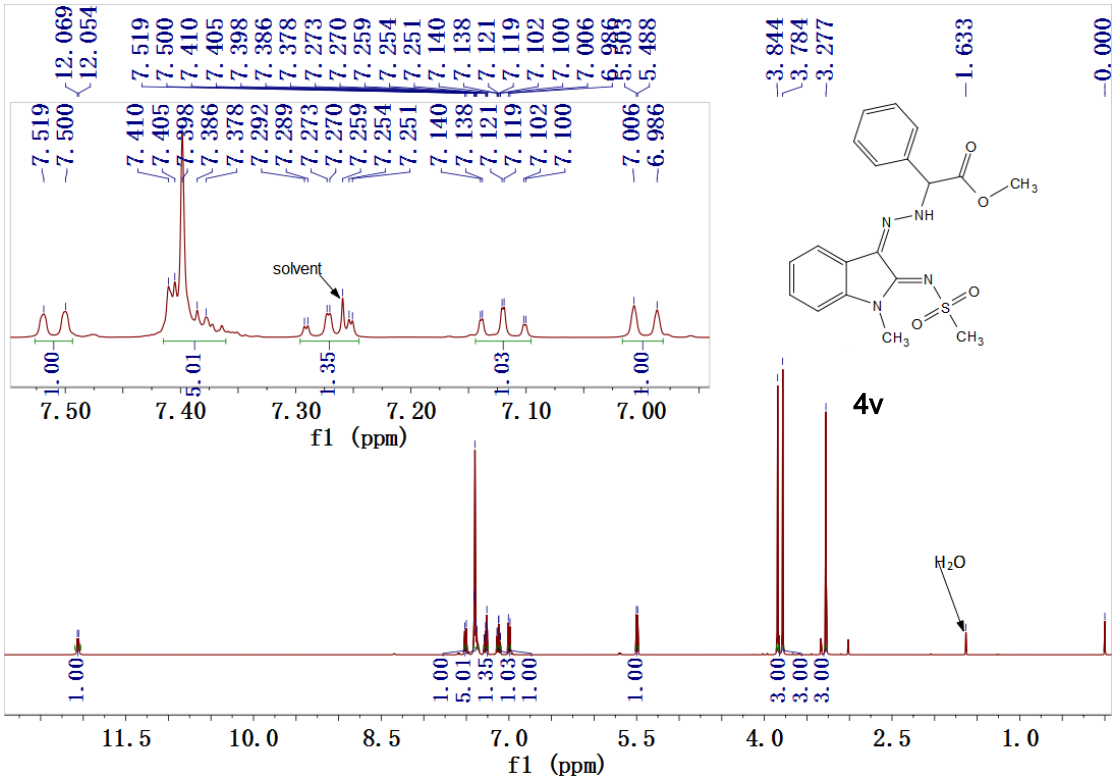
4u
f1 (ppm)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7.270
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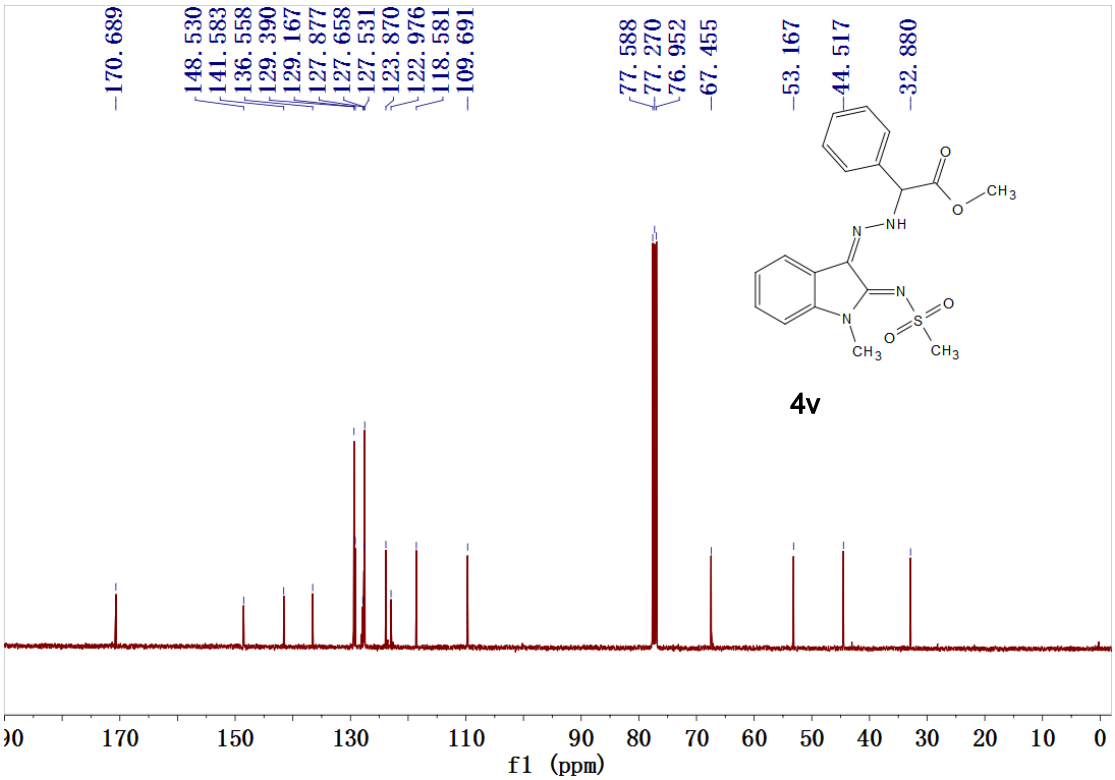
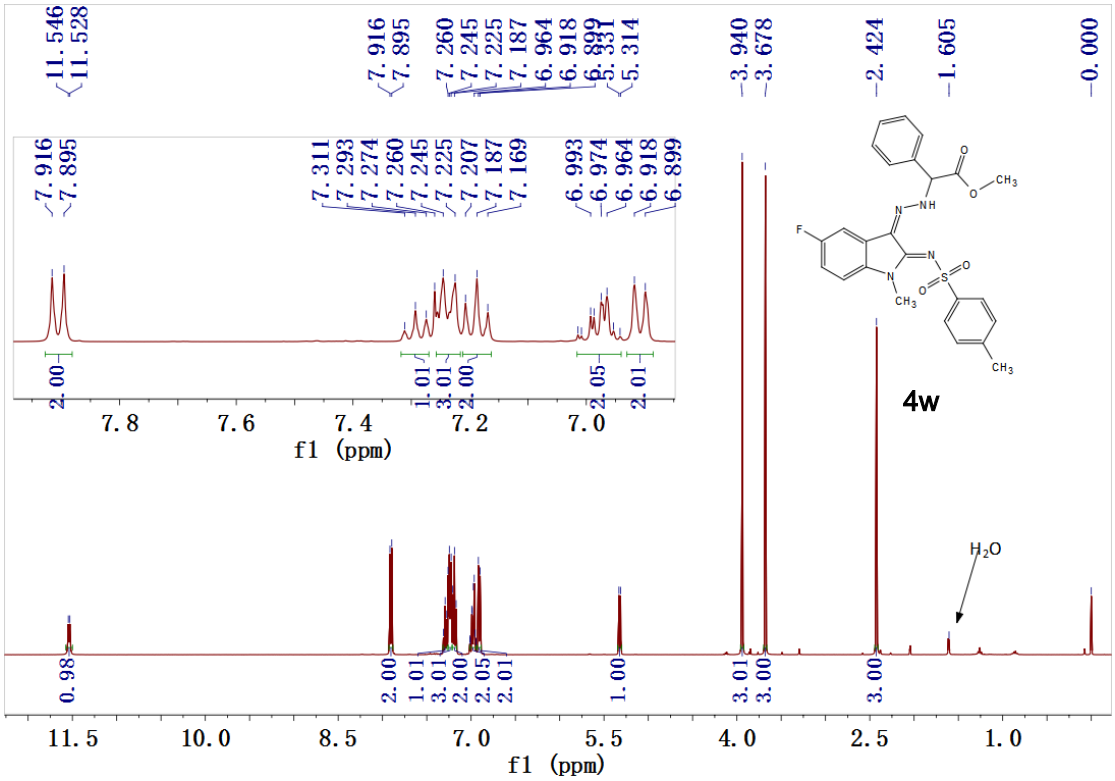
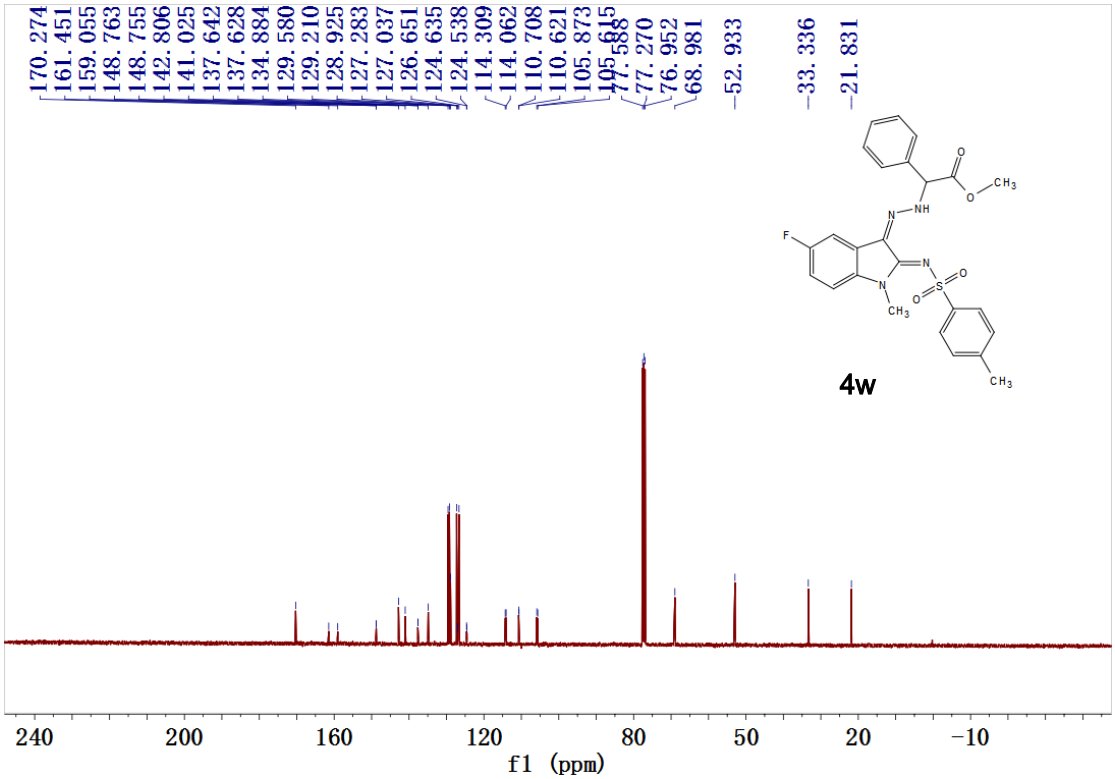
