Diastereoselective synthesis of polycyclic indolines via dearomative [4+2] cycloaddition of 3-nitroindoles with *ortho*-aminophenyl *p*-quinone methides

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Supporting Information

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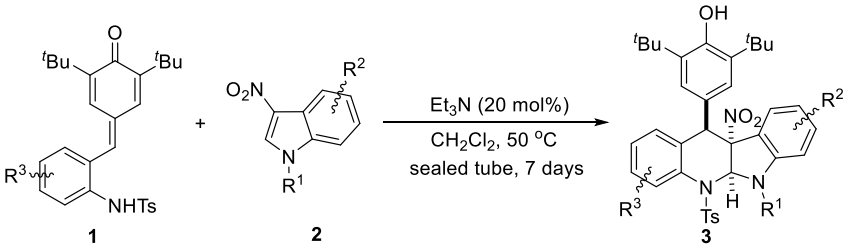
1. General experimental information

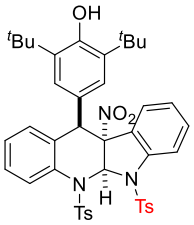
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). The enantiomeric excesses were determined by chiral HPLC analysis. HPLC analysis was performed on Shimadzu SCL-10AVP HPLC systems and Agilent 1260 Infinity Ⅱ consisting of the followings: pump, LC-10AD and G7129A; detector, SPD-10A and G7114A measured at 254 nm. Melting points products were recorded on a Büchi Melting Point B-545. The HRMS were recorded by Agilent 6545 LC/Q-TOF mass spectrometer.

2. General procedure for the synthesis of 3



In a sealed tube equipped with a magnetic stirring bar, the 3-nitroindoles **1** (0.05 mmol, 1 equiv), *ortho*-tosylaminophenyl *p*-QMs **2** (0.05 mmol, 1.0 equiv), triethylamine (20 mol%) and dichloromathane (0.5 mL) were added. And then, the mixture was stirred at 50 ℃ for 7 days. After completion of the reaction as indicated by TLC. the products **3** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 ~ 5/1).

2,6-di-*tert*-butyl-4-(10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5*H*-indolo[2,3-b]quinolin-11-yl)phenol (3a)



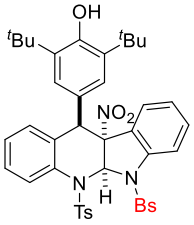
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (33.5 mg, 86% yield); m.p. 226.3-227.1 ℃; 91:9 er. The er was determined by HPLC, Chiralpak IA, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 10.5 min, t_{minor} = 13.2 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 3H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.21 (m, 5H), δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.02 (m, 2H), 6.86 (m, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 2H), 5.31 (s, 1H), 3.82 (s, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.37 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 145.2, 144.3, 143.8, 136.1, 135.2, 134.6, 133.5, 132.0, 131.9, 131.1, 130.0, 129.3, 128.8, 128.5, 128.1, 127.9, 127.8, 127.5, 122.6, 121.1, 120.3, 115.0, 104.6, 81.6, 51.8, 34.4, 30.3, 27.0, 21.8, 21.8.

HRMS (ESI-TOF) calcd. for $C_{43}H_{45}N_3O_7S_2Na$ $[M + Na]^+$ 802.2591; found: 802.2612.

2,6-di-*tert*-butyl-4-(10b-nitro-6-(phenylsulfonyl)-5-tosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3b)



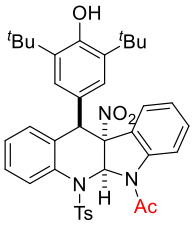
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (29.1 mg, 76% yield); m.p. 242.5-243.5 ℃;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.75 (q, *J* = 6.9, 6.1 Hz, 1H), 7.69 – 7.56 (m, 3H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.37 – 7.28 (m, 5H), 7.26 – 7.18 (m, 2H), 7.07 – 6.95 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 3.52 (s, 1H), 2.31 (s, 3H), 1.99 (s, 1H), 1.31 (s, 18H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.1, 145.1, 143.3, 136.6, 135.2, 135.1, 134.2, 133.0, 132.9, 131.6, 131.1, 130.7, 130.3, 130.0, 129.2, 128.2, 128.1, 127.6, 127.4, 127.3, 123.3, 120.5, 119.9, 114.7, 104.3, 81.8, 51.7, 34.9, 30.5, 21.6.

HRMS (ESI-TOF) calcd. for $C_{42}H_{43}N_3O_7S_2Na$ $[M + Na]^+$ 788.2435; found: 788.2439.

1-(11-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10b-nitro-5-tosyl-5,5a,10b,11-tetrahydro-6H-indolo[2,3-b]quinolin-6-yl)ethan-1-one (3c)



It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (24.7 mg, 74% yield); m.p. 220.7-221.4 ℃; 81:19 er. The er was determined by HPLC, Chiralpak IA, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 17.4 min, t_{minor} = 36.2 min.

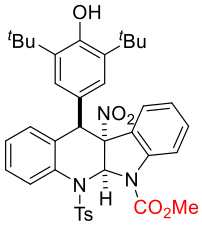
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), δ 7.41 – 7.33 (m, 2H), 7.32 – 7.21 (m, 1H), 7.21 – 7.13 (m, 3H), 7.09 (dt, *J* = 7.9, 1.3 Hz, 1H), 6.87 (td, *J* = 7.6, 1.1 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.51 (s, 2H), 5.33 (s, 1H), 3.63 (s, 1H), 2.79 (s, 3H), 2.36 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.4, 144.7, 144.7, 135.8, 134.7, 133.8, 132.4, 131.8, 130.6, 129.3, 128.8, 128.7, 128.5, 128.1, 127.7, 122.9, 122.0, 119.9, 119.3, 116.1, 104.7, 80.8, 52.0, 34.3, 30.2, 25.5, 21.7.

HRMS (ESI-TOF) calcd. for $C_{38}H_{41}N_3O_6SNa$ $[M + Na]^+$ 690.2608; found: 690.2603.

methyl 11-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10b-nitro-5-tosyl-5,5a,10b,11-

tetrahydro-6H-indolo[2,3-b]quinoline-6-carboxylate (3d)



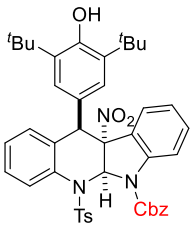
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (29.4 mg, 86% yield); m.p. 223.7-224.6 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 14.4, 8.1 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.41 – 7.03 (m, 7H), 6.91 – 6.80 (m, 2H), 6.63(s, 2H), 5.31 (s, 1H), 4.05 (d, *J* = 1.5 Hz, 3H), 3.78 (s, 1H), 2.32 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 152.5, 144.1, 144.0, 135.7, 134.2, 131.9, 131.8, 131.0, 129.1, 128.6, 128.4, 128.0, 127.9, 127.8, 127.3, 121.4, 120.1, 119.2, 114.1, 104.4, 79.7, 53.3, 52.2, 34.4, 30.2, 21.7.

HRMS (ESI-TOF) calcd. for $C_{38}H_{41}N_3O_7SNa$ $[M + Na]^+$ 706.2557; found: 706.2567.

benzyl-11-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10b-nitro-5-tosyl-5,5a,10b,11-tetrahydro-6H-indolo[2,3-b]quinoline-6-carboxylate (3e)



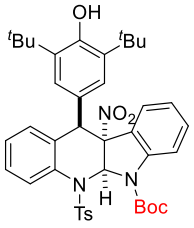
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (26.6 mg, 70% yield); m.p. 193.9-195.0 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.33 (m, 4H), 7.33 – 7.17 (m, 2H), 7.17 – 7.03 (m, 4H), 6.89 – 6.78 (m, 2H), 6.62 (s, 2H), 5.52 (d, *J* = 11.9 Hz, 1H), 5.46 (d, *J* = 11.9 Hz, 1H), 5.31 (s, 1H), 3.75 (s, 1H), 2.33 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 151.9, 144.0, 135.9, 135.8, 134.3, 131.9, 131.8, 130.9, 129.6, 129.4, 129.1, 128.7, 128.5, 128.4, 128.2, 127.9, 127.8, 127.3, 127.3, 121.4, 120.2, 119.3, 114.3, 104.4, 79.8, 68.2, 52.2, 34.3, 30.2, 21.6.

HRMS (ESI-TOF) calcd. for $C_{44}H_{45}N_3O_7SNa$ $[M + Na]^+$ 782.2870; found: 782.2880.

***tert*-butyl-11-(3,5-di-tert-butyl-4-hydroxyphenyl)-10b-nitro-5-tosyl-5,5a,10b,11-tetrahydro-6H-indolo[2,3-b]quinoline-6-carboxylate (3f)**



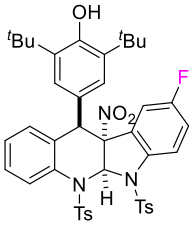
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (30.5 mg, 84% yield); m.p. 215.8-216.5 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 12.3, 8.1 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.18 (m, 3H), 7.16 – 7.00 (m, 4H), 6.80 (d, *J* = 4.3 Hz, 2H), 6.64 (s, 2H), 5.30 (s, 1H), 3.69 (s, 1H), 2.32 (s, 3H), 1.75 (s, 9H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 151.1, 144.5, 143.9, 135.7, 134.4, 132.2, 131.7, 130.8, 129.1, 128.7, 128.5, 128.3, 127.9, 127.8, 127.4, 120.9, 120.2, 119.0, 114.1, 104.4, 84.0, 80.0, 52.2, 34.3, 30.2, 28.6, 21.7.

HRMS (ESI-TOF) calcd. for $C_{41}H_{47}N_3O_7SNa$ $[M + Na]^+$ 748.3027; found: 748.3036.

2,6-di-*tert*-butyl-4-(9-fluoro-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3g)



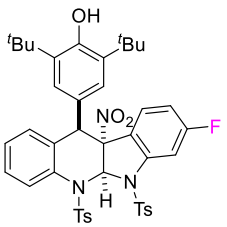
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford yellow solid (29.1 mg, 73% yield); m.p. 209.3-210.2 ℃; 84.5:15.5 er. The er was determined by HPLC, Chiralpak IC, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 29.8 min, t_{minor} = 33.6 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.72 – 7.63 (m, 2H), 7.67 – 7.57 (m, 2H), 7.34 – 7.23 (m, 4H), 7.22 – 6.95 (m, 5H), 6.63 (s, 2H), 6.47 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.35 (s, 1H), 3.84 (s, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (d, *J* = 242.4 Hz), 154.5, 145.3, 144.2, 139.82, 139.8, 135.9, 134.5, 132.9, 131.5, 130.0, 129.2, 128.6, 128.5, 128.5, 128.0, 127.9, 127.6, 127.4, 122.6 (d, *J* = 8.7 Hz), 119.7, 119.0 (d, *J* = 23.3 Hz), 117.9 (d, *J* = 26.1 Hz), 116.1 (d, *J* = 8.0 Hz), 103.9 (d, *J* = 2.0 Hz), 81.8, 51.8, 34.3, 30.1, 21.6.

HRMS (ESI-TOF) calcd. for $C_{43}H_{44}FN_3O_7S_2Na$ $[M + Na]^+$ 820.2497 found: 820.2514.

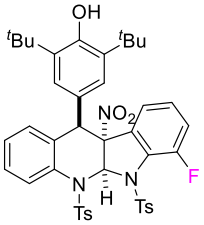
2,6-di-*tert*-butyl-4-(8-fluoro-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3h)



It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford yellow solid (28.7 mg, 82% yield); m.p. 202.2-203.1 ℃; 83.5:16.5 er. The er was determined by HPLC, Chiralpak IA, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 9.3 min, t_{minor} = 15.2 min.

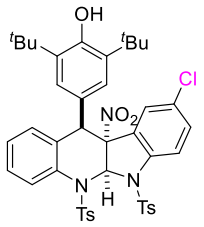
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.67 – 7.58 (m, 2H), 7.55 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.36 – 7.22 (m, 4H), 7.21 – 7.03 (m, 4H), 6.69 (dd, *J* = 8.8, 5.7 Hz, 1H), 6.56 (m, 3H), 5.32 (s, 1H), 3.77 (s, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 1.38 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9 (d, *J* = 250.6 Hz), 154.4, 145.5, 145.3, 144.2, 135.8, 134.3, 133.4, 132.5, 132.4, 131.6, 130.1, 129.2, 128.5, 128.5, 128.5, 128.0, 127.9, 127.7, 127.4, 120.0, 116.4 (d, *J* = 2.8 Hz), 109.7 (d, *J* = 22.9 Hz), 103.9, 102.6 (d, *J* = 28.7 Hz), 81.9, 51.6, 34.3, 30.2, 21.7, 21.6.
HRMS (ESI-TOF) calcd. for $C_{43}H_{44}FN_3O_7S_2Na$ $[M + Na]^+$ 820.2497; found: 820.2502.

2,6-di-*tert*-butyl-4-(7-fluoro-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3i)



It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (21.9 mg, 55% yield); m.p. 215.6-216.5 ℃;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.94 (m, 2H), 7.82 (s, 1H), 7.67 – 7.59 (m, 2H), 7.47 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.27 – 7.15 (m, 3H), 7.08 – 6.95 (m, 3H), 6.85 (td, *J* = 8.0, 4.4 Hz, 1H), 6.73 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.57 (s, 2H), 5.32 (s, 1H), 3.87 (s, 1H), 2.47 (s, 3H), 2.36 (s, 3H), 1.38 (s, 18H).
^{13}C NMR (101MHz, $CDCl_3$) δ 154.4, 150.0 (d, *J* = 251.6 Hz), 144.7, 144.4, 136.2, 135.4, 134.3, 132.0, 131.8, 131.6, 129.5, 129.3, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.3, 126.4 (d, *J* = 3.7 Hz), 125.3, 123.6 (d, *J* = 6.6 Hz), 119.9, 119.3 (d, *J* = 19.8 Hz), 104.1 (d, *J* = 1.7 Hz), 82.4, 51.6, 34.4, 30.2, 21.7.
HRMS (ESI-TOF) calcd. for $C_{43}H_{44}FN_3O_7S_2Na$ $[M + Na]^+$ 820.2497; found: 820.2502.

2,6-di-*tert*-butyl-4-(9-chloro-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3j)

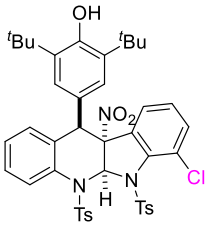


It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford yellow solid (31.7 mg, 78% yield); m.p. 232.8-233.7 ℃; 79:21 er. The er was determined by HPLC, Chiralpak IA, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 17.5 min, t_{minor} = 27.4 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.66 – 7.55 (m, 4H), 7.26 (m, 5H), 7.20 – 7.02 (m, 4H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.40 (s, 2H), 5.33 (s, 1H), 3.76 (s, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 145.3, 144.3, 142.4, 136.1, 135.8, 134.4, 133.1, 132.1, 131.4, 130.6, 130.1, 129.3, 128.6, 128.5, 128.0, 127.9, 127.6, 127.3, 122.4, 120.9, 119.6, 117.8, 115.9, 103.9, 81.8, 51.8, 34.3, 30.1, 21.7.

HRMS (ESI-TOF) calcd. for $C_{43}H_{44}ClN_3O_7S_2Na$ $[M + Na]^+$ 836.2201; found: 836.2204.

2,6-di-*tert*-butyl-4-(7-chloro-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3k)



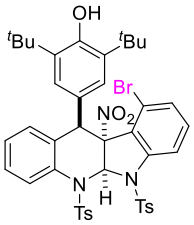
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (18.3 mg, 45% yield); m.p. 225.7-226.4 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.66 – 7.52 (m, 3H), 7.42 – 7.32 (m, 3H), 7.25 – 7.18 (m, 3H), 7.11 – 6.86 (m, 4H), 6.65 (s, 2H), 5.31 (s, 1H), 3.90 (s, 1H), 2.47 (s, 3H), 2.37 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 152.8, 144.6, 144.4, 142.0, 136.0, 135.4, 134.1, 133.1, 132.2, 131.4, 129.5, 129.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.5, 127.4, 127.0, 125.1, 124.4, 124.2, 124.0, 120.2, 117.8, 103.6, 82.7, 51.3, 34.4, 30.2, 21.7.

HRMS (ESI-TOF) calcd. for $C_{43}H_{44}ClN_3O_7S_2Na$ $[M + Na]^+$ 836.2201; found: 836.2204.

4-(10-bromo-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)-2,6-di-*tert*-butylphenol (3l)



It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (19.8 mg, 46% yield); m.p. 240.6-241.3 ℃; 78.5:21.5 er. The er was determined by HPLC, Chiralpak IA, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 18.2 min, t_{major} = 20.2 min,.

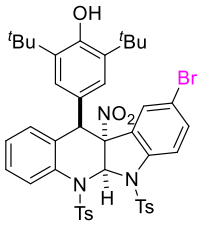
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.71 (s, 1H), 7.65 – 7.60 (m, 2H), 7.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.49 – 7.28 (m, 3H), 7.27 – 7.11 (m, 3H), 7.06 (ddd, *J* = 7.5, 6.3, 1.3 Hz, 2H), 6.98 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.94 – 6.82 (m, 1H), 6.60 (s, 2H), 5.30 (s, 1H), 3.88 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 144.8, 144.4, 143.5, 136.3, 135.5, 135.3, 134.1, 132.1, 129.5, 128.7, 128.5, 128.4, 128.2, 128.2, 127.9, 127.9, 126.9, 125.6, 124.2, 124.0, 120.2, 117.8, 113.0, 103.7, 82.5, 51.6, 34.4, 30.2, 21.7.

HRMS (ESI-TOF) calcd. for $C_{43}H_{44}BrN_3O_7S_2Na$ $[M + Na]^+$ 880.1696; found: 880.1700,.

4-(9-bromo-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)

-2,6-di-*tert*-butylphenol (3m)



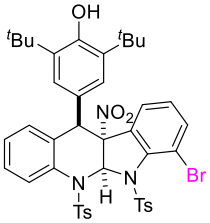
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (35.2 mg, 82% yield); m.p. 232.8-233.5 ℃; 80:20 er. The er was determined by HPLC, Chiralpak IC, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 30.0 min, t_{minor} = 33.3 min.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.61 – 7.49 (m, 4H), 7.42 – 7.35 (m, 1H), 7.32 – 7.24 (m, 3H), 7.21 (d, *J* = 2.2 Hz, 1H), 7.18 – 7.03 (m, 4H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.74 (s, 2H), 5.45 (s, 1H), 3.70 (s, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 154.5, 145.4, 144.3, 142.9, 135.7, 134.9, 134.3, 133.3, 133.2, 131.4, 130.1, 129.5, 129.2, 128.6, 128.4, 128.1, 128.0, 127.9, 127.5, 127.3, 122.7, 119.5, 116.2, 115.3, 103.9, 81.7, 51.7, 34.3, 30.1, 21.6.

HRMS (ESI-TOF) calcd. for $C_{43}H_{44}BrN_3O_7S_2Na$ $[M + Na]^+$ 880.1696, found: 880.1692.

4-(7-bromo-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl) -2,6-di-tert-butylphenol (3n)



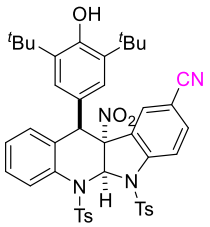
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (20.7 mg, 48% yield); m.p. 230.4-231.0 ℃;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.66 – 7.52 (m, 3H), 7.42 – 7.32 (m, 3H), 7.25 – 7.18 (m, 3H), 7.11 – 6.86 (m, 4H), 6.65 (s, 2H), 5.31 (s, 1H), 3.90 (s, 1H), 2.47 (s, 3H), 2.37 (s, 3H), 1.39 (s, 18H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 154.3, 144.8, 144.4, 143.5, 136.3, 135.5, 135.3, 134.1, 132.1, 129.5, 128.7, 128.5, 128.4, 128.2, 128.2, 127.9, 127.8, 127.5, 126.9, 125.6, 124.0, 120.2, 117.8, 113.0, 103.7, 82.5, 51.6, 34.4, 30.2, 21.7.

HRMS (ESI-TOF) calcd. for $C_{43}H_{44}BrN_3O_7S_2Na$ $[M + Na]^+$ 880.1696, found: 880.1711.

11-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinoline-9-carbonitrile (3o)



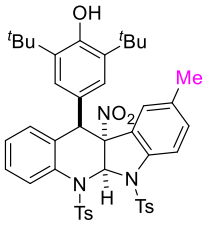
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (28.6 mg, 71% yield); m.p. 184.5-185.3 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.58 (td, *J* = 8.9, 8.4, 1.7 Hz, 3H), 7.47 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.34 – 7.28 (m, 4H), 7.20 – 7.05 (m, 5H), 6.52 (s, 2H), 5.38 (s, 1H), 3.71 (s, 1H), 2.43 (s, 3H), 2.35 (s, 3H), 1.40 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 147.2, 145.8, 144.5, 135.7, 135.6, 135.1, 134.2, 133.6, 131.0, 130.2, 129.3, 128.8, 128.5, 128.1, 128.0, 127.6, 127.4, 121.5, 119.3, 118.0, 114.9, 106.0, 103.4, 81.7, 51.7, 34.3, 30.1, 21.7, 21.7.

HRMS (ESI-TOF) calcd. for $C_{44}H_{44}N_4O_7S_2Na$ $[M + Na]^+$ 827.2544; found: 827.2549.

2,6-di-*tert*-butyl-4-(9-methyl-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3p)



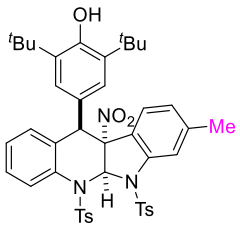
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (32.9 mg, 83% yield); m.p. 181.3-182.1 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.67 – 7.58 (m, 3H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.34 – 6.96 (m, 9H), 6.60 (s, 3H), 5.29 (s, 1H), 3.80 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 1.38 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 144.9, 144.1, 142.7, 142.4, 141.5, 136.0, 134.5, 133.2, 132.8, 132.1, 131.9, 130.8, 129.9, 129.2, 128.4, 128.4, 128.0, 127.7, 127.6, 127.3, 121.0, 120.3, 114.7, 104.7, 81.7, 51.7, 34.3, 30.2, 21.7, 21.6, 21.2.

HRMS (ESI-TOF) calcd. for $C_{44}H_{47}N_3O_7S_2Na$ $[M + Na]^+$ 816.2748; found: 816.2758.

2,6-di-*tert*-butyl-4-(8-methyl-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3q)



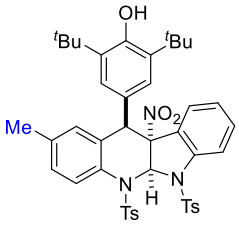
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (30.2 mg, 76% yield); m.p. 176.6-177.3 ℃; 92:8 er. The er was determined by HPLC, Chiralpak IA, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 9.4 min, t_{minor} = 12.0 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.56 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.35 – 7.15 (m, 4H), 7.17 – 7.13 (m, 2H), 7.13 – 7.01 (m, 2H), 6.88 – 6.25 (m, 4H), 5.28 (s, 1H), 3.79 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H), 1.36 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 144.9, 144.1, 143.9, 142.6, 136.0, 134.5, 133.6, 132.0, 131.3, 130.5, 129.9, 129.2, 128.7, 128.4, 128.3, 128.0, 127.7, 127.6, 127.4, 123.5, 120.3, 118.1, 115.2, 104.5, 81.7, 51.6, 34.3, 30.2, 21.9, 21.6.

HRMS (ESI-TOF) calcd. for $C_{44}H_{47}N_3O_7S_2Na$ $[M + Na]^+$ 816.2748; found: 816.2753.

2,6-di-*tert*-butyl-4-(2-methyl-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3r)



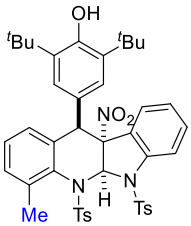
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (32.1 mg, 81% yield); m.p. 193.8-194.7 ℃;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.34 (m, 6H), 7.34 – 7.27 (m, 4H), 7.23 (ddd, *J* = 8.6, 6.1, 2.9 Hz, 1H), 7.17 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.47 (m, 3H), 3.51 (s, 1H), 2.36 (s, 3H), 2.29 (d, *J* = 11.3 Hz, 6H), 1.31 (s, 18H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.0, 145.8, 145.1, 143.6, 143.3, 135.3, 134.2, 133.6, 131.8, 130.7, 131.3, 130.6, 130.0, 129.2, 128.3, 128.1, 127.6, 127.6, 127.5, 124.2, 121.3, 120.0, 117.8, 115.1, 104.4, 82.0, 51.6, 34.9, 30.5, 21.8, 21.5, 21.5.

HRMS (ESI-TOF) calcd. for $C_{44}H_{47}N_3O_7S_2$ $[M + Na]^+$ 816.2748; found: 816.2745.

2,6-di-*tert*-butyl-4-(4-methyl-10b-nitro-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)phenol (3s)



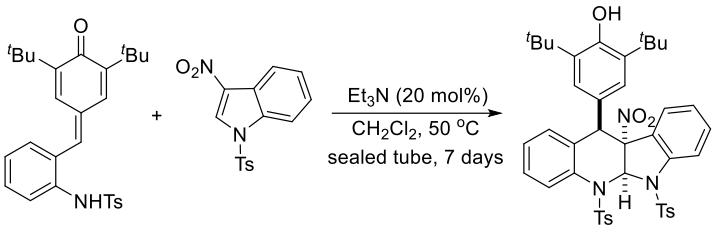
It was purified by flash chromatography (petroleum ether / EtOAc, 8:1) to afford white solid (22.2 mg, 56% yield); m.p. 197.0-197.7 ℃;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.36 (m, 6H), 7.29 (dt, *J* = 29.7, 7.4 Hz, 5H), 7.16 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 3H), 3.54 (s, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 2.16 (s, 3H), 1.32 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 147.3, 145.9, 144.6, 143.1, 135.3, 135.3, 134.7, 134.4, 133.3, 132.6, 131.8, 130.6, 130.6, 130.0, 130.0, 129.5, 128.6, 127.5, 127.5, 120.1, 120.1, 119.3, 114.7, 104.6, 82.0, 51.8, 36.0, 30.5, 27.1, 21.4, 21.1.

HRMS (ESI-TOF) calcd. for $C_{44}H_{47}N_3O_7S_2$ $[M + Na]^+$ 816.2748; found: 816.2766.

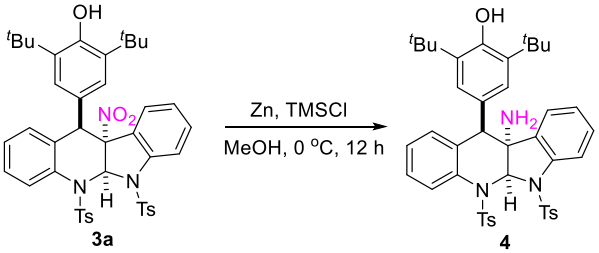
3. Scale-up reaction for the synthesis of 3



1a 1.5 mmol **2a** 1.5 mmol **3a**, 882 mg >20:1 dr, 75% yield

Compound **1a** (695 mg, 1.5 mmol) and Compound **2a** (473 mg, 1.5 mmol) was dissolved in DCM (15 mL) and triethylamine (42 μL, 0.3 mmol) was added in sealed tube. The mixture was stirred at 50 °C for 7 days. The solution concentrated under rotatory evaporation and the crude was purified by column chromatography (petroluem ether / EtOAc = 8/1), affording compound **3a** as a white solid (882 mg, 75% yield).

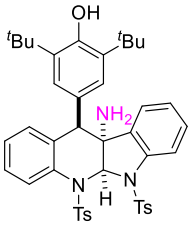
4. Synthesis of compound 4



3a **4** >20:1 dr, 55% yield

Zinc powder (65 mg, 1 mmol, 20 equiv) was added to a solution of **3a** (39.0 mg, 0.05 mmol, 1 equiv) and trimethylsilyl chloride (0.13 mL, 1 mmol, 20 equiv) in methanol at 0 °C. The mixture stirred at 0 °C for 12 h. The suspension was filtered and washed by saturated $NaHCO_3$.The filtrate extracted with DCM. The combined organic ftactions were dried by $MgSO_4$, filtered and concentrated by rotatory evaporation. Then the residue was purified by column chromatography(petroluem ether / EtOAc = 5/1), affording compound **4** as a white solid (20.6 mg, 55% yield).

