Supporting Information

Facile Synthesis of *N*-(α-furanyl) alkyl sulfoximines via Gold Catalyzed Michael addition / Cyclization of Enynones and Sulfoximines

A. Antony Haritha Mercy,[a] V. R. Padma Priya,[a] R. Hariprasad,[a] K. Gayathri,[a] S. Ravindra,[a] Ganesh Chandra Nandi*[a] and Ramesh Kataria[b]

[a]*Department of Chemistry, National Institute of Technology-Tiruchirappalli, Tamilnadu – 620015, India.*

Email ID: ganeshnandi@gmail.com, nandi@nitt.edu

[b]*Department of Chemistry, Panjab University, Chandigarh-160014, India*

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1. General Information

The starting materials (enynone and sulfoximine) were synthesized in the laboratory following the reported methods.[1,2] The aldehydes, catalysts and anhydrous solvents were purchased from various suppliers and used as received. ^{1}H (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on BRUKER NMR spectrophotometer. $CDCl_3$ was used as solvent to record NMR spectra. Mass spectra were recorded with Agilent QTOF G6545 spectrometer at 50,000 resolutions using ESI mode. Melting points were uncorrected.

2. General Procedure for the synthesis of 3a

A clean 20 mL Schlenk tube equipped with a magnetic bar was charged with the corresponding enynone **1a** (30 mg, 0.109 mmol, 1.0 equiv.) and PPh_3AuCl (5 mol %). Then, anhydrous toluene (1 mL) and corresponding sulfoximine **2a** (37 mg, 0.217 mmol, 2.0 equiv.) were added sequentially. The reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (checked by TLC), the reaction mixture was cooled down, diluted with water and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate and then concentrated under reduced pressure. The crude product was purified through column chromatography (100-200 mesh SiO_2) using 15 % of ethyl acetate in hexane as eluent.

Similar protocol was used to prepare **3b-3y, 3a', 3b'**. The products were isolated using 7-25 % of ethyl acetate in hexane as eluent.

For unsymmetrical sulfoximines, the products were formed in approximately 1:1 diastereomeric ratio and were inseparable via column chromatography.

3. General procedure for Suzuki-Miyaura coupling reaction of bromine containing *N*-(α-furanyl) alkyl sulfoximine

A mixture of bromine containing *N*-(α-furanyl) alkyl sulfoximine (**3d**, 40 mg, 0.076 mmol), arylboronic acid (**4a**, 17.4 mg, 0.114 mmol), K_2CO_3 (32.0 mg, 0.232 mmol), PPh_3 (1.2 mg, 10 mol %) in 1,4-dioxane (3.0 mL), and distilled water (1.2 mL) was degassed with a stream of argon passing through the solution for 15 min. Thereafter, $Pd(PPh_3)_2Cl_2$ (1.6 mg, 5 mol %) was added, and the reaction mixture was stirred under argon atmosphere for 30 min at 90 °C. After completion, the reaction mixture was cooled, diluted with water (15 mL), and extracted with DCM (3 × 20 mL). The collected organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 15 - 20 % of EtOAc/Hexane as the eluent to give product **5a**.

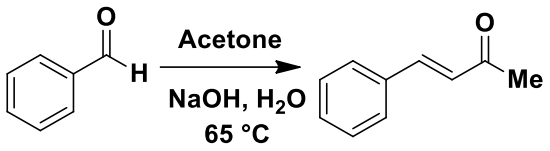
4. General procedure for furan ring opening of 3f

A clean 20 mL Schlenk tube equipped with a magnetic bar was charged with **3f** (20 mg, 0.0405 mmol). Then, anhydrous acetonitrile (400 μL) was added. The reaction mixture was stirred under oxygen atmosphere and blue LEDs for 30 min. After completion of the reaction (checked by TLC), the reaction mixture was cooled down, diluted with water and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium

sulfate and then concentrated under reduced pressure. The crude product was purified through column chromatography (100-200 mesh SiO_2) using 15 % of ethyl acetate in hexane as eluent.

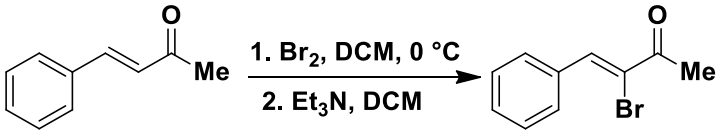
5. General procedure for the synthesis of enynone 1a

Step 1:



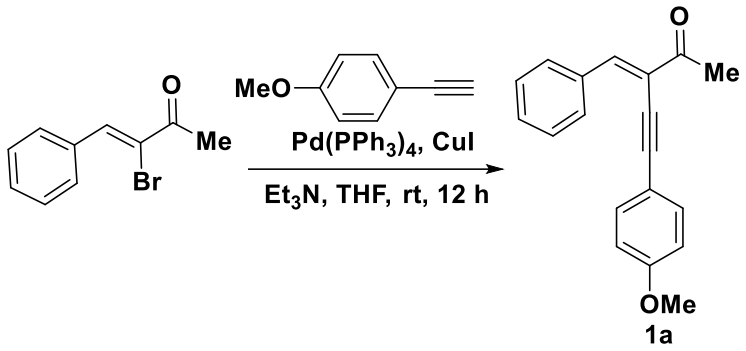
Benzaldehyde (7.07 mmol, 1.0 *equiv.*) was suspended in a mixture of acetone/water (3 mL/3 mL). Aqueous solution of sodium hydroxide (1 %, 7 mL) was slowly added to the reaction mixture. The reaction mixture was heated to 65 °C and stirred until no benzaldehyde was detected by TLC. After completion of the reaction (checked by TLC), the reaction mixture was cooled down, diluted with water and extracted with DCM. The combined organic extracts were dried over anhydrous sodium sulfate and then concentrated under reduced pressure. The crude product was purified through column chromatography (100-200 mesh SiO_2) using 3 % of ethyl acetate in hexane as eluent to give the benzalacetone (96 % yield).

Step 2:



To a solution of benzalacetone (1.0 g, 6.84 mmol, 1.0 equiv.) in DCM (20 mL), Br_2 (0.42 mL, 8.20 mmol, 12 equiv.) was added at 0 °C. The reaction mixture was stirred for 15 min, followed by the addition of Et_3N (1.62 mL, 11.6 mmol, 1.7 equiv.). After stirring for additional 5 hrs, the reaction mixture was diluted with DCM and washed sequentially with a 10 % $NaHSO_3$ solution, H_2O and brine. The organic layer was separated and dried over Na_2SO_4, filtered and concentrated in vacuo. Crude product was purified on a silica gel column to give α-bromobezalacetone (1.38 g, 6.1 mmol, 90 %) as brown oil.

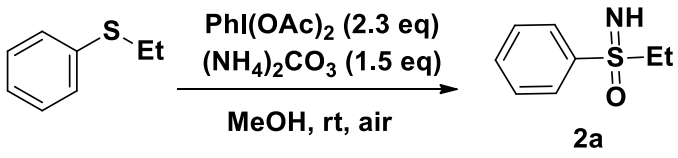
Step 3:



A round bottom flask was charged with $Pd(PPh_3)_4$ (17.6 mg, 0.015 mmol, 0.25 mol%) and CuI (14.5 mg, 0.076 mmol, 1.25 mol%). To this was added freshly distilled THF (10 mL) and Et_3N (10 mL). The mixture was kept stirring and α-bromobezalacetone (1.38 g, 6.13 mmol, 1 equiv.) was added. Finally, 4-ethynyl anisole (0.97 g, 7.36 mmol, 1.2 equiv.) in THF was added using a syringe over 30 min. Then the mixture was stirred for 12 hrs at room temperature. Upon completion, the reaction mixture was quenched with aqueous NH_4Cl. The crude product was extracted with DCM and concentrated in vacuo. The residue was purified on a silica gel column to give **1a** (73 %).

All the enynones were synthesised using the above mentioned procedure and characterisation data were exactly matching with the reported data.[1] ^1H and ^{13}C of enynone **1b** is included at the end as representative example.

6. General procedure for the synthesis of Sulfoximine 2a

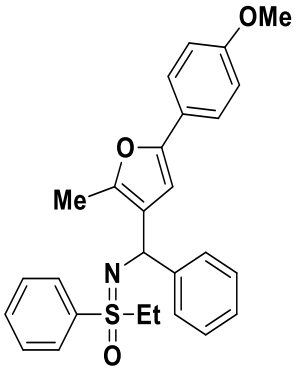


To a stirred solution of sulfide (12 mmol) in MeOH (20 mL) was added the $(NH_4)_2CO_3$ (1.5 equiv.). Subsequently, $(PhI(OAc)_2$ (2.3 equiv.) was added and the solution was stirred at rt. After the disappearance of the sulfide (checked by TLC, the solvent was removed under reduced pressure. The crude product was purified by column chromatography to give **2a** (80 %).

All the sulfoximines were synthesised using the above mentioned procedure and characterisation data were exactly matching with the reported data.[2]

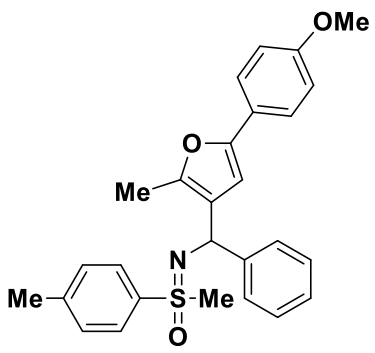
7. Characterization data of the synthesized compounds

Compound 3a (Obtained as diastereomeric mixture in the ratio of 3:2)



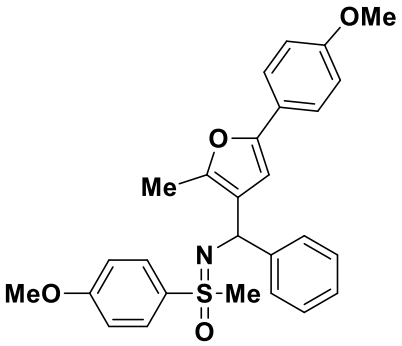
Yellow sticky liquid. Yield: 89 % (43 mg from 0.1086 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1.2H), 7.73 (d, J = 8.5 Hz, 2H), 7.54 (t, J = 8.5 Hz, 0.9H), 7.50 – 7.42 (m, 8H), 7.38 (t, J = 8.0 Hz, 3.5H), 7.29 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.20 – 7.14 (m, 1.8H), 6.87 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 1.4H), 6.46 (s, 0.7H), 6.38 (s, 1H), 5.32 (s, 1H), 5.26 (s, 0.7H), 3.81 (s, 3H), 3.80 (s, 2.1H), 3.32 – 3.24 (m, 2H), 3.22 – 3.18 (m, 1.5H), 2.18 (s, 2.1H), 1.88 (s, 3H), 1.27 (t, J = 7.5 Hz, 3H), 1.20 (t, J = 7.5 Hz, 2.1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.7, 158.5, 151.6, 151.2, 146.3, 146.1, 145.2, 145.1, 138.6, 138.0, 132.7, 132.6, 129.4, 129.4, 129.1, 128.9, 128.2, 128.1, 127.2, 127.2, 126.5, 126.5, 126.2, 125.1, 124.8, 124.8, 124.7, 124.5, 114.1, 114.0, 105.0, 104.6, 55.4, 55.4, 53.5, 52.1, 51.3, 51.3, 12.2, 11.5, 7.9, 7.4. HRMS (ESI) calcd for $C_{27}H_{27}NNaO_3S$ $[M+Na]^+$ 468.1604; found 468.1607.

Compound 3b (Obtained as diastereomeric mixture in the ratio of 4:3)



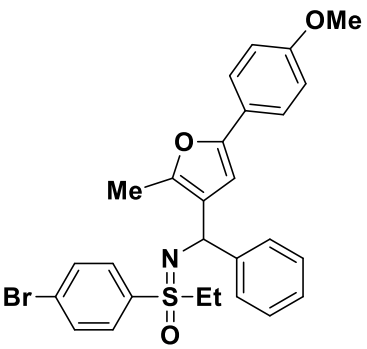
Brown sticky liquid. Yield: 91 % (44 mg from 0.1086 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.5 Hz, 1.3H), 7.66 (d, J = 8.0 Hz, 2H), 7.51 – 7.48 (m, 3.5H), 7.45 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.0 Hz, 1.3H), 7.29 (t, J = 7.5 Hz, 2.4H), 7.24 (d, J = 8.0 Hz, 1.8H), 7.20 – 7.16 (m, 4H), 6.86 (t, J = 8.5 Hz, 3.5H), 6.48 (s, 0.7H), 6.33 (s, 1H), 5.29 (s, 1H), 5.23 (s, 0.7H), 3.81 (s, 3H), 3.80 (s, 2H), 3.13 (s, 3H), 3.10 (s, 2H), 2.41 (s, 2H), 2.33 (s, 3H), 2.20 (s, 2H), 1.92 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.6, 158.5, 151.5, 146.2, 146.1, 145.0, 145.0, 143.7, 143.5, 143.3, 137.3, 136.9, 129.9, 129.8, 129.6, 128.6, 128.6, 128.2, 128.2, 127.1, 126.5, 126.5, 126.0, 124.9, 124.8, 124.8, 124.6, 124.5, 114.1, 114.0, 104.9, 104.7, 55.4, 55.4, 53.6, 52.5, 45.8, 45.7, 21.6, 21.5, 12.2, 11.6. HRMS (ESI) calcd for $C_{27}H_{27}NNaO_3S$ $[M+Na]^+$ 468.1604; found 468.1607

Compound 3c (Obtained as diastereomeric mixture in the ratio of 4:3)



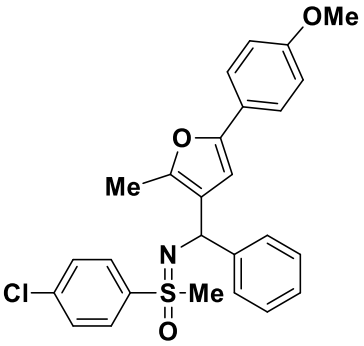
Yellow sticky liquid. Yield: 86 % (43 mg from 0.1086 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, J = 9.0 Hz, 1.6H), 7.70 (d, J = 9.0 Hz, 2H), 7.51 – 7.48 (m, 4H), 7.46 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.0 Hz, 1.6H), 7.29 (t, J = 7.5 Hz, 2.4H), 7.24 (d, J = 7.5 Hz, 1.3H), 7.20 – 7.15 (m, 2H), 6.91 (d, J = 9.0 Hz, 1.6H), 6.87 – 6.84 (m, 5.4H), 6.48 (s, 0.7H), 6.37 (s, 1H), 5.29 (s, 1H), 5.24 (s, 0.7H), 3.85 (s, 2.4H), 3.81 (s, 3H), 3.80 (s, 2.2H), 3.76 (s, 3H), 3.12 (s, 3H), 3.10 (s, 2.2H), 2.20 (s, 2.3H), 1.93 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 163.2, 163.1, 158.7, 158.6, 151.6, 151.3, 146.3, 146.1, 145.1, 145.1, 134.6, 131.7, 131.4, 130.8, 130.7, 128.2, 128.2, 127.2, 126.5, 126.5, 126.0, 125.0, 124.9, 124.8, 124.7, 124.5, 114.5, 114.2, 114.1, 114.0, 105.0, 104.7, 55.7, 55.7, 55.4, 55.4, 53.6, 52.5, 46.1, 45.9, 12.3, 11.6. HRMS (ESI) calcd for $C_{27}H_{27}NNaO_4S$ $[M+Na]^+$ 484.1553; found 484.1556.

Compound 3d (Obtained as diastereomeric mixture in the ratio of 5:4)



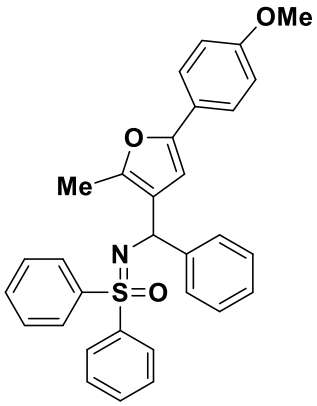
Brown sticky liquid. Yield: 56 % (48 mg from 0.1630 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.02 (t, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 0.9H), 7.51 (d, J = 8.0 Hz, 2.2H), 7.47 (d, J = 8.5 Hz, 1.8H), 7.43 (d, J = 7.5 Hz, 1H), 7.34 – 7.29 (m, 7H), 7.20 – 7.15 (m, 2.8H), 7.11– 7.08 (m, 2H), 6.83 (t, J = 8.0 Hz, 3.8H), 6.46 (s, 0.8H), 6.20 (s, 1H), 5.41 (s, 1H), 5.27 (s, 0.8H), 3.80 (s, 3H), 3.80 (s, 2.4H), 3.76 – 3.69 (m, 2H), 3.60 – 3.52 (m, 1.9H), 2.10 (s, 2.5H), 2.07 (s, 3H), 1.25 (d, J = 7.5 Hz, 3H), 1.22 (t, J = 7.5 Hz, 2.7H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.6, 158.6, 151.1, 151.1, 146.4, 146.3, 145.0, 144.2, 138.9, 138.1, 135.3, 135.0, 133.7, 133.5, 133.2, 132.7, 128.2, 128.0, 127.9, 127.7, 127.4, 127.2, 126.5, 124.9, 124.7, 124.00, 121.0, 121.0, 114.0, 114.0, 105.4, 105.2, 55.4, 55.4, 54.5, 52.7, 49.2, 49.1, 12.1, 11.7, 7.1, 6.7. HRMS (ESI) calcd for $C_{27}H_{26}BrNNaO_3S$ $[M+Na]^+$ 546.0709; found 546.0714.

Compound 3e (Obtained as diastereomeric mixture in the ratio of 5:4)



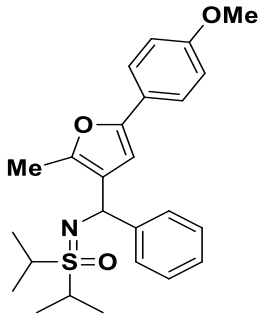
Yellow sticky liquid. Yield: 67 % (34 mg from 0.1086 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.5 Hz, 1.6H), 7.70 (d, J = 7.0 Hz, 2H), 7.51 – 7.48 (m, 4H), 7.45 (d, J = 6.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 1.8H), 7.35 – 7.31 (m, 5H), 7.25 – 7.20 (m, 3H), 6.88 – 6.84 (m, 4H), 6.47 (s, 0.8H), 6.31 (s, 1H), 5.31 (s, 1H), 5.24 (s, 0.8H), 3.82 (s, 3H), 3.80 (s, 2.4H), 3.13 (s, 3H), 3.10 (s, 2.4H), 2.21 (s, 2.4H), 1.94 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.3, 158.1, 151.3, 150.9, 145.8, 145.7, 144.2, 144.1, 138.9, 138.8, 138.6, 138.3, 129.6, 129.6, 129.5, 129.0, 128.7, 127.8, 127.8, 126.7, 126.6, 126.2, 126.2, 125.2, 124.4, 124.1, 124.0, 123.8, 113.6, 113.4, 104.3, 103.9, 55.0, 54.9, 53.2, 51.9, 45.3, 45.2, 12.3, 11.6. HRMS (ESI) calcd for $C_{26}H_{24}ClNNaO_3S$ $[M+Na]^+$ 488.1058; found 488.1059.

Compound 3f



Yellow solid. Yield: 65 % (35 mg from 0.1086 mmol of the corresponding enynone), mp 105-110 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.5 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.55 – 7.51 (m, 7H), 7.44 (d, J = 7.5 Hz, 2H), 7.40 – 7.38 (m, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 6.51 (s, 1H), 5.37 (s, 1H), 3.81 (s, 3H), 2.01 (s, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.6, 151.5, 146.0, 145.2, 141.2, 134.3, 134.2, 132.5, 132.3, 132.1, 129.4, 129.1, 129.0, 128.6, 128.2, 127.1, 126.5, 124.8, 114.1, 104.8, 55.4, 53.2, 11.8. HRMS (ESI) calcd for $C_{31}H_{27}NNaO_3S$ $[M+Na]^+$ 516.1604; found 516.1604.

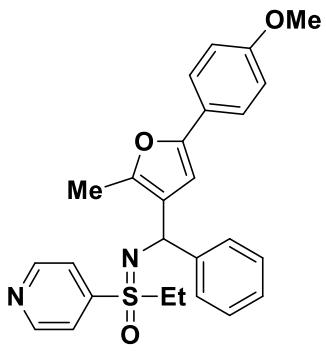
Compound 3g



Off white solid, Yield: 67 % (31 mg from 0.1086 mmol of the corresponding enynone), mp 110-115 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.51 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.17 (t, J = 7.0 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 6.47 (s, 1H), 5.59 (s, 1H), 3.80 (s, 3H), 3.31 – 3.26 (m, 2H), 2.34 (s, 3H), 1.32 (d, J = 7.0 Hz, 3H), 1.28 (d, J = 6.5 Hz, 3H), 1.26 (d, J = 7 Hz, 3H), 1.25 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.6, 151.2, 146.6, 145.8,

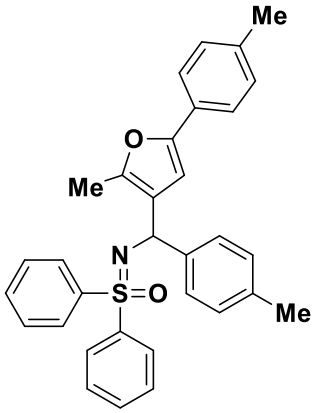
128.1, 127.2, 127.1, 126.3, 124.8, 124.7, 114.1, 104.9, 55.4, 52.5, 52.0, 51.3, 16.3, 16.2, 15.7, 15.6, 12.3. HRMS (ESI) calcd for $C_{25}H_{31}NNaO_3S$ $[M+Na]^+$ 448.1917; found 448.1920.

Compound 3h (Obtained as diastereomeric mixture in the ratio of 1:0.6)



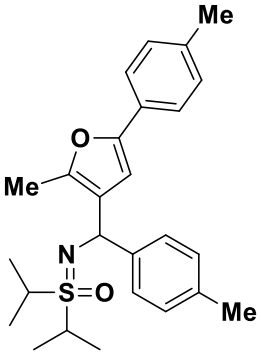
Brown sticky liquid. Yield: 71 % (46mg from 0.1447 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.60 – 8.59 (m, 0.6H), 8.50 – 8.49 (m, 1.2H), 7.86-7.84 (m, 0.6H), 7.80-7.78 (m, 1.3H), 7.70 – 7.66 (m, 0.6H), 7.59 – 7.56 (m, 1.3H), 7.50-7.47 (m, 4H), 7.29 – 7.27 (m, 4H), 7.19-7.16 (m, 1.3H), 7.13-7.10 (m, 1.2H), 7.07 – 7.04 (m, 2H), 6.84 (d, J = 8.5 Hz, 1.2H), 6.81 (d, J = 9 Hz, 1.9H), 6.45 (s, 0.6H), 5.96 (s, 1H), 5.51 (s, 1H), 5.42 (s, 0.6H), 3.80 (s, 3H), 3.80 (s, 2.1H), 3.62 – 3.58 (m, 1.4H), 3.53-3.46(m, 2H), 2.22 (s, 1.4H), 2.17 (s, 3H), 1.27 (t, J = 7.5Hz, J = 7.5 Hz, 3H), 1.20 (t, J = 7.5 Hz, J = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 158.6, 158.5, 158.5, 158.5, 151.2, 151.0, 149.9, 149.7, 146.4, 146.4, 144.8, 137.4, 136.9, 128.1, 127.9, 127.4, 127.1, 126.5, 125.9, 125.7, 124.8, 124.6, 124.5, 124.2, 123.7, 122.9, 114.0, 113.9, 105.2, 104.9, 55.4, 55.4, 53.6, 52.4, 47.6, 47.5, 12.3, 11.9, 7.1, 6.6. HRMS (ESI) calcd for $C_{26}H_{26}N_2NaO_3S$ $[M+Na]^+$ 469.1556; found 469.1564.

Compound 3i



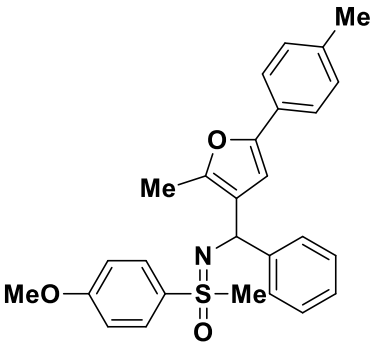
Pale yellow solid, Yield: 52 % (28 mg from 0.1093 mmol of the corresponding enynone), mp 120-123 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 7.5 Hz, 2H), 7.49 – 7.43 (m, 6H), 7.40 – 7.37 (m, 4H), 7.13 – 7.09 (m, 4H), 6.58 (s, 1H), 5.34 (s, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.02 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.7, 146.3, 142.4, 141.3, 136.4, 136.0, 132.4, 132.3, 129.4, 129.3, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 127.1, 125.9, 123.4, 105.8, 53.1, 22.9, 21.3, 11.9. HRMS (ESI) calcd for $C_{32}H_{29}NNaO_2S$ $[M+Na]^+$ 514.1811; found 514.1821.

Compound 3j



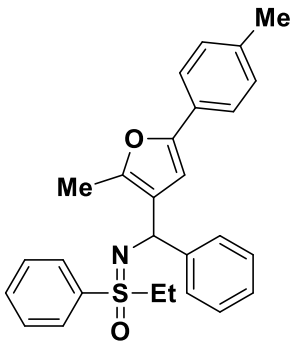
Pale yellow solid, Yield: 63 % (29 mg from 0.1093 mmol of the corresponding enynone), mp 123-125 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.47 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.54 (s, 1H), 5.56 (s, 1H), 3.31 – 3.23 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 1.32 (d, J = 7.0 Hz, 3H), 1.27 (d, J = 7 Hz, 3H), 1.25 (d, J = 7 Hz, 3H), 1.25 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.4, 146.1, 143.7, 136.3, 135.7, 129.3, 128.9, 128.8, 127.5, 127.0, 123.3, 105.9, 52.6, 52.1, 51.1, 21.3, 21.2, 16.3, 16.3, 15.7, 15.7, 12.3. HRMS (ESI) calcd for $C_{26}H_{33}NNaO_2S$ $[M+Na]^+$ 446.2124; found 446.2135.

Compound 3k (Obtained as diastereomeric mixture in the ratio of 5:4)



Yellow sticky liquid, Yield: 72 % (43 mg from 0.1344 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, J = 7.0 Hz, 1.7H), 7.70 (d, J = 7.0 Hz, 2H), 7.50 – 7.47 (m, 3H), 7.46 – 7.42 (m, 3H), 7.37 (d, J = 7 Hz, 1.3H), 7.30 (t, J = 7 Hz, 2H), 7.24 (d, J = 7.5 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.14 – 7.10 (m, 4H), 6.92 (d, J = 7.0 Hz, 1.7H), 6.85 (d, J = 9.0 Hz, 2H), 6.56 (s, 0.8H), 6.45 (s, 1H), 5.30 (s, 1H), 5.24 (s, 0.8H), 3.84 (s, 2.6H), 3.75 (s, 3H), 3.13 (s, 3H), 3.10 (s, 2.4H), 2.33 (s, 3H), 2.32 (s, 2.2H), 2.21 (s, 2.4H), 1.94 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 163.2, 163.1, 151.7, 151.5, 146.6, 146.4, 145.0, 145.0, 136.5, 136.3, 131.6, 131.3, 130.7, 130.7, 129.3, 129.2, 128.7, 128.6, 128.2, 128.2, 127.2, 127.2, 126.5, 126.5, 126.0, 125.0, 123.4, 123.3, 114.5, 114.2, 105.8, 105.6, 55.7, 55.7, 53.6, 52.4, 46.1, 45.9, 21.3, 21.3, 12.3, 11.6. HRMS (ESI) calcd for $C_{27}H_{27}NNaO_3S$ $[M+Na]^+$ 468.1604; found 468.1605.

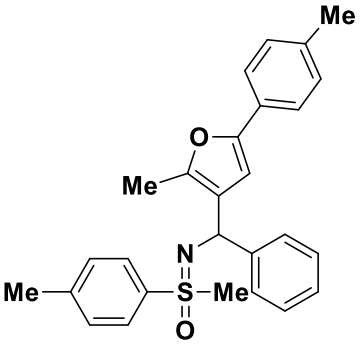
Compound 3l (Obtained as diastereomeric mixture in the ratio of 5:4)



Brown sticky liquid. Yield: 79 % (39 mg from 0.1152 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.0 Hz, 1.6H), 7.73 (d, J = 7.0 Hz, 2H), 7.55 – 7.49 (m, 4.1H), 7.47 – 7.42 (m, 5.4H), 7.39 – 7.37 (m, 3.4H), 7.29 (t, J = 7.5 Hz, 2.2H), 7.25 – 7.16 (m, 3.3H), 7.14 – 7.10 (m, 3.4H), 6.54 (s, 0.8H), 6.45 (s, 1H), 5.33 (s, 1H), 5.27 (s, 0.8H), 3.33 – 3.25 (m, 2H), 3.23 – 3.18 (m,

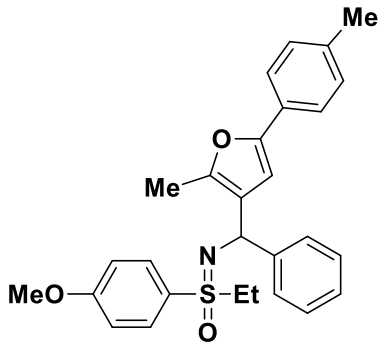
1.8H), 2.34 (s, 3H), 2.32 (s, 2H), 2.19 (s, 2H), 1.88 (s, 3H), 1.27 (d, *J* = 7.5 Hz, 3H), 1.20 (t, *J* = 7.5 Hz, 2.4H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): *δ* 151.8, 151.4, 146.6, 146.4, 145.2, 145.1, 138.6, 138.0, 136.5, 136.3, 134.3, 134.2, 132.7, 132.6, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.2, 128.2, 127.2, 126.5, 126.5, 126.2, 125.2, 123.4, 123.3, 105.9, 105.6, 53.5, 52.0, 51.3, 51.3, 21.4, 21.3, 12.3, 11.5, 7.9, 7.4. HRMS (ESI) calcd for $C_{27}H_{27}NNaO_2S$ $[M+Na]^+$ 452.1655; found 452.1659.

Compound 3m (Obtained as diastereomeric mixture in the ratio of 4:3)



Brown sticky liquid. Yield: 67 % (43 mg from 0.1536 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.71 (d, *J* = 8.0 Hz, 1.3H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.45 (m, 4H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1.5H), 7.30 (t, *J* = 7.5 Hz, 2.6H), 7.24 – 7.23 (m, 2H), 7.20 – 7.17 (m, 3.5H), 7.13 – 7.10 (m, 3.3H), 6.56 (s, 0.7H), 6.42 (s, 1H), 5.29 (s, 1H), 5.24 (s, 0.7H), 3.14 (s, 3H), 3.11 (s, 2H), 2.41 (s, 2.1H), 2.33 (s, 3H), 2.32 (s, 5.3H), 2.21 (s, 2H), 1.92 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): *δ* 151.7, 151.5, 146.6, 146.5, 144.9, 144.9, 143.7, 143.6, 136.5, 136.3, 134.4, 134.3, 129.9, 129.6, 129.4, 129.3, 129.3, 129.2, 128.7, 128.6, 128.6, 128.2, 128.2, 127.2, 127.2, 126.6, 126.5, 124.9, 123.4, 123.4, 105.8, 105.6, 53.6, 52.5, 45.8, 45.7, 21.7, 21.6, 21.5, 21.4, 12.3, 11.6. HRMS (ESI) calcd for $C_{27}H_{27}NNaO_2S$ $[M+Na]^+$ 452.1655; found 452.1661.

