Supporting Information

$CoCl_2$-Promoted TEMPO Oxidative Homocoupling of Indoles: Acess to Tryptanthrin Derivatives

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CONTENTS

1. General Methods

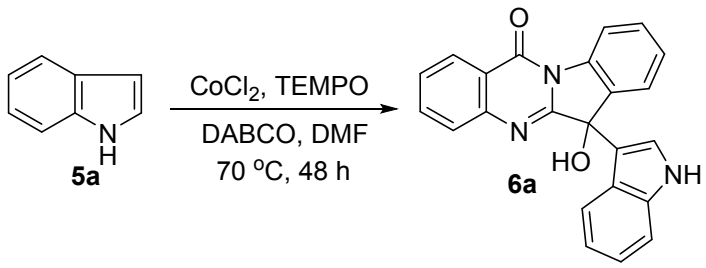
^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

Materials

Commercially available starting materials and solvents were used as supplied, without further purification.

2. Selected optimization of the reaction conditions

Table S1: Influence of $CoCl_2$ loadings[a]



Entry	$CoCl_2$ (mmol)	Yield (%)[b]
1	0.02	trace
2	0.04	35
3	0.05	59
4	0.06	72
5	0.07	72
6	0.08	64

[a] Conditions: **5** (0.3 mmol), TEMPO (0.135 mmol), DABCO (0.15 mmol), and DMF (1 mL), 48 h, under open air. [b] Isolated yield.

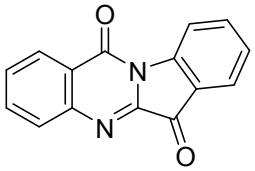
3. General Procedure and Characterization Data of the Products 6.

To a solution of indole (0.3 mmol), $CoCl_2$ (0.06 mmol), and TEMPO (0.135 mmol) in DMF (1 mL) was added DABCO (0.15 mmol) under an air atmosphere and the mixture was stirred at 70 ^{o}C for 48 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:1) to yield the corresponding product **6**.

spectrometer.

4. Spectroscopic Data of the Products 1, 6, and 8.

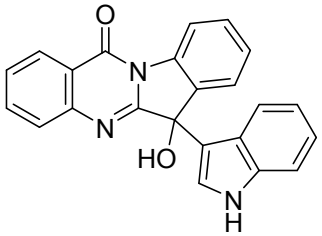
Indolo[2,1-*b*]quinazoline-6,12-dione (tryptanthrin) (**1**)



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.49 (d, J = 7.9 Hz, 1H, Ar-H), 8.33 (d, J = 7.9 Hz, 1H, Ar-H), 7.95 (d, J = 3.7 Hz, 2H, Ar-H), 7.89 (d, J = 7.9 Hz, 1H, Ar-H), 7.87 (d, J = 7.9 Hz, 1H, Ar-H),

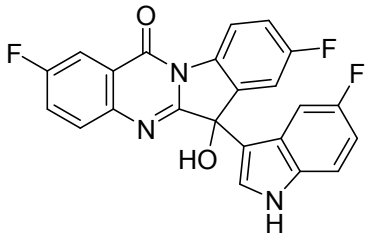
7.78-7.73 (m, 1H, Ar-H), 7.49 (d, J = 7.5 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.9, 158.2, 146.9, 146.5, 145.5, 138.2, 135.6, 130.4, 130.3, 127.4, 127.3, 125.2, 123.8, 122.7, 117.5. MS (ESI): 249 (M+H$^+$, 100). These assignments matched with those previously published.[1]

6-Hydroxy-6-(1*H*-indol-3-yl)indolo[2,1-*b*]quinazolin-12(6*H*)-one (**6a**)



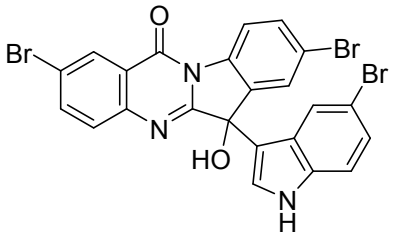
Yellow amorphous solid, 27.6 mg, 78% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.13 (d, J = 1.6 Hz, 1H, NH), 8.55 (d, J = 8.0 Hz, 1H, Ar-H), 8.32 (dd, J = 8.0, 1.6 Hz, 1H, Ar-H), 7.83 (dt, J = 1.5, 8.4 Hz, 1H, Ar-H), 7.67 (d, J = 7.7 Hz, 1H, Ar-H), 7.58 (t, J = 8.0 Hz, 1H, Ar-H), 7.55 (t, J = 8.8 Hz, 1H, Ar-H), 7.50 (d, J = 7.7 Hz, 1H, Ar-H), 7.37-7.33 (m, 3H, Ar-H), 7.07 (d, J = 8.0 Hz, 1H, Ar-H), 6.99 (t, J = 7.8 Hz, 1H, Ar-H), 6.88 (s, 1H, OH), 6.80 (t, J = 7.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.0, 159.5, 147.6, 138.6, 137.3, 136.2, 135.2, 130.2, 128.2, 127.9, 127.4, 126.9, 125.5, 125.0, 124.3, 121.8, 121.6, 119.8, 119.3, 116.7, 116.0, 112.2, 77.3. MS (ESI): 366 (M+H$^+$, 100), 388 (M+Na$^+$, 30). Anal calcd for $C_{23}H_{15}N_3O_2$: C, 75.60; H, 4.14; N, 11.50. Found C, 75.32; H, 4.41; N, 11.25.

2,8-Difluoro-6-(5-fluoro-1*H*-indol-3-yl)-6-hydroxyindolo[2,1-*b*]quinazolin-12(6*H*)-one (**6b**)



Yellow amorphous solid, 29.2 mg, 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.26 (s, 1H, NH), 8.52 (dd, J = 8.7, 4.5 Hz, 1H, Ar-H), 7.96 (d, J = 8.4 Hz, 1H, Ar-H), 7.77-7.69 (m, 2H, Ar-H), 7.45-7.31 (m, *3*H, Ar-H), 7.25 (d, J = 1.9 Hz, 1H, Ar-H), 7.18 (d, J = 8.9 Hz, 1H, Ar-H), 7.02 (s, 1H, OH), 6.90 (t, J = 8.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.2 (d, J = 244.6 Hz), 161.1 (d, J = 246.5 Hz), 161.0, 158.6 (d, J = 3.3 Hz), 157.1 (d, J = 231.4 Hz), 144.3, 138.3 (d, J = 8.0 Hz), 134.7 (d, J = 1.9 Hz), 134.0, 131.0 (d, J = 8.5 Hz), 126.6, 125.4 (d, J = 10.5 Hz), 123.5 (d, J = 24.0 Hz), 123.2 (d, J = 8.6 Hz), 118.5 (d, J = 8.4 Hz), 117.1 (d, J = 23.6 Hz), 115.5 (d, J = 4.6 Hz), 113.2 (d, J = 9.8 Hz), 112.8 (d, J = 24.7 Hz), 111.8 (d, J = 13.9 Hz), 110.1 (d, J = 26.1 Hz), 105.4 (d, J = 24.0 Hz), 77.0 (d, J = 1.4 Hz). MS (ESI): 420 (M+H$^+$, 100). Anal calcd for $C_{23}H_{12}F_3N_3O_2$: C, 65.87; H, 2.88; N, 10.02. Found C, 65.57; H, 3.14; N, 9.90.

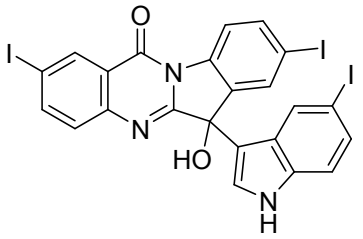
2,8-Dibromo-6-(5-bromo-1*H*-indol-3-yl)-6-hydroxyindolo[2,1-*b*]quinazolin-12(6*H*)-one (**6c**)



Yellow amorphous solid, 43.5 mg, 72% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.37 (d, J = 2.2

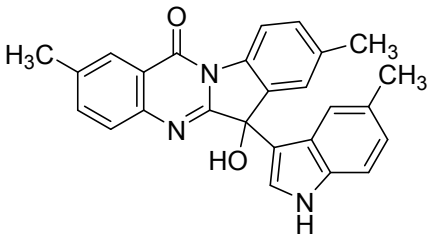
Hz, 1H, NH), 8.43 (d, *J* = 8.6 Hz, 1H, Ar-H), 8.34 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.99 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.79 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar-H), 7.69 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.62 (d, *J* = 8.6 Hz, 1H, Ar-H),, 7.34 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.19 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar-H), 7.16 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.08 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.5, 158.2, 146.5, 138.2, 138.1, 137.6, 136.1, 133.4, 130.5, 129.0, 128.2, 127.1, 126.2, 124.4, 123.4, 123.3, 120.6, 119.8, 118.8, 114.9, 114.3, 112.0, 77.1. MS (ESI): 600 (M+H$^+$, 30), 602 (M+H$^+$, 100), 604 (M+H$^+$, 100). Anal calcd for $C_{23}H_{12}Br_3N_3O_2$: C, 45.88; H, 2.01; N, 6.98. Found C, 46.19; H, 2.25; N, 6.61.

6-Hydroxy-2,8-diiodo-6-(5-iodo-1*H*-indol-3-yl)indolo[2,1-*b*]quinazolin-12(6*H*)-one (**6d**)



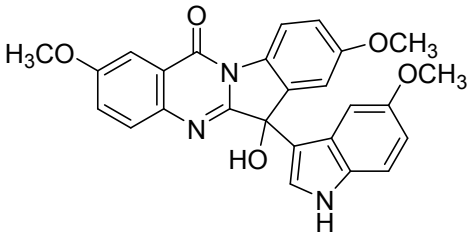
Yellow amorphous solid, 55.6 mg, 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.29 (s, 1H, NH), 8.51 (s, 1H, Ar-H), 8.27 (s, 1H, Ar-H), 8.12 (s, 1H, Ar-H), 8.03 (s, 1H, Ar-H), 7.93 (s, 1H, Ar-H), 7.82 (s, 1H, Ar-H), 7.43 (s, 1H, Ar-H), 7.32 (s, 1H, Ar-H), 7.22 (s, 1H, Ar-H), 7.07 (s, 1H, OH), 6.99 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.4, 158.1, 146.9, 143.8, 139.2, 138.1, 138.0, 136.4, 135.1, 133.8, 130.2, 129.8, 129.6, 128.0, 125.7, 123.5, 118.9, 114.8, 114.7, 93.3, 92.1, 83.3, 77.0. MS (ESI): 744 (M+H$^+$, 100). Anal calcd for $C_{23}H_{12}I_3N_3O_2$: C, 37.18; H, 1.63; N, 5.65. Found C, 37.43; H, 2.96; N, 5.52.

6-Hydroxy-2,8-dimethyl-6-(5-methyl-1*H*-indol-3-yl)indolo[2,1-*b*]quinazolin-12(6*H*)-one (**6e**)



Yellow amorphous solid, 33.6 mg, 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.95 (s, 1H, NH), 8.41 (s, 1H, Ar-H), 8.10 (s, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.56 (s, 1H, Ar-H), 7.34 (s, 1H, Ar-H), 7.26-7.21 (m, 3H, Ar-H), 6.85 (s, 1H, Ar-H),, 6.82 (s, 1H, Ar-H),, 6.75 (s, 1H, OH), 2.48 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.3, 159.3, 145.7, 137.6, 136.7, 136.4, 136.3, 136.2, 135.6, 130.5, 128.0, 127.5, 126.3, 125.8, 125.3, 124.2, 123.1, 121.5, 119.5, 116.4, 115.7, 111.8, 77.3, 21.8, 21.4, 21.3. MS (ESI): 408 (M+H$^+$, 100). Anal calcd for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.19; N, 10.31. Found C, 76.57; H, 5.39; N, 9.96.

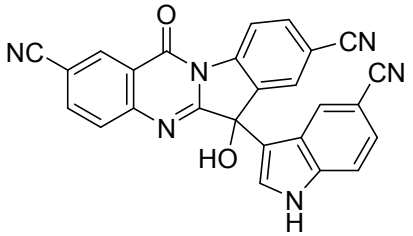
6-Hydroxy-2,8-dimethoxy-6-(5-methoxy-1*H*-indol-3-yl)indolo[2,1-*b*]quinazolin-12(6*H*)-one (**6f**)



Yellow amorphous solid, 39.5 mg, 87% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.92 (d, *J* = 2.3

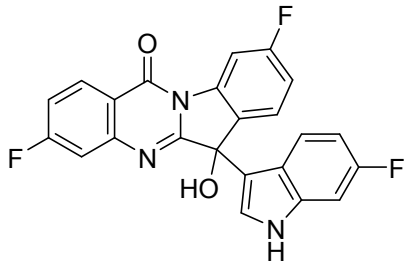
Hz, 1H, NH), 8.45 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.66 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.60 (d, *J* = 8.9 Hz, 1H, Ar-H), 7.41 (dd, *J* = 8.9, 3.0 Hz, 1H, Ar-H), 7.22 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.19 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.11 (dd, *J* = 8.9, 2.6 Hz, 1H, Ar-H), 7.05 (d, *J* = 2.6 Hz, 1H, Ar-H), 6.82 (s, 1H, OH), 6.67-6.63 (m, 2H, Ar-H), 3.89 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.8, 158.8, 158.7, 158.6, 153.3, 141.9, 137.9, 132.5, 132.0, 129.7, 125.5, 124.9, 124.1, 122.6, 117.7, 115.8, 115.1, 112.7, 111.4, 111.2, 107.2, 102.3, 77.2, 56.2, 56.1, 55.5. MS (ESI): 456 ($M+H^+$, 100). Anal calcd for $C_{26}H_{21}N_3O_5$: C, 68.56; H, 4.65; N, 9.23. Found C, 68.72; H, 4.70; N, 8.91.

6-(5-Cyano- 1*H*-indol-3-yl) 6-hydroxy-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazoline-2,8-dicarbonitrile (**6g**)



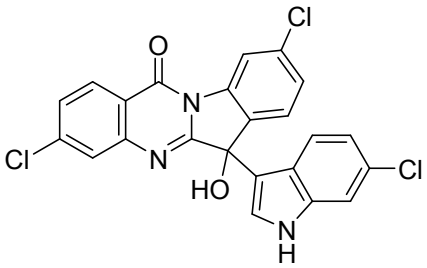
Yellow amorphous solid, 23.4 mg, 53% yield. ^1H NMR (400 MHz, DMSO-d_6): δ 11.27 (s, 1H, NH), 8.53 (d, *J* = 4.4 Hz, 1H, Ar-H), 7.98 (s, 1H, Ar-H), 7.80-7.52 (m, 2H, Ar-H), 7.48-7.33 (m, 3H, Ar-H), 7.26 (s, 1H, Ar-H), 7.18 (d, *J* = 9.6 Hz, 1H, Ar-H), 7.03 (s, 1H, OH), 6.95-6.87 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.4, 162.3, 161.1, 160.0, 159.8, 158.6, 158.2, 155.9, 144.3, 138.4, 134.7, 134.0, 131.0, 126.6, 125.4, 123.7, 123.2, 118.5, 117.2, 115.5, 113.3, 112.7, 111.7, 110.2, 105.5, 77.0. MS (ESI): 441 ($M+H^+$, 100). Anal calcd for $C_{26}H_{12}N_6O_2$: C, 70.91; H, 2.75; N, 19.08. Found C, 70.56; H, 2.94; N, 18.77.

3,9-Difluoro-6-(6-fluoro-1*H*-indol-3-yl)-6-hydroxyindolo[2,1-*b*]quinazolin-12(6*H*)-one (**6h**)



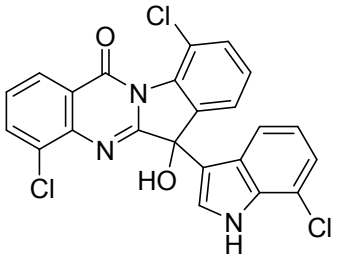
Yellow amorphous solid, 26.7 mg, 64% yield. ^1H NMR (400 MHz, DMSO-d_6): δ 11.21 (s, 1H, NH), 8.35 (dd, *J* = 8.8, 5.9 Hz, 1H, Ar-H), 8.25 (dd, *J* = 9.5, 2.3 Hz, 1H, Ar-H), 7.57-7.43 (m, 3H, Ar-H), 7.34 (dd, *J* = 8.8, 5.9 Hz, 1H, Ar-H), 7.23 (dt, *J* = 9.9, 2.3 Hz, 2H, Ar-H), 7.12 (dd, *J* = 9.9, 2.3 Hz, 1H, Ar-H), 6.95 (s, 1H, OH), 6.76 (dt, *J* = 9.5, 2.3 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.4 (d, *J* = 252.5 Hz), 163.2, 162.8 (d, *J* = 244.4 Hz), 159.2 (d, *J* = 234.9 Hz), 158.8, 149.7 (d, *J* = 13.2 Hz), 139.4 (d, *J* = 12.7 Hz), 137.2 (d, *J* = 12.6 Hz), 131.9 (d, *J* = 2.8 Hz), 130.0 (d, *J* = 11.0 Hz), 127.1 (d, *J* = 9.9 Hz), 125.2 (d, *J* = 3.0 Hz), 122.0, 121.5 (d, *J* = 10.1 Hz), 118.7 (d, *J* = 10.7 Hz), 116.5 (d, *J* = 23.5 Hz), 115.6, 114.1 (d, *J* = 22.6 Hz), 113.7 (d, *J* = 22.2 Hz), 108.0 (d, *J* = 24.3 Hz), 104.7 (d, *J* = 29.0 Hz), 98.1 (d, *J* = 25.4 Hz), 77.0. MS (ESI): 420 ($M+H^+$, 100). Anal calcd for $C_{23}H_{12}F_3N_3O_2$: C, 65.87; H, 2.88; N, 10.02. Found C, 65.70; H, 2.97; N, 9.76.

3,9-Dichloro-6-(6-chloro-1*H*-indol-3-yl)-6-hydroxyindolo[2,1-*b*]quinazolin-12(6*H*)-one (**6i**)



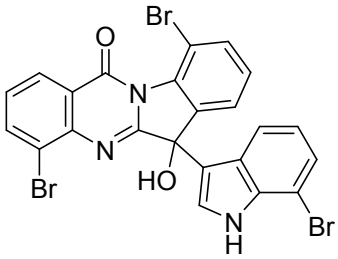
Yellow amorphous solid, 32.5 mg, 69% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.28 (s, 1H, NH), 8.50 (s, 1H, Ar-H), 8.28 (s, 1H, Ar-H), 7.78 (s, 1H, Ar-H), 7.65 (s, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 7.47 (dd, J = 9.8, 5.9 Hz, 2H, Ar-H), 7.40 (s, 1H, Ar-H), 7.23 (s, 1H, Ar-H), 7.01 (s, 1H, OH), 6.94 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.8, 158.9, 148.6, 140.1, 139.4, 137.7, 134.7, 134.3, 128.9, 128.4, 127.5, 127.4, 127.0, 126.6, 125.7, 124.0, 122.2, 120.6, 119.8, 116.7, 115.4, 111.7, 77.0. MS (ESI): 468 (M+H$^+$, 100), 470 (M+H$^+$, 100), 472 (M+H$^+$, 30). Anal calcd for $C_{23}H_{12}Cl_3N_3O_2$: C, 58.94; H, 2.58; N, 8.97. Found C, 59.06; H, 2.73; N, 8.66.

4,10-Dichloro-6-(7-chloro-1*H*-indol-3-yl)-6-hydroxyindolo[2,1-*b*]quinazolin-12(6*H*)-one (**6j**)



Yellow amorphous solid, 34.4 mg, 73% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.55 (s, 1H, NH), 8.18 (dd, J = 7.8, 1.3 Hz, 1H, Ar-H), 7.97 (d, J = 7.8 Hz, 1H, Ar-H), 7.64 (t, J = 8.0 Hz, 2H, Ar-H), 7.54 (t, J = 8.0 Hz, 2H, Ar-H), 7.44 (t, J = 7.8 Hz, 1H, Ar-H), 7.16 (s, 1H, Ar-H), 7.15 (d, J = 8.0 Hz, 1H, Ar-H), 7.02 (s, 1H, OH), 6.96 (t, J = 8.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.5, 157.6, 143.8, 139.7, 135.6, 135.4, 134.2, 132.9, 131.1, 129.3, 128.5, 127.1, 126.2, 125.8, 124.4, 124.3, 121.6, 121.4, 120.5, 120.4, 116.8, 116.4, 77.4. MS (ESI): 468 (M+H$^+$, 100), 470 (M+H$^+$, 100), 472 (M+H$^+$, 30). Anal calcd for $C_{23}H_{12}Cl_3N_3O_2$: C, 58.94; H, 2.58; N, 8.97. Found C, 58.79; H, 2.67; N, 8.82.

