

Supplementary Information

The peroxodisulfate-assisted three-component benzylation of coumarins with styrenes and KSCN: A transition-metal-free approach for the synthesis of 3-(1-aryl-2-thiocyanatoethyl)-2H-chromen-2-one in ethyl lactate

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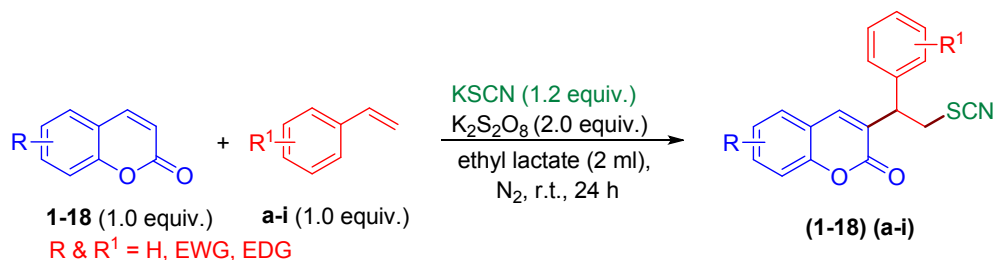
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1. General Information

All reactions were carried out under nitrogen gas atmosphere using standard Schlenk-tube. All solvents were distilled according to the established procedures¹ and de-aerated prior to use. Reactions were monitored by analytical thin layer chromatography on silica gel and visualization was accomplished by irradiation with short wave UV light at 254 nm and near UV 366 nm lights. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded using a 300 MHz spectrometer in CD₂Cl₂. Chemical shifts are expressed as δ value in parts per million (ppm) and were calibrated using the residual protonated solvent as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet and so on. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectra were collected by positive mode electrospray ionization (ESI) using Waters-Q-TOF-Premier mass spectrometer.

2. Experimental Section

2.1. General procedure for the synthesis of 3-(1-aryl-2-thiocyanatoethyl)-2H-chromen-2-ones



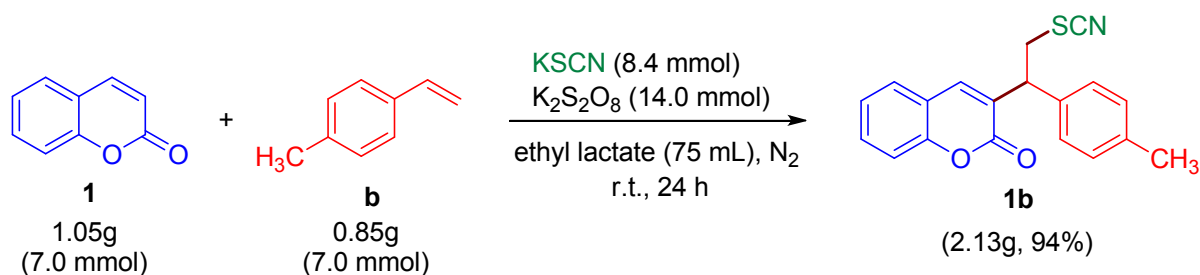
An oven-dried Schlenk-tube equipped with a magnetic stir bar was charged with coumarins (0.2 mmol, 1.0 equiv.), styrenes (0.2 mmol, 1.0 equiv.), KSCN (0.24 mmol, 1.2 equiv.), and K₂S₂O₈ (0.4 mmol, 2.0 equiv.). To this mixture, ethyl lactate (2 mL) was added. Then, the tube was sealed and inlet/outlet for N₂ gas was provided by a side-neck. Resultant mixture was vigorously stirred under nitrogen gas atmosphere at ambient conditions and the progress of reaction was monitored by TLC. After completion (as indicated by TLC, \approx 24 h), volatiles were removed under reduced pressure and then admixed with cold brine solution. Organic matter (product) precipitated was collected by filtration and washed with cold water (1 mL) followed by cold n-hexane (1 mL) to remove inorganic and organic (unreacted styrene), respectively, impurities. Subsequently, in many cases, the final purification was done by recrystallization (at low

temperature 0-10 °C) using either ethanol or ethanol-water mixture (cf. Section 2.2). The identity and purity of the product was confirmed by spectroscopic analysis, *vide infra*.

2.2. General procedure for the isolation of products by recrystallization

The product precipitate obtained (from 0.2 mmol scale) was transferred completely in to a round bottom flask (10 mL) and then dissolved using minimum amount of 30% aqueous ethanol (\approx 2 mL) or ethanol (\approx 1.5-2 mL) at elevated temperature (60 °C). Resultant clear solution was allowed to stand at 8-10 °C for overnight. Afterwards, so-formed precipitate particles were collected in a G5-crucible (porosity 1-5 μ m) by filtration and dried under vacuum for overnight.

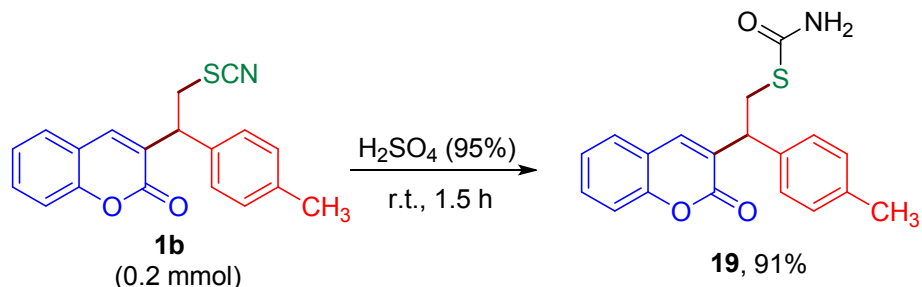
2.3. Large-scale synthesis of 1b (7.0 mmol scale)



An oven-dried three-neck round bottom flask equipped with a magnetic stir bar was charged with coumarins (1.05g, 7.0 mmol, 1.0 equiv.), *p*-methylstyrene (0.85g, 7.0 mmol, 1.0 equiv.), KSCN (0.82g, 8.4 mmol, 1.2 equiv.), and K₂S₂O₈ (3.8g, 14 mmol, 2.0 equiv.). To this mixture, ethyl lactate (75 mL) was added. Then, the flask was connected with a condenser and inlet/outlet for N₂ gas was provided. Resultant mixture was vigorously stirred under nitrogen gas atmosphere at ambient conditions for 24 h. Afterwards, solvent was distilled under reduced pressure and the residue was then admixed with cold brine solution (30 mL). The precipitate formed was collected by filtration and washed with cold water (10 mL) followed by cold *n*-hexane (10 mL) to remove inorganic and organic (unreacted styrene), respectively, impurities. Finally, product was purified by recrystallization by following the general recrystallization procedure described in Section 2.2.

