Supporting Information

Photocatalyst-Free Visible-Light-Induced Cross-Dehydrogenative Sulfenylation of Aminocoumarins and Amino-1,4-naphthoquinones

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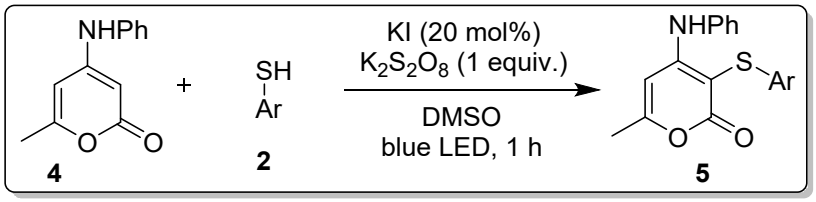
Contents

General Information: All the reactions were carried out under aerobic atmosphere using oven dried reaction vials. Chemicals, reagents, and solvents were procured from the commercial sources and used without purification. The reactions were monitored by using aluminium TLC silica plates and visualized in UV chamber (254 or 365 nm). Photochemical reactions were carried out under the irradiation of white/blue/green LED. Column chromatography was carried out using 100-200 mesh silica gel and a mixture of ethyl acetate-hexane as eluent. ^{1}H NMR and ^{13}C NMR were recorded in 400 MHz and 100 MHz NMR spectrometer respectively using $CDCl_3$ as solvent. Chemical shifts were given in parts per million (δ) and coupling constants (J) were expressed in Hertz. The signals were expressed as s for singlet, d for doublet, dd for doublet of doublet, t for triplet. Melting points were recorded using capillary tubes in the melting point apparatus and data were uncorrected.

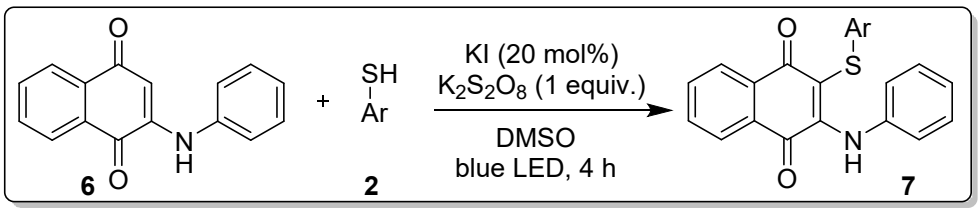
General procedure for the synthesis of 4-(phenylamino)-3-(phenylthio)-2*H*-chromen-2-one derivatives (3): In an oven-dried reaction vial, 4-(phenylamino)-2*H*-chromen-2-one derivatives (**1**, 0.2 mmol) and thiophenols (**2**, 0.2 mmol) were taken. Then KI (20 mol%, 7 mg), $K_2S_2O_8$ (0.2 mmol, 1 equiv., 54 mg), and 1 mL DMSO were added to the reaction vial. The reaction mixture was then stirred under the irradiation of blue LED (435-445 nm) for 7 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (DCM)-water and dried over anhydrous sodium sulfate. After that, dichloromethane was evaporated to get the crude product. Column chromatography was not required for the purification of the desired products.

General procedure for the synthesis of 6-methyl-4-(phenylamino)-3-(phenylthio)-5,6-dihydro-2*H*-pyran-2-ones (5): In an oven-dried reaction vial, 6-methyl-4-(phenylamino)-2*H*-pyran-2-one (**4**, 0.2 mmol, 40 mg) and thiophenols (**2**, 0.2 mmol) were taken. Then KI (20 mol%, 7 mg), $K_2S_2O_8$ (0.2 mmol, 1 equiv., 54 mg), and 1 mL DMSO were added to the reaction vial. The reaction mixture was then stirred under the irradiation of blue LED (435-445 nm) for 1 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (DCM)-water and dried over anhydrous sodium sulfate. After that, dichloromethane was evaporated to get the crude product. Finally, the crude product was

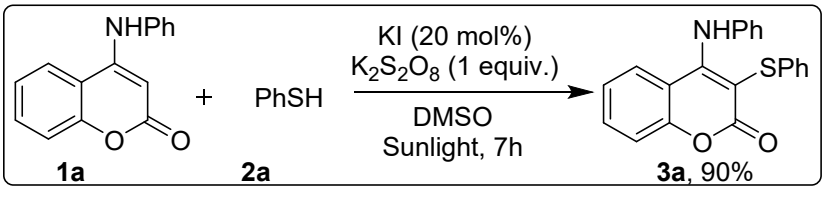
purified by column chromatography (100-200 mesh silica gel) employing ethyl acetate-petroleum ether (1:2) as eluent.



General procedure for the synthesis of 2-(Phenylamino)-3-(phenylthio)naphthalene-1,4-diones (7): In an oven-dried reaction vial, 2-(phenylamino)naphthalene-1,4-dione (**6**, 0.2 mmol, 50 mg) and thiophenol (**2**, 0.2 mmol) were taken. Then KI (20 mol%, 7 mg), $K_2S_2O_8$ (0.2 mmol, 1 equiv., 54 mg), and 1 mL DMSO were added to the reaction vial. The reaction mixture was then stirred under the irradiation of blue LED (435-445 nm) for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (DCM)-water and dried over anhydrous sodium sulfate. After that, dichloromethane was evaporated to get the crude product. Finally, the crude product was purified by column chromatography (100-200 mesh silica gel) employing ethyl acetate-petroleum ether (1:15) as eluent.



Procedure for the synthesis of 4-(phenylamino)-3-(phenylthio)-2*H*-chromen-2-one under sunlight: In an oven-dried reaction vial, 4-(phenylamino)-2*H*-chromen-2-one (**1a**, 0.2 mmol) and thiophenol (**2a**, 0.2 mmol) were taken. Then KI (20 mol%, 7 mg), $K_2S_2O_8$ (0.2 mmol, 1 equiv., 54 mg), and 1 mL DMSO were added to the reaction vial. The reaction mixture was then kept under sunlight for 7 h (Figure S1). After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (DCM)-water and dried over anhydrous sodium sulfate. After that, dichloromethane was evaporated to get the crude product. Column chromatography was not required for the purification of the desired product.



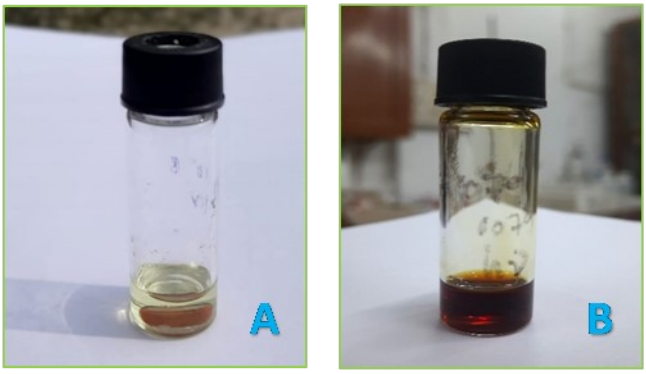
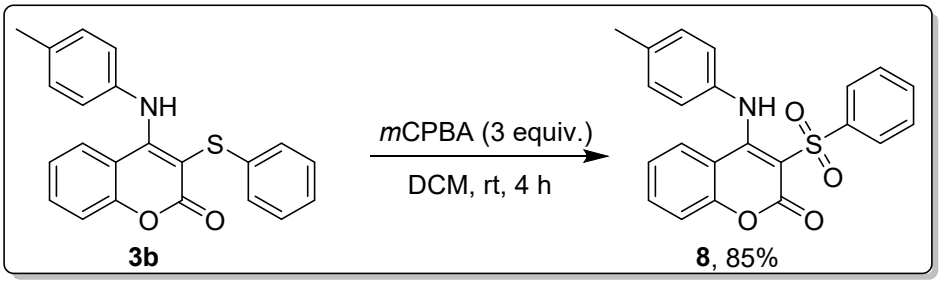


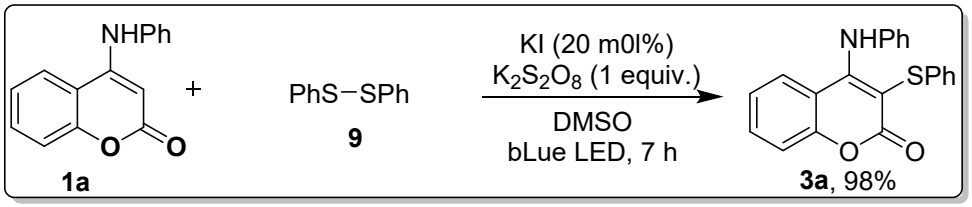
Figure 1. (A) Reaction mixture at t = 0; (B) Reaction mixture after the irradiation of sunlight for 7 h.

Procedure for the synthesis of 3-(phenylsulfonyl)-4-(p-tolylamino)-2*H*-chromen-2-one (8): In an oven-dried reaction vial, 3-(phenylthio)-4-(*p*-tolylamino)-2*H*-chromen-2-one (**3b**, 0.2 mmol, 72 mg) and *m*CPBA (0.6 mmol, 3 equiv., 103 mg) were taken. Then, 1 mL of dichloromethane was added to the reaction mixture. The reaction mixture was stirred at room temperature for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (DCM)-water and dried over anhydrous sodium sulfate. After that, dichloromethane was evaporated to get the crude product. Finally, the crude product was purified by column chromatography (100-200 mesh silica gel) employing ethyl acetate-petroleum ether (1:5) as eluent.

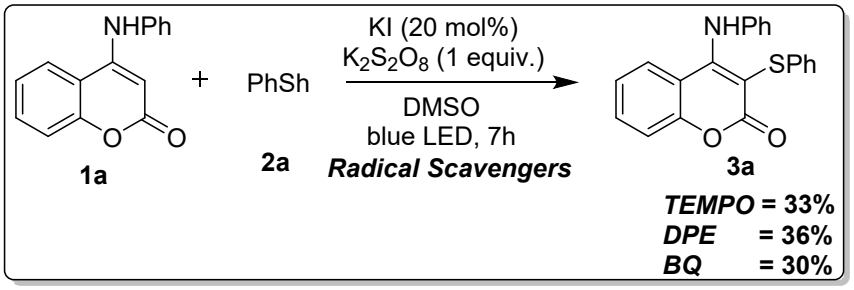


Procedure for control experiment:

Reaction of 4-(phenylamino)-2*H*-chromen-2-one with diphenyldisulphide: In an oven-dried reaction vial, 4-(phenylamino)-2*H*-chromen-2-one (**1a**, 0.2 mmol, 47 mg) and diphenyl disulphide (**9**, 0.1 mmol, 22 mg) were taken. Then KI (20 mol%, 7 mg), $K_2S_2O_8$ (0.2 mmol, 1 equiv., 54 mg), and 1 mL DMSO were added to the reaction vial. The reaction mixture was then stirred under the irradiation of blue LED (435-445 nm) for 7 h. After standard time, the starting compound was fully converted to the desired sulfenylated product.



Reaction of 4-(phenylamino)-2*H*-chromen-2-one with thiophenol in presence of radical scavengers: In an oven-dried reaction vial, 4-(phenylamino)-2*H*-chromen-2-one (**1a**, 0.2 mmol, 47 mg), thiophenol (**2a**, 0.2 mmol, 22 μL), and radical scavengers like TEMPO, DPE, BQ (0.4 mmol, 2 equiv.) were taken. Then KI (20 mol%, 7 mg), $K_2S_2O_8$ (0.2 mmol, 1 equiv., 54 mg), and 1 mL DMSO were added to the reaction vial. The reaction mixture was then stirred under the irradiation of blue LED (435-445 nm) for 7 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (DCM)-water and dried over anhydrous sodium sulfate. After that, dichloromethane was evaporated to get the crude product. Finally, the crude product was purified by column chromatography (100-200 mesh silica gel) employing ethyl acetate-petroleum ether (1:3) as eluent.



Test for the detection of the I_2 formed during the reaction: The formation of I_2 during the reaction was confirmed by using starch solution. Upon the addition of a starch solution, the reaction mixture (RM: 1a + 2a + KI + $K_2S_2O_8$ + DMSO) turned blue, which upon the addition of sodium thiosulfate ($Na_2S_2O_3$) solution, turned colourless.

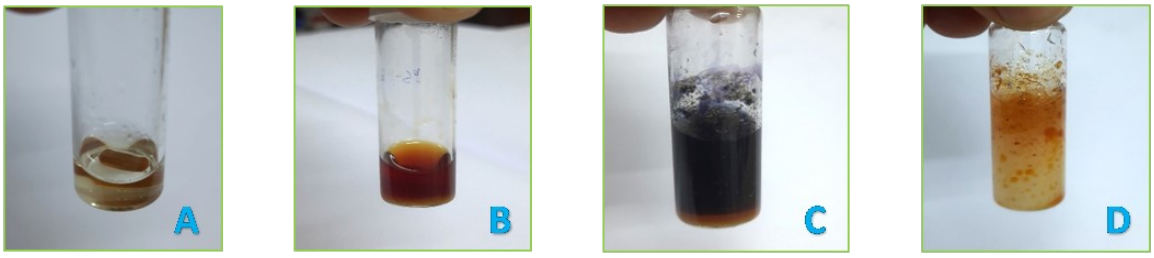
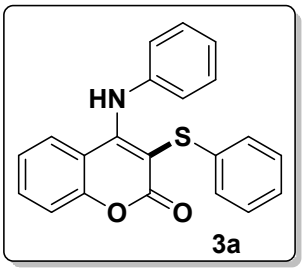
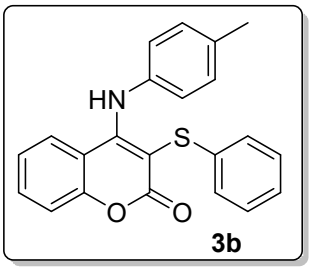


Figure 2. (A) Reaction mixture (RM: 1a + 2a + KI + $K_2S_2O_8$ + DMSO) at t = 0; (B) Reaction mixture at t = 7 h; (C) Reaction on addition of starchsolution (RM + starch solution); (D) Reaction mixture on addition of sodium thiosulfate solution (RM + starch solution+$Na_2S_2O_3$ solution).

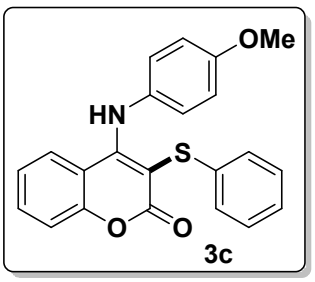
Characterization Data of the Synthesized Compounds:



4-(Phenylamino)-3-(phenylthio)-2H-chromen-2-one **(3a)**[1]. Yellow solid (67 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.09 (S, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37-7.29 (m, 6H), 7.27-7.23 (m, 2H), 7.20-7.14 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 8 Hz, 1H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 161.0, 156.5, 154.1, 140.7, 134.4, 132.7, 129.7, 129.3, 127.2, 126.8, 126.3, 124.2, 122.9, 117.8, 113.6, 97.1 ppm.

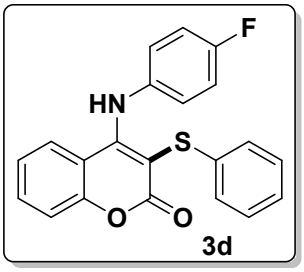


3-(Phenylthio)-4-(p-tolylamino)-2H-chromen-2-one **(3b)**[1]. Yellow solid (70 mg, 97%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.23 (s, 1H), 7.61-7.54 (m, 2H), 7.38 (d, *J* = 8 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.17-7.13 (m, 1H), 7.11-7.05 (m, 5H), 6.95 (d, *J* = 8.4 Hz, 2H), 2.24 (s, 3H) ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ: 160.7, 156.2, 153.5, 139.1, 136.5, 134.6, 133.2, 129.8, 129.4, 126.5, 125.9, 125.8, 124.0, 123.8, 117.7, 115.3, 94.7, 20.9 ppm.

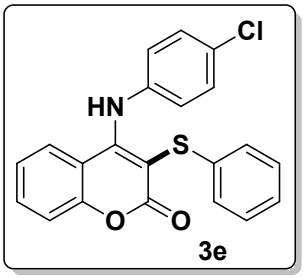


4-((4-Methoxyphenyl)amino)-3-(phenylthio)-2H-chromen-2-one **(3c)**[1]. Yellow solid (73 mg, 98%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.22 (s, 1H), 7.59 (t, *J* = 8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.07-7.05 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H)

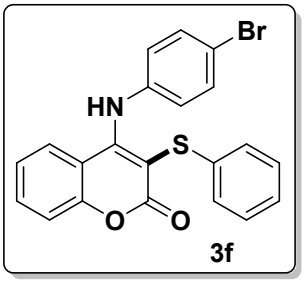
ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ: 160.9, 157.4, 156.4, 153.6, 136.7, 134.2, 133.2, 129.4, 126.3, 126.2, 125.8, 125.7, 123.7, 117.7, 115.1, 114.5, 92.8, 55.7 ppm.



4-((4-Fluorophenyl)amino)-3-(phenylthio)-2H-chromen-2-one **(3d)**[1]. Yellow solid (69 mg, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.32 (s, 1H), 7.66-7.60 (m, 2H), 7.40 (d, J = 8 Hz, 1H), 7.24-7.18 (m, 3H), 7.11-7.01 (m, 7H) ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ: 160.3 159.3 (J_{C-F} = 240 Hz), 155.3, 153.0, 137.4, 136.1, 132.8, 128.9, 125.9, 125.6, 125.4 (J_{C-F} = 23 Hz), 125.1, 123.6, 117.3, 115.5, 115.3 (J_{C-F} = 8 Hz), 94.1 ppm. ^{19} F NMR (DMSO-d_6, 376 MHz) δ: -117.7 ppm.

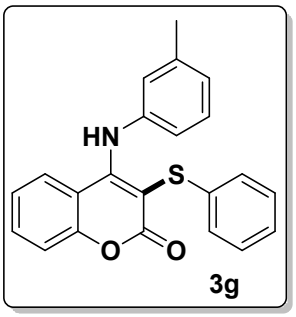


4-((4-Chlorophenyl)amino)-3-(phenylthio)-2H-chromen-2-one **(3e)**[1]. Yellow solid (73 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.97 (s, 1H), 7.50 (t, J = 8 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.32-7.24 (m, 6H), 7.21 (d, J = 8 Hz, 1H), 7.18-7.15 (m, 1H), 7.02-6.99 (m, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 160.8, 156.1, 154.0, 139.4, 134.2, 132.8, 131.6, 129.7, 129.3, 127.3, 126.6, 126.5, 125.1, 123.2, 117.9, 113.5, 98.4 ppm.

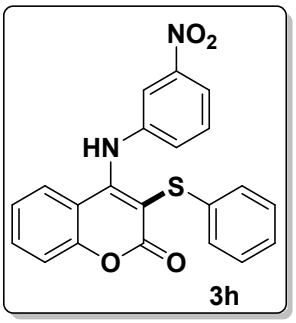


4-((4-Bromophenyl)amino)-3-(phenylthio)-2H-chromen-2-one **(3f)**[1]. Brown solid (80 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.35 (s, 1H), 7.70 (d, J = 8 Hz, 1H), 7.63 (t, J = 8 Hz, 1H), 7.42-7.37 (m, 3H), 7.26 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 2H), 7.10 (t, J = 7.2 Hz,

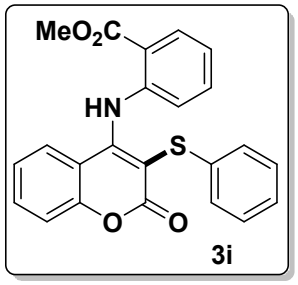
1H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 160.7, 155.0, 153.3, 141.1, 136.1, 133.3, 131.9, 129.4, 126.7, 126.0, 125.4, 125.0, 124.2, 117.6, 116.5, 115.7, 97.2 ppm.



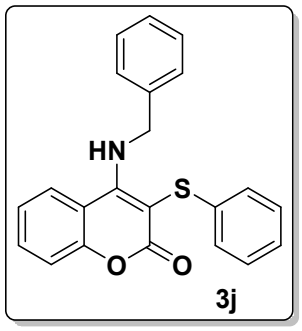
3-(Phenylthio)-4-(m-tolylamino)-2H-chromen-2-one **(3g)**[1]. Yellow solid (70 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.09 (s, 1H), 7.49-7.47 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.33-7.31 (m, 2H), 7.29-7.27 (m, 2H), 7.25-7.18 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.99-6.94 (m, 2H), 6.88 (d, *J* = 8 Hz, 1H), 2.33 (s, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 161.0, 156.5, 154.1, 140.5, 139.8, 134.5, 132.6, 129.4, 129.2, 127.2, 127.1, 126.8, 126.3, 124.9, 122.9, 121.4, 117.8, 113.7, 96.5, 21.3 ppm.



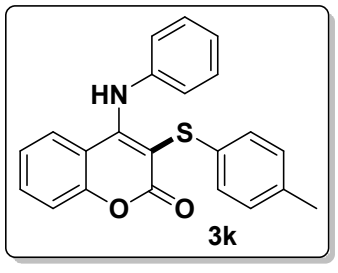
4-((3-Nitrophenyl)amino)-3-(phenylthio)-2H-chromen-2-one **(3h)**[1]. Yellowish white solid (65 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H), 7.88 (s, 1H), 7.58-7.54 (m, 1H), 7.48 (t, *J* = 8 Hz, 1H), 7.43 (d, *J* = 8 Hz, 1H), 7.31-7.27 (m, 4H), 7.25-7.17 (m, 3H), 7.06 (t, *J* = 8 Hz, 1H), ppm.^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 160.4, 154.9, 153.9, 148.9, 142.3, 133.8, 133.1, 130.2, 129.4, 128.3, 127.8, 126.9, 126.0, 123.5, 119.9, 118.1, 117.3, 113.6, 102.2 ppm.



Methyl 2-((2-oxo-3-(phenylthio)-2H-chromen-4-yl)amino)benzoate **(3i)**. Pale yellow solid (64 mg, 80%). Melting point = 117-120 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.12 (s, 1H), 7.93 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 1H), 7.54 (dt, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 7.48 (dd, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 7.40 (d, J = 8 Hz, 1H), 7.36-7.32 (m, 1H), 7.21-7.10 (m, 6H), 7.04 (t, J = 8 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 167.9, 161.0, 153.1, 151.6, 142.2, 133.9, 133.0, 132.4, 131.1, 128.8, 126.6, 125.2, 123.6, 121.8, 120.2, 117.6, 116.7, 115.8, 105.4, 52.2 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{23}H_{18}NO_4S^+$: 404.0957, found: 404.0963.

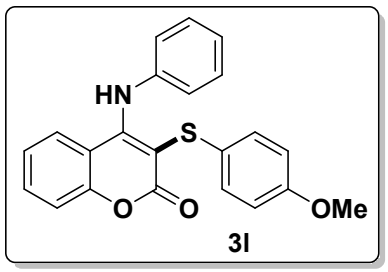


4-(Benzylamino)-3-(phenylthio)-2H-chromen-2-one **(3j)**. Yellow solid (66 mg, 92%). Melting point = 153-156 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.87 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 8 Hz, 1H), 7.41 (d, J = 8 Hz, 1H), 7.34-7.33 (m, 3H), 7.28-7.14 (m, 8H), 6.75 (brs, 1H), 4.95 (d, J = 6 Hz, 2H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 161.6, 158.8, 154.0, 137.2, 135.3, 132.9, 129.1, 128.2, 127.1, 126.6, 126.0, 125.0, 123.5, 118.3, 114.1, 91.1, 51.6 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{22}H_{18}NO_2S^+$: 360.1058, found: 360.1066.



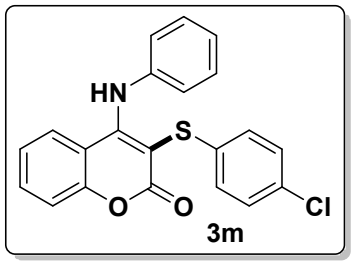
4-(Phenylamino)-3-(p-tolylthio)-2H-chromen-2-one **(3k)**. Yellow solid (69 mg, 96%). Melting point = 245-248 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.09 (s, 1H), 7.46-7.44 (m, 1H),

7.34 (t, J = 8 Hz, 3H),7.26-7.24 (m, 3H), 7.19 (dd, J_1= 7.2 Hz, J_2= 1.2 Hz, 1H), 7.08-7.06 (m, 4H), 6.95-6.91 (m, 1H), 2.28 (s, 3H) ppm. ^{13}C {^{1}H} NMR($CDCl_3$, 100 MHz) δ:160.9, 156.1, 154.0, 140.8, 136.6, 132.5, 130.7, 130.0, 129.6, 127.9, 126.8, 126.1, 124.1, 122.9, 117.8, 113.8, 98.3, 20.9 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{22}H_{18}NO_2S^+$: 360.1058, found: 360.1066.



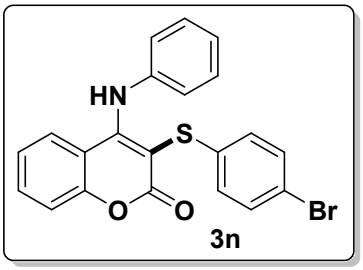
3l

3-((4-Methoxyphenyl)thio)-4-(phenylamino)-2H-chromen-2-one **(3l)**. Yellow solid (72 mg, 97%). Melting point = 212-215 ºC. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.25 (s, 1H), 7.60-7.56 (m, 2H), 7.38(d, J = 8.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.13-703 (m, 5H), 6.78 (d, J = 8.8 Hz, 2H),3.67 (s, 3H) ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ: 160.0, 158.0, 154.2, 152.9, 141.6, 132.5, 129.6, 128.9, 126.2, 125.3, 124.2, 123.4, 122.8, 117.1, 115.3, 114.6, 98.3 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{22}H_{18}NO_3S^+$: 376.1007, found: 376.0998.