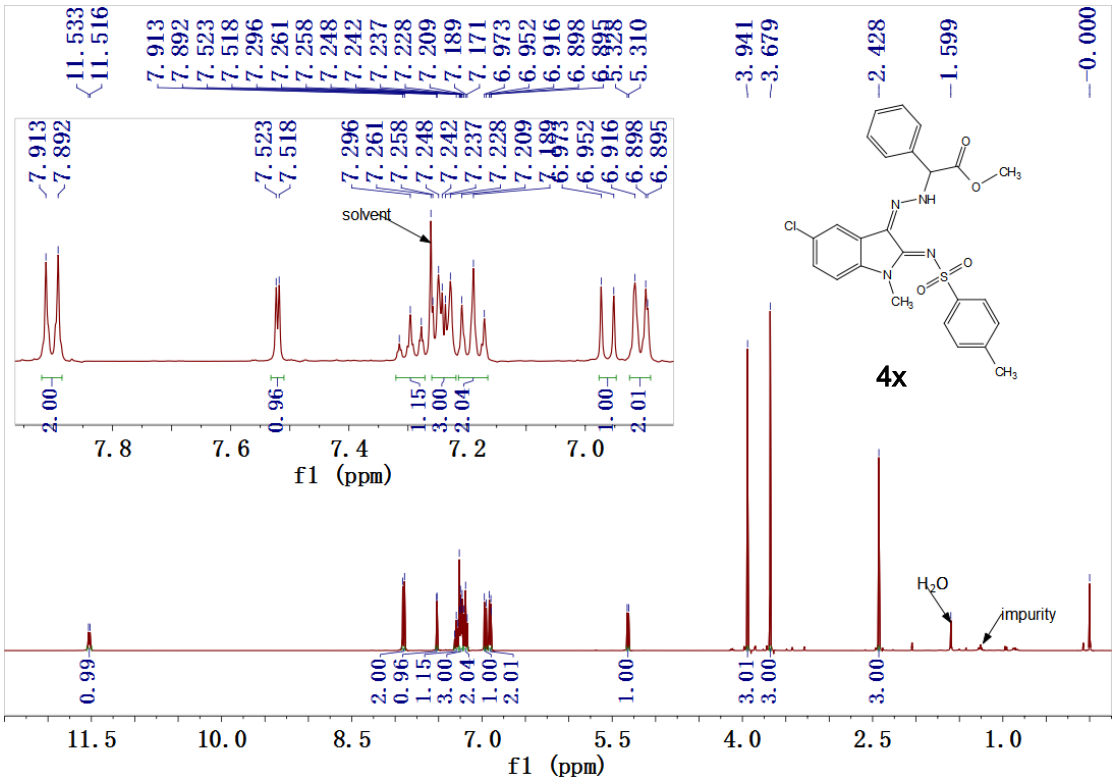
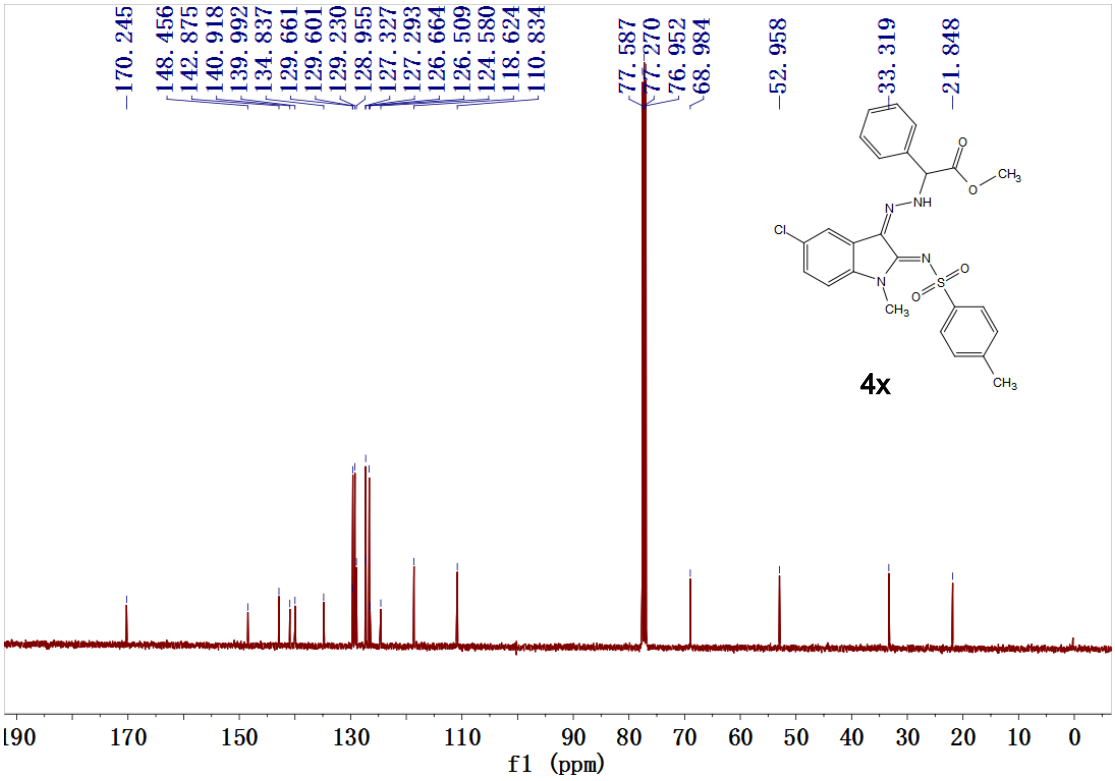
7.140
7.138
7.121
7.119
7.102
7.100
7.006
6.986
5.503
5.488
3.844
3.784
3.277
1.633
0.000
solvent
4v
H2O
1.00
5.01
1.35
1.03
1.00
1.00
1.00
3.00
3.00
3.00
11.5
10.0
8.5
7.0
5.5
4.0
2.5
1.0
f1 (ppm)
7.50
7.40
7.30
7.20
7.10
7.00

