

Electronic Supplementary Information

**Enantioselective Construction of Dihydropyranone-Fused
Indoles by [3+3] Annulation of in Situ-Derived Indolin-3-
ones and Unsaturated Carboxylic Ester**

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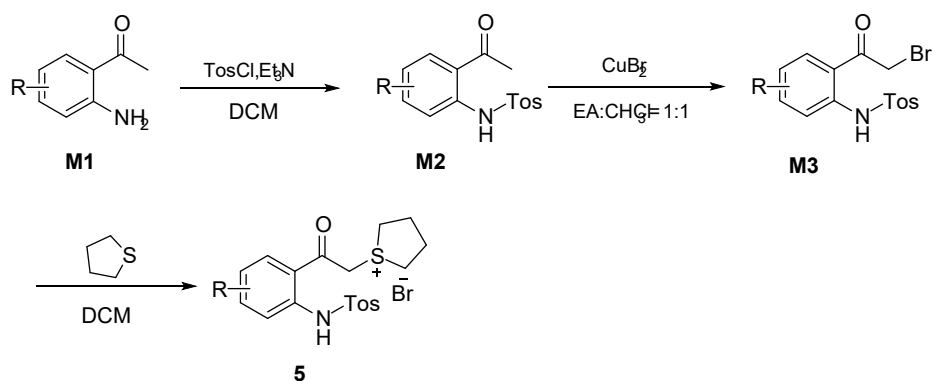
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General Information

Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich were used as received. Solvents were dried over Na metal, K metal, or CaH₂ and were distilled under nitrogen prior to use. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker BBFO (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). ¹H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), etc. All first-order splitting patterns were assigned based on 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 (¹³C NMR) spectra were recorded on a Bruker BBFO (100 MHz) spectrometer. Fluorine (¹⁹F) nuclear magnetic resonance (¹⁹F NMR) spectra were recorded on a Bruker BBFO (376 MHz) spectrometer. High-resolution mass spectral analysis (HRMS) was performed on Agilent 6546 LC/Q-TOF mass spectrometer. The determination of enantiomeric excess was performed *via* chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractometer. Optical rotations were measured using a 1 mL cell with a 10 mm path length on a Jasco P-1030 polarimeter and are reported as follows: [α]_D^T (c in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished with UV light.

Preparing Materials



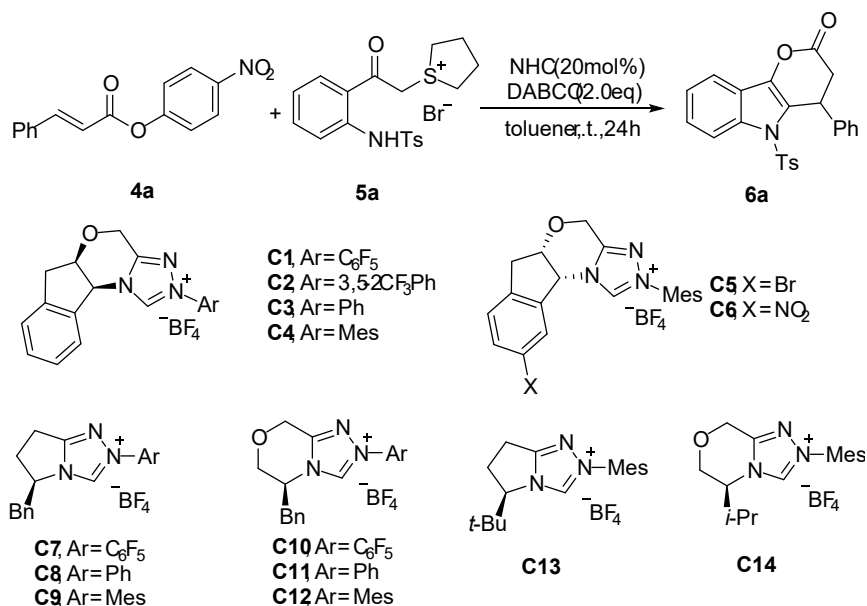
M1 (1.0 mmol, 1.0 equiv) was dissolved in DCM (40 mL), and 4-toluenesulfonyl chloride (TosCl) (1.5 mmol, 1.5 equiv) and Et₃N (3.0 mmol, 3.0 equiv) were sequentially added to the reaction mixture, which was then stirred overnight (monitored by TLC). The reaction mixture was washed twice with water (40 mL), then once with saturated brine (40 mL) and dry with anhydrous Na₂SO₄. After the removal of the solvent by evaporation, the crude residue was subjected to silica column purification using ethyl acetate/petroleum as an eluent to give the desired product **M2**.

M2 (1.0 mmol, 1.0 equiv) and bromide copper (2.0 mmol, 2.0 equiv) were dissolved in a mixed solvent of ethyl acetate (20 mL) and chloroform (20 mL) under nitrogen protection and reacted at 85°C for 12 hours (monitored by TLC). Filter the solid matter in the reactant with diatomic soil, after the removal of the solvent by evaporation. Dissolving crude product added to DCM (40 mL). The crude product was washed twice with water (40 mL), then once with saturated brine (40 mL) and dry with anhydrous Na₂SO₄. After the removal of the solvent by evaporation, the crude residue was subjected to silica column purification using ethyl acetate/petroleum as an eluent to give the desired product **M3**.

Tetrahydrothiophene (1.2 mmol, 1.2 equiv) was added to a solution of **M3** (1.0 mmol, 1.0 equiv) in DCM (5 mL). The mixture was stirred at room temperature until there was solid precipitation, then the solid was filtered and washed with a small amount of cold dichloromethane.

Reaction Conditions Optimization

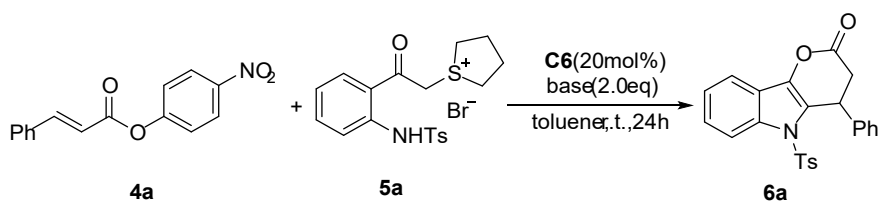
Table S1. Screening of NHC Catalysts^a



entry	NHC	yield (%) ^b	er ^c
1	C1	n.r.	--
2	C2	n.r.	--
3	C3	n.r.	--
4	C4	40	75:25
5	C5	53	4:96
6	C6	56	2:98
7	C7	n.r.	--
8	C8	n.r.	--
9	C9	trace	--
10	C10	n.r.	--
11	C11	n.r.	--
12	C12	18	71:29
13	C13	15	58:42
14	C14	15	75:25

[a]The reactions were carried under glove box using **1a** (0.12 mmol), **2a** (0.10 mmol), NHC (0.02 mmol), DABCO (2.0 mmol), toluene (2.0 mL), rt, 24 hours. All of the bases and solvents need dry. [b] Yields were isolated yields after column chromatography. [c] er was determined via HPLC on a chiral stationary phase

Table S2. Screening of Bases^a

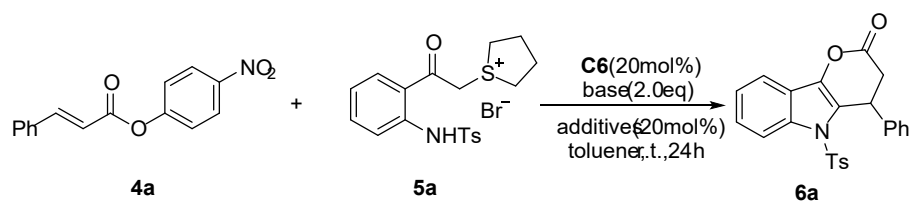


entry	Base	yield (%) ^b	er ^c
1	K ₂ CO ₃	n.r.	--
2	Cs ₂ CO ₃	n.r.	--
3	Na ₂ CO ₃	n.r.	--
4	DBU	n.r.	--
5	DIEA	n.r.	--
6	DABCO	56	2:98
7	t-BuOK	n.r.	--
8	NaOMe	n.r.	--
9	NaHCO ₃	n.r.	--
10	DMAP	trace	--
11	Et ₃ N	n.r.	--
12	NaOAc	n.r.	--

[a]The reactions were carried under glove box using **1a** (0.12 mmol), **2a** (0.10 mmol), NHC (0.02 mmol), base (2.0 mmol), toluene (2.0 mL), rt, 24 hours. All of the bases and solvents need dry.

[b]Yields were isolated yields after column chromatography. [c] er was determined via HPLC on a chiral stationary phase.

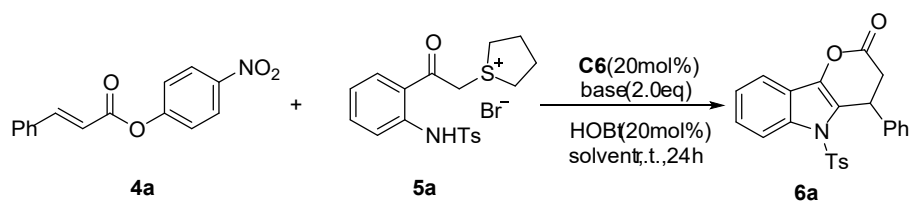
Table S3. Screening of Additives^a



entry	Additives	yield (%) ^b	er ^c
1	Mg(<i>O</i> - <i>t</i> -Bu) ₂	43	5:95
2	Sm(OTf) ₃	40	2:98
3	AgOTf	38	2:98
4	Sc(OTf) ₂	34	10:90
5	LiCl	36	2:98
6	Fe ₃ Cl	34	2:98
7	Urea	48	2:98
8	Thiourea	50	2:98
9	Ti(<i>O</i> - <i>i</i> -Pr) ₄	47	6:94
10	LiBr	38	2:98
11	diphenylmethanol	50	2:98
12	HOBt	73	2:98

[a]The reactions were carried under glove box using **1a** (0.12 mmol), **2a** (0.10 mmol), NHC (0.02 mmol), DABCO (2.0 mmol), additives (0.02mmol), toluene (2.0 mL), rt, 24 hours. All of the bases and solvents need dry. [b]Yields were isolated yields after column chromatography. [c]Er was determined via HPLC on a chiral stationary phase.

Table S4. Screening of Solvents^a

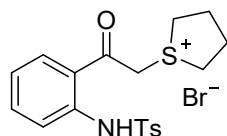


entry	Solvent	yield (%) ^b	er ^c
1	DCM	n.r.	--
2	CH ₃ Cl	n.r.	--
3	CCl ₄	24	3:97
4	DCE	36	3:97
5	EA	83	12:88
6	THF	94	4:96
7	Et ₂ O	48	5:95
8	DME	80	12:88
9	1,4-Dioxane	70	4:96
10	CH ₃ CN	17	10:90
11	Toluene	73	2:98
12	PhCF ₃	55	3:97
13	Xylene	61	5:95
14	1,2-Dichlorbenzene	24	3:97
15	DMF	n.r.	--
16	DMSO	32	8:92
17	H ₂ O	n.r.	--
18	Toluene:H ₂ O (v:v = 4:1)	68	3:97

[a]The reactions were carried under glove box using **1a** (0.12 mmol), **2a** (0.10 mmol), NHC (0.02 mmol), DABCO (2.0 mmol), HOBT (0.02mmol), solvent (2.0 mL), rt, 24 hours. All of the bases and solvents need dry. [b]Yields were isolated yields after column chromatography. [c] Er was determined via HPLC on a chiral stationary phase.

Characterizations of Products

1-(2-(2-((4-methylphenyl)sulfonamido)phenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide



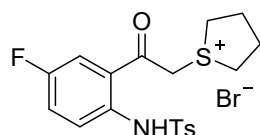
White solid, 42% total yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.70 (s, 1H), 7.93 (d, *J* = 7.1 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 5.35 (s, 2H), 3.59 (dq, *J* = 18.8, 6.3 Hz, 4H), 2.36 (s, 3H), 2.24 (dt, *J* = 14.6, 7.1 Hz, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 195.1, 144.3, 138.1, 135.8, 135.5, 132.1, 120.0, 127.0, 123.7, 123.0, 119.5, 52.9, 42.6, 28.2, 21.0.

HRMS (ESI, *m/z*): calcd. for C₁₉H₂₂NO₃S₂⁺ 376.1036, found 376.1039.

1-(2-(5-fluoro-2-((4-methylphenyl)sulfonamido)phenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide



Grey solid, 45% total yield.

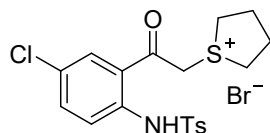
¹H NMR (400 MHz, DMSO-*d*₆) δ 10.41 (s, 1H), 7.77 (dd, *J* = 9.2, 3.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.50 (td, *J* = 8.7, 2.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 9.1, 4.8 Hz, 1H), 5.31 (s, 2H), 3.64 (dd, *J* = 12.7, 6.5 Hz, 2H), 3.54 (dd, *J* = 12.2, 5.9 Hz, 2H), 2.36 (s, 3H), 2.26 (dq, *J* = 14.0, 7.5, 6.8 Hz, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 193.8, 158.2 (d, *J* = 243.6 Hz), 144.3, 135.4, 133.6 (d, *J* = 2.6 Hz), 130.0, 127.6 (d, *J* = 6.8 Hz), 127.1, 124.2 (d, *J* = 8.0 Hz), 122.1 (d, *J* = 22.7 Hz), 117.8 (d, *J* = 24.3 Hz), 52.8, 42.9, 28.3, 21.1.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -116.9.

HRMS (ESI, *m/z*): calcd. for C₁₉H₂₁FNO₃S₂⁺ 394.0941, found 394.0943.

1-(2-(5-chloro-2-((4-methylphenyl)sulfonamido)phenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide



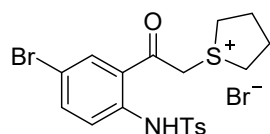
Grey solid, 50% total yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.58 (s, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.75 - 7.66 (m, 3H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 1H), 5.33 (s, 2H), 3.59 (dq, *J* = 20.2, 6.4 Hz, 4H), 2.37 (s, 3H), 2.25 (dt, *J* = 14.7, 7.0 Hz, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 194.1, 144.5, 136.6, 135.4, 135.1, 131.1, 130.1, 128.2, 127.1, 125.6, 122.3, 52.8, 42.8, 28.3, 21.1.

HRMS (ESI, m/z): calcd. for $C_{19}H_{21}ClNO_3S_2^+$ 410.0646, found 410.0649.

1-(2-(5-bromo-2-((4-methylphenyl)sulfonamido)phenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide



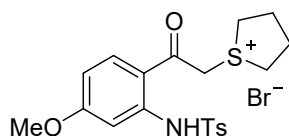
Brown solid, 50% total yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.59 (s, 1H), 8.09 (d, *J* = 2.3 Hz, 1H), 7.80 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 1H), 5.32 (s, 2H), 3.66 – 3.53 (m, 4H), 2.37 (s, 3H), 2.25 (ddd, *J* = 22.1, 11.3, 5.0 Hz, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 194.4, 144.9, 138.4, 137.5, 135.9, 134.4, 130.7, 130.5, 127.8, 127.5, 126.1, 122.7, 116.4, 53.2, 43.3, 28.7, 21.5.

HRMS (ESI, m/z): calcd. for $C_{19}H_{21}BrNO_3S_2^+$ 454.0141, found 454.0152.

1-(2-(4-methoxy-2-((4-methylphenyl)sulfonamido)phenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide



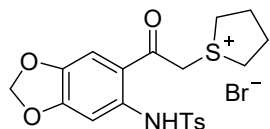
White solid, 46% total yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.13 (s, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.37 (s, 2H), 3.83 (s, 3H), 3.58 (dtd, *J* = 18.3, 12.1, 5.8 Hz, 4H), 2.37 (s, 3H), 2.24 (ddd, *J* = 20.8, 13.5, 6.6 Hz, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 194.1, 165.5, 145.1, 142.3, 135.8, 130.7, 127.7, 114.0, 109.4, 102.9, 56.6, 53.2, 43.1, 28.7, 21.5.

HRMS (ESI, m/z): calcd. for $C_{19}H_{24}NO_4S_2^+$ 406.1141, found 406.1141.

1-(2-(6-((4-methylphenyl)sulfonamido)benzo[d][1,3]dioxol-5-yl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide



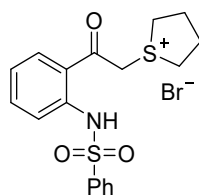
Grey solid, 62% total yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.12 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.49 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 1H), 6.18 (s, 2H), 5.29 (s, 2H), 3.60 (dt, *J* = 13.1, 6.4 Hz, 2H), 3.54 – 3.47 (m, 2H), 2.37 (s, 3H), 2.32 – 2.14 (m, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 193.6, 154.1, 145.0, 144.0, 137.5, 136.0, 130.6, 127.5, 115.3, 110.4, 103.7, 99.7, 53.5, 43.1, 28.65, 21.5.

HRMS (ESI, m/z): calcd. for $C_{20}H_{22}NO_5S_2^+$ 420.0934, found 420.0939.

1-(2-oxo-2-(2-(phenylsulfonamido)phenyl)ethyl)tetrahydro-1H-thiophen-1-ium bromide



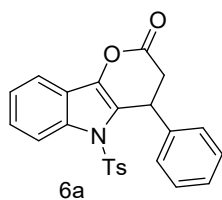
White solid, 54% total yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.73 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.88 - 7.84 (m, 2H), 7.69 (ddd, *J* = 6.7, 3.9, 1.2 Hz, 1H), 7.64 - 7.57 (m, 3H), 7.36 - 7.27 (m, 2H), 5.37 (s, 2H), 3.60 (qt, *J* = 12.2, 5.9 Hz, 4H), 2.32 - 2.16 (m, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 195.5, 138.9, 138.4, 136.2, 134.2, 132.5, 130.1, 127.5, 124.5, 123.9, 120.4, 53.4, 43.2, 28.7.

HRMS (ESI, *m/z*): calcd. for C₁₈H₂₀NO₃S₂⁺ 362.0879, found 362.0880.

4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6a)



39.2 mg, 94% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.45 - 7.37 (m, 1H), 7.36 - 7.30 (m, 1H), 7.29 - 7.24 (m, 5H), 7.18 - 7.08 (m, 4H), 6.92 (d, *J* = 8.1 Hz, 2H), 5.09 (dd, *J* = 7.7, 1.3 Hz, 1H), 3.29 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.02 (dd, *J* = 15.9, 1.5 Hz, 1H), 2.26 (s, 3H).

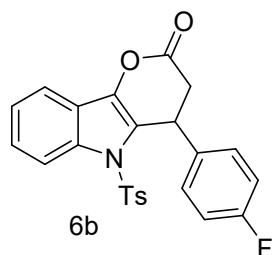
¹³C NMR (100 MHz, CDCl₃) δ 166.3, 145.1, 140.4, 138.4, 134.8, 134.7, 129.7, 129.4, 127.9, 127.4, 126.7, 126.2, 124.3, 120.9, 120.1, 117.7, 115.0, 38.5, 37.1, 21.6.

HPLC analysis: 4:96 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 24.2 min, *tr*(R) = 27.1 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₂₀NO₄S⁺ 418.1109, found 418.1108.

[α]_D²⁵ = 18.8 (*c* = 4.2 in CHCl₃).

4-(4-fluorophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6b)



40.1 mg, 92% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.66 - 7.57 (m, 1H), 7.46 - 7.38 (m, 1H), 7.37 - 7.30 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.07 (ddd, *J* = 8.2, 5.2, 2.5 Hz, 2H), 7.01 - 6.89 (m, 4H), 5.08 (dd, *J* = 7.7, 1.2 Hz, 1H), 3.28 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.99 (dd, *J* = 15.9, 1.5 Hz, 1H), 2.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.0, 162.4 (d, *J* = 245.0 Hz), 145.2, 138.4, 136.1 (d, *J* = 3.0 Hz), 134.8, 134.7, 129.7, 128.9 (d, *J* = 8.0 Hz), 126.5, 125.3 (d, *J* = 198.0 Hz), 120.8, 119.7, 117.7, 116.3, 116.0, 114.9, 38.4, 36.4, 21.6.

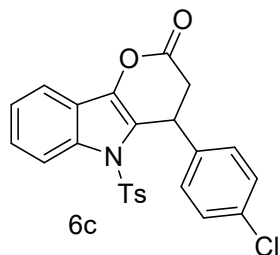
¹⁹F NMR (376 MHz, CDCl₃) δ -114.4.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 14.9 min, *tr*(R) = 25.5 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉FNO₄S⁺ 436.1013, found 436.1013.

[α]_D²⁵ = 45.6 (*c* = 4.7 in CHCl₃).

4-(4-chlorophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6c)



40.7 mg, 90% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.43 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.38 - 7.32 (m, 1H), 7.23 - 7.14 (m, 4H), 7.04 - 6.91 (m, 4H), 5.05 (d, *J* = 9.0 Hz, 1H), 3.29 (dd, *J* = 16.0, 7.8 Hz, 1H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.29 (s, 3H).

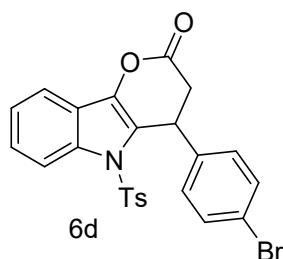
¹³C NMR (100 MHz, CDCl₃) δ 165.9, 145.3, 138.8, 138.6, 134.9, 133.8, 129.7, 129.5, 128.7, 126.4, 126.4, 124.4, 120.7, 119.3, 117.7, 115.0, 38.3, 36.5, 21.6.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 15.2 min, *tr*(R) = 24.6 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉ClNO₄S⁺ 452.0718, found 452.0714.

[α]_D²⁵ = 44.9 (*c* = 2.6 in CHCl₃).

4-(4-bromophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6d)



43.7 mg, 88% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.46 - 7.40 (m, 1H), 7.39 - 7.31 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.00 - 6.89 (m, 4H), 5.04 (d, *J* = 8.8 Hz, 1H), 3.29 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.97 (dd, *J* = 16.0, 1.5 Hz, 1H), 2.30 (s, 3H).

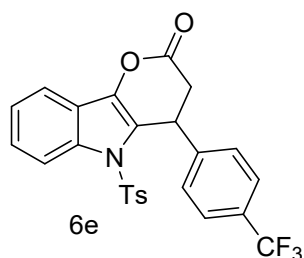
¹³C NMR (100 MHz, CDCl₃) δ 166.0, 145.2, 143.5, 138.0, 134.9, 134.7, 129.8, 127.4, 126.7, 126.4, 125.3, 125.3, 124.4, 120.9, 120.0, 117.9, 115.0, 39.1, 32.5, 21.7.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 15.9 min, *tr*(R) = 25.5 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉BrNO₄S⁺ 496.0213, found 496.0209.

[α]_D²⁵ = 56.0 (*c* = 2.0 in CHCl₃).

5-tosyl-4-(4-(trifluoromethyl)phenyl)-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6e)



44.2 mg, 91% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.52 - 7.41 (m, 3H), 7.40 - 7.34 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 5.15 (d, *J* = 6.8 Hz, 1H), 3.33 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.99 (dd, *J* = 16.0, 1.5 Hz, 1H), 2.26 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 165.6, 145.3, 144.3, 144.2 138.7, 135.0, 134.9, 130.2 (q, *J* = 32.6 Hz), 129.7, 127.7, 126.6, 126.3 (q, *J* = 3.7 Hz), 124.4, 124.0 (q, *J* = 270 Hz), 120.6, 118.6, 117.8, 115.0, 38.0, 36.8, 21.5.

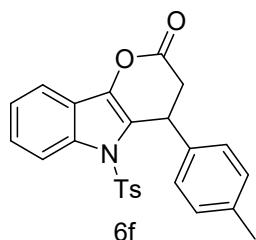
¹⁹F NMR (376 MHz, CDCl₃) δ -62.6.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 12.5 min, *tr*(R) = 20.1 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₁₉F₃NO₄S⁺ 486.0981, found 486.0979.

[α]_D²⁵ = 87.0 (*c* = 1.1 in CHCl₃).

4-(*p*-tolyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6f)



34.5 mg, 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.43 - 7.37 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 - 7.14 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 7.0 Hz, 1H), 3.27 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.99 (dd, *J* = 15.9, 1.2 Hz, 1H), 2.33 (s, 3H), 2.26 (s, 3H).

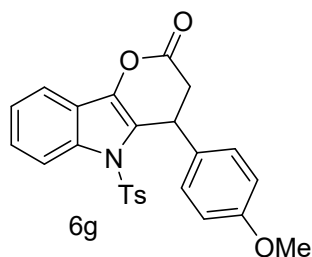
¹³C NMR (100 MHz, CDCl₃) δ 166.4, 145.0, 138.3, 137.6, 137.4, 134.9, 134.7, 130.0, 129.6, 127.2, 126.7, 126.1, 124.2, 120.9, 120.3, 117.6, 115.0, 38.6, 36.8, 21.6, 21.2.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 13.4 min, *tr*(R) = 17.9 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₄S⁺ 432.1264, found 432.1269.

[α]_D²⁵ = 32.2 (*c* = 4.0 in CHCl₃).

4-(4-methoxyphenyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6g)



39.4 mg, 88% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.43 - 7.37 (m, 1H), 7.35 - 7.29 (m, 1H), 7.21 - 7.15 (m, 2H), 7.05 - 7.00 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.80 - 6.75 (m, 2H), 5.04 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 3.26 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.99 (dd, *J* = 15.9, 1.5 Hz, 1H), 2.26 (s, 3H).

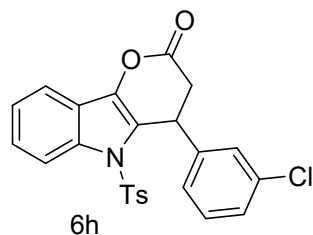
¹³C NMR (100 MHz, CDCl₃) δ 166.5, 159.4, 145.0, 138.2, 134.9, 134.7, 132.5, 129.7, 128.4, 126.7, 126.1, 124.3, 120.9, 120.4, 117.6, 115.0, 114.7, 55.5, 38.7, 36.4, 21.6.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 30.8 min, *tr*(R) = 33.4 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₅S⁺ 448.1213, found 448.1211.

[α]_D²⁵ = 38 (*c* = 3.0 in CHCl₃).

4-(3-chlorophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6h)



41.6 mg, 92% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.48 - 7.41 (m, 1H), 7.39 - 7.33 (m, 1H), 7.23 (dd, *J* = 3.3, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.1, 6.5 Hz, 3H), 7.02 (dt, *J* = 7.1, 1.5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 3H), 5.11 - 5.00 (m, 1H), 3.29 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.99 (dd, *J* = 16.0, 1.5 Hz, 1H), 2.28 (s, 3H).

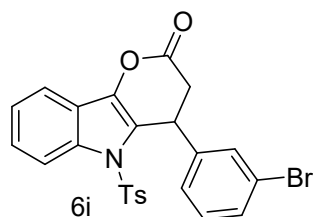
¹³C NMR (100 MHz, CDCl₃) δ 165.8, 145.3, 142.2, 138.7, 135.2, 134.9, 134.8, 130.6, 129.7, 128.1, 127.3, 126.4, 126.4, 125.5, 124.4, 120.7, 118.7, 117.8, 115.0, 38.2, 36.7, 21.6.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 20.2 min, *tr*(R) = 22.7 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉ClNO₄S⁺ 452.0718, found 452.0720.

[α]_D²⁵ = 8.4 (*c* = 1.0 in CHCl₃).

4-(3-bromophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6i)



44.2 mg, 89% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 - 7.42 (m, 1H), 7.37 (q, *J* = 8.2, 7.3 Hz, 2H), 7.20 - 7.09 (m, 4H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 6.9 Hz, 1H), 3.29 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.98 (dd, *J* = 16.0, 1.4 Hz, 1H), 2.28 (s, 3H).

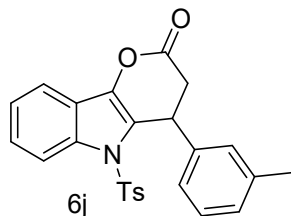
¹³C NMR (100 MHz, CDCl₃) δ 165.8, 145.3, 142.6, 138.8, 135.0, 134.8, 131.1, 131.0, 130.2, 130.8, 126.5, 126.4, 126.1, 124.4, 123.5, 120.7, 118.7, 117.8, 115.0, 38.3, 36.7, 21.7.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 22.1 min, *tr*(R) = 24.4 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉BrNO₄S⁺ 496.0213, found 496.0215.

$[\alpha]_{\text{D}}^{25} = 28.2$ (*c* = 2.9 in CHCl₃).

4-(*m*-tolyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6j)



39.3 mg, 91% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.44 - 7.38 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.19 - 7.11 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 9.2 Hz, 3H), 6.82 (s, 1H), 5.05 (d, *J* = 6.9 Hz, 1H), 3.28 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.00 (dd, *J* = 15.9, 1.3 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H).

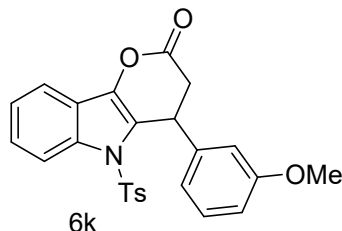
¹³C NMR (100 MHz, CDCl₃) δ 166.4, 145.0, 140.3, 139.1, 138.4, 134.9, 134.7, 129.6, 129.3, 128.6, 127.8, 126.8, 126.1, 124.5, 124.2, 120.9, 120.1, 117.7, 115.0, 38.5, 37.0, 21.6, 21.5.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 19.7 min, *tr*(R) = 22.4 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₄S⁺ 432.1264, found 432.1264.

$[\alpha]_{\text{D}}^{25} = 18.8$ (*c* = 4.2 in CHCl₃).

4-(3-methoxyphenyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6k)



40.3 mg, 90% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.70 - 7.54 (m, 1H), 7.41 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.37 - 7.30 (m, 1H), 7.22 - 7.14 (m, 3H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.61 - 6.55 (m, 1H), 5.05 (dd, *J* = 7.7, 1.2 Hz, 1H), 3.69 (s, 3H), 3.27 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.01 (dd, *J* = 15.9, 1.5 Hz, 1H), 2.26 (s, 3H).

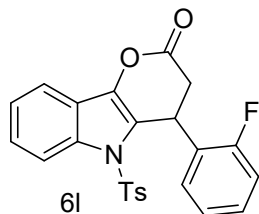
¹³C NMR (100 MHz, CDCl₃) δ 166.2, 160.3, 145.0, 141.8, 138.4, 134.8, 134.7, 130.4, 129.6, 126.6, 126.1, 124.2, 120.8, 119.7, 119.5, 117.6, 114.9, 113.1, 112.9, 55.2, 38.4, 37.0, 21.5.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 17.3 min, *tr*(R) = 20.7 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₅S⁺ 448.1213, found 448.1216.

$[\alpha]_{\text{D}}^{25} = 14$ (*c* = 0.5 in CHCl₃).

4-(2-fluorophenyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6l)



28.7 mg, 66% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.48 - 7.40 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28 - 7.23 (m, 2H), 7.16 - 7.08 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.74 (td, *J* = 7.7, 1.5 Hz, 1H), 5.40 (d, *J* = 6.8 Hz, 1H), 3.26 (dd, *J* = 16.2, 7.9 Hz, 1H), 3.05 (dd, *J* = 16.1, 1.4 Hz, 1H), 2.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 165.9, 160.1 (d, *J* = 245 Hz), 145.1, 139.2, 134.8, 134.8, 129.7, 129.5 (d, *J* = 8.0 Hz), 128.5 (d, *J* = 4.0 Hz), 127.0 (d, *J* = 14.0 Hz), 126.4, 126.3, 124.6 (d, *J* = 4.0 Hz), 124.2, 120.7, 117.7, 117.6, 116.1 (d, *J* = 21 Hz), 114.9, 36.9, 30.7 (d, *J* = 4.0 Hz), 21.5.

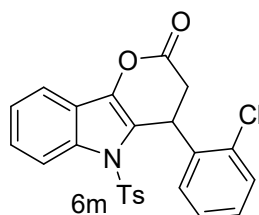
¹⁹F NMR (376 MHz, CDCl₃) δ -118.2.

HPLC analysis: 4:96 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 14.2 min, *tr*(R) = 15.1 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉FNO₄S⁺ 436.1013, found 436.1012.

[α]_D²⁵ = 90.1 (*c* = 3.6 in CHCl₃).

4-(2-chlorophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6m)



25.3 mg, 56% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.50 - 7.42 (m, 2H), 7.40 - 7.31 (m, 3H), 7.20 (td, *J* = 7.8, 1.5 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.96 - 6.89 (m, 1H), 6.58 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.60 - 5.54 (m, 1H), 3.24 (dd, *J* = 16.1, 7.8 Hz, 1H), 3.07 (dd, *J* = 16.1, 1.6 Hz, 1H), 2.28 (s, 3H).

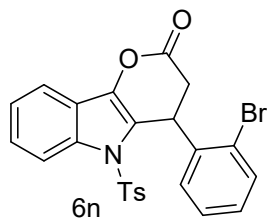
¹³C NMR (100 MHz, CDCl₃) δ 165.9, 145.2, 139.3, 136.9, 135.1, 134.9, 133.2, 130.5, 129.8, 129.0, 127.8, 127.5, 126.6, 126.4, 124.2, 120.5, 118.1, 117.7, 114.9, 36.5, 33.7, 21.6.

HPLC analysis: 95:5 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 23.8 min, *tr*(R) = 25.6 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉ClNO₄S⁺ 452.0718, found 452.0720.

[α]_D²⁵ = 10.8 (*c* = 1.1 in CHCl₃)

4-(2-bromophenyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6n)



21.8 mg, 44% yield. CCDC number: 2204888.

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 1H), 7.70 - 7.62 (m, 2H), 7.50 - 7.42 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 3H), 7.11 (td, *J* = 7.8, 1.5 Hz, 1H), 6.97 (dd, *J* = 13.8, 7.7 Hz, 3H), 6.57 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.54 (d, *J* = 6.6 Hz, 1H), 3.23 (dd, *J* = 16.1, 7.8 Hz, 1H), 3.08 (dd, *J* = 16.1, 1.5 Hz, 1H), 2.28 (s, 3H).

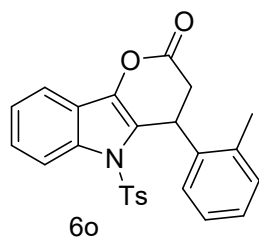
¹³C NMR (100 MHz, CDCl₃) δ 166.0, 145.2, 139.3, 138.5, 135.2, 135.0, 133.9, 129.8, 129.4, 128.2, 127.9, 126.6, 126.5, 124.3, 123.7, 120.5, 118.3, 117.7, 114.9, 36.6, 36.3, 21.7.

HPLC analysis: 95:5 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 26.5 min, *tr*(R) = 28.4 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉BrNO₄S⁺ 496.0213, found 496.0213.

[α]_D²⁵ = 8.1 (*c* = 1.2 in CHCl₃).

4-(*o*-tolyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6o)



32.8 mg, 76% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.45 - 7.39 (m, 1H), 7.37 - 7.32 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.87 (dd, *J* = 11.9, 7.9 Hz, 3H), 6.60 (d, *J* = 7.2 Hz, 1H), 5.40 - 5.33 (m, 1H), 3.27 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.89 (dd, *J* = 15.8, 1.3 Hz, 1H), 2.57 (s, 3H), 2.25 (s, 3H).

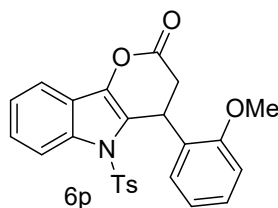
¹³C NMR (100 MHz, CDCl₃) δ 166.2, 144.9, 138.7, 138.0, 135.4, 134.9, 134.5, 131.4, 129.6, 127.7, 126.9, 126.7, 126.3, 126.0, 124.1, 120.6, 120.0, 117.5, 114.7, 37.1, 32.7, 21.6, 19.4.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 24.2 min, *tr*(R) = 31.9 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₄S⁺ 432.1264, found 432.1266.

[α]_D²⁵ = -6.1 (*c* = 0.2 in CHCl₃).

4-(2-methoxyphenyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6p)



37.6 mg, 84% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.43 - 7.36 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 - 7.22 (m, 3H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.91 - 6.83 (m, 2H), 6.75 (t, *J* = 7.5 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 3.81 (s, 3H), 3.19 (dd, *J* = 16.2, 8.3 Hz, 1H), 3.02 (dd, *J* = 16.2, 1.3 Hz, 1H), 2.27 (s, 3H).

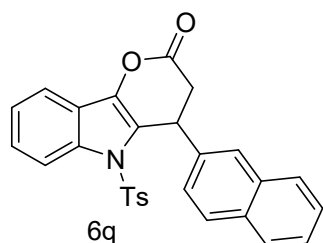
¹³C NMR (100 MHz, CDCl₃) δ 166.8, 157.1, 144.9, 139.1, 135.0, 134.9, 129.7, 129.3, 129.1, 128.2, 126.7, 126.0, 124.2, 121.2, 120.9, 118.8, 117.6, 115.1, 111.1, 55.2, 36.4, 32.9, 21.6.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 14.8 min, *tr*(R) = 18.1 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₅S⁺ 448.1213, found 444.81212.

[α]_D²⁵ = 107.6 (*c* = 3.8 in CHCl₃).

4-(naphthalen-2-yl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6q)



38.8 mg, 83% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.49 - 7.35 (m, 4H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.05 - 6.98 (m, 2H), 6.53 (d, *J* = 8.2 Hz, 2H), 5.23 (d, *J* = 7.2 Hz, 1H), 3.36 (dd, *J* = 16.0, 7.9 Hz, 1H), 3.09 (dd, *J* = 16.0, 1.1 Hz, 1H), 2.00 (s, 3H).

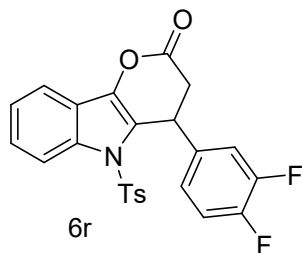
¹³C NMR (100 MHz, CDCl₃) δ 166.2, 144.9, 138.5, 137.5, 134.9, 134.8, 133.6, 132.9, 129.4, 129.4, 128.1, 127.7, 126.4, 126.3, 126.3, 126.3, 126.0, 125.4, 124.3, 120.8, 119.7, 117.7, 115.0, 38.4, 37.1, 21.4.

HPLC analysis: 94:6 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 28.6 min, *tr*(R) = 32.3 min.

HRMS (ESI, *m/z*): calcd. for C₂₈H₂₂NO₄S⁺ 468.1264, found 468.1269.

[α]_D²⁵ = 9.3 (*c* = 3.2 in CHCl₃).

4-(3,4-difluorophenyl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6r)



36.7 mg, 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.48 - 7.41 (m, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 - 7.04 (m, 1H), 7.01 (d, *J* = 8.1 Hz, 2H),

6.88 - 6.78 (m, 2H), 5.05 (d, $J = 7.2$ Hz, 1H), 3.28 (dd, $J = 16.0, 7.8$ Hz, 1H), 2.99 (dd, $J = 16.0, 1.3$ Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 150.6 (dd, $J = 248.0, 12.0$ Hz), 150.0 (dd, $J = 247.0, 12.0$ Hz), 145.4, 138.7, 137.2 (t, $J = 4.3$ Hz), 135.0, 134.9, 129.7, 126.6, 126.3, 124.5, 123.2 (dd, $J = 6.4, 3.6$ Hz), 120.6, 118.6, 118.1 (d, $J = 17.4$ Hz), 117.8, 116.3 (d, $J = 17.9$ Hz), 115.0, 38.2, 36.3, 21.5;

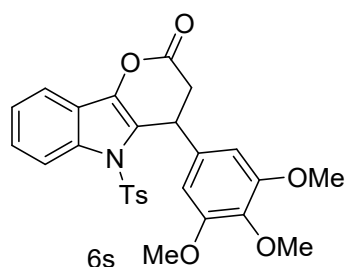
^{19}F NMR (376 MHz, CDCl_3) δ -135.9, -138.7.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) $tr(S) = 16.9$ min, $tr(R) = 18.7$ min.

HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{18}\text{F}_2\text{NO}_4\text{S}^+$ 454.0919, found 454.0922.

$[\alpha]_D^{25} = 20.4$ ($c = 3.1$ in CHCl_3).

5-tosyl-4-(3,4,5-trimethoxyphenyl)-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6s)



47.7 mg, 94% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.4$ Hz, 1H), 7.62 (d, $J = 7.7$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.17 (d, $J = 8.3$ Hz, 2H), 6.96 (d, $J = 8.2$ Hz, 2H), 6.27 (s, 2H), 5.01 (d, $J = 7.1$ Hz, 1H), 3.84 (s, 3H), 3.68 (s, 6H), 3.27 (dd, $J = 15.9, 7.8$ Hz, 1H), 3.02 (d, $J = 15.8$ Hz, 1H), 2.26 (s, 3H).

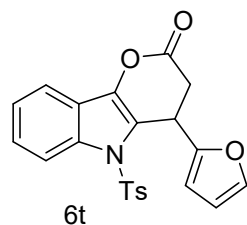
^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 153.8, 145.3, 138.4, 137.7, 135.8, 134.8, 134.8, 129.5, 126.6, 126.3, 124.3, 120.7, 119.7, 117.7, 115.0, 104.1, 61.0, 56.1, 38.5, 37.2, 21.6.

HPLC analysis: 7:93 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) $tr(S) = 21.0$ min, $tr(R) = 23.9$ min.

HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{NO}_7\text{S}^+$ 508.1424, found 508.1428.

$[\alpha]_D^{25} = -8.3$ ($c = 6.5$ in CHCl_3).

4-(furan-2-yl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (6t)



36.7 mg, 90% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.41 - 7.36 (m, 3H), 7.33 - 7.28 (m, 2H), 7.09 (d, $J = 8.2$ Hz, 2H), 6.27 (dd, $J = 3.1, 1.9$ Hz, 1H), 6.15 (d, $J = 3.2$ Hz, 1H), 5.19 (dd, $J = 5.5, 3.5$ Hz, 1H), 3.19 - 3.14 (m, 2H), 2.30 (s, 3H).

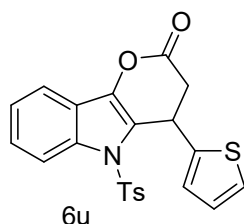
¹³C NMR (100 MHz, CDCl₃) δ 166.2, 152.4, 145.3, 142.7, 138.8, 134.9, 134.8, 129.9, 126.6, 126.3, 124.4, 121.2, 117.8, 117.6, 115.0, 110.7, 107.4, 35.9, 31.2, 21.7.

HPLC analysis: 4:96 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 23.3 min, *tr*(R) = 27.5 min.

HRMS (ESI, *m/z*): calcd. for C₂₂H₁₈NO₅S⁺ 408.0900, found 408.0908.

[α]_D²⁵ = 50.0 (*c* = 3.3 in CHCl₃).

4-(thiophen-2-yl)-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6u)



39.4 mg, 93% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.41 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 7.32 (dd, *J* = 11.1, 7.9 Hz, 3H), 7.19 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.88 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.79 (d, *J* = 3.3 Hz, 1H), 5.40 (d, *J* = 5.8 Hz, 1H), 3.26 (d, *J* = 7.2 Hz, 1H), 3.15 (dd, *J* = 15.9, 1.7 Hz, 1H), 2.29 (s, 3H).

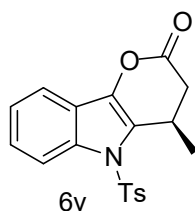
¹³C NMR (100 MHz, CDCl₃) δ 165.9, 145.2, 143.5, 137.9, 134.9, 134.6, 129.8, 127.3, 126.6, 126.3, 125.3, 124.3, 120.9, 120.0, 117.8, 115.0, 39.0, 32.4, 21.6.

HPLC analysis: 5.5:94.5 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 29.9 min, *tr*(R) = 33.3 min.

HRMS (ESI, *m/z*): calcd. for C₂₂H₁₈NO₄S₂⁺ 424.0672, found 424.0676.

[α]_D²⁵ = 30.1 (*c* = 0.6 in CHCl₃).

4-methyl-5-tosyl-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (6v)



27.0 mg, 76% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.33 - 7.26 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 3.87 (td, *J* = 6.9, 1.7 Hz, 1H), 2.95 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.83 (dd, *J* = 16.0, 1.8 Hz, 1H), 2.35 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H).

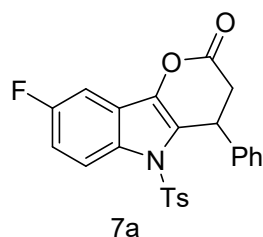
¹³C NMR (100 MHz, CDCl₃) δ 167.0, 145.4, 137.1, 135.1, 134.9, 130.1, 126.3, 125.9, 124.4, 122.6, 121.5, 117.4, 115.2, 37.2, 27.3, 21.7, 21.1.

HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 12.1 min, *tr*(R) = 13.4 min.

HRMS (ESI, *m/z*): calcd. for C₁₉H₁₈NO₄S⁺ 356.0951, found 356.0955.

[α]_D²⁵ = 26.7 (*c* = 0.5 in CHCl₃).

