Supporting Information

Asymmetric Kinetic Resolution of Sulfides for the Construction of Unsymmetric Sulfides and Chiral 3,3-Disubstituted Oxindoles

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Contents

General Information

The NMR spectra were recorded on a Bruker NMR spectrometers. Chemical shifts (δ) for ^{1}H NMR (400 Hz), ^{13}C NMR (100 Hz) were given in ppm. Data were reported as follows: chemical shift, intergration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics maXis UHR-TOF MS. Analytical high performance liquid chromatography (HPLC) was carried out on a SHIMADZU equipment with a series of chiral columns. Melting points were determined on a SGW X-4 microscope melting point apparatus and were uncorrected. Optical rotations were measured on a Hanon P810 NEW instrument at λ =589 nm. Reactions were powered by magnetic stirrers. Flash column chromatography was carried out on silica gel (300-400 mesh) using a forced flow of eluent. For TLC, silica gel plates were used and visualized by fluorescence quenching under UV light.

The commercial available materials were purchased from Sigma-Aldrich®, Adamas-beta®, Energy Chemical® and Heowns®. Solvents for the kinetic resolution reaction were treated by the standard methods. The synthesis of the *para*-quinone methides (**VIII**) was according to our previous study[1].

Figure S1a: The Addition Reaction of *p*-QMs Derived from Aldehydes

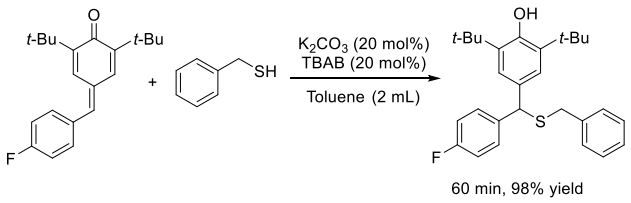
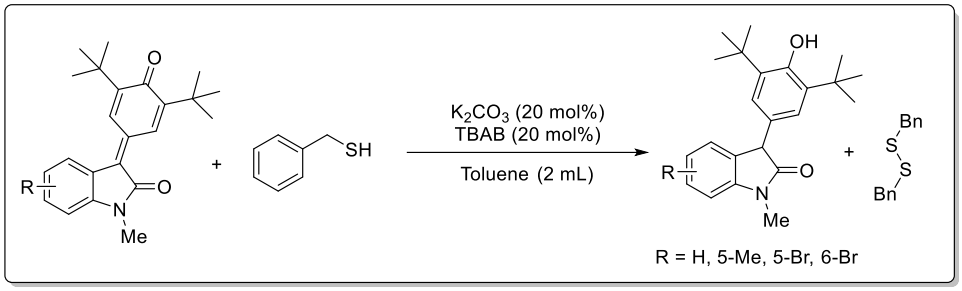


Table S1: Solvent Optimization

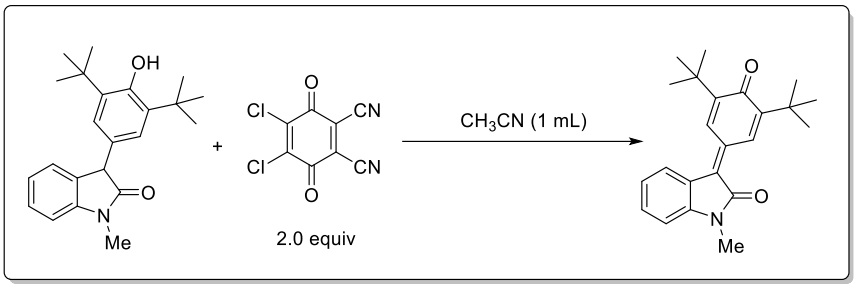
solvent	yield	ee%
Tol	45%	86%
DCM	95%	7%
EtOAc	80%	16%
EtOH	99%	0%
Acetone	91%	4%
CH_3CN	76%	3%

*All the reactions were carried out with **1a** (0.1 mmol) in the presence of chiral catalyst (5 mol%) in solvent (2.0 mL) at r.t. for 30 min. Yields of isolated products are given, and the ee value was determined by HPLC analysis.

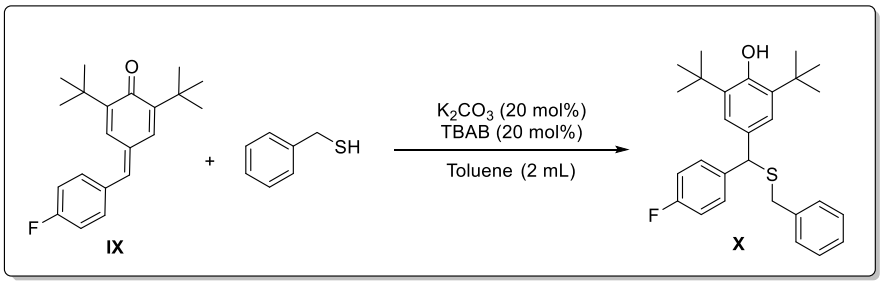
The Addition-S_N2 Reaction Circulation



The thiophenol **2** (0.4 mmol) was added to a suspension of K_2CO_3 (0.02 mmol, 20 mol%) and tetrabutylammonium bromide (0.02 mmol, 20 mol%) in toluene (2 mL), then the mixture was stirred for 10 min at surrounding temperature. The solution was stirred sequentially for another 30 min at room temperature after the *para*-quinone methides (0.1 mmol) was added. The final products **4** were obtained by flash column chromatography (PE:EA = 5:1) as white solids. And the disulfides were repurified by flash column chromatography (PE).



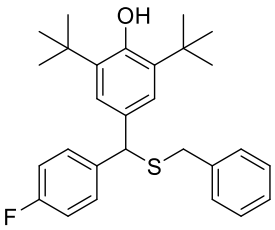
To a solution of 3-aryl oxoindole (0.1 mmol) in CH_3CN was added DDQ (0.2 mmol), and the mixture was stirred for 10 min at surrounding temperature. The *para*-quinone methide product was obtained by flash column chromatography (PE:EA = 10:1) as dark red solid.



The thiophenol (0.4 mmol) was added to a suspension of K_2CO_3 (0.02 mmol, 20 mol%) and tetrabutylammonium bromide (0.02 mmol, 20 mol%) in toluene (2 mL), then the mixture was stirred for 10 min at surrounding temperature. The solution was stirred sequentially for another 60 min at room temperature after the *para*-quinone methides (0.1 mmol) were added. The final product was obtained by flash column

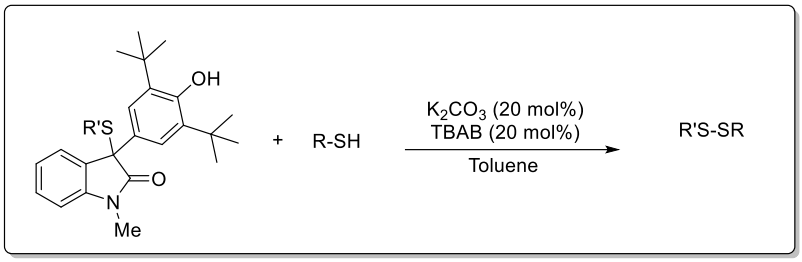
chromatography (PE:EA = 20:1) as white solid.

4-((benzylthio)(4-fluorophenyl)methyl)-2,6-di-tert-butylphenol (X)



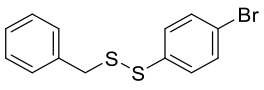
White soild, (m.p.: 81-83 ºC); 42.5 mg, 98% yield, R_f = 0.29 (PE); ^{1}H NMR (400 MHz, DMSO) δ 7.38-7.34 (m, 2H), 7.28-7.26 (m, 2H), 7.24-7.23 (m, 1H), 7.12 (s, 2H), 7.01-6.97 (t, *J* = 8 Hz, 2H), 5.14 (s, 1H), 4.84 (s, 1H), 3.51 (s, 2H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.98, 160.54, 152.91, 138.07, 137.54, 137.51, 135.83, 131.11, 130.04, 129.96, 129.04, 128.39, 126.96, 125.00, 115.38, 115.16, 77.38, 77.06, 76.74, 52.89, 36.76, 34.43, 30.31; HRMS (ESI) *m/z* calcd for $C_{28}H_{33}FNaOS^+$ [(M+Na)$^+$]: 459.2128, found: 459.2199.

The Synthesis of Unsymmetrical Disulfides



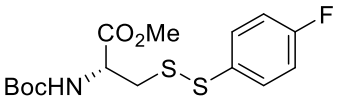
The thiophenol (0.2 mmol) was added to a suspension of K_2CO_3 (0.02 mmol, 20 mol%) and tetrabutylammonium bromide (0.02 mmol, 20 mol%) in toluene (2 mL), then the mixture was stirred for 10 min at surrounding temperature. The solution was stirred sequentially at room temperature after the compound **1** (0.1 mmol) was added and determined by TLC. The final product was obtained by flash column chromatography as white solid.

1-benzyl-2-(4-bromophenyl)disulfane (3a)



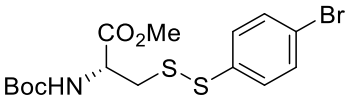
White solid (m.p.: 43-45 ℃); 27.5 mg, 90% yield, R_f = 0.65 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.27-7.24 (m, 7H), 3.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.36, 131.86, 129.38, 129.20, 128.58, 127.65, 120.64, 43.42; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}BrNaS_2^+$ [(M+Na)$^+$]: 332.9378, found: 332.9349.

methyl N-(tert-butoxycarbonyl)-S-((4-fluorophenyl)thio)-L-cysteinate (3b)



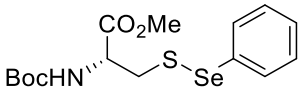
Colourless oil; 18.2 mg, 50% yield, R_f = 0.45 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.06-7.02 (t, *J* = 8 Hz, 2H), 5.29-5.27 (m, 1H), 4.65-4.61 (m, 1H), 3.75 (s, 3H), 3.23-3.12 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ171.06, 163.81, 161.34, 154.96, 131.51, 116.43, 116.21, 80.29, 52.77, 52.67, 40.78, 28.29; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}FNNaO_4S_2^+$ [(M+Na)$^+$]: 384.0710, found: 384.0640.

methyl N-(tert-butoxycarbonyl)-S-(phenylthio)-L-cysteinate (3c)



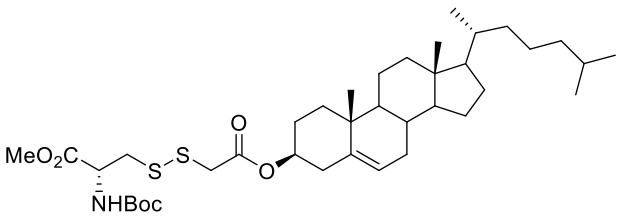
White solid (m.p.: 50-52 ℃); 24 mg, 57% yield, R_f = 0.45 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (d, *J* = 8 Hz, 2H), 7.40-7.38 (d, *J* = 8 Hz, 2H), 5.28-5.27 (m, 1H), 4.62-4.60 (m, 1H), 3.75 (s, 3H), 3.24-3.13 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.98, 132.19, 129.85, 121.42, 52.68, 40.96, 28.30; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}BrNNaO_4S_2^+$ [(M+Na)$^+$]: 443.9909, found: 443.9898.

methyl N-(tert-butoxycarbonyl)-S-(phenylselanyl)-L-cysteinate (3d)



White solid (m.p.: 40-42 ℃); 15.6 mg, 40% yield, R_f = 0.40 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (d, *J* = 8 Hz, 2H), 7.35-7.29 (m, 3H), 5.28-5.26 (m, 1H), 4.63-4.59 (m, 1H), 3.74 (s, 3H), 3.37-3.24 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.10, 154.98, 130.71, 129.32, 127.92, 80.20, 53.60, 52.58, 40.17, 28.30; HRMS (ESI) *m/z* calcd for $C_{15}H_{21}NNaO_4S_2^+$ [(M+Na)$^+$]: 414.0249, found: 414.0200.

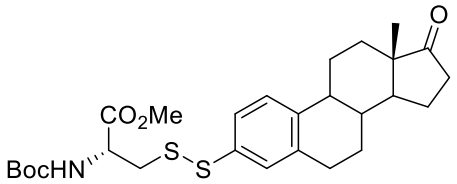
methyl N-(tert-butoxycarbonyl)-S-((2-(((3S,10R,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-2-oxoethyl)thio)-L-cysteinate (3e)



White solid (m.p.: 48-50 ℃); 41.6 mg, 60% yield, R_f = 0.78 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43-5.38 (m, 2H), 4.71-4.60 (m, 2H), 3.77 (s, 3H), 3.47 (s, 2H), 3.25 (br, 2H), 2.36-2.34 (d, *J* = 8 Hz, 2H), 2.05 (s, 1H), 2.03-1.89 (m, 5H), 1.67-

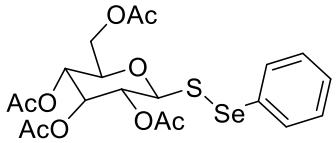
1.50 (m, 6H), 1.45 (s, 9H), 1.39-1.08 (m, 15H), 1.03 (s, 3H), 0.92-0.91 (d, *J* = 4 Hz, 3H), 0.87-0.85 (d, *J* = 8 Hz, 6H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.21, 168.79, 155.08, 139.32, 122.99, 80.27, 75.55, 60.43, 56.67, 56.11, 52.81, 52.68, 49.99, 42.31, 41.69, 41.24, 39.70, 39.52, 37.99, 36.94, 36.58, 36.18, 35.80, 31.90, 31.83, 30.22, 28.32, 28.25, 28.03, 27.67, 24.29, 23.83, 22.85, 22.59, 21.03, 19.33, 18.73, 14.23, 11.87; HRMS (ESI) *m/z* calcd for $C_{38}H_{63}NNaO_6S_2^+$ [$(M+Na)^+$]: 716.3989, found: 716.3928.

methyl N-(tert-butoxycarbonyl)-S-(((13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)thio)-L-cysteinate (3f)



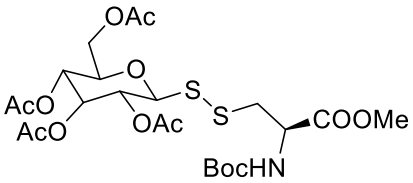
White solid (m.p.: 85-87 ℃); 29.6 mg, 57% yield, R_f = 0.43 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.29 (m, 1H), 7.27-7.26 (m, 2H), 5.36-5.34 (d, *J* = 8 Hz, 1H), 4.66-4.61 (m, 1H), 3.76 (s, 3H), 3.23-3.12 (m, 2H), 2.94-2.92 (m, 2H), 2.55-2.48 (dd, *J* = 20 Hz, *J* = 8 Hz, 1H), 2.42-2.39 (m, 1H), 2.29-1.96 (m, 5H), 1.87-1.84 (m, 2H), 1.67-1.52 (m, 4H), 1.45 (s, 9H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.19, 155.02, 139.63, 137.73, 133.50, 129.34, 126.35, 126.30, 80.25, 68.00, 52.82, 52.67, 50.44, 47.95, 44.29, 40.74, 37.98, 35.86, 31.53, 29.35, 28.33, 26.35, 25.67, 25.63, 21.60, 13.84; HRMS (ESI) *m/z* calcd for $C_{27}H_{37}NNaO_5S_2^+$ [$(M+Na)^+$]: 542.2005, found: 542.1978.

(2R,3R,4R,5R,6S)-2-(acetoxymethyl)-6-((phenylselanyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3g)



White solid (m.p.: 95-97 ℃); 30.2 mg, 58% yield, R_f = 0.37 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.26 (br, 3H), 5.29-5.21 (m, 2H), 5.14-5.10 (t, *J* = 8 Hz, 1H), 4.63-4.61 (d, *J* = 8 Hz, 1H), 4.18-4.14 (dd, *J* = 12 Hz, *J* = 4 Hz, 1H), 4.10-4.07 (d, *J* = 12 Hz, 1H), 3.78-3.74 (m, 1H), 2.02-2.00 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.56, 170.19, 169.35, 169.21, 132.14, 131.38, 128.96, 127.99, 85.75, 76.03, 73.76, 70.72, 68.07, 61.99, 20.65, 20.61, 20.57; HRMS (ESI) *m/z* calcd for $C_{20}H_{24}NaO_9SSe^+$ [$(M+Na)^+$]: 543.0198, found: 543.0161.

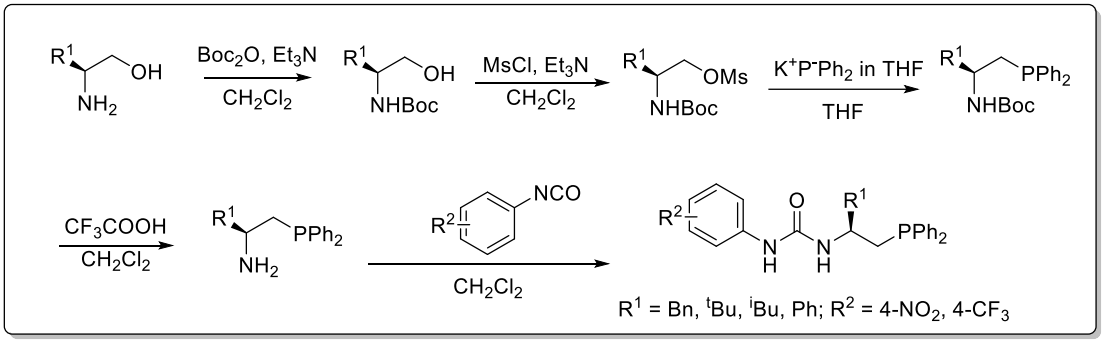
(2R,3R,4R,5R,6S)-2-(acetoxymethyl)-6-(((R)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)disulfanyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3h)



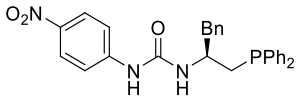
White solid (m.p.: 125-127 ℃); 37.0 mg, 62% yield, R_f = 0.24 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35-5.33 (d, *J* = 8 Hz, 1H), 5.31-5.24 (m, 2H), 5.16-5.12 (t, *J* = 8 Hz, 1H), 4.71-4.66 (m, 1H), 4.59-4.57 (d, *J* = 8 Hz, 1H), 4.31-4.26 (m, 1H), 4.18-4.15 (m, 1H), 3.82-3.79 (br, 1H), 3.77 (s, 3H), 3.34-3.29 (dd, *J* = 16 Hz, *J* = 4 Hz,1H), 3.08-3.03 (dd, *J* = 12 Hz, *J* = 8 Hz,1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.40, 170.63, 170.20, 169.40, 169.17, 155.05, 87.88, 80.27, 76.14, 73.79, 68.88, 67.84, 61.96, 52.91, 52.65, 42.62, 28.31, 20.68, 20.64, 20.62; HRMS (ESI) *m/z* calcd for $C_{23}H_{35}NNaO_{13}S_2^+$ [$(M+Na)^+$]: 620.1442, found: 620.1423.

The Synthesis of Chiral Catalysts

The preparation of chiral catalysts referred to the foregone literatures[2].



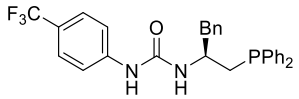
(S)-1-(1-(diphenylphosphanyl)-3-phenylpropan-2-yl)-3-(4-nitrophenyl)urea (E)



Bright yellow solid (m.p.: 61-63 ℃); R_f = 0.47 (PE/EA = 2:1); $[\alpha]_D^{21.5}$ = 6.73 (*c* 0.37, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.03 (d, *J* = 12 Hz, 2H), 7.56-7.28 (m, 14H), 7.24-7.22 (d, *J* = 8 Hz, 2H), 7.20-7.18 (d, *J* = 8 Hz, 1H), 7.15-7.13 (d, *J* = 8 Hz, 2H), 5.55-5.53 (d, *J* = 8 Hz, 1H), 4.22-4.19 (m, 1H), 3.03-2.93 (m, 2H), 2.44-2.39 (m, 1H), 2.26-2.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.88, 145.82, 141.74, 138.04, 137.94, 137.59, 137.53, 137.42, 132.87, 132.77, 132.68, 132.58, 129.47, 128.97, 128.83, 128.69, 128.66, 128.62, 128.59, 128.53, 126.69, 125.23, 117.66, 49.89, 42.06, 33.75; ^{31}P NMR (163 MHz, $CDCl_3$) δ -23.87; HRMS (ESI) *m/z* calcd for $C_{28}H_{26}N_3NaO_3P^+$ [$(M+Na)^+$]: 506.1604, found: 506.1666.

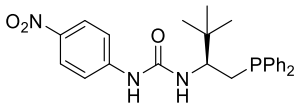
(S)-1-(1-(diphenylphosphanyl)-3-phenylpropan-2-yl)-3-(4-

(trifluoromethyl)phenyl)urea (F)



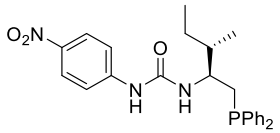
White solid (m.p.: 52-54 ℃); R_f = 0.64 (PE/EA = 2:1); $[\alpha]_D^{21.7}$ = 11.9 (*c* 0.44, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 4H), 7.28-7.18 (m, 9H), 7.16-7.14 (m, 5H), 7.07-7.05 (d, *J* = 8 Hz, 2H), 5.49-5.47 (d, *J* = 8 Hz, 1H), 4.14-4.11 (m, 1H), 2.91-2.84 (m, 2H), 2.34-2.30 (m, 1H), 2.17-2.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.77, 142.01, 138.10, 137.99, 137.68, 137.65, 137.56, 132.89, 132.76, 132.70, 132.57, 129.46, 128.96, 128.82, 128.68, 128.61, 128.53, 126.67, 126.25, 126.22, 126.18, 126.14, 125.03, 124.70, 124.38, 124.05, 122.90, 118.96, 49.93, 49.77, 42.16, 42.08, 33.89, 33.75, 29.74; ^{31}P NMR (163 MHz, $CDCl_3$) δ -24.01; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.84; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}F_3N_2NaO_2P^+$ [$(M+Na)^+$]: 529.1627, found: 529.1569.

(S)-1-(1-(diphenylphosphanyl)-3,3-dimethylbutan-2-yl)-3-(4-nitrophenyl)urea (G)



Bright yellow solid (m.p.: 79-81 ℃); R_f = 0.50 (PE/EA = 2:1); $[\alpha]_D^{21.71}$ = 34.7 (*c* 0.37, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.03-8.01 (d, *J* = 8 Hz, 2H), 7.50-7.48 (d, *J* = 8 Hz, 2H), 7.43-7.37 (m, 4H), 6.30-6.21 (m, 3H), 7.21-7.20 (m, 3H), 5.70-5.68 (d, *J* = 8 Hz, 1H), 3.89-3.82 (m, 1H), 2.47-2.44 (d, *J* = 12 Hz, 1H), 2.47-2.44 (d, *J* = 12 Hz, 1H), 2.04-1.98 (t, *J* = 12 Hz, 1H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.83, 146.55, 141.31, 138.92, 138.80, 138.31, 138.18, 133.01, 132.84, 132.82, 132.65, 128.92, 128.64, 128.57, 128.51, 128.45, 125.31, 117.74, 56.33, 35.84, 35.77, 31.22, 31.10, 26.28; ^{31}P NMR (163 MHz, $CDCl_3$) δ -20.59; HRMS (ESI) *m/z* calcd for $C_{25}H_{28}N_3NaO_3P^+$ [$(M+Na)^+$]: 472.1760, found: 472.1725.

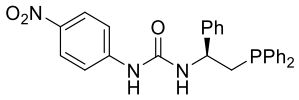
1-((2S,3S)-1-(diphenylphosphanyl)-3-methylpentan-2-yl)-3-(4-nitrophenyl)urea (H)



Bright yellow solid (m.p.: 66-68 ℃); R_f = 0.50 (PE/EA = 2:1); $[\alpha]_D^{21.7}$ = 7.9 (*c* 0.35, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-8.02 (m, 3H), 7.47-7.45 (d, *J* = 8 Hz, 1H), 7.41-7.35 (m, 4H), 7.30-7.28 (m, 3H), 7.24-7.23 (m, 3H), 5.77-5.75 (d, *J* = 8 Hz, 1H), 3.92 (br, 1H), 2.32-2.29 (d, *J* = 12 Hz, 1H), 2.09-2.03 (t, *J* = 12 Hz, 1H), 1.70 (br, 1H), 1.34-1.27 (m, 1H), 1.07-1.00 (m, 1H), 0.85-0.83 (d, *J* = 8 Hz, 3H), 0.77-0.73 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ154.47, 146.37, 141.41, 138.55, 138.43, 138.05, 137.92, 133.08, 132.89, 132.67, 132.48, 129.05, 128.68, 128.61, 128.56, 128.50, 125.33, 117.62, 52.43, 52.28, 39.71, 39.64, 31.09, 30.96, 25.24, 14.86; ^{31}P NMR (163 MHz, $CDCl_3$) δ -22.57; HRMS (ESI) *m/z* calcd for $C_{25}H_{28}N_3NaO_3P^+$ [$(M+Na)^+$]:

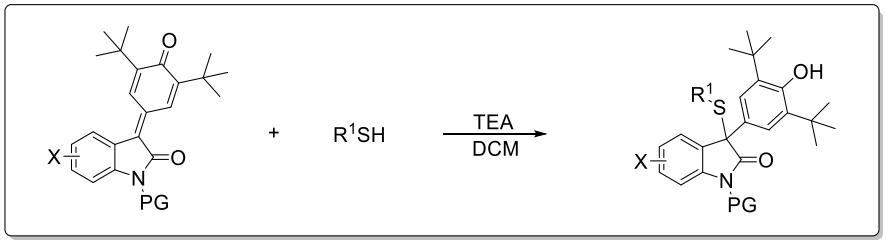
472.1760, found: 472.1711.

(S)-1-(2-(diphenylphosphanyl)-1-phenylethyl)-3-(4-nitrophenyl)urea (I)



Bright yellow solid (m.p.: 90-92 ℃); R_f = 0.43 (PE/EA = 2:1); $[\alpha]_D^{21.9}$ = -51.0 (*c* 0.38, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (d, *J* = 8 Hz, 2H), 7.43 (br, 1H), 7.38-7.33 (m, 5H), 7.31-7.27 (m, 7H), 7.24-7.17 (m, 5H), 5.93-5.91 (t, *J* = 4 Hz, 1H), 4.92-4.85 (m, 1H), 2.54-2.52 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.76, 145.39, 142.59, 142.53, 142.00, 137.55, 137.44, 137.33, 137.21, 132.89, 132.82, 132.70, 132.63, 129.11, 128.95, 128.88, 128.74, 128.68, 128.67, 128.61, 127.80, 126.00, 125.21, 117.79, 52.88, 52.72, 37.26, 37.10; ^{31}P NMR (163 MHz, $CDCl_3$) δ -23.35; HRMS (ESI) *m/z* calcd for $C_{27}H_{24}N_3NaO_3P^+$ [$(M+Na)^+$]: 492.1447, found: 492.1391.

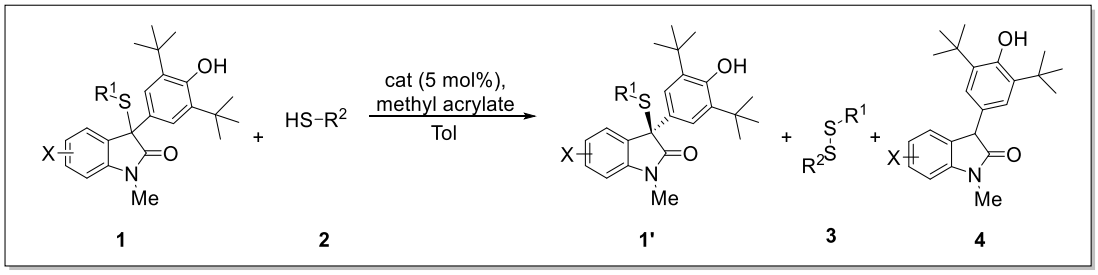
The Preparation of Racemic Compounds

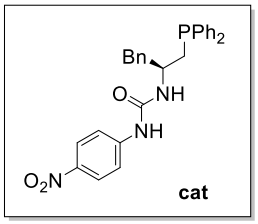


To a solution of triethylamine (0.01 mmol) in dichloromethane (2 mL) was added thiol (0.4 mmol), and the mixture was stirred for 5 minutes, then the *para*-quinone methides (0.2 mmol) was added. The solution was stirred at room temperature until finished (determined by the color change), and the racemic compounds were purified via flash column chromatography, dried under vacuum to afford the products **1** as white solid.

General Procedures for the Asymmetric Kinetic Resolution

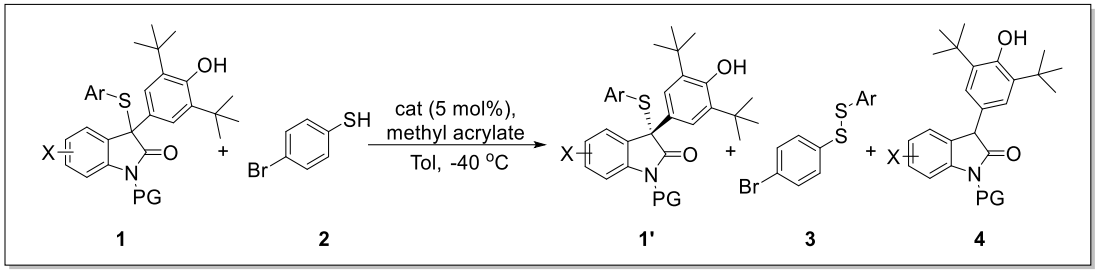
General Procedures for alkyl sulphide (GP 1)

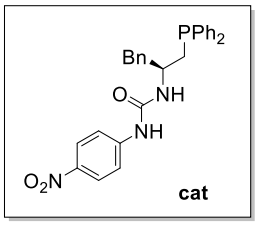




To a solution of the catalyst (5 mol%) in toluene (1.0 mL) was added methyl acrylate (1 μL), and the mixture was stirred for 5 min at room temperature, and then the thiophenol **2** (0.2 mmol) was added. The resulting mixture was vigorously stirred for 10 min at room temperature, after that, compound **1** (0.1 mmol) in 1 mL toluene was introduced and the solution kept stirring at room temperature until half of **1** worked out. The crude product was purified by flash column chromatography to afford the products **1'**, **3** and **4**.

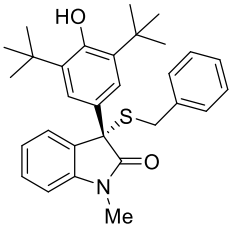
General Procedures for aryl sulfide (GP 2)





To a solution of the catalyst (5 mol%) in toluene (1.0 mL) was added methyl acrylate (1 μL), and the mixture was stirred for 5 min, and then the thiophenol **2** (0.2 mmol) was added. Then the resulting mixture was transferred to a cryogenic stirrer and stirred for 10 min at -40 ℃, after that, compound **1** (0.1 mmol) in 1 mL toluene was introduced and the solution kept stirring at cryogenic surroundings until half of **1** worked out. The crude product was purified by flash column chromatography to afford the products **1'**, **3** and **4**.

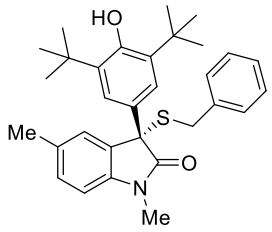
(S)-3-(benzylthio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'a)



The product **1'a** was prepared according to the **GP 1**. White solid (m.p.: 162-164 ℃); 15.6 mg, 44% yield, R_f = 0.50 (PE/EA = 5:1); $[\alpha]_D^{21.7}$ = -16.1 (*c* 0.41, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.43-7.41 (d, *J* = 8 Hz, 1H), 7.32-7.28 (t, *J* = 8 Hz, 1H), 7.21-7.08 (m, 6H), 6.84-6.82 (d, *J* = 8 Hz, 1H), 5.21 (s, 1H), 3.67-3.64 (d, *J* = 12 Hz, 1H), 3.56-3.53 (d, *J* = 12 Hz, 1H), 3.15 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.99, 153.60, 142.81, 136.61, 135.78, 130.04, 129.12, 128.84, 128.27, 126.98, 126.96, 125.52, 124.63, 122.76, 108.35, 58.54, 35.16, 34.56, 30.27, 26.51; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}NNaO_2S^+$ $[(M+Na)^+]$: 496.2281, found: 496.2235; Enantiomeric excess: 96%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 11.9 min; t_{minor} = 14.3

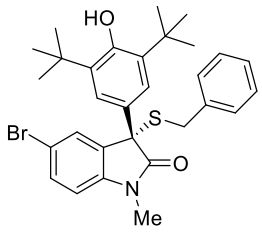
min).

(S)-3-(benzylthio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,5-dimethylindolin-2-one (1'b)



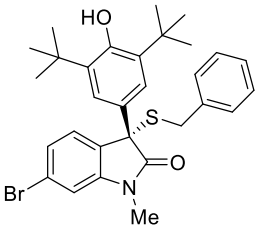
The product **1'b** was prepared according to the **GP 1**. White solid (m.p.: 170-172 °C); 20.5 mg, 42% yield, R_f = 0.48 (PE/EA = 5:1); $[\alpha]_D^{21.5}$ = -28.3 (*c* 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.23-7.16 (m, 4H), 7.13-7.10 (m, 3H), 6.75-6.73 (d, *J* = 8 Hz, 1H), 5.24 (s, 1H), 3.73-3.70 (d, *J* = 12 Hz, 1H), 3.60-3.57 (d, *J* = 12 Hz, 1H), 3.17 (s, 3H), 2.36 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.97, 153.56, 140.39, 136.79, 135.76, 132.29, 130.09, 129.14, 129.11, 128.26, 127.10, 126.95, 126.22, 124.67, 108.07, 58.66, 35.12, 34.57, 30.29, 26.56, 21.24; HRMS (ESI) *m/z* calcd for $C_{31}H_{37}NNaO_2S^+$ [$(M+Na)^+$]: 510.2437, found: 510.2364; Enantiomeric excess: 81%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 10.1 min; t_{minor} = 11.5 min).

(S)-3-(benzylthio)-5-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'c)



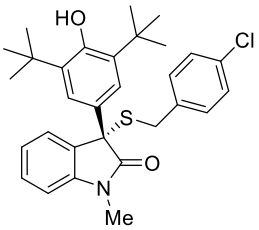
The product **1'c** was prepared according to the **GP 1**. White solid (m.p.: 157-159 °C); 19.3 mg, 35% yield, R_f = 0.44 (PE/EA = 5:1); $[\alpha]_D^{23.5}$ = -21.7 (*c* 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.47 (d, *J* = 4 Hz, 1H), 7.43 (s, 2H), 7.41-7.38 (dd, *J* = 8 Hz, *J* = 4 Hz, 1H), 7.22-7.13 (m, 3H), 7.11-7.09 (d, *J* = 8 Hz, 2H), 6.70-6.68 (d, *J* = 8 Hz, 1H), 5.25 (s, 1H), 3.73-3.70 (d, *J* = 12 Hz, 1H), 3.59-3.56 (d, *J* = 12 Hz, 1H), 3.14 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.45, 153.81, 141.69, 136.30, 136.02, 132.23, 131.64, 129.07, 128.67, 128.34, 127.16, 126.26, 124.50, 115.37, 109.76, 58.53, 35.23, 34.59, 30.26, 26.63; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}BrNNaO_2S^+$ [$(M+Na)^+$]: 574.1386, found: 574.1285; Enantiomeric excess: 96%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.5 mL/min; t_{major} = 25.1 min; t_{minor} = 26.3 min).

(S)-3-(benzylthio)-6-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'd)



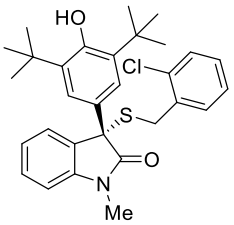
The product **1'd** was prepared according to the **GP 1**. White solid (m.p.: 144-146 ℃); 21.5 mg, 39% yield, R_f = 0.56 (PE/EA = 5:1); $[\alpha]_D^{21.3}$ = -49.4 (*c* 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.26-7.14 (m, 5H), 7.09-7.07 (d, *J* = 8 Hz, 2H), 6.96 (s, 1H), 5.25 (s, 1H), 3.68-3.65 (d, *J* = 12 Hz, 1H), 3.56-3.53 (d, *J* = 12 Hz, 1H), 3.11 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.78, 153.80, 144.07, 136.38, 135.99, 129.09, 128.35, 127.12, 126.83, 126.37, 125.57, 124.52, 122.46, 111.86, 58.28, 35.31, 34.61, 30.30, 26.65; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}BrNNaO_2S^+$ $[(M+Na)^+]$: 574.1386, found: 574.1316; Enantiomeric excess: 95%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 10.3 min; t_{minor} = 12.4 min).

(S)-3-((4-chlorobenzyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'e)



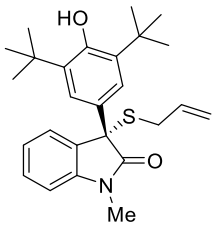
The product **1'e** was prepared according to the **GP 1**. White solid (m.p.: 102-104 ℃); 20.3 mg, 40% yield, R_f = 0.50 (PE/EA = 5:1); $[\alpha]_D^{21.2}$ = -69.9 (*c* 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.42-7.40 (d, *J* = 8 Hz, 1H), 7.33-7.29 (t, *J* = 8 Hz, 1H), 7.15-7.13 (d, *J* = 8 Hz, 2H), 7.13-7.09 (t, *J* = 8 Hz, 1H), 7.01-6.99 (d, *J* = 8 Hz, 2H), 6.83-6.81 (d, *J* = 8 Hz, 1H), 5.73-5.62 (m, 1H), 5.22 (s, 1H), 3.63-3.54 (q, *J* = 12 Hz, 2H), 3.15 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.86, 153.65, 142.72, 135.80, 135.36, 132.68, 130.43, 129.85, 128.92, 128.32, 126.81, 125.52, 124.60, 122.81, 108.40, 58.38, 34.55, 34.51, 30.25, 26.51; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}ClNNaO_2S^+$ $[(M+Na)^+]$: 530.1891, found: 530.1821; Enantiomeric excess: 94%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 10.4 min; t_{minor} = 12.4 min).

(S)-3-((2-chlorobenzyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'f)



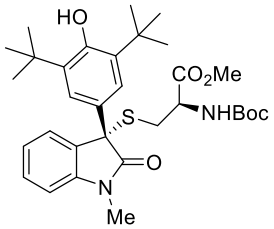
The product **1'f** was prepared according to the **GP 1**. White solid (m.p.: 162-164 ℃); 22.8 mg, 45% yield, R_f = 0.52 (PE/EA = 5:1); $[\alpha]_D^{21.9}$ = -22.5 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.41-7.39 (d, *J* = 8 Hz, 1H), 7.30-7.26 (t, *J* = 8 Hz, 1H), 7.24-7.22 (d, *J* = 8 Hz, 1H), 7.12-7.03 (m, 4H), 6.86-6.84 (d, *J* = 8 Hz, 1H), 5.20 (s, 1H), 3.82 (s, 2H), 3.26 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.90, 153.58, 142.53, 135.72, 134.86, 134.11, 131.42, 130.12, 129.34, 128.88, 128.34, 126.75, 126.59, 125.47, 124.75, 122.80, 108.37, 58.21, 34.54, 32.32, 30.27, 26.61; HRMS (ESI) *m/z* calcd for $C_{30}H_{34}ClNNaO_2S^+$ $[(M+Na)^+]$: 530.1891, found: 530.1793; Enantiomeric excess: 76%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.5 mL/min; t_{major} = 19.6 min; t_{minor} = 21.1 min).

(S)-3-(allylthio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'g)



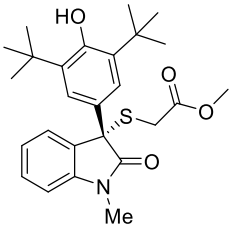
The product **1'g** was prepared according to the **GP 1**. White solid (m.p.: 130-132 ℃); 16.1 mg, 38% yield, R_f = 0.48 (PE/EA = 5:1); $[\alpha]_D^{23.4}$ = 32.9 (*c* 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.45-7.43 (d, *J* = 8 Hz, 1H), 7.33-7.29 (td, *J* = 8 Hz, *J* = 1.2 Hz, 1H), 7.15-7.11 (td, *J* = 8 Hz, *J* = 0.8 Hz, 1H), 6.86-6.84 (d, *J* = 8 Hz, 1H), 5.73-5.62 (m, 1H), 5.22 (s, 1H), 4.90-4.83 (m, 2H), 3.22 (s, 3H), 3.07-2.05 (m, 2H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.49, 153.63, 142.96, 135.73, 133.63, 130.09, 128.86, 126.99, 125.73, 124.68, 122.74, 117.14, 108.28, 58.19, 34.55, 34.09, 30.24, 26.50; HRMS (ESI) *m/z* calcd for $C_{26}H_{33}NNaO_2S^+$ $[(M+Na)^+]$: 446.2124, found: 446.2070; Enantiomeric excess: 86%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 14.2 min; t_{minor} = 16.1 min).

methyl N-(tert-butoxycarbonyl)-S-((S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methyl-2-oxoindolin-3-yl)-L-cysteinate (1'h)



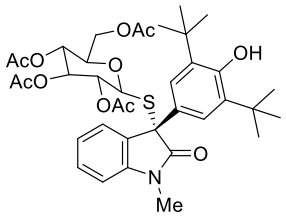
The product **1'h** was prepared according to the **GP 1**. White solid (m.p.: 88-90 °C); 17.5 mg, 30% yield, R_f = 0.51 (PE/EA = 2:1); $[\alpha]_D^{23.1}$ = -11.6 (*c* 0.38, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.38-7.36 (d, *J* = 8 Hz, 1H), 7.33-7.29 (t, *J* = 8 Hz, 1H), 7.13-7.09 (t, *J* = 8 Hz, 1H), 6.89-6.87 (d, *J* = 8 Hz, 1H), 5.28-5.24 (m, 2H), 4.32-4.29 (m, 1H), 3.67 (s, 3H), 3.29 (s, 3H), 2.92-2.76 (m, 2H), 1.43 (s, 9H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.19, 171.33, 153.71, 142.52, 135.95, 130.09, 129.10, 126.38, 125.40, 124.64, 122.94, 108.48, 79.99, 57.71, 52.76, 52.44, 34.54, 32.08, 30.22, 28.33, 26.66; HRMS (ESI) *m/z* calcd for $C_{32}H_{44}N_2NaO_6S^+$ [$(M+Na)^+$]: 607.2812, found: 607.2733; Enantiomeric excess: >99%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 95:5, λ = 254 nm, flow rate 1 mL/min; t_{major} = 12.9 min; t_{minor} = 11.0 min).

methyl (S)-2-((3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methyl-2-oxoindolin-3-yl)thio)acetate (1'i)



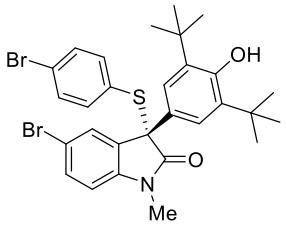
The product **1'i** was prepared according to the **GP 1**. White solid (m.p.: 151-153 °C); 10 mg, 21% yield, R_f = 0.6 (PE/EA = 2:1); $[\alpha]_D^{23.1}$ = -9.83 (*c* 0.37, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.46-7.44 (d, *J* = 8 Hz, 1H), 7.34-7.30 (t, *J* = 8 Hz, 1H), 7.14-7.10 (t, *J* = 8 Hz, 1H), 6.89-6.87 (d, *J* = 8 Hz, 1H), 5.26 (s, 1H), 3.53 (s, 3H), 3.29-3.25 (m, 4H), 3.18-3.15 (d, *J* = 12 Hz, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.58, 169.85, 153.78, 142.94, 135.87, 129.35, 129.20, 126.16, 125.73, 124.76, 122.79, 108.53, 57.85, 52.33, 34.56, 32.73, 30.22, 26.62; HRMS (ESI) *m/z* calcd for $C_{26}H_{33}NNaO_4S^+$ [$(M+Na)^+$]: 478.2023, found: 478.1967; Enantiomeric excess: 98%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 15.9 min; t_{minor} = 13.9 min).

(2R,3R,4R,5R,6S)-2-(acetoxymethyl)-6-(((S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methyl-2-oxoindolin-3-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (1'j)



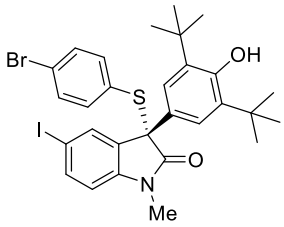
The product **1'j** was prepared according to the **GP 1**. White solid (m.p.: 81-83 °C); 26.4 mg, 37% yield, R_f = 0.38 (PE/EA = 2:1); $[\alpha]_D^{123.3}$ = -9.7 (*c* 0.48, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 3H), 7.41-7.37 (t, *J* = 8 Hz, 1H), 7.21-7.17 (t, *J* = 8 Hz, 1H), 6.91-6.89 (d, *J* = 8 Hz, 1H), 6.96 (s, 1H), 5.26 (s, 1H), 5.01-4.93 (m, 3H), 4.36-4.33 (d, *J* = 12 Hz, 1H), 4.18-4.14 (m, 1H), 3.75-3.71 (m. 1H), 3.23 (s, 3H), 3.07-3.04 (m, 1H), 2.07 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.08, 170.62, 170.21, 169.21, 169.16, 153.87, 143.39, 135.82, 129.58, 128.08, 126.35, 126.22, 124.80, 122.76, 108.34, 82.73, 75.40, 73.87, 69.40, 68.27, 61.81, 57.43, 34.58, 30.19, 26.65, 20.77, 20.72, 20.58, 20.52; HRMS (ESI) *m/z* calcd for $C_{37}H_{47}NNaO_{11}S^+$ $[(M+Na)^+]$: 736.2762, found: 736.2691; Enantiomeric excess: 99%, determined by HPLC (Lux® 5 μm Cellulose-1, hexane/*i*-PrOH 90:10, λ = 254 nm, flow rate 1 mL/min; t_{major} = 16.1 min; t_{minor} = 10.0 min).

(S)-5-bromo-3-((4-bromophenyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'k)



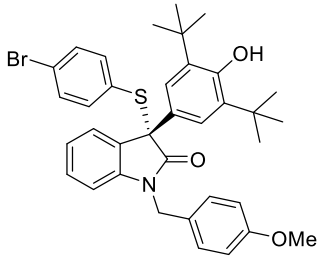
The product **1'k** was prepared according to the **GP 2**. Light red solid (m.p.: 178-180 °C); 21.0 mg, 34% yield, R_f = 0.33 (PE/EA = 10:1); ^1H R- (400 MHz, $CDCl_3$) δ 7.66-7.65 (d, *J* = 4 Hz, 1H), 7.50 (s, 2H), 7.37-7.34 (dd, *J* = 8 Hz, *J* = 4 Hz 1H), 7.26-7.24 (d, *J* = 8 Hz, 2H), 7.03-7.01 (d, *J* = 8 Hz, 2H), 6.45-6.43 (d, *J* = 8 Hz, 1H), 5.31 (s, 1H), 2.85 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.57, 154.13, 141.79, 137.90, 135.99, 132.15, 131.62, 131.42, 129.28, 129.23, 124.94, 124.81, 124.58, 115.12, 109.59, 62.43, 34.61, 30.19, 26.26; HRMS (ESI) *m/z* calcd for $C_{29}H_{31}Br_2NNaO_2S^+$ $[(M+Na)^+]$: 638.0334, found: 638.0260; Enantiomeric excess: 94%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 98:2, λ = 254 nm, flow rate 0.8 mL/min; t_{major} = 8.7 min; t_{minor} = 10.9 min).

(S)-3-((4-bromophenyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-iodo-1-methylindolin-2-one (1'l)



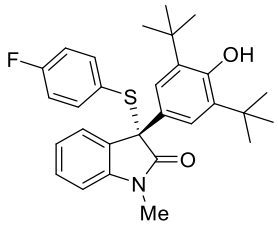
The product **1'l** was prepared according to the **GP 2**. Light red solid (m.p.: 185-187 ℃); 25.2 mg, 38% yield, R_f = 0.39 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.55-7.53 (d, *J* = 8 Hz, 1H), 7.49 (s, 2H), 7.26-7.24 (d, *J* = 8 Hz, 2H), 7.02-7.00 (d, *J* = 8 Hz, 2H), 6.36-6.34 (d, *J* = 8 Hz, 1H), 5.31 (s, 1H), 2.84 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.38, 154.12, 142.47, 137.93, 137.51, 135.97, 135.00, 132.37, 131.41, 129.31, 124.99, 124.78, 124.58, 110.16, 84.67, 62.21, 34.62, 30.20, 26.21; HRMS (ESI) *m/z* calcd for $C_{29}H_{31}BrINNaO_2S^+$ [$(M+Na)^+$]: 686.0196, found: 686.0124; Enantiomeric excess: 94%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 98:2, λ = 254 nm, flow rate 0.8 mL/min; t_{major} = 9.1 min; t_{minor} = 10.6 min).

(S)-3-((4-bromophenyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxybenzyl)indolin-2-one (1'm)



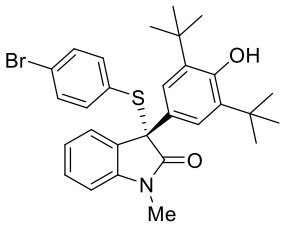
The product **1'm** was prepared according to the **GP 2**. Light red solid (m.p.: 72-74 ℃); 25.1 mg, 39% yield, R_f = 0.60 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 1H), 7.56 (s, 2H), 7.17-7.12 (m, 4H), 7.05-7.02 (m, 2H), 6.81-6.76 (m, 4H),6.52-6.50 (m, 1H), 5.29 (s, 1H), 4.71-4.67 (d, *J* = 16 Hz, 1H), 4.49-4.45 (d, *J* = 16 Hz, 1H), 3.78 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.08, 158.90, 153.96, 142.18, 137.92, 135.83, 131.58, 130.18, 129.82, 128.86, 128.44, 127.28, 126.30, 126.25, 125.05, 124.27, 122.57, 114.04, 109.44, 62.58, 55.32, 43.63, 34.64, 30.25; HRMS (ESI) *m/z* calcd for $C_{36}H_{38}BrNNaO_3S^+$ [$(M+Na)^+$]: 666.1648, found: 666.1621; Enantiomeric excess: 94%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 95:5, λ = 254 nm, flow rate 1.0 mL/min; t_{major} = 5.2 min; t_{minor} = 16.7 min).

(S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-((4-fluorophenyl)thio)-1-methylindolin-2-one (1'n)



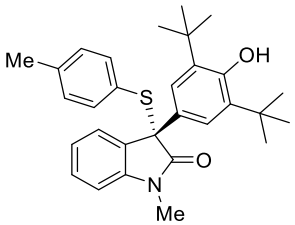
The product **1'n** was prepared according to the **GP 2**. Light red solid (m.p.: 175-177 ℃); 20.0 mg, 42% yield, R_f = 0.34 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.57-7.55 (d, *J* = 8 Hz, 1H), 7.23-7.19 (t, *J* = 8 Hz, 1H), 7.17-7.7.13 (t, *J* = 8 Hz, 1H),7.12-7.08 (m, 2H), 6.77-6.73 (t, *J* = 8 Hz, 2H), 6.54-6.52 (d, *J* = 8 Hz, 1H), 5.27 (s, 1H), 2.85 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.15, 164.90, 162.41, 153.93, 142.86, 138.55, 138.47, 135.77, 129.93, 128.77, 126.21, 126.01, 125.97, 125.51, 125.20, 122.57, 115.23, 115.02, 108.08, 62.64, 34.61, 30.25, 26.11; HRMS (ESI) *m/z* calcd for $C_{29}H_{32}FNNaO_2S^+$ [$(M+Na)^+$]: 500.2030, found: 500.2010; Enantiomeric excess: 90%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 98:2, λ = 254 nm, flow rate 0.6 mL/min; t_{major} = 8.7 min; t_{minor} = 10.6 min).

(S)-3-((4-bromophenyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'o)



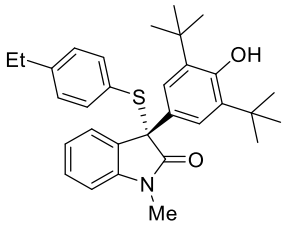
The product **1'o** was prepared according to the **GP 2**. Light red solid (m.p.: 88-90 ℃); 21.5 mg, 40% yield, R_f = 0.23 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.56-7.54 (d, *J* = 8 Hz, 1H), 7.25-7.21 (t, *J* = 8 Hz, 1H), 7.20-7.18 (d, *J* = 8 Hz, 2H), 7.17-7.13 (t, *J* = 8 Hz, 1H), 6.99-6.97 (d, *J* = 8 Hz, 2H), 6.57-6.55 (d, *J* = 8 Hz, 1H), 5.27 (s, 1H), 2.87 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.05, 153.94, 142.87, 137.84, 135.79, 131.18, 129.86, 129.79, 128.86, 126.19, 125.48, 125.18, 124.22, 122.57, 108.16, 62.46, 34.59, 30.23, 26.14; HRMS (ESI) *m/z* calcd for $C_{29}H_{32}BrNNaO_2S^+$ [$(M+Na)^+$]: 560.1229, found: 560.1206; Enantiomeric excess: 92%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 8.7 min; t_{minor} = 14.0 min).

(S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methyl-3-(p-tolylthio)indolin-2-one (1'p)



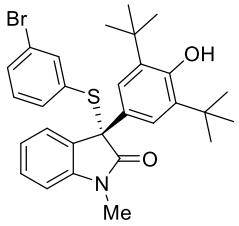
The product **1'p** was prepared according to the **GP 2**. Light red solid (m.p.: 72-74 ℃); 16.1 mg, 34% yield, R_f = 0.26 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.55-7.53 (d, *J* = 8 Hz, 1H), 7.20-7.13 (m, 2H), 7.00-6.98 (d, *J* = 8 Hz, 2H), 6.87-6.85 (d, *J* = 8 Hz, 2H), 5.51-5.49 (d, *J* = 8 Hz, 1H), 5.25 (s, 1H), 2.82 (s, 3H), 2.23 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.37, 153.80, 142.94, 139.48, 136.31, 135.63, 130.32, 128.78, 128.49, 127.10, 126.21, 125.90, 125.22, 122.39, 107.94, 62.47, 34.59, 30.26, 26.09, 21.26; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}NNaO_2S^+$ [$(M+Na)^+$]: 496.2281, found: 496.2252; Enantiomeric excess: 95%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 98:2, λ = 254 nm, flow rate 0.8 mL/min; t_{major} = 6.5 min; t_{minor} = 8.2 min).

