Supporting Information

N-Heterocyclic carbene catalyzed asymmetric [3 + 3] cycloaddtion of β,β-disubstituted, α,β-unsaturated carboxylic esters with 3-aminobenzofurans

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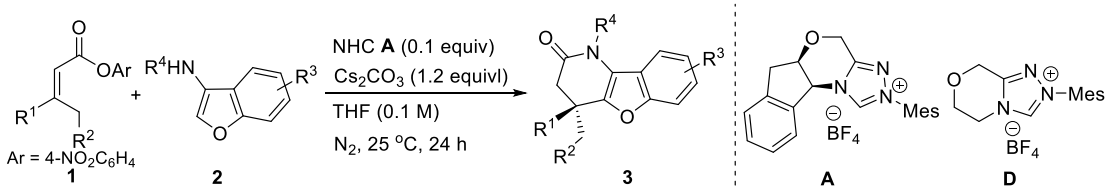
Table of Contents

General Information

Commercially available materials purchased from Energy-Chemical were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AV 400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV 400 (400 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Waters Xevo G2-S QTof mass spectrometer. The determination of ee was performed via chiral HPLC analysis using Waters Empower 3 HPLC system. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Rudolph Autopol IV automatic polarimeter and are reported as follows: $[\alpha]^{rt}_{D}$ (*c* in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on GF 254 silica gel coated plates. Flash column chromatography was carried out using 200−300 mesh silica gel. Melting points are uncorrected. β,β-disubstituted, α,β-unsaturated carboxylic esters[1] and 3-aminobenzofurans[2] were synthesized according to reported method. NHC pre-catalyst **A**[3] and **D**[4] were prepared by known protocol.

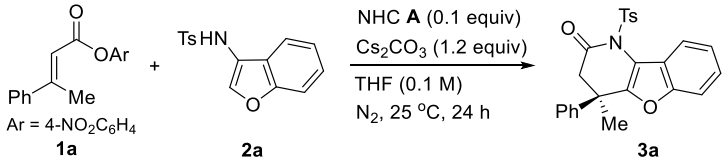
General procedure for the [3 + 3] cycloaddition reaction:



To a dry 10 mL Schlenk tube equipped with a magnetic stir bar, were added chiral NHC pre-catalyst **A** (4.2 mg, 0.01 mmol), β,β-disubstituted, α,β-unsaturated carboxylic esters **1** (0.12 mmol), 3-aminobenzofurans **2** (0.1 mmol), and Cs_2CO_3 (39.1 mg, 0.12 mmol). The tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). THF (1 mL) was then added and the reaction mixture was stirred at 25 °C for 24 hours. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and the residue was subjected to column chromatography using petroleum ether/EtOAc = 5/1 as eluent to afford the desired products **3**.

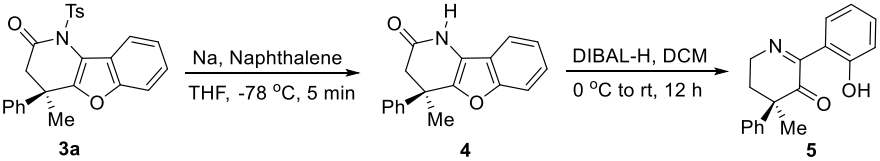
Note: The corresponding racemic products for HPLC analysis were synthesized following the same procedure by using NHC pre-catalyst **D** as the achiral catalyst.

Gram-scale preparation of 3a:



To a 100 mL two-neck round-bottom flask equipped with a magnetic stir bar, were added chiral NHC pre-catalyst **A** (125.7 mg, 0.3 mmol), β,β-disubstituted, α,β-unsaturated carboxylic ester **1a** (1.021 g, 3.6 mmol), 3-aminobenzofuran **2a** (861.9 mg, 3 mmol), and Cs_2CO_3 (1.173 g, 3.6 mmol). The flask was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). THF (30 mL) was then added and the reaction mixture was stirred at 25 °C for 24 hours. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and the residue was subjected to column chromatography using petroleum ether/EtOAc = 5/1 as eluent to afford the desired product **3a** (1.176 g, 2.73 mmol, 91% yield, 98% ee).

Synthetic transformation of 3a:



Under a nitrogen atmosphere, to a freshly prepared solution of Na (23 mg, 1 mmol, 10 equiv.) and naphthalene (128 mg, 1 mmol, 10 equiv.) in anhydrous THF (7 mL) at -78 °C, was added a solution of **3a** (43.2 mg, 0.1 mmol, 98% ee) in THF (3 mL). The reaction mixture was stirred at that temperature for 5 minutes and then quenched with saturated NH_4Cl aq. (10 mL). The aqueous phase was extracted with CH_2Cl_2, and the combined organic phase was washed with brine, dried over Na_2SO_4. Filtration and

removal of solvent under reduced pressure afforded a residue, which was purified by column chromatography using petroleum ether/EtOAc = 3/1 as eluent to afford the desired product **4** (23.1 mg, 0.083 mmol, 83% yield, 98% ee).

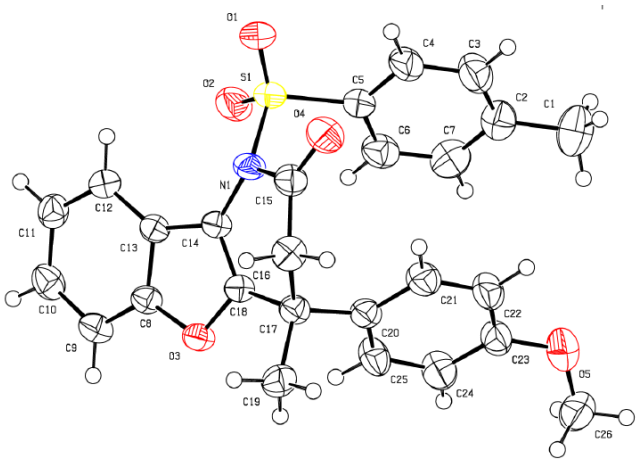
Under a nitrogen atmosphere, to a solution of **4** (27.7 mg, 0.1 mmol, 98% ee) in anhydrous DCM (2 mL) at 0 ^{o}C, was added DIBAL-H (2 mL of a 1.5 M solution in toluene, 3 mmol, 30 equiv.) dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 hours before it was quenched with brine (10 mL). The aqueous phase was extracted with EtOAc, and the combined organic phase was dried over Na_2SO_4. Filtration and removal of solvent under reduced pressure afforded a residue, which was purified by column chromatography using petroleum ether/EtOAc = 5/1 as eluent to afford the desired product **5** (19.9 mg, 0.071 mmol, 71% yield, 98% ee).

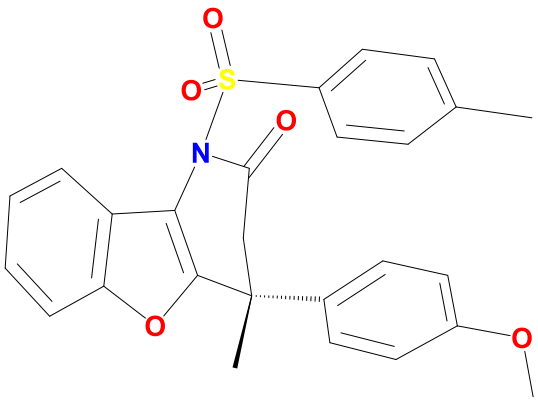
References cited in the SI:

1. J. Xu, Z. Jin and Y. R. Chi, *Org. Lett.*, 2013, **15**, 5028.
2. X. F. Ding, R. H. Su, W. L. Yang and W. P. Deng, *Adv. Synth. Catal.*, 2018, **360**, 4168.
3. M. He, J. R. Struble and J. W. Bode, *J. Am. Chem. Soc.*, 2006, **128**, 8418.
4. P. C. Chiang, M. Rommel and J. W. Bode, *J. Am. Chem. Soc.*, 2009, **131**, 8714.

X-ray structure of product 3b (ellipsoid contour at 30% probability)

Absolute configurations of the products **3** were assigned based on the crystal X-ray structures of **3b**. CCDC 2040018 (**3b**, obtained as colorless needles *via* evaporation of a petroleum ether/CH_2Cl_2 solution) contains the supplementary X-ray crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



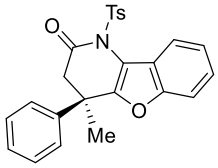


3b

Table S1. Crystal data and structure refinement for 3b.

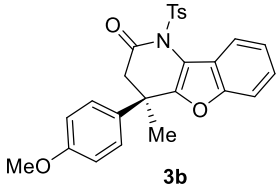
Empirical formula	$C_{26}H_{23}NO_5S$	
Formula weight	461.51	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system, Space group	orthorhombic,	P 21 21 21
Unit cell dimensions	a = 9.5921(4) Å	α = 90 °
	b = 9.8807(3) Å	β = 90 °
	c = 23.3768(10) Å	γ = 90 °
Volume	2215.58(15) $Å^3$	
Z	4	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	1.628 mm^{-1}	
F(000)	968	
Crystal size	0.12*0.12*0.11 mm^3	
Theta range for data collection	3.78 to 67.21 ^{o}	
Index ranges	-11 <= h <= 7, -11 <= k <= 10, -27 <= l <= 27	
Reflections collected	5570	
Independent reflections	3472 [*R*(int) = 0.0281]	
Completeness to theta= 67.23	99.8%	
Absorption correction	Multi-scan from equivalents	
Max. and min. transmission	0.8413 and 0.8286	
Refinement method	Full-matrix least-squares on F2	
Data/restraints/parameters	3472 / 0 / 302	
Goodness-of-fit on F2	1.026	
Final R indices [I>2sigma(I)]	*R1* = 0.0404, *wR2* = 0.0964	
R indices(all data)	*R1* = 0.0472, *wR2* = 0.1021	
Extinction coefficient	0.0046(3)	
Largest diff. peak and hole	0.169 and -0.209 e.$Å^{-3}$	

Characterization of products:



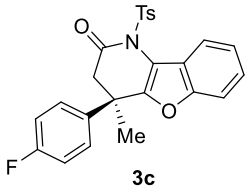
3a

(R)-4-Methyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b] pyridin-2(1H)-one (3a)*:* 40.2 mg, 93% yield; yellow solid, 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H), 7.57-7.55 (m, 1H), 7.40-7.35 (m, 4H), 7.18 (t, *J* = 6.4 Hz, 1H), 7.13-7.08 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.24 (d, *J* = 15.6 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 154.2, 150.9, 144.4, 143.6, 134.6, 128.9, 128.8, 128.6, 126.9, 125.4, 124.7, 123.5, 123.4, 122.7, 118.0, 111.6, 47.6, 39.6, 27.2, 21.6; HRMS (ESI, m/z): calcd. for $C_{25}H_{21}NO_4SH^+$ 432.1264, found 432.1266. $[\alpha]^{27}_D$ = -90.0 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 8.2 min (minor), 14.0 min (major)].



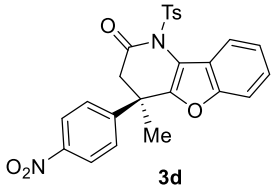
3b

(R)-4-(4-Methoxyphenyl)-4-methyl-1-tosyl-3,4-dihydro benzofuro[3,2-b]pyridin-2(1H)-one (3b)*:* 45.2 mg, 98% yield; yellow solid, 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.56-7.54 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.37-7.33 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.19 (d, *J* = 15.6 Hz, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 158.6, 154.1, 151.4, 144.4, 135.6, 134.7, 128.8 128.6, 126.5, 124.6, 123.5, 122.6, 117.8, 115.6, 114.1, 111.6, 55.2, 47.6, 39.0, 27.2, 21.5; HRMS (ESI, m/z): calcd. for $C_{26}H_{23}NO_5SH^+$ 462.1370, found 462.1370. $[\alpha]^{27}_D$ = -89.2 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 99% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 10.2 min (minor), 15.4 min (major)].



3c

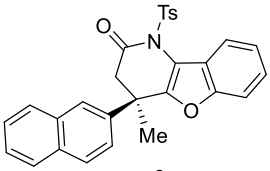
(R)-4-(4-Fluorophenyl)-4-methyl-1-tosyl-3,4-dihydrobenzo furo[3,2-b]pyridin-2(1H)-one (3c)*:* 43.1 mg, 96% yield; yellow solid, 194-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H), 7.56-7.54 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 2H), 7.05-7.01 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 8.4 Hz, 2H), 3.19 (d, *J* = 15.6 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 161.7 (d, $J_{C\text{-}F}$ = 244.7 Hz), 154.1, 151.0, 144.8, 139.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 134.5, 128.8, 128.7, 127.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 124.8, 123.6, 123.4, 122.7, 118.1, 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 111.6, 47.6, 39.1, 27.2, 21.4; HRMS (ESI, m/z): calcd. for $C_{25}H_{20}FNO_4SH^+$ 450.1170, found 450.1173. $[\alpha]^{27}_D$ = -77.2 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 99% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 7.6 min (minor), 13.4 min (major)].



3d

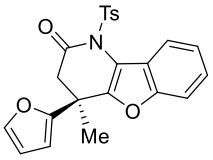
(R)-4-Methyl-4-(4-nitrophenyl)-1-tosyl-3,4-dihydrobenzo furo[3,2-b]pyridin-2(1H)-one (3d)*:* 42.9 mg, 90% yield; yellow solid, 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-

8.07 (m, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.59-7.57 (m, 1H), 7.45-7.36 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.25 (d, *J* = 15.6 Hz, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.29 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 154.3, 151.0, 149.6, 146.7, 145.4, 134.4, 128.9, 128.7, 126.6, 125.2, 123.9, 123.8, 123.2, 122.9, 118.7, 111.7, 47.2, 39.7, 26.5, 21.3; HRMS (ESI, m/z): calcd. for $C_{25}H_{20}N_2O_6SH^+$ 477.1115, found 477.1115. $[\alpha]^{27}_D$ = -74.4 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 96% ee, [CHIRALPAK IB column; 1 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 23.2 min (major), 26.4 min (mionr)].



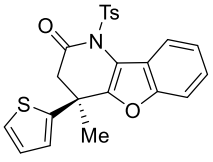
3e

(R)-4-Methyl-4-(naphthalen-2-yl)-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3e)*:* 46.7 mg, 97% yield; yellow solid, 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.62-7.60 (m, 1H), 7.55-7.44 (m, 3H), 7.42-7.35 (m, 3H), 7.33-7.30 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 8.0 Hz, 2H), 3.39 (d, *J* = 16.0 Hz, 1H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.86 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 154.3, 151.1, 144.4, 141.2, 134.3, 133.2, 132.4, 128.7, 128.3, 128.2, 128.1, 127.4, 126.4, 126.2, 124.7, 124.2, 123.6, 123.4, 122.7, 118.4, 111.6, 47.1, 39.7, 26.9, 21.2; HRMS (ESI, m/z): calcd. for $C_{29}H_{23}NO_4SH^+$ 482.1421, found 482.1424. $[\alpha]^{27}_D$ = -16.8 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 8.8 min (minor), 11.7 min (major)].



3f

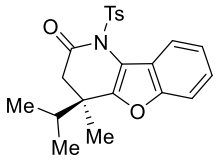
(R)-4-(Furan-2-yl)-4-methyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3f)*:* 33.3 mg, 79% yield; yellow solid, 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.50-7.48 (m, 1H), 7.35-7.33 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 6.08 (d, *J* = 1.6 Hz, 1H), 5.83 (d, *J* = 3.2 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 2.82 (d, *J* = 15.6 Hz, 1H), 2.43 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 154.5, 154.0, 147.4, 144.9, 142.2, 135.0 129.4, 129.1, 124.8, 123.4, 123.0, 122.8, 118.3, 111.6, 110.1, 105.4, 47.2, 35.6, 22.8, 21.6; HRMS (ESI, m/z): calcd. for $C_{23}H_{19}NO_5SH^+$ 422.1057, found 422.1060. $[\alpha]^{27}_D$ = -137.2 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 97% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 8.8 min (minor), 12.6 min (major)].



3g

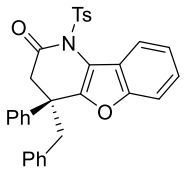
(S)-4-Methyl-4-(thiophen-2-yl)-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3g)*:* 38.1 mg, 87% yield; white solid, 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.54-7.52 (m, 1H), 7.39-7.33 (m, 2H), 7.12-7.07 (m, 3H), 6.67 (t, *J* = 3.6 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 3.11 (d, *J* = 15.6 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 154.0, 149.2, 147.6, 144.7, 134.8, 129.0 128.9, 126.7, 124.9, 124.6, 123.6, 123.5, 123.1, 122.8, 118.1, 111.7, 49.4, 37.3, 27.6, 21.6; HRMS (ESI,

m/z): calcd. for $C_{23}H_{19}NO_4S_2H^+$ 438.0828, found 438.0832. $[\alpha]^{27}_D$ = -82.0 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 99% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 9.4 min (minor), 13.9 min (major)].



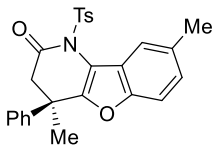
3h

(R)-4-Isopropyl-4-methyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3h)*:* 39.3 mg, 99% yield; yellow solid, 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.47-7.44 (m, 1H), 7.33-7.30 (m, 4H), 2.66 (d, *J* = 15.6 Hz, 1H), 2.49 (d, *J* = 15.6 Hz, 1H), 2.44 (s, 3H), 1.29-1.22 (m, 1H), 1.18 (s, 3H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.73 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.1, 152.5, 145.3, 134.7, 129.2, 129.1, 124.3, 123.3, 123.2, 122.4, 117.3, 111.4, 46.6, 38.5, 34.5, 21.6, 18.4, 17.1, 16.5; HRMS (ESI, m/z): calcd. for $C_{22}H_{23}NO_4SH^+$ 398.1421, found 398.1422. $[\alpha]^{27}_D$ = -142.8 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 97% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 6.5 min (minor), 7.8 min (major)].



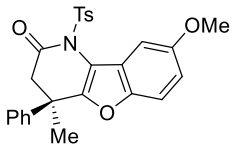
3i

(R)-4-Benzyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3i)*:* 42.3 mg, 83% yield; yellow solid, 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.41-7.34 (m, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.19-7.00 (m, 6H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 3.38 (d, *J* = 13.6 Hz, 1H), 3.28 (d, *J* = 13.2 Hz, 1H), 3.02 (d, *J* = 15.6 Hz, 1H), 2.83 (d, *J* = 15.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 154.0, 150.8, 144.2, 141.7, 134.7, 134.4, 130.4, 128.8, 128.4, 128.3, 127.9, 127.0, 126.9, 126.5, 124.7, 123.5, 123.4, 122.8, 118.1, 111.5, 45.5, 43.9, 43.5, 21.5; HRMS (ESI, m/z): calcd. for $C_{31}H_{25}NO_4SH^+$ 508.1577, found 508.1583. $[\alpha]^{27}_D$ = +32.8 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 94% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 11.5 min (minor), 15.6 min (major)].



3j

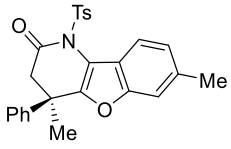
(R)-4,8-Dimethyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3j)*:* 40.1 mg, 90% yield; orange solid, 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12-7.06 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.22 (d, *J* = 15.6 Hz, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 152.6, 151.1, 144.3, 143.7, 134.5, 133.1, 128.9, 128.8, 128.5, 126.8, 126.0, 125.4, 123.4, 122.2, 117.7, 111.1, 47.3, 39.5, 27.3, 21.5; HRMS (ESI, m/z): calcd. for $C_{26}H_{23}NO_4SH^+$ 446.1421, found 446.1422. $[\alpha]^{27}_D$ = -66.4 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 96% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 6.2 min (minor), 8.9 min (major)].



3k

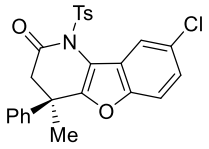
(R)-8-Methoxy-4-methyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3k)*:* 33.2 mg, 72% yield; yellow

solid, 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.19-7.15 (m, 1H), 7.12-7.05 (m, 4H), 6.99-6.96 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H), 2.32 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.3, 151.8, 149.1, 144.4, 143.6, 134.5 128.9, 128.8, 128.5, 126.8, 125.4, 123.9, 118.1, 114.2, 112.0, 104.6, 56.0, 47.3, 39.6, 27.3, 21.5; HRMS (ESI, m/z): calcd. for $C_{26}H_{23}NO_5SH^+$ 462.1370, found 462.1373. $[\alpha]^{27}_D$ = -85.2 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 7.3 min (minor), 12.8 min (major)].



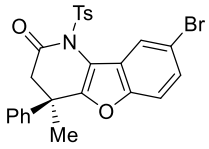
3l

(R)-4,7-Dimethyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3l)*:* 37.4 mg, 84% yield; yellow solid, 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 2H), 7.19-7.14 (m, 2H), 7.11-7.06 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.21 (d, *J* = 15.6 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H), 2.51 (s, 3H), 2.31 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 154.5, 150.2, 144.3, 143.7, 135.1, 134.6, 128.9, 128.7, 128.5, 126.8, 125.4, 124.9, 122.1, 120.9, 117.9, 111.7, 47.4, 39.5, 27.2, 21.5; HRMS (ESI, m/z): calcd. for $C_{26}H_{23}NO_4SH^+$ 446.1421, found 446.1426. $[\alpha]^{24}_D$ = -89.0 (*c* = 0.3 in CH_2Cl_2); HPLC analysis: 97% ee, [CHIRALPAK ADH column; 1 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 15.5 min (minor), 37.0 min (major)].



3m

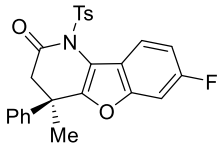
(R)-8-Chloro-4-methyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro [3,2-b]pyridin-2(1H)-one (3m)*:* 35.9 mg, 77% yield; yellow solid, 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.33-7.30 (m, 1H), 7.20-7.16 (m, 1H), 7.11 (t, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.24 (d, *J* = 15.6 Hz, 1H), 2.87 (d, *J* = 15.6 Hz, 1H), 2.32 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 152.5, 152.4, 144.6, 143.2, 134.3, 129.3, 128.9, 128.8, 128.5, 127.0, 125.3, 125.0, 124.6, 122.3, 117.6, 112.5, 47.1, 39.6, 27.1, 21.6; HRMS (ESI, m/z): calcd. for $C_{25}H_{20}ClNO_4SH^+$ 466.0874, found 466.0876. $[\alpha]^{27}_D$ = -89.6 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 6.7 min (minor), 11.9 min (major)].