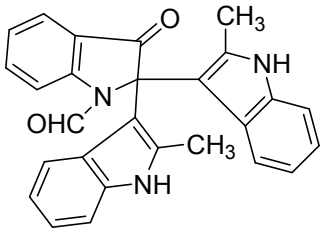
4,10-Dibromo-6-(7-bromo-1*H*-indol-3-yl)-6-hydroxyindolo[2,1-*b*]quinazolin-12(6*H*)-one (**6k**)



Yellow amorphous solid, 43.6 mg, 72% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.38 (d, J = 2.3 Hz, 1H, NH), 8.20 (dd, J = 7.9, 1.2 Hz, 1H, Ar-H), 8.13 (dd, J = 7.9, 1.3 Hz, 1H, Ar-H), 7.84 (d, J = 7.9 Hz, 1H, Ar-H), 7.82 (d, J = 7.9 Hz, 1H, Ar-H), 7.61 (dd, J = 7.4, 1.2 Hz, 1H, Ar-H), 7.47 (t, J = 7.9 Hz, 1H, Ar-H), 7.37 (t, J = 7.9 Hz, 1H, Ar-H), 7.30 (d, J = 7.1 Hz, 1H, Ar-H), 7.06 (d, J = 2.3 Hz, 1H, Ar-H), 7.00 (s, 1H, OH), 6.94 (t, J = 7.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.5, 157.5, 144.8, 139.9, 138.6, 137.6, 136.1, 135.7, 129.5, 128.9, 127.0, 126.8, 125.7,

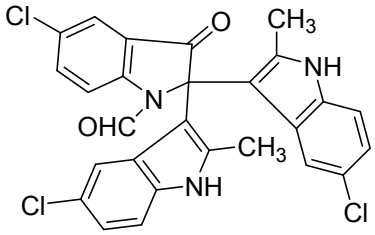
124.7, 124.6, 124.3, 121.9, 121.6, 120.8, 116.9, 109.4, 104.6, 77.5. MS (ESI): 600 ($M+H^+$, 30), 602 ($M+H^+$, 100), 604 ($M+H^+$, 100). Anal calcd for $C_{23}H_{12}Br_3N_3O_2$: C, 45.88; H, 2.01; N, 6.98. Found C, 46.02; H, 2.31; N, 6.79.

2,2''-Dimethyl-3'-oxo-(3,2':2',3''-terindoline)-1'-carbaldehyde (**8a**)



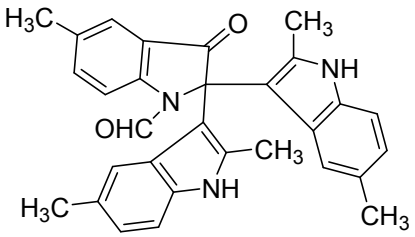
Yellow solid, 285-288 °C (from CH_2Cl_2), 30.6 mg, 73% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.67 (s, 1H, CHO), 8.64 (d, J = 8.3 Hz, 1H, Ar-H), 8.45-8.35 (bs, 2H, NH), 7.83 (d, J = 7.5 Hz, 1H, Ar-H), 7.77 (dt, J = 1.2, 8.3 Hz, 1H, Ar-H), 7.30 (t, J = 7.5 Hz, 1H, Ar-H), 7.21 (d, J = 7.5 Hz, 2H, Ar-H), 7.19 (d, J = 7.9 Hz, 1H, Ar-H), 7.04 (t, J = 8.3 Hz, 2H, Ar-H), 6.93 (d, J = 8.1 Hz, 1H, Ar-H), 6.88 (d, J = 8.1 Hz, 1H, Ar-H), 6.83 (d, J = 7.9 Hz, 1H, Ar-H), 2.08 (s, 3H, CH_3), 2.04 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 162.2, 150.0, 137.4, 135.2, 135.1, 134.9, 134.4, 127.6, 126.7, 125.3, 125.2, 123.4, 121.5, 121.4, 120.3, 120.2, 119.9, 119.8, 117.7, 110.6, 110.5, 107.9, 107.2, 71.3, 14.2, 14.0. MS (ESI): 420 ($M+H^+$, 100). Anal calcd for $C_{27}H_{21}N_3O_2$: C, 77.31; H, 5.05; N, 10.02. Found C, 77.16; H, 5.40; N, 9.83.

5,5',5''-Trichloro-2,2''-dimethyl-3'-oxo-(3,2':2',3''-terindoline)-1'-carbaldehyde (**8b**)



Yellow solid, 212-215 °C (from EtOAc/PE = 1:1), 35.2 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 8.7 Hz, 1H, Ar-H), 8.56 (s, 1H, CHO), 8.40 (s, 1H, NH), 8.37 (s, 1H, NH), 7.79 (d, J = 2.1 Hz, 1H, Ar-H), 7.75 (dd, J = 8.7, 2.1 Hz, 1H, Ar-H), 7.16 (dd, J = 8.8, 2.8 Hz, 2H, Ar-H), 7.05-7.01 (m, 3H, Ar-H), 6.86 (d, J = 1.7 Hz, 1H, Ar-H), 2.12 (s, 3H, CH_3), 2.06 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 161.5, 148.1, 137.5, 136.2, 135.7, 133.5, 133.4, 131.2, 128.2, 127.7, 126.2, 126.1, 125.0, 124.4, 122.4, 122.2, 119.2, 119.1, 118.9, 111.8, 111.7, 106.8, 106.3, 71.2, 14.3, 14.1. MS (ESI): 522 ($M+H^+$, 100), 524 ($M+H^+$, 100), 526 ($M+H^+$, 30). Anal calcd for $C_{27}H_{18}Cl_3N_3O_2$: C, 62.03; H, 3.47; N, 8.04. Found C, 62.35; H, 3.61; N, 7.73.

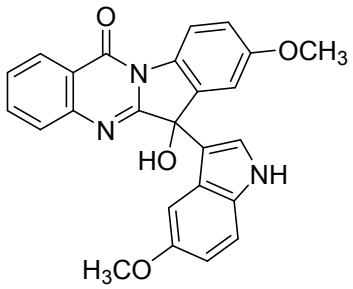
2,2'',5,5',5''-Pentamethyl-3'-oxo-(3,2':2',3''-terindoline)-1'-carbaldehyde (**8c**)



Yellow amorphous solid, 37.3 mg, 81% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.14 (s, 1H, NH), 11.09 (s, 1H, NH), 8.39 (s, 1H, CHO), 8.37 (d, J = 8.3 Hz, 1H, Ar-H), 7.70 (dd, J = 8.5, 1.5 Hz, 1H, Ar-H), 7.62 (s, 1H, Ar-H), 7.18 (t, J = 8.3 Hz, 2H, Ar-H), 6.81 (d, J = 8.3 Hz, 2H, Ar-H),

6.80 (s, 1H, Ar-H), 6.53 (s, 1H, Ar-H), 2.38 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.94 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.4, 161.5, 147.8, 138.8, 136.3, 135.5, 133.9, 127.8, 127.6, 127.3, 126.8, 125.0, 123.6, 122.5, 122.4, 119.6, 118.7, 117.1, 111.2, 111.0, 106.2, 105.6, 71.8, 22.1, 22.0, 20.9, 13.9, 13.8. HRESIMS calcd for [$C_{30}H_{27}N_3O_2$ + Na^+] 484.20010 (100%), found 484.19823 (100%).

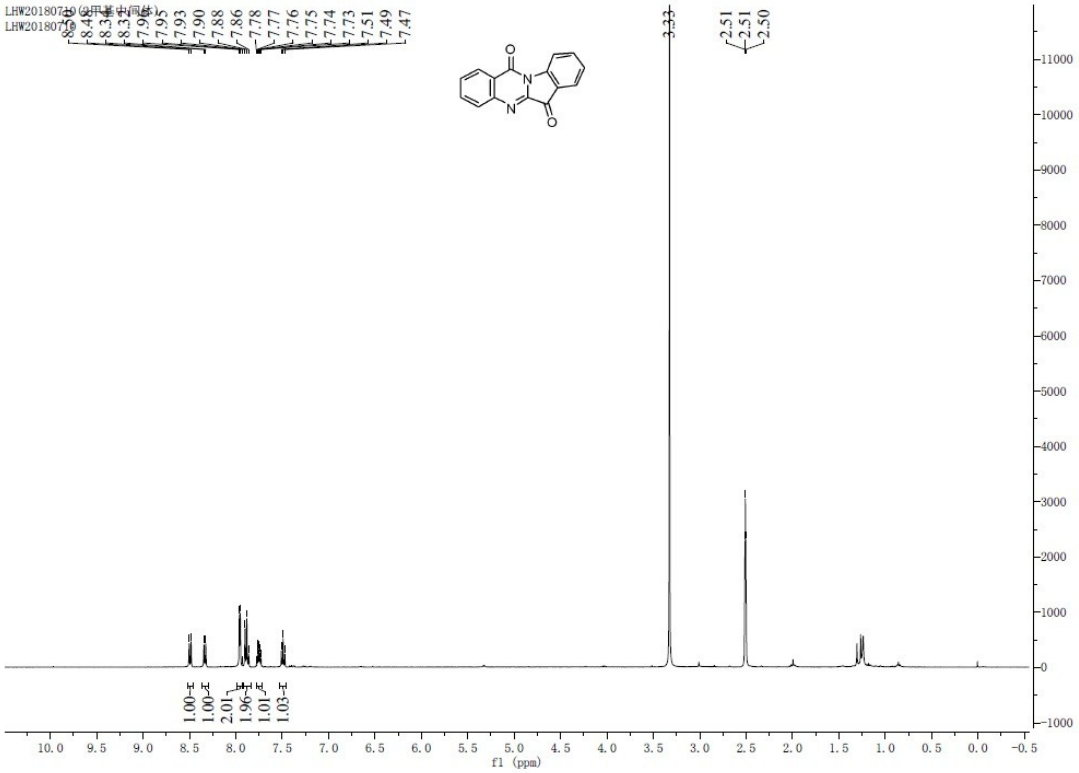
6-Hydroxy-8-methoxy-6-(5-methoxy-1*H*-indol-3-yl)indolo[2,1-*b*]quinazolin-12(6*H*)-one (**10**)

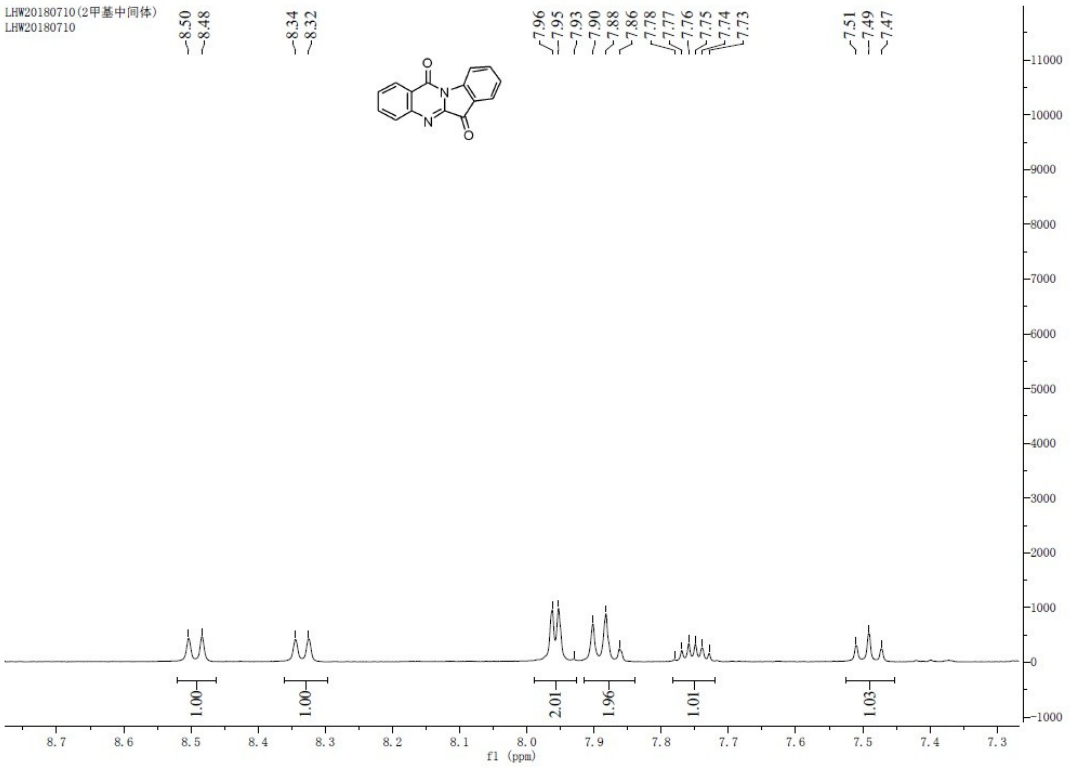


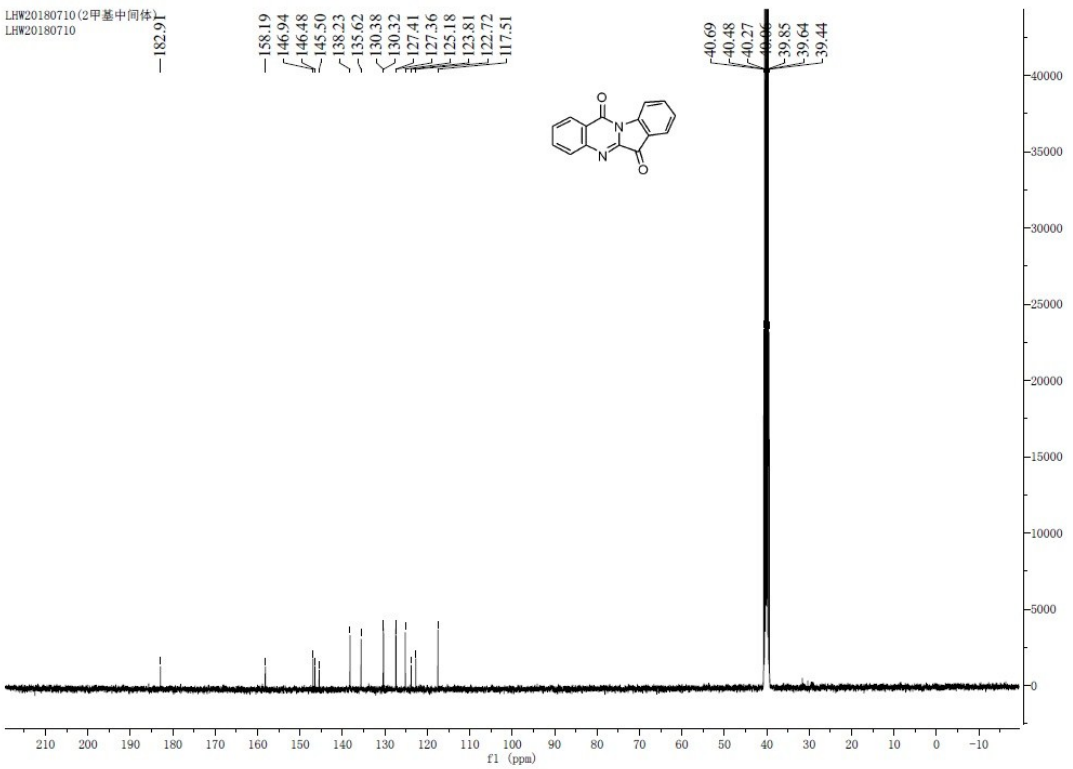
Yellow amorphous solid, 23.8 mg, 56% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.97 (s, 1H, NH), 8.46 (d, J = 8.8 Hz, 1H, Ar-H), 8.30 (dd, J = 7.9, 1.2 Hz, 1H, Ar-H), 7.84 (dt, J = 1.2, 8.4 Hz, 1H, Ar-H), 7.68 (d, J = 7.9 Hz, 1H, Ar-H), 7.59 (t, J = 7.9 Hz, 1H, Ar-H), 7.24 (d, J = 8.8 Hz, 1H, Ar-H), 7.21 (d, J = 2.6 Hz, 1H, Ar-H), 7.14 (dd, J = 8.8, 2.6 Hz, 1H, Ar-H), 7.08 (d, J = 2.6 Hz, 1H, Ar-H), 6.88 (s, 1H, OH), 6.75 (d, J = 2.3 Hz, 1H, Ar-H), 6.69 (dd, J = 8.8, 2.3 Hz, 1H, Ar-H), 3.78 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.0, 159.1, 158.8, 153.4, 147.6, 137.8, 135.1, 132.5, 132.0, 128.1, 127.8, 126.7, 125.5, 125.0, 121.7, 117.7, 115.6, 115.2, 112.8, 111.5, 111.2, 102.4, 77.5, 56.1, 55.6. MS (ESI): 426 ($M+H^+$, 100). Anal calcd for $C_{25}H_{19}N_3O_4$: C, 70.58; H, 4.50; N, 9.88. Found C, 70.25; H, 4.73; N, 9.61.