8-fluoro-4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7a)



40.1 mg, 92% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, *J* = 9.2, 4.2 Hz, 1H), 7.28 (td, *J* = 5.8, 5.3, 2.6 Hz, 3H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.14 - 7.08 (m, 5H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.14 - 4.99 (m, 1H), 3.28 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.02 (dd, *J* = 16.0, 1.5 Hz, 1H), 2.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 165.8, 159.9 (d, *J* = 241.0 Hz), 145.2, 140.1, 138.0 (d, *J* = 4.0 Hz), 134.5, 130.8, 129.7, 129.4, 127.9, 127.2, 126.6, 121.8 (d, *J* = 11.0 Hz), 116.3 (d, *J* = 9.0 Hz), 114.1 (d, *J* = 25.0 Hz), 103.5 (d, *J* = 25.0 Hz), 38.3, 37.1, 21.6.

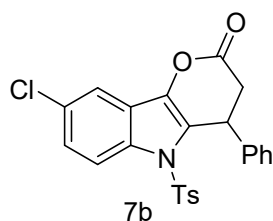
¹⁹F NMR (376 MHz, CDCl₃) δ -117.5.

HPLC analysis: 6:94 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 14.3 min, *tr*(R) = 21.2 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉FNO₄S⁺ 436.1013, found 436.1016.

[α]_D²⁵ = 20.8 (*c* = 2.9 in CHCl₃).

8-chloro-4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7b)



39.8 mg, 88% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.31 - 7.24 (m, 3H), 7.15 - 7.06 (m, 4H), 6.93 (d, *J* = 8.2 Hz, 2H), 5.07 (d, *J* = 6.8 Hz, 1H), 3.28 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.02 (dd, *J* = 16.0, 1.4 Hz, 1H), 2.26 (s, 3H).

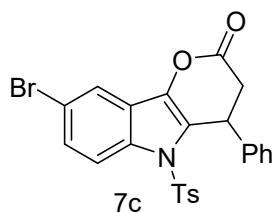
¹³C NMR (100 MHz, CDCl₃) δ 165.8, 145.4, 140.1, 137.5, 134.5, 132.9, 130.3, 129.8, 129.5, 128.0, 127.3, 126.7, 126.4, 122.0, 121.6, 117.4, 116.1, 38.3, 37.1, 21.6.

HPLC analysis: 7:93 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 15.0 min, *tr*(R) = 19.9 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉ClNO₄S⁺ 452.0718, found 452.0720.

[α]_D²⁵ = 85.1 (*c* = 3.1 in CHCl₃)

8-bromo-4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7c)



44.7 mg, 90% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.30 - 7.26 (m, 3H), 7.10 (d, *J* = 6.6 Hz, 4H), 6.93 (d, *J* = 8.2 Hz, 2H), 5.07 (d, *J* = 6.7 Hz, 1H), 3.28 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.01 (dd, *J* = 16.0, 1.4 Hz, 1H), 2.27 (s, 3H).

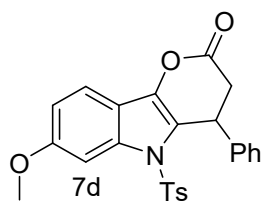
¹³C NMR (100 MHz, CDCl₃) δ 165.8, 145.4, 140.1, 137.3, 134.5, 133.3, 129.8, 129.5, 129.0, 128.0, 127.3, 126.7, 122.4, 121.4, 120.5, 117.8, 116.4, 38.3, 37.1, 21.6.

HPLC analysis: 7:93 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 16.4 min, *tr*(R) = 21.1 min.

HRMS (ESI, *m/z*): calcd. for C₂₄H₁₉BrNO₄S⁺ 496.0213, found 496.0216.

[α]_D²⁵ = 84.0 (*c* = 2.0 in CHCl₃).

8-methoxy-4-phenyl-5-tosyl-4,5-dihydro-3H-indolo[3,2-b]indol-2(3H)-one (7d)



26.0 mg, 58% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.26 (q, *J* = 4.1, 3.7 Hz, 4H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.11 (dd, *J* = 6.4, 3.0 Hz, 2H), 6.95 (td, *J* = 6.1, 2.9 Hz, 3H), 5.03 (d, *J* = 6.7 Hz, 1H), 3.90 (s, 3H), 3.27 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.99 (dd, *J* = 15.9, 1.4 Hz, 1H), 2.27 (s, 3H).

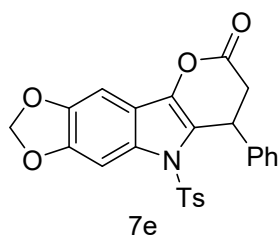
¹³C NMR (100 MHz, CDCl₃) δ 166.4, 159.1, 145.0, 140.6, 138.5, 135.9, 134.8, 129.6, 129.3, 127.7, 127.2, 126.6, 118.3, 118.2, 114.8, 113.3, 99.6, 56.0, 38.4, 37.2, 21.6.

HPLC analysis: 1:99 *er* (S) - isomer as determined by HPLC (ID, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 29.9 min, *tr*(R) = 32.5 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₂NO₅S⁺ 448.1213, found 448.1215.

[α]_D²⁵ = -20.3 (*c* = 0.9 in CHCl₃).

8-phenyl-9-tosyl-8,9-dihydro-[1,3]dioxolo[4,5-f]pyrano[3,2-b]indol-6(7H)-one (7e)



27.7 mg, 60% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.67 - 7.63 (m, 1H), 7.29 - 7.26 (m, 3H), 7.16 - 7.08 (m, 4H), 7.01 - 6.90 (m, 3H), 6.03 (dd, *J* = 6.6, 1.2 Hz, 2H), 5.01 (dd, *J* = 7.7, 1.4 Hz, 1H), 3.25 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.98 (dd, *J* = 15.9, 1.5 Hz, 1H), 2.28 (s, 3H).

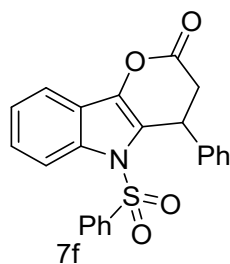
¹³C NMR (100 MHz, CDCl₃) δ 166.4, 147.8, 145.8, 145.1, 140.7, 138.7, 134.7, 129.8, 129.7, 129.4, 127.8, 127.3, 126.7, 118.6, 115.2, 101.8, 96.8, 96.5, 38.5, 37.3, 21.7.

HPLC analysis: 3:97 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 19.8 min, *tr*(R) = 30.8 min.

HRMS (ESI, *m/z*): calcd. for C₂₅H₂₀NO₆S⁺ 462.1006, found 462.1009.

[α]_D²⁵ = 44.4 (*c* = 0.9 in CHCl₃)

5-phenyl-5-(phenylsulfonyl)-4,5-dihydropyrano[3,2-*b*]indol-2(3H)-one (7f)



38.3 mg, 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.61 (m, 1H), 7.45 - 7.32 (m, 3H), 7.26 (tt, *J* = 4.0, 2.0 Hz, 6H), 7.18 - 7.09 (m, 4H), 5.09 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.30 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.02 (dd, *J* = 15.9, 1.5 Hz, 1H).

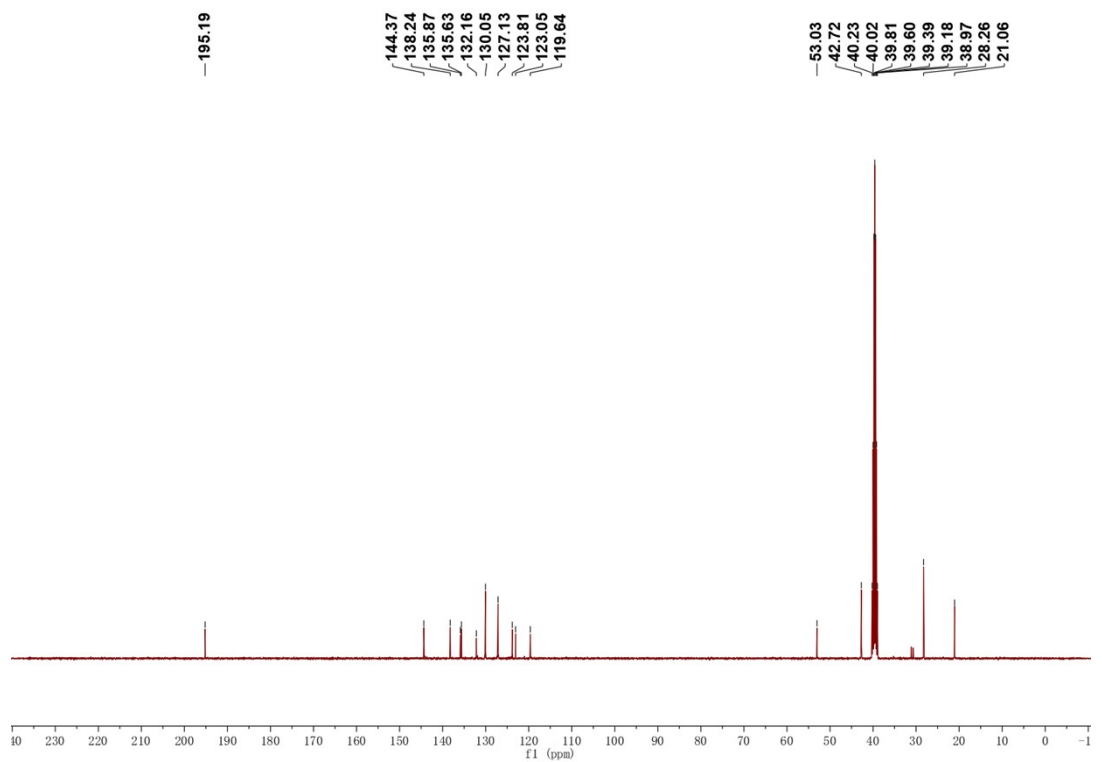
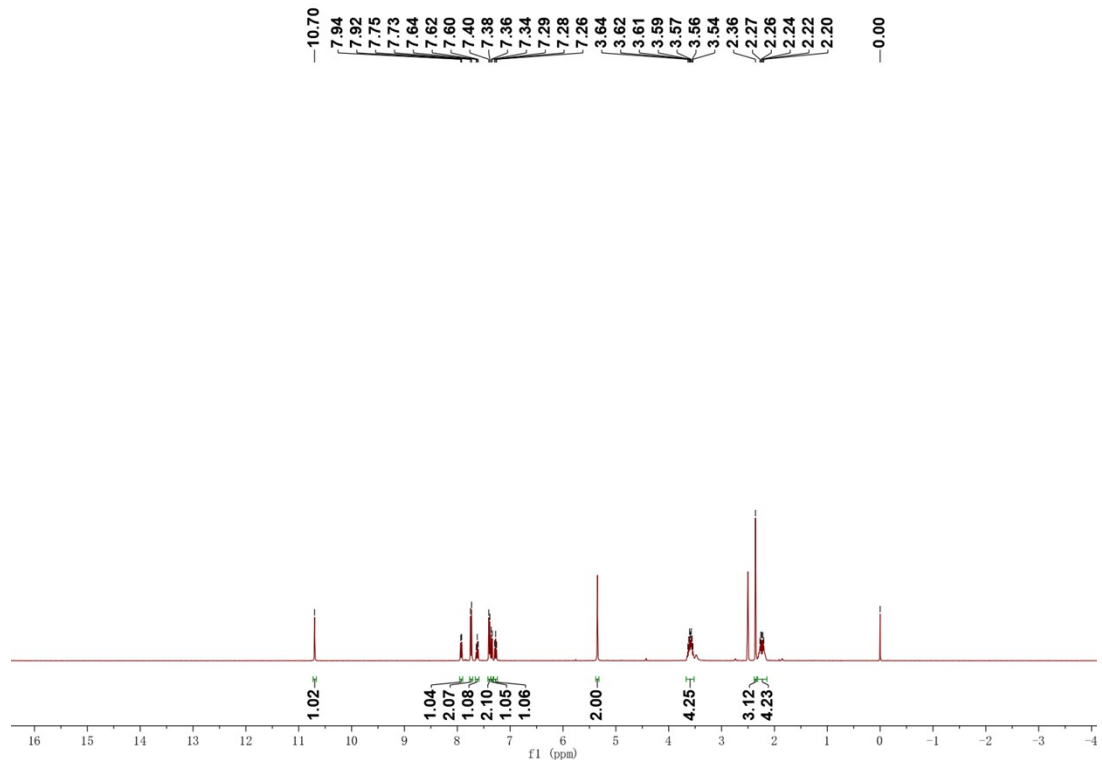
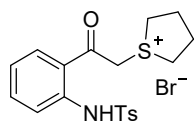
¹³C NMR (100 MHz, CDCl₃) δ 166.2, 140.3, 138.4, 137.7, 134.6, 133.8, 129.4, 129.0, 127.9, 127.2, 126.6, 126.2, 124.3, 120.9, 119.9, 117.7, 114.9, 38.4, 37.1.

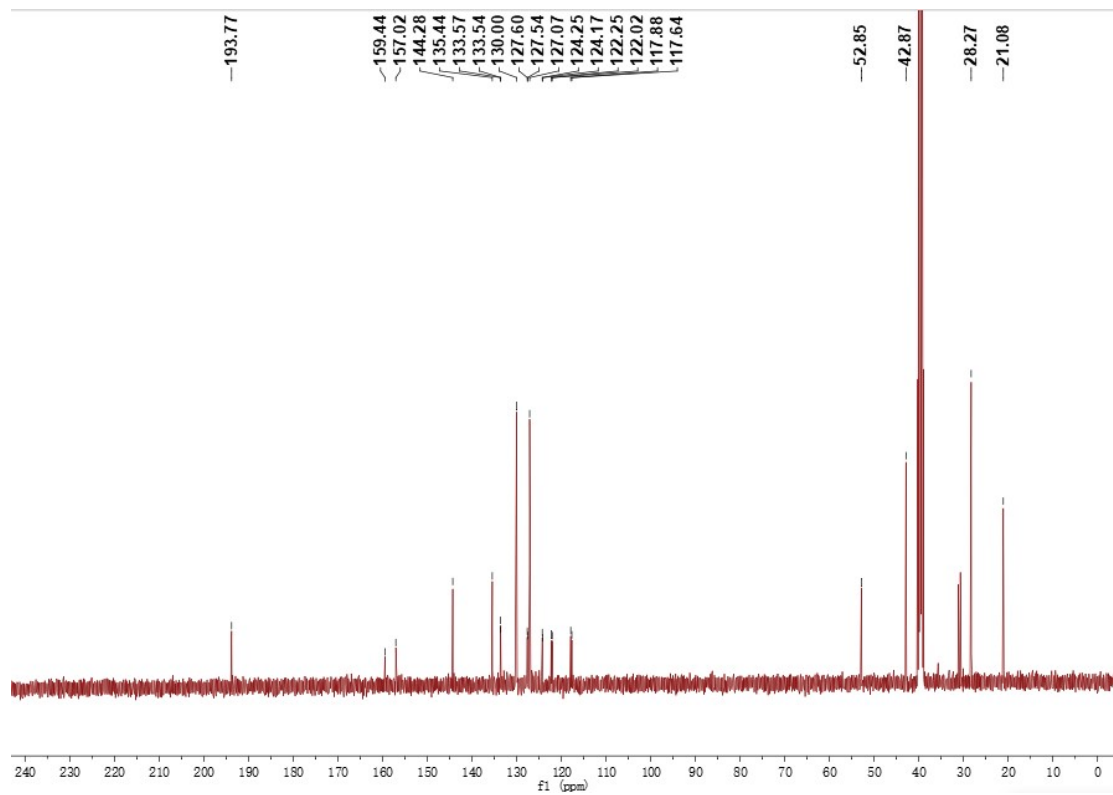
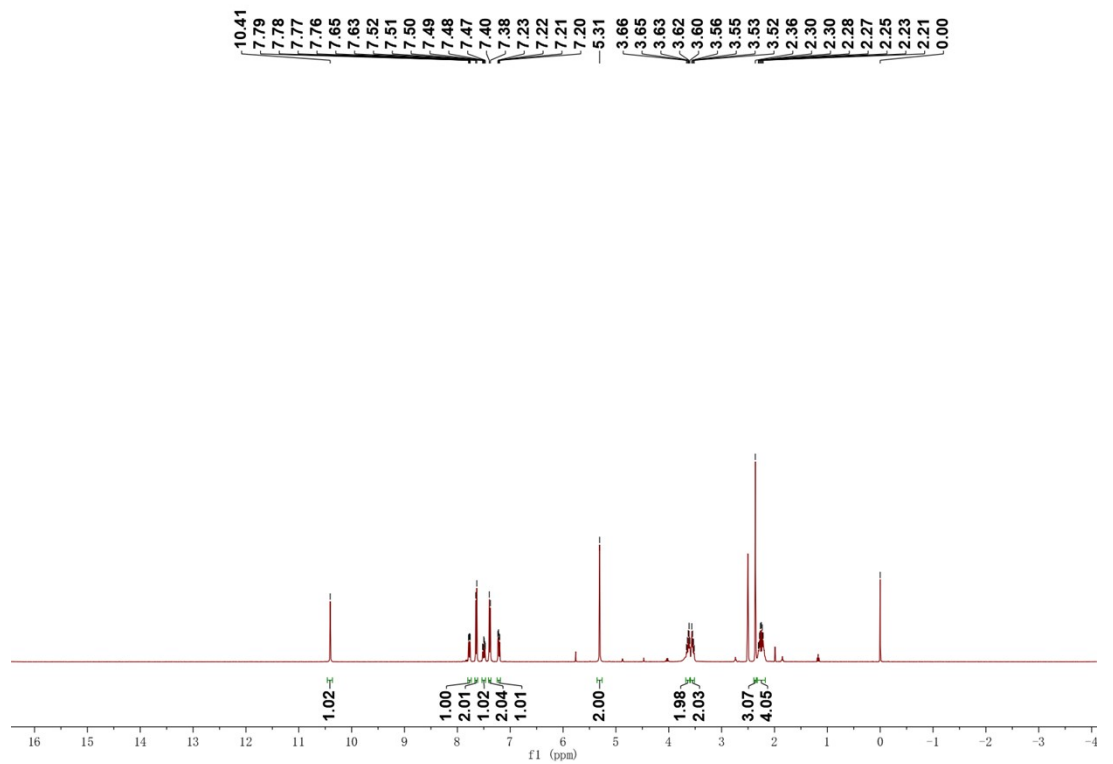
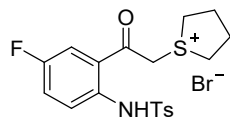
HPLC analysis: 5:95 *er* (S) - isomer as determined by HPLC (IA, 80:20 hexanes/iso-propanol, 0.6 ml/min) *tr*(S) = 14.2 min, *tr*(R) = 17.5 min.

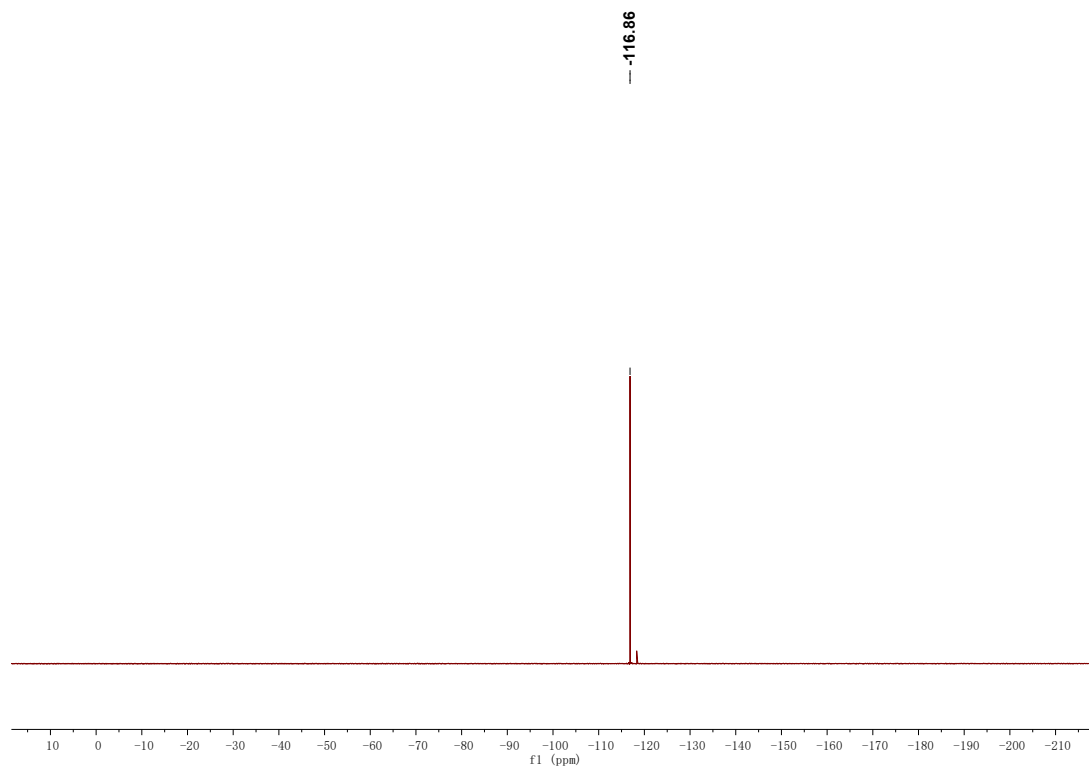
HRMS (ESI, *m/z*): calcd. for C₂₃H₁₈NO₄S⁺ 404.0951, found 404.0955.

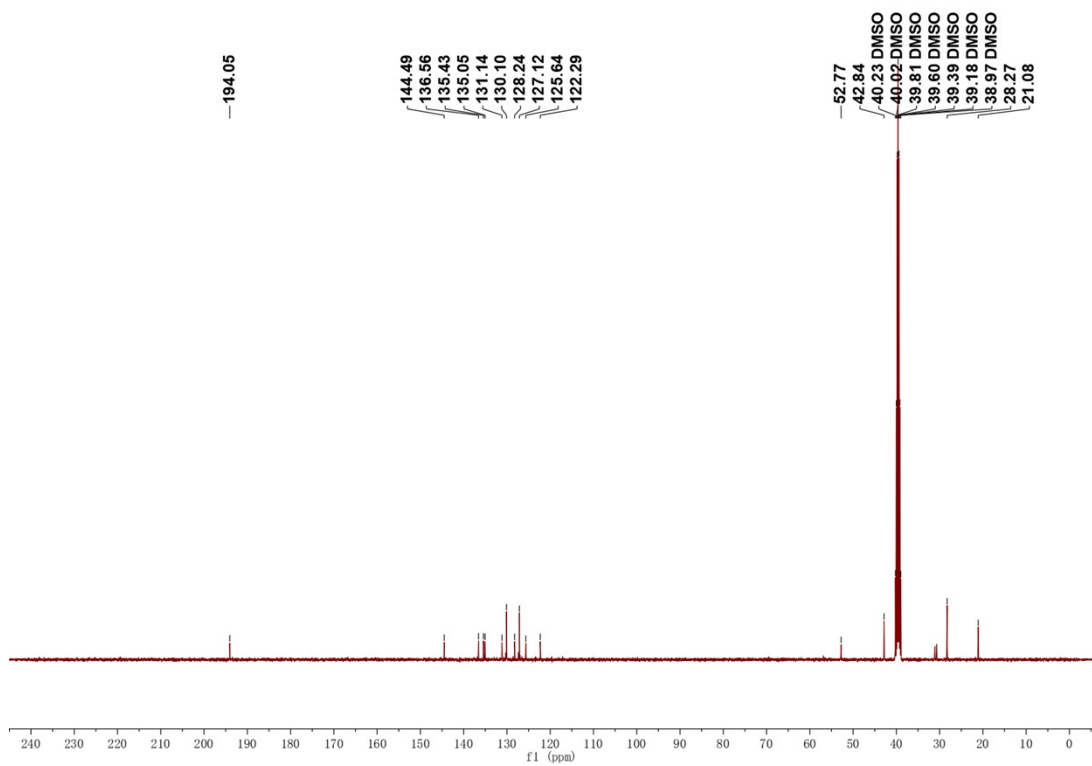
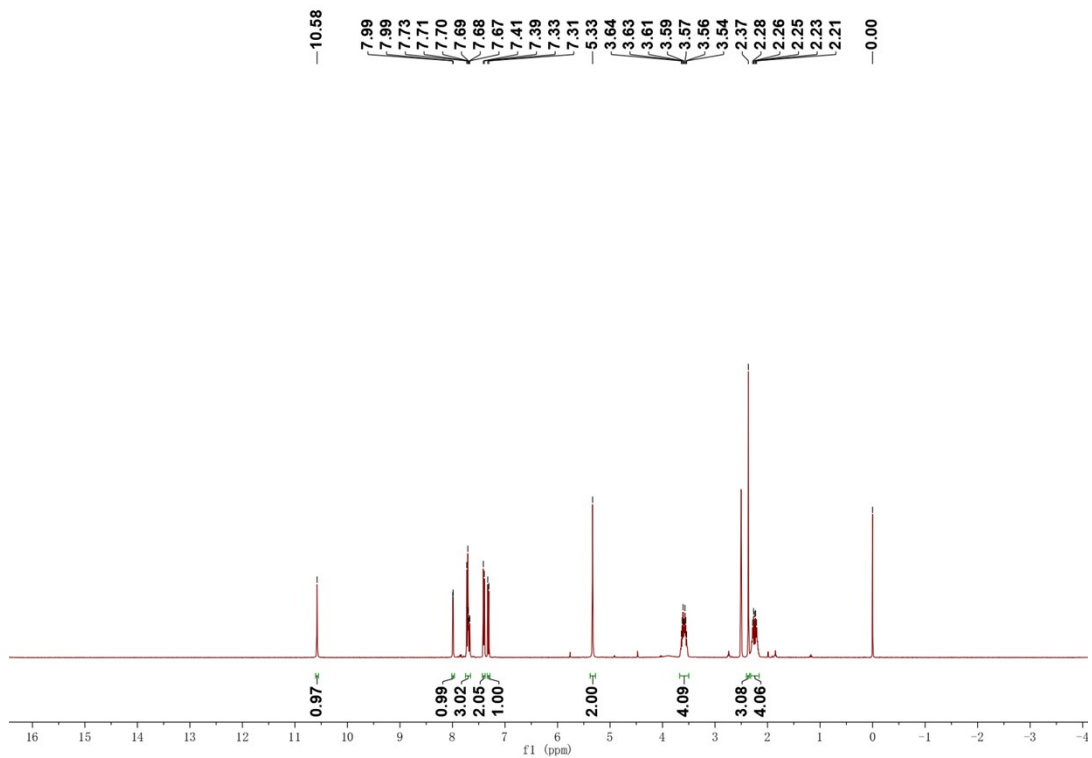
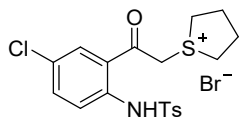
[α]_D²⁵ = 32.9 (*c* = 1.6 in CHCl₃).

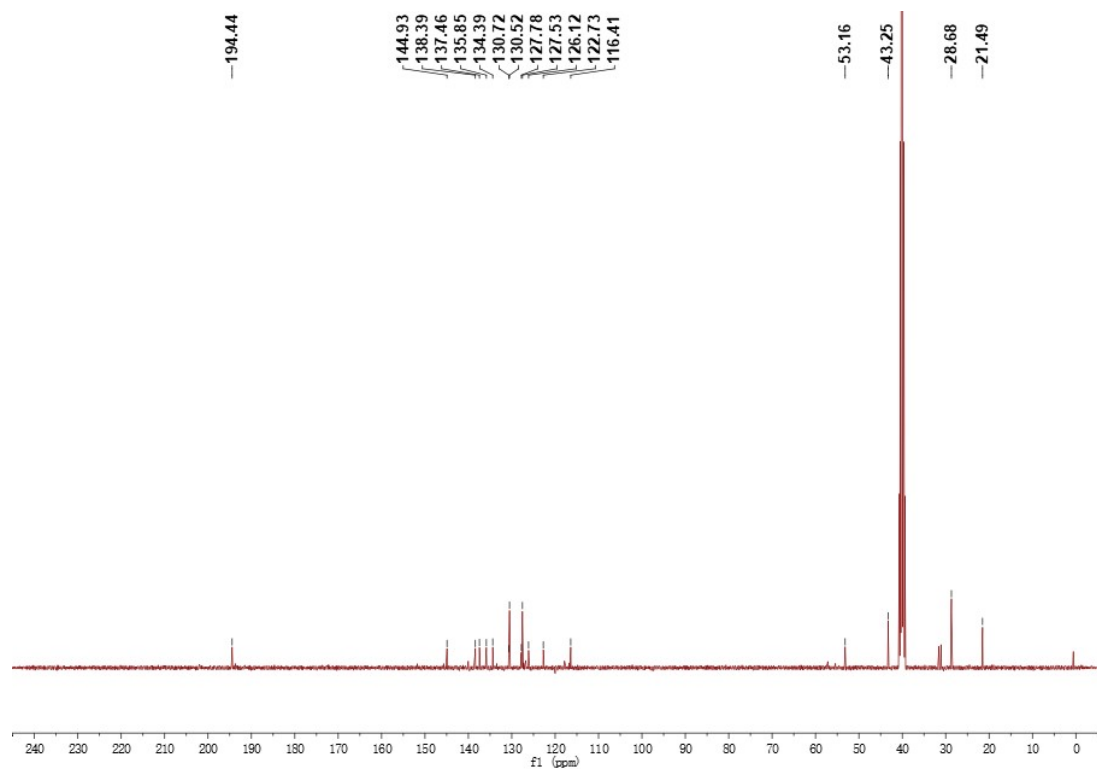
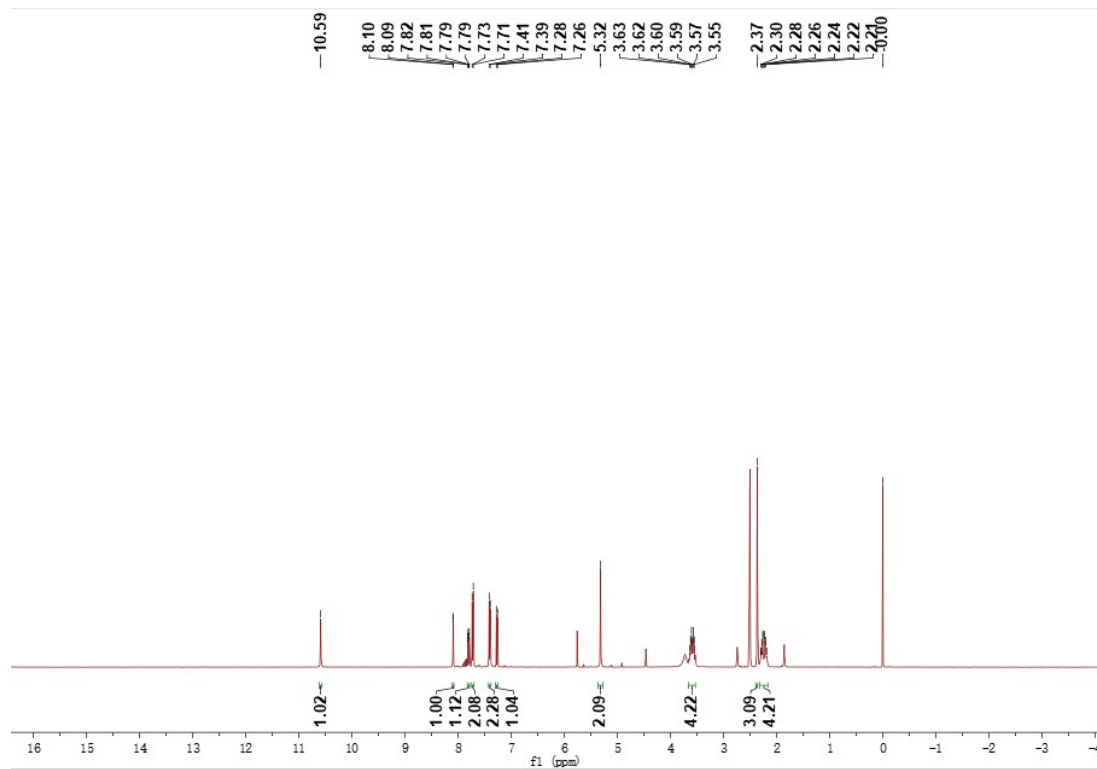
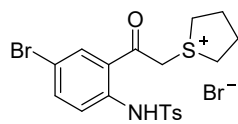
Spectra
 ^1H , ^{13}C , ^{19}F NMR

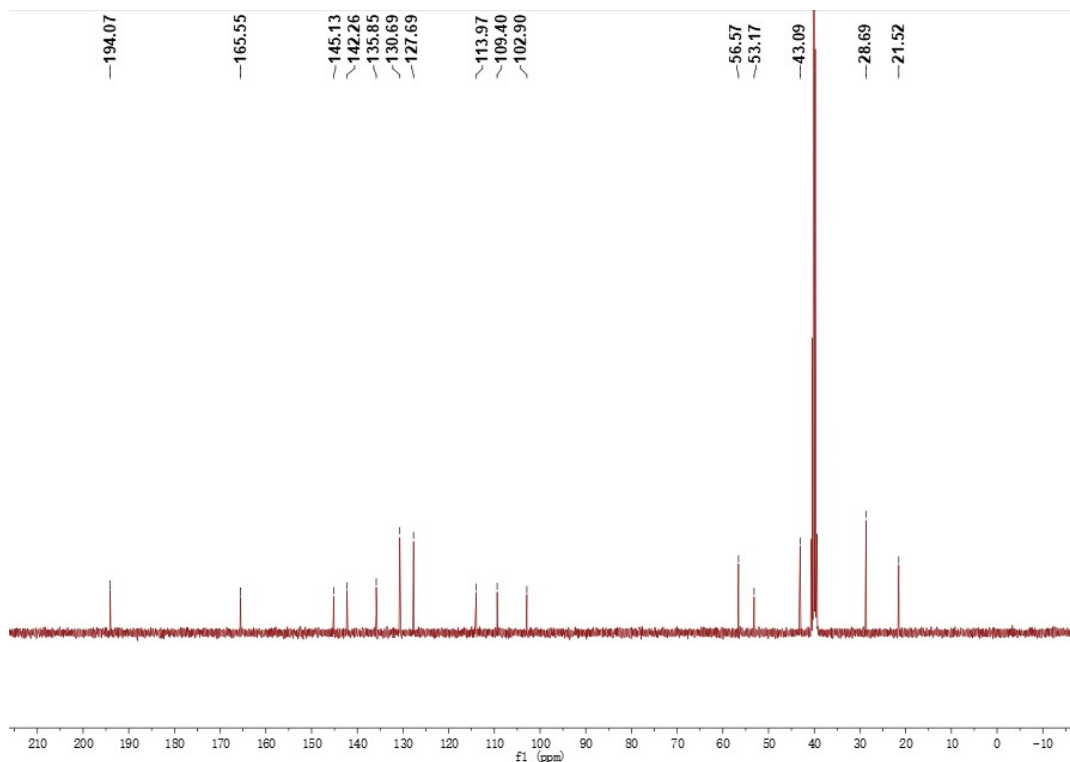
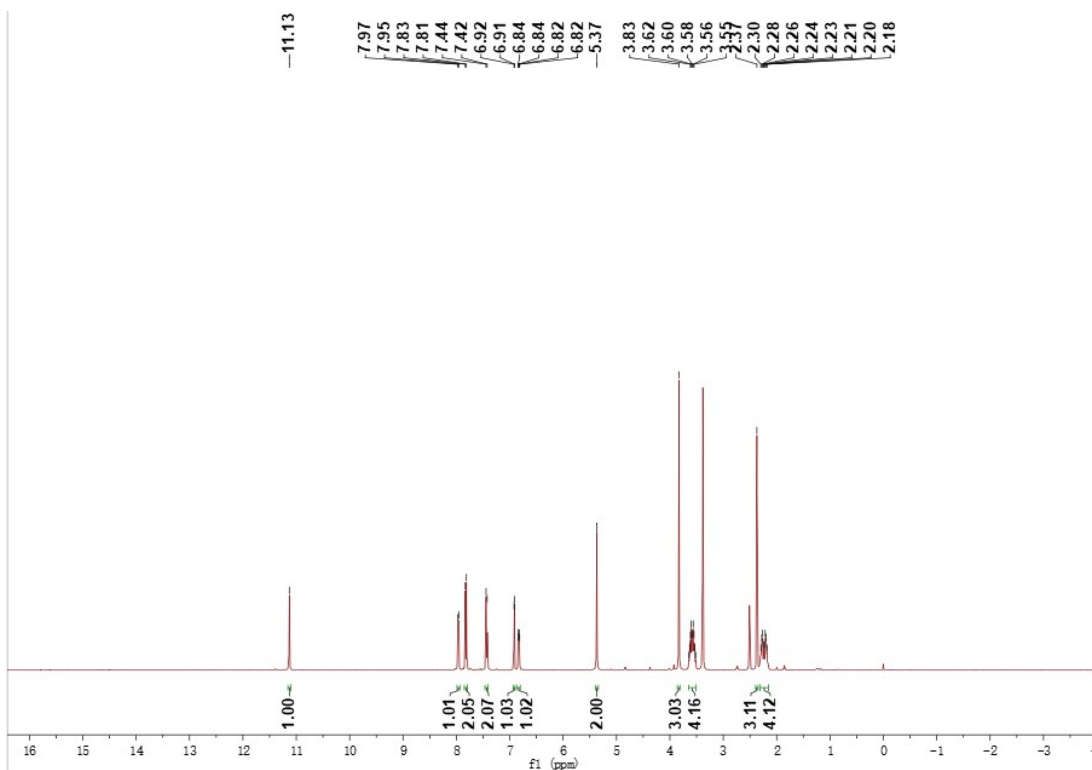
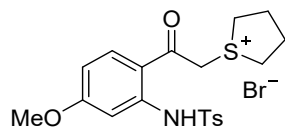


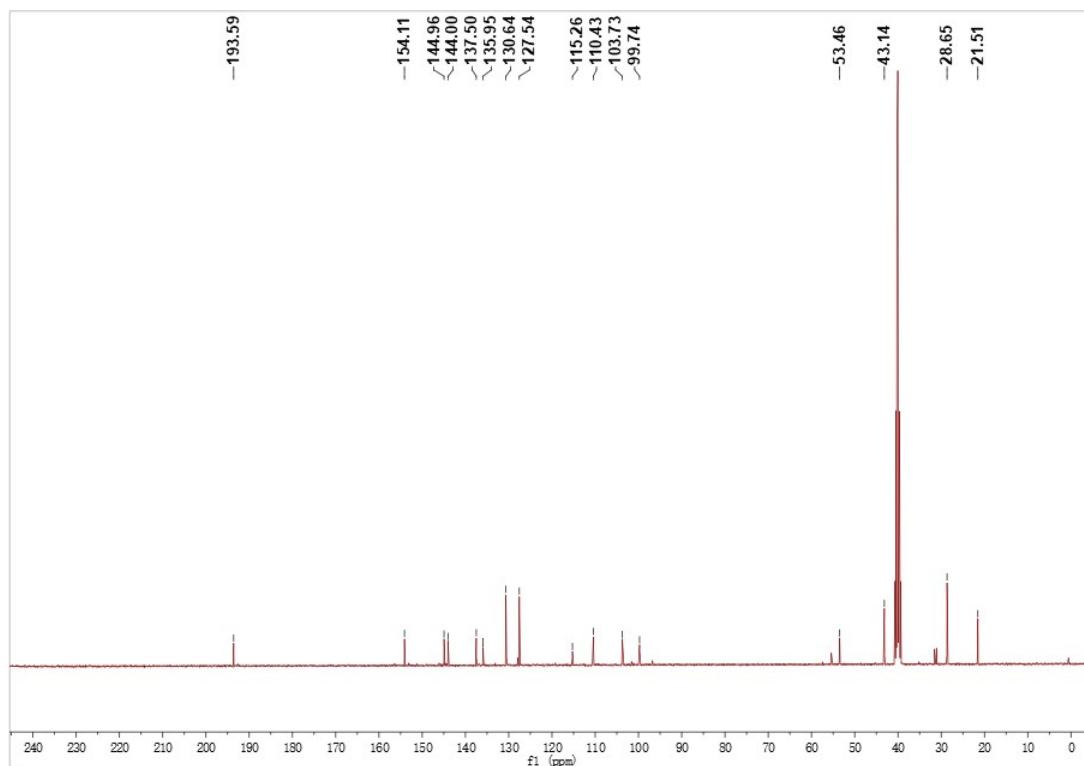
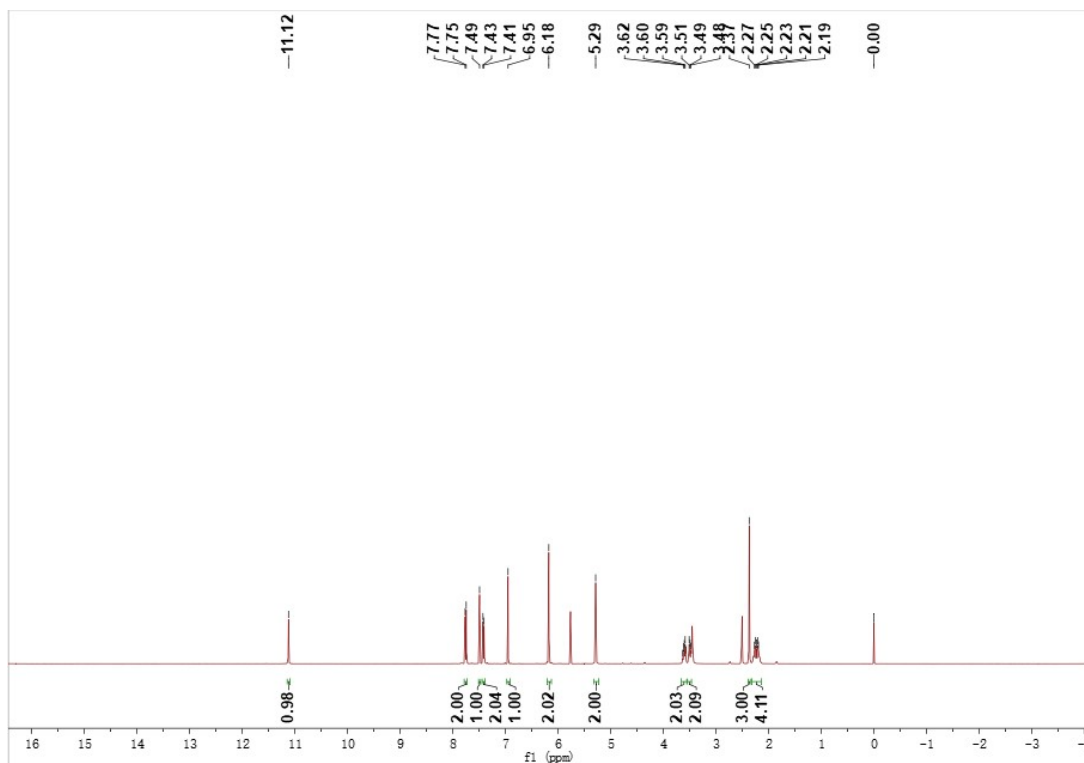
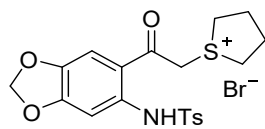


