Supporting Information

Facile Synthesis of Pyrroloindoles via a Rhodium(II)-Catalyzed Annulation of 3-Benzylidene-indolin-2-ones and α-Imino Carbenes

Xueji Ma,[a] Xuemei Xie,[a] Li Liu,[a] Ran Xia,[a] Tongyu Li,[b] Hangxiang Wang[b]*

[a] *Department of Chemistry and Chemical Engineering, Xinxiang University, Xinxiang 453003, China.*

[b] *The First Affiliated Hospital; Collaborative Innovation Center for Diagnosis and Treatment of Infectious Diseases; Key Laboratory of Combined Multi-Organ Transplantation, Ministry of Public Health, School of Medicine, Zhejiang University, Hangzhou, 310003, China.*

Email: wanghx@zju.edu.cn

Contents

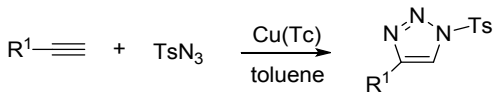
I. General Information.

^{1}H NMR spectra were recorded in deuterated solvents on a Bruker 400 (400 MHz) or Bruker 600 (600 MHz) spectrometer and calibrated to the residual solvent peak or tetramethylsilane (δ = 0 ppm). $CDCl_3$ or d_6-DMSO was used as solvent. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, br = broad. *J*-values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer or a GCT Premier (7000FWHM). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Organocatalysts were synthesized according to the literatures. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

II. Experimental Section

1. Synthesis of starting materials 1.

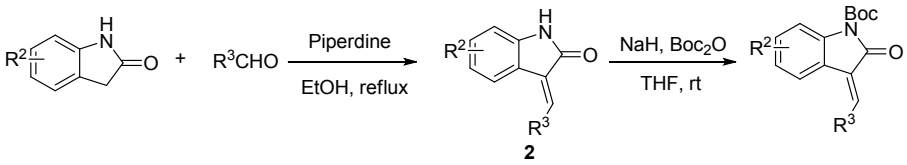
N-Sulfonyl-1,2,3-triazoles **1** were prepared from the corresponding alkynes and sulfonyl azides according to previously reported synthetic procedures,[1] and all data correspond to previously reported material.



Following the reported procedure,[1] copper(I) thiophene-2-carboxylate (0.2 mmol), sulfonyl azide (4 mmol), alkyne (4.4 mmol) in wet toluene (10 mL) was stirred at room temperature until the total consumption of sulfonyl azide. The mixture as then diluted with 30 mL of saturated NH_4Cl and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The mixture obtained was then filtrated over a pad of silica gel with a mixture of n-hexane/EtOAc to afford the desired product as white or brown solid.

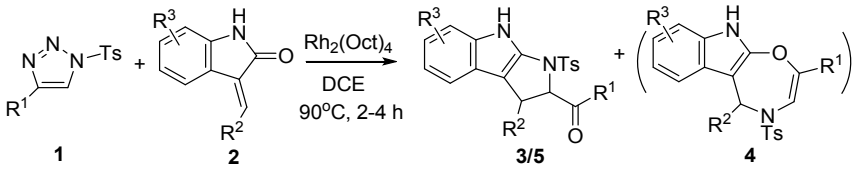
2. Synthesis of starting materials 2 and their derivatives.

3-Benzylideneindolin-2-one **2** was prepared from the corresponding oxindole and aldehyde according to previously reported synthetic procedures. [2]

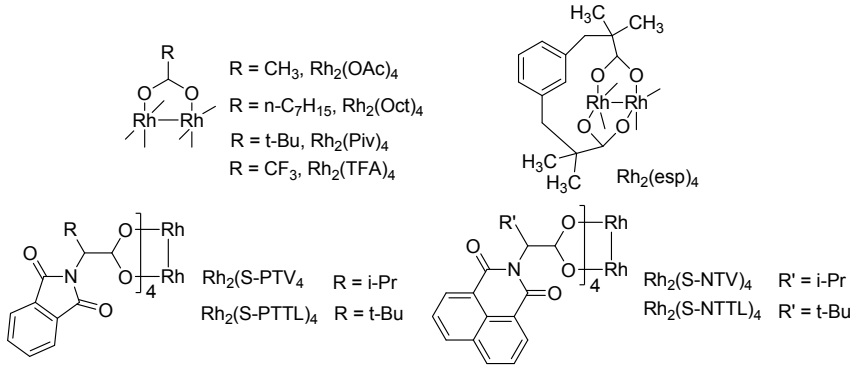


To the solution of oxindole (10 mmol) in EtOH (15 mL) was added the corresponding aldehyde (12 mmol) and piperdine (1 mmol). After refluxing for 8 hours, the reaction was cooled to room temperature. Crude product was collected by flash filtration. After washed by EtOH and hexane, the pure products were obtained as yellow or orange solid. [2-3] *N*-protected derivatives of **2** were synthesized through nucleophilic substitution in the presence of NaH as base.

3. General Procedure for synthesizing pyrroloindoles 3-5.



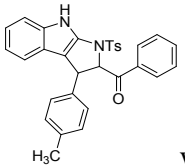
A 15 mL tube was filled with N_2 before it was charged with a solution of *N*- Sulfonyl-1,2,3-triazole **1** (0.30 mmol), 3-benzylideneindolin-2-one **2** (0.20 mmol) and $Rh_2(Oct)_4$ (9.0 μmol) in dry DCE (1.0 mL). The tube was sealed, and the reaction mixture was stirred at 90° C in an oil bath. The reaction was monitored by TLC. After completion and the removal of solvent, the resulting product was isolated by column chromatography on silica gel using ethylacetate-petroleum ether mixture as eluent.



(Structures of the rhodium catalysts)

4. Compound characterizations

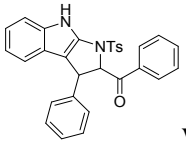
Phenyl(3-(*p*-tolyl)-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)methanone (3a)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.39-7.42 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.2 Hz, 2H), 6.32 (d, *J* = 7.2 Hz, 2H), 5.12 (d, *J* = 4.2 Hz, 1H), 4.43 (d, *J* = 4.2 Hz, 1H), 2.43 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.0, 145.1,

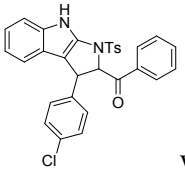
141.1, 138.4, 138.2, 136.9, 134.3, 133.7, 131.5, 130.3，129.2, 129.1, 128.7, 128.0, 127.2, 123.6, 121.1, 120.8, 117.8, 112.1, 104.6, 80.4, 48.4, 21.6, 21.1; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}N_2O_3S^+$ (M+H)+: requires 507.1736, found: 507.1740.

Phenyl(3-phenyl)-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)methanone (3b)



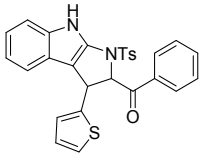
white solid; ^{1}H NMR (600 MHz, *d6*-DMSO): δ = 11.88 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.69-7.70 (m, 3H), 7.53 (t, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.97-7.01 (m, 3H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.27 (d, *J* = 7.8 Hz, 2H), 5.35 (d, *J* = 4.8Hz, 1H) , 4.37 (d, *J* = 4.8Hz, 1H) , 2.42 (d, 3H) ; ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 193.7, 145.4, 141.4, 140.8, 139.0, 134.1, 133.9, 131.2, 130.5, 129.0, 128.6, 128.3, 127.5, 127.2, 126.8, 122.5, 120.2, 120.0, 116.6, 112.7, 103.9, 79.1, 47.1, 21.0; HRMS (ESI, m/z): calcd. for $C_{30}H_{25}N_2O_3S^+$ (M+H)+: requires 493.1580, found: 493.1582.

(3-(4-Chlorophenyl)-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3c)



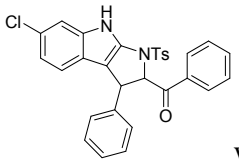
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.90 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.58-7.60 (m, 3H), 7.41-7.44 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.92-6.97 (m, 3H), 6.40 (d, *J* = 7.8 Hz, 2H), 5.09 (d, *J* = 4.8 Hz, 1H), 4.44 (d, *J* = 4.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.0, 145.4, 141.4, 139.9, 138.5, 133.9, 133.1, 131.3, 130.3, 129.1, 128.8, 128.7, 128.6, 127.9, 123.4, 121.4, 121.0, 117.7, 112.3, 103.9, 80.2, 47.9, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}ClN_2O_3S^+$ (M+H)+: requires 527.1190, found: 527.1189.

Phenyl (3-(thiophen-2-yl)-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl) Methanone (3d)



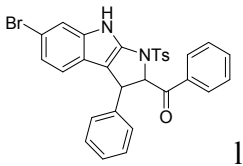
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.88 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.58-7.62 (m, 3H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.01-7.04 (m, 2H), 6.69 (t, *J* = 3.6 Hz, 1H), 5.26 (s, br, 1H), 5.29 (d, *J* = 4.8 Hz, 1H), 4.74 (d, *J* = 4.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.6, 1455, 145.2, 141.1, 138.3, 134.3, 133.9, 131.4, 130.3, 129.1, 128.8, 127.9, 126.7, 124.9, 123.4, 121.3, 120.9, 117.8, 112.2, 104.4, 80.0, 43.5, 21.6; HRMS (ESI, m/z): calcd. for $C_{28}H_{23}N_2O_3S_2^+$ (M+H)+: requires 499.1144, found: 499.1143.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3e)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.00 (s, br, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.38-7.42 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 7.2 Hz, 2H), 5.21 (d, *J* = 4.8 Hz, 1H), 4.41 (d, *J* = 4.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.8, 145.3, 141.8, 140.9, 138.8, 134.2, 133.9, 131.4, 130.4，129.1, 128.8, 128.6, 127.9, 127.4, 127.2, 126.8, 122.0, 121.4, 118.3, 112.3, 104.4, 79.9, 48.5, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}ClN_2O_3S^+$ (M+H)+: requires 527.1190, found: 527.1191.

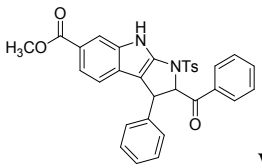
(6-Bromo-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3f)



light brown solid; ^{1}H NMR (600 MHz, CDCl3): δ = 8.96 (s, 1H), 7.67

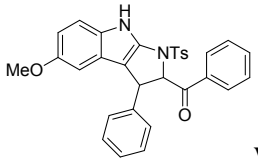
(d, *J* = 7.2 Hz, 2H), 7.58-7.62 (m, 3H), 7.54 (s, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 6.6 Hz, 2H), 5.20 (d, *J* = 3.6 Hz, 1H), 4.41 (d, *J* = 3.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.8, 145.3, 141.7, 140.9, 139.1, 134.2, 133.9, 131.5, 130.4，129.1, 128.8, 128.6, 128.0, 127.4, 127.2, 124.1, 122.4, 118.8, 115.1, 114.2, 104.4, 80.0, 48.5, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}BrN_2O_3S^+$ (M+H)+: requires 571.0685, found: 571.0688.

Methyl 2-benzoyl-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indole-6-carboxylate (3g)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.12 (s, 1H), 8.16 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 6.6 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 6.0 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 6.6 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 2H), 5.27 (d, *J* = 3.6 Hz, 1H), 4.44 (d, *J* = 3.6 Hz, 1H), 3.92 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 192.9, 166.9, 145.6, 143.9, 141.1, 138.2, 134.2, 133.7, 131.5, 130.6, 129.0, 128.7, 128.4, 127.5, 127.3, 126.8, 126.2, 121.2, 121.0, 116.2, 114.3, 104.6, 78.9, 51.7, 46.7, 21.0; HRMS (ESI, m/z): calcd. for $C_{32}H_{27}N_2O_5S^+$ (M+H)+: requires 551.1641, found: 551.1642.

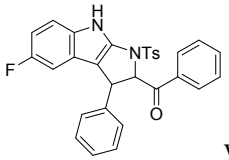
(5-Methoxyl-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3h)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.79 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.56-7.61 (m, 3H), 7.40-7.43 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.95-7.01 (m, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.07

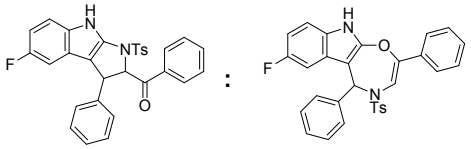
(s, 1H), 6.04 (d, *J* = 7.2 Hz, 1H), 5.15 (d, *J* = 4.2 Hz, 1H), 4.44 (d, *J* = 4.2 Hz, 1H), 3.60 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.1, 145.3, 142.8, 141.2, 134.3, 133.8, 131.3, 130.3, 129.5, 129.1, 128.7, 127.9, 123.7, 121.1, 120.8, 119.6, 117.8, 113.2, 112.4, 112.0, 104.4, 80.1, 55.1, 48.7, 21.6; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}N_2O_4S^+$ (M+H)+: requires 523.1686, found: 523.1688.

(5-Fluoro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3i)



white solid; ^{1}H NMR (600 MHz, *d6*-DMSO): δ = 11.81 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.41-7.43 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.83 (dt, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.45 (d, *J* =9.0 Hz, 1H), 6.26 (d, *J* = 7.8Hz, 2H), 5.40 (d, *J* = 4.2Hz, 1H), 4.36 (d, *J* = 4.2Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 193.5, 145.5, 142.4, 141.1, 135.5, 134.2, 133.8, 131.5, 130.6, 129.0, 128.7, 128.4, 127.5, 127.2, 126.7, 122.8, 113.7, 107.9, 107.7, 104.1, 101.9, 78.8, 46.8, 21.0; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}FN_2O_3S^+$ (M+H)+: requires 511.1486, found: 511.1489.

(5-Fluoro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3i) and 7-Fluoro-2,5-diphenyl-4-tosyl-5,10-dihydro-4*H*-[1,4] oxazepino[7,6-b]indole (4i)

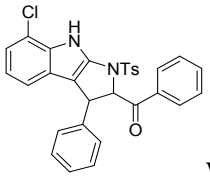


1.0 : 1.5

white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.16 (s, 1.5H), 8.84 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 3H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.52-7.55 (m, 1.5H), 7.41(t, *J* = 7.2 Hz, 2H), 7.21-7.27 (m, 5.5H), 7.22 (t, *J* = 9.0 Hz, 1.5H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.00-7.05 (m, 7H), 6.95 (s, 1.5H), 6.83-6.90 (m, 11.5H), 6.57 (d, *J* = 9.0 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 2H), 5.20 (d, *J* = 4.8 Hz, 1H), 4.94 (s, 1.5H), 4.40 (d, *J* = 4.8 Hz, 1H), 3.34 (s, 1.5H), 2.44 (s, 3H), 2.40

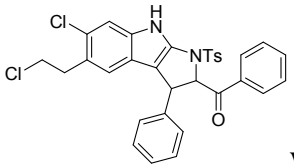
(s, 4.5H); ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 193.4, 174.3, 145.3, 145.2, 145.0, 144.9, 144.2, 144.1, 142.7, 142.1, 141.9, 140.8, 136.8, 136.0, 134.1, 133.7, 130.4, 130.1, 129.2, 129.0, 128.8, 128.6, 128.0, 127.9, 127.8, 127.4, 127.3, 127.2, 127.1, 127.0, 126.5, 123.1, 118.9, 118.8, 118.5, 115.9, 114.8, 113.1, 112.6, 109.2, 108.9, 102.2, 93.1, 79.7, 55.8, 47.1, 21.1, 21.0; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}FN_2O_3S^+$ (M+H)+: requires 511.1486, found: 511.1489.

(7-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3j)



white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.11-7.16 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 2H), 5.21 (d, *J* = 5.2 Hz, 1H), 4.30 (d, *J* = 5.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 145.3, 141.6, 140.8, 135.3, 134.1, 133.9, 131.5, 130.4, 129.1, 128.8, 128.6, 127.9, 127.4, 127.2, 124.8, 121.7, 120.8, 117.1, 116.3, 105.4, 79.9, 46.4, 21.7; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}ClN_2O_3S^+$ (M+H)+: requires 527.1190, found: 527.1181.

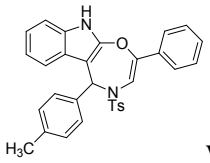
(6-Chloro-5-(2-chloroethyl)-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(phenyl) methanone (3k)



white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.97 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.77 (s, 1H), 6.39 (d, *J* = 8.0 Hz, 2H), 5.20 (d, *J* = 4.8 Hz, 1H), 4.41 (d, *J* = 4.8 Hz, 1H), 3.61 (t, *J* = 7.6 Hz, 2H), 2.99-3.16 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100

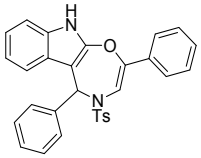
MHz, $CDCl_3$): δ = 193.7, 145.3, 142.2, 140.8, 137.8, 134.1, 133.9, 131.4, 130.4, 129.1, 128.8, 128.6,128.0, 127.9, 127.4, 127.2, 126.8, 122.5, 119.6, 112.9, 104.0, 79.9, 48.4, 43.7, 37.3, 21.7; HRMS (ESI, m/z): calcd. for $C_{32}H_{27}Cl_2N_2O_3S^+$ (M+H)+: requires 589.1113, found: 589.1107.

5-Phenyl-2-(4-tolyl)-4-tosyl-5,10-dihyro-4*H*-[1,4]oxazepino[7,6-b]indole (4a)



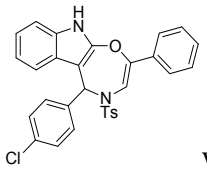
white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.00-7.06 (m, 4H), 6.89 (d, *J* = 6.8 Hz, 2H), 6.78(d, *J* = 8.4 Hz, 2H), 6.69(d, *J* = 8.0 Hz, 2H), 4.95 (s, 1H), 3.31 (s, 1H), 2.39 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 145.9, 145.4, 143.9, 139.2, 137.2, 136.9, 136.6, 132.9, 129.7, 129.4, 129.2, 127.9, 127.7, 127.1, 126.9, 126.4, 123.2, 123.1, 121.4, 113.7, 93.2, 56.0, 21.6, 20.9; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}N_2O_3S^+$ (M+H)+: requires 507.1742, found: 507.1743.

2,5-Diphenyl-4-tosyl-5,10-dihyro-4*H*-[1,4]oxazepino[7,6-b]indole (4b)



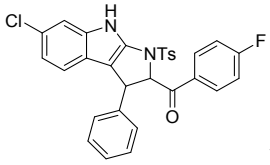
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.12 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.03-7.07 (m, 2H), 7.00-7.03 (m, 2H), 6.89-6.94 (m, 7H), 4.97 (s, 1H), 3.32 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.3, 145.9, 145.5, 144.0, 142.2, 137.2, 136.5, 132.9, 129.6, 129.5, 129.3, 127.7, 127.4, 127.3, 127.0, 126.9, 126.5, 123.2, 123.1, 121.5, 113.8, 93.2, 56.0, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{25}N_2O_3S^+$ (M+H)+: requires 493.1580, found: 493.1582.

2-(4-Fluorophenyl)-5-phenyl-4-tosyl-5,10-dihyro-4*H*-[1,4]oxazepino[7,6-b]indole (4c)



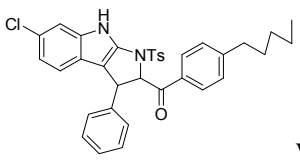
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.05-7.08 (m, 4H), 6.85-6.90 (m, 6H), 4.97 (s, 1H), 3.34 (s, br, 1H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, d_6-DMSO): δ = 175.0, 146.4, 144.4, 144.1, 141.9, 138.1, 137.2, 133.1, 131.7, 130.1, 129.2, 128.5, 128.1, 127.3, 127.2, 127.1, 122.5, 124.4, 121.6, 115.8, 93.1, 56.6, 21.5; HRMS (ESI, m/z): calcd. for $C_{30}H_{24}ClN_2O_3S^+$ (M+H)+: requires 527.1190, found: 527.1191.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(4-fluorophenyl)methanone (5a)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 7.79-7.81 (m, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.39 (s, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 6.6 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 2H), 5.11 (d, *J* = 4.2 Hz, 1H), 4.41 (d, *J* = 4.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.3, 145.4, 141.6, 140.8, 138.7, 131.9, 131.8, 131.2, 130.4, 128.7, 127.9, 127.5, 127.2, 127.0, 121.9, 121.5, 118.4, 116.1, 116.0, 112.2, 104.4, 80.1, 48.6, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{23}ClFN_2O_3S^+$ (M+H)+: requires 545.1096, found: 545.1091.

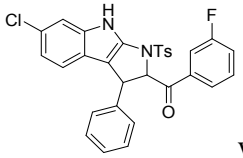
(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(4-pentylphenyl)methanone (5b)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.38 (s, 1H), 7.24-7.26 (m, 2H), 7.21 (d, *J*

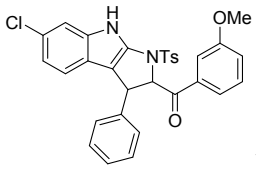
= 7.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 2H), 5.18 (d, *J* = 4.8 Hz, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.61-1.64 (m, 2H), 1.26-1.35 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.3, 149.9, 145.2, 141.8, 141.0, 138.6, 131.8, 130.3, 129.3, 128.8, 128.5, 127.9, 127.3, 127.2, 126.8, 122.1, 121.4, 118.3, 112.2, 104.4, 79.8, 48.6, 36.0, 31.4, 30.6, 22.5, 21.6, 14.0; HRMS (ESI, m/z): calcd. for $C_{35}H_{34}ClN_2O_3S^+$ (M+H)+: requires 597.1973, found: 597.1976.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(3-flurophenyl)methanone (5c)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.90 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 6.0 Hz, 2H), 7.39 (s, 1H), 7.38 (d, *J* = 6.6 Hz, 1H), 7.25-7.30 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 7.2 Hz, 2H), 5.11 (d, *J* = 4.8 Hz, 1H), 4.42 (d, *J* = 4.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.8, 145.4, 141.6, 140.7, 138.7, 136.3, 136.2, 131.2, 130.5, 130.4, 128.7, 128.0, 127.5, 127.0, 124.7, 122.0, 121.6, 121.0, 118.4, 116.0, 115.8, 112.2, 104.3, 80.2, 48.5, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{23}ClFN_2O_3S^+$ (M+H)+: requires 545.1096, found: 545.1092.