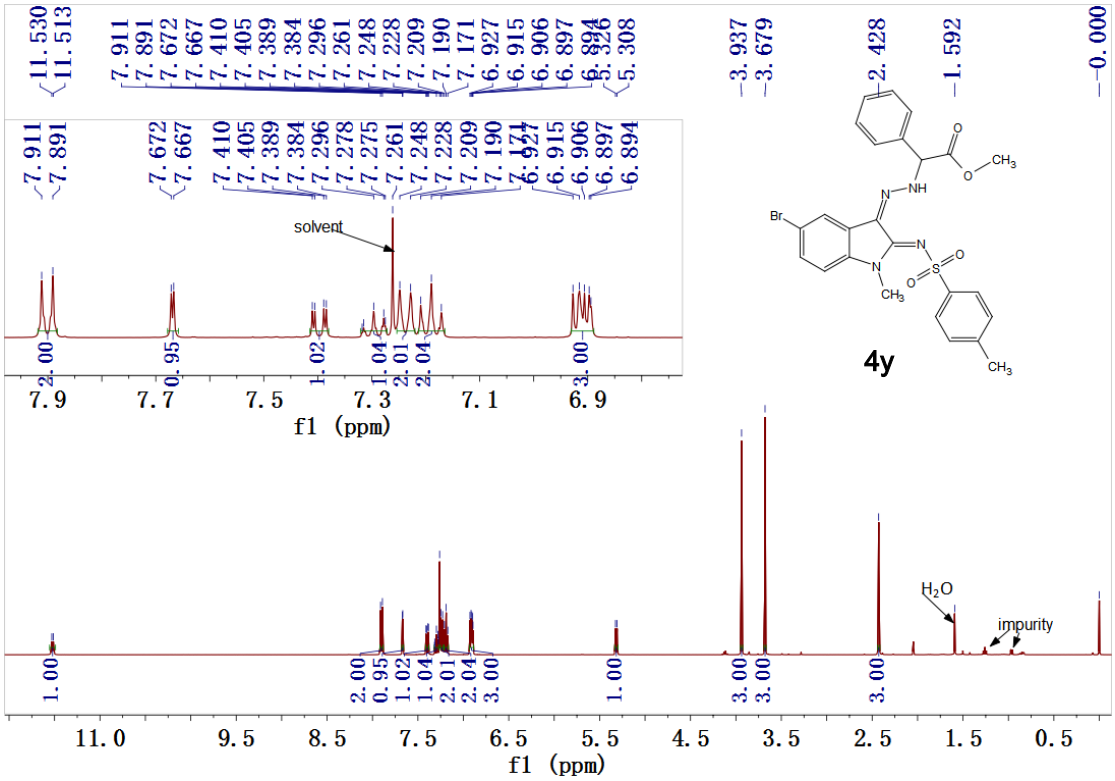

170.689
148.530
141.583
136.558
129.390
129.167
127.877
127.658
127.531
123.870
122.976
118.581
109.691
77.588
77.270
76.952
67.455
53.167
44.517
32.880
4v
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

