Electronic Supplementary Material (ESI) for RSC Advances.

Highly efficient microwave synthesis of rhodanine and 2-thiohydantoin derivatives and determination of relationships between their chemical structures and antibacterial activity

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Electronic Supplementary Information

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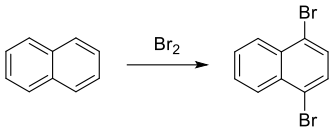
1,4-dibromonaphthalene



A solution of naphthalene (8.97 g, 70.0 mmol) in 70 mL of DCM in round-bottom reactor was vigorously stirred and cooled to -15 °C in a cryostat. Next, bromine (33.6 g, 10.77 mL, 208.0 mmol) was added dropwise not to overcome -10 °C. The mixture was stirred at -10 °C for 24 h. Then, reaction progress was analyzed by GC-MS technique, resulting in 73% of desired product among other bromonaphthalenes, based on chromatogram integration. The excess of bromine was quenched with sodium thiosulfate and sodium hydroxide aqueous solution. The organic layer was washed 3 times with water, dried with anhydrous magnesium sulfate and filtered. All volatiles were removed under reduced pressure, the residue was adsorbed on celite and loaded into a Biotage samplet. The product purified by column chromatography using hexanes as eluent. The fractions containing over 90 % of the desired product were collected and concentrated. The residue was recrystallized form hexanes giving pure product as colorless needles (8.4 g, 29.4 mmol). Yield: 42.0 %.

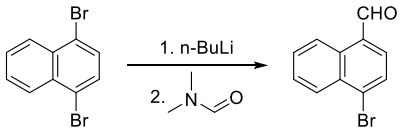
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 – 8.21 (m, 2H), 7.69 – 7.60 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.08, 130.20, 128.31, 127.92, 122.71.

MS (GC-LRMS): 288.0 (41.1 %), 286.0 (84.4 %), 283.9 (45.8 %), 207.1 (20.0 %), 205.0 (20.4 %), 126.0 (100.0 %), 74.0 (23.4 %), 63.0 (33.1 %).

Elemental analysis calculated (%) for $C_{10}H_6Br_2$: C 42.00, H 2.11. Found: C 42.05, H 2.12.

4-bromo-1-naphthalenecarbaldehyde



A three-necked 100 mL round-bottom flask equipped with thermometer, gas inlet and septum was loaded with 1,4-dibromonaphthalene (2.0 g, 6.99 mmol). The reaction set was evacuated and backfilled with argon three times. Next, 40 mL of anhydrous THF was added and the formed solution was cooled to -80 °C in dry ice – acetone bath. Subsequently, n-butyllithium (1.6 M in hexanes, 4.37 mL, 6.99 mmol) was added dropwise not to exceed -70 °C. After addition complete, the mixture was stirred at –80 °C for 1 h. Next, DMF (0.562 g, 0.596 mL, 7.69 mmol) was dropwise added not to exceed -70 °C. After addition, the mixture was stirred at -80 °C for 0.5 h, left to reach room temperature slowly and stirred further for 3 h. After reaction was complete, the volume of the mixture was reduced to approx. 1/5 under reduced pressure. The residue was dissolved in 20 mL of ethyl acetate and washed three times with 50 mL of water. The organic layer was evaporated to dryness, the residue was adsorbed on celite and loaded into a Biotage samplet. The product was purified by column chromatography with a gradient elution from 100 % hexanes to 20 % ethyl acetate : 80 % hexanes. Fractions containing the product were collected and concentrated under reduced pressure. The residue was recrystallized from hexanes giving pure product as colorless crystals. Yield: 54 %.

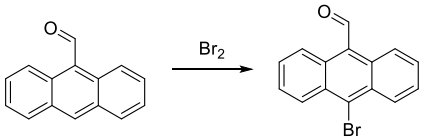
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.32 – 9.23 (m, 1H), 8.41 – 8.31 (m, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.65 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.79, 136.26, 132.31, 131.60, 131.49, 131.08, 129.95, 129.51, 128.44, 127.89, 125.28.

MS (GC-LRMS): 236.0 (32.1 %), 234.0 (26.9 %), 235.0 (20.6 %), 155.0 (20.0 %), 127.0 (77.5 %), 126.0 (100.0 %), 75.1 (22.3 %), 74.1 (22.3 %), 63.1 (25.5 %).

Elemental analysis calculated (%) for $C_{11}H_7BrO$: C 56.20, H 3.00. Found: C 56.27, H 3.01.

10-bromo-9-anthracenecarbaldehyde



9-anthracenecarbaldehyde (1.0 g, 4.7 mmol) was loaded to a round-bottom flask and dissolved in 30 mL of DCM. Subsequently, solution of bromine (0.759 g, 0.243 mL, 4.7 mmol) was added under stirring. The formed mixture was refluxed to the disappearance of bromine vapors (approx. 2 h). At this stage the reaction mixture was analyzed by GC-MS technique and if substrate was present, the additional amount of bromine was added (calculated with 1 : 1 molar ratio to the residual substrate which amount was estimated on the basis of chromatogram integration) and the mixture was refluxed once again to the bromine

vapors disappearance. After reaction complete, the solvent was evaporated under reduced pressure. The residual was adsorbed on celite and loaded into a Biotage samplet. The product was purified by column chromatography, starting with 10 % DCM : 90 % hexanes elution to remove 9,10-dibromoanthracene side-product and then eluent composition was gradient changed to 70 % DCM : 30 % hexanes to elute the product. The fractions containing the product were concentrated under reduced pressure and the residue was recrystallized from hexane giving the product as yellow needles (0.85 g, 2.98 mmol). Yield: 63 %.

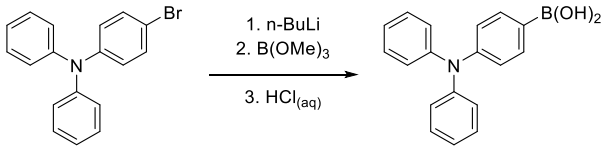
^{1}H NMR (300 MHz, $CDCl_3$) δ 11.42 (s, 1H), 8.88 – 8.77 (m, 2H), 8.66 – 8.55 (m, 2H), 7.63 (ddt, *J* = 10.2, 6.6, 3.4 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.33, 131.95, 131.88, 130.29, 129.08, 128.95, 127.46, 125.68, 123.90.

MS (GC-LRMS): 286.1 (32.5 %), 284.1 (33.2 %), 205.2 (36.2 %), 177.2 (57.8 %), 176.1 (100.0 %), 175.1 (20.8 %), 150.1 (31.2 %), 88.2 (42.1 %).

Elemental analysis calculated (%) for $C_{15}H_9BrO$: C 63.18, H 3.18. Found: C 63.25, H 3.20.

4-(diphenylamino)phenylboronic acid



A three-necked 100 mL round-bottom flask equipped with thermometer, gas inlet and septum was loaded with 4-bromo-*N*,*N*-diphenylaniline (8.0 g, 24.68 mmol). The reaction set was evacuated and backfilled with argon three times. Next, 40 mL of anhydrous THF was added and the formed solution was cooled to -80 °C in dry ice – acetone bath. Subsequently, n-butyllithium (1.6 M in hexanes, 18.5 mL, 29.6 mmol) was added dropwise not to exceed -70 °C. After addition complete, the mixture was stirred at –80 °C for 1 h. Next, the mixture was cooled to -90 °C and trimethyl borate (3.11 g, 3.33 mL, 29.6 mmol) was added in a one shot. After addition, the mixture was stirred at -80 °C for 2 h and then left to reach room temperature overnight. The volume of the mixture was reduced to approx. 1/3 under reduced pressure and acidified to pH = 5-6 with 5 % aqueous HCl. The product was extracted with 100 mL of DCM. The organic phase was washed 3 times with 50 mL of water and dried with anhydrous sodium sulfate and filtered. The resulting solution was concentrated under reduced pressure and the residue was washed with hexanes. The product was obtained as a white powder (5.5 g, 19.02 mmol). Yield: 77 %.

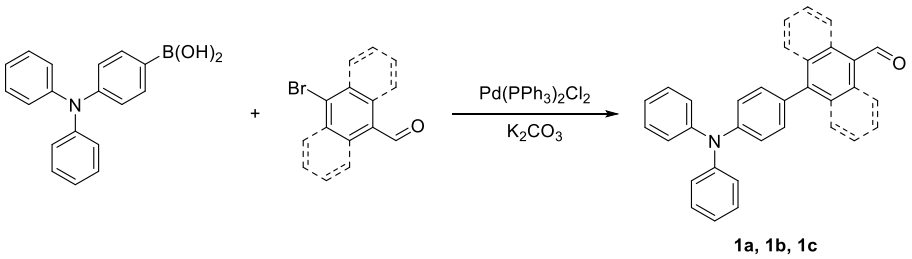
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90 (s, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 4H), 7.08 – 6.96 (m, 6H), 6.88 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 149.08, 147.09, 135.55, 129.68, 124.51, 123.47, 121.37.

MS (ESI-HRMS): calculated for $[C_{19}H_{19}BNO_2]^+$ (monomethyl ester) 304.1507, measured 304.1530 (error 7.6 ppm).

Elemental analysis calculated (%) for $C_{18}H_{16B}NO_2$: C 74.77, H 5.58, N 4.84. Found: C 74.80, H 5.60, N 4.83.

General procedure for the synthesis of 1a, 1b and 1c

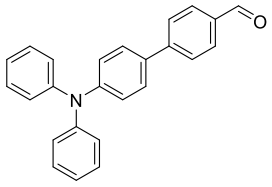


1a, 1b, 1c

A 100 mL Schlenk flask was loaded with 4-(diphenylamino)phenylboronic acid, aryl bromoaldehyde and dichlorobis(triphenylophosphine)palladium(II). Subsequently, the flask was evacuated and backfilled with argon three times. Next, toluene, ethanol and deoxygenated aqueous potassium carbonate solution was added. The reaction mixture was vigorously stirred at 90 °C for 6 h. After complete consumption of bromoaldehyde confirmed by GC-MS, the volume of the organic phase was almost completely reduced under reduced pressure. Then, 20 mL of DCM was added and water phase was removed. The organic phase was washed three times with 50 mL of water and evaporated to dryness under reduced pressure. The residue was adsorbed on celite and loaded into a Biotage samplet. The product was purified by column chromatography using gradient elution from 100 % hexanes to 60 % DCM : 40 % hexanes. The fractions containing desired product were collected and concentrated under reduced pressure. The residue was recrystallized by slow evaporation from DCM : hexanes and subsequently washed twice with pentane.

4'-(diphenylamino)-[1,1'-biphenyl]-4-carbaldehyde (1a)

Synthetic procedures and analytical data



1a

The product was synthesized according to the general procedure, using the following substances: 4-(diphenylamino)phenylboronic acid (1.272 g, 4.40 mmol), 4-bromobenzaldehyde (0.74 g, 4.0 mmol), dichlorobis(triphenylophosphine)palladium(II) (28.0 mg, 0.04 mmol), 2M potassium carbonate aqueous solution (11.99 mL, 23.96 mmol), 23 mL of toluene 7.6 mL of ethanol. The product was obtained as yellow needles (1.36 g, 3.90 mmol). Yield: 90 %.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 10.02 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.23 (m, 4H), 7.18 – 7.02 (m, 8H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 192.20, 149.00, 147.93, 146.97, 135.40, 133.30, 130.72, 129.95, 128.54, 127.39, 125.45, 124.05, 123.57.

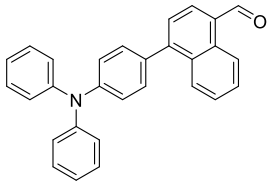
IR (ATR, ν_{max}, cm^{-1}): 1690 (C=O).

MS (DEP-LRMS): 350.3 (28.0 %), 349.2 (100.0 %).

MS (ESI-HRMS): calculated for $[C_{25}H_{20}NO]^+$ 350.1539, measured 350.1565 (error 7.4 ppm).

Elemental analysis calculated (%) for $C_{25}H_{19}NO$: C 85.93, H 5.48, N 4.01. Found: C 85.98, H 5.49, N 4.00.

4-(4-(diphenylamino)phenyl)-1-naphthalenecarbaldehyde (1b)



1b

The product was synthesized according to the general procedure, using the following substances: 4-(diphenylamino)phenylboronic acid (1.178 g, 4.08 mmol), 4-bromo-1-naphthalenecarbaldehyde (0.871 g, 3.71 mmol), dichlorobis(triphenylophosphine)palladium(II) (26.0 mg, 0.037 mmol), 2M potassium carbonate aqueous solution (11.12 mL, 23.96 mmol), 22 mL of toluene 7 mL of ethanol. The product was obtained as yellow powder (1.05 g, 2.63 mmol). Yield: 71 %.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 10.40 (s, 1H), 9.34 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 6.9 Hz, 1H), 7.65 – 7.53 (m, 2H), 7.42 – 7.26 (m, 6H), 7.24 – 7.14 (m, 6H), 7.09 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 193.74, 148.51, 148.11, 147.70, 136.88, 133.82, 132.56, 131.73, 131.30, 130.85, 129.95, 129.25, 127.40, 127.36, 126.60, 125.48, 125.37, 123.92, 123.28.

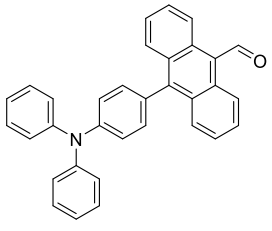
IR (ATR, ν_{max}, cm^{-1}): 1680 (C=O).

MS (DEP-LRMS): 400.3 (31.4 %), 399.3 (100 %).

MS (ESI-HRMS): calculated for $[C_{29}H_{22}NO]^+$ 400.1696, measured 400.1728 (error 8.0 ppm).

Elemental analysis calculated (%) for $C_{29}H_{21}NO$: C 87.19, H 5.30, N 3.51. Found: C 87.25, H 5.32, N 3.49.

10-(4-(diphenylamino)phenyl)anthracene-9-carbaldehyde (1c)



1c

The product was synthesized according to the general procedure, using the following substances: 4-(diphenylamino)phenylboronic acid (0.829 g, 2.87 mmol), 10-bromo-9-anthracenecarbaldehyde (0.743 g, 2.61 mmol),

dichlorobis(triphenylophosphine)palladium(II) (18.0 mg, 0.026 mmol), 2M potassium carbonate aqueous solution(7.82 mL, 15.63 mmol), 15 mL of toluene 5 mL of ethanol. The product was obtained as orange powder (1.06g, 2.36 mmol). Yield: 90 %.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 11.55 (s, 1H), 9.00 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.73 – 7.62 (m, 2H), 7.53 – 7.42 (m, 2H), 7.41 – 7.31 (m, 4H), 7.30 – 7.22 (m, 8H), 7.10 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 193.79, 148.32, 148.20, 146.06, 132.20, 132.09, 132.01, 130.68, 129.98, 129.08, 128.67, 125.98, 125.53, 125.36, 124.00, 123.90, 123.29.

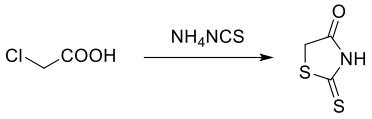
IR (ATR, ν_{max}, cm^{-1}): 1664 (C=O).

MS (DEP-LRMS): 450.3 (36.2 %), 449.3 (100.0 %).

MS (ESI-HRMS): calculated for $[C_{33}H_{24}NO]^+$ 450.1852, measured 400.1876 (error 5.3 ppm).

Elemental analysis calculated (%) for $C_{33}H_{23}NO$: C 88.17, H 5.16, N 3.12. Found: C 88.23, H 5.18, N 3.10.

Rhodanine (2a)



2a

A solution of chloroacetic acid (23.62 g, 0.25 mol) and ammonium thiocyanate (38.06 g, 0.50 mol) in 150 mL of water was heated for 20 minutes under reflux. After cooling down, a precipitate was formed. The crude product was filtered and recrystallized from water. The product was obtained as a yellowish powder (14.96 g, 0.113 mol), yield: 45 %.

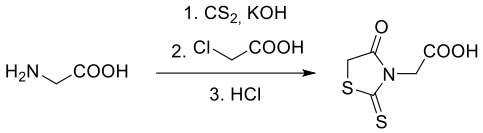
^{1}H NMR (300 MHz, DMSO-d_6) δ 13.14 (s, 1H), 4.26 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 205.43, 176.81, 39.42.

MS (ESI-HRMS): calculated for $[C_3H_2NOS_2]^-$ 131.9583, measured 131.9572 (error 8.3 ppm).

Elemental analysis calculated (%) for $C_3H_3NOS_2$: C 27.06, H 2.27, N 10.52, S 48.14. Found: C 27.09, H 2.28, N 10.55, S 48.16.

Rhodanine-3-acetic acid (2b)



2b

A solution of potassium hydroxide (28.00 g, 0.5 mol) in 100 mL of water was added to the suspension of aminoethanoic acid (18.75 g, 0.25 mol). The resulting solution was cooled to 5 °C and carbon disulfide (19.03 g, 0.25 mol) was added. The content of the flask was mixed at 5 °C for 6 h. The cooling bath was removed and mixing was continued at room temperature for 20 h. Then, a solution of chloroacetic acid (23.62 g, 0.25 mol) in 100 mL of water was added. The reaction mixture was stirred for 8 h at the temperature below 15°C. Next, a mixture of 150 mL concentrated hydrochloric acid and 200 mL of water was added slowly. The resulting mixture was heated at 90°C for 25 min. After cooling down, a precipitate was formed, which was next filtered and recrystallized from water. The product was obtained as a white crystalline solid (21.49 g, 0.275 mol), yield: 55 %.

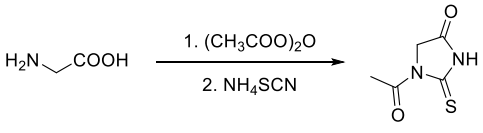
^{1}H NMR (300 MHz, DMSO-d_6) δ 4.55 (s, 2H), 4.40 (s, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 202.96, 173.88, 167.47, 44.90, 36.08.

MS (ESI-HRMS): calculated for $[C_5H_4NO_3S_2]^-$ 189.9638, measured 189.9625 (error 6.8 ppm).

Elemental analysis calculated (%) for $C_5H_5NOS_2$: C 31.41, H 2.64, N 7.33, S 33.53. Found: C 31.47, H 2.65, N 7.35, S 33.60.

1-acetyl-2-thiohydantoin (3a)



3a

A flask containing a mixture of aminoethanoic acid (37.5 g, 0.5 mol), ammonium thiocyanate (38.06 g, 0.5 mol), 150 mL of acetic anhydride and 15 mL of acetic acid was heated in a water bath at 110 ºC for 30 minutes under reflux. Next, the flask was

cooled to 60 °C and heated again at 100 °C for 15 minutes. Then, the reaction mixture was poured into a beaker containing 1000 mL of cold water. The resulting precipitate was filtered and recrystallized from acetic acid. The product was obtained as a brown crystalline solid (55.3 g, 0.35 mol), yield: 70 %.

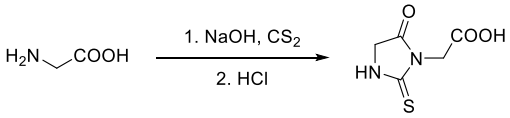
^{1}H NMR (300 MHz, DMSO-d_6) δ 12.58 (s, 1H), 4.39 (s, 2H), 2.67 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 182.57, 170.46, 169.44, 52.26, 26.70, 26.67.

MS (ESI-HRMS): calculated for $[C_5H_5N_2O_2S]^-$ 157.0077, measured 157.0052 (error 15.9 ppm).

Elemental analysis calculated (%) for $C_5H_6N_2O_2S$: C 37.97, H 3.82, N 17.71, S 20.27. Found: C 37.95, H 3.80, N 17.75, S 20.30.

2-thiohydantoin-3-acetic acid (3b)



3b

A solution of sodium hydroxide (12.0 g, 0.3 mol) was added to a well stirred suspension of aminoethanoic acid (18.75 g, 0.25 mol) in 20 mL of water. To the resulting solution carbon disulfide (11.42 g, 0.15 mol) was added under nitrogen atmosphere and the reaction mixture was refluxed for 8 h. After the heating was finished, the excess of carbon disulfide was evaporated on a rotary evaporator. Next, a mixture of 100 mL of concentrated hydrochloric acid and 200 mL of water was added. The resulting mixture was refluxed for 2 h. After cooling, a precipitate was formed, which was filtered and subsequently recrystallized from water. The product was obtained as a white crystalline solid (39.15 g, 0.225 mol), yield: 75 %.

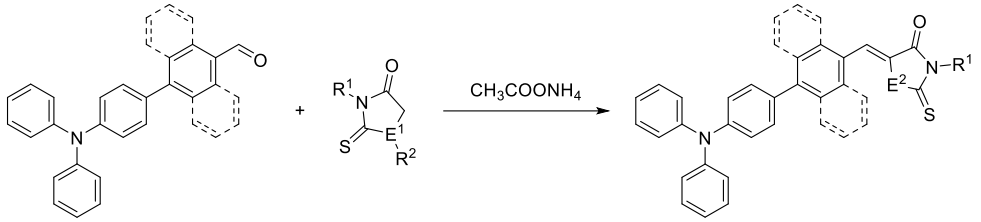
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.34 (s, 1H), 4.34 (s, 2H), 4.23 (d, J = 1.3 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 182.87, 172.27, 168.44, 48.64, 41.47.

MS (ESI-HRMS): calculated for $[C_5H_5N_2O_3S]^-$ 173.0026, measured 173.0008 (error 10.4 ppm).

Elemental analysis calculated (%) for $C_7H_{11}N_3O_5S$: C 33.73, H 4.45, N 16.86, S 12.86. Found: C 33.75, H 4.47, N 16.90, S 12.88.

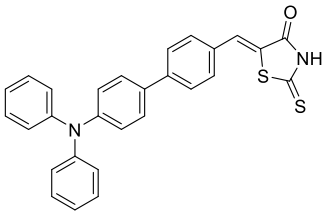
General procedure for the synthesis of 4a – 7c



E^1 = N, S; E^2 = NH, S; R^1 = H, CH_2COOH; R^2 = H, $COCH_3$ **4a - 7c**

4-bromo-1-benzaldehyde (0.1 g, 0.286 mmol), **4-bromo-1-naphthalenecarbaldehyde** (0.114 g, 0.286 mmol) or **10-bromo-9-anthracenecarbaldehyde** (0.129 g, 0.286 mmol), respective rhodanine (0.046 g, 0.343 mmol), rhodanine-3-acetic acid (0.066 g, 0.343 mmol), 1-acetyl-2-thiohydantoin (0.054 g, 0.343 mmol) or 2-thiohydantoin-3-acetic acid (0.06 g, 0.343 mmol) and ammonium acetate (44 mg, 0.57 mmol) were added to a CEM microwave vial. Subsequently, 2 mL of AA was added and the vessel was closed with a cap. The mixture was heated with maximum power 200 W at 180 °C for 5-7 min (5 min for **4-bromo-1-benzaldehyde**, 6 min for **4-bromo-1-naphthalenecarbaldehyde** and 7 min for **10-bromo-9-anthracenecarbaldehyde**). During heating the color of the mixtures turned red very quickly and became homogenous. After cooling back to room temperature the precipitate was formed (some products tended to form supercooled solutions, in that case precipitation was initiated by ultrasonification). The solid was centrifuged and the supernatant was sucked off with a syringe. The solid was washed with 1 mL of AA and 4 times with 4 mL portions of water in the same manner. The obtained product was dried in an oven at 110 °C overnight. In some cases the product was purified by subsequent recrystallization from 2-propanol.

(*Z*)-5-((4'-(diphenylamino)-(1,1'-biphenyl)-4-yl)methylene)-2-thioxothiazolidin-4-one (4a)



4a

Brick-red crystalline solid (128 mg, 0.276 mmol). Yield: 96 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.79 (d, J = 8.2 Hz, 2H), 7.71 – 7.55 (m, 5H), 7.33 (t, J = 7.8 Hz, 4H), 7.14 – 6.95 (m, 8H).

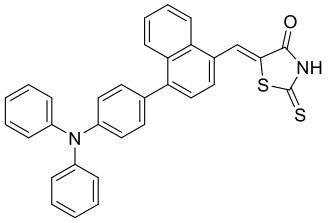
^{13}C NMR (75 MHz, DMSO-d_6) δ 195.64, 169.62, 147.75, 146.89, 141.66, 132.02, 131.50, 131.42, 129.84, 127.94, 126.90, 124.86, 124.72, 123.82, 122.64.

IR (ATR, ν_{max}, cm^{-1}): 1689 (C=O), 1068 (C=S).

MS (ESI-HRMS): calculated for $[C_{28}H_{19}N_2OS_2]^-$ 463.0944, measured 463.0947 (error 0.6 ppm).

Elemental analysis calculated (%) for $C_{28}H_{20}N_2OS_2$: C 72.39, H 4.34, N 6.03, S 13.80. Found: C 72.37, H 4.34, N 6.05, S 13.79.

(*Z*)-5-((4-(4-(diphenylamino)phenyl)naphthalen-1-yl)methylene)-2-thioxothiazolidin-4-one (4b)



4b

Dark-brown crystalline solid (139 mg, 0.270 mmol). Yield: 94 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.75 – 7.53 (m, 4H), 7.45 – 7.30 (m, 6H), 7.18 – 7.04 (m, 8H).

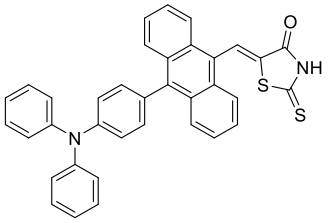
^{13}C NMR (151 MHz, DMSO-d_6) δ 196.17, 168.97, 147.16, 146.97, 142.33, 132.77, 131.66, 131.19, 130.85, 129.75, 129.34, 128.60, 128.17, 127.52, 127.17, 126.68, 126.63, 126.57, 124.58, 123.93, 123.60, 122.26.

IR (ATR, ν_{max}, cm^{-1}): 1683 (C=O), 1073 (C=S).

MS (ESI-HRMS): calculated for $[C_{32}H_{21}N_2OS_2]^-$ 513.1101, measured 513.1103 (error 0.4 ppm).

Elemental analysis calculated (%) for $C_{32}H_{22}N_2OS_2$: C 74.68, H 4.31, N 5.44, S 12.46. Found: C 74.65, H 4.29, N 5.45, S 12.44.

(*Z*)-5-((10-(4-(diphenylamino)phenyl)anthracen-9-yl)methylene)-2-thioxothiazolidin-4-one (4c)



4c

Orange powder (145 mg, 0.257 mmol). Yield: 90 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.10 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.68 – 7.58 (m, 2H), 7.58 – 7.47 (m, 2H), 7.39 (t, J = 7.9 Hz, 4H), 7.30 (d, J = 8.5 Hz, 2H), 7.24 – 7.08 (m, 8H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 147.24, 132.02, 129.97, 129.56, 127.88, 127.42, 127.04, 126.27, 125.58, 124.76, 124.70, 123.78, 122.36.

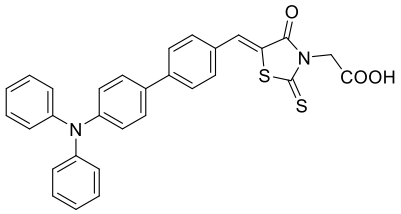
IR (ATR, ν_{max}, cm^{-1}): 1734 (C=O), 1068 (C=S).

MS (ESI-HRMS): calculated for $[C_{36}H_{23}N_2OS_2]^-$ 563.1257, measured 563.1259 (error 0.4 pm).

Elemental analysis calculated (%) for $C_{36}H_{24}N_2OS_2$: C 76.57, H 4.28, N 4.96, S 11.35. Found: C 76.60, H 4.29, N 4.95, S 11.35.

Synthetic procedures and analytical data

(*Z*)-2-(5-((4'-(diphenylamino)-(1,1'-biphenyl)-4-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (5a)



5a

Red powder (140 mg, 0.268 mmol). Yield: 94 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.70 (dd, *J* = 8.5, 6.3 Hz, 4H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.15 – 7.04 (m, 6H), 7.02 (d, *J* = 8.6 Hz, 2H), 4.74 (s, 2H).

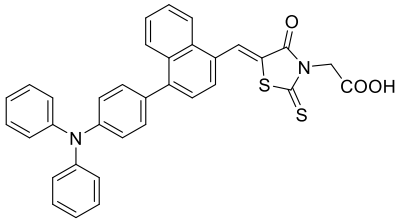
^{13}C NMR (151 MHz, DMSO) δ 193.21, 167.49, 166.56, 147.89, 146.88, 142.17, 133.79, 131.89, 131.76, 131.28, 129.87, 128.01, 127.01, 124.80, 123.90, 122.56, 121.12, 45.19.

IR (ATR, ν_{max}, cm^{-1}): 1722 (C=O), 1701 (C=O), 1056 (C=S).

MS (ESI-HRMS): calculated for $[C_{30}H_{21}N_2O_3S_2]^-$ 521.0999, measured 521.0994 (error 1.0 ppm).

Elemental analysis calculated (%) for $C_{30}H_{22}N_2O_3S_2$: C 68.94, H 4.24, N 5.36, S 12.27. Found: C 68.99, H 4.23, N 5.34, S 12.28.

(*Z*)-2-(5-((4-(4-(diphenylamino)phenyl)naphthalen-1-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (5b)



5b

Orange crystalline solid (148 mg, 0.258 mmol). Yield: 90 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.55 (s, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.61 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.17 – 7.04 (m, 8H), 4.78 (s, 2H).

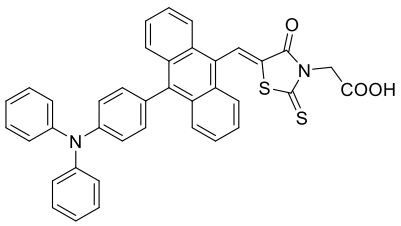
^{13}C NMR (151 MHz, DMSO-d_6) δ 193.84, 167.51, 166.03, 147.34, 147.06, 142.95, 132.76, 131.79, 131.32, 130.97, 130.73, 129.89, 129.21, 127.82, 127.41, 127.18, 126.79, 126.73, 124.95, 124.73, 124.09, 123.78, 122.29, 45.22.

IR (ATR, ν_{max}, cm^{-1}): 1725 (C=O), 1708 (C=O), 1062 (C=S).

MS (ESI-HRMS): calculated for $[C_{34}H_{23}N_2O_3S_2]^-$ 571.1156, measured 571.1137 (error 3.3 ppm).

Elemental analysis calculated (%) for $C_{34}H_{24}N_2O_3S_2$: C 71.31, H 4.22, N 4.89, S 11.20. Found: C 71.35, H 4.24, N 4.90, S 11.22.

(*Z*)-2-(5-((10-(4-(diphenylamino)phenyl)anthracen-9-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (5c)



5c

Red crystalline solid (159 mg, 0.255 mmol). Yield: 89 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.83 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.69 – 7.58 (m, 2H), 7.59 – 7.48 (m, 2H), 7.38 (t, *J* = 7.8 Hz, 4H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.07 (m, 8H), 4.79 (s, 2H).

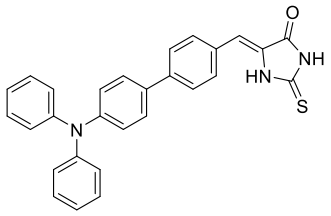
^{13}C NMR (151 MHz, DMSO-d_6) δ 193.63, 167.57, 165.05, 147.18, 139.73, 132.57, 131.94, 131.10, 130.85, 129.92, 129.53, 127.89, 127.51, 127.27, 126.99, 126.31, 125.30, 124.76, 123.75, 122.25, 45.29.

IR (ATR, ν_{max}, cm^{-1}): 1727 (C=O), 1713 (C=O), 1056 (C=S).

MS (ESI-HRMS): calculated for $[C_{38}H_{25}N_2O_3S_2]^-$ 621.1312, measured 621.1289 (error 3.7 ppm).

Elemental analysis calculated (%) for $C_{38}H_{26}N_2O_3S_2$: C 73.29, H 4.21, N 4.50, S 10.30. Found: C 73.27, H 4.20, N 4.51, S 10.32.

(*Z*)-5-((4'-(diphenylamino)-(1,1'-biphenyl)-4-yl)methylene)-2-thioxoimidazolidin-4-one (6a)



6a

Orange crystalline solid (92 mg, 0.206 mmol). Yield: 72 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.38 (s, 1H), 12.20 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 8.2 Hz, 4H), 7.33 (t, *J* = 7.8 Hz, 4H), 7.13 – 6.97 (m, 8H), 6.51 (s, 1H).

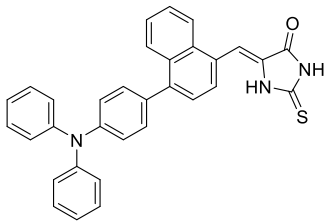
^{13}C NMR (151 MHz, DMSO-d_6) δ 179.17, 166.05, 147.45, 147.05, 140.32, 132.81, 131.06, 129.88, 127.83, 127.61, 126.46, 124.59, 123.73, 123.05, 111.63.

IR (ATR, ν_{max}, cm^{-1}): 1720 (C=O), 1080 (C=S).

MS (ESI-HRMS): calculated for $[C_{28}H_{20}N_3OS]^-$ 446.1333, measured 446.1321 (error 2.7 ppm).

Elemental analysis calculated (%) for $C_{28}H_{21}N_3OS$: C 75.14, H 4.73, N 9.39, S 7.16. Found: C 75.18, H 4.75, N 9.41, S 7.14.

(*Z*)-5-((4-(4-(diphenylamino)phenyl)naphthalen-1-yl)methylene)-2-thioxoimidazolidin-4-one (6b)



6b

Yellow crystalline solid (122 mg, 0.245 mmol). Yield: 86 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.34 (s, 2H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.53 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.17 – 7.05 (m, 9H).

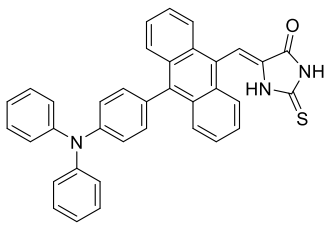
^{13}C NMR (151 MHz, DMSO-d_6) δ 130.99, 129.93, 124.64, 123.72.

IR (ATR, ν_{max}, cm^{-1}): 1714 (C=O), 1087 (C=S).

MS (ESI-HRMS): calculated for $[C_{32}H_{22}N_3OS]^-$ 496.1489, measured 496.1465 (error 4.8 ppm).

Elemental analysis calculated (%) for $C_{32}H_{23}N_3OS$: C 77.24, H 4.66, N 8.44, S 6.44. Found: C 77.27, H 4.68, N 8.46, S 6.43.

(*Z*)-5-((10-(4-(diphenylamino)phenyl)anthracen-9-yl)methylene)-2-thioxoimidazolidin-4-one (6c)



6c

The pure product was obtained after recrystallization from 2-propanol. Red crystalline solid (116 mg, 0.212 mmol). Yield: 74 %

Synthetic procedures and analytical data

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.37 (s, 1H), 11.67 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.46 (m, 4H), 7.46 – 7.35 (m, 4H), 7.34 – 7.25 (m, 3H), 7.22 (d, *J* = 7.1 Hz, 6H), 7.12 (t, *J* = 7.3 Hz, 2H).

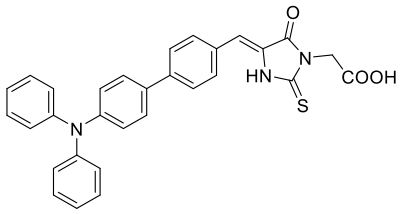
^{13}C NMR (151 MHz, DMSO-d_6) δ 179.13, 164.64, 147.15, 146.88, 137.76, 133.63, 131.86, 131.51, 129.79, 129.64, 129.08, 127.09, 126.77, 126.18, 125.85, 125.68, 124.57, 123.54, 122.38, 108.17.

IR (ATR, ν_{max}, cm^{-1}): 1742 (C=O), 1099 (C=S).

MS (ESI-HRMS): calculated for $[C_{36}H_{24}N_3OS]^-$ 546.1646, measured 546.1629 (error 3.1 ppm).

Elemental analysis calculated (%) for $C_{36}H_{25}N_3OS$: C 78.95, H 4.60, N 7.67, S 5.85. Found: C 78.93, H 4.58, N 7.65, S 5.86.

(*Z*)-2-(5-((4'-(diphenylamino)-(1,1'-biphenyl)-4-yl)methylene)-4-oxo-2-thioxoimidazolidin-3-yl)acetic acid (7a)



7a

Orange crystalline solid (122 mg, 0.241 mmol). Yield: 84 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.58 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 4H), 7.15 – 6.97 (m, 8H), 6.72 (s, 1H), 4.51 (s, 2H).

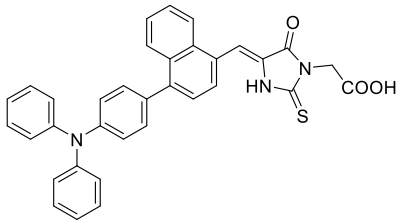
^{13}C NMR (151 MHz, DMSO-d_6) δ 178.26, 168.37, 163.78, 147.49, 147.00, 140.67, 132.65, 131.27, 130.76, 129.84, 127.84, 126.47, 125.72, 124.60, 124.58, 123.73, 122.93, 113.61, 41.97.

IR (ATR, ν_{max}, cm^{-1}): 1735 (C=O), 1647 (C=O), 1076 (C=S).

MS (ESI-HRMS): calculated for $[C_{30}H_{22}N_3O_3S]^-$ 504.1387, measured 504.1383 (error 0.8 ppm).

Elemental analysis calculated (%) for $C_{30}H_{23}N_3O_3S$: C 71.27, H 4.59, N 8.31, S 6.34. Found: C 71.30, H 4.60, N 8.29, S 6.35.

(*Z*)-2-(5-((4-(4-(diphenylamino)phenyl)naphthalen-1-yl)methylene)-4-oxo-2-thioxoimidazolidin-3-yl)acetic acid (7b)



7b

Yellow powder (135 mg, 0.243 mmol). Yield: 85 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.55 (m, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.29 (m, 7H), 7.17 – 7.05 (m, 8H), 4.54 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 178.48, 168.44, 163.38, 147.15, 147.09, 141.08, 133.36, 131.75, 131.19, 130.94, 129.88, 128.57, 128.37, 128.14, 127.25, 126.86, 126.73, 126.48, 124.63, 124.58, 124.38, 123.69, 123.64, 122.59, 122.53, 110.33, 42.00.

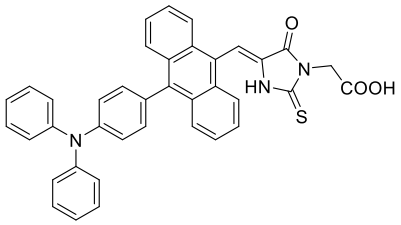
IR (ATR, ν_{max}, cm^{-1}): 1707 (C=O), 1649 (C=O), 1073 (C=S).

MS (ESI-HRMS): calculated for $[C_{34}H_{24}N_3O_3S]^-$ 554.1544, measured 554.1527 (error 3.1 ppm).

Elemental analysis calculated (%) for $C_{34}H_{25}N_3O_3S$: C 73.49, H 4.54, N 7.56, S 5.77. Found: C 73.53, H 4.55, N 7.54, S 5.78.

(*Z*)-2-(5-((10-(4-(diphenylamino)phenyl)anthracen-9-yl)methylene)-4-oxo-2-thioxoimidazolidin-3-yl)acetic acid (7c)

Synthetic procedures and analytical data



7c

The pure product was obtained after recrystallization from 2-propanol. Orange powder (128 mg, 0.211 mmol). Yield: 74 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.09 (s, 1H), 8.05 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.64 – 7.48 (m, 5H), 7.40 (t, J = 7.7 Hz, 4H), 7.33 – 7.26 (m, 2H), 7.25 – 7.17 (m, 6H), 7.12 (t, J = 7.3 Hz, 2H), 4.55 (s, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 178.29, 172.10, 168.35, 162.43, 147.16, 146.93, 138.11, 131.85, 131.81, 131.42, 129.81, 129.66, 129.09, 127.15, 126.36, 125.76, 125.69, 124.61, 123.58, 122.36, 110.38, 41.85.

IR (ATR, ν_{max}, cm^{-1}): 1718 (C=O), 1643 (C=O), 1075 (C=S).

MS (ESI-HRMS): calculated for $[C_{38}H_{26}N_3O_3S]^-$ 604.1700, measured 604.1692 (error 1.3 ppm).

Elemental analysis calculated (%) for $C_{38}H_{27}N_3O_3S$: C 75.35, H 4.49, N 6.94, S 5.29. Found: C 75.30, H 4.48, N 6.96, S 5.30.