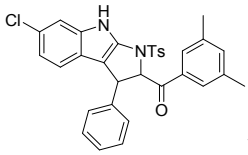
(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(3-methoxyphenyl)methanone (5d)



white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.35 (s, 1H), 7.25-7.29 (m, 4H), 7.12-7.15 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.93 (dd, *J* = 2.0 Hz, 2.0Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 2H), 5.19(d, *J* = 5.2Hz, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 3.71 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.5, 159.9, 145.3, 141.7, 140.9, 138.6,

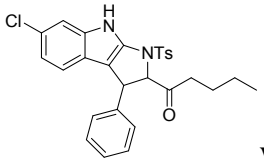
135.4, 131.4, 130.4, 129.7, 128.6, 128.0, 127.4, 127.2, 127.0, 122.0, 121.5, 121.4, 121.0, 118.3, 112.9, 112.1, 104.4, 79.9, 55.3, 48.6, 21.6; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}ClN_2O_4S^+$ (M+H)+: requires 557.1396, found: 557.1390.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(3,5-dimethylphenyl)methanone (5e)



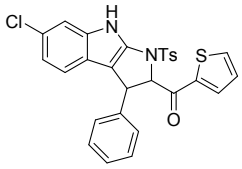
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.37 (s, 1H), 7.25-7.29 (m, 4H), 7.21 (s, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 2H),5.26 (d, *J* = 4.8 Hz, 1H), 4.32 (d, *J* = 4.8 Hz, 1H), 2.45 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.6, 145.2, 141.8, 141.1, 138.6, 138.4, 135.6, 134.1, 131.7, 130.3, 128.5, 127.9, 127.4, 127.0, 126.7, 122.0, 121.4, 118.3, 112.1, 104.4, 79.8, 48.6, 21.6, 21.2; HRMS (ESI, m/z): calcd. for $C_{32}H_{28}ClN_2O_3S^+$ (M+H)+: requires 555.1503, found: 555.1504.

1-(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)pentan-1-one (5f)



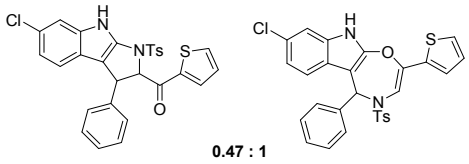
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 7.41 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.00-7.03 (m, 3H), 6.94-7.00 (m, 3H), 6.51 (d, *J* = 7.2 Hz, 2H), 4.48 (d, *J* = 2.4 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 3.00-3.06 (m, 1H), 2.75-2.79 (m, 1H), 2.32 (s, 3H), 1.60-1.64 (m, 2H), 1.33-1.37 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 208.5, 145.3, 141.5, 141.3, 138.6, 130.6, 130.1, 128.4, 127.8, 127.2, 126.8, 126.5, 122.2, 121.7, 118.9, 112.2, 105.4, 83.5, 46.8, 39.0, 25.1, 22.2, 21.6, 13.9; HRMS (ESI, m/z): calcd. for $C_{28}H_{28}ClN_2O_3S^+$ (M+H)+: requires 507.1503, found: 507.1502.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(thiophen-2-yl)methanone (5g)



white solid; ^{1}H NMR (600 MHz, *d6*-DMSO): δ = 11.92 (s, 1H), 8.15 (d, *J* = 4.2 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 3.0 Hz, 1H), 7.46 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 3.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 2H), 5.07 (d, *J* = 4.2 Hz, 1H), 4.45 (d, *J* = 4.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (400 MHz, *d6*-DMSO): δ = 186.7, 145.7, 141.6, 141.2, 139.8, 139.4, 137.2, 134.1, 130.7, 130.6, 129.0, 128.4, 127.6, 127.2, 126.8, 124.8, 121.2, 120.3, 118.0, 112.4, 104.2, 79.8, 59.7, 47.4, 21.0, 14.0; HRMS (ESI, m/z): calcd. for $C_{28}H_{22}ClN_2O_3S_2^+$ (M+H)+: requires 533.0760, found: 533.0756.

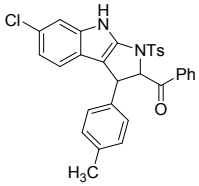
(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(thiophen-2-yl)methanone (5g) and 5g'



5g 5g'

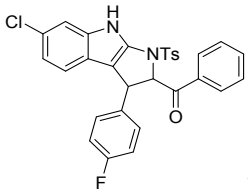
white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.15 (s, 1H), 9.11 (s, 0.47H), 8.63 (s, 1H), 7.89 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.70-7.73 (m, 2H), 7.54-7.63 (m, 2.1H), 7.41-7.49 (m, 2.1H), 7.28 (s, 1H), 7.05-7.28 (m, 4.6H), 6.95-7.01 (m, 2.1H), 6.82-6.89 (m, 2.4H), 6.57 (t, *J* = 4.4 Hz, 1H), 6.46-6.50 (m, 1.0H), 4.99 (s, 1H), 4.89 (d, *J* = 4.8 Hz, 0.47H), 4.51 (d, *J* = 4.8 Hz, 0.47H), 4.10 (s, 1H), 2.42 (s, 1.41H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 186.7, 173.2, 146.5, 145.6, 143.8, 142.4, 141.6, 141.2, 139.8, 139.4, 137.4, 137.3, 137.1, 136.3, 134.1, 133.0, 132.6, 130.7, 130.6, 129.8, 129.7, 129.0, 128.7, 128.4, 127.6, 127.2, 127.0, 126.8, 126.7, 125.5, 124.9, 124.8, 124.2, 123.4, 121.9, 121.3, 120.6, 120.3, 118.0, 114.6, 112.4, 104.2, 91.8, 79.8, 55.7, 47.4, 21.1, 21.0; HRMS (ESI, m/z): calcd. for $C_{28}H_{22}ClN_2O_3S_2^+$ (M+H)+: requires 533.0760, found: 533.0756.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(thiophen-2-yl)methanone (5h)



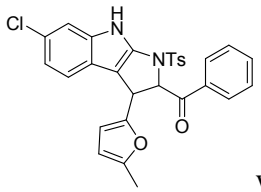
white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.39 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4Hz, 1H), 6.79(d, *J* = 7.8 Hz, 2H), 6.29 (d, *J* = 7.2 Hz, 2H), 5.16 (d, *J* = 4.8 Hz, 1H), 4.38 (d, *J* = 4.8 Hz, 1H), 2.45(s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 193.5, 145.5, 141.5, 139.3, 138.2, 136.4, 134.2, 133.8, 131.3, 130.6, 129.0, 128.9, 128.7, 127.5, 126.7, 124.7, 121.3, 120.2, 117.8, 112.3, 104.0, 79.0, 46.6, 21.0, 20.5; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}ClN_2O_3S^+$ (M+H)+: requires 541.1347, found: 541.1342.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(thiophen-2-yl)methanone (5i)



white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.97 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.59-7.62 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 6.95 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.69 (t, *J* = 8.4 Hz, 2H), 6.36-6.40 (m, 2H), 5.12 (d, *J* = 4.8 Hz, 1H), 4.41 (d, *J* = 4.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8, 145.4, 141.8, 138.7, 136.8, 134.2, 134.0, 131.4, 130.4, 129.1, 128.8, 128.7, 127.9, 127.0, 121.9, 121.6, 118.3, 115.5, 115.3, 112.3, 104.1, 80.0, 47.7, 21.6; HRMS (ESI, m/z): calcd. for $C_{30}H_{23}ClFN_2O_3S^+$ (M+H)+: requires 545.1096, found: 545.1093.

(6-Chloro-3-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-2-yl)(thiophen-2-yl)methanone (5j)



white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 6.6 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.38(s, 1H), 7.18 (d, *J* = 8.4Hz, 2H), 7.00-7.05 (m, 2H), 5.62 (s, 1H), 5.55 (d, *J* = 4.2Hz, 1H), 5.28 (d, *J* = 2.4Hz, 1H), 4.43 (d, *J* = 3.0Hz, 1H), 2.37 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, *d6*-DMSO): δ = 192.9, 150.1, 150.7, 145.0, 141.7, 139.0, 134.2, 133.5, 131.7, 130.2, 129.0, 128.8, 127.3, 124.6, 121.4, 120.3, 118.0, 112.3, 107.2, 106.2, 101.8, 75.4, 40.4, 21.0, 13.1; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}ClN_2O_4S^+$ (M+H)+: requires 531.1139, found: 531.1138.

III Reference

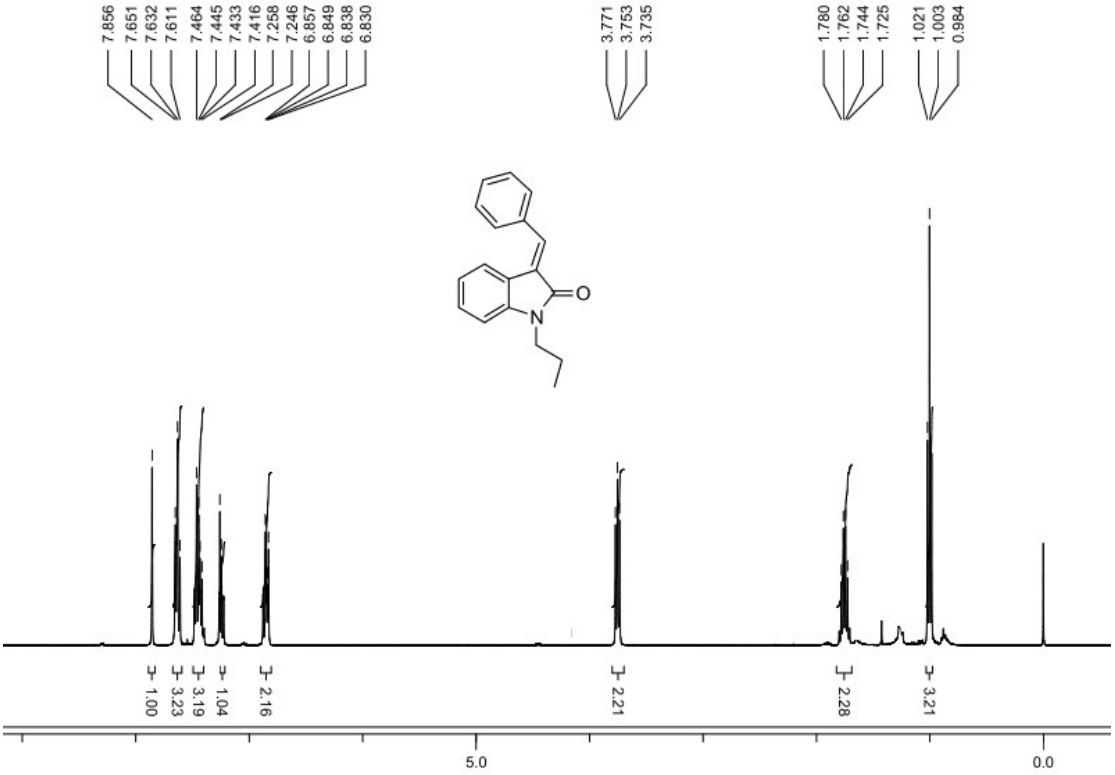
[1] a) Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V. *J. Am. Chem.Soc.,* **2009**, *131*, 18034. b) Miura, T.; Biyajima, T.; Fujii, T.; Murakami, M. *J. Am.Chem. Soc.*, **2012**, *134*, 194. c) Yadagiri, D.; Anbarasan, P. Chem. *Eur. J.*, **2013**, *19*, 15115. d) Xueji, M.; Shanfei, P. Hangxiang, W.; Wanzhi, C. *Org. Lett.*, **2014**, *16*, 4554.

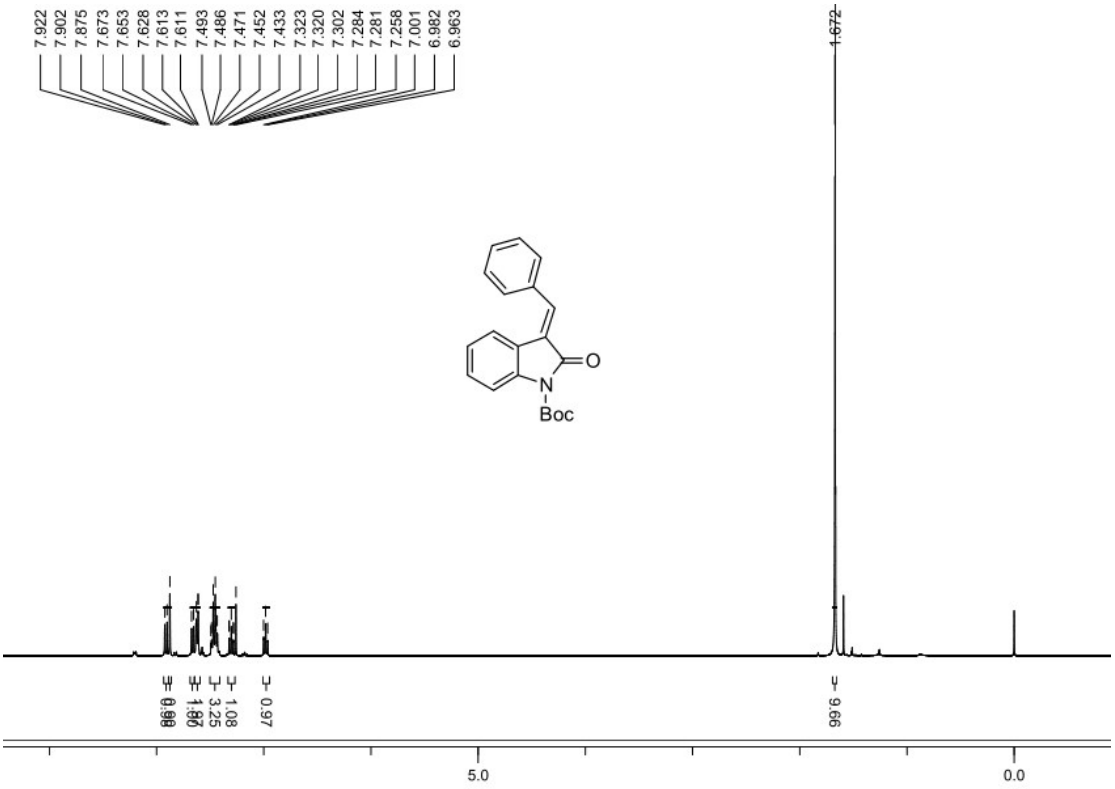
[2] a) Elloit, I. W.; Rivers, P. *J. Org. Chem.,* **1964**, *29*, 2438. b) Trost, B. M.; Cramer, N. ; Silverman, S. M. *J. Am. Chem. Soc.,* **2007**, *129*, 12396. c) Tan, B.; Candeias, N. R.; Barbas, C. F. *J. Am. Chem. Soc.,* **2011**, *133*, 4672. d) Gang, W.; Xiaohua, L.; Tianyu, H.; Yulong, K.; Lili, L.; Xiaoming, F. *Org. Lett.,* **2013**, *15* , 76.

[3] a) Satoshi, U.; Takahiro, O.; Hideko, N. *Chem. Commun.,* **2010**, *46*, 2462. b)Wei, Z.; Mei, L. G. *Bioorg. Med. Chem.*, **2009**, *17*, 2077.

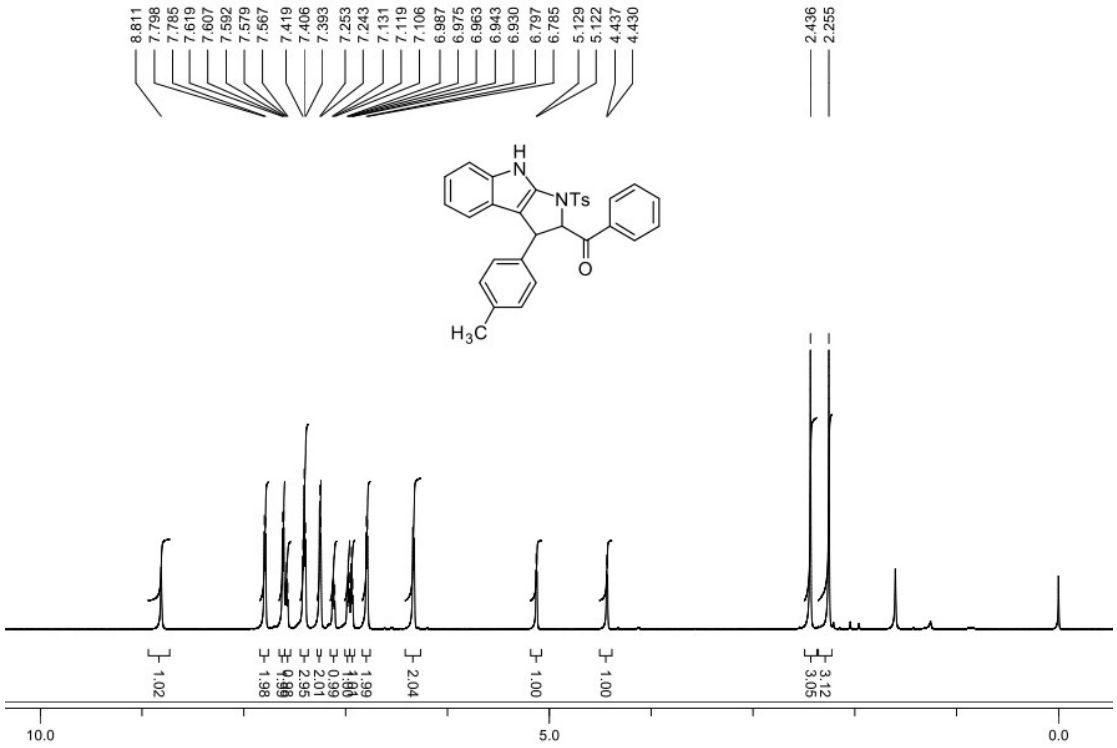
IV ^{1}H NMR and ^{13}C NMR spectra

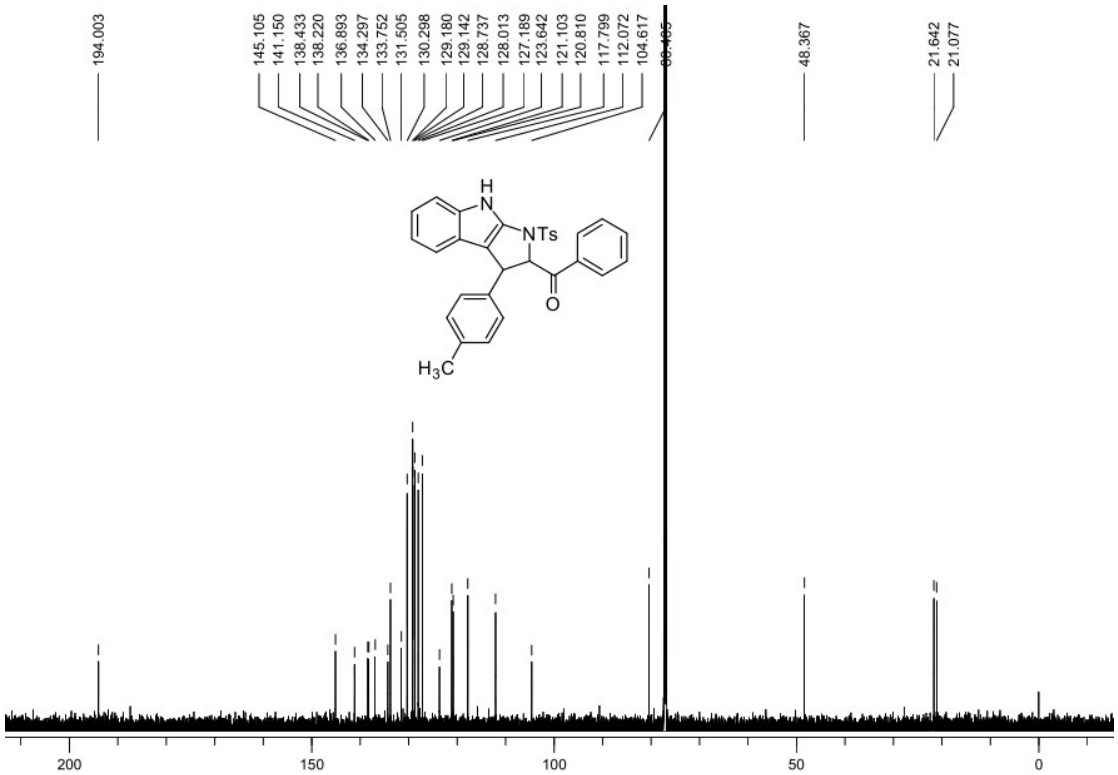
^{1}H NMR spectrum of *N*-substituded derivatives of **2**.