3n

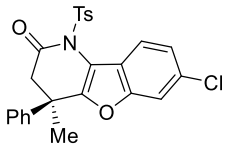
(R)-8-Bromo-4-methyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro [3,2-b]pyridin-2(1H)-one (3n)*:* 35.2 mg, 69% yield; yellow solid, 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.6 Hz, 1H), 7.48-7.41 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.20-7.16 (m, 1H), 7.11 (t, *J* = 8.9 Hz, 2H), 7.06-7.04 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 152.9, 152.3, 144.6, 143.2, 134.3, 128.9, 128.8, 128.5, 127.7, 127.0, 125.3, 125.1, 117.4, 116.8, 113.0, 47.1, 39.6, 27.1, 21.6; HRMS (ESI, m/z): calcd. for $C_{25}H_{20}BrNO_4SH^+$ 510.0369, found 510.0372. $[\alpha]^{27}_D$ = -100.0 (*c*

= 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 7.0 min (minor), 12.0 min (major)].



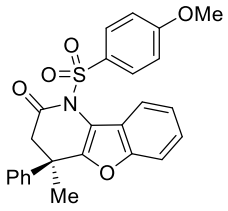
3o

(R)-7-Fluoro-4-methyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro [3,2-b]pyridin-2(1H)-one (3o)*:* 38.3 mg, 85% yield; white solid, 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 1H), 7.20-7.06 (m, 6H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.87 (d, *J* = 15.6 Hz, 1H), 2.32 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 160.8 (d, $J_{C\text{-}F}$ = 242.8 Hz), 154.0 (d, $J_{C\text{-}F}$ = 13.2 Hz), 151.5, 144.5, 143.4, 134.4 128.9, 128.8, 128.5, 126.9, 125.3, 123.3 (d, $J_{C\text{-}F}$ = 9.6 Hz), 119.8, 117.9, 111.9 (d, $J_{C\text{-}F}$ = 23.5 Hz), 99.2 (d, $J_{C\text{-}F}$ = 26.5 Hz), 47.3, 39.6, 27.2, 21.6; HRMS (ESI, m/z): calcd. for $C_{25}H_{20}FNO_4SH^+$ 450.1170, found 450.1171. $[\alpha]^{27}_D$ = -45.2 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 96% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 7.2 min (minor), 11.0 min (major)].



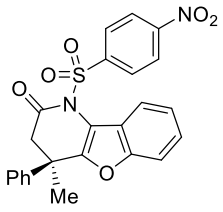
3p

(R)-7-Chloro-4-methyl-4-phenyl-1-tosyl-3,4-dihydrobenzofuro [3,2-b]pyridin-2(1H)-one (3p)*:* 41.5 mg, 89% yield; yellow solid, 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34-7.32 (m, 1H), 7.20-7.16 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.06-7.04 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 154.1, 151.6, 144.6, 143.3, 134.3, 130.6, 128.9, 128.8, 128.5, 127.0, 125.3, 124.2, 123.4, 122.1, 117.9, 112.1, 47.2, 39.6, 27.1, 21.5; HRMS (ESI, m/z): calcd. for $C_{25}H_{20}ClNO_4SH^+$ 466.0874, found 466.0871. $[\alpha]^{27}_D$ = -32.4 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 7.9 min (minor), 13.7 min (major)].



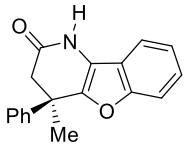
3q

(R)-1-((4-Methoxyphenyl)sulfonyl)-4-methyl-4-phenyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (3q)*:* 41.6 mg, 93% yield; brown solid, 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.05 (m, 1H), 7.57-7.55 (m, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.39-7.34 (m, 2H), 7.18-7.09 (m, 5H), 6.56 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.24 (d, *J* = 16.0 Hz, 1H), 2.88 (d, *J* = 15.6 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.4, 154.2, 150.9, 143.7, 130.9, 129.0, 128.9, 128.8, 127.1, 125.4, 124.6, 123.5, 122.6, 118.1, 113.4, 111.6, 55.5, 47.4, 39.5, 27.2; HRMS (ESI, m/z): calcd. for $C_{25}H_{21}NO_5SH^+$ 448.1213, found 448.1217. $[\alpha]^{27}_D$ = -59.2 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 11.0 min (minor), 20.7 min (major)].



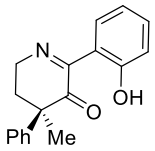
3r

(R)-4-Methyl-1-((4-nitrophenyl)sulfonyl)-4-phenyl-3,4-dihydro benzofuro[3,2-b]pyridin-2(1H)-one (3r)*:* 43.4 mg, 94% yield; yellow solid, 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 3H), 7.44-7.37 (m, 2H), 7.20-7.17 (m, 1H), 7.10-7.04 (m, 4H), 3.29 (d, *J* = 15.6 Hz, 1H), 2.91 (d, *J* = 15.6 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 154.2, 151.7, 150.1, 143.7, 142.5, 129.7, 128.9, 127.4, 125.3, 125.1, 123.8, 123.3, 123.1, 122.4, 117.5, 111.8, 46.6, 39.8, 27.4; HRMS (ESI, m/z): calcd. for $C_{24}H_{18}N_2O_6SH^+$ 463.0958, found 463.0977. $[\alpha]^{27}_D$ = -54.4 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 10.5 min (minor), 17.7 min (major)].



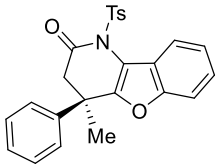
4

(R)-4-Methyl-4-phenyl-3,4-dihydrobenzofuro[3,2-b]pyridin-2(1H)-one (4)*:* 23.1 mg, 83% yield; white solid, 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (br, 1H), 7.59-7.57 (m, 1H), 7.47-7.45 (m, 1H), 7.32-7.27 (m, 6H), 7.22-7.17 (m, 1H), 3.24 (d, *J* = 16.4 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.0, 143.9, 143.8, 128.8, 127.1, 125.6, 124.4, 123.0, 120.7, 118.0, 117.8, 111.9, 47.5, 40.4, 26.2; HRMS (ESI, m/z): calcd. for $C_{18}H_{15}NO_2H^+$ 278.1176, found 278.1179. $[\alpha]^{27}_D$ = +12.4 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 6.8 min (major), 10.6 min (minor)].



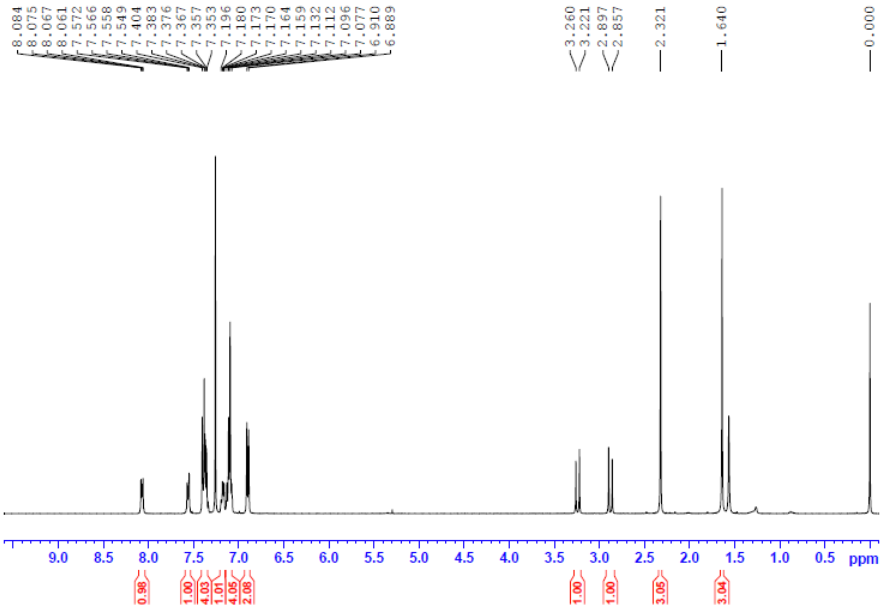
5

(R)-2-(2-Hydroxyphenyl)-4-methyl-4-phenyl-5,6-dihydropyridin-3(4H)-one (5)*:* 19.9 mg, 71% yield; yellow solid, 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.74 (br, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.36-7.27 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 4.10-4.03 (m, 1H), 3.88-3.79 (m, 1H), 2.83-2.78 (m, 1H), 2.47-2.39 (m, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 165.5, 162.0, 139.6, 132.6, 130.0, 129.3, 127.7, 125.7, 118.2, 117.9, 115.8, 50.4, 45.4, 37.0, 26.4; HRMS (ESI, m/z): calcd. for $C_{18}H_{17}NO_2H^+$ 280.1332, found 280.1343. $[\alpha]^{27}_D$ = +102.8 (*c* = 0.25 in CH_2Cl_2); HPLC analysis: 98% ee, [CHIRALPAK IA column; 1 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 6.3 min (major), 7.3 min (minor)].

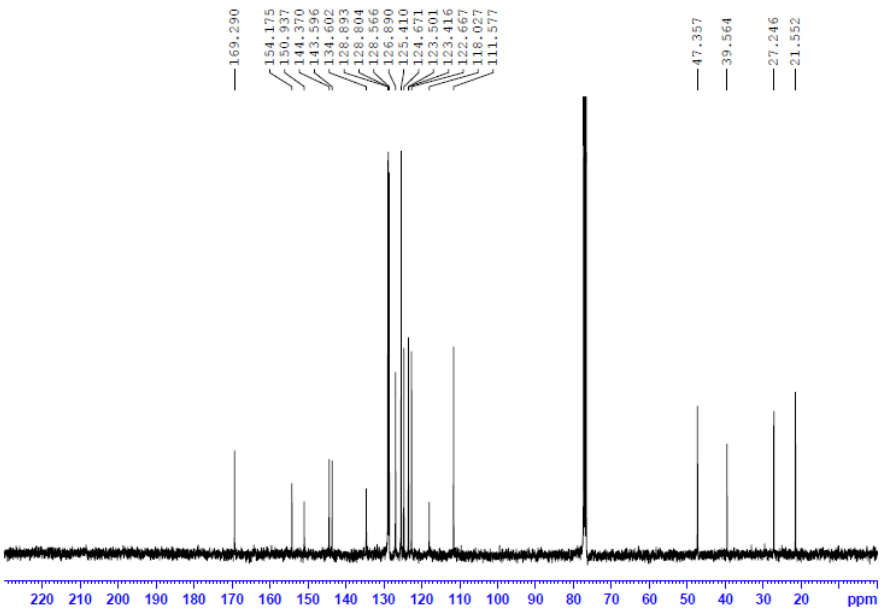


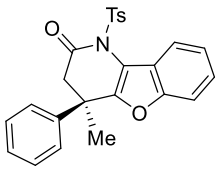
3a

$CDCl_3$, ^1H NMR, 400 MHz

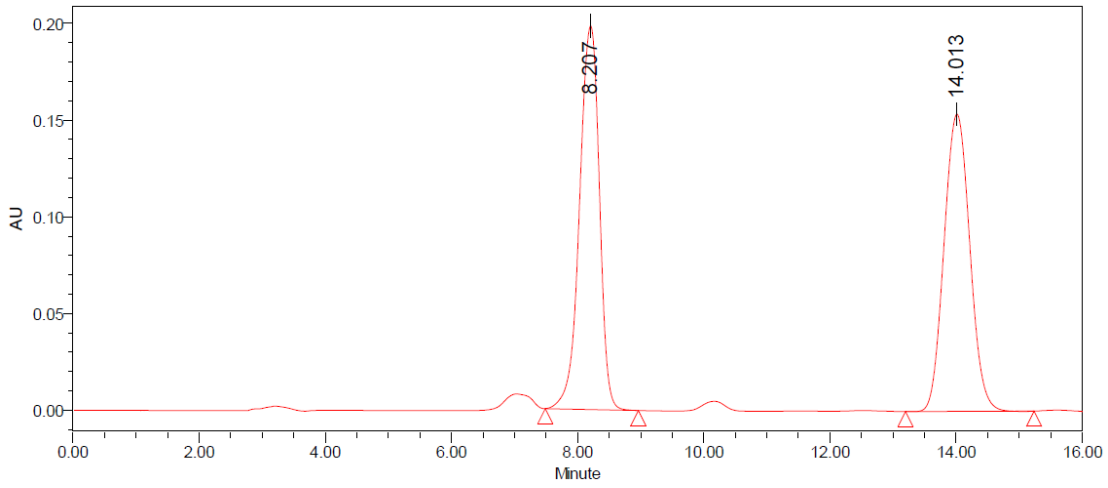


$CDCl_3$, ^{13}C NMR, 100 MHz





3a



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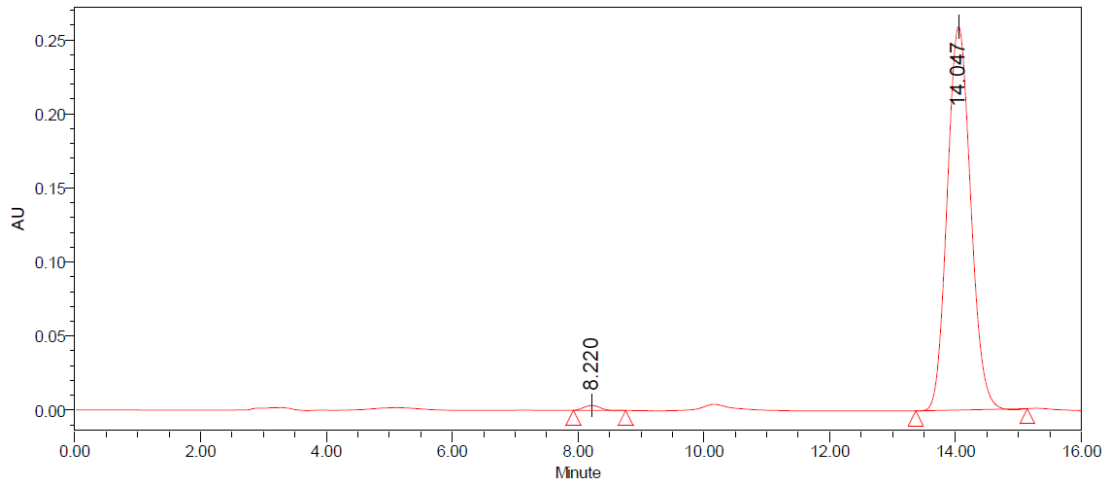
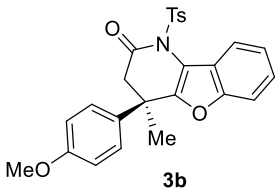
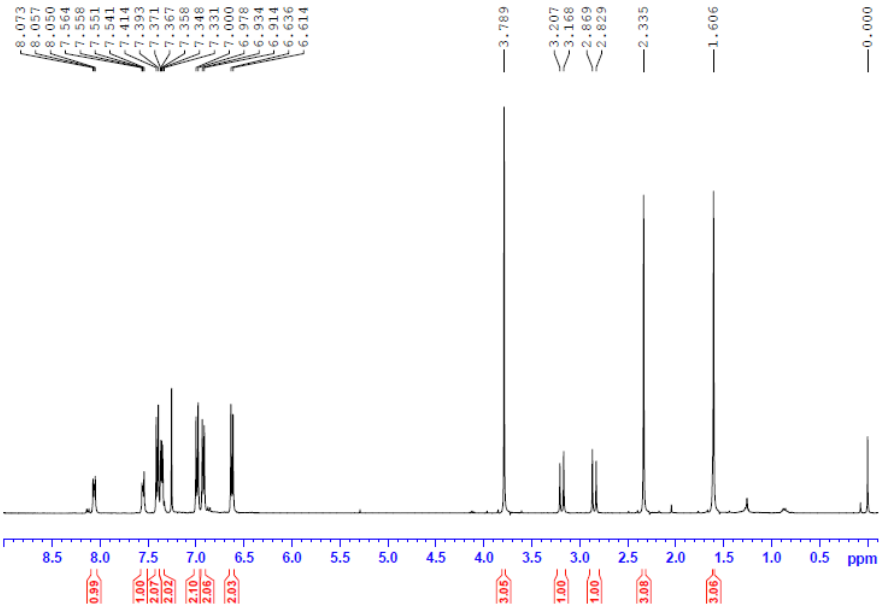


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	8.220	58823	0.87	3236	1.23	7.925	8.757
2	14.047	6718781	99.13	259009	98.77	13.367	15.140

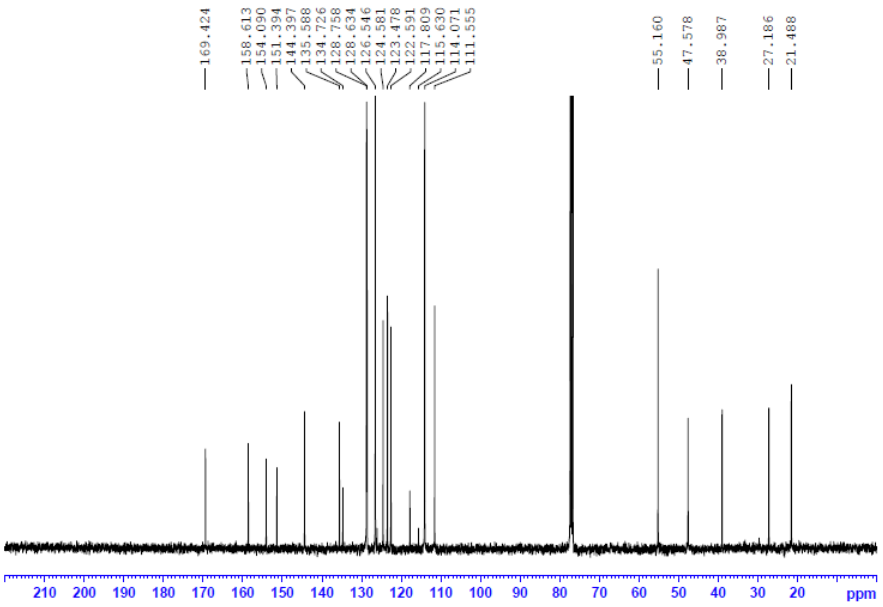


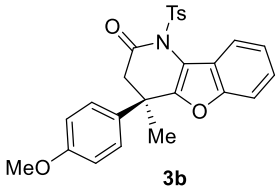
3b

$CDCl_3$, ^1H NMR, 400 MHz

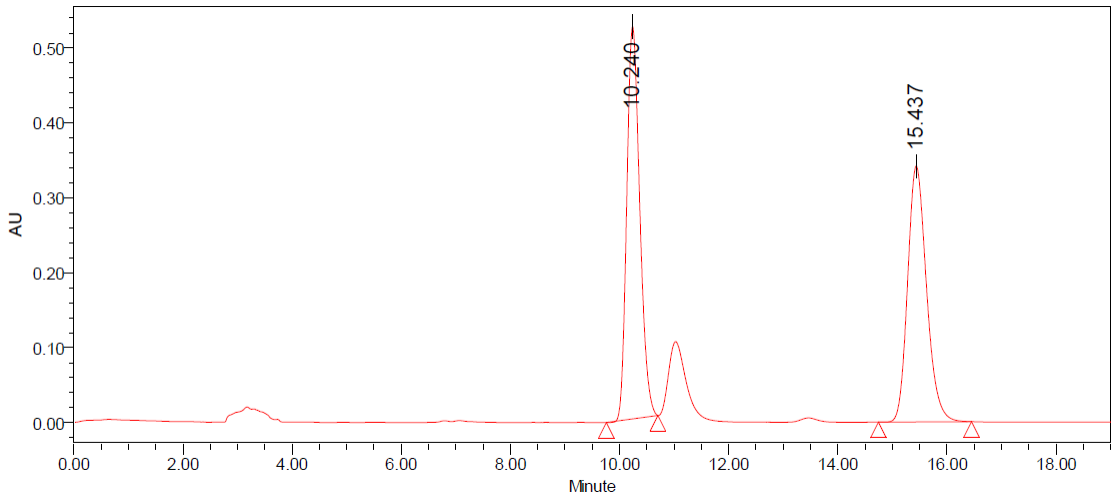


$CDCl_3$, ^{13}C NMR, 100 MHz

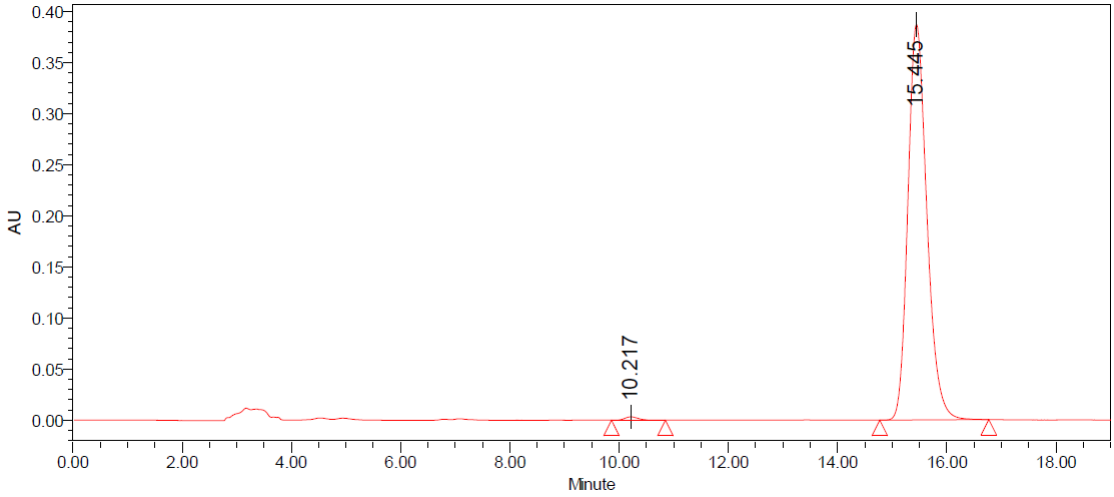




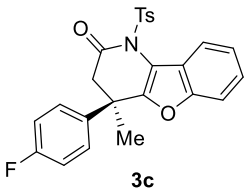
3b



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	10.240	8656287	51.36	523662	60.53	9.760	10.703
2	15.437	8198091	48.64	341504	39.47	14.745	16.450