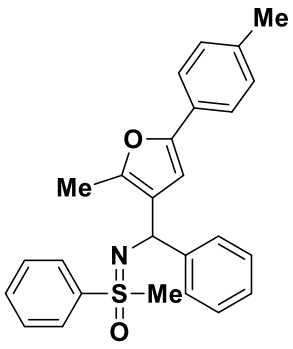
Compound 3n (Obtained as diastereomeric mixture in the ratio of 4:3)



Yellow sticky liquid. Yield: 74 % (38 mg from 0.1152 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.68 (d, *J* = 9.0 Hz, 1.3H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.43 (m, 3.5H), 7.39 (d, *J* = 7.5 Hz, 1.4H), 7.29 (t, *J* = 7.5 Hz, 2.2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2.2H), 7.10 (d, *J* = 8.0 Hz, 1.5H), 6.90 (d, *J* = 9.0 Hz, 1.5H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.53 (s, 0.7H), 6.46 (s, 1H), 5.33 (s, 1H), 5.26 (s, 0.7H), 3.84 (s, 2.4H), 3.75 (s, 3H), 3.29 – 3.22 (m, 1.9H), 3.20 – 3.16 (m, 2H), 2.34 (s, 3H), 2.31 (s, 2.2H), 2.19 (s, 2.3H), 1.95 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.5 Hz, 2.5H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): *δ* 163.2, 163.1, 151.7, 151.3, 146.6, 146.4, 145.3, 145.3, 136.5, 136.2, 131.6, 131.5, 129.8, 129.3, 129.2, 129.0, 128.8, 128.7, 128.2, 128.1, 127.2, 127.2, 126.5, 126.4, 126.4, 125.3, 123.4, 123.3, 114.4,

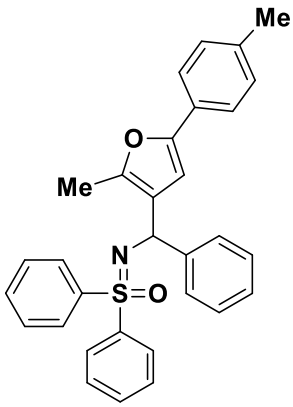
114.1, 105.9, 105.7, 55.7, 55.6, 53.4, 52.0, 51.63, 51.5, 21.3, 21.3, 12.3, 11.6, 8.0, 7.5. HRMS (ESI) calcd for $C_{28}H_{29}NNaO_3S$ $[M+Na]^+$ 482.1760; found 482.1765.

Compound 3o (Obtained as diastereomeric mixture in the ratio of 4:3)



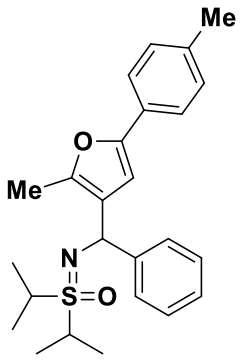
Yellow sticky liquid. Yield: 66 % (42 mg from 0.1536 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 1.3H), 7.79 (d, J = 8.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 0.8H), 7.50 – 7.48 (m, 3.8H), 7.47 – 7.45 (m, 1.6H), 7.43 – 7.39 (m, 4H), 7.38 – 7.35 (m, 1.7H), 7.30 (t, J = 7.5 Hz, 2.5H), 7.25 – 7.21 (m, 1.9H), 7.20 – 7.16 (m, 1.4H), 7.14 – 7.11 (m, 3H), 6.56 (s, 0.7H), 6.45 (s, 1H), 5.30 (s, 1H), 5.27 (s, 0.7H), 3.14 (s, 3H), 3.11 (s, 2.1H), 2.34 (s, 3H), 2.32 (s, 2.1H), 2.21 (s, 2.1H), 1.88 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.8, 151.5, 146.6, 146.5, 144.9, 144.8, 140.3, 140.1, 136.5, 136.4, 132.8, 132.7, 129.3, 129.3, 129.2, 129.0, 128.7, 128.6, 128.6, 128.5, 128.2, 128.2, 127.2, 127.2, 126.6, 126.6, 125.9, 124.9, 123.4, 123.4, 105.8, 105.5, 53.6, 52.4, 45.7, 45.6, 21.3, 21.3, 12.3, 11.5. HRMS (ESI) calcd for $C_{26}H_{25}NNaO_2S$ $[M+Na]^+$ 438.1498; found 438.1503.

Compound 3p



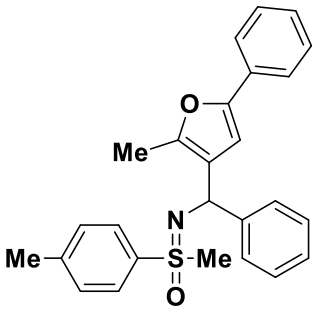
White solid, Yield: 60 % (33 mg from 0.1152 mmol of the corresponding enynone), mp 116-118 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.01 (d, J = 7.0 Hz, 2H), 7.90 (d, J = 7.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.49 – 7.42 (m, 6H), 7.40 – 7.37 (m, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.13 (d, J = 7.5 Hz, 2H), 6.58 (s, 1H), 5.38 (s, 1H), 2.33 (s, 3H), 2.02 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.7, 146.4, 145.2, 141.2, 141.2, 136.4, 132.5, 132.3, 129.3, 129.1, 129.0, 129.0, 128.7, 128.6, 128.2, 127.2, 126.6, 125.8, 123.3, 105.7, 53.2, 21.4, 11.9. HRMS (ESI) calcd for $C_{31}H_{27}NNaO_2S$ $[M+Na]^+$ 500.1655; found 500.1656.

Compound 3q



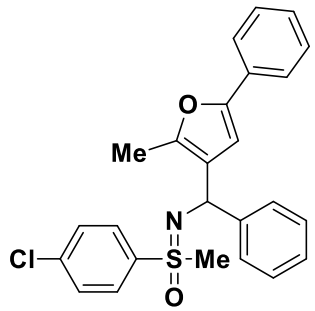
Yellow solid, Yield: 61 % (29 mg from 0.1152 mmol of the corresponding enynone), mp 123-124 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.0 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.55 (s, 1H), 5.60 (s, 1H), 3.32 – 3.25 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 1.32 (d, J = 6.5 Hz, 3H), 1.27 (d, J = 6.5 Hz, 3H), 1.25 (d, J = 7.0 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.4, 146.6, 146.1, 136.4, 129.3, 128.8, 128.1, 127.1, 126.5, 126.3, 123.3, 105.8, 52.5, 52.0, 51.3, 21.3, 16.3, 16.2, 15.7, 15.6, 12.3. HRMS (ESI) calcd for $C_{25}H_{31}NNaO_2S$ $[M+Na]^+$ 432.1968; found 432.1971.

Compound 3r (Obtained as diastereomeric mixture in the ratio of 4:3)



Brown sticky liquid. Yield: 65 % (33 mg from 0.1218 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.5 Hz, 1.4H), 7.66 (d, J = 8.5 Hz, 2H), 7.58(d, J = 8.5 Hz, 1.5H), 7.53 – 7.48 (m, 4.6H), 7.37 (d, J = 7.5 Hz, 1.5H), 7.33 – 7.29 (m, 6.5H), 7.25 – 7.23 (m, 2H), 7.21 – 7.14 (m, 6H), 6.62 (s, 0.7H), 6.47 (s, 1H), 5.31 (s, 1H), 5.24 (s, 0.7H), 3.13 (s, 3H), 3.11 (s, 2.1H), 2.41 (s, 2.1H), 2.31 (s, 3H), 2.21 (s, 2.1H), 1.95 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.5, 151.3, 147.1, 146.9, 145.0, 144.9, 143.7, 143.5, 137.3, 136.9, 131.4, 131.2, 129.9, 129.6, 128.6, 128.6, 128.5, 128.2, 128.2, 127.1, 126.7, 126.6, 126.6, 126.5, 126.5, 126.2, 126.2, 125.0, 123.4, 123.3, 106.6, 106.4, 53.6, 52.5, 45.8, 45.7, 21.6, 21.4, 12.3, 11.6. HRMS (ESI) calcd for $C_{26}H_{25}NNaO_2S$ $[M+Na]^+$ 438.1498; found 438.1501.

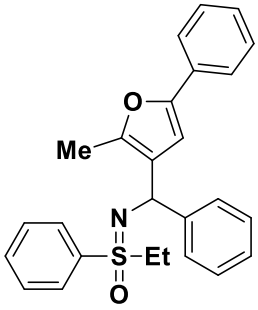
Compound 3s (Obtained as diastereomeric mixture in the ratio of 5:4)



Yellow sticky liquid. Yield: 60 % (48 mg from 0.1827 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (dd, J = 14.5, 8.5 Hz, 4H), 7.57 (d, J = 8.5 Hz, 1.8H), 7.52 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 1.6H), 7.36 – 7.29 (m, 9H), 7.24 – 7.15 (m, 5H), 6.62 (s, 0.8H), 6.46 (s, 1H), 5.32 (s, 1H), 5.25 (s, 0.8H), 3.14 (s, 3H), 3.11 (s, 2.5H), 2.23 (s, 2.6H), 1.96 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.8, 151.3, 147.1, 146.9, 144.6, 144.5, 139.4, 139.3, 139.0, 138.7, 131.3, 131.0, 130.0, 130.0, 129.5, 129.2, 128.7, 128.6, 128.3, 128.3, 127.2, 127.1, 127.1, 126.9, 126.7, 126.7, 126.7, 125.9, 124.8, 123.4, 106.4, 106.2, 53.6,

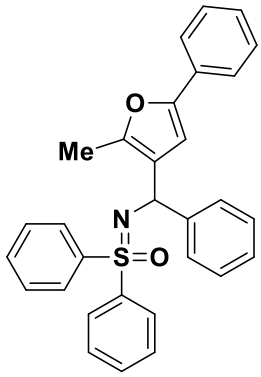
52.4, 45.7, 45.7, 12.3, 11.6. HRMS (ESI) calcd for $C_{25}H_{22}ClNNaO_2S$ $[M+Na]^+$ 458.0952; found 458.0953.

Compound 3t (Obtained as diastereomeric mixture in the ratio of 5:4)



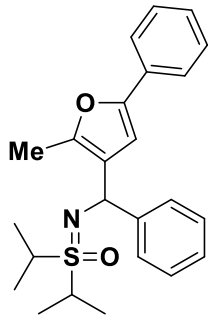
Yellow sticky liquid. Yield: 63 % (32 mg from 0.1218 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.5 Hz, 1.6H), 7.74 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 3H), 7.51 – 7.48 (m, 3H), 7.47 – 7.43 (m, 2H), 7.38 (t, J = 7.5 Hz, 4H), 7.34 – 7.28 (m, 6.1H), 7.24 – 7.16 (m, 4.9H), 6.61 (s, 0.8H), 6.52 (s, 1H), 5.34 (s, 1H), 5.27 (s, 0.8H), 3.33 – 3.26 (m, 1.9H), 3.24 – 3.18 (m, 2H), 2.19 (s, 2.4H), 1.90 (s, 3H), 1.27 (t, J = 7.5 Hz, 3H), 1.21 (t, J = 7.5 Hz, 2.7H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.5, 151.1, 147.1, 146.9, 145.2, 145.1, 138.6, 138.0, 132.8, 132.6, 131.4, 131.3, 129.4, 129.2, 128.9, 128.6, 128.5, 128.2, 128.2, 127.2, 126.8, 126.7, 126.6, 126.5, 126.5, 126.5, 126.4, 125.3, 123.4, 123.4, 106.7, 106.4, 53.5, 53.4, 52.0, 51.4, 12.3, 11.5, 7.9, 7.4. HRMS (ESI) calcd for $C_{26}H_{25}NNaO_2S$ $[M+Na]^+$ 438.1498; found 438.1503.

Compound 3u



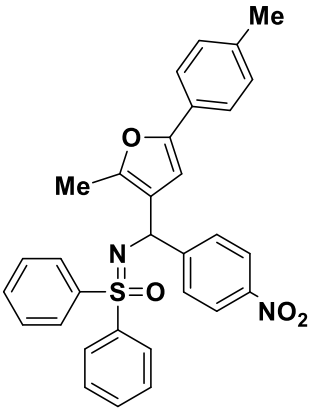
Off white solid, Yield: 64 % (36 mg from 0.1218 mmol of the corresponding enynone), mp 113-118 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, J = 7.5 Hz, 2H), 7.91 (d, J = 7.0 Hz, 2H), 7.57 (d, J = 7.0 Hz, 2H), 7.53 – 7.48 (m, 3H), 7.45 – 7.42 (m, 3H), 7.40 – 7.37 (m, 2H), 7.34 – 7.29 (m, 4H), 7.22 – 7.17 (m, 2H), 6.65 (s, 1H), 5.39 (s, 1H), 2.03 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.5, 146.9, 145.2, 141.2, 141.2, 132.5, 132.4, 131.3, 129.2, 129.0, 129.0, 128.6, 128.6, 128.3, 127.2, 126.7, 126.6, 125.9, 123.4, 106.5, 53.2, 11.9. HRMS (ESI) calcd for $C_{30}H_{25}NNaO_2S$ $[M+Na]^+$ 486.1498;found486.1501.

Compound 3v



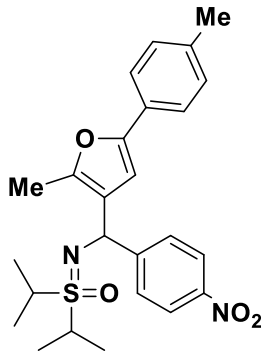
Yellow solid, Yield: 62 % (30 mg from 0.1218 mmol of the corresponding enynone), mp 123-127 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, J = 7.0 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.17 (t, J = 7.5 Hz, 2H), 6.62 (s, 1H), 5.61 (s, 1H), 3.31 – 3.25 (m, 2H), 2.36 (s, 3H), 1.32 (d, J = 7.0 Hz, 3H), 1.28 (d, J = 6.5 Hz, 3H), 1.26 (d, J = 7 Hz, 3H), 1.26 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 151.2, 146.6, 146.5, 131.4, 128.6, 128.1, 127.4, 127.1, 126.6, 126.3, 123.3, 106.6, 52.5, 52.1, 51.3, 16.2, 16.2, 15.7, 15.6, 12.3. HRMS (ESI) calcd for $C_{24}H_{29}NNaO_2S$ $[M+Na]^+$ 418.1811; found 418.1815.

Compound 3w



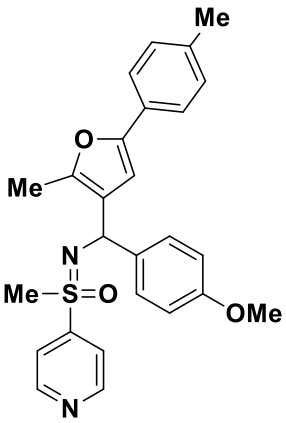
Yellow sticky liquid. Yield: 51 % (52 mg from 0.1965 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.15 (d, J = 9.0 Hz, 2H), 8.02 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.49 – 7.45 (m, 6H), 7.40 (t, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.49 (s, 1H), 5.43 (s, 1H), 2.34 (s, 3H), 2.02 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 152.8, 152.3, 146.8, 146.7, 140.8, 140.5, 136.9, 134.3, 134.2, 132.9, 132.7, 129.4, 129.3, 129.2, 128.9, 128.4, 128.1, 123.6, 123.4, 105.0, 52.8, 21.4, 11.8. HRMS (ESI) calcd for $C_{31}H_{27}N_2O_4S$ $[M+H]^+$ 523.1686; found 523.1692.

Compound 3x



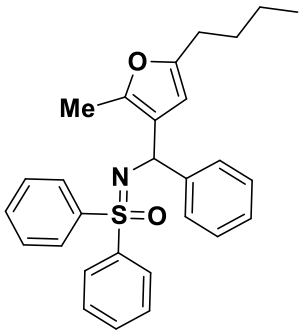
Yellow solid. Yield: 56 % (50 mg from 0.1965 mmol of the corresponding enynone), mp 120-123 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.14 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.50 (s, 1H), 5.65 (s, 1H), 3.34 – 3.27 (m, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 1.33 (d, J = 6.5 Hz, 3H), 1.27 (t, J = 6.5 Hz, 6H), 1.25 (d, J = 5.5 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 152.0, 146.6, 146.4, 136.8, 134.3, 134.2, 129.4, 128.4, 127.9, 123.6, 123.4, 105.1, 53.0, 51.8, 51.1, 21.3, 16.2, 16.0, 15.6, 15.6, 12.3. HRMS (ESI) calcd for $C_{25}H_{31}N_2O_4S$ $[M+H]^+$ 455.1999; found 455.2002.

Compound 3y (Obtained as diastereomeric mixture in the ratio of 5:4)



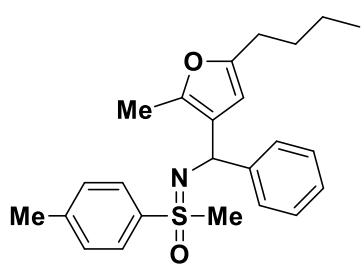
Brown sticky liquid. Yield: 75 % (46 mg from 0.1377 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.60 – 8.59 (m, 0.81H), 8.50 – 8.49 (m, 1H), 7.86 – 7.84 (m, 0.9H), 7.81 – 7.79 (m, 1H), 7.71 – 7.68 (m, 1H), 7.61 – 7.57 (m, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.31 (m, 0.9H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 1.8H), 7.12 – 7.06 (m, 4H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 1.7H), 6.55 (s, 0.8H), 6.08 (s, 1H), 5.45 (s, 1H), 5.39 (s, 0.8H), 3.77 (s, 3H), 3.72 (s, 2.6H), 3.29 (s, 3H), 3.27 (s, 2.6H), 2.32 (s, 5.7H), 2.25 (s, 2.6H), 2.16 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 159.4, 159.2, 158.4, 158.2, 151.5, 151.2, 149.8, 149.6, 146.6, 146.5, 137.5, 137.1, 136.9, 136.4, 136.3, 129.2, 129.2, 128.4, 128.1, 126.0, 125.9, 124.5, 123.4, 123.2, 122.6, 121.9, 113.6, 113.4, 105.8, 105.7, 55.4, 55.3, 53.1, 52.2, 41.9, 41.8, 21.3, 21.3, 12.3, 11.9.HRMS (ESI) calcd for $C_{26}H_{26}N_2O_3S$ $[M+Na]^+$ 469.1556; found 469.1562.

Compound 3z



Yellow sticky liquid, Yield: 37 % (22 mg from 0.1326 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.45 (m, 4H), 7.43 – 7.39 (m, 4H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 5.93 (s, 1H), 5.32 (s, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.90 (s, 3H), 1.57 – 1.54 (m, 2H), 1.38 – 1.33 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 154.0, 145.6, 144.7, 141.5, 141.4, 132.4, 132.2, 129.1, 129.0, 128.9, 128.6, 128.1, 127.2, 126.4, 123.8, 105.6, 53.3, 30.3, 28.0, 22.5, 14.0, 11.7. HRMS (ESI) calcd for $C_{28}H_{29}NNaO_2S$ $[M+Na]^+$ 466.1811; found 466.1812.

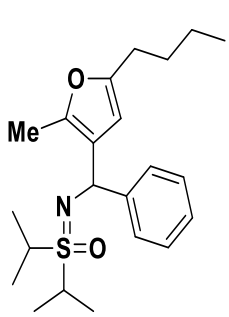
Compound 3a' (Obtained as diastereomeric mixture in the ratio of 5:4)



Brown sticky liquid. Yield: 67 % (30 mg from 0.1126 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.5 Hz, 1.8H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1.7H), 7.29 – 7.28 (m, 1.5H), 7.24 – 7.21 (m, 5.3H), 7.18 – 7.14 (m, 2H), 5.91 (s, 0.8H), 5.80 (s, 1H), 5.23 (s, 1H), 5.18 (s, 0.8H), 3.09 (s, 3H), 3.05 (s, 2.6H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.44 (d, *J* = 7.0 Hz, 2.2H), 2.41 (s, 3H), 2.40 (s, 2.8H), 2.09 (s, 2.7H),

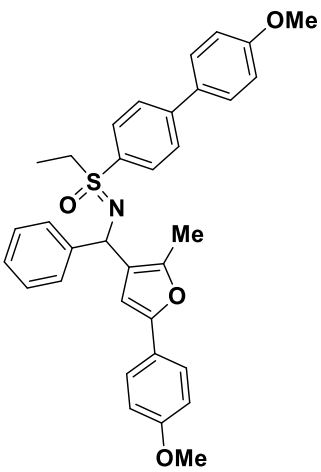
1.80 (s, 3H), 1.57 – 1.50 (m, 4H), 1.38 – 1.32 (m, 4H), 0.92 (d, *J* = 7.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): *δ* 154.0, 153.8, 145.4, 145.3, 145.0, 144.7, 143.5, 143.3, 137.6, 137.2, 129.9, 129.6, 128.7, 128.6, 128.1, 128.1, 127.2, 126.4, 126.4, 124.1, 123.1, 123.1, 105.7, 105.5, 53.7, 52.5, 45.9, 45.7, 30.3, 30.2, 28.0, 27.9, 22.5, 22.5, 21.6, 21.6, 14.0, 13.9, 12.0, 11.3. HRMS (ESI) calcd for $C_{24}H_{29}NNaO_2S$ $[M+Na]^+$ 418.1811; found 418.1812.

Compound 3b'



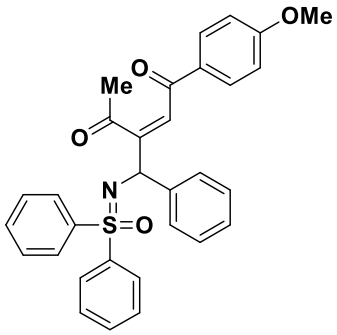
Yellow sticky liquid, Yield: 68 % (45 mg from 0.1198 mmol of the corresponding enynone).**^{1}H NMR (**500 MHz, $CDCl_3$): *δ* 7.41 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.16 – 7.13 (m, 1H), 5.89 (s, 1H), 5.51 (s, 1H), 3.28 – 3.22 (m, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 1.56 – 1.52 (m, 2H), 1.35 – 1.32 (m, 2H), 1.30 (d, *J* = 6.5 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.24 (d, *J* = 7.0 Hz, 6H), 0.89 (t, *J* = 7.5 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): *δ* 153.7, 146.9, 144.4, 134.1, 128.1, 127.2, 126.1, 105.9, 52.6, 52.0, 51.5, 30.3, 27.9, 22.4, 16.3, 16.2, 15.8, 15.7, 13.9, 12.1. HRMS (ESI) calcd for $C_{22}H_{33}NNaO_2S$ $[M+Na]^+$ 398.2124; found 398.2130.

Compound 5a (Obtained as diastereomeric mixture in the ratio of 1:1 approximately)



Yellow sticky liquid, Yield: 71 % (30 mg from 0.0763 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 8.20 – 8.18 (m, 0.9H), 8.15 – 8.13 (m, 1H), 7.56 – 7.53 (m, 1H), 7.50 – 7.46 (m, 7.7H), 7.43 – 7.40 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.28 (m, 2.19H), 7.25 – 7.23 (m, 2.4H), 7.20 – 7.15 (m, 5.9H), 6.85 (d, *J* = 8.5 Hz, 4H), 6.80 – 6.77 (m, 4H), 6.44 (s, 0.9H), 6.36 (s, 1H), 5.42 (s, 1H), 5.38 (s, 0.9H), 3.81 (s, 3H), 3.80 (s, 2.9H), 3.78 (s, 3H), 3.78 (s, 3H), 2.91 – 2.84 (m, 2H), 2.64 –2.54 (m, 2H), 2.22 (s, 3H), 1.97 (s, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): *δ* 159.5, 159.5, 158.7, 158.6, 151.6, 151.2, 146.3, 145.6, 145.6, 145.2, 141.3, 137.7, 136.9, 133.3, 133.1, 132.1, 131.5, 131.4, 131.1, 131.0, 130.5, 130.4, 128.2, 128.1, 127.6, 127.4, 127.3, 127.2, 126.5, 126.5, 125.4, 124.8, 124.6, 124.5, 114.1, 114.0, 113.2, 113.1, 105.2, 104.8, 55.4, 55.3, 53.8, 53.8, 52.7, 52.7, 48.9, 48.9, 12.3, 11.5, 7.8, 7.2. HRMS (ESI) calcd for $C_{34}H_{34}NO_4S$ $[M+H]^+$ 552.2203; found 552.2210.

Compound 6a



Yellow sticky liquid, Yield: 73 % (15 mg from 0.0405 mmol of the corresponding enynone). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 7.5 Hz, 2H), 7.50 – 7.48 (m, 4H), 7.42 – 7.39 (m, 2H), 7.34 – 7.29 (m, 6H), 6.94 (d, J = 8.5 Hz, 2H), 5.11 (d, J = 1.5 Hz, 1H), 3.87 (s, 3H), 1.92 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 206.7, 188.8, 163.9, 162.5, 141.4, 140.4, 140.3, 132.9, 132.8, 131.2, 130.6, 129.4, 129.3, 128.9, 128.8, 128.7, 127.9, 127.8, 121.2, 114.0, 61.7, 55.6, 31.1. HRMS (ESI) calcd for $C_{31}H_{28}NO_4S$ $[M+H]^+$ 510.1734; found 510.1744.

8. Data for single X-ray crystal structures

Table S1: Crystal data and structure refinement parameters for compound **3v**.

CCDC Number	2310379
Identification code	RK-112
Empirical formula	$C_{24}H_{29}NO_2S$
Formula weight	395.54
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1$
a [Å]	7.3206(4)
b [Å]	9.0166(4)
c [Å]	16.8696(8)
α/°	90
β/°	97.364(5)
γ/°	90
Volume/Å^{-3}	1104.33(9)
Z	2
ρ_{calc} g/cm^3	1.190
μ/mm^{-1}	0.165
F(000)	424.0
Crystal size/mm^3	0.24 x 0.22 x 0.2
Radiation Mo K_α	Mo *Ka* (A.= 0.71073)
2Θ range for data collection/°	6.398 to 51.188

Reflections collected	8334
R_{int}	3495
Data/restraints/parameters	3495/1/259
Goodness-of-fit on F^2	0.961
Final R indexes [I>=2σ (I)]	R1 = 0.0426, wRz = 0.0869
Final R indexes [all data]	R1 = 0.0615, wRz = 0.0956
Largest diff peak/hole [e $Å^{-3}$]	0.12/-0.18

Crystal Structure of compound 3v

The single crystal of the compound **3v** was mounted on Hampton cryoloops. All geometric and intensity data for the crystal was collected using a Super-Nova (Mo) X-ray diffractometer equipped with a micro-focus sealed X-ray tube Mo-Kα (λ = 0.71073 Å) X-ray source and HyPix3000 detector with increasing (width of 0.3 per frame) at a scan speed of 10 s per frame. The CrysAlisPro software was used for data acquisition and data extraction. Using Olex2 [1], the structure was solved with the SIR2004 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters.

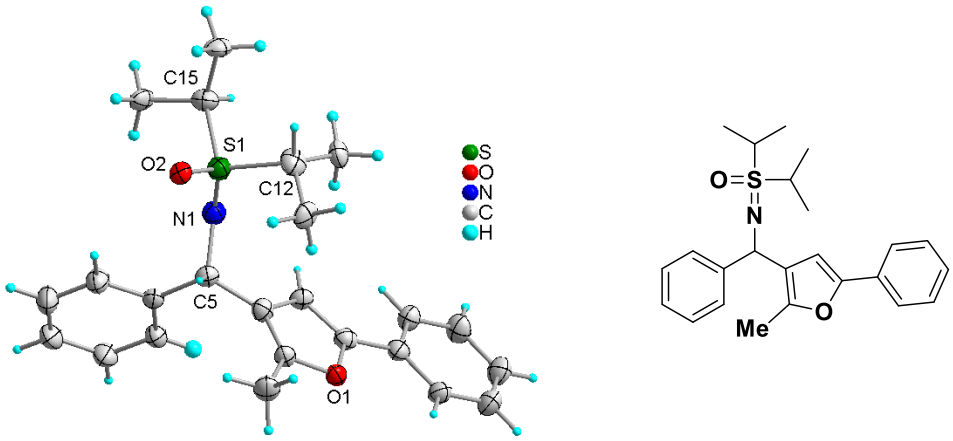


Figure 1: ORTEP diagram of compound 3v with thermal ellipsoids set to 50% probability level.

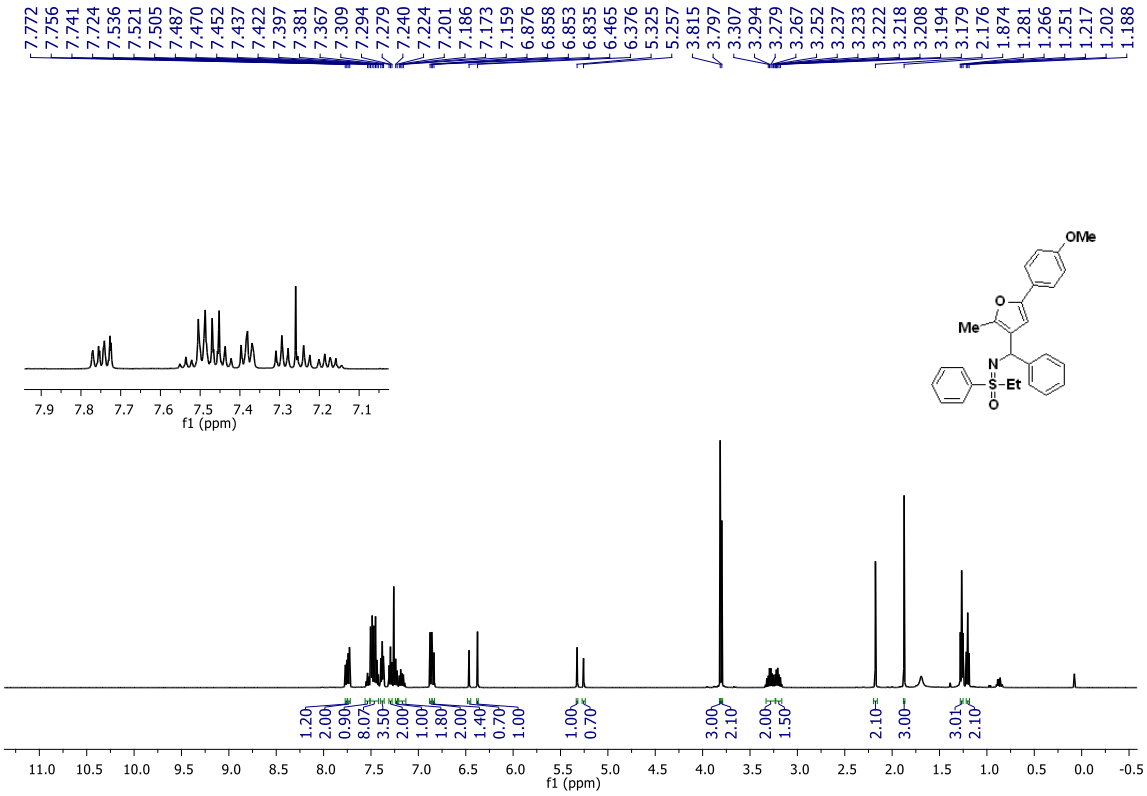
REFERENCE

[1]. (a) R. D. Kardile, T. H. Chao, M. J. Cheng and R. S. Liu, *Angew. Chem. Int. Ed.*, 2020, **59**, 10396-10400. (b) P.H. Poulsen, Y. Li, V.H. Lauridsen, D.K. Jørgensen, T.A. Palazzo, M. Meazza, K.A. Jørgensen, *Angew. Chem. Int. Ed.*, 2018, **57**,10661-10665.