4-(10b-amino-5,6-ditosyl-5a,6,10b,11-tetrahydro-5H-indolo[2,3-b]quinolin-11-yl)-2,6-di-*tert*-butylphenol (4)



It was purified by flash chromatography (petroleum ether / EtOAc, 5:1) to afford white solid (20.6 mg, 55% yield); >20:1 dr; m.p. 164.2-165.0 ℃;

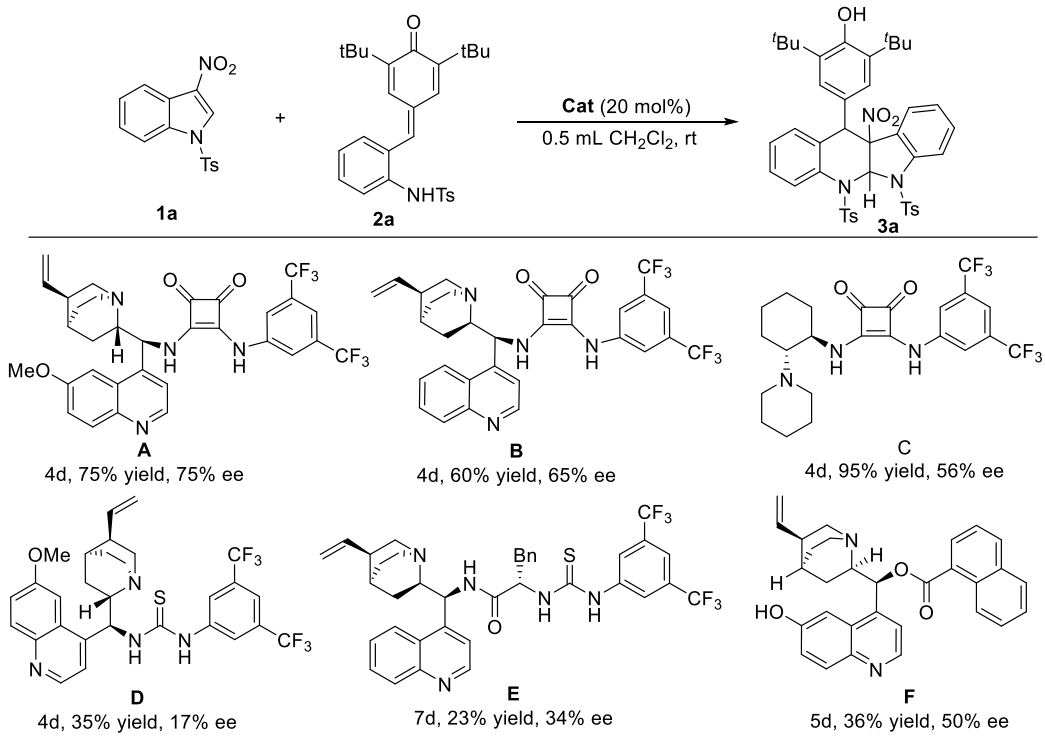
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.81 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.10 (m, 4H), 7.07 – 6.92 (m, 2H), 6.84 (s, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.62 (s, 2H), 6.16 (dd, *J* = 7.7, 1.3 Hz, 1H), 5.25 (s, 1H), 4.32 (s, 2H), 3.50 (s, 1H), 2.37 (d, *J* = 6.0 Hz, 6H), 1.37 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 144.2, 143.8, 143.5, 136.8, 134.8, 134.6, 134.3, 129.8, 129.5, 129.2, 129.1, 128.2, 128.0, 128.0, 127.3, 127.1, 127.0, 126.1, 122.5, 121.9, 114.3, 80.5, 79.6, 47.9, 34.3, 30.25, 21.7, 21.6.

HRMS (ESI-TOF) calcd. for $C_{43}H_{47}N_3O_5S_2$ $[M + K]^+$ 788.2589; found: 788.2877.

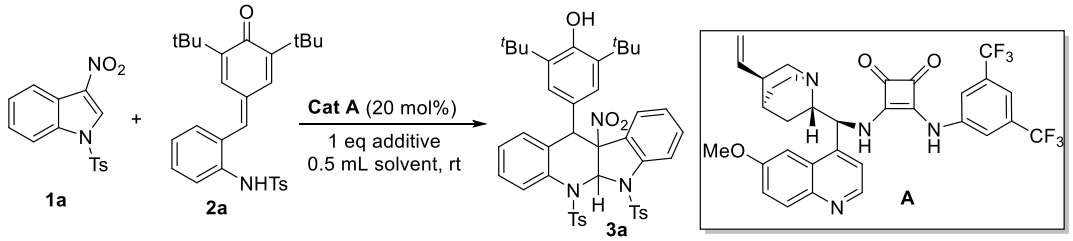
5. Optimization of conditions for catalytic asymmetric version

Table S1 Optimization of reaction conditions with catalysts



The reaction was carried out with **1a** (0.05 mmol), **2a** (0.05 mmol) and **cat** (20 mol%) in 0.5 mL of DCM at room temperature. The yield refers to the isolated yield.

Table S2 Optimization of reaction conditions with other parameters



entry	solvent	additive	time (days)	yield (%)[b]	ee (%)[c]
1	DCM	-	4	75	75
2	toluene	-	8	40	65
3	MTBE	-	8	34	71
4	THF	-	8	trace	-
5	$CHCl_3$	-	4	97	72
6	CH_3CN	-	3	84	33
7	EA	-	3	62	59
8	DMF	-	2	80	1
9	DCM	(D)-ethyl tartrate	7	72	57

10	DCM	(L)-ethyl tartrate	7	67	56
11	**DCM**	**(R)-BINOL**	**7**	**78**	**82**
12	DCM	(S)-BINOL	7	75	74
13[d]	DCM	-	7	96	73
14[d]	$CHCl_3$	-	7	98	72
15[f]	DCM	-	7	70	80

[a]Unless otherwise noted, the reaction was carried out with **1a** (0.05 mmol), **2a** (0.05 mmol) and **cat** (20 mol%) in 0.5 mL of solvent at room temperature. [b]Isolated yield. [c]Determined by chiral HPLC. [d]Run at 0 °C. [e]Run at -10 °C.

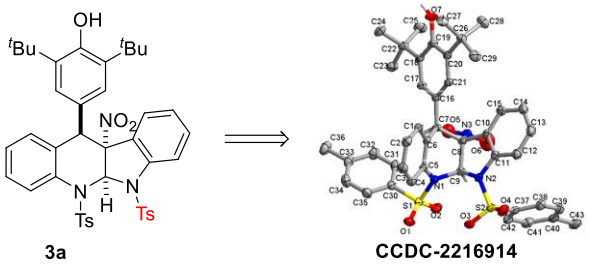
6. X-ray crystal structure of compound 3a

Single crystals of compound **3a** were prepared from the mixture solvent of dichloromethane and EtOH. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

[3] Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.



ORTEP of **3a** (at 50% level)

Table 1 Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	$C_{43}H_{45}N_3O_7S_2$
Formula weight	779.94
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.5995(2)
b/Å	10.0324(2)
c/Å	27.7318(5)
α/°	90
β/°	104.9954(18)
γ/°	90

Volume/Å^3	3923.48(13)
Z	4
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	1.680
F(000)	1648.0
Crystal size/mm^3	0.17 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	6.6 to 142.102
Index ranges	-17 ≤ h ≤ 12, -11 ≤ k ≤ 11, -34 ≤ l ≤ 33
Reflections collected	17801
Independent reflections	7407 [R_{int} = 0.0350, R_{sigma} = 0.0407]
Data/restraints/parameters	7407/7/511
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1513
Final R indexes [all data]	R_1 = 0.0696, wR_2 = 0.1659
Largest diff. peak/hole / e Å^{-3}	0.70/-0.49

7. Determination of the absolute configuration of 3a by ECD spectrum

Based on the experimental crystal structure of enantiomers, there are only two possible configurations (*C7R,C8R,C9R*)-**3a** and (*C7S,C8S,C9S*)-**3a**. To further determine the precise configuration of our chiral product, theoretical calculation of the ECD spectrum has been performed and compared with the experimental spectrum. For the ECD spectrum calculations, all structures were optimized at B3LYP[1] level of theory with 6-311+g(d,p)[2] basis set for all atoms. Empirical dispersion correction has been considered by using Grimme's DFT empirical dispersion correction with the Becke-Jonson (D3BJ) damping function.[3] Optimized minima were verified at the same level of theory by harmonic vibrational analysis to have no imaginary frequency. CD spectra were calculated by TDDFT at the CAM-B3LYP[4]/Def2SVP[5] level. All DFT geometry optimizations and TDDFT calculations were performed with Gaussian 16 program.[6]

[1] (a) Becke, A. D. Phys. Rev. 1988, A38, 3098. (b) Becke, A. D. J.Chem. Phys. 1993, 98, 5648.(c) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. 1988, B37, 785.

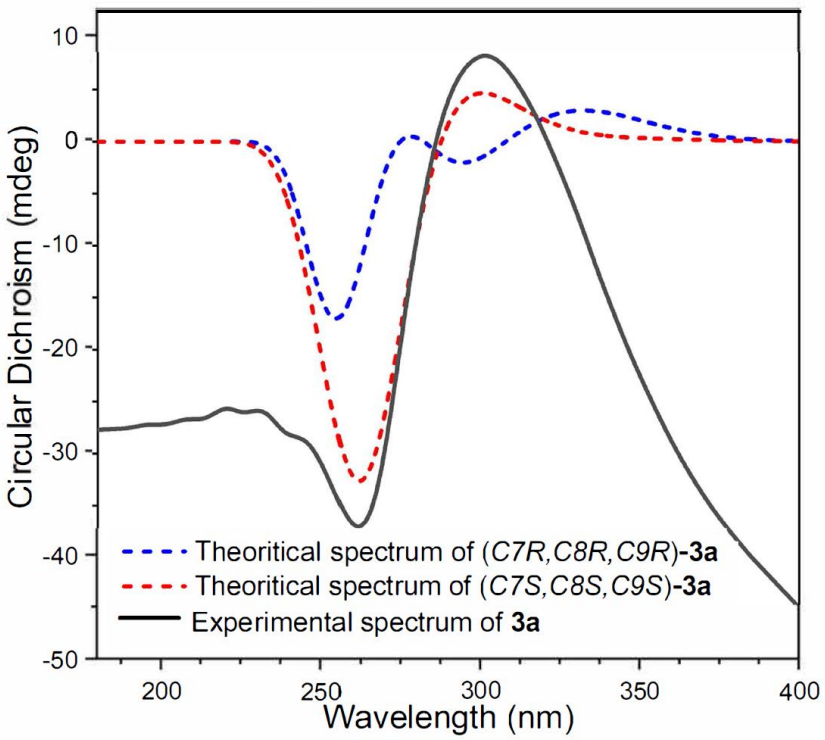
[2] (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. J. Chem. Phys. 1980, 72, 650−654. (b) McLean, A. D.; Chandler, G. S. J. Chem. Phys. 1980, 72, 5639−5648.

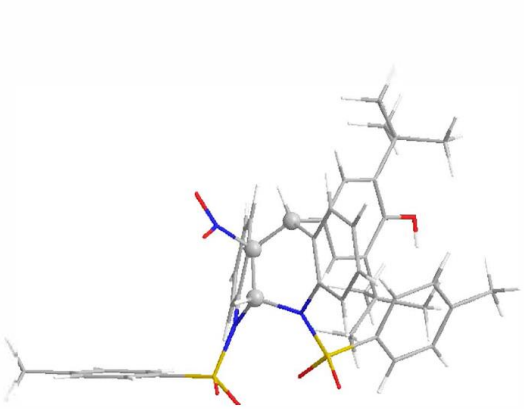
[3] Grimme, S.; Ehrlich, S.; Georigk, L. *J. Compt. Chem*. **2011**, *32*, 1456-1465.

[4] Yanai, T. V.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett*. **2004**, *393*, 51-57.

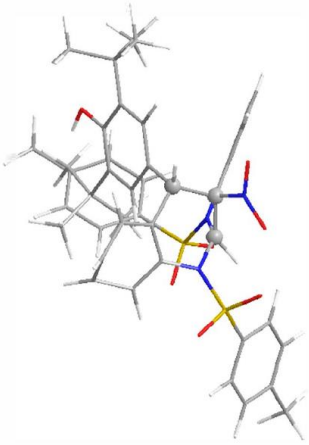
[5] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E. *et al*. Gaussian, Inc., Wallingford CT, 2019.





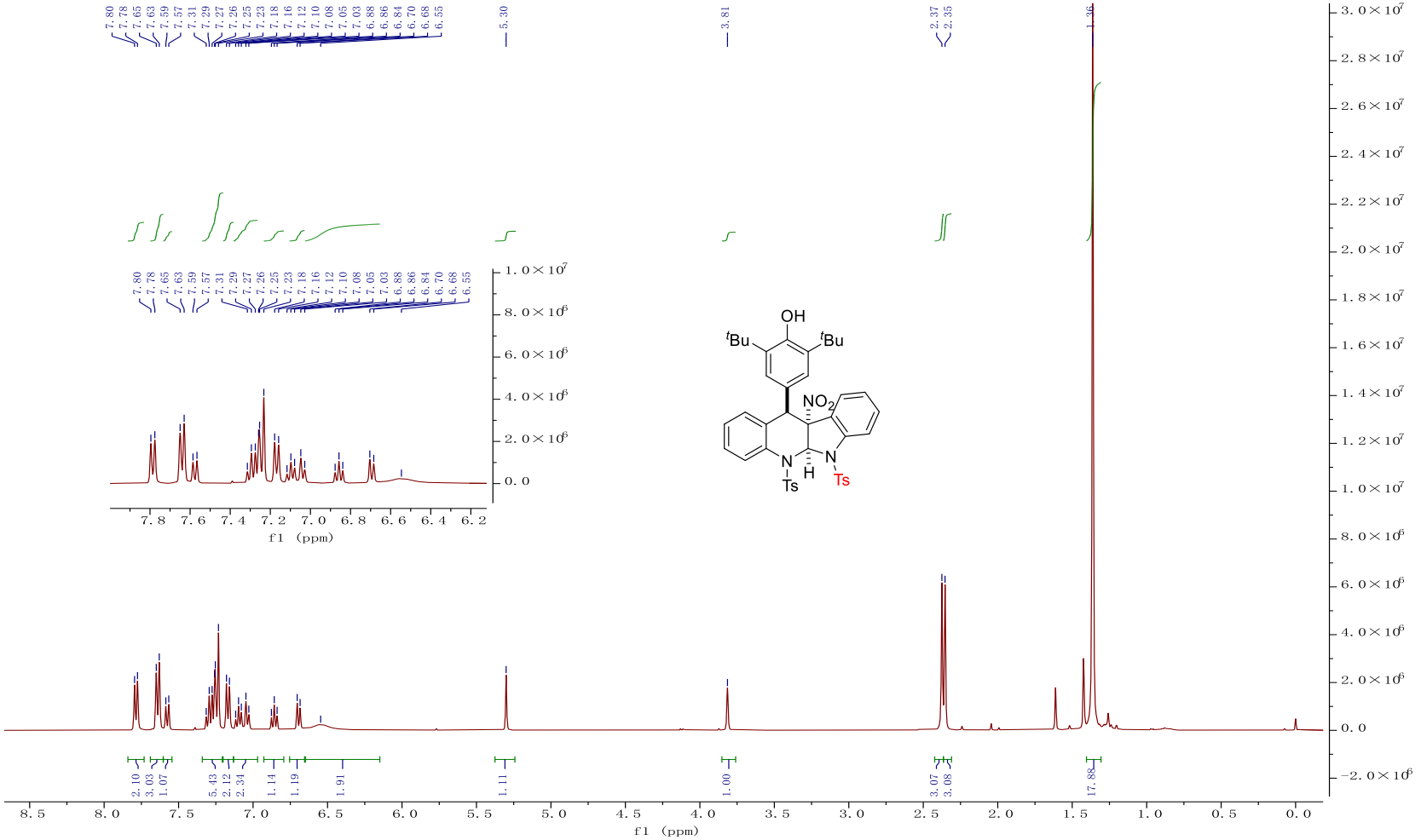
(*C7R, C8R, C9R*)-**3a**



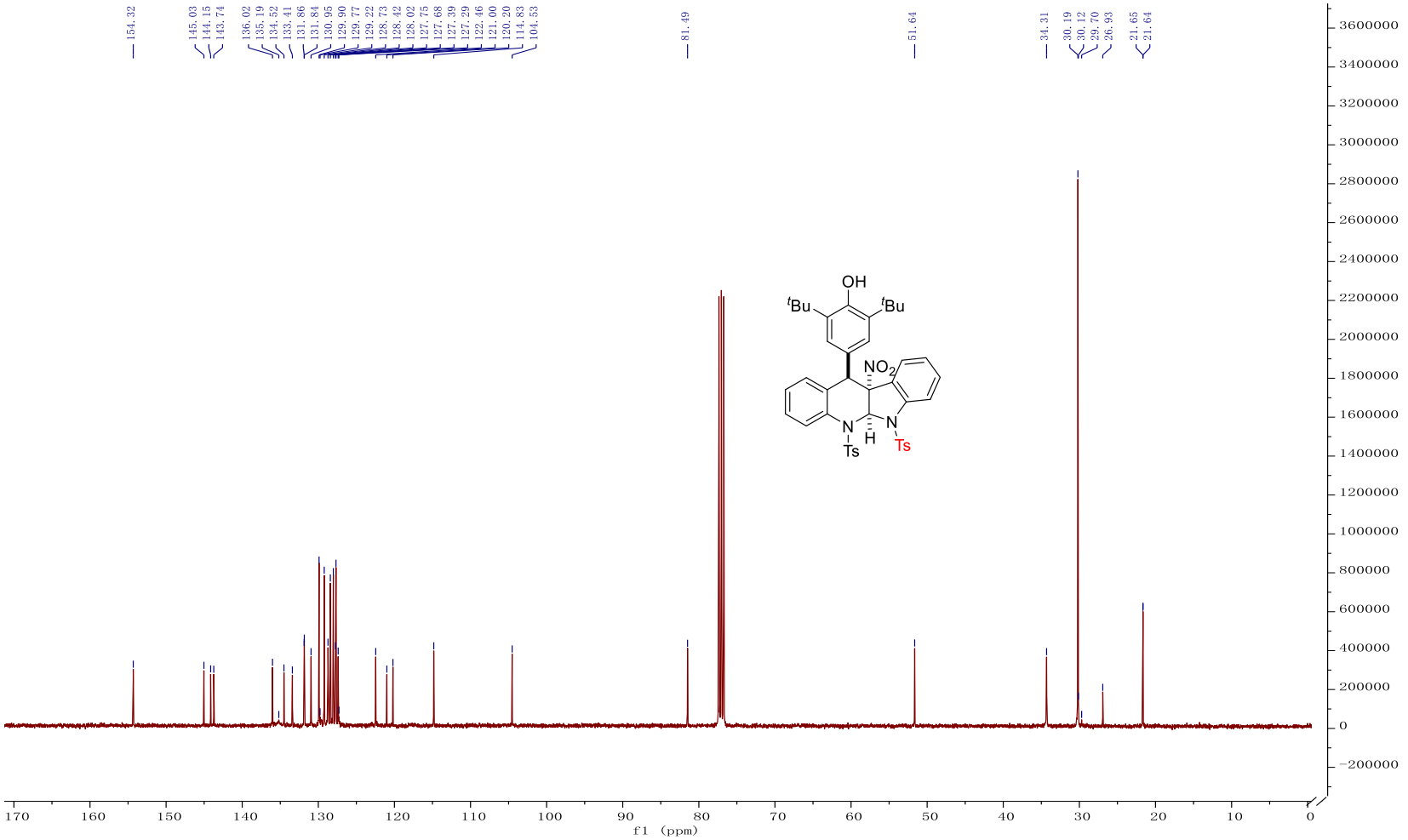
(*C7S, C8S, C9S*)-**3a**

8. ^{1}H NMR and ^{13}C NMR spectra for compounds 3 and 4

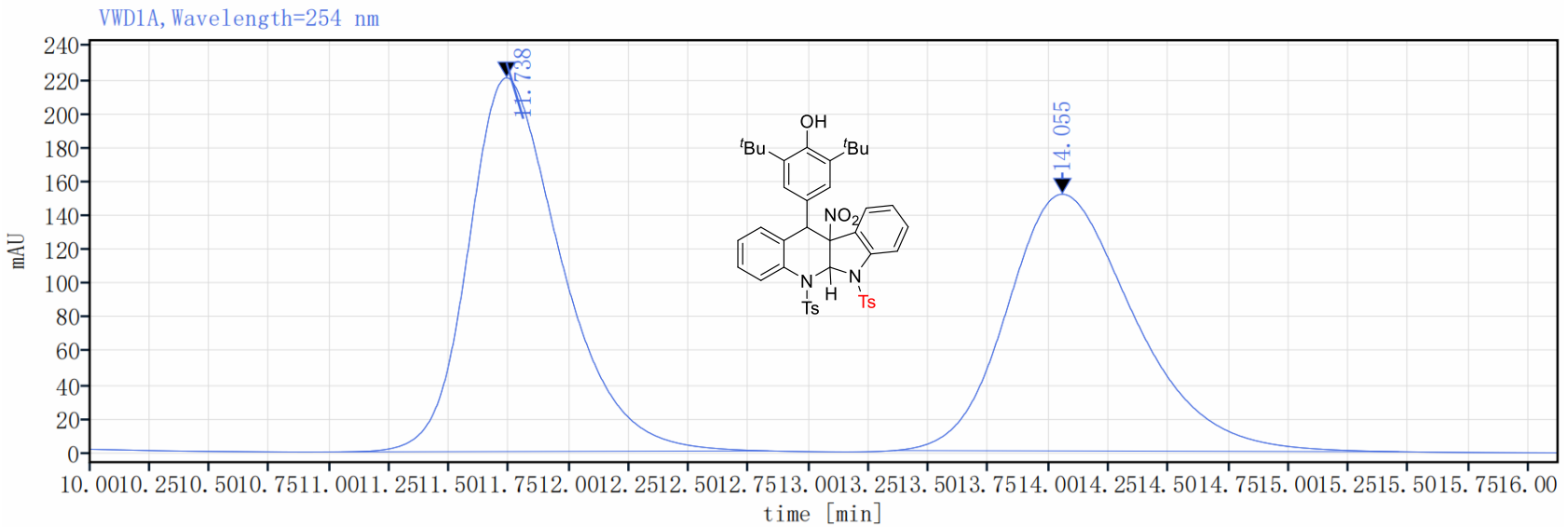
^{1}H NMR spectrum of 3a



^{13}C NMR spectrum of 3a

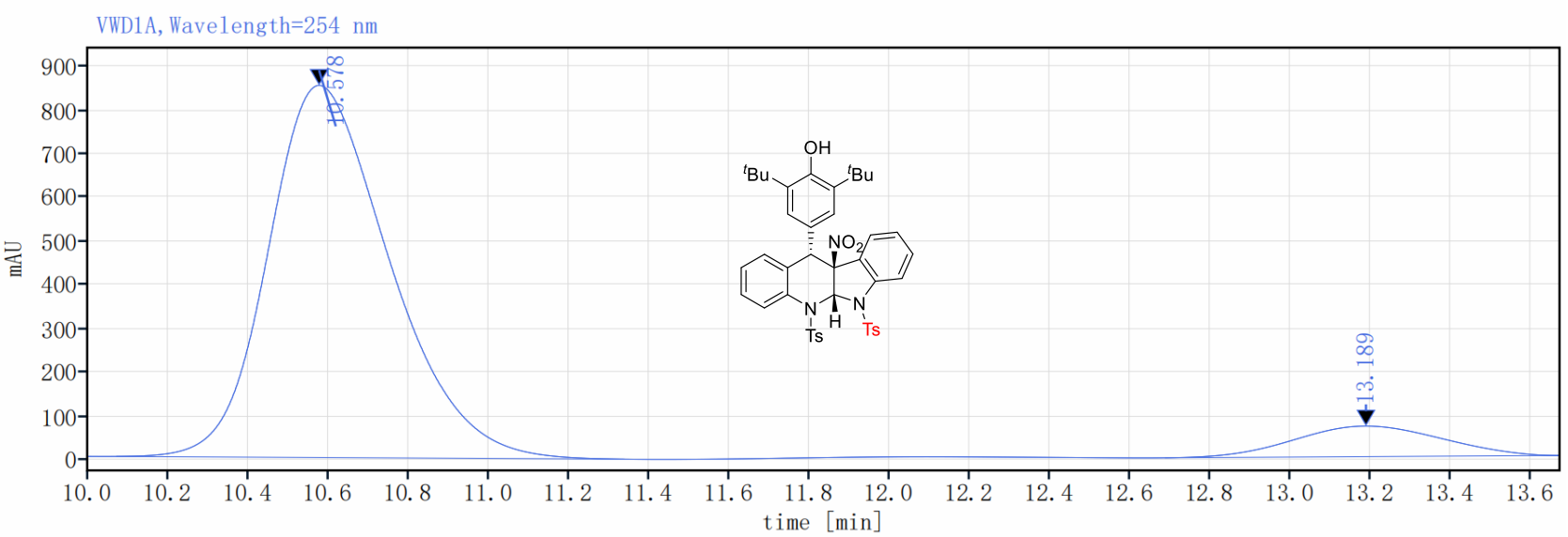


HPLC spectra of 3a



Detector VWD1A,Wavelength=254 nm

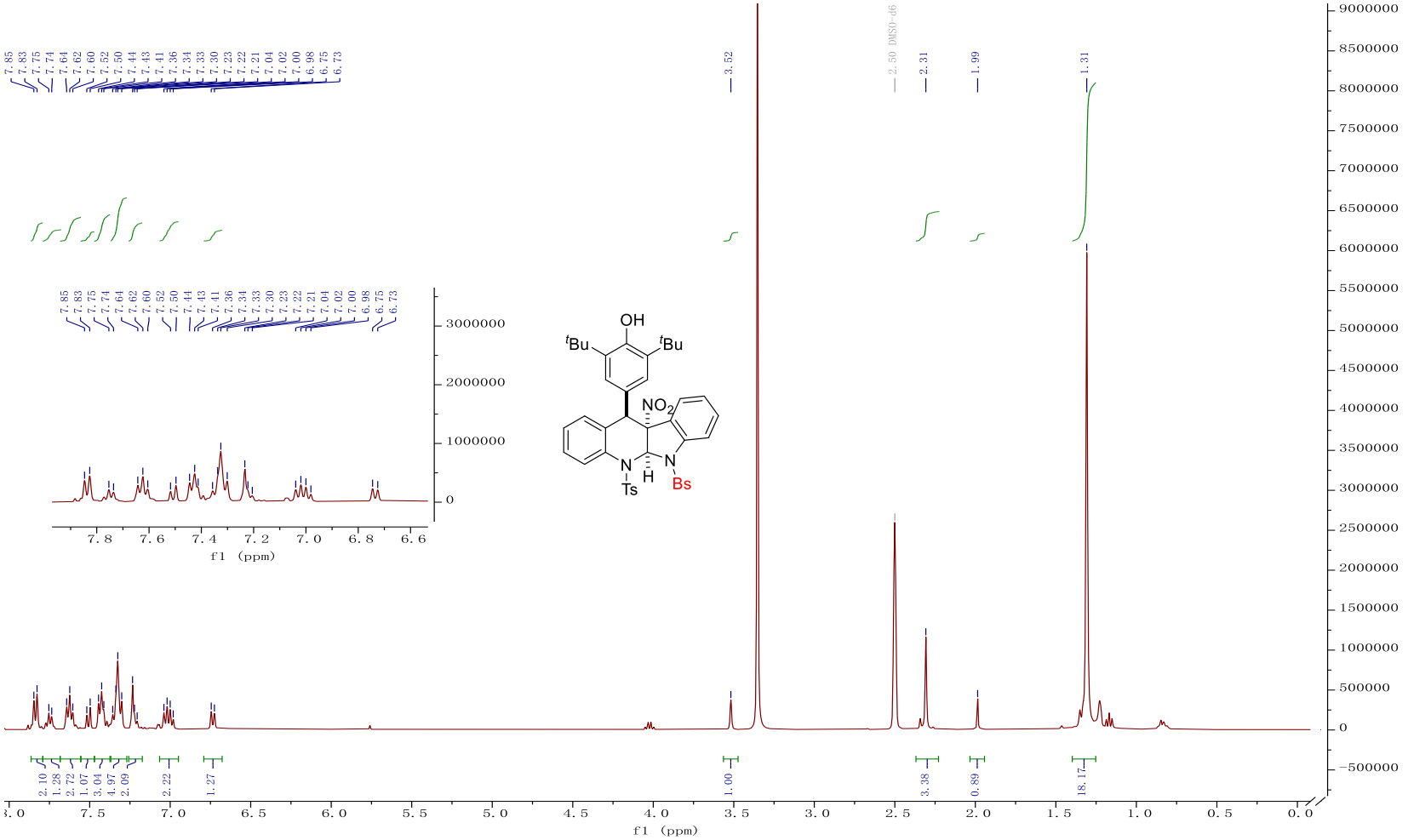
Peak	Ret.Time [min]	Area	Height	Area%
	11.738	5928.79	220.19	51.45
	14.055	5595.53	151.29	48.55
		11524.32		100.00