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

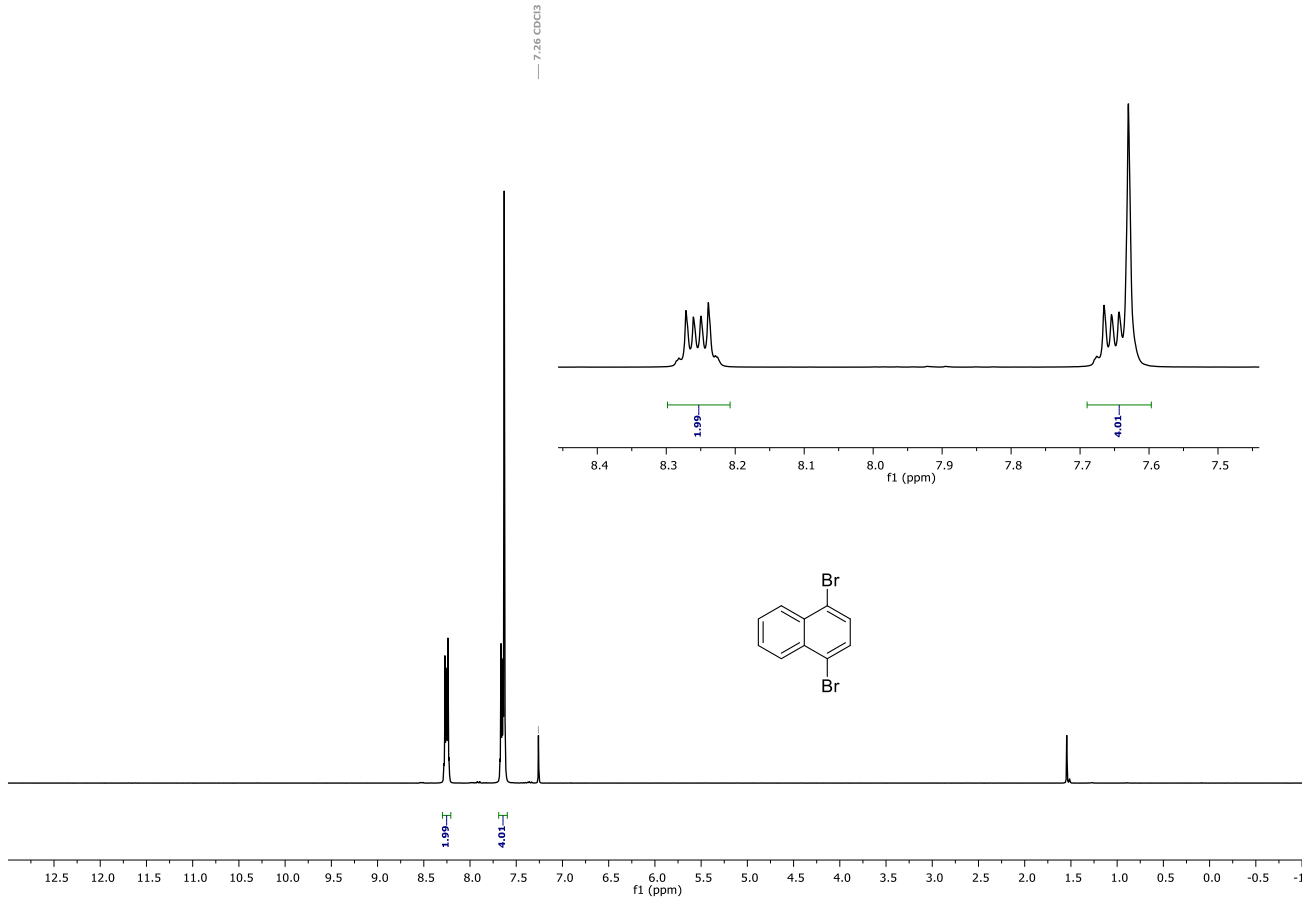


Figure 1S. *^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of* ***1,4-dibromonaphthalene.***

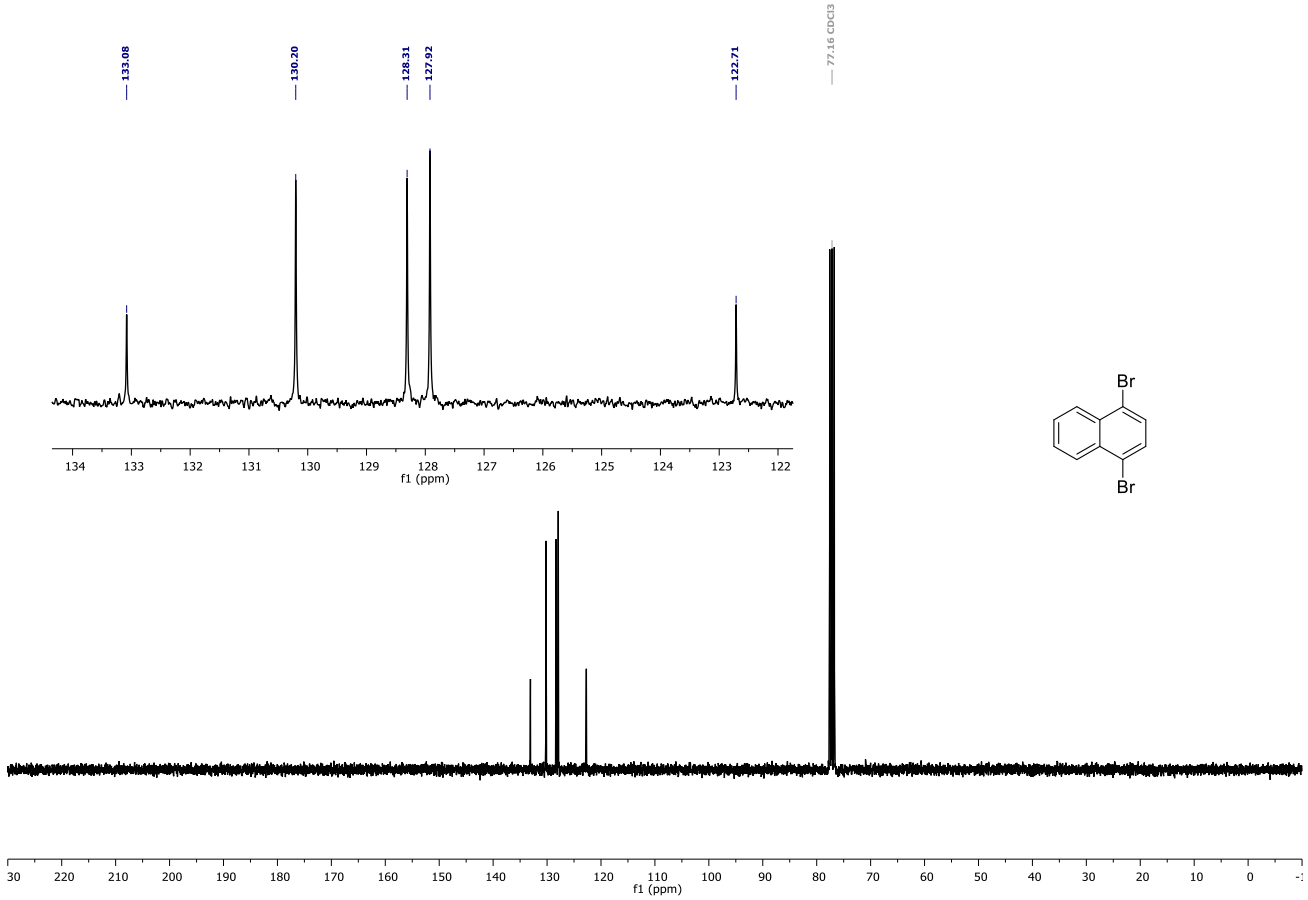


Figure 2S. *^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of* ***1,4-dibromonaphthalene.***

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

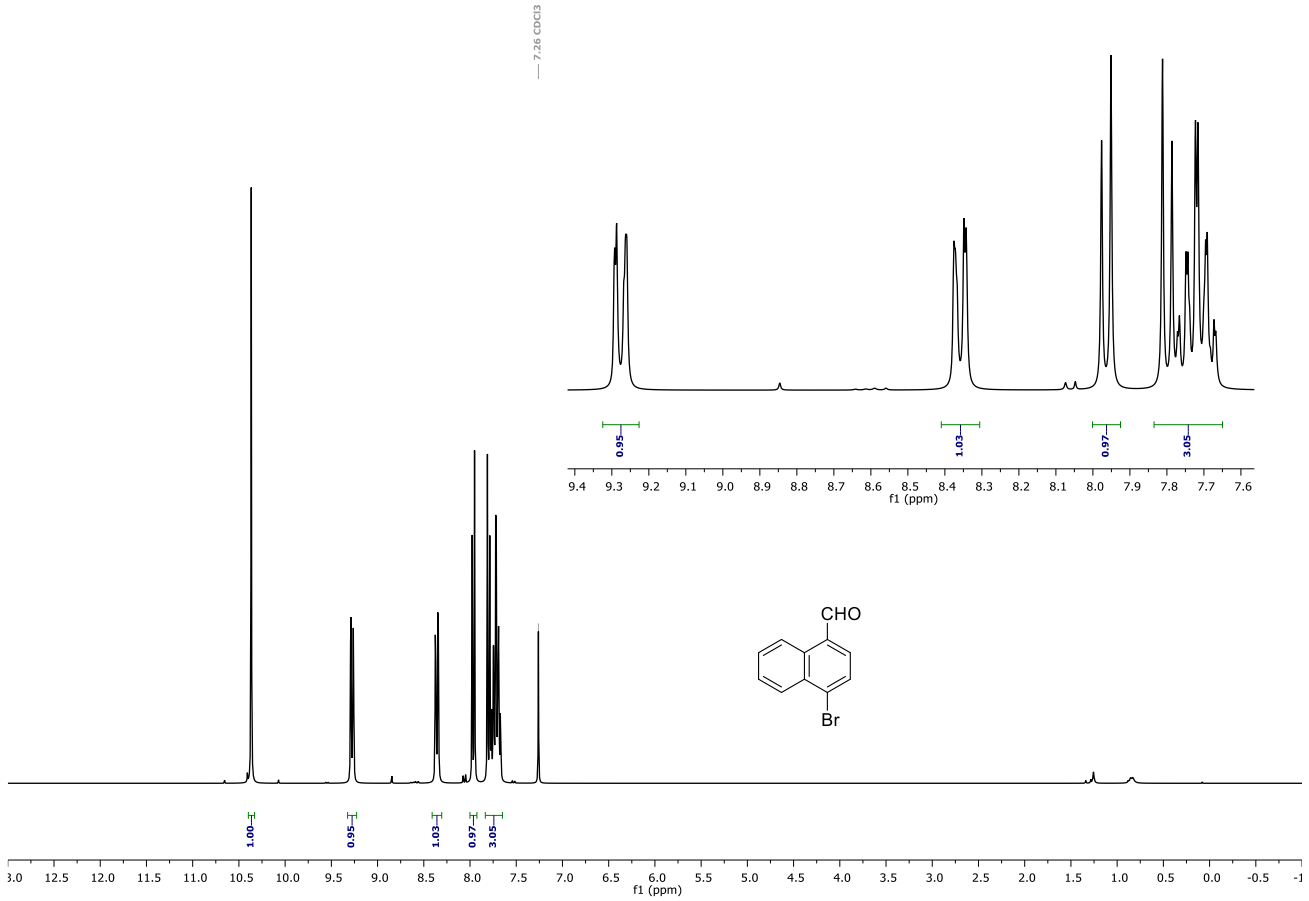


Figure 3S. *^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of* ***4-bromo-1-naphthalenecarbaldehyde.***

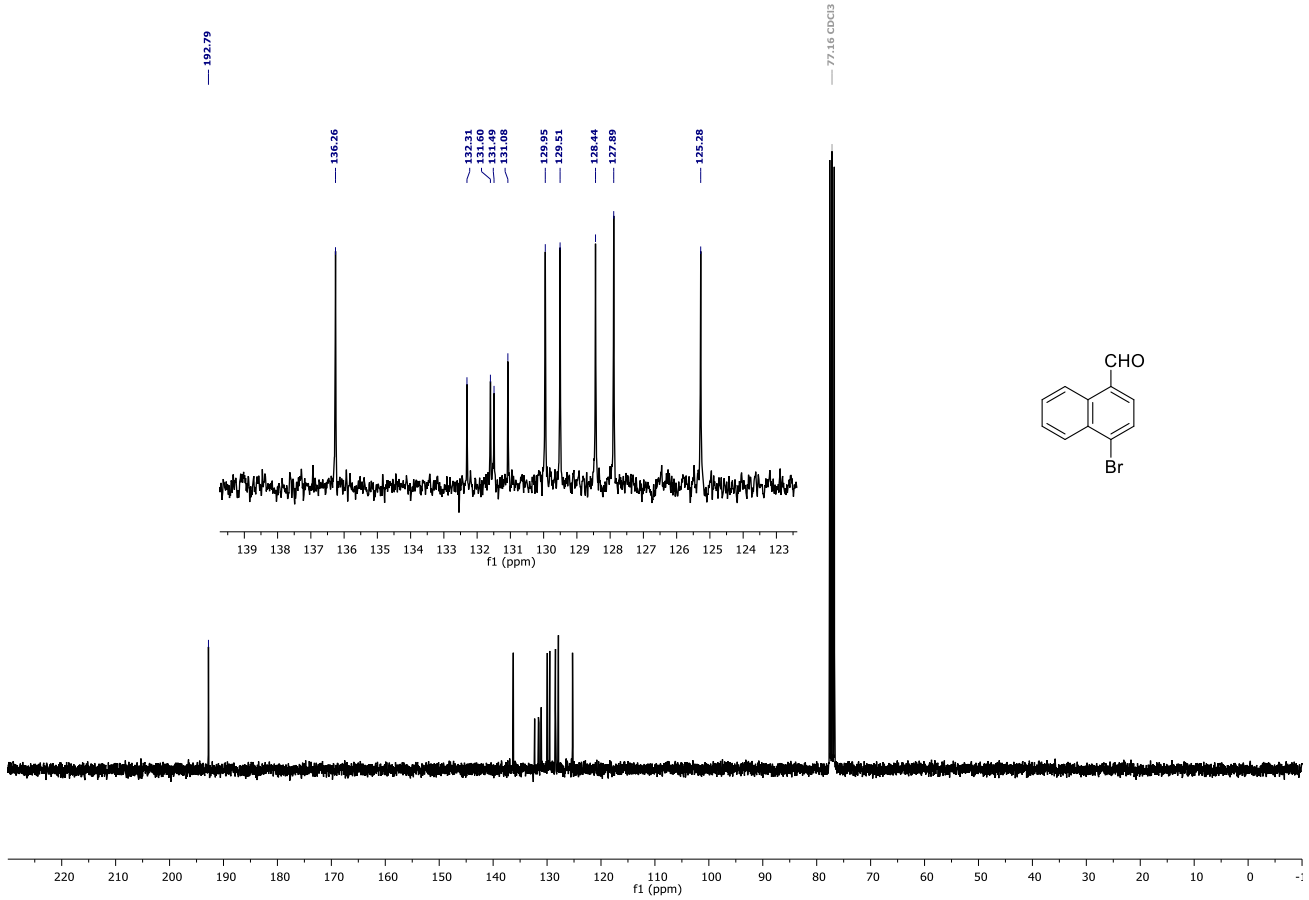


Figure 4S. *^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of* ***4-bromo-1-naphthalenecarbaldehyde.***

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

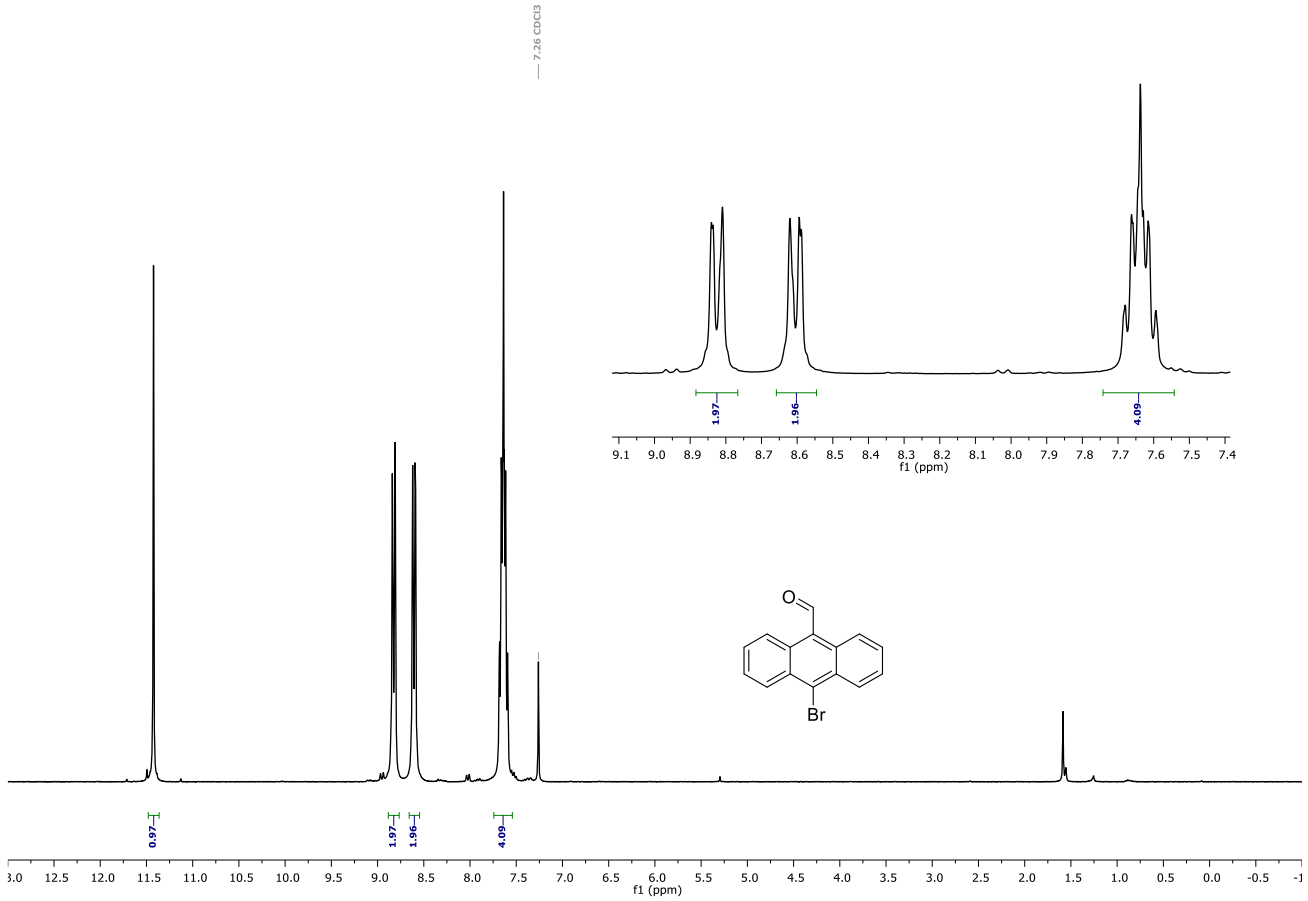


Figure 5S. *^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of* ***10-bromo-9-anthracenecarbaldehyde.***

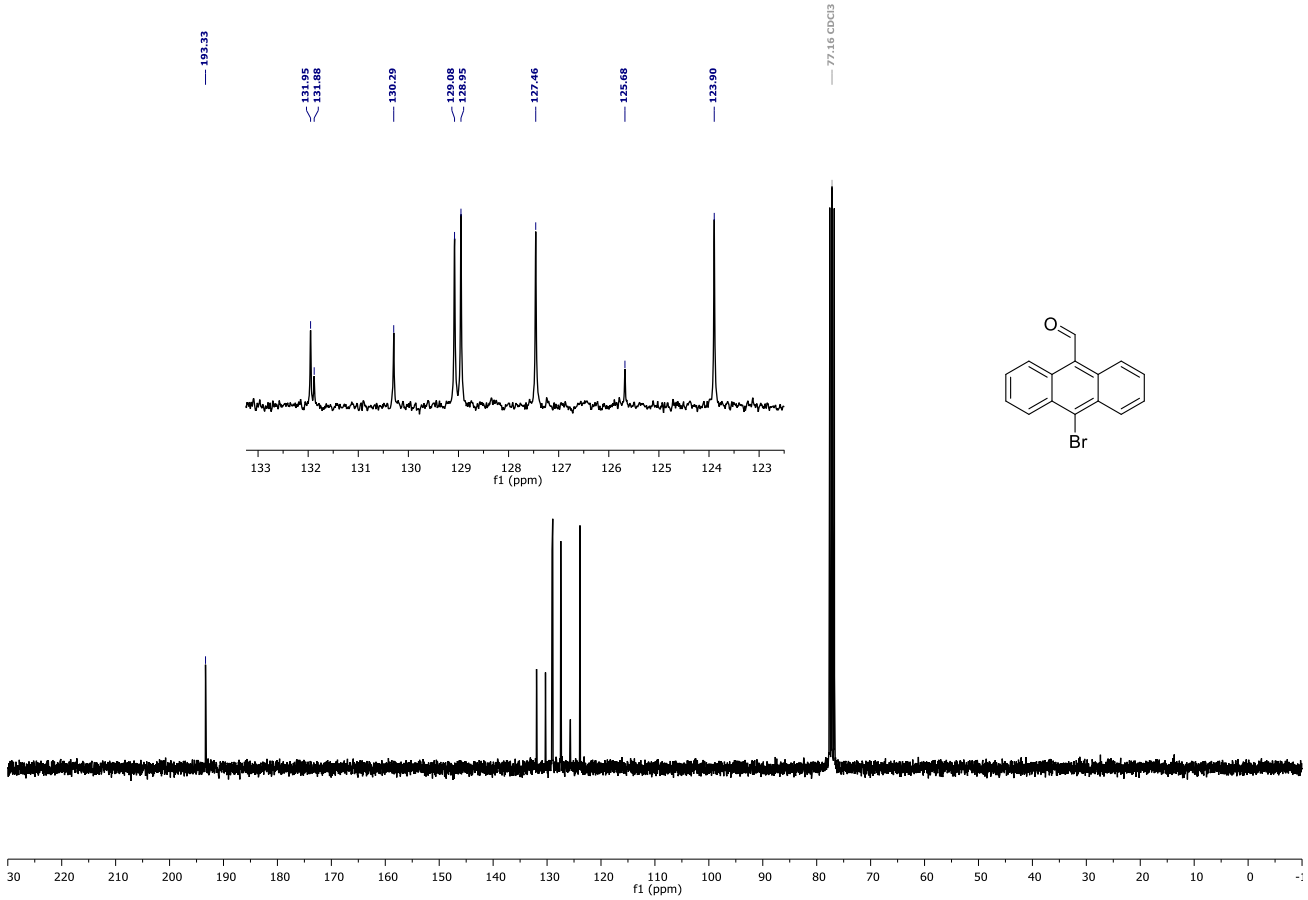


Figure 6S. *^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of* ***10-bromo-9-anthracenecarbaldehyde.***

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

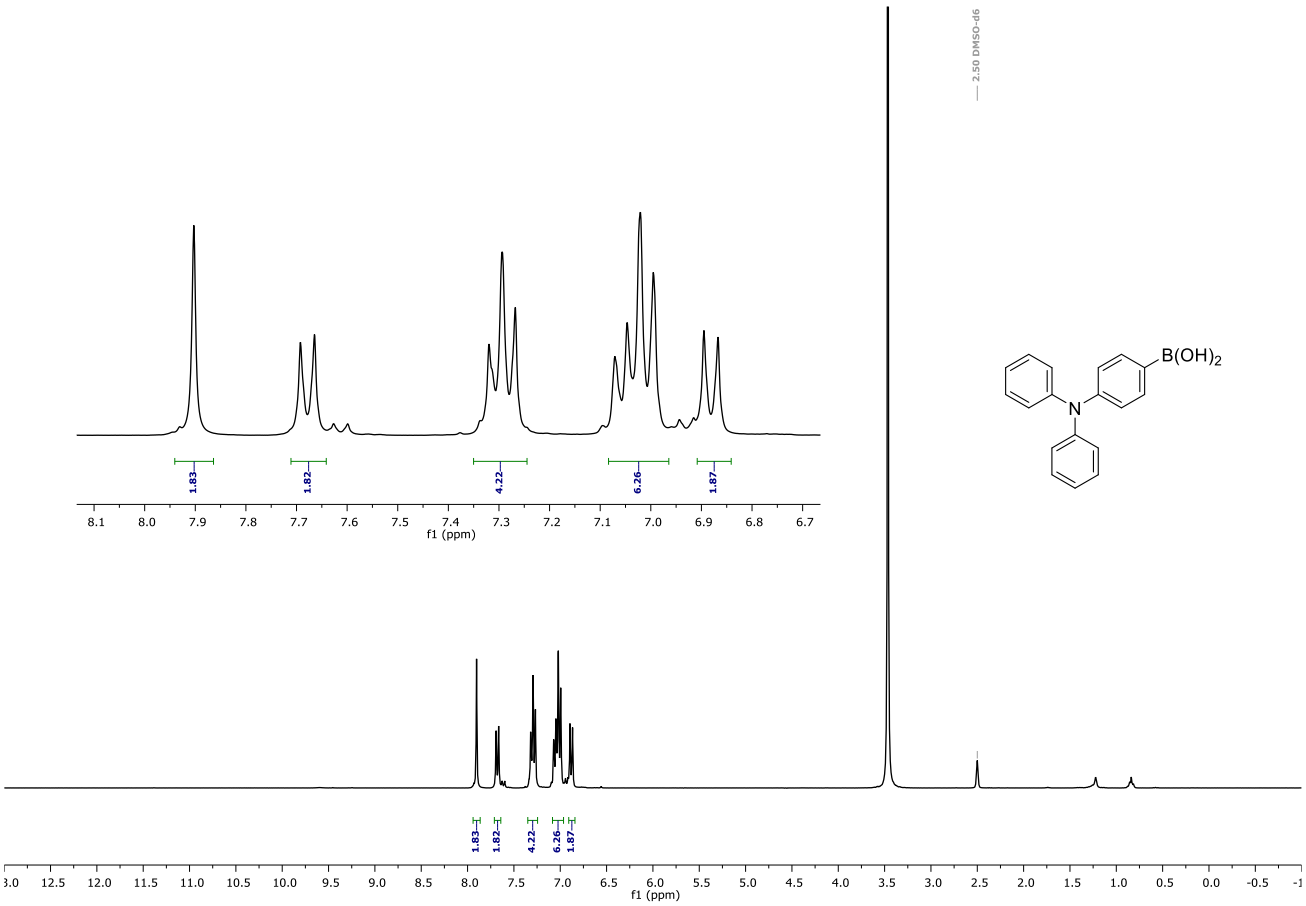


Figure 7S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***4-(diphenylamino)phenylboronic acid.***

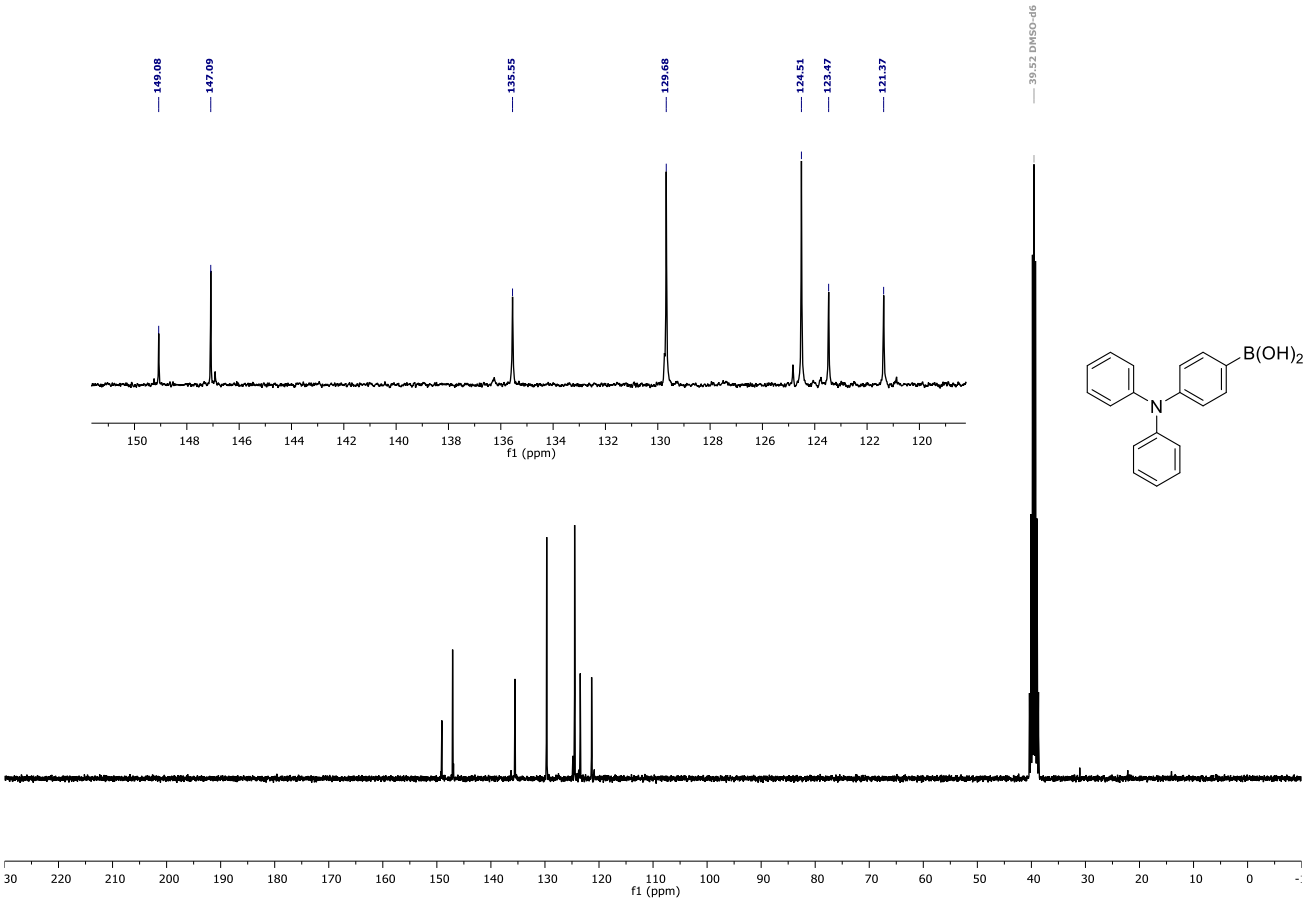


Figure 8S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***4-(diphenylamino)phenylboronic acid.***

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

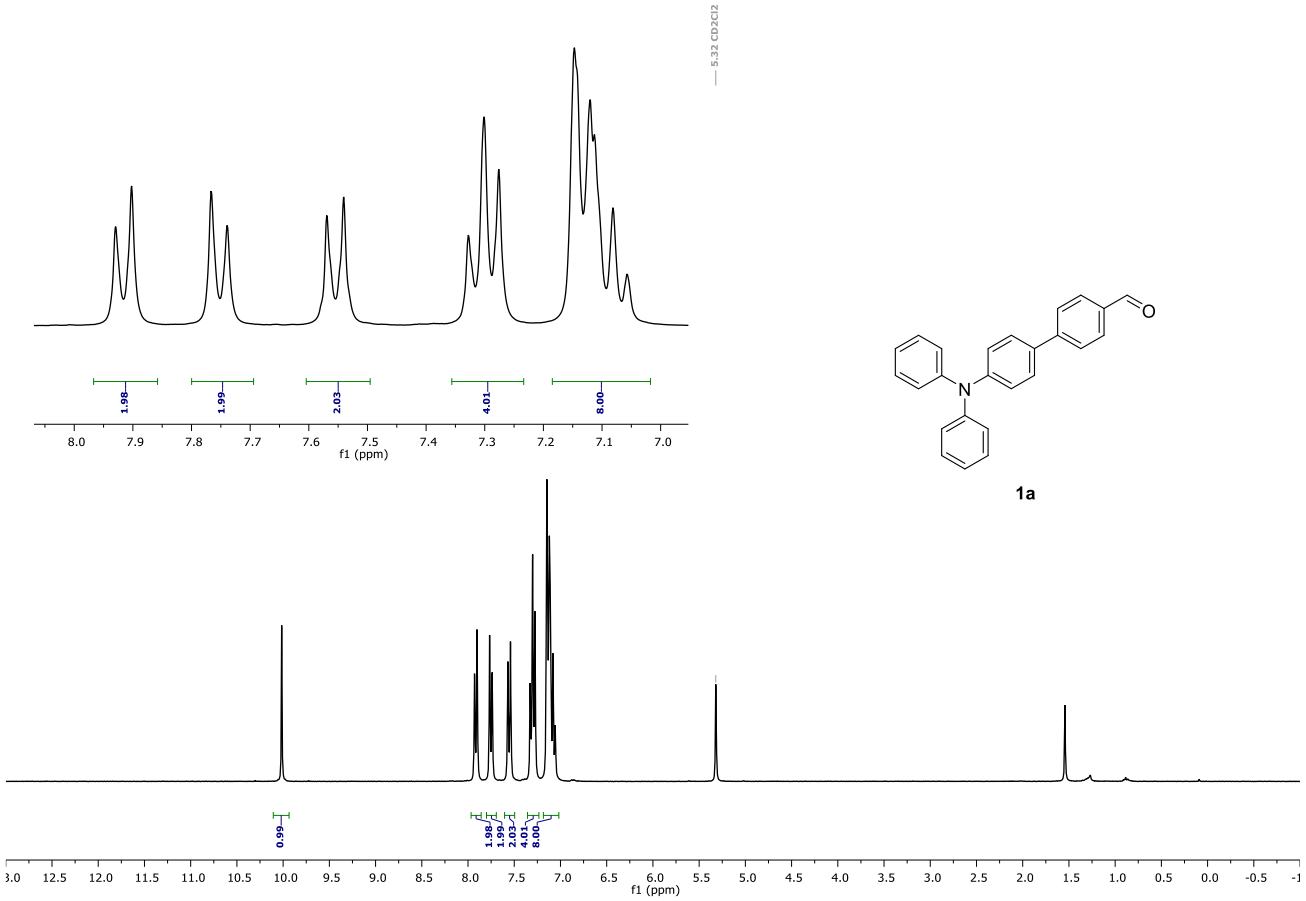


Figure 9S. *^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) spectrum of* ***1a.***

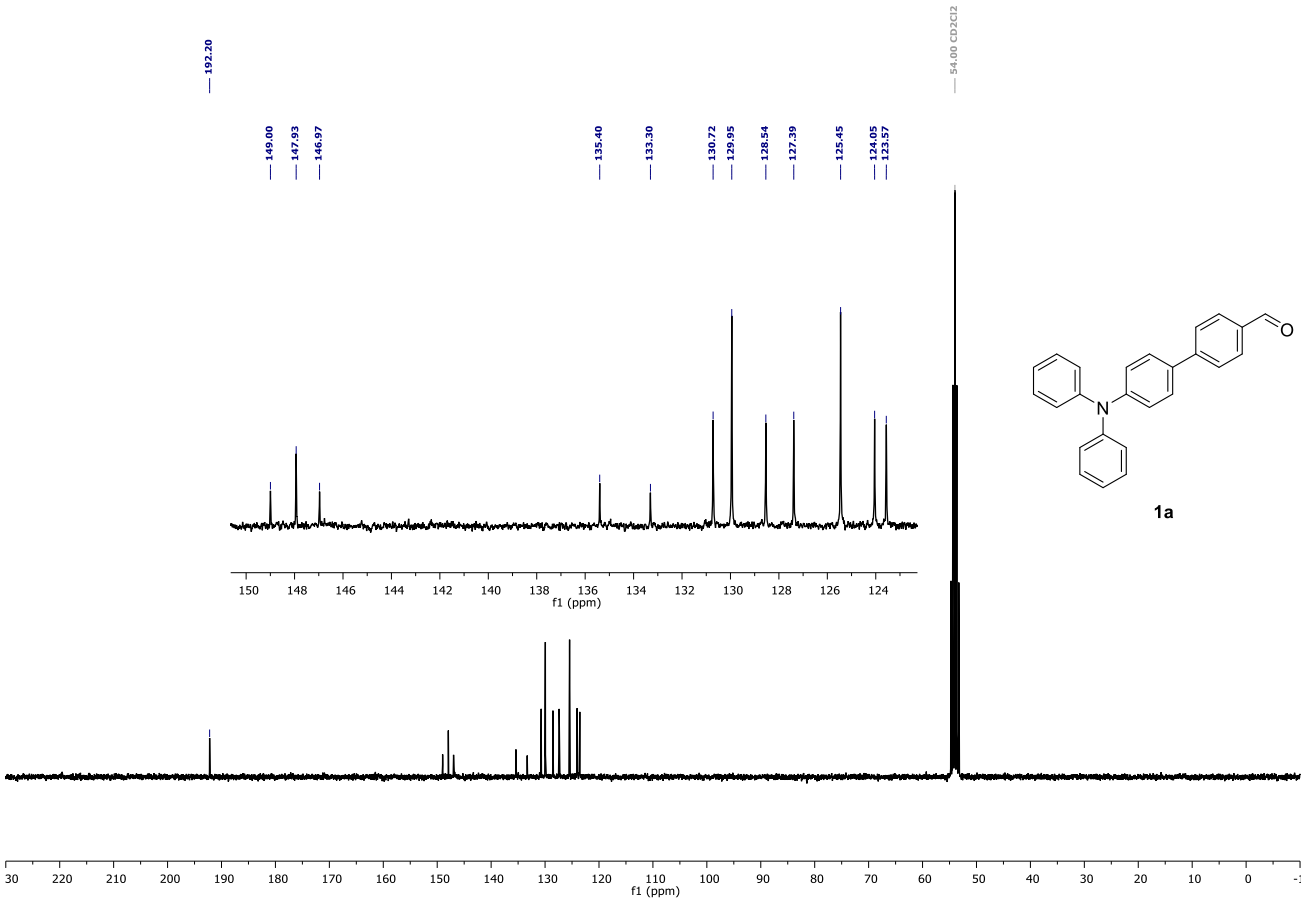


Figure 10S. *^{13}C NMR (75 MHz, CD_2Cl_2, 298 K) spectrum of* ***10-bromo-9-anthracenecarbaldehyde.***

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

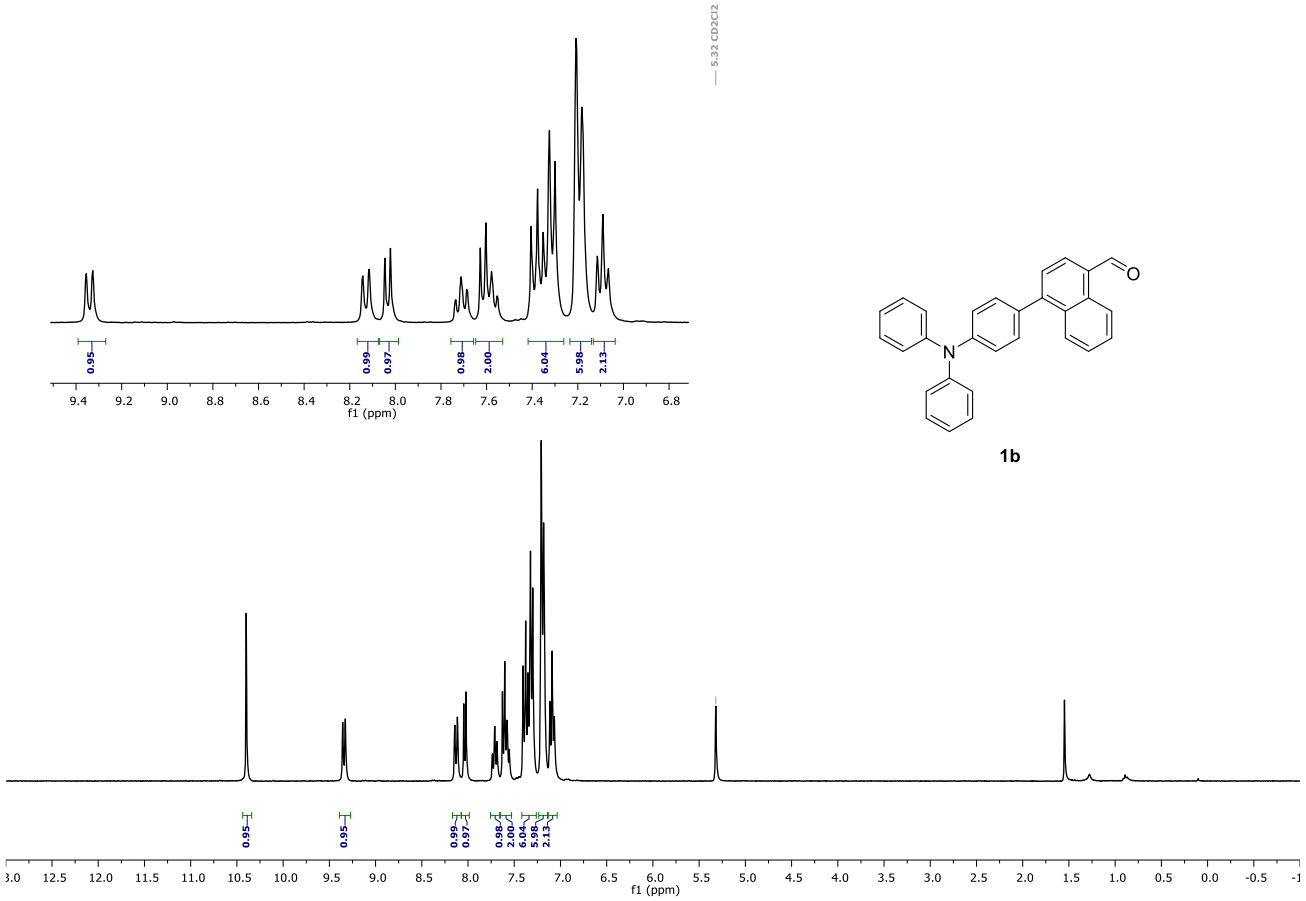


Figure 11S. *^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) spectrum of* ***1b.***

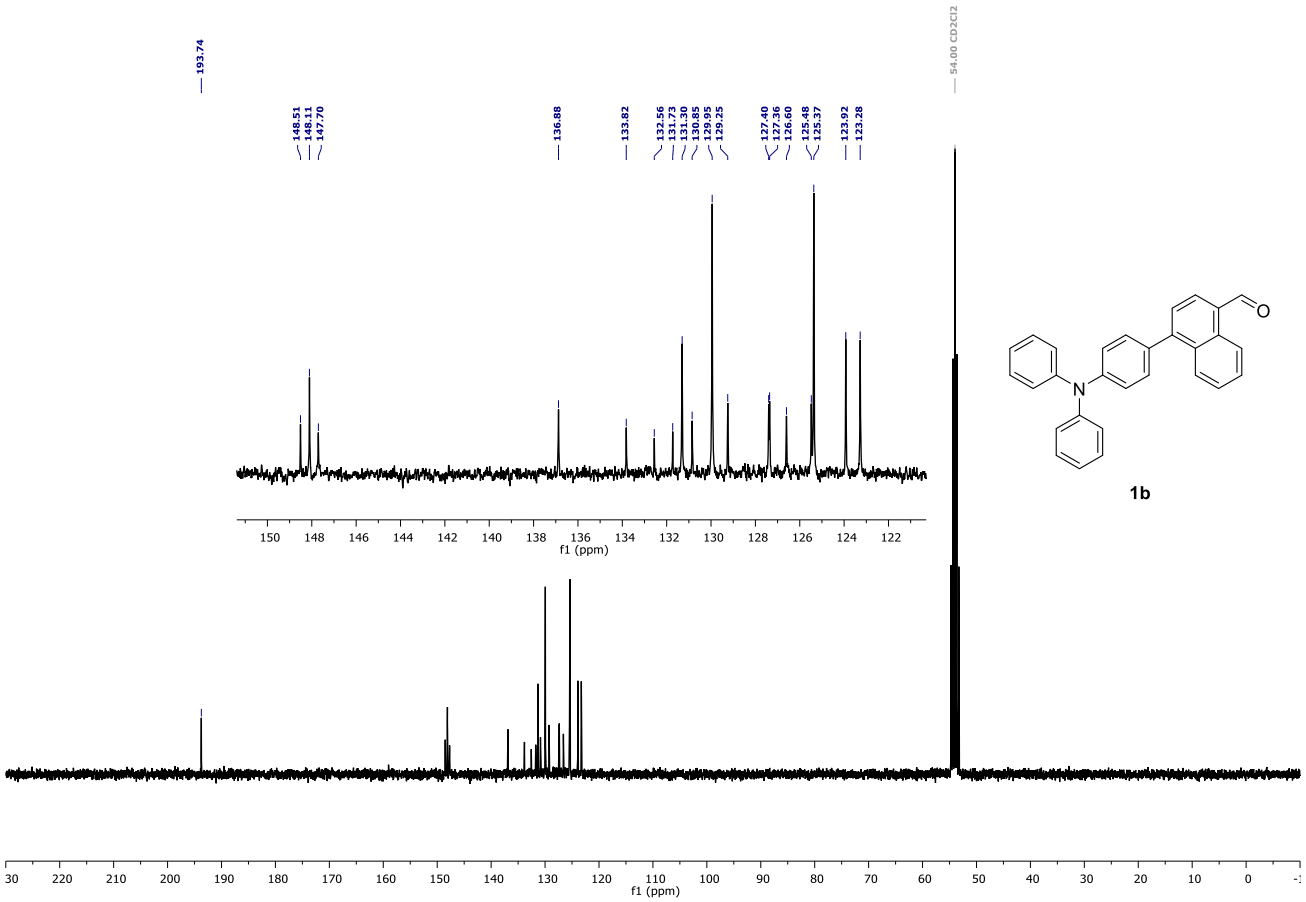


Figure 12S. *^{13}C NMR (75 MHz, CD_2Cl_2, 298 K) spectrum of* ***1b.***

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

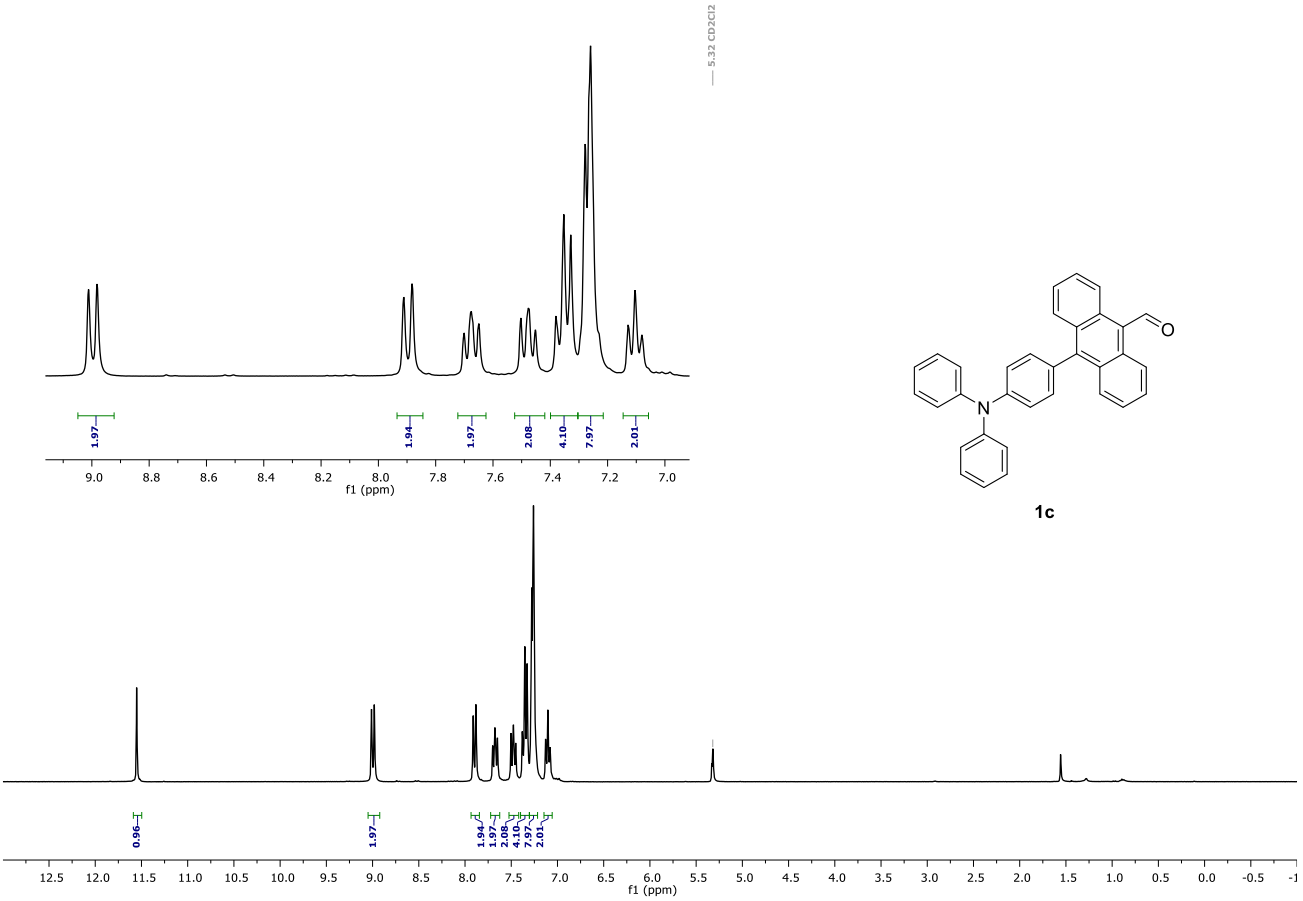


Figure 13S. *^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) spectrum of* ***1c.***