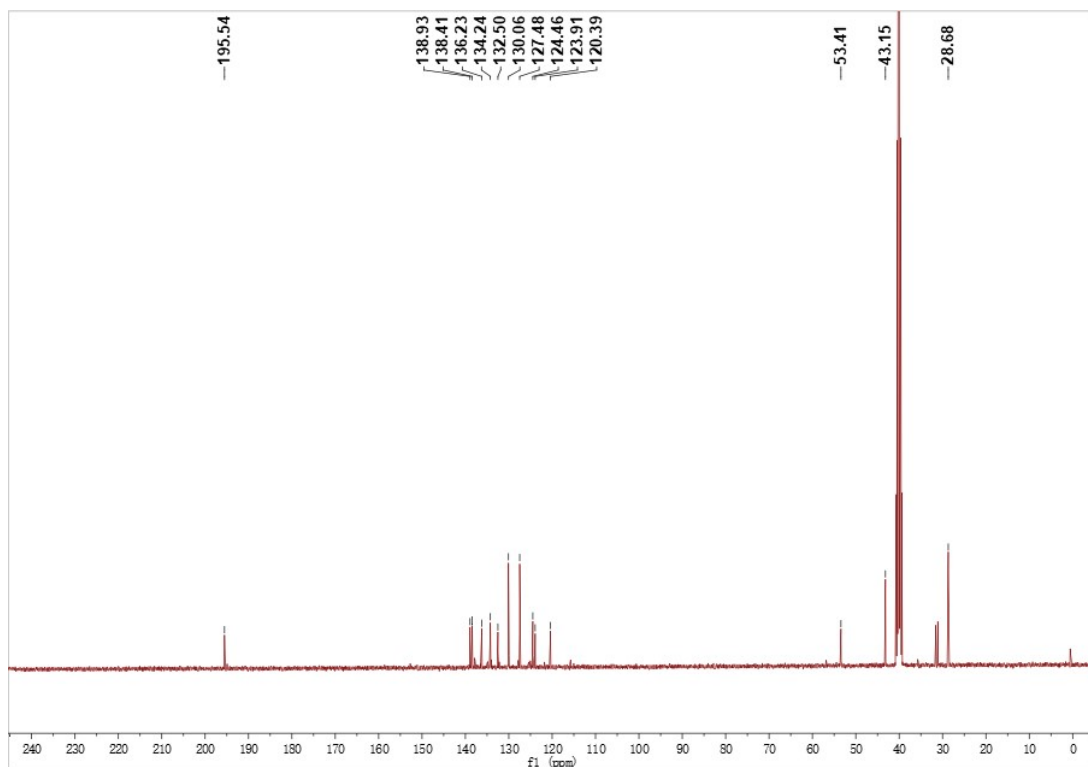
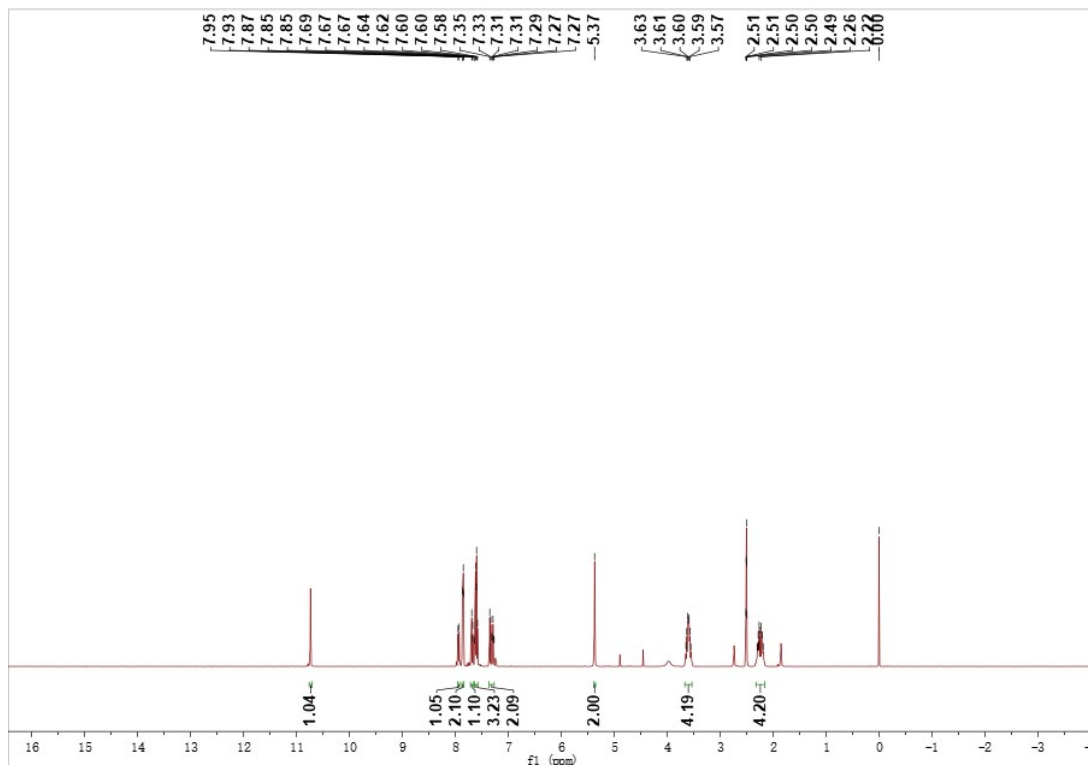
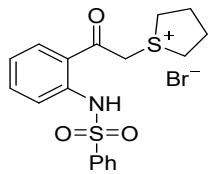


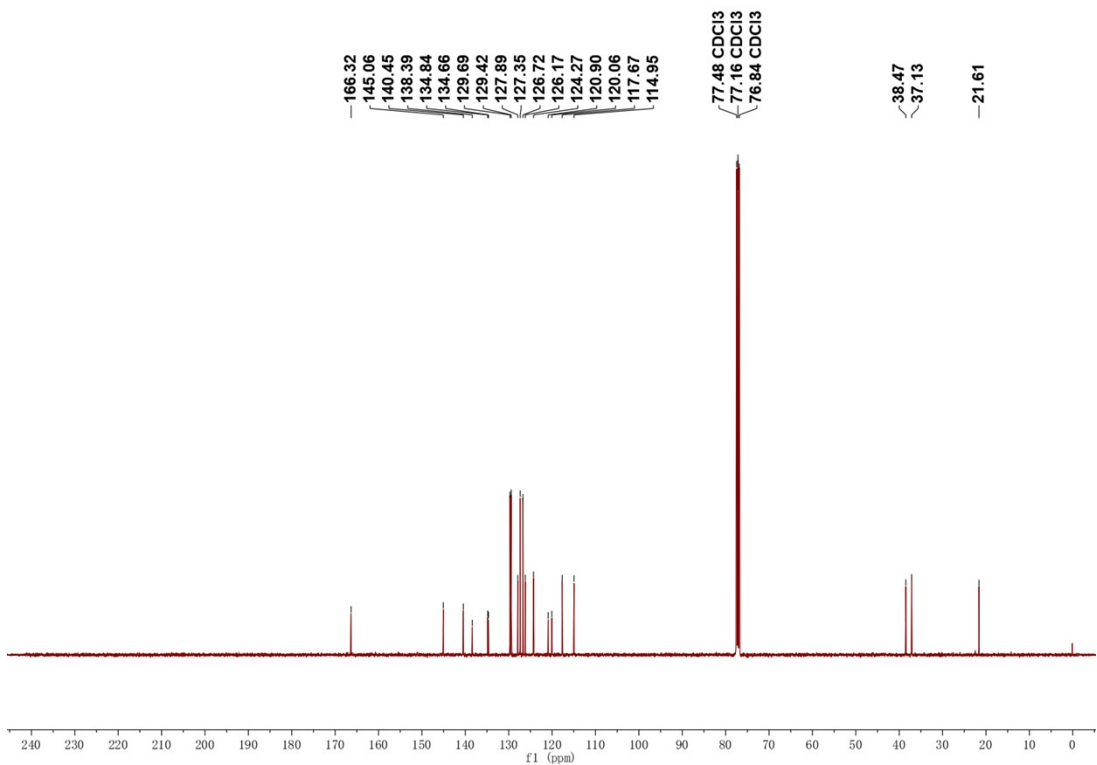
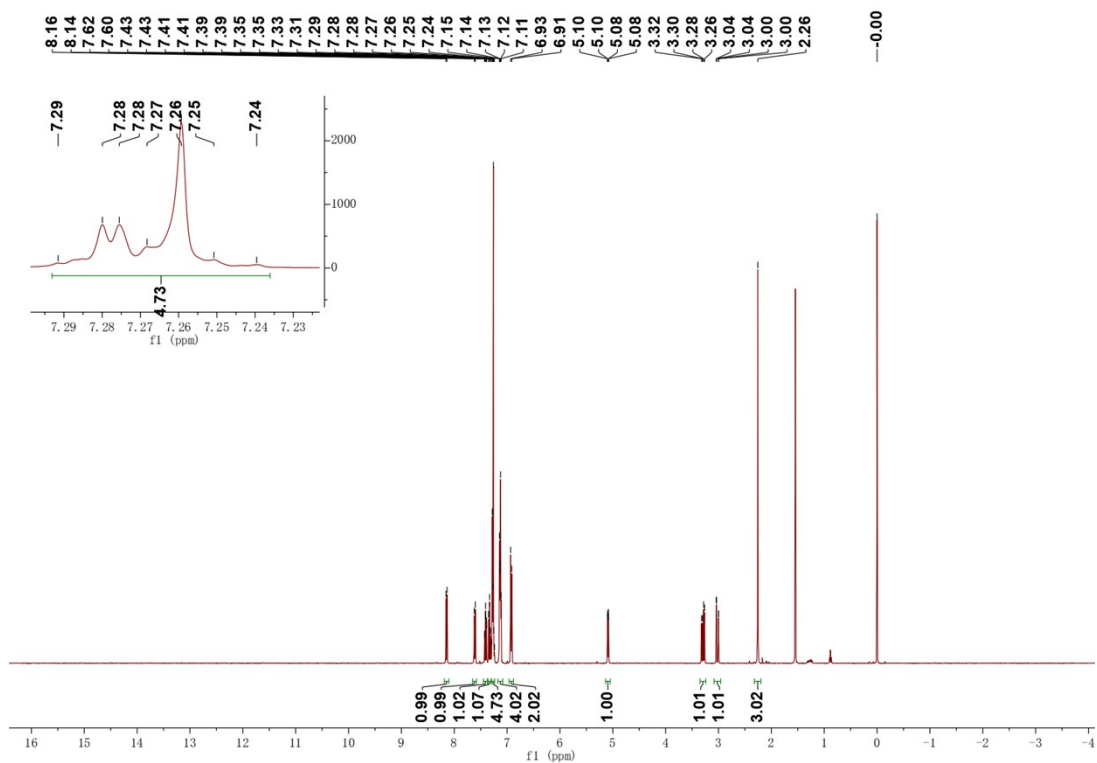
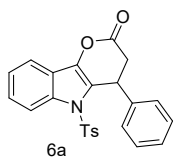


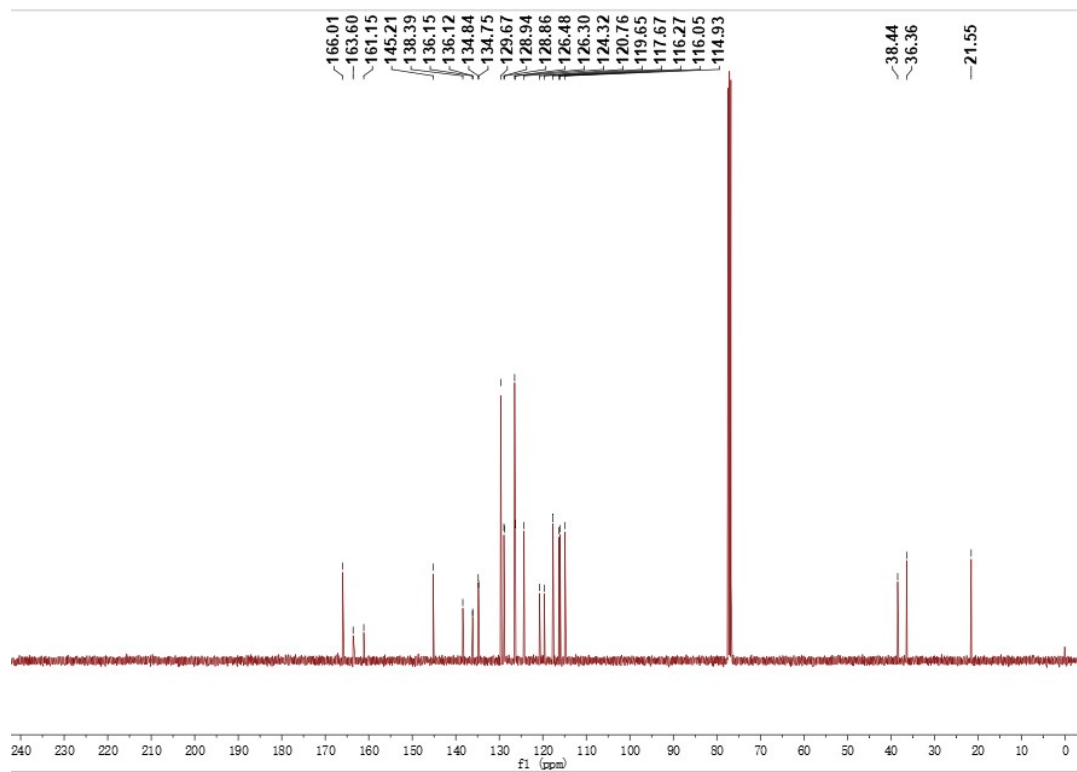
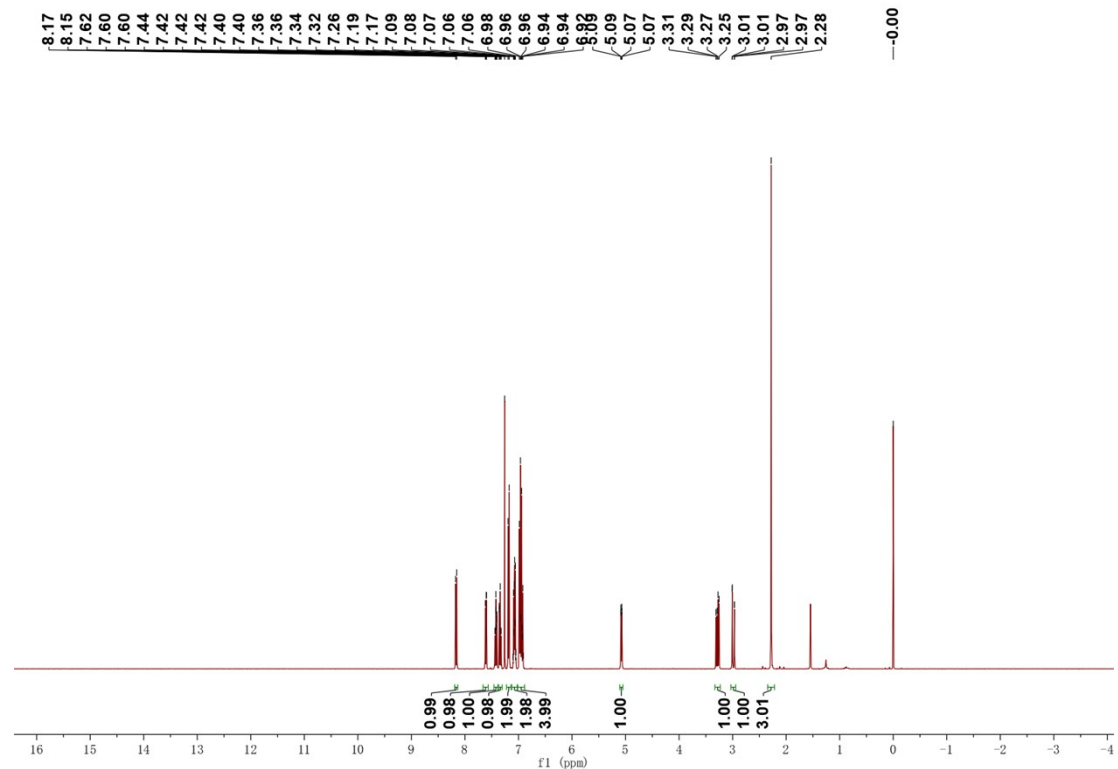
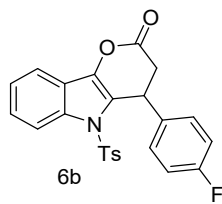


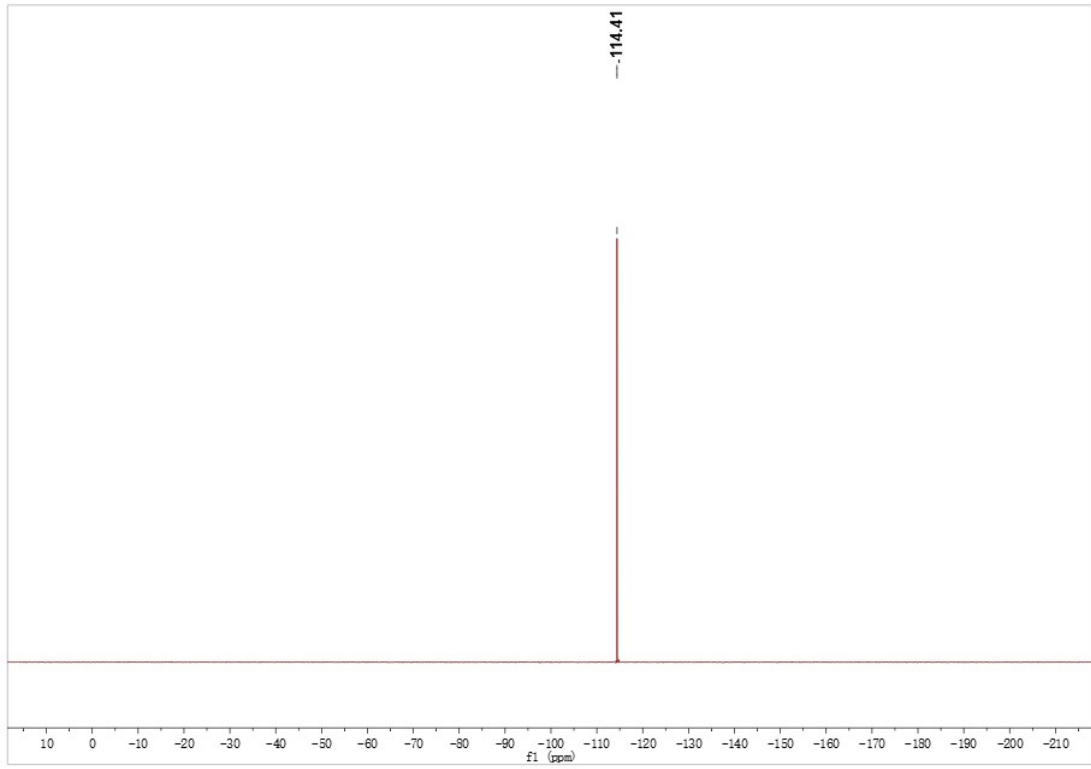


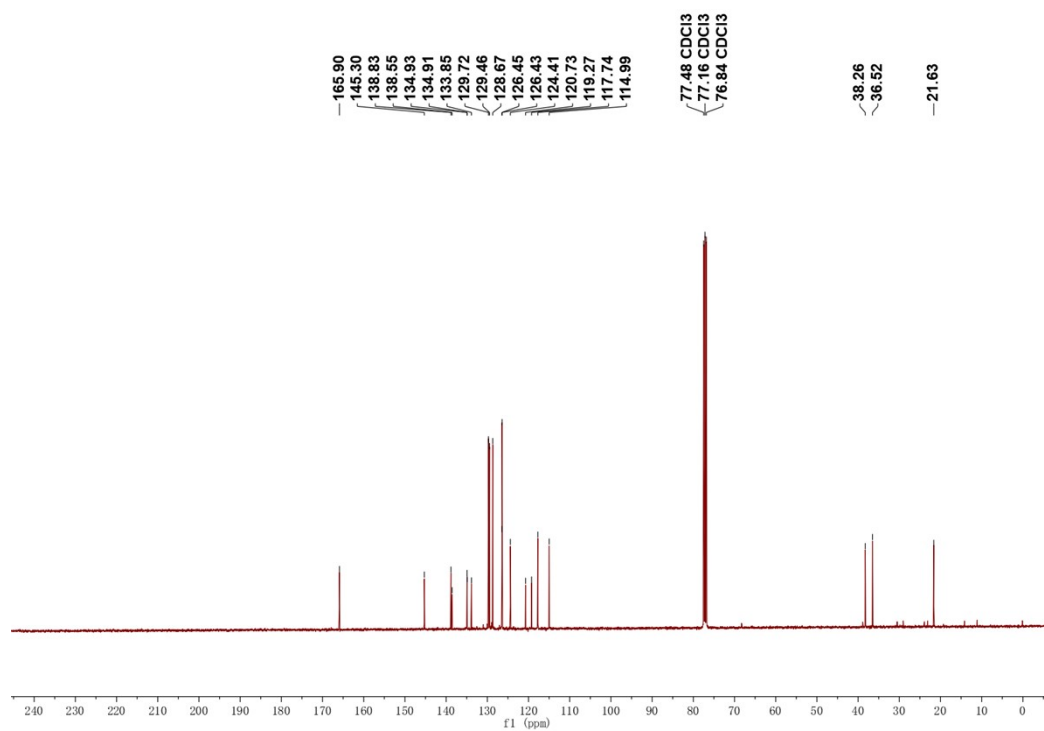
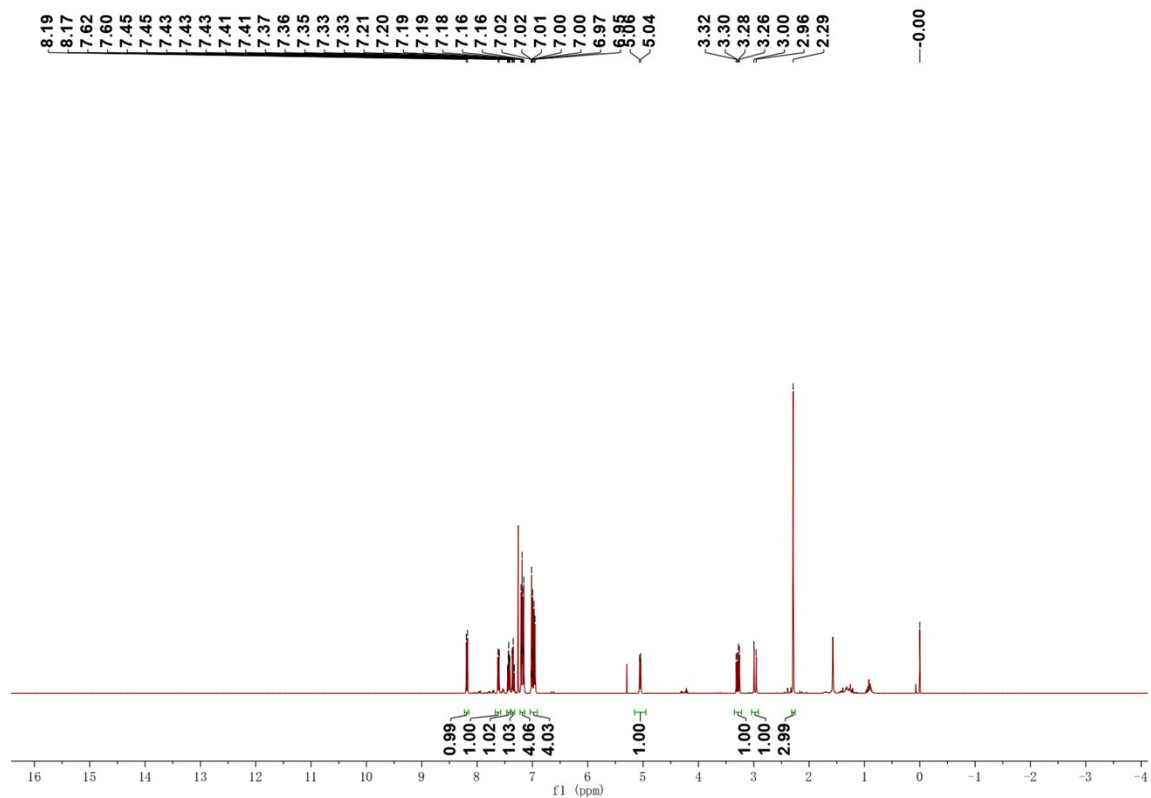
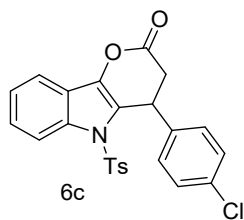


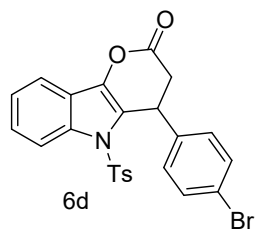




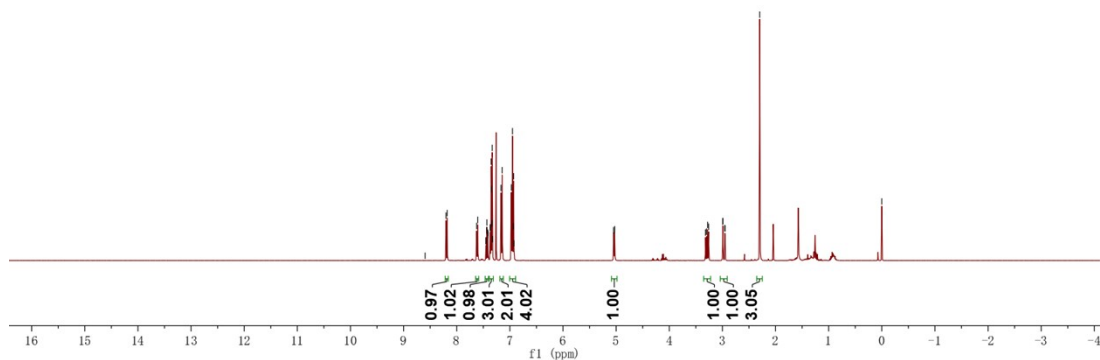




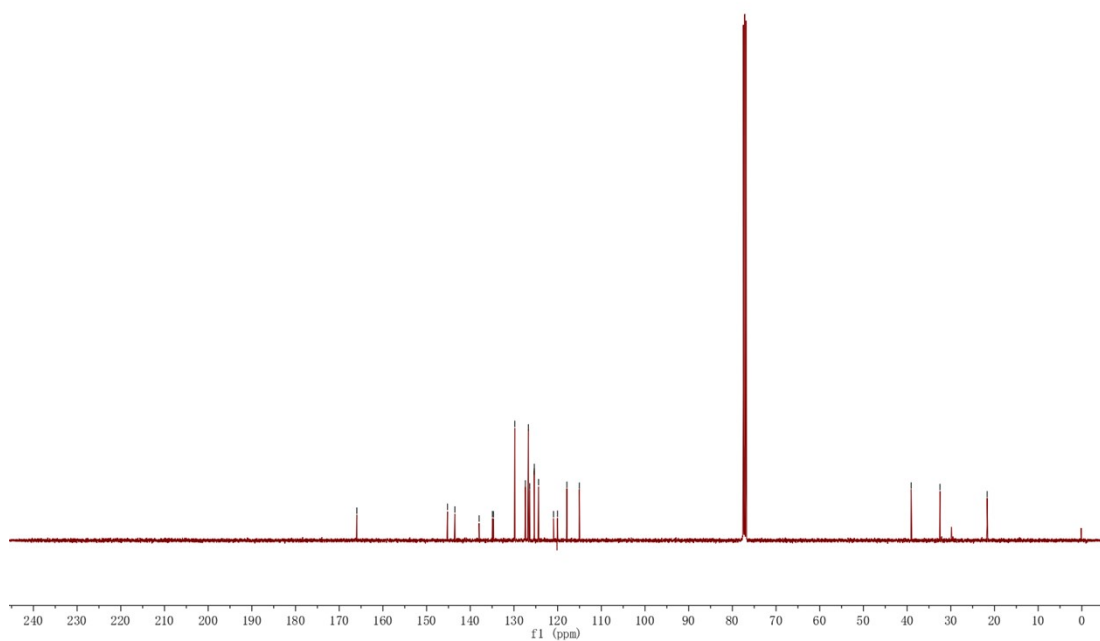


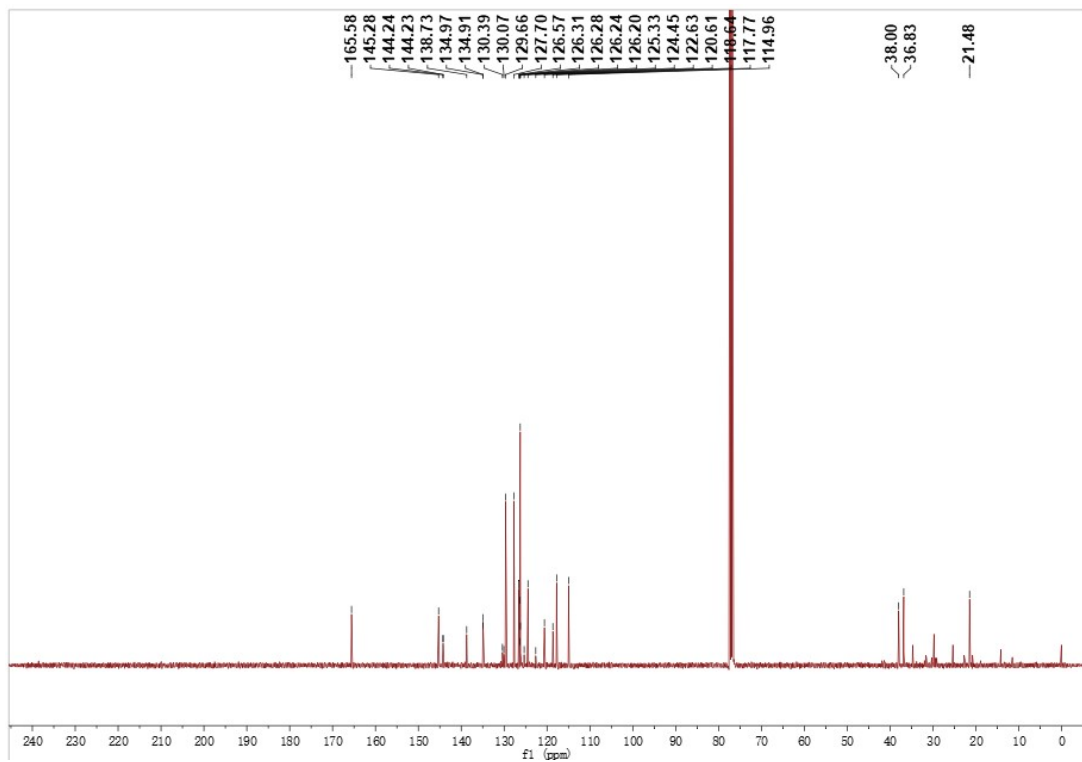
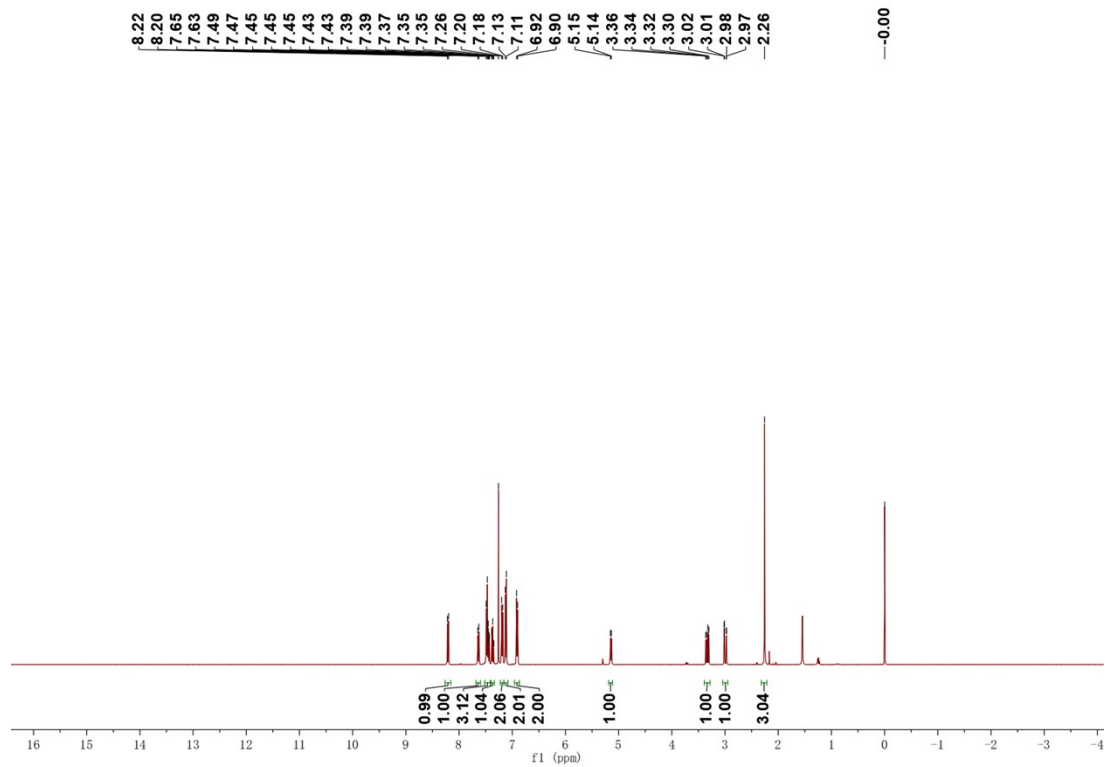
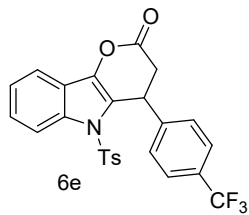


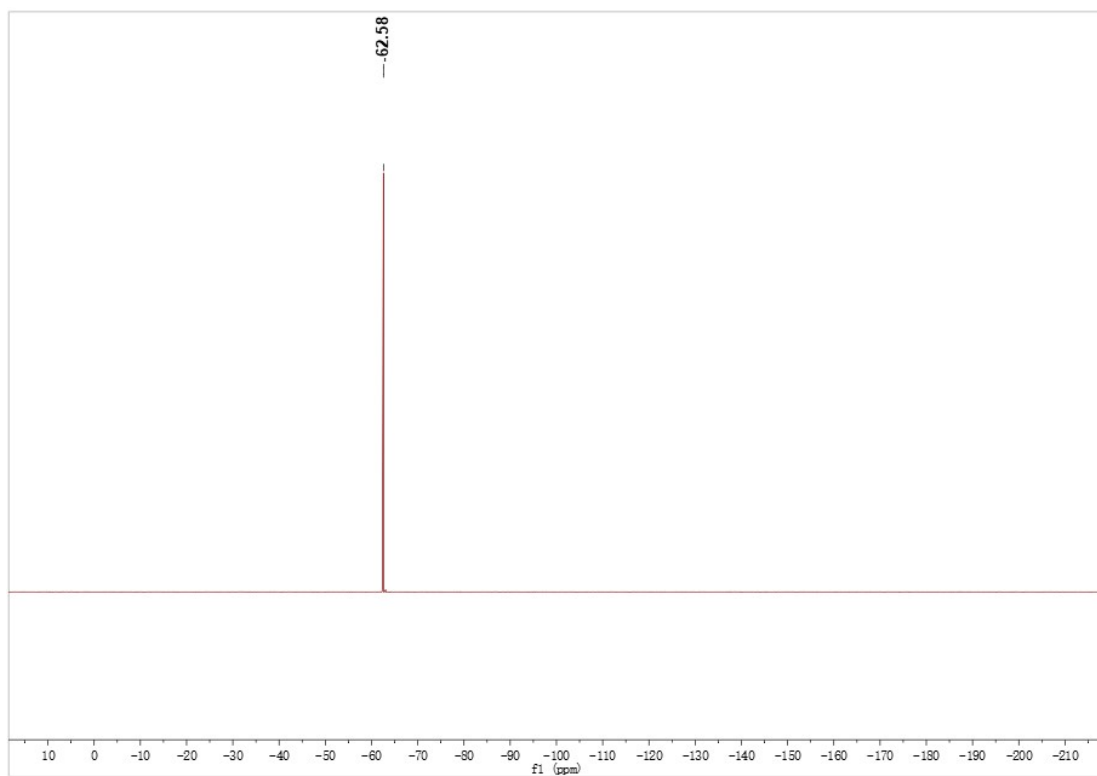
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7.35
7.35
7.34
7.33
7.33
7.17
7.15
6.97
6.95
6.93
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6.92
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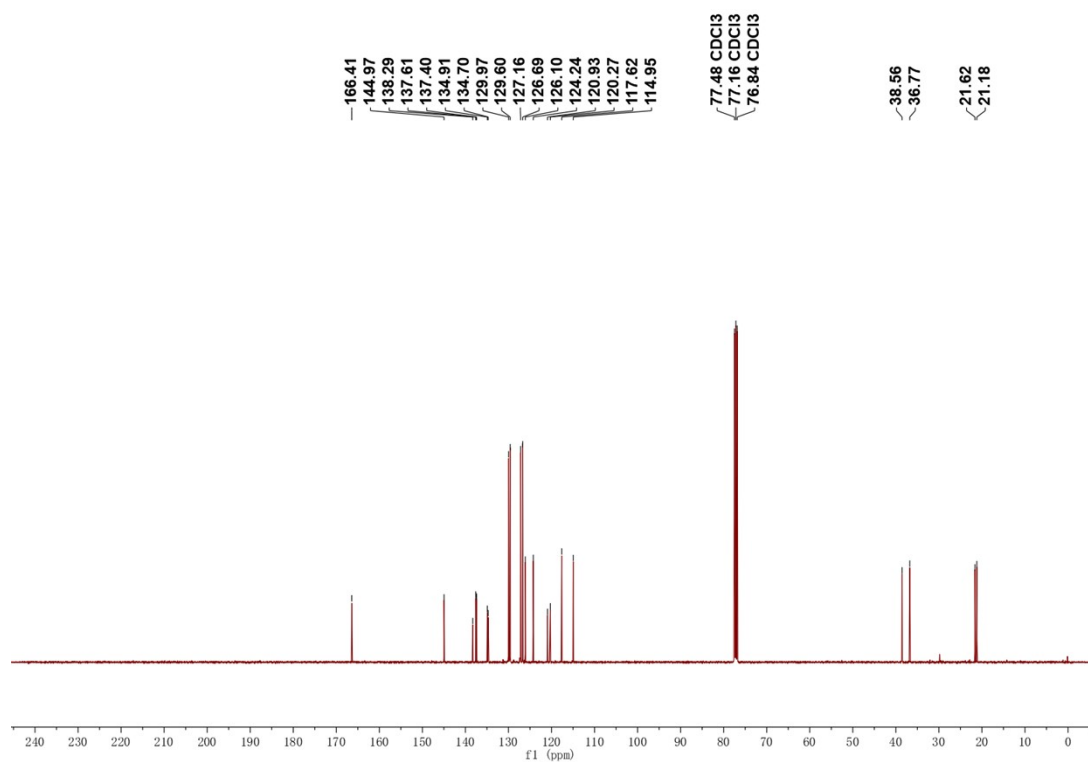
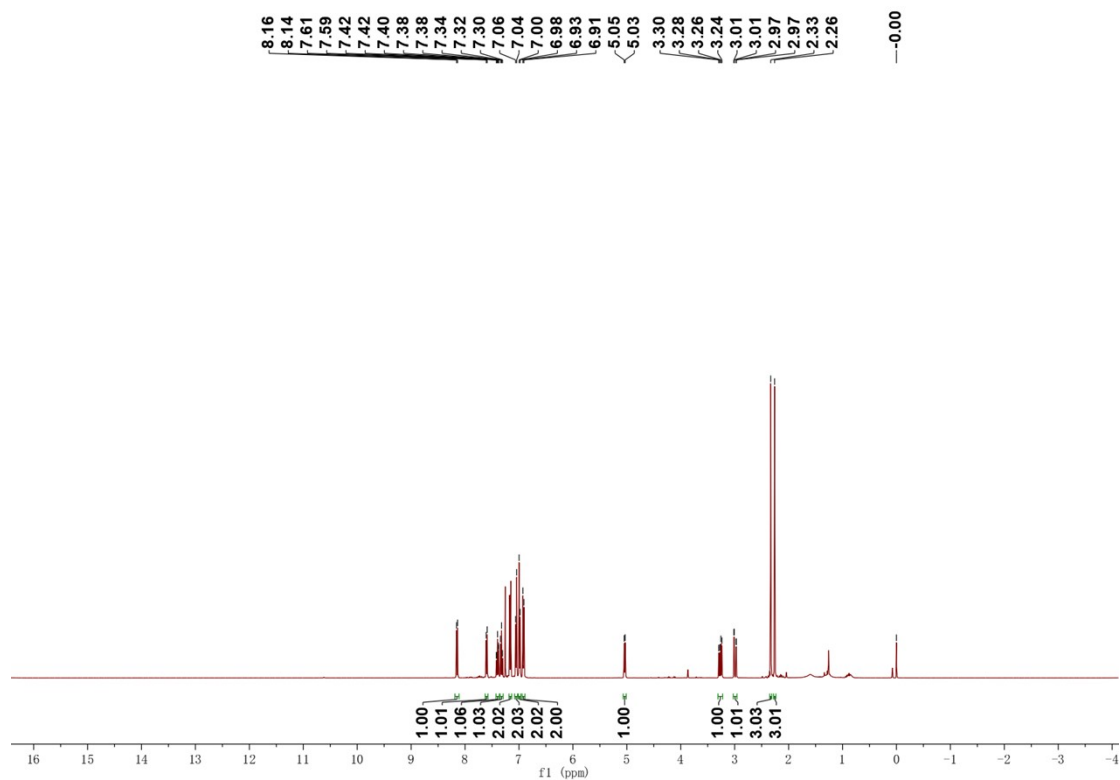
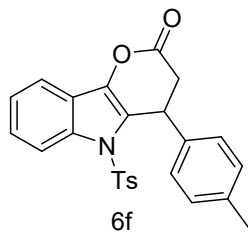


