Supporting Information

Phosphine-Catalyzed Intramolecular Rauhut-Currier Reaction: Enantioselective Synthesis of Hydro-2H-Indole Derivatives

Hongxing Jin,[a] Qinglong Zhang,[a] Erqing Li,[a] Penghao Jia,[a] Ning Li[a] and You Huang*[ab]

a. State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 30071, China

b. Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 30071, China

E-mail: hyou@nankai.edu.cn

I. General Information S2

II. Preparation of the N-tosylacrylamide S2

III. Preparation of the Catalysts S4

IV. References S5

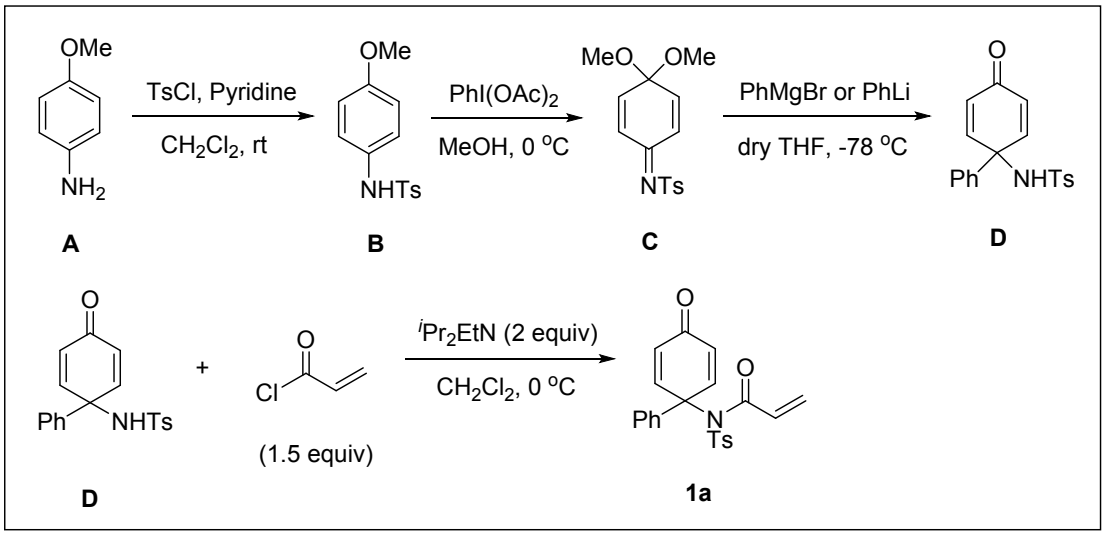
V. General Procedure and Spectroscopic Data and HPLC Chromatogram S5

VI. X-ray crystal structure S106

I. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Yields referred to isolated compounds through flash column chromatography performed using 300-400 mesh silica gel. NMR spectra were recorded on Varian Brucker ARX 400 spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (ppm) relative to internal standard TMS (0 ppm) for ^1H NMR and chloroform-*d* (77.0 ppm) for ^{13}C NMR. Coupling constants were given in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), brs (broad singlet) and m (multiplet). Enantiomeric excesses of the RC products were determined by Agilent 6890 chiral-phase high performance liquid chromatography (HPLC) or LabAlliance PC2001, using chiralcel AD-H, OD-H, and IC. Optical rotations were performed on Perkin-Elmer-341 MC digital polarimeter. Infrared spectra (IR) spectra were recorded on a Perkin-Elmer 983G instrument. High resolution mass spectrometry (HRMS) were obtained on an IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected.

II. Preparation of the N-tosylacrylamide *



* Unless otherwise specified, all starting materials N-tosylacrylamide (**1a** to **1v**) were prepared as above process.

The Synthesis of B: A round bottom flask was charged with a methlene chloride solution of *p*-anisidine **A** (100 mmol, 12.3 g), followed by the addition of pyridine (200 mmol, 16.1 mL). Tosyl chloride (105 mmol, 20 g) was added in many ports. The reaction mixture was allowed to stir at room temperature until completion of the reaction monitored by TLC. The reaction was then quench with dilute hydrochloric acid solution, extracted with methylene chloride, washed with sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the crude product **B** was obtained without further purification and used for next synthesis step.

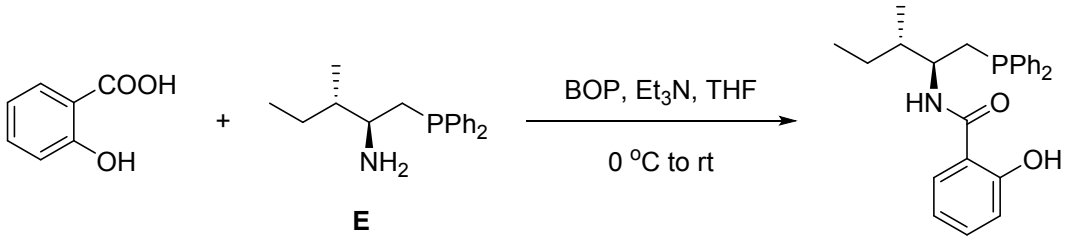
The Synthesis of C: To a stirred solution of sulfonamide **B** (50 mmol, 13.9 g) in anhydrous methanol (80 mL) at 0 °C (ice bath) was added (Diacetoxyiodo)benzene[1] (50 mmol, 16.1 g) slowly. And the reaction mixture was stir at same temperature for another 1h after the addition of (Diacetoxyiodo)benzene. Then the precipitates was filtered from reaction mixture, collected and dried and was used directly in the next step.

The Synthesis of D: To a flame dried round bottle flask with a magnetic stirring bar under Argon atmosphere were added bromobenzene (12 mmol, 1.26 mL) and anhydrous tetrahydrofuran (15 mL). The resulting mixture was cooled to –78 °C for 20 min, and *n*-butyllithium solution (3.52 mL) (2.5 mol/L in hexane) was added in one port under Argon atmosphere. The reaction mixture was kept at –78 °C for another 2 h. And then a solution of sulfonyl imides **C** (8 mmol, 2.46 g) in anhydrous tetrahydrofuran was added, and the reaction mixture was still kept at –78 °C for 10 h. The reaction was then quenched at –78 °C with hydrochloric acid solution, and another 3 h were needed for the reaction at room temperature. After that the mixture was extracted with ethyl acetate (2 × 100 mL). The combined organic extracts were washed by water (2 × 100 mL) and dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was recrystallization with ethyl acetate and *n*-hexane.

The Synthesis of 1a: A round bottom flask was charged with a methlene chloride solution of amine **D** (3 mmol, 1.017 g)，which were easily accessible from the corresponding *p*-anisidine, followed by the addition of ethyldiisopropylamine (6

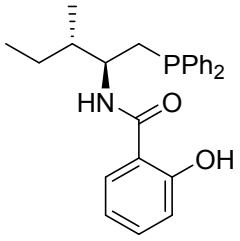
mmol, 990 μL). And the reaction mixture was cooled to 0 °C (ice bath) for 10 min. Acrolyl chloride (4.5 mmol, 365 μL) in methlene chloride (5 mL) was added drop wise slowly. The reaction mixture was allowed to stir for another 10 minutes at same temperature after the addition of acrolyl chloride. The solvent was removed in vacuo and the crude product was directly purified by silica gel flash column chromatography using petroleum ether/ethyl acetate as an elutant to give the desired product **1a** as a white or pale solid and recovered **D**.

III. Preparation of the Catalysts



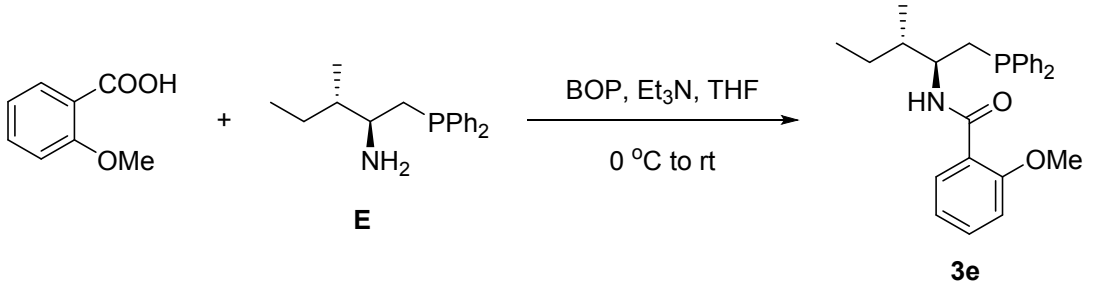
To a stirred solution of salicylic acid (0.6 mmol, 83 mg), triethylamine (3 mmol, 416 μL), BOP (0.625 mmol, 277 mg) in anhydrous tetrahydrofuran (3 mL) at 0 °C under Ar, a solution of aminophosphine **E**[2,3](0.5 mmol, 143 mg) in anhydrous tetrahydrofuran (3 mL) was added. After 1 h at 0 °C, the solution was then stirred at room temperature for 10 h until completion of the reaction monitored by TLC. Then saturated sodium bicarbonate solution (10 mL) was added to quench the reaction. The reaction mixture was extracted with ethyl acetate, the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate as the eluent to afford the catalyst **3c**.

N-((2S,3S)-1-(diphenylphosphino)-3-methylpentan-2-yl)-2-hydroxybenzamide



$[\alpha]^{29}_{D}$ = +8.8 (*c* = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 7.37 (dt,

J = 36.5, 12.5 Hz, 11H), 6.94 (d, J = 8.2 Hz, 1H), 6.78 (d, J = 7.4 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.00 (d, J = 7.7 Hz, 1H), 4.28 (s, 1H), 2.41 (d, J = 12.0 Hz, 1H), 2.37 – 2.29 (m, 1H), 1.84 (m, 1H), 1.48 (d, J = 6.2 Hz, 1H), 1.15 (dt, J = 21.6, 7.6 Hz, 1H), 0.94 (d, J = 6.5 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.14 (s), 161.52 (s), 138.12 (dd, J = 31.7, 12.7 Hz), 138.12 (dd, J = 31.7, 12.7 Hz), 133.98 (s), 132.82 (t, J = 18.8 Hz), 129.25 – 128.49 (m), 125.13 (s), 118.40 (d, J = 6.4 Hz), 114.25 (s), 51.80 (d, J = 13.5 Hz), 39.12 (d, J = 7.7 Hz), 30.33 (d, J = 14.7 Hz), 25.48 (s), 14.90 (s), 11.63 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ -23.40 (s); HRMS (ESI) m/z calcd for $C_{25}H_{28}NO_2P$ $[M+H]^+$ =406.1930, found = 406.1937.



Catalyst **3e** was prepared from 2-methoxybenzoic acid following the procedure described for the preparation of **3c**.

IV. References

[1] S. C. Banfield, M. A. Kerr, *Can. J. Chem*. **2004**, *82*, 131-138.

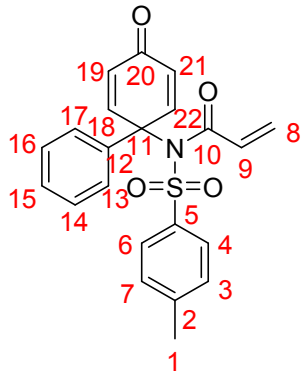
[2] K. Kawamura, H. Fukuzawa, M. Hayashi, *Org. Lett*. **2008**, *10*, 3509-3512.

[3] X. Dong, L. Liang, E. Li, Y. Huang, *Angew. Chem. Int. Ed*. **2015**, *54*, 1621-1624.

V. General Procedure and Spectroscopic Data and HPLC Chromatogram

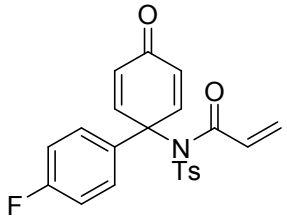
To a stirred solution of **1** (0.1 mmol) in toluene (1.0 mL) at 0 °C, chiral aminophosphine catalyst **3c** (0.02 mmol) was added in one portion. Then the reaction mixture was stirred at this temperature. After completion of the reaction (monitored by TLC), the reaction mixture was directly applied to a silica gel dropper column plug (petroleum ether/ethyl acetate as eluent) to give desired product **2**.

N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



(**1a**) 70% yield; white solid; mp 121-124°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.32 (s, 1H), 7.27 (ddd, *J* = 12.8, 6.3, 3.9 Hz, 8H), 6.94 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.22 (d, *J* = 16.8 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 2H), 5.78 (d, *J* = 10.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.76 (C=O, C20), 169.49 (C=O, C10), 148.01 (CH, C18, C22), 145.73 (C, Ar), 138.68 (C, Ar), 136.46 (C, Ar), 133.32 (CH, C9), 130.93 (CH_2, C8), 129.86 (CH, C19, C21), 129.42 (CH, Ar), 128.62 (CH, Ar), 128.56 (CH, Ar), 127.73 (CH, Ar), 125.09 (CH, Ar), 65.66 (C11), 21.77 (CH_3, C1)；IR (neat): ν 2989, 2377, 2349, 2320, 1700, 1626, 1398, 1177, 984, 763 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_4S$ $[M+H]^+$ = 394.1113, found = 394.1113.

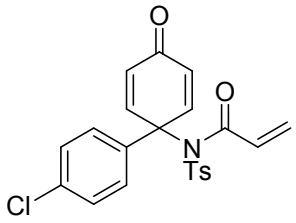
N-(4'-fluoro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



(**1b**) 78% yield; white solid; mp 108-110°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.28 (dd, *J* = 12.1, 5.1 Hz, 6H), 6.94 (dt, *J* = 16.9, 9.5 Hz, 3H), 6.23 (d, *J* = 16.8 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 2H), 5.80 (d, *J* = 10.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.48, 169.45, 163.63, 161.16, 147.69, 145.82, 136.29, 134.51 (d, *J* = 3.4 Hz), 133.19, 131.16, 129.86, 128.50, 127.72, 126.91 (d, *J* = 8.3 Hz), 116.39 (d, *J* = 21.9 Hz), 65.02, 21.74; IR (neat): ν 2989, 2377, 2350, 2314, 1671, 1504, 1275, 1261, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}FNO_4S$

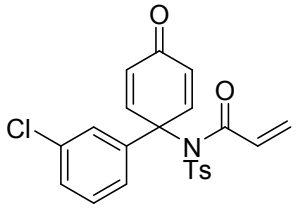
$[M+H]^+$ = 412.1019, found = 412.1044.

N-(4'-chloro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



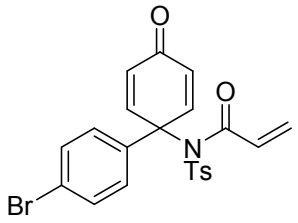
(**1c**) 88% yield; white solid; mp 122-124°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.22 (m, 8H), 6.95 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.24 (dd, *J* = 16.8, 1.0 Hz, 1H), 6.05 (d, *J* = 10.3 Hz, 2H), 5.81 (dd, *J* = 10.2, 1.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.43, 169.35, 147.44, 145.88, 137.36, 136.26, 134.52, 133.07, 131.28, 129.88, 129.58, 128.49, 127.91, 126.37, 65.11, 21.74; IR (neat): ν 2989, 2377, 2350, 2320, 1698, 1671, 1398, 1359, 1275, 1261, 1192, 1087, 987, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_4S$ $[M+H]^+$ = 428.0723, found = 428.0728.

N-(3'-chloro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



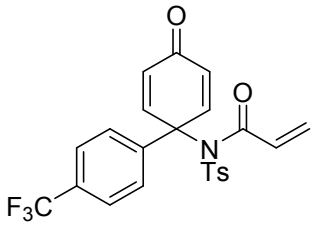
(**1d**) 52% yield; white solid; mp 158-160°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.19 (dd, *J* = 20.6, 9.7 Hz, 8H), 6.89 (dd, *J* = 16.7, 10.2 Hz, 1H), 6.17 (d, *J* = 16.8 Hz, 1H), 6.00 (d, *J* = 9.9 Hz, 2H), 5.76 (d, *J* = 10.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.45, 169.33, 147.26, 145.91, 140.76, 136.24, 135.32, 133.03, 131.32, 130.57, 129.90, 128.80, 128.48, 128.10, 125.32, 123.15, 65.14, 21.76; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1671, 1398, 1361, 1275, 1261, 1086, 991, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_4S$ $[M+H]^+$ = 428.0723, found = 428.0728.

N-(4'-bromo-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



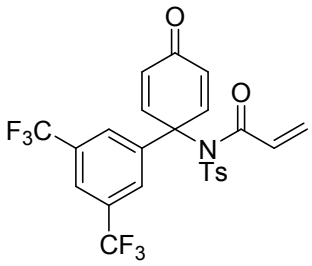
(**1e**) 75% yield; white solid; mp 123-126°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.29 (t, *J* = 10.0 Hz, 4H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.98 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.27 (d, *J* = 16.8 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 2H), 5.84 (d, *J* = 10.3 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.42, 169.33, 147.38, 145.89, 137.93, 136.25, 133.04, 132.52, 131.32, 129.89, 128.48, 127.94, 126.64, 122.66, 65.18, 21.75; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1670, 1397, 1360, 1275, 1261, 1085, 986, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}BrNO_4S$ $[M+H]^+$ = 472.0218, found = 472.0218.

N-(4-oxo-4'-(trifluoromethyl)-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



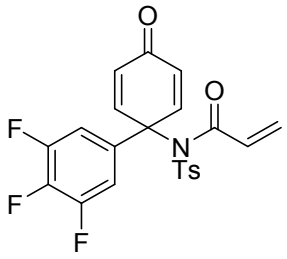
(**1f**) 79% yield; white solid; mp 140-142°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (dd, *J* = 13.6, 6.9 Hz, 4H), 6.93 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.17 (d, *J* = 16.8 Hz, 1H), 6.02 (d, *J* = 10.2 Hz, 2H), 5.76 (d, *J* = 10.3 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.29, 169.20, 147.06, 145.99, 142.97, 136.24, 132.79, 131.49, 130.44, 129.94, 128.45, 128.27, 126.40 (d, *J* = 3.7 Hz), 126.35, 125.27, 65.34, 21.73; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1672, 1398, 1325, 1275, 1261, 1086, 988, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{18}F_3NO_4S$ $[M+H]^+$ = 462.0987, found = 462.0977.

N-(4-oxo-3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



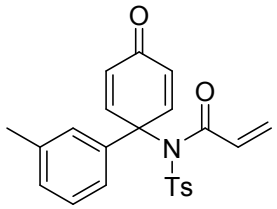
(**1g**) 85% yield; white solid; mp 169-172°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (s, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.01 (dd, *J* = 16.8, 10.3 Hz, 1H), 6.24 (d, *J* = 16.8 Hz, 1H), 6.15 (d, *J* = 10.2 Hz, 2H), 5.86 (d, *J* = 10.3 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.87, 169.34, 146.21 (d, *J* = 17.0 Hz), 142.18, 136.00, 132.91, 132.55 (d, *J* = 3.8 Hz), 132.05, 130.05, 128.93, 128.41, 125.02 (d, *J* = 3.2 Hz), 124.11, 122.46, 121.40, 64.86, 21.76; IR (neat): ν 2989, 2377, 2349, 2314, 1697, 1673, 1364, 1277, 1261, 1178, 1136, 918, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{17}F_6NO_4S$ $[M+H]^+$ = 530.0861, found = 530.0873.

N-tosyl-N-(3',4',5'-trifluoro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)acrylamide



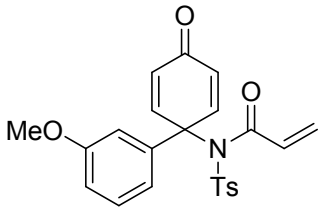
(**1h**) 37% yield; white solid; mp 139-141°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (t, *J* = 8.6 Hz, 4H), 7.03 – 6.85 (m, 3H), 6.28 (d, *J* = 16.8 Hz, 1H), 6.21 (d, *J* = 10.2 Hz, 2H), 5.82 (d, *J* = 10.3 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.06, 168.30, 145.80, 145.23, 136.53, 131.91, 131.12, 129.89, 129.09, 128.28, 123.42, 120.98, 112.79 (d, *J* = 3.4 Hz), 112.62 (d, *J* = 3.0 Hz), 63.45, 21.73; IR (neat): ν 2989, 2377, 2349, 2319, 1693, 1673, 1510, 1473, 1275, 1261, 1089, 926, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{17}F_6NO_4S$ $[M+H]^+$ = 530.0861, found = 530.0873.

N-(3'-methyl-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



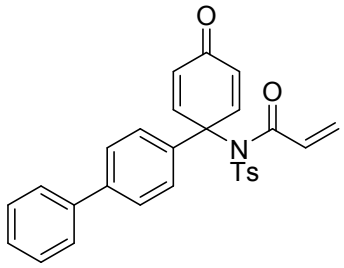
(**1i**) 88% yield; white solid; mp 139-140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.31 (s, 1H), 7.29 (d, *J* = 2.1 Hz, 2H), 7.26 (s, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 7.1 Hz, 2H), 6.93 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.22 (d, *J* = 16.8 Hz, 1H), 6.03 (d, *J* = 10.2 Hz, 2H), 5.79 (d, *J* = 10.4 Hz, 1H), 2.44 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.82, 169.53, 148.11, 145.65, 139.24, 138.41, 136.45, 133.38, 130.80, 129.78, 129.44, 129.23, 128.54, 127.59, 125.72, 122.22, 65.62, 21.73, 21.58; IR (neat): ν 2989, 2377, 2349, 2320, 1699, 1669, 1397, 1359, 1275, 1261, 1086, 984, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_4S$ $[M+H]^+$ = 408.1270, found = 408.1292.

N-(3'-methoxy-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



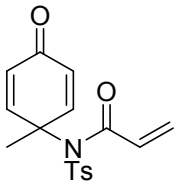
(**1j**) 28% yield; white solid; mp 149-152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.42 (m, 3H), 7.30 – 7.15 (m, 4H), 6.95 (dd, J = 16.2, 10.7 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H), 6.78 (d, J = 12.9 Hz, 2H), 6.24 (d, J = 16.4 Hz, 1H), 6.04 (d, J = 9.4 Hz, 2H), 5.80 (d, J = 9.7 Hz, 1H), 3.73 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.74, 169.45, 160.15, 147.81, 145.68, 140.09, 136.43, 133.30, 130.88, 130.40, 129.80, 128.51, 127.71, 117.36, 113.51, 111.38, 65.55, 55.24, 21.72; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1670, 1275, 1261, 1133, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_5S$ $[M+H]^+$ = 424.1219 , found = 424.1231.

N-(4-oxo-[1,1':4',1''-terphenyl]-1(4H)-yl)-N-tosylacrylamide



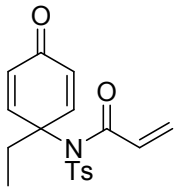
(**1k**) 59% yield; white solid; mp 113-115°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 4H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 9.3 Hz, 5H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.98 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.25 (d, *J* = 16.8 Hz, 1H), 6.07 (d, *J* = 10.1 Hz, 2H), 5.81 (d, *J* = 10.3 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.73, 169.51, 147.92, 145.74, 141.44, 139.84, 137.38, 136.41, 133.28, 131.03, 129.85, 129.61, 128.84, 128.53, 128.03, 127.73, 127.03, 125.51, 65.49, 21.76; IR (neat): ν 2989, 2377, 2349, 2319, 1699, 1669, 1485, 1397, 1359, 1275, 1261, 1086, 985, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{23}NO_4S$ $[M+H]^+$ = 470.1426, found = 470.1437.

N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-N-tosylacrylamide



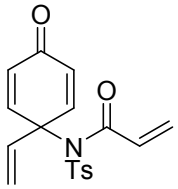
(**1l**) 30% yield; white solid; mp 76-78°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.10 (d, *J* = 10.2 Hz, 2H), 6.77 (dd, *J* = 16.9, 10.2 Hz, 1H), 6.47 (d, *J* = 16.9 Hz, 1H), 6.00 (d, *J* = 10.2 Hz, 2H), 5.95 (d, *J* = 10.3 Hz, 1H), 2.43 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.39, 170.42, 150.29, 145.39, 136.59, 134.02, 131.70, 129.78, 128.36, 127.46, 60.25, 26.93, 21.67; IR (neat): ν 2989, 2377, 2350, 2319, 1700, 1668, 1397, 1350, 1275, 1261, 1176, 1159, 1086, 1042, 971, 860, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_4S$ $[M+H]^+$ = 332.0956, found = 332.0960.

N-(1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)-N-tosylacrylamide



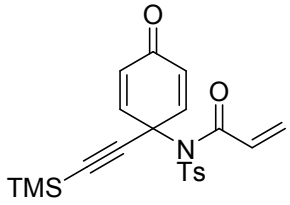
(**1m**) 61% yield; white solid; mp 89-91°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.8 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.07 (d, *J* = 9.3 Hz, 2H), 6.82 (dd, *J* = 16.2, 10.4 Hz, 1H), 6.50 (d, *J* = 16.9 Hz, 1H), 5.99 (dd, *J* = 20.5, 9.8 Hz, 3H), 2.42 (s, 3H), 1.94 (d, *J* = 6.7 Hz, 2H), 0.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.67, 170.84, 148.67, 145.41, 136.54, 134.56, 131.53, 129.68, 128.87, 128.57, 64.10, 31.02, 21.68, 8.19; IR (neat): ν 2988, 2377, 2350, 2319, 1699, 1669, 1455, 1398, 1354, 1275, 1261, 1175, 1085, 975, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_4S$ $[M+H]^+$ = 346.1113, found = 346.1112.

N-(4-oxo-1-vinylcyclohexa-2,5-dien-1-yl)-N-tosylacrylamide



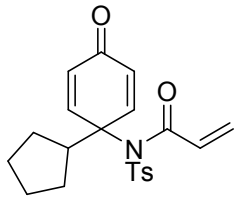
(**1n**) 68% yield; white solid; mp 111-114°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.29 (s, 2H), 7.07 (d, *J* = 10.1 Hz, 2H), 6.85 (dd, *J* = 16.9, 10.2 Hz, 1H), 6.43 (d, *J* = 16.8 Hz, 1H), 6.06 (d, *J* = 10.1 Hz, 2H), 5.91 (d, *J* = 10.3 Hz, 1H), 5.69 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.72, 169.31, 147.07, 145.57, 136.58, 134.99, 133.31, 131.37, 129.82, 128.39, 128.03, 117.09, 64.22, 21.70; IR (neat): ν 2989, 2377, 2349, 2319, 1699, 1669, 1398, 1355, 1275, 1261, 1176, 1086, 983, 924, 764, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_4S$ $[M+H]^+$ = 344.0956, found = 344.0966.

N-(4-oxo-1-((trimethylsilyl)ethynyl)cyclohexa-2,5-dien-1-yl)-N-tosylacrylamide



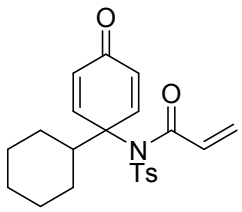
(**1o**) 87% yield; white solid; mp 136-138°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 10.0 Hz, 2H), 6.70 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.44 (d, *J* = 16.8 Hz, 1H), 6.13 (d, *J* = 10.0 Hz, 2H), 5.89 (d, *J* = 10.2 Hz, 1H), 2.45 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.89, 168.86, 145.93, 145.70, 137.80, 133.28, 132.08, 130.48, 128.65, 128.45, 96.38, 95.08, 78.03, 77.71, 77.39, 57.14, 22.34, -0.00 (TMS); IR (neat): ν 2989, 2377, 2350, 2319, 1702, 1671, 1456, 1398, 1357, 1275, 1261, 1176, 1149, 853, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{23}NO_4SSi$ $[M+H]^+$ = 414.1195, found = 414.1207.

N-(1-cyclopentyl-4-oxocyclohexa-2,5-dien-1-yl)-N-tosylacrylamide



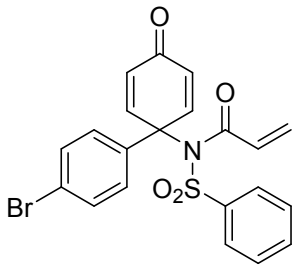
(**1p**) 20% yield; oil solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 10.2 Hz, 2H), 6.82 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.50 (d, *J* = 16.9 Hz, 1H), 6.01 (d, *J* = 10.2 Hz, 2H), 5.94 (d, *J* = 10.1 Hz, 1H), 2.93 – 2.72 (m, 1H), 2.40 (s, 3H), 1.46 (s, 6H), 1.28 – 1.18 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.82, 171.16, 147.31, 145.37, 136.52, 134.76, 130.89, 129.72, 129.61, 128.70, 66.26, 43.10, 27.62, 26.11, 21.68; IR (neat): ν 2988, 2377, 2350, 2319, 1698, 1670, 1398, 1355, 1275, 1261, 1175, 1085, 980, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{23}NO_4S$ $[M+H]^+$ = 386.1426, found = 386.1473.

N-(4-oxo-[1,1'-bi(cyclohexane)]-2,5-dien-1-yl)-N-tosylacrylamide



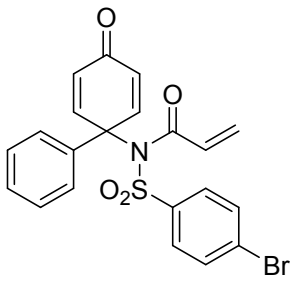
(**1q**) 44% yield; oil solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 10.2 Hz, 2H), 6.90 (dd, *J* = 16.9, 10.1 Hz, 1H), 6.48 (d, *J* = 16.9 Hz, 1H), 6.01 (d, *J* = 10.2 Hz, 2H), 5.89 (d, *J* = 10.1 Hz, 1H), 2.40 (s, 3H), 2.17 (t, *J* = 11.9 Hz, 1H), 1.69 (d, *J* = 12.5 Hz, 2H), 1.58 (d, *J* = 11.2 Hz, 3H), 1.17 – 0.98 (m, 3H), 0.89 (dd, *J* = 23.6, 11.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.94, 170.62, 147.30, 145.31, 136.84, 134.60, 130.34, 129.75, 129.60, 128.53, 67.56, 42.04, 27.55, 26.27, 26.05, 21.66; IR (neat): ν 2988, 2933, 2857, 2377, 2350, 2319, 1698, 1670, 1398, 1355, 1275, 1261, 1175, 1085, 980, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_4S$ $[M+H]^+$ =400.1583, found =400.1592.

N-(4'-bromo-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-(phenylsulfonyl)acrylamide



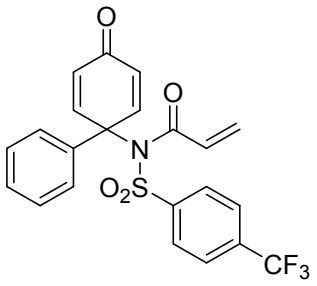
(**1r**) 72% yield; white solid; mp 125-127°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 10.0 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.95 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.26 (d, *J* = 16.8 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 2H), 5.83 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.33, 169.34, 147.23, 139.20, 137.79, 134.52, 133.06, 132.55, 131.52, 129.33, 128.44, 127.97, 126.69, 122.74, 65.14; IR (neat): ν 2989, 2924, 2377, 2349, 2319, 1699, 1670, 1397, 1360, 1275, 1261, 1183, 1134, 1086, 985, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_4S$ $[M+H]^+$ =458.0062, found =458.0049.

N-((4-bromophenyl)sulfonyl)-N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)acrylamide



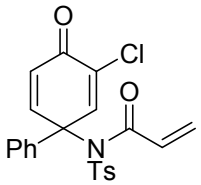
(**1s**) 71% yield; white solid; mp 121-123°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.35 – 7.27 (m, 7H), 6.87 (dd, *J* = 16.9, 10.2 Hz, 1H), 6.25 (d, *J* = 16.8 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 2H), 5.82 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.45, 169.36, 147.80, 138.32, 138.19, 133.08, 132.55, 131.68, 129.84, 129.67, 129.45, 128.81, 127.94, 125.23, 65.68; IR (neat): ν 3007, 2989, 2377, 2349, 2319, 1701, 1670, 1548, 1394, 1361, 1275, 1261, 1185, 1132, 1085, 1068, 984, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_4S$ $[M+H]^+$ =458.0062, found =458.0056.

N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-((4-(trifluoromethyl)phenyl)sulfonyl)acrylamide



(**1t**) 37% yield; white solid; mp 111-113°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.31 (s, 1H), 7.27 (d, *J* = 4.8 Hz, 5H), 6.85 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.28 (d, *J* = 16.7 Hz, 1H), 6.10 (d, *J* = 10.2 Hz, 2H), 5.84 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.25, 169.25, 147.60, 142.85, 137.93, 135.93, 135.59, 132.94, 132.12, 129.46, 128.96 (d, *J* = 5.5 Hz), 128.05, 126.35 (d, *J* = 3.7 Hz), 125.38, 124.23, 121.52, 65.72; IR (neat): ν 3007, 2989, 2377, 2350, 2319, 1701, 1671, 1401, 1364, 1275, 1261, 1177, 1133, 1062, 984, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_4S$ $[M+H]^+$ =448.0830, found =448.0823.

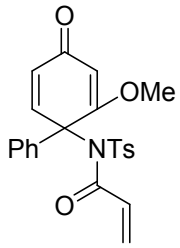
N-(3-chloro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



(**1u**) 70% yield; white solid; mp 132-134°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 –

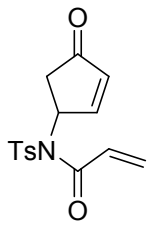
7.52 (m, 2H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.37 (dt, *J* = 10.1, 2.9 Hz, 1H), 7.34 – 7.23 (m, 7H), 6.96 (ddd, *J* = 16.8, 10.2, 2.9 Hz, 1H), 6.24 (dd, *J* = 16.9, 1.9 Hz, 1H), 6.14 (dd, *J* = 10.1, 3.0 Hz, 1H), 5.82 (dd, *J* = 10.2, 1.9 Hz, 1H), 2.45 (d, *J* = 2.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.74, 169.50, 148.81, 146.26, 143.21, 137.92, 135.76, 133.33, 132.74, 131.11, 130.10, 129.58, 128.95, 128.33, 125.53, 124.96, 66.93, 21.76; IR (neat): ν 3007, 2989, 2377, 2350, 2319, 1699, 1677, 1275, 1261, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_4S$ $[M+H]^+$ =428.0723, found =428.0778.

N-(2-methoxy-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide



(**1v**) 30% yield; white solid; mp 63-65°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.35 – 7.22 (m, 6H), 6.78 (dd, *J* = 16.8, 10.3 Hz, 1H), 6.42 (d, *J* = 10.0 Hz, 1H), 6.08 (d, *J* = 16.8 Hz, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 5.52 (s, 1H), 3.73 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.20, 173.38, 168.70, 145.15, 143.98, 137.87, 137.30, 131.54, 131.26, 129.63, 129.28, 128.62, 128.60, 128.28, 126.23, 102.32, 67.94, 56.20, 21.69; IR (neat): ν 3007, 2989, 2377, 2349, 2314, 1699, 1661, 1594, 1356, 1275, 1261, 1226, 1151, 1058, 985, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_4S$ $[M+H]^+$ =424.1219, found =424.1225.

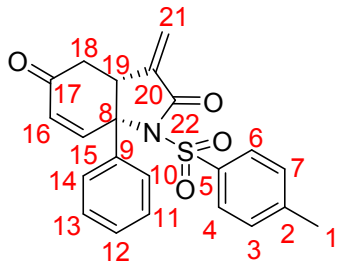
N-(4-oxocyclopent-2-en-1-yl)-N-tosylacrylamide



(**1w**) 30% yield; white solid; mp 88-90°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.39 (s, 1H), 7.06 (dd, *J* = 16.7, 10.4 Hz, 1H), 6.34 (dd, *J* = 16.7, 1.5 Hz, 1H), 6.26 (dd, *J* = 5.7, 2.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.5 Hz,

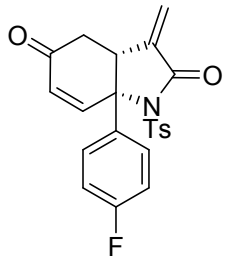
1H), 5.49 (ddd, *J* = 7.3, 4.9, 2.4 Hz, 1H), 2.59 (s, 1H), 2.58 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.65, 166.12, 161.08, 145.75, 136.43, 134.42, 131.73, 130.39, 129.40, 127.25, 58.33, 39.87, 21.72; IR (neat): ν 3007, 2989, 2377, 2349, 2319, 1717, 1687, 1548, 1275, 1261, 1159, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{15}NO_4S$ $[M+H]^+$ = 306.0800, found = 306.0834.

(3aR,7aR)-3-methylene-7a-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



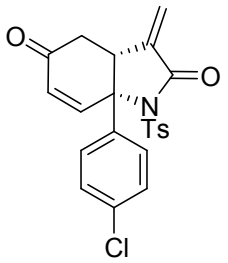
(**2a**) 94% yield; white solid; mp 150-152°C; $[\alpha]^{28}_D$ = -70.1 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 10.5 Hz, 1H), 7.45 (d, *J* = 6.5 Hz, 3H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.33 (d, *J* = 10.5 Hz, 1H), 6.24 (d, *J* = 3.0 Hz, 1H), 5.45 (d, *J* = 2.6 Hz, 1H), 3.42 (s, 1H), 2.69 (dd, *J* = 16.8, 3.0 Hz, 1H), 2.60 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.59 (C=O, C17), 165.83 (C=O, C22), 145.70 (C20), 144.65 (C, Ar), 139.54 (CH, C15), 138.41 (C, Ar), 135.56 (C, Ar), 130.33 (CH, C16), 129.40 (CH, Ar), 129.22 (CH, Ar), 128.99 (CH, Ar), 128.90 (CH, Ar), 125.84 (CH, Ar), 120.69 (CH_2, C21), 69.98 (C8), 48.81 (CH, C19), 35.09 (CH_2, C18), 21.78 (CH_3, C1); IR (neat): ν 3006, 2989, 2321, 1730, 1694, 1359, 1275, 1261, 1173, 1153, 1068, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_4S$ $[M+H]^+$ =394.1113, found =394.1131; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 18.3 min, second peak: t_R = 23.3 min.

(3aR,7aR)-7a-(4-fluorophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2b**) 75% yield; white solid; mp 181-183°C; $[\alpha]^{28}_D$ = -64.9 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 10.2 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 8.2 Hz, 2H), 6.33 (d, *J* = 10.4 Hz, 1H), 6.24 (s, 1H), 5.46 (s, 1H), 3.38 (s, 1H), 2.70 (d, *J* = 15.8 Hz, 1H), 2.59 (dd, *J* = 16.8, 5.1 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.25, 165.64, 164.00, 161.53, 145.85, 144.23, 138.14, 135.48, 130.43, 129.48, 129.14, 127.76 (d, *J* = 8.3 Hz), 120.91, 116.04 (d, *J* = 21.9 Hz), 69.40, 48.86, 34.99, 21.78; IR (neat): ν 3007, 2989, 2377, 2349, 2320, 1734, 1697, 1511, 1275, 1261, 1173, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}FNO_4S$ $[M+H]^+$ =412.1019, found =412.1031; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 16.0 min, second peak: t_R = 21.2 min.

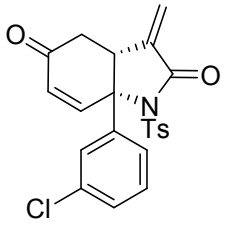
(3aR,7aR)-7a-(4-chlorophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2c**) 77% yield; white solid; mp 105-107°C; $[\alpha]^{28}_D$ = -84.6 (*c* = 0.4, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.45 (dd, *J* = 13.9, 9.2 Hz, 3H), 7.40 – 7.30 (m, 4H), 6.34 (d, *J* = 10.4 Hz, 1H), 6.25 (s, 1H), 5.46 (s, 1H), 3.36 (s, 1H), 2.70 (d, *J* = 16.7 Hz, 1H), 2.58 (dd, *J* = 16.9, 4.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.16, 165.61, 145.90, 143.95, 138.28, 138.05, 135.39, 134.92, 130.59, 129.50, 129.23, 129.18, 127.25, 121.01, 69.37, 48.73, 34.97, 21.78; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1733, 1696, 1572, 1275, 1261, 1173, 1120, 1087,

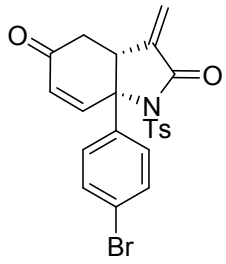
763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_4S$ $[M+H]^+$ =428.0723, found =428.0721; Enantiomeric excess: 87%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 17.5 min, second peak: t_R = 22.5 min.

(3aR,7aR)-7a-(3-chlorophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



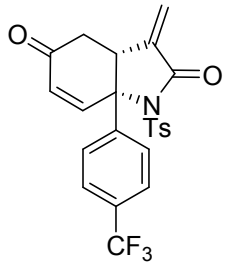
(**2d**) 82% yield; white solid; mp 214-217°C; $[\alpha]^{28}_D$ = -58.5 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 10.5 Hz, 1H), 7.41 (d, *J* = 5.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 6.5 Hz, 2H), 6.35 (d, *J* = 10.4 Hz, 1H), 6.27 (d, *J* = 2.6 Hz, 1H), 5.47 (s, 1H), 3.37 (s, 1H), 2.72 (d, *J* = 15.0 Hz, 1H), 2.60 (dd, *J* = 16.9, 5.2 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.13, 165.61, 145.93, 143.86, 141.66, 138.03, 135.35, 135.14, 130.67, 130.32, 129.60, 129.17, 129.15, 126.13, 124.18, 121.05, 69.45, 48.62, 34.90, 21.79; IR (neat): ν 3007, 2989, 2377, 2349, 2320, 1733, 1696, 1572, 1275, 1261, 1173, 1120, 1087, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_4S$ $[M+H]^+$ =428.0723, found =428.0717; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 20.8 min, second peak: t_R = 23.1 min.

(3aR,7aR)-7a-(4-bromophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



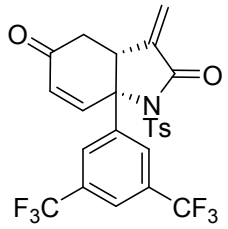
(**2e**) 68% yield; white solid; mp 108-110°C; $[\alpha]^{28}_D$ = -82.9 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.8 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.46 (d, *J* = 9.9 Hz, 1H), 7.33 (dd, *J* = 18.9, 7.2 Hz, 4H), 6.33 (d, *J* = 10.1 Hz, 1H), 6.24 (s, 1H), 5.46 (s, 1H), 3.35 (s, 1H), 2.70 (d, *J* = 16.0 Hz, 1H), 2.58 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.13, 165.60, 145.90, 143.87, 138.84, 138.03, 135.38, 132.18, 130.62, 129.50, 129.19, 127.52, 123.06, 121.03, 69.42, 48.69, 34.97, 21.78; IR (neat): ν 3007, 2989, 2377, 2350, 2320, 1733, 1697, 1572, 1275, 1261, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}BrNO_4S$ $[M+H]^+$ =472.0218, found =472.0223; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 20.1 min, second peak: t_R = 24.9 min.

(3aR,7aR)-3-methylene-1-tosyl-7a-(4-(trifluoromethyl)phenyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



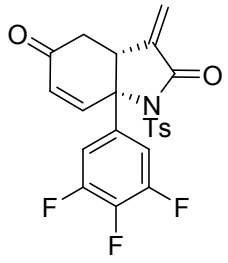
(**2f**) 66% yield; white solid; mp 206-208°C; $[\alpha]^{28}_D$ = -80.1 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 10.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 10.5 Hz, 1H), 6.27 (d, *J* = 2.8 Hz, 1H), 5.48 (d, *J* = 2.3 Hz, 1H), 3.38 (s, 1H), 2.77 – 2.66 (m, 1H), 2.58 (dd, *J* = 16.9, 5.3 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.97, 165.54, 146.06, 143.85, 143.49, 137.86, 135.22, 130.90, 129.57, 129.20, 126.24, 126.15, 126.10 (d, *J* = 3.6 Hz), 126.04, 121.32, 69.33, 48.62, 34.97, 21.79; IR (neat): ν 3007, 2989, 2377, 2350, 2320, 1734, 1698, 1548, 1327, 1275, 1261, 1172, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{18}F_3NO_4S$ $[M+H]^+$ =462.0987, found =462.0981; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 17.3 min, second peak: t_R = 24.2 min.

(3aR,7aR)-7a-(3,5-bis(trifluoromethyl)phenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2g**) 93% yield; white solid; mp 112-114°C; $[\alpha]^{28}_D$ = -71.3 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 – 7.78 (m, 4H), 7.49 (d, *J* = 10.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.44 (d, *J* = 10.4 Hz, 1H), 6.34 (d, *J* = 2.6 Hz, 1H), 5.53 (s, 1H), 3.35 (s, 1H), 2.78 (d, *J* = 16.8 Hz, 1H), 2.56 (dd, *J* = 17.0, 5.2 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.28, 165.41, 146.40, 142.93, 142.41, 137.32, 134.88, 132.78, 132.44, 131.64, 129.72, 129.11, 125.98 (d, *J* = 2.3 Hz), 123.09 (d, *J* = 3.4 Hz), 121.95, 68.93, 48.54, 34.62, 21.78; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1732, 1696, 1366, 1277, 1261, 1175, 1136, 1018, 901, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{17}F_6NO_4S$ $[M+H]^+$ =530.0861, found =530.0867; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 6.9 min, second peak: t_R = 12.1 min.

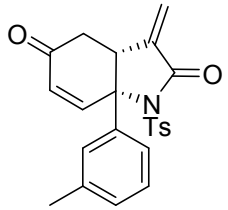
(3aR,7aR)-3-methylene-1-tosyl-7a-(3,4,5-trifluorophenyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2h**) 83% yield; white solid; mp 197-199°C; $[\alpha]^{28}_D$ = -118.1 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 10.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 14.0, 6.4 Hz, 1H), 7.10 (dd, *J* = 16.2, 7.7 Hz, 1H), 6.30 (t, *J* = 7.3 Hz, 2H), 5.50 (d, *J* = 2.7 Hz, 1H), 3.67 (s, 1H), 2.76 (dd, *J* = 17.0, 2.6 Hz, 1H), 2.58 (dd, *J* = 16.9, 5.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.70, 163.86, 145.01, 142.15, 136.61, 133.89, 129.14, 128.48, 127.73, 122.88, 121.70, 120.38, 111.43 (d, *J* = 3.9 Hz), 111.26 (d, *J* = 3.8 Hz), 65.79, 44.06, 34.36,

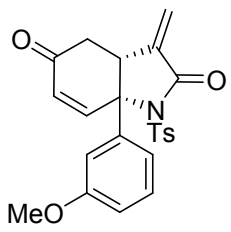
20.75; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1732, 1697, 1513, 1476, 1275, 1261, 1188, 1173, 1153, 1170, 1011, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{16}F_3NO_4S$ $[M+H]^+$ =448.0830, found =448.0834; Enantiomeric excess: 97%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 16.1 min, second peak: t_R = 18.6 min.

(3aR,7aR)-3-methylene-7a-(m-tolyl)-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



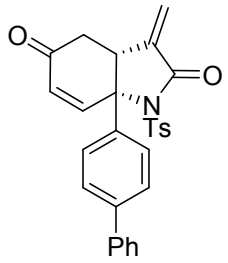
(**2i**) 91% yield; white solid; mp 152-154°C; $[\alpha]^{28}_D$ = -64.1 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 10.5, 1.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 6.32 (d, *J* = 10.5 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 5.44 (d, *J* = 2.9 Hz, 1H), 3.40 (s, 1H), 2.68 (dd, *J* = 16.8, 2.9 Hz, 1H), 2.60 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.69, 165.87, 145.64, 144.88, 139.36, 138.67, 138.53, 135.68, 130.20, 129.69, 129.36, 129.18, 128.84, 126.47, 123.06, 120.55, 70.07, 48.78, 35.08, 21.76, 21.60; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1732, 1694, 1275, 1260, 1231, 1173, 1151, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_4S$ $[M+Na]^+$ = 430.1089, found = 430.1153; Enantiomeric excess: 98%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 13.3 min, second peak: t_R = 15.8 min.

(3aR,7aR)-7a-(3-methoxyphenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



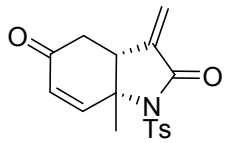
(**2j**) 73% yield; white solid; mp 162-164°C; $[\alpha]^{28}_D$ = -70.8 (*c* = 0.45, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 10.3 Hz, 1H), 7.35 (dd, *J* = 17.8, 8.0 Hz, 3H), 7.02 – 6.93 (m, 2H), 6.91 (s, 1H), 6.32 (d, *J* = 10.4 Hz, 1H), 6.23 (d, *J* = 1.8 Hz, 1H), 5.44 (s, 1H), 3.80 (s, 3H), 3.42 (s, 1H), 2.69 (dd, *J* = 16.9, 2.1 Hz, 1H), 2.62 (dd, *J* = 16.9, 5.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.64, 165.82, 160.00, 145.69, 144.54, 141.13, 138.42, 135.56, 130.28, 130.09, 129.40, 129.24, 120.67, 118.10, 113.94, 111.97, 69.91, 55.34, 48.66, 35.18, 21.77; IR (neat): ν 3006, 2989, 2377, 2349, 2320, 1733, 1696, 1275, 1261, 1151, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_5S$ $[M+Na]^+$ = 446.1038, found = 446.1026; Enantiomeric excess: >99%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 27.4 min, second peak: t_R = 34.1 min.

(3aR,7aR)-7a-([1,1'-biphenyl]-4-yl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



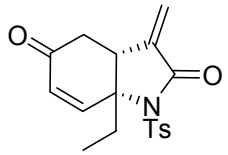
(**2k**) 77% yield; white solid; mp 103-105°C; $[\alpha]^{28}_D$ = -78.9 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.65 (dd, *J* = 15.4, 7.8 Hz, 4H), 7.55 (d, *J* = 10.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.36 (d, *J* = 10.4 Hz, 1H), 6.26 (d, *J* = 2.9 Hz, 1H), 5.46 (d, *J* = 2.5 Hz, 1H), 3.45 (s, 1H), 2.71 (dd, *J* = 16.8, 2.9 Hz, 1H), 2.65 (dd, *J* = 16.9, 5.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.58, 165.83, 145.75, 144.58, 141.77, 140.04, 138.46, 138.38, 135.54, 130.39, 129.44, 129.24, 128.96, 127.85, 127.64, 127.17, 126.30, 120.78, 69.84, 48.81, 35.15, 21.79; IR (neat): ν 3006, 2989, 2377, 2351, 2321, 1731, 1694, 1359, 1275, 1261, 1152, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{23}NO_4S$ $[M+H]^+$ =470.1426, found =470.1414; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 32.4 min, second peak: t_R = 36.7 min.

(3aR,7aR)-7a-methyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2l**) 77% yield; white solid; mp 161-163°C; $[\alpha]^{28}_{D}$ = -65.1 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 10.4 Hz, 1H), 6.17 (d, *J* = 3.0 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 5.46 (d, *J* = 2.7 Hz, 1H), 3.17 (s, 1H), 2.80 (dd, *J* = 16.9, 5.6 Hz, 1H), 2.73 (dd, *J* = 16.9, 4.4 Hz, 1H), 2.45 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.38, 165.40, 146.87, 145.52, 138.44, 135.94, 129.64, 128.63, 128.17, 120.83, 64.82, 45.26, 36.28, 25.19, 21.75; IR (neat): ν 3006, 2989, 2377, 2351, 2320, 1688, 1572, 1275, 1261, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_4S$ $[M+H]^+$ =332.0956, found =332.0990; Enantiomeric excess: 72%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 61.0 min, second peak: t_R = 66.2 min.

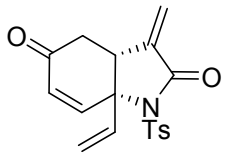
(3aR,7aR)-7a-ethyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2m**) 66% yield; white solid; mp 72-74°C; $[\alpha]^{28}_{D}$ = -60.1 (*c* = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 9.8 Hz, 1H), 6.17 (s, 1H), 6.12 (d, *J* = 10.4 Hz, 1H), 5.47 (s, 1H), 3.36 (s, 1H), 2.69 (dd, *J* = 16.7, 5.8 Hz, 1H), 2.61 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.44 (s, 3H), 2.39 (d, *J* = 6.8 Hz, 1H), 2.17 (td, *J* = 14.2, 6.9 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.91, 165.68, 146.51, 145.51, 139.08, 135.65, 129.51, 129.35, 128.96, 120.94, 68.22, 40.53, 37.97, 30.40, 21.74, 8.80; IR (neat): ν 2985, 2925, 2377, 2350, 2320, 1728, 1691, 1595, 1357, 1275, 1261, 1187, 1158, 1085, 1039, 909, 764, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_4S$ $[M+H]^+$ =346.1113, found =346.1118; Enantiomeric excess: 84%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 98/2; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R =

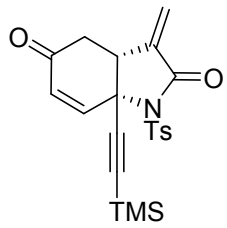
115.6 min, second peak: t_R = 127.0 min.

(3aR,7aR)-3-methylene-1-tosyl-7a-vinyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2n**) 87% yield; white solid; mp 157-159°C; $[\alpha]^{28}_D$ = -101.0 (*c* = 0.45, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.13 (dd, *J* = 10.4, 1.3 Hz, 1H), 6.27 – 6.15 (m, 3H), 5.50 (d, *J* = 10.6 Hz, 1H), 5.45 (d, *J* = 2.8 Hz, 1H), 5.35 (d, *J* = 17.4 Hz, 1H), 3.19 (s, 1H), 2.75 (d, *J* = 4.5 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.45, 165.17, 145.65, 143.67, 138.04, 136.83, 135.84, 130.43, 129.69, 128.80, 120.94, 117.32, 68.31, 44.09, 34.55, 21.77; IR (neat): ν 3007, 2989, 2377, 2350, 2320, 1732, 1695, 1275, 1261, 1172, 1086, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_4S$ $[M+H]^+$ =344.0956, found =344.0994; Enantiomeric excess: 85%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 14.8 min, second peak: t_R = 18.8 min.

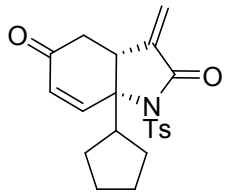
(3aR,7aR)-3-methylene-1-tosyl-7a-((trimethylsilyl)ethynyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2o**) 42% yield; white solid; mp 102-105°C; $[\alpha]^{28}_D$ = +19.6 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 10.0 Hz, 1H), 6.18 (s, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 5.45 (s, 1H), 3.59 (s, 1H), 3.07 – 2.93 (m, 1H), 2.82 (d, *J* = 16.7 Hz, 1H), 2.46 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.12, 164.52, 145.96, 143.70, 137.83, 136.01, 129.89, 129.14, 128.34, 121.34, 100.04, 94.17, 59.54, 46.85, 36.21, 22.13, 0.00; IR (neat): ν 3007, 2988, 2965, 2377, 2350, 2320, 1737, 1697, 1596, 1365, 1275, 1260, 1175, 1087, 1017,

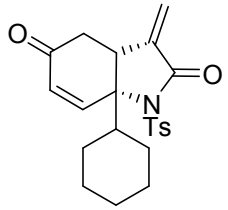
920, 844, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_4S$ $[M+Na]^+$ = 436.1015, found = 436.1012; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 9.4 min, second peak: t_R = 10.7 min.

(3aR,7aR)-7a-cyclopentyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2p**) 88% yield; white solid; mp 127-130°C; $[\alpha]^{28}_D$ = +24.0 (*c* = 0.25, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 10.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 10.6 Hz, 1H), 6.13 (s, 1H), 5.47 (s, 1H), 3.35 (t, *J* = 7.6 Hz, 1H), 3.07 – 2.92 (m, 1H), 2.57 (dd, *J* = 16.3, 6.3 Hz, 1H), 2.43 (s, 3H), 2.41 – 2.33 (m, 1H), 1.85 – 1.74 (m, 2H), 1.68 (d, *J* = 15.8 Hz, 4H), 1.31 (dd, *J* = 23.4, 13.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.57, 165.36, 146.48, 145.40, 140.70, 135.56, 129.63, 129.47, 128.81, 120.45, 68.62, 49.16, 41.19, 38.87, 28.42, 27.52, 25.43, 25.03, 21.72; IR (neat): ν 3006, 2988, 2377, 2350, 2321, 1725, 1694, 1275, 1261, 1159, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{23}NO_4S$ $[M+H]^+$ =386.1426, found =386.1424; Enantiomeric excess: 95%, determined by HPLC (Chiralpak IC, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 72.5 min, second peak: t_R = 95.0 min.

