Supporting information

A Metal-free Petasis reaction towards the synthesis of *N*-(α-substituted)alkyl sulfoximines / sulfonimidamides

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1. General Information

The starting material sulfoximine and sulfonimidamides were synthesized in the laboratory following the reported methods.[1] The 2-hydroxyarylaldehydes, arylboronic acids and anhydrous dichloromethane were purchased from various suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on BRUKER NMR spectrophotometer operating at 500 MHz and 126 MHz respectively. $CDCl_3$ was used as solvent to record NMR spectra. HR Mass spectra were recorded on HR mass spectrometer using TOF mass analyzer. Melting points were uncorrected.

2. A typical procedure for one pot synthesis of *N*-(α-substituted)alkyl sulfoximines (5) / sulfonimidamides (6)

A 15 mL screw cap seal tube was charged with a magnetic stirring bar, sulfoximine **1** or sulfonimidamides **2** (30 mg, 0.2457 mmol), salicylaldehyde **3** (30 mg, 0.2457 mmol, 1.0 equiv.), phenylboronic acid **4** (37 mg, 0.2457 mmol, 1.0 equiv.), and dichloromethane (1.5 mL) and firmly closed. The resulting mixture was stirred at 100 °C for 15 h. After the completion of reaction, it was quenched by water and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were dried over anhydrous sodium sulphate and filtered. The filtrate was evaporated, and purified by column chromatography over silica gel (100-200 mesh) using EtOAc/Hexane (15-25%) as eluent to afford desired *N*-(α-substituted)alkyl sulfoximines/sulfonimidamides in moderate to very good yields.

The products were obtained as diastereomeric mixture (almost 1: 1 ratio), and we were able to separate two diastereomers in most of the cases.

3. General procedure for O-allylation of *N*-(α-substituted)alkyl sulfoximines (7a-b)

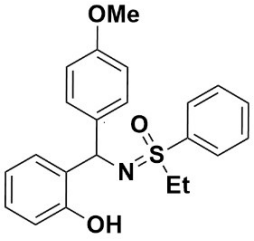
To a stirring solution of diastereomerically pure *N*-(α-substituted)alkyl sulfoximines **5** (60 mg, 0.1113 mmol) in DMF (2.0 mL), allyl bromide (27 mg, 0.2226 mmol, 2.0 equiv.) and K_2CO_3 (30 mg, 0.2226 mmol, 2.0 equiv.) were added and heated at 80 °C for 10 h. After completion of reaction (checked by TLC), the reaction mixture was cooled down, diluted with water and extracted with ethyl ether (3 x 10 mL). The organic layer was then washed with brine solution, dried and purified by column chromatography over silica gel (100-200 mesh) using EtOAc/Hexane (7%) as the eluent to give *O*-allylated product **7a/b** from corresponding precursor **5c/d**.

4. General procedure for the synthesis of benzofuran derivatives (8a/b) via intramolecular Heck coupling of 7a/b

A solution of *O*-allylated product **7a/b** (42 mg, 0.0725 mmol), in anhydrous DMF (1.5 mL) was heated at 110 °C in the presence of $Pd(OAc)_2$ (5 mol%), NaOAc (29 mg, 0.3625 mmol, 5.0 equiv.) for 10 h under argon atmosphere. After completion of the reaction, it was cooled down, diluted with water and extracted with ethyl ether (3 x 10 mL). The organic layer was then purified by column chromatography over silica gel (100-200 mesh) using EtOAc/Hexane (12%) as the eluent.

5. Characterisation Data of the isolated compounds

For most of the cases we were able to separate the diastereomers of compounds **5** and **6**. Yields were calculated by accumulating the amount of diastereomers for compounds **5** and **6** as we got some mixtures also during purification. The HRMS data of one of the pure diastereomer is included (when the mixtures were separated).



Compound 5a (Yield: 65%, 61 mg of total products from 30 mg (0.2457 mmol) of aldehyde)

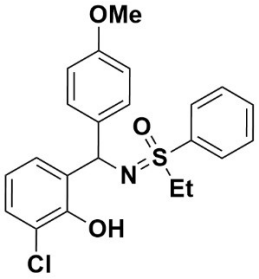
Diastereomer – 1

Brown sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 7.12 - 7.09 (m, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.79 (d, J = 8.5 Hz, 2H), 6.66 - 6.64 (m, 2H), 5.30 (s, 1H), 3.74 (s, 3H), 3.32 - 3.22 (m, 2H), 1.26 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 156.6, 136.7, 136.2, 133.5, 129.5, 129.4, 128.8, 128.6, 128.2, 127.9, 119.2, 117.4, 113.7, 61.6, 55.2, 51.3, 7.4. HRMS (ESI) calcd for $C_{22}H_{24}NO_3S$ $[M+H]^+$ 382.1472; found 382.1485.

Diastereomer - 2

Pale yellow solid, mp 118-120 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.14 (d, J = 8.5 Hz 2H), 7.12 – 7.08 (m, 1H), 6.90 – 6.87 (m, 2H), 6.72 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 8.5 Hz, 2H), 5.45 (s, 1H), 3.71 (s, 3H), 3.32 – 3.19 (m, 2H), 1.25 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 156.4, 136.9, 136.5, 133.1, 129.5, 129.1, 129.1, 128.9, 128.2, 128.1, 119.4, 117.5, 113.6, 61.2, 55.2, 51.3, 7.2.

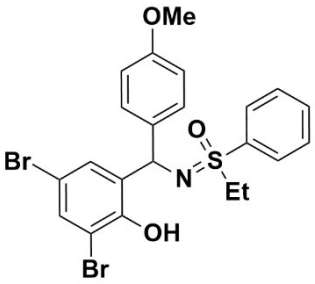
Compound 5b (Obtained as diastereomeric mixture (approx. 1:1); Yield: 36%, 38 mg of total products from 40 mg (0.2555 mmol) of aldehyde)



Yellow sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.27 (s, 1H), 11.02 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.5 Hz, 2H), 7.27 (s, 1H), 7.19 - 7.16 (m, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.80 (t, J = 9.0 Hz, 2H), 6.65 – 6.57 (m, 5H), 5.46 (s, 1H), 5.32 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.33 – 3.29 (m, 2H), 3.26 – 3.21 (m, 2H), 1.27 – 1.24 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 158.5, 152.4, 152.3, 137.5, 136.7, 136.4, 135.9, 135.9, 133.6, 133.2, 130.3, 129.5, 129.4, 129.4, 129.2, 129.1, 128.5, 128.4, 128.2, 128.1,

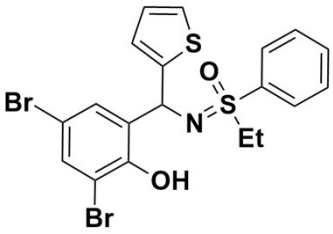
126.6, 126.5, 121.9, 119.6, 119.5, 113.8, 113.8, 61.4, 61.1, 55.2 (Two peaks are merged), 51.4, 51.2, 7.3, 7.2. HRMS (ESI) calcd for $C_{22}H_{23}ClNO_3S$ $[M+H]^+$ 416.1082; found 416.1082.

Compound 5c (Obtained as diastereomeric mixture (approx. 1:1); Yield: 83%, 144 mg of total products from 90 mg (0.3215 mmol) of aldehyde)



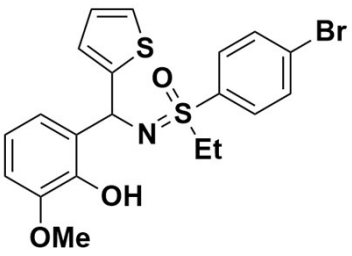
Yellowish sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.53 (s, 1H), 11.31 (s, 1H), 7.75 - 7.74 (m, 2H), 7.66 – 7.61 (m, 3H), 7.57 – 7.51 (m, 3H), 7.48-7.46 (m, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 6.96 (dd, J = 2.5, 0.5 Hz, 1H), 6.81 (d, J = 9.0 Hz, 2H), 6.78 (dd, J = 2.5, 0.5 Hz, 1H), 6.65 (d, J = 8.5 Hz, 2H), 5.35 (s, 1H), 5.24 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.36 – 3.29 (m, 2H), 3.28 – 3.21 (m, 2H), 1.29 – 1.24 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 158.7, 152.7, 152.8, 136.3, 135.8, 135.6, 135.3, 133.8, 133.5, 133.4, 133.4, 131.6, 130.7, 129.8, 129.6, 129.2 (two peaks merged), 129.2, 129.2, 128.1, 127.9, 113.9, 113.8, 112.2, 112.1, 110.9, 110.8, 61.5, 60.9, 55.2 (two peaks merged), 51.4, 51.1, 7.2, 7.1. HRMS (ESI) calcd for $C_{22}H_{22}Br_2NO_3S$ $[M+H]^+$ 537.9682; found 537.9644.

Compound 5d (We were able to isolate only one diastereomer in pure form, Yield: 86%, 158 mg of total products from 100 mg (0.3572 mmol) of aldehyde)



Off white solid, mp 118-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.84 – 7.81 (m, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.11 (dd, J = 5.0, 1.5 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.77 - 6.75 (m, 1H), 6.60 - 6.59 (m, 1H), 5.51 (s, 1H), 3.38 – 3.28 (m, 2H), 1.30 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 147.3, 135.5, 133.9, 133.7, 131.5, 129.5, 129.4, 129.2, 126.7, 124.8, 124.3, 112.2, 110.9, 57.2, 51.3, 7.1. HRMS (ESI) calcd for $C_{19}H_{18}Br_2NO_2S_2$ $[M+H]^+$ 515.9120; found 515.9114.

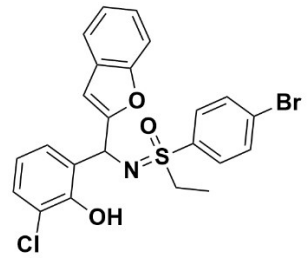
Compound 5e (We were able to isolate only one diastereomer in pure form, Yield: 78%, 36 mg of total products from 15 mg (0.0986 mmol) of aldehyde)



Diastereomer 1: Brownish sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.59-7.54 (m, 4H), 7.14 (d, J = 5.0 Hz, 1H), 6.86 - 6.84 (m, 1H), 6.81 - 6.77 (m, 2H), 6.70 (t, J = 8.0 Hz, 1H), 6.53 (d, J = 7.5 Hz, 1H), 5.62 (s, 1H), 3.88 (s, 3H), 3.33 -

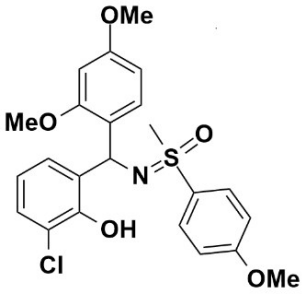
3.21(m, 2H), 1.32 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 148.3, 145.0, 135.7, 132.6, 130.9, 128.8, 128.3, 126.6, 124.5, 124.1, 119.9, 119.2, 110.4, 56.3, 55.9, 51.2, 7.3. HRMS (ESI) calcd for $C_{21}H_{20}BrNO_3S_2$ $[M+H]^+$ 468.0121; found 468.0123.

Compound 5f (Obtained as diastereomeric mixture (approx. 1:1); Yield: 81%, 39 mg of total products from 15 mg (0.0958 mmol) of aldehyde)



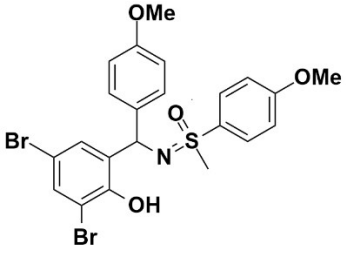
Brown sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 10.27 (s, 1H), 7.64 - 7.62 (m, 5H), 7.46 – 7.44 (m, 3H), 7.38 – 7.33 (m, 2H), 7.27 – 7.24 (m, 2H), 7.21 (s, 1H), 7.20- 7.16 (m, 3H), 7.16 - 7.11(m, 2H), 6.93 - 6.92 (m, 1H), 6.87 - 6.83 (m, 1H), 6.74 - 6.68 (m, 2H), 6.60 (s, 1H), 6.32 (s, 1H), 5.68 (s, 1H), 5.47 (s, 1H), 3.42 – 3.22 (m, 4H), 1.31 (t, J = 7.5 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 156.9, 155.0, 154.4, 152.6, 152.3, 135.7, 134.6, 132.8, 132.3, 130.8, 130.3, 129.3, 129.2, 128.6, 128.2, 127.7, 126.8, 126.1, 124.5, 124.1, 123.8, 122.9, 122.7, 122.6, 121.2, 120.9, 120.8, 119.8, 119.7, 111.3, 111.2, 111.1, 104.3, 104.1, 103.3, 55.9, 55.1, 51.5, 51.2, 7.2, 6.8. HRMS (ESI) calcd for $C_{23}H_{20}BrClNO_3S$ $[M+H]^+$ 504.0031; found 504.0017.

Compound 5g (Obtained as diastereomeric mixture (approx. 1:1); Yield: 45%, 20 mg of total products from 15 mg (0.0958 mmol) of aldehyde)



Yellowish sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 8.5 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.85 – 6.83 (m, 3H), 6.77 - 6.59 (m, 1H), 6.62 - 6.56 (m, 2H), 6.46 – 6.43 (m, 1H), 6.40 – 6.36 (m, 2H), 6.13 (d, J = 2.5 Hz, 1H), 5.96 (s, 1H), 5.81 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.72 (s, 3H), 3.47 (s, 3H), 3.14 (s, 3H), 3.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 163.3, 159.8, 159.8, 156.1, 155.9, 152.6, 137.5, 130.7, 130.6, 130.3, 129.8, 129.6, 129.2, 128.9, 128.6, 128.0, 127.9, 126.6, 126.5, 125.8, 125.5, 121.6, 121.5, 119.4, 119.3, 114.7, 114.1, 104.8, 104.7, 98.4, 97.7, 55.7, 55.7, 55.3, 55.3, 55.3, 55.0, 54.9, 53.6, 45.4, 45.4. HRMS (ESI) calcd for $C_{23}H_{25}ClNO_5S$ $[M+H]^+$ 462.1136; found 462.1138.

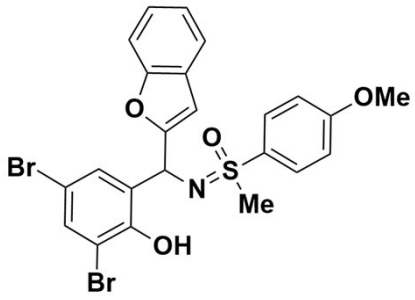
Compound 5h (Obtained as diastereomeric mixture (approx. 1:1); Yield: 55%, 65 mg of total products from 60 mg (0.2143 mmol) of aldehyde)



Colourless sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.52 (s, 1H), 11.40 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 9.0 Hz,

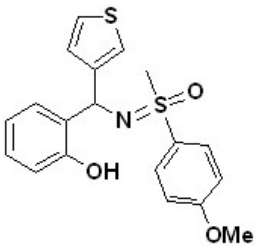
2H), 7.47 (dd, *J* = 7.5, 2.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.28 (s, 1H), 5.21 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.18 (s, 3H), 3.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 163.6, 158.8, 158.7, 152.6, 152.5, 135.7, 135.3, 133.4, 133.4, 131.7, 130.7, 130.6, 130.6, 129.9, 129.8, 128.7, 128.2, 127.9, 127.9, 114.9, 114.6, 113.9, 113.7, 112.2, 112.1, 110.9, 110.8, 61.6, 61.0, 55.8, 55.7, 55.2 (Two peaks merged), 45.5, 45.4. HRMS (ESI) calcd for $C_{22}H_{22}Br_2NO_4S$ $[M+H]^+$ 555.9611; found 555.9600.

Compound 5i (Obtained as diastereomeric mixture (approx. 1:1); Yield: 80%, 24 mg of total products from 15 mg (0.0534 mmol) of aldehyde)



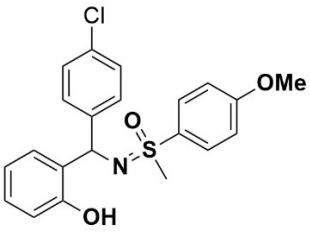
Yellowish sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.04 (s, 1H), 10.92 (s, 1H), 7.75 -7.72 (m, 4H), 7.54 - 7.53 (m, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.11 (m, 4H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 3H), 6.83 (s, 1H), 6.82 (s, 1H), 6.64 (s, 1H), 6.38 (s, 1H), 5.51 (s, 1H), 5.38 (s, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 3.25 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 163.7, 157.6, 156.6, 155.0, 154.7, 153.0, 152.9, 134.2 (Two peaks merged), 130.7, 130.5, 130.1, 130.1, 128.4, 128.2, 127.9, 127.7, 127.6, 127.3, 124.0, 123.9, 122.6 (Two peaks merged), 121.0, 120.9, 115.0, 114.5, 112.2, 112.1, 111.2, 111.2, 110.9, 110.8, 103.9, 103.4, 56.03 55.8, 55.6, 55.3, 45.7, 45.3. HRMS (ESI) calcd for $C_{23}H_{20}Br_2NO_4S$ $[M+H]^+$ 563.9474; found 563.9475.

Compound 5j (We were able to isolate only one diastereomer in pure form. Yield: 78%, 36 mg of total products from 15 mg (0.1228 mmol) of aldehyde)



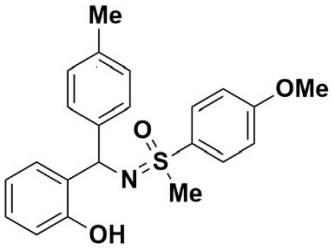
Yellowish Sticky liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.16 - 7.13 (m, 2H), 6.92 - 6.88 (m, 3H), 6.87 - 6.85 (m, 1H), 6.81 (d, *J* = 3.5 Hz, 1H), 6.77 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.70 (t, *J* = 7.0 Hz, 1H), 5.51 (s, 1H), 3.85 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.77, 156.33, 149.56, 130.93, 128.79, 128.69, 127.82, 127.78, 126.73, 124.64, 124.22, 119.28, 117.58, 114.72, 57.96, 55.75, 45.38. HRMS (ESI) calcd for $C_{19}H_{20}NO_3S_2$ $[M+H]^+$ 374.0880 ; found 374.0892.

Compound 5k (We were able to isolate only one diastereomer in pure form. Yield: 71%, 23 mg of total products from 10 mg (0.0819 mmol) of aldehyde)



Diastereomer 1: White solid, mp 103-105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 7.15 – 7.12 (m, 1H), 6.92 - 6.89 (m, 3H), 6.70 – 6.67 (m, 2H), 5.23 (s, 1H), 3.86 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 156.6, 142.9, 132.7, 131.1, 128.6, 128.6, 128.6, 128.5, 128.3, 127.4, 119.5, 117.7, 114.8, 61.7, 55.8, 45.8. HRMS (ESI) calcd for $C_{21}H_{21}ClNO_3S$ $[M+H]^+$ 402.0926 ; found 402.0926.

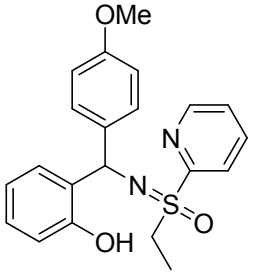
Compound 5l (Yield: 59%, 55 mg of total products from 30 mg (0.2456 mmol) of aldehyde)



Diastereomer 1: White Solid, mp 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 7.12 - 7.09 (m, 1H), 7.07 (d, J = 8 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.89 - 6.88 (m, 1H), 6.69 – 6.65 (m, 2H), 5.27 (s, 1H), 3.85 (s, 3H), 3.14 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 156.6, 141.5, 136.5, 130.9, 129.1, 128.9, 128.3, 128.2, 127.8, 126.9, 119.3, 117.5, 114.7, 62.1, 55.7, 45.6, 21.1. HRMS (ESI) calcd for $C_{22}H_{24}NO_3S$ $[M+H]^+$ 382.1471; found 382.1472.

Diastereomer 2: White Solid, mp 94-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 6.5 Hz, 2H), 7.12 – 7.06 (m, 2H), 6.98 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.89 - 6.87 (m, 1H), 6.75 - 6.72 (m, 1H), 5.40 (s, 1H), 3.86 (s, 3H), 3.14 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 156.3, 141.1, 136.4, 130.9, 130.6, 129.6, 128.9, 128.2, 128.0, 126.8, 119.5, 117.5, 114.5, 61.7, 55.7, 45.3, 21.0. HRMS (ESI) calcd for $C_{22}H_{24}NO_3S$ $[M+H]^+$ 382.1471; found 382.1472.

Compound 5m (Yield: 43%, 41 mg of total products from 60 mg (0.4912 mmol) of aldehyde)



Diastereomer 1

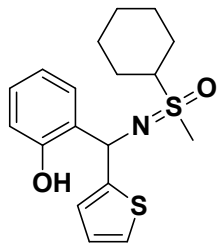
Colourless sticky liquid, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.43 (s, 1H), 8.52 (dd, J = 4.5, 1.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.77 (t, J = 7.5 1H), 7.35-7.32 (m, 1H), 7.26 (d, J = 8.5 Hz, 2H), 7.00 – 6.96 (m, 1H), 6.80 (d, J = 8.5 Hz, 2H), 6.73 (dd, J = 8.0, 1.0 Hz, 1H), 6.59 – 6.53 (m, 2H), 5.42 (s, 1H), 3.75 (s, 3H), 3.64-3.48 (m, 2H), 1.28 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 156.3, 155.6, 150.1, 137.6, 136.1, 128.3, 128.1, 128.0, 127.7, 126.5,

123.6, 118.9, 117.2, 113.6, 60.3, 55.2, 47.1, 6.7. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3S$ $[M+H]^+$ 383.1424; found 383.1428.

Diastereomer 2

Colourless sticky liquid, 22% yield (21 mg from 0.2456 mmol of corresponding aldehyde), ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (s, 1H), 8.58-8.56 (m, 1H), 7.76-7.74 (m, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.34-7.32 (m, 1H), 7.12 – 7.07 (m, 1H), 7.05 (d, J = 8.5 Hz, 2H), 6.87 (dd, J = 8.0, 1.0 Hz, 1H), 6.85 (dd, J = 7.5, 1.5 Hz, 1H), 6.71 (t, J = 7.5, 1H), 6.50 (d, J = 9.0 Hz, 2H), 5.57 (s, 1H), 3.66 (s, 3H), 3.56-5.53 (m, 2H), 1.26 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.3, 156.7, 156.4, 149.9, 137.4 135.7, 128.7, 128.3, 128.2, 128.1, 126.1, 123.5, 119.3, 117.6, 113.3, 61.4, 55.1, 47.4, 6.3.

Compound 5n (Yield: 33%, 29 mg of total products from 30 mg (0.4912 mmol) of aldehyde)



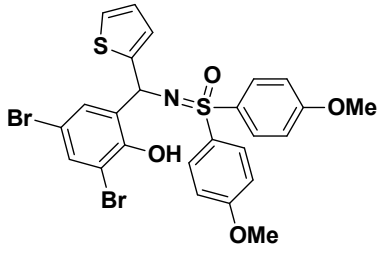
Diastereomer 1

Colourless sticky liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.20 – 7.13 (m, 3H), 6.86-6.84 (m, 3H), 6.69-6.68 (m, 1H), 5.85 (s, 1H), 2.98-2. 91 (m, 1H), 2.70 (s, 3H), 2.34-3.26 (m, 2H), 1.98-1.95 (m, 2H), 1.76-1.74 (m, 1H), 1.63 – 1.57 (m, 2H), 1.33 – 1.28 (m, 2H). 1.23 – 1.16 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 150.0, 128.9, 128.2, 127.9, 126.6, 124.6, 123.9, 119.5, 117.5, 63.7, 56.2, 37.1, 26.0, 25.3, 25.3, 25.3, 25.0. HRMS (ESI) calcd for $C_{18}H_{24}NO_2S_2$ $[M+H]^+$ 350.1243; found 350.1241

Diastereomer 2

Colourless sticky liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16-7.12 (m, 2H), 7.05 (dd, J = 8.0, 1.5 Hz, 1H), 6.88 – 6.85 (m, 2H), 6.84 – 6.83 (m, 1H), 6.79 (td, J = 7.5, 1.5 Hz, 1H), 5.90 (s, 1H), 2.97-2. 92 (m, 1H), 2.77 (s, 3H), 2.25-2.22 (m, 2H), 1.94-1.88 (m, 2H), 1.72 – 1.69 (m, 1H). 1.54-1.44 (m, 2H 1H), 1.33-1.28 (m, 2H), 1.23 – 1.16 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 150.1, 128.6, 128.2, 127.8, 126.7, 124.7, 123.9, 119.4, 117.5, 64.1, 56.5, 36.7, 26.4, 25.5, 25.3, 25.3, 24.9. HRMS (ESI) calcd for $C_{18}H_{24}NO_2S_2$ $[M+H]^+$ 350.1243; found 350.1240

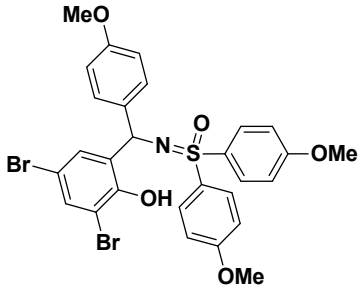
Compound 5o



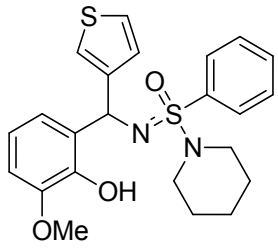
White crystalline solid, 75% yield, (47 mg from 30mg (0.1 mmol) of corresponding aldehyde), mp 161-162 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.80-7.77 (m, 4H), 7.51-

7.50 (m, 1H), 7.20-7.19 (m, 1H), 7.06 – 7.05 (m, 2H), 6.95 – 6.91 (m, 5H), 5.41 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 163.3, 152.7, 144.3, 133.6, 131.0, 130.7, 130.4, 130.3, 130.2, 129.5, 126.7, 126.1, 121.3, 114.7, 114.6, 112.1, 110.8, 58.1, 55.6, 55.6. HRMS (ESI) calcd for $C_{25}H_{24}NO_4S_2$ $[M+H]^+$ 466.1141; found 466.1145.

Compound 5p



White crystalline solid, yield 72% (46.5 mg from 30 mg (0.1 mmol) of corresponding aldehyde), mp 162-163 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.37 (s, 1H), 7.80 (d, J = 9.0 Hz, 2H), 7.75 (d, J = 9.0 Hz, 2H), 7.47 (d, J = 2.5 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 6.94-6.89 (m, 5H), 6.78 (d, J = 8.5 Hz, 2H), 5.33 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 163.3, 158.7, 152.6, 135.8, 133.4, 131.6, 130.9, 130.6, 130.3, 130.2, 129.7, 127.8, 114.7, 114.6, 113.8, 112.2, 110.8, 61.6, 55.7, 55.6, 55.2. HRMS (ESI) calcd for $C_{28}H_{28}NO_5S$ $[M+H]^+$ 490.1683; found 490.1688.

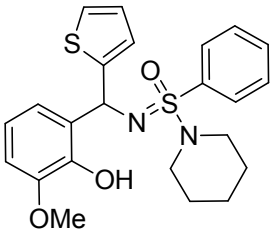


Compound 6a (Yield: 79%, 35.5 mg of total products from 30 mg (0.2 mmol) of aldehyde)

Diastereomer 1: Brown solid, mp 123-124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.16 (dd, J = 5.0, 3.0 Hz, 1H), 7.10 (dd, J = 5.5, 1.5 Hz, 1H), 7.05 – 7.04 (m, 1H), 6.86 – 6.82 (m, 3H), 5.94 (s, 1H), 3.90 (s, 3H), 2.90 – 2.89 (m, 2H), 2.81 – 2.79 (m, 2H), 1.43 – 1.41 (m, 4H), 1.32 – 1.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 145.4, 145.2, 135.1, 132.5, 128.9, 128.2, 127.5, 127.5, 125.4, 121.4, 120.2, 119.1, 110.4, 55.8, 55.5, 47.7, 25.1, 23.4. HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3S_2$ $[M+H]^+$ 443.1458; found 443.1460.

Diastereomer 2: Brown solid, mp 119-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.85 – 7.81 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.27 – 7.26 (m, 1H), 7.25 – 7.25 (m, 1H)7.20 (dd, J = 5.0, 2.9 Hz, 1H), 6.71 (s, 3H), 5.94 (s, 1H), 3.83 (s, 3H), 2.86-2.84 (m, 2H), 2.76-2.75 (m, 2H), 1.47 – 1.38 (m, 4H), 1.31 – 1.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 145.9, 145.2, 134.9, 132.4, 128.9, 128.8, 127.5, 126.9, 125.9, 120.5, 120.0, 118.9, 109.8, 55.7, 55.4, 47.7, 25.1, 23.4.

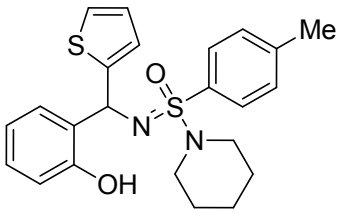
Compound 6b (Yield: 69%, 30.5 mg of total products from 30 mg (0.2 mmol) of aldehyde)



Diastereomer 1: Off white solid, mp 130-132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.89 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.0 Hz, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.11 (dd, J = 5, 1 Hz, 1H), 6.89 (dd, J = 6.5, 2 Hz, 1H), 6.87 – 6.86 (m, 1H), 6.84 – 6.82 (m, 3H), 6.11 (s, 1H), 3.90 (s, 3H), 2.92 – 2.89 (m, 2H), 2.81 – 2.78 (m, 2H), 1.42 – 1.39 (m, 4H), 1.32 – 1.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 148.4, 145.2, 135.0, 132.6, 128.9, 128.4, 127.5, 126.6, 124.4, 124.3, 120.1, 119.2, 110.6, 55.8, 55.0, 47.7, 25.1, 23.4. HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3S_2$ $[M+H]^+$ 443.1458; found 443.1462

Diastereomer 2: Off white solid, mp 132-134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.87 (d, J = 7.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.15 (dd, J = 5.0, 1.0 Hz, 1H), 6.97 (dd, J = 3.5, 1.0 Hz, 1H), 6.87 (dd, J = 5.0, 3.5 Hz, 1H), 6.81 (dd, J = 6.0, 3.0 Hz, 1H), 6.75 – 6.73 (m, 2H), 6.12 (s, 1H), 3.82 (s, 3H), 2.90 (bs, 4H), 1.51 – 1.48 (m, 4H), 1.35 – 1.32 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 148.4, 144.8, 135.1, 132.5, 129.4, 128.8, 127.6, 126.5, 124.1, 123.7, 119.9, 119.0, 110.1, 55.8, 54.8, 47.7, 25.2, 23.5.

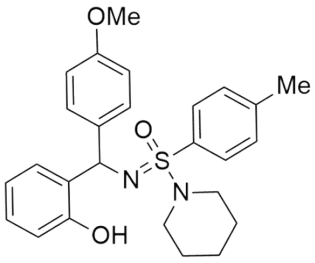
Compound 6c (Yield: 80%, 56 mg of total products from 40 mg (0.3278 mmol) of aldehyde)



Diastereomer 1: Off white solid, mp 116-118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 5.0, 1.5 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.91 – 6.90 (m, 1H), 6.88-6.87 (m, 1H), 6.82 (dd, J = 8.5, 1.5 Hz, 1H), 6.79-6.76 (m, 1H), 6.01 (s, 1H), 2.91 (brs, 4H), 2.43 (s, 3H), 1.53-1.49 (m, 4H), 1.38 – 1.32 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 149.8, 143.6, 132.1, 129.7, 128.9, 128.5, 127.9, 127.8, 126.7, 124.3, 123.8, 119.5, 117.7, 56.4, 47.9, 25.4, 23.6, 21.6. HRMS (ESI) calcd for $C_{23}H_{26}N_2NaO_2S_2$ $[M+Na]^+$ 449.1328; found 449.1336.

Diastereomer 2: Off white solid, mp 117-119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 5.0, 1.0 Hz, 1H), 7.09 (dd, J = 15.5, 7.5 Hz, 2H), 6.92 – 6.90 (m, 1H), 6.88 (dd, J = 5.0, 3.5 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.02 (s, 1H), 2.91 (bs, 4H), 2.43 (s, 3H), 1.53 - 1.50 (m, 4H), 1.36 – 1.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 149.6, 143.5, 131.8, 129.6, 128.8, 128.4, 127.7, 127.7, 126.5, 124.2, 123.7, 119.3, 117.6, 56.2, 47.7, 25.2, 23.5, 21.5.

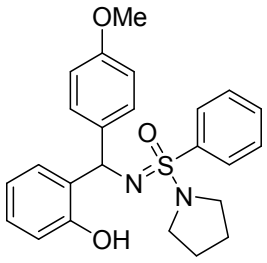
Compound 6d (Yield: 76%, 56.6 mg of total products from 40 mg (0.3278 mmol) of aldehyde)



Diastereomer 1: White solid, mp 116-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.33-7.30 (m, 4H), 7.17 (t, J = 7.0 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 2H), 5.82 (s, 1H), 3.73 (s, 3H), 2.89 – 2.87 (m, 2H), 2.78 – 2.74 (m, 2H), 2.42 (s, 3H), 1.43 – 1.41 (m, 4H), 1.31 – 1.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 156.4, 143.3 136.2, 132.4, 129.6, 128.4, 128.4, 128.2, 128.1, 127.6, 119.4, 117.3, 113.6, 59.3, 55.2, 47.8, 25.2, 23.5, 21.4. HRMS (ESI) calcd for $C_{26}H_{31}N_2O_3S$ $[M+H]^+$ 451.2050; found 451.2055.

Diastereomer 2: White solid, mp 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.33-7.29 (m, 4H), 7.17 – 7.13 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.84-6.81 (m, 1H), 6.78 (d, J = 8.5 Hz, 2H), 5.82 (s, 1H), 3.73 (s, 3H), 2.92 – 2.85 (m, 2H), 2.80 – 2.73 (m, 2H), 2.42 (s, 3H), 1.46 – 1.38 (m, 4H), 1.32 – 1.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 156.6, 143.5, 136.4, 132.6, 129.8, 128.6, 128.6, 128.4, 128.3, 127.8, 119.6, 117.5, 113.8, 59.5, 55.4, 47.9, 25.4, 23.7, 21.6.

Compound 6e (Yield: 52%, 36 mg of total products from 40 mg (0.3278 mmol) of aldehyde)

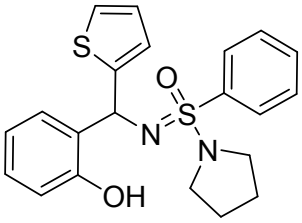


Diastereomer 1: Pale yellow sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.92 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 2H), 5.87 (s, 1H), 3.73 (s, 3H), 3.15 (dd, J = 7.0, 3.0 Hz, 2H), 2.99 (dd, J = 7.0, 3.0 Hz, 2H), 1.63 – 1.60 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 156.5, 136.3, 135.9, 132.5, 129.0, 128.4, 128.3, 128.2, 128.1, 127.6, 119.4, 117.4, 113.6, 59.7, 55.2, 48.5, 25.1. HRMS (ESI) calcd for $C_{24}H_{26}N_2NaO_3S$ $[M+Na]^+$ 445.1556; found 445.1578.

Diastereomer 2: Pale yellow sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.06 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 7.4 Hz, 1H), 6.82 (t, J = 7.8 Hz, 3H), 6.72 (t, J = 7.4 Hz, 1H), 5.76 (s, 1H), 3.77 (s, 3H), 3.13 – 3.07 (m, 2H), 2.93 – 2.88 (m, 2H), 1.60-1.59 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 156.2, 137.3, 135.8, 132.6, 129.1, 128.8, 128.2, 128.1, 127.9, 127.7, 119.3, 117.5, 113.7, 60.2, 55.2, 48.4, 25.1.

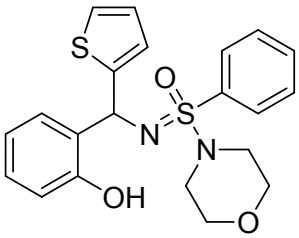
Compound 6f (Yield: 86%, 42 mg of total products from 30 mg (0.2458 mmol) of aldehyde)



Diastereomer 1: Pale brown sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.94 (d, J = 7.0 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.0 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.12 (t, J = 3 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.85-6.84 (m, 3H), 6.06 (s, 1H), 3.17 – 3.12 (m, 2H), 3.01 - 2.97 (m, 2H), 1.64 – 1.61 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 149.3, 135.7, 132.7, 129.1, 128.8, 128.0, 127.9, 127.6, 126.6, 124.5, 124.3, 119.4, 117.5, 56.3, 48.5, 25.1. HRMS (ESI) calcd for $C_{21}H_{22}N_2NaO_2S_2$ $[M+Na]^+$ 421.1015; found 421.1020.

Diastereomer 2: Pale brown sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.16 (dd, J = 4.5, 1.0 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.90 – 6.86 (m, 2H), 6.82 – 6.77 (m, 2H), 6.01 (s, 1H), 3.22 – 3.20 (m, 2H), 3.11 – 3.09 (m, 2H), 1.71 – 1.66 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 149.7, 135.6, 132.7, 129.1, 128.7, 128.5, 127.8, 127.7, 126.7, 124.1, 123.8, 119.3, 117.6, 56.5, 48.5, 25.2.

Compound 6g (Yield: 65%, 33.5 mg of total products from 30 mg (0.2458 mmol) of aldehyde)

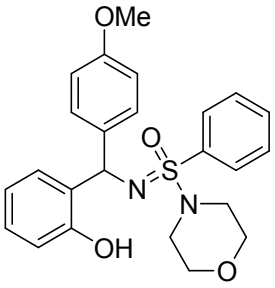


Diastereomer 1: Colourless sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 7.15 (d, J = 5.0 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.89 – 6.86 (m, 2H), 6.83 – 6.82 (m, 1H), 6.08 (s, 1H), 3.54 – 3.42 (m, 4H), 2.93 – 2.90 (m, 2H), 2.77 – 2.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 148.6, 133.9, 133.2, 129.2, 129.2, 127.9, 127.8, 127.6, 126.7, 124.7, 124.5, 119.7, 117.5, 66.0, 55.8, 47.0. HRMS (ESI) calcd for $C_{21}H_{22}N_2NaO_3S_2$ $[M+Na]^+$ 437.0964; found 437.0971.

Diastereomer 2: Colourless sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.17 (dd, J = 5.0, 1.0 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.95 (d, J = 3.5 Hz, 1H), 6.90 – 6.88 (m, 1H), 6.84 - 6.83 (m, 1H), 6.81 – 6.78 (m, 1H), 6.10 (s, 1H), 3.61 – 3.59 (m, 4H), 2.93 – 2.87 (m, 4H). ^{13}C NMR (126

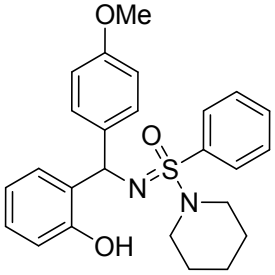
MHz, $CDCl_3$) δ 155.7, 149.1, 133.6, 133.2, 129.2, 128.6, 128.4, 127.8, 127.7, 126.7, 124.4, 123.9, 119.5, 117.7, 66.1, 56.1, 47.0.

Compound 6h (We were able to isolate only one isomer in its pure form. Yield: 73%, 39 mg of total products from 15 mg (0.1229 mmol) of aldehyde)



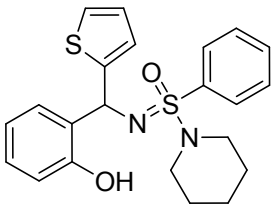
Light yellowish sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 9.0 Hz, 2H), 7.22 – 7.15 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 9.0 Hz, 2H), 5.89 (s, 1H), 3.74 (s, 3H), 3.56 – 3.50 (m, 2H), 3.48 – 3.42 (m, 2H), 2.90 (brs, 2H), 2.75 (brs, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 155.9, 137.4, 133.0, 129.2, 129.1, 128.2, 128.1, 128.0, 127.5, 126.4, 119.5, 117.6, 113.9, 65.9, 60.0, 55.3, 46.9. HRMS (ESI) calcd for $C_{24}H_{27}N_2O_4S$ $[M+H]^+$ 439.1686; found 439.1695.

Compound 6i (We were able to isolate only one isomer in its pure form. Yield: 74%, 39.5 mg of total products from 15 mg (0.1229 mmol) of aldehyde)



Off white solid, mp 115-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.86 (d, J = 7.0 Hz, 2H), 7.58(t, J = 7.0 Hz, 1H), 7.53 (t, J = 6.0 Hz, 2H), 7.33 – 7.31 (m, 2H), 7.18 – 7.14 (m, 2H), 6.85 (d, J = 7.0 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 5.84 (s, 1H), 3.74 (s, 3H), 2.91 – 2.89 (m, 2H), 2.81 – 2.79 (m, 2H), 1.44 – 1.41 (m, 4H), 1.33 – 1.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 156.4, 136.1, 135.5, 132.5, 130.2, 128.9, 128.4, 128.2, 127.5, 119.5, 117.4, 114.0, 113.6, 59.3, 55.2, 47.8, 25.2, 23.5. HRMS (ESI) calcd for $C_{25}H_{29}N_2O_3S$ $[M+H]^+$ 437.1893; found 437.1891.

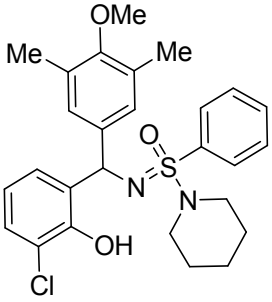
Compound 6j (We were able to isolate only one isomer in its pure form. Yield: 84%, 42.5 mg of total products from 15 mg (0.1229 mmol) of aldehyde)



Brownish sticky liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 5.0 Hz, 1H), 7.11 – 7.08 (m, 2H), 6.91 (bs, 1H), 6.88 (t, J = 4.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.03 (s, 1H), 2.93 (bs, 4H), 1.54 – 1.50 (m, 4H), 1.38 – 1.35 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 149.5, 135.0, 132.7, 128.9, 128.8, 128.5, 127.7, 127.7, 126.6, 124.2, 123.8,

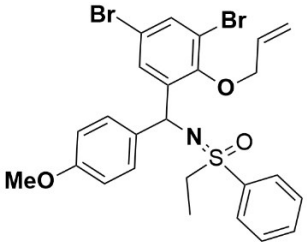
119.4, 117.6, 56.2, 47.8, 25.2, 23.5. HRMS (ESI) calcd for $C_{22}H_{25}N_2O_2S_2$ $[M+H]^+$ 413.1352; found 413.1358.

Compound 6k (We were able to isolate only one isomer in its pure form. Yield: 54%, 33 mg of total products from 15 mg (0.1229 mmol) of aldehyde)



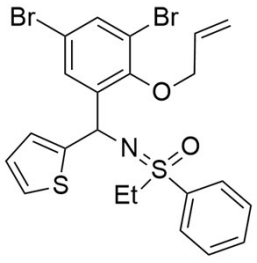
Pale yellow sticky liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.60 (t, J = 7.0 Hz, 1H), 7.54 (t, J = 7.0 Hz, 2H), 7.26 – 7.25 (m, 1H), 7.07 (dd, J = 7.5, 1 Hz, 1H), 7.02 (s, 2H), 6.78 (t, J = 7.5 Hz, 1H), 5.79 (s, 1H), 3.64 (s, 3H), 2.92 – 2.90 (m, 2H), 2.78 – 2. 75 (m, 2H), 2.20 (s, 6H), 1.47 - 1.45 (m, 2H), 1.39 – 1.37 (m, 2H), 1.33 – 1.31 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 152.1, 138.4, 135.0, 132.7, 130.5, 129.6, 129.1, 128.7, 127.4, 127.2, 126.8, 121.7, 119.8, 59.5, 59.4, 47.7, 25.1, 23.4, 16.2. HRMS (ESI) calcd for $C_{27}H_{32}ClN_2O_3S$+ $[M+H]^+$ 499.1817; found 499.1821.

Compound 7a



Brownish sticky liquid. Yield: 91% (59 mg from 60 mg (0.1113 mmol) of one of the pure diastereomer of **5c**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 2.5 Hz, 1H), 7.71 - 7.70 (m, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.49 (d, J = 2.5 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 5.80 - 5.74 (m, 1H), 5.59 (s, 1H), 5.13 – 5.09 (m, 1H), 5.03 - 5.0 (m, 1H), 4.18 - 4.15 (m, 2H), 3.74 (s, 3H), 3.29 - 3.18 (m, 2H), 1.25 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 151.3, 144.1, 137.7, 136.9, 133.6, 133.1, 132.8, 131.4, 129.4, 129.1, 128.1, 117.7, 117.6, 117.5, 113.5, 73.7, 55.2, 54.6, 51.4, 7.5. HRMS (ESI) calcd for $C_{25}H_{26}Br_2NO_3S$ $[M+H]^+$ 579.9975; found 579.9951.