5. Copies of ^{1}H, ^{13}C Spectra

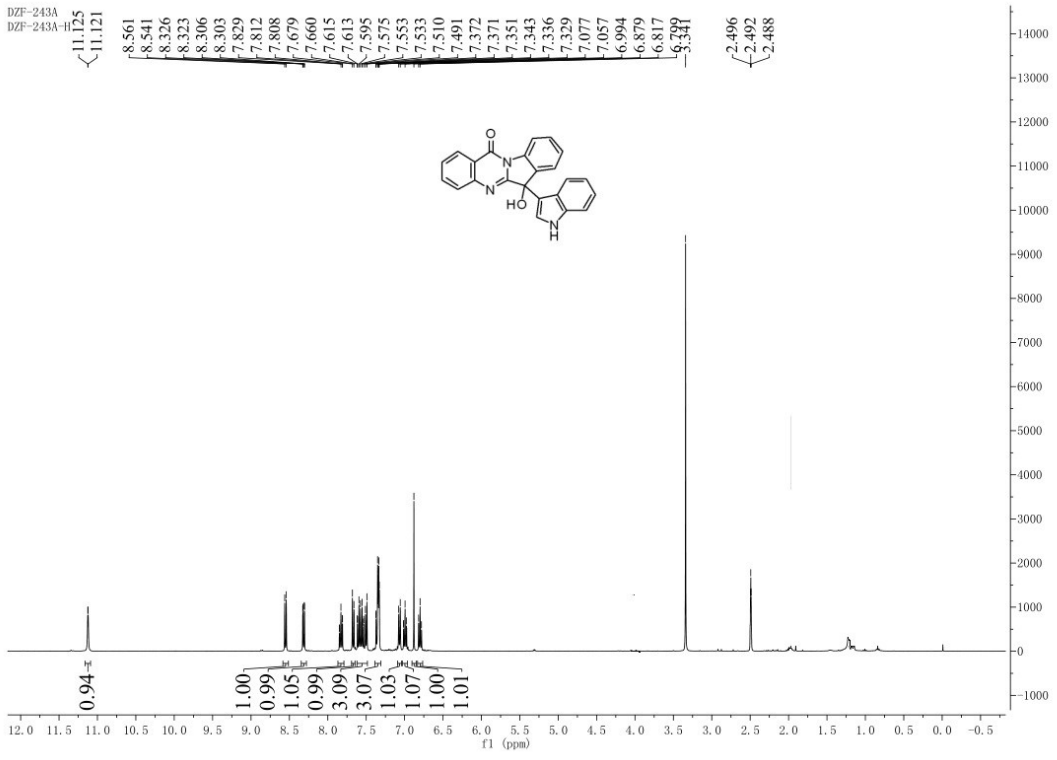
^{1}H and ^{13}C NMR Spectra for **1**

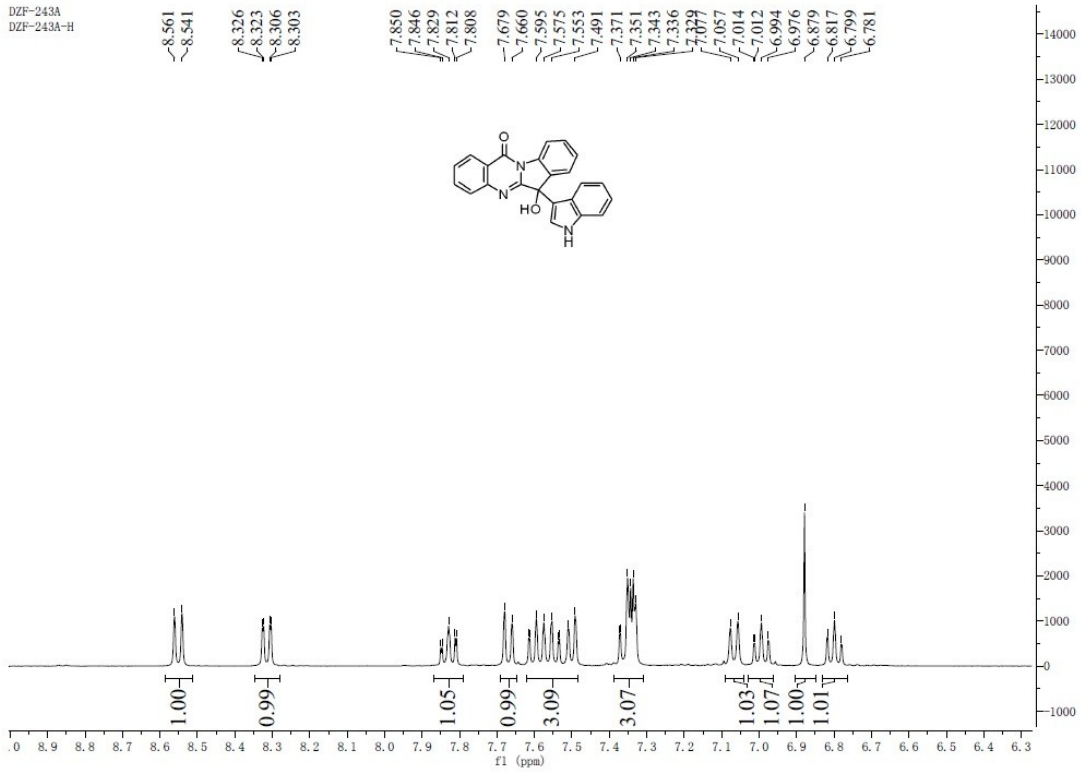


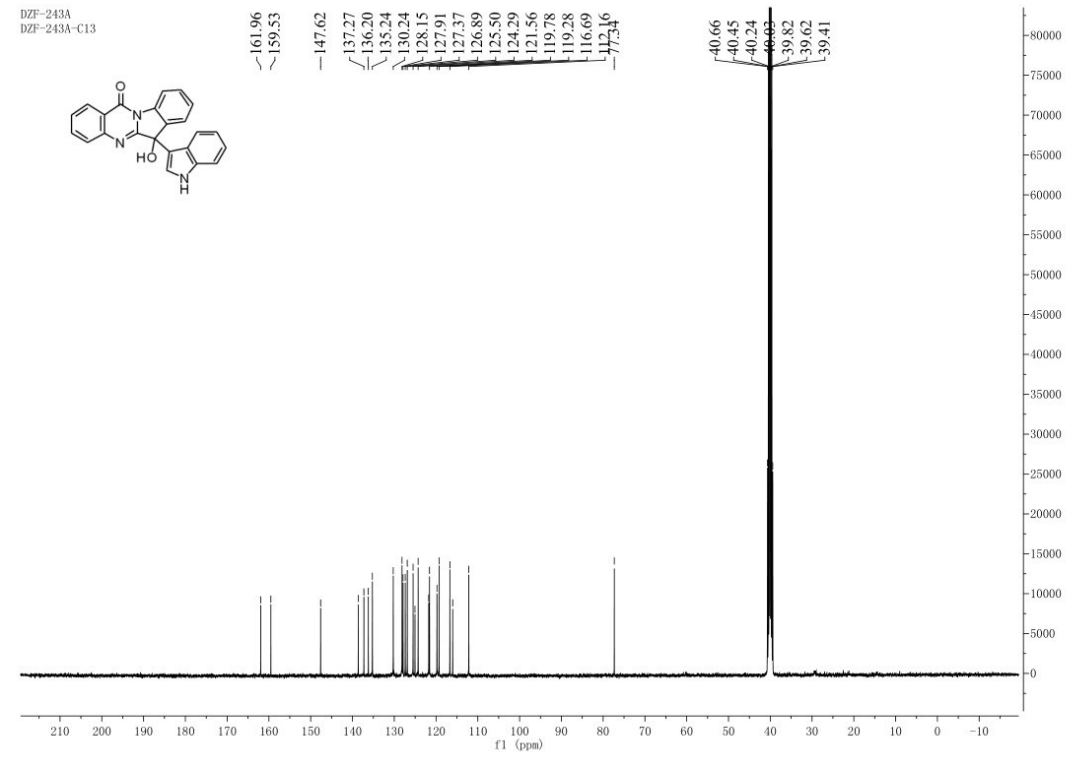




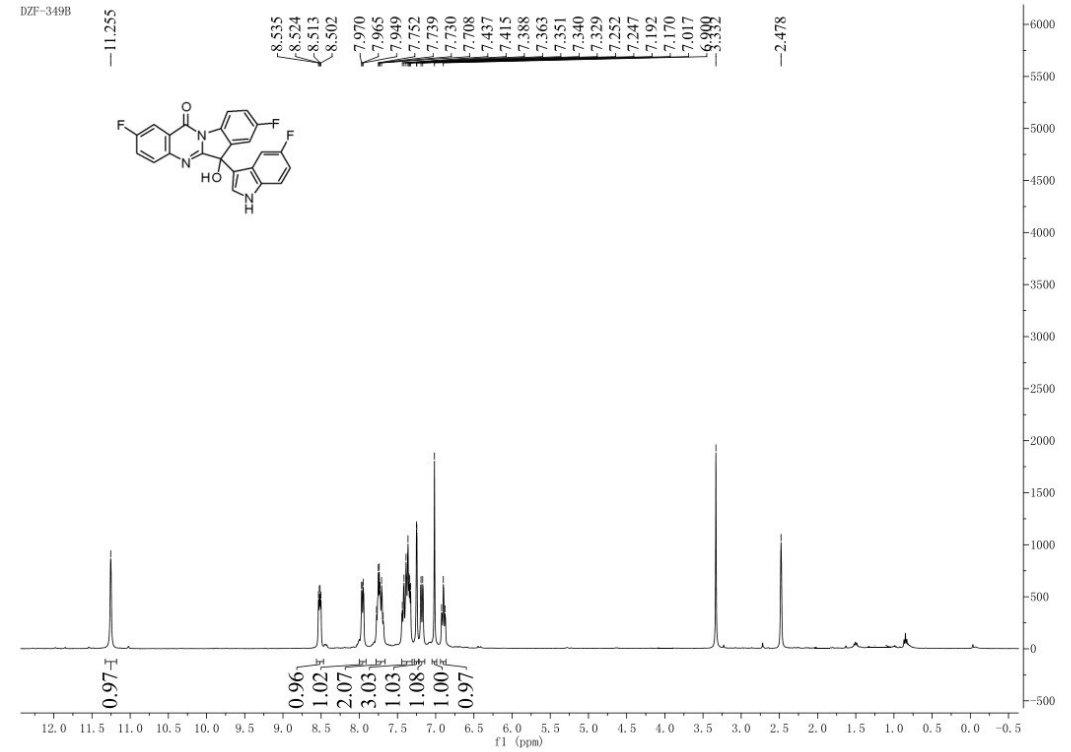
^{1}H and ^{13}C NMR Spectra for **6a**

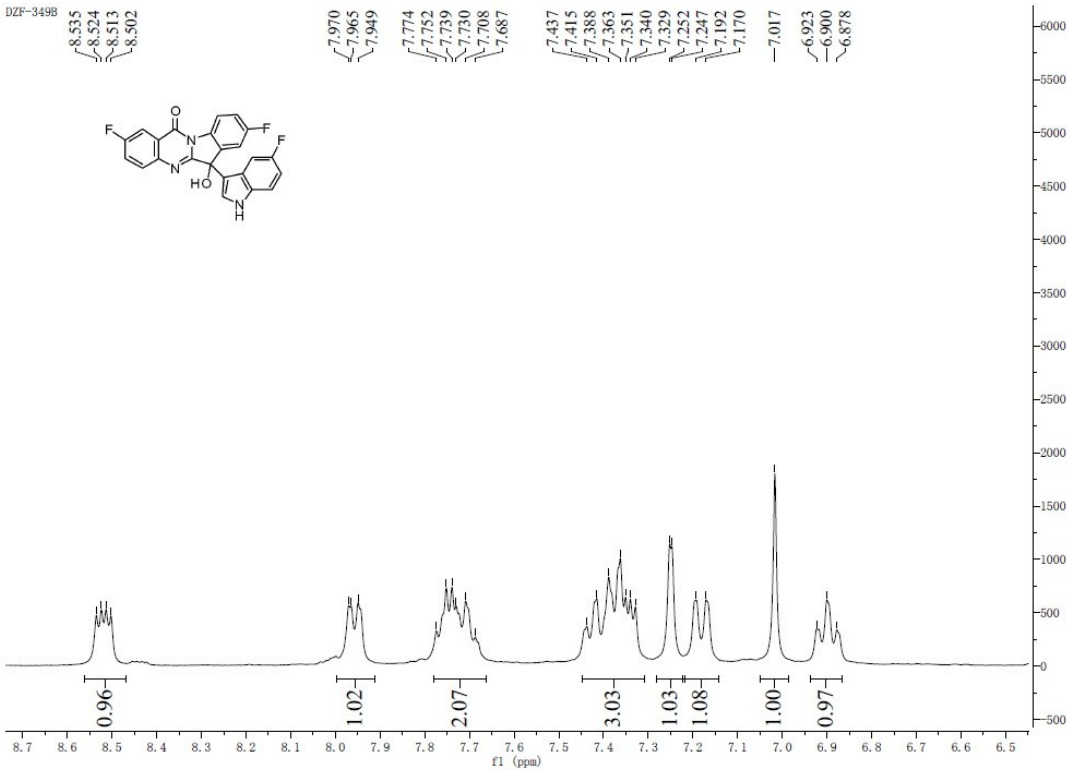


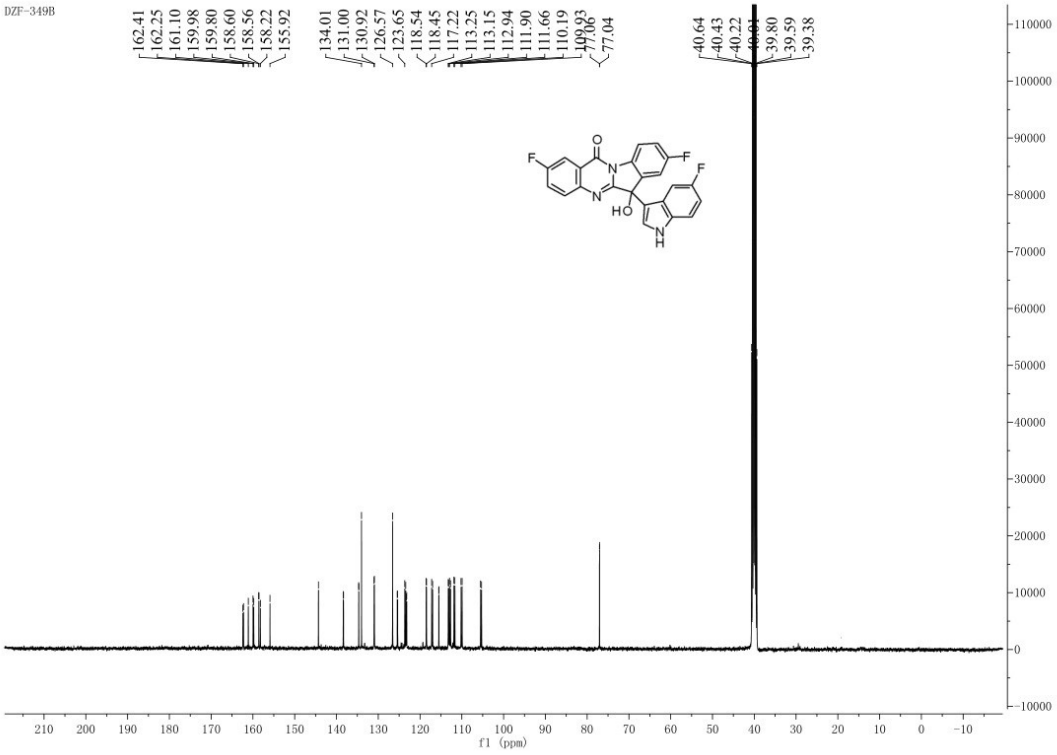

DZF-243A
DZF-243A-H
8.561
8.541
8.326
8.323
8.306
8.303
7.850
7.846
7.829
7.812
7.808
7.679
7.660
7.595
7.575
7.553
7.491
7.371
7.351
7.343
7.336
7.329
7.077
7.057
7.014
7.012
6.994
6.976
6.879
6.817
6.799
6.781
1.00
0.99
1.05
0.99
3.09
3.07
1.03
1.07
1.00
1.01
f1 (ppm)


DZF-243A
DZF-243A-C13
161.96
159.53
147.62
137.27
136.20
135.24
130.24
128.15
127.91
127.37
126.89
125.50
124.29
121.56
119.78
119.28
116.69
112.16
77.34
40.66
40.45
40.24
40.03
39.82
39.62
39.41
f1 (ppm)