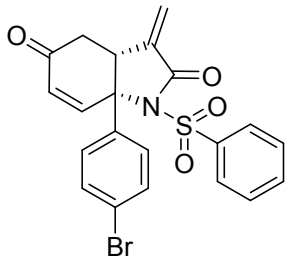
(3aR,7aR)-7a-cyclohexyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2q**) 87% yield; white solid; mp 169-171°C; $[\alpha]^{28}_D$ = -9.2 (*c* = 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 10.6 Hz, 1H), 7.33 (d, *J* =

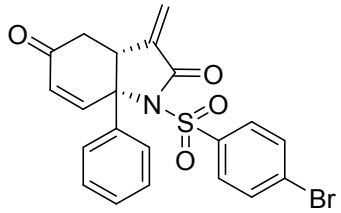
8.0 Hz, 2H), 6.23 (d, *J* = 10.6 Hz, 1H), 6.13 (d, *J* = 1.7 Hz, 1H), 5.45 (s, 1H), 3.44 (t, *J* = 6.8 Hz, 1H), 2.62 (dd, *J* = 16.5, 6.4 Hz, 1H), 2.52 (dd, *J* = 21.8, 9.8 Hz, 2H), 2.43 (s, 3H), 1.79 (dt, *J* = 26.5, 13.1 Hz, 5H), 1.31 (dt, *J* = 20.7, 10.5 Hz, 2H), 1.18 – 0.93 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.49, 165.67, 147.07, 145.45, 140.36, 135.50, 130.28, 129.41, 128.97, 120.49, 70.69, 45.80, 40.86, 37.82, 28.85, 27.17, 26.41, 26.13, 26.04, 21.71; IR (neat): ν 3006, 2989, 2378, 2350, 2320, 1722, 1690, 1573, 1275, 1261, 1157, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_4S$ $[M+H]^+$ =400.1583, found =400.1579; Enantiomeric excess: 97%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 38.0 min, second peak: t_R = 42.1 min, third peak: t_R = 46.4 min, fourth peak: t_R = 56.6 min.

(3aR,7aR)-7a-(4-bromophenyl)-3-methylene-1-(phenylsulfonyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



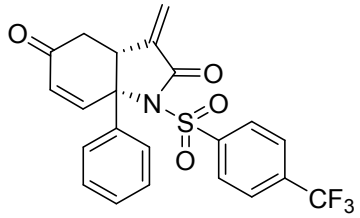
(**2r**) 79% yield; white solid; mp 93-96°C; $[\alpha]^{28}_D$ = -64.1 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.7 Hz, 2H), 7.68 (d, *J* = 6.0 Hz, 1H), 7.58 (s, 4H), 7.47 (d, *J* = 9.9 Hz, 1H), 7.34 – 7.26 (m, 2H), 6.35 (d, *J* = 10.2 Hz, 1H), 6.26 (s, 1H), 5.47 (s, 1H), 3.37 (s, 1H), 2.71 (d, *J* = 16.2 Hz, 1H), 2.59 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.10, 165.61, 143.81, 138.69, 138.33, 137.93, 134.60, 132.21, 130.70, 129.09, 128.91, 127.56, 123.13, 121.24, 69.49, 48.69, 34.96; IR (neat): ν 3007, 2989, 2378, 2350, 2320, 1732, 1695, 1275, 1261, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_4S$ $[M+H]^+$ =458.0062, found =458.0058; Enantiomeric excess: 91%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 22.9 min, second peak: t_R = 45.7 min.

(3aR,7aR)-1-((4-bromophenyl)sulfonyl)-3-methylene-7a-phenyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2s**) 51% yield; white solid; mp 147-149°C; $[\alpha]^{28}_{D}$ = -100.1 (*c* = 0.25, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.39 (s, 2H), 6.34 (d, *J* = 10.4 Hz, 1H), 6.27 (s, 1H), 5.49 (s, 1H), 3.44 (s, 1H), 2.71 (d, *J* = 16.3 Hz, 1H), 2.60 (dd, *J* = 16.7, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.36, 165.82, 144.30, 139.22, 138.10, 137.39, 132.12, 130.63, 130.50, 129.99, 129.06, 128.15, 125.86, 121.18, 70.15, 48.80, 35.01; IR (neat): ν 3006, 2989, 2378, 2350, 2320, 1731, 1694, 1572, 1275, 1261, 1150, 1067, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_4S$ $[M+H]^+$ =458.0062, found =458.0066; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 17.3 min, second peak: t_R = 33.5 min.

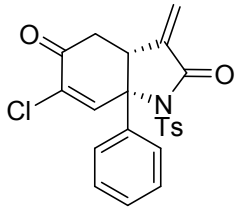
(3aR,7aR)-3-methylene-7a-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2t**) 76% yield; white solid; mp 83-85°C; $[\alpha]^{28}_{D}$ = -54.1 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 17.8 Hz, 4H), 7.40 (s, 2H), 6.36 (d, *J* = 10.3 Hz, 1H), 6.28 (s, 1H), 5.51 (s, 1H), 3.47 (s, 1H), 2.72 (d, *J* = 16.7 Hz, 1H), 2.66 – 2.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.22, 165.83, 144.14, 141.80, 139.08, 137.94, 136.06, 135.73, 130.63, 129.73, 129.15 (d, *J* = 7.9 Hz), 125.94 (d, *J* = 3.7 Hz), 125.89, 124.40, 121.47, 70.27, 48.81, 35.01; IR (neat): ν 3006, 2989, 2378, 2350, 2320, 1731, 1694, 1572, 1275, 1261, 1150, 1067, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{16}F_3NO_4S$ $[M+H]^+$ =448.0830, found =448.0838; Enantiomeric excess: 86%, determined by HPLC

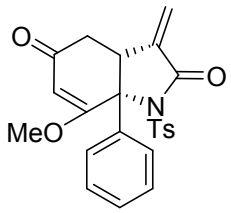
(Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 12.0 min, second peak: t_R = 17.3 min.

(3aR,7aS)-6-chloro-3-methylene-7a-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2u**) 33% yield; white solid; mp 223-225°C; $[\alpha]^{28}_D$ = -27.4 (*c* = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.74 (s, 1H), 7.46 (s, 3H), 7.40 (s, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 6.27 (s, 1H), 5.47 (s, 1H), 3.44 (s, 1H), 2.88 (d, *J* = 15.0 Hz, 1H), 2.71 (dd, *J* = 16.7, 5.0 Hz, 1H), 2.46 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 187.07, 165.46, 145.93, 140.96, 139.13, 137.67, 135.31, 134.22, 129.48, 129.17, 125.71, 121.30, 71.09, 48.56, 35.29, 21.79; IR (neat): ν 3006, 2989, 2370, 2350, 2320, 1732, 1710, 1364, 1275, 1261, 1188, 1158, 1085, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClNO_4S$ $[M+H]^+$ =428.0723, found =428.0769; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 20.9 min, second peak: t_R = 23.4 min.

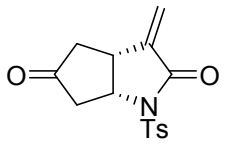
(3aR,7aR)-7-methoxy-3-methylene-7a-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione



(**2u**) 47% yield; white solid; mp 215-217°C; $[\alpha]^{28}_D$ = -82.5 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.47 (s, 4H), 7.34 (d, *J* = 8.2 Hz, 3H), 6.20 (d, *J* = 3.2 Hz, 1H), 5.64 (s, 1H), 5.43 (d, *J* = 2.9 Hz, 1H), 3.87 (s, 3H), 3.47 (dd, *J* = 5.1, 2.5 Hz, 1H), 2.65 (dd, *J* = 17.2, 1.9 Hz, 1H), 2.45 (s, 3H), 2.41 (dd, *J* = 13.3, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.24, 170.50, 165.95, 145.22, 137.93, 137.03, 136.34, 129.89, 129.08, 128.72, 128.07, 126.54, 119.61, 104.87,

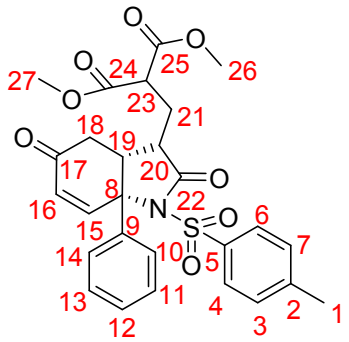
73.29, 56.46, 50.33, 33.51, 21.71; IR (neat): ν 3007, 2989, 2370, 2350, 2320, 1732, 1671, 1608, 1454, 1364, 1275, 1261, 1226, 1169, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_5S$ $[M+H]^+$ =424.1219, found =424.1211; Enantiomeric excess: 73%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 21.8 min, second peak: t_R = 27.3 min.

(3aR,6aR)-3-methylene-1-tosyltetrahydrocyclopenta[b]pyrrole-2,5(1H,3H)-dione



(**2w**) 49% yield; white solid; mp 94-96°C; $[\alpha]^{28}_D$ = -10.3 (*c* = 0.35, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 6.27 (s, 1H), 5.56 (s, 1H), 4.96 (dd, *J* = 14.2, 6.5 Hz, 1H), 3.71 (s, 1H), 2.97 (dd, *J* = 19.3, 8.1 Hz, 1H), 2.79 (dd, *J* = 19.3, 10.0 Hz, 1H), 2.45 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.99, 165.10, 145.78, 141.24, 135.12, 129.83, 128.53, 122.94, 57.06, 44.46, 42.98, 37.41, 21.74; IR (neat): ν 3006, 2958, 2923, 2851, 2370, 2350, 2320, 1728, 1657, 1595, 1358, 1275, 1261, 1226, 1169, 1088, 1038, 763, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{15}NO_4S$ $[M+H]^+$ = 306.0800, found = 306.0896; Enantiomeric excess: 91%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 75.4 min, second peak: t_R = 83.3 min.

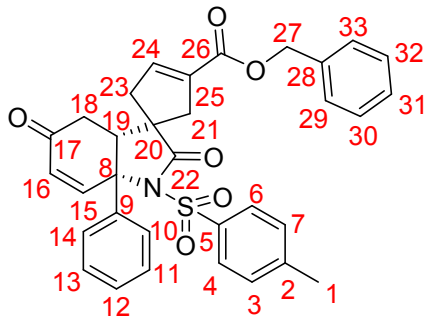
Dimethyl-2-(((3R,3aR,7aR)-2,5-dioxo-7a-phenyl-1-tosyl-2,3,3a,4,5,7a-hexahydro-1H-indol-3-yl)methyl)malonate



(**4a**) 82% yield; white solid; mp 115-117°C; $[\alpha]^{25}_D$ = -52.0 (*c* = 0.5, CH_2Cl_2); ^1H

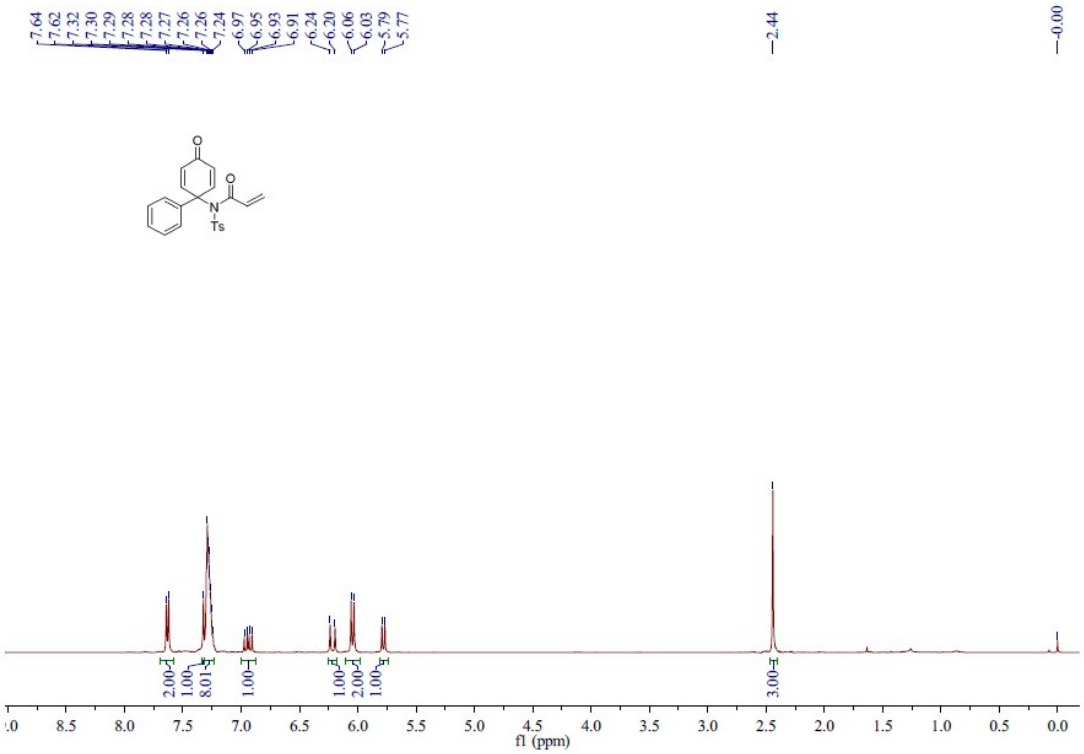
NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 10.4 Hz, 1H), 7.42 (s, 3H), 7.37 – 7.28 (m, 4H), 6.43 (d, *J* = 10.4 Hz, 1H), 3.95 (t, *J* = 7.3 Hz, 1H), 3.70 (d, *J* = 2.6 Hz, 6H), 2.62 – 2.48 (m, 3H), 2.46 (s, 3H), 2.42 (d, *J* = 5.9 Hz, 1H), 2.17 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.49 (C=O, C17), 173.95 (C=O, C22), 169.17 (C=O, C24, C25), 168.88 (C, Ar), 145.65 (C, Ar), 144.43 (CH, C15), 139.22 (C, Ar), 135.48 (C, C16), 130.79 (CH, Ar), 129.34 (CH, Ar), 129.25 (CH, Ar), 128.91 (CH, Ar), 126.05 (CH, Ar), 69.67 (C8), 52.90 (CH_3, C26), 52.81 (CH_3, C27), 49.61 (CH, C23), 48.53 (CH, C19), 42.21 (CH, C20), 34.65 (CH_2, C18), 27.08 (CH_2, C21), 21.77 (CH_3, C1); IR (neat): ν 2961, 2924, 2853, 2360, 2340, 2271, 1749, 1717, 1684, 1558, 1261, 1155, 1074, 871, 805, 764 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{27}NO_8S$ $[M+H]^+$ = 526.1536, found = 526.1544; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 20.4 min, second peak: t_R = 48.5 min.

Benzyl-(1R,3a'R,7a'R)-2',5'-dioxo-7a'-phenyl-1'-tosyl-1',2',3a',4',5',7a'-hexahydrospiro[cyclopentane-1,3'-indol]-3-ene-3-carboxylate

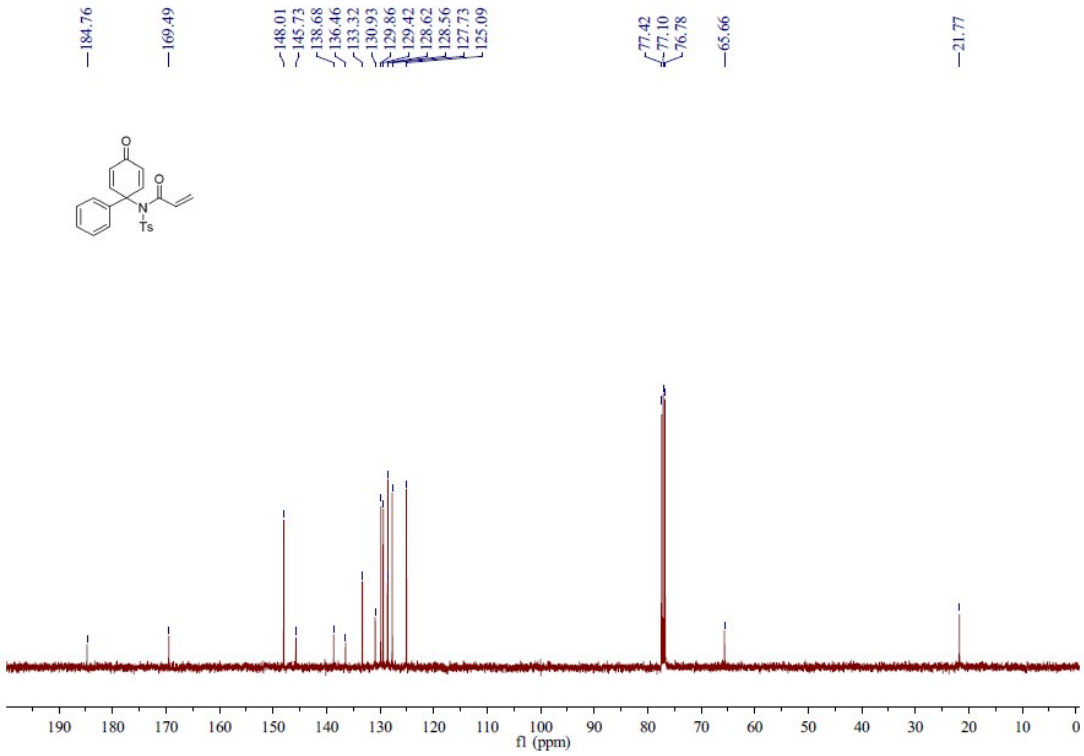


(**4b**) 95% yield; white solid; mp > 230°C; $[\alpha]^{25}_D$ = -77.7 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 10.3 Hz, 1H), 7.41 (d, *J* = 2.7 Hz, 5H), 7.37 – 7.27 (m, 7H), 6.66 (s, 1H), 6.51 (d, *J* = 10.4 Hz, 1H), 5.12 (q, *J* = 12.4 Hz, 2H), 3.01 (d, *J* = 18.6 Hz, 1H), 2.85 (s, 1H), 2.58 (s, 2H), 2.50 (d, *J* = 6.3 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 1H), 2.33 (d, *J* = 19.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.82 (C=O, C17), 176.76 (C=O, C22), 163.28 (C=O, C26), 145.70 (C25), 145.54 (CH, C24), 140.66 (CH, C15), 140.55 (C, Ar), 135.77 (C, Ar), 135.13 (C, Ar), 133.74 (C, Ar), 131.08 (CH, C16), 129.43 (CH, Ar), 129.15 (CH, Ar), 129.01 (CH, Ar), 128.78 (CH, Ar), 128.55 (CH, Ar), 128.24 (CH, Ar), 128.21 (CH, Ar), 125.83 (CH, Ar), 68.86 (C8), 66.34 (CH_2, C27), 53.05 (C20), 52.86 (CH, C19), 42.92 (CH_2, C21),

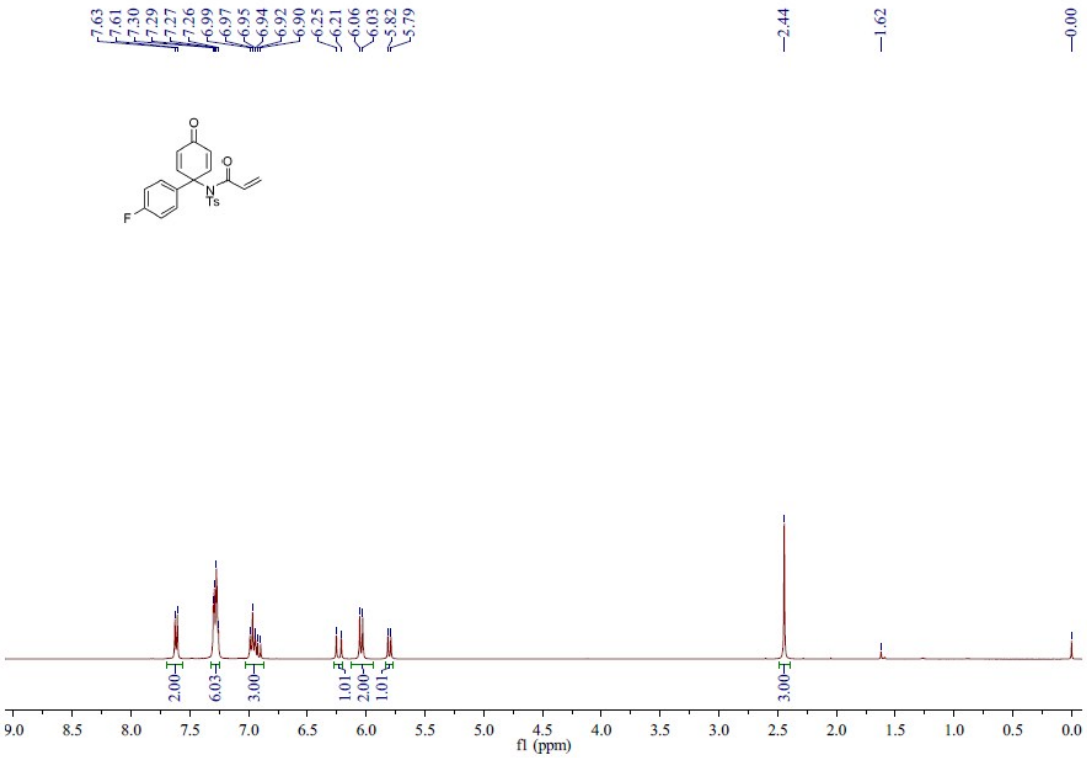
37.70 (CH_2, C23), 33.40 (CH_2, C18), 21.76 (CH_3, C1); IR (neat): ν 2961, 2924, 2853, 2360, 2340, 2271, 1761, 1699, 1647, 1576, 1075, 860, 804 cm^{-1}; HRMS (ESI) m/z calcd for $C_{33}H_{29}NO_6S$ $[M+H]^+$ = 568.1794, found = 568.1792; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 49.1 min, second peak: t_R = 93.2 min.