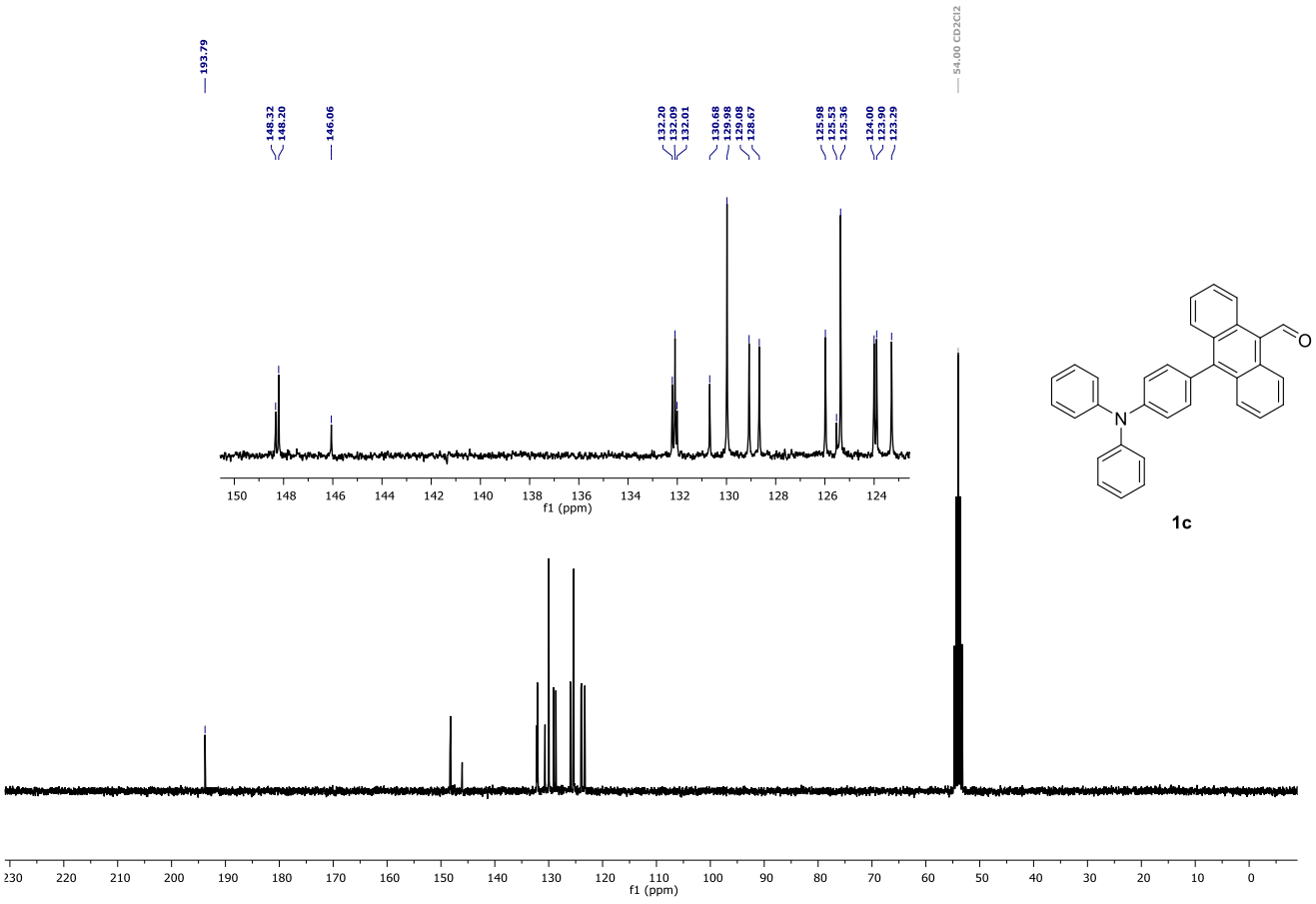


Figure 14S. *^{13}C NMR (75 MHz, CD_2Cl_2, 298 K) spectrum of* ***1c.***

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

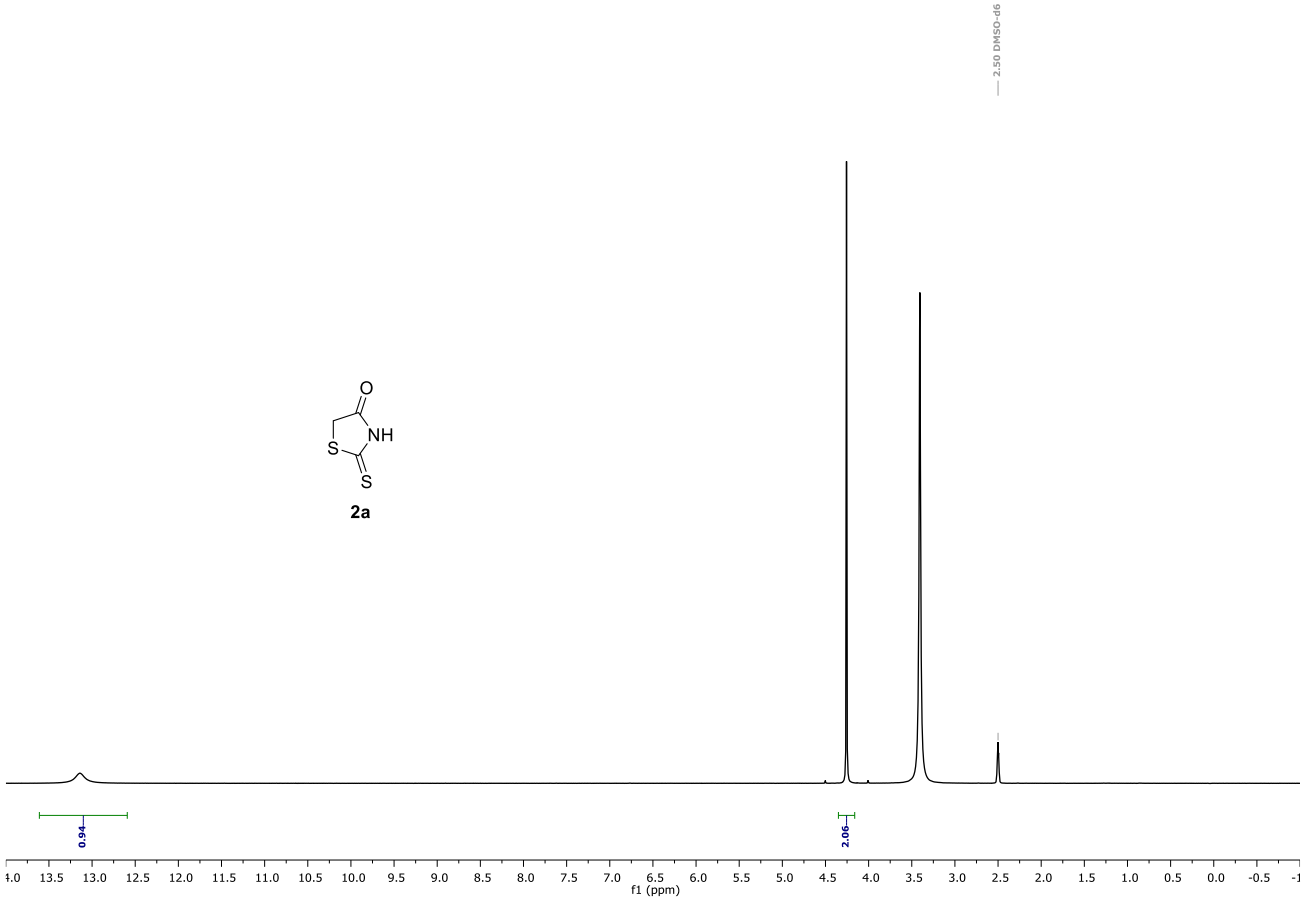


Figure 15S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***2a.***

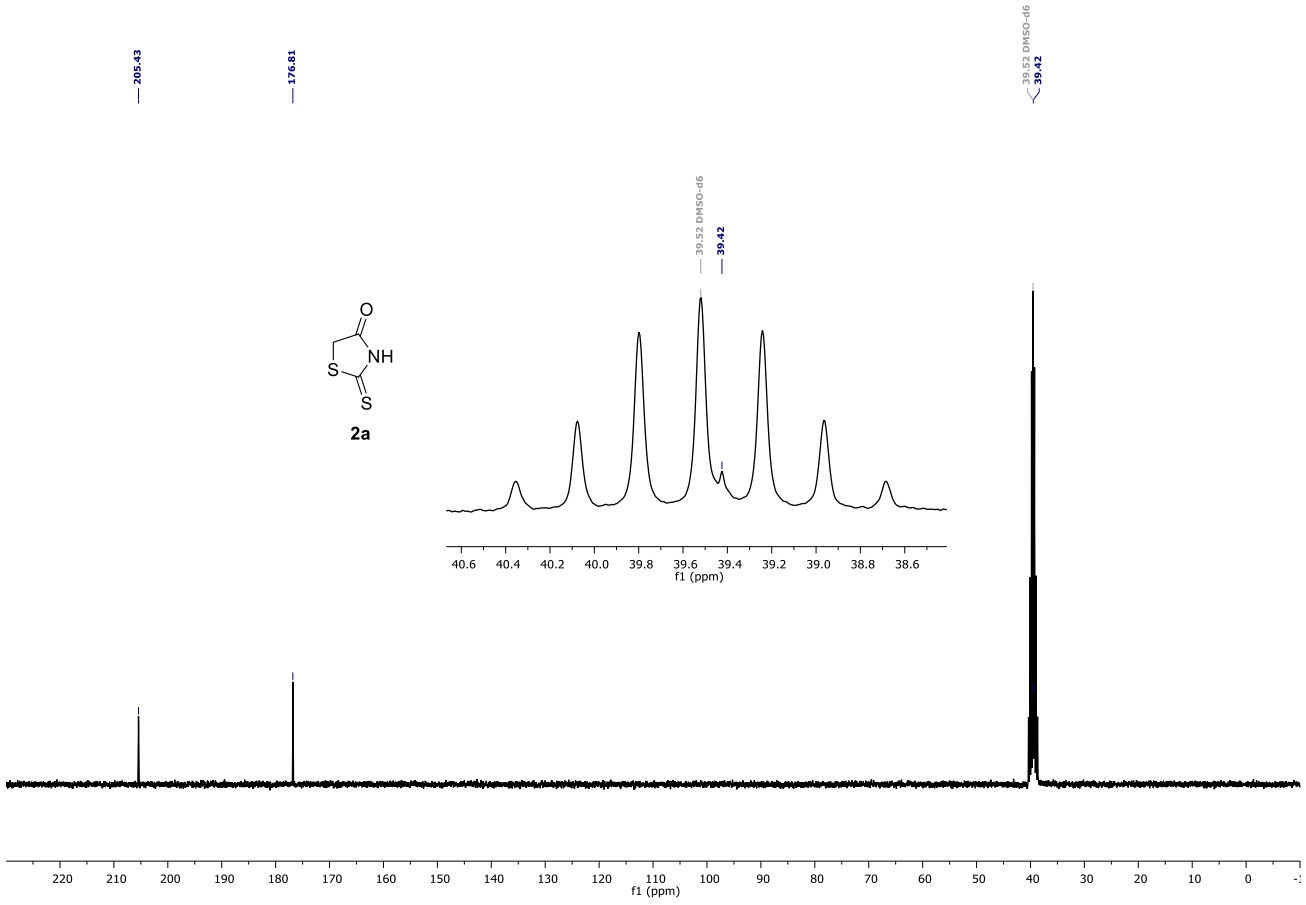


Figure 16S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***2a.***

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

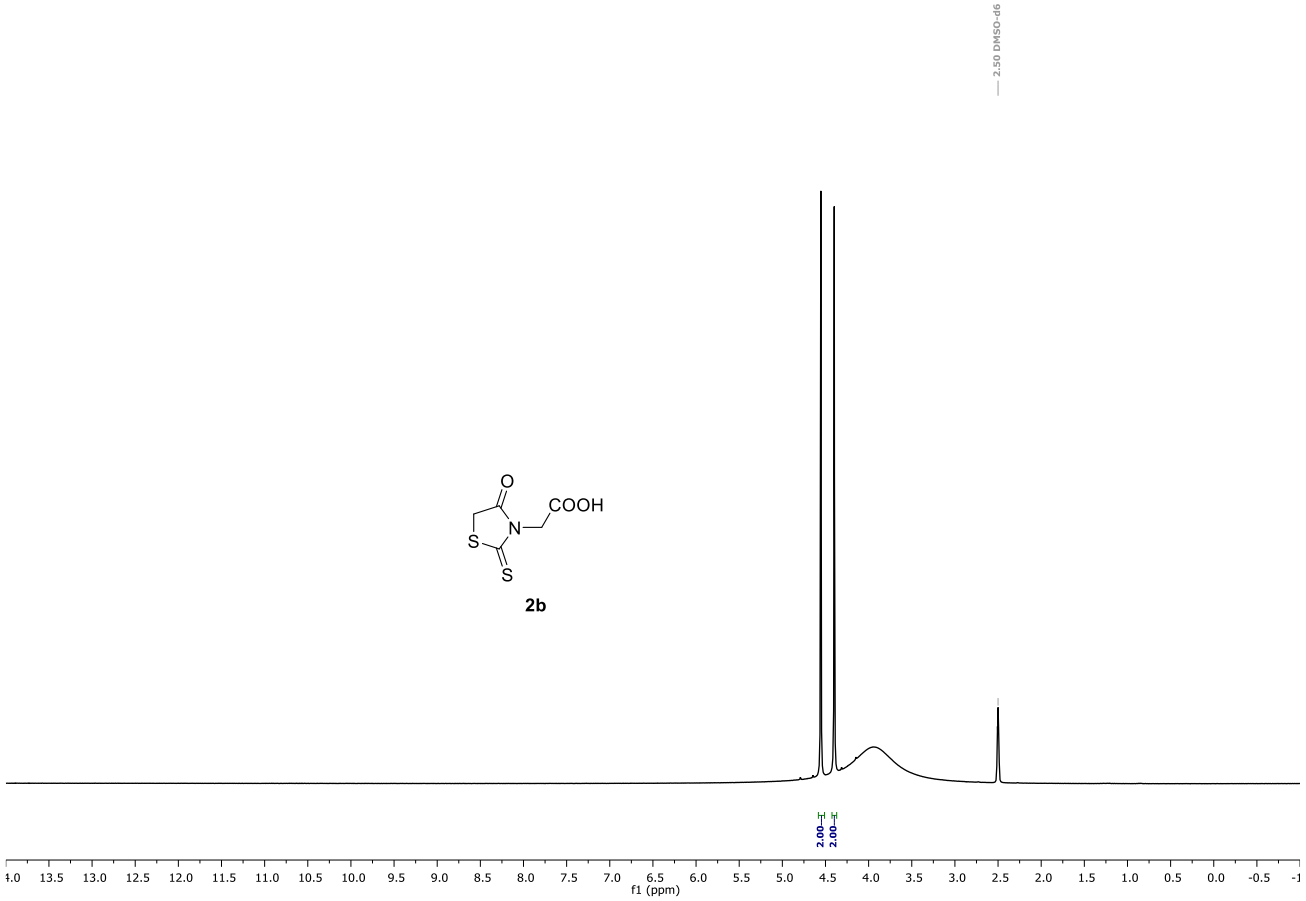


Figure 17S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***2b.***

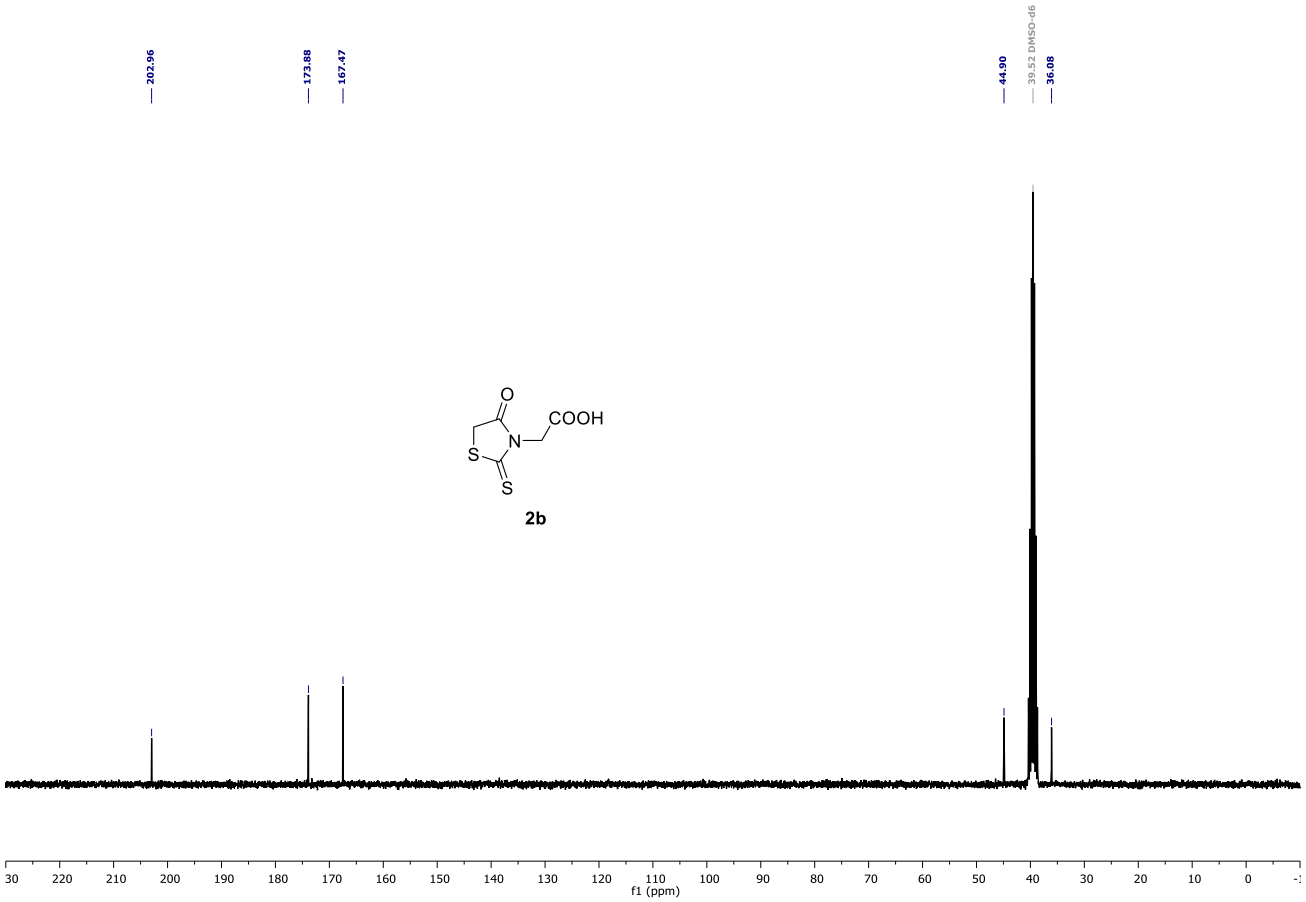


Figure 18S. *^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of* ***2b.***

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

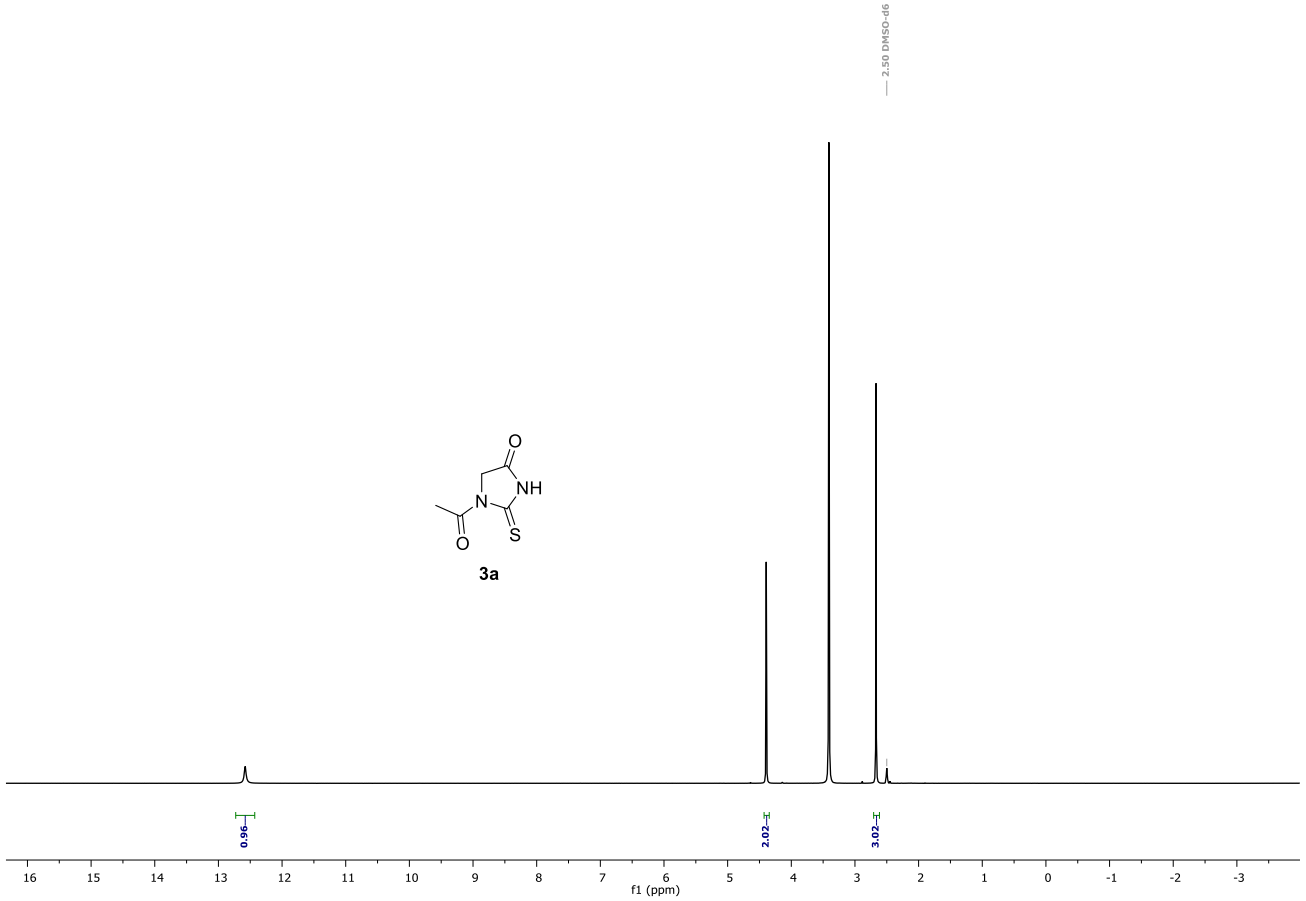


Figure 19S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***3a.***

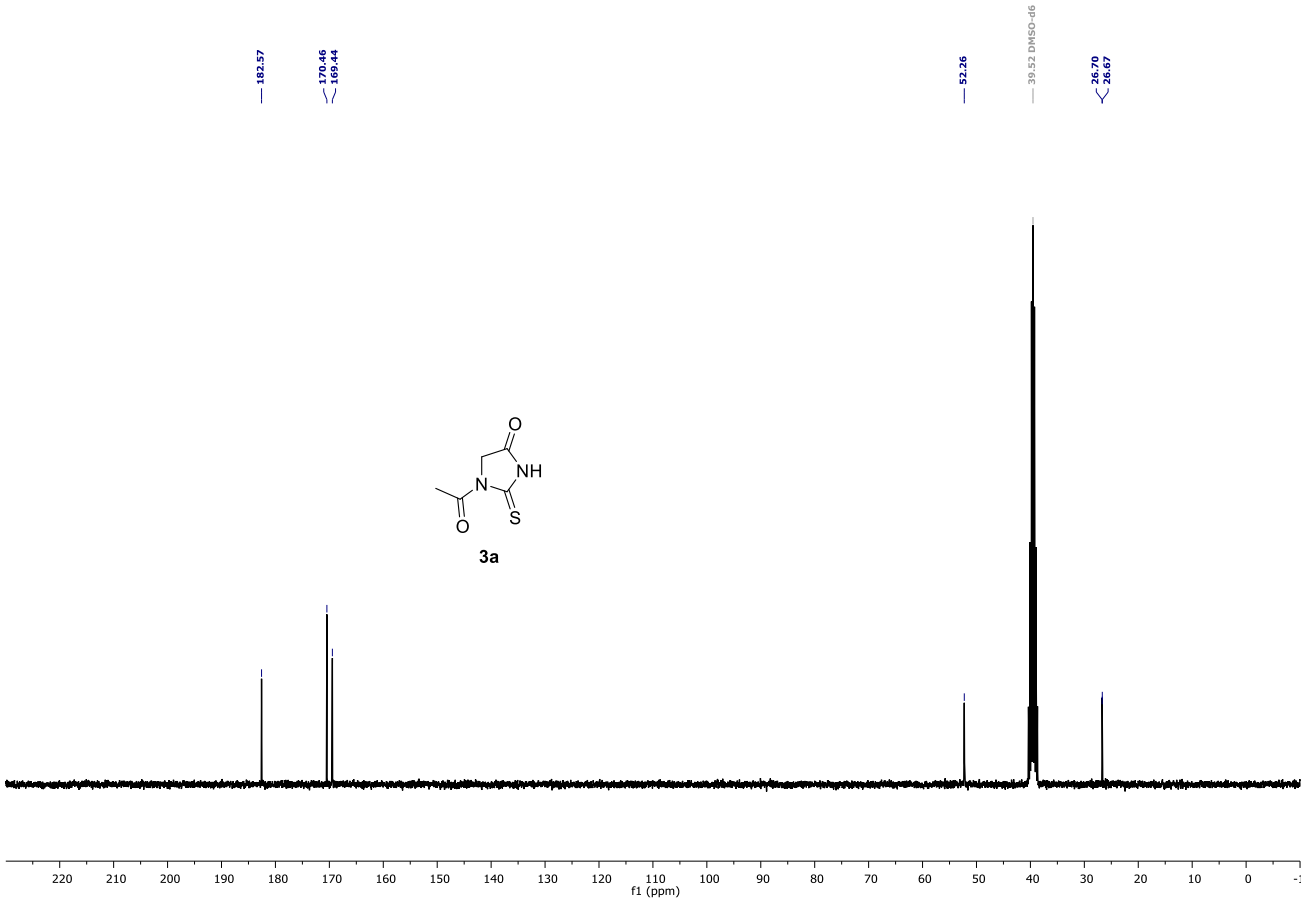


Figure 20S. *^{13}C NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***3a.***