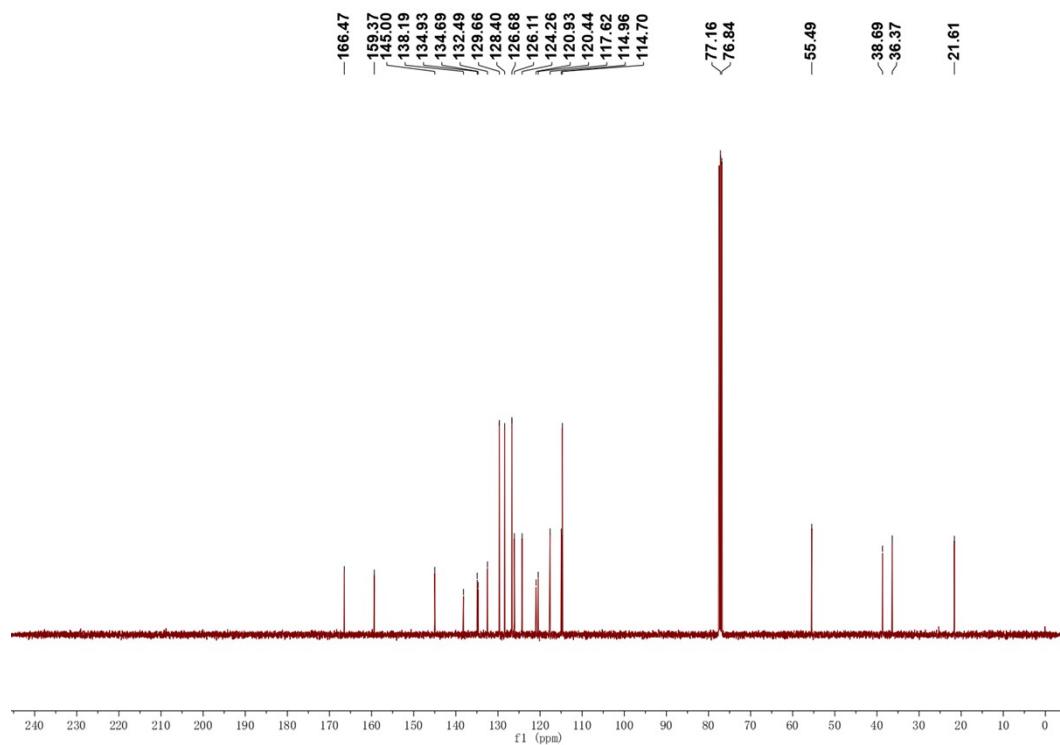
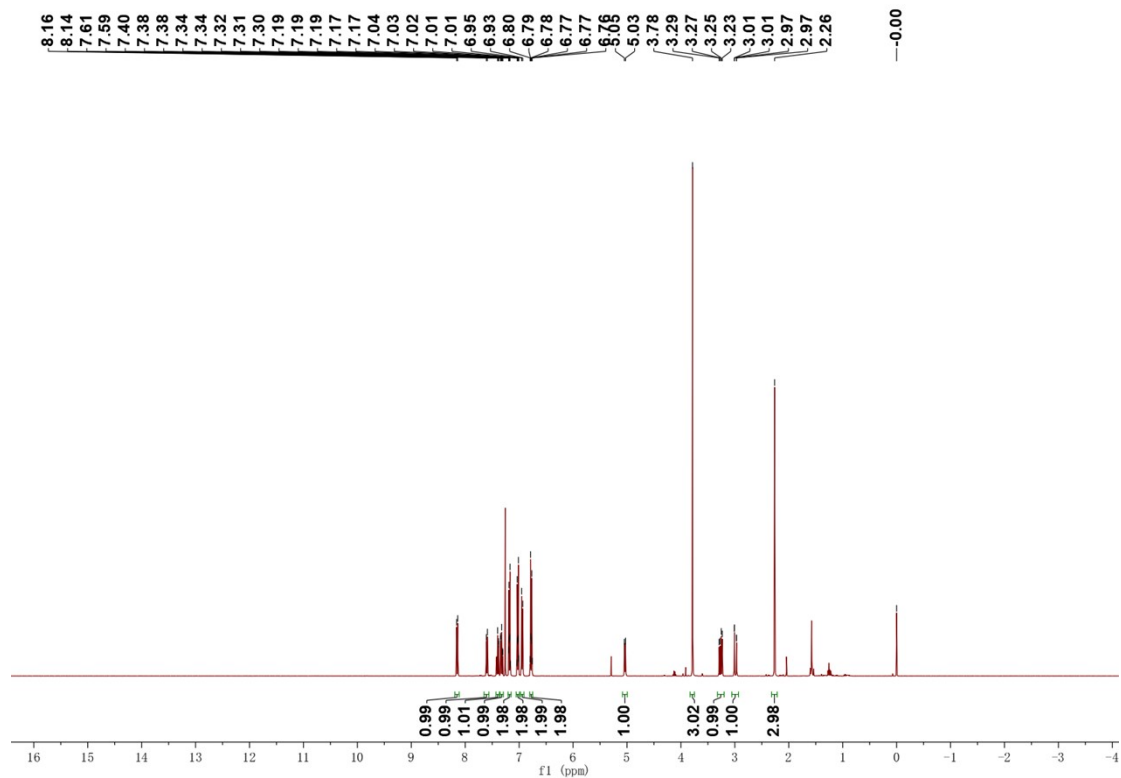
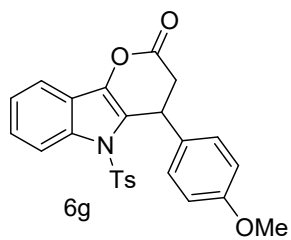
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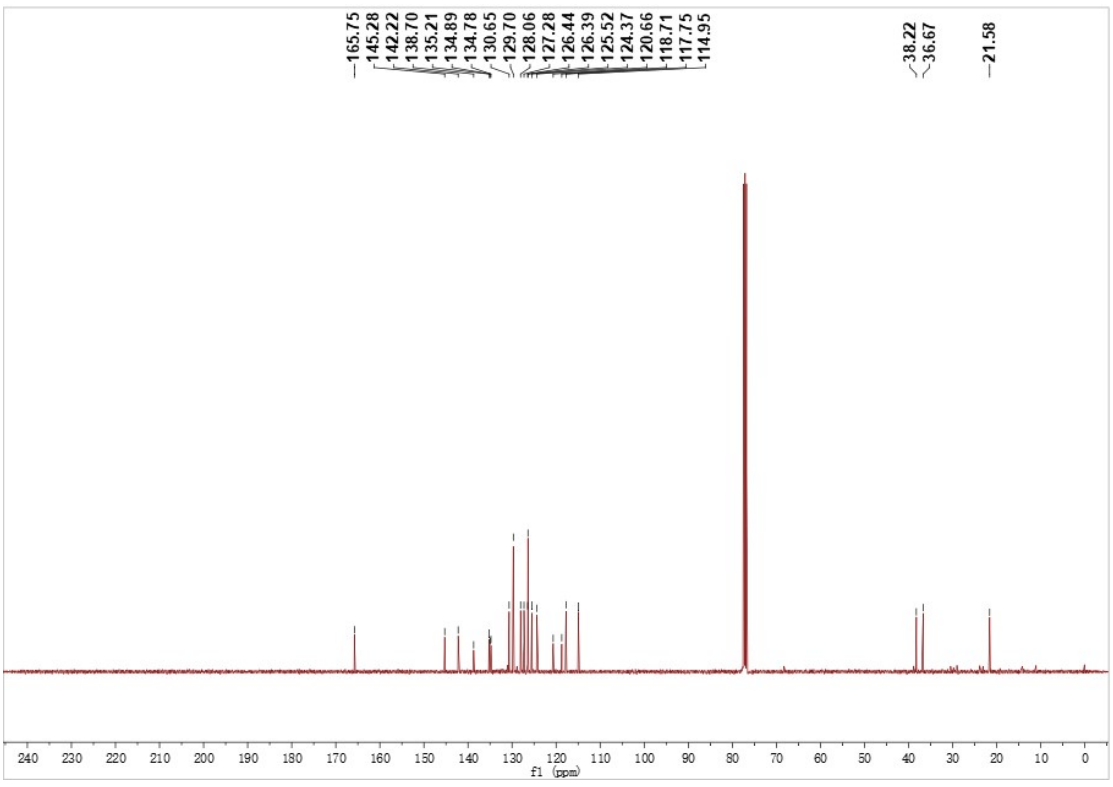
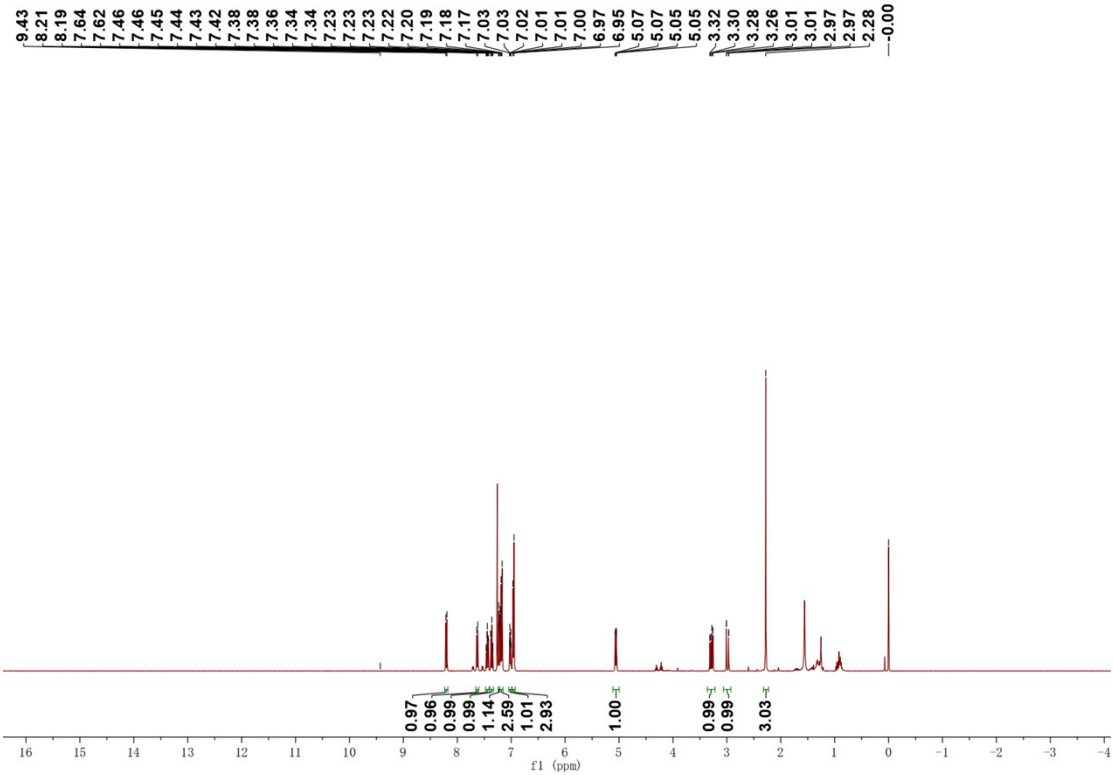
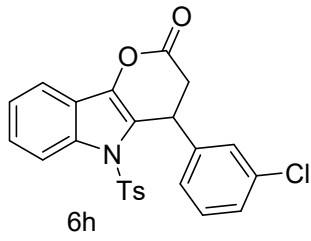


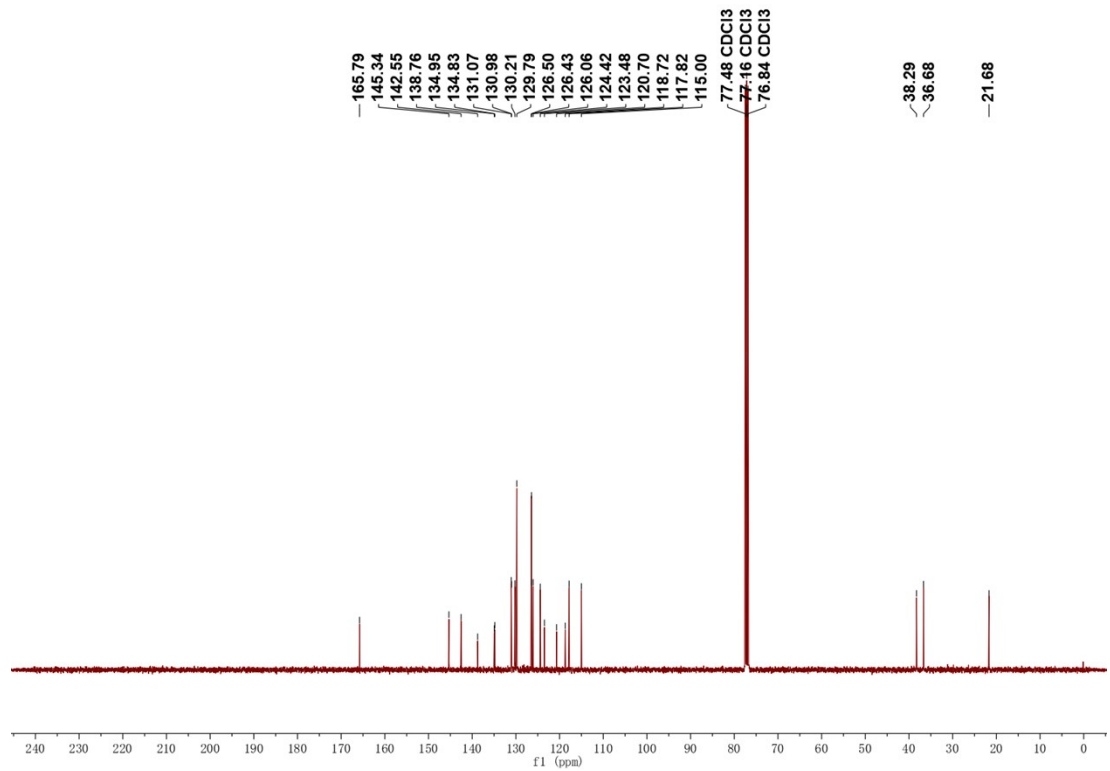
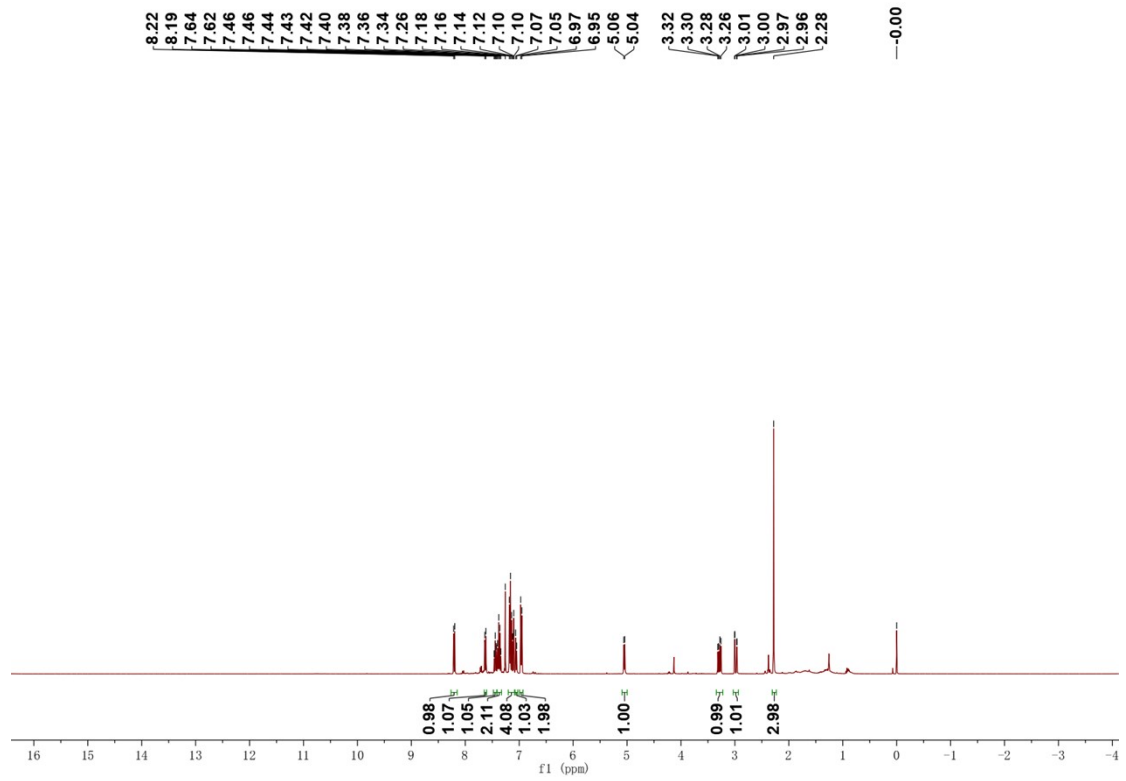
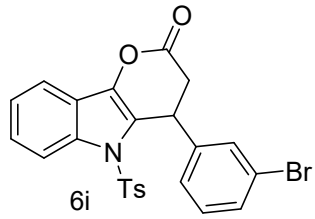


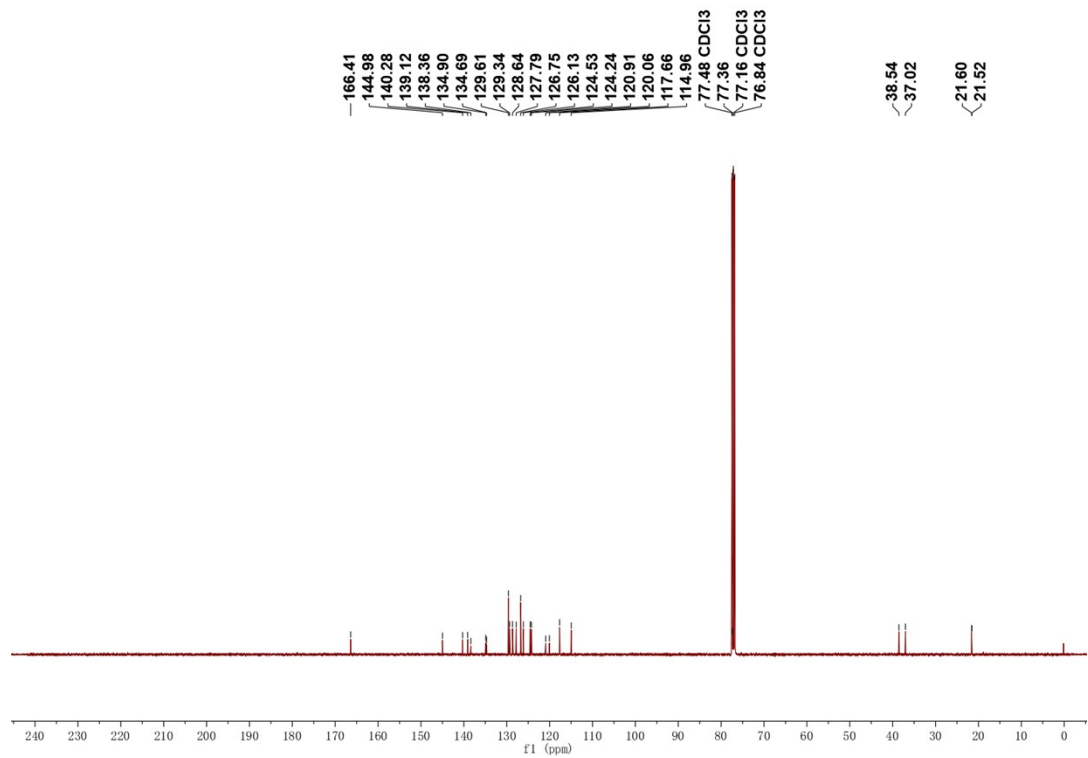
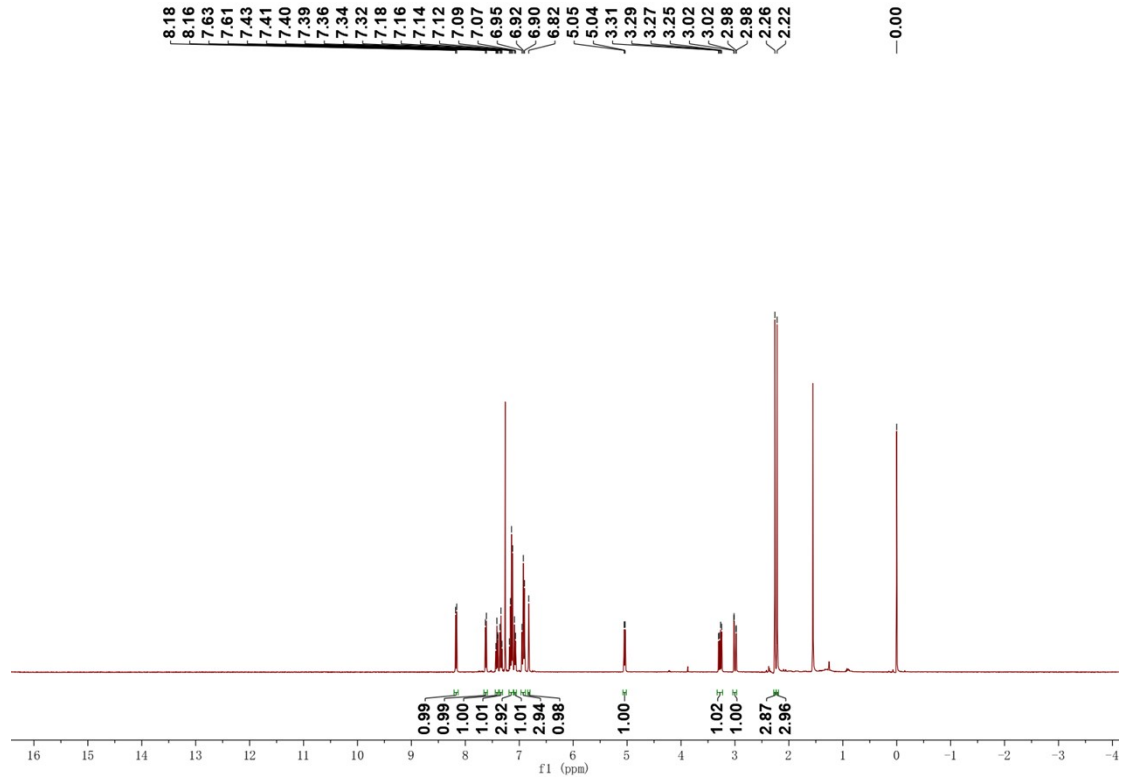
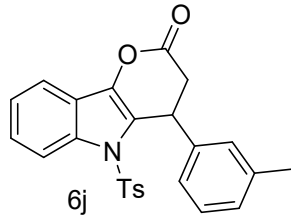


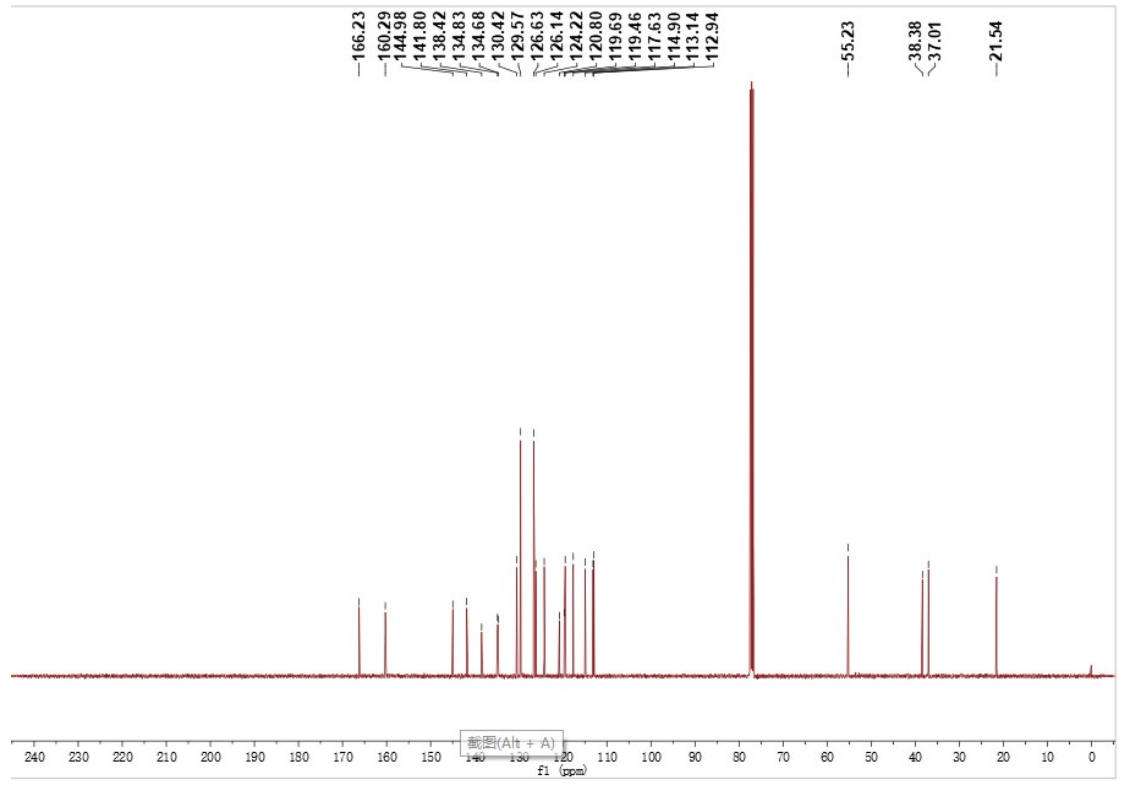
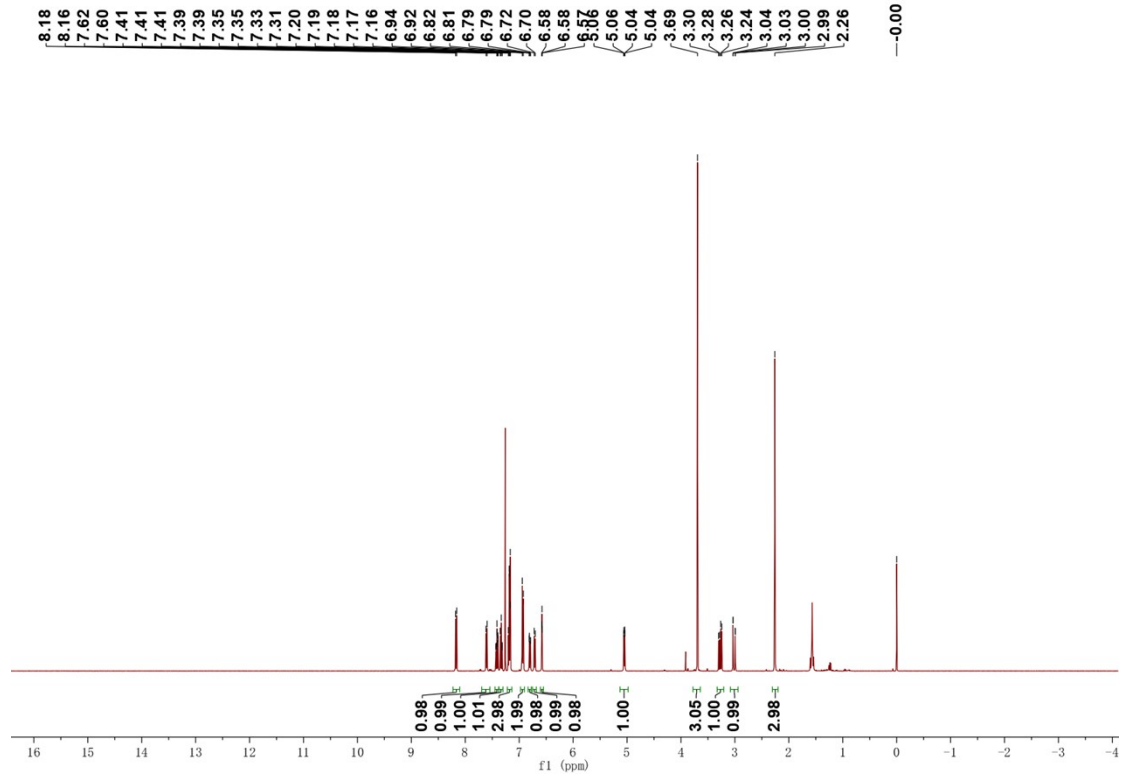
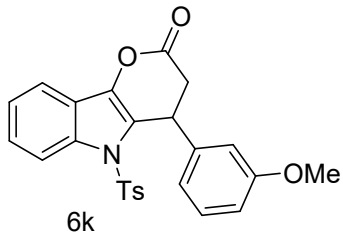


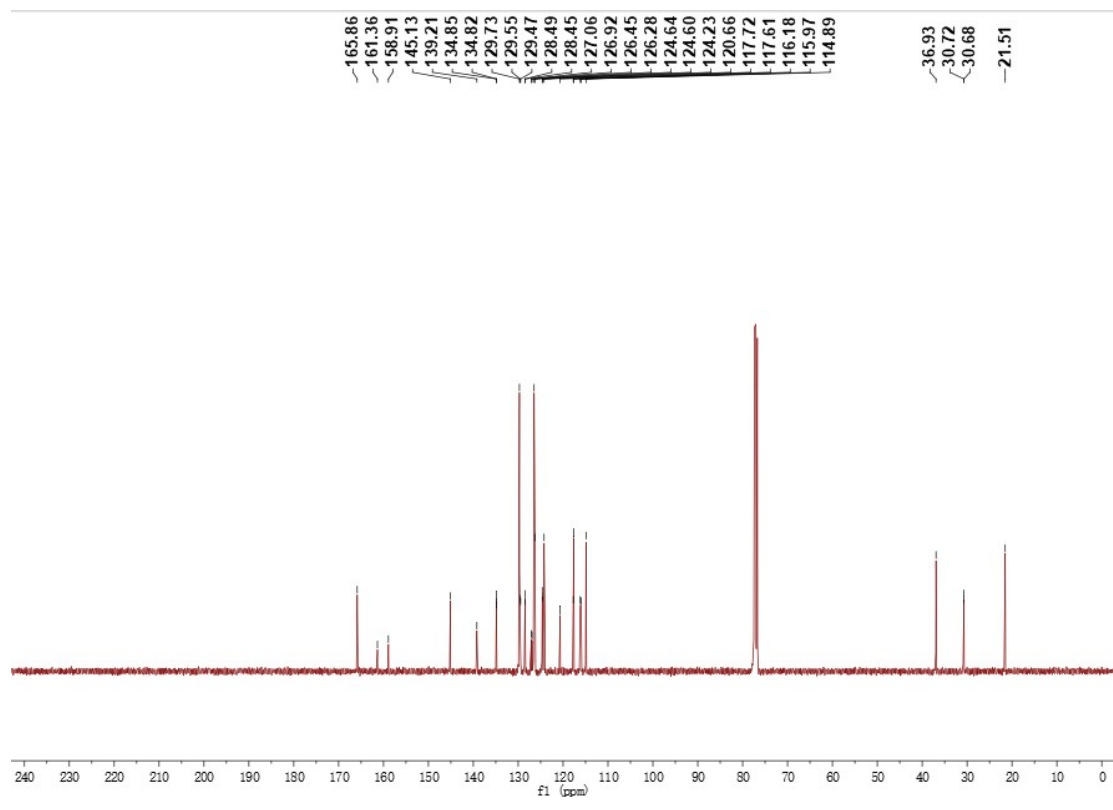
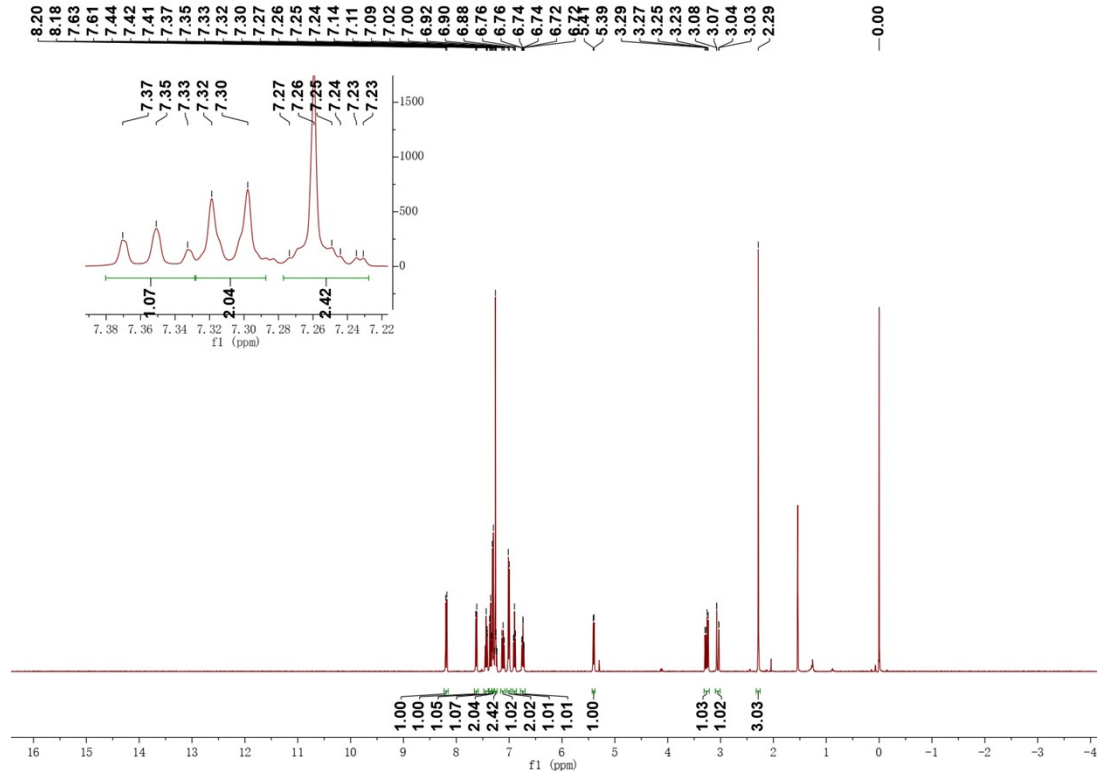
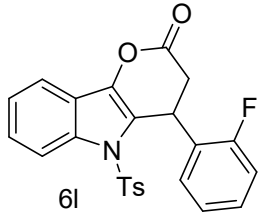


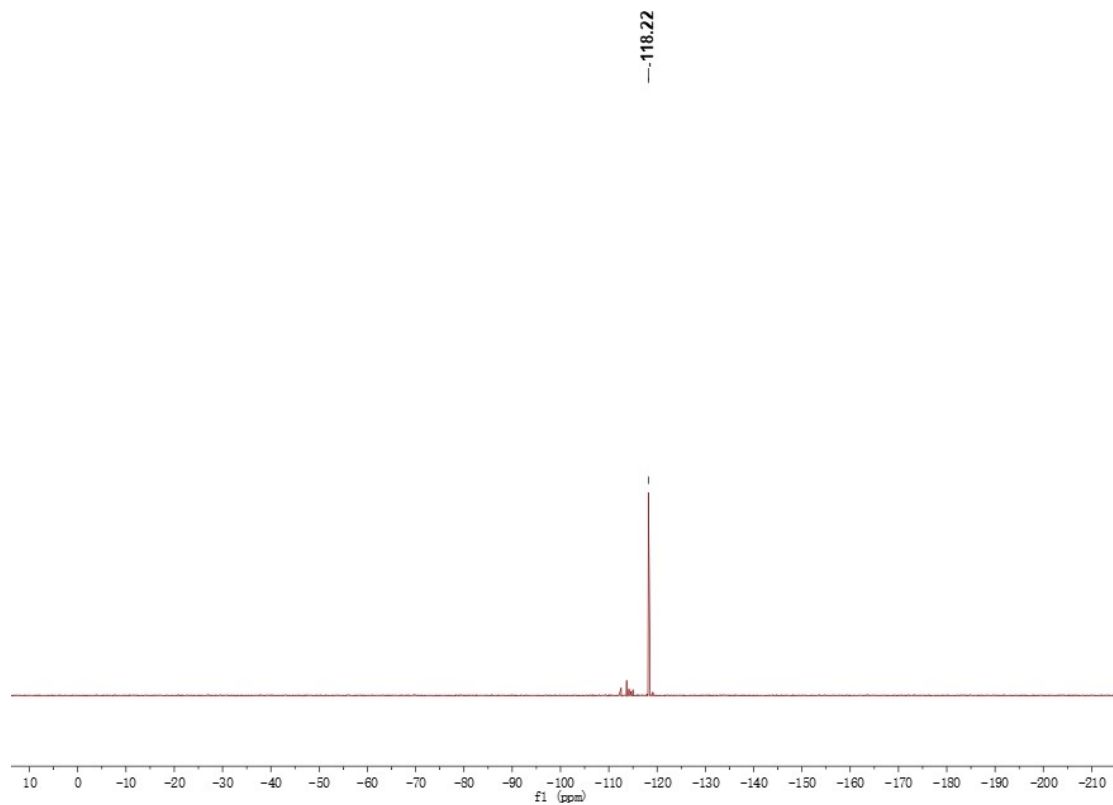


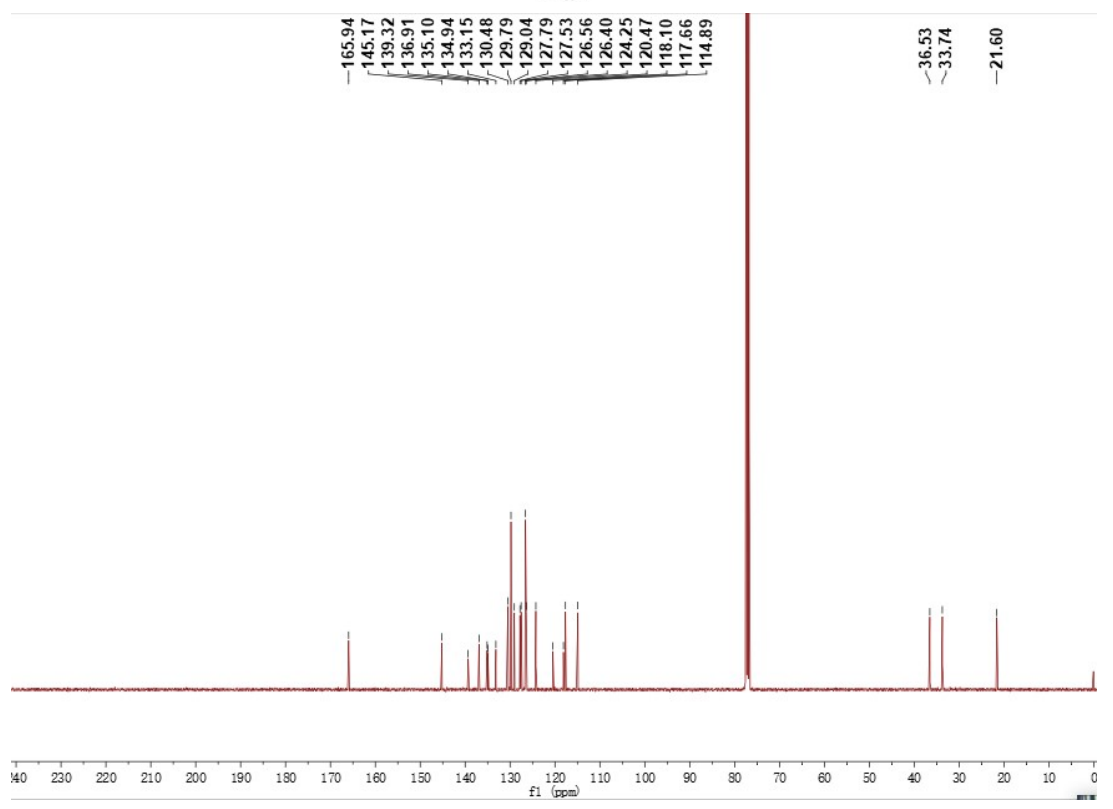
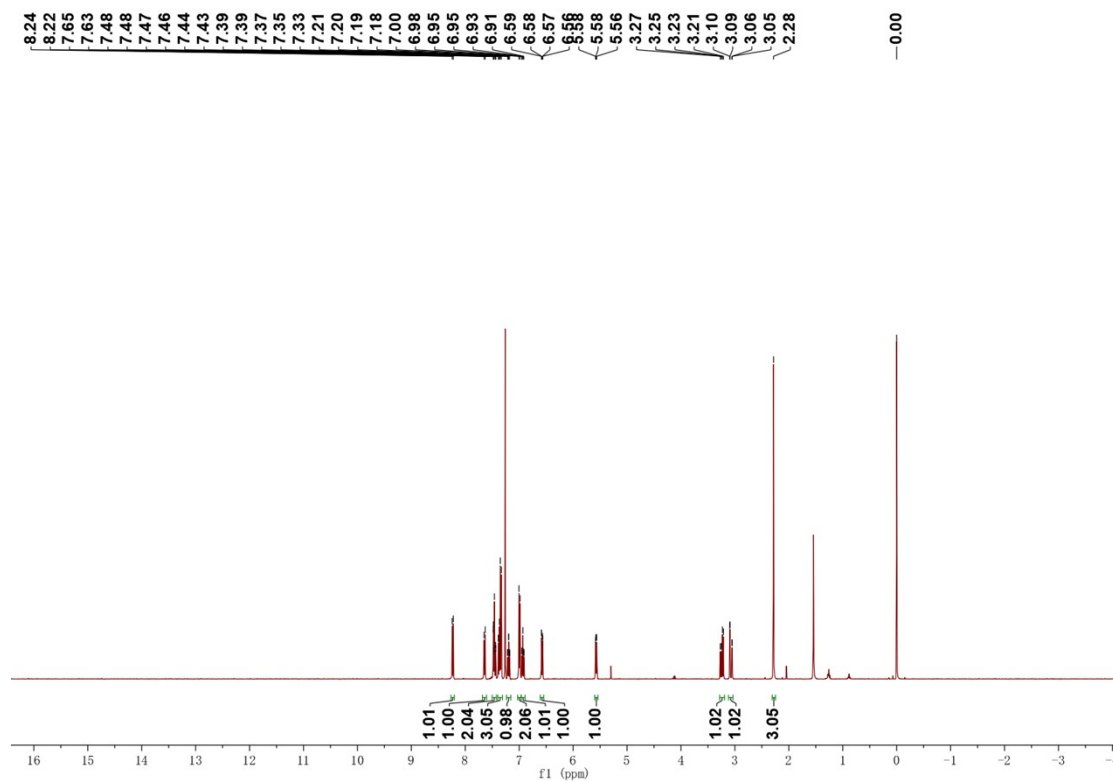
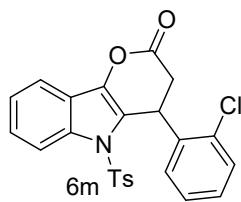


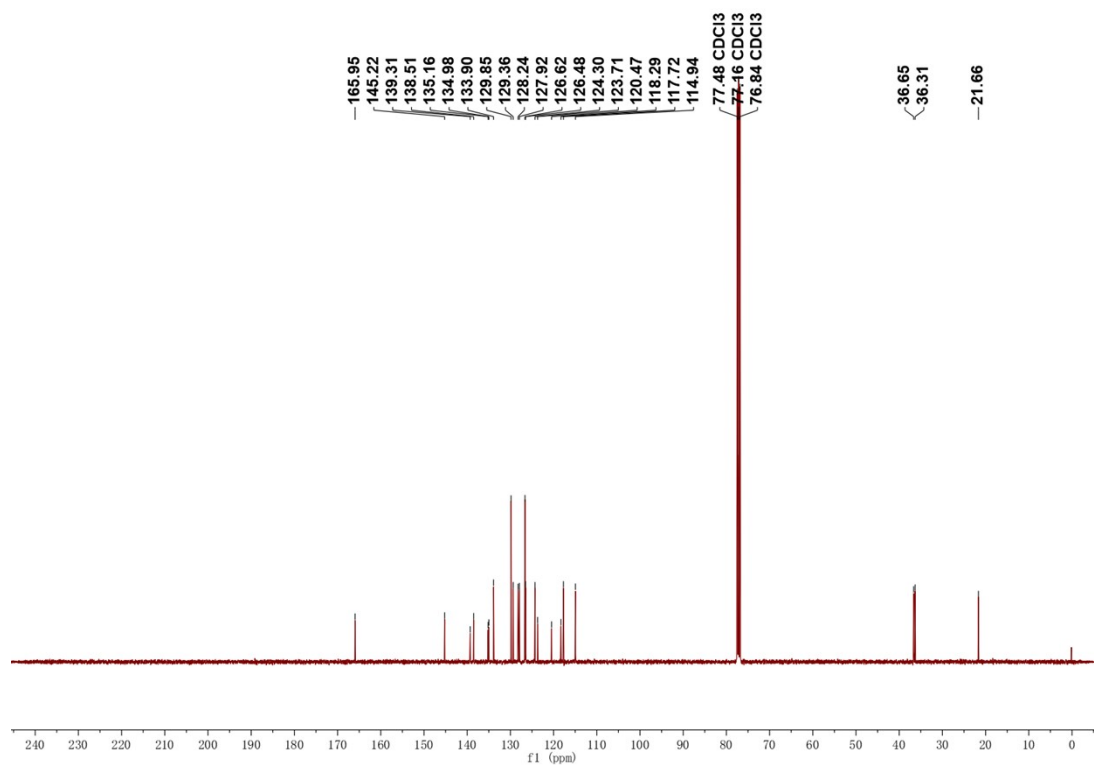
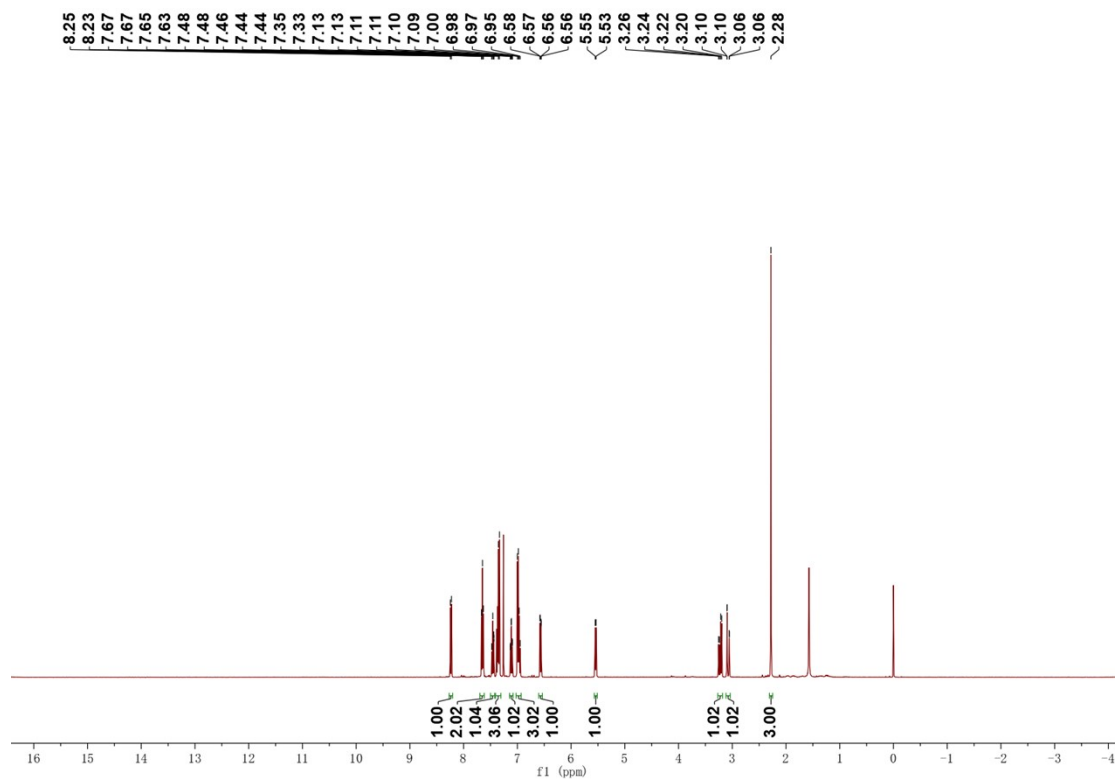
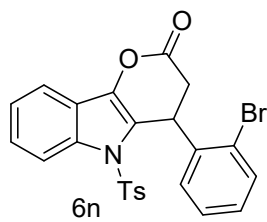