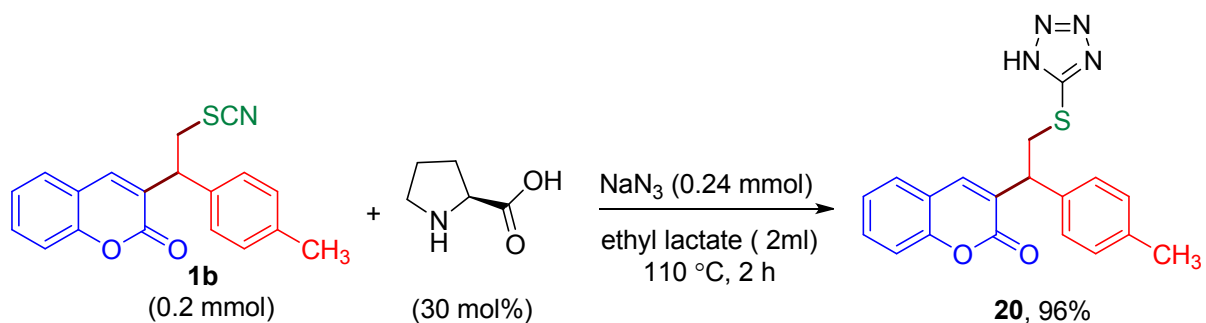
3. Follow-up transformations of product

3.1. Procedure for the preparation of *S*-2-(2-oxo-2*H*-chromen-3-yl)-2-*p*-tolylethyl carbamothioate (**19**)



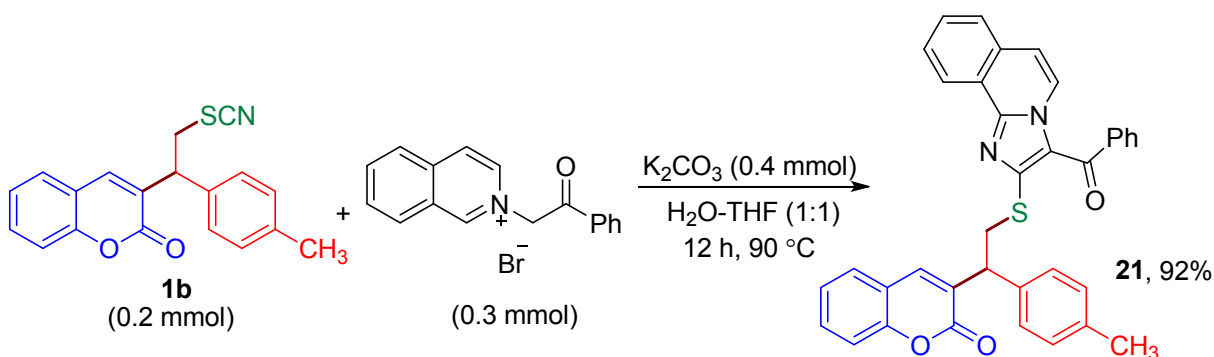
To an oven-dried Schlenk-tube (10 mL) was added **1b** (65 mg, 0.2 mmol) and sulfuric acid (1 mL, 95%). The resulting mixture was stirred at room temperature for 1.5 h. After completion of the reaction (monitored by TLC), the mixture was cooled to 5 °C and neutralized with dilute aqueous NaHCO₃ solution. The precipitate noticed was collected by filtration and recrystallized using water-ethanol (7:3, 2 mL) mixture at 10 °C to afford product **19** (62 mg, 91% Yield). White solid. $R_f = 0.17$ in 9:1 dichloromethane-methanol mixture. ¹H NMR (300 MHz, methanol-*d*₄) δ 7.49-7.44 (m, 1H), 7.37-7.34 (m, 1H), 7.32-7.27 (m, 2H), 7.25-7.16 (m, 5H), 4.21 (t, $J = 7.4$ Hz, 1H), 3.41 (d, $J = 7.4$ Hz, 1H), 3.19 (d, $J = 7.4$ Hz, 1H), 2.41 (s, 3H). ¹³C NMR (75 MHz, methanol-*d*₄) δ 168.1, 161.6, 152.9, 139.3, 136.2, 134.3, 130.5, 129.6, 129.4, 129.2, 127.3, 124.2, 119.3, 116.2, 42.8, 39.6, 24.3. HRMS (ESI) calcd for C₁₉H₁₈NO₃S⁺ [M+H]⁺ 340.0931, found 340.0938.

3.2. Procedure for the preparation of 3-(2-(1*H*-tetrazol-5-ylthio)-1-*p*-tolylethyl)-2*H*-chromen-2-one (**20**)



To an oven-dried Schlenk-tube (10 mL) was added **1b** (65 mg, 0.2 mmol), L-proline (10 mg, 30 mol%), NaN₃ (16 mg, 0.24 mmol), and ethyl lactate (2 mL). The resulting mixture was heated to 110 °C and stirred vigorously for 2 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and then admixed with cold brine solution. Organic matter (product) precipitated was collected by filtration and washed with cold water (3 mL) followed by recrystallized using water-ethanol (7:3, 2 mL) mixture at 10 °C to afford product **20** (70 mg, 96% Yield). White solid. R_f = 0.31 in 4:1 dichloromethane-methanol mixture. ¹H NMR (300 MHz, methanol-*d*₄) δ 7.51-7.47 (m, 1H), 7.38-7.29 (m, 3H), 7.25-7.16 (m, 5H), 4.15 (t, J = 7.2 Hz, 1H), 3.37 (d, J = 7.2 Hz, 1H), 3.16 (d, J = 7.2 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (75 MHz, methanol-*d*₄) δ 161.9, 154.3, 152.9, 139.4, 136.3, 134.5, 130.5, 129.4, 129.3, 129.0, 127.5, 124.1, 119.2, 116.5, 41.1, 37.9, 22.4. HRMS (ESI) calcd for C₁₉H₁₇N₄O₂S⁺ [M+H]⁺ 365.0995, found 365.0997.

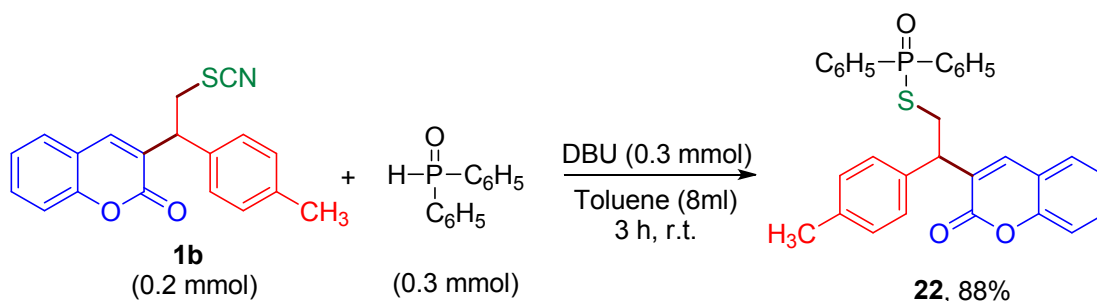
3.3. Procedure for the preparation of 3-(2-((3-benzoylimidazo[2,1-*a*]isoquinolin-2-yl)thio)-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (**21**)



To an oven-dried Schlenk-tube (10 mL) was added **1b** (65 mg, 0.2 mmol), isoquinoliniumbromide (98 mg, 0.3 mmol), potassium carbonate (55 mg, 0.4 mmol.) and water-THF (1:1, 5 mL). The resulting mixture was refluxed for 12 h at 90 °C and the solvents were removed under reduced pressure. Residue obtained was treated with water and then extracted with ethyl acetate (3 × 10 mL), the organic phase was dried over sodium sulfate and evaporated under reduced pressure to get the crude product which was purified by filtration thru a short-pad of silica gel column (hexane-ethyl acetate-methanol) to afford **21** (105 mg, 92%). Yellow solid. R_f = 0.12 in 9:1 dichloromethane-methanol mixture. ¹H NMR (300 MHz, CD₂Cl₂) δ 9.18 (d, J =

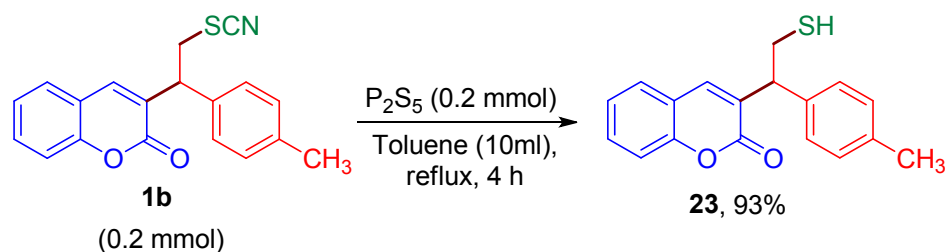
7.4 Hz, 1H), 8.77-8.75 (m, 1H), 7.86-7.83 (m, 1H), 7.79-7.76 (m, 2H), 7.74-7.71 (m, 2H), 7.67-7.64 (m, 1H), 7.59-7.55 (m, 2H), 7.49-7.44 (m, 1H), 7.37-7.33 (m, 1H), 7.32-7.26 (m, 3H), 7.23-7.14 (m, 5H), 3.99 (t, $J = 7.1$ Hz, 1H), 3.29 (d, $J = 7.1$ Hz, 1H), 3.05 (d, $J = 7.1$ Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 186.6, 161.7, 153.7, 152.9, 146.5, 140.3, 139.2, 136.4, 134.3, 132.2, 131.6, 130.7, 130.4, 129.6, 129.3, 129.2, 129.0, 128.9, 128.7, 127.3, 127.1, 125.1, 124.9, 124.2, 122.4, 119.3, 116.4, 114.4, 39.3, 35.7, 20.1. HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{27}\text{N}_2\text{O}_3\text{S}^+$ $[\text{M}+\text{H}]^+$ 567.1665, found 567.1672.