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

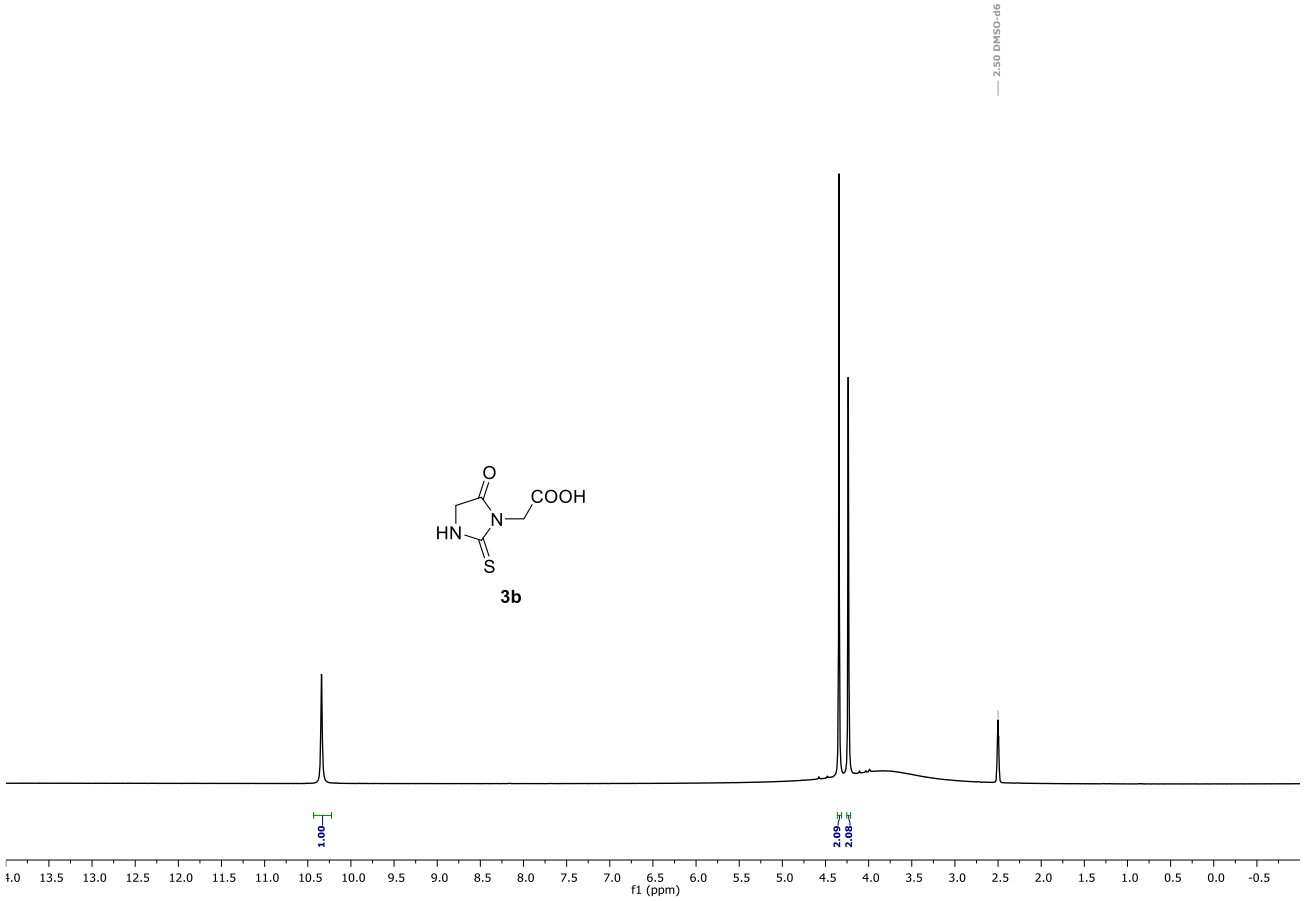


Figure 21S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***3b.***

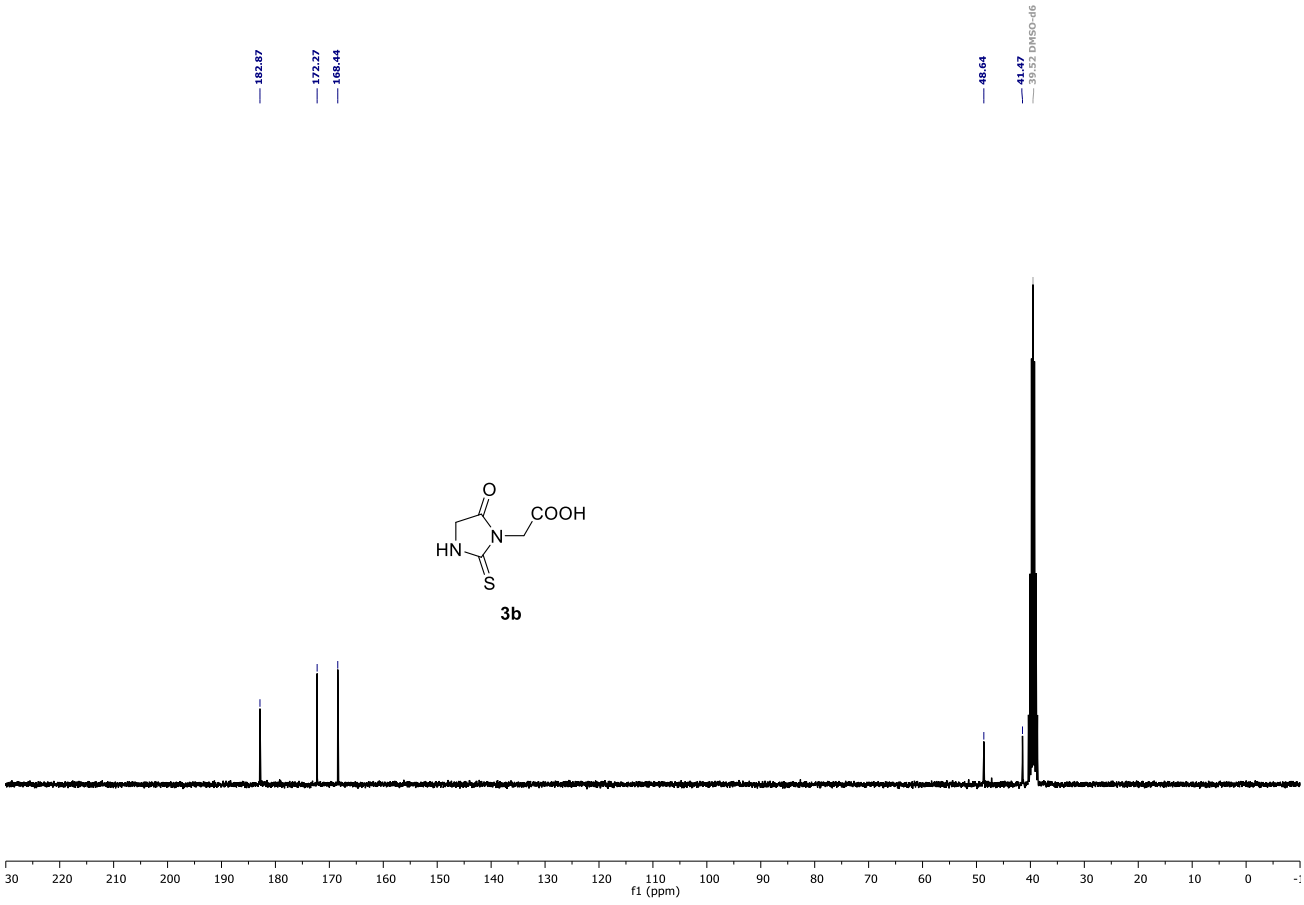


Figure 22S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***3b.***

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

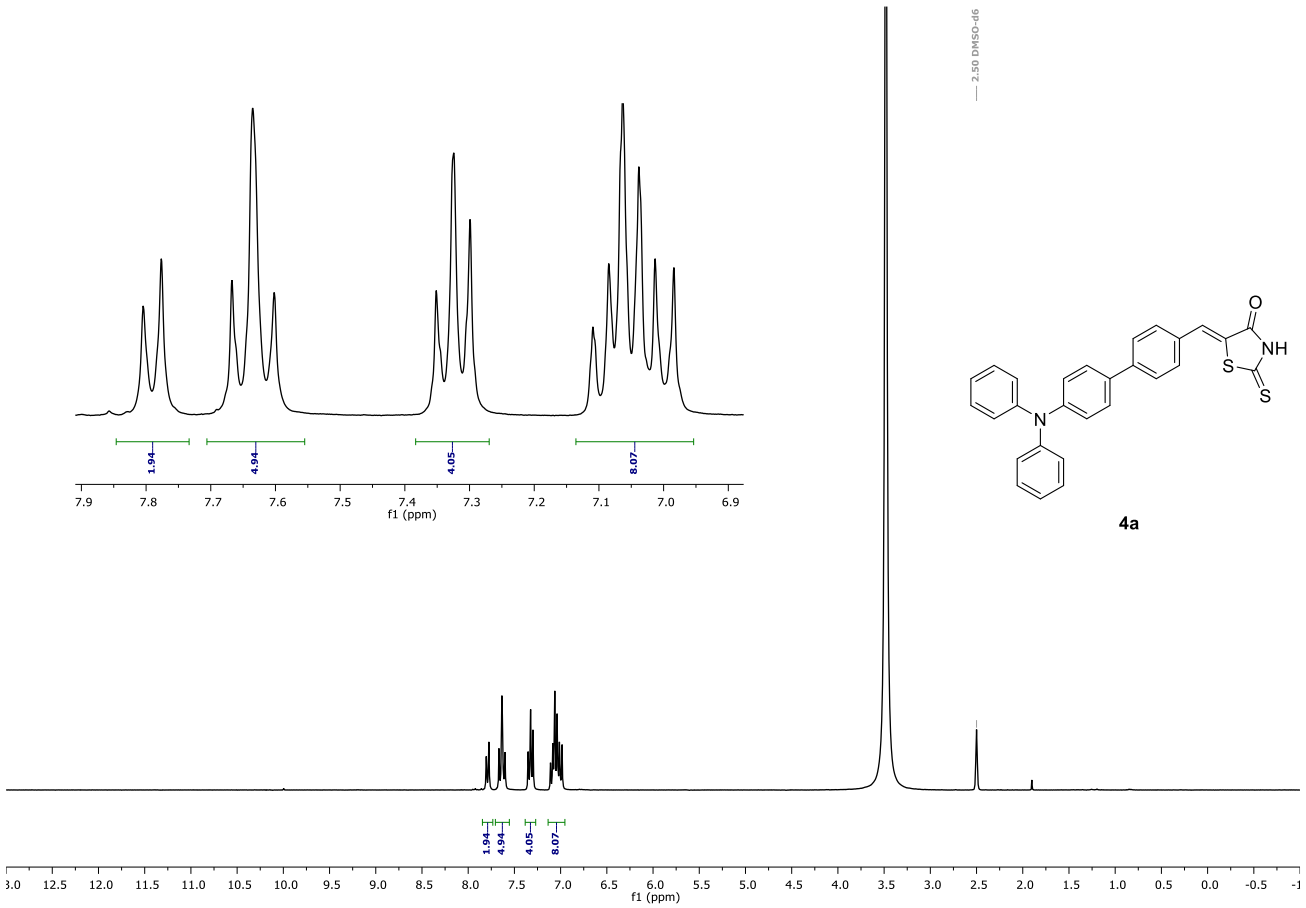


Figure 23S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***4a.***

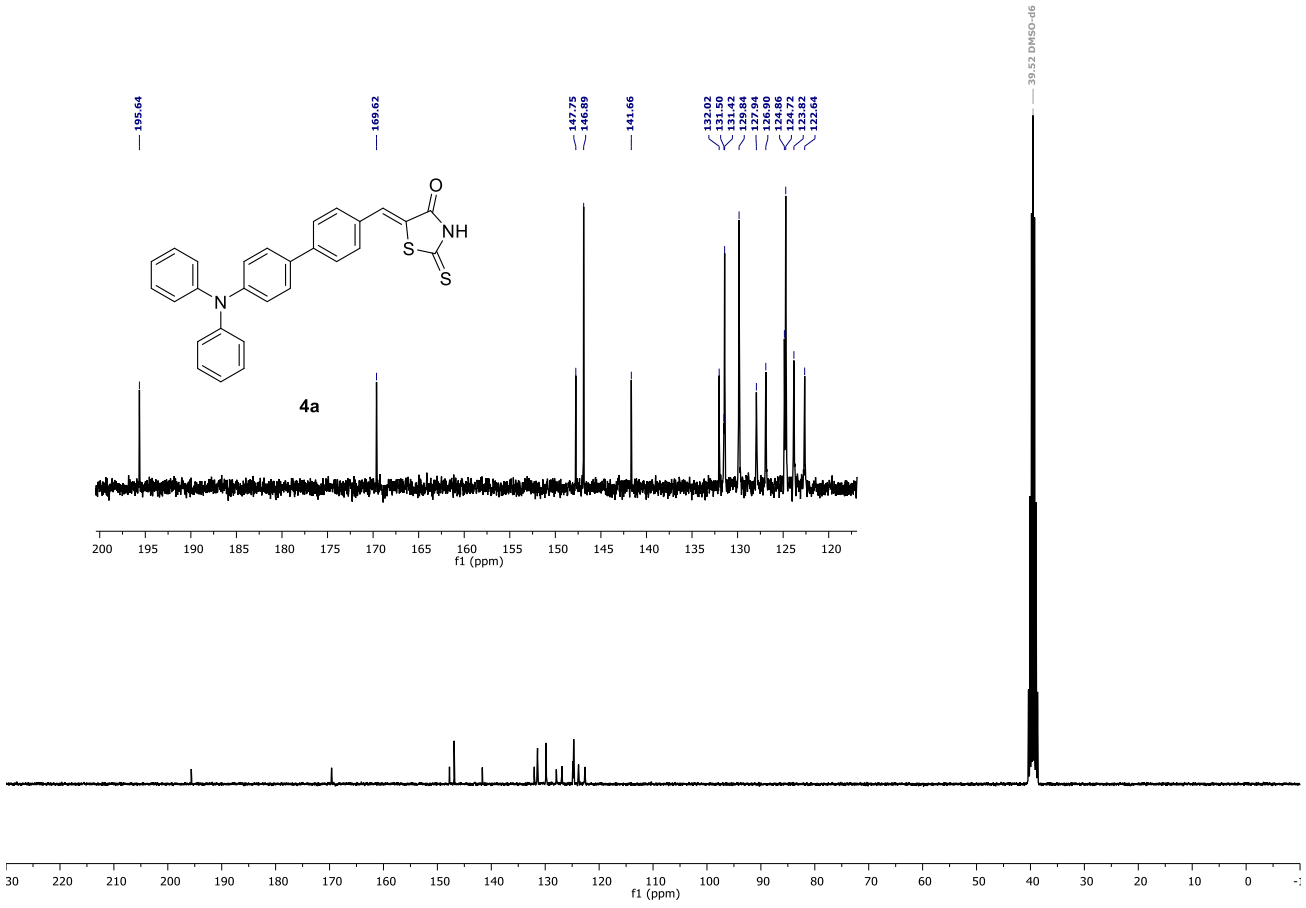


Figure 24S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***4a.***

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

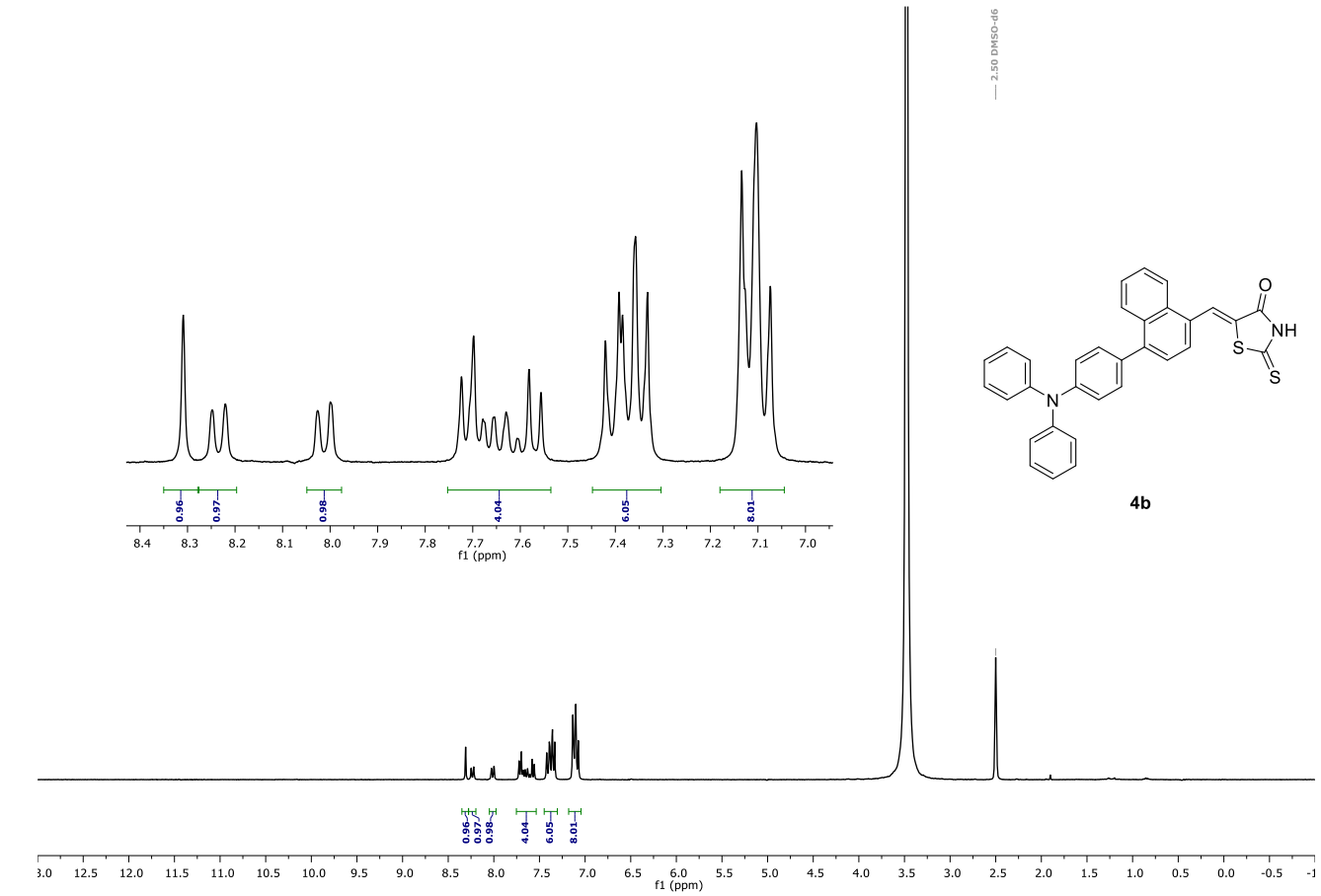


Figure 25S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***4b.***

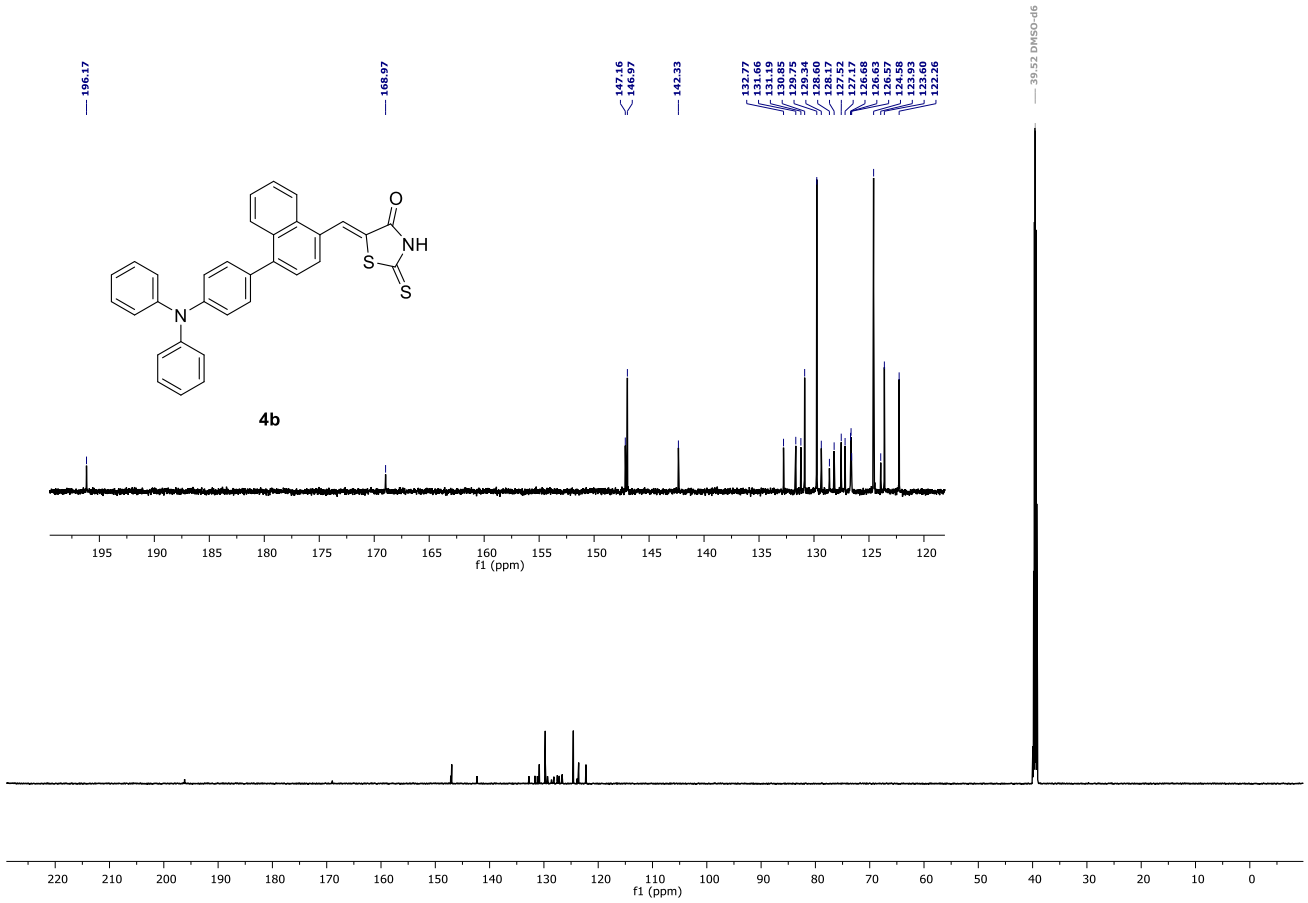


Figure 26S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***4b.***

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

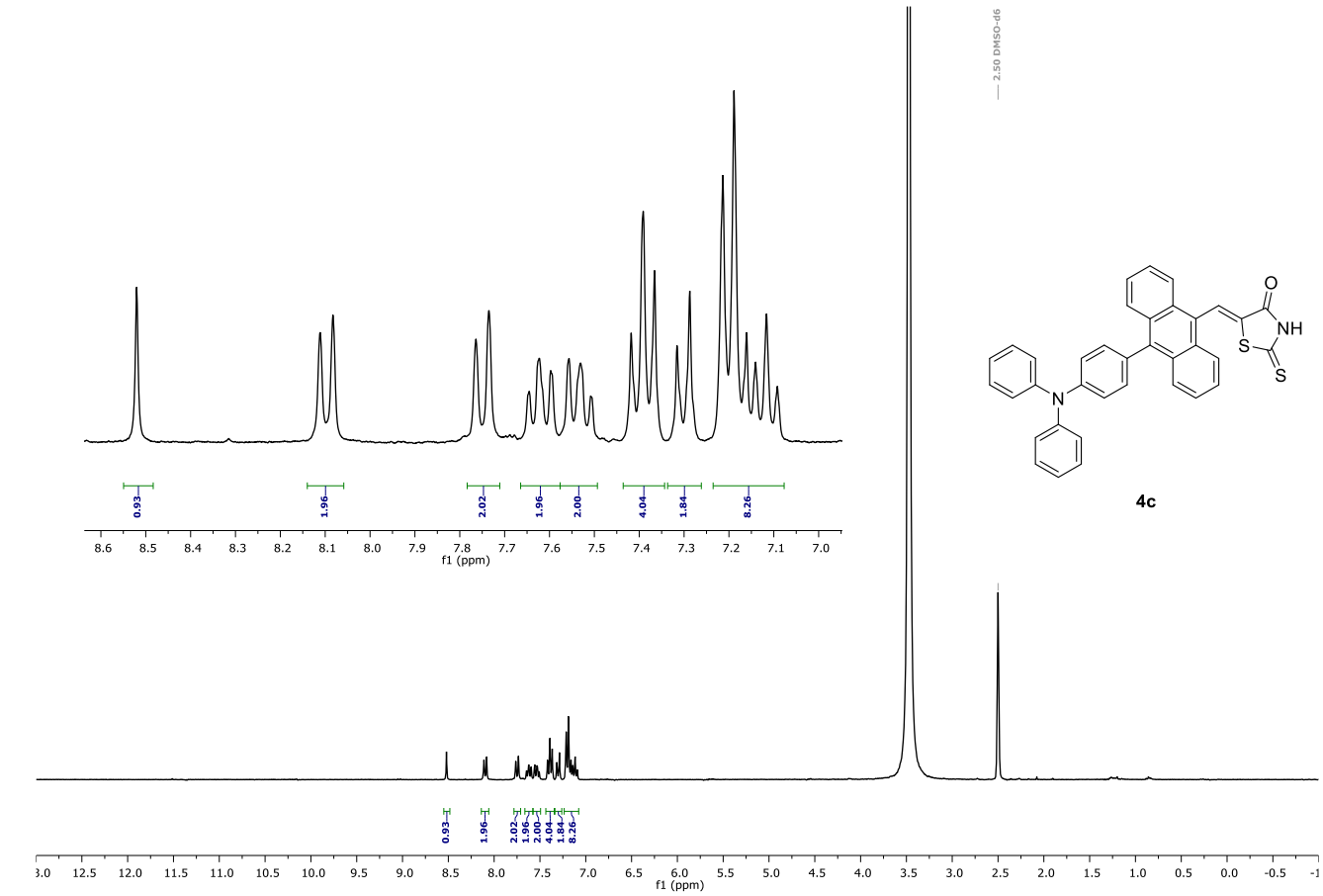


Figure 27S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***4c.***

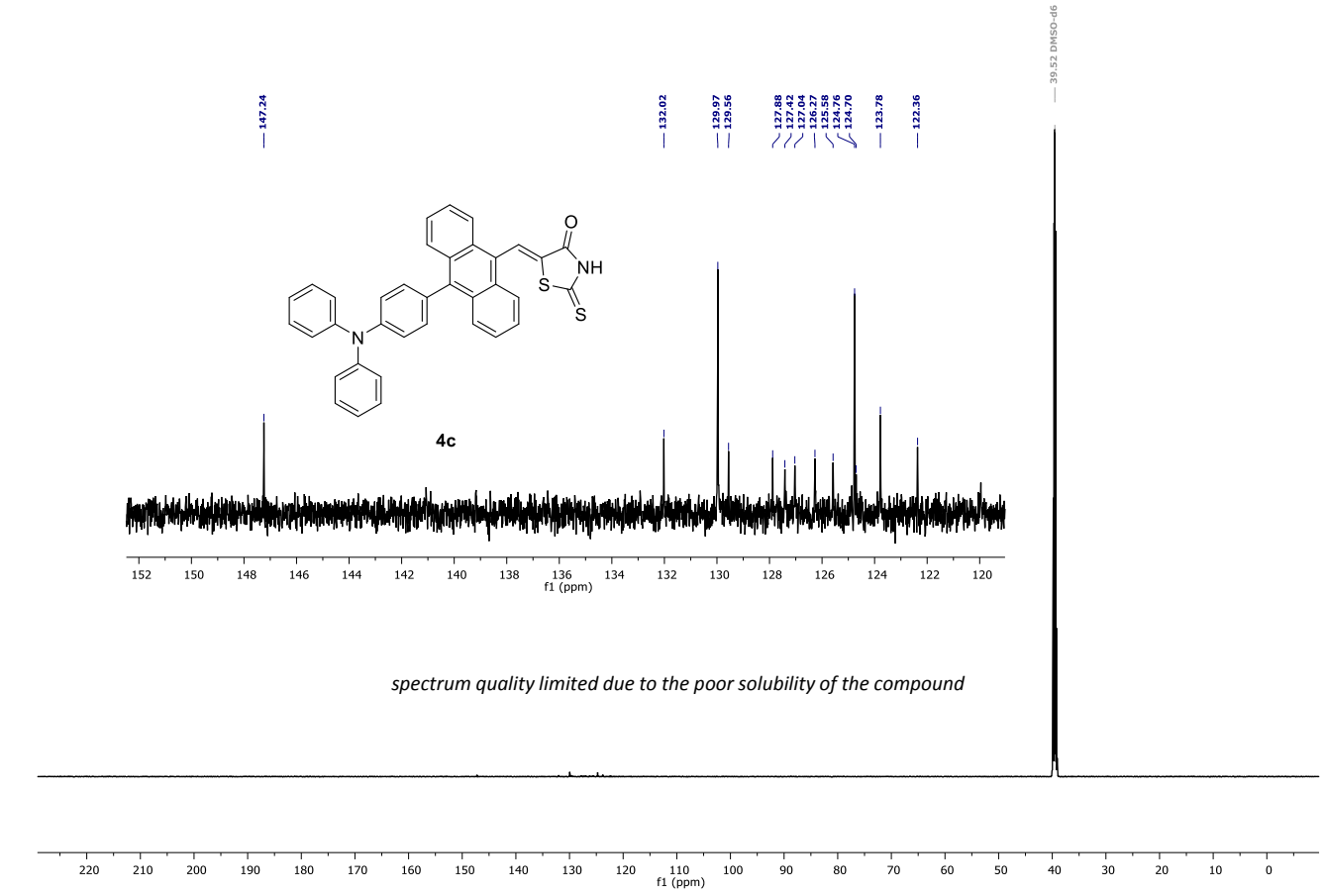


Figure 28S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***4c.***

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

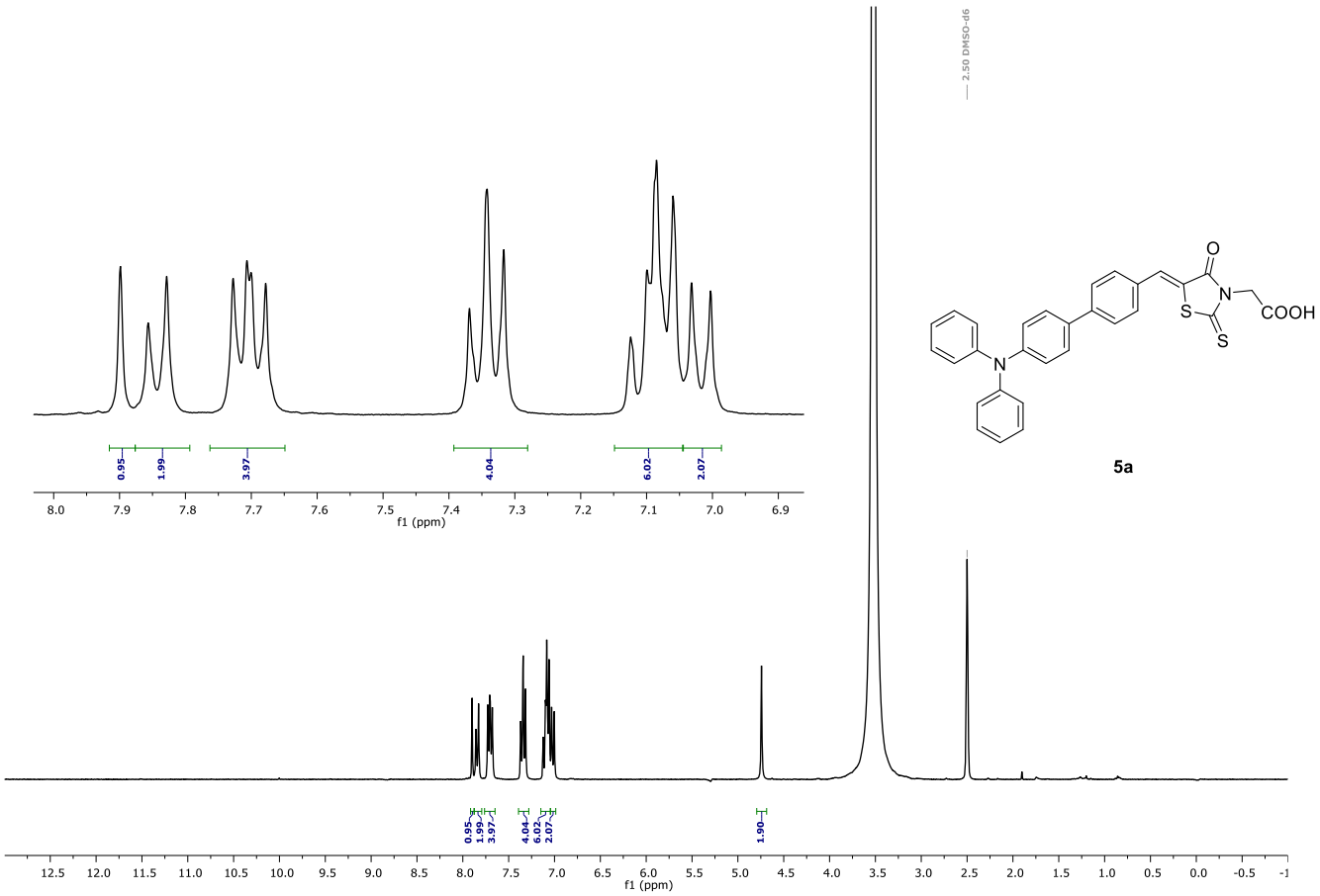


Figure 29S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***5a.***

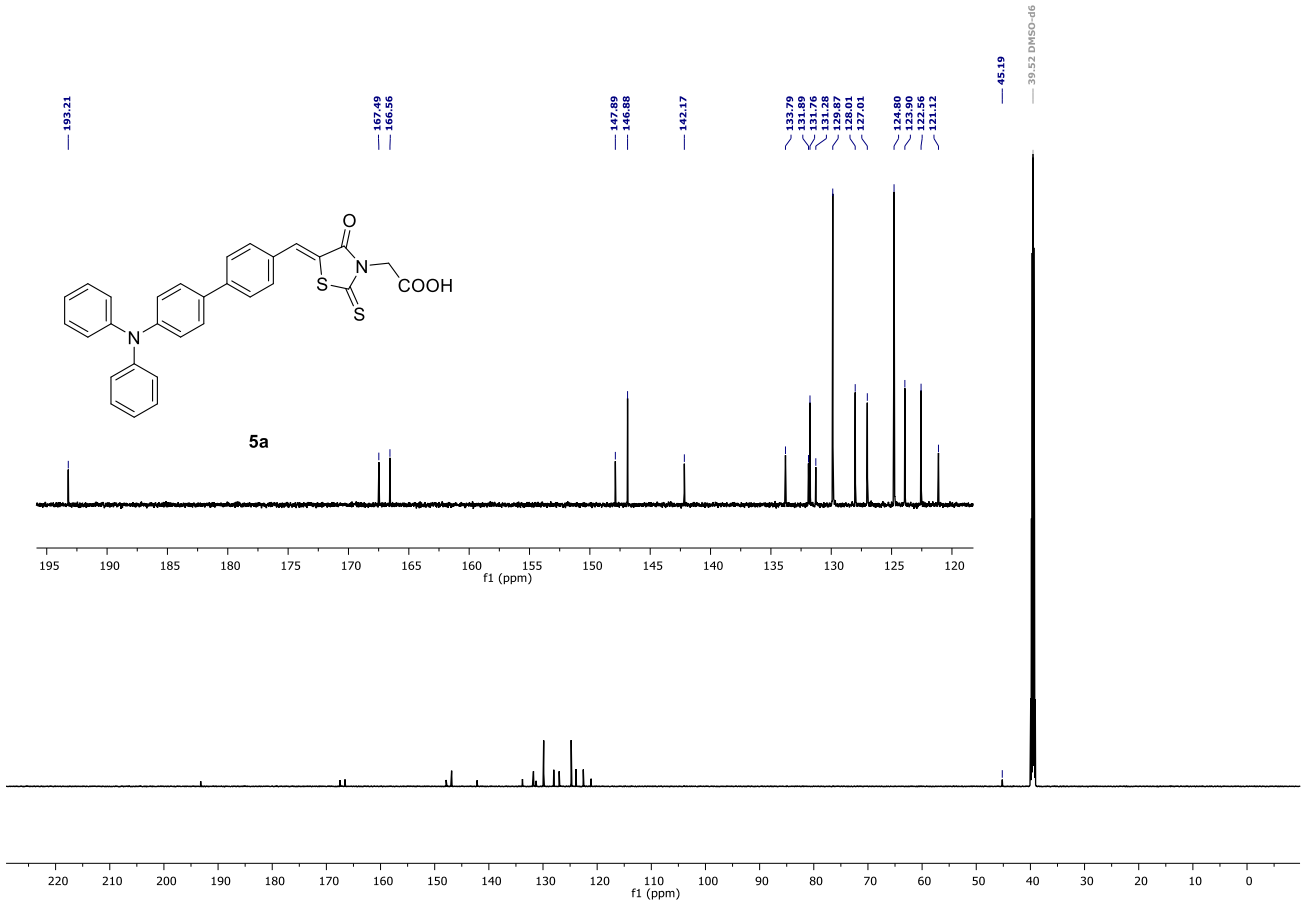


Figure 30S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***5a.***

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

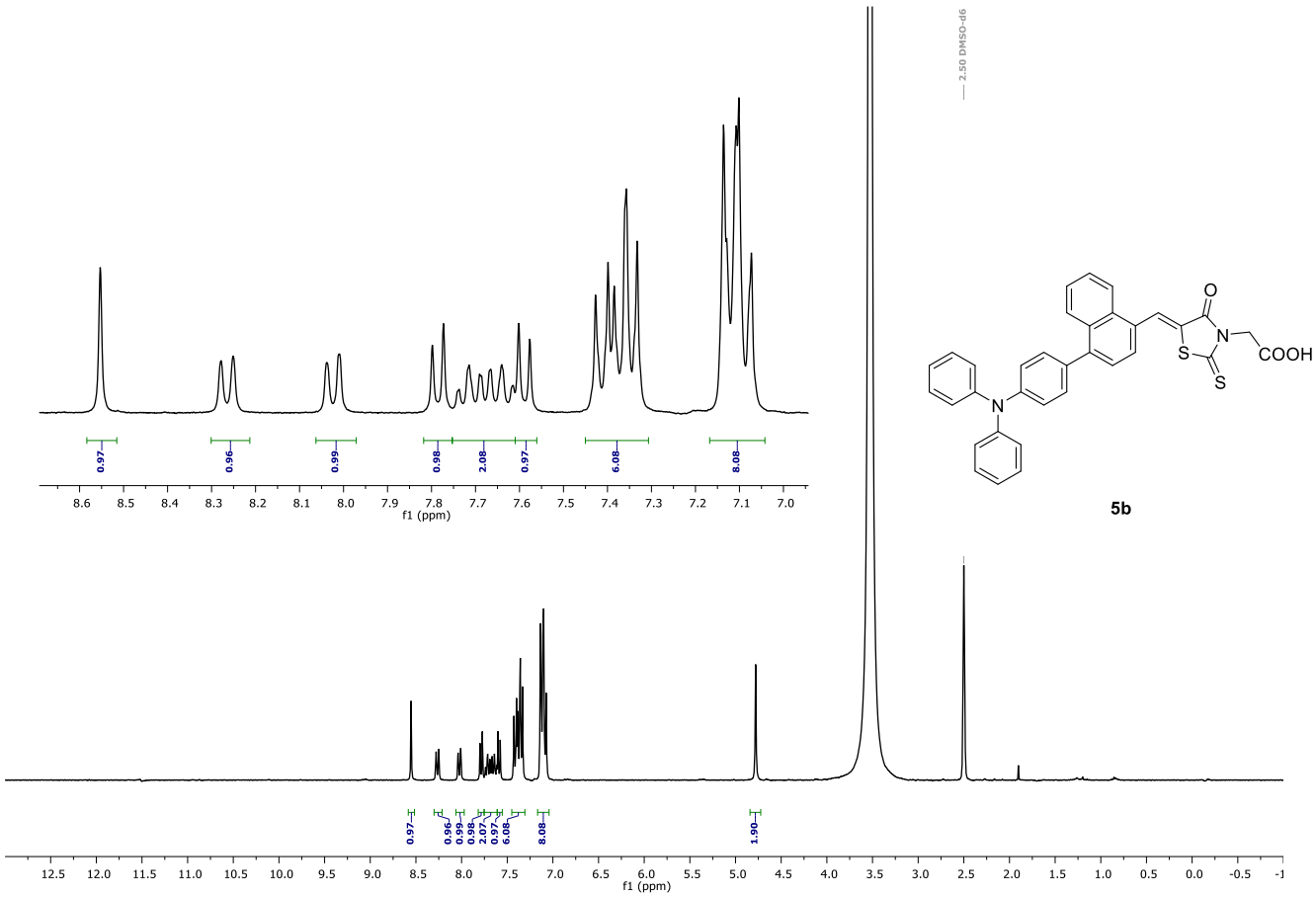


Figure 31S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***5b.***

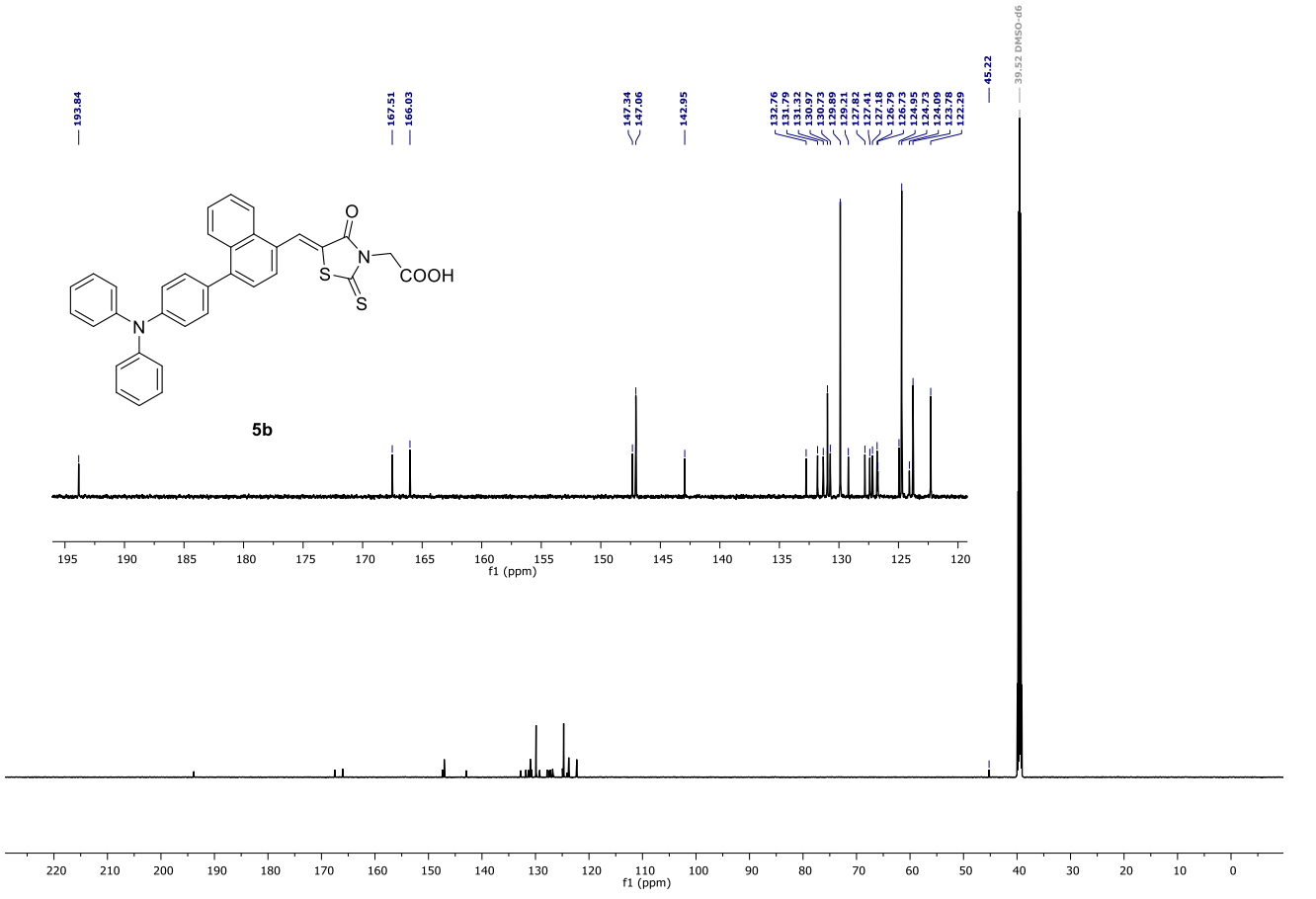


Figure 32S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***5b.***

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

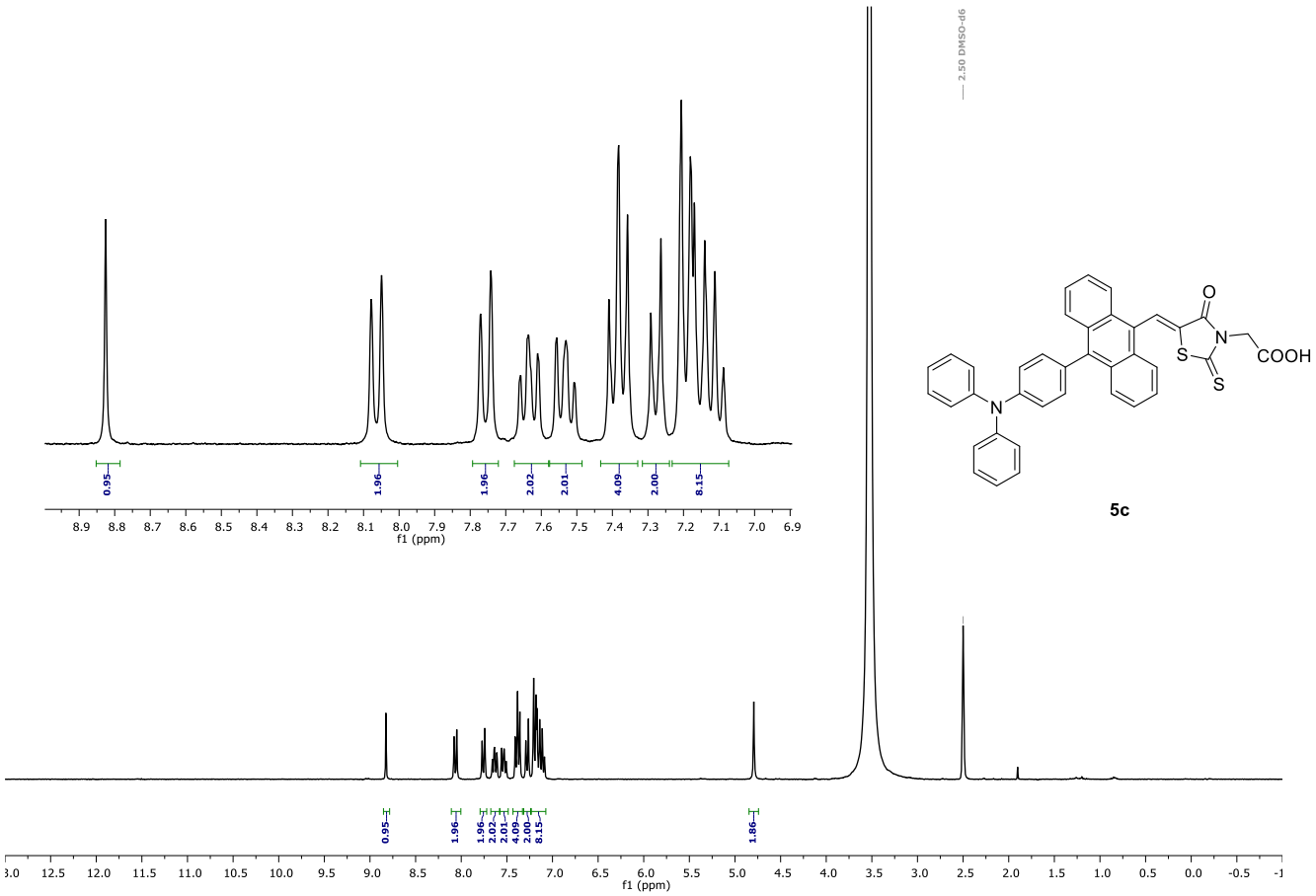


Figure 33S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***5c.***

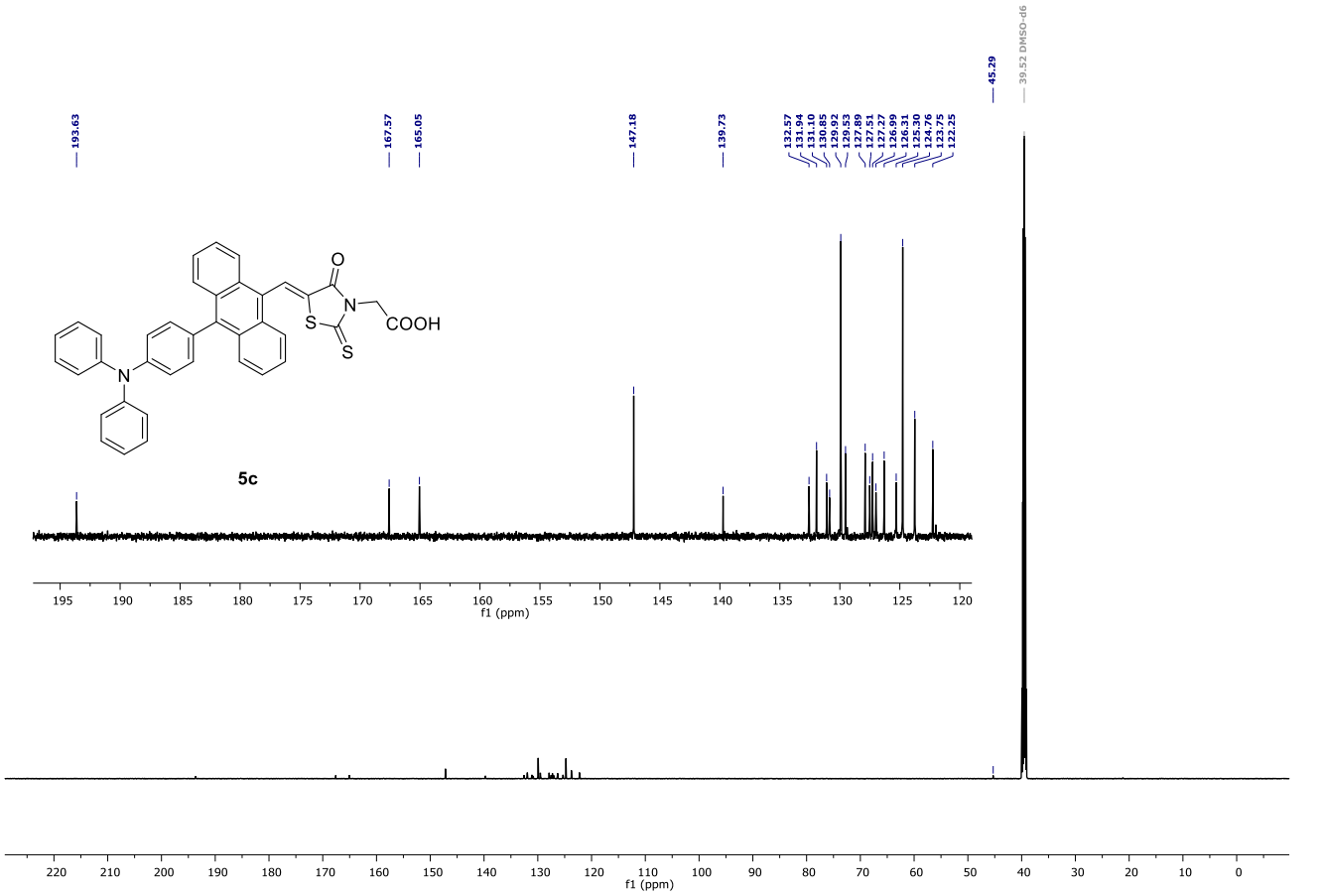