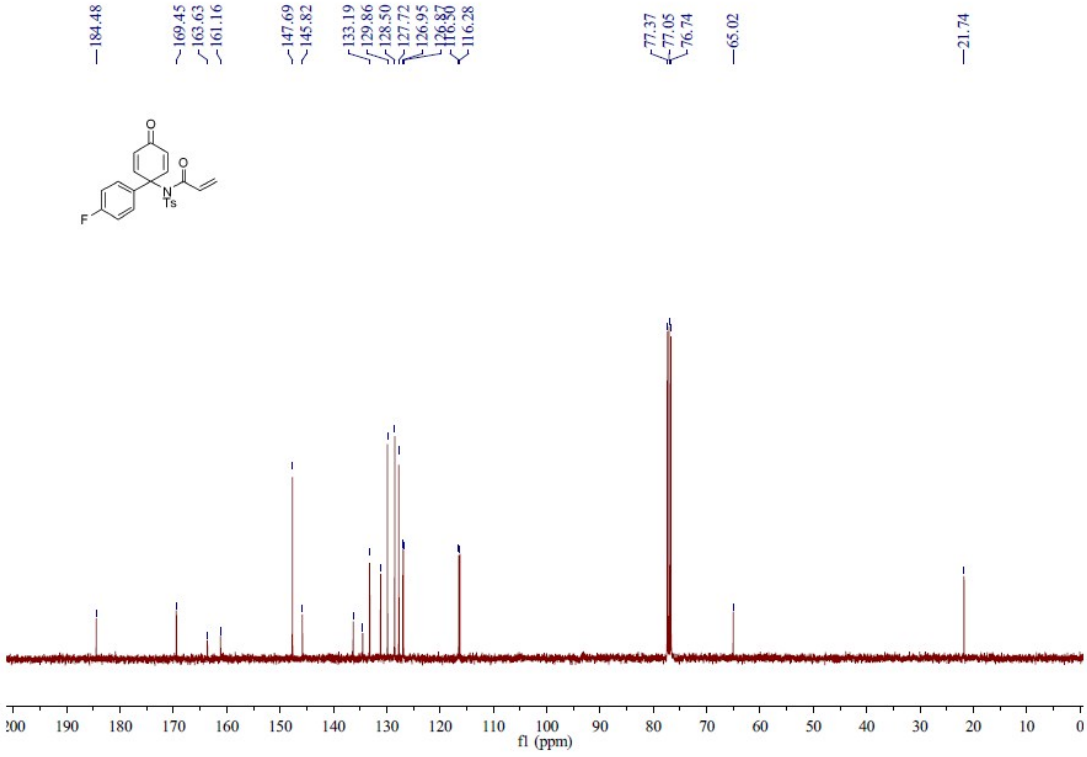
^{1}H NMR spectra of **1a**



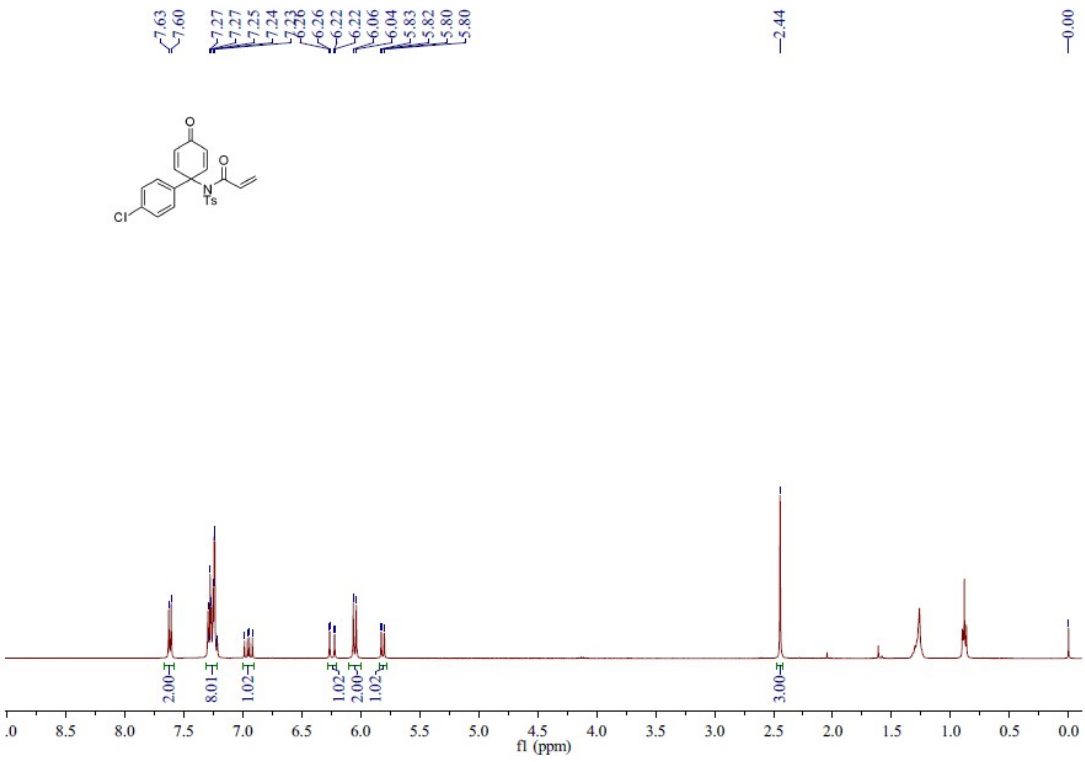
^{13}C NMR spectra of **1a**



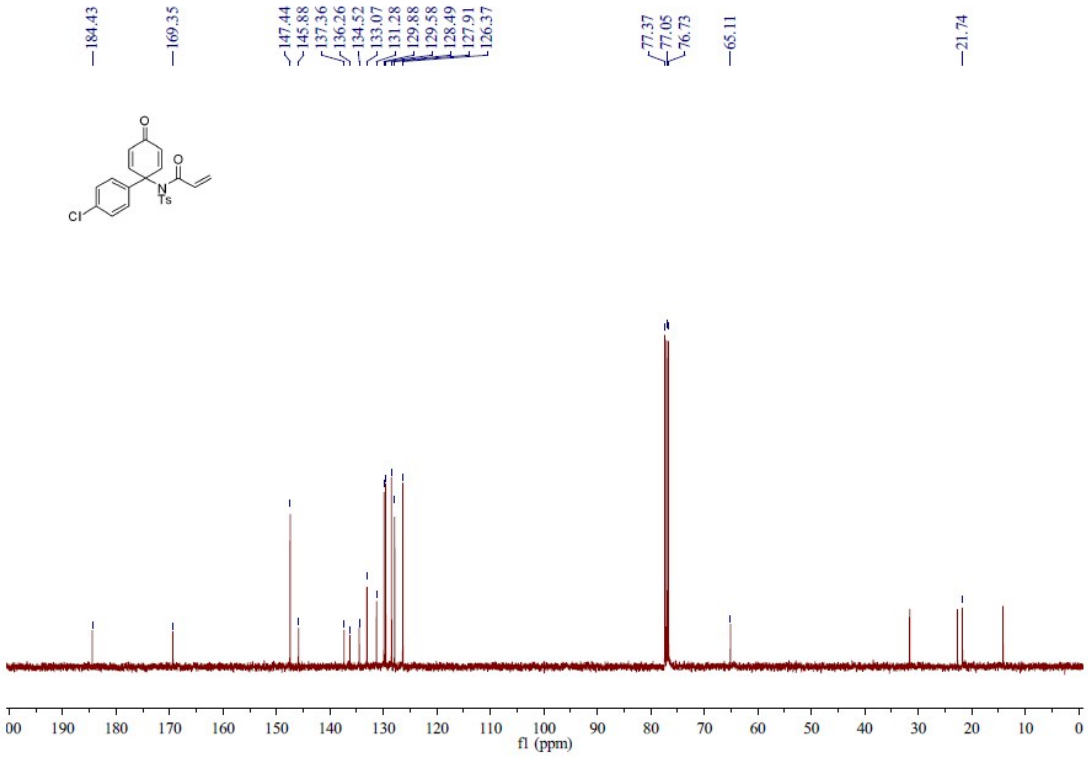
^{1}H NMR spectra of **1b**



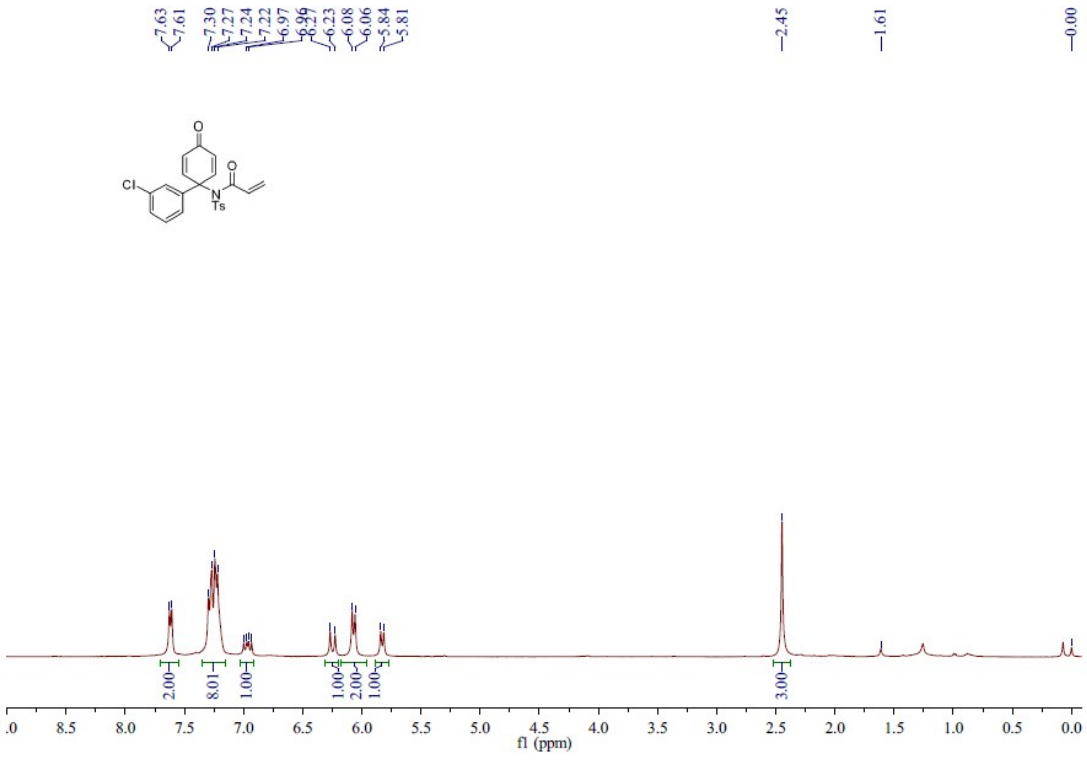
^{13}C NMR spectra of **1b**



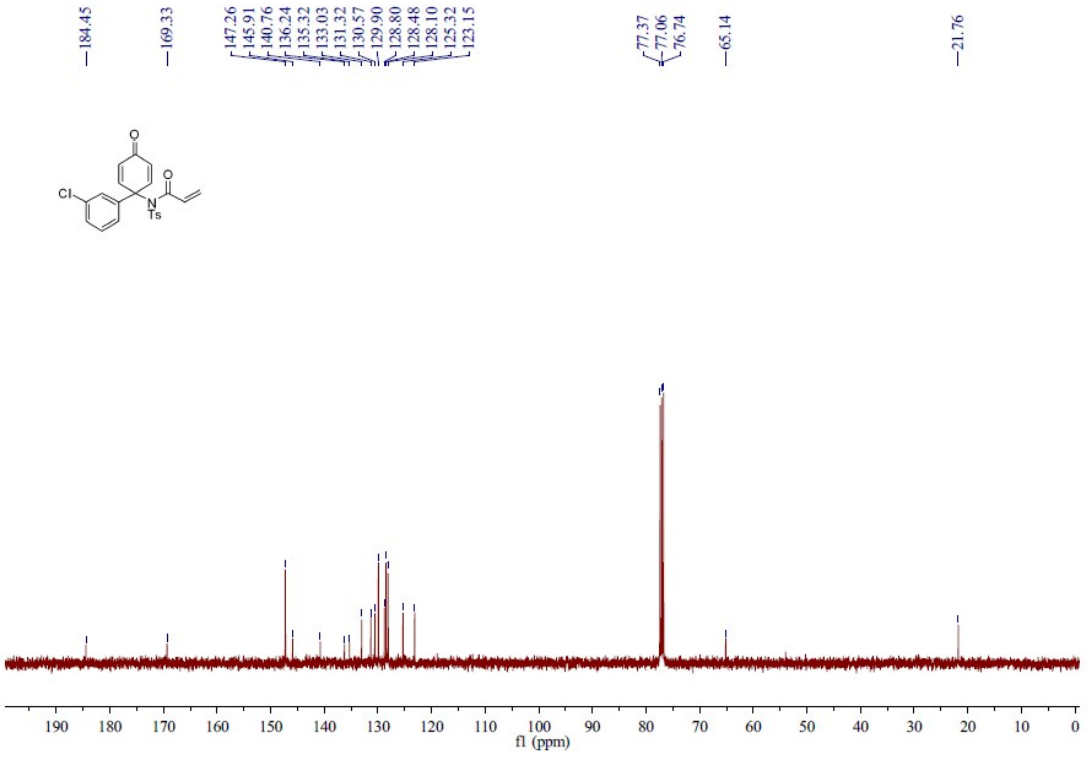
^{1}H NMR spectra of **1c**



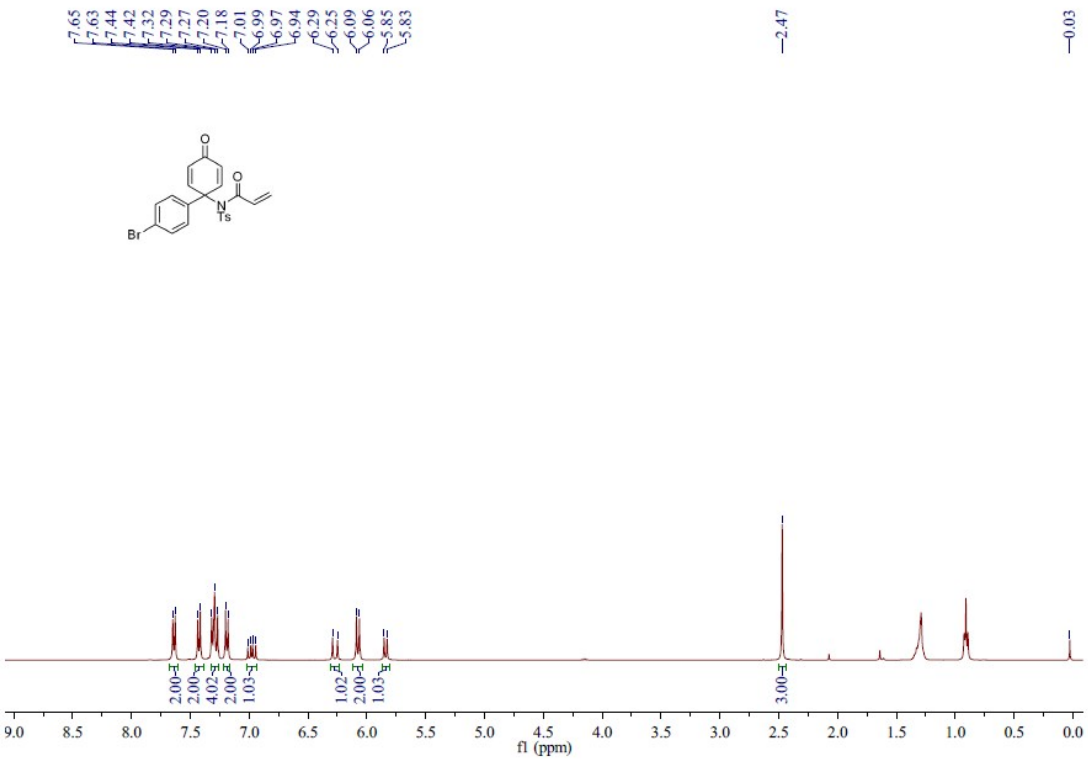
^{13}C NMR spectra of **1c**



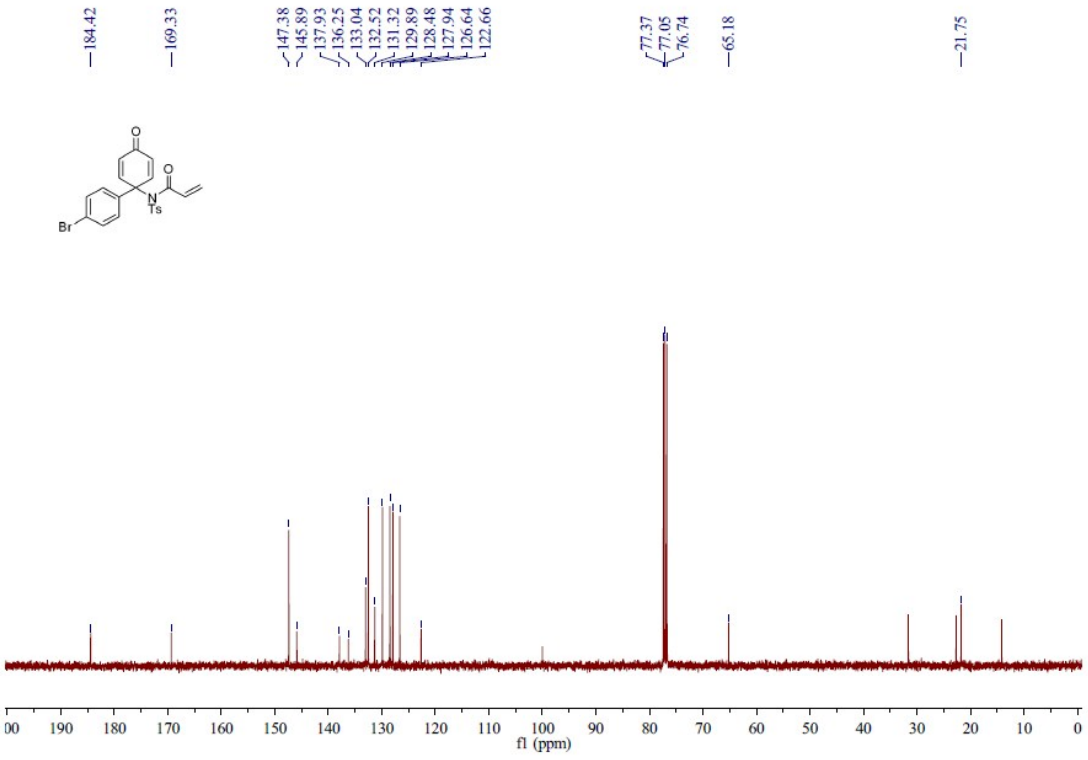
^{1}H NMR spectra of **1d**



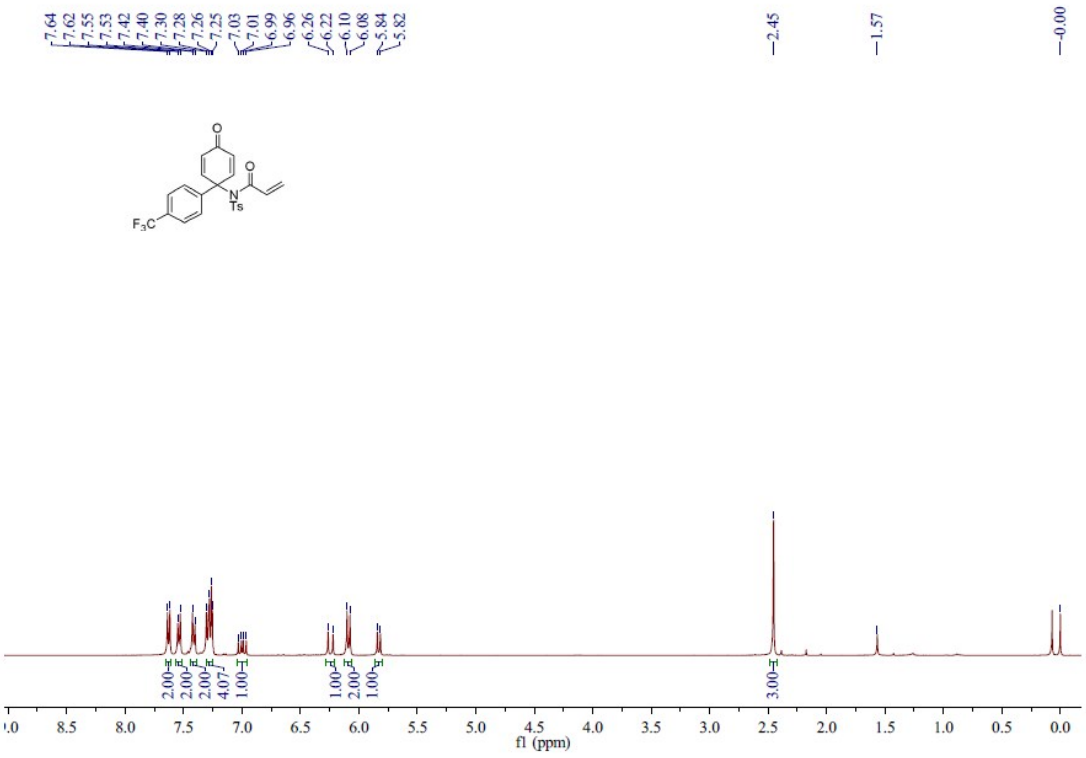
^{13}C NMR spectra of **1d**



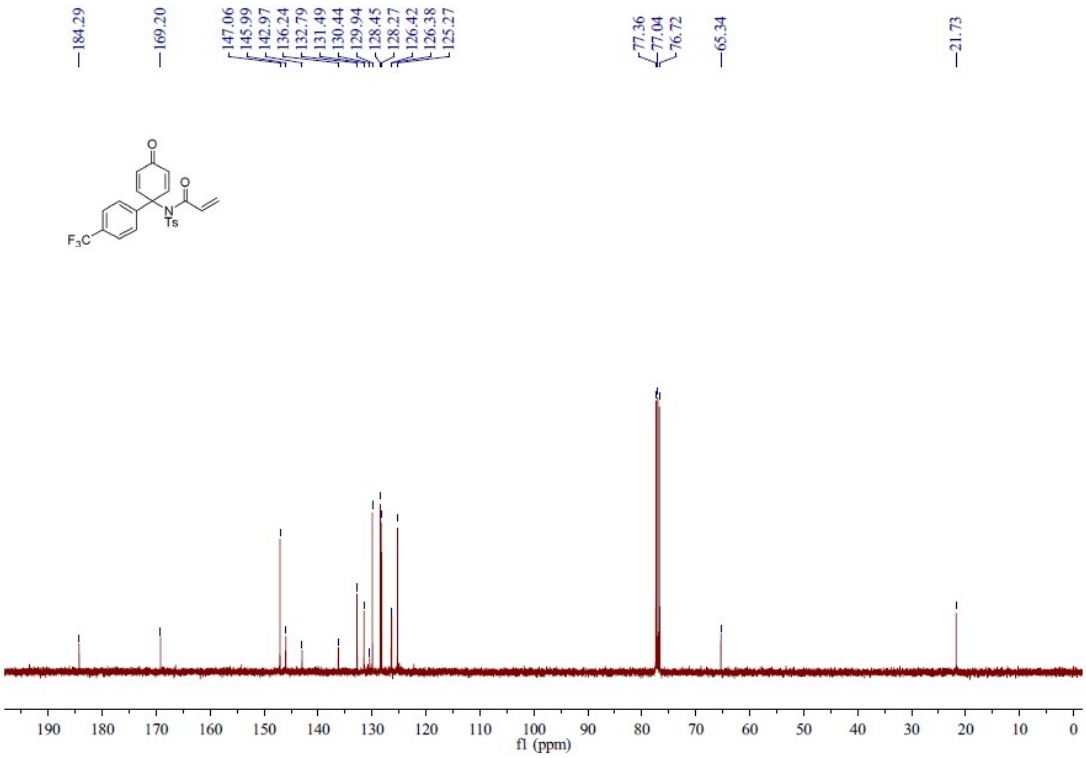
^{1}H NMR spectra of **1e**



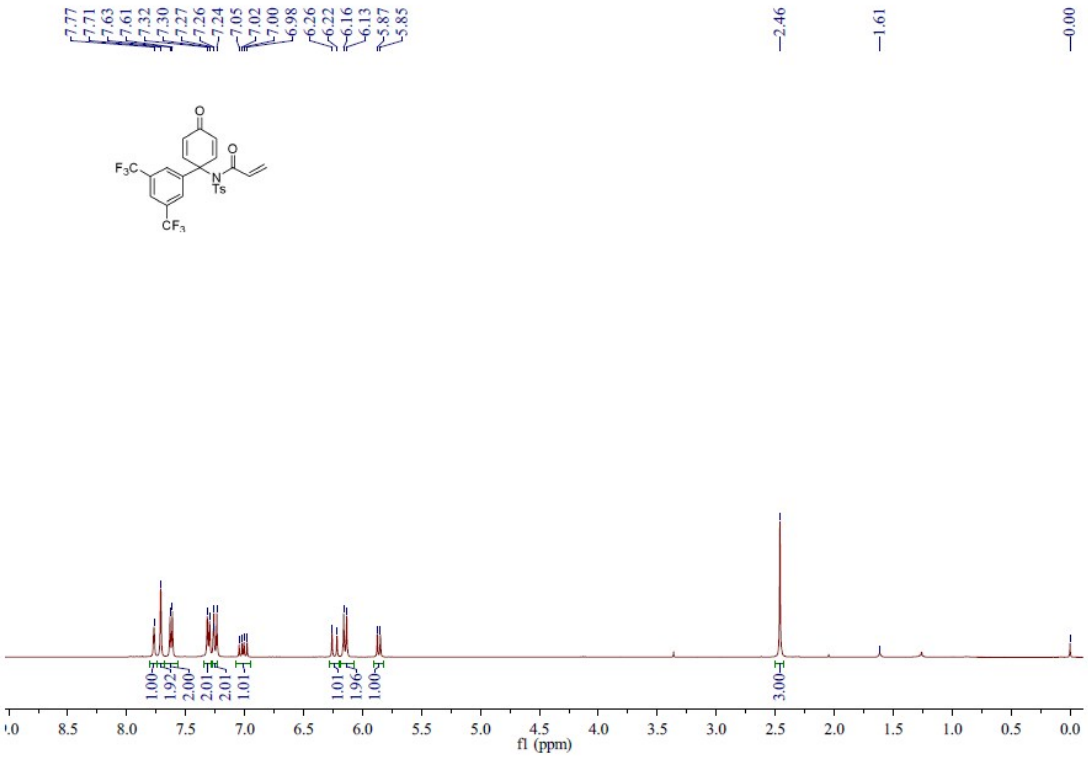
^{13}C NMR spectra of **1e**



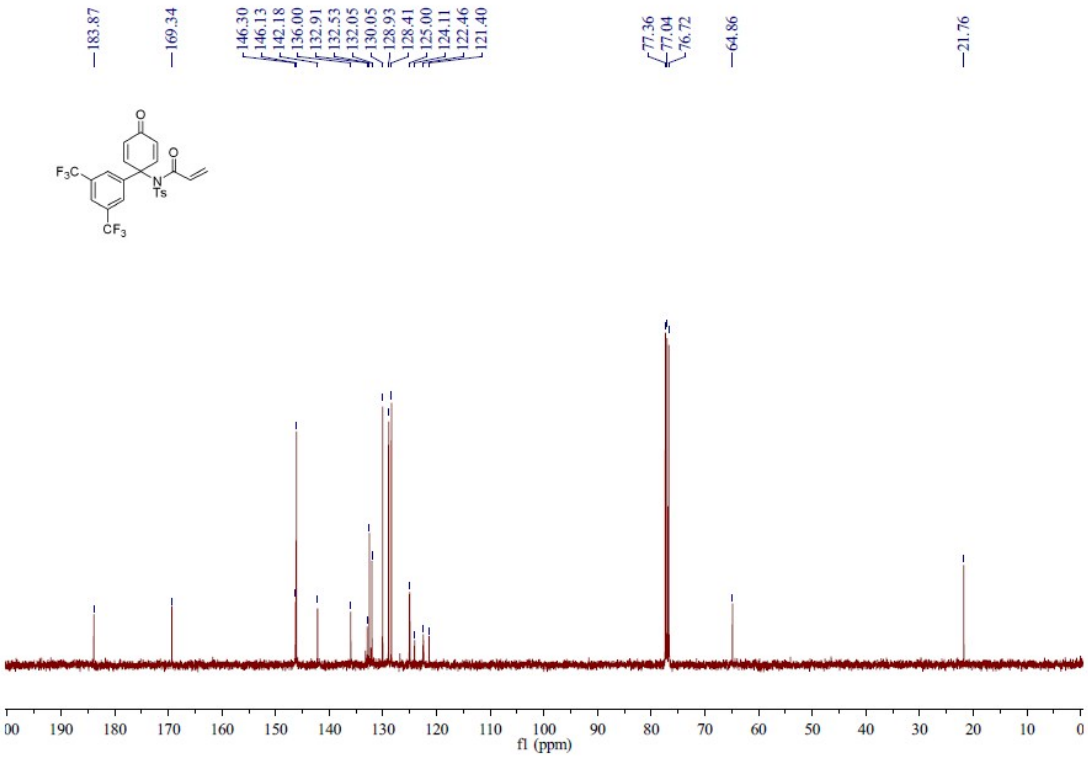
^{1}H NMR spectra of **1f**



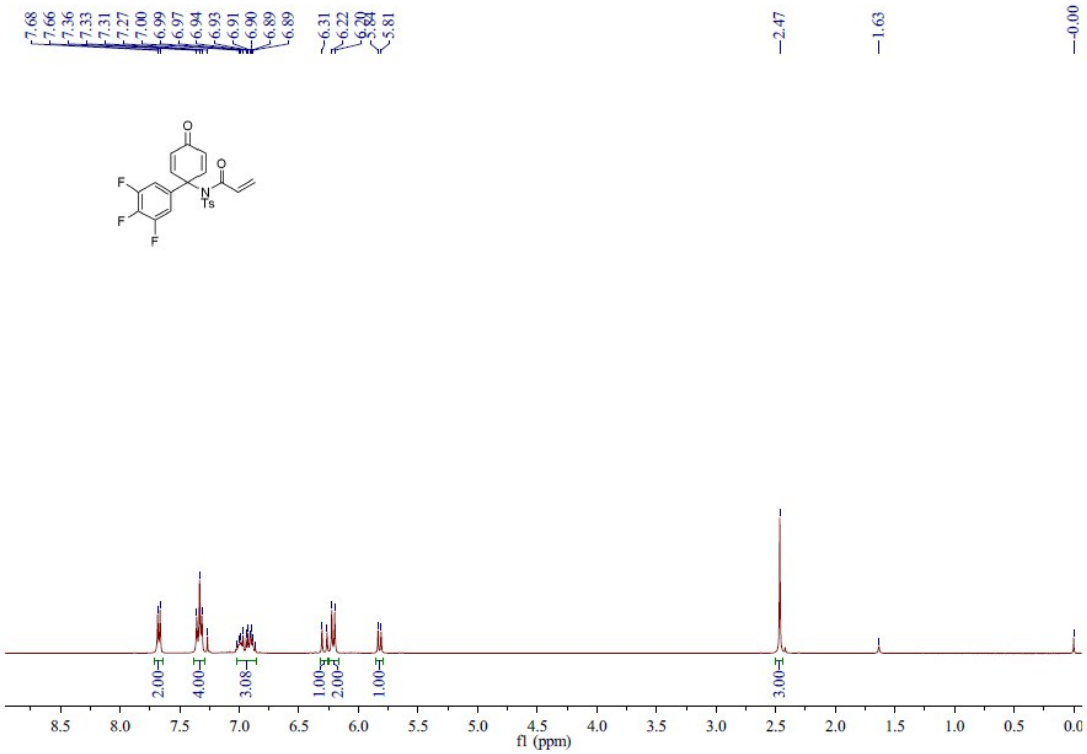
^{13}C NMR spectra of **1f**



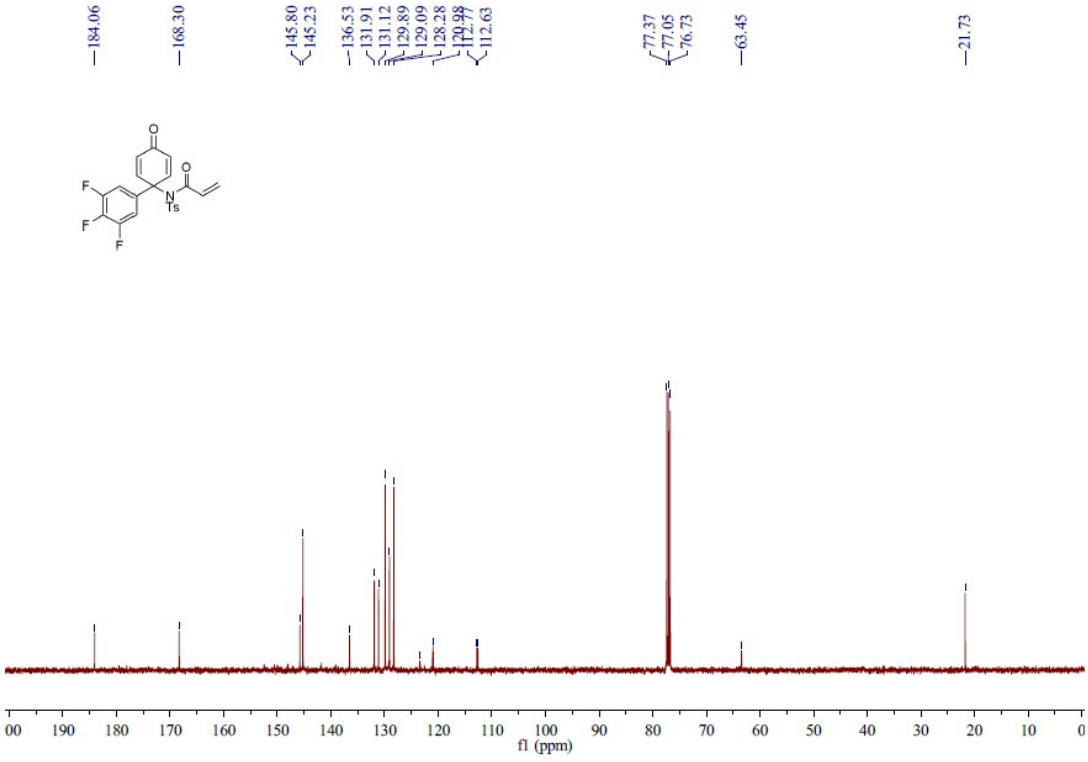
^{1}H NMR spectra of **1g**



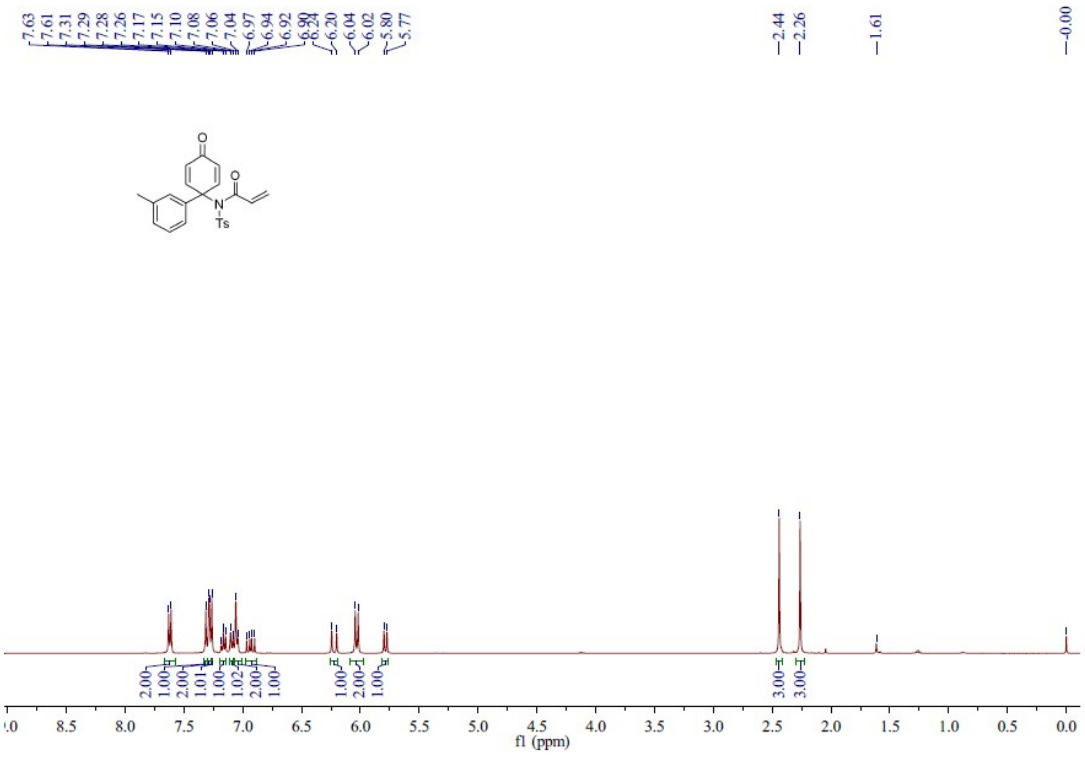
^{13}C NMR spectra of **1g**



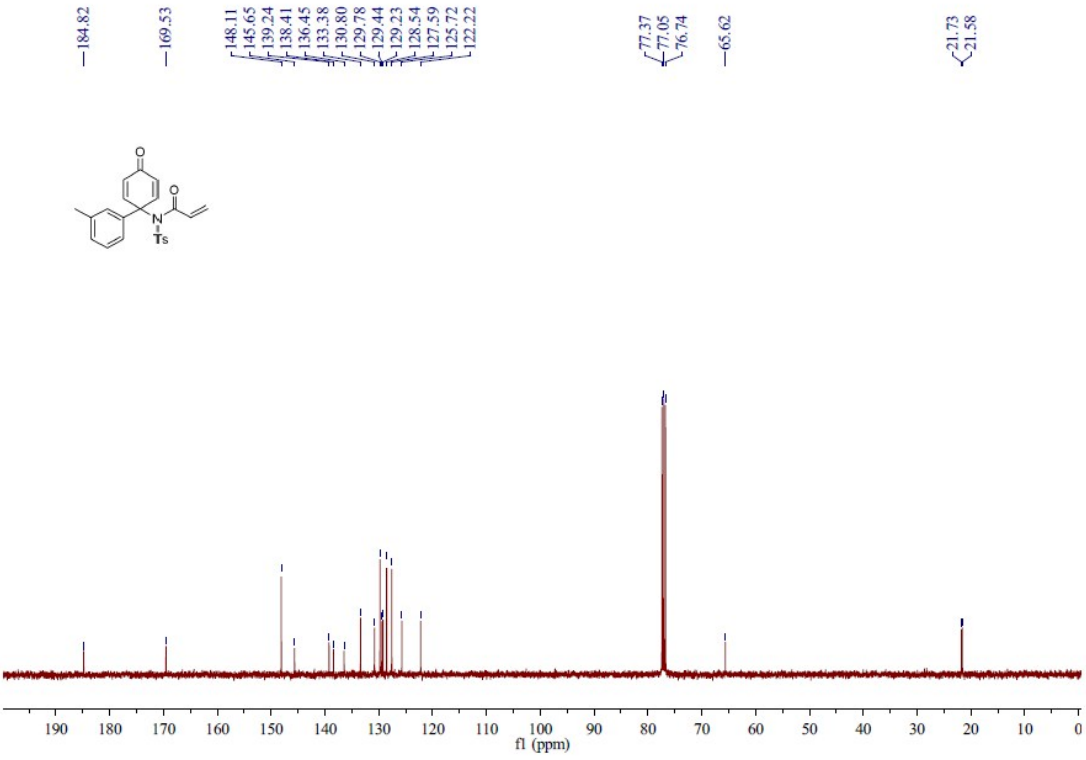
^{1}H NMR spectra of **1h**



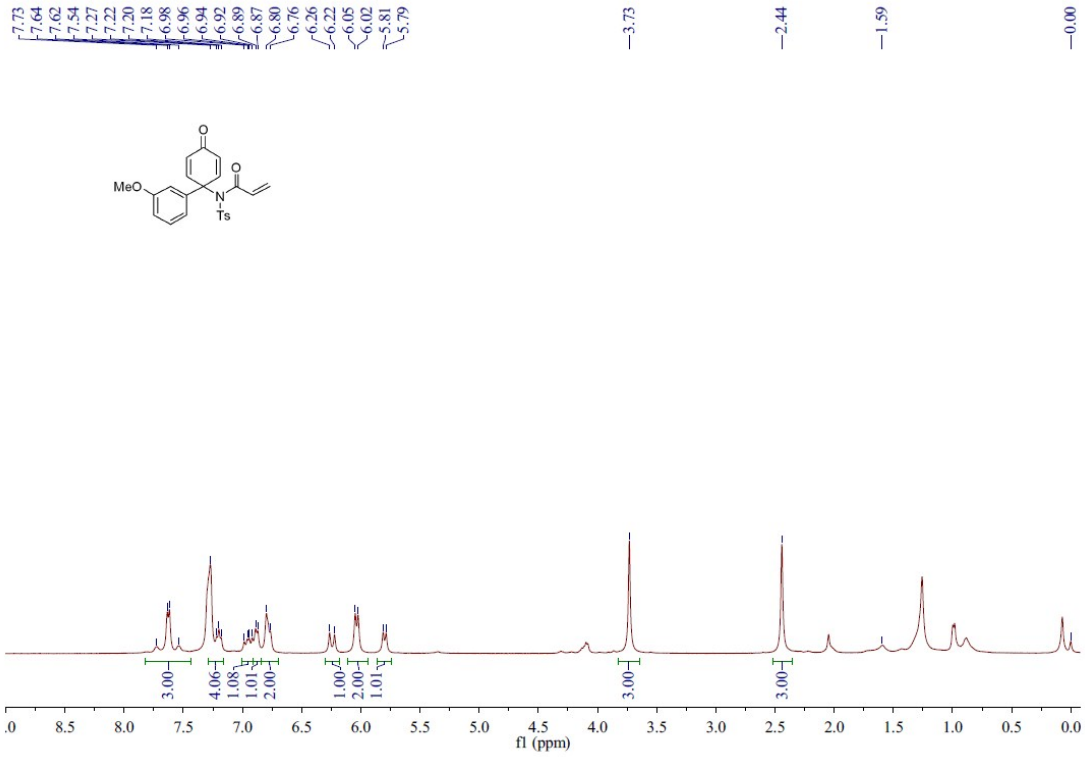
^{13}C NMR spectra of **1h**



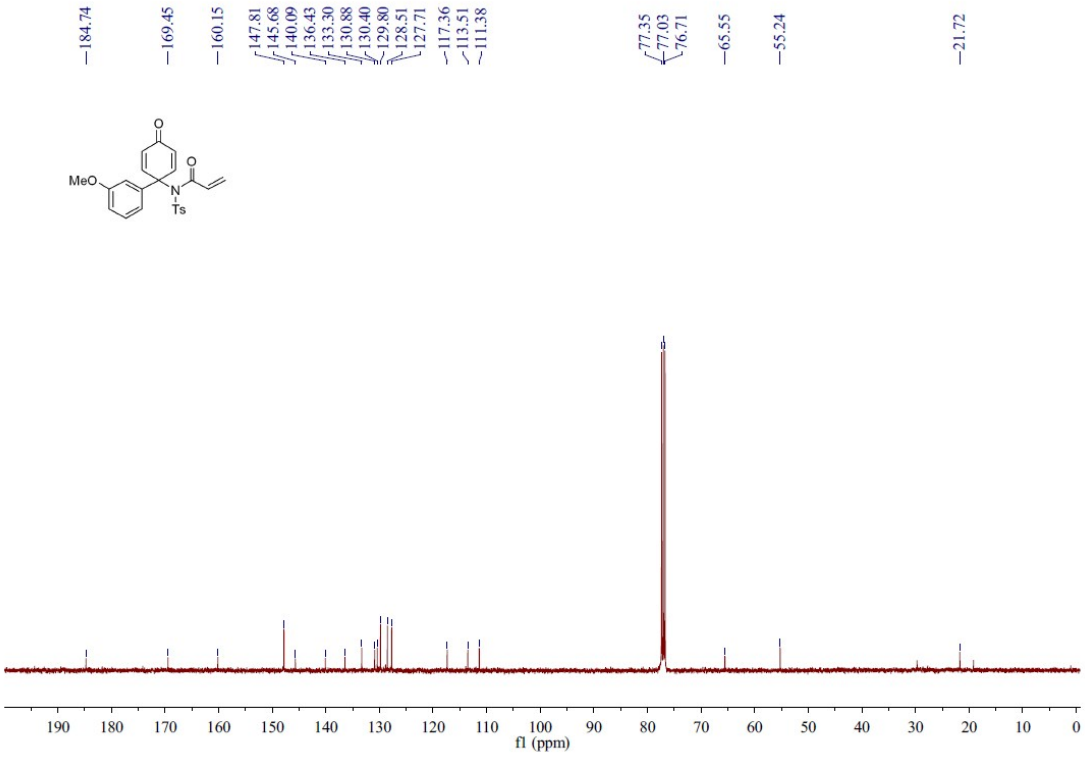
^{1}H NMR spectra of **1i**



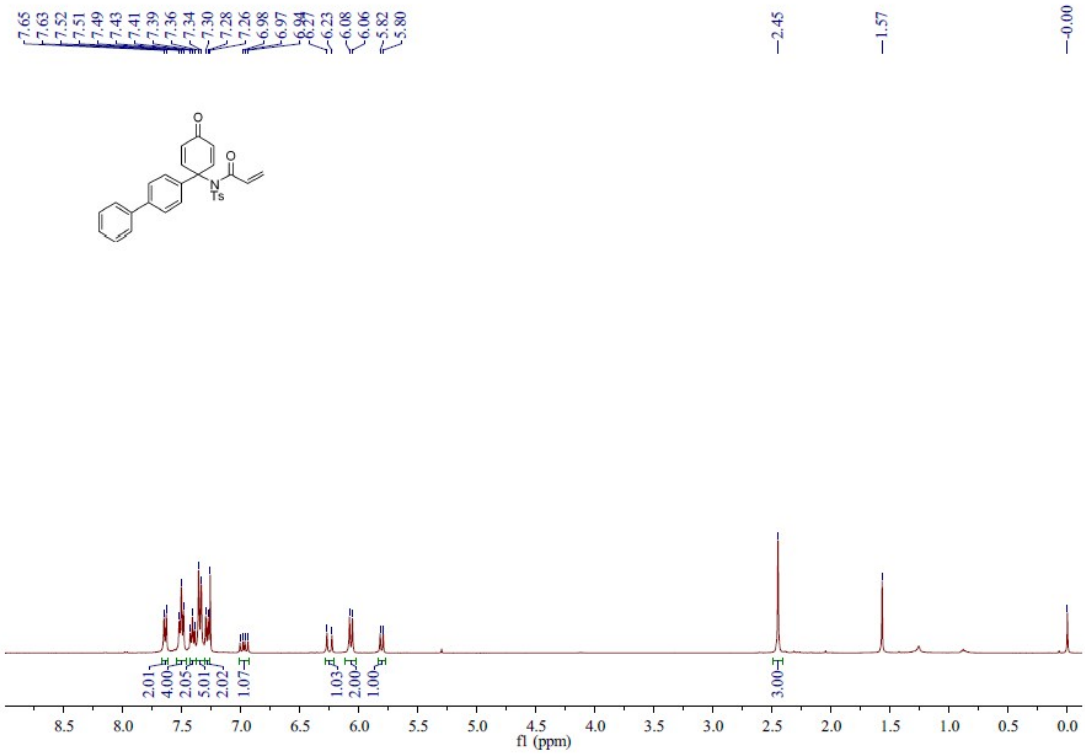
^{13}C NMR spectra of **1i**



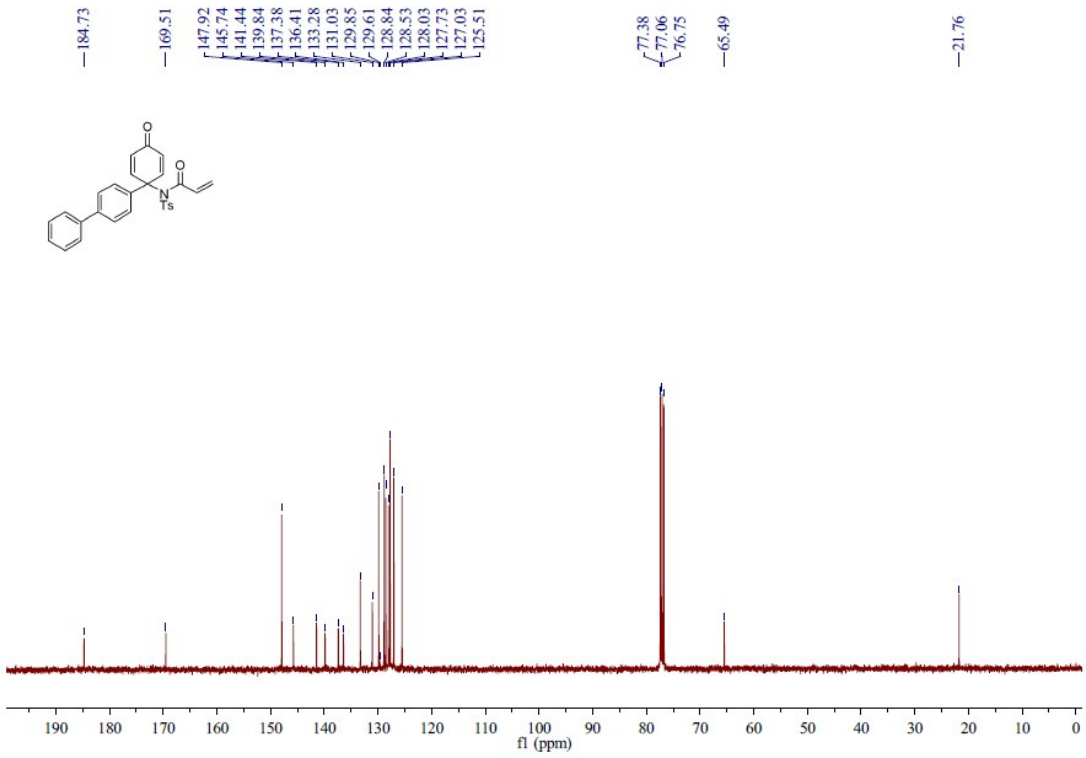
^{1}H NMR spectra of **1j**



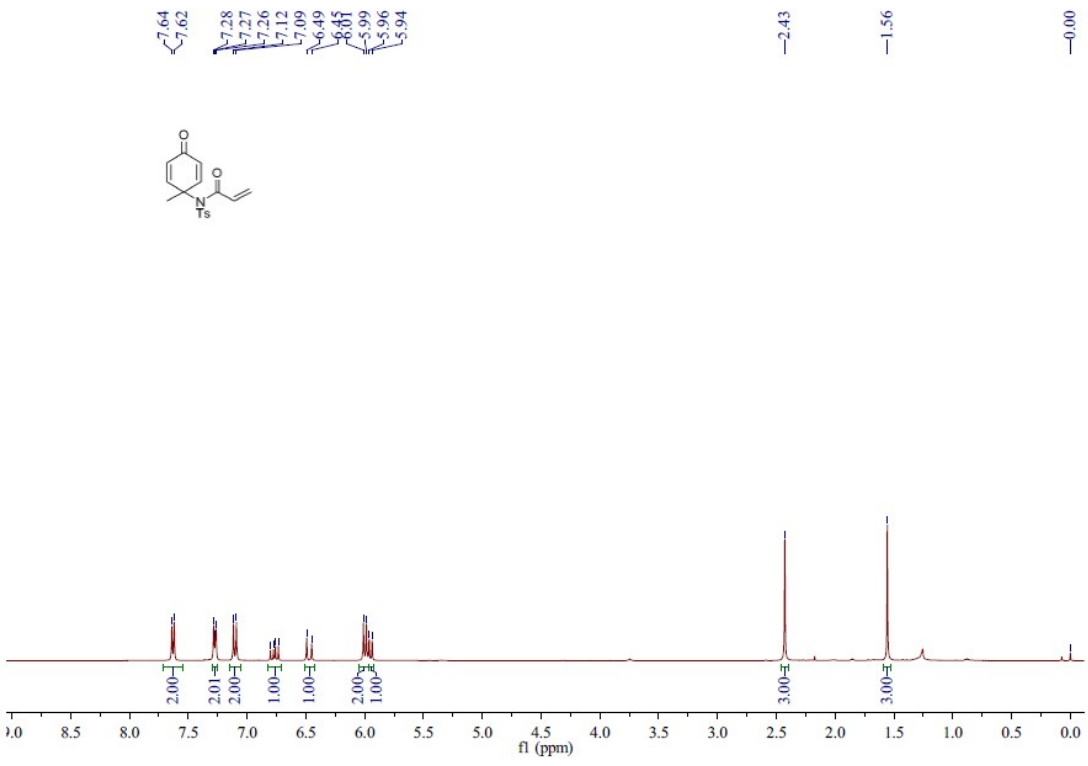
^{13}C NMR spectra of **1j**



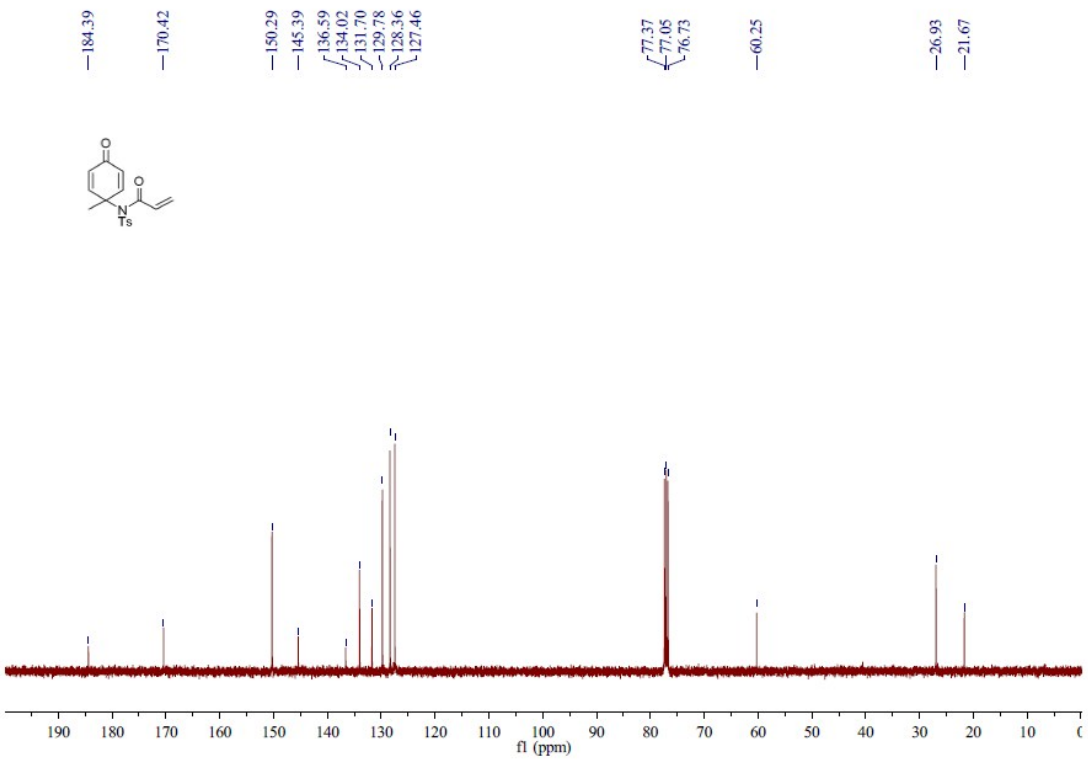
^{1}H NMR spectra of **1k**



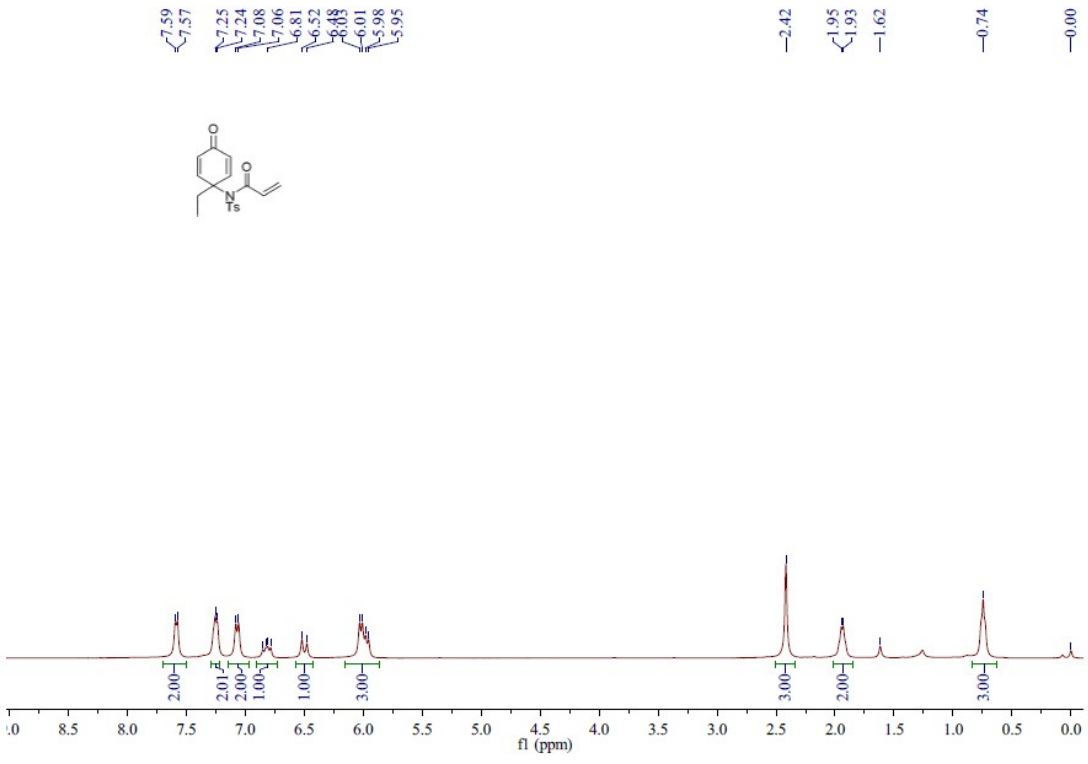
^{13}C NMR spectra of **1k**



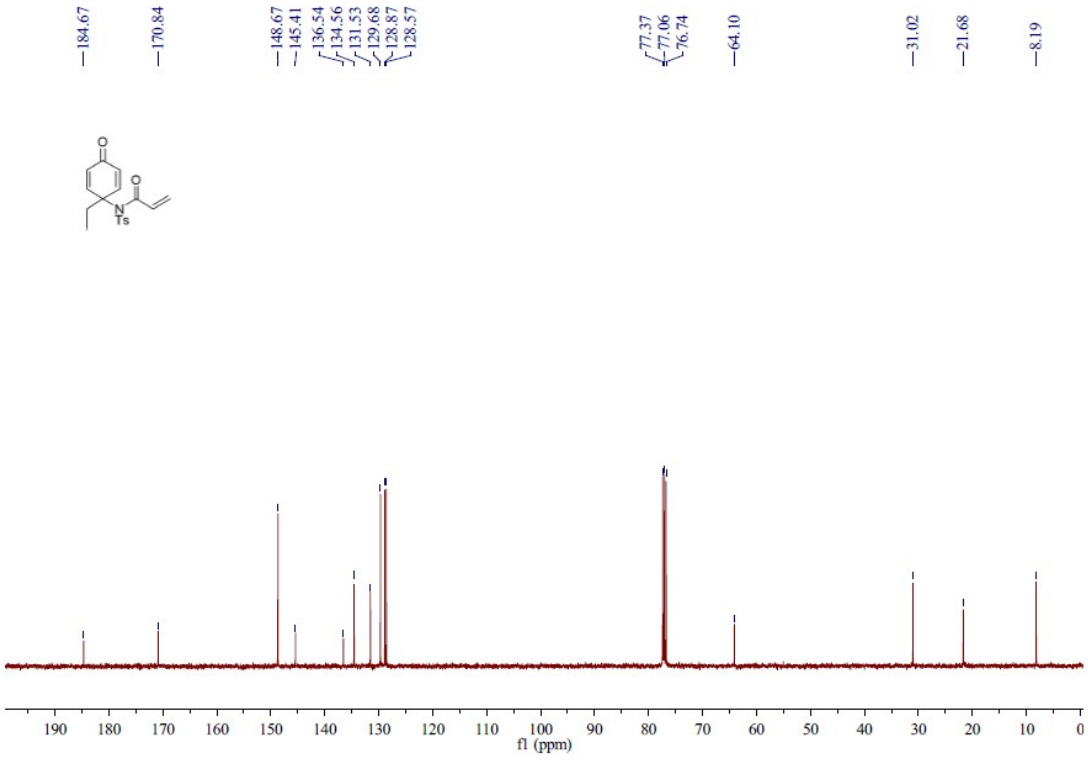
^{1}H NMR spectra of **1l**



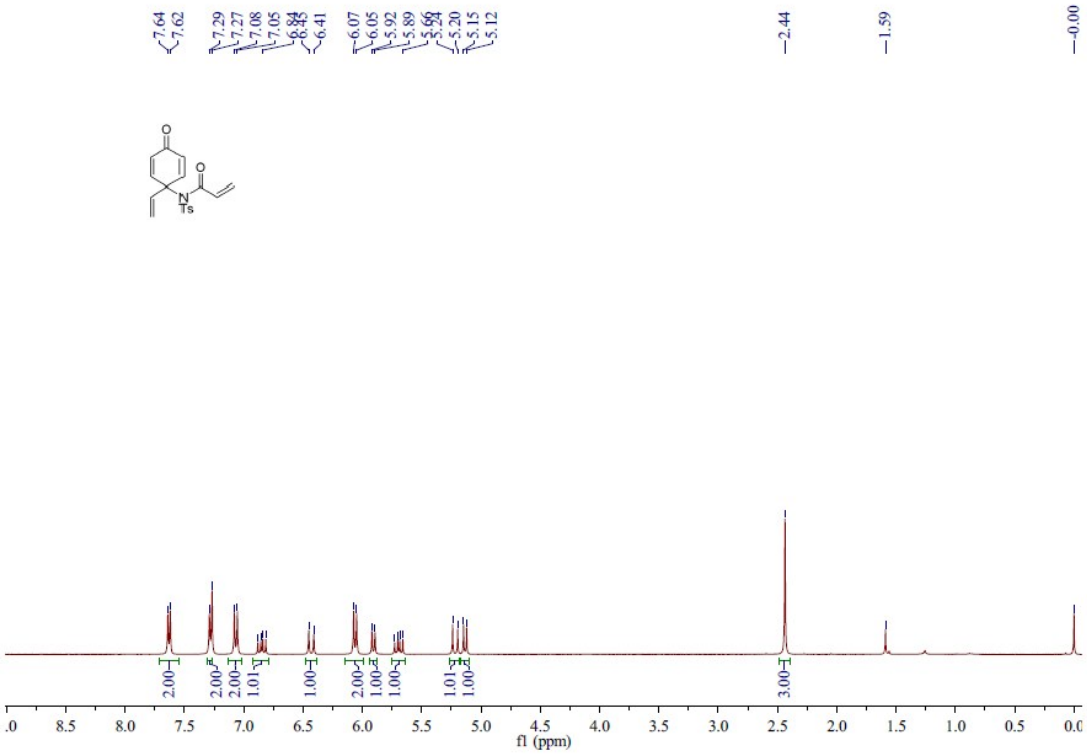
^{13}C NMR spectra of **1l**



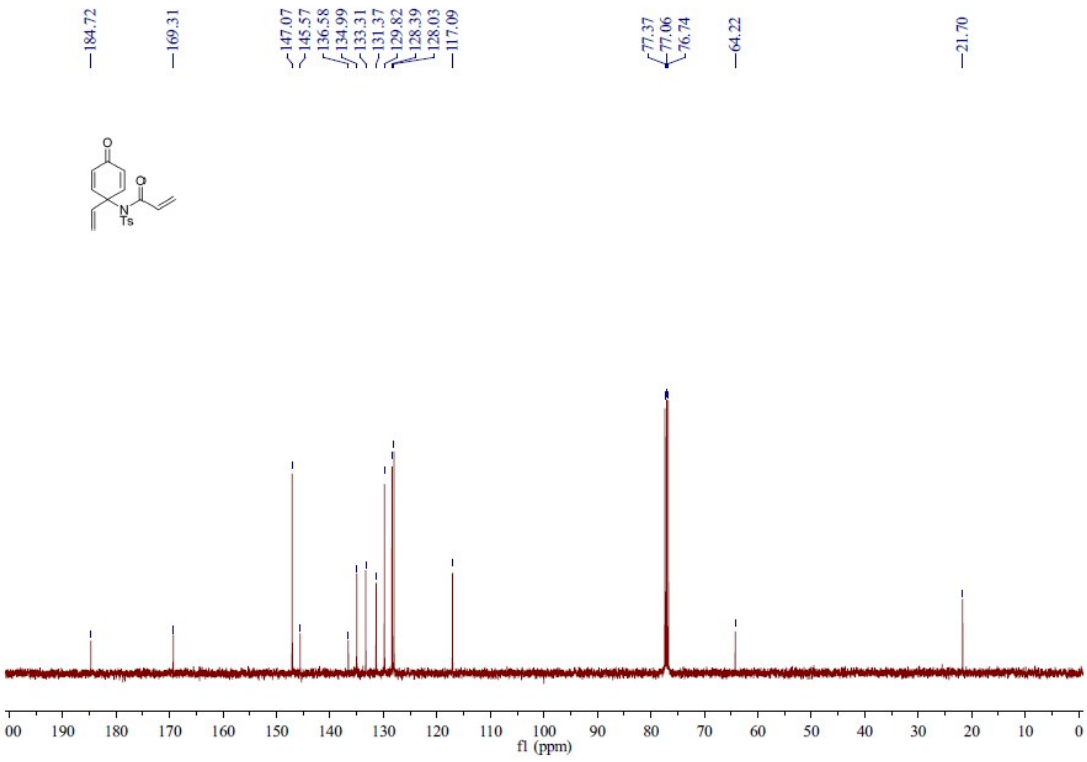