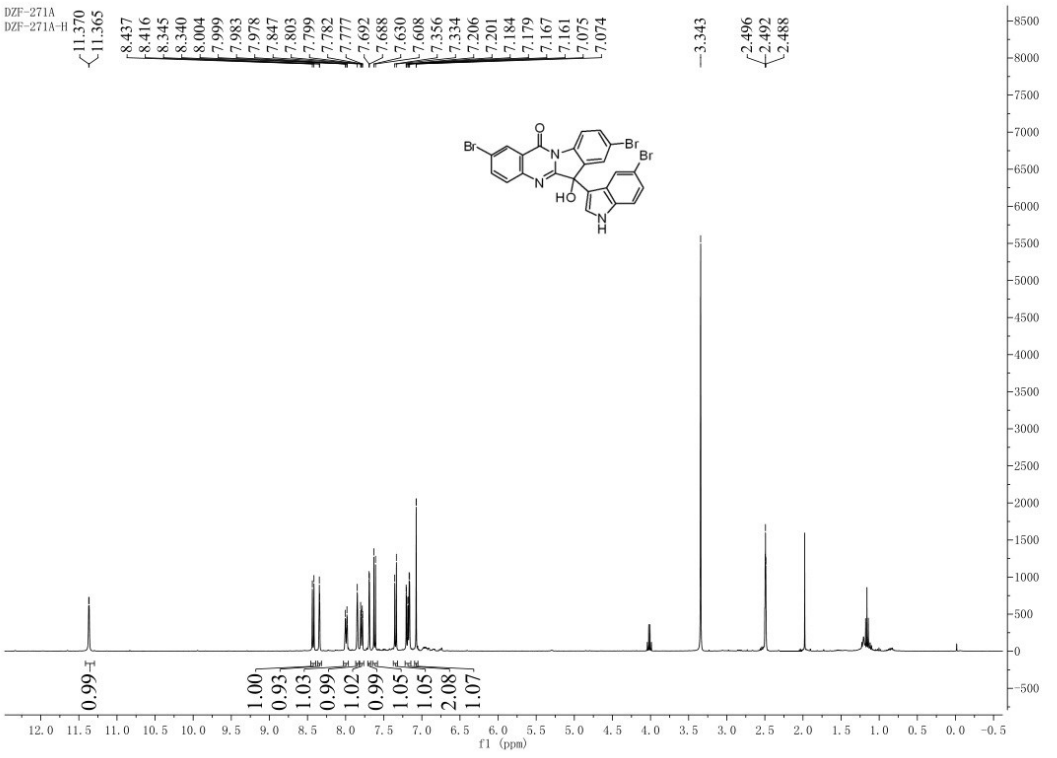
^{1}H and ^{13}C NMR Spectra for **6b**

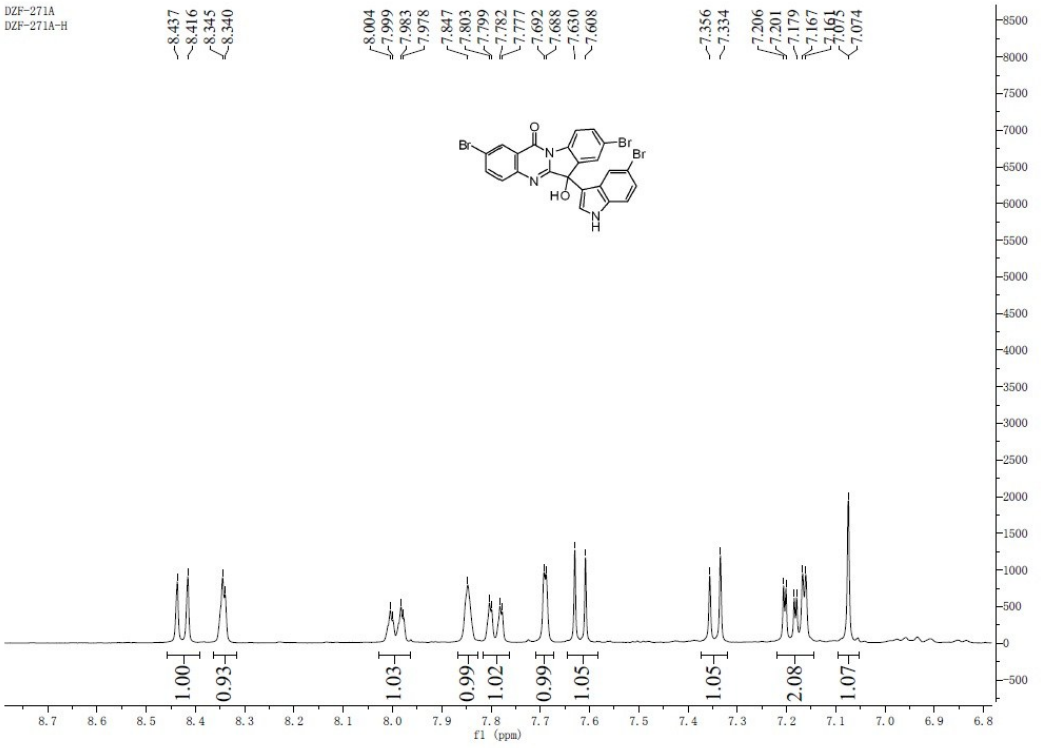


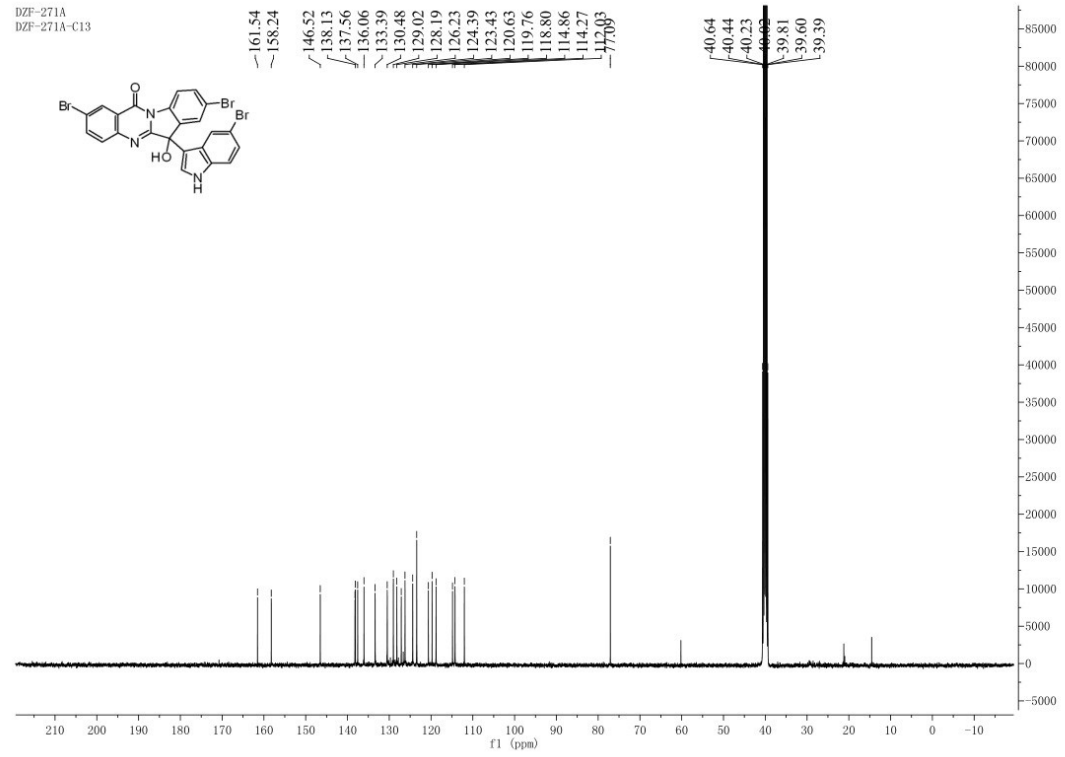




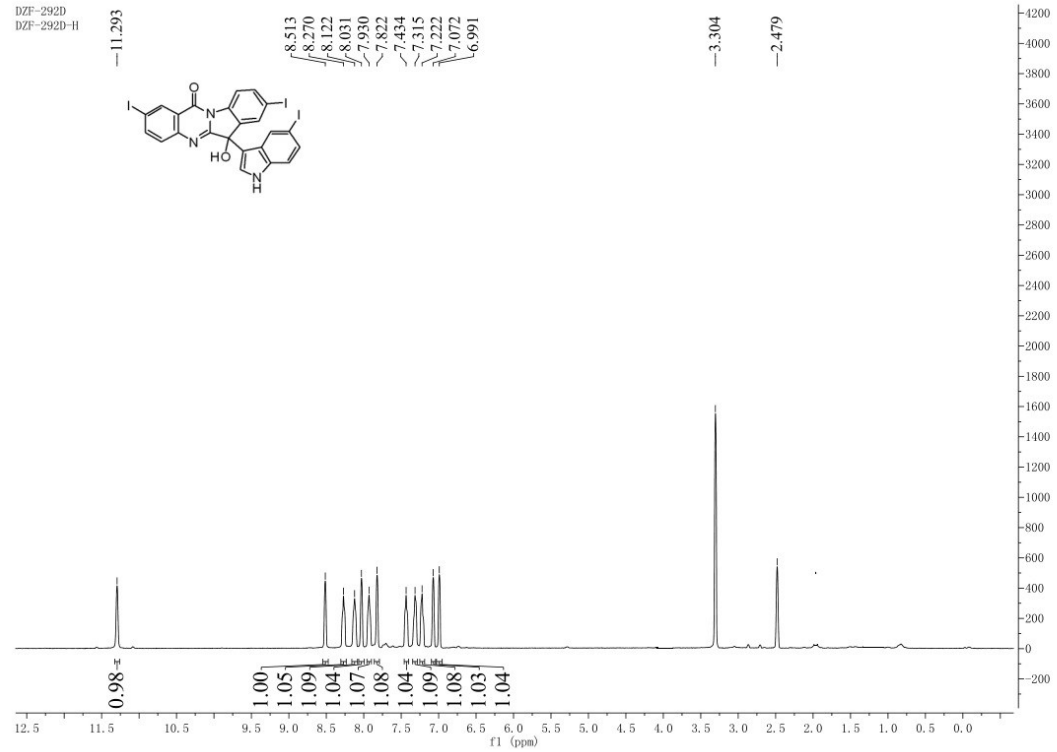
^{1}H and ^{13}C NMR Spectra for **6c**

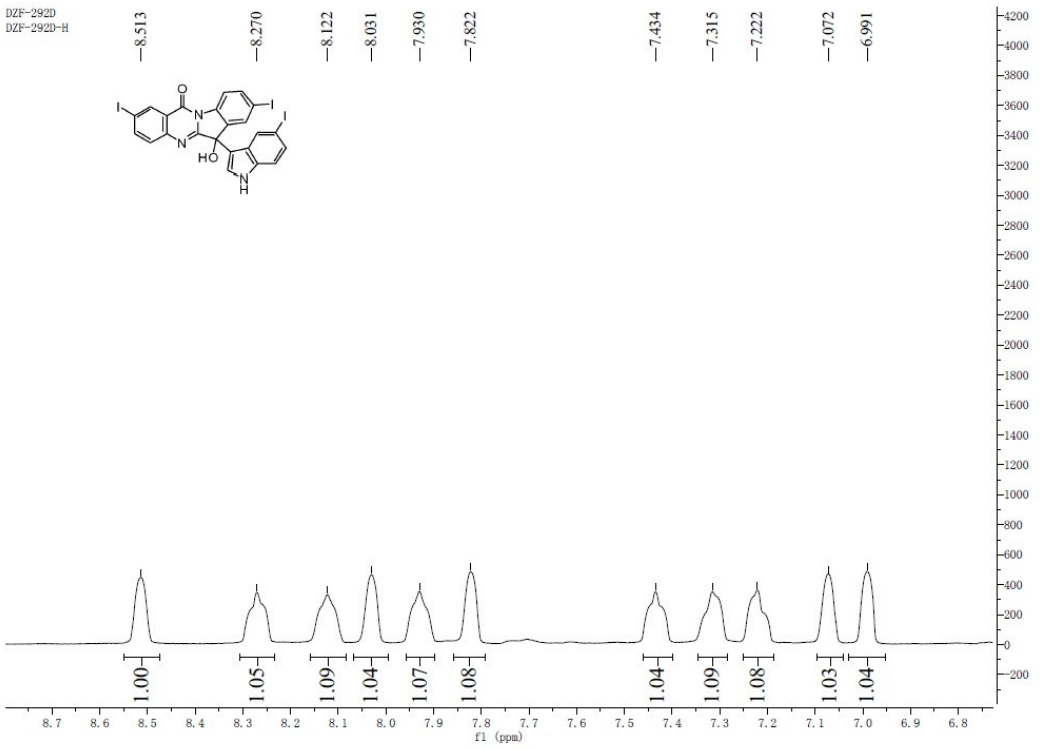


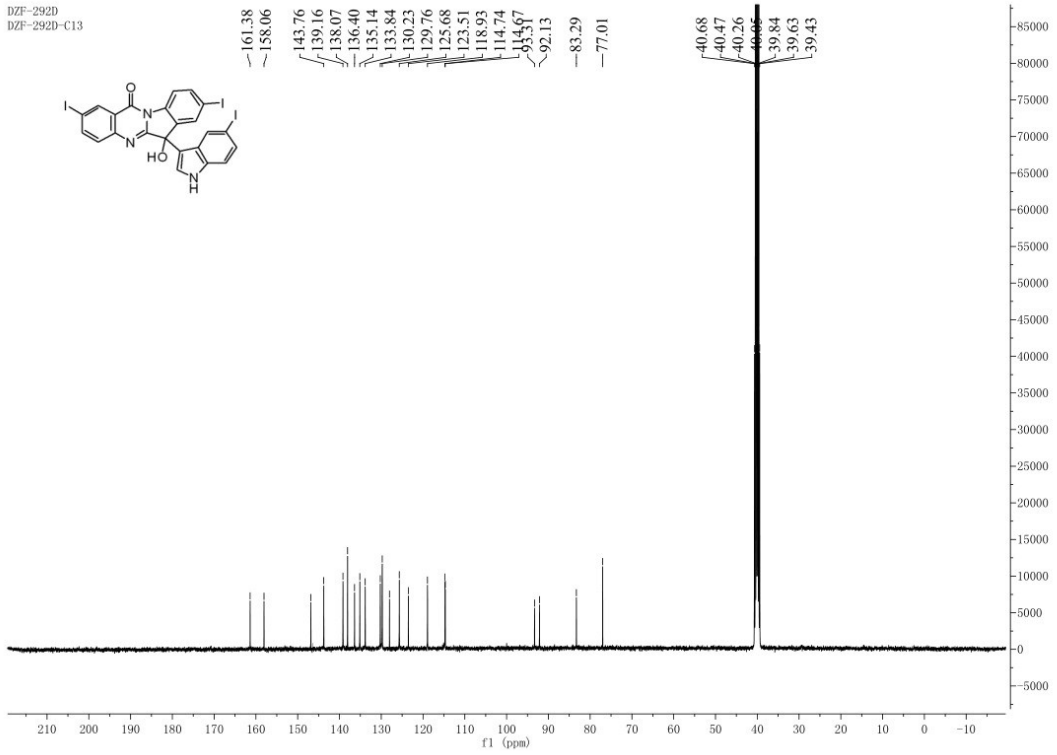

DZF-271A
DZF-271A-H
8.437
8.416
8.345
8.340
8.004
7.999
7.983
7.978
7.847
7.803
7.799
7.782
7.777
7.692
7.688
7.630
7.608
7.356
7.334
7.206
7.201
7.179
7.167
7.161
7.075
7.074
1.00
0.93
1.03
0.99
1.02
0.99
1.05
1.05
2.08
1.07
f1 (ppm)


DZF-271A
DZF-271A-C13
161.54
158.24
146.52
138.13
137.56
136.06
133.39
130.48
129.02
128.19
126.23
124.39
123.43
120.63
119.76
118.80
114.86
114.27
77.09
40.64
40.44
40.23
39.81
39.60
39.39
f1 (ppm)

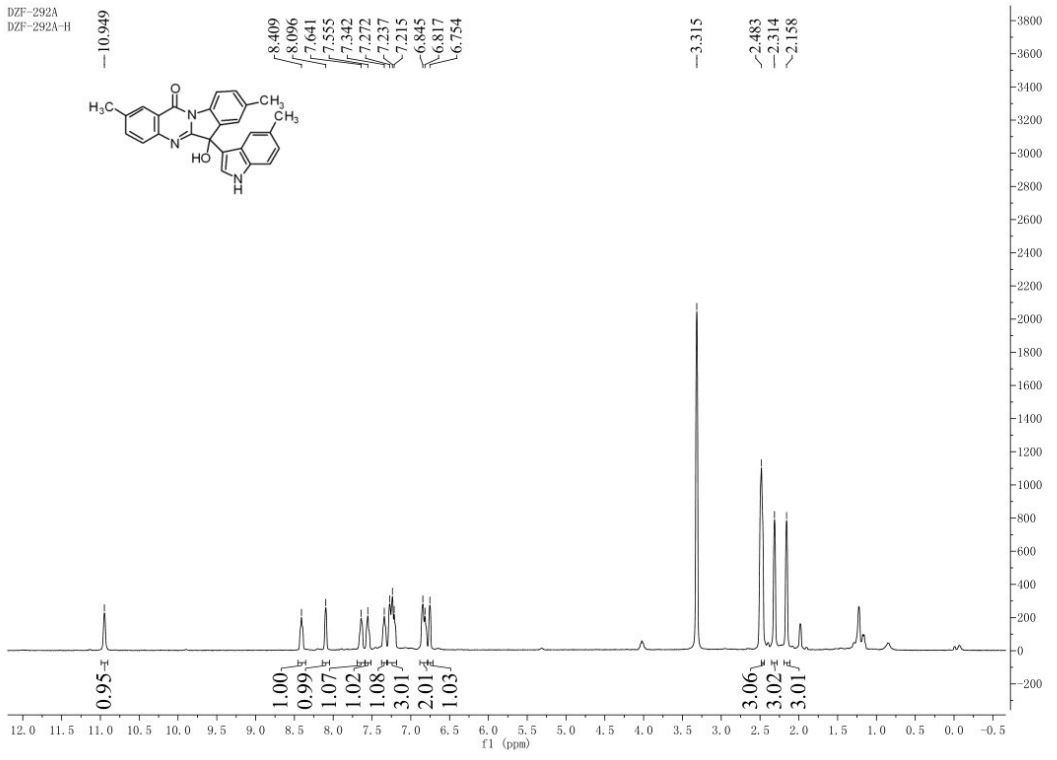
^{1}H and ^{13}C NMR Spectra for **6d**

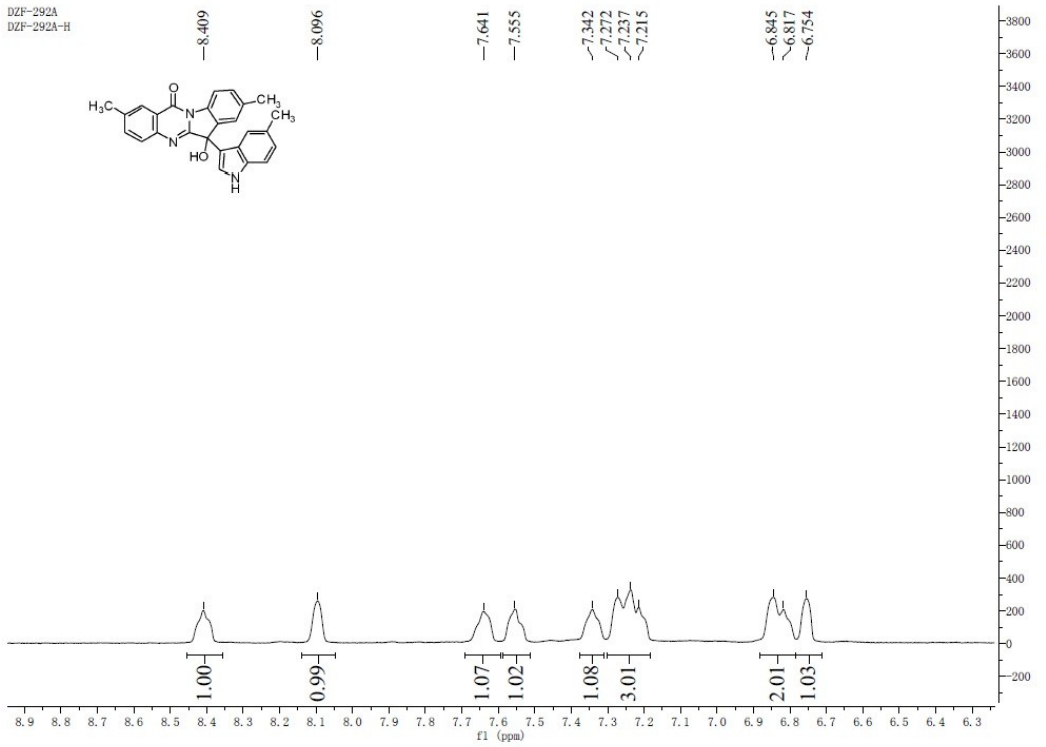


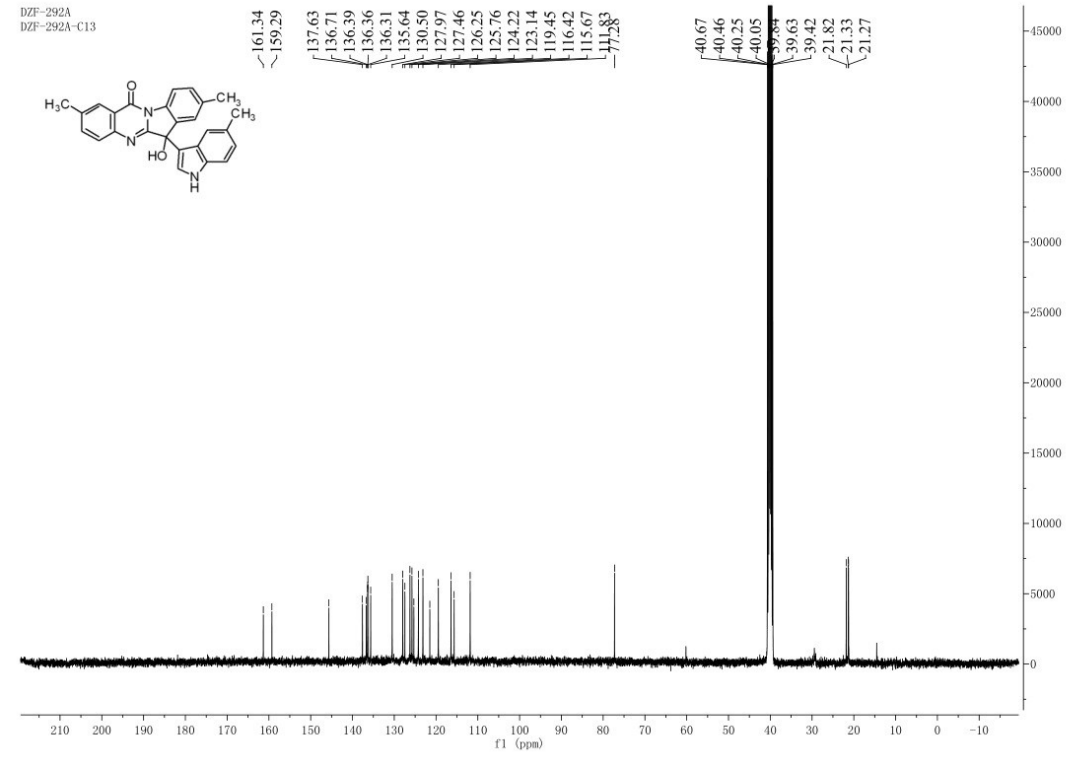




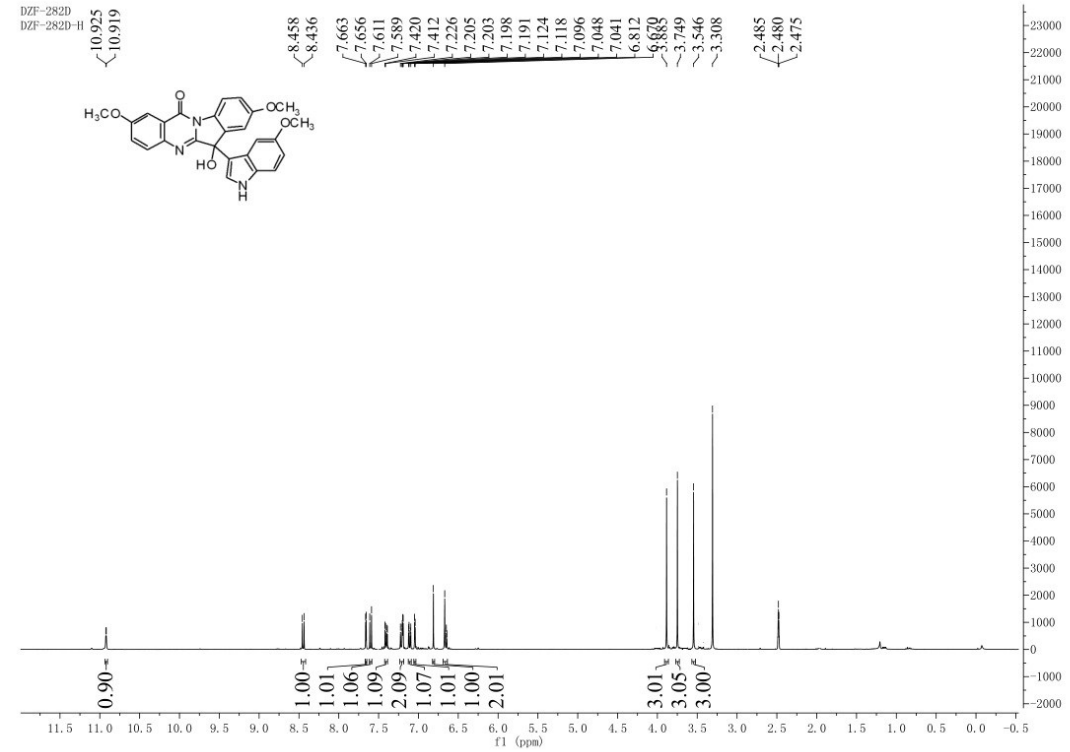
^{1}H and ^{13}C NMR Spectra for **6e**

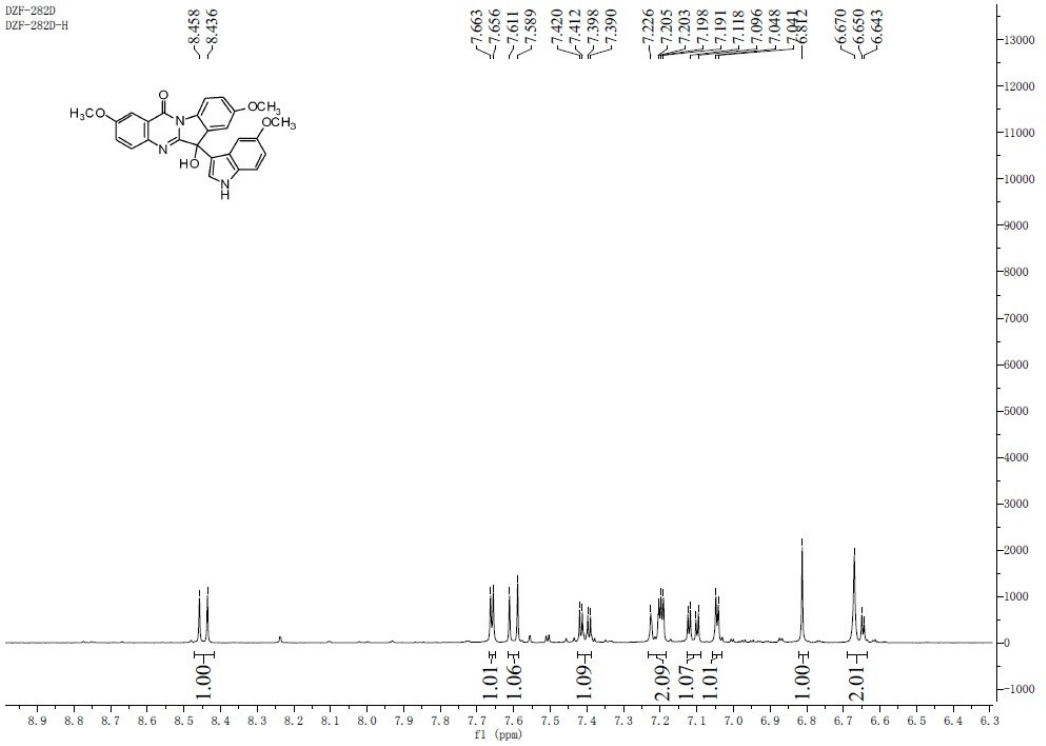


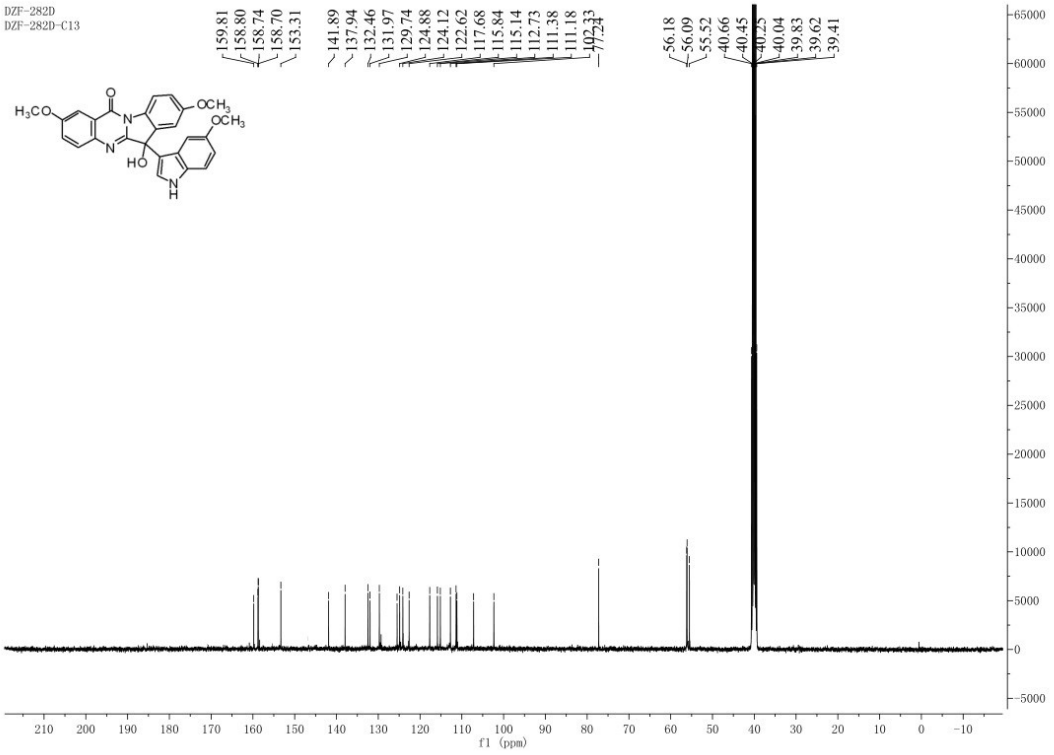

DZF-292A
DZF-292A-H
8.409
8.096
7.641
7.555
7.342
7.272
7.237
7.215
6.845
6.817
6.754
1.00
0.99
1.07
1.02
1.08
3.01
2.01
1.03
f1 (ppm)


DZF-292A
DZF-292A-C13
161.34
159.29
137.63
136.71
136.39
136.36
136.31
135.64
130.50
127.97
127.46
126.25
125.76
124.22
123.14
119.45
116.42
115.67
77.28
40.67
40.46
40.25
40.05
39.84
39.63
39.42
21.82
21.33
21.27
f1 (ppm)