Figure 34S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***5c.***

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

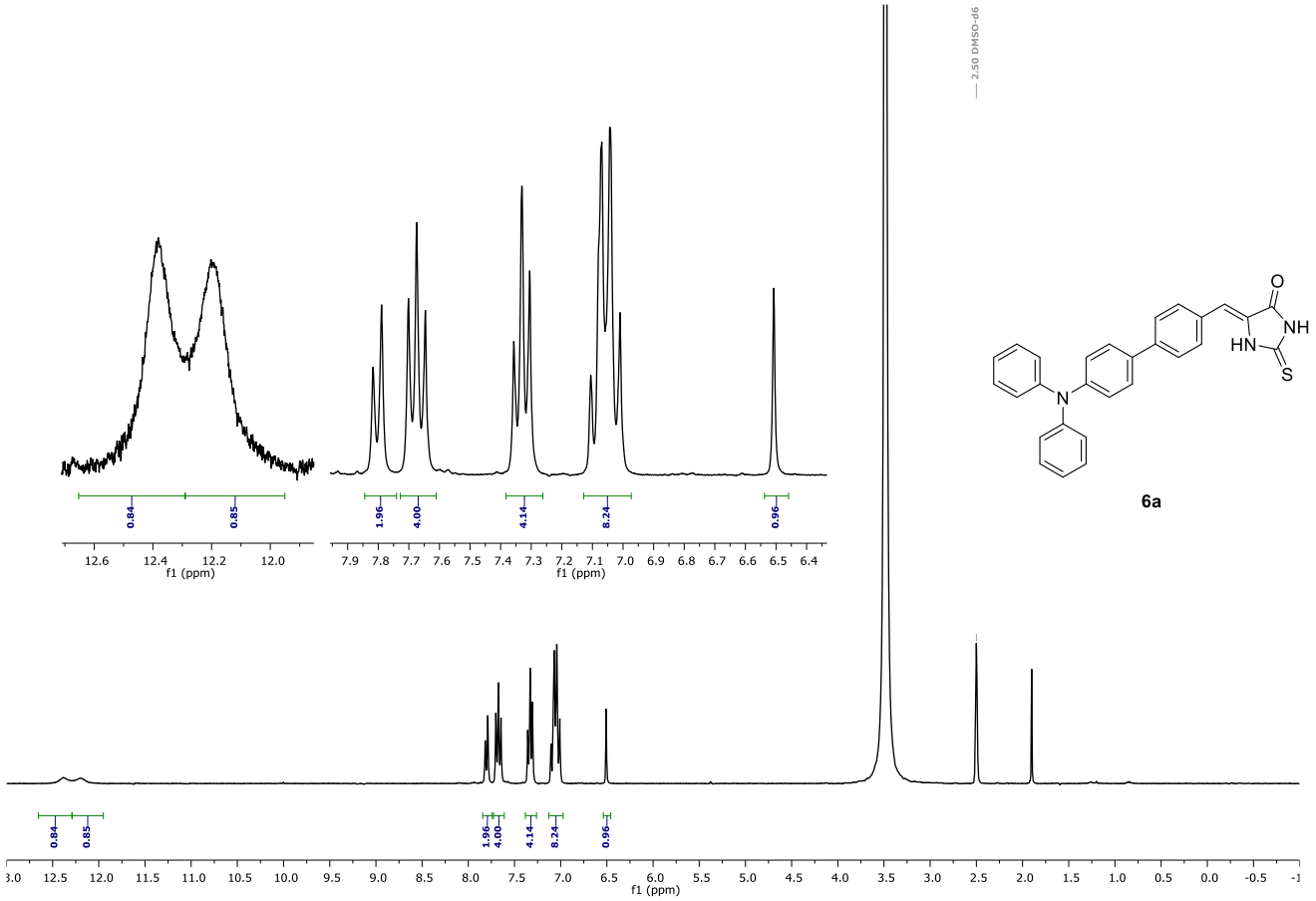


Figure 35S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***6a.***

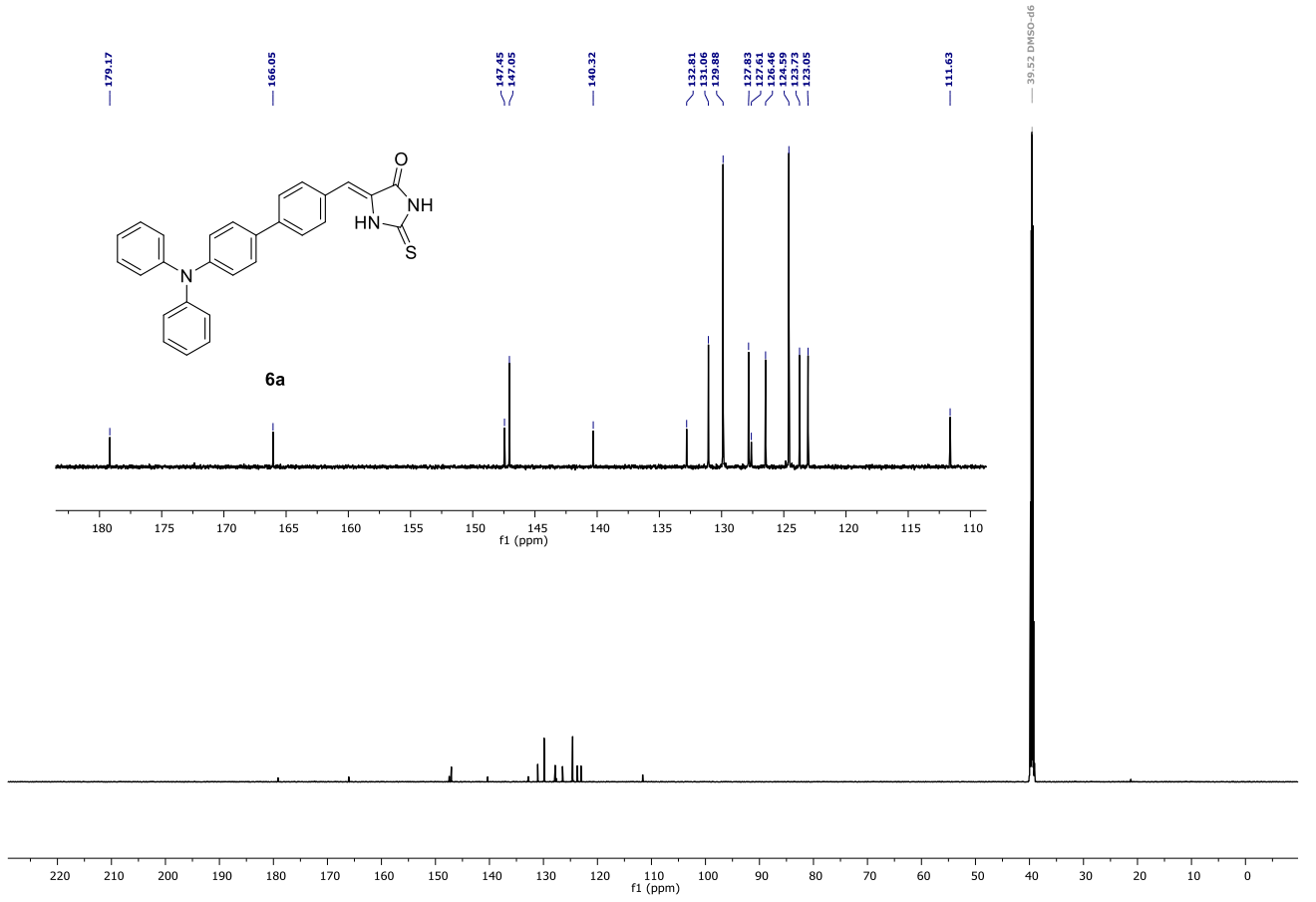


Figure 36S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***6a.***

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

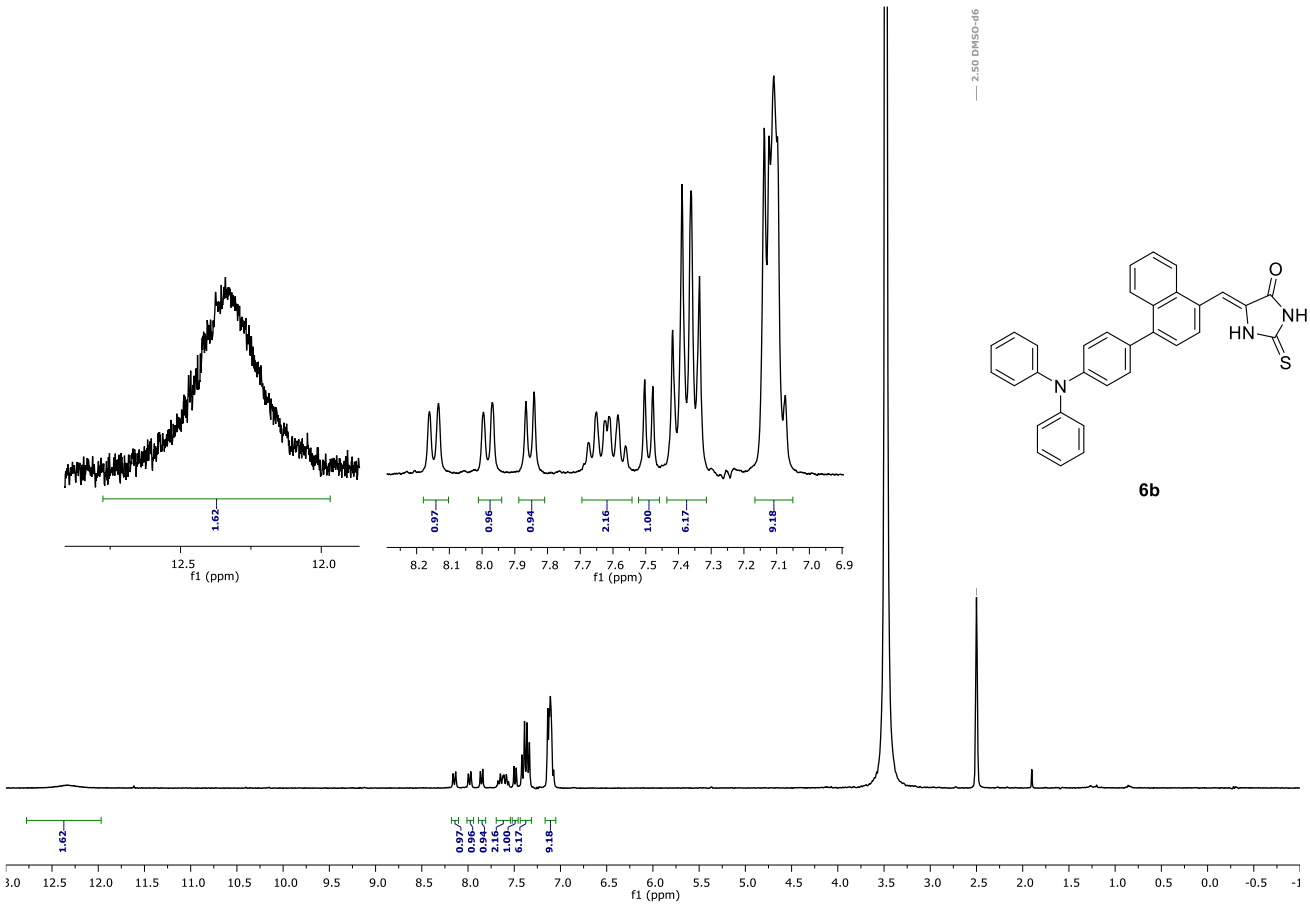


Figure 37S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***6b.***

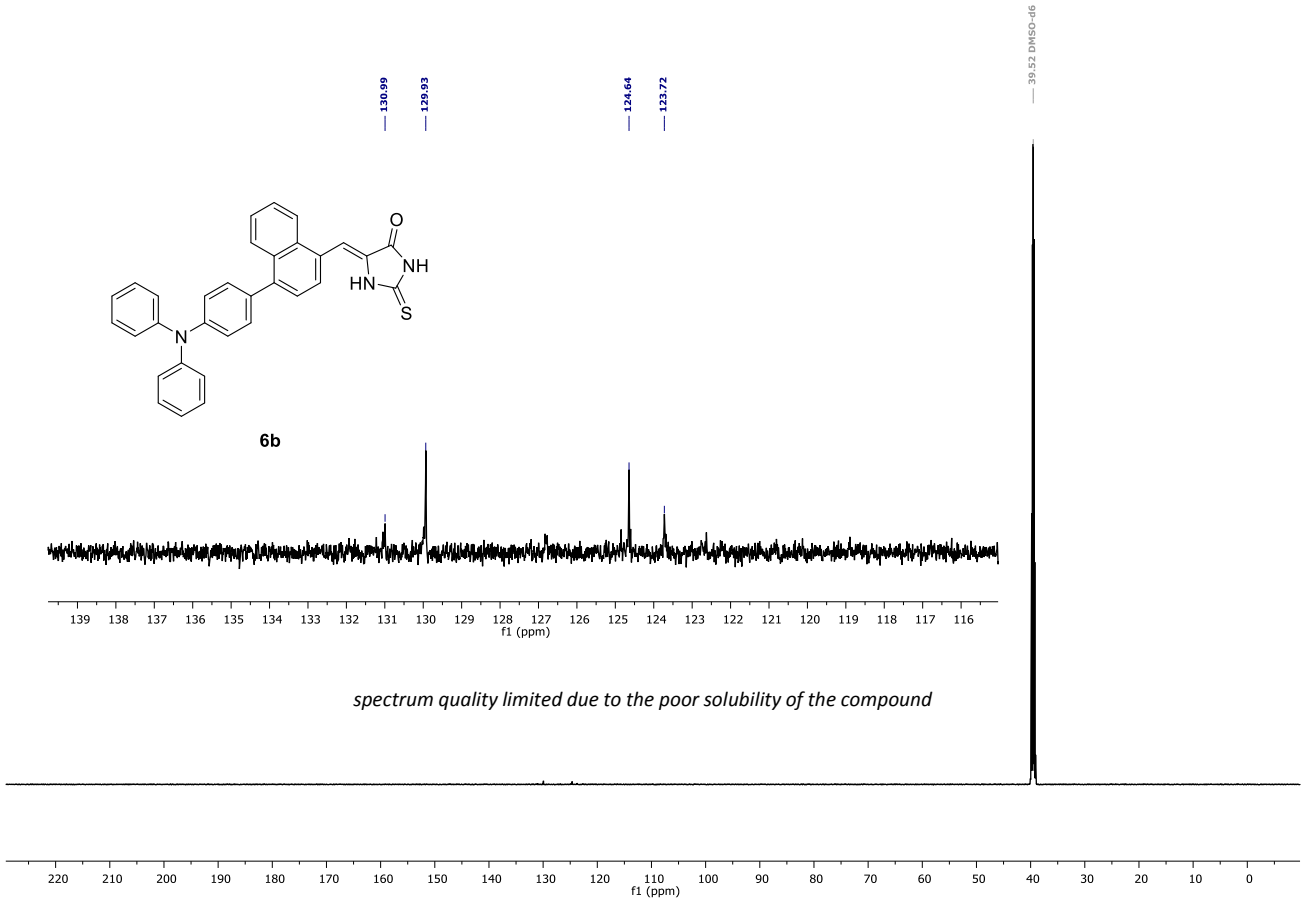


Figure 38S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***6b.***

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

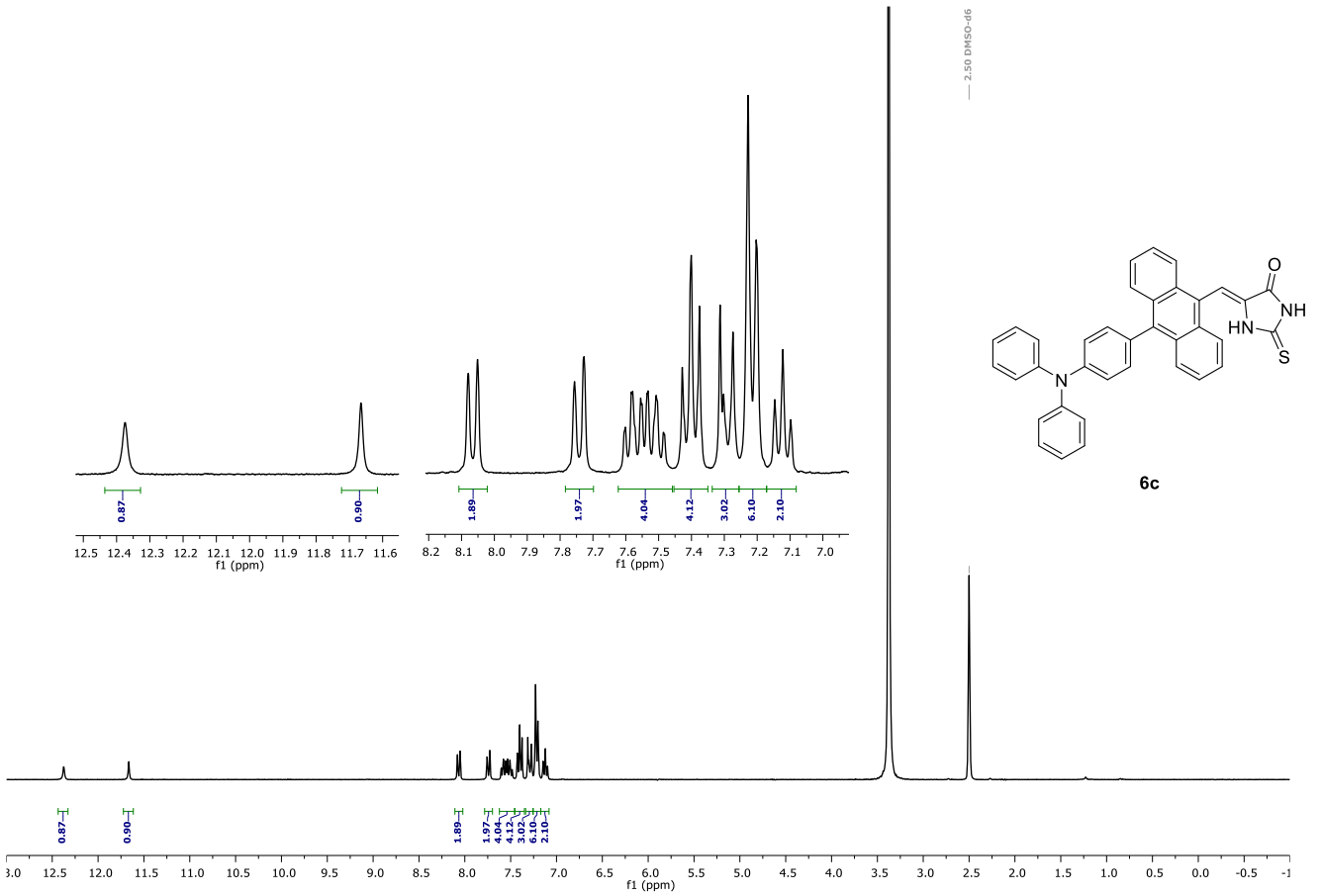


Figure 39S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***6c.***

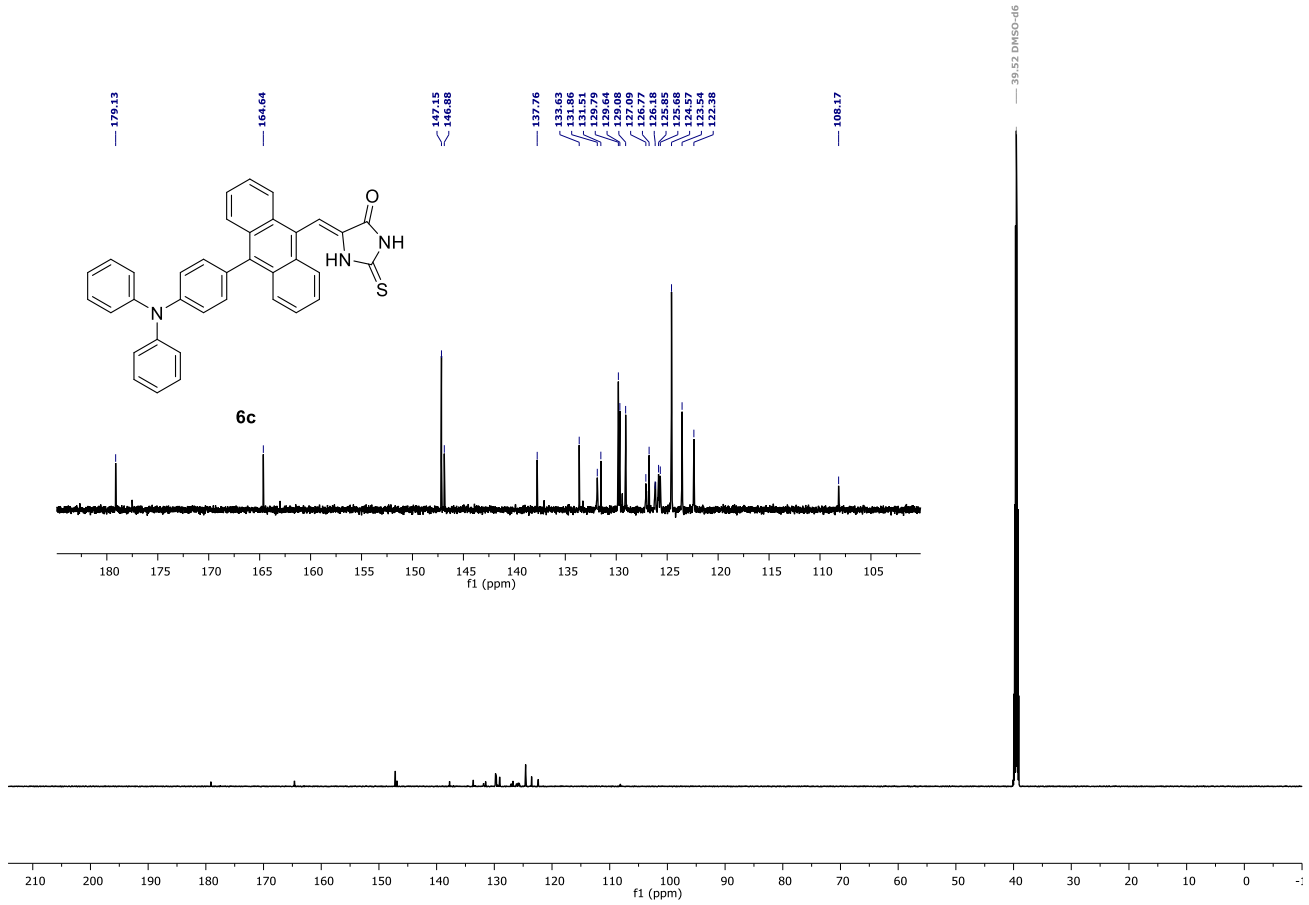


Figure 40S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***6c.***

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

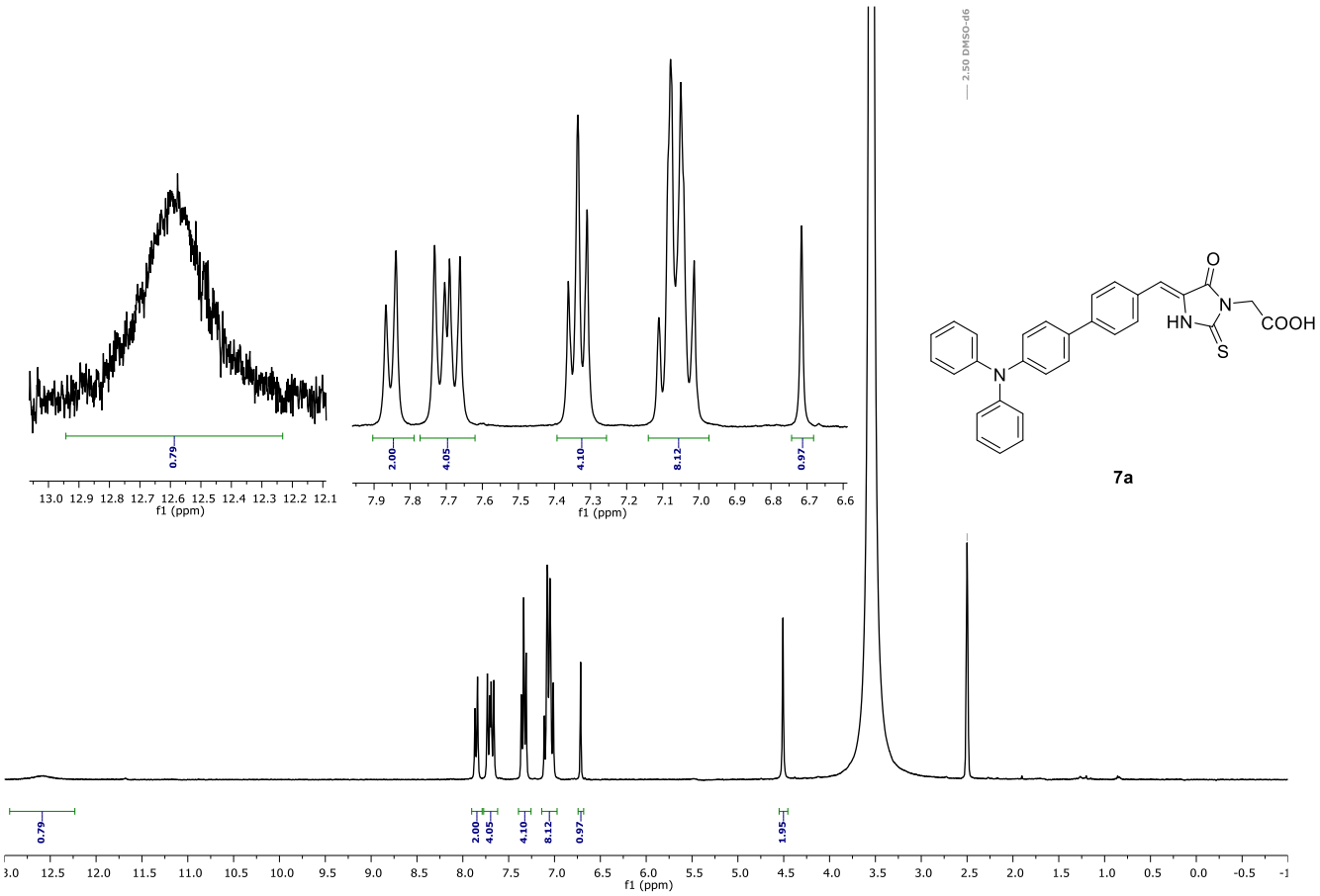


Figure 41S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***7a.***

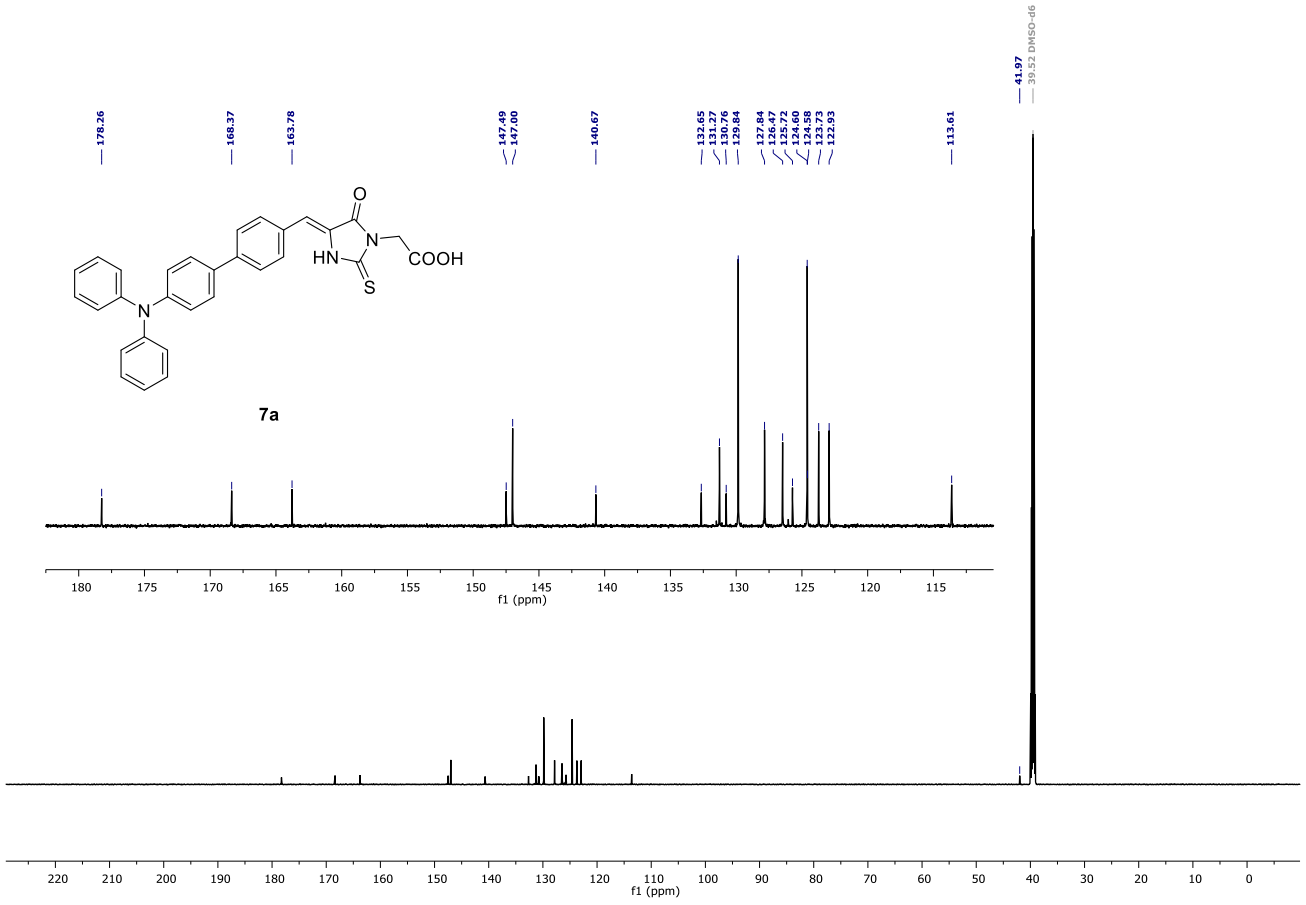


Figure 42S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***7a.***

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

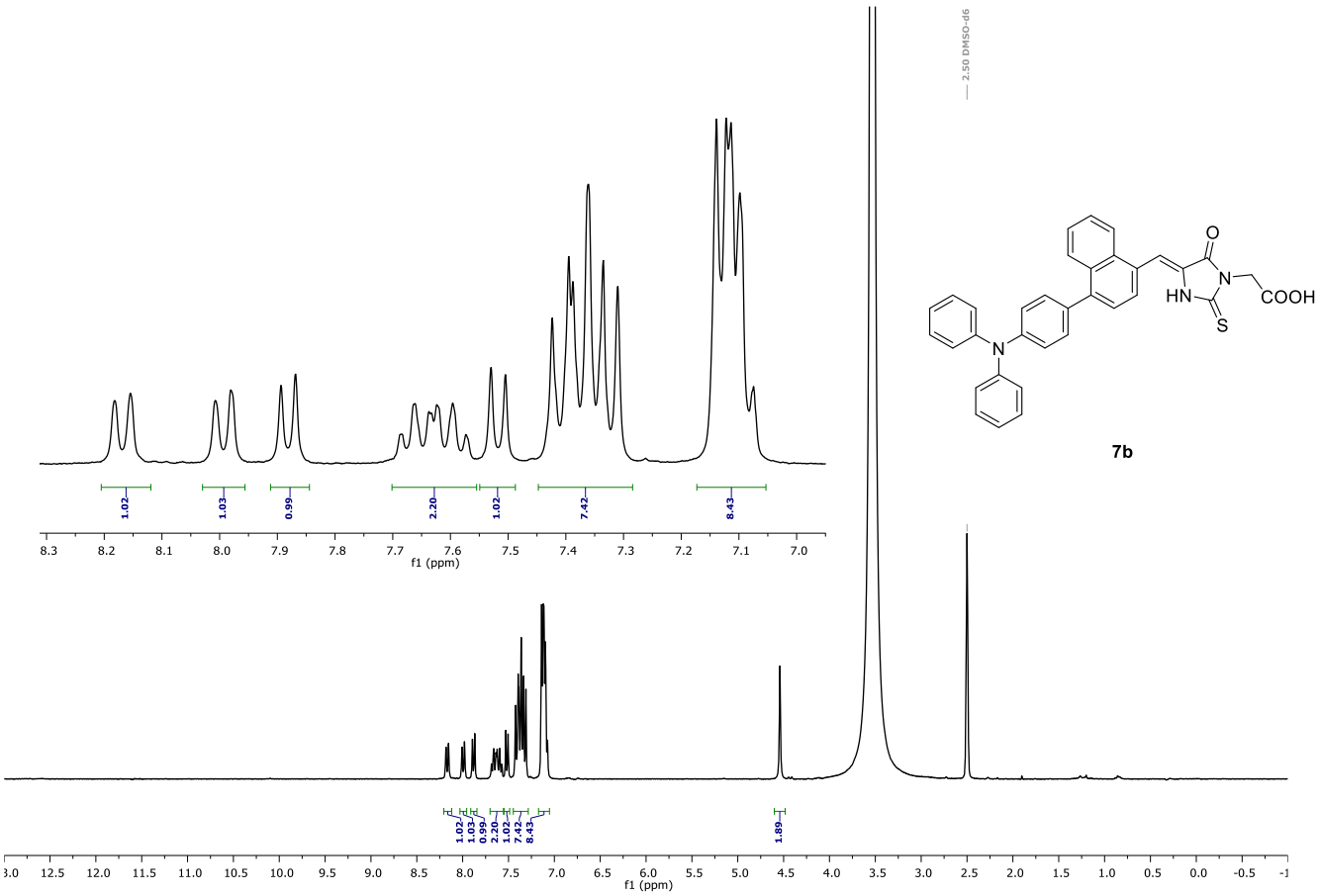


Figure 43S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***7b.***

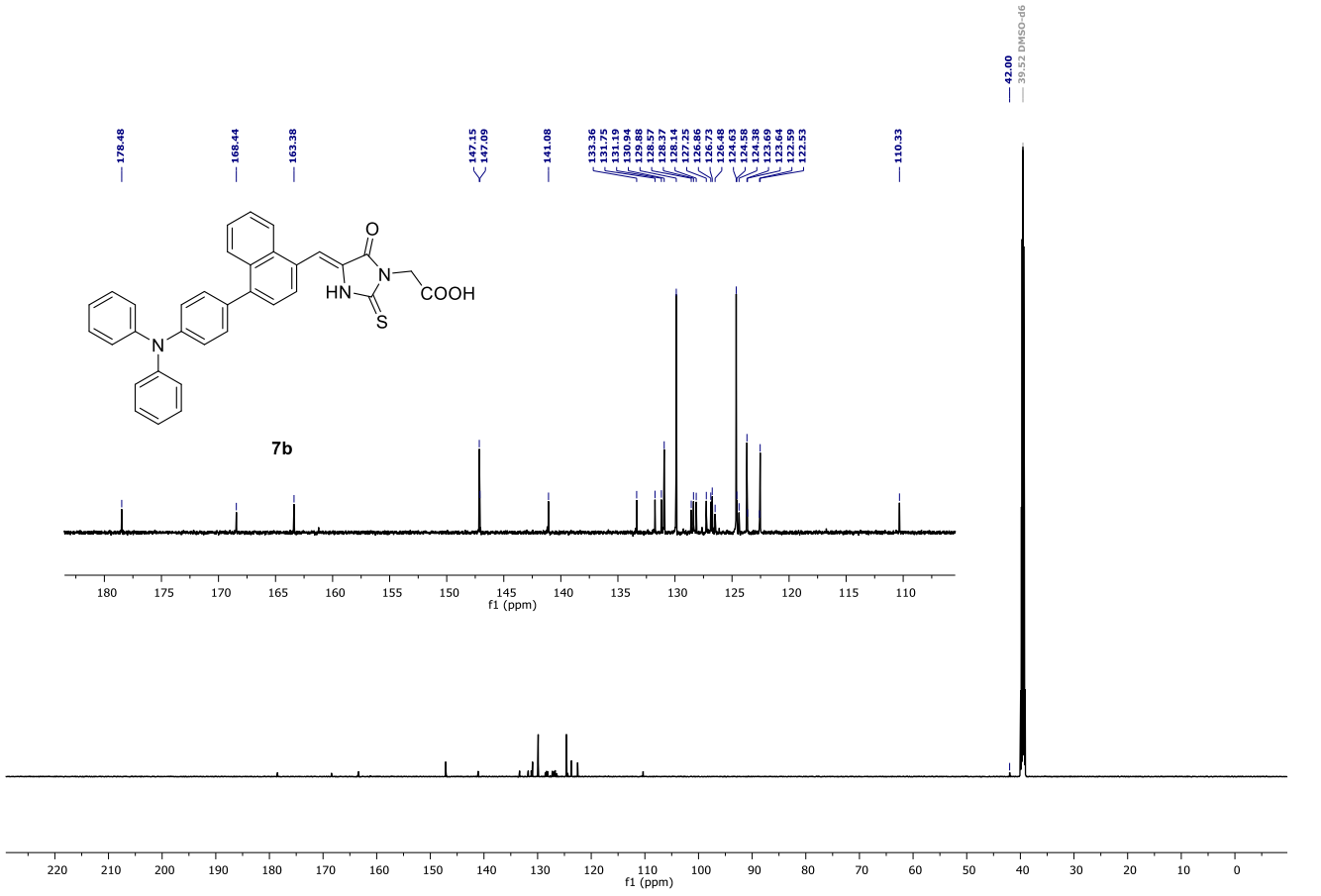


Figure 44S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***7b.***

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

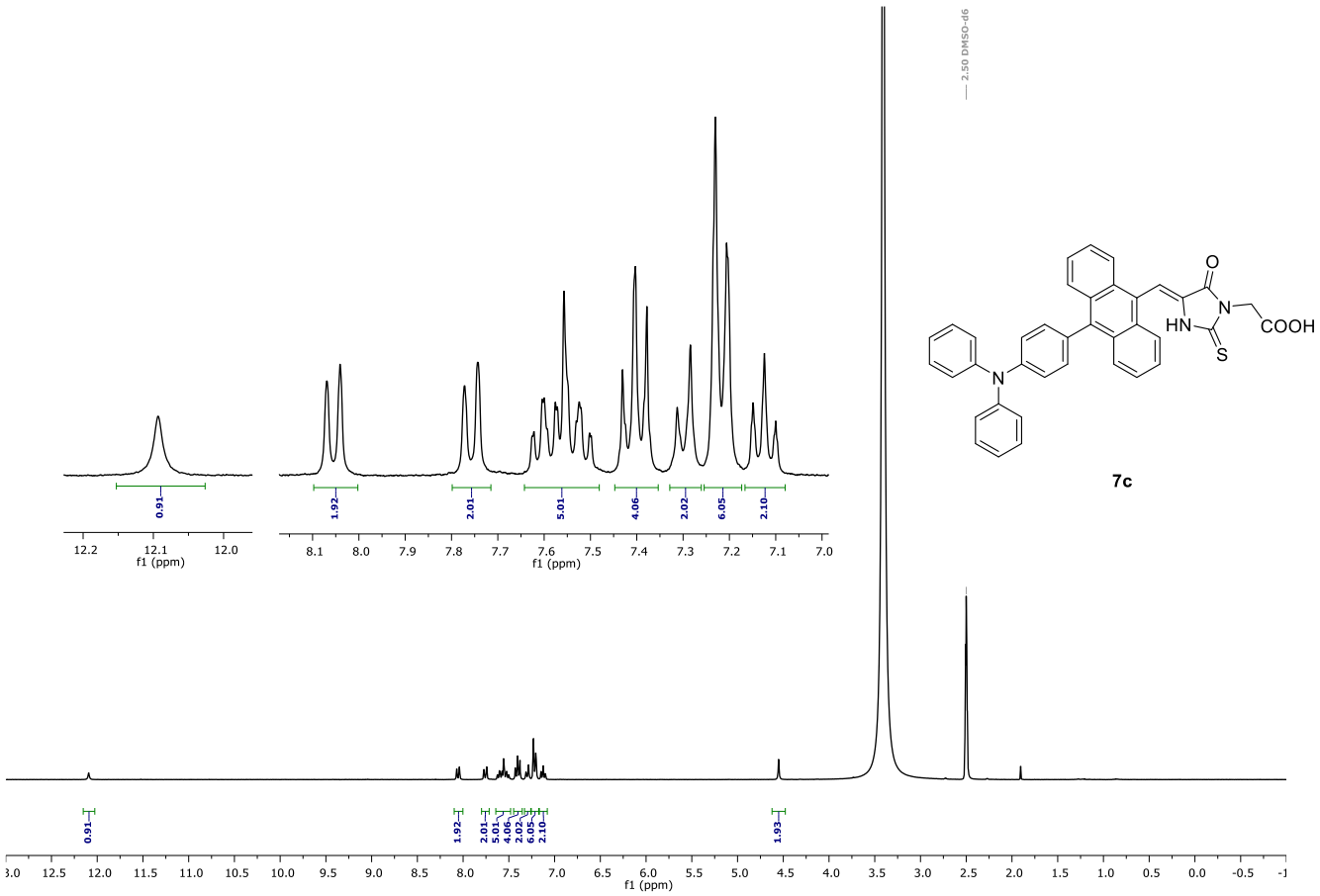


Figure 45S. *^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of* ***7c.***

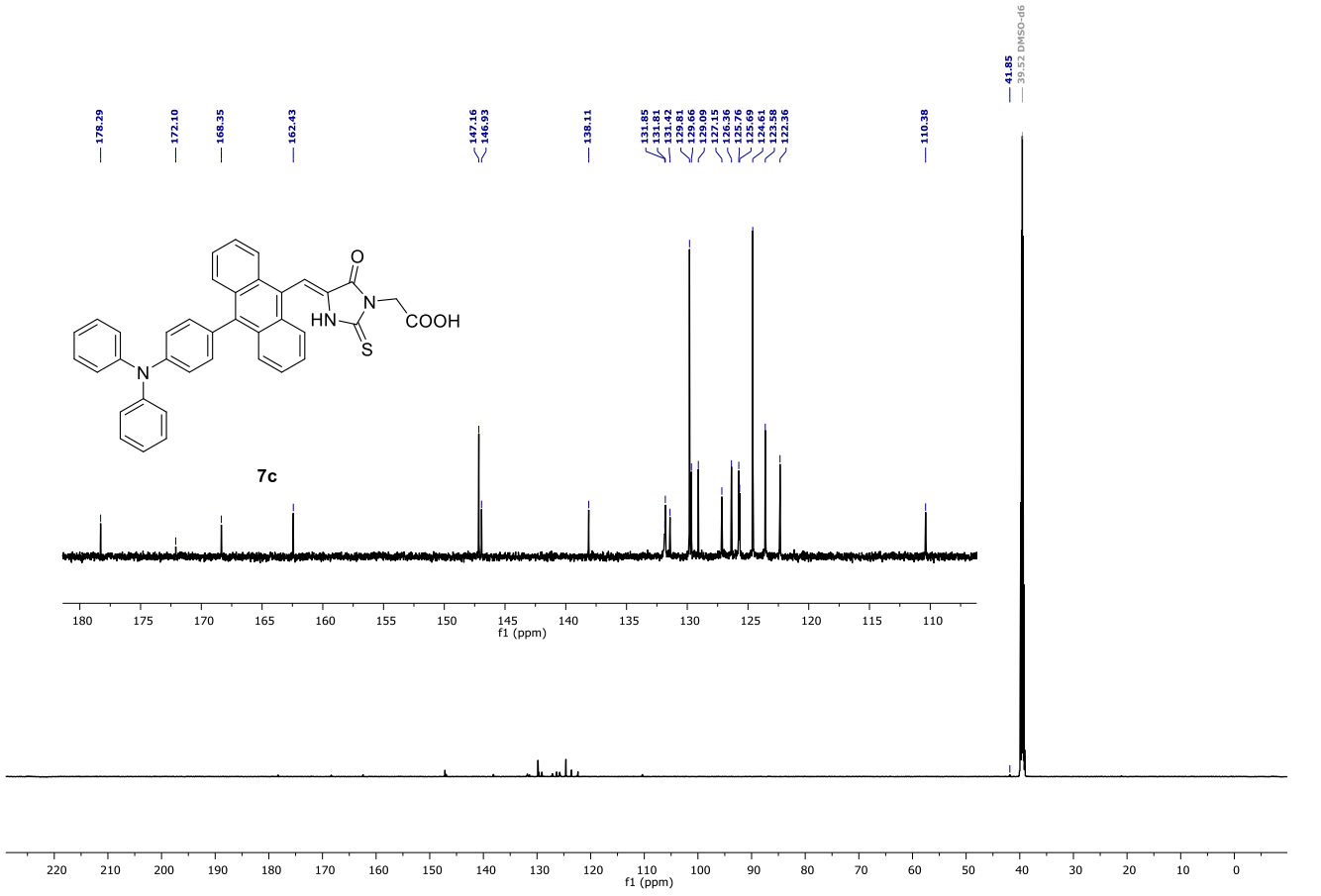


Figure 46S. *^{13}C NMR (75 MHz, DMSO-d_6, 298 K) spectrum of* ***7c.***

IR spectra

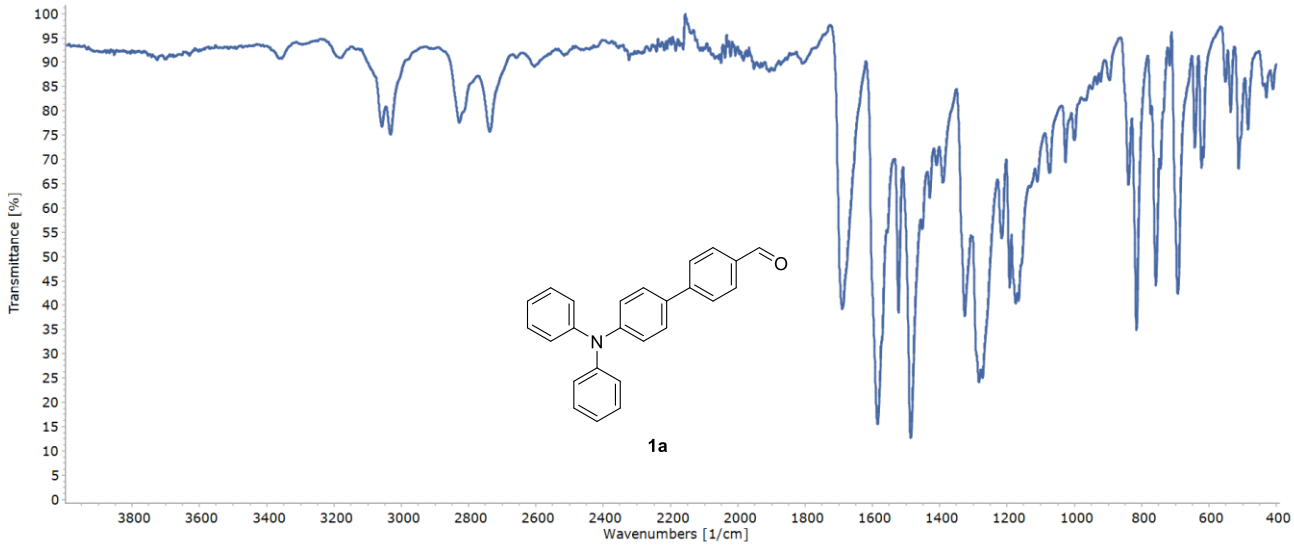


Figure 47S. *FT-IR (ATR) spectrum of* ***1a.***

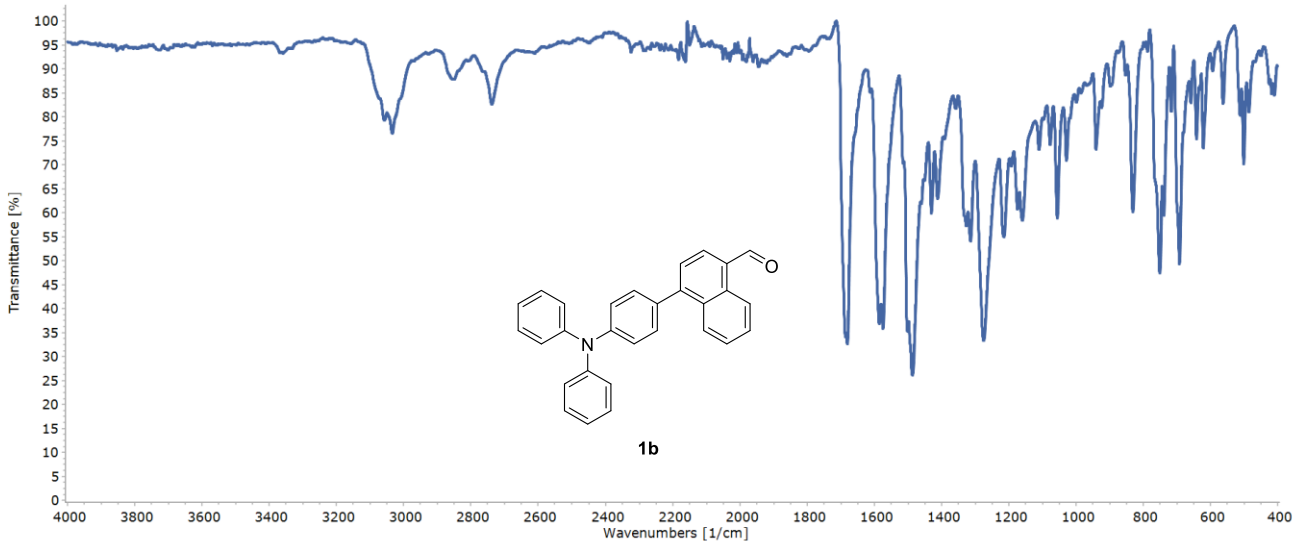


Figure 48S. *FT-IR (ATR) spectrum of* ***1b.***