^{1}H NMR spectra of **1m**



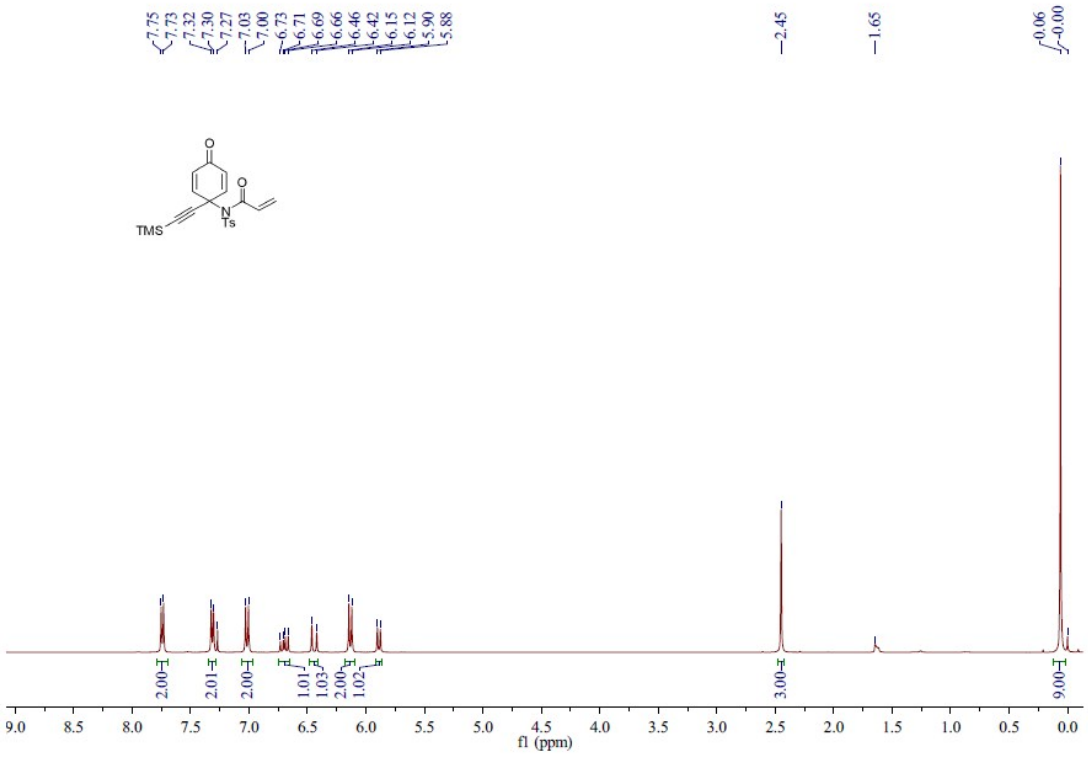
^{13}C NMR spectra of **1m**



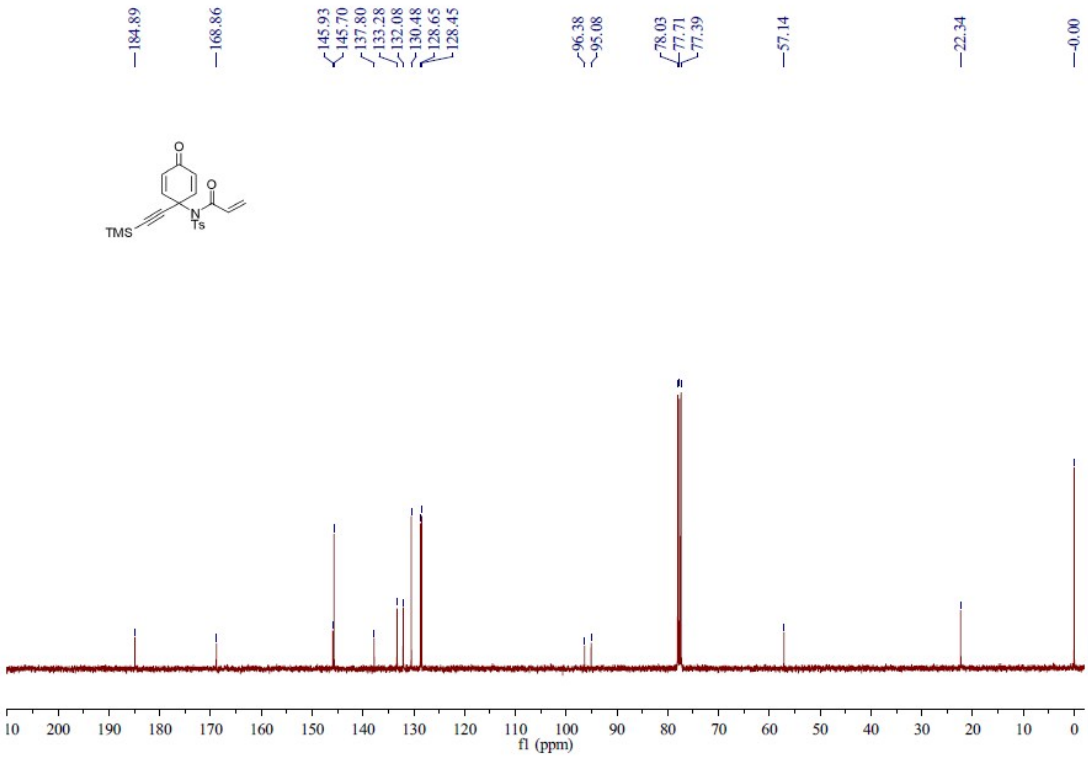
^{1}H NMR spectra of **1n**



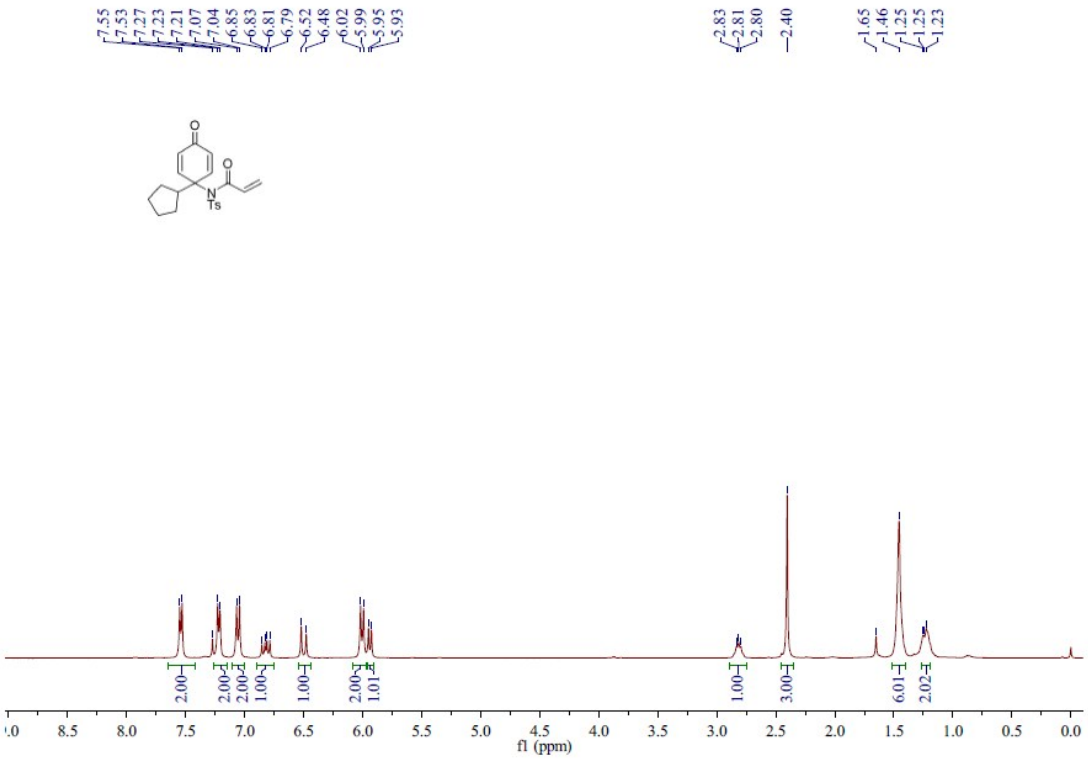
^{13}C NMR spectra of **1n**



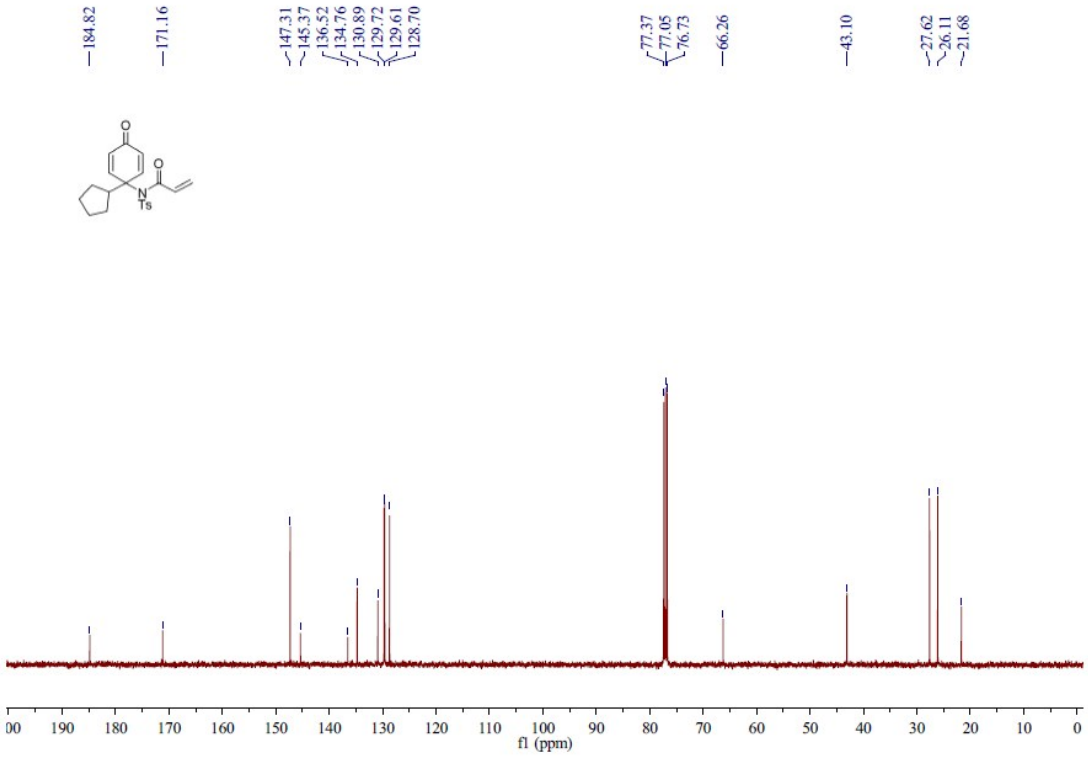
^{1}H NMR spectra of **1o**



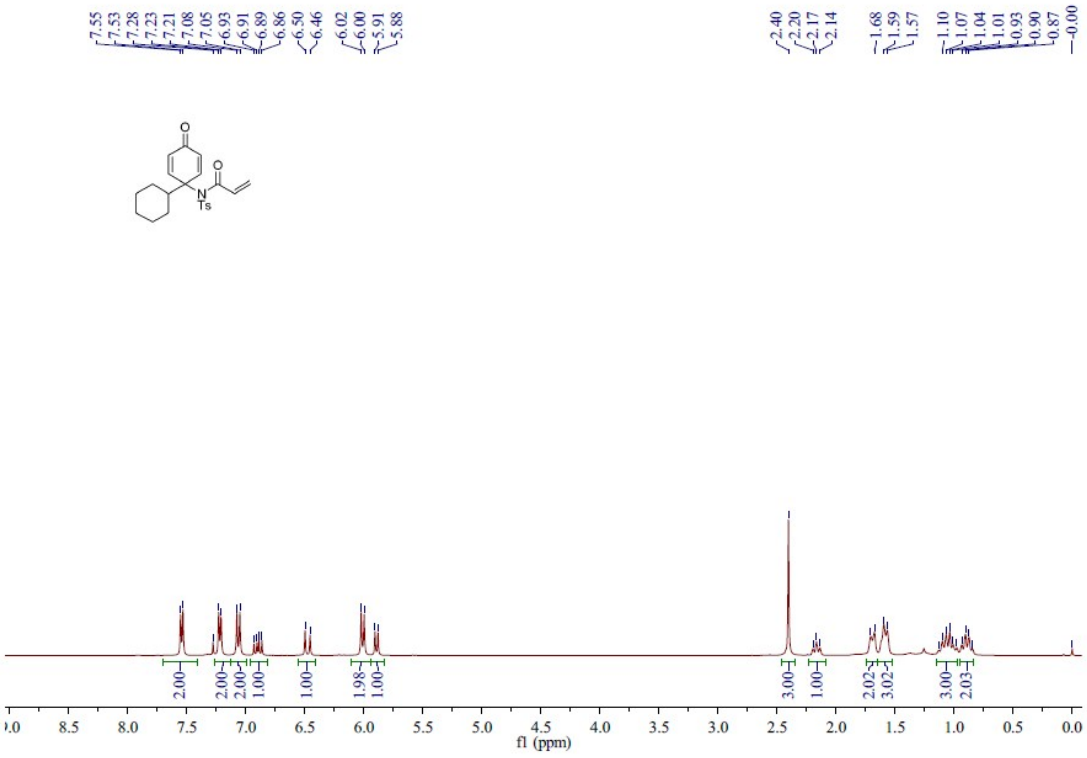
^{13}C NMR spectra of **1o**



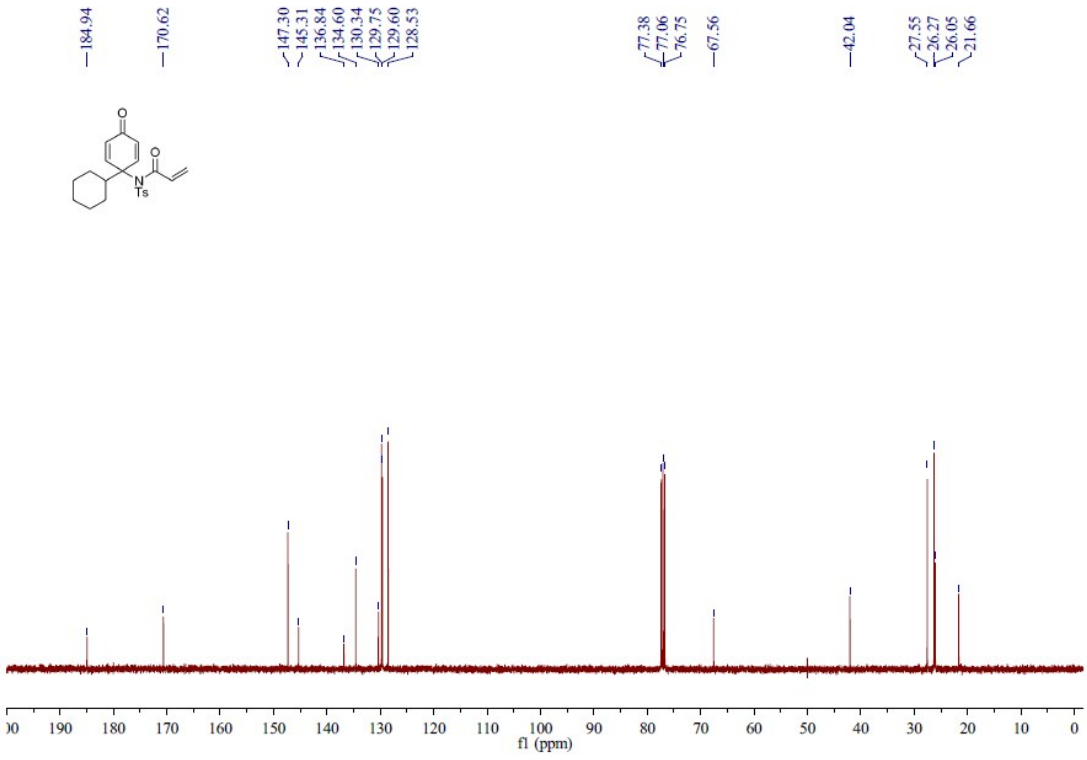
^{1}H NMR spectra of **1p**



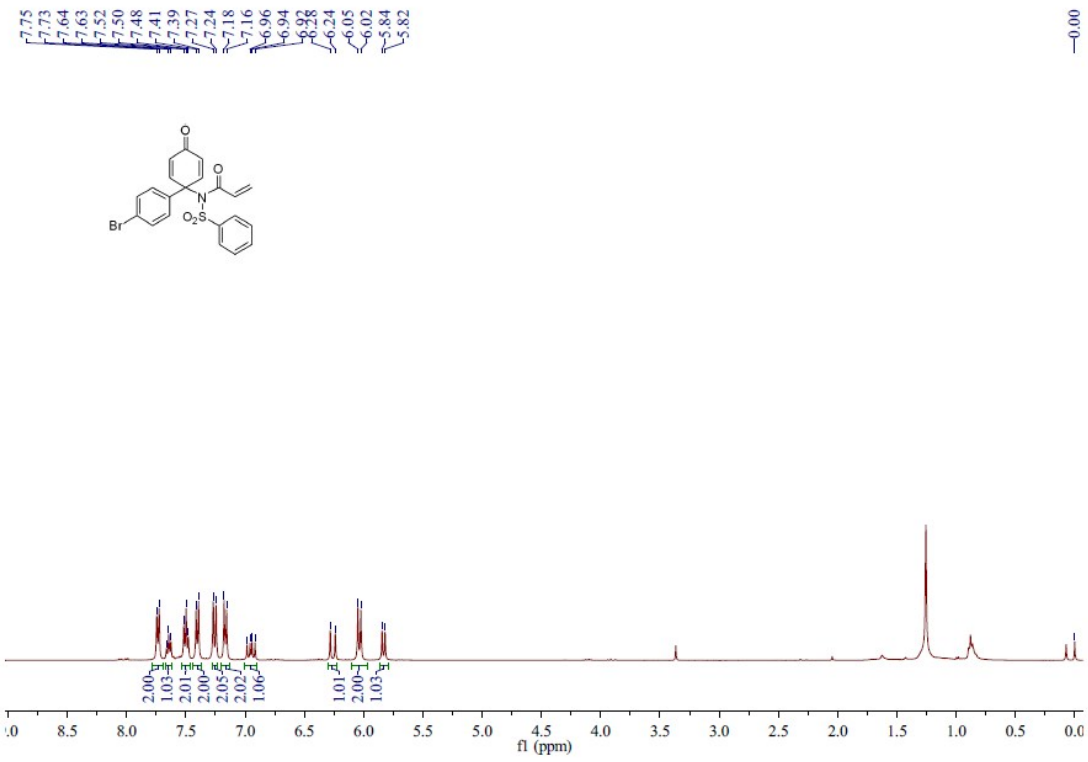
^{13}C NMR spectra of **1p**



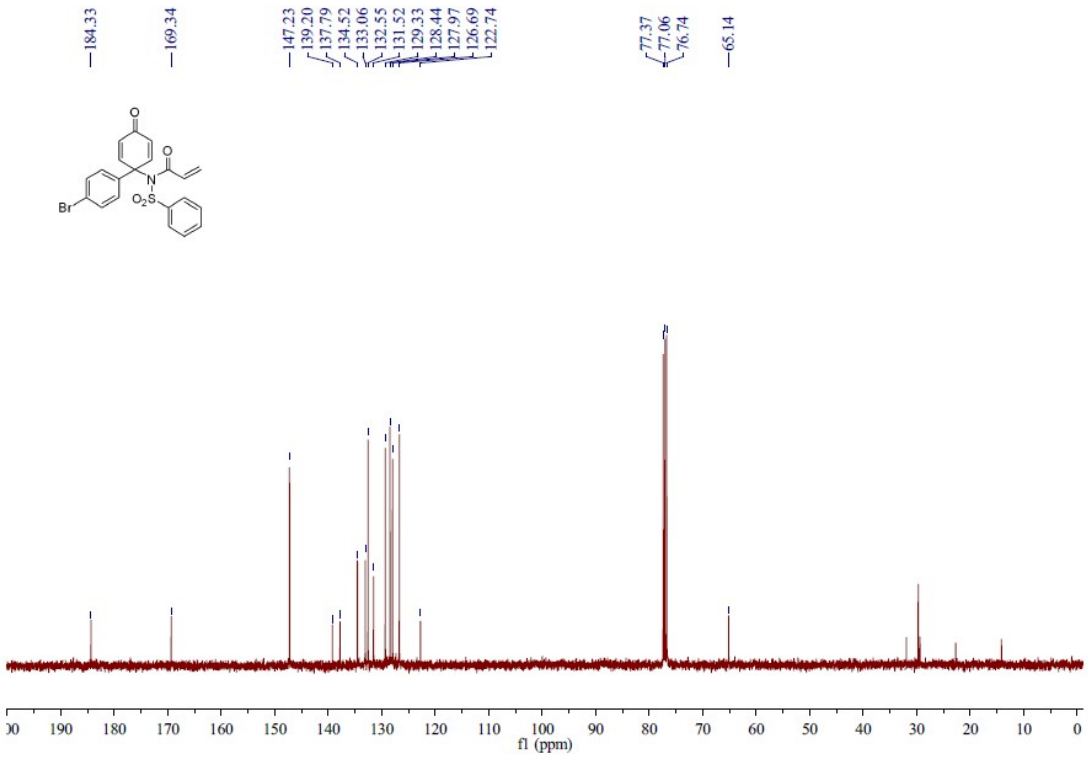
^{1}H NMR spectra of **1q**



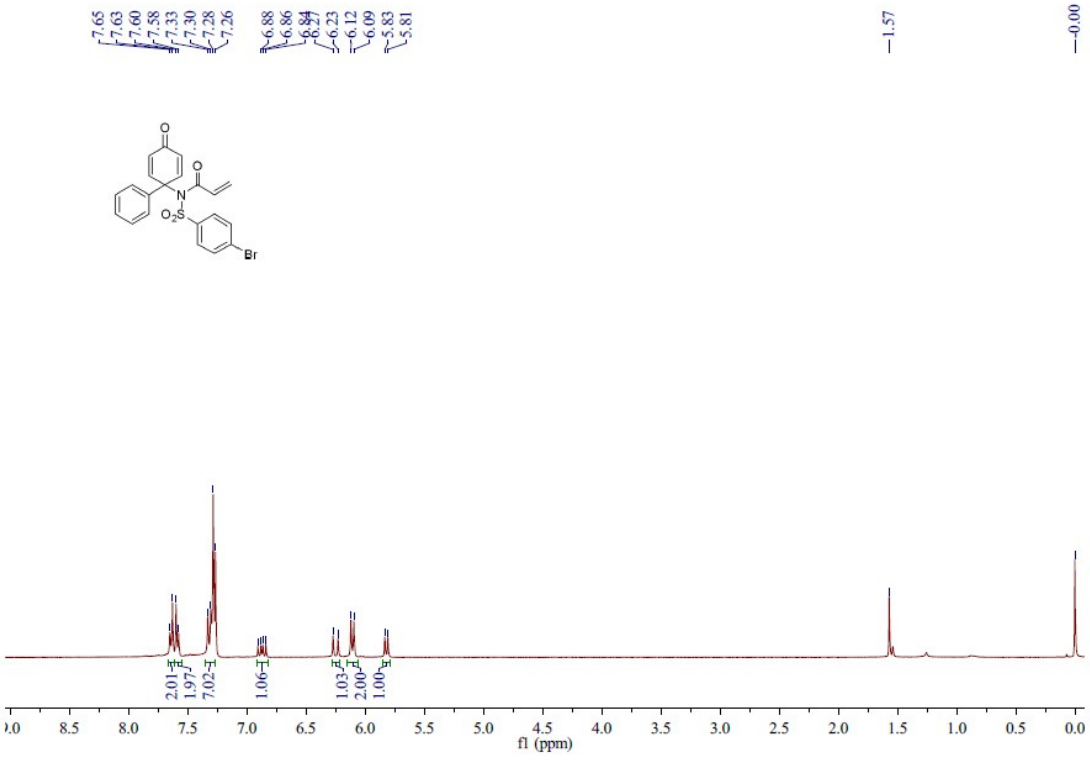
^{13}C NMR spectra of **1q**



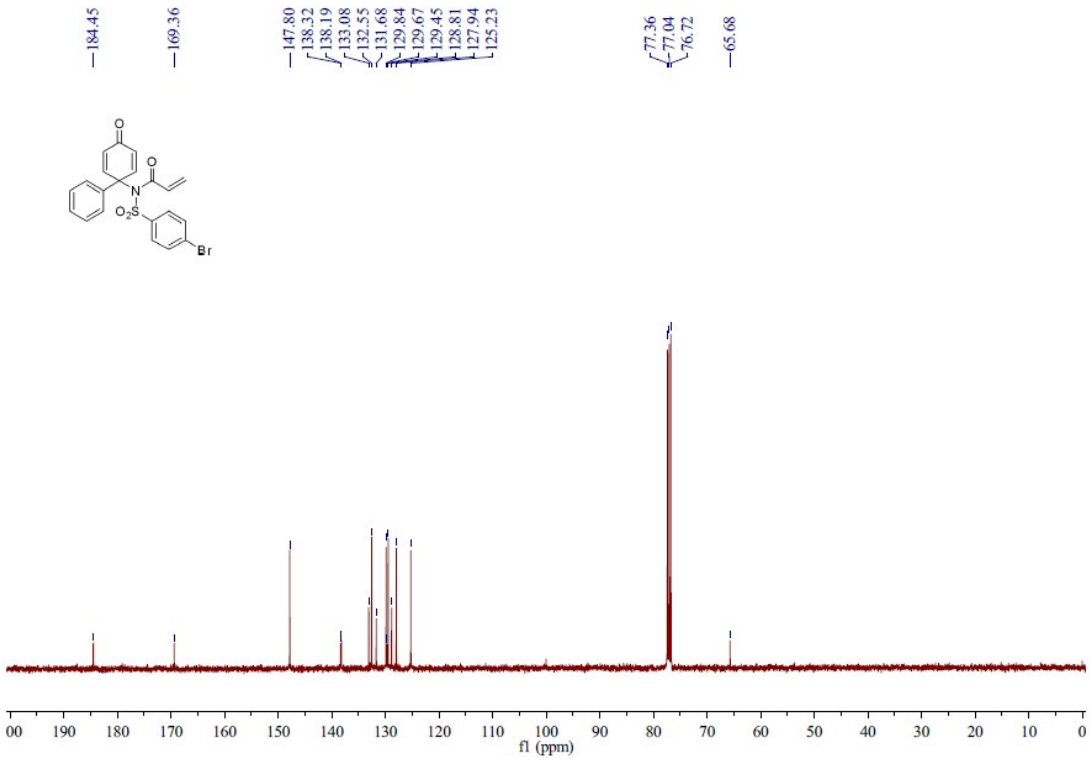
^{1}H NMR spectra of **1r**



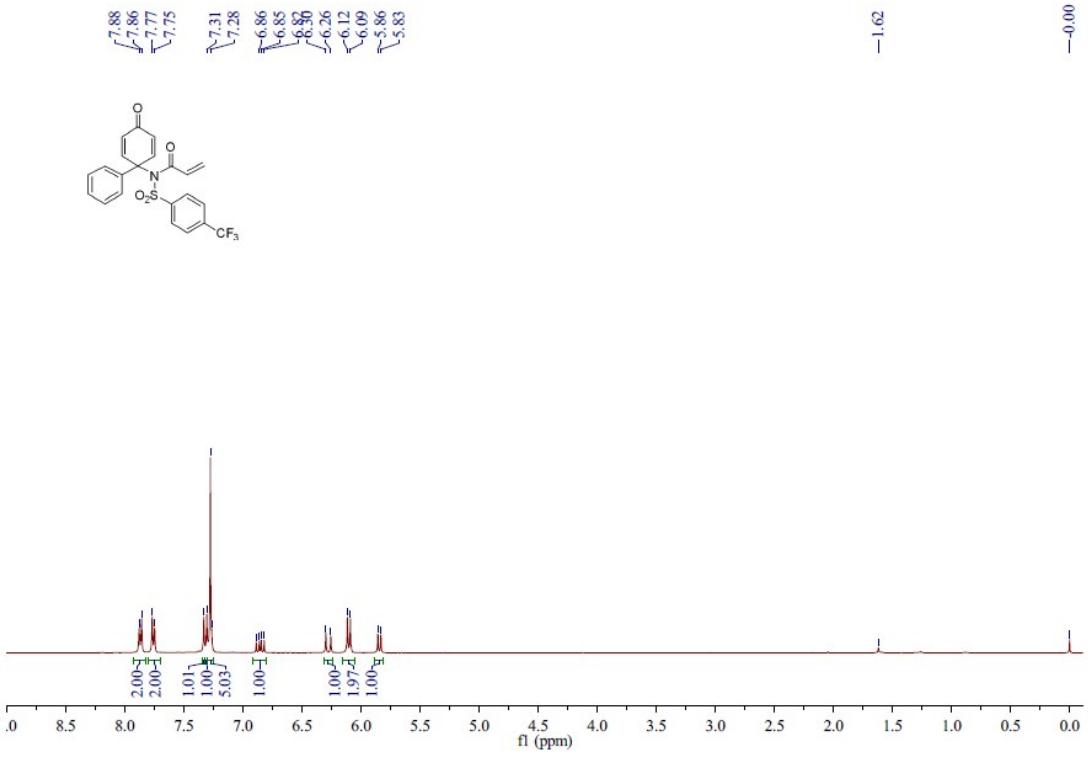
^{13}C NMR spectra of **1r**



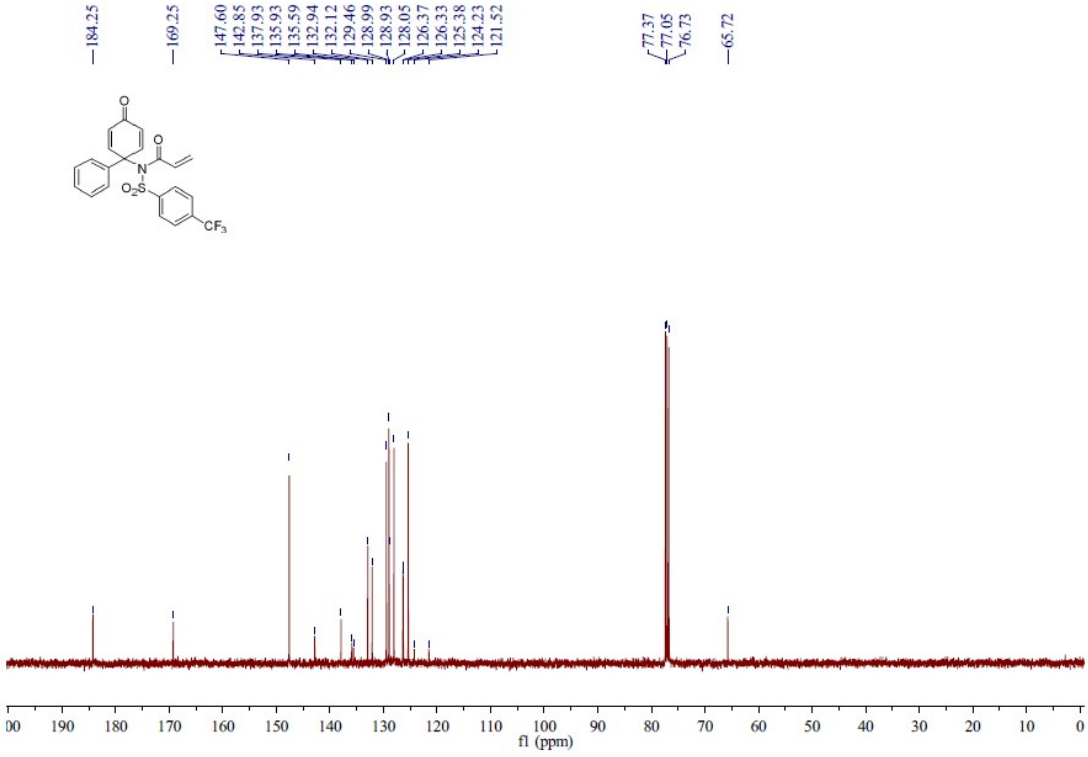
^{1}H NMR spectra of **1s**



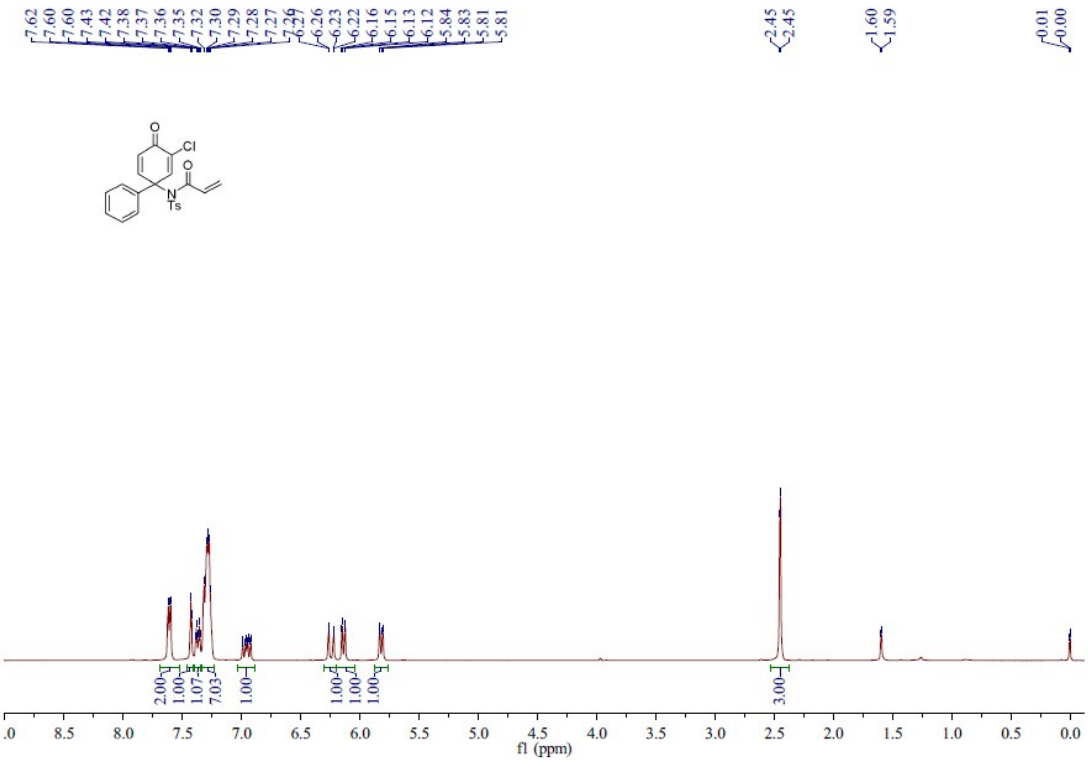
^{13}C NMR spectra of **1s**



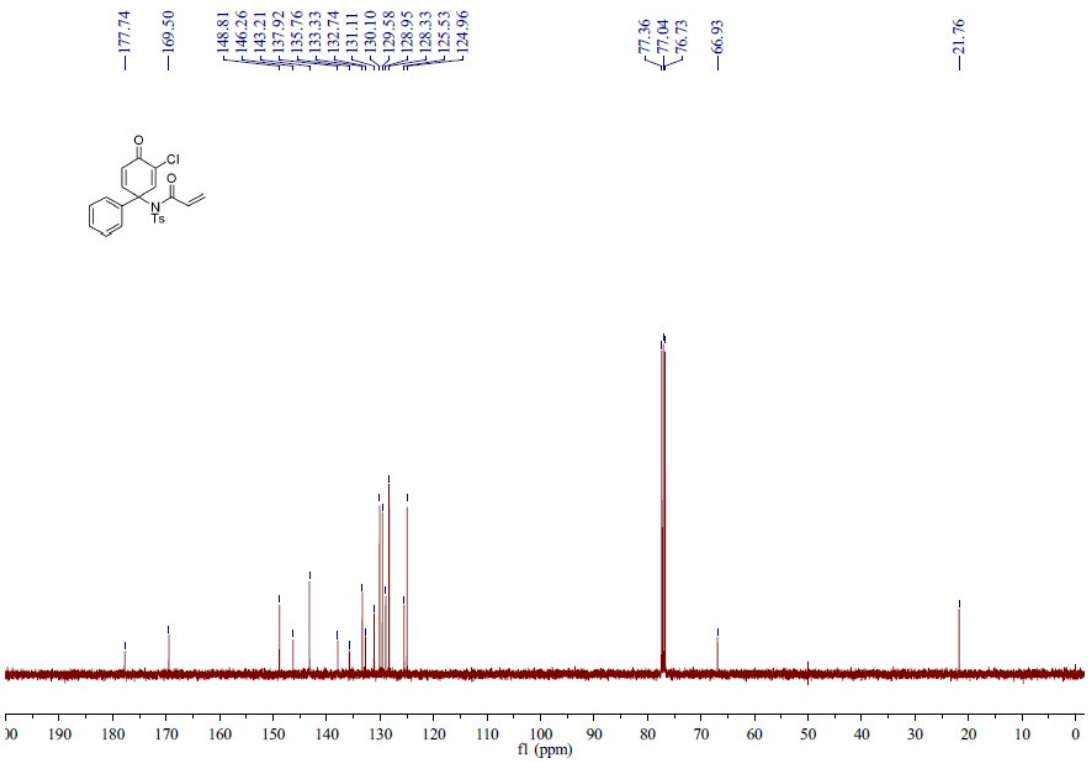
^{1}H NMR spectra of **1t**



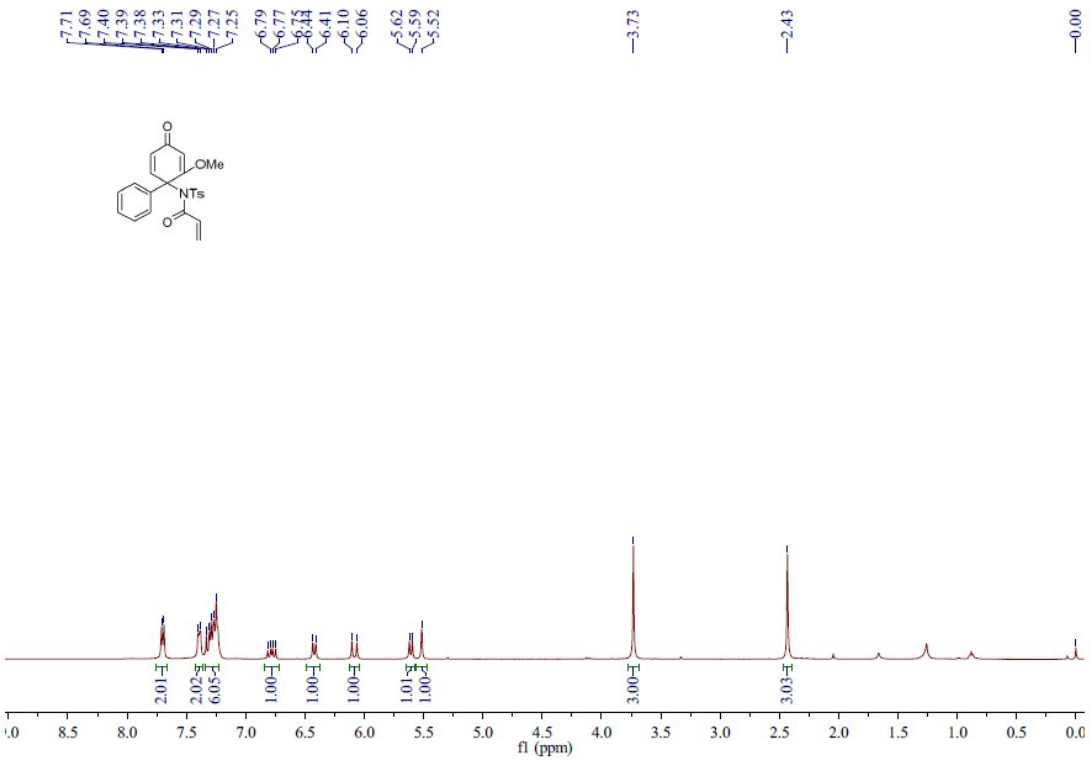
^{13}C NMR spectra of **1t**



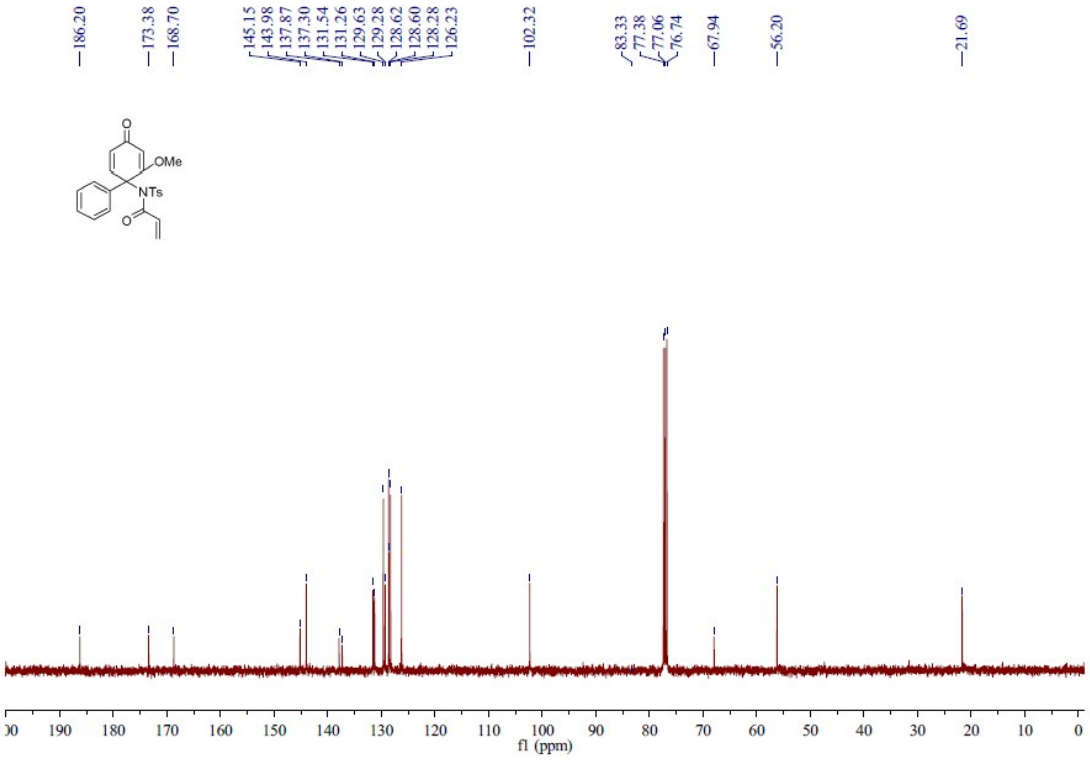
^{1}H NMR spectra of **1u**



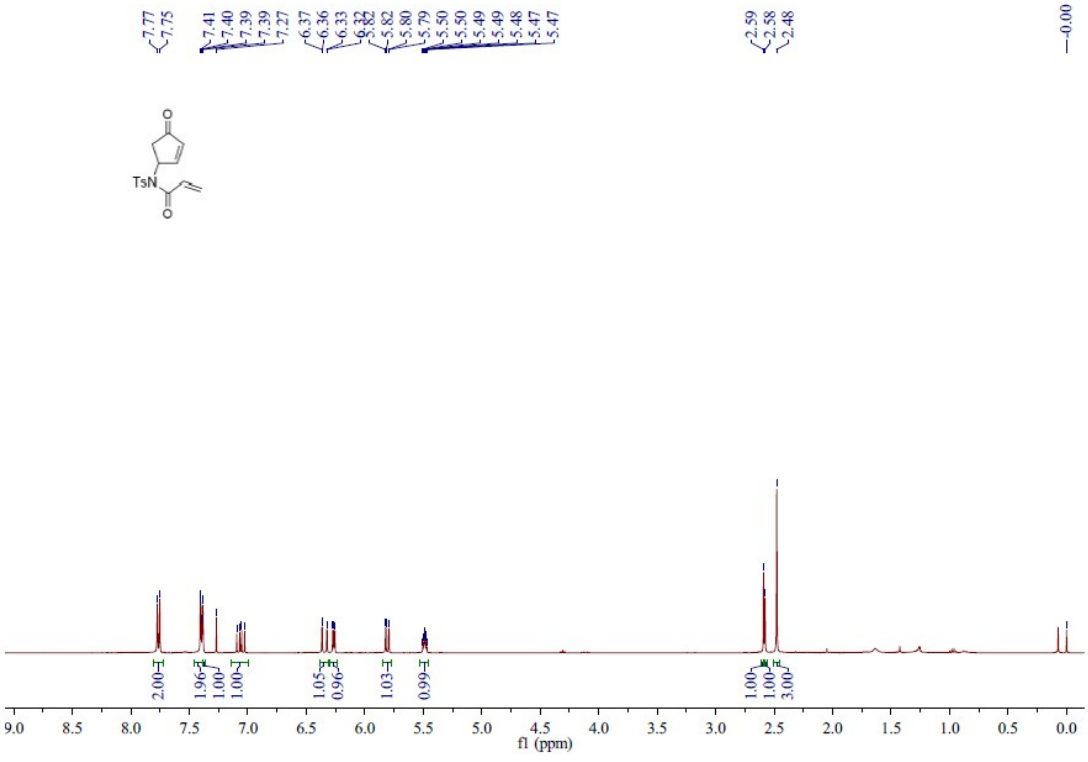
^{13}C NMR spectra of **1u**



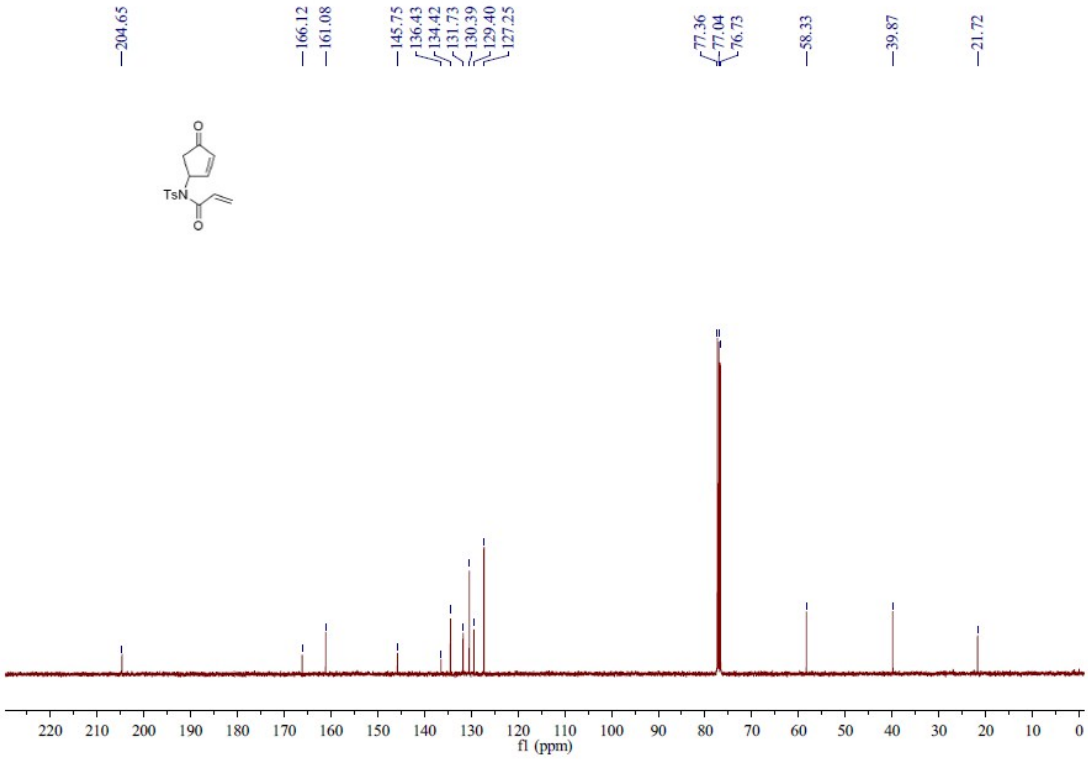
^{1}H NMR spectra of **1v**



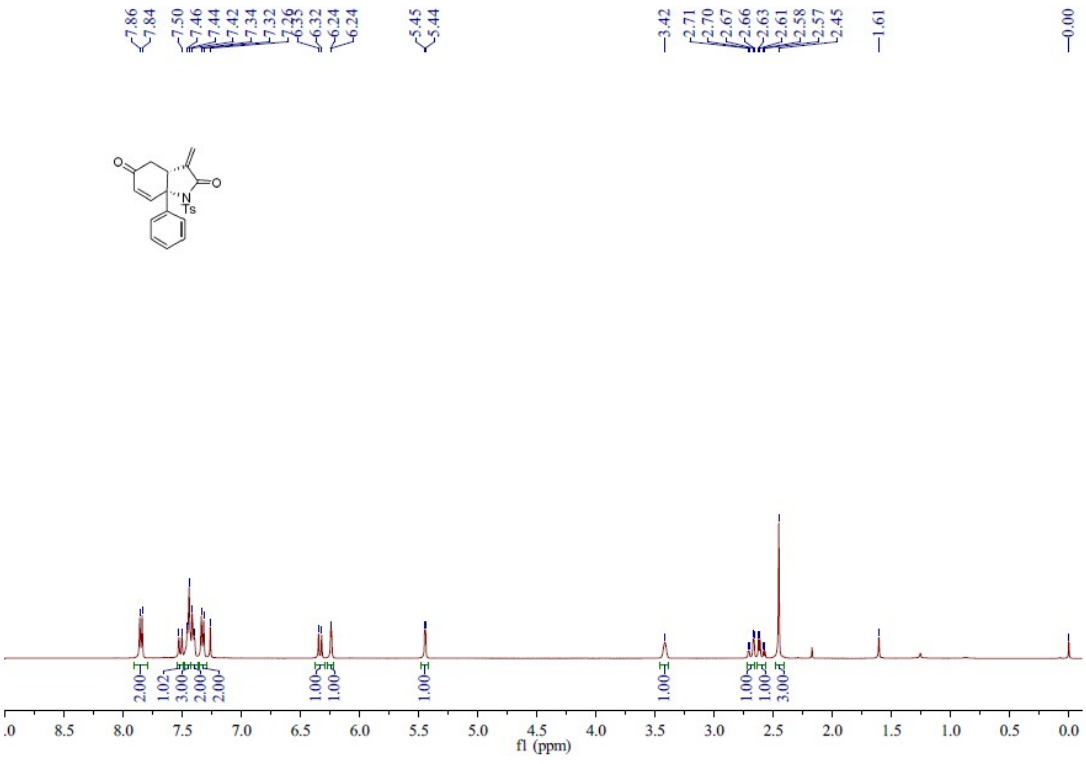
^{13}C NMR spectra of **1v**



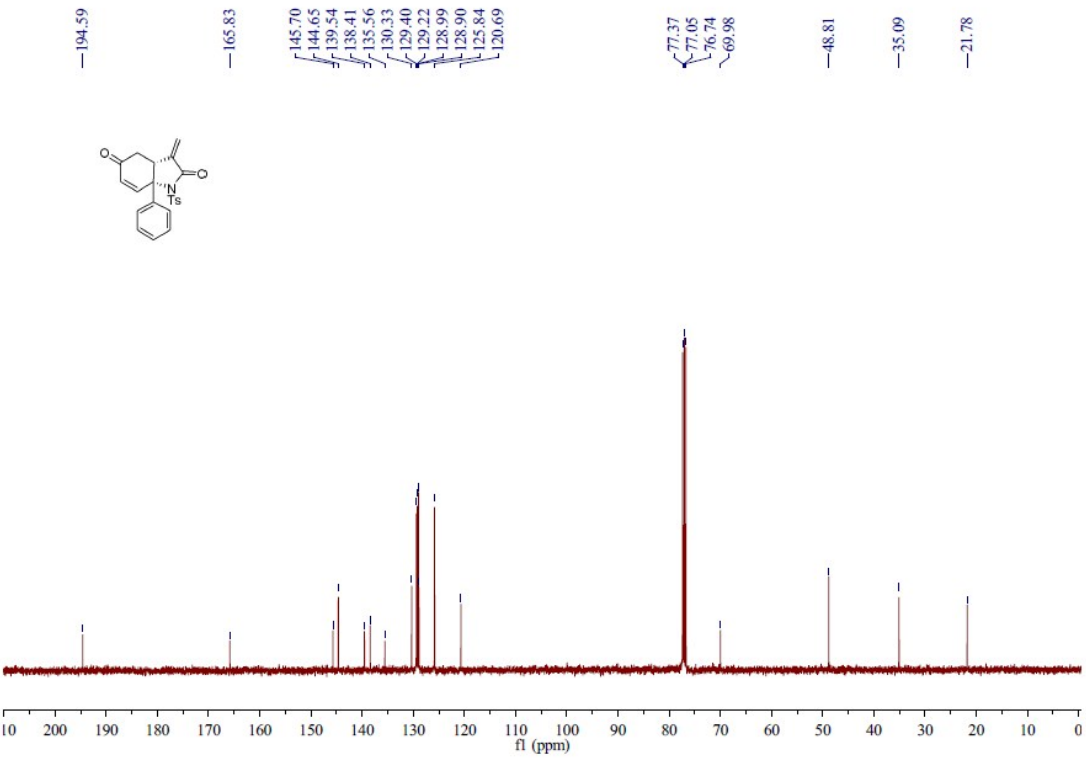
^{1}H NMR spectra of **1w**



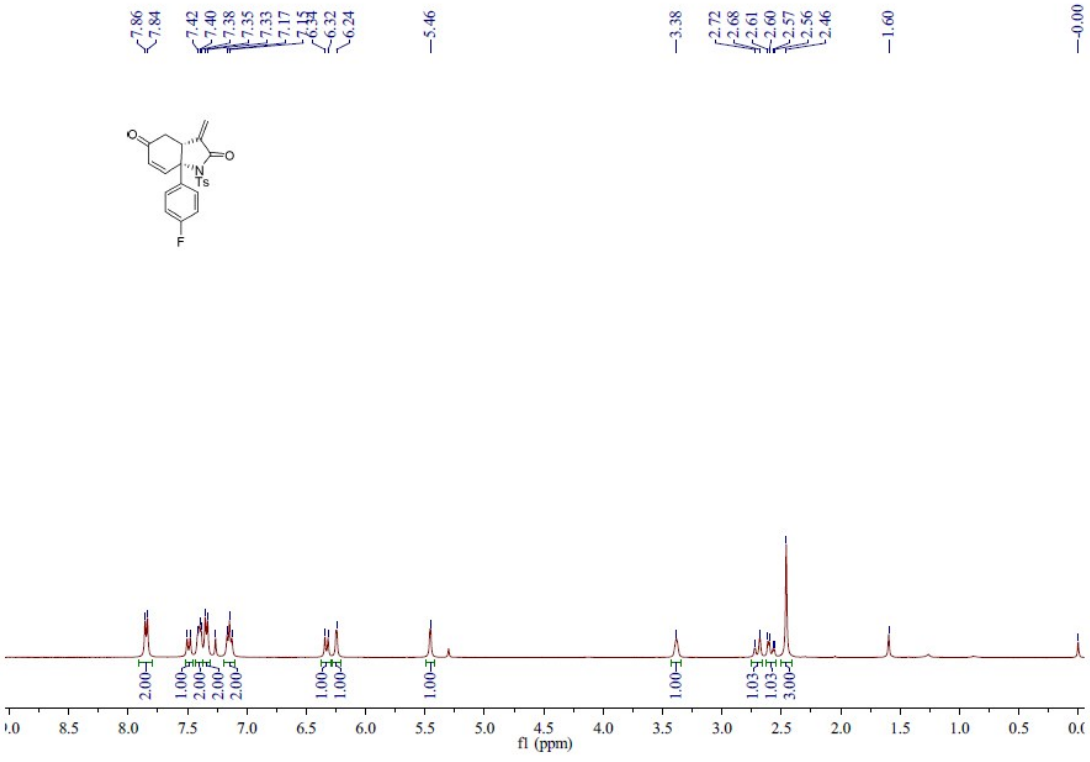
^{13}C NMR spectra of **1w**



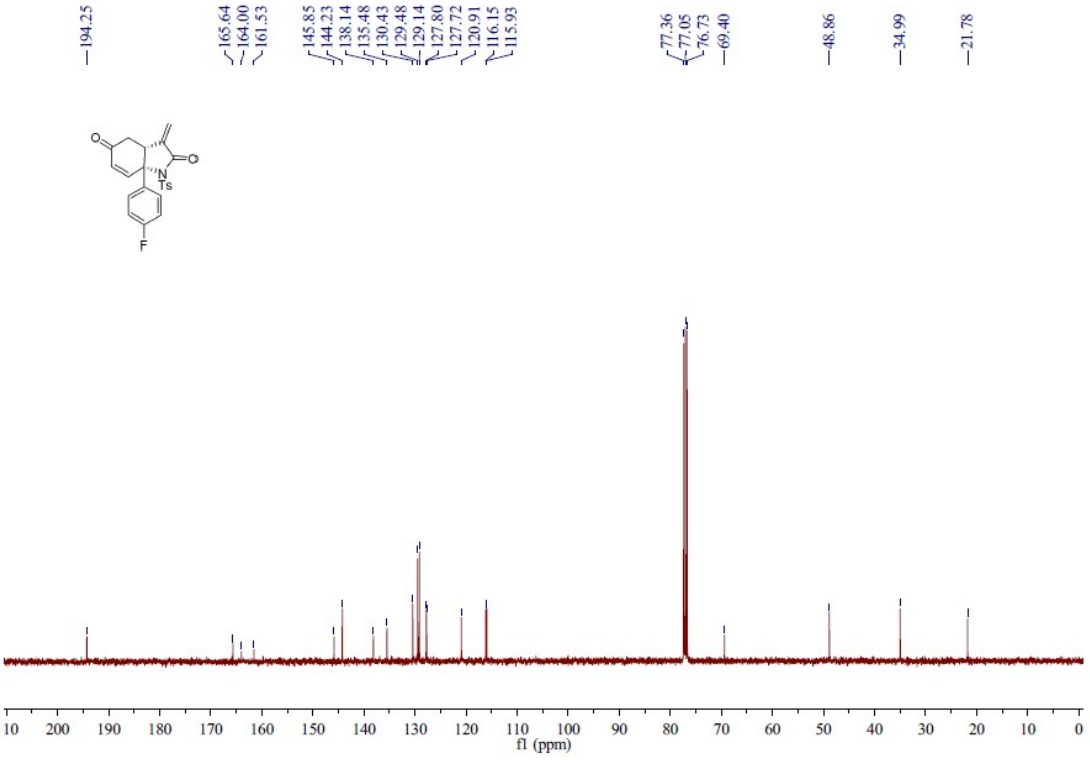
^{1}H NMR spectra of **2a**



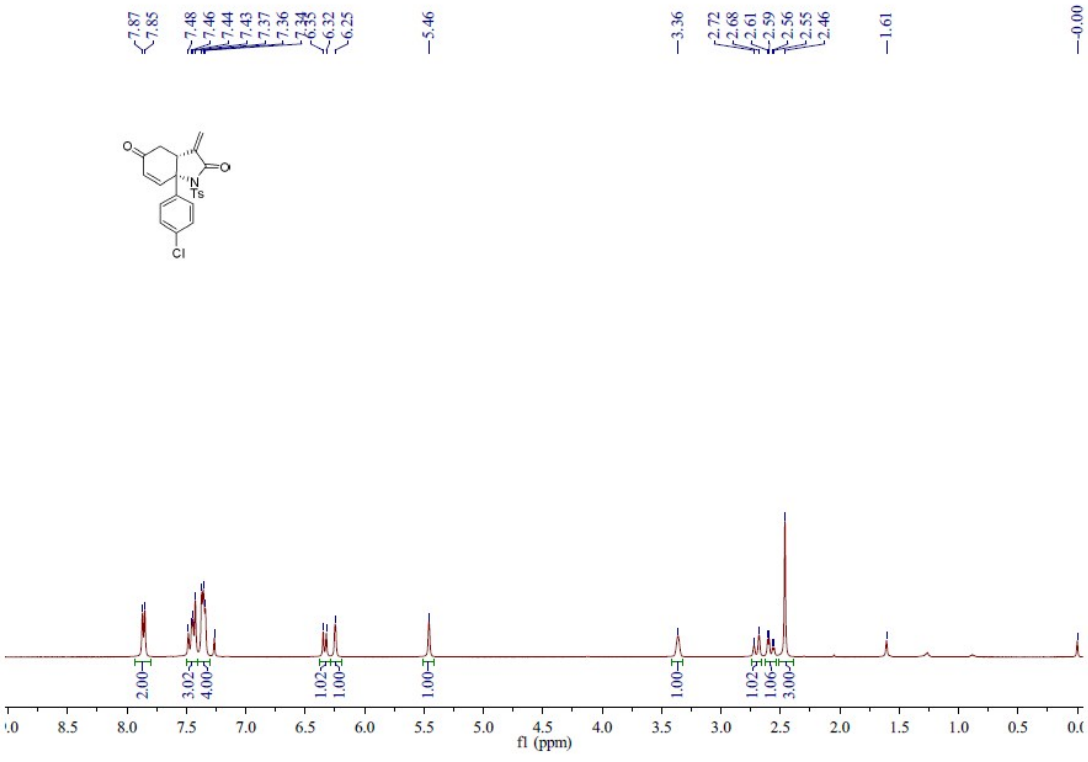
^{13}C NMR spectra of **2a**



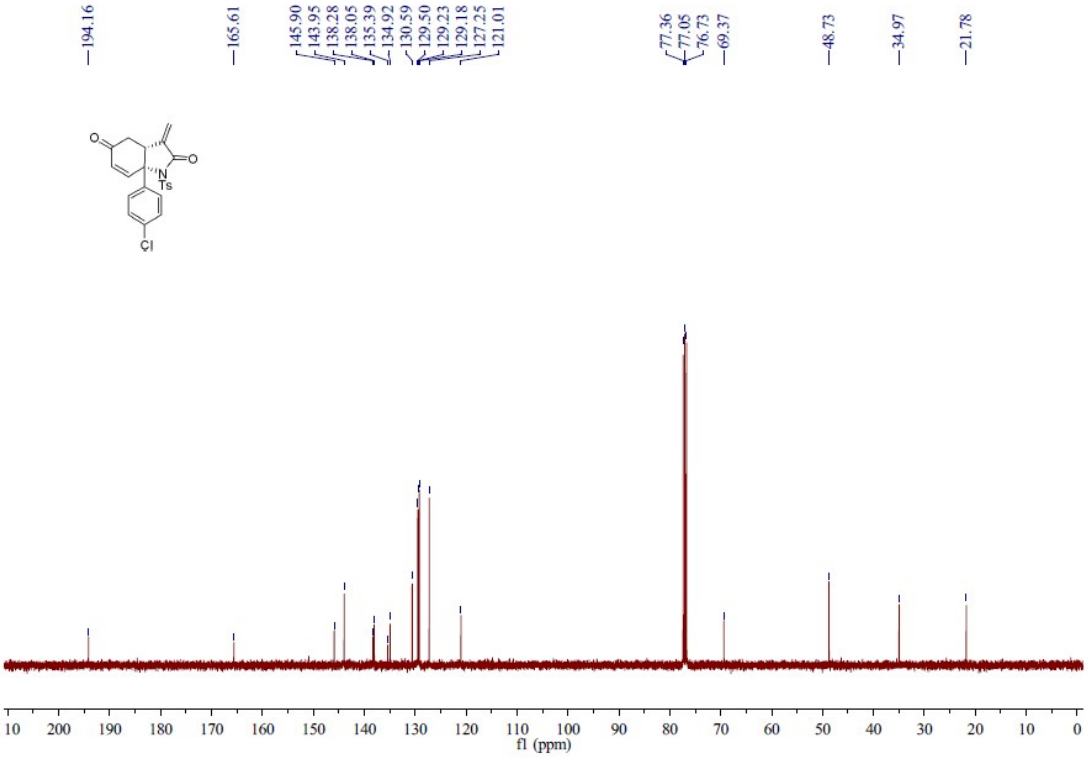
^{1}H NMR spectra of **2b**