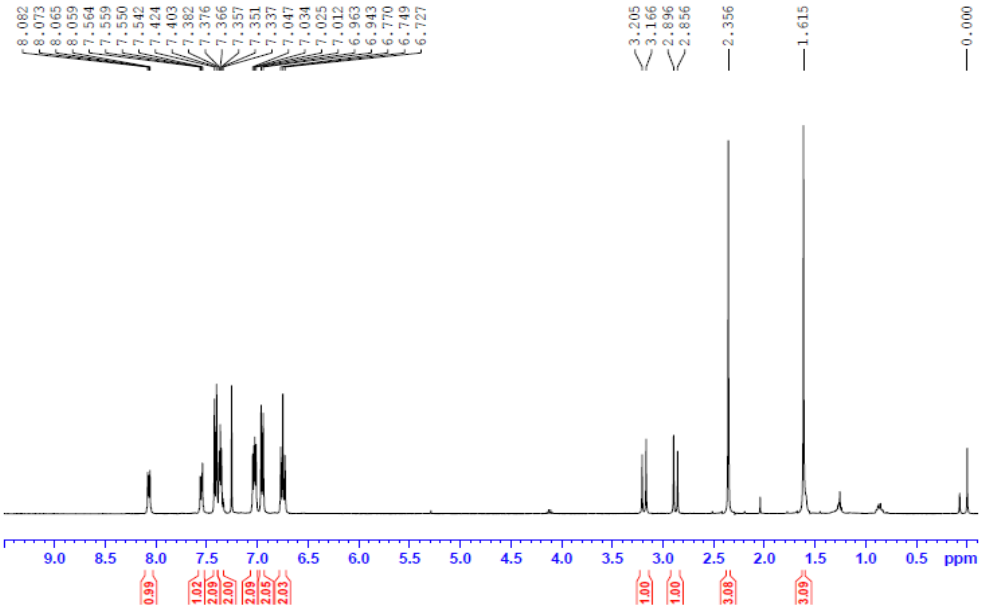


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	10.217	55615	0.59	3290	0.84	9.862	10.847
2	15.445	9351079	99.41	387067	99.16	14.773	16.768

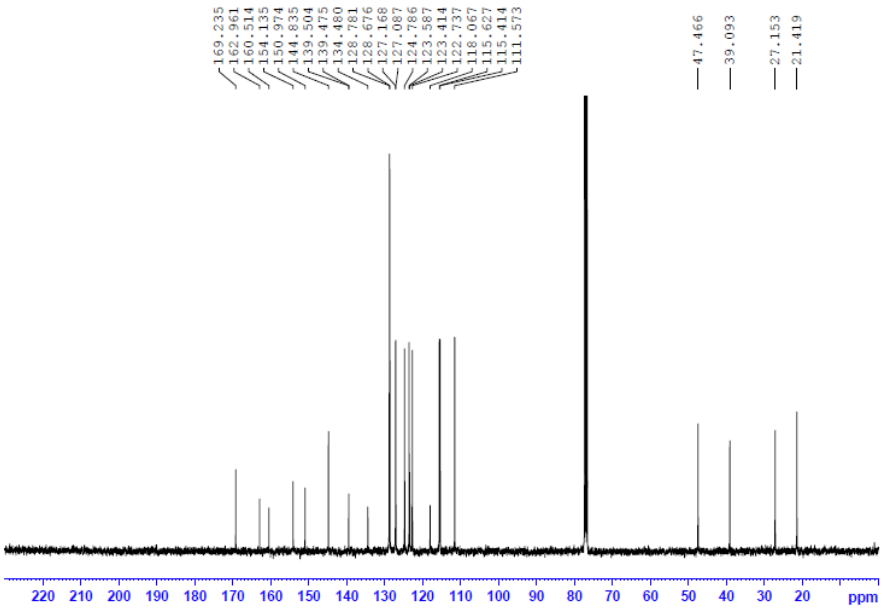


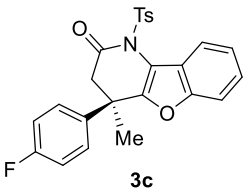
3c

$CDCl_3$, ^1H NMR, 400 MHz

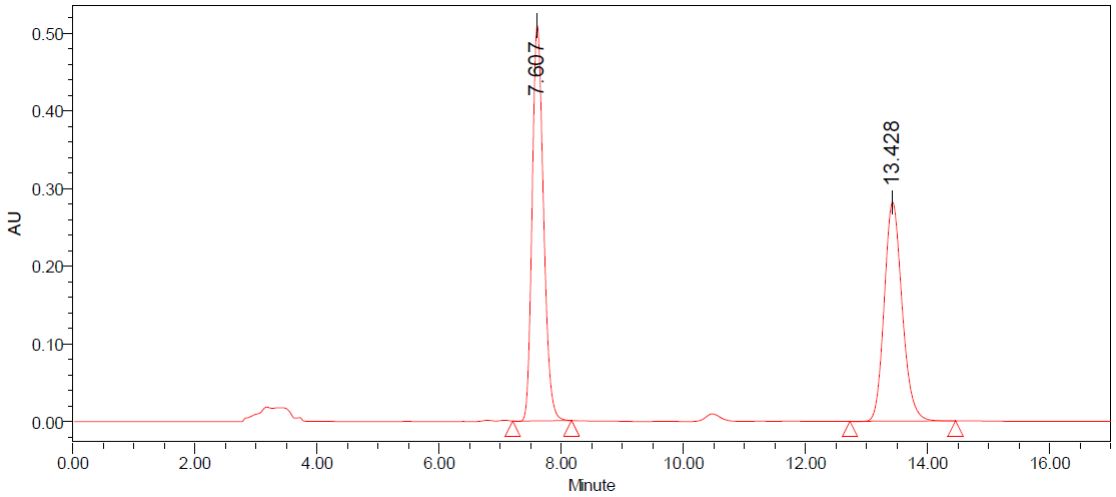


$CDCl_3$, ^{13}C NMR, 100 MHz

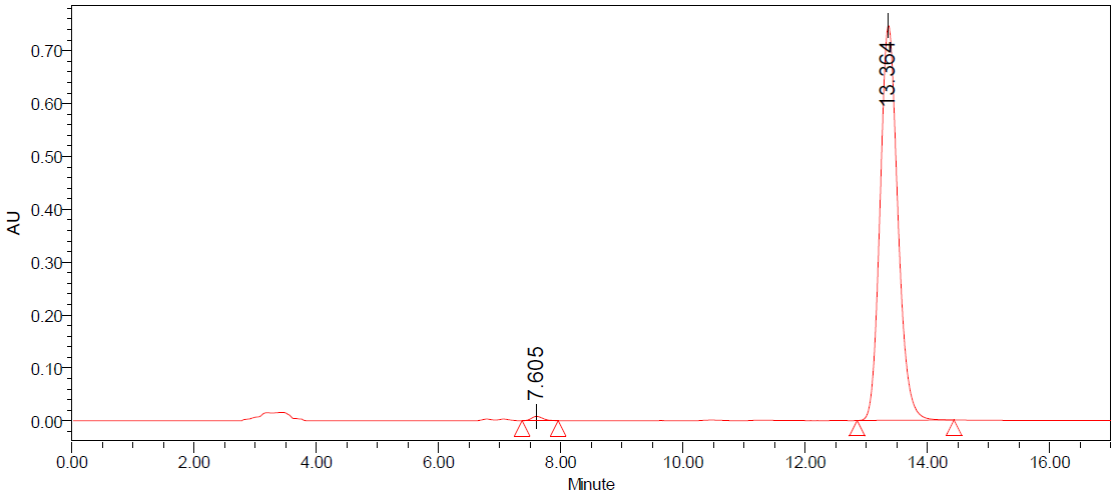




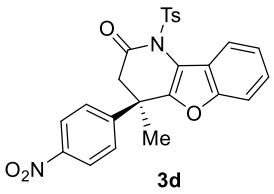
3c



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.607	6591532	53.46	508923	64.35	7.205	8.170
2	13.428	5738094	46.54	281985	35.65	12.730	14.458

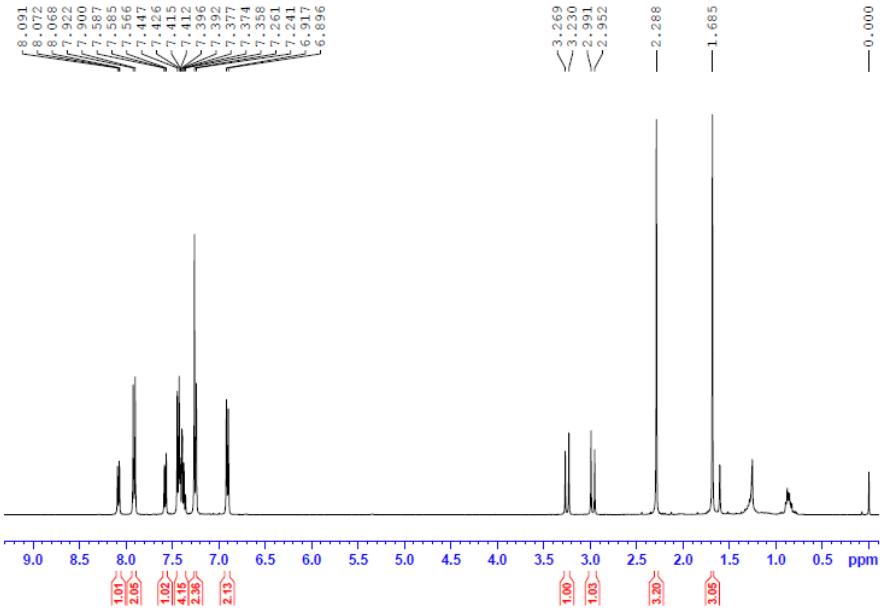


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.605	100765	0.66	7909	1.05	7.368	7.958
2	13.364	15113659	99.34	746980	98.95	12.852	14.437

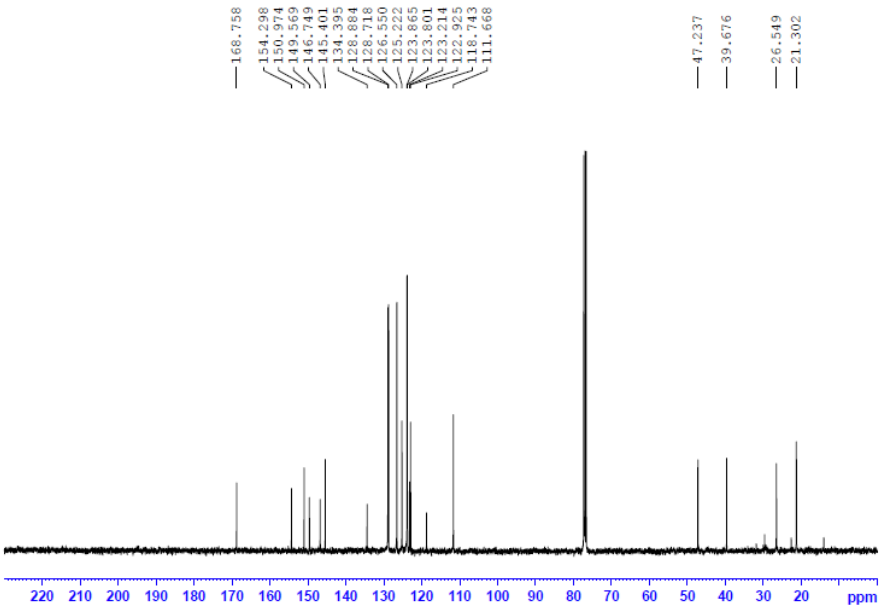


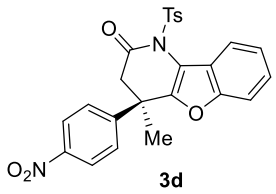
3d

$CDCl_3$, ^1H NMR, 400 MHz

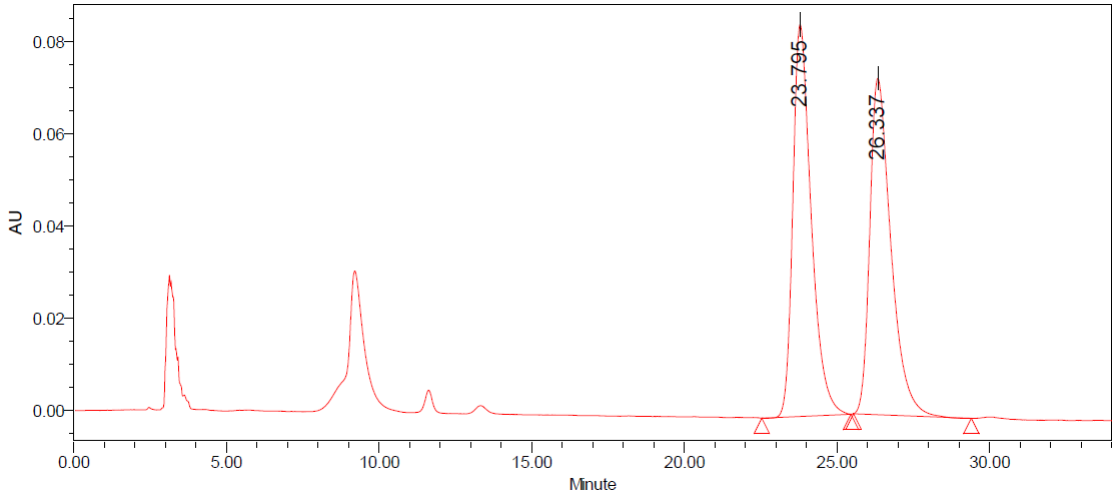


$CDCl_3$, ^{13}C NMR, 100 MHz

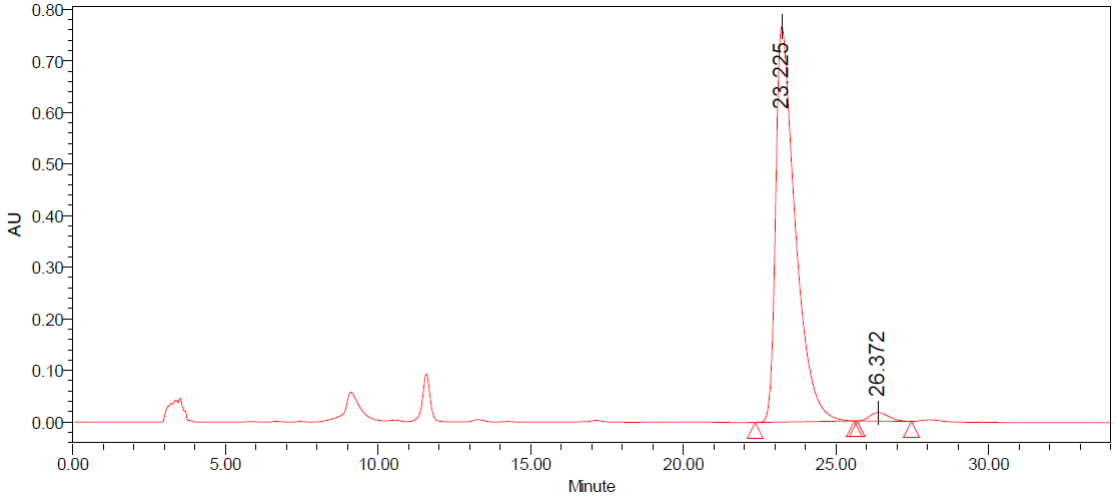




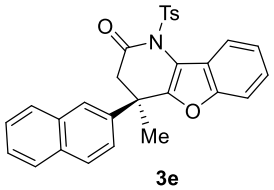
3d



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	23.795	3561427	50.36	85000	53.81	22.538	25.460
2	26.337	3510324	49.64	72954	46.19	25.547	29.402

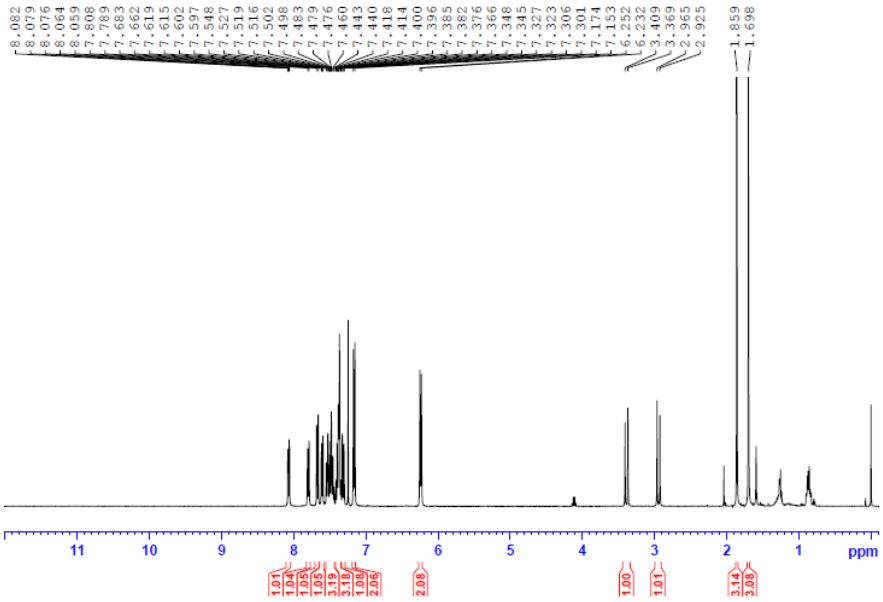


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	23.225	34303157	97.95	766931	97.87	22.353	25.602
2	26.372	717087	2.05	16730	2.13	25.690	27.475

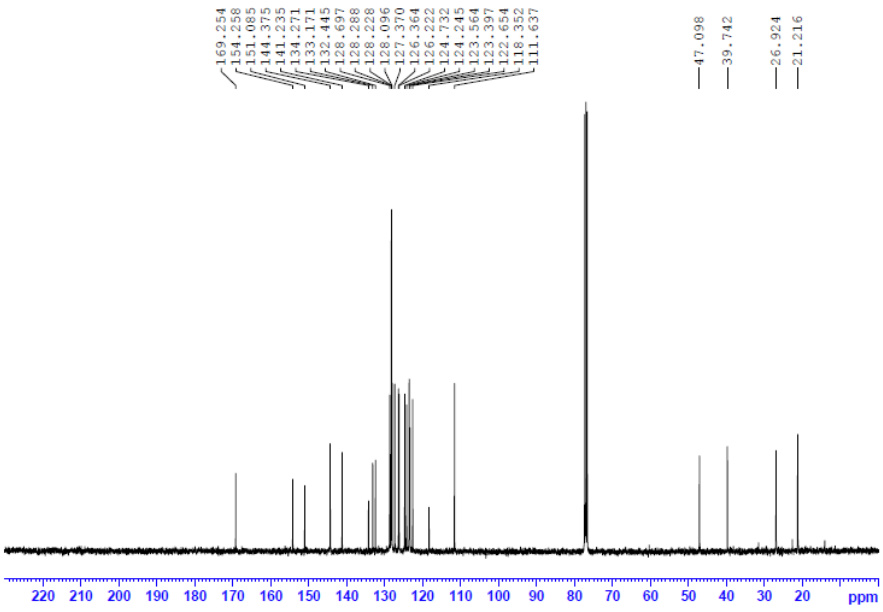


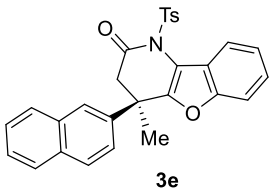
3e

$CDCl_3$, ^1H NMR, 400 MHz

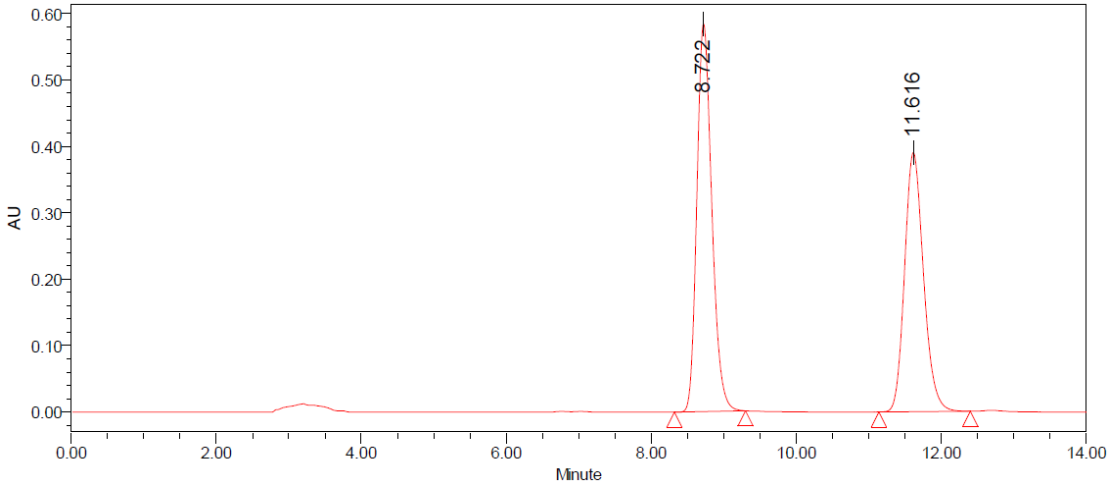


$CDCl_3$, ^{13}C NMR, 100 MHz

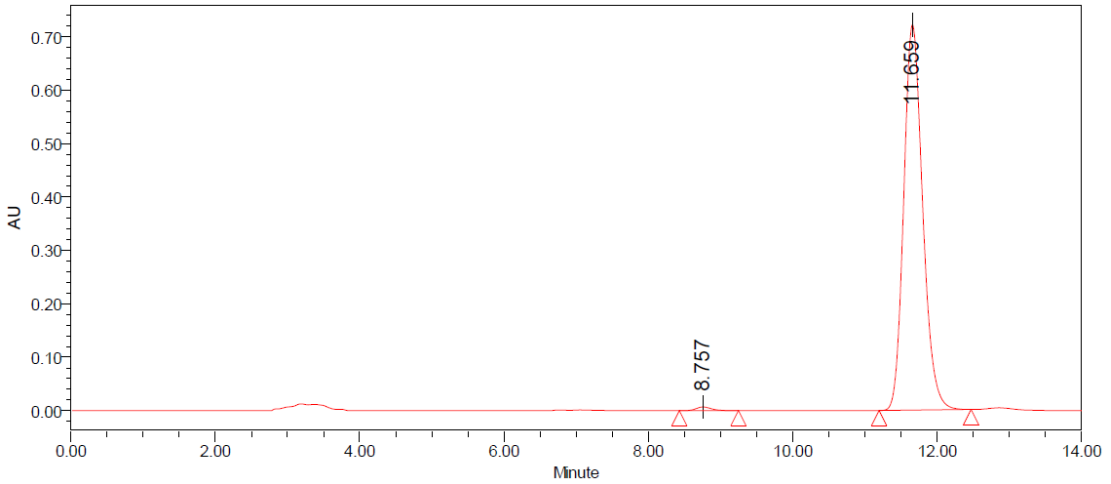




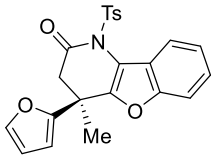
3e



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	8.722	8351247	54.14	583578	59.94	8.320	9.300
2	11.616	7072792	45.86	390030	40.06	11.142	12.402