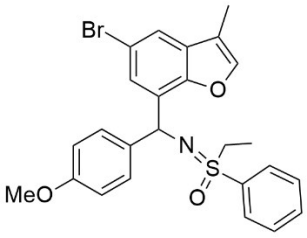
Compound 7b



Brown liquid. Yield: 90% (71 mg from 74 mg (0.1429 mmol) of one of the pure diastereomer of **5d**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 2.0 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.54 – 7.51 (m, 1H), 7.48 (d, J = 2.5 Hz, 1H), 7.44 - 7.41 (m, 2H), 7.15 (dd, J = 5.0, 1.0 Hz, 1H), 6.87 - 6.85 (m, 1H), 6.77 - 6.76 (m, 1H), 5.94 (d, J = 0.5 Hz, 1H), 5.85 – 5.78 (m, 1H), 5.19 – 5.10 (m, 2H), 4.12 - 4.08 (m, 1H), 3.94 - 3.90 (m, 1H), 3.35 - 3.28 (m, 1H), 3.24 - 3.17 (m, 1H), 1.28 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 150.6, 142.4,

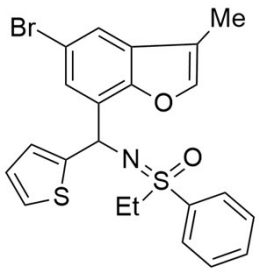
137.9, 134.2, 132.9, 132.8, 131.5, 129.1, 129.0, 126.6, 124.3, 123.9, 117.8, 117.7, 117.5, 74.2, 50.9, 50.4, 7.3. HRMS (ESI) calcd for $C_{22}H_{22}Br_2NO_2S_2$ $[M+H]^+$ 553.9453; found 553.9455.

Compound 8a



Yellowish sticky liquid. Yield: 52% (19 mg from 42 mg (0.0725 mmol) of **7a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 2.0 Hz, 1H), 7.72 - 7.71 (m, 2H), 7.54 - 7.53(m, J = 6.0, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.24 – 7.22 (m, 3H), 6.69 (d, J = 9.0 Hz, 2H), 5.80 (s, 1H), 3.72 (s, 3H), 3.29 – 3.19 (m, 2H), 2.12 (s, 3H), 1.22 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 150.8, 142.0, 138.1, 136.7, 132.6, 132.2, 130.7, 129.4, 128.9, 128.3, 125.2, 120.3, 115.7, 115.2, 113.4, 55.2, 54.8, 51.3, 7.8, 7.5. HRMS (ESI) calcd for $C_{25}H_{25}BrNO_3S$ $[M+H]^+$ 498.0734; found 498.0720.

Compound 8b



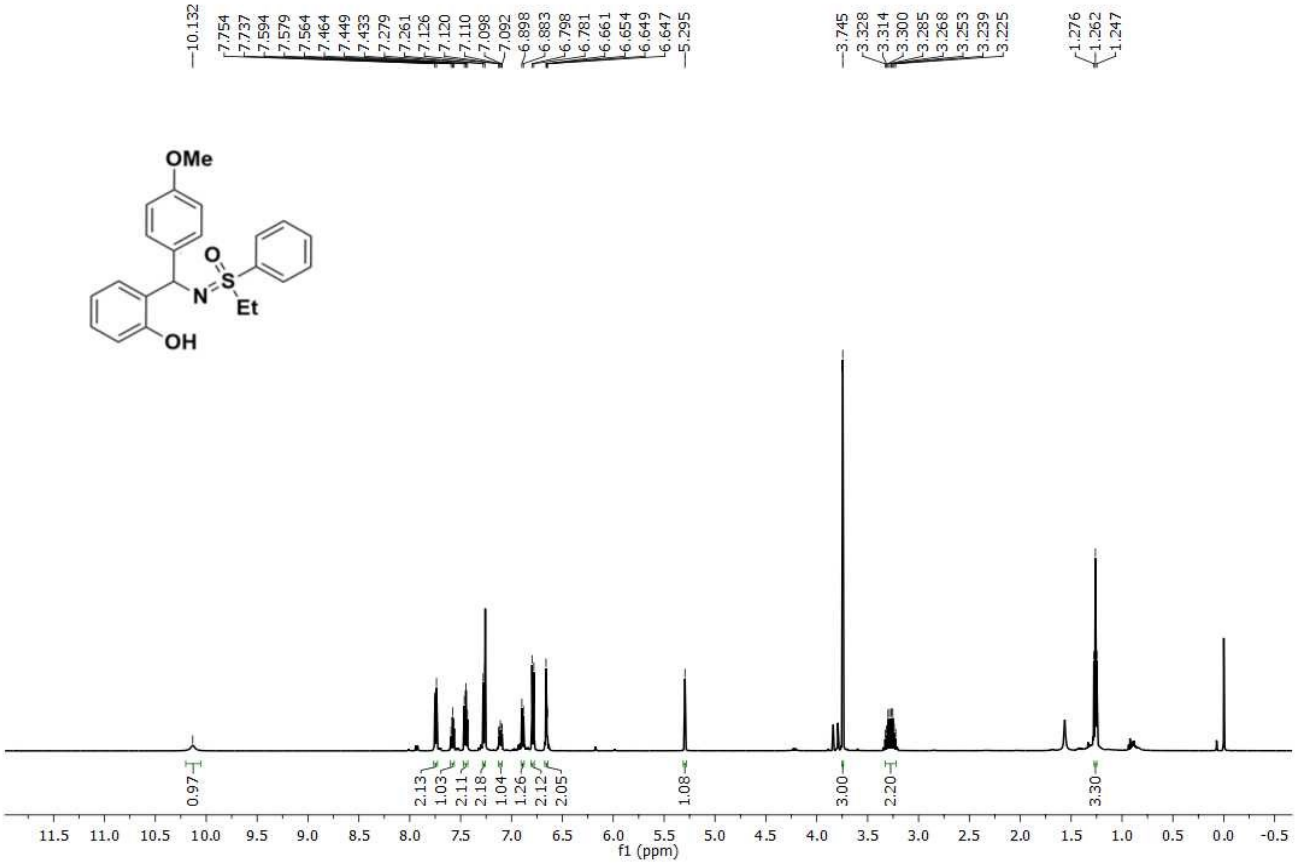
Off white solid, Yield: 65% (25 mg from 45 mg (0.0804 mmol) of **7b**), mp 127-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.5, 1.0 Hz, 2H), 7.51 (d, J = 2.0 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.20 (d, J = 2.0 Hz, 1H), 7.17 – 7.15 (m, 2H), 7.01 (dd, J = 4.5, 1.5 Hz, 1H), 5.90 (s, 1H), 3.33 – 3.19 (m, 2H), 2.13 (s, 3H), 1.25 (t, J = 7.5 Hz 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 145.8, 142.2, 137.7, 132.5, 130.8, 130.4, 128.9, 128.7, 127.3, 125.8, 125.2, 121.3, 120.5, 115.7, 115.1, 51.5, 51.1, 7.8, 7.4. HRMS (ESI) calcd for $C_{22}H_{21}BrNO_2S_2$ [M+H]+ 474.0192; found 474.0185.

Reference

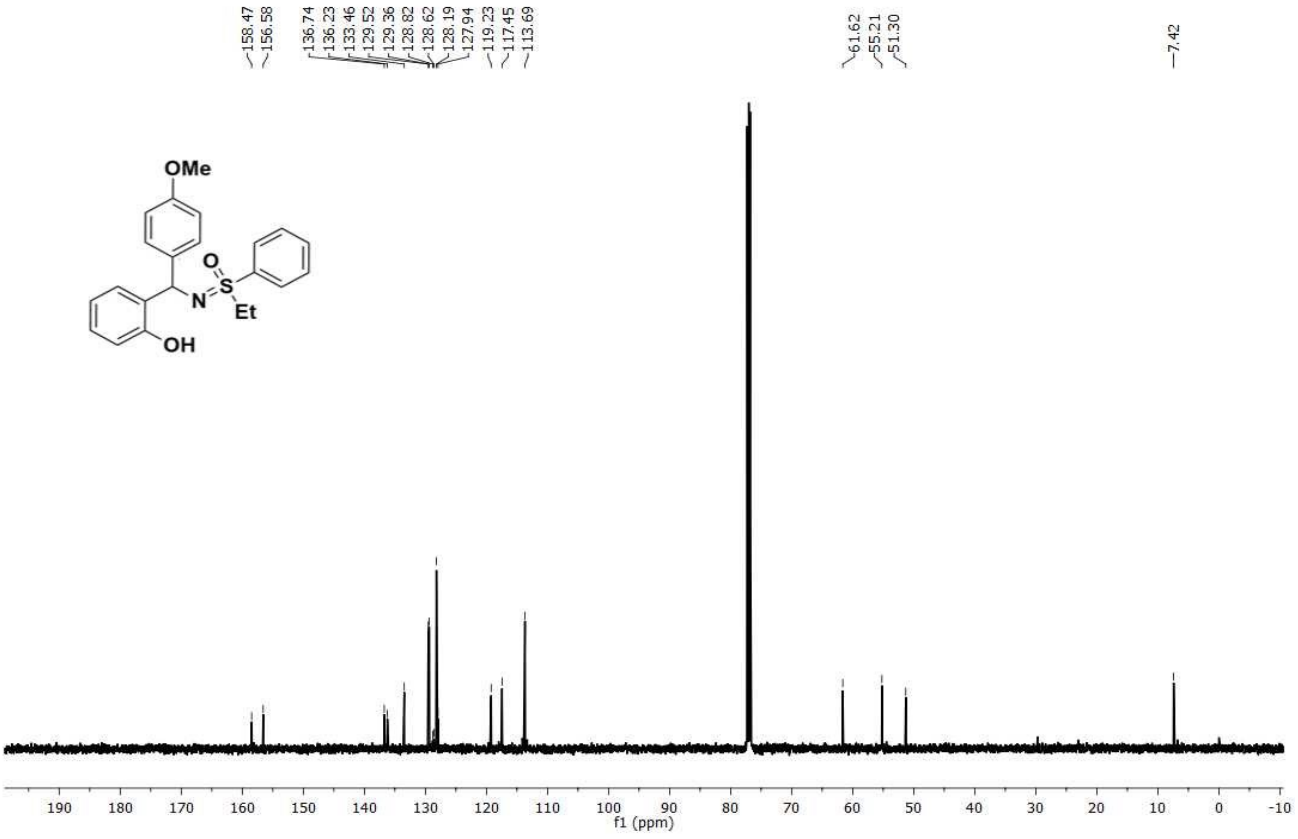
1. (a) Y. Xie, B. Zhou, S. Zhou, S. Zhou, W. Wei, J. Liu, Y. Zahn, D. Cheng, M. Chen, Y. Li, B. Wang, X. Xue and Z. Li, *ChemistrySelect* 2017, **2**, 1620; (b) F. Izzo, M. Schäfer, R. Stockman and U. Lücking, *Chem. Eur. J.*, 2017, **23**, 15189.

6. NMR Spectra of Synthesized Compound

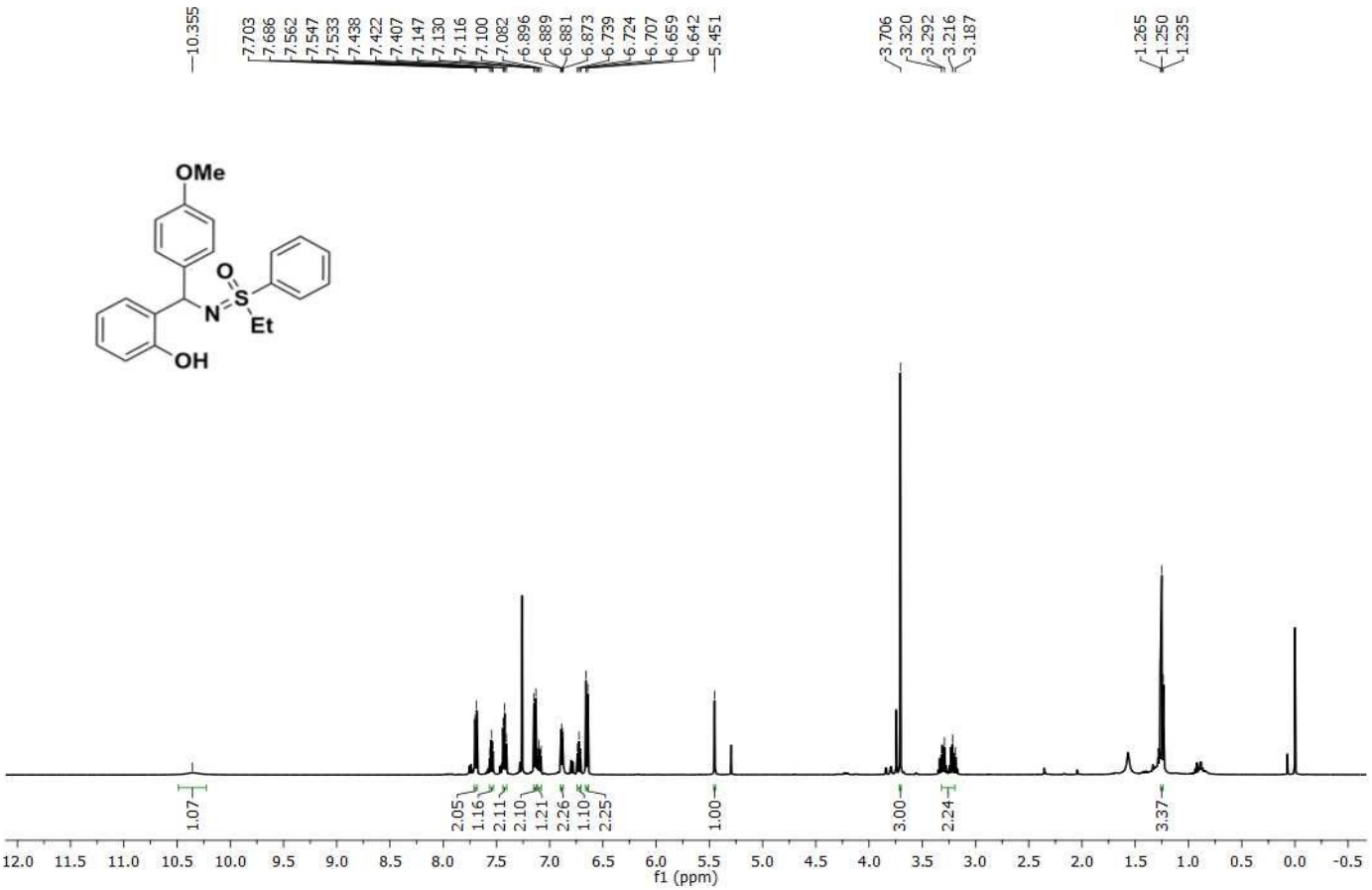
^{1}H NMR of **5a** (Diastereomer- 1)



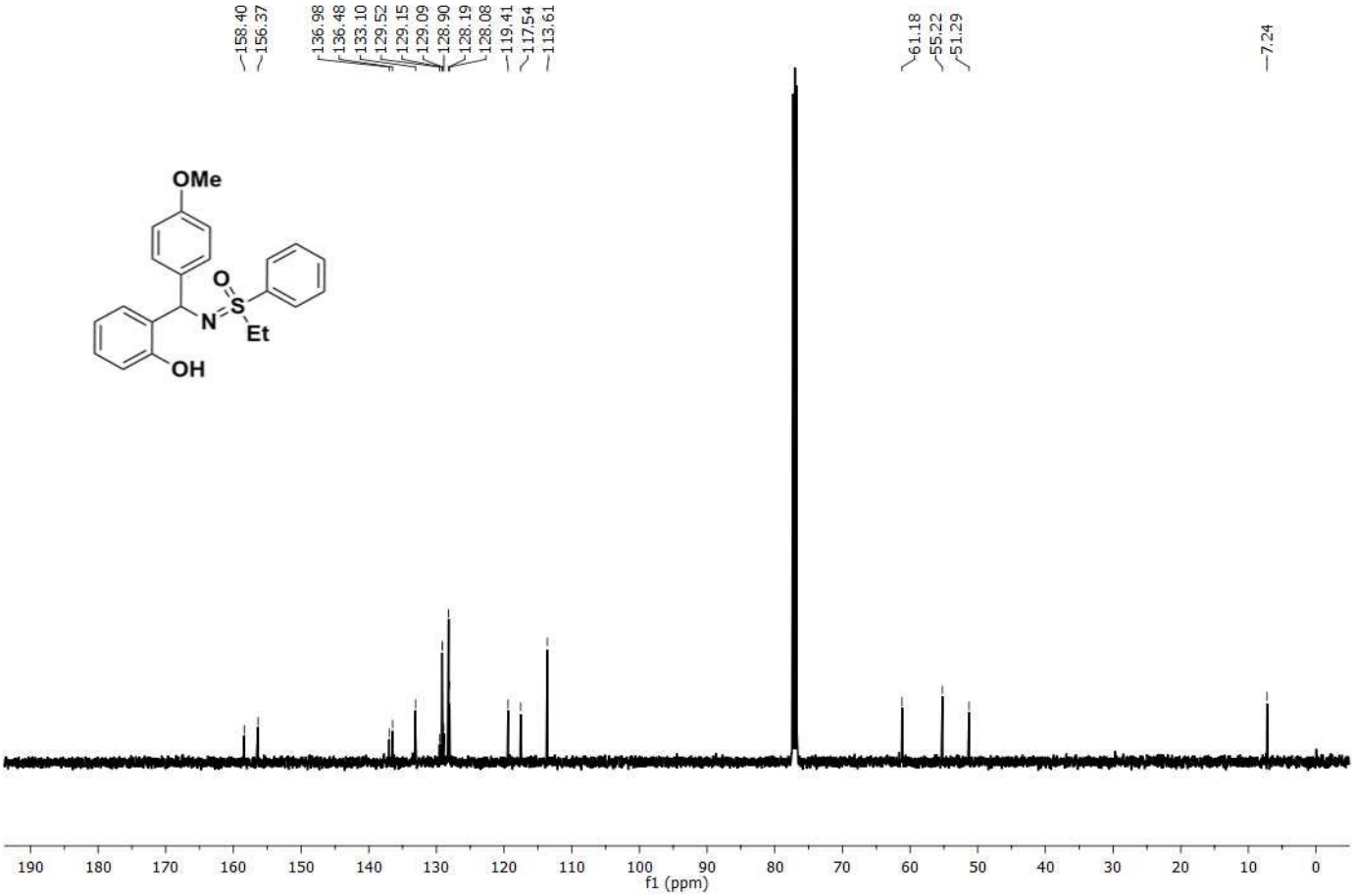
^{13}C {^{1}H} NMR of **5a** (Diastereomer- 1)



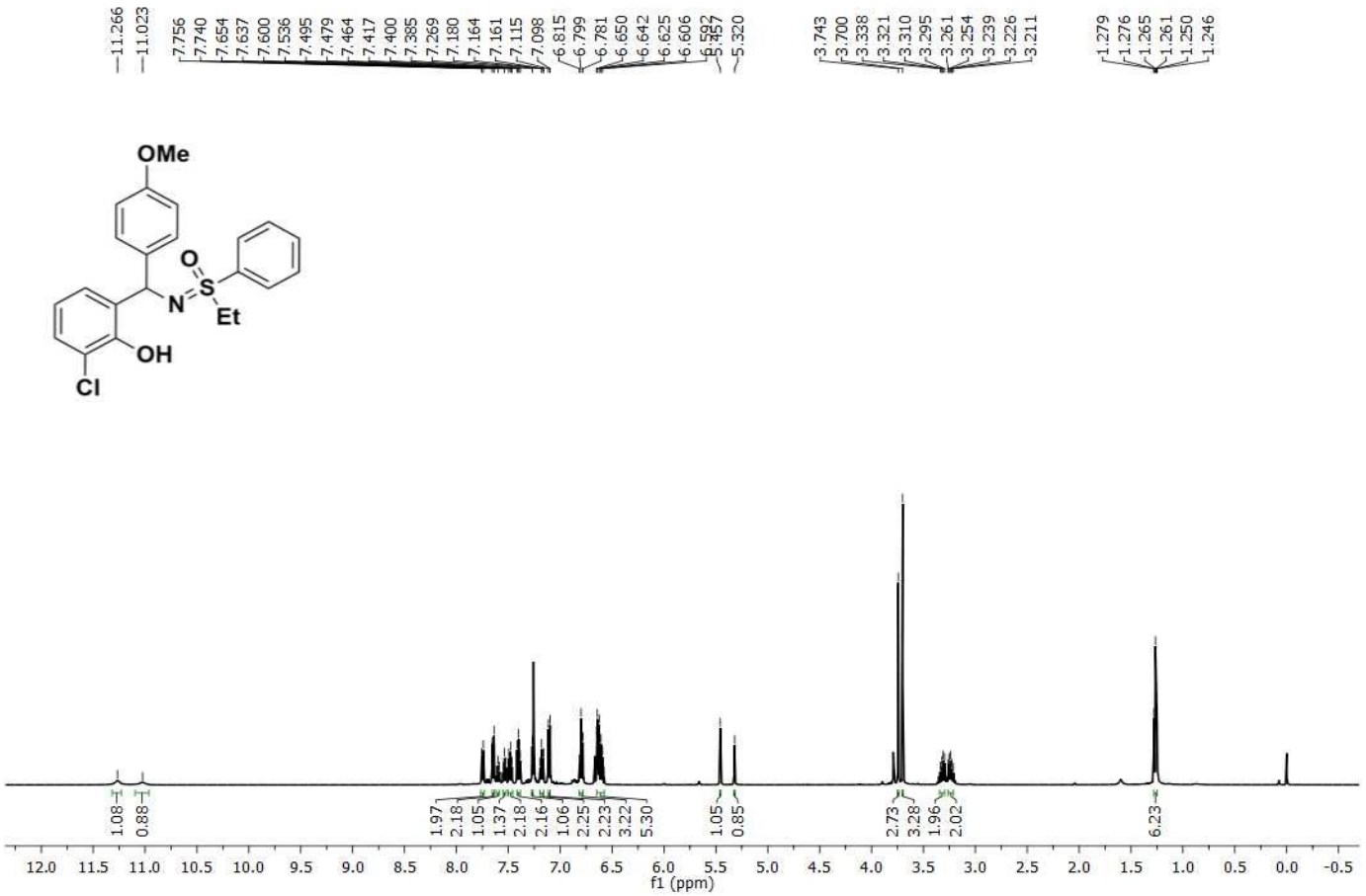
^{1}H NMR of **5a** (Diastereomer- 2)



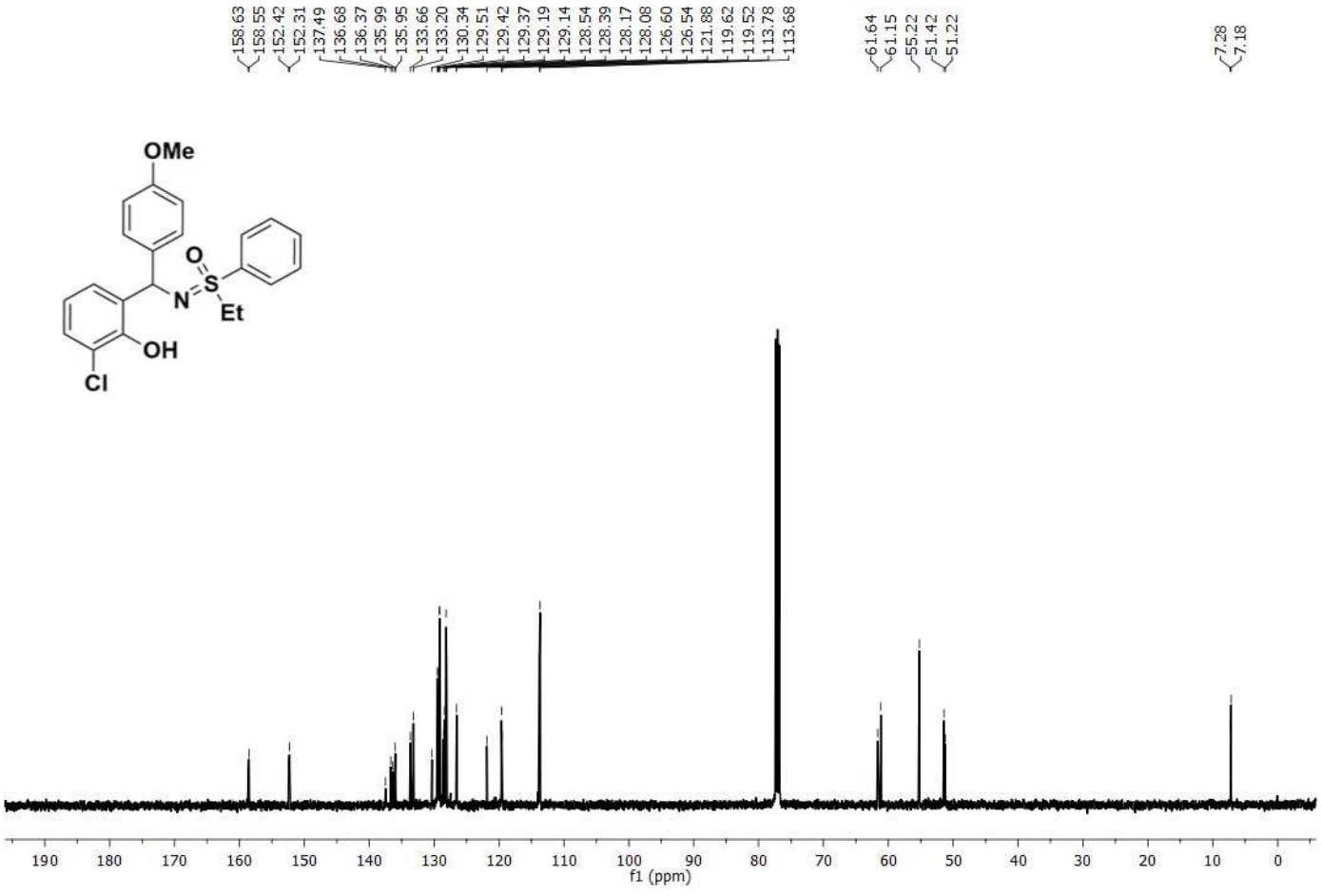
^{13}C {^{1}H} NMR of **5a** (Diastereomer- 2)



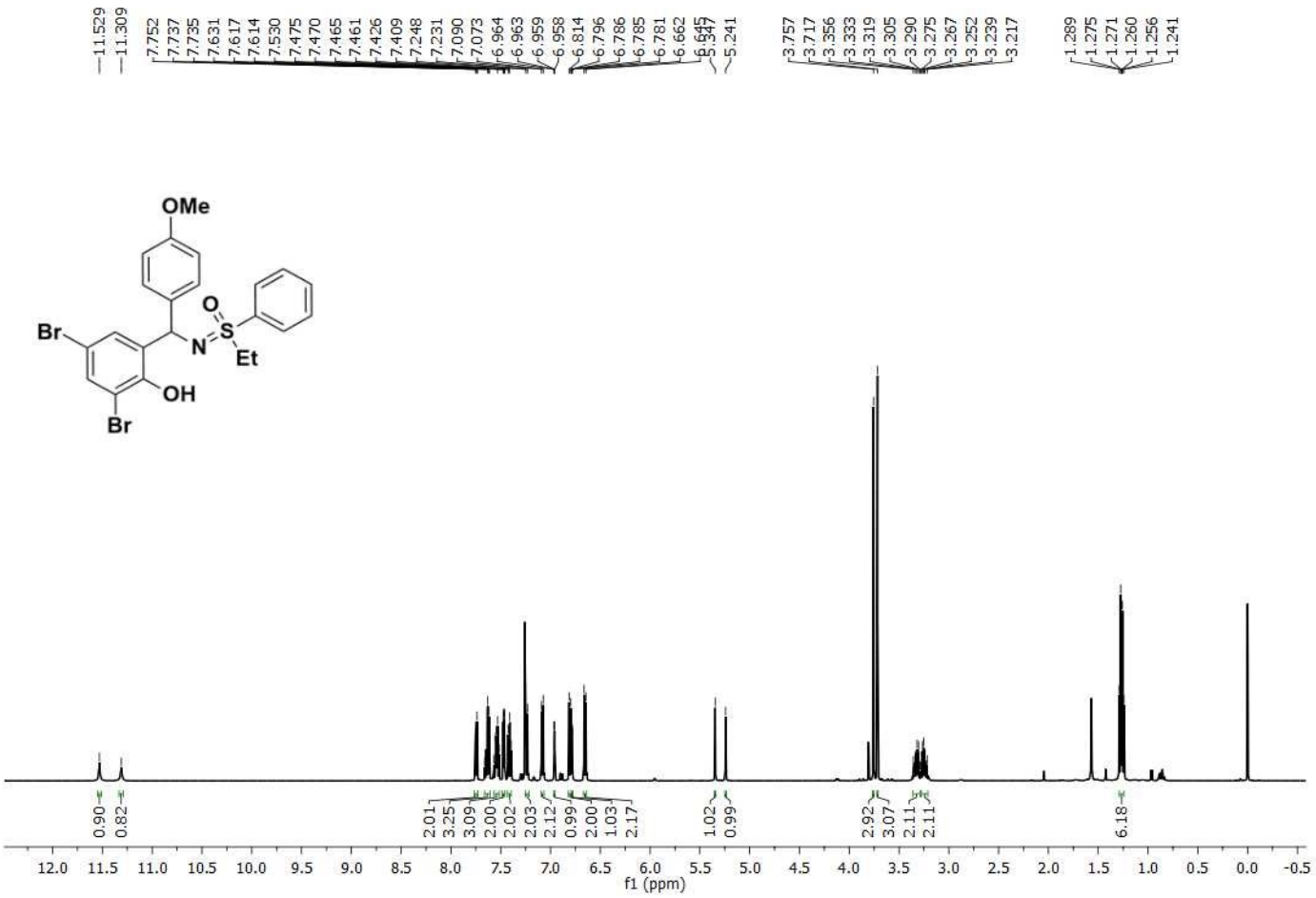
^{1}H NMR of **5b** (Mixture of Diastereomers)



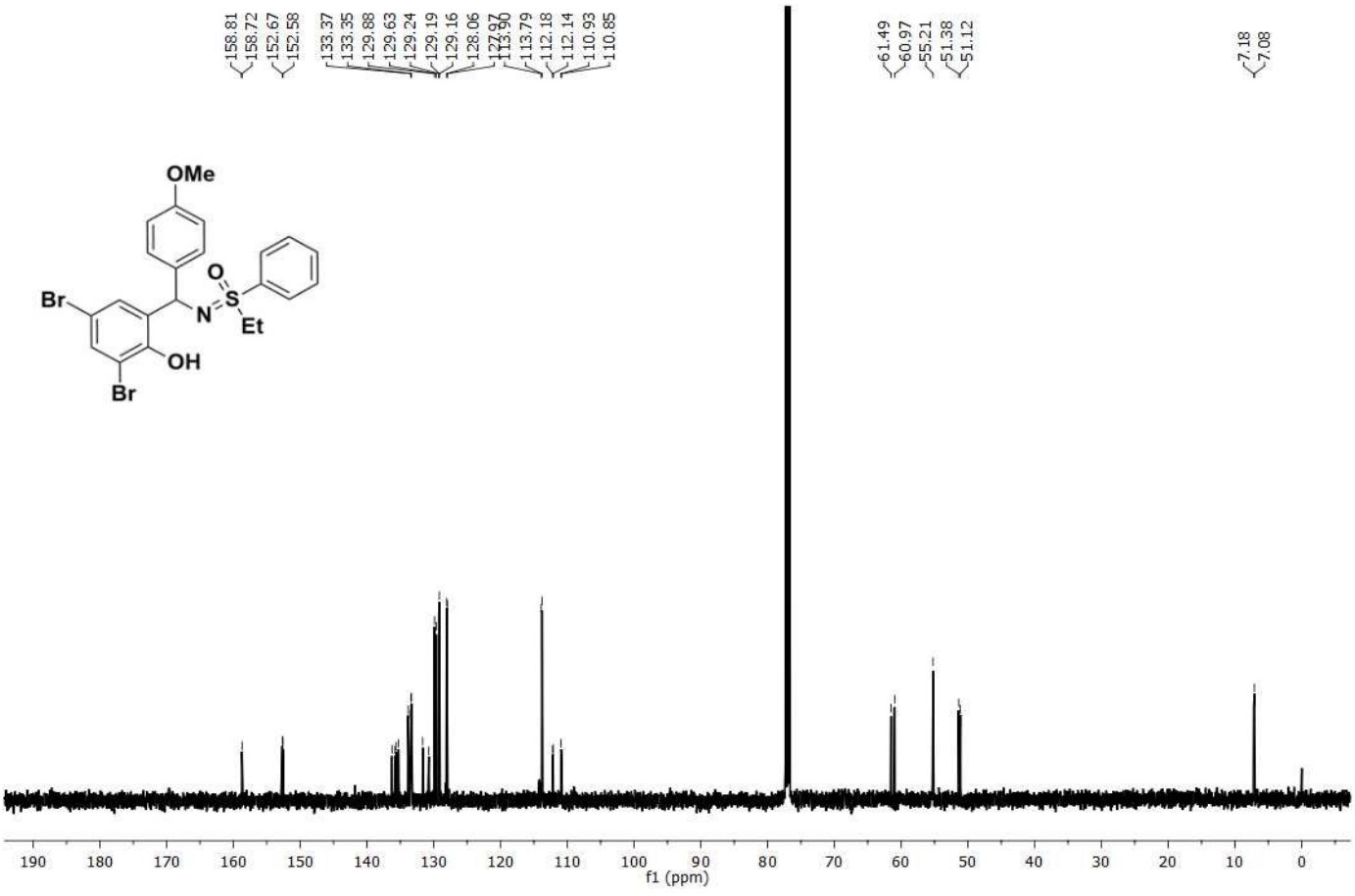
^{13}C {^{1}H} NMR of **5b** (Mixture of Diastereomers)



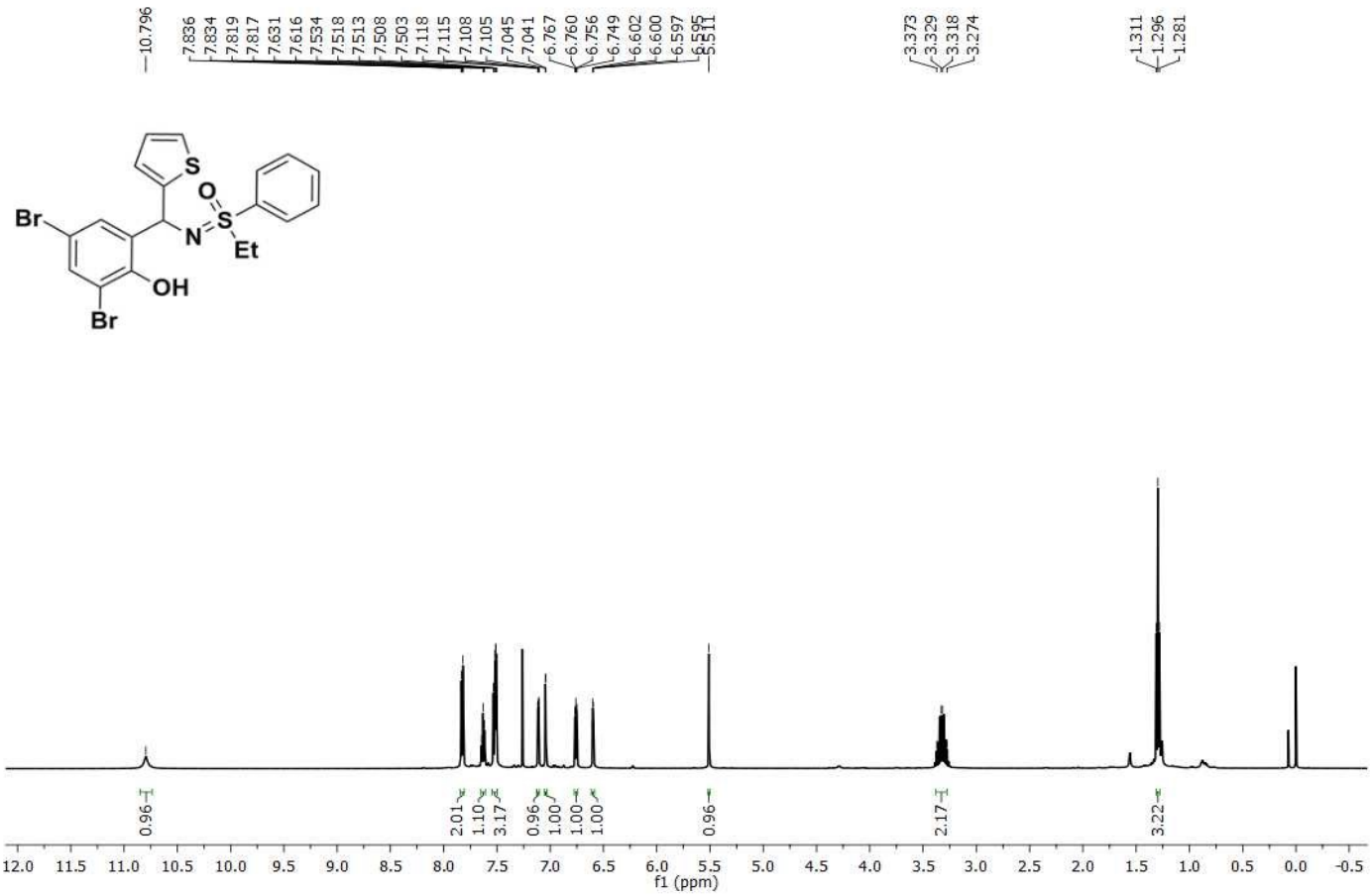
^{1}H NMR of **5c** (Mixture of Diastereomers)



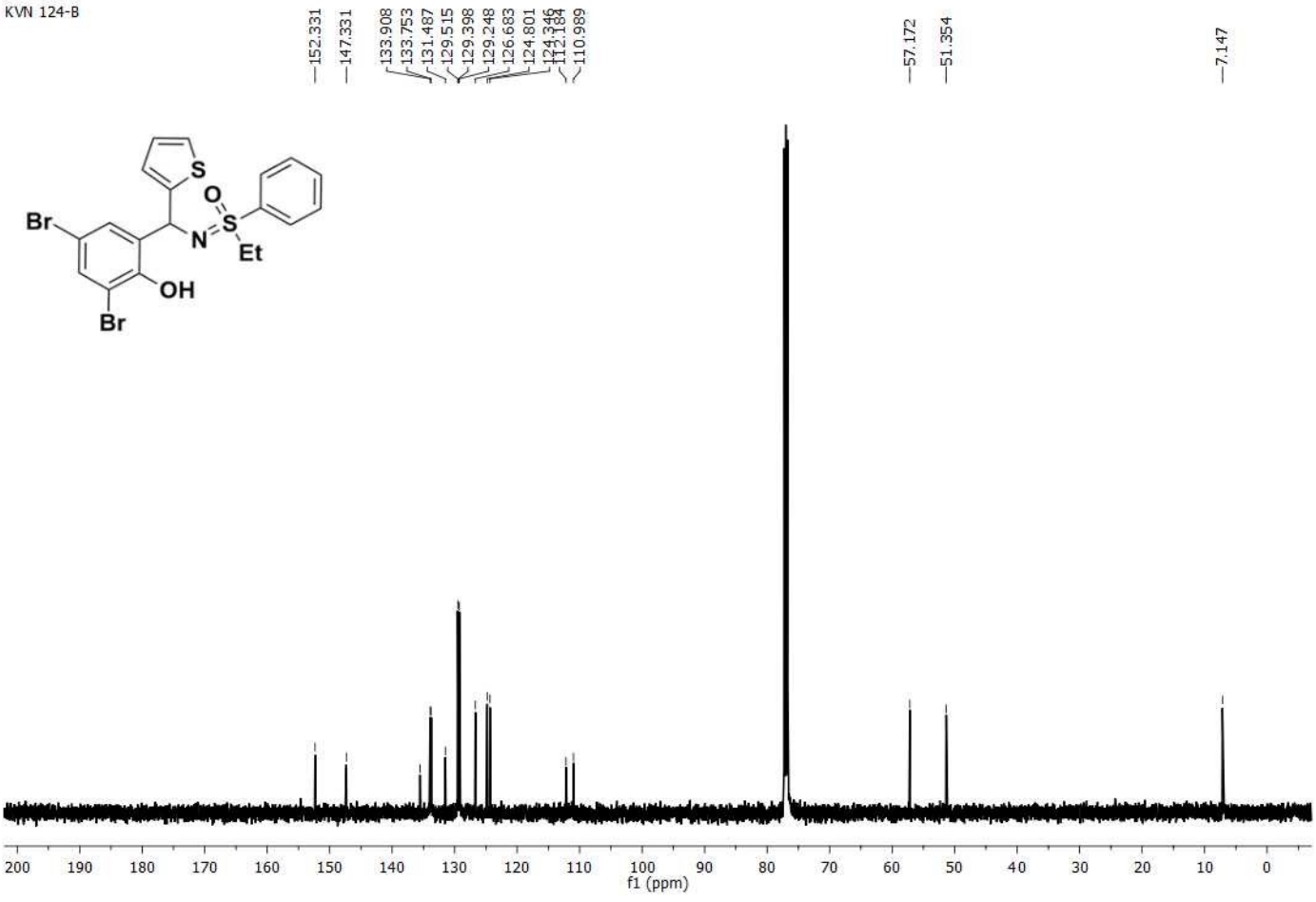
^{13}C {^{1}H} NMR of **5c** (Mixture of Diastereomers)



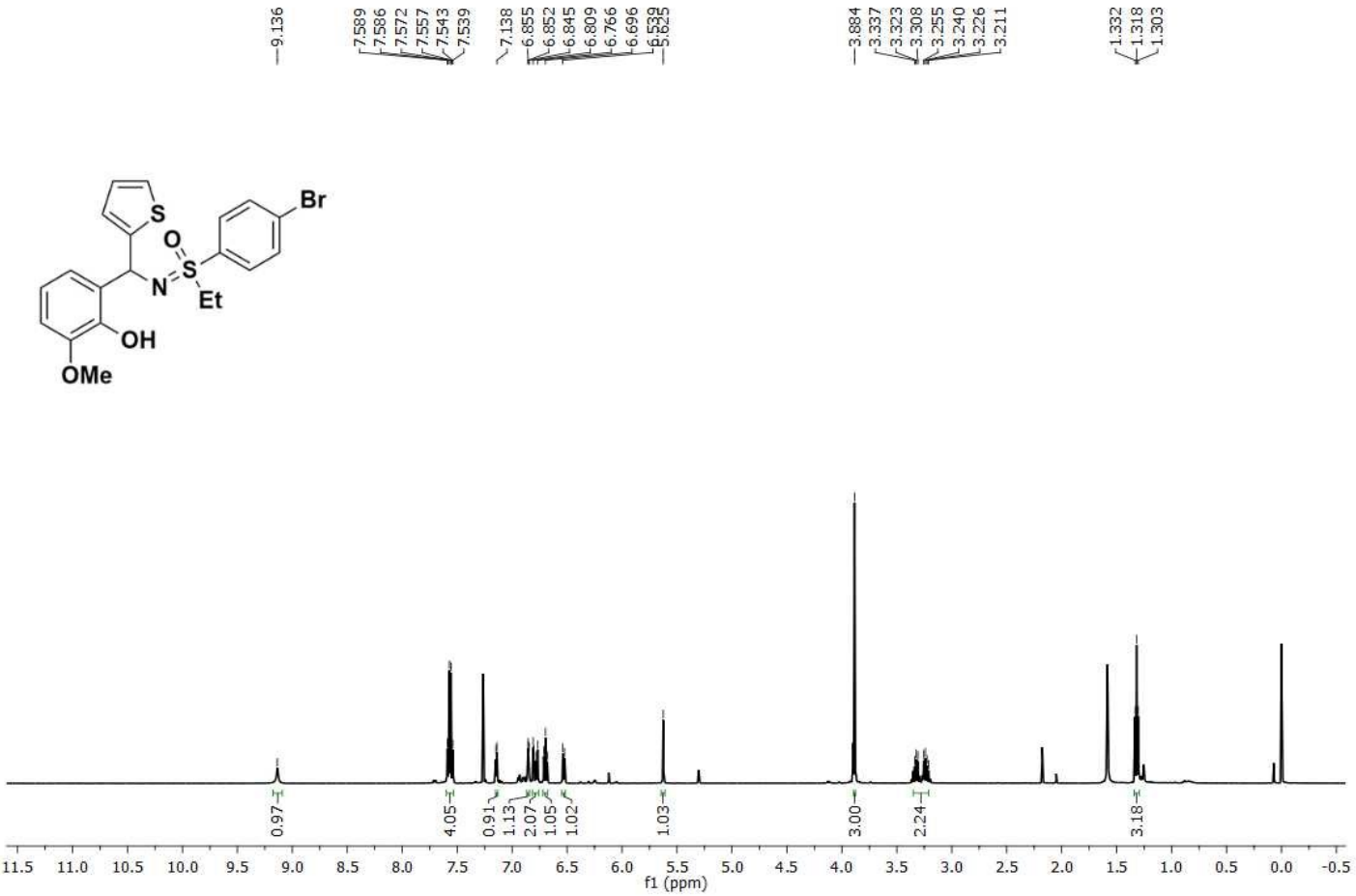
^{1}H NMR of **5d** (Diastereomer-1, able to purify only one diastereomer)