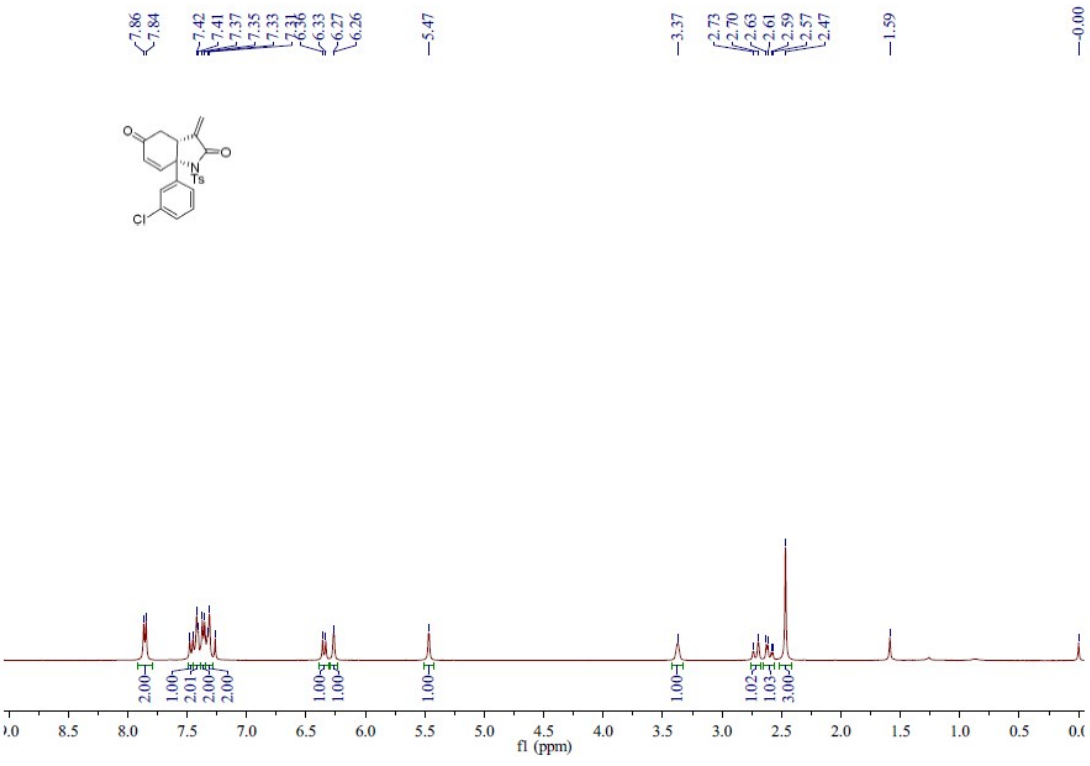
^{13}C NMR spectra of **2b**



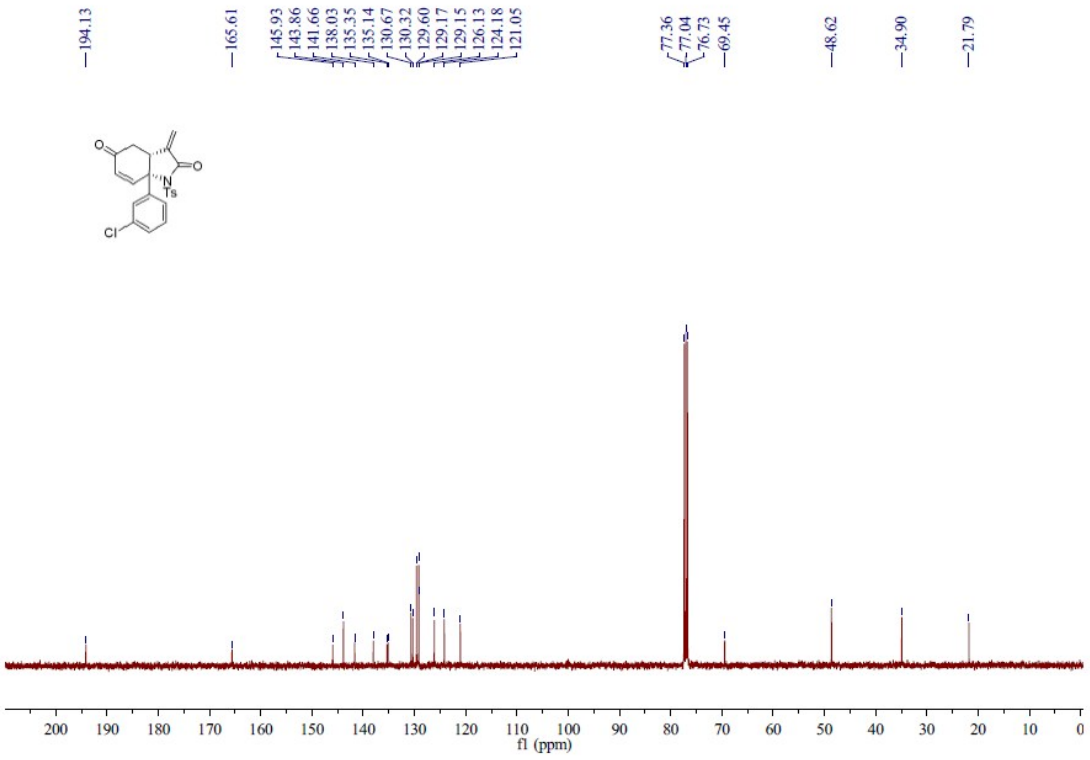
^{1}H NMR spectra of **2c**



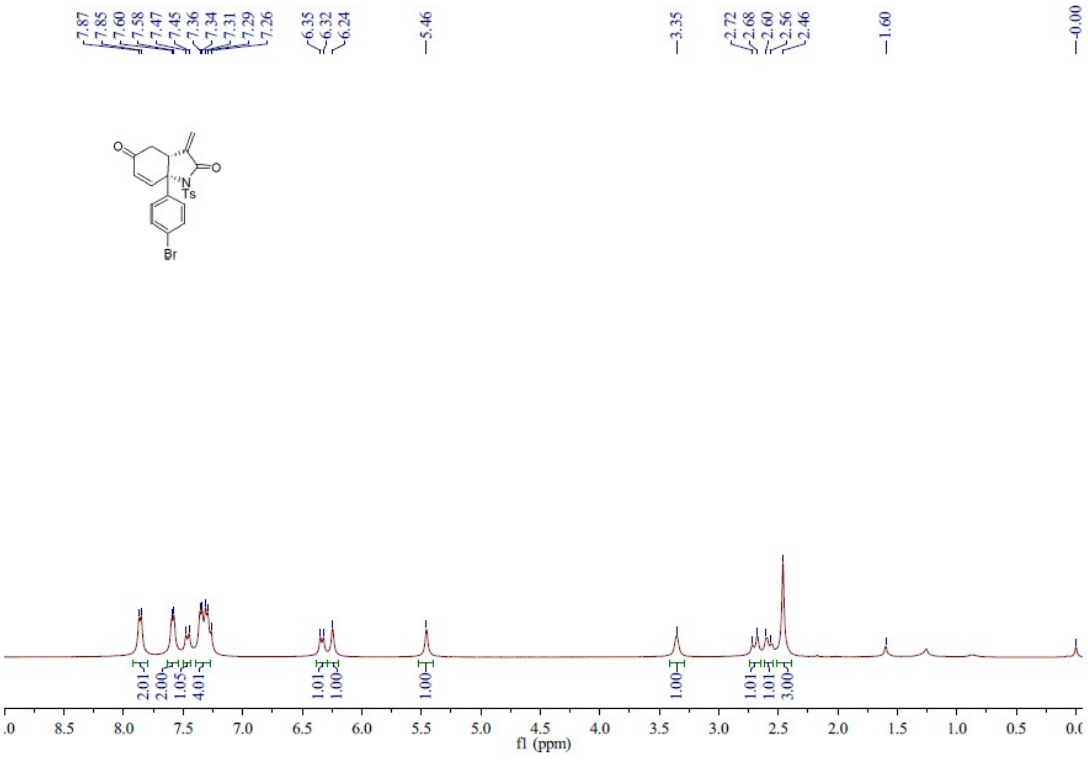
^{13}C NMR spectra of **2c**



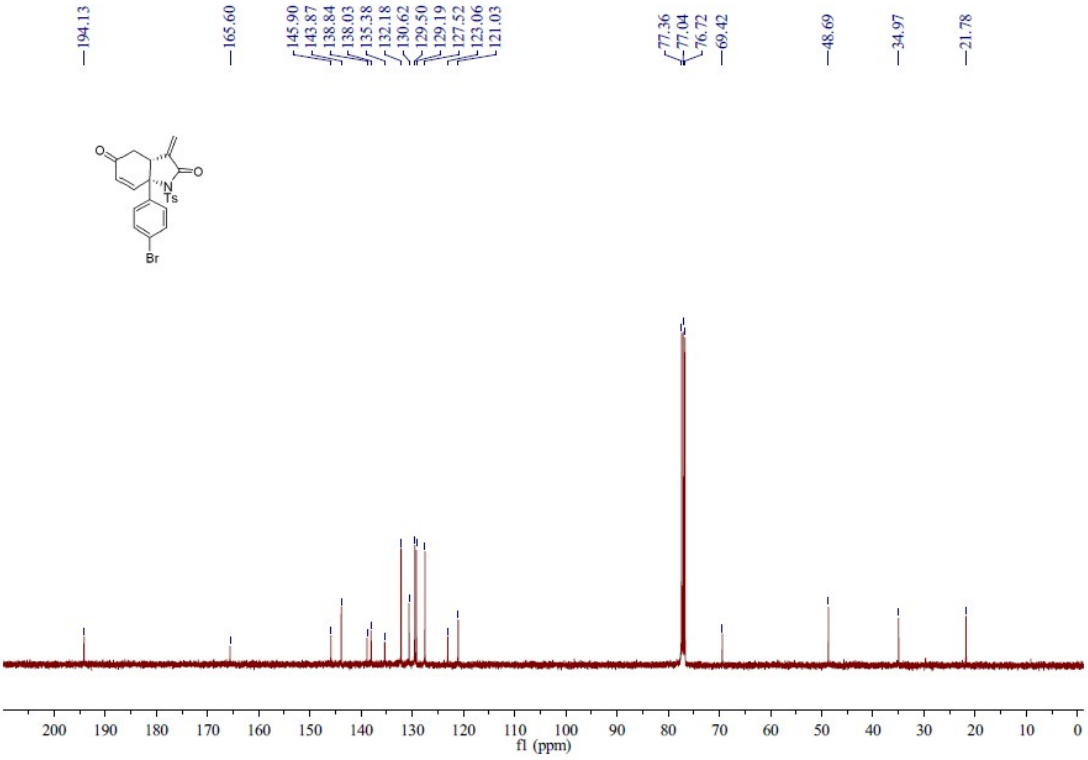
^{1}H NMR spectra of **2d**



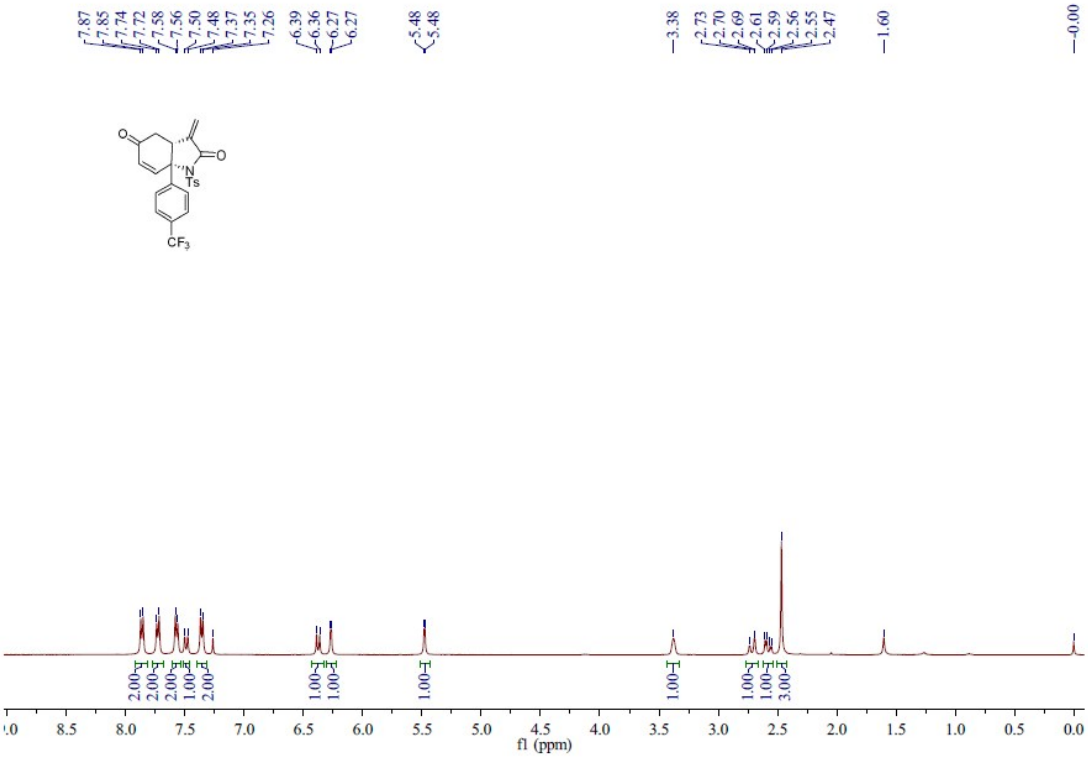
^{13}C NMR spectra of **2d**



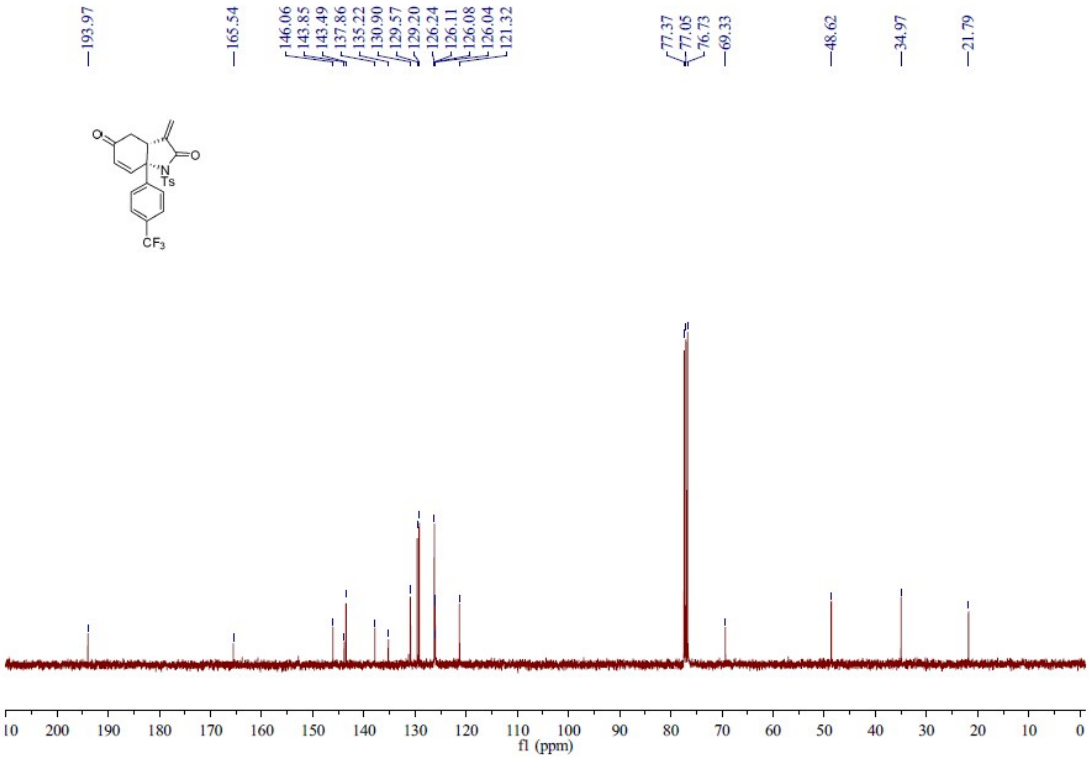
^{1}H NMR spectra of **2e**



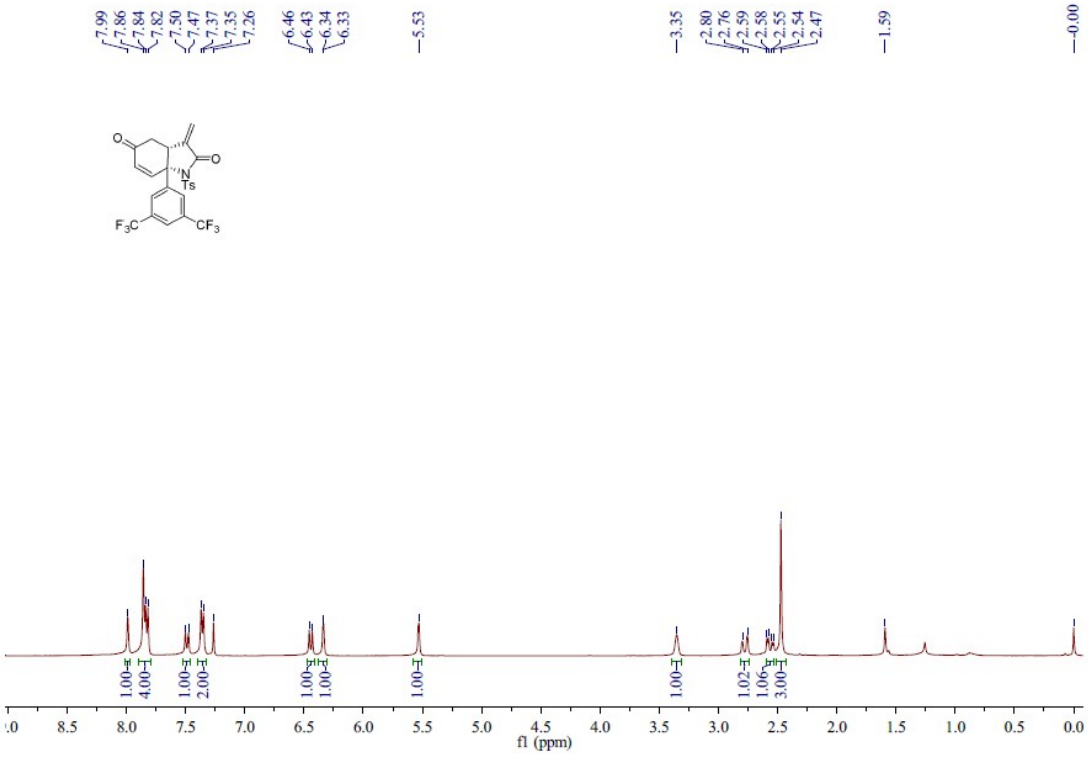
^{13}C NMR spectra of **2e**



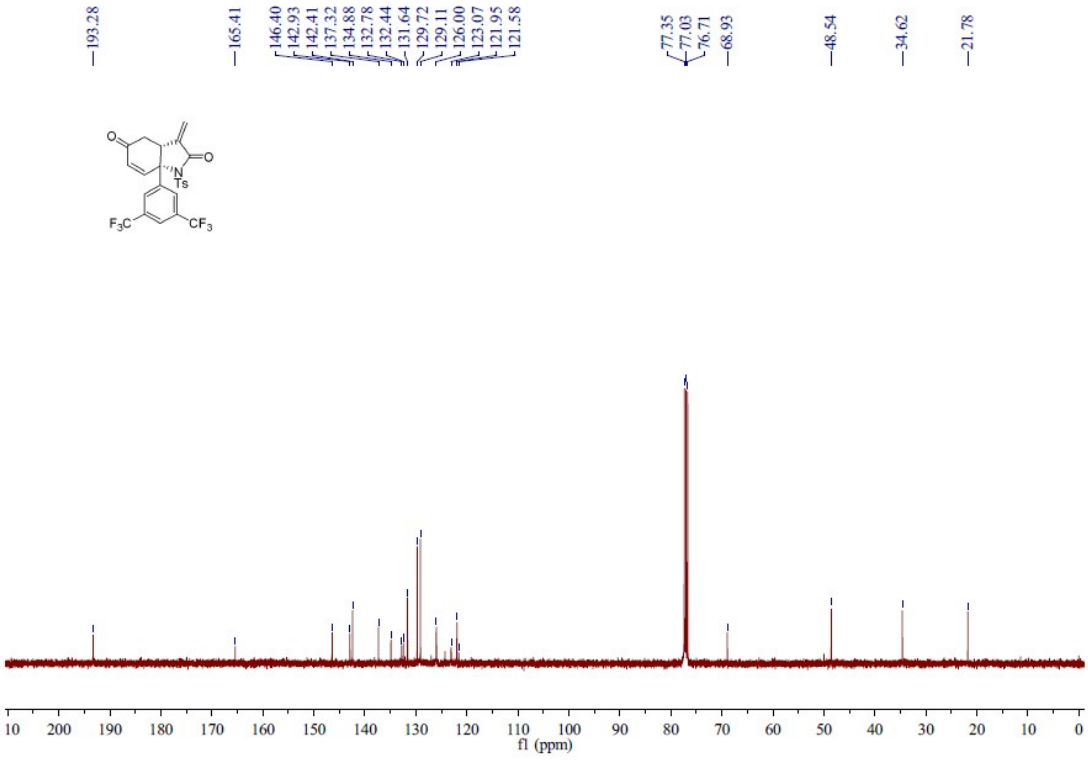
^{1}H NMR spectra of **2f**



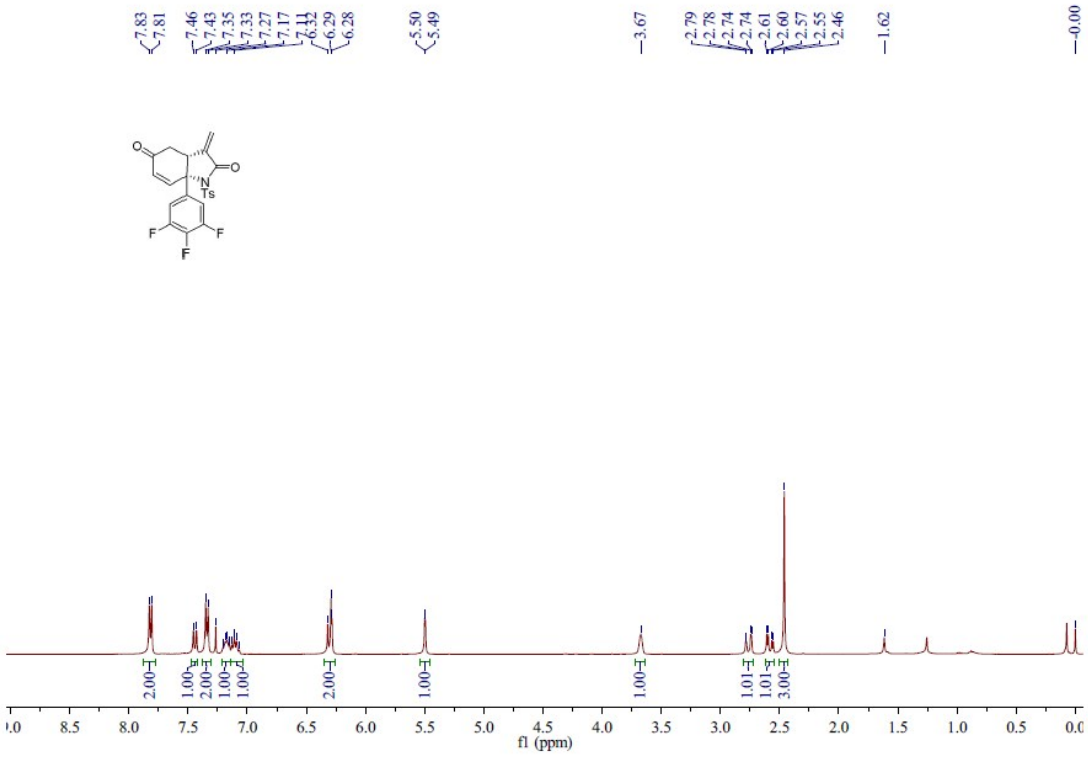
^{13}C NMR spectra of **2f**



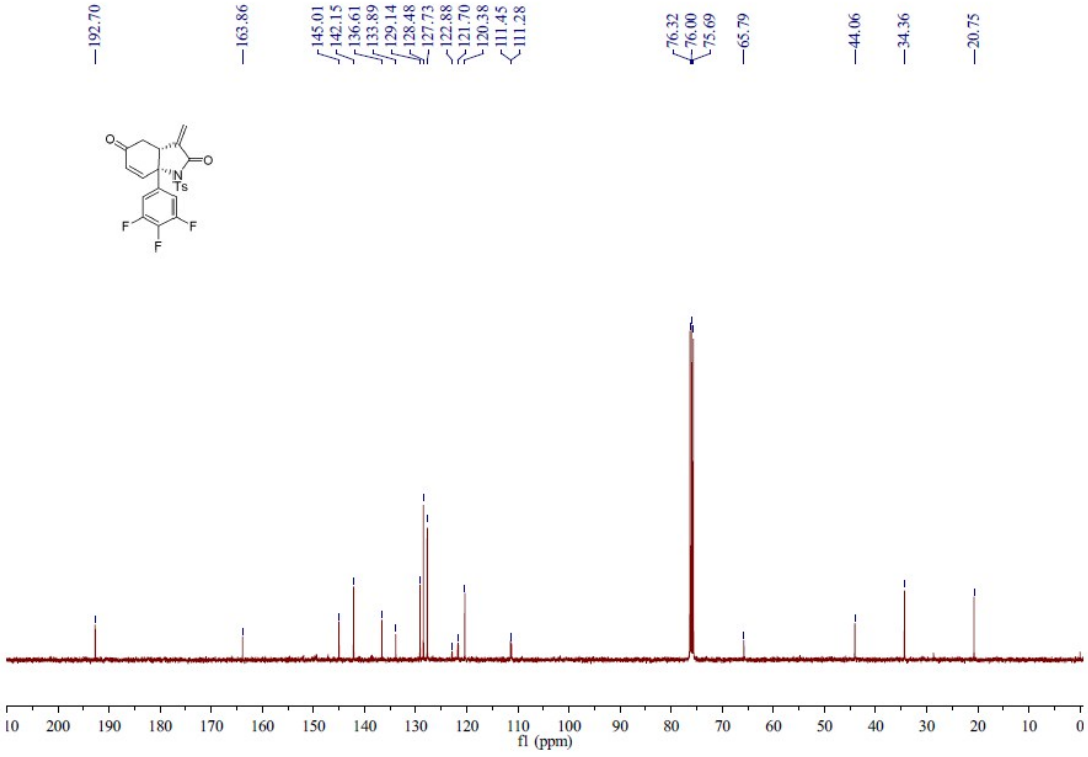
^{1}H NMR spectra of **2g**



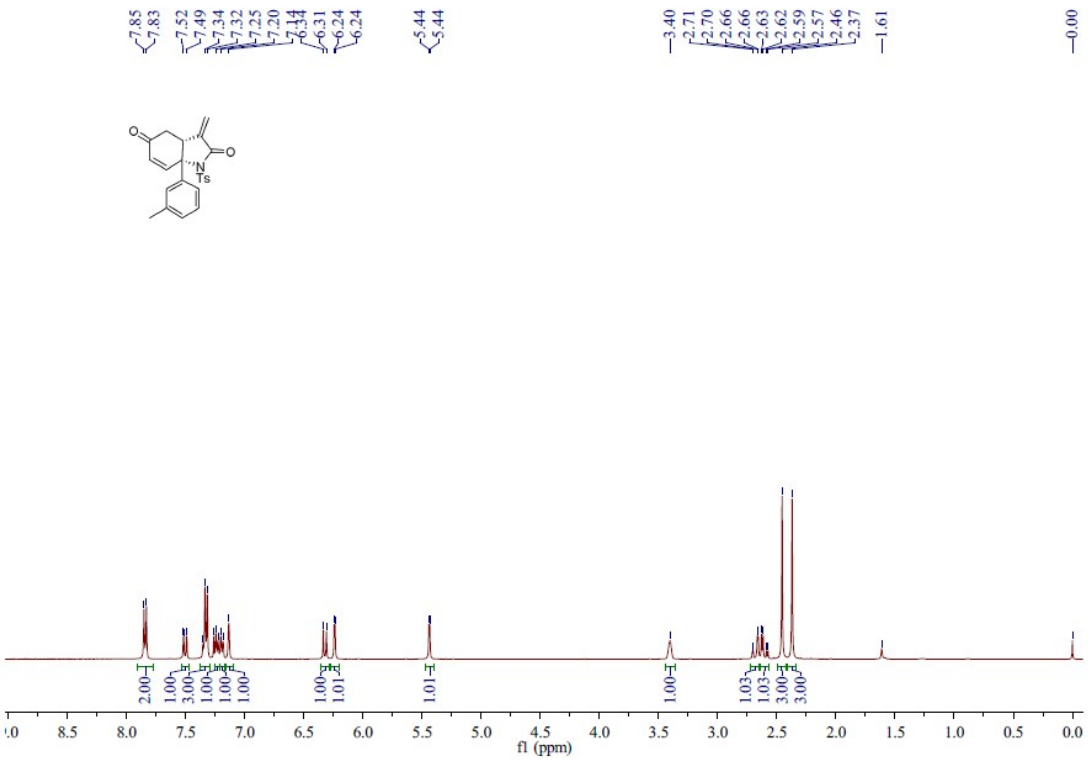
^{13}C NMR spectra of **2g**



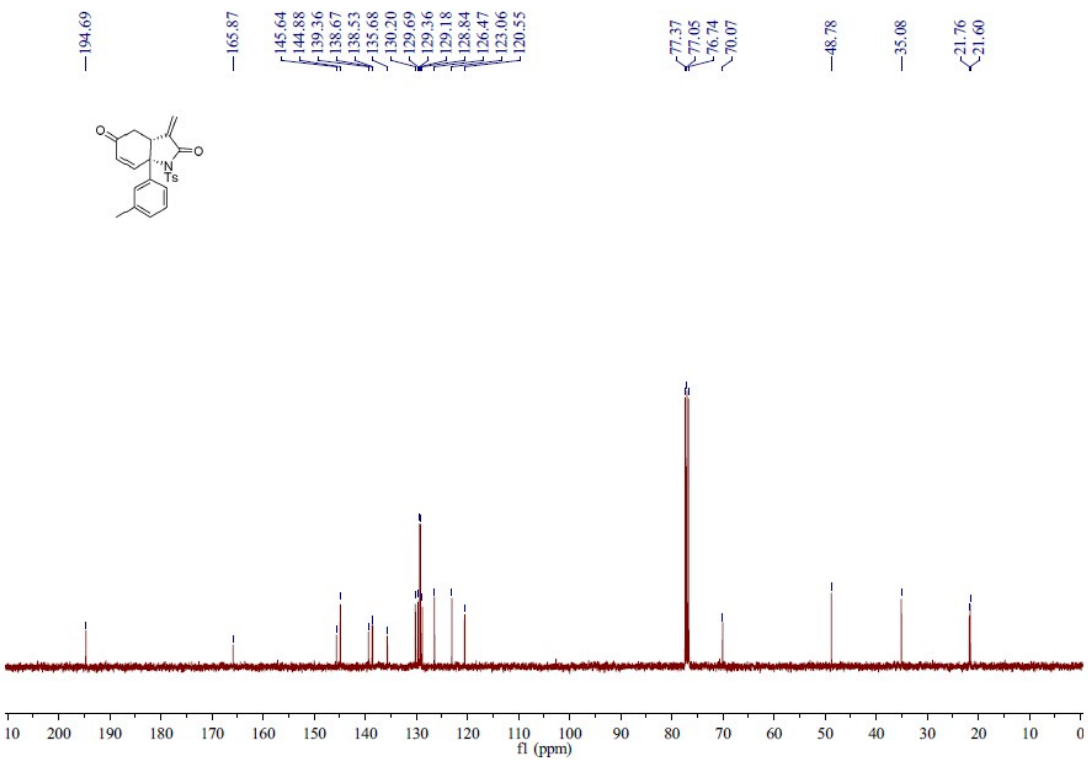
^{1}H NMR spectra of **2h**



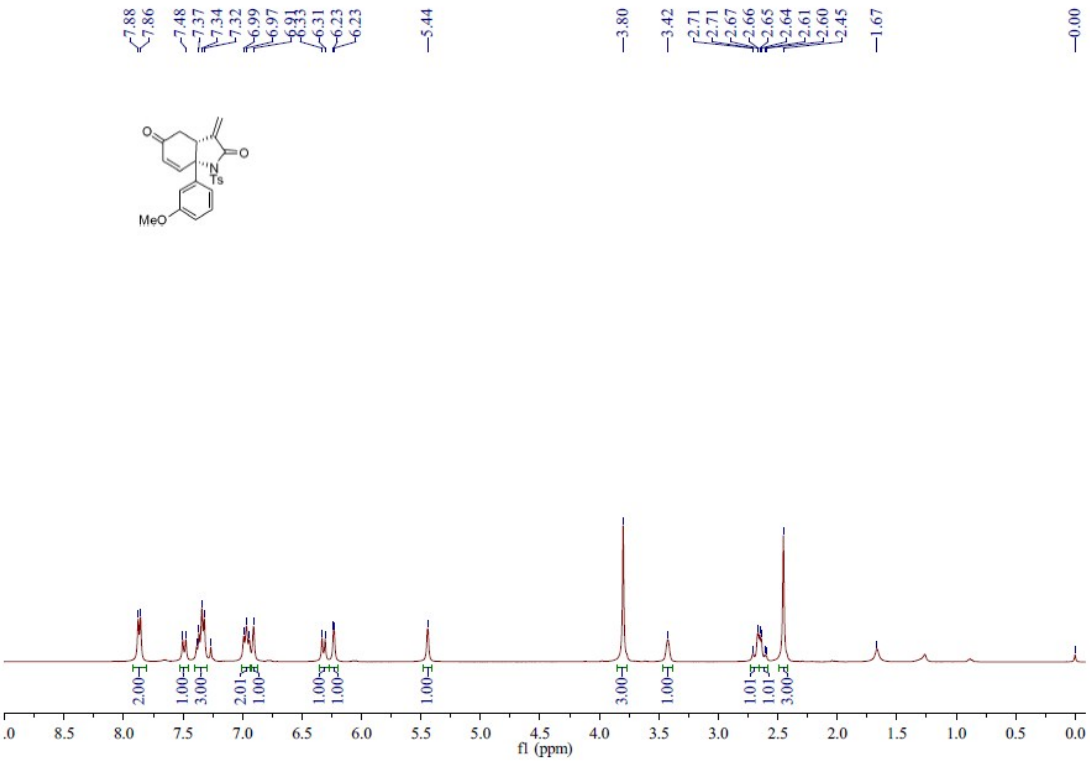
^{13}C NMR spectra of **2h**



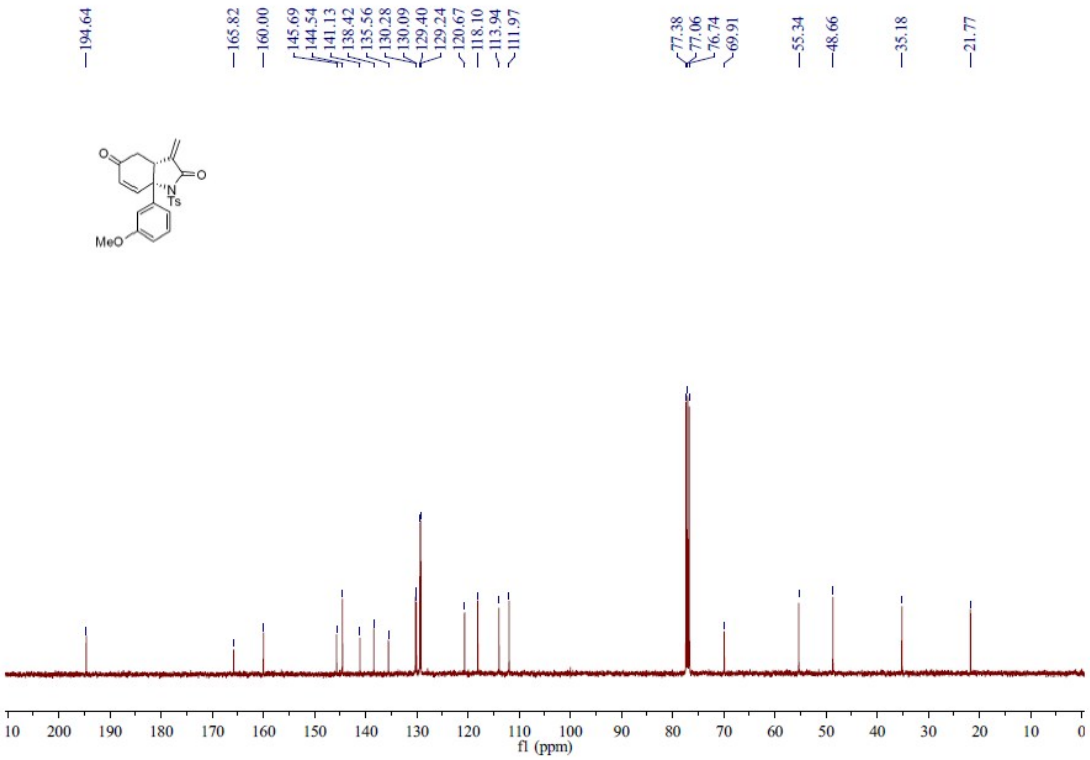
^{1}H NMR spectra of **2i**



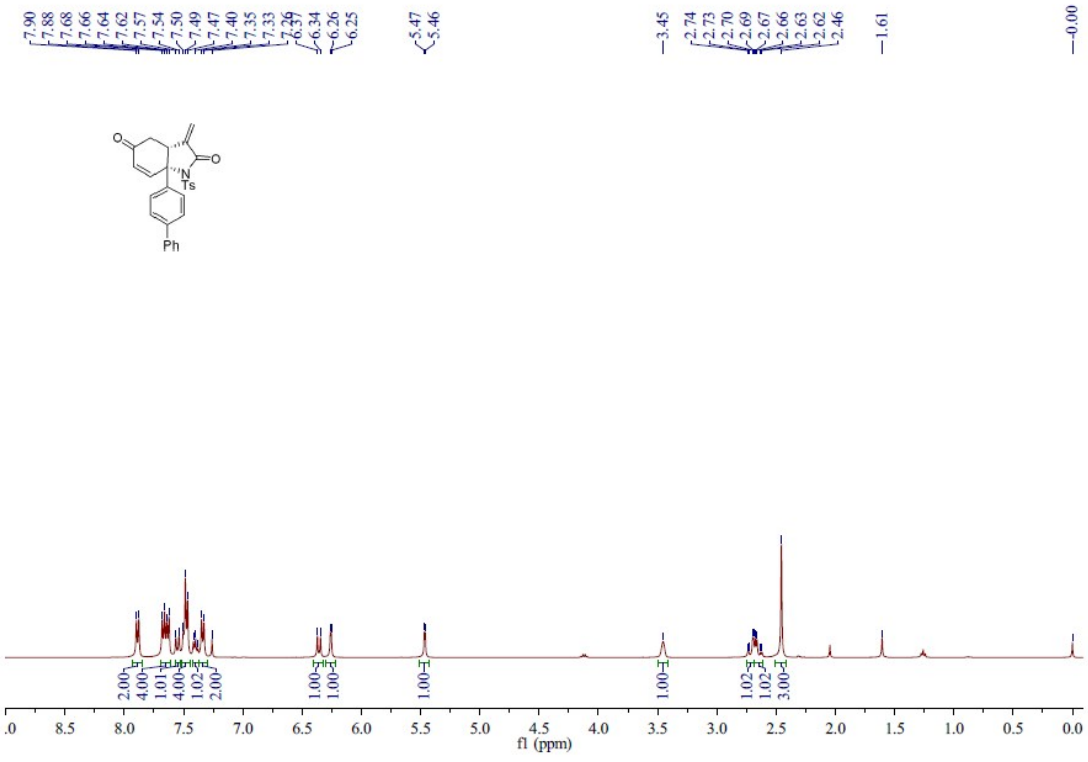
^{13}C NMR spectra of **2i**



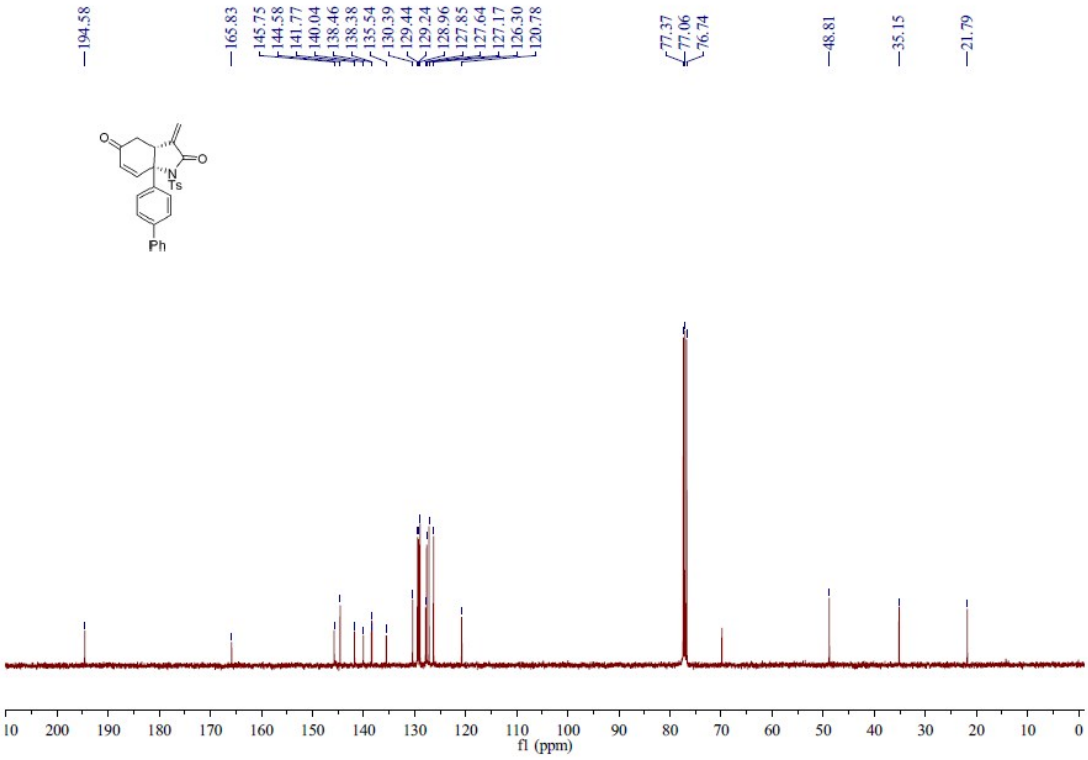
^{1}H NMR spectra of **2j**



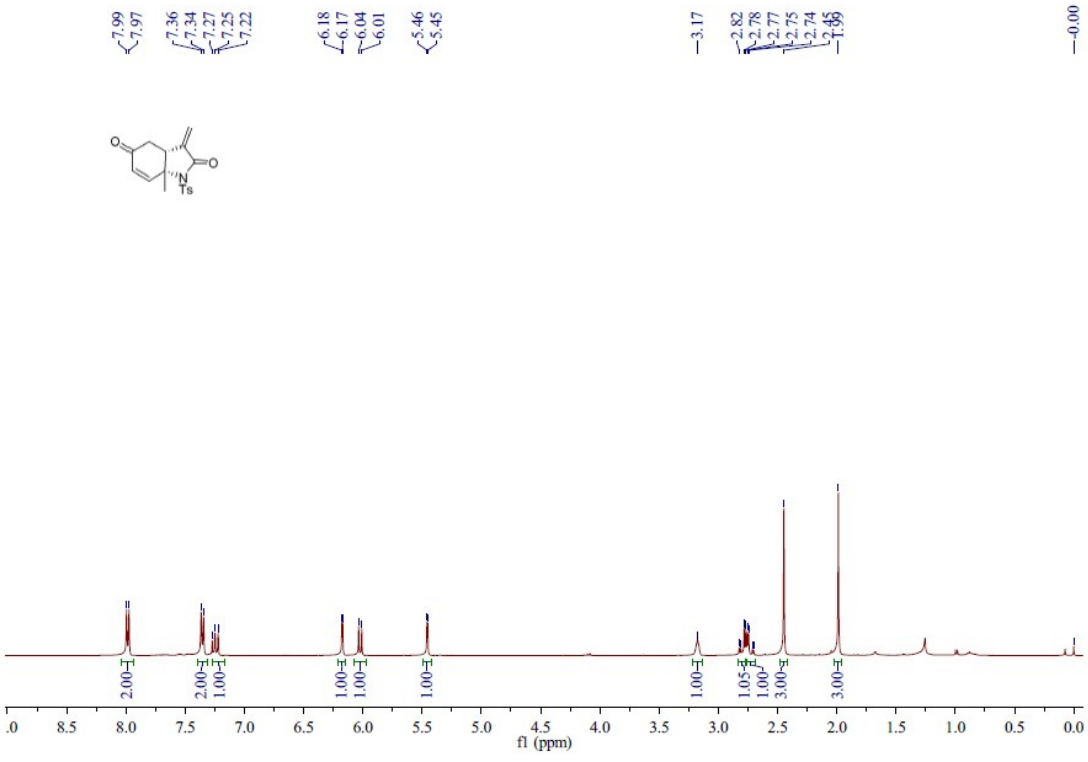
^{13}C NMR spectra of **2j**



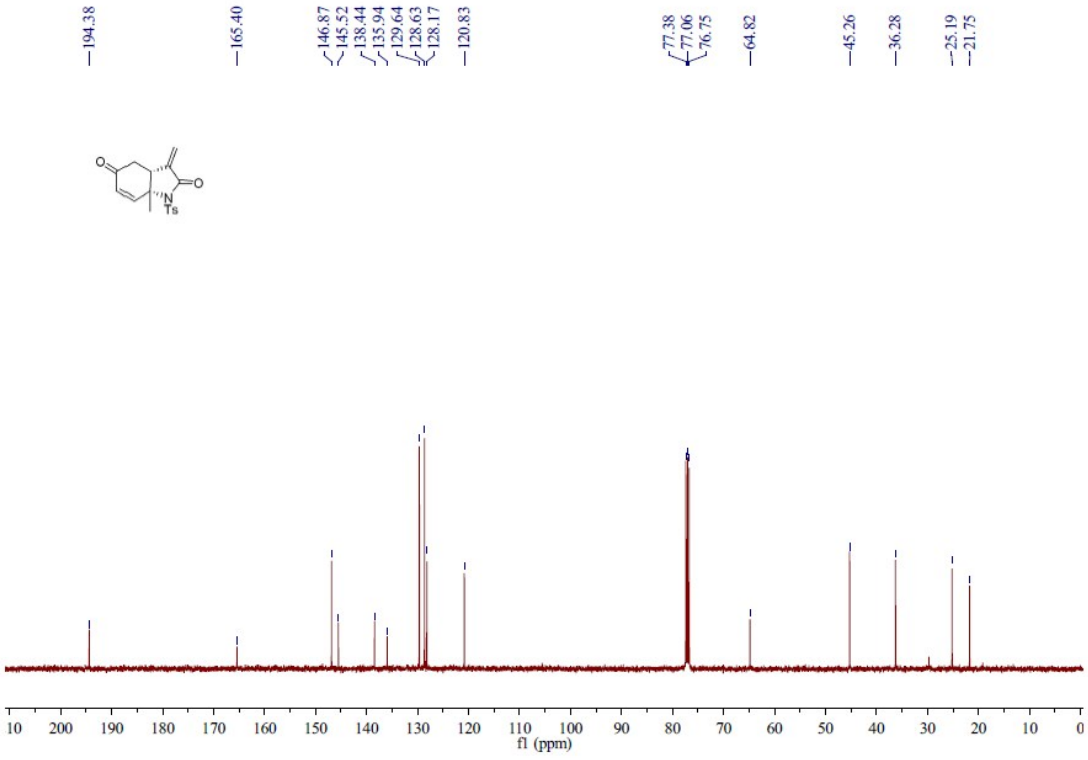
^{1}H NMR spectra of **2k**



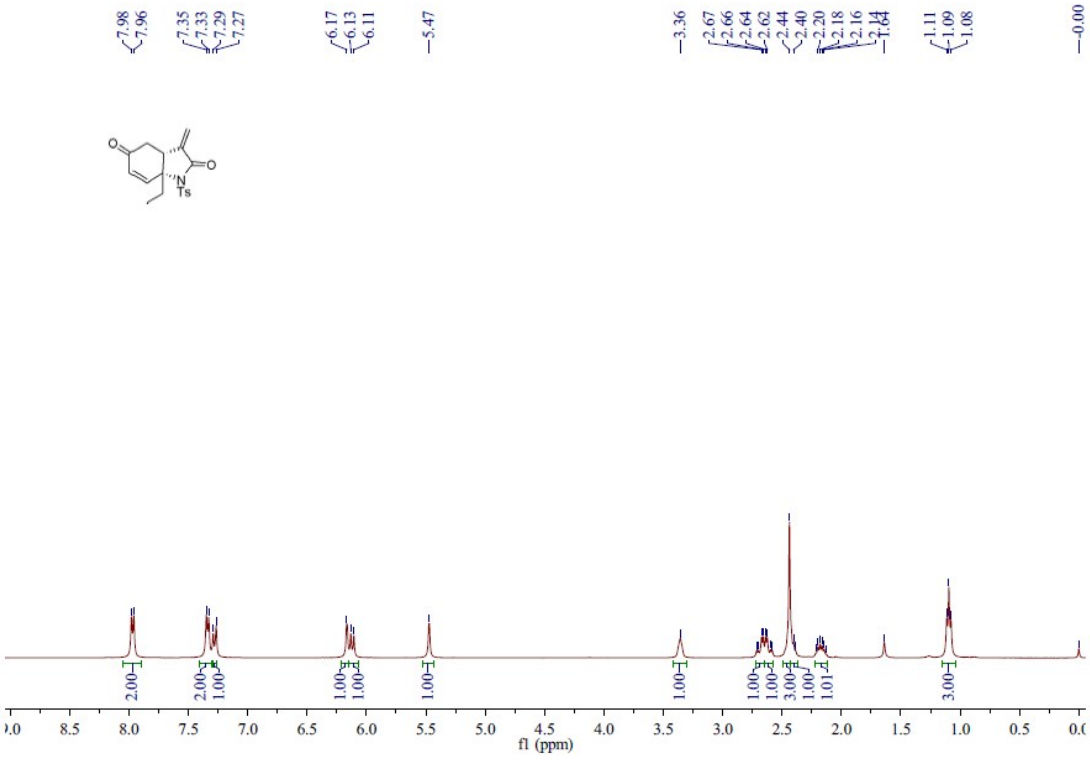
^{13}C NMR spectra of **2k**



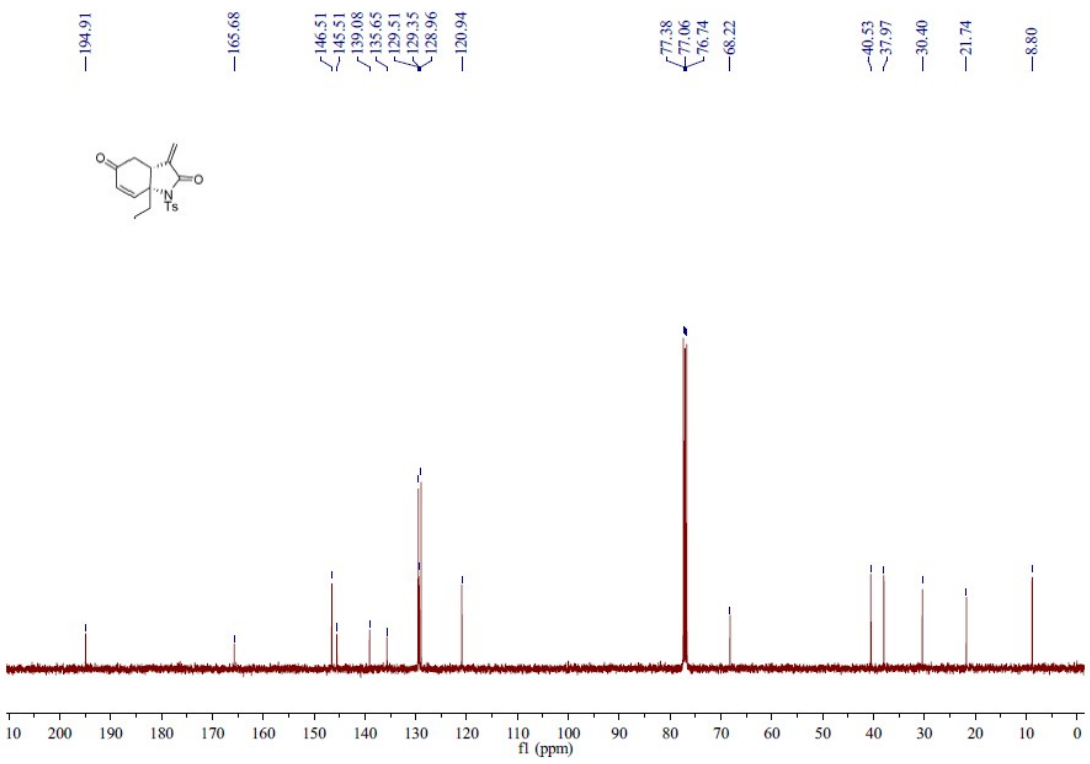
^{1}H NMR spectra of **2l**



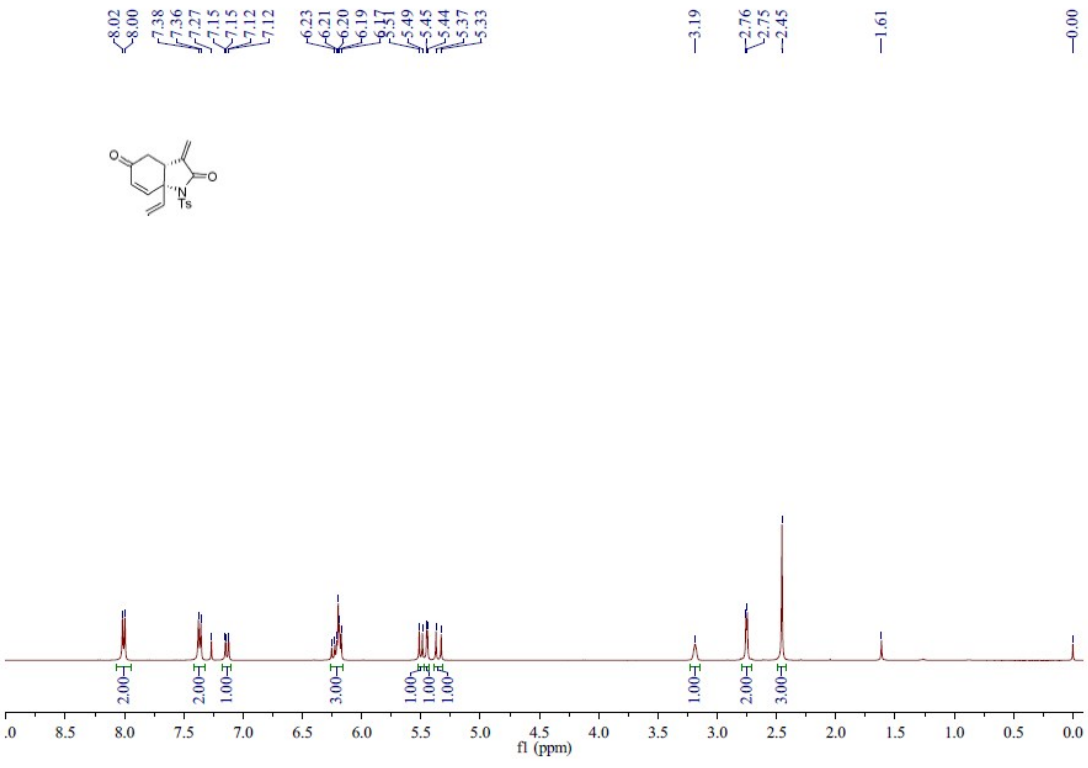
^{13}C NMR spectra of **2l**



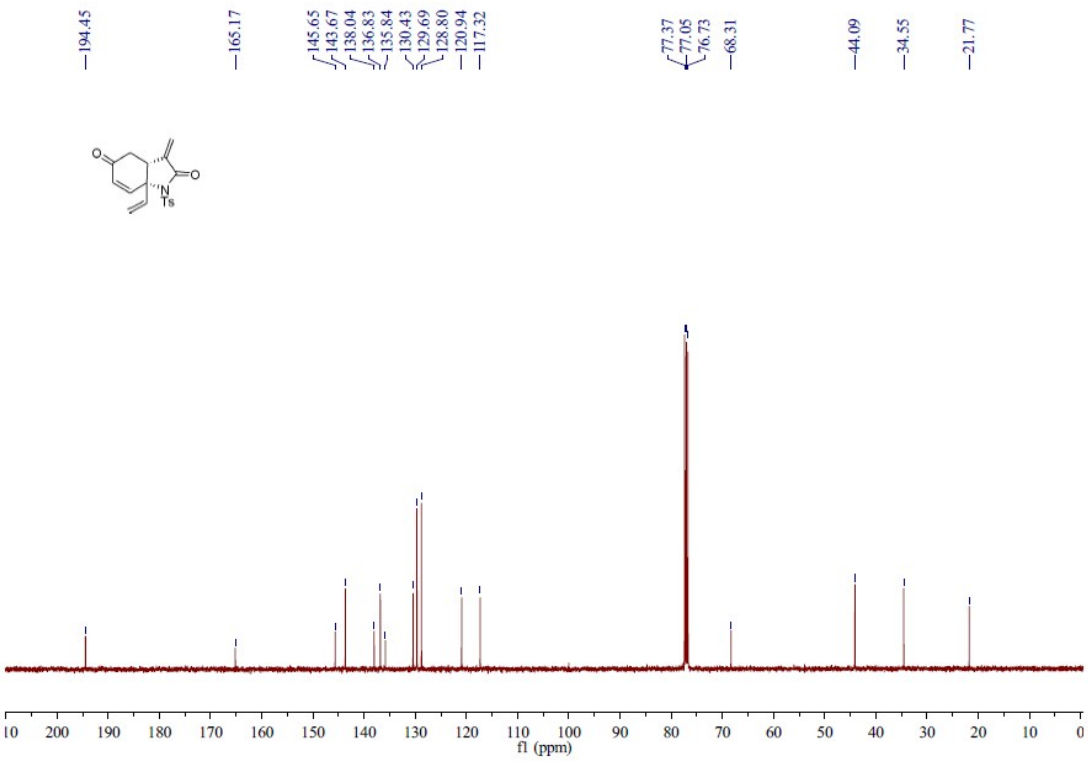
^{1}H NMR spectra of **2m**



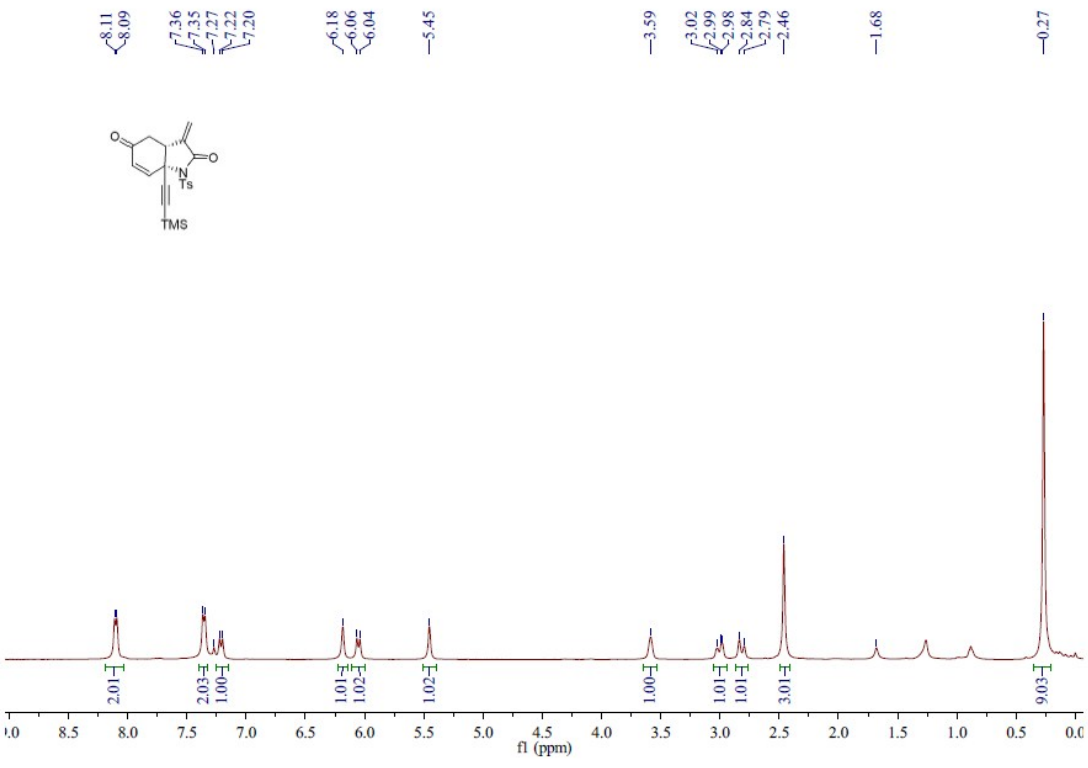
^{13}C NMR spectra of **2m**



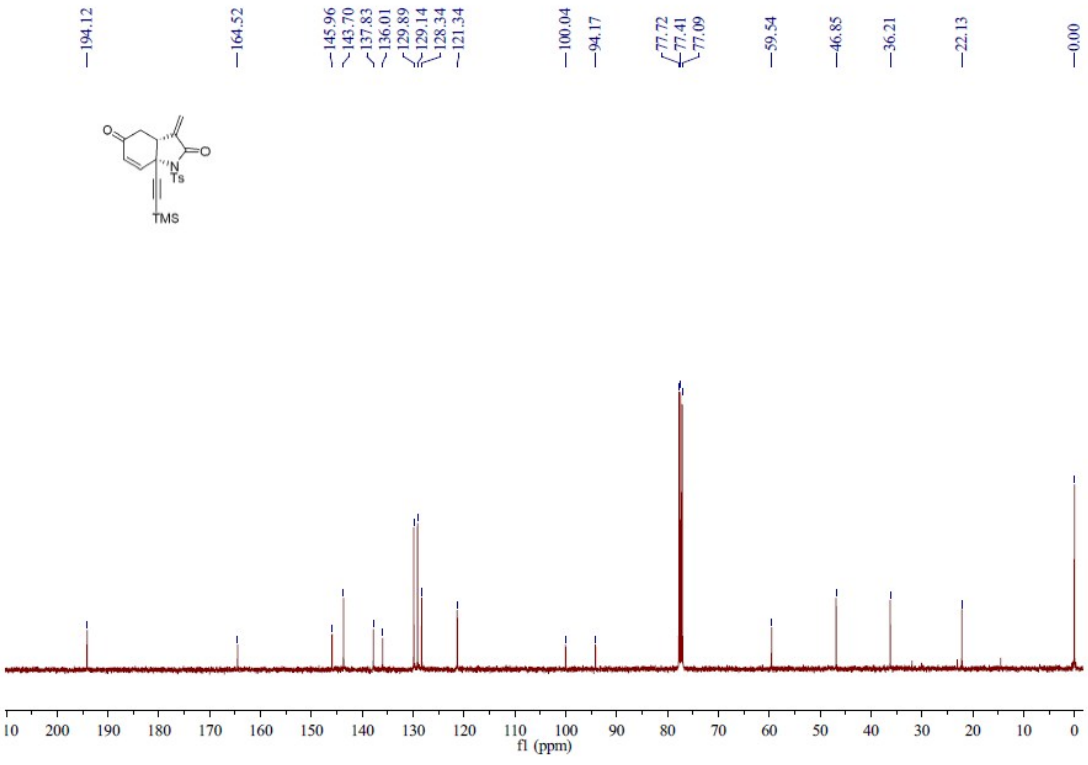
^{1}H NMR spectra of **2n**



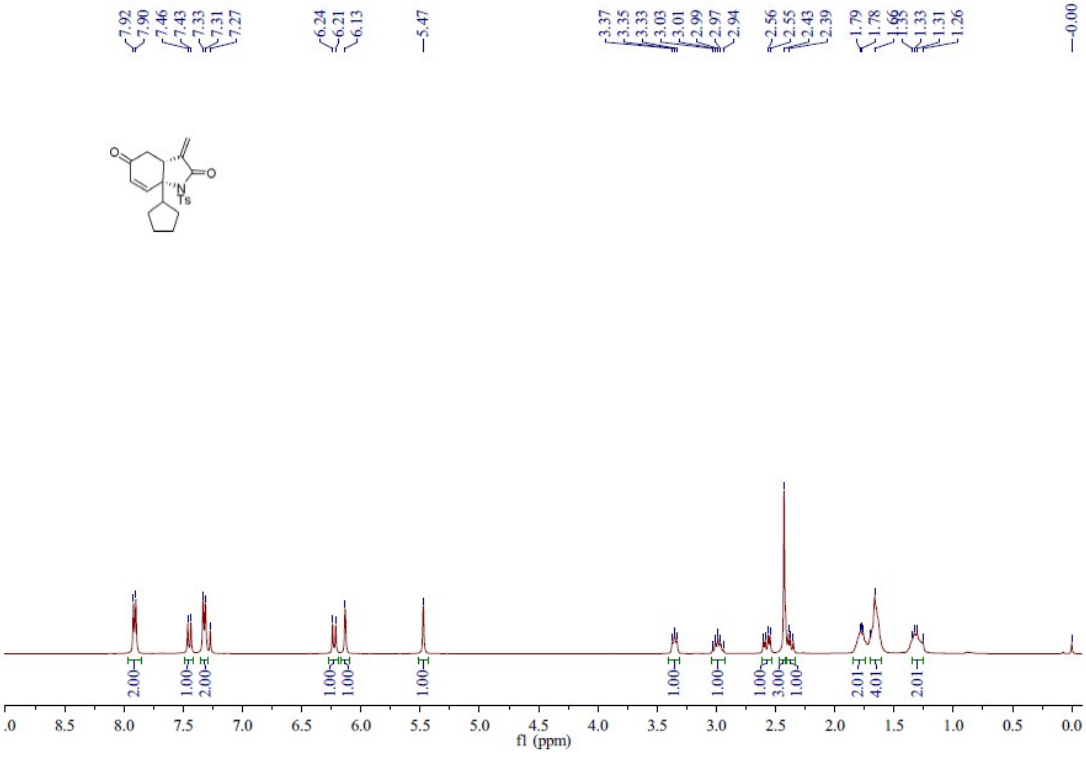