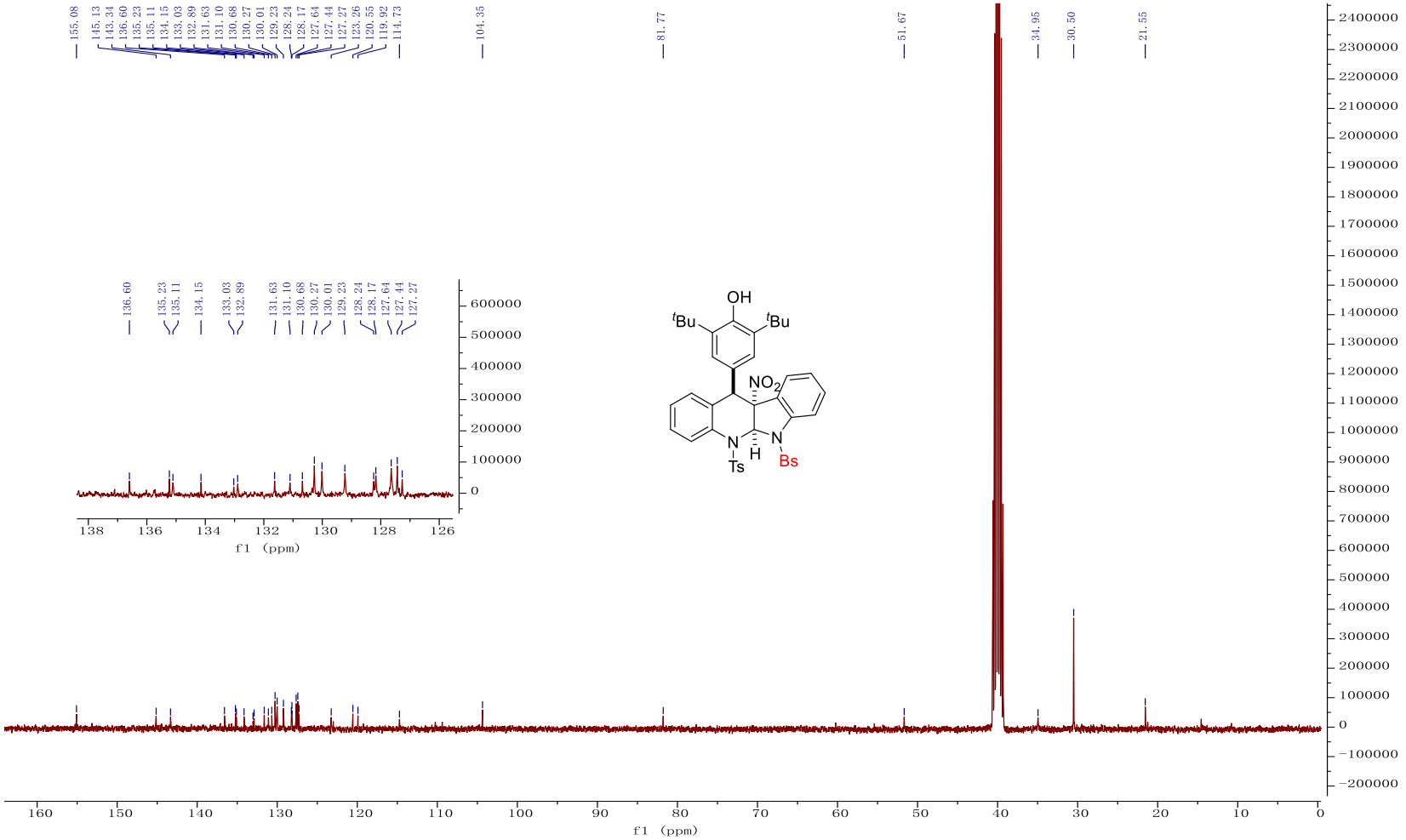
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	10.578	17907.24	851.46	90.98
	13.189	1774.45	69.77	9.02
		19681.68		100.00

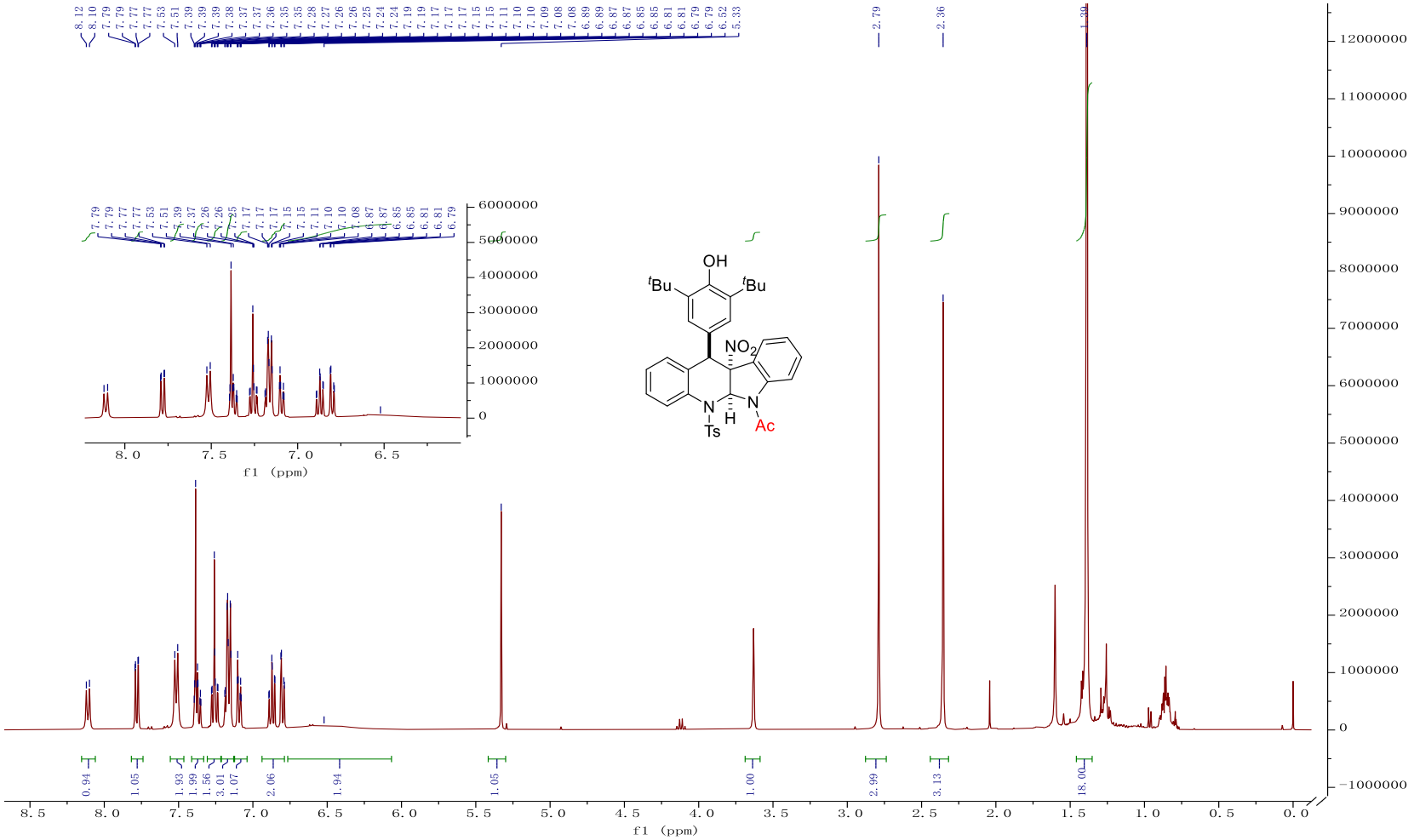
^{1}H NMR spectrum of 3b



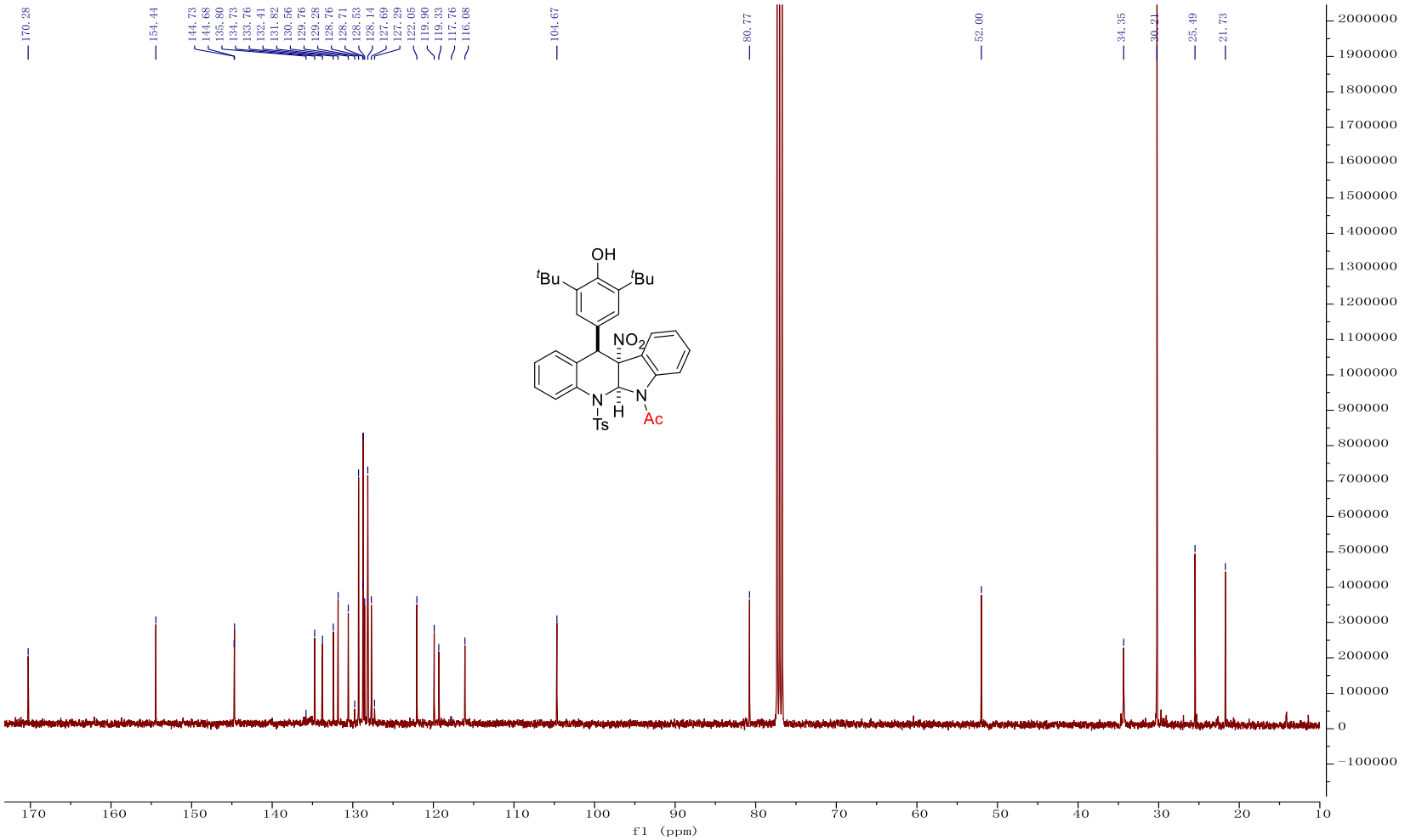
^{13}C NMR spectrum of 3b



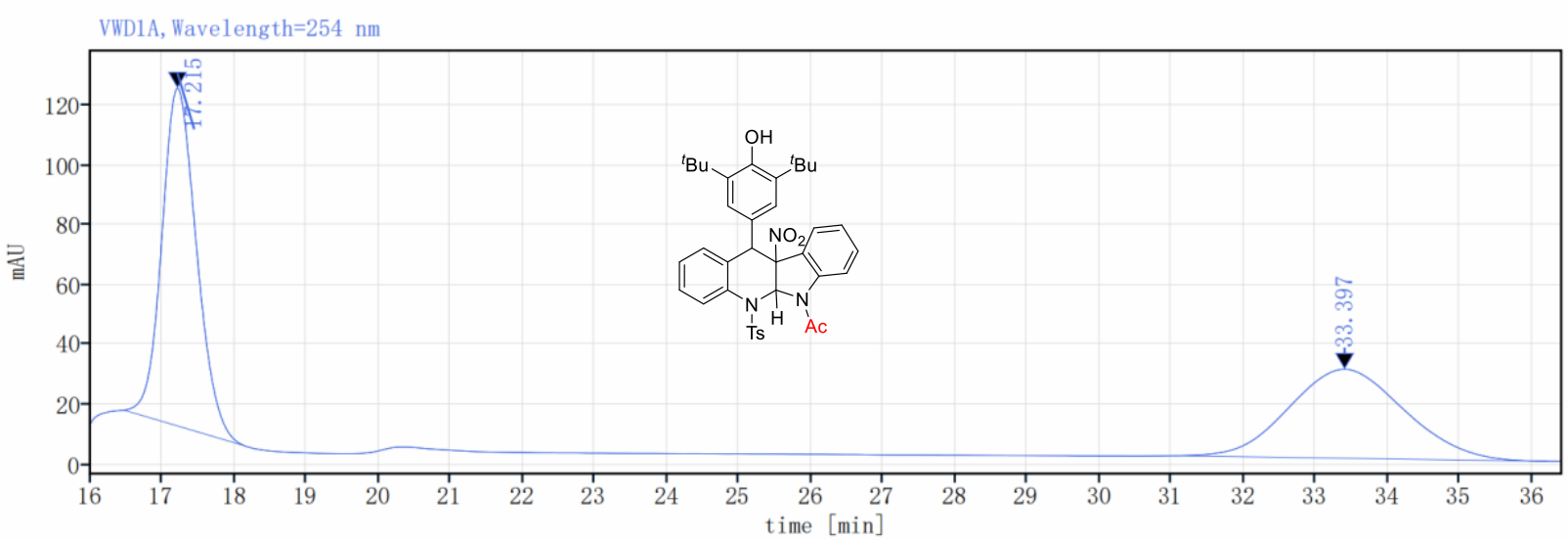
^{1}H NMR spectrum of 3c



^{13}C NMR spectrum of 3c

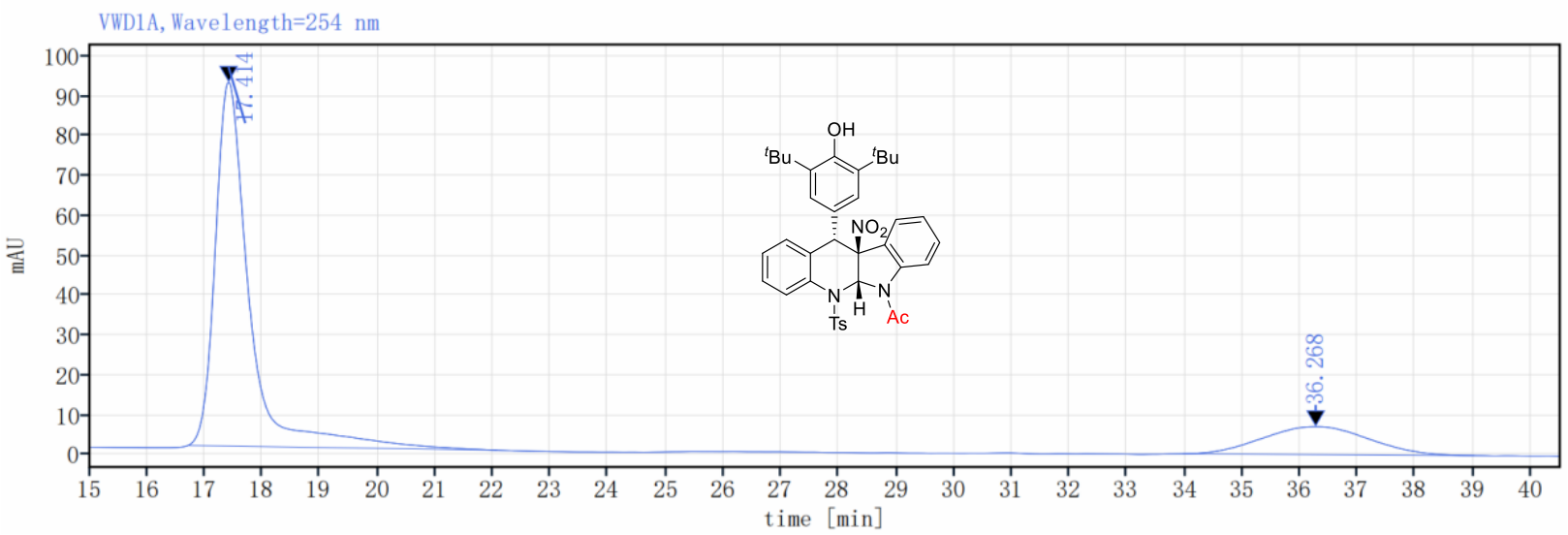


HPLC spectra of 3c



Detector VWD1A,Wavelength=254 nm

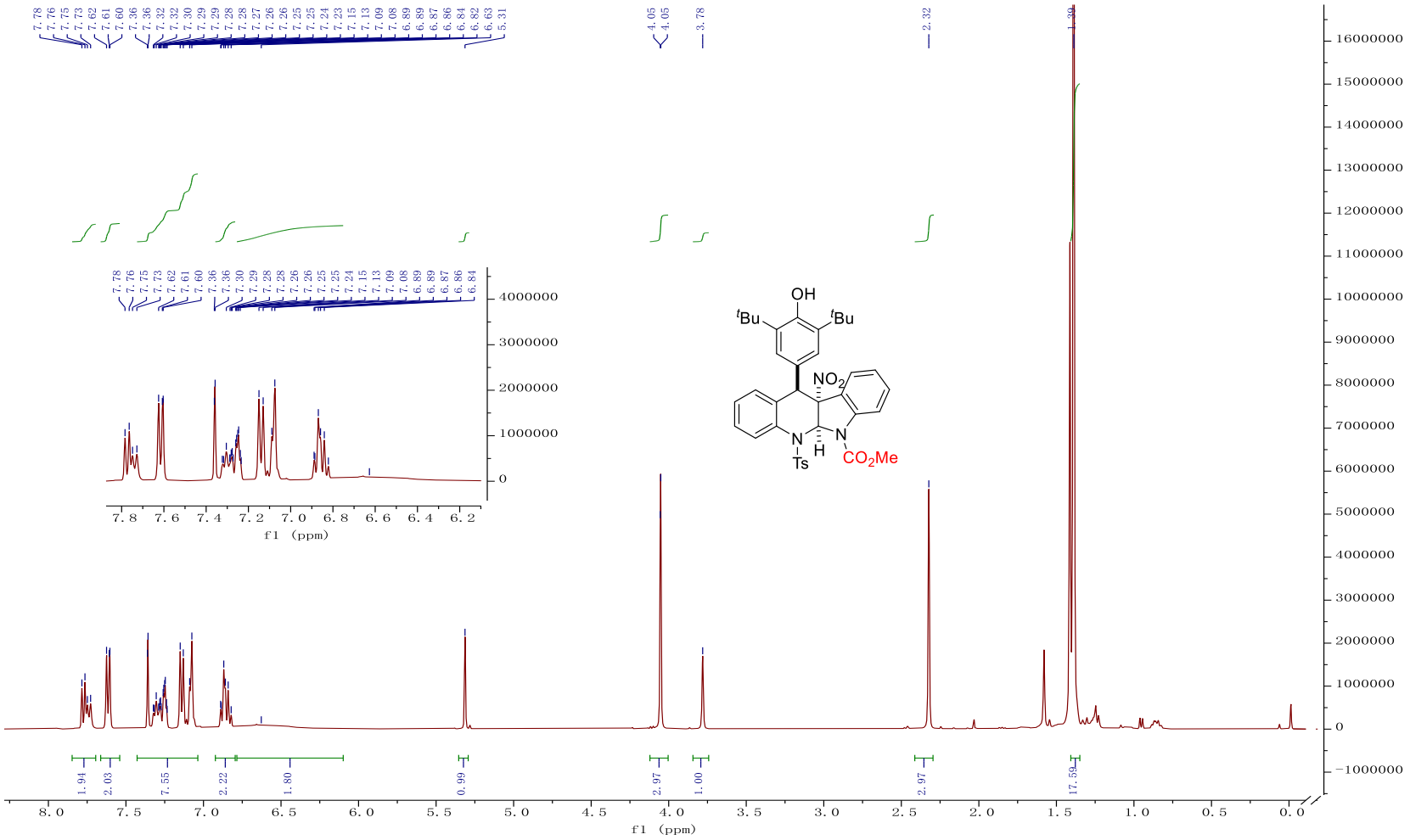
Peak	Ret.Time [min]	Area	Height	Area%
	17.215	3770.37	112.66	53.45
	33.397	3283.96	29.66	46.55
		7054.33		100.00



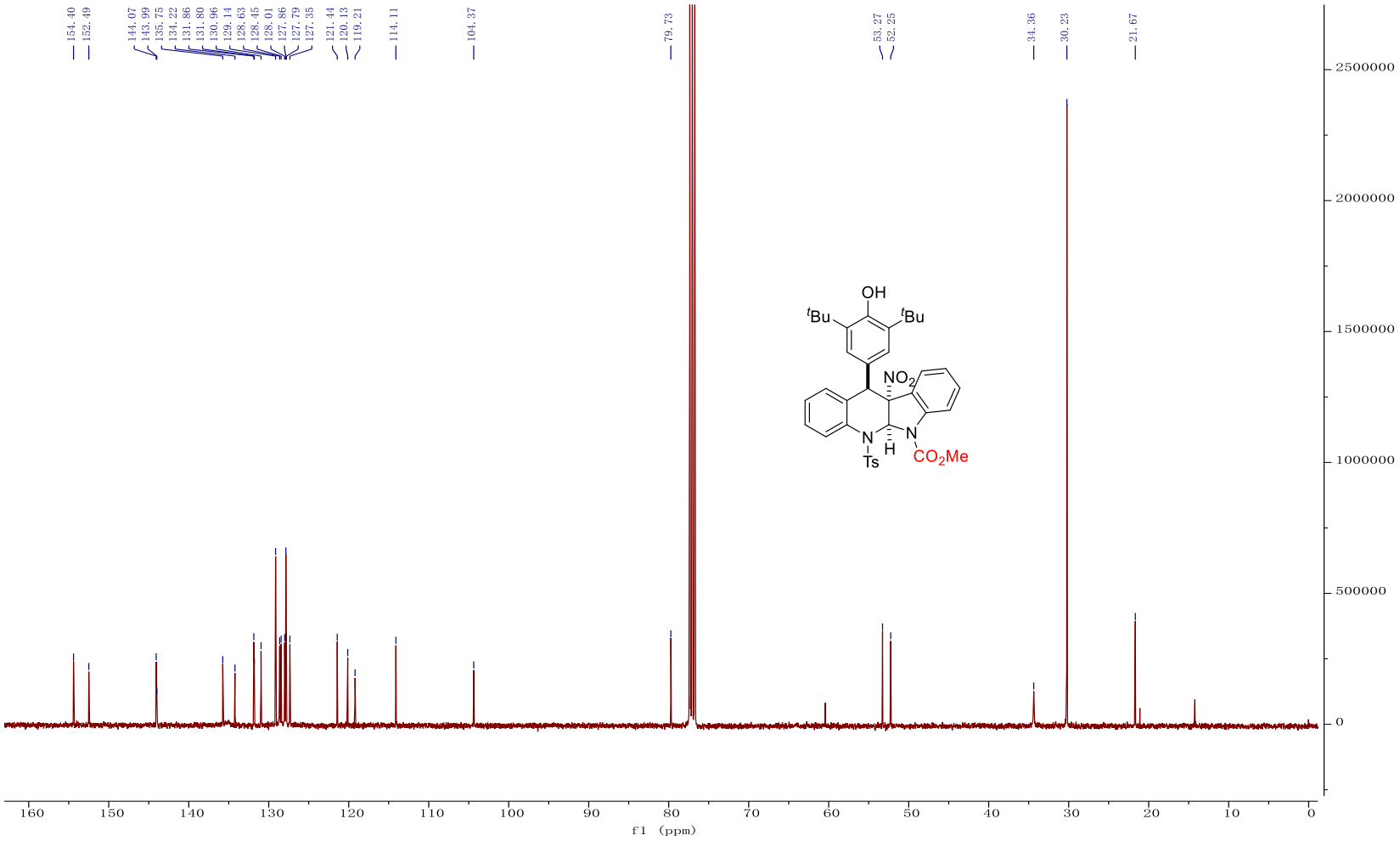
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	17.414	3754.16	91.18	80.76
	36.268	894.17	7.00	19.24
		4648.34		100.00