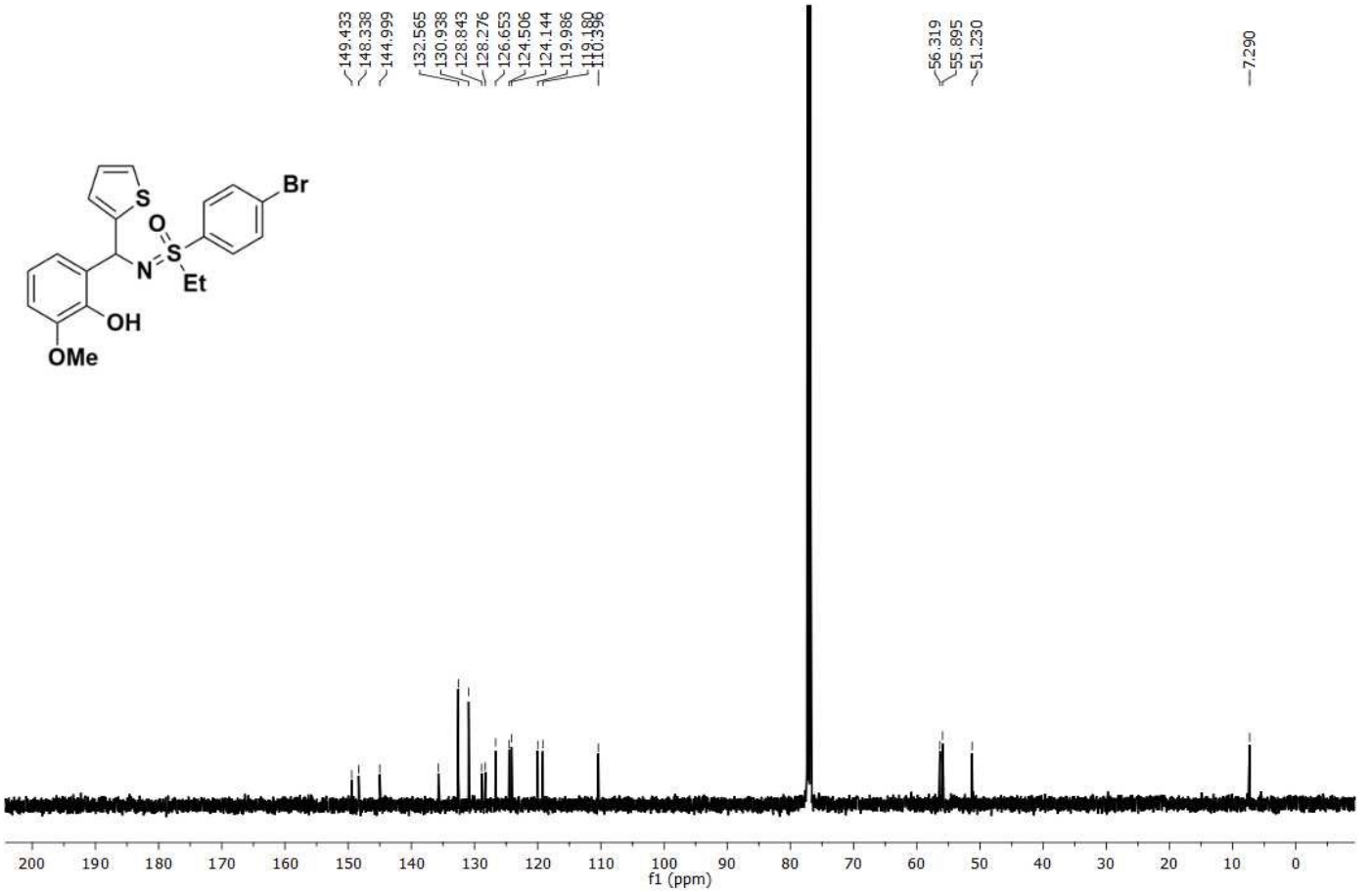
^{13}C {^{1}H} NMR of **5d** (Diastereomer-1, able to purify only one diastereomer)



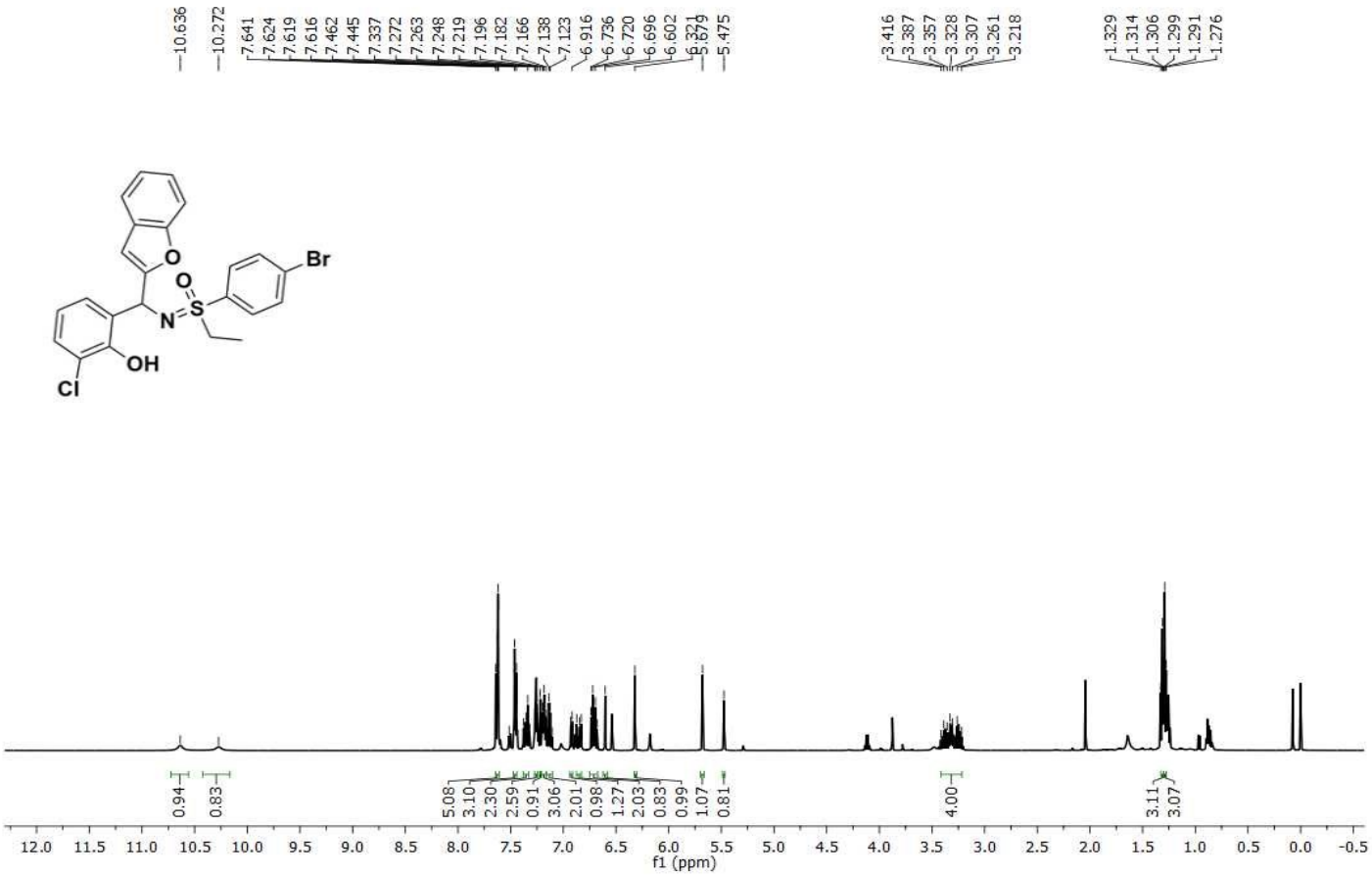
^{1}H NMR of **5e** (Diastereomer-1, able to purify only one diastereomer)



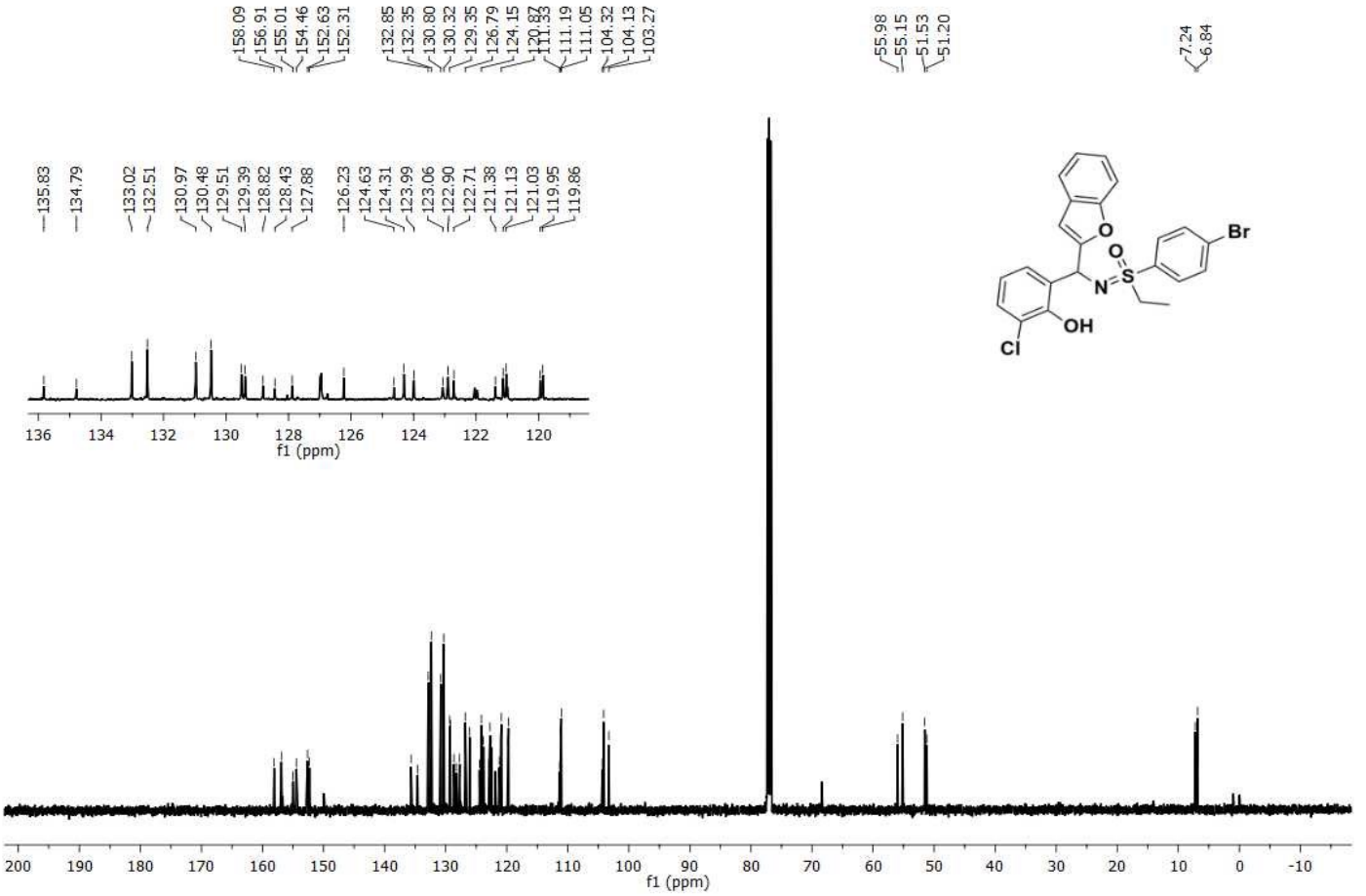
^{13}C {^{1}H} NMR of **5e** (Diastereomer-1, able to purify only one diastereomer)



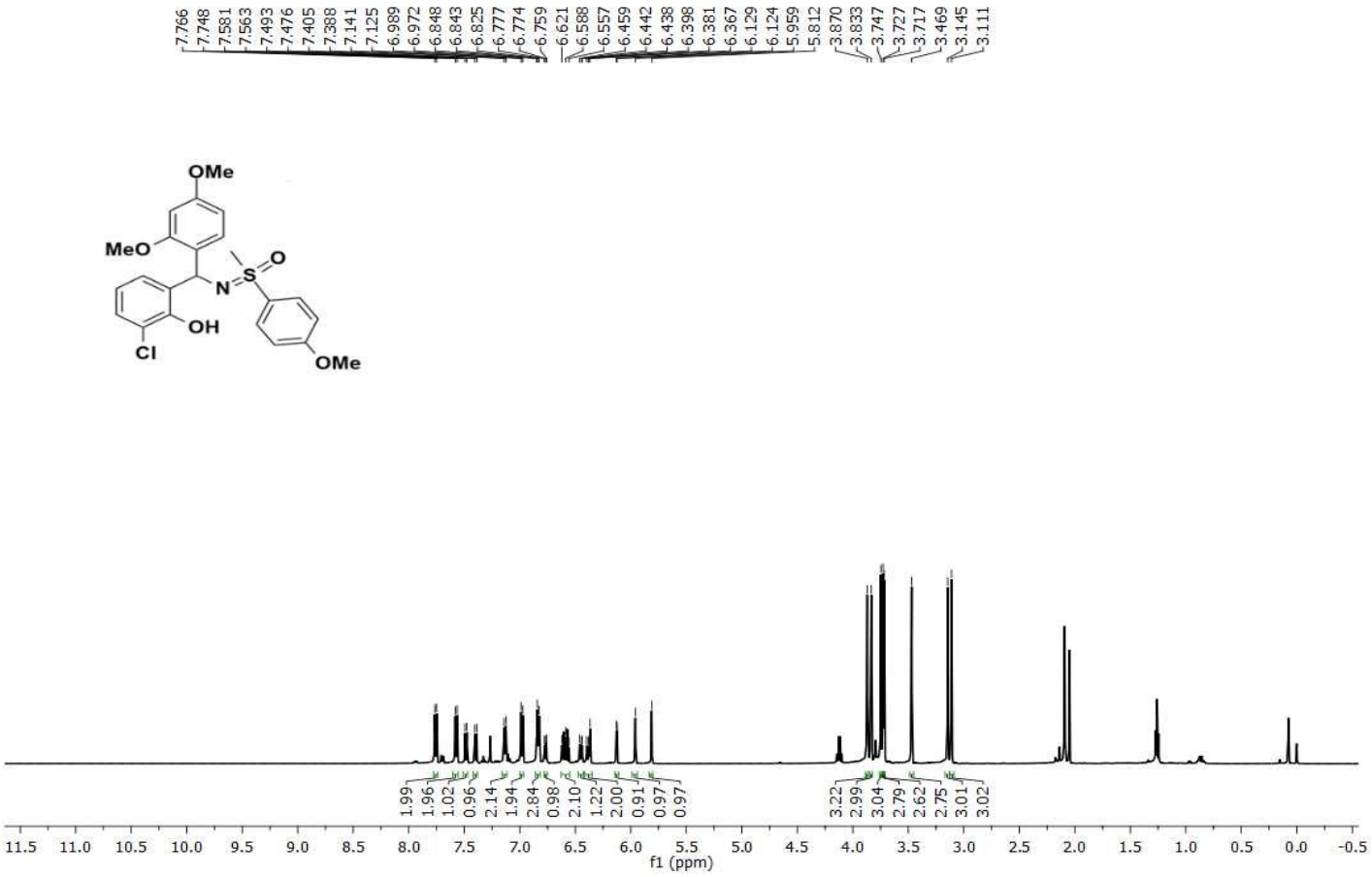
^{1}H NMR of **5f** (Mixture of Diastereomers)



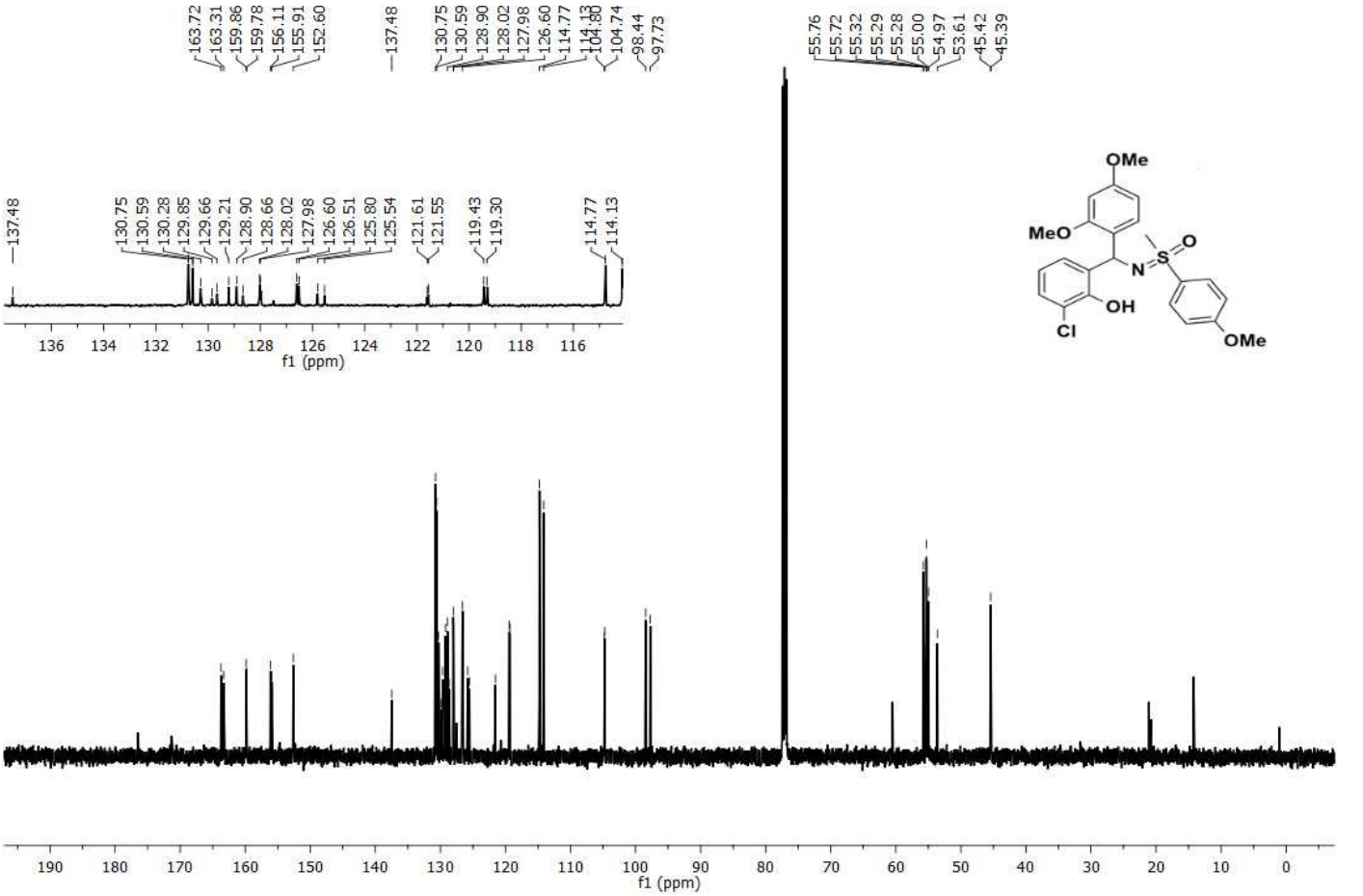
^{13}C {^{1}H} NMR of **5f** (Mixture of Diastereomers)



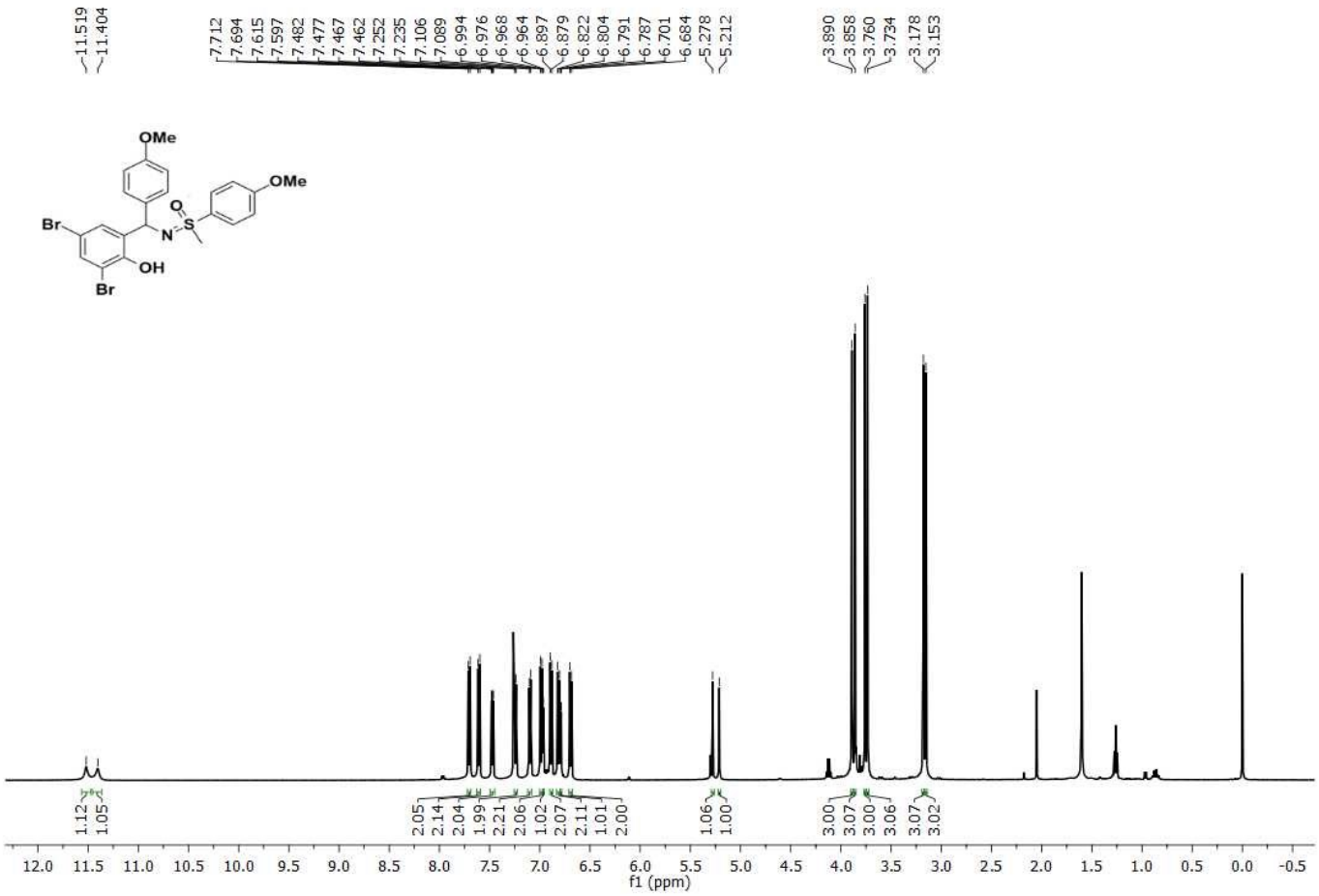
^{1}H NMR of **5g** (Mixture of Diastereomers)



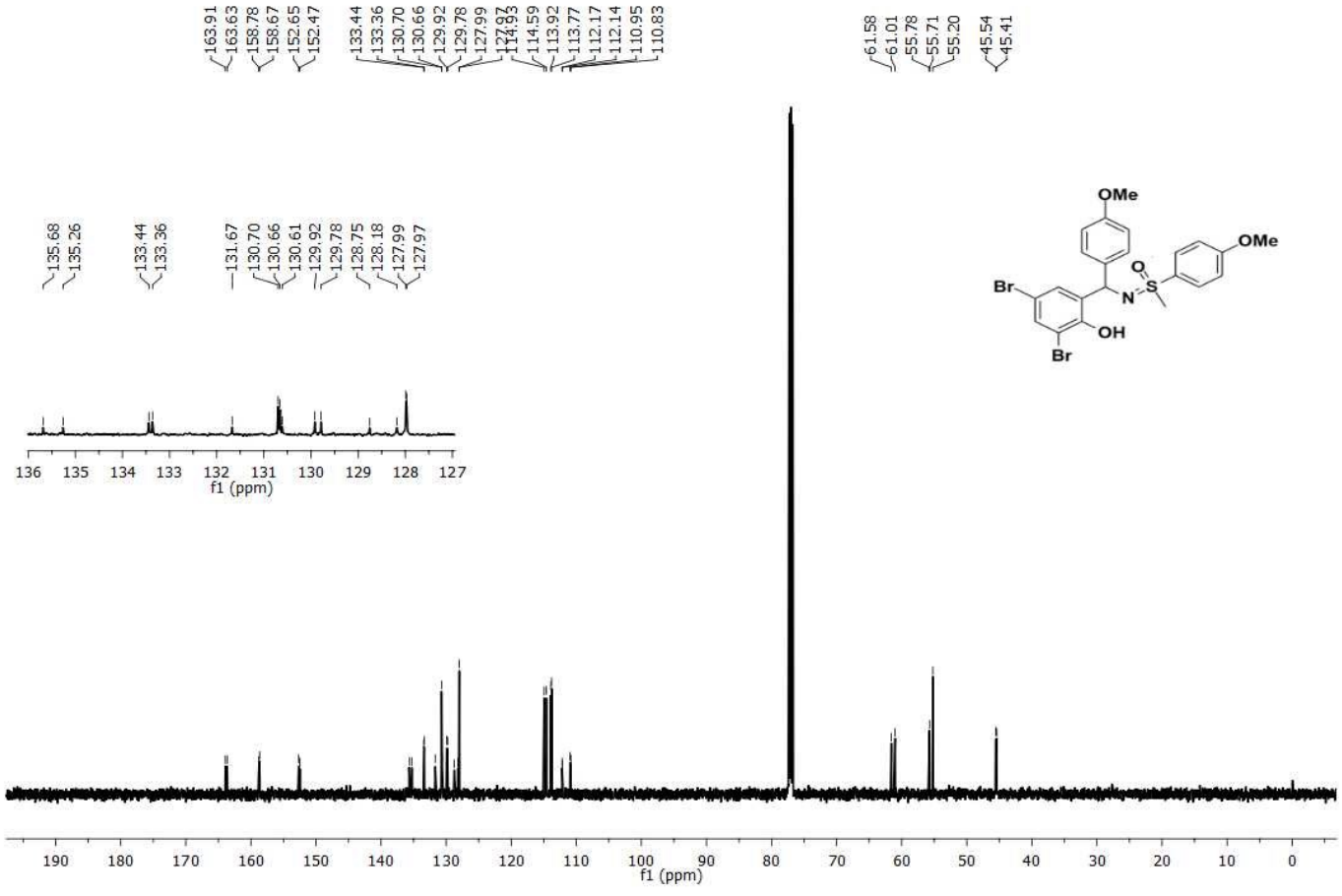
^{13}C {^{1}H} NMR of **5g** (Mixture of Diastereomers)



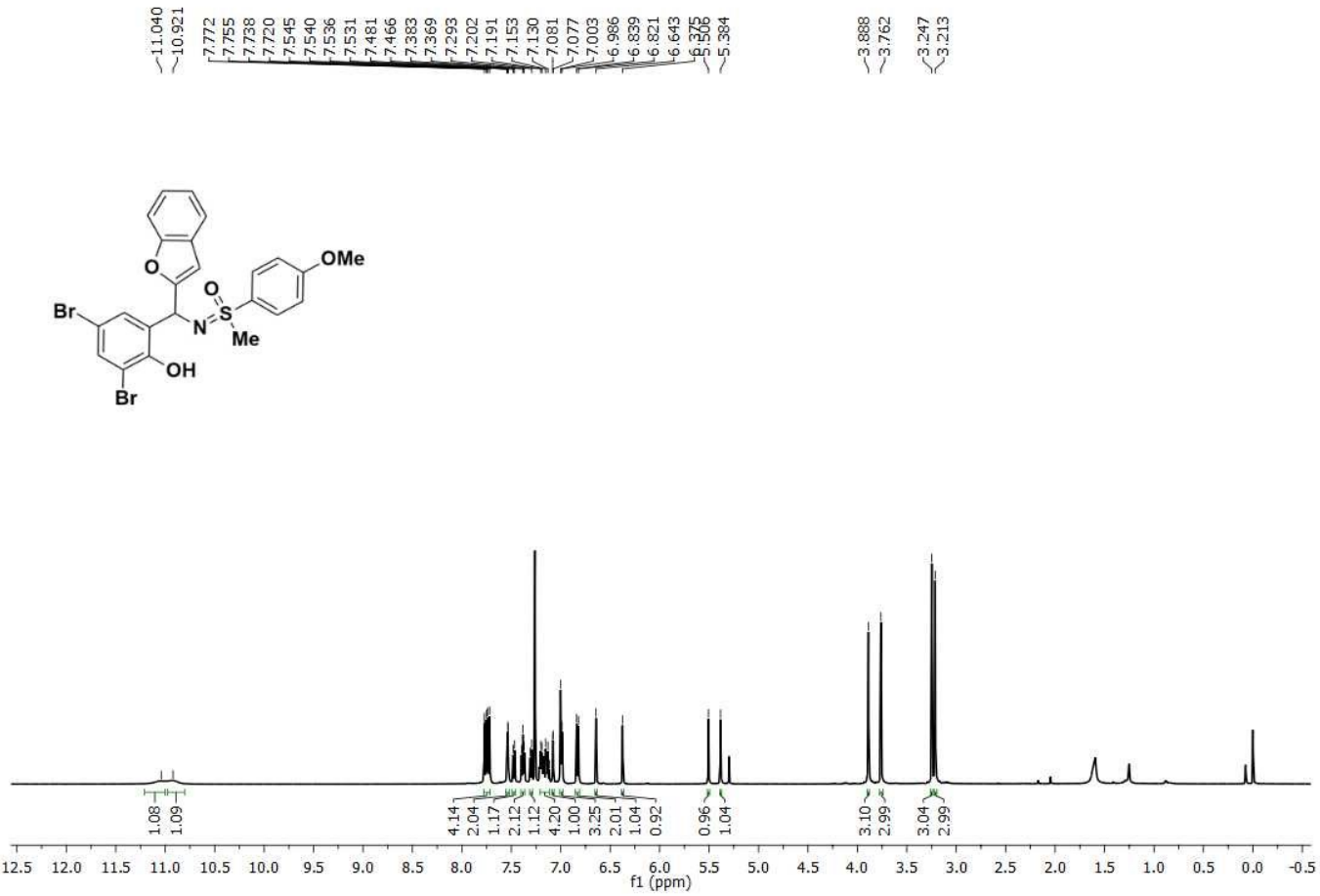
^{1}H NMR of **5h** (Mixture of Diastereomers)



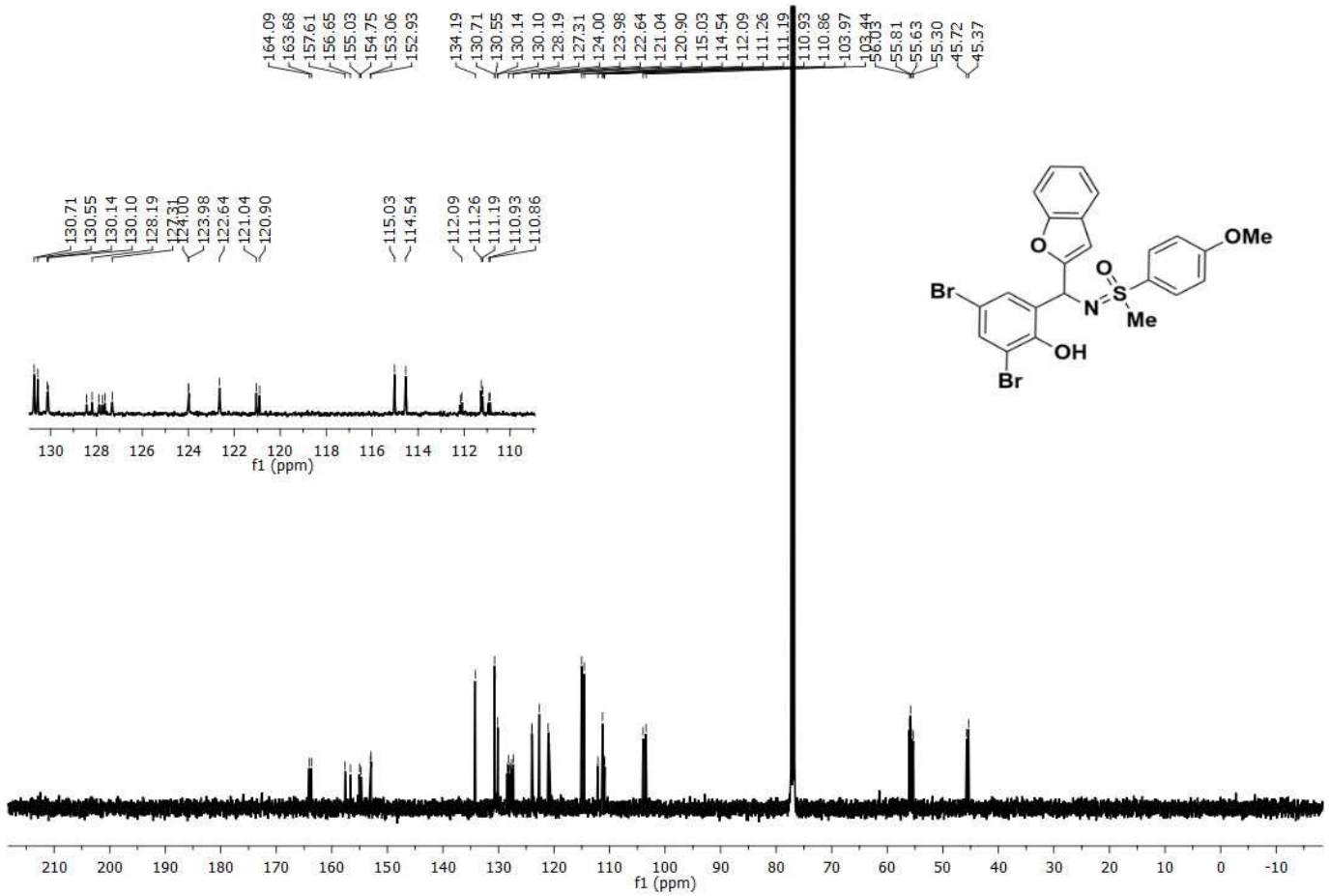
^{13}C {^{1}H} NMR of **5h** (Mixture of Diastereomers)



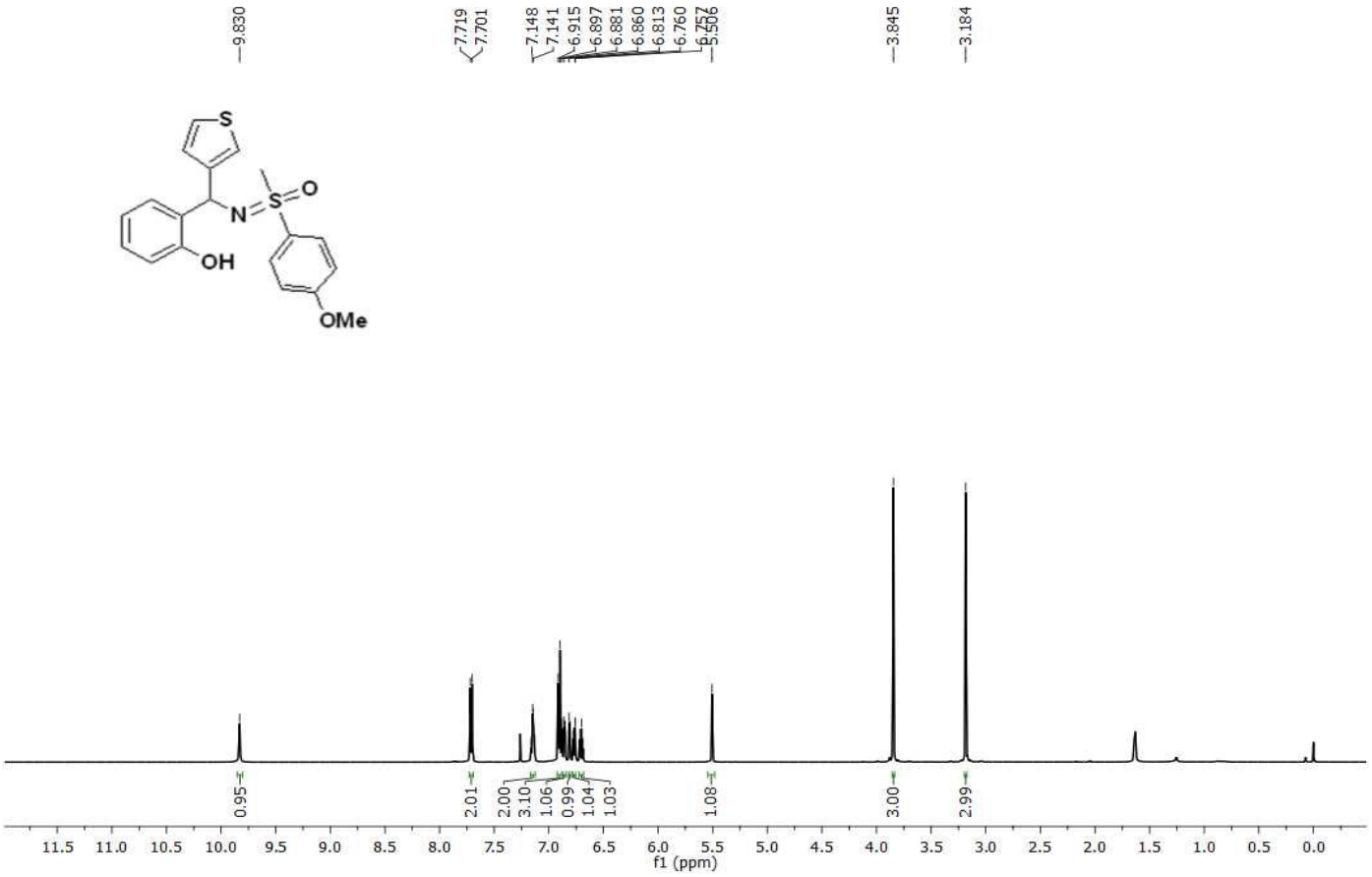
^{1}H NMR of **5i** (Mixture of Diastereomers)



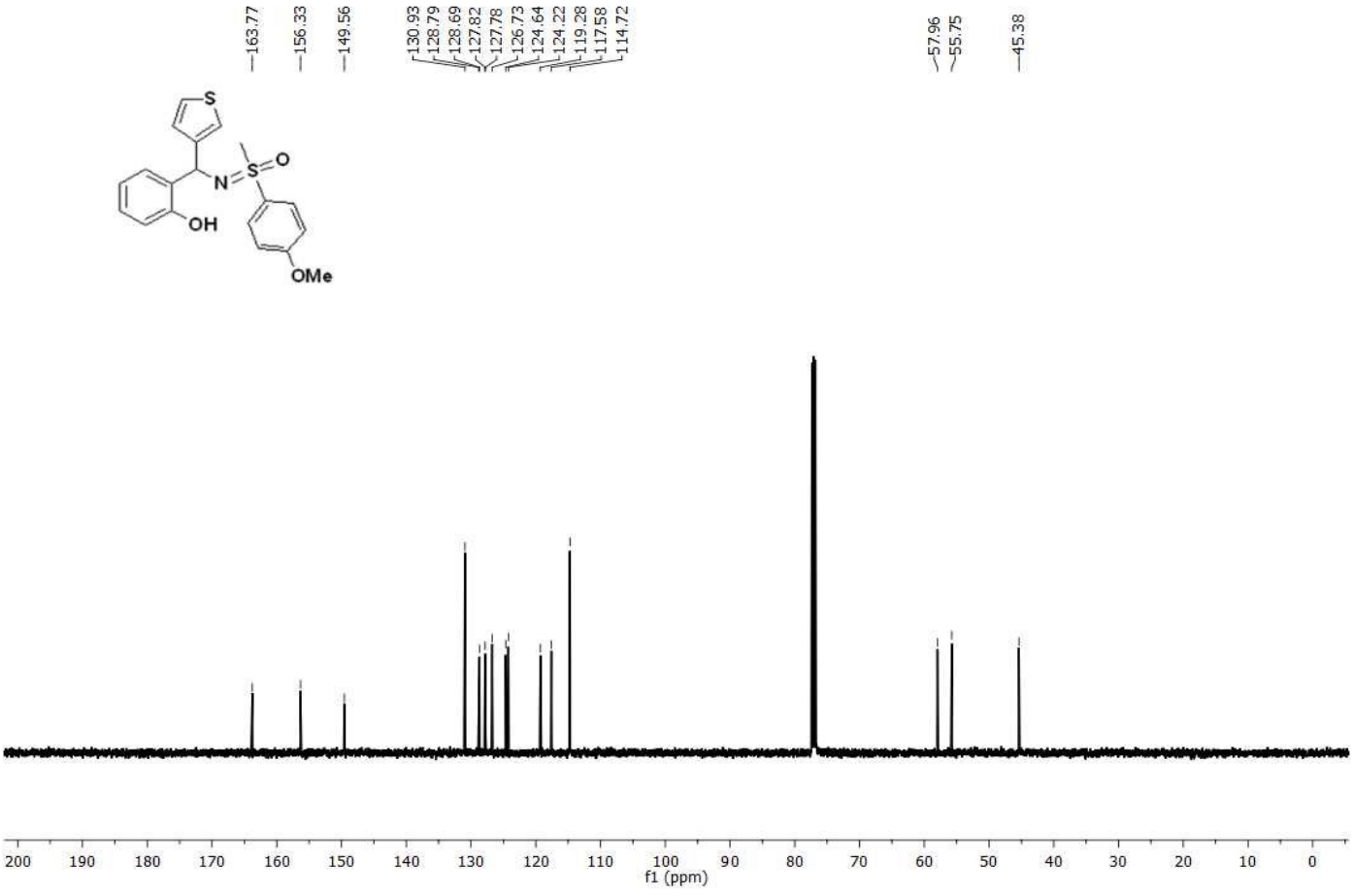
^{13}C {^{1}H} NMR of **5i** (Mixture of Diastereomers)



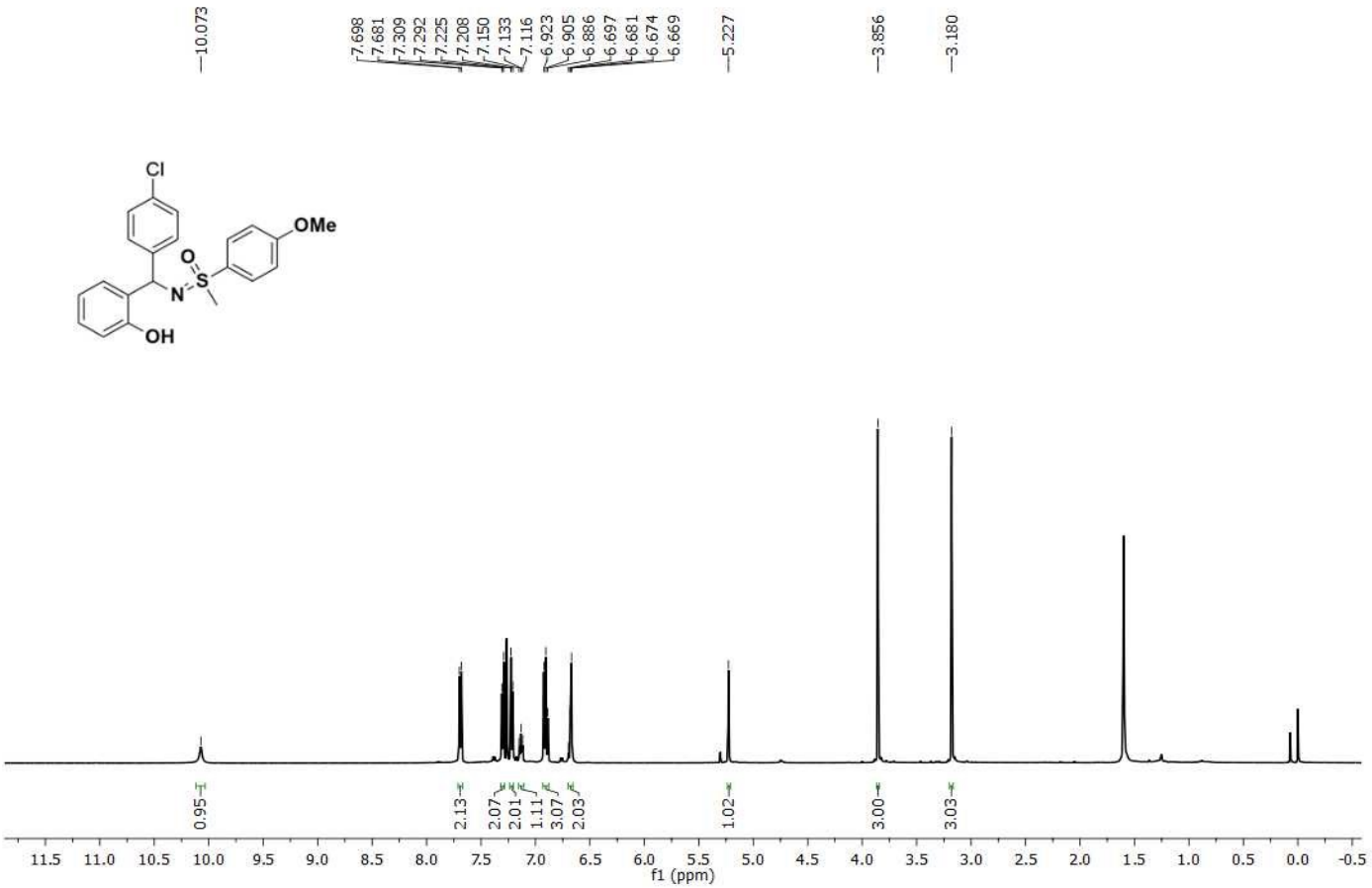
^{1}H NMR of **5j** (Diastereomer-1, able to purify only one diastereomer)