(S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-((4-ethylphenyl)thio)-1-methylindolin-2-one (1'q)



The product **1'q** was prepared according to the **GP 2**. Light red solid (m.p.: 144-146 ℃); 20.4 mg, 42% yield, R_f = 0.26 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.55-7.53 (d, *J* = 8 Hz, 1H), 7.20-7.16 (t, *J* = 8 Hz, 1H), 7.15-7.11 (t, *J* = 8 Hz, 1H), 7.02-7.00 (d, *J* = 8 Hz, 2H), 6.89-6.87 (d, *J* = 8 Hz, 2H), 6.48-6.46 (d, *J* = 8 Hz, 1H), 5.26 (s, 1H), 2.80 (s, 3H), 2.55-2.49 (q, *J* = 8 Hz, 2H), 1.42 (s, 18H), 1.14-1.10 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.33, 153.81, 145.91, 142.94, 136.47, 135.64, 130.35, 128.50, 127.55, 127.33, 126.23, 125.87, 125.25, 122.41, 107.90, 62.52, 34.60, 30.27, 28.61, 26.06, 15.69; HRMS (ESI) *m/z* calcd for $C_{31}H_{37}NNaO_2S^+$ [$(M+Na)^+$]: 510.2437, found: 510.2404; Enantiomeric excess: 86%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 99:1, λ = 254 nm, flow rate 0.9 mL/min; t_{major} = 8.9 min; t_{minor} = 13.7 min).

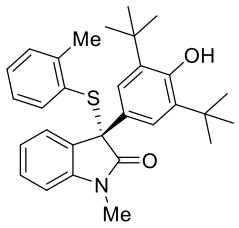
(S)-3-((3-bromophenyl)thio)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (1'r)



The product **1'r** was prepared according to the **GP 2**. White solid (m.p.: 64-66 ºC); 16.1 mg, 30% yield, R_f = 0.23 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.55-7.53 (d, *J* = 8 Hz, 1H), 7.34-7.32 (d, *J* = 8 Hz, 1H), 7.23-7.21 (t, *J* = 8 Hz, 1H), 720-7.19 (m, 1H), 7.19-7.15 (t, *J* = 8 Hz, 1H), 713-7.11 (d, *J* = 8 Hz, 1H), 6.97-6.93 (d, *J* = 8 Hz, 1H), 5.29 (s, 1H), 2.89 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz,

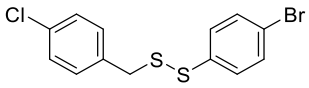
$CDCl_3$) δ 175.07, 153.98, 142.86, 138.49, 135.80, 134.92, 132.79, 132.22, 129.59, 129.27, 128.96, 126.24, 125.30, 125.22, 122.63, 121.44, 108.13, 62.56, 34.60, 30.23, 26.15; HRMS (ESI) *m/z* calcd for $C_{29}H_{32}BrNNaO_2S^+$ [$(M+Na)^+$]: 560.1229, found: 560.1206; Enantiomeric excess: 92%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 98:2, λ = 254 nm, flow rate 0.8 mL/min; t_{major} = 8.0 min; t_{minor} = 10.3 min).

(S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methyl-3-(o-tolylthio)indolin-2-one (1's)



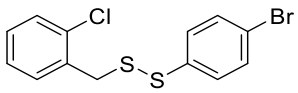
The product **1's** was prepared according to the **GP 2**. White solid (m.p.: 155-157 °C); 14.2 mg, 30% yield, R_f = 0.28 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.47-7.45 (d, *J* = 8 Hz, 1H), 7.25-7.21 (t, *J* = 8 Hz, 1H), 7.13-7.09 (t, *J* = 8 Hz, 2H), 7.07-7.03 (t, *J* = 8 Hz, 2H), 6.90-6.86 (t, *J* = 8 Hz, 1H), 6.60-6.58 (d, *J* = 8 Hz, 1H), 5.28 (s, 1H), 2.92 (s, 3H), 2.26 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.26, 153.81, 143.89, 142.96, 137.11, 135.50, 130.20, 130.03, 129.85, 129.43, 128.69, 126.40, 125.88, 125.46, 125.27, 122.22, 108.02, 62.00, 34.60, 30.25, 26.19, 21.06; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}NNaO_2S^+$ [$(M+Na)^+$]: 496.2281, found: 496.2267; Enantiomeric excess: 90%, determined by HPLC (Chiral ND, hexane/*i*-PrOH 98:2, λ = 254 nm, flow rate 0.8 mL/min; t_{major} = 6.8 min; t_{minor} = 9.4 min).

1-(4-bromophenyl)-2-(4-chlorobenzyl)disulfane (3i)



The product **3i** was prepared according to the **GP 1**. White solid (m.p.: 50-52 °C); 11.3 mg, 33% yield, R_f = 0.65 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.26-7.24 (m, 2H), 7.24-7.22 (m, 2H), 7.17-7.15 (m, 2H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.06, 134.89, 133.61, 131.92, 130.70, 129.34, 128.68, 120.85, 42.49.; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}BrClNaS_2^+$ [$(M+Na)^+$]: 366.8988, found: 366.8977.

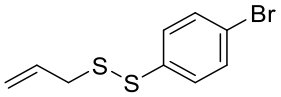
1-(4-bromophenyl)-2-(2-chlorobenzyl)disulfanee (3j)



The product **3j** was prepared according to the **GP 1**. White solid (m.p.: 44-46 °C); 9.3 mg, 27% yield, R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 3H), 7.27-7.22 (m, 3H), 7.20-7.15 (td, *J* = 8 Hz, *J* = 4 Hz, 1H), 7.14-7.09 (td, *J* = 8 Hz, *J* = 4 Hz, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.22, 134.23, 134.11, 131.78, 131.61, 129.70, 129.10, 128.75, 126.67, 120.48, 41.10; HRMS (ESI) *m/z* calcd for

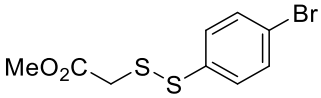
$C_{13}H_{10}BrClNaS_2^+$ [(M+Na)$^+$]: 366.8988, found: 366.8919.

1-allyl-2-benzyldisulfane (3k)



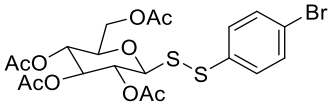
The product **3k** was prepared according to the **GP 1**. R_f = 0.74 (PE); HRMS (ESI) *m/z* calcd for $C_9H_9BrNaS_2^+$ [(M+Na)$^+$]: 282.9221, found: 282.9136.

methyl 2-(phenyldisulfanyl)acetate (3l)



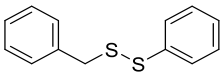
The product **3l** was prepared according to the **GP 1**. Colorless oil; 9.6 mg, 33% yield, R_f = 0.70 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (d, *J* = 8 Hz, 2H), 7.43-7.41 (d, *J* = 8 Hz, 2H), 3.61 (s, 3H), 3.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.16, 135.39, 132.11, 130.12, 121.55, 52.48, 40.59; HRMS (ESI) *m/z* calcd for $C_9H_9NaO_2S_2^+$ [(M+ Na)$^+$]: 314.9120., found: 314.9001.

(*2R,3R,5R,6S*)-2-(acetoxymethyl)-6-((4-bromophenyl)disulfanyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3m)



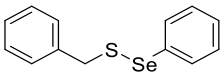
The product **3m** was prepared according to the **GP 1**. White solid (m.p.: 132-134 ℃); 12.6 mg, 23% yield, R_f = 0.31 (PE/EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (d, *J* = 8 Hz, 2H), 7.41-7.39 (d, *J* = 8 Hz, 2H), 5.30-5.22 (m, 2H), 5.11-5.06 (m, 1H), 4.61-4.59 (m, 1H), 4.17-4.08 (m, 2H), 3.76-3.72 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.47, 170.17, 169.33, 169.15, 136.15, 131.76, 130.38, 121.49, 87.46, 76.16, 73.72, 69.25, 67.90, 61.81, 20.64, 20.60, 20.59, 20.56; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}BrNaO_9S_2^+$ [(M+Na)$^+$]: 572.9859, found: 572.9786.

1-benzyl-2-phenyldisulfane (3n)



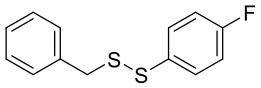
The product **3n** was prepared according to the **GP 1**. Colorless oil; 8.1 mg, 35% yield, R_f = 0.55 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.30-7.18 (m, 7H), 3.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.03, 136.56, 129.37, 128.90, 128.52, 127.68, 127.54, 126.80, 43.40; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}NaS_2^+$ [(M+Na)$^+$]: 255.0273, found: 255.0236.

benzyl(phenylselanyl)sulfane (3o)



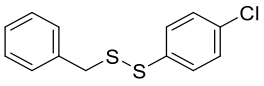
The product **3o** was prepared according to the **GP 1**. White solid (m.p.: 28-30 ℃); 9.2 mg, 33% yield, R_f = 0.55 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.27-7.23 (m, 8H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.77, 131.82, 130.10, 129.19, 129.08, 128.47, 127.44, 127.33, 42.32; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}NaSSe^+$ [$(M+Na)^+$]: 302.9717, found: 302.9719.

1-benzyl-2-(4-fluorophenyl)disulfane (3p)



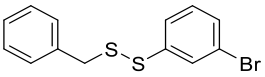
The product **3p** was prepared according to the **GP 1**. White solid (m.p.: 31-33 ℃); 8 mg, 32% yield, R_f = 0.68 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.30-7.22 (m, 5H), 6.97-6.93 (m, 2H), 3.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.39, 160.94, 136.50, 132.33, 132.30, 130.67, 130.59, 129.39, 128.53, 127.56, 116.07, 115.85, 43.44; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}FNaS_2^+$ [$(M+Na)^+$]: 273.0178, found: 273.0126.

1-benzyl-2-(4-chlorophenyl)disulfane (3q)



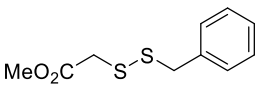
The product **3q** was prepared according to the **GP 1**. White solid (m.p.: 55-57 ℃); 7.5 mg, 28% yield, R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.28-7.20 (m, 7H), 3.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.39, 135.69, 132.78, 129.38, 129.06, 128.96, 128.58, 127.64, 43.45; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}ClNaS_2^+$ [$(M+Na)^+$]: 288.9883, found: 288.9864.

1-benzyl-2-(3-bromophenyl)disulfane (3r)



The product **3r** was prepared according to the **GP 1**. White solid (m.p.: 34-36 ℃); 11.5 mg, 37% yield, R_f = 0.68 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.31-7.25 (m, 7H), 7.12-7.08 (t, J = 8 Hz, 7H), 3.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.43, 136.27, 130.07, 129.64, 129.35, 128.57, 127.72, 125.71, 122.91, 43.51; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}BrNaS_2^+$ [$(M+Na)^+$]: 332.9378, found: 332.9370.

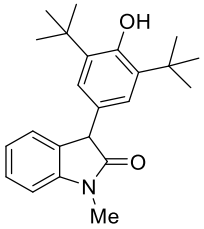
methyl 2-(benzyldisulfanyl)acetate (3s)



The product **3s** was prepared according to the **GP 1**. Colorless oil; 5.2 mg, 23% yield, R_f = 0.55 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.33 (m, 4H), 7.31-

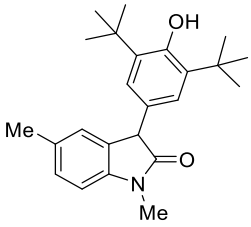
7.27 (m, 1H), 3.97 (s, 2H), 3.74 (s, 3H), 3.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.98, 136.87, 129.39, 128.61, 127.61, 52.49, 43.34, 41.05; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}NaO_2S_2^+$ [$(M+Na)^+$]: 251.0171, found: 251.0172.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (4a)



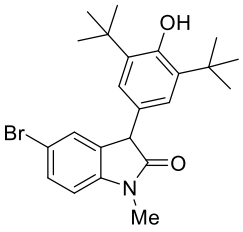
The product **4a** was prepared according to the **GP 1**. White solid (m.p.: 154-156 ℃); 23.9 mg, 68% yield, R_f = 0.69 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (t, *J* = 8 Hz, 1H), 7.22-7.20 (d, *J* = 8 Hz, 1H), 7.08-7.04 (t, *J* = 8 Hz, 1H), 6.99 (s, 2H), 6.90-6.88 (d, *J* = 8 Hz, 1H), 5.16 (s, 1H), 4.54 (s, 1H), 3.25 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.63, 153.24, 144.38, 136.03, 129.17, 128.15, 126.90, 125.14, 125.02, 122.53, 108.07, 51.78, 34.38, 30.24, 26.44; HRMS (ESI) *m/z* calcd for $C_{22}H_{29}NNaO_2^+$ [$(M+Na)^+$]: 374.2091, found: 374.2065.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,5-dimethylindolin-2-one (4b)



The product **4b** was prepared according to the **GP 1**. White solid (m.p.: 190-192 ℃); 20.8 mg, 57% yield, R_f = 0.69 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.20-7.15 (m, 4H), 7.11-7.09 (m, 3H), 6.73-6.71 (d, *J* = 8 Hz, 1H), 5.21 (s, 1H), 3.70-3.67 (d, *J* = 12 Hz, 1H), 3.57-3.54 (d, *J* = 12 Hz, 1H), 3.16 (s, 3H), 2.34 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.63, 153.20, 141.97, 136.05, 132.00, 129.36, 128.29, 127.21, 125.90, 125.05, 107.71, 51.96, 34.37, 30.25, 26.44, 21.10; HRMS (ESI) *m/z* calcd for $C_{24}H_{31}NNaO_2^+$ [$(M+Na)^+$]: 388.2247, found: 388.2227.

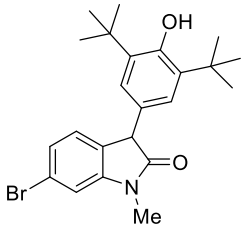
5-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (4c)



The product **4c** was prepared according to the **GP 1**. White solid (m.p.: 124-126 ℃); 27.9 mg, 65% yield, R_f = 0.66 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ

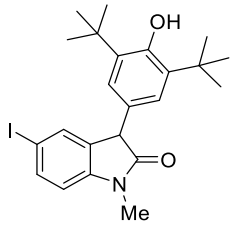
7.45-7.43 (d, *J* = 8 Hz, 1H), 7.30 (s, 1H), 6.93 (s, 2H), 6.78-6.76 (d, *J* = 8 Hz, 1H), 5.19 (s, 1H), 4.52 (s, 1H), 3.24 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.09, 153.47, 143.34, 136.26, 131.45, 131.00, 128.19, 126.27, 124.97, 115.19, 109.47, 51.91, 34.39, 30.20, 26.55; HRMS (ESI) *m/z* calcd for $C_{23}H_{28}BrNNaO_2^+$ [$(M+Na)^+$]: 452.1196, found: 452.1145.

6-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (4d)



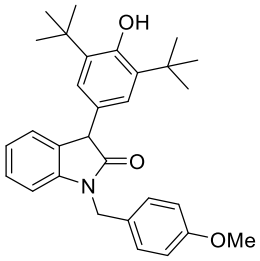
The product **4d** was prepared according to the **GP 1**. White solid (m.p.: 181-183 ℃); 25.7 mg, 60% yield, R_f = 0.77 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.18 (d, *J* = 8 Hz, 1H), 7.07-7.05 (d, *J* = 8 Hz, 1H), 7.04-7.03 (d, *J* = 4 Hz, 1H), 6.95 (s, 2H), 5.18 (s, 1H), 4.47 (s, 1H), 3.22 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.40, 153.41, 145.72, 136.21, 128.09, 126.40, 126.24, 125.29, 124.94, 121.67, 111.58, 51.46, 34.39, 30.23, 26.55; HRMS (ESI) *m/z* calcd for $C_{23}H_{28}BrNNaO_2^+$ [$(M+Na)^+$]: 452.1196, found: 452.1151.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-iodo-1-methylindolin-2-one (4e)



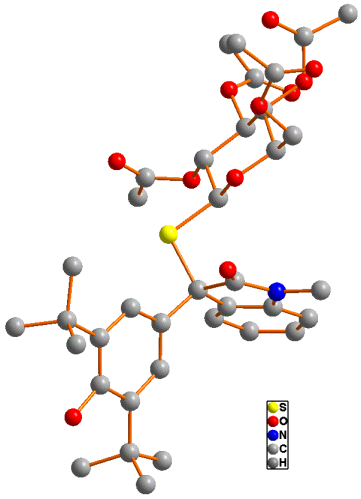
The product **4e** was prepared according to the **GP 2**. White solid (m.p.: 139-141 ^{o}C); 28.6 mg, 60% yield, R_f = 0.37 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (d, *J* = 8 Hz, 1H), 7.47 (s, 1H), 6.93 (s, 2H), 6.68-6.66 (d, *J* = 8 Hz, 1H), 5.19 (s, 1H), 4.50 (s, 1H), 3.22 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.91, 153.47, 144.04, 136.98, 136.26, 133.76, 131.75, 126.27, 124.99, 110.11, 85.02, 51.71, 34.40, 30.22, 26.50; HRMS (ESI) *m/z* calcd for $C_{23}H_{28}INNaO_2^+$ [$(M+Na)^+$]: 500.1057, found: 500.1045.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxybenzyl)indolin-2-one (4f)



The product **4f** was prepared according to the **GP 2**. White solid (m.p.: 145-147 ^{o}C); 26.5 mg, 58% yield, R_f = 0.43 (PE/EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (d, *J* = 8 Hz, 2H), 7.21-7.17 (t, *J* = 8 Hz, 1H), 7.18-7.16 (d, *J* = 8 Hz, 1H), 7.02-6.98 (t, *J* = 8 Hz, 1H), 6.97 (s, 2H), 6.84-6.82 (d, *J* = 8 Hz, 1H), 6.81-6.79 (d, *J* = 8 Hz, 1H), 5.16 (s, 1H), 5.05-5.01 (d, *J* = 16 Hz, 1H), 4.76-4.73 (t, *J* = 16 Hz, 1H), 4.59 (s, 1H), 3.77 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.84, 159.01, 153.26, 143.34, 136.15, 129.70, 128.72, 128.20, 128.01, 127.47, 125.10, 124.98, 122.55, 114.13, 109.05, 55.28, 52.00, 43.26, 34.39, 30.25; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}NNaO_3^+$ [$(M+Na)^+$]: 480.2509, found: 480.2495.

Crystal Data and Structure Refinement for 1906989 (1'j)



Empirical formula	C37H47NO11S
Formula weight	713.81
Temperature	173.00(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 10.2529(2) A alpha = 90 deg.
	b = 11.3156(3) A beta = 90 deg.
	c = 39.0323(9) A gamma = 90 deg.
Volume	4528.44(18) A^3
Z, Calculated density	4, 1.047Mg/m^3
Absorption coefficient	1.046 mm^-1
F(000)	1520
Theta range for data collection	4.068 to 71.058 deg.
Limiting indices	-12< = h< = 11, -7< = k< = 13, -38< = l< = 47
Reflections collected / unique	11429 / 7480 [R(int) = 0.0348]
Completeness to theta = 71.01	98.4 %
Absorption correction	multi-scan

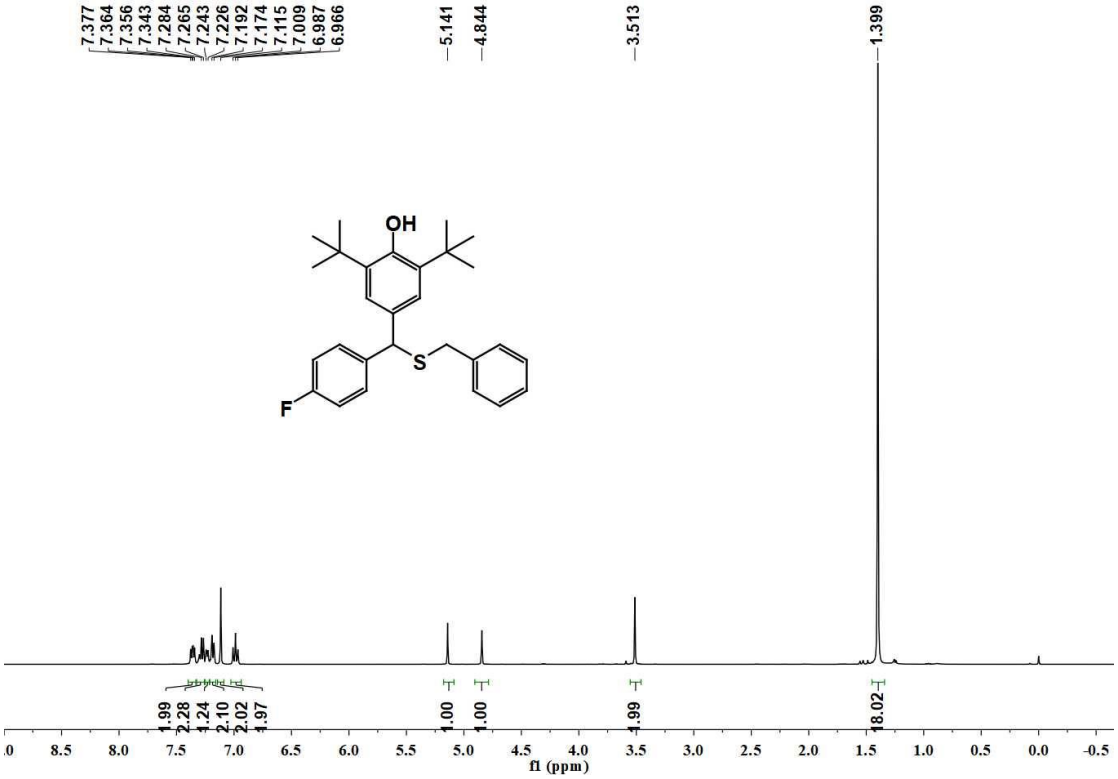
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7480 / 0 / 466
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1740
R indices (all data)	R1 = 0.0726, wR2 = 0.1793
Absolute structure Flack parameter	0.11(3)
Largest diff. peak and hole	-0.61 and 1.46 e. A^-3

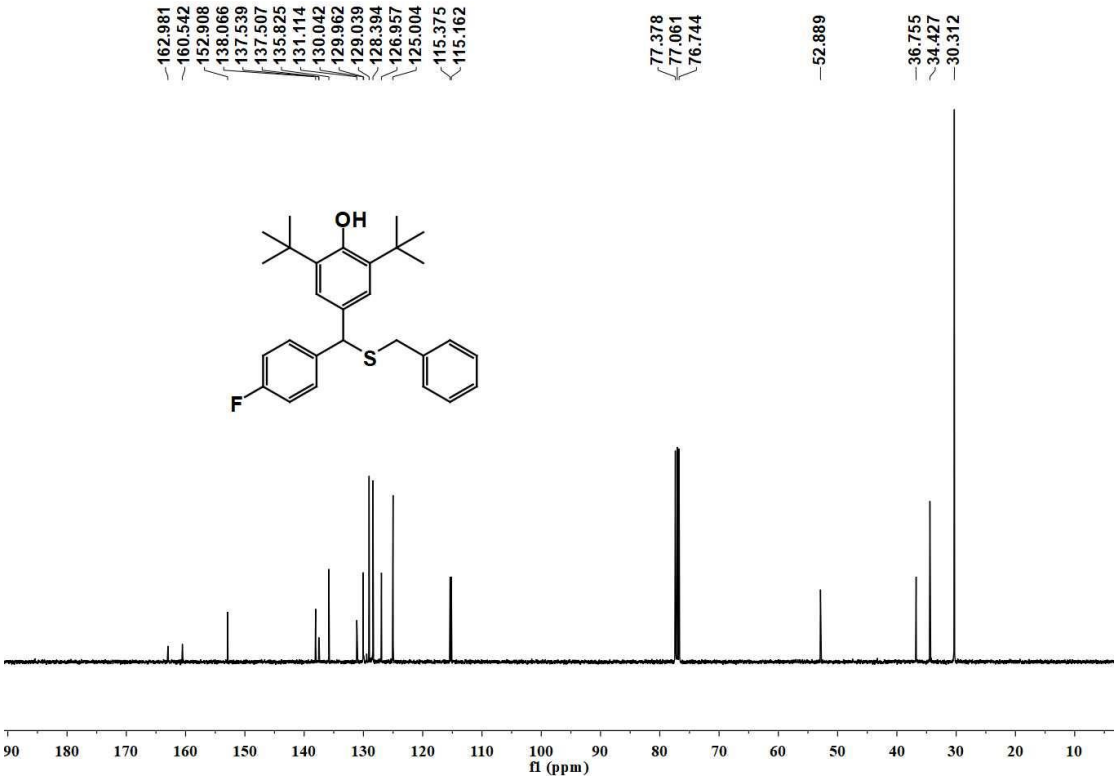
References

1. H.-Y. Wang, K.-Y. Wang, Y.-Q. Man, X.-N. Gao, L.-M. Yang, Y.-F Ren, N. Li, , B. Tang, G. Zhao, *Adv. Synth. Catal.*, 2017, **359**, 3934.
2. a) H.-Y. Wang, K. Zhang, C.-W. Zheng, Z. Chai, D.-D. Cao, J.-X. Zhang, G. Zhao, *Angew. Chem. Int. Ed.* 2015, **54**, 1775. b) D.-D. Cao, Z. Chai, J.-X. Zhang, Z.-Q. Ye, H. Xiao, H.-Y. Wang, J.-H. Chen, X.-Y. Wu, G. Zhao, *Chem. Commun.* 2013, **49**, 5972. c)H. Xiao, Z.Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang, G. Zhao, *Angew. Chem. Int. Ed.* 2010, **49**, 4467.

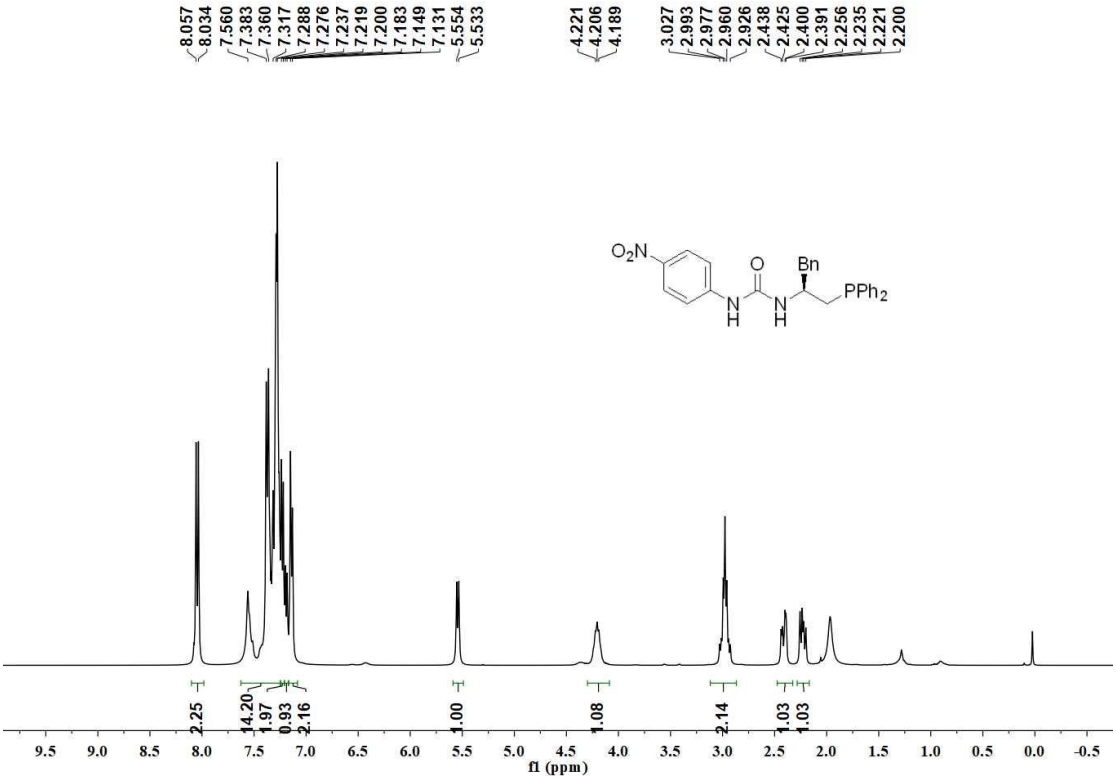
^{1}H, ^{13}C, ^{19}F and ^{31}P-NMR spectra.

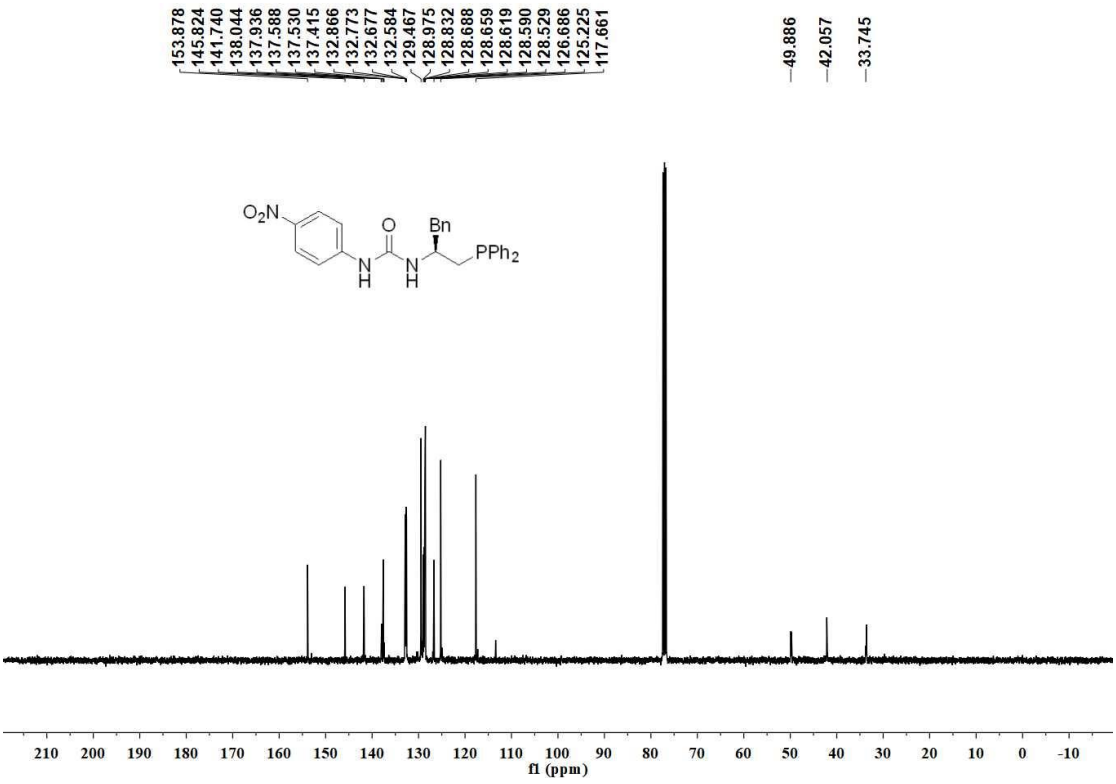
^{1}H and ^{13}C-NMR spectra of **X**.

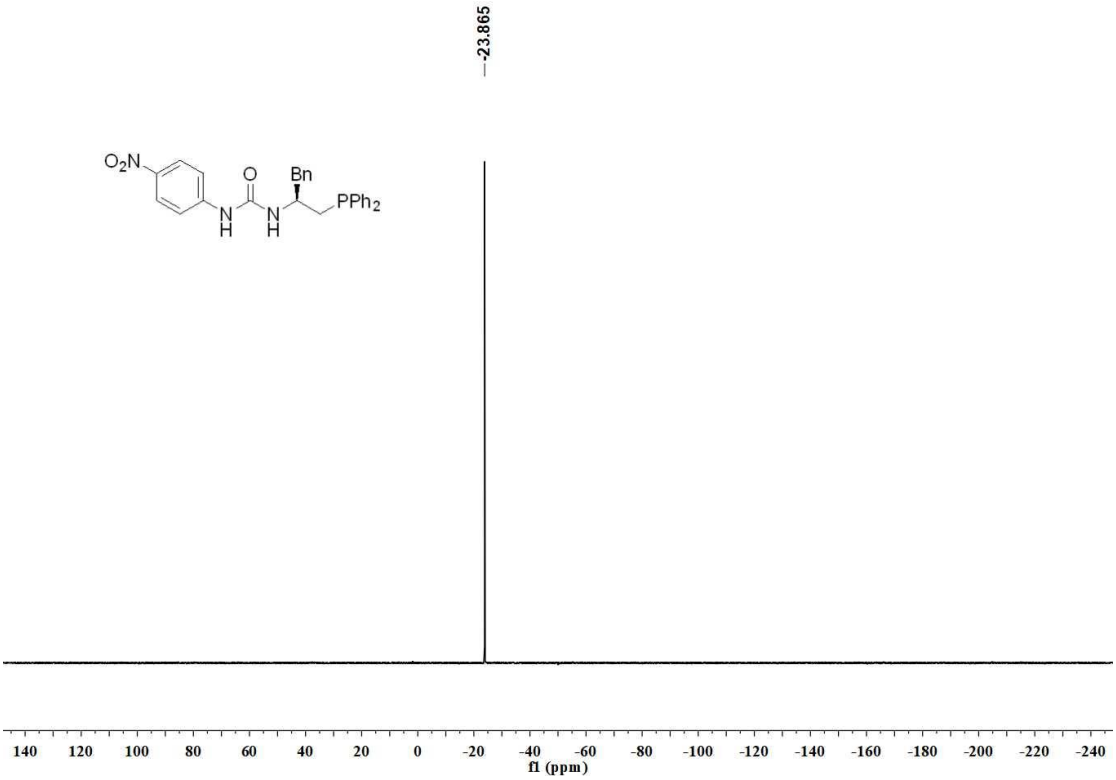




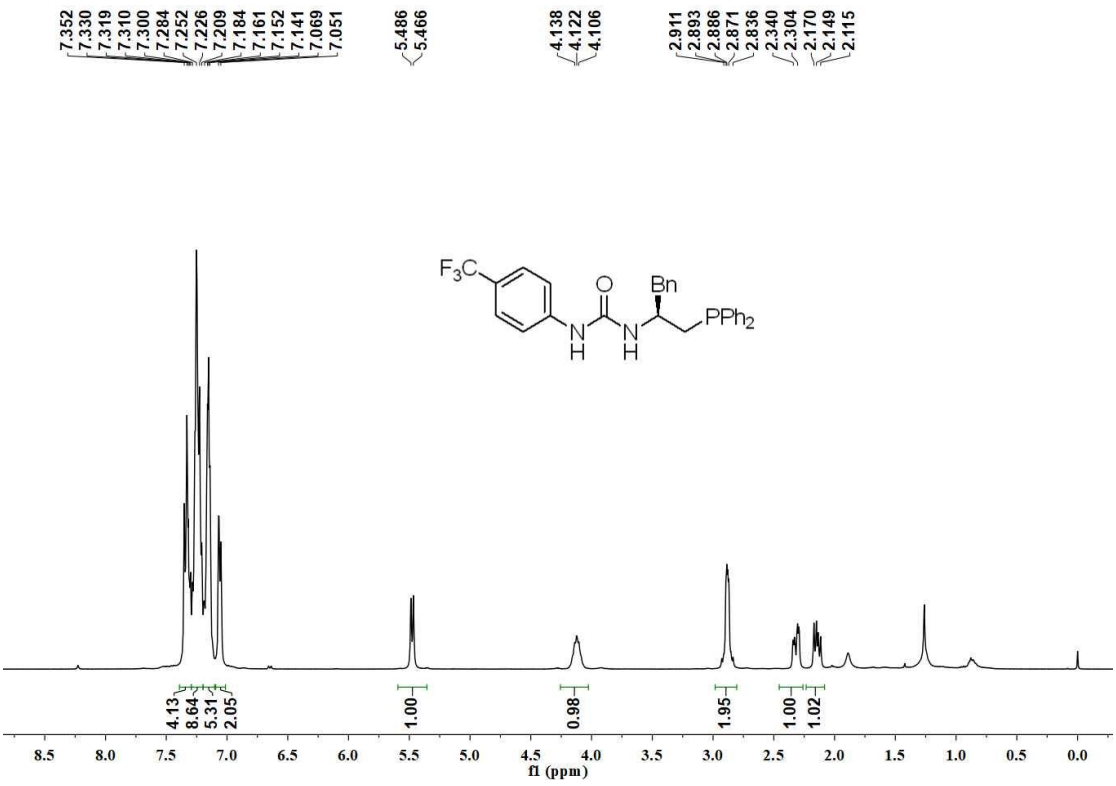
^{1}H, ^{13}C and ^{31}P-NMR spectra of **E**.

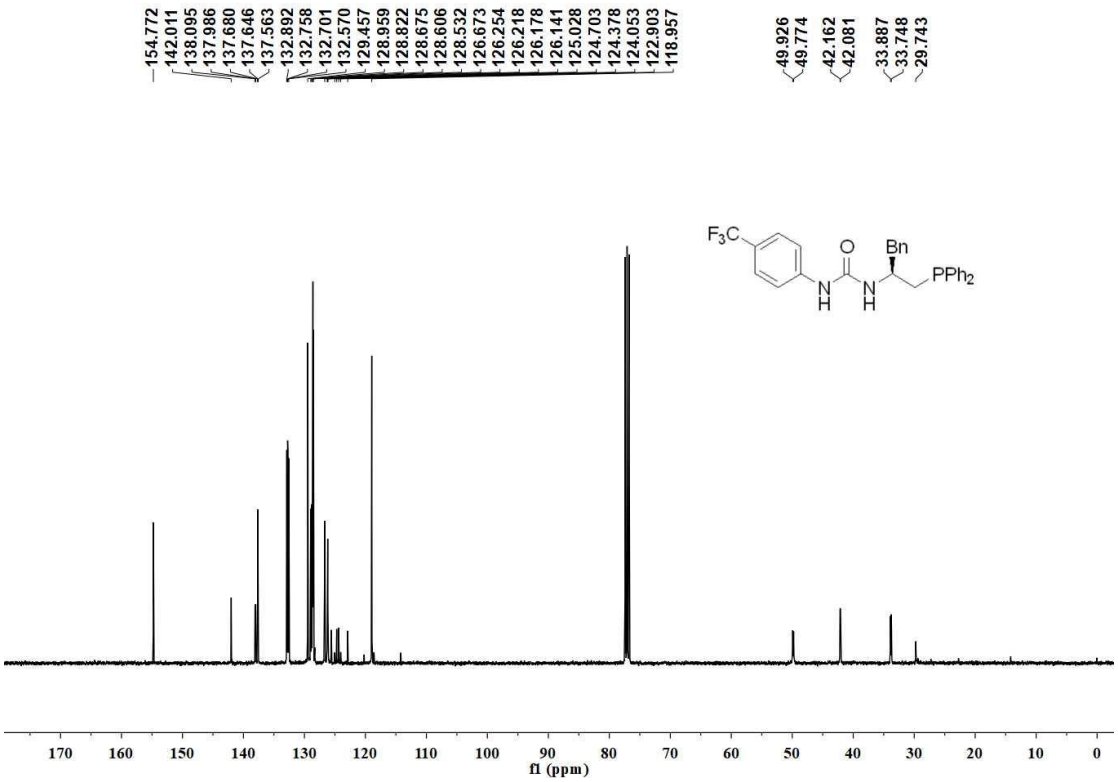






^{1}H, ^{13}C, ^{31}P and ^{19}F -NMR spectra of **F**.

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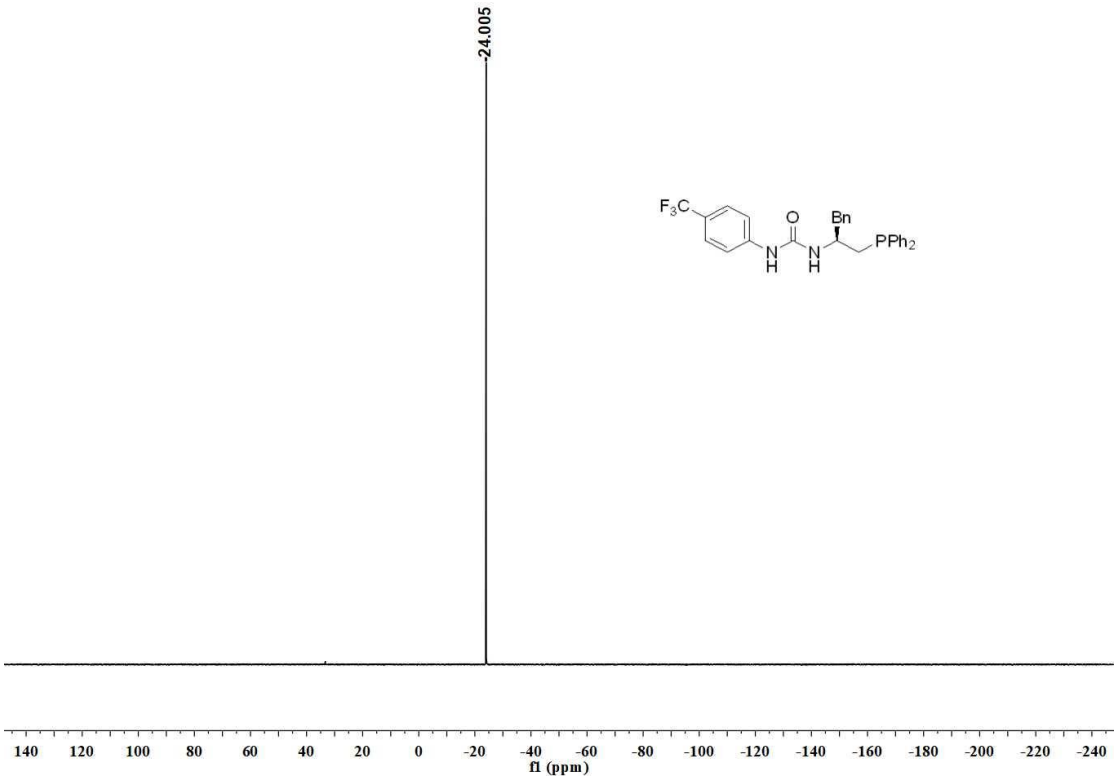
142.011
138.095
137.986
137.680
137.646
137.563
132.892
132.758
132.701
132.570
129.457
128.959
128.822
128.675
128.606
128.532
126.673
126.254
126.218
126.178
126.141
125.028
124.703
124.378
124.053
122.903
118.957
49.926
49.774
42.162
42.081
33.887
33.748
29.743
F3C
O
Bn
N
H
N
H
PPh2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-24.005
F3C
O
Bn
N
H
N
H
PPh2
140
120
100
80
60
40
20
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-60
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-140
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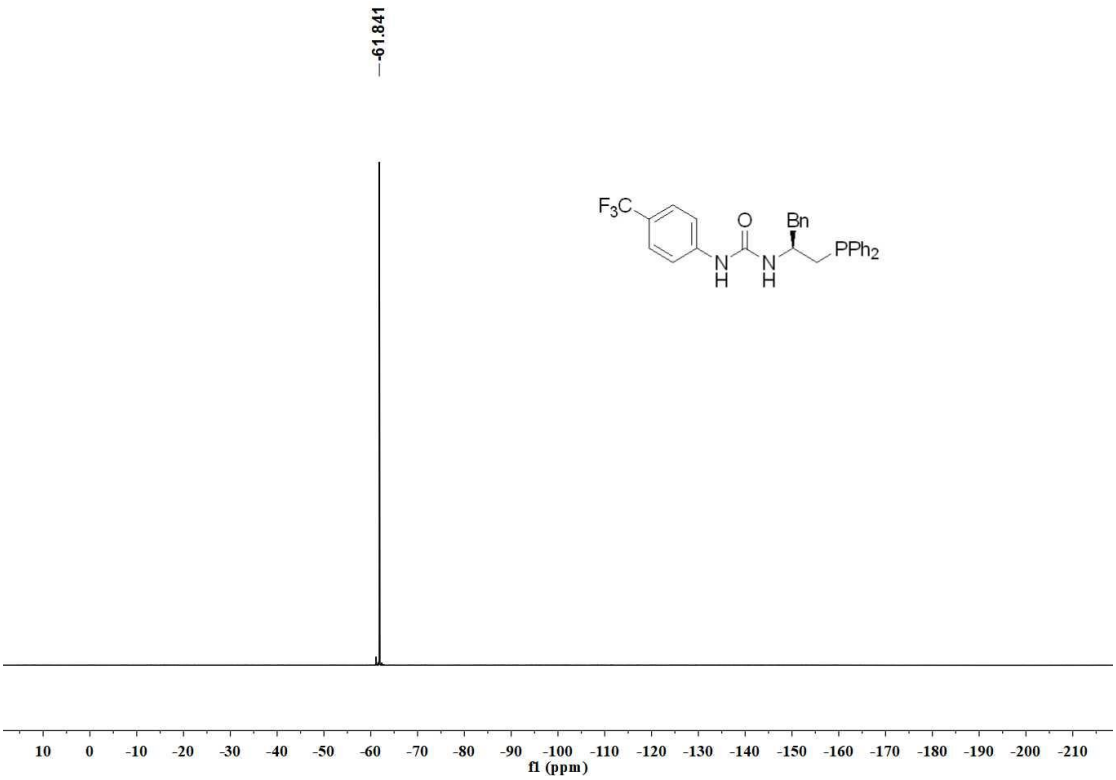
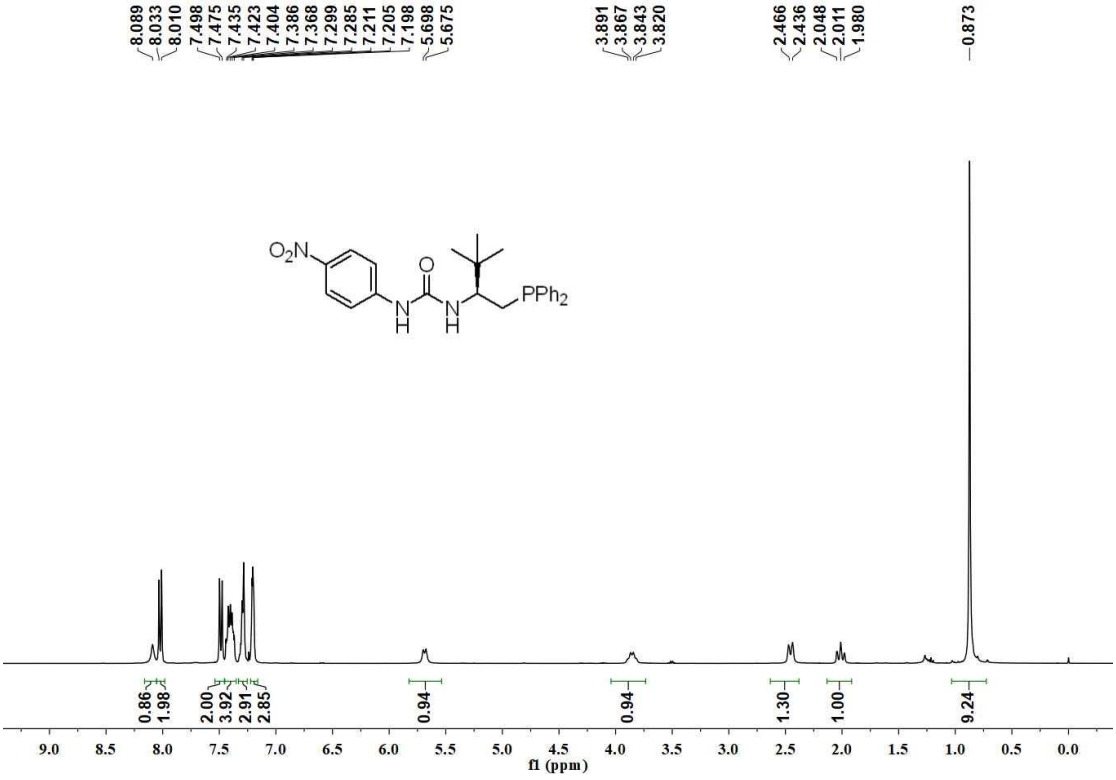
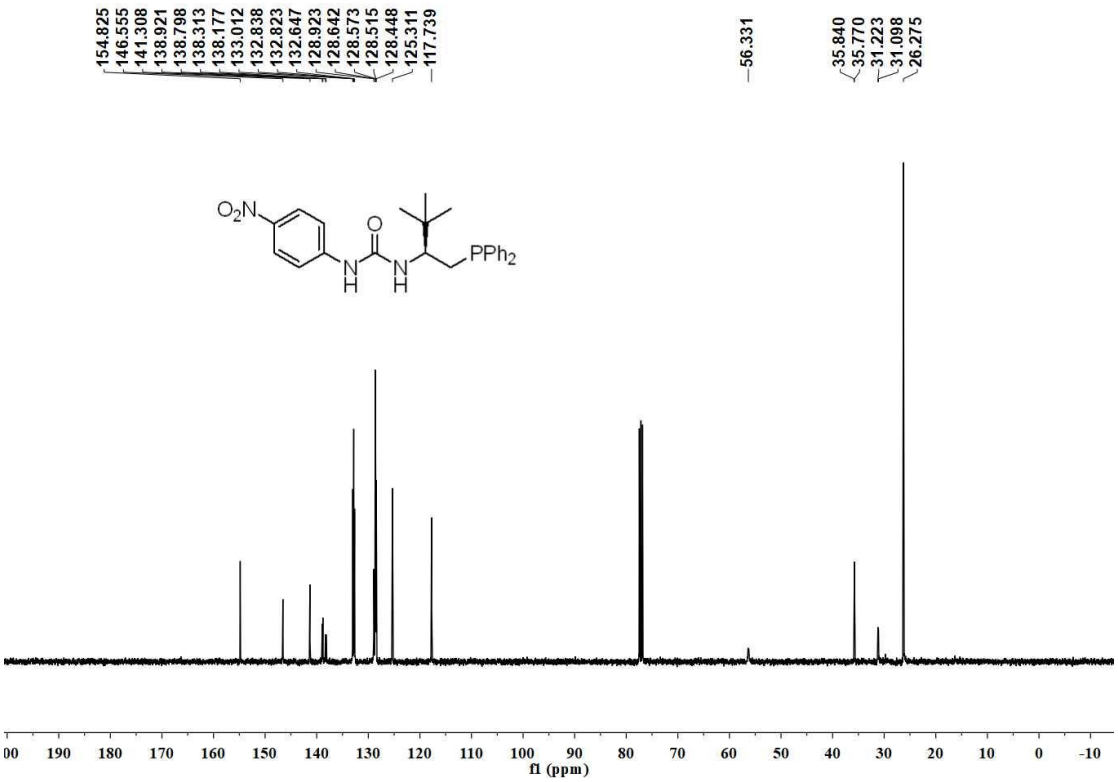
-180
-200
-220
-240
f1 (ppm)



^{1}H, ^{13}C and ^{31}P-NMR spectra of **G**.