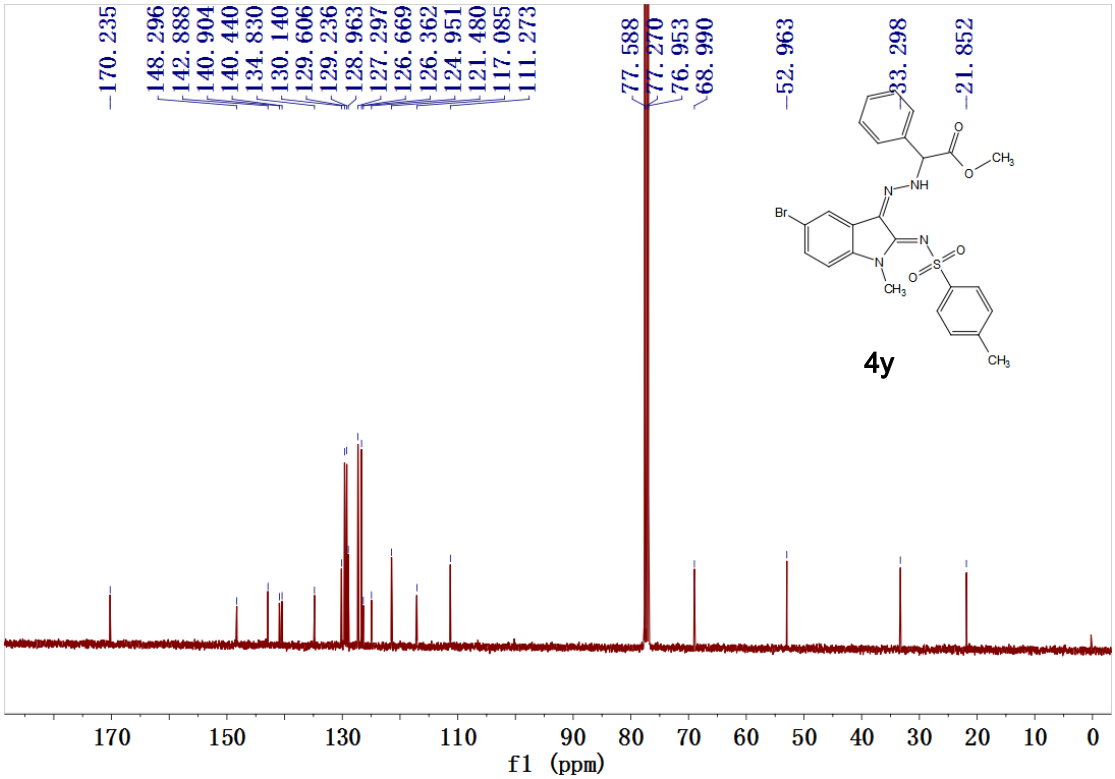

11.546
11.528
7.916
7.895
7.260
7.245
7.225
7.187
6.964
6.918
6.899
5.331
5.314
3.940
3.678
2.424
1.605
0.000
7.311
7.293
7.274
7.260
7.245
7.225
7.207
7.187
7.169
6.993
6.974
6.964
6.918
6.899
2.00
1.01
3.01
2.00
2.05
2.01
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
4w
H2O
0.98
2.00
1.01
3.01
2.00
2.05
2.01
1.00
3.01
3.00
3.00
11.5
10.0
8.5
7.0
5.5
4.0
2.5
1.0
f1 (ppm)

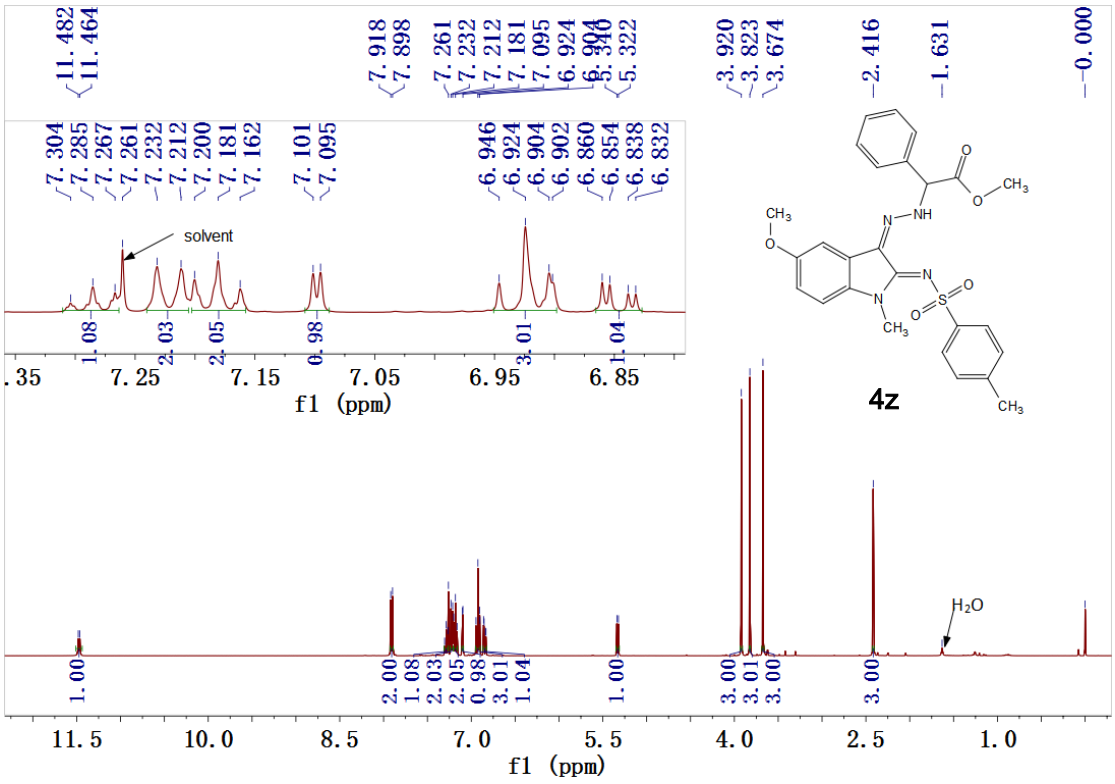

170.274
161.451
159.055
148.763
148.755
142.806
141.025
137.642
137.628
134.884
129.580
129.210
128.925
127.283
127.037
126.651
124.635
124.538
114.309
114.062
110.708
110.621
105.873
105.615
77.588
77.270
76.952
68.981
52.933
33.336
21.831
4w
240
200
160
120
80
50
20
-10
f1 (ppm)

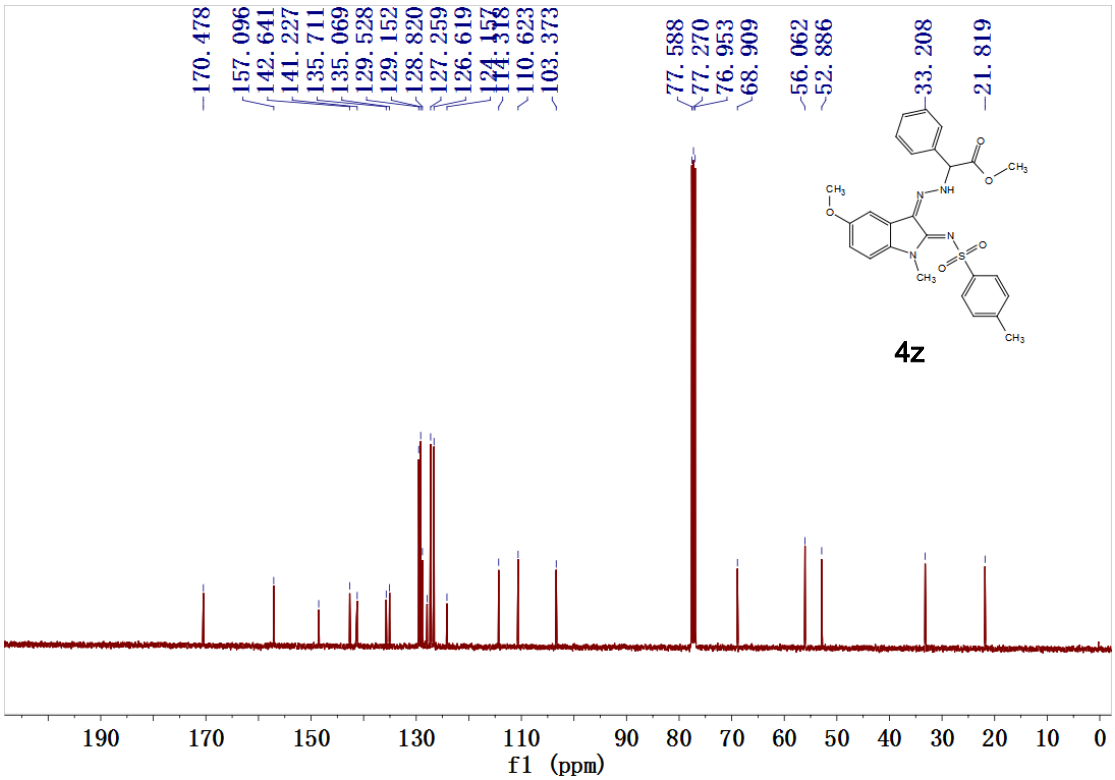

11.533
11.516
7.913
7.892
7.523
7.518
7.296
7.261
7.258
7.248
7.242
7.237
7.228
7.209
7.189
7.171
6.973
6.952
6.916
6.898
6.895
5.328
5.310
3.941
3.679
2.428
1.599
0.000
solvent
4x
H2O
impurity
f1 (ppm)