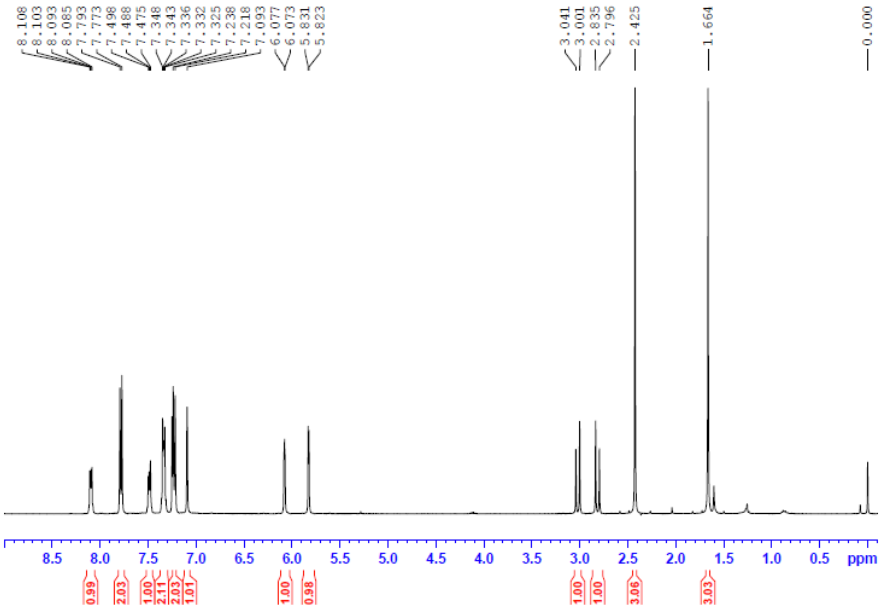


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	8.757	95665	0.72	6656	0.91	8.428	9.248
2	11.659	13164958	99.28	721533	99.09	11.197	12.472

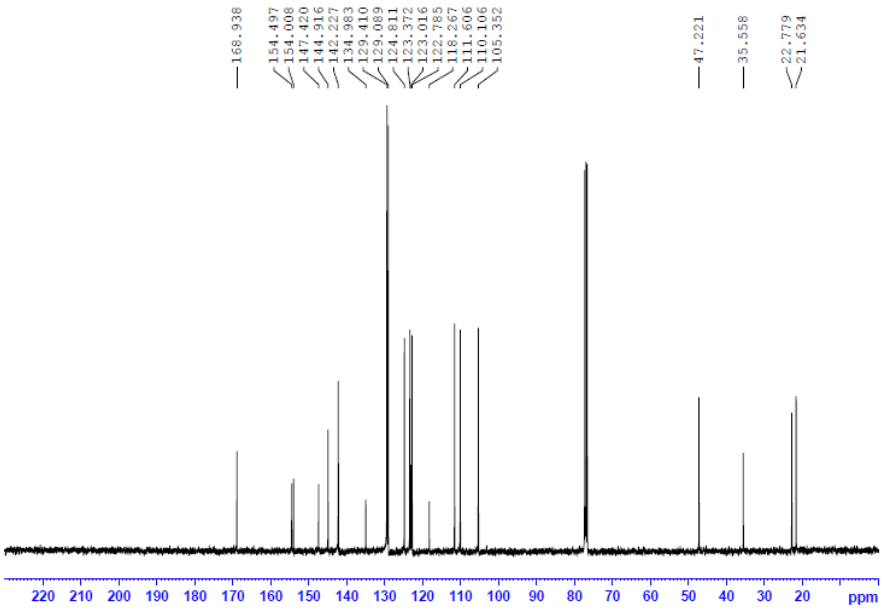


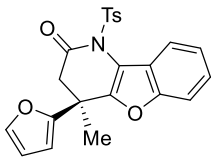
3f

$CDCl_3$, ^1H NMR, 400 MHz

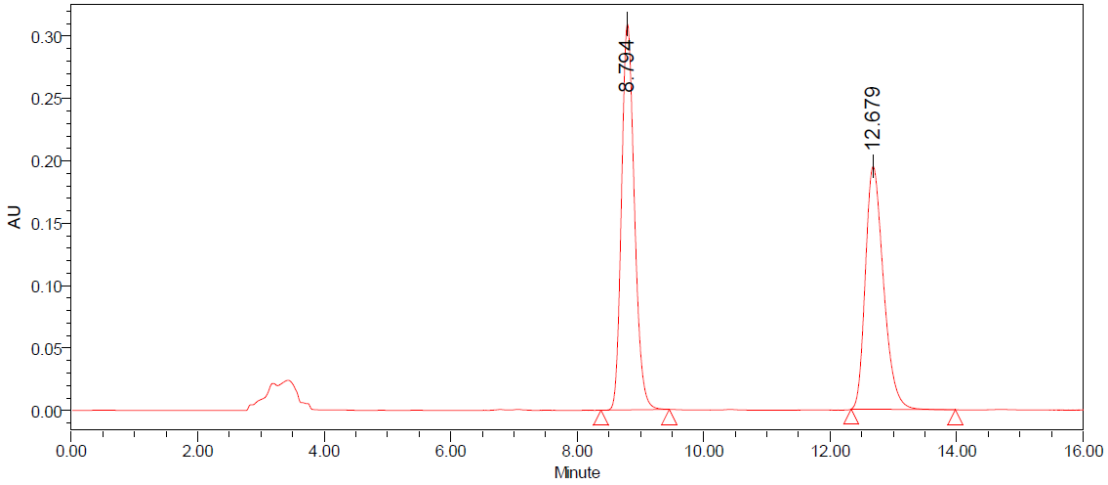


$CDCl_3$, ^{13}C NMR, 100 MHz

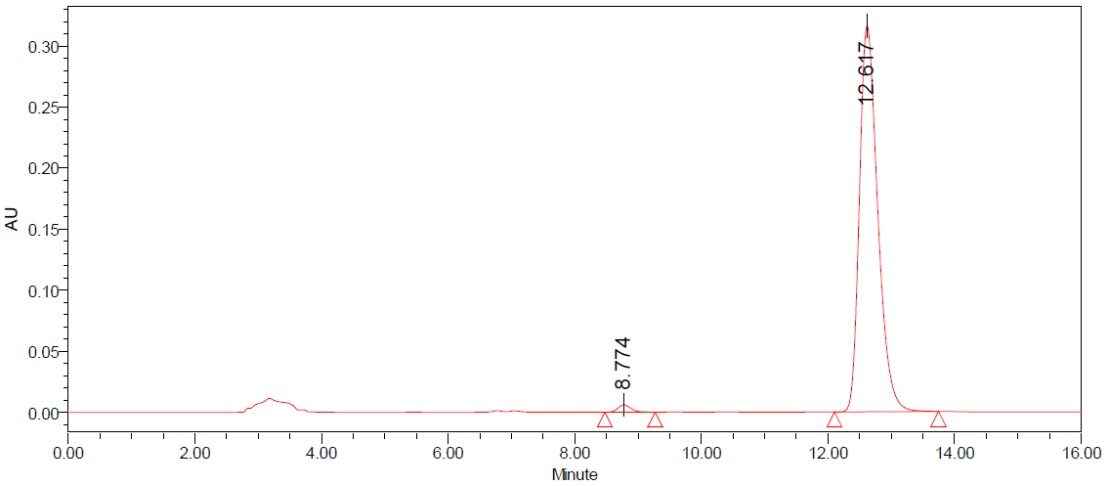




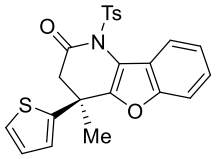
3f



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	8.794	4390033	53.13	309343	61.39	8.377	9.457
2	12.679	3872450	46.87	194539	38.61	12.332	13.978

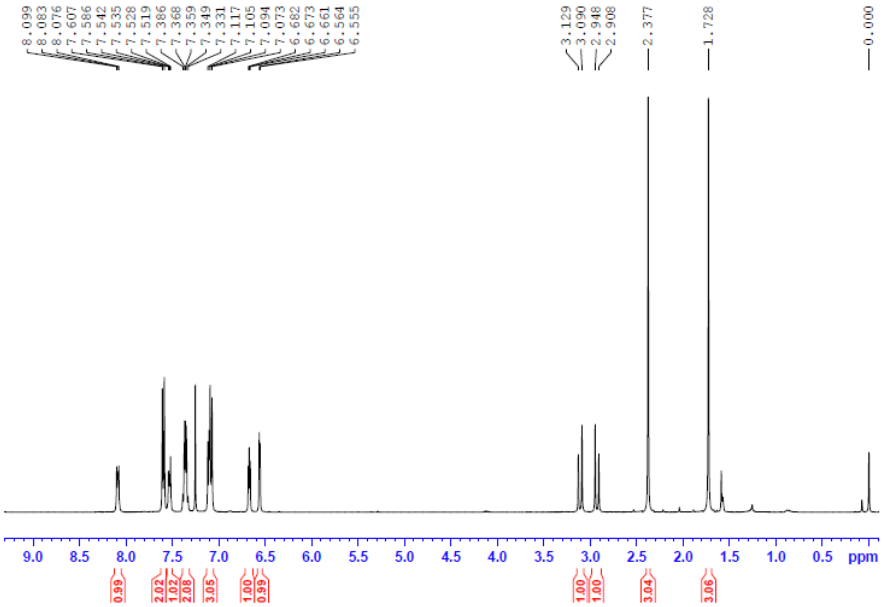


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	8.774	83758	1.30	5929	1.84	8.473	9.268
2	12.617	6352054	98.70	316014	98.16	12.102	13.745

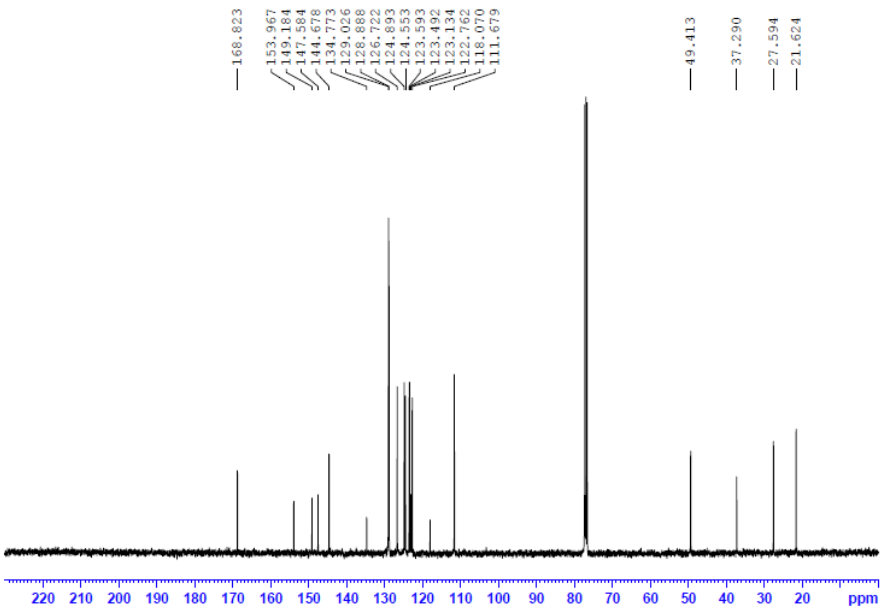


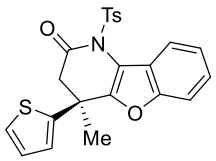
3g

$CDCl_3$, ^1H NMR, 400 MHz

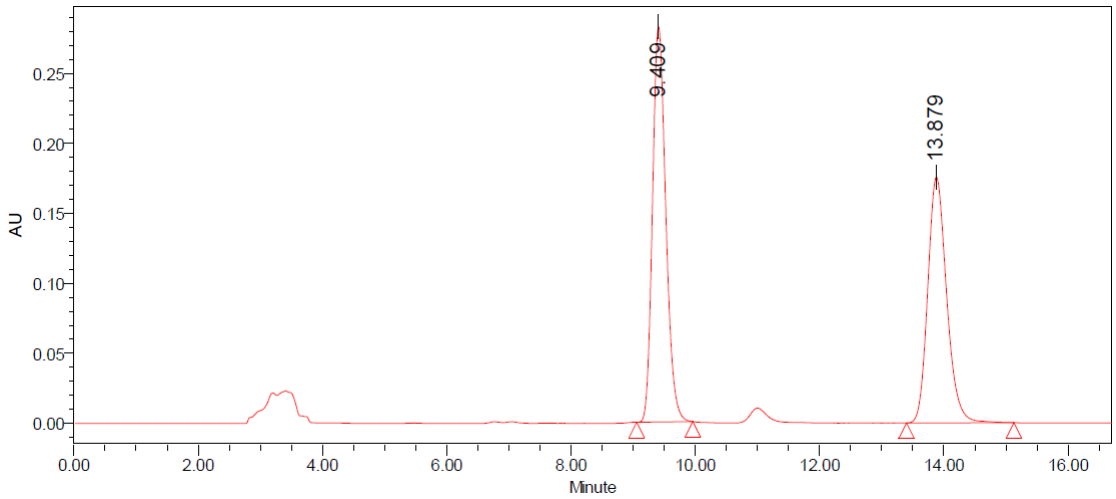


$CDCl_3$, ^{13}C NMR, 100 MHz

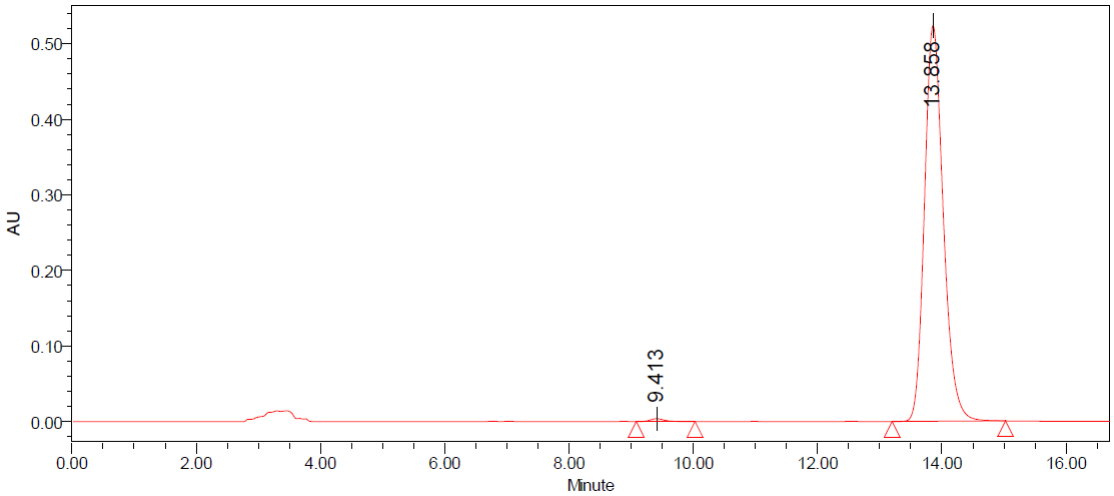




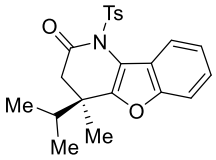
3g



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	9.409	4201292	53.13	282472	61.67	9.057	9.960
2	13.879	3706035	46.87	175557	38.33	13.398	15.127

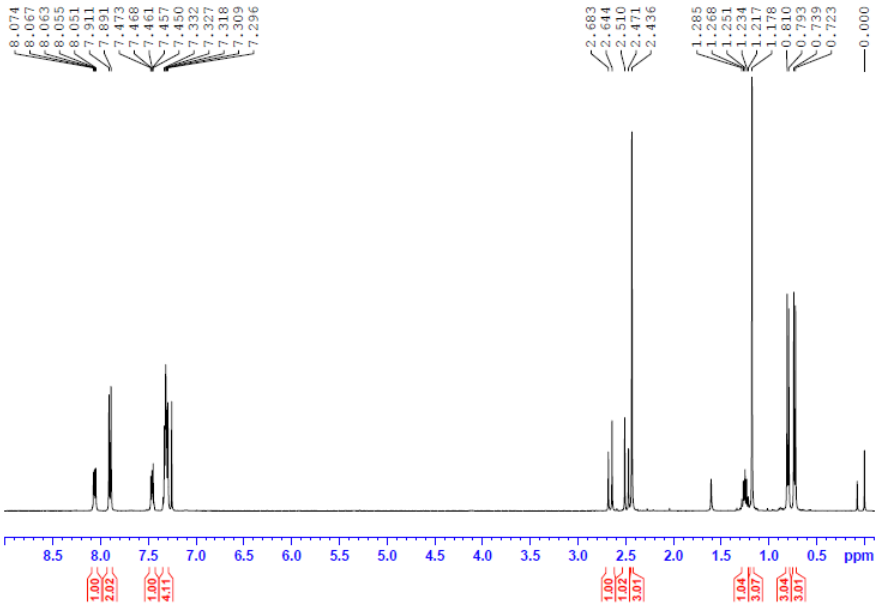


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	9.413	56080	0.51	3734	0.71	9.083	10.028
2	13.858	11017295	99.49	523620	99.29	13.198	15.023

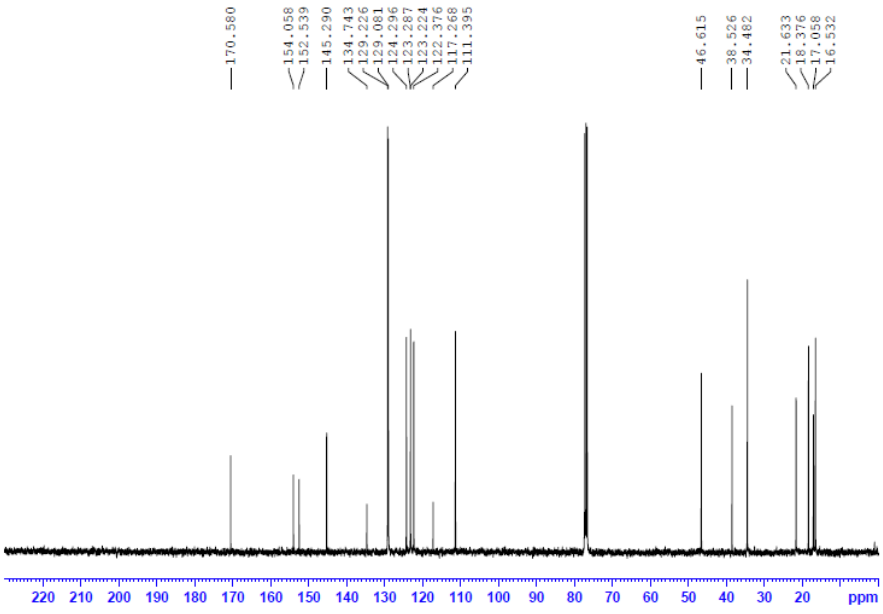


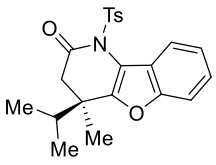
3h

$CDCl_3$, ^1H NMR, 400 MHz

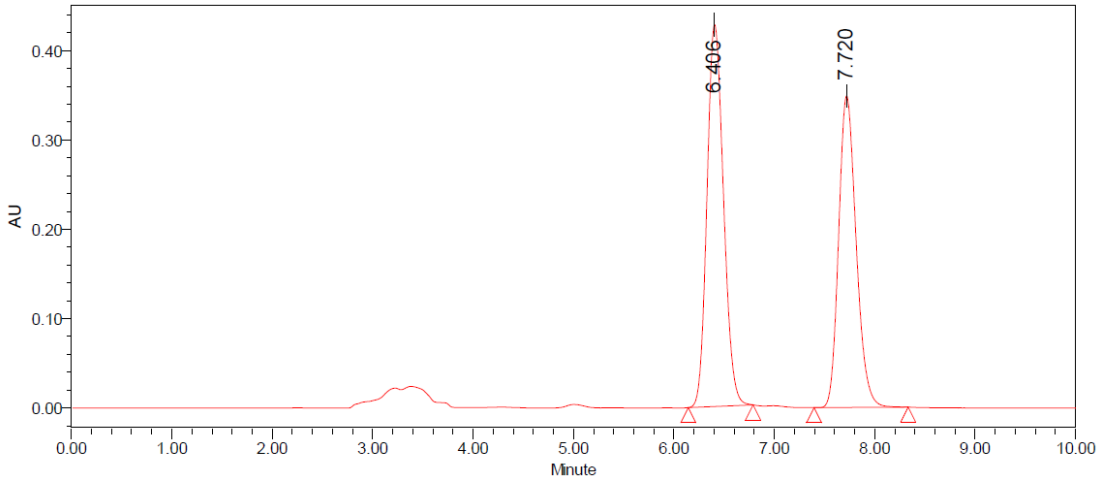


$CDCl_3$, ^{13}C NMR, 100 MHz

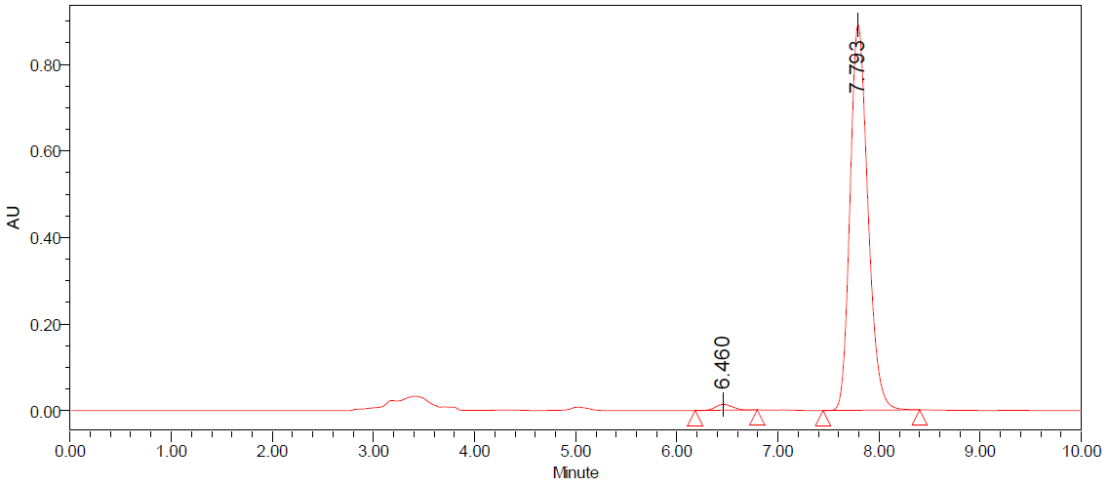




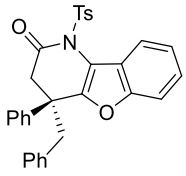
3h



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.406	4881447	53.58	427473	55.06	6.143	6.788
2	7.720	4228853	46.42	348855	44.94	7.397	8.333