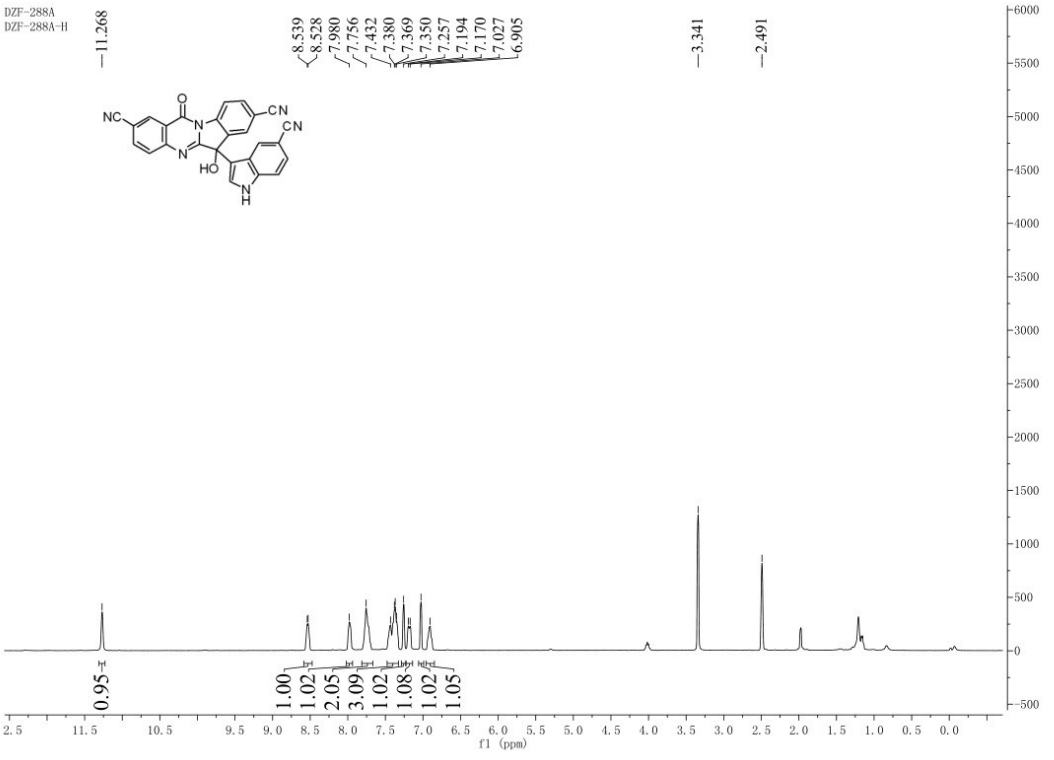
^{1}H and ^{13}C NMR Spectra for **6f**

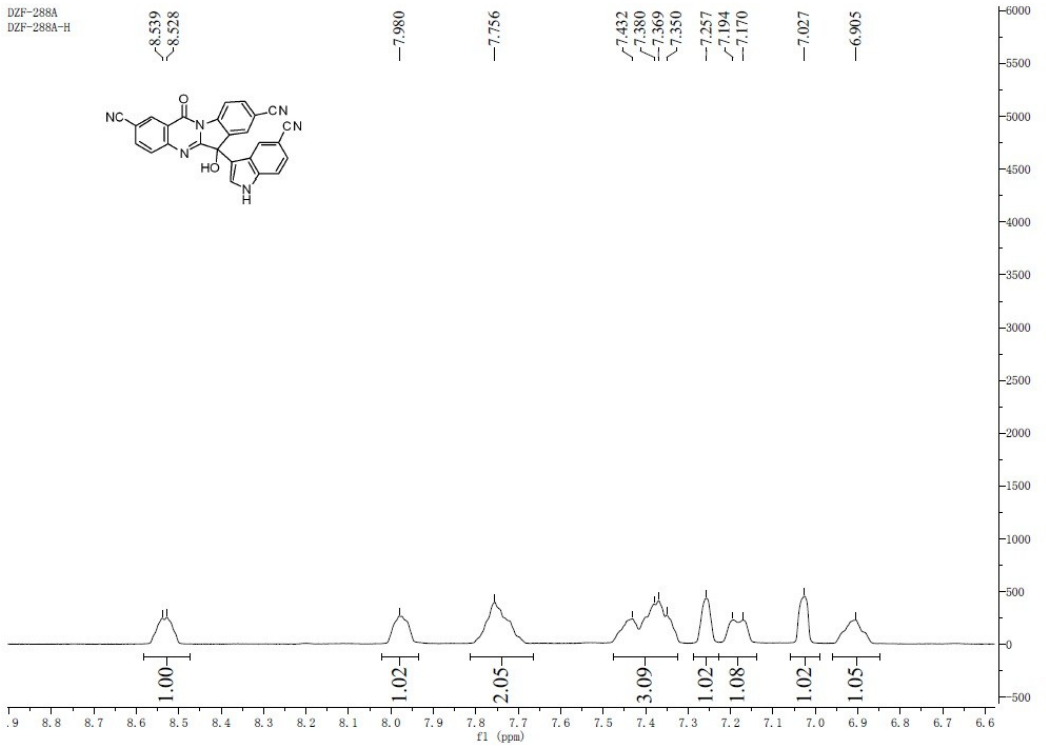


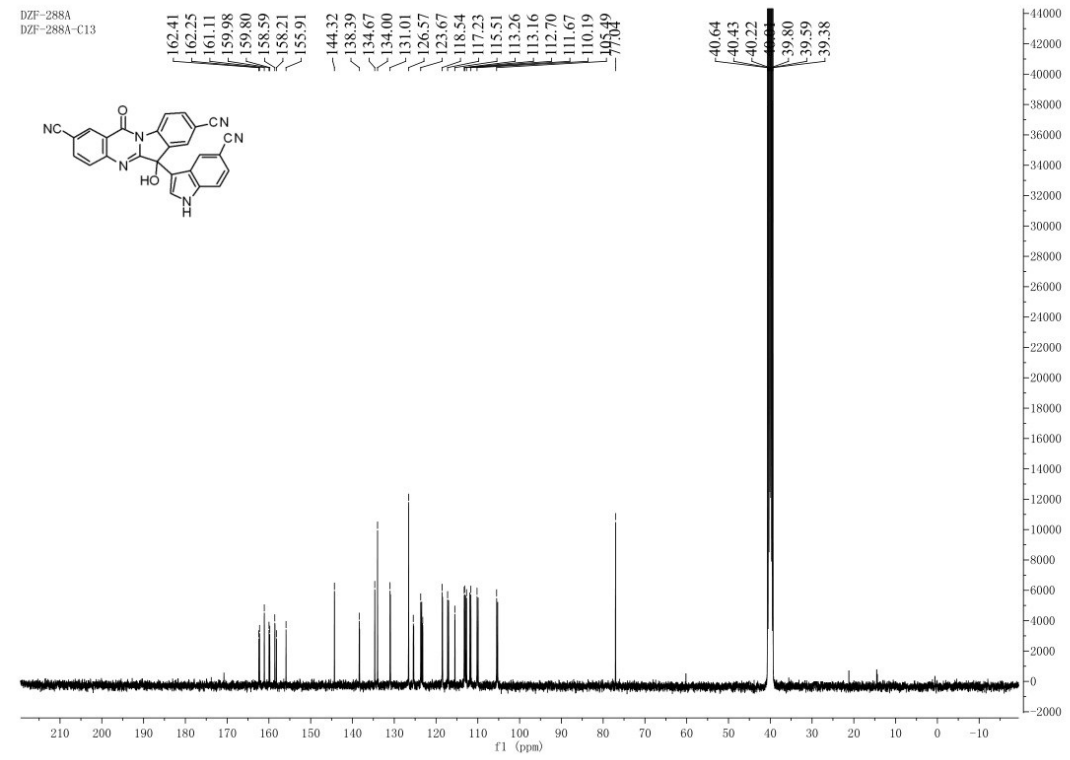




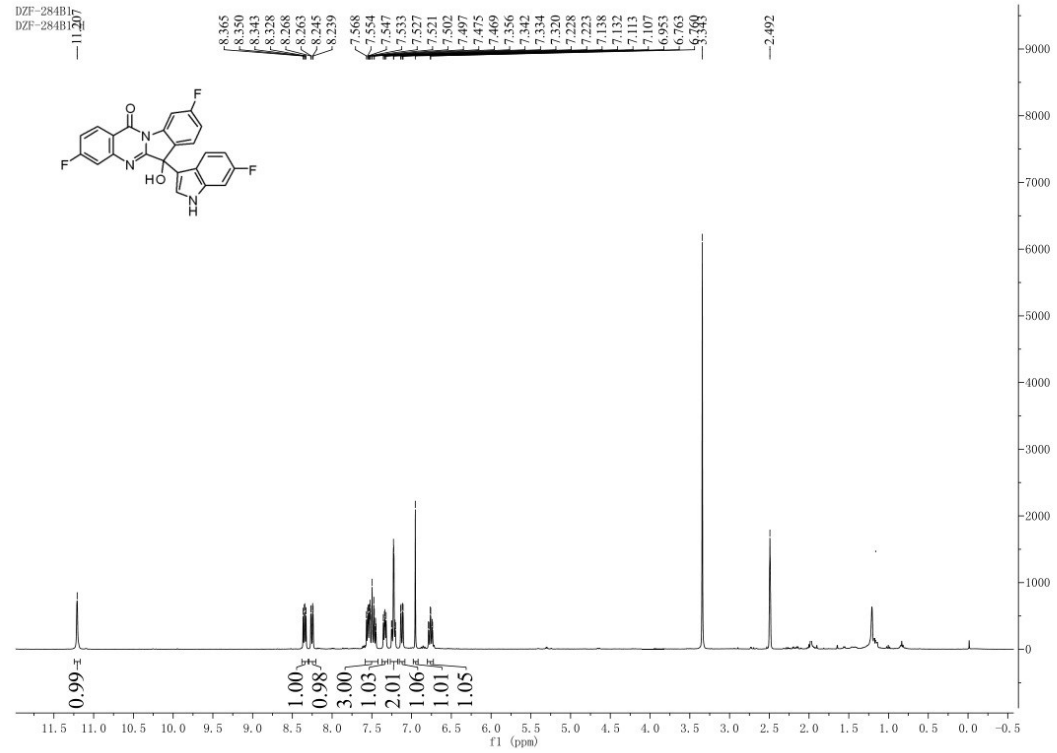
^{1}H and ^{13}C NMR Spectra for **6g**

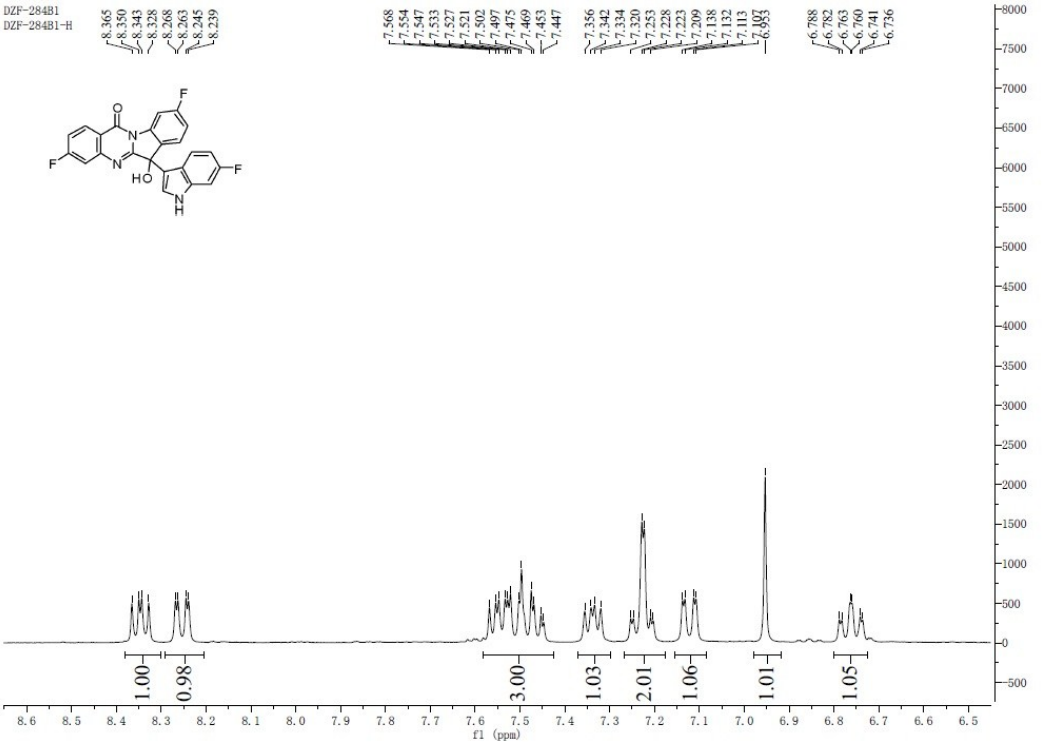


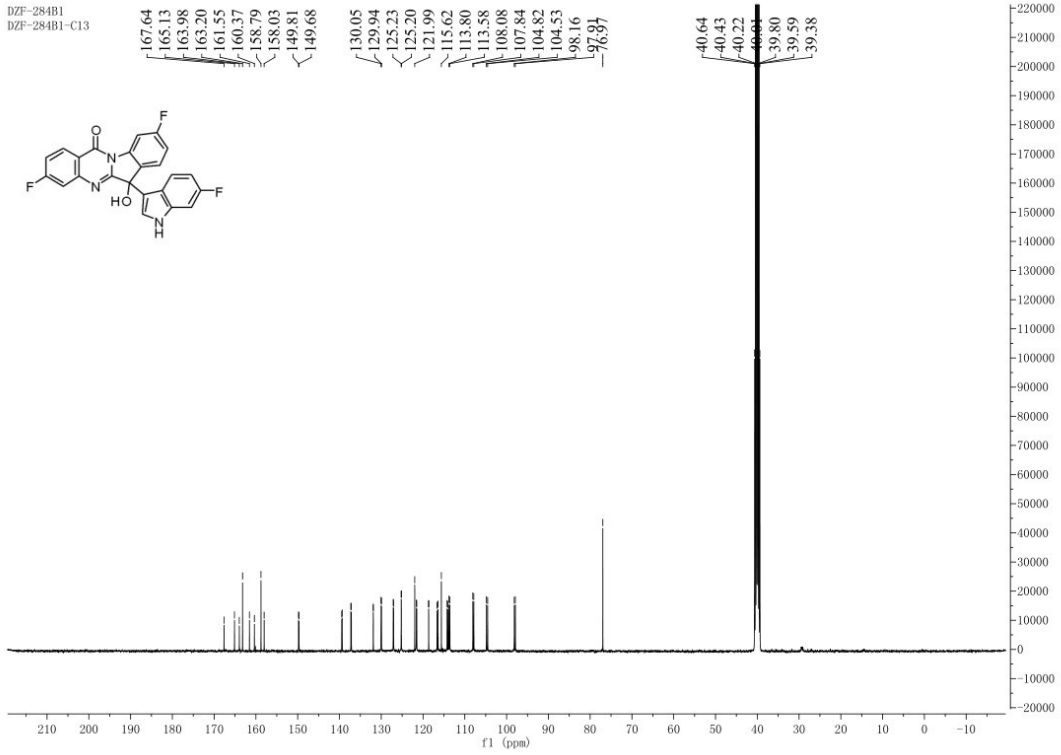

DZF-288A
DZF-288A-H
8.539
8.528
7.980
7.756
7.432
7.380
7.369
7.350
7.257
7.194
7.170
7.027
6.905
1.00
1.02
2.05
3.09
1.02
1.08
1.02
1.05
f1 (ppm)


DZF-288A
DZF-288A-C13
162.41
162.25
161.11
159.98
159.80
158.59
158.21
155.91
144.32
138.39
134.67
134.00
131.01
126.57
123.67
118.54
117.23
115.51
113.26
113.16
112.70
111.67
110.19
105.49
77.04
40.64
40.43
40.22
39.80
39.59
39.38
f1 (ppm)