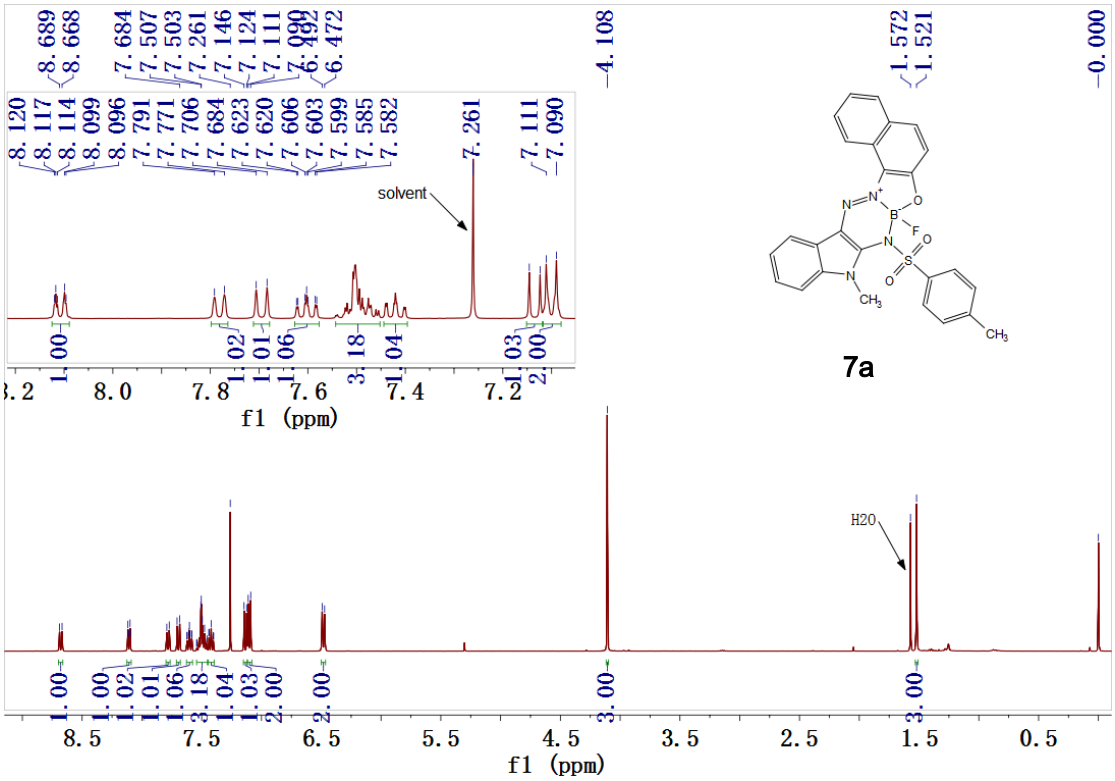

170.245
148.456
142.875
140.918
139.992
134.837
129.661
129.601
129.230
128.955
127.327
127.293
126.664
126.509
124.580
118.624
110.834
77.587
77.270
76.952
68.984
52.958
33.319
21.848
4x
f1 (ppm)

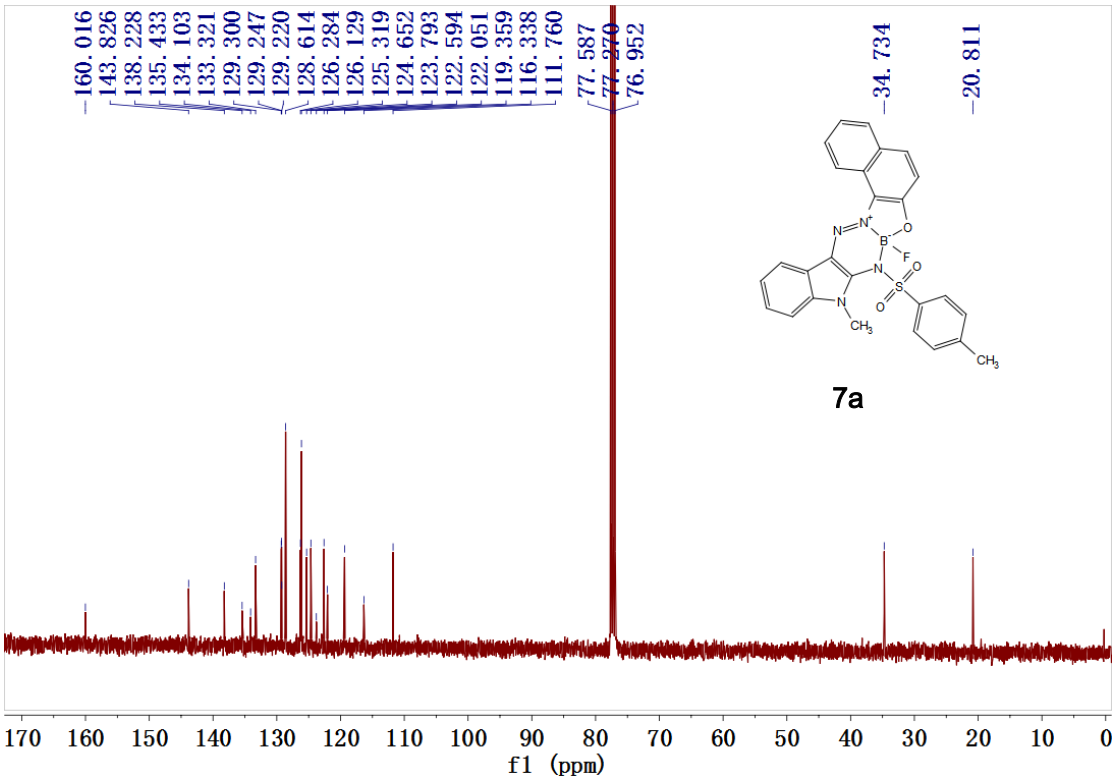

solvent
4y
H2O
impurity
f1 (ppm)