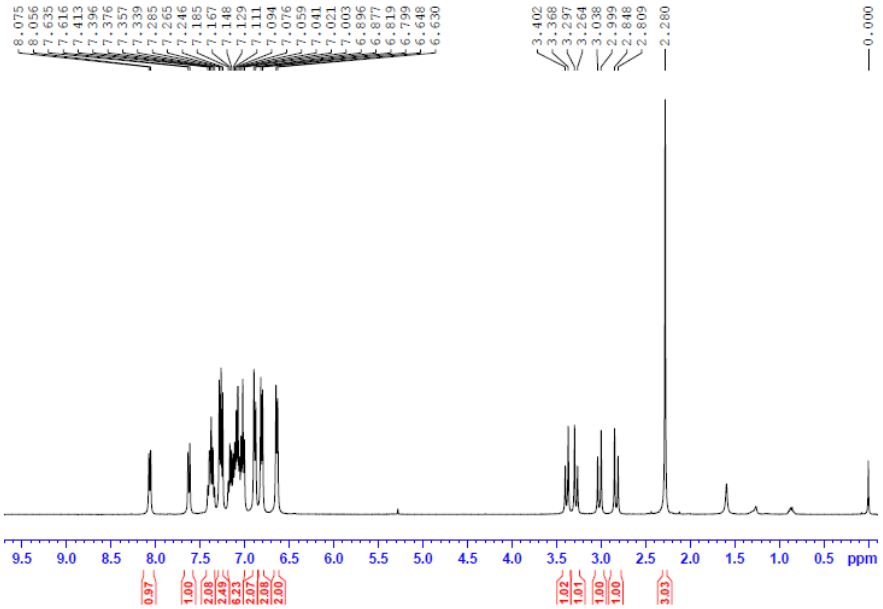


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.460	151535	1.37	13232	1.46	6.182	6.795
2	7.793	10928163	98.63	890583	98.54	7.445	8.400

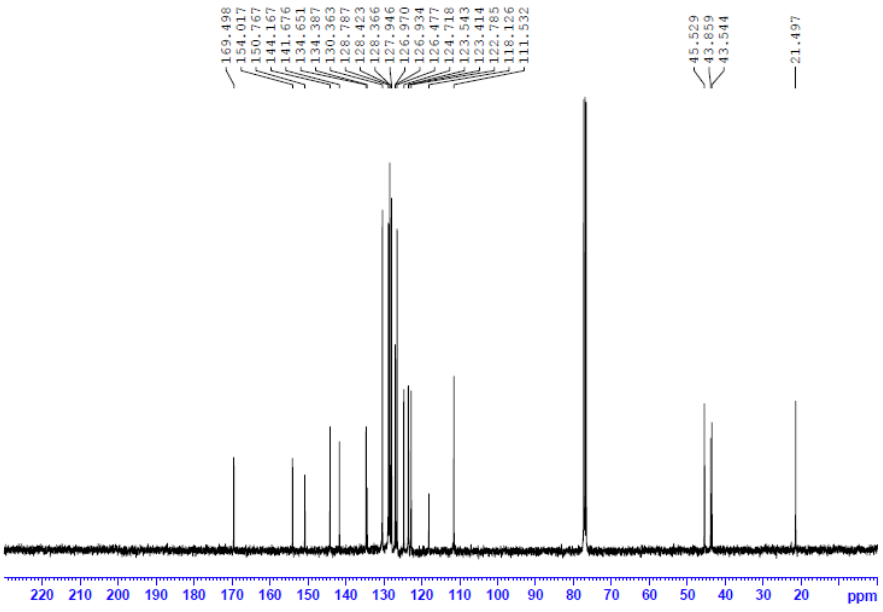


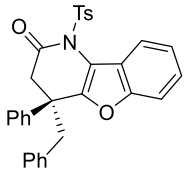
3i

$CDCl_3$, ^1H NMR, 400 MHz

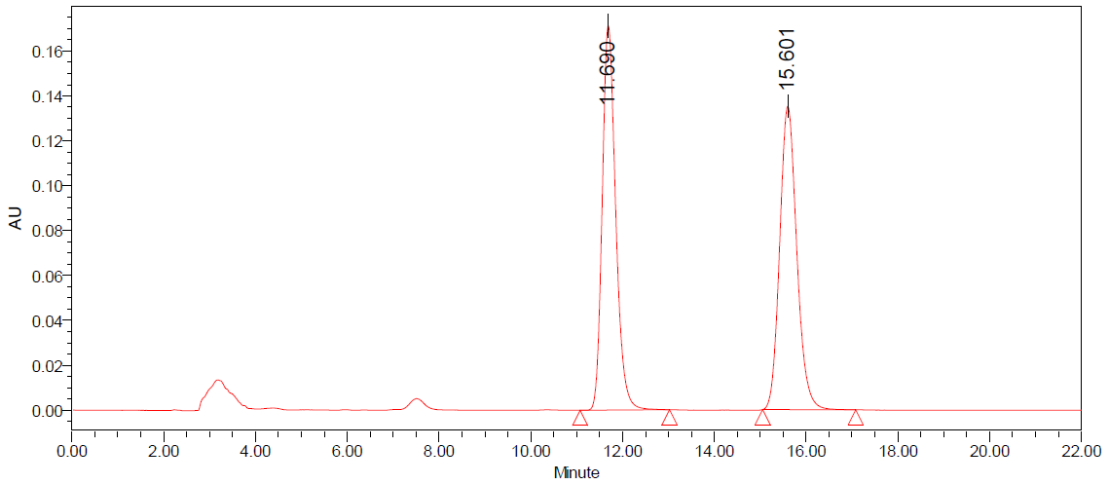


$CDCl_3$, ^{13}C NMR, 100 MHz

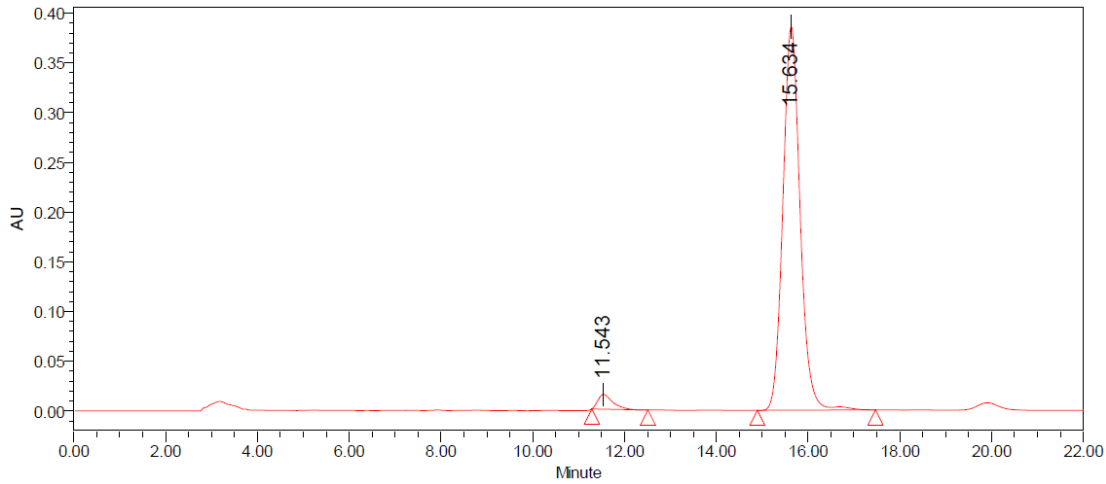




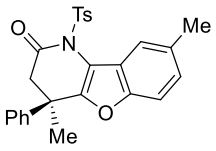
3i



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	11.690	3491155	49.97	171218	55.89	11.075	13.025
2	15.601	3496037	50.03	135114	44.11	15.055	17.083

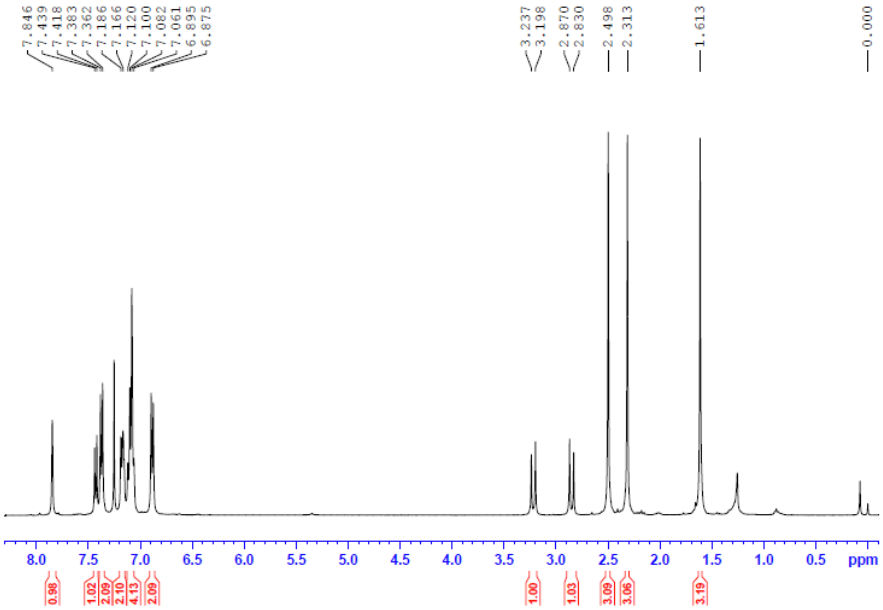


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	11.543	333671	3.21	14864	3.71	11.288	12.510
2	15.634	10075913	96.79	385654	96.29	14.897	17.470

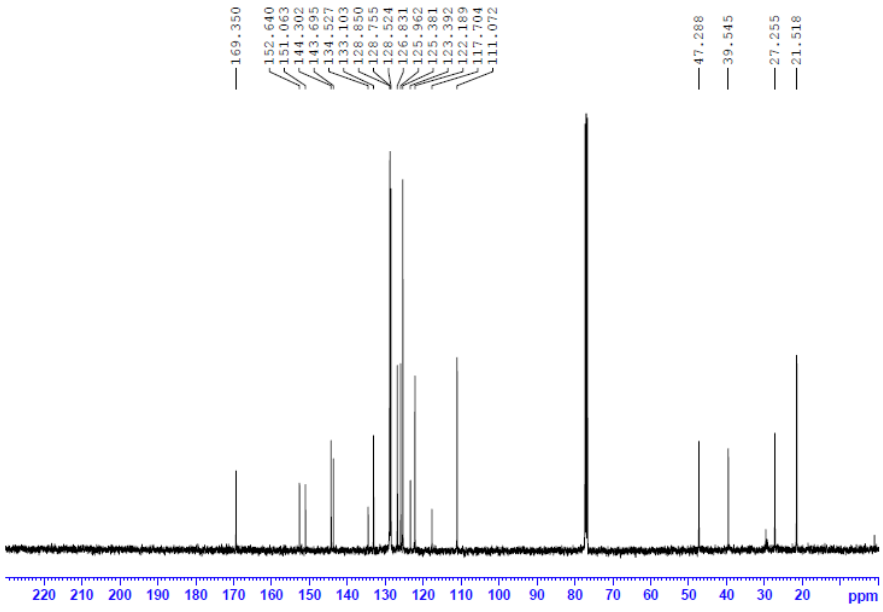


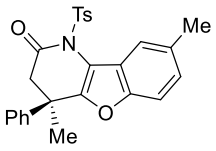
3j

$CDCl_3$, ^1H NMR, 400 MHz

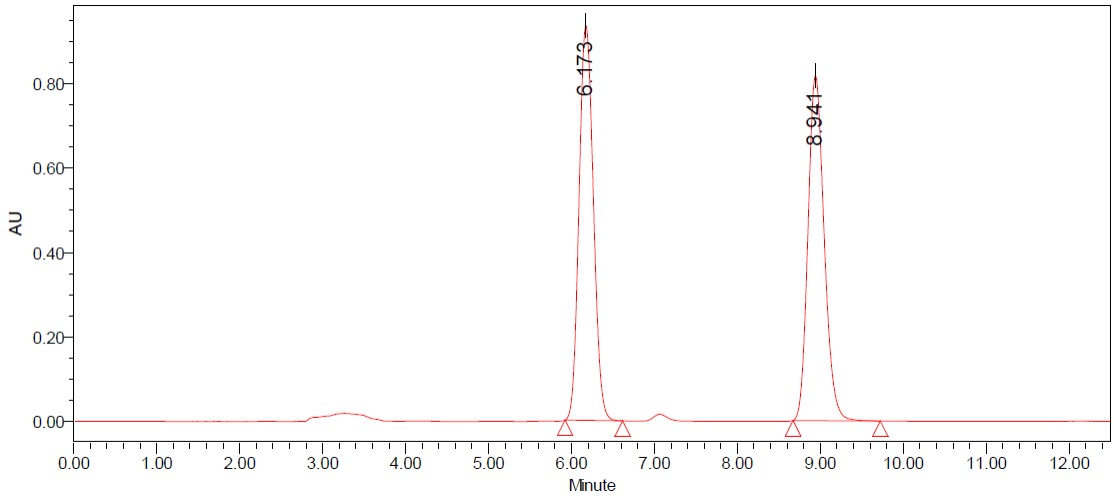


$CDCl_3$, ^{13}C NMR, 100 MHz

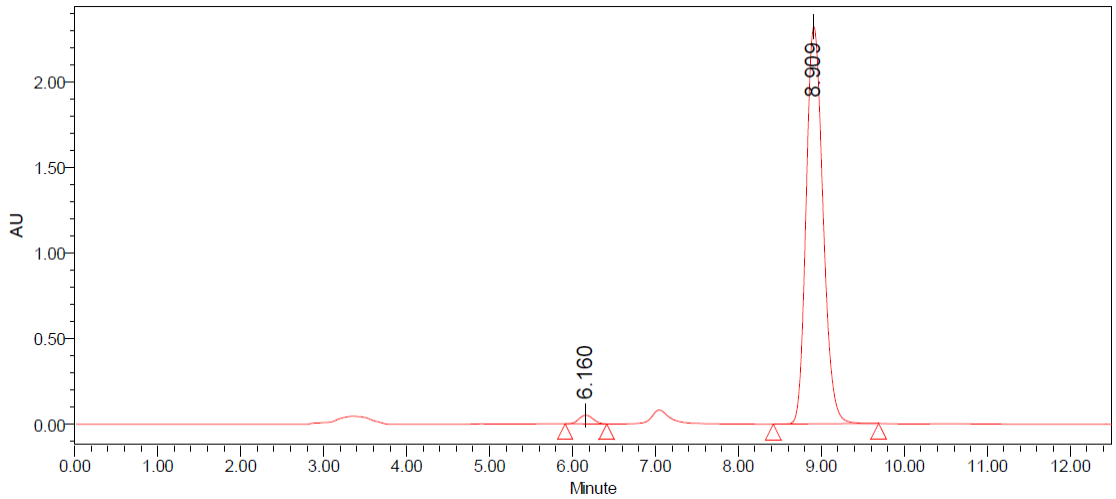




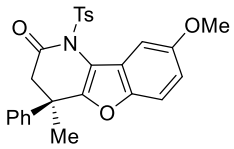
3j



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.173	11230665	50.31	935555	53.38	5.922	6.617
2	8.941	11092842	49.69	817016	46.62	8.672	9.722

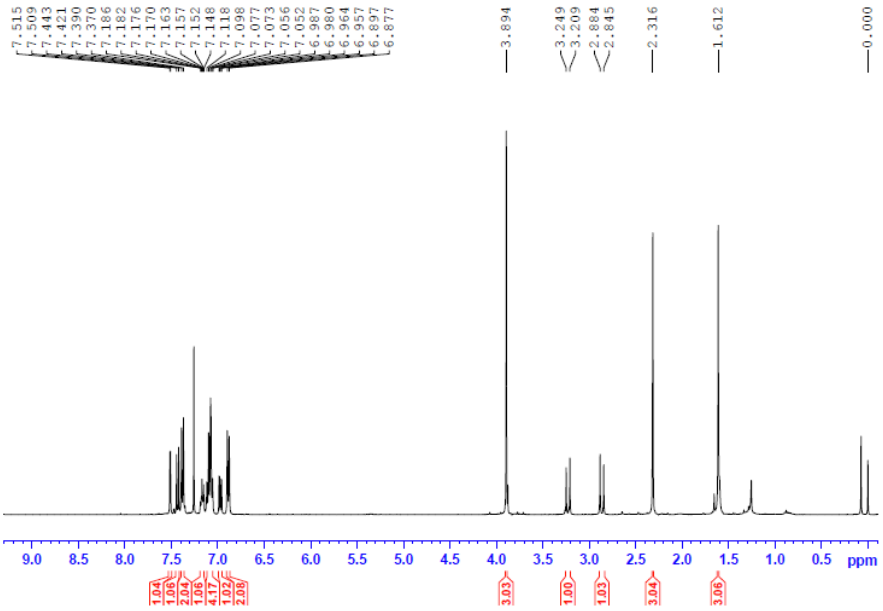


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.160	601866	1.81	50795	2.14	5.912	6.413
2	8.909	32730520	98.19	2320483	97.86	8.420	9.690

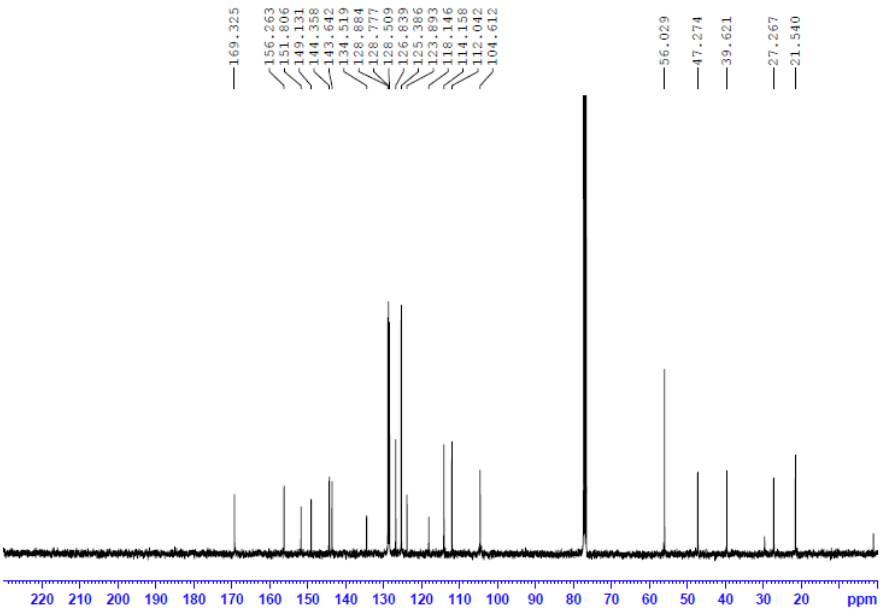


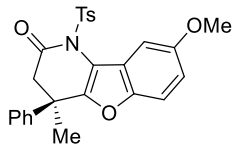
3k

$CDCl_3$, ^1H NMR, 400 MHz

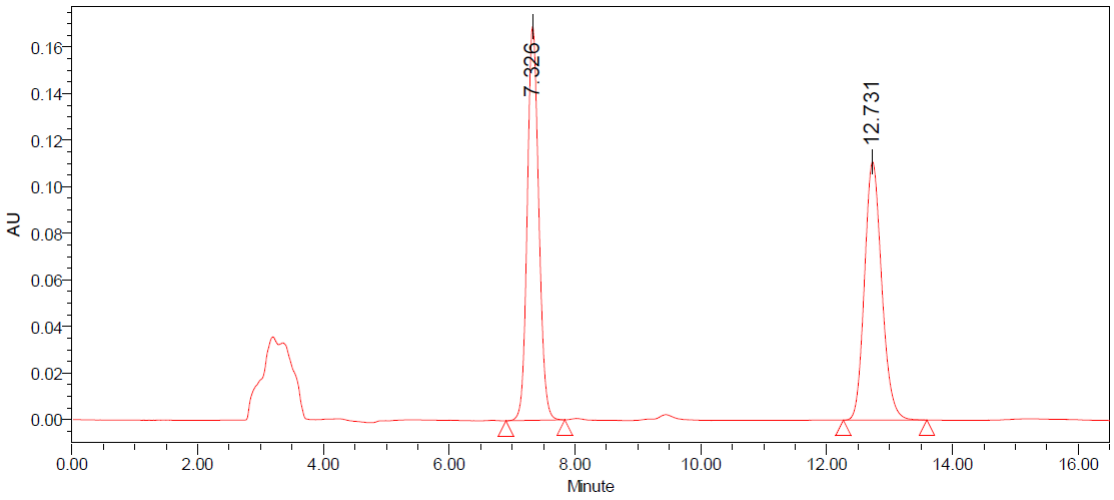


$CDCl_3$, ^{13}C NMR, 100 MHz

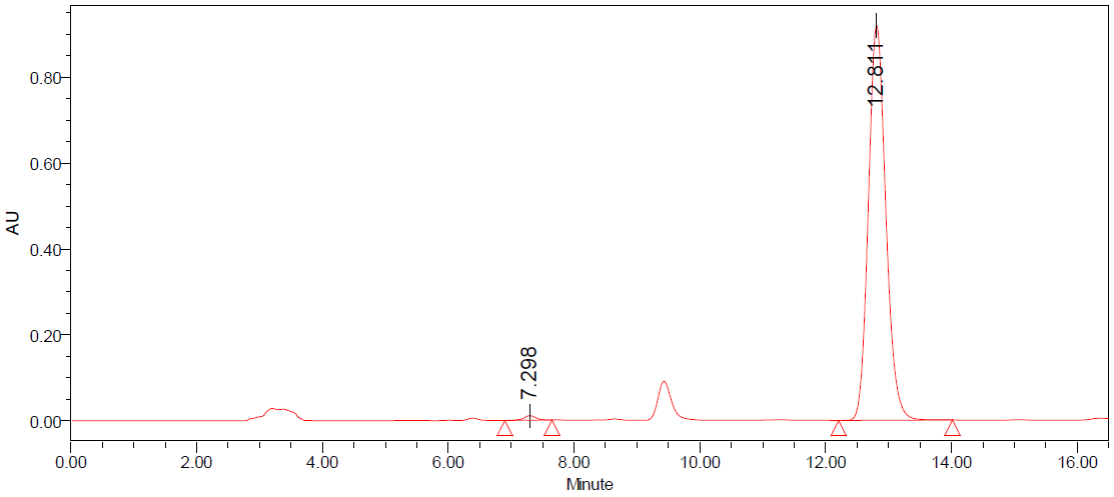




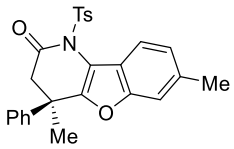
3k



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.326	2149444	50.43	169124	60.40	6.902	7.837
2	12.731	2112493	49.57	110891	39.60	12.267	13.593