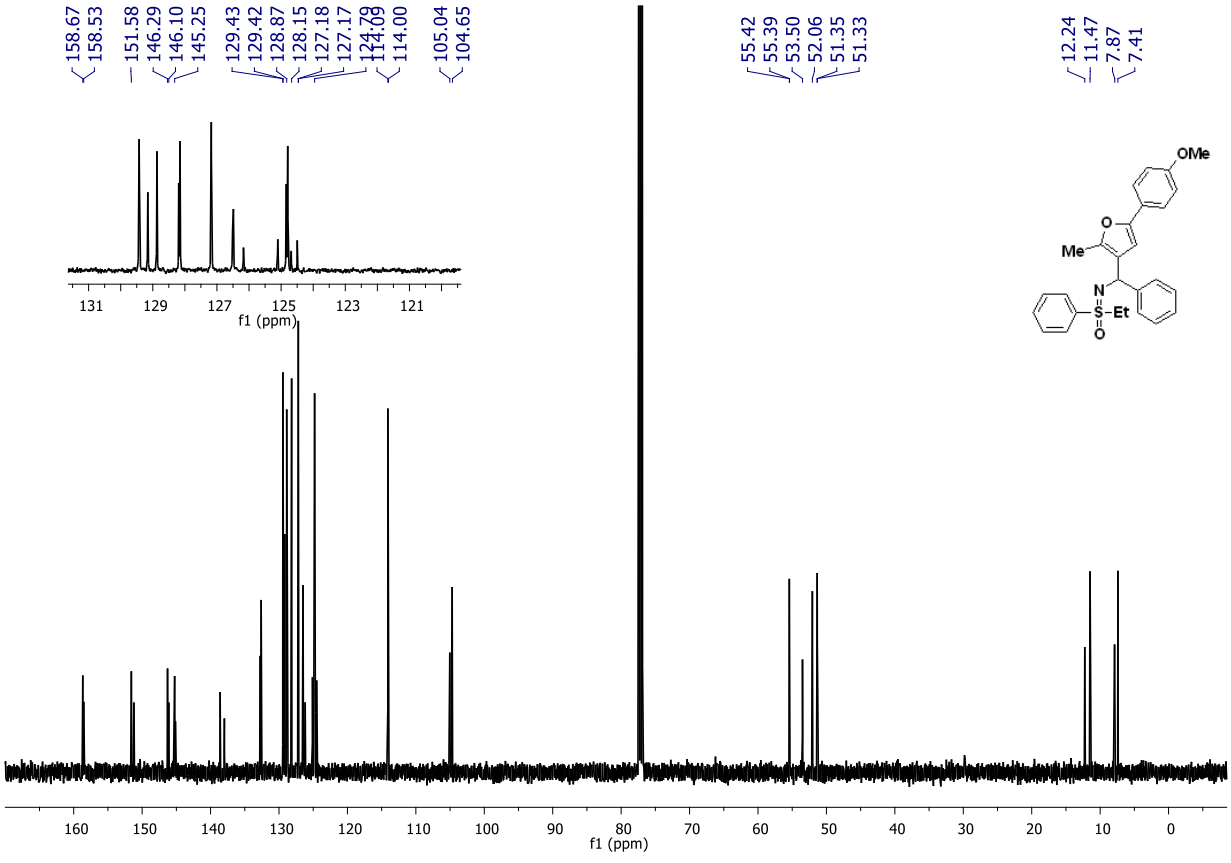
[2]. Y. Xie, B. Zhou, S. Zhou, S. Zhou, W. Wei, J. Liu, Y. Zhan, D. Cheng, M. Chen, Y. Li, B. Wang, X.-s. Xue, Z. Li, *ChemistrySelect*, 2017, **2**, 1620-1624.

9. ^{1}H and ^{13}C spectra of synthesized compounds

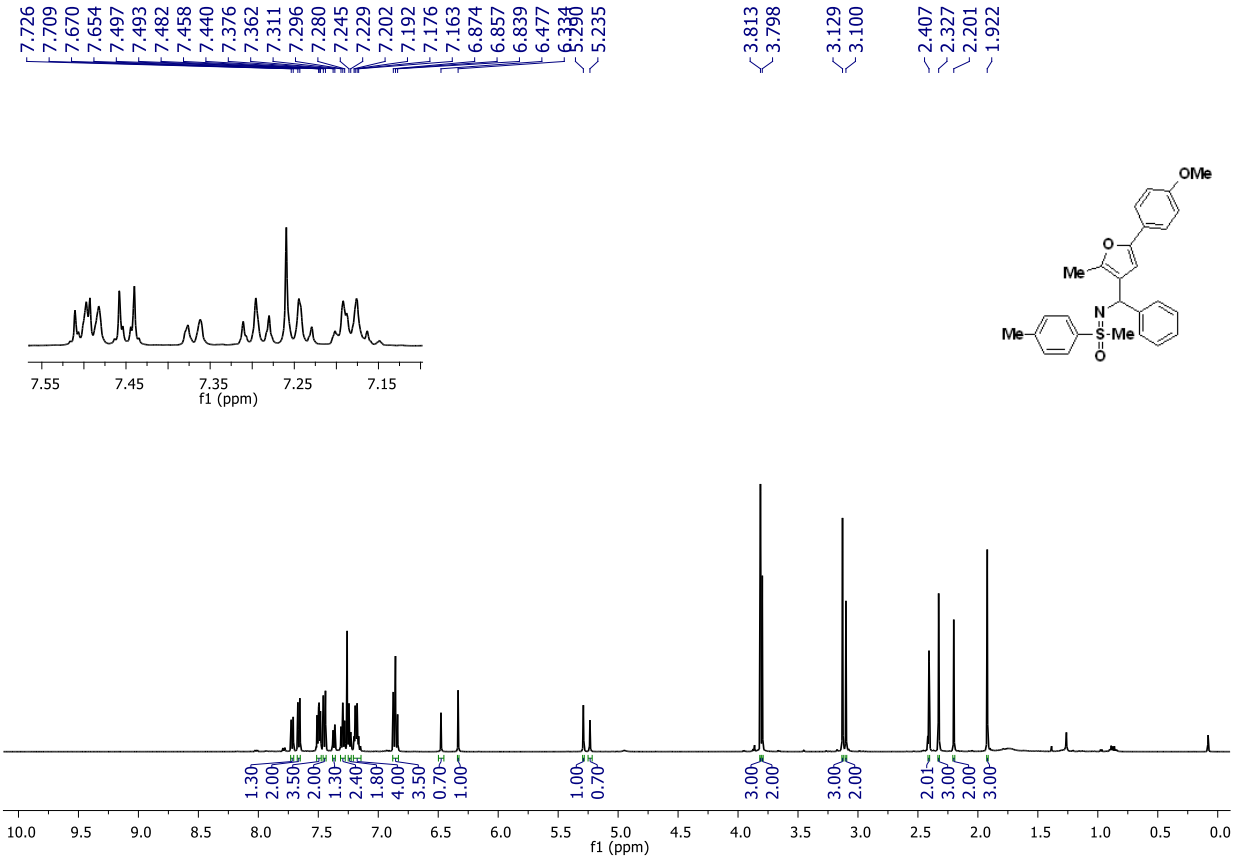
^{1}H NMR of **3a** (Mixture of diastereomers in the ratio of 3:2)



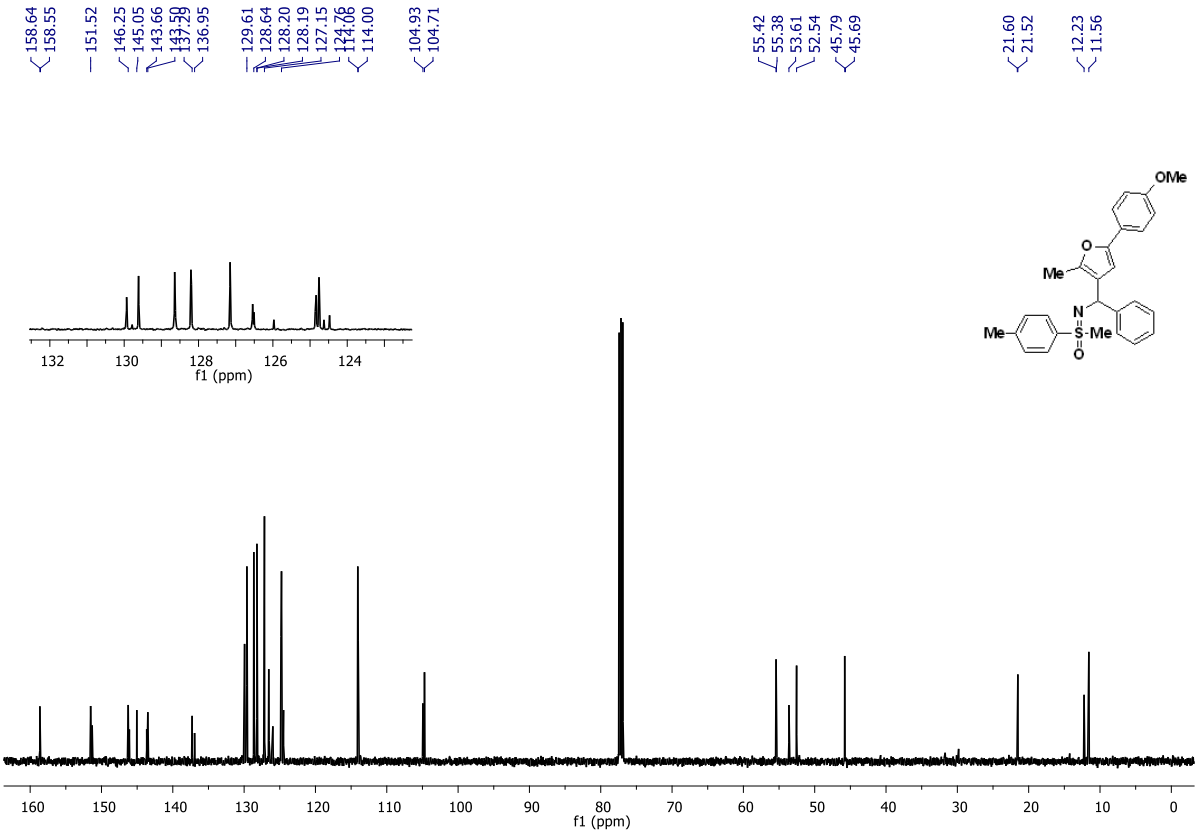
^{13}C {^{1}H} NMR of **3a** (Mixture of diastereomers in the ratio of 3:2)



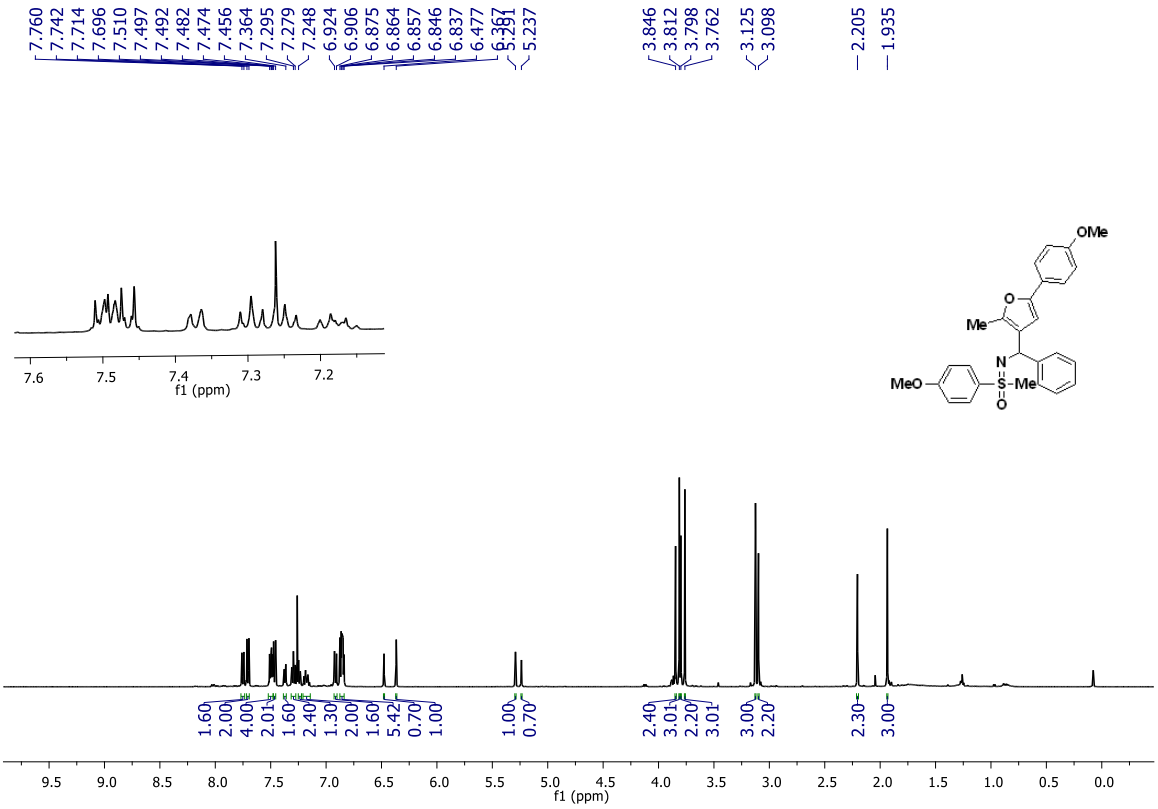
^{1}H NMR of **3b** (Mixture of diastereomers in the ratio of 4:3)



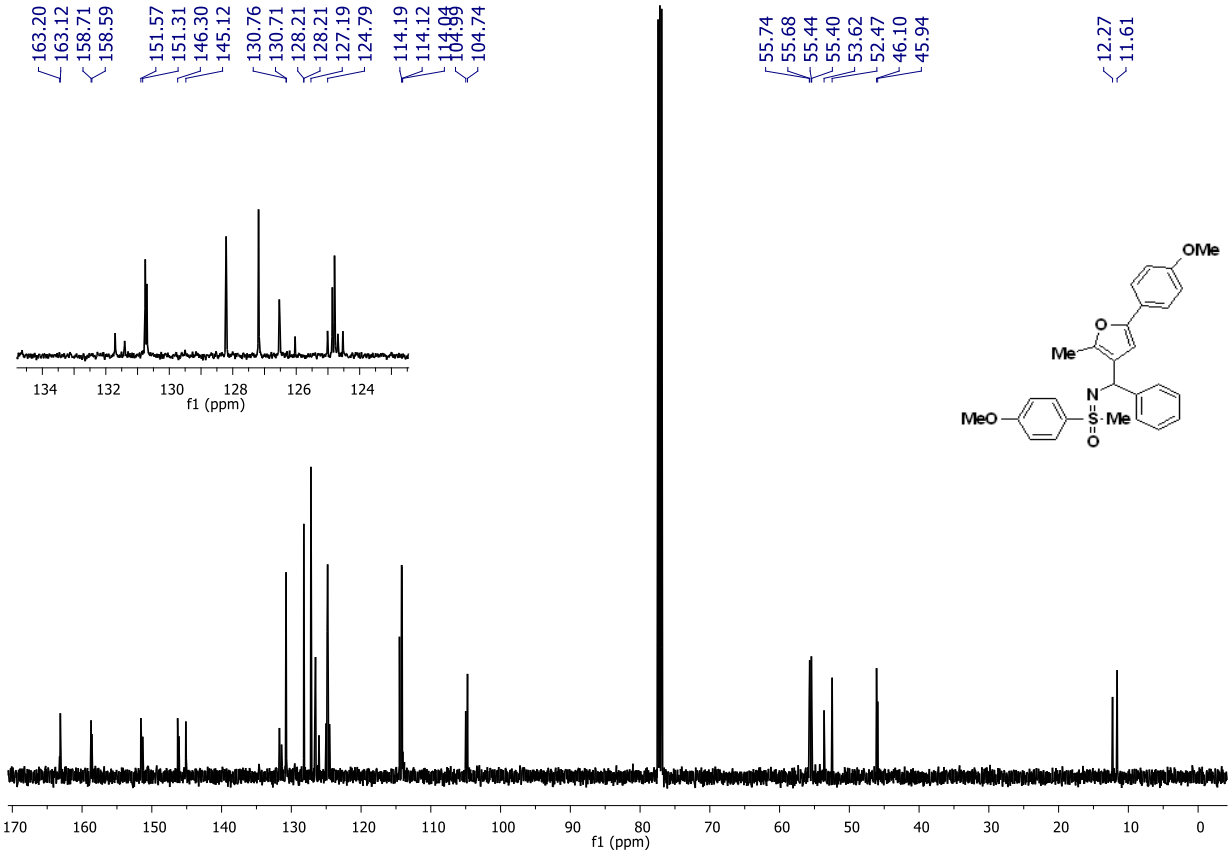
^{13}C {^{1}H} NMR of **3b** (Mixture of diastereomers in the ratio of 4:3)



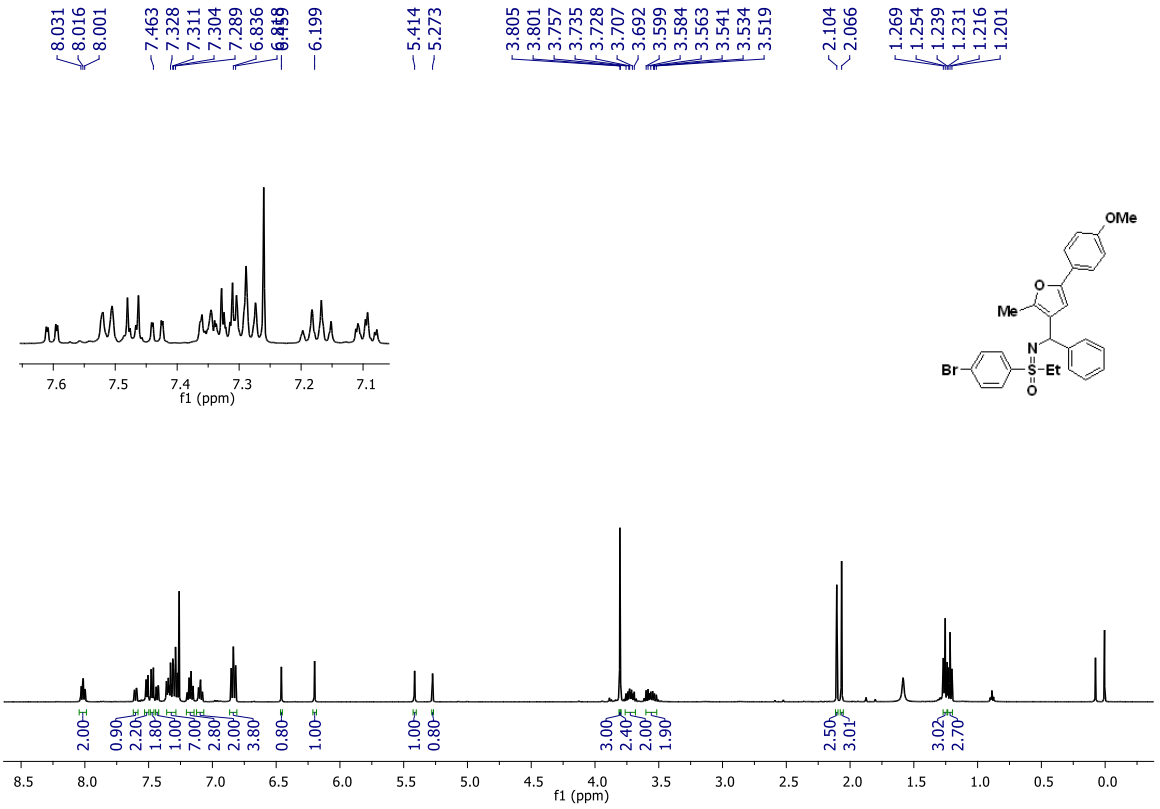
^{1}H NMR of **3c** (Mixture of diastereomers in the ratio of 4:3)



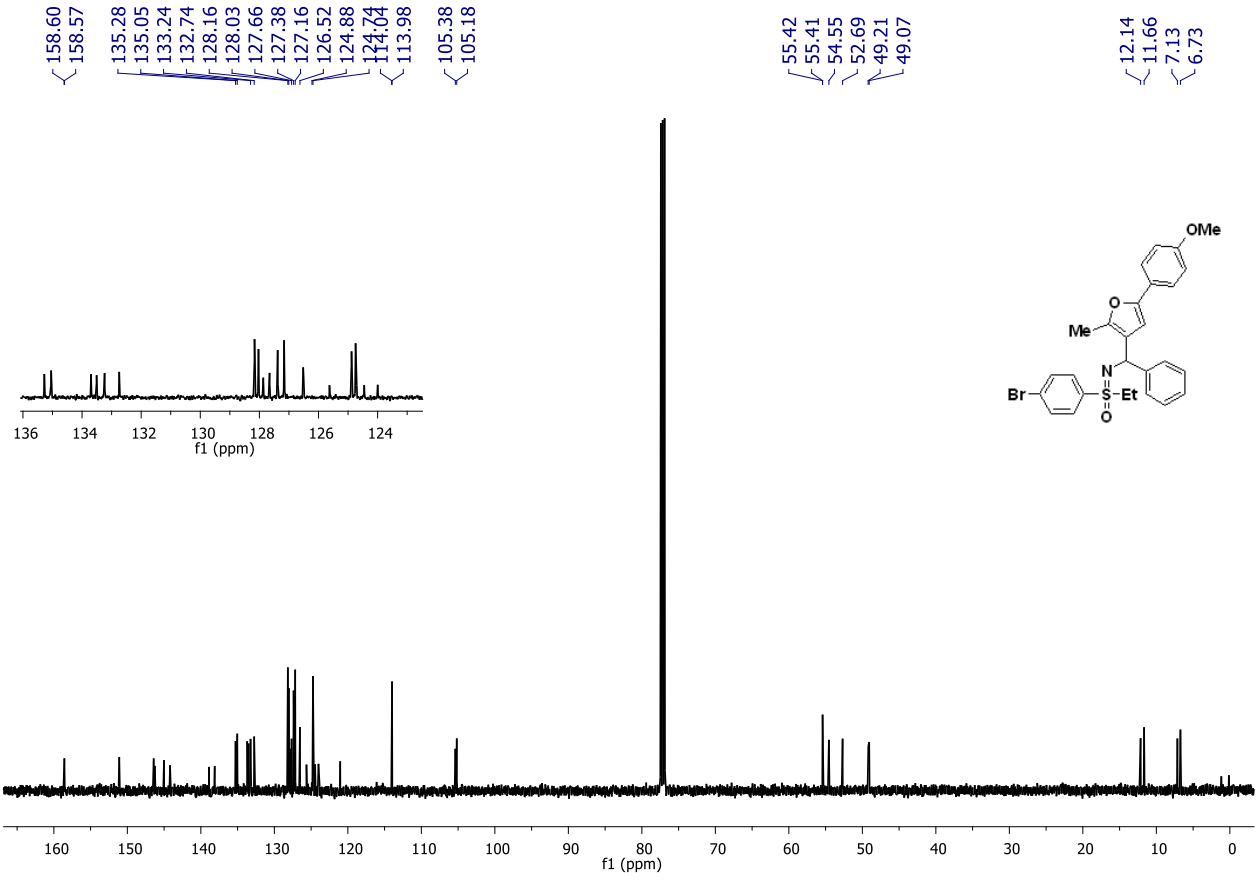
^{13}C {^{1}H} NMR of **3c** (Mixture of diastereomers in the ratio of 4 :3)



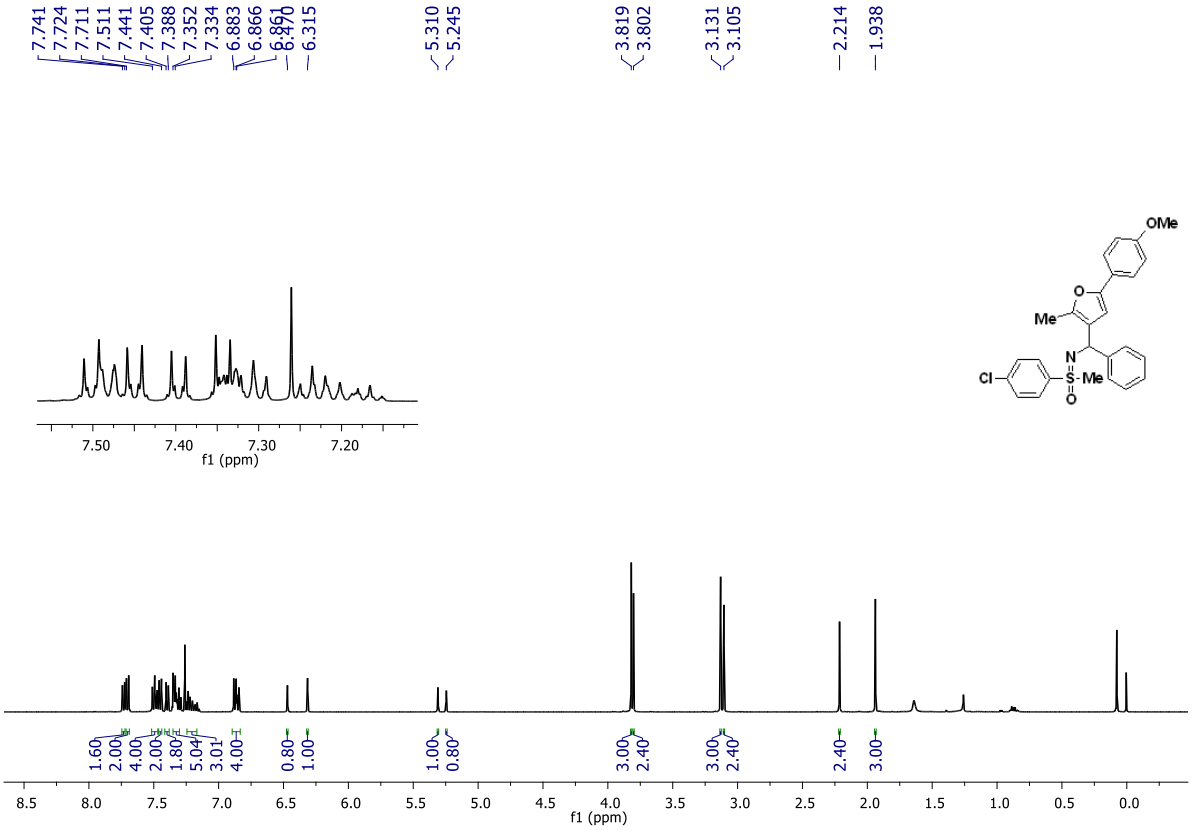
^{1}H NMR of **3d** (Mixture of diastereomers in the ratio of 5:4)



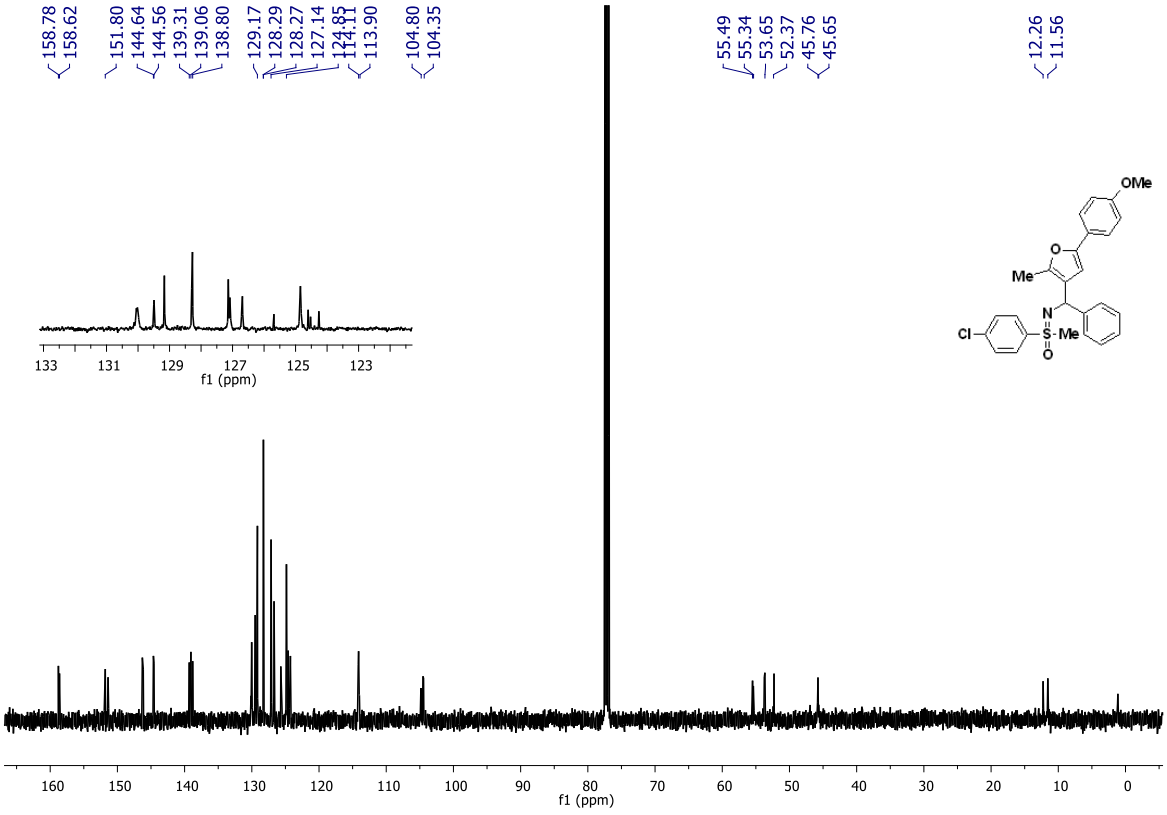
^{13}C {^{1}H} NMR of **3d** (Mixture of diastereomers in the ratio of 5:4)



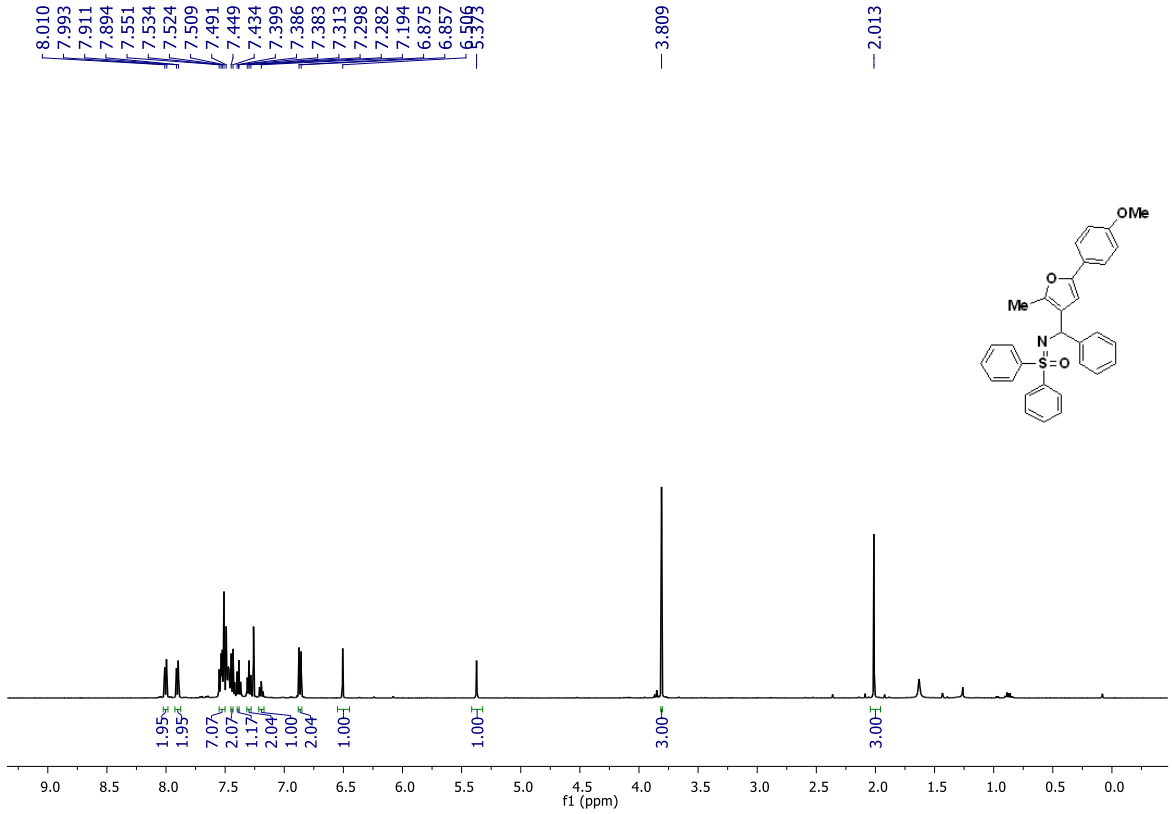
^{1}H NMR of **3e** (Mixture of diastereomers in the ratio of 5:4)