3.4. Procedure for the preparation of 3-(2-(diphenylphosphinothioate)-1-p-tolyethyl)-2H-chromen-2-one (**22**)



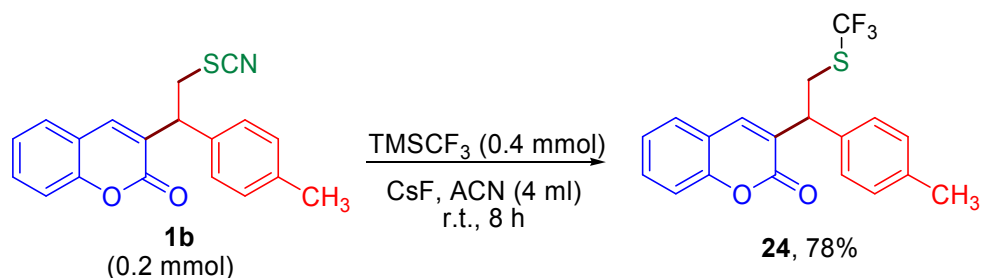
To an oven-dried Schlenk-tube (25 mL) was added **1b** (65 mg, 0.2 mmol), diphenylphosphine oxide (62 mg, 0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 45 mg, 0.3 mmol) and toluene (8 mL). The resulting mixture was stirred for 3 h at room temperature and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using 1-50% hexane-ethyl acetate mixture to afford pure **22** (87 mg, 88% Yield). White solid. $R_f = 0.29$ in 1:1 hexane-ethyl acetate mixture. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.87-7.70 (m, 4H), 7.53-7.40 (m, 7H), 7.37-7.34 (m, 1H), 7.32-7.28 (m, 2H), 7.25-7.17 (m, 5H), 4.29 (t, $J = 7.4$ Hz, 1H), 3.44 (d, $J = 7.4$ Hz, 1H), 3.22 (d, $J = 7.4$ Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.1, 153.0, 139.7, 136.8, 134.7, 133.9, 133.8, 133.0, 132.7, 131.5, 131.4, 130.5, 129.5, 129.3, 129.2, 128.8, 128.4, 127.3, 124.1, 119.2, 116.3, 43.8, 40.3, 26.2. HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{26}\text{PO}_3\text{S}^+$ $[\text{M}+\text{H}]^+$ 497.1263, found 497.1271.

3.5. Procedure for the preparation of 3-(2-mercapto-1-p-tolyethyl)-2H-chromen-2-one (**23**)



To an oven-dried Schlenk-tube (25 mL) was added **1b** (65 mg, 0.2 mmol), P_2S_5 (90 mg, 0.2 mmol) and toluene (10 mL). The resulting suspension was refluxed for 4 h and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using 1-50% hexane-ethyl acetate mixture to afford pure **23** (55 mg, 93% Yield). Pale yellow solid. $R_f = 0.6$ in 1:1 hexane-ethyl acetate mixture. 1H NMR (300 MHz, CD_2Cl_2) δ 7.45-7.41 (m, 1H), 7.35-7.33 (m, 1H), 7.30-7.26 (m, 2H), 7.22-7.12 (m, 5H), 3.86 (t, $J = 7.0$ Hz, 1H), 2.97 (d, $J = 7.0$ Hz, 1H), 2.73 (d, $J = 7.0$ Hz, 1H), 2.33 (s, 3H), 1.39 (s, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 161.4, 152.7, 139.2, 136.2, 134.3, 130.1, 129.5, 129.3, 129.1, 126.9, 124.1, 119.3, 116.3, 39.4, 29.7, 20.8. HRMS (ESI) calcd for $C_{18}H_{17}O_2S^+$ $[M+H]^+$ 297.0872, found 297.0884.

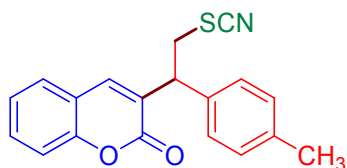
3.6 Procedure for the preparation of 3-(1-p-tolyl-2-(trifluoromethylthio)ethyl)-2H-chromen-2-one (**24**)



To an oven-dried Schlenk-tube (10 mL) was added **1b** (65 mg, 0.2 mmol), CsF (30 mg, 0.2 mmol) and MeCN (4 mL). Then trimethyl(trifluoromethyl)silane (60 μ l, 0.4 mmol) was added at 0 °C. The resulting mixture was stirred at room temperature for 8 h. After completion of the reaction (monitored by TLC), the mixture was filtered through a short pad of celite and diluted with ethyl acetate (10 mL). Resulting organic layer was washed with water (5 mL), dried over sodium sulfate and concentrated under vacuum. The residue obtained was purified by a column chromatography on silica-gel using 1-30% hexane-ethyl acetate mixture to afford product **24** (58

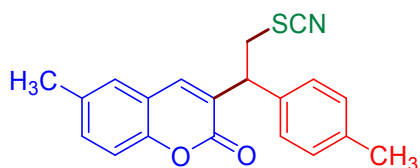
mg, 78%). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.47-7.43 (m, 1H), 7.36-7.32 (m, 1H), 7.31-7.26 (m, 2H), 7.23-7.14 (m, 5H), 3.93 (t, $J = 7.2$ Hz, 1H), 3.29 (d, $J = 7.2$ Hz, 1H), 3.07 (d, $J = 7.2$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 161.6, 152.9, 139.1, 136.3, 134.2, 130.8 (q, $J = 306.6$), 130.4, 129.6, 129.3, 129.1, 127.2, 124.0, 119.1, 116.1, 39.9, 32.7, 20.7. ^{19}F NMR (282 MHz, CD_2Cl_2) δ (ppm): -41.81. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{O}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 365.0746, found 365.0752.

4. Experimental characterization data for products



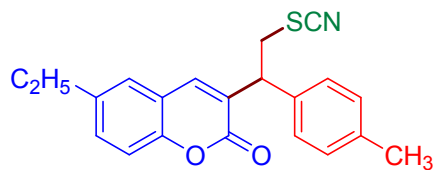
1b, 93%

3-(2-Thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (1b): Synthesized from **1** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 59.7 mg, 93% Yield. White solid. $R_f = 0.64$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.48-7.44 (m, 1H), 7.36-7.33 (m, 1H), 7.32-7.27 (m, 2H), 7.25-7.15 (m, 5H), 4.06 (t, $J = 7.2$ Hz, 1H), 3.37 (d, $J = 7.2$ Hz, 1H), 3.13 (d, $J = 7.2$ Hz, 1H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.7, 152.9, 139.2, 136.3, 134.3, 130.5, 129.5, 129.3, 129.2, 127.3, 124.1, 119.2, 116.3, 112.1, 40.1, 36.7, 21.2. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 322.0902, found 322.0908.



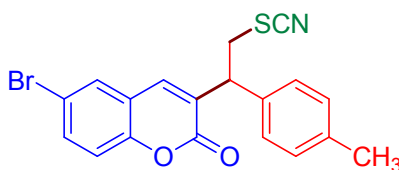
2b, 84%

6-Methyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (2b): Synthesized from **2** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 56.3 mg, 84% Yield. Off-white solid. $R_f = 0.61$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.53 (s, 1H), 7.34-7.26 (m, 3H), 7.25 (s, 1H), 7.24-7.14 (m, 3H), 4.08 (t, $J = 7.0$ Hz, 1H), 3.35 (d, $J = 7.0$ Hz, 1H), 3.12 (d, $J = 7.0$ Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.5, 151.4, 140.2, 139.1, 134.2, 132.3, 130.6, 129.5, 129.1, 127.2, 127.0, 118.9, 116.3, 112.0, 40.2, 36.6, 23.9, 21.1. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 336.1058, found 336.1061.



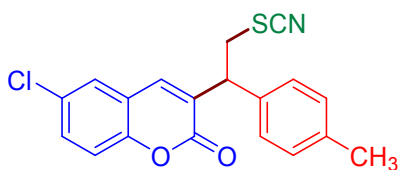
3b, 83%

6-Ethyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (3b): Synthesized from **3** and **b** according to the general procedure. The precipitate obtained was purified by chromatography on a silica gel column using 0 to 25% ethyl acetate/hexane solution. Obtained 57.9 mg, 83% Yield. Off-white solid. $R_f = 0.6$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.54 (s, 1H), 7.32-7.26 (m, 3H), 7.25 (s, 1H), 7.24-7.14 (m, 3H), 4.07 (t, $J = 7.2$ Hz, 1H), 3.37 (d, $J = 7.2$ Hz, 1H), 3.14 (d, $J = 7.2$ Hz, 1H), 2.48 (q, $J = 7.6$ Hz, 2H), 2.37 (s, 3H), 1.22 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.5, 151.5, 140.3, 139.1, 134.2, 132.3, 130.6, 129.6, 129.3, 127.2, 127.0, 118.9, 116.3, 112.1, 40.3, 36.7, 31.9, 21.2, 13.8. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 350.1215, found 350.1219.