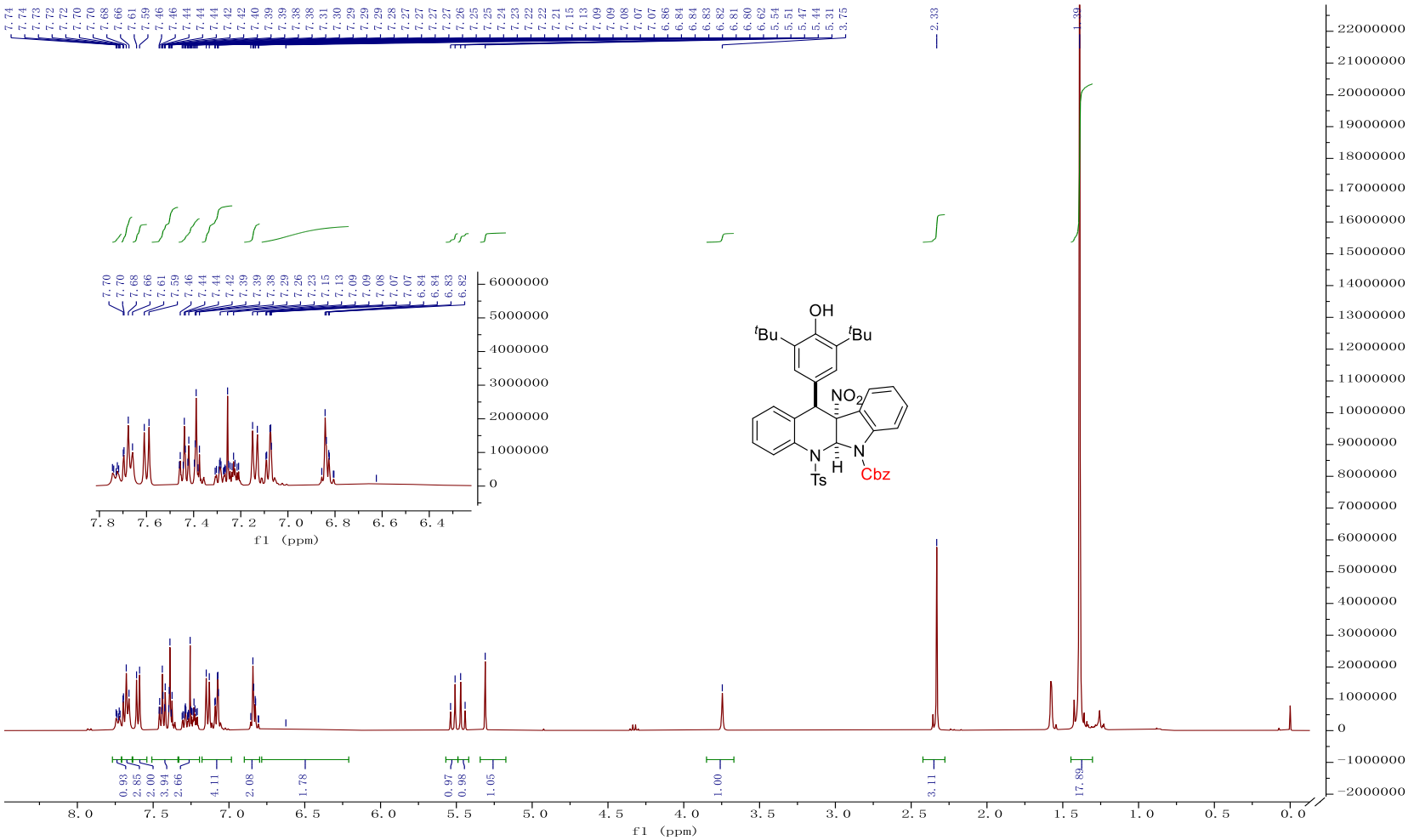
^{1}H NMR spectrum of 3d



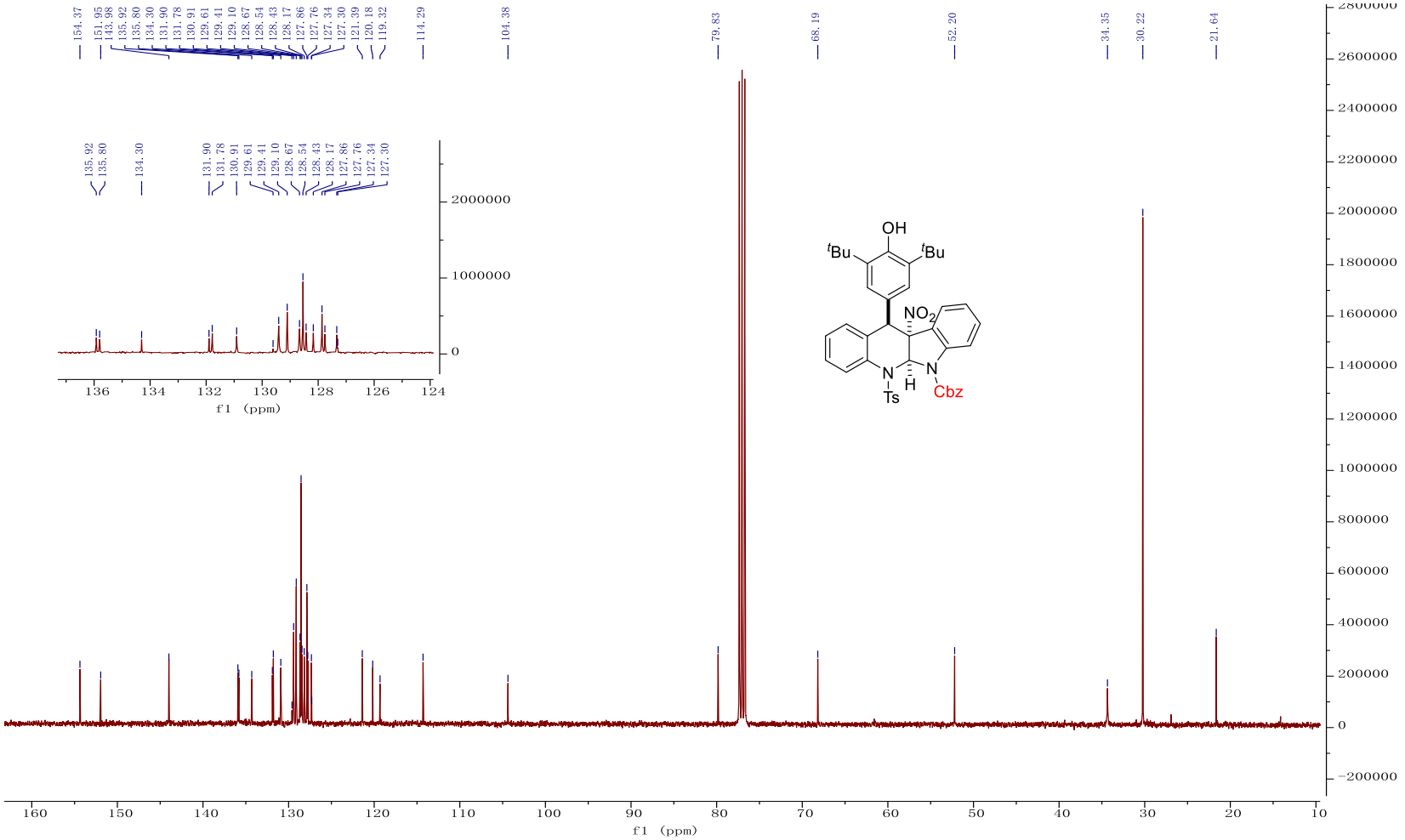
^{13}C NMR spectrum of 3d



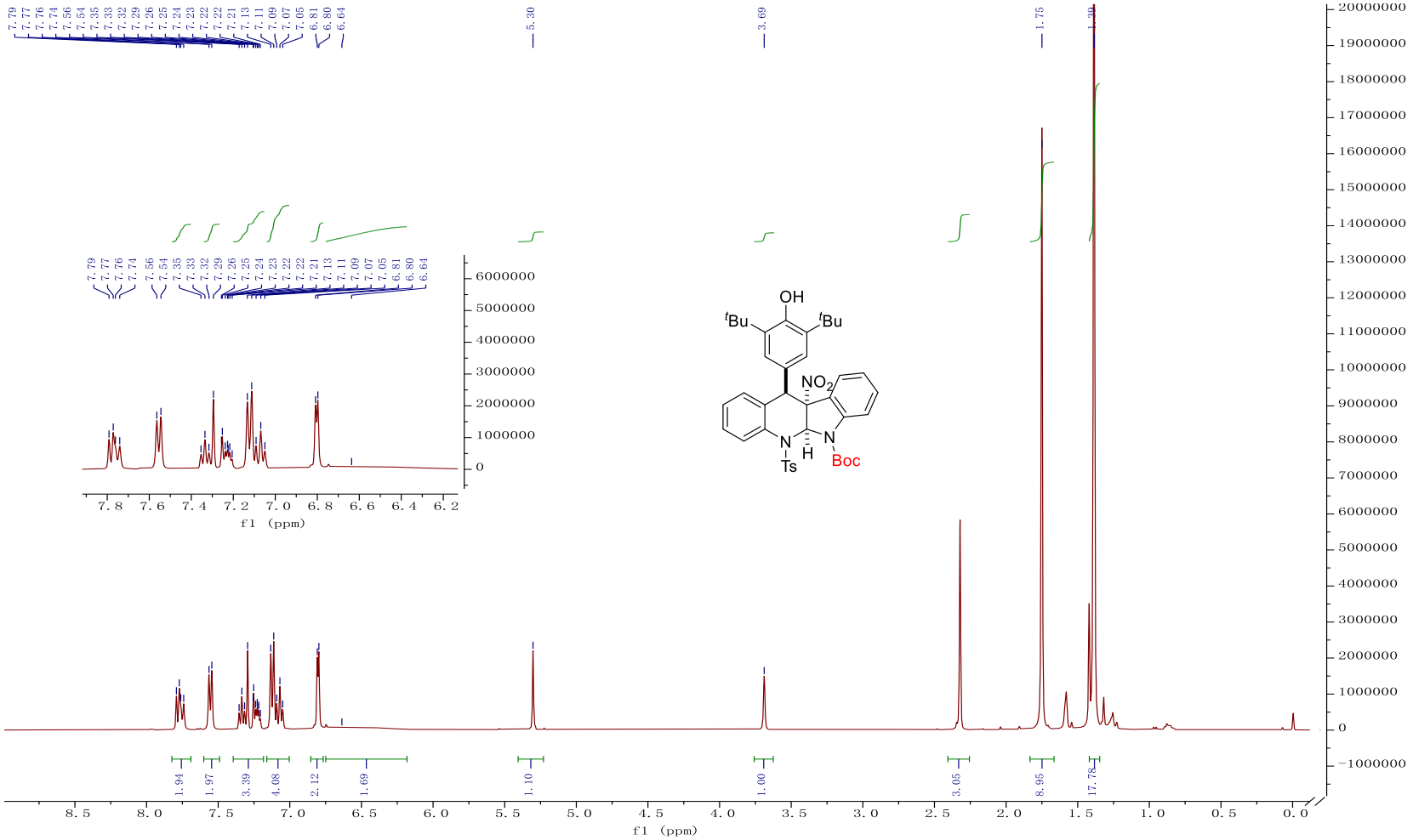
^{1}H NMR spectrum of 3e



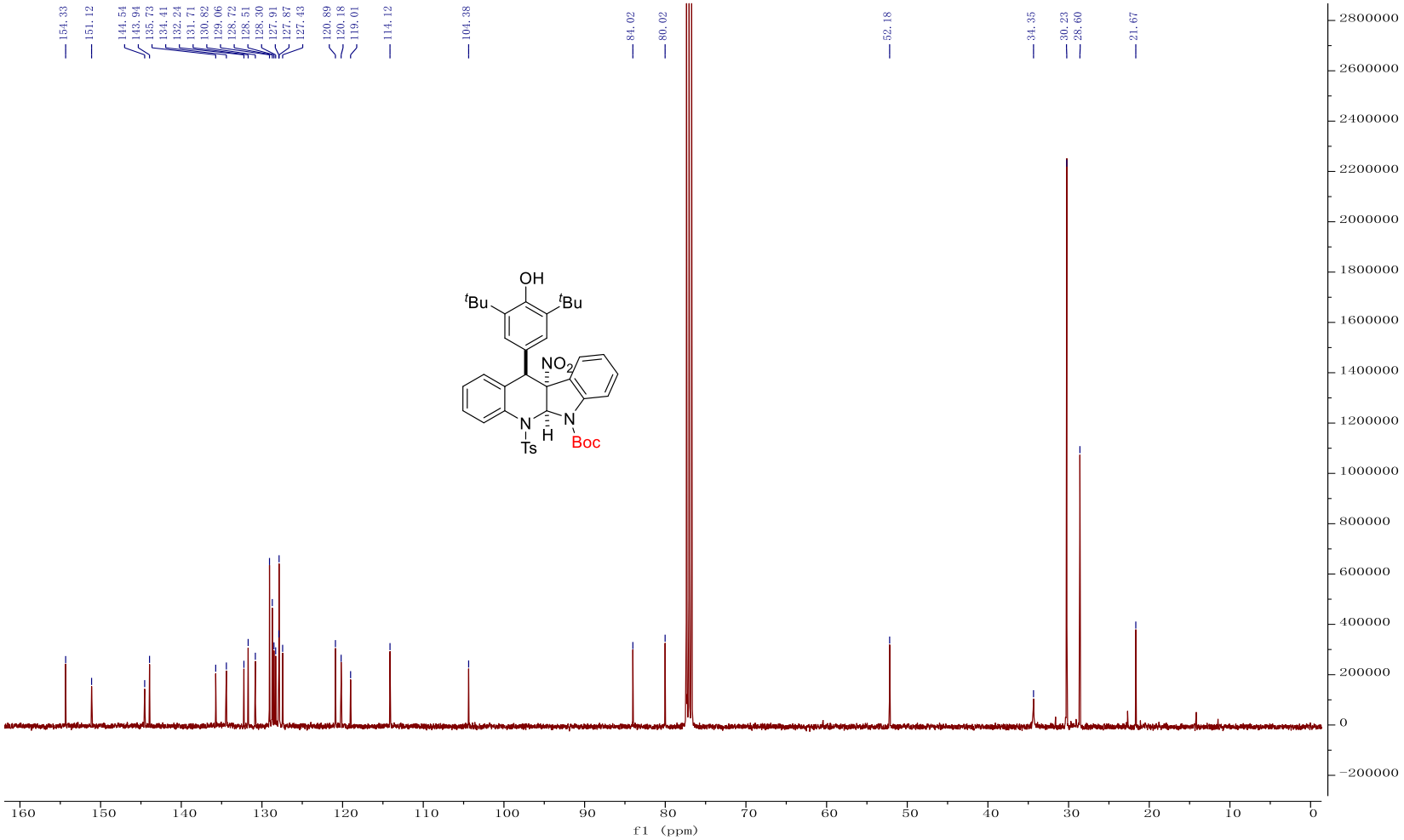
^{13}C NMR spectrum of 3e



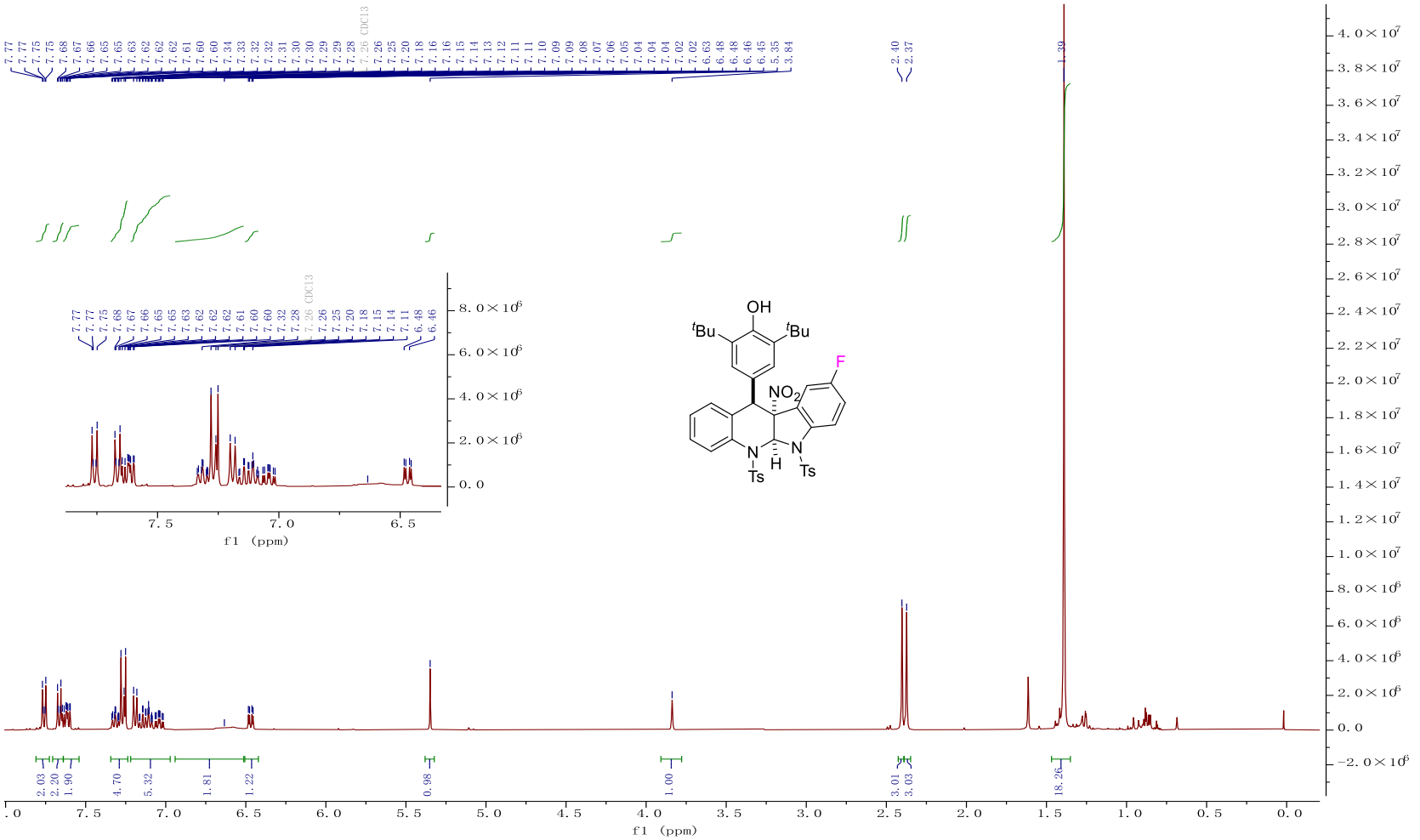
^{1}H NMR spectrum of 3f



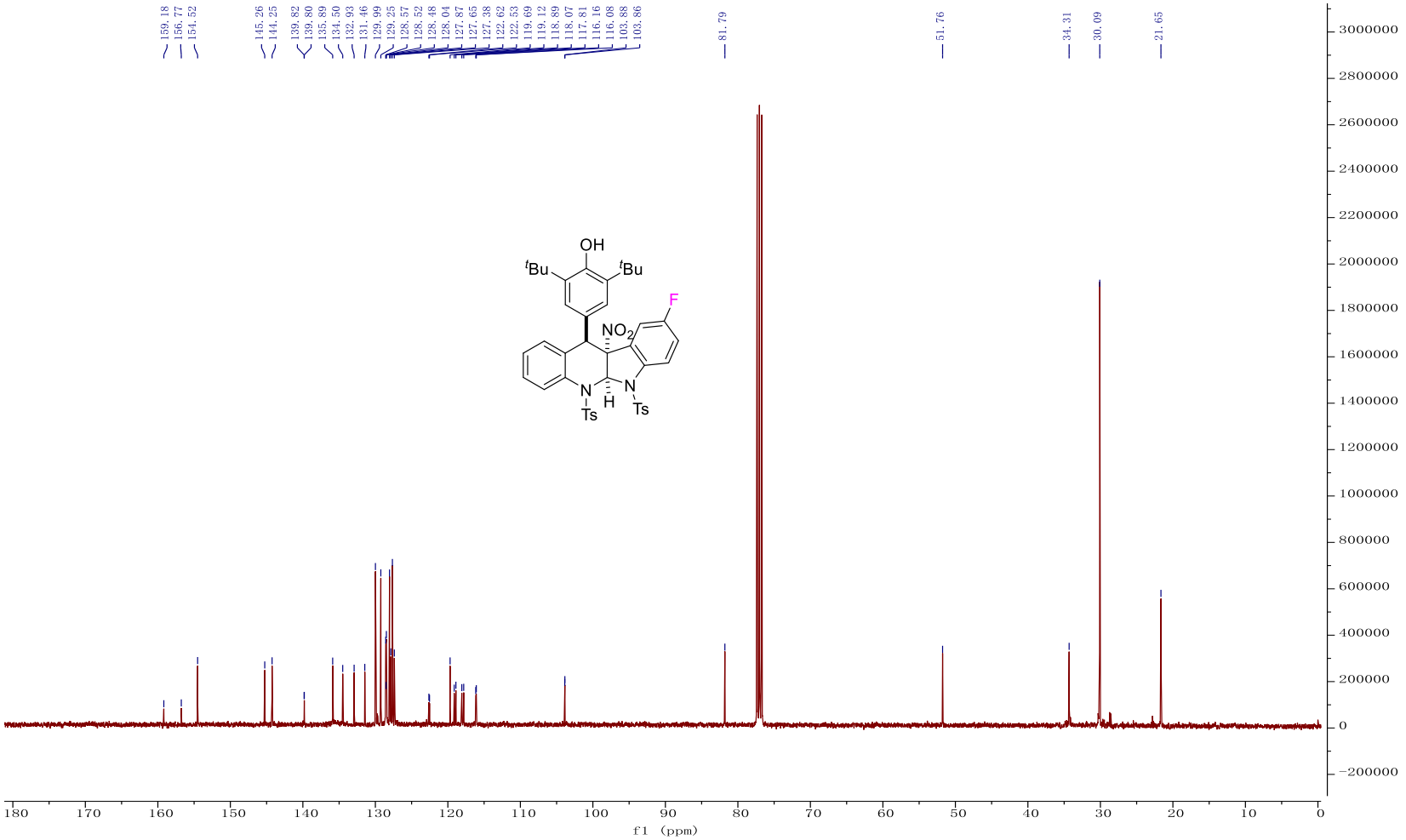
^{13}C NMR spectrum of 3f



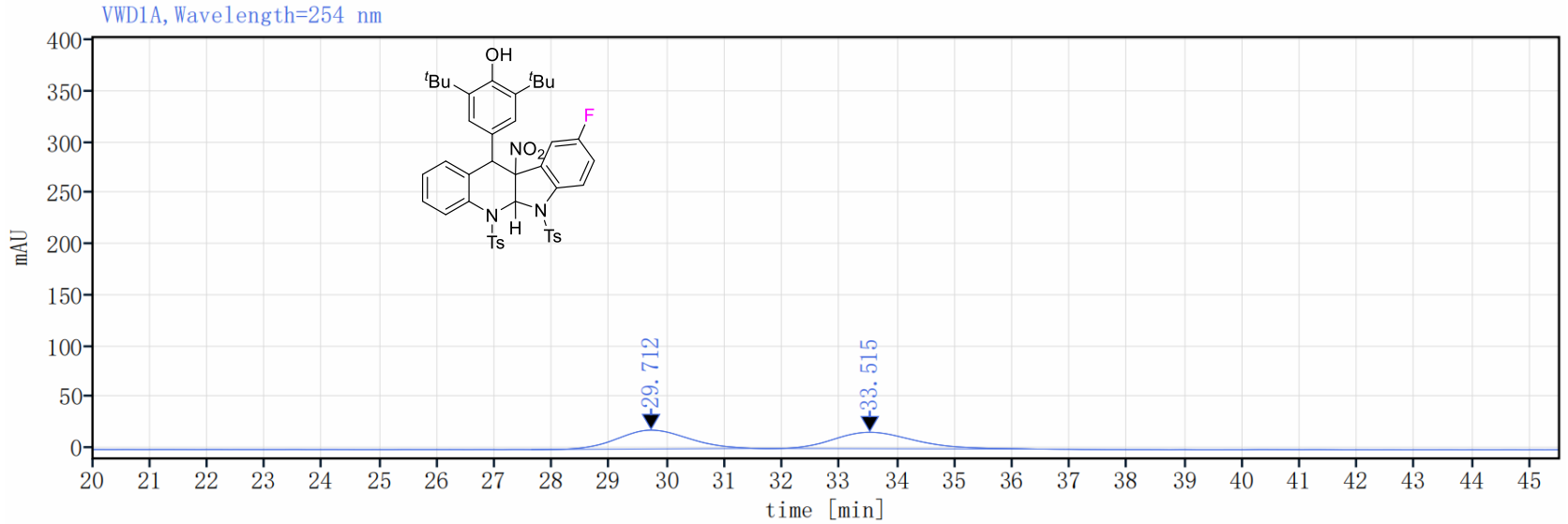
^{1}H NMR spectrum of 3g



^{13}C NMR spectrum of 3g

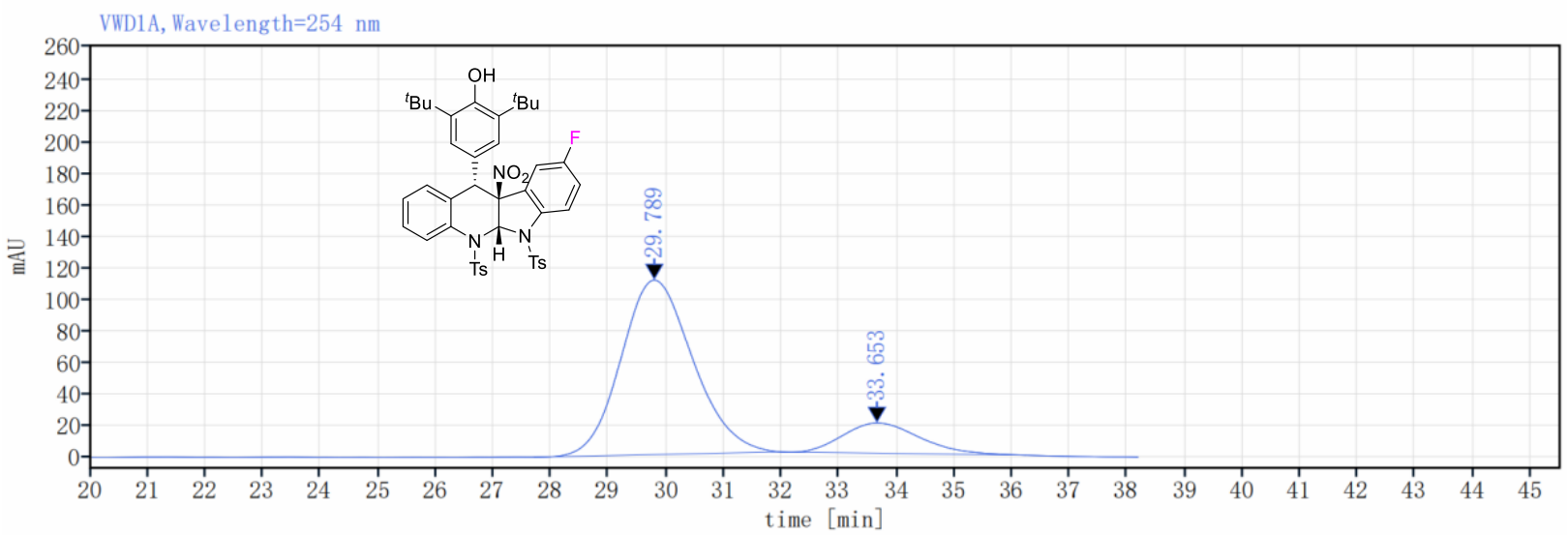


HPLC spectra of 3g



Detector VWD1A,Wavelength=254 nm

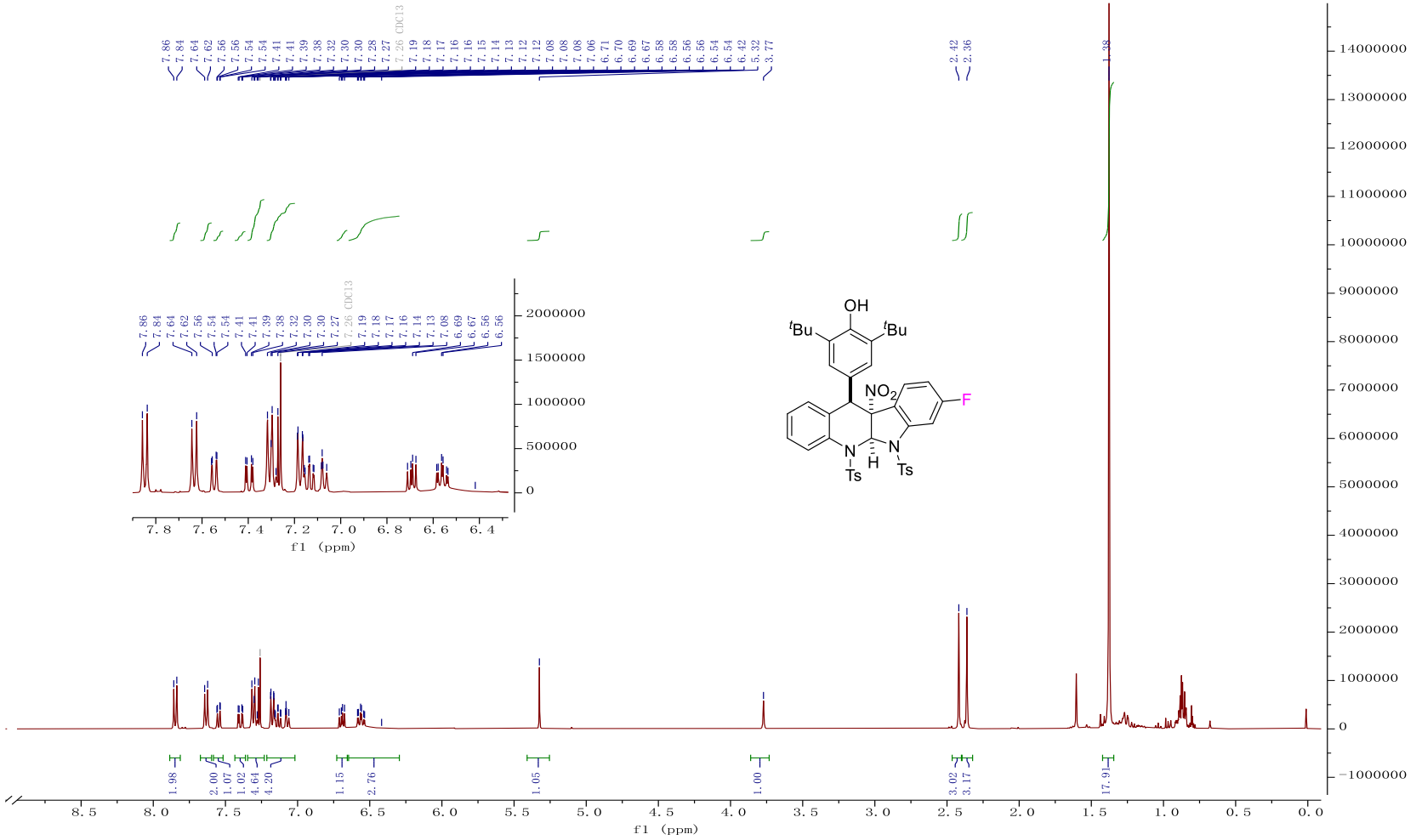
Peak	Ret.Time [min]	Area	Height	Area%
	29.712	1587.86	18.47	50.38
	33.515	1563.64	16.10	49.62
		3151.50		100.00



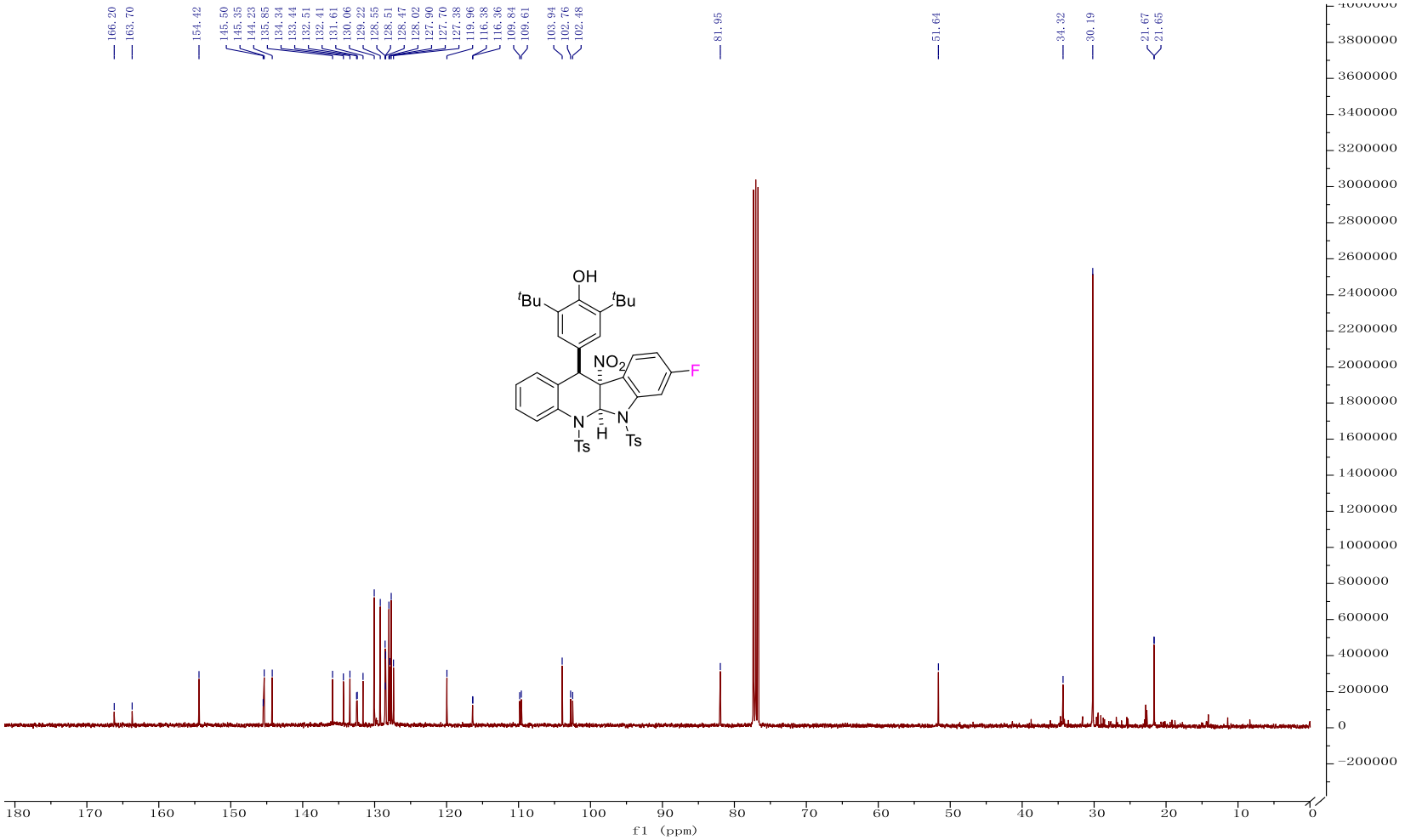
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	29.789	9564.71	110.50	84.40
	33.653	1767.98	19.05	15.60
		11332.69		100.00