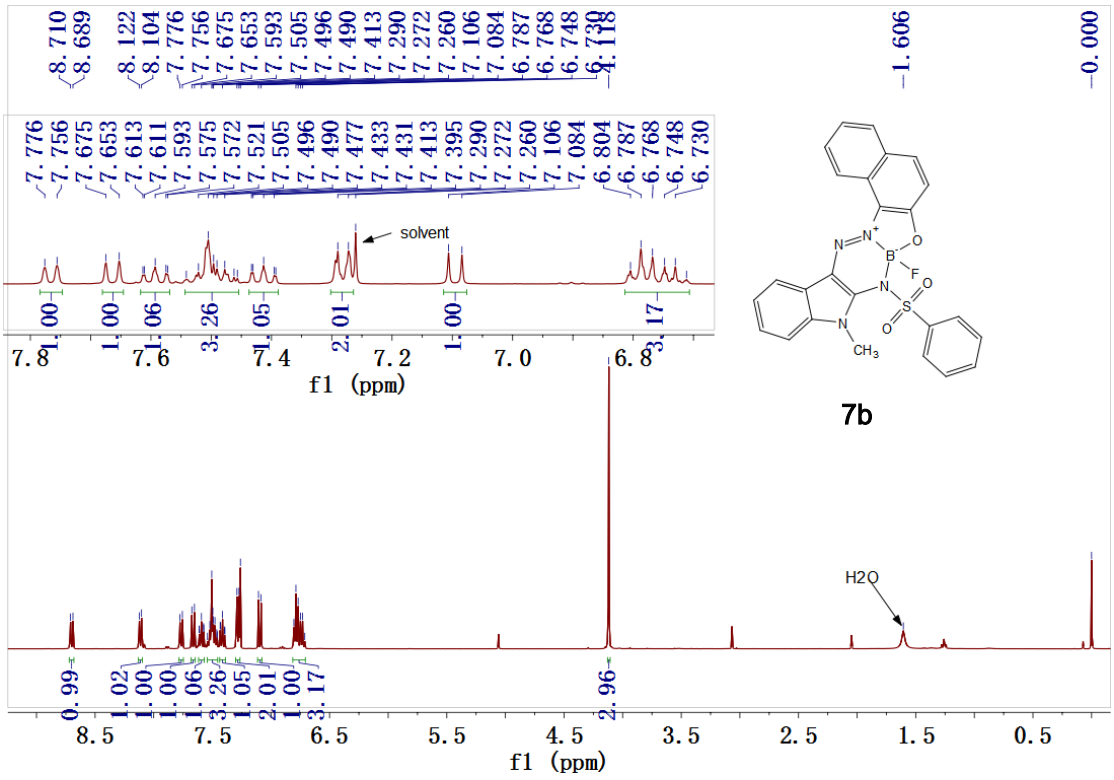

4y
f1 (ppm)

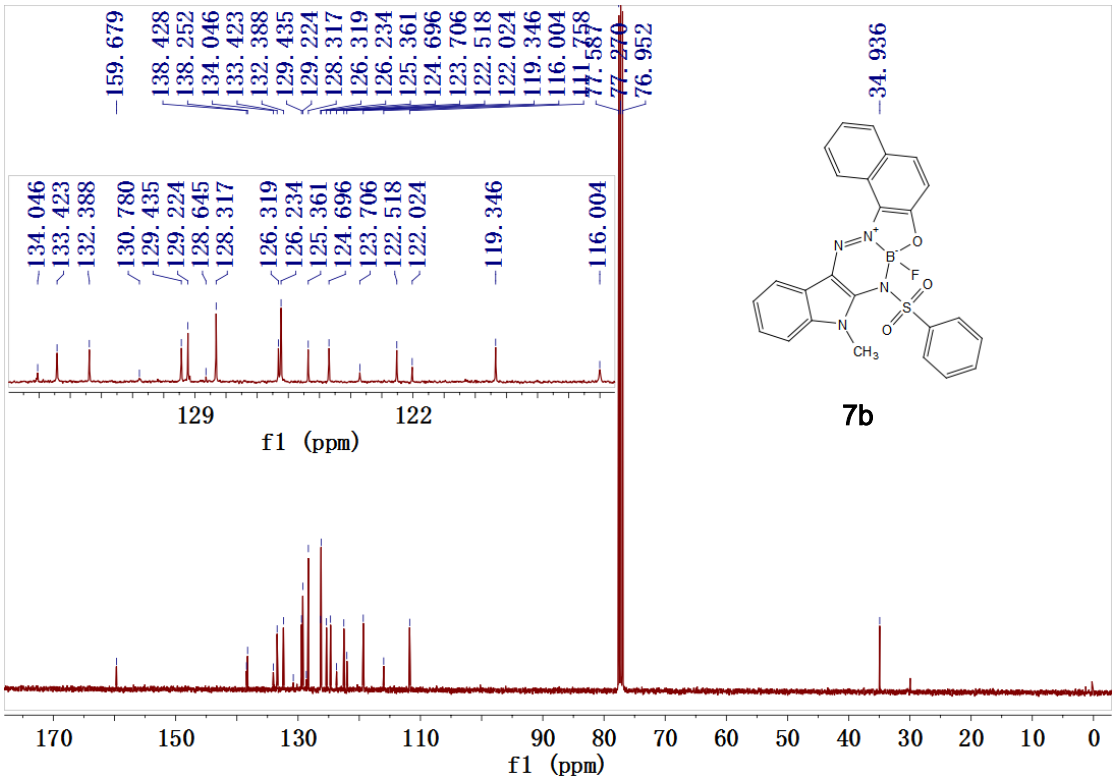

11.482
11.464
7.918
7.898
7.261
7.232
7.212
7.181
7.095
6.924
6.904
6.340
5.322
3.920
3.823
3.674
2.416
1.631
0.000
7.304
7.285
7.267
7.261
7.232
7.212
7.200
7.181
7.162
7.101
7.095
6.946
6.924
6.904
6.902
6.860
6.854
6.838
6.832
solvent
1.08
2.03
2.05
0.98
3.01
1.04
7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
4z
H2O
1.00
2.00
1.08
2.03
2.05
0.98
3.01
1.04
1.00
3.00
3.01
3.00
3.00
11.5
10.0
8.5
7.0
5.5
4.0
2.5
1.0
f1 (ppm)