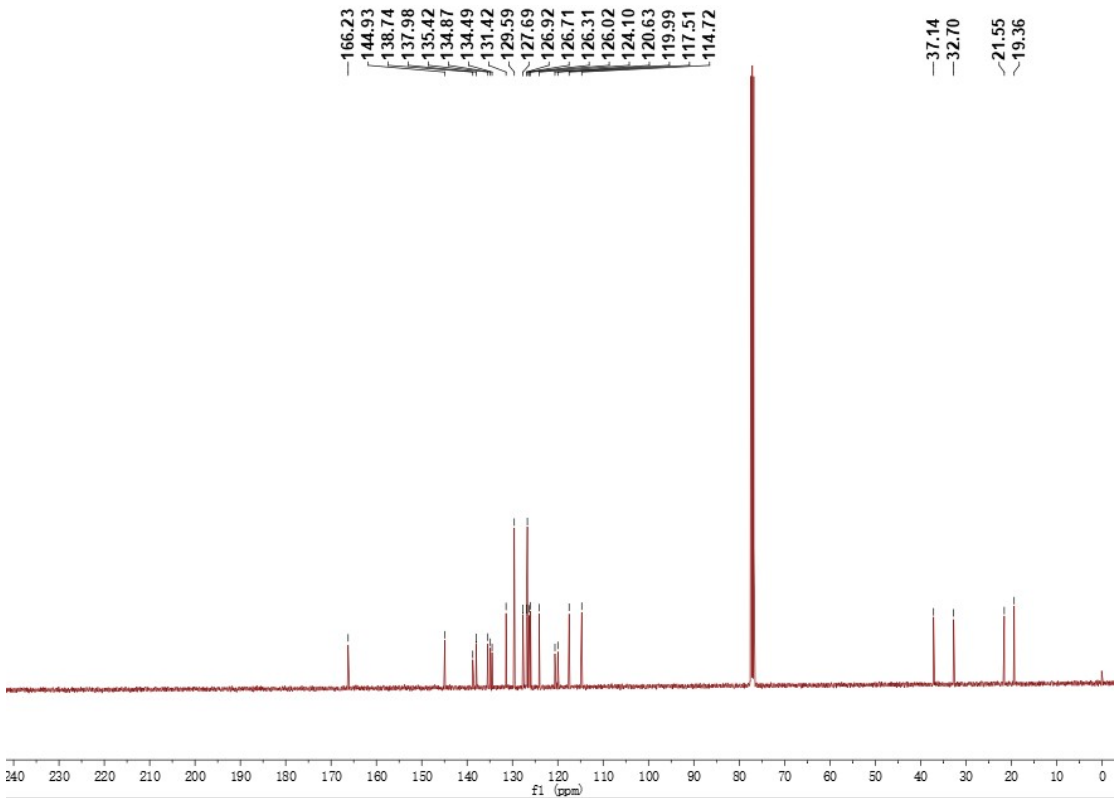
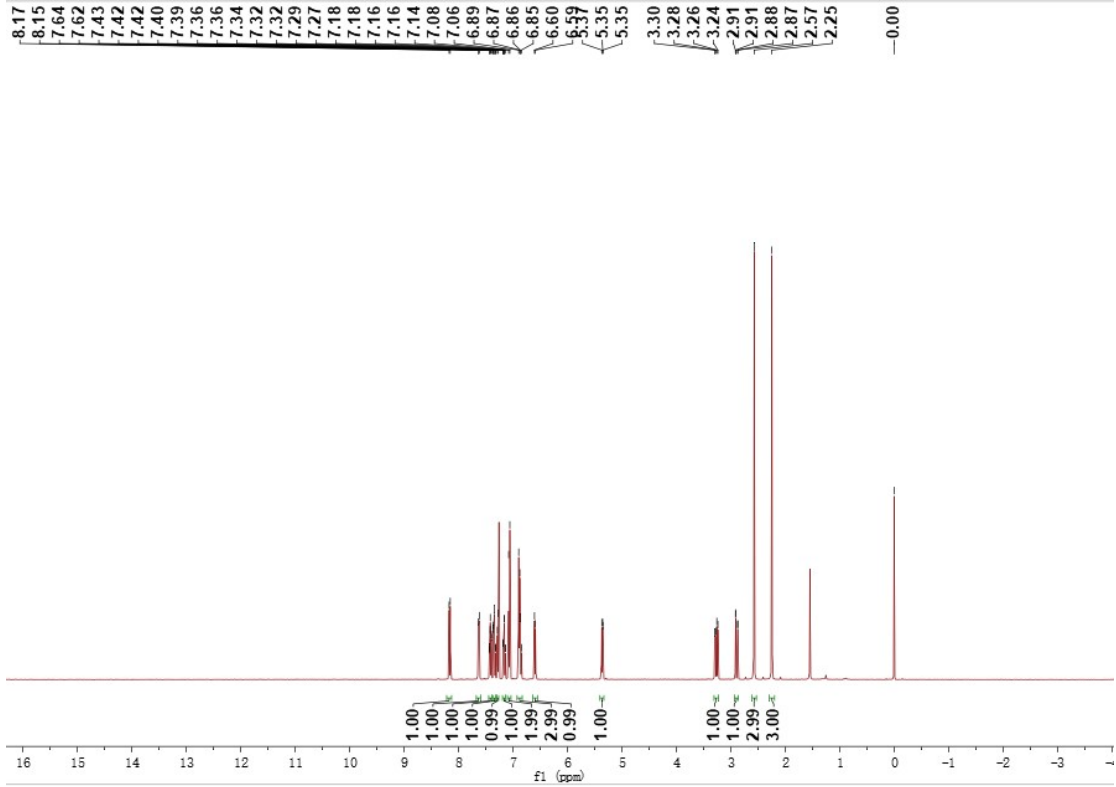
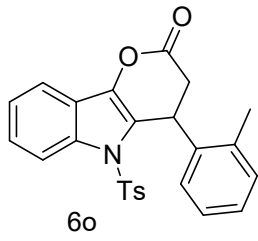


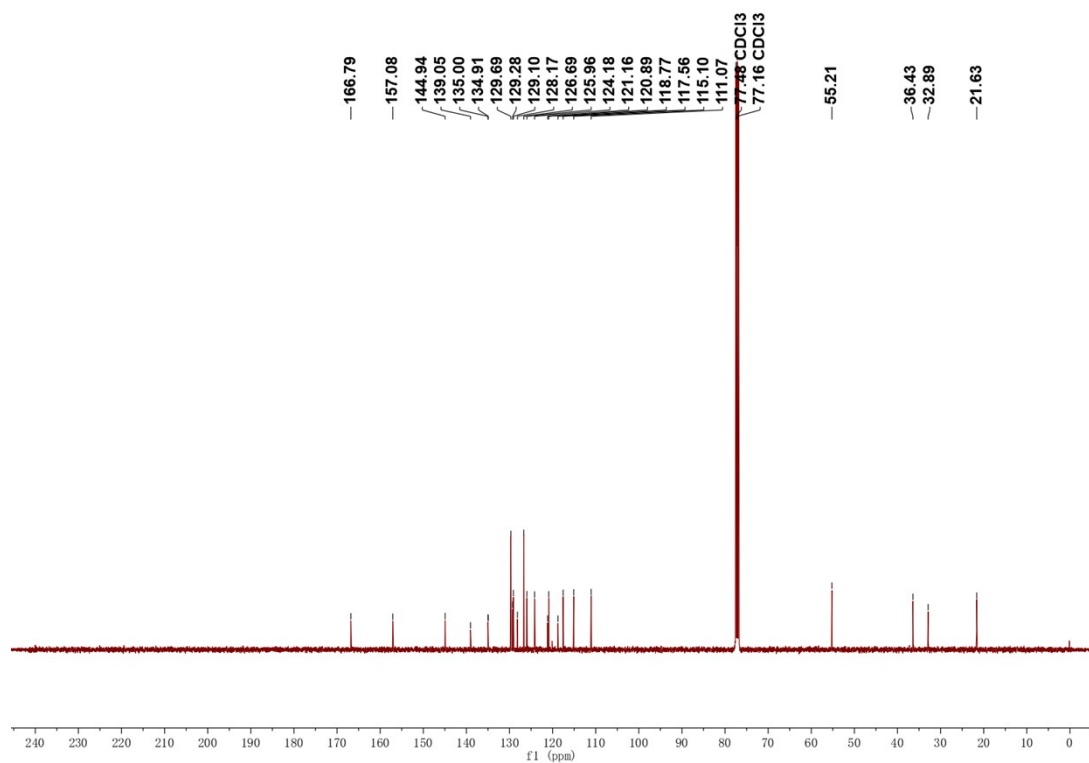
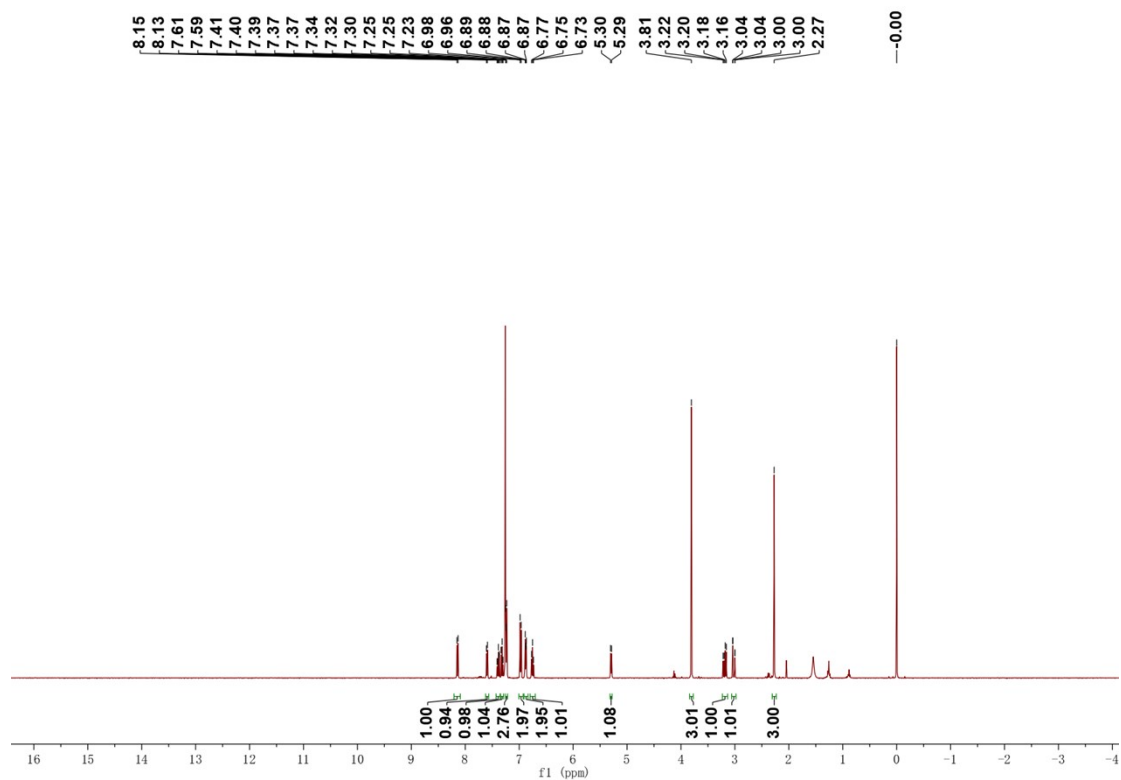
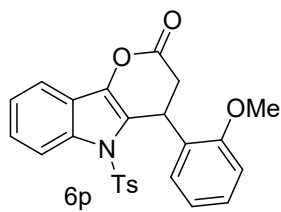


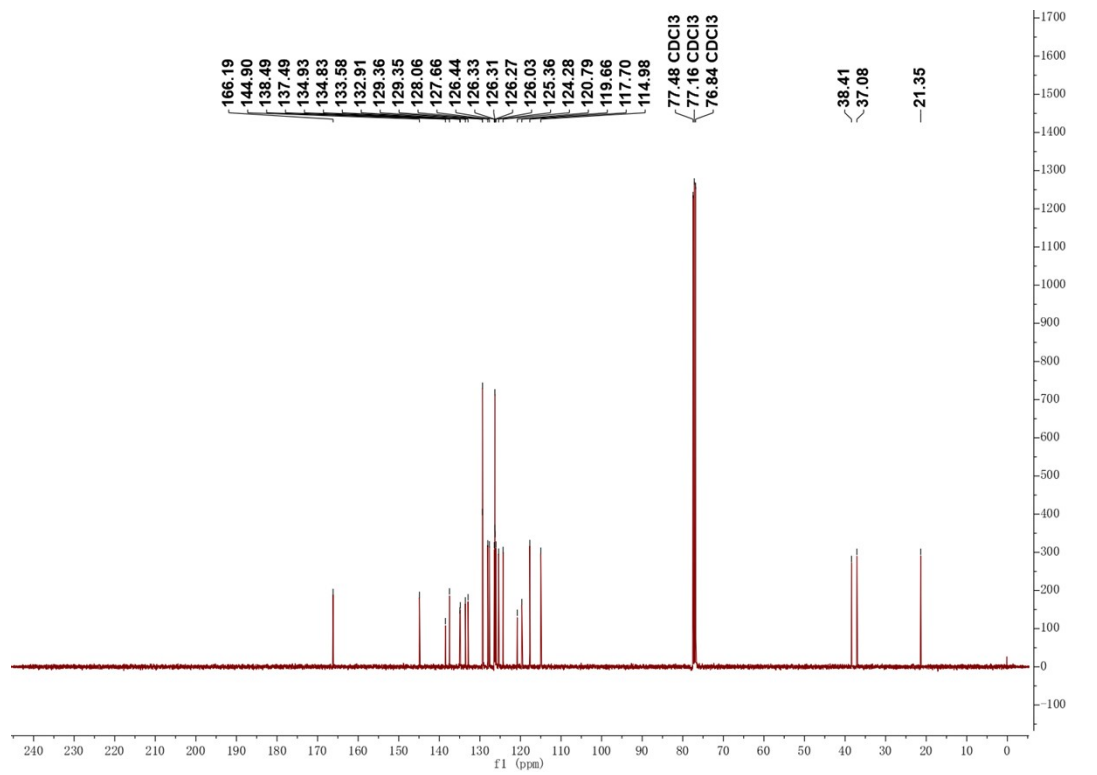
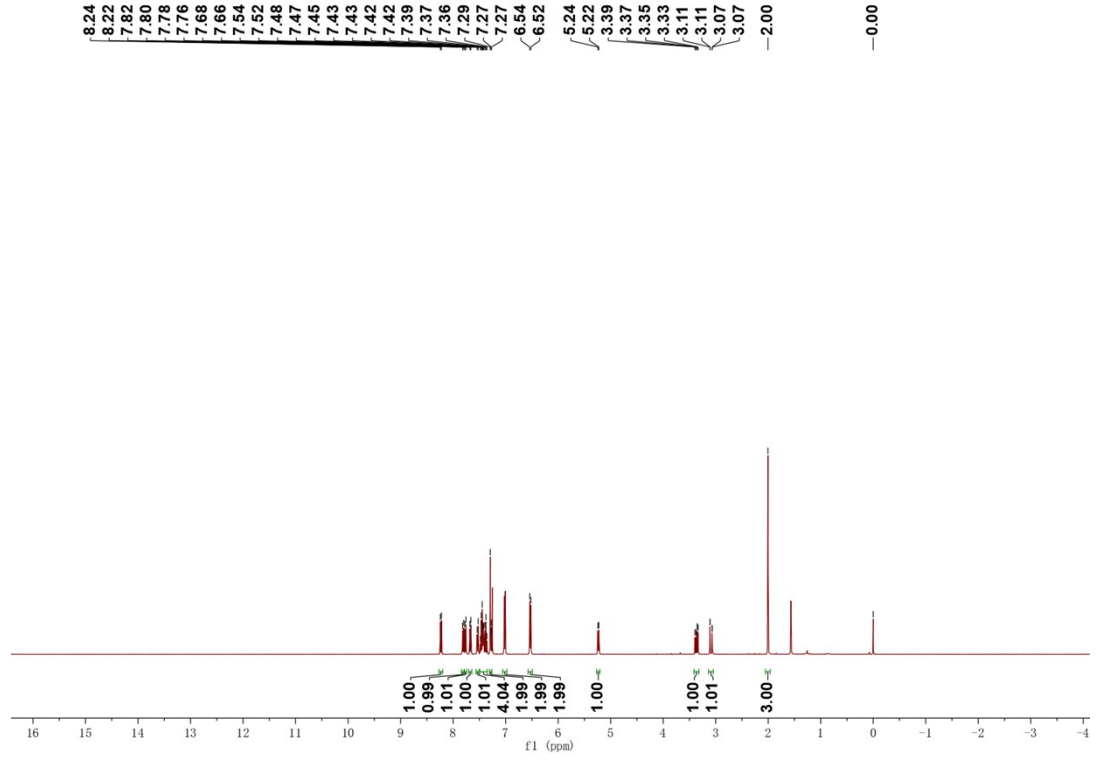
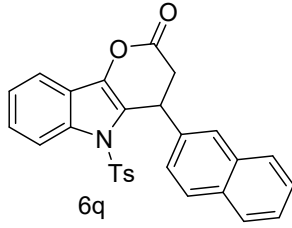


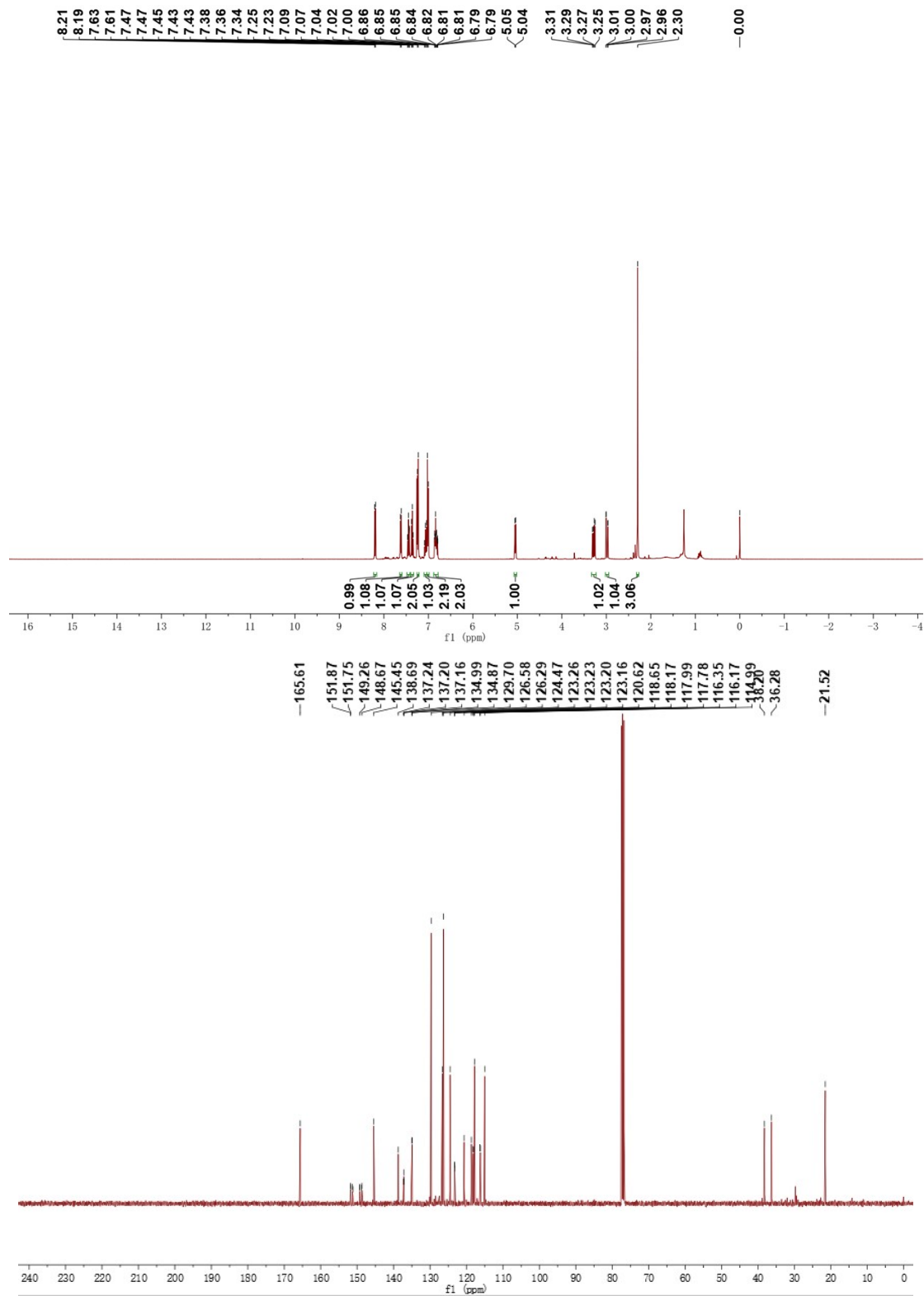
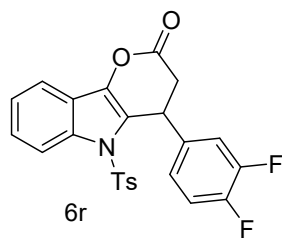


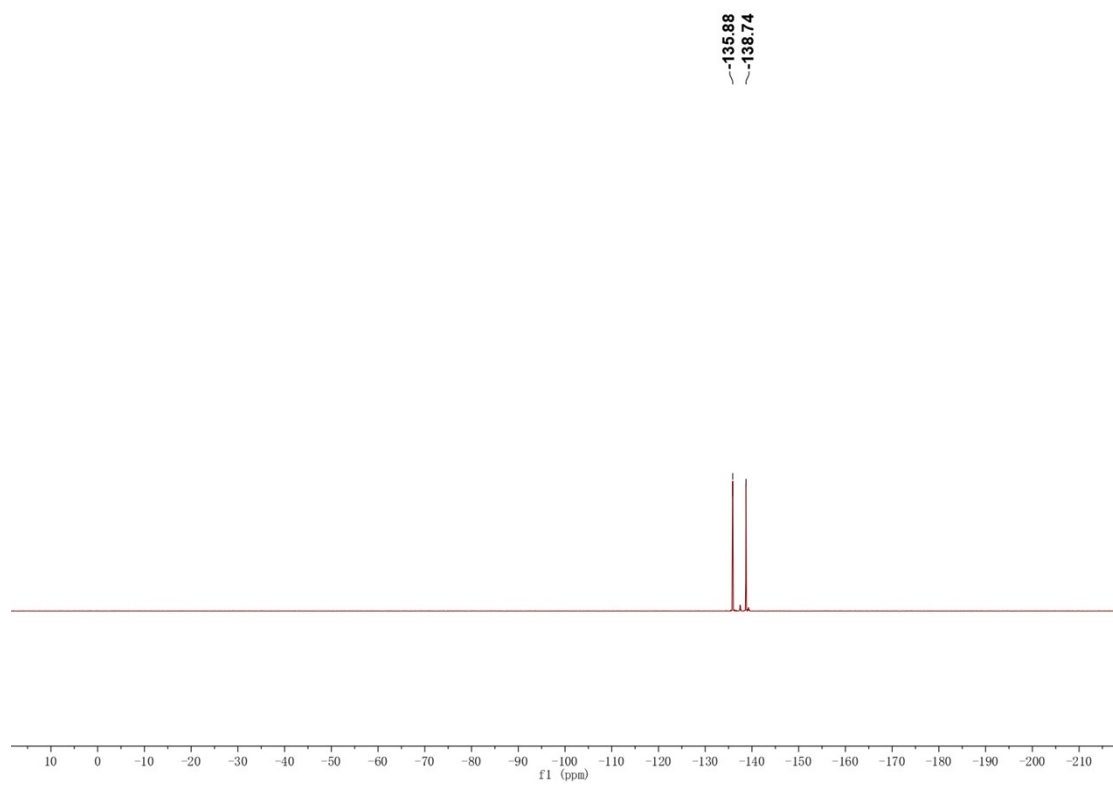


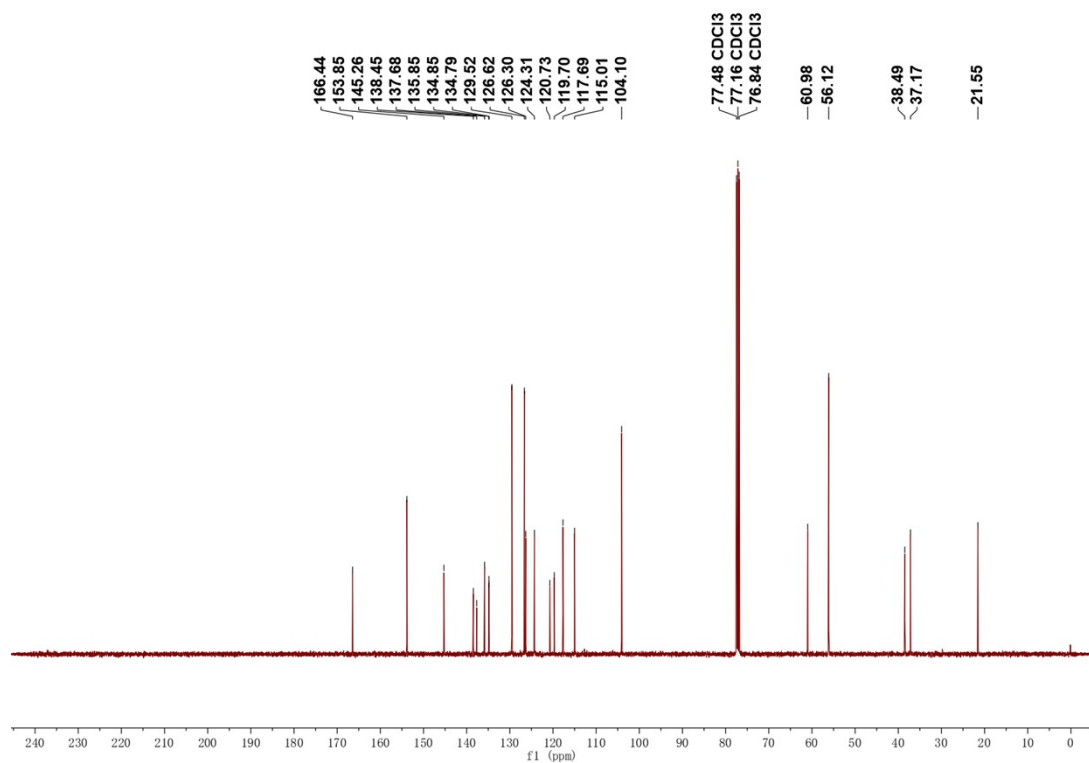
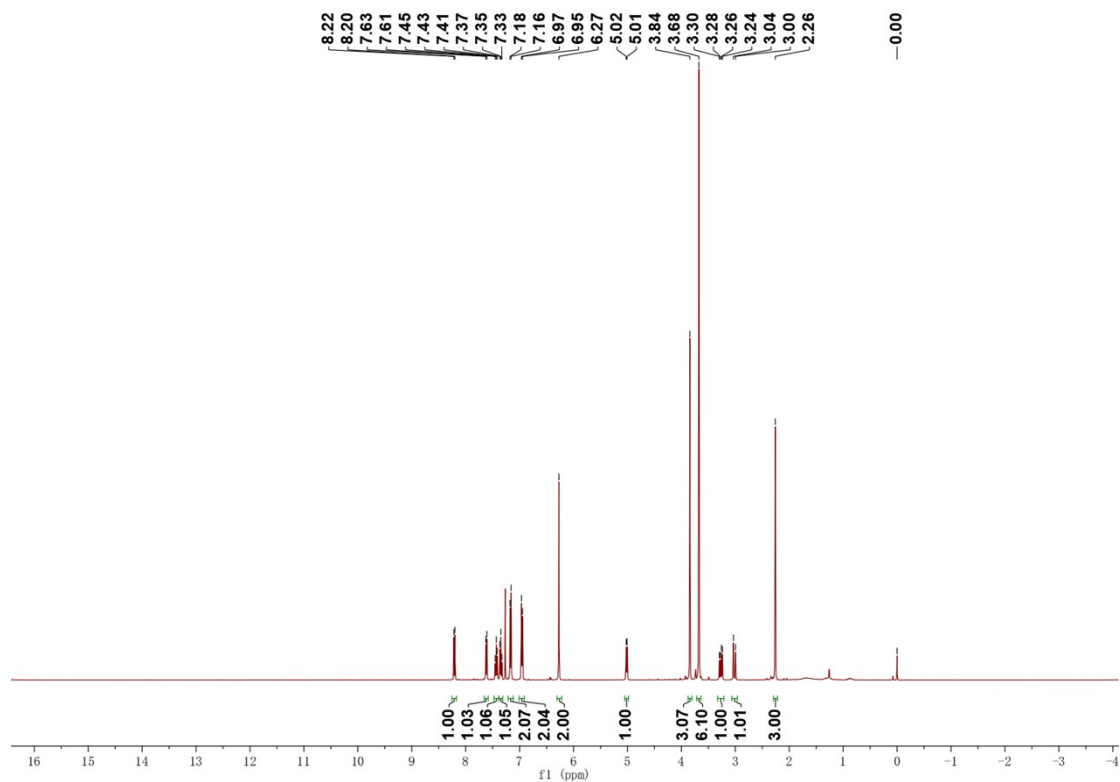
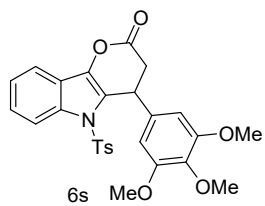


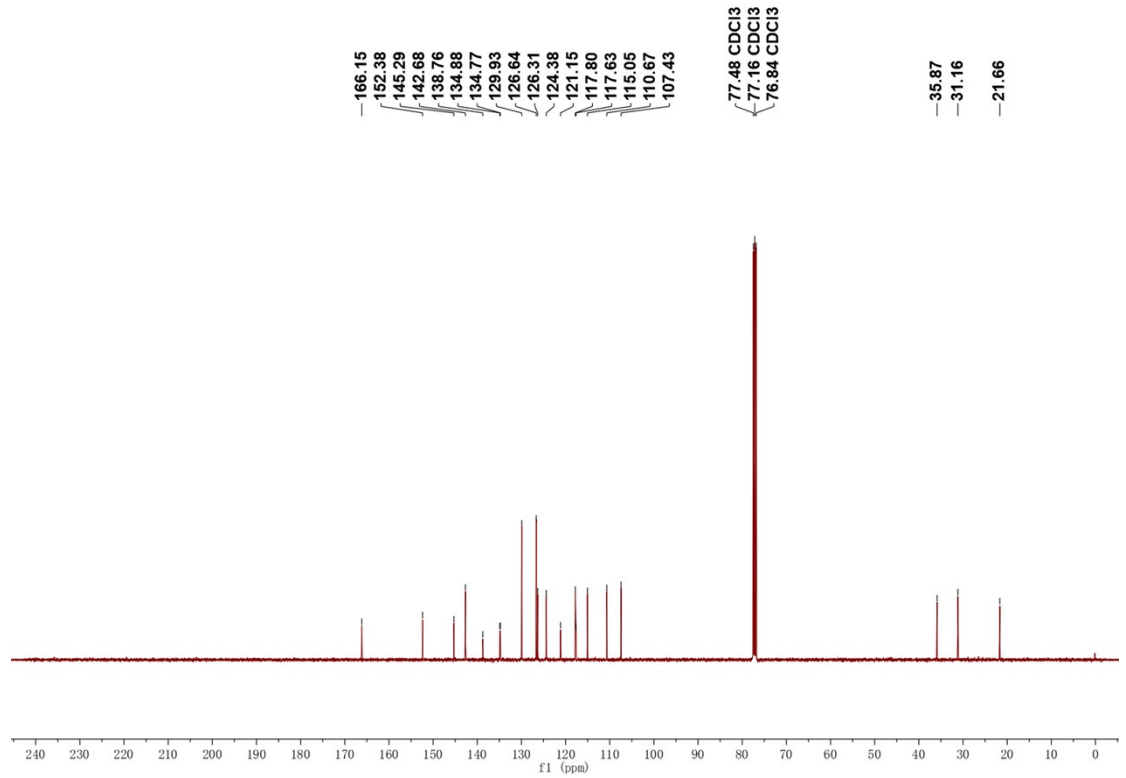
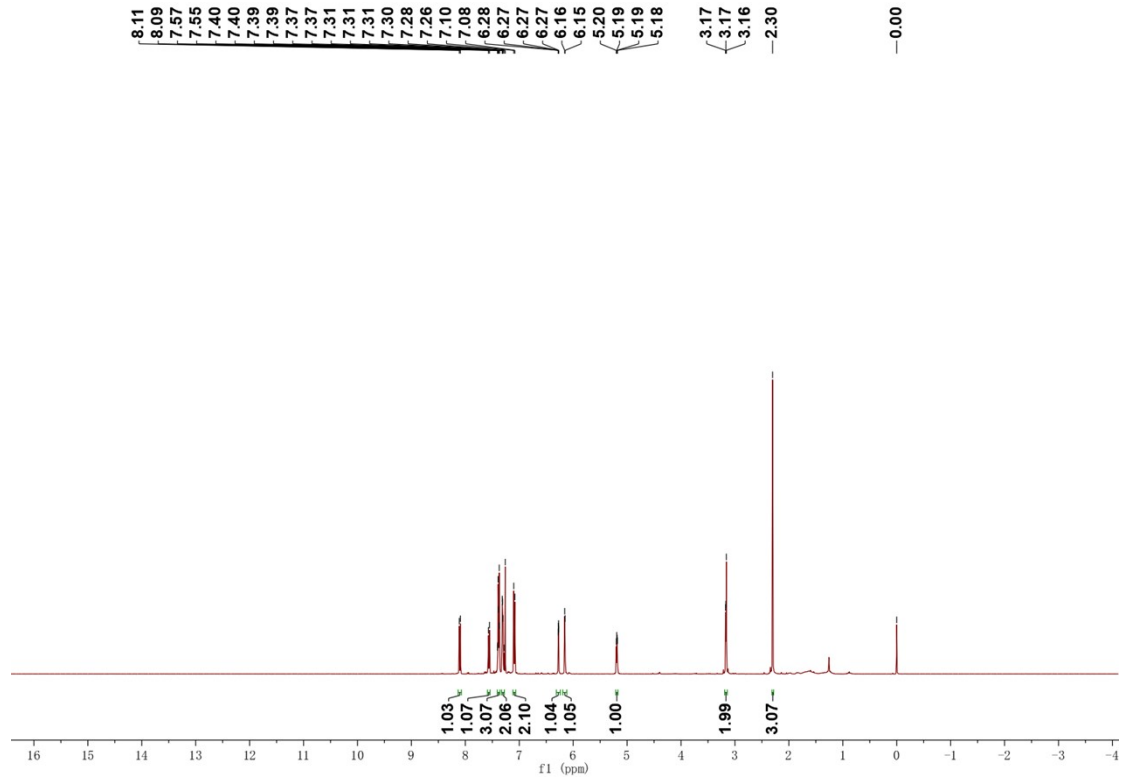
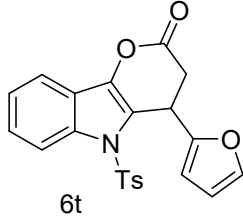


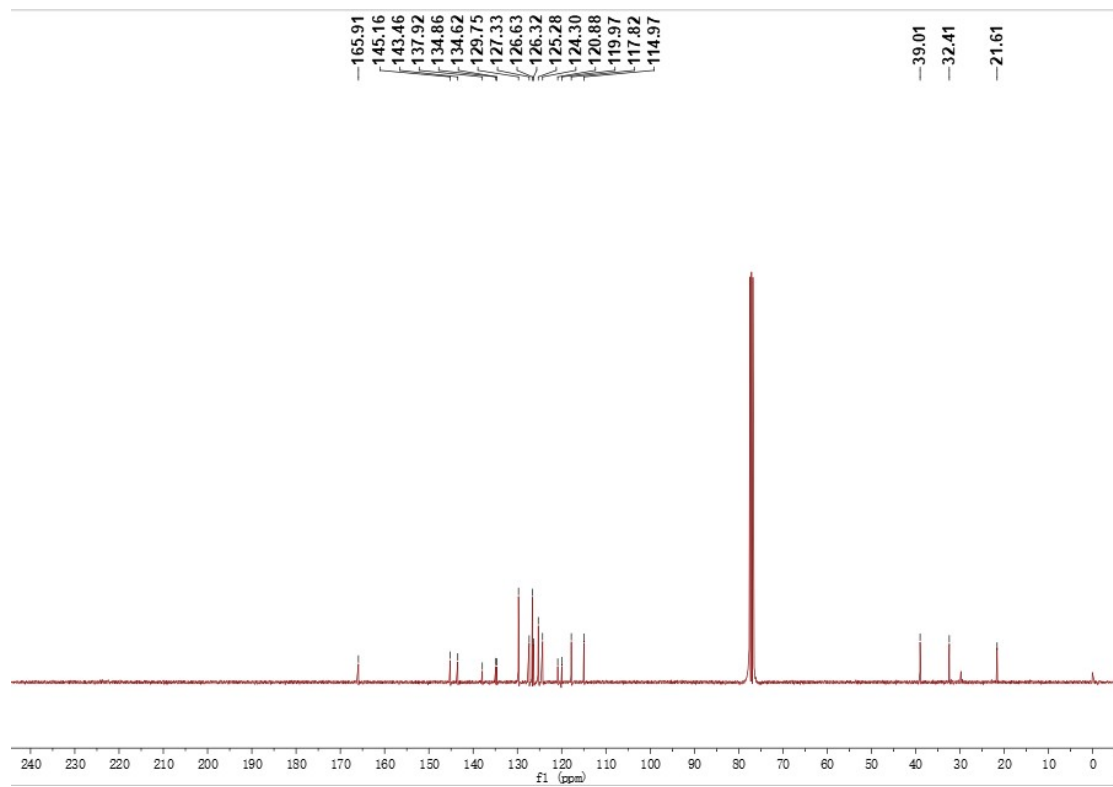
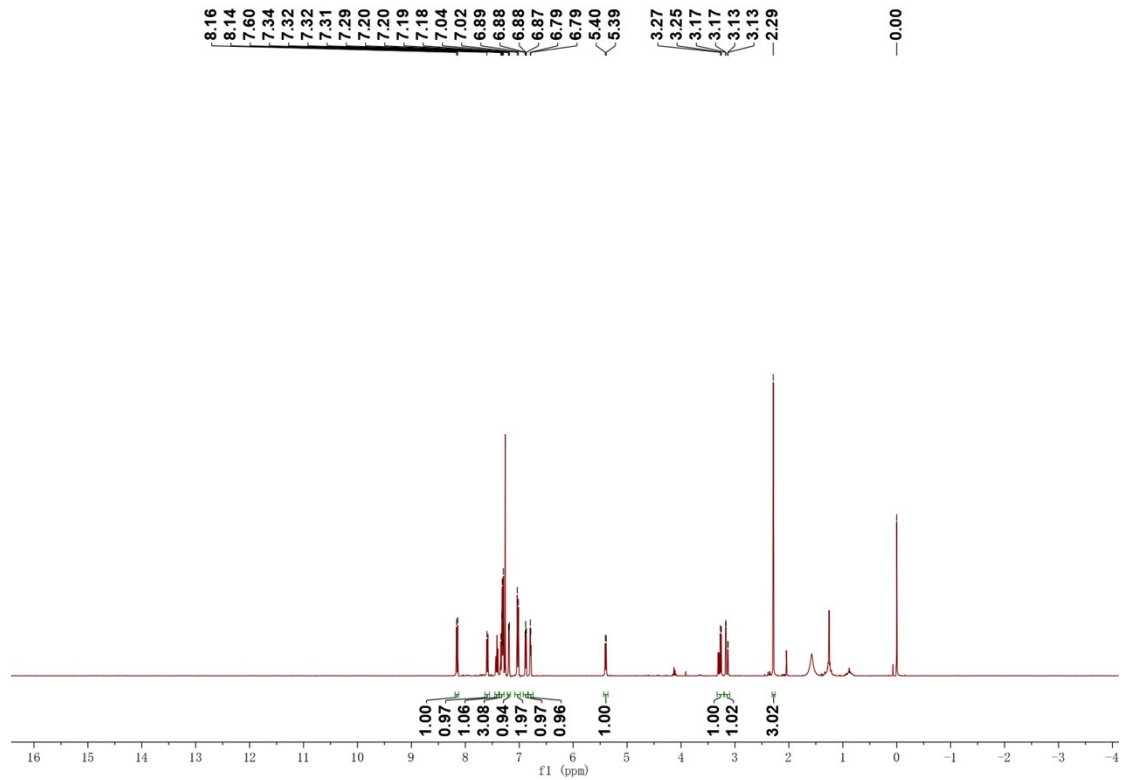
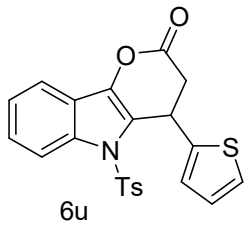


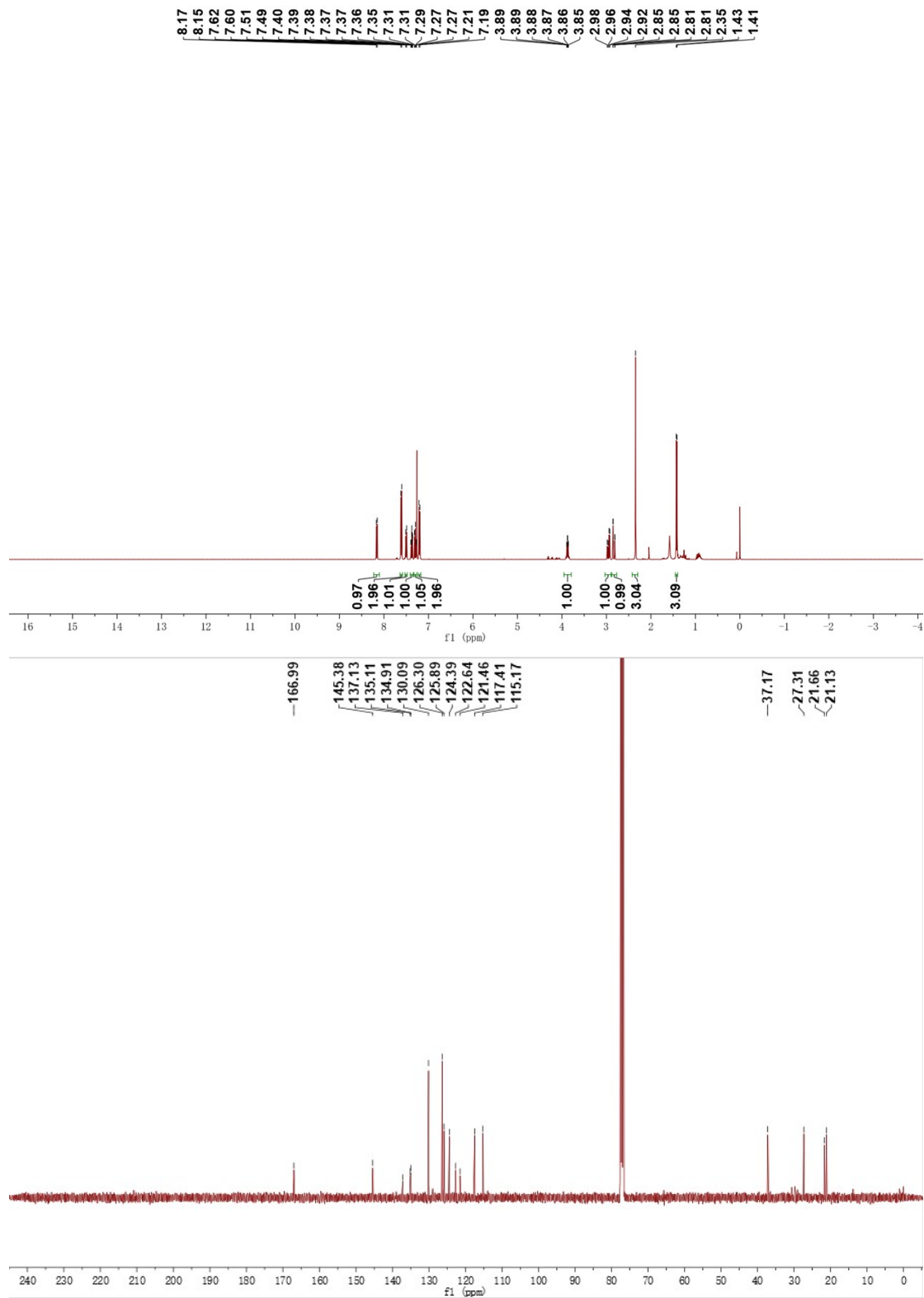
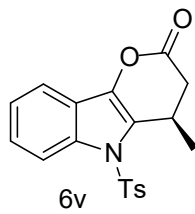


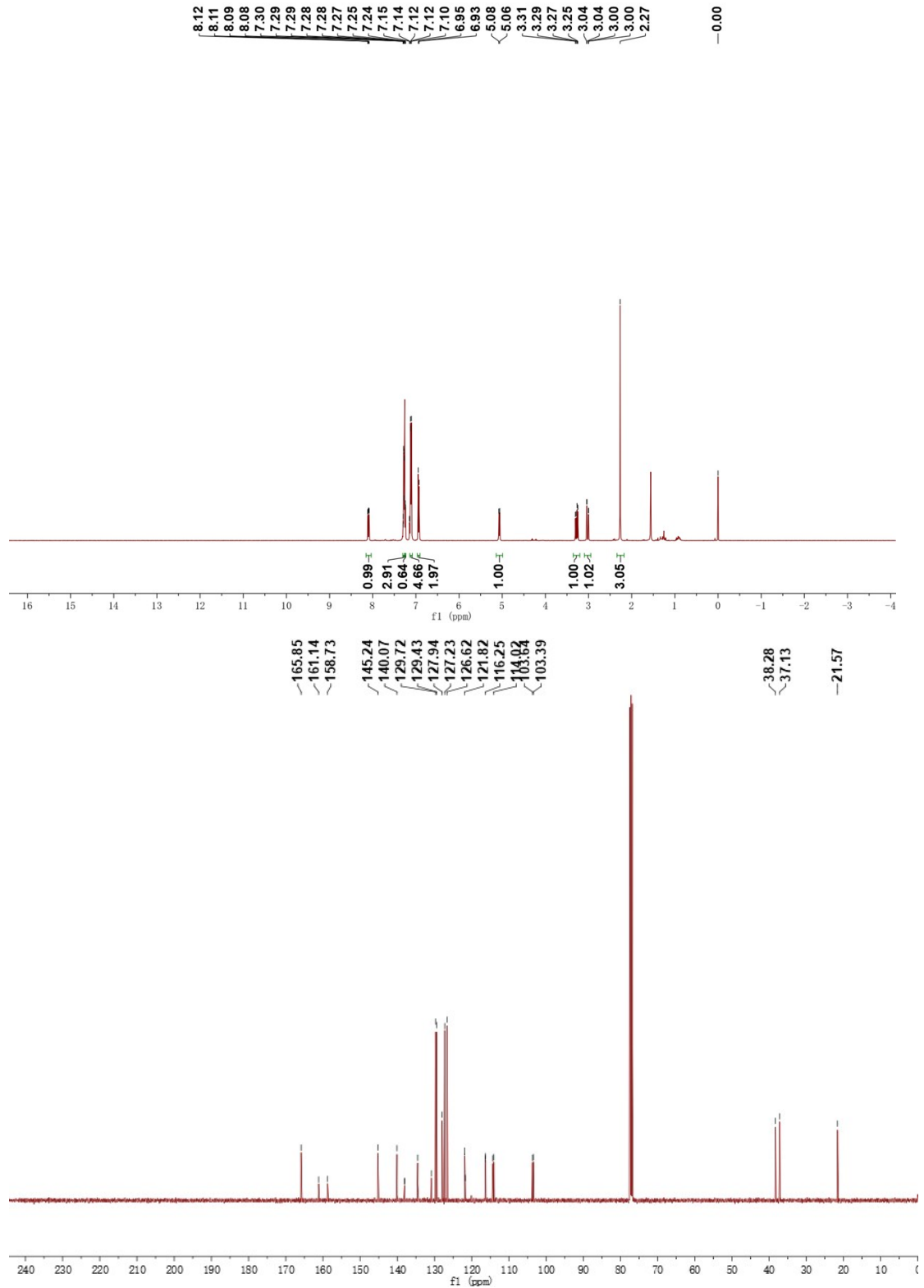
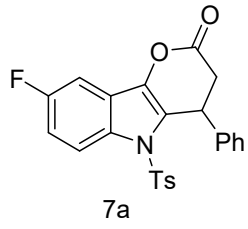