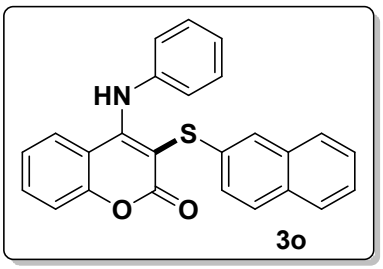


3m

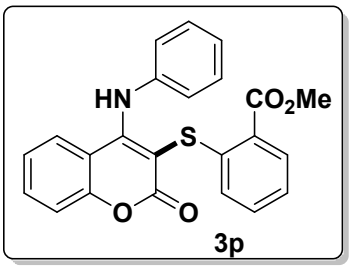
3-((4-Chlorophenyl)thio)-4-(phenylamino)-2H-chromen-2-one **(3m)**. Yellow solid (73 mg, 96%). Melting point = 235-238 ºC. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.39 (s, 1H), 7.67-7.60 (m, 2H), 7.41 (d, J = 8 Hz, 1H), 7.26-7.19 (m, 5H), 7.11 (t, J = 7.6 Hz, 1H), 7.06-7.04 (m, 4H) ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ:160.1, 155.2, 153.0, 141.2, 135.4, 132.8, 129.7, 128.8, 128.7, 127.8, 125.2, 124.7, 123.5, 123.4, 117.2, 115.3, 94.3 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{21}H_{15}ClNO_2S^+$: 380.0512, found: 380.0506.



3-((4-Bromophenyl)thio)-4-(phenylamino)-2H-chromen-2-one **(3n)**. Yellow solid (82 mg, 97%). Melting point = 236-239 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (s, 1H), 7.51-7.46 (m, 1H), 7.38-7.34 (m, 5H), 7.28-7.23 (m, 1H), 7.20-7.16 (m, 3H), 7.09 (d, *J* = 8 Hz, 2H), 6.97-6.93 (m, 1H) ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ: 160.1, 155.3, 153.0, 141.2, 136.0, 132.8, 131.6, 128.8, 128.0, 125.2, 124.7, 123.5, 123.4, 117.9, 117.3, 115.3. 94.1 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{21}H_{15}BrNO_2S^+$: 424.0007, found: 424.0009.

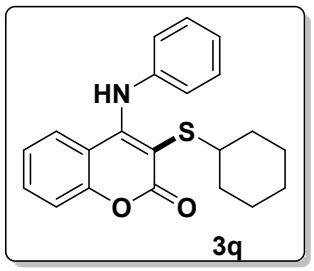


3-(Naphthalen-2-ylthio)-4-(phenylamino)-2H-chromen-2-one **(3o)**. Reddish yellow solid (75 mg, 95%). Melting point = 190-193 ºC. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.37 (s, 1H), 7.80 (d, *J* = 8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.65-7.61 (m, 2H), 7.55 (d, *J* = 1.2 Hz, 1H), 7.44-7.40 (m, 3H), 7.22 (q, *J* = 7.6 Hz, 4H), 7.11-7.06 (m, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$ + DMSO-d_6, 100 MHz) δ: 153.5, 141.8, 134.0, 133.7, 133.3, 131.5, 129.2, 128.8, 128.0, 127.2, 127.0, 125.9, 125.7, 125.2, 125.1, 124.1, 123.9, 123.6, 117.7, 115.6 ppm. HRMS (ESI-TOF), m/z, $[M + H]^+$: Calcd Mass for $C_{25}H_{18}NO_2S^+$: 396.1058, found: 396.1053.

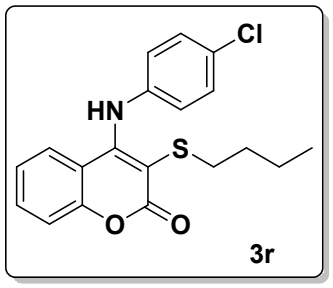


Methyl 2-((2-oxo-4-(phenylamino)-2H-chromen-3-yl)thio)benzoate **(3p)**. Yellow crystalline solid (64 mg, 80%). Melting point = 220-223 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.22 (s, 1H), 8.05-8.03 (m, 1H), 7.53-7.49 (m, 1H), 7.40-7.32 (m, 4H), 7.28-7.25 (m, 1H), 7.22-7.19 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 2H),6.98-6.94 (m, 1H), 3.95 (s, 3H) ppm. ^{13}C {^{1}H} NMR($CDCl_3$, 100 MHz) δ: 166.9, 160.9, 157.4, 154.3, 140.6, 138.9, 132.9, 132.8, 131.7, 129.6, 127.5, 126.9,

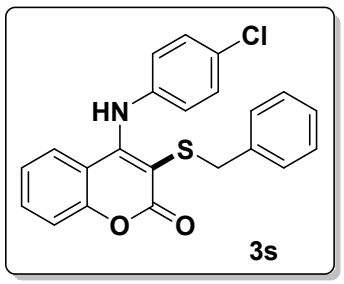
126.3, 125.4, 125.1, 124.4, 122.9, 117.9, 113.6, 95.7, 52.2 ppm. HRMS (ESI-TOF), m/z, [M + H]$^+$: Calcd Mass for $C_{23}H_{18}NO_4S^+$: 404.0957, found: 404.0948.



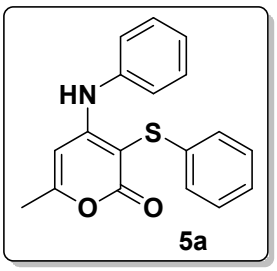
3-(Cyclohexylthio)-4-(phenylamino)-2H-chromen-2-one **(3q)**. Yellow gummy mass (55 mg, 79%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.88 (s, 1H), 7.55-7.51 (m, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 8 Hz, 2H), 7.13-7.07 (m, 2H), 7.04 (d, J = 8 Hz, 2H),3.17-3.12 (m, 1H), 1.75-1.73 (m, 2H), 1.61-1.60 (m, 2H), 1.47-1.45 (m, 1H), 1.22-1.12 (m, 5H) ppm. ^{13}C {^{1}H} NMR (DMSO-d_6, 100 MHz) δ: 160.7, 155.1, 153.2, 142.3, 132.6, 129.5, 125.9, 124.6, 123.6, 122.9, 117.5, 115.3, 99.7, 45.0, 32.7, 25.7, 25.6 ppm. HRMS (ESI-TOF), m/z, [M + H]$^+$: Calcd Mass for $C_{21}H_{22}NO_2S^+$: 352.1371, found: 352.1364.



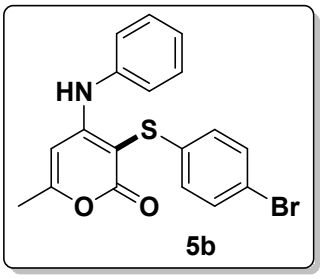
3-(Butylthio)-4-((4-chlorophenyl)amino)-2H-chromen-2-one **(3r)**. Yellow gummy mass (56 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.94 (s, 1H), 7.47 (t, J = 8 Hz, 1H), 7.36-7.28 (m, 3H), 7.20 (d, J = 8.4 Hz, 1H), 7.02-6.99 (m, 3H), 2.89 (t, J = 7.6 Hz, 2H), 1.59-1.52 (m, 2H), 1.44-1.35 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 160.6, 155.2, 153.6, 140.0, 132.1, 130.8, 129.6, 126.3, 124.4, 123.1, 117.7, 113.4, 101.4, 33.6, 31.8, 21.9, 13.6 ppm. HRMS (ESI-TOF), m/z, [M + H]$^+$: Calcd Mass for $C_{19}H_{19}ClNO_2S^+$: 360.0825, found: 360.0851.



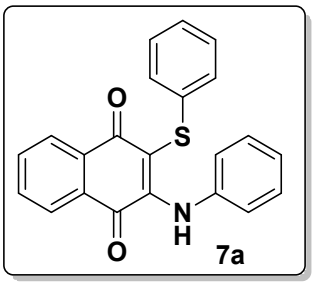
3-(Benzylthio)-4-((4-chlorophenyl)amino)-2H-chromen-2-one **(3s)**. Yellow gummy mass (64 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61 (s, 1H), 7.46-7.42 (m, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.19-7.17 (m, 4H), 7.13-7.11 (m, 3H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 4.07 (s, 1H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 160.7, 155.9, 153.7, 139.4, 138.2, 132.2, 131.0, 129.3, 128.7, 128.5, 127.1, 126.4, 124.9, 122.9, 117.7, 113.4, 98.7. 37.6 ppm. HRMS (ESI-TOF), m/z, [M + H]$^{+}$: Calcd Mass for $C_{22}H_{17}ClNO_2S^{+}$: 394.0669, found: 394.0676.



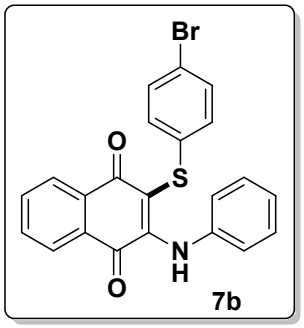
6-Methyl-4-(phenylamino)-3-(phenylthio)-5,6-dihydro-2H-pyran-2-one **(5a)**. Yellow gummy mass (54 mg, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.87 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.29-7.26 (m, 4H), 7.18-7.12 (m, 3H), 5.96 (s, 1H), 2.21 (s, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ:164.1, 163.3, 159.0, 136.9, 135.1, 129.7, 129.1, 127.1, 126.3, 125.9, 125.4, 95.4, 85.8, 20.5 ppm.



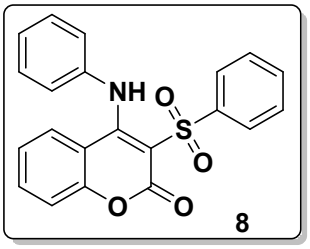
3-((4-Bromophenyl)thio)-6-methyl-4-(phenylamino)-5,6-dihydro-2H-pyran-2-one **(5b)**. Yellow gummy mass (65 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 3H), 7.06-7.04 (m, 4H), 5.86 (s, 1H), 2.12 (s, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 164.3, 163.1, 159.0, 136.7, 134.5, 132.1, 129.8, 127.9, 127.3, 125.5, 119.6, 95.4, 85.3, 20.5 ppm. HRMS (ESI-TOF), m/z, [M + H]$^{+}$: Calcd Mass for $C_{18}H_{16}BrNNaO_2S^{+}$: 411.9983, found: 411.9936.



2-(Phenylamino)-3-(phenylthio)naphthalene-1,4-dione **(7a)**[2]. Violet solid (64 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.20 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.97 (s, 1H), 7.80-7.76 (m, 1H), 7.73-7.69 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06-7.01 (m, 3H), 6.76-6.74 (m, 2H), 6.71 (d, *J* = 7.6 Hz, 2H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 181.1, 180.8, 142.5, 136.3, 134.8, 133.4, 133.1, 132.8, 130.4, 128.3, 127.7, 127.1, 126.8, 125.8, 124.6, 122.9, 113.0 ppm.



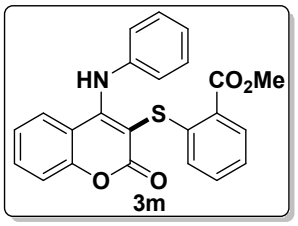
2-((4-Bromophenyl)thio)-3-(phenylamino)naphthalene-1,4-dione **(7b)**[2]. Violet solid (77 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.10 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.93 (s, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.06-7.01 (m, 3H), 6.63 (d, *J* = 7.6 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 181.0, 180.7, 136.0, 135.0, 133.3, 132.9, 132.5, 131.3, 130.3, 129.7, 127.8, 127.1, 126.9, 124.9, 123.1, 119.6, 112.0 ppm



4-(Phenylamino)-3-(phenylsulfonyl)-2H-chromen-2-one **(8)**. White solid (64 mg, 85%).^{1}H NMR ($CDCl_3$, 400 MHz) δ: 11.02 (s, 1H), 8.15-8.13 (m, 2H), 7.64-7.60 (m, 1H), 7.56-7.52 (m, 2H), 7.49-7.45 (m, 1H), 7.28-7.22 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.92-6.88 (m, 1H), 2.42 (s, 3H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ:156.9, 156.0, 154.4, 141.3, 137.4, 137.3, 134.0, 133.4, 130.6, 128.6, 128.4, 128.2, 124.6, 122.9, 117.9, 113.2, 101.3, 21.1 ppm

X-Ray crystallographic analysis of the compound 3m:

Procedure for crystal growth: Compound **3m** (15 mg) was dissolved in DCM/Petroleum ether (v/v = 2 mL/3 mL). At room temperature, yellow cubic crystals of the compound **3m** were grown by slow evaporation of solvent.



CCDC: 2483055

Bond precision:	C-C = 0.0075 A		Wavelength=0.71073
Cell:	a=9.8696(9)	b=9.9403(8)	c=19.5879(17)
alpha=90	beta=90	gamma=90	
Temperature:	301 K		
Calculated		Reported	
Volume	1921.7(3)		1921.7(3)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	C23 H17 N O4 S		C23 H17 N O4 S
Sum formula	C23 H17 N O4 S		C23 H17 N O4 S
Mr	403.44		403.43
Dx, g cm-3	1.394		1.394
Z	4		4
Mu (mm-1)	0.199		0.199
F000	840.0		840.0
F000’	840.89		
h, k, lmax	12,12,24		12,12,24
Nref	3938[2257]		3929
Tmin, Tmax			0.677,0.745
Tmin’			

Correction method= # Reported T Limits: Tmin=0.677 Tmax=0.745

AbsCorr = MULTI-SCAN

Data completeness= 1.74/1.00 Theta(max)= 26.370

R(reflections)= 0.0752(3069) wR2(reflections)=

S = 1.260 Npar= 266 0.1123(3929)

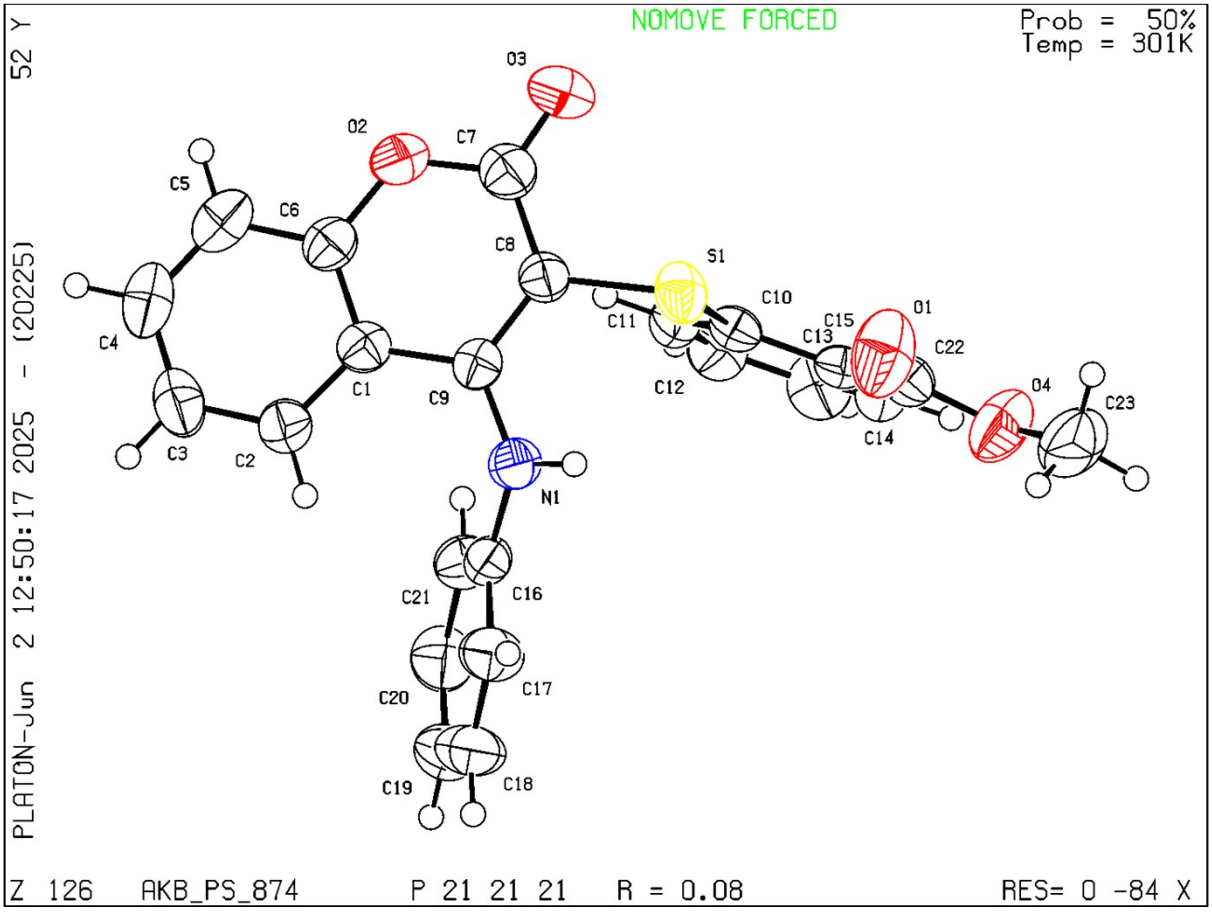
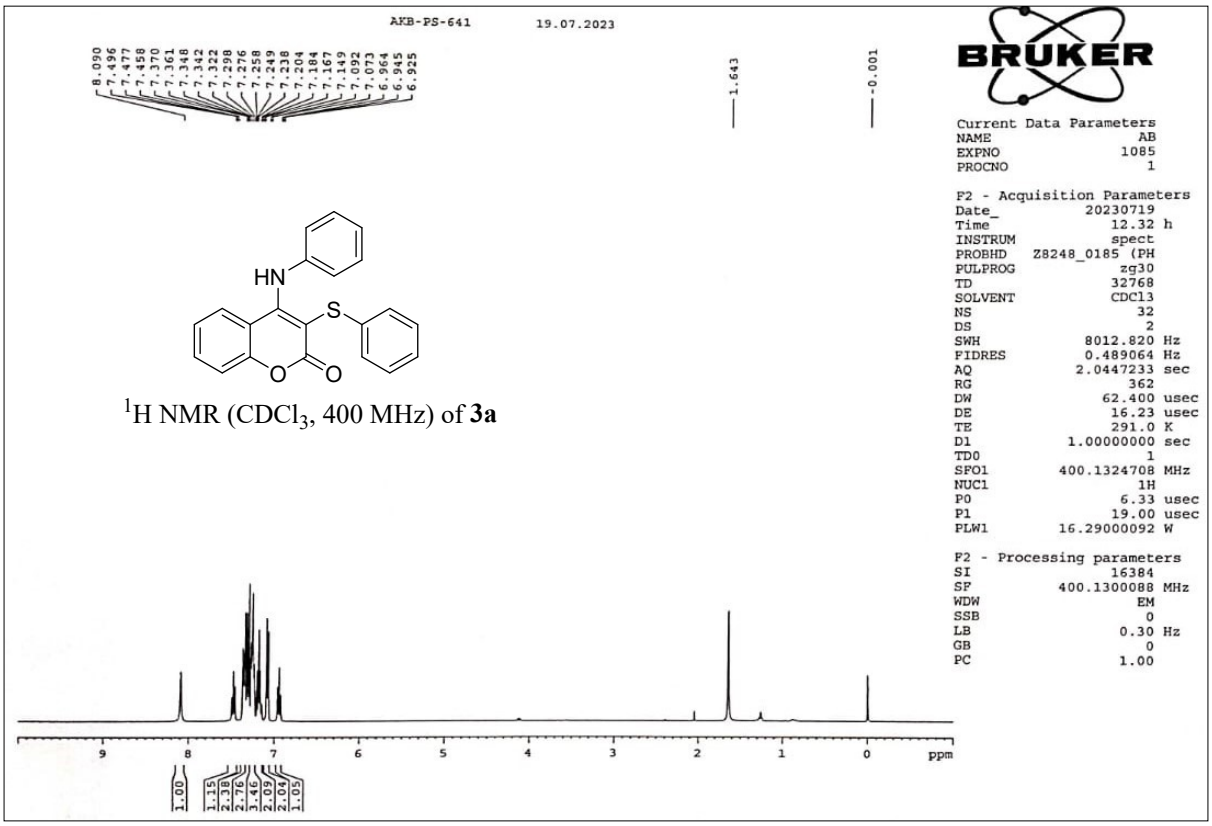


Figure: X-Ray crystal structure of the compound**3m.**

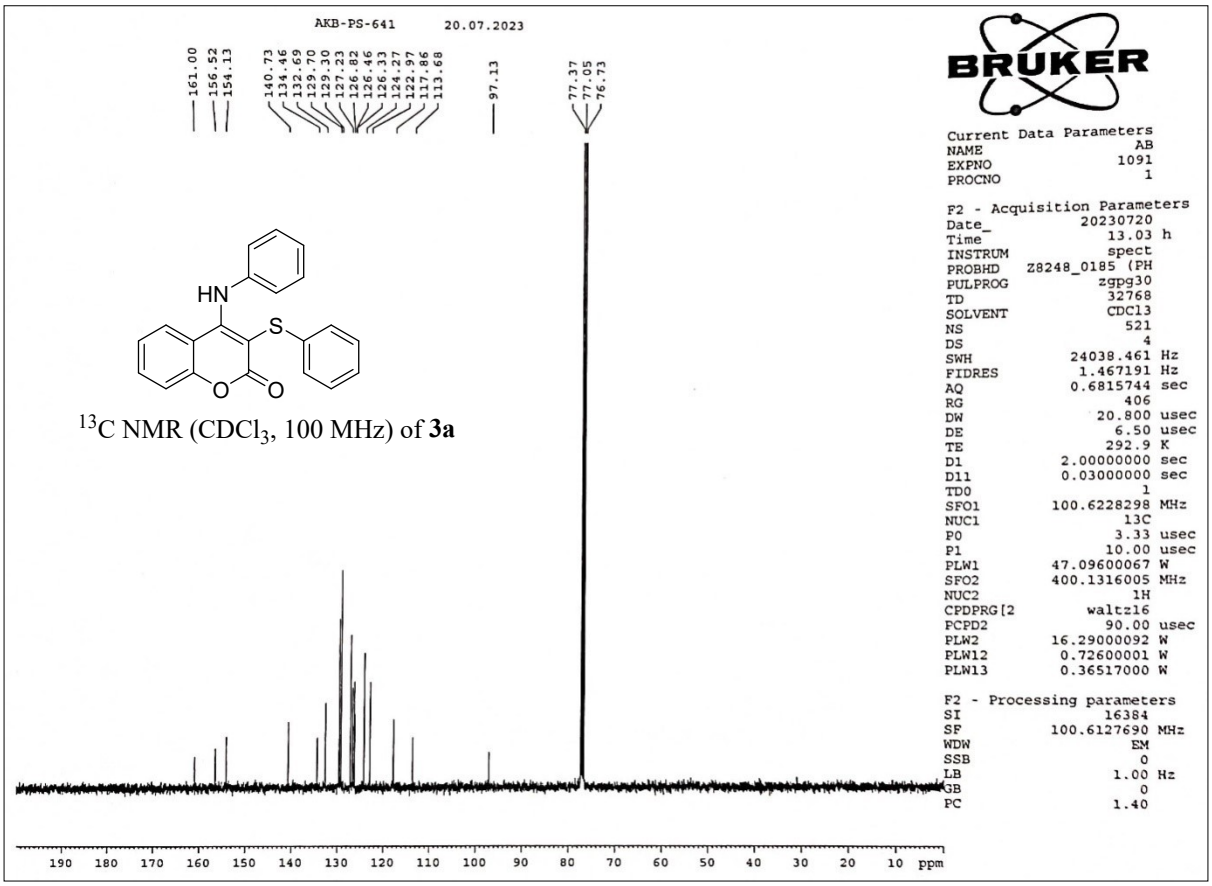
Reference:

1. S. S. Sahay, S. Rahaman, R. Das and S. Dey, *Eur. J. Org. Chem.*, 2025, **28**, e202401163.
2. N. Nayek and G. Brahmachari, *Eur. J. Org. Chem.*, 2023, **26**, e202201343.