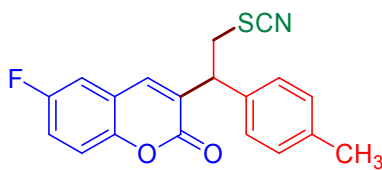
4b, 91%

6-Bromo-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (4b): Synthesized from **4** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 72.6 mg, 91% Yield. Pale yellow solid. $R_f = 0.63$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.72 (s, 1H), 7.64 (d, $J = 2.4$ Hz, 1H), 7.56 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.30-7.28 (m, 2H), 7.24-7.16 (m, 3H), 4.06 (t, $J = 6.8$ Hz, 1H), 3.36 (d, $J = 6.8$ Hz, 1H), 3.15 (d, $J = 6.8$ Hz, 1H), 2.38 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.8, 151.9, 139.1, 135.2, 133.7, 132.5, 130.6, 130.1, 129.6, 129.3, 120.7, 118.2, 116.9, 112.2, 40.3, 36.7, 21.4. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 400.0007, found 400.0013.



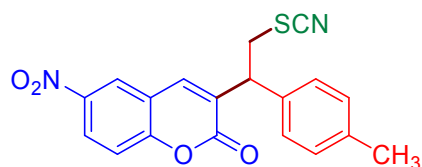
5b, 93%

6-Chloro-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (5b): Synthesized from **5** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 66.2 mg, 93% Yield. Pale yellow solid. $R_f = 0.64$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.74 (d, $J = 0.7$ Hz, 1H), 7.46 (d, $J = 2.4$ Hz, 1H), 7.44 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.33-7.15 (m, 5H), 4.07 (t, $J = 7.0$ Hz, 1H), 3.37 (d, $J = 7.0$ Hz, 1H), 3.16 (d, $J = 7.0$ Hz, 1H), 2.38 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.7, 151.4, 139.1, 135.2, 132.4, 130.9, 130.6, 129.5, 129.4, 129.2, 127.0, 120.4, 117.8, 112.3, 40.1, 36.8, 21.3. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 356.0512, found 356.0521.



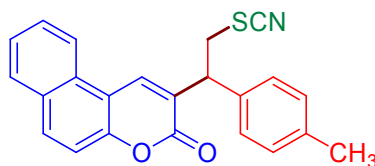
6b, 97%

6-Fluoro-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (6b): Synthesized from **6** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 65.9 mg, 97% Yield. White solid. $R_f = 0.62$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.51 (s, 1H), 7.32-7.28 (m, 2H), 7.25 (dd, $J = 8.8, 4.2$ Hz, 1H), 7.23-7.12 (m, 4H), 4.08 (t, $J = 7.0$ Hz, 1H), 3.38 (d, $J = 7.0$ Hz, 1H), 3.18 (d, $J = 7.0$ Hz, 1H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.4, 158.7 (d, $J = 242.1$ Hz), 149.2 (d, $J = 2.0$ Hz), 139.1, 138.4, 135.6 (d, $J = 2.7$ Hz), 130.6, 129.5, 129.3, 120.1 (d, $J = 9.2$ Hz), 117.9 (d, $J = 24.6$ Hz), 117.5 (d, $J = 8.2$ Hz), 112.9 (d, $J = 23.8$ Hz), 112.2, 40.4, 36.8, 21.4. $^{19}\text{F NMR}$ (282 MHz, CD_2Cl_2): -118.56 to -118.61 (m, 1F). HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{FNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 340.0808, found 340.0812.



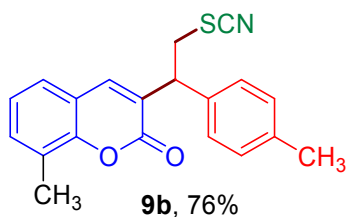
7b, 75%

6-Nitro-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (7b): Synthesized from **7** and **b** according to the general procedure. The precipitate obtained was purified by chromatography on a silica gel column using 0 to 30% ethyl acetate/hexane solution. Obtained 55.1 mg, 75% Yield. Yellow solid. $R_f = 0.38$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 8.40 (d, $J = 2.2$ Hz, 1H), 8.34 (d, $J = 9.4$ Hz, 1H), 7.52 (s, 1H), 7.41 (d, $J = 9.0$ Hz, 1H), 7.32-7.28 (m, 2H), 7.24-7.16 (m, 2H), 4.09 (t, $J = 7.2$ Hz, 1H), 3.39 (d, $J = 7.2$ Hz, 1H), 3.19 (d, $J = 7.2$ Hz, 1H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 160.2, 156.6, 144.2, 139.1, 137.7, 135.3, 130.6, 129.6, 129.2, 125.4, 123.5, 119.9, 117.7, 112.3, 40.4, 36.8, 21.6. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_4\text{S}^+$ $[\text{M}+\text{H}]^+$ 367.0753, found 367.0757.

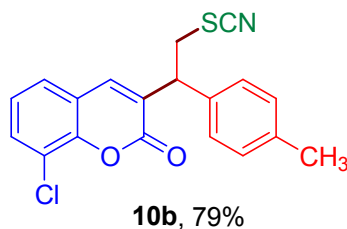


8b, 87%

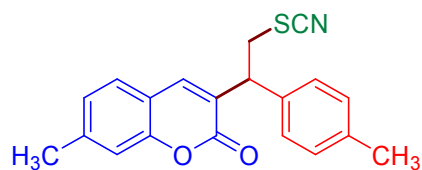
2-(2-Thiocyanato-1-(*p*-tolyl)ethyl)-3H-benzo[f]chromen-3-one (8b): Synthesized from **8** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 65.2 mg, 87% Yield. Pale yellow solid. $R_f = 0.58$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 8.26 (d, $J = 8.4$ Hz, 1H), 8.23 (s, 1H), 7.92 (t, $J = 8.4$ Hz, 2H), 7.66 (t, $J = 7.8$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 7.32-7.28 (m, 2H), 7.23-7.14 (m, 2H), 4.07 (t, $J = 6.8$ Hz, 1H), 3.37 (d, $J = 6.8$ Hz, 1H), 3.19 (d, $J = 6.8$ Hz, 1H), 2.35 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.7, 152.3, 139.1, 134.3, 132.3, 131.9, 130.6, 130.5, 129.6, 129.3, 129.2, 128.0, 125.8, 121.7, 116.9, 113.7, 112.1, 40.1, 36.6, 21.3. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 372.1058, found 372.1061.



8-Methyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (9b): Synthesized from **9** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 51.3 mg, 76% Yield. Off-white solid. $R_f = 0.59$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.59 (s, 1H), 7.34 (dd, $J = 7.4, 0.8$ Hz, 1H), 7.30-7.26 (m, 3H), 7.24-7.16 (m, 3H), 4.08 (t, $J = 7.0$ Hz, 1H), 3.36 (d, $J = 7.0$ Hz, 1H), 3.20 (d, $J = 7.0$ Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.5, 151.7, 140.4, 139.2, 132.5, 130.6, 129.6, 129.2, 126.8, 126.1, 125.2, 124.1, 119.3, 112.2, 40.3, 36.8, 21.3, 15.4. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 336.1058, found 336.1063.

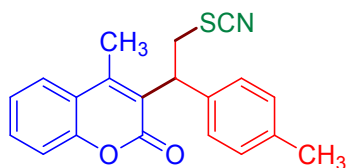


8-Chloro-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (10b): Synthesized from **10** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 56.4 mg, 79% Yield. Pale yellow solid. $R_f = 0.6$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.55 (d, $J = 8.2$ Hz, 1H), 7.48 (s, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.32-7.28 (m, 2H), 7.23-7.14 (m, 3H), 4.08 (t, $J = 7.2$ Hz, 1H), 3.37 (d, $J = 7.2$ Hz, 1H), 3.19 (d, $J = 7.2$ Hz, 1H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 158.6, 148.9, 139.2, 138.0, 136.1, 130.9, 130.7, 129.6, 129.1, 126.0, 124.3, 120.9, 120.7, 112.1, 40.1, 36.8, 21.3. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 356.0512, found 356.0519.



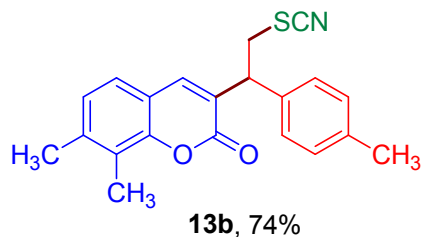
11b, 77%

7-Methyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (11b): Synthesized from **11** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 51.8 mg, 77% Yield. Off-white solid. $R_f = 0.61$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.51 (s, 1H), 7.33 (d, $J = 7.8$ Hz, 1H), 7.31-7.28 (m, 2H), 7.25-7.16 (m, 2H), 7.08 (s, 1H), 7.02 (d, $J = 7.8$ Hz, 1H), 4.08 (t, $J = 6.8$ Hz, 1H), 3.36 (d, $J = 6.8$ Hz, 1H), 3.20 (d, $J = 6.8$ Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 160.3, 153.4, 141.5, 139.0, 136.7, 135.9, 130.5, 129.6, 129.2, 127.2, 125.1, 117.1, 116.3, 112.2, 40.1, 36.8, 21.7, 21.3. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 336.1058, found 336.1064.