154.825
146.555
141.308
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138.798
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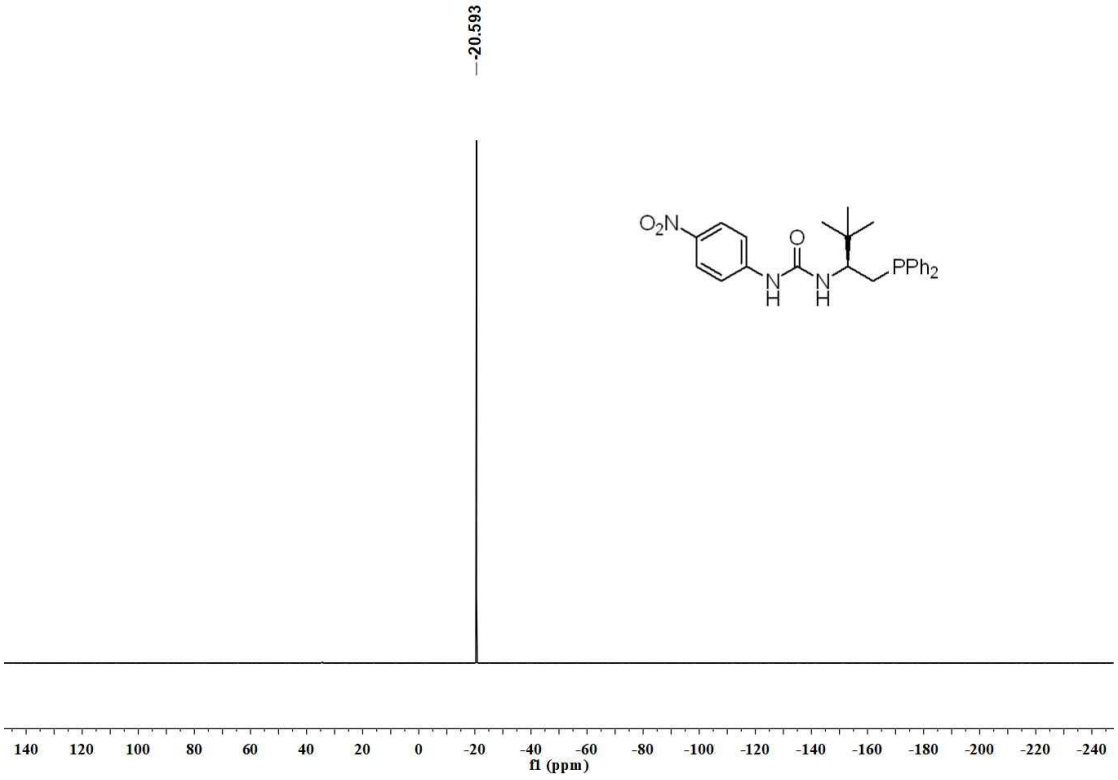
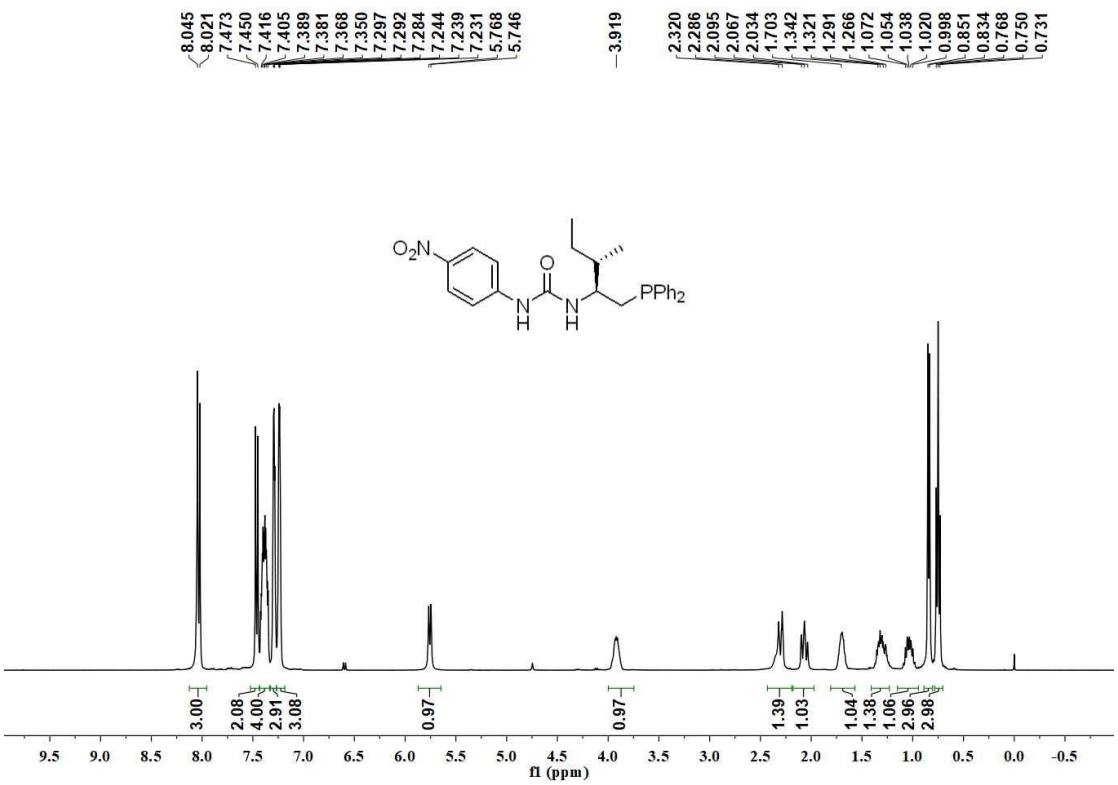
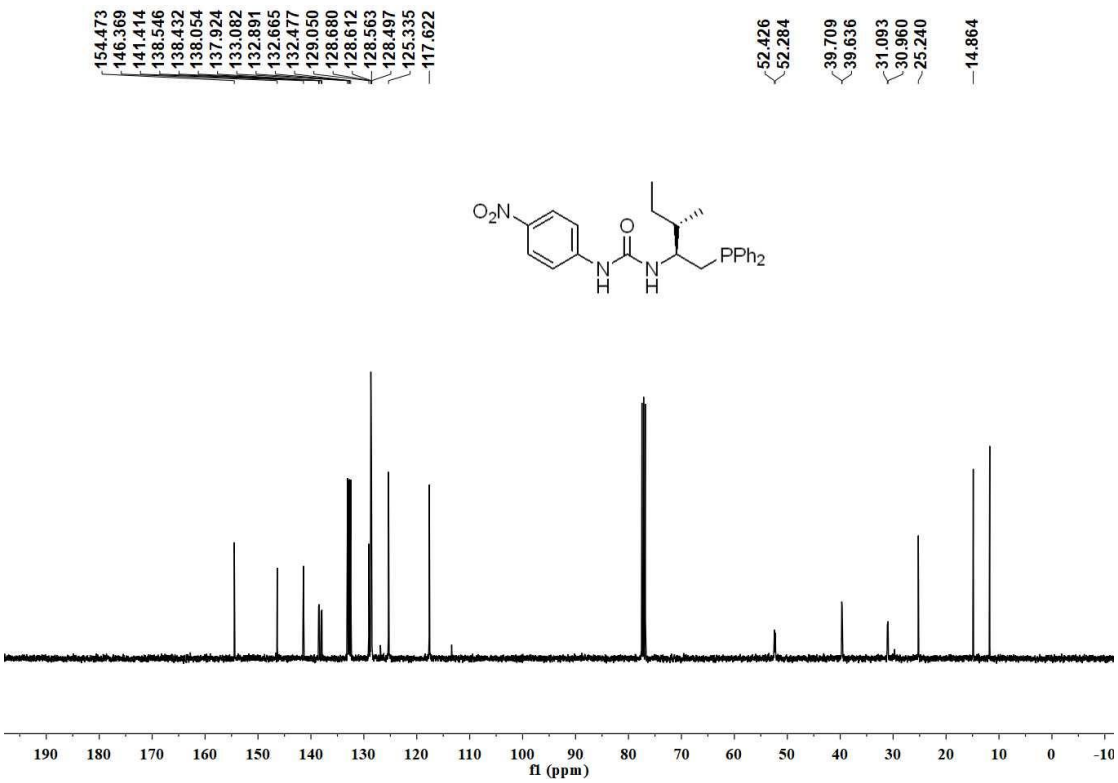
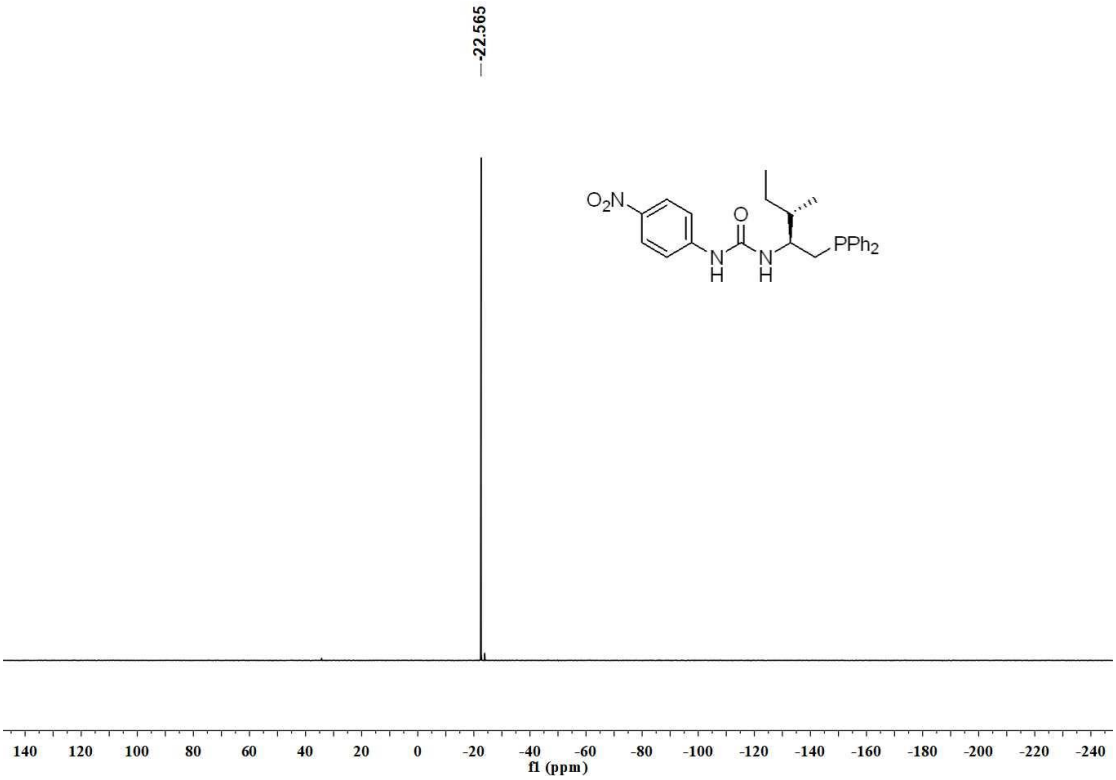
138.177
133.012
132.838
132.823
132.647
128.923
128.642
128.573
128.515
128.448
125.311
117.739
56.331
35.840
35.770
31.223
31.098
26.275
O2N
O
N
H
N
H
PPh2
f1 (ppm)


-20.593
O2N
O
N
H
N
H
PPh2
f1 (ppm)

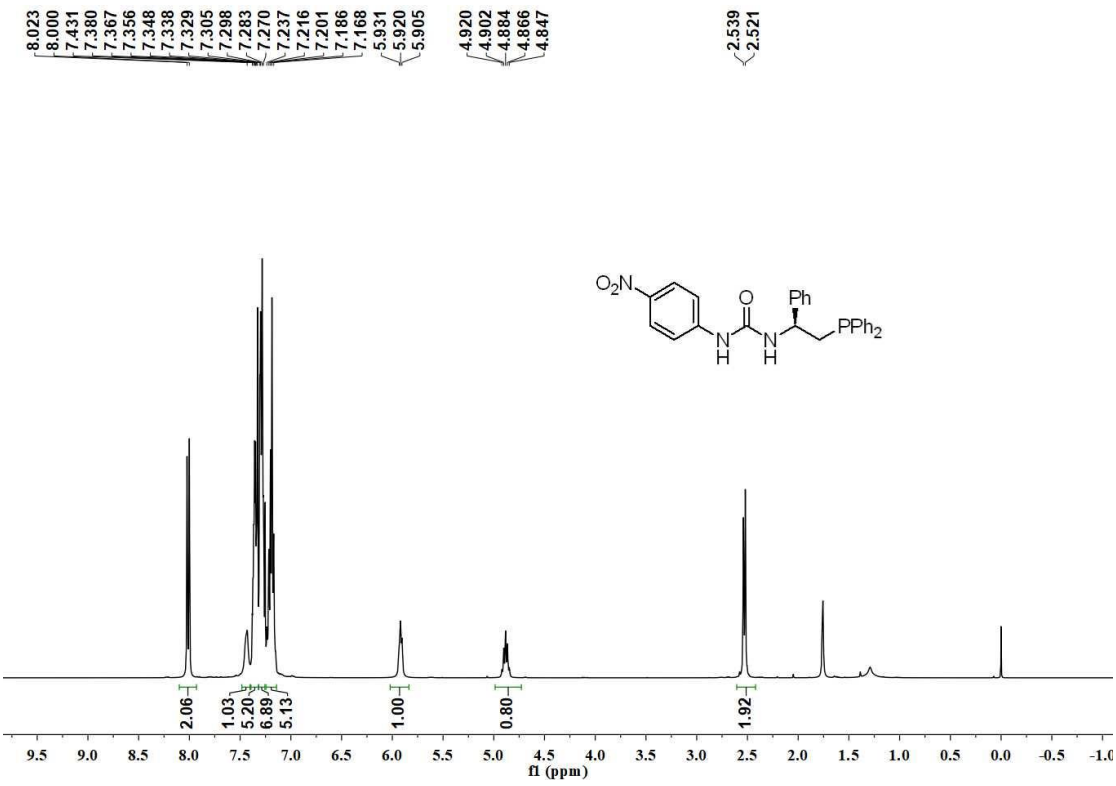
^{1}H, ^{13}C and ^{31}P-NMR spectra of **H**.

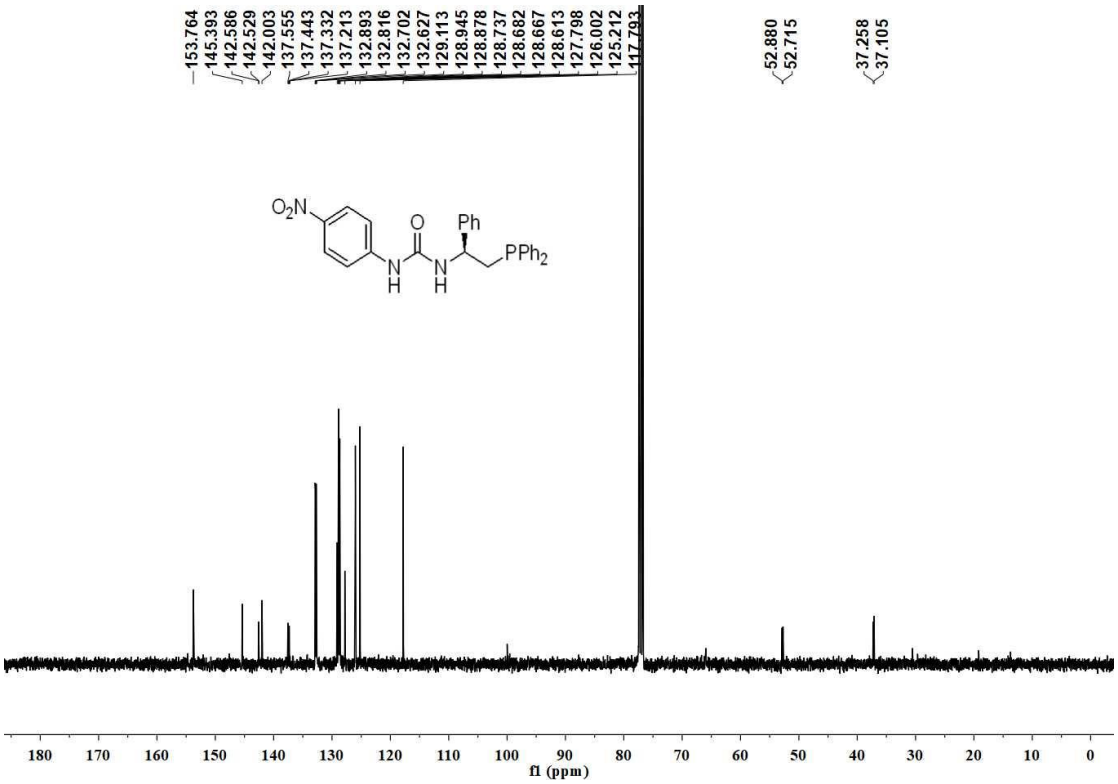






^{1}H, ^{13}C and ^{31}P-NMR spectra of **I**.

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142.586
142.529
142.003
137.555
137.443
137.332
137.213
132.893
132.816
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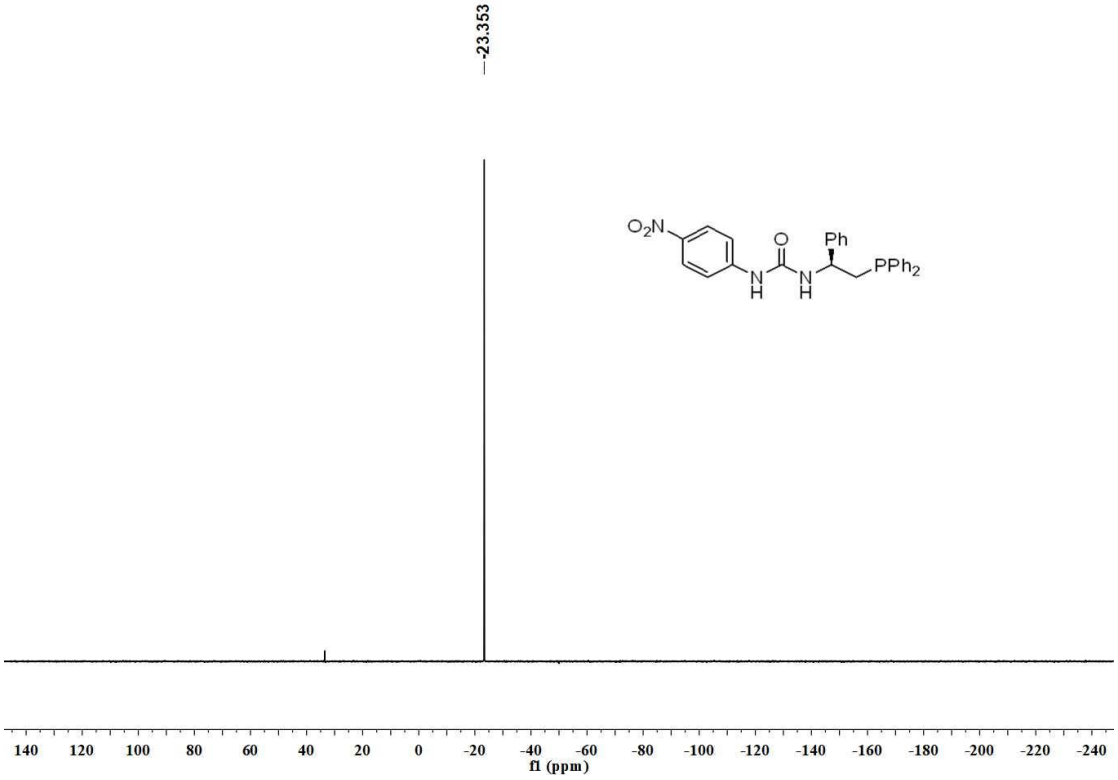
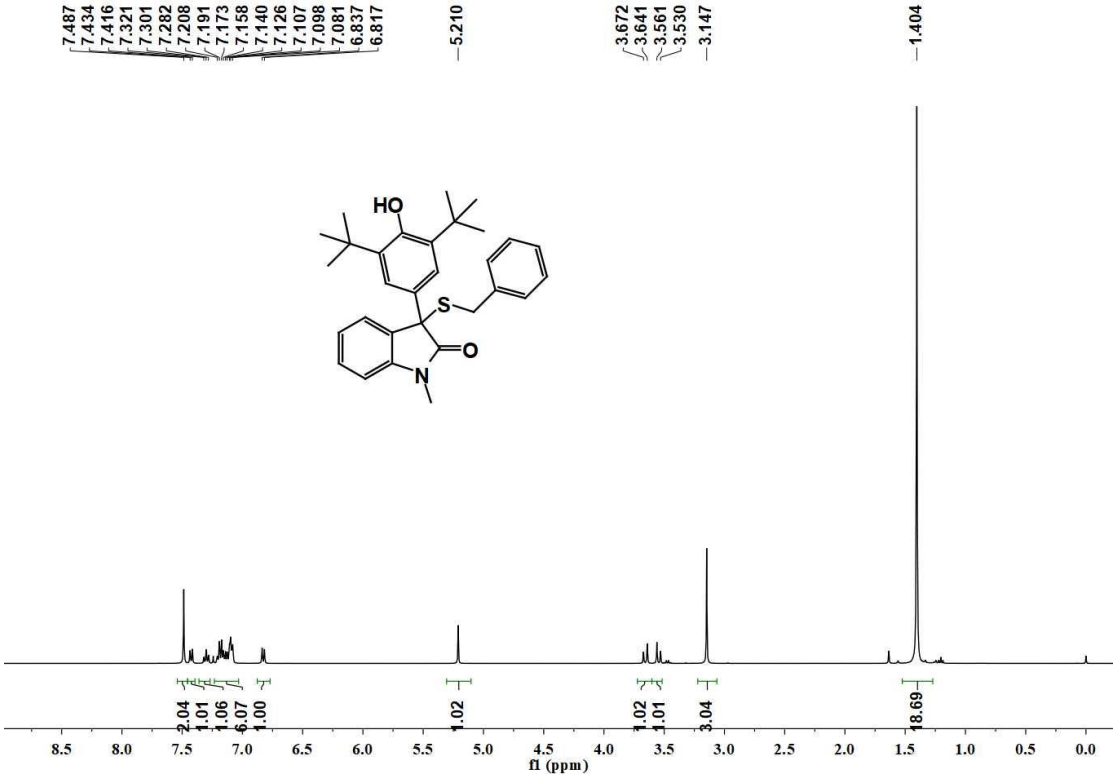
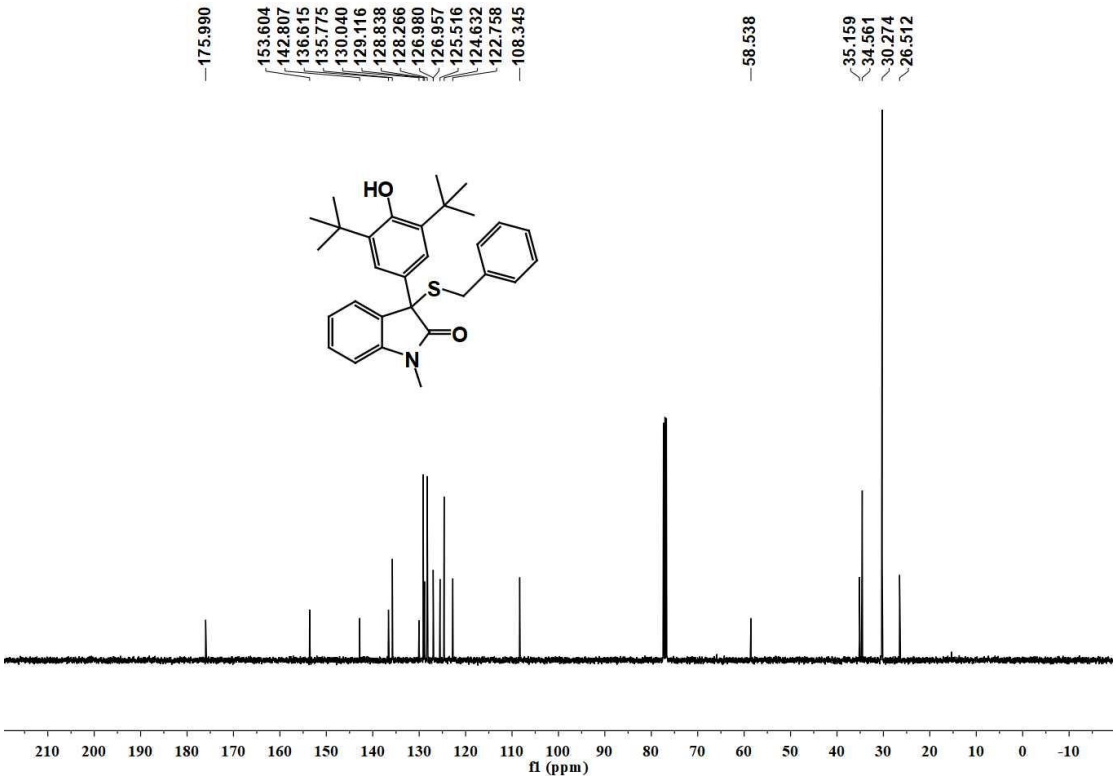
132.627
129.113
128.945
128.878
128.737
128.682
128.667
128.613
127.798
126.002
125.212
117.792
52.880
52.715
37.258
37.105
O2N
O
Ph
PPh2
N
H
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

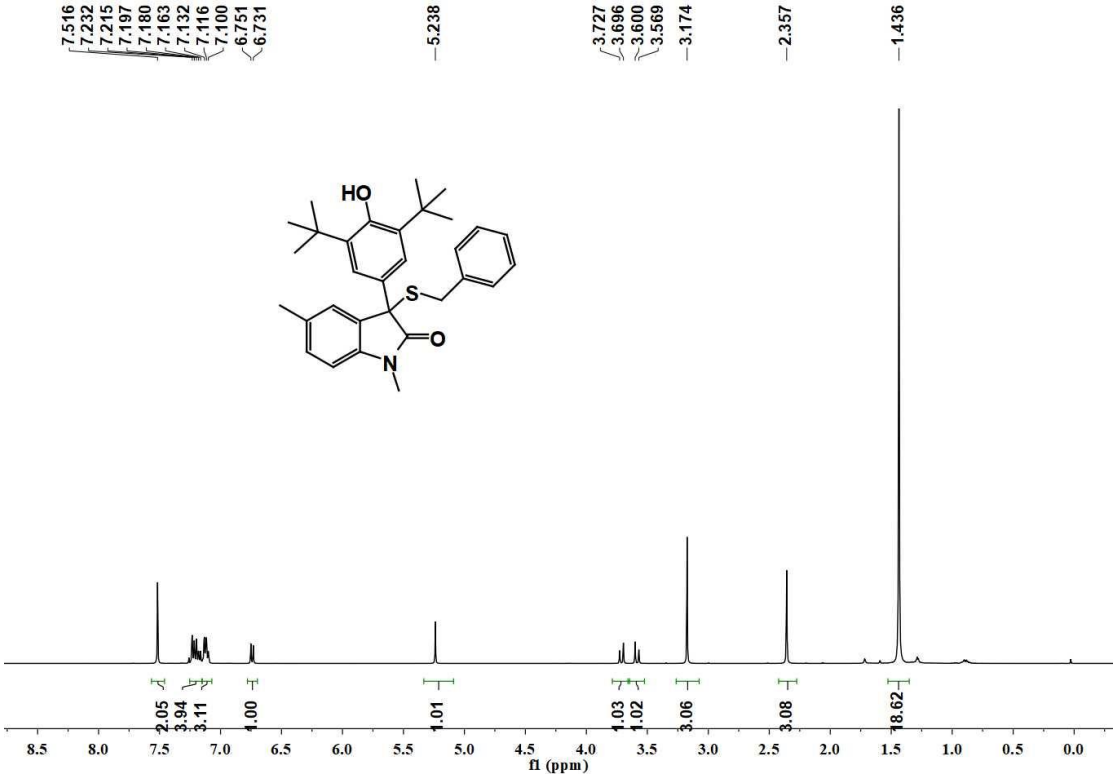

-23.353
O2N
O
Ph
PPh2
N
H
N
H
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

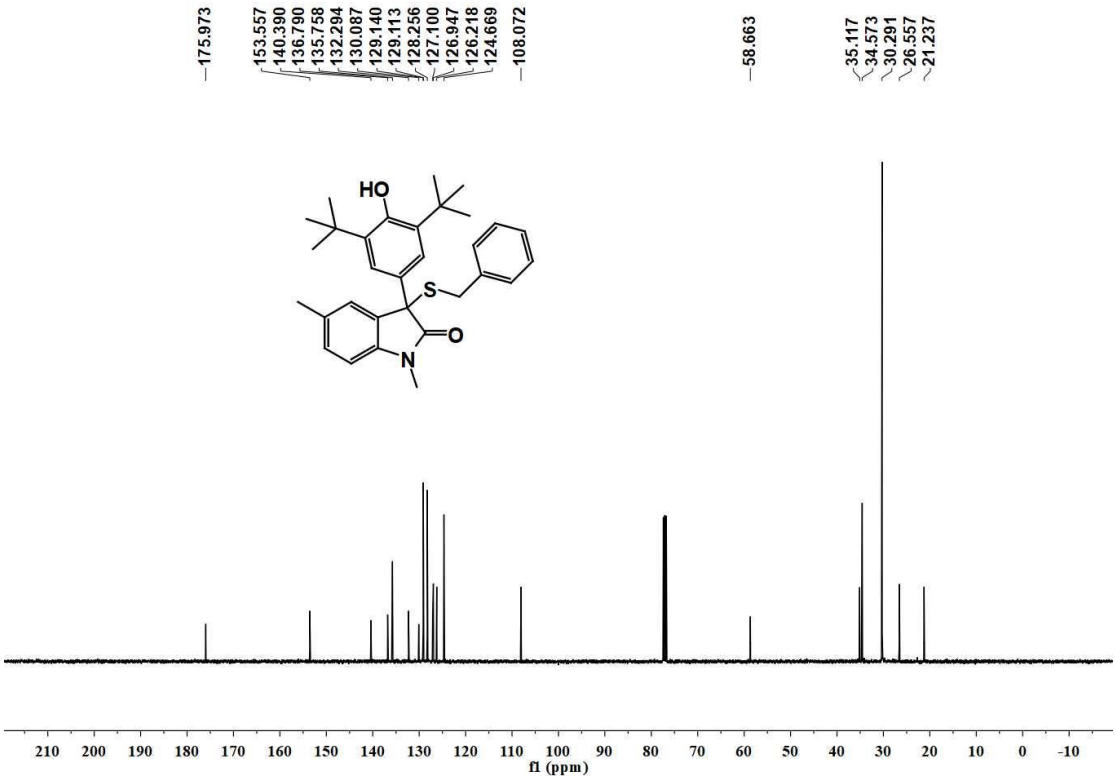
^{1}H and ^{13}C-NMR spectra of **1a**.



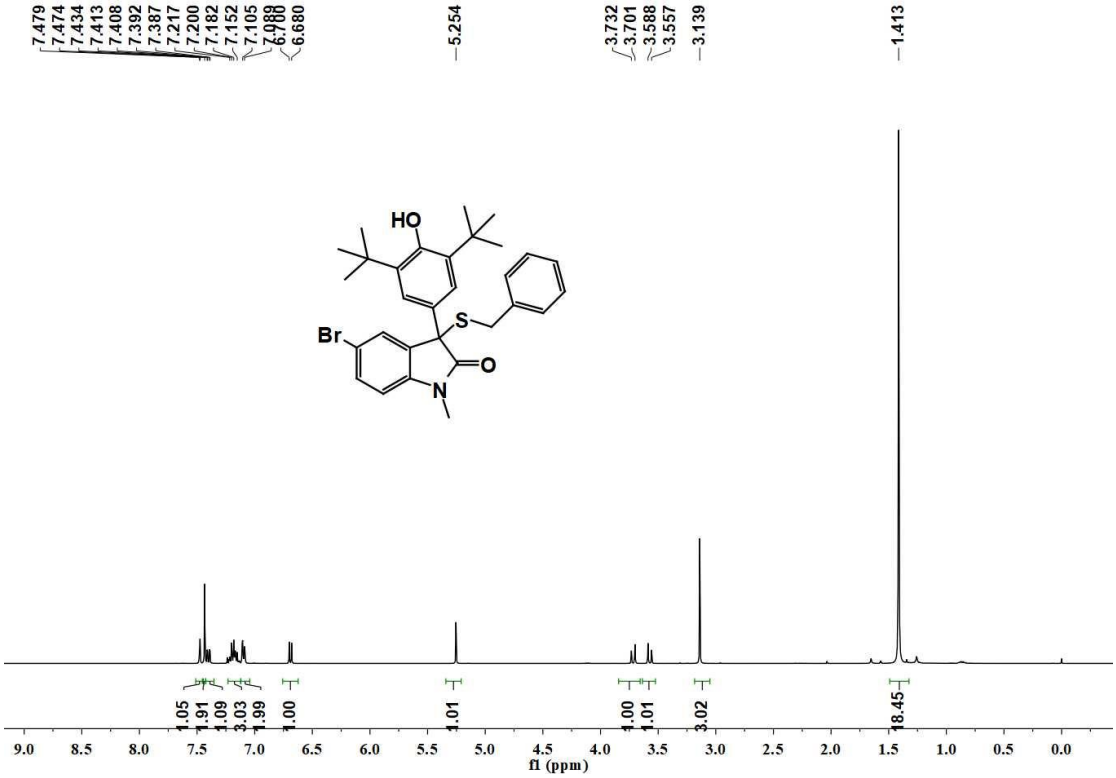


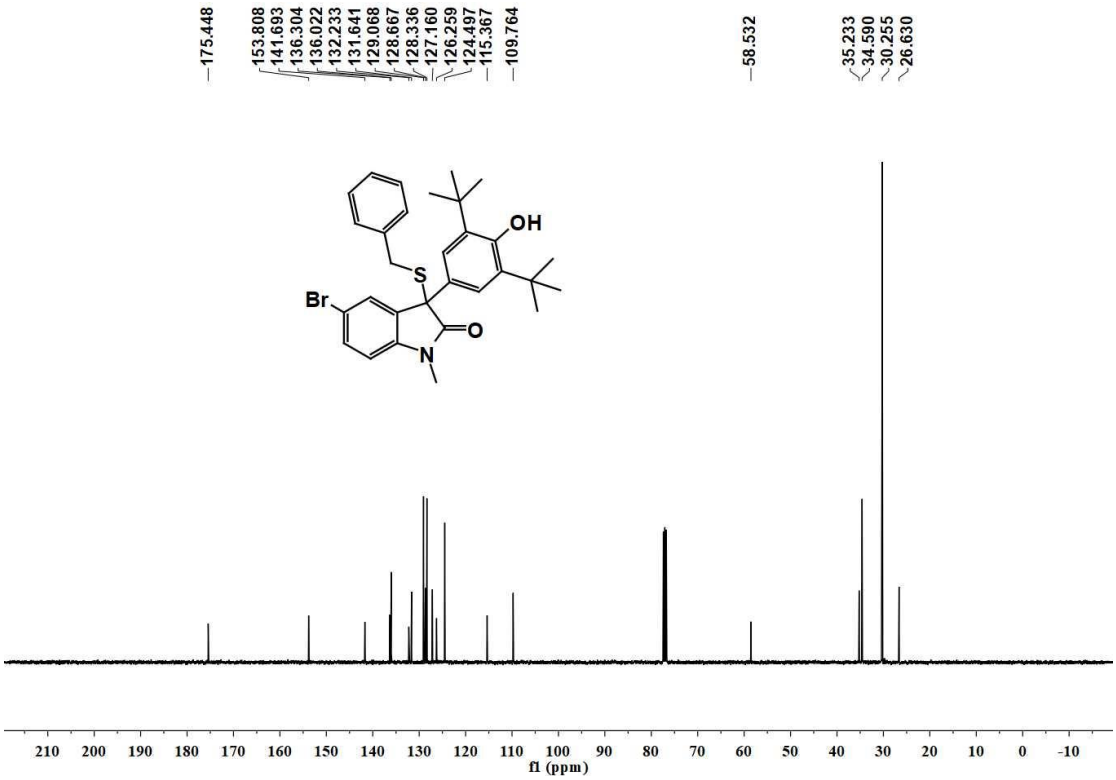
^{1}H and ^{13}C-NMR spectra of **1b**.



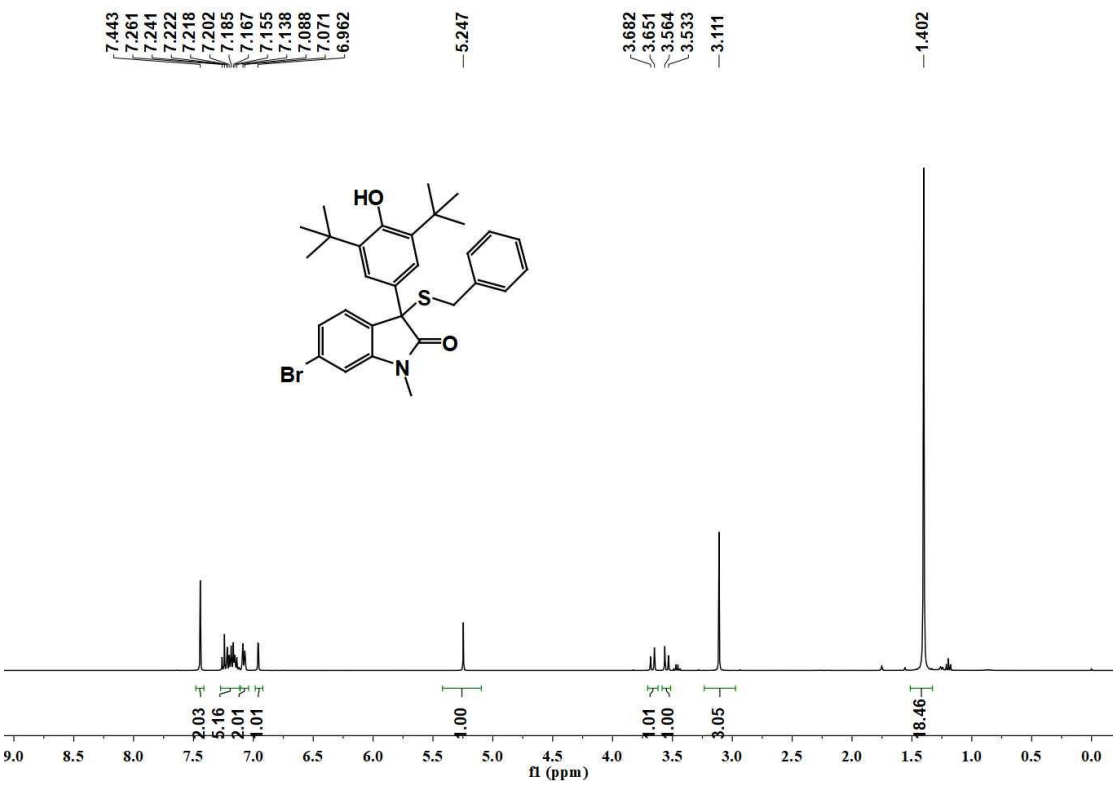


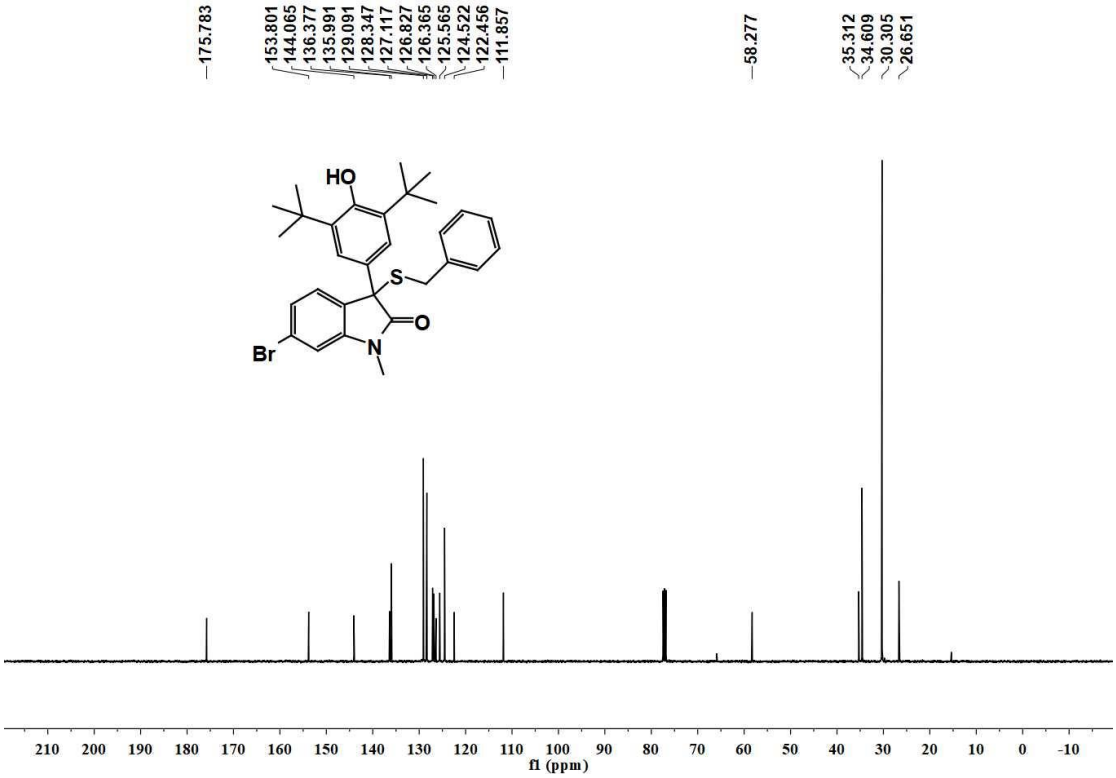
^{1}H and ^{13}C-NMR spectra of **1c**.



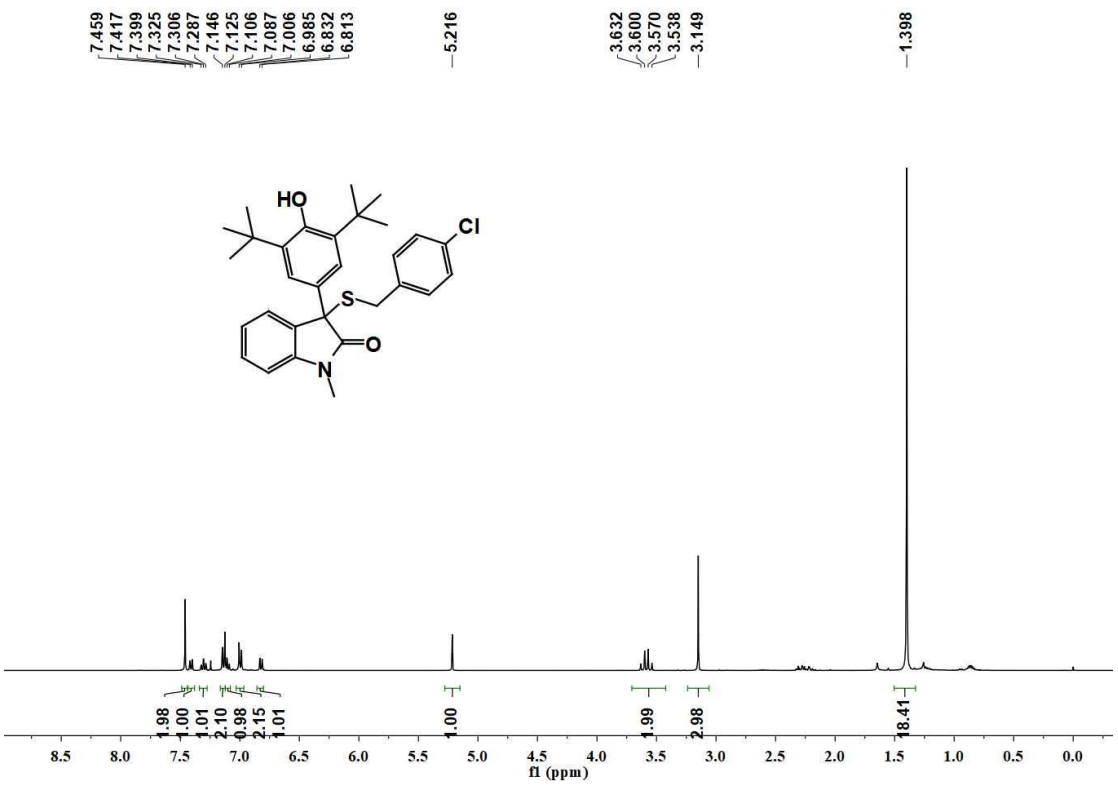


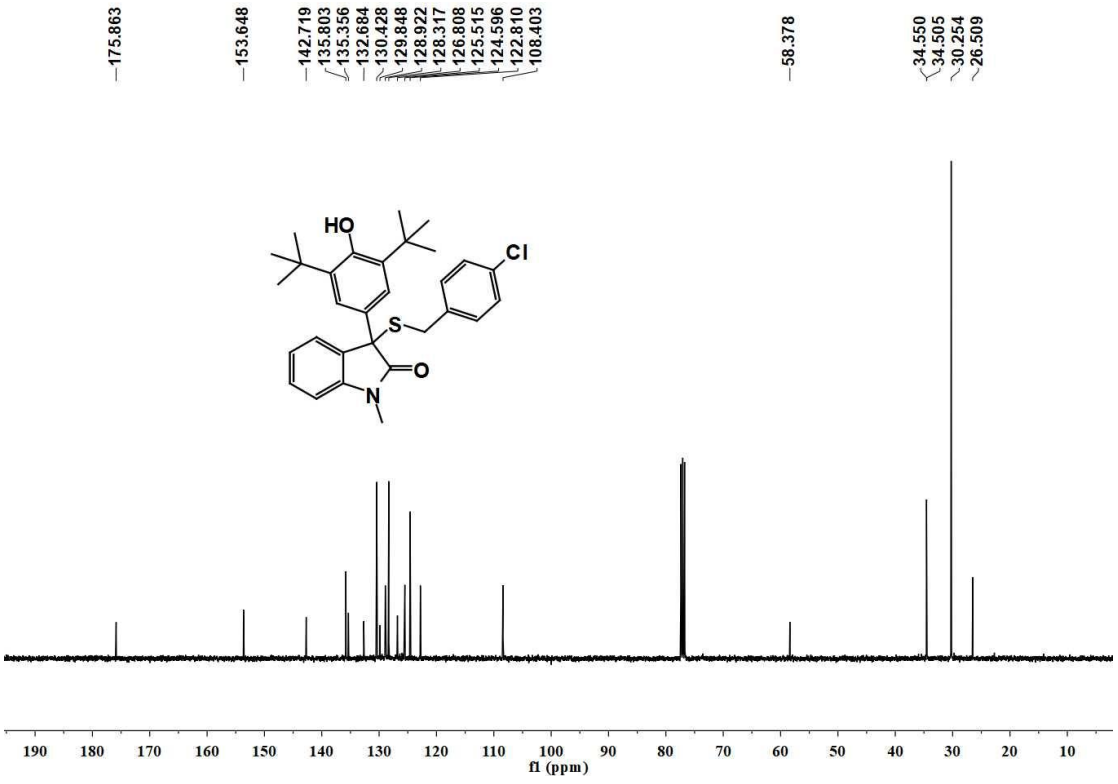
^{1}H and ^{13}C-NMR spectra of **1d**.



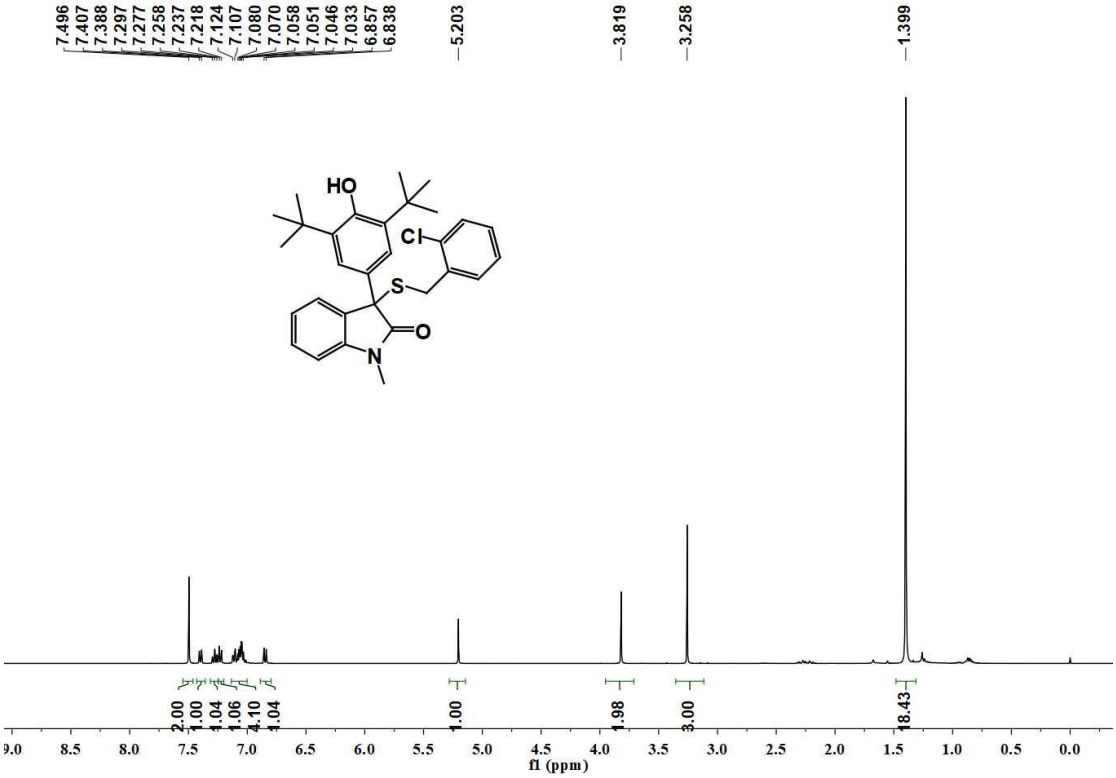


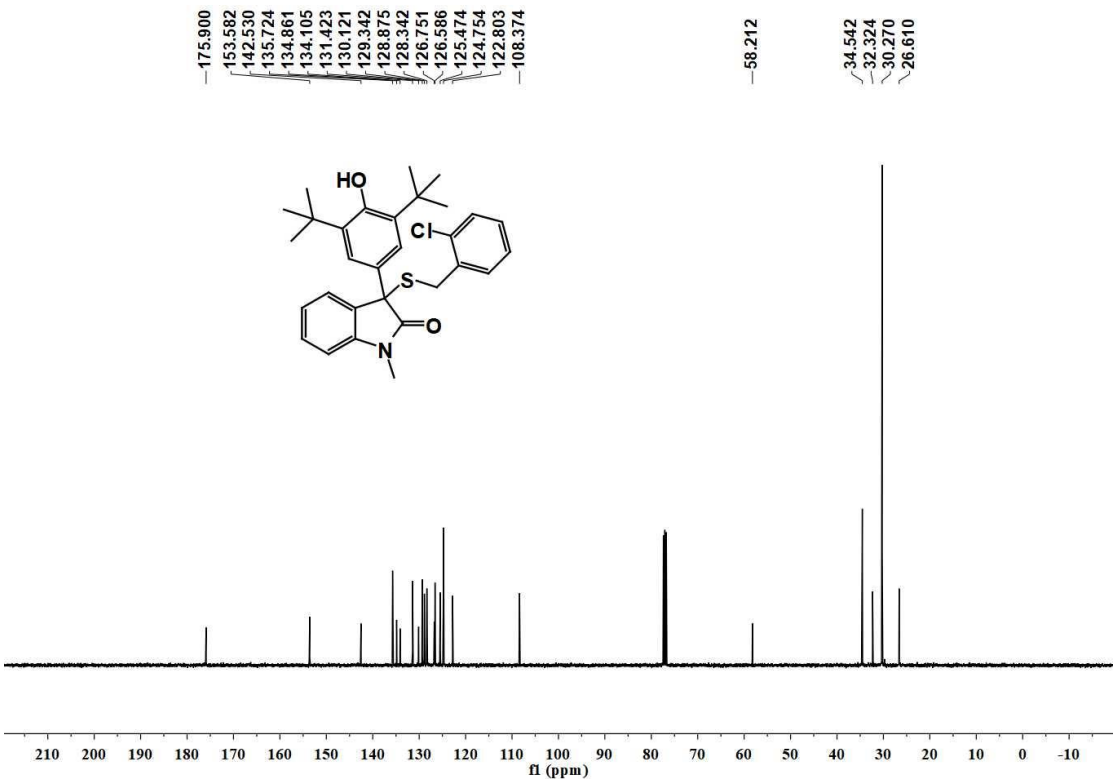
^{1}H and ^{13}C-NMR spectra of **1e**.



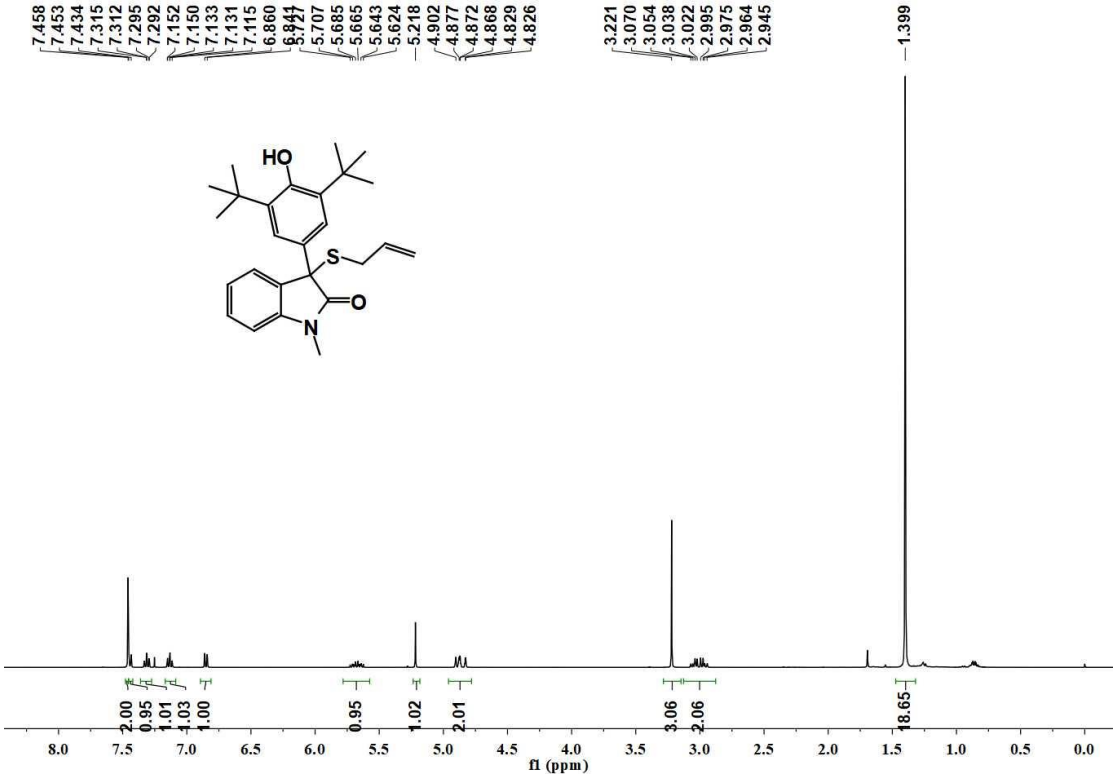


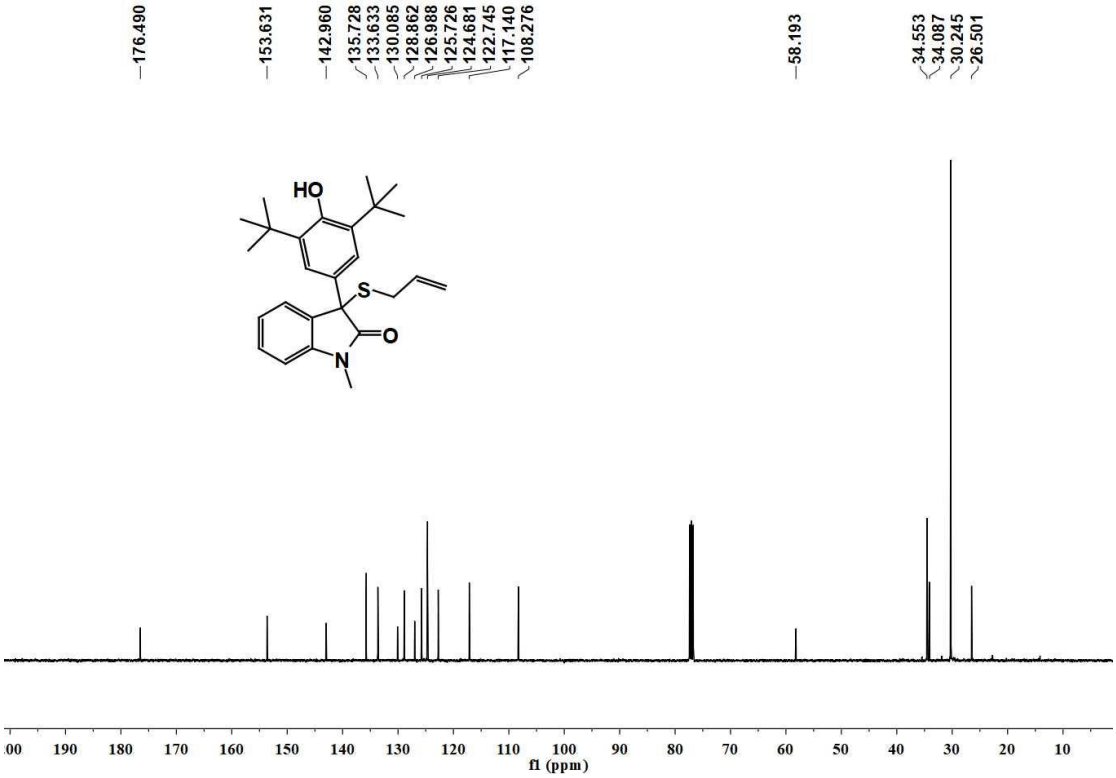
^{1}H and ^{13}C-NMR spectra of **1f**.