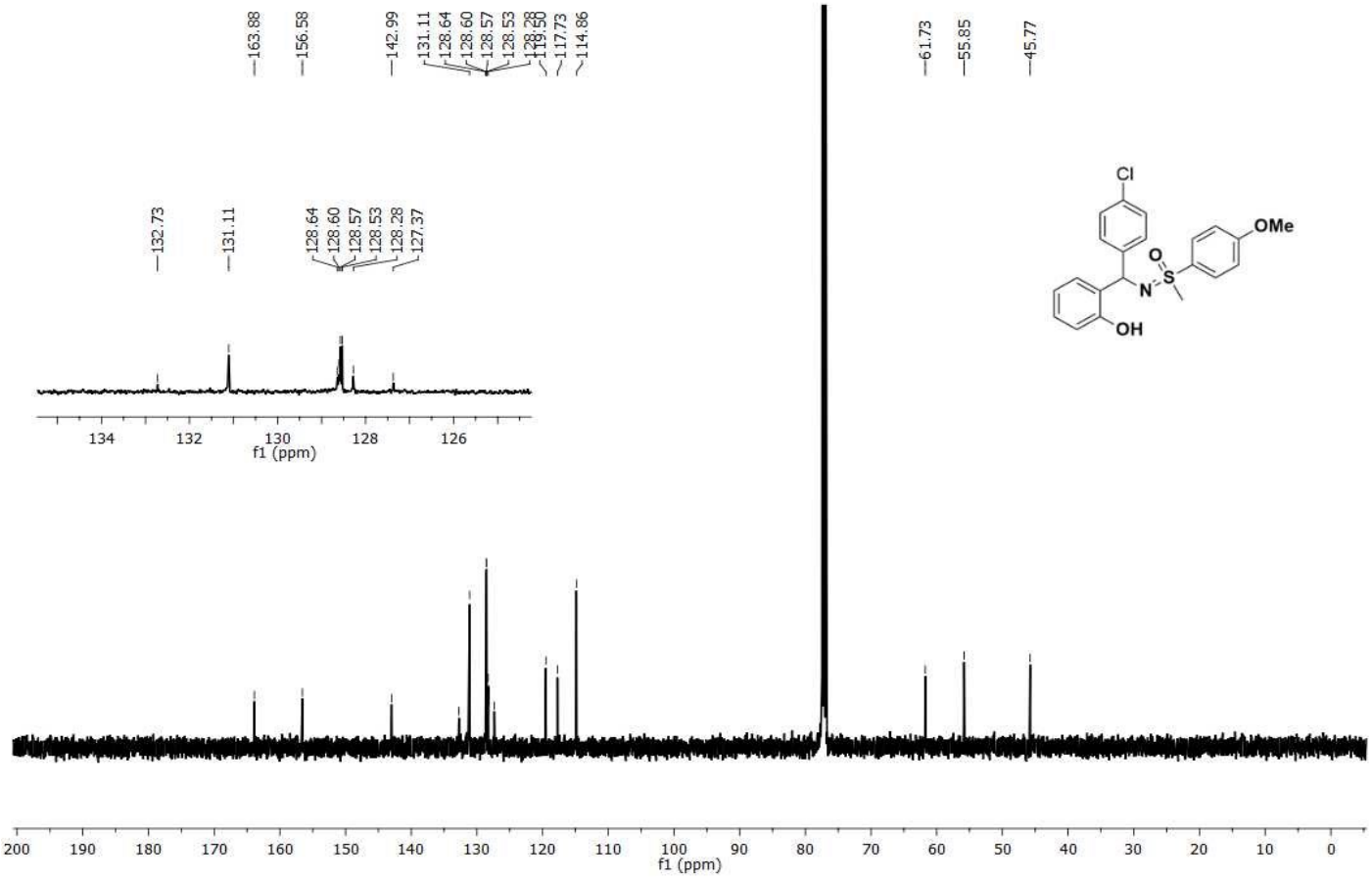
^{13}C {^{1}H} NMR of **5j** (Diastereomer-1, able to purify only one diastereomer)



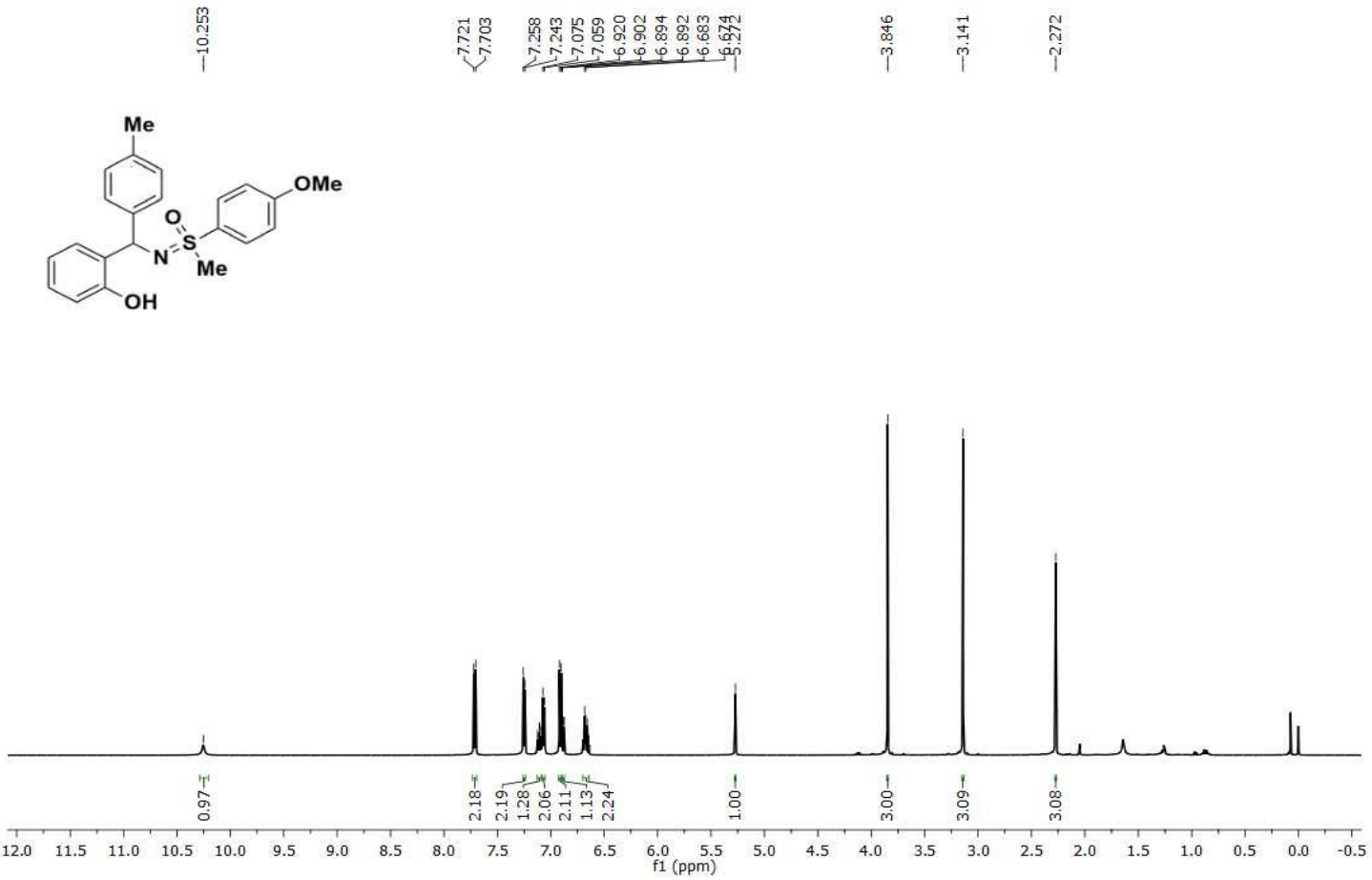
^{1}H NMR of 5**k** (Diastereomer-1, able to purify only one diastereomer)



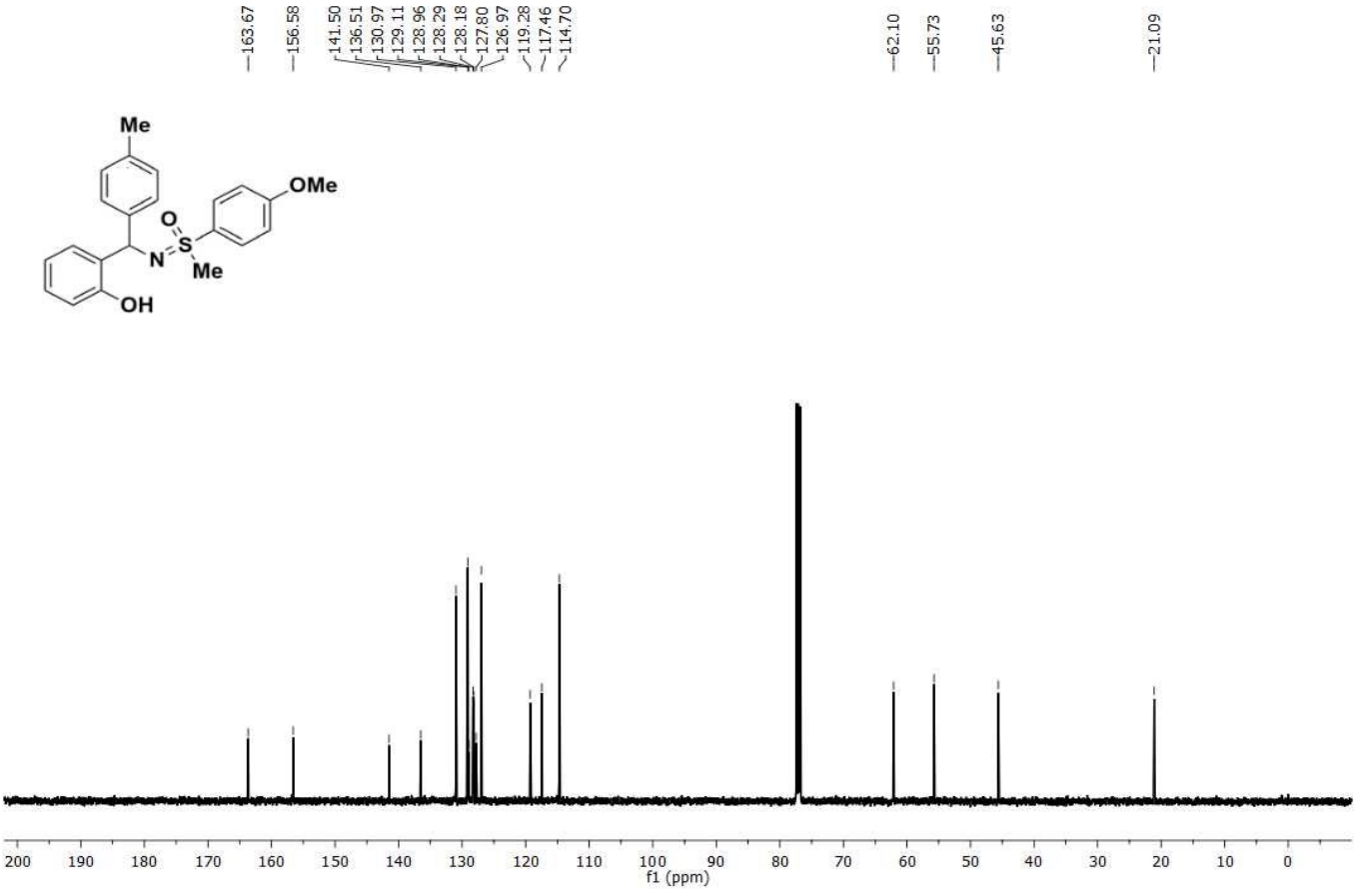
^{13}C {^{1}H} NMR of **5k** (Diastereomer-1, able to purify only one diastereomer)



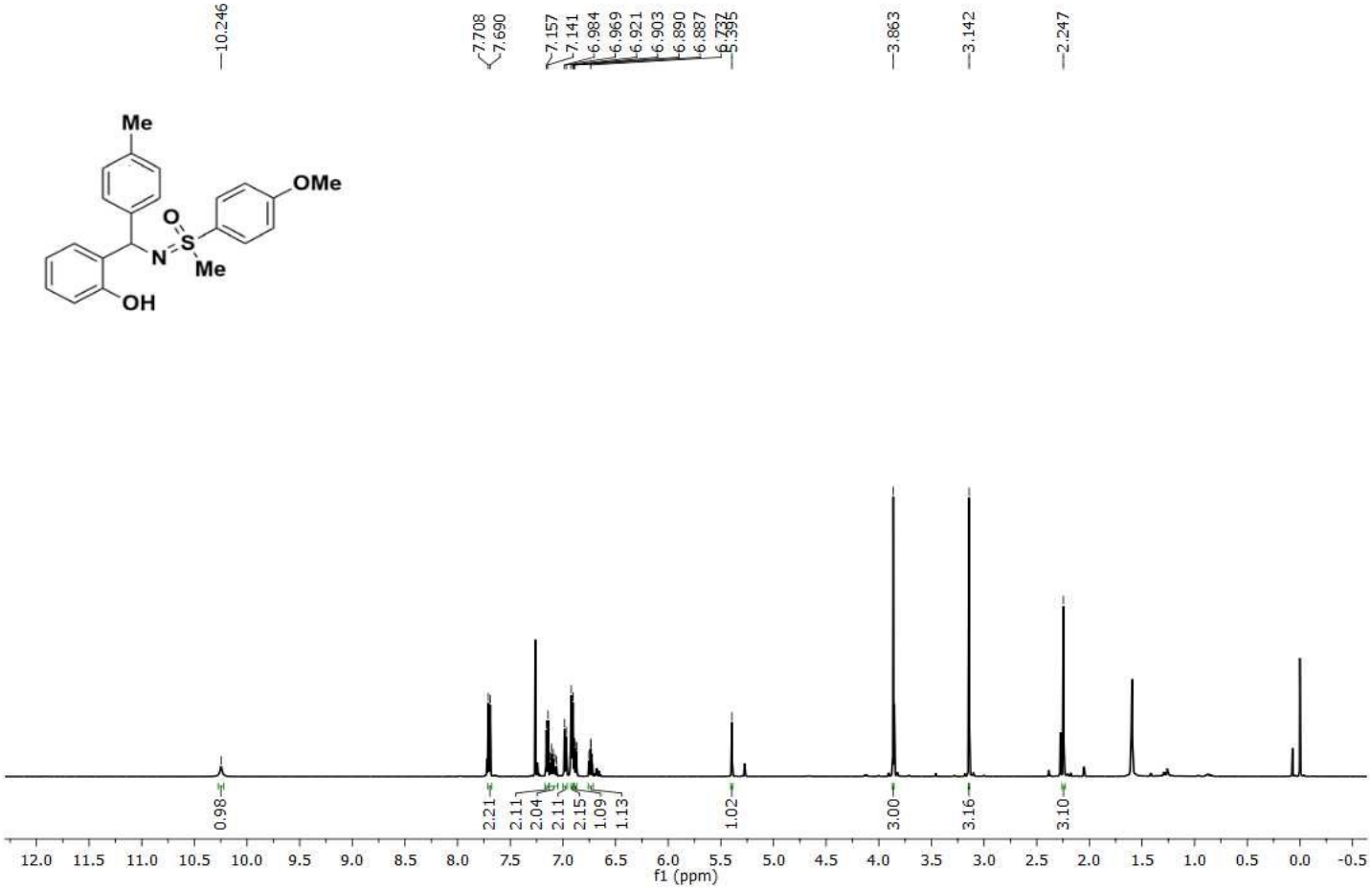
^{1}H NMR of **5l** (Diastereomer-1)



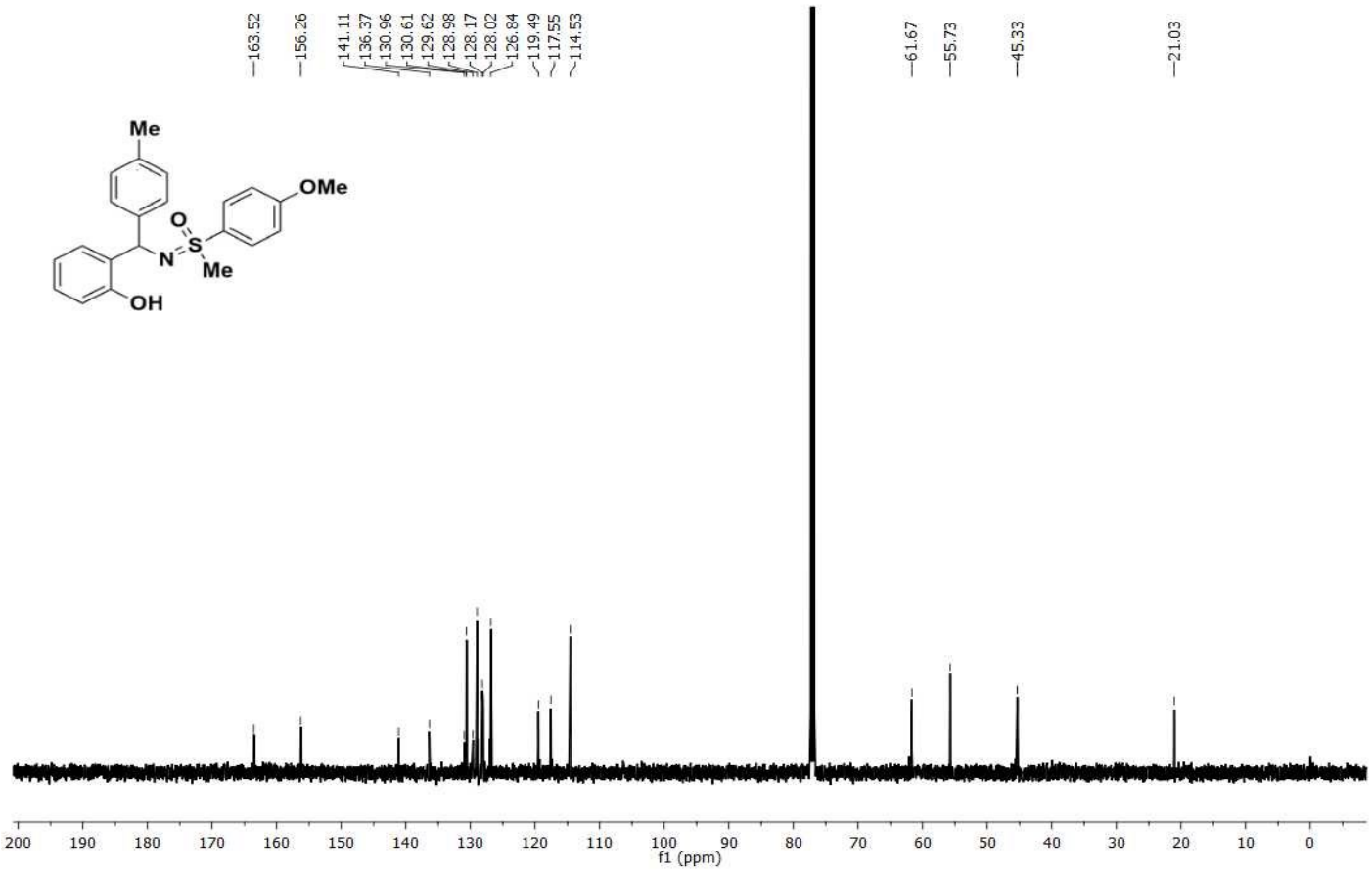
^{13}C {^{1}H} NMR of **5l** (Diastereomer-1)



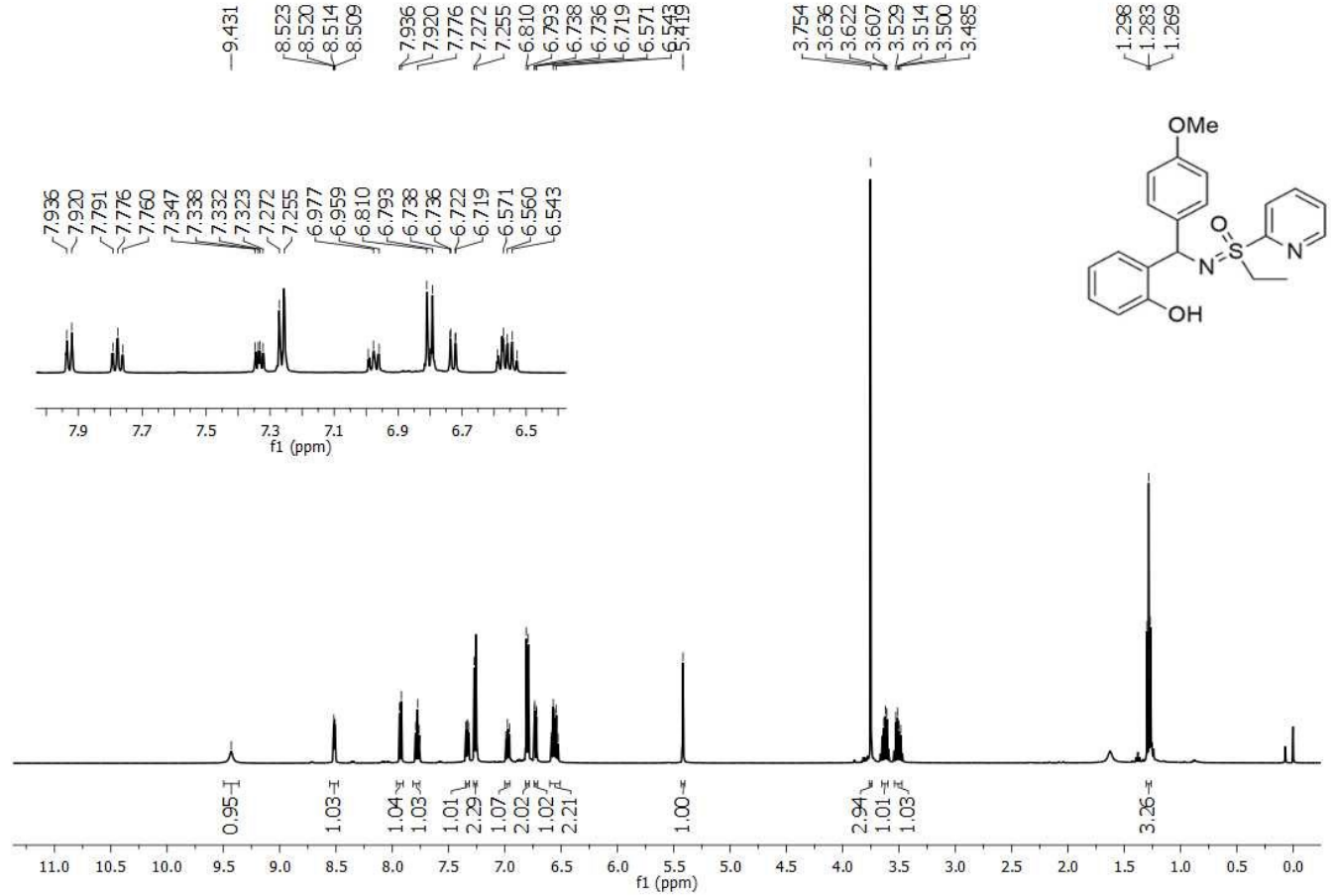
^{1}H NMR of **5l** (Diastereomer-2)



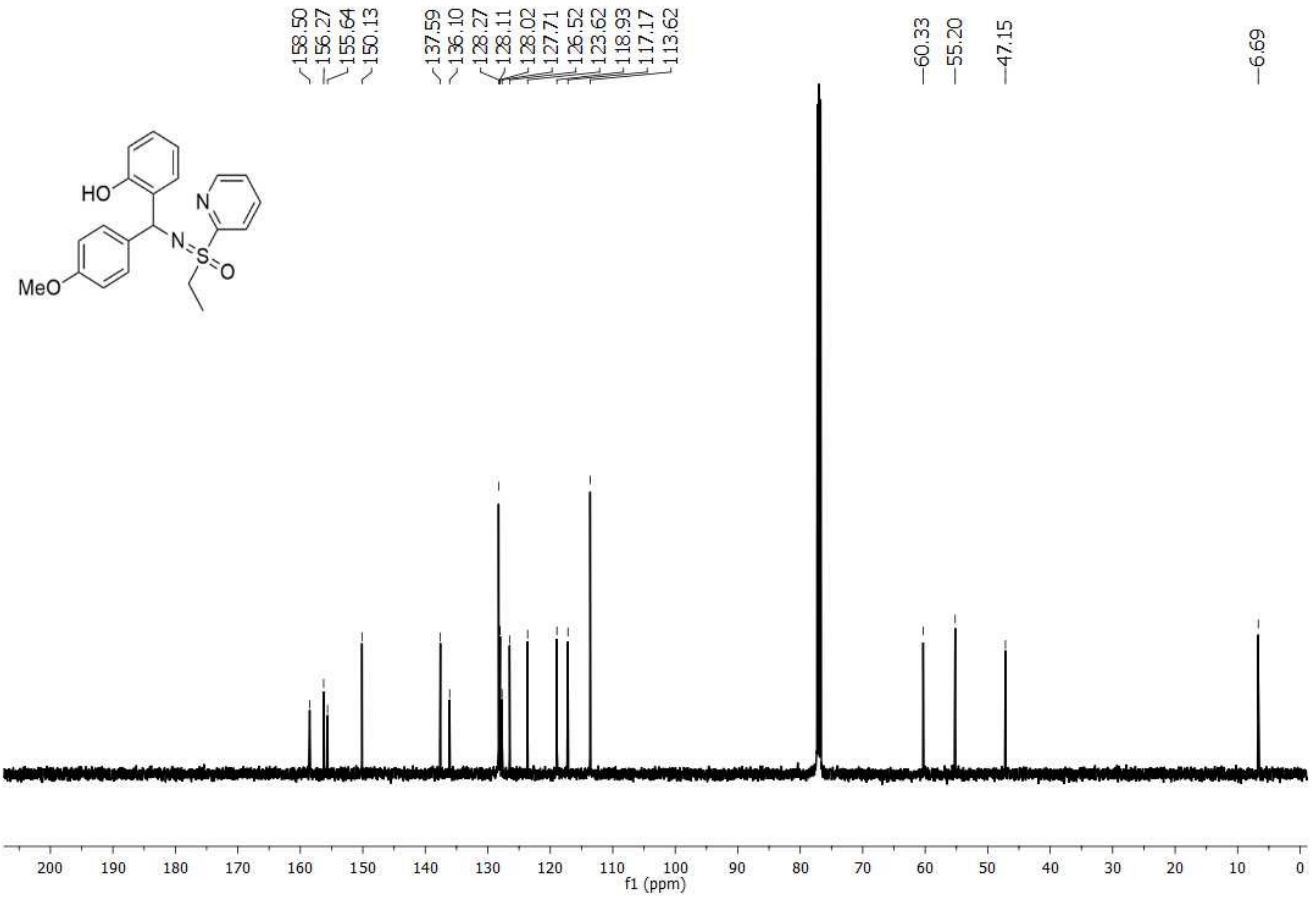
^{13}C {^{1}H} NMR of **5l** (Diastereomer-2)



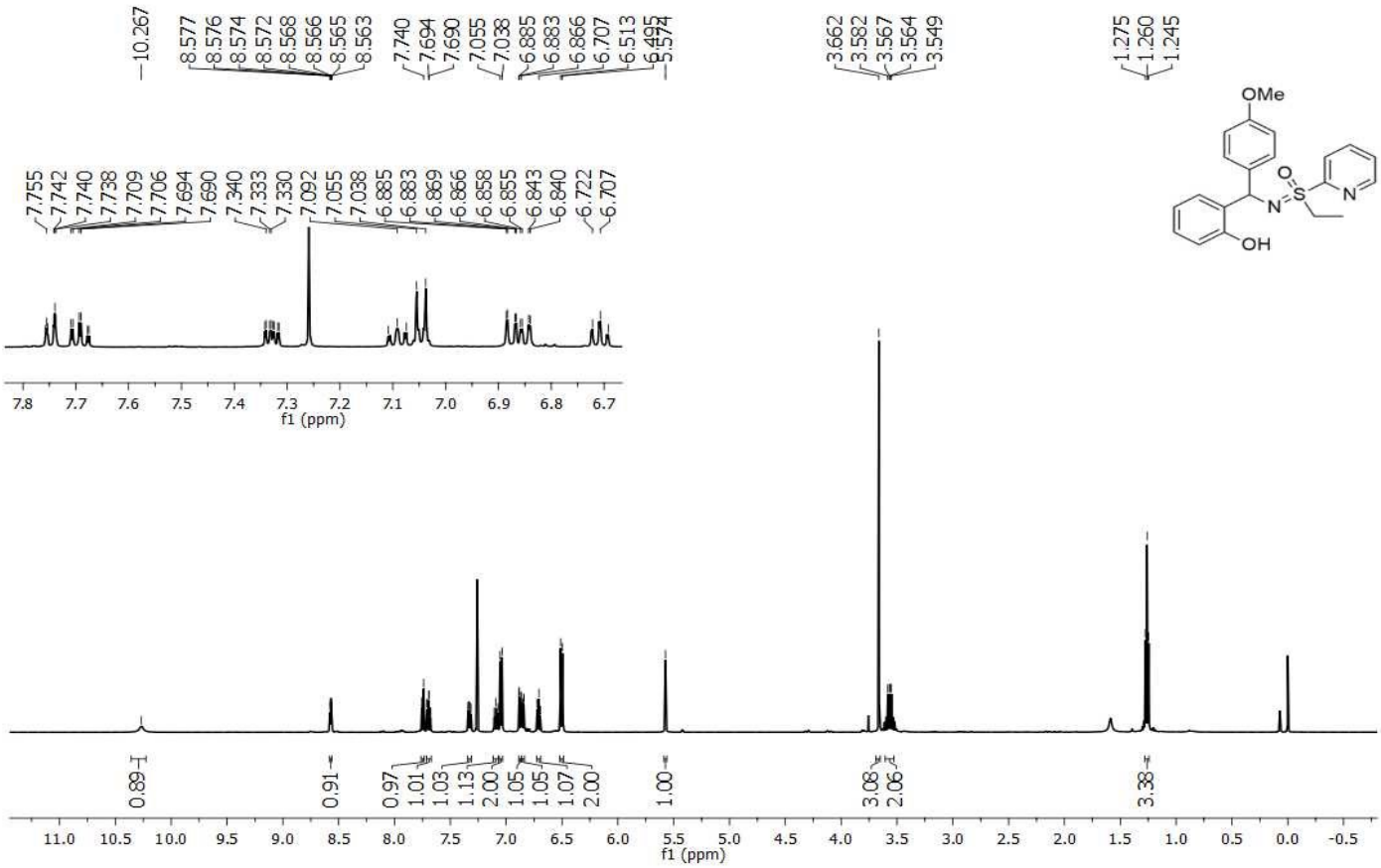
^{1}H NMR of **5m** (Diastereomer-1)



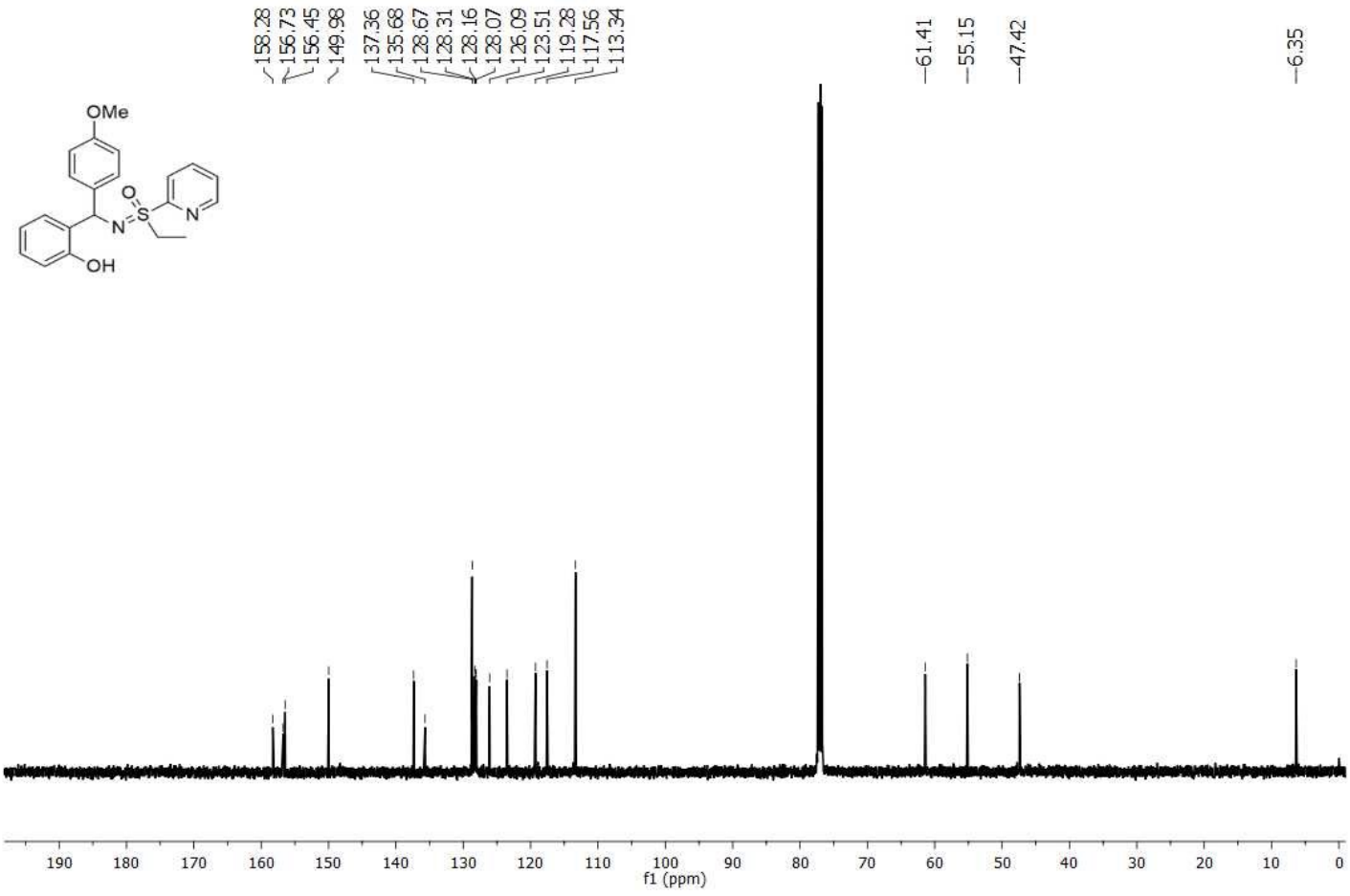
^{13}C {^{1}H} NMR of **5m** (Diastereomer-1)



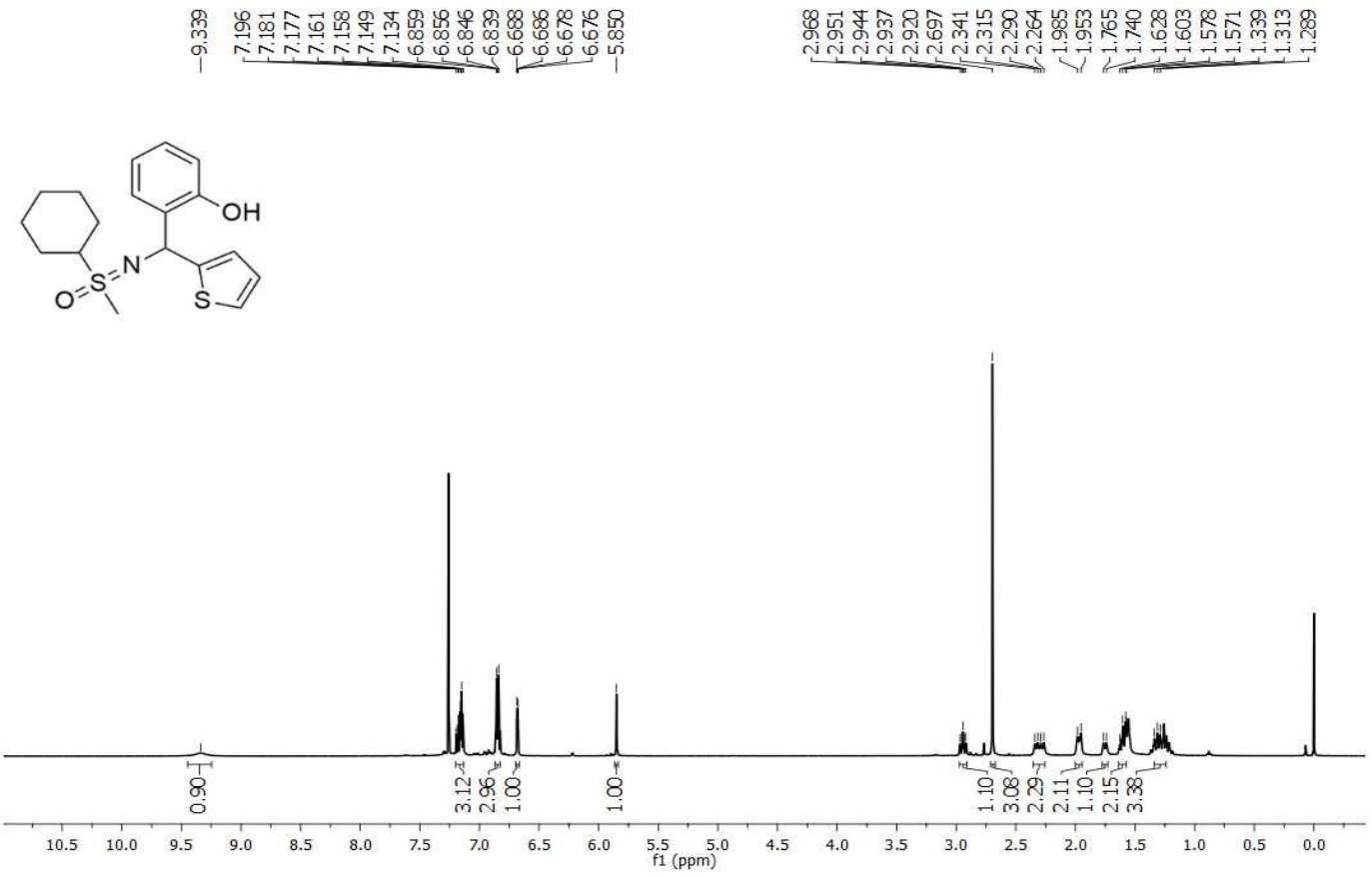
^{1}H NMR of **5m** (Diastereomer-2)



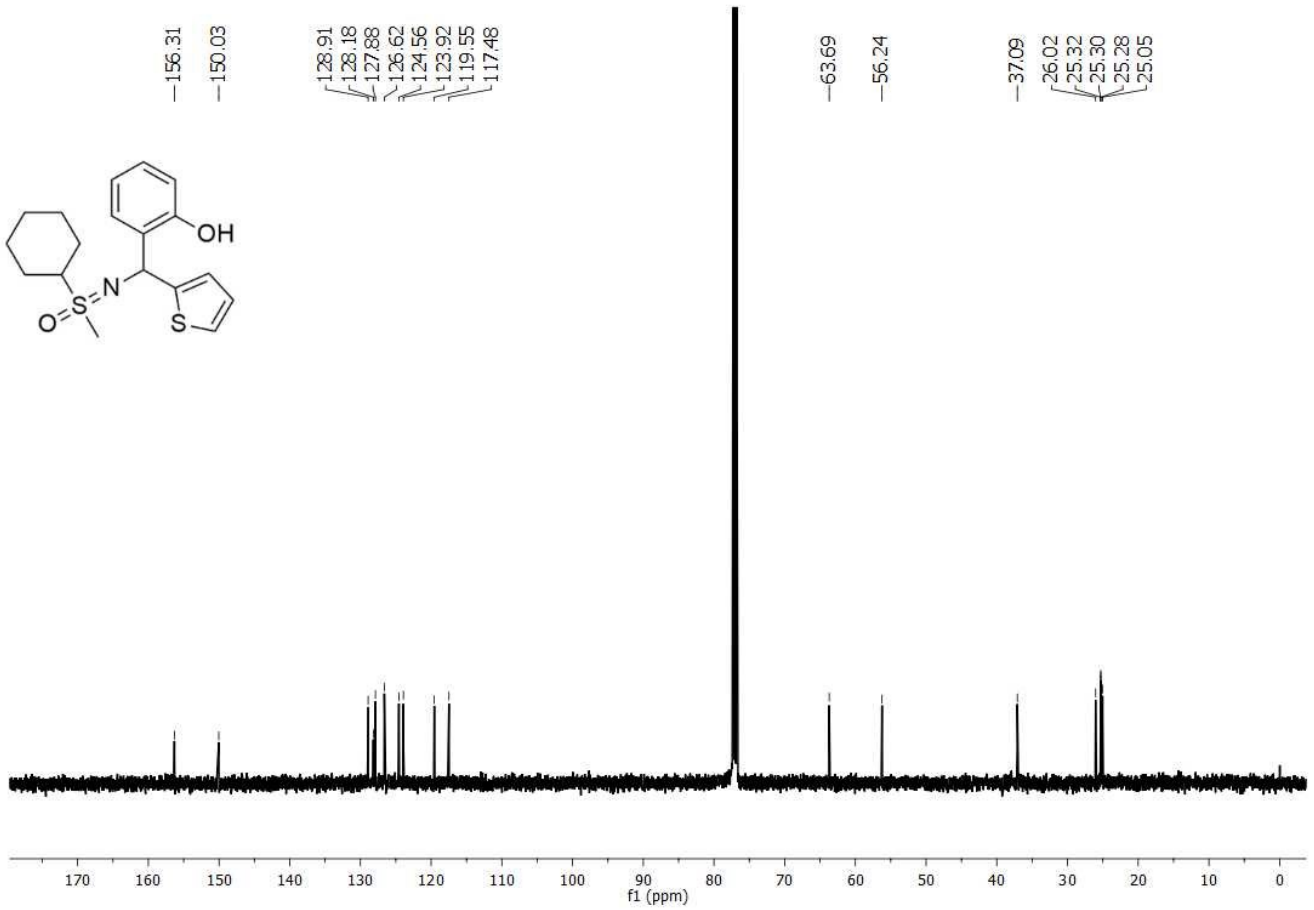
^{13}C {^{1}H} NMR of **5m** (Diastereomer-2)



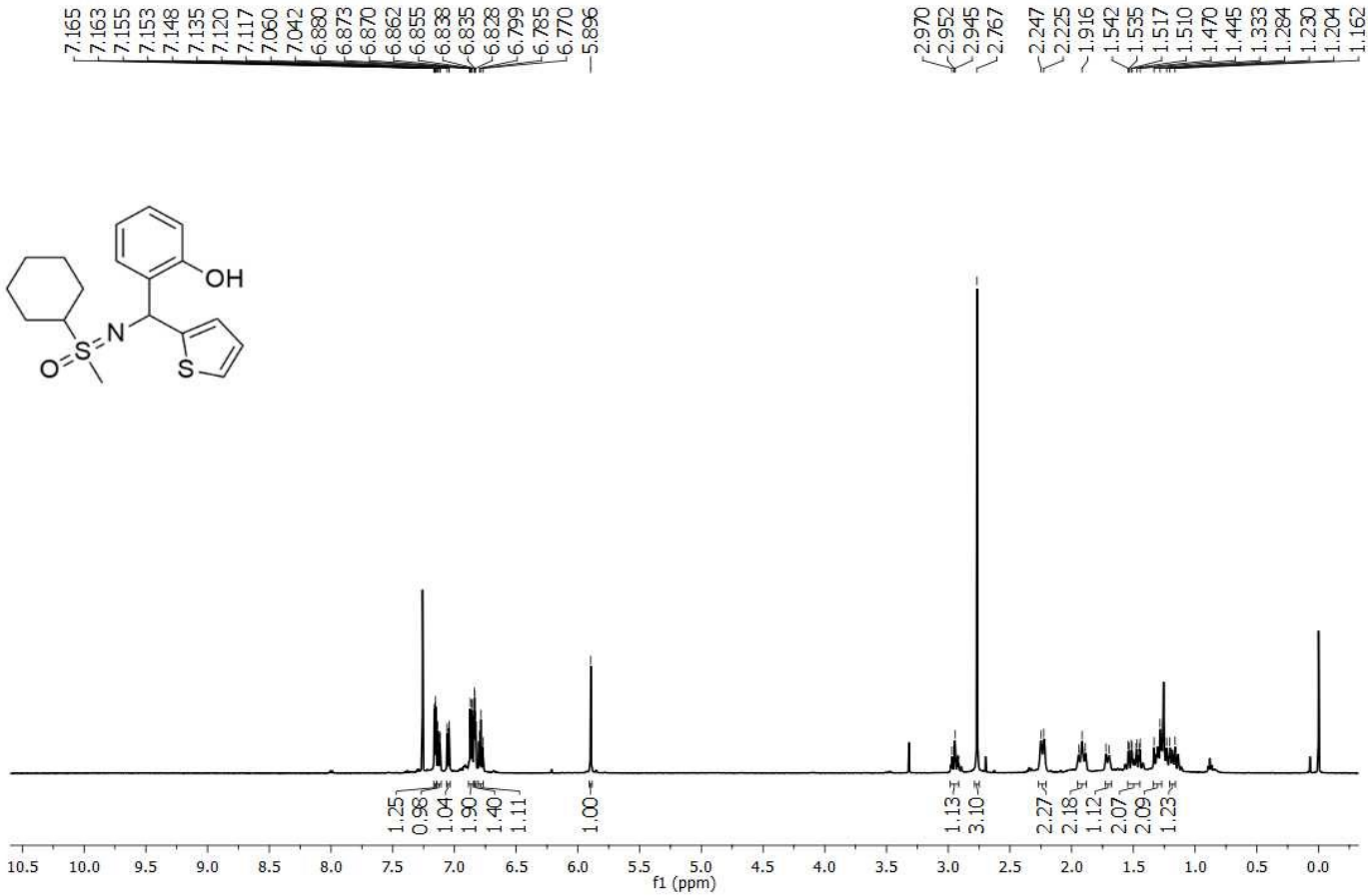
^{1}H NMR of **5n** (Diastereomer-1)