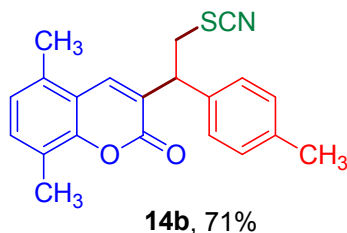


12b, 81%

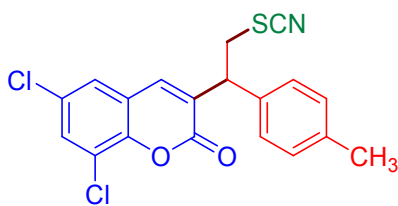
4-Methyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (12b): Synthesized from **12** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 54.7 mg, 81% Yield. Off-white solid. $R_f = 0.58$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.65-7.62 (m, 1H), 7.53-7.48 (m, 1H), 7.32-7.28 (m, 2H), 7.27-7.26 (m, 1H), 7.23-7.14 (m, 3H), 4.07 (t, $J = 6.8$ Hz, 1H), 3.38 (d, $J = 6.8$ Hz, 1H), 3.22 (d, $J = 6.8$ Hz, 1H), 2.48 (s, 3H), 2.35 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.7, 152.9, 139.1, 136.3, 134.5, 130.6, 129.6, 129.5, 129.3, 127.4, 124.2, 119.4, 116.3, 112.1, 40.2, 36.7, 21.2, 15.5. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 336.1058, found 336.1060.



7,8-Dimethyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (13b): Synthesized from **13** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 51.9 mg, 74% Yield. Pale yellow solid. $R_f = 0.52$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.77 (d, $J = 1.0$ Hz, 1H), 7.32-7.28 (m, 2H), 7.25-7.15 (m, 3H), 7.11 (d, $J = 8.0$ Hz, 1H), 4.06 (t, $J = 6.8$ Hz, 1H), 3.37 (d, $J = 6.8$ Hz, 1H), 3.18 (d, $J = 6.8$ Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 160.7, 151.3, 140.4, 139.1, 136.8, 130.7, 129.6, 129.3, 129.1, 125.8, 124.5, 124.1, 116.9, 112.2, 40.1, 36.8, 21.2, 20.3, 11.4. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 350.1215, found 350.1222.

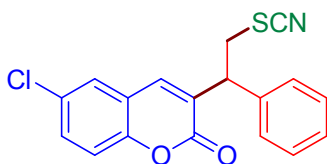


5,8-Dimethyl-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (14b): Synthesized from **14** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 50.2 mg, 71% Yield. Yellow solid. $R_f = 0.51$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.79 (s, 1H), 7.32-7.27 (m, 2H), 7.24-7.16 (m, 3H), 7.01 (d, $J = 7.4$ Hz, 1H), 4.06 (t, $J = 6.8$ Hz, 1H), 3.36 (d, $J = 6.8$ Hz, 1H), 3.21 (d, $J = 6.8$ Hz, 1H), 2.51 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 161.6, 152.2, 139.1, 137.7, 133.0, 132.1, 130.6, 129.5, 129.2, 125.9, 125.4, 123.7, 117.6, 112.0, 40.3, 36.6, 21.3, 18.2, 15.3. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 350.1215, found 350.1221.



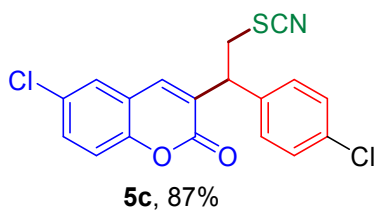
15b, 80%

6,8-Dichloro-3-(2-thiocyanato-1-(*p*-tolyl)ethyl)-2H-chromen-2-one (15b): Synthesized from **15** and **b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 62.5 mg, 80% Yield. Yellow solid. $R_f = 0.59$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.54 (d, $J = 2.2$ Hz, 1H), 7.51 (s, 1H), 7.35 (d, $J = 2.2$ Hz, 1H), 7.31-7.28 (m, 2H), 7.25-7.14 (m, 2H), 4.10 (t, $J = 7.2$ Hz, 1H), 3.38 (d, $J = 7.2$ Hz, 1H), 3.23 (d, $J = 7.2$ Hz, 1H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.9, 147.4, 139.2, 137.4, 134.9, 130.7, 130.6, 129.7, 129.5, 129.3, 125.4, 122.3, 121.8, 112.4, 40.4, 36.9, 21.4. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 390.0122, found 390.0127.

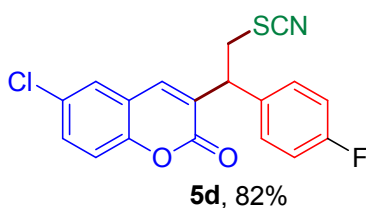


5a, 91%

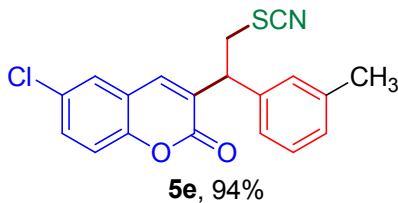
6-Chloro-3-(1-phenyl-2-thiocyanatoethyl)-2H-chromen-2-one (5a): Synthesized from **5** and **a** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 62.4 mg, 91% Yield. Pale yellow solid. $R_f = 0.65$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.71 (d, $J = 0.8$ Hz, 1H), 7.50 (d, $J = 2.2$ Hz, 1H), 7.44 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.34-7.20 (m, 6H), 4.07 (t, $J = 7.0$ Hz, 1H), 3.37 (d, $J = 7.0$ Hz, 1H), 3.21 (d, $J = 7.0$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.7, 151.2, 135.1, 134.3, 132.4, 130.8, 129.7, 129.2, 129.0, 128.9, 127.1, 120.4, 117.8, 112.1, 40.3, 36.6. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{13}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 342.0356, found 342.0361.



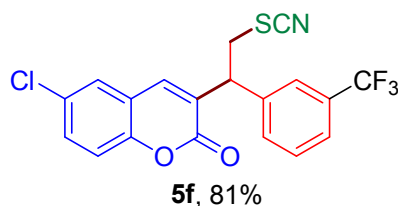
6-Chloro-3-(1-(4-chlorophenyl)-2-thiocyanatoethyl)-2H-chromen-2-one (5c): Synthesized from **5** and **c** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 65.7 mg, 87% Yield. Yellow solid. $R_f = 0.64$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.74 (d, $J = 0.9$ Hz, 1H), 7.51 (d, $J = 2.4$ Hz, 1H), 7.46 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.37-7.33 (m, 2H), 7.32-7.23 (m, 3H), 4.10 (t, $J = 7.2$ Hz, 1H), 3.38 (d, $J = 7.2$ Hz, 1H), 3.23 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.8, 151.3, 135.2, 134.9, 133.0, 132.5, 130.8, 130.4, 129.6, 129.2, 127.1, 120.3, 117.8, 112.2, 40.2, 36.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 375.9966, found 375.9973.



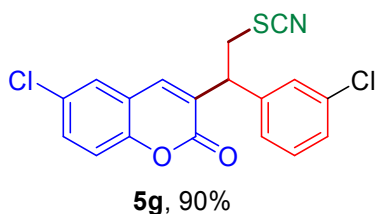
6-Chloro-3-(1-(4-fluorophenyl)-2-thiocyanatoethyl)-2H-chromen-2-one (5d): Synthesized from **5** and **d** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 60.0 mg, 82% Yield. Pale yellow solid. $R_f = 0.64$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.77 (d, $J = 1.0$ Hz, 1H), 7.52 (d, $J = 2.6$ Hz, 1H), 7.45 (dd, $J = 9.0, 2.6$ Hz, 1H), 7.33 (dd, $J = 8.6, 5.0$ Hz, 2H), 7.31-7.21 (m, 1H), 7.08 (t, $J = 8.6$ Hz, 2H), 4.09 (t, $J = 7.1$ Hz, 1H), 3.40 (d, $J = 7.1$ Hz, 1H), 3.25 (d, $J = 7.1$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 162.8 (d, $J_{\text{C-F}} = 248.4$ Hz), 159.7, 151.3, 135.2, 132.4, 130.9, 130.8 (d, $J_{\text{C-F}} = 9.0$ Hz), 130.2 (d, $J_{\text{C-F}} = 3.7$ Hz), 129.7, 127.2, 120.4, 117.9, 116.3 (d, $J_{\text{C-F}} = 21.2$ Hz), 112.3, 40.4, 36.8. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{12}\text{ClFNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 360.0261, found 360.0269.