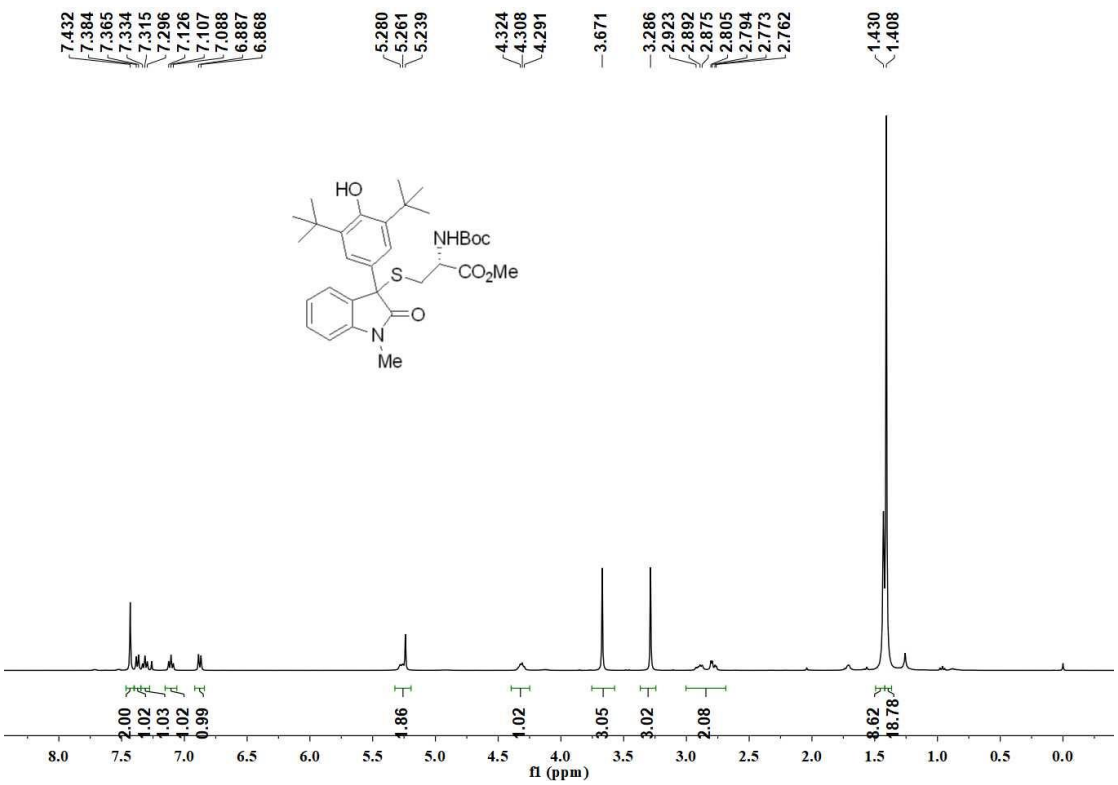


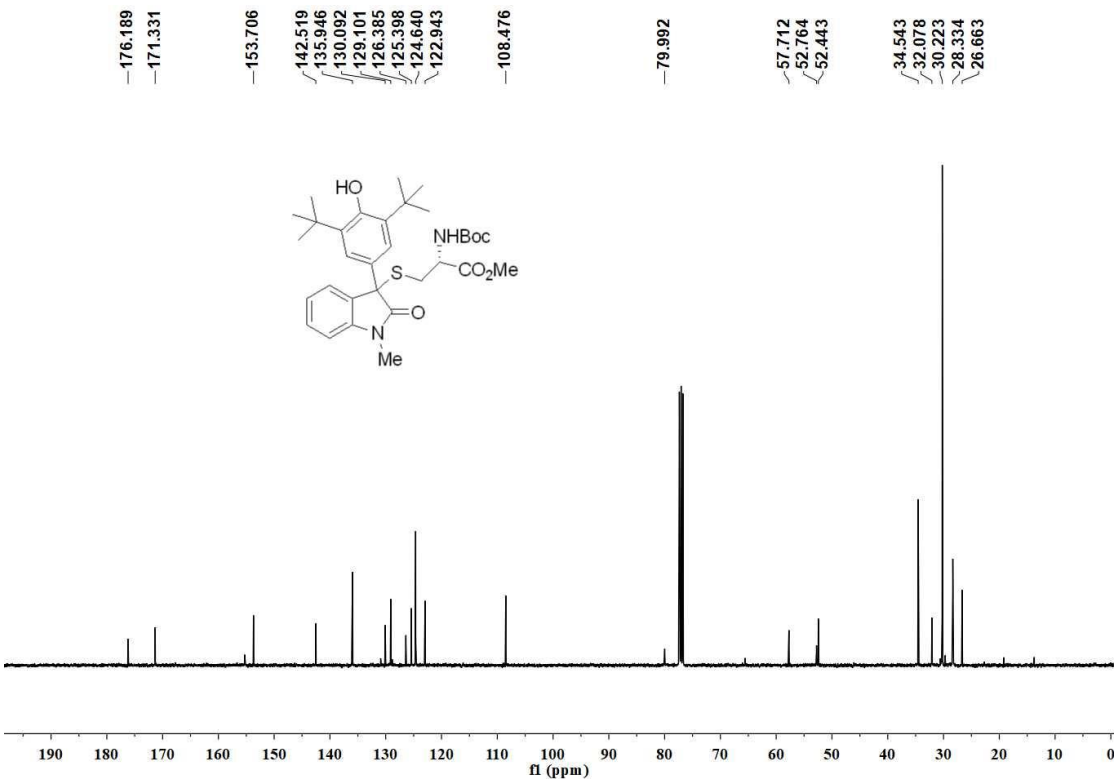
^{1}H and ^{13}C-NMR spectra of **1g**.



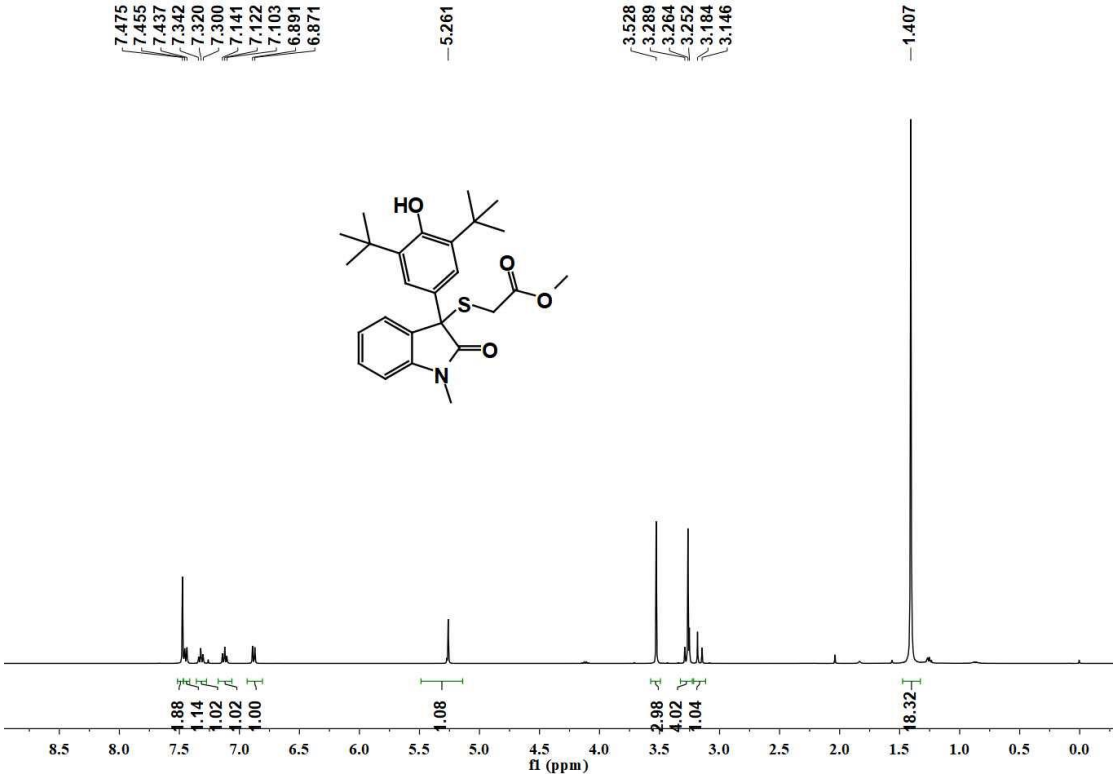


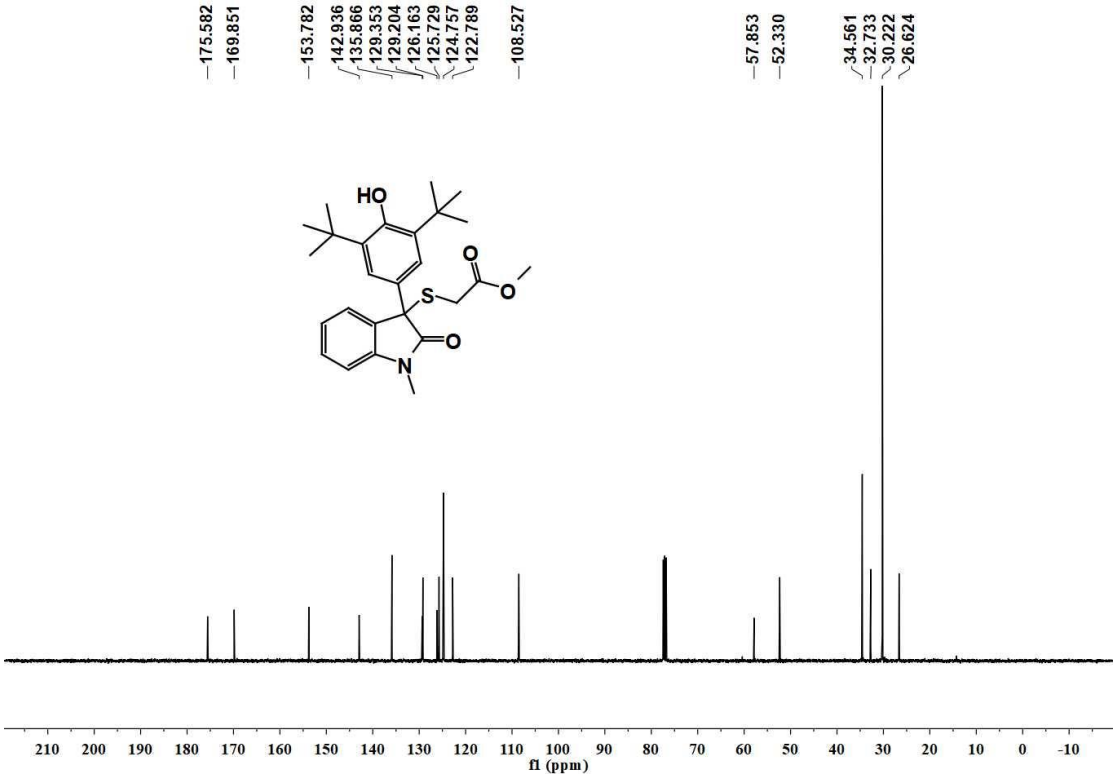
^{1}H and ^{13}C-NMR spectra of **1'h**.



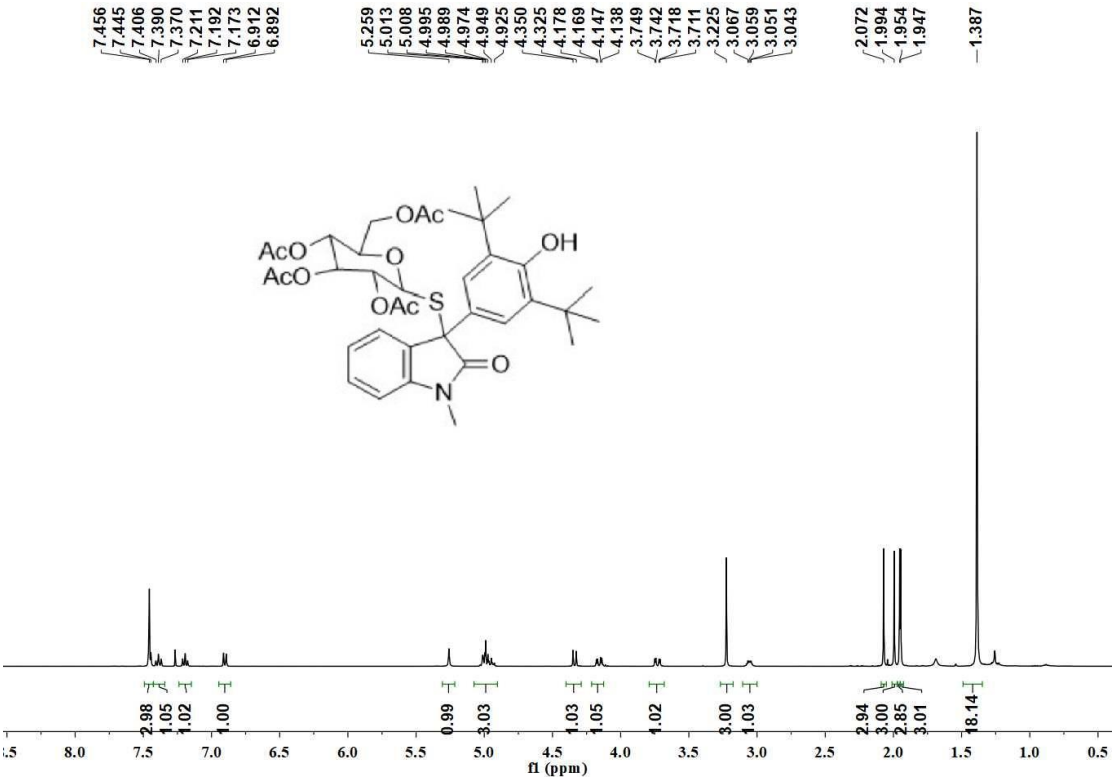


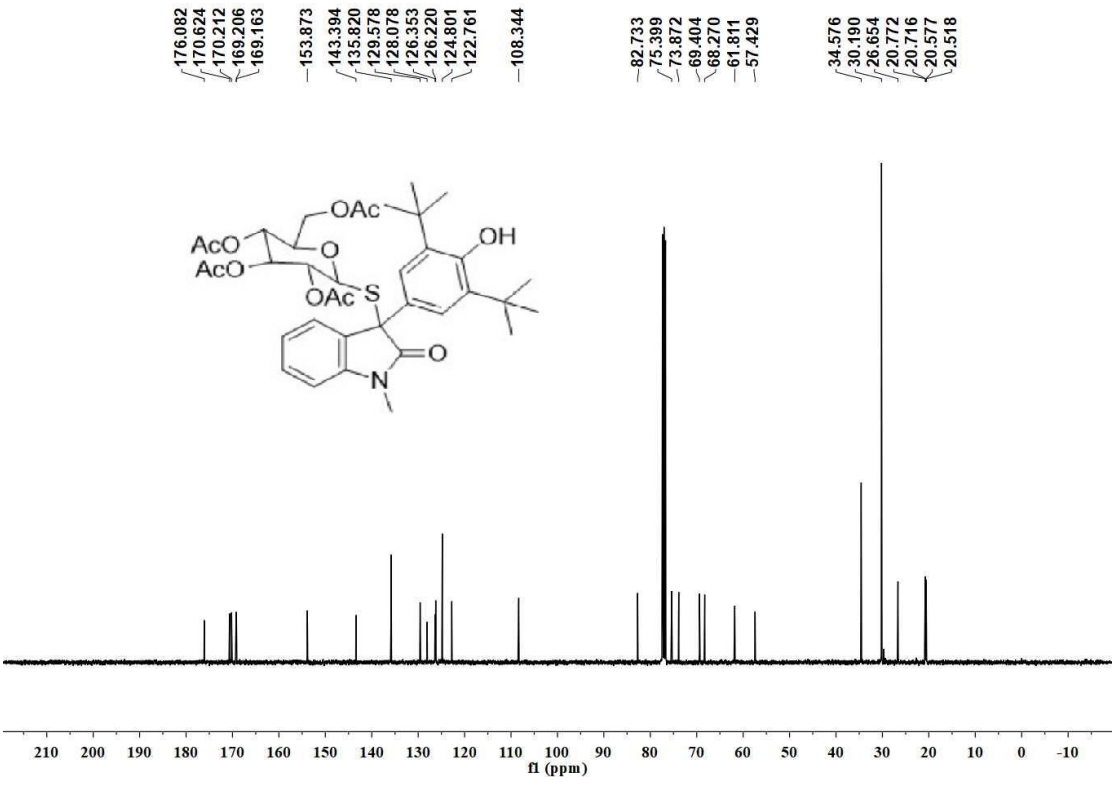
^{1}H and ^{13}C-NMR spectra of **1i**.



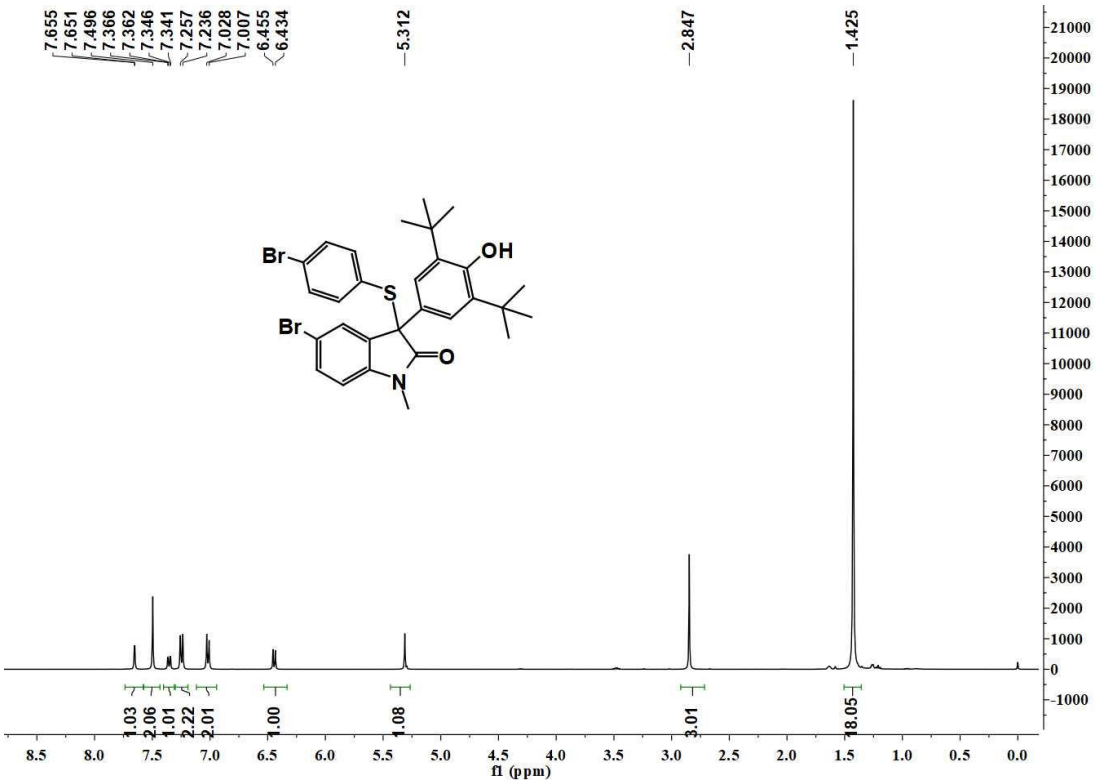


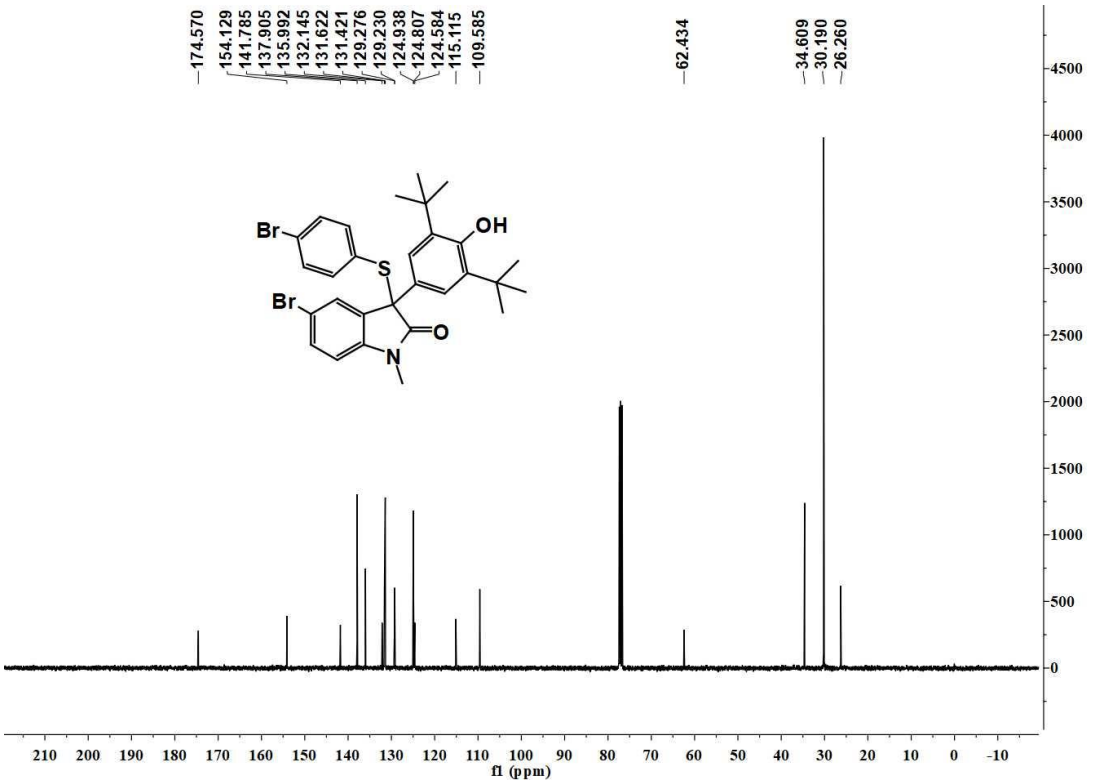
^{1}H and ^{13}C-NMR spectra of **1'j**.



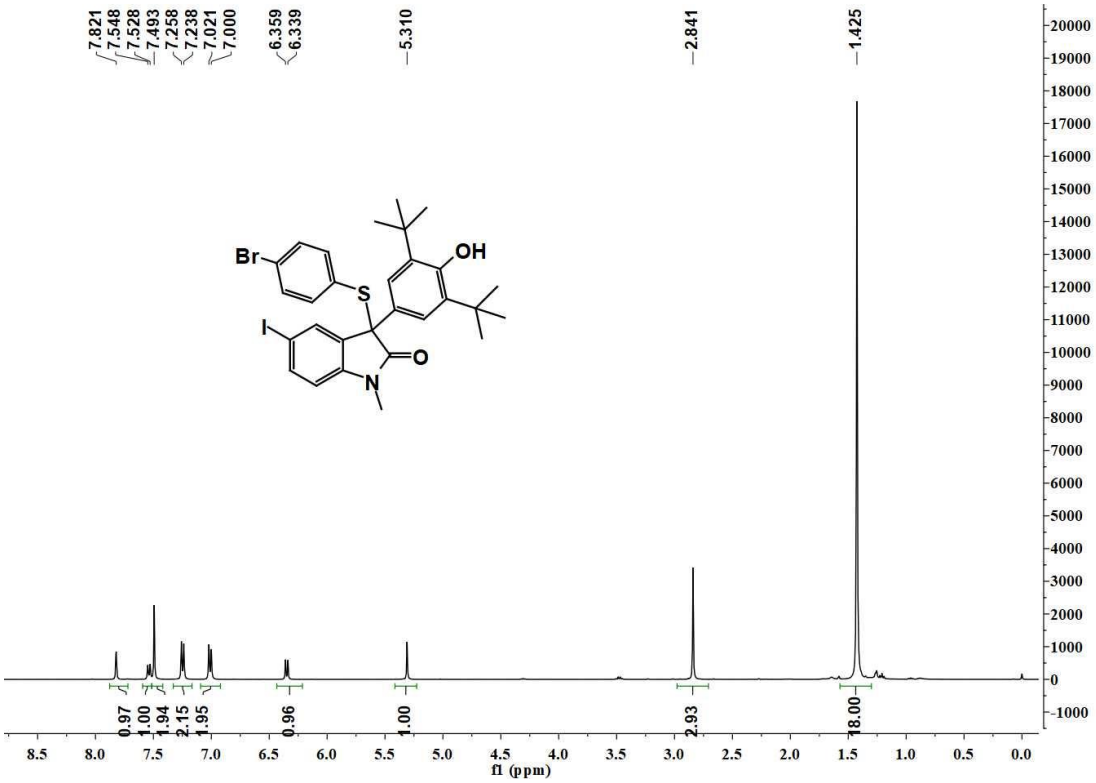


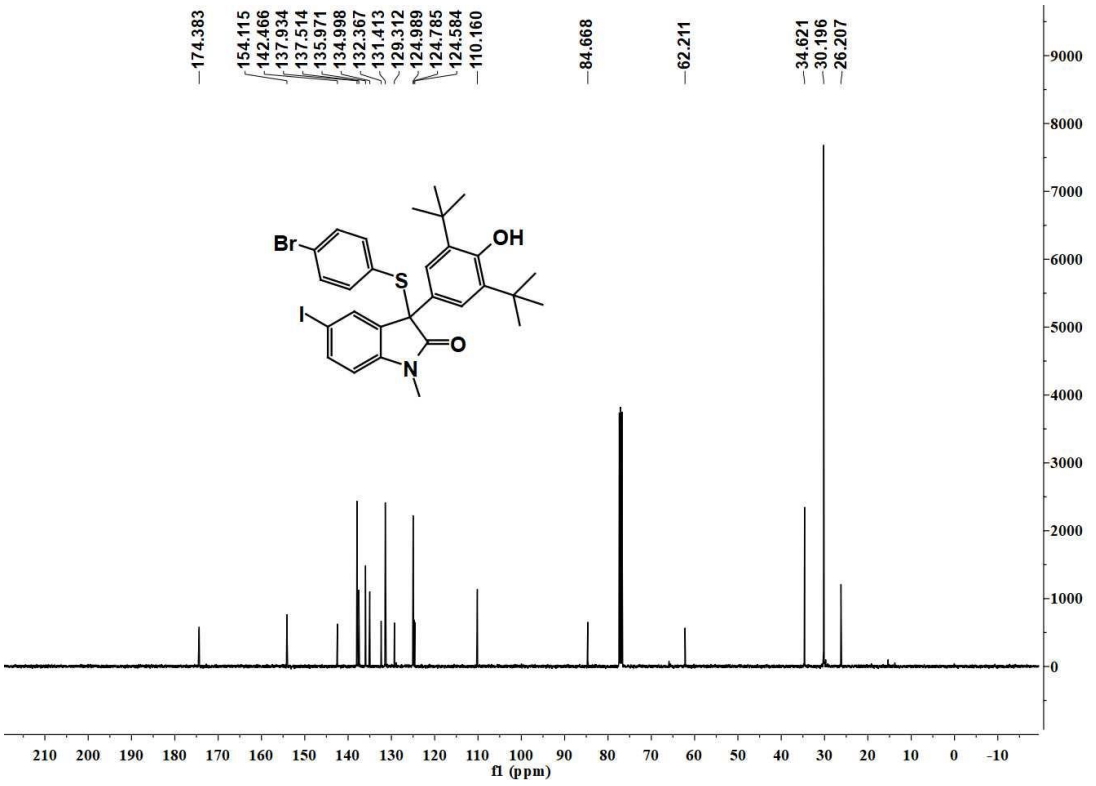
^{1}H and ^{13}C-NMR spectra of **1k**.



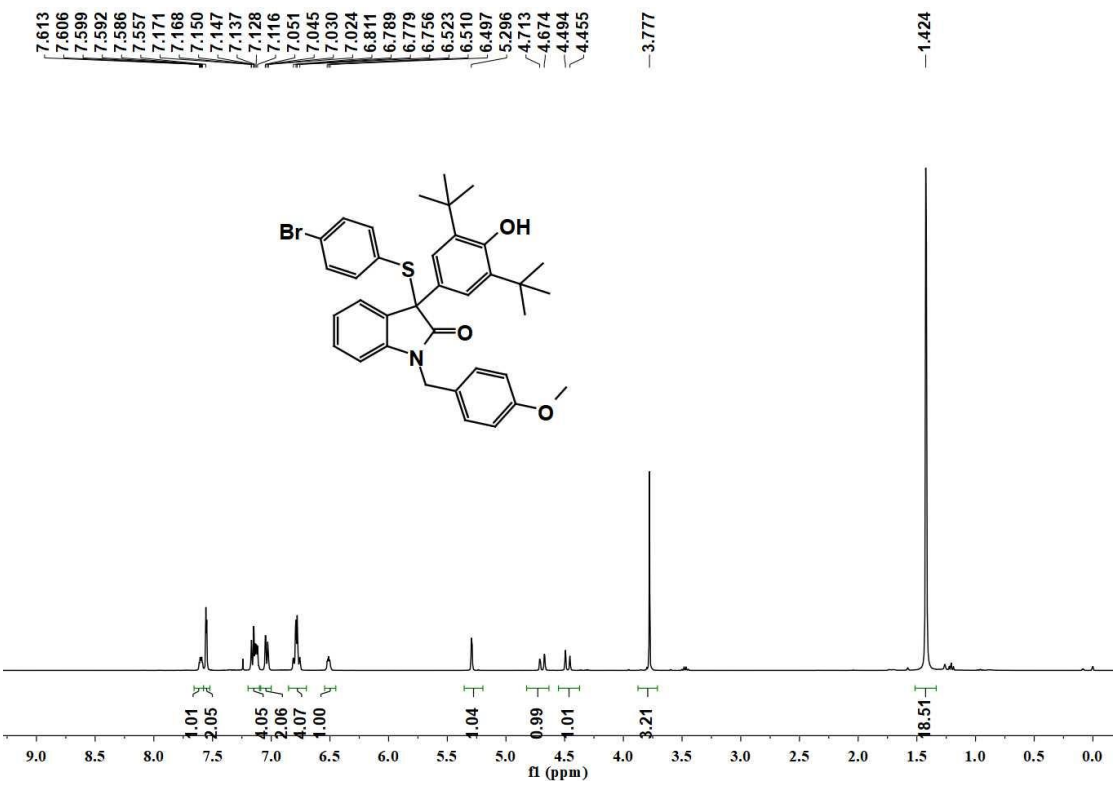


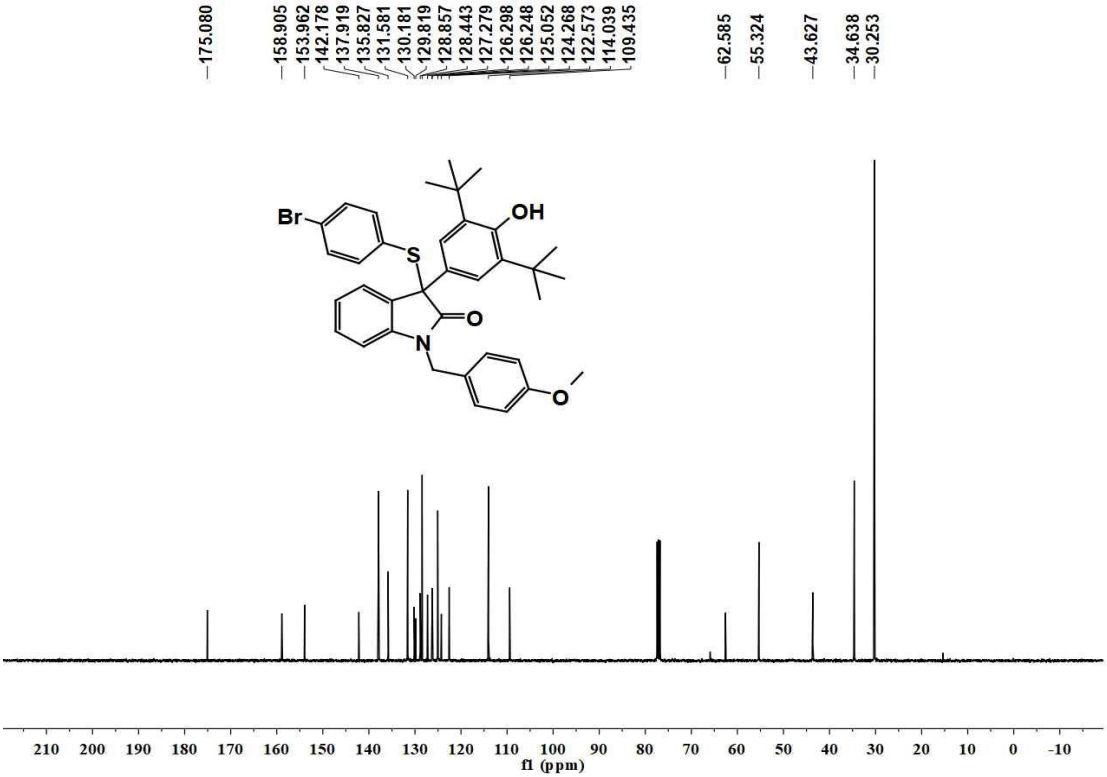
^{1}H and ^{13}C-NMR spectra of **1l**.



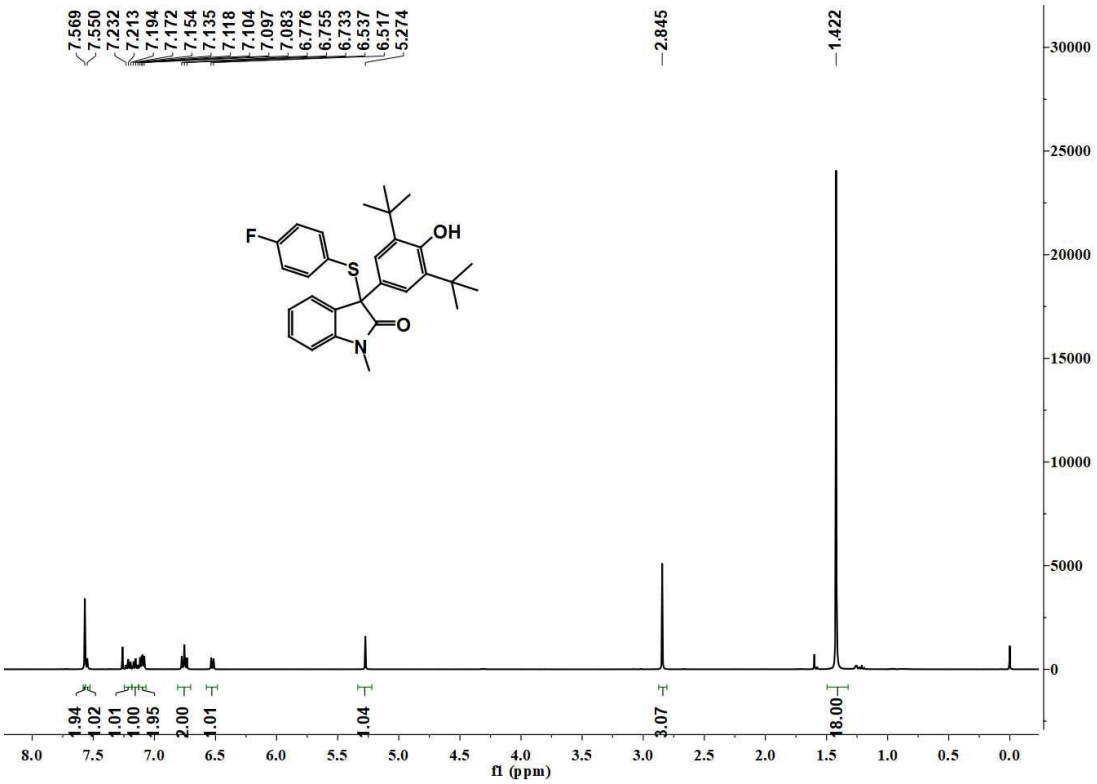


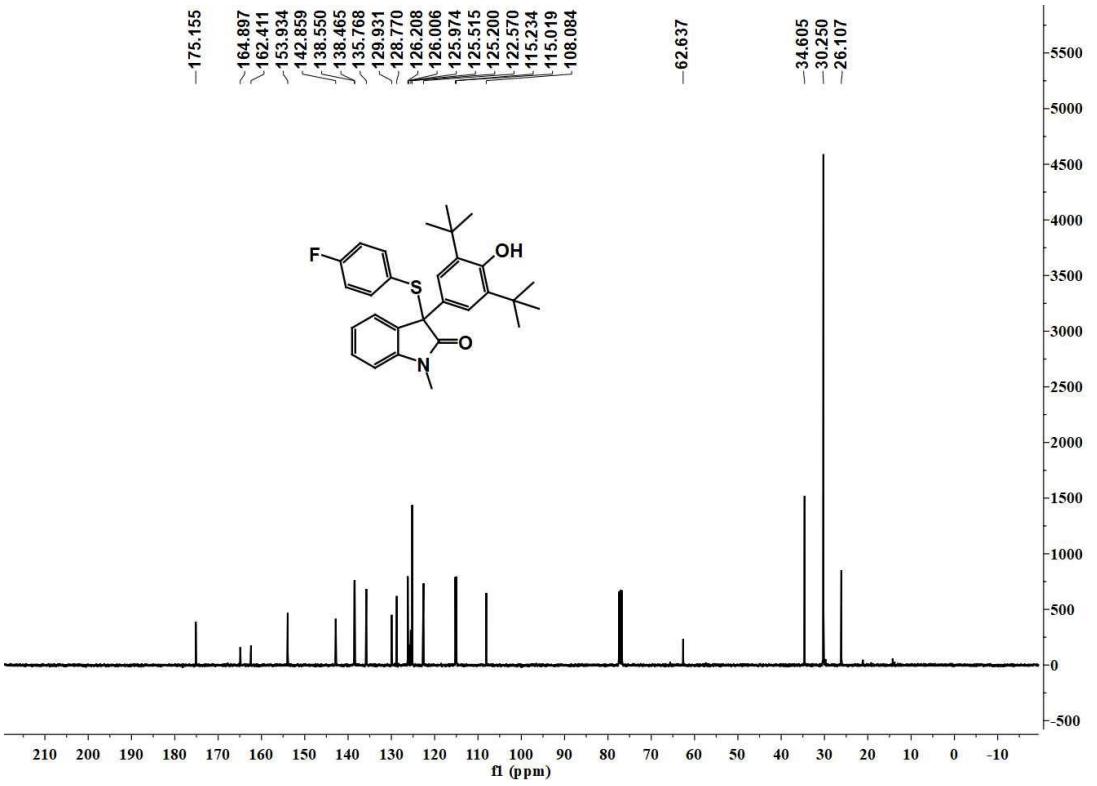
^{1}H and ^{13}C-NMR spectra of **1m**.



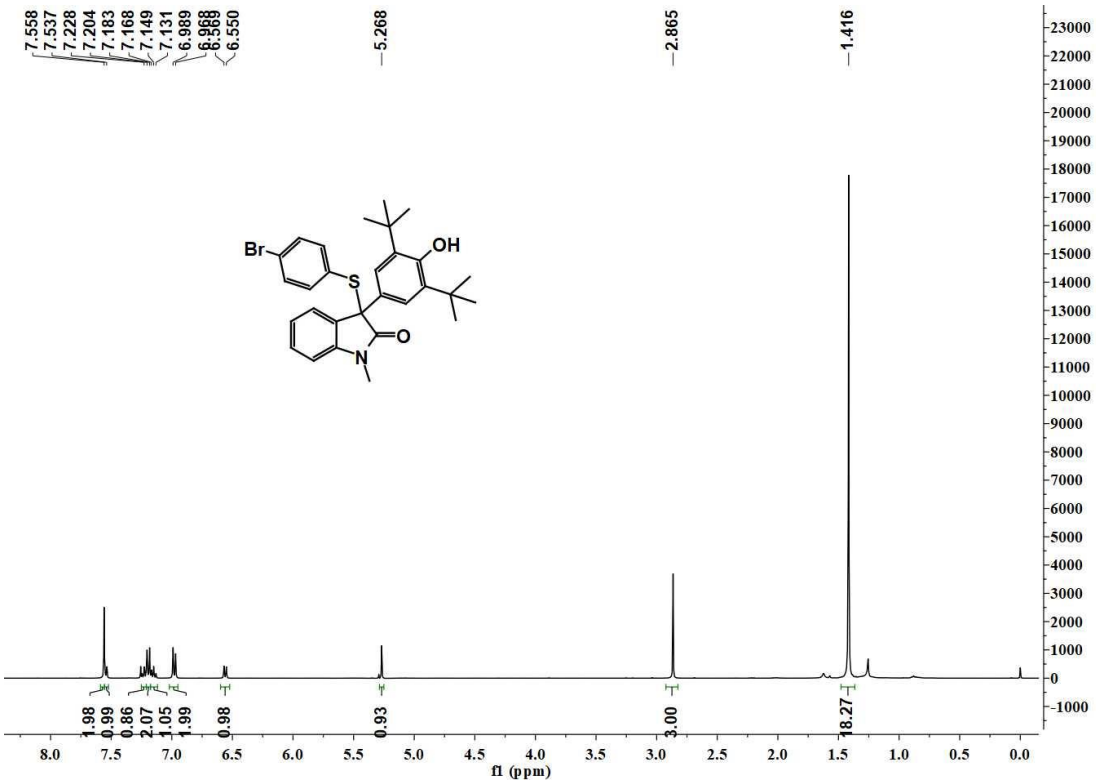


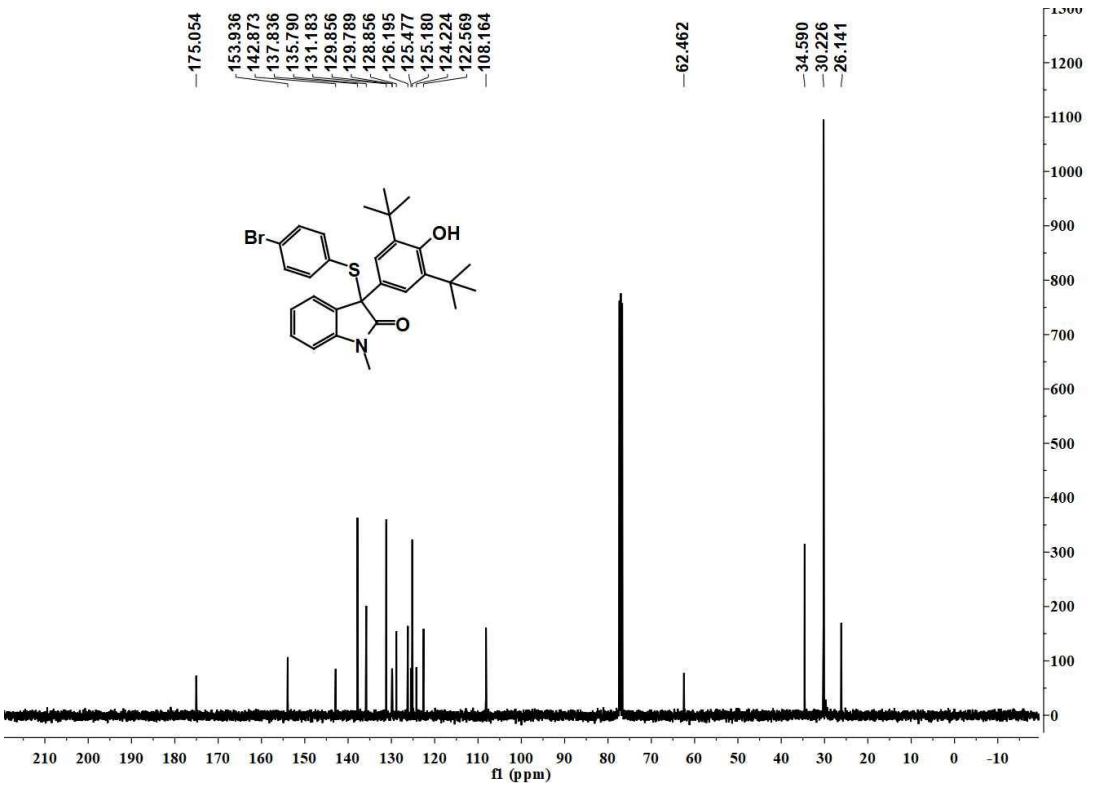
^{1}H and ^{13}C-NMR spectra of **1n**.



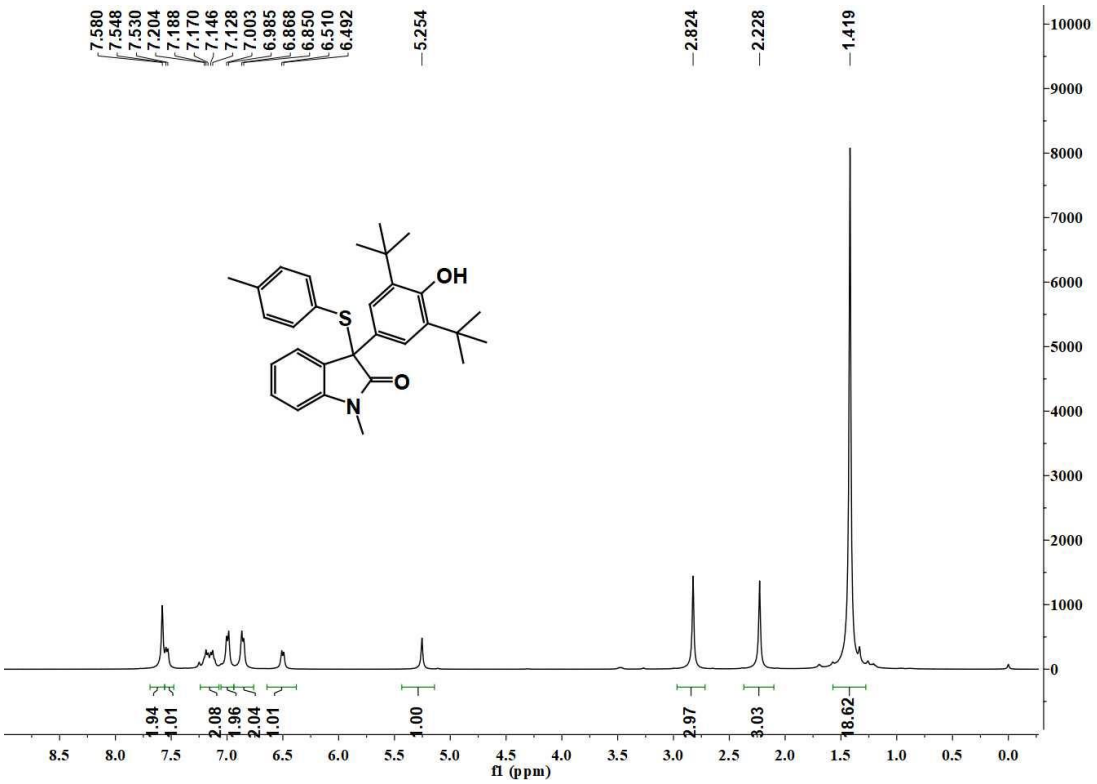


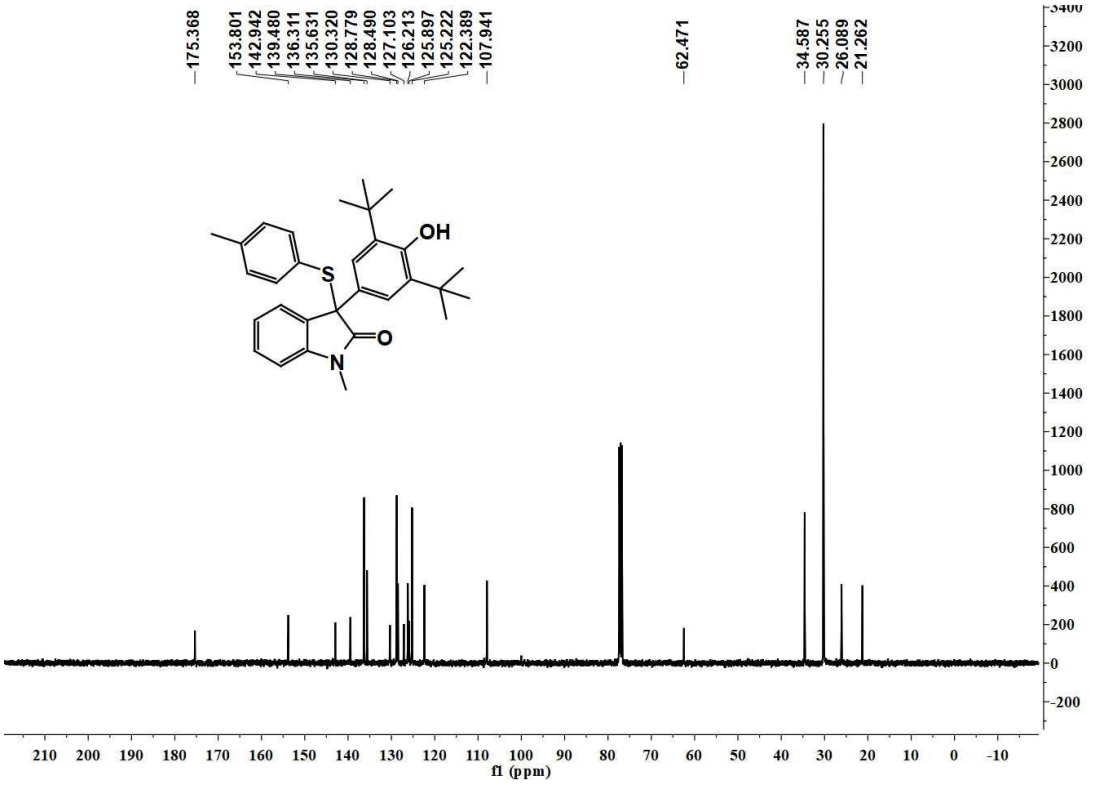
^{1}H and ^{13}C-NMR spectra of **1o**.