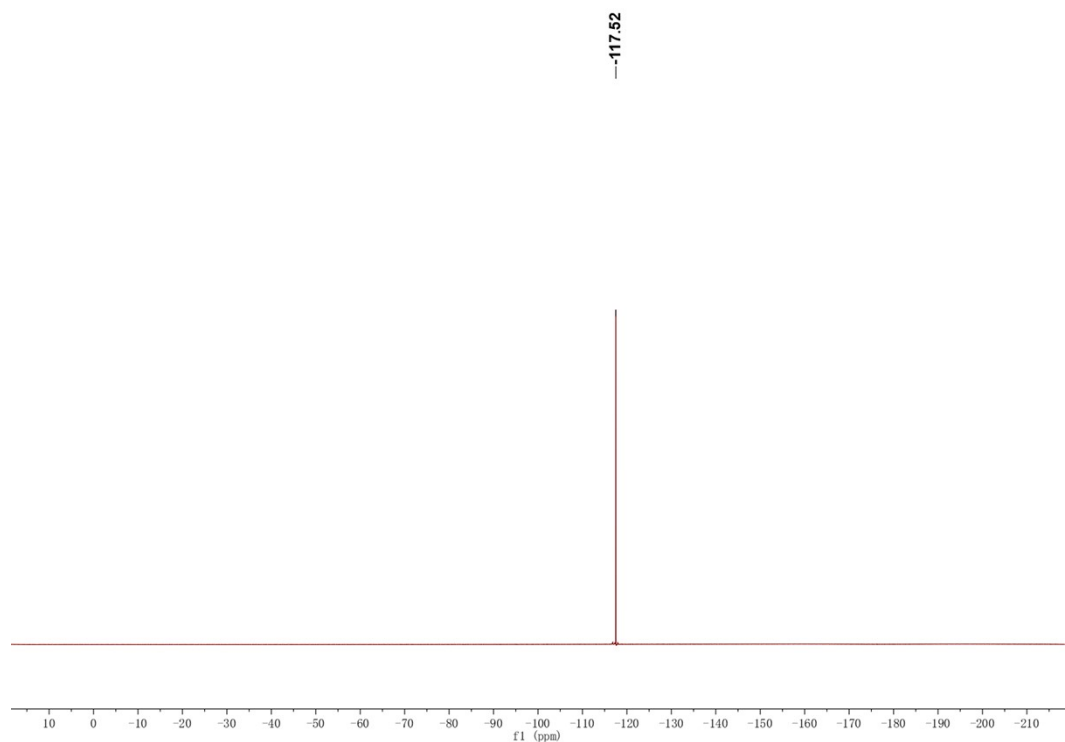


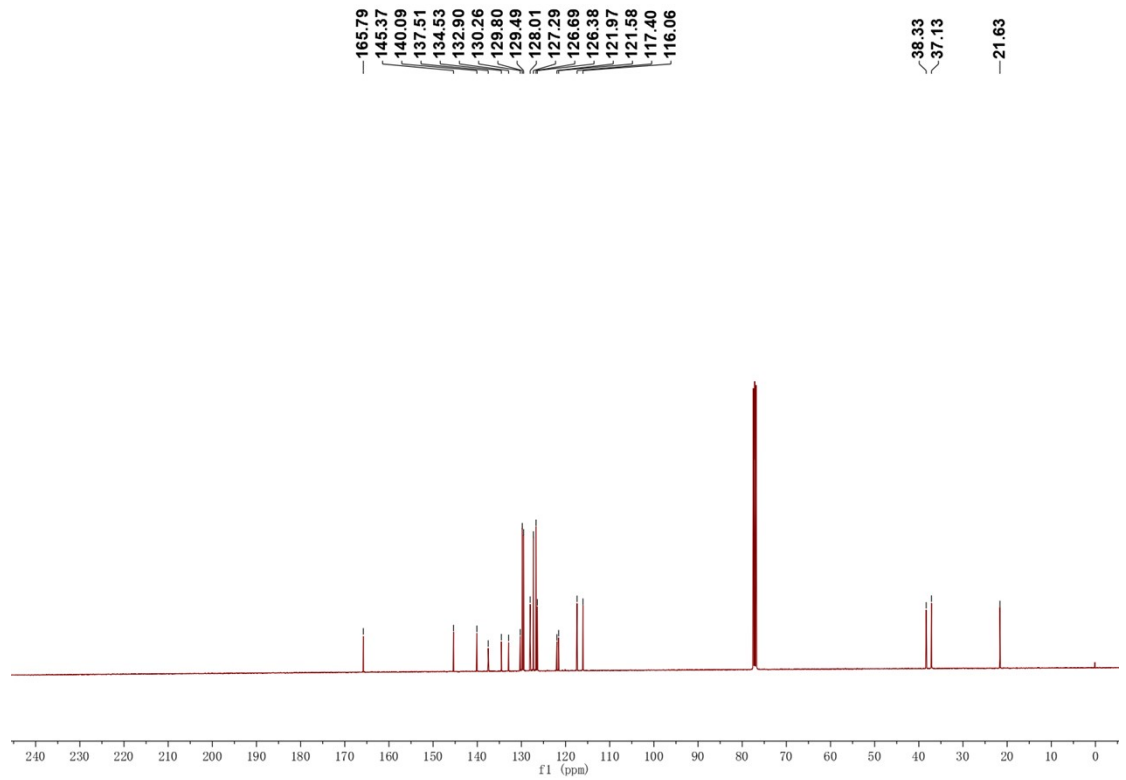
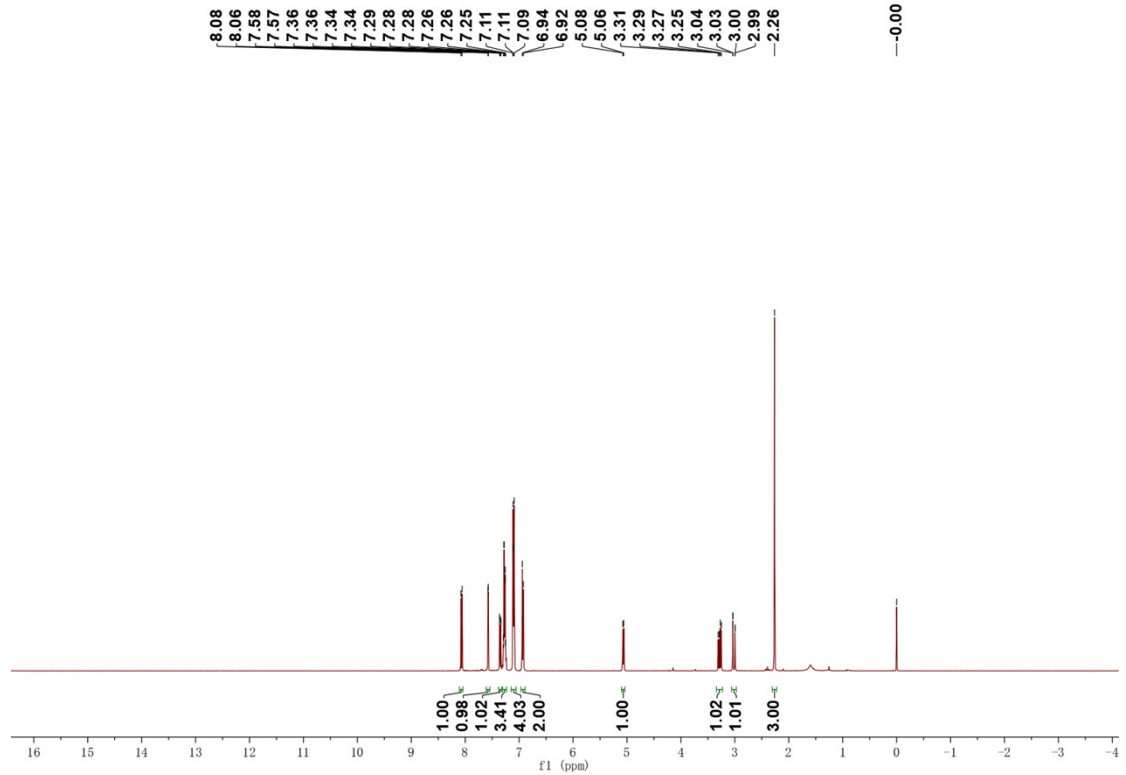
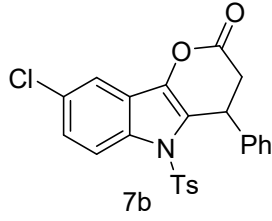


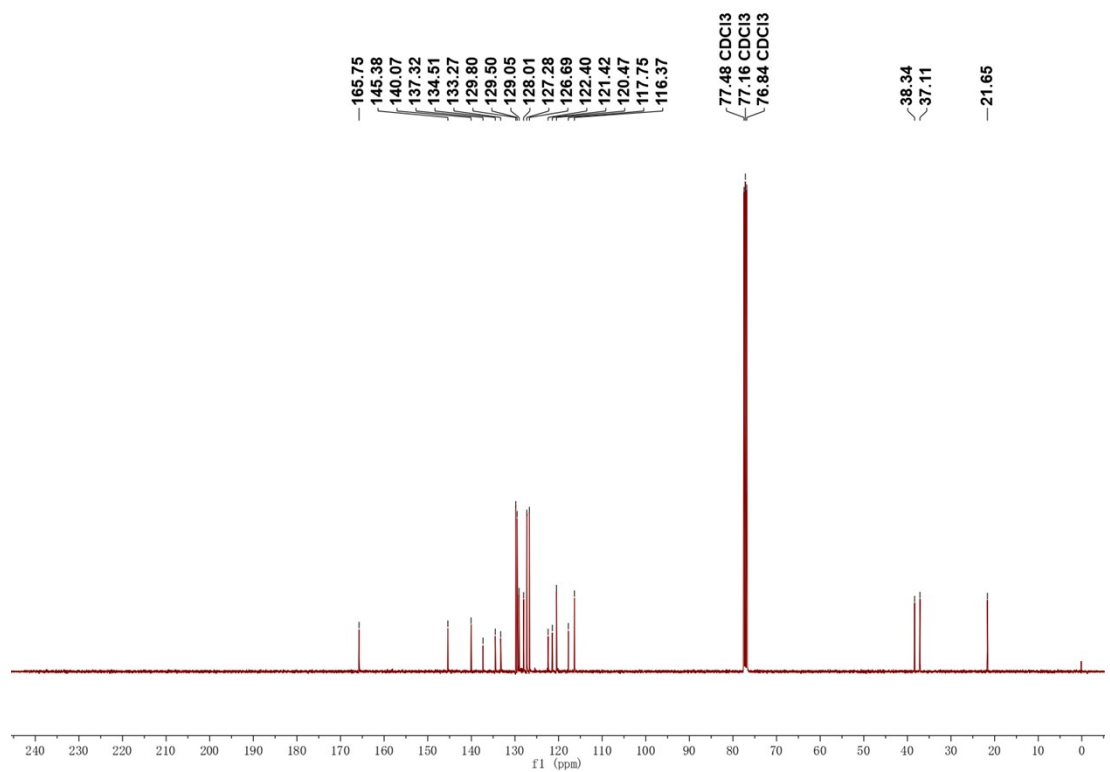
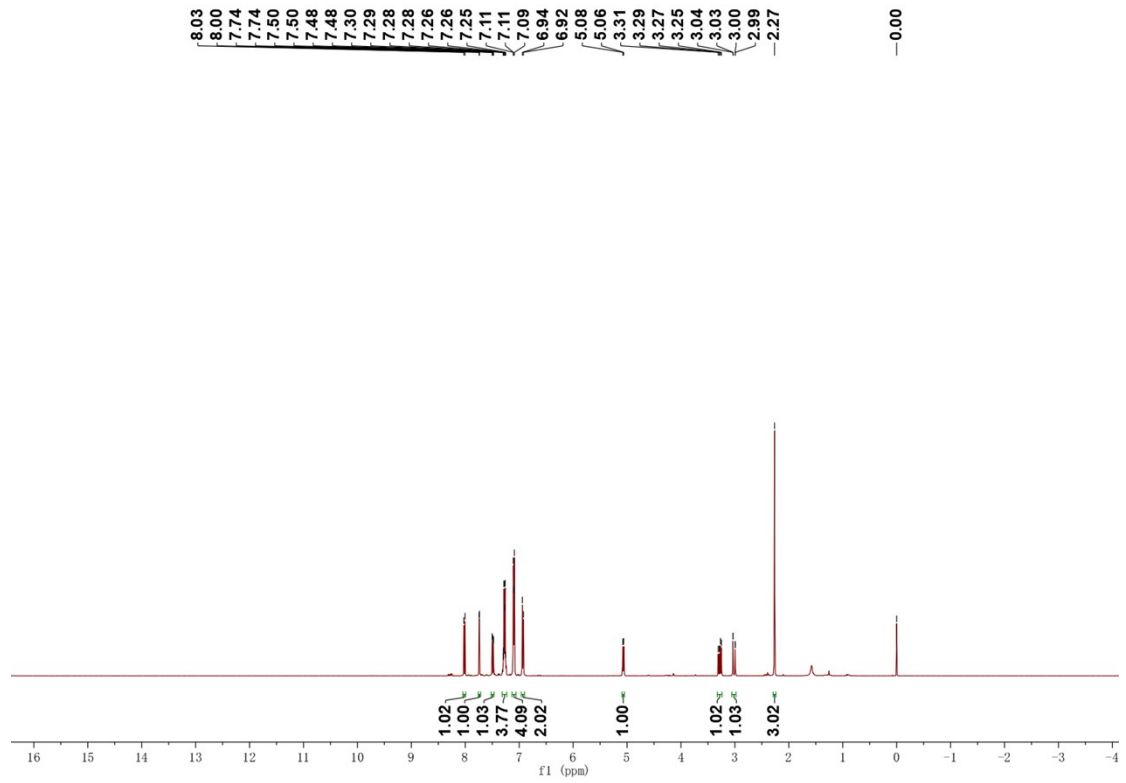
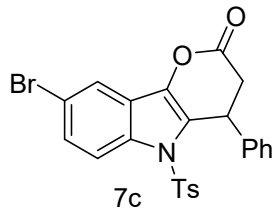


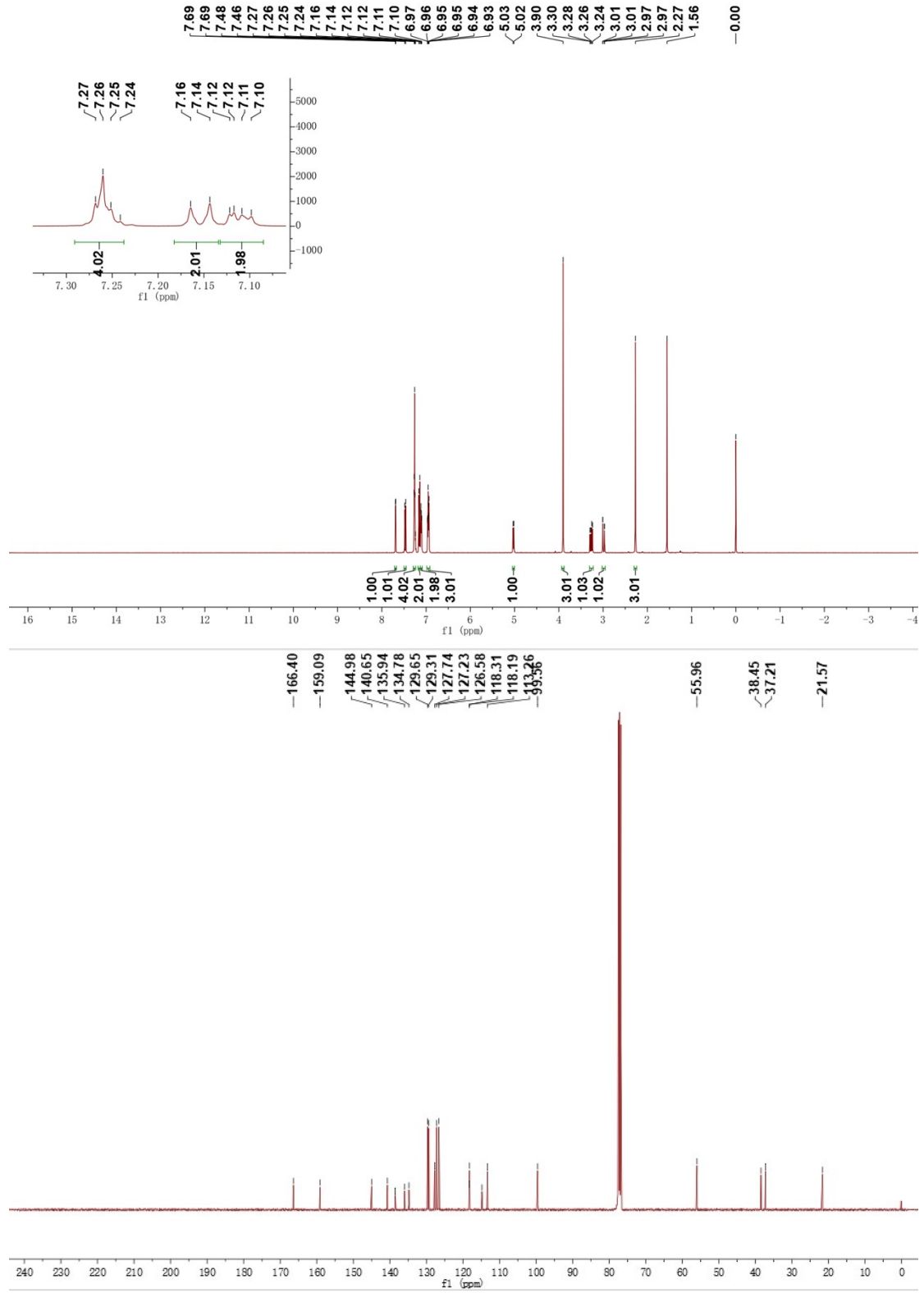
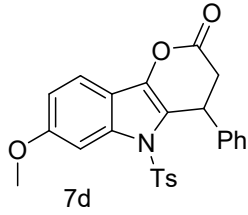


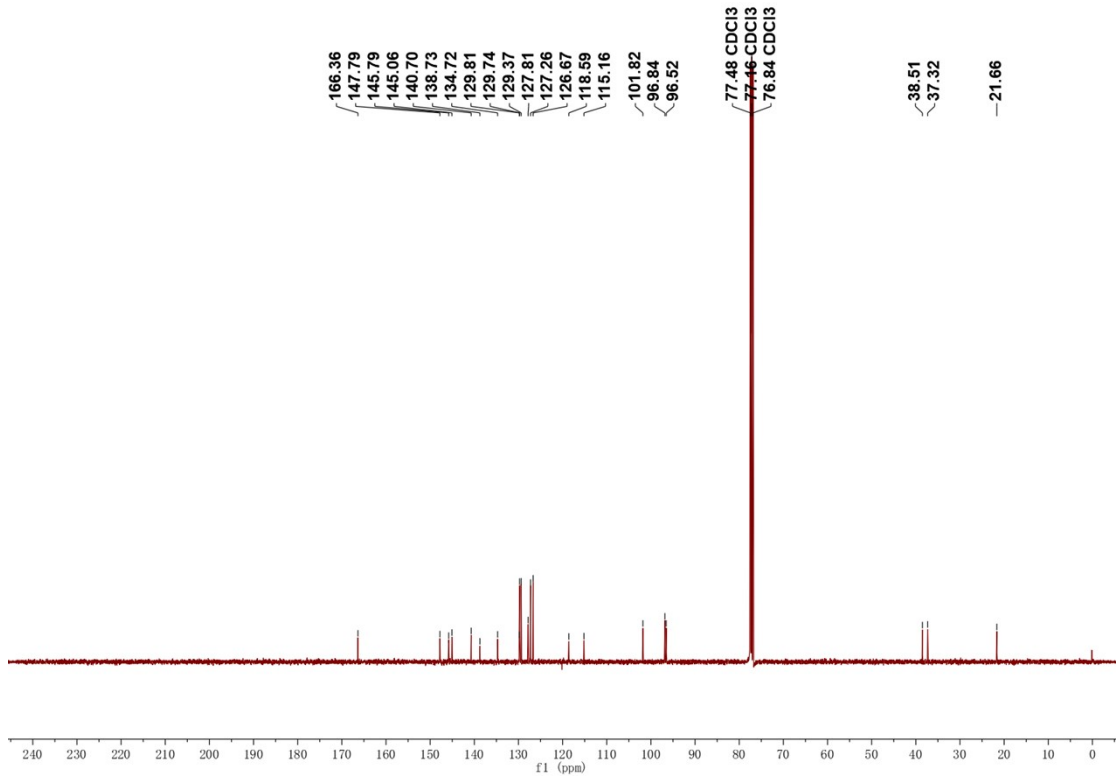
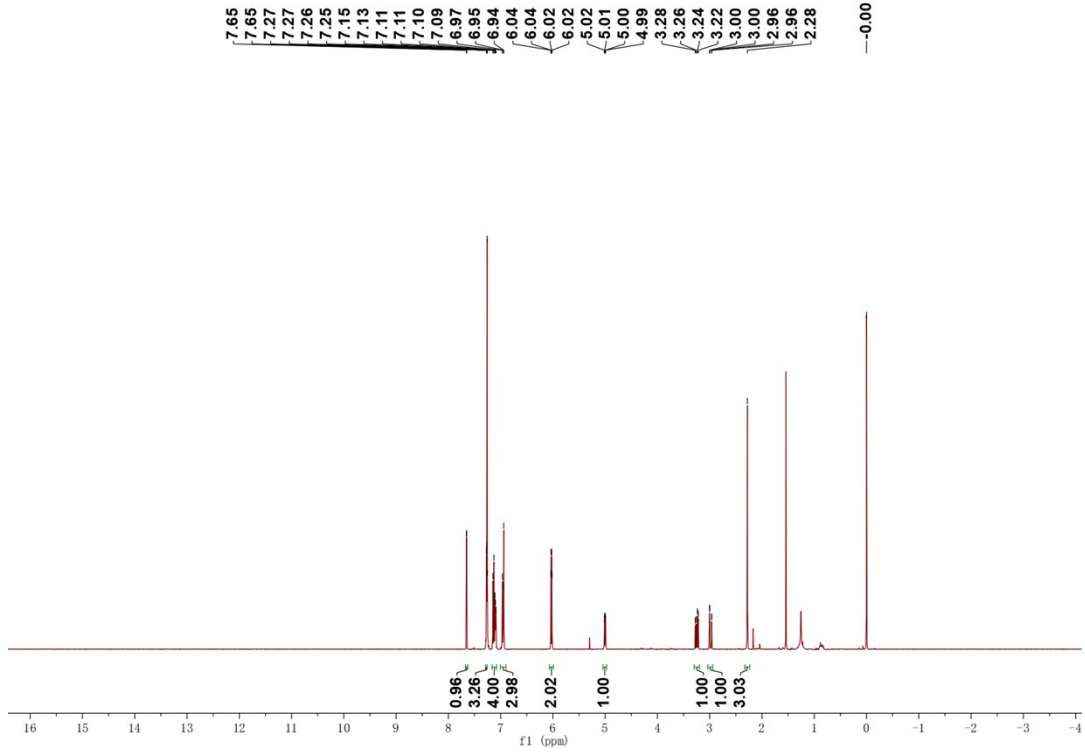
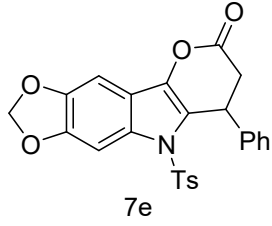


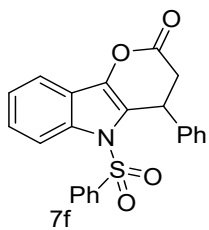






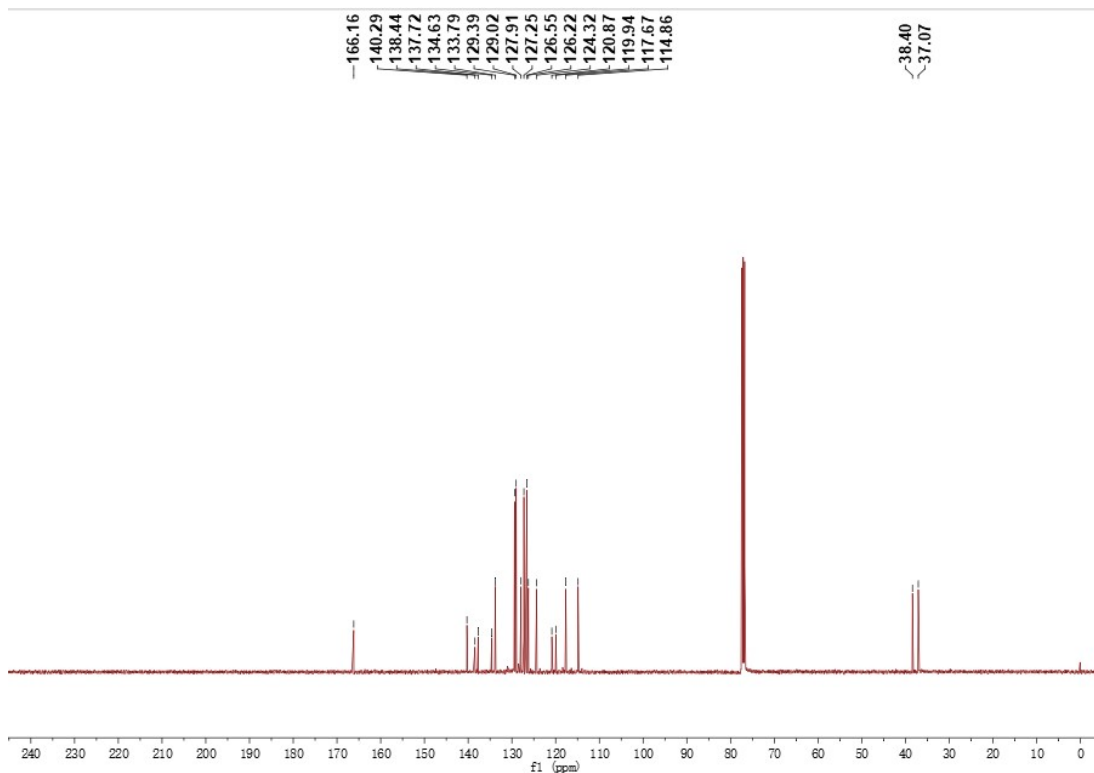
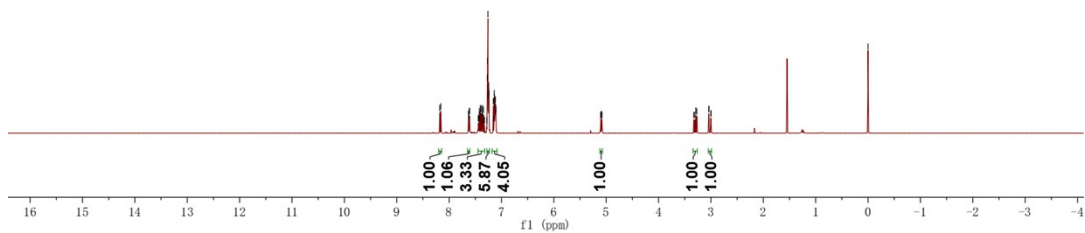
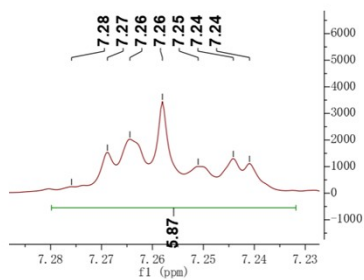




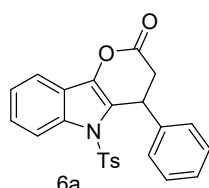


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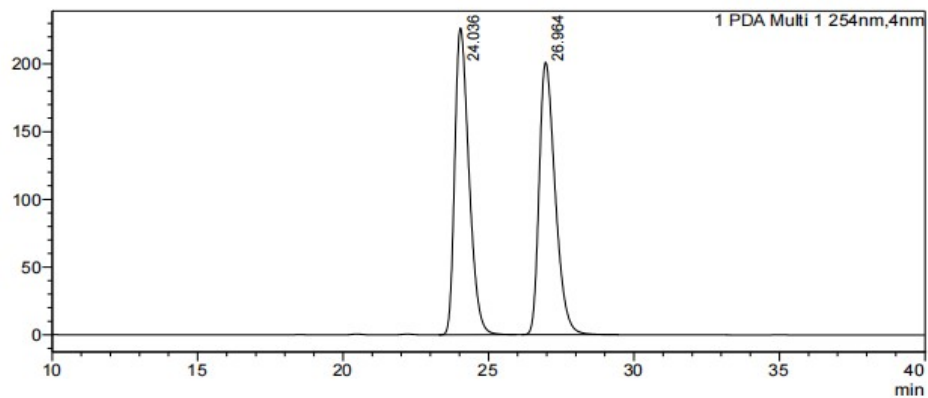
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HPLC spectra of products



mAU

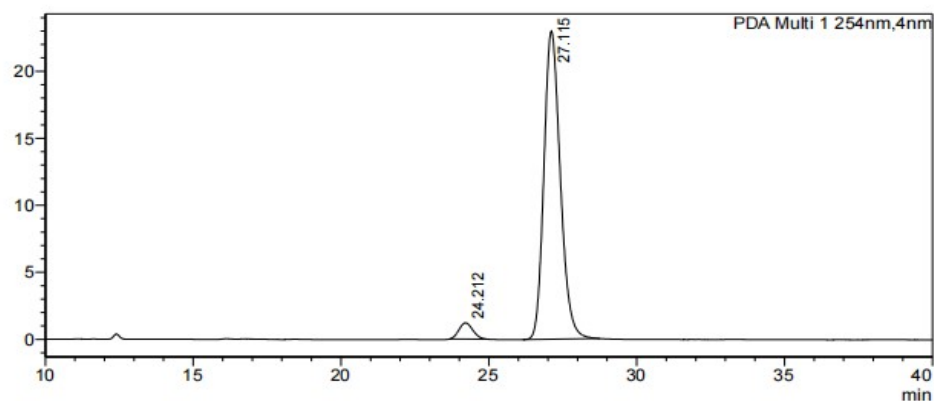


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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.036	7702983	226490	50.018
2	26.964	7697443	201091	49.982
Total		15400427	427581	100.000

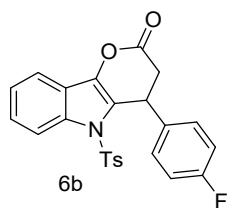
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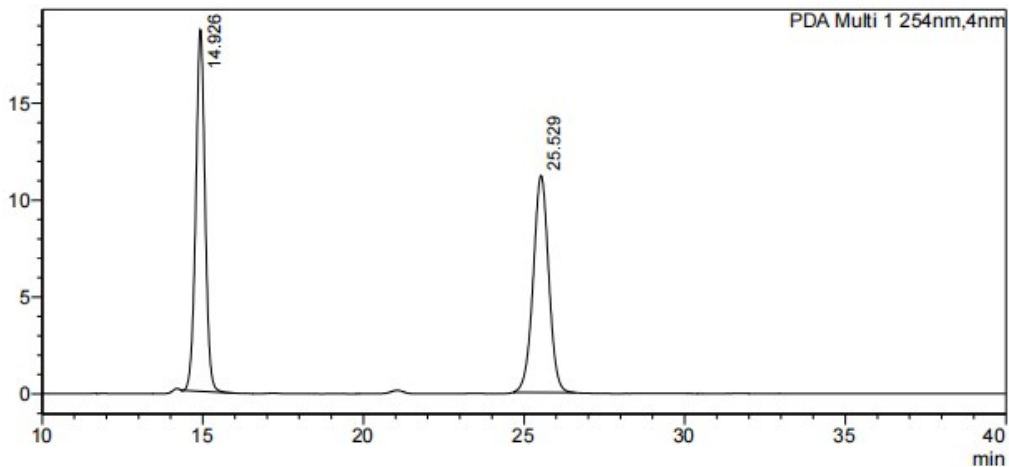
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.212	39166	1204	4.235
2	27.115	885556	22983	95.765
Total		924722	24187	100.000



mAU

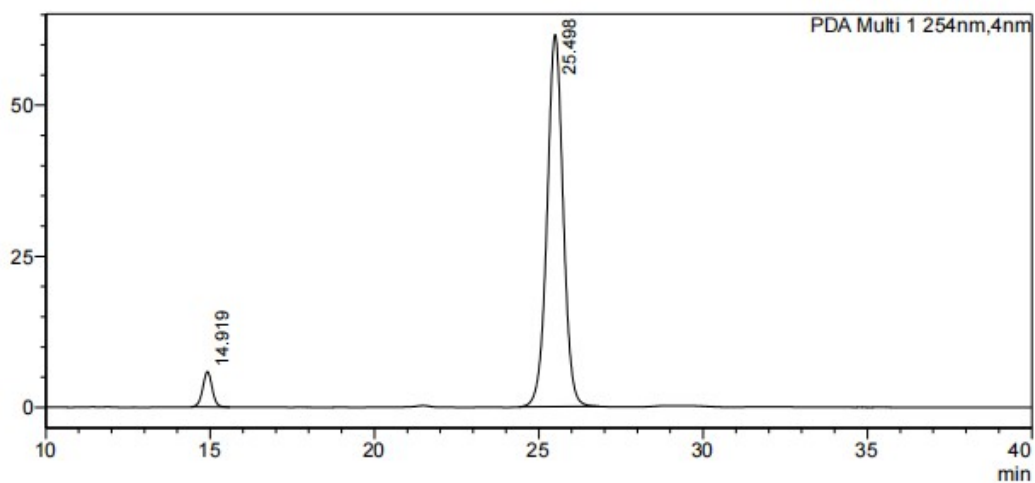


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.926	374091	18644	49.810
2	25.529	376942	11193	50.190
Total		751032	29837	100.000

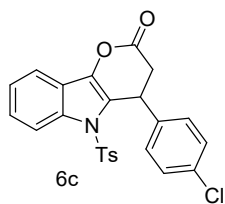
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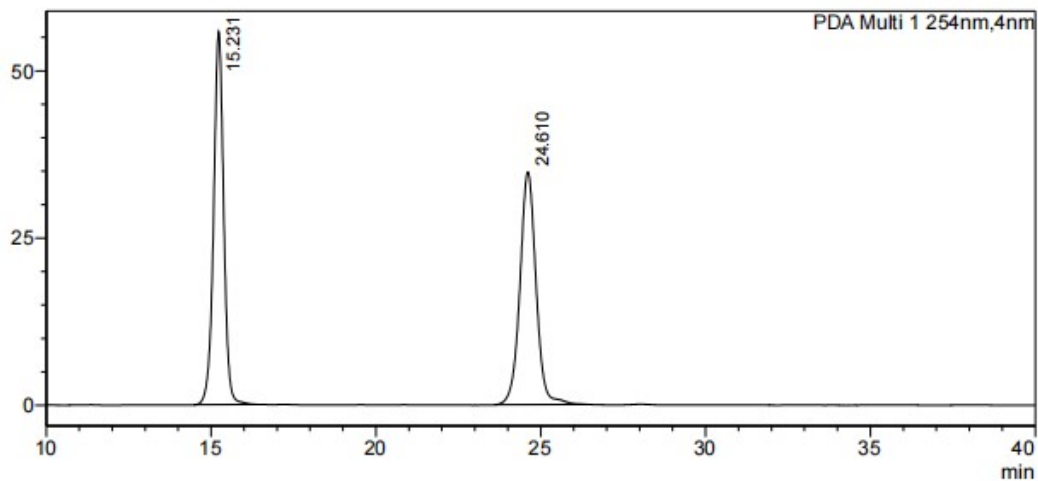
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.919	116818	5837	5.289
2	25.498	2091925	61545	94.711
Total		2208743	67382	100.000



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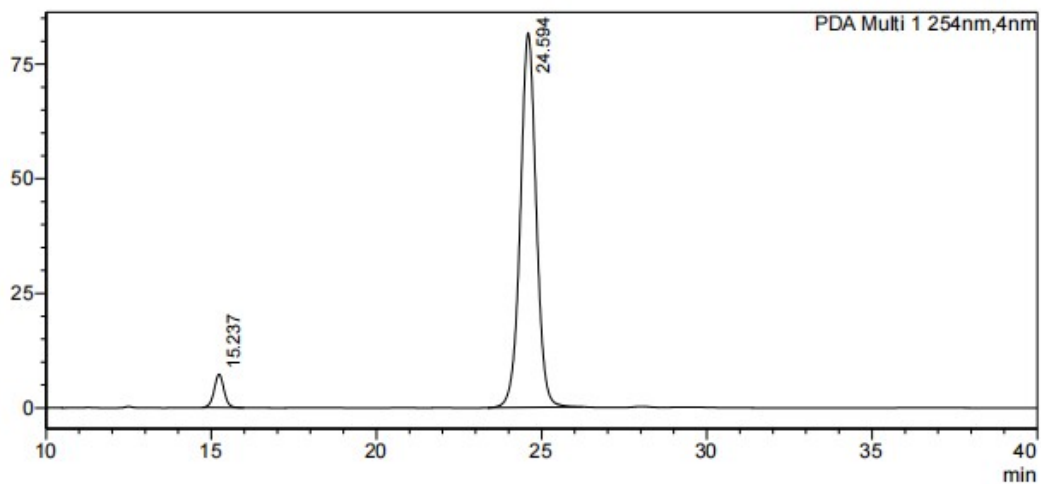


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.231	1186980	55728	50.000
2	24.610	1186973	34816	50.000
Total		2373953	90544	100.000

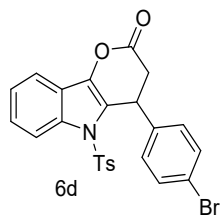
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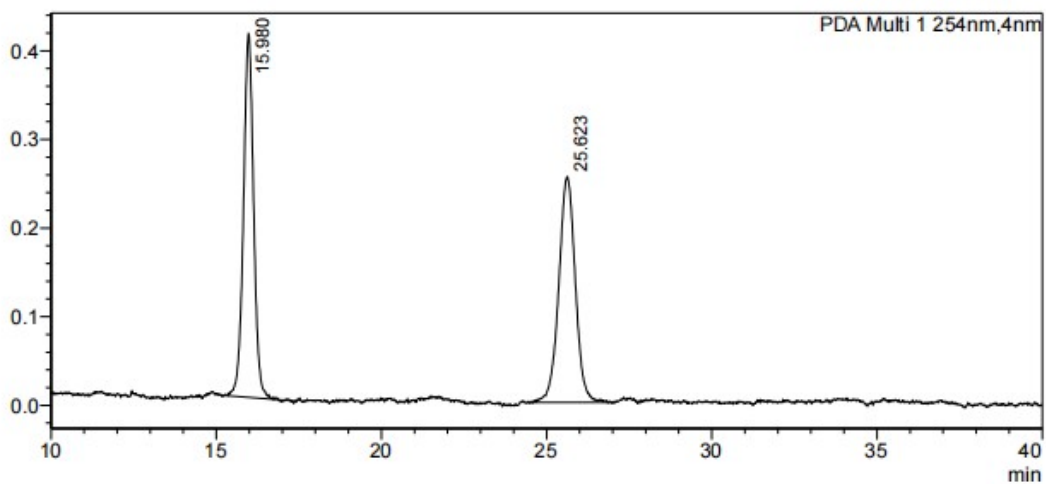
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.237	149693	7242	5.189
2	24.594	2735134	81648	94.811
Total		2884828	88890	100.000



mAU

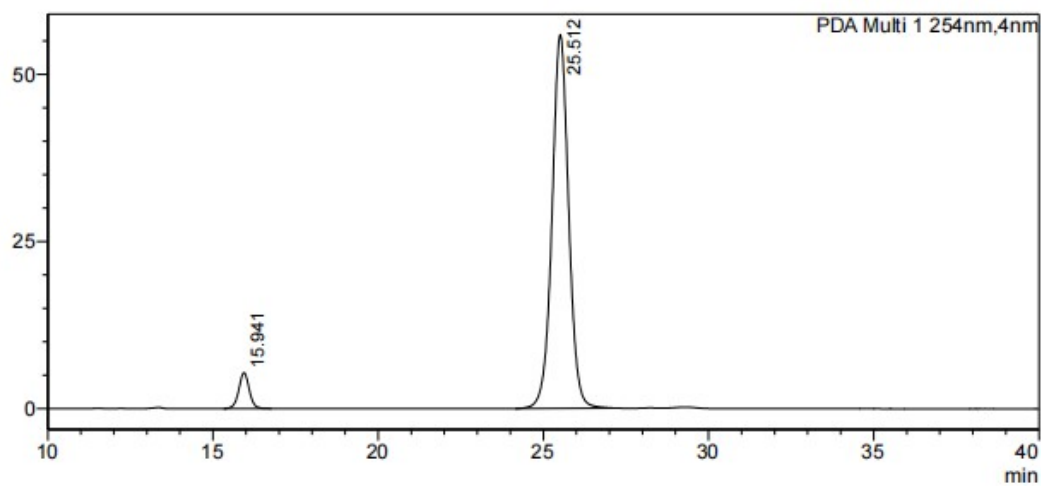


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.980	8775	410	49.734
2	25.623	8868	255	50.266
Total		17643	664	100.000

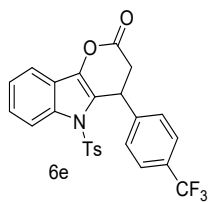
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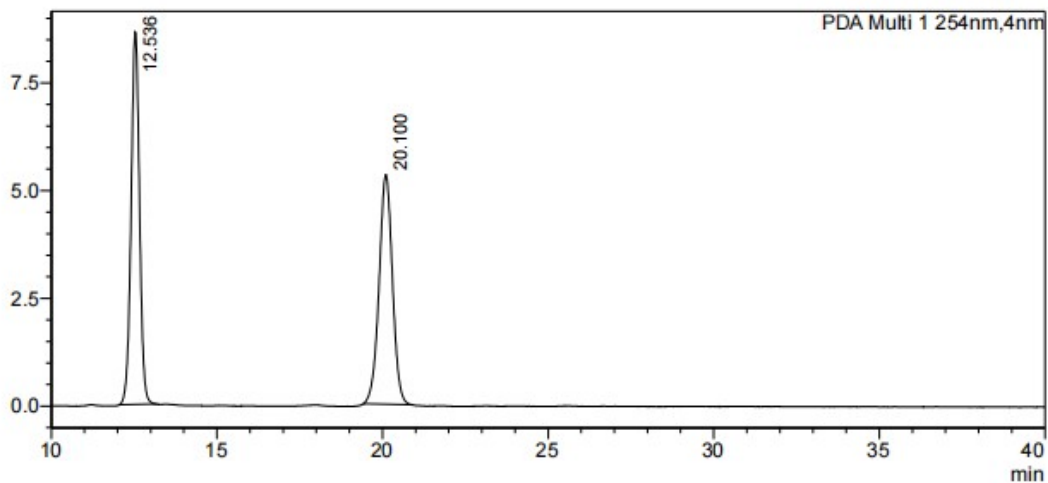
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.941	117491	5349	5.658
2	25.512	1958904	55831	94.342
Total		2076395	61180	100.000