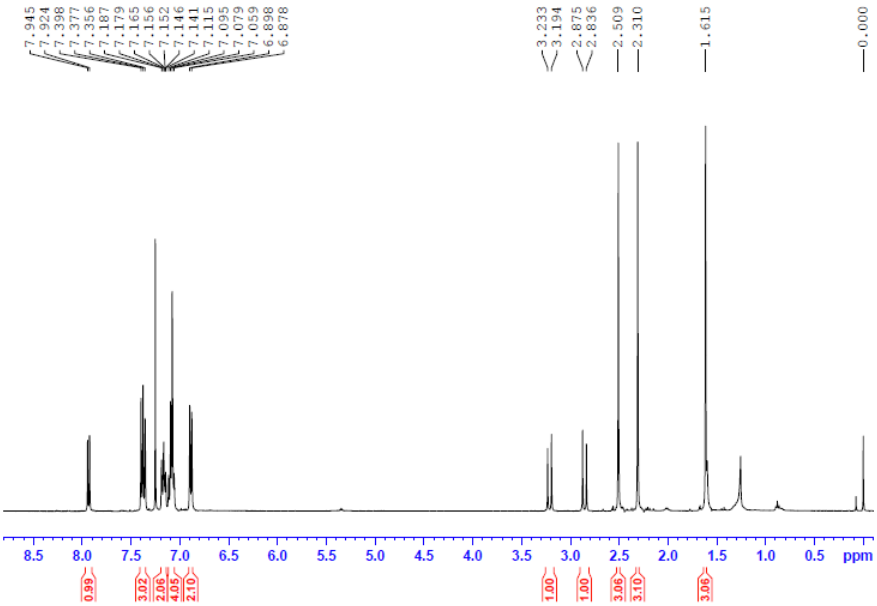


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.298	137296	0.77	10438	1.12	6.898	7.650
2	12.811	17746852	99.23	919580	98.88	12.207	14.017

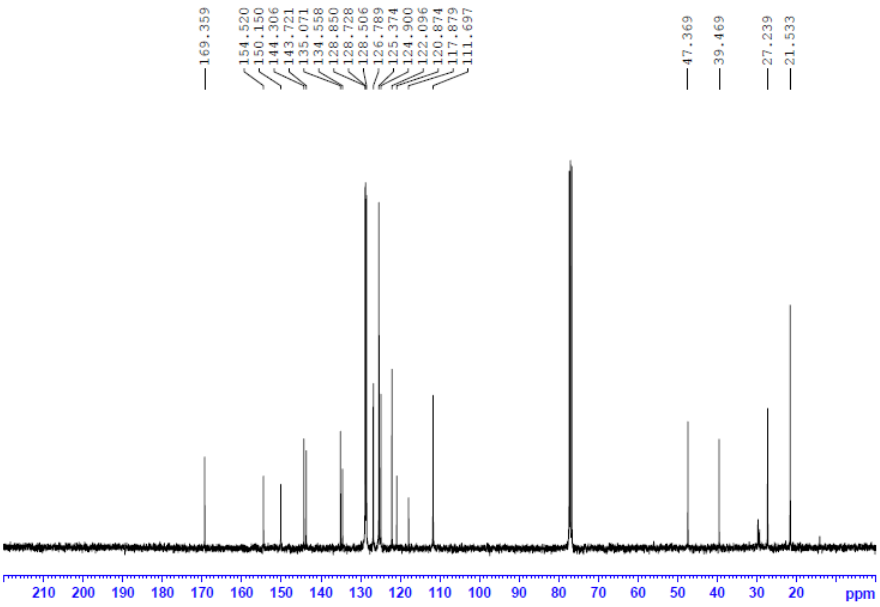


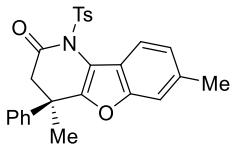
3l

$CDCl_3$, ^1H NMR, 400 MHz

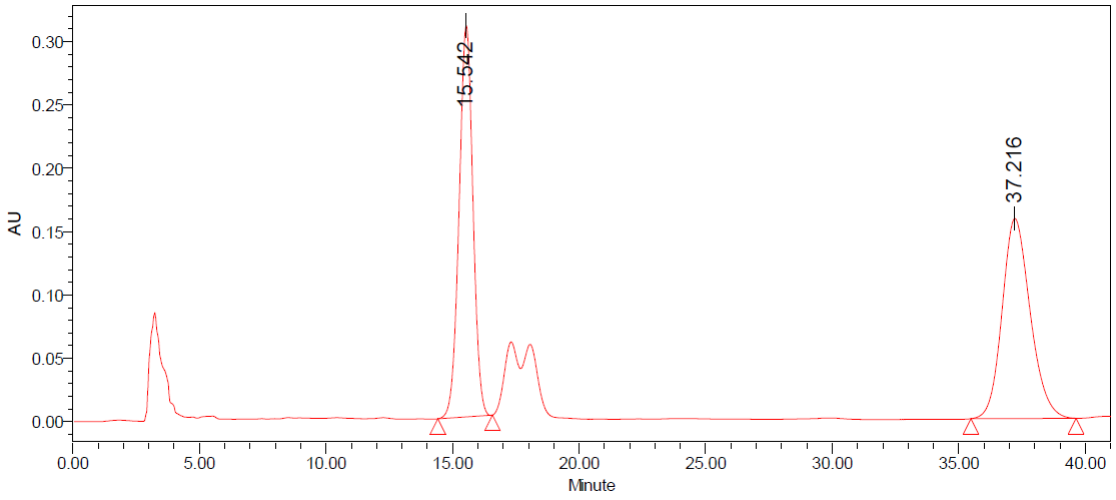


$CDCl_3$, ^{13}C NMR, 100 MHz

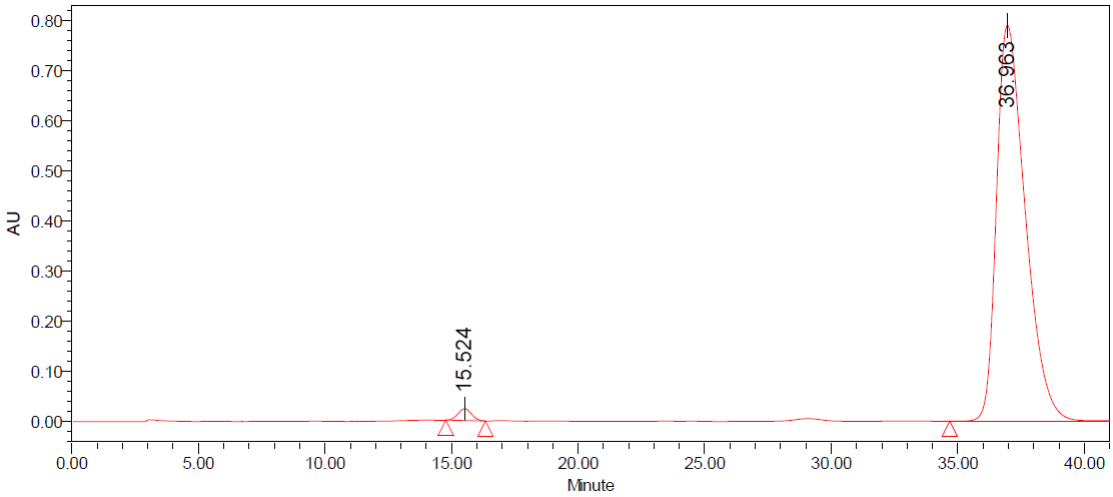




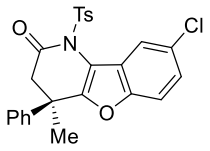
3l



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	15.542	11784032	49.16	309041	66.18	14.420	16.578
2	37.216	12187296	50.84	157962	33.82	35.482	39.635

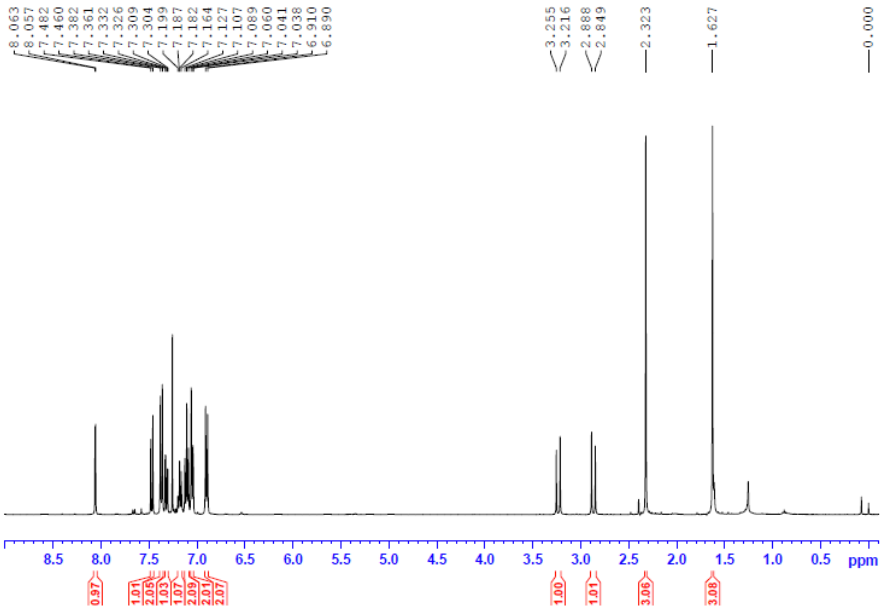


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	15.524	878913	1.39	23804	2.93	14.773	16.338
2	36.963	62432681	98.61	789219	97.07	34.682	42.120

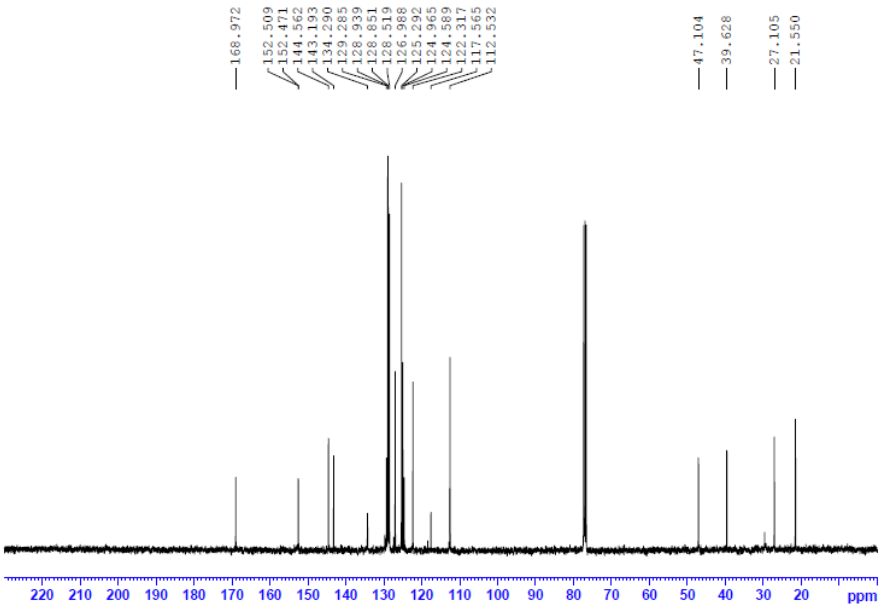


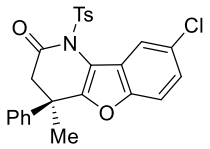
3m

$CDCl_3$, ^1H NMR, 400 MHz

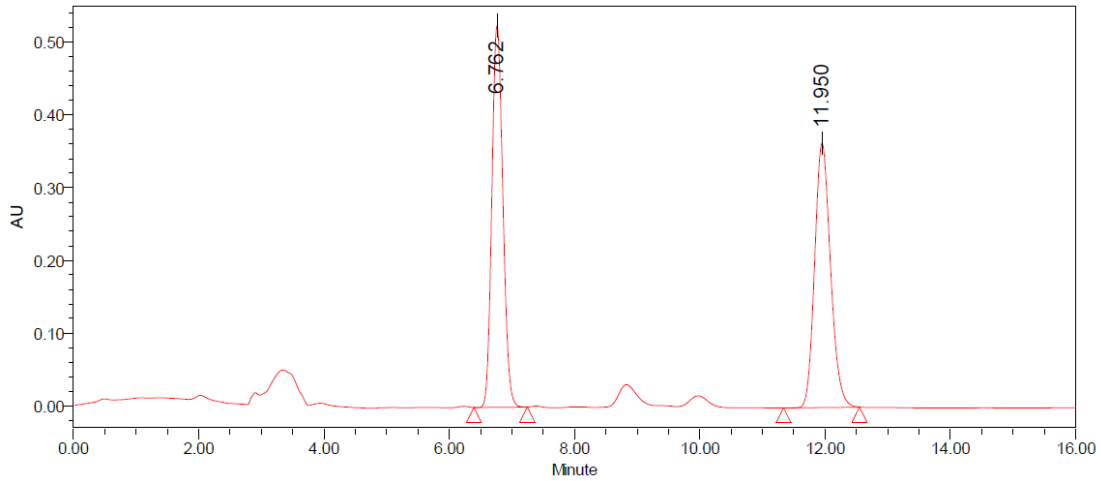


$CDCl_3$, ^{13}C NMR, 100 MHz

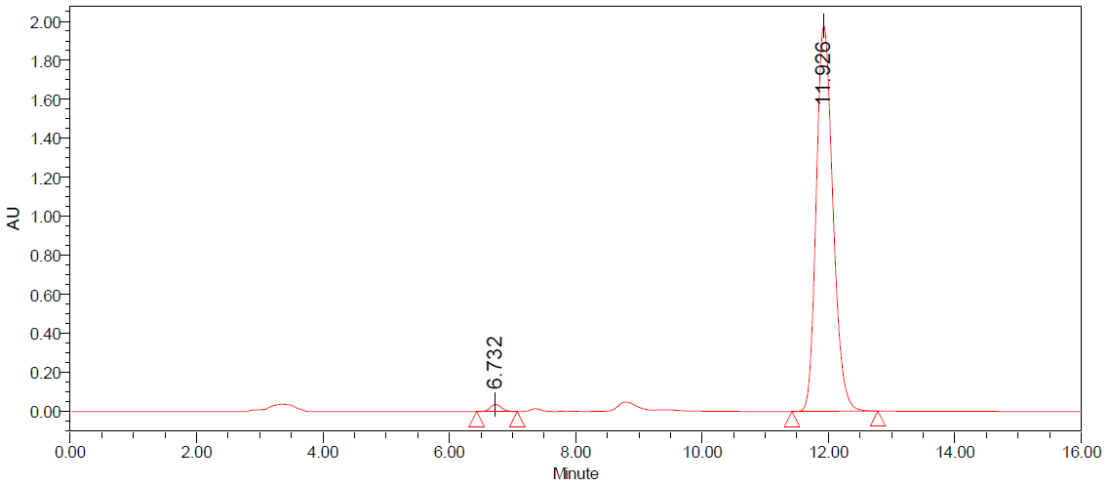




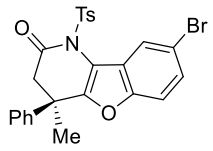
3m



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.762	6417412	50.07	525477	59.08	6.393	7.245
2	11.950	6399422	49.93	364004	40.92	11.337	12.548

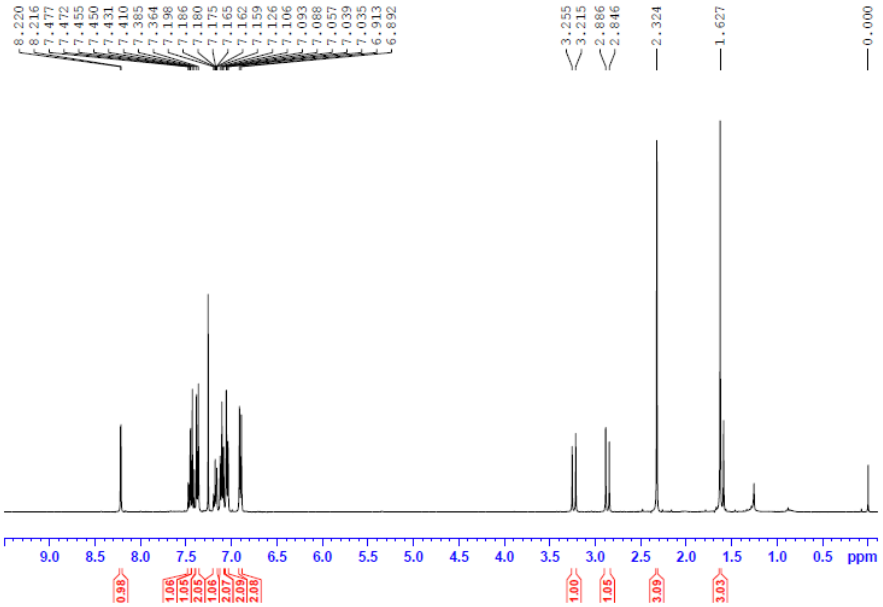


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.732	431122	1.18	35489	1.76	6.433	7.077
2	11.926	36244522	98.82	1976460	98.24	11.422	12.780

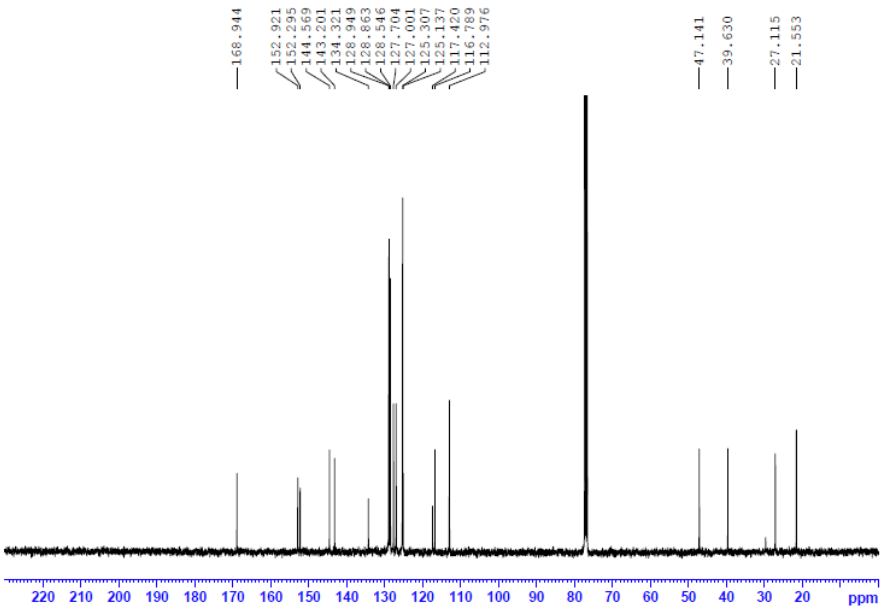


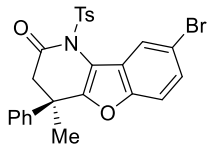
3n

$CDCl_3$, ^1H NMR, 400 MHz

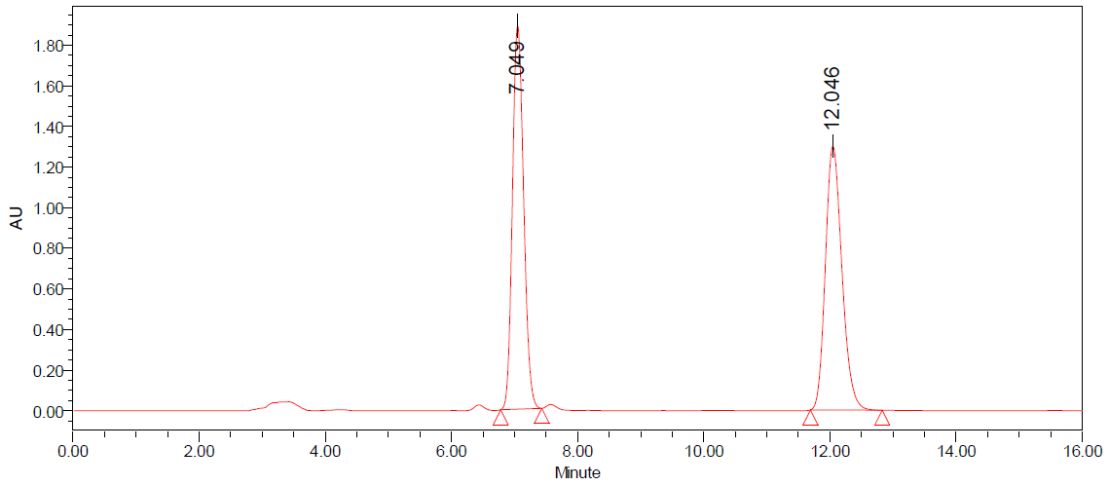


$CDCl_3$, ^{13}C NMR, 100 MHz

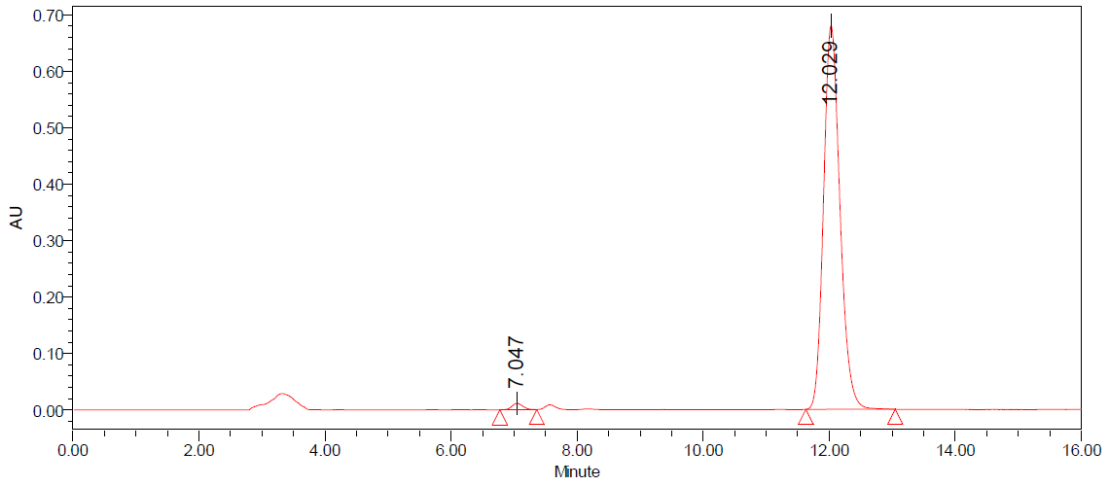




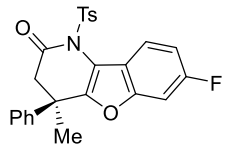
3n



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.049	23336223	49.61	1888320	59.23	6.780	7.433
2	12.046	23705516	50.39	1299746	40.77	11.690	12.828