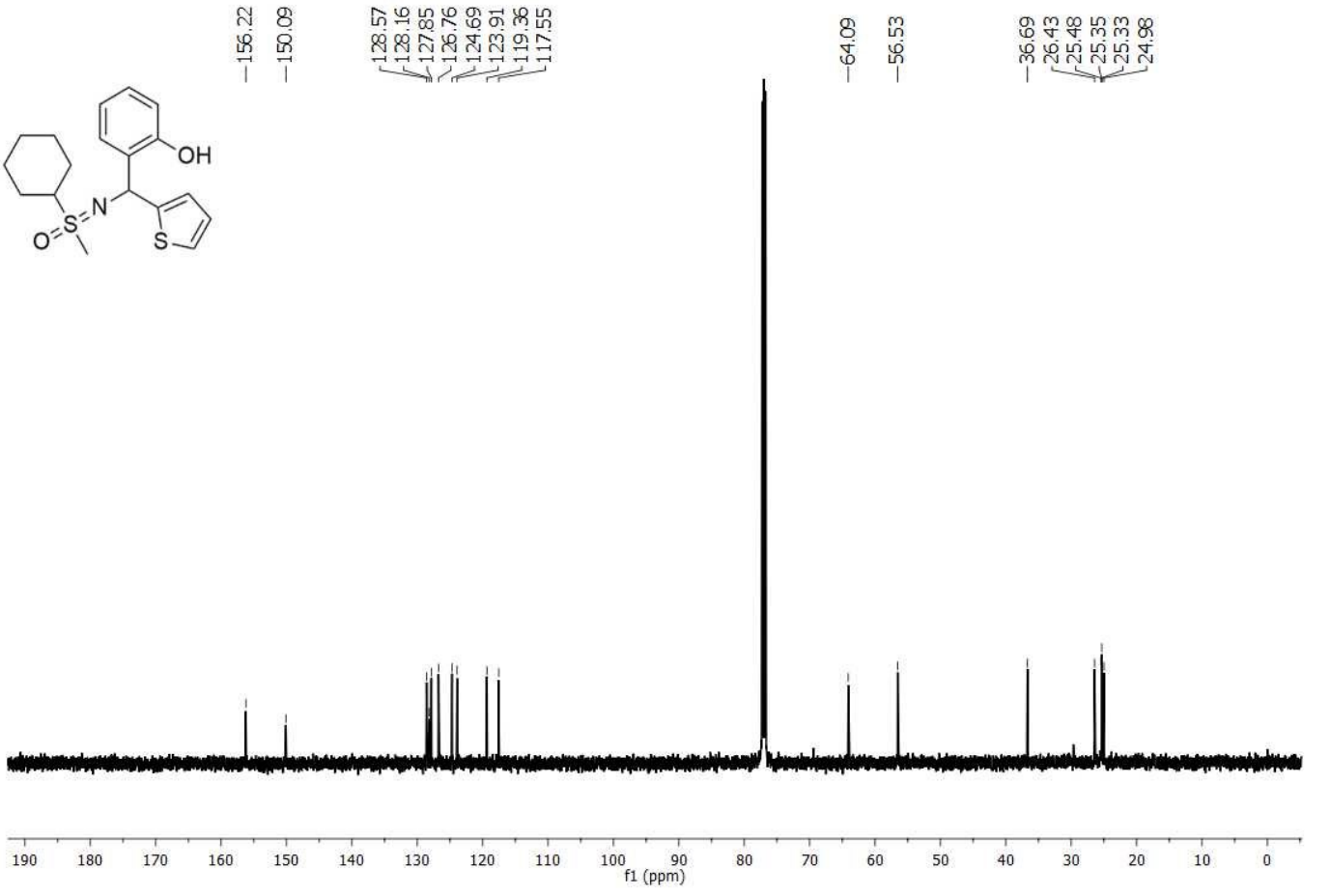
^{13}C {^{1}H} NMR of **5n** (Diastereomer-1)



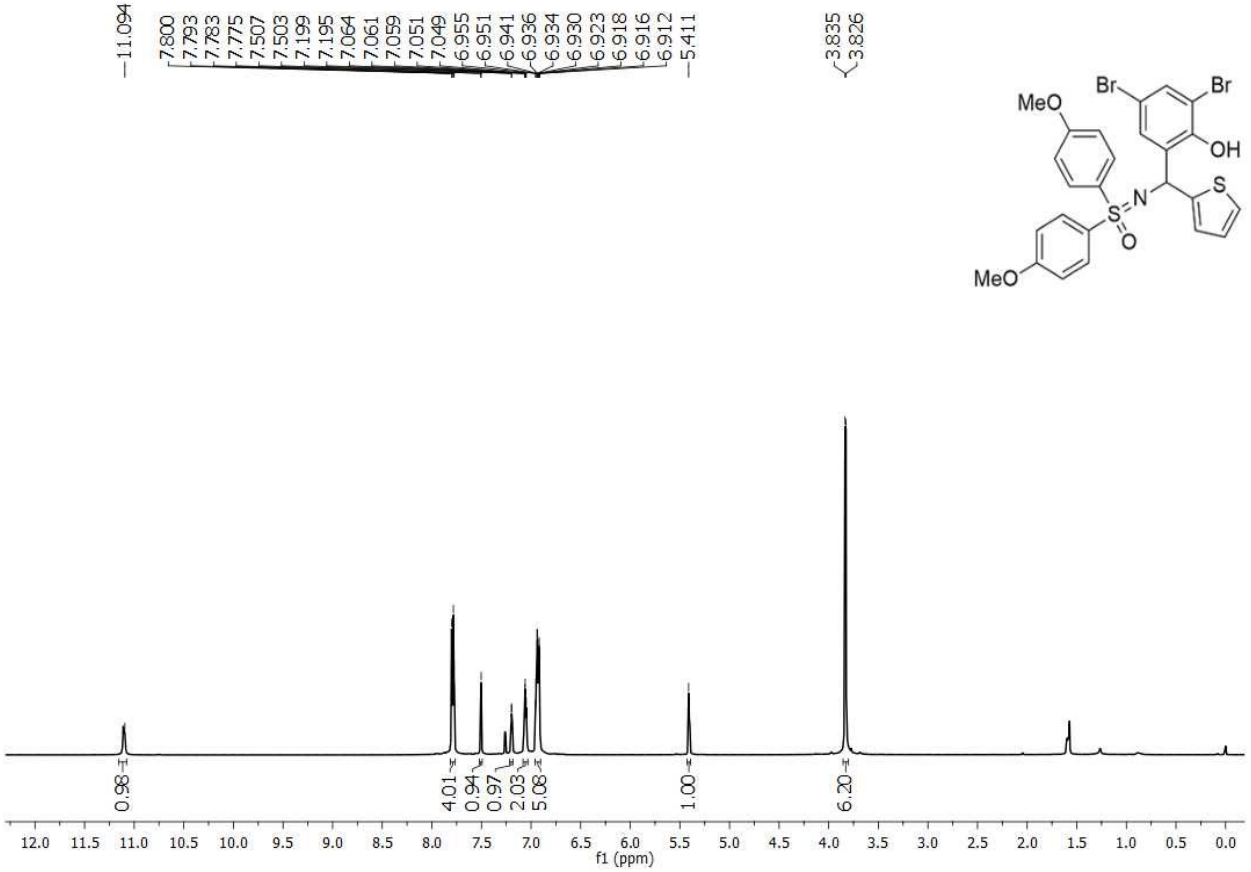
^{1}H NMR of **5n** (Diastereomer-2)



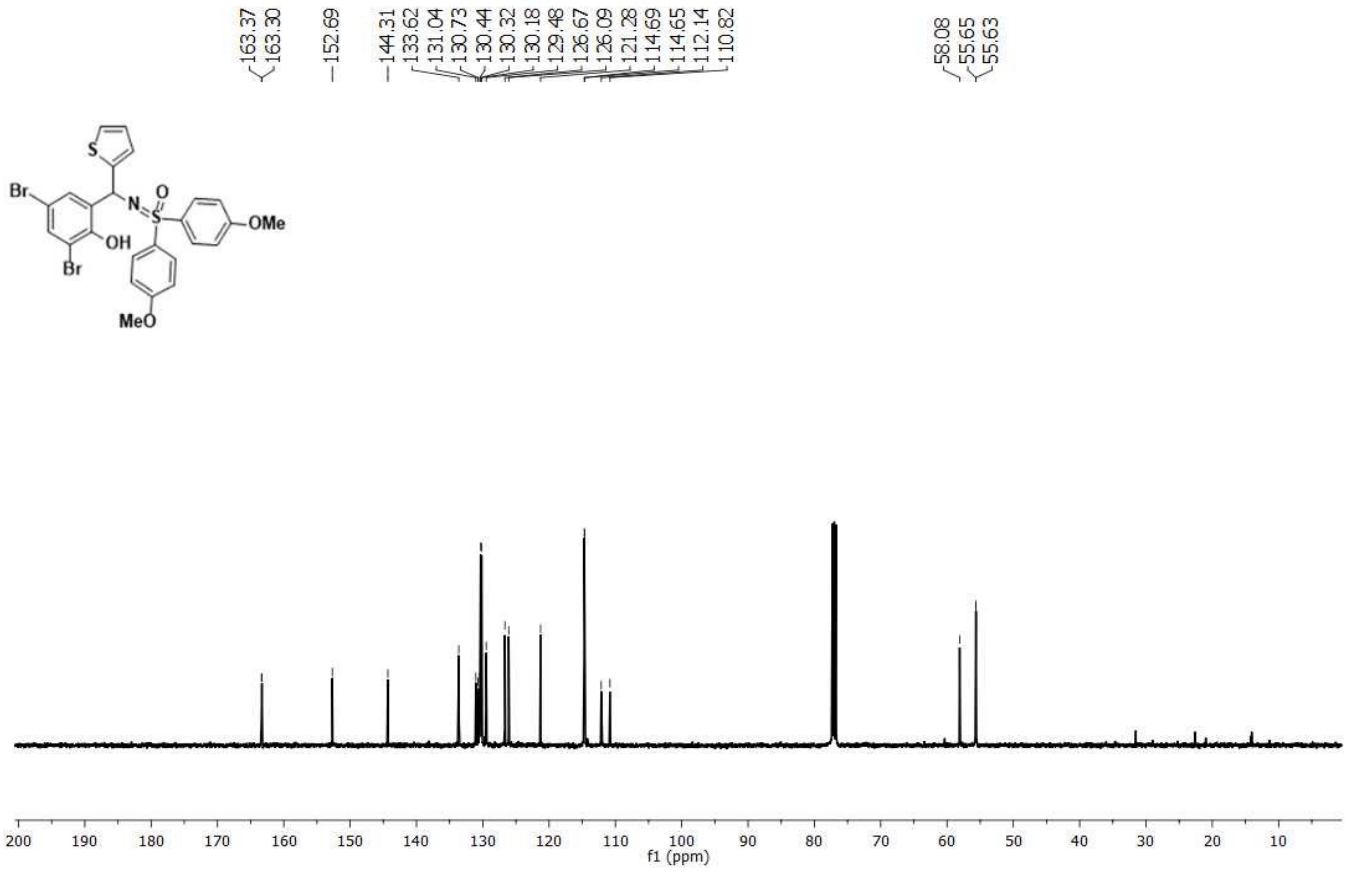
^{13}C {^{1}H} NMR of **5n** (Diastereomer-2)



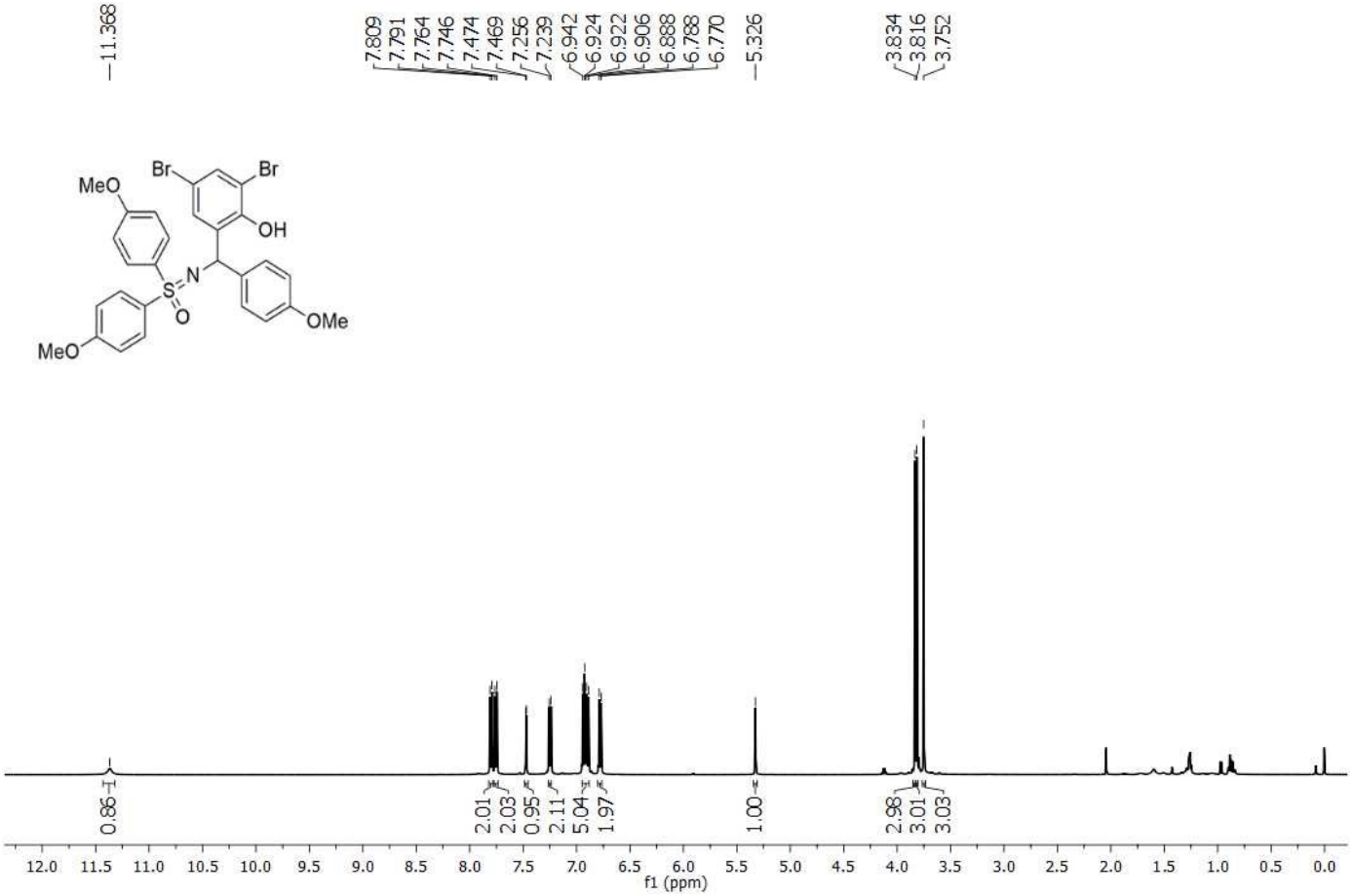
^{1}H NMR of **5o**



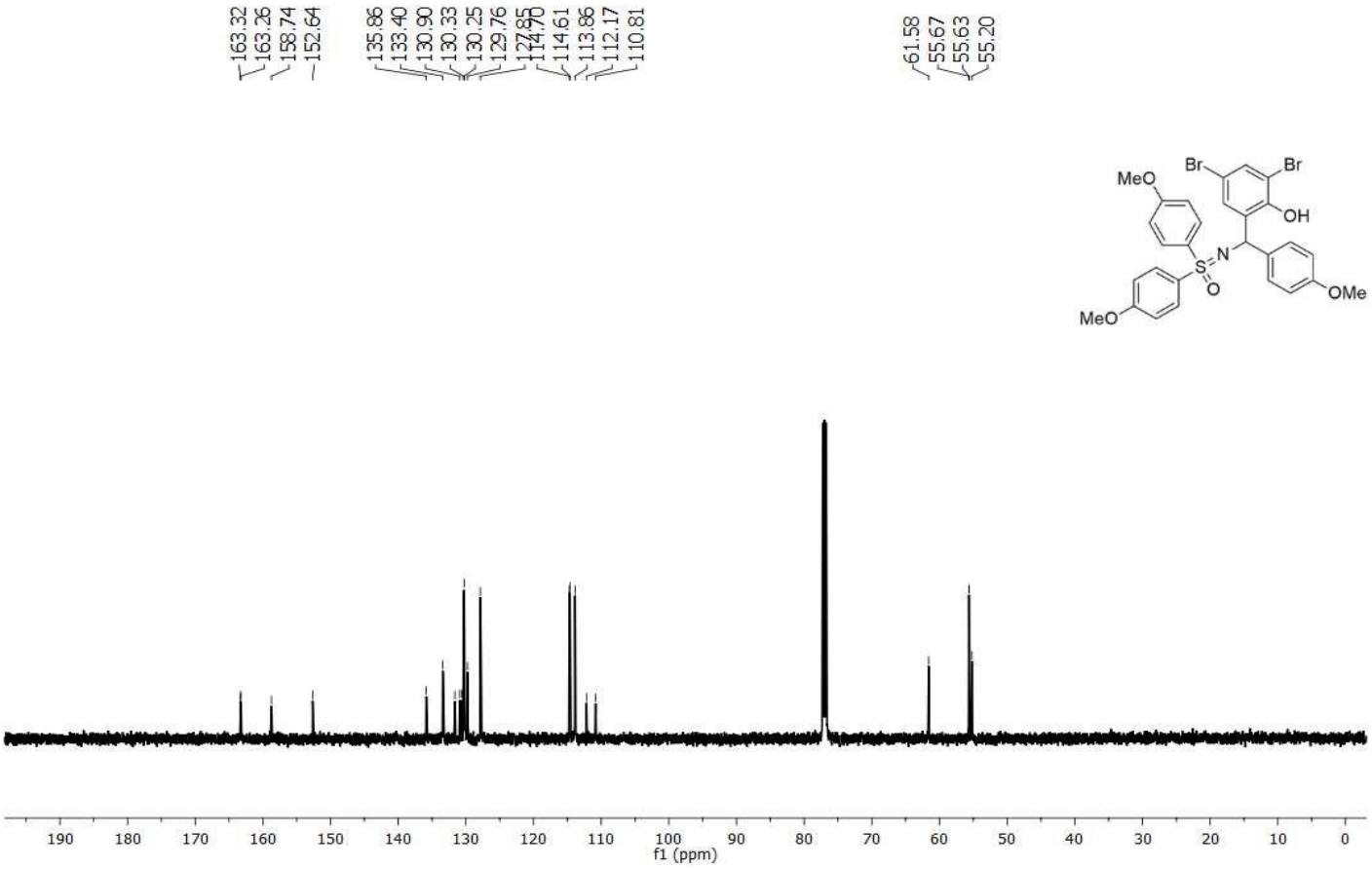
^{13}C {^{1}H} NMR of **5o**



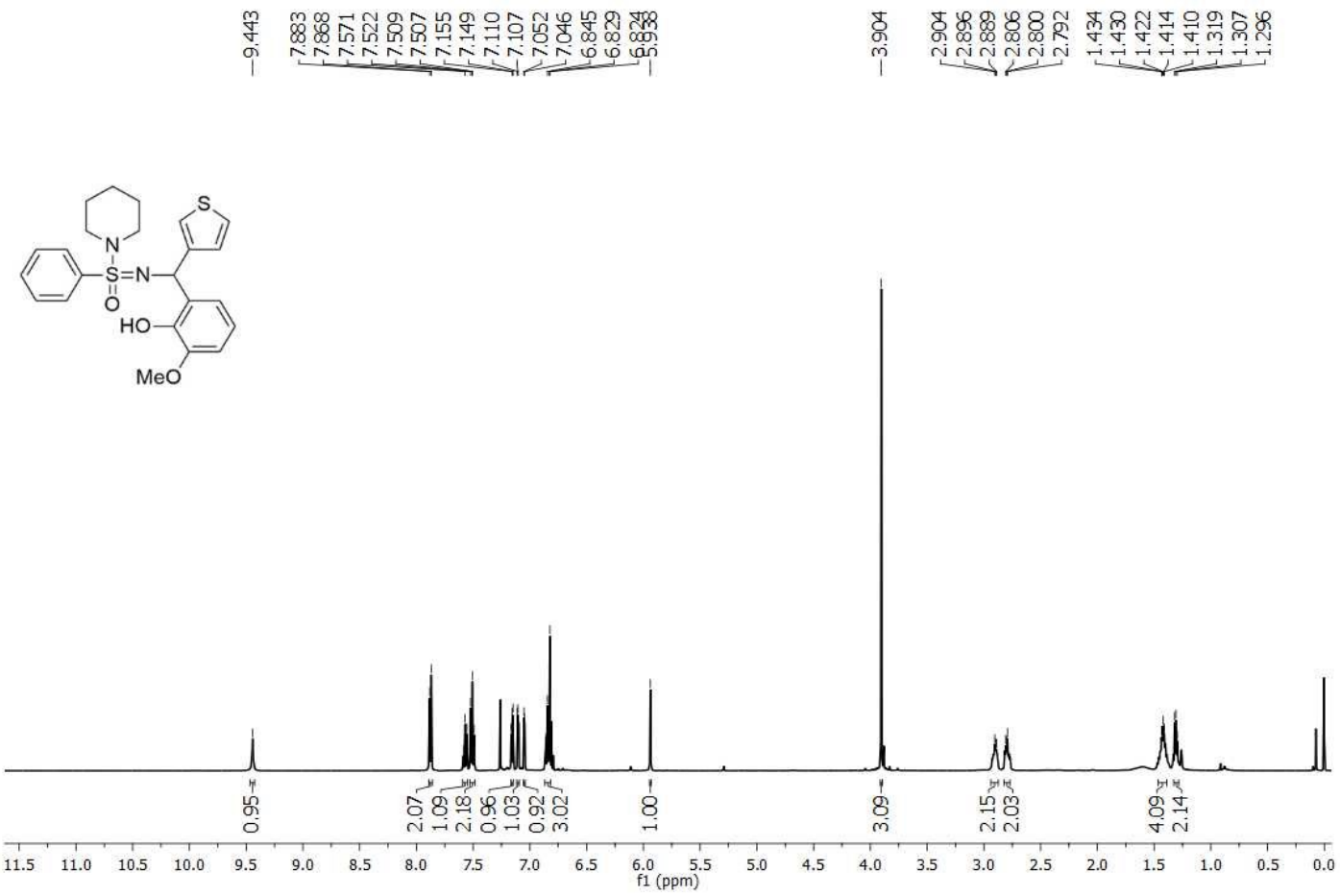
^{1}H NMR of **5p**



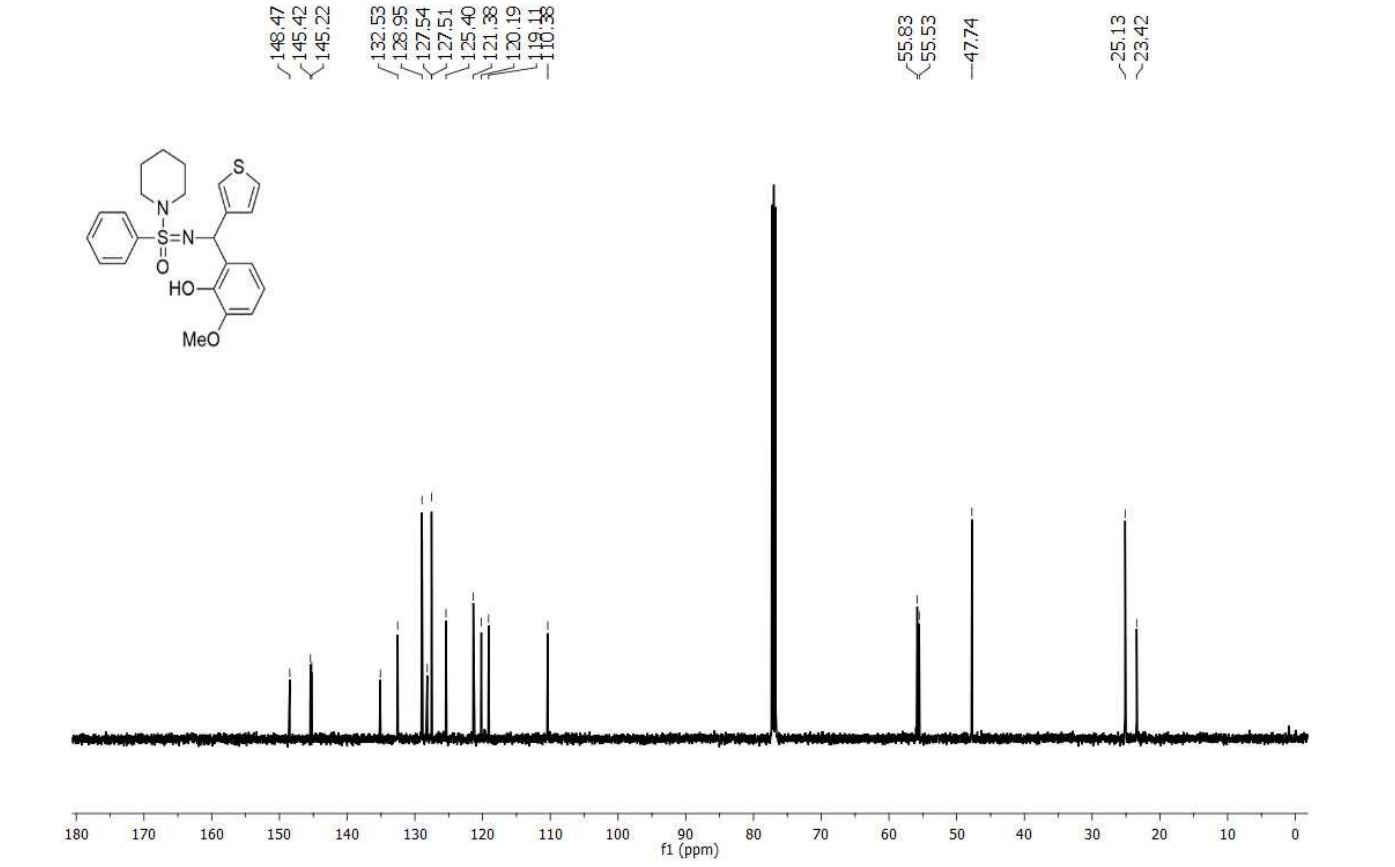
^{13}C {^{1}H} NMR of **5p**



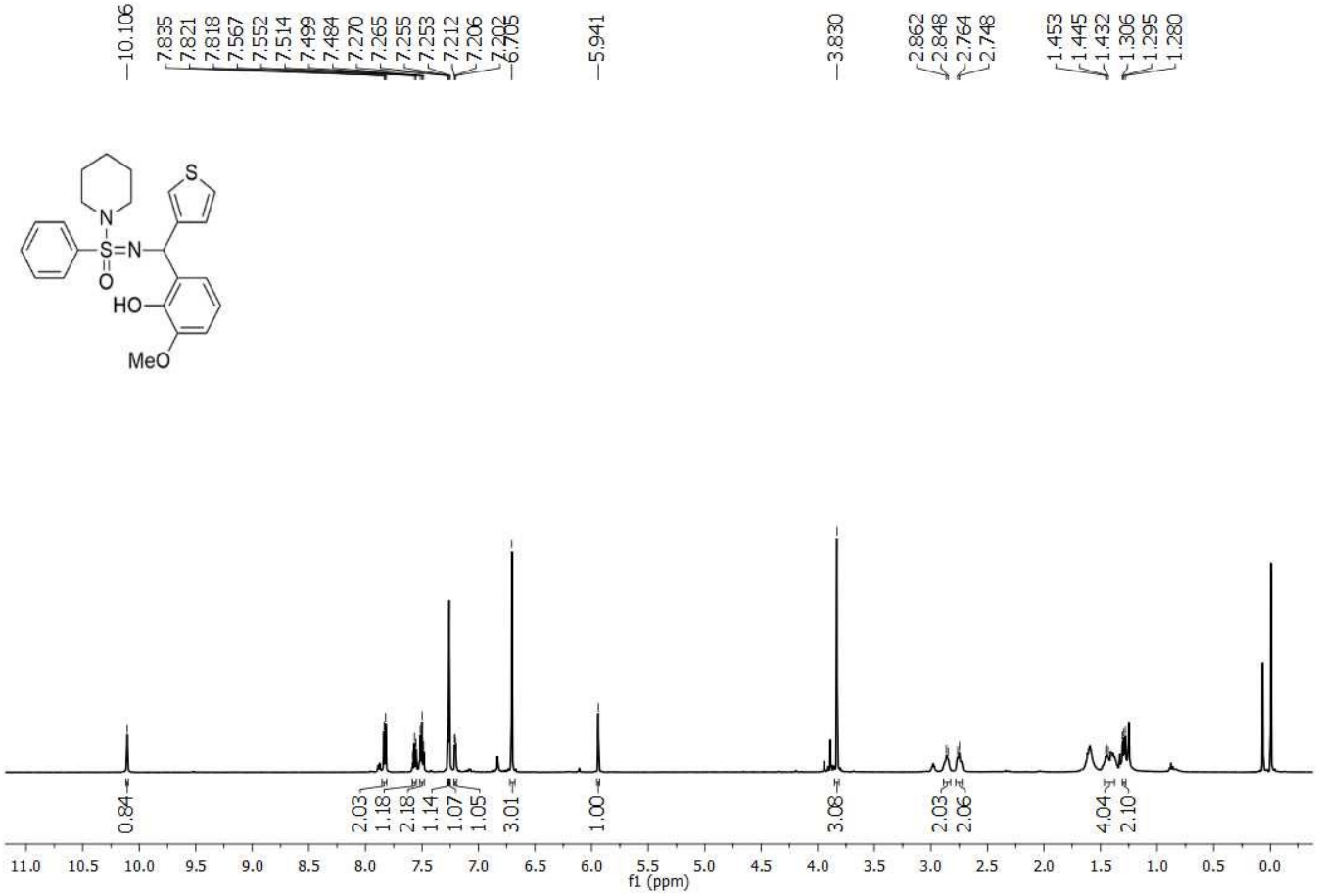
^{1}H NMR of **6a** (Diastereomer-1)



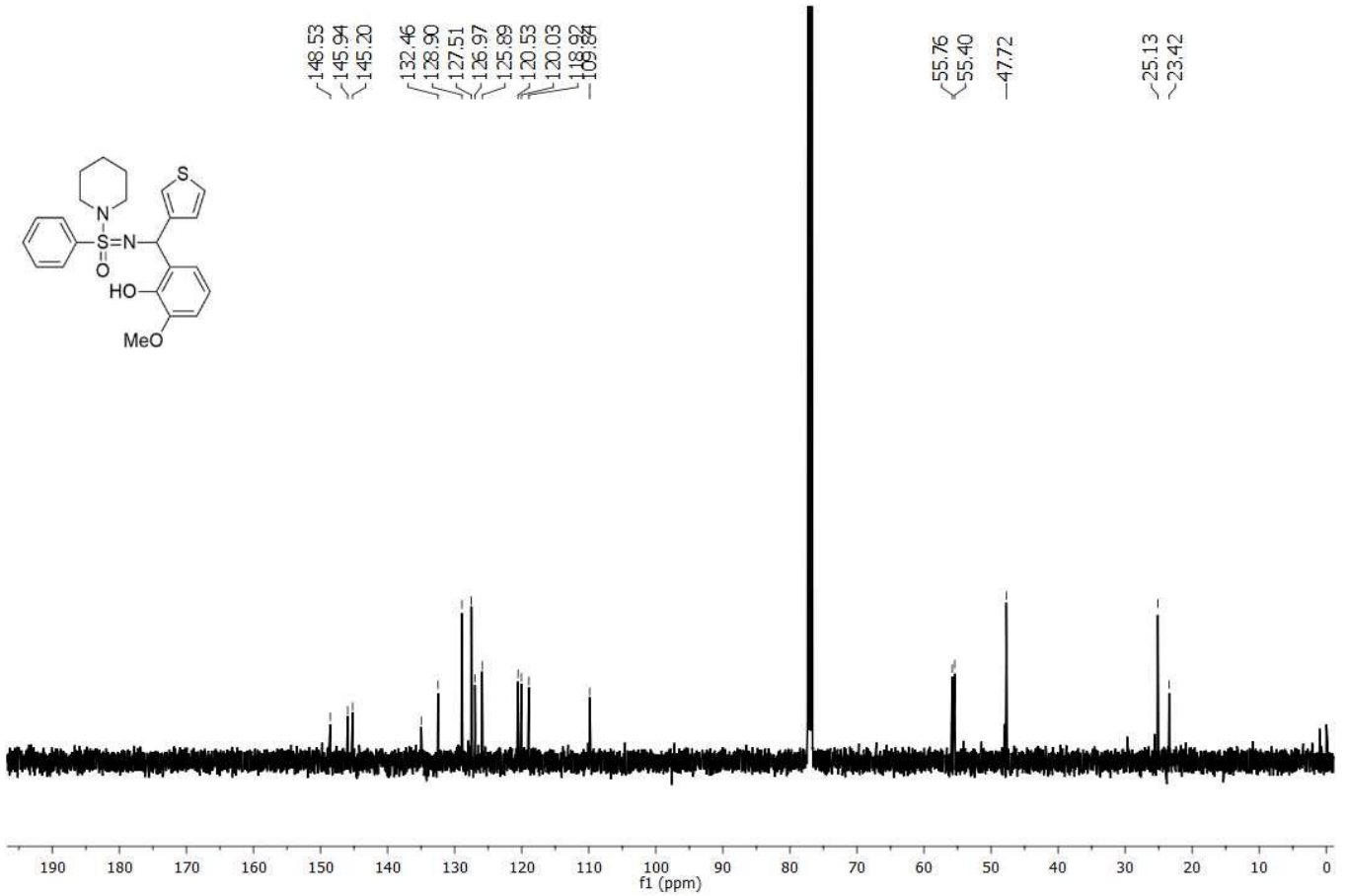
^{13}C {^{1}H} NMR of **6a** (Diastereomer-1)



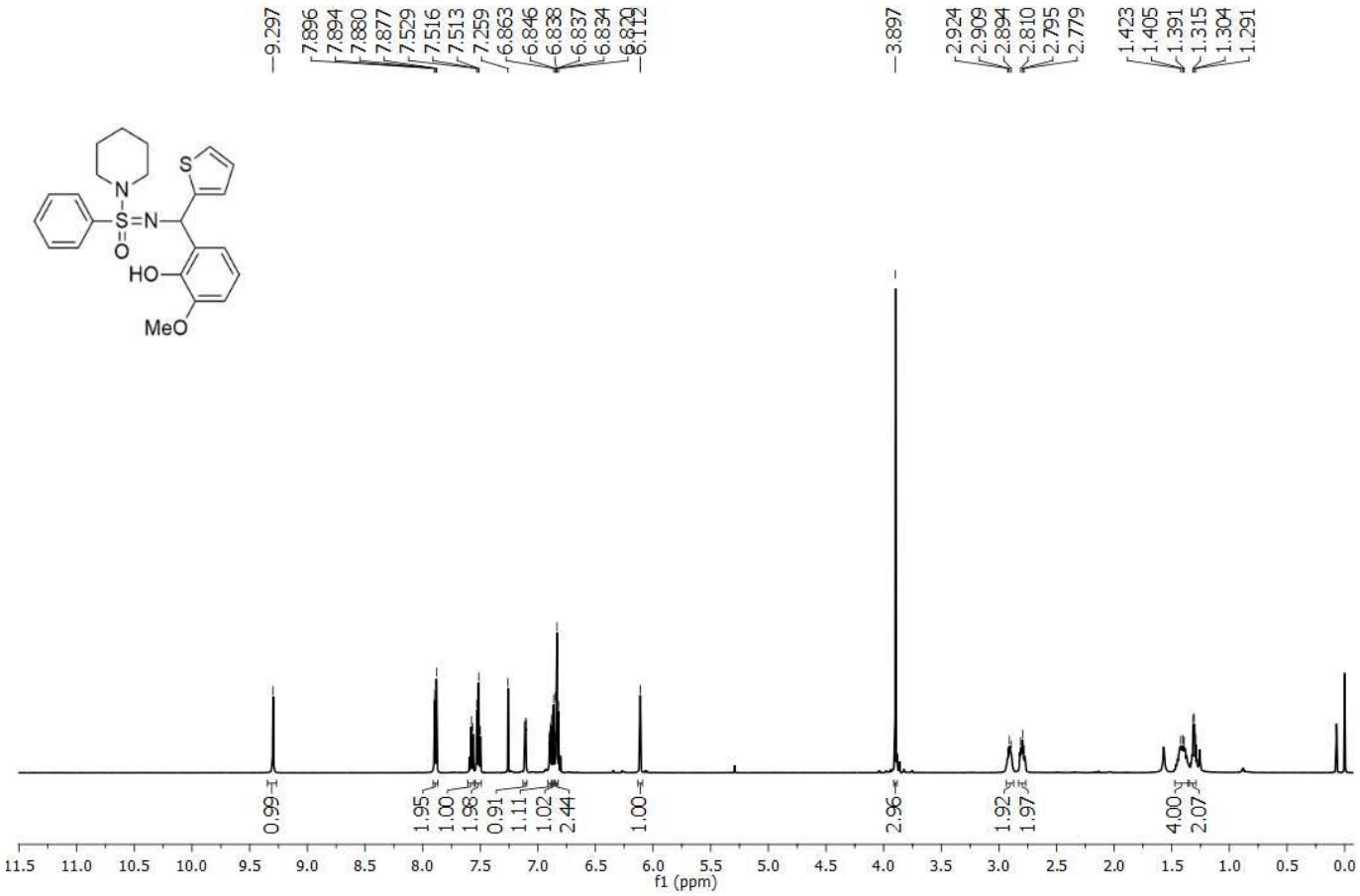
^{1}H NMR of **6a** (Diastereomer-2)



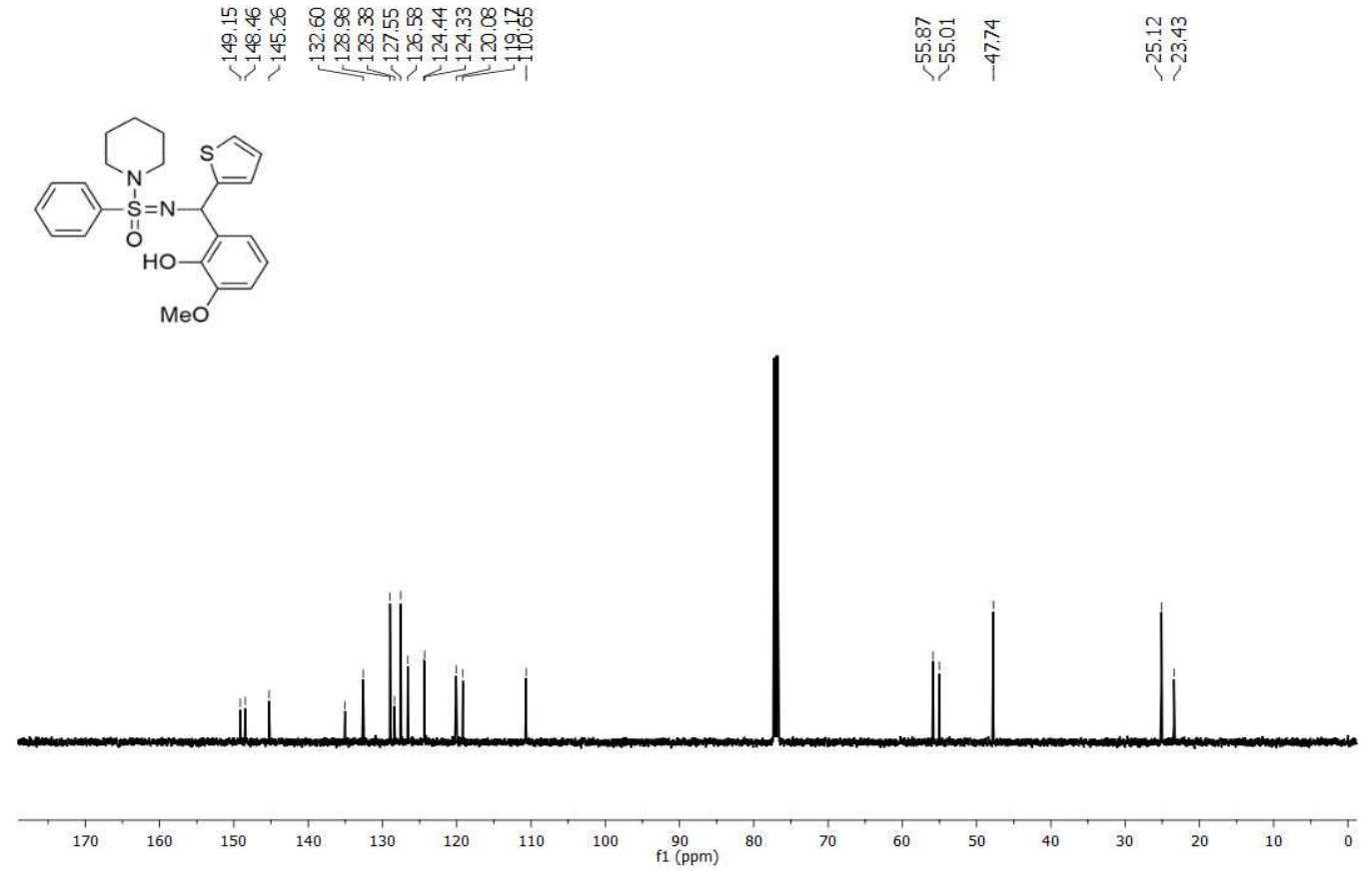
^{13}C {^{1}H} NMR of **6a** (Diastereomer-2)