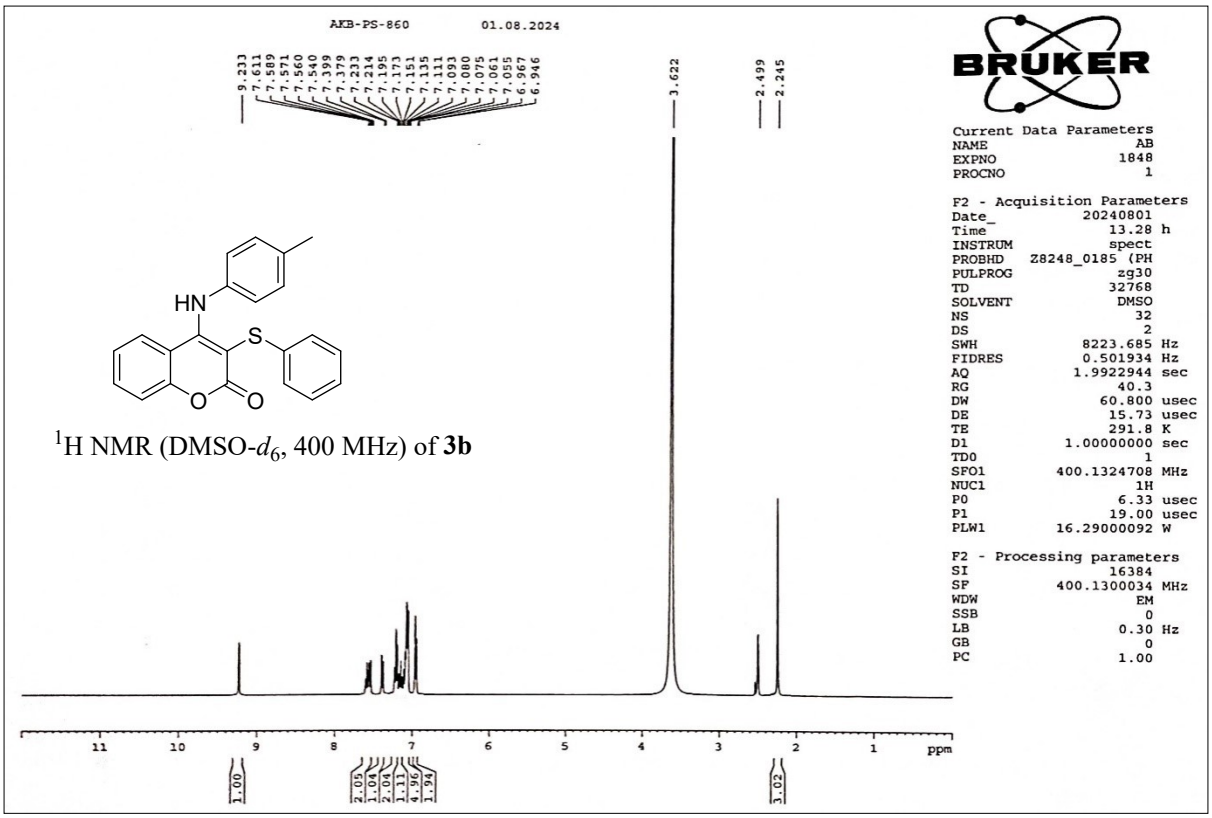
^{1}H and ^{13}C NMR Spectra:



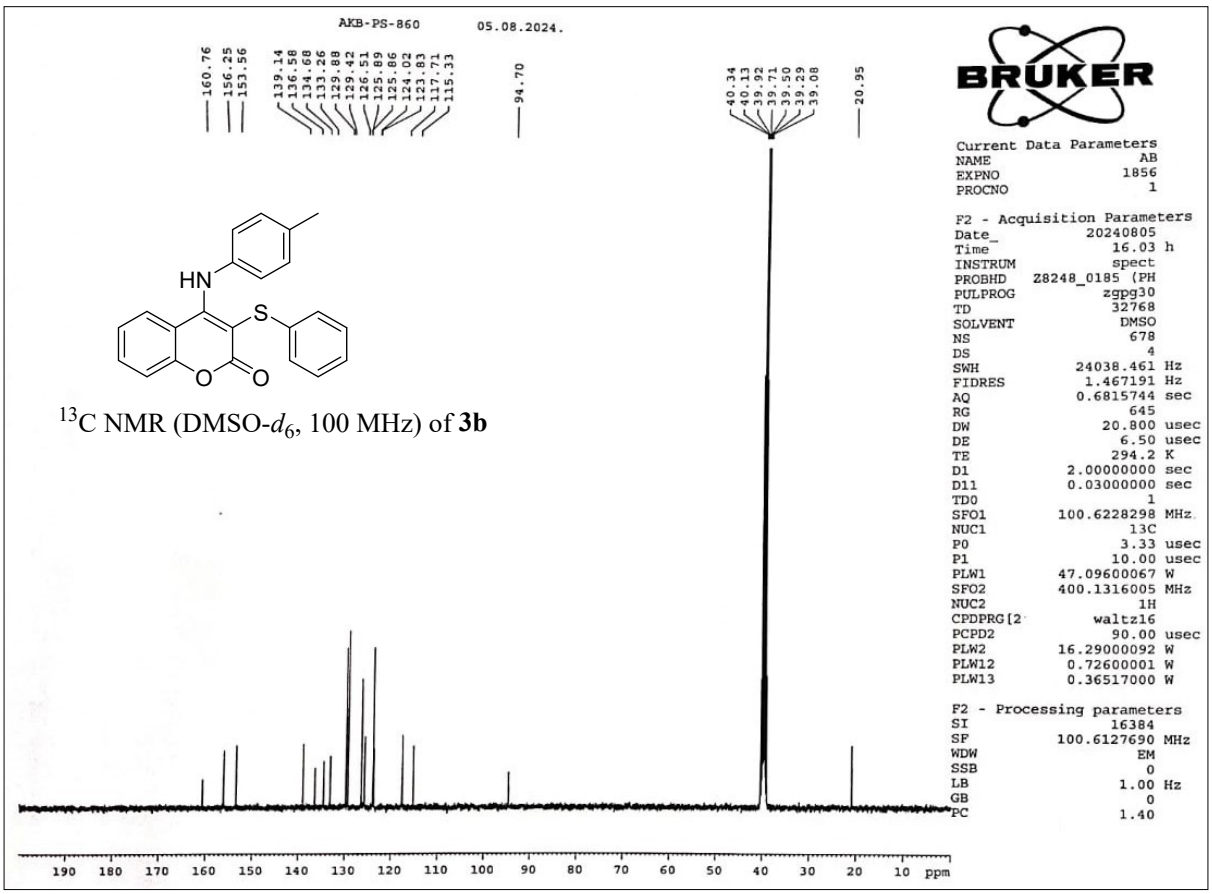
^{1}H NMR ($CDCl_3$, 400 MHz) of **3a**



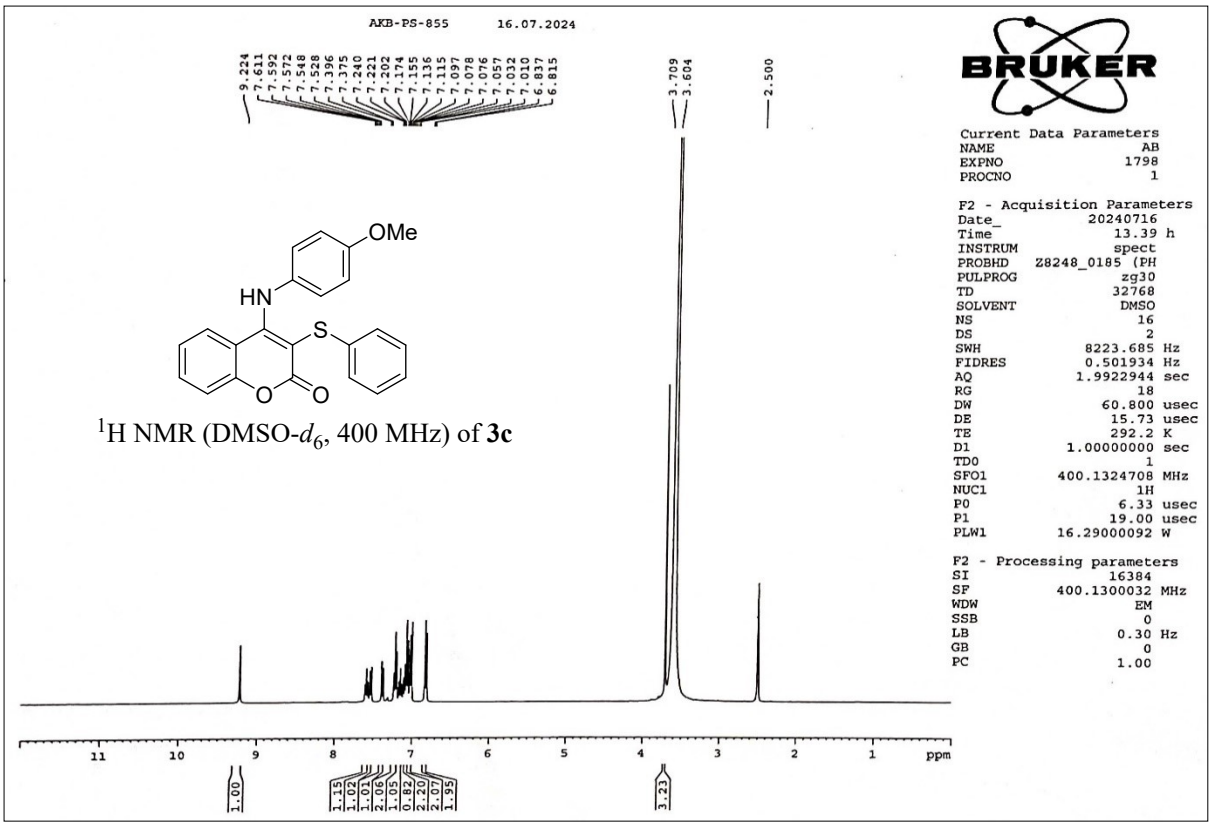
^{13}C NMR ($CDCl_3$, 100 MHz) of **3a**



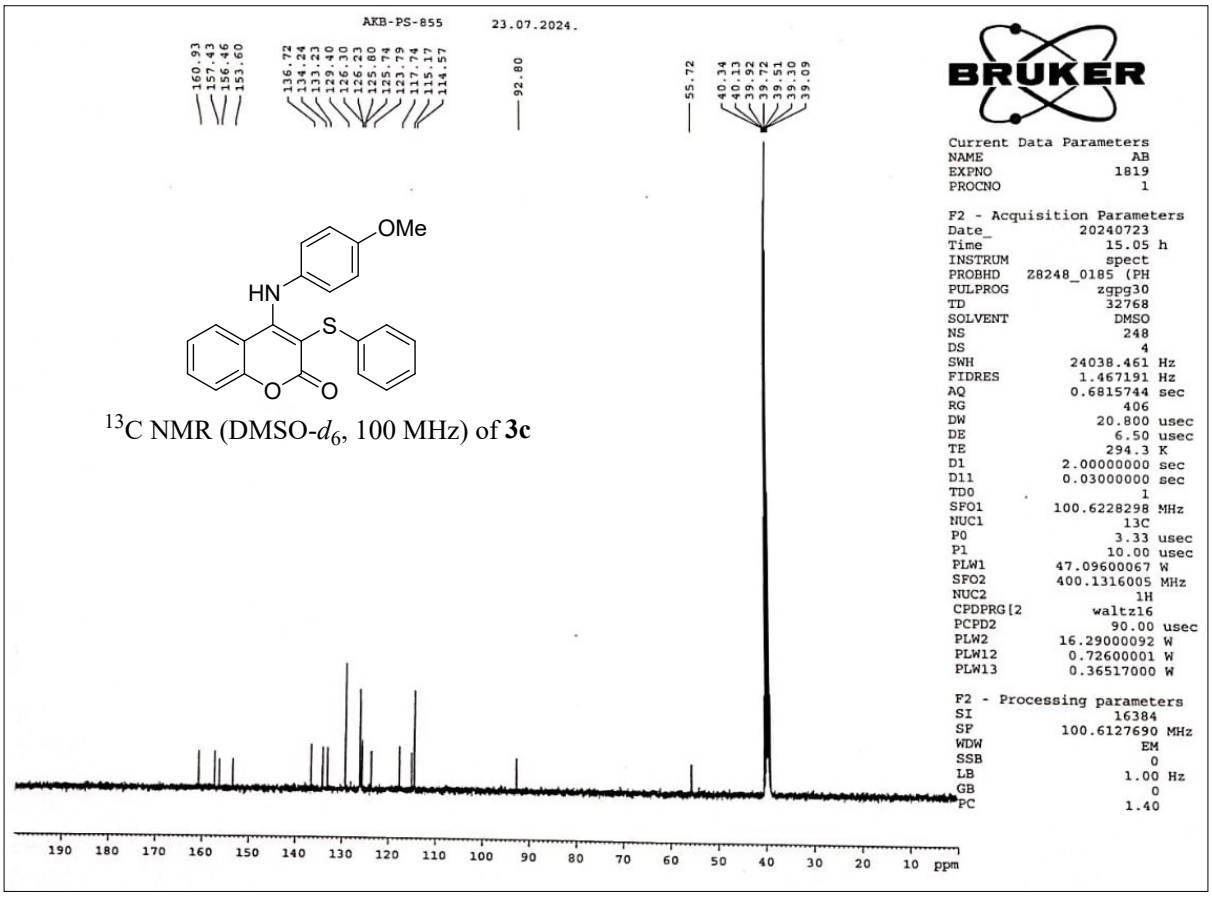
^{1}H NMR (DMSO-d_6, 400 MHz) of **3b**



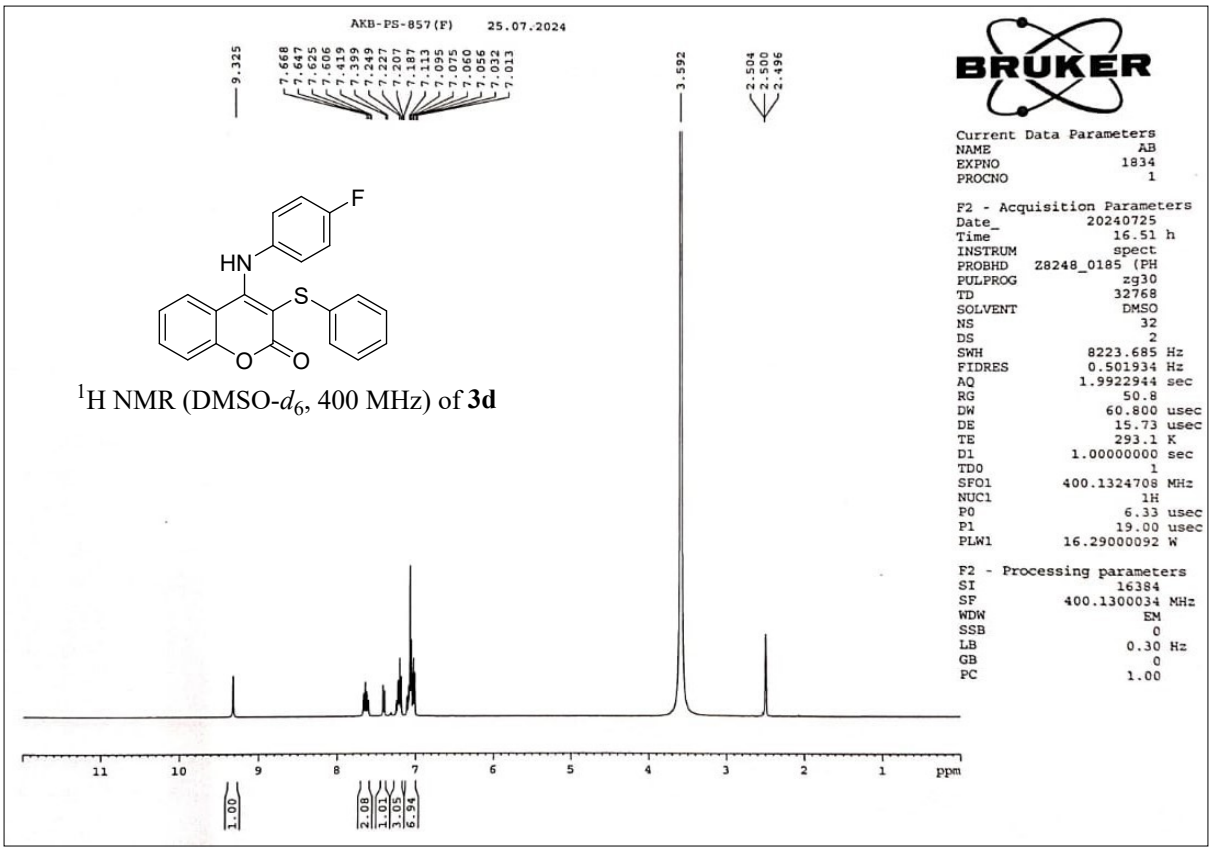
^{13}C NMR (DMSO-d_6, 100 MHz) of **3b**



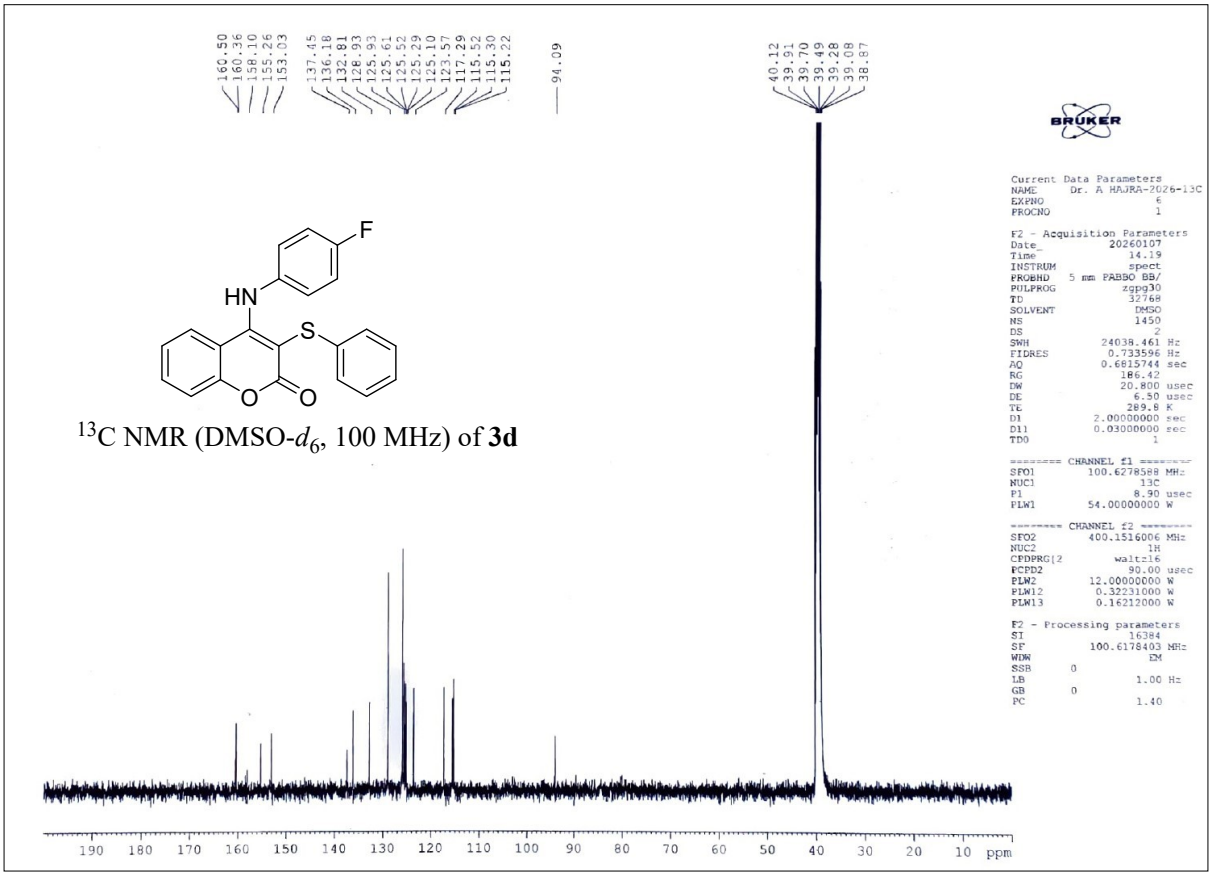
^{1}H NMR (DMSO-d_6, 400 MHz) of **3c**



^{13}C NMR (DMSO-d_6, 100 MHz) of **3c**

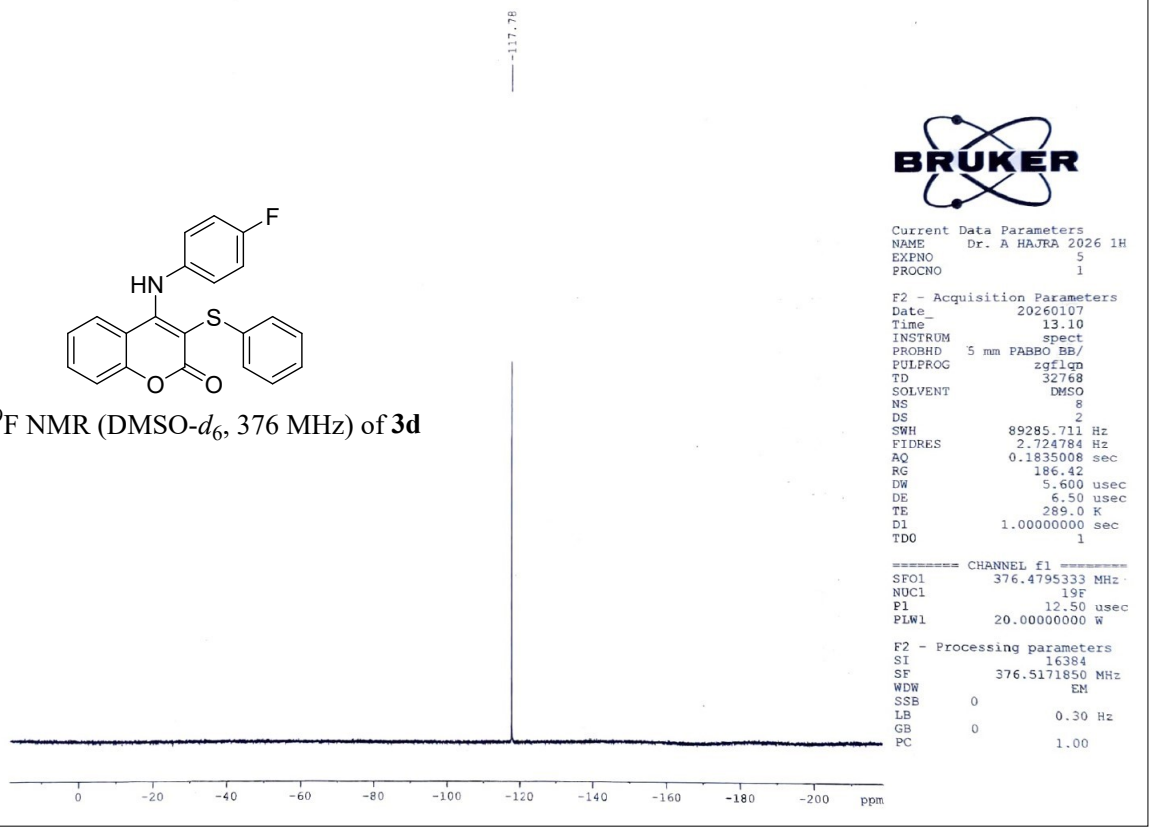


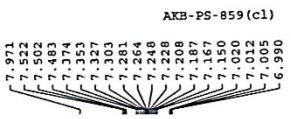
^{1}H NMR (DMSO-d_6, 400 MHz) of **3d**

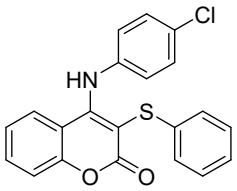


^{13}C NMR (DMSO-d_6, 100 MHz) of **3d**

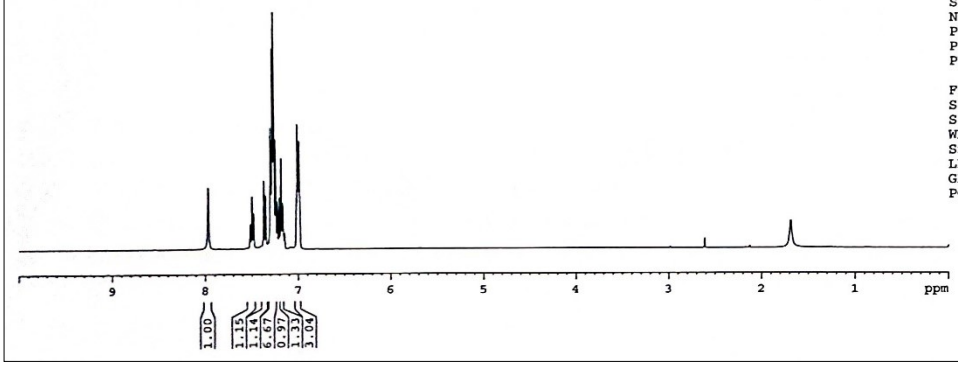
^{19}F NMR (DMSO-d_6, 376 MHz) of **3d**