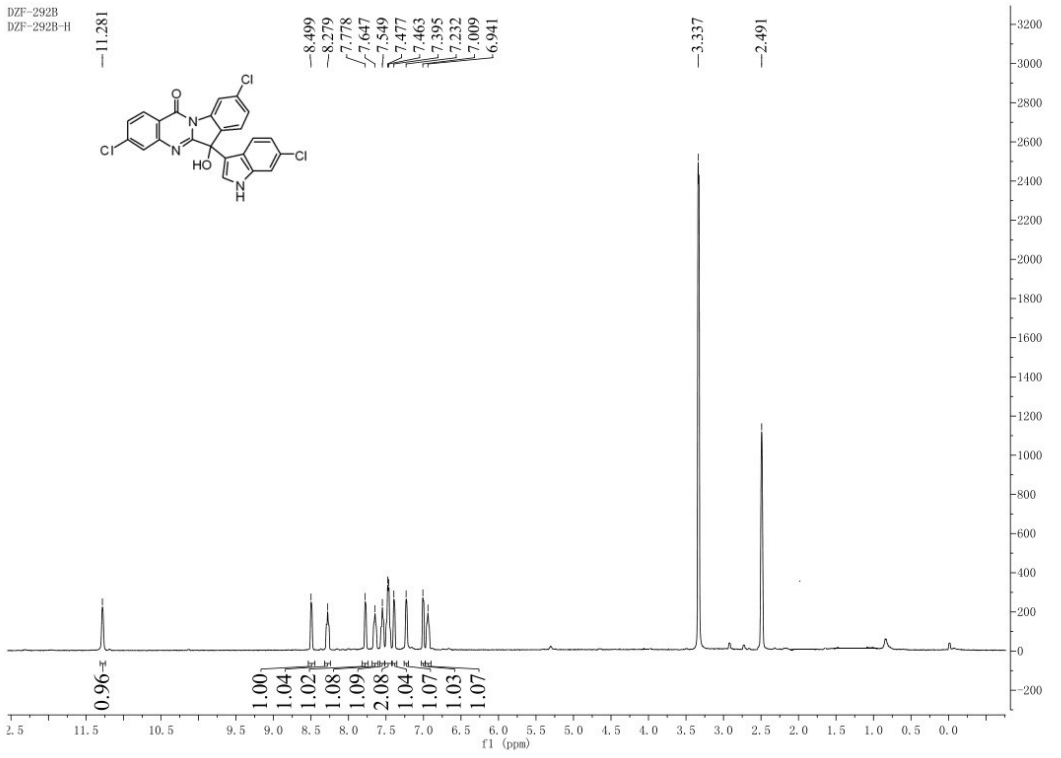
^{1}H and ^{13}C NMR Spectra for **6h**

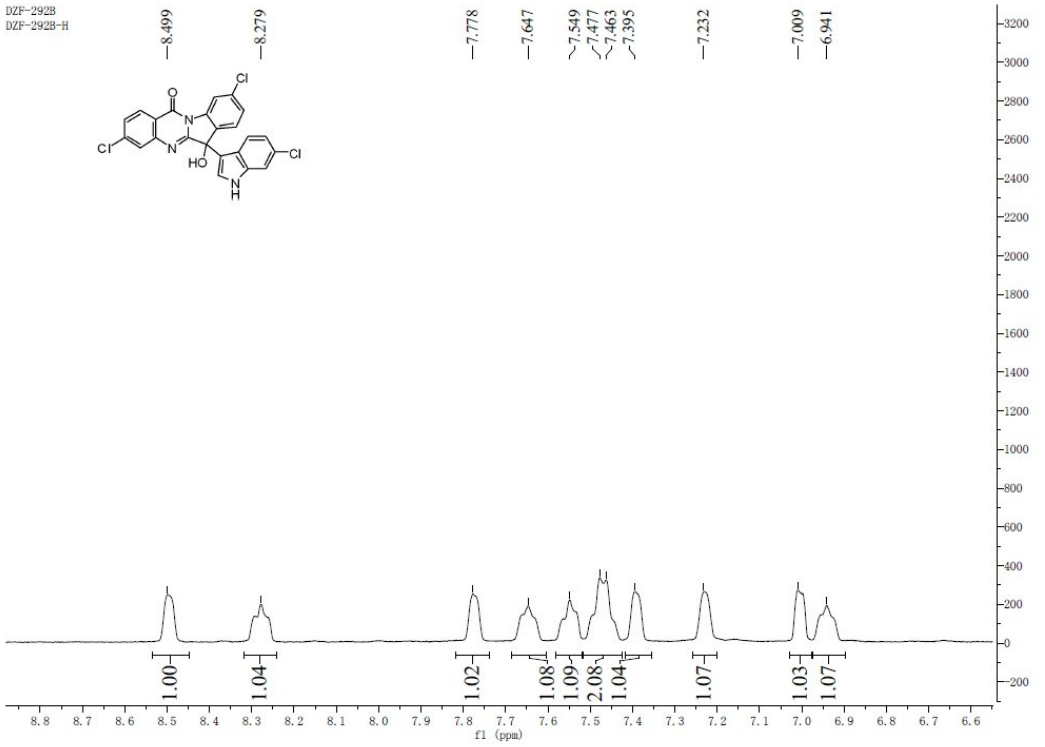


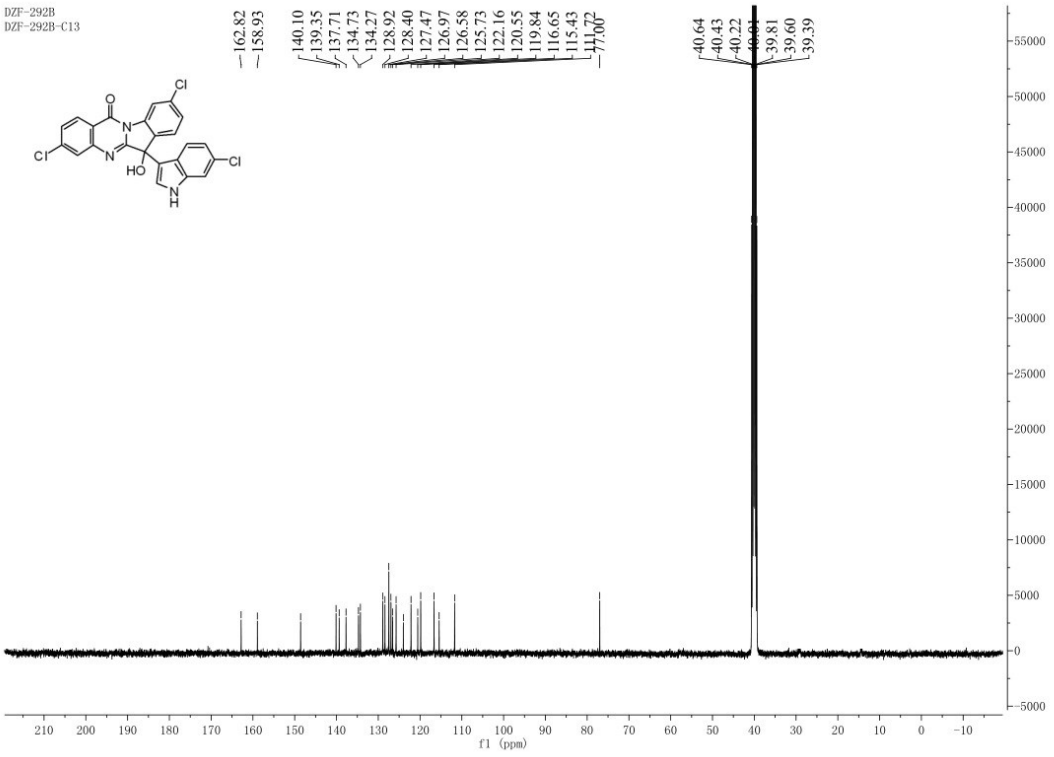




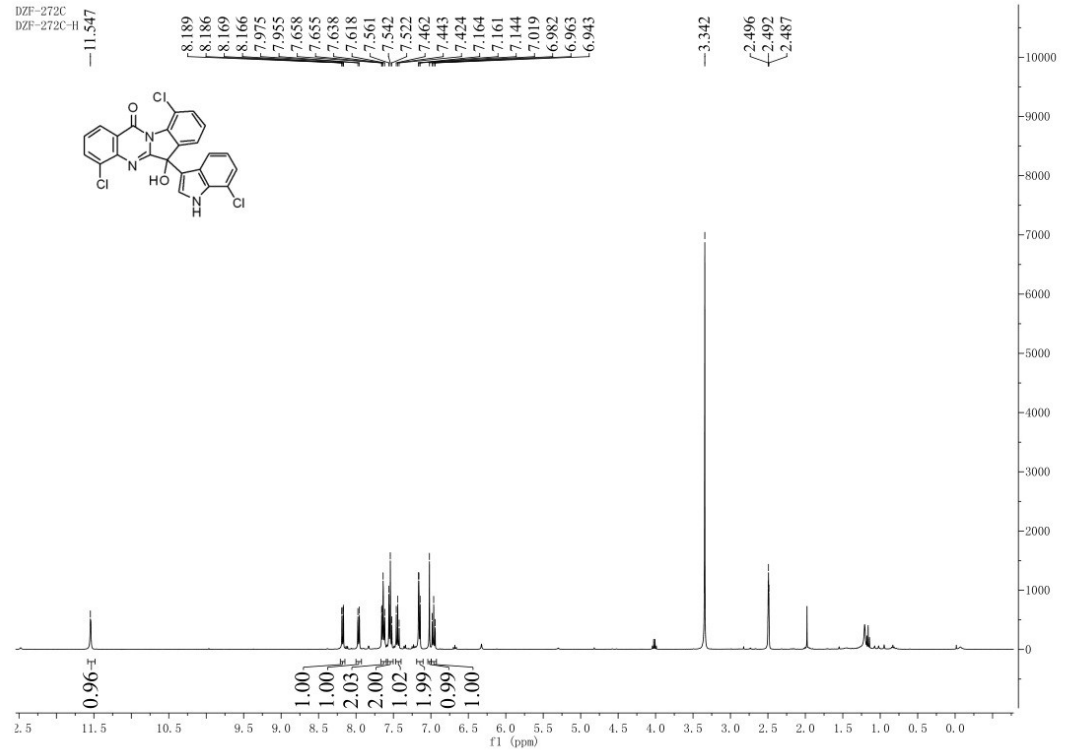
^{1}H and ^{13}C NMR Spectra for **6i**

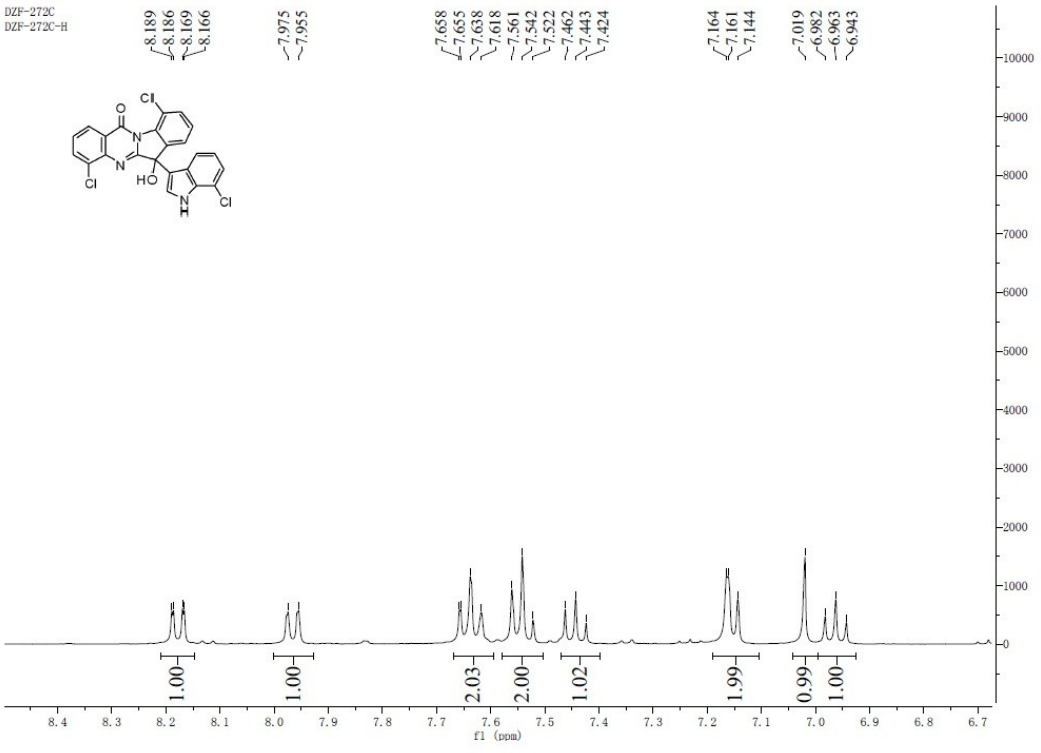


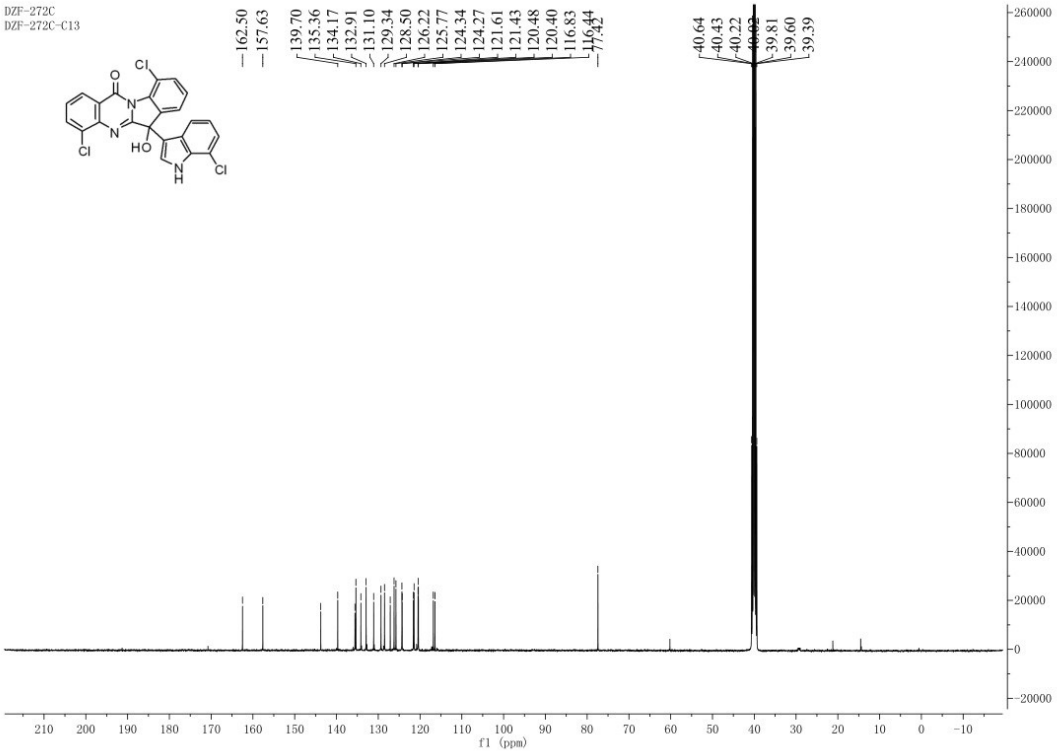

DZF-292B
DZF-292B-H
8.499
8.279
7.778
7.647
7.549
7.477
7.463
7.395
7.232
7.009
6.941
1.00
1.04
1.02
1.08
1.09
2.08
1.04
1.07
1.03
1.07
f1 (ppm)


DZF-292B
DZF-292B-C13
162.82
158.93
140.10
139.35
137.71
134.73
134.27
128.92
128.40
127.47
126.97
126.58
125.73
122.16
120.55
119.84
116.65
115.43
111.72
77.00
40.64
40.43
40.22
40.01
39.81
39.60
39.39
f1 (ppm)