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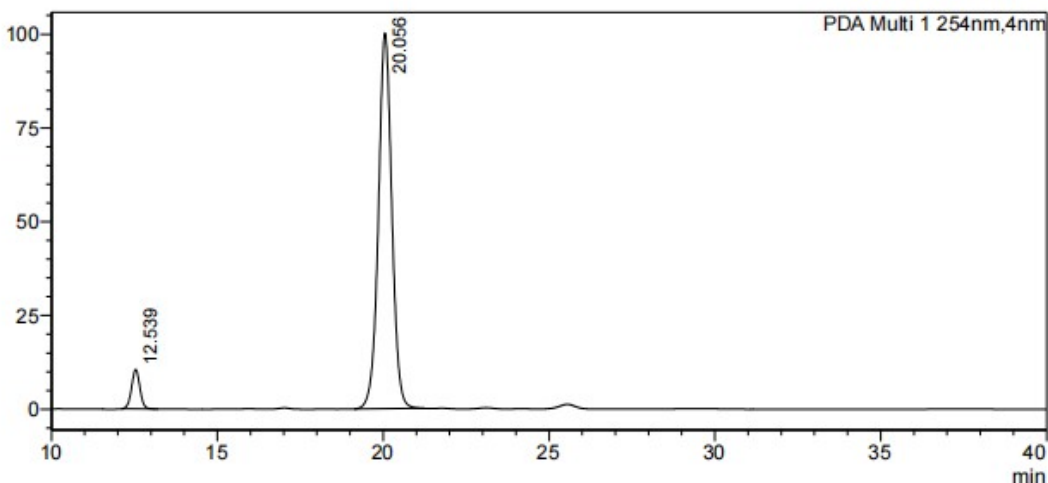


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.536	152227	8639	50.425
2	20.100	149664	5325	49.575
Total		301891	13964	100.000

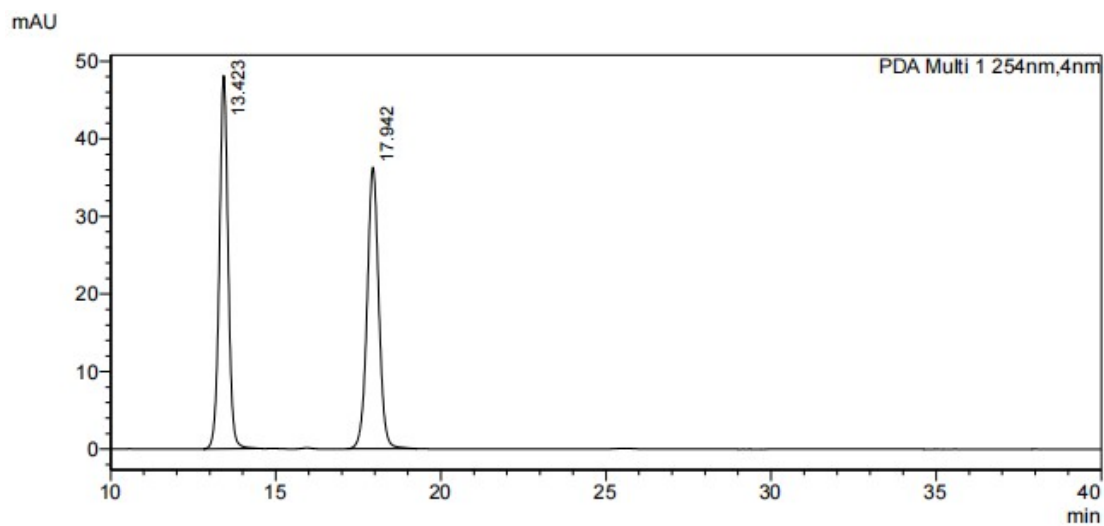
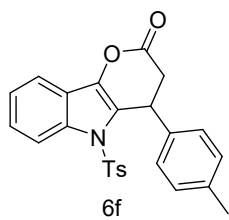
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PDA Ch1 254nm

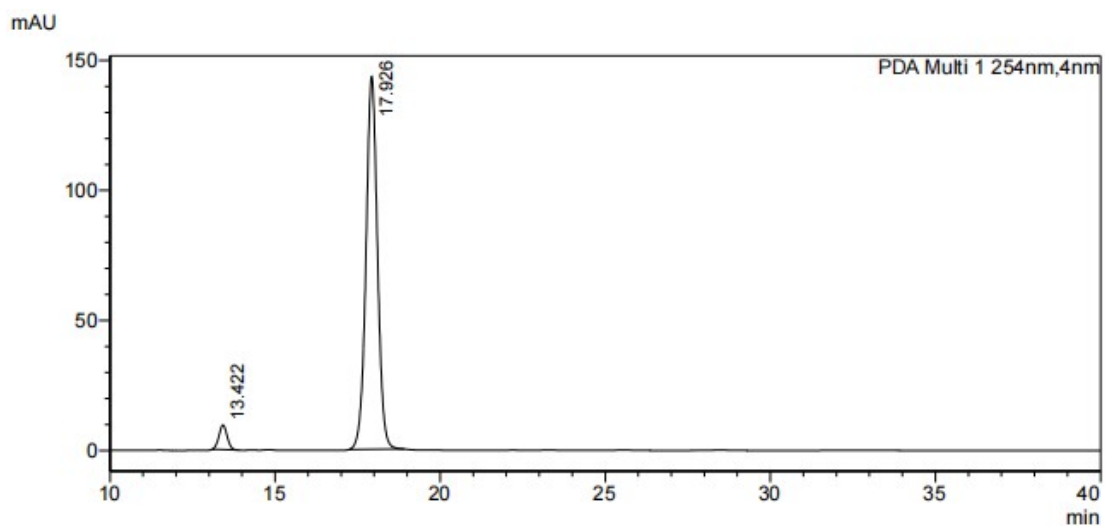
Peak#	Ret. Time	Area	Height	Area%
1	12.539	183356	10486	6.083
2	20.056	2830870	100091	93.917
Total		3014226	110577	100.000



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PDA Ch1 254nm

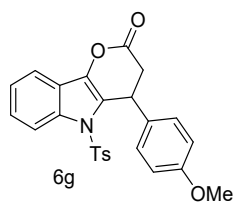
Peak#	Ret. Time	Area	Height	Area%
1	13.423	888098	48068	50.001
2	17.942	888057	36261	49.999
Total		1776155	84330	100.000



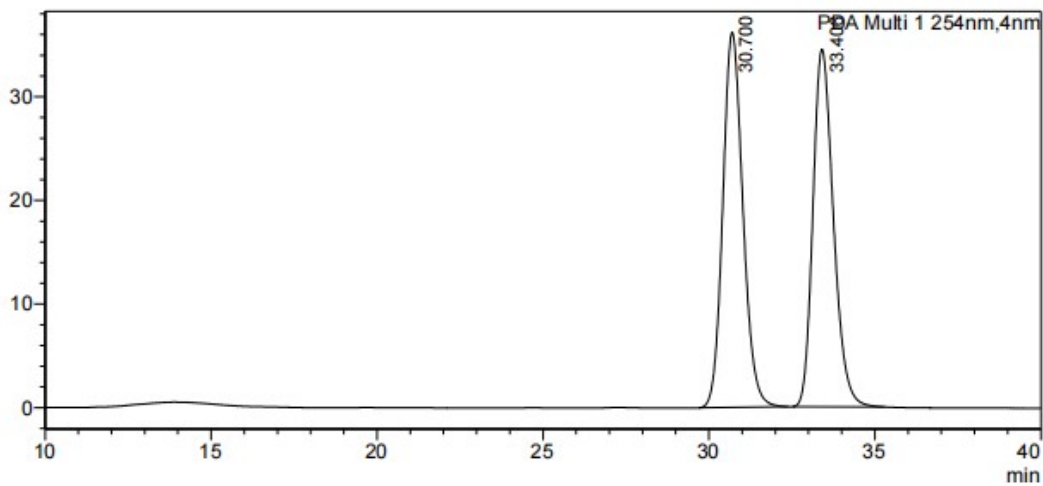
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.422	163499	9444	4.514
2	17.926	3458197	143217	95.486
Total		3621696	152661	100.000



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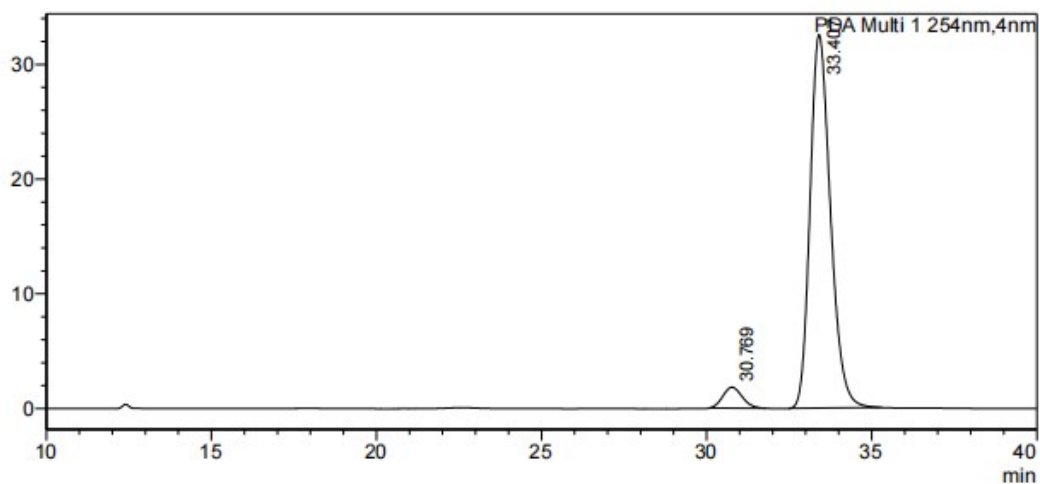


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	30.700	1522367	36190	50.711
2	33.406	1479671	34491	49.289
Total		3002037	70682	100.000

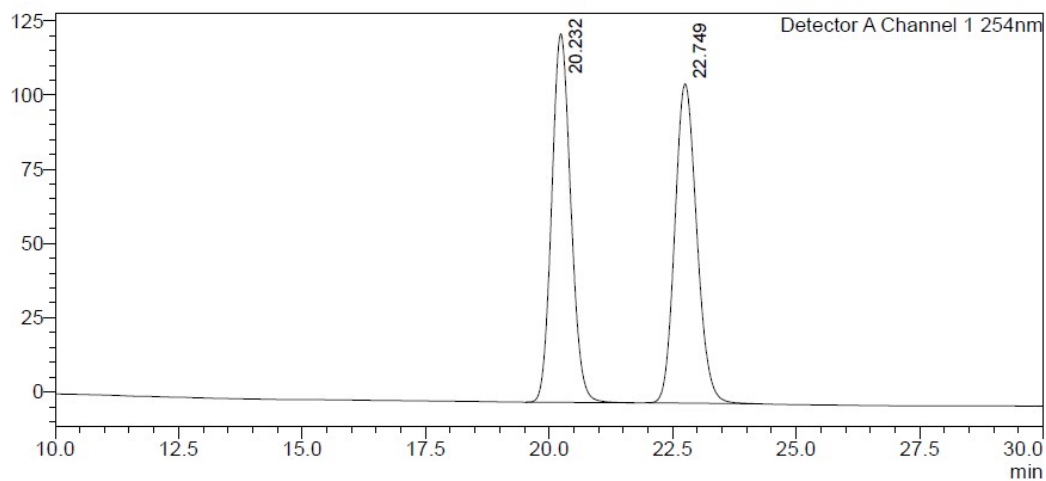
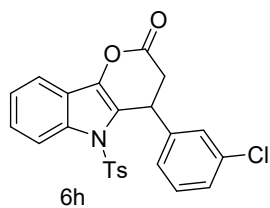
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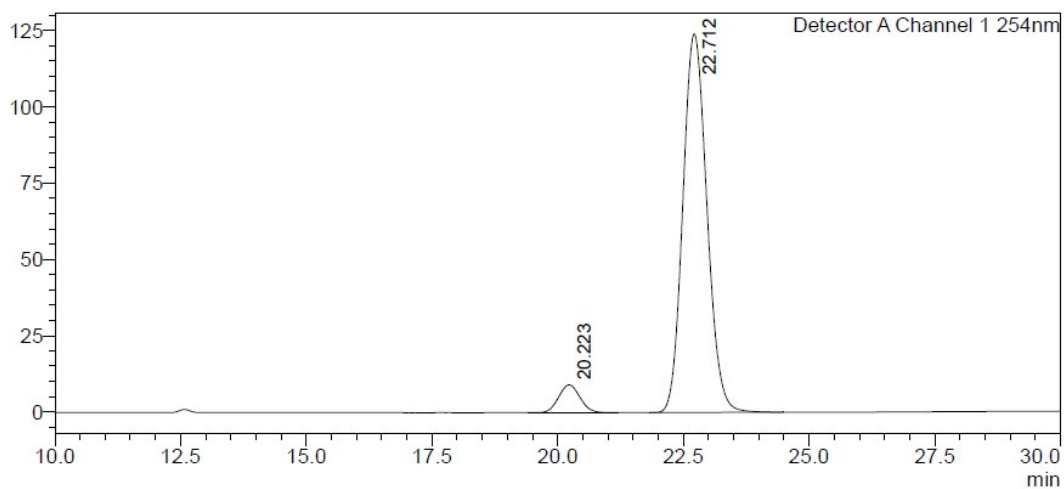
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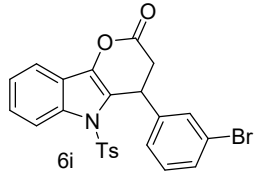
Peak#	Ret. Time	Area	Height	Area%
1	30.769	73763	1813	5.012
2	33.407	1398068	32546	94.988
Total		1471832	34359	100.000



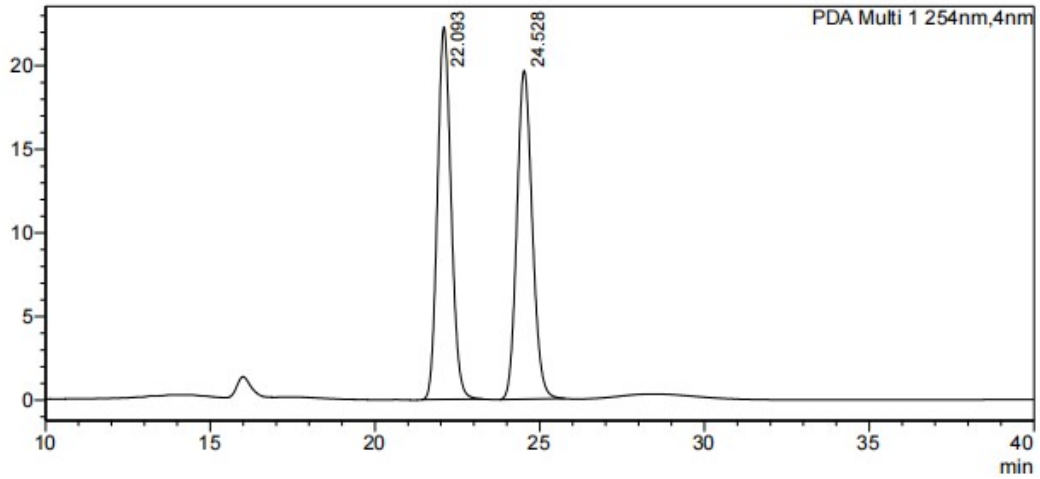
Peak#	Ret. Time	Area	Height	Area%
1	20.232	3338051	124113	50.083
2	22.749	3326948	107600	49.917
Total		6664998	231713	100.000



Peak#	Ret. Time	Area	Height	Area%
1	20.223	271239	9117	6.161
2	22.712	4131455	124025	93.839
Total		4402694	133143	100.000



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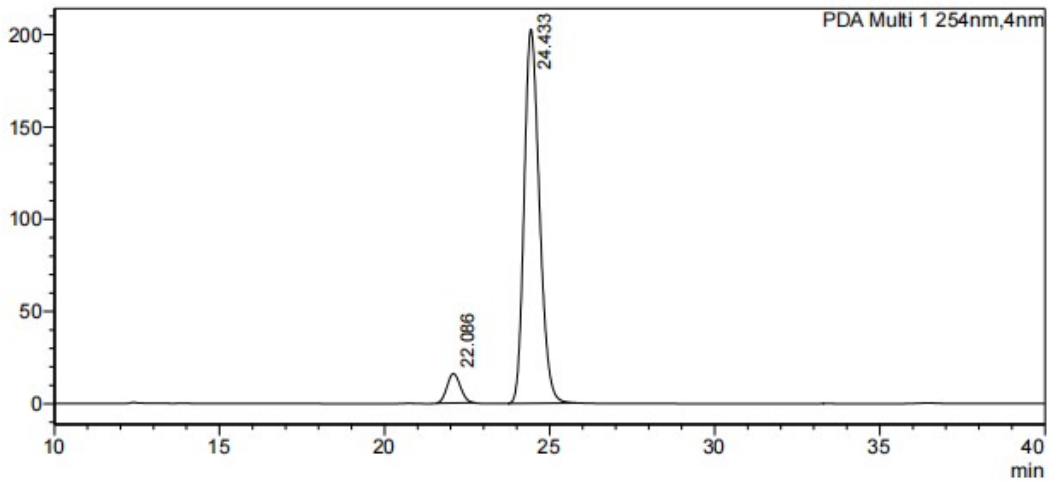


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	22.093	642001	22266	50.160
2	24.528	637900	19644	49.840
Total		1279901	41910	100.000

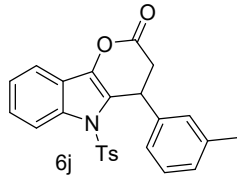
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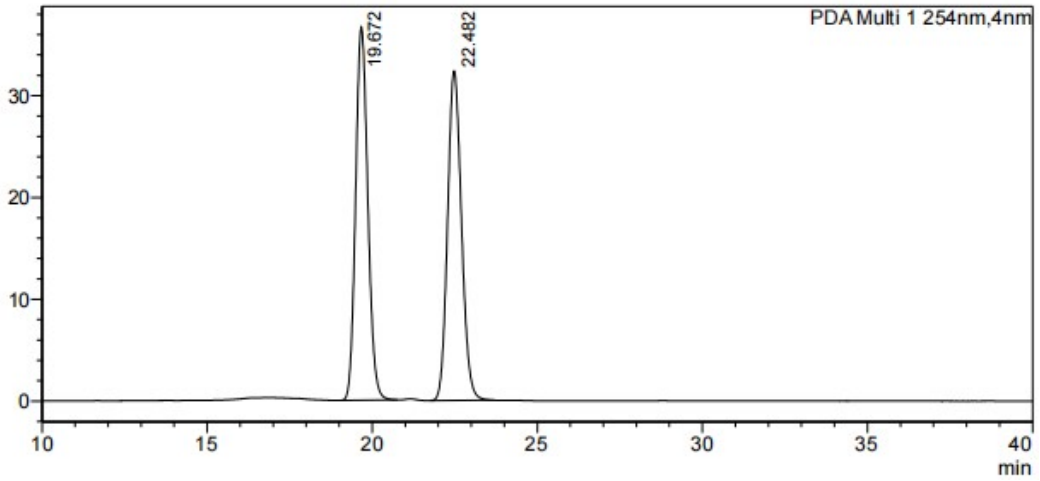
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	22.086	446468	15943	6.417
2	24.433	6511311	202521	93.583
Total		6957779	218464	100.000



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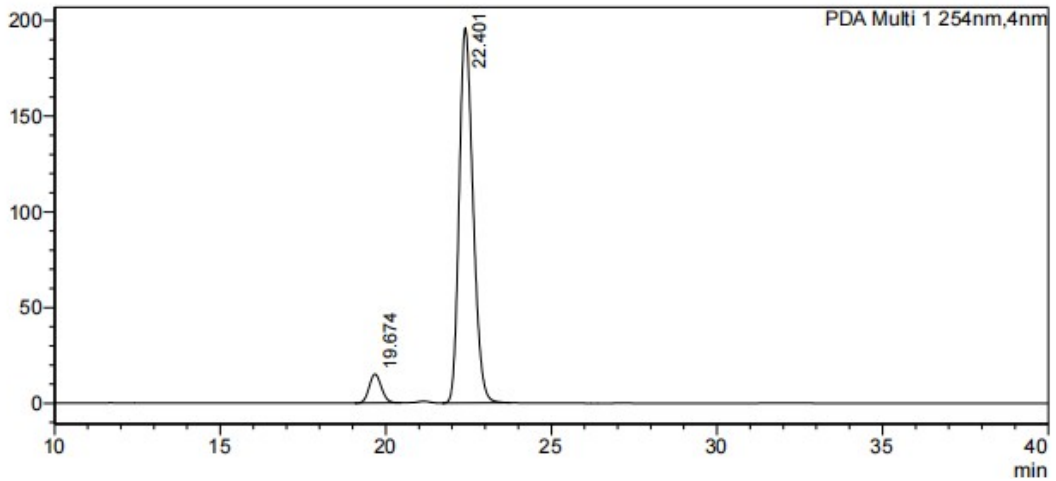


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.672	941312	36634	49.853
2	22.482	946847	32366	50.147
Total		1888159	69000	100.000

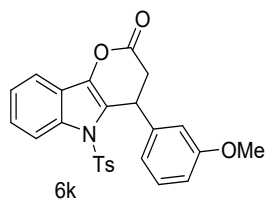
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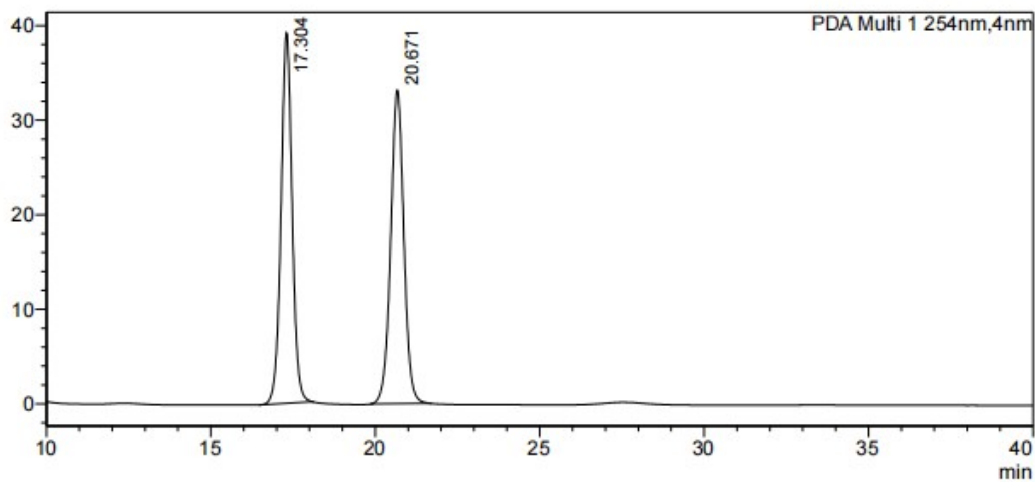
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.674	389218	15119	6.394
2	22.401	5697965	195819	93.606
Total		6087182	210938	100.000



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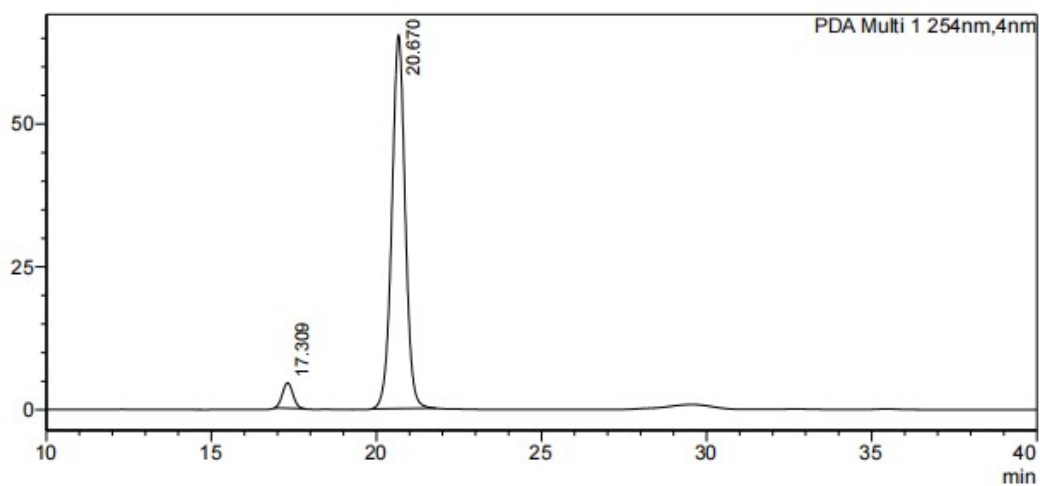


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.304	920783	39147	49.958
2	20.671	922334	33138	50.042
Total		1843117	72286	100.000

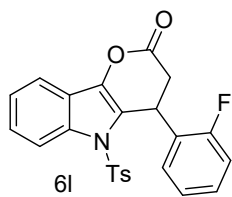
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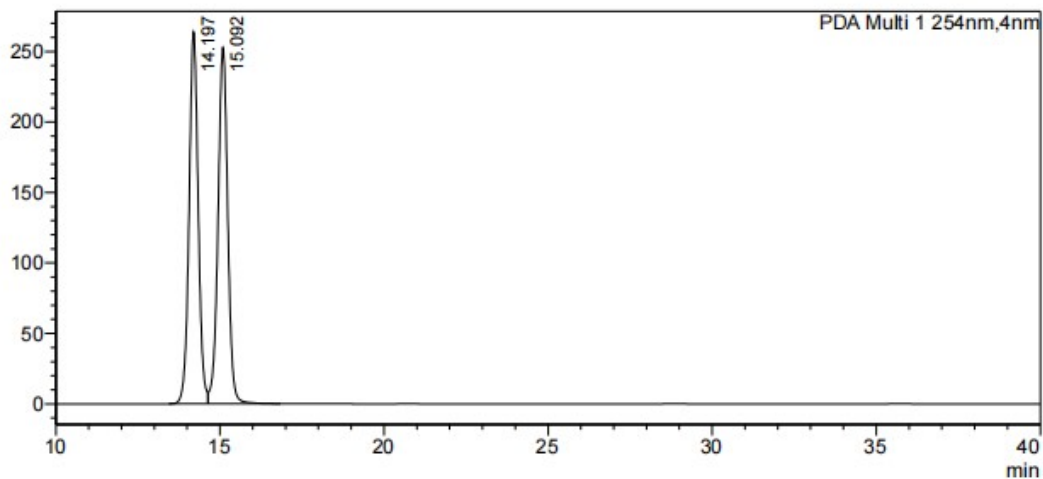
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.309	98666	4457	5.089
2	20.670	1840065	65304	94.911
Total		1938731	69761	100.000



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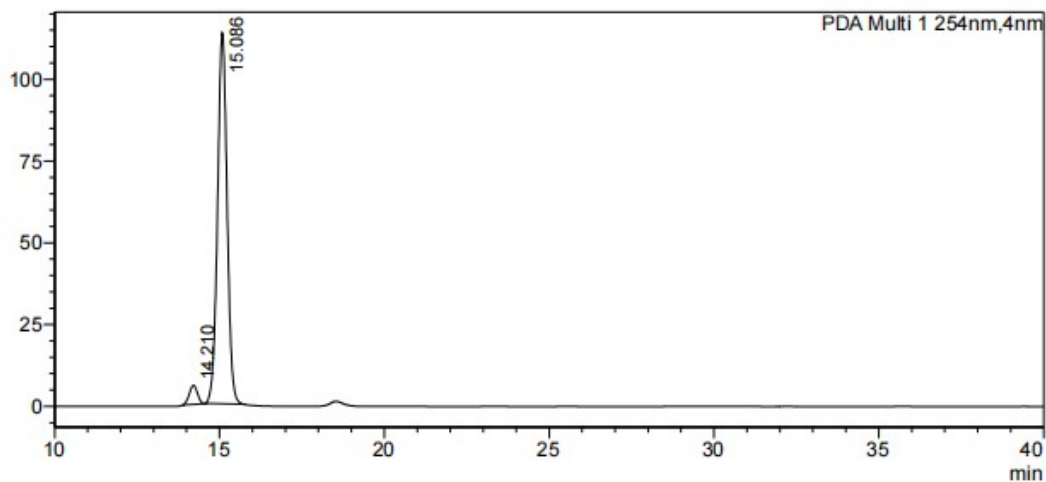


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.197	5117544	263706	49.504
2	15.092	5220097	252743	50.496
Total		10337641	516449	100.000

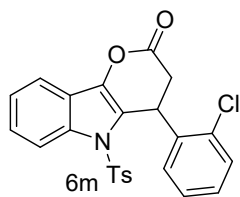
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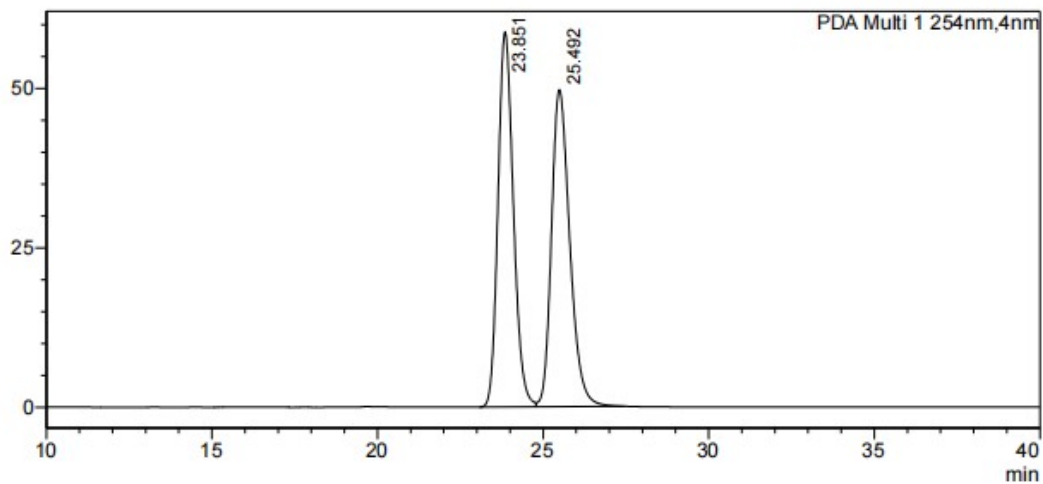
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.210	100463	5813	4.204
2	15.086	2289470	113379	95.796
Total		2389933	119192	100.000



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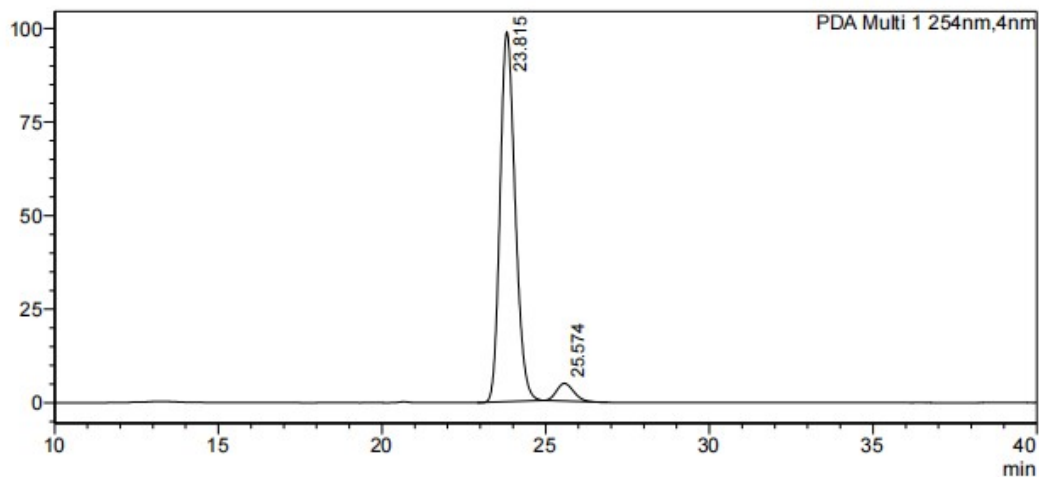


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.851	1902166	58765	49.909
2	25.492	1909135	49661	50.091
Total		3811300	108426	100.000

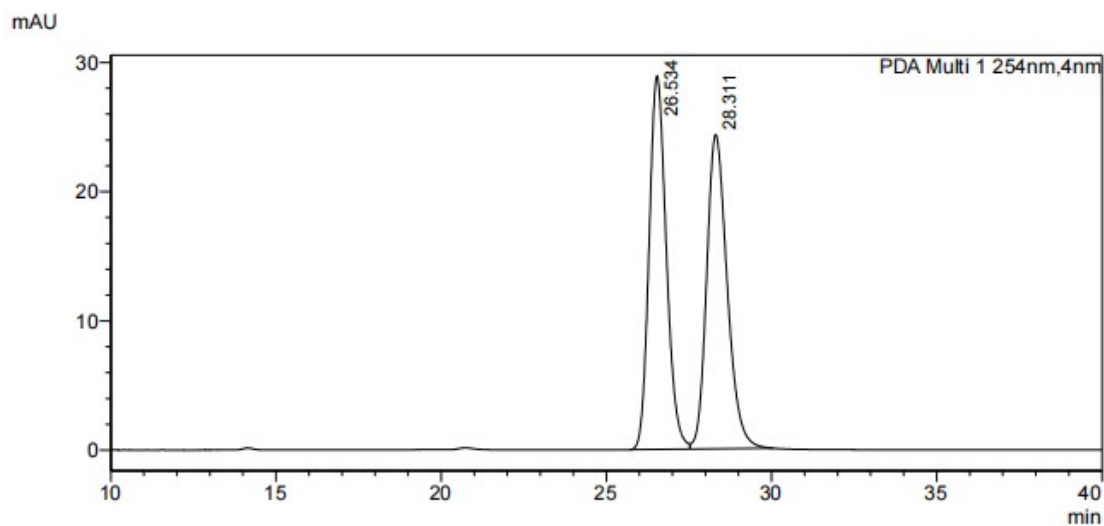
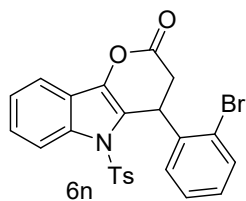
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PDA Ch1 254nm

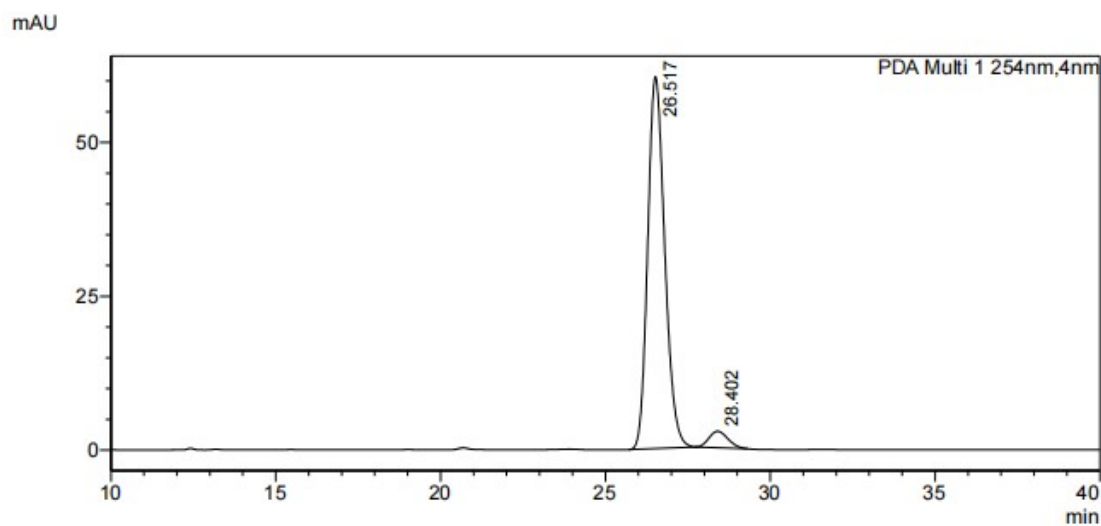
Peak#	Ret. Time	Area	Height	Area%
1	23.815	3171409	98702	94.916
2	25.574	169864	4694	5.084
Total		3341273	103397	100.000



<Peak Table>

PDA Ch1 254nm

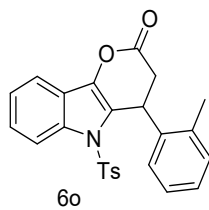
Peak#	Ret. Time	Area	Height	Area%
1	26.534	1046738	28886	49.947
2	28.311	1048980	24315	50.053
Total		2095718	53202	100.000



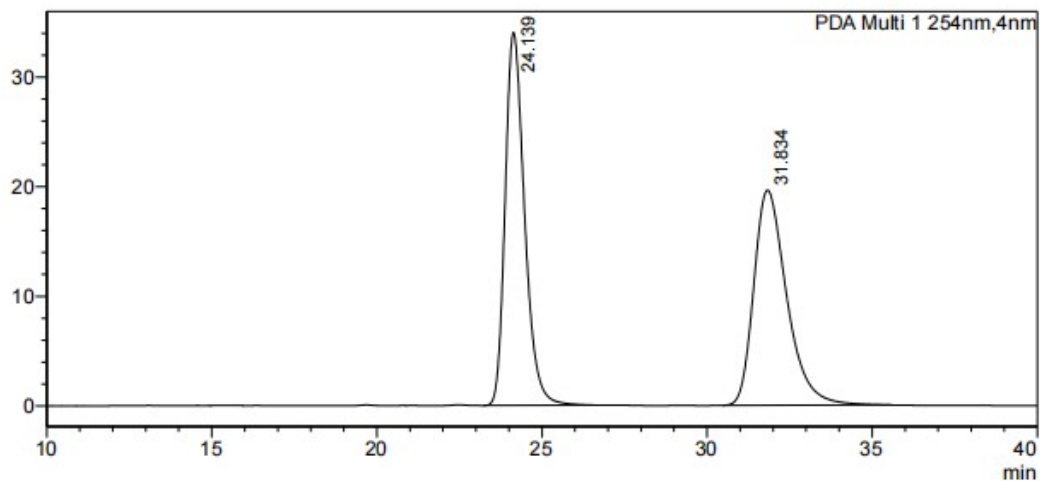
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.517	2169069	60415	95.304
2	28.402	106874	2678	4.696
Total		2275943	63093	100.000



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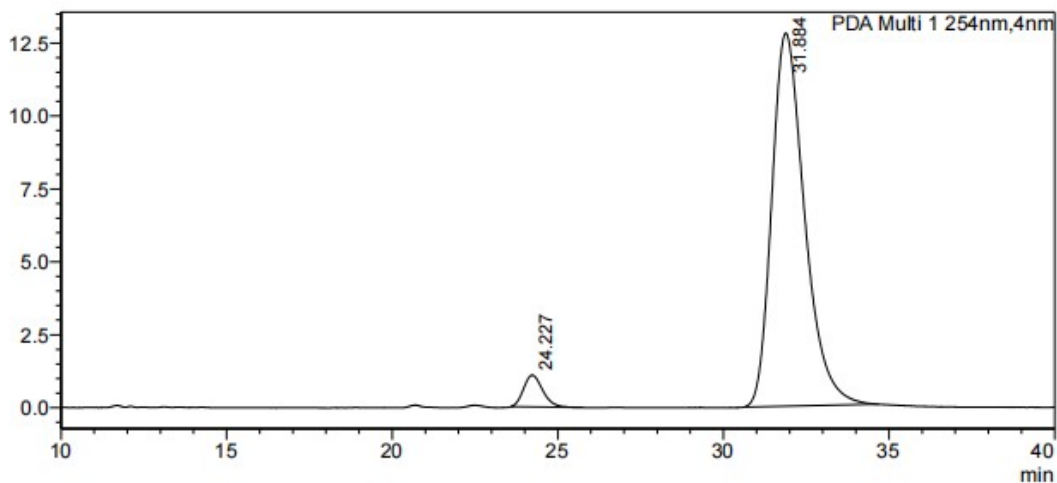


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.139	1389974	34042	50.529
2	31.834	1360878	19627	49.471
Total		2750852	53669	100.000

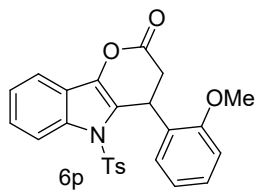
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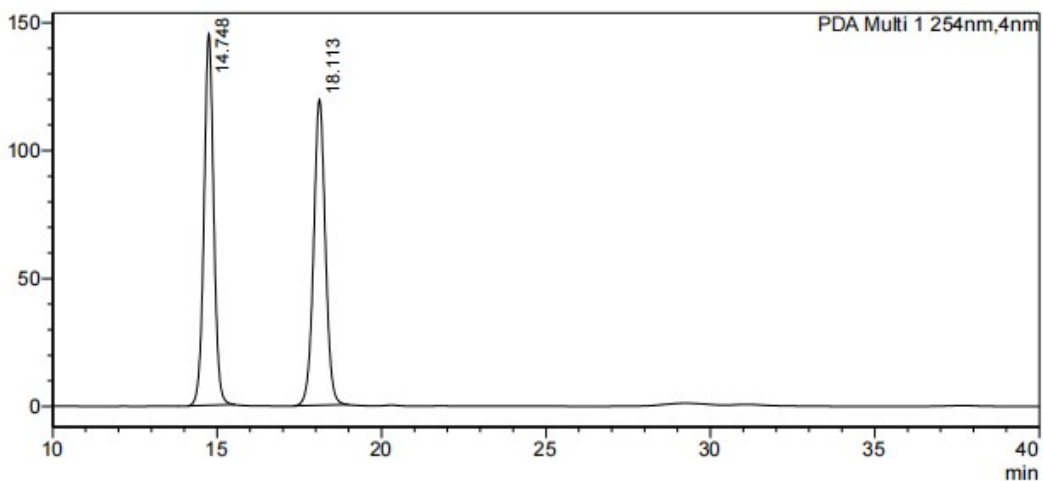
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.227	43675	1090	4.719
2	31.884	881908	12794	95.281
Total		925583	13883	100.000



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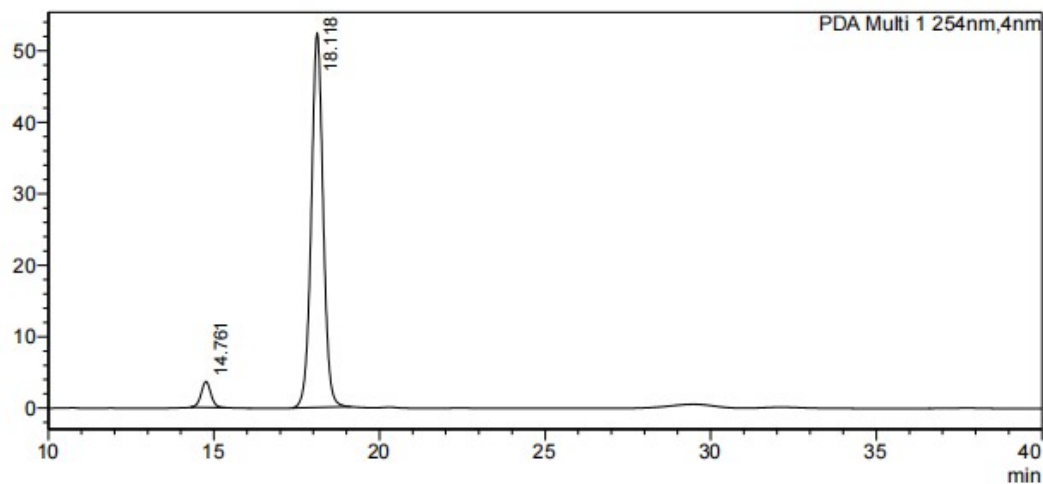


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.748	2974233	145224	50.065
2	18.113	2966494	119531	49.935
Total		5940727	264755	100.000

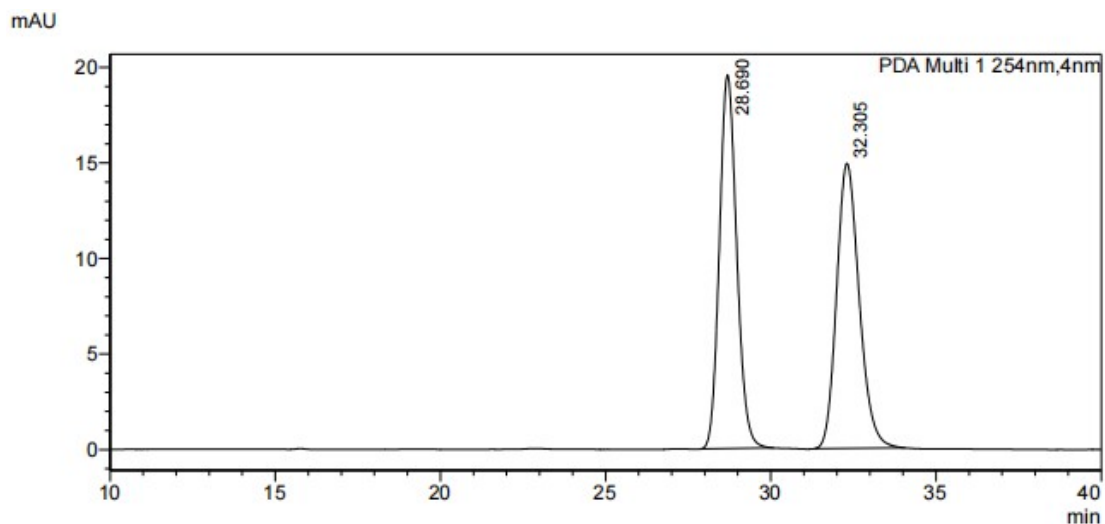
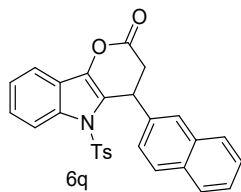
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<Peak Table>