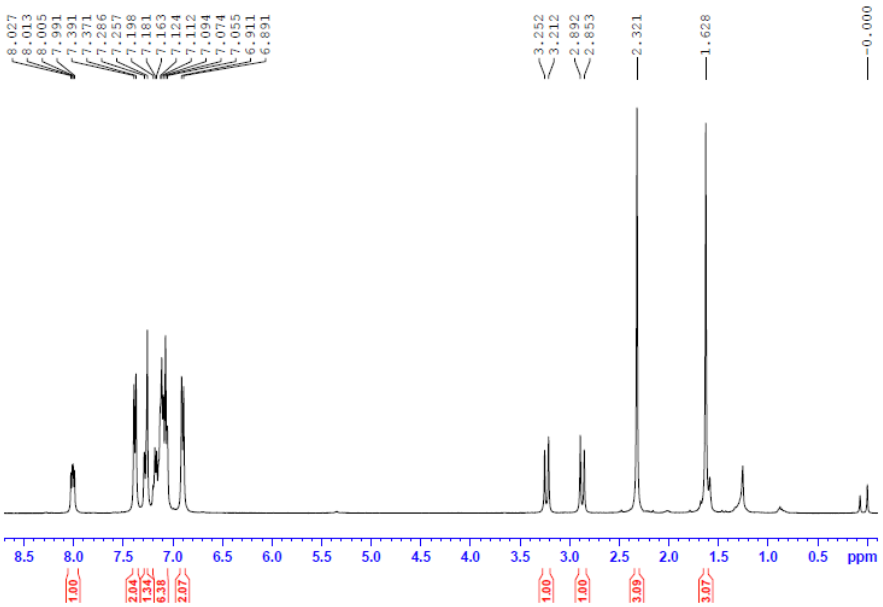


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.047	133172	1.07	11062	1.60	6.773	7.360
2	12.029	12296779	98.93	679663	98.40	11.628	13.045

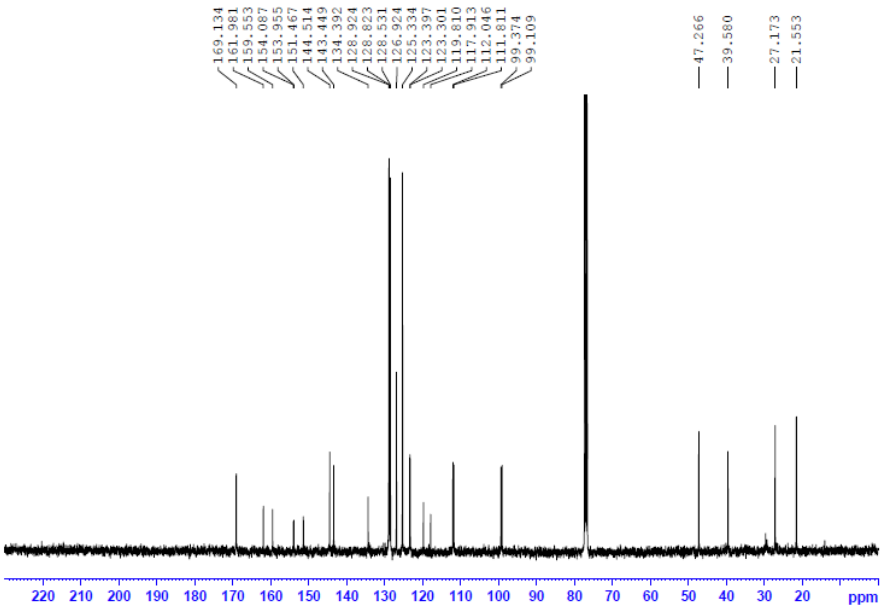


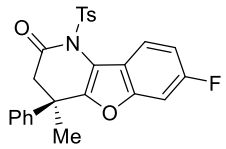
3o

$CDCl_3$, ^1H NMR, 400 MHz

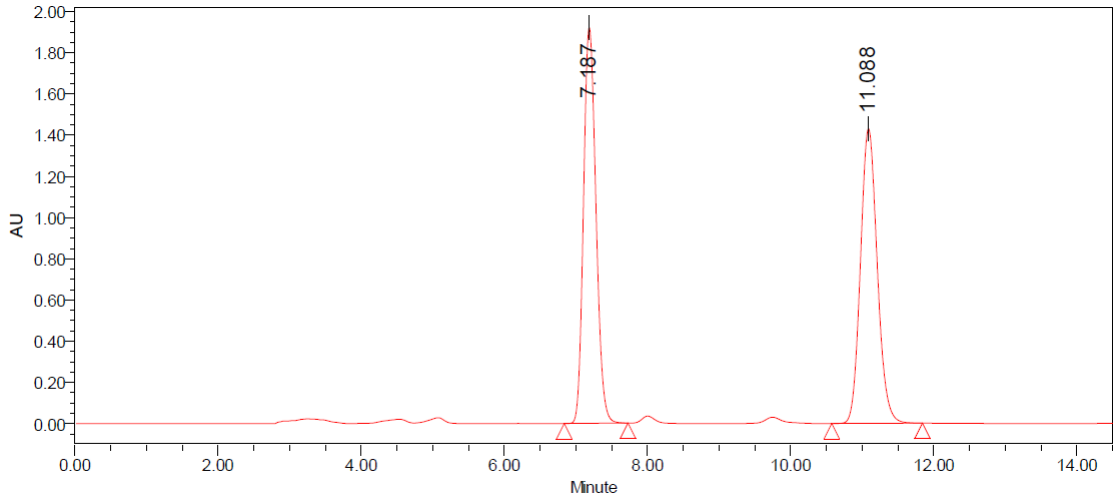


$CDCl_3$, ^{13}C NMR, 100 MHz

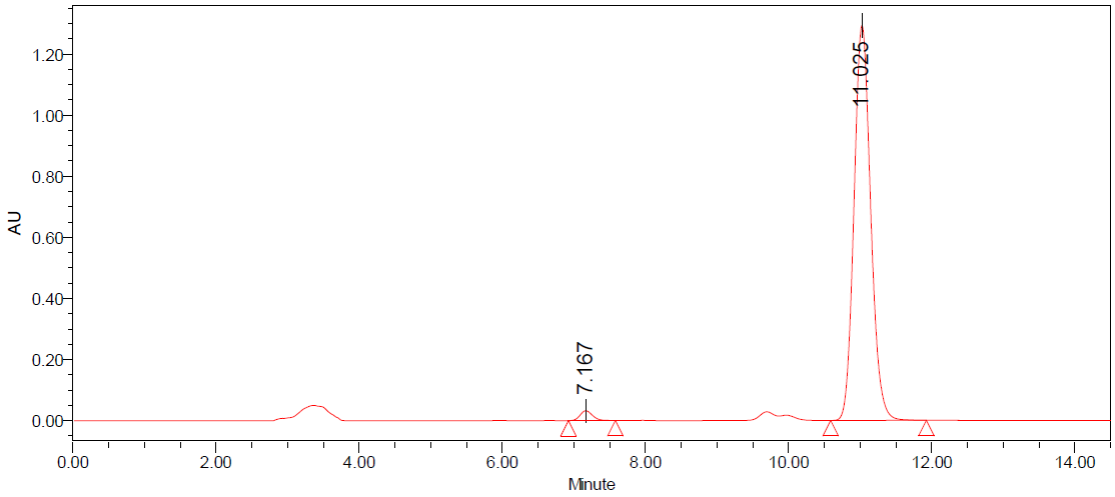




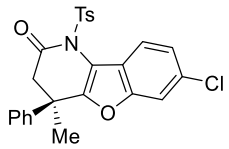
3o



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.187	23138302	49.81	1920579	57.33	6.837	7.727
2	11.088	23316568	50.19	1429466	42.67	10.575	11.843

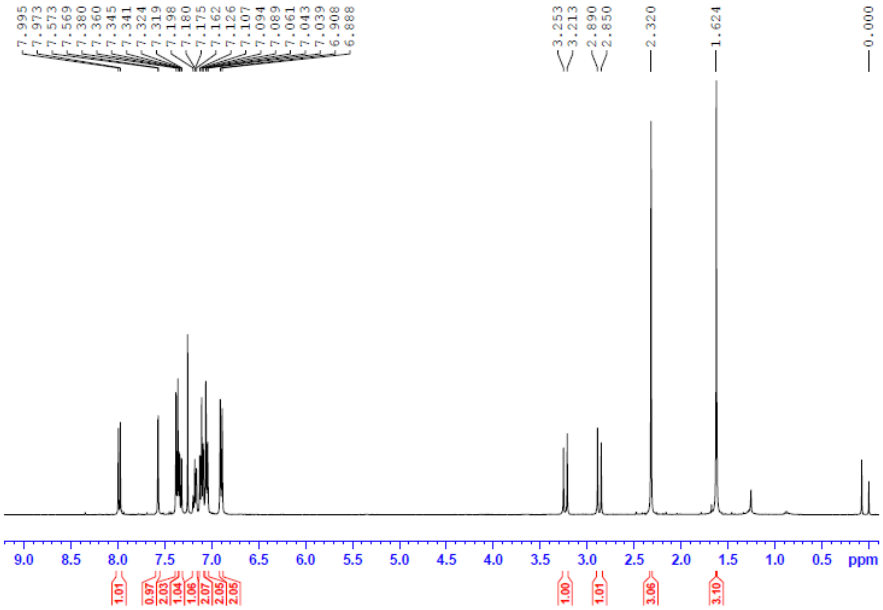


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.167	381227	1.79	31930	2.41	6.925	7.580
2	11.025	20928423	98.21	1292433	97.59	10.588	11.925

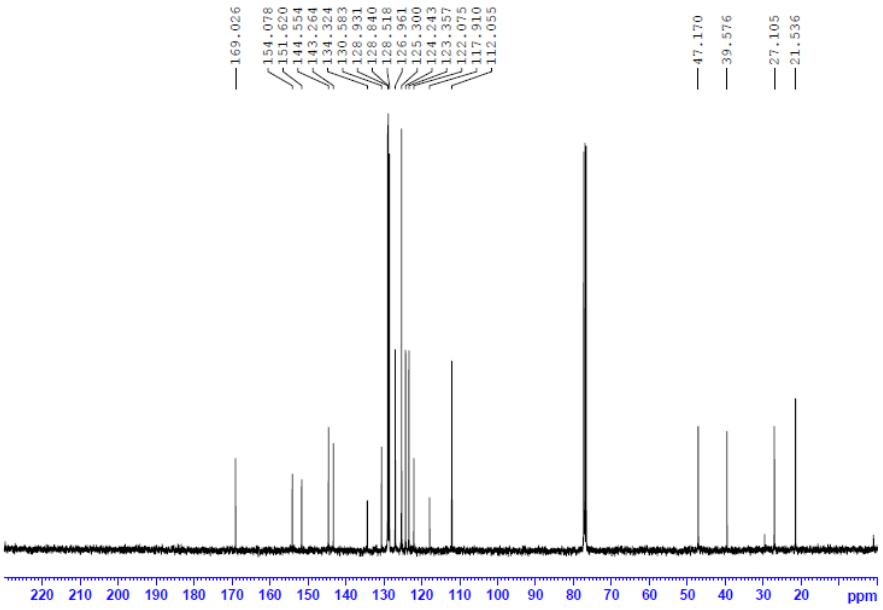


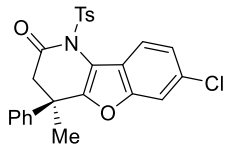
3p

$CDCl_3$, ^1H NMR, 400 MHz

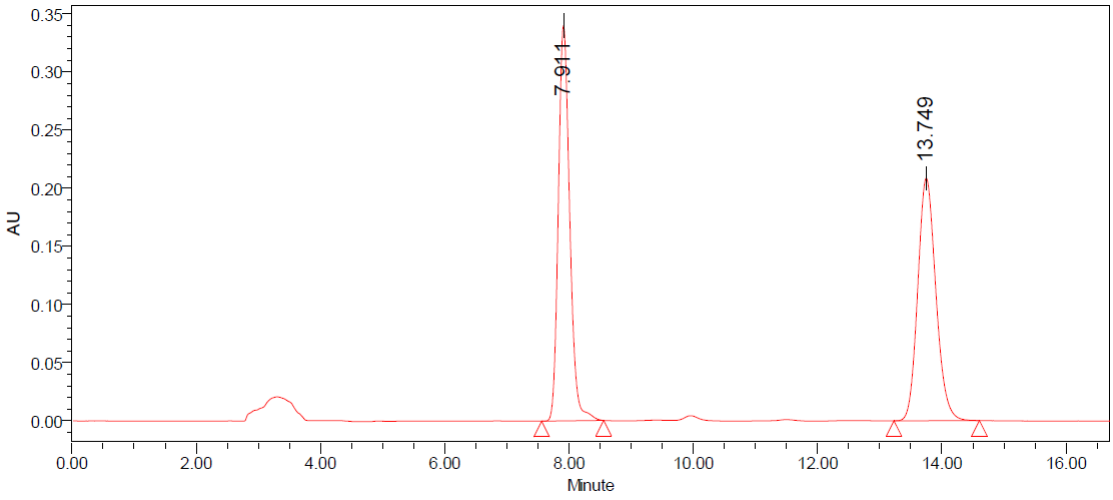


$CDCl_3$, ^{13}C NMR, 100 MHz

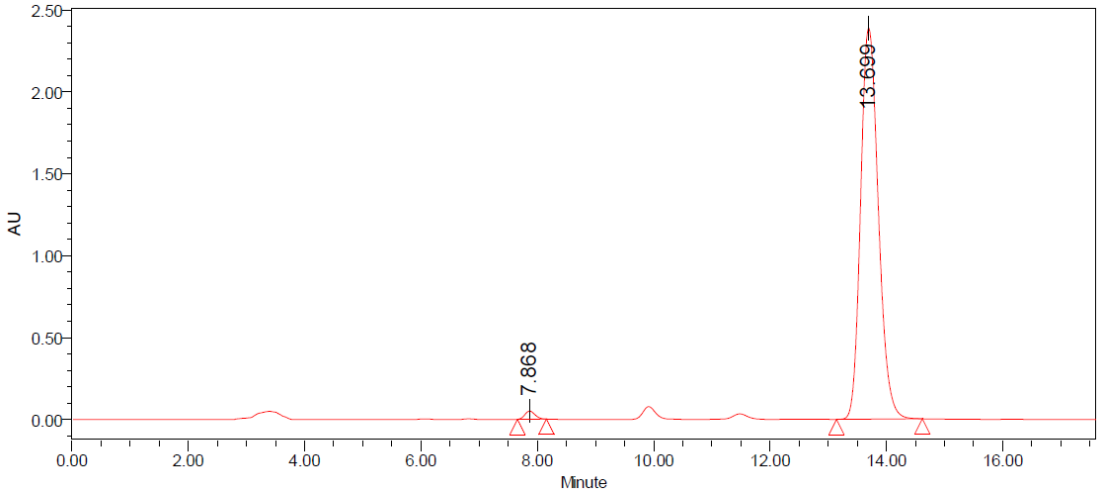




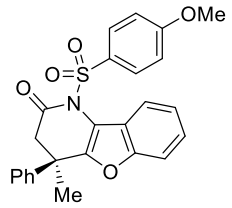
3p



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.911	4325396	50.59	339815	61.97	7.560	8.558
2	13.749	4224622	49.41	208524	38.03	13.228	14.605

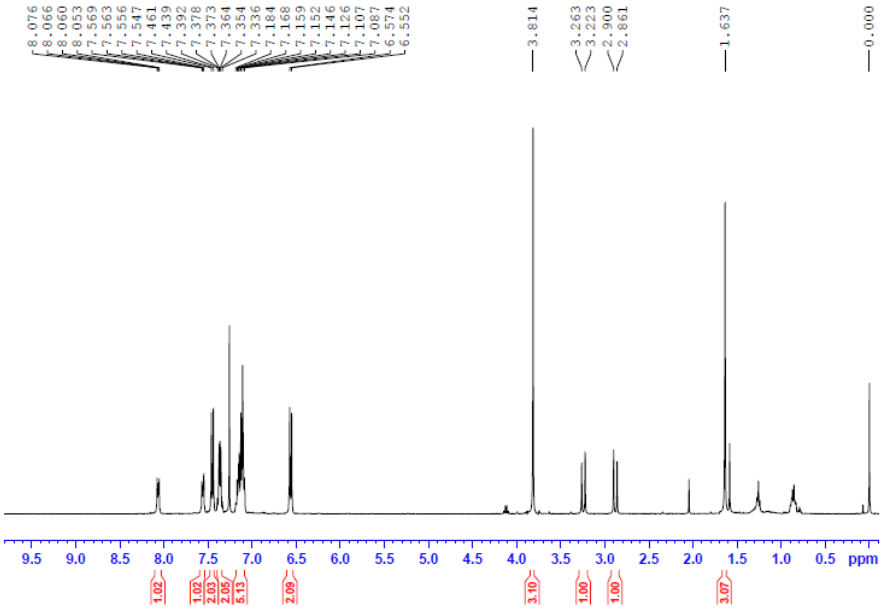


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	7.868	599442	1.17	49661	2.04	7.658	8.157
2	13.699	50550294	98.83	2386212	97.96	13.143	14.620

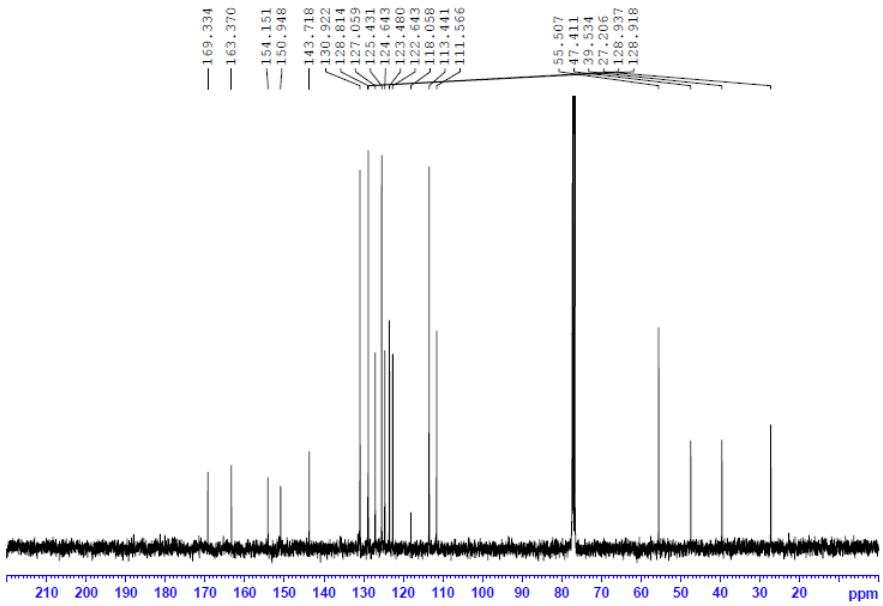


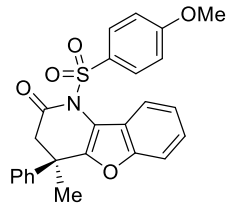
3q

$CDCl_3$, ^1H NMR, 400 MHz

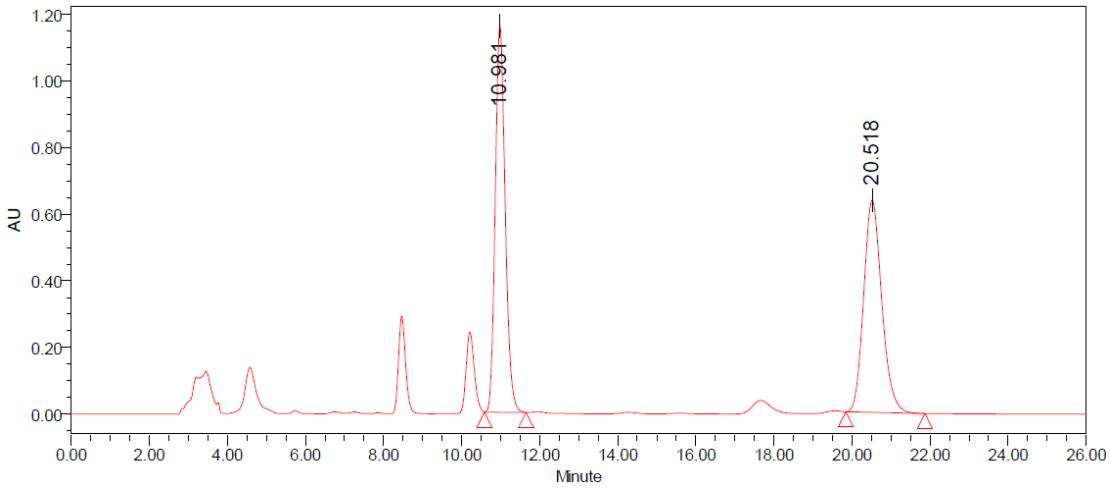


$CDCl_3$, ^{13}C NMR, 100 MHz

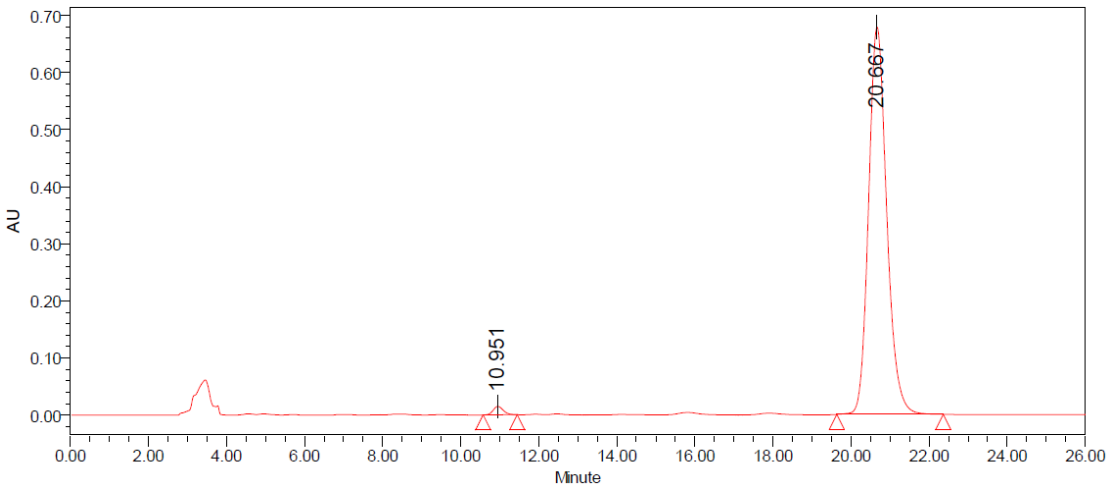




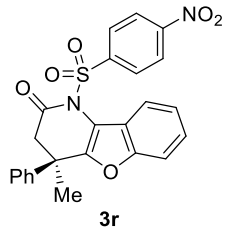
3q



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	10.981	20595299	50.15	1159684	64.58	10.585	11.648
2	20.518	20473122	49.85	636095	35.42	19.843	21.868