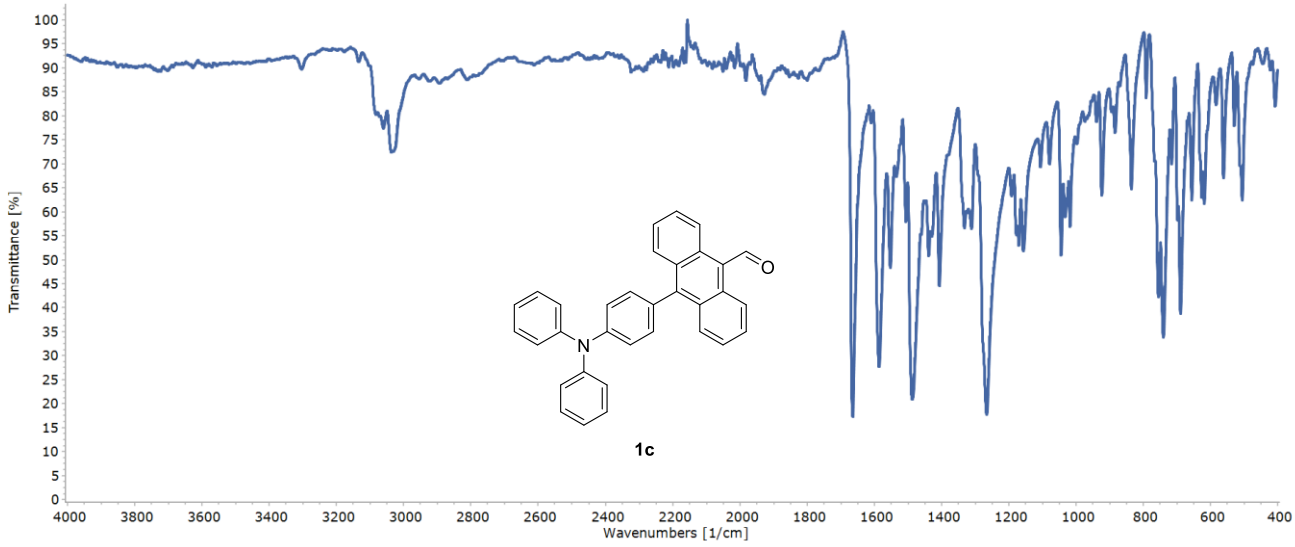


Figure 49S. *FT-IR (ATR) spectrum of* ***1c.***

IR spectra

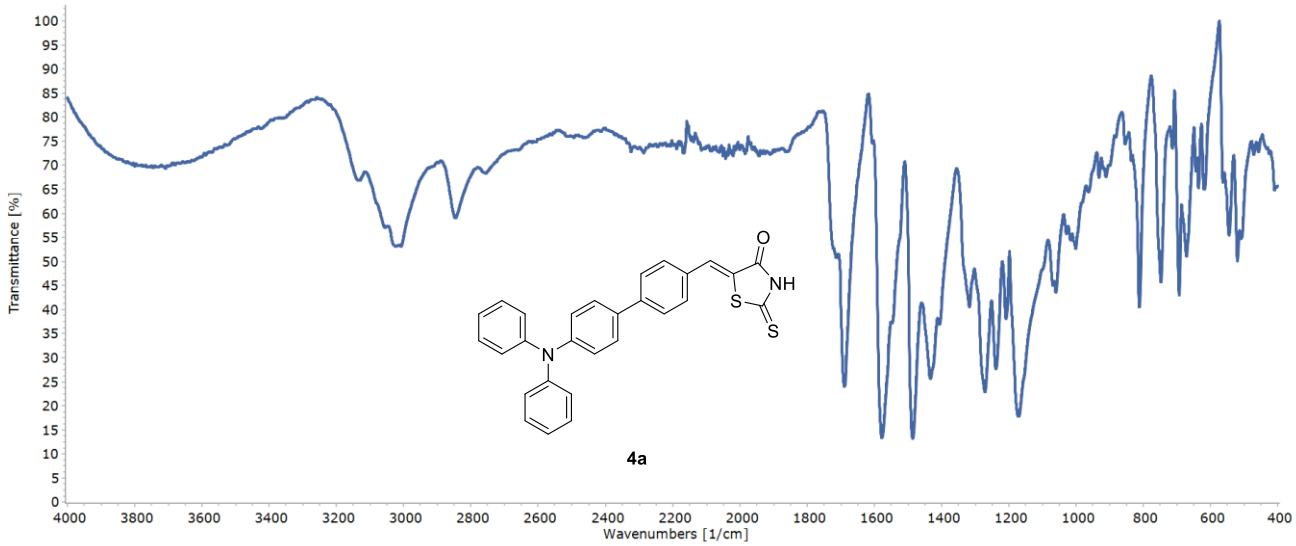


Figure 50S. *FT-IR (ATR) spectrum of* ***4a.***

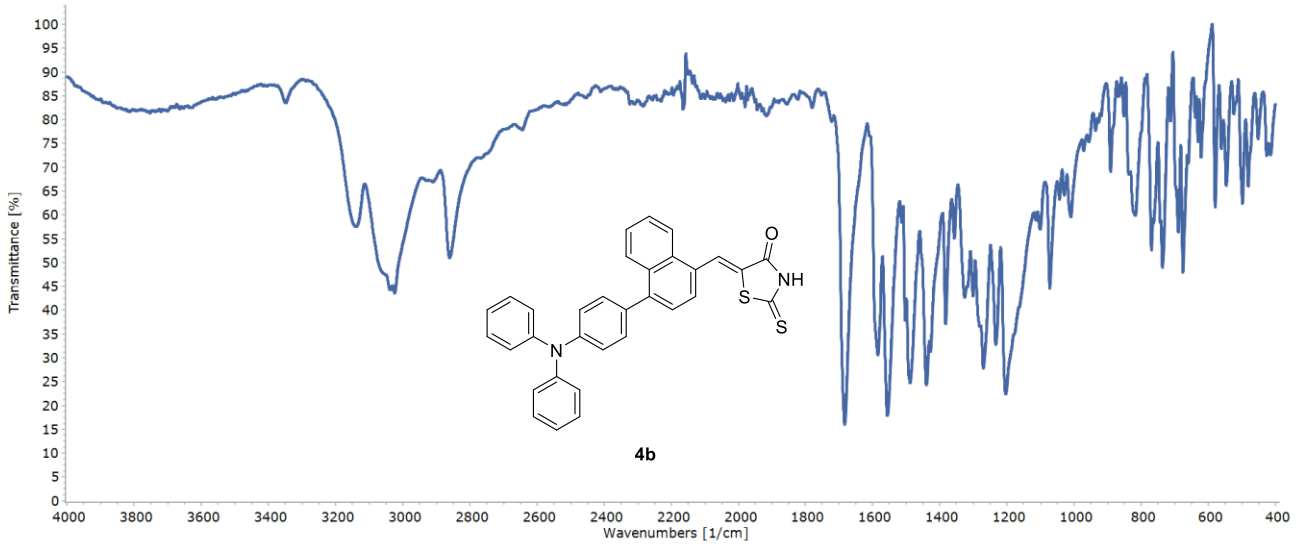


Figure 51S. *FT-IR (ATR) spectrum of* ***4b.***

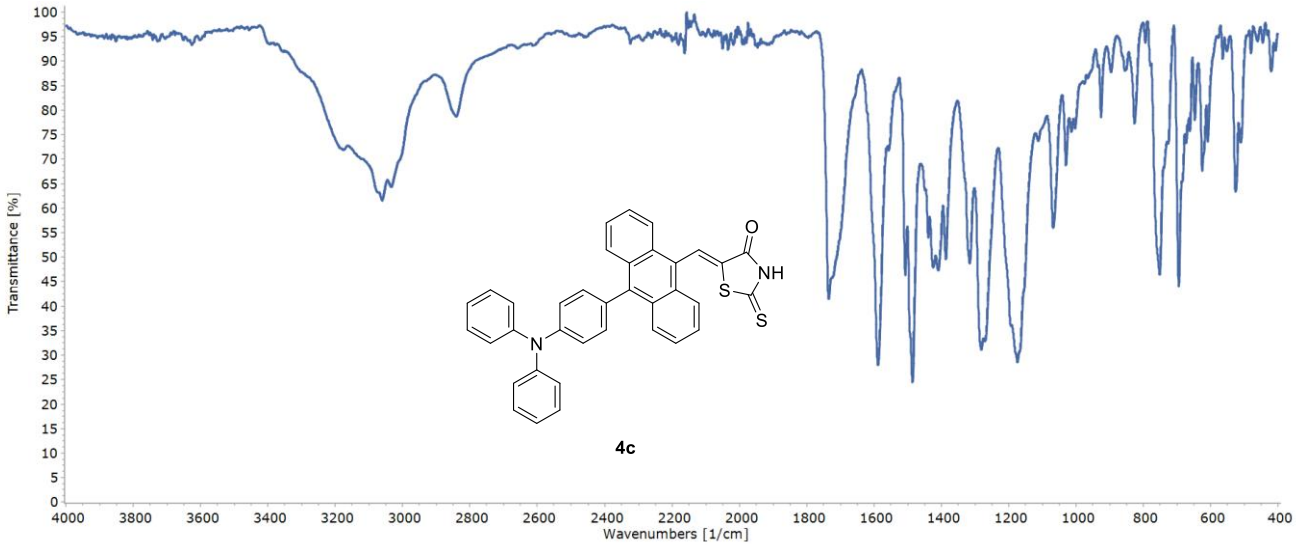


Figure 52S. *FT-IR (ATR) spectrum of* ***4c.***

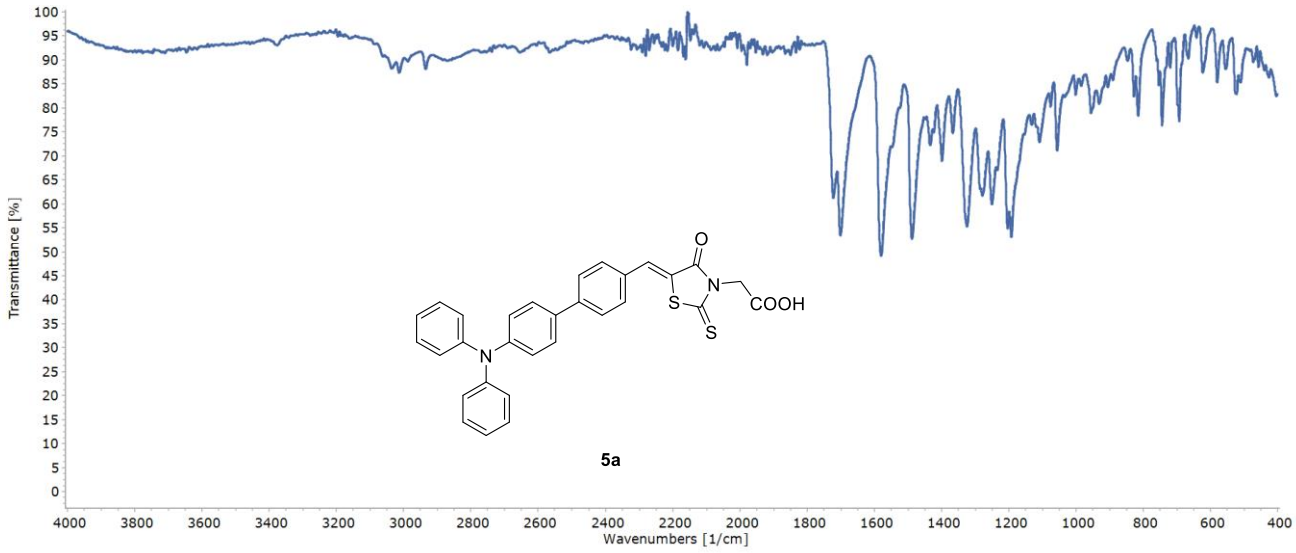


Figure 53S. *FT-IR (ATR) spectrum of* ***5a.***

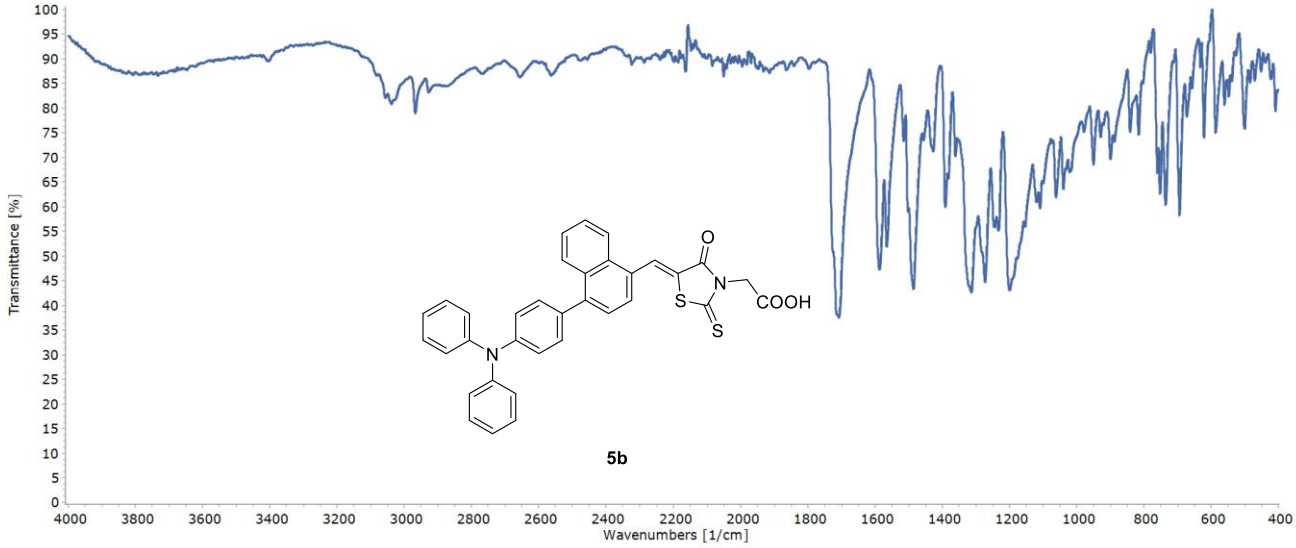


Figure 54S. *FT-IR (ATR) spectrum of* ***5b.***

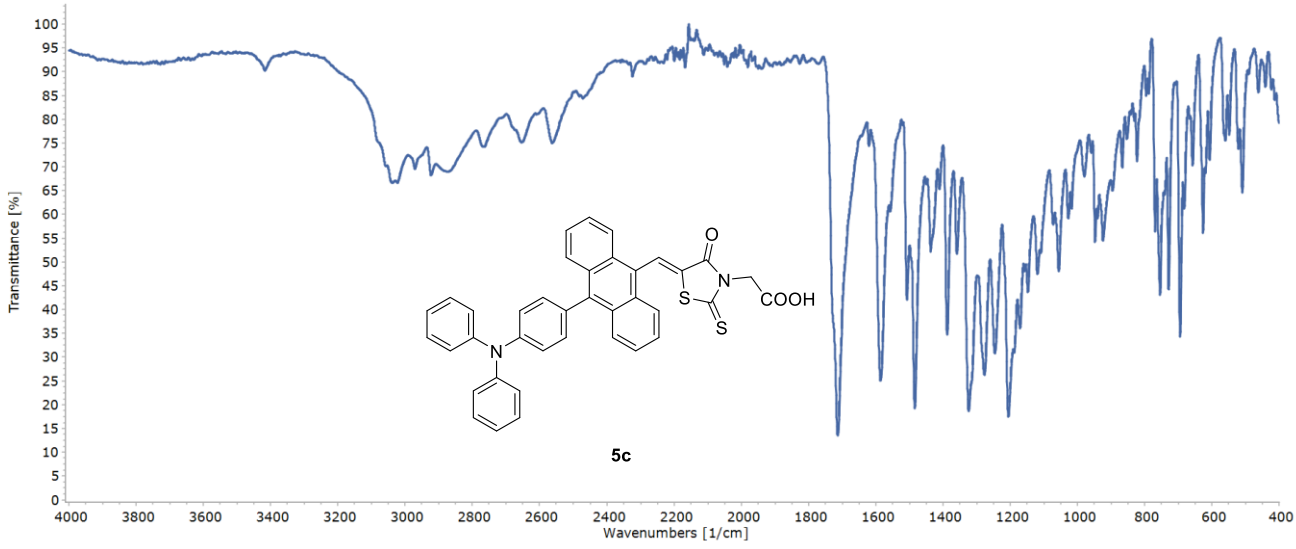


Figure 55S. *FT-IR (ATR) spectrum of* ***5c.***

IR spectra

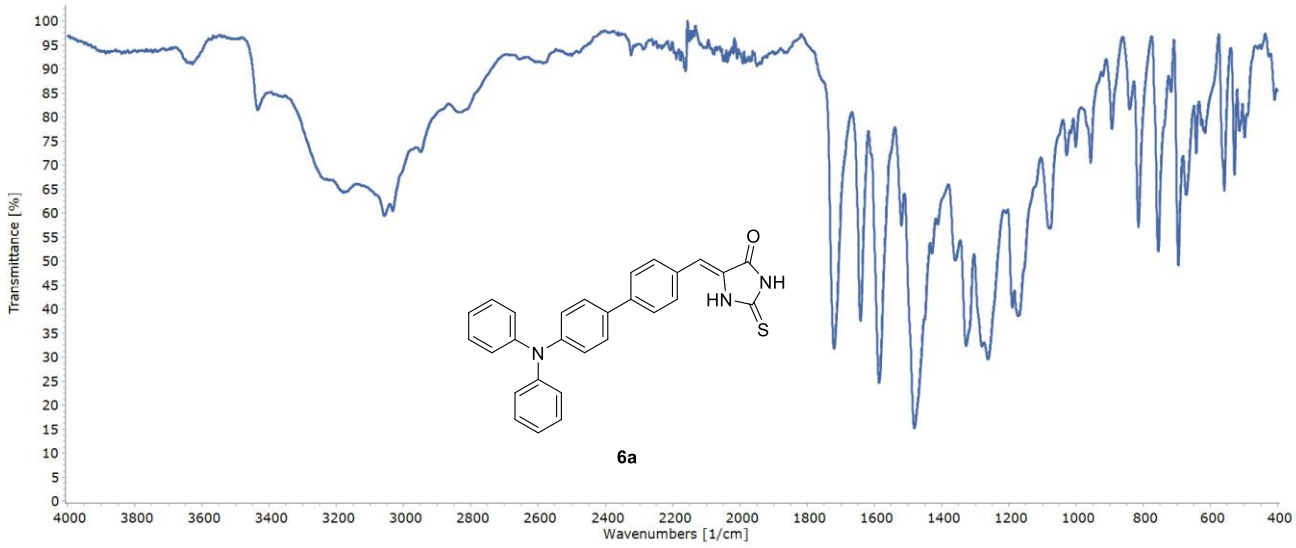


Figure 56S. *FT-IR (ATR) spectrum of* ***6a.***

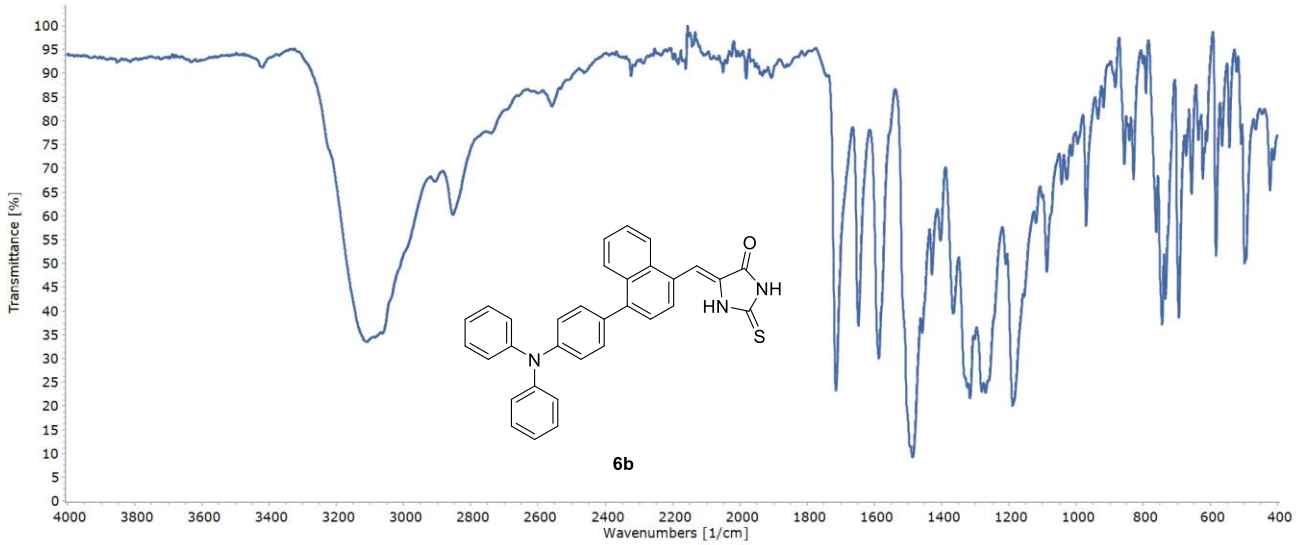


Figure 57S. *FT-IR (ATR) spectrum of* ***6b.***

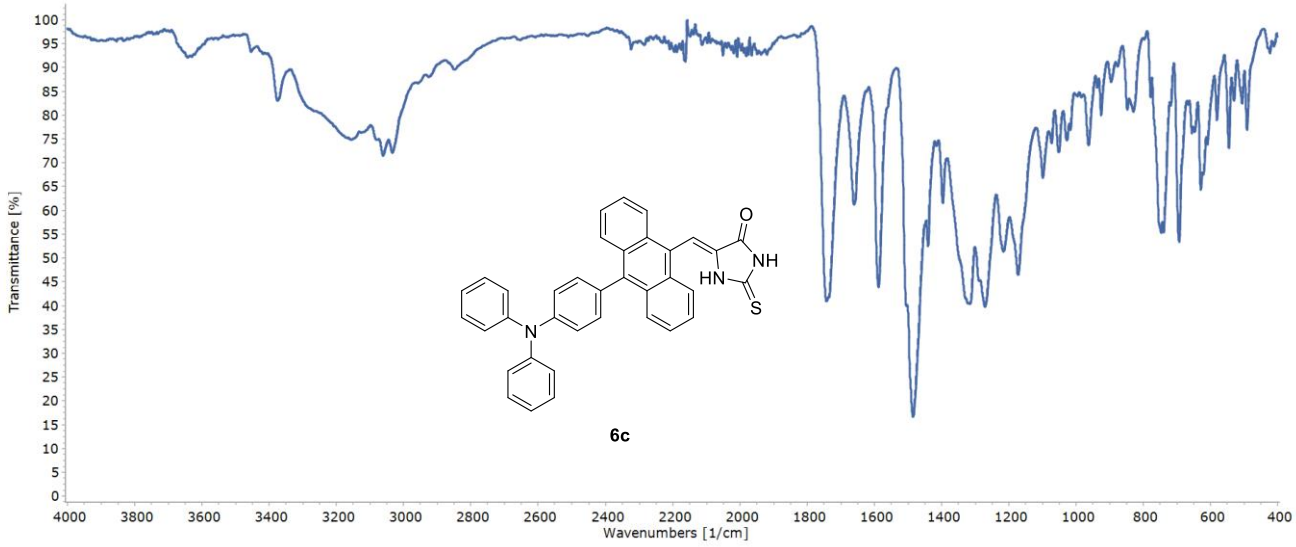


Figure 58S. *FT-IR (ATR) spectrum of* ***6c.***

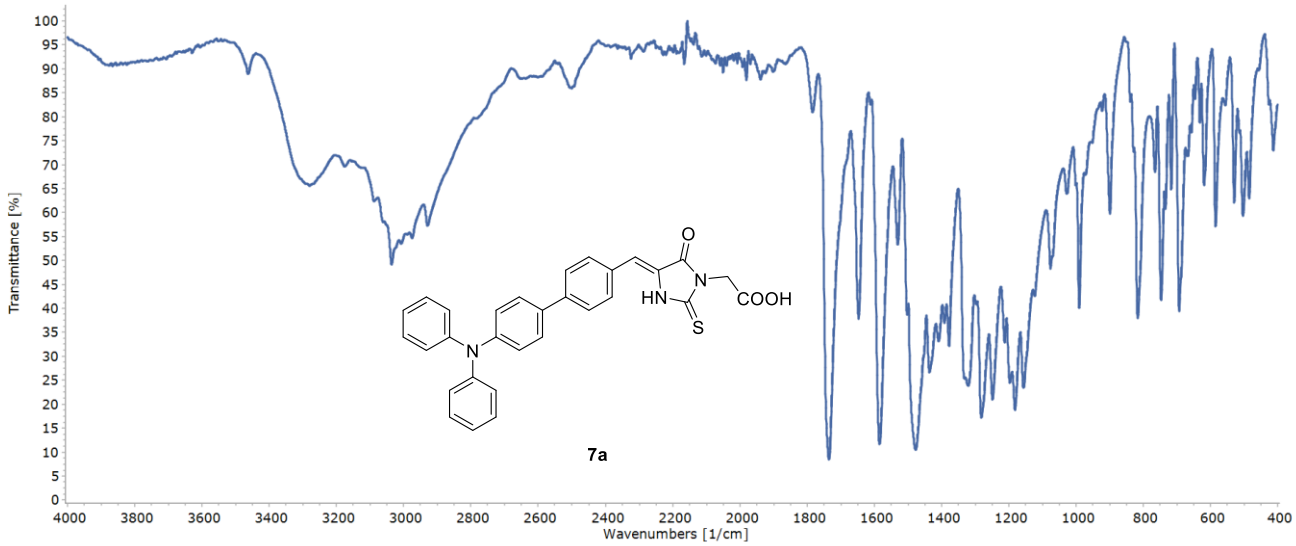


Figure 59S. *FT-IR (ATR) spectrum of* ***7a.***

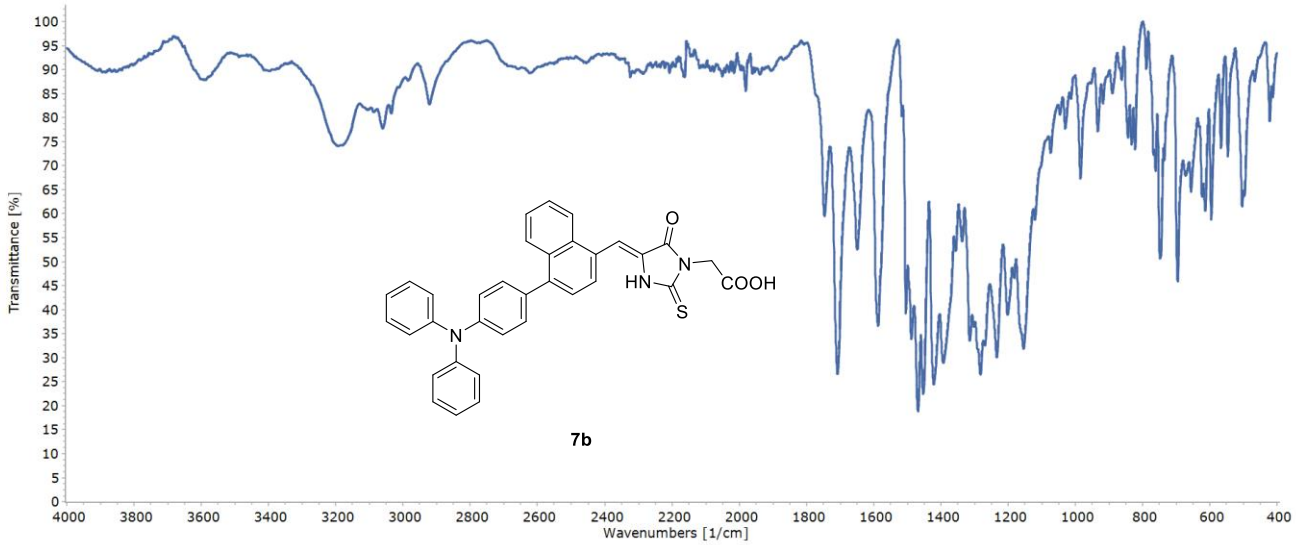


Figure 60S. *FT-IR (ATR) spectrum of* ***7b.***

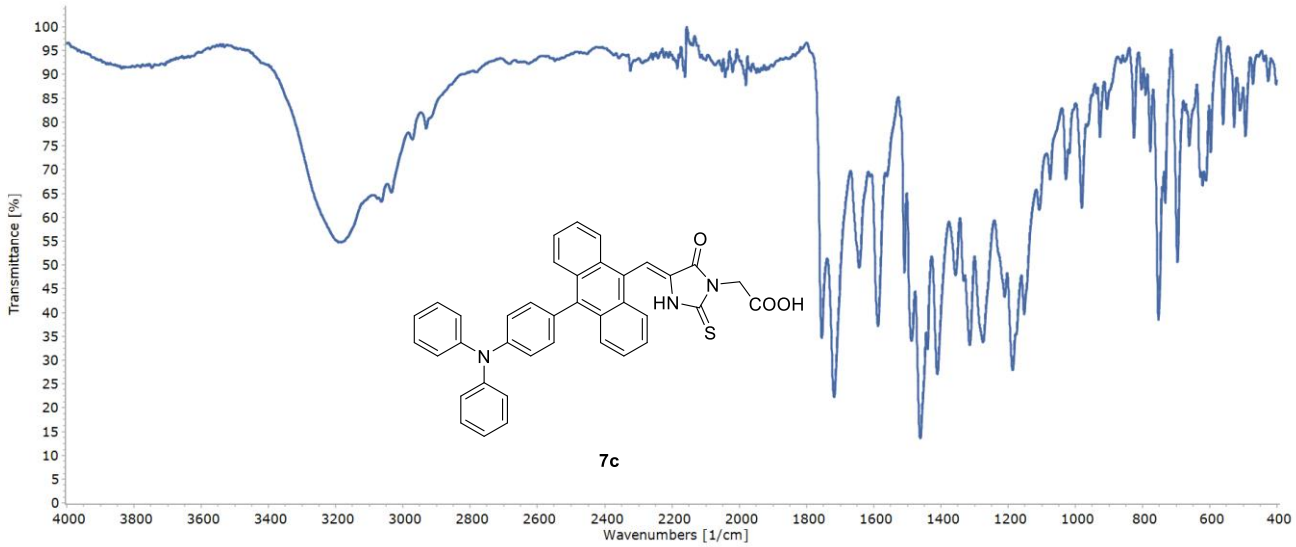


Figure 61S. *FT-IR (ATR) spectrum of* ***7c.***

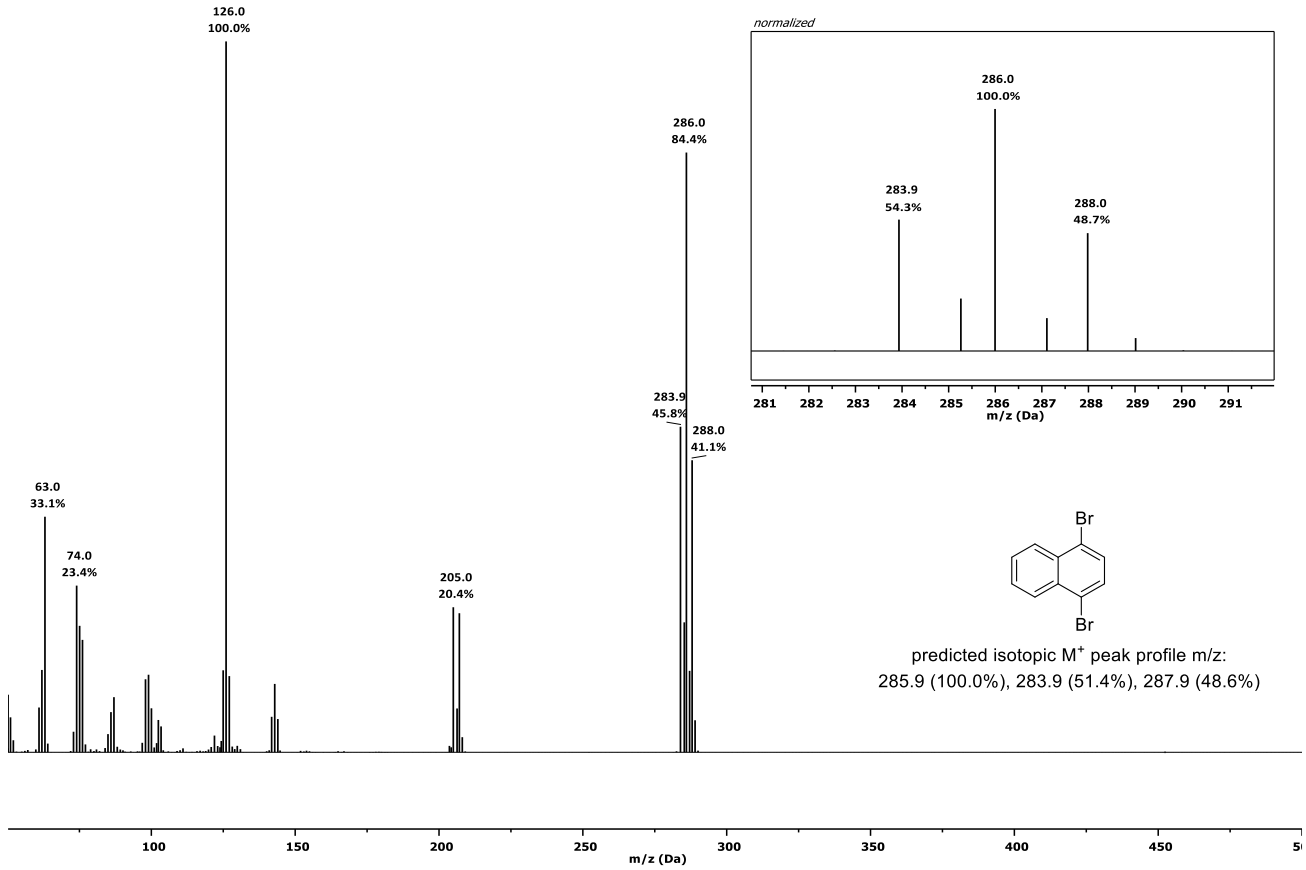


Figure 62S. *EI-LRMS spectrum of* ***1,4-dibromonaphthalene.***

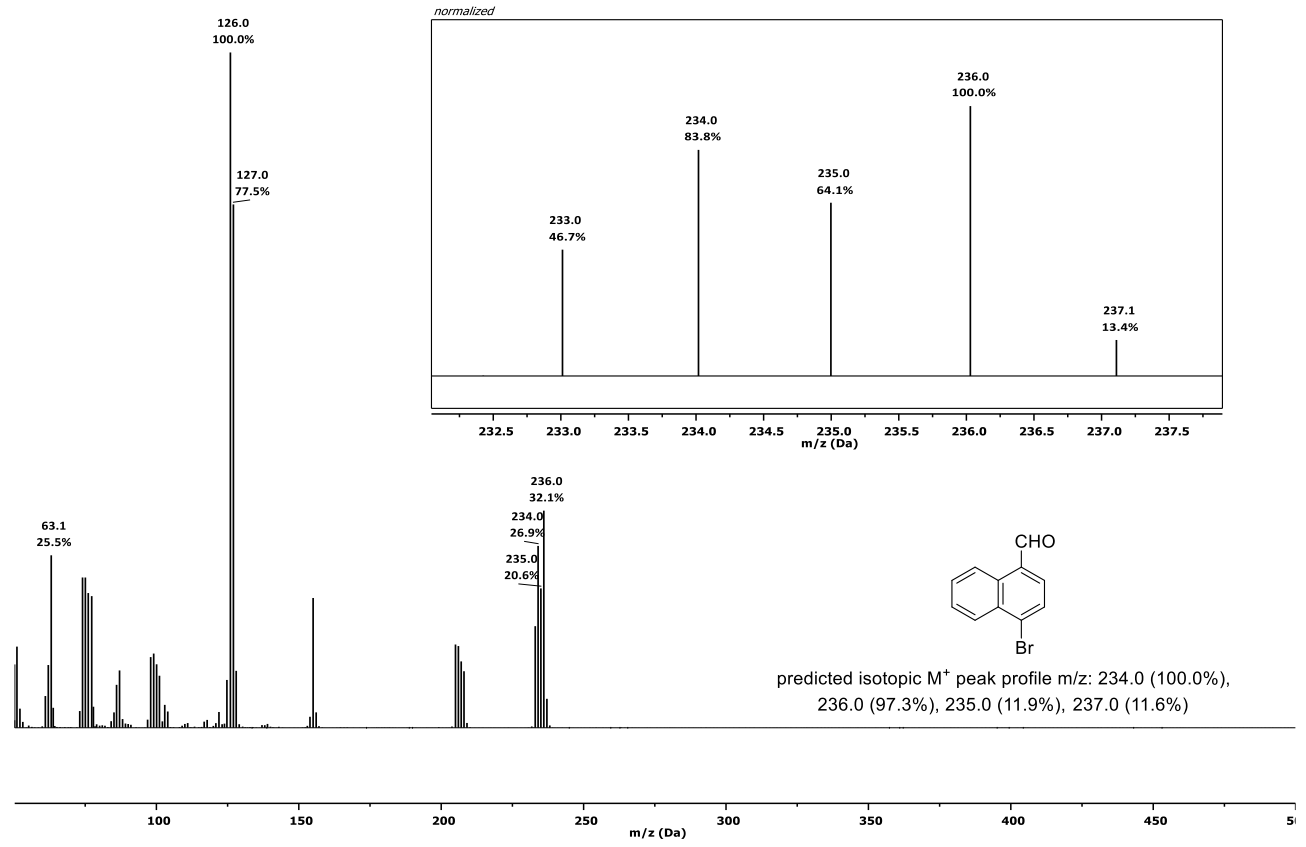


Figure 63S. *EI-LRMS spectrum of* ***4-bromo-1-naphthalenecarbaldehyde.***

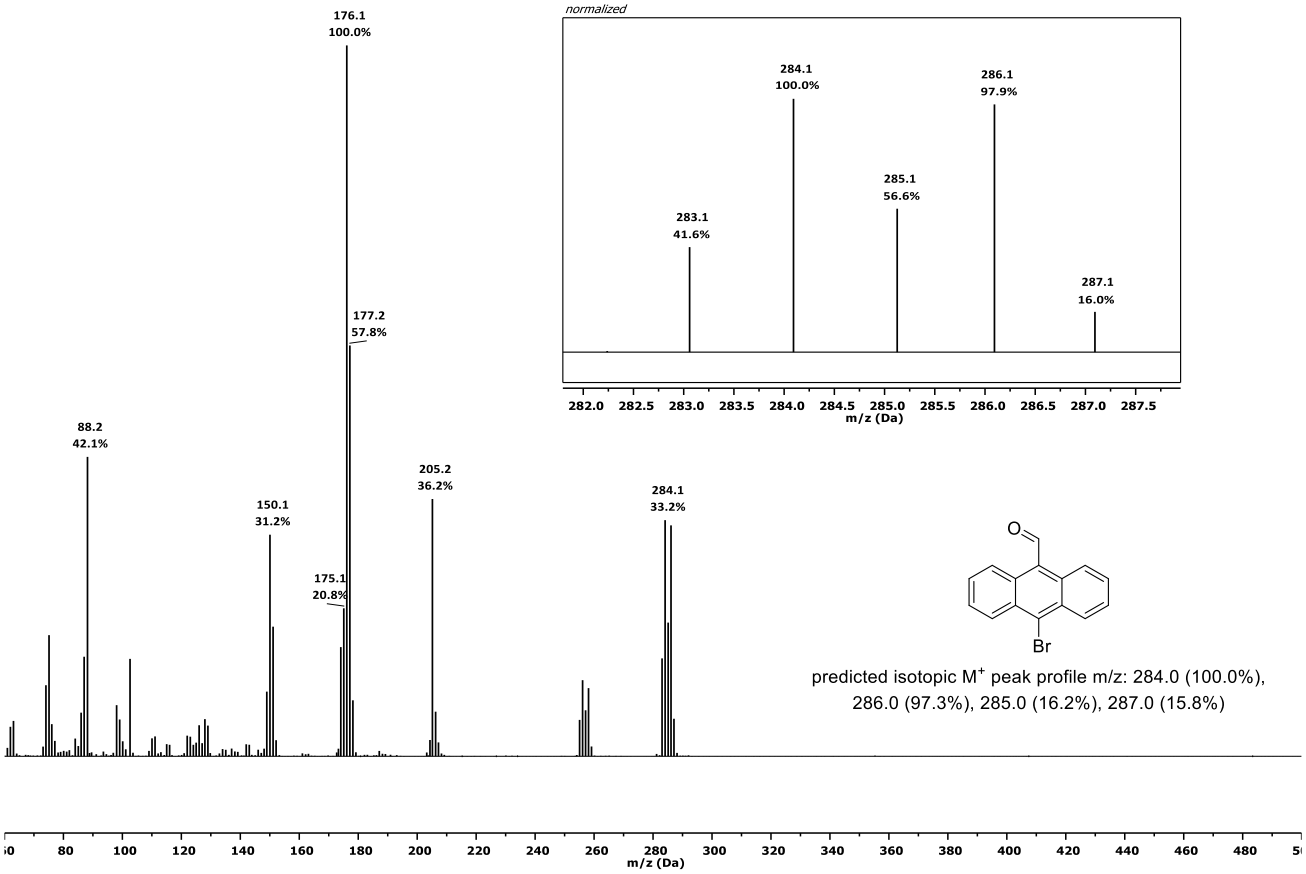


Figure 64S. *EI-LRMS spectrum of* ***10-bromo-9-anthracenecarbaldehyde.***

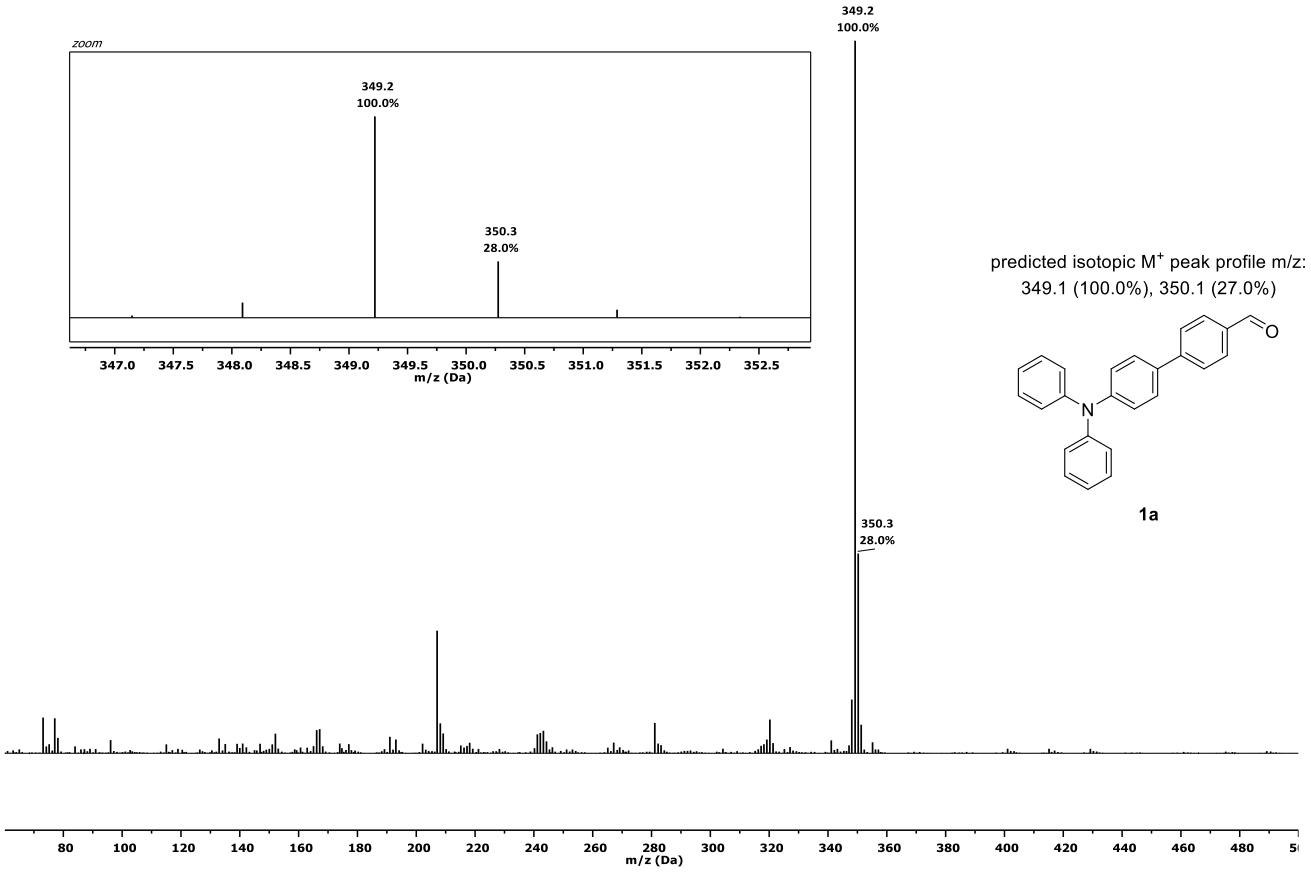


Figure 65S. *DEP-LRMS spectrum of* ***1a.***

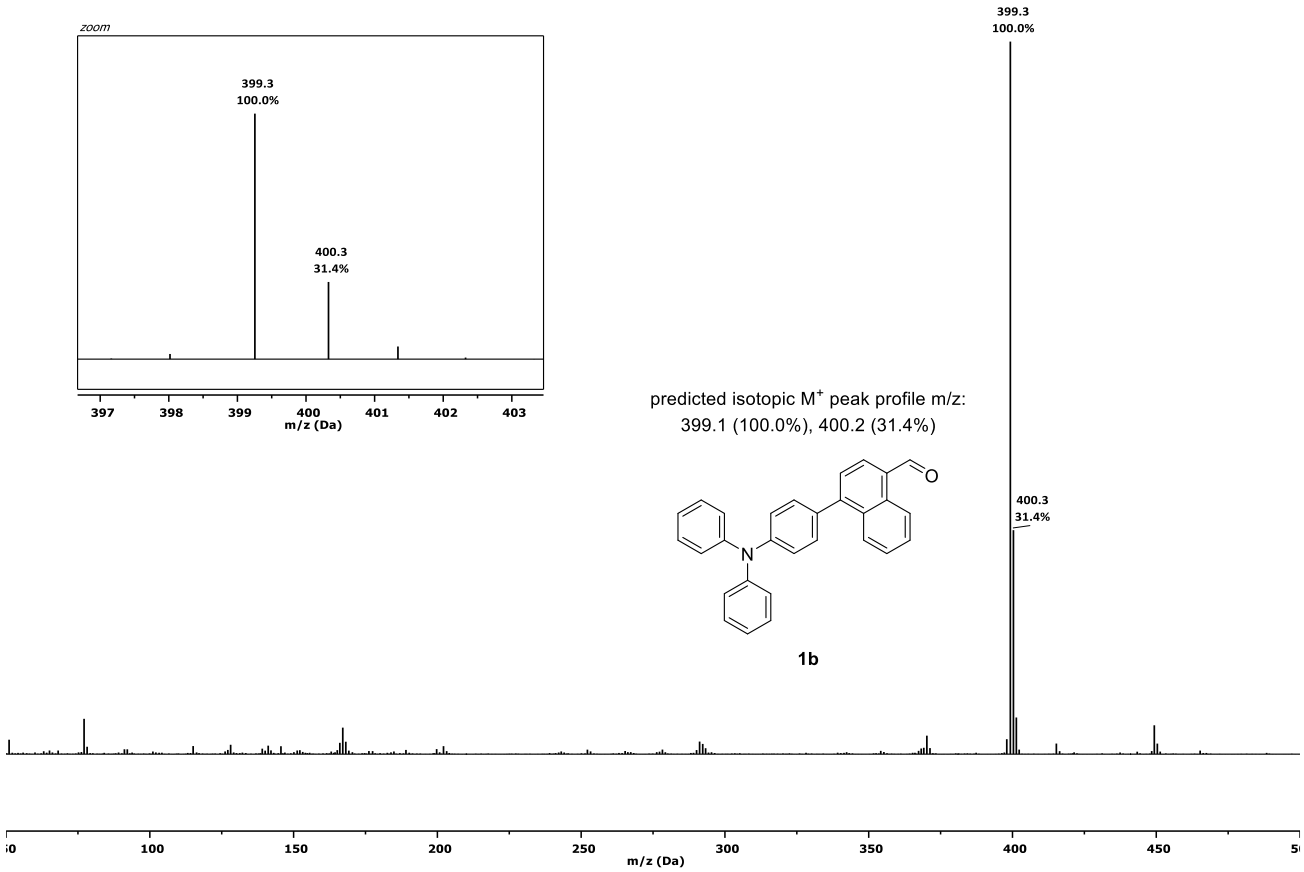


Figure 66S. *DEP-LRMS spectrum of* ***1b.***

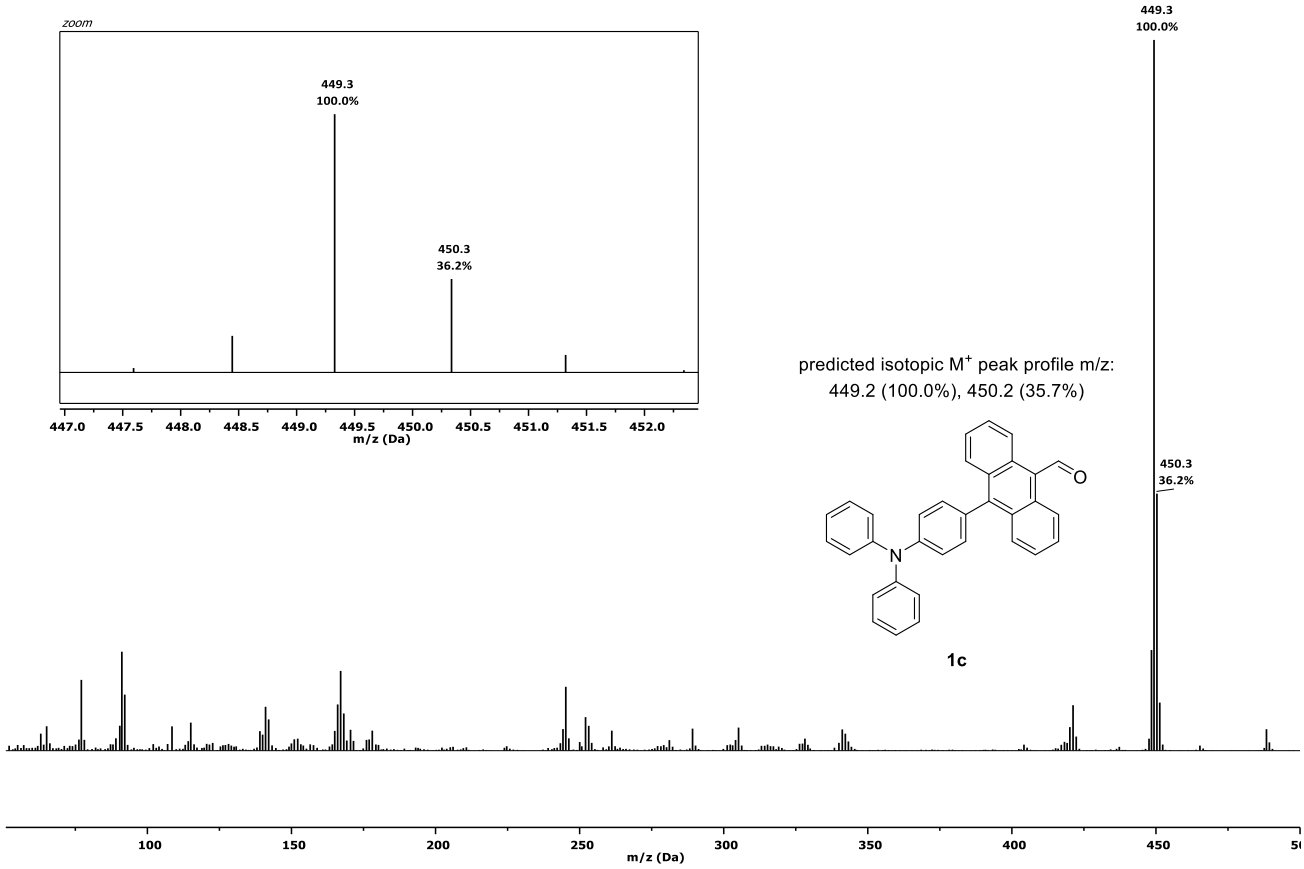


Figure 67S. *DEP-LRMS spectrum of* ***1c.***

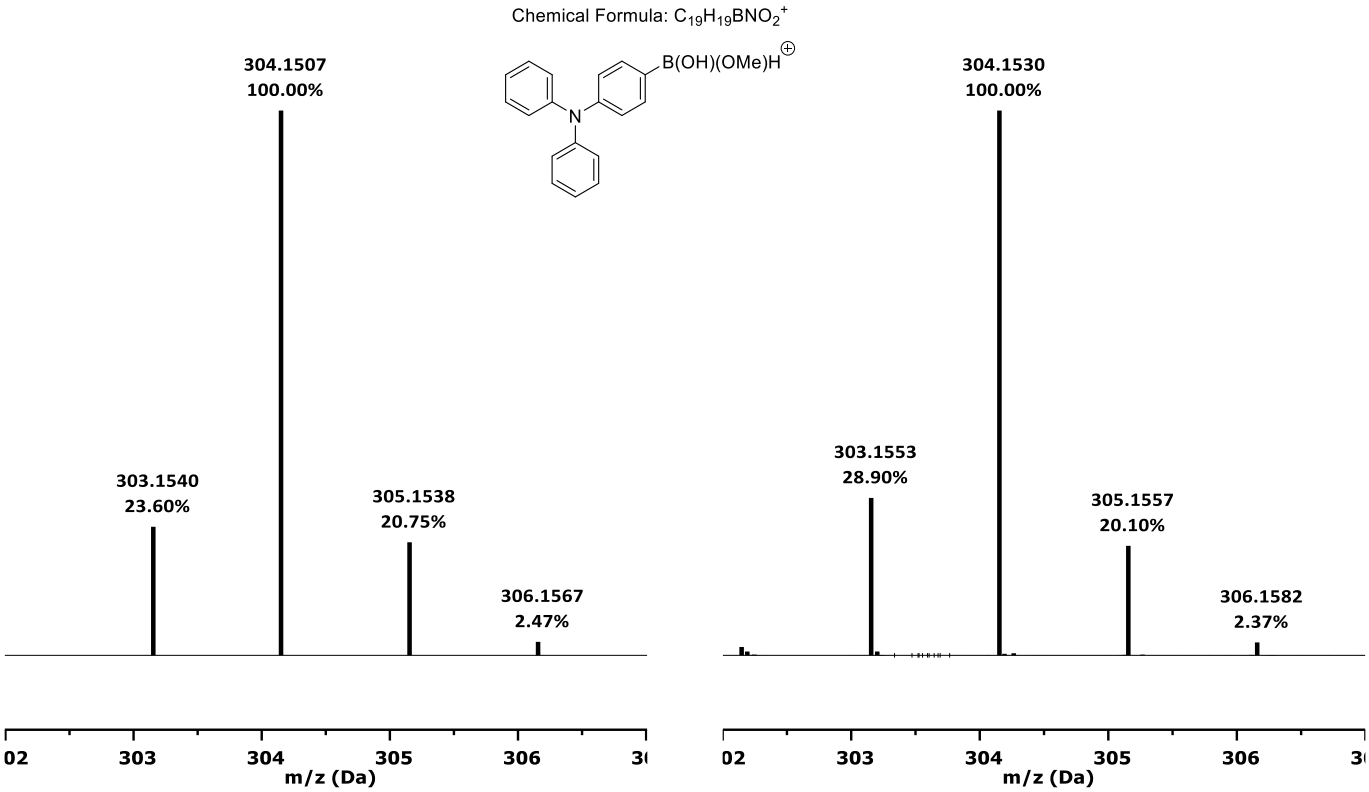


Figure 68S. *ESI-HRMS spectrum of* ***4-(diphenylamino)phenylboronic acid****, predicted (left) and measured (right).*