^{13}C NMR spectra of **2n**



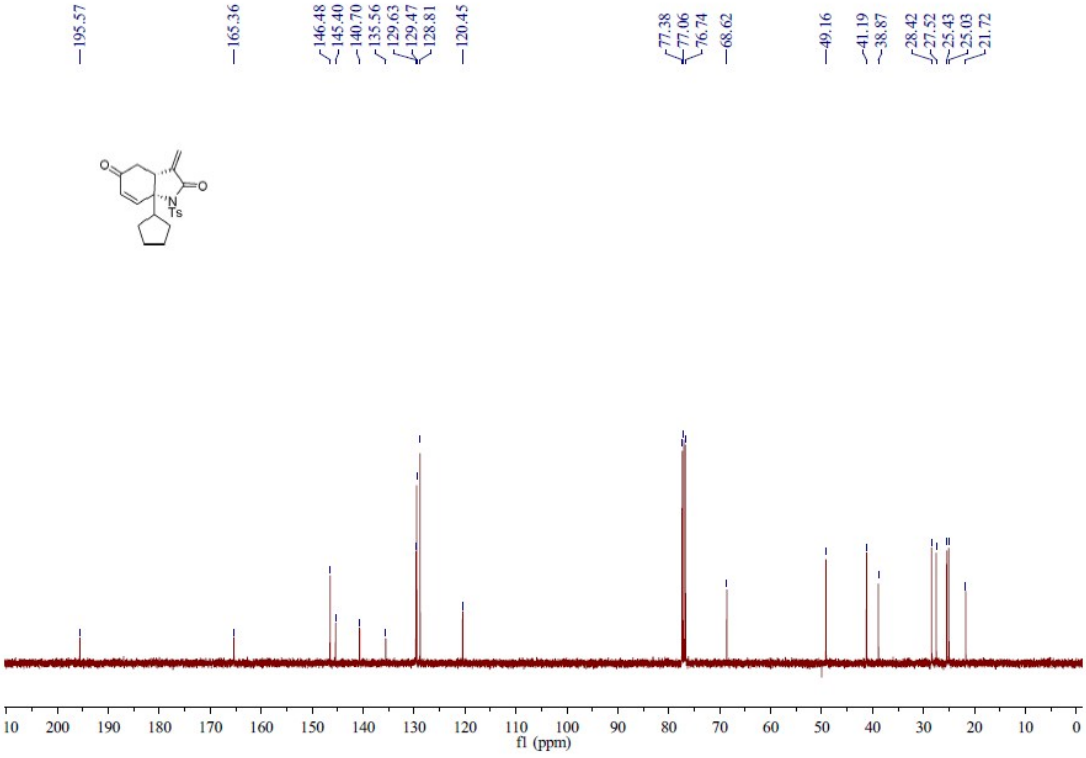
^{1}H NMR spectra of **2o**



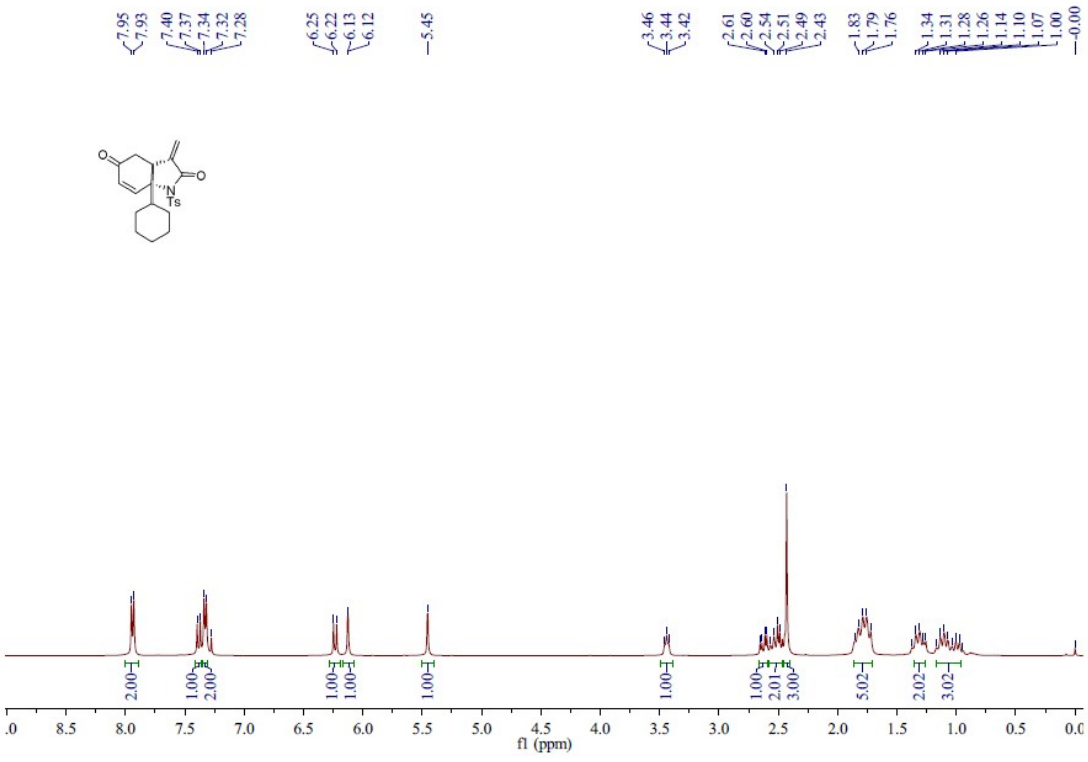
^{13}C NMR spectra of **2o**



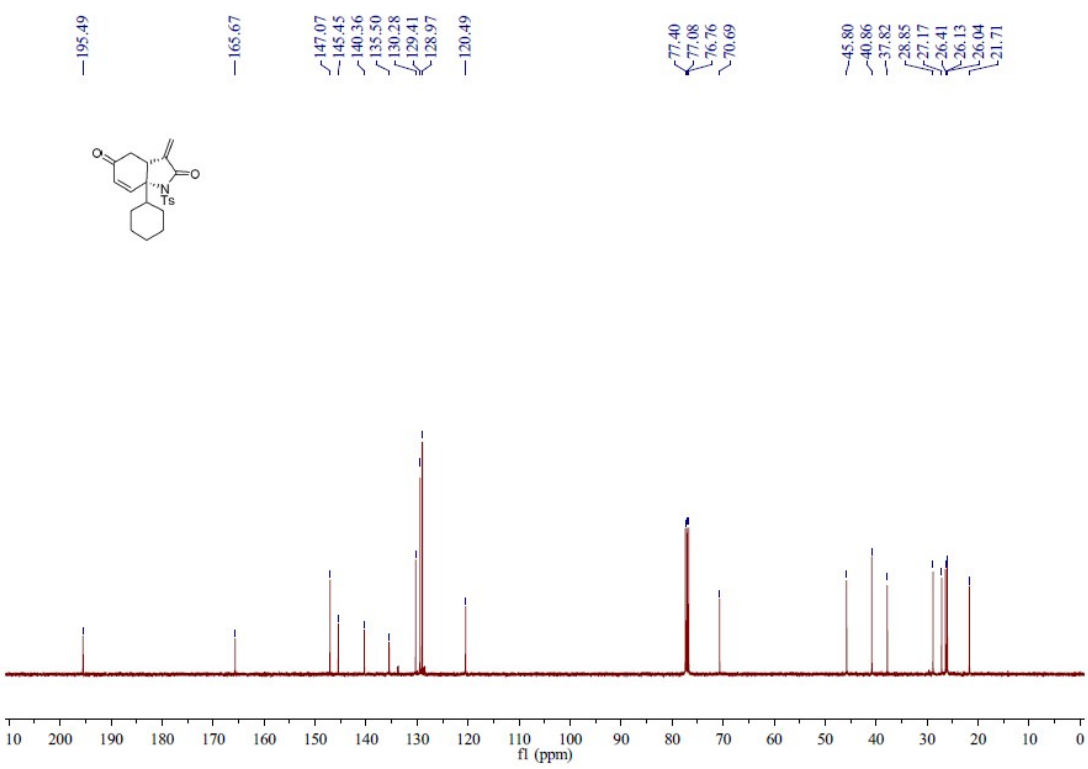
^{1}H NMR spectra of **2p**



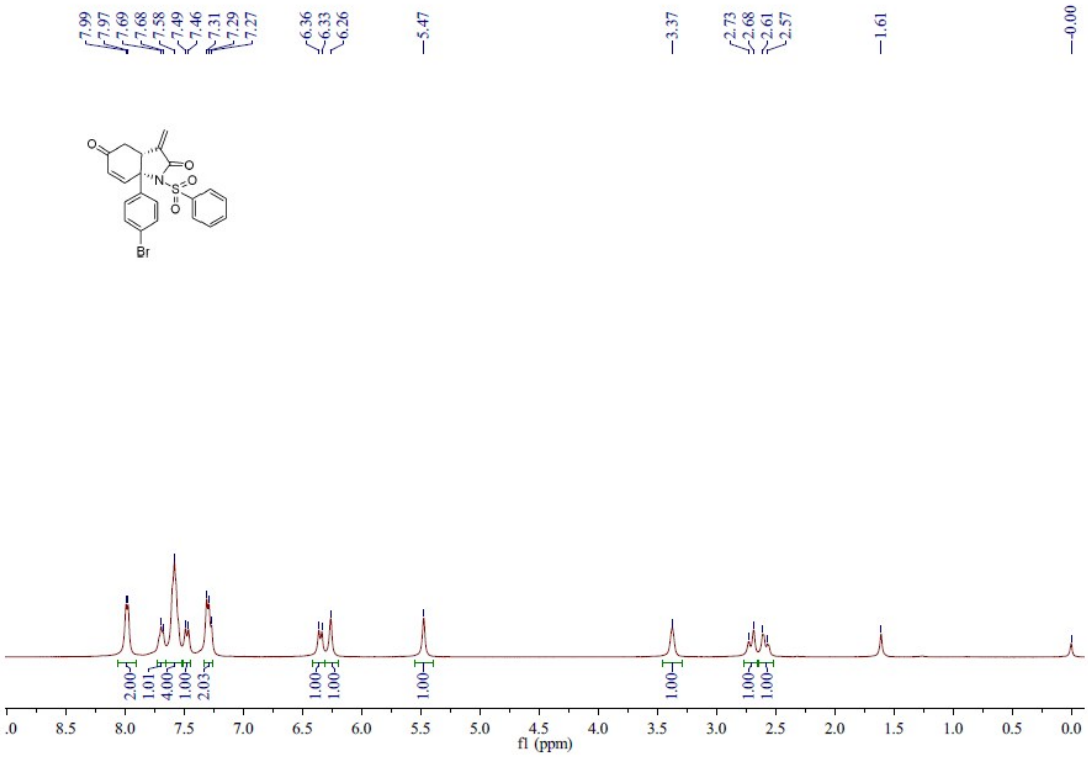
^{13}C NMR spectra of **2p**



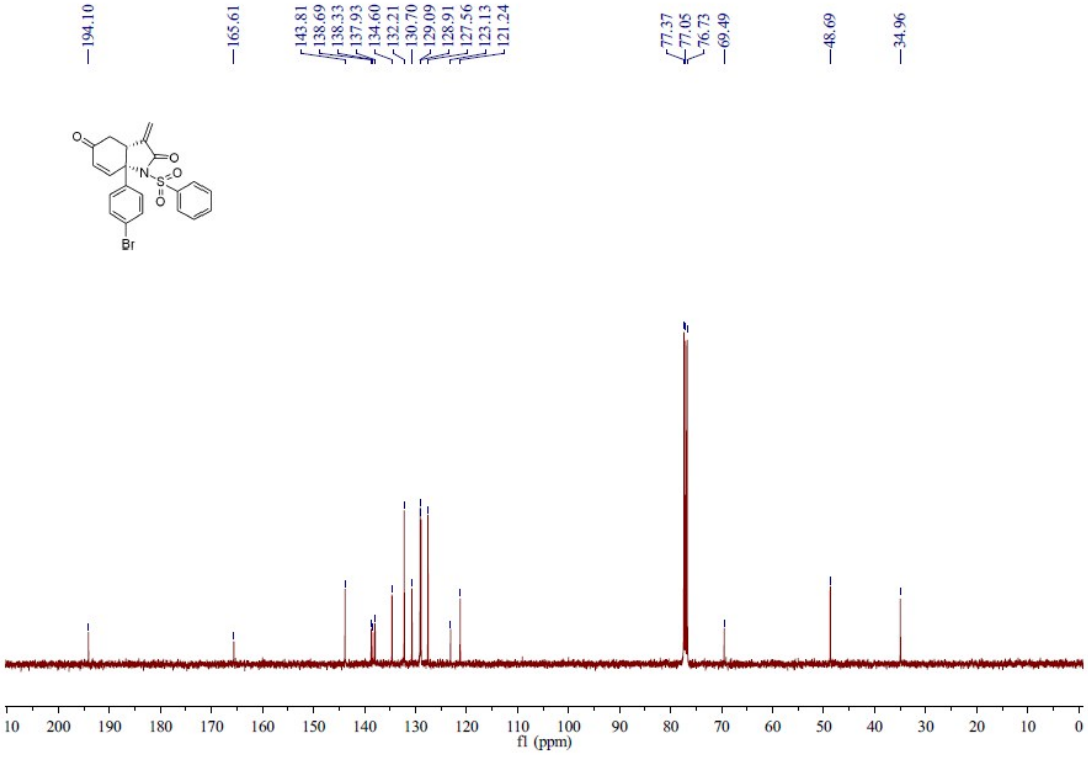
^{1}H NMR spectra of **2q**



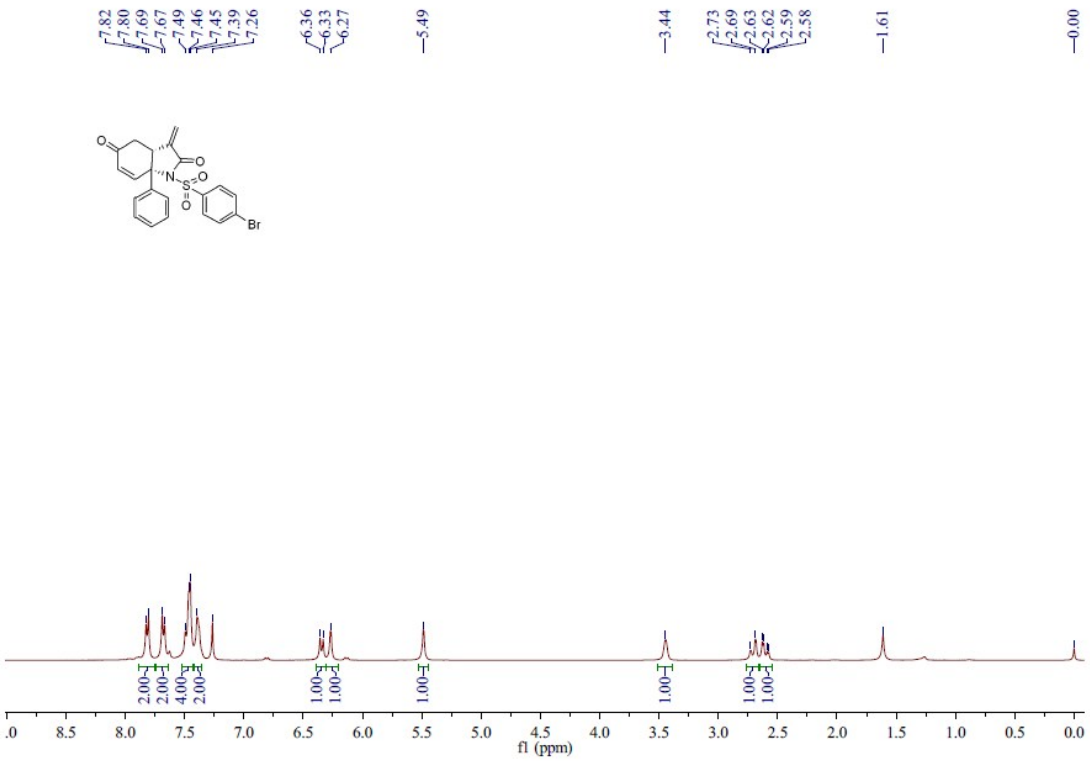
^{13}C NMR spectra of **2q**



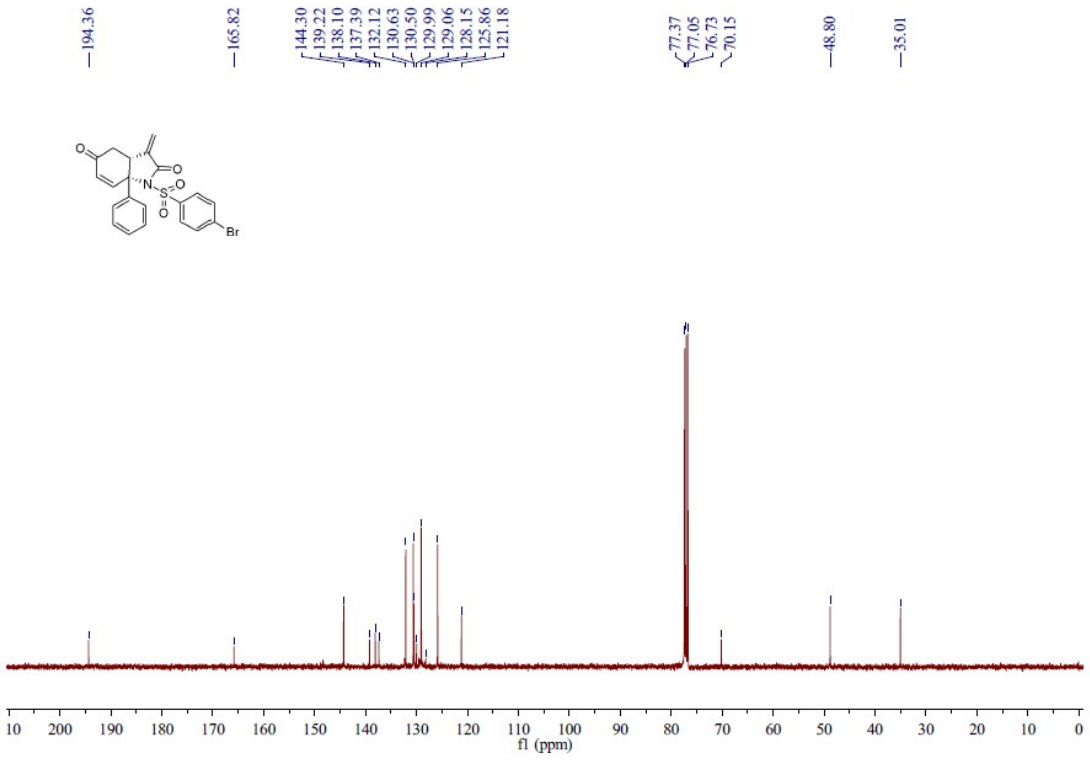
^{1}H NMR spectra of **2r**



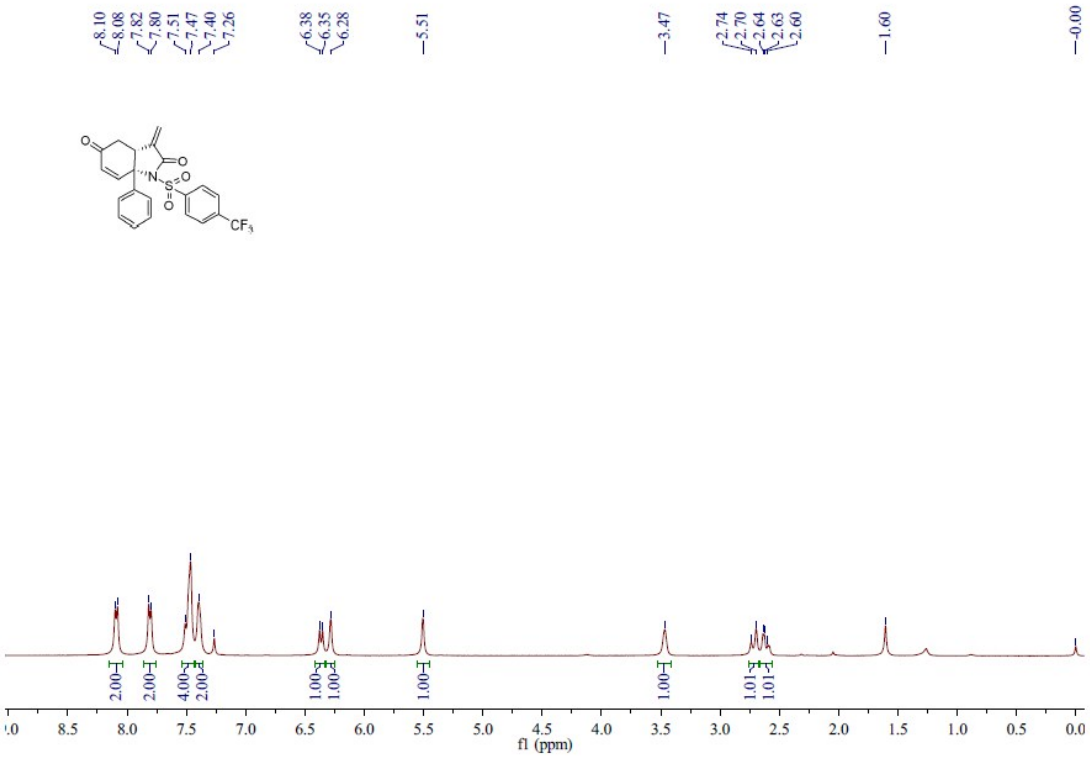
^{13}C NMR spectra of **2r**



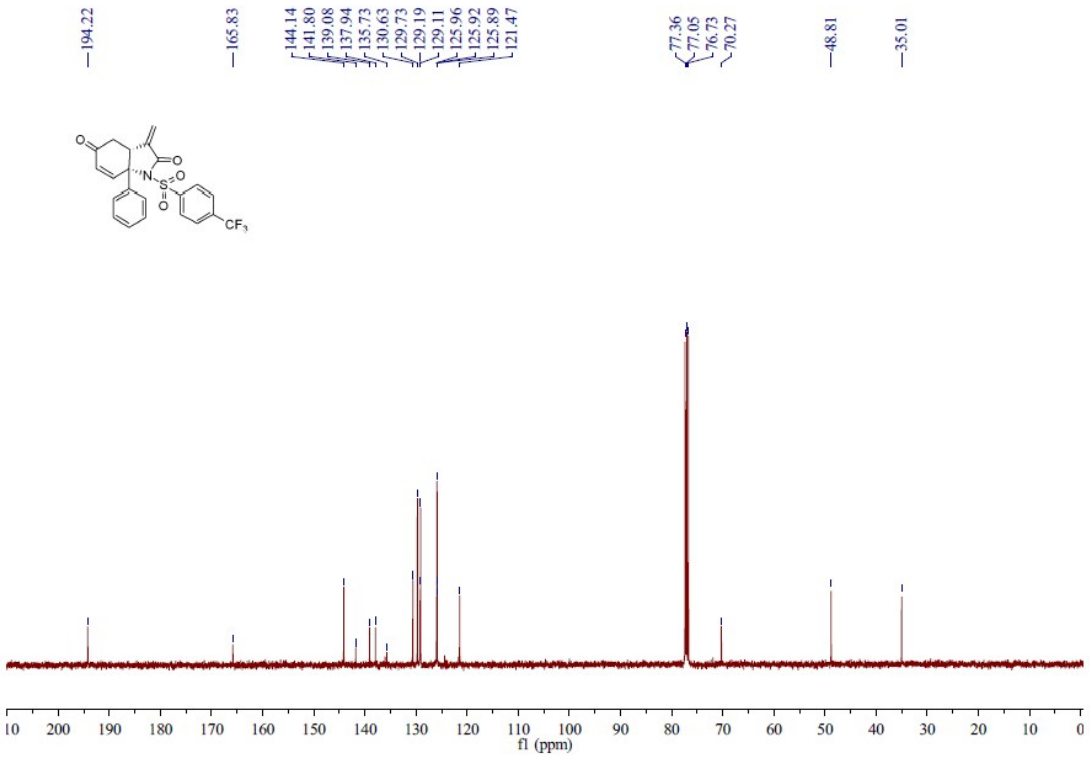
^{1}H NMR spectra of **2s**



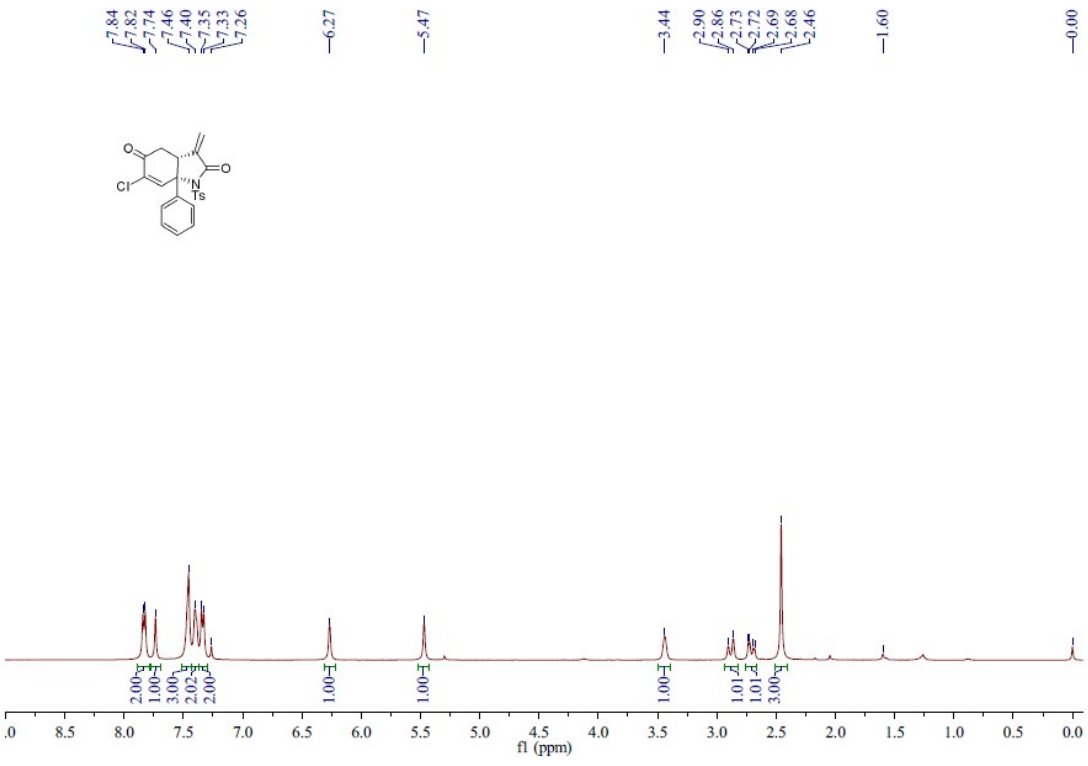
^{13}C NMR spectra of **2s**



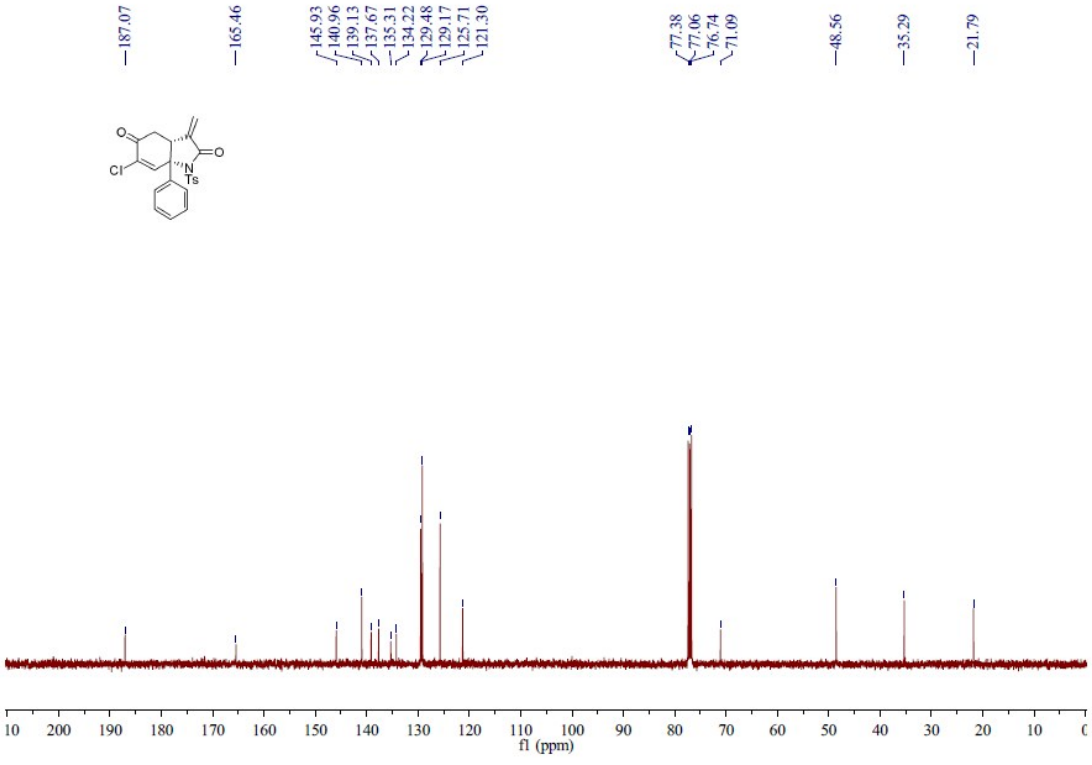
^{1}H NMR spectra of **2t**



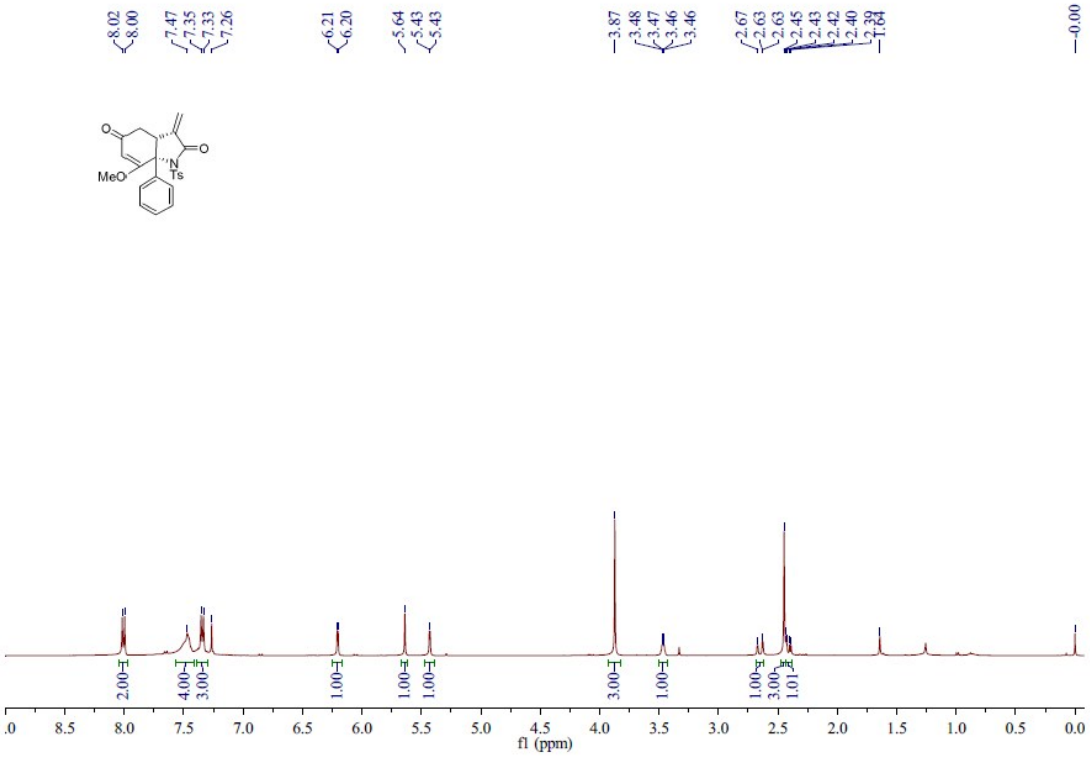
^{13}C NMR spectra of **2t**



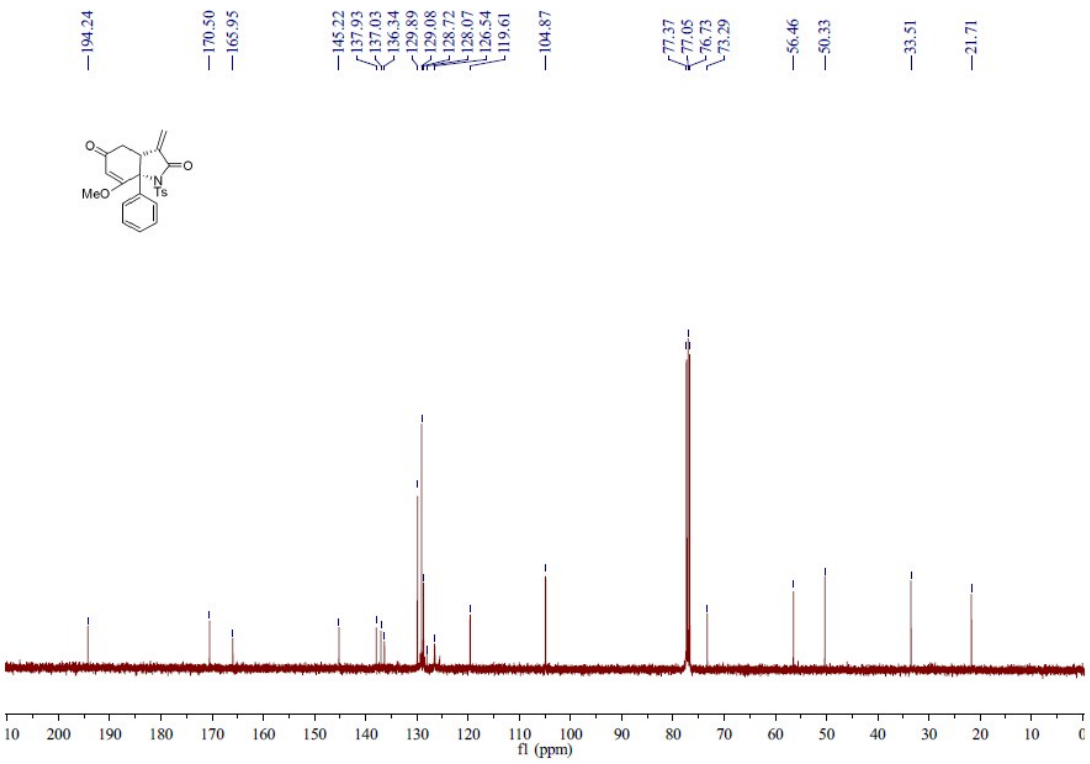
^{1}H NMR spectra of **2u**



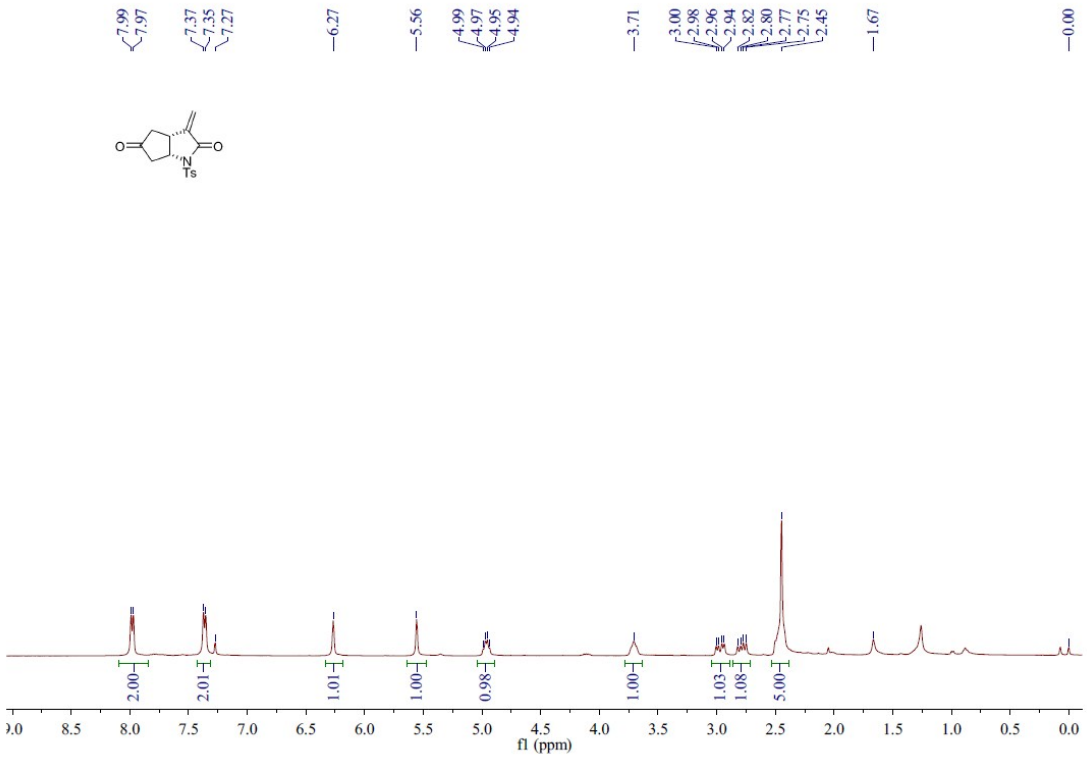
^{13}C NMR spectra of **2u**



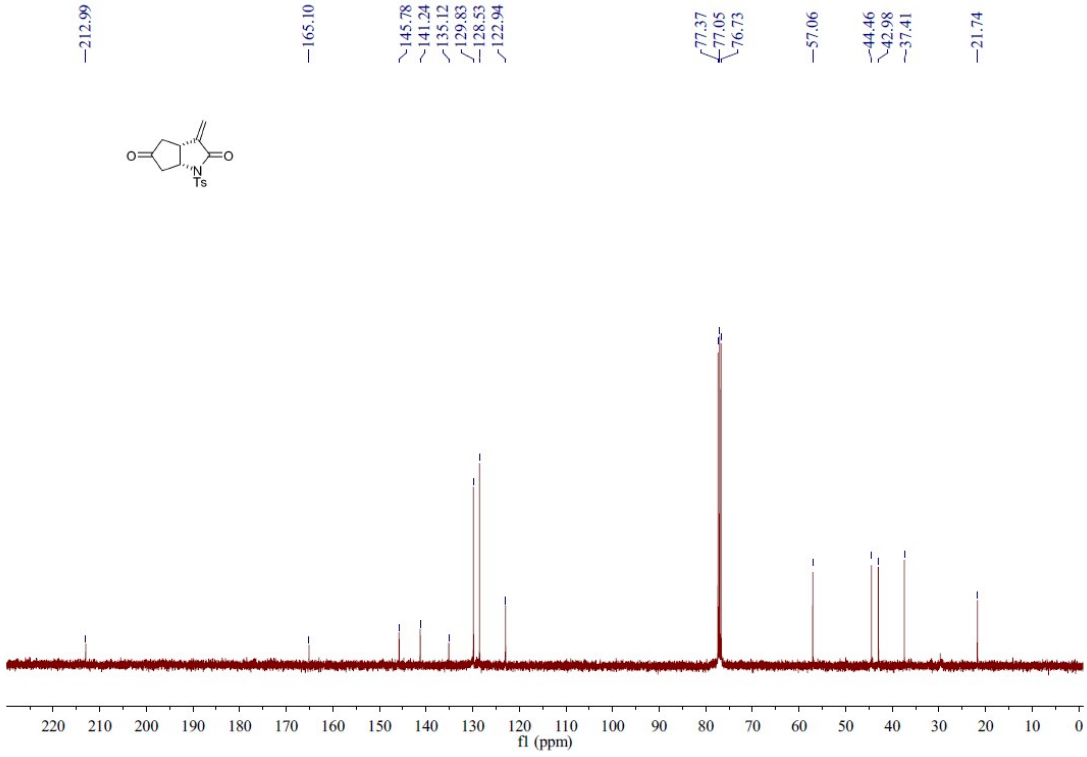
^{1}H NMR spectra of **2v**



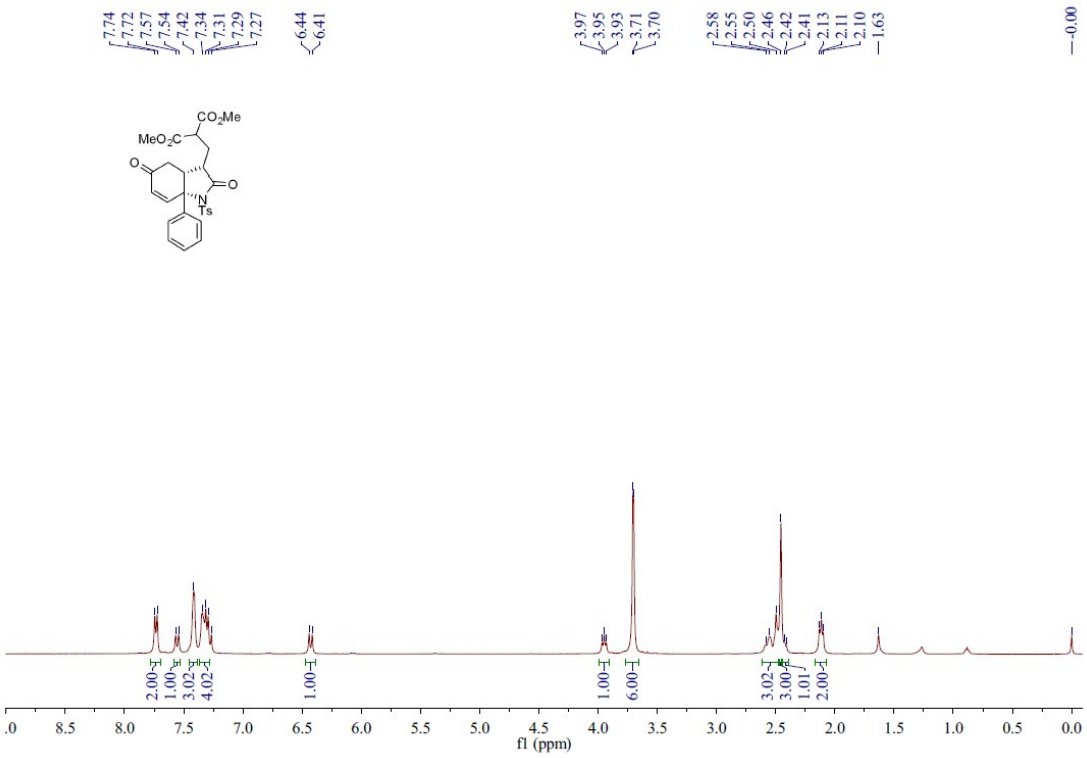
^{13}C NMR spectra of **2v**



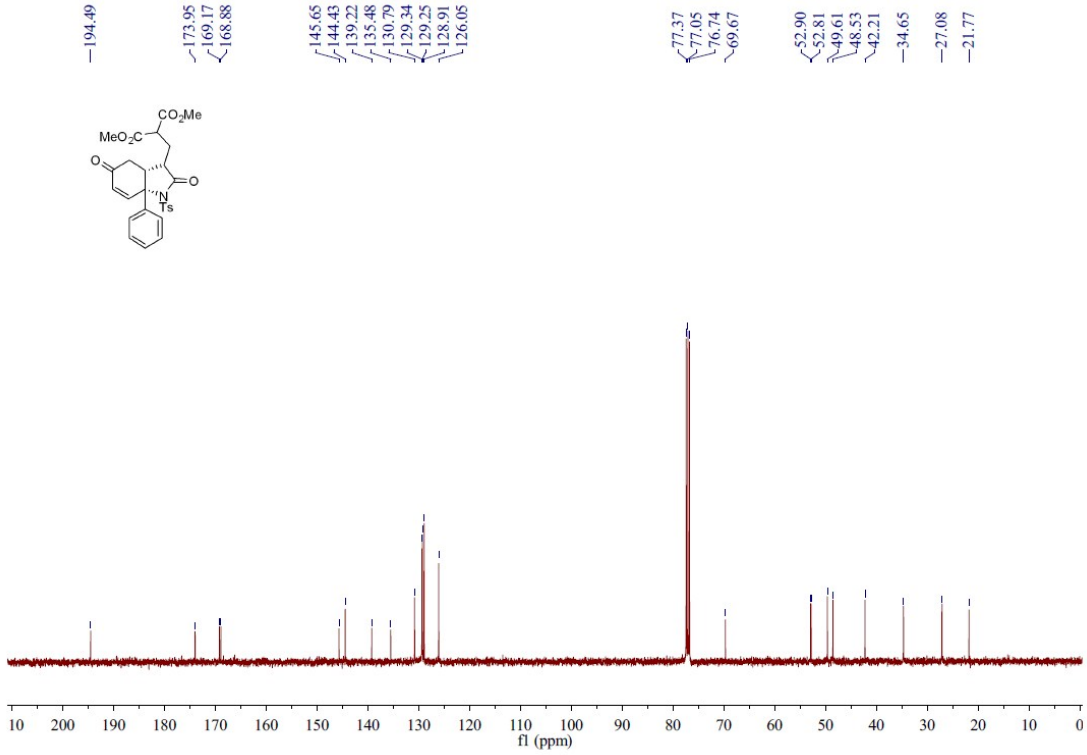
^{1}H NMR spectra of **2w**



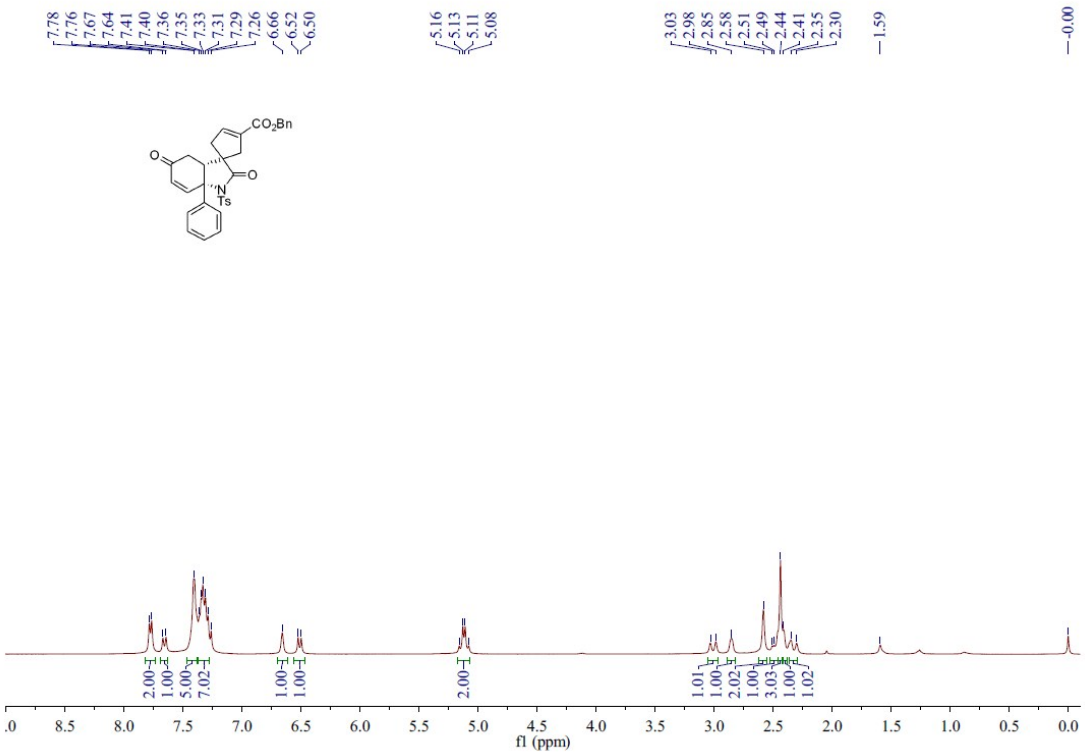
^{13}C NMR spectra of **2w**



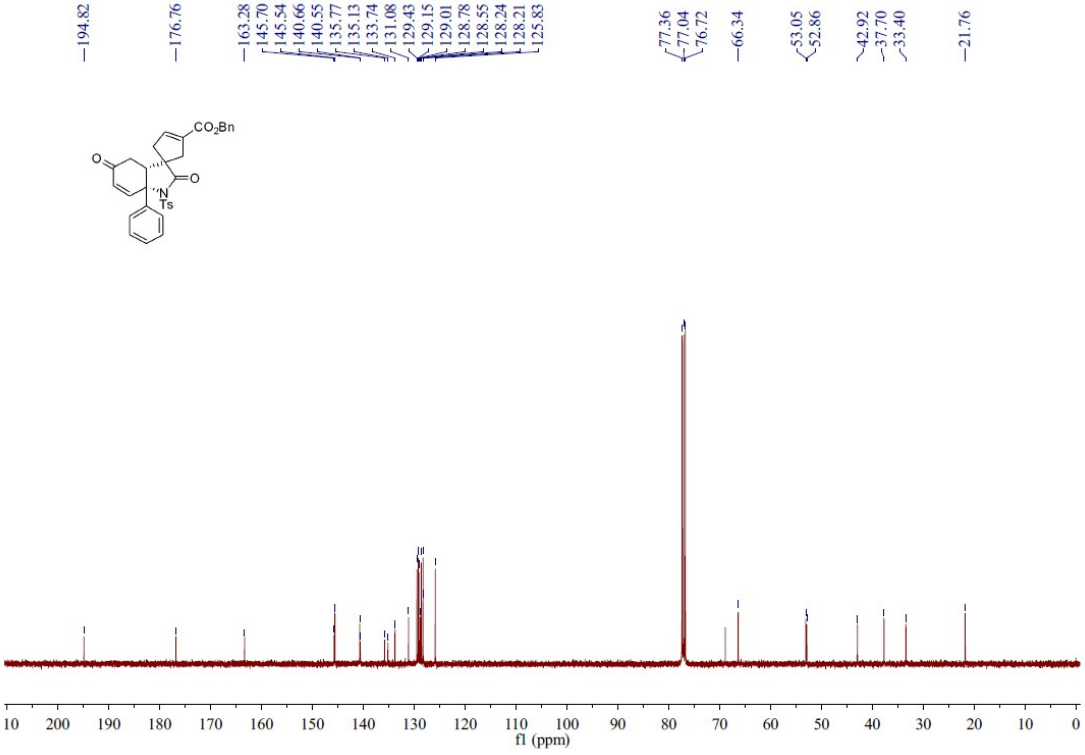
^{1}H NMR spectra of **4a**



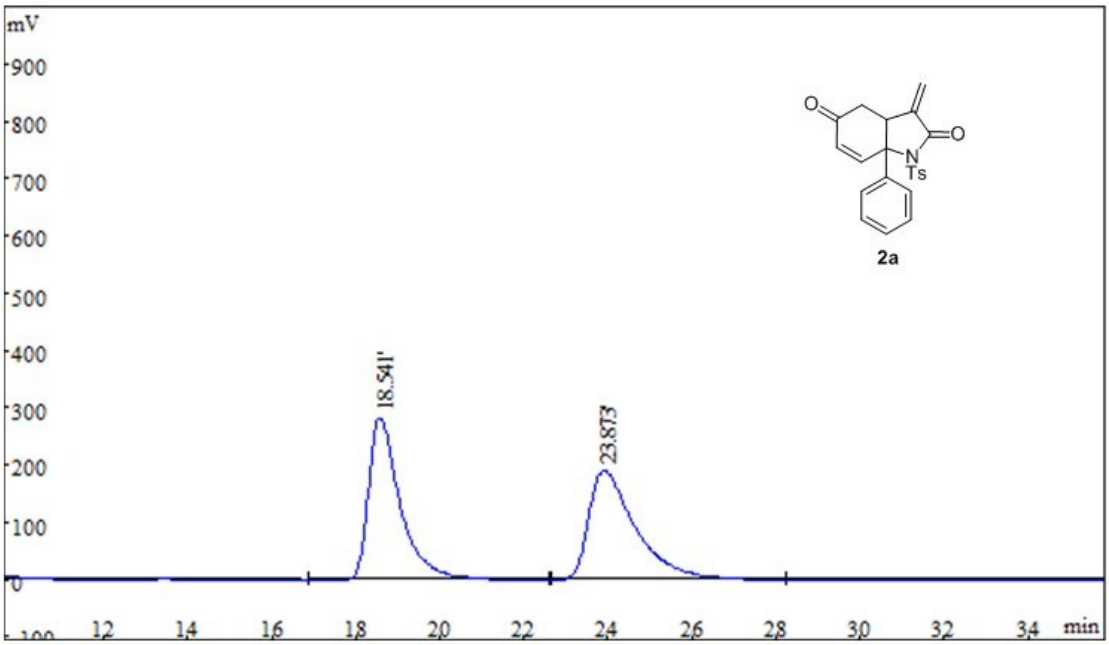
^{13}C NMR spectra of **4a**



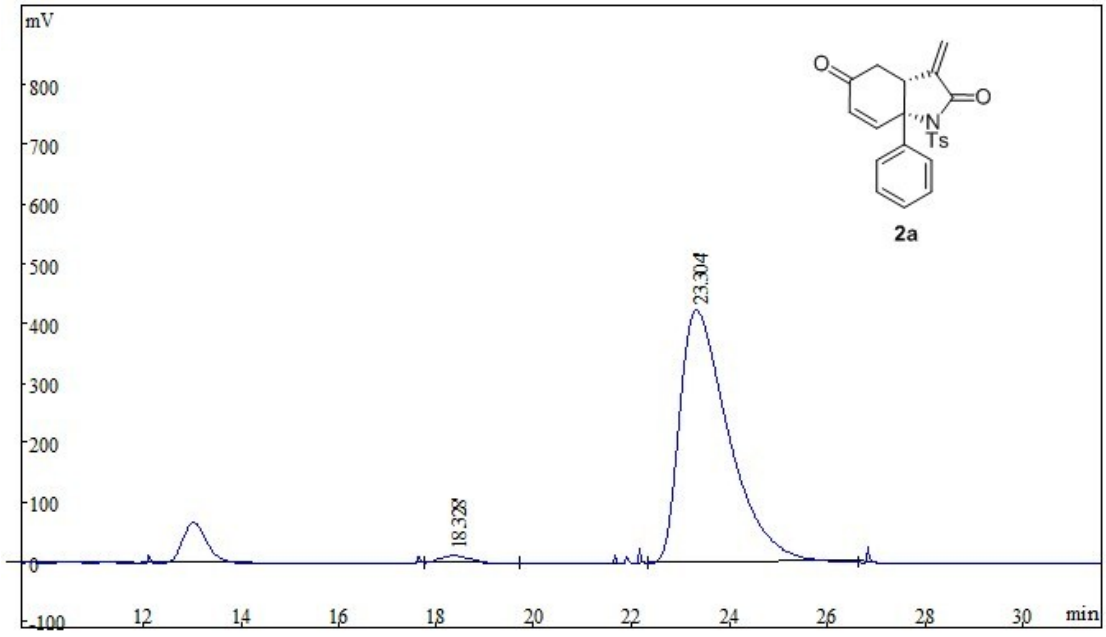
^{1}H NMR spectra of **4b**



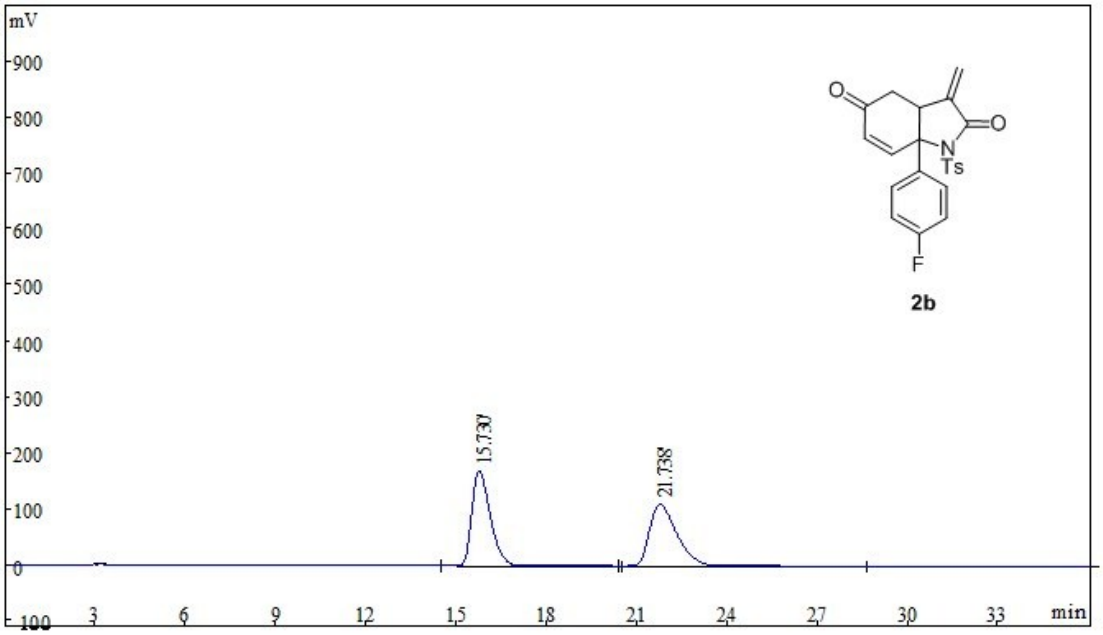
^{13}C NMR spectra of **4b**



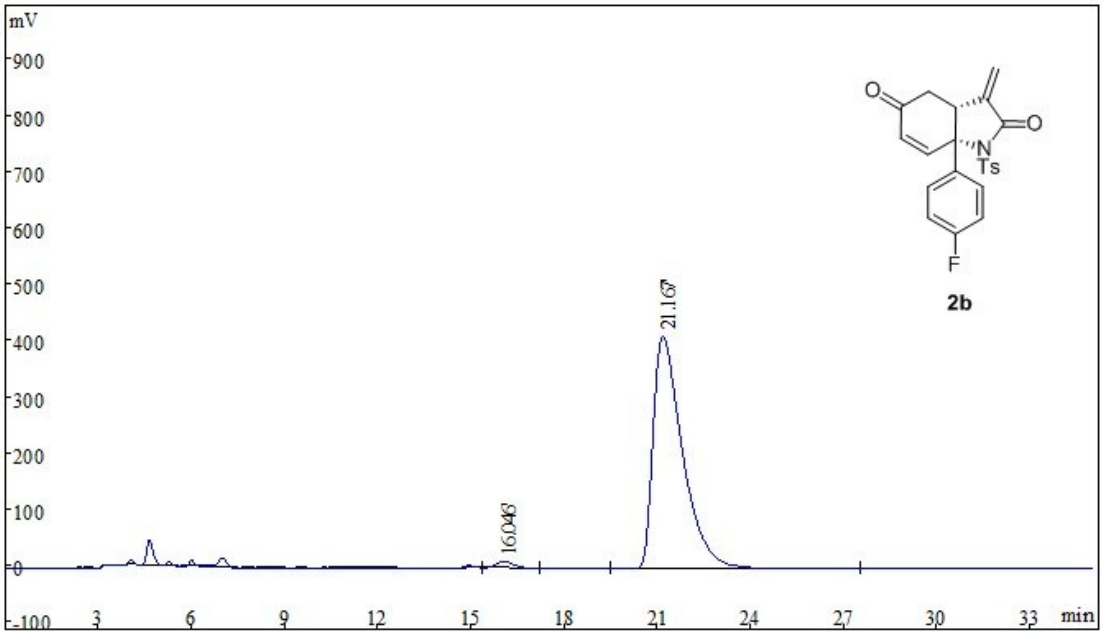
Rank	Time(min)	Area%	Area
1	18.541	50.08	14816973
2	23.873	49.92	14767594
Total		100	29584567