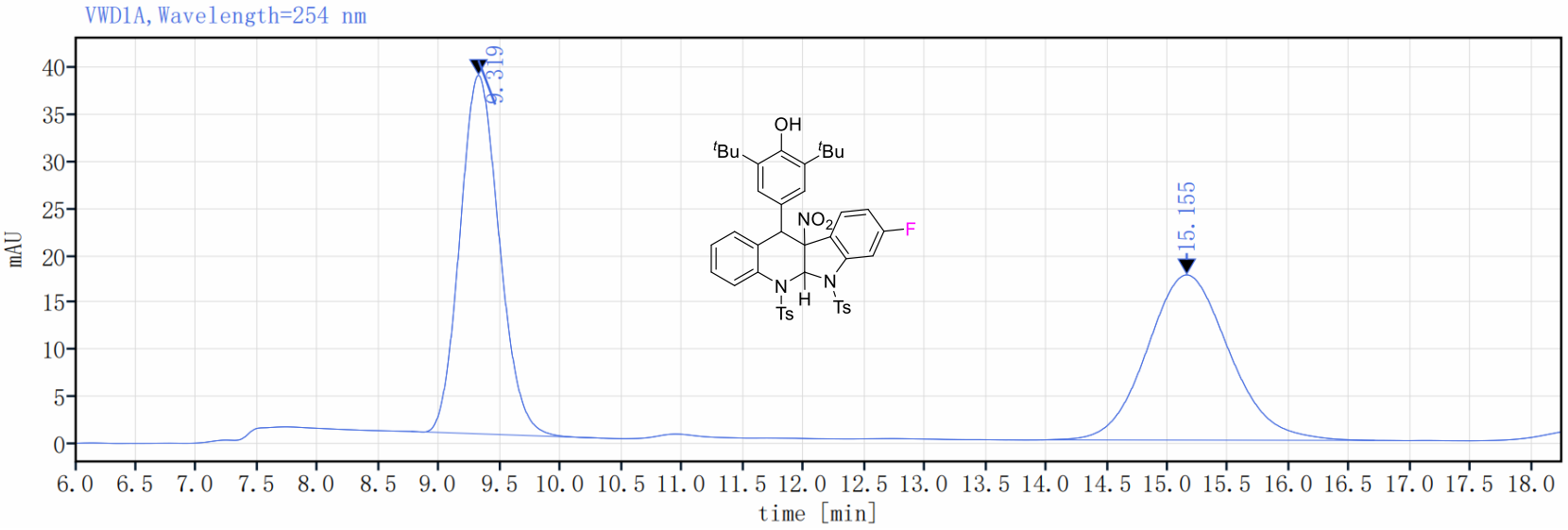
^{1}H NMR spectrum of 3h



^{13}C NMR spectrum of compound of 3h

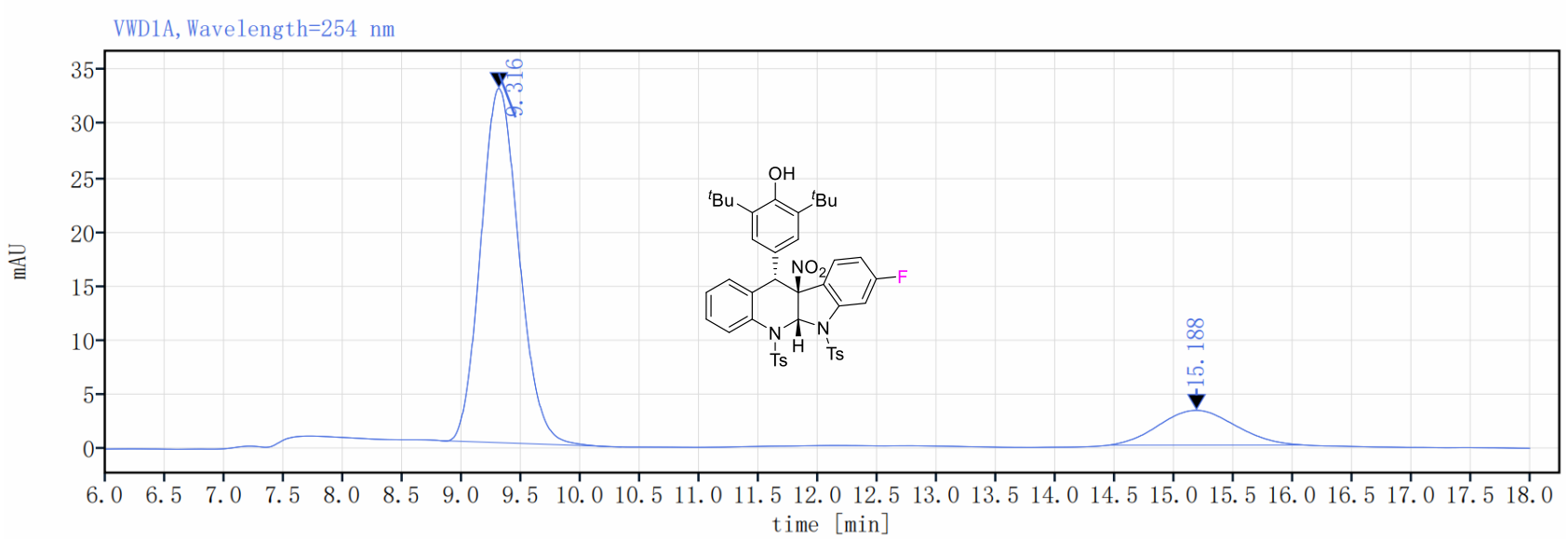


HPLC spectra of 3h



Detector VWD1A,Wavelength=254 nm

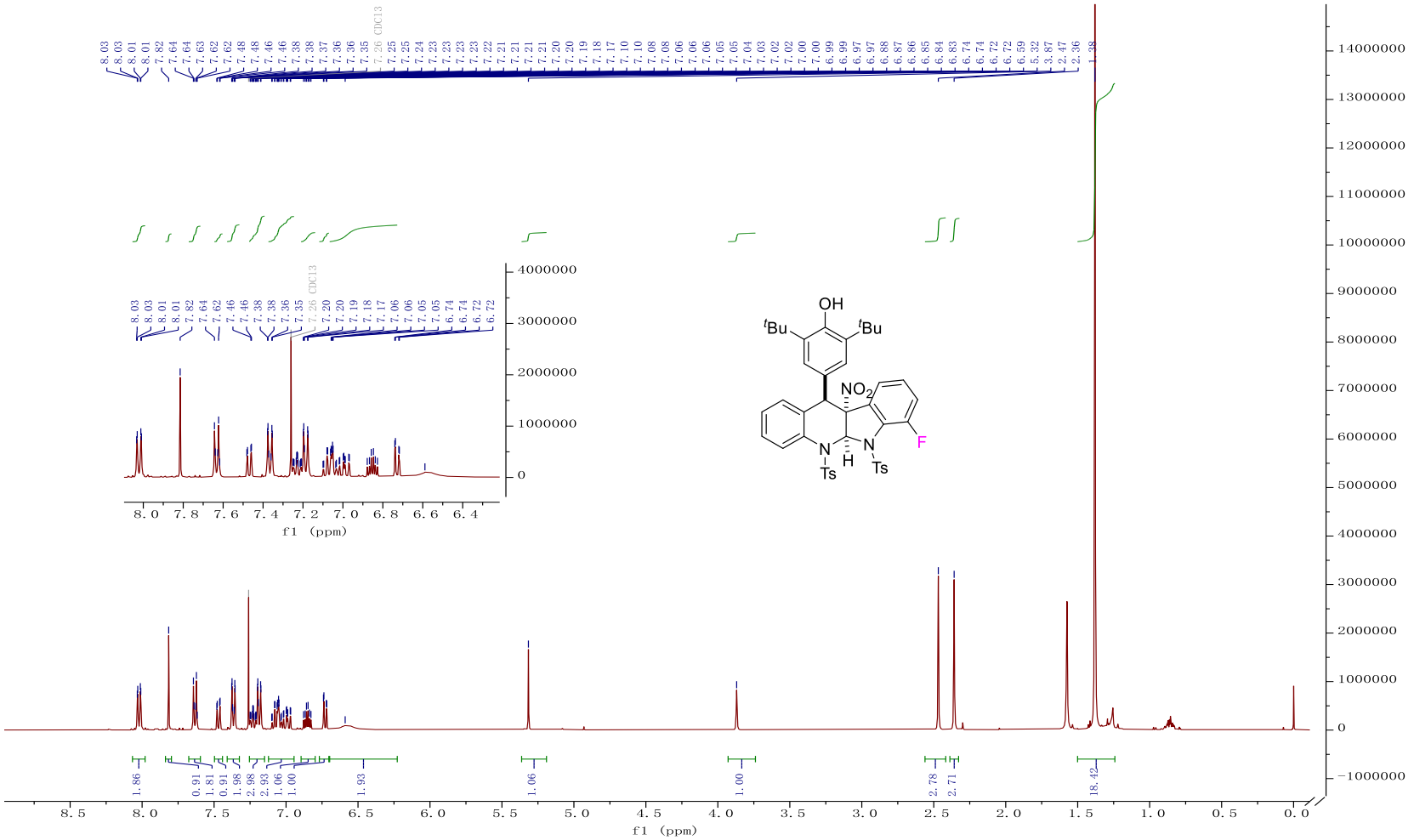
Peak	Ret.Time [min]	Area	Height	Area%
	9.319	857.98	38.07	50.93
	15.155	826.70	17.55	49.07
		1684.68		100.00



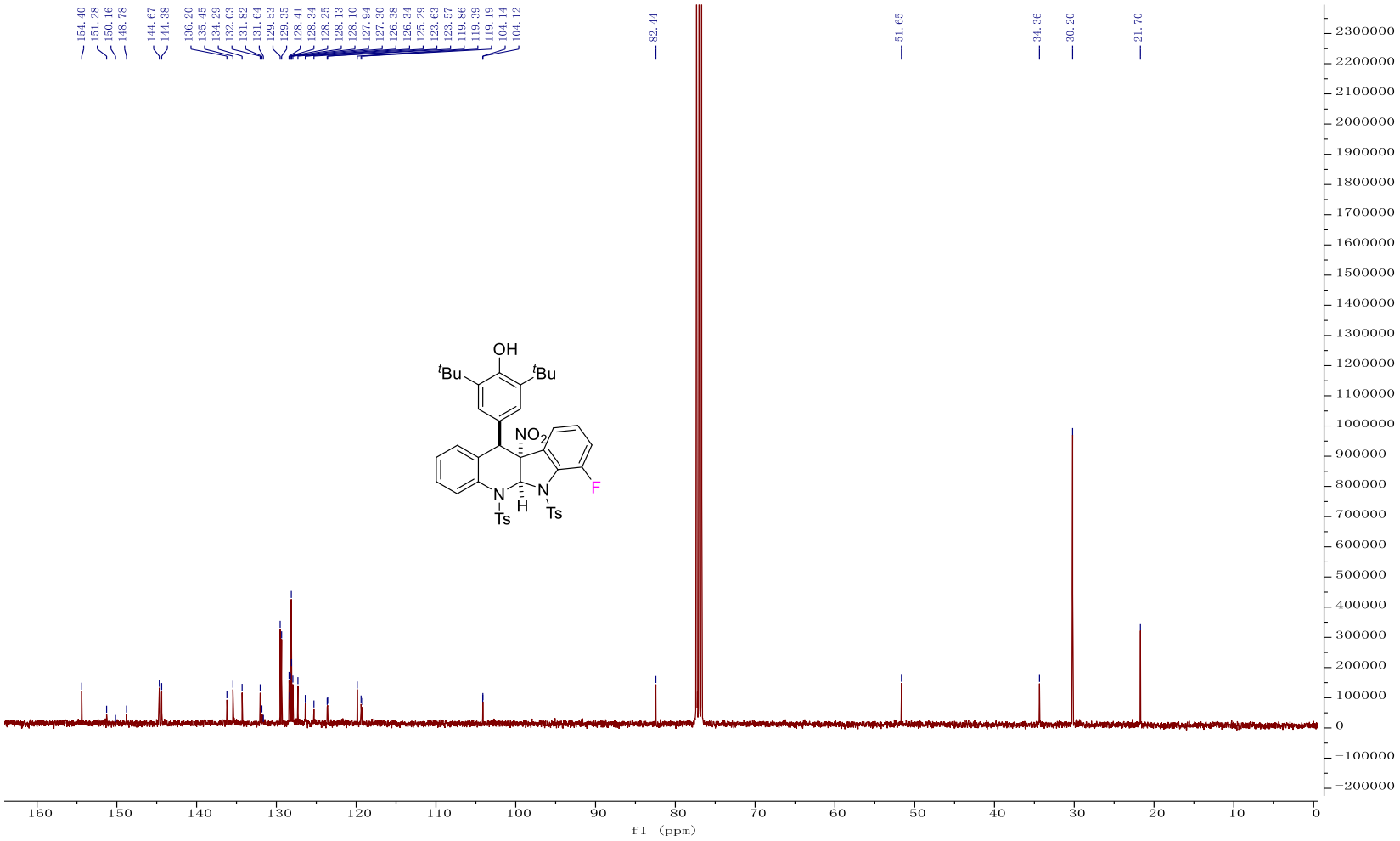
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	9.316	733.17	32.68	83.64
	15.188	143.37	3.21	16.36
		876.54		100.00

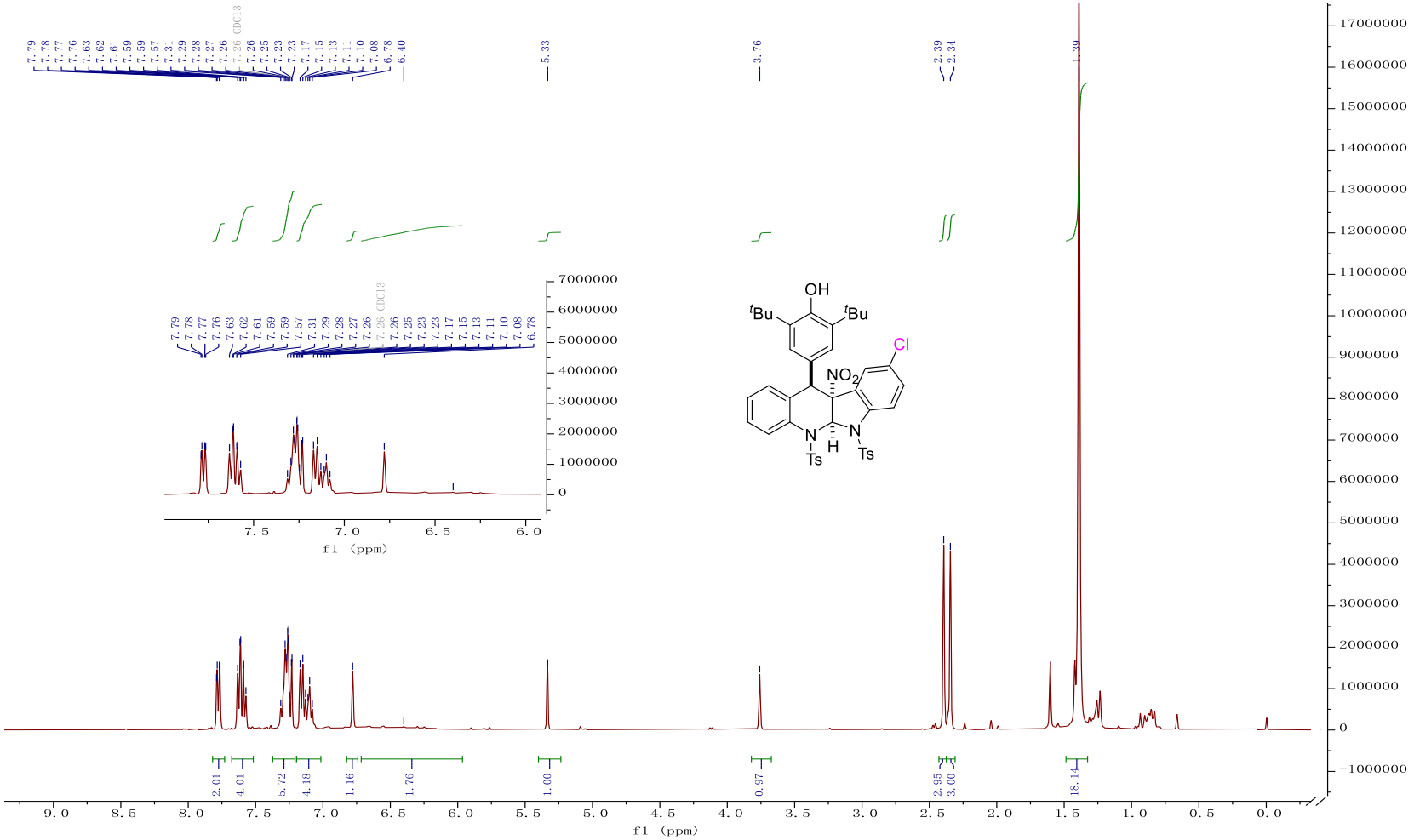
^{1}H NMR spectrum of 3i



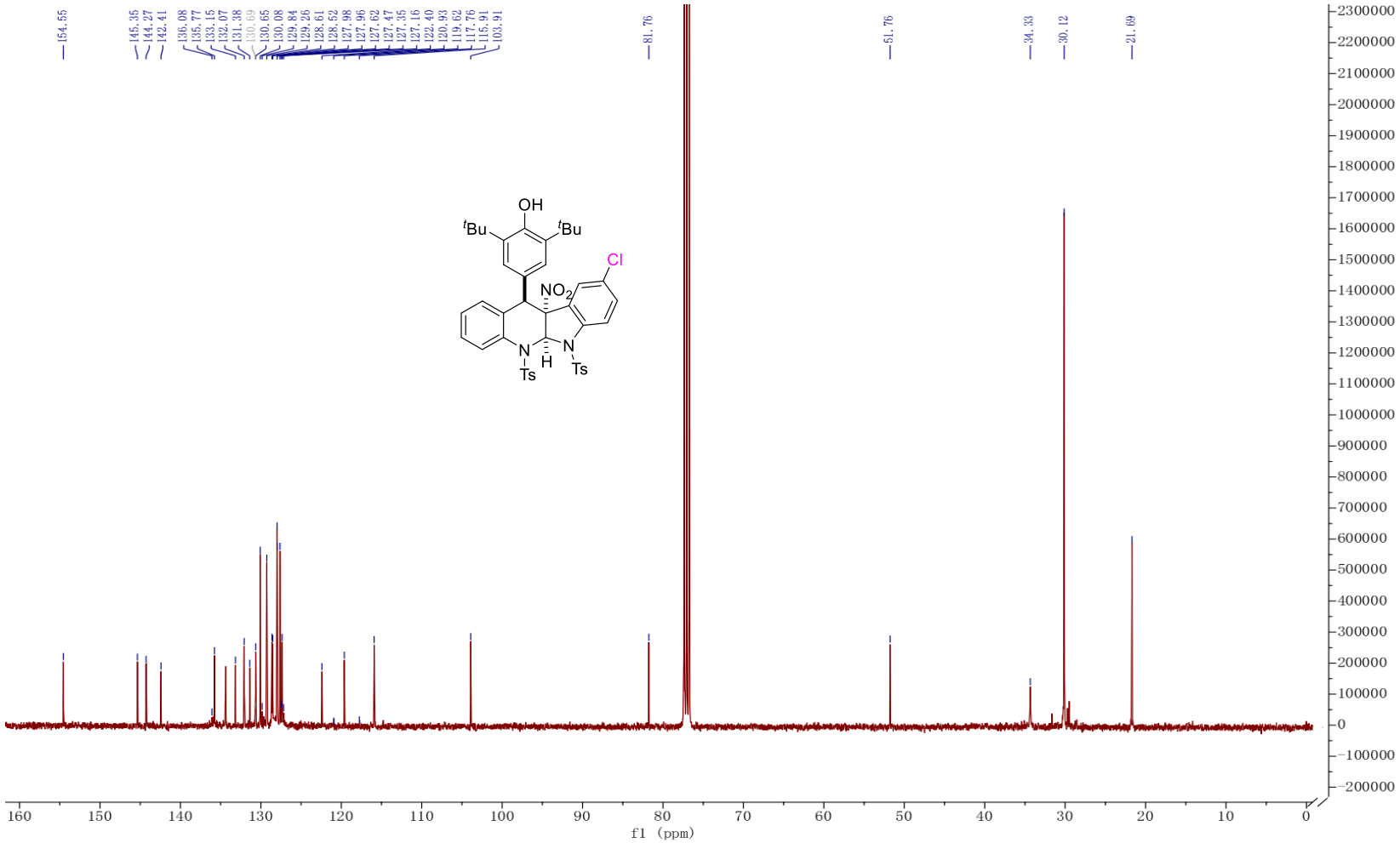
^{13}C NMR spectrum of 3i



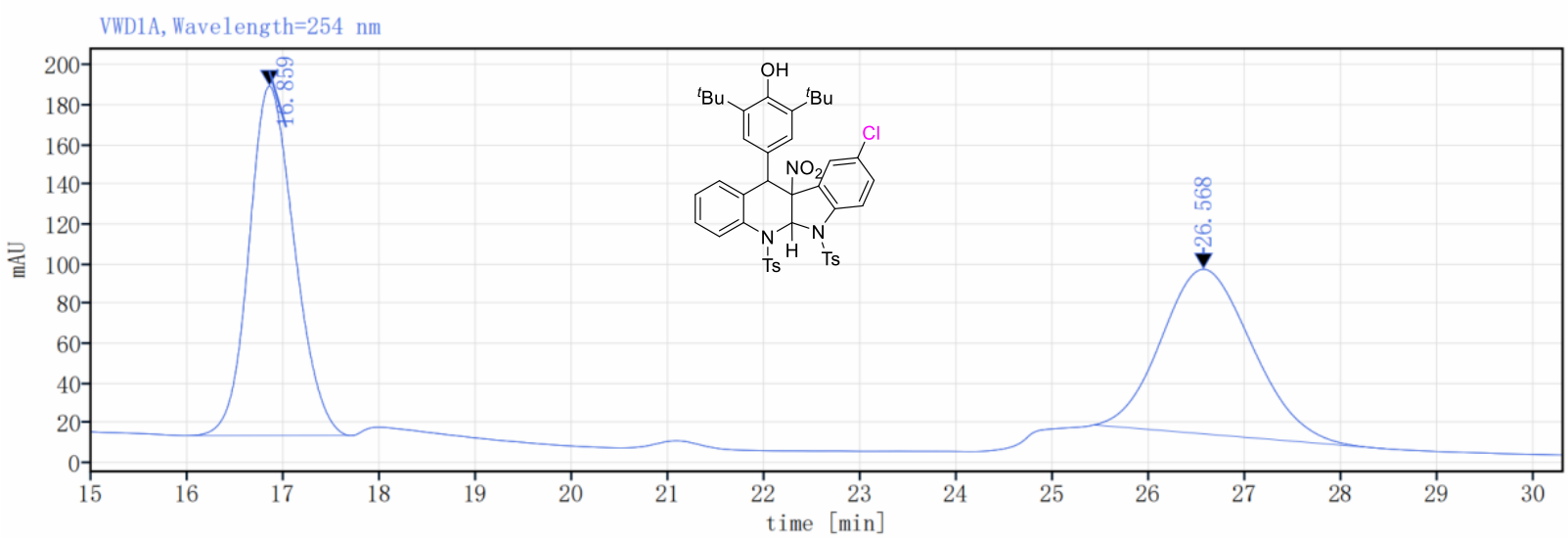
^{1}H NMR spectrum of 3j



^{13}C NMR spectrum of 3j

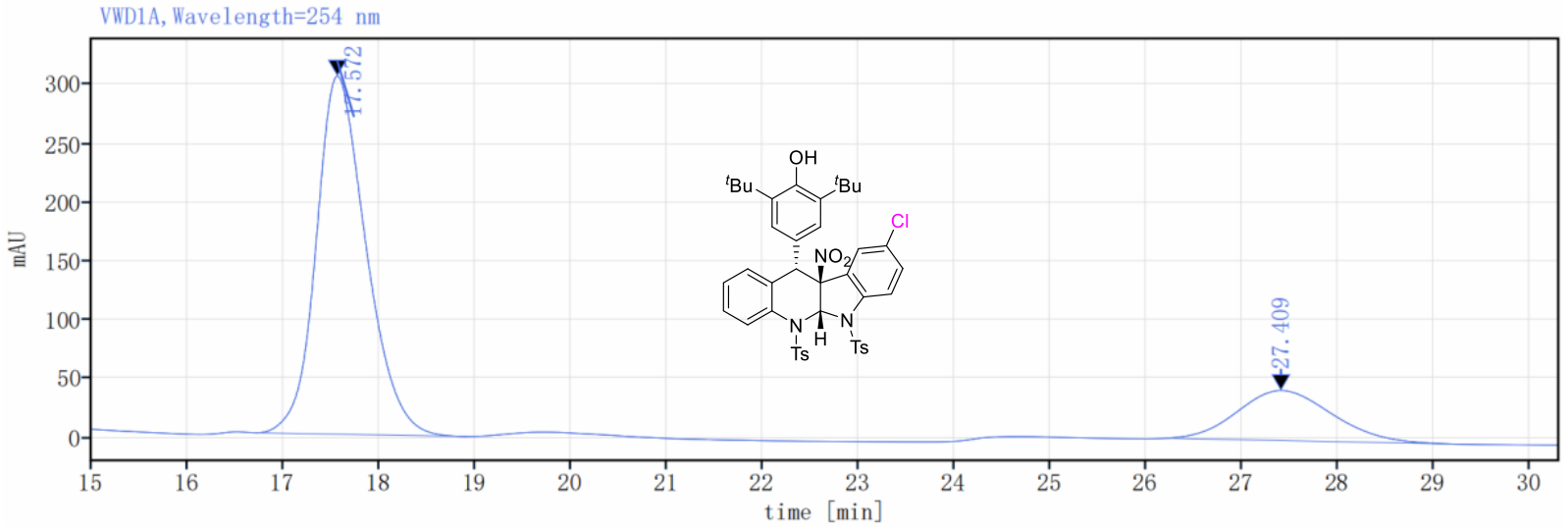


HPLC spectra of 3j



Detector VWD1A, Wavelength=254 nm

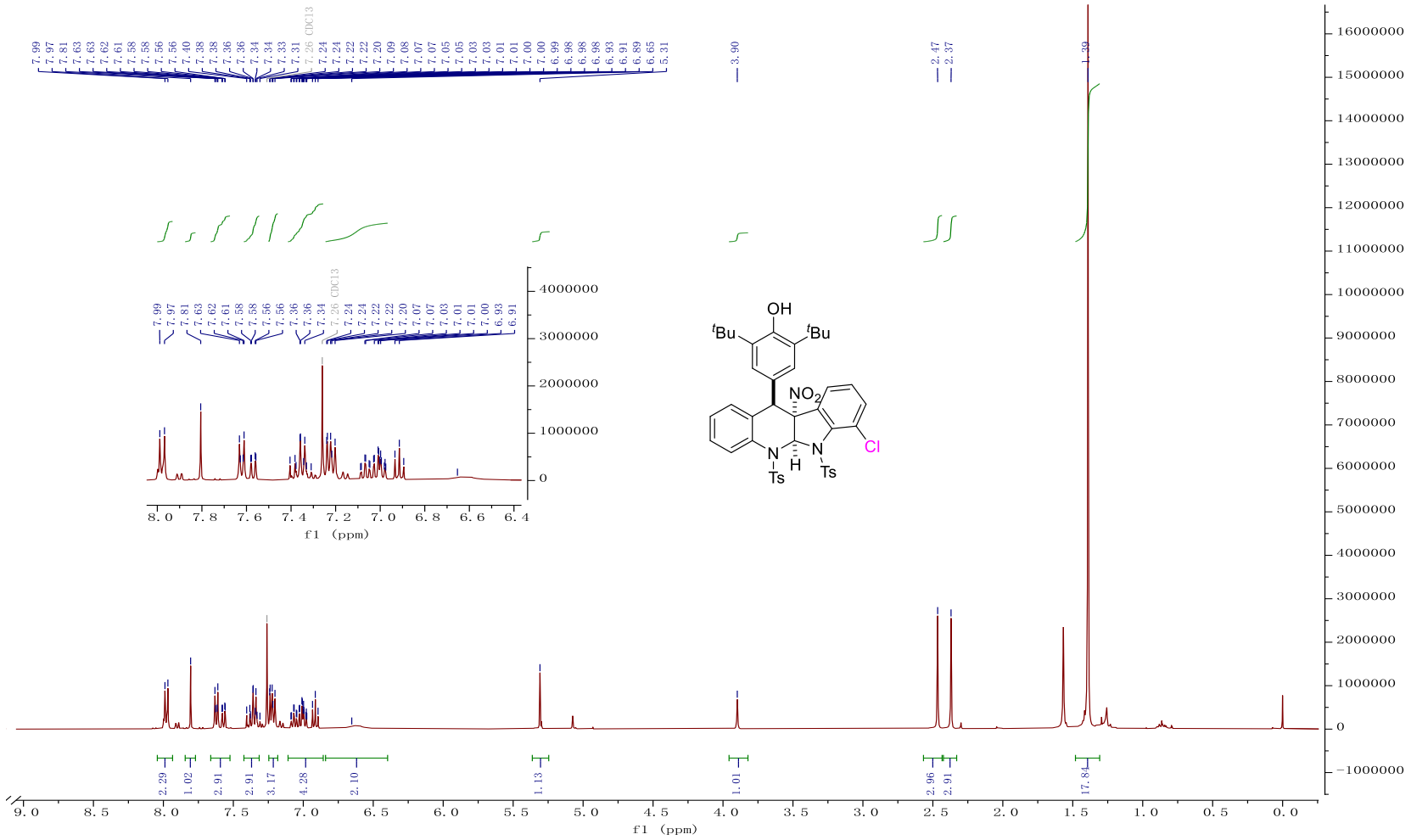
Peak	Ret.Time [min]	Area	Height	Area%
	16.859	5765.13	175.42	51.48
	26.568	5433.61	82.71	48.52
		11198.73		100.00