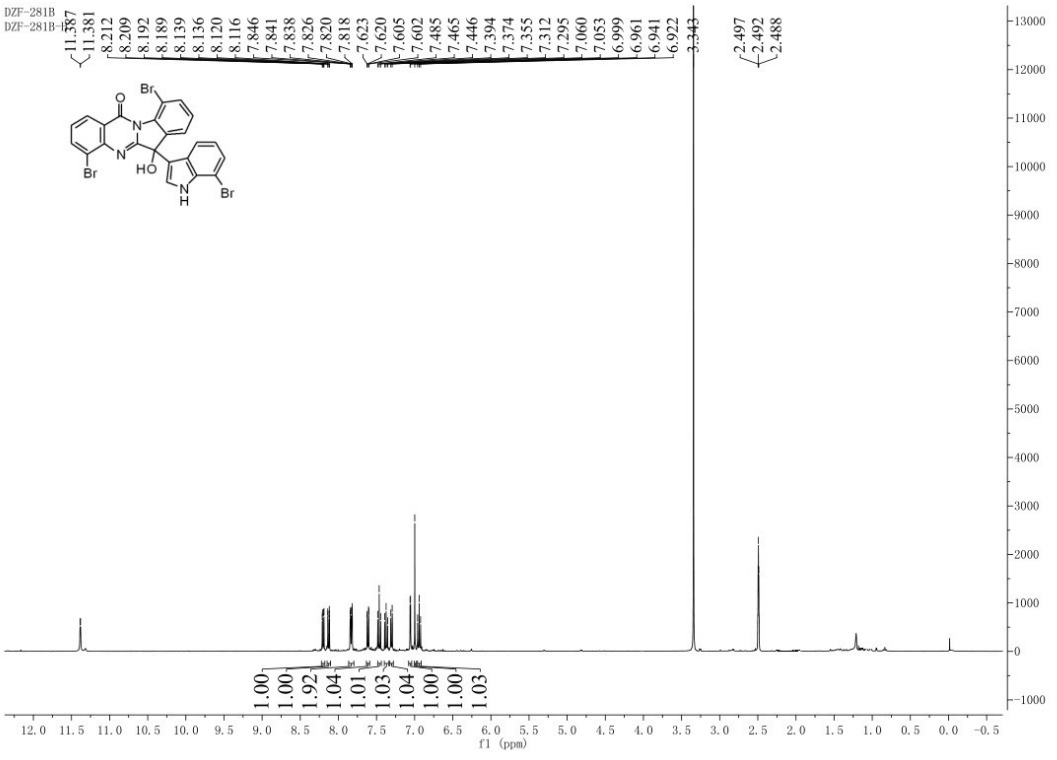
^{1}H and ^{13}C NMR Spectra for **6j**

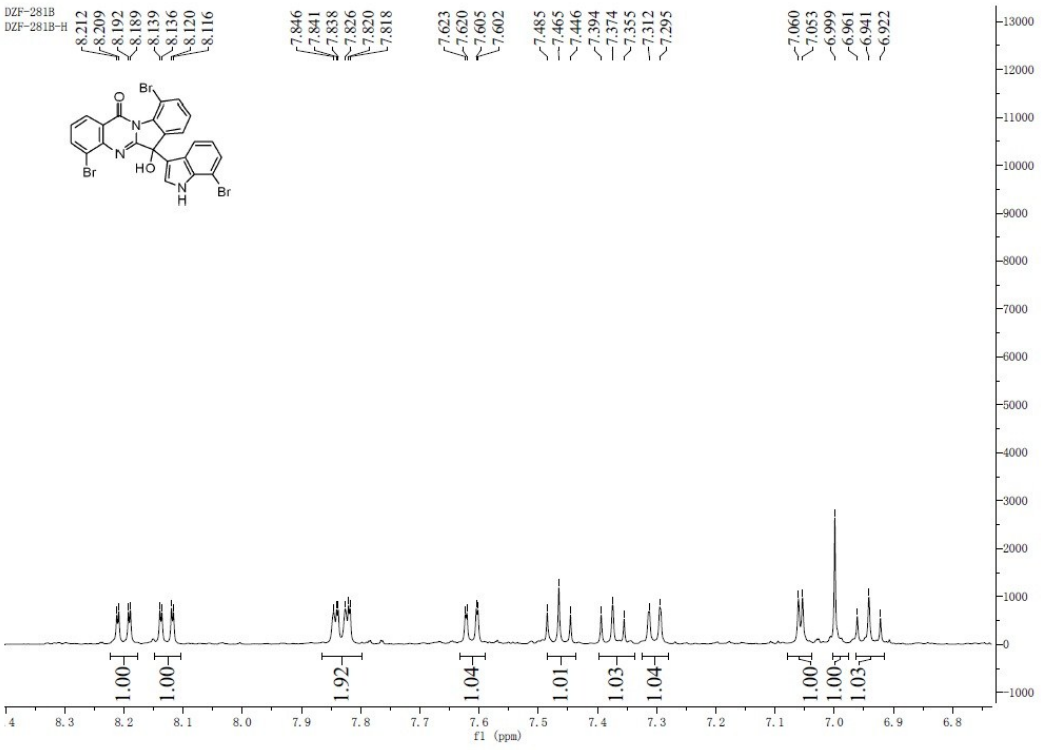


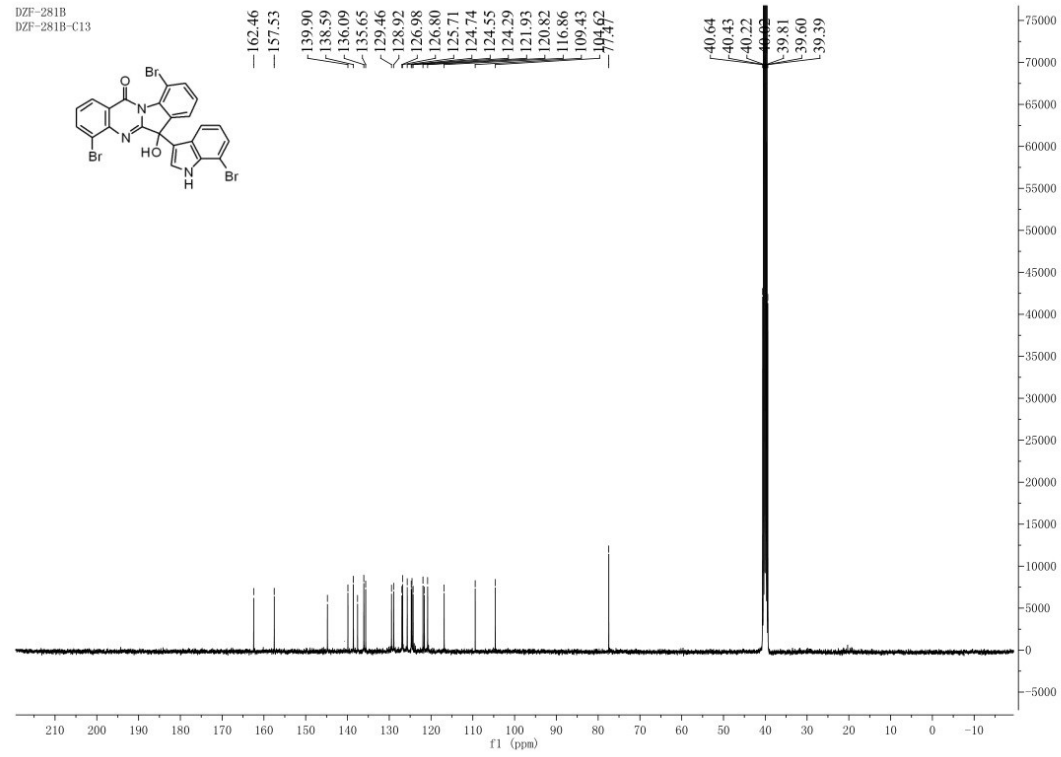




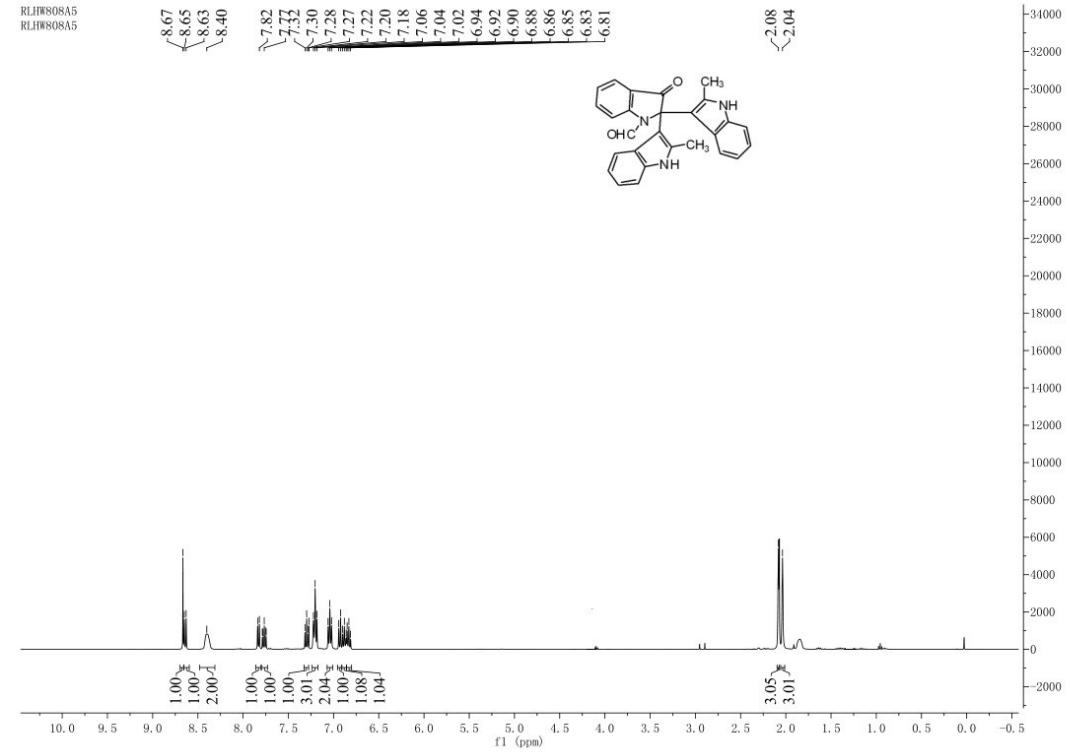
^{1}H and ^{13}C NMR Spectra for **6k**

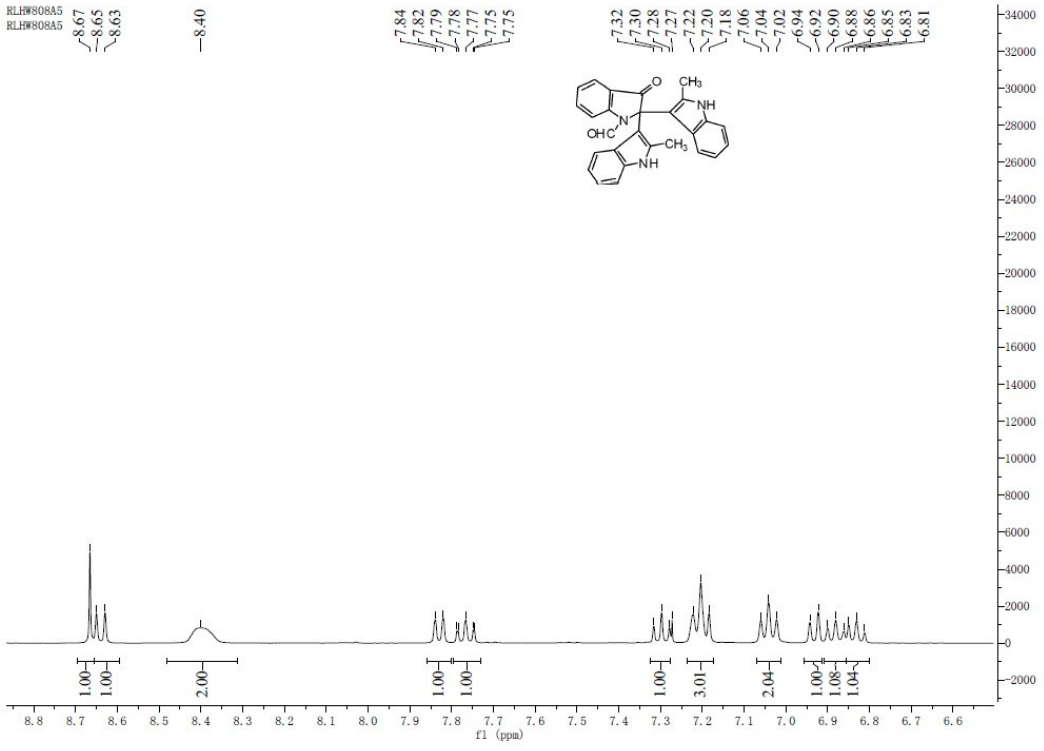


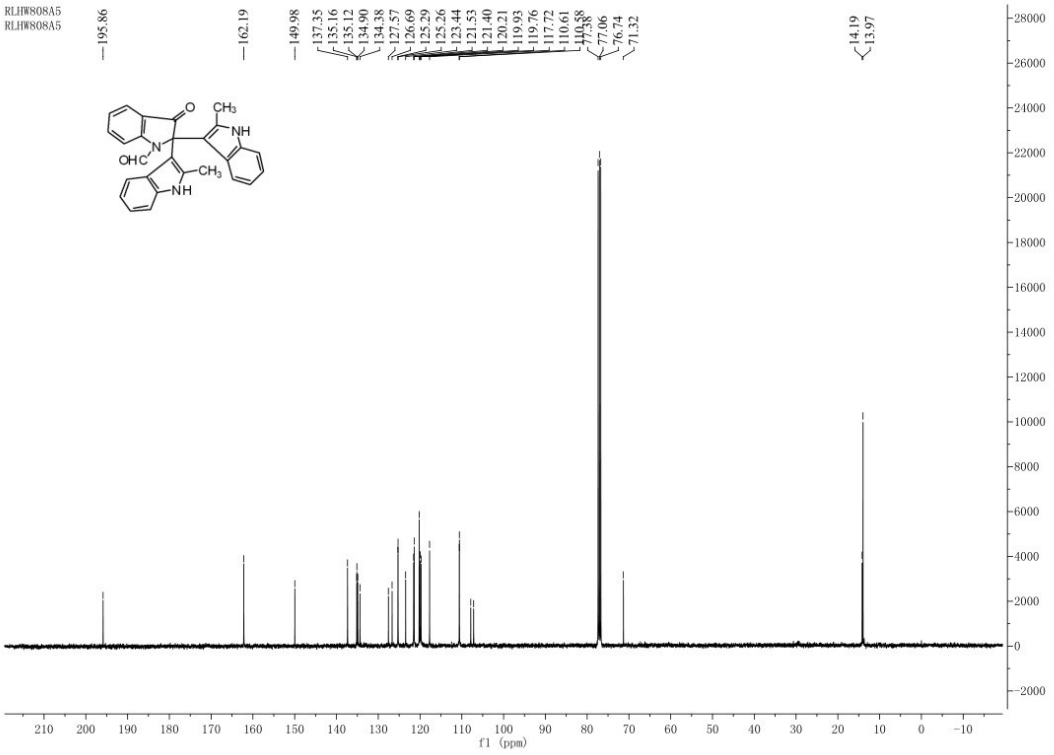

DZF-281B
DZF-281B-H
8.212
8.209
8.192
8.189
8.139
8.136
8.120
8.116
7.846
7.841
7.838
7.826
7.820
7.818
7.623
7.620
7.605
7.602
7.485
7.465
7.446
7.394
7.374
7.355
7.312
7.295
7.060
7.053
6.999
6.961
6.941
6.922
1.00
1.00
1.92
1.04
1.01
1.03
1.04
1.00
1.00
1.03
f1 (ppm)


DZF-281B
DZF-281B-C13
162.46
157.53
139.90
138.59
136.09
135.65
129.46
128.92
126.98
126.80
125.71
124.74
124.55
124.29
121.93
120.82
116.86
109.43
40.64
40.43
40.22
39.81
39.60
39.39
f1 (ppm)

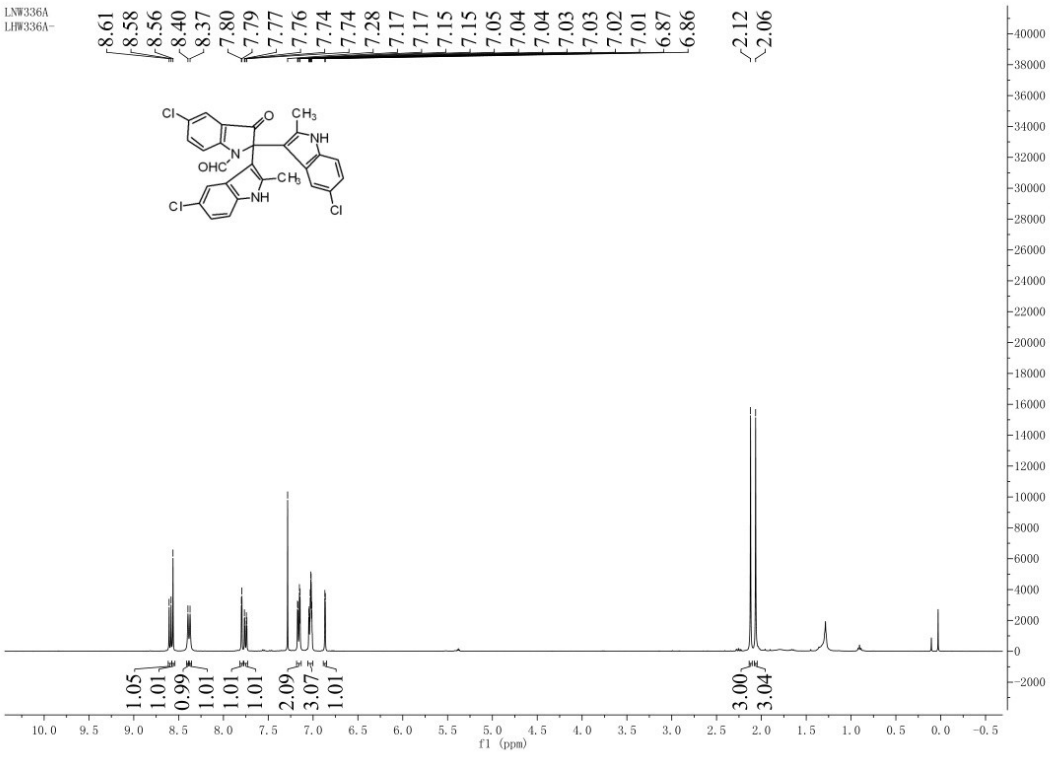
^{1}H and ^{13}C NMR Spectra for **8a**

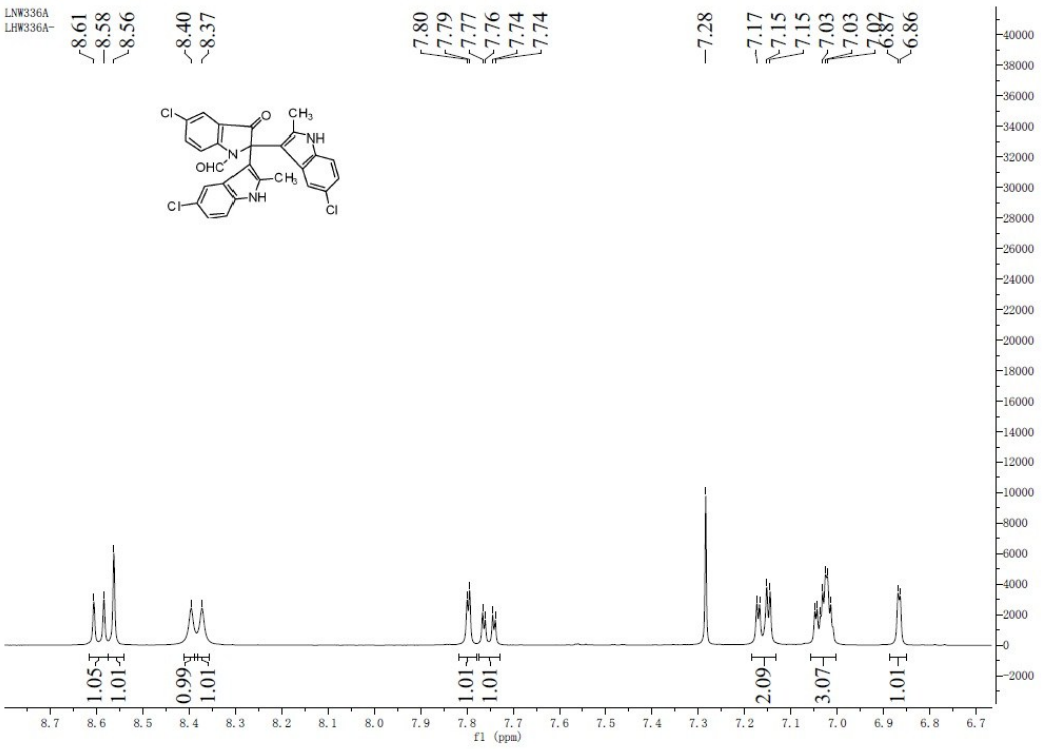


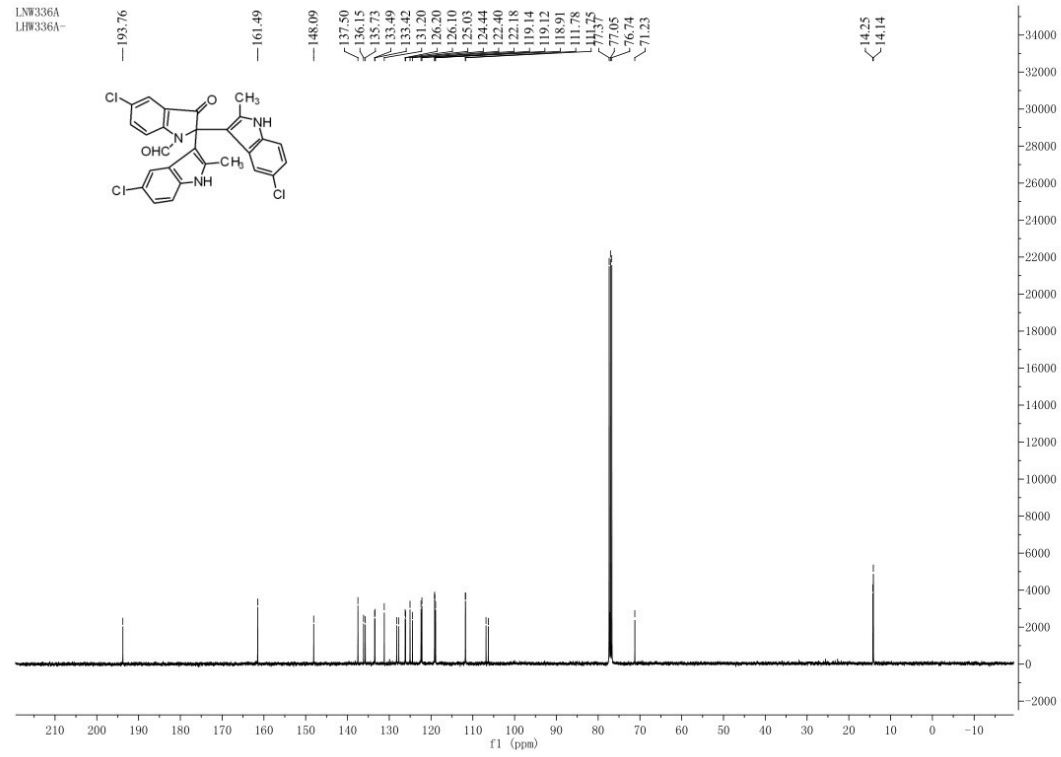




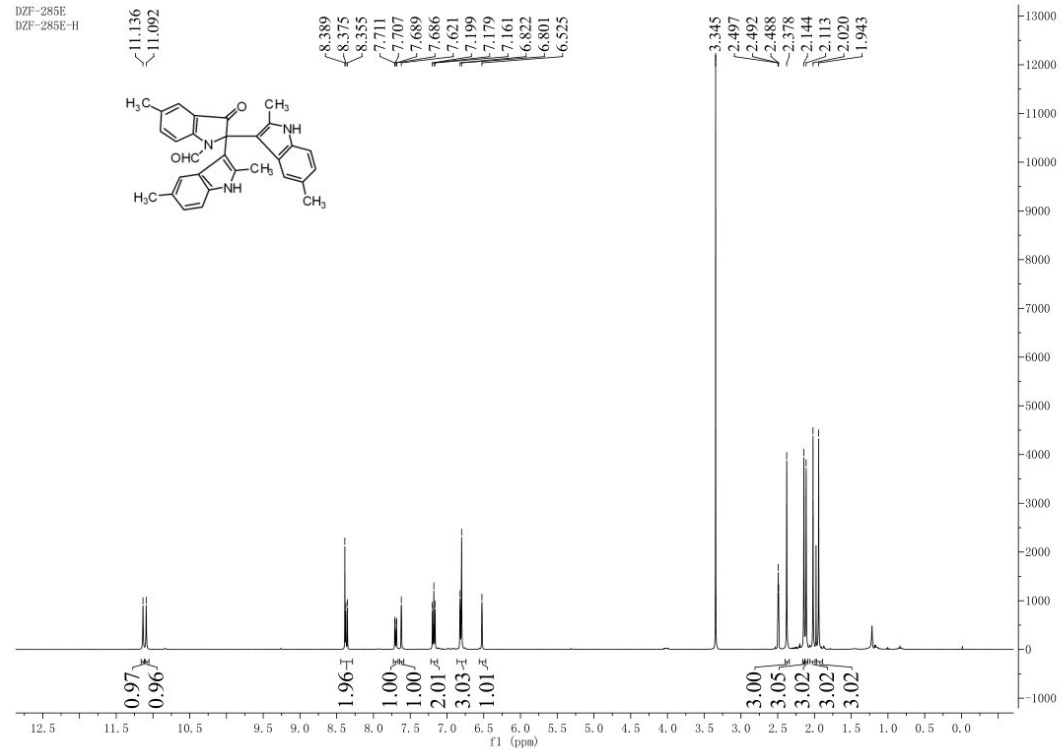
^{1}H and ^{13}C NMR Spectra for **8b**

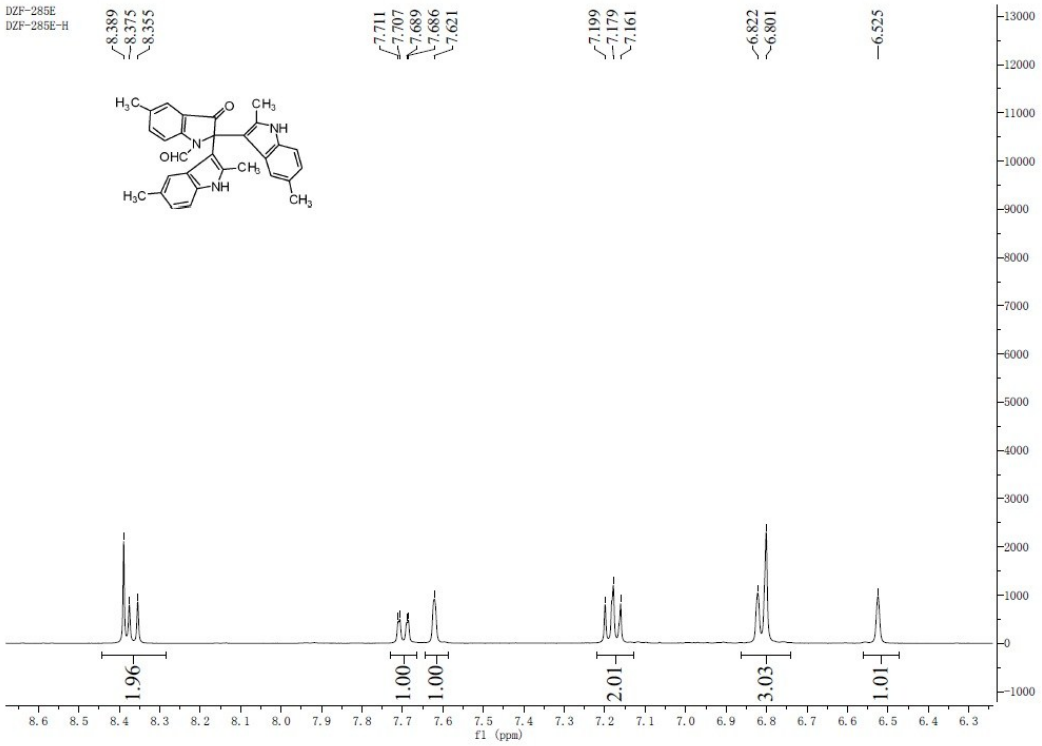


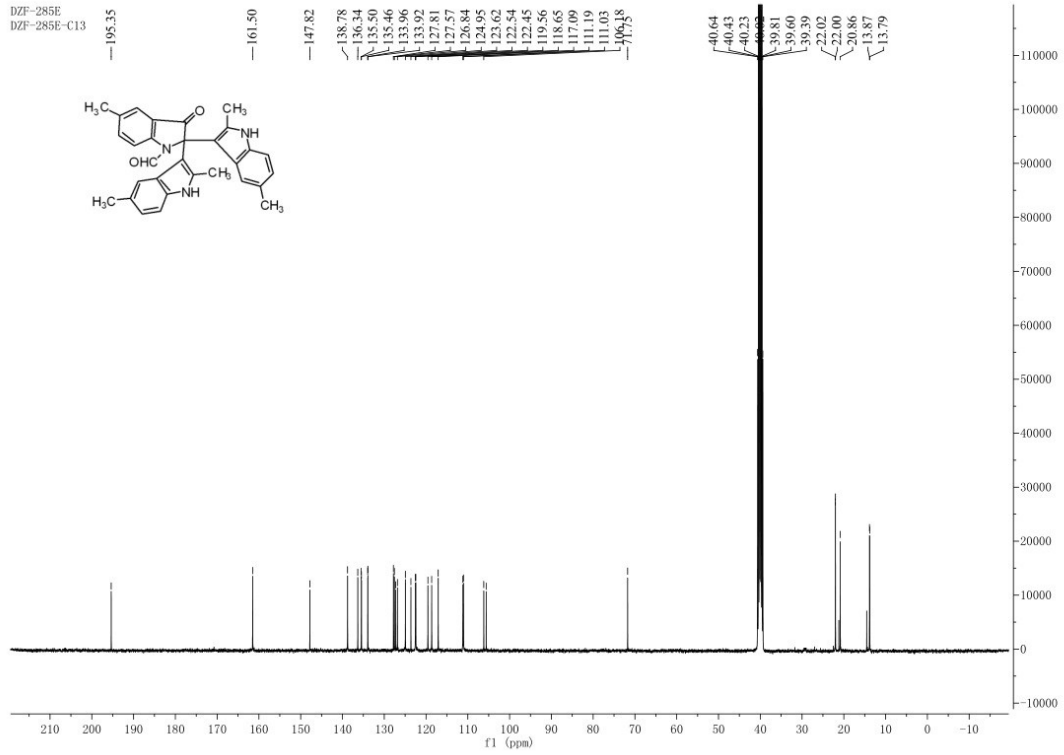

LNW336A
LHW336A-
8.61
8.58
8.56
8.40
8.37
7.80
7.79
7.77
7.76
7.74
7.74
7.28
7.17
7.15
7.15
7.03
7.03
7.02
6.87
6.86
1.05
1.01
0.99
1.01
1.01
1.01
2.09
3.07
1.01
f1 (ppm)


LNW336A
LHW336A-
193.76
161.49
148.09
137.50
136.15
135.73
133.49
133.42
131.20
126.20
126.10
125.03
124.44
122.40
122.18
119.14
119.12
118.91
111.78
111.75
77.37
77.05
76.74
71.23
14.25
14.14
f1 (ppm)