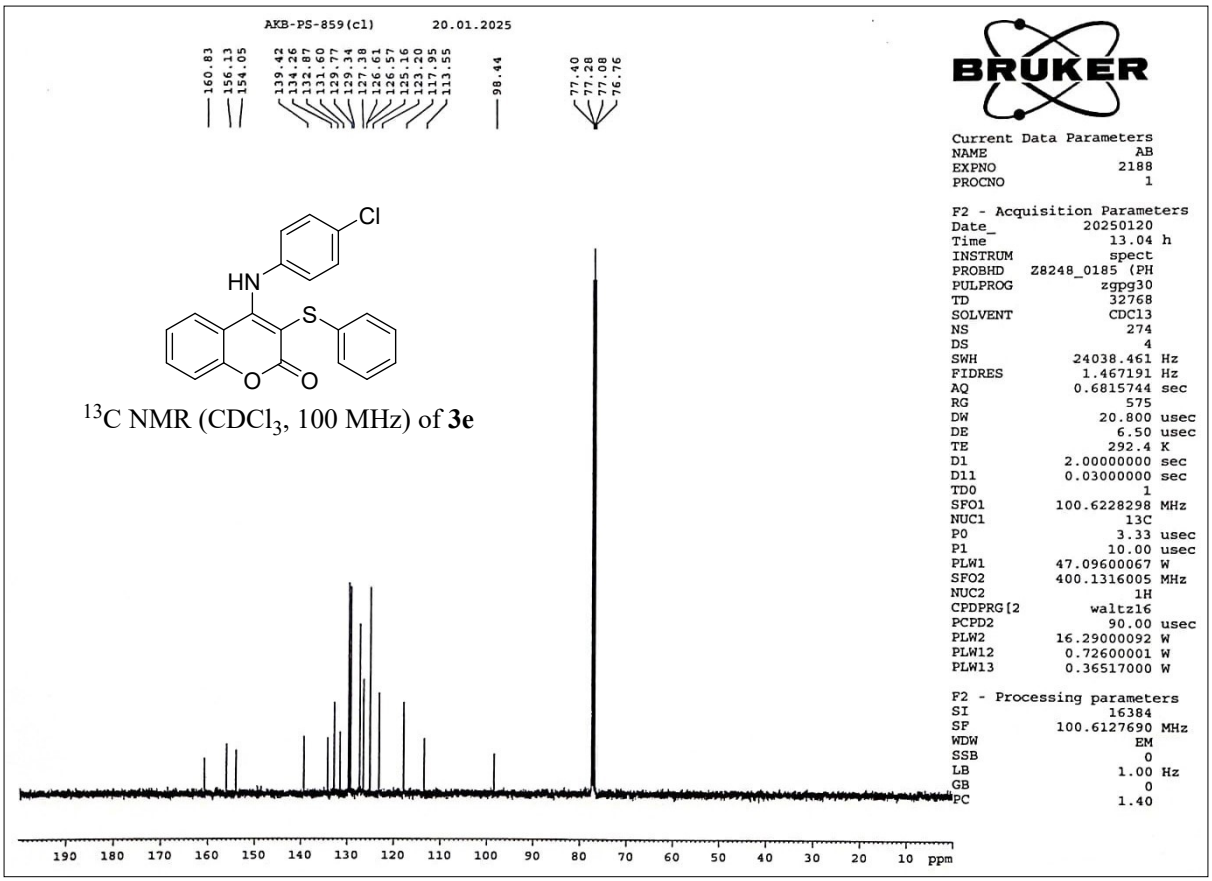




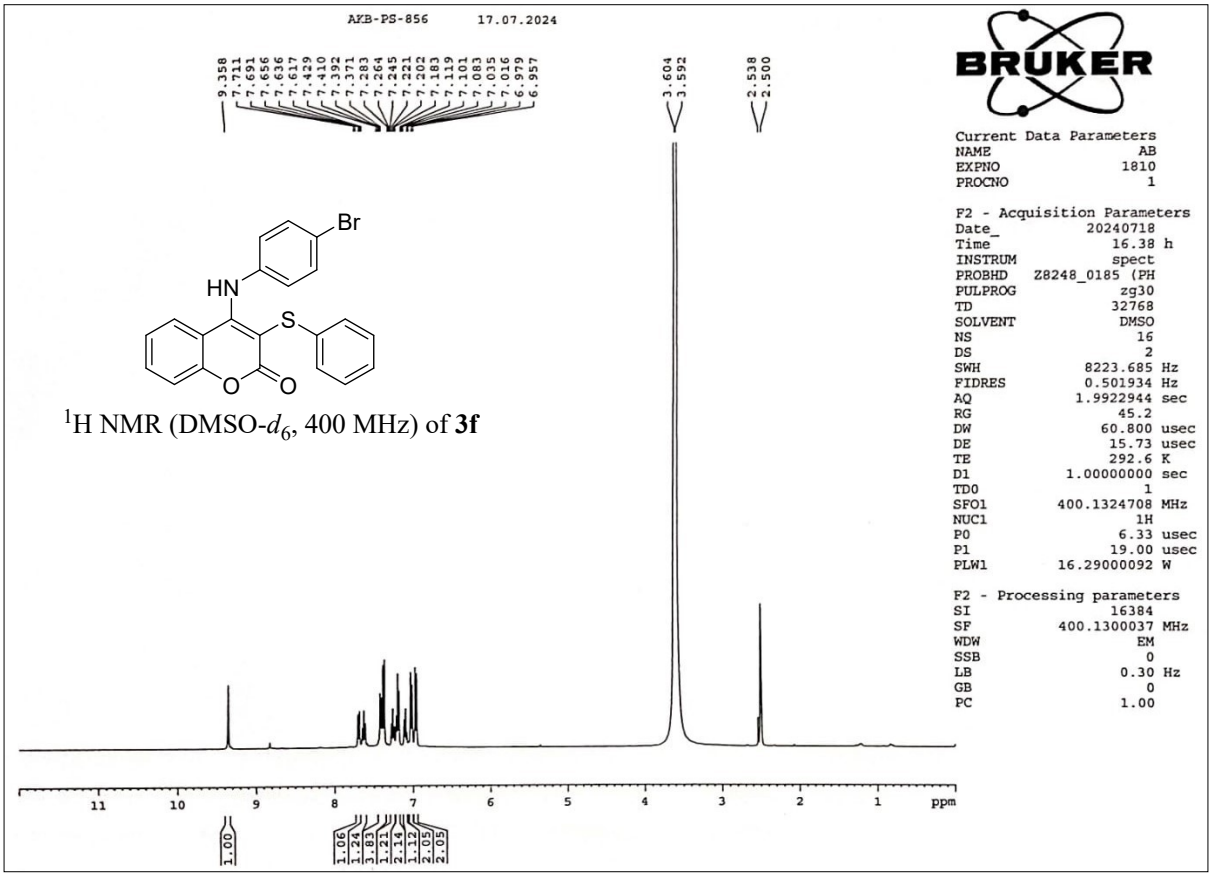


^{1}H NMR ($CDCl_3$, 400 MHz) of **3e**

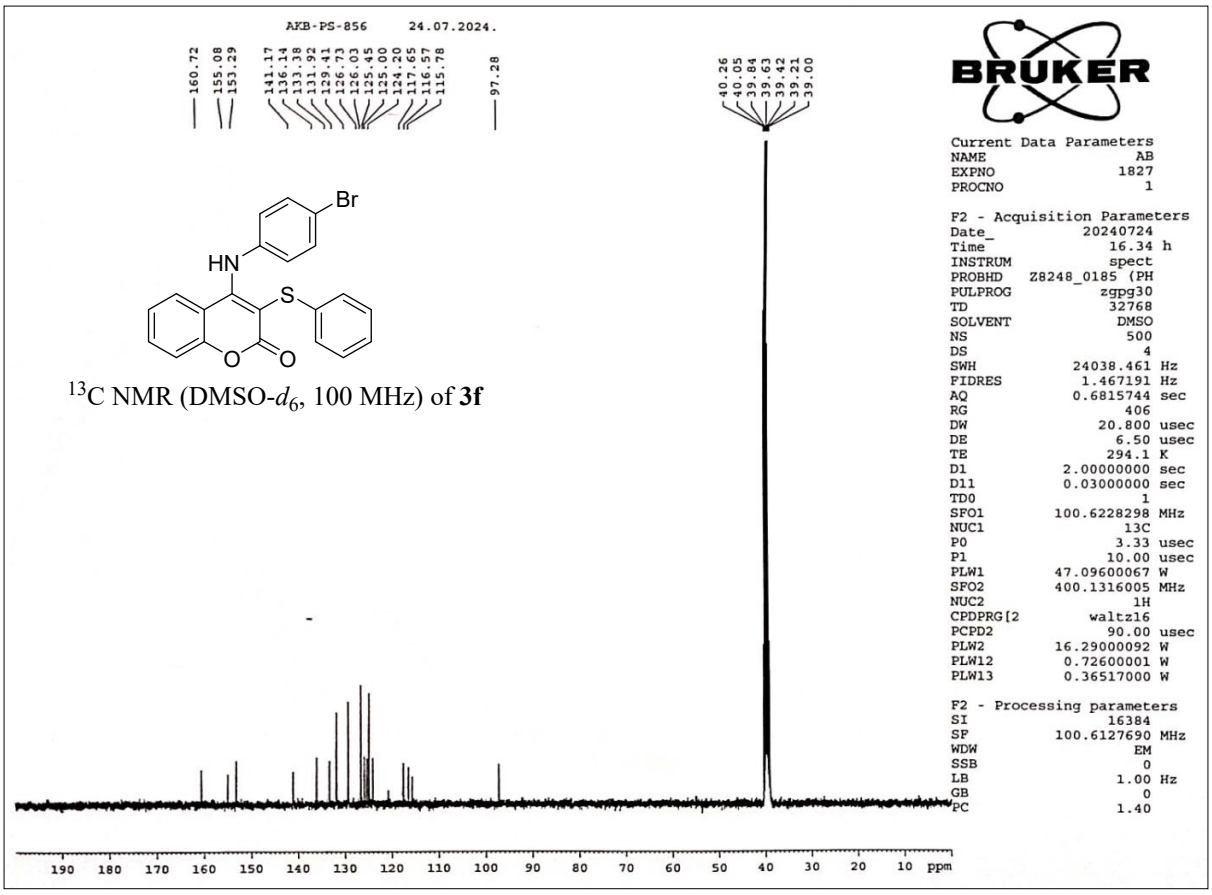




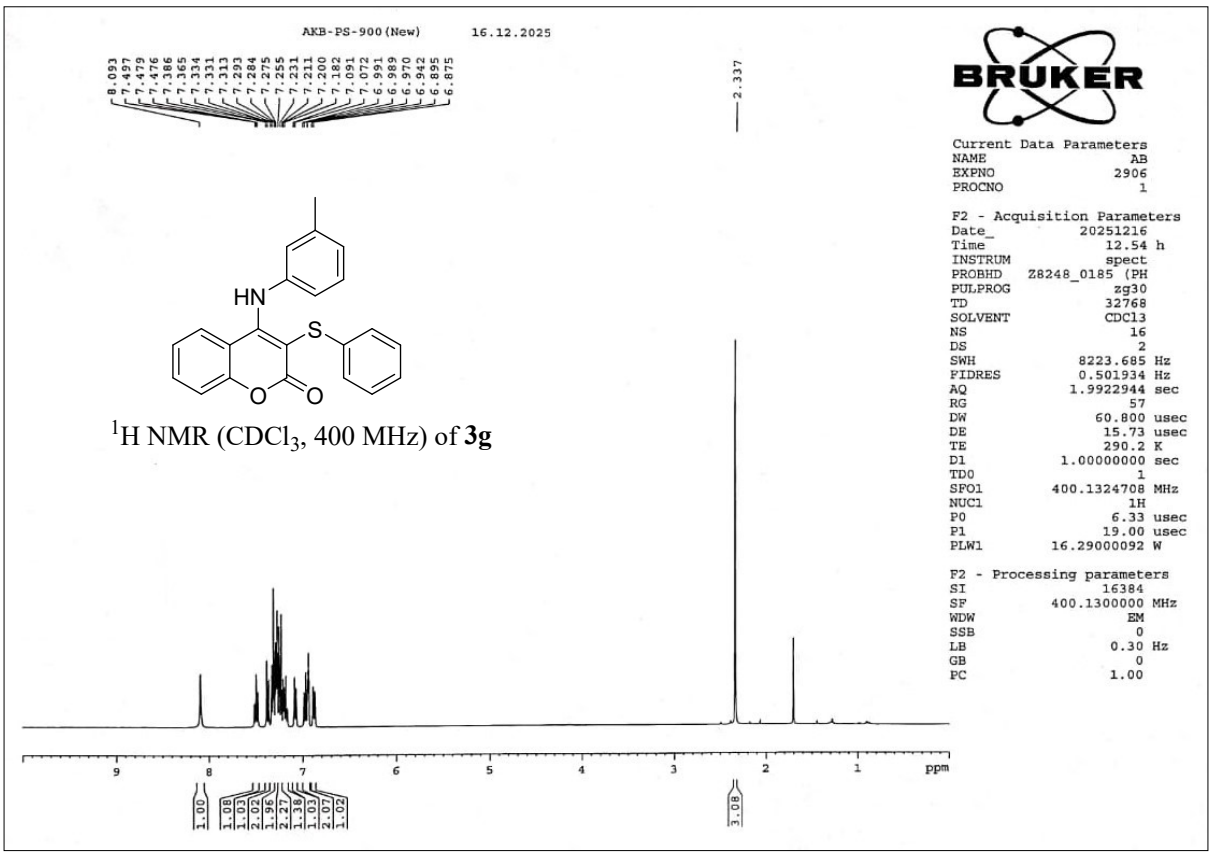
^{13}C NMR ($CDCl_3$, 100 MHz) of **3e**



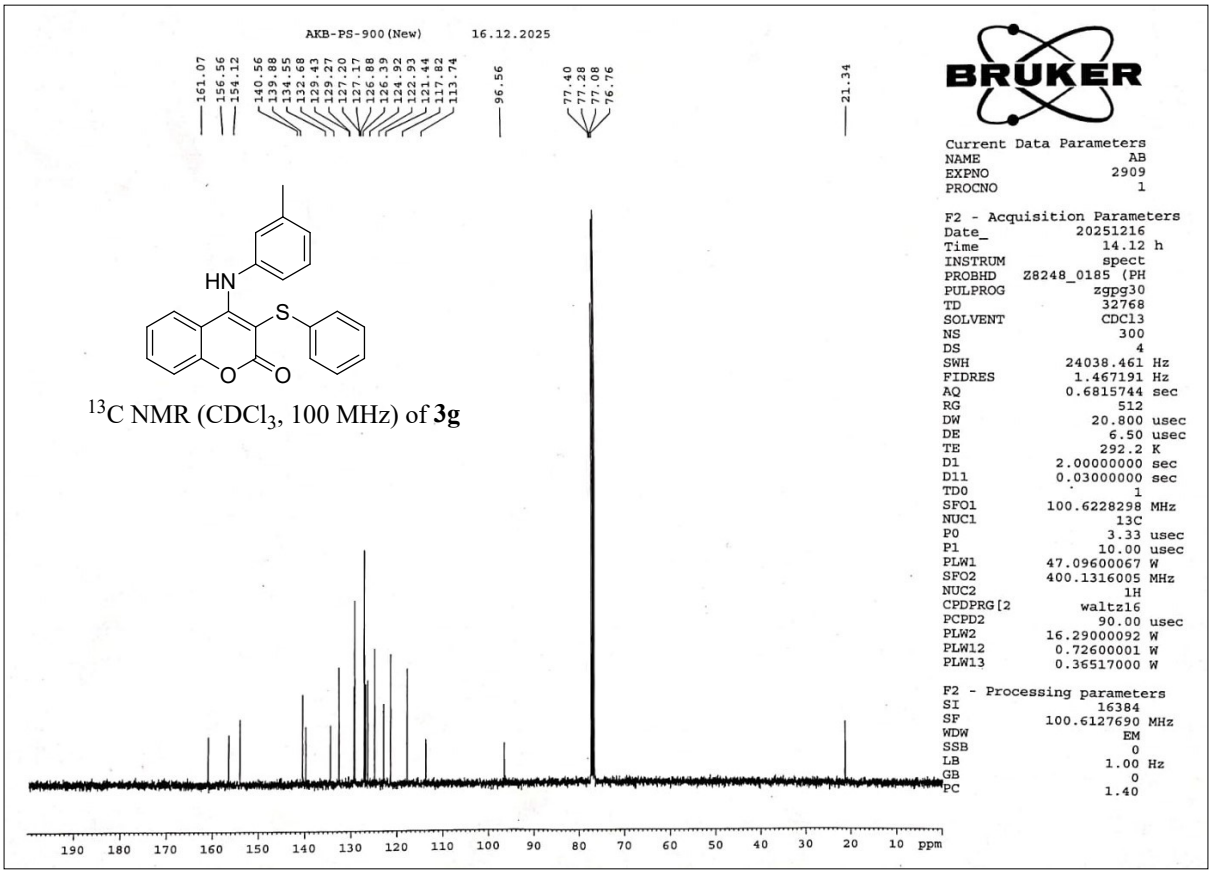
^{1}H NMR (DMSO-d_6, 400 MHz) of **3f**



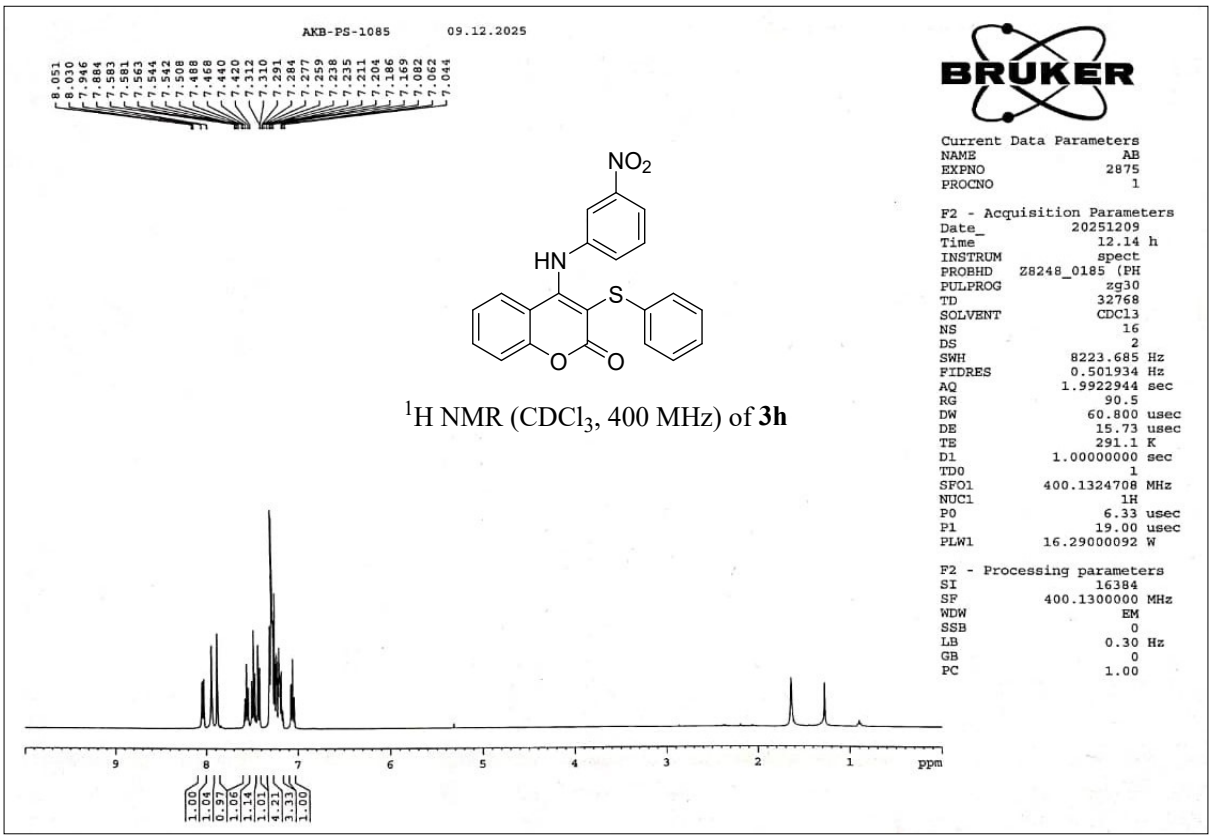
^{13}C NMR (DMSO-d_6, 100 MHz) of **3f**



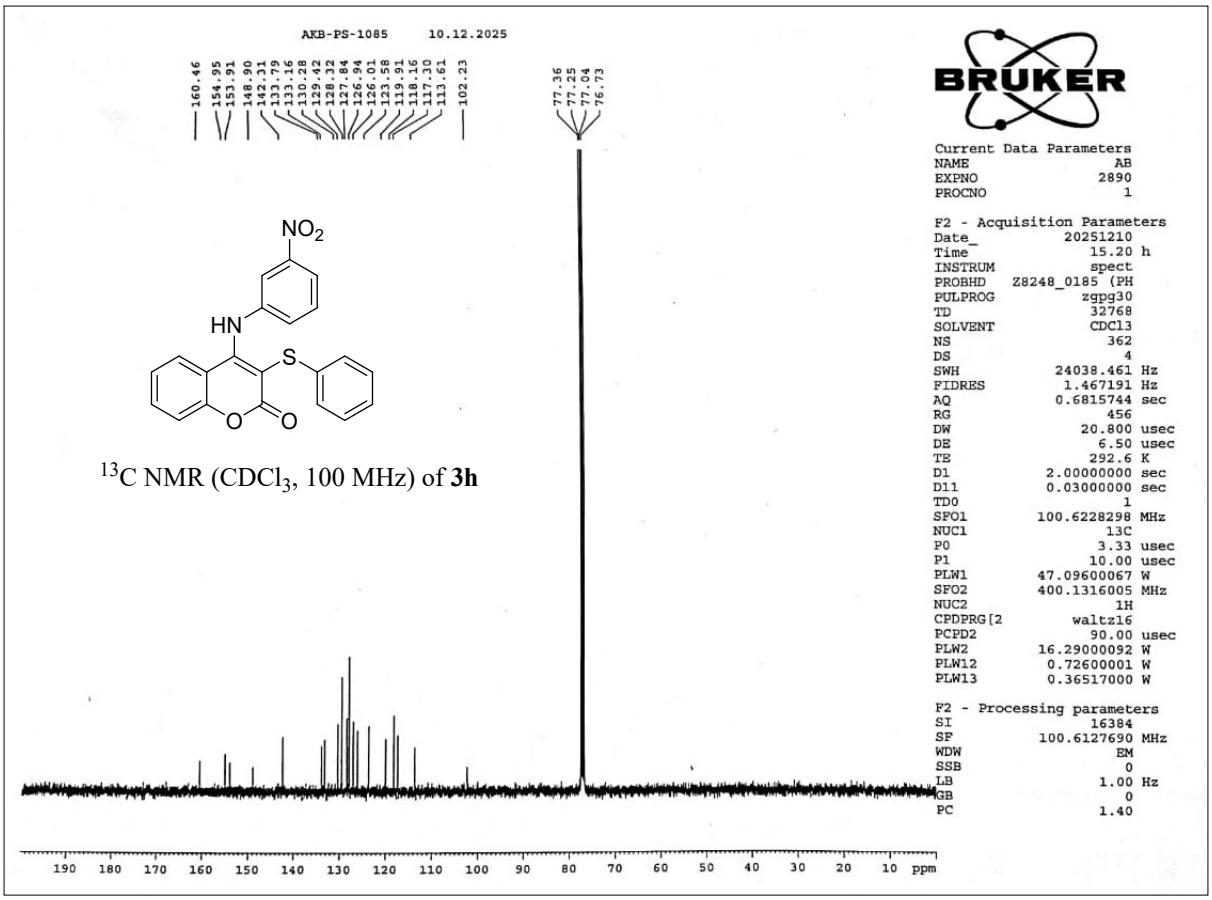
^{1}H NMR ($CDCl_3$, 400 MHz) of **3g**



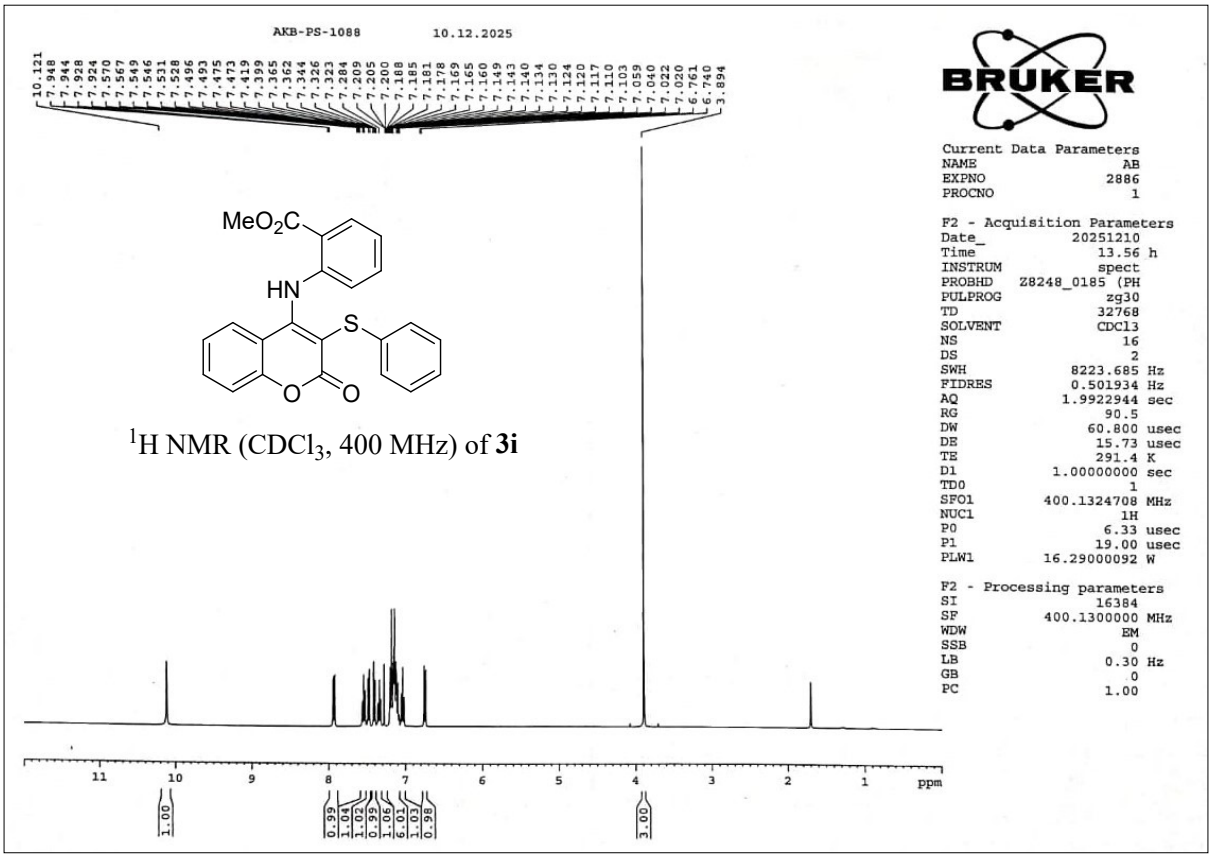
^{13}C NMR ($CDCl_3$, 100 MHz) of **3g**