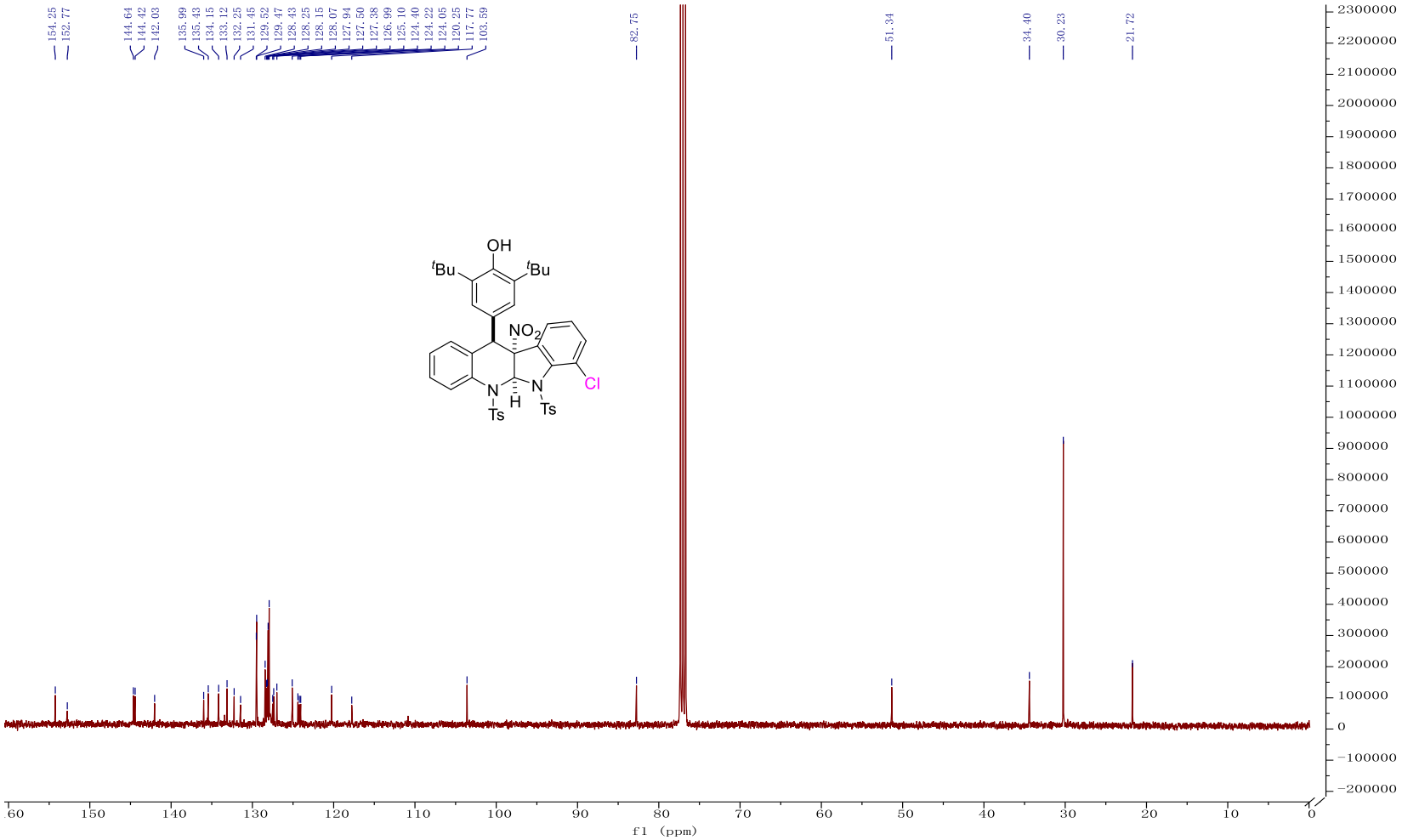
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	17.572	10997.89	304.53	79.08
	27.409	2909.90	42.47	20.92
		13907.79		100.00

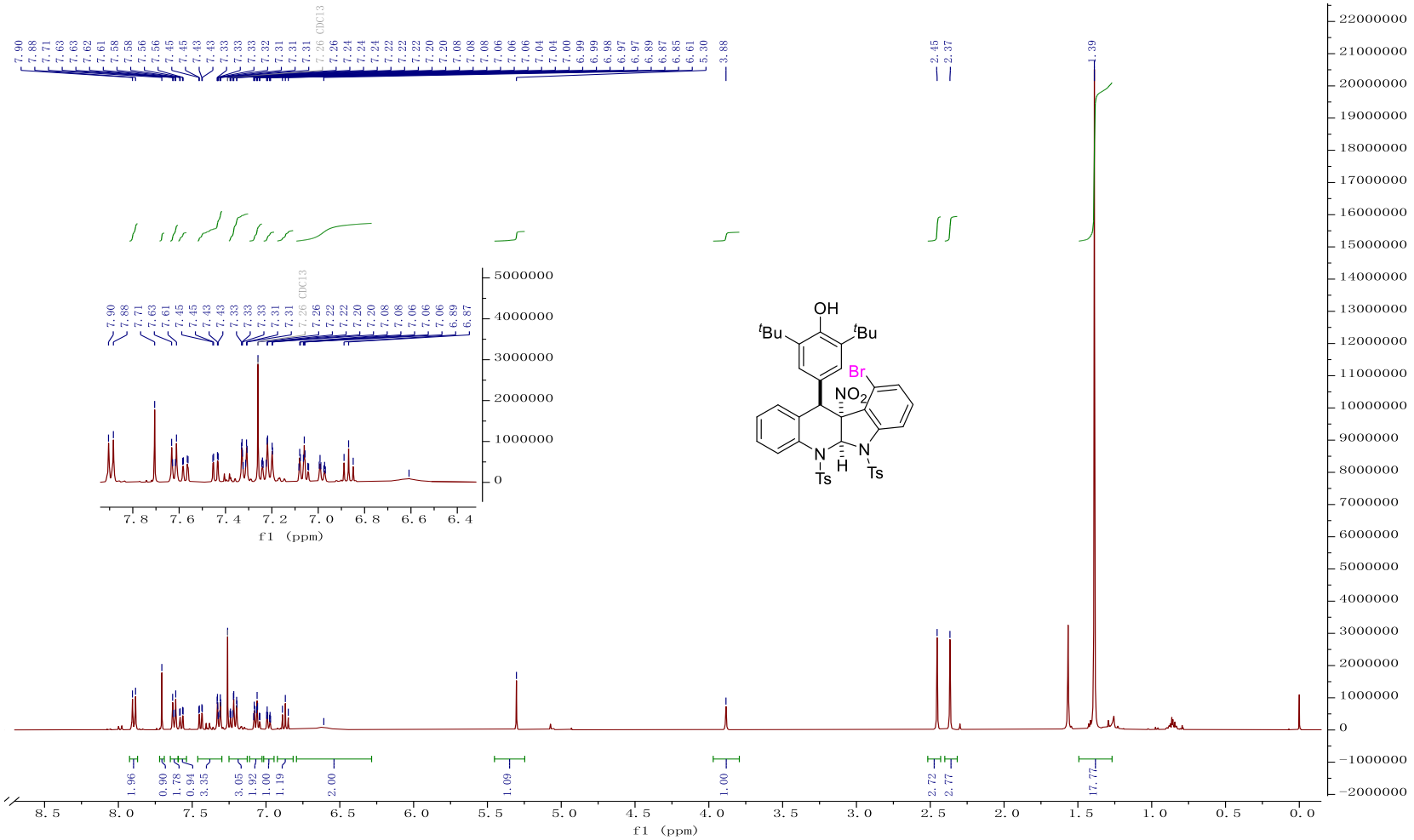
^{1}H NMR spectrum of 3k



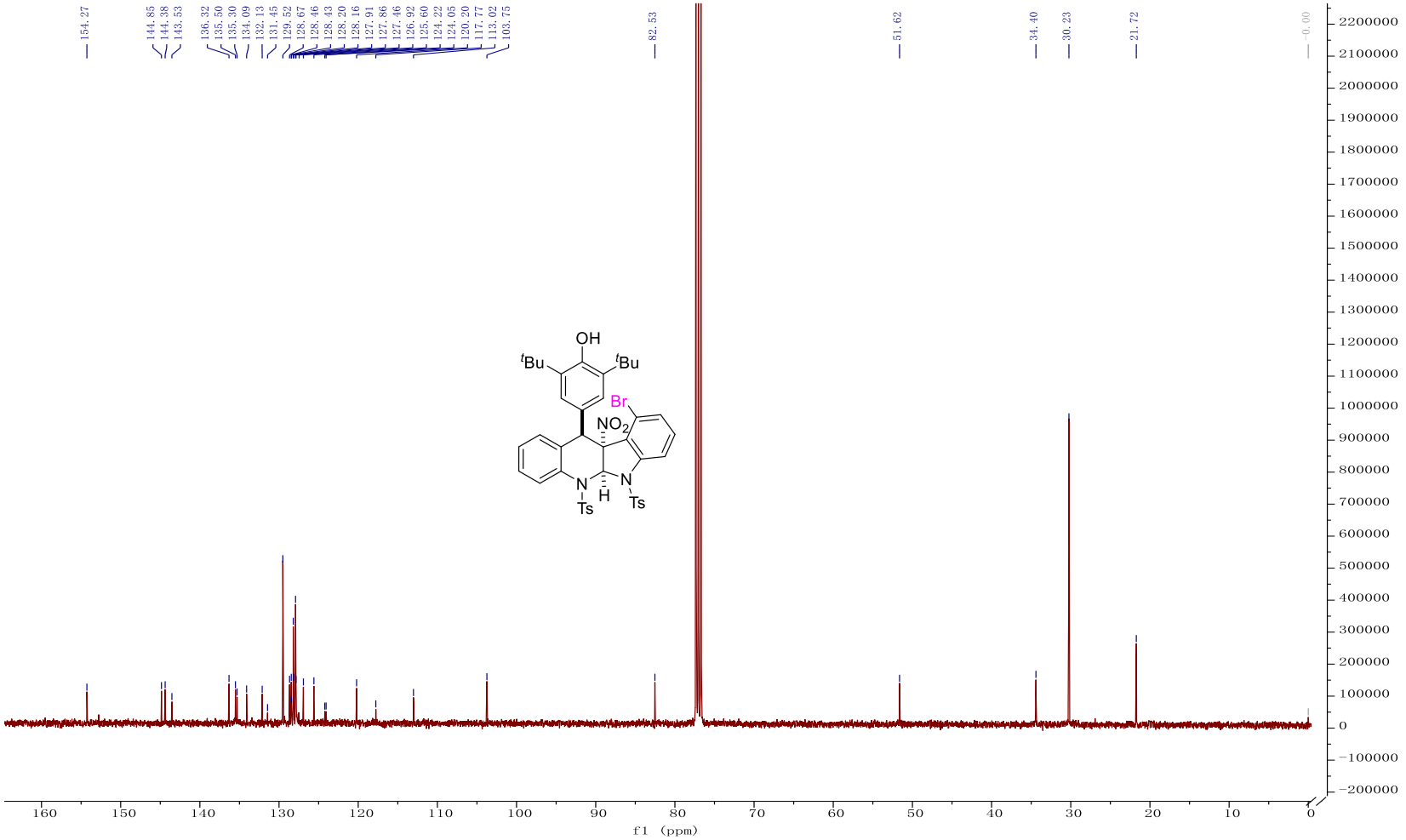
^{13}C NMR spectrum of 3k



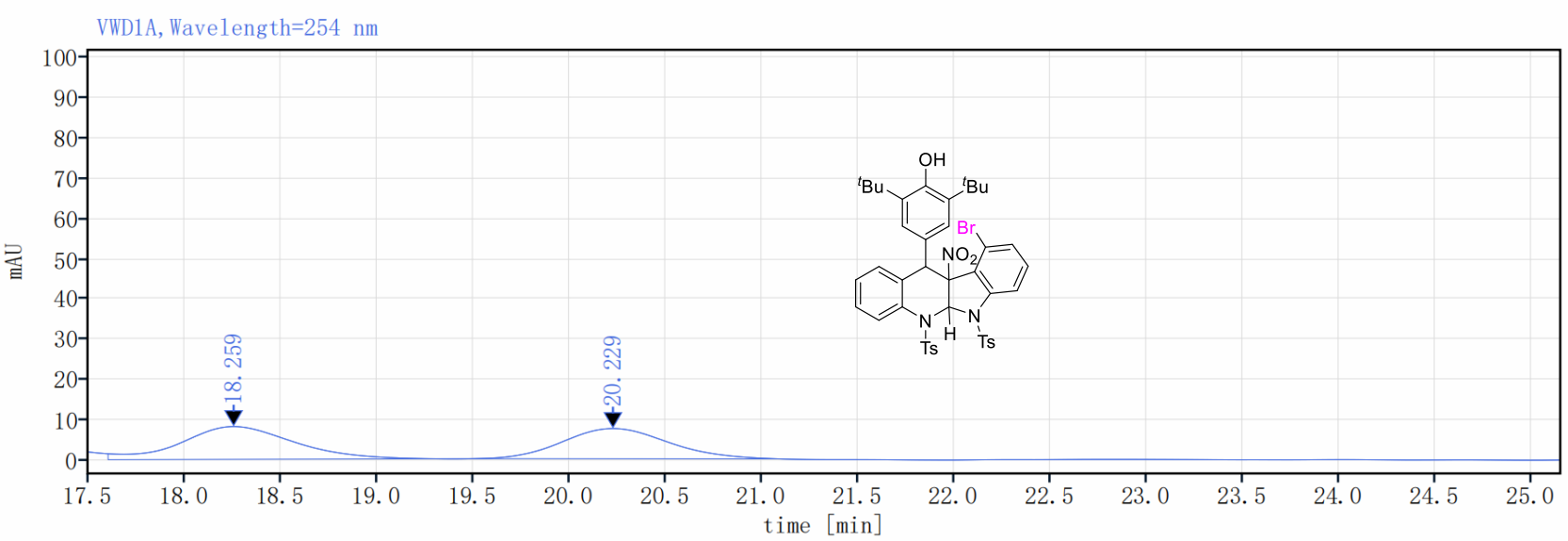
^{1}H NMR spectrum of 3l



^{13}C NMR spectrum of 3l

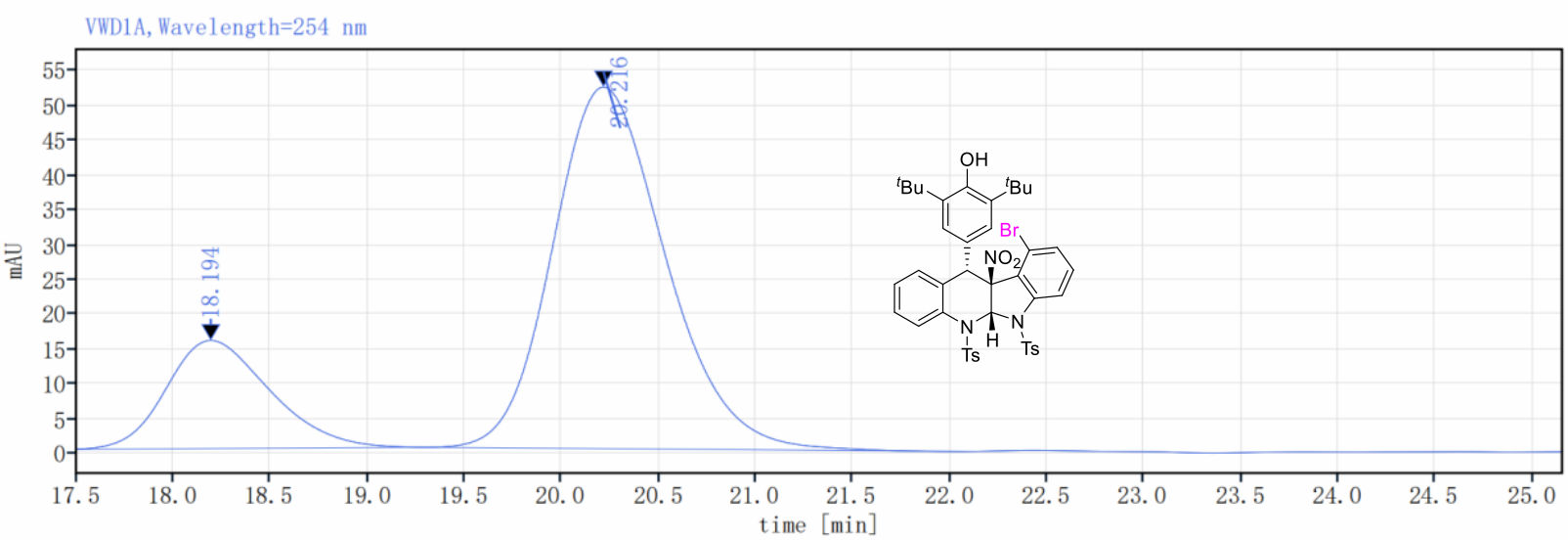


HPLC spectra of 3l



Detector VWD1A,Wavelength=254 nm

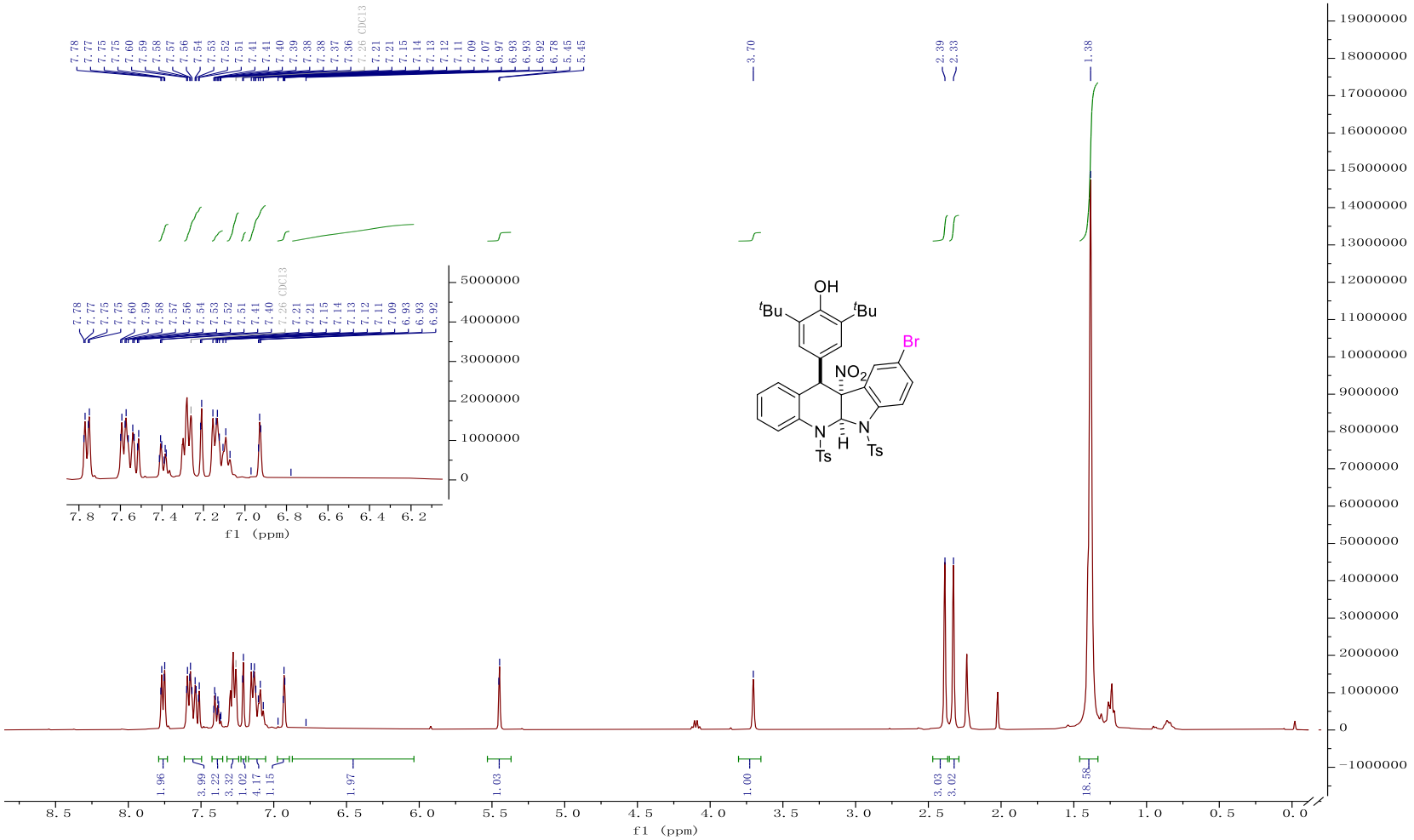
Peak	Ret.Time [min]	Area	Height	Area%
	18.259	330.64	8.14	53.59
	20.229	286.40	7.50	46.41
		617.04		100.00



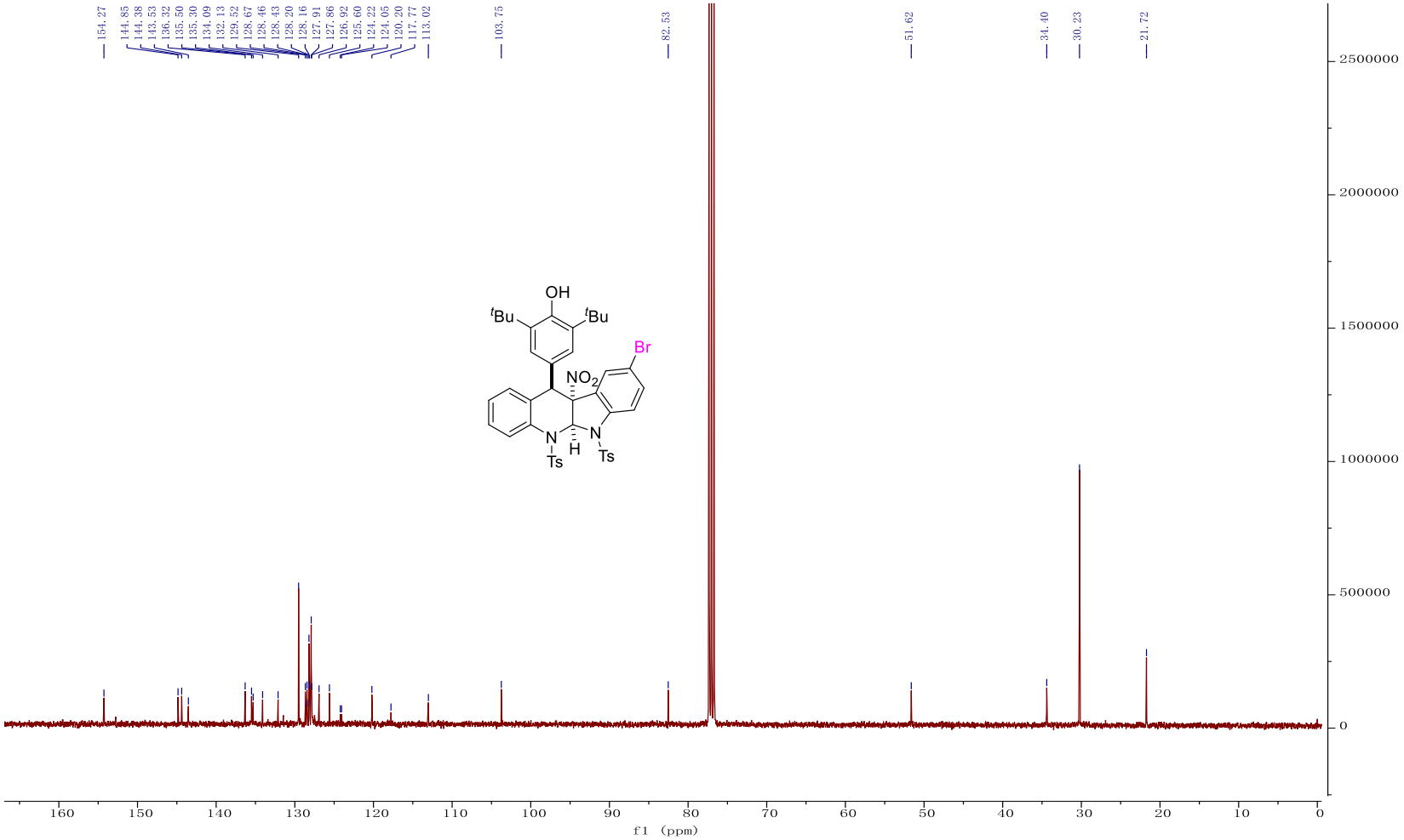
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	18.194	575.99	15.55	21.51
	20.216	2101.71	52.05	78.49
		2677.70		100.00