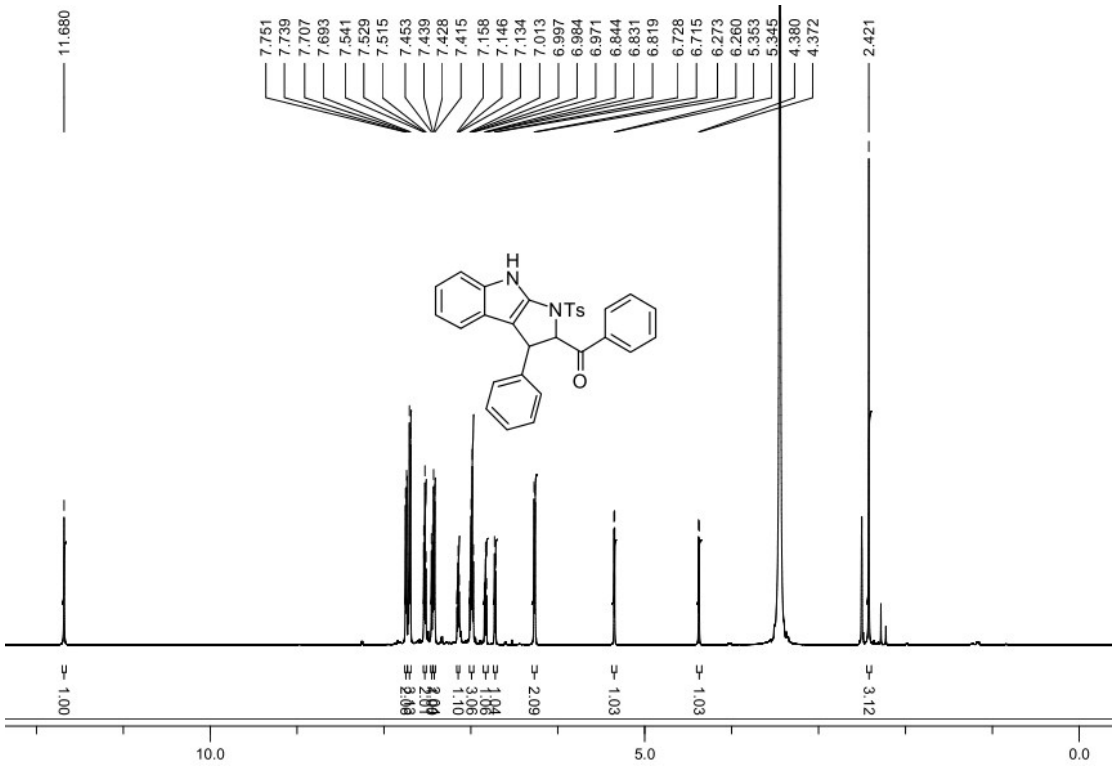


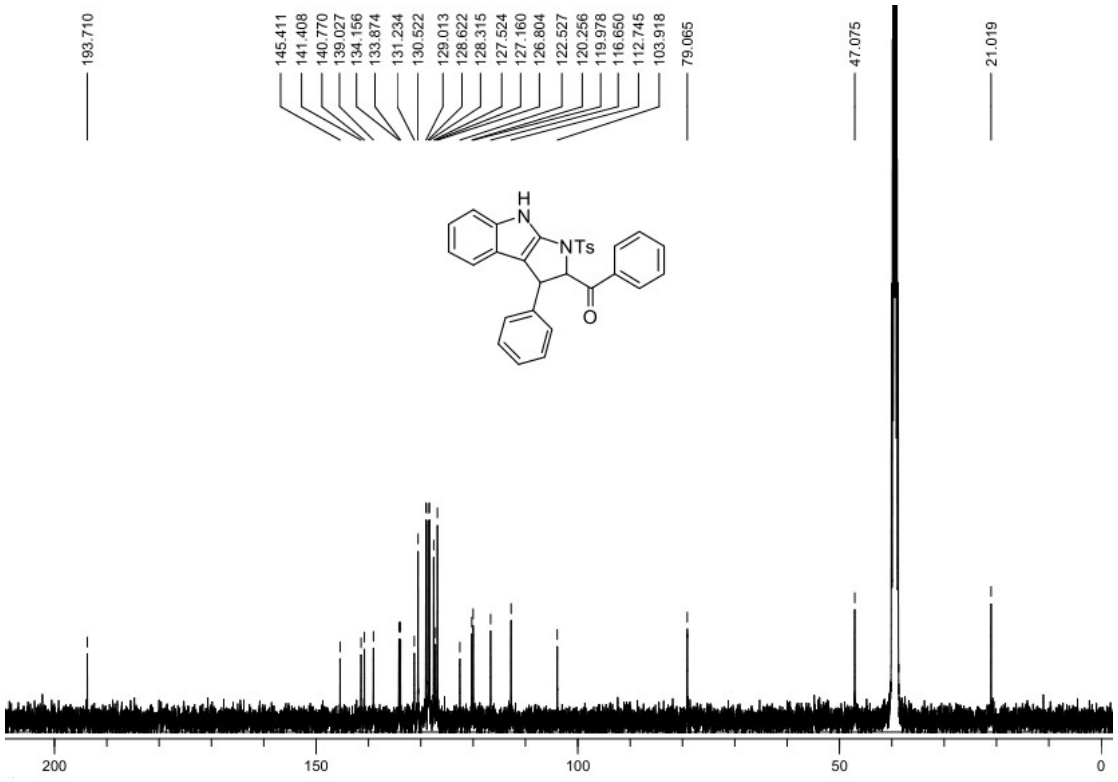
^{1}H NMR and ^{13}C NMR spectrum of **3a**



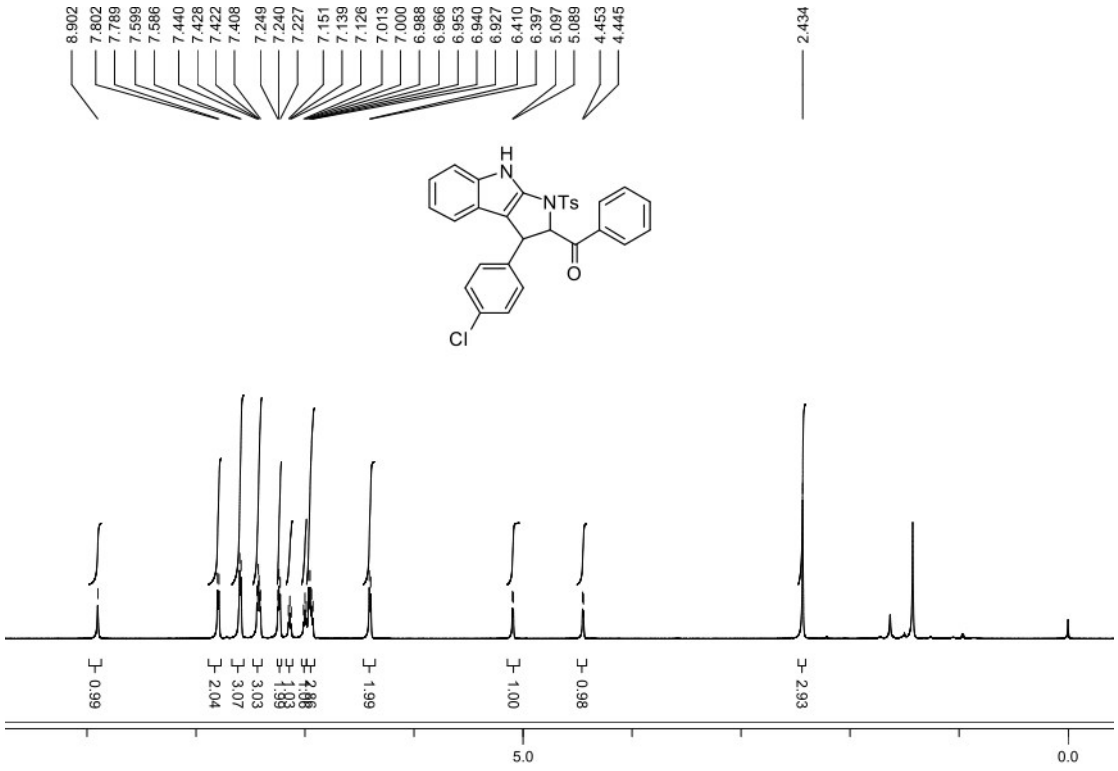


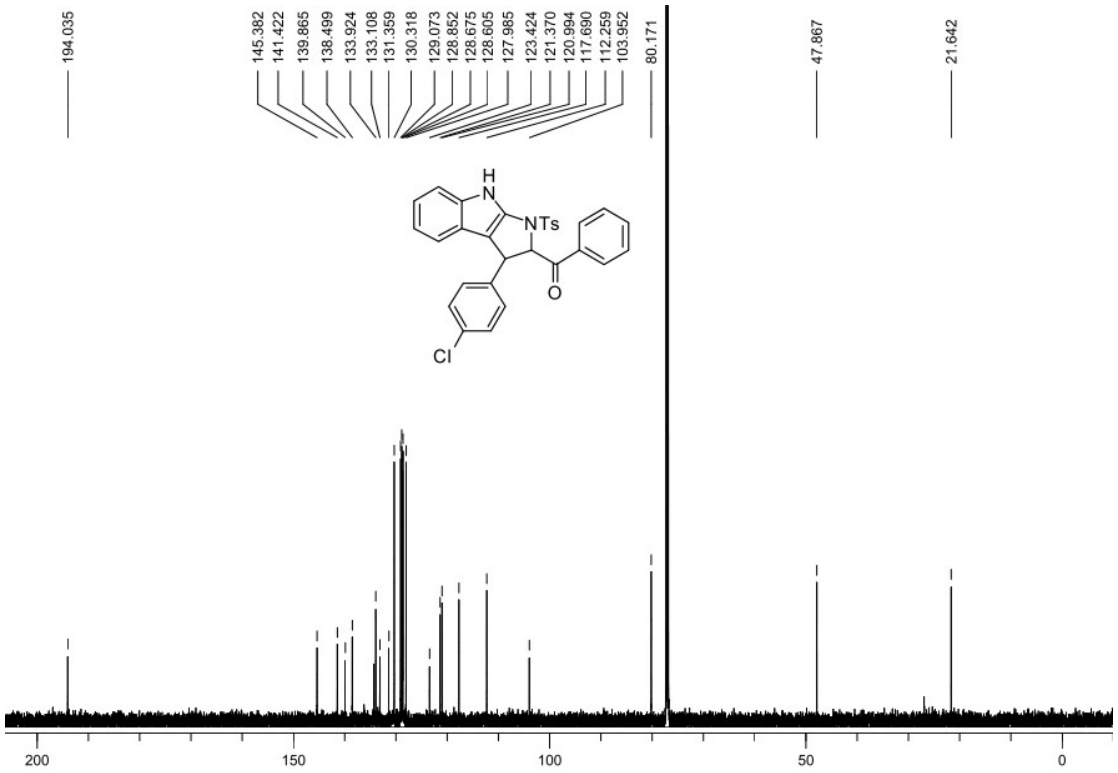
^{1}H NMR and ^{13}C NMR spectrum of **3b**



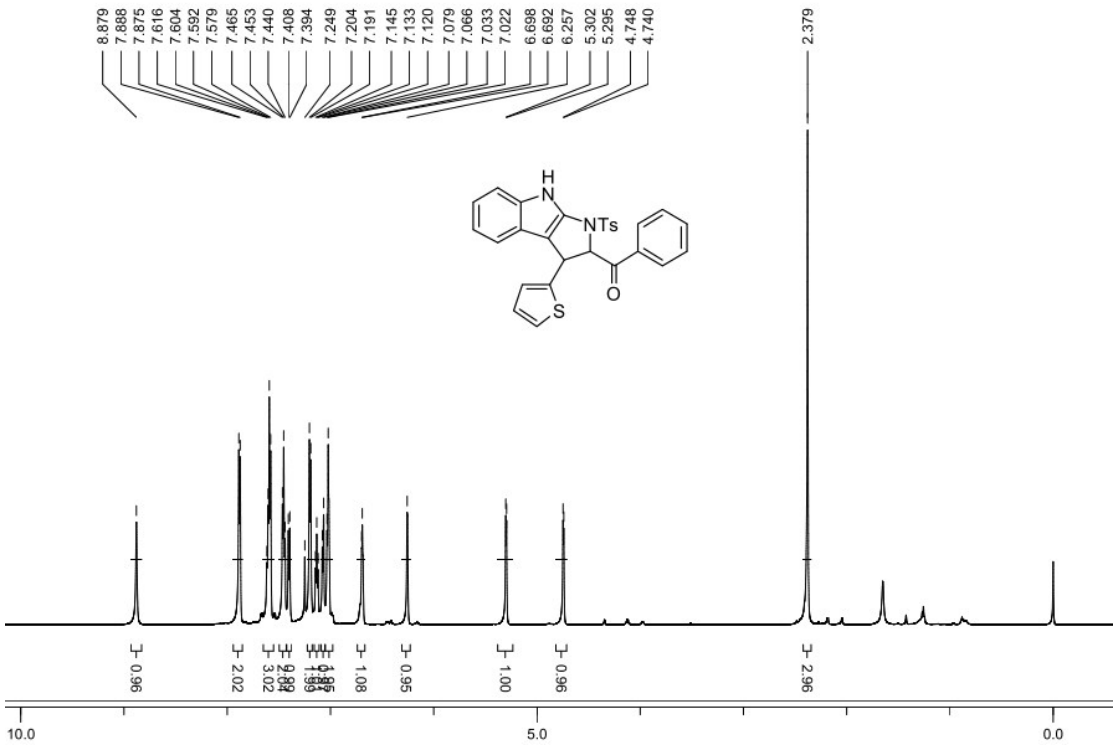


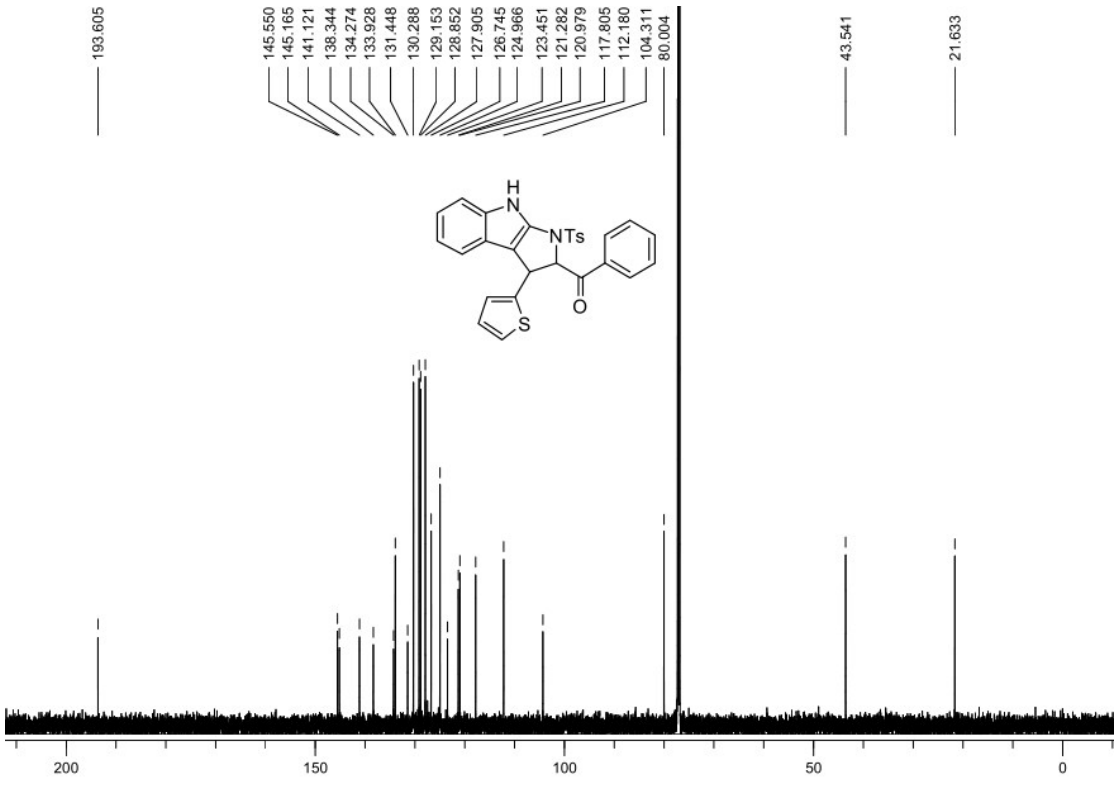
^{1}H NMR and ^{13}C NMR spectrum of **3c**



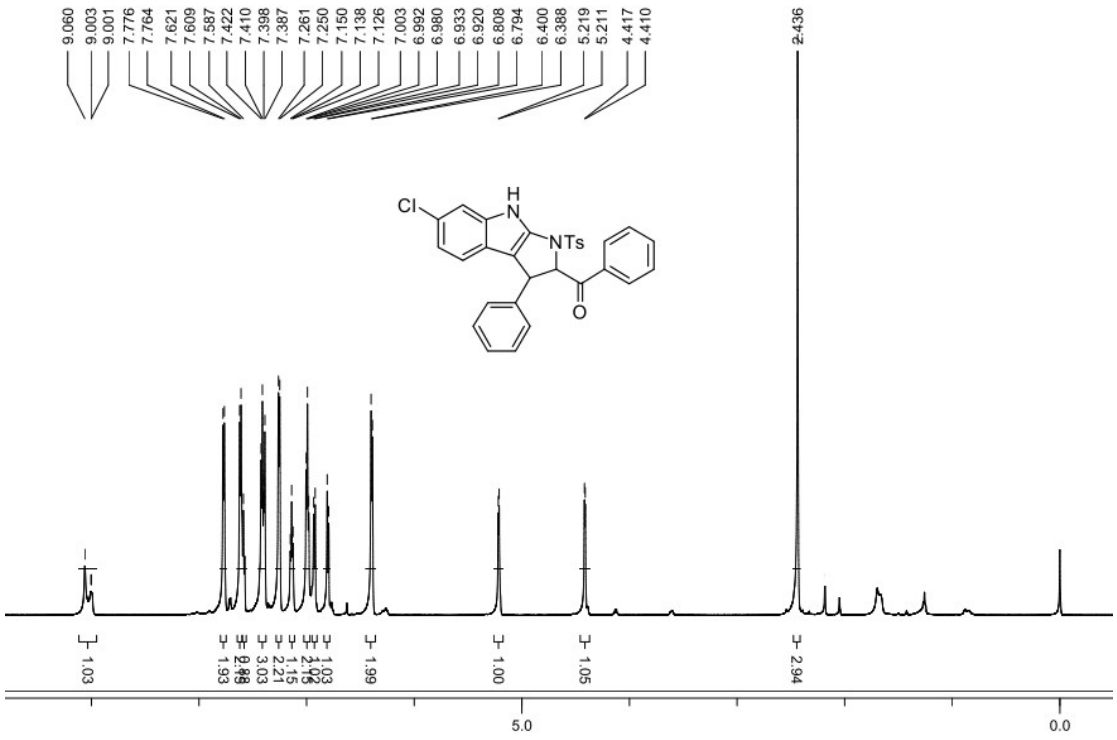


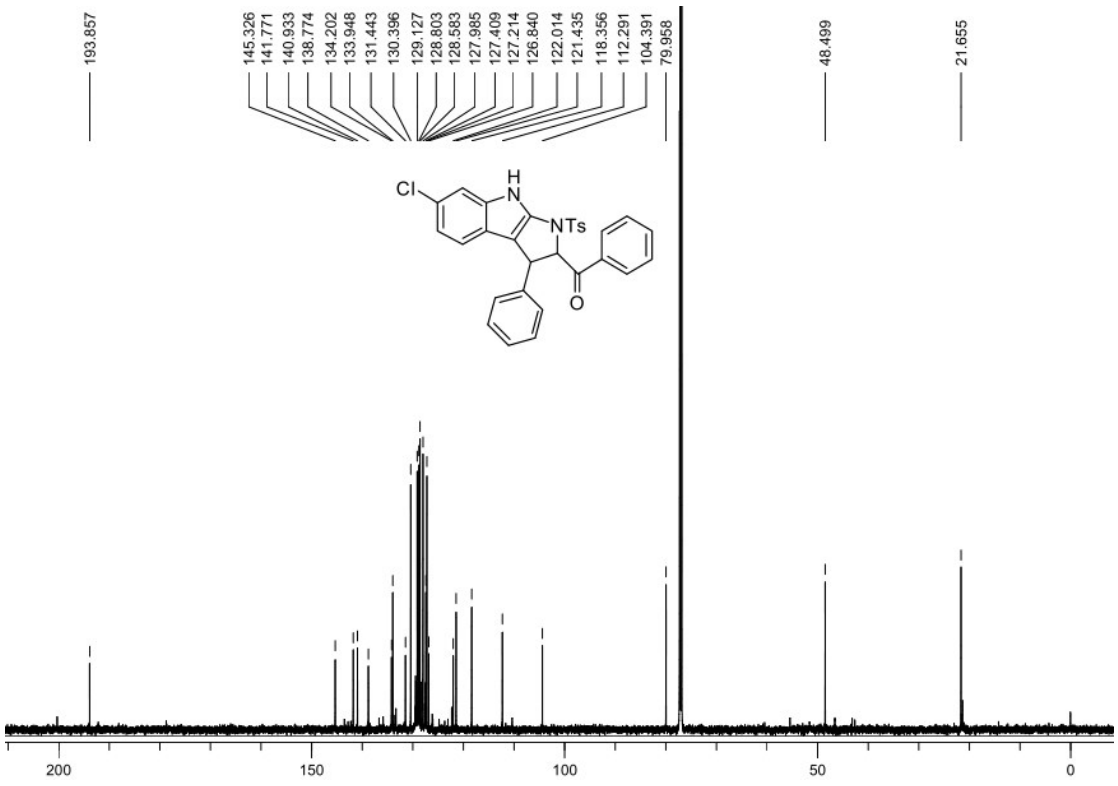
^{1}H NMR and ^{13}C NMR spectrum of **3d**



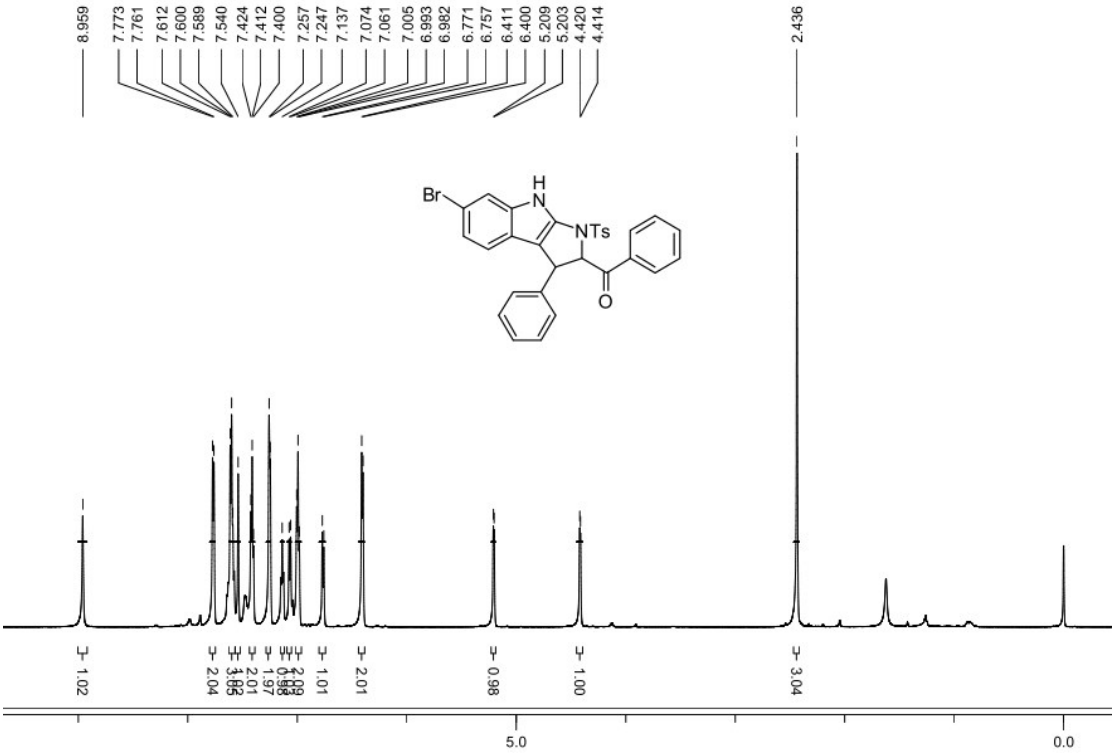


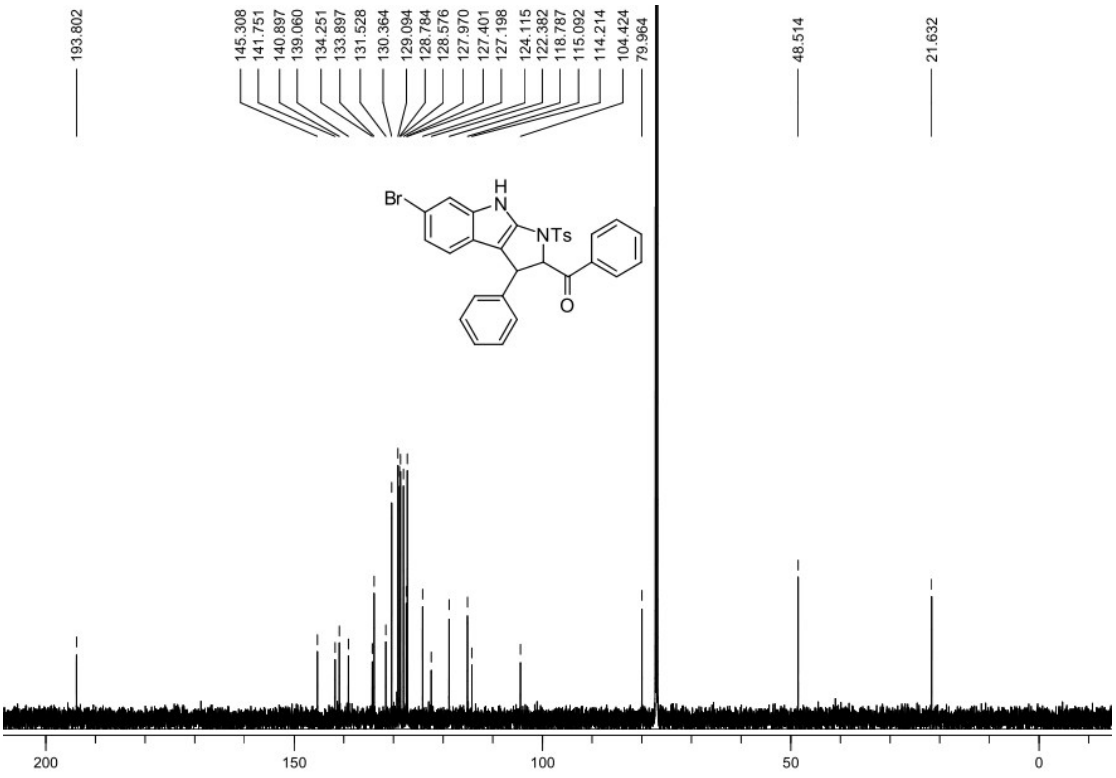
^{1}H NMR and ^{13}C NMR spectrum of **3e**