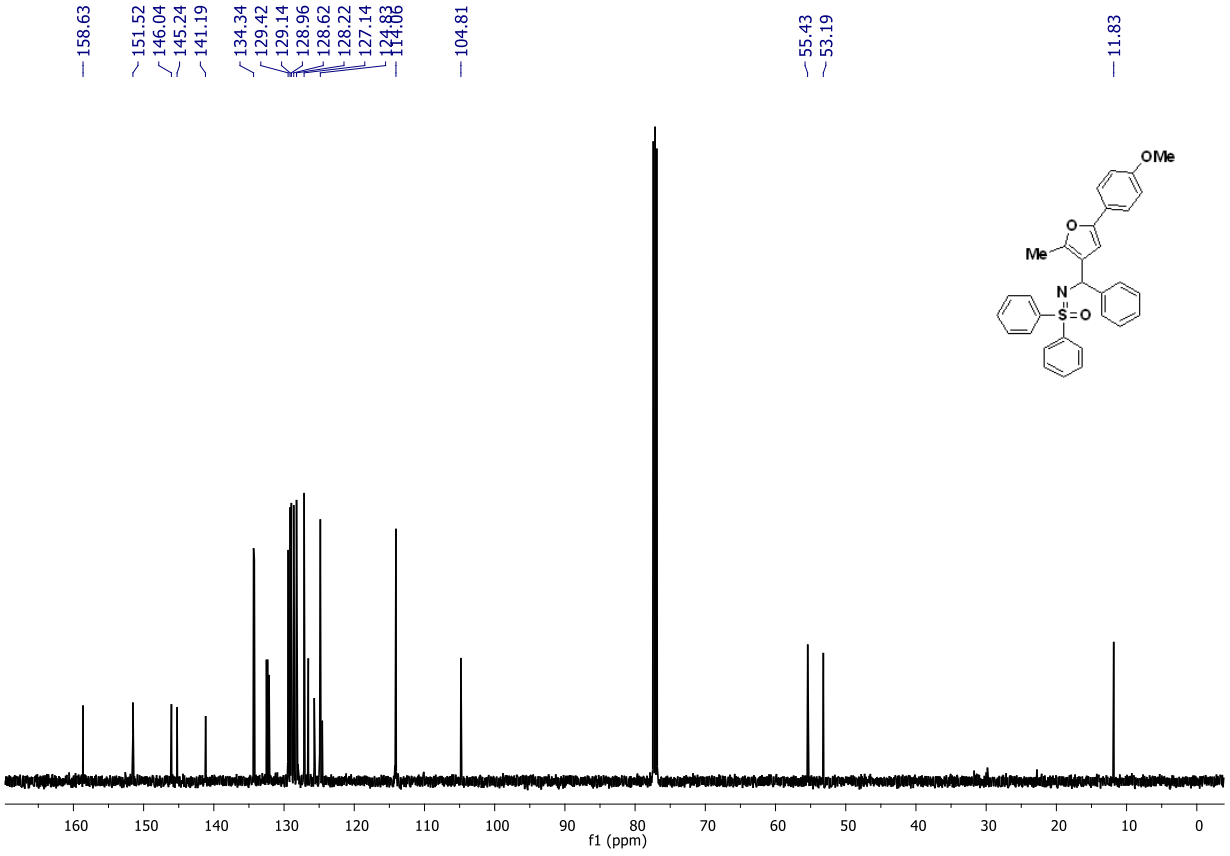
^{13}C {^{1}H} NMR of **3e** (Mixture of diastereomers in the ratio of 5:4)



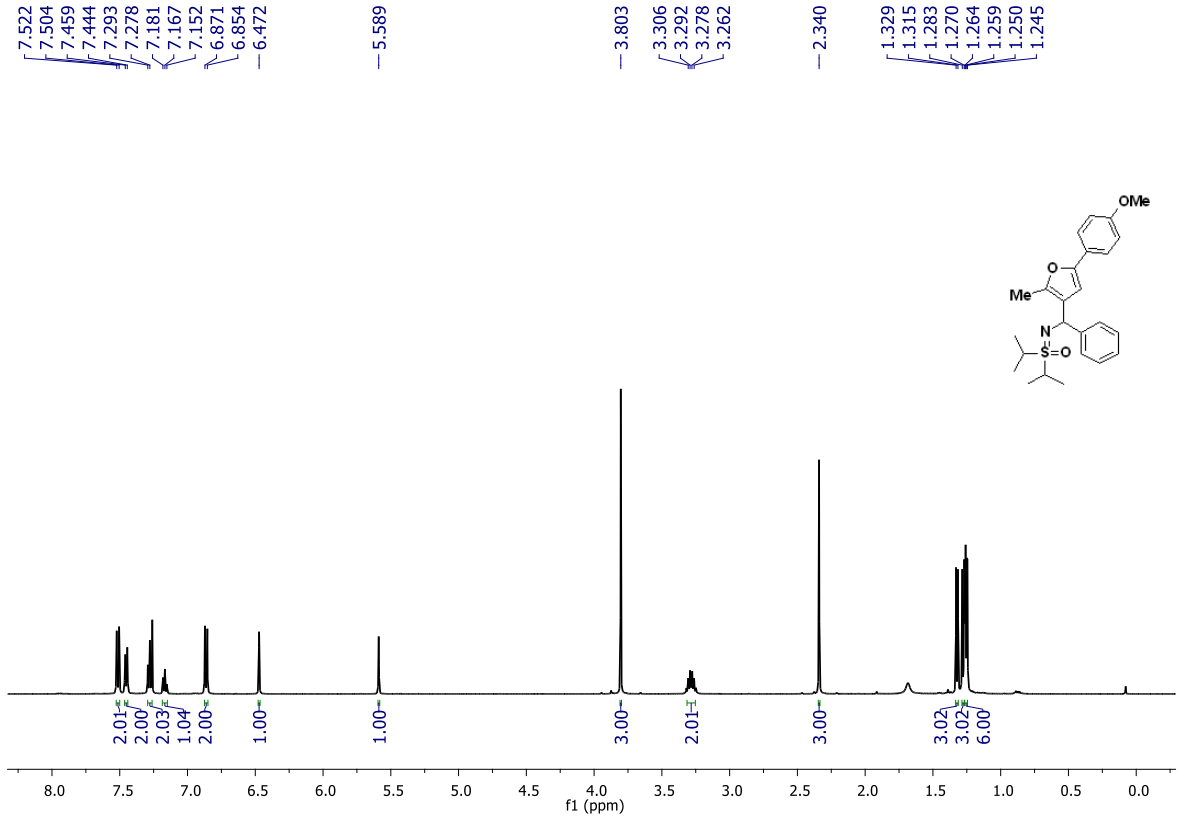
^{1}H NMR of **3f**



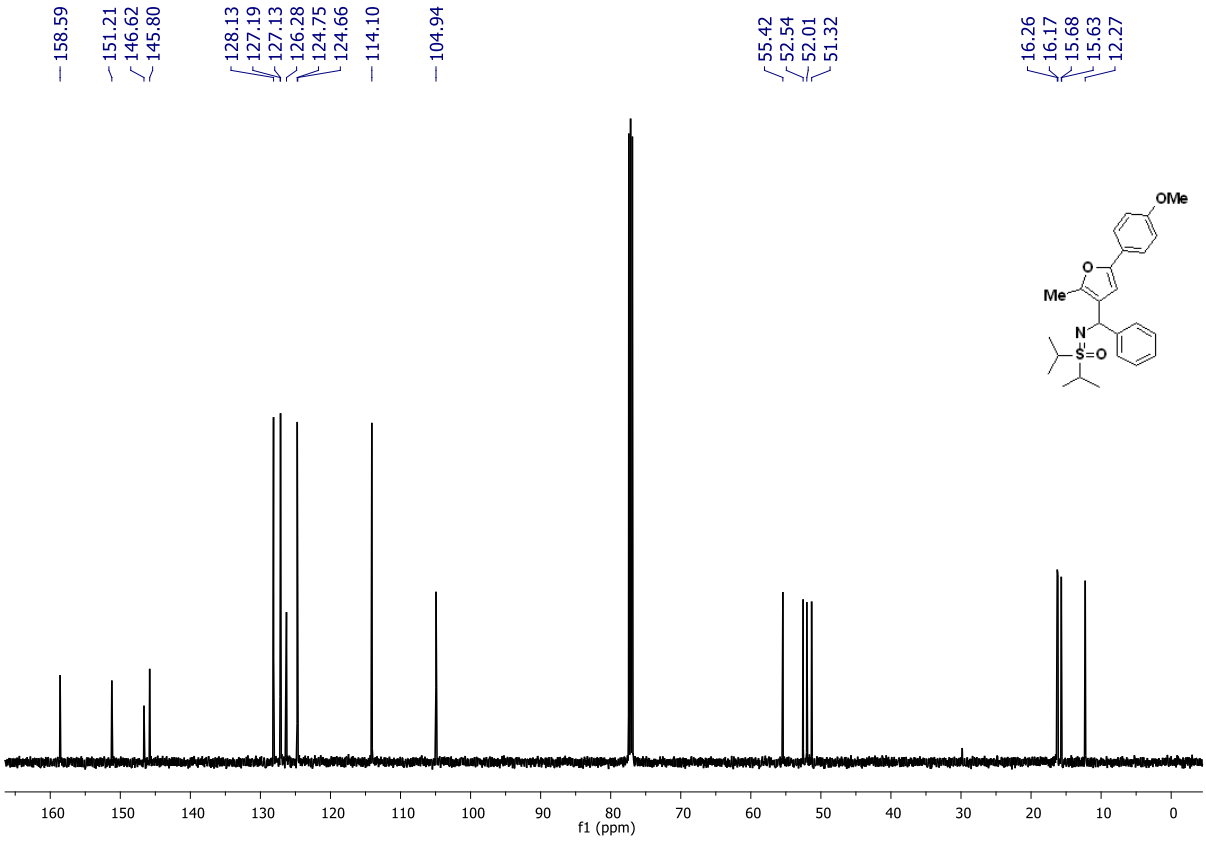
^{13}C {^{1}H} NMR of **3f**



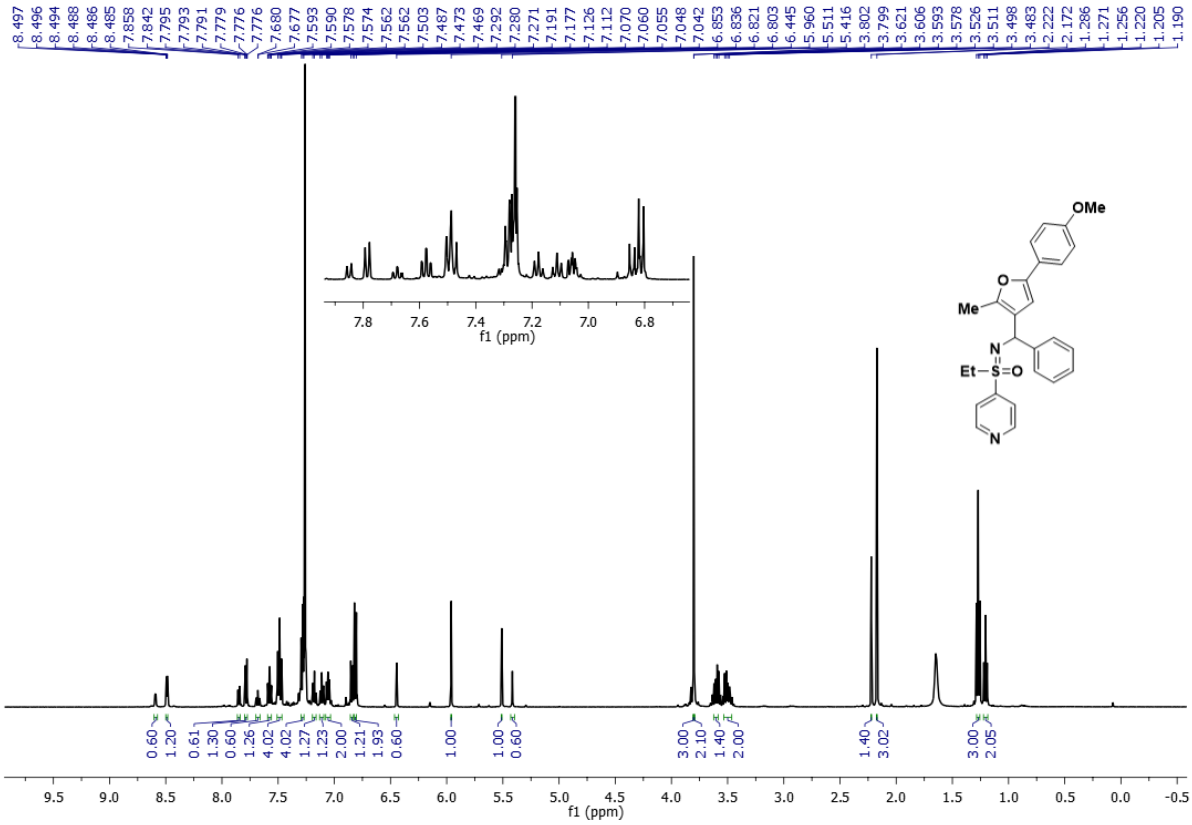
^{1}H NMR of **3g**



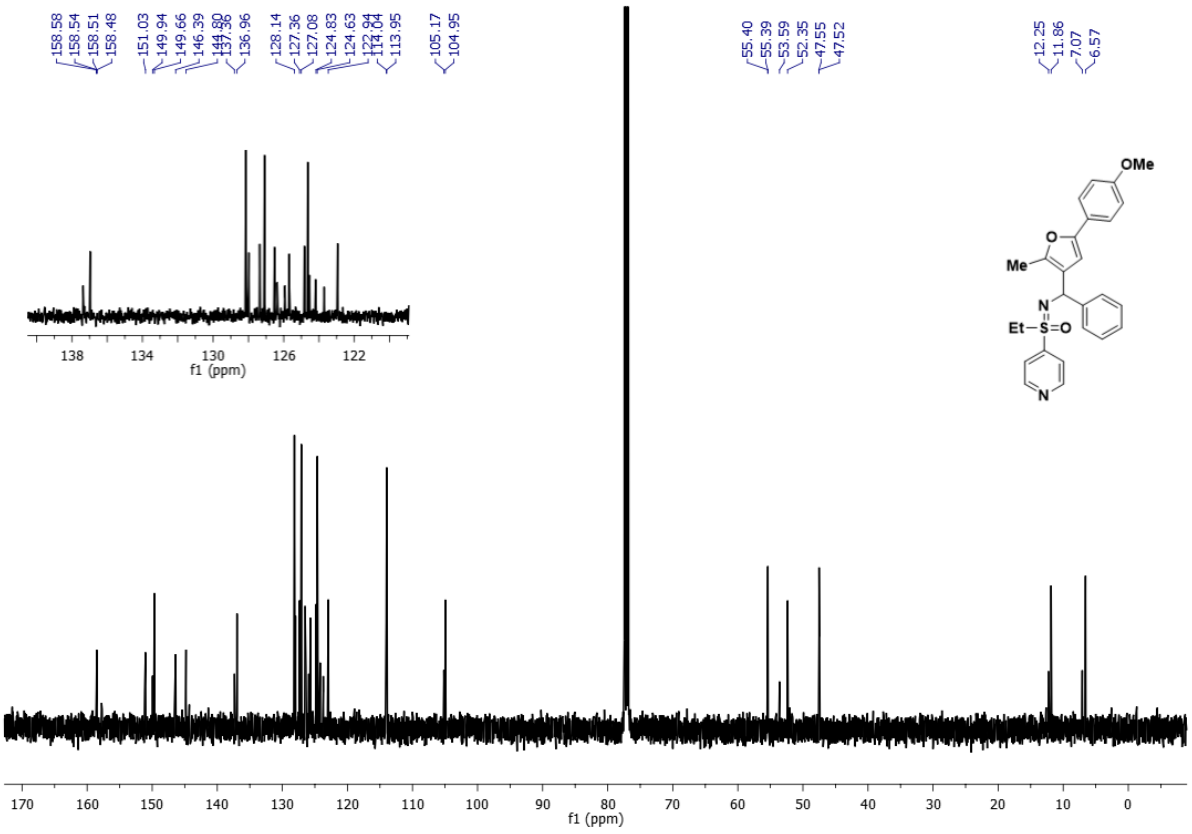
^{13}C {^{1}H} NMR of **3g**



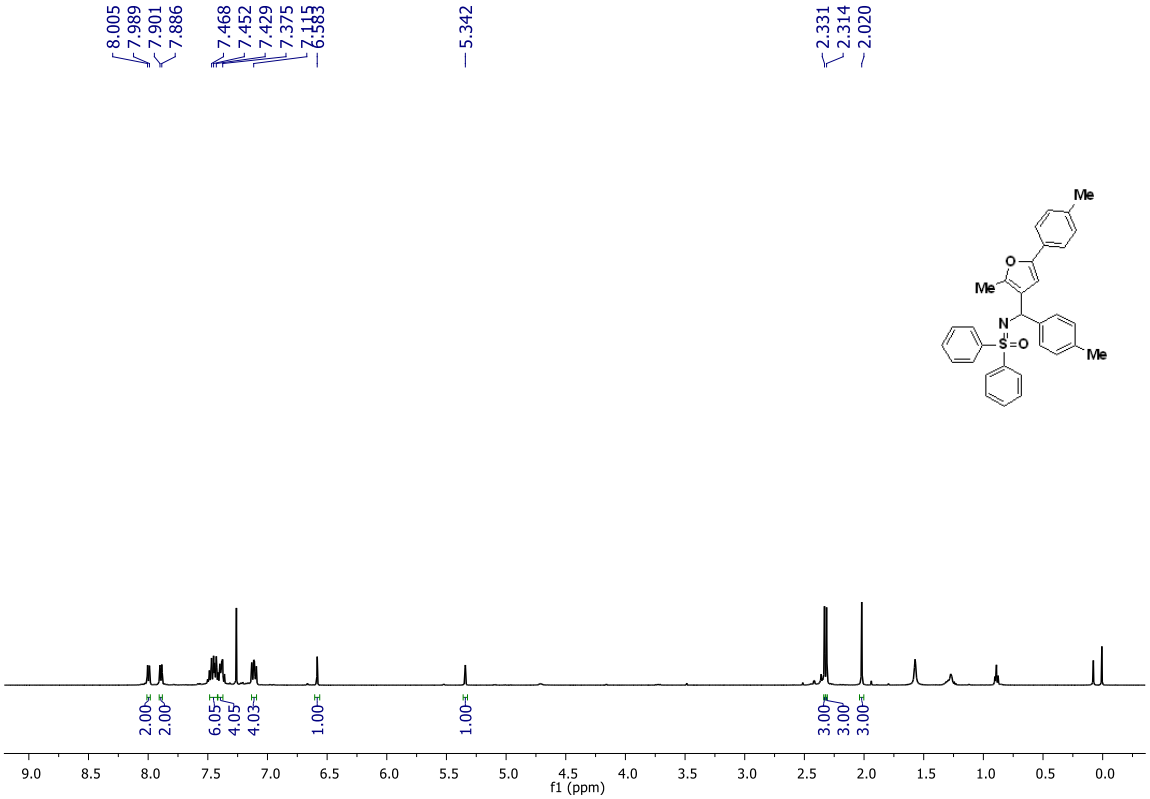
^{1}H NMR of **3h** (Mixture of diastereomers in the ratio of 1:0.6)



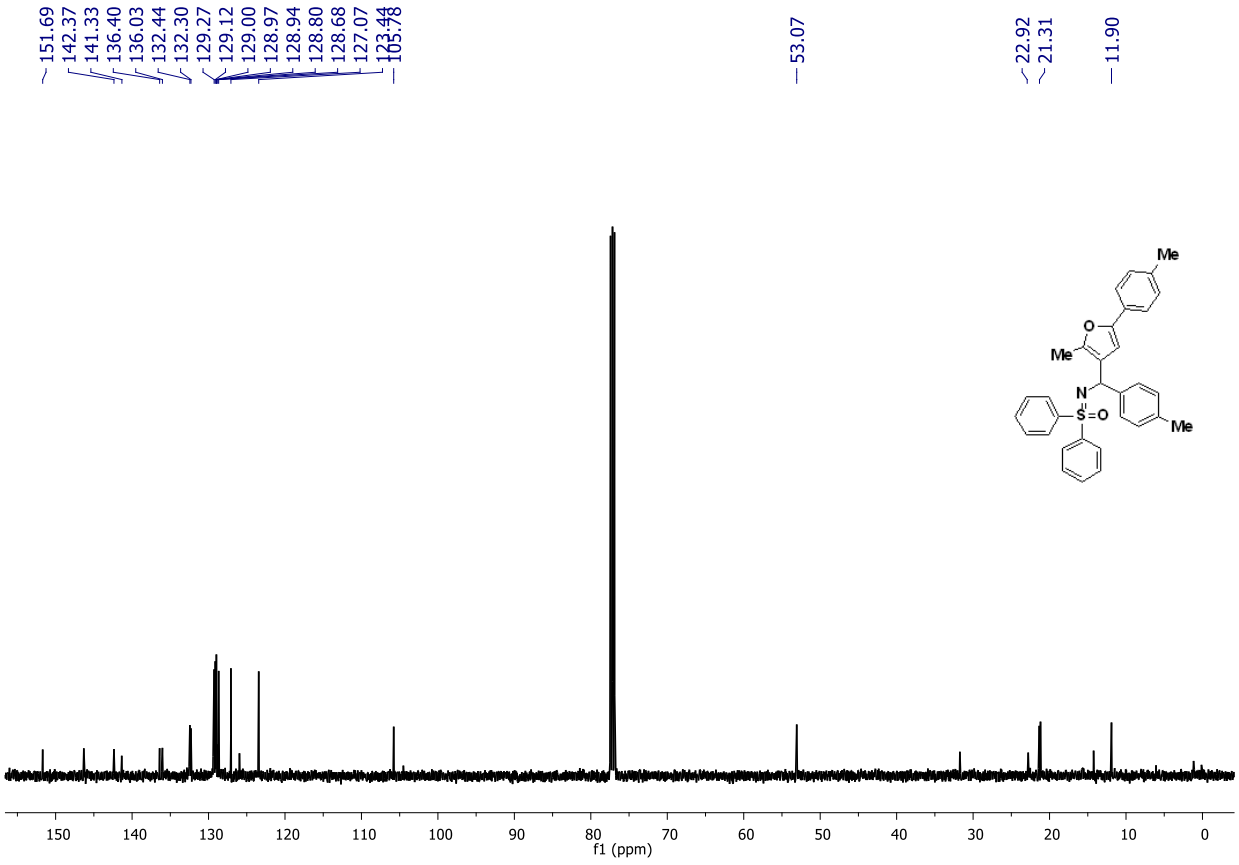
^{13}C {^{1}H} NMR of **3h** (Mixture of diastereomers in the ratio of 1:0.6)