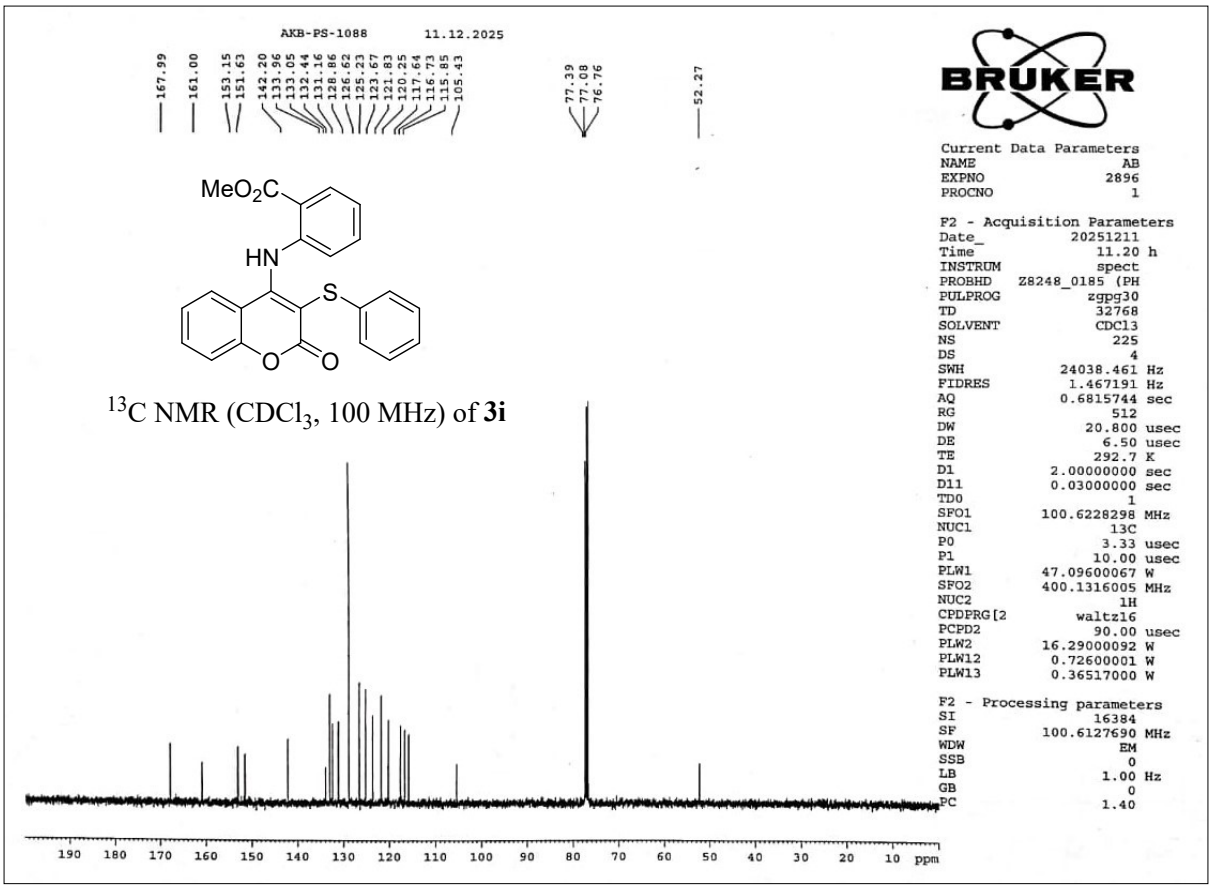
^{1}H NMR ($CDCl_3$, 400 MHz) of **3h**



^{13}C NMR ($CDCl_3$, 100 MHz) of **3h**



^{1}H NMR ($CDCl_3$, 400 MHz) of **3i**


AKB-PS-1088 11.12.2025
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151.63
142.20
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123.67
121.83
120.25
117.64
116.73
115.85
105.43
77.39
77.08
76.76
52.27
MeO2C
HN
S
O
O
13C NMR (CDCl3, 100 MHz) of 3i
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BRUKER
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PROCNO 1
F2 - Acquisition Parameters
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Time 11.20 h
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SWH 24038.461 Hz
FIDRES 1.467191 Hz
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DE 6.50 usec
TE 292.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
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P0 3.33 usec
P1 10.00 usec
PLW1 47.09600067 W
SFO2 400.1316005 MHz
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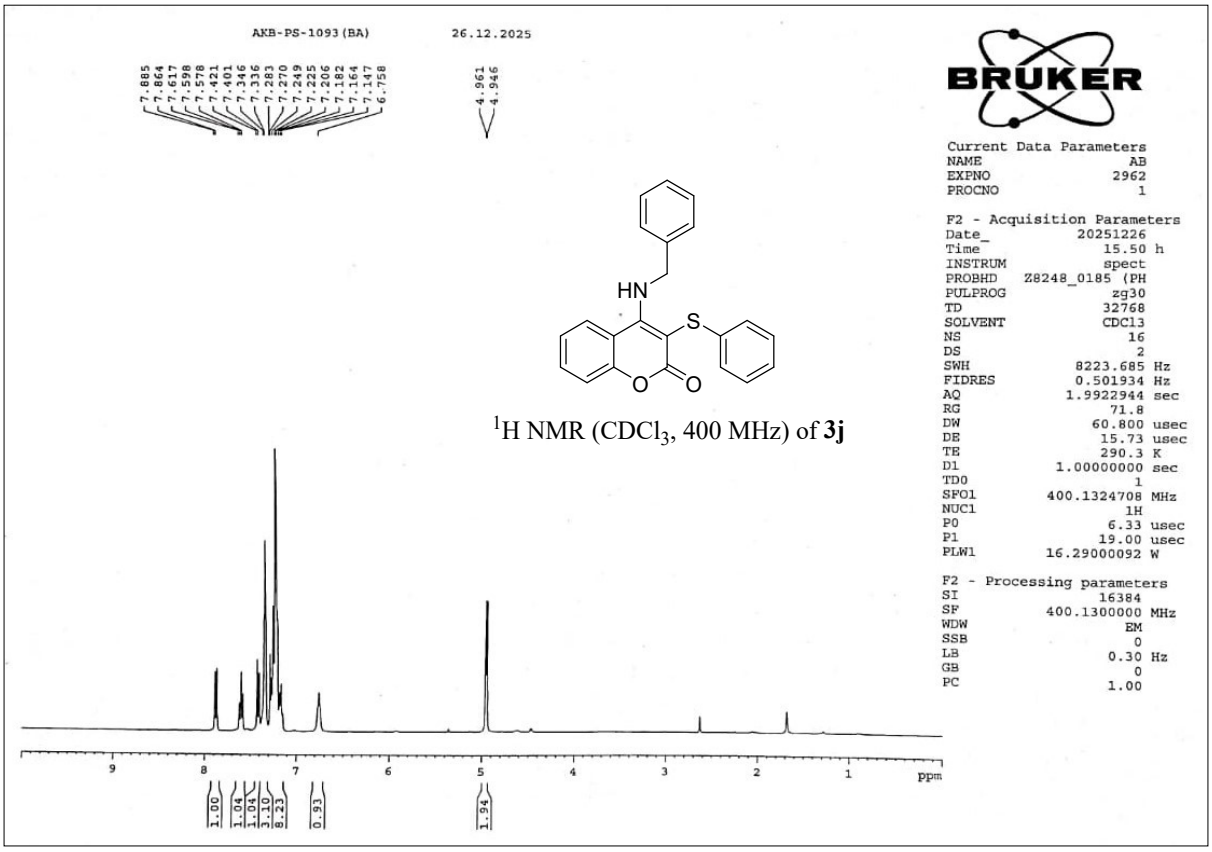
AKB-PS-1093(BA) 26.12.2025
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7.346
7.336
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7.270
7.249
7.225
7.206
7.182
7.164
7.147
6.758
4.961
4.946
HN
S
O
O
1H NMR (CDCl3, 400 MHz) of 3j
9 8 7 6 5 4 3 2 1 ppm
1.00
1.04
1.04
3.10
8.23
0.93
1.94
BRUKER
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P0 6.33 usec
P1 19.00 usec
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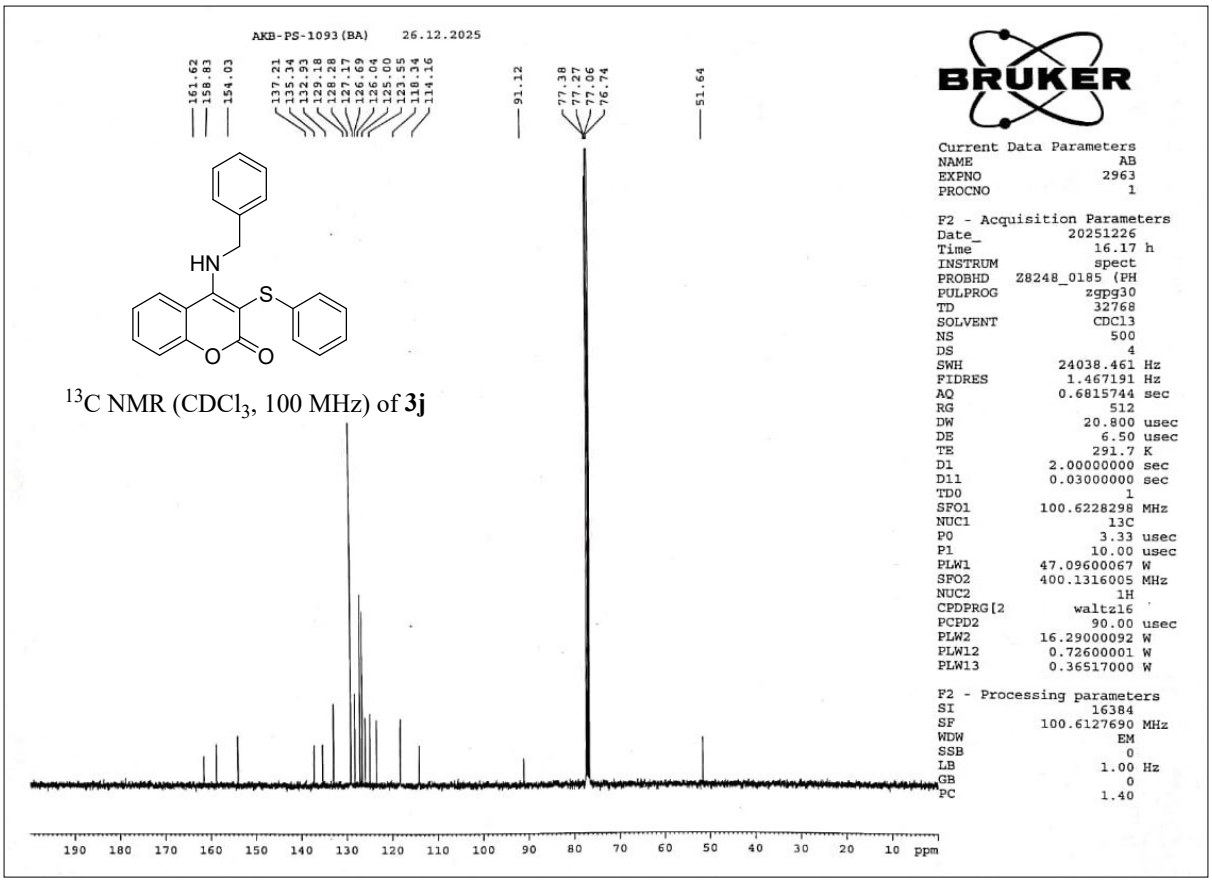
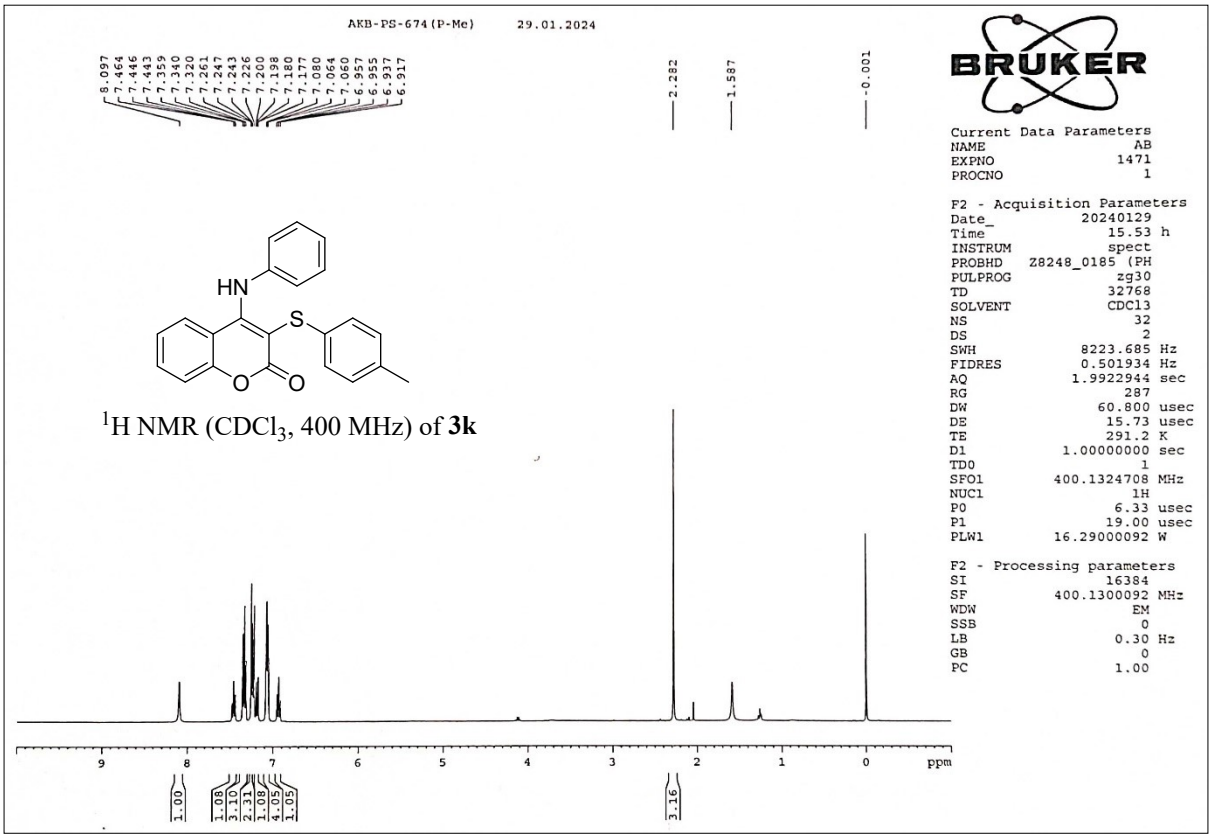
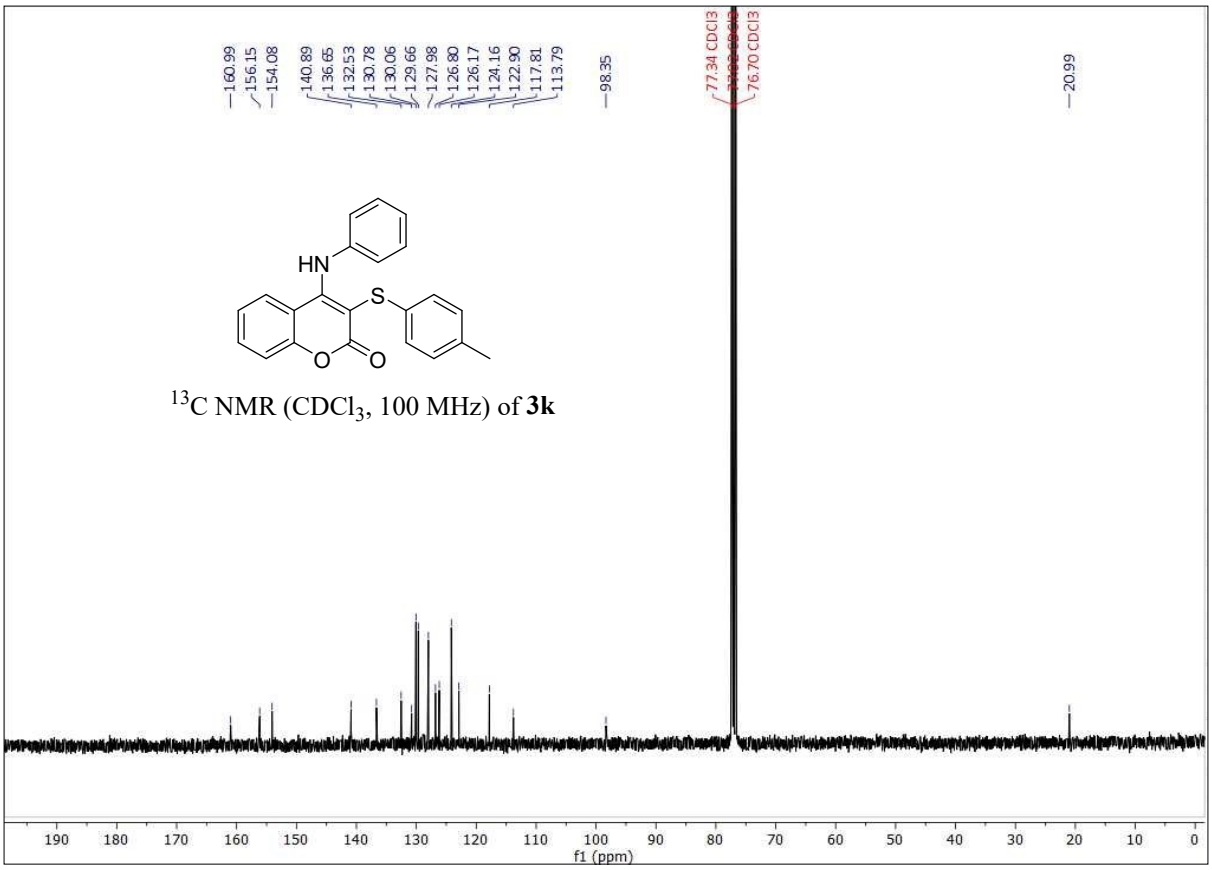


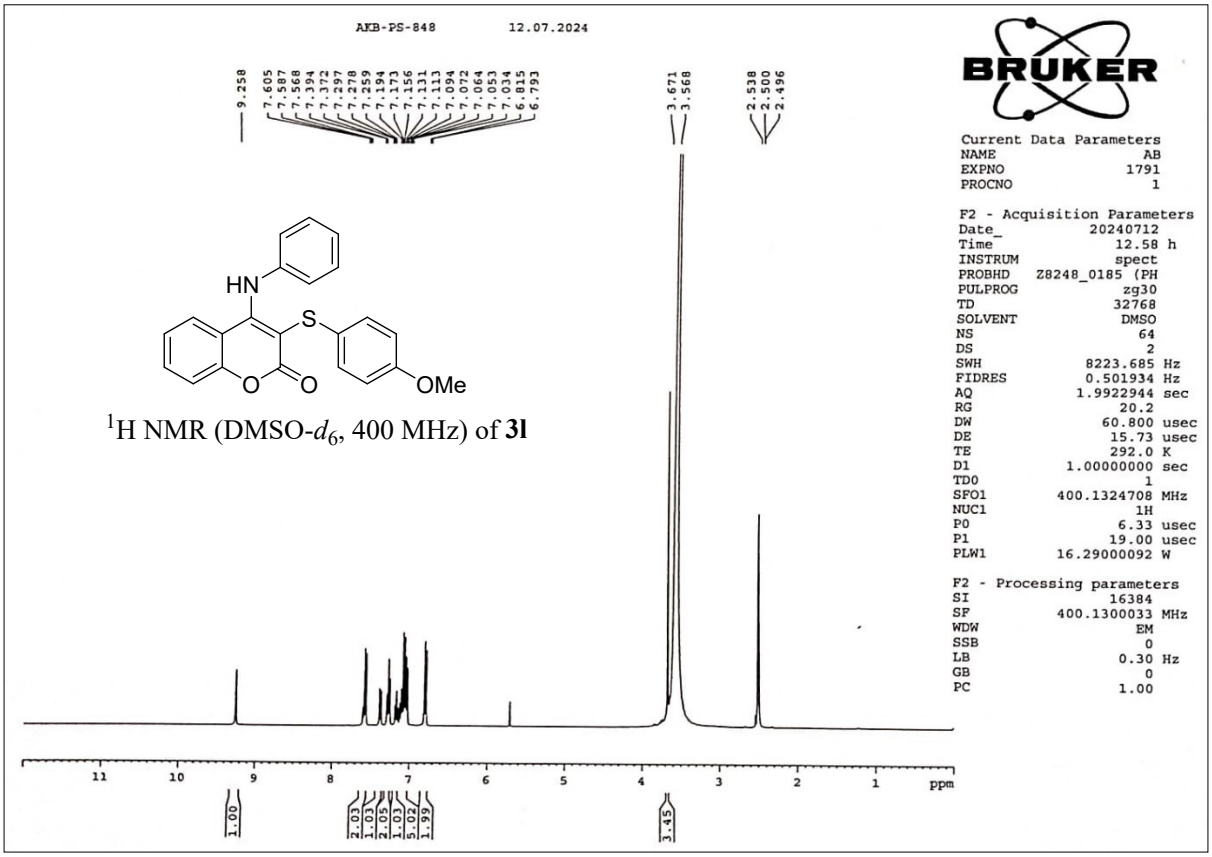
^{13}C NMR ($CDCl_3$, 100 MHz) of **3j**



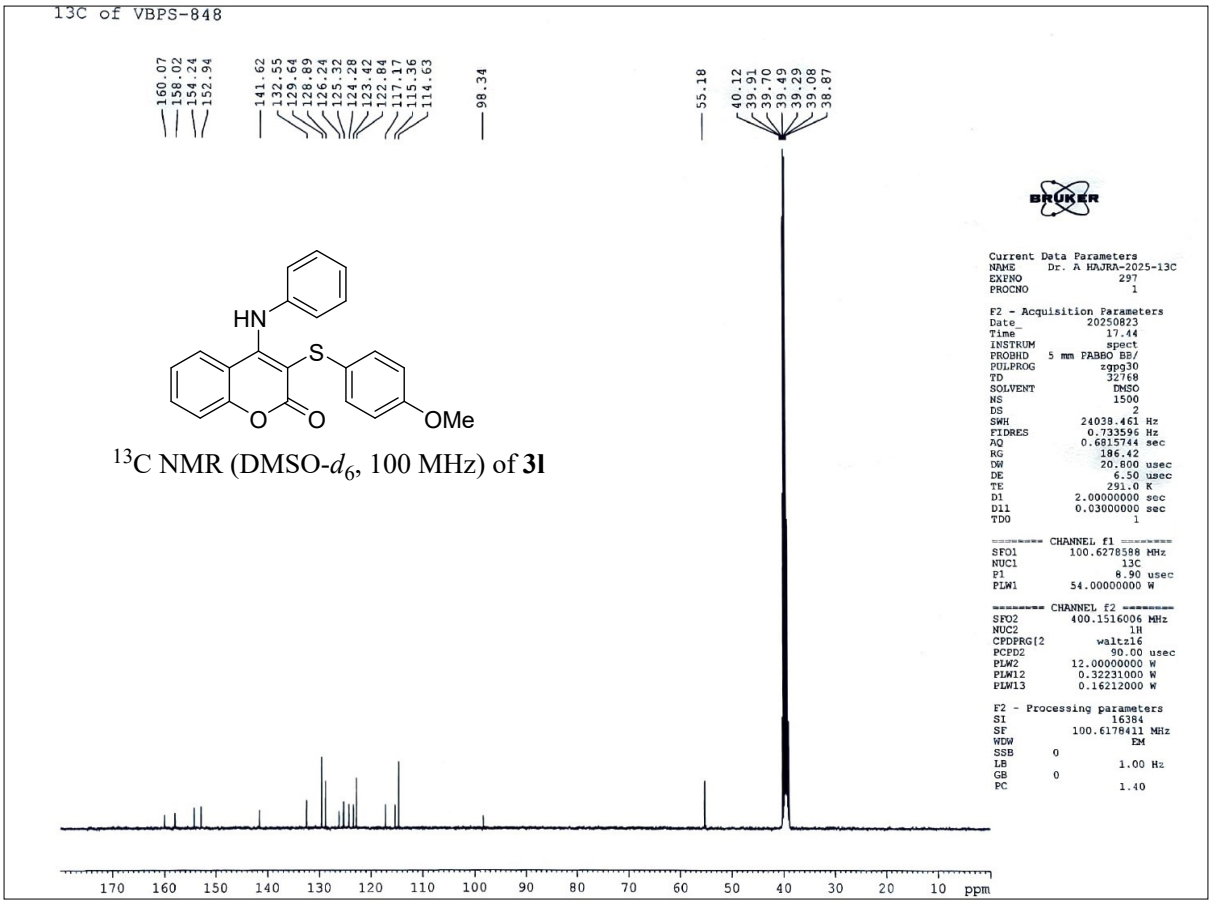
^{1}H NMR ($CDCl_3$, 400 MHz) of **3k**



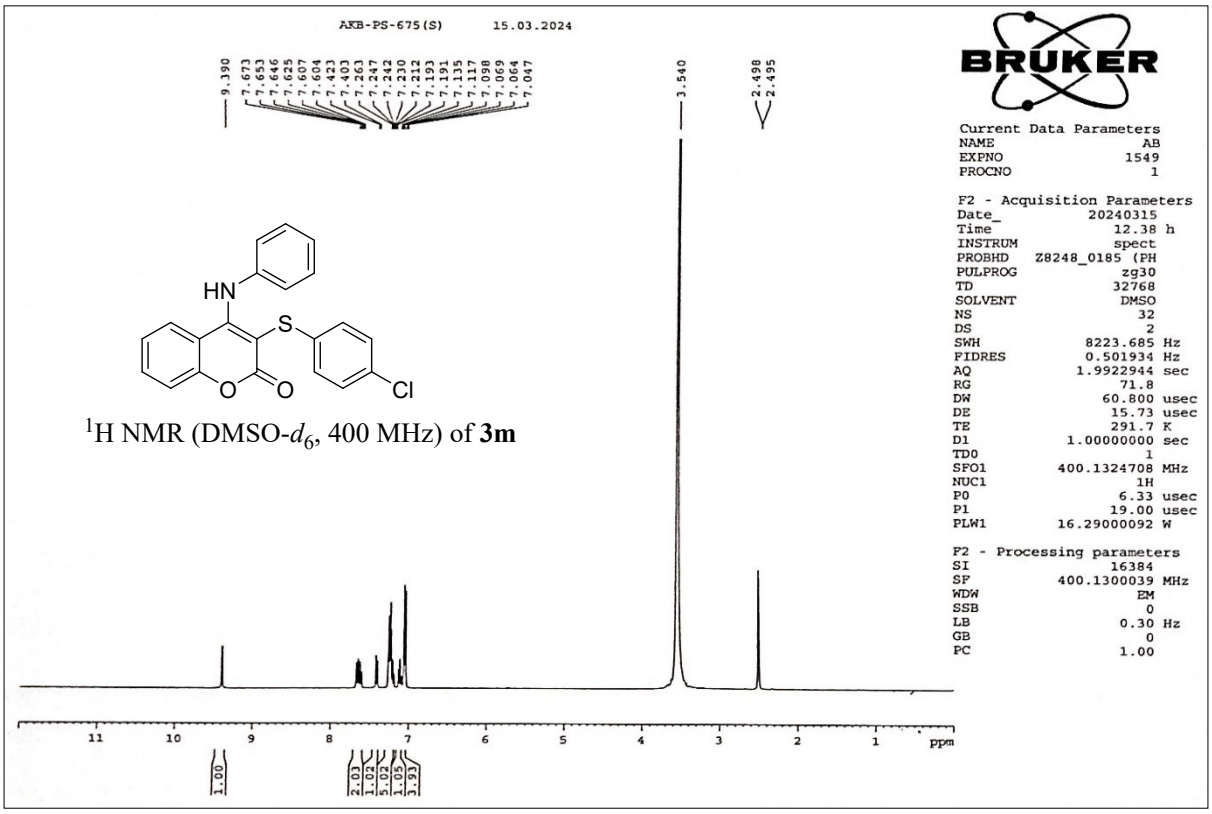
^{13}C NMR ($CDCl_3$, 100 MHz) of **3k**