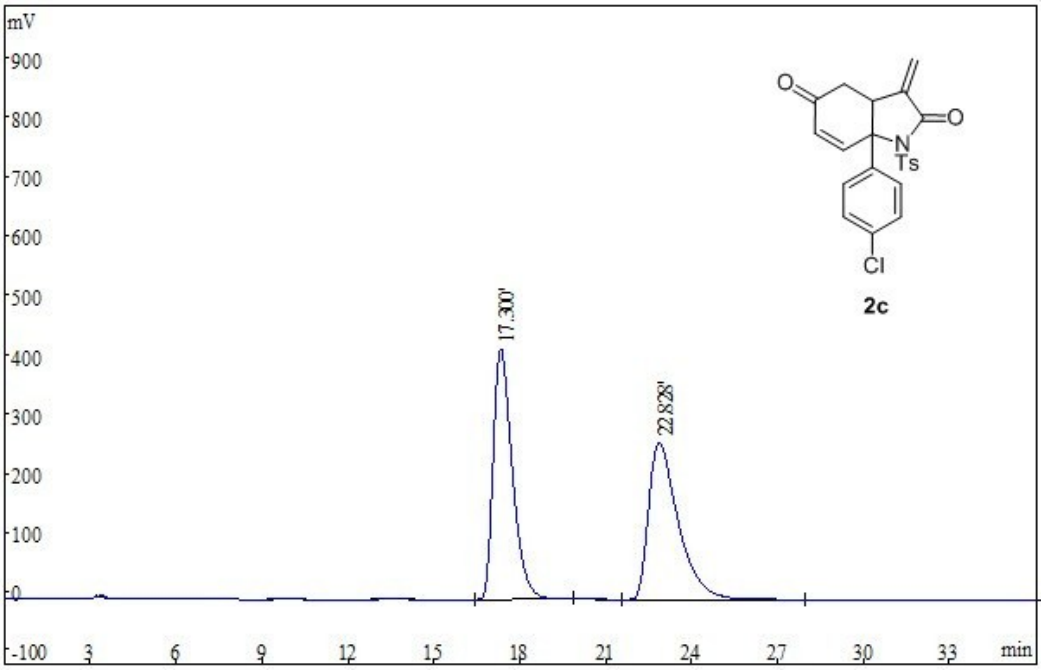
Rank	Time(min)	Area%	Area
1	18.328	1.798	545735
2	23.304	98.2	29806518
Total		100	30352253



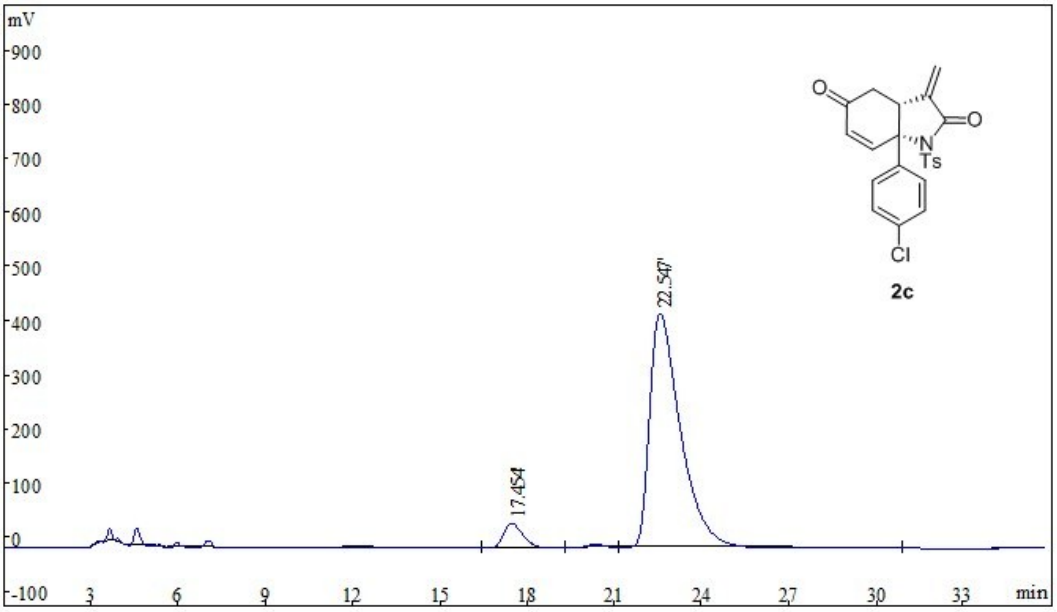
Rank	Time(min)	Area%	Area
1	15.730	49.89	7593594
2	21.738	50.11	7626408
Total		100	15220002



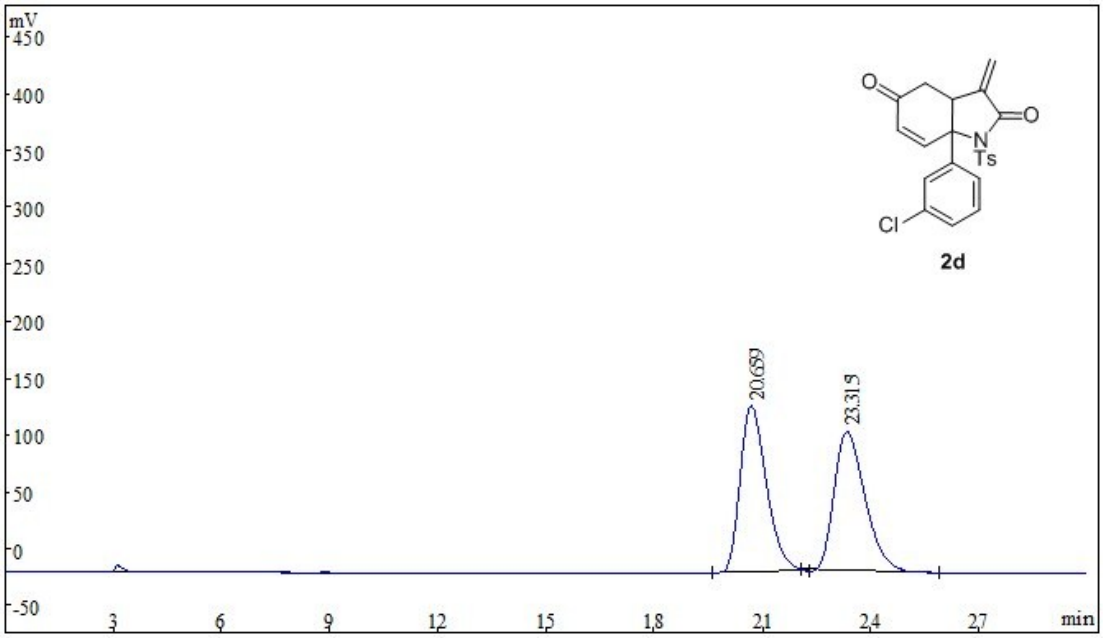
Rank	Time(min)	Area%	Area
1	16.046	1.784	499433
2	21.167	98.21	27501216
Total		100	28000649



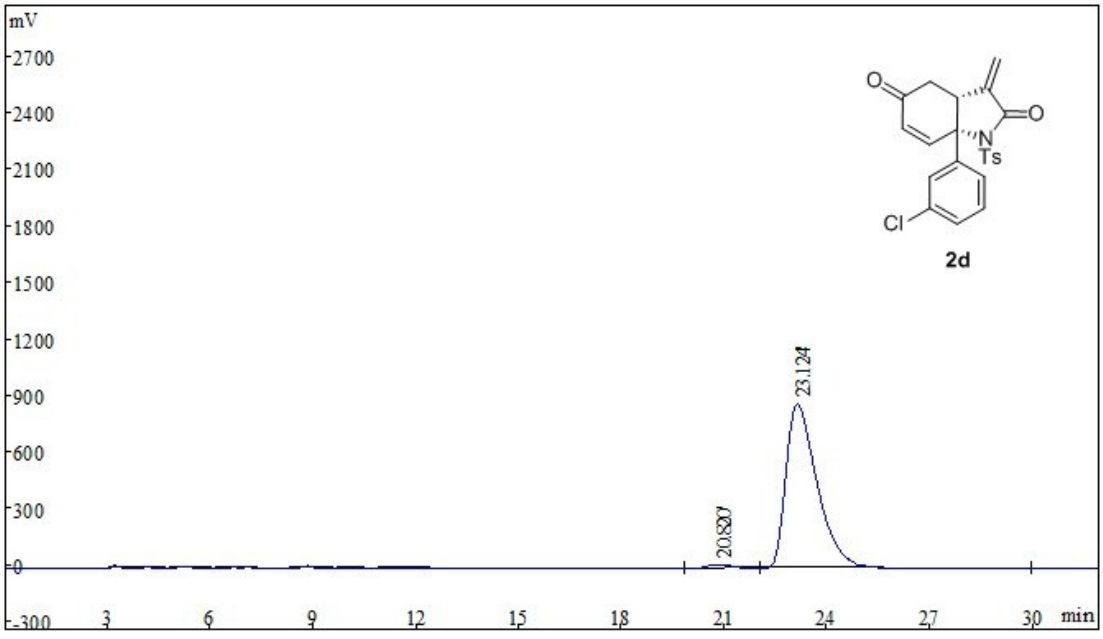
Rank	Time(min)	Area%	Area
1	17.300	50.17	19864966
2	22.828	49.83	19726907
Total		100	39591873



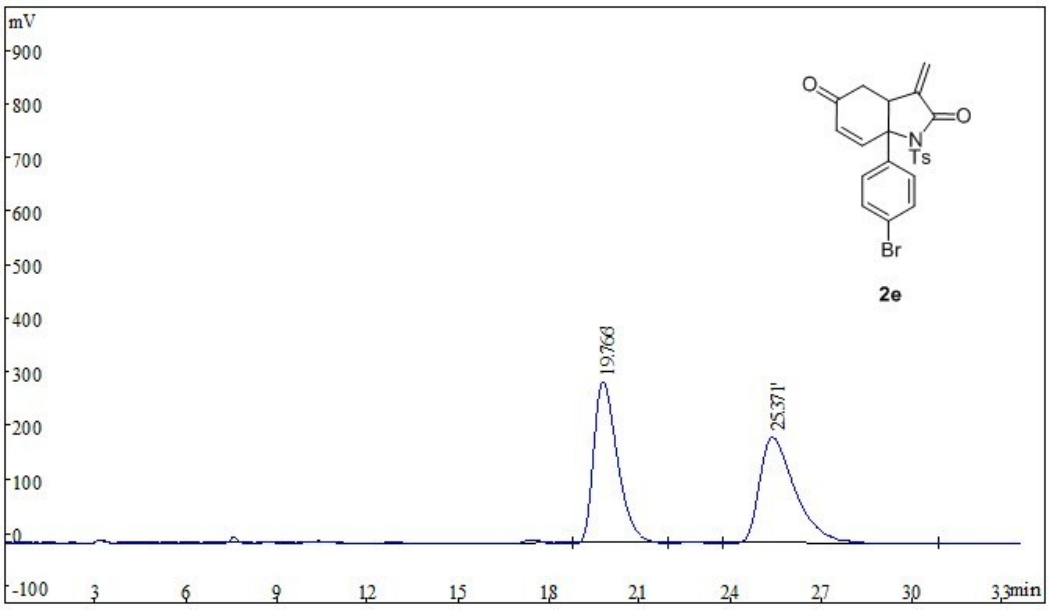
Rank	Time(min)	Area%	Area
1	17.454	6.389	2195258
2	22.547	93.61	32165456
Total		100	39591873



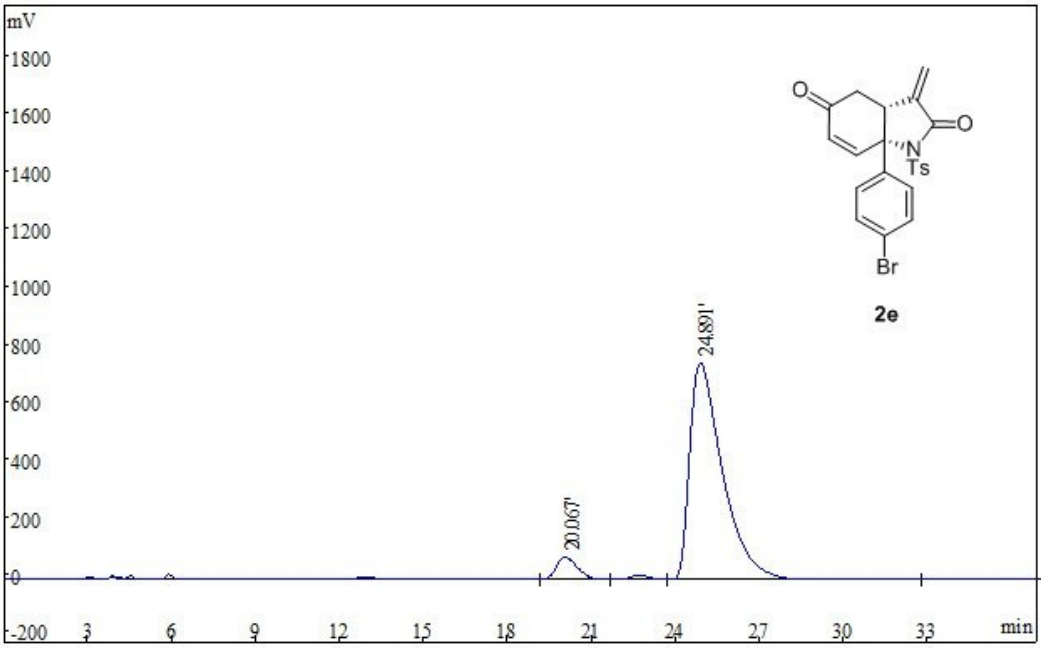
Rank	Time(min)	Area%	Area
1	20.659	50.51	7510626
2	23.315	49.49	7359526
Total		100	14870152



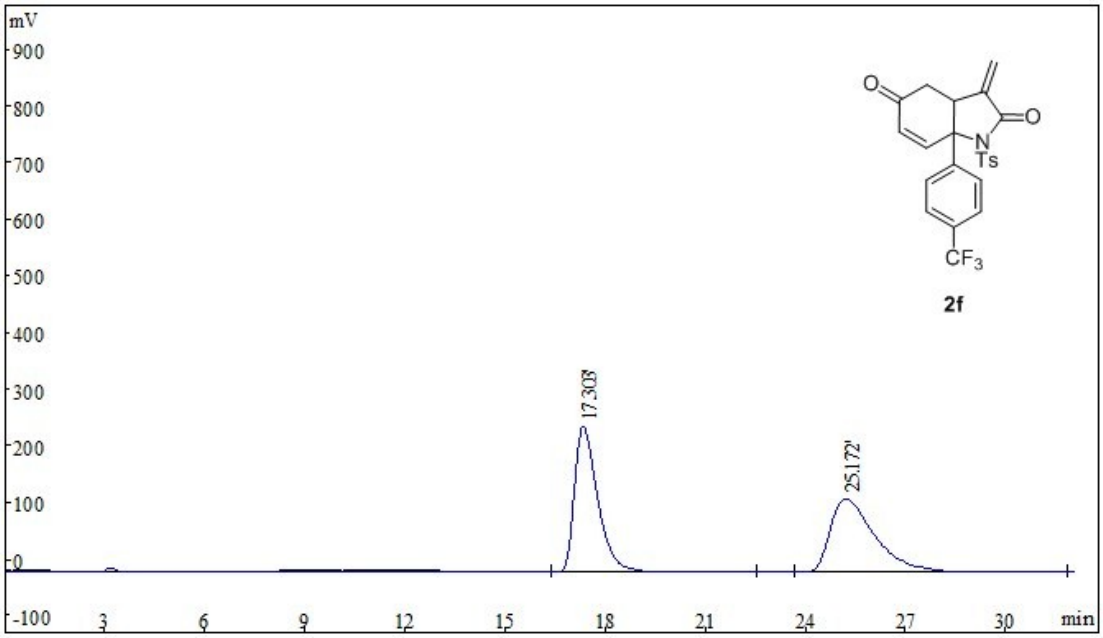
Rank	Time(min)	Area%	Area
1	20.820	2.029	1160566
2	23.124	97.97	56039821
Total		100	57200387



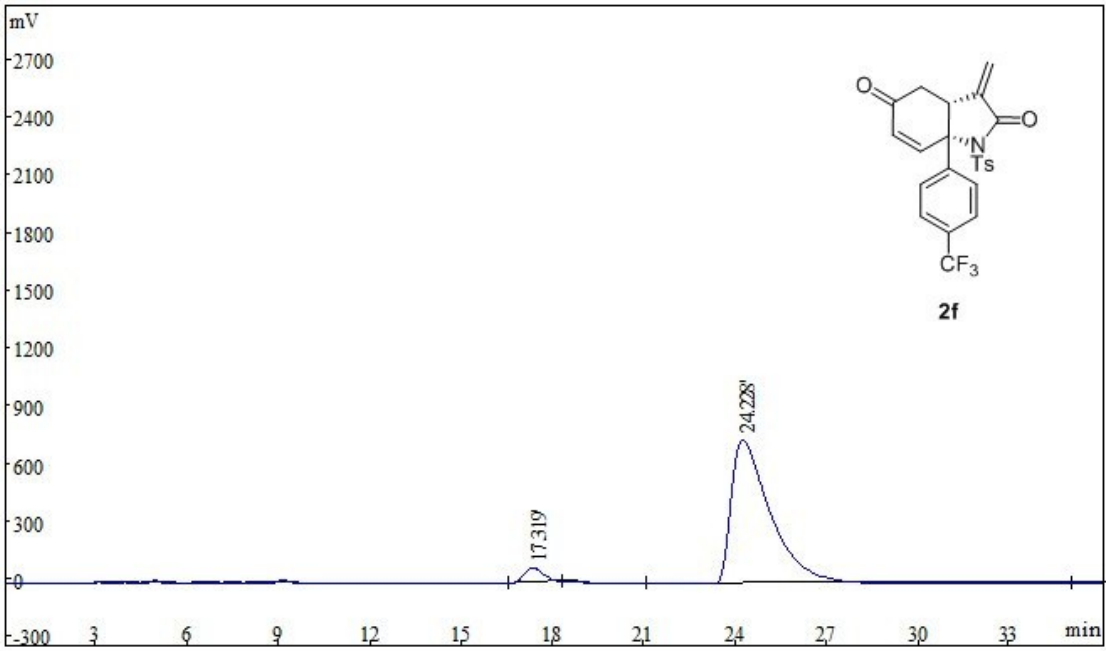
Rank	Time(min)	Area%	Area
1	19.766	49.8	16601266
2	25.371	50.2	16731392
Total		100	33332658



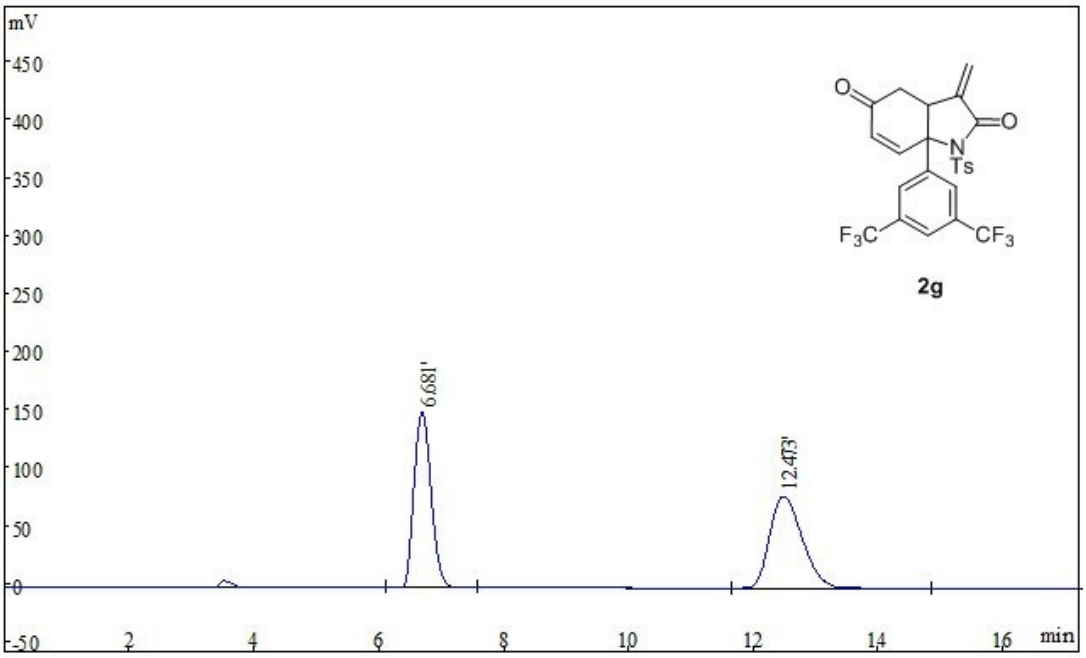
Rank	Time(min)	Area%	Area
1	20.067	6.222	4094131
2	24.891	93.78	61705798
Total		100	65799929



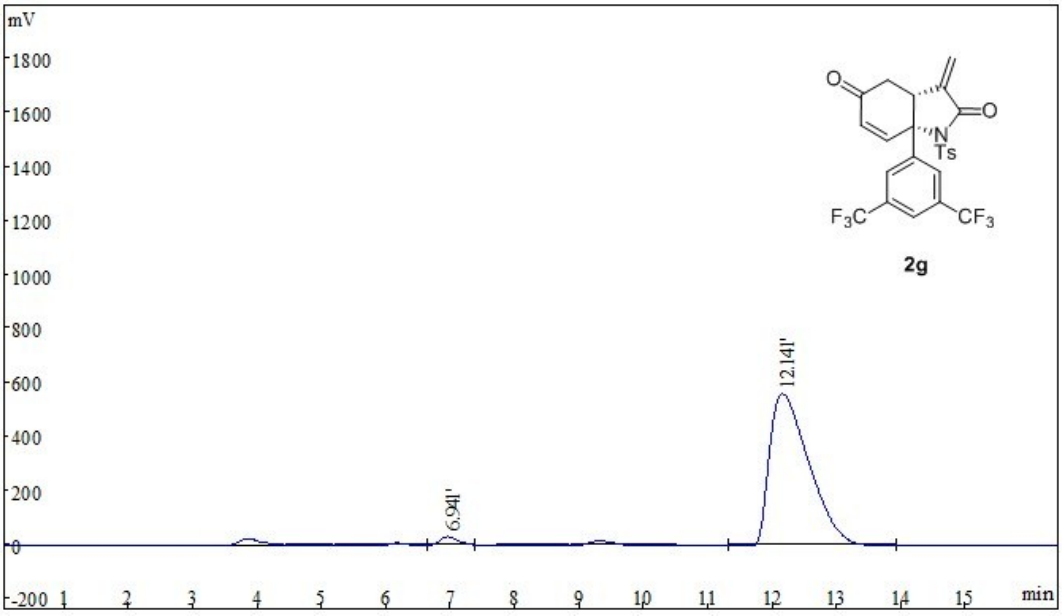
Rank	Time(min)	Area%	Area
1	17.303	50.39	12583542
2	25.172	49.61	12387802
Total		100	24971344



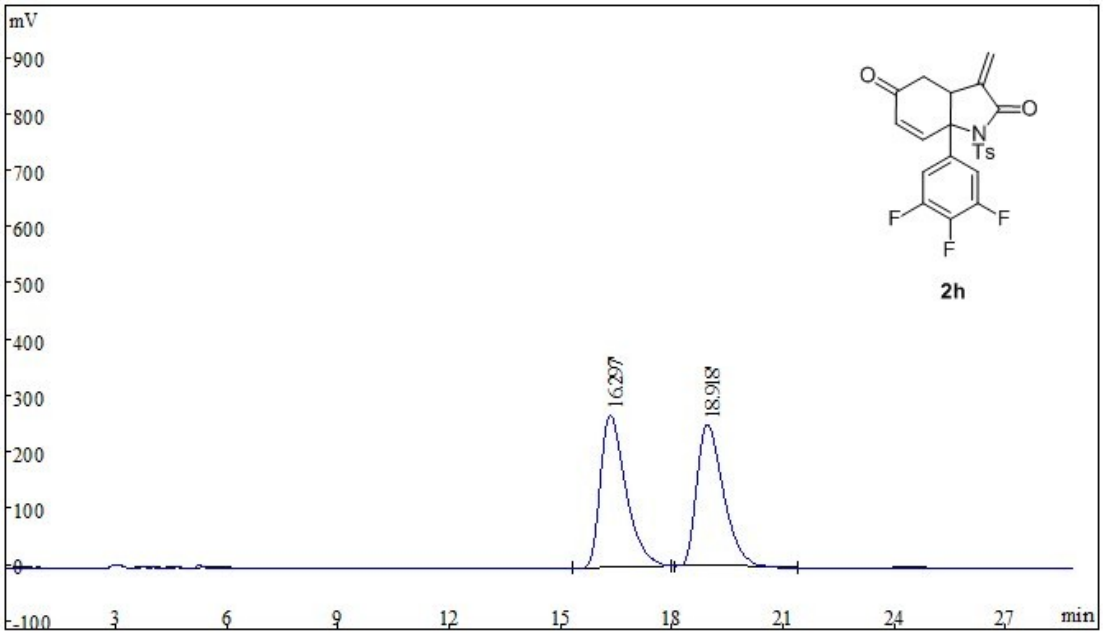
Rank	Time(min)	Area%	Area
1	17.319	4.869	3446609
2	24.228	95.13	67343808
Total		100	70790417



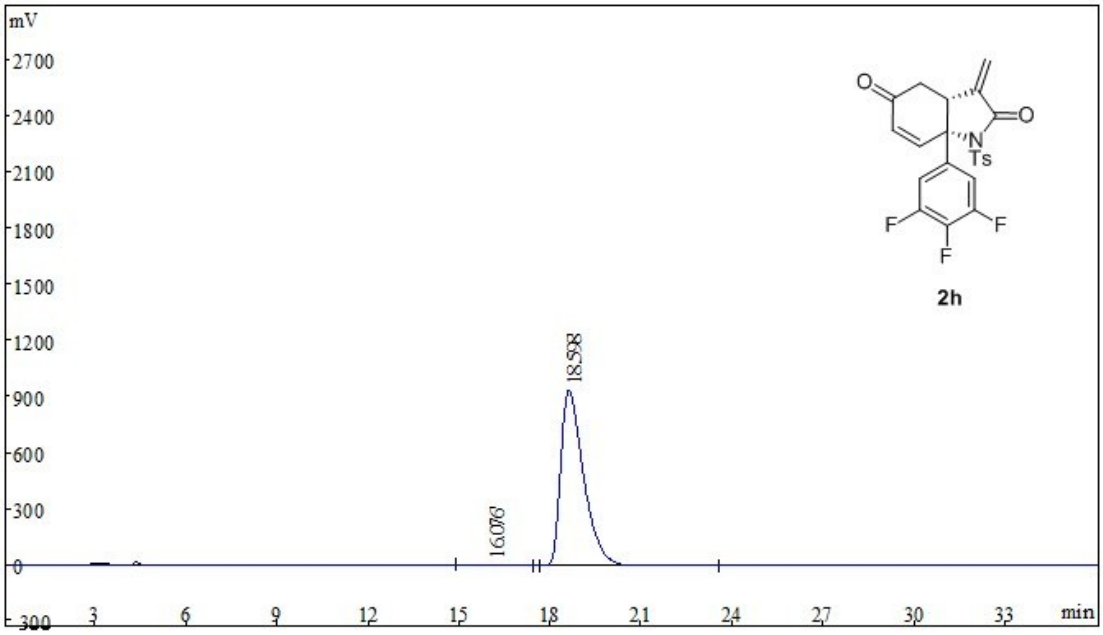
Rank	Time(min)	Area%	Area
1	6.681	49.65	2916083
2	12.473	50.35	2956894
Total		100	5872977



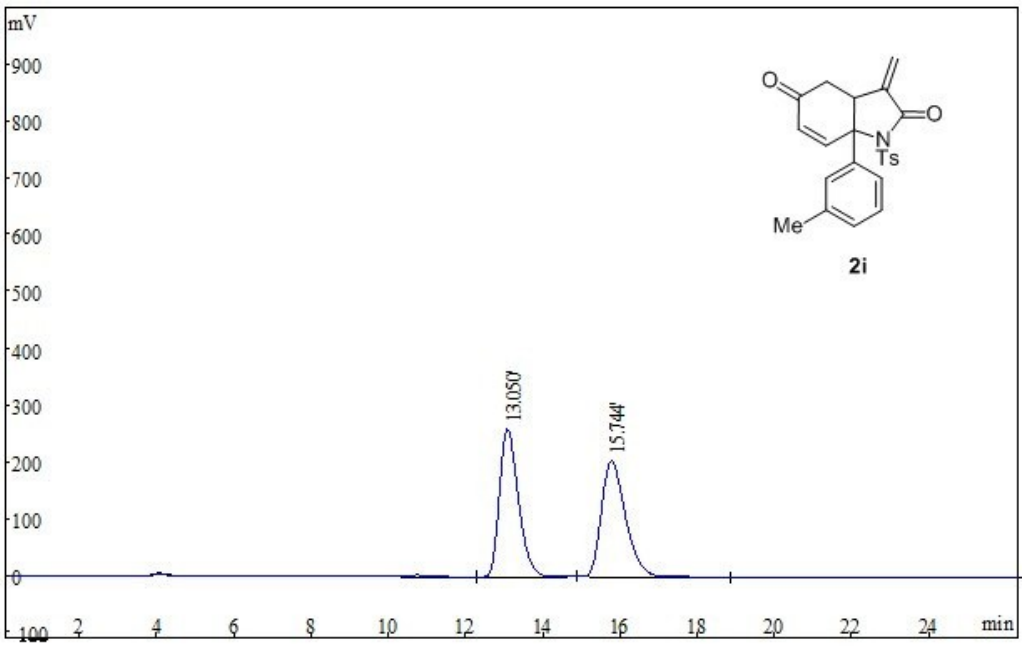
Rank	Time(min)	Area%	Area
1	6.941	2.596	642306
2	12.141	97.41	24096230
Total		100	24738536



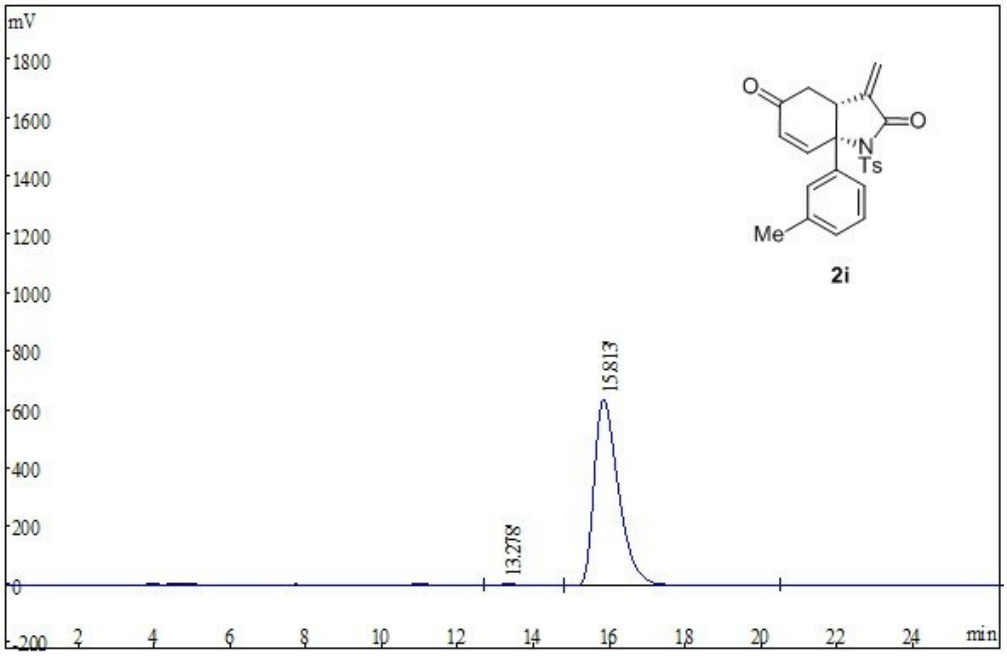
Rank	Time(min)	Area%	Area
1	16.297	50.63	13086445
2	18.918	49.37	12759405
Total		100	25845850



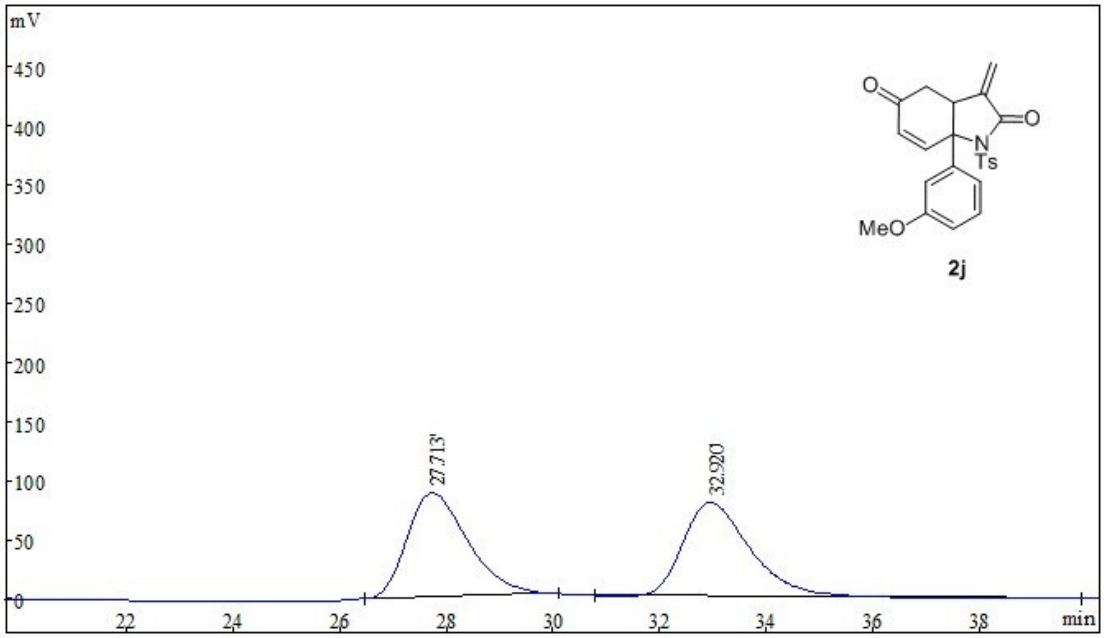
Rank	Time(min)	Area%	Area
1	16.076	1.736	876061
2	18.598	98.27	49579590
Total		100	50455651



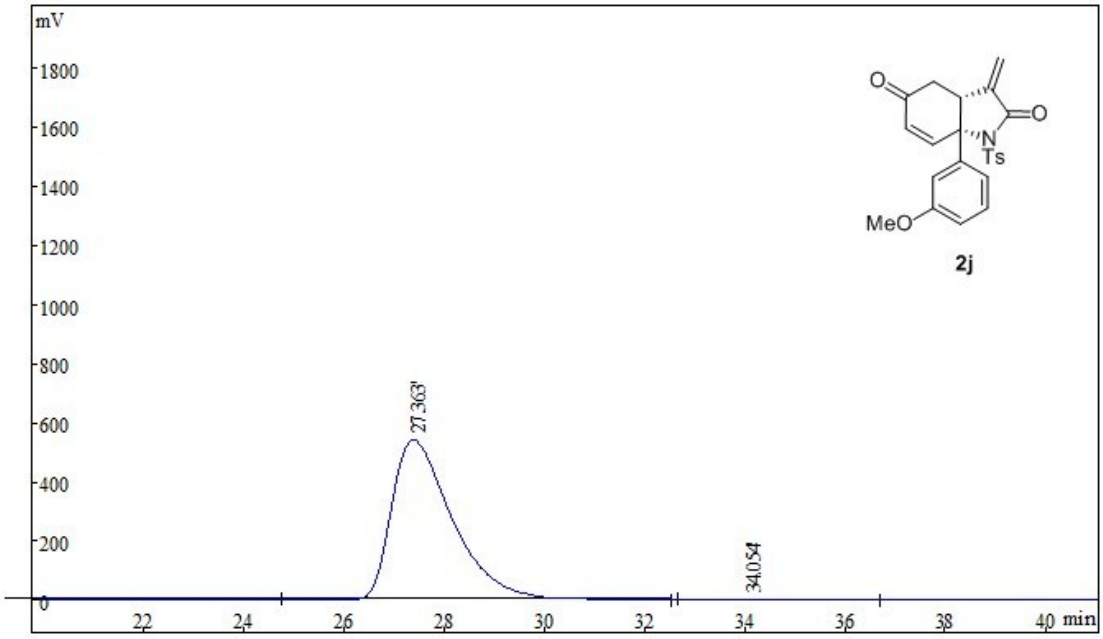
Rank	Time(min)	Area%	Area
1	13.050	49.85	9162012
2	15.744	50.15	9217637
Total		100	18379649



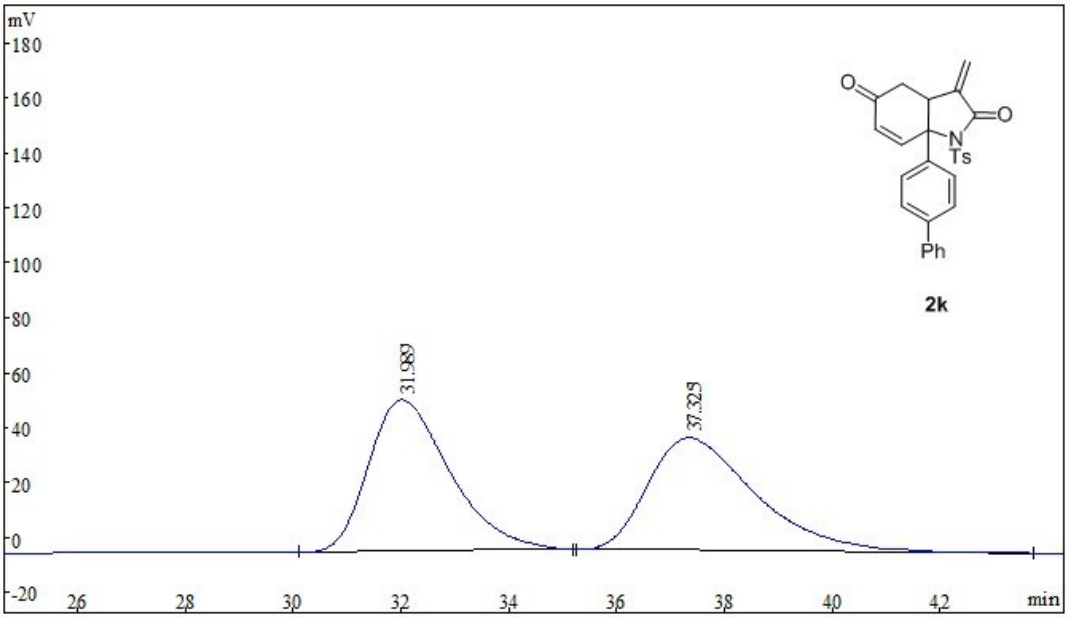
Rank	Time(min)	Area%	Area
1	13.278	0.9748	286690
2	15.813	99.02	29121478
Total		100	18379649



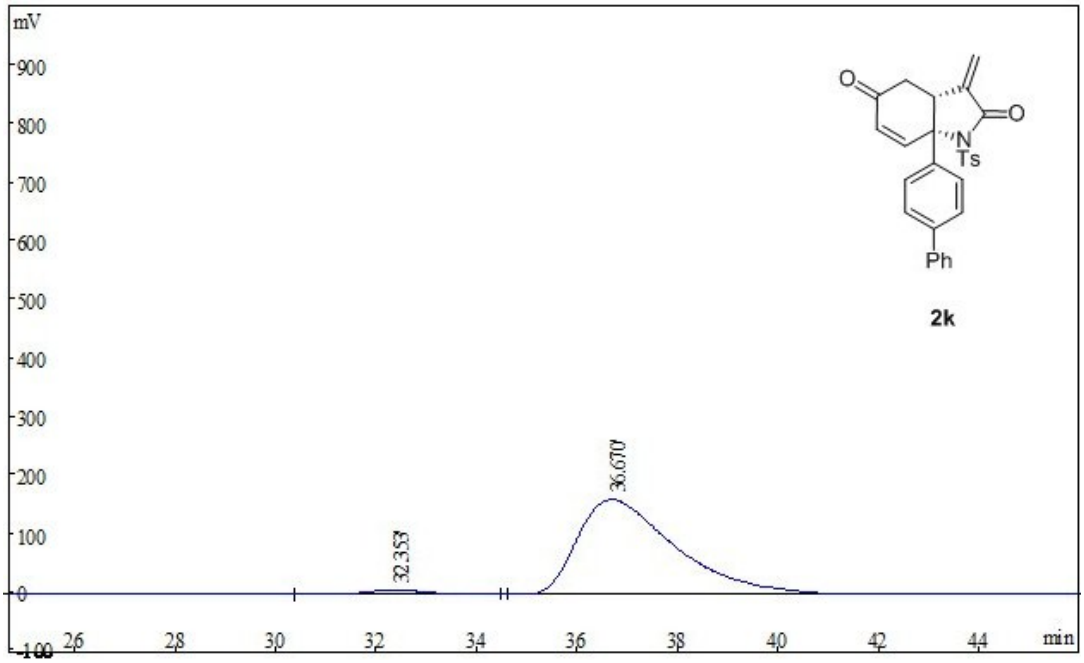
Rank	Time(min)	Area%	Area
1	27.713	50.26	7091435
2	32.920	49.74	7017488
Total		100	14108923



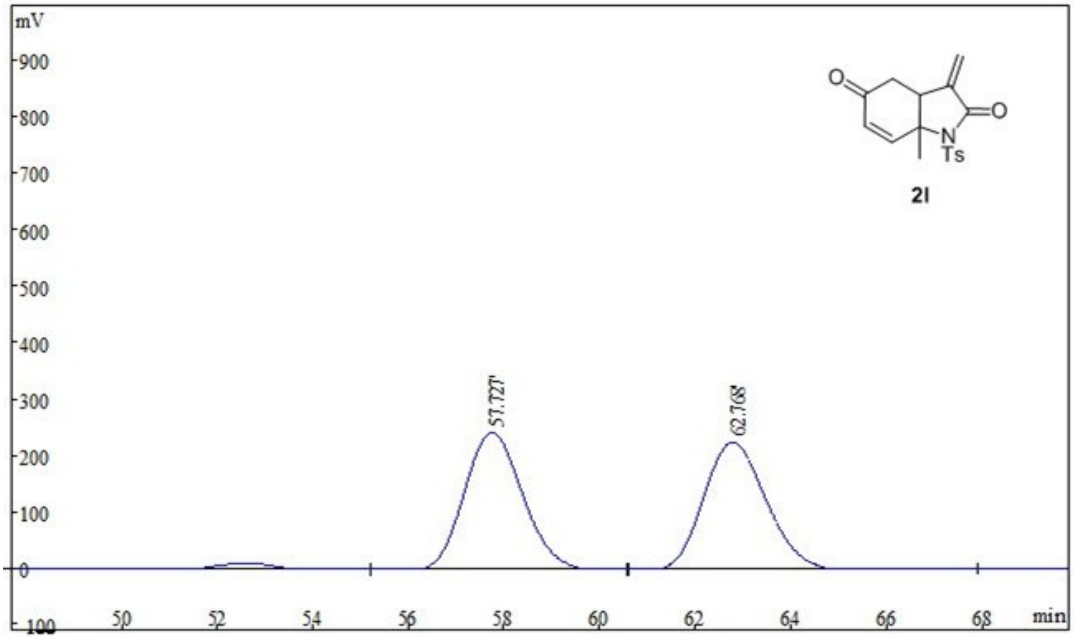
Rank	Time(min)	Area%	Area
1	27.363	99.4	46269683
2	34.054	0.6062	282180
Total		100	46551863



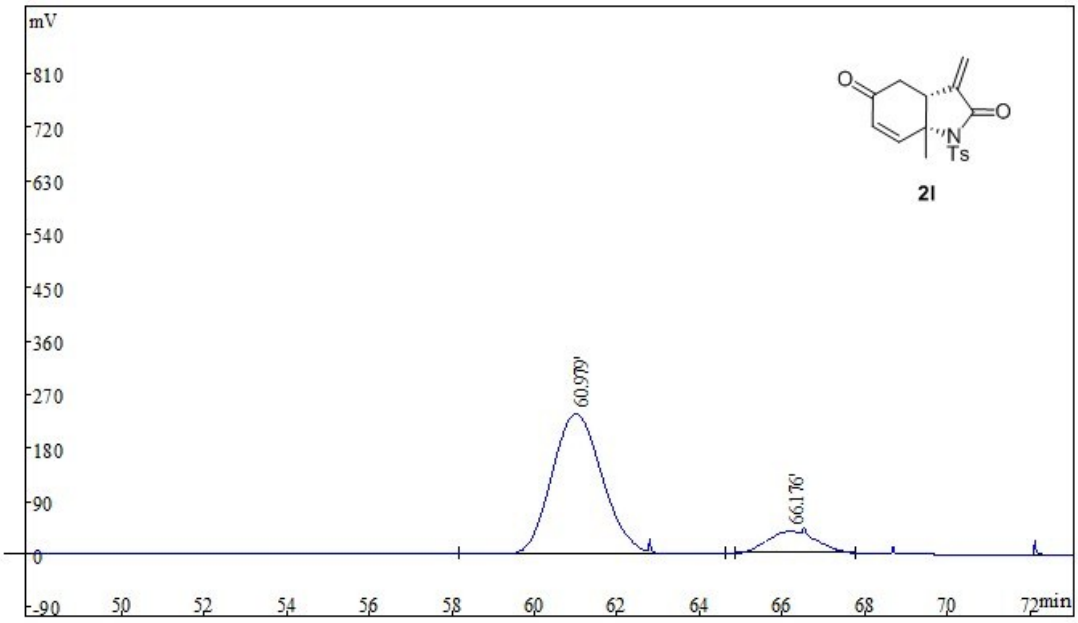
Rank	Time(min)	Area%	Area
1	31.989	50.33	5801236
2	37.325	49.67	5724531
Total		100	11525767



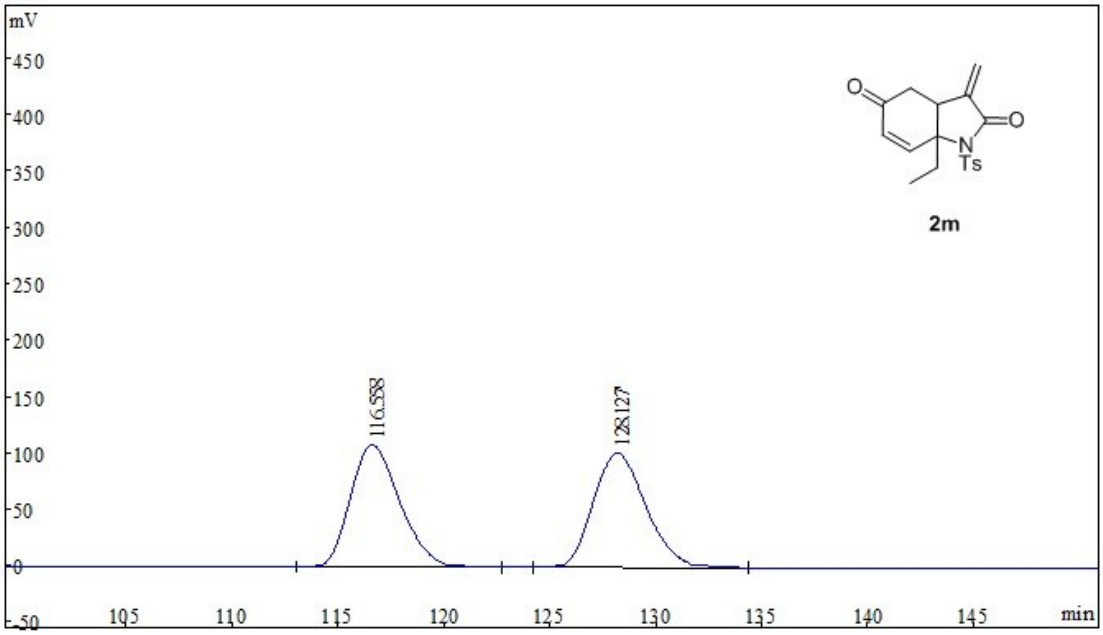
Rank	Time(min)	Area%	Area
1	32.353	3.897	917832
2	36.670	96.11	22633830
Total		100	23551662



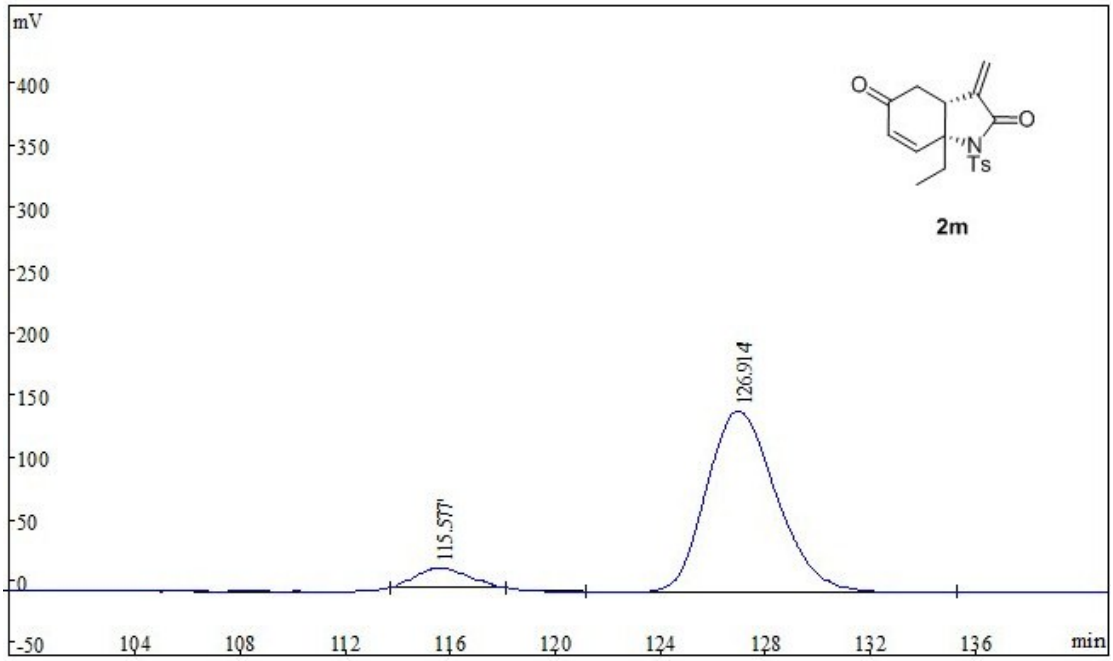
Rank	Time(min)	Area%	Area
1	57.727	49.99	20860410
2	62.768	50.01	20870883
Total		100	23551662



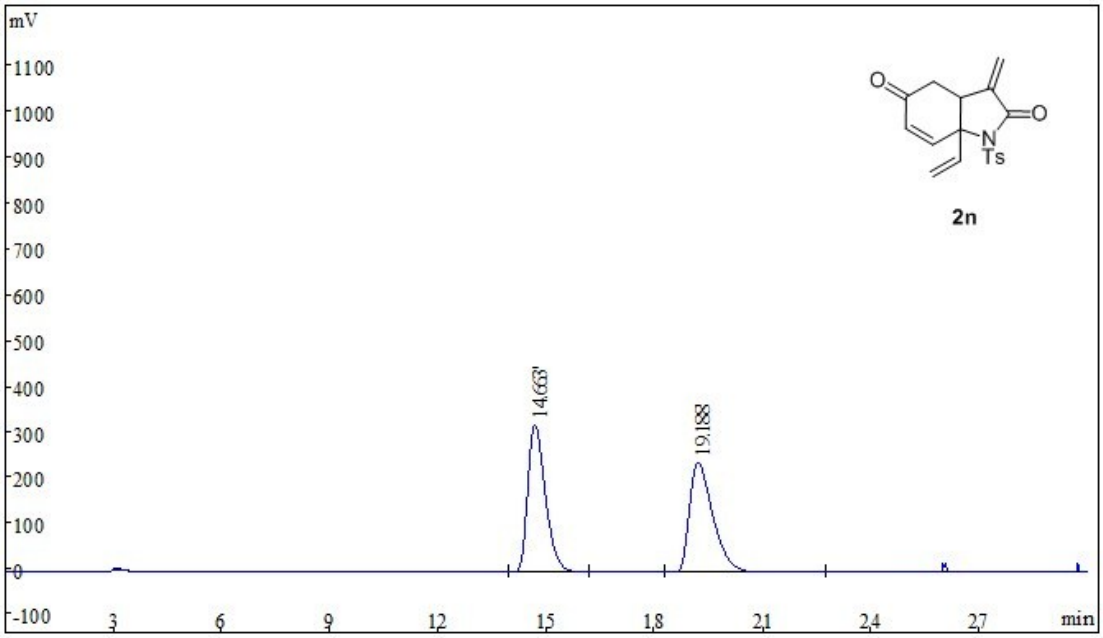
Rank	Time(min)	Area%	Area
1	60.979	86.05	20476722
2	66.176	13.95	3318349
Total		100	23795071



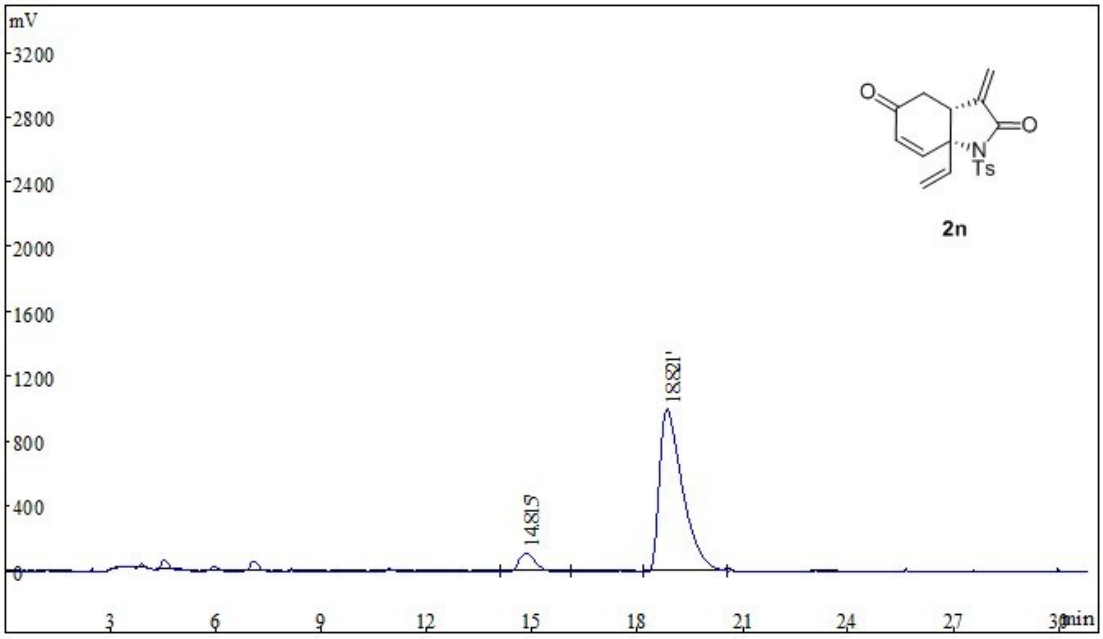
Rank	Time(min)	Area%	Area
1	116.558	50.23	18148317
2	128.127	49.77	17982581
Total		100	36130898