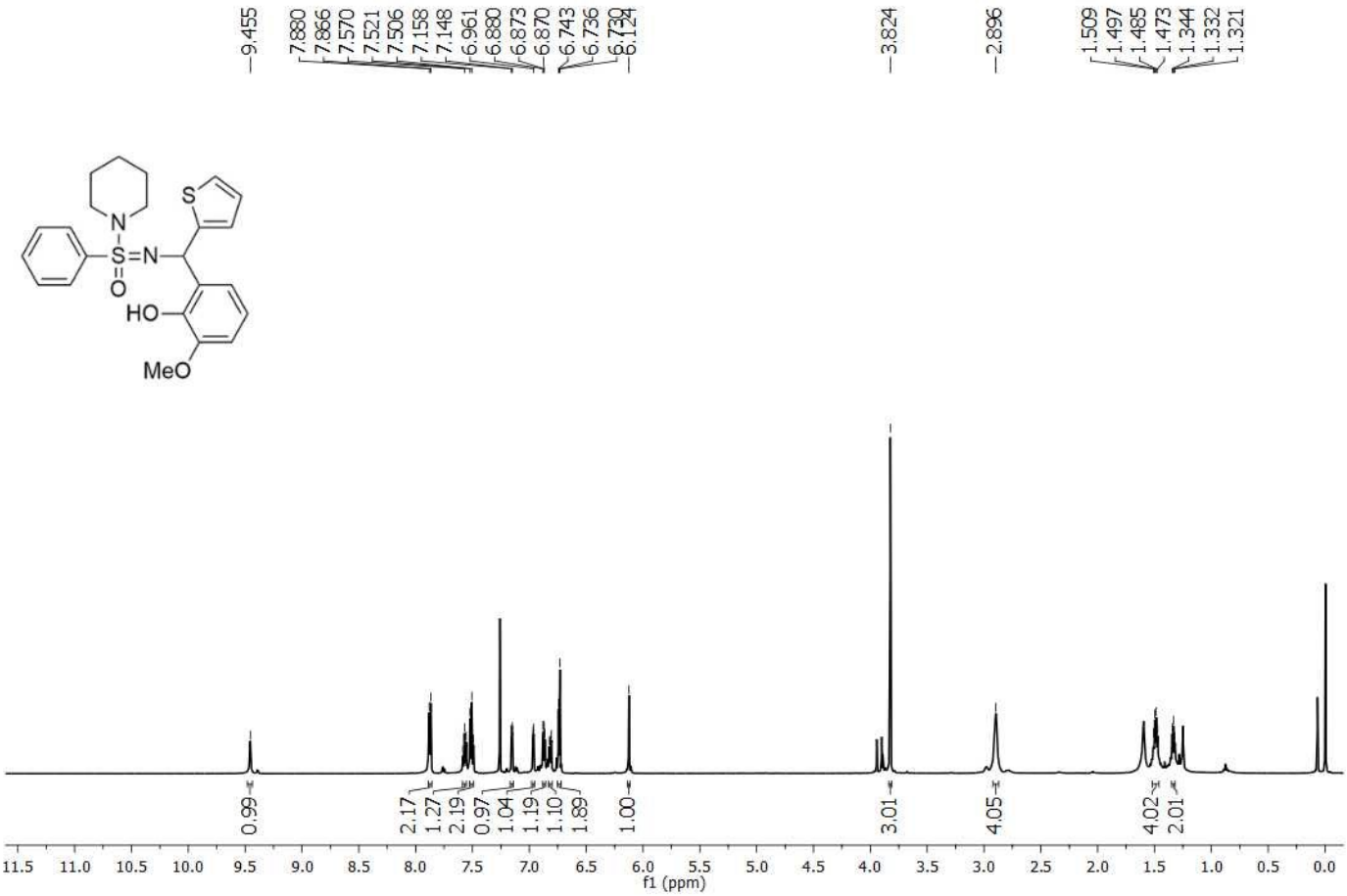
^{1}H NMR of **6b** (Diastereomer-1)



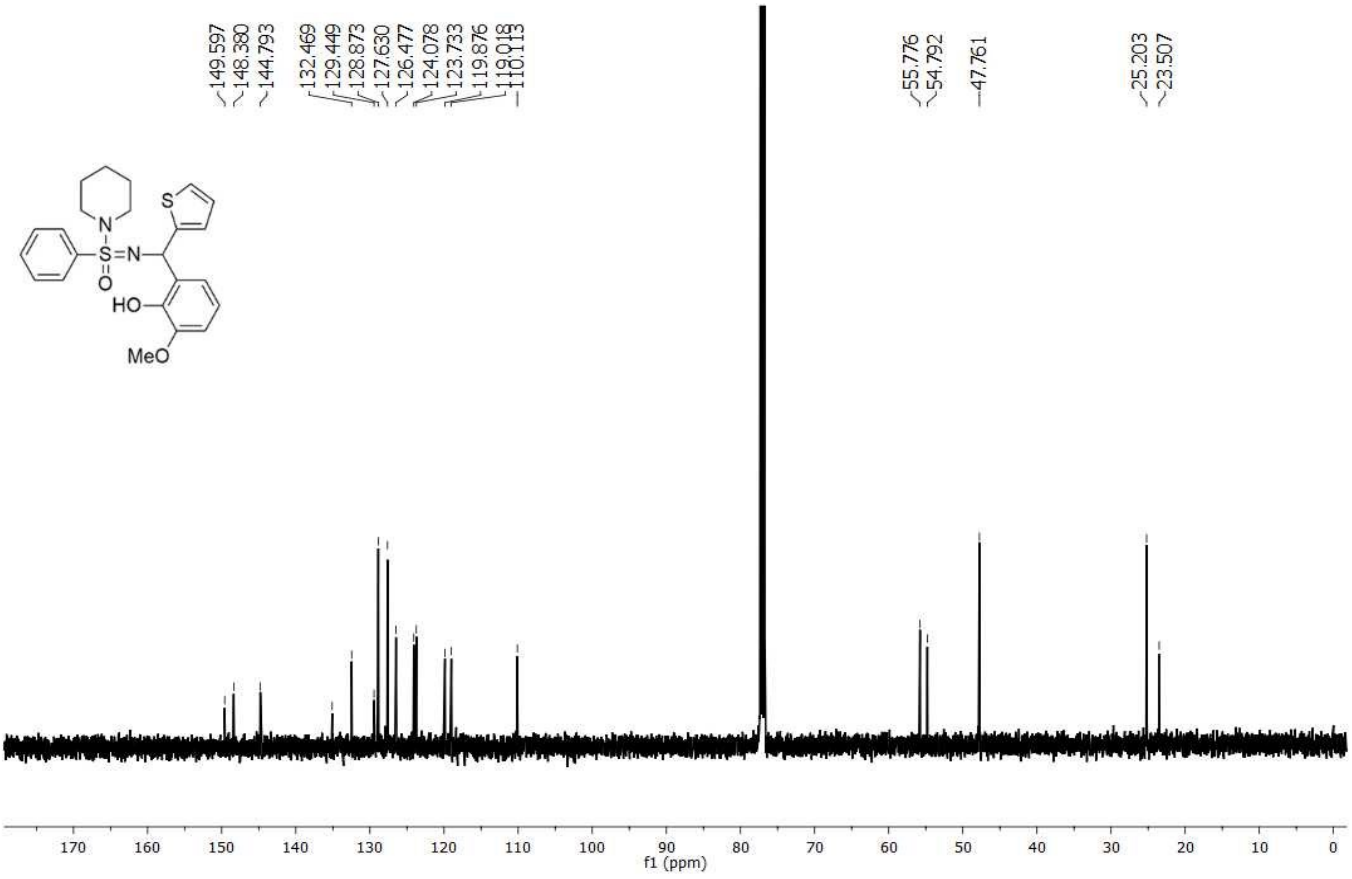
^{13}C {^{1}H} NMR of **6b** (Diastereomer-1)



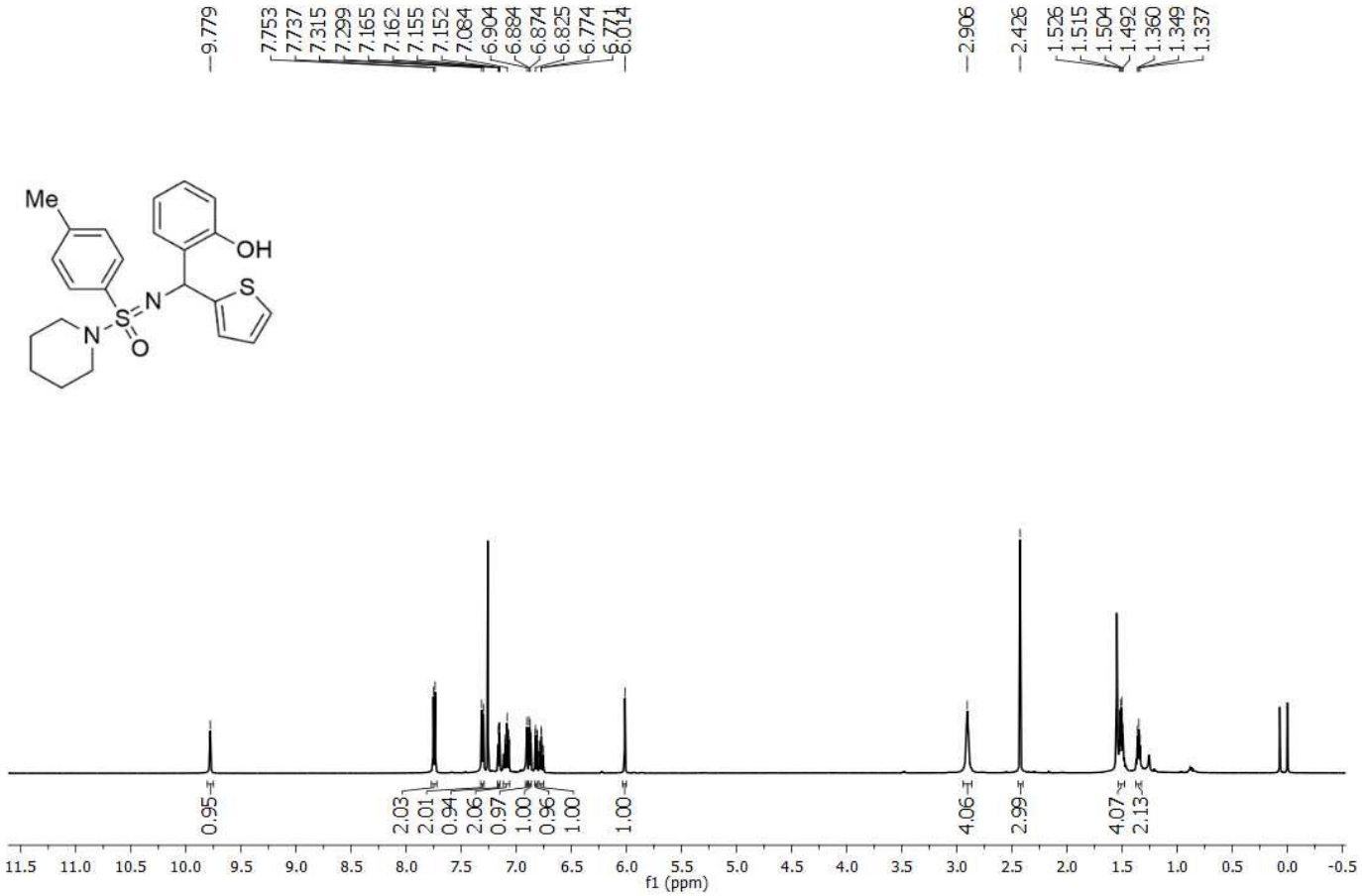
^{1}H NMR of **6b** (Diastereomer-2)



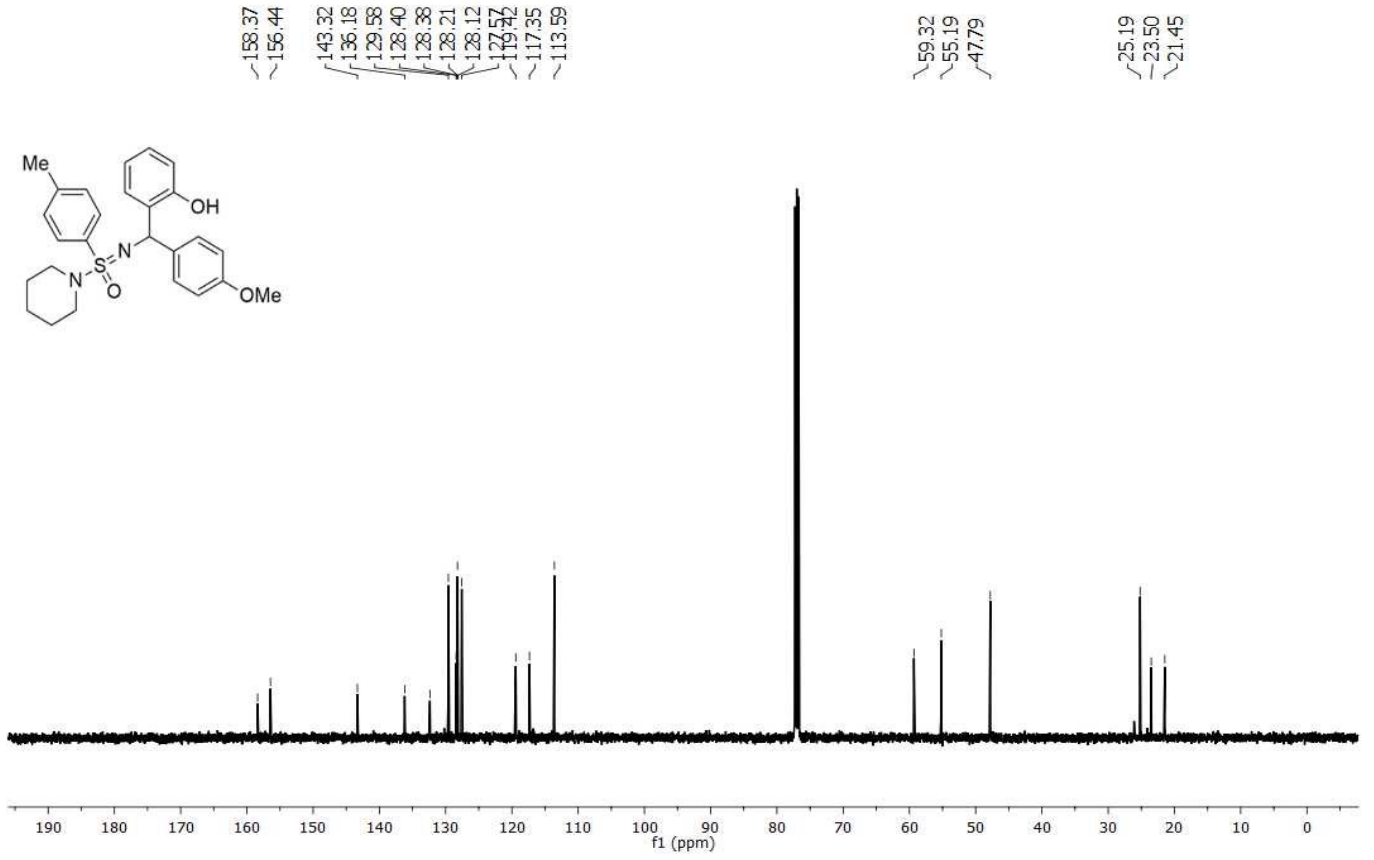
^{13}C NMR of **6b** (Diastereomer-2)



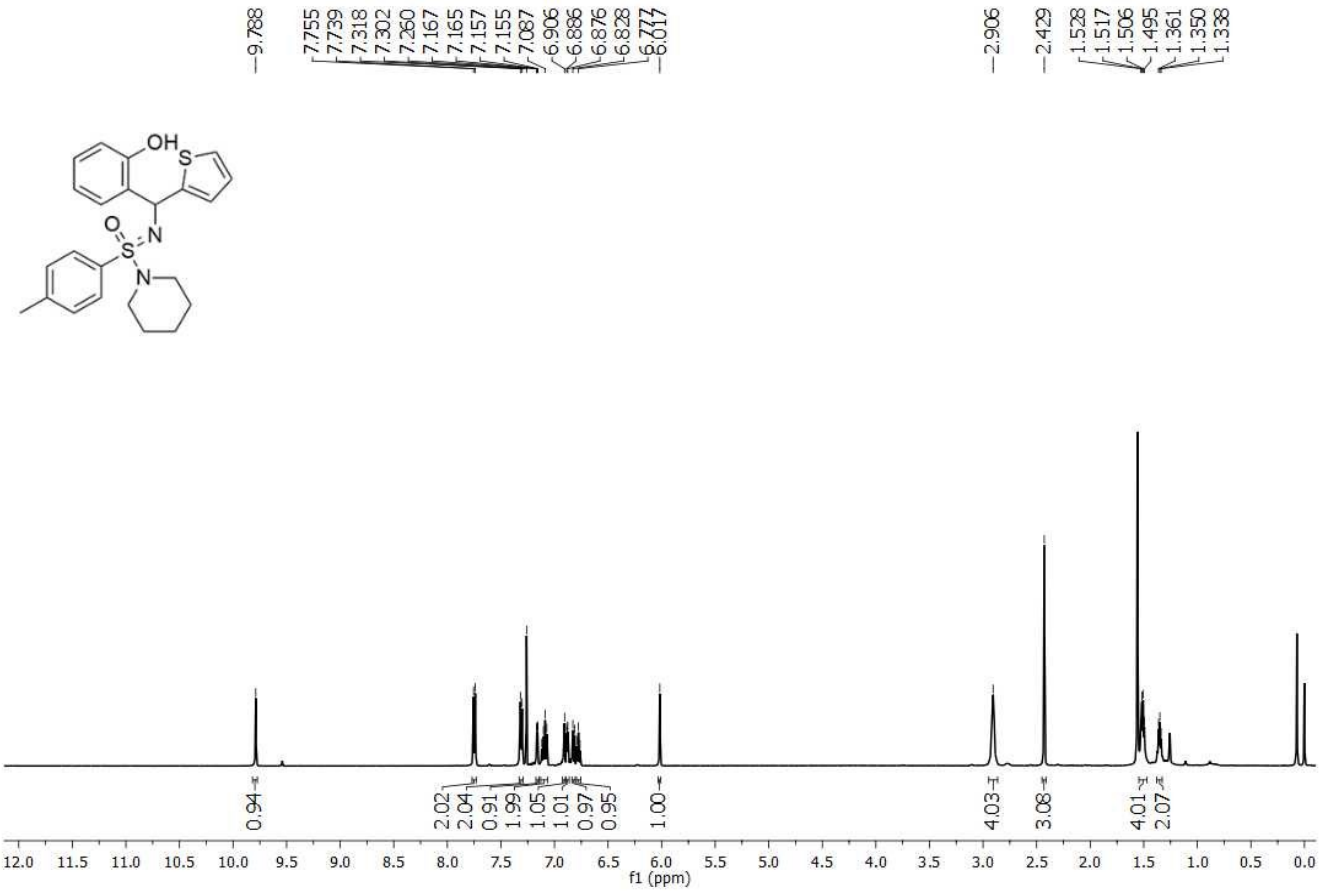
^{1}H NMR of **6c** (Diastereomer-1)



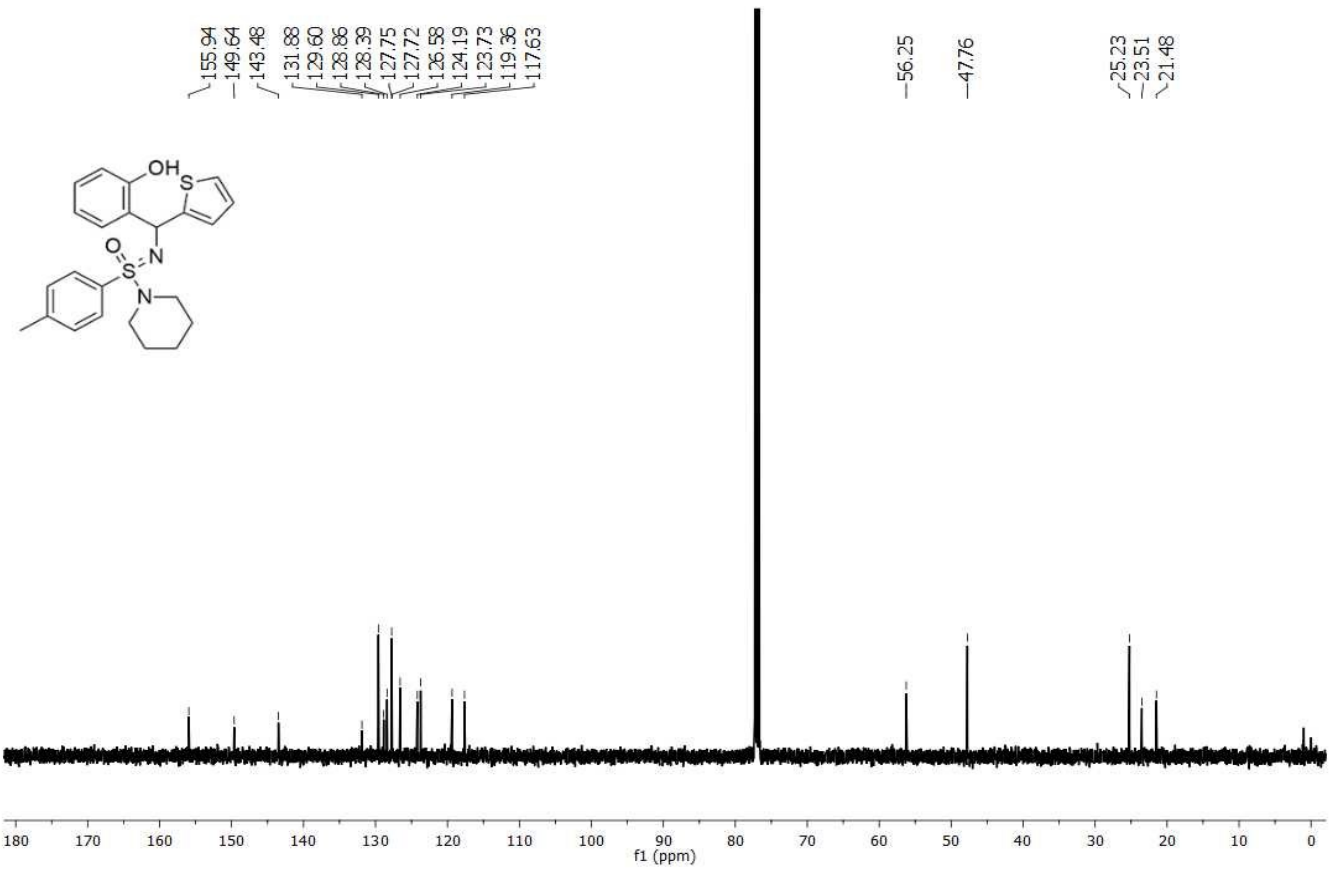
^{13}C {^{1}H} NMR of **6c** (Diastereomer-1)



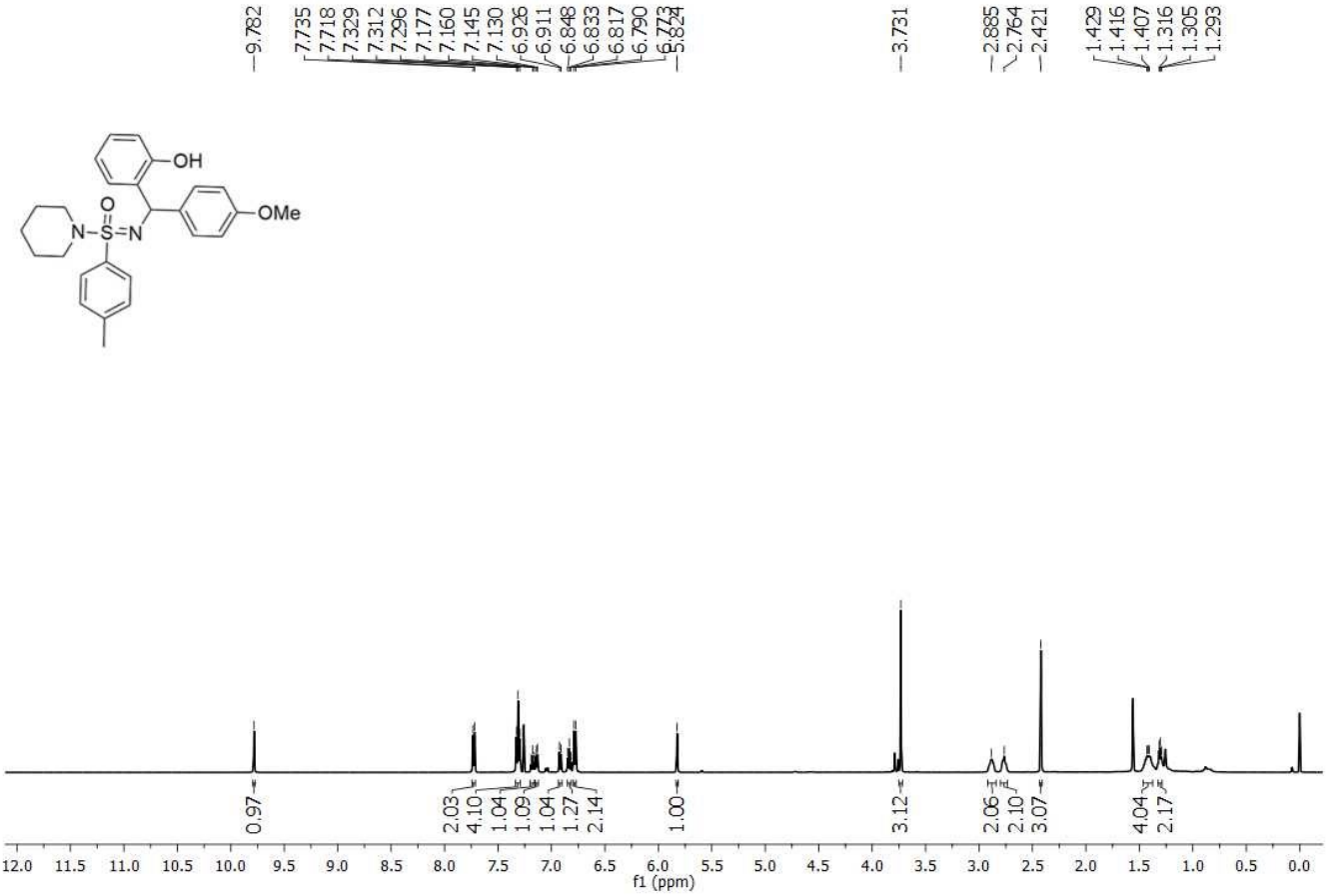
^{1}H NMR of **6c** (Diastereomer-2)



^{13}C {^{1}H} NMR of **6c** (Diastereomer-2)

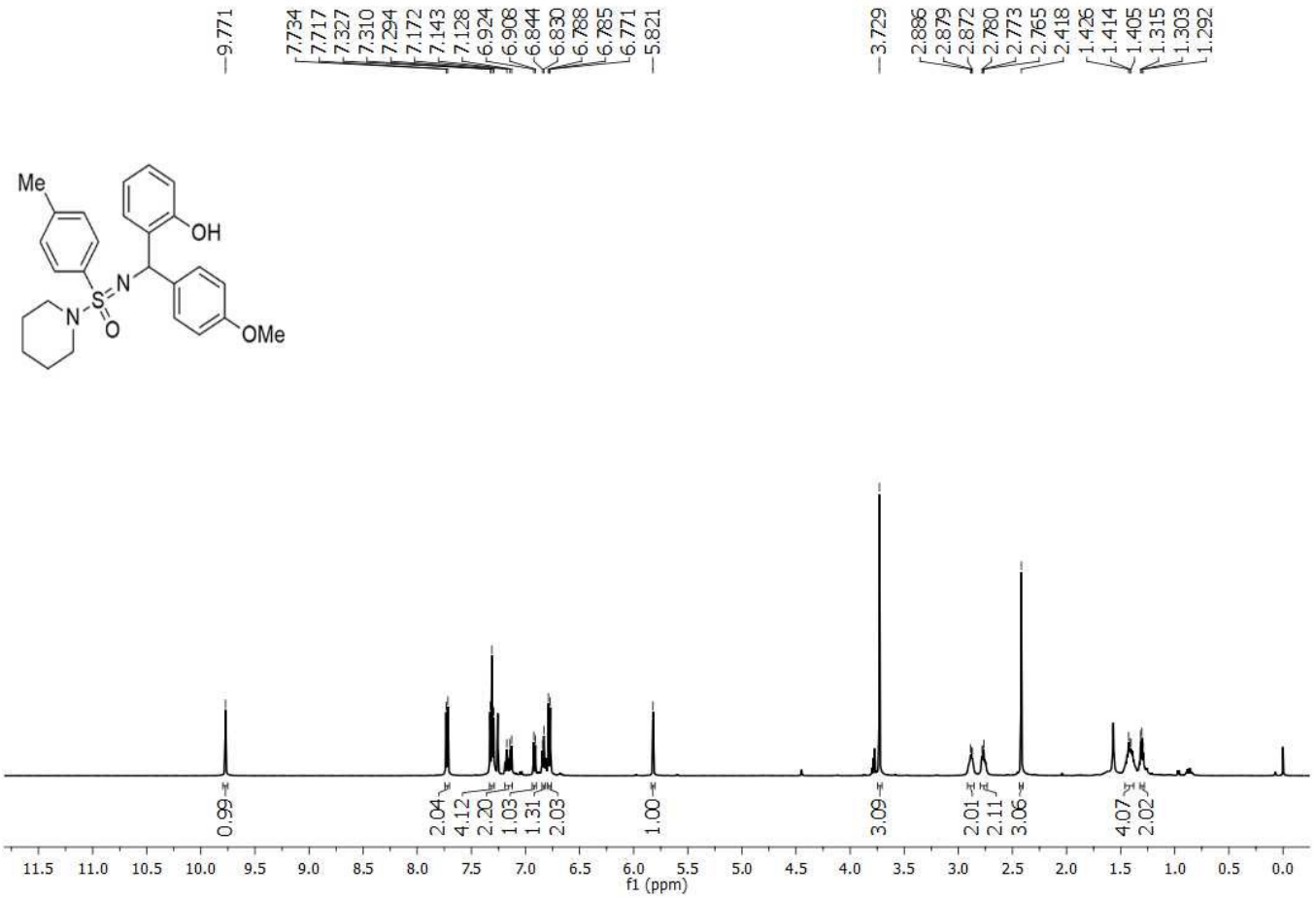


^{1}H NMR of **6d** (Diastereomer-1)

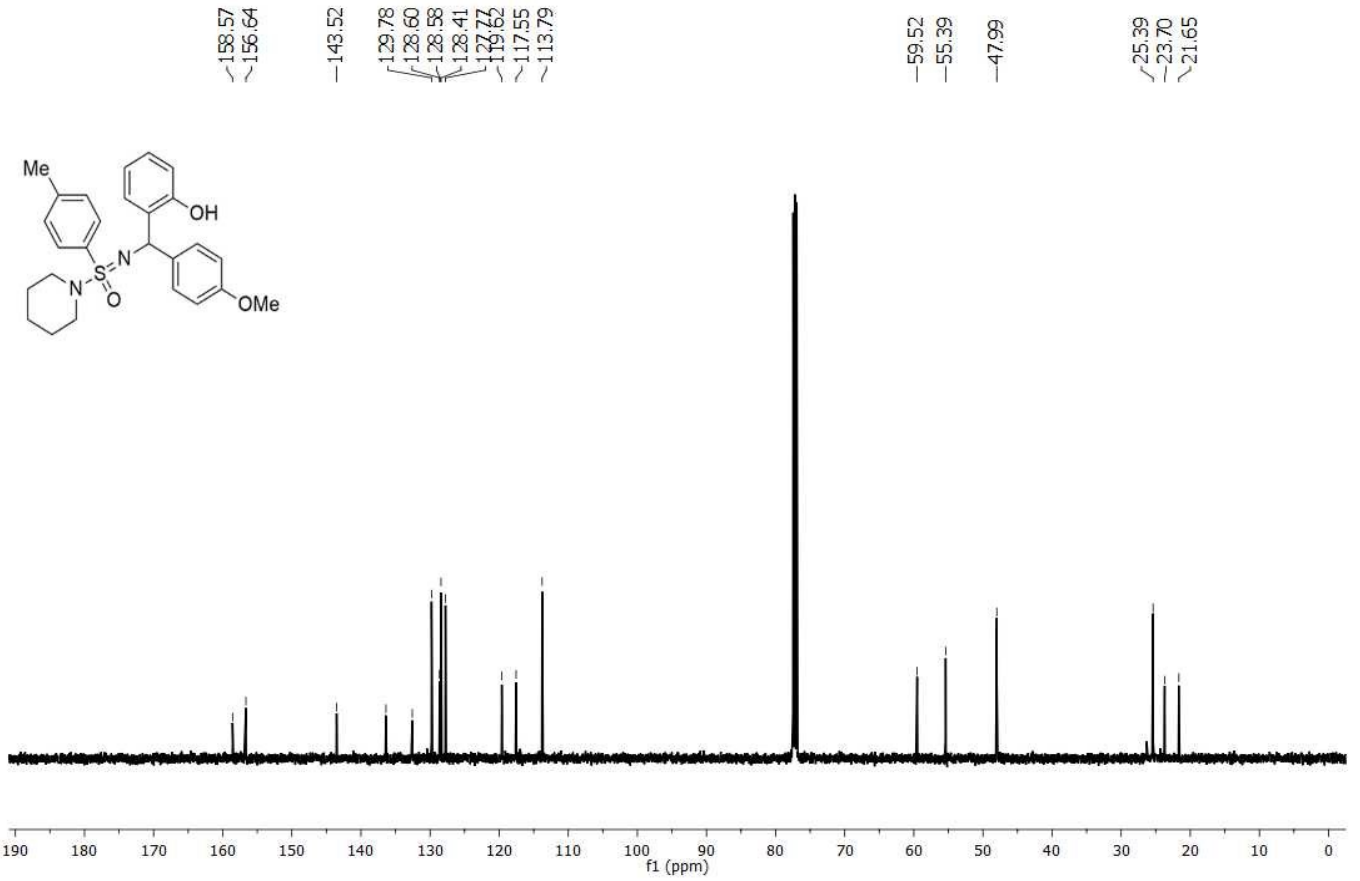


^{13}C {^{1}H} NMR of **6d** (Diastereomer-1)

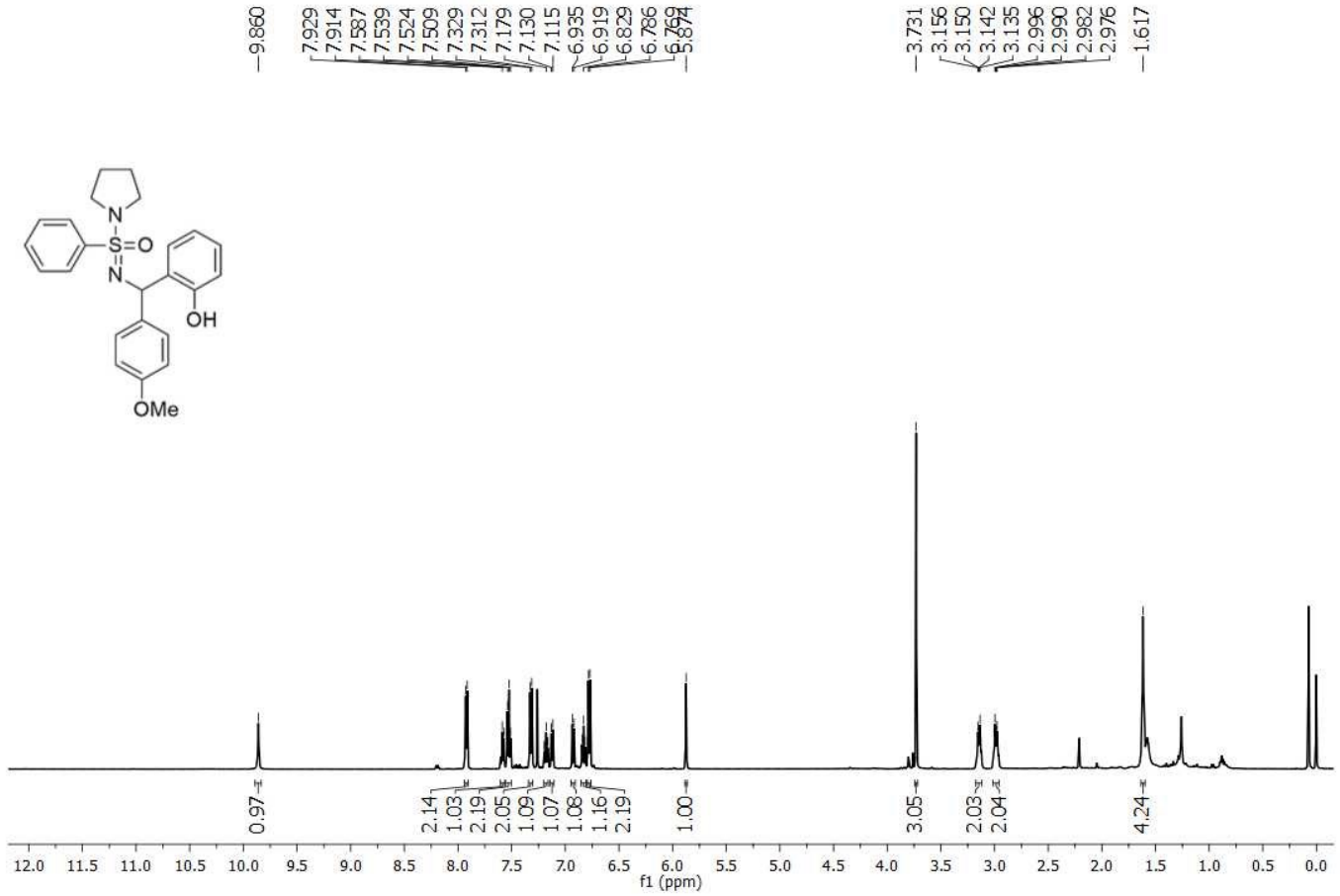
^{1}H NMR of **6d** (Diastereomer-2)



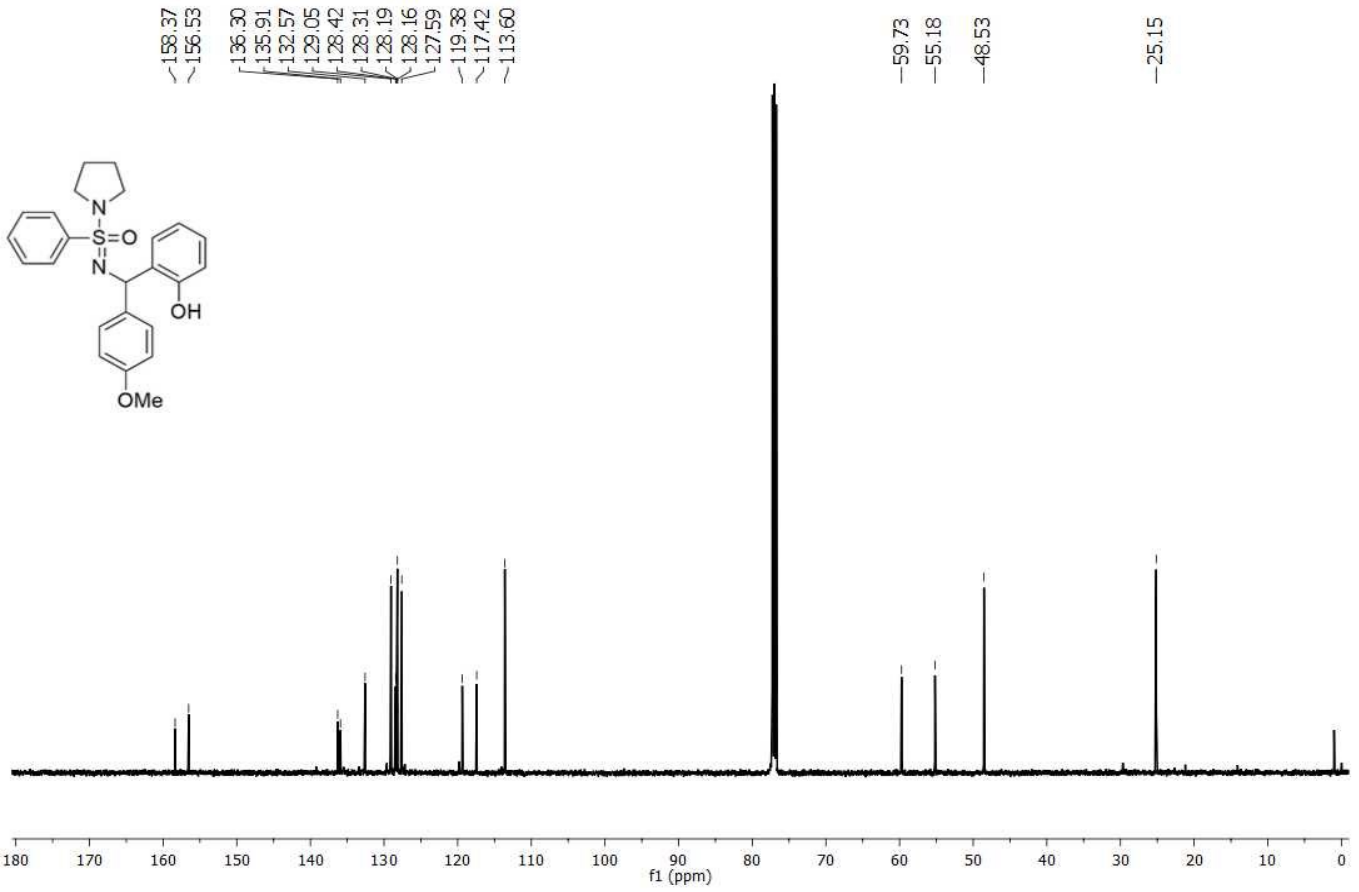
^{13}C {^{1}H} NMR of **6d** (Diastereomer-2)



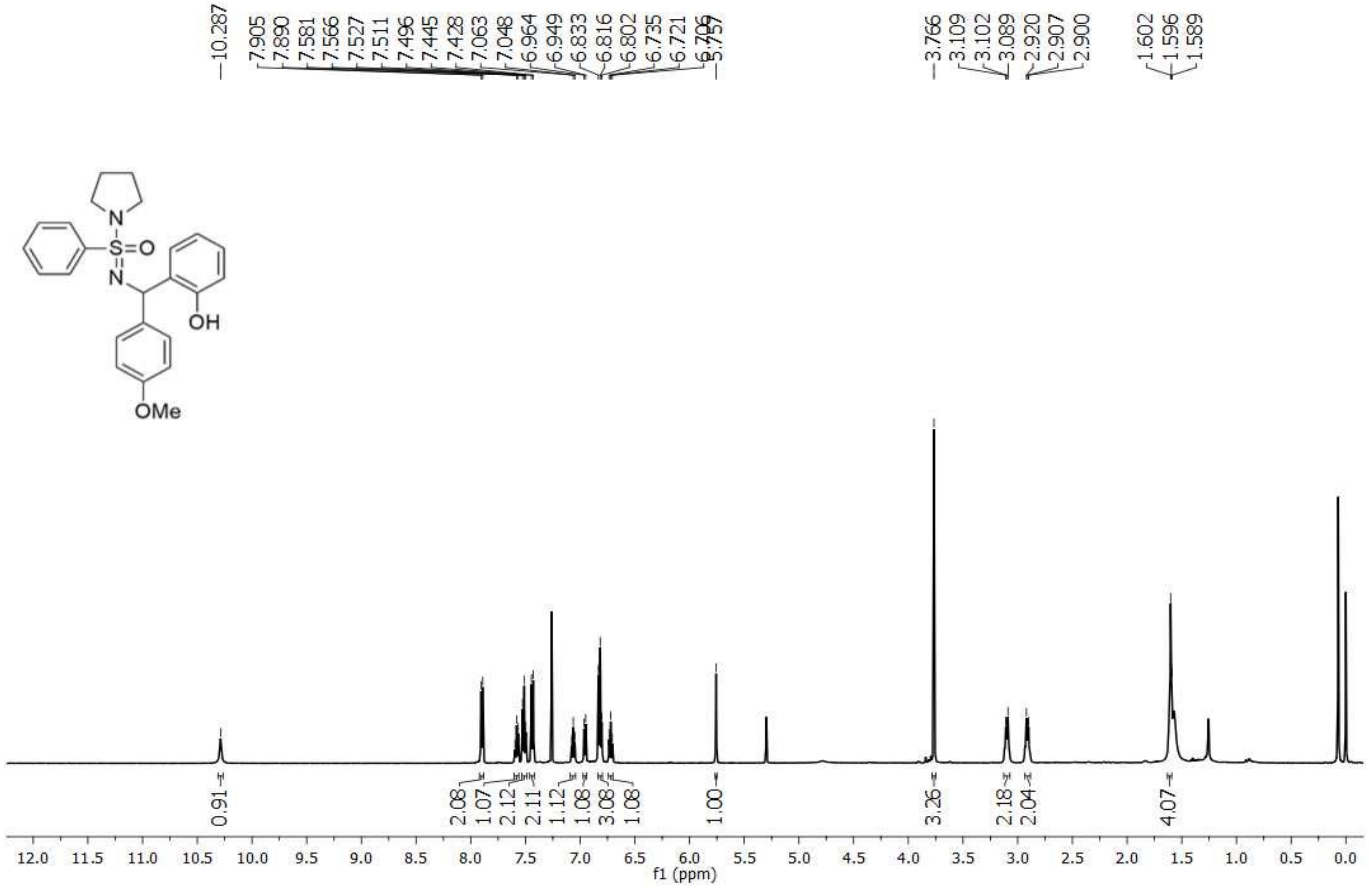
^{1}H NMR of **6e** (Diastereomer-1)