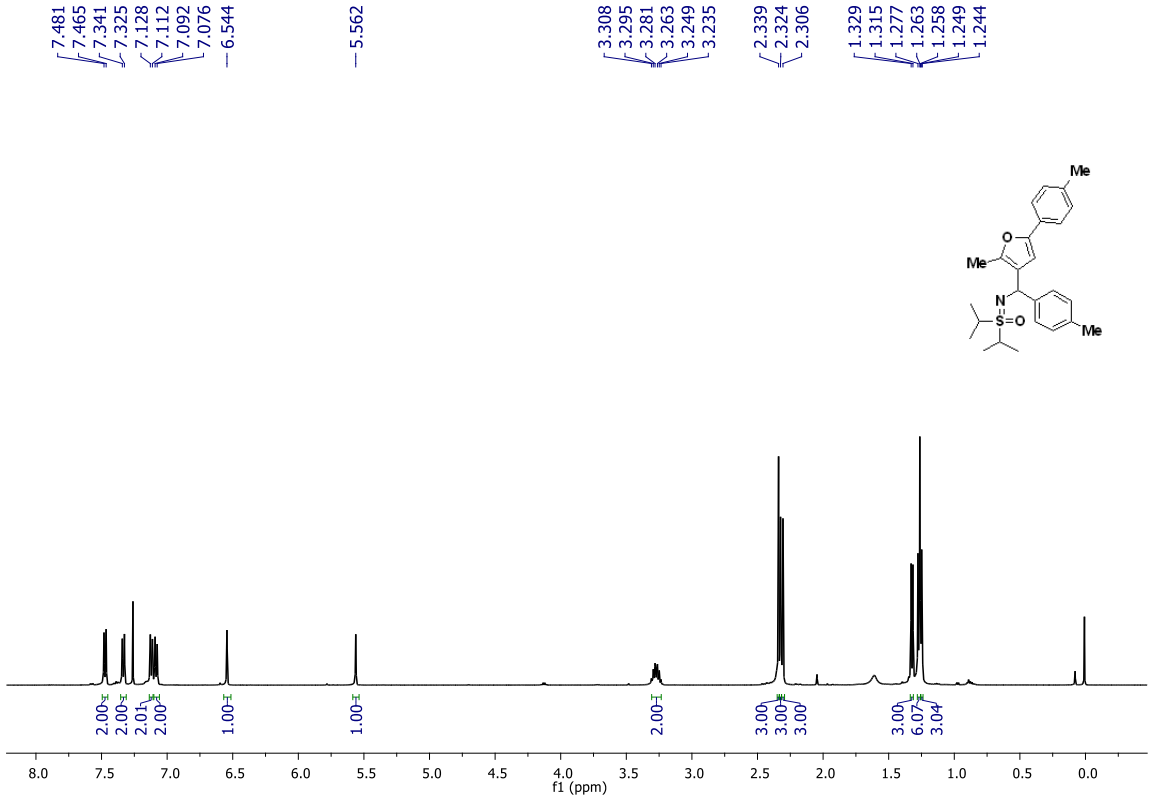
^{1}H NMR of **3i**



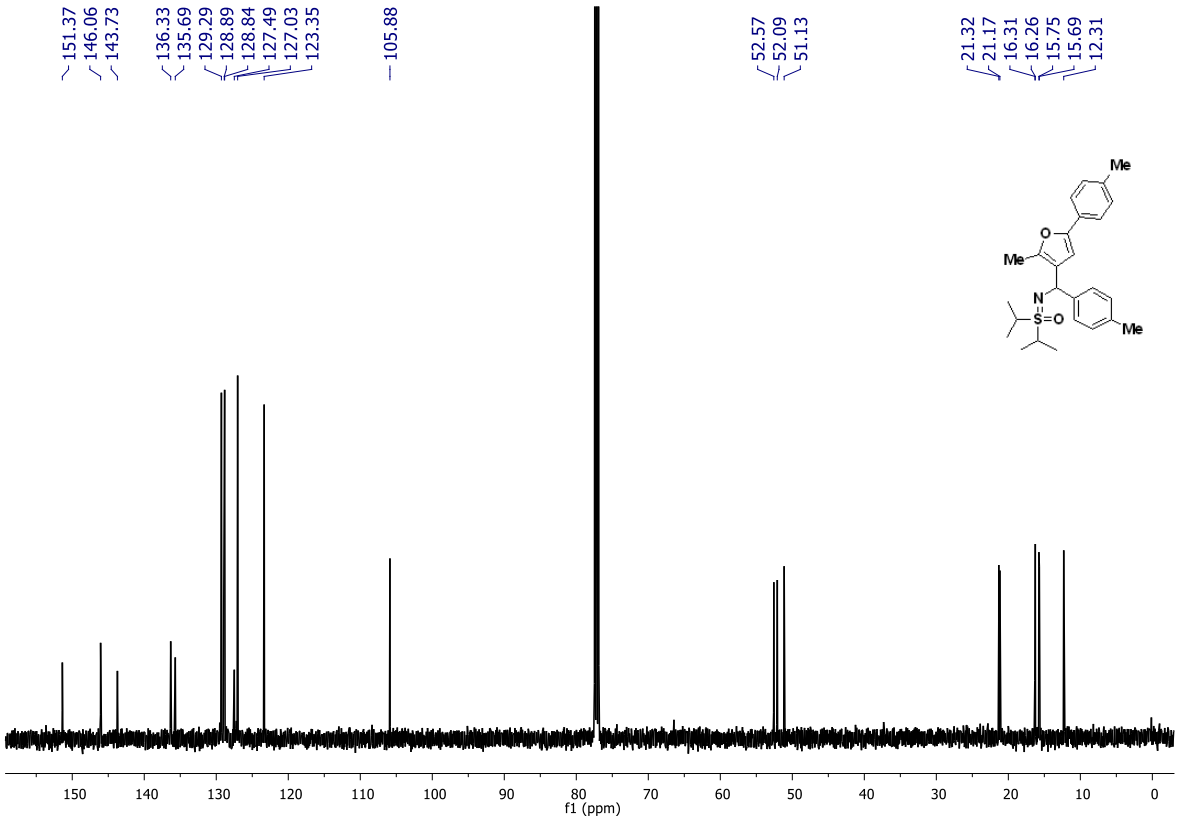
^{13}C {^{1}H} NMR of **3i**



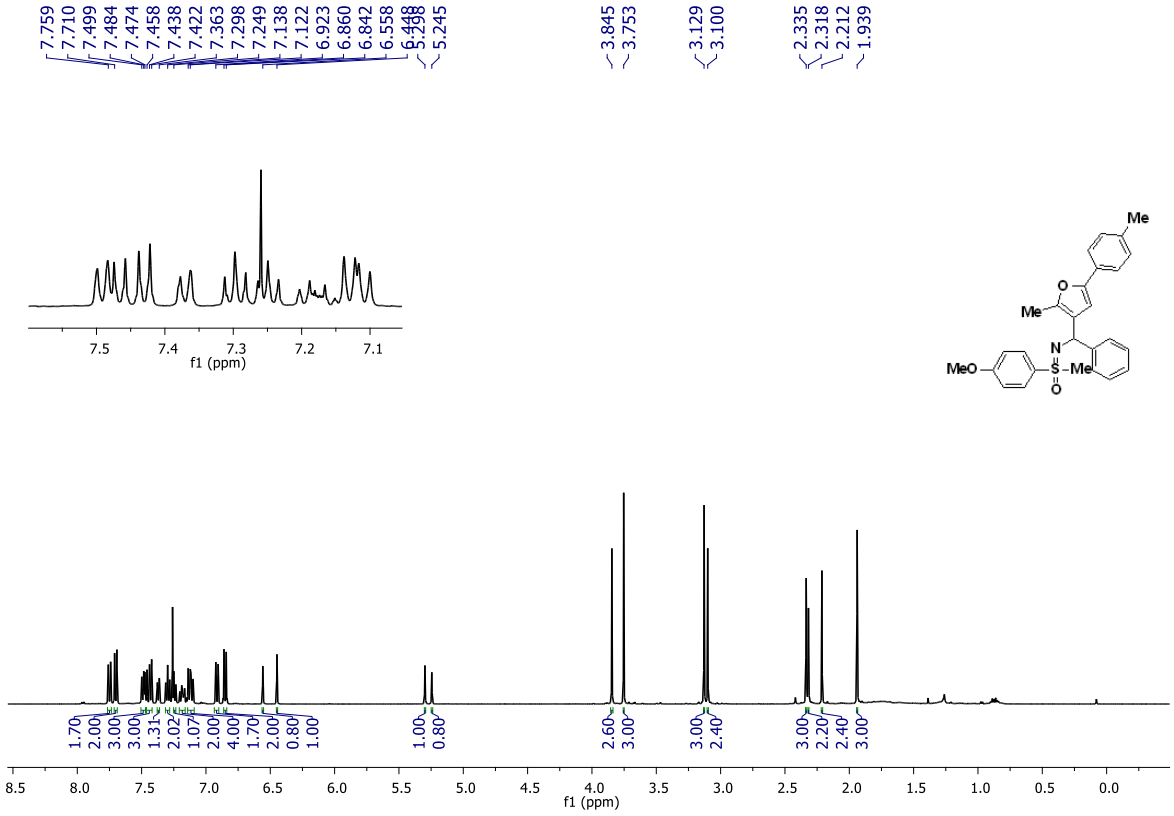
^{1}H NMR of **3j**



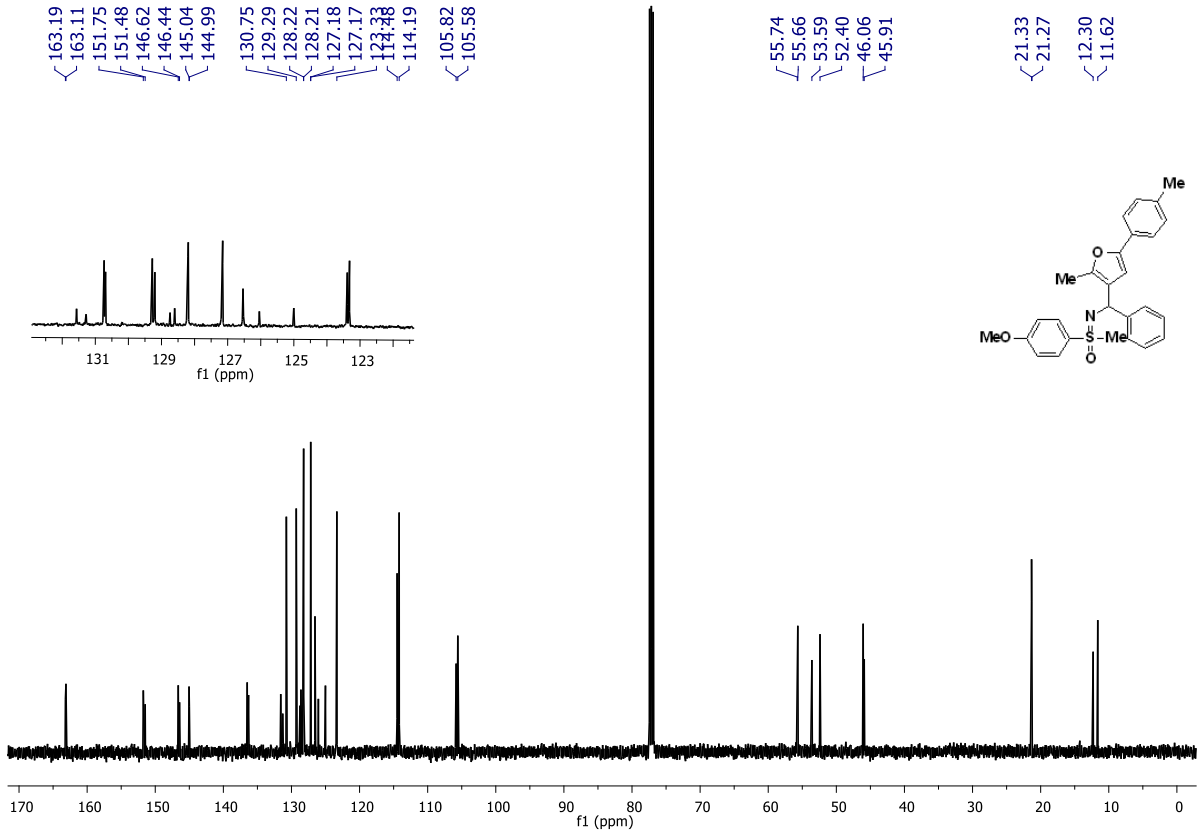
^{13}C {^{1}H} NMR of **3j**



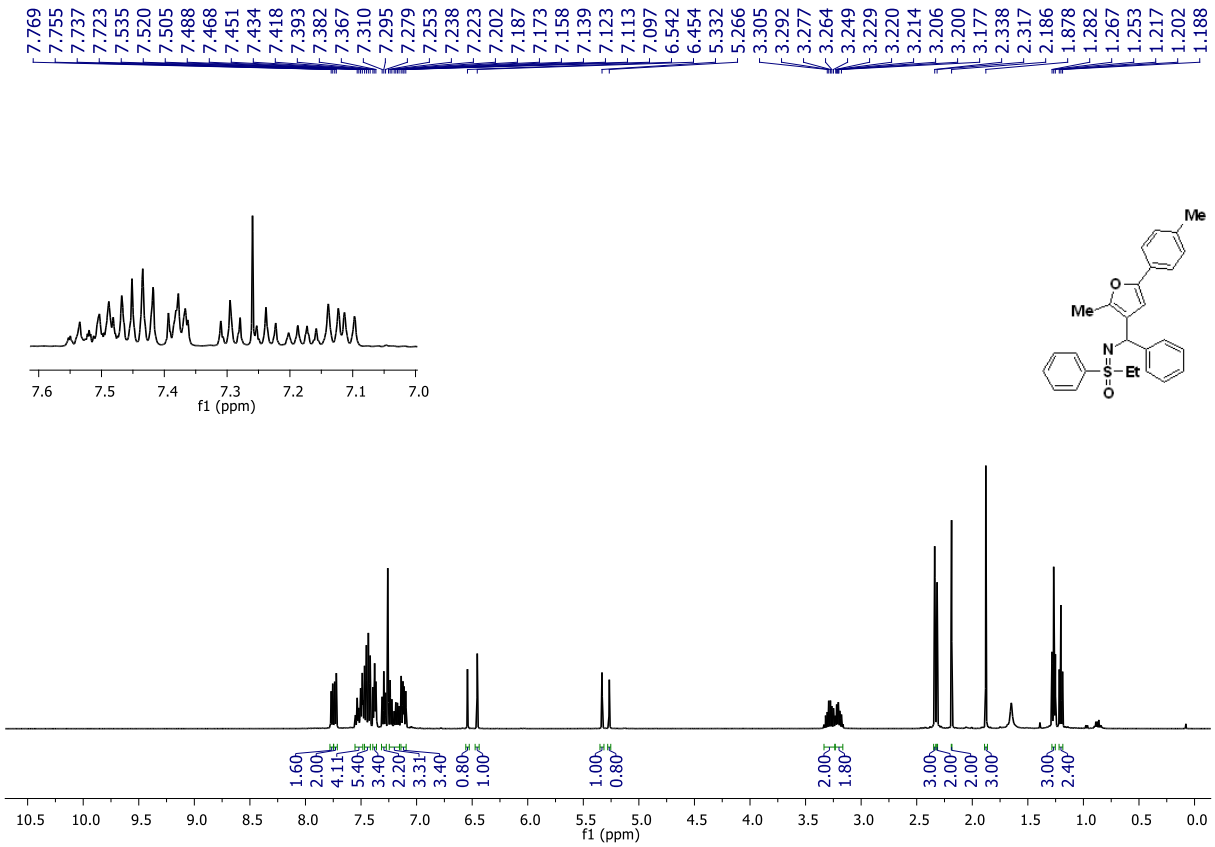
^{1}H NMR of **3k** (Mixture of diastereomers in the ratio of 5:4)



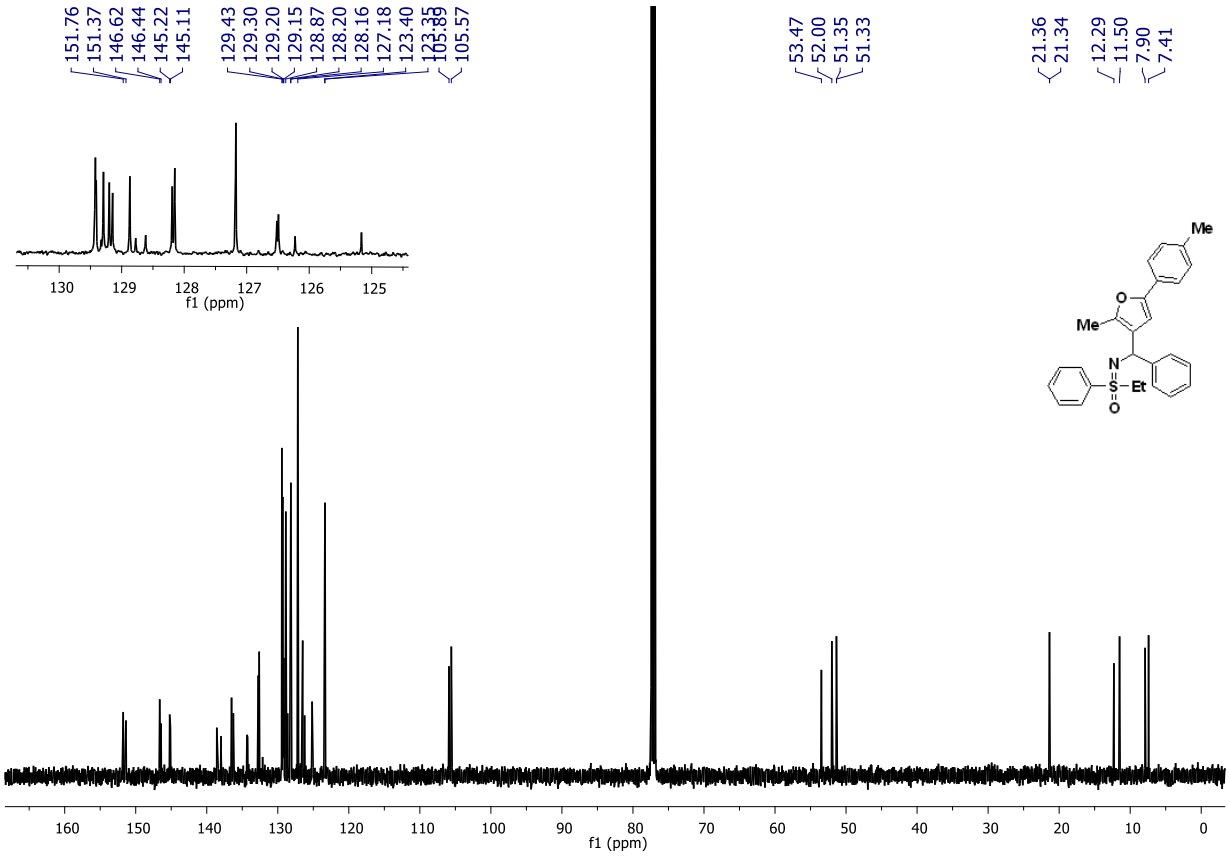
^{13}C {^{1}H} NMR of **3k** (Mixture of diastereomers in the ratio of 5:4)



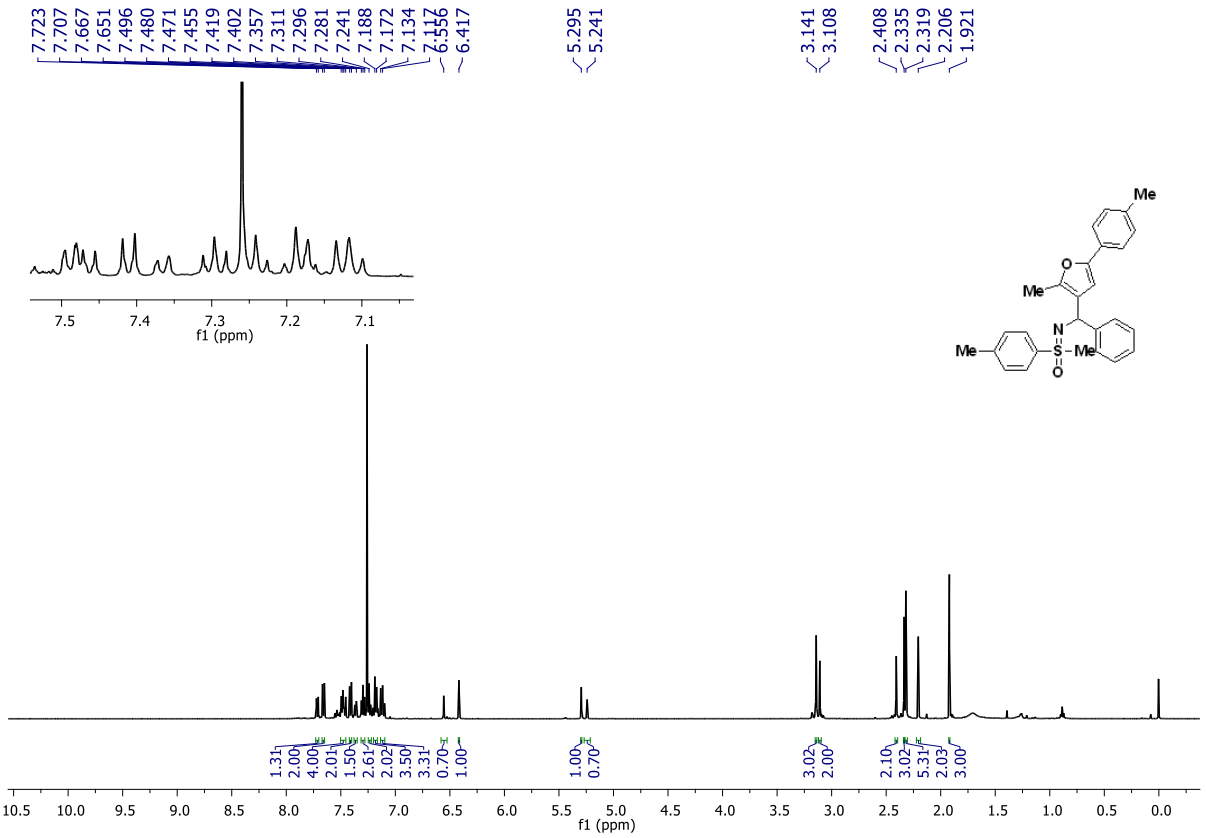
^{1}H NMR of **3l** (Mixture of diastereomers in the ratio of 5:4)



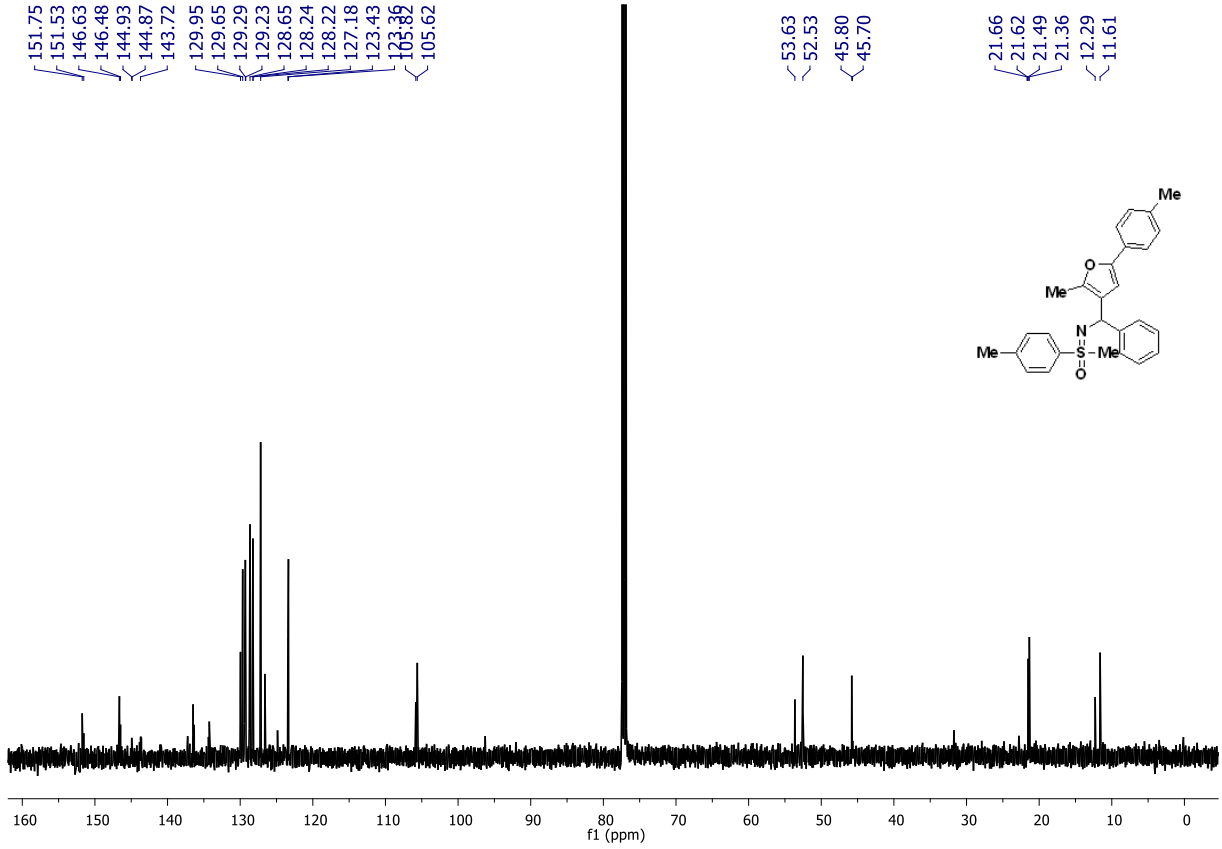
^{13}C {^{1}H} NMR of **3l** (Mixture of diastereomers in the ratio of 5:4)



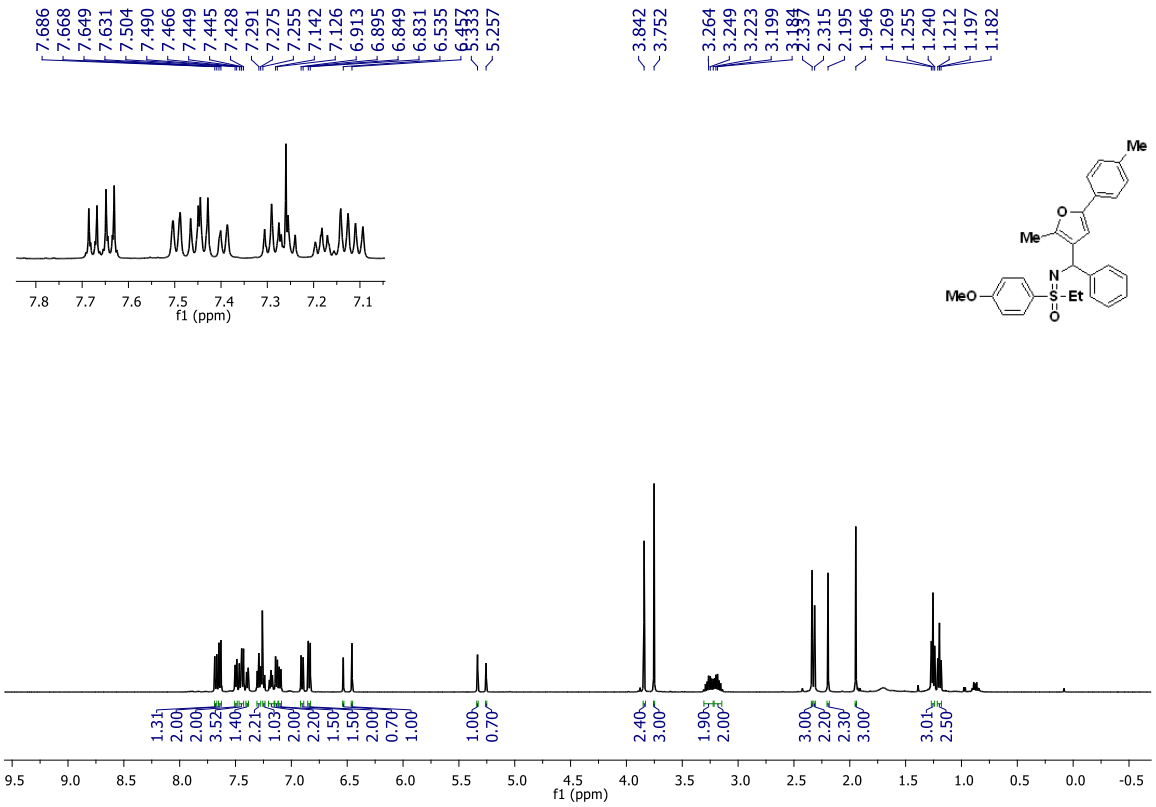
^{1}H NMR of **3m** (Mixture of diastereomers in the ratio of 4:3)



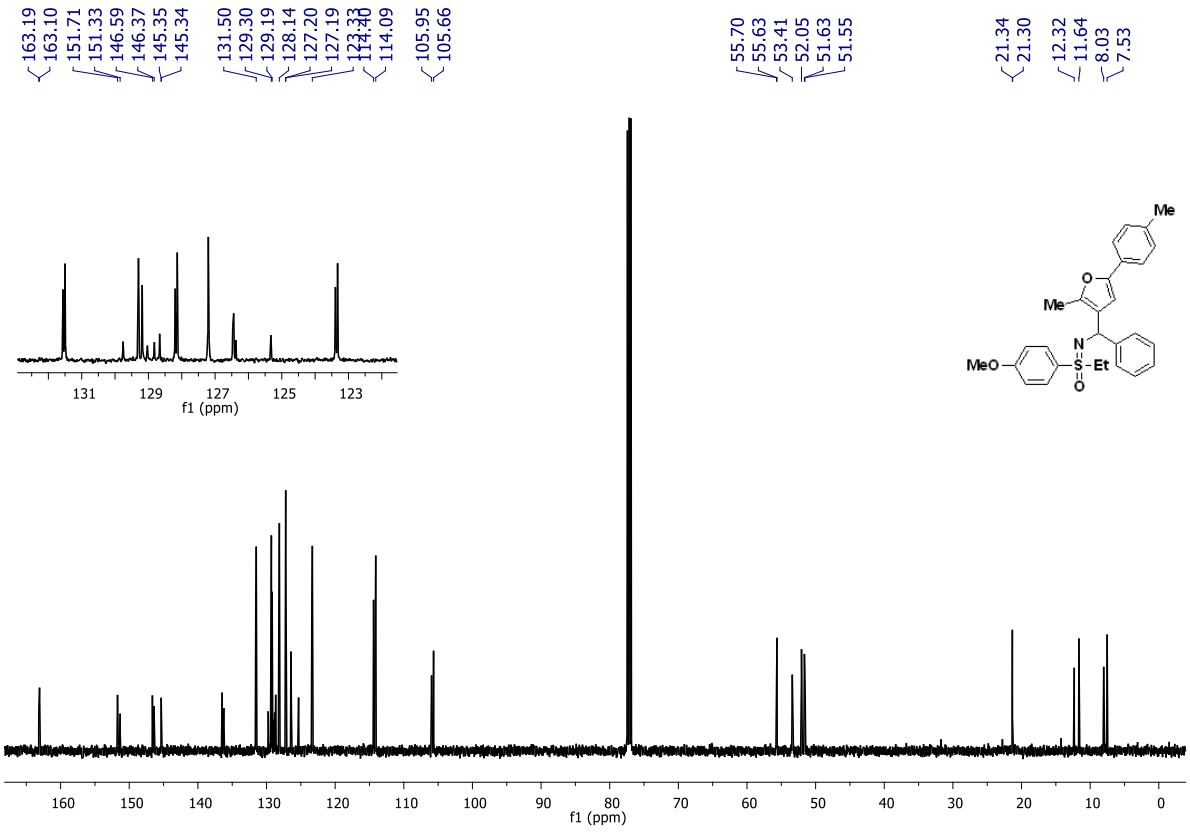
^{13}C {^{1}H} NMR of **3m** (Mixture of diastereomers in the ratio of 4:3)



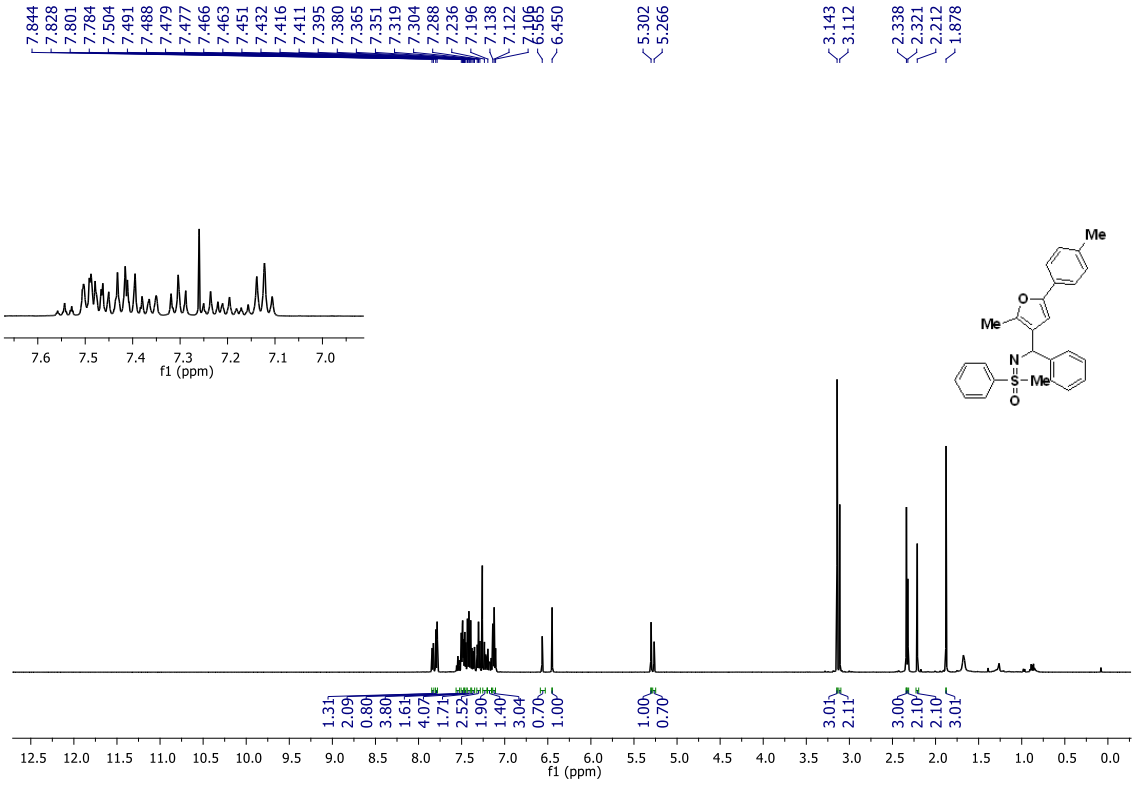
^{1}H NMR of **3n** (Mixture of diastereomers in the ratio of 4:3)



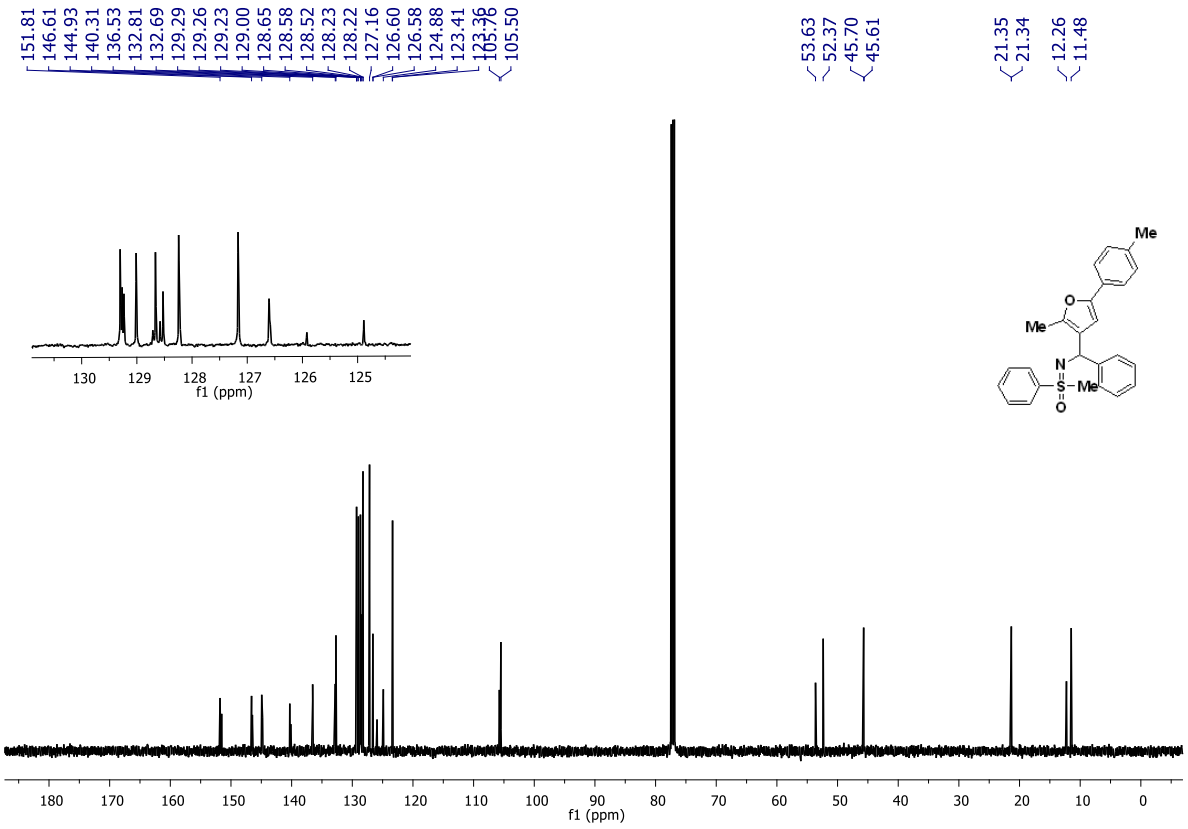
^{13}C {^{1}H} NMR of **3n** (Mixture of diastereomers in the ratio of 4:3)



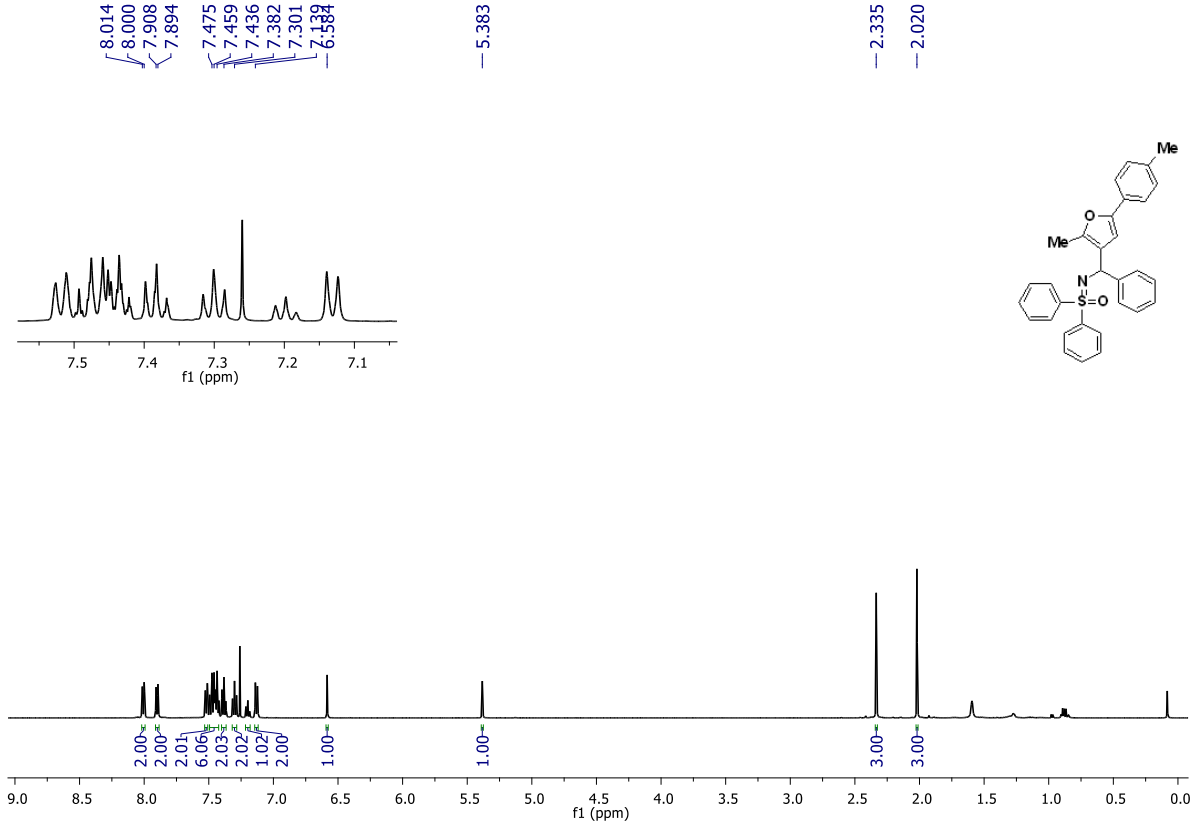
^{1}H NMR of **3o** (Mixture of diastereomers in the ratio of 4:3)