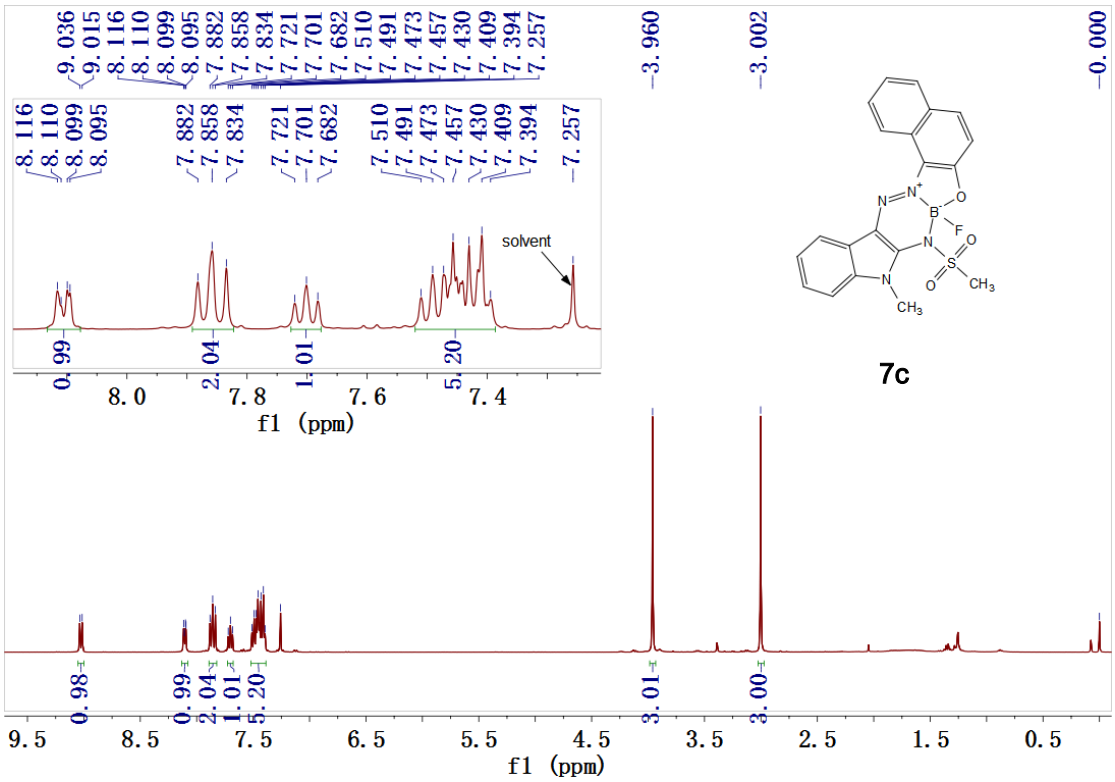

170.478
157.096
142.641
141.227
135.711
135.069
129.528
129.152
128.820
127.259
126.619
124.157
114.318
110.623
103.373
77.588
77.270
76.953
68.909
56.062
52.886
33.208
21.819
4z
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

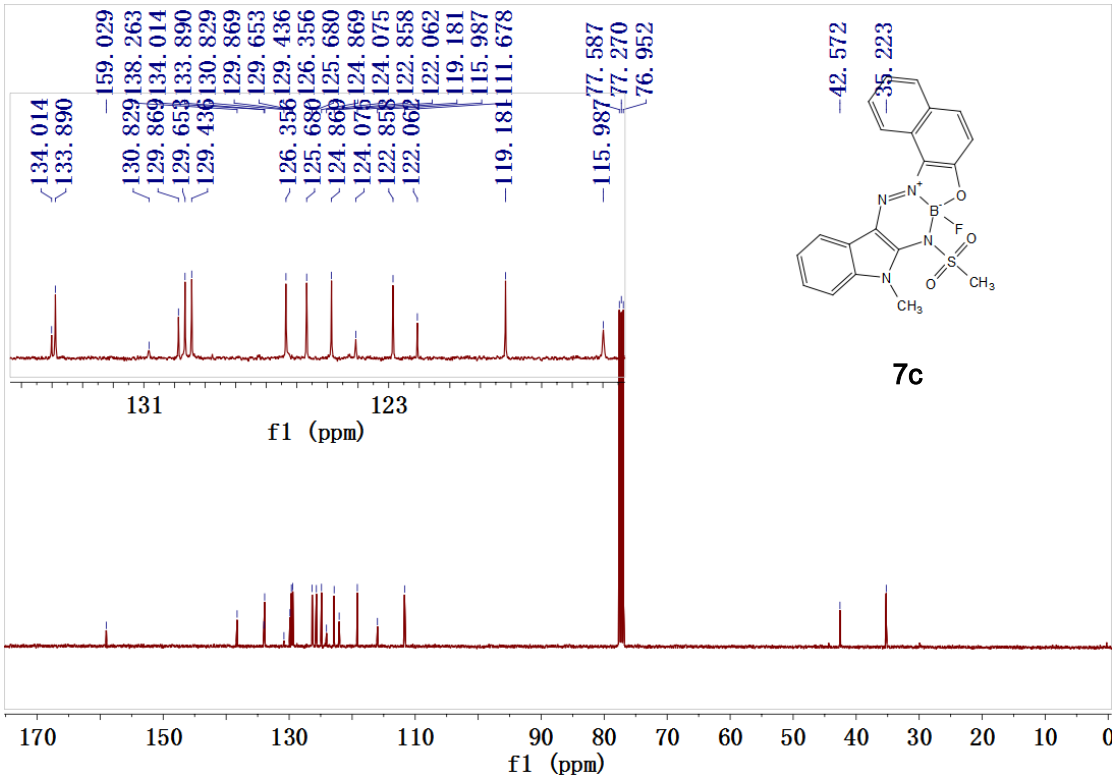

8.689
8.668
7.684
7.507
7.503
7.261
7.146
7.124
7.111
6.492
6.472
4.108
1.572
1.521
0.000
solvent
H2O
7a
f1 (ppm)

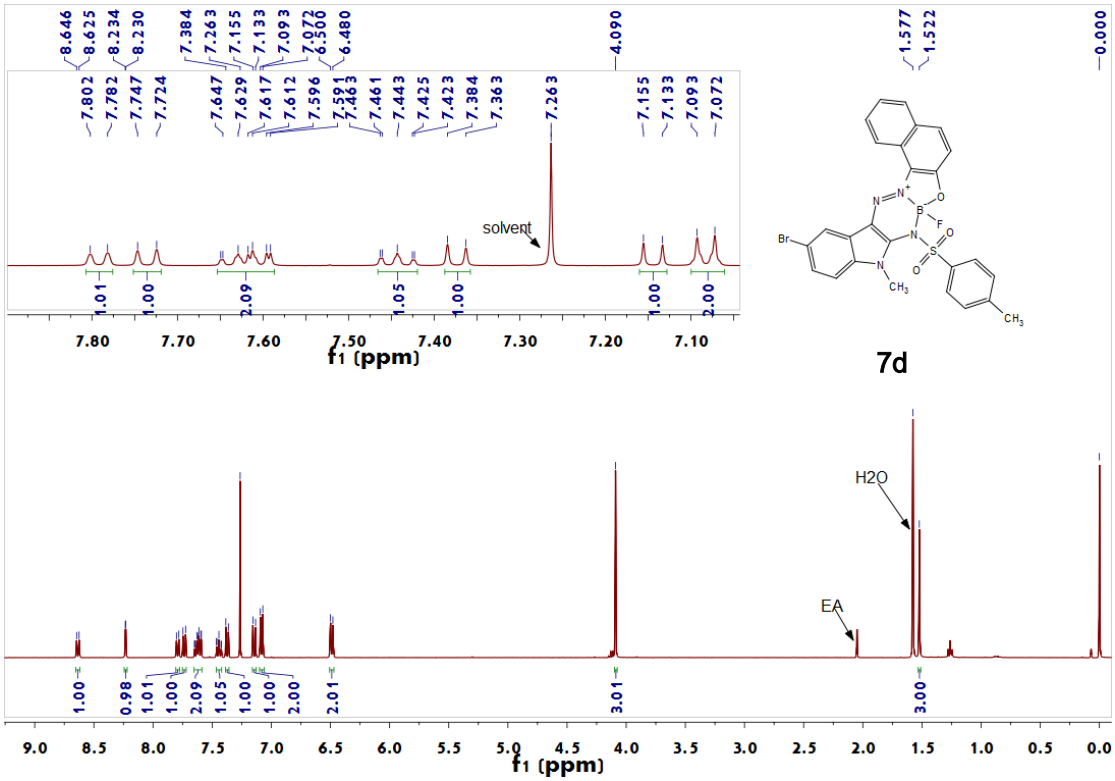

160.016
143.826
138.228
135.433
134.103
133.321
129.300
129.247
129.220
128.614
126.284
126.129
125.319
124.652
123.793
122.594
122.051
119.359
116.338
111.760
77.587
77.270
76.952
34.734
20.811
7a
f1 (ppm)


solvent
H2O
7b
f1 (ppm)