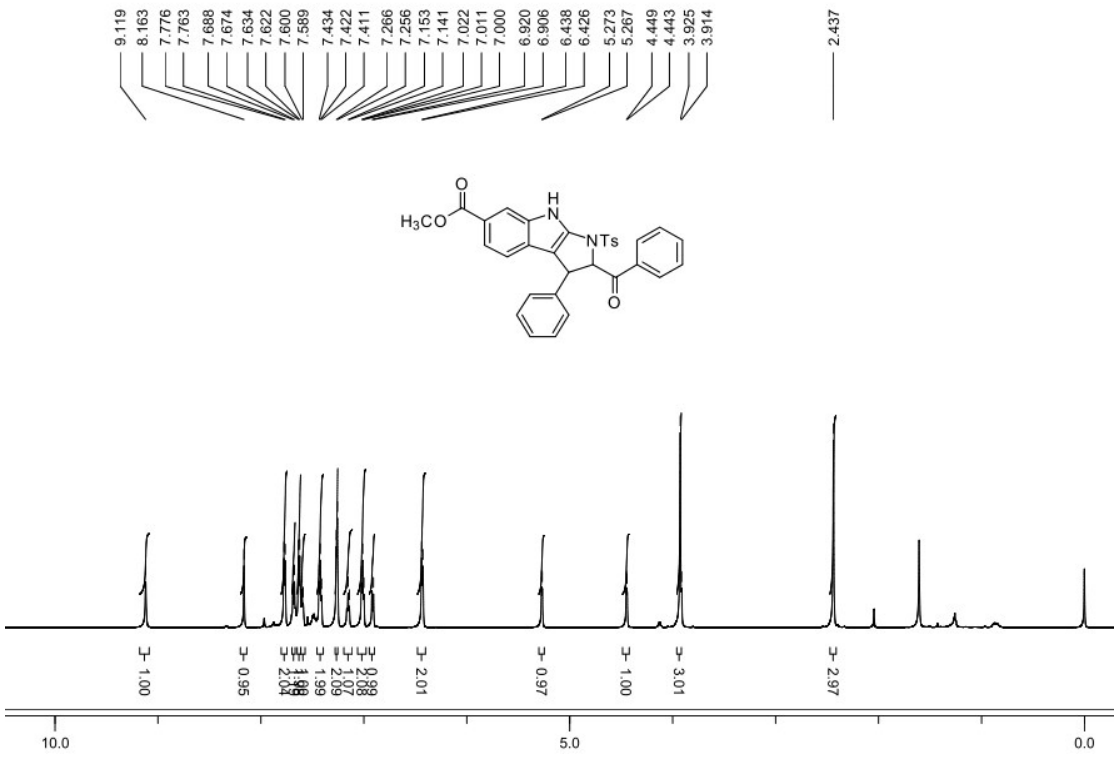


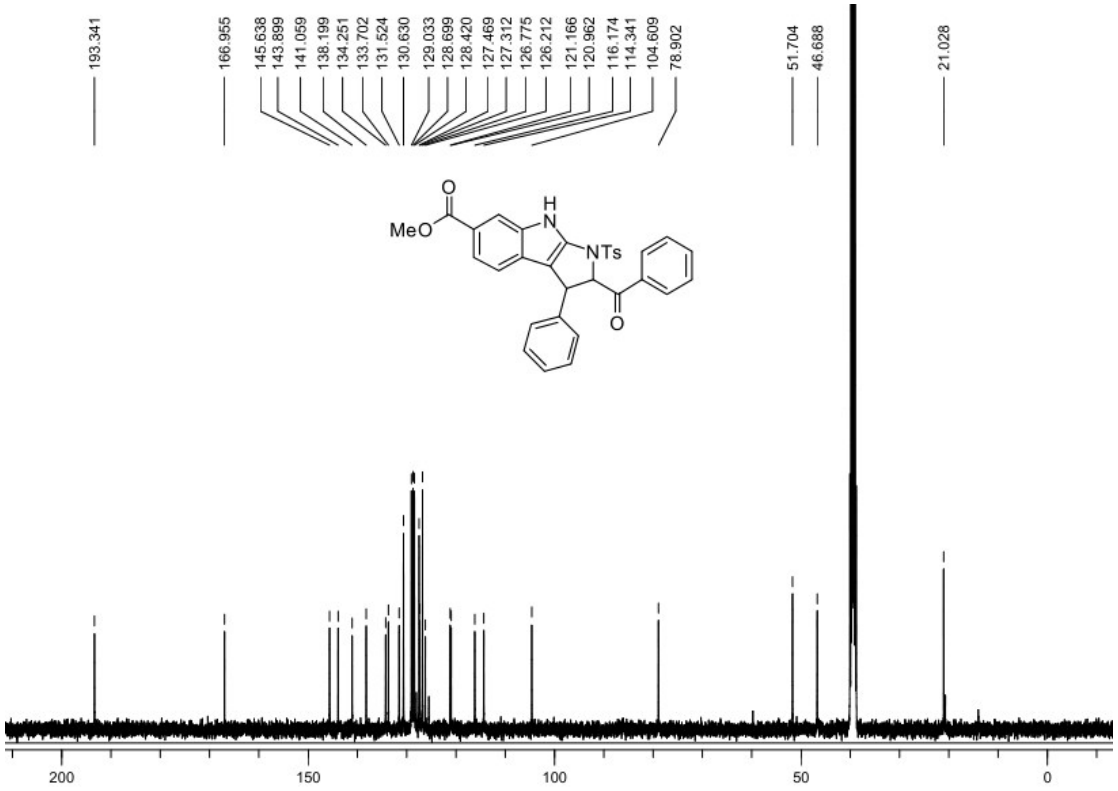
^{1}H NMR and ^{13}C NMR spectrum of **3f**



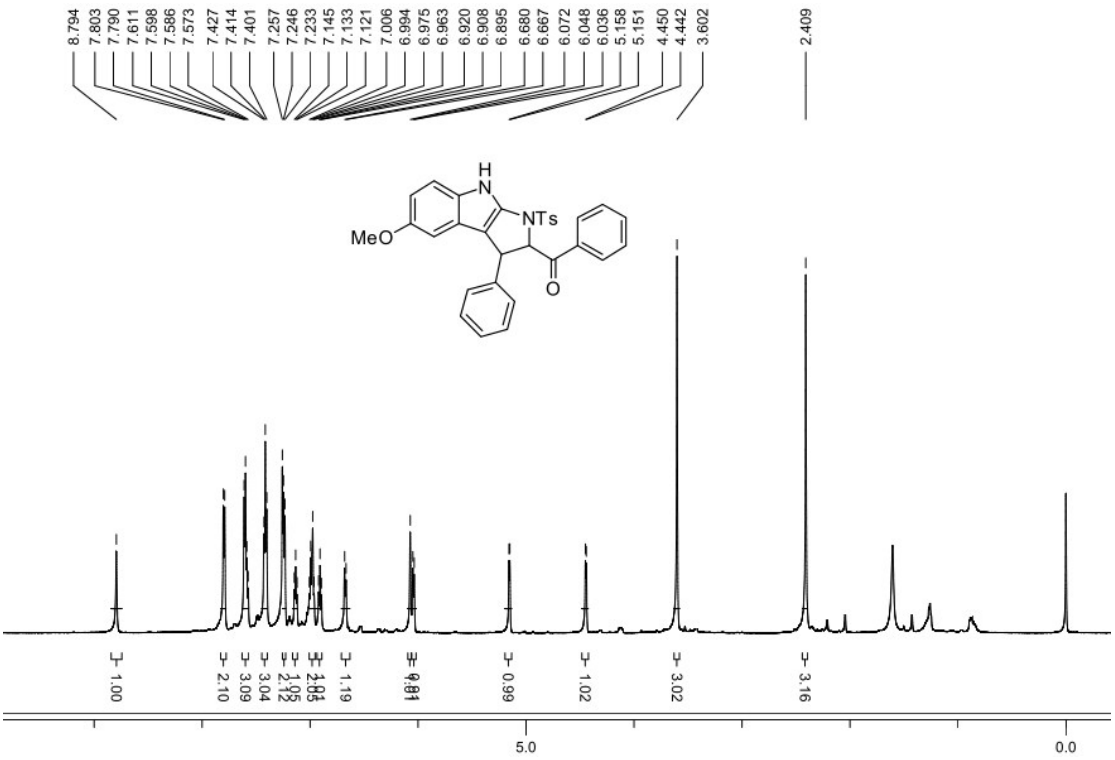


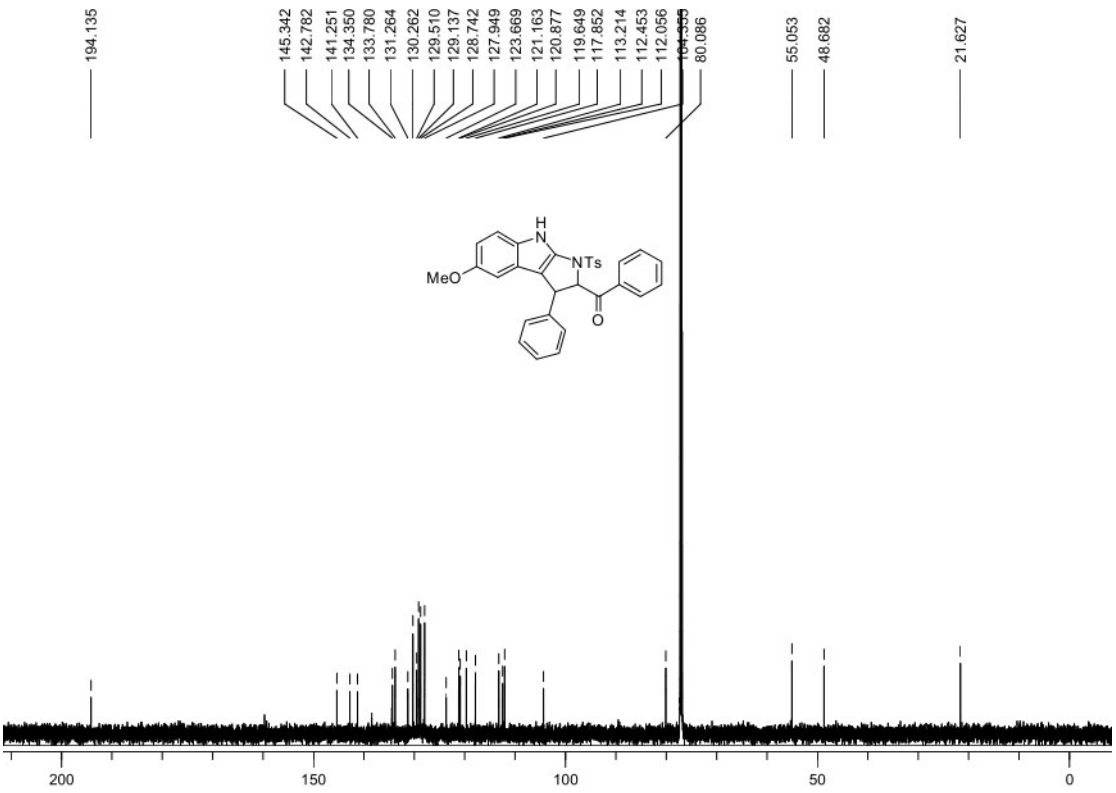
^{1}H NMR and ^{13}C NMR spectrum of **3g**



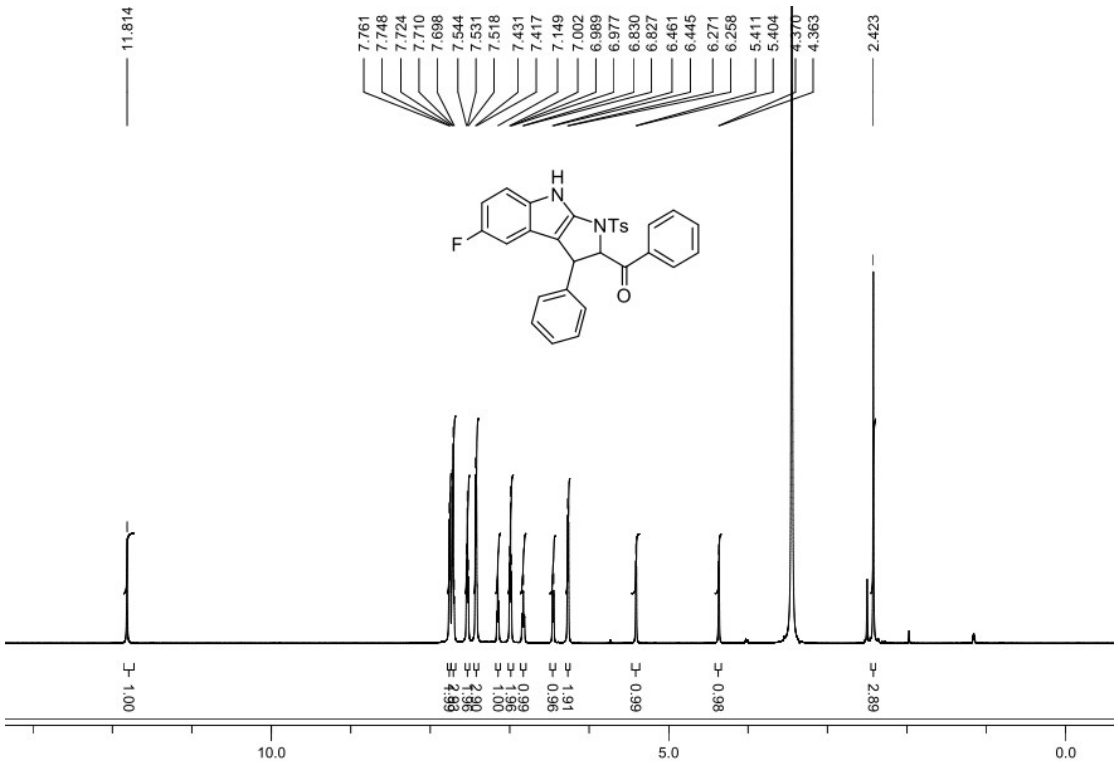


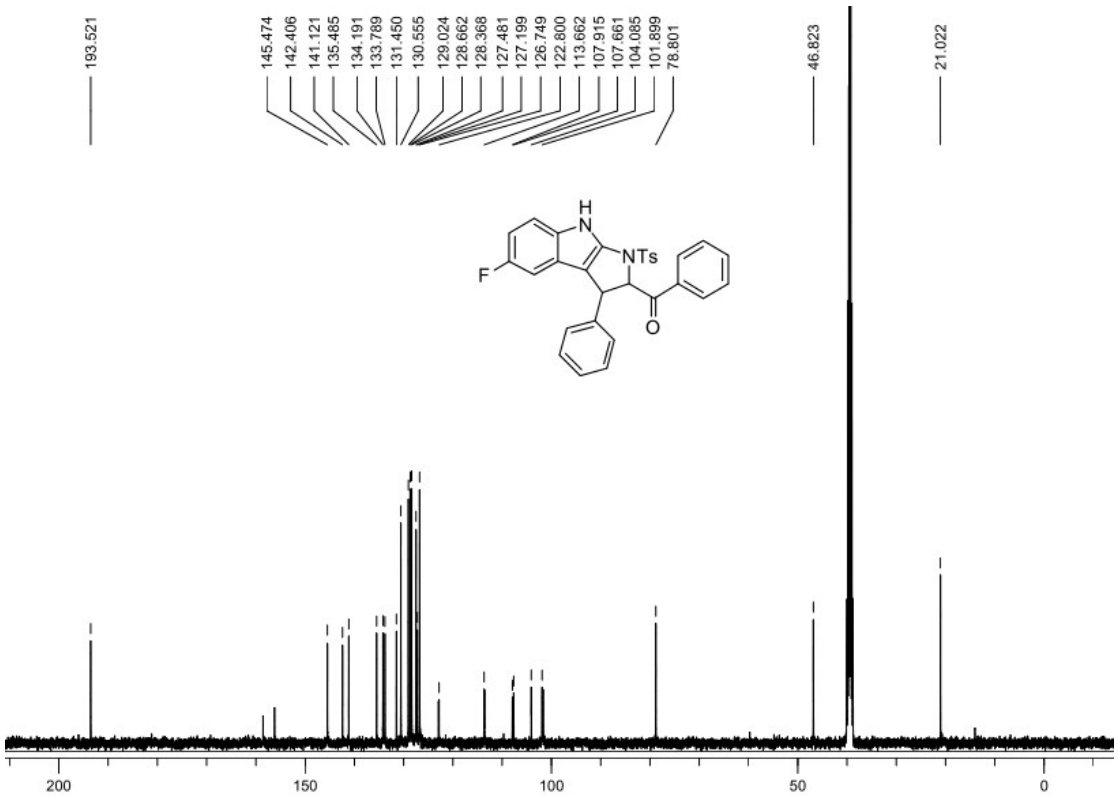
^{1}H NMR and ^{13}C NMR spectrum of **3h**



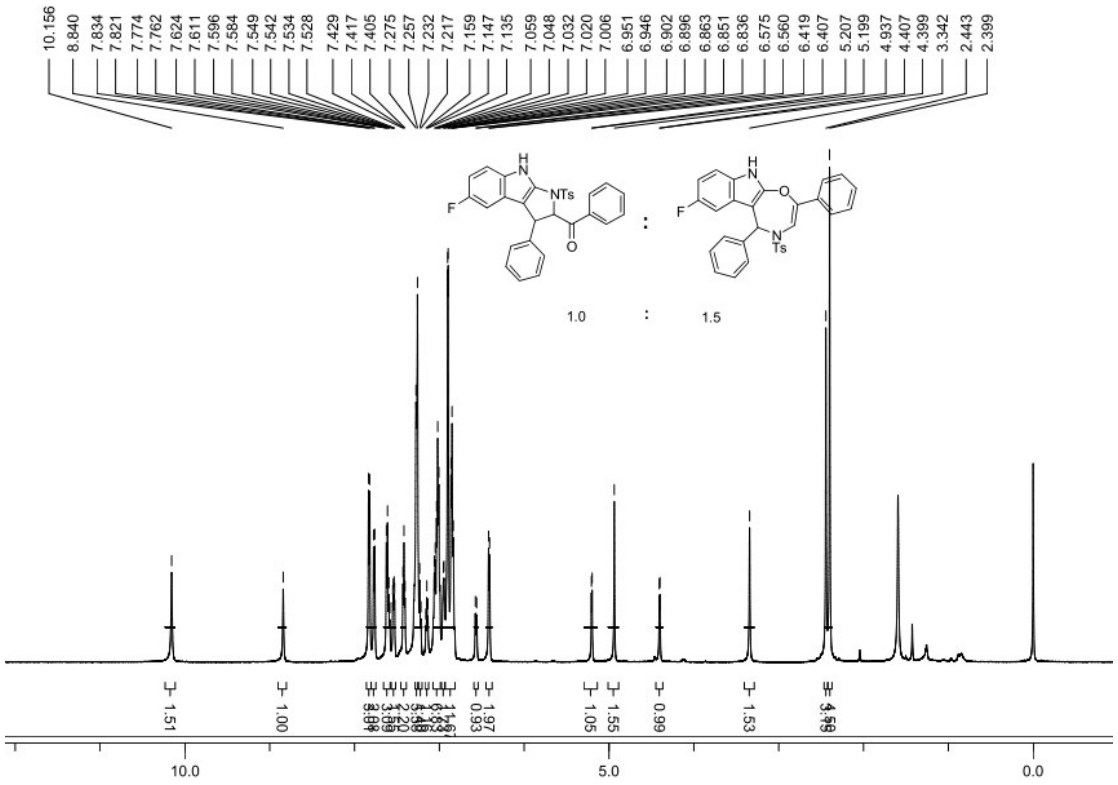


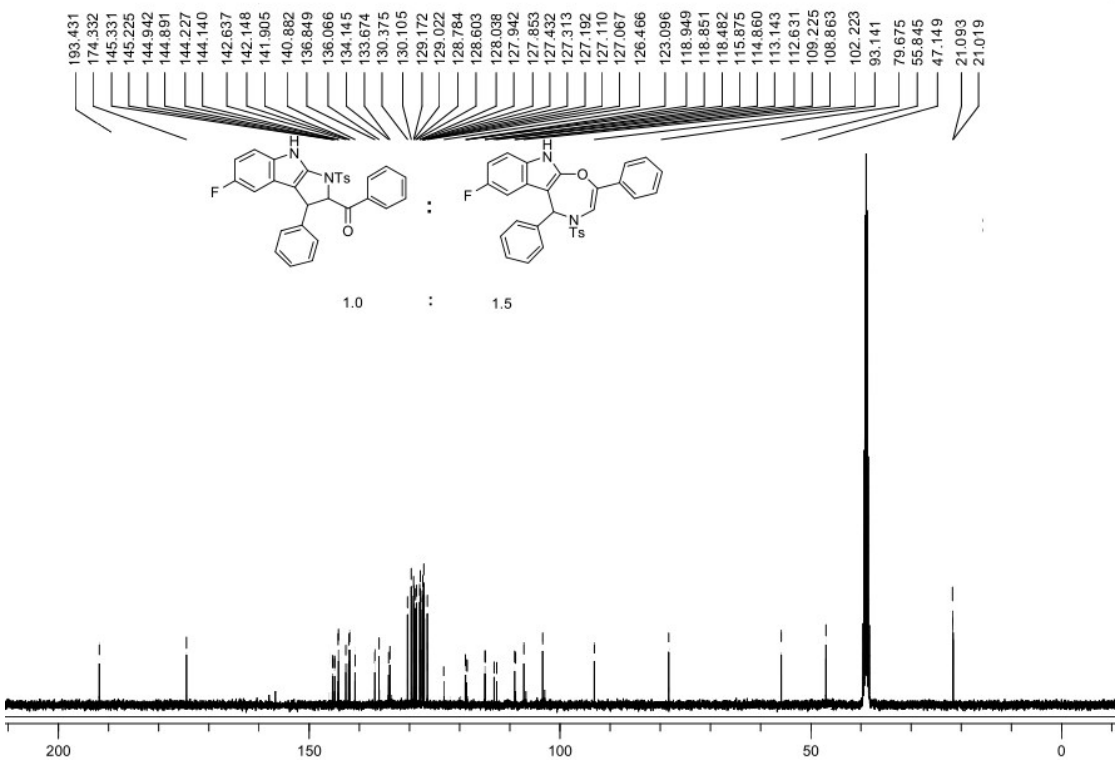
^{1}H NMR and ^{13}C NMR spectrum of **3i**