PDA Ch1 254nm

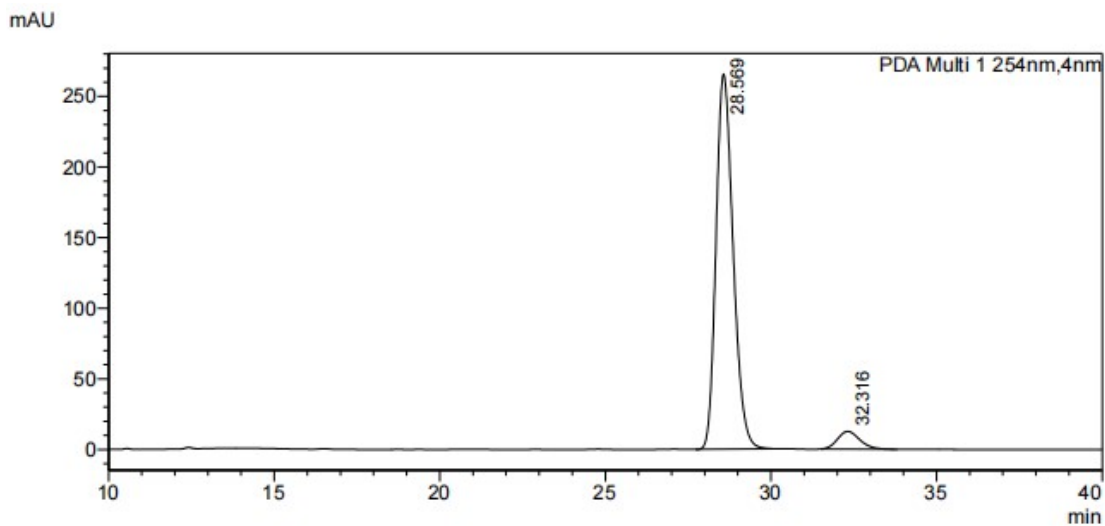
Peak#	Ret. Time	Area	Height	Area%
1	14.761	74088	3611	5.369
2	18.118	1305912	52353	94.631
Total		1380000	55964	100.000



<Peak Table>

PDA Ch1 254nm

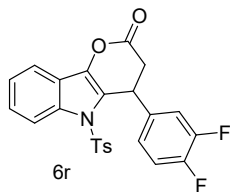
Peak#	Ret. Time	Area	Height	Area%
1	28.690	711972	19541	50.137
2	32.305	708084	14909	49.863
Total		1420056	34450	100.000



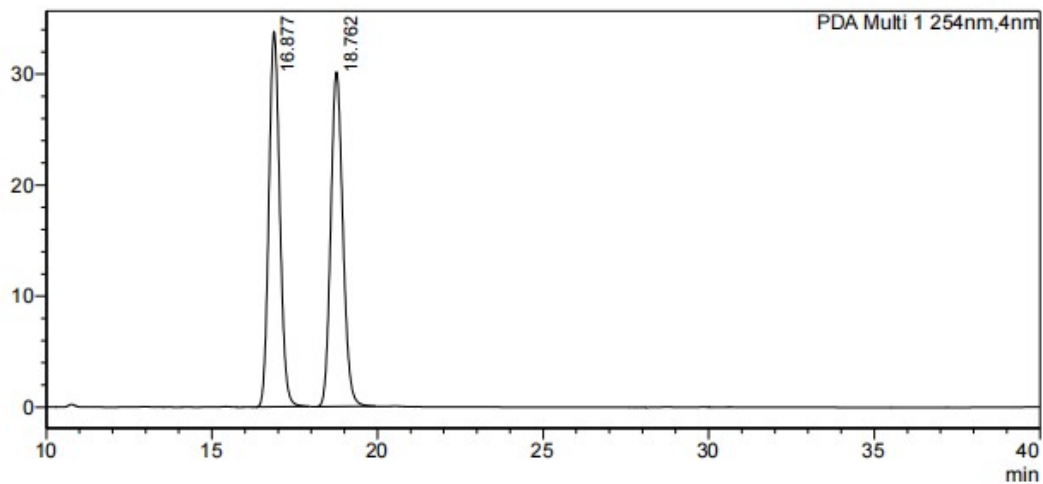
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.569	9553747	265368	94.235
2	32.316	584448	12525	5.765
Total		10138195	277893	100.000



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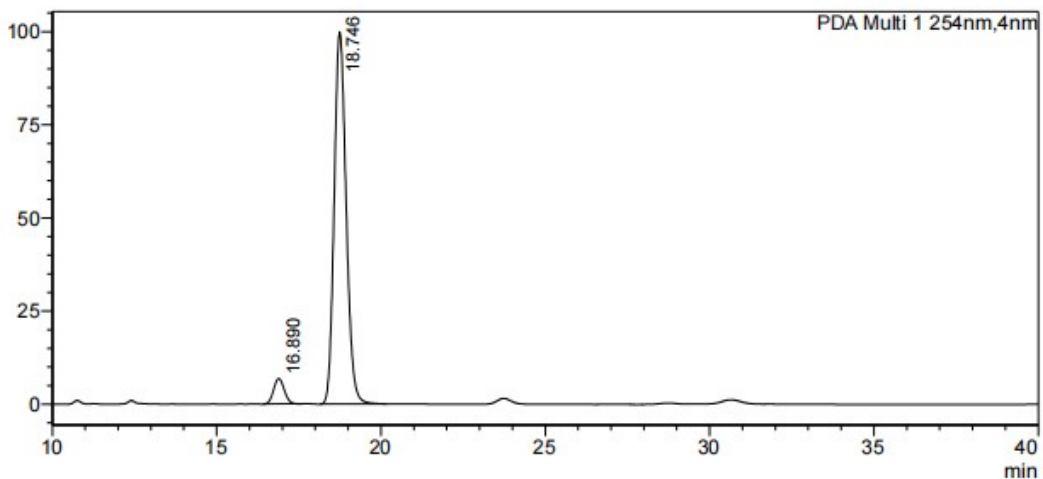


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.877	772733	33760	50.116
2	18.762	769144	30135	49.884
Total		1541877	63894	100.000

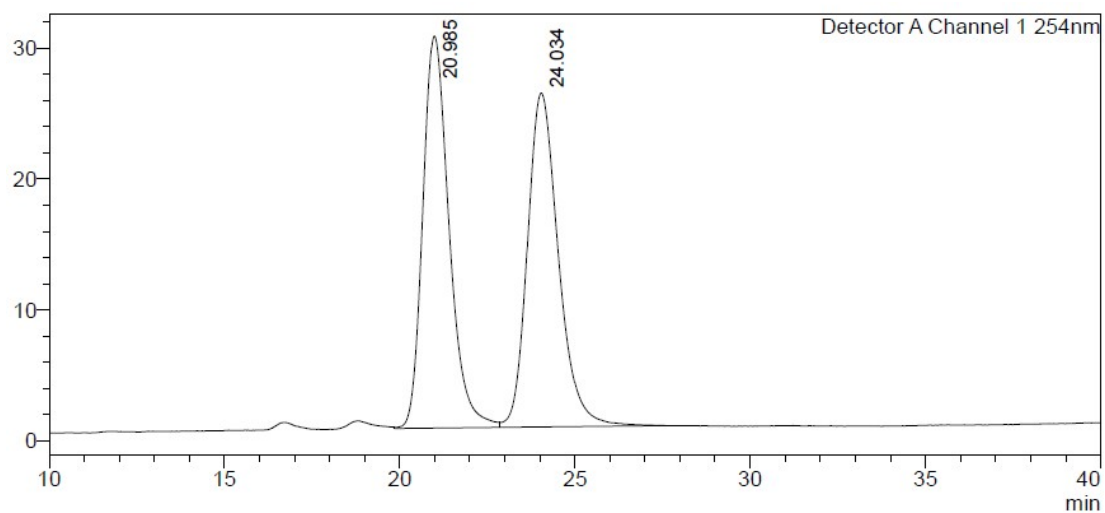
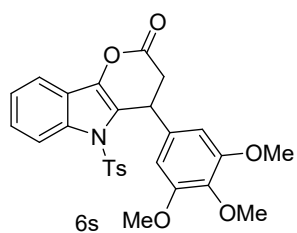
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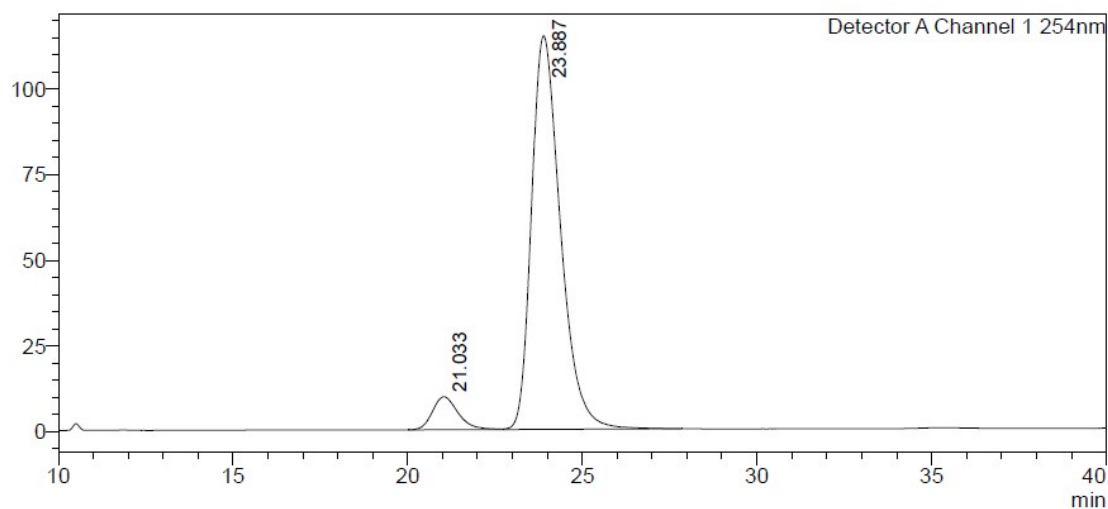
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PDA Ch1 254nm

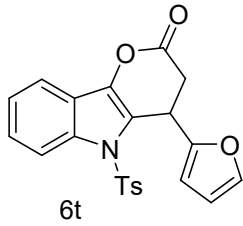
Peak#	Ret. Time	Area	Height	Area%
1	16.890	154026	6831	5.733
2	18.746	2532517	99732	94.267
Total		2686543	106563	100.000



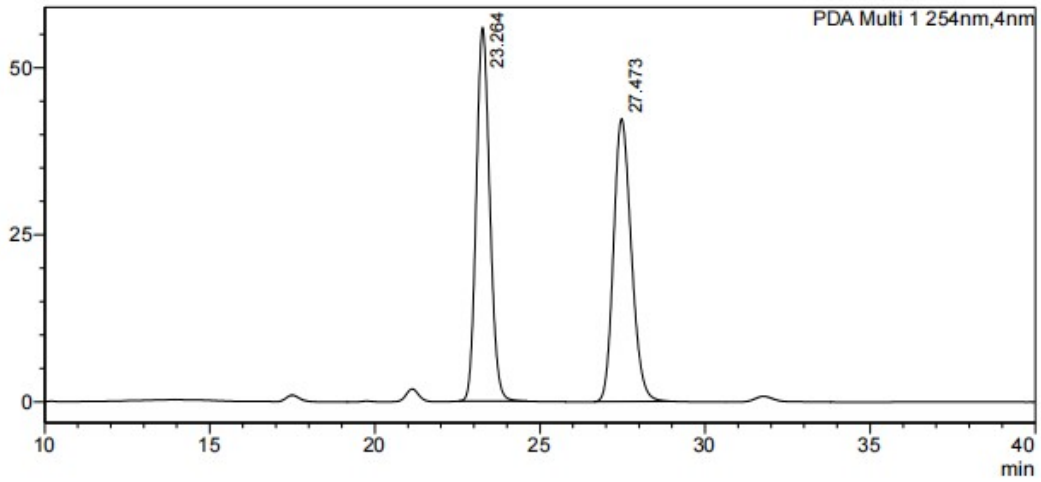
Peak#	Ret. Time	Area	Height	Area%
1	20.985	1561099	29932	49.849
2	24.034	1570559	25493	50.151
Total		3131657	55425	100.000



Peak#	Ret. Time	Area	Height	Area%
1	21.033	489244	9582	6.887
2	23.887	6614350	114777	93.113
Total		7103594	124359	100.000



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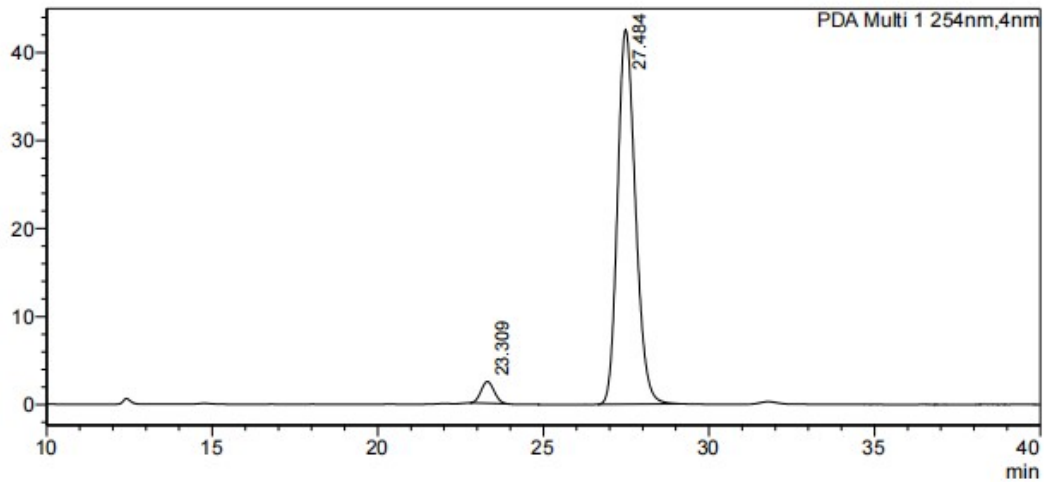


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.264	1591099	55821	50.065
2	27.473	1586979	42317	49.935
Total		3178078	98138	100.000

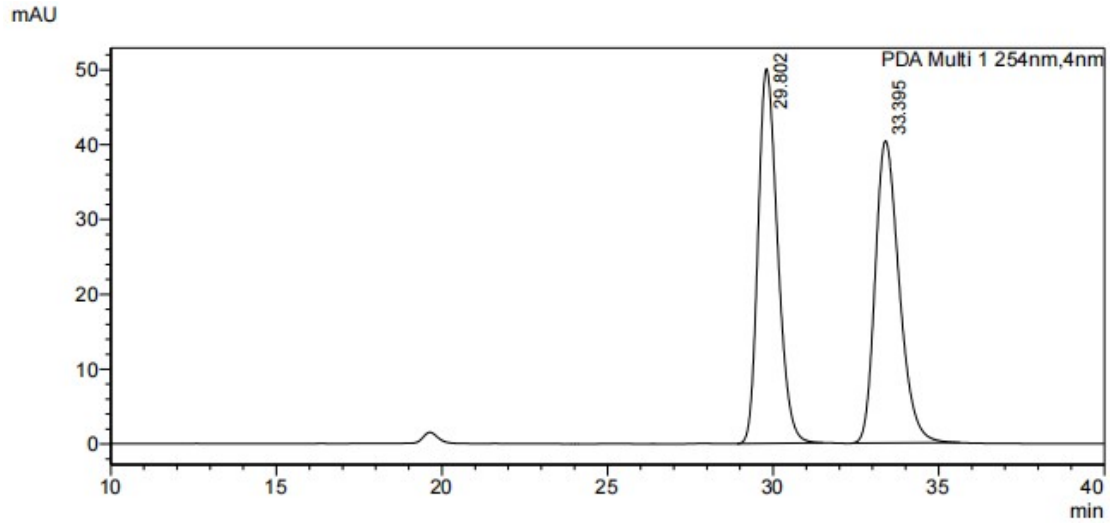
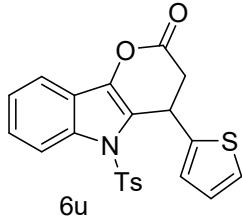
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<Peak Table>

PDA Ch1 254nm

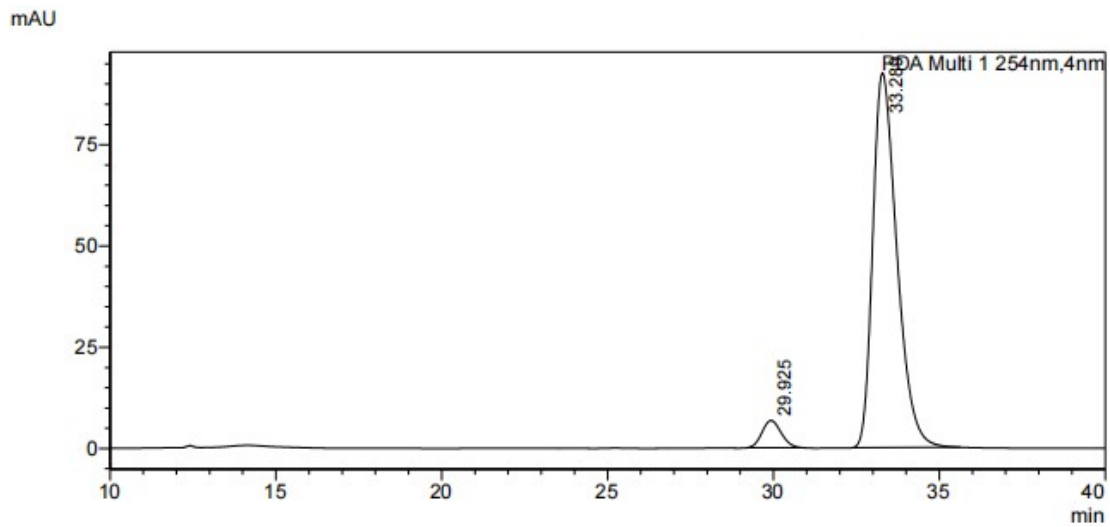
Peak#	Ret. Time	Area	Height	Area%
1	23.309	68458	2475	4.102
2	27.484	1600517	42557	95.898
Total		1668974	45032	100.000



<Peak Table>

PDA Ch1 254nm

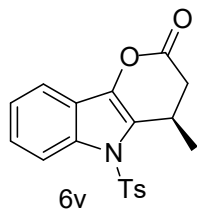
Peak#	Ret. Time	Area	Height	Area%
1	29.802	2050597	50034	50.124
2	33.395	2040469	40383	49.876
Total		4091066	90417	100.000



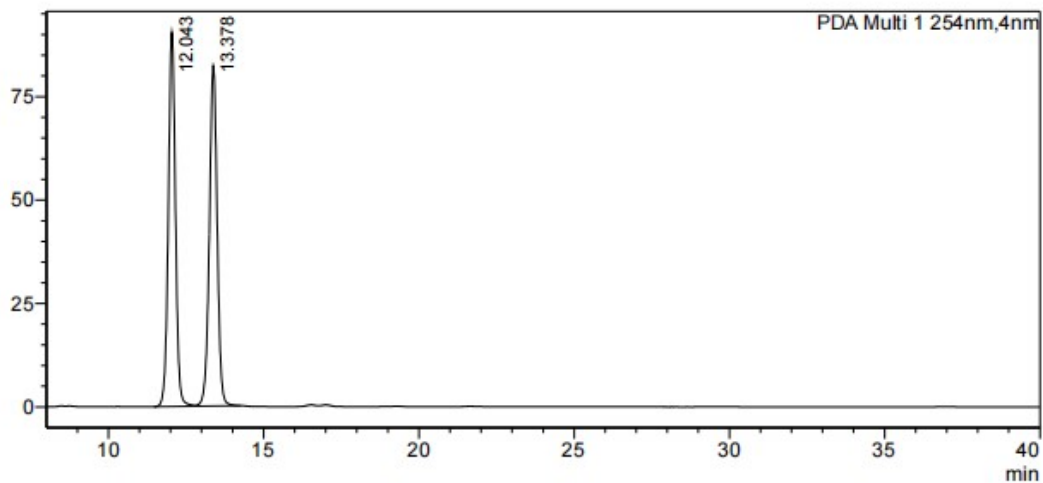
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	29.925	271472	6728	5.488
2	33.289	4674770	92513	94.512
Total		4946242	99241	100.000



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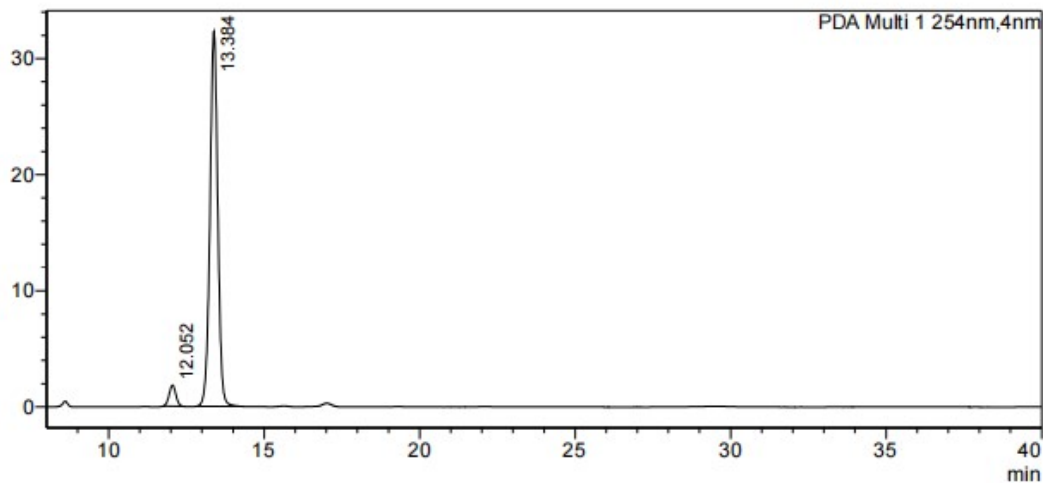


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.043	1443154	90430	49.981
2	13.378	1444243	82317	50.019
Total		2887397	172746	100.000

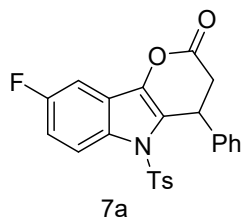
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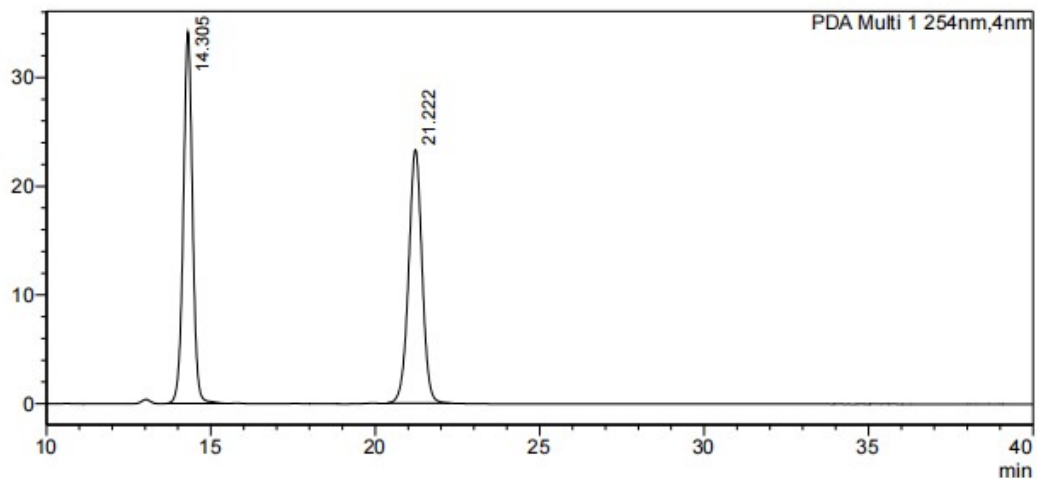
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.052	27194	1803	4.585
2	13.384	565957	32264	95.415
Total		593151	34068	100.000



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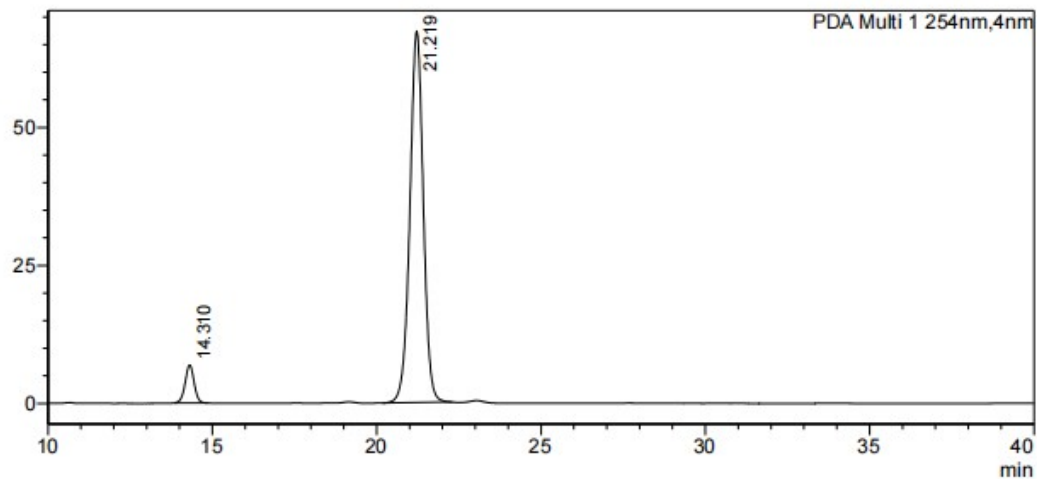


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.305	664448	34136	50.140
2	21.222	660728	23305	49.860
Total		1325175	57440	100.000

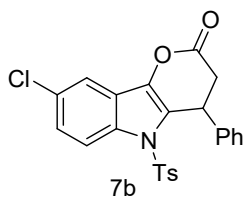
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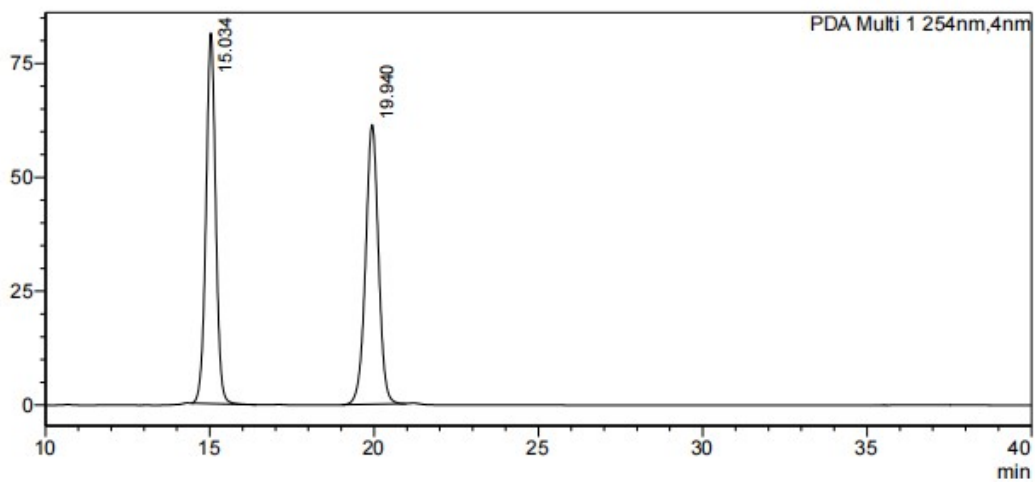
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.310	130452	6860	6.386
2	21.219	1912366	67249	93.614
Total		2042818	74109	100.000



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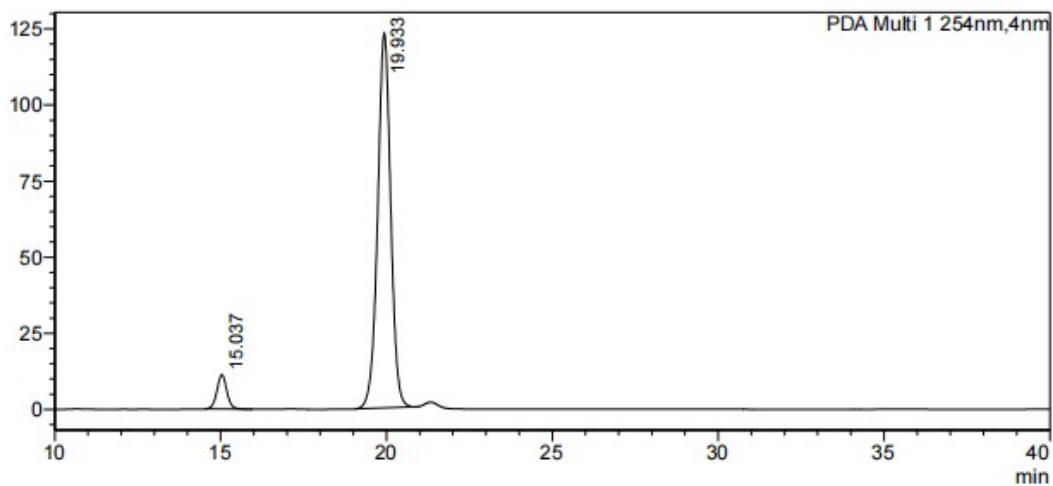


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.034	1671867	81287	49.916
2	19.940	1677480	61328	50.084
Total		3349347	142615	100.000

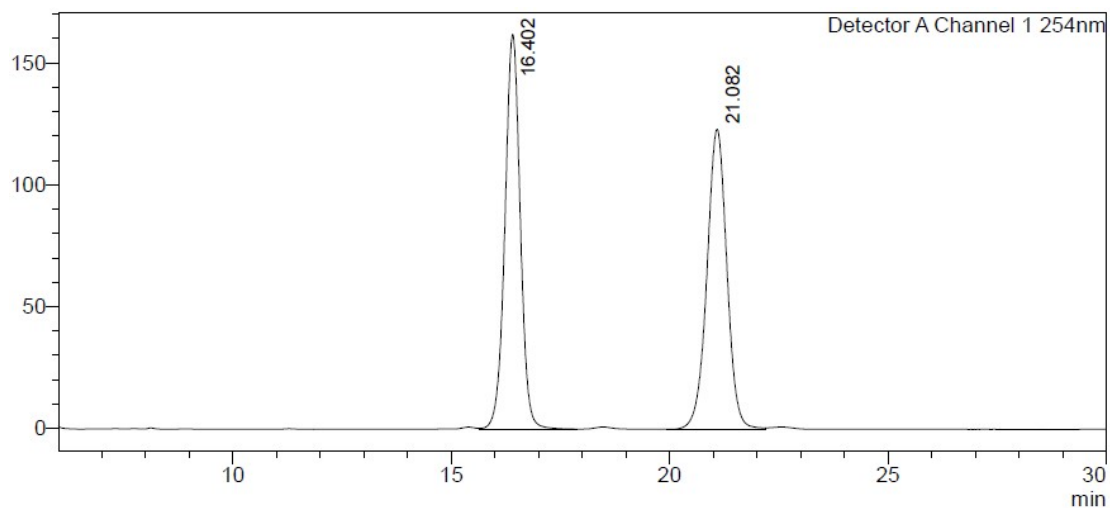
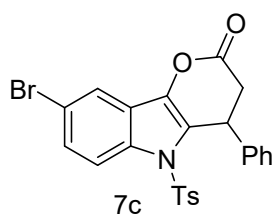
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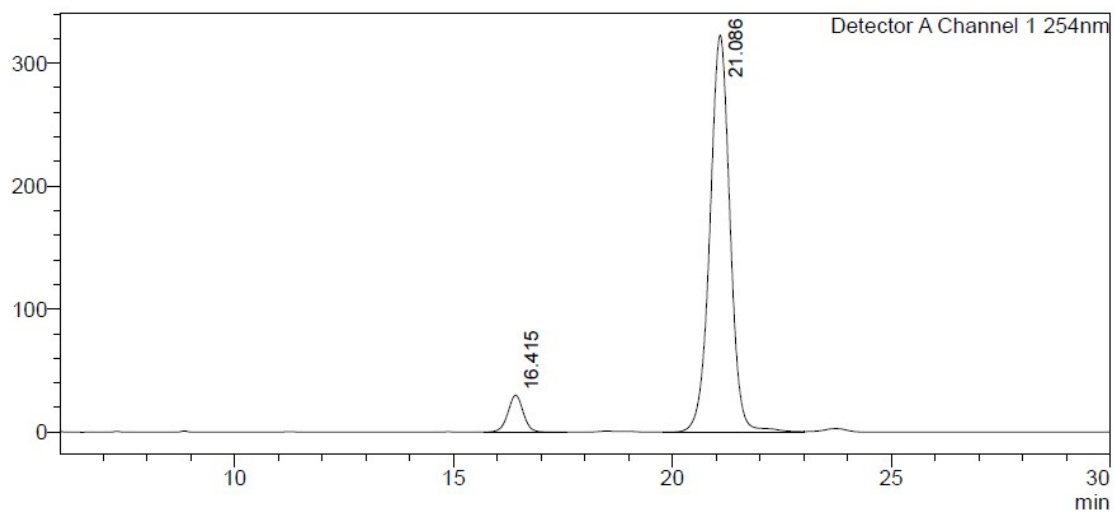
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PDA Ch1 254nm

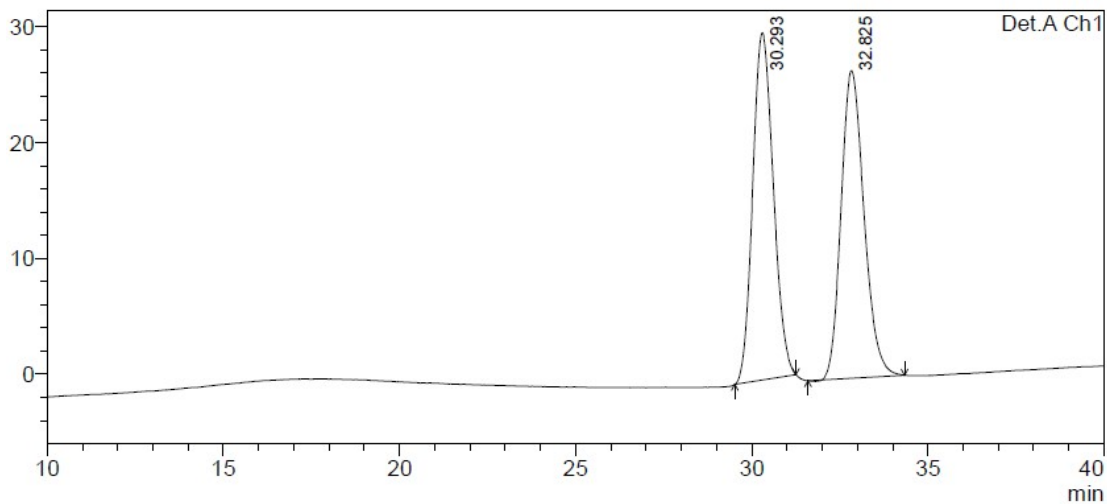
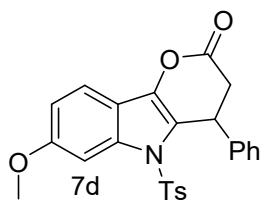
Peak#	Ret. Time	Area	Height	Area%
1	15.037	234967	11317	6.522
2	19.933	3367742	123064	93.478
Total		3602709	134381	100.000



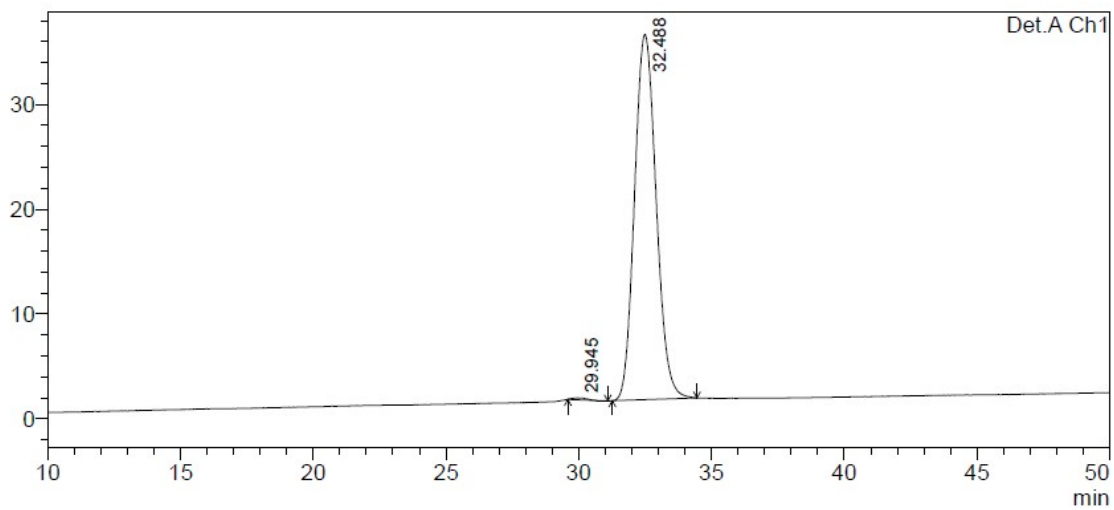
Peak#	Ret. Time	Area	Height	Area%
1	16.402	3971492	162076	50.347
2	21.082	3916706	123227	49.653
Total		7888198	285303	100.000



Peak#	Ret. Time	Area	Height	Area%
1	16.415	736794	29947	6.665
2	21.086	10317195	322541	93.335
Total		11053990	352488	100.000

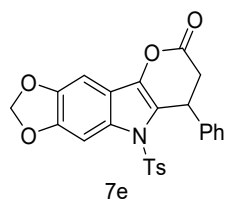


Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.293	1219916	29997	50.387	53.022
2	32.825	1201193	26578	49.613	46.978
Total		2421109	56575	100.000	100.000

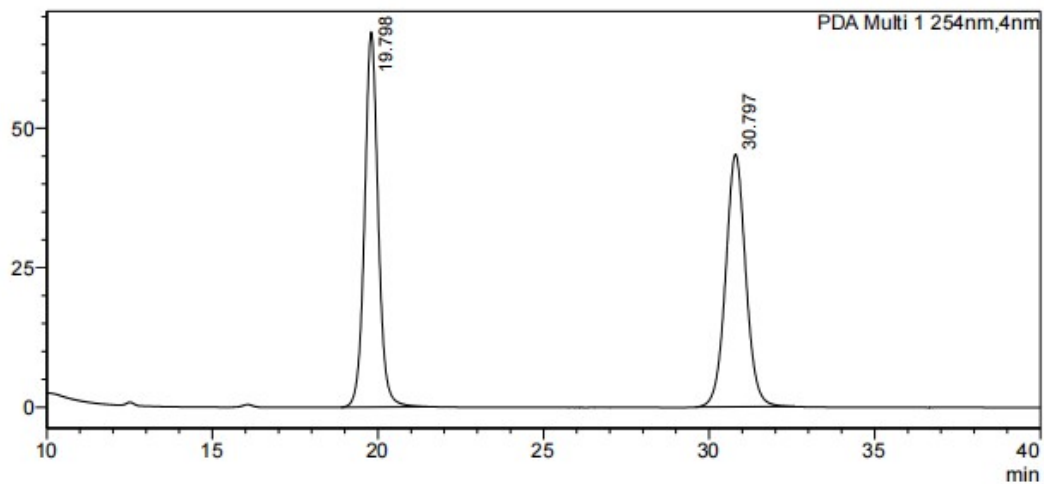


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.945	6217	188	0.314	0.537
2	32.488	1974146	34854	99.686	99.463
Total		1980363	35042	100.000	100.000



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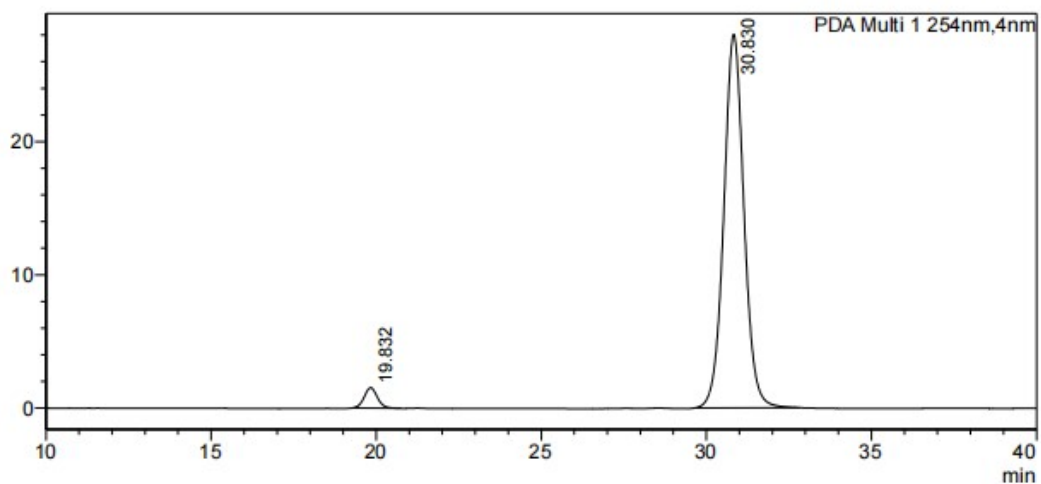


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.798	1915595	67179	50.019
2	30.797	1914127	45263	49.981
Total		3829723	112442	100.000

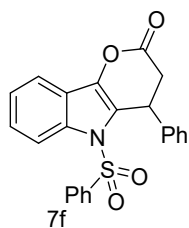
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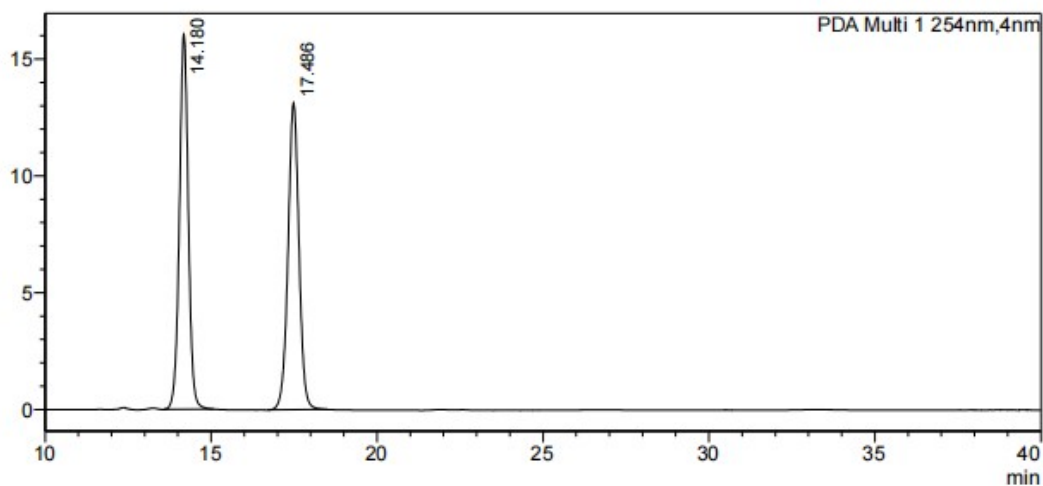
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.832	42921	1537	3.481
2	30.830	1190045	28024	96.519
Total		1232966	29561	100.000



mAU

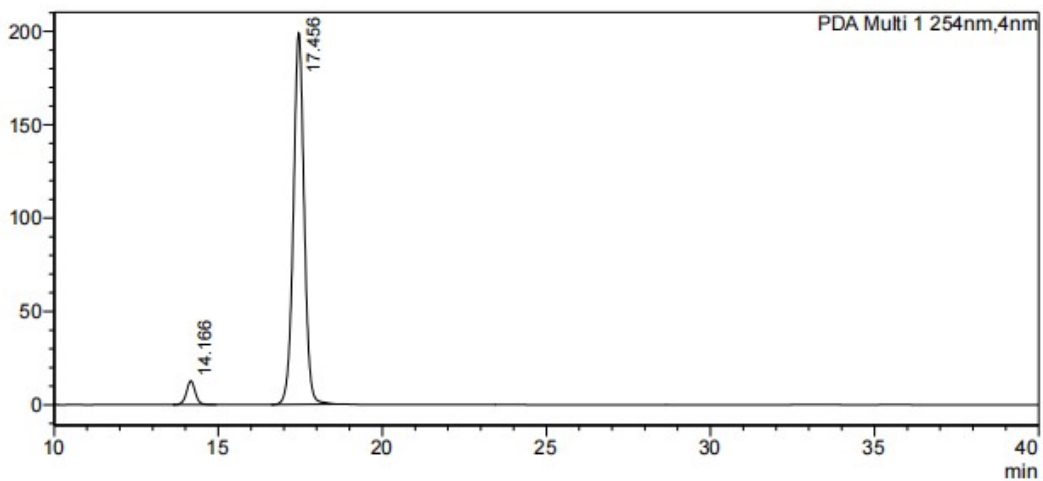


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.180	301063	16047	49.980
2	17.486	301301	13132	50.020
Total		602364	29178	100.000

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<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.166	238538	12709	4.981
2	17.456	4550410	198938	95.019
Total		4788948	211647	100.000