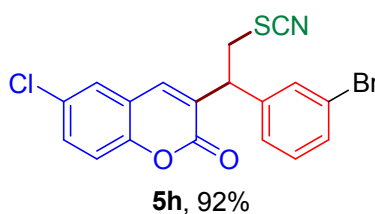
6-Chloro-3-(2-thiocyanato-1-*m*-tolylethyl)-2H-chromen-2-one (5e): Synthesized from **5** and **e** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 66.9 mg, 94% Yield. Off-white solid. $R_f = 0.63$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.71 (d, $J = 0.6$ Hz, 1H), 7.46 (d, $J = 2.3$ Hz, 1H), 7.42 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.32-7.22 (m, 2H), 7.19-7.11 (m, 3H), 4.07 (t, $J = 6.9$ Hz, 1H), 3.36 (d, $J = 6.9$ Hz, 1H), 3.21 (d, $J = 6.9$ Hz, 1H). 2.37 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.7, 151.5, 138.9, 135.2, 134.1, 132.4, 130.8, 129.7, 129.6, 129.5, 129.0, 127.1, 126.0, 120.3, 117.8, 112.1, 40.2, 36.8, 21.4. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 356.0512, found 356.0518.



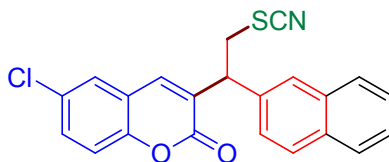
6-Chloro-3-(1-(3-(trifluoromethyl)phenyl)-2-thiocyanatoethyl)-2H-chromen-2-one (5f): Synthesized from **5** and **f** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 66.5 mg, 81% Yield. Yellow solid. $R_f = 0.58$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.81 (d, $J = 1.1$ Hz, 1H), 7.66 (s, 1H), 7.60 (d, $J = 7.8$ Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.48 (d, $J = 2.4$ Hz, 1H), 7.44-7.41 (m, 2H), 7.32-7.19 (m, 1H), 4.11 (t, $J = 7.2$ Hz, 1H), 3.38 (d, $J = 7.2$ Hz, 1H), 3.24 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.7, 151.4, 144.7, 135.1, 132.5, 130.8 (q, $J_{\text{C-F}} = 32.4$ Hz), 130.6, 130.4, 129.8, 129.1, 127.1, 125.6, 124.2, 124.1 (q, $J_{\text{C-F}} = 272.2$ Hz), 120.4, 117.8, 112.3, 40.4, 36.6. $^{19}\text{F NMR}$ (282 MHz, CD_2Cl_2): -62.54 (s, 3F). HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{12}\text{ClF}_3\text{NO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 410.0229, found 410.0234.



6-Chloro-3-(1-(3-chlorophenyl)-2-thiocyanatoethyl)-2H-chromen-2-one (5g): Synthesized from **5** and **g** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 67.8 mg, 90% Yield. Pale yellow solid. $R_f = 0.62$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.76 (d, $J = 0.9$ Hz, 1H), 7.52 (d, $J = 2.4$ Hz, 1H), 7.46 (dd, $J = 8.6, 2.4$ Hz, 1H), 7.38-7.33 (m, 3H), 7.32-7.21 (m, 2H), 4.09 (t, $J = 7.1$ Hz, 1H), 3.36 (d, $J = 7.1$ Hz, 1H), 3.23 (d, $J = 7.1$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.9, 151.5, 136.3, 135.2, 134.9, 132.6, 130.8, 130.5, 129.6, 129.2, 129.1, 127.4, 127.1, 120.3, 117.8, 112.2, 40.4, 36.9. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{NO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 375.9966, found 375.9969.

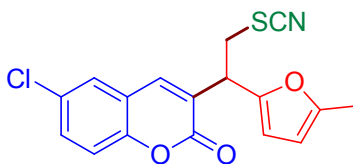


3-(1-(3-Bromophenyl)-2-thiocyanatoethyl)-6-chloro-2H-chromen-2-one (5h): Synthesized from **5** and **h** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 77.3 mg, 92% Yield. Yellow solid. $R_f = 0.61$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.75 (d, $J = 0.8$ Hz, 1H), 7.49 (d, $J = 2.2$ Hz, 1H), 7.44 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.35-7.21 (m, 3H), 7.13-7.09 (m, 2H), 4.07 (t, $J = 7.0$ Hz, 1H), 3.37 (d, $J = 7.0$ Hz, 1H), 3.22 (d, $J = 7.0$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.9, 151.4, 140.2, 135.3, 132.4, 132.2, 130.8, 129.7, 129.7, 128.5, 127.7, 127.2, 122.3, 120.4, 117.8, 112.2, 40.2, 36.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{12}\text{BrClNO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 419.9461, found 419.9469.



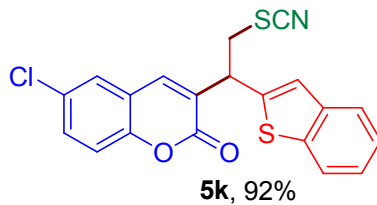
5i, 93%

6-Chloro-3-(1-(naphthalen-3-yl)-2-thiocyanatoethyl)-2H-chromen-2-one (5i): Synthesized from **5** and **i** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in ethanol solution. Obtained 72.9 mg, 93% Yield. Yellow solid. $R_f = 0.54$ in 1:1 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.89-7.79 (m, 4H), 7.74 (d, $J = 0.8$ Hz, 1H), 7.52 (dt, $J = 6.2, 3.2$ Hz, 2H), 7.49 (d, $J = 2.2$ Hz, 1H), 7.45 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.43 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.32-7.21 (m, 1H), 4.06 (t, $J = 6.8$ Hz, 1H), 3.34 (d, $J = 6.8$ Hz, 1H), 3.19 (d, $J = 6.8$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.5, 151.3, 135.1, 133.2, 132.5, 131.6, 130.8, 129.6, 129.4, 128.3, 128.0, 127.8, 127.2, 126.8, 126.7, 126.2, 120.3, 117.9, 112.1, 40.1, 36.6. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{15}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 392.0512, found 392.0516.



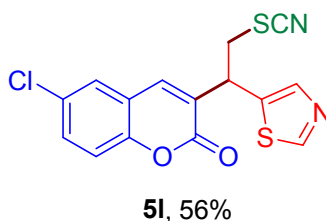
5j, 78%

6-chloro-3-(1-(5-methylfuran-2-yl)-2-thiocyanatoethyl)-2H-chromen-2-one (5j): Synthesized from **5** and **j** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol. Obtained 55 mg, 78% Yield. Pale Yellow solid. $R_f = 0.48$ in 7:3 hexane-ethyl acetate mixture. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.71 (d, $J = 1.0$ Hz, 1H), 7.49-7.43 (m, 2H), 7.32-7.29 (m, 1H), 6.234 (d, $J = 3.2$ Hz, 1H), 5.934 (d, $J = 3.2$ Hz, 1H), 3.52 (t, $J = 7.0$ Hz, 1H), 2.91 (d, $J = 7.0$ Hz, 1H), 2.63 (d, $J = 7.0$ Hz, 1H), 2.262 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 159.6, 155.8, 151.3, 151.0, 135.1, 133.2, 130.9, 129.5, 127.2, 120.3, 117.6, 112.3, 105.7, 104.5, 31.2, 23.7, 13.8. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{13}\text{ClNO}_3\text{S}^+$ $[\text{M}+\text{H}]^+$ 346.0227, found 346.0232.



3-(1-(benzo[b]thiophen-2-yl)-2-thiocyanatoethyl)-6-chloro-2H-chromen-2-one (5k):

Synthesized from **5** and **k** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 73.7 mg, 92% Yield. Yellow solid. $R_f = 0.37$ in 7:3 hexane-ethyl acetate mixture. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.74-7.71 (m, 2H), 7.61-7.59 (m, 1H), 7.50-7.45 (m, 2H), 7.31-7.27 (m, 3H), 7.02 (s, 1H), 3.61 (t, $J = 7.2$ Hz, 1H), 3.02 (d, $J = 7.2$ Hz, 1H), 2.83 (d, $J = 7.2$ Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.4, 151.3, 151.1, 140.4, 139.7, 135.3, 133.1, 130.5, 129.6, 127.2, 124.4, 124.1, 123.4, 122.5, 120.4, 119.6, 117.5, 112.1, 39.8, 36.4. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{13}\text{ClNO}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$ 398.0002, found 398.0011.