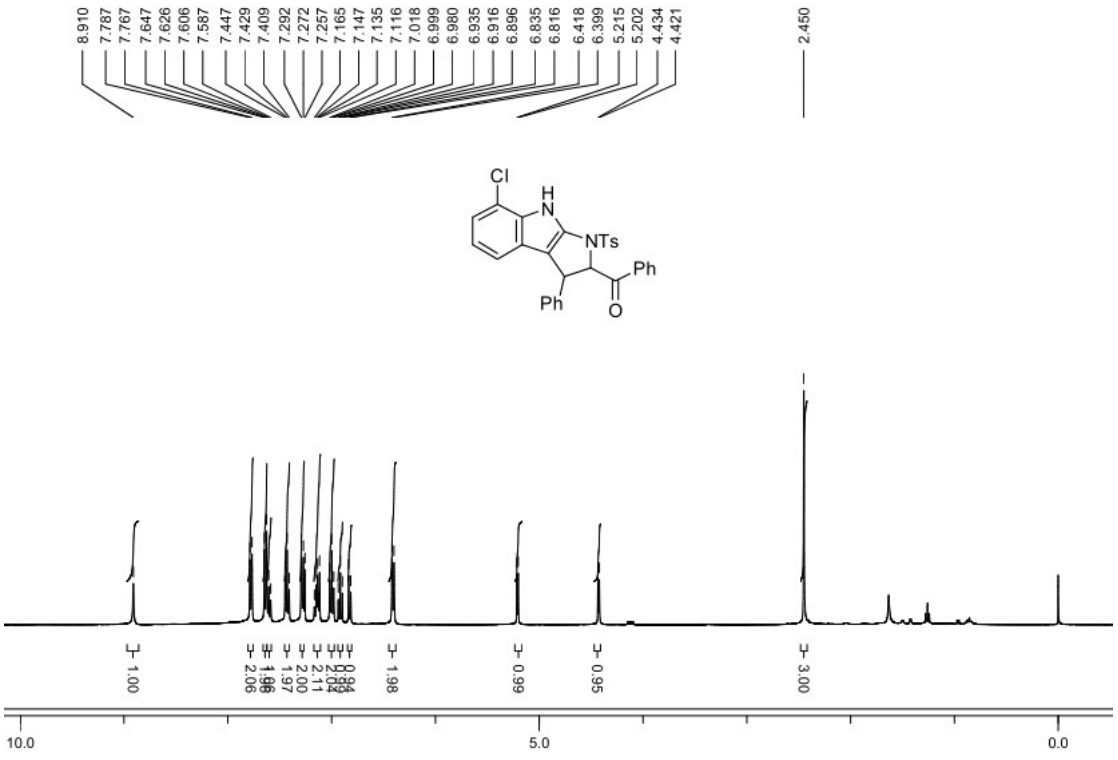


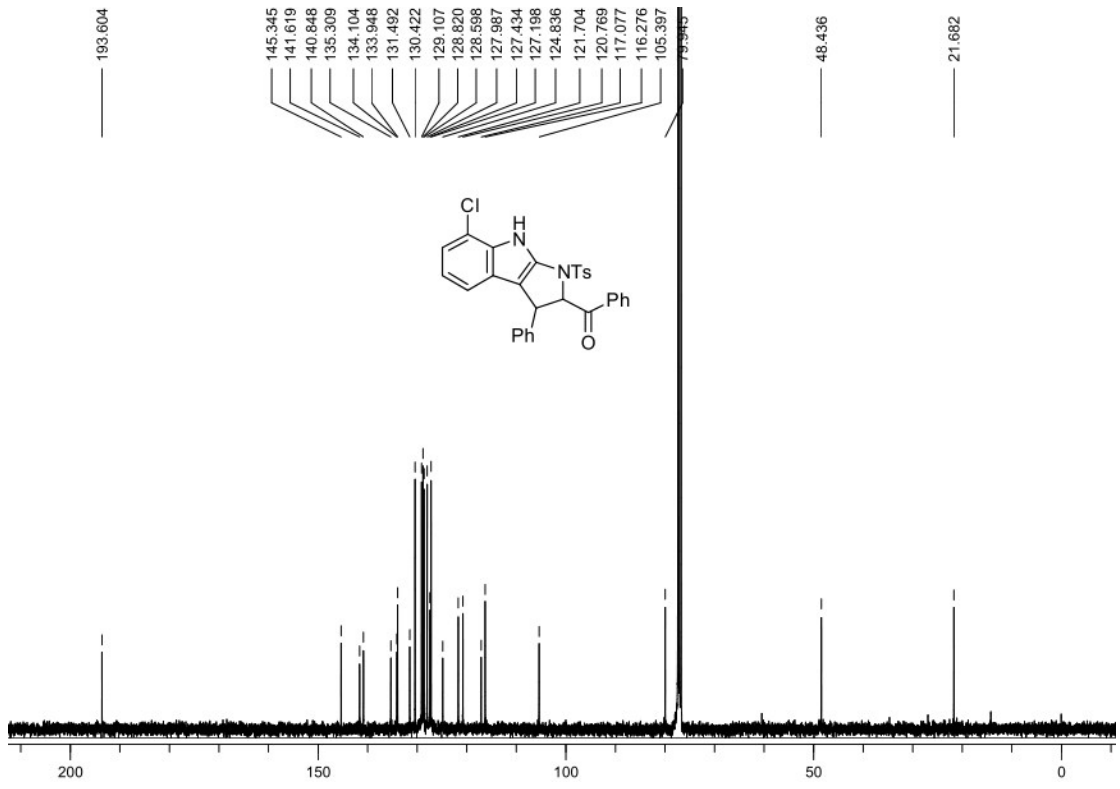
^{1}H NMR and ^{13}C NMR spectrum of **3i** + **4i**



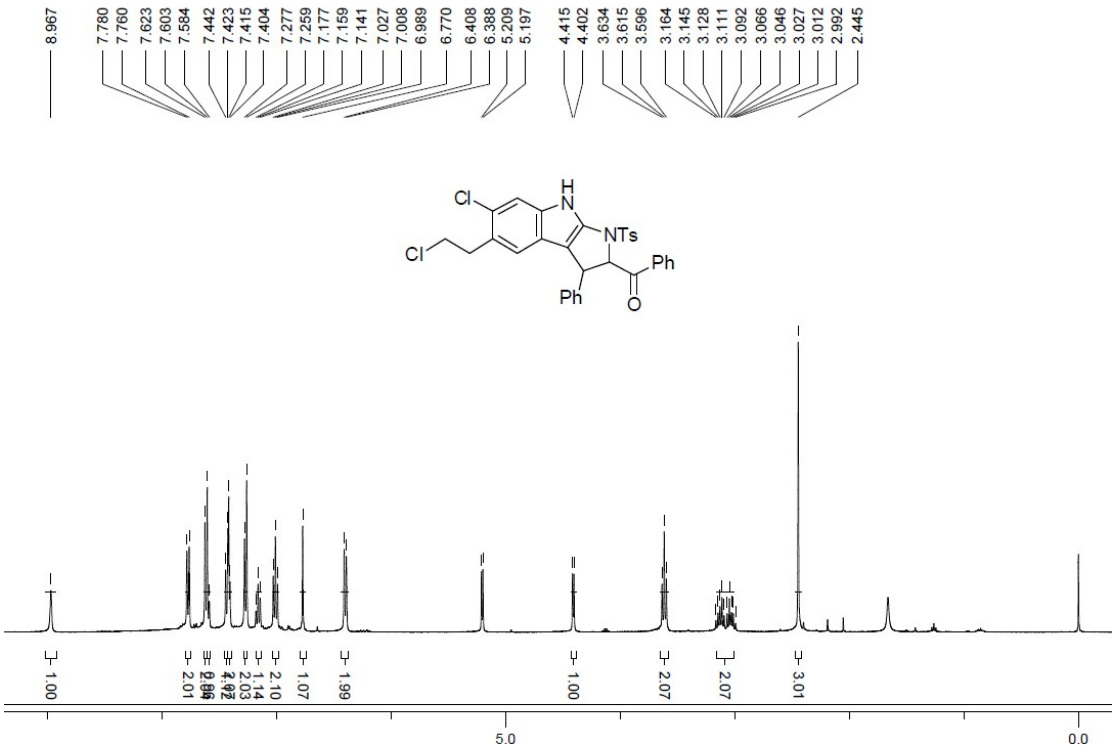


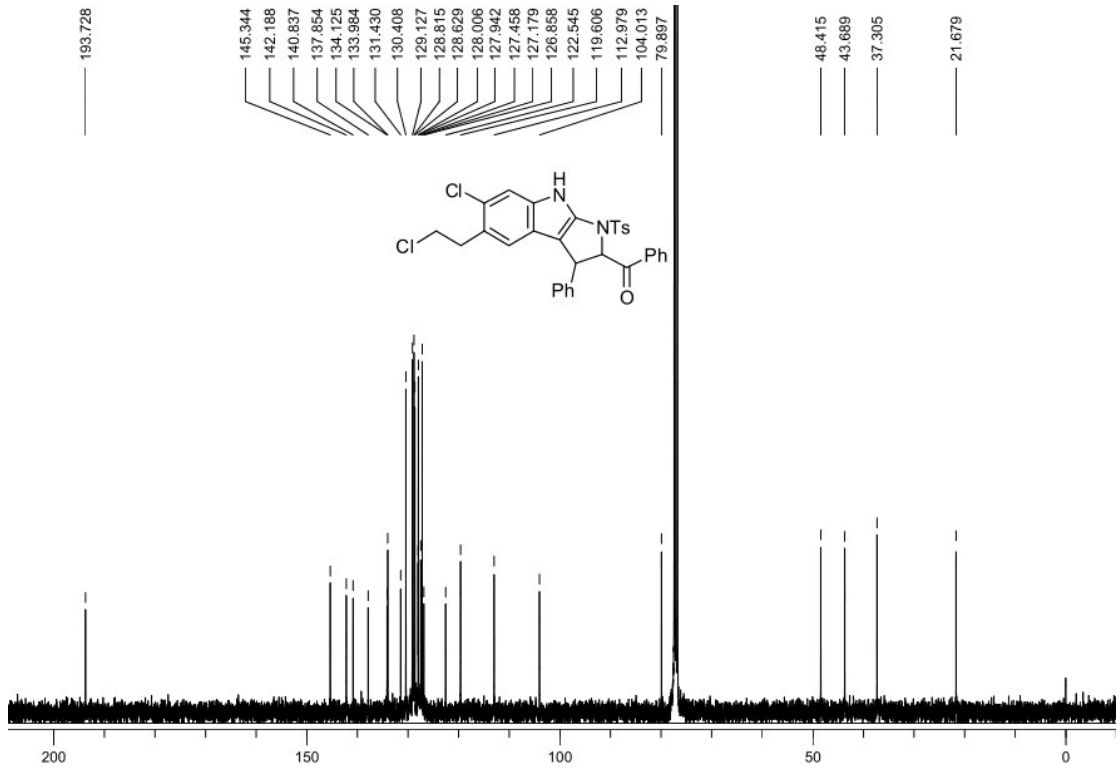
^{1}H NMR and ^{13}C NMR spectrum of **3j**



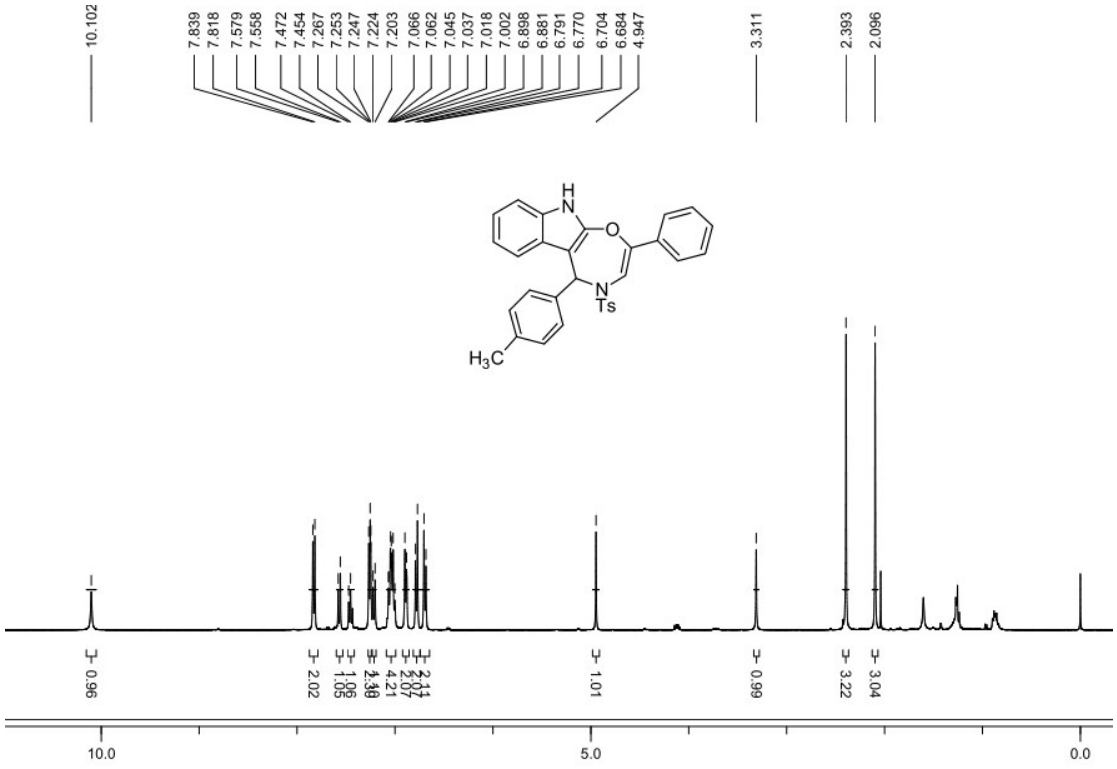


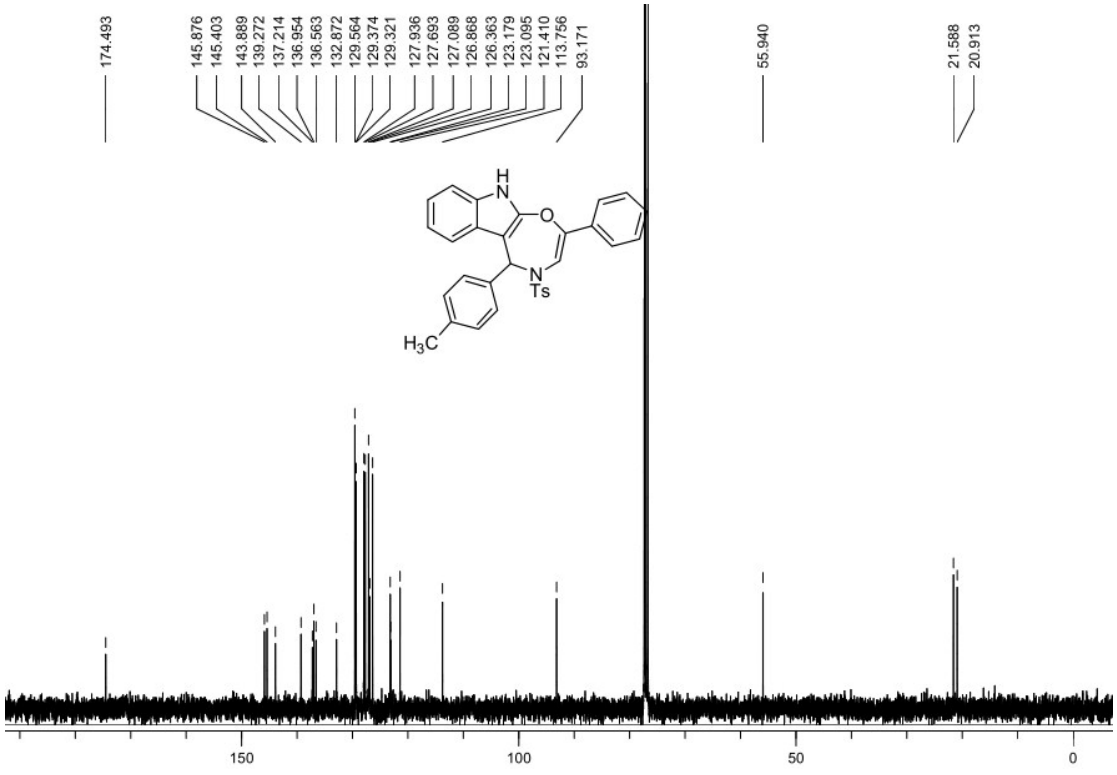
^{1}H NMR and ^{13}C NMR spectrum of **3k**



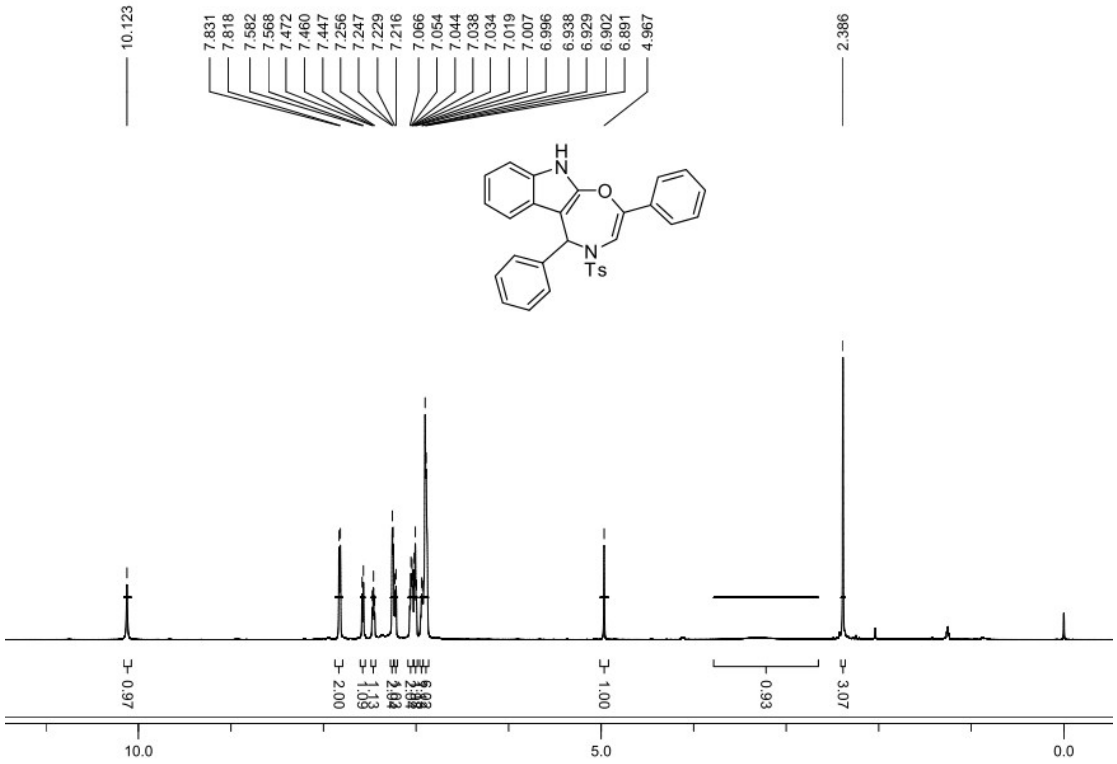


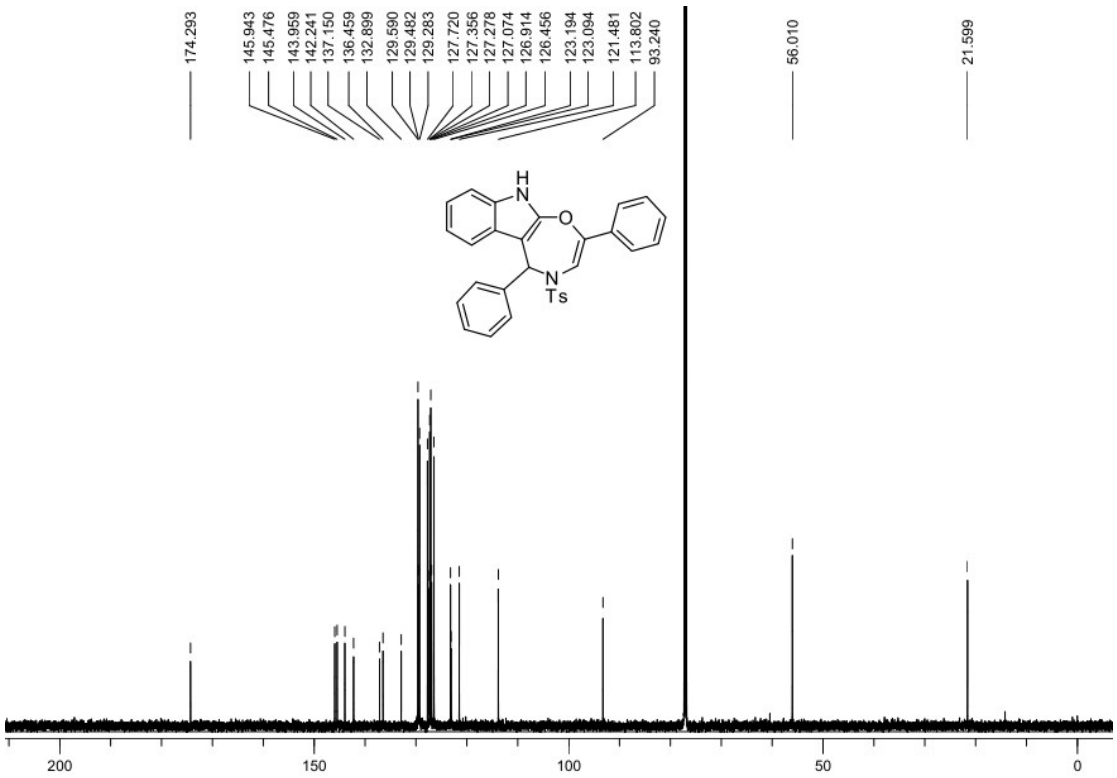
^{1}H NMR and ^{13}C NMR spectrum of **4a**