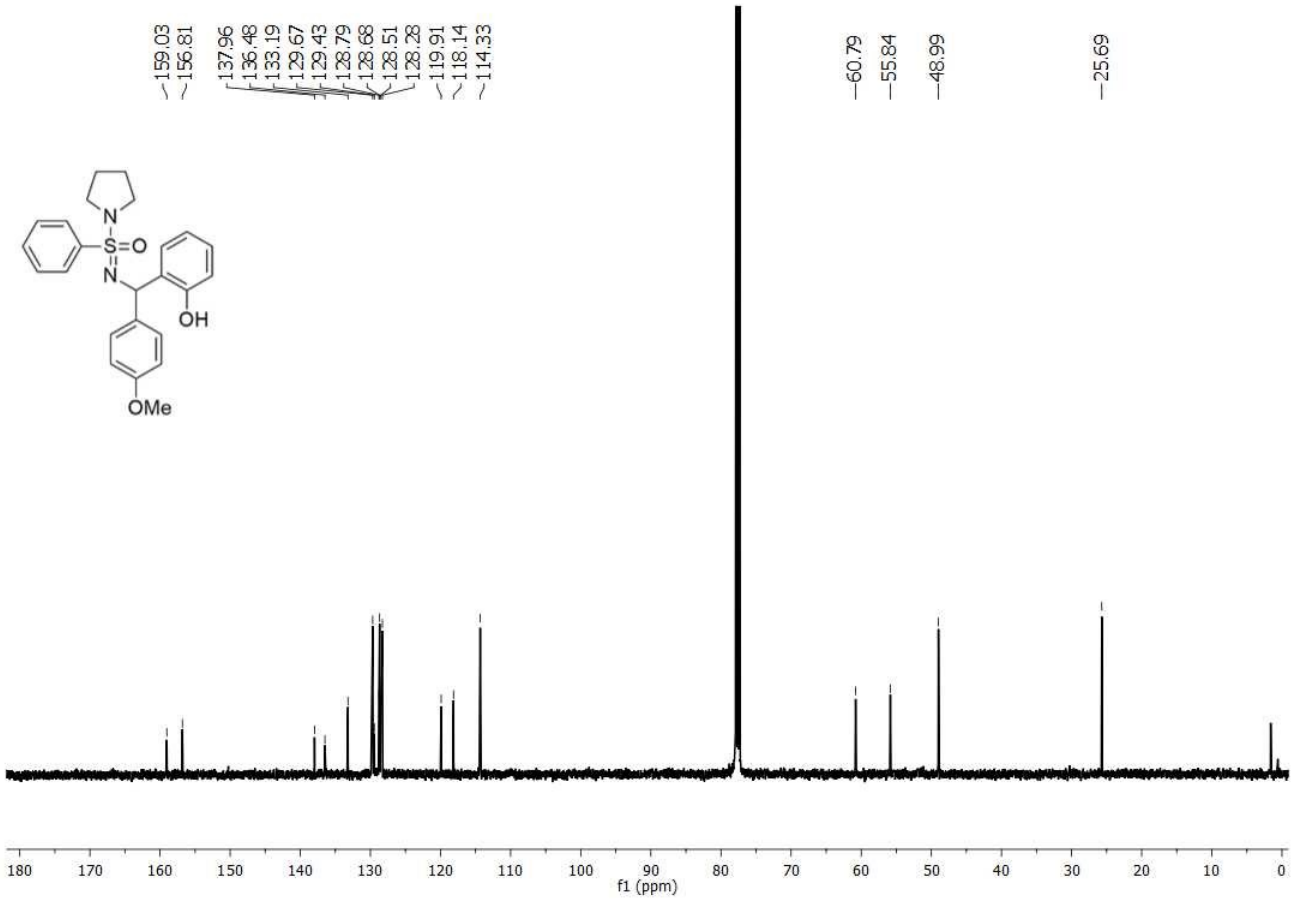
^{13}C {^{1}H} NMR of **6e** (Diastereomer-1)



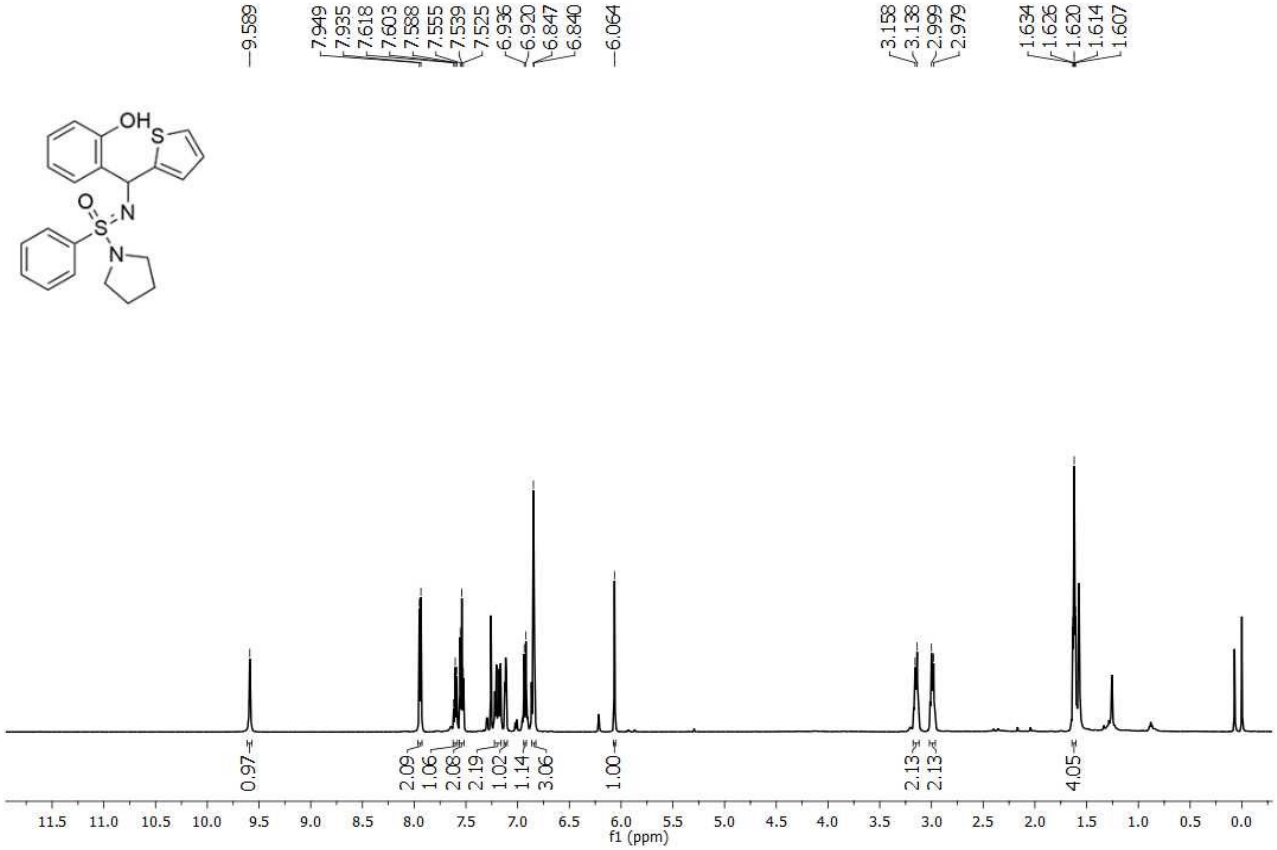
^{1}H NMR of **6e** (Diastereomer-2)



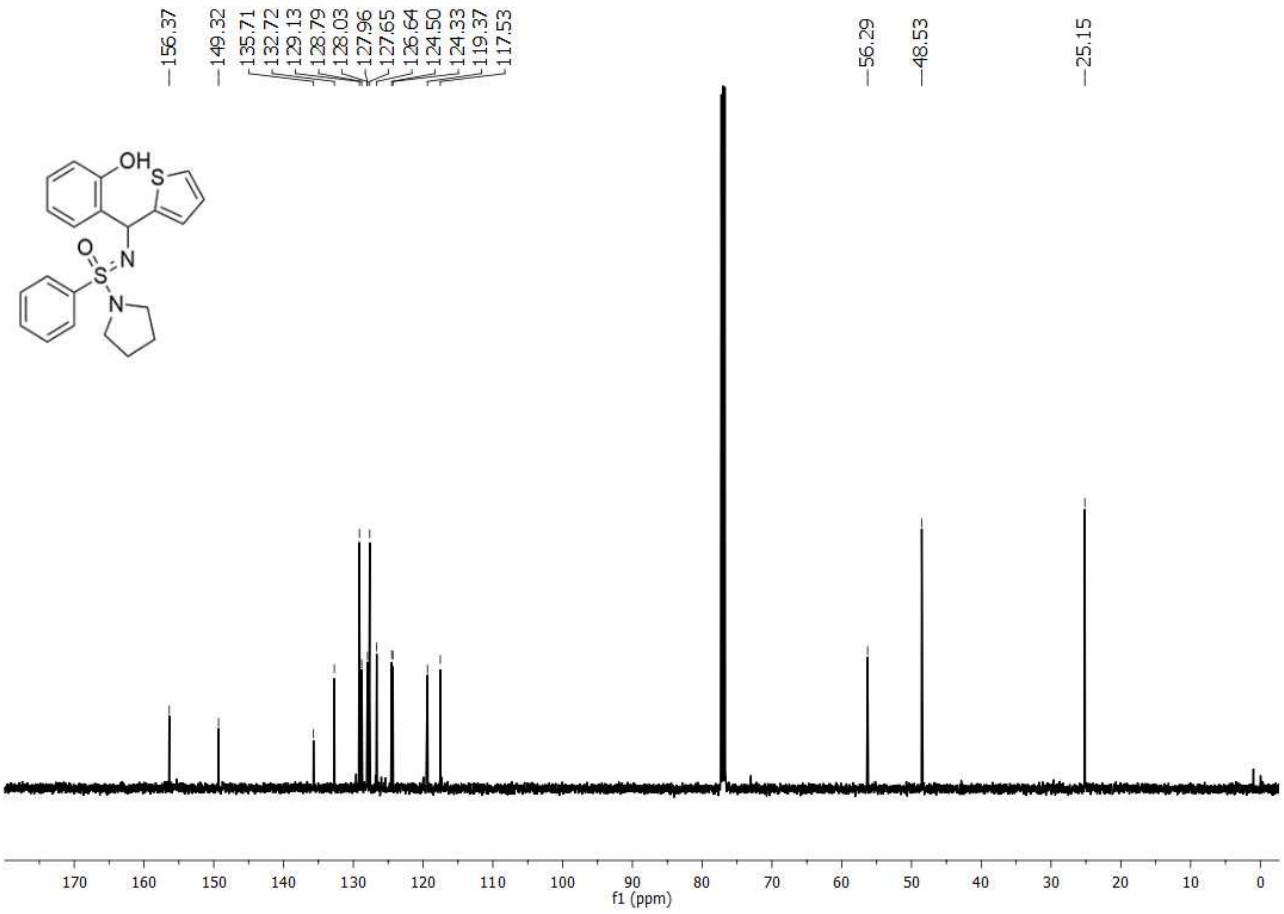
^{13}C {^{1}H} NMR of **6e** (Diastereomer-2)



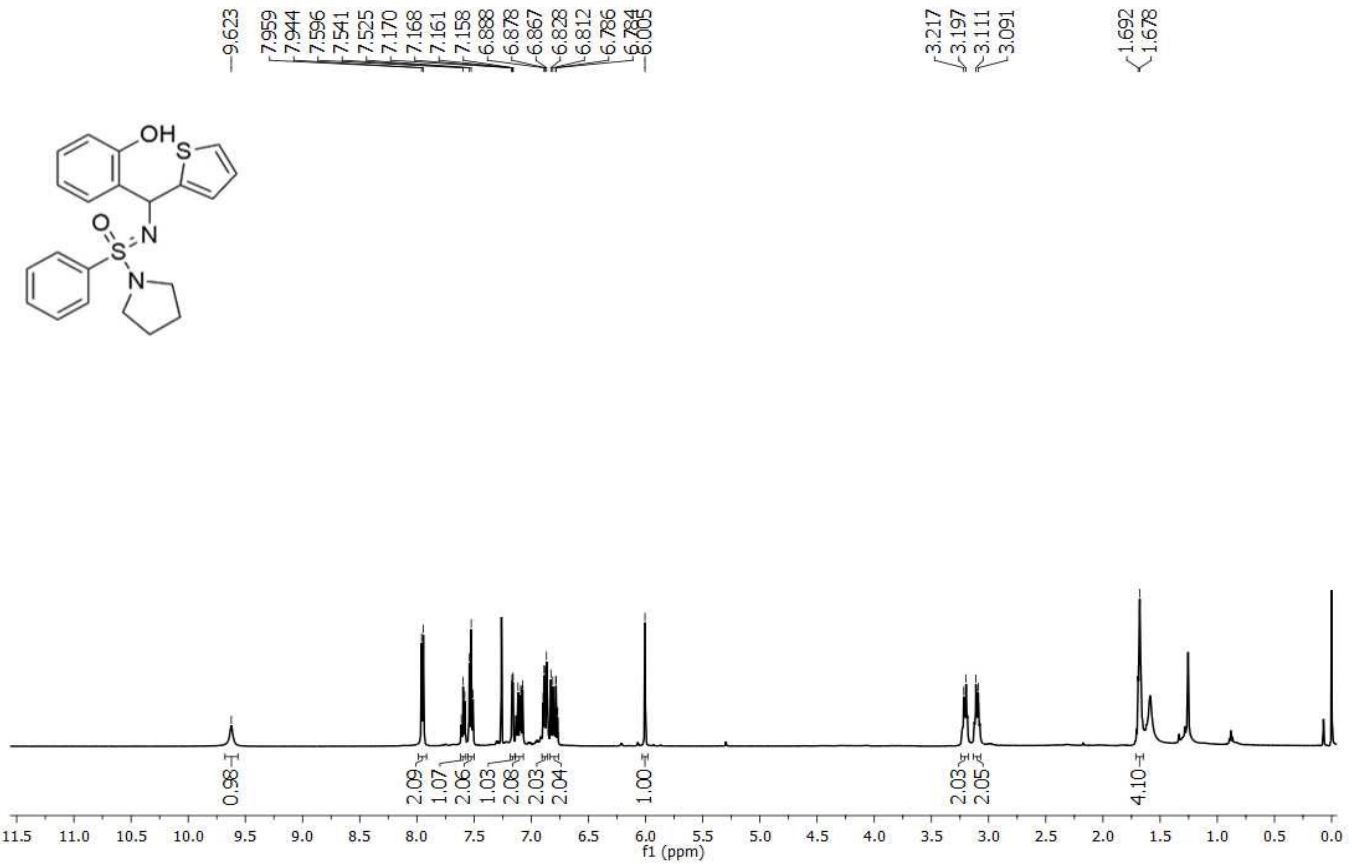
^{1}H NMR of **6f** (Diastereomer-1)



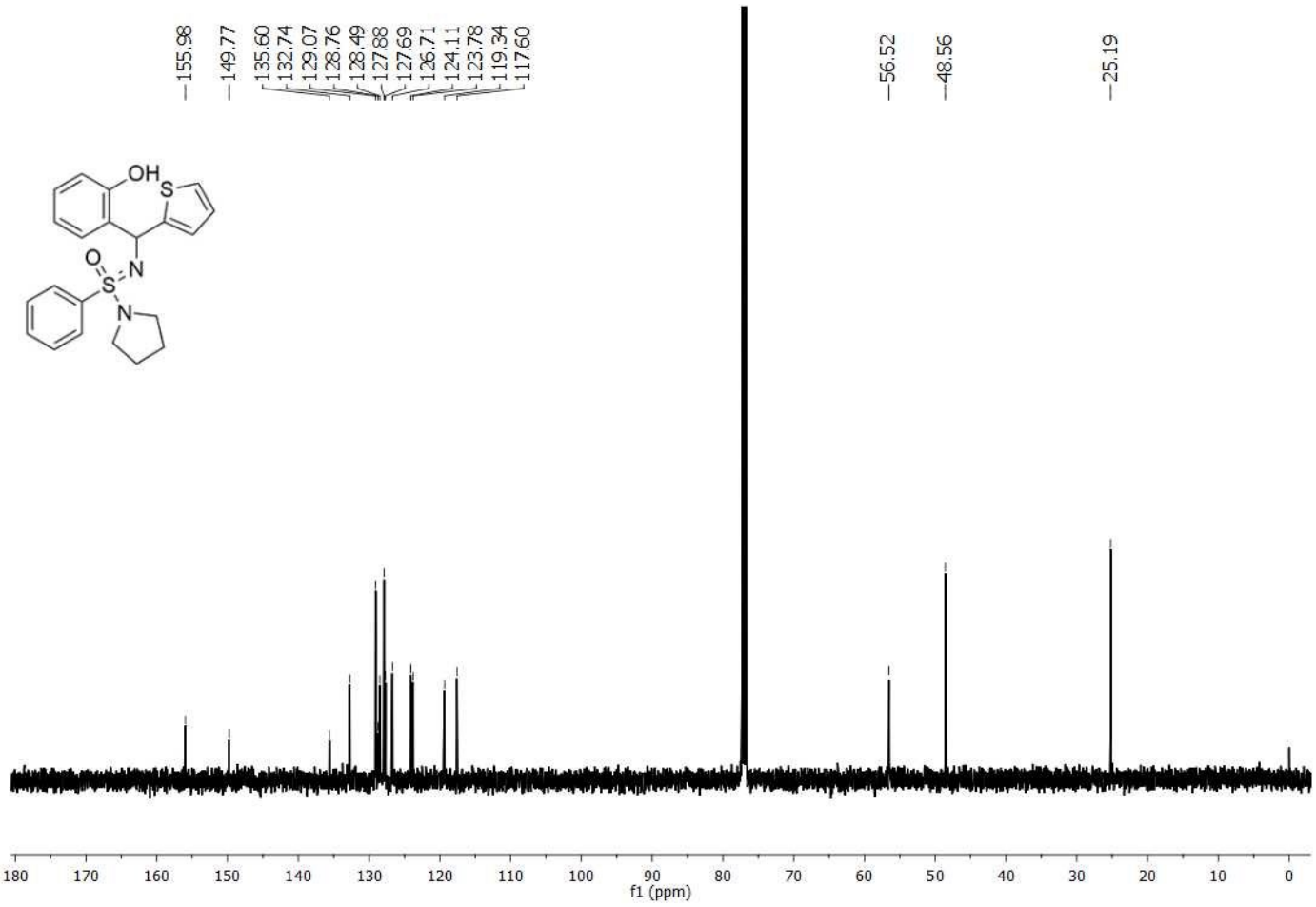
^{13}C {^{1}H} NMR of **6f** (Diastereomer-1)



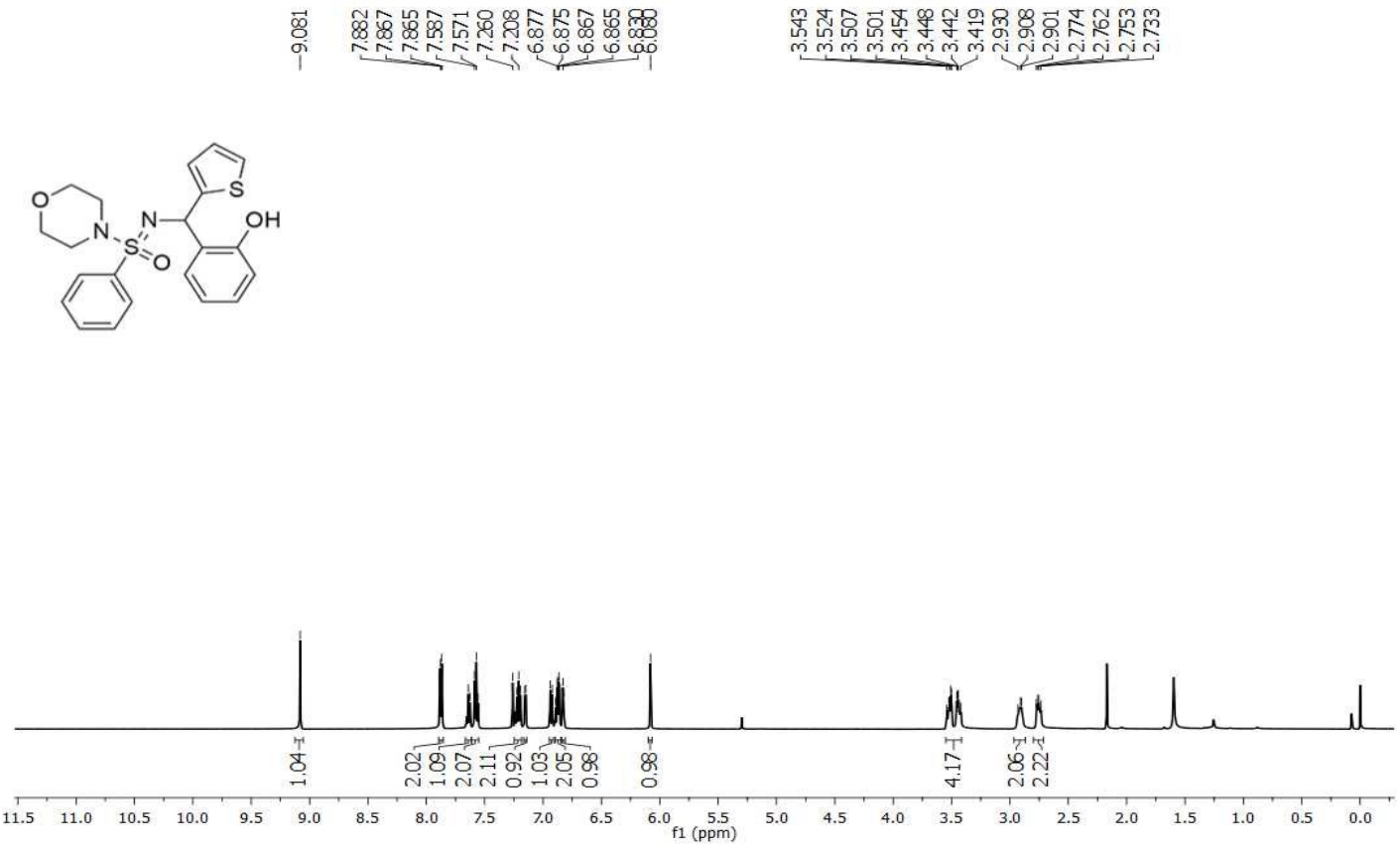
^{1}H NMR of **6f** (Diastereomer-2)



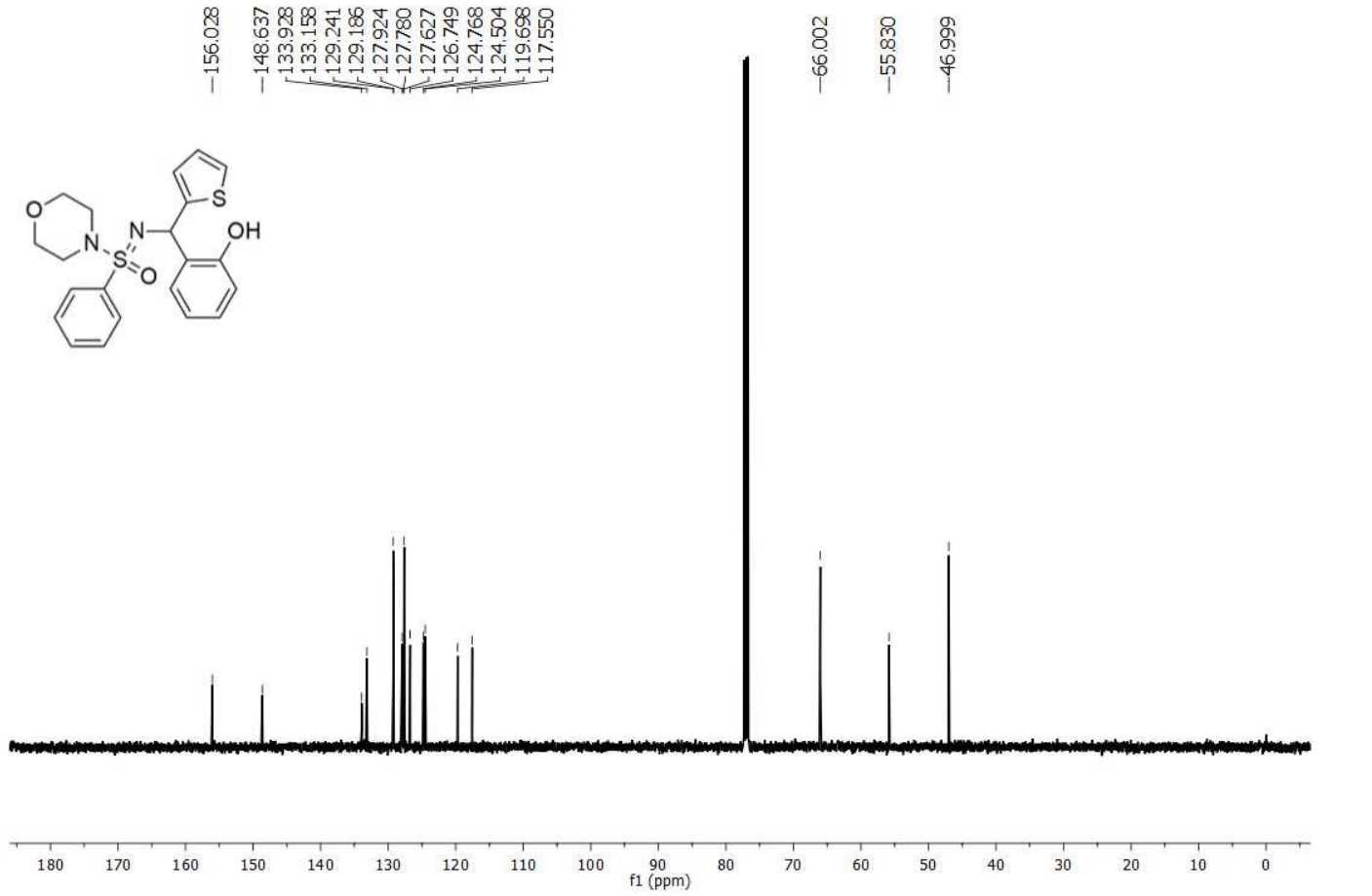
^{13}C {^{1}H} NMR of **6f** (Diastereomer-2)



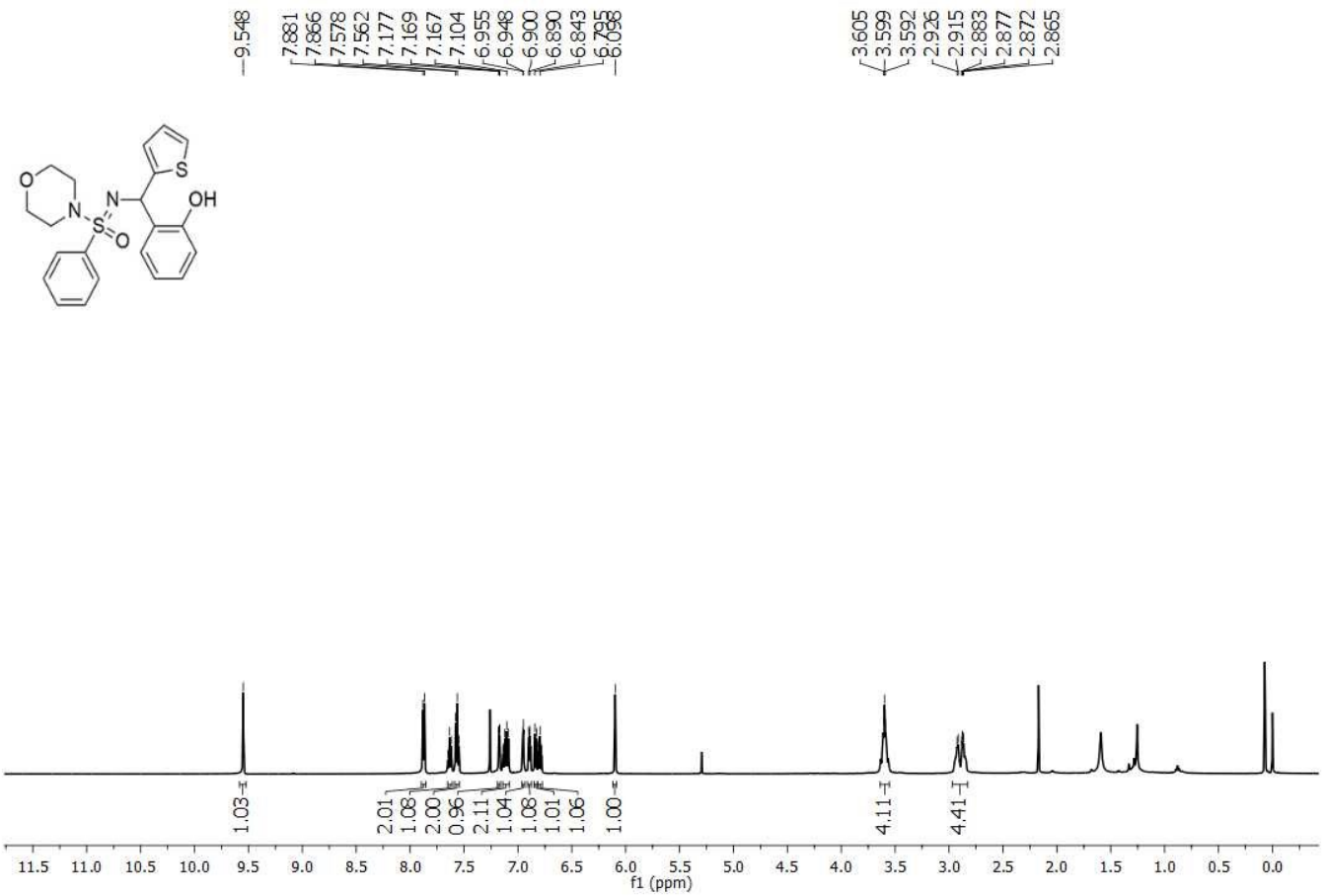
^{1}H NMR of **6g** (Diastereomer-1)



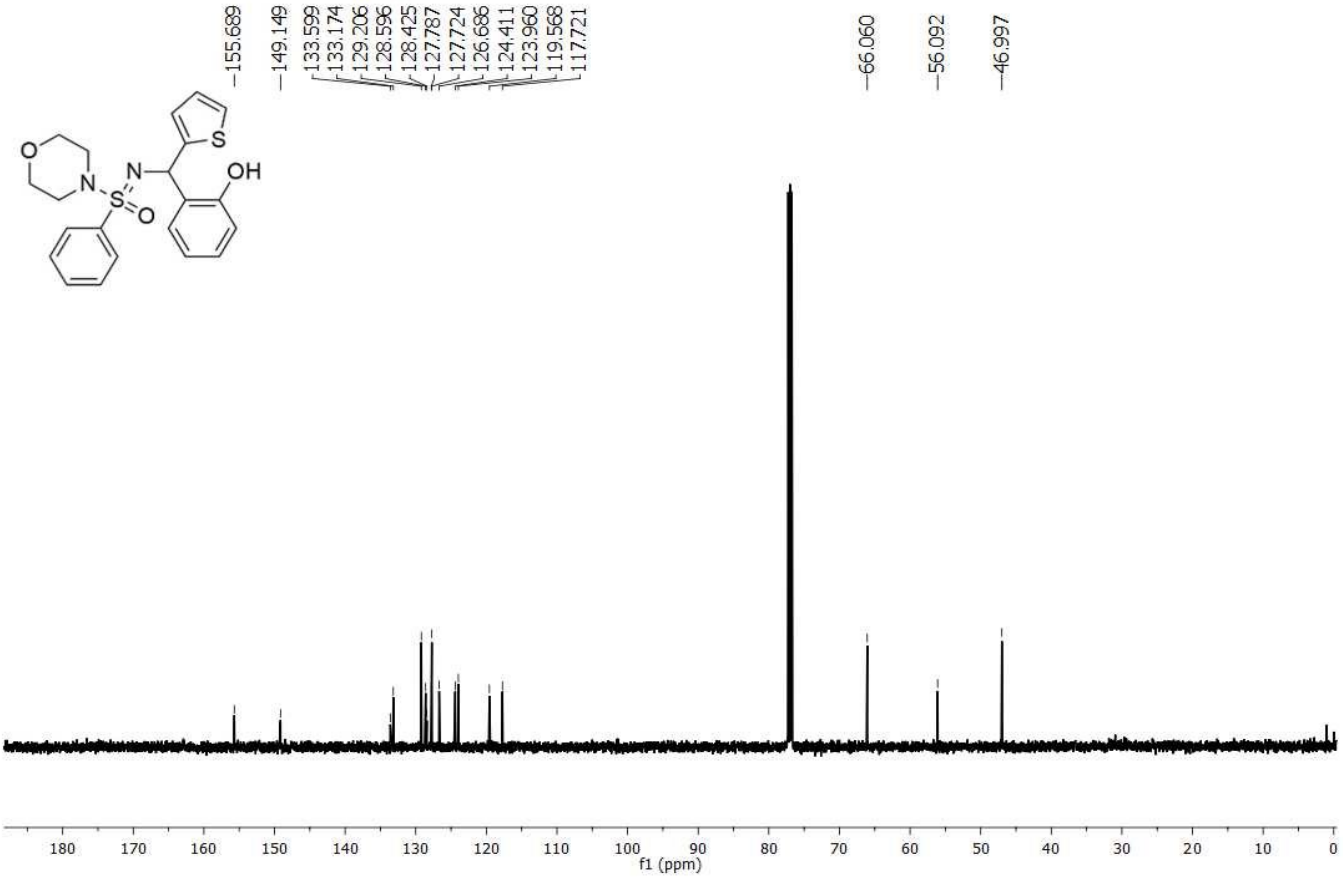
^{13}C {^{1}H} NMR of **6g** (Diastereomer-1)



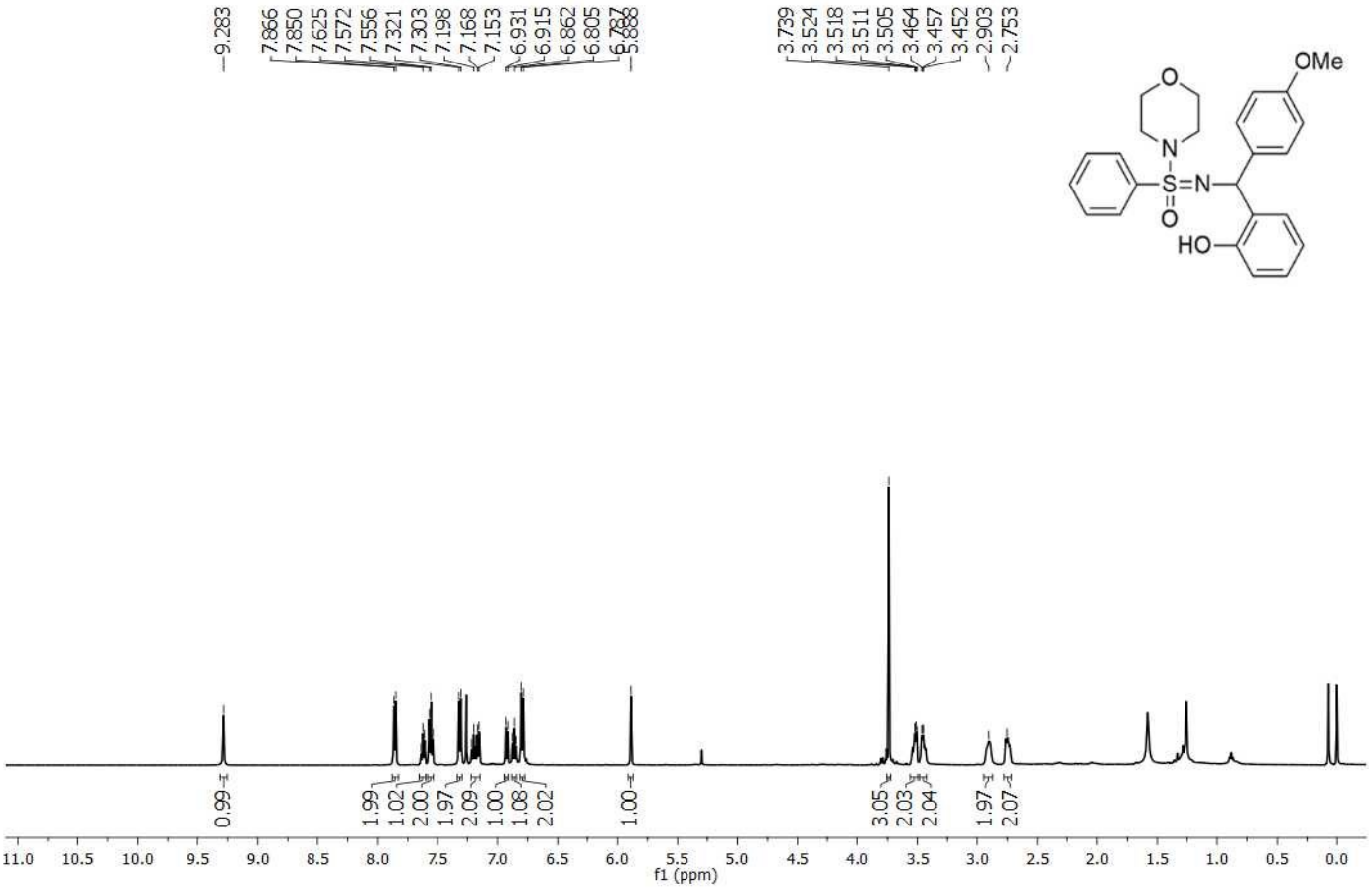
^{1}H NMR of **6g** (Diastereomer-2)



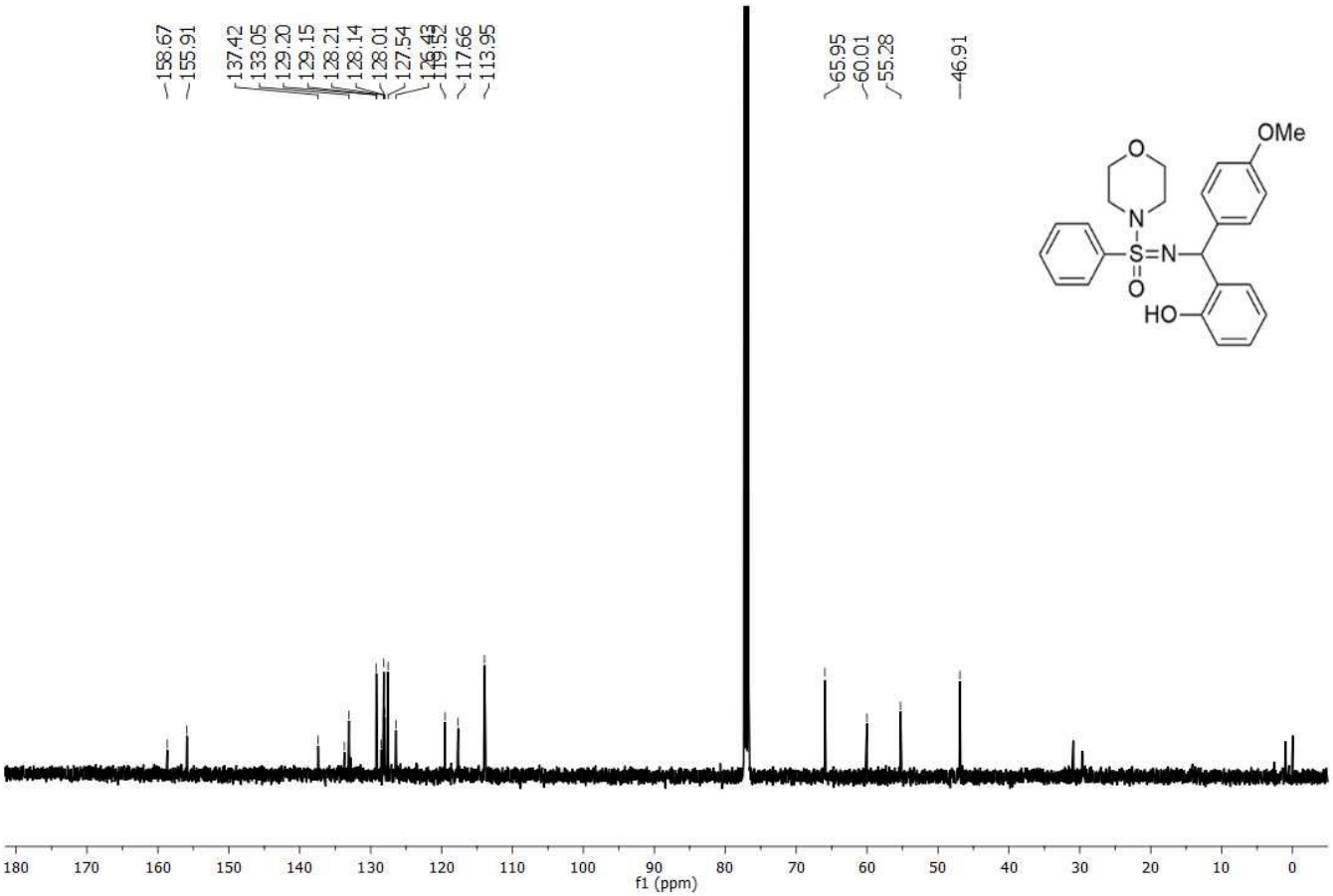
^{13}C {^{1}H} NMR of **6g** (Diastereomer-2)



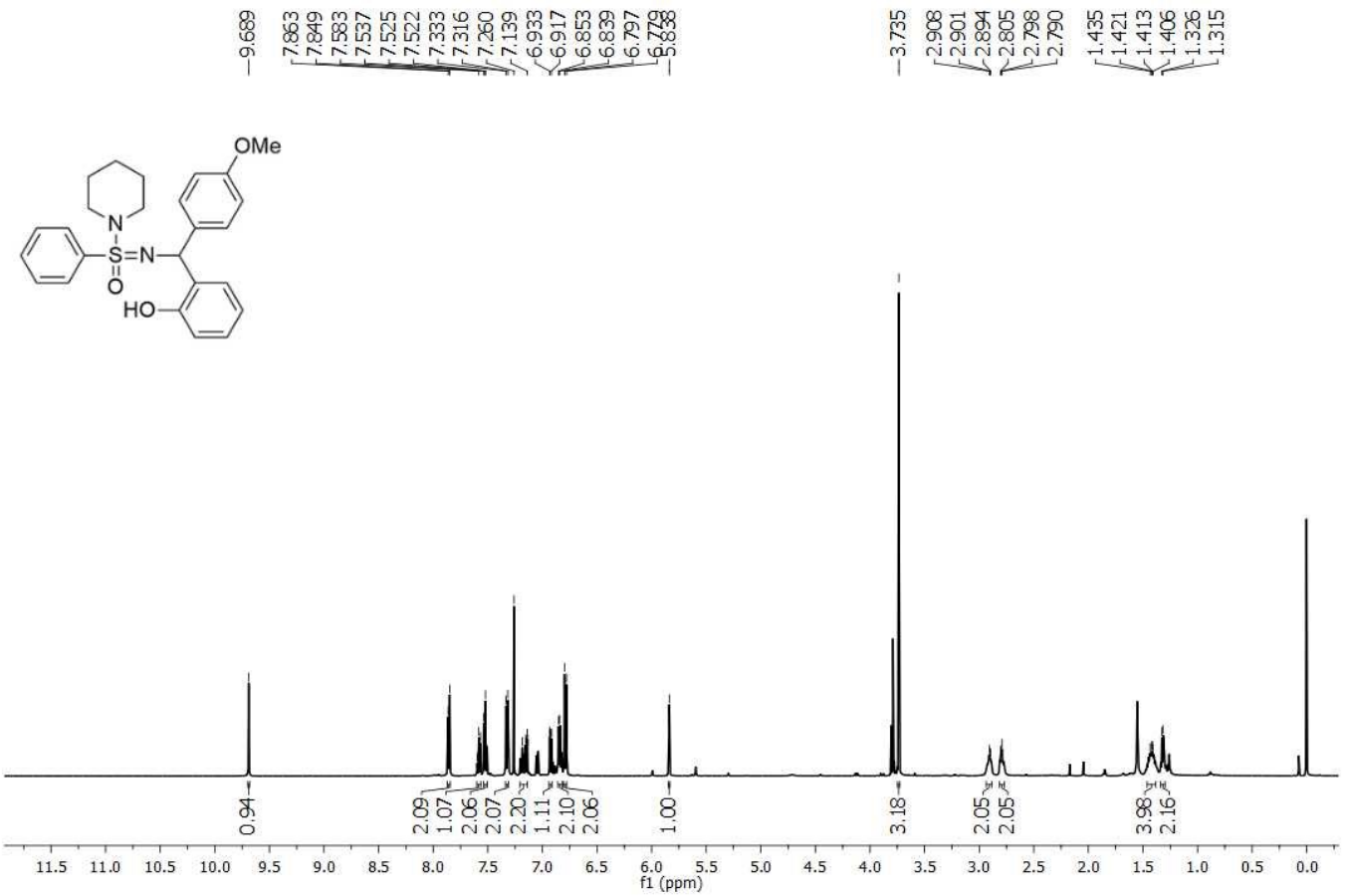
^{1}H NMR of **6h** (Diastereomer-1, able to purify only one diastereomer)