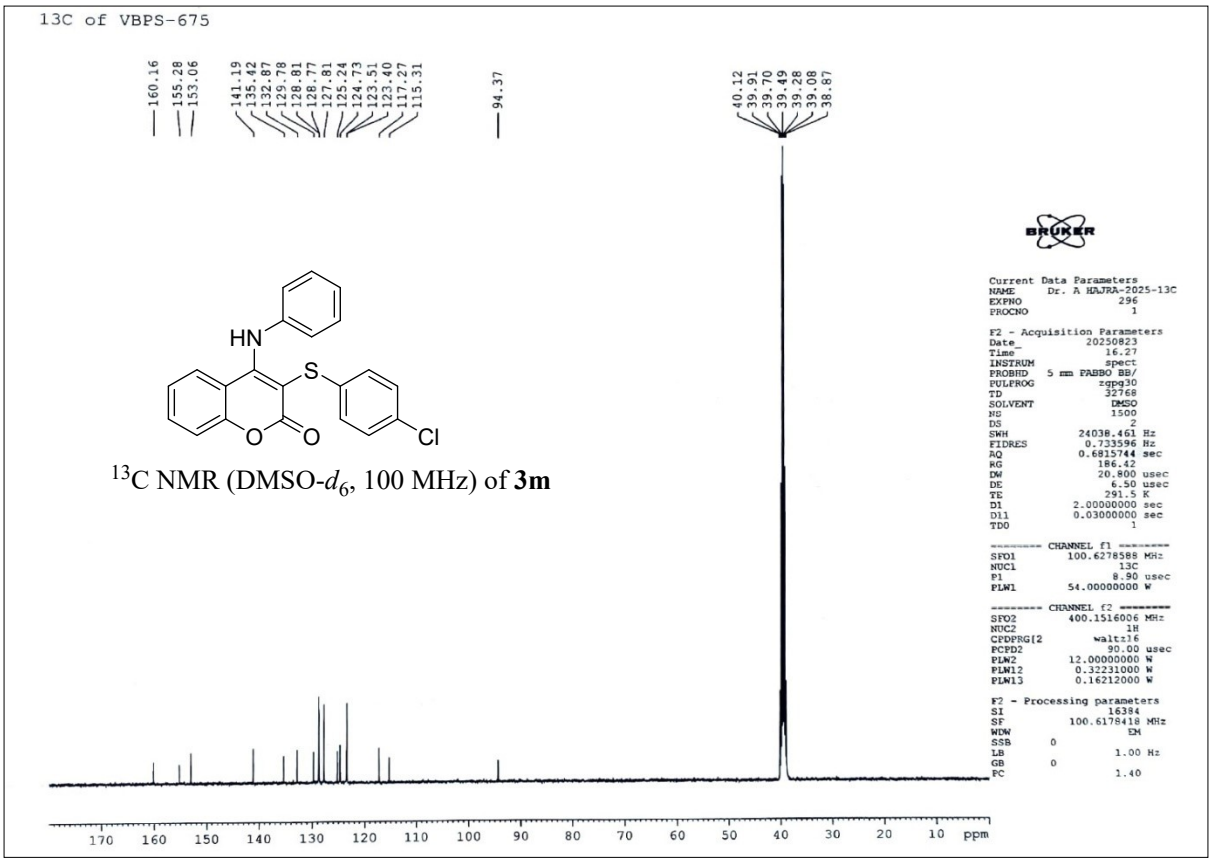
^{1}H NMR (DMSO-d_6, 400 MHz) of **3l**



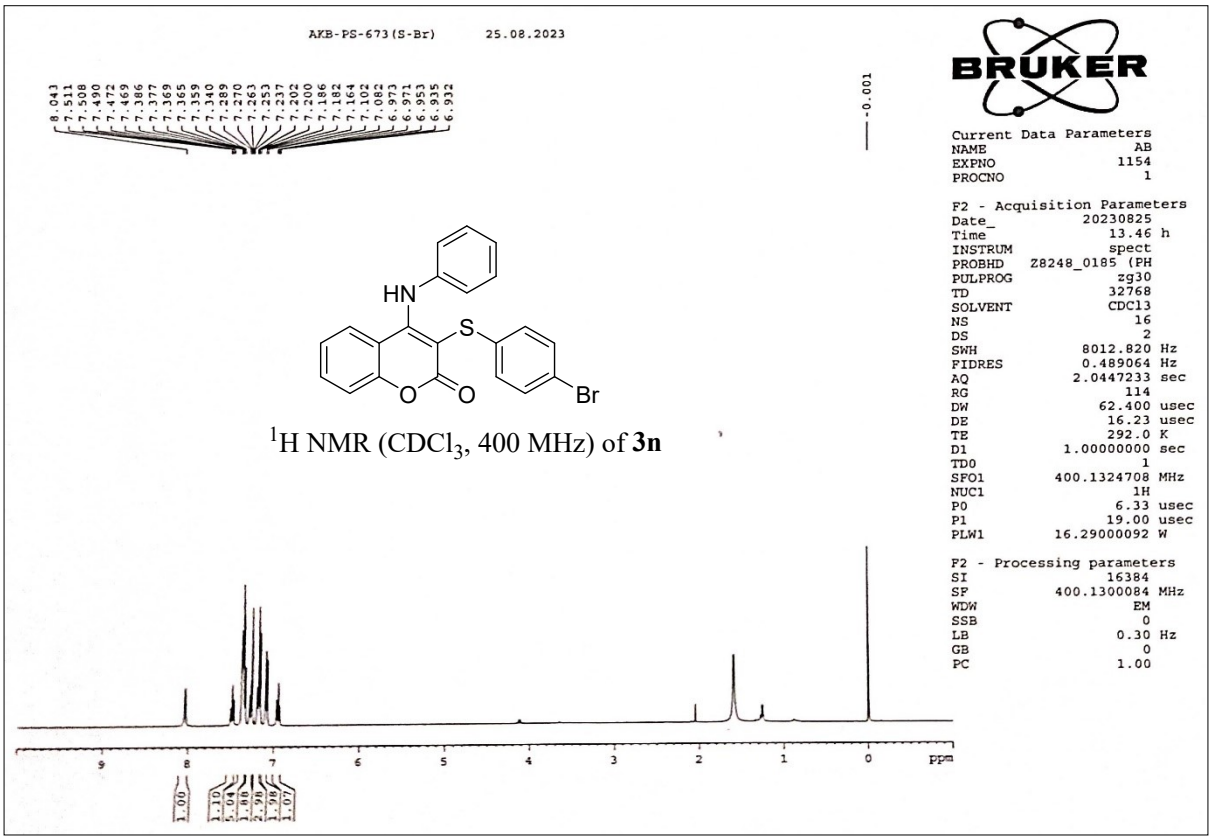
^{13}C NMR (DMSO-d_6, 100 MHz) of **3l**



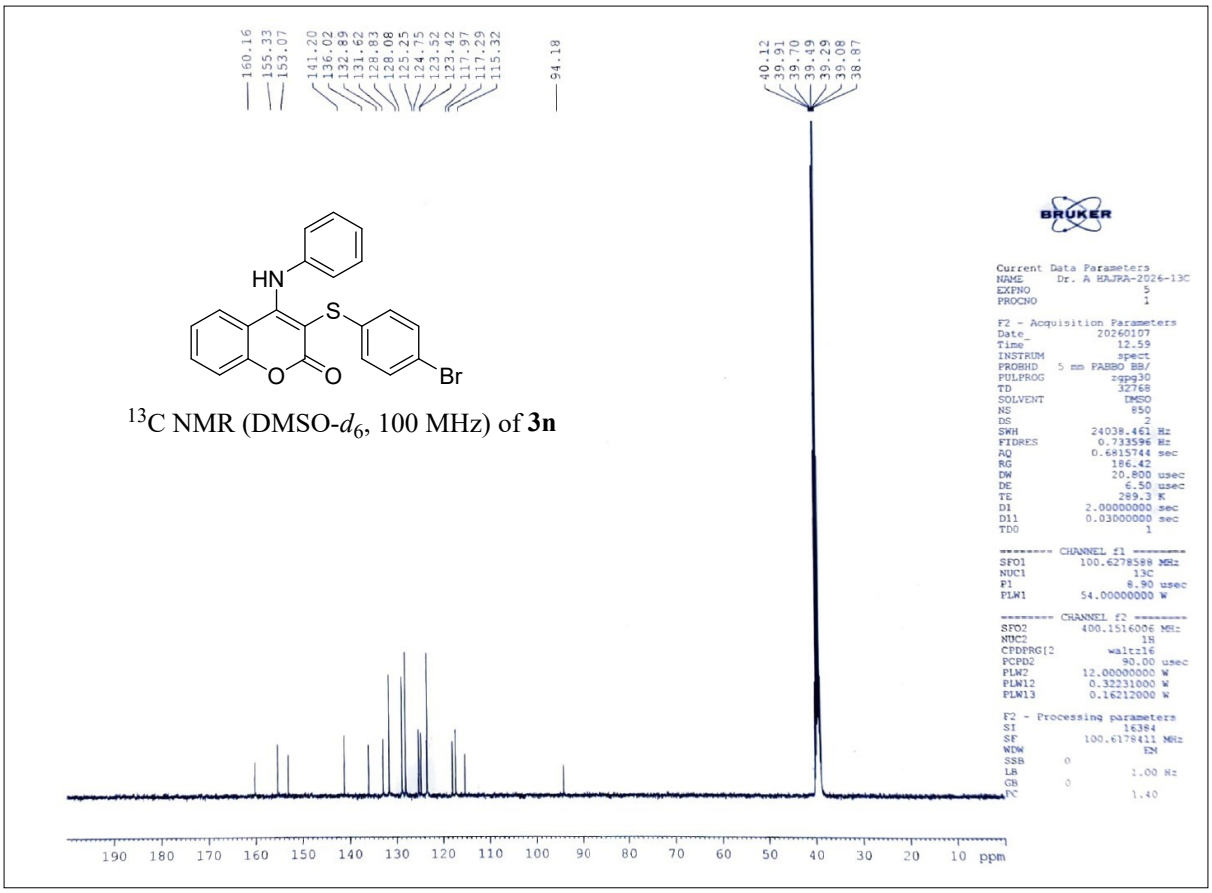
^{1}H NMR (DMSO-d_6, 400 MHz) of **3m**



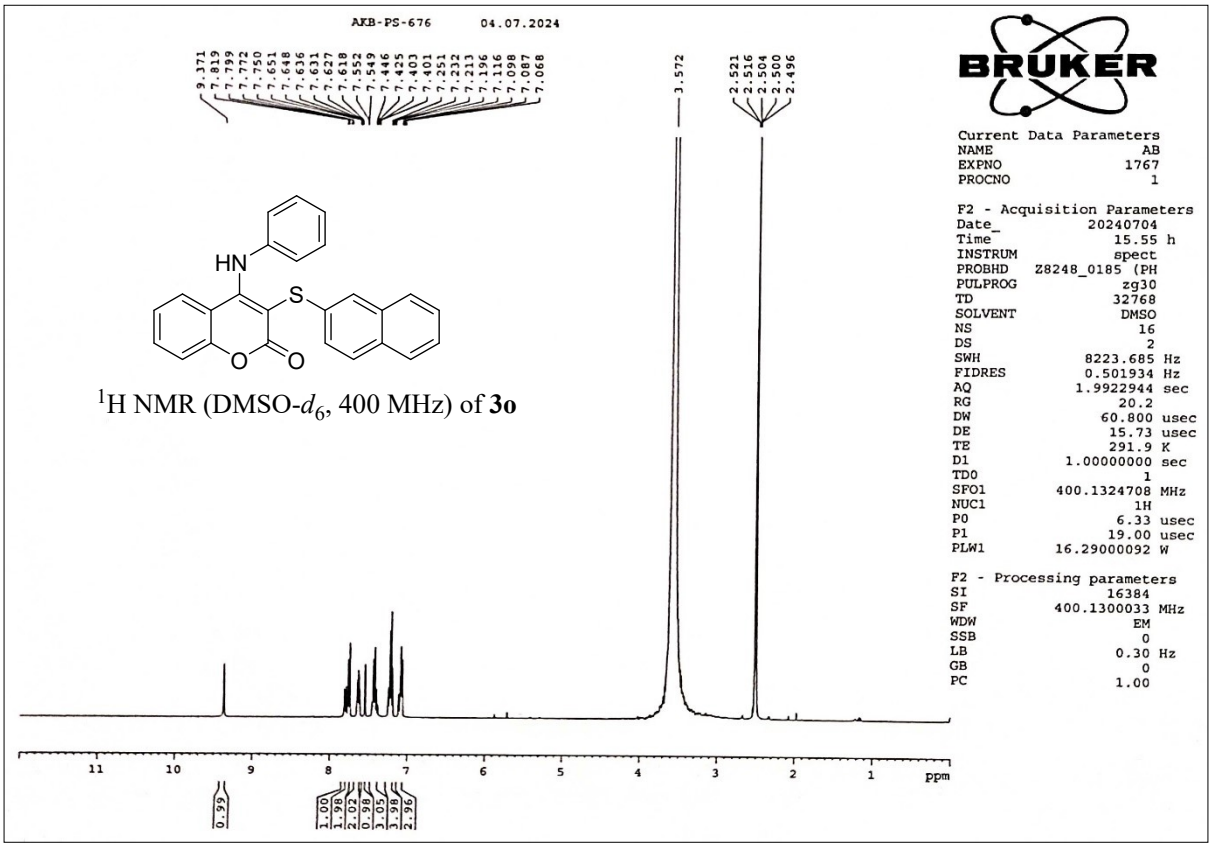
^{13}C NMR (DMSO-d_6, 100 MHz) of **3m**



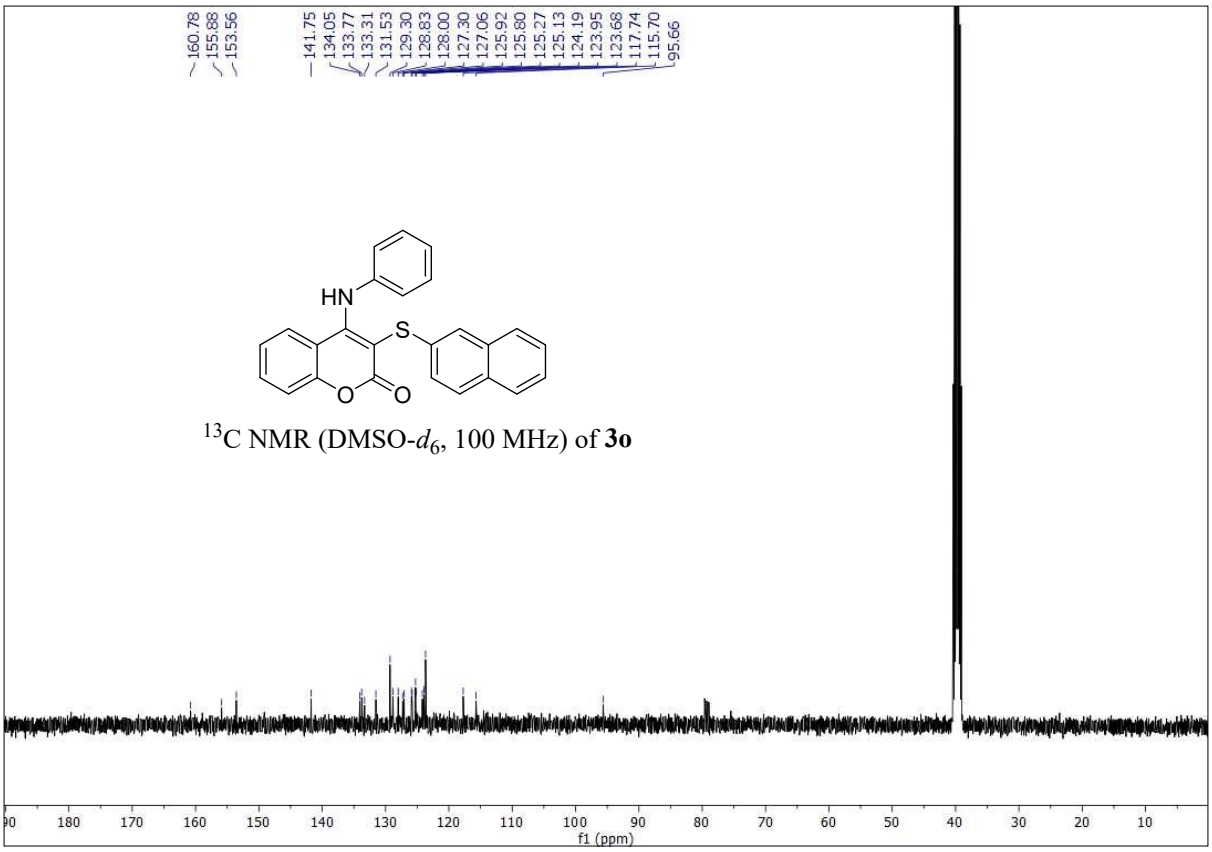
^{1}H NMR ($CDCl_3$, 400 MHz) of **3n**



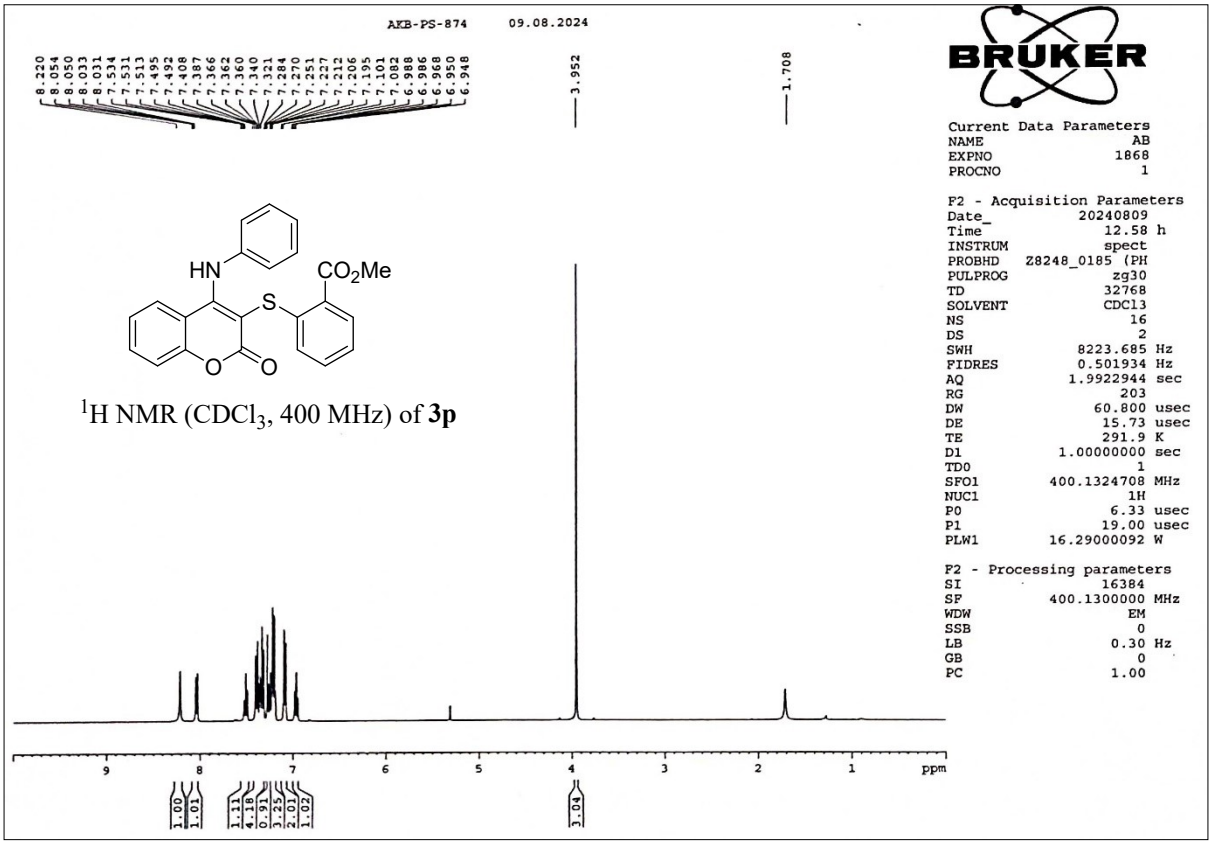
^{13}C NMR (DMSO-d_6, 100 MHz) of **3n**



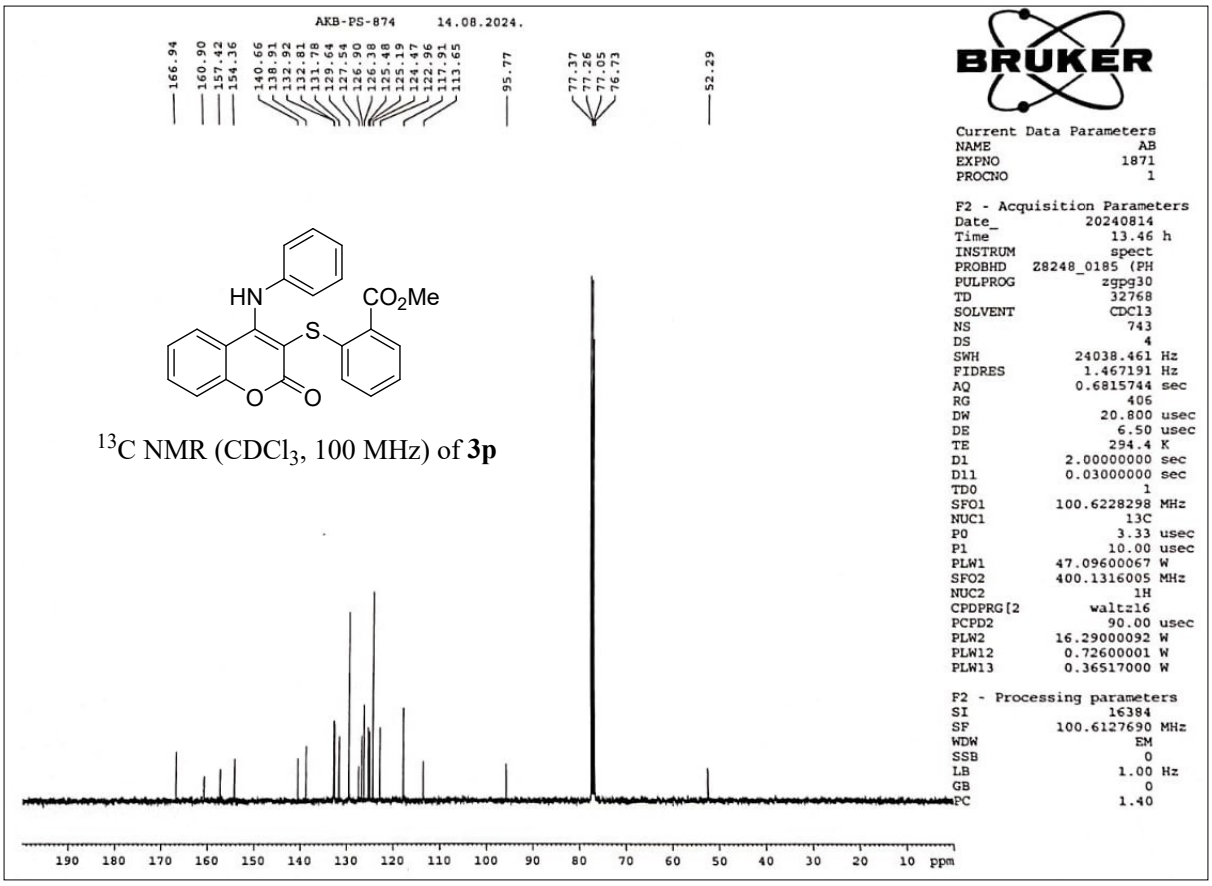
^{1}H NMR (DMSO-d_6, 400 MHz) of **3o**



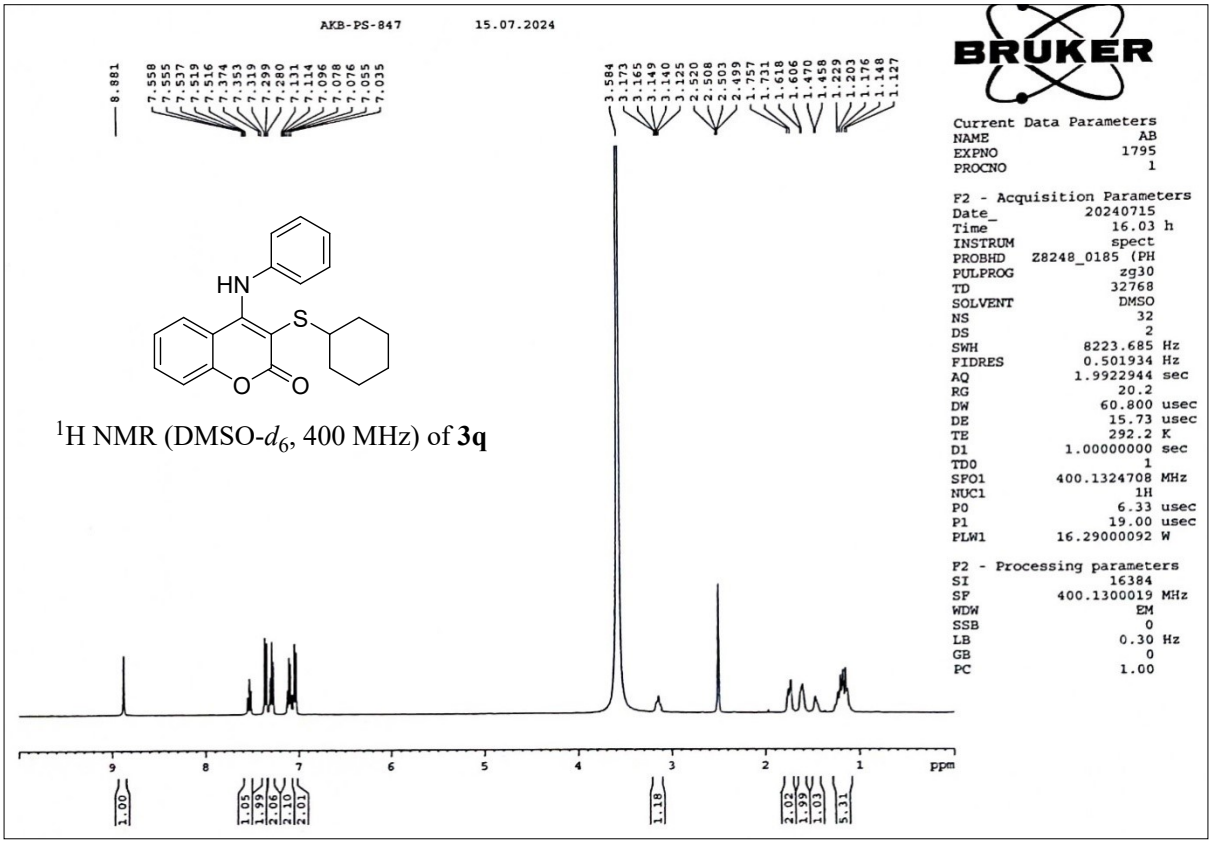
^{13}C NMR (DMSO-d_6, 100 MHz) of **3o**