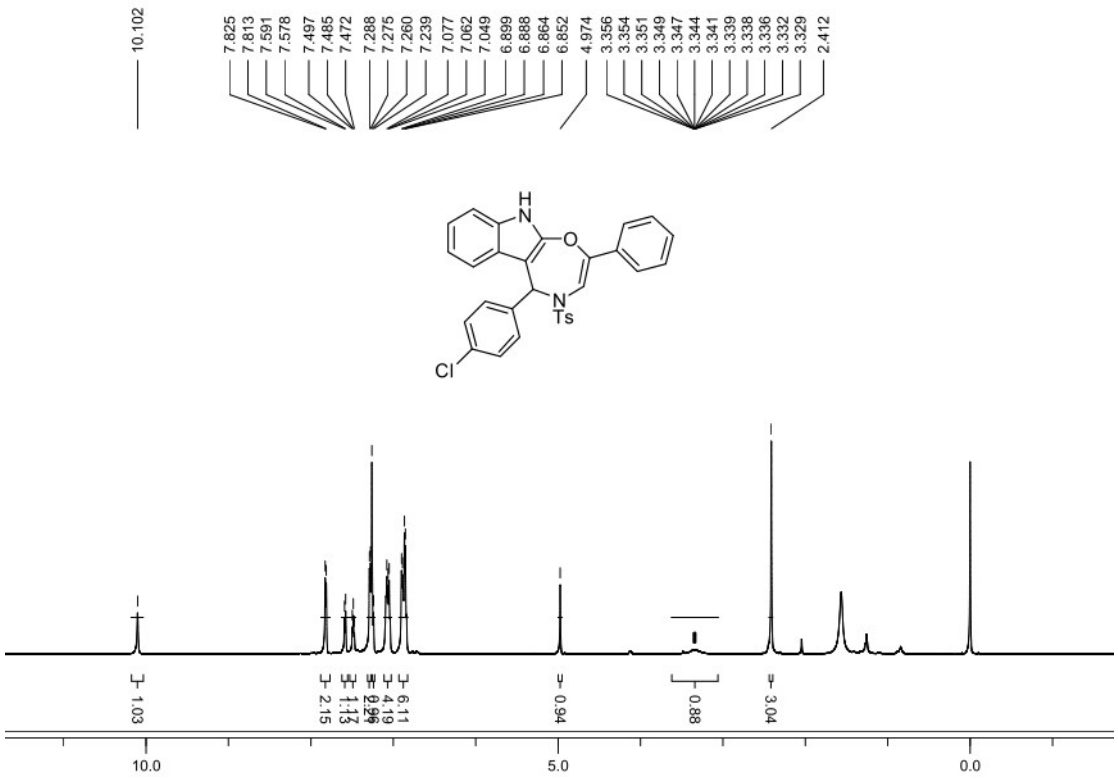


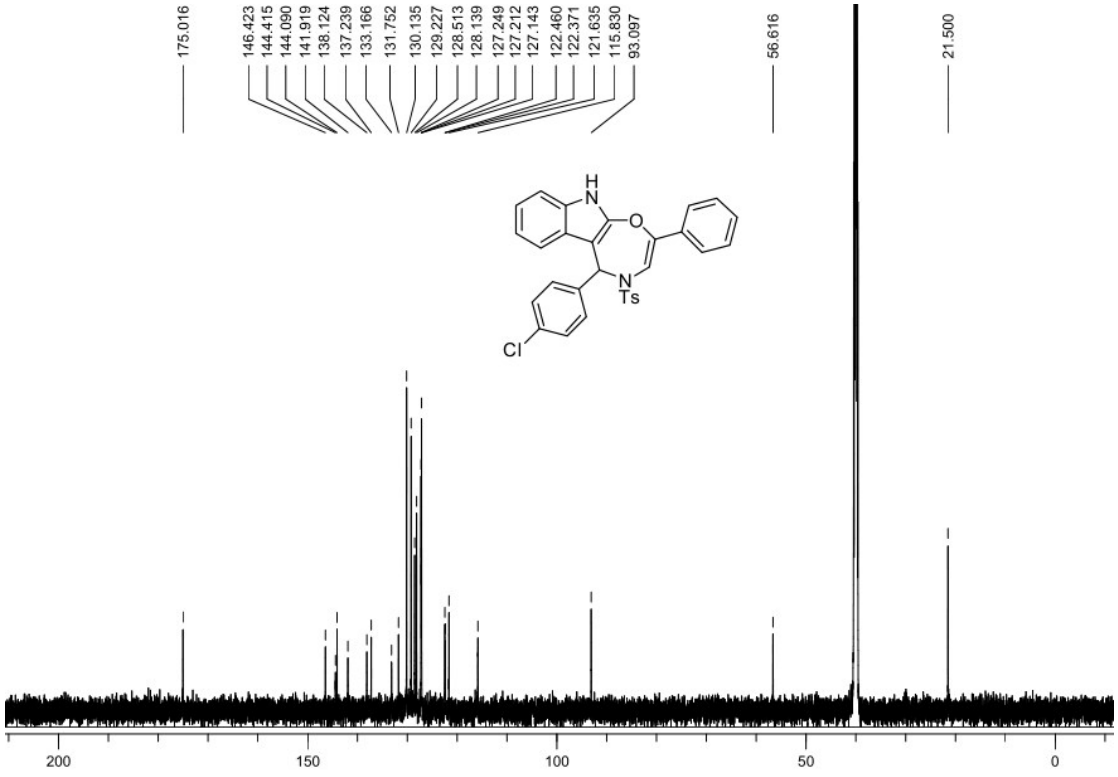
^{1}H NMR and ^{13}C NMR spectrum of **4b**



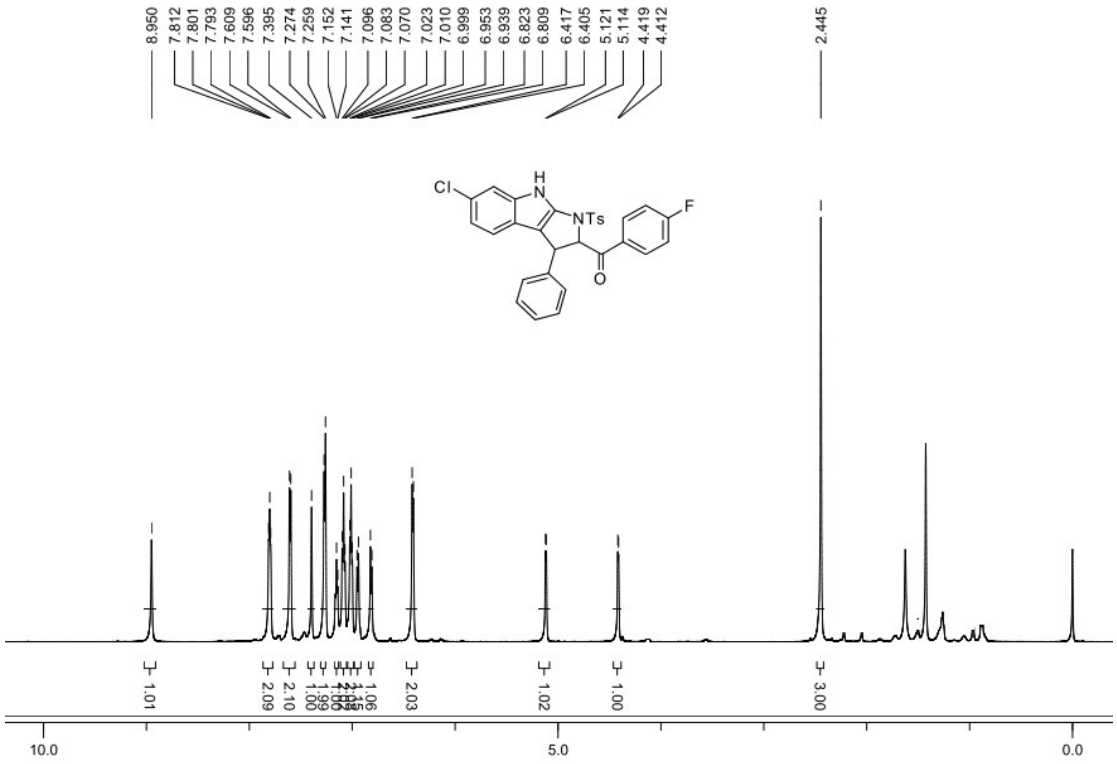


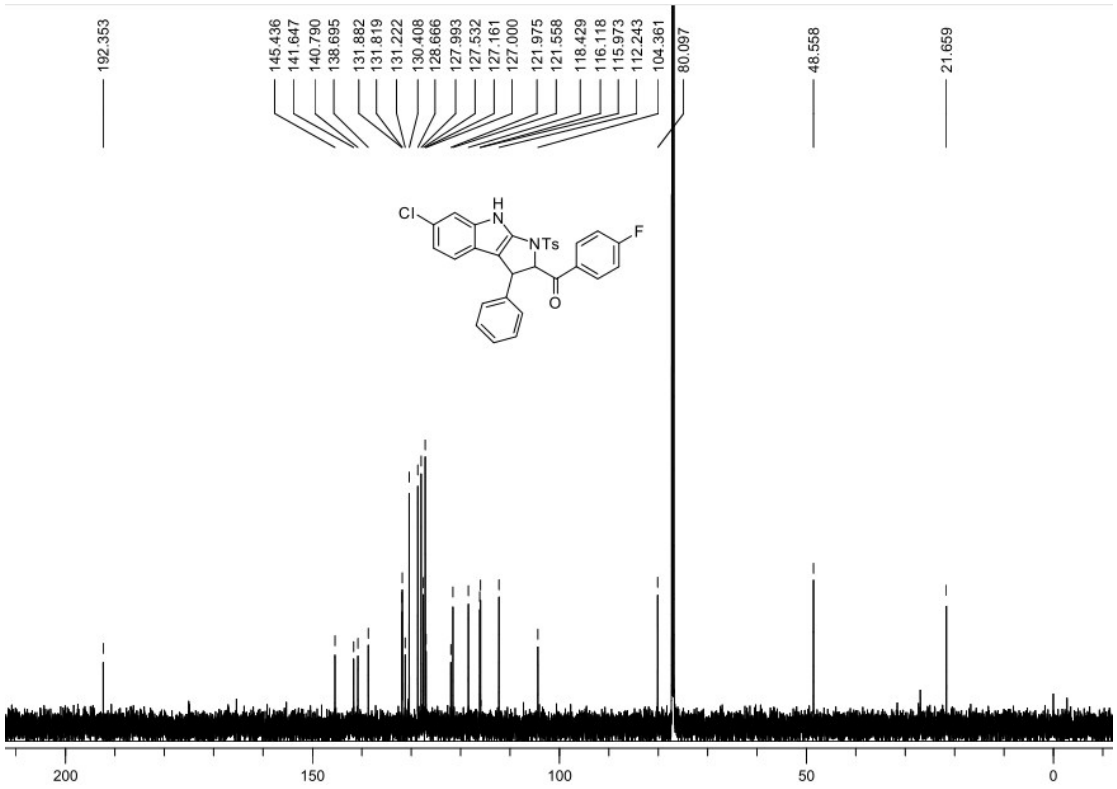
^{1}H NMR and ^{13}C NMR spectrum of **4c**



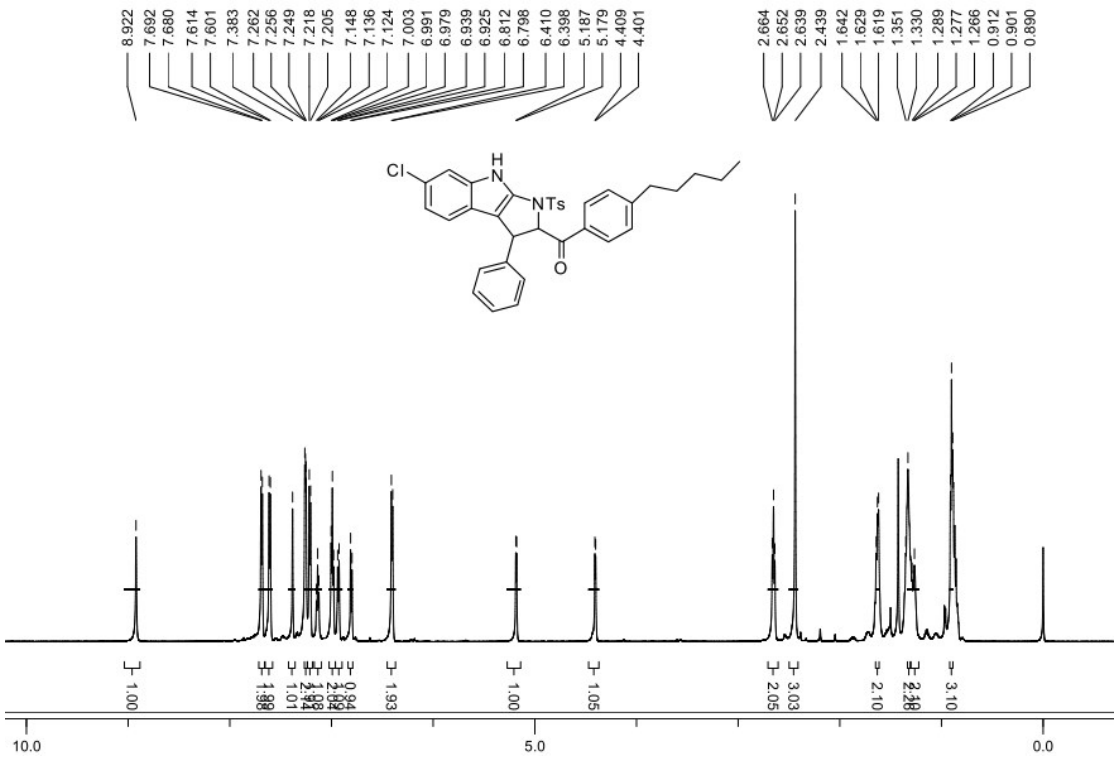


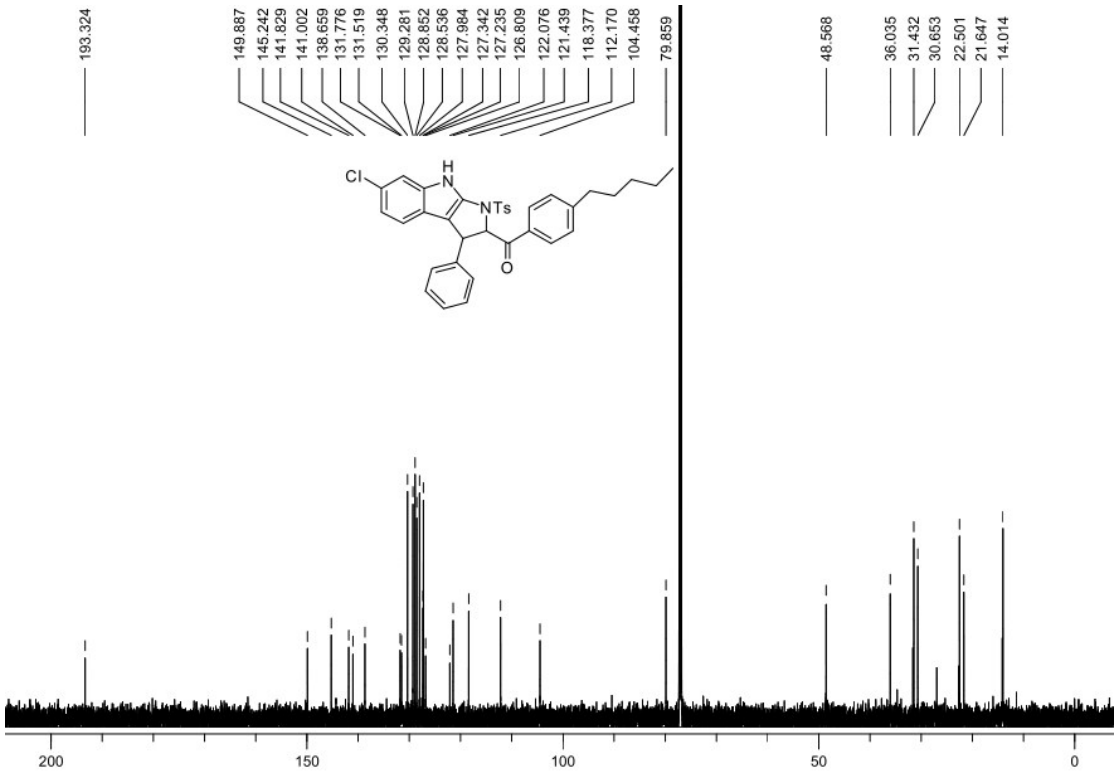
^{1}H NMR and ^{13}C NMR spectrum of **5a**



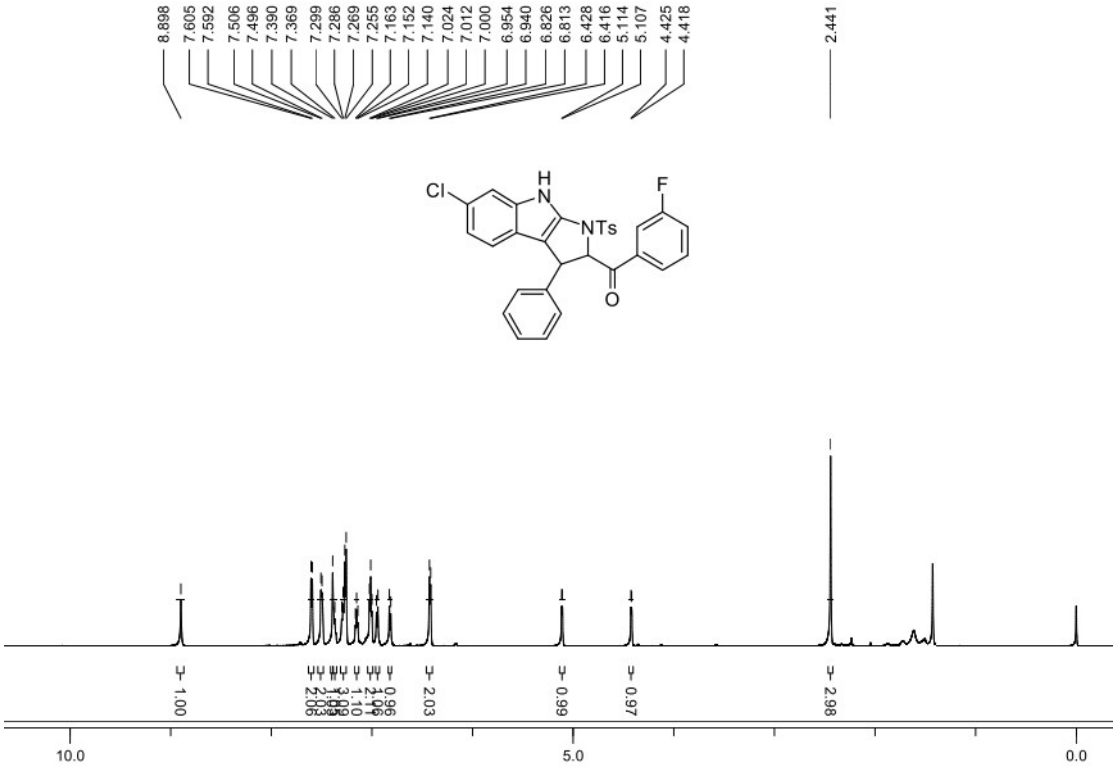


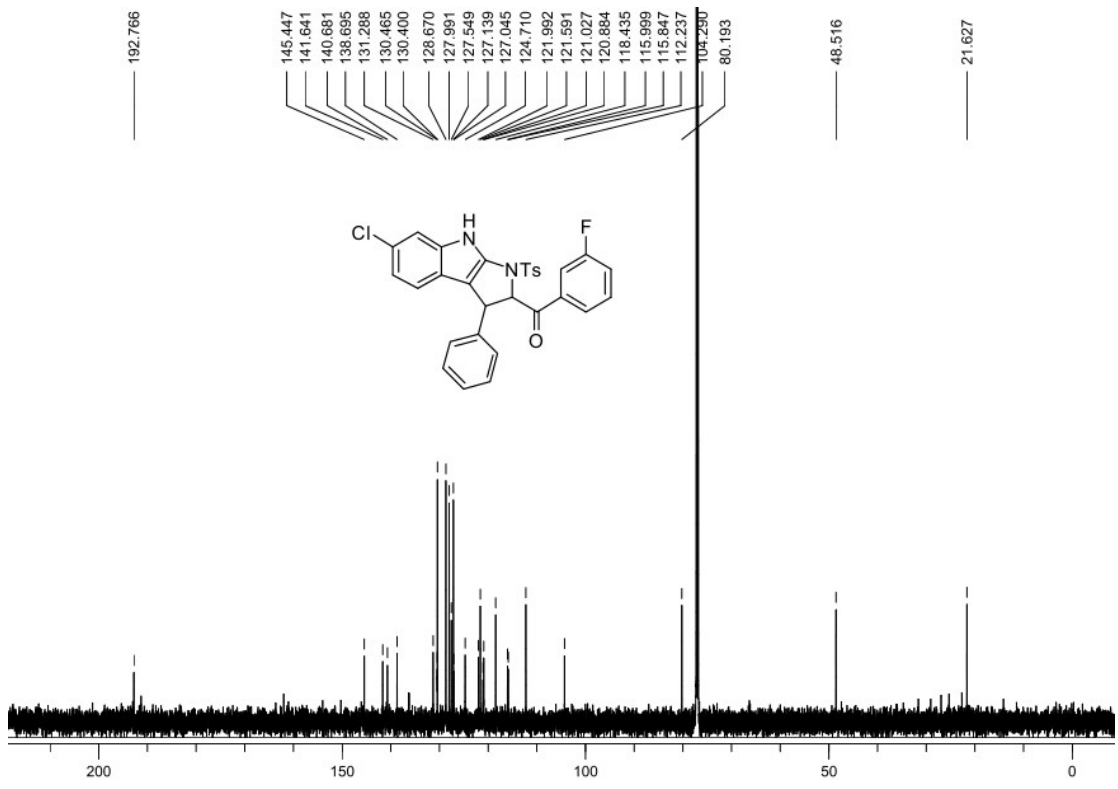
^{1}H NMR and ^{13}C NMR spectrum of **5b**