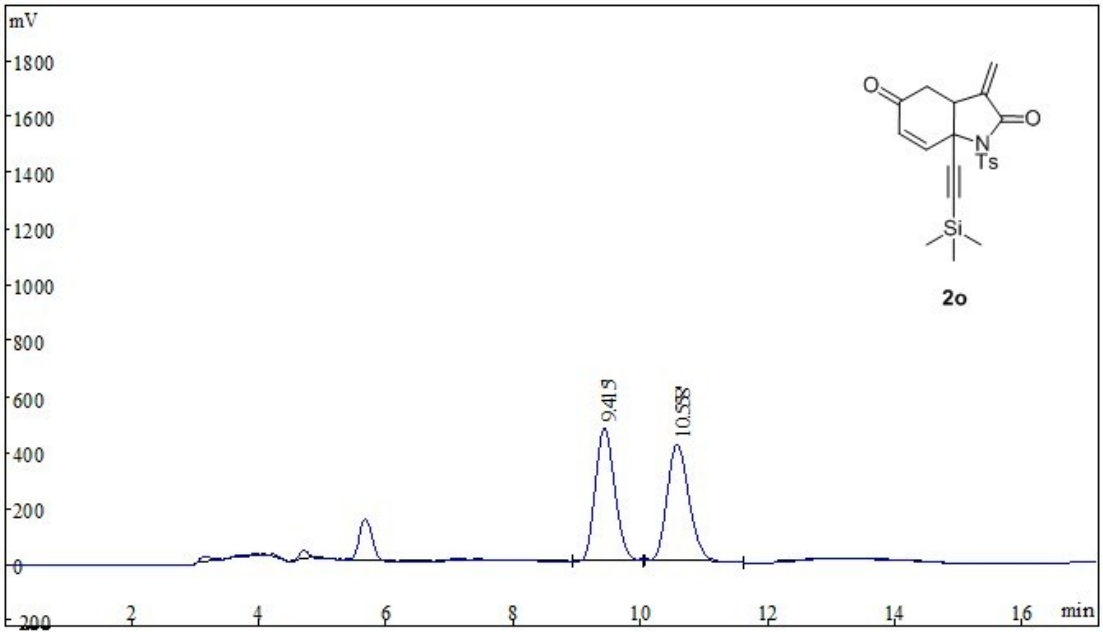
Rank	Time(min)	Area%	Area
1	115.577	7.937	2344141
2	126.914	92.07	27193139
Total		100	29537280



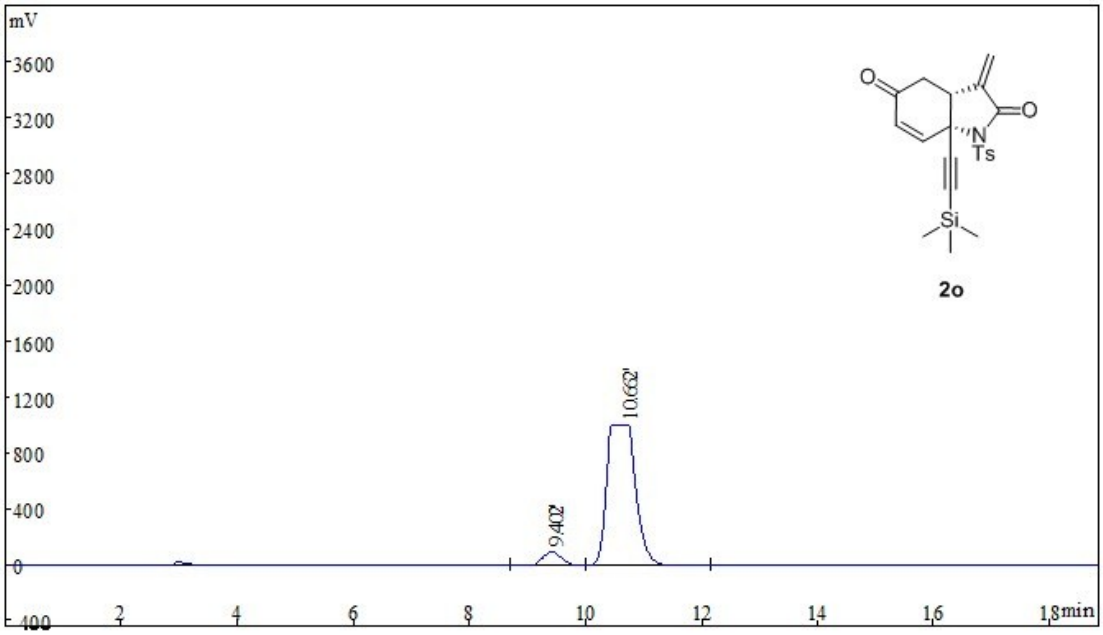
Rank	Time(min)	Area%	Area
1	14.663	50.21	11036975
2	19.188	49.79	10943034
Total		100	21980009



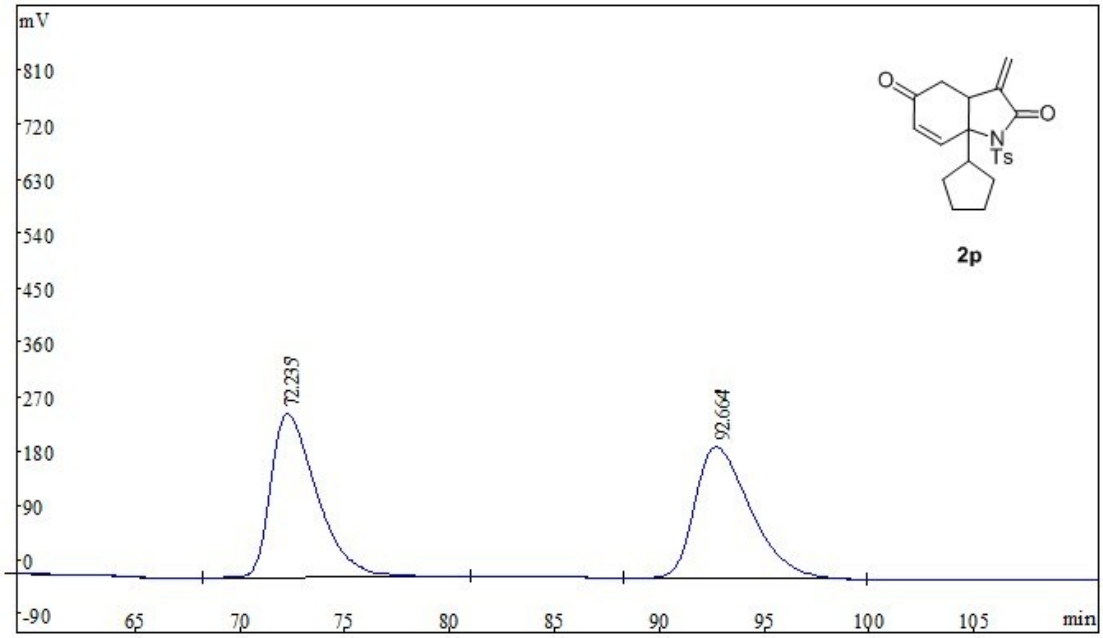
Rank	Time(min)	Area%	Area
1	14.815	7.539	3721539
2	18.821	92.46	45639898
Total		100	49361437



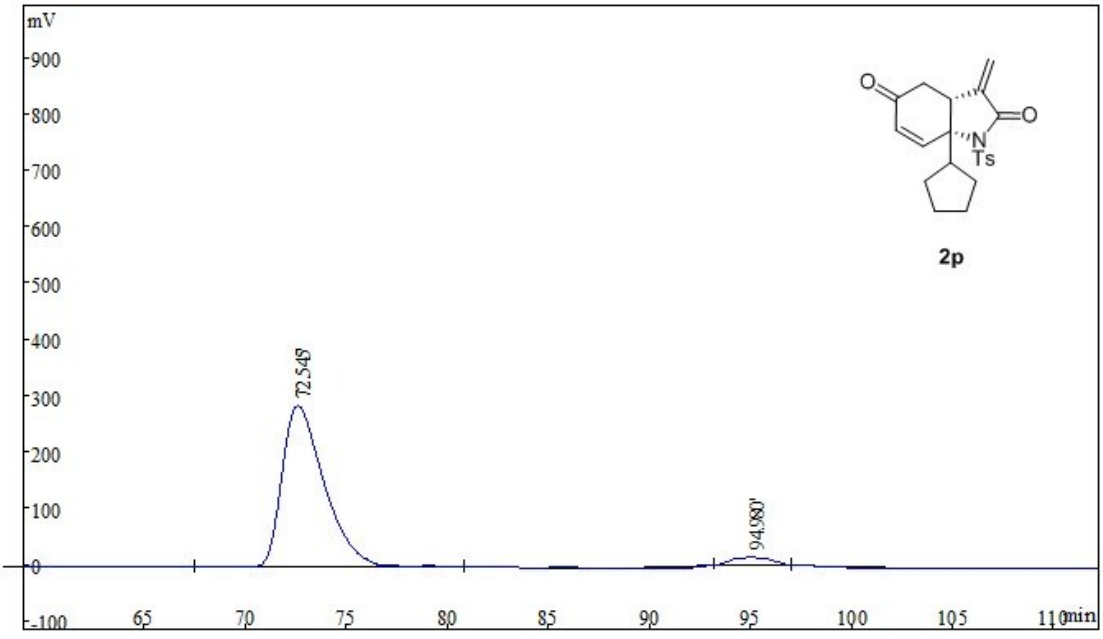
Rank	Time(min)	Area%	Area
1	9.415	50.14	10143171
2	10.558	49.86	10084792
Total		100	20227963



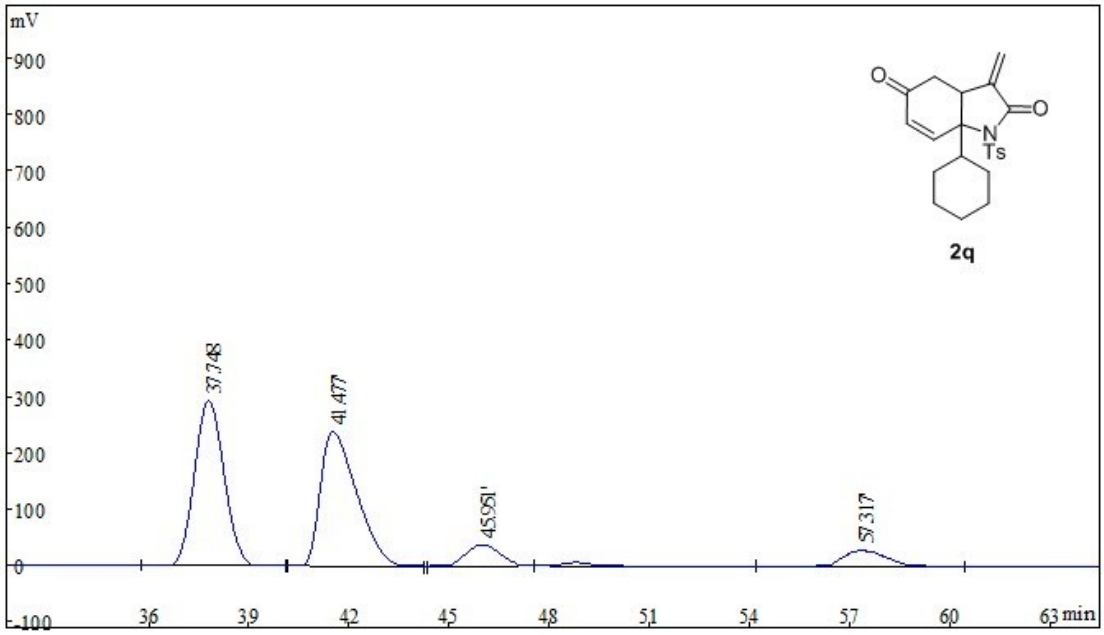
Rank	Time(min)	Area%	Area
1	9.402	6.164	2276488
2	10.662	93.83	34655869
Total		100	36932357



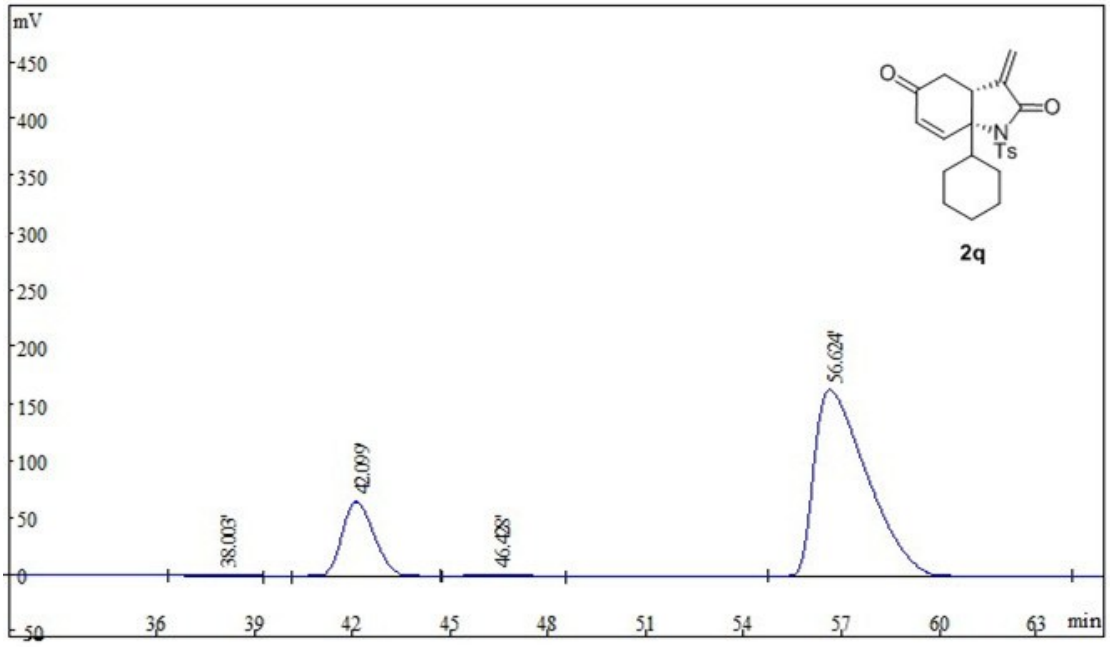
Rank	Time(min)	Area%	Area
1	72.235	50.69	42143910
2	92.664	49.31	40992422
Total		100	83136332



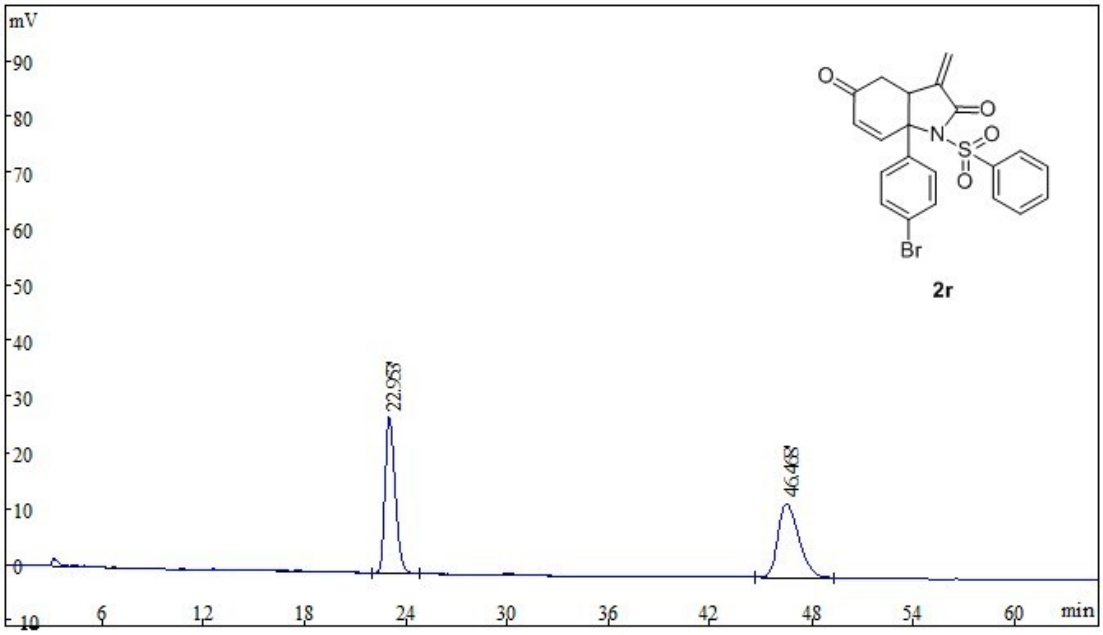
Rank	Time(min)	Area%	Area
1	72.545	95.49	42371254
2	94.980	4.505	1998819
Total		100	44370073



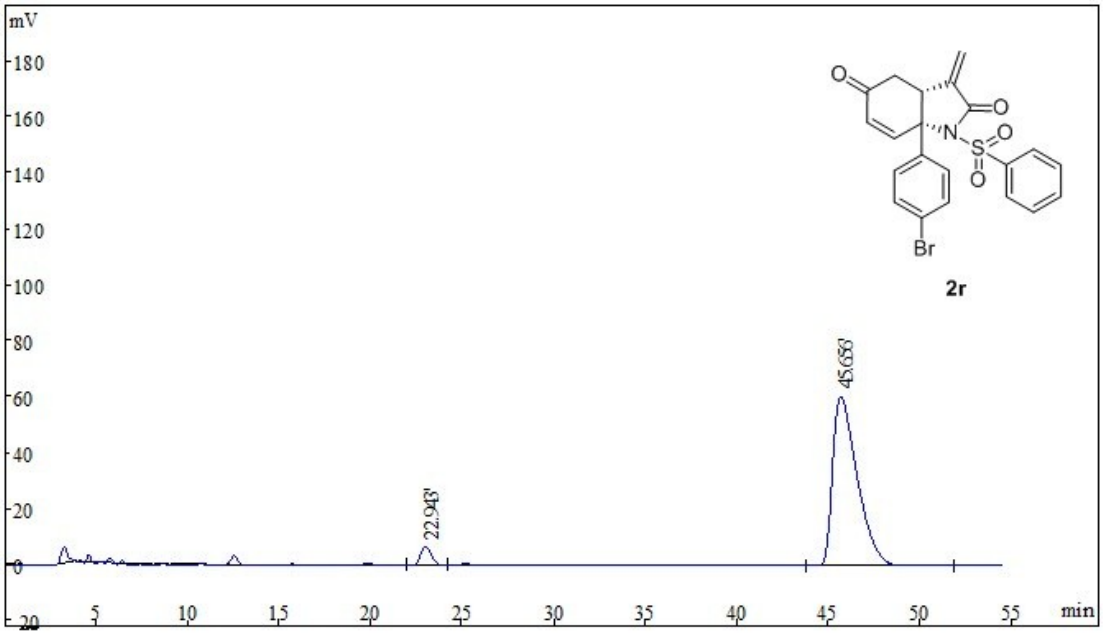
Rank	Time(min)	Area%	Area	Rank	Time(min)	Area%	Area
1	37.748	42.9	18499835	3	45.951	6.949	2996894
2	41.477	42.76	18439848	4	57.317	7.395	3189425
Total		100	43126002				



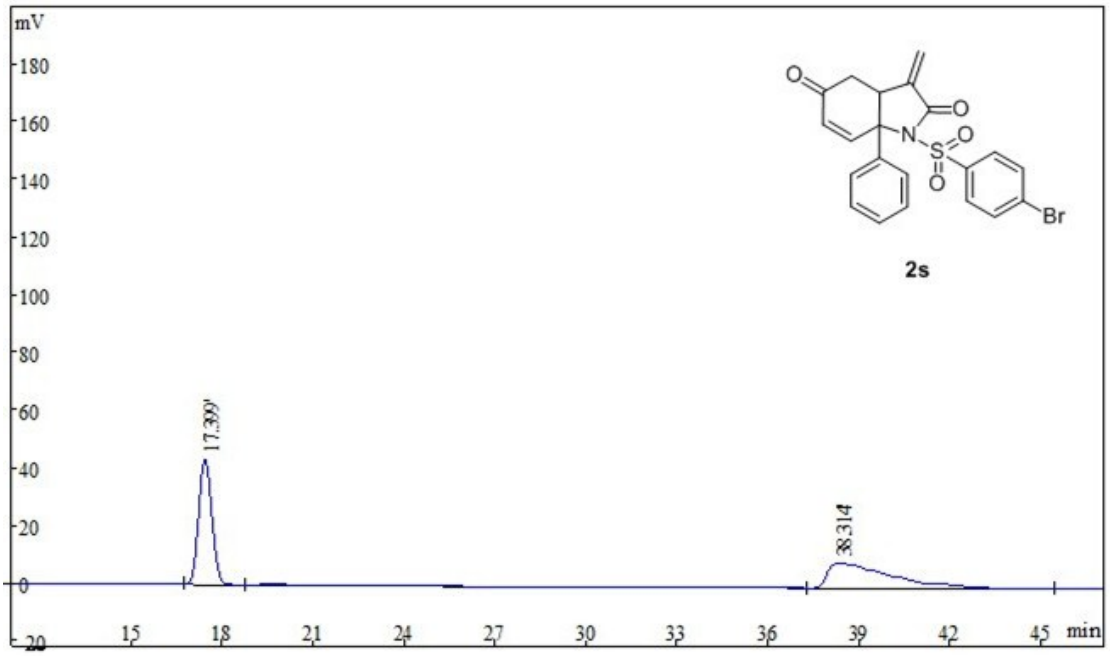
Rank	Time(min)	Area%	Area	Rank	Time(min)	Area%	Area
1	38.003	0.5924	141884	3	46.428	1.048	250999
2	42.099	19.3	4622132	4	56.624	79.06	18936269
Total		100	23951284				



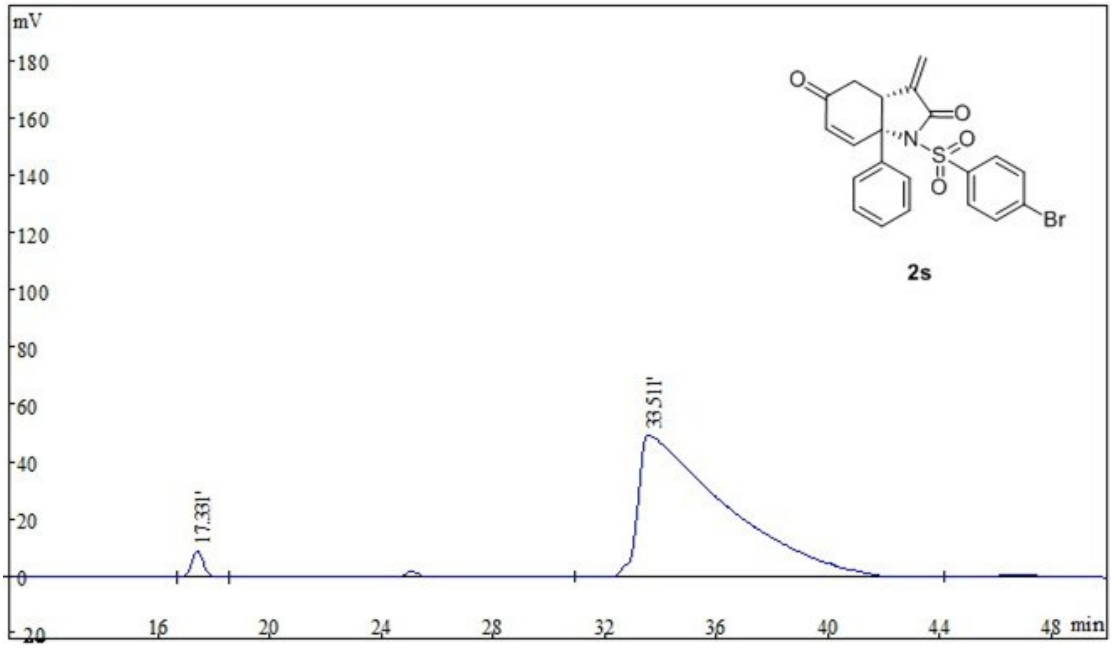
Rank	Time(min)	Area%	Area
1	22.953	50.14	1179187
2	46.468	49.86	1172772
Total		100	2351959



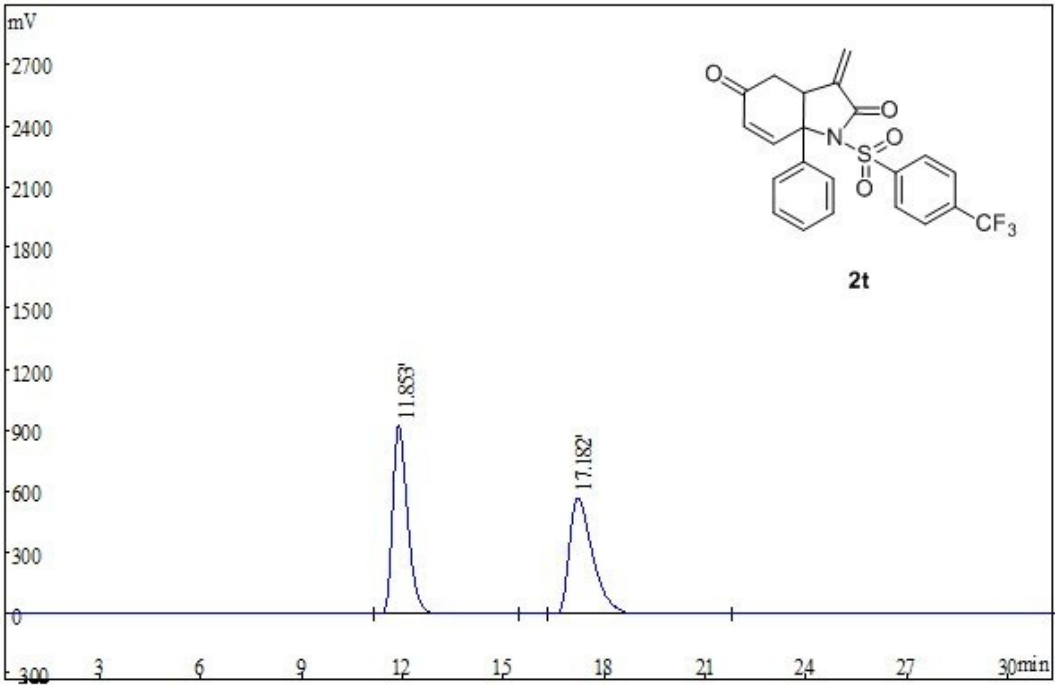
Rank	Time(min)	Area%	Area
1	22.943	4.664	280582
2	45.656	95.33	5734586
Total		100	6015168



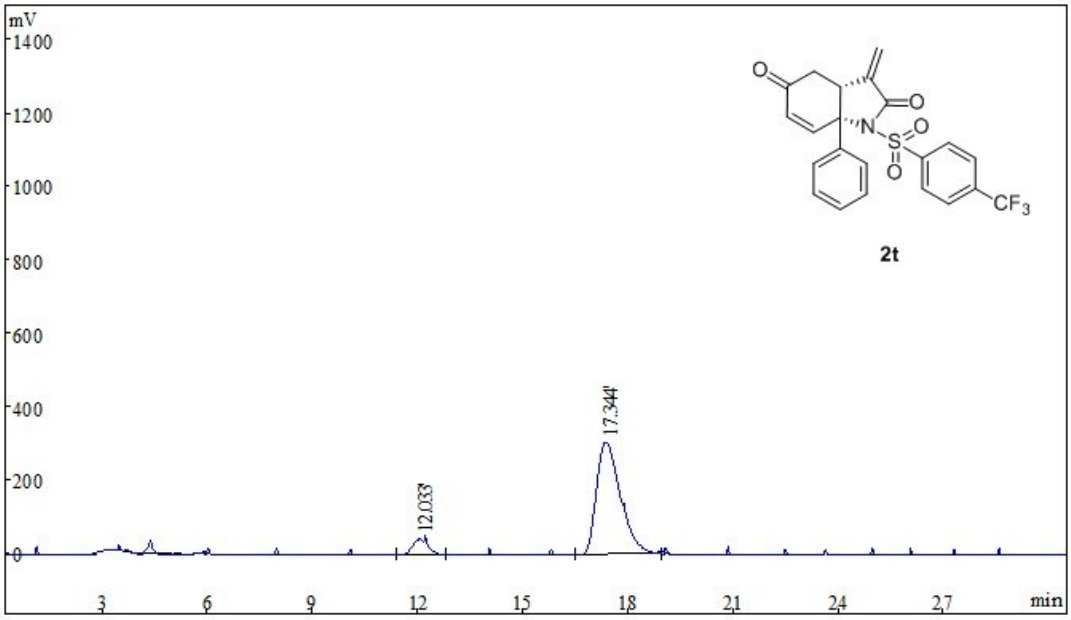
Rank	Time(min)	Area%	Area
1	17.399	50.33	1352250
2	38.314	49.67	1334558
Total		100	2686808



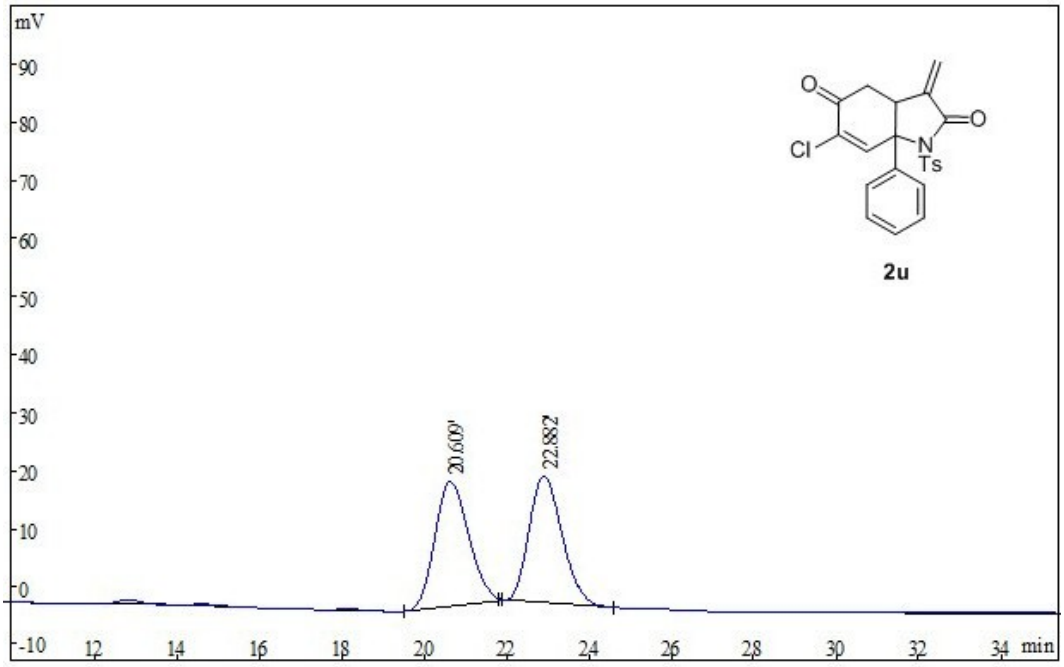
Rank	Time(min)	Area%	Area
1	17.331	2.499	286567
2	33.511	97.5	11182633
Total		100	11469200



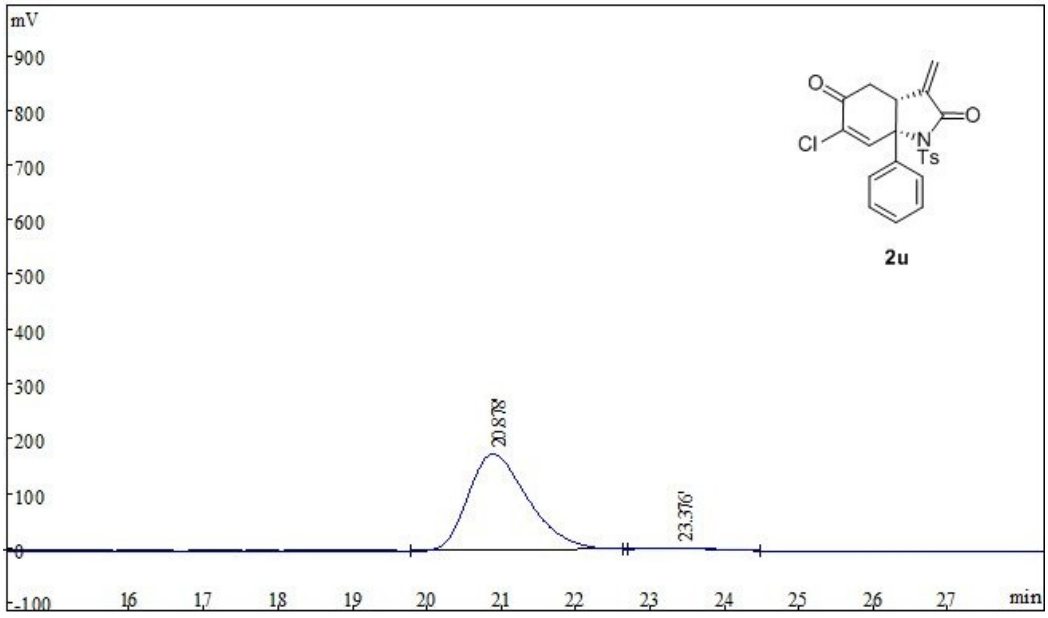
Rank	Time(min)	Area%	Area
1	11.853	50.62	28893187
2	17.182	49.38	28185555
Total		100	57078742



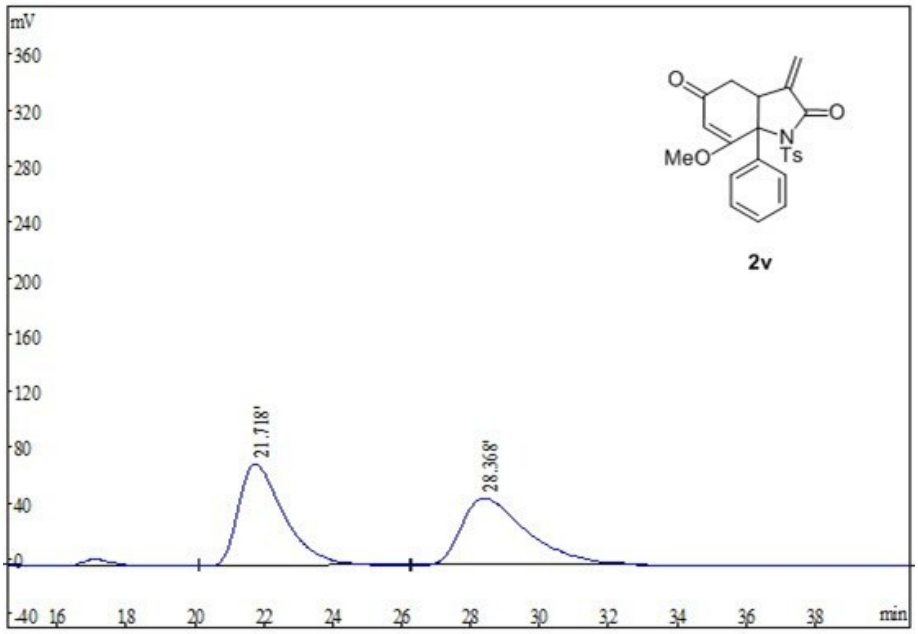
Rank	Time(min)	Area%	Area
1	12.033	6.802	1074220
2	17.344	93.2	14718549
Total		100	15792769



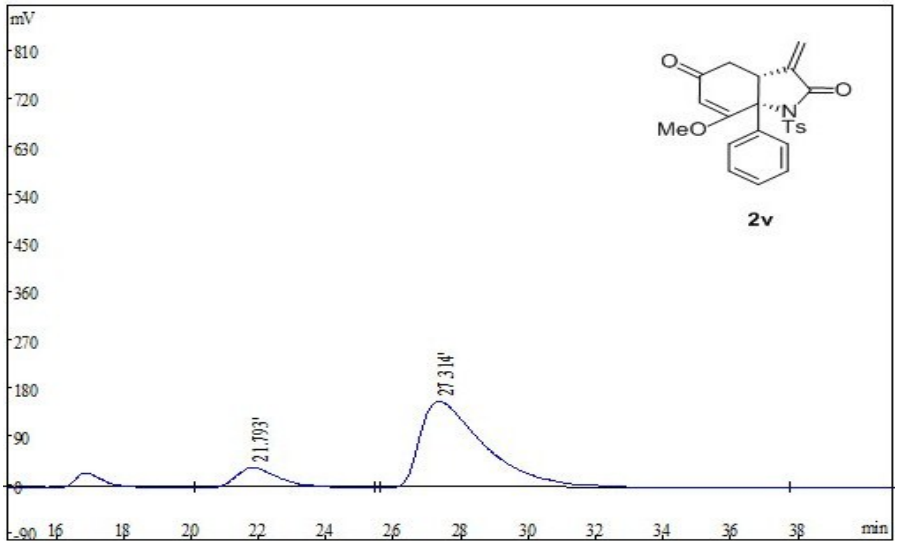
Rank	Time(min)	Area%	Area
1	20.609	50.27	1249969
2	22.882	49.73	1236612
Total		100	2486581



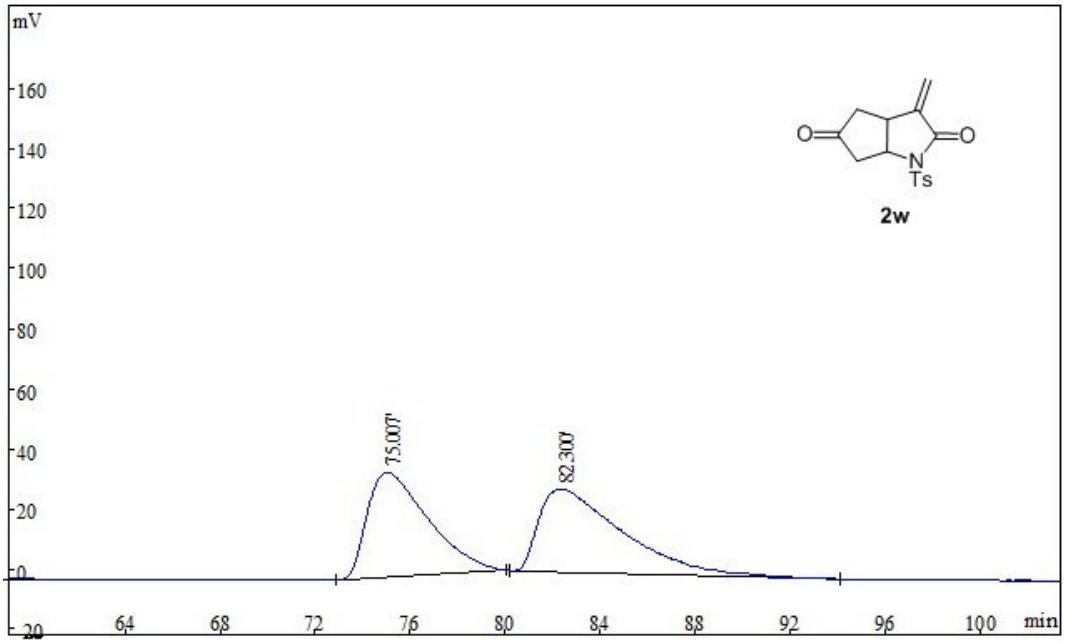
Rank	Time(min)	Area%	Area
1	20.878	98.11	9963502
2	23.376	1.888	191771
Total		100	10155273



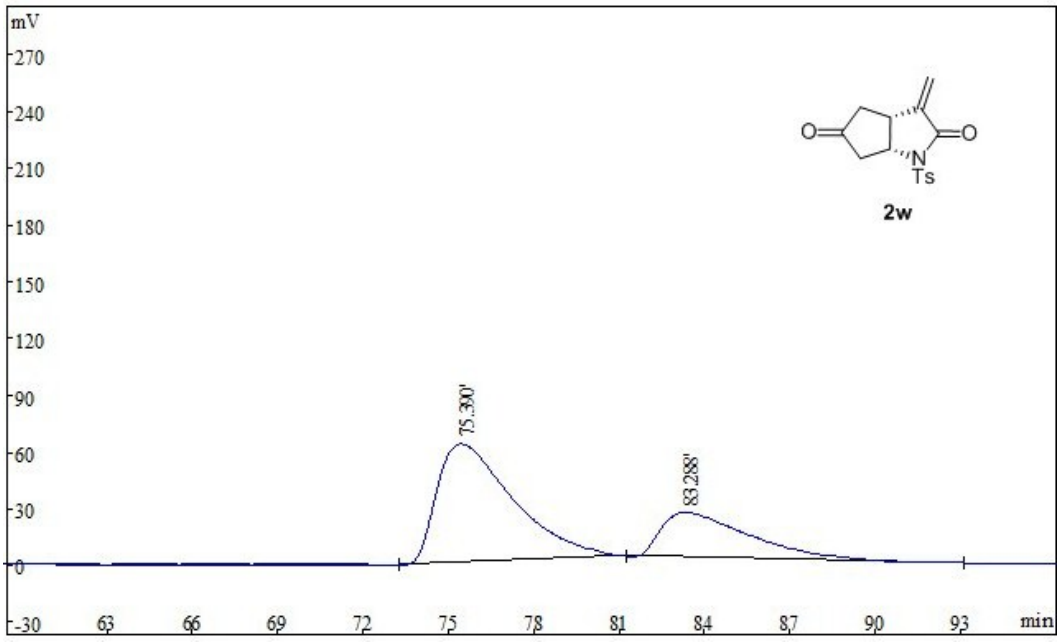
Rank	Time(min)	Area%	Area
1	21.718	49.87	6759183
2	28.368	50.13	6794099
Total		100	13553282



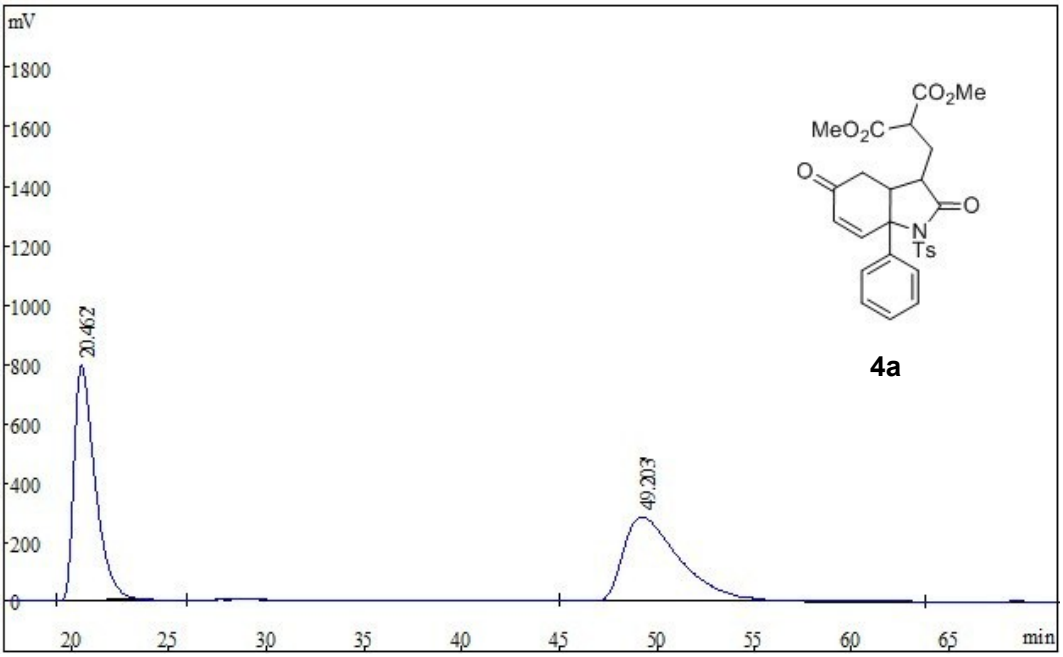
Rank	Time(min)	Area%	Area
1	21.793	13.43	3393466
2	27.314	86.57	21872883
Total		100	25266349



Rank	Time(min)	Area%	Area
1	75.007	48.03	6345513
2	82.300	51.97	6865154
Total		100	13210667

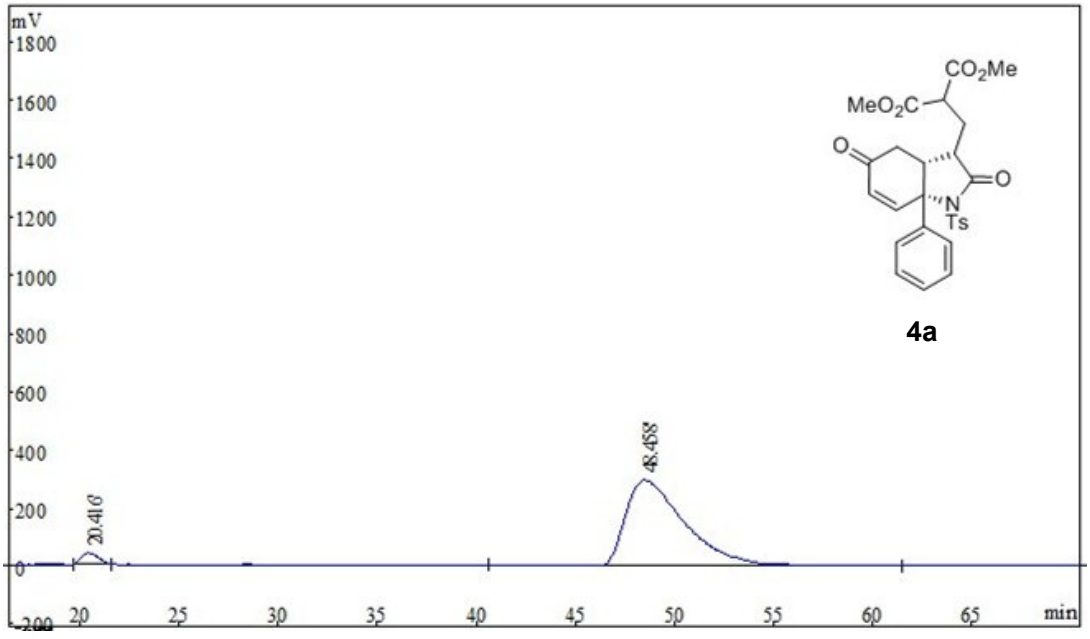


Rank	Time(min)	Area%	Area
1	75.390	69.17	11821162
2	83.288	30.83	5269055
Total		100	17090217



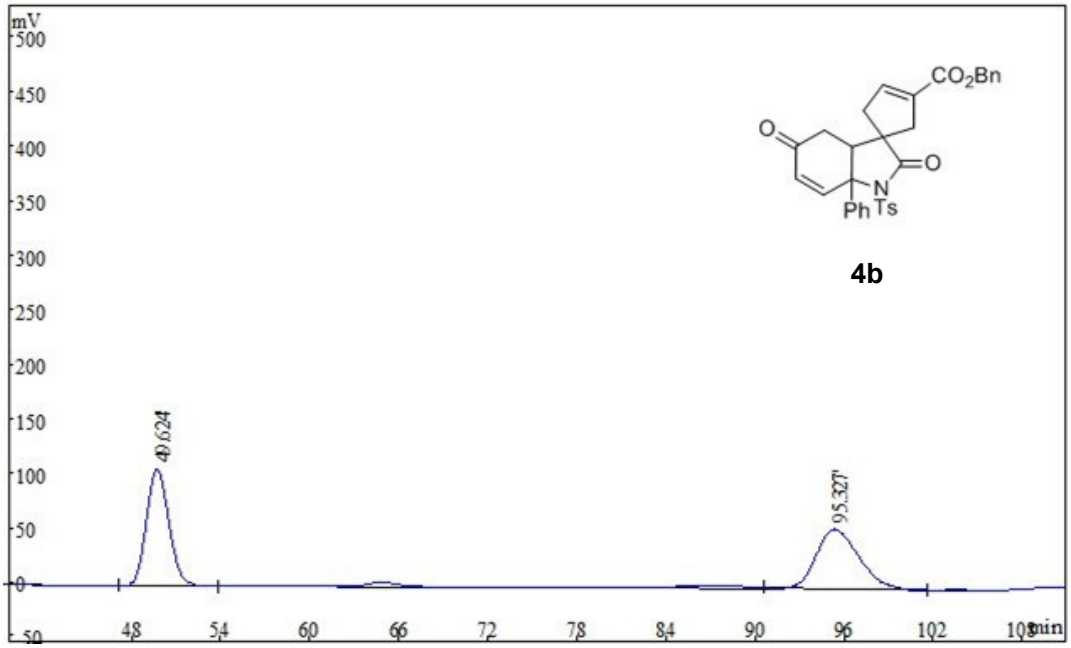
4a

Rank	Time(min)	Area%	Area
1	20.462	50.34	60795776
2	49.203	49.66	59964525
Total		100	120760301



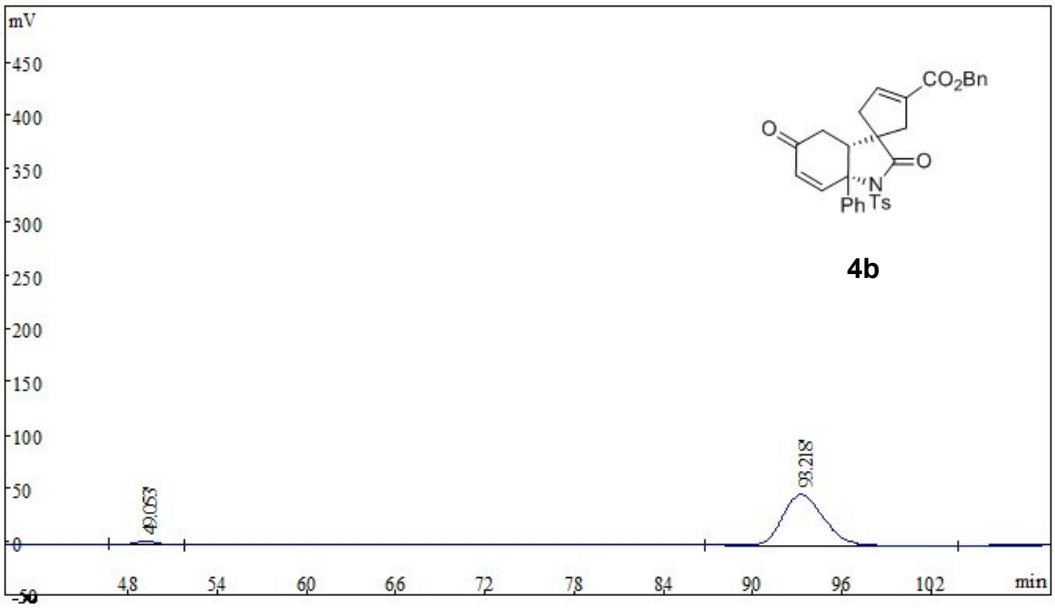
4a

Rank	Time(min)	Area%	Area
1	20.416	3.52	2284864
2	48.458	96.48	62603430
Total		100	64888294



4b

Rank	Time(min)	Area%	Area
1	49.624	50.86	11521064
2	95.327	49.14	11131507
Total		100	22652571



4b

Rank	Time(min)	Area%	Area
1	49.053	3.104	310872
2	93.218	96.89	9703847
Total		100	10014719

VI. X-ray crystal structure

Crystallographic data for compound **1e** (CCDC-1524099)* has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

* A tool (PLATON SQUEEZE) for the calculation of the disordered solvent contribution to the calculated structure factors was used, see: L. S. Anthony, *Acta Cryst*. **2015**, *C71*, 9-18.

Crystallographic data for compound **2b** (CCDC-1524100) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

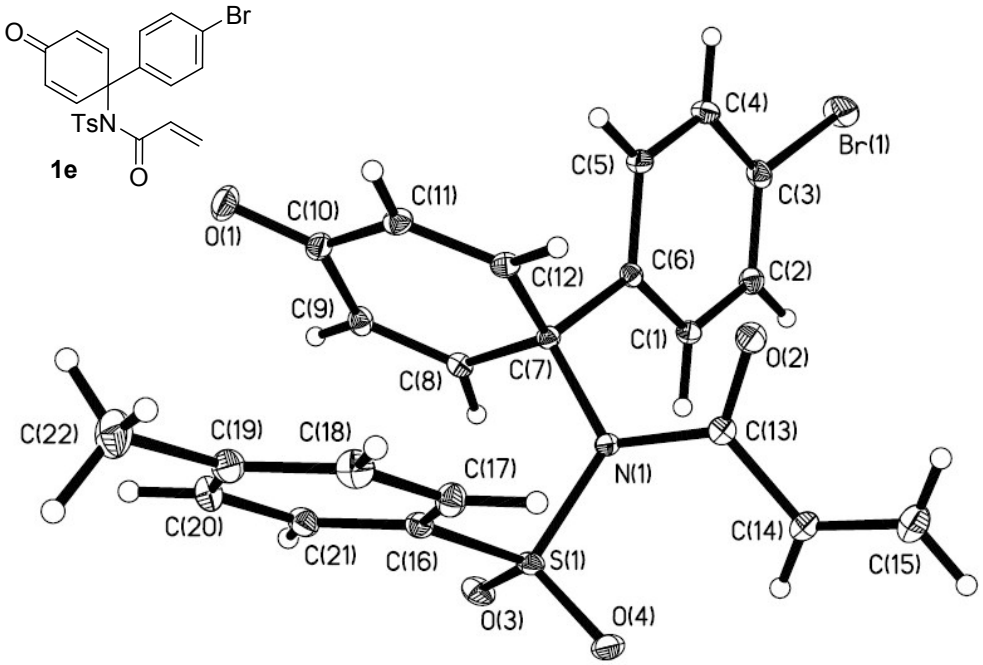


Figure S1: X-ray structure of **1e** (The H-atoms are omitted for clarity) CCDC NO.1524099

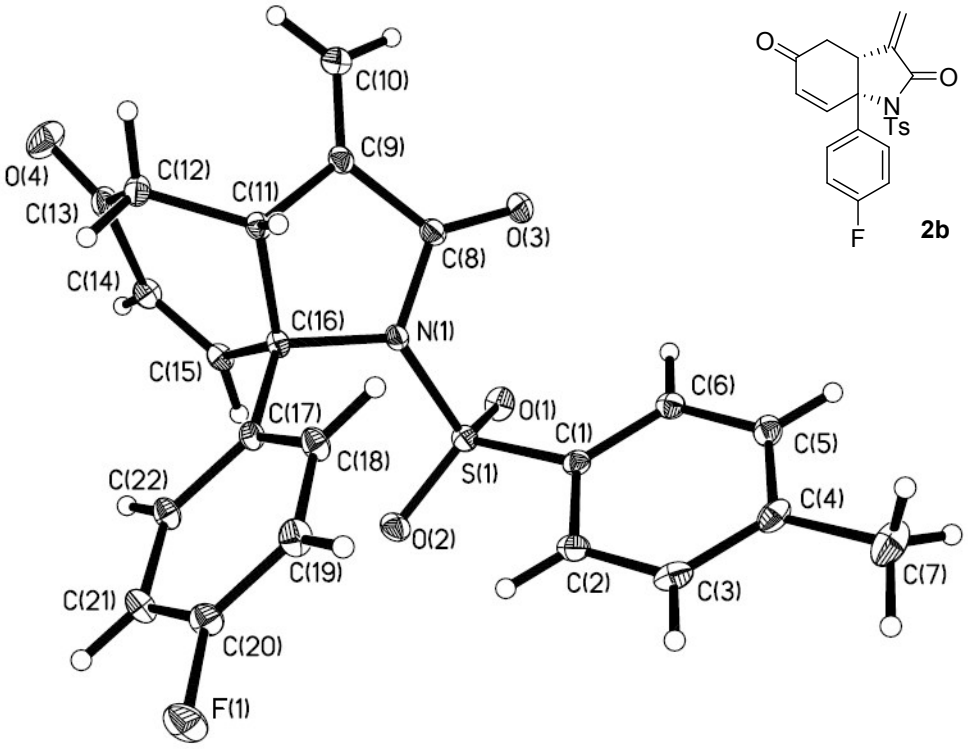


Figure S2: X-ray structure of **2b** (The H-atoms are omitted for clarity) CCDC NO. 1524100