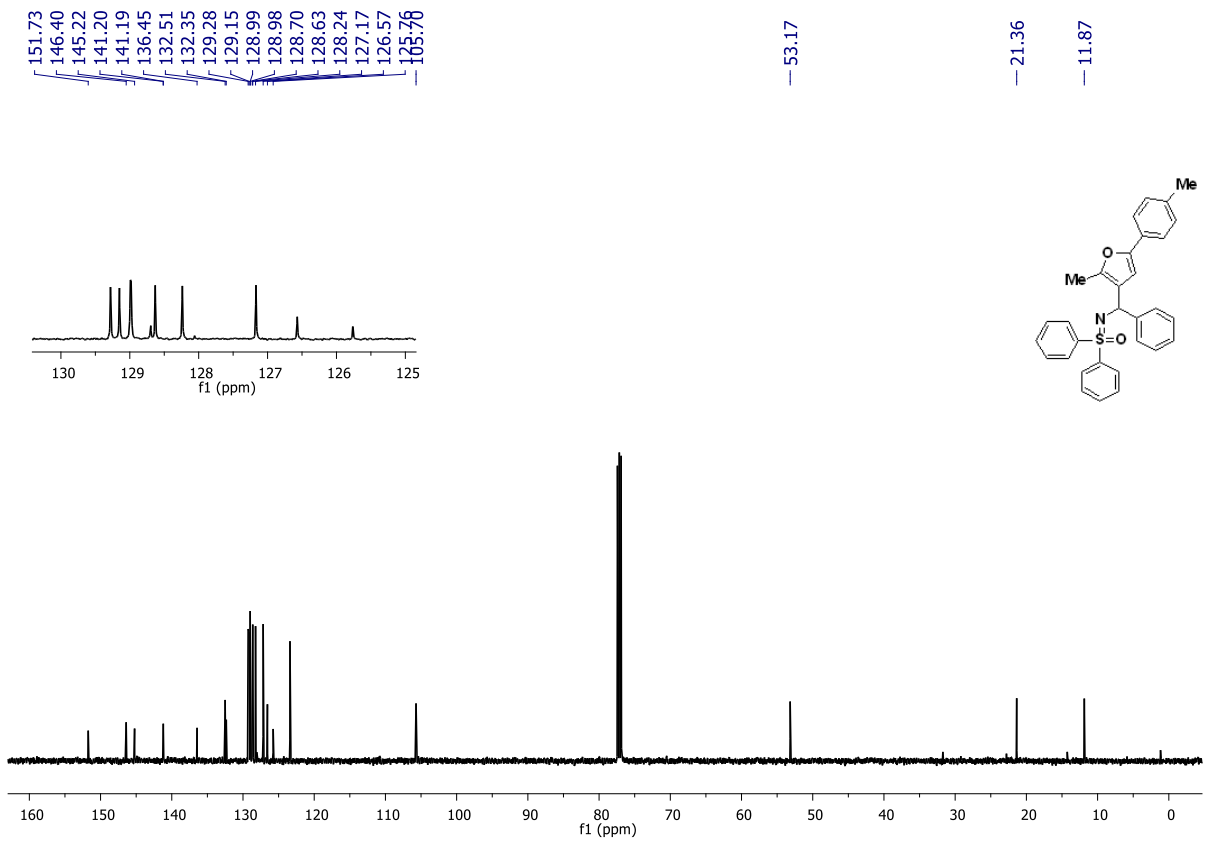
^{13}C {^{1}H} NMR of **3o** (Mixture of diastereomers in the ratio of 4:3)



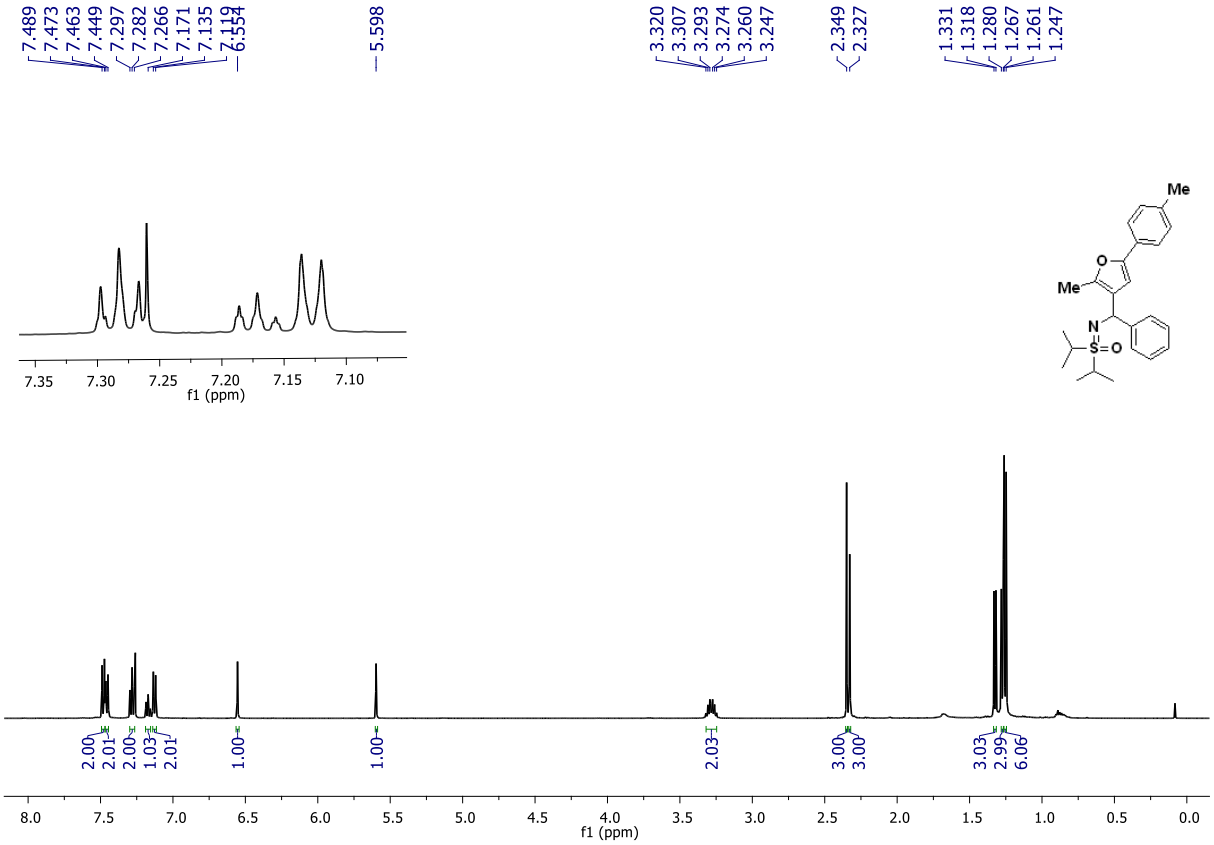
^{1}H NMR of **3p**



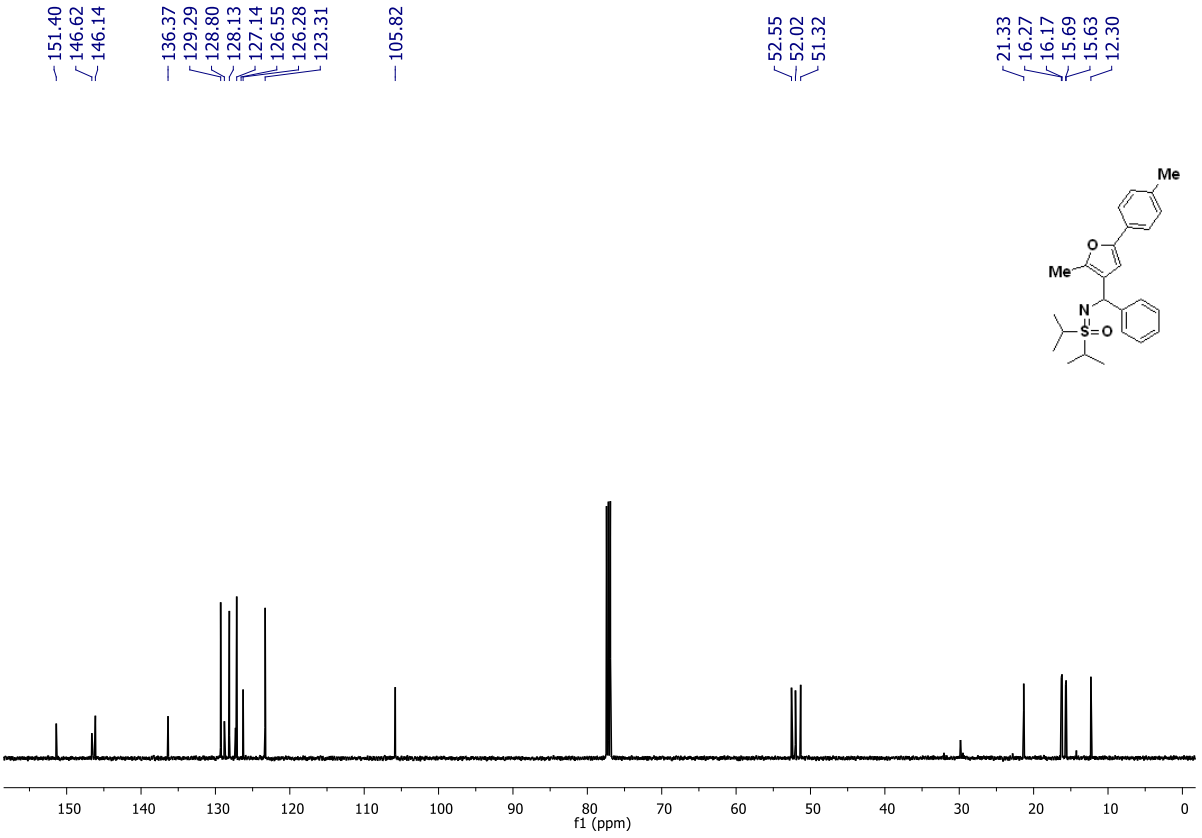
^{13}C {^{1}H} NMR of **3p**



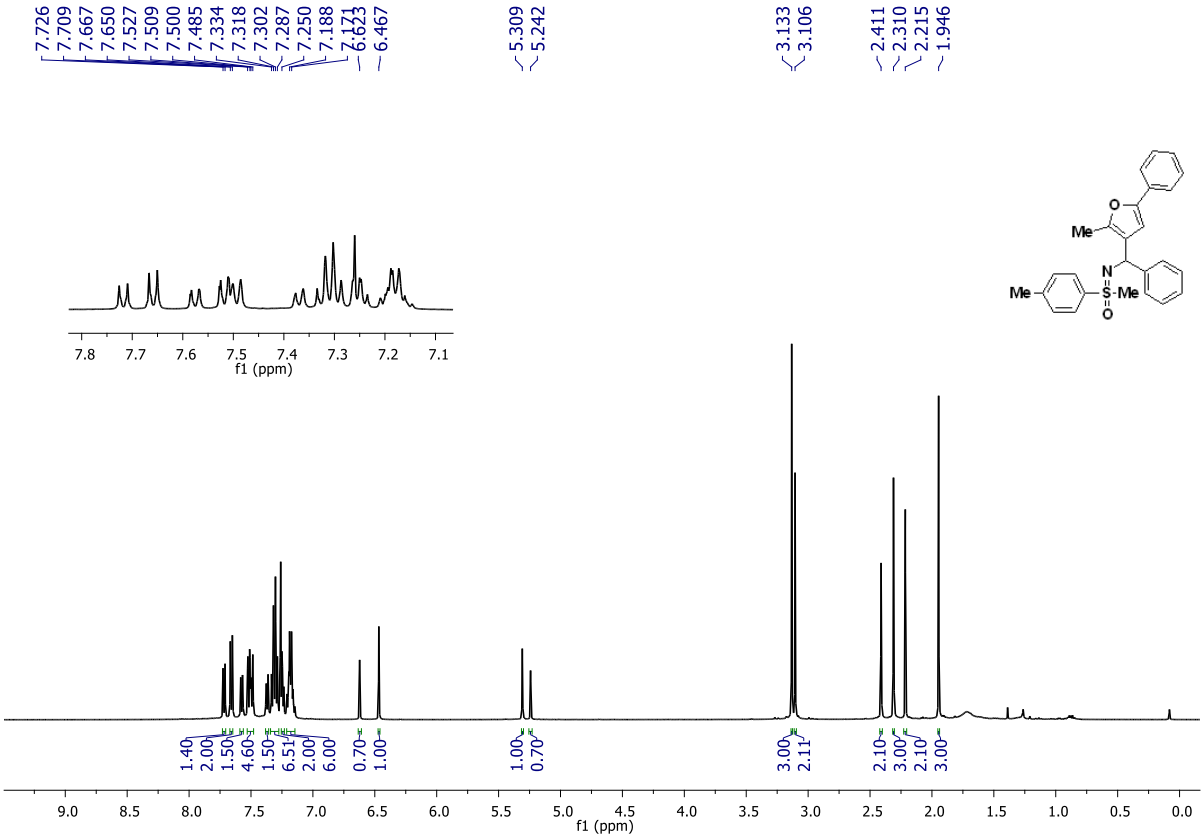
^{1}H NMR of **3q**



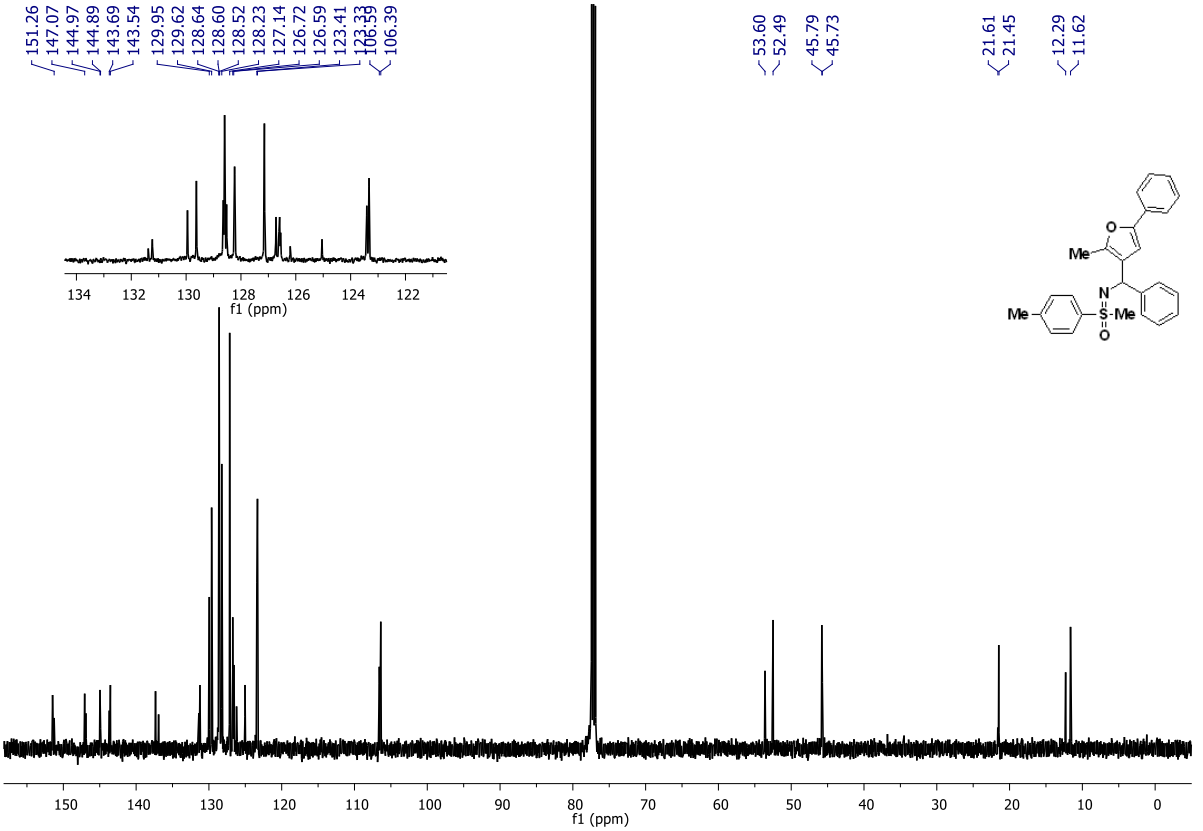
^{13}C {^{1}H} NMR of **3q**



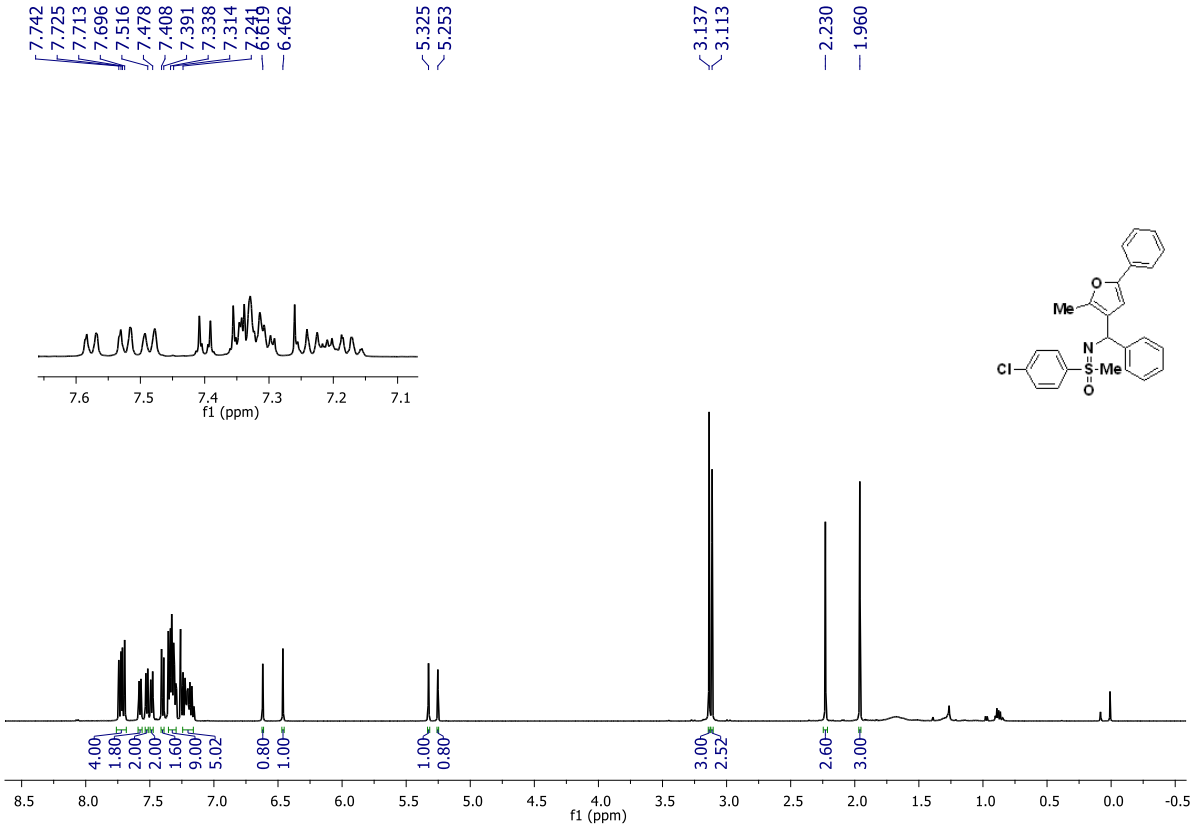
^{1}H NMR of **3r** (Mixture of diastereomers in the ratio of 4:3)



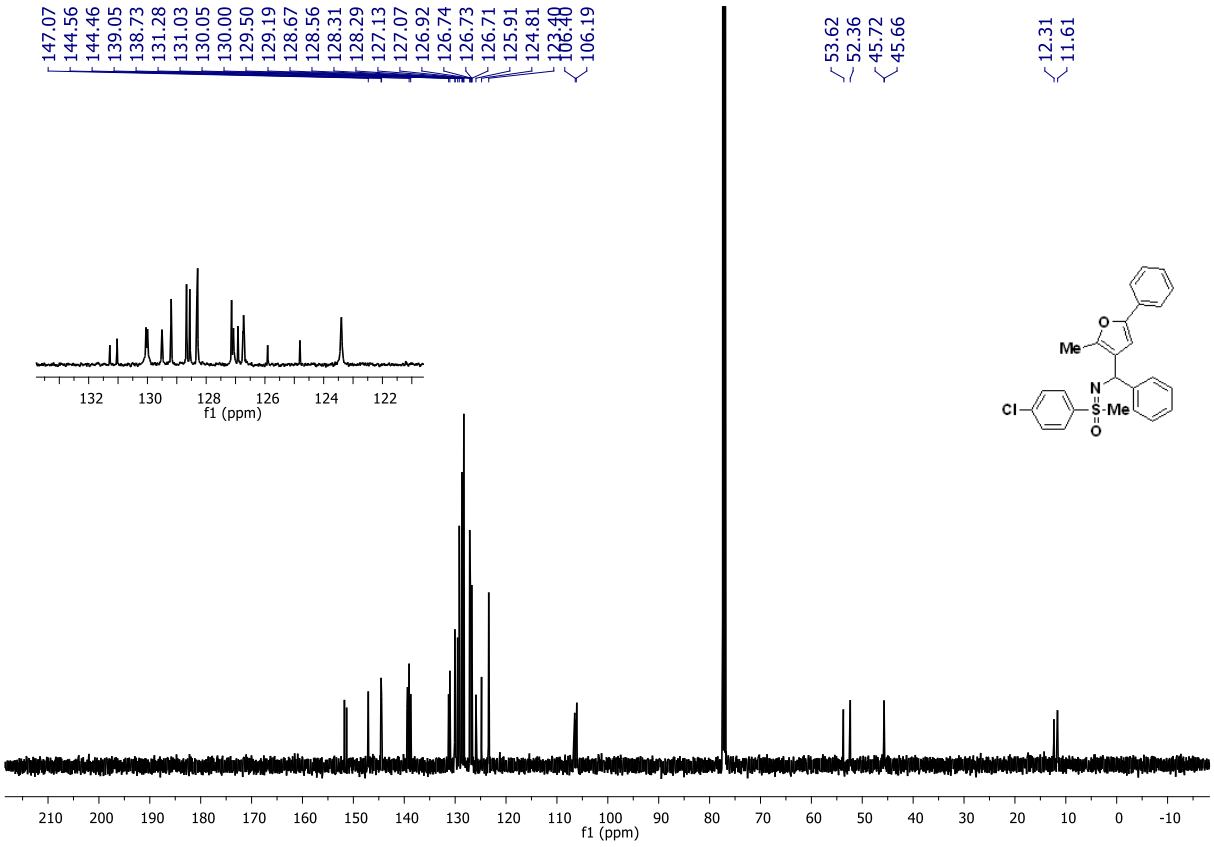
^{13}C {^{1}H} NMR of **3r** (Mixture of diastereomers in the ratio of 4:3)



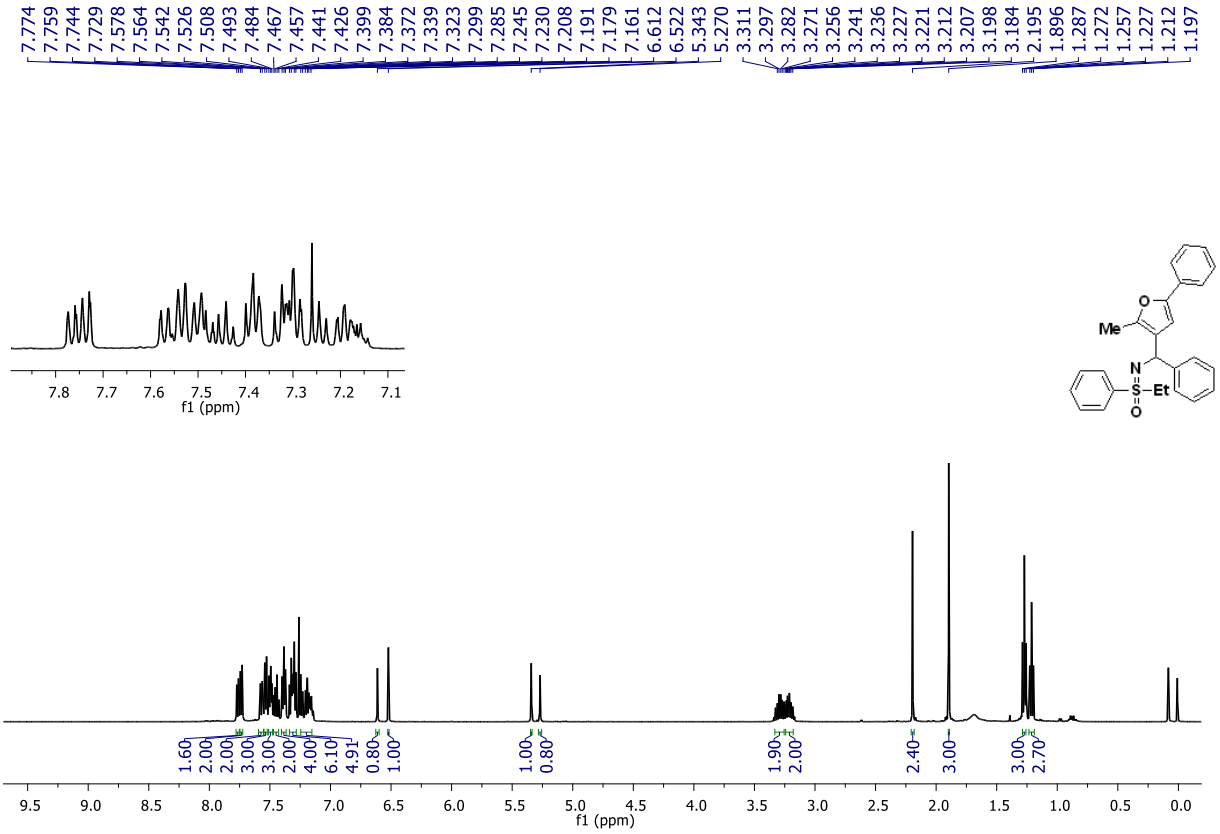
^{1}H NMR of **3s** (Mixture of diastereomers (Mixture of diastereomers in the ratio of 5:4)



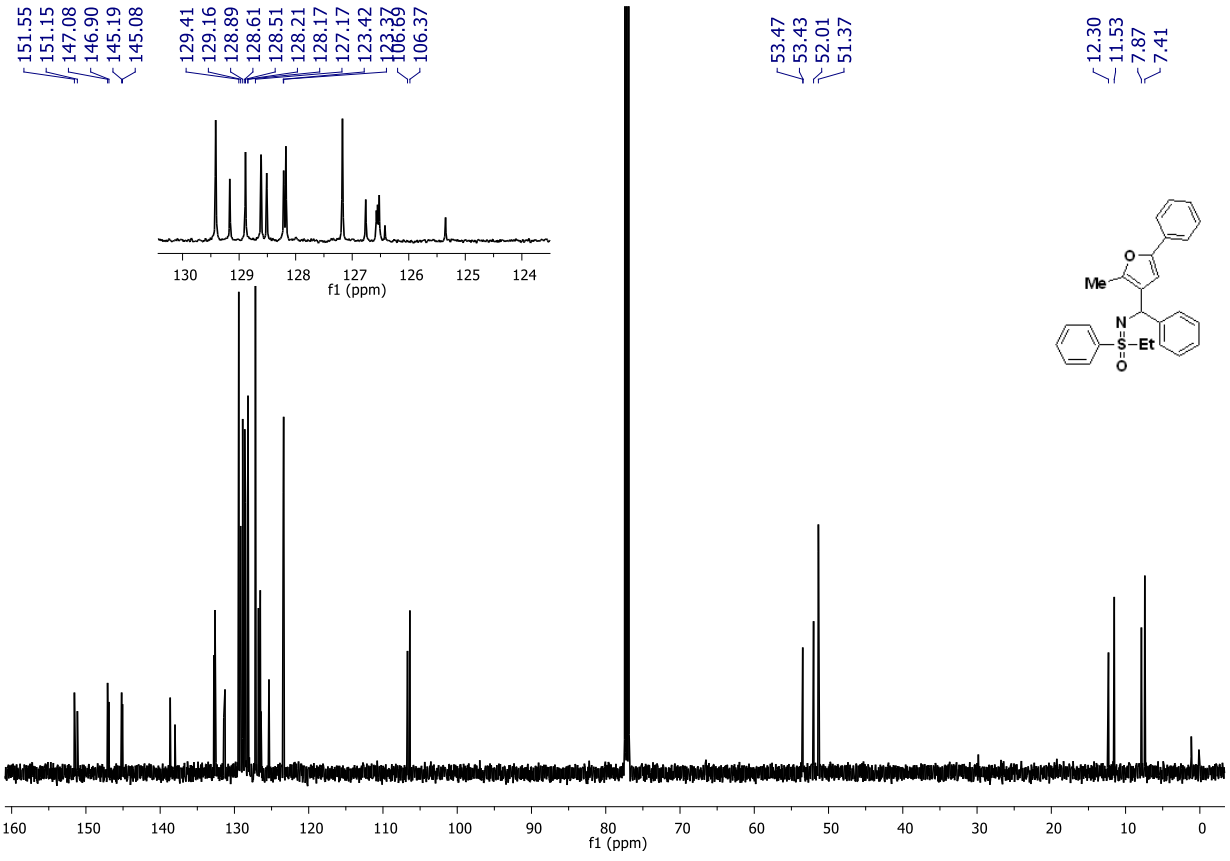
^{13}C {^{1}H} NMR of **3s** (Mixture of diastereomers in the ratio of 5:4)



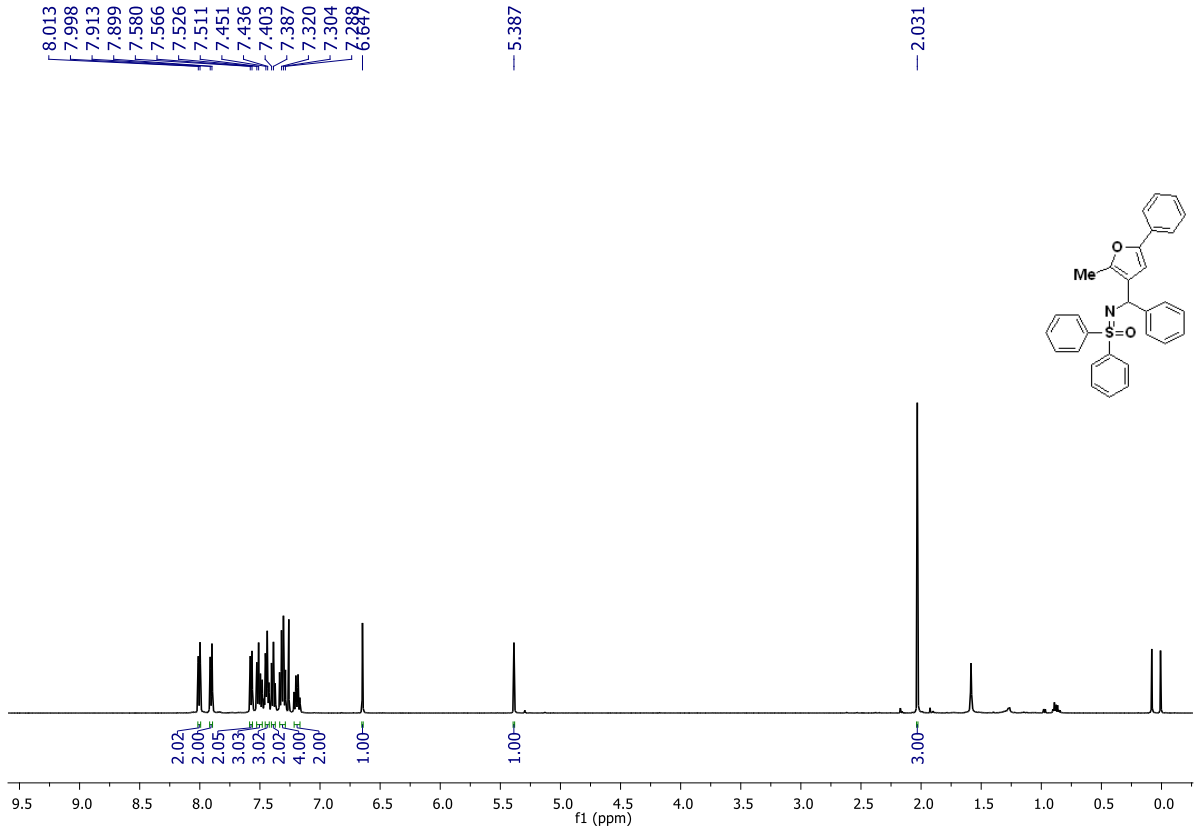
^{1}H NMR of **3t** (Mixture of diastereomers in the ratio of 5:4)