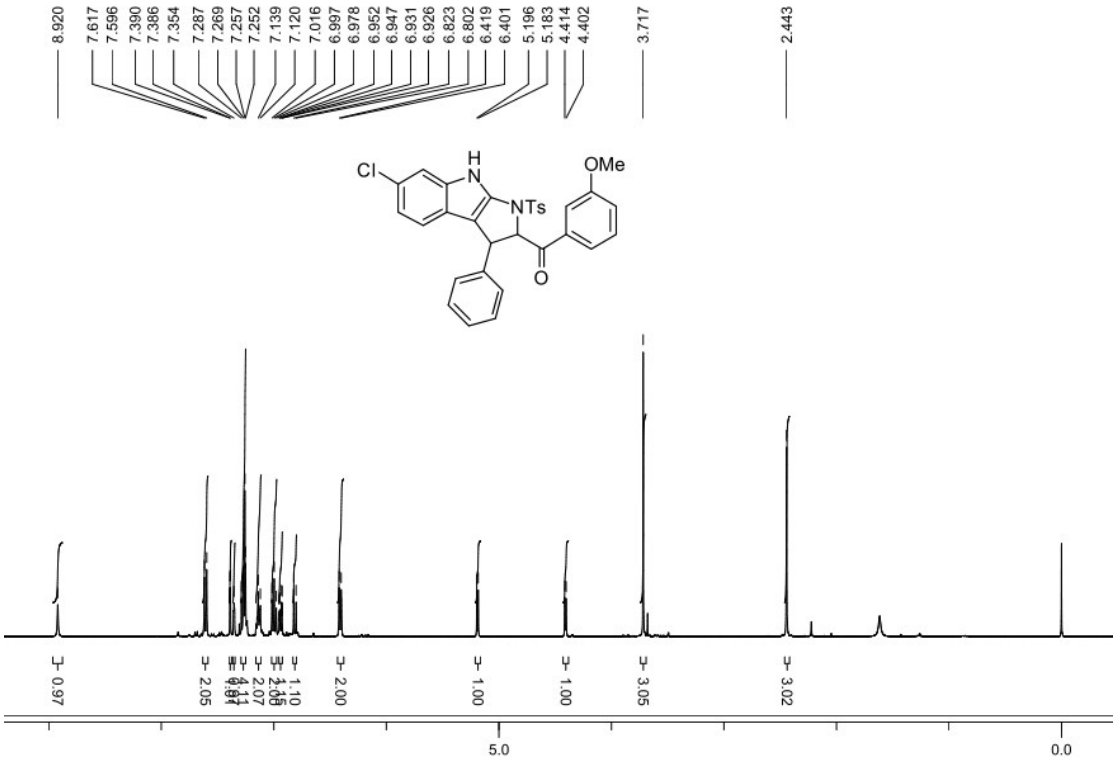


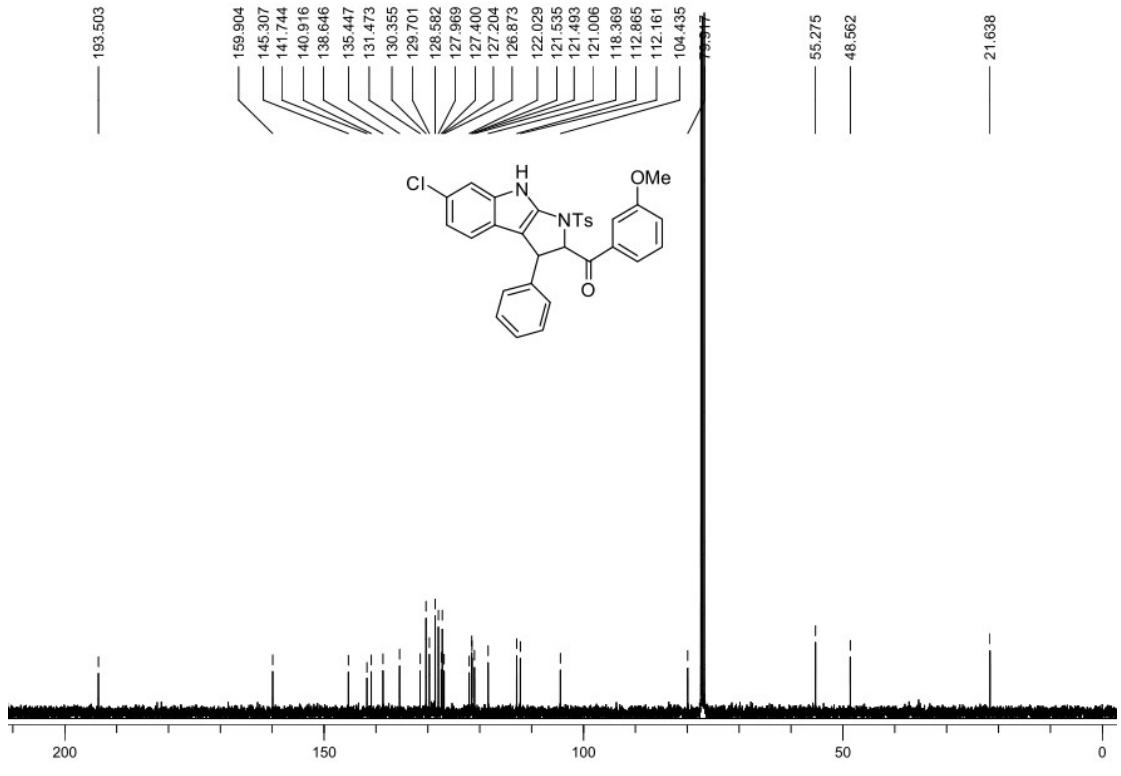
^{1}H NMR and ^{13}C NMR spectrum of **5c**



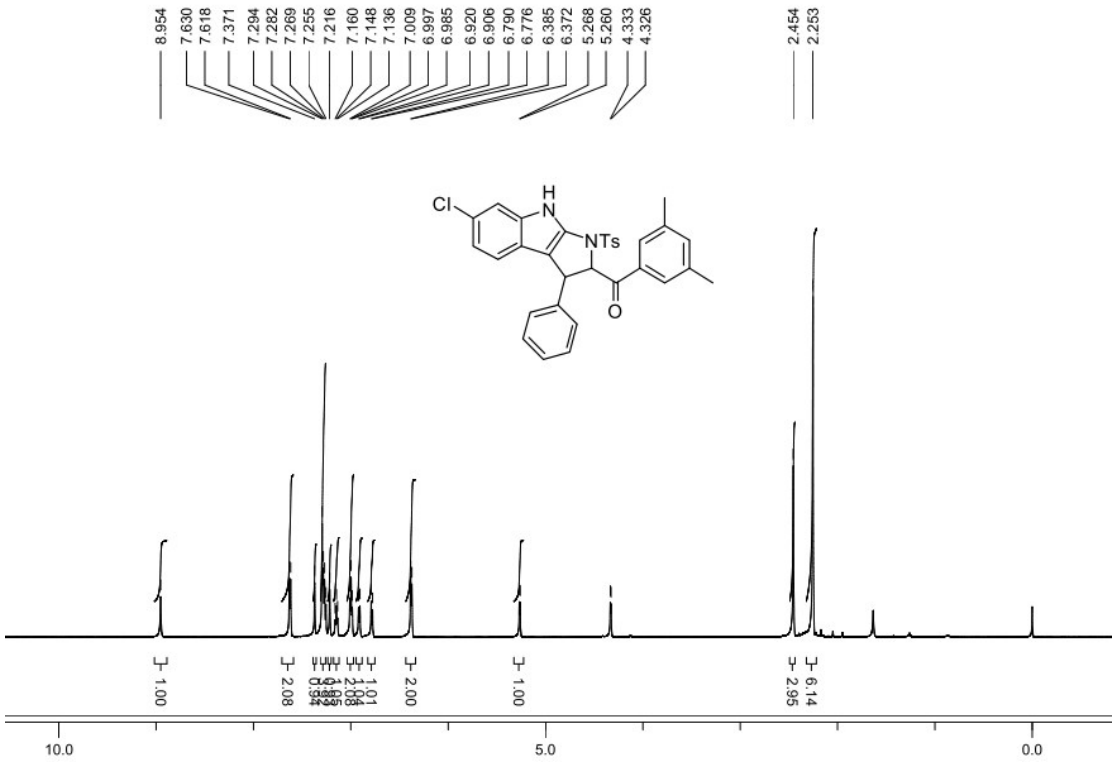


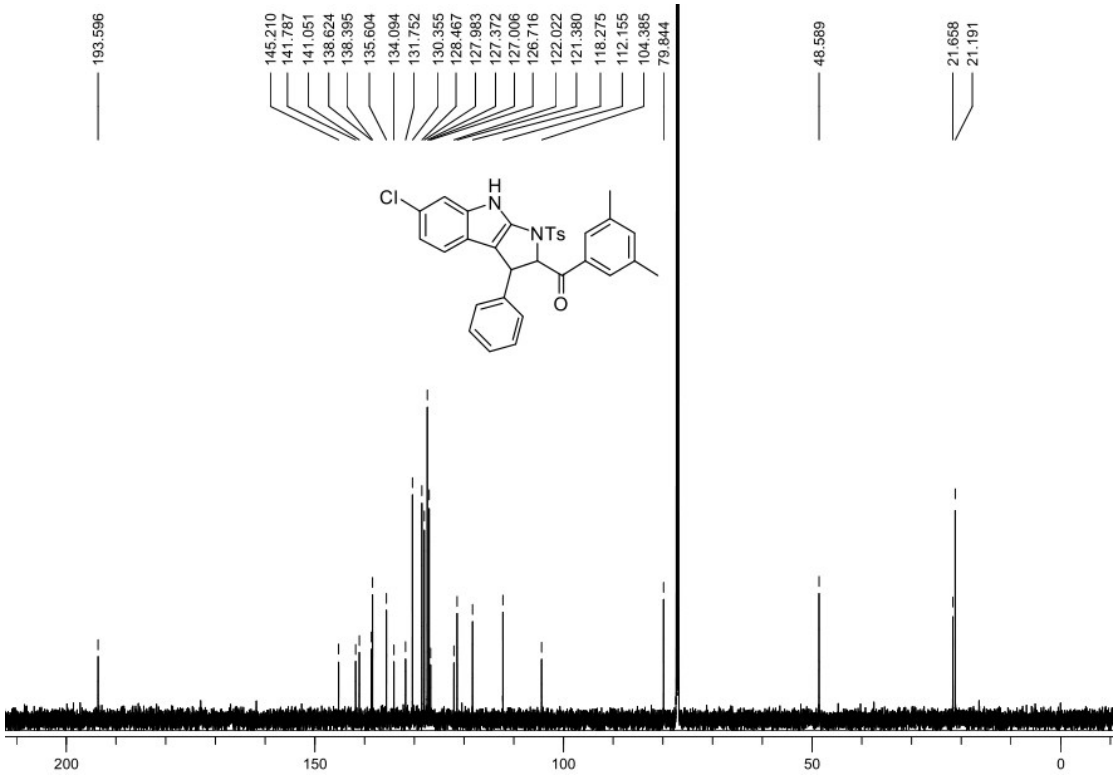
^{1}H NMR and ^{13}C NMR spectrum of **5d**



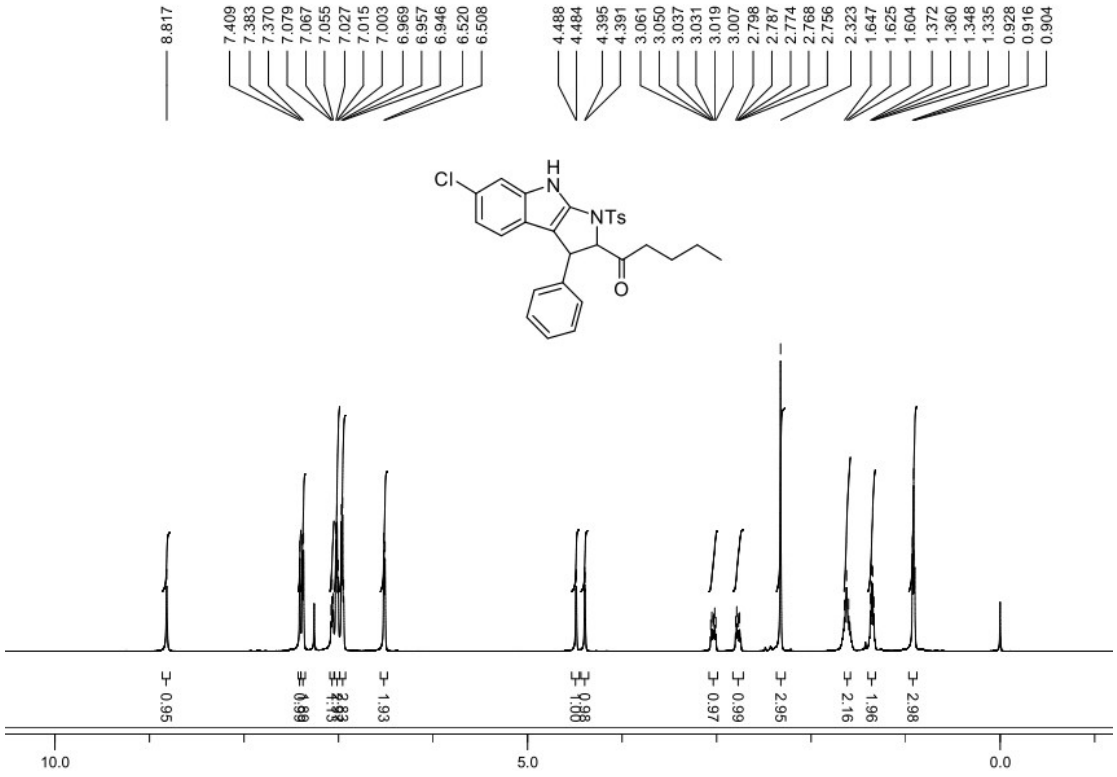


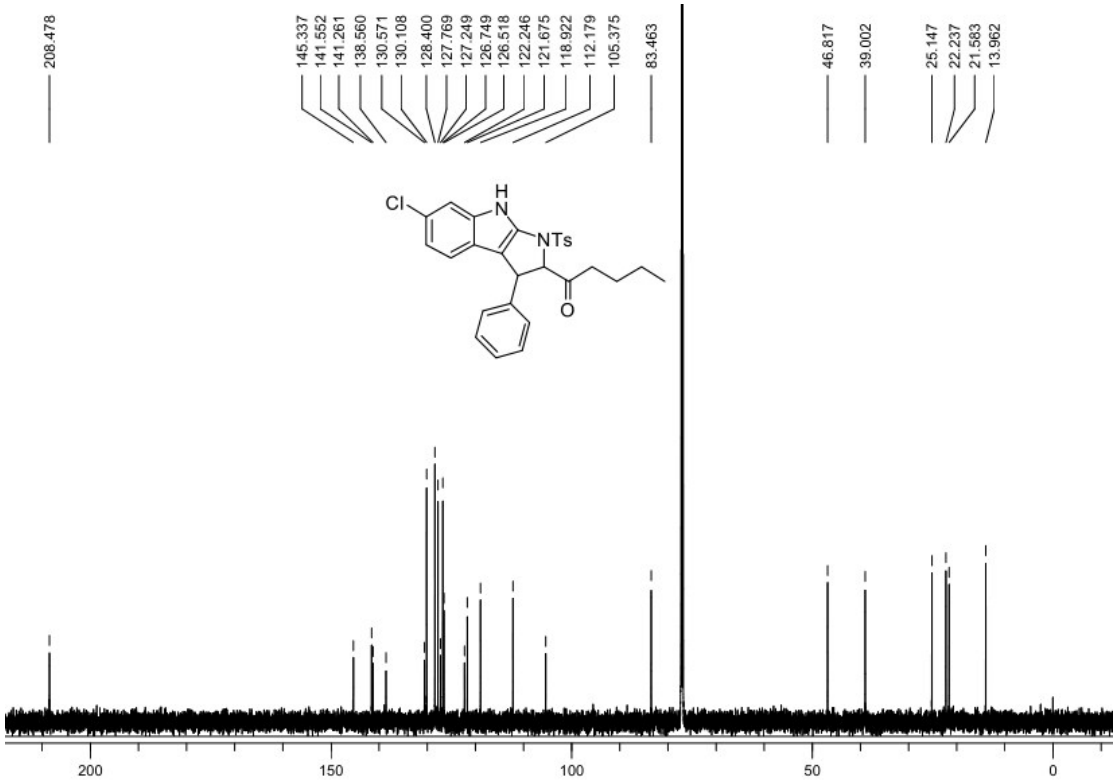
^{1}H NMR and ^{13}C NMR spectrum of **5e**



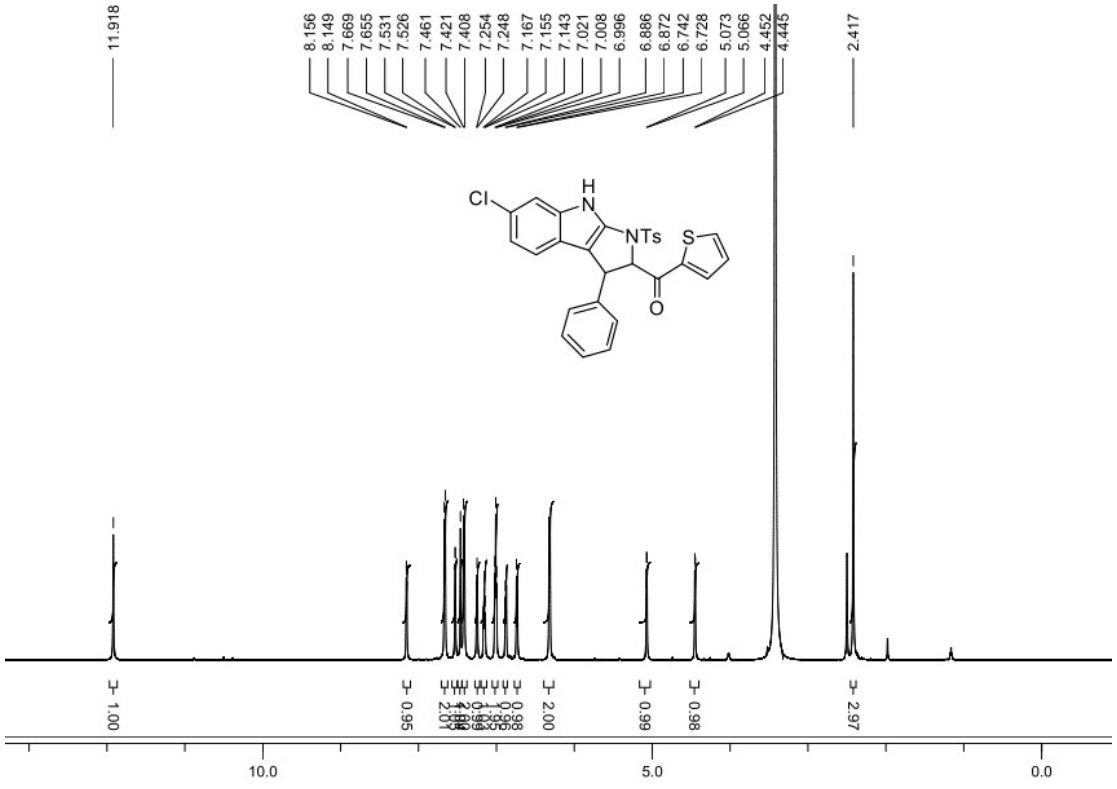


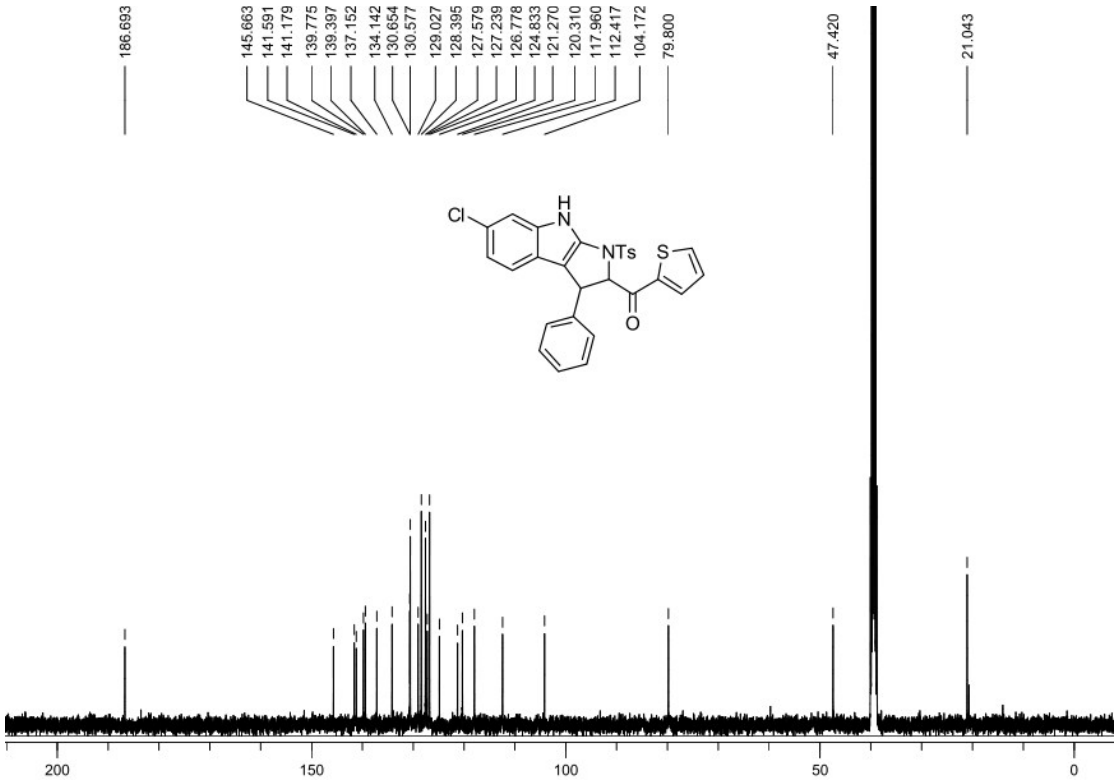
^{1}H NMR and ^{13}C NMR spectrum of **5f**