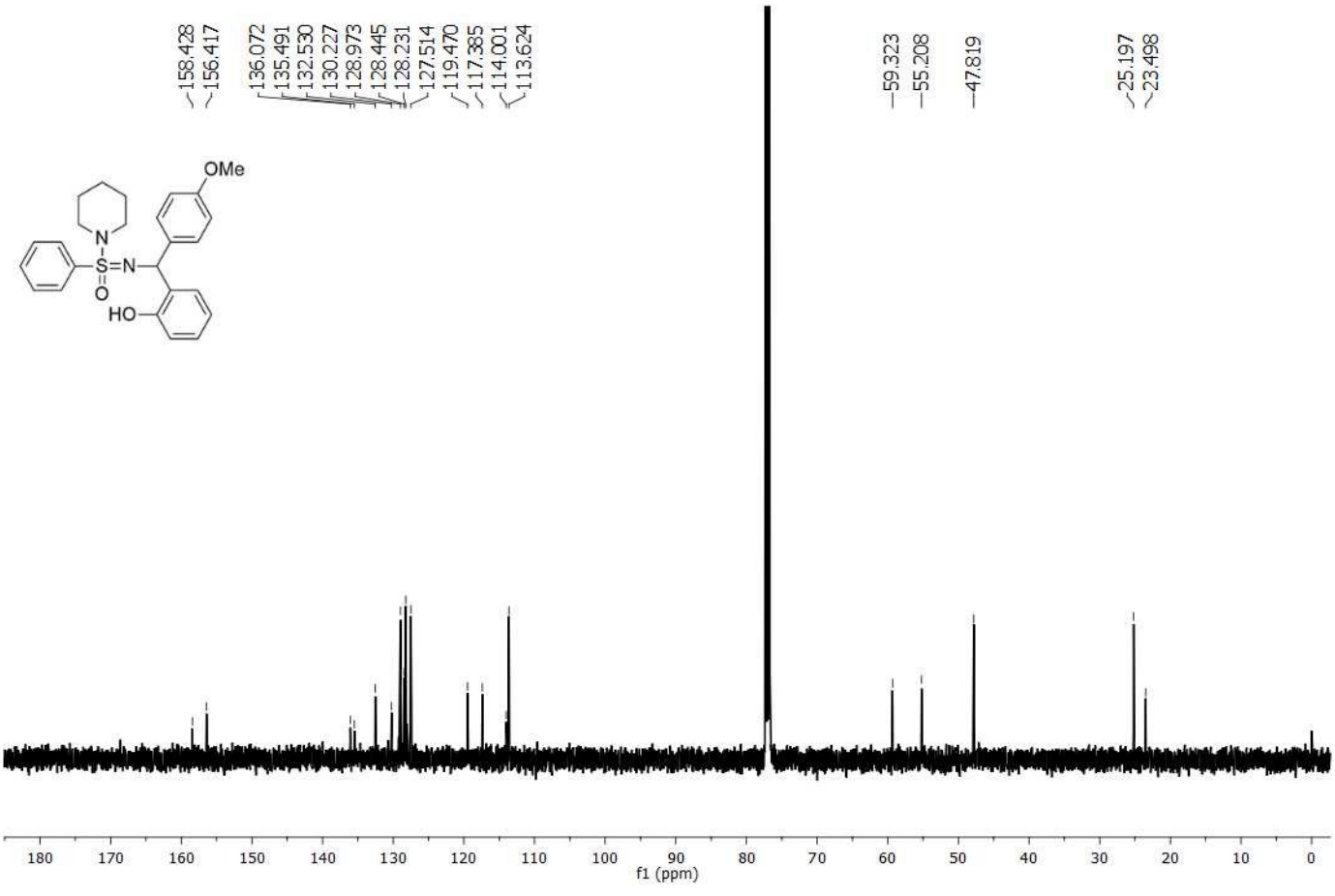
^{13}C {^{1}H} NMR of **6h** (Diastereomer-1, able to purify only one diastereomer)



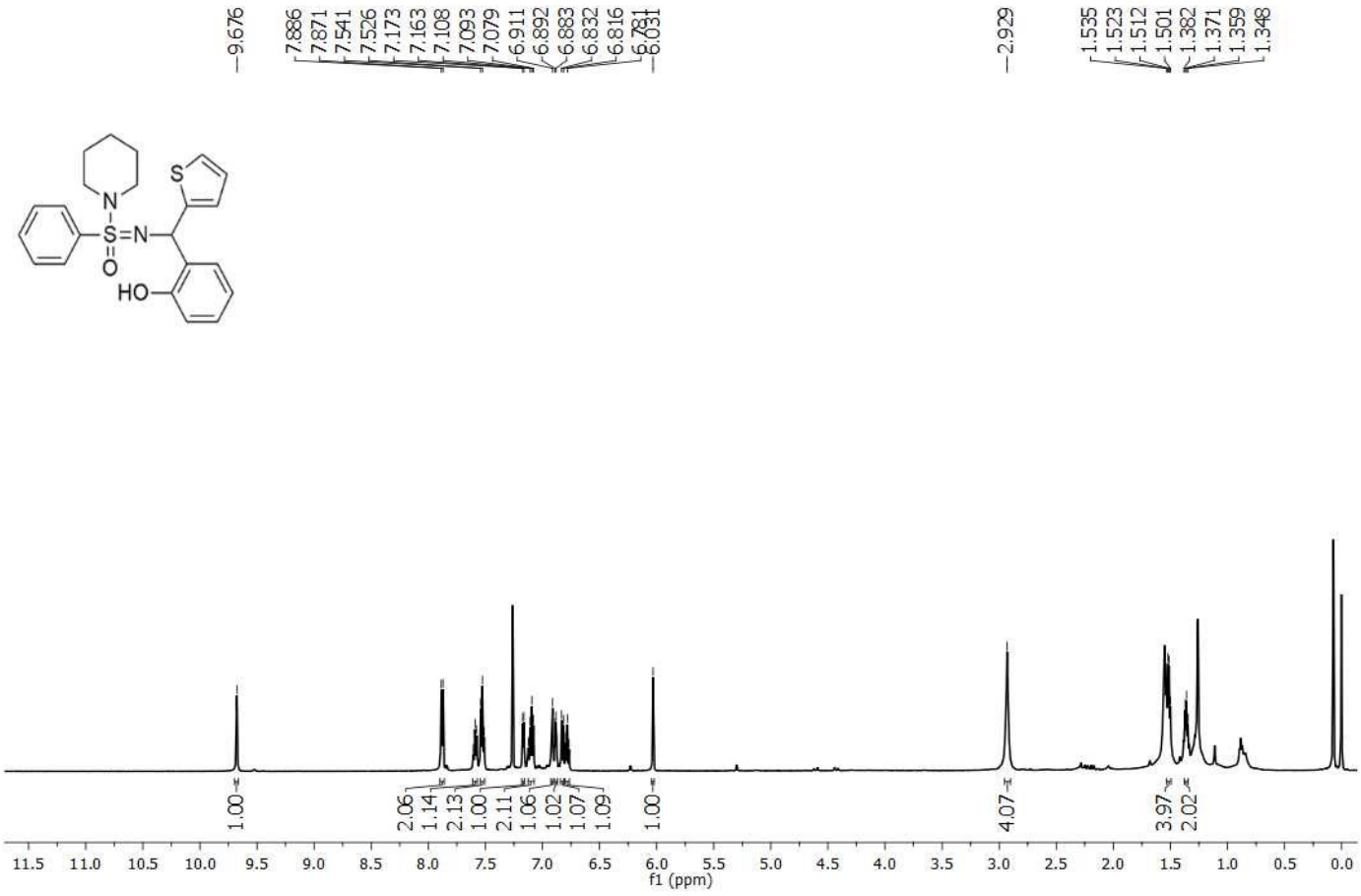
^{1}H NMR of **6i** (Diastereomer-1, able to purify only one diastereomer)



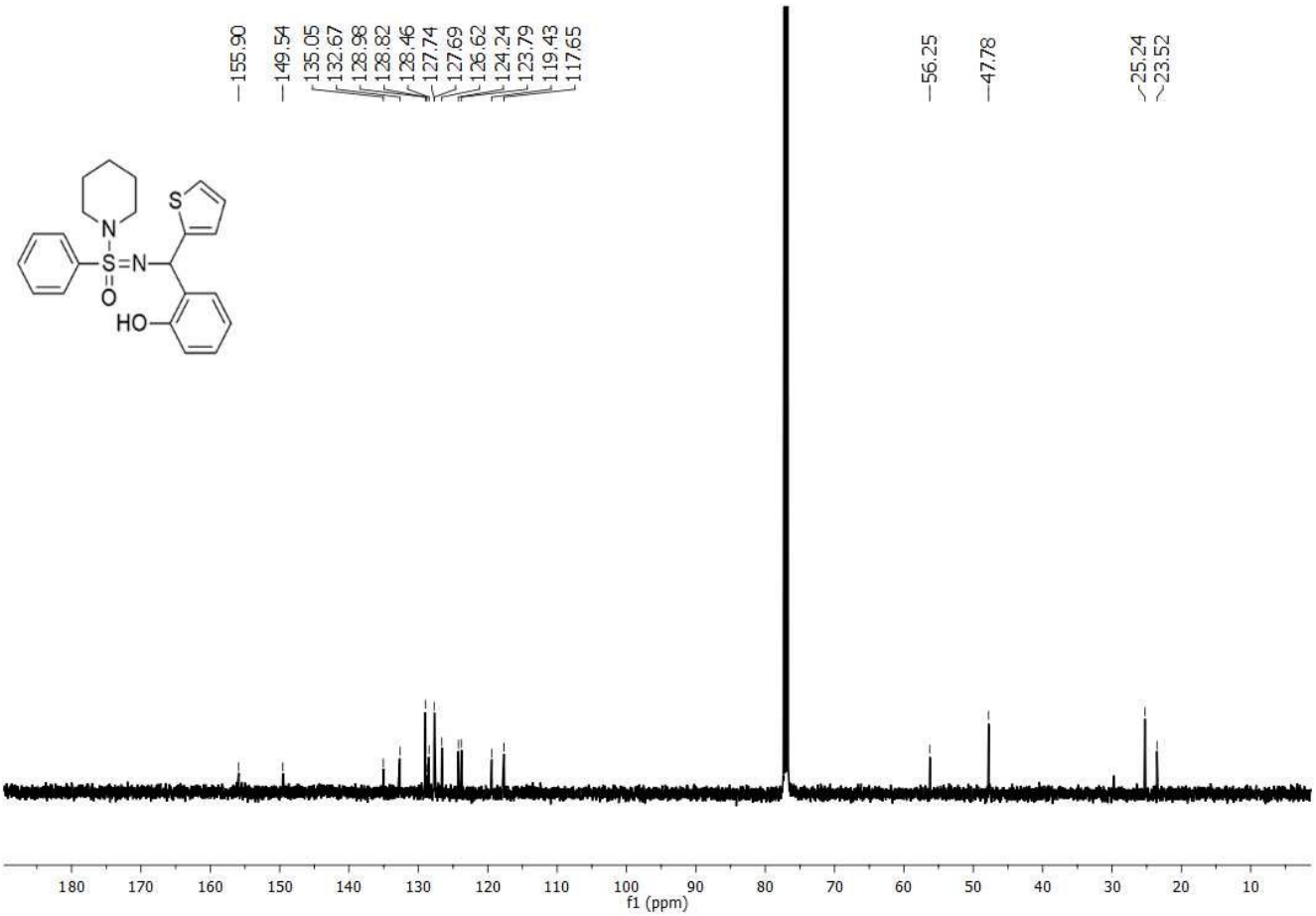
^{13}C {^{1}H} NMR of **6i** (Diastereomer-1, able to purify only one diastereomer)



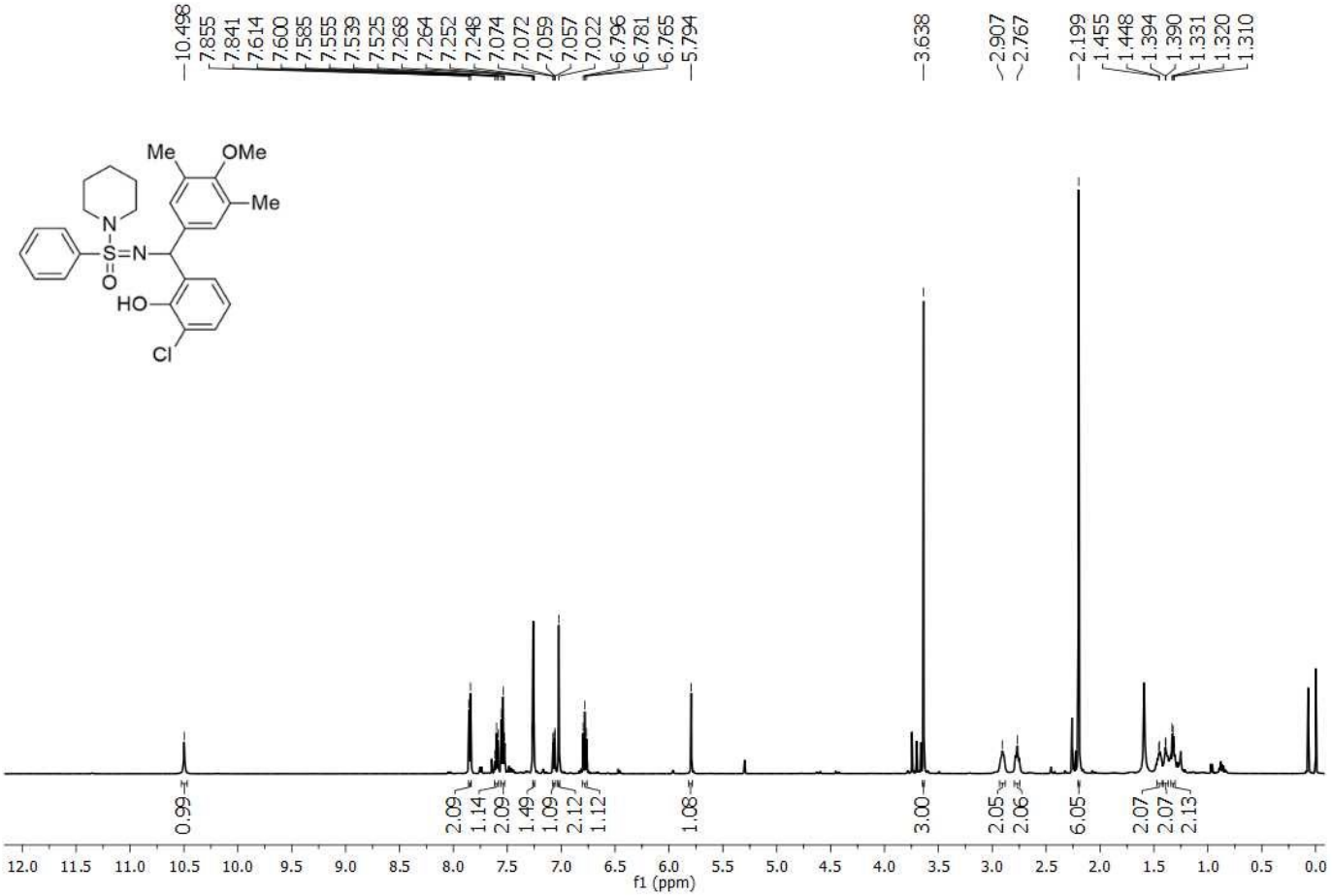
^{1}H NMR of **6j** (Diastereomer-1, able to purify only one diastereomer)



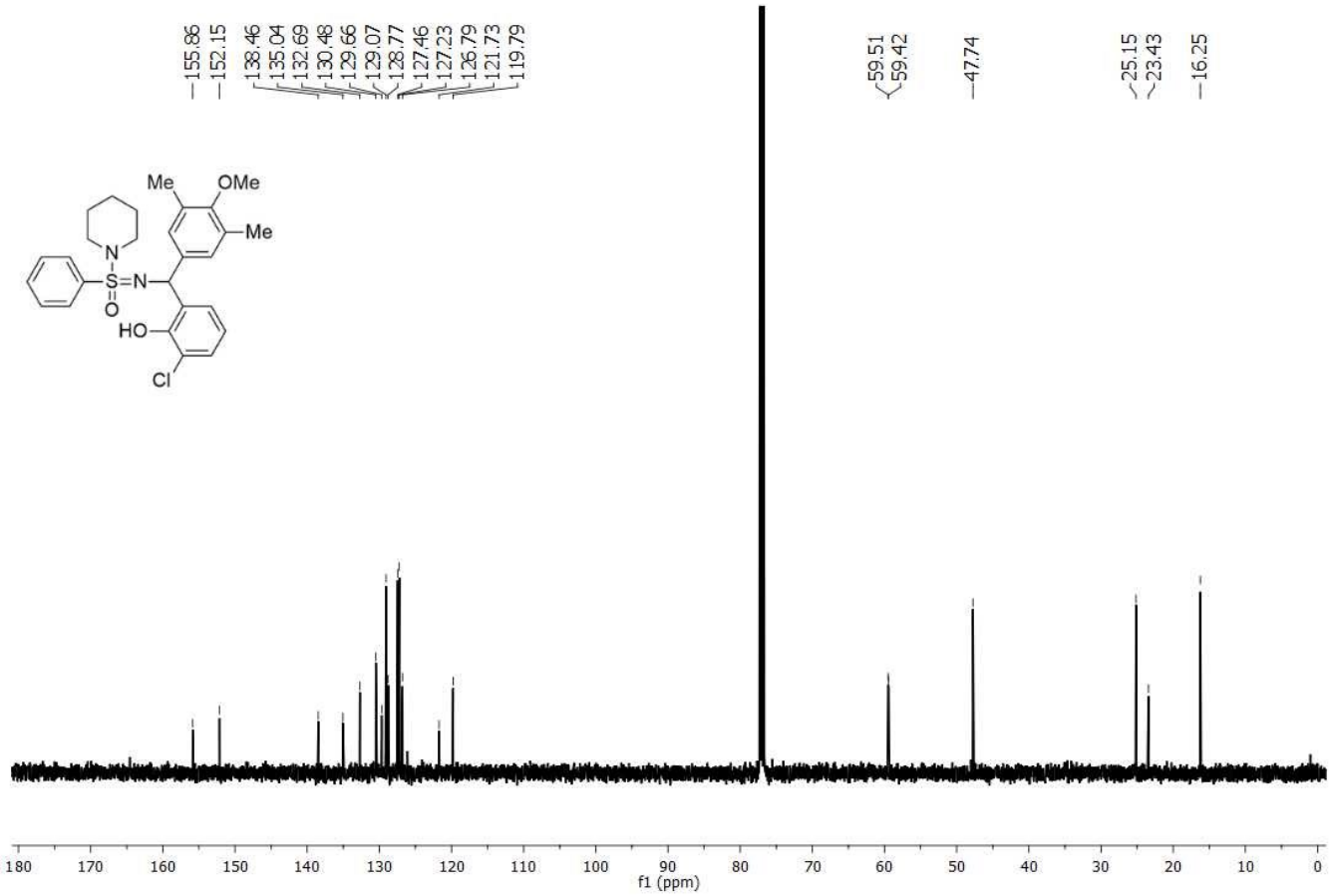
^{13}C {^{1}H} NMR of **6j** (Diastereomer-1, able to purify only one diastereomer)



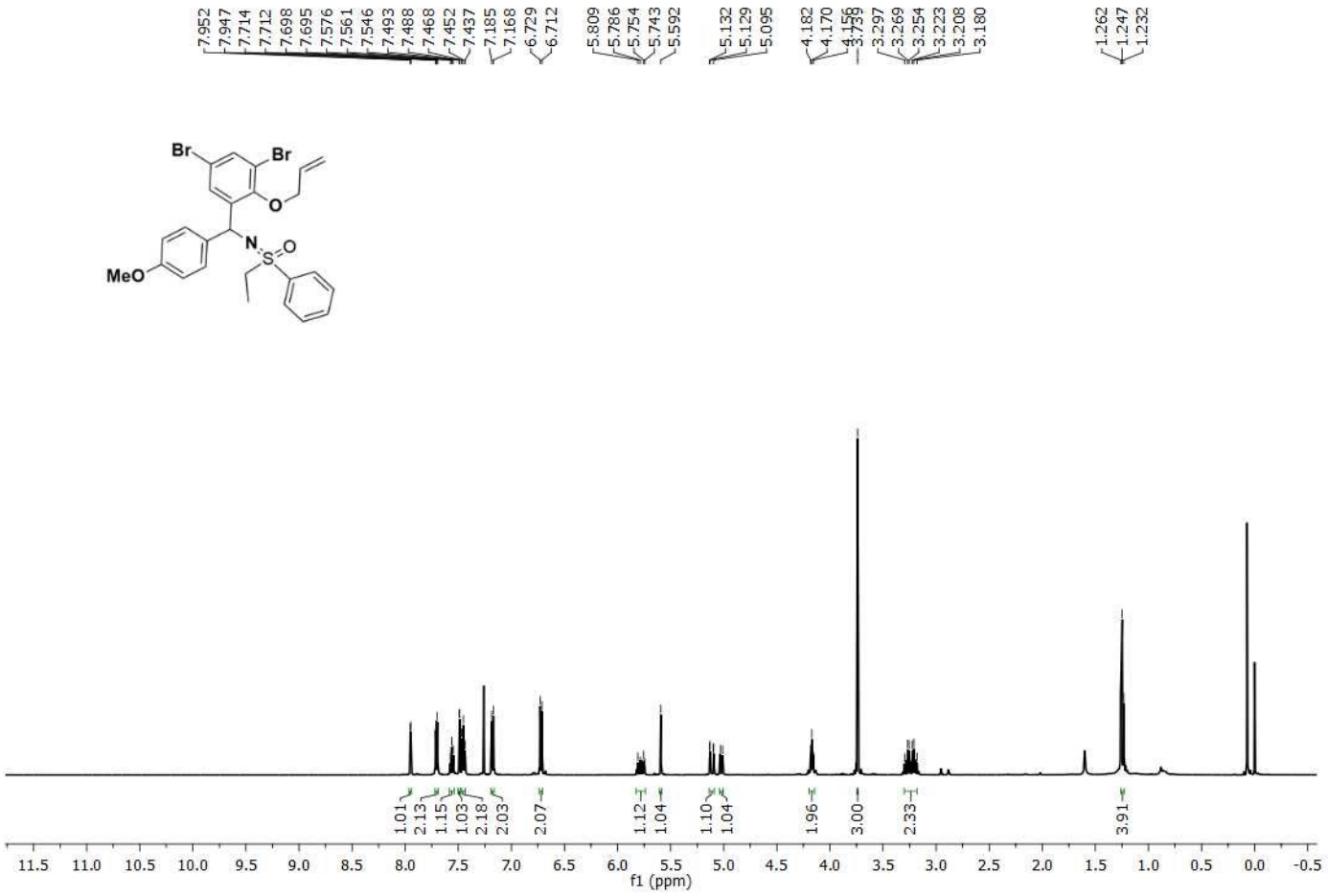
^{1}H NMR of **6k** (Diastereomer-1, able to purify only one diastereomer)



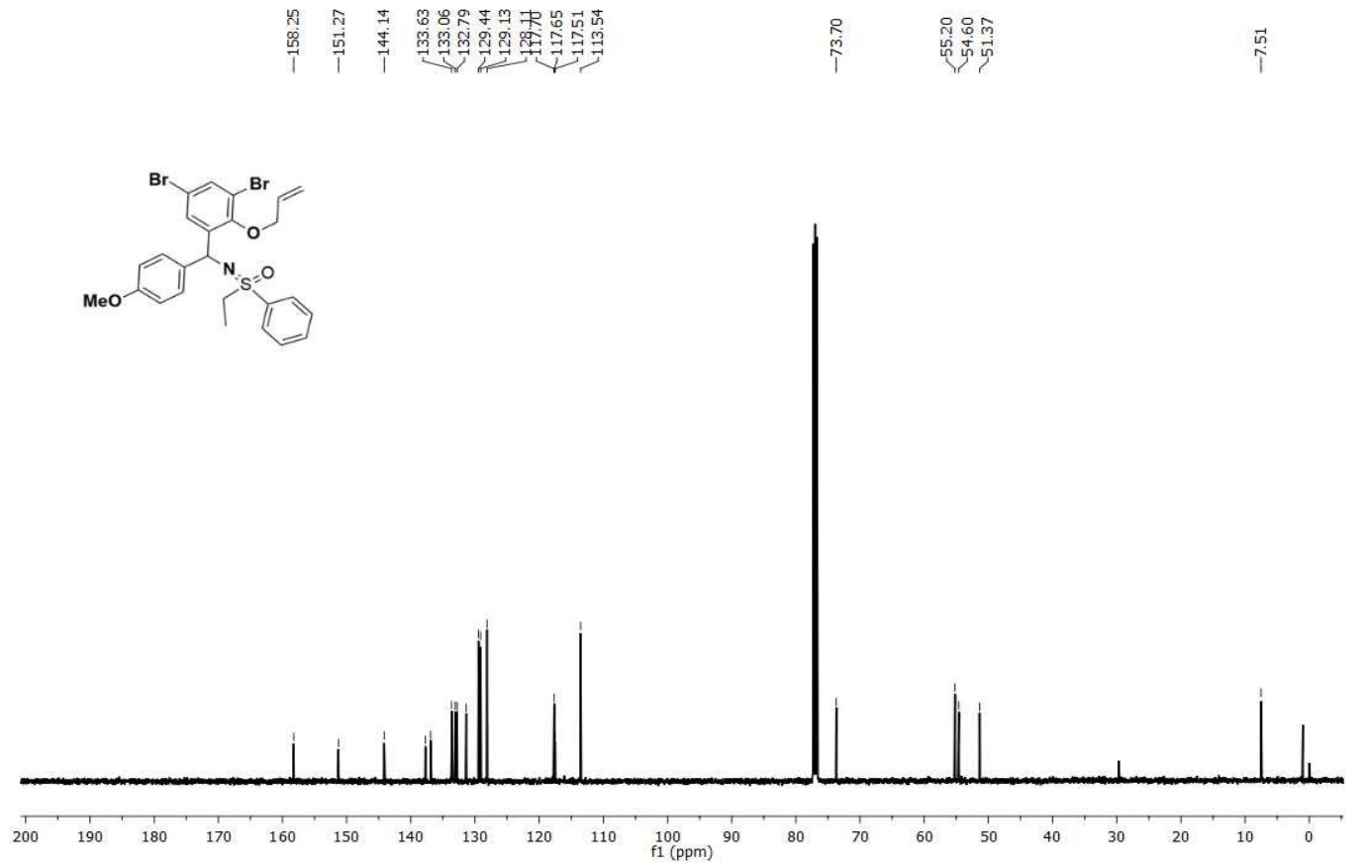
^{13}C {^{1}H} NMR of **6k** (Diastereomer-1, able to purify only one diastereomer)



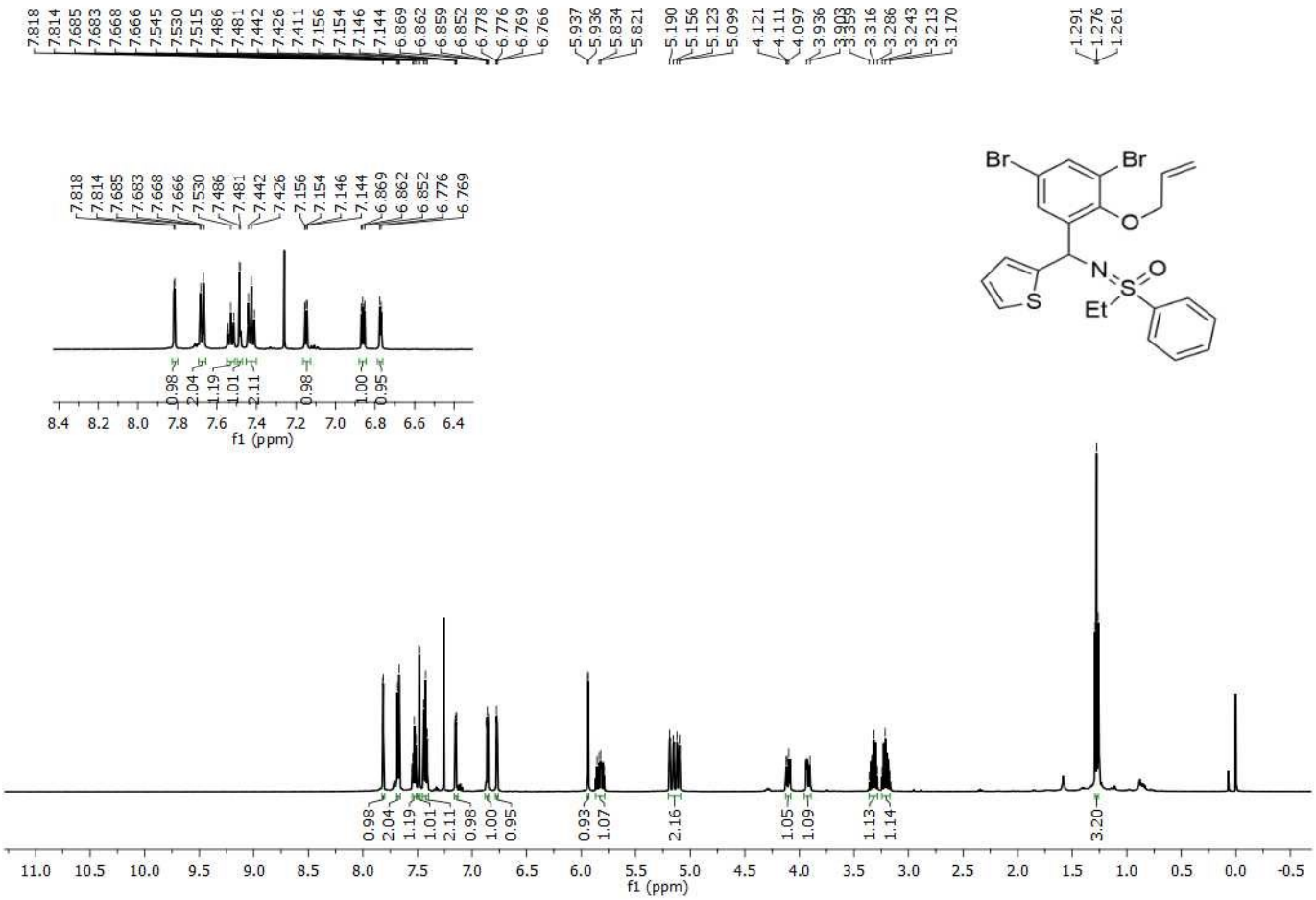
^{1}H NMR of **7a**



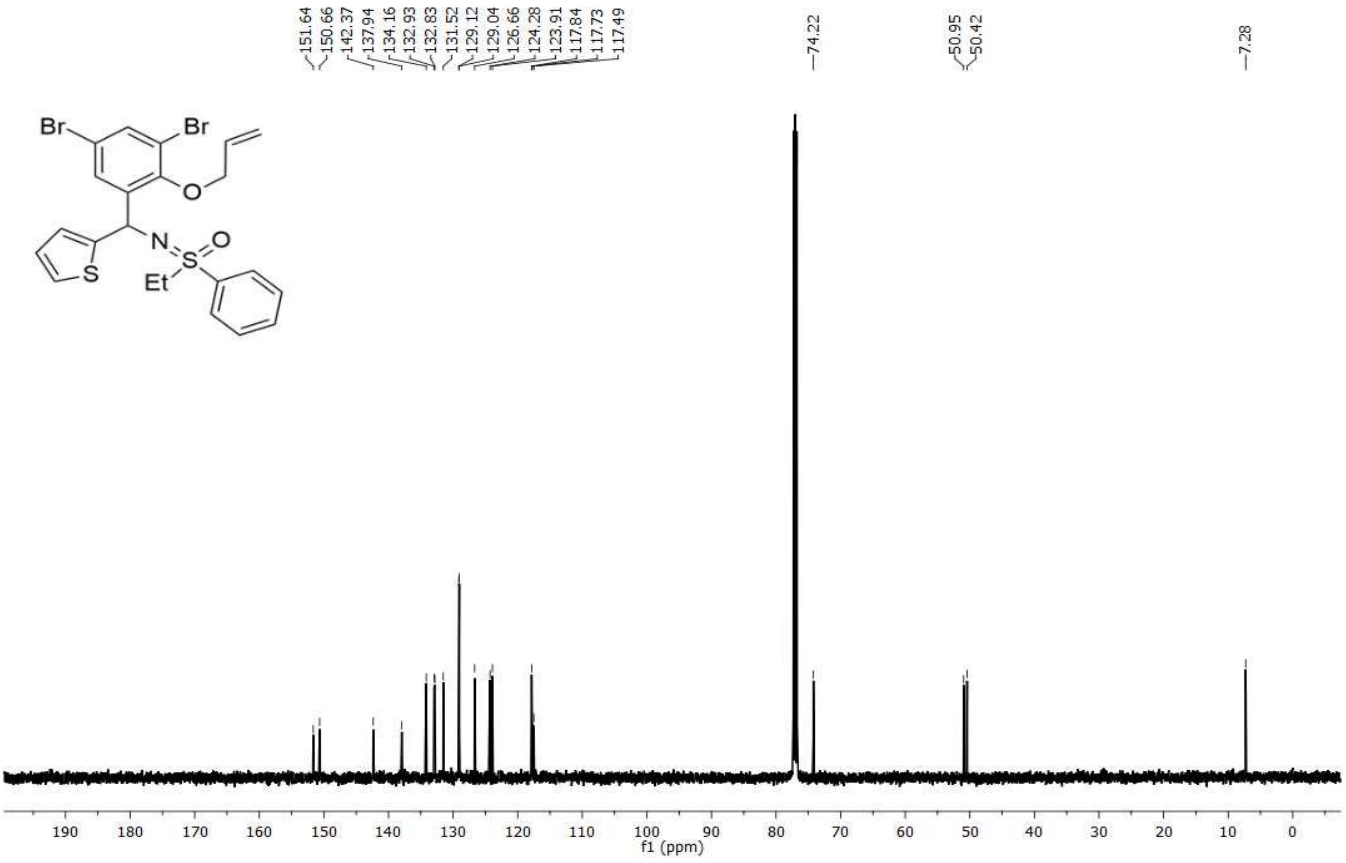
^{13}C {^{1}H} NMR of **7a**



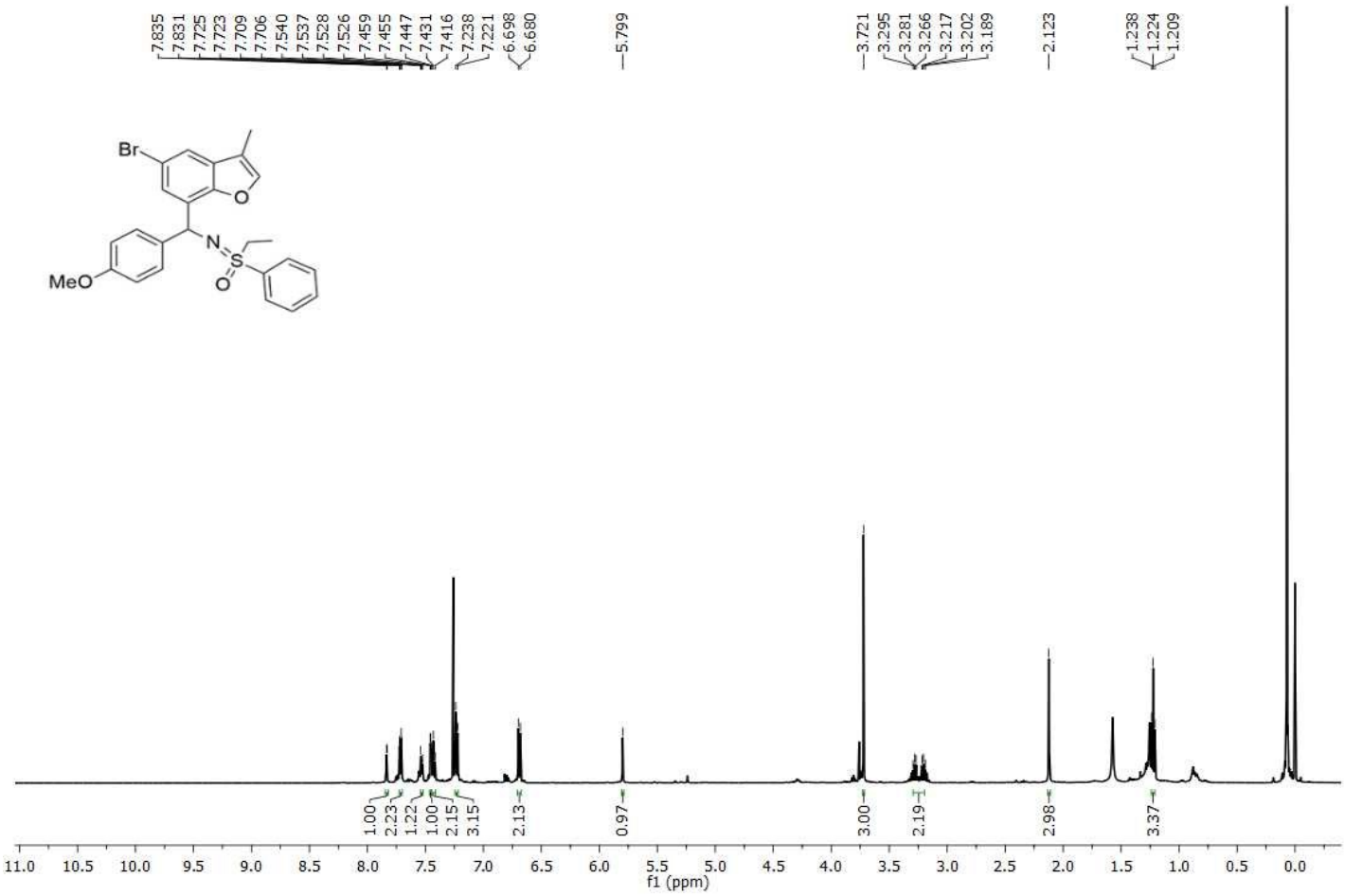
^{1}H NMR of **7b**



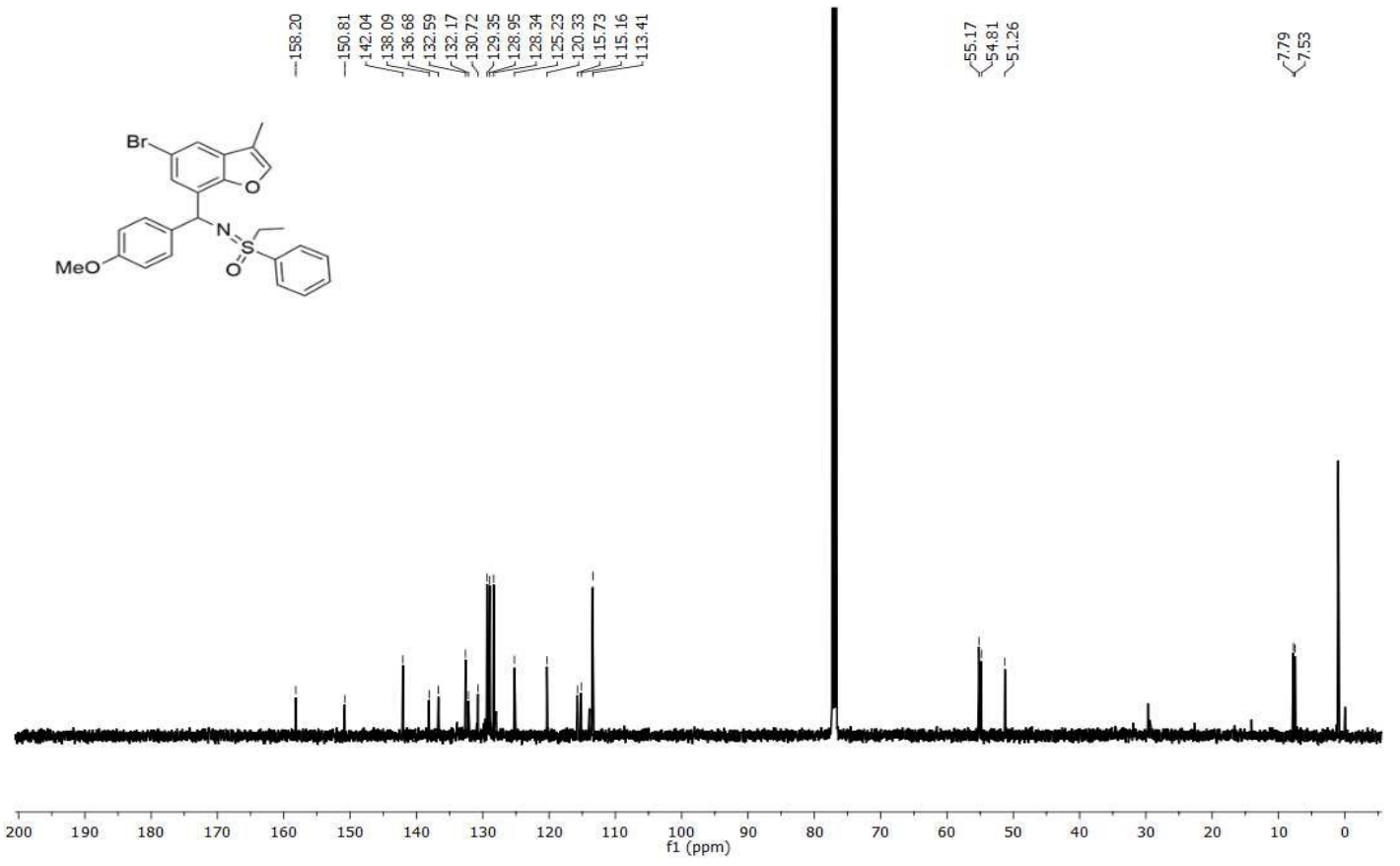
^{13}C {^{1}H} NMR of **7b**



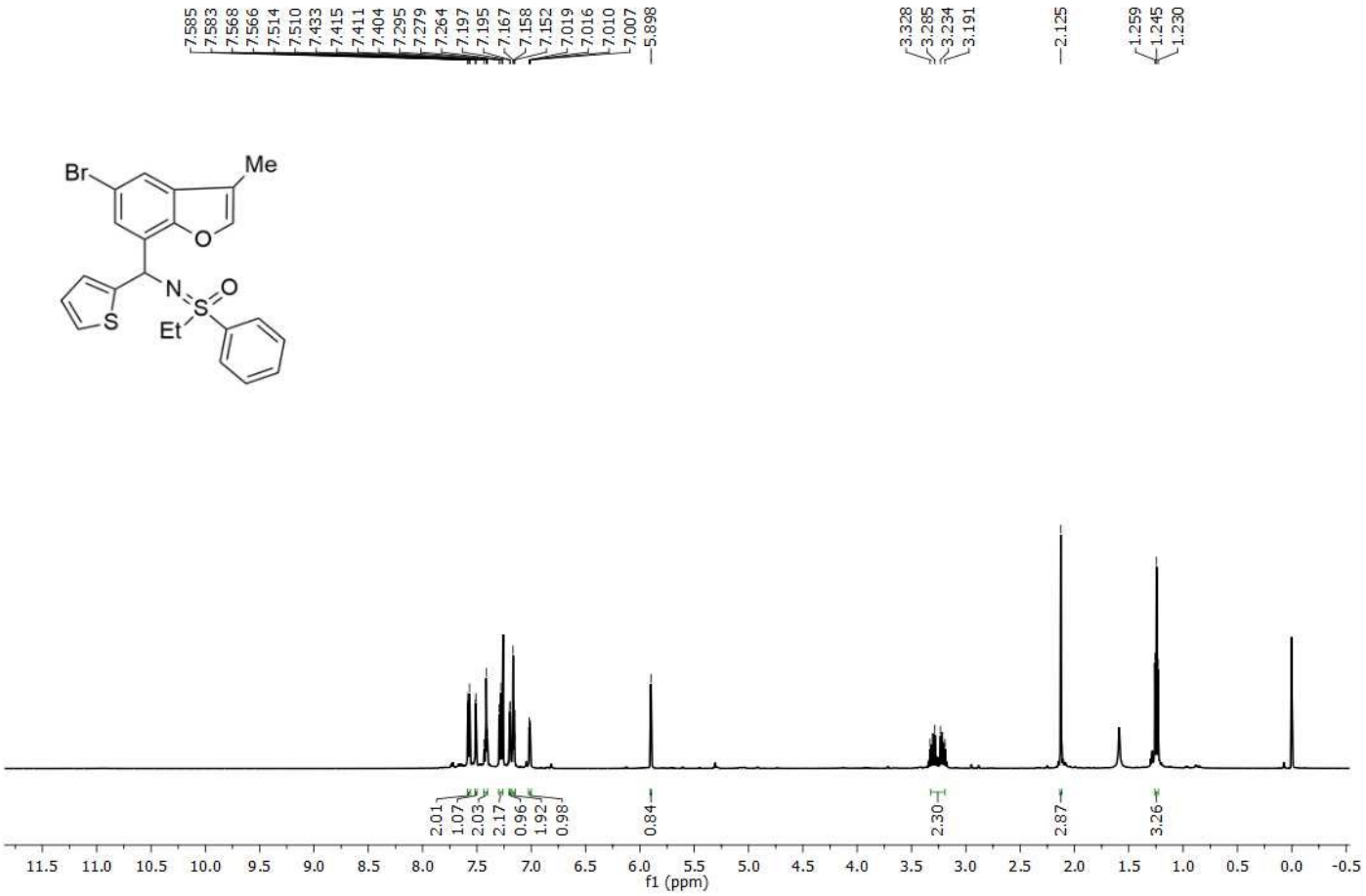
^{1}H NMR of **8a**



^{13}C {^{1}H} NMR of **8a**



^{1}H NMR of **8b**



^{13}C {^{1}H} NMR of **8b**