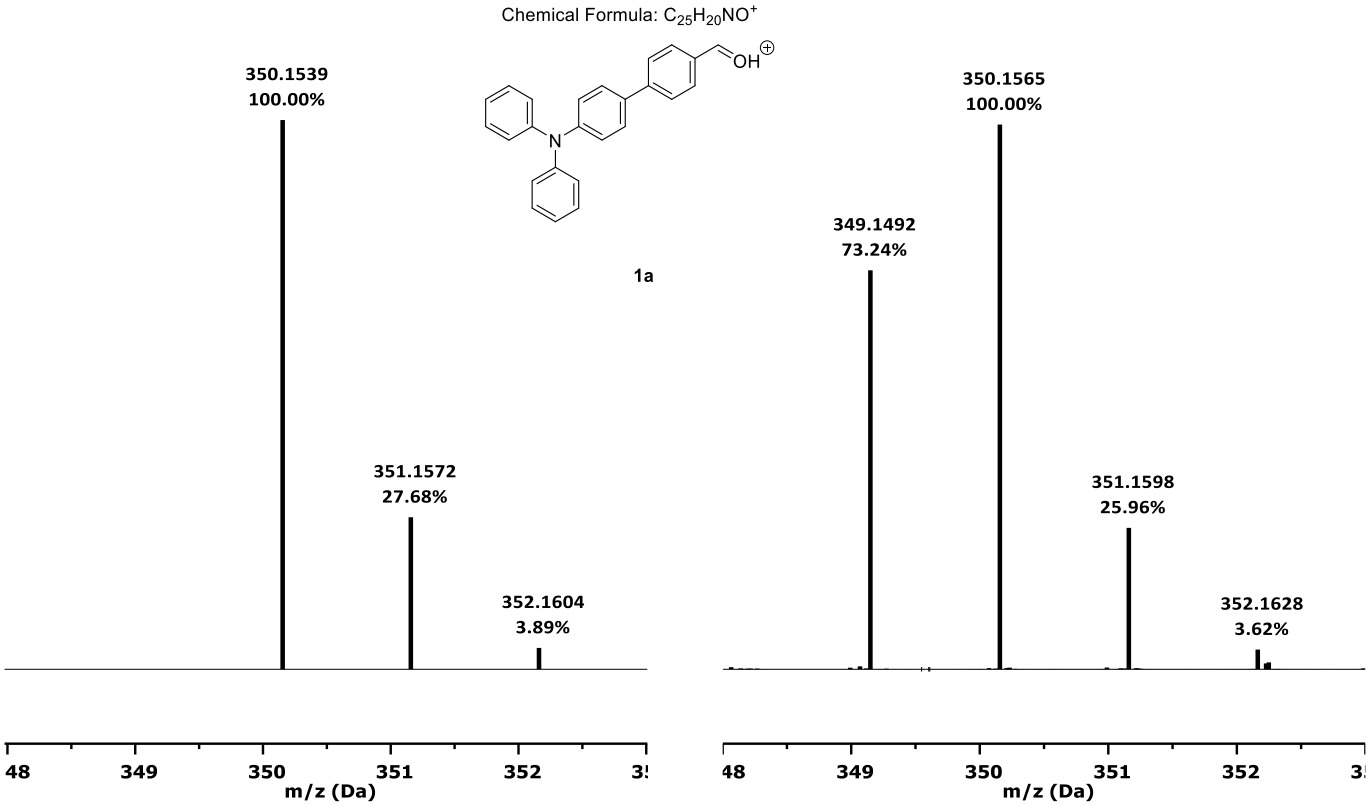


Figure 69S. *ESI-HRMS spectrum of* ***1a****, predicted (left) and measured (right).*

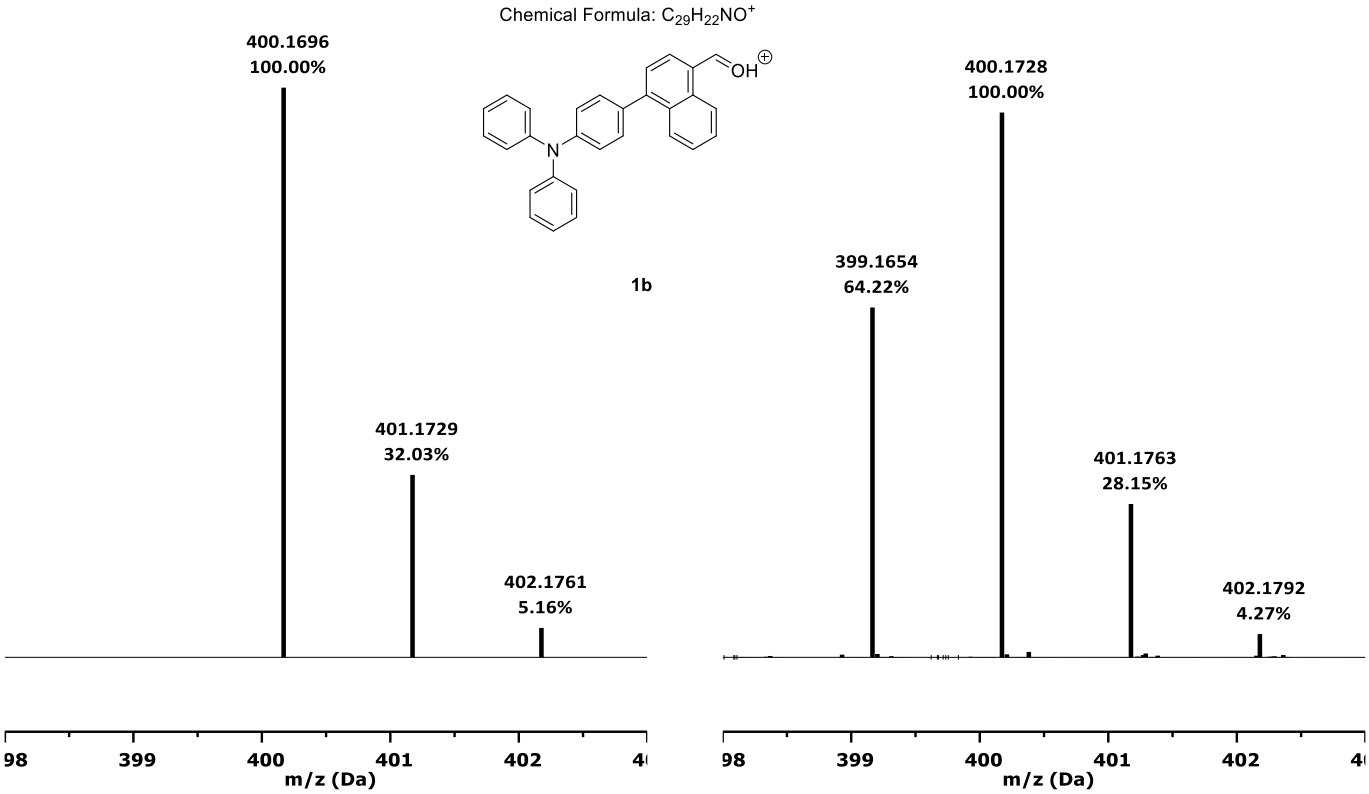


Figure 70S. *ESI-HRMS spectrum of* ***1b****, predicted (left) and measured (right).*

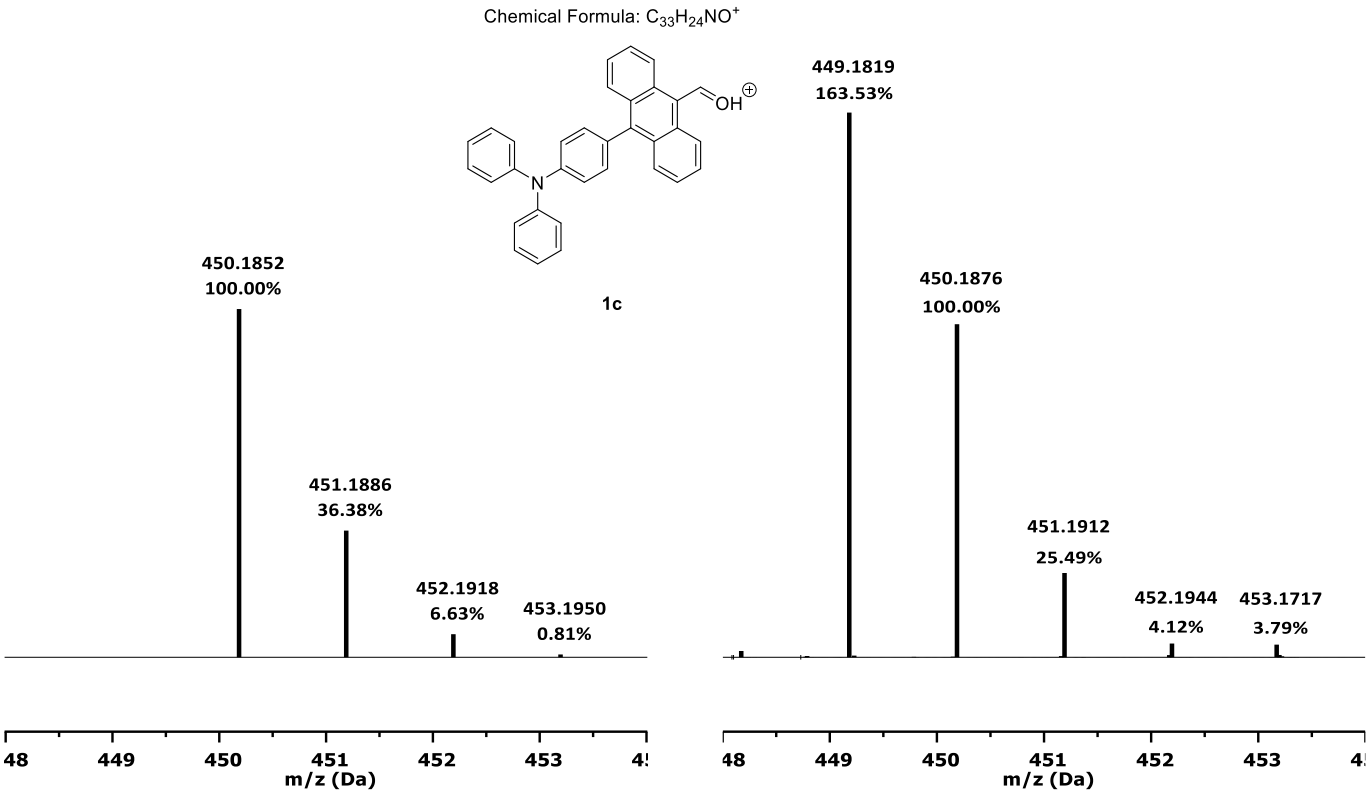


Figure 71S. *ESI-HRMS spectrum of* ***1c****, predicted (left) and measured (right, normalized).*

ESI-HRMS spectra

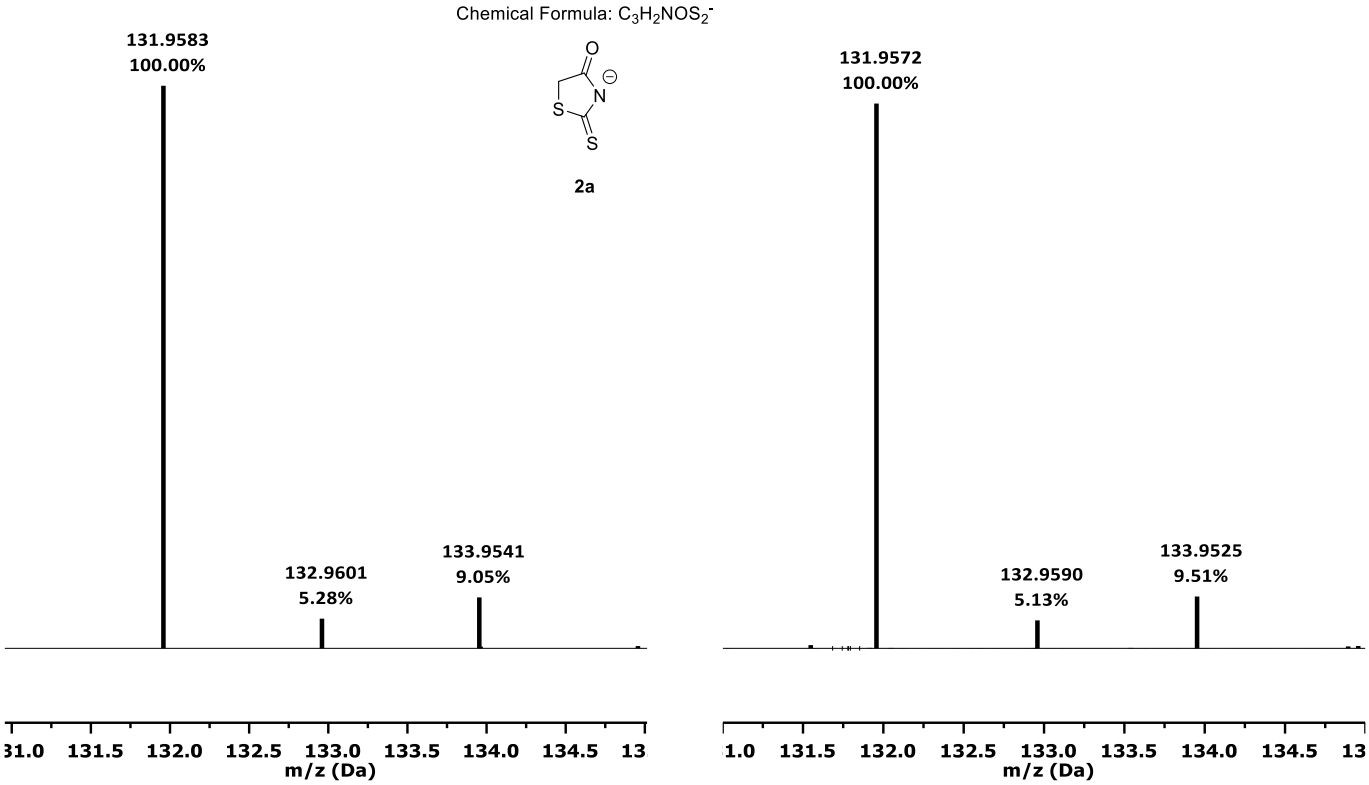


Figure 72S. *ESI-HRMS spectrum of* ***2a****, predicted (left) and measured (right).*

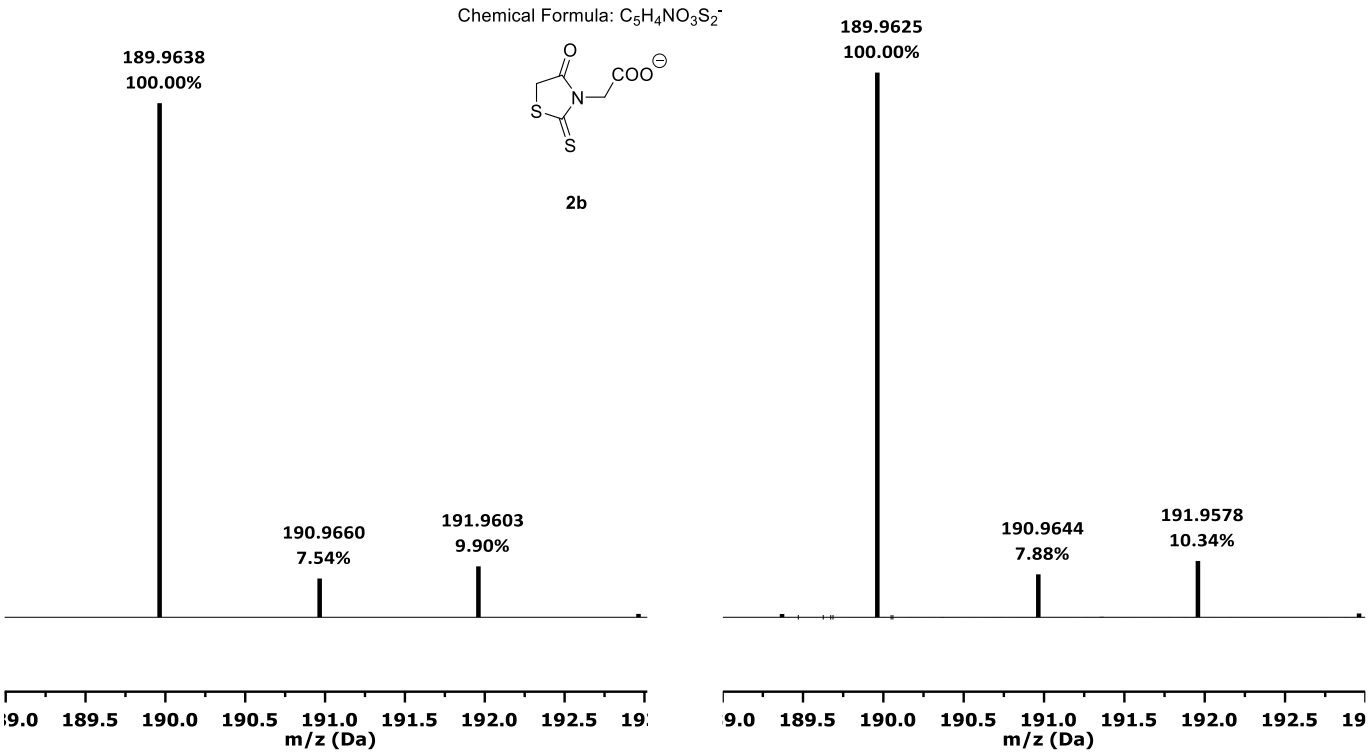


Figure 73S. *ESI-HRMS spectrum of* ***2b****, predicted (left) and measured (right).*

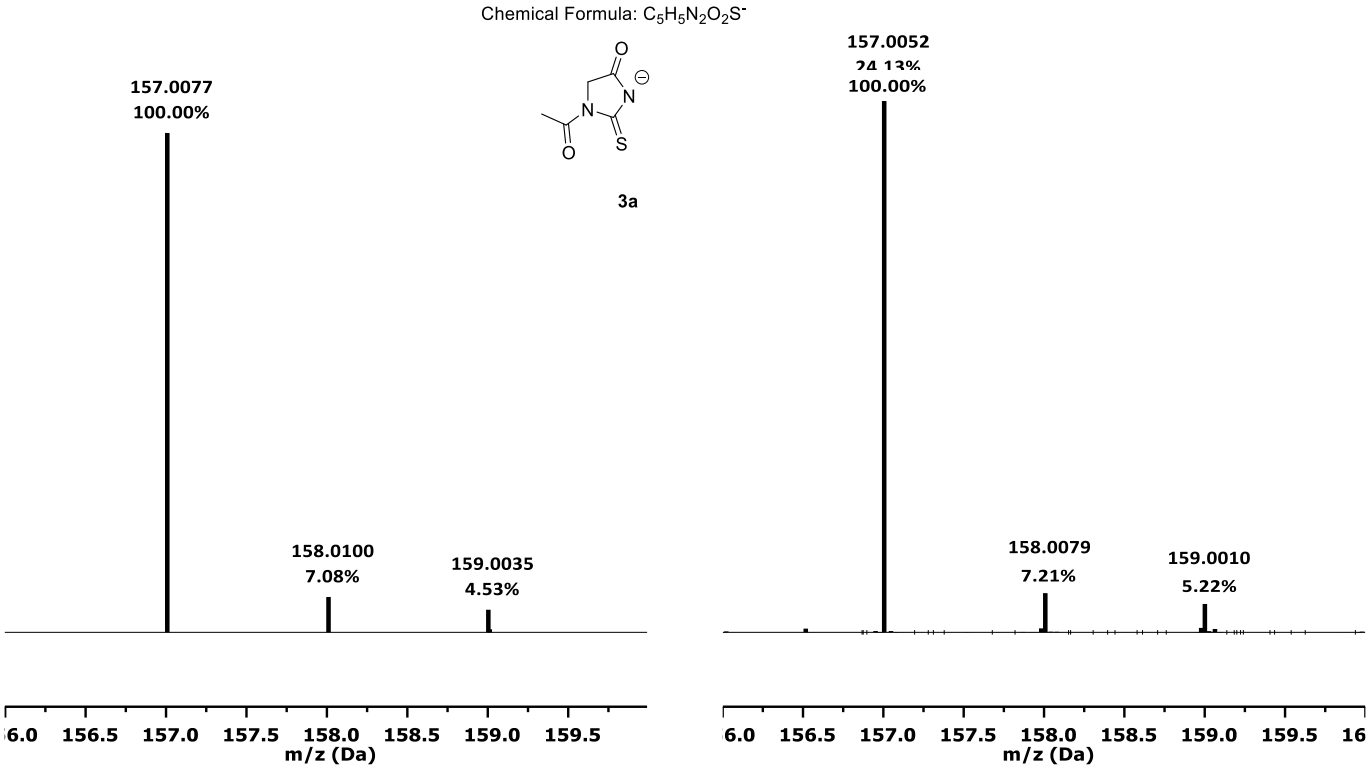


Figure 74S. *ESI-HRMS spectrum of* ***3a****, predicted (left) and measured (right).*

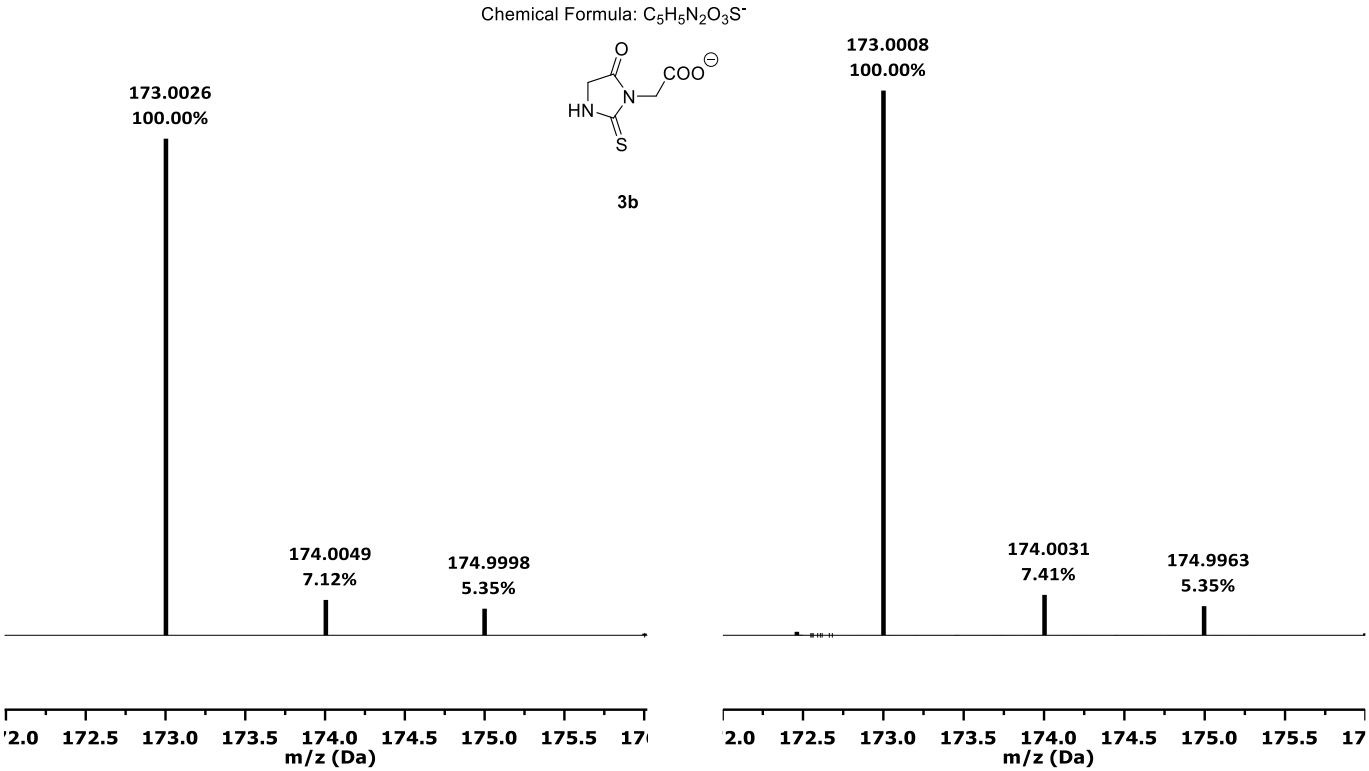


Figure 75S. *ESI-HRMS spectrum of* ***3b****, predicted (left) and measured (right).*

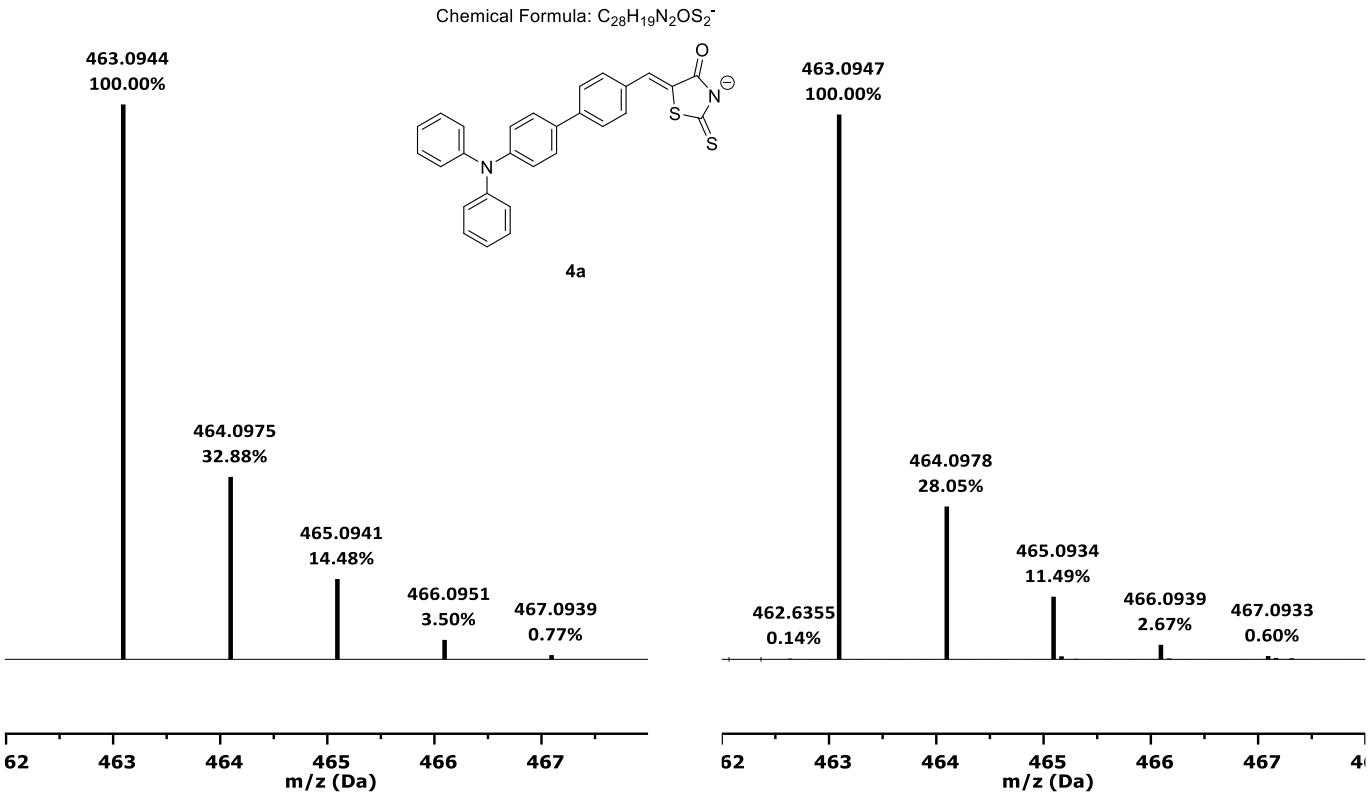


Figure 76S. *ESI-HRMS spectrum of* ***4a****, predicted (left) and measured (right).*

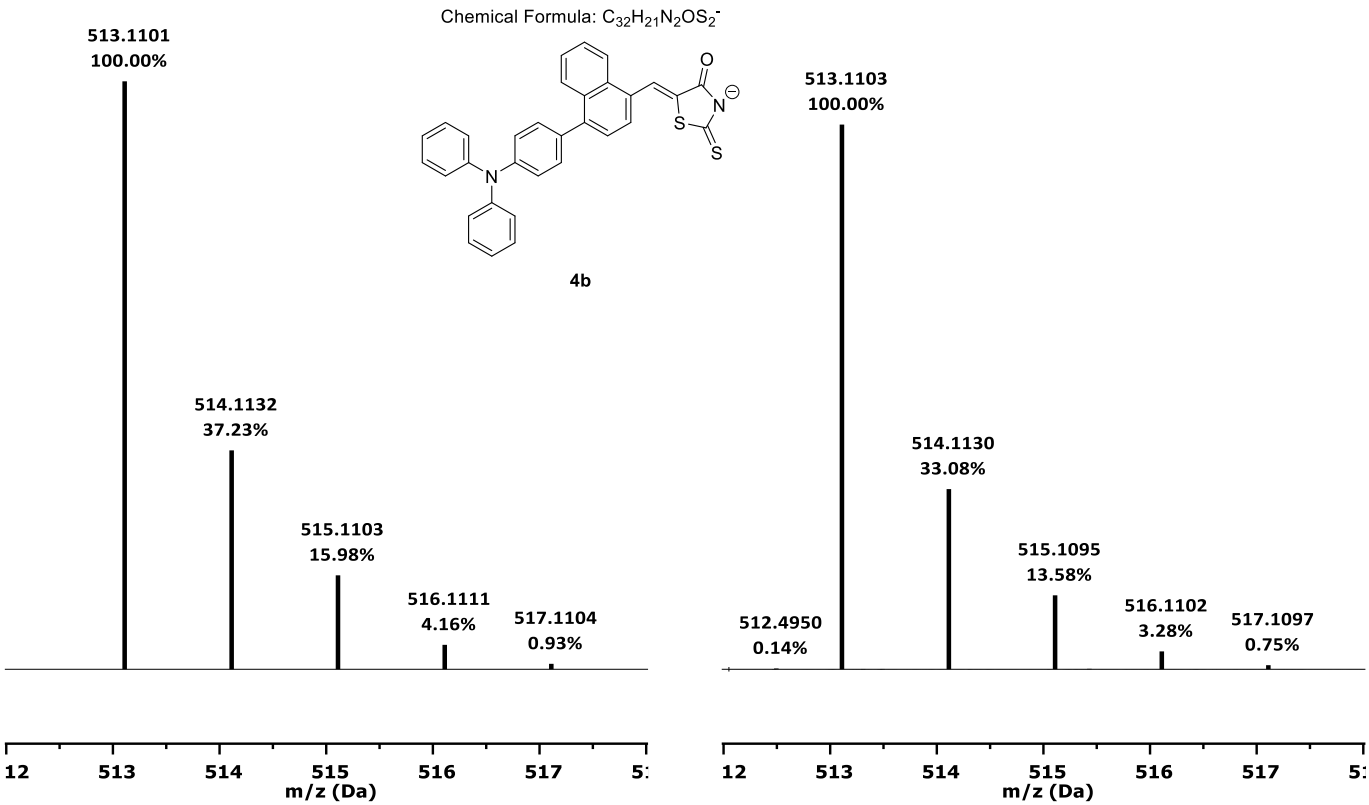


Figure 77S. *ESI-HRMS spectrum of* ***4b****, predicted (left) and measured (right).*

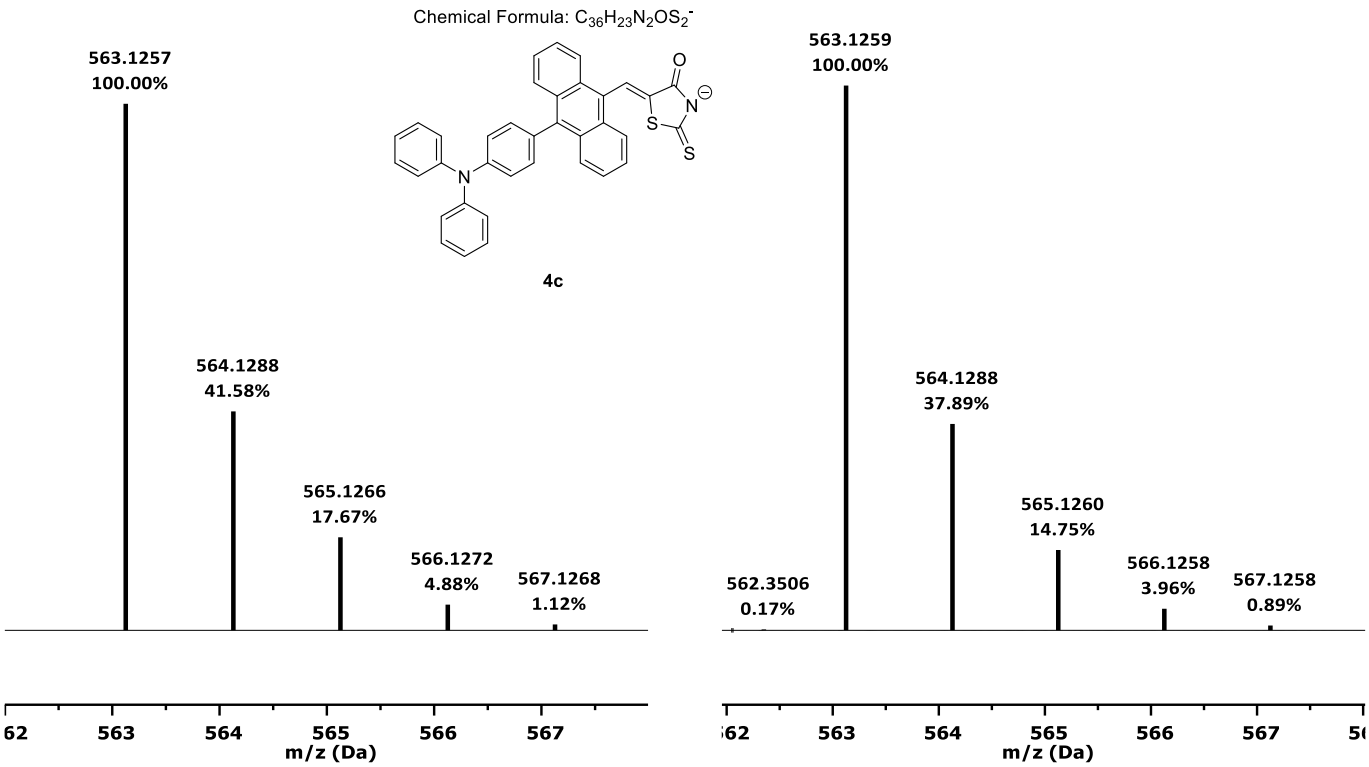


Figure 78S. *ESI-HRMS spectrum of* ***4c****, predicted (left) and measured (right).*

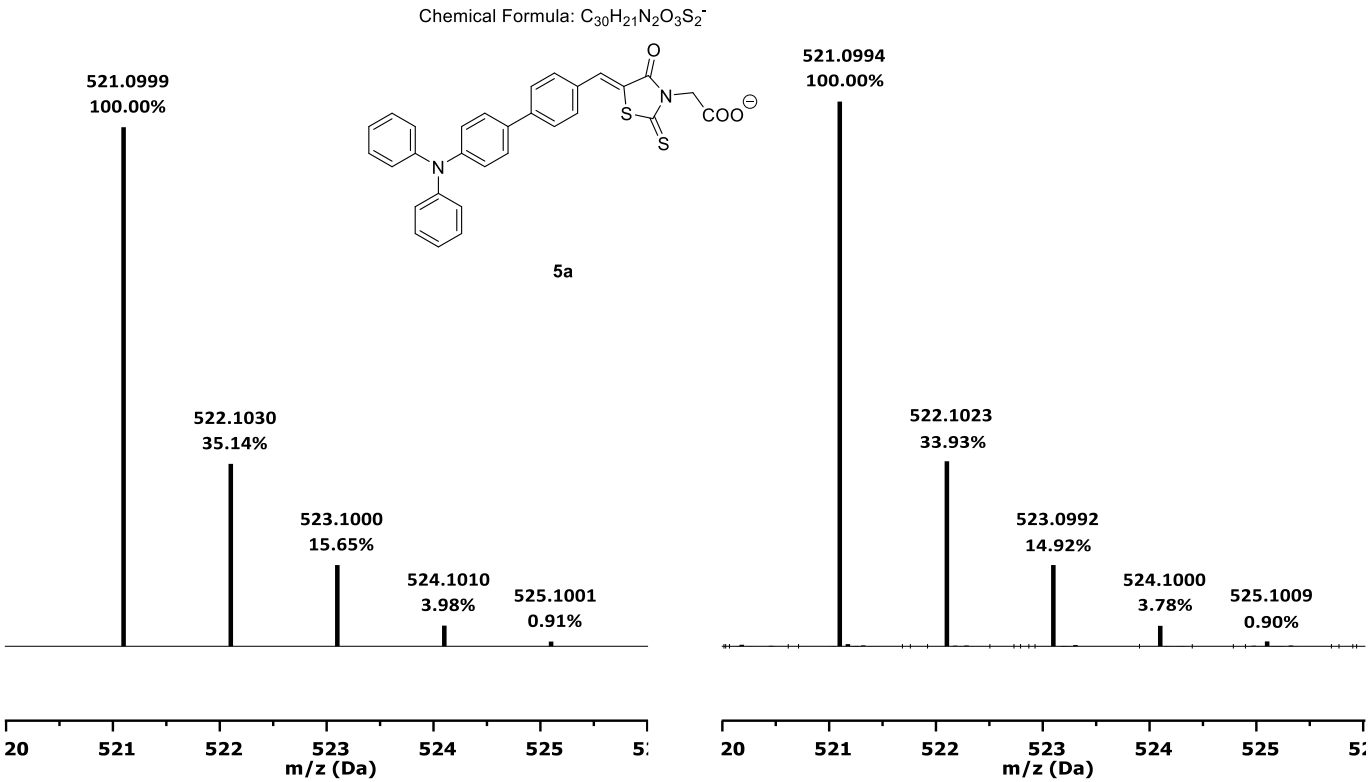


Figure 79S. *ESI-HRMS spectrum of* ***5a****, predicted (left) and measured (right, normalized).*