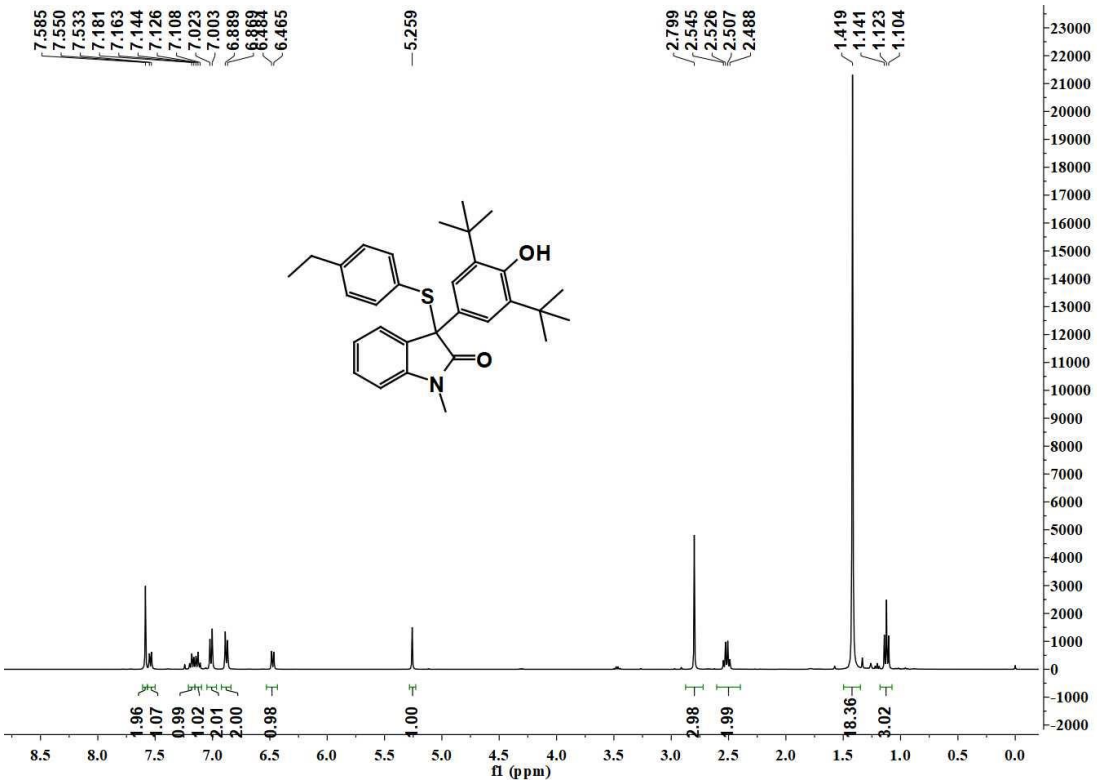


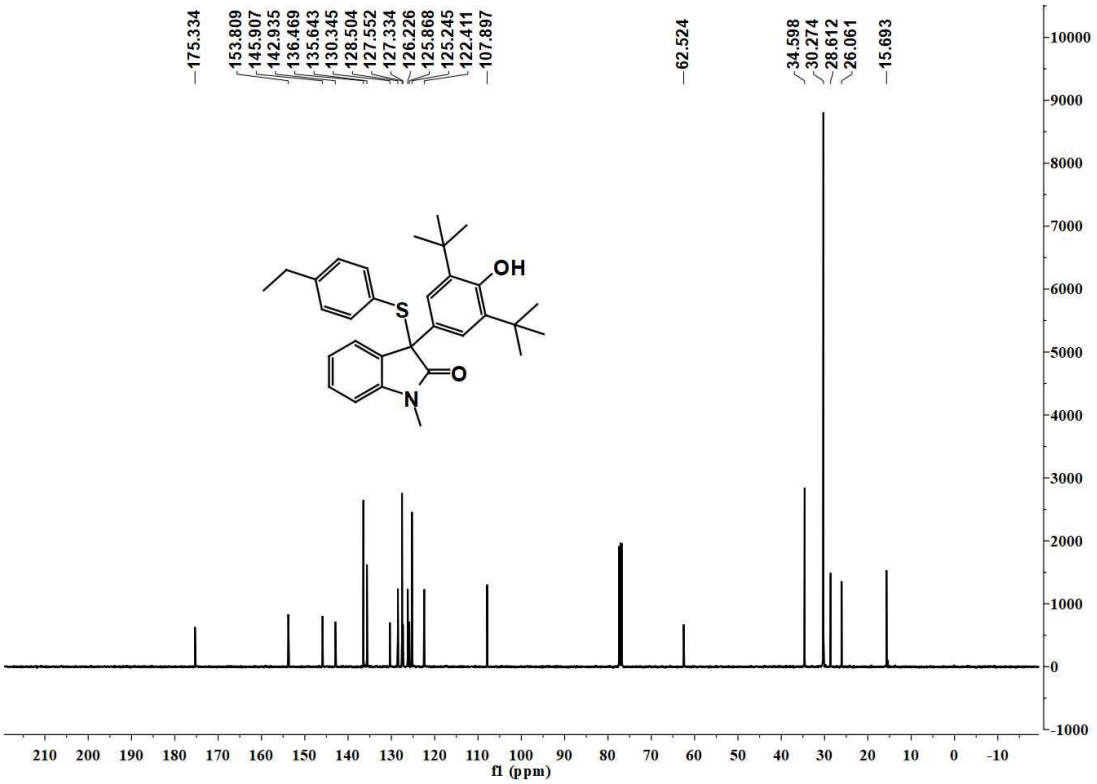
^{1}H and ^{13}C-NMR spectra of **1p**.



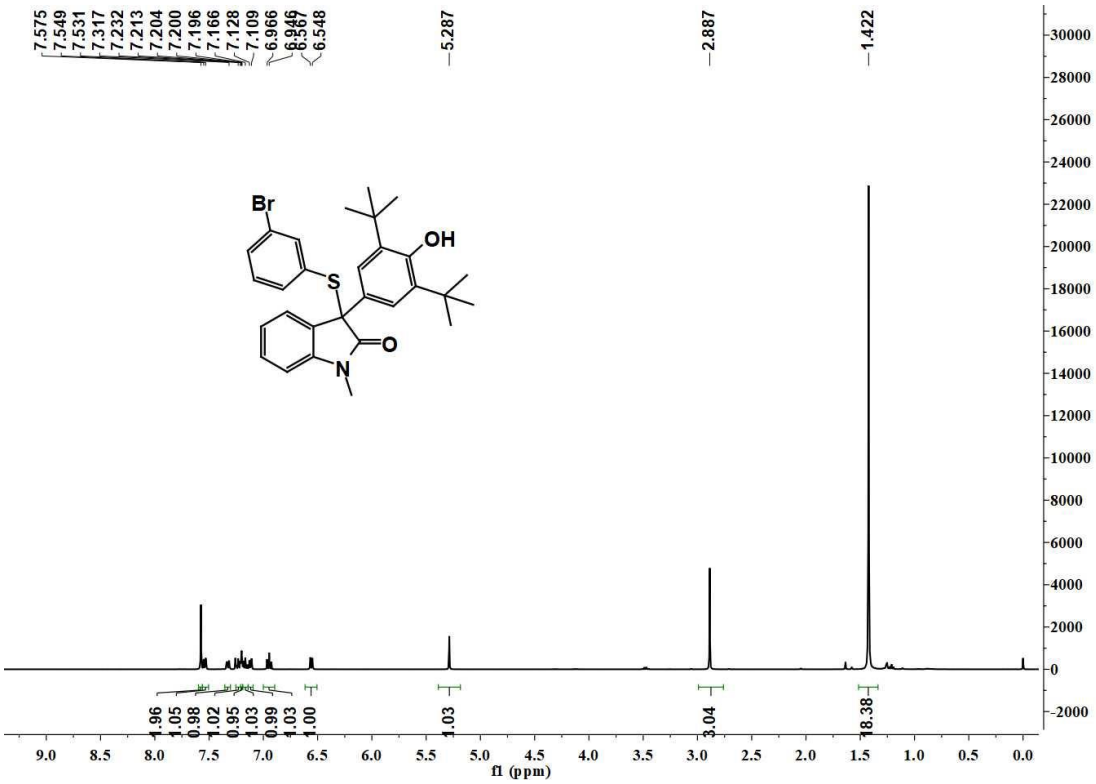


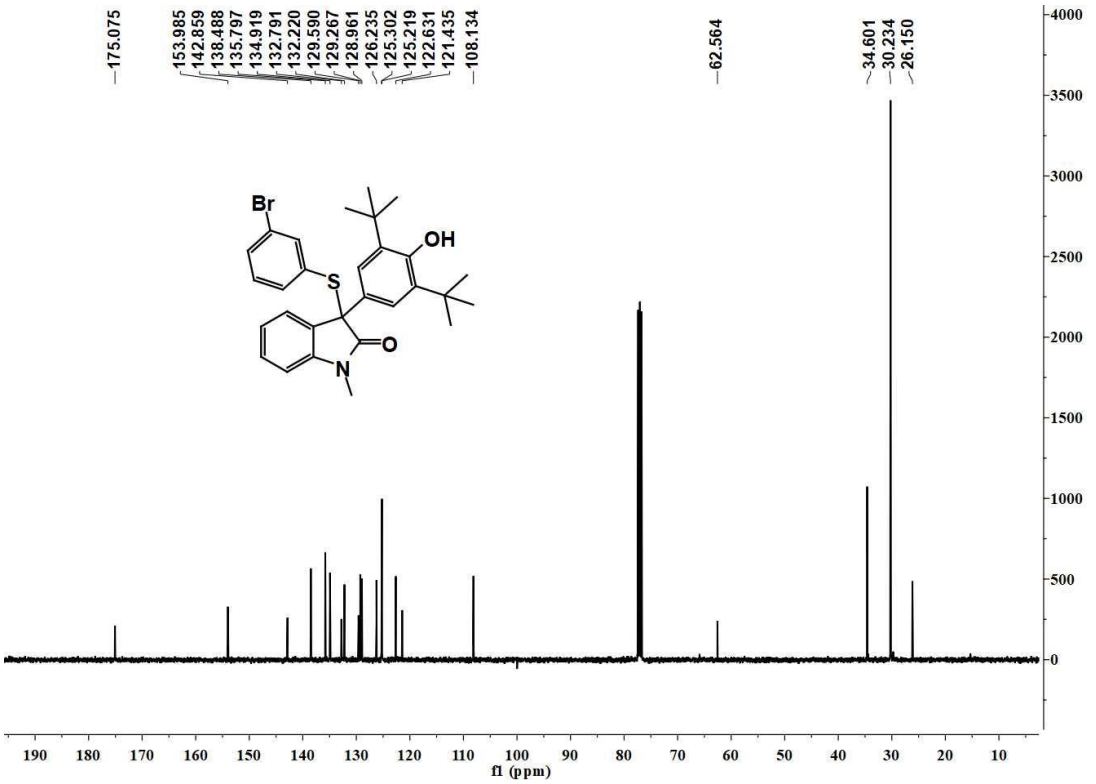
^{1}H and ^{13}C-NMR spectra of **1q**.



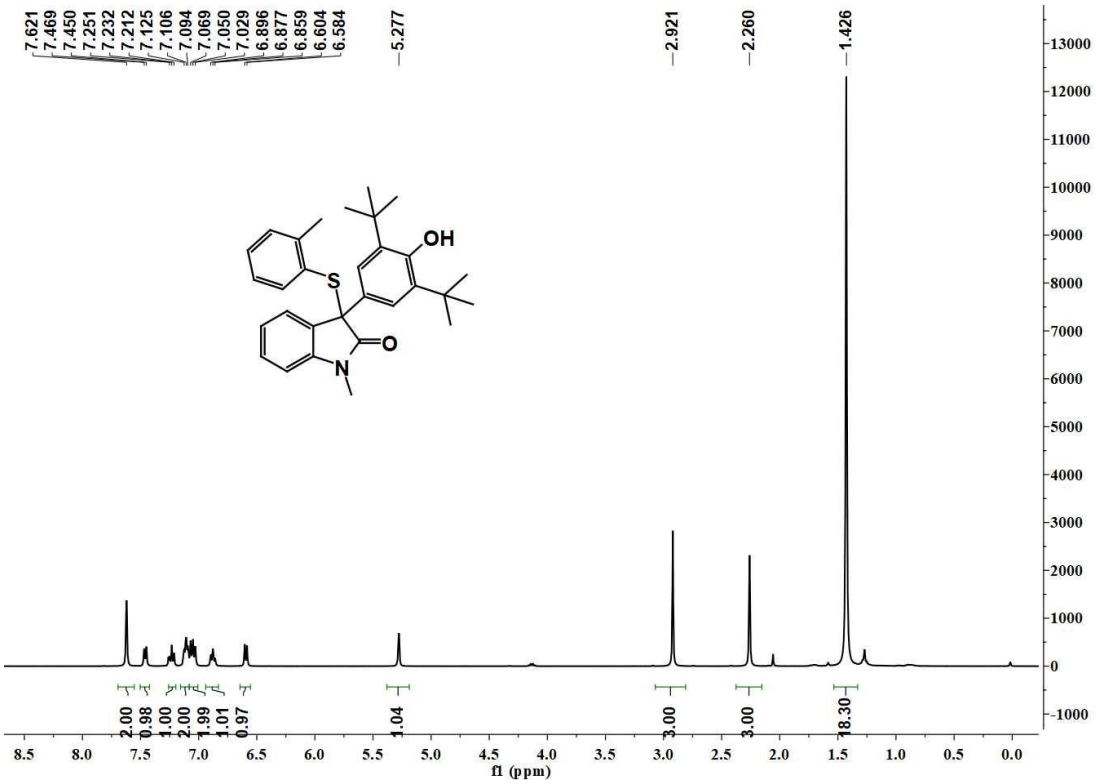


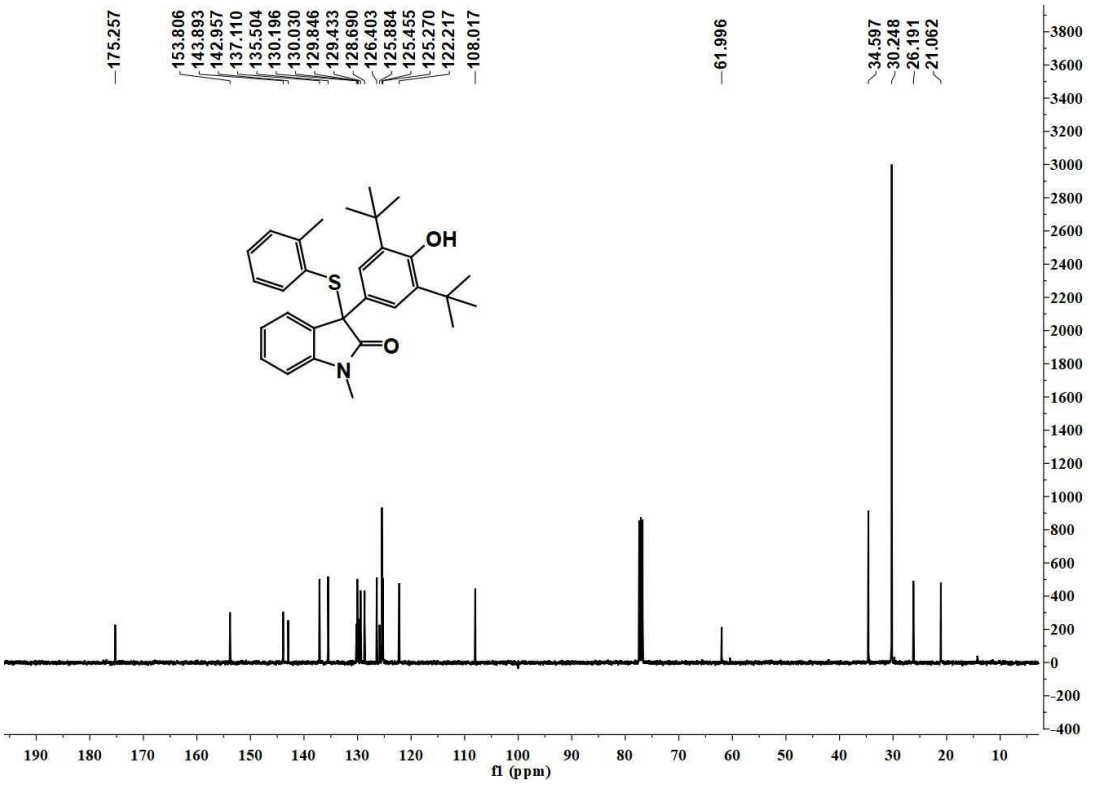
^{1}H and ^{13}C-NMR spectra of **1r**.



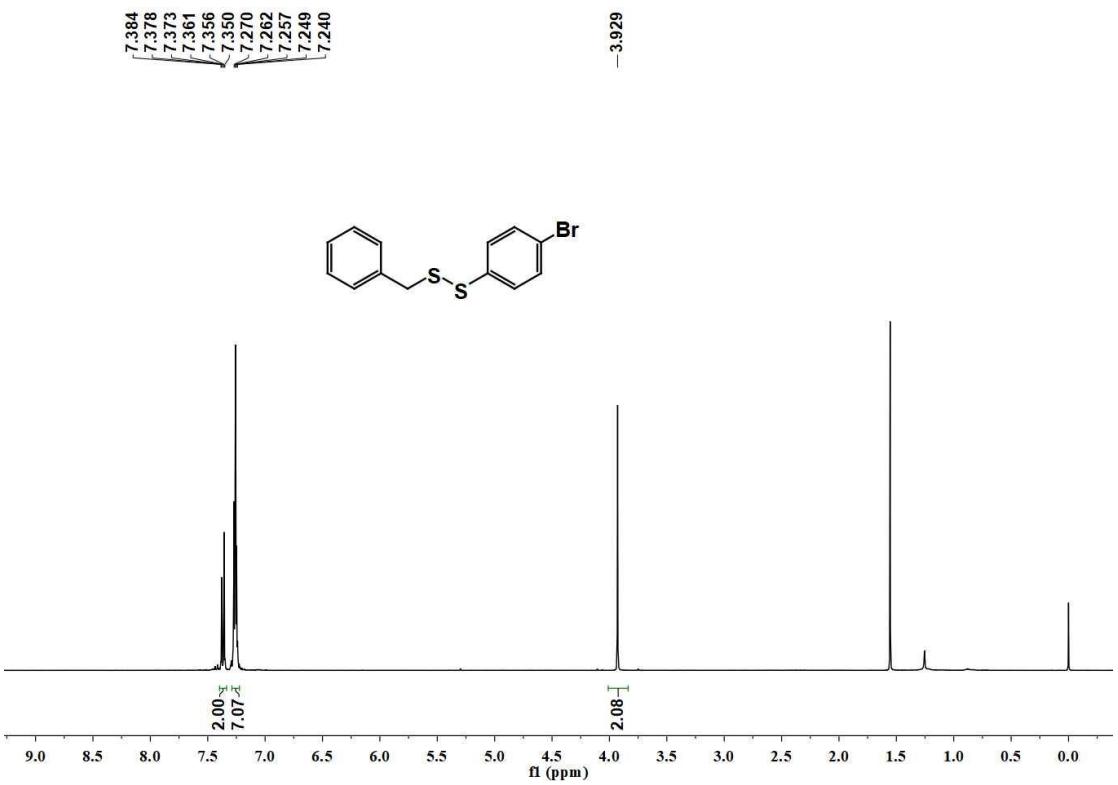


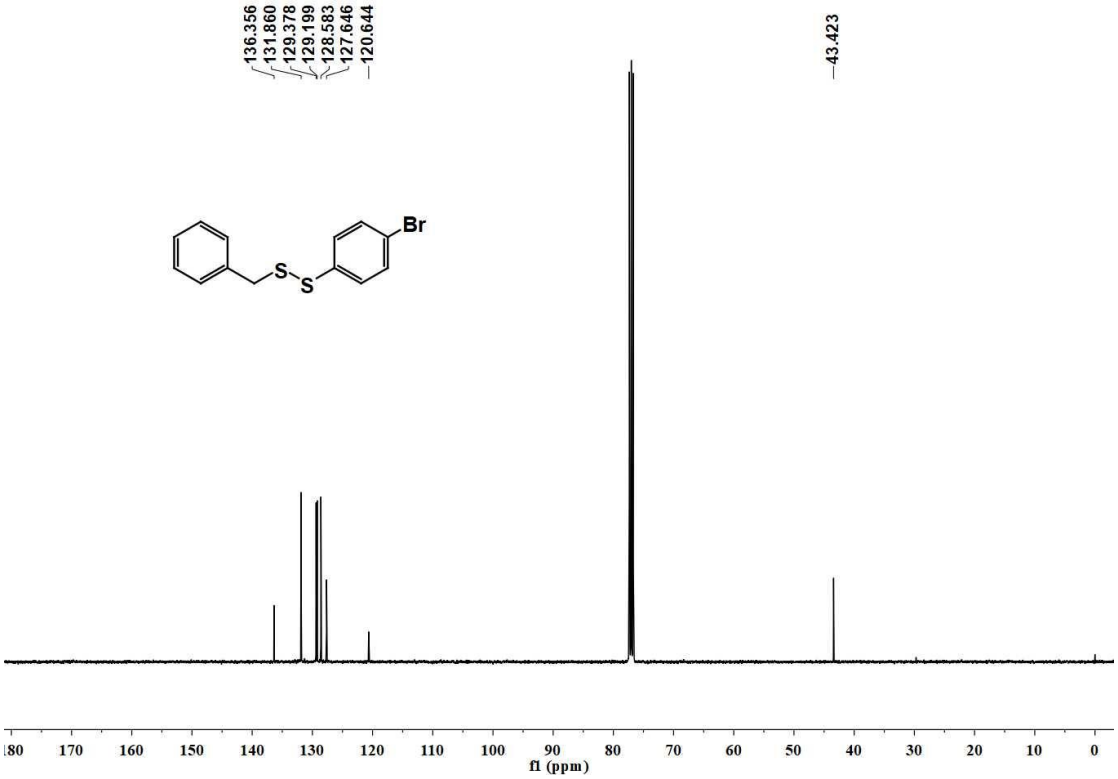
^{1}H and ^{13}C-NMR spectra of **1s**.



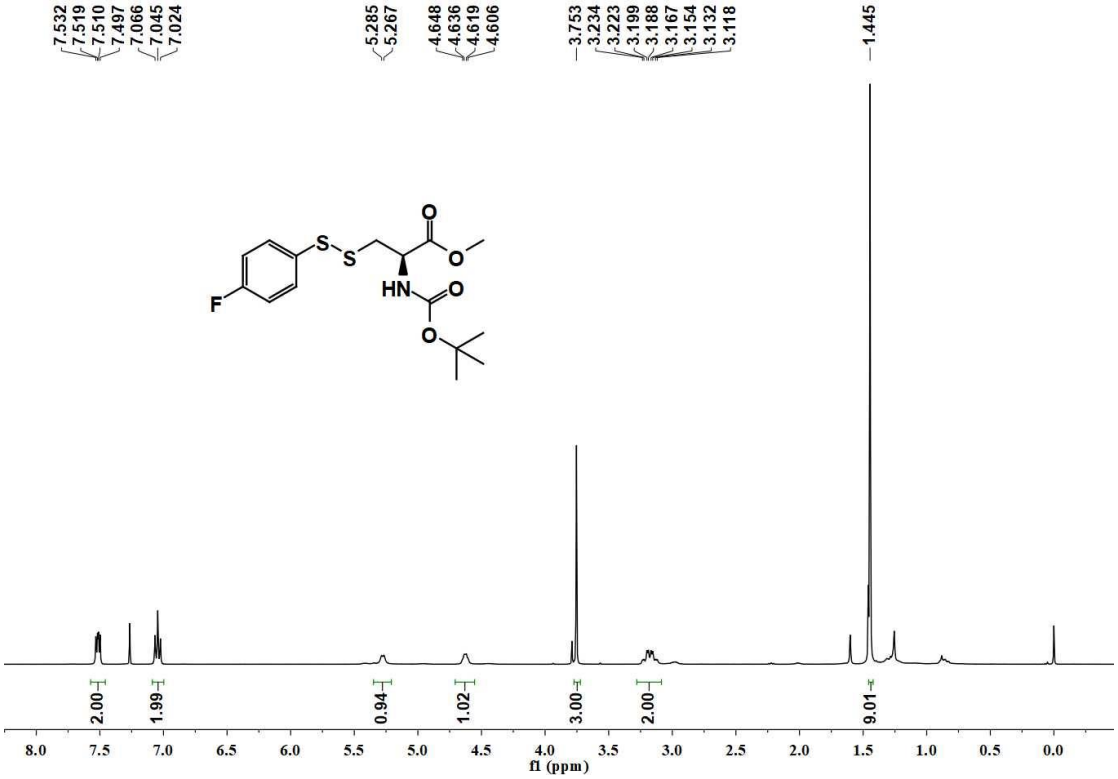


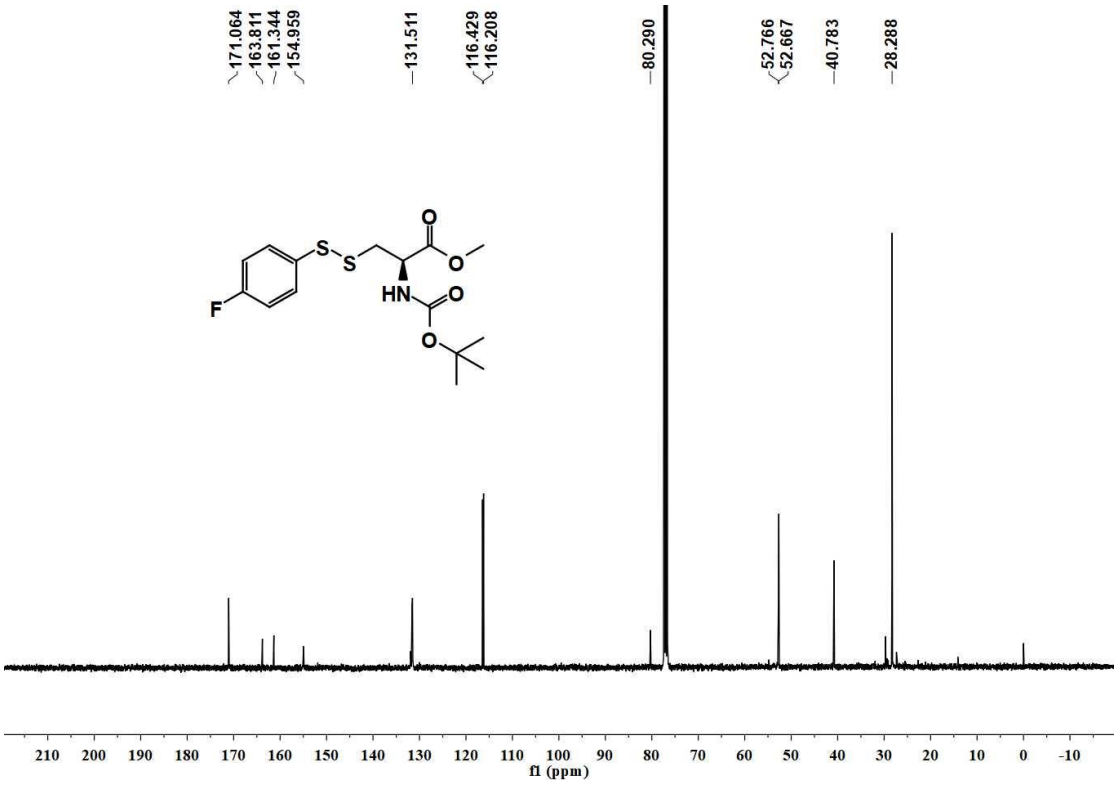
^{1}H and ^{13}C-NMR spectra of **3a**.



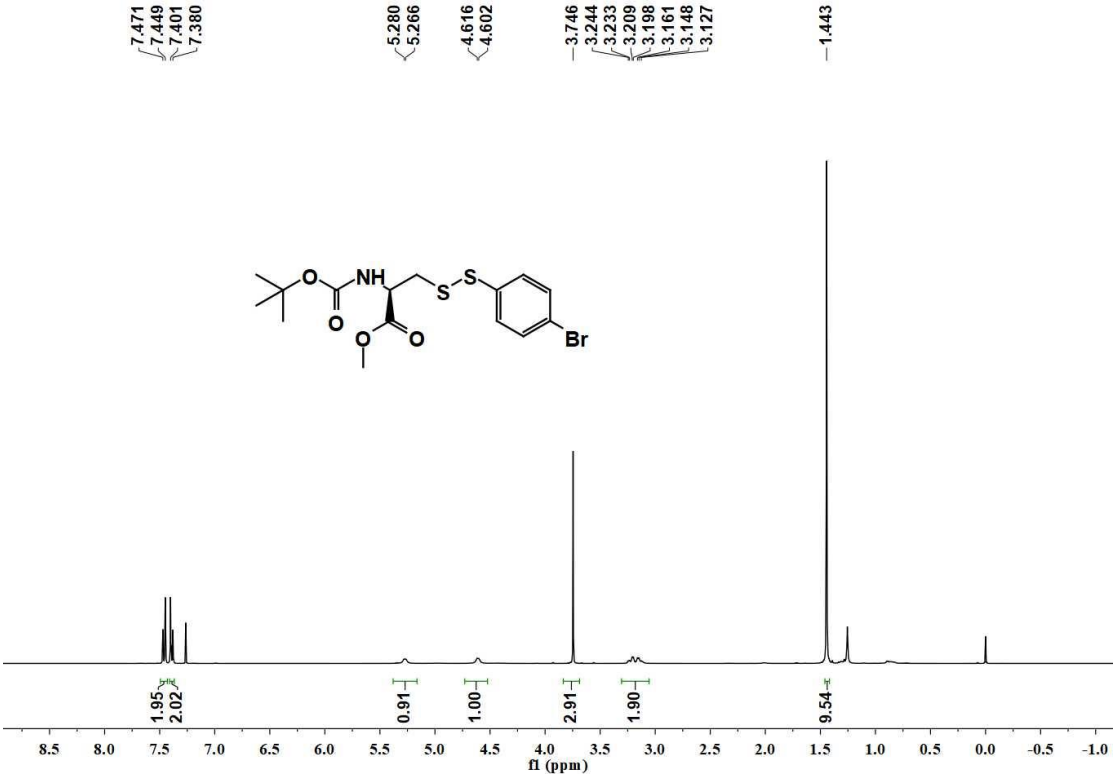


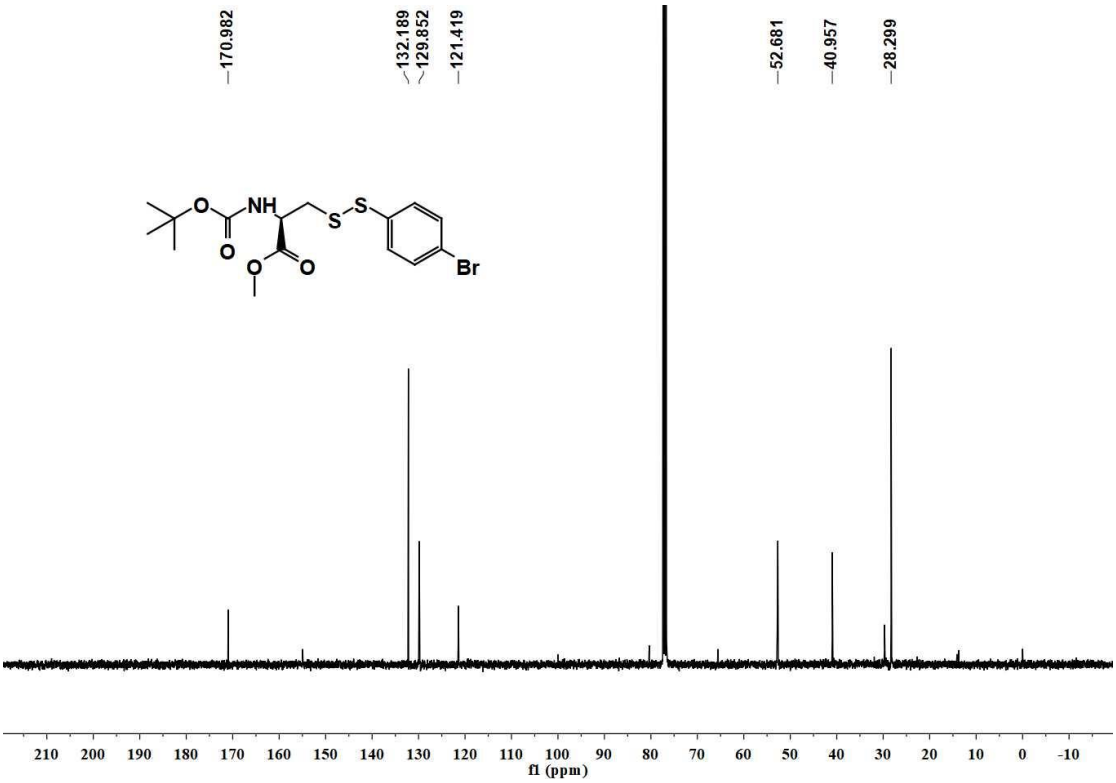
^{1}H and ^{13}C-NMR spectra of **3b**.



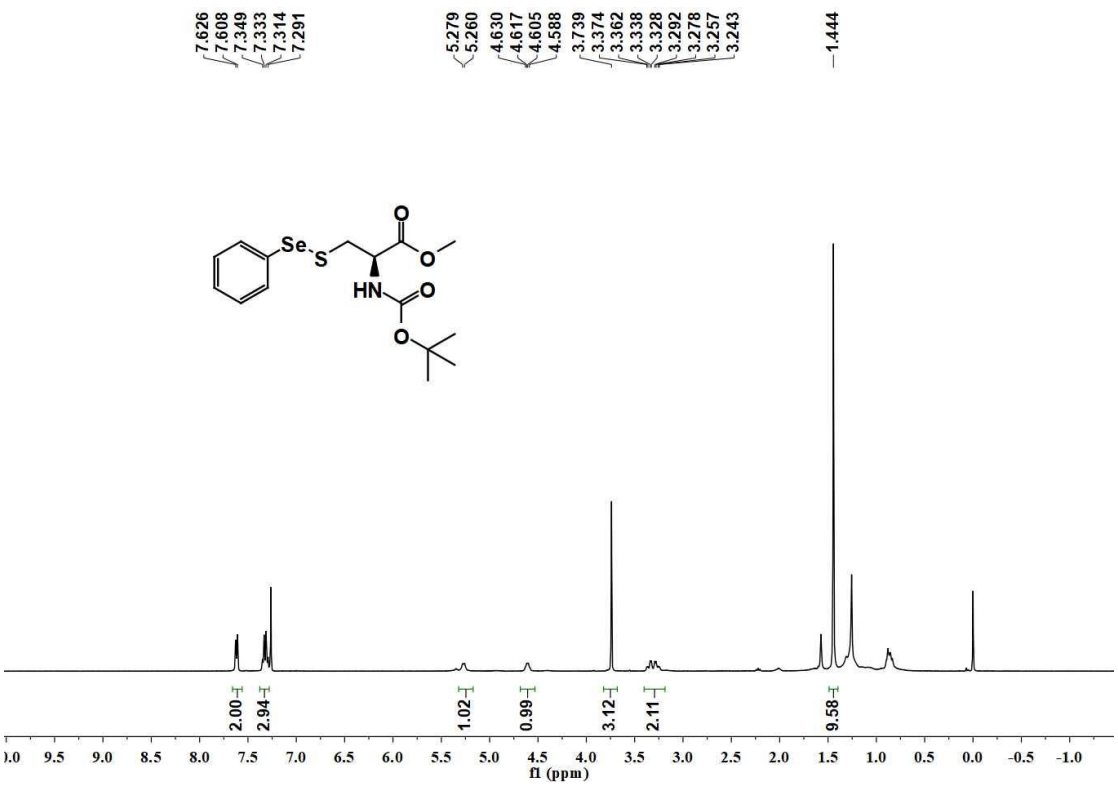


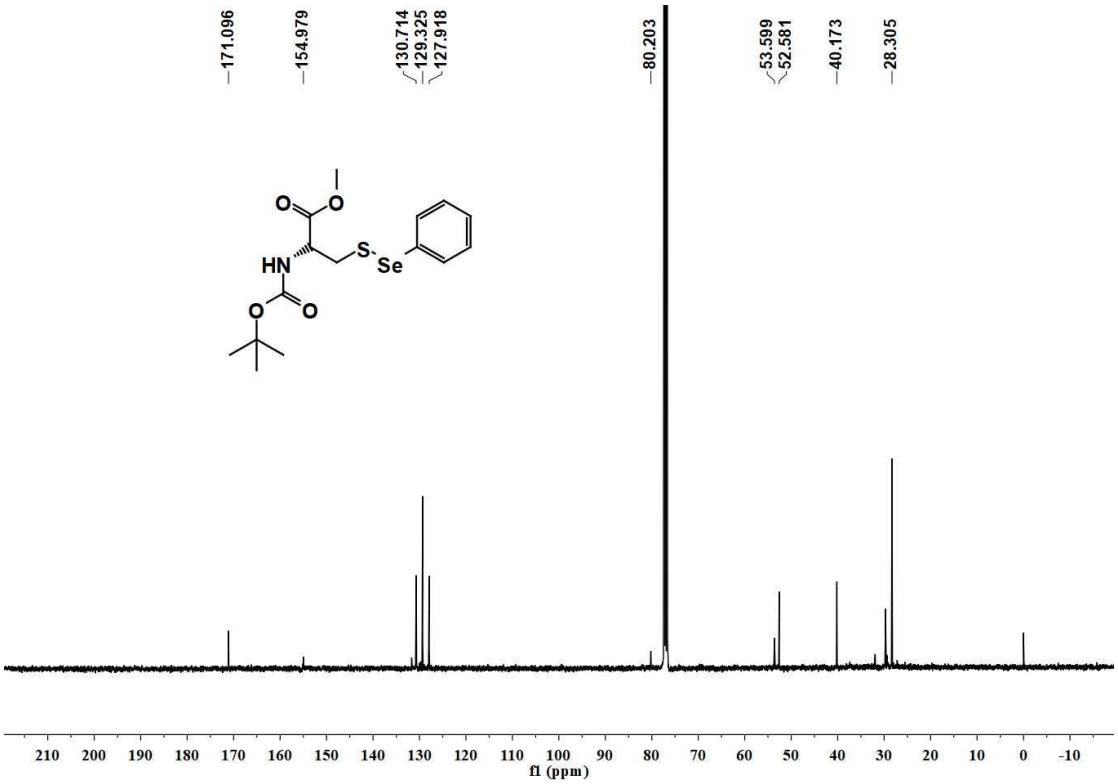
^{1}H and ^{13}C-NMR spectra of **3c**.



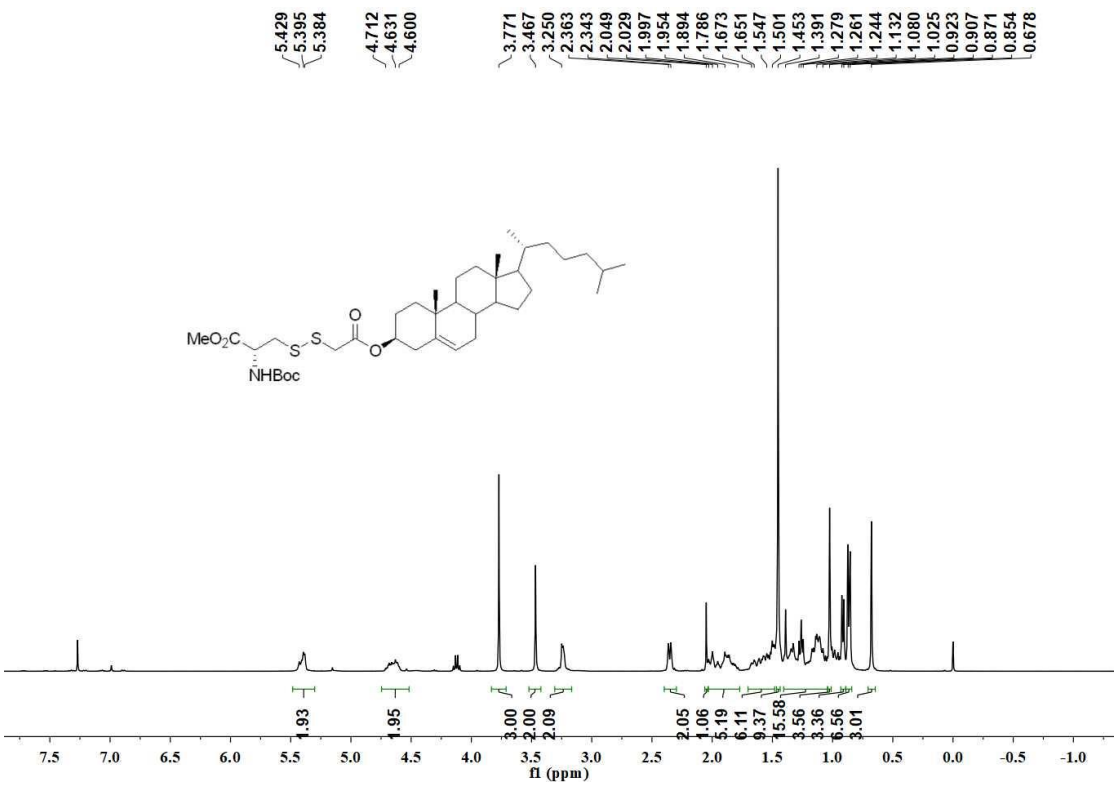


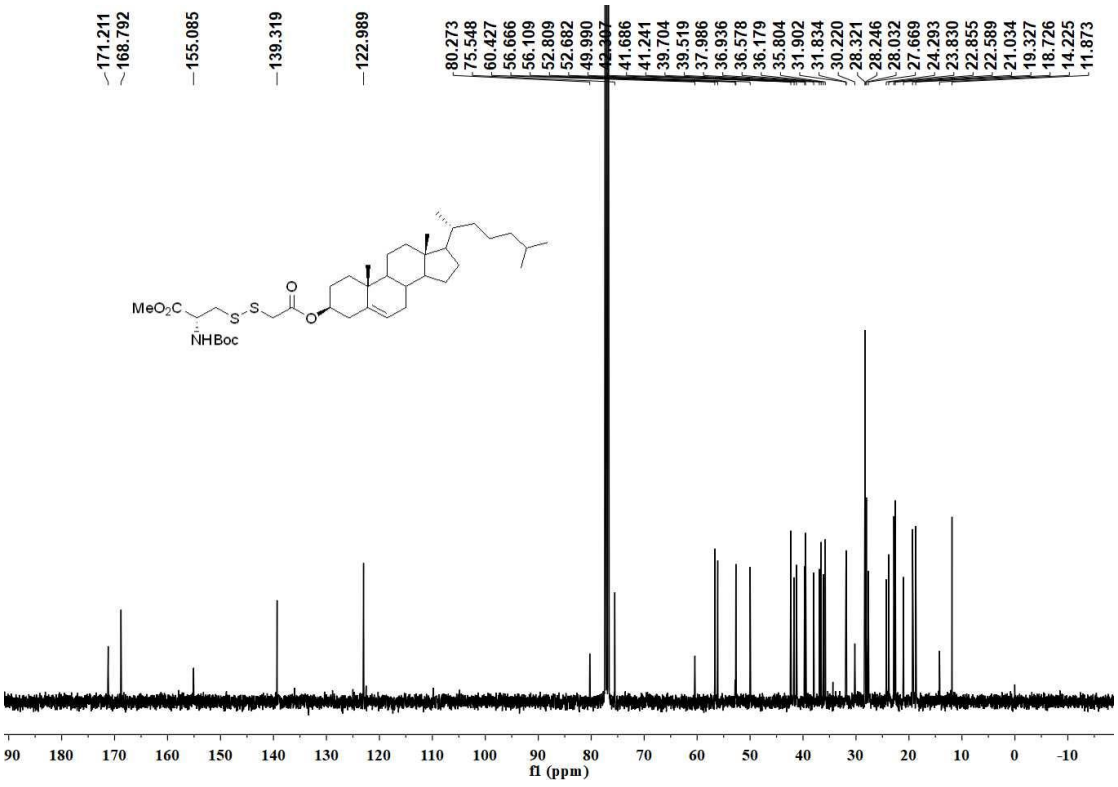
^{1}H and ^{13}C-NMR spectra of **3d**.



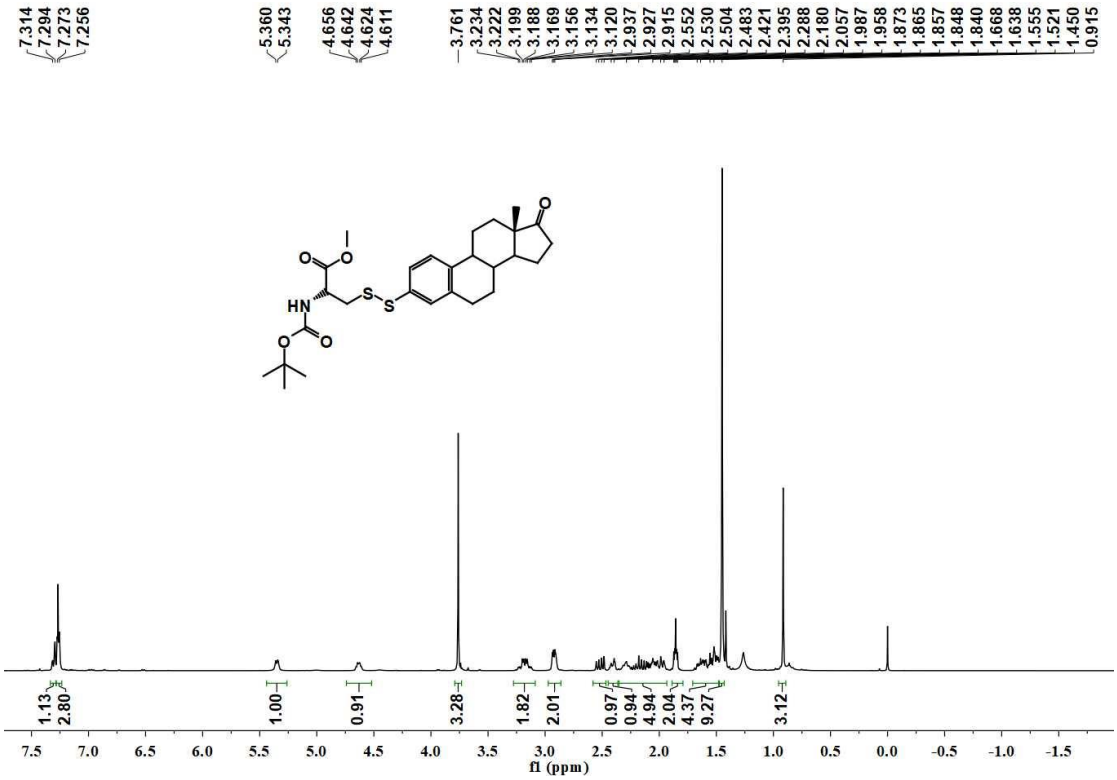


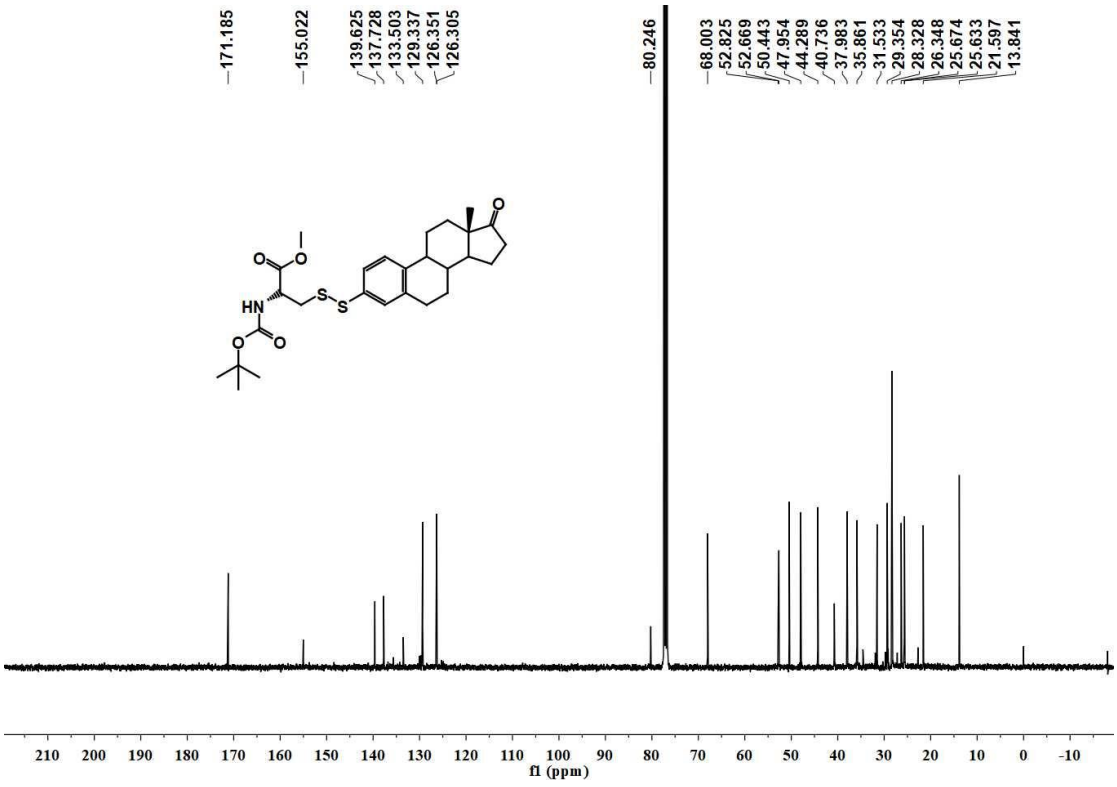
^{1}H and ^{13}C-NMR spectra of **3e**.



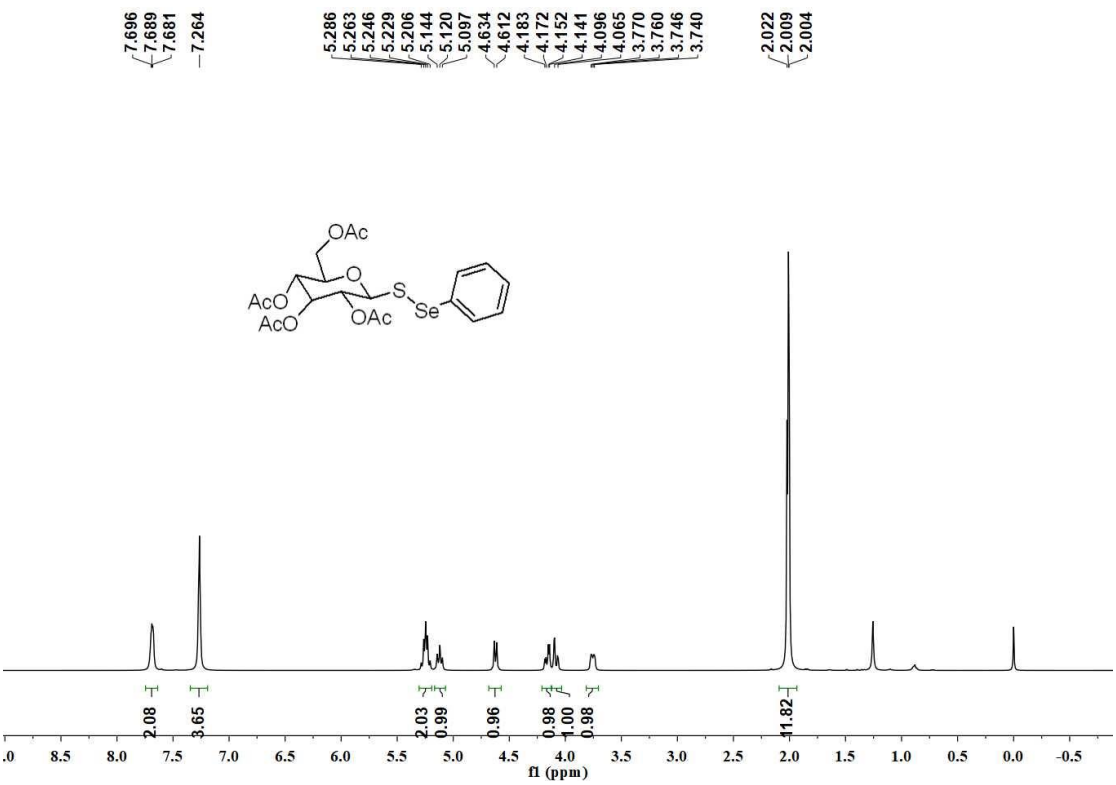


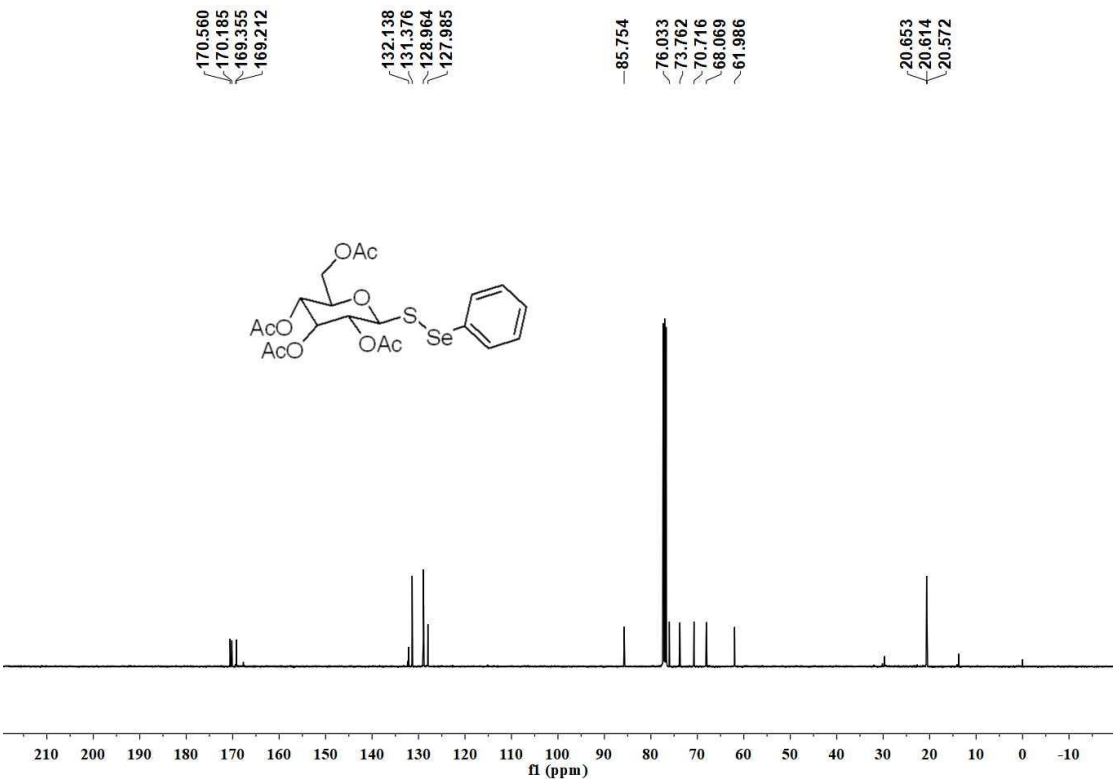
^{1}H and ^{13}C-NMR spectra of **3f**.