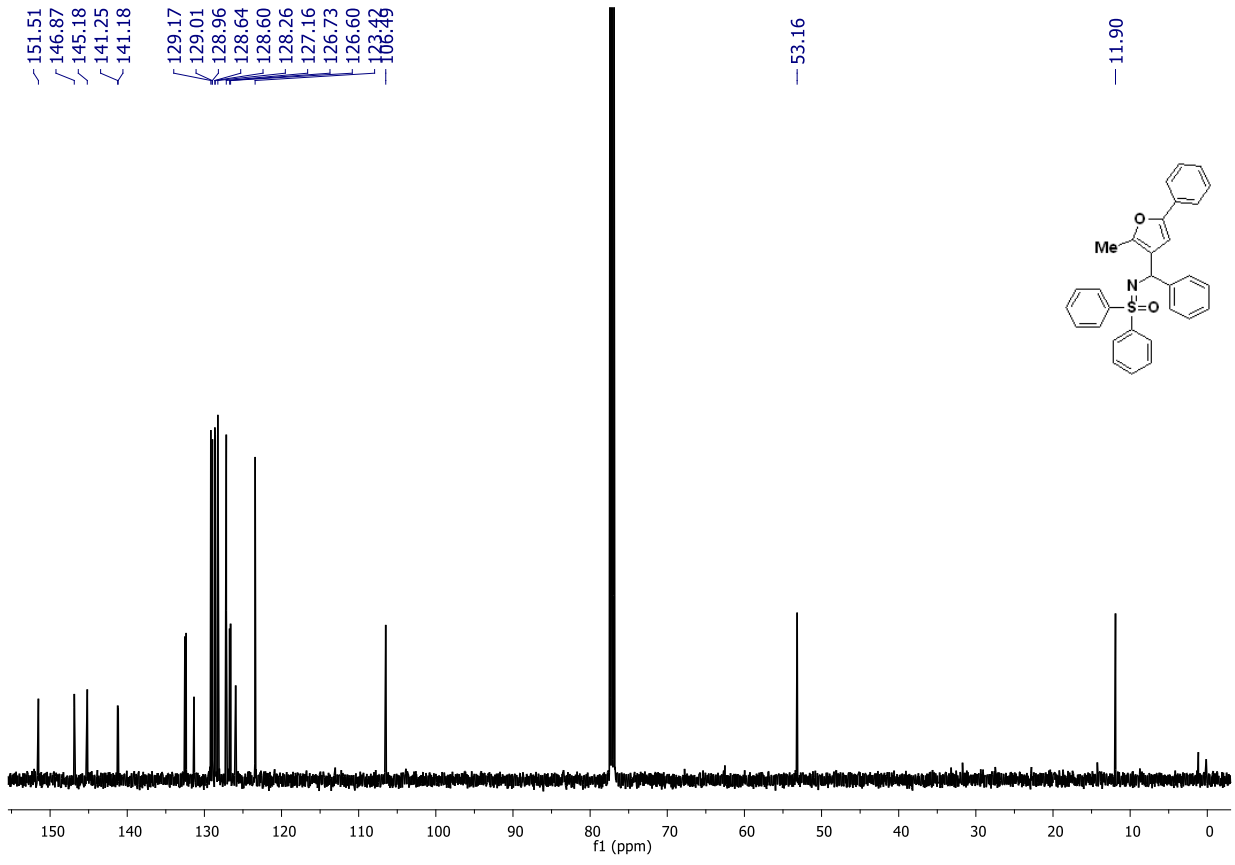
^{13}C {^{1}H} NMR of **3t** (Mixture of diastereomers in the ratio of 5:4)



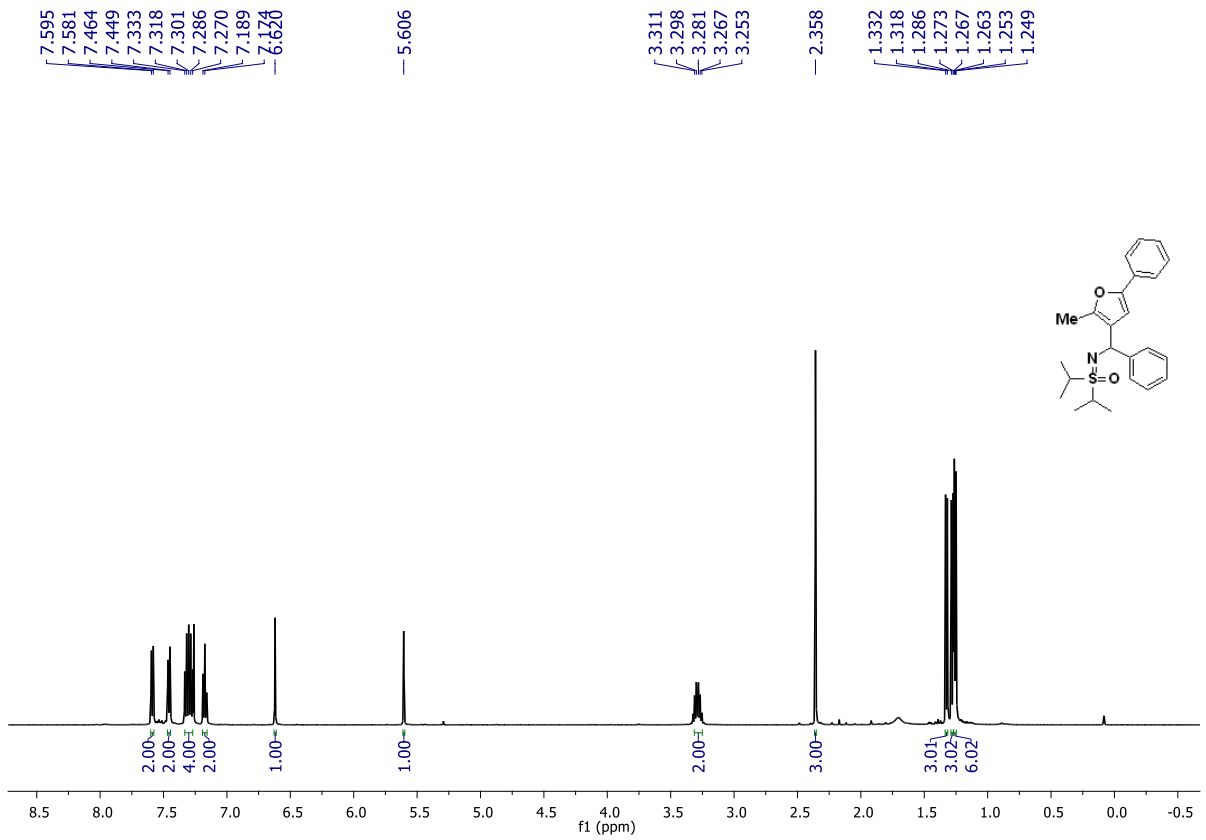
^{1}H NMR of **3u**



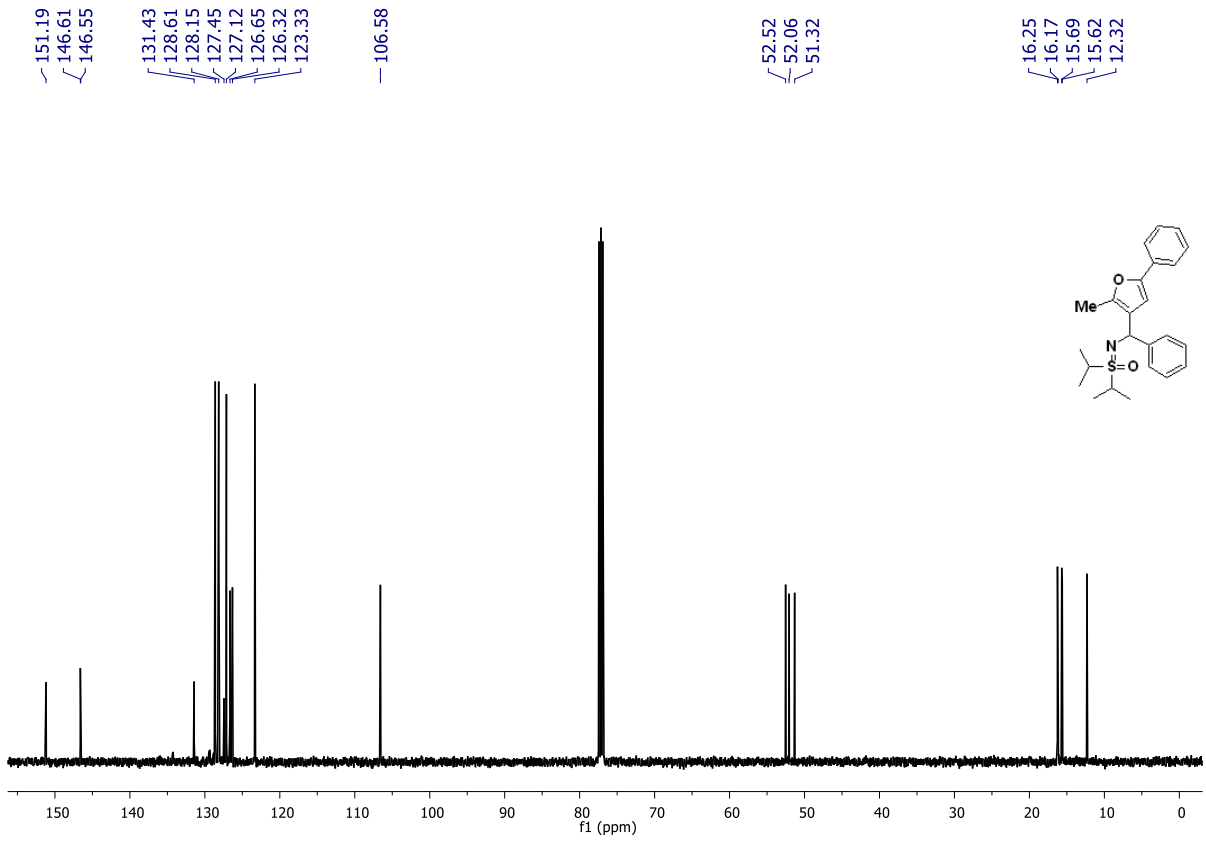
^{13}C {^{1}H} NMR of **3u**



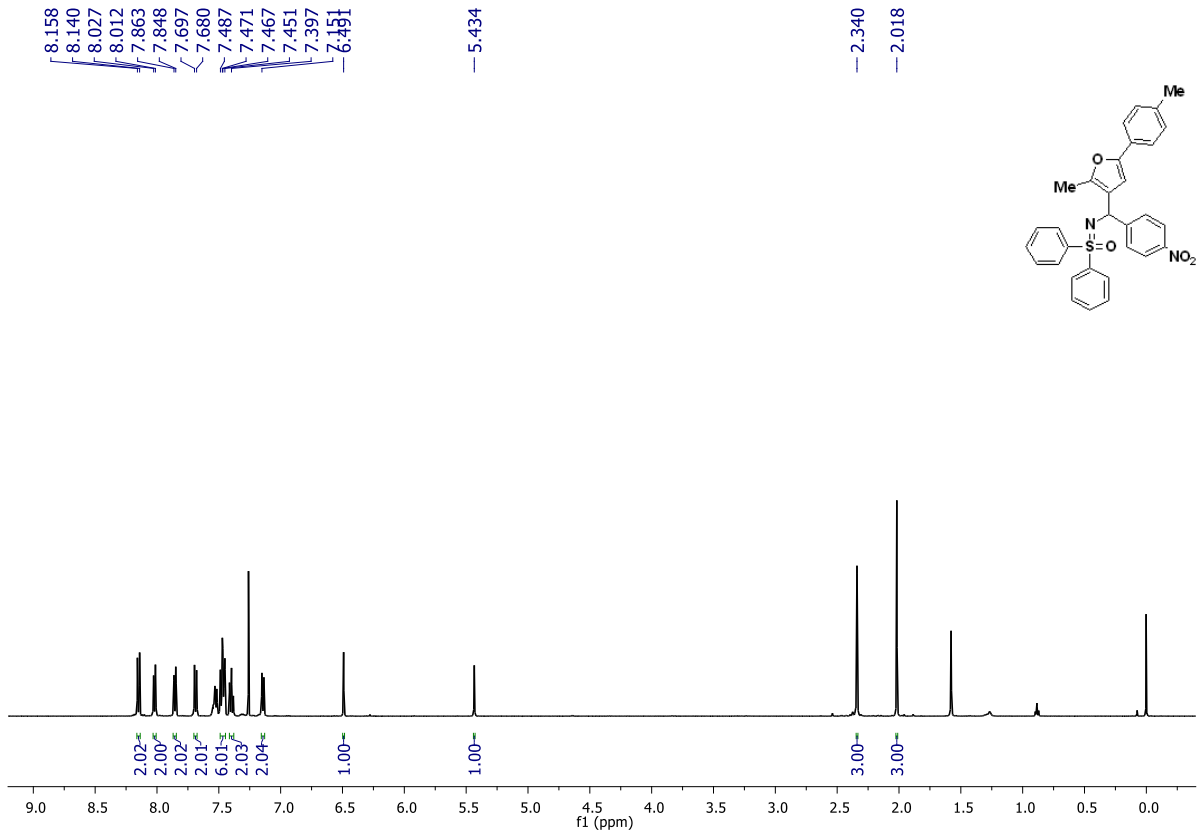
^{1}H NMR of **3v**



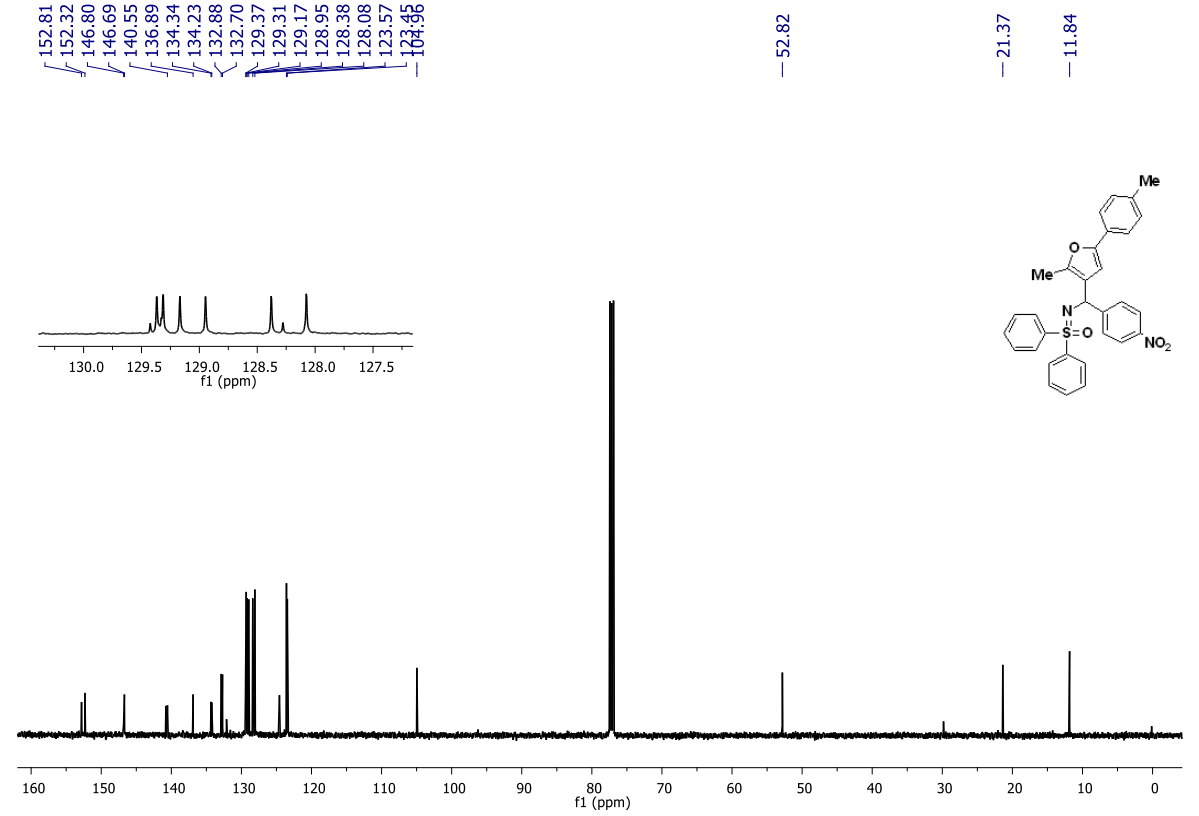
^{13}C {^{1}H} NMR of **3v**



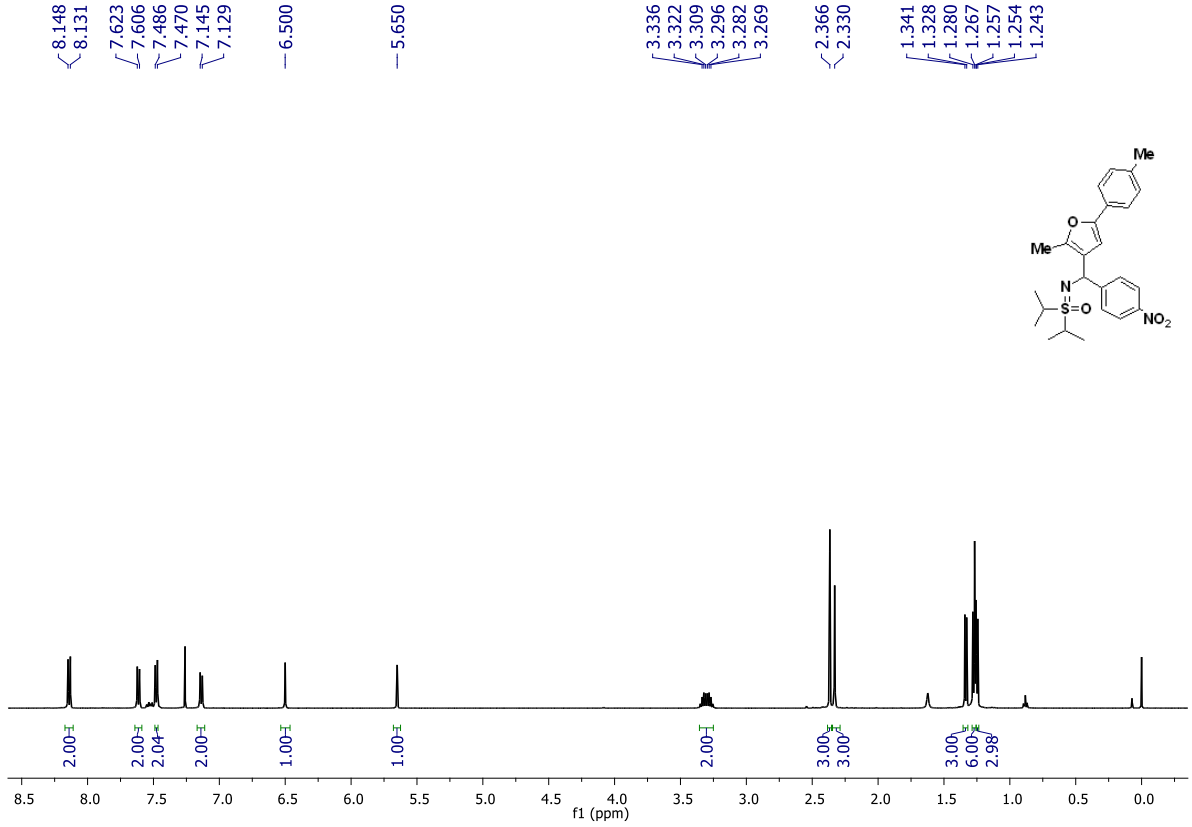
^{1}H NMR of **3w**



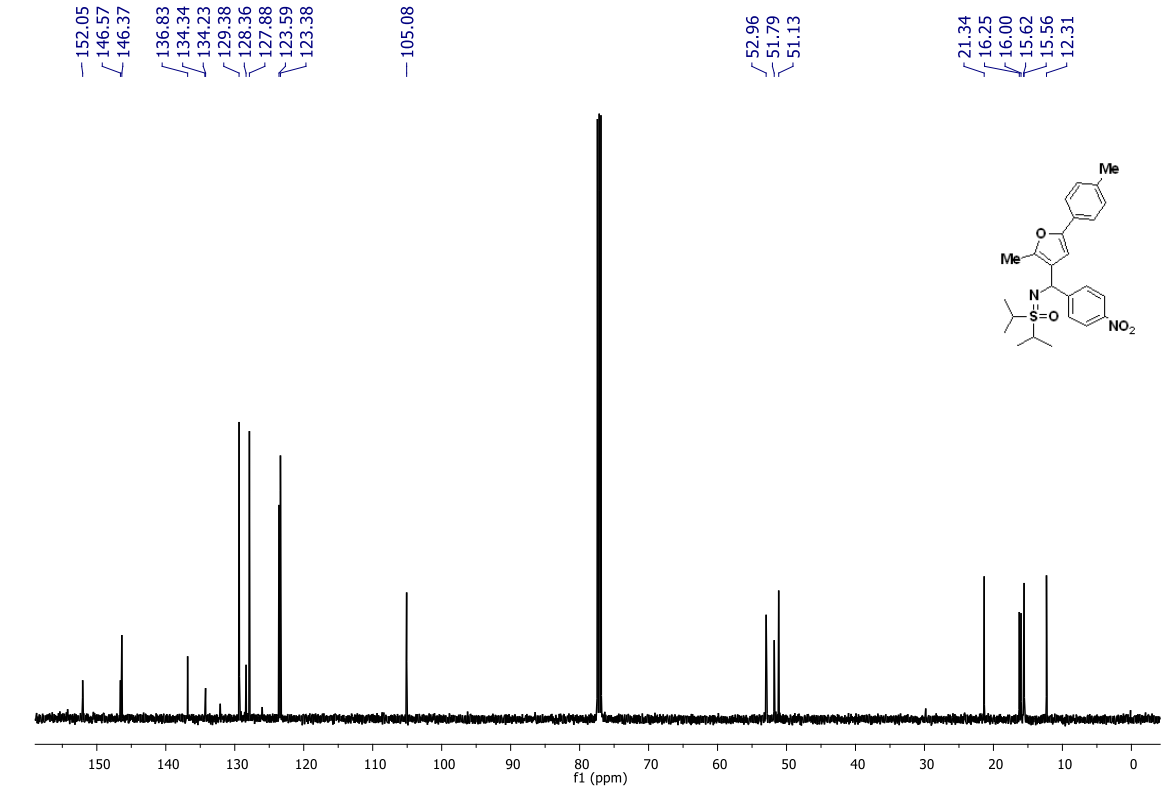
^{13}C {^{1}H} NMR of **3w**



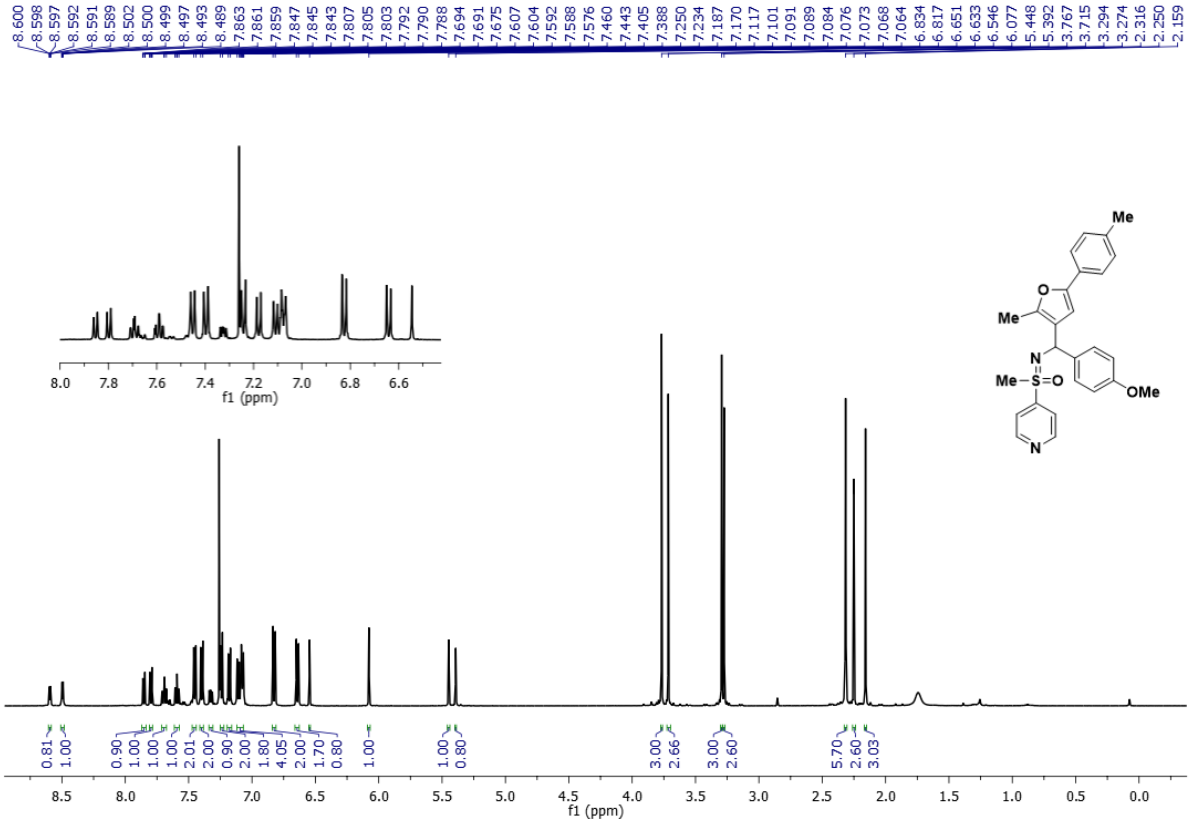
^{1}H NMR of **3x**



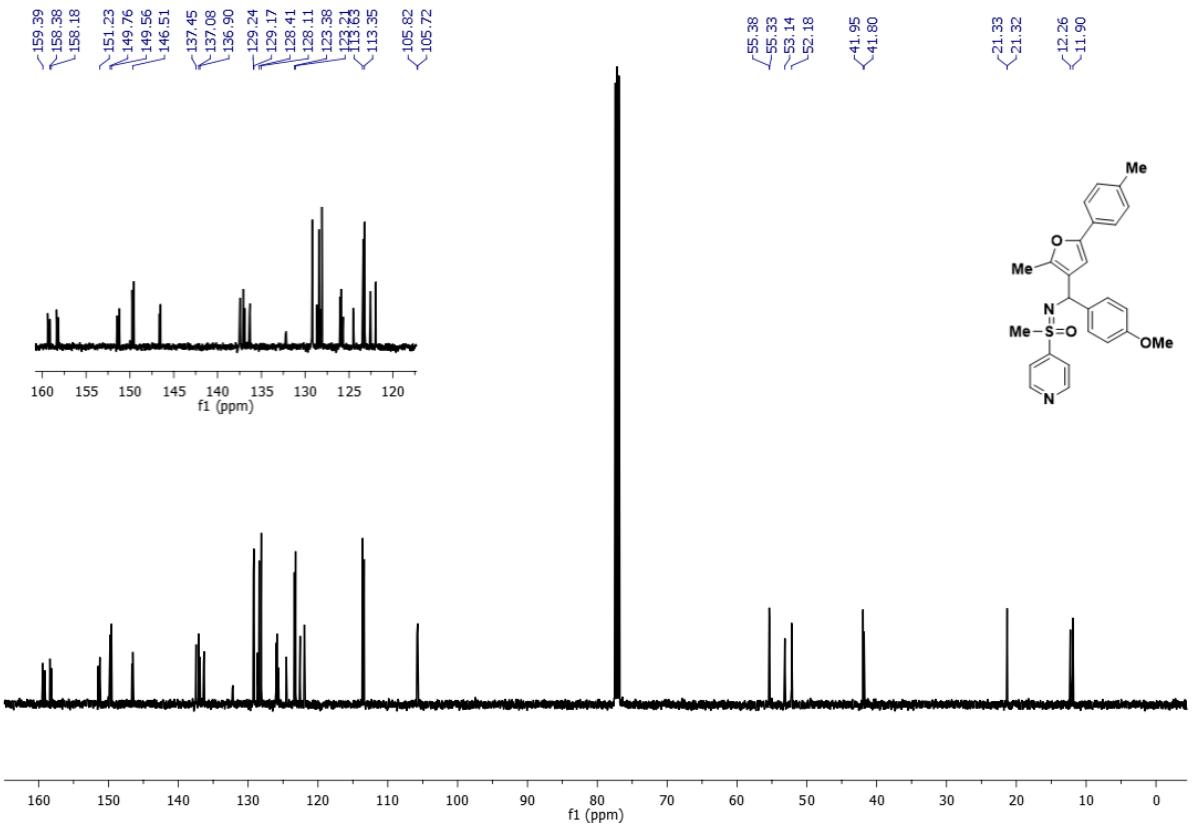
^{13}C {^{1}H} NMR of **3x**



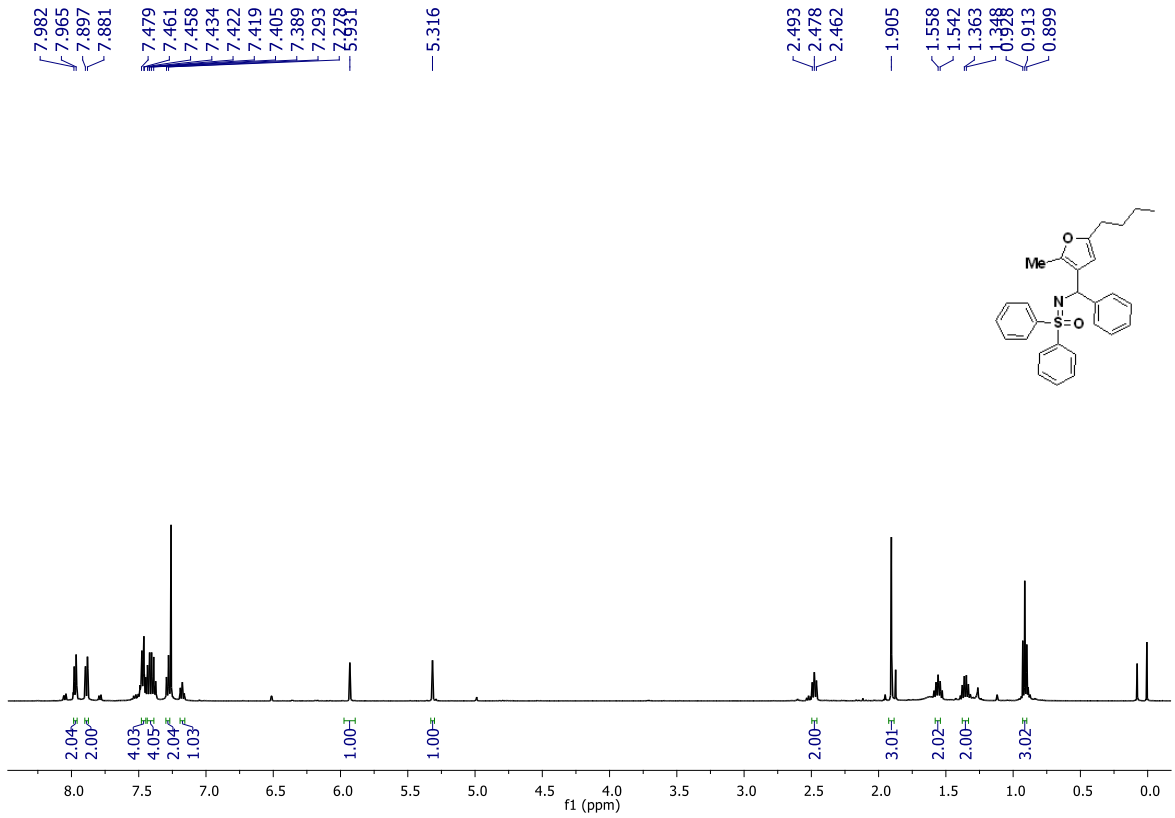
^{1}H NMR of **3y** (Mixture of diastereomers in the ratio of 5:4)