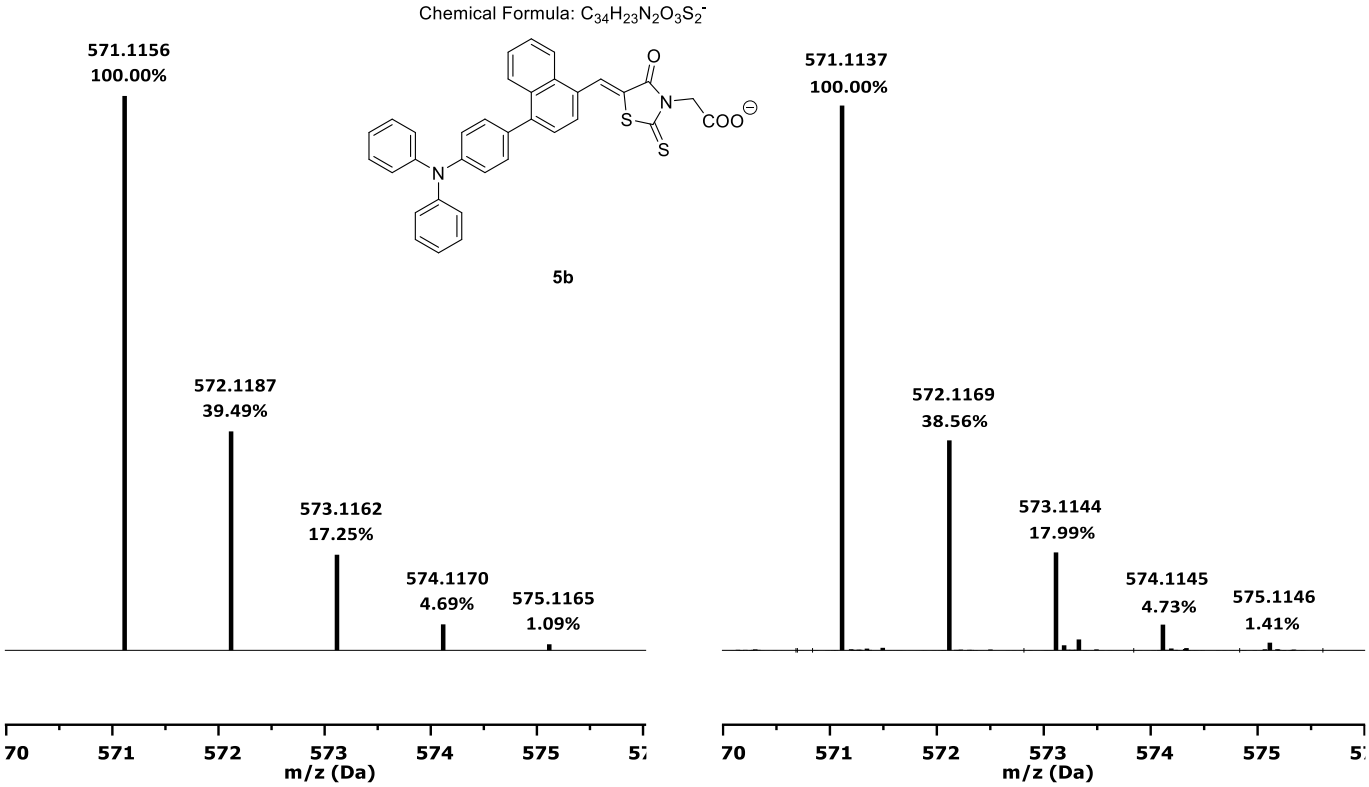


Figure 80S. *ESI-HRMS spectrum of* ***5b****, predicted (left) and measured (right, normalized).*

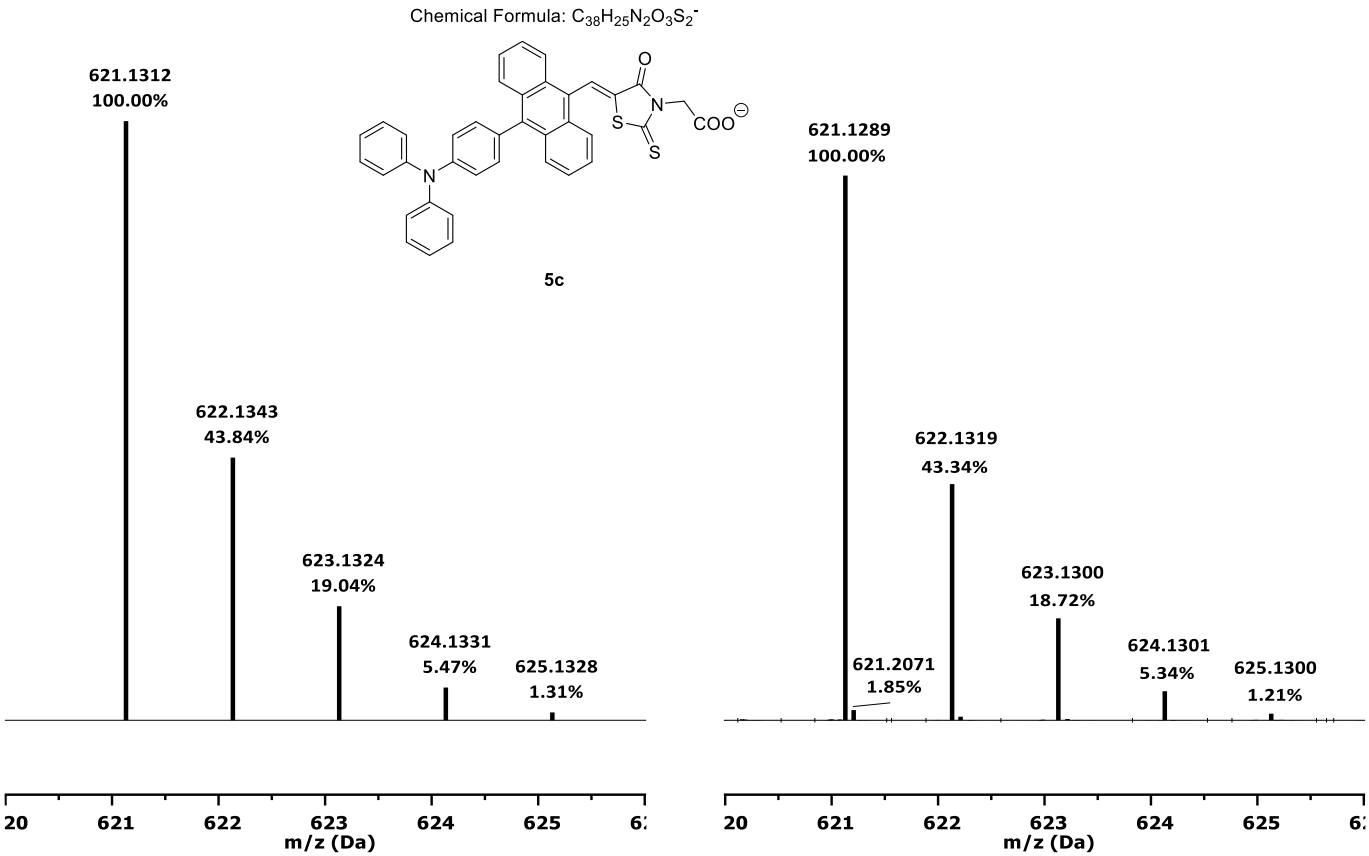


Figure 81S. *ESI-HRMS spectrum of* ***5c****, predicted (left) and measured (right, normalized).*

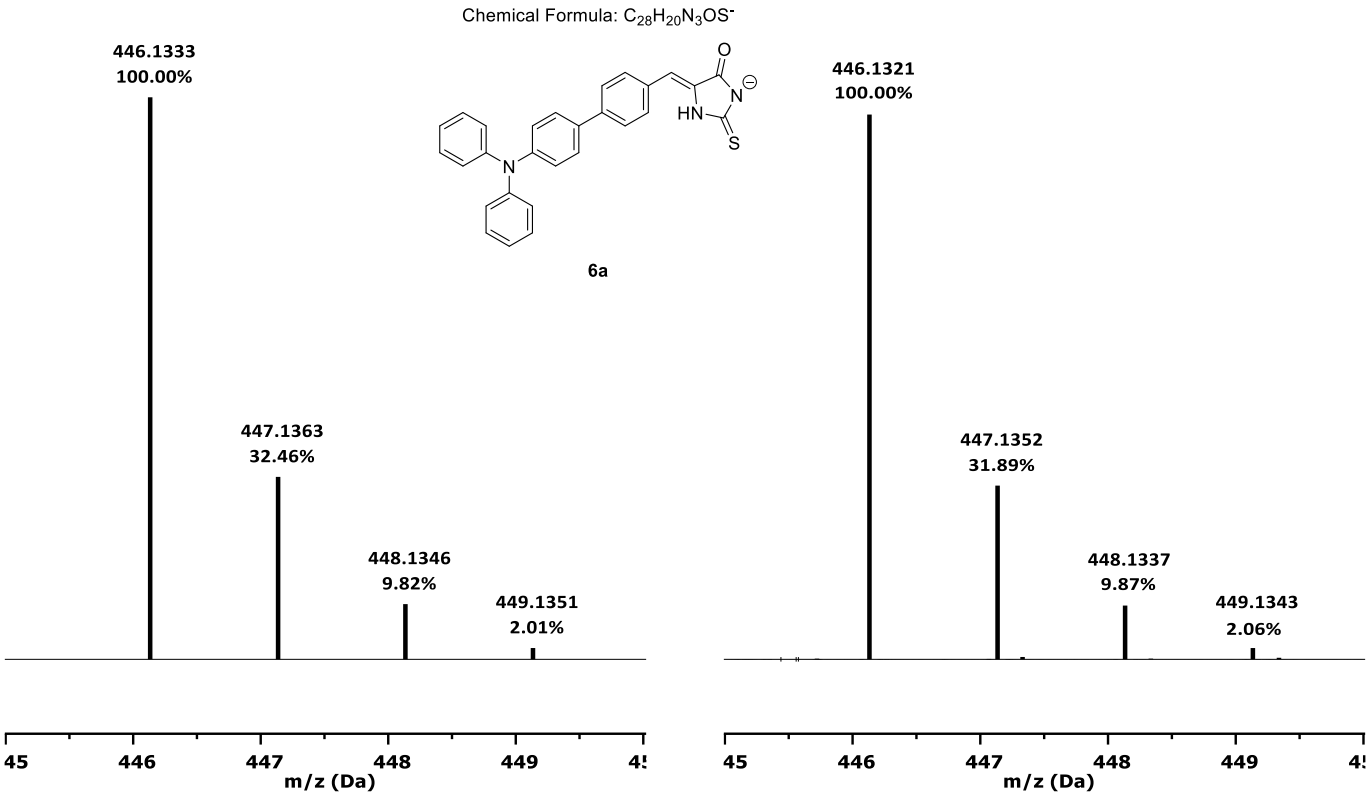


Figure 82S. *ESI-HRMS spectrum of* ***6a****, predicted (left) and measured (right).*

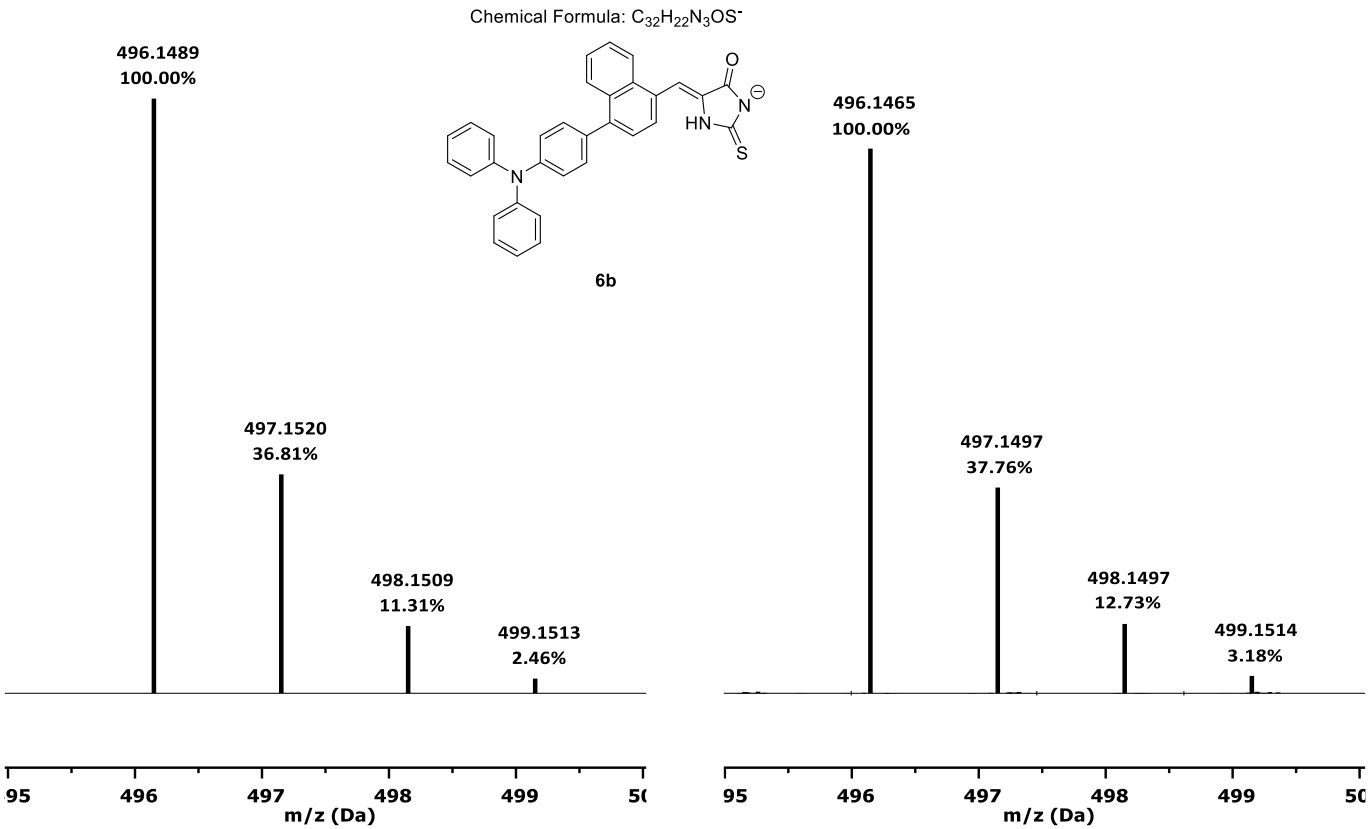


Figure 83S. *ESI-HRMS spectrum of* ***6b****, predicted (left) and measured (right, normalized).*

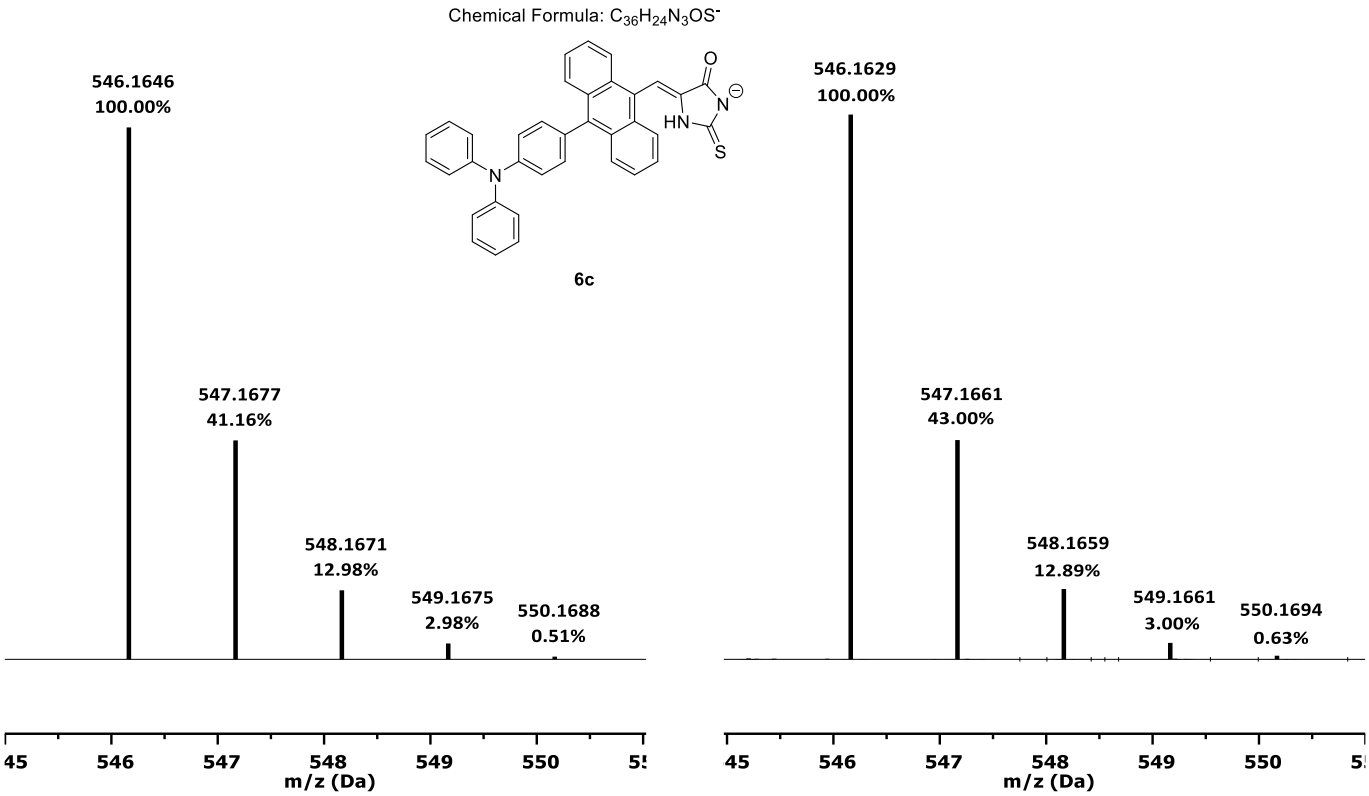


Figure 84S. *ESI-HRMS spectrum of* ***6c****, predicted (left) and measured (right, normalized).*

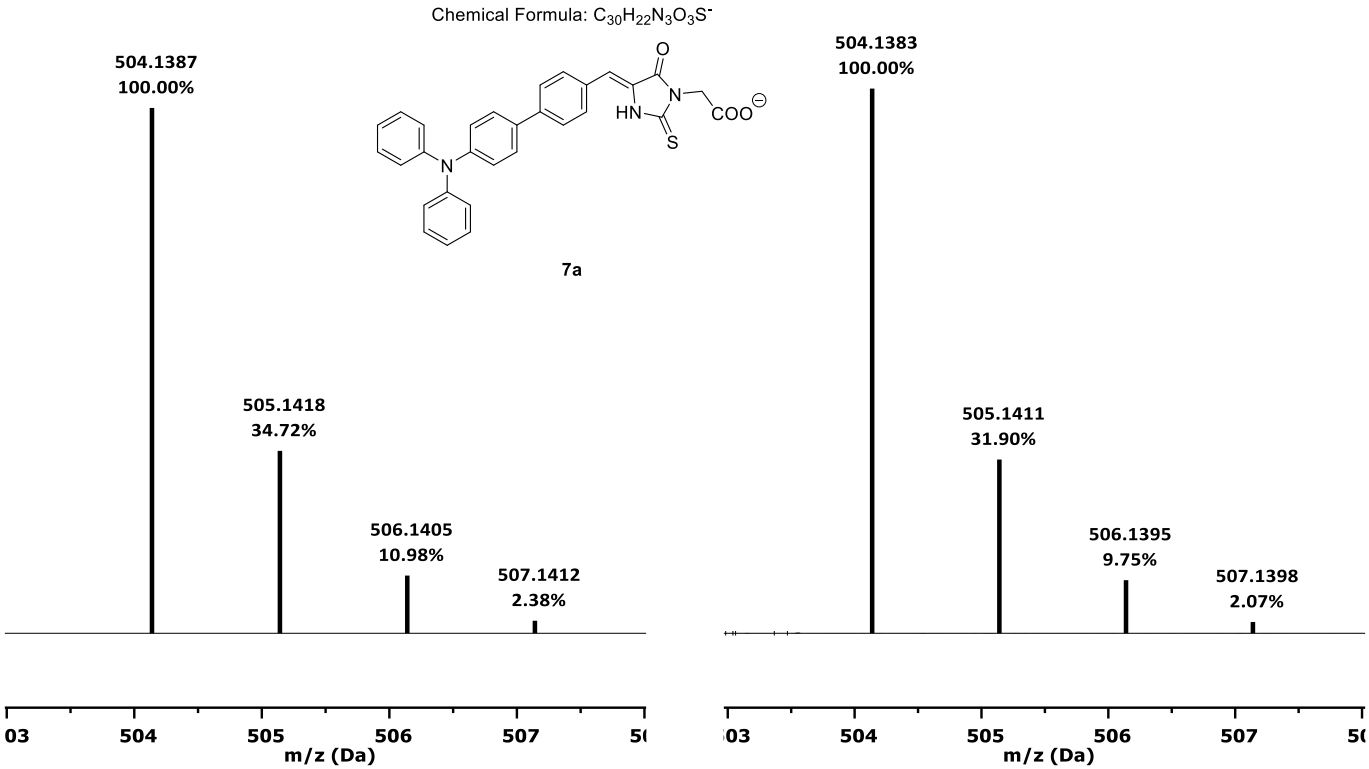


Figure 85S. *ESI-HRMS spectrum of* ***7a****, predicted (left) and measured (right).*

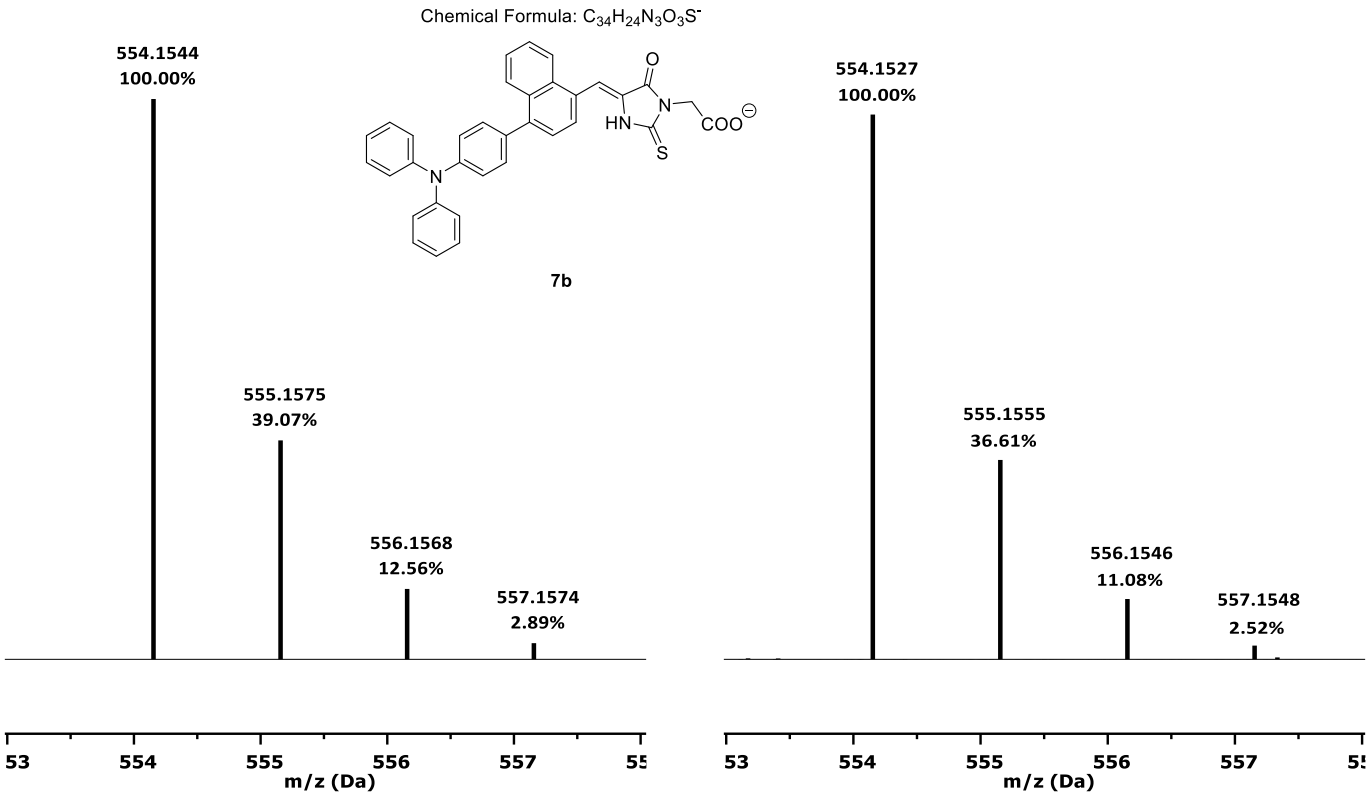


Figure 86S. *ESI-HRMS spectrum of* ***7b****, predicted (left) and measured (right, normalized).*

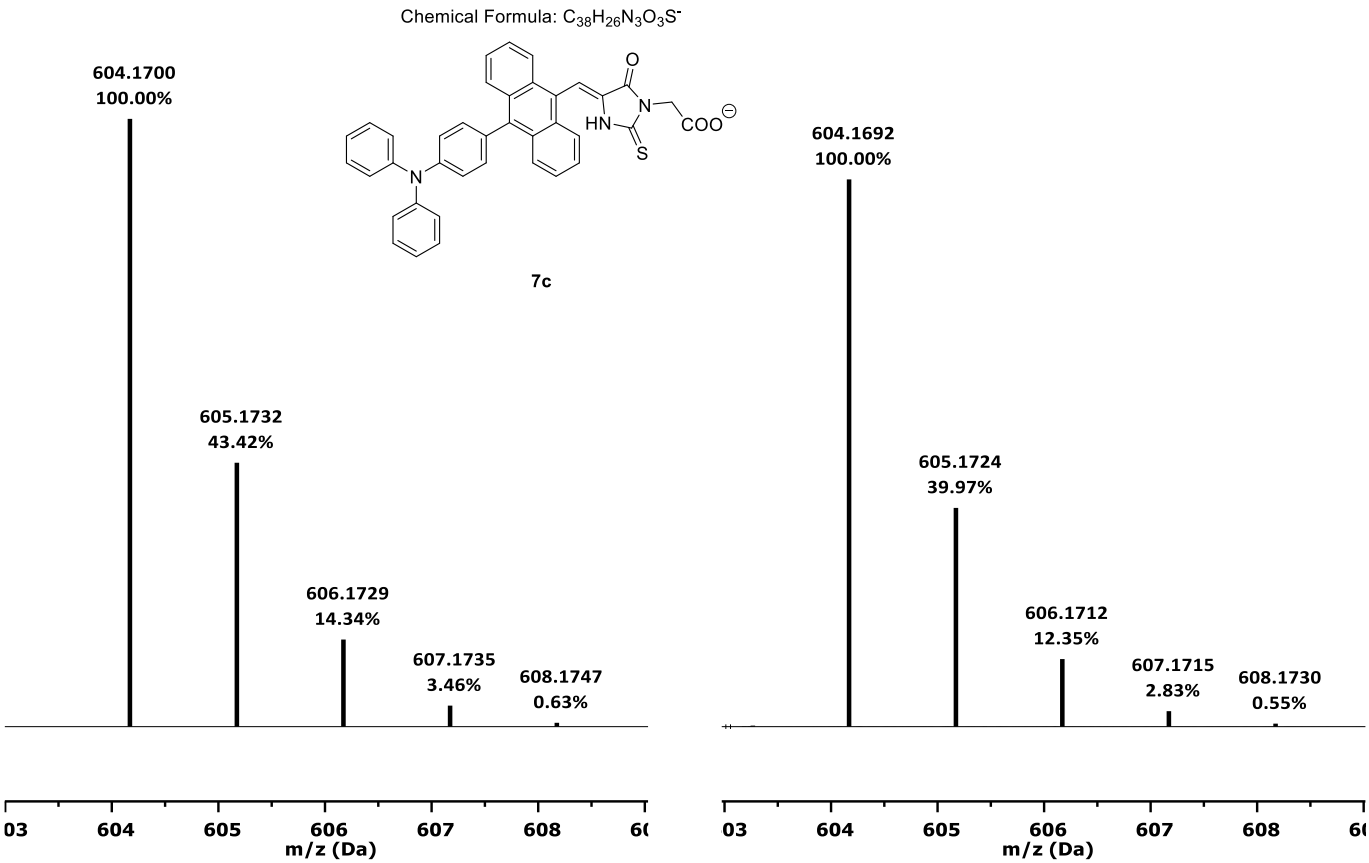


Figure 87S. *ESI-HRMS spectrum of* ***7c****, predicted (left) and measured (right).*

MIC & MBC

Table 1S. Activity of rhodanine and rhodanine-3-acetic acid derivatives against selected gram positive bacteria.

Compound	4a		4b		4c		5a		5b		5c	
Bacteria strain	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]
***S. aureus* ATCC 25923**	250	1000	500	>1000	>1000	>1000	3,9	31,3	1000	>1000	>1000	>1000
***S. aureus* ATCC 6538**	500	>1000	500	>1000	>1000	>1000	3,9	7,8	1000	>1000	>1000	>1000
***S. aureus* ATCC 43300**	250	>1000	1000	>1000	>1000	>1000	3,9	7,8	1000	>1000	>1000	>1000
***S. epidermidis* ATCC 12228**	125	250	1000	>1000	>1000	>1000	0,98	7,8	500	1000	>1000	>1000
***M. luteus* ATCC 10240**	31,1	500	250	>1000	>1000	>1000	0,98	31,3	31,3	62,5	125	125
***B. subtilis* ATCC 6633**	1000	>1000	1000	>1000	>1000	>1000	1,95	1,95	500	1000	>1000	>1000
***B. cereus* ATCC 10876**	1000	>1000	1000	>1000	>1000	>1000	7,8	31,3	1000	>1000	>1000	>1000
***S. pyogenes* ATCC 19615**	1000	>1000	1000	>1000	>1000	>1000	15,6	500	1000	>1000	>1000	>1000
***S. pneumoniae* ATCC 49619**	1000	>1000	1000	>1000	>1000	>1000	15,6	500	1000	>1000	>1000	>1000
***S. mutans* ATCC 25175**	1000	>1000	1000	>1000	>1000	>1000	1000	>1000	1000	>1000	>1000	>1000

Table 2S. Activity of 2-thiohydantoin and 2-thiohydantoin-3-acetic acid derivatives against selected gram positive bacteria.

Compound	6a		6b		6c		7a		7b		7c	
Bacteria strain	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]	MIC [mg/L]	MBC [mg/L]
***S. aureus* ATCC 25923**	>1000	>1000	>1000	>1000	>1000	>1000	3,9	3,9	>1000	>1000	>1000	>1000
***S. aureus* ATCC 6538**	>1000	>1000	>1000	>1000	>1000	>1000	1,95	3,9	>1000	>1000	>1000	>1000
***S. aureus* ATCC 43300**	>1000	>1000	>1000	>1000	>1000	>1000	1,95	3,9	>1000	>1000	>1000	>1000
***S. epidermidis* ATCC 12228**	>1000	>1000	>1000	>1000	>1000	>1000	1,95	3,9	>1000	>1000	>1000	>1000
***M. luteus* ATCC 10240**	62,5	>1000	>1000	>1000	>1000	>1000	1,95	31,3	>1000	>1000	>1000	>1000
***B. subtilis* ATCC 6633**	>1000	>1000	>1000	>1000	>1000	>1000	3,9	3,9	>1000	>1000	>1000	>1000
***B. cereus* ATCC 10876**	>1000	>1000	>1000	>1000	>1000	>1000	125	250	>1000	>1000	>1000	>1000
***S. pyogenes* ATCC 19615**	>1000	>1000	>1000	>1000	>1000	>1000	31,3	125	>1000	>1000	>1000	>1000
***S. pneumoniae* ATCC 49619**	>1000	>1000	>1000	>1000	>1000	>1000	62,5	125	>1000	>1000	>1000	>1000
***S. mutans* ATCC 25175**	>1000	>1000	>1000	>1000	>1000	>1000	62,5	>1000	>1000	>1000	>1000	>1000

Table 3S. Determined MIC values [mg/L] of ciprofloxacin and vancomycin for bacterial strains.

Microorganism	Vancomycin	Ciprofloxacin
S. aureus ATCC25923	0.98	0.49
S. aureus ATCC6538	0.49	0.24
S. aureus ATCC43300	1.96	0.24
S. epidermidis ATCC12228	0.98	0.49
M. luteus ATCC10240	0.12	0.98
B. subtilis ATCC6633	0.24	0.03
B. cereus ATCC10876	0.98	0.12
S. pyogenes ATCC19615	0.24	-
S. pneumoniae ATCC49619	0.24	-
S. mutans ATCC25175	0.98	-

Cytotoxicity tests

Table 4S. Determined average lethal dose (LD_{50}) for 24 h incubation of human cell lines in the presence of compounds **4a**-**7c.**

Compound	LD_{50} [mg/L/1x10^6 cells]		
	U-937	**HUT-78**	**COLO-720L**
4a	17.81	34.71	22.71
4b	23.63	41.02	28.83
4c	29.10	42.50	31.08
5a	18.46	38.48	16.50
5b	25.50	15.93	24.35
5c	21.93	17.92	24.16
6a	34.44	18.47	41.70
6b	22.17	22.31	20.63
6c	30.99	67.63	35.11
7a	29.35	20.96	29.63
7b	29.70	63.42	28.11
7c	25.54	27.89	23.41

Membrane permeability test results

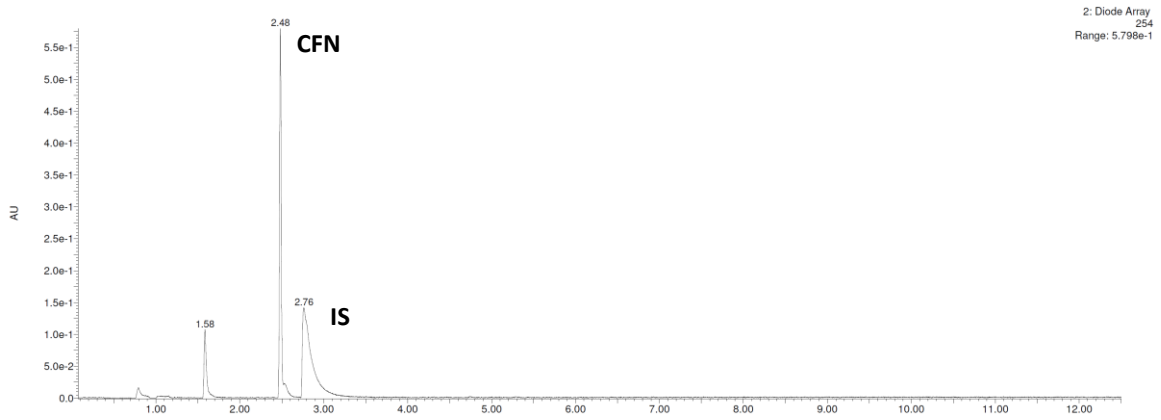


Figure 88S. *HPLC chromatogram of reference donor well.*

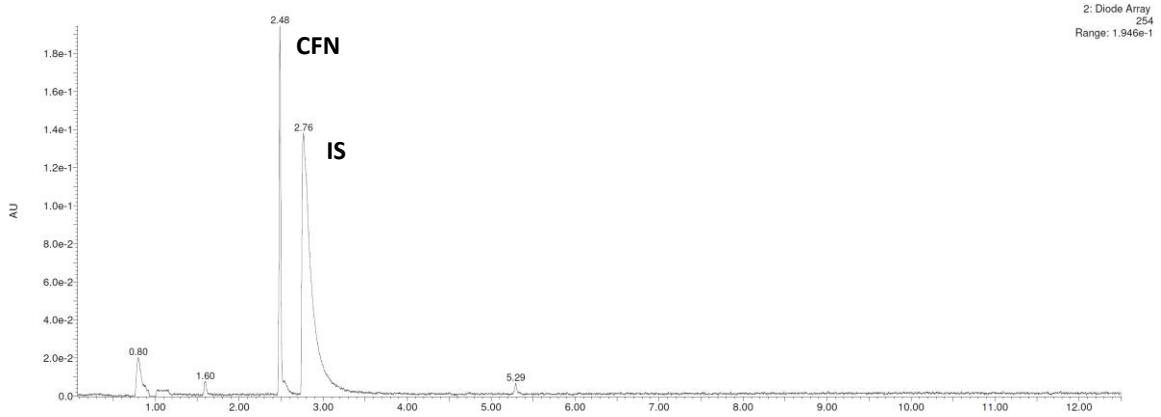


Figure 89S. *HPLC chromatogram of reference acceptor well.*

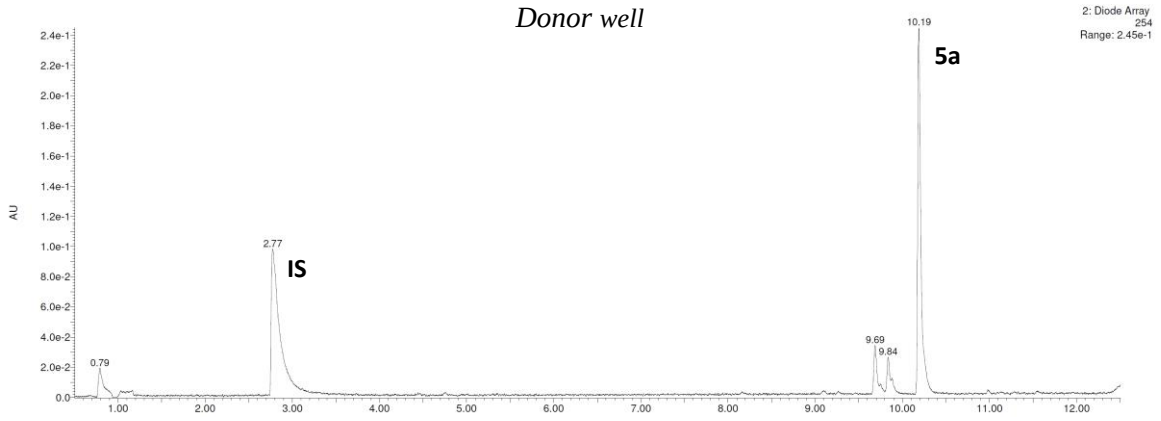


Figure 90S. *HPLC chromatogram of **5a** test donor well.*

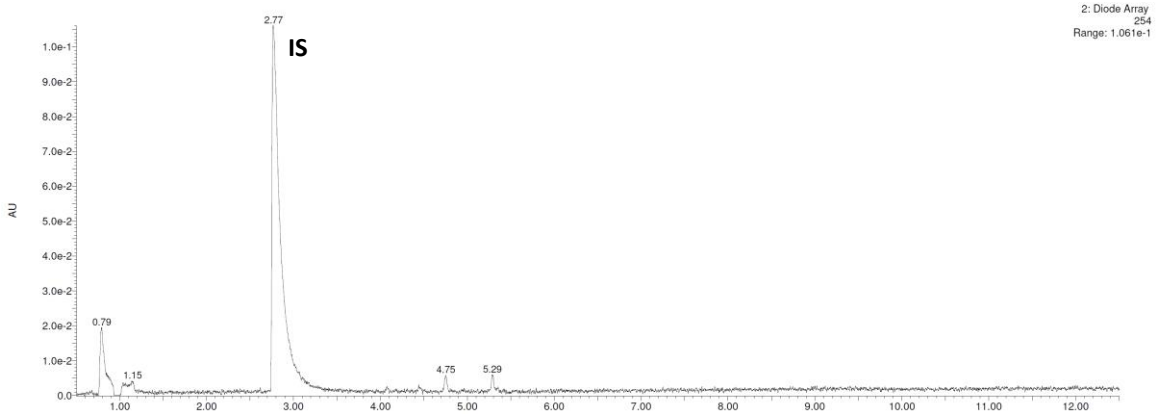


Figure 91S. *HPLC chromatogram of **5a** test acceptor well.*

Membrane permeability test results

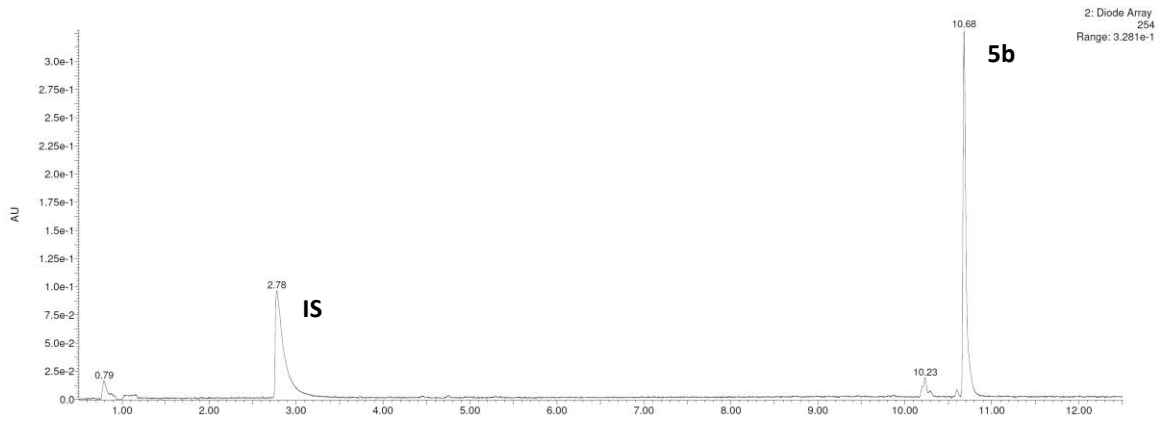


Figure 92S. *HPLC chromatogram of* ***5b*** *test donor well .*

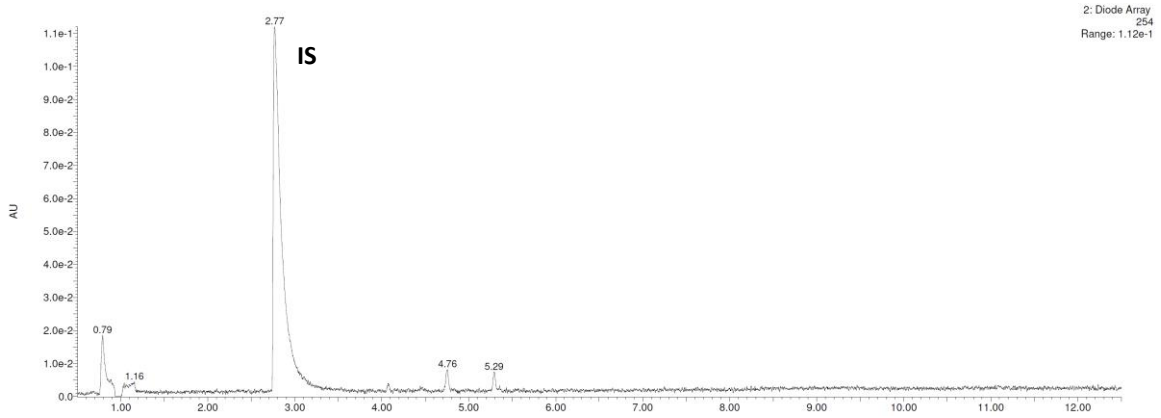


Figure 93S. *HPLC chromatogram of* ***5b*** *test acceptor well.*

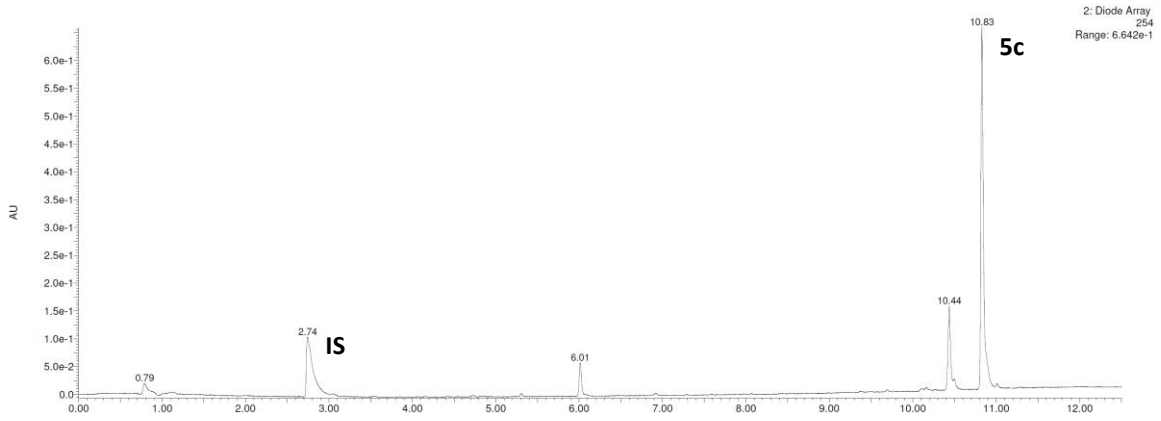


Figure 94S. *HPLC chromatogram of* ***5c*** *test donor well.*

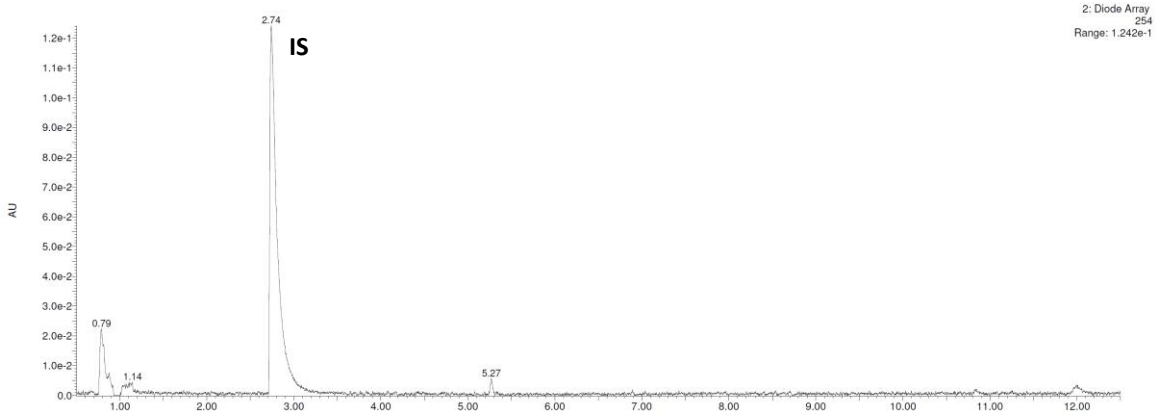


Figure 95S. *HPLC chromatogram of* ***5c*** *test acceptor well.*