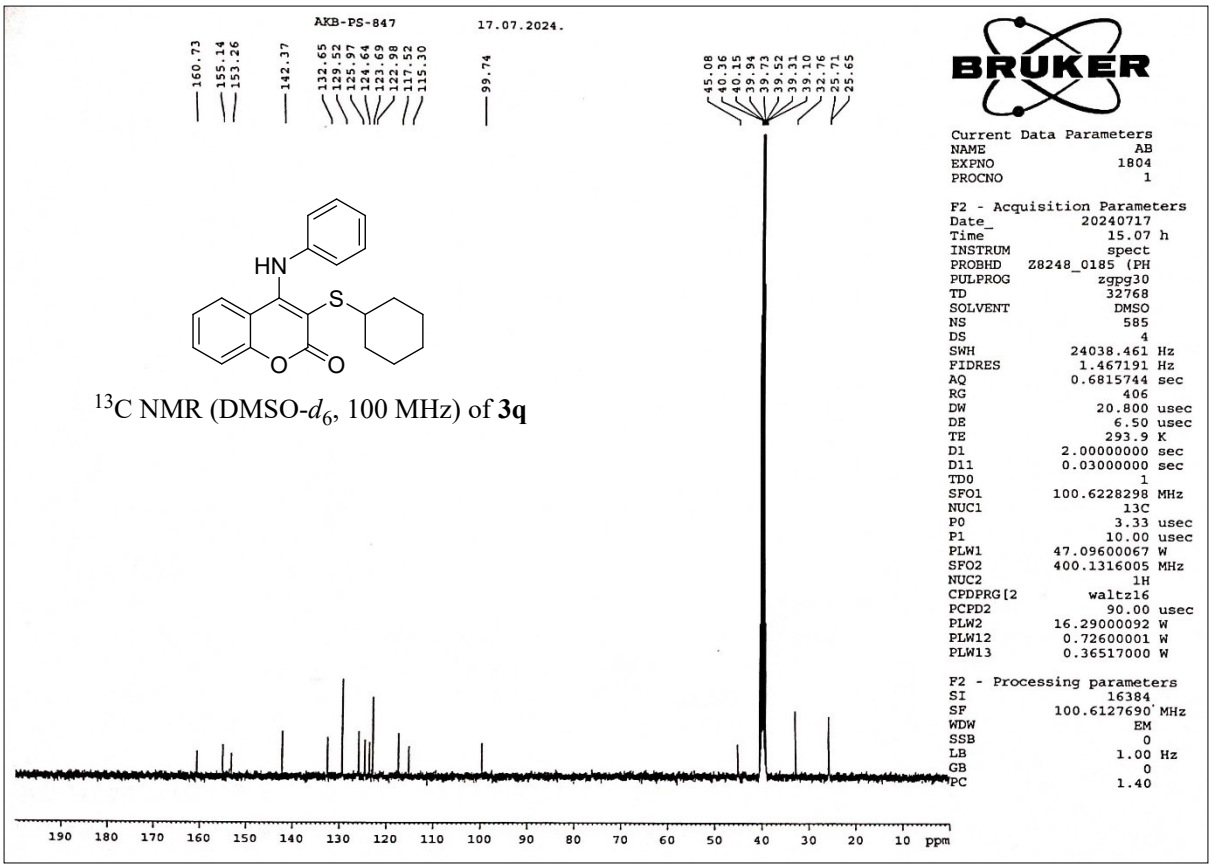
^{1}H NMR ($CDCl_3$, 400 MHz) of **3p**



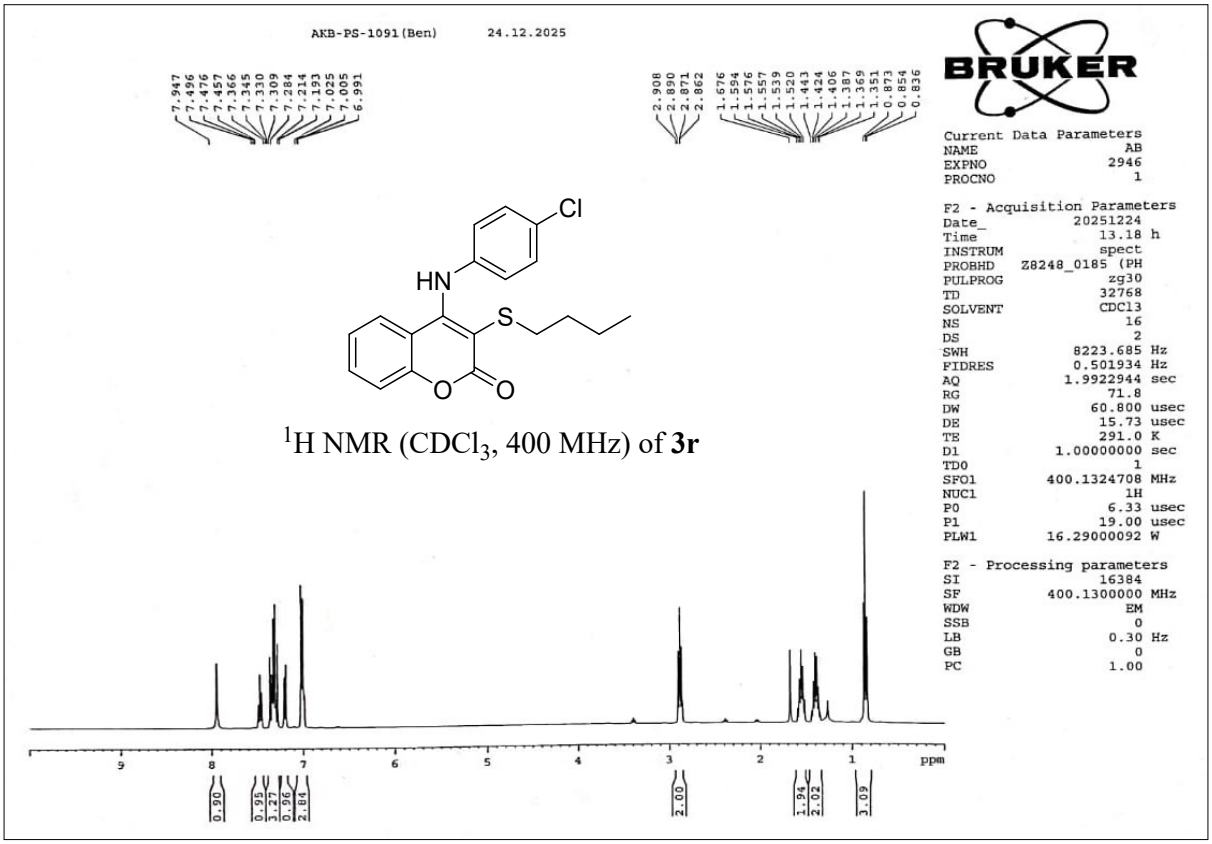
^{13}C NMR ($CDCl_3$, 100 MHz) of **3p**



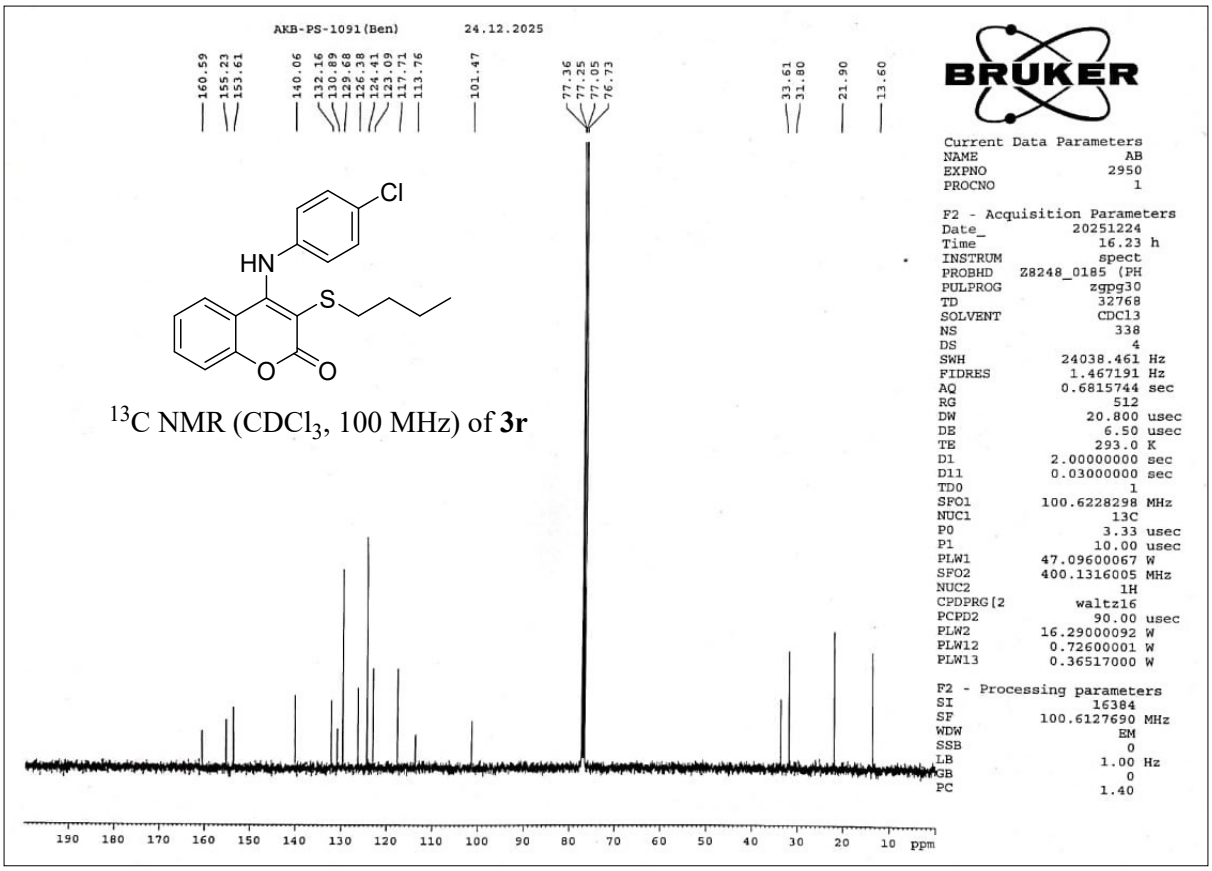
^{1}H NMR (DMSO-d_6, 400 MHz) of **3q**



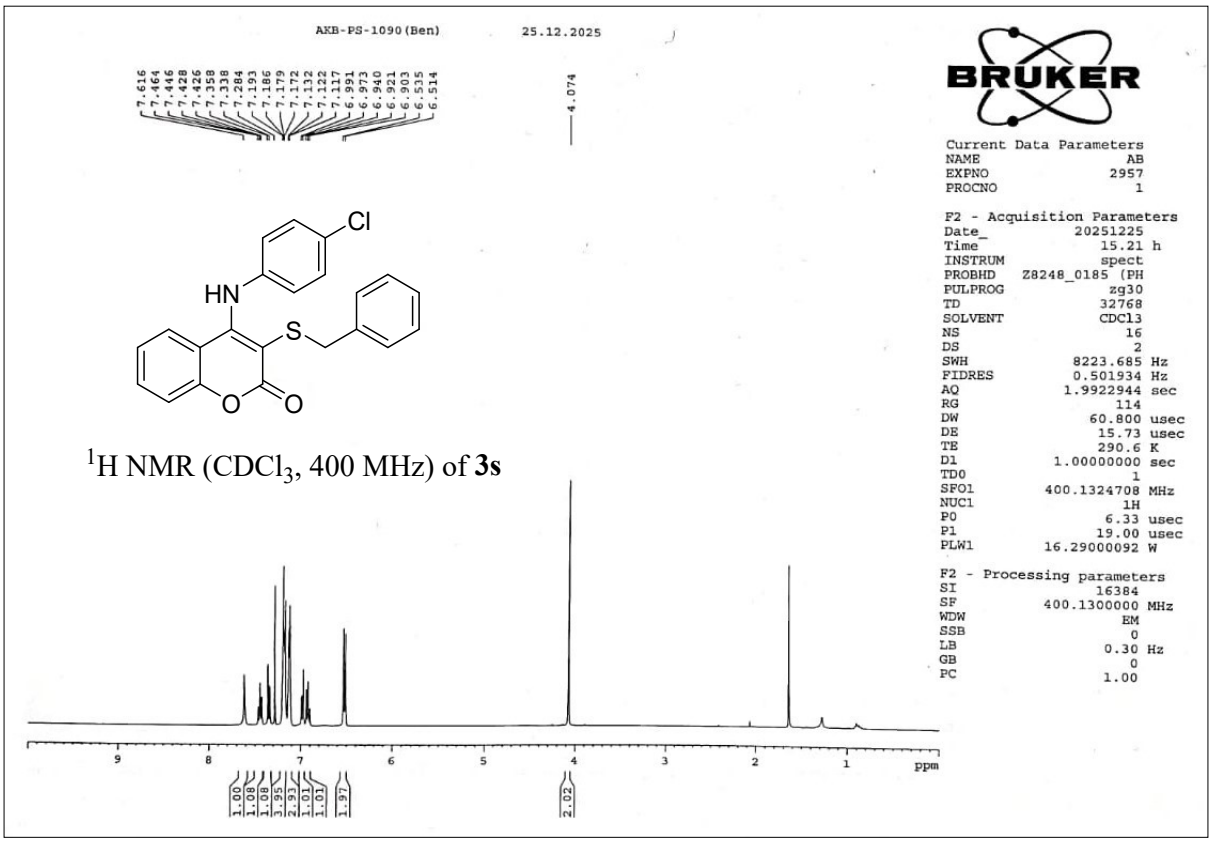
^{13}C NMR (DMSO-d_6, 100 MHz) of **3q**



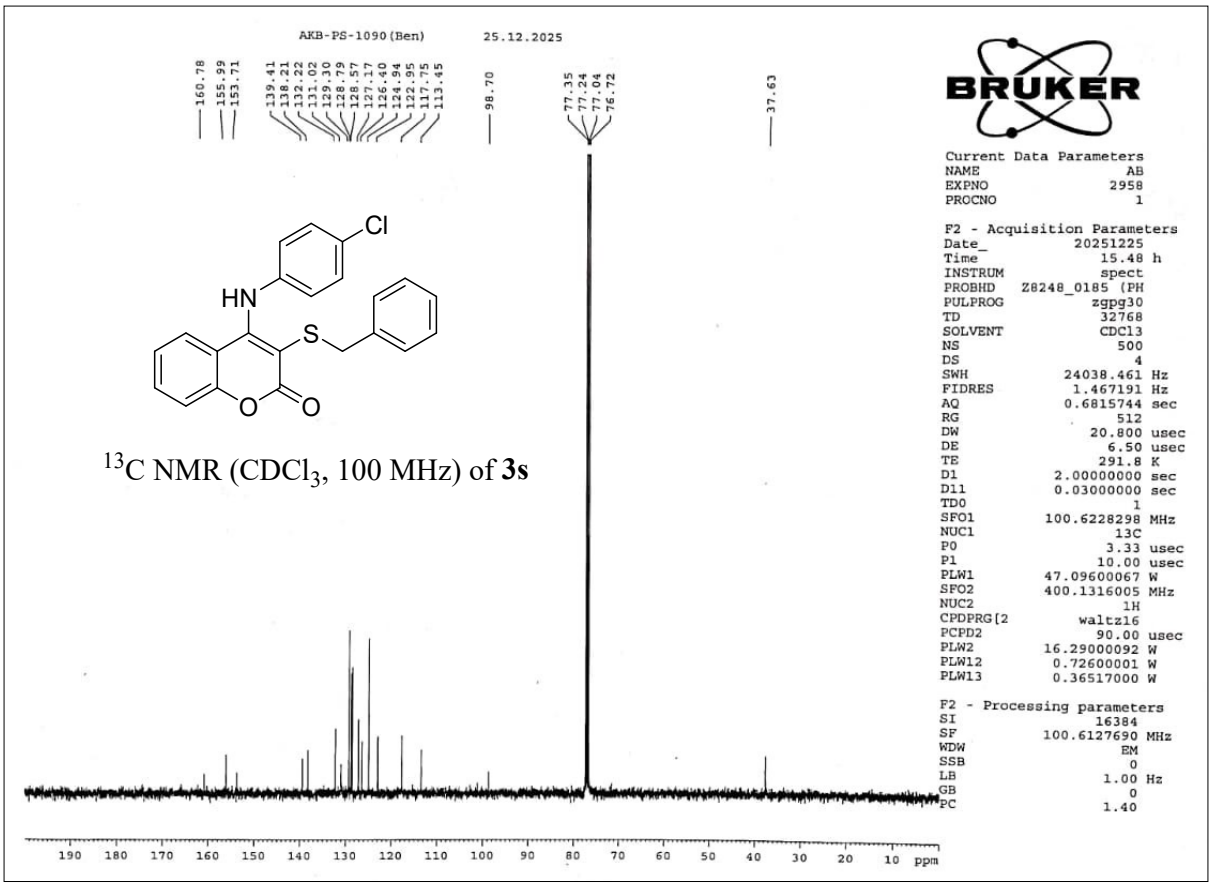
^{1}H NMR ($CDCl_3$, 400 MHz) of **3r**



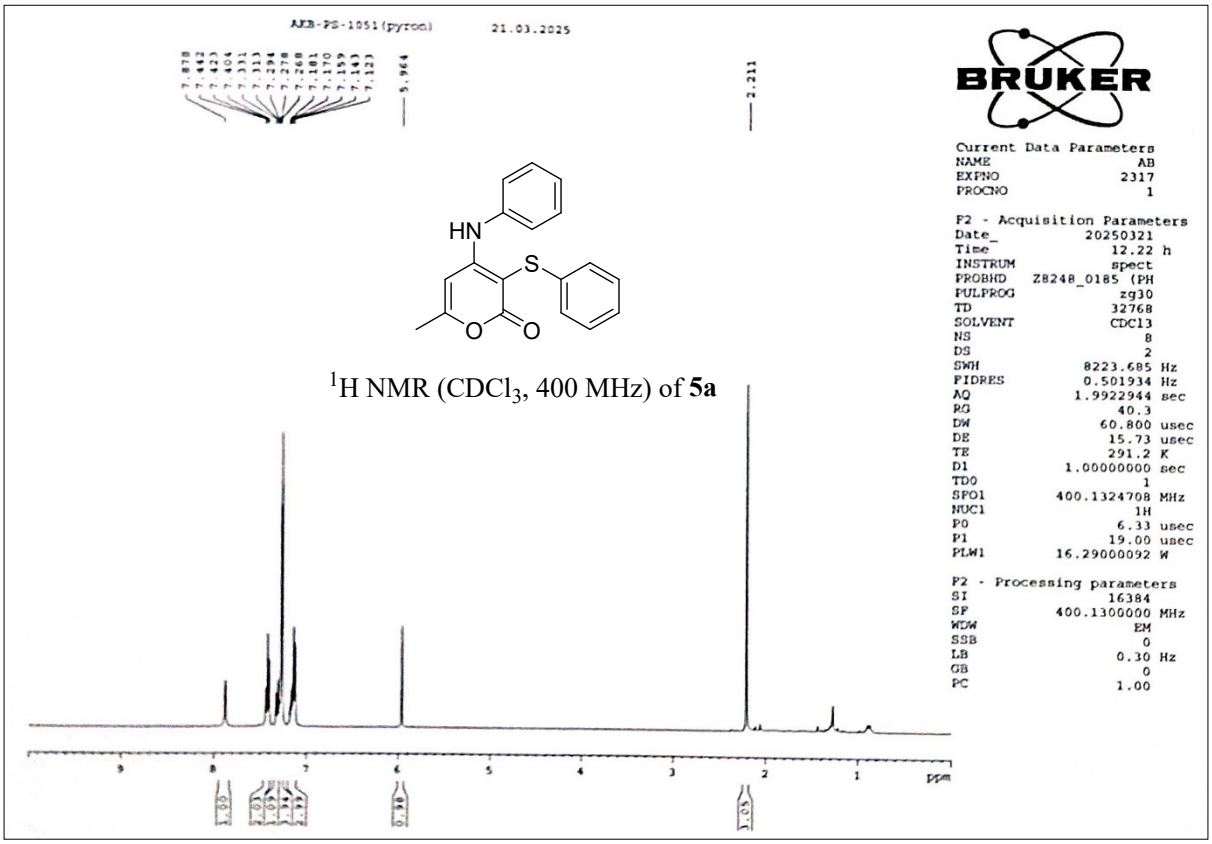
^{13}C NMR ($CDCl_3$, 100 MHz) of **3r**



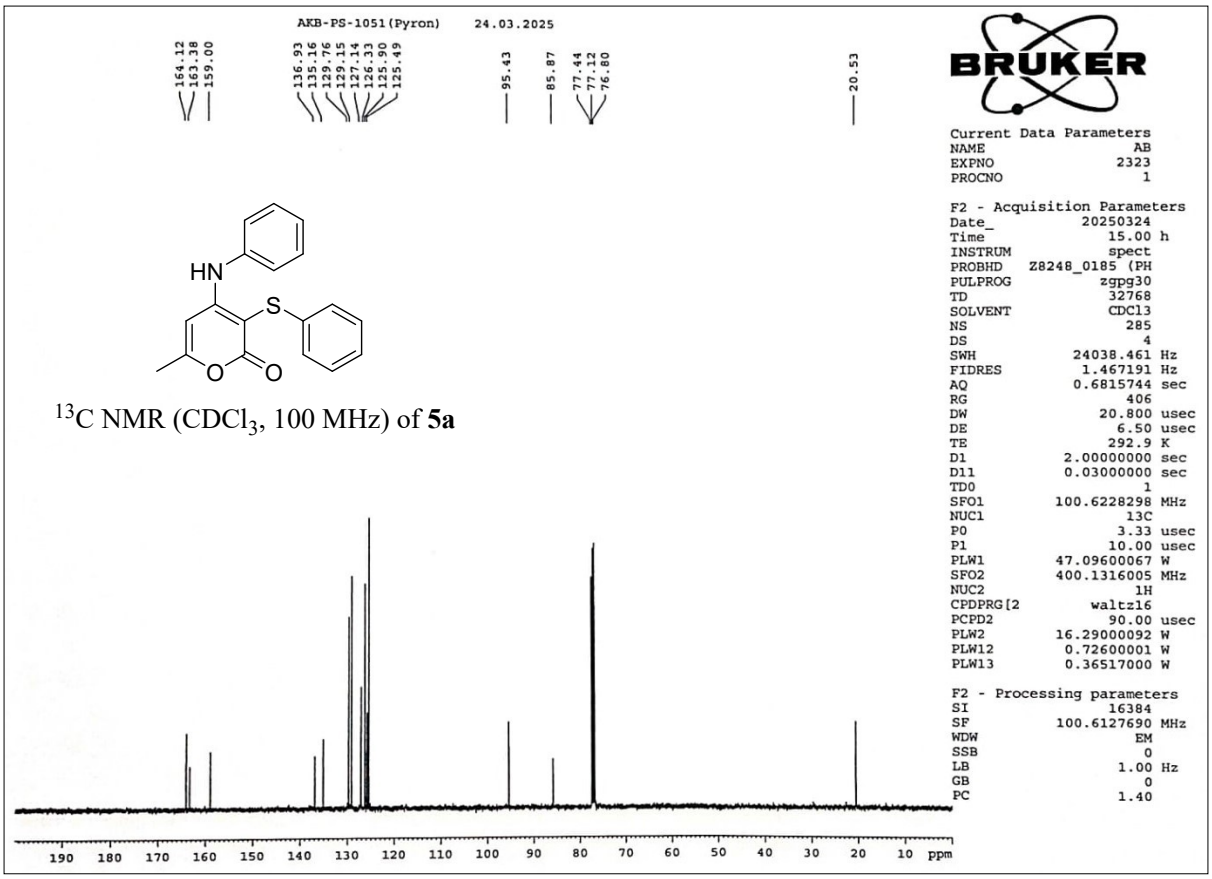
^{1}H NMR ($CDCl_3$, 400 MHz) of **3s**



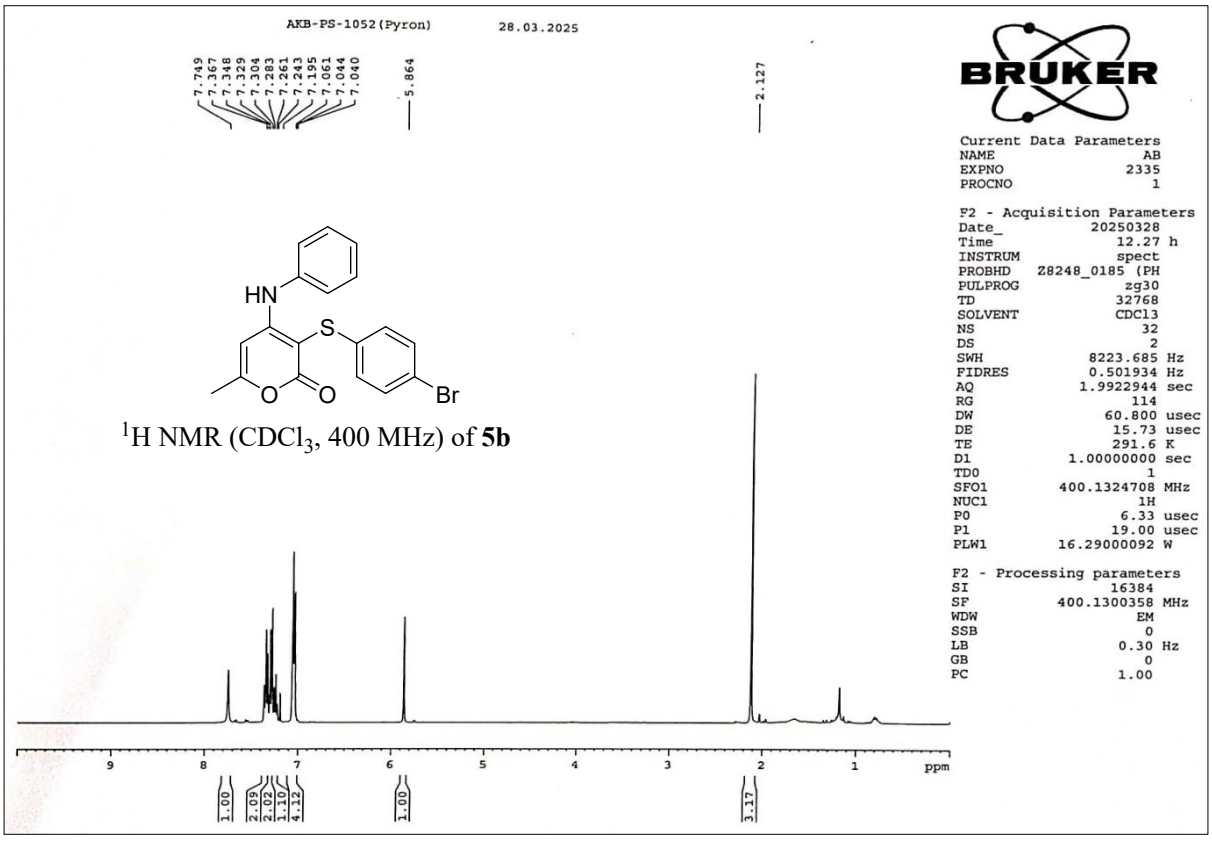
^{13}C NMR ($CDCl_3$, 100 MHz) of **3s**