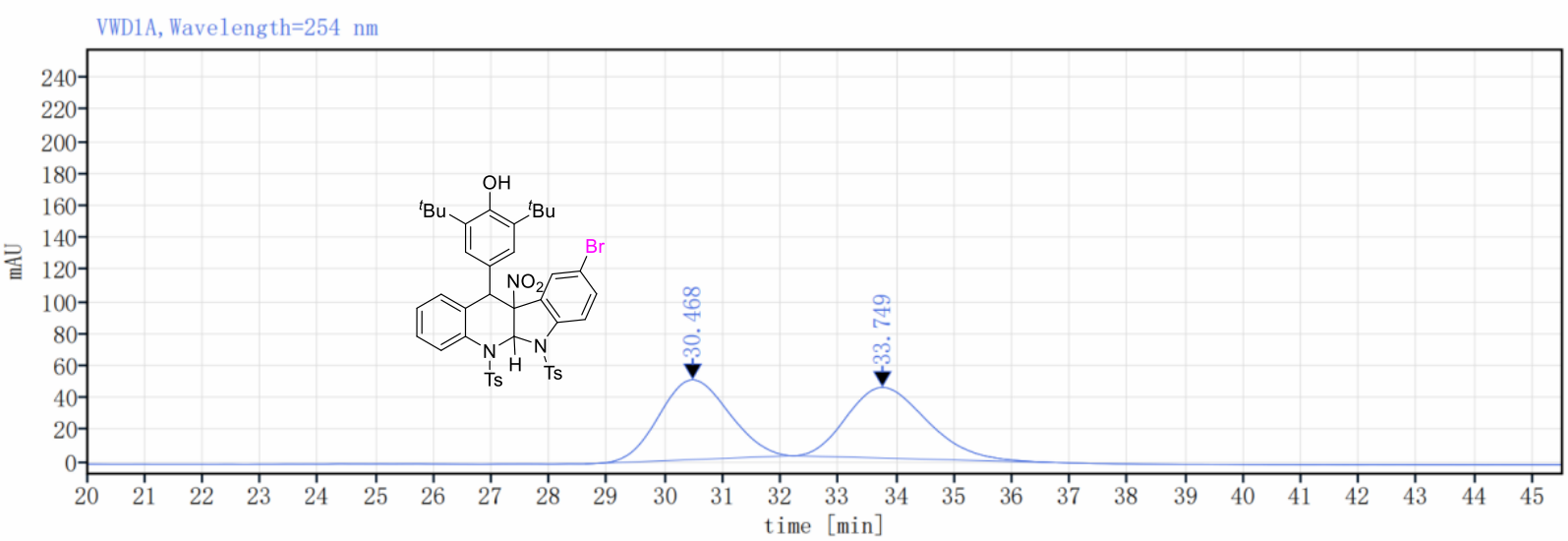
^{1}H NMR spectrum of 3m



^{13}C NMR spectrum of 3m

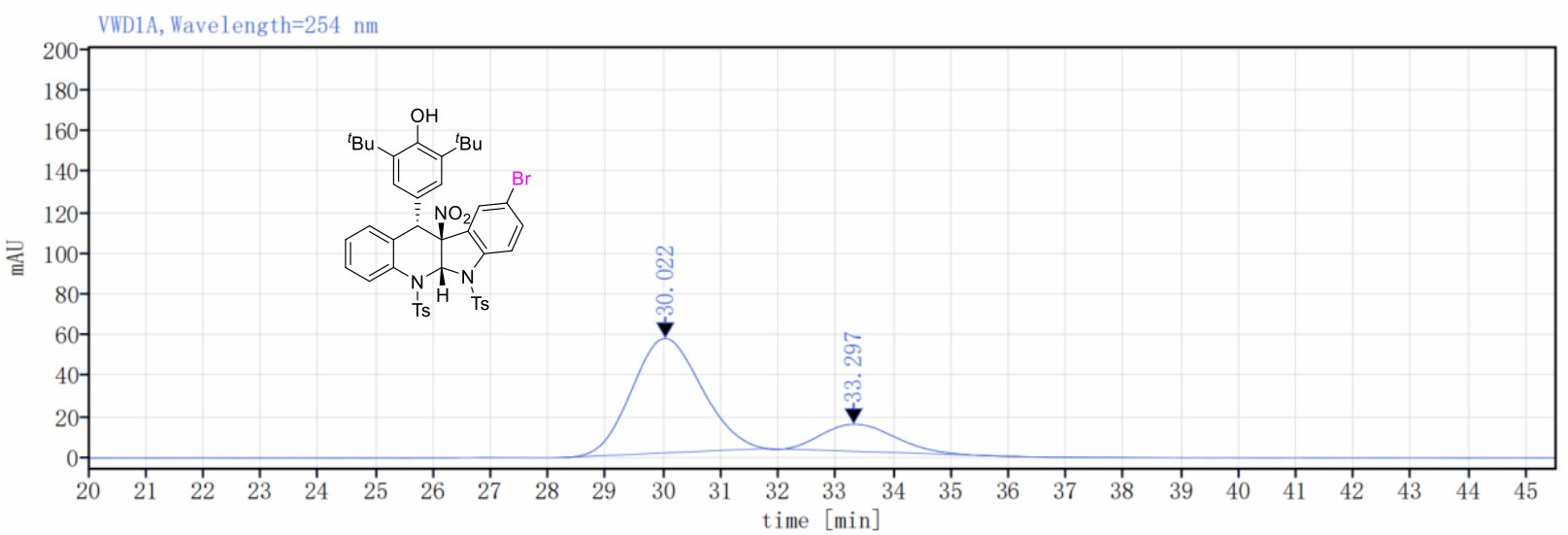


HPLC spectra of 3m



Detector VWD1A, Wavelength=254 nm

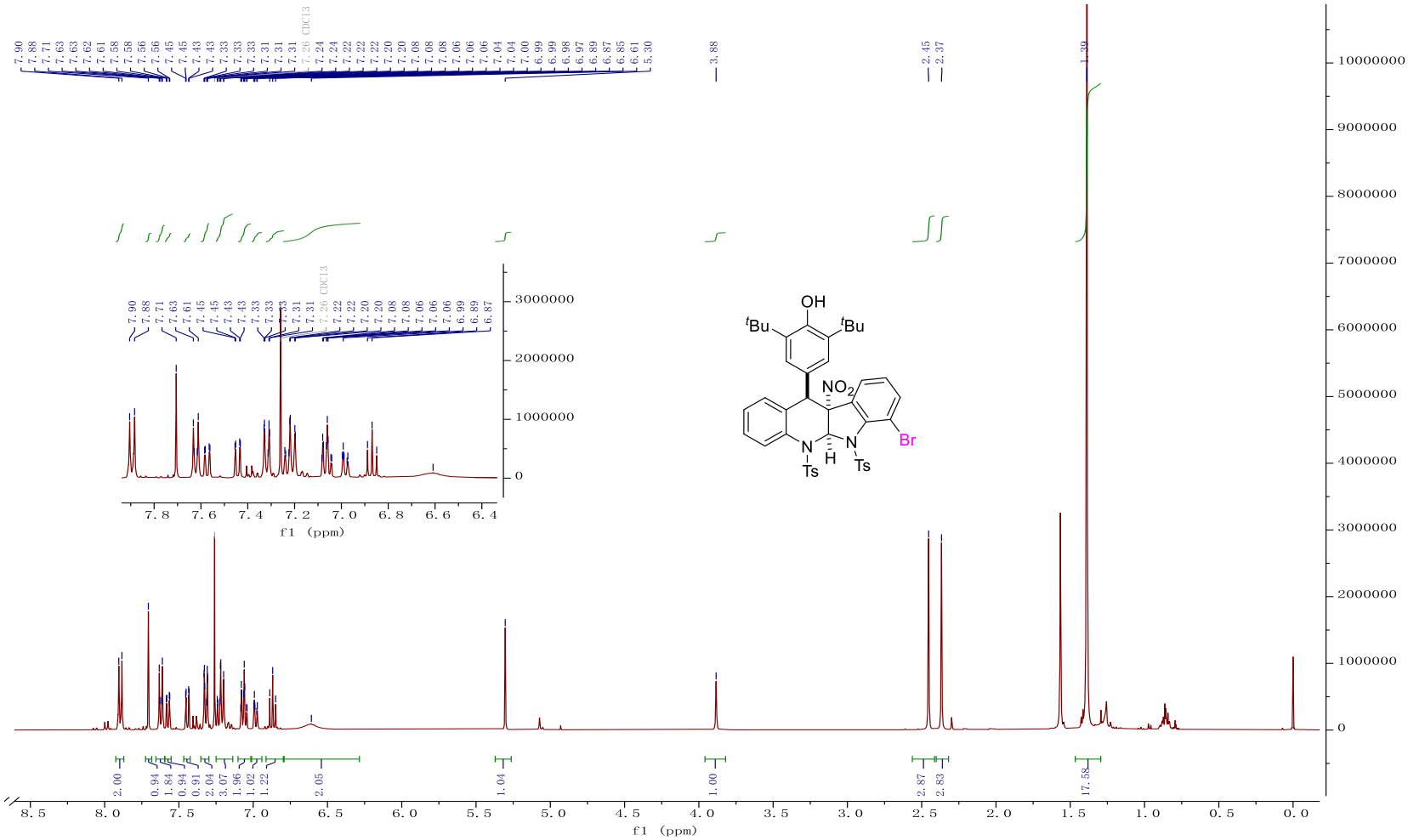
Peak	Ret.Time [min]	Area	Height	Area%
	30.468	4187.63	49.77	49.55
	33.749	4264.29	44.09	50.45
		8451.93		100.00



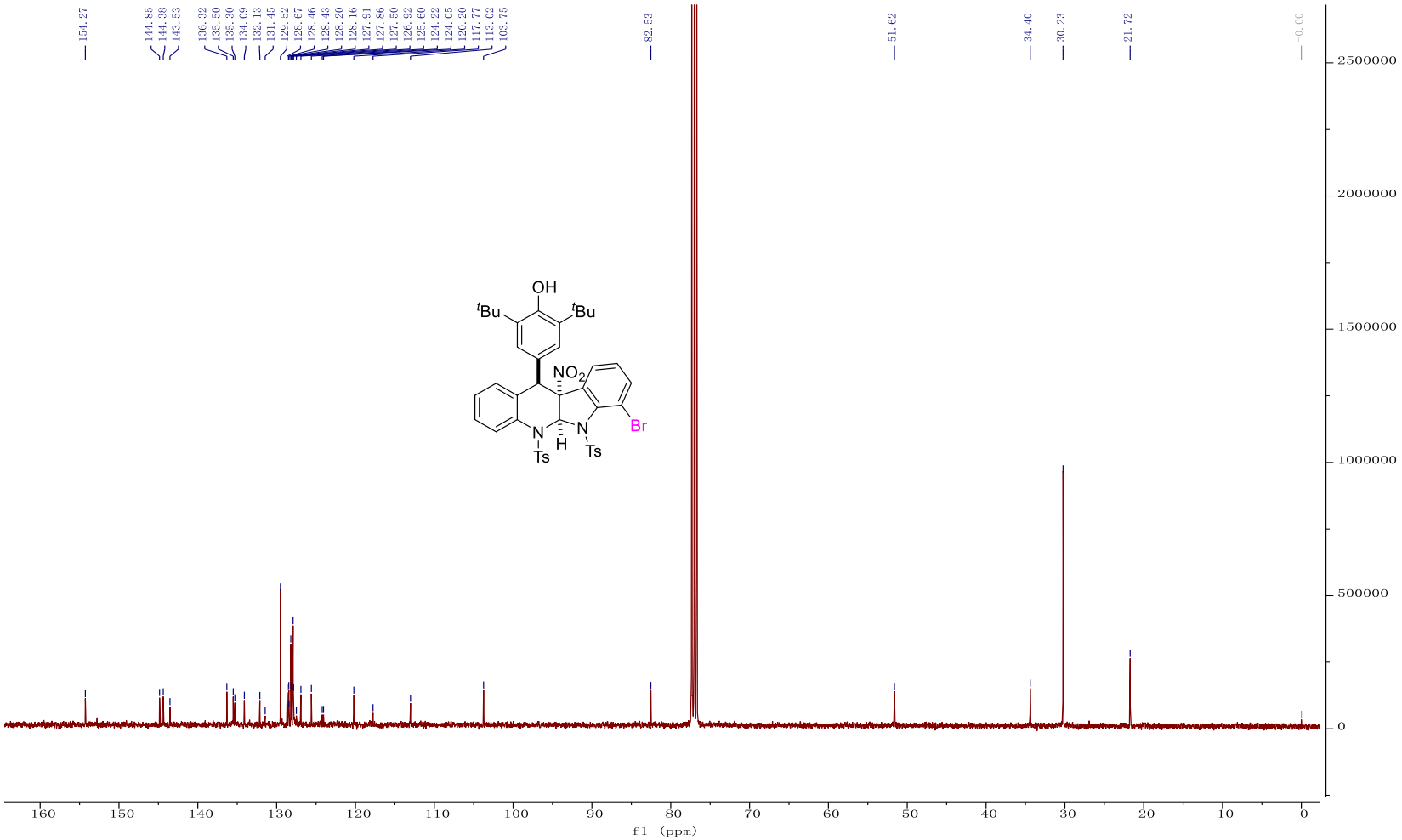
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	30.022	4721.38	56.05	80.14
	33.297	1169.83	13.15	19.86
		5891.21		100.00