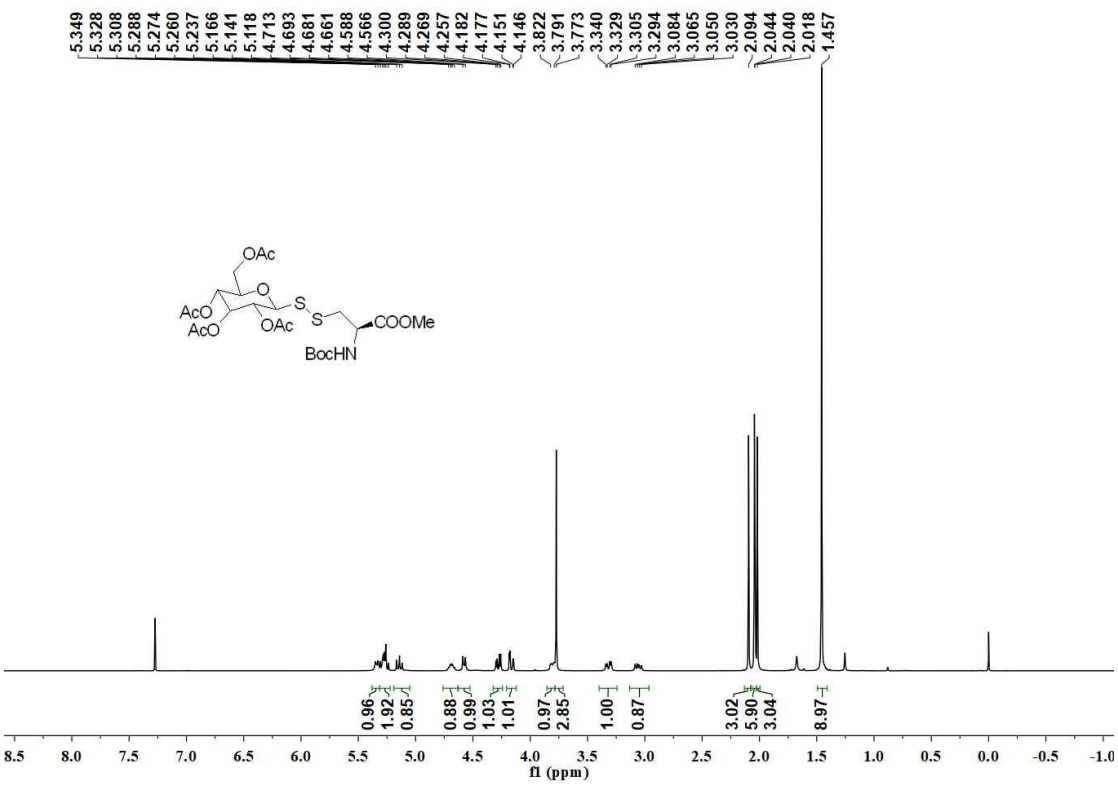


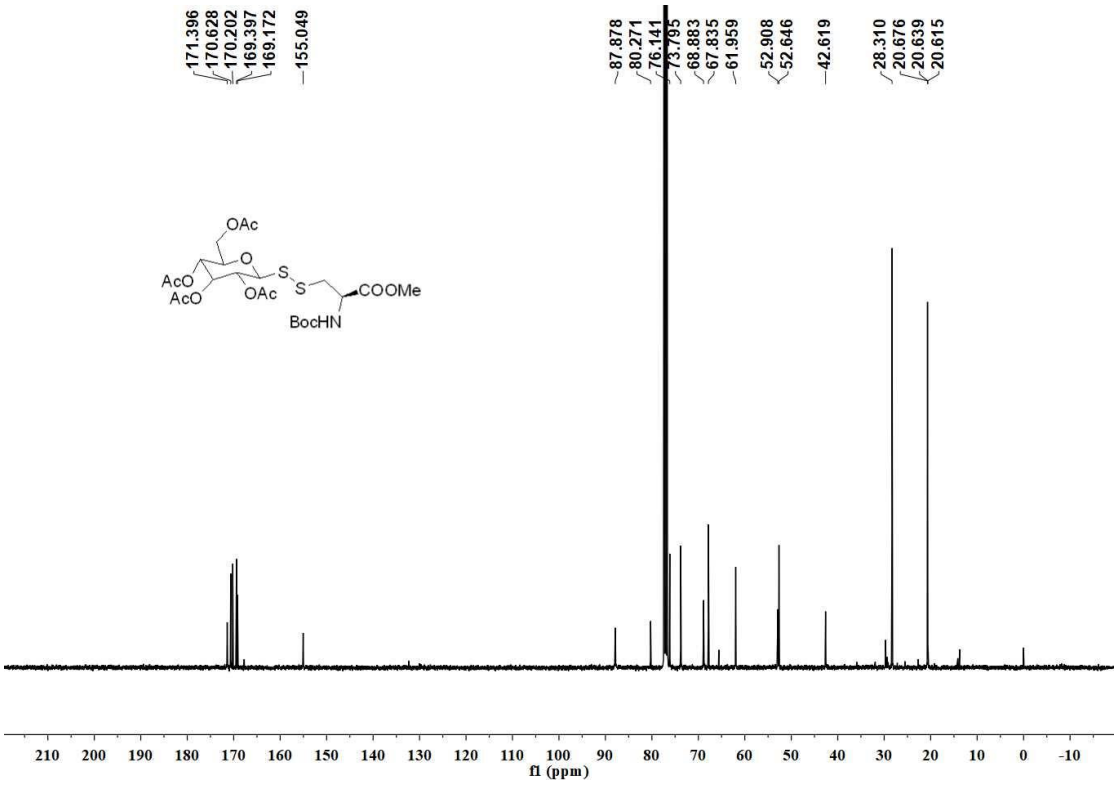
^{1}H and ^{13}C-NMR spectra of **3g**.



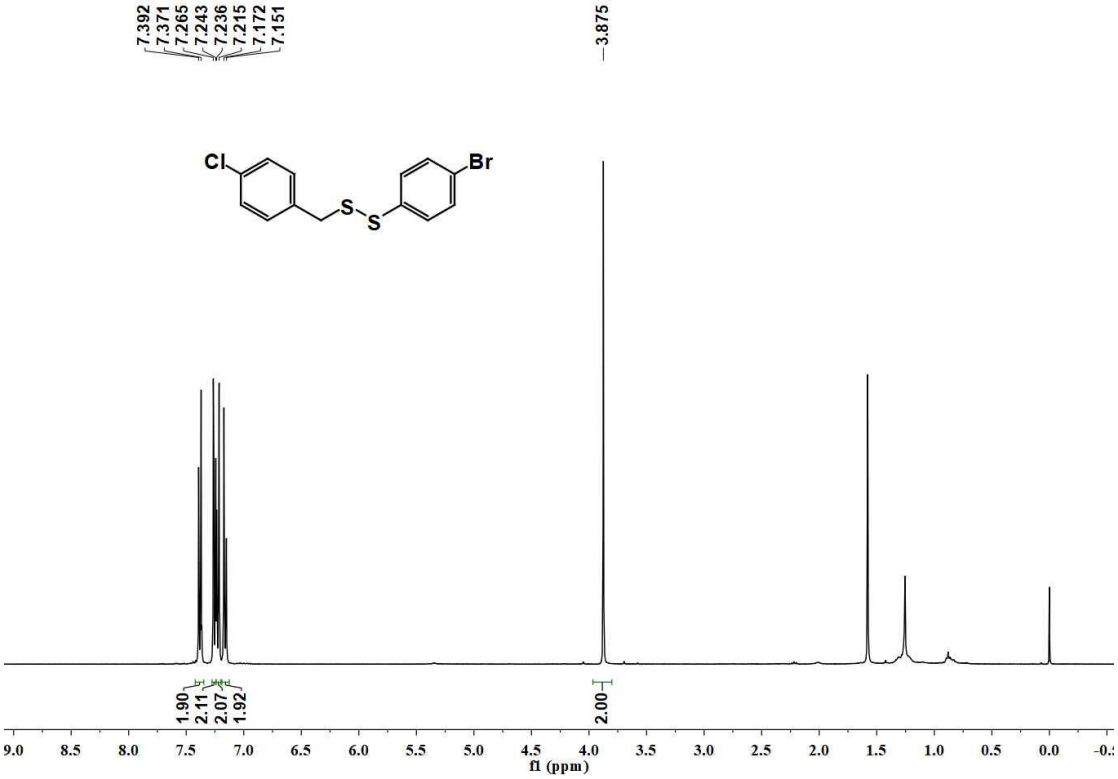


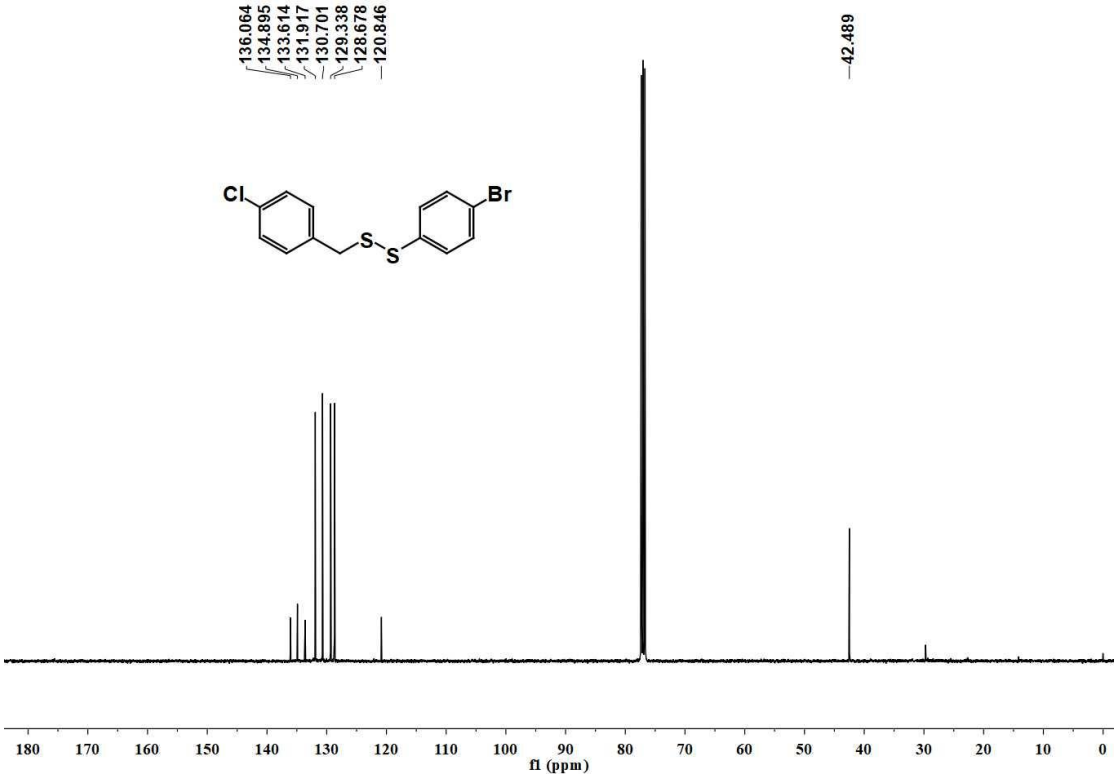
^{1}H and ^{13}C-NMR spectra of **3h**.



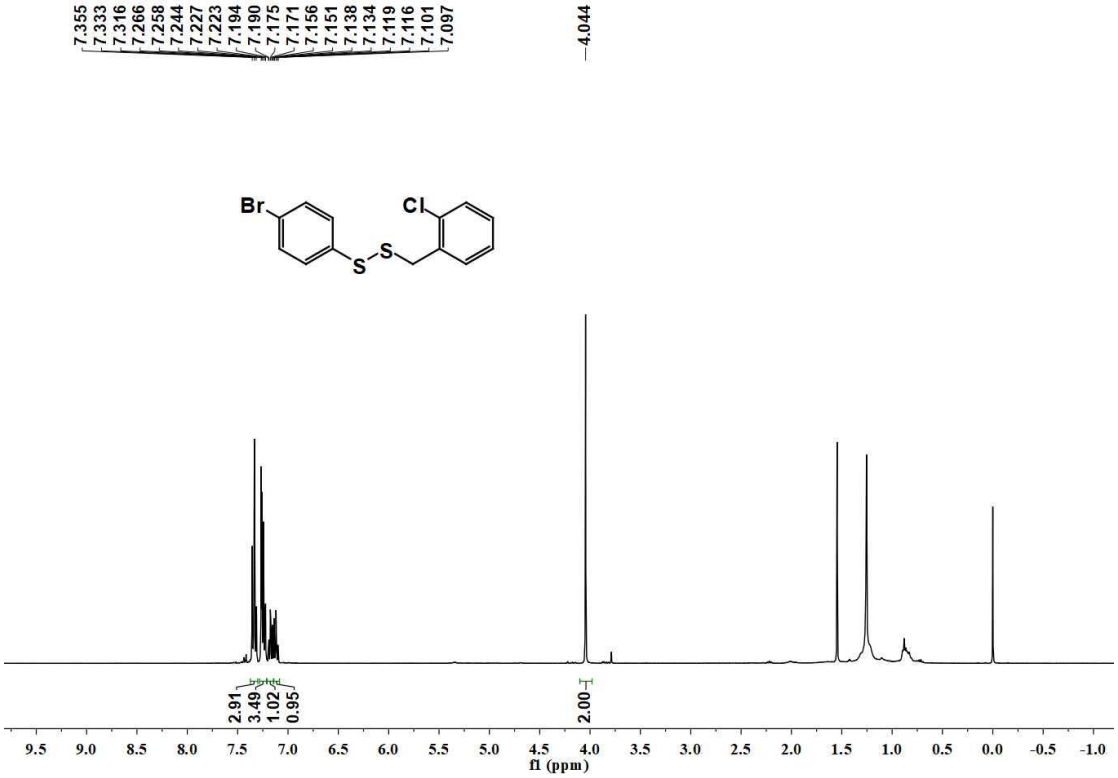


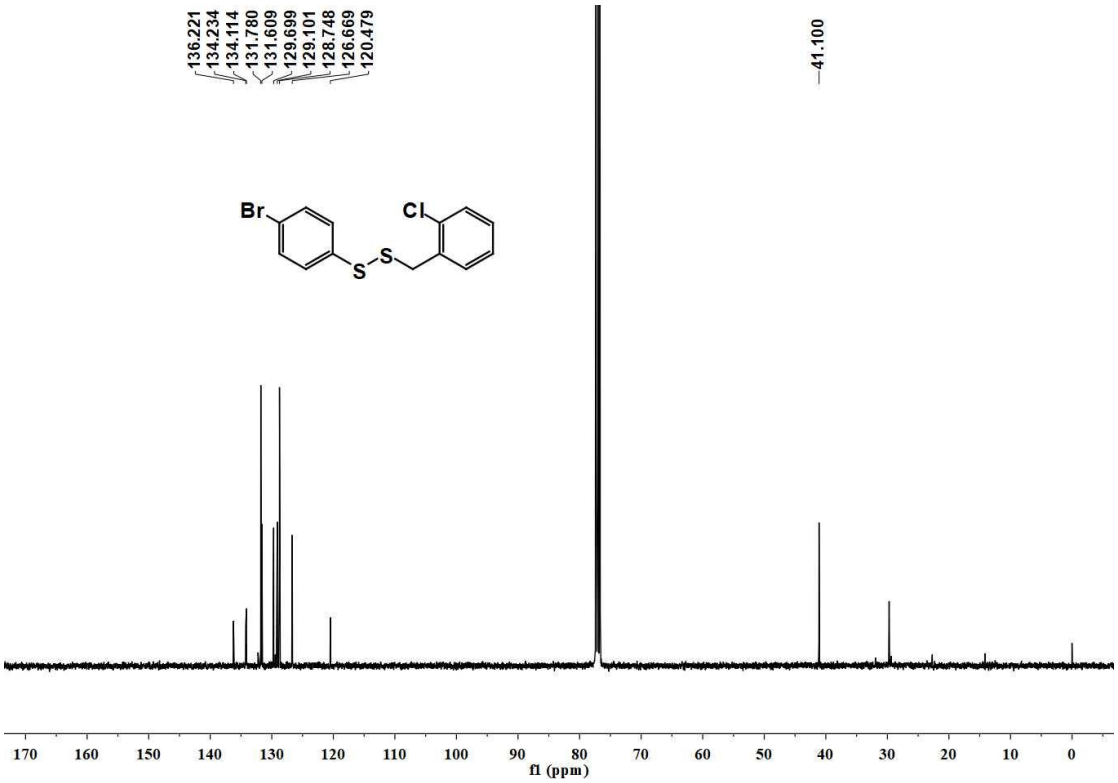
^{1}H and ^{13}C-NMR spectra of **3i**.



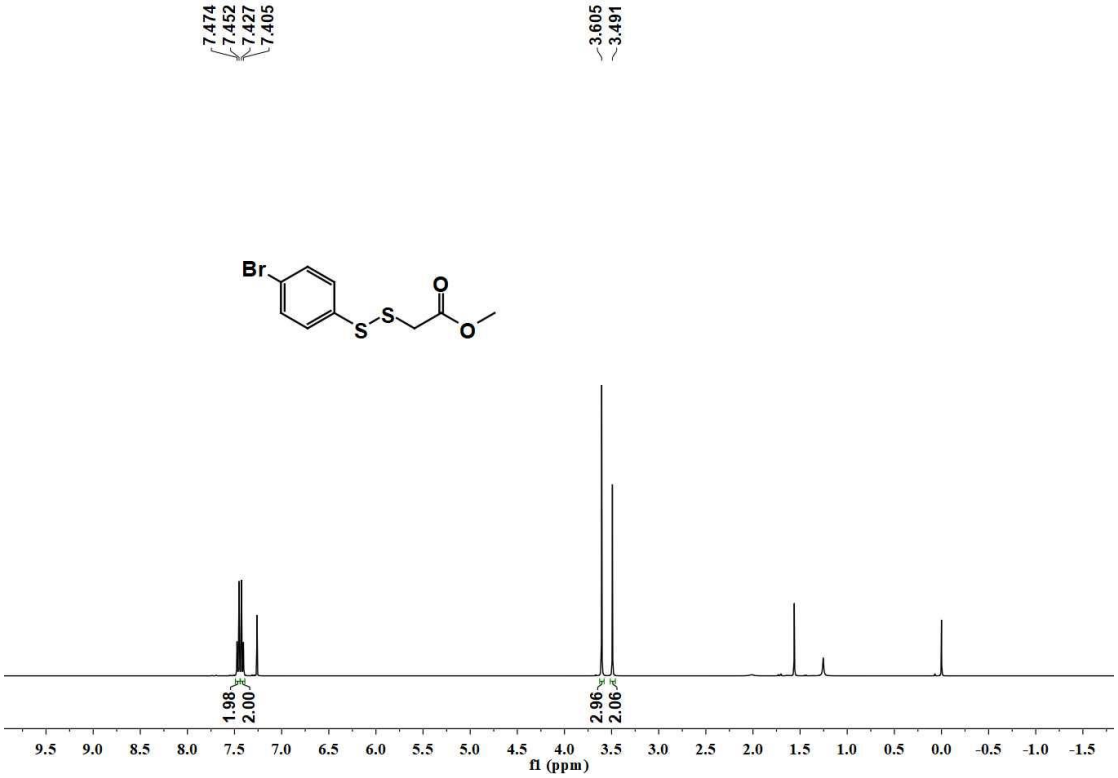


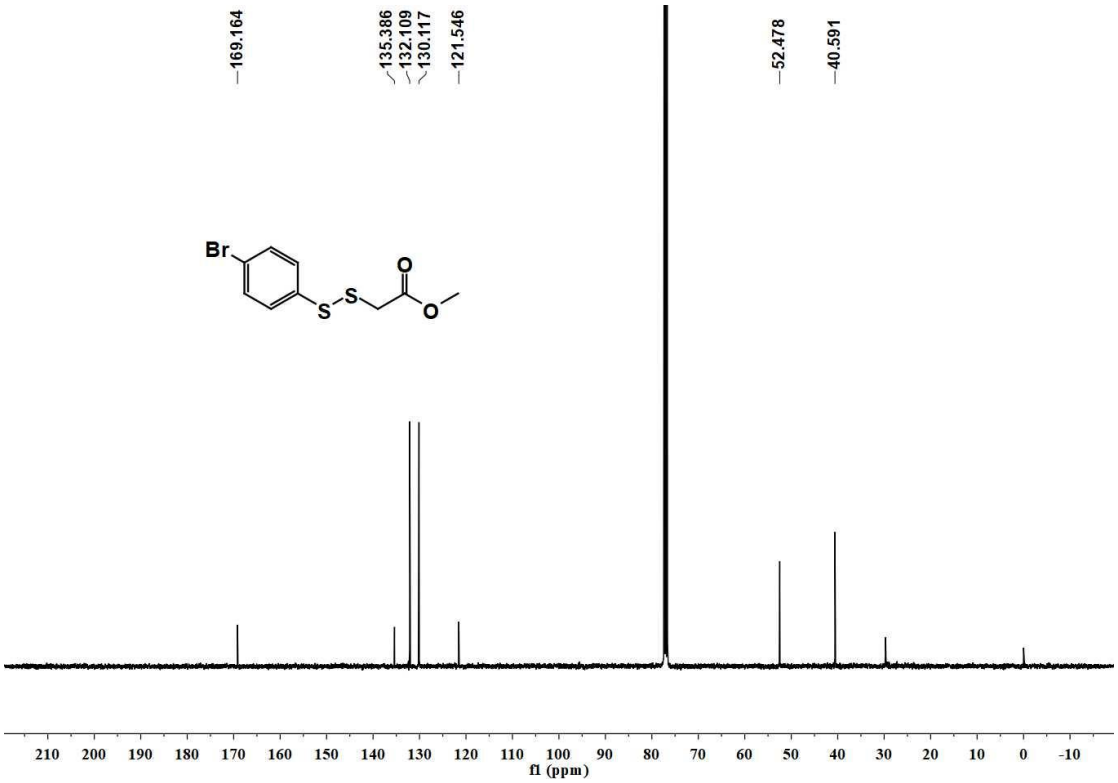
^{1}H and ^{13}C-NMR spectra of **3j**.



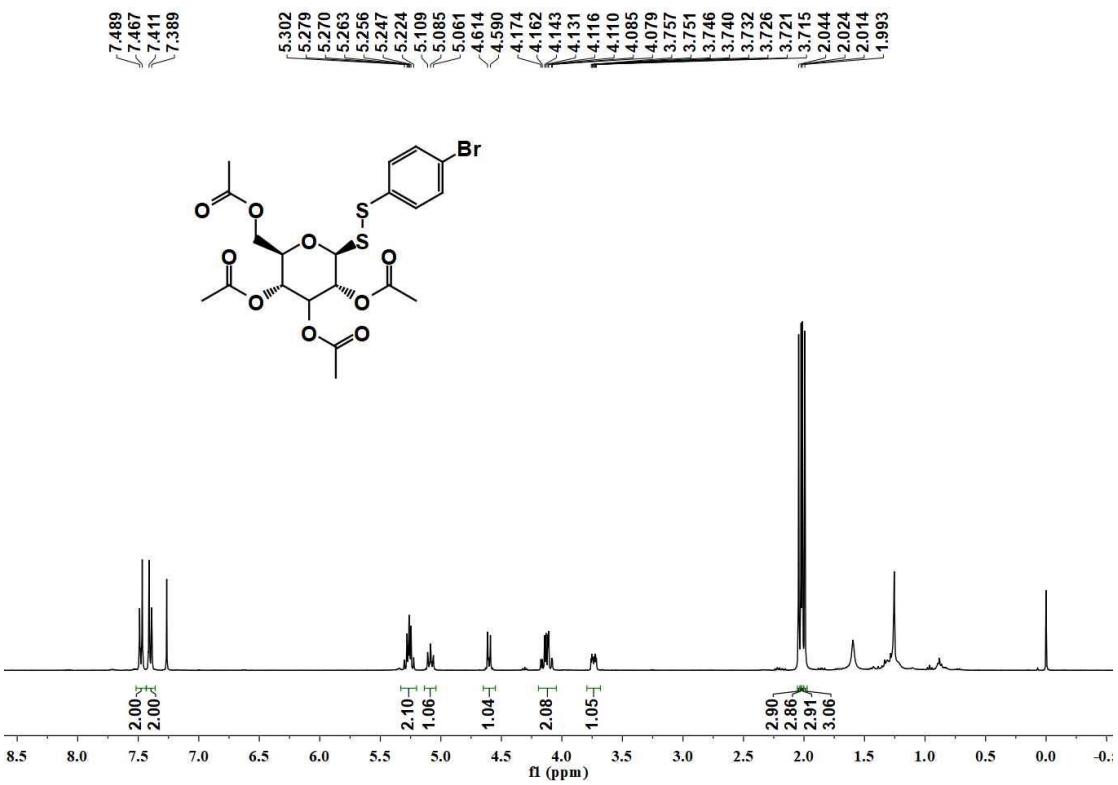


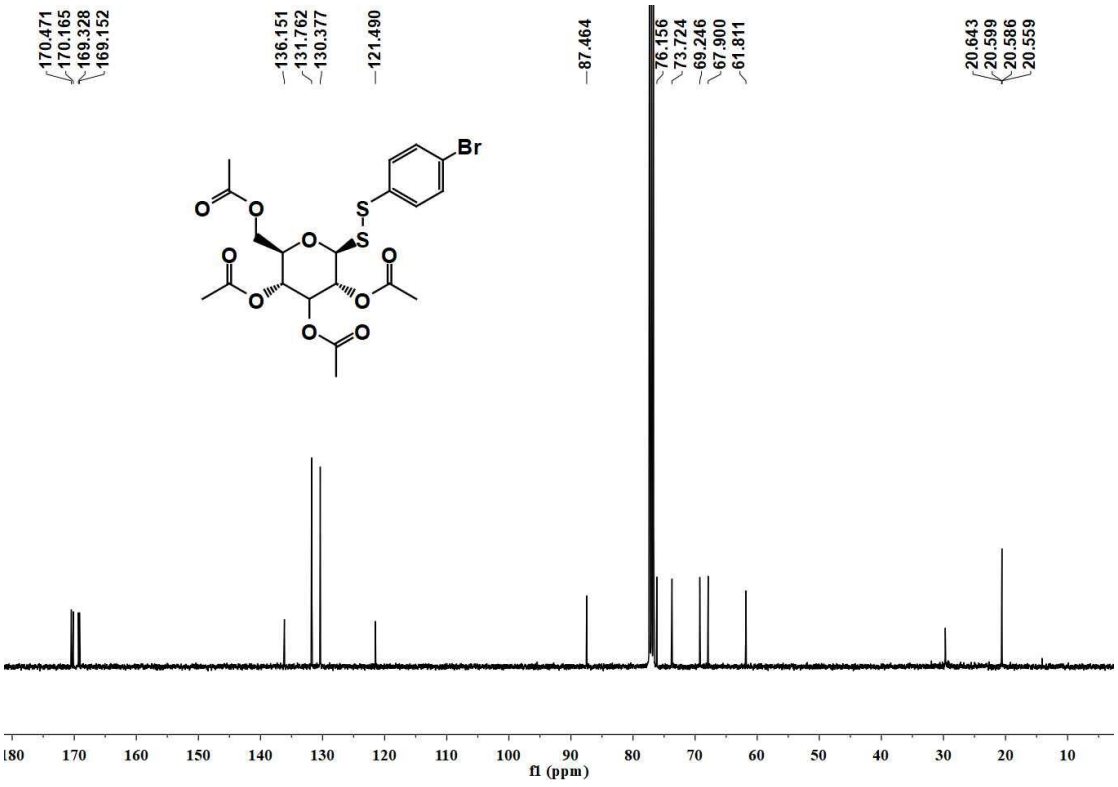
^{1}H and ^{13}C-NMR spectra of **3l**.



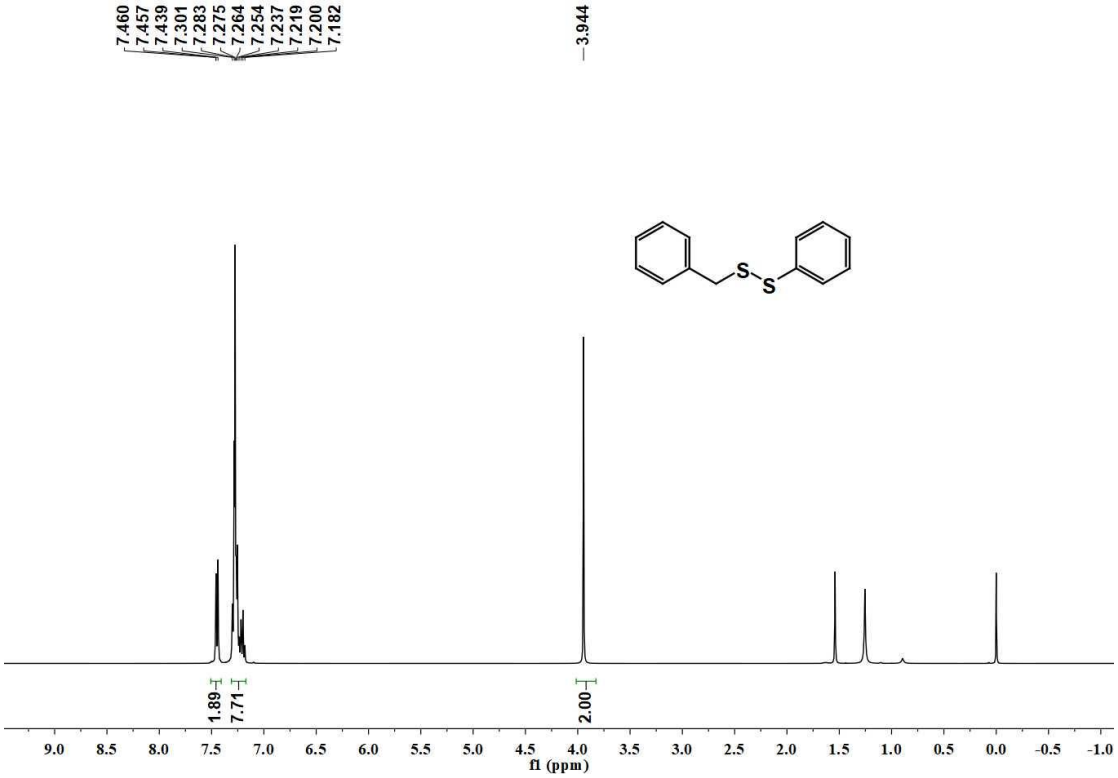


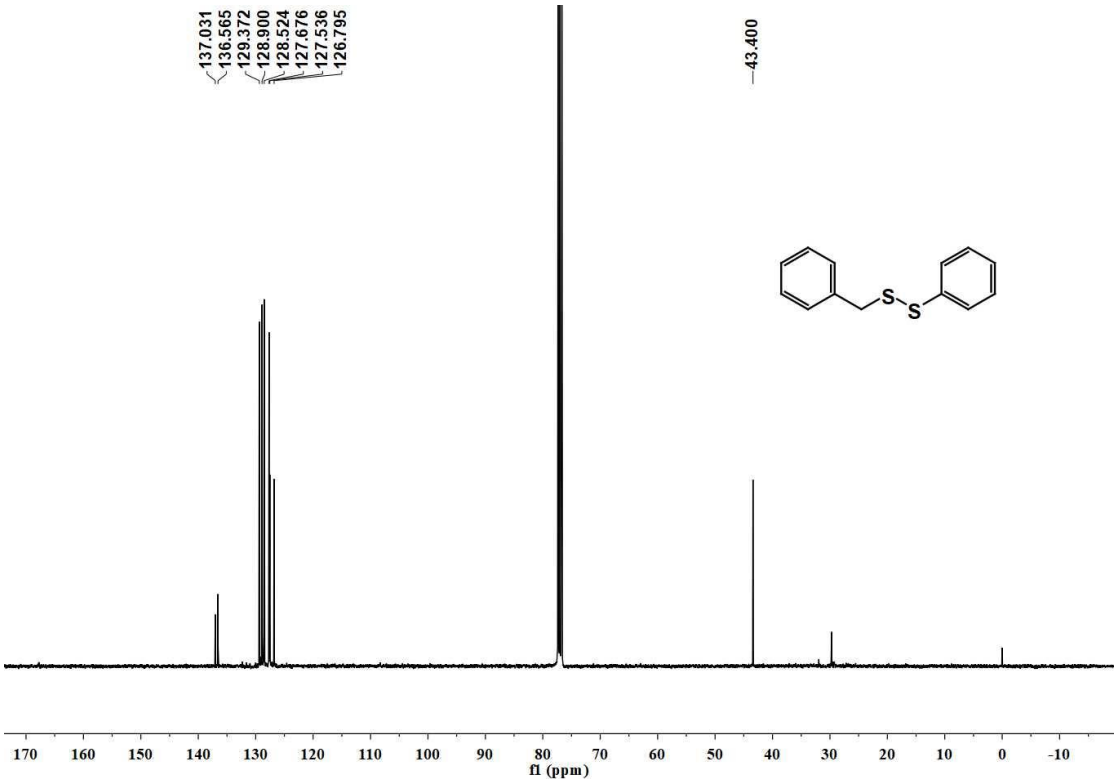
^{1}H and ^{13}C-NMR spectra of **3m**.



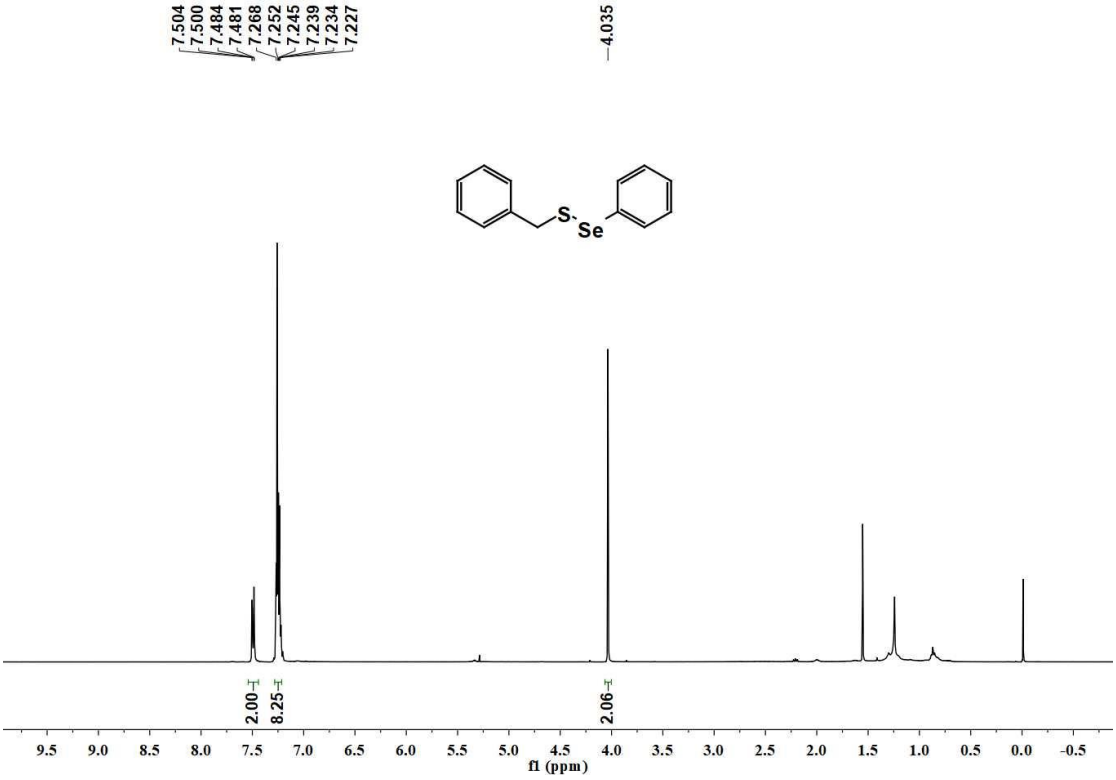


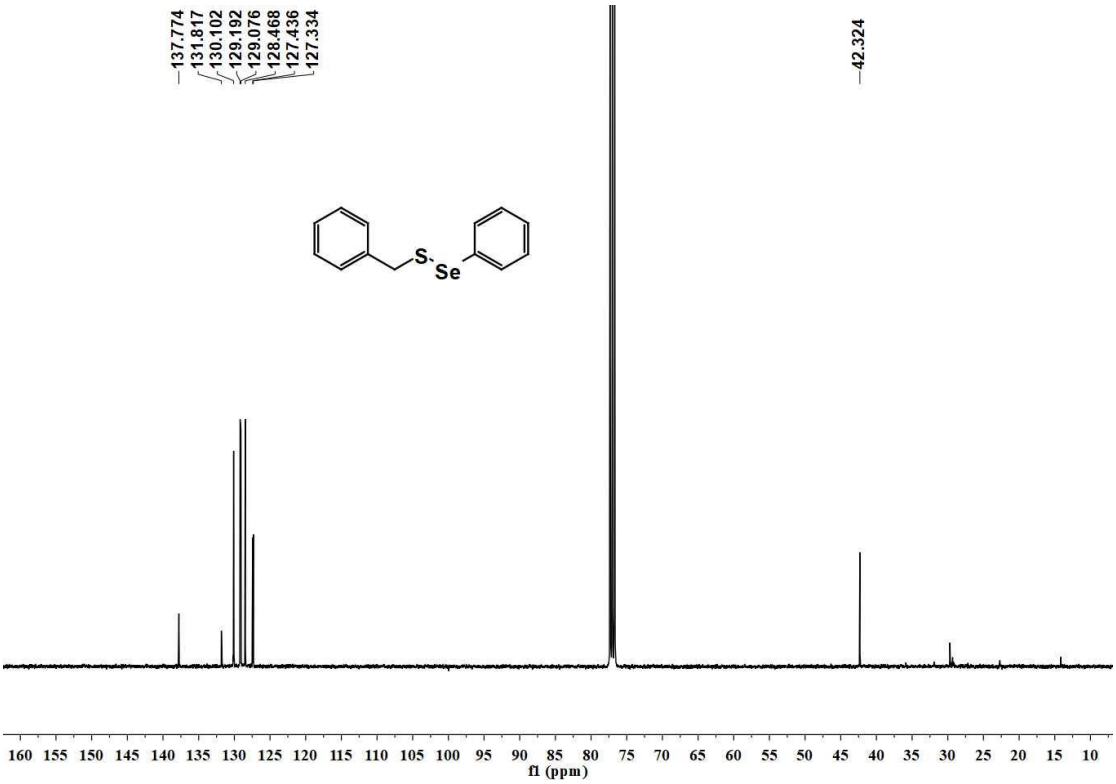
^{1}H and ^{13}C-NMR spectra of **3n**.



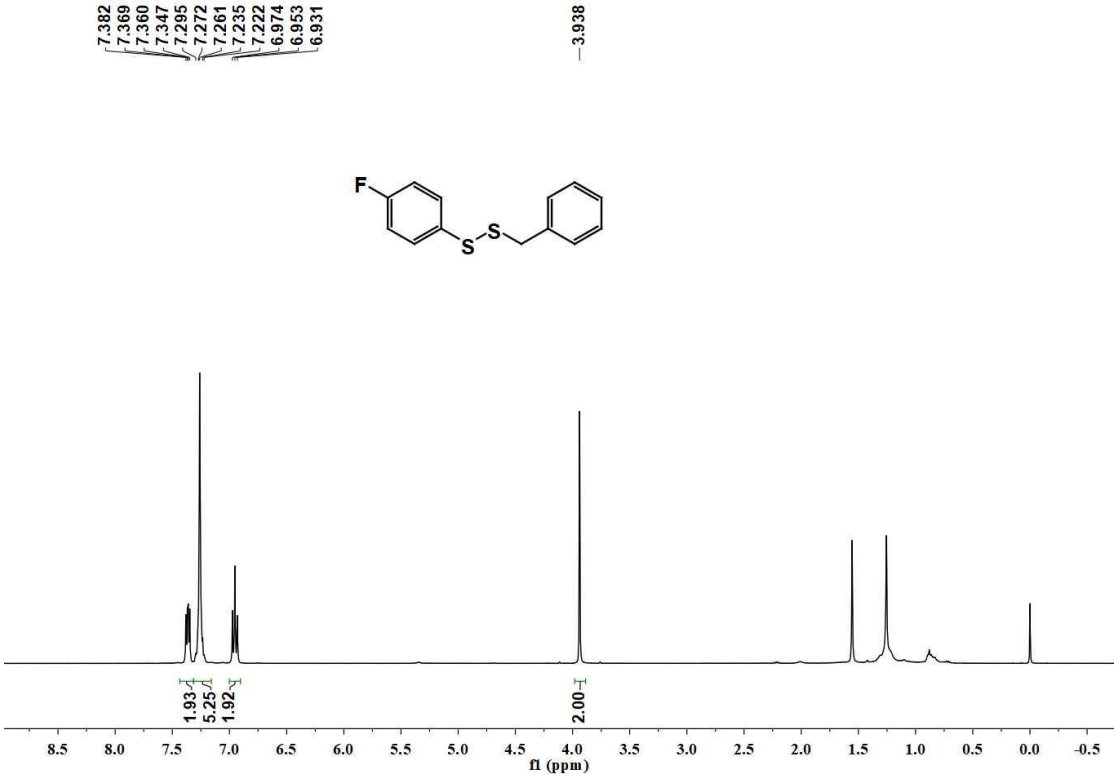


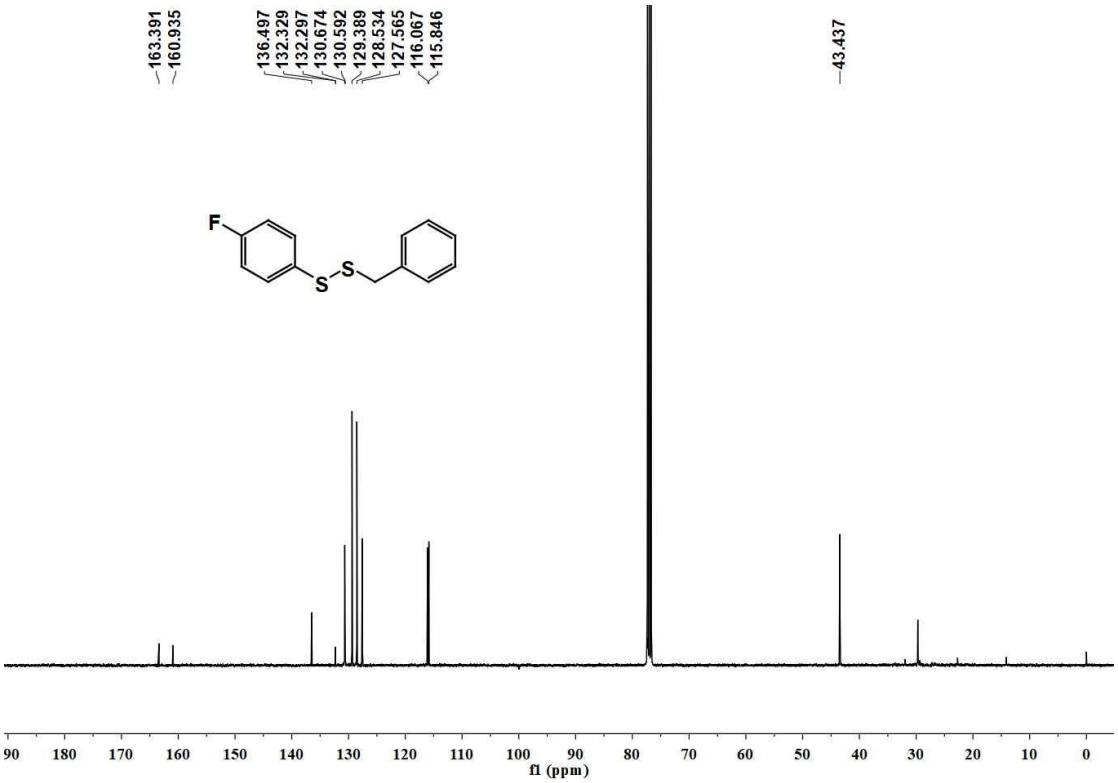
^{1}H and ^{13}C-NMR spectra of **3o**.



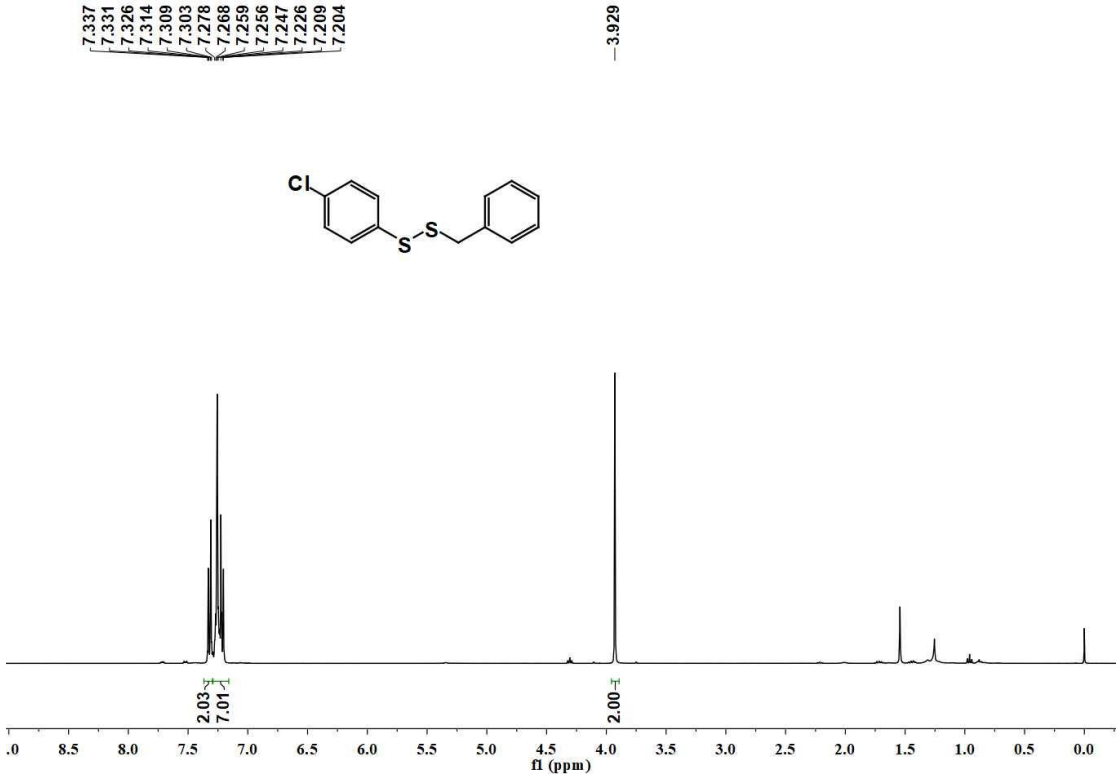


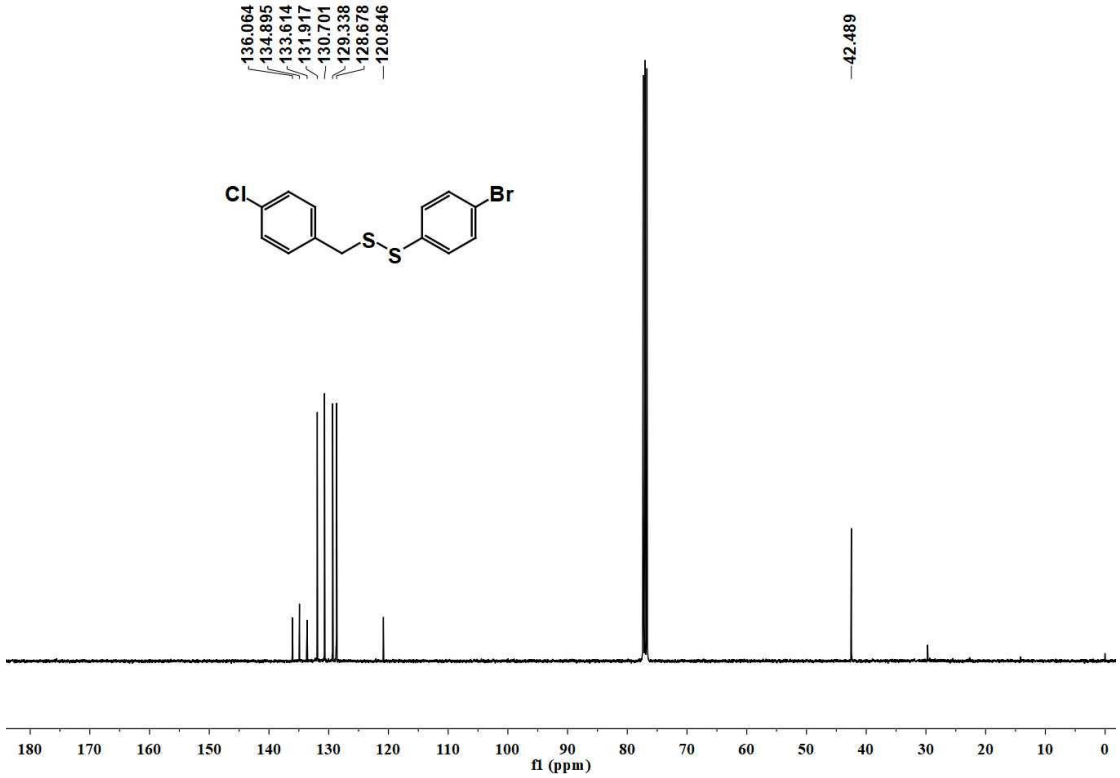
^{1}H and ^{13}C-NMR spectra of **3p**.



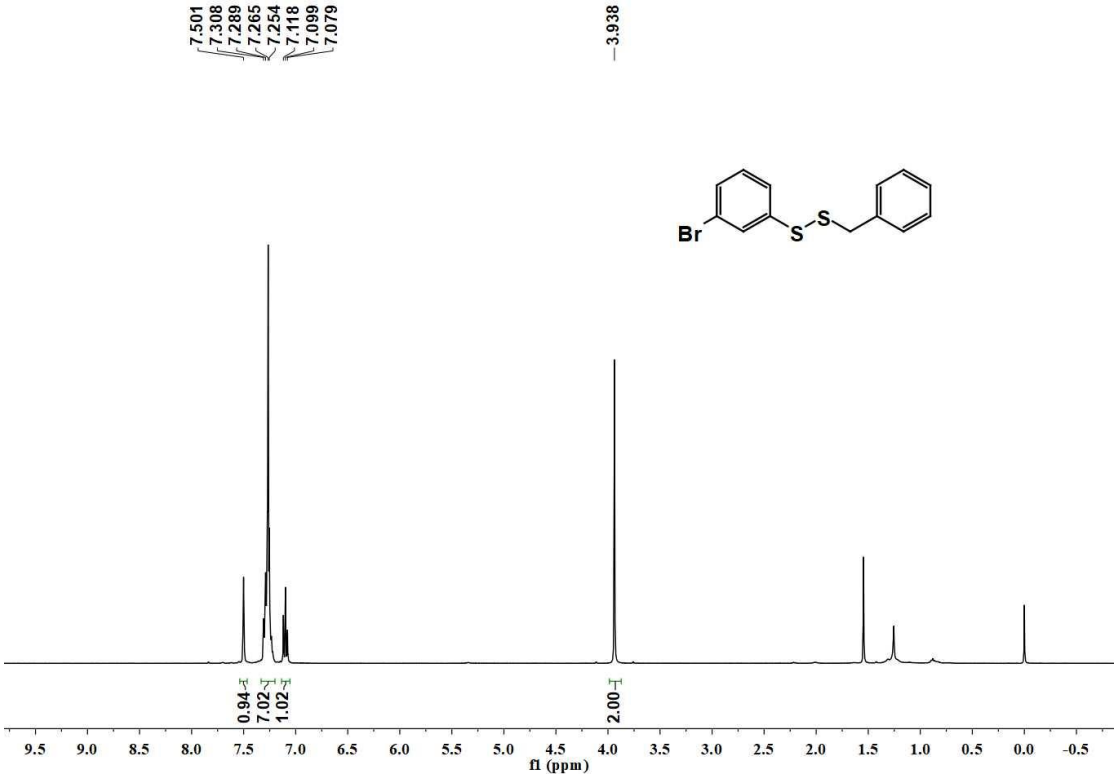


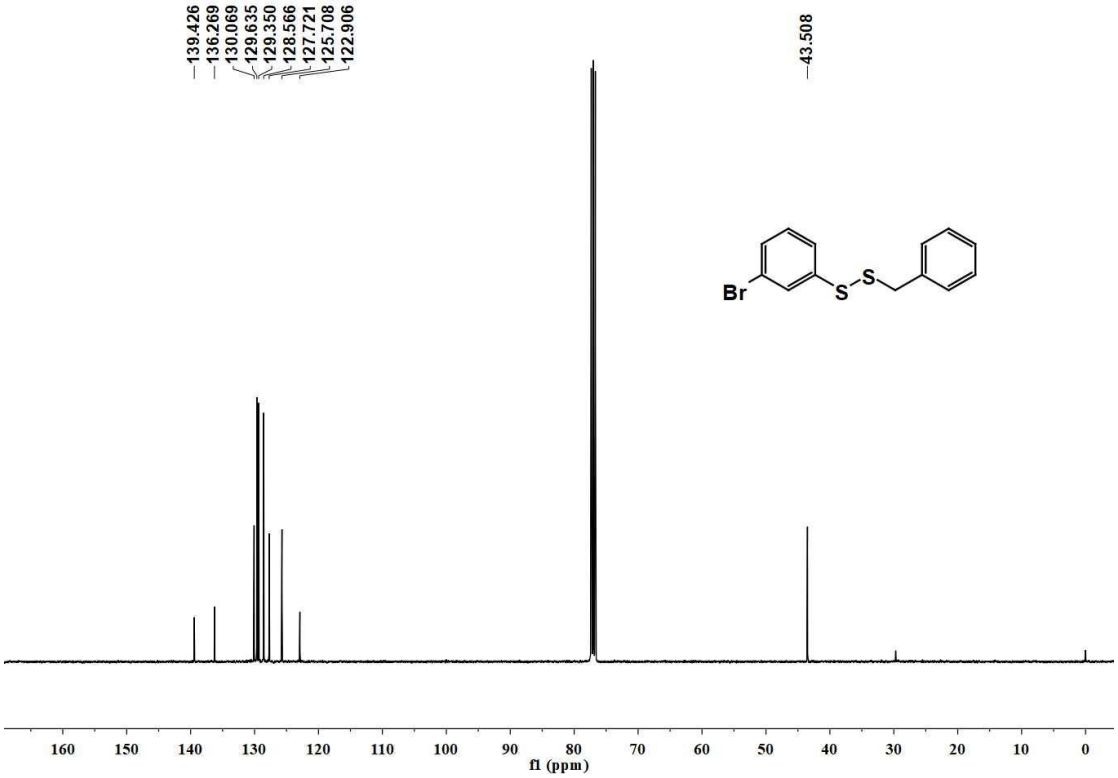
^{1}H and ^{13}C-NMR spectra of **3q**.