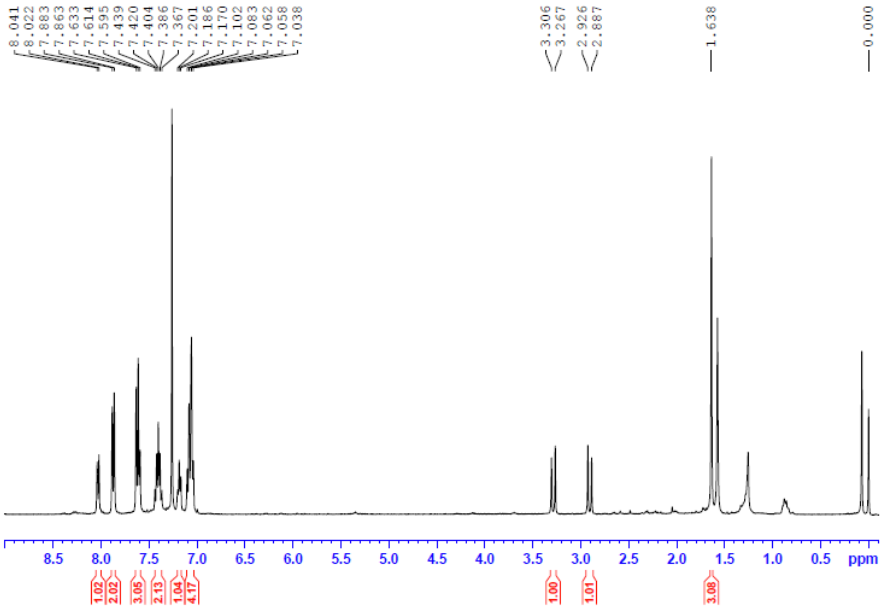


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	10.951	266170	1.20	14803	2.14	10.577	11.448
2	20.667	21918646	98.80	678432	97.86	19.633	22.363

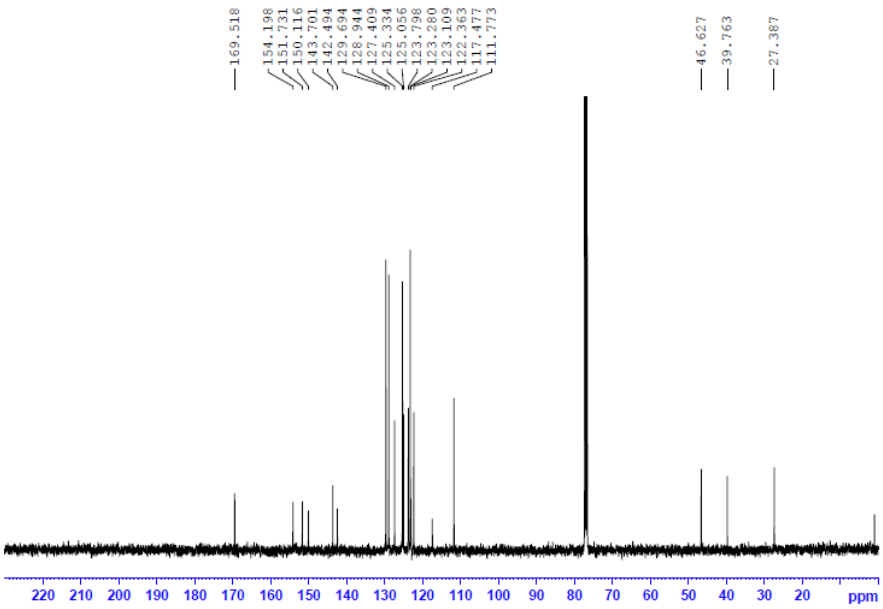


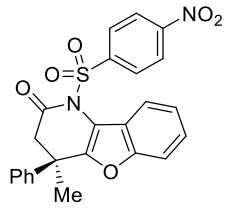
3r

$CDCl_3$, ^1H NMR, 400 MHz

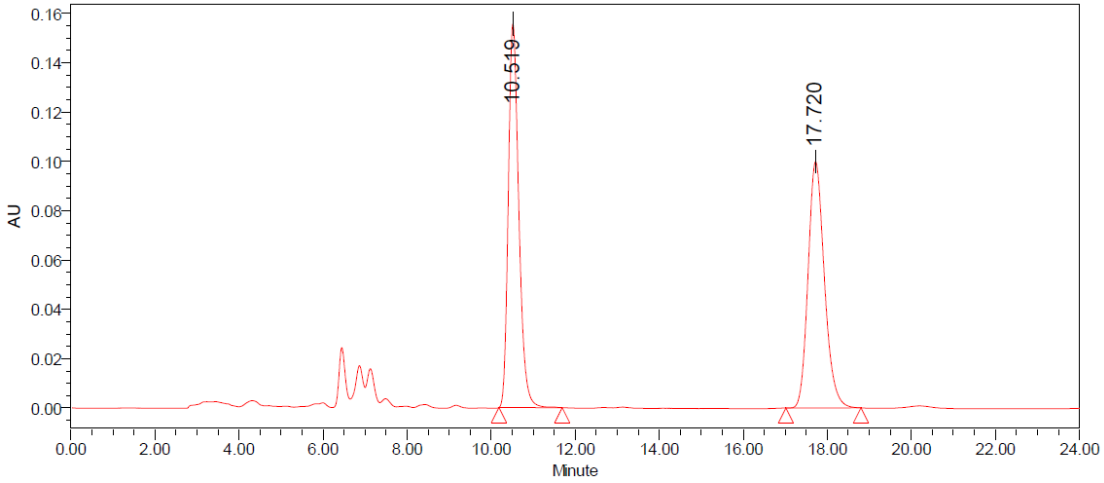


$CDCl_3$, ^{13}C NMR, 100 MHz

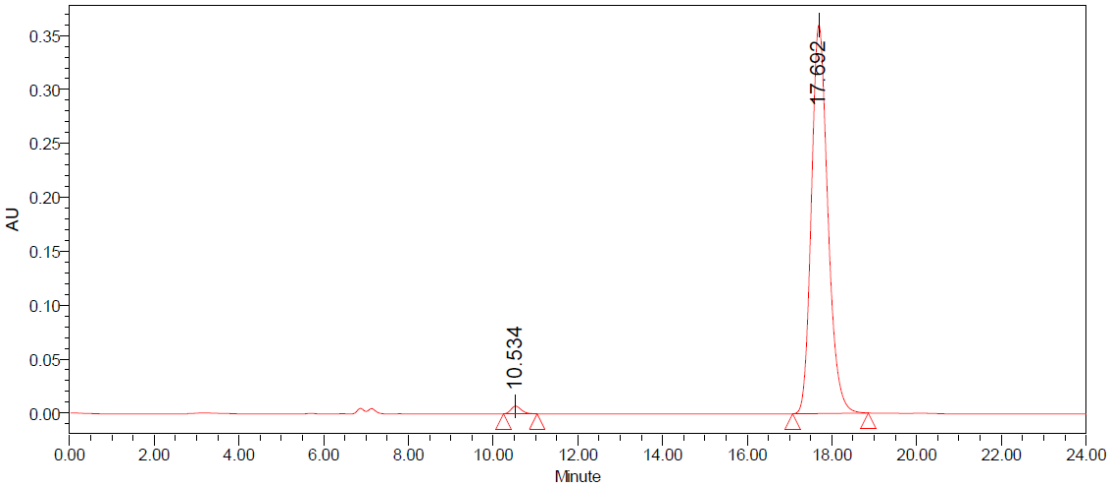




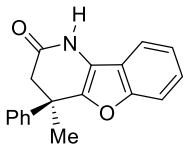
3r



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	10.519	2701996	50.05	155680	60.92	10.187	11.690
2	17.720	2696220	49.95	99872	39.08	17.013	18.800

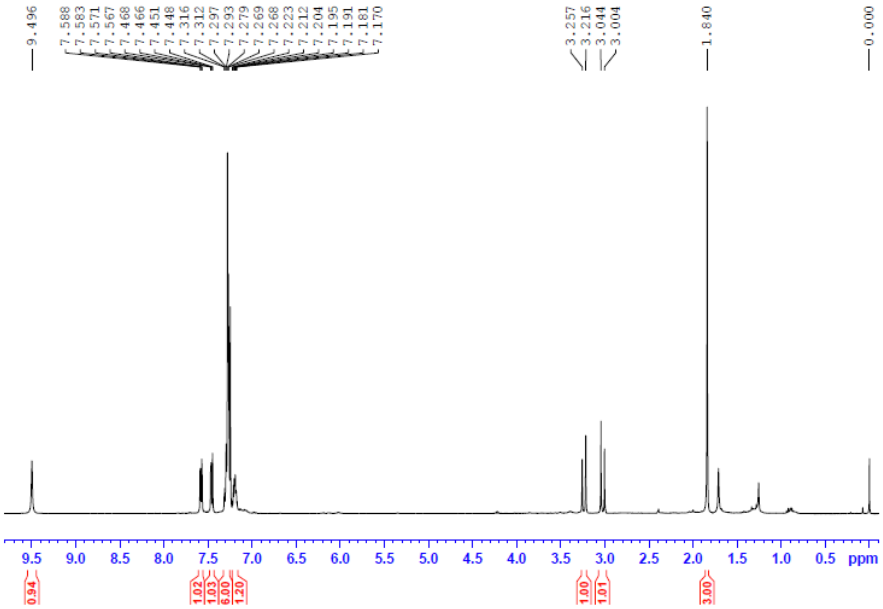


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	10.534	120331	1.22	7104	1.93	10.247	11.040
2	17.692	9714534	98.78	360188	98.07	17.073	18.858

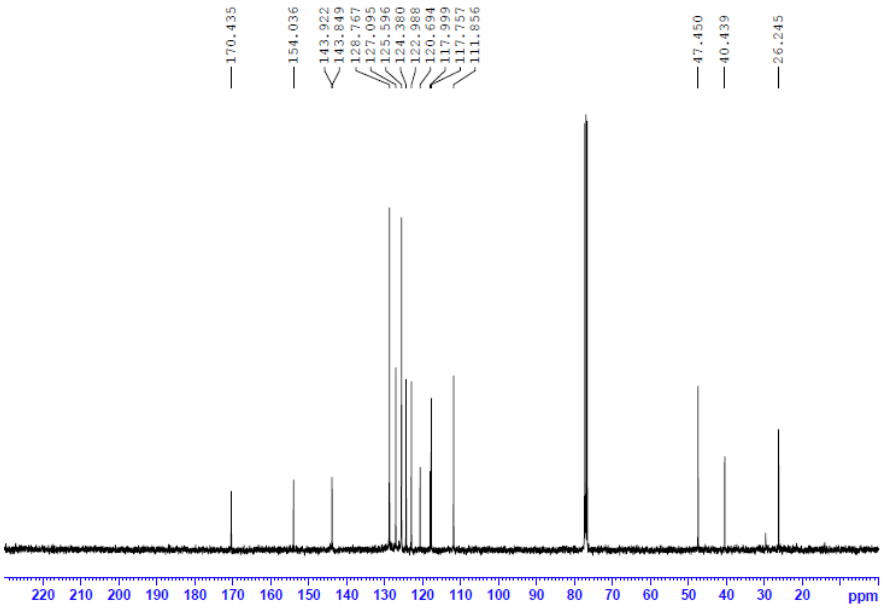


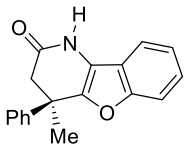
4

$CDCl_3$, ^1H NMR, 400 MHz

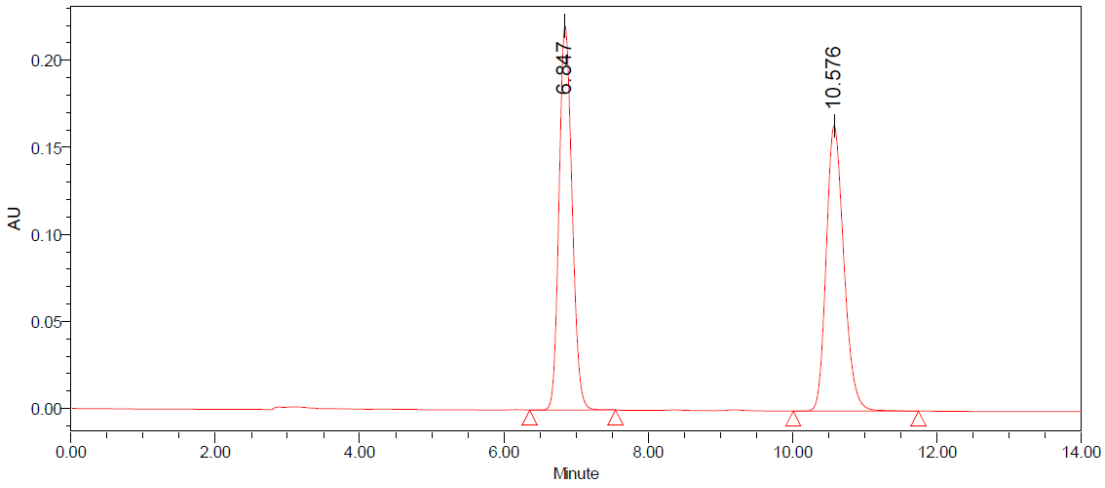


$CDCl_3$, ^{13}C NMR, 100 MHz

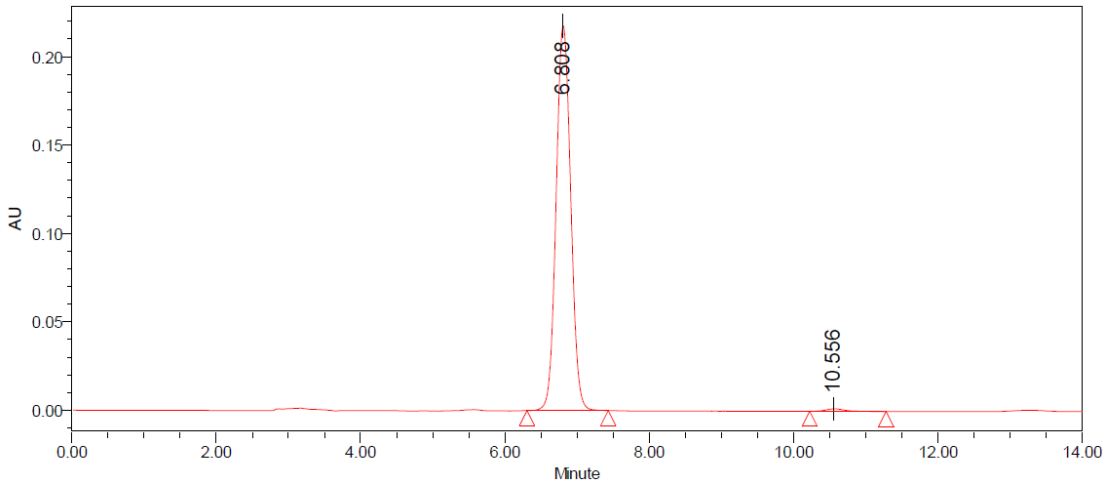




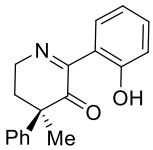
4



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.847	2764066	49.90	220657	57.39	6.357	7.547
2	10.576	2775221	50.10	163858	42.61	10.008	11.743

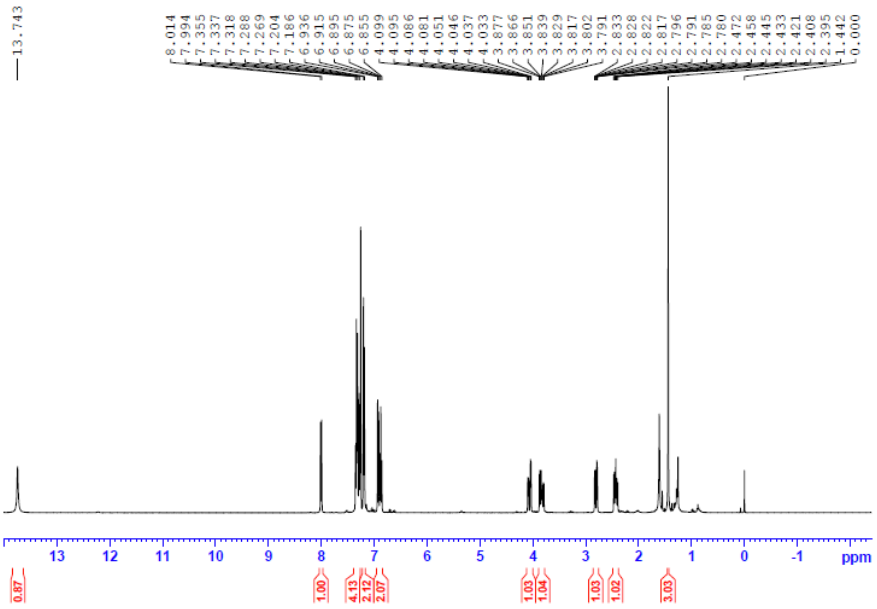


	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.808	3056706	99.22	217568	99.36	6.307	7.432
2	10.556	23949	0.78	1409	0.64	10.223	11.282

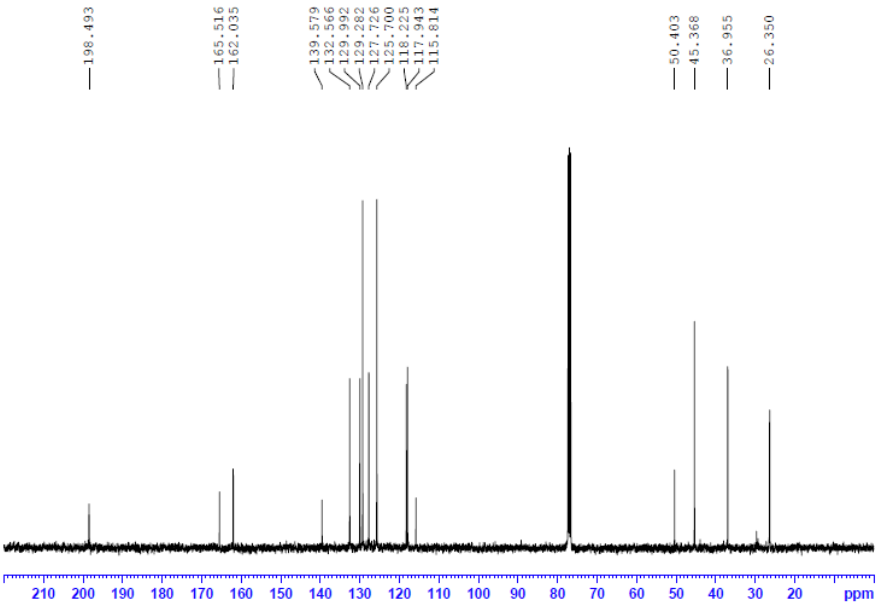


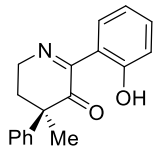
5

$CDCl_3$, ^1H NMR, 400 MHz

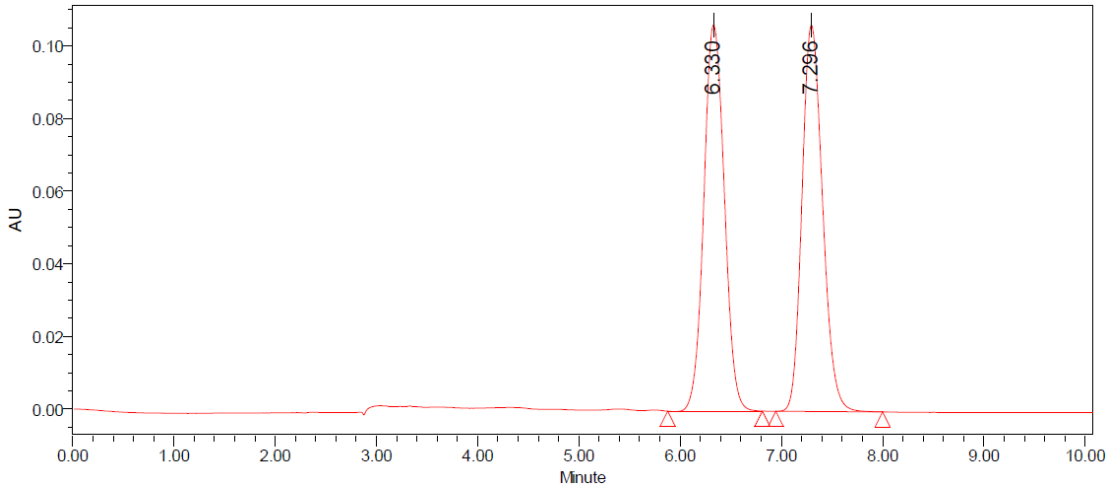


$CDCl_3$, ^{13}C NMR, 100 MHz

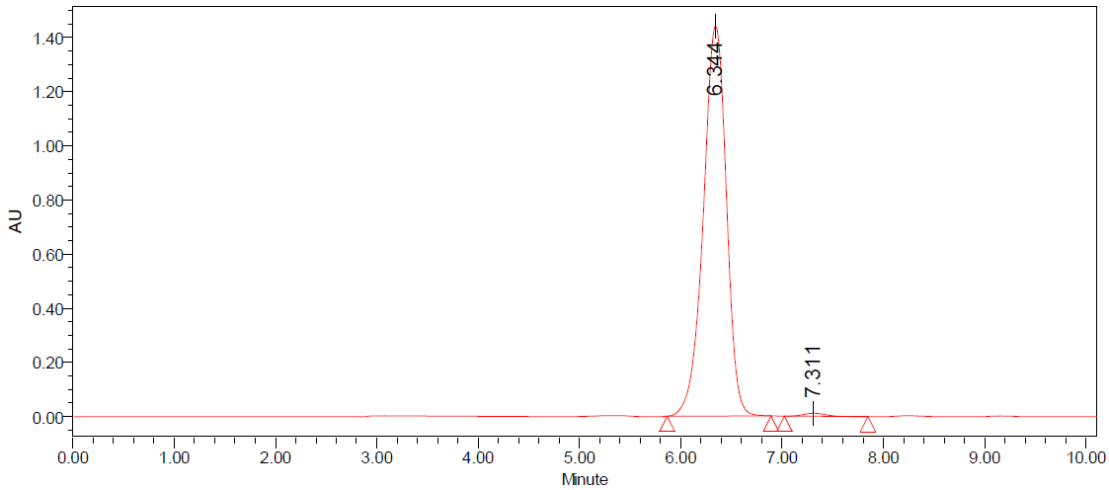




5



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.330	1497800	49.94	106338	49.98	5.877	6.812
2	7.296	1501122	50.06	106429	50.02	6.945	7.998



	RT (分钟)	Area (微伏*秒)	% Area	Height (微伏)	% Height	Start Time (分钟)	End Time (分钟)
1	6.344	22764210	99.30	1439731	99.25	5.865	6.892
2	7.311	160286	0.70	10820	0.75	7.023	7.847