6-chloro-3-(1-(thiazol-5-yl)-2-thiocyanatoethyl)-2H-chromen-2-one (5l): Synthesized from **5** and **l** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 40 mg, 56% Yield. Yellow solid. $R_f = 0.48$ in 1:1 hexane-ethyl acetate mixture. ^1H NMR (300 MHz, CD_2Cl_2) δ 8.14 (s, 1H), 7.73 (d, $J = 1.0$ Hz, 1H), 7.54 (d, $J = 2.2$ Hz, 1H), 7.48 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.29-7.25 (m, 1H), 7.08 (s, 1H), 3.67 (t, $J = 7.2$ Hz, 1H), 3.21 (d, $J = 7.2$ Hz, 1H), 3.07 (d, $J = 7.2$ Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.9, 151.7, 151.2, 138.8, 135.3, 133.1, 131.6, 130.7, 129.6, 127.1, 120.5, 117.8, 112.1, 40.3, 36.9. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{ClN}_2\text{O}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$ 348.9795, found 348.9799.

5. References

1 B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, in *Vogel's Textbook of Practical Organic Chemistry*, Pearson Education, 5th edn, 1989, ch. 4, 395-409 (ISBN: 978-81-7758-957-3).

6. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra for products

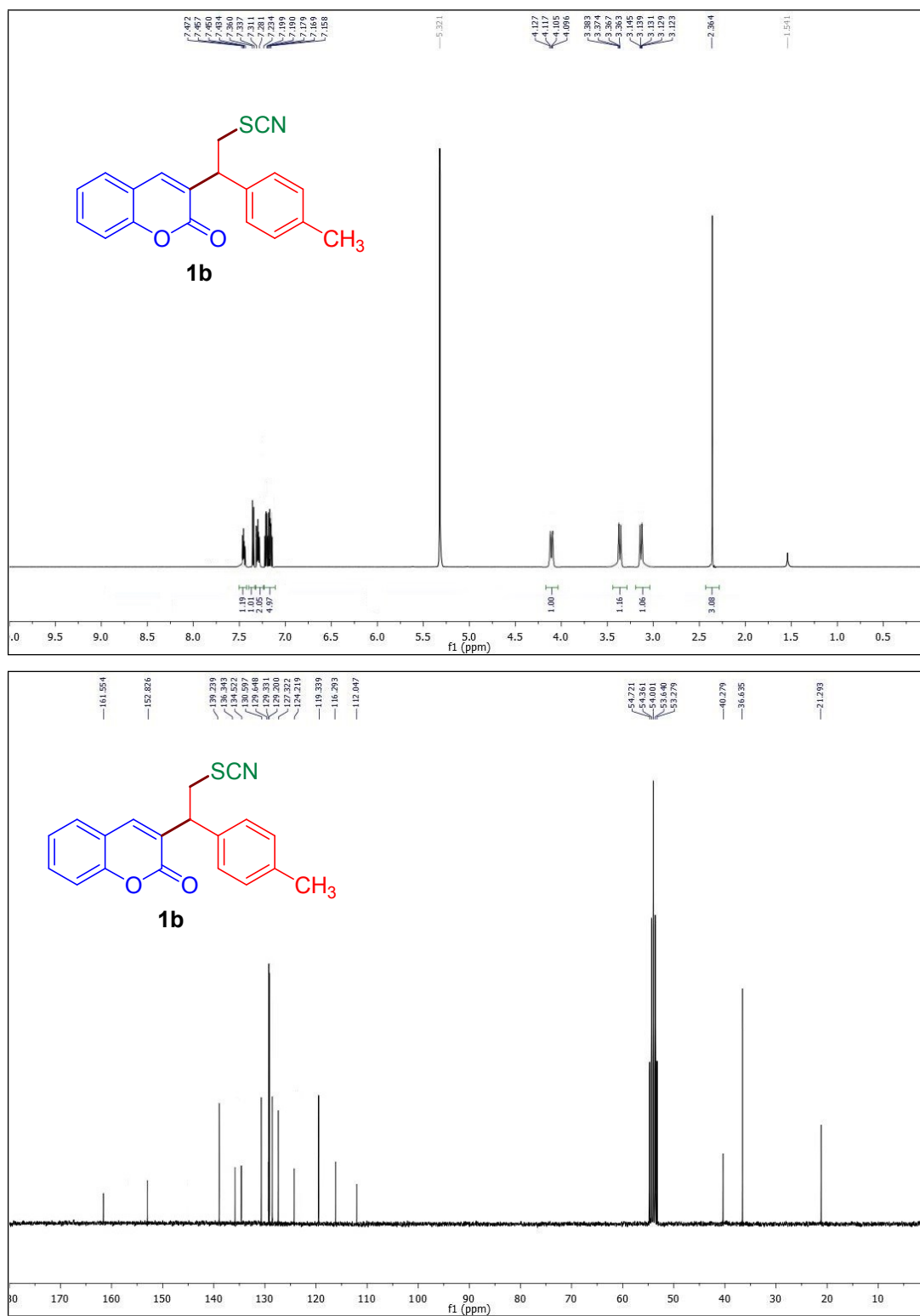


Figure S1. ^1H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **1b** in CD_2Cl_2 .

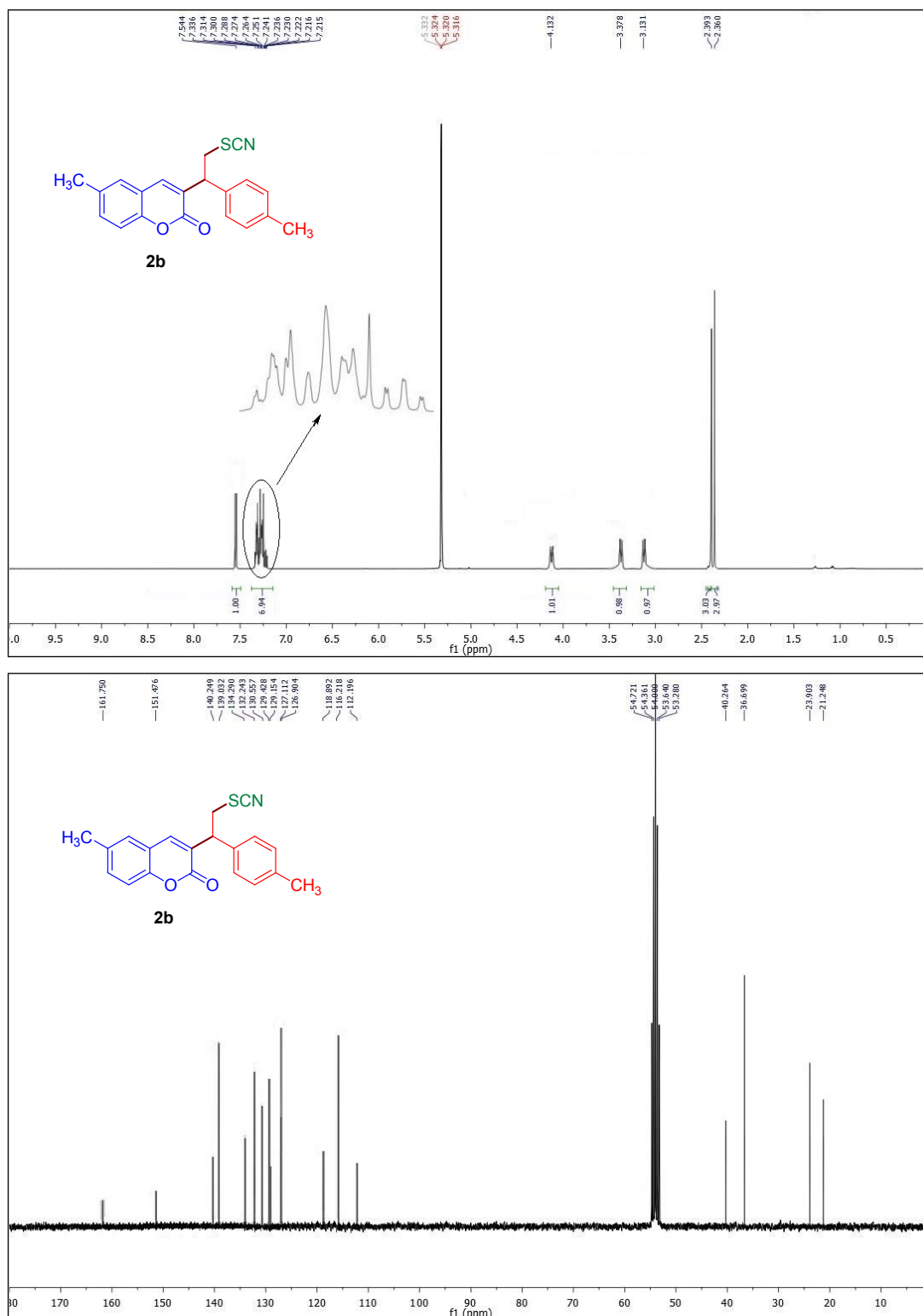


Figure S2. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **2b** in CD₂Cl₂.