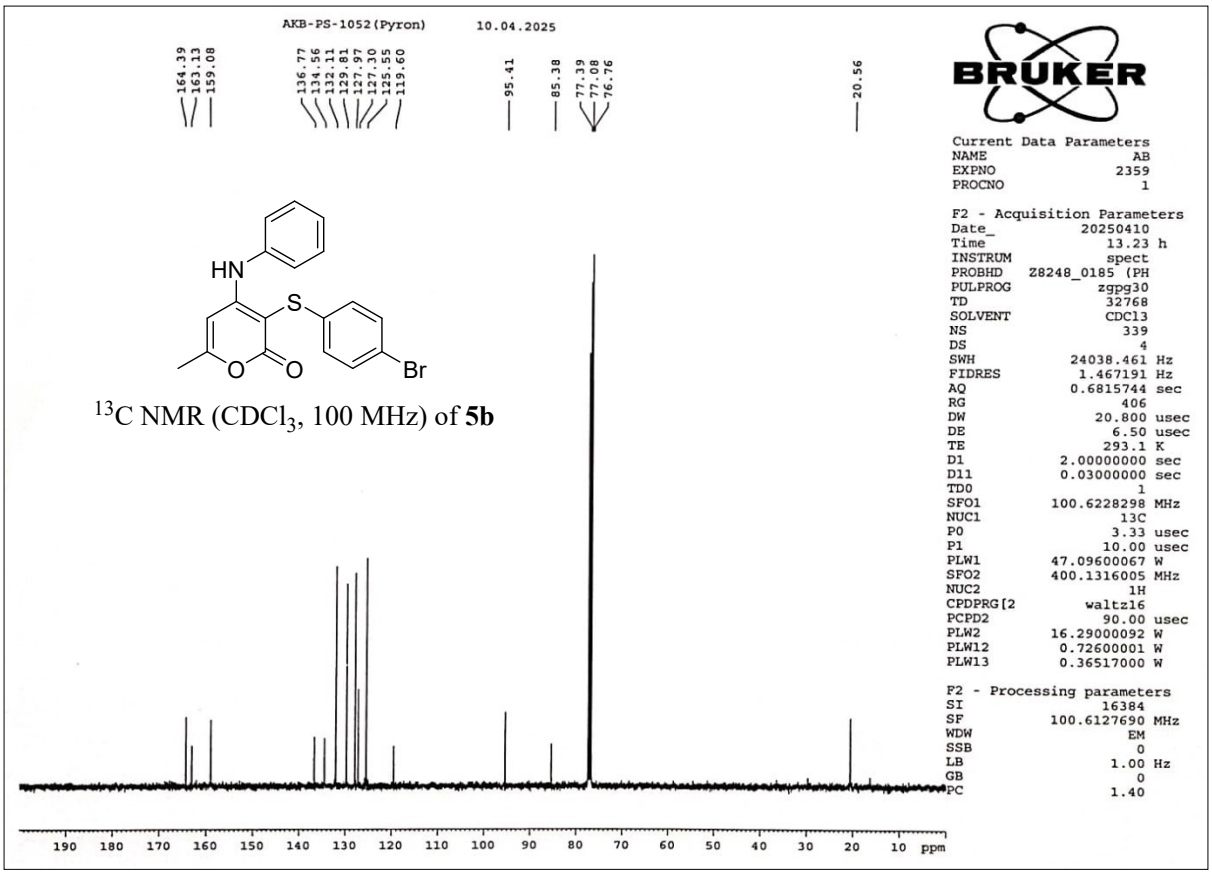
^{1}H NMR ($CDCl_3$, 400 MHz) of **5a**



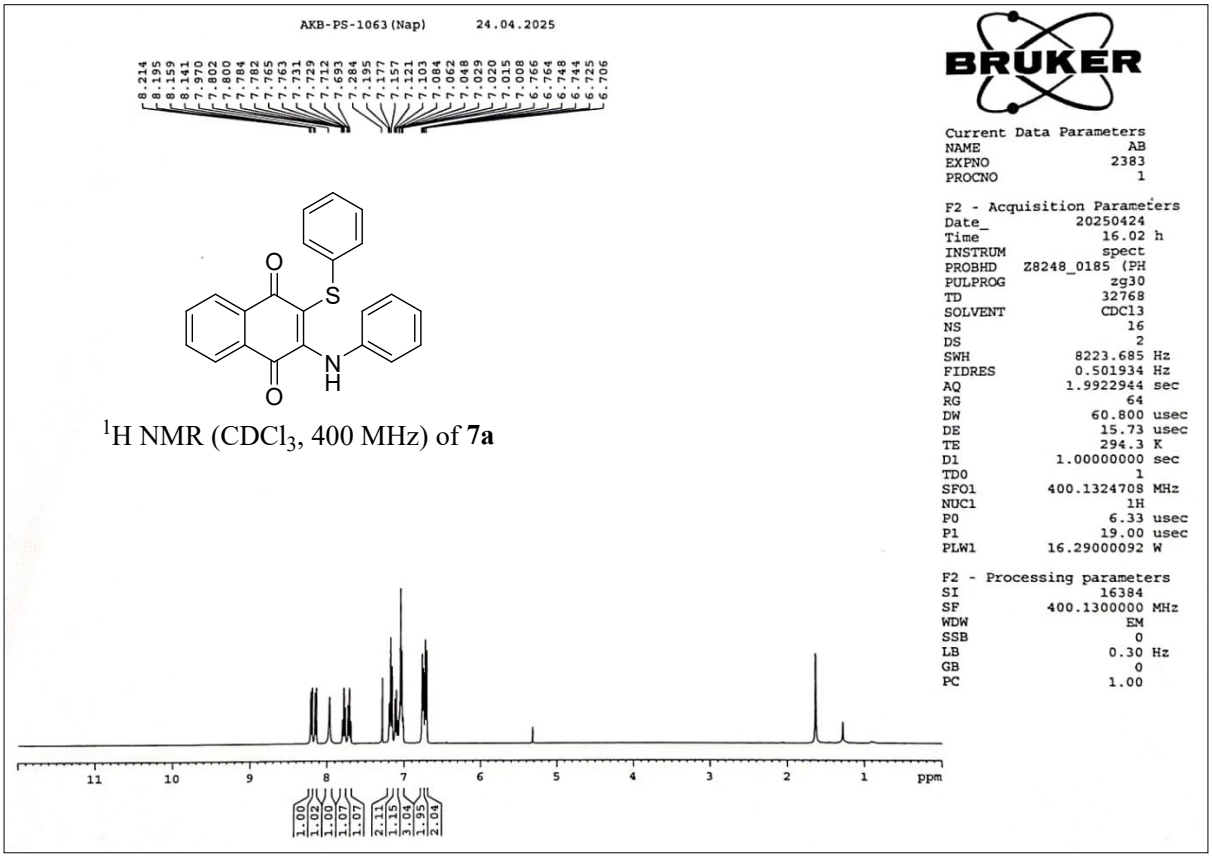
^{13}C NMR ($CDCl_3$, 100 MHz) of **5a**



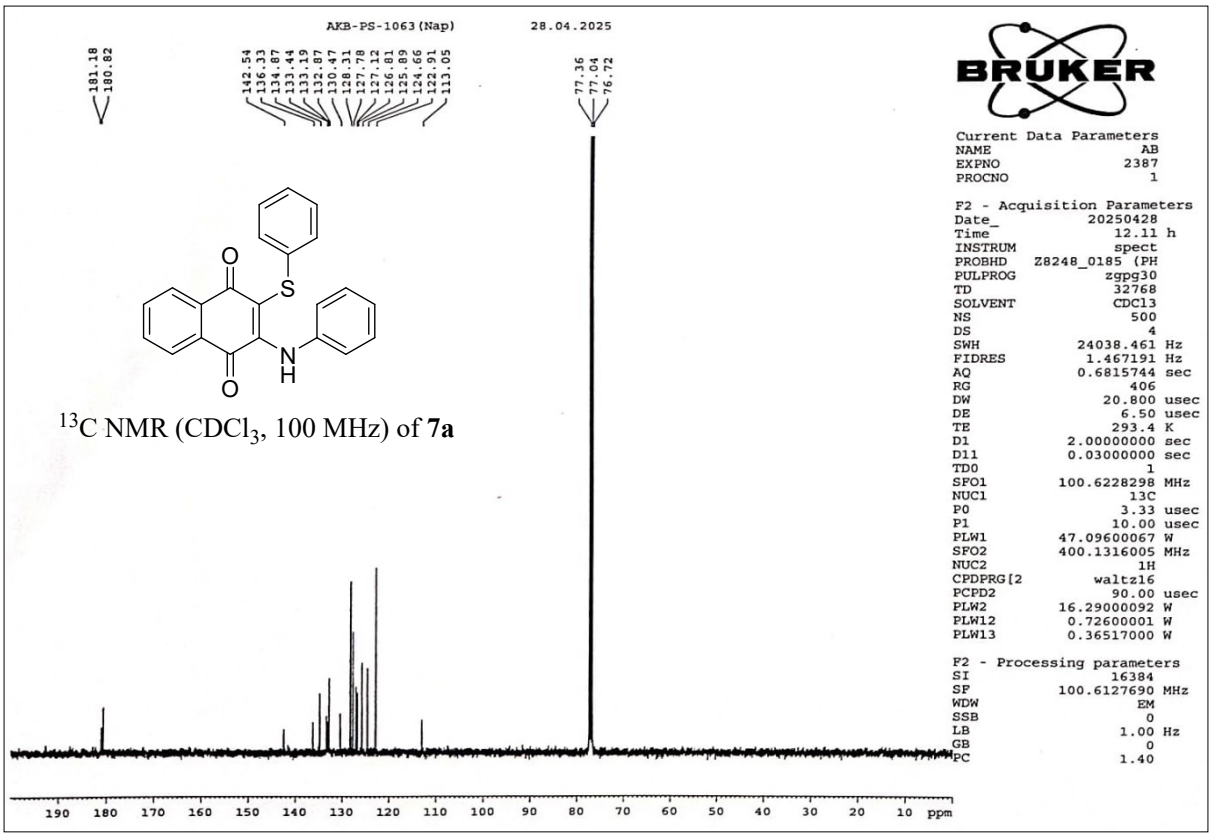
^{1}H NMR ($CDCl_3$, 400 MHz) of **5b**



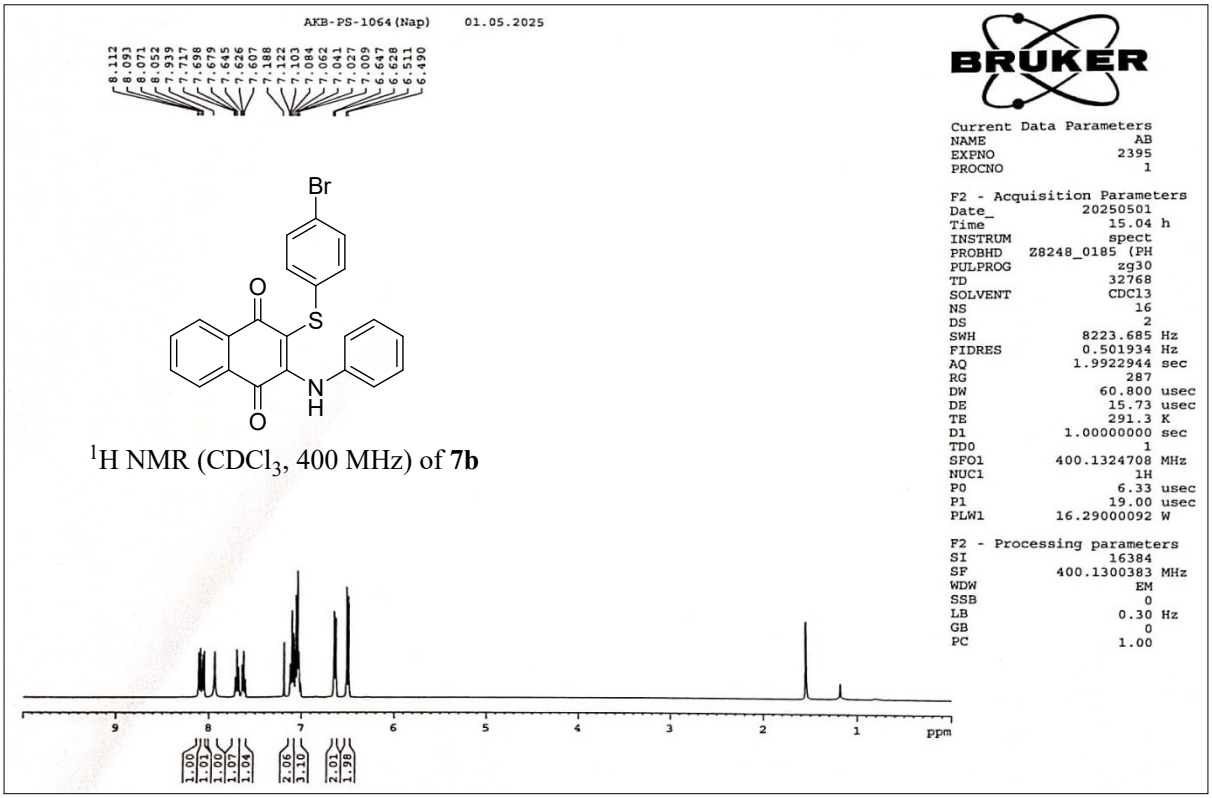
^{13}C NMR ($CDCl_3$, 100 MHz) of **5b**



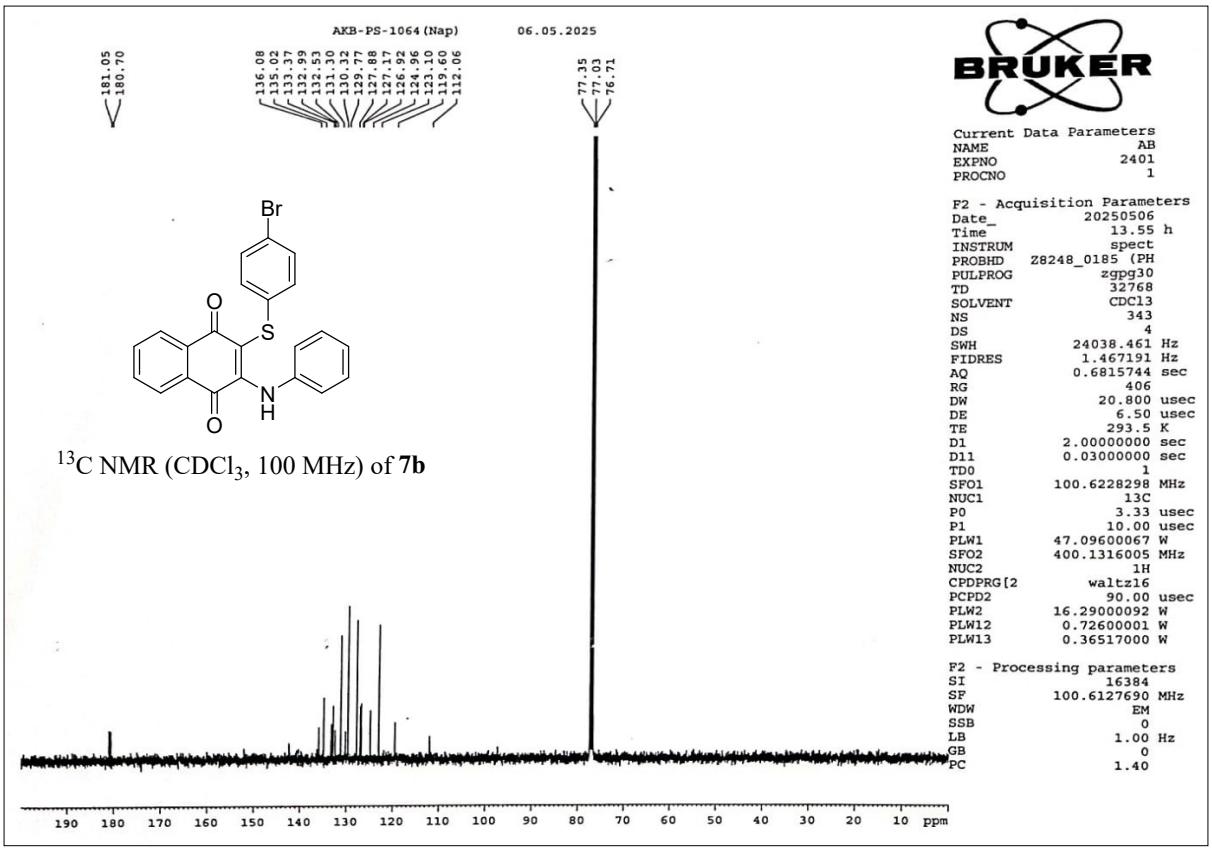
^{1}H NMR ($CDCl_3$, 400 MHz) of **7a**



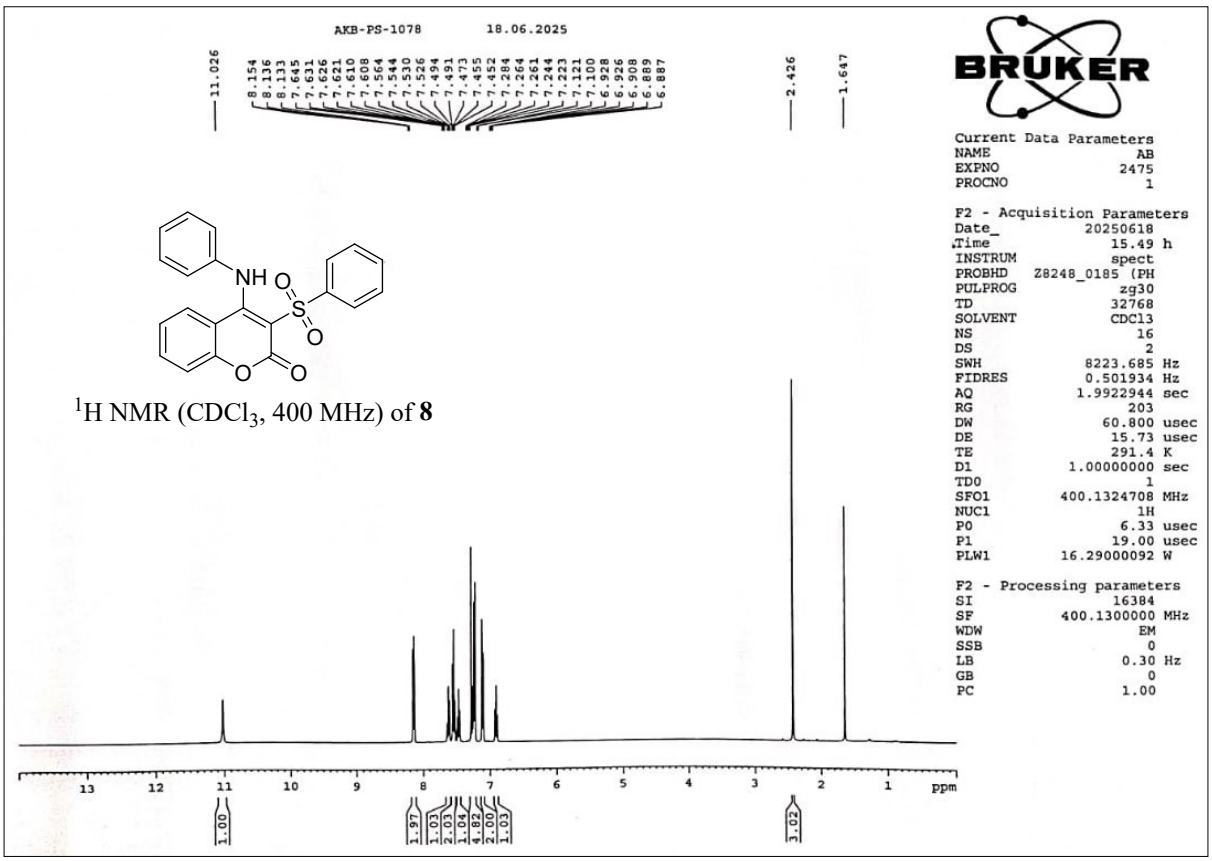
^{13}C NMR ($CDCl_3$, 100 MHz) of **7a**



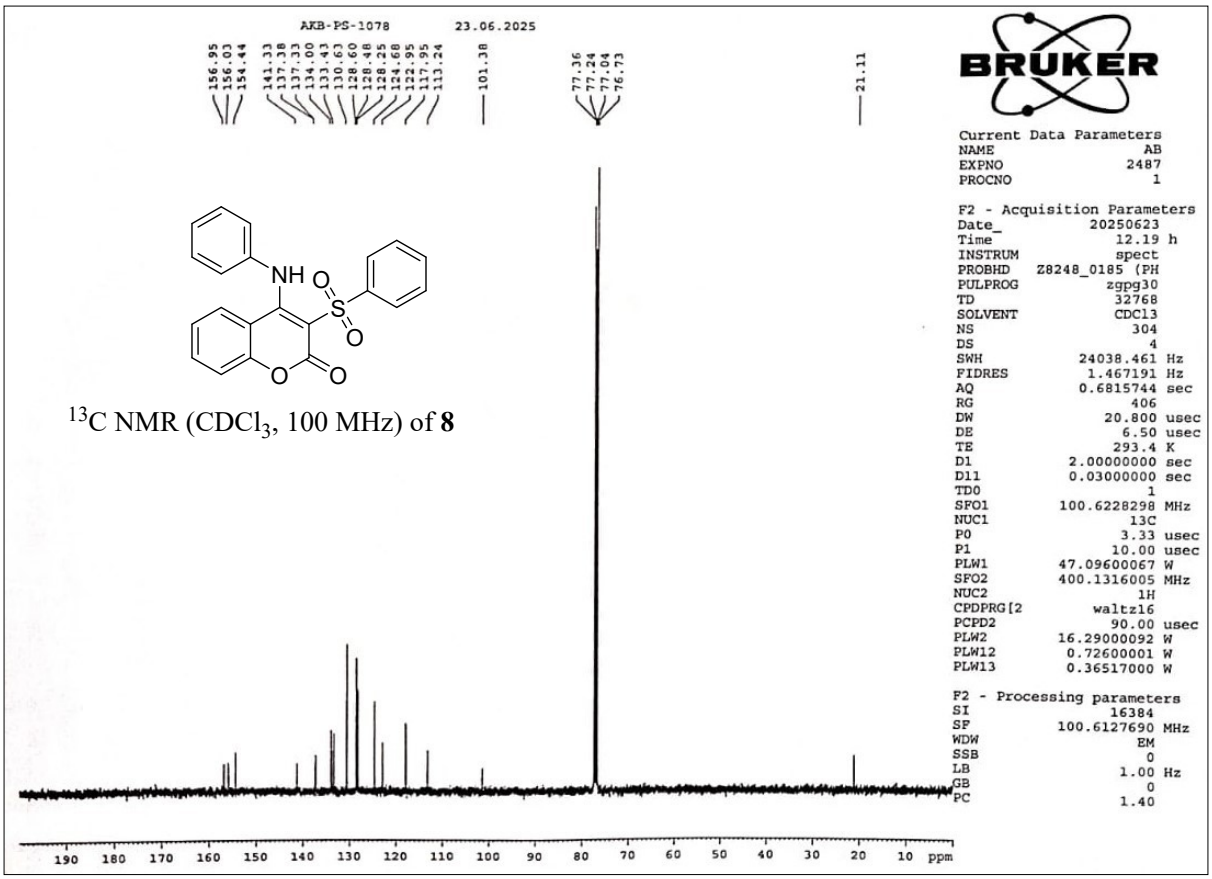
^{1}H NMR ($CDCl_3$, 400 MHz) of **7b**



^{13}C NMR ($CDCl_3$, 100 MHz) of **7b**



^{1}H NMR ($CDCl_3$, 400 MHz) of **8**



^{13}C NMR ($CDCl_3$, 100 MHz) of **8**