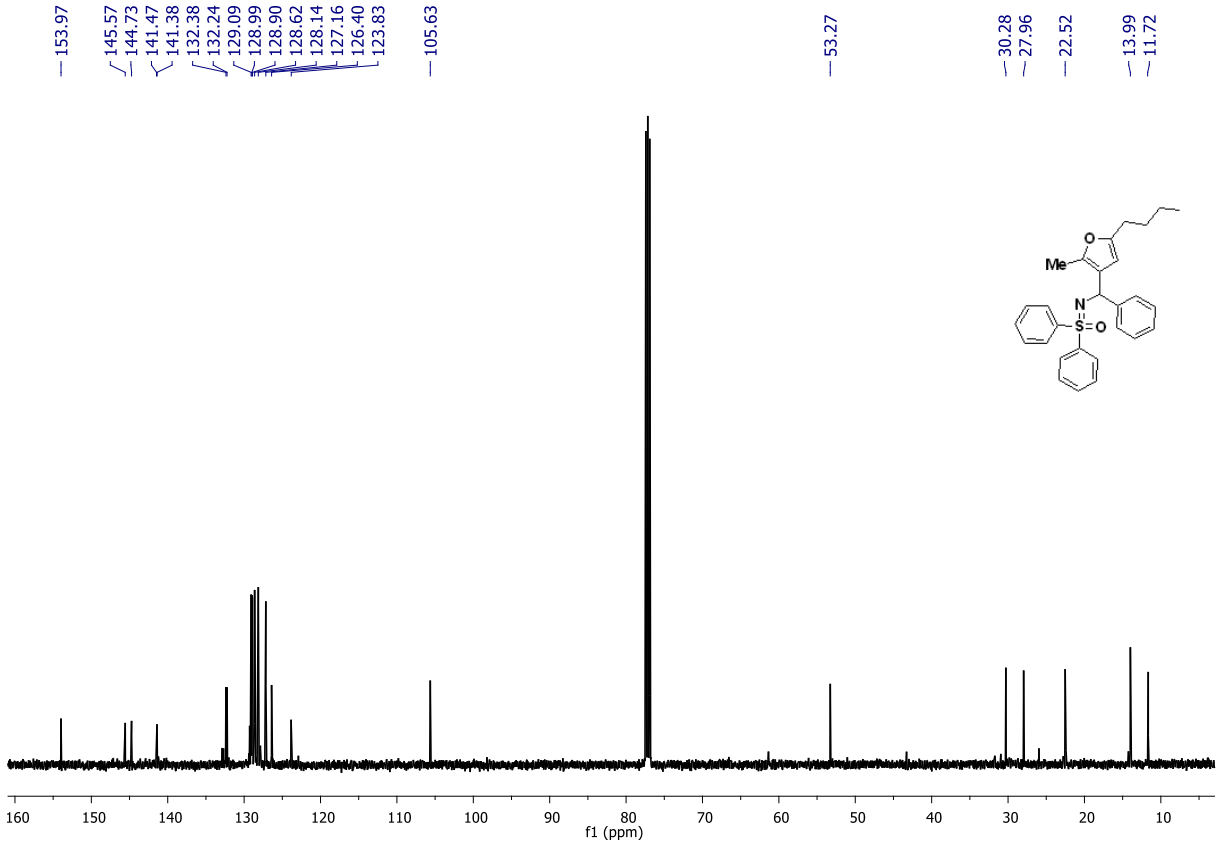
^{13}C {^{1}H} NMR of **3y** (Mixture of diastereomers in the ratio of 5:4)



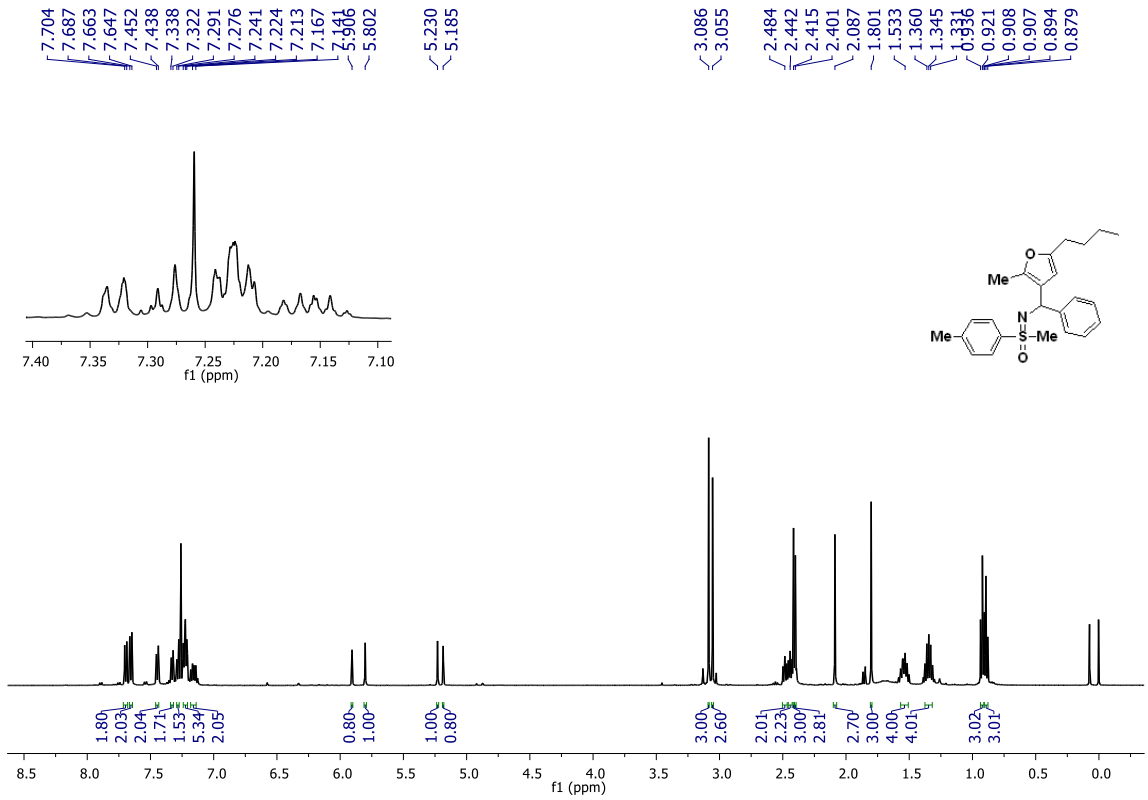
^{1}H NMR of **3z**



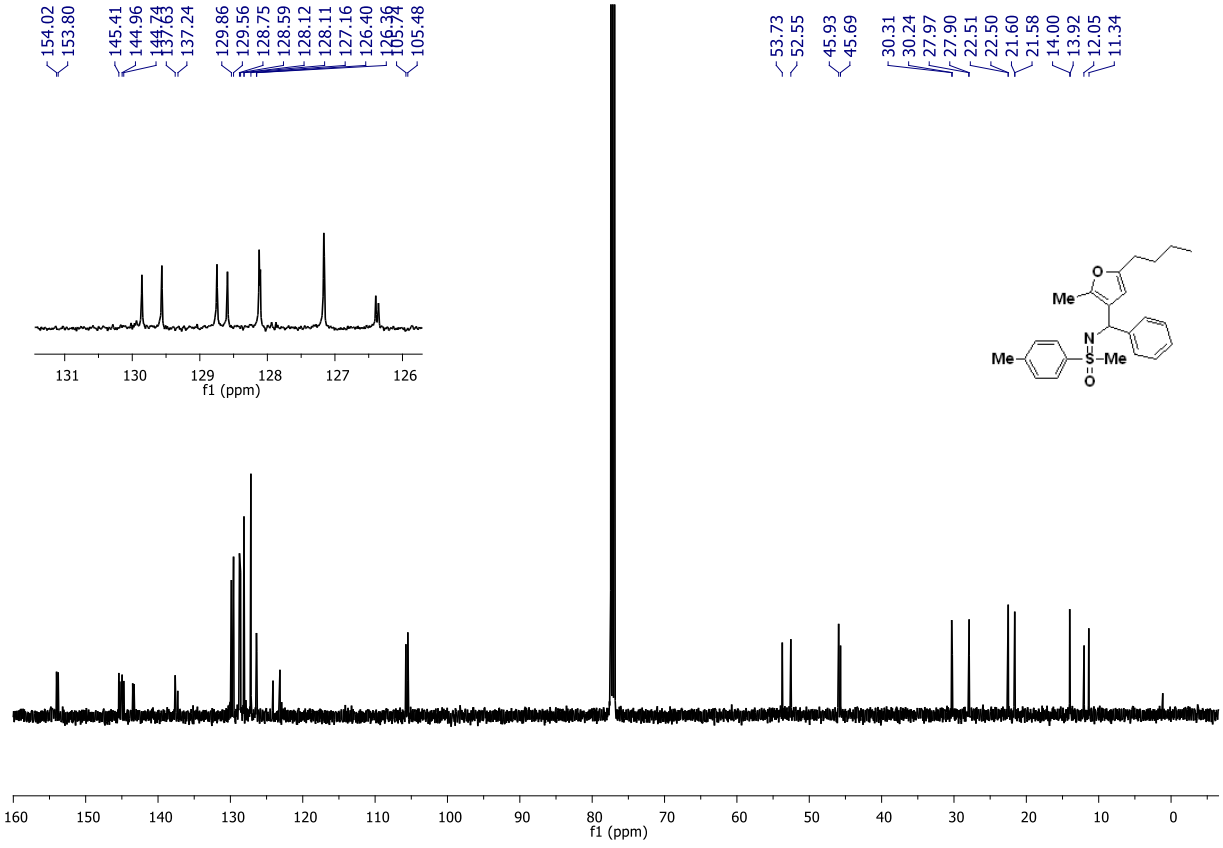
^{13}C {^{1}H} NMR of **3z**



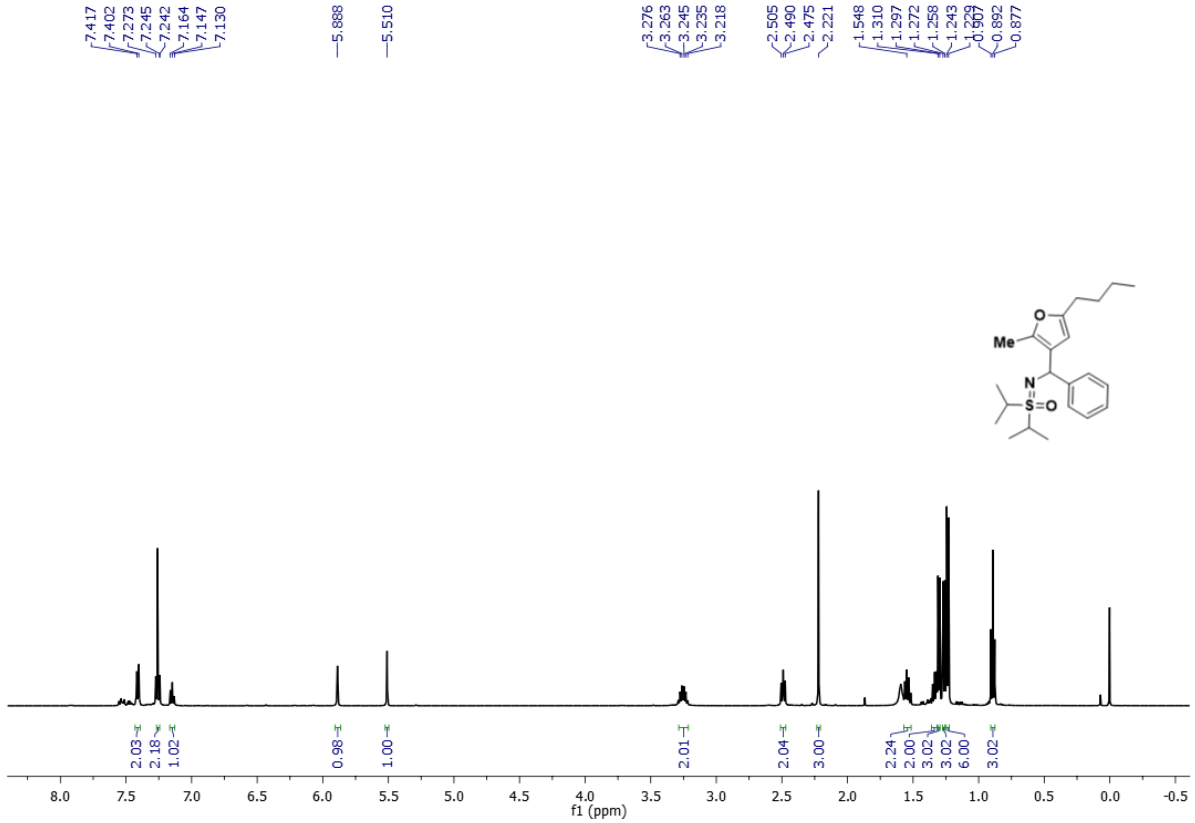
^{1}H NMR of **3a'** (Mixture of diastereomers in the ratio of 5:4)



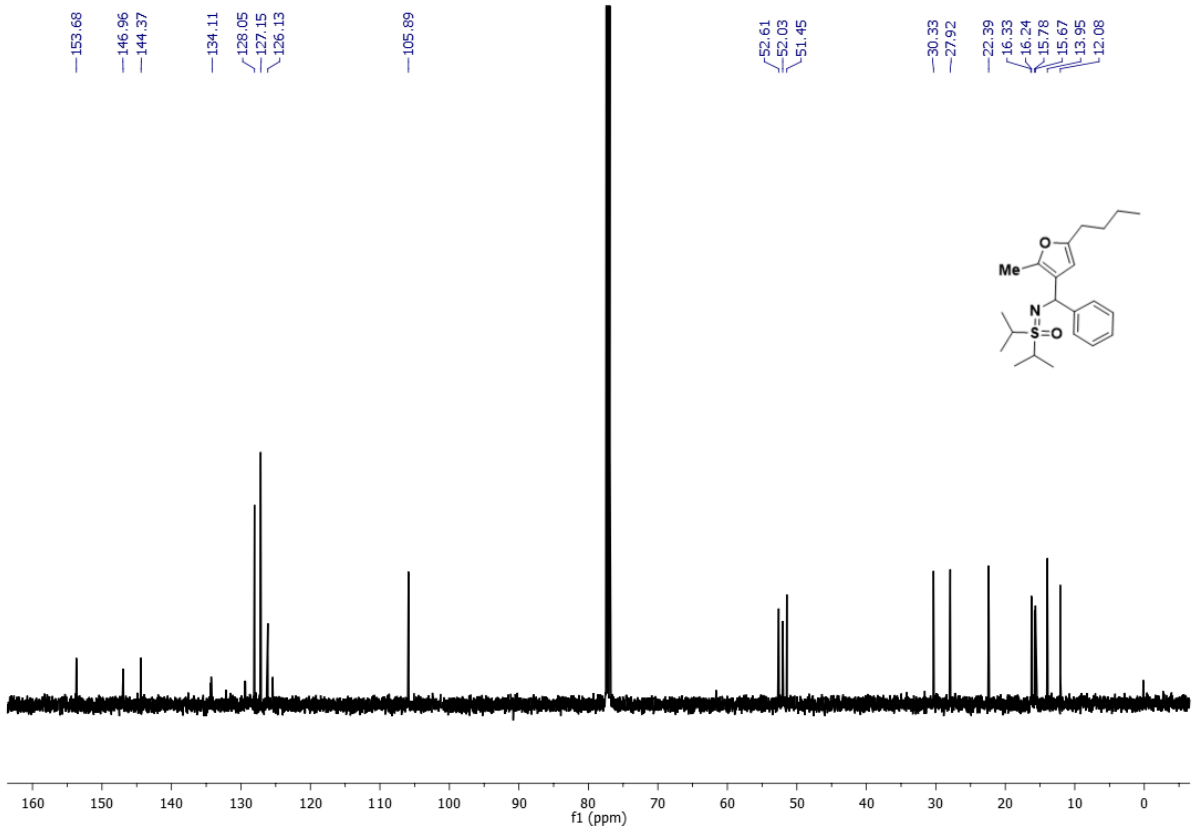
^{13}C {^{1}H} NMR of **3a'** (Mixture of diastereomers in the ratio of 5:4)



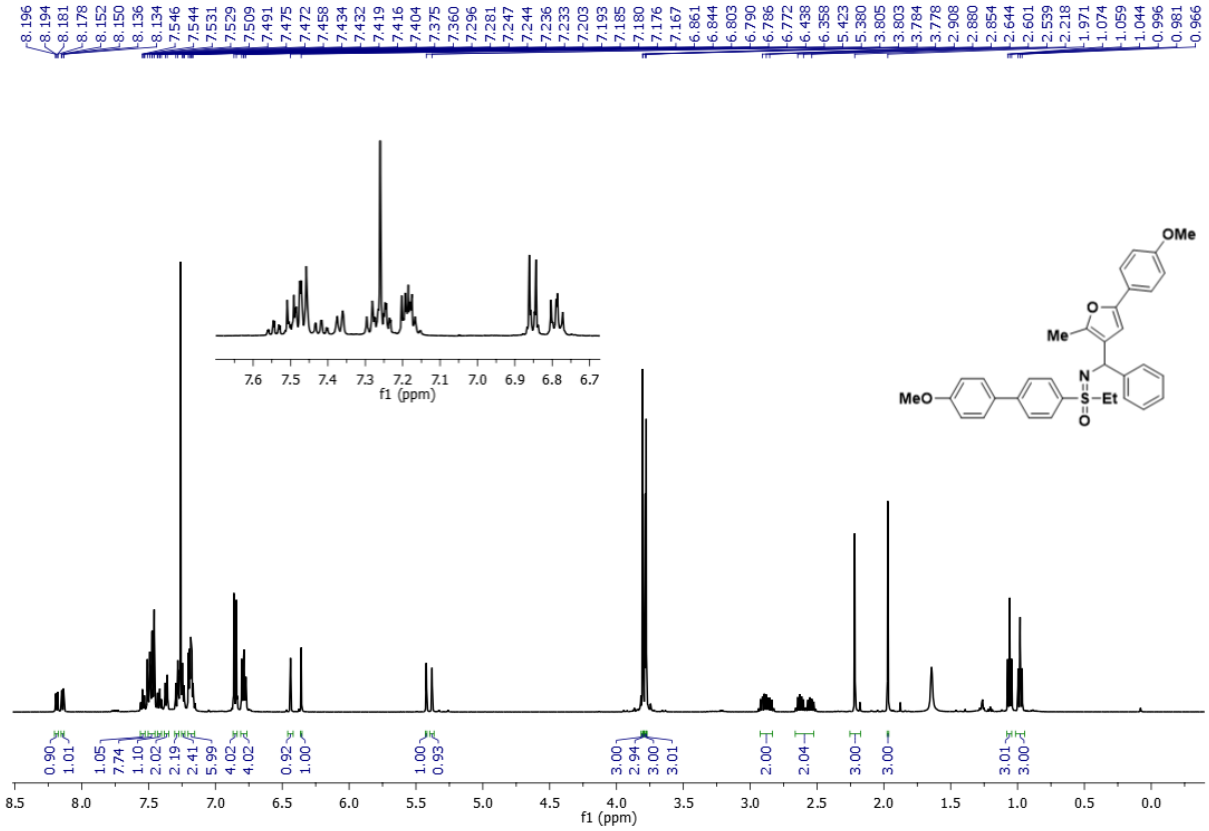
^{1}H NMR of **3b'**



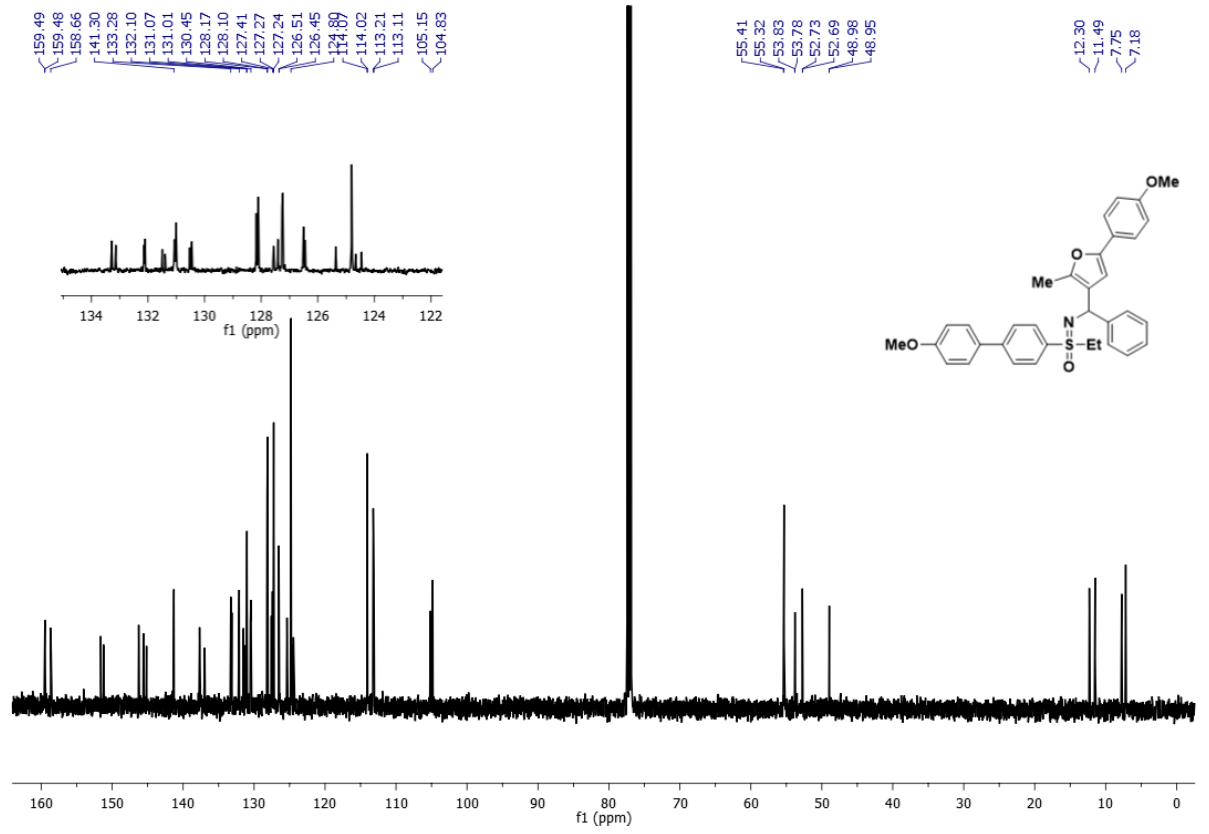
^{13}C {^{1}H} NMR of **3b'**



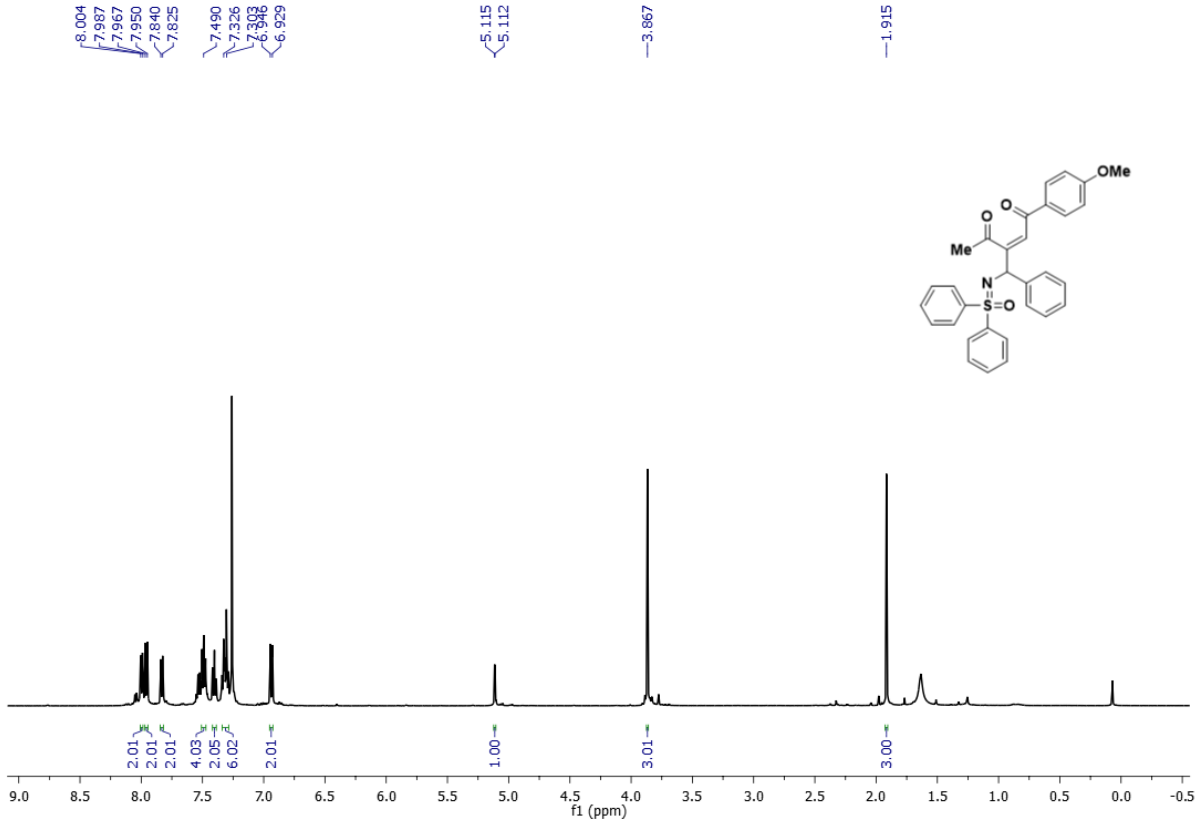
^{1}H NMR of **5a** (Mixture of diastereomers in the ratio of 1:1 approximately)



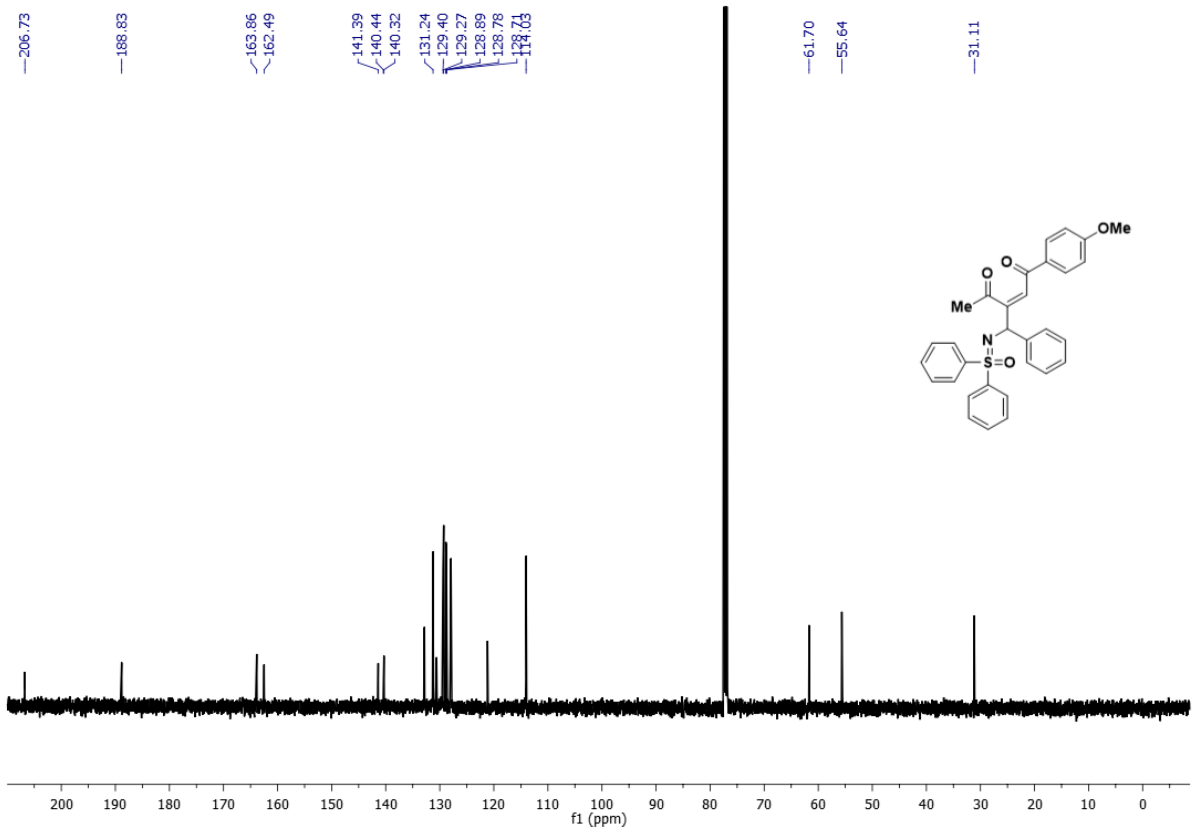
^{13}C {^{1}H} NMR of 5a (Mixture of diastereomers in the ratio of 1:1 approximately)



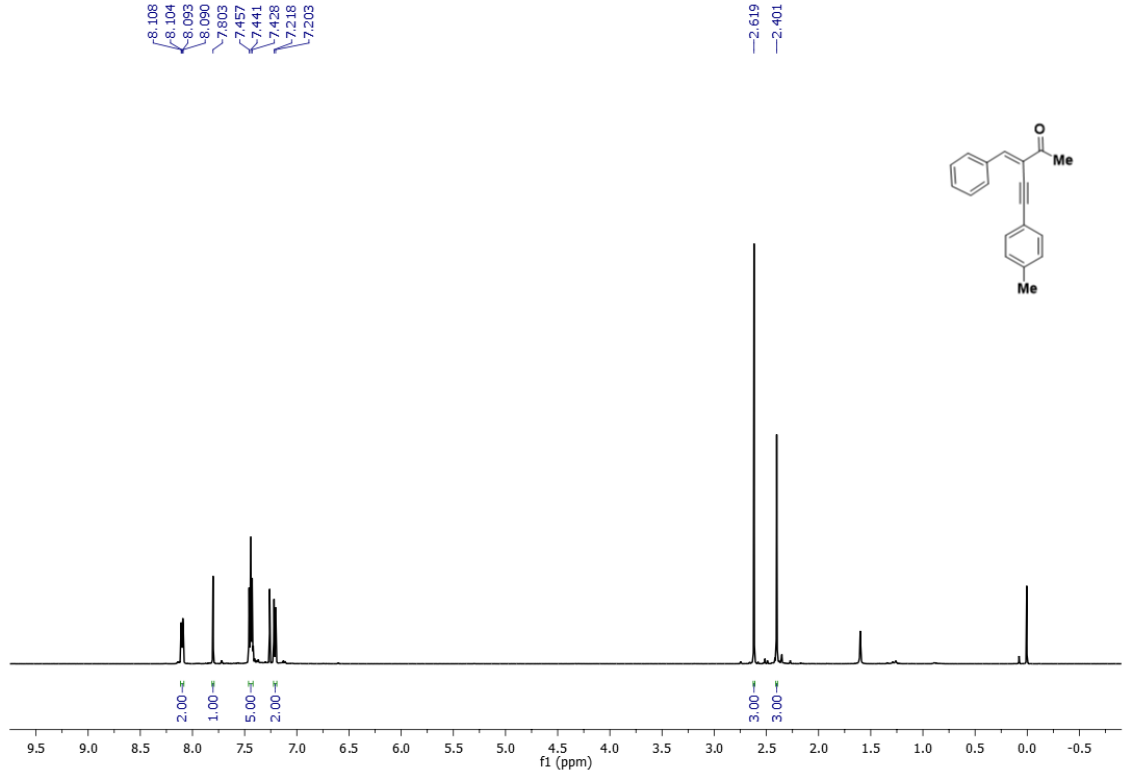
^{1}H NMR of 6**a**



^{13}C {^{1}H} NMR of 6a



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



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