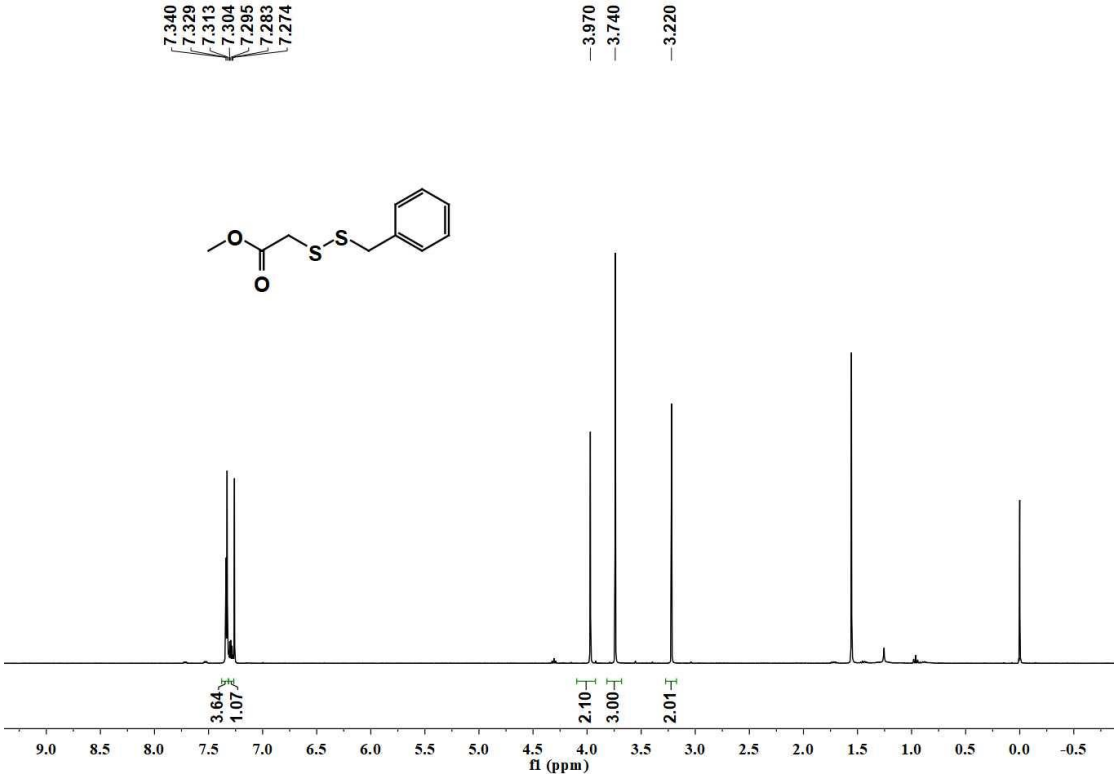


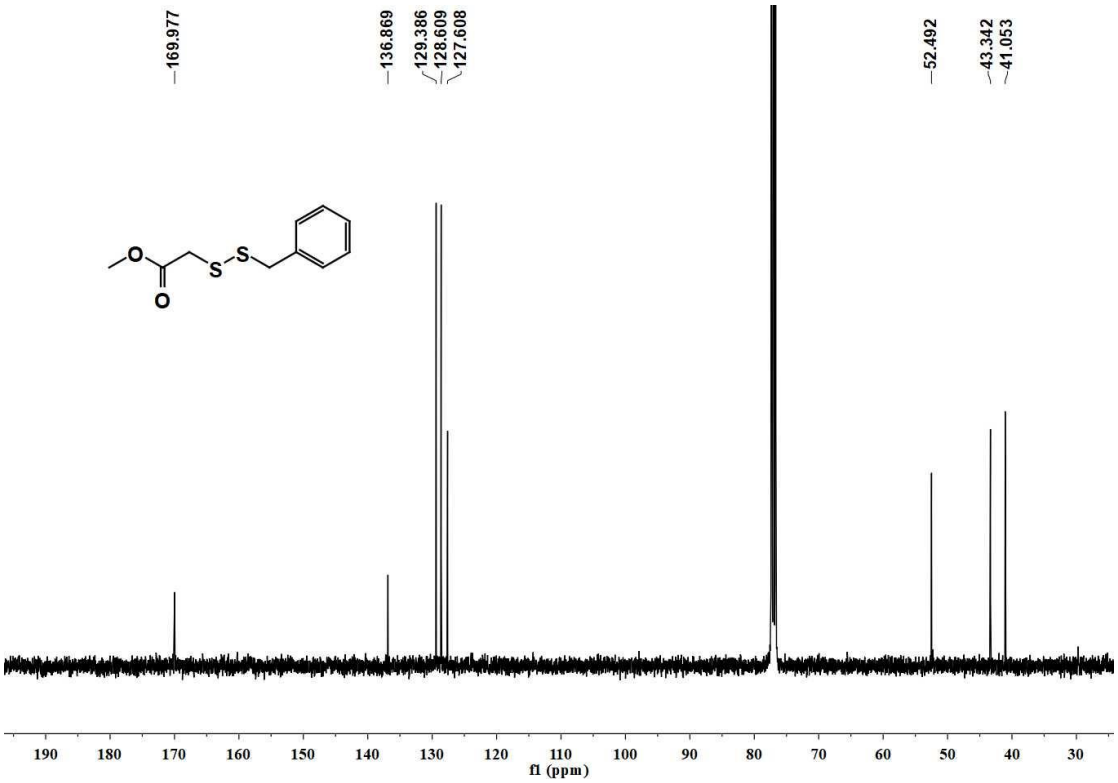
^{1}H and ^{13}C-NMR spectra of **3r**.



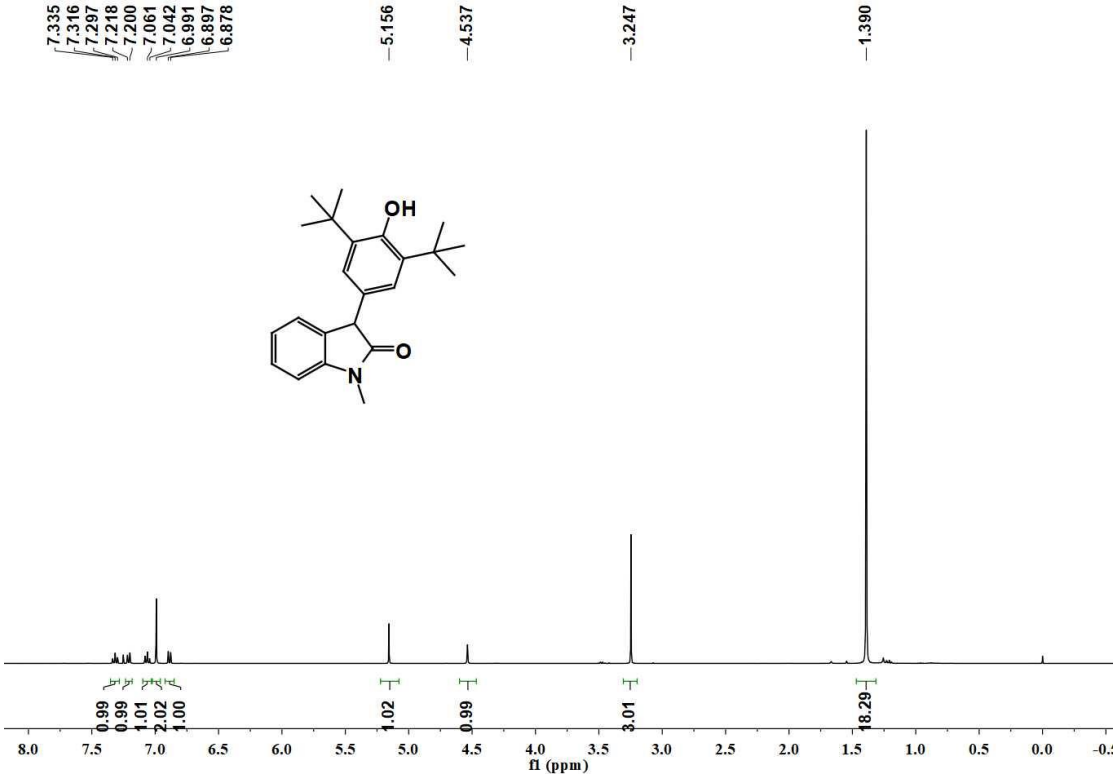


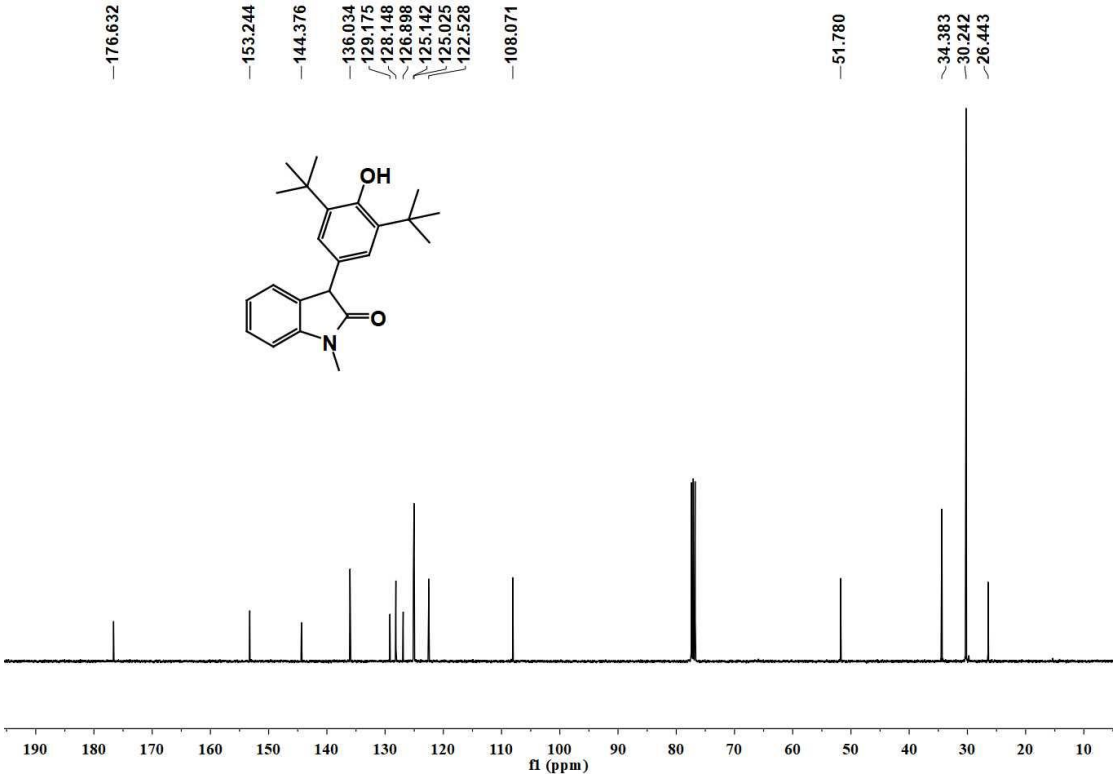
^{1}H and ^{13}C-NMR spectra of **3s**.



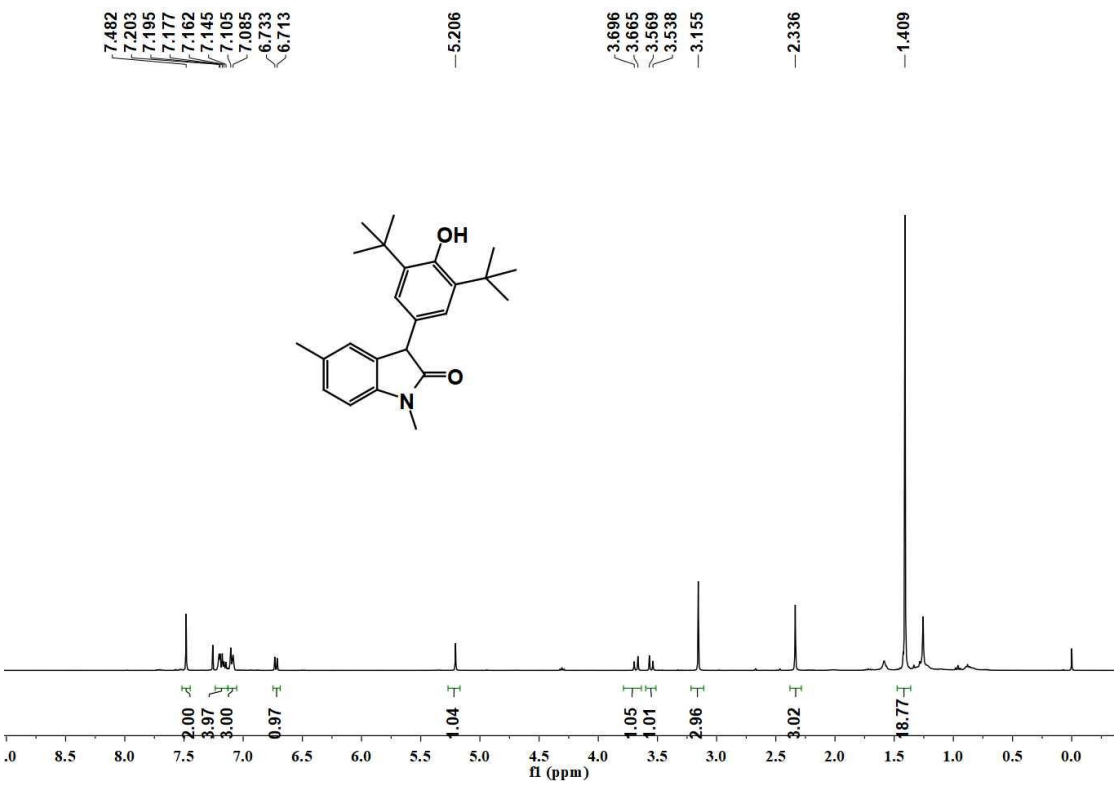


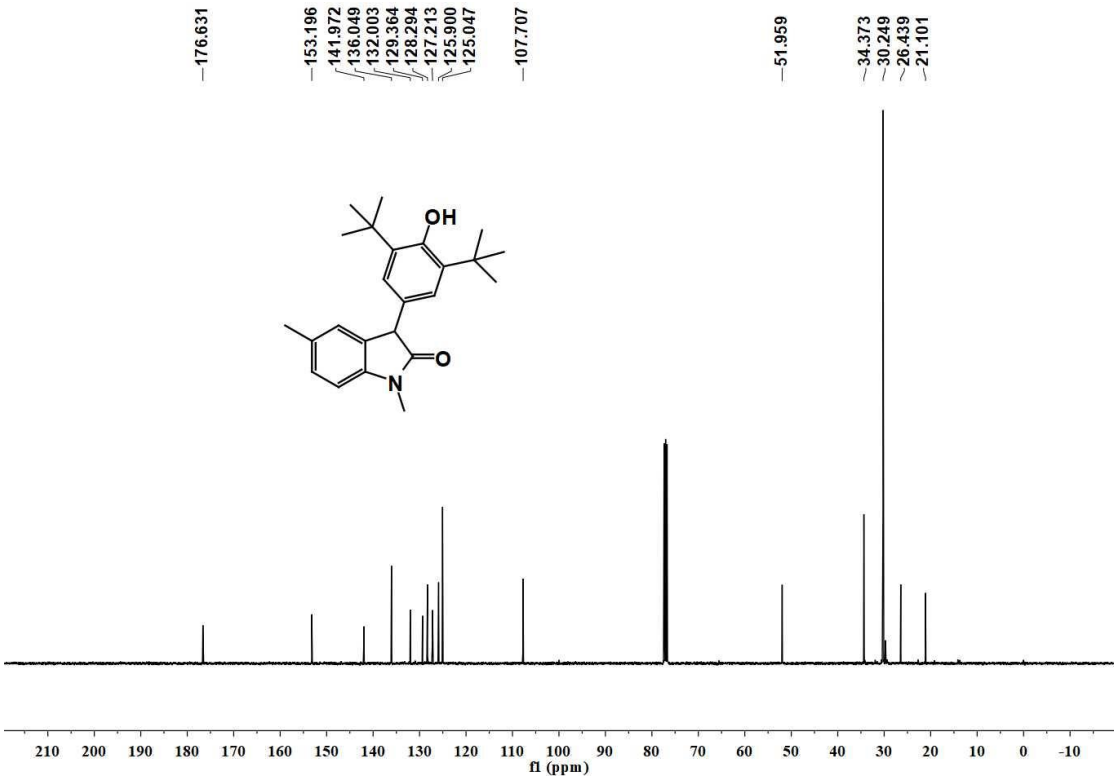
^{1}H and ^{13}C-NMR spectra of **4a**.



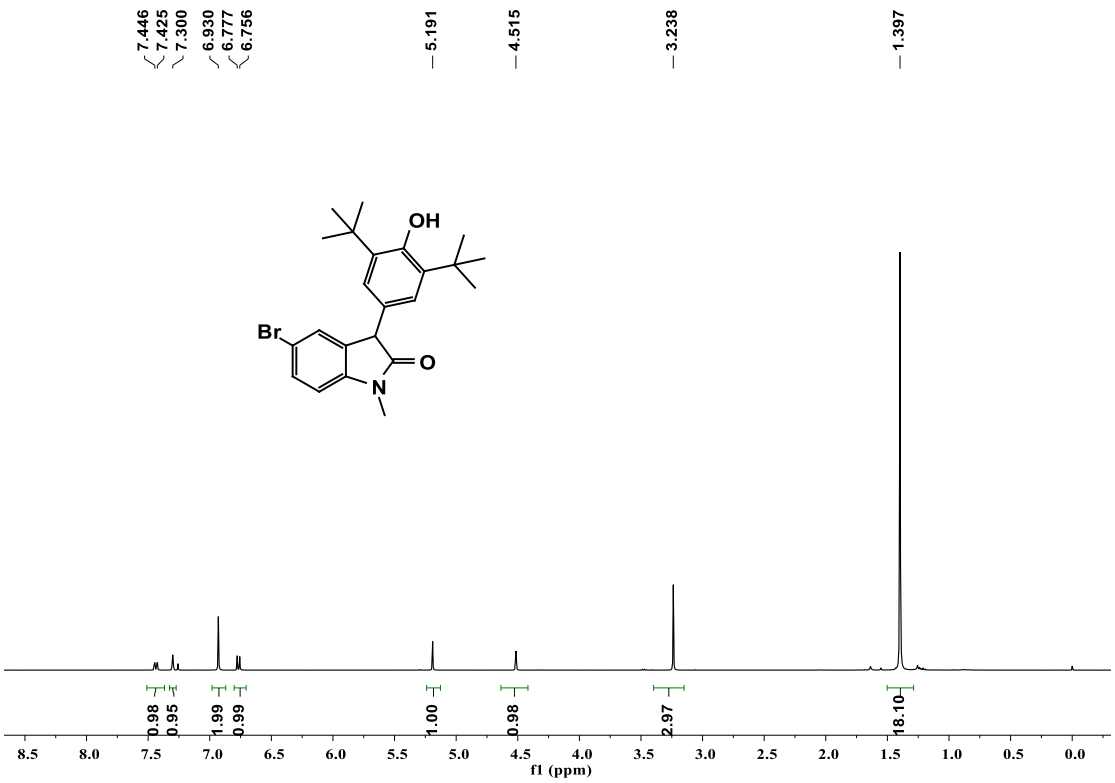


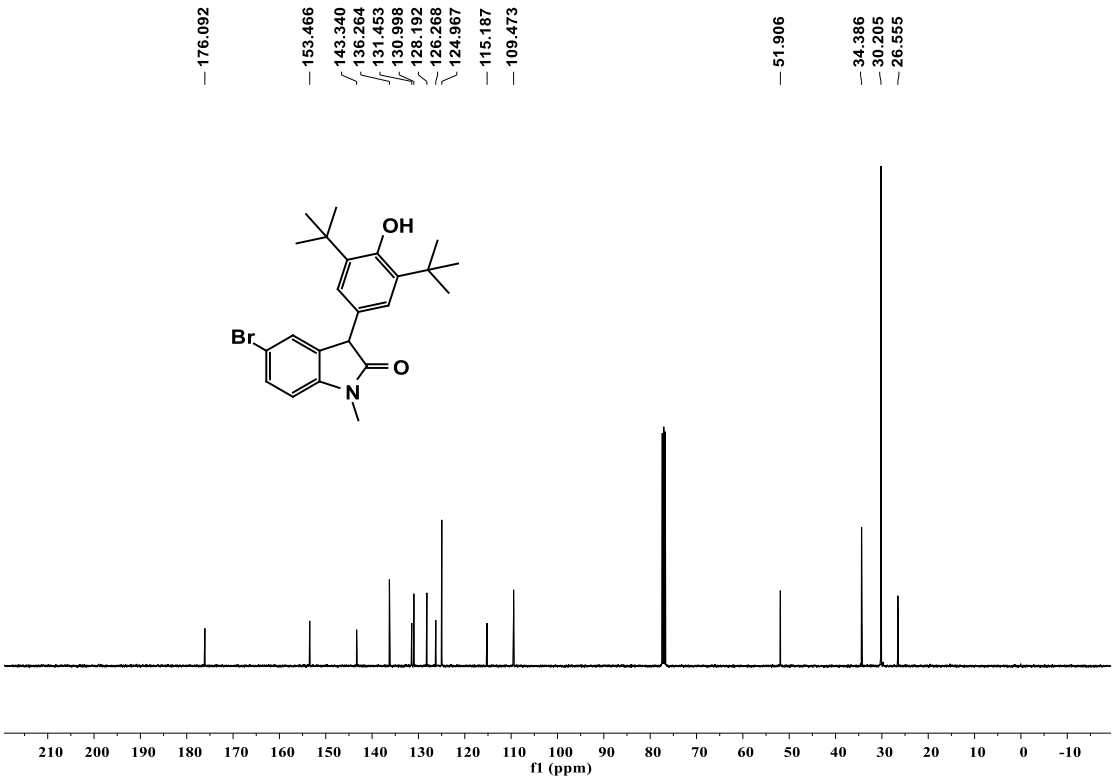
^{1}H and ^{13}C-NMR spectra of **4b**.



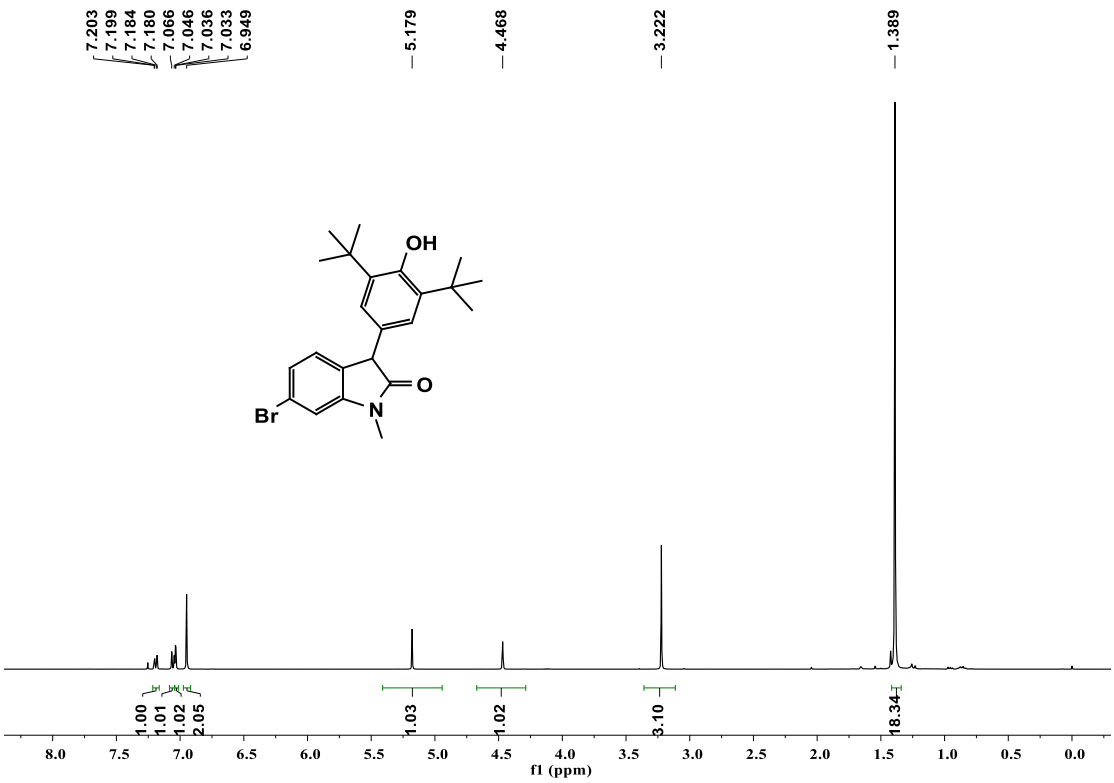


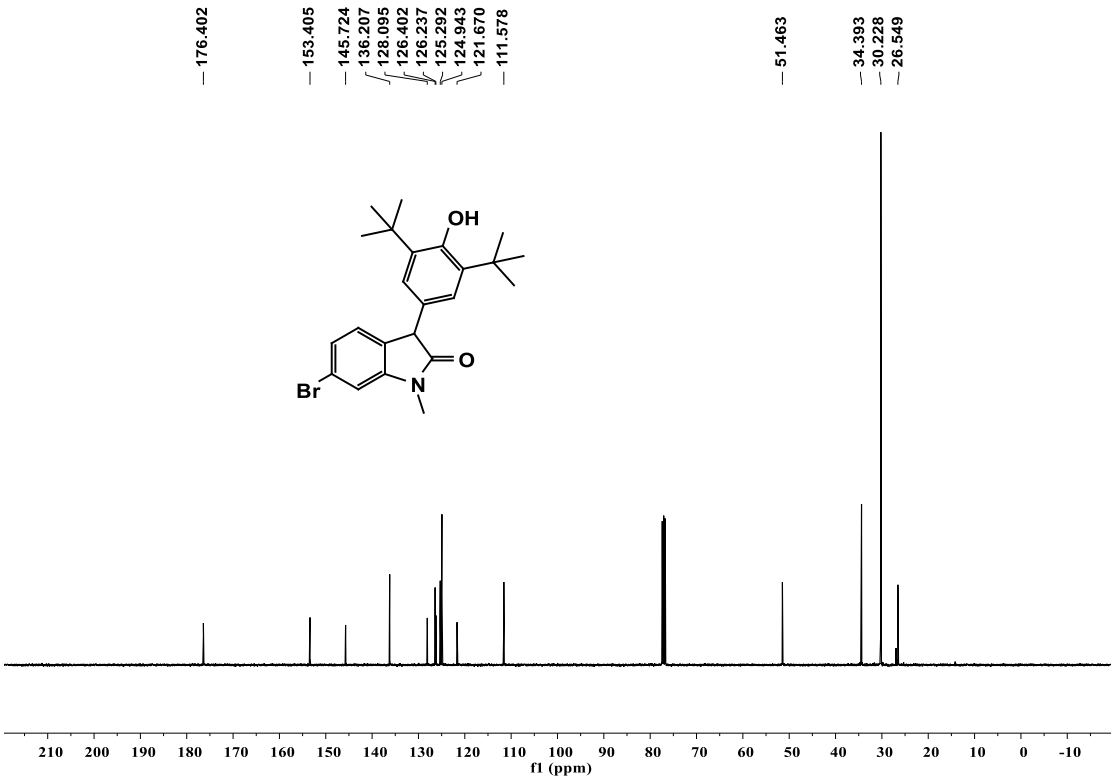
^{1}H and ^{13}C-NMR spectra of **4c**.



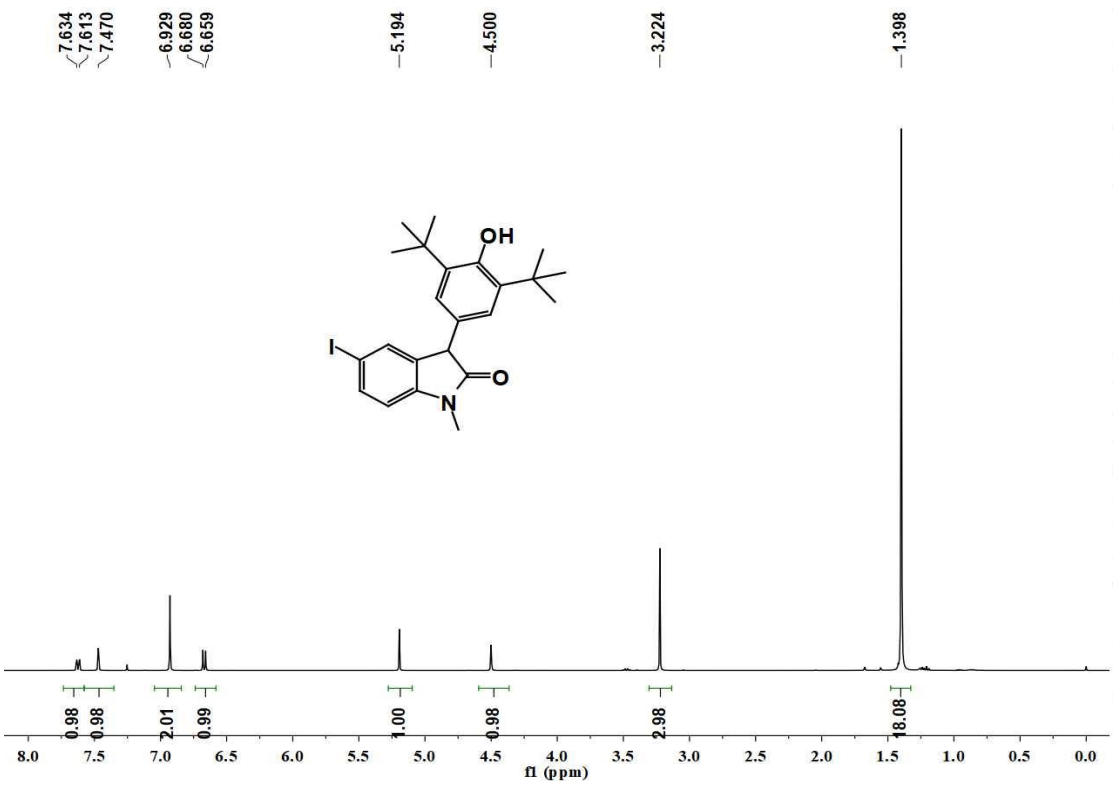


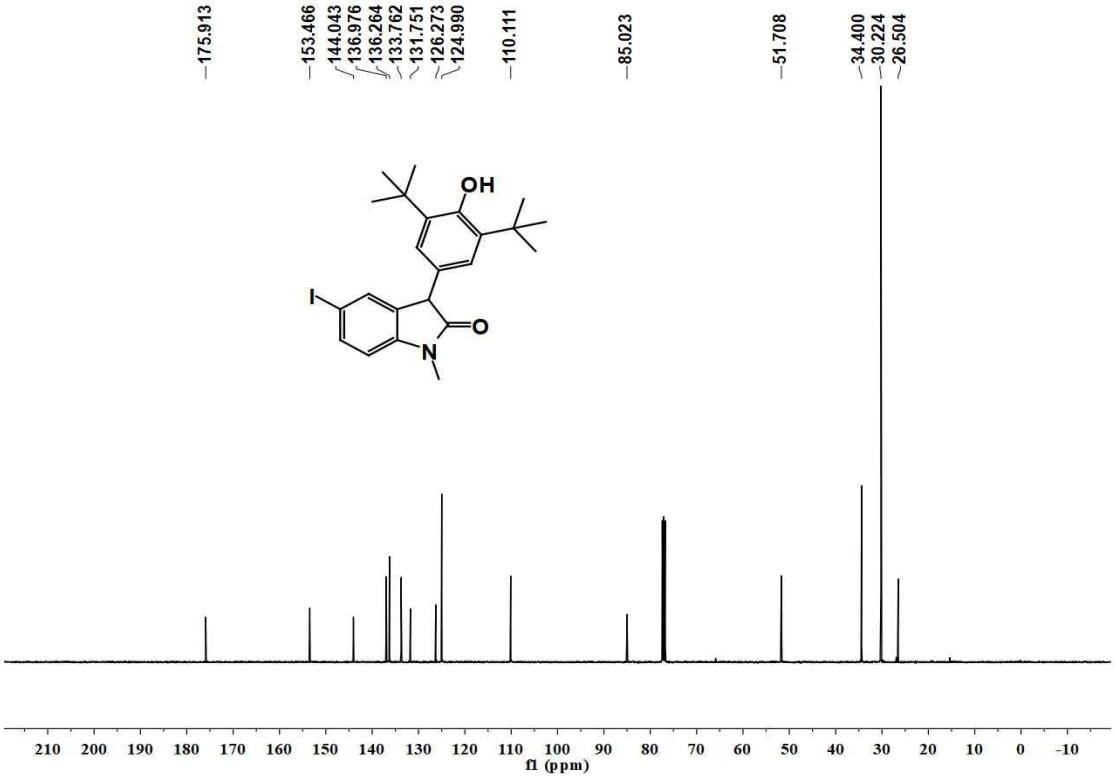
^{1}H and ^{13}C-NMR spectra of **4d**.



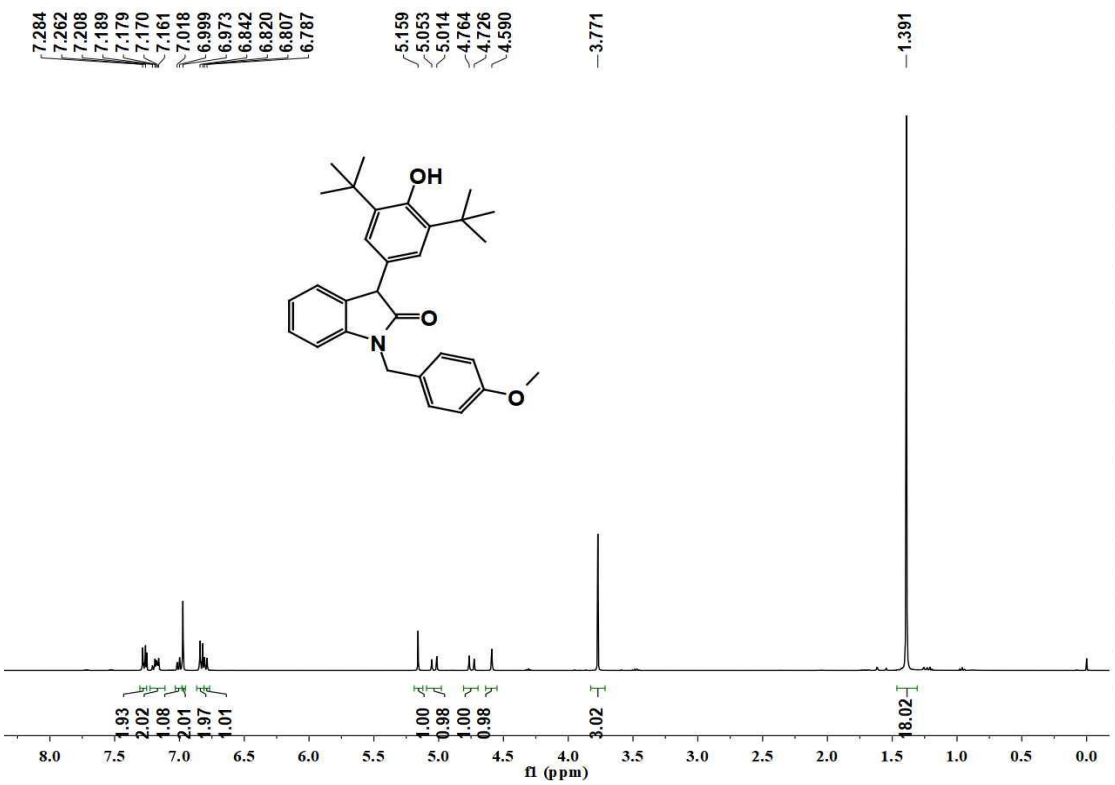


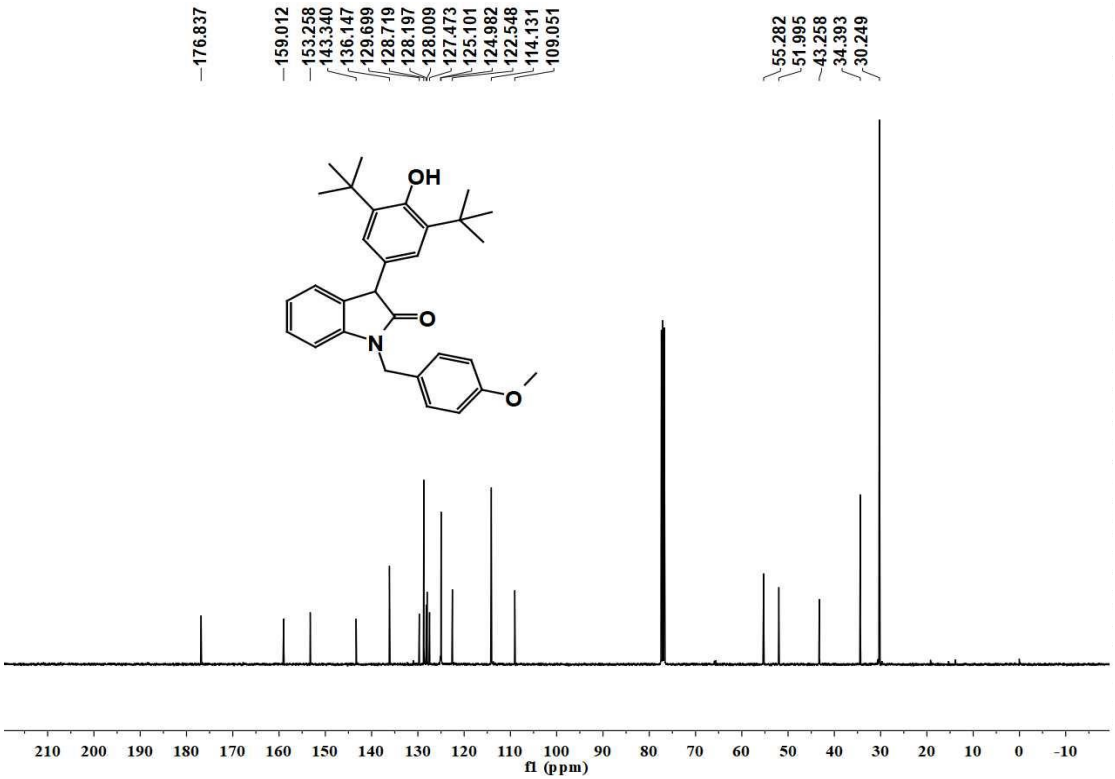
^{1}H and ^{13}C-NMR spectra of **4e**.





^{1}H and ^{13}C-NMR spectra of **4f**.

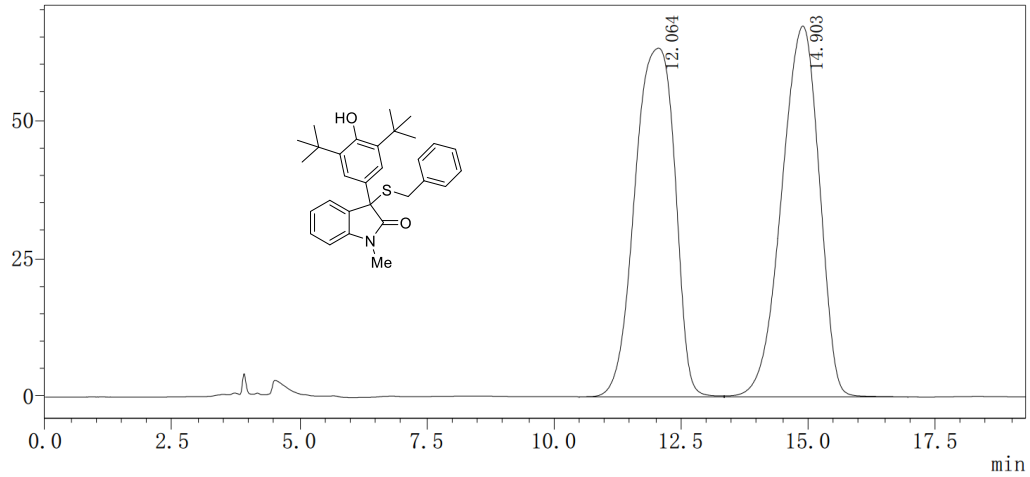




HPLC Spectra of Products 1’

HPLC spectra of product **1’a**.

<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	12.064	50.048	3464968	63088	
2	14.903	49.952	3458371	67084	

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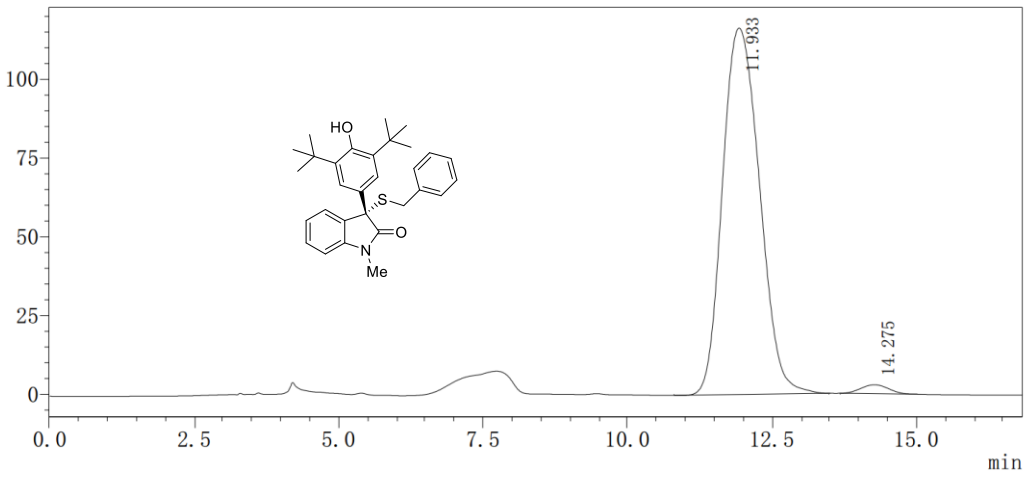
mV

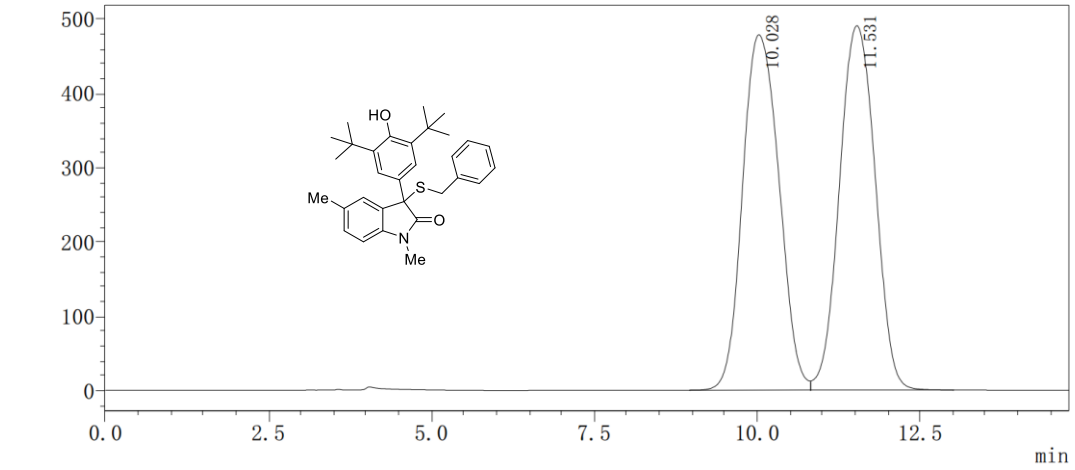


<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	11.933	98.186	5183590	116223	
2	14.275	1.814	95790	2838	

HPLC spectra of product **1'b**.

<Chromatogram>



<Peak Table>

检测器A 254nm

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1	10.028	49.843	18592491	477700	
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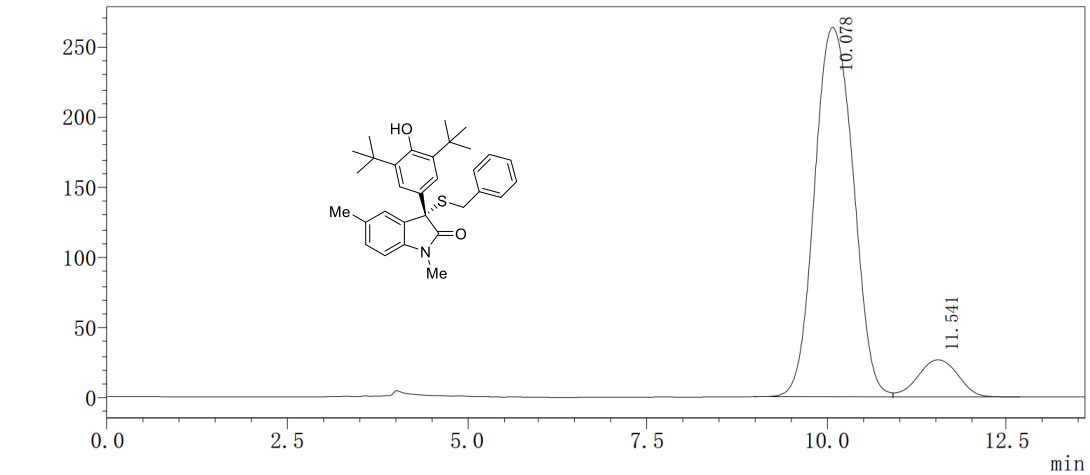


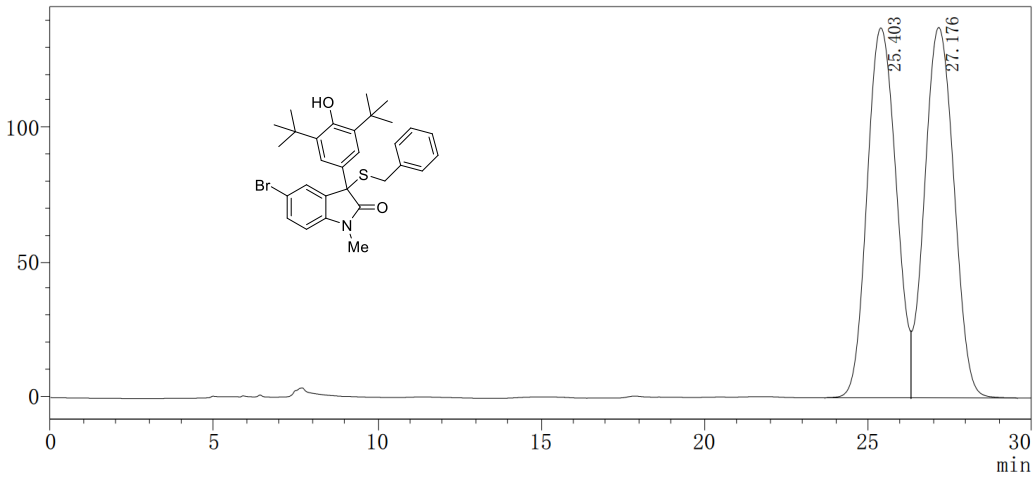
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	10.078	90.582	9855126	263051	
2	11.541	9.418	1024650	26411	

HPLC spectra of product **1'c**.

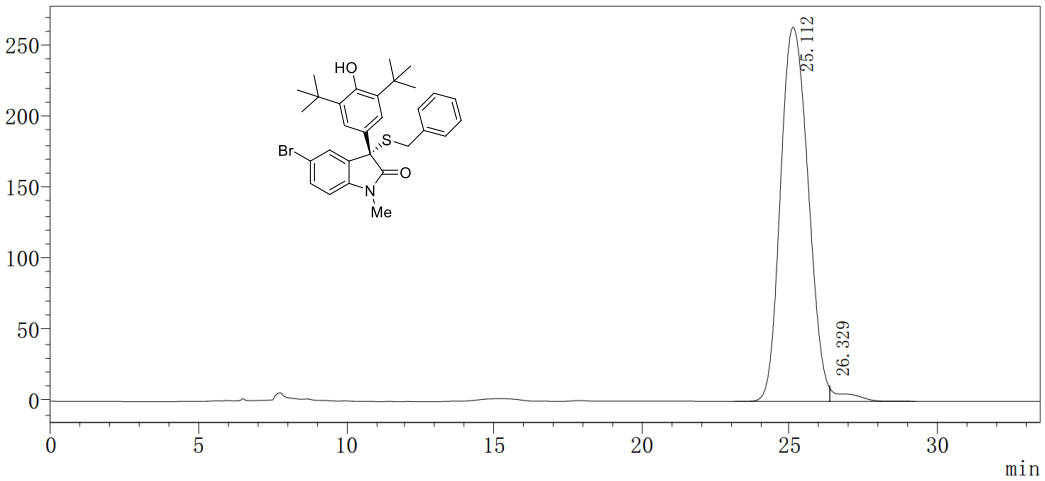
<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	25.403	49.640	8505725	137415	
2	27.176	50.360	8629224	137617	

<Chromatogram>
mV

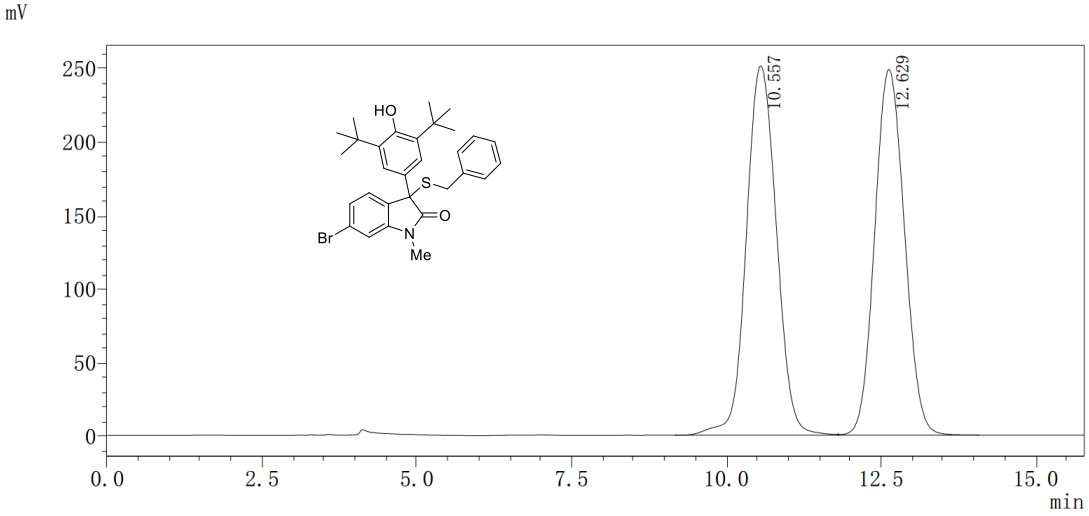


<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	25.112	97.730	17134897	263202	
2	26.329	2.270	398078	10308	

HPLC spectra of product **1'd**.

<Chromatogram>

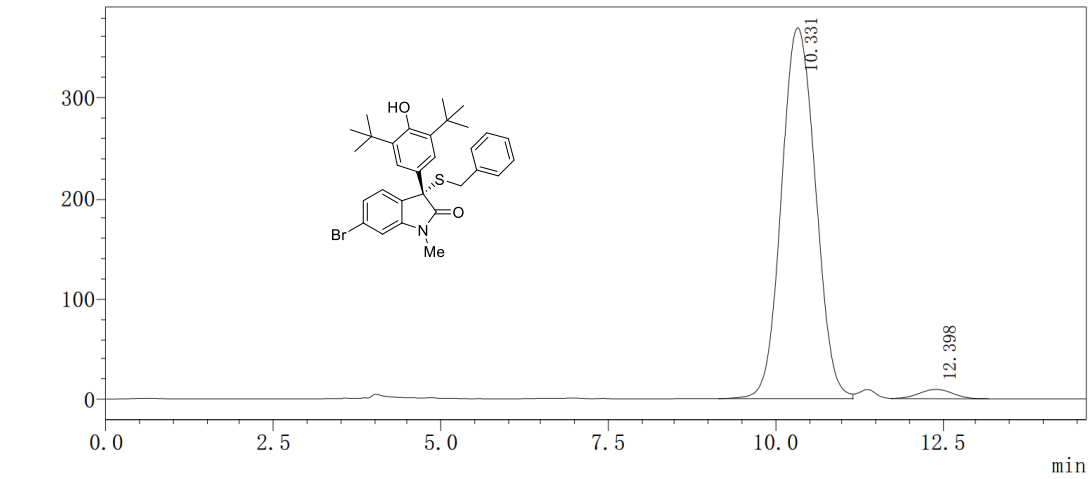


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	10.557	50.632	8521664	251074	
2	12.629	49.368	8309008	248590	

<Chromatogram>



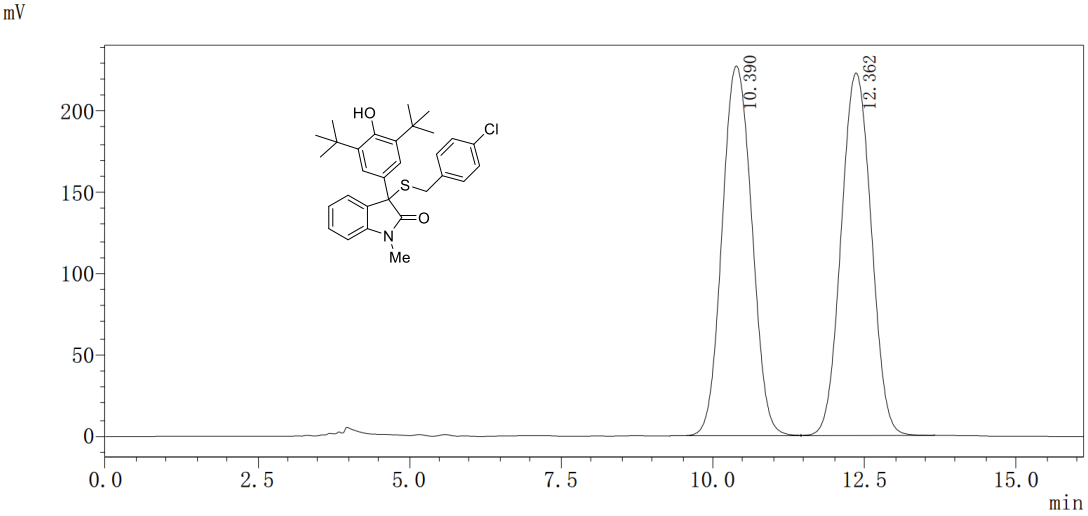
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	10.331	97.569	13080311	368744	
2	12.398	2.431	325858	9255	

HPLC spectra of product **1'e**.