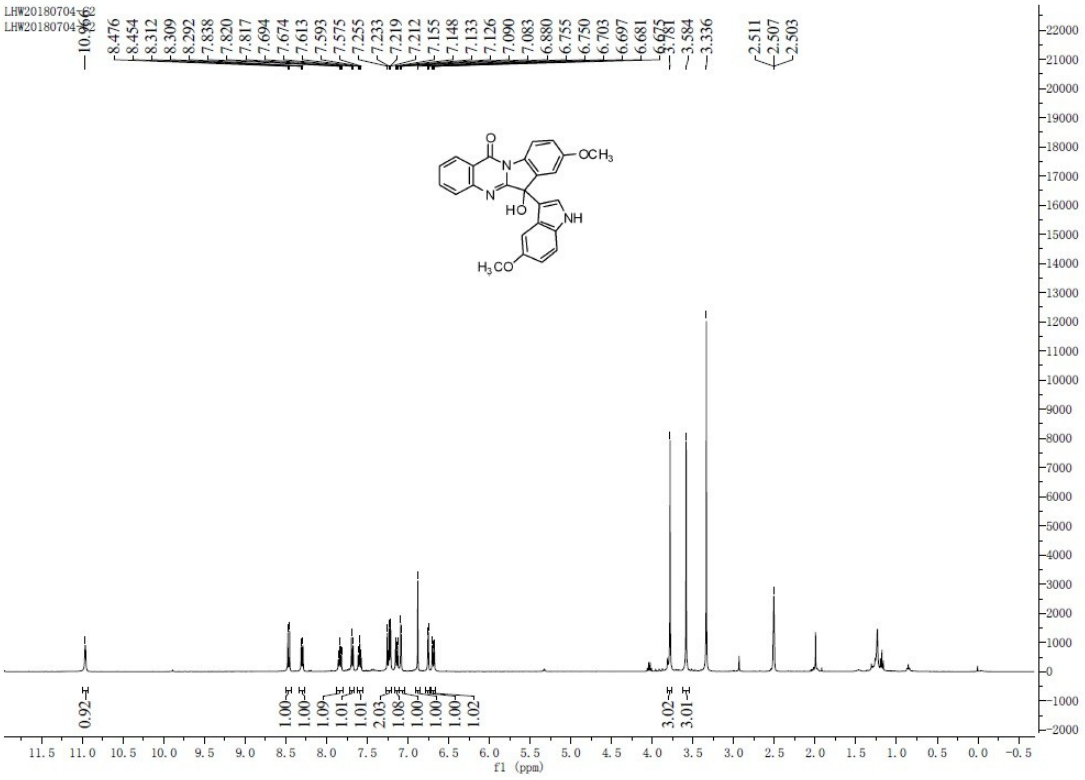
^{1}H and ^{13}C NMR Spectra for **8c**

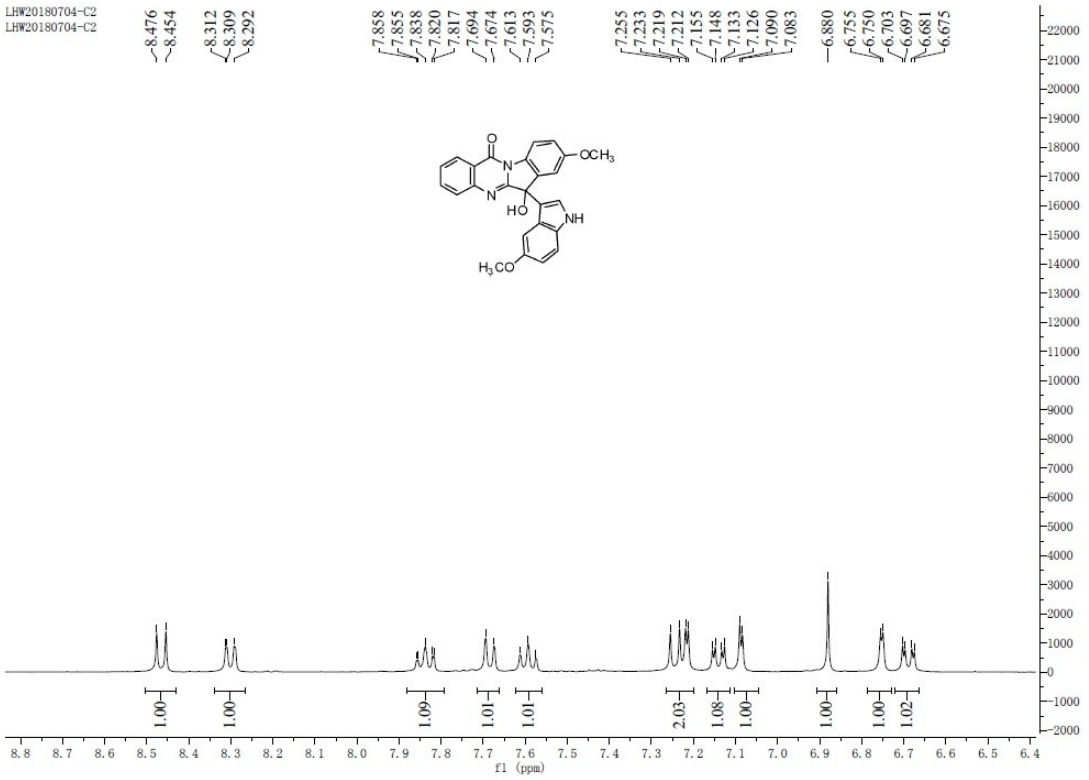


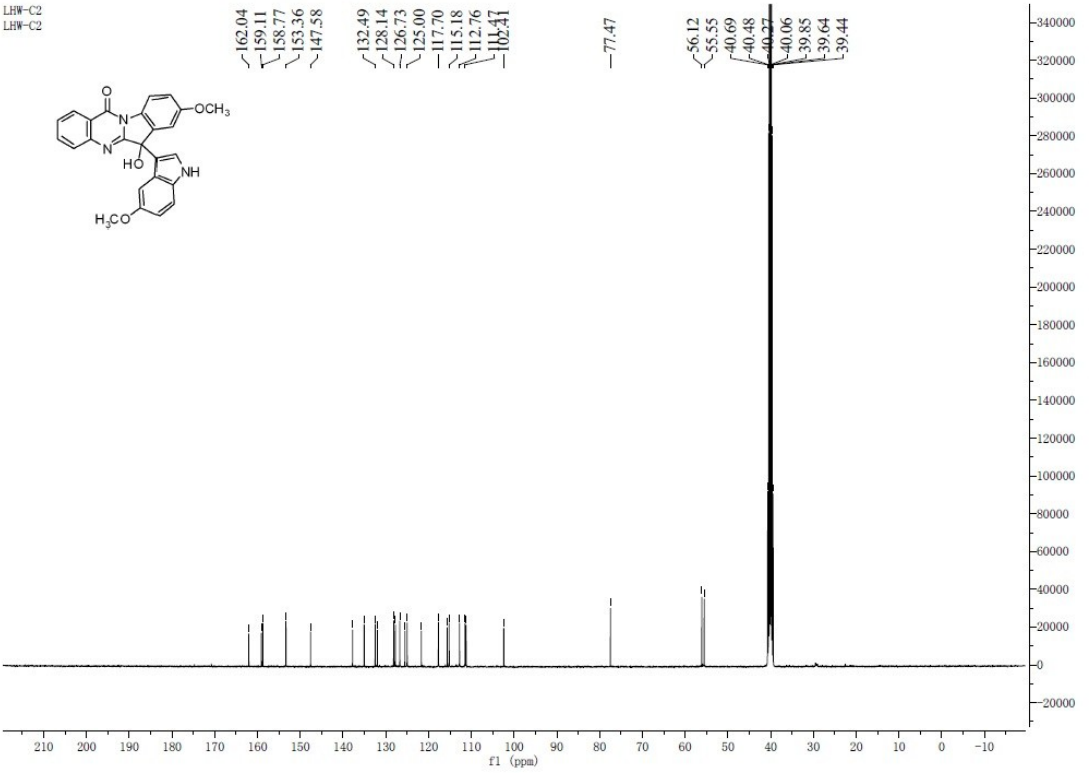




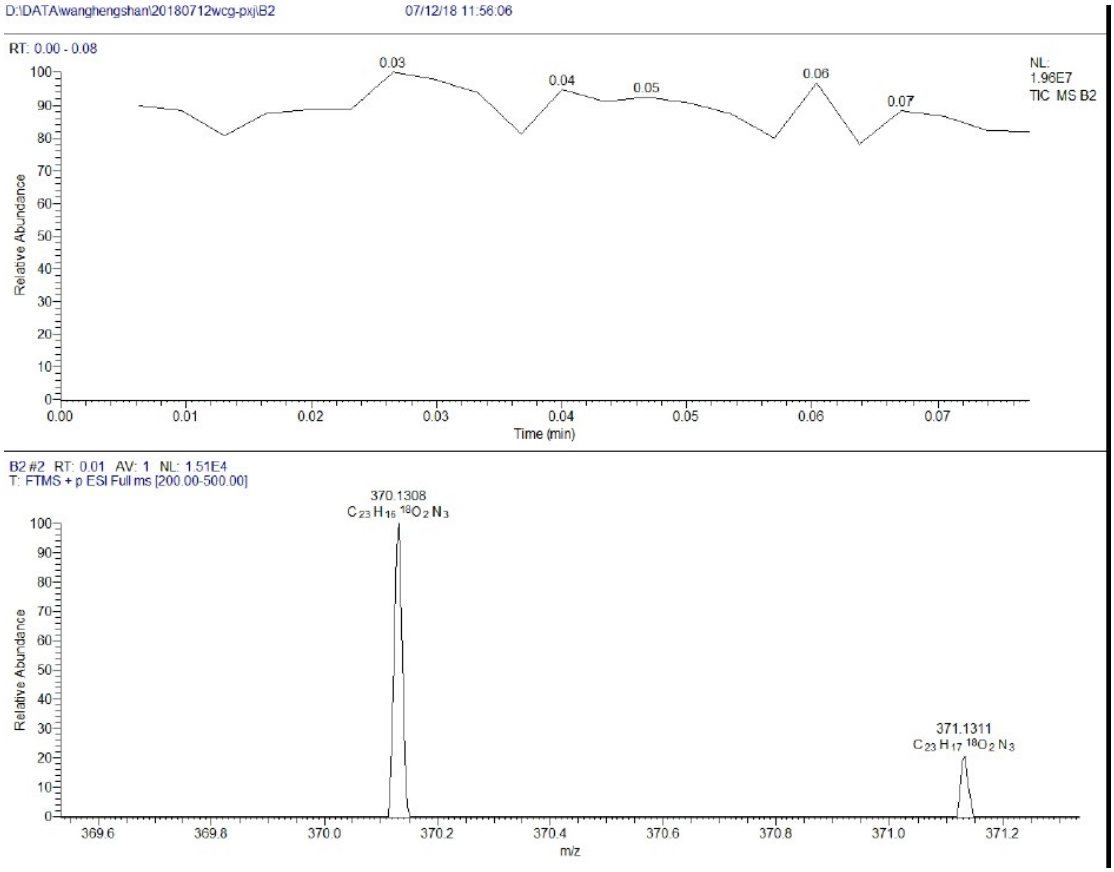
^{1}H and ^{13}C NMR Spectra for **10**




LHW20180704-C2
LHW20180704-C2
8.476
8.454
8.312
8.309
8.292
7.858
7.855
7.838
7.820
7.817
7.694
7.674
7.613
7.593
7.575
7.255
7.233
7.219
7.212
7.155
7.148
7.133
7.126
7.090
7.083
6.880
6.755
6.750
6.703
6.697
6.681
6.675
OCH3
HO
NH
H3CO
1.00
1.00
1.09
1.01
1.01
2.03
1.08
1.00
1.00
1.00
1.02
f1 (ppm)


LHW-C2
LHW-C2
162.04
159.11
158.77
153.36
147.58
132.49
128.14
126.73
125.00
117.70
115.18
112.76
111.47
102.41
77.47
56.12
55.55
40.69
40.48
40.27
40.06
39.85
39.64
39.44
OCH3
HO
NH
H3CO
f1 (ppm)

6. Copies of HRESIMS Spectra for ***[18]*O-6a**



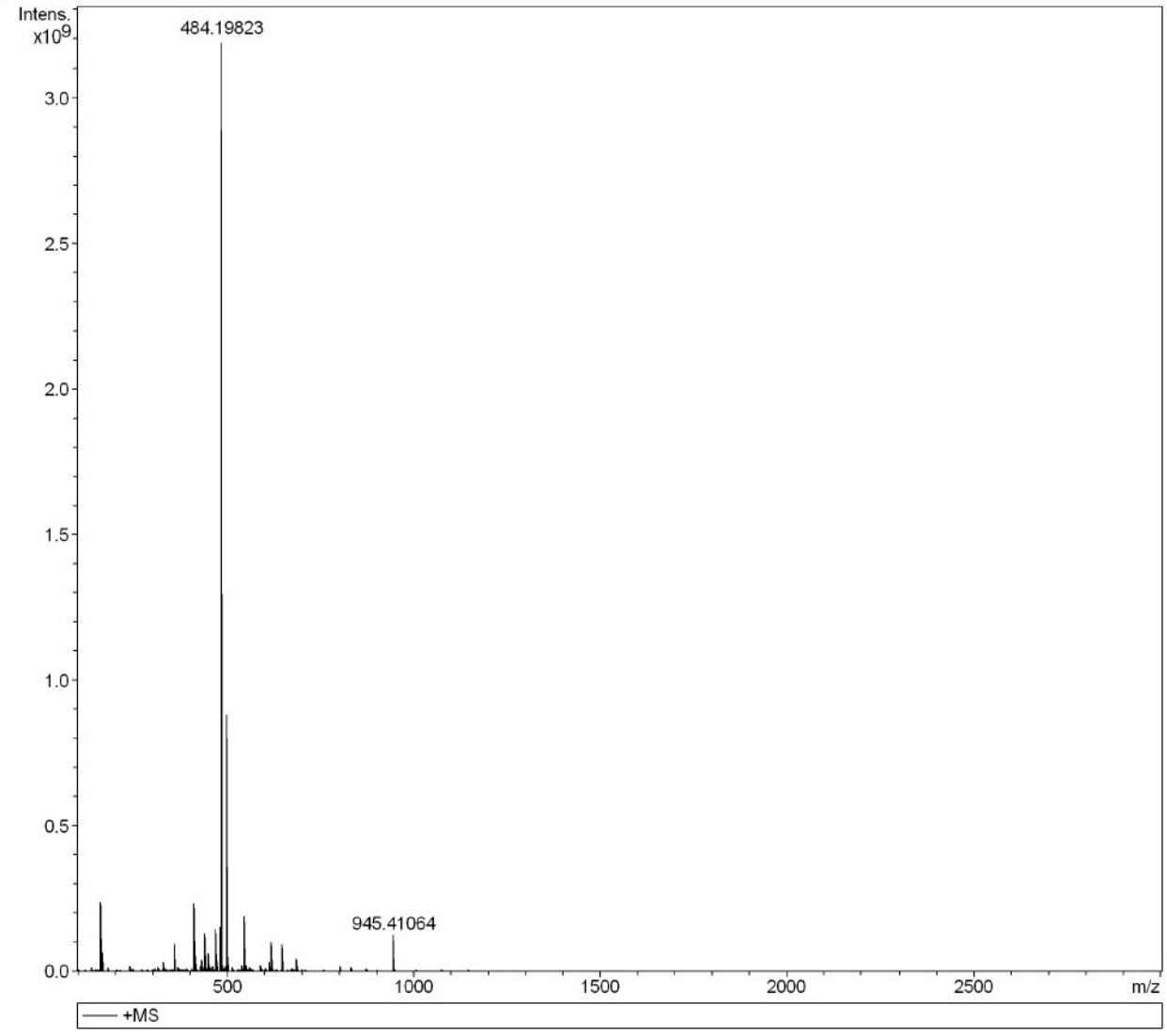
Copies of HRESIMS Spectra for **8c**

Analysis Info

Analysis Name	D:\Data\origin data\zhanghuijun\wujiajun\20170801\POS_ESI_20170801_285E_000002.d	Acquisition Date	8/1/2017 10:47:37
Method	APEX_Pos_NaFA_400_20100407	Operator	
Sample Name		Instrument	apex-Ultra
Comment			

Acquisition Parameter

Polarity	Positive	Source	ESI	No. of Laser Shots	20
Averaged Scans	2	No. of Cell Fills	1	Laser Power	51.0 %
Broadband Low Mass	100.4 m/z	End Plate	3900.0 V	MALDI Plate	300.0 V
Broadband High Mass	3000.0 m/z	Capillary Entrance	4400.0 V	Imaging Spot Diameter	2000.0 µm
Acquisition Mode	Single MS	Skimmer 1	36.0 V		
Pulse Program	basic	Drying Gas Temperature	200.0 °C	Calibration Date	Fri Jul 28 08:24:01 2017
Source Accumulation	0.0 sec	Drying Gas Flow Rate	4.0 L/min	Data Acquisition Size	1048576
Ion Accumulation Time	1.0 sec	Nebulizer Gas Flow Rate	1.0 L/min	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.0 sec				



Bruker Compass DataAnalysis 4.0 printed: 8/1/2017 10:49:05 Page 1 of 1

7. X-ray Data of Compound 6a.

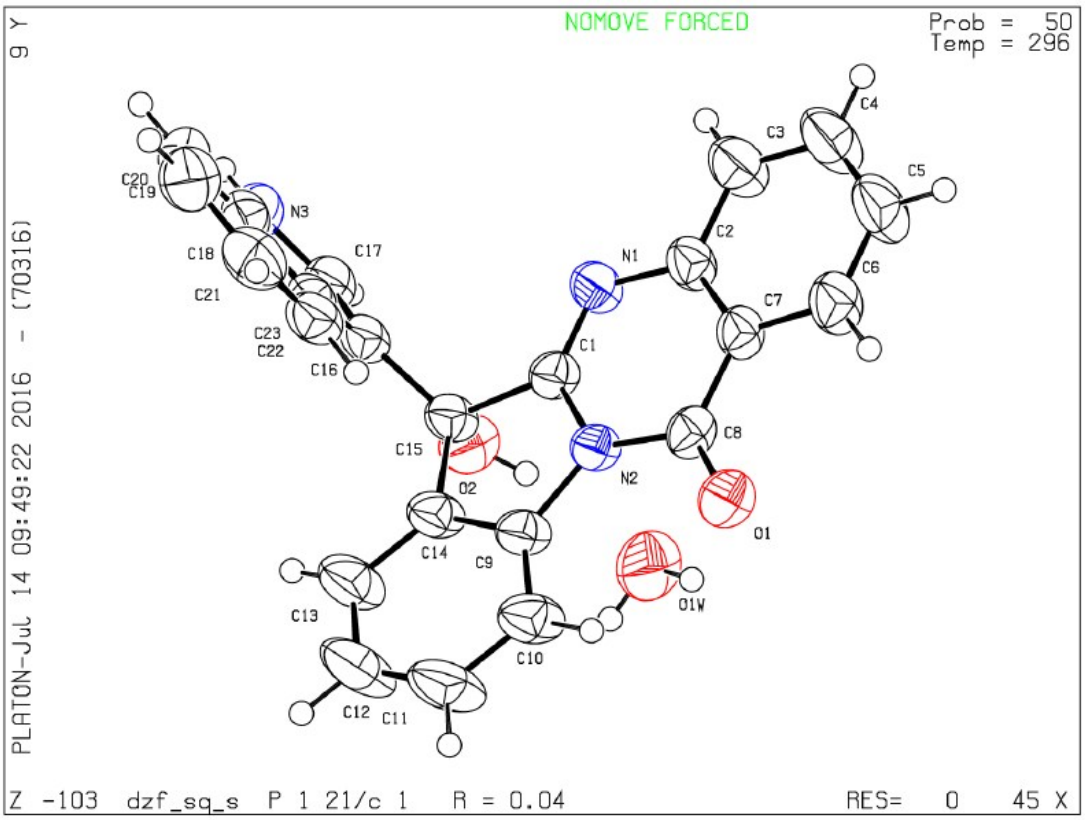


Figure 1. ORTEP representation of the molecular structure of **6a**. The data have been assigned the following deposition numbers, **CCDC 1842423**.

8. X-ray Data of Compound 8a.

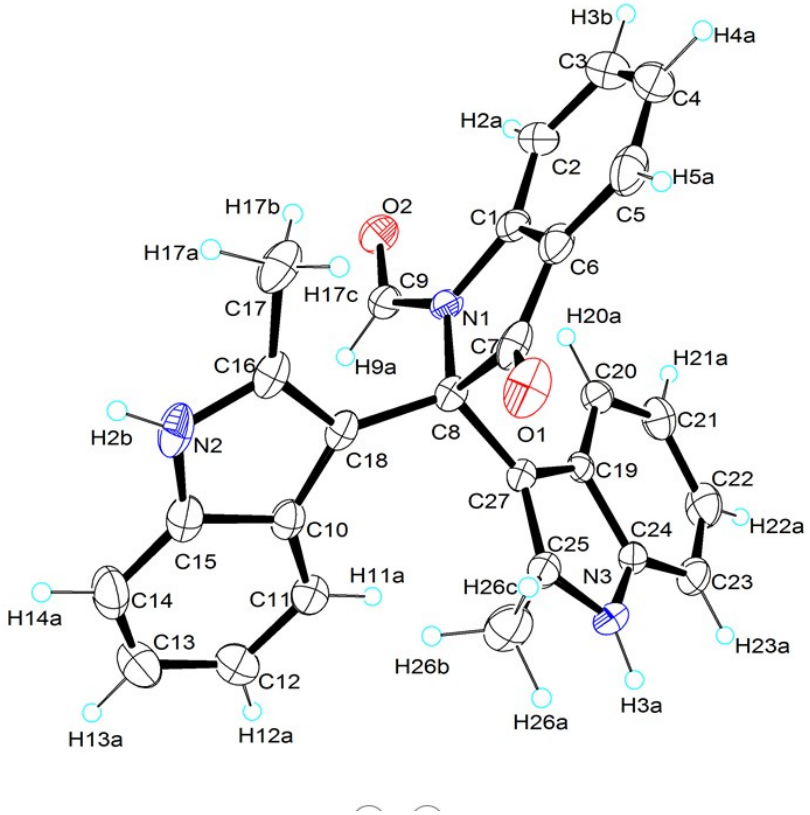


Figure 2. ORTEP representation of the molecular structure of **8a**. The data have been assigned the following deposition numbers, **CCDC 1556114**.

9. References

(1) B. V. S. Reddy, D. M. Reddy, G. N. Reddy, M. R. Reddy and V. K. Reddy, *Eur. J. Org. Chem.* **2015**, 8018–8022.