7b
f1 (ppm)


9.036
9.015
8.116
8.110
8.099
8.095
7.882
7.858
7.834
7.721
7.701
7.682
7.510
7.491
7.473
7.457
7.430
7.409
7.394
7.257
3.960
3.002
0.000
solvent
0.99
2.04
1.01
5.20
8.0
7.8
7.6
7.4
f1 (ppm)
0.98
0.99
2.04
1.01
5.20
3.01
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
7c


159.029
138.263
134.014
133.890
130.829
129.869
129.653
129.436
126.356
125.680
124.869
124.075
122.858
122.062
119.181
115.987
111.678
77.587
77.270
76.952
42.572
35.223
131
123
f1 (ppm)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
7c


8.646
8.625
8.234
8.230
7.802
7.782
7.747
7.724
7.384
7.263
7.155
7.133
7.093
7.072
6.500
6.480
7.647
7.629
7.617
7.612
7.596
7.591
7.483
7.461
7.443
7.425
7.423
7.384
7.363
4.090
1.577
1.522
0.000
solvent
1.01
1.00
2.09
1.05
1.00
1.00
2.00
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
f1 (ppm)
7d
H2O
EA
1.00
0.98
1.01
1.00
2.09
1.05
1.00
1.00
2.00
2.01
3.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

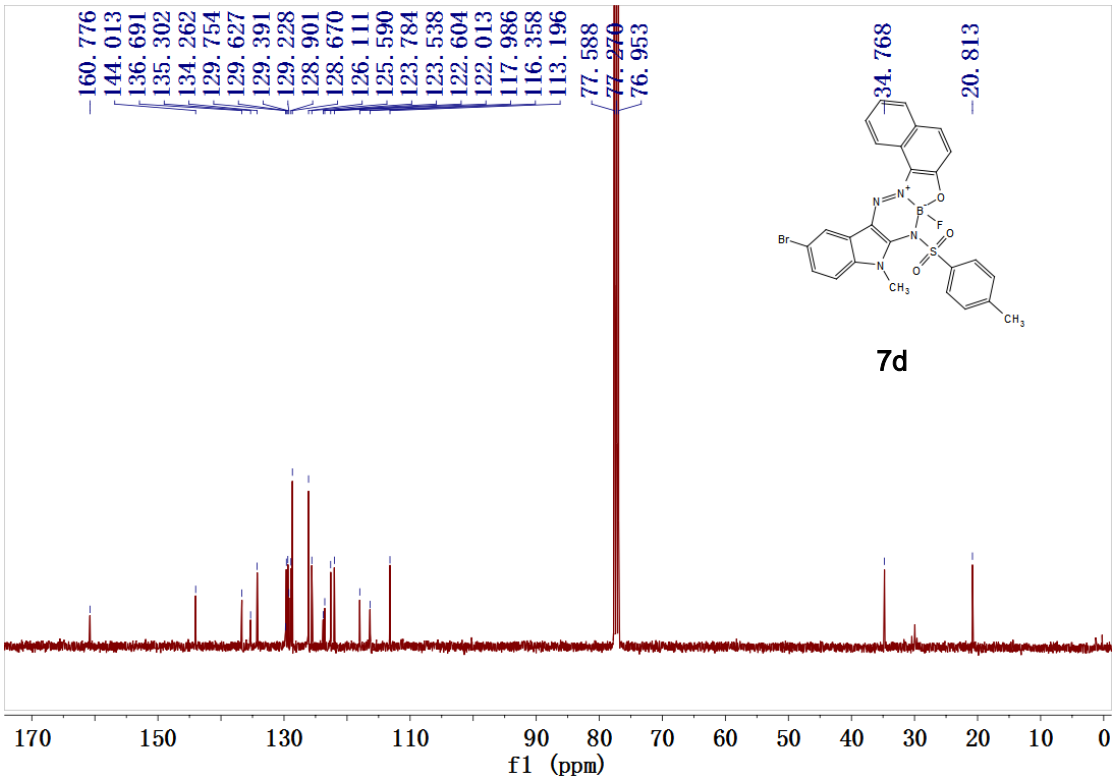

160.776
144.013
136.691
135.302
134.262
129.754
129.627
129.391
129.228
128.901
128.670
126.111
125.590
123.784
123.538
122.604
122.013
117.986
116.358
113.196
77.588
77.270
76.953
34.768
20.813
7d
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure S1 Absorption spectra of**3** in DCM

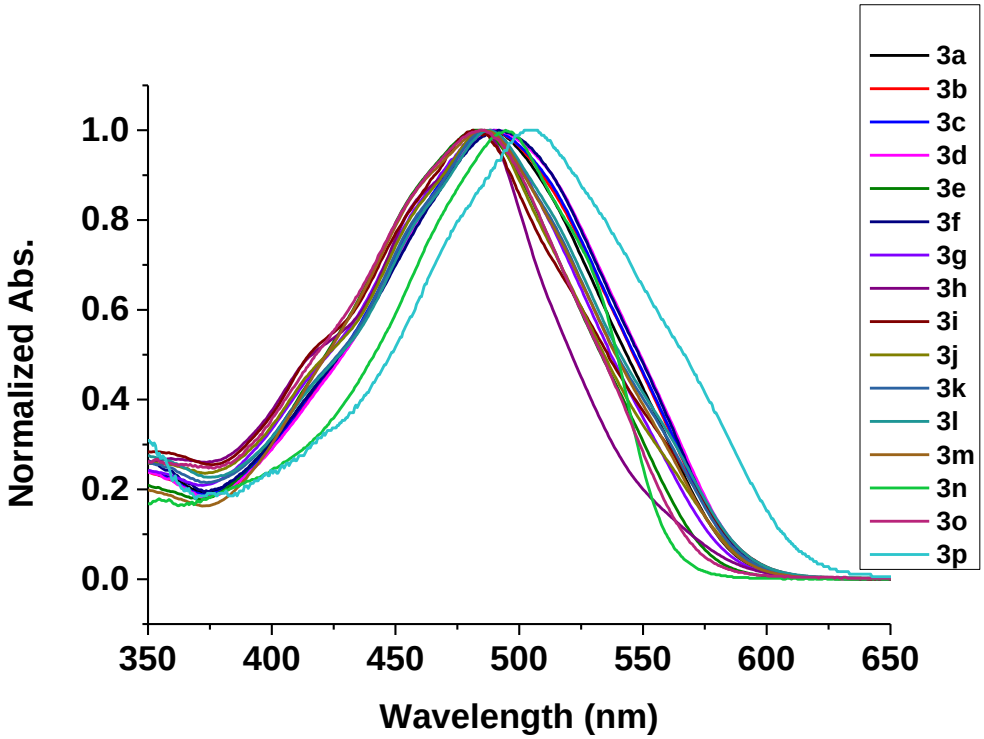


Figure S2 Absorption spectra of **7**in DCM