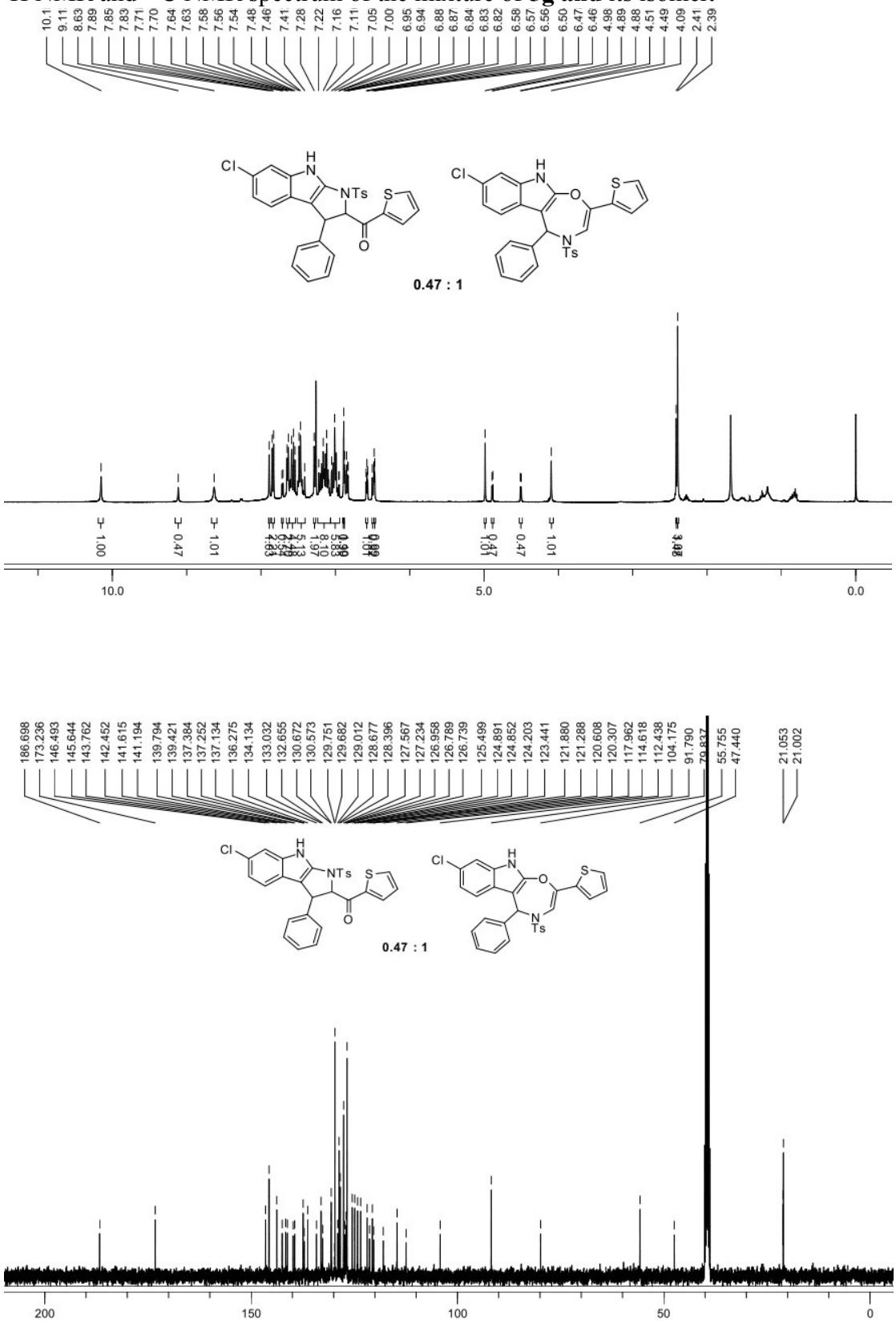


^{1}H NMR and ^{13}C NMR spectrum of **5g**

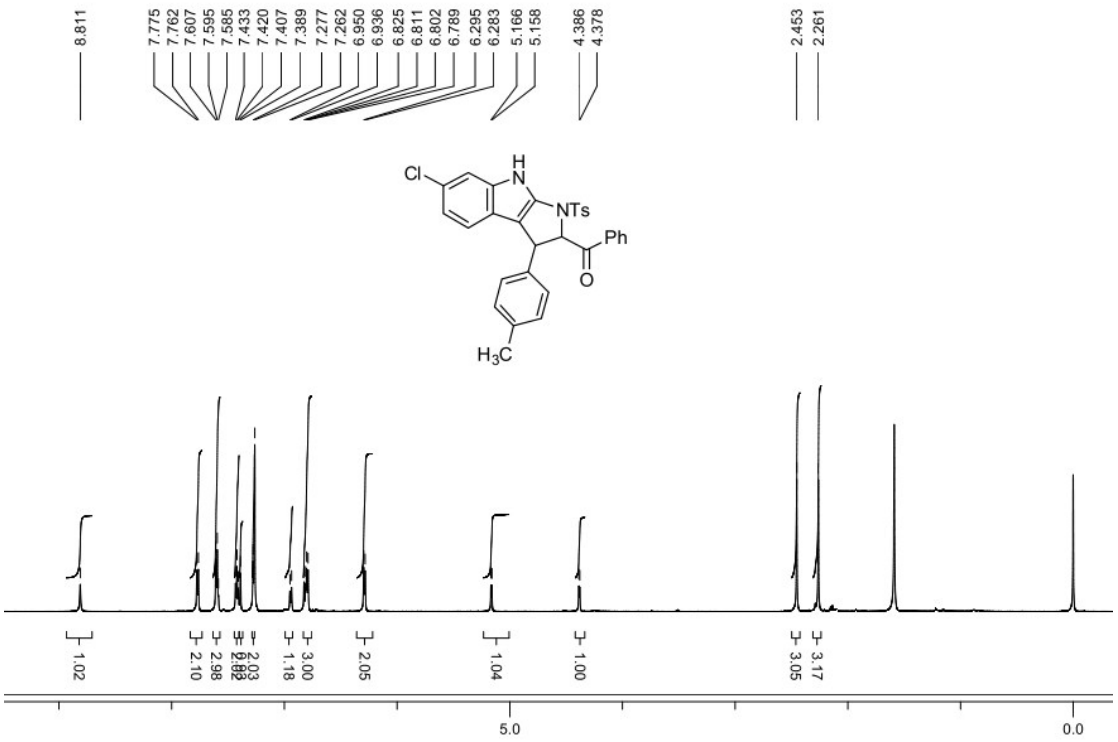


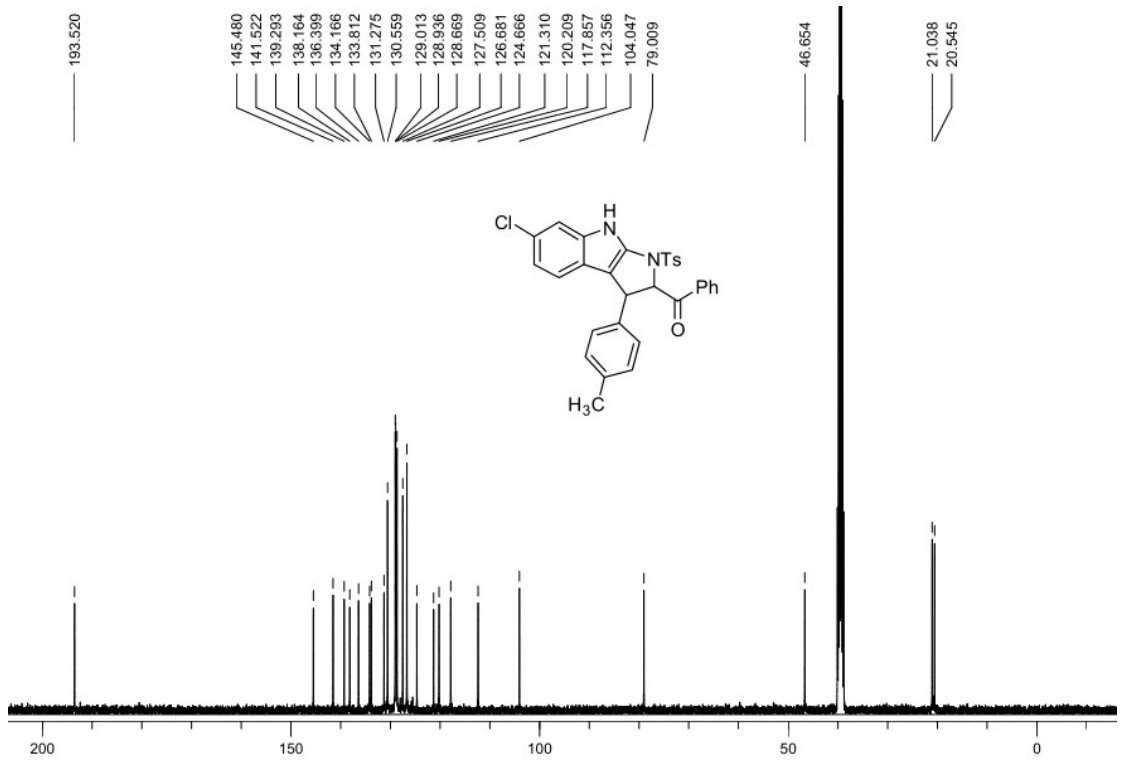


^{1}H NMR and ^{13}C NMR spectrum of the mixture of **5g and** its isomer**.**

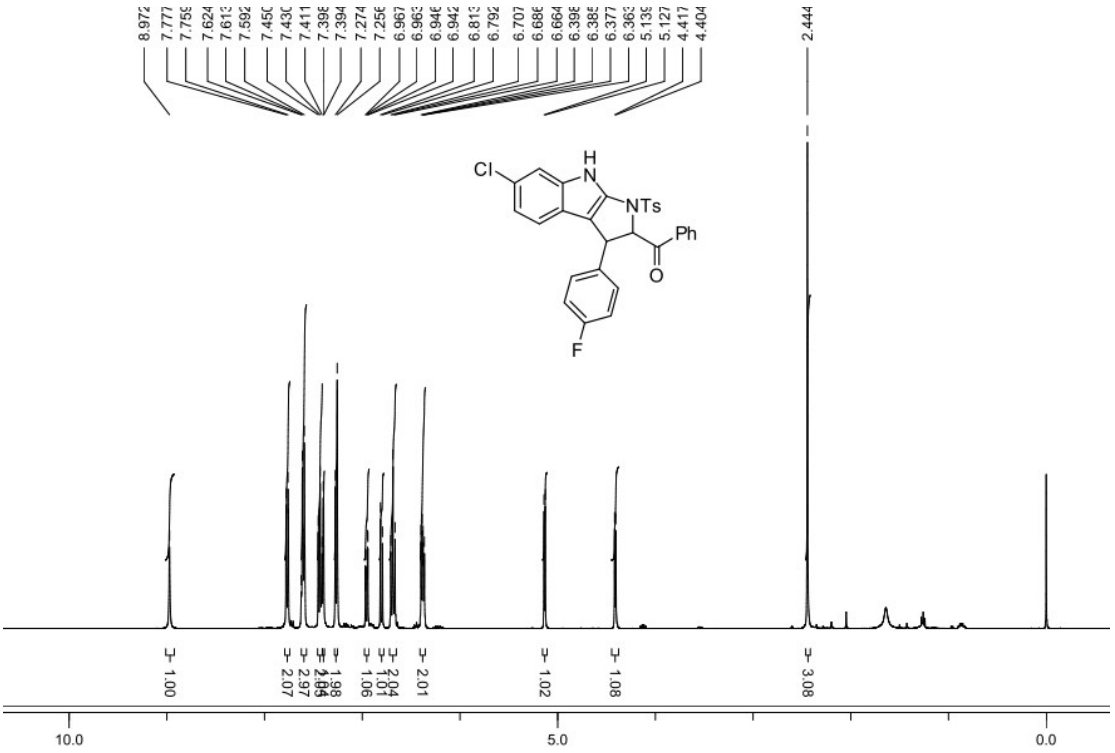


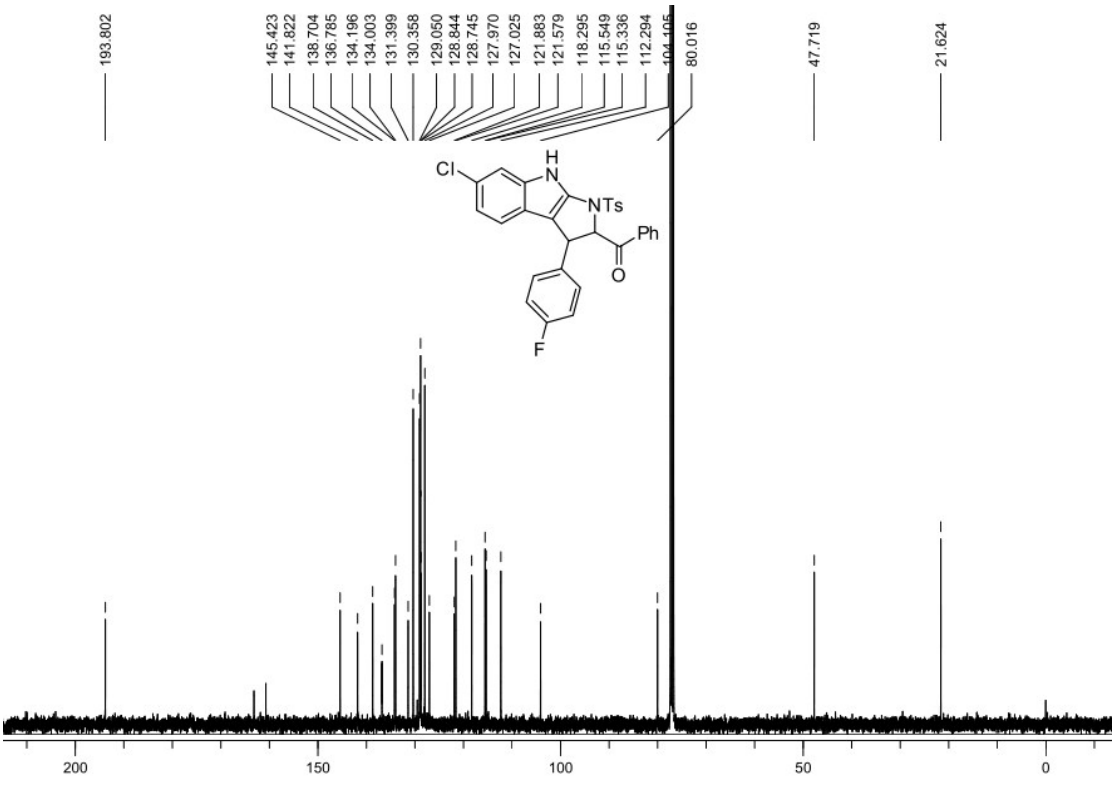
^{1}H NMR and ^{13}C NMR spectrum of **5h**



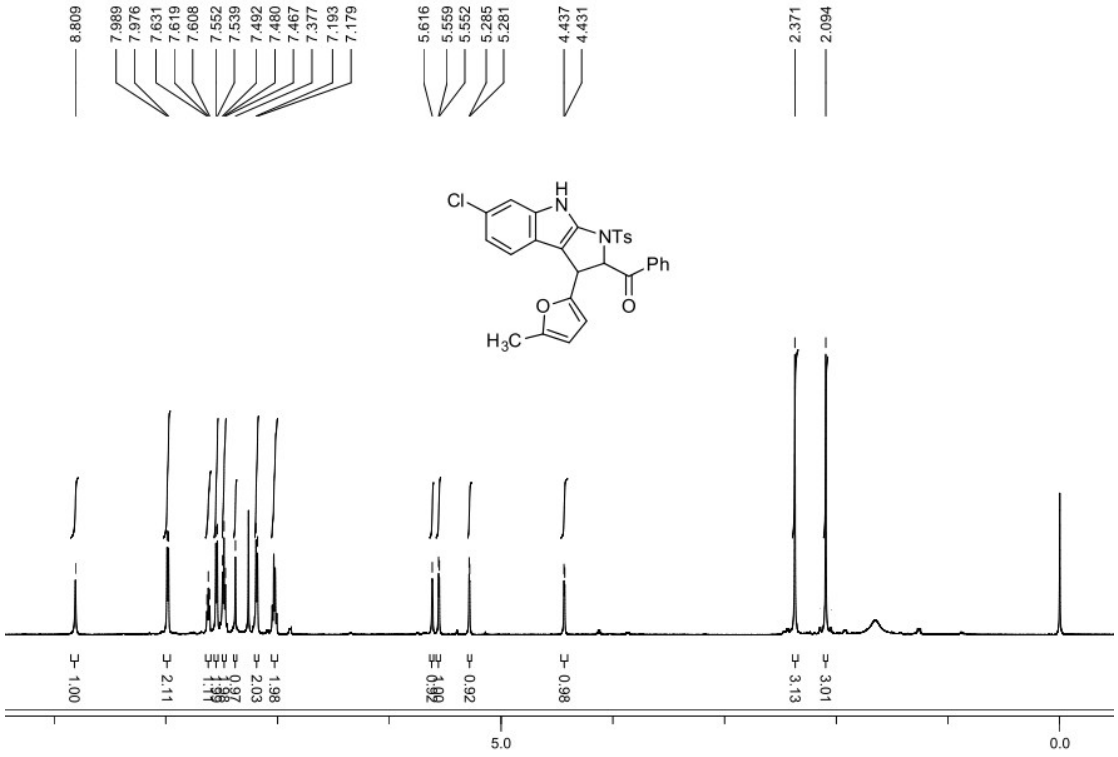


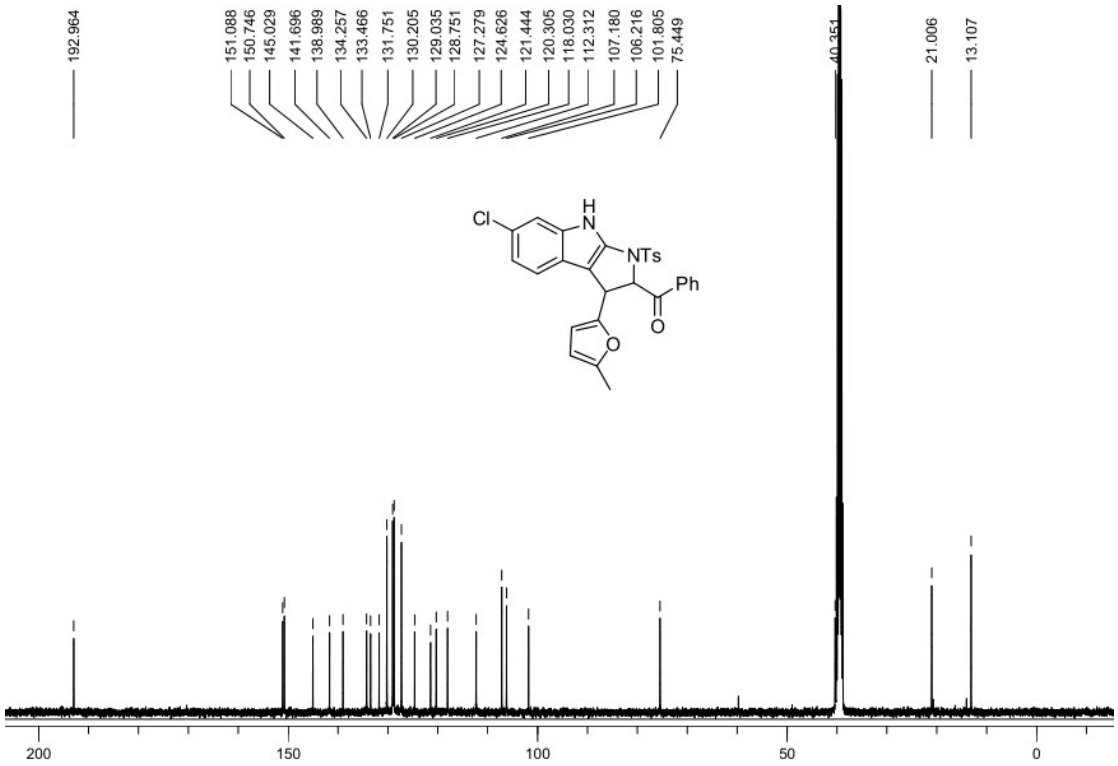
^{1}H NMR and ^{13}C NMR spectrum of **5i**



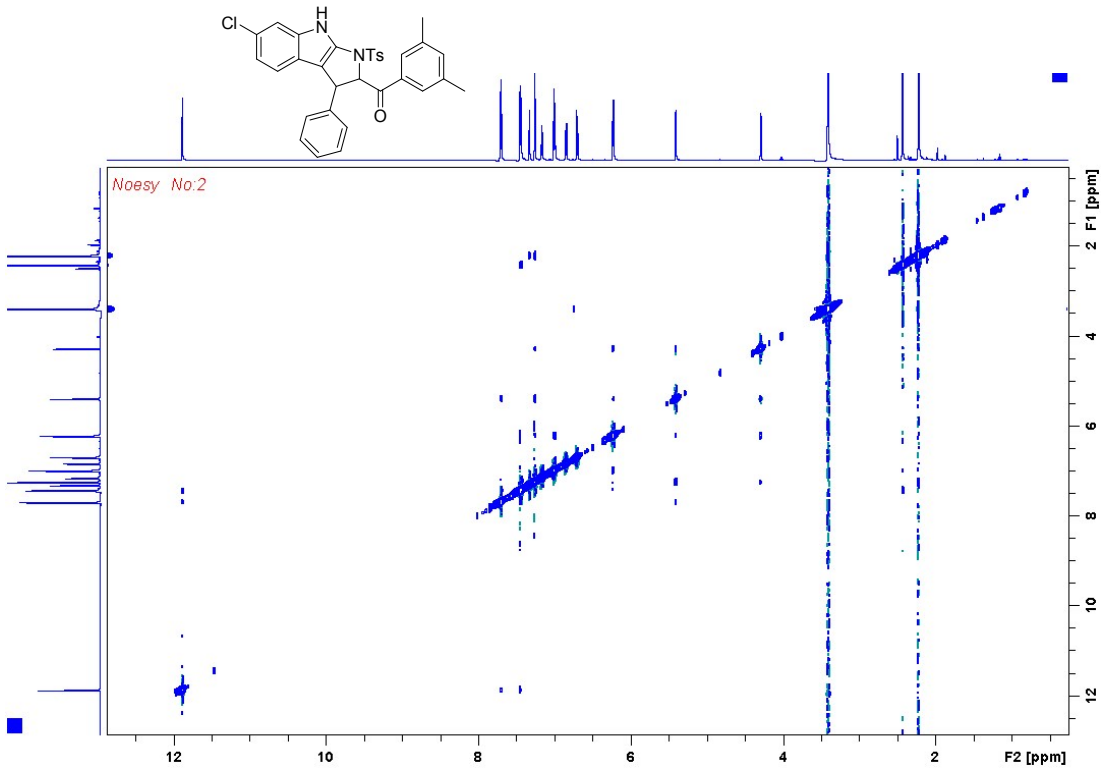


^{1}H NMR and ^{13}C NMR spectrum of **5j**





NOE of Compounds **5e** (400 MHz, d_6-DMSO)



NOE of Compounds **5j** (400 MHz, d_6-DMSO)