<Chromatogram>

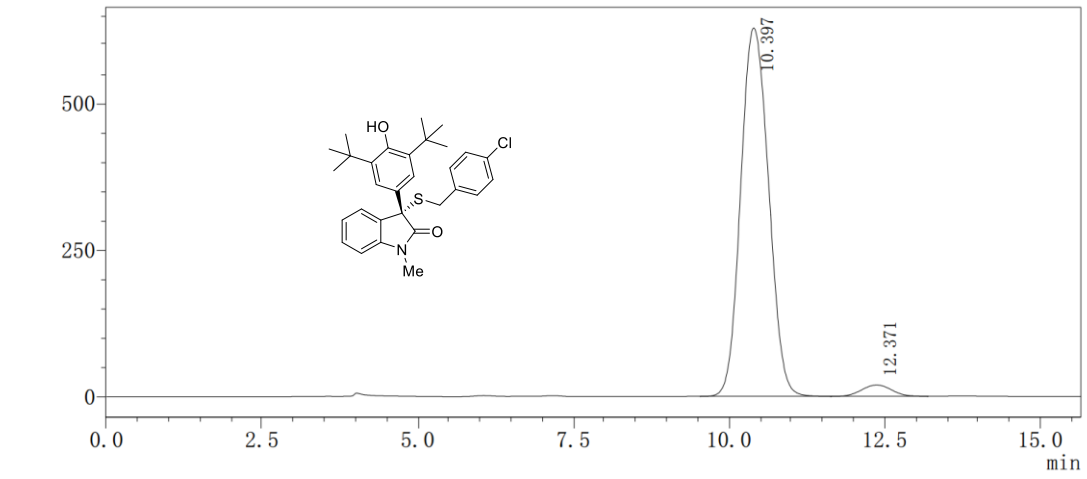


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	10.390	50.166	7764105	227768	
2	12.362	49.834	7712689	223289	

<Chromatogram>



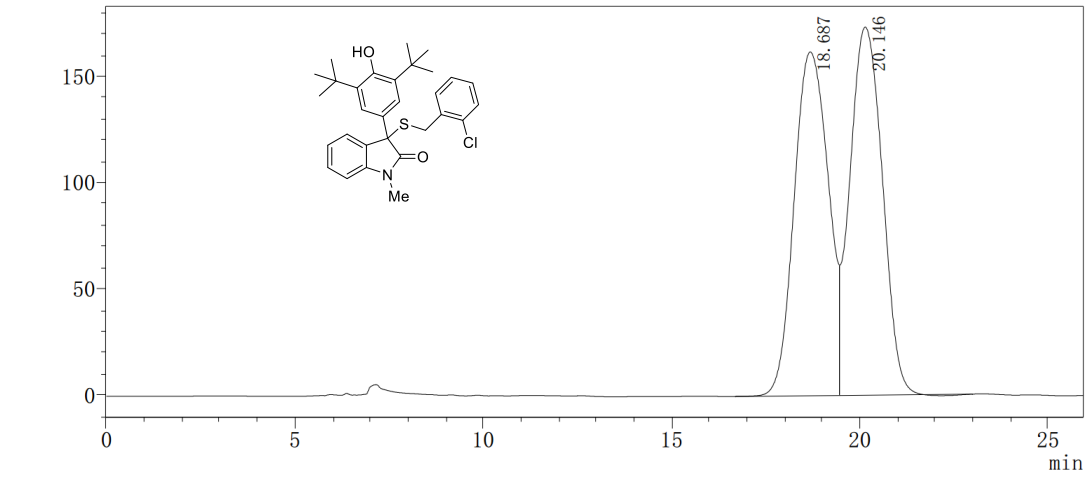
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	10.397	96.802	19583670	627662	
2	12.371	3.198	646896	19284	

HPLC spectra of product **1'f**.

<Chromatogram>

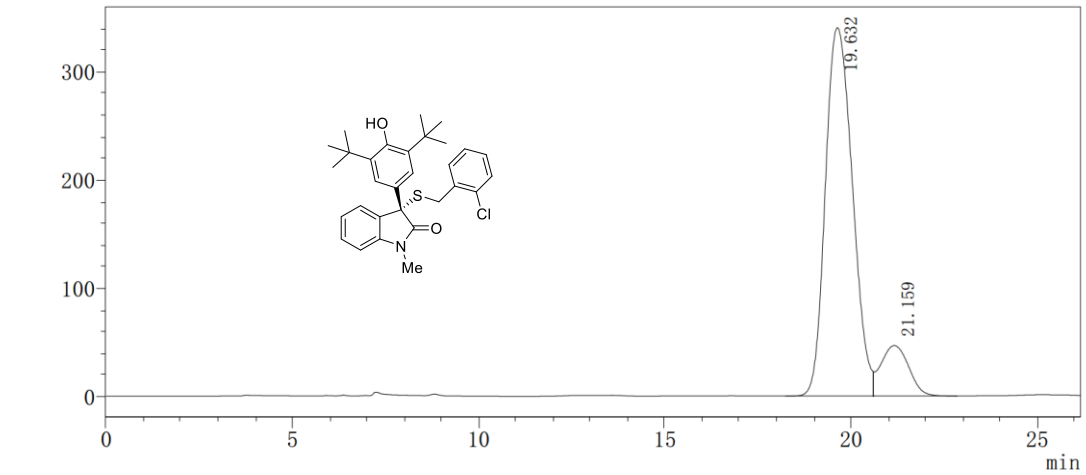


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	18.687	49.604	10208960	161737	
2	20.146	50.396	10372011	173155	

<Chromatogram>



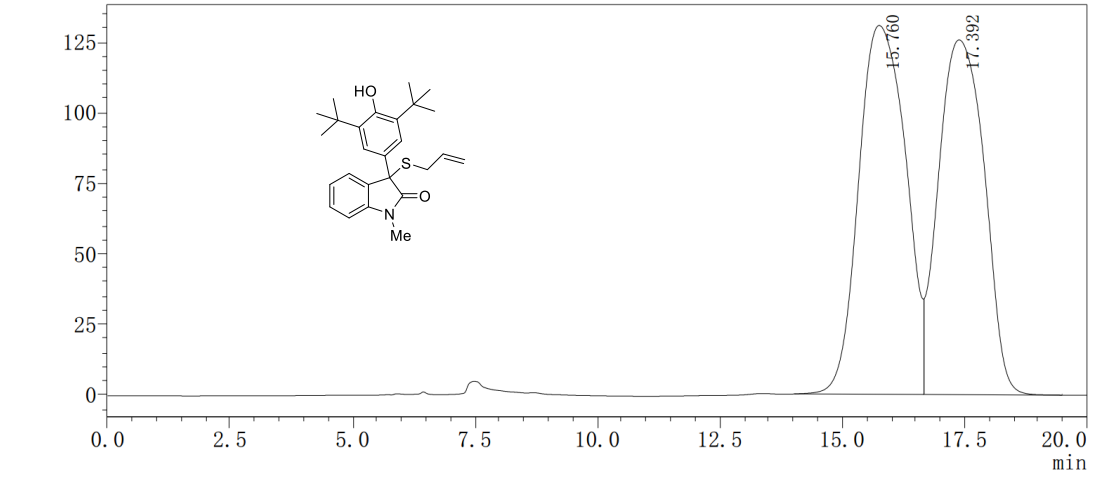
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	19.632	87.781	17198619	339817	
2	21.159	12.219	2394136	46517	

HPLC spectra of product **1'g**.

<Chromatogram>

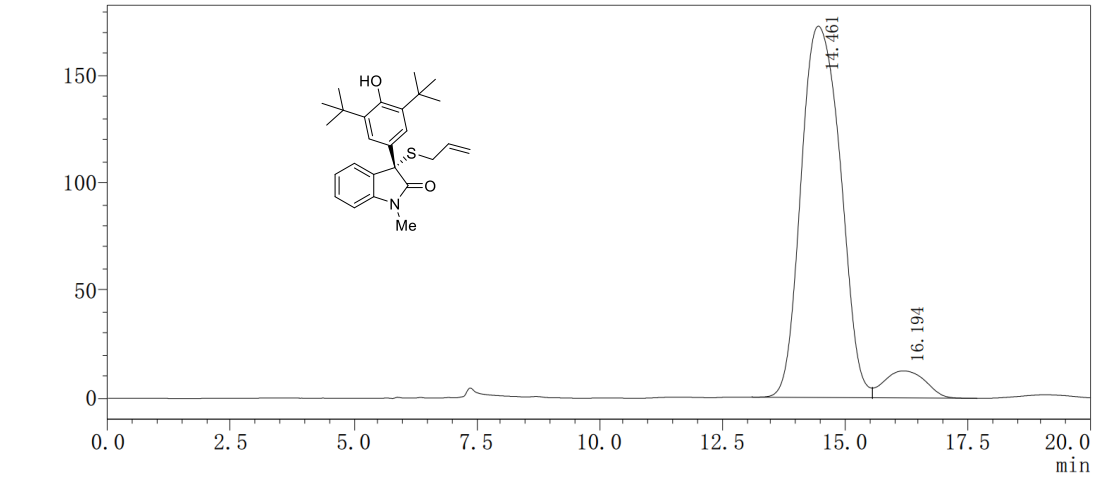


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	15.760	51.430	8726258	130673	
2	17.392	48.570	8240949	125684	

<Chromatogram>



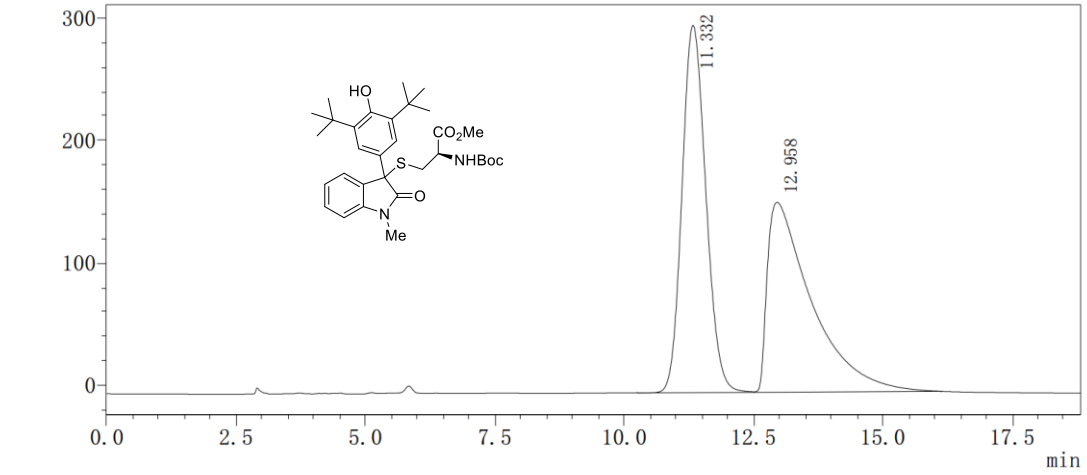
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	14.461	92.942	9665808	172803	
2	16.194	7.058	734047	12594	

HPLC spectra of product **1'h**.

<Chromatogram>

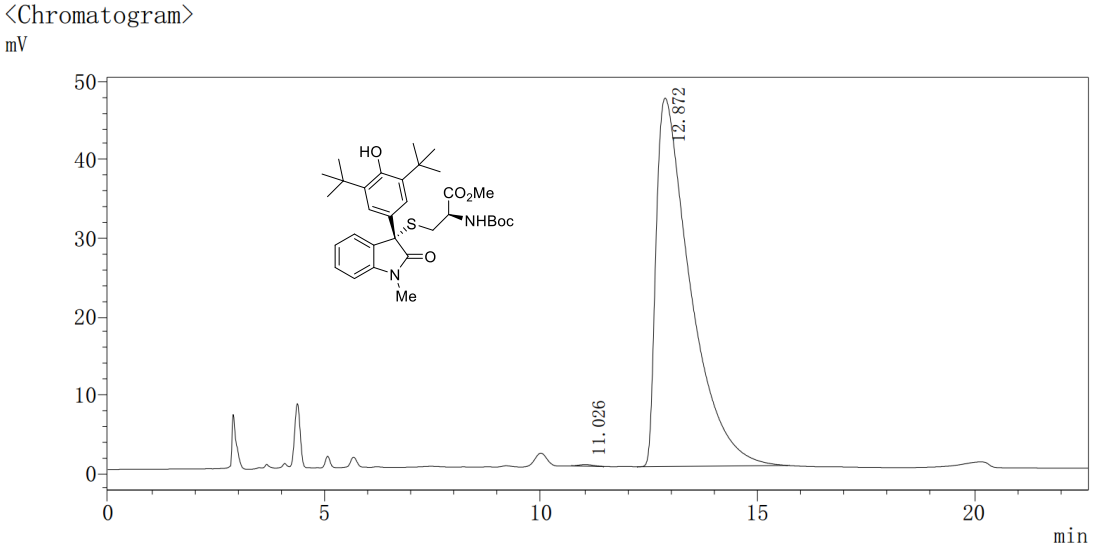


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	11.332	50.968	9635484	300336	
2	12.958	49.032	9269553	155336	

<Chromatogram>



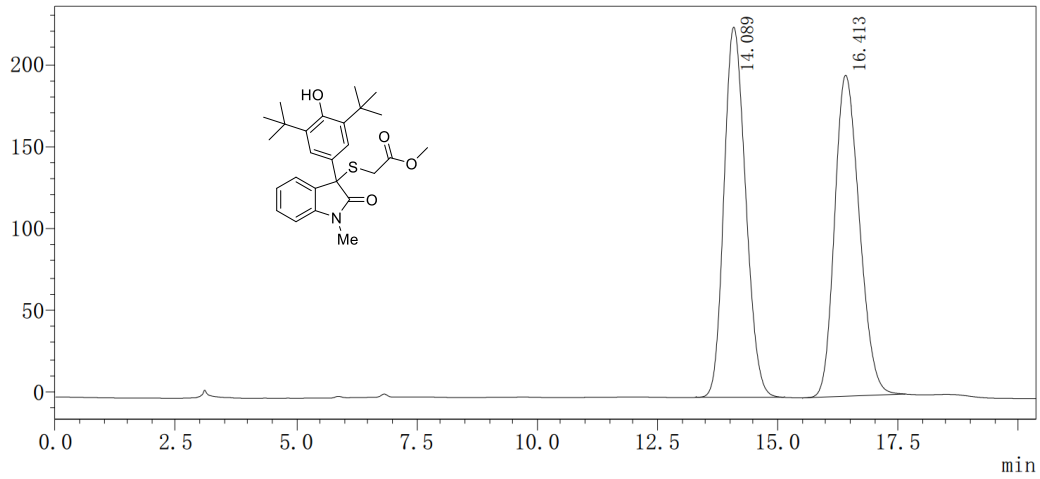
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	11.026	0.170	4410	189	
2	12.872	99.830	2587960	47018	

HPLC spectra of product **1'i**.

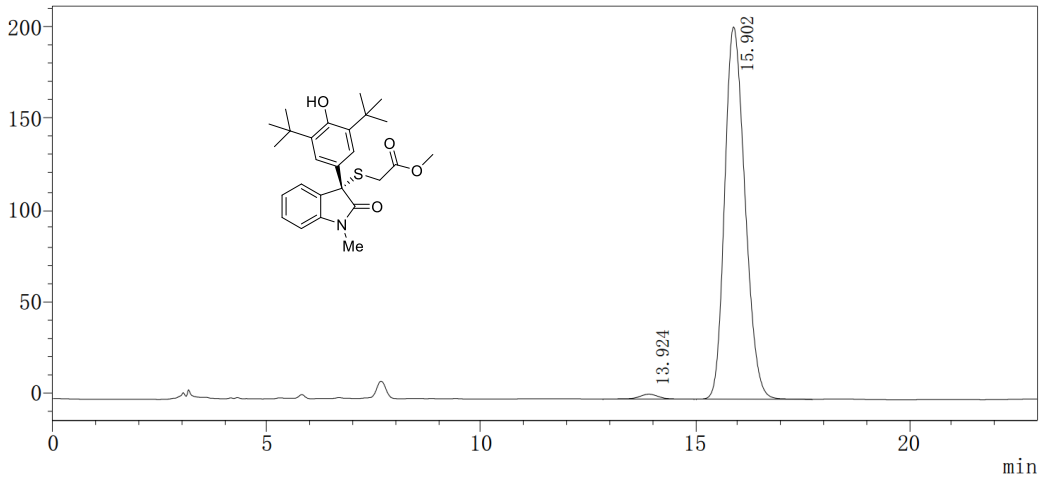
<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	14.089	50.193	7060497	225648	
2	16.413	49.807	7006311	195651	

<Chromatogram>
mV

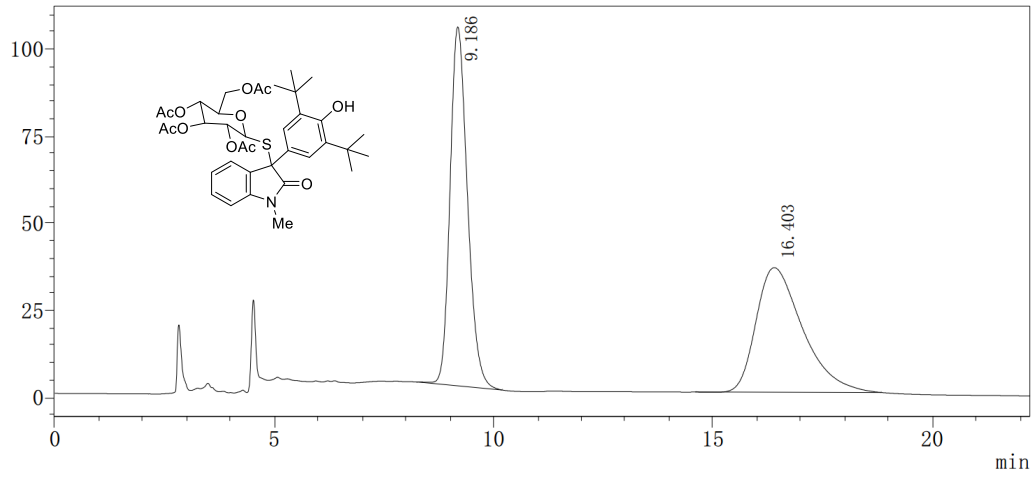


<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	13.924	1.243	84675	2695	
2	15.902	98.757	6728499	203834	

HPLC spectra of product **1'j**.

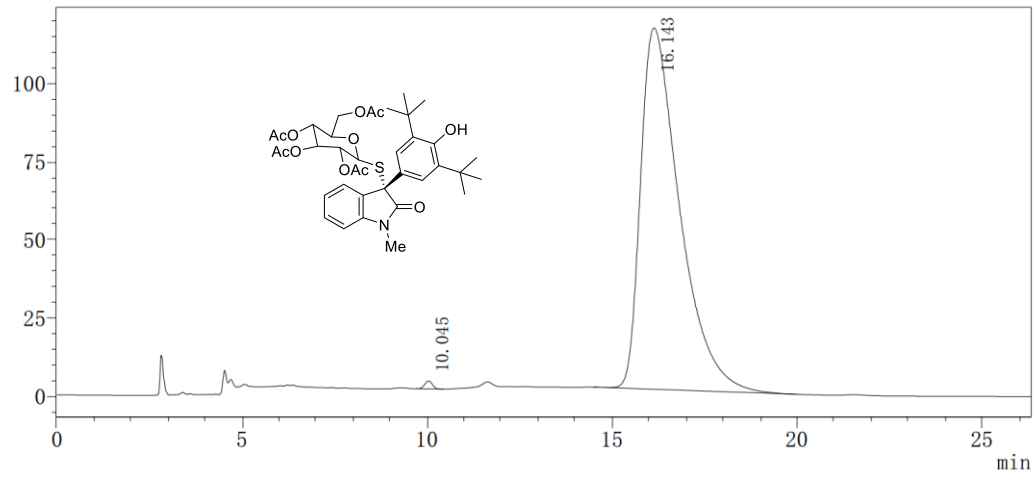
<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	9.186	51.780	2838599	103071	
2	16.403	48.220	2643434	35775	

<Chromatogram>
mV

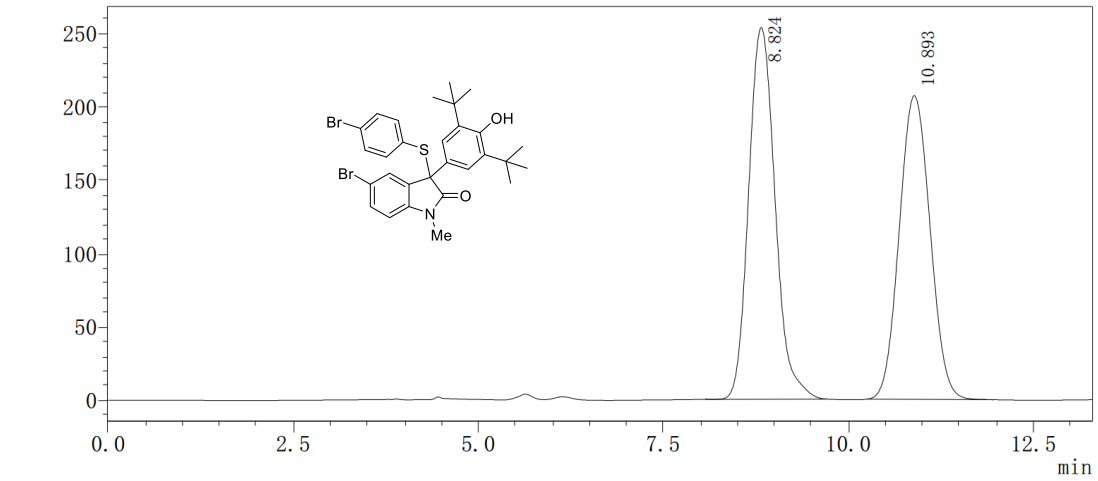


<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	10.045	0.431	36680	2561	
2	16.143	99.569	8481518	115287	

HPLC spectra of product **1'k**.

<Chromatogram>

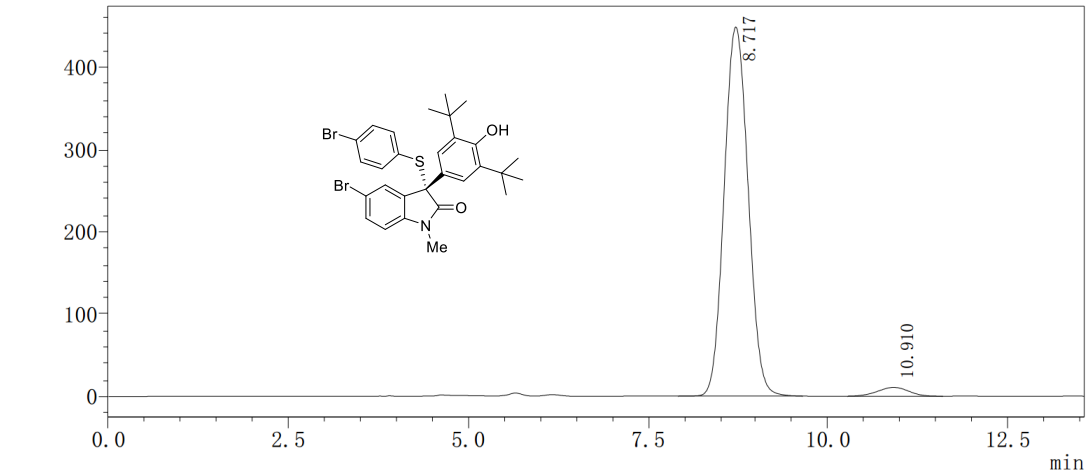


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.824	51.242	6297376	253255	
2	10.893	48.758	5992016	206924	

<Chromatogram>



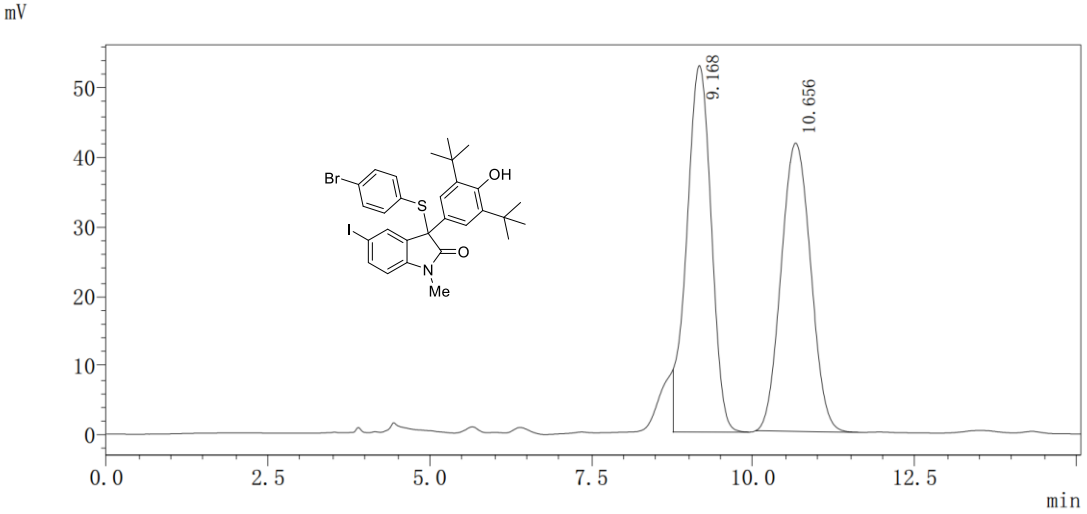
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.717	96.992	10390017	448163	
2	10.910	3.008	322272	10669	

HPLC spectra of product **1'l**.

<Chromatogram>

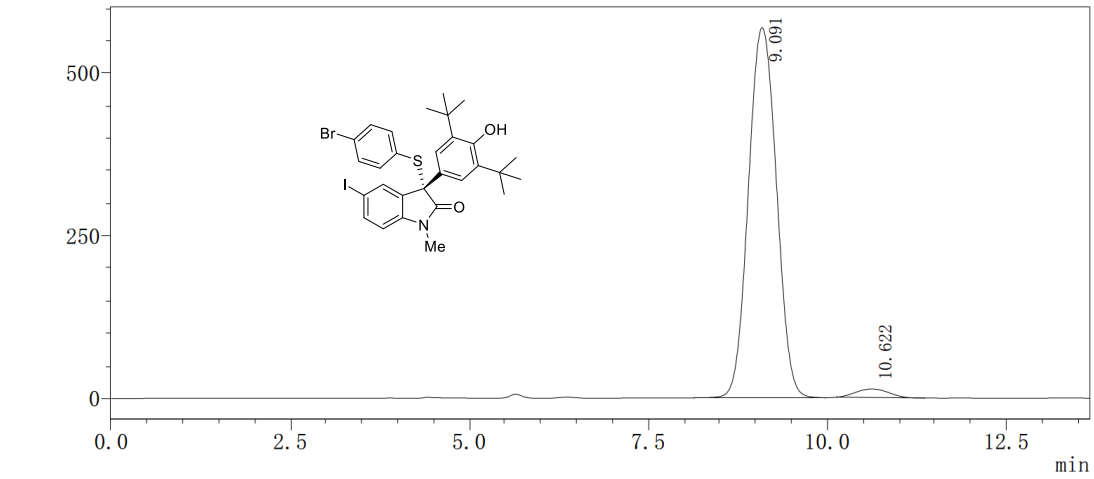


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	9.168	51.332	1394771	52833	
2	10.656	48.668	1322389	41565	

<Chromatogram>



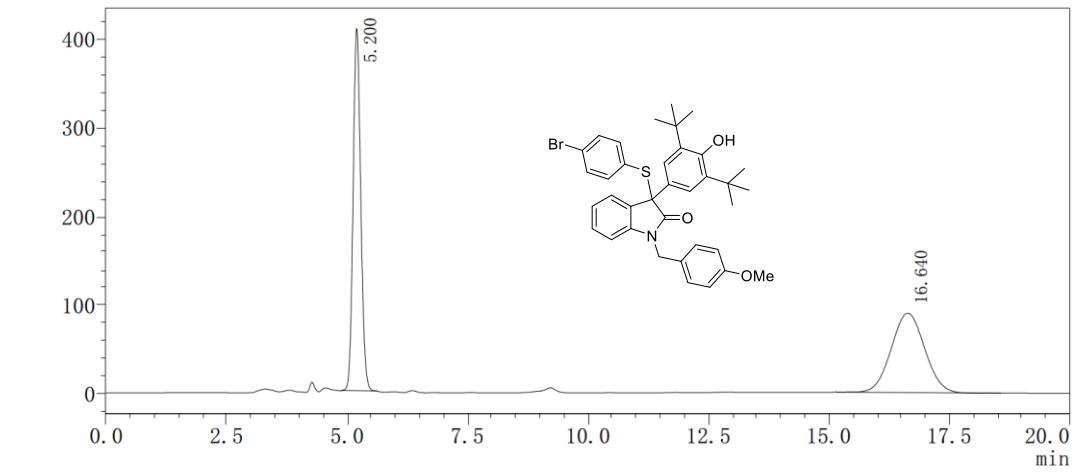
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	9.091	97.355	15525545	569021	
2	10.622	2.645	421769	13131	

HPLC spectra of product **1'm**

<Chromatogram>

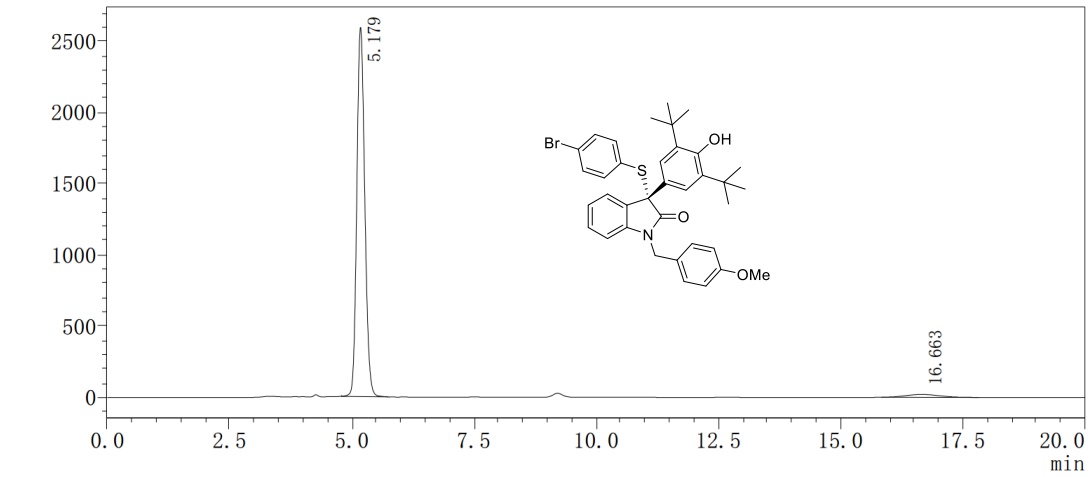


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	5.200	50.965	4510847	408824	
2	16.640	49.035	4340052	89661	

<Chromatogram>



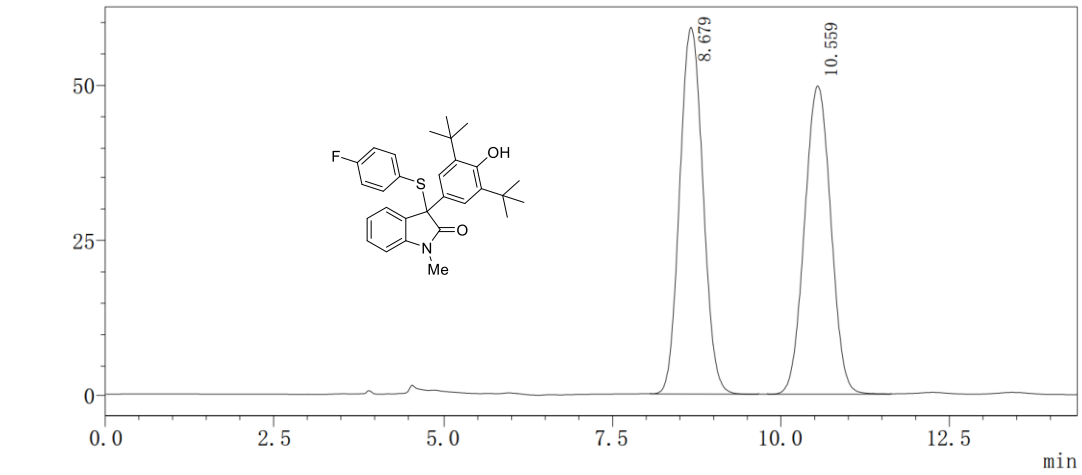
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	5.179	96.856	29388345	2588780	
2	16.663	3.144	953938	19922	

HPLC spectra of product **1'n**

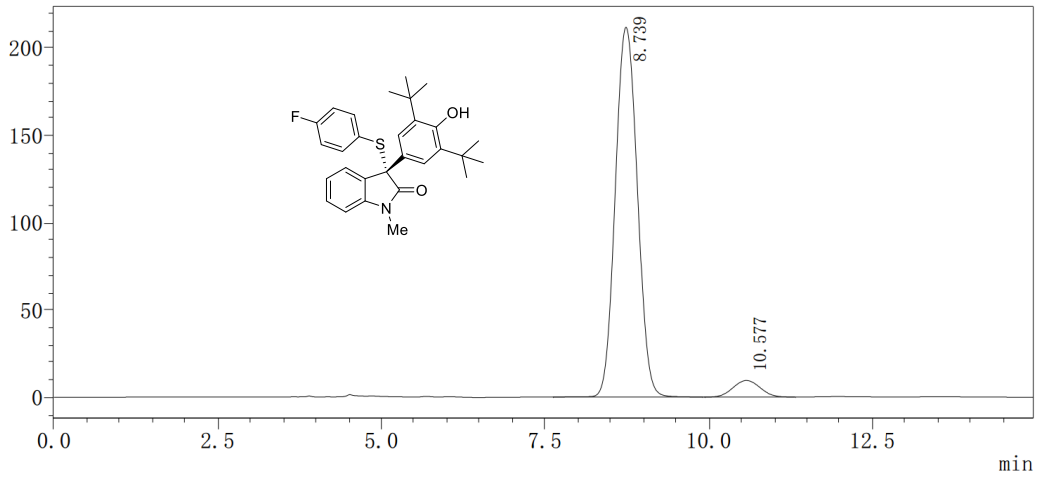
<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.679	51.282	1419824	59003	
2	10.559	48.718	1348848	49616	

<Chromatogram>
mV

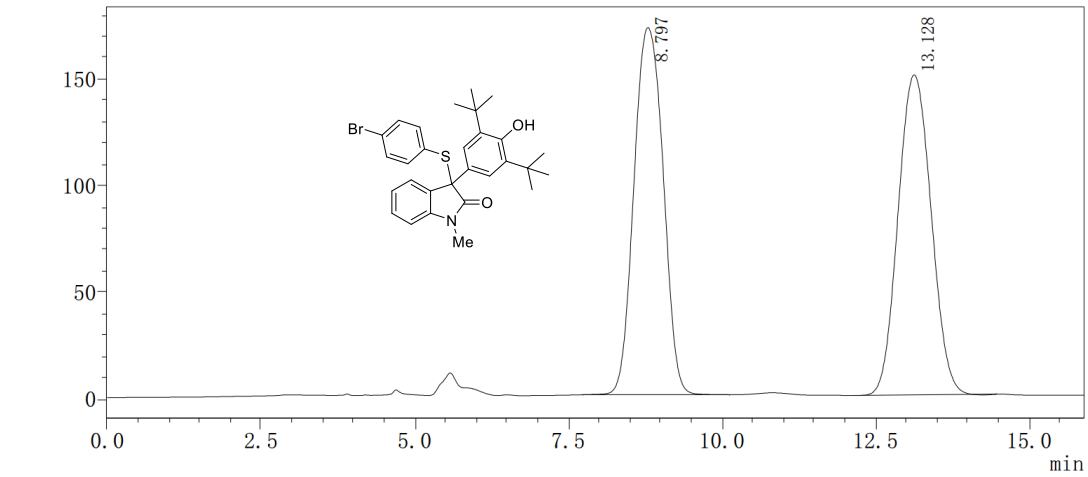


<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.739	94.813	4947826	211465	
2	10.577	5.187	270659	9427	

HPLC spectra of product **1'o**

<Chromatogram>

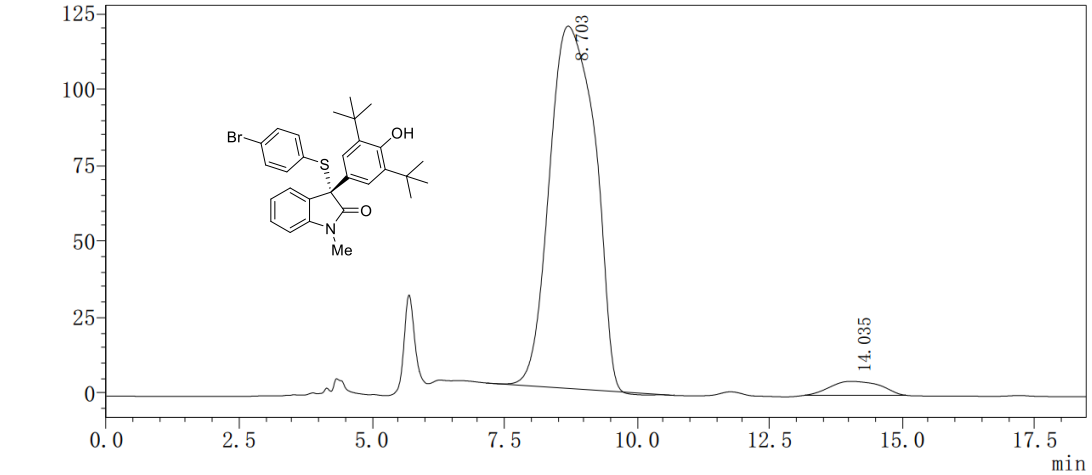


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.797	50.410	5706840	172095	
2	13.128	49.590	5613993	149973	

<Chromatogram>



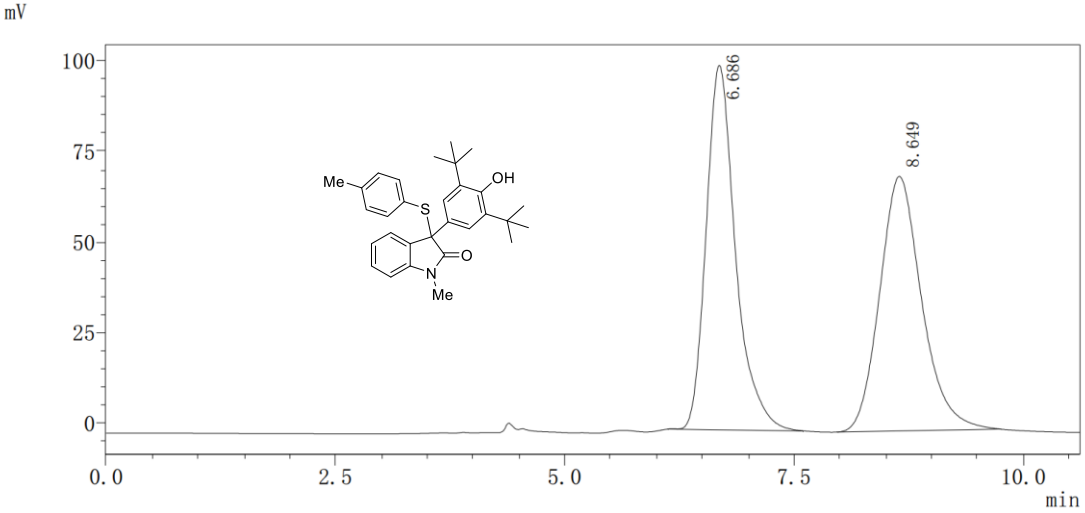
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.703	95.935	7116548	119202	
2	14.035	4.065	301536	4581	

HPLC spectra of product **1'p**

<Chromatogram>

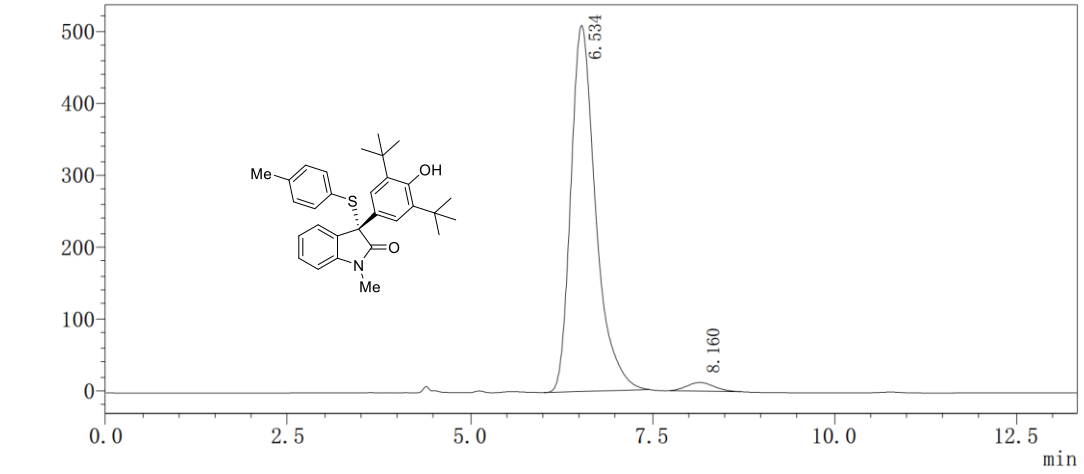


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	6.686	50.031	2241899	100653	
2	8.649	49.969	2239132	70303	

<Chromatogram>



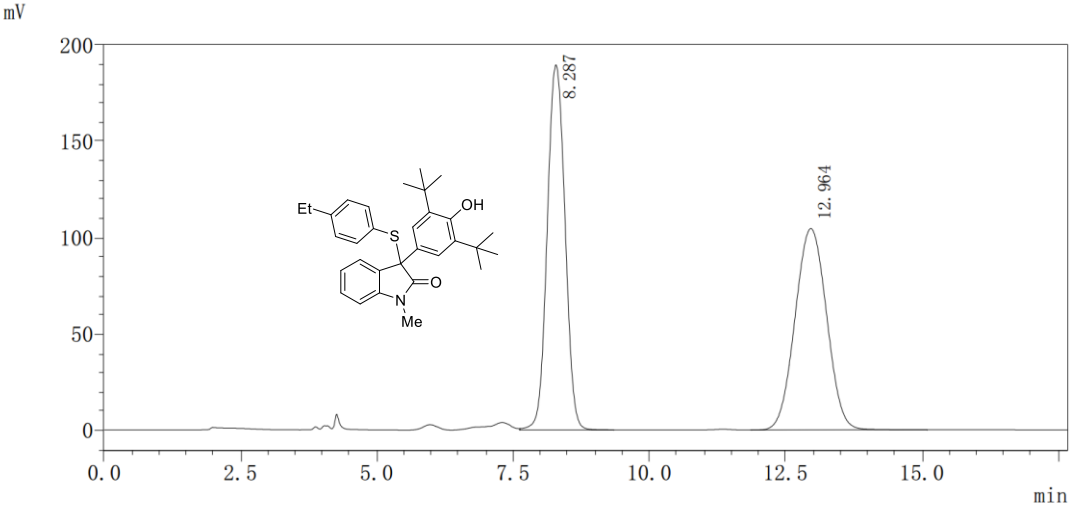
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	6.534	97.509	12113001	508965	
2	8.160	2.491	309385	12029	

HPLC spectra of product **1'q**

<Chromatogram>

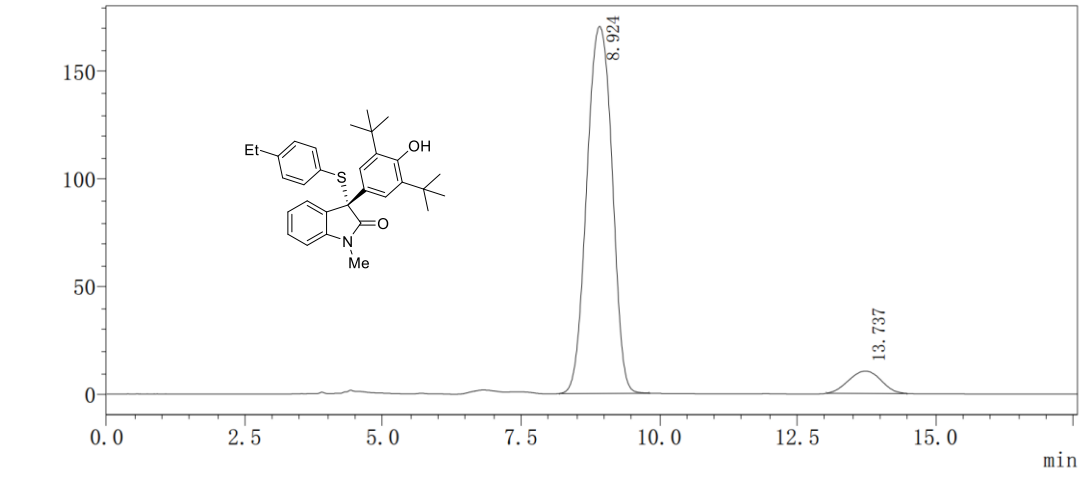


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.287	50.518	4313786	189533	
2	12.964	49.482	4225392	104574	

<Chromatogram>



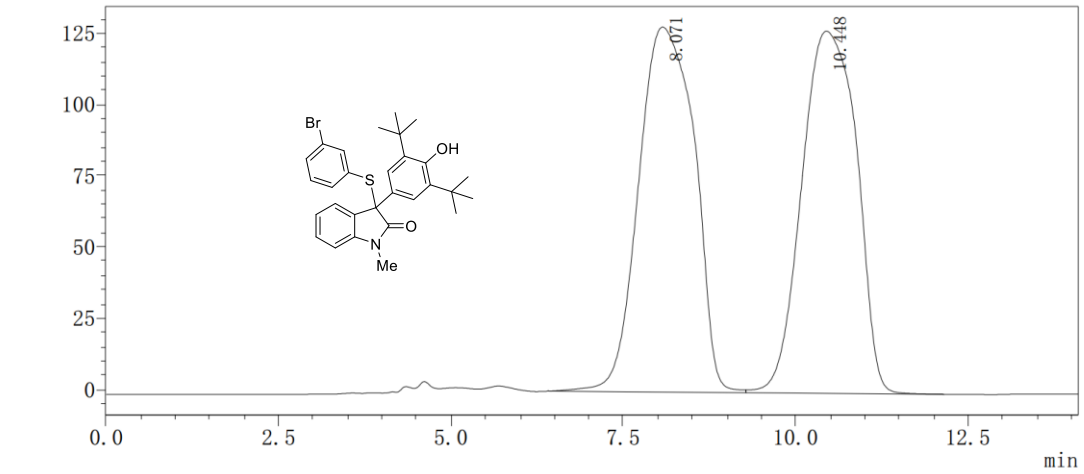
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.924	92.841	5447698	170537	
2	13.737	7.159	420046	10363	

HPLC spectra of product **1'r**

<Chromatogram>

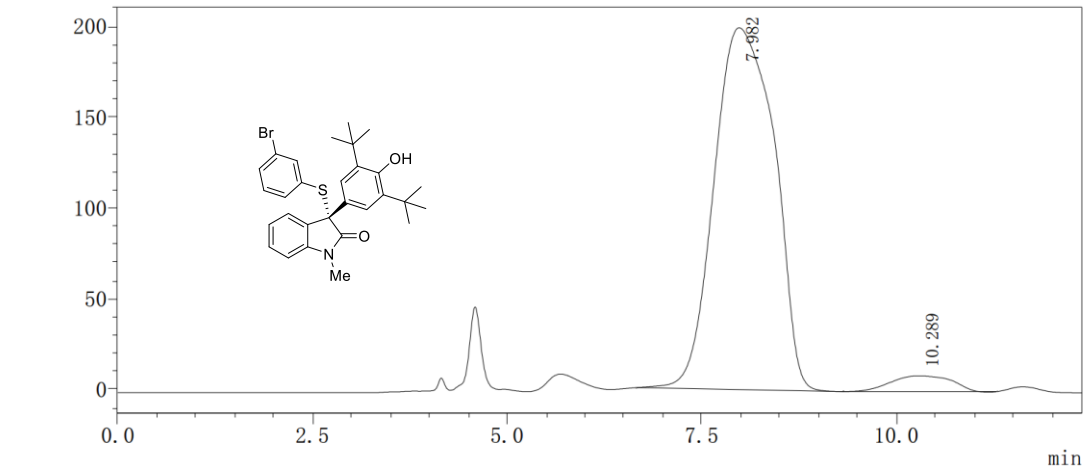


<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	8.071	50.585	7225965	128013	
2	10.448	49.415	7058728	127043	

<Chromatogram>



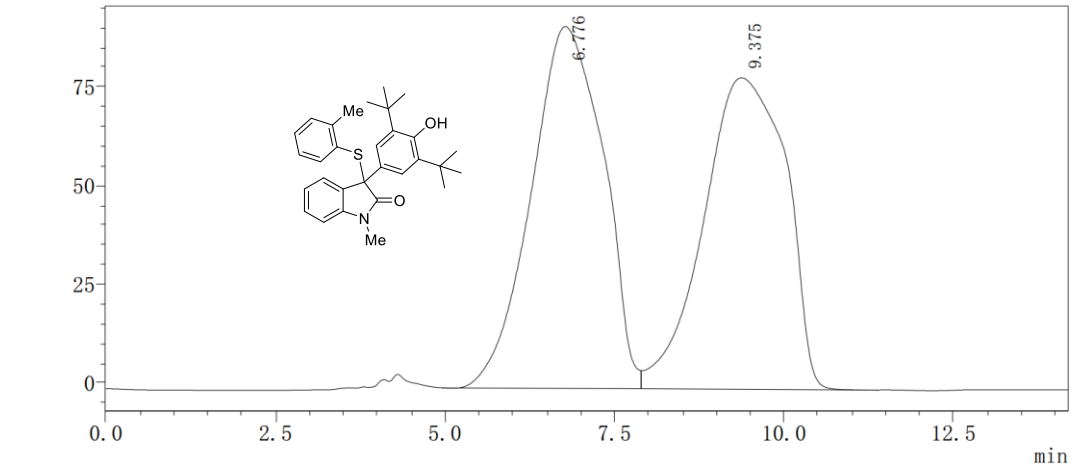
<Peak Table>

检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	7.982	95.790	10738038	199147	
2	10.289	4.210	471951	8634	

HPLC spectra of product **1's**

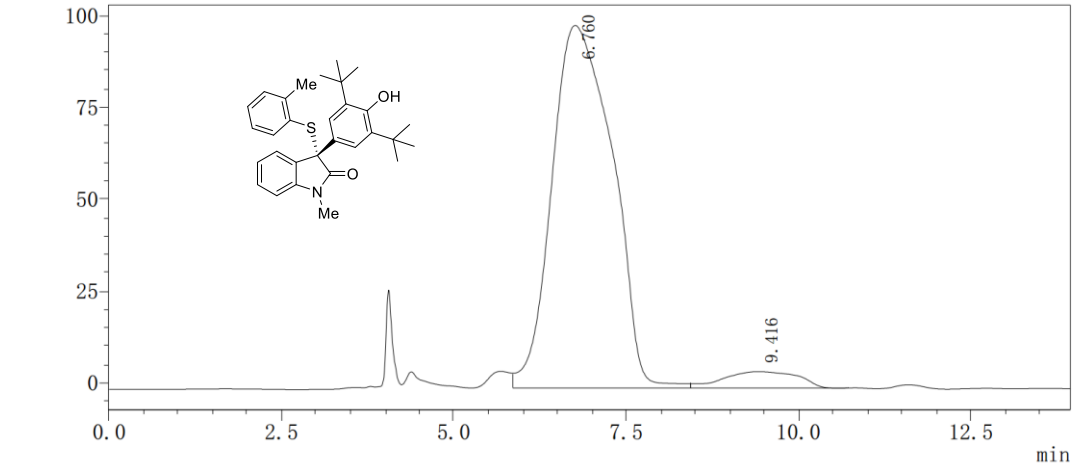
<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	6.776	50.380	6798416	91610	
2	9.375	49.620	6695808	78872	

<Chromatogram>
mV



<Peak Table>
检测器A 254nm

	Time	Area%	Area	Height	Compound Name
1	6.760	94.743	6053032	98729	
2	9.416	5.257	335880	4464	