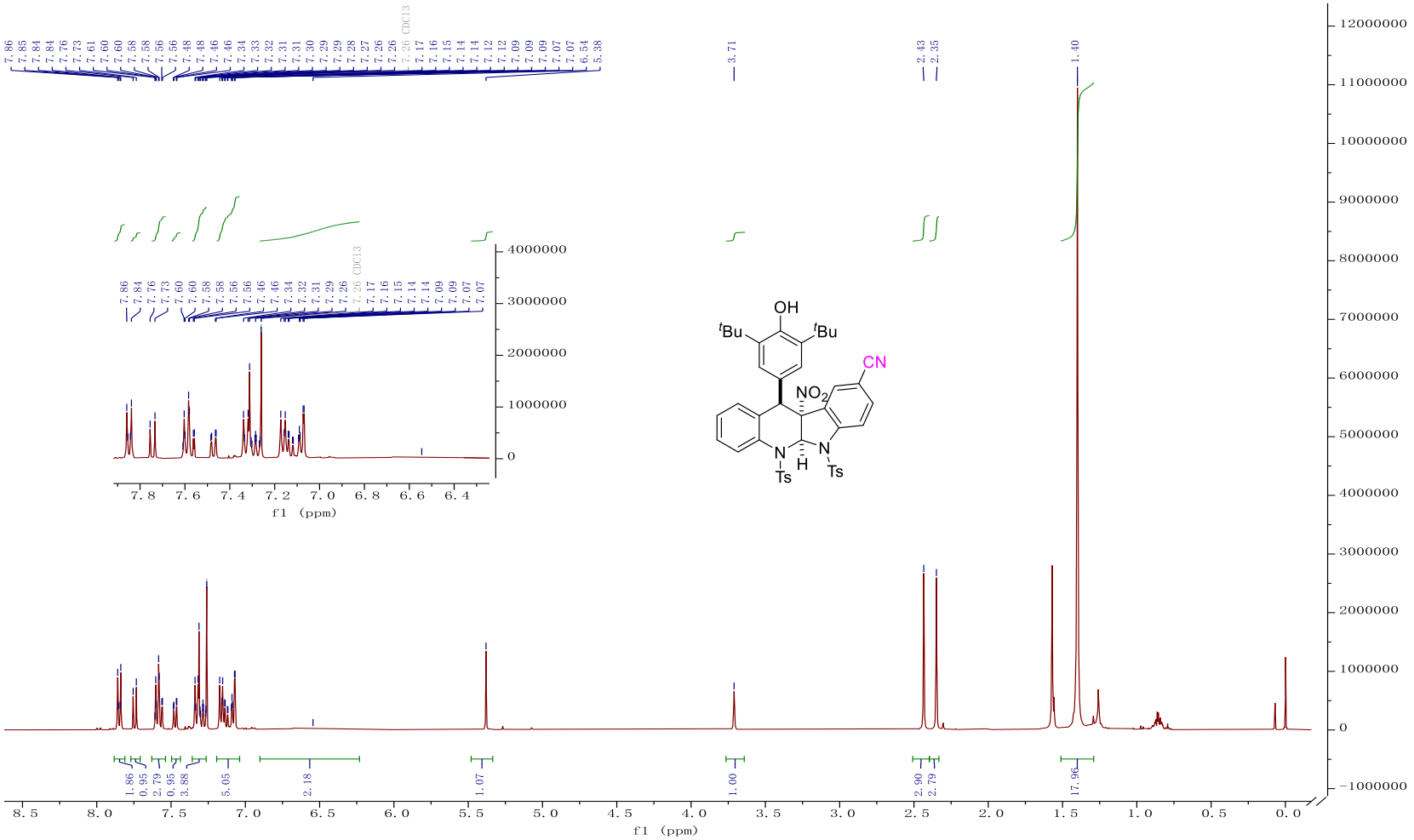
^{1}H NMR spectrum of 3n



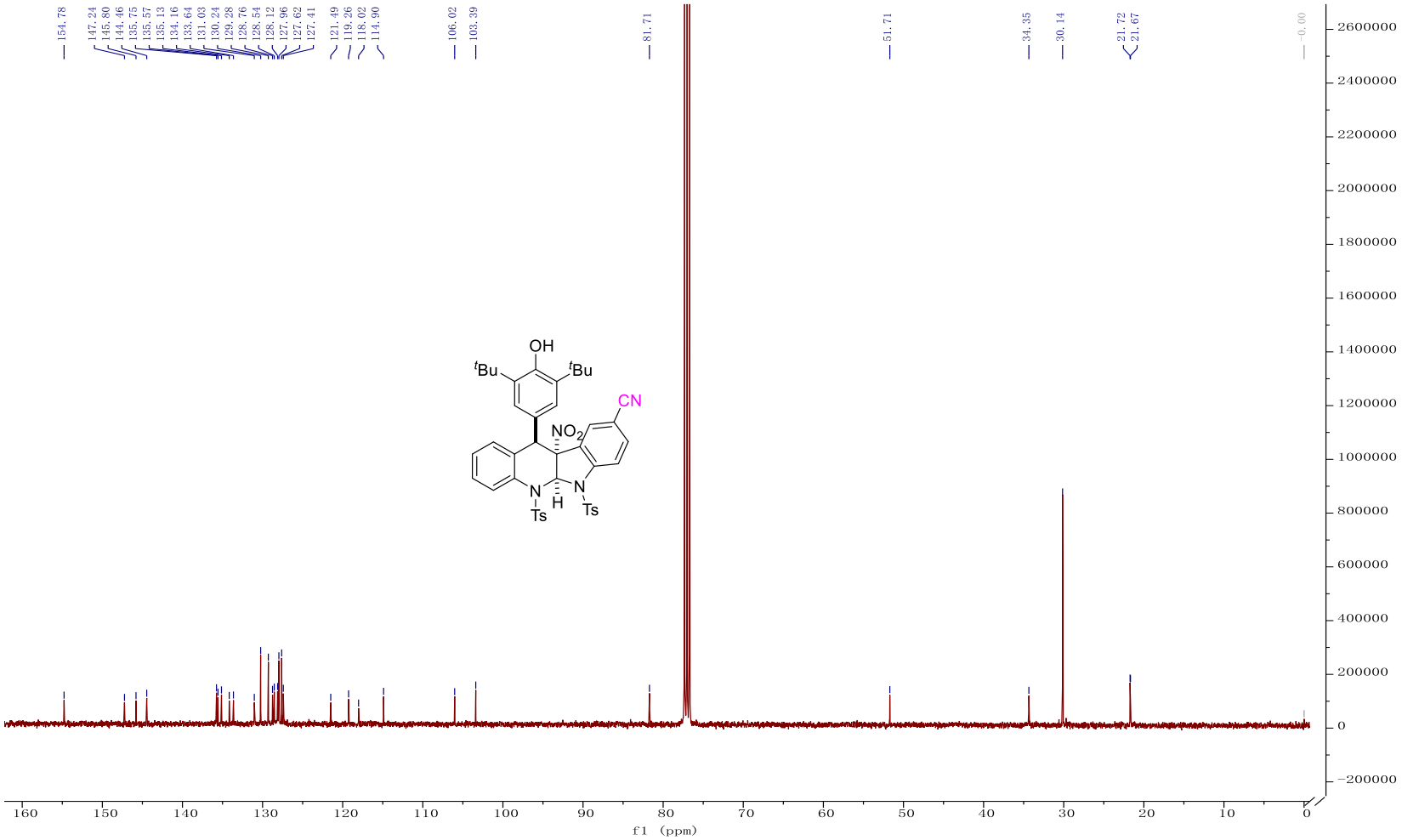
^{13}C NMR spectrum of 3n



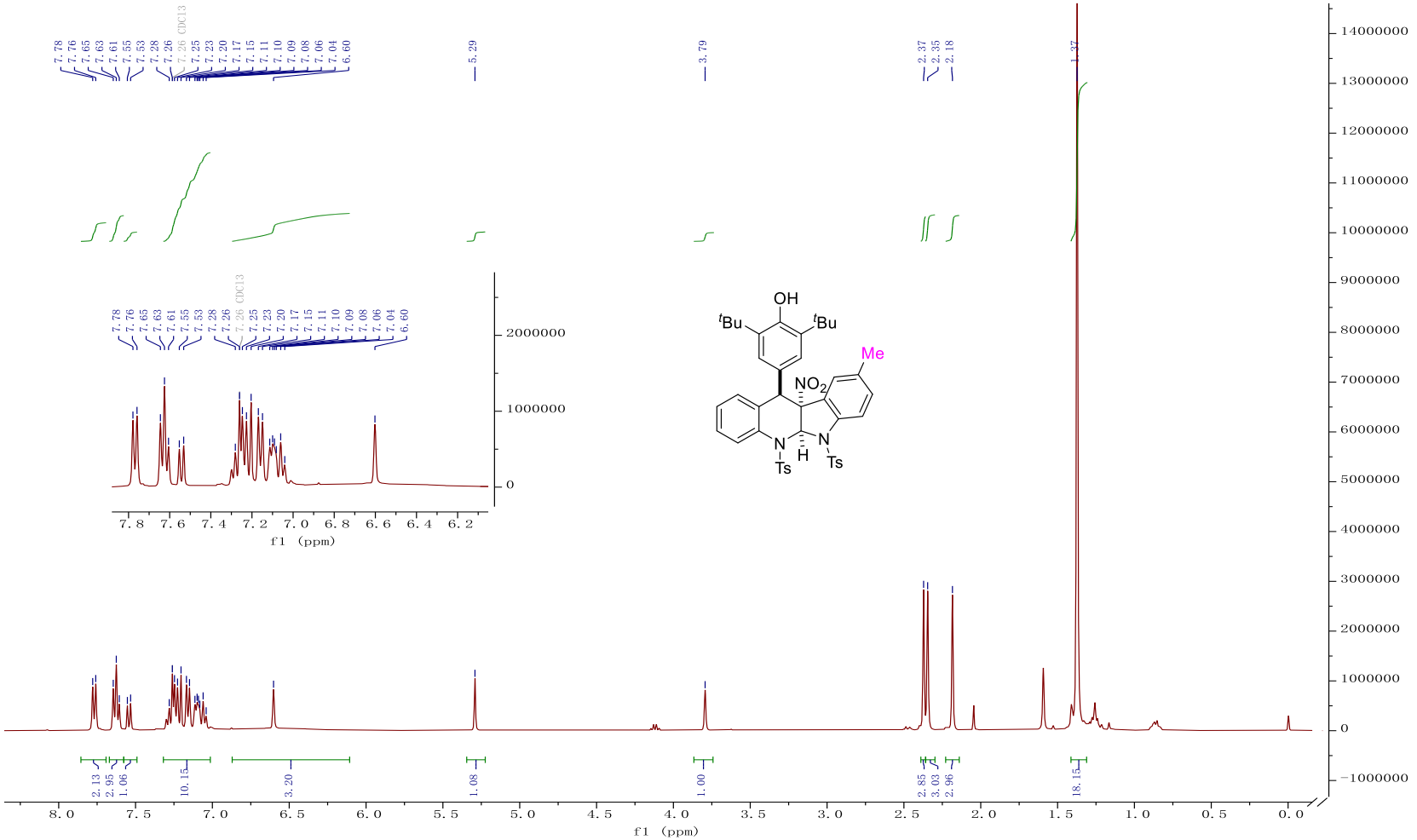
^{1}H NMR spectrum of 3o



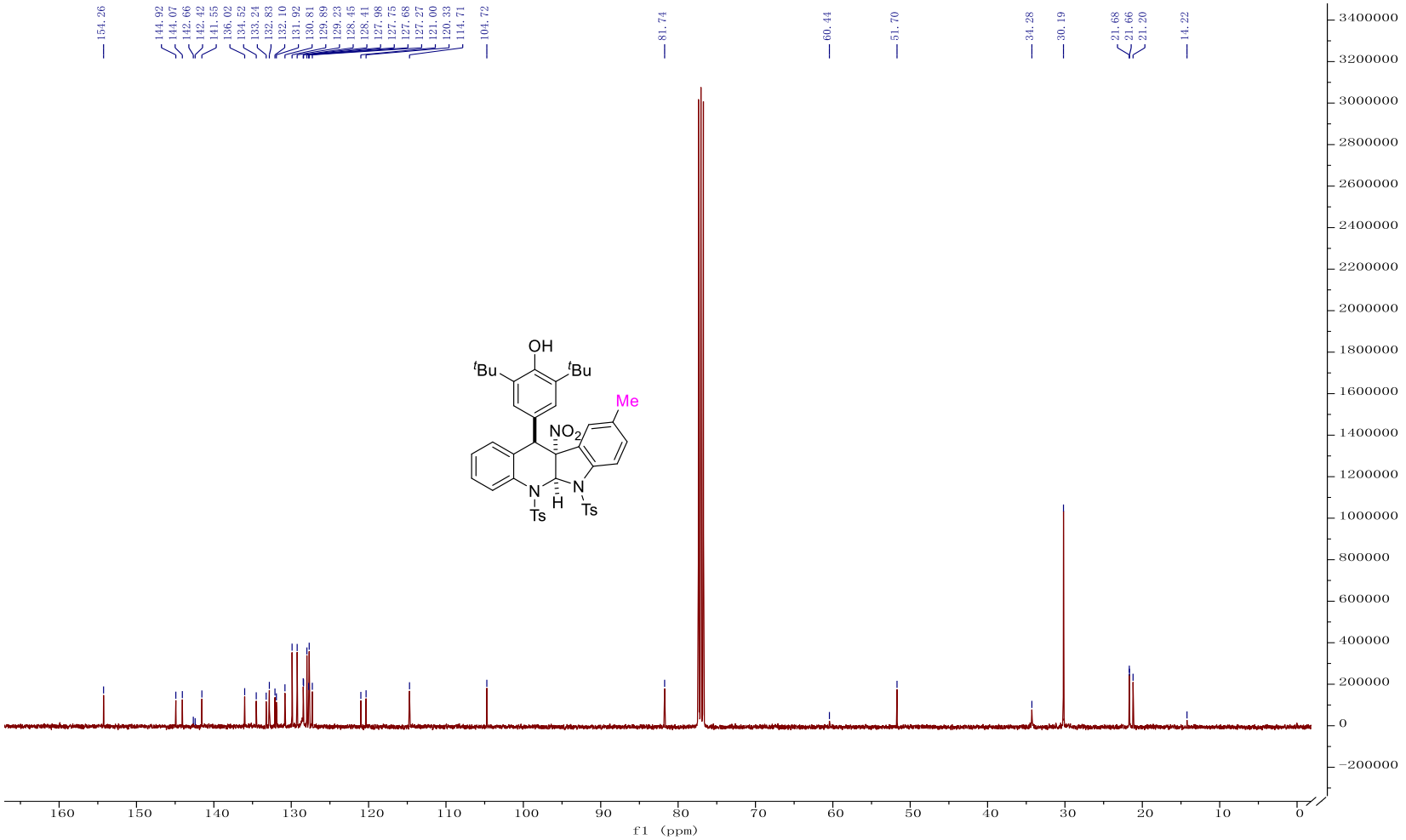
^{13}C NMR spectrum of 3o



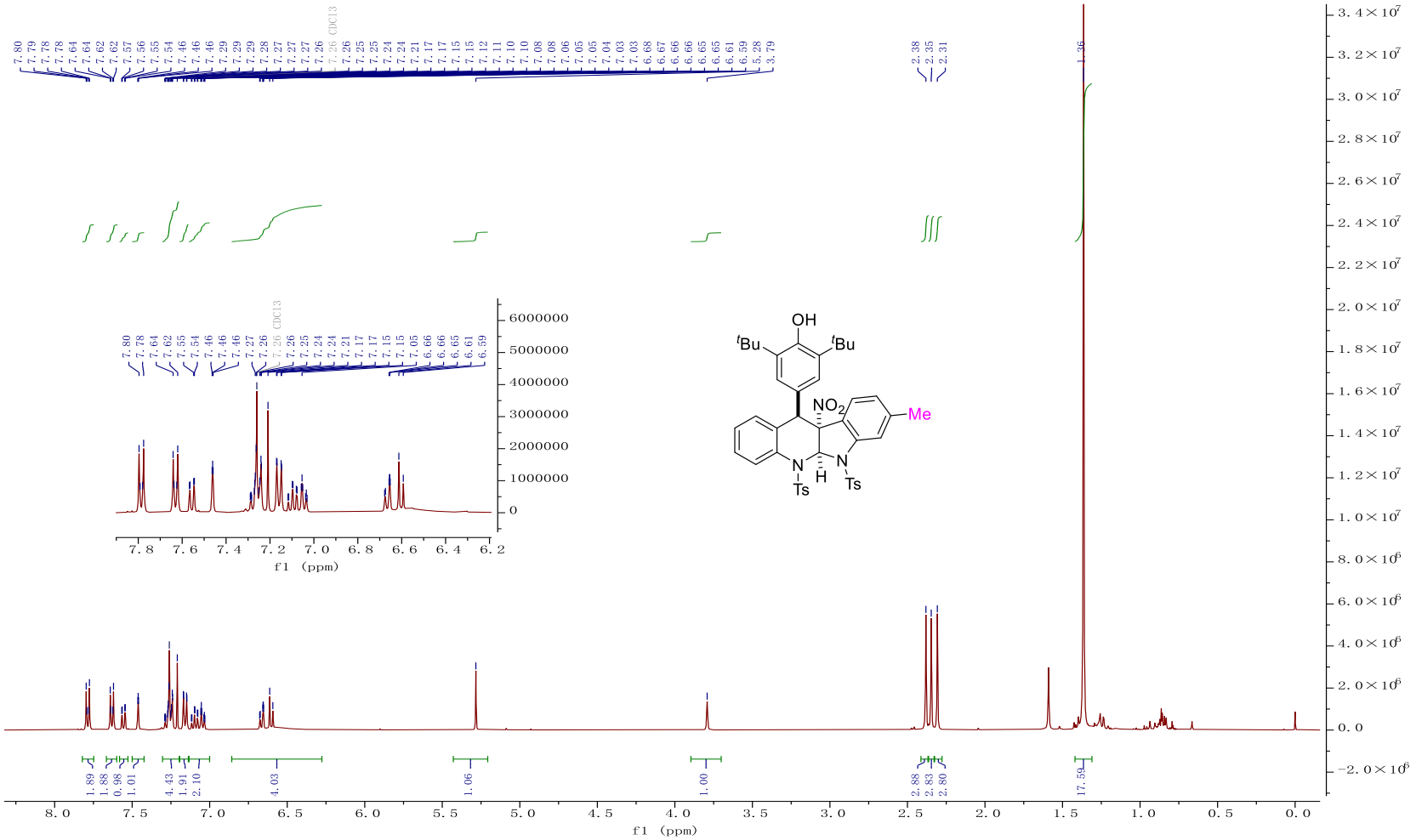
^{1}H NMR spectrum of 3p



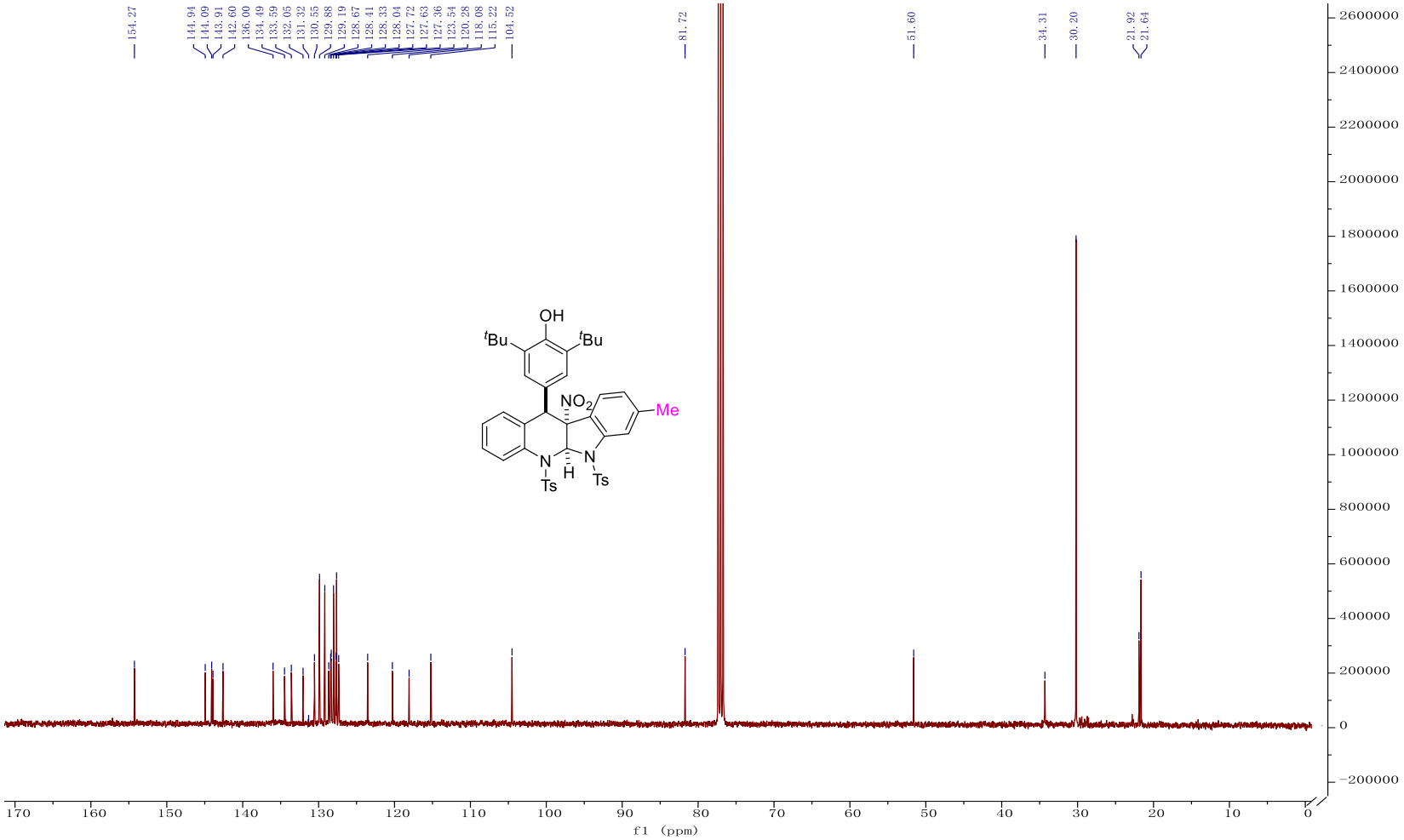
^{13}C NMR spectrum of 3p



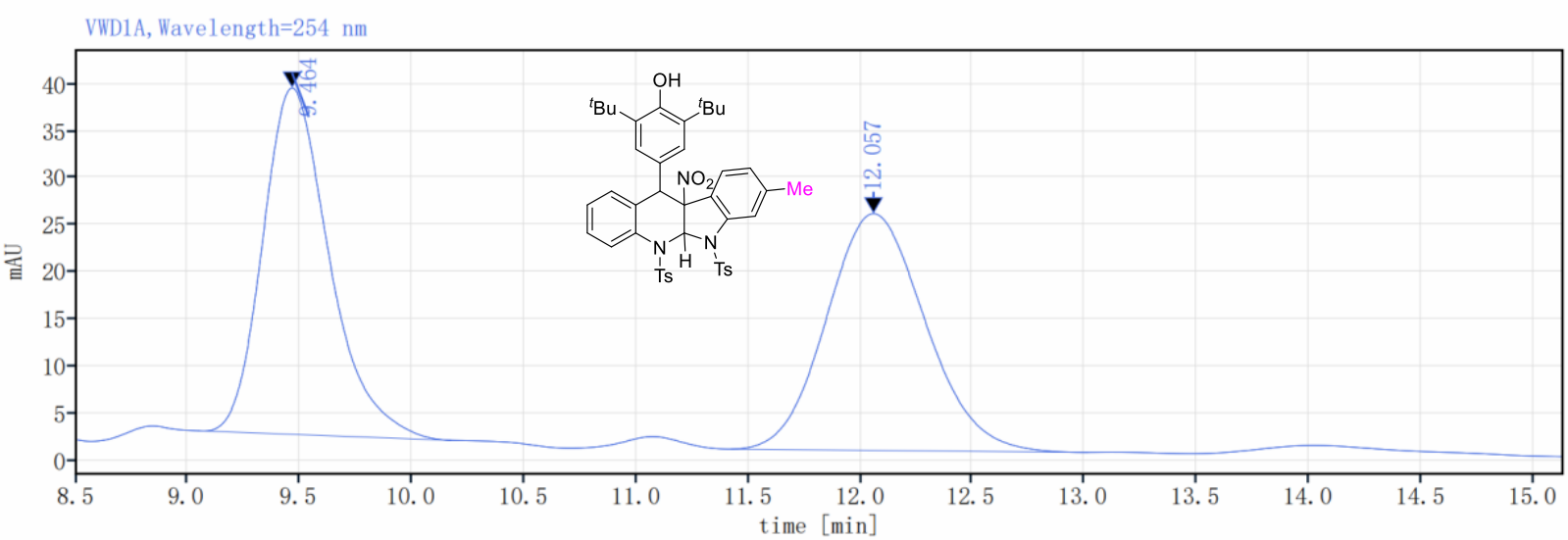
^{1}H NMR spectrum of 3q



^{13}C NMR spectrum of 3q

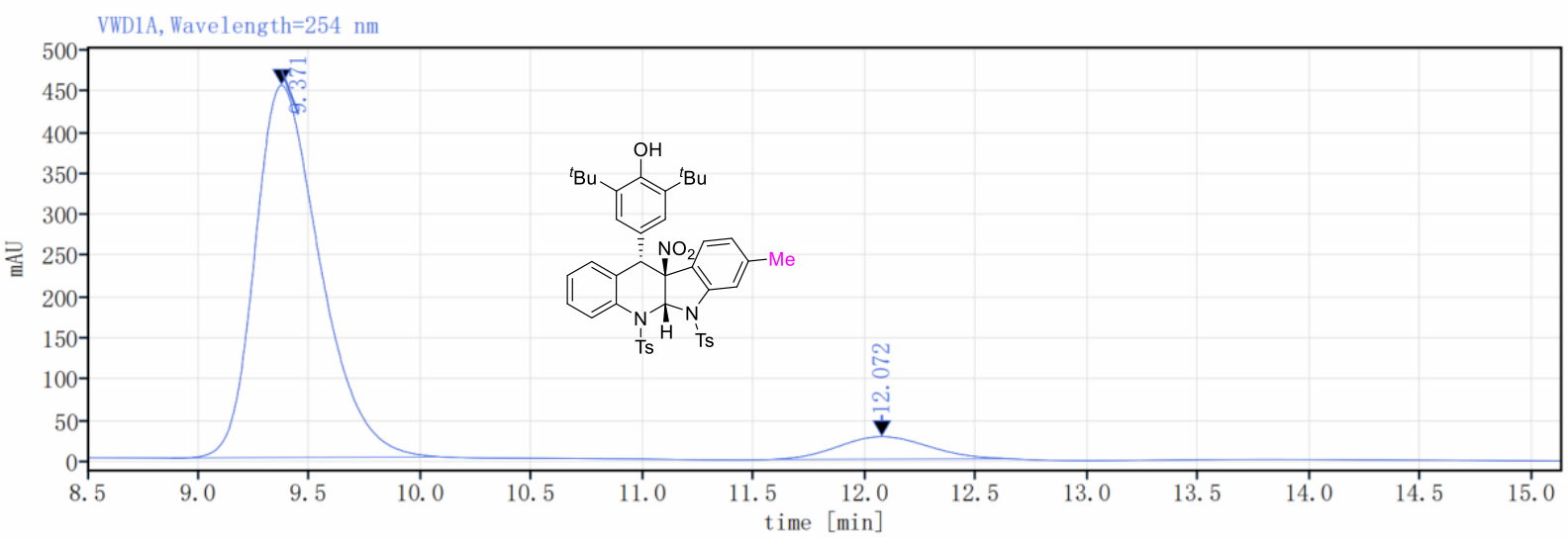


HPLC spectra of 3q



Detector VWD1A,Wavelength=254 nm

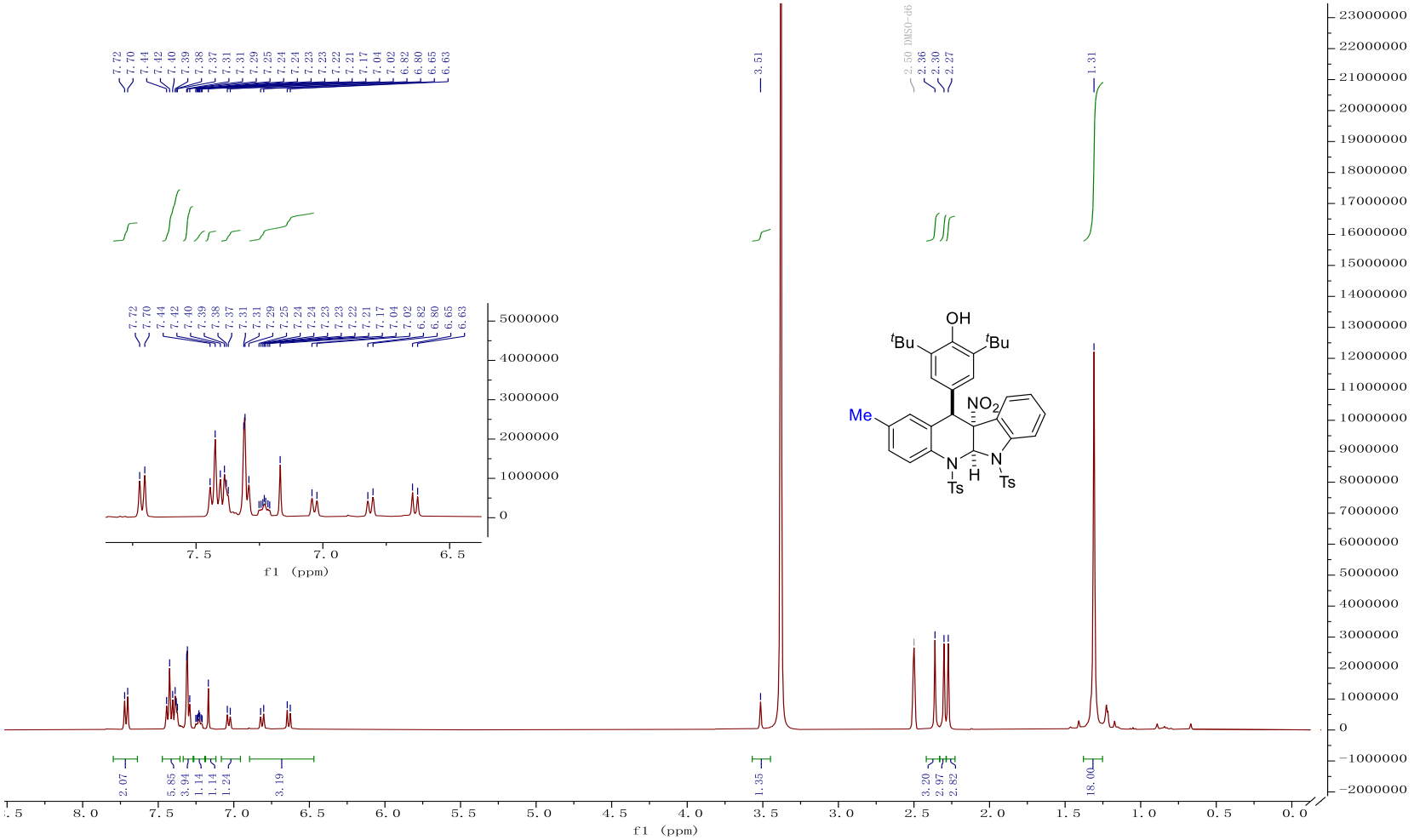
Peak	Ret.Time [min]	Area	Height	Area%
	9.464	759.40	36.77	49.70
	12.057	768.50	25.14	50.30
		1527.90		100.00



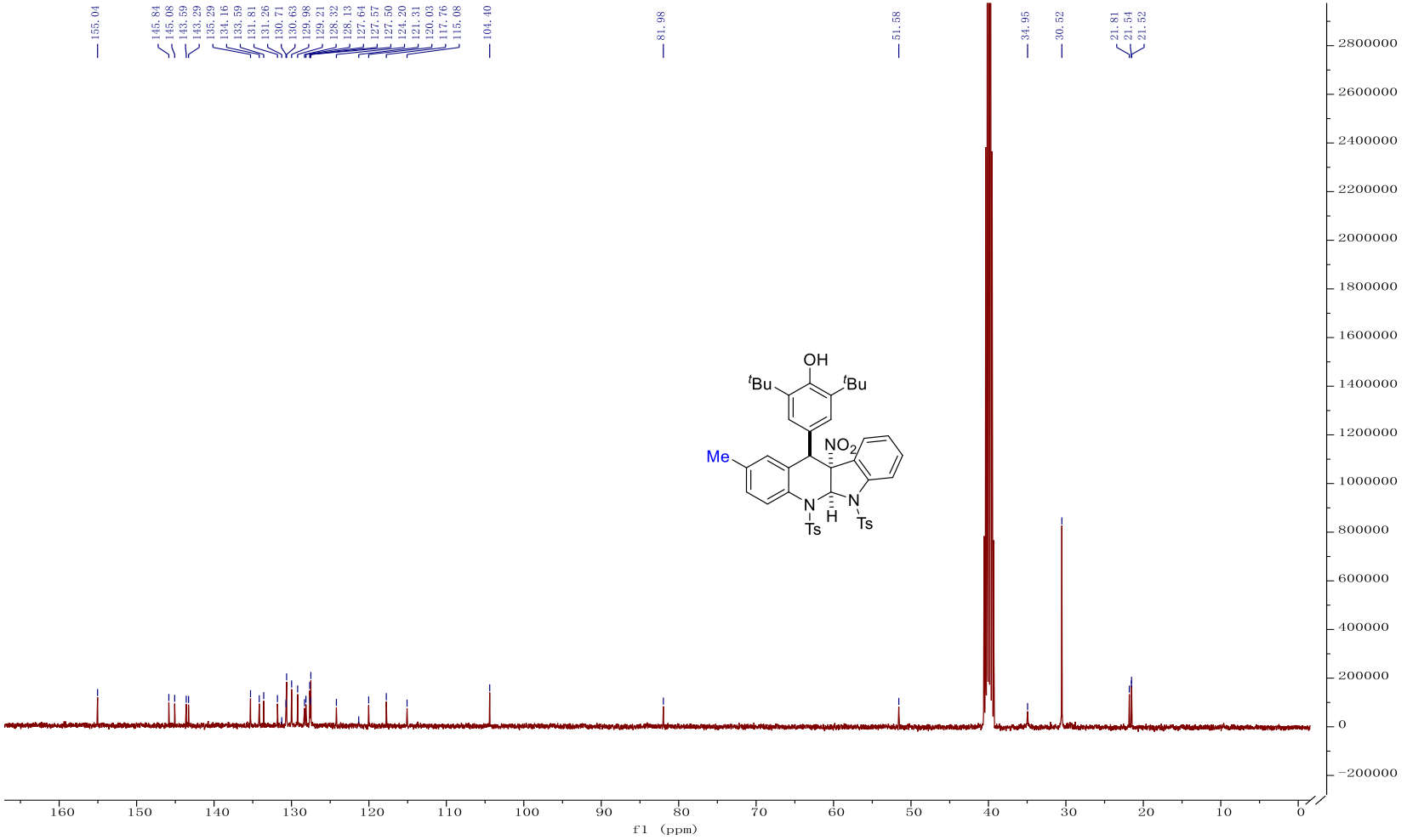
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	9.371	9205.78	452.60	92.28
	12.072	769.68	27.24	7.72
		9975.46		100.00

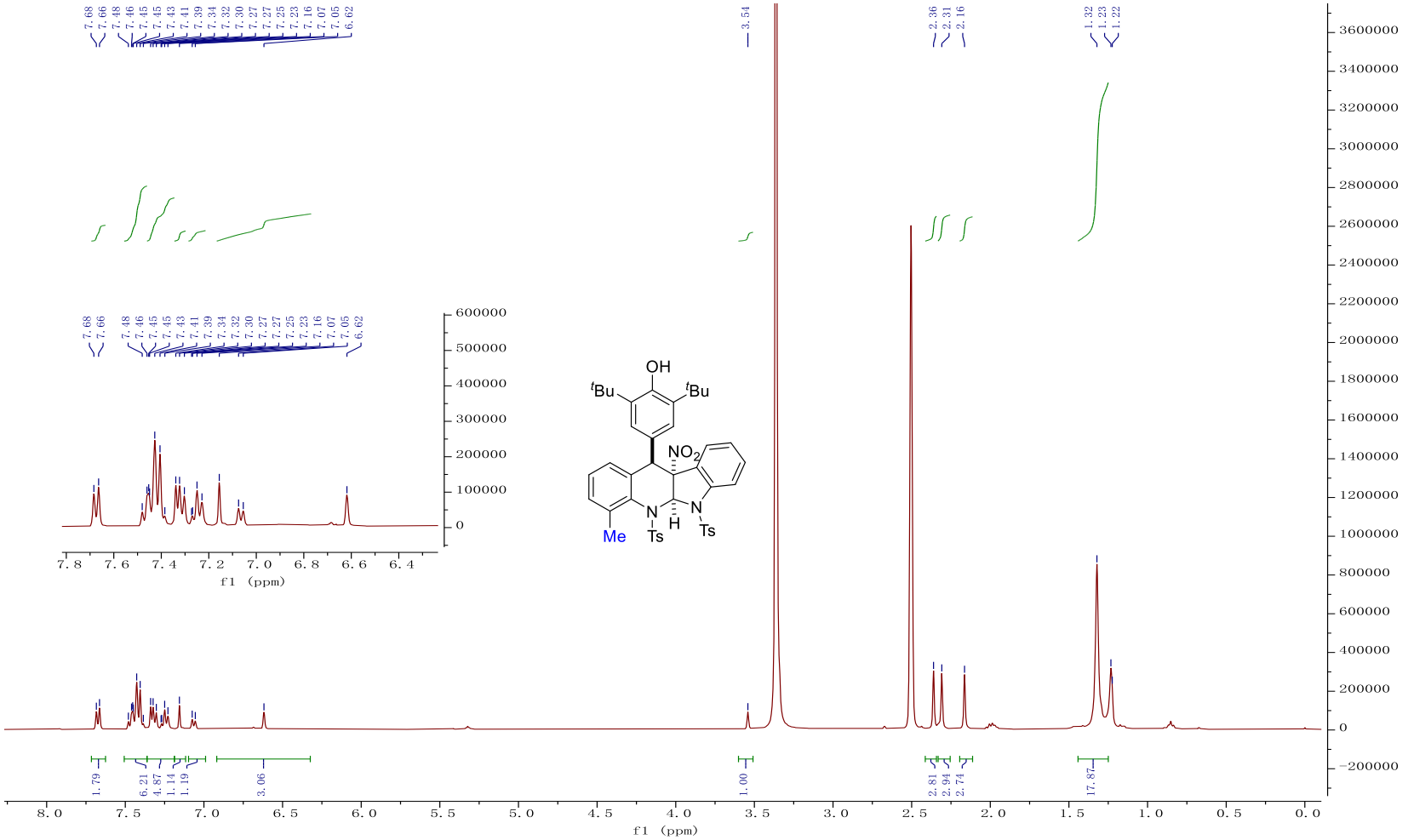
^{1}H NMR spectrum of 3r



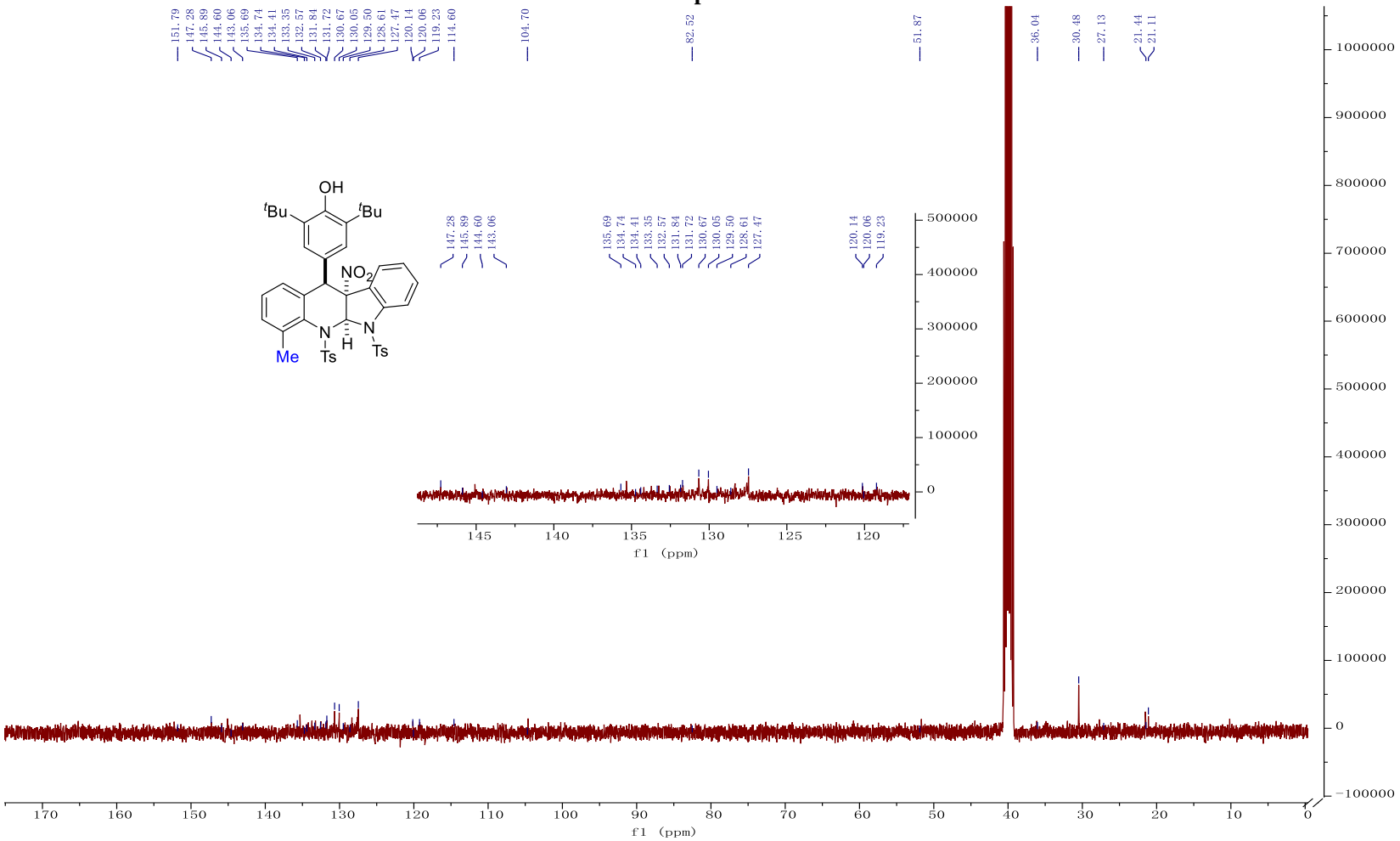
^{13}C NMR spectrum of 3r



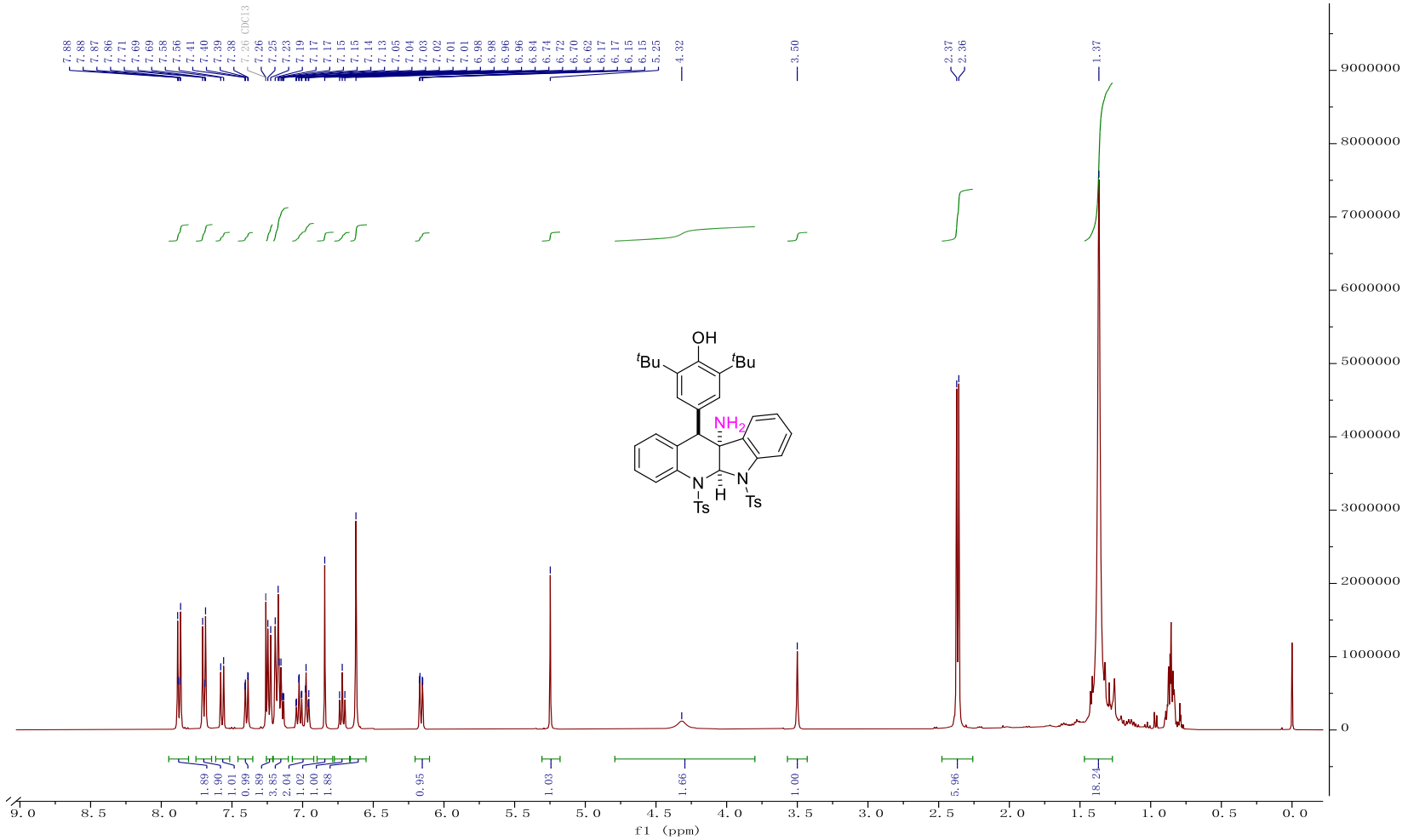
^{1}H NMR spectrum of 3s



^{13}C NMR spectrum of 3s



^{1}H NMR spectrum of compound of 4



^{13}C NMR spectrum of compound of 4