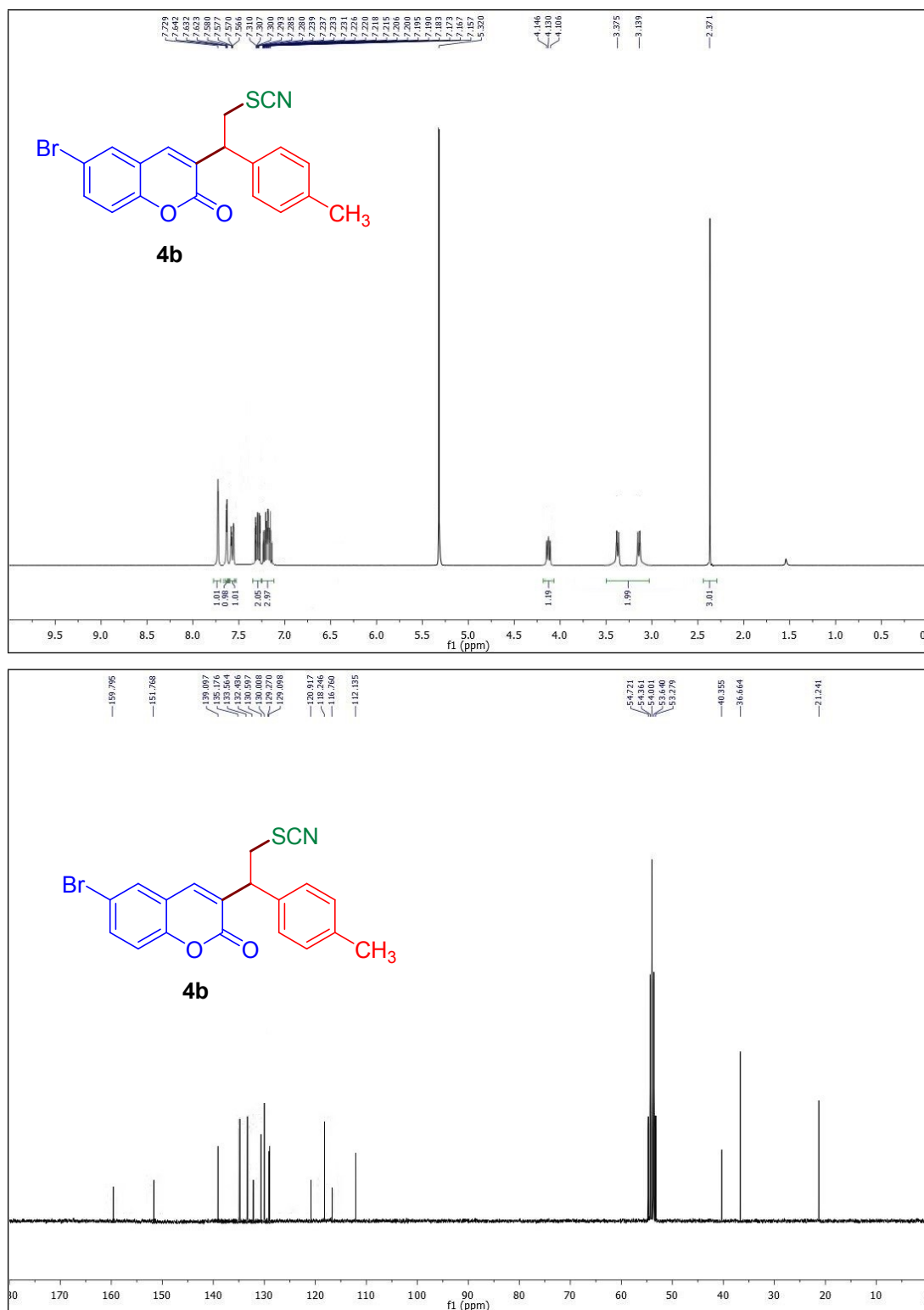


Figure S3. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **4b** in CD₂Cl₂.

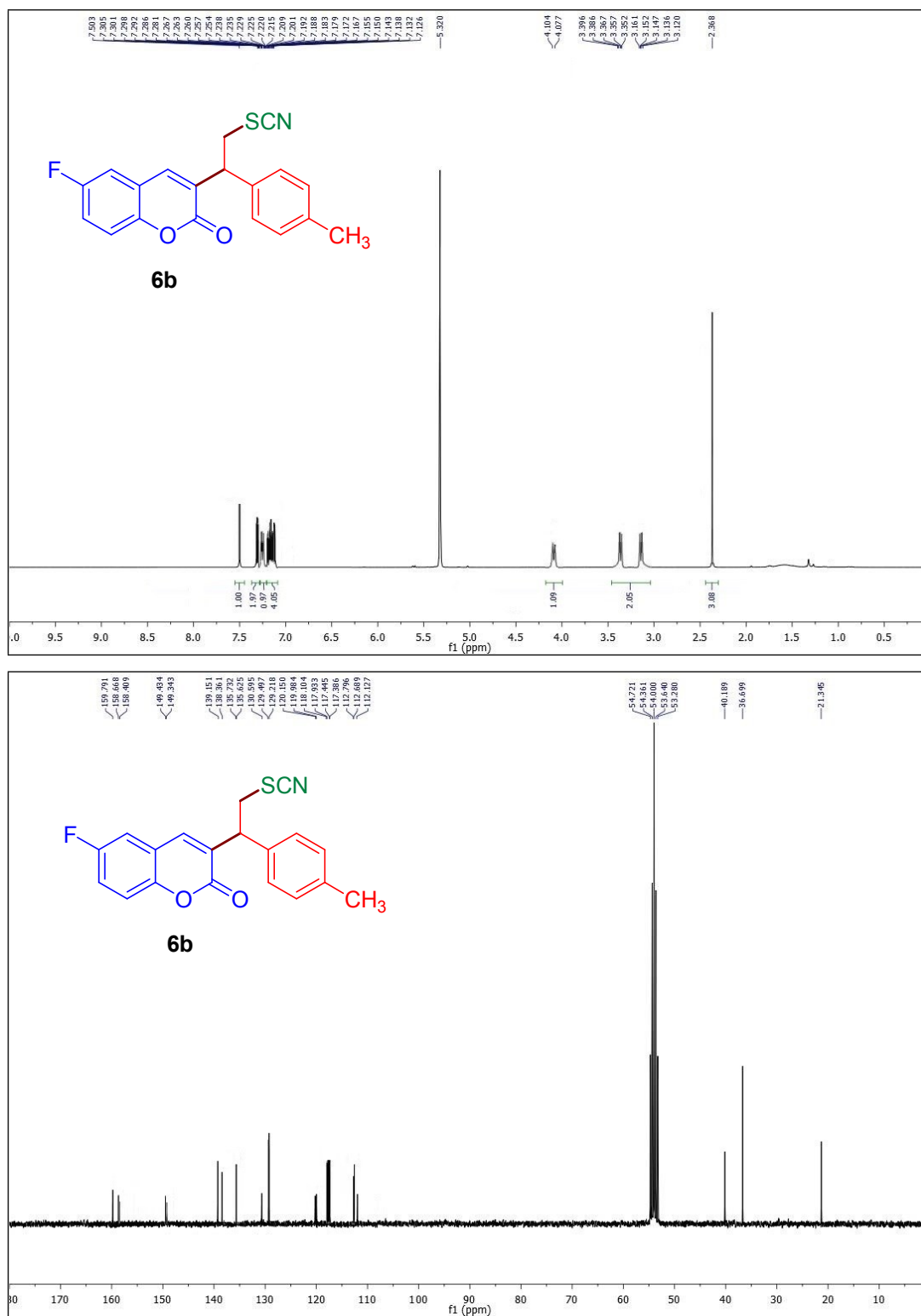


Figure S4. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **6b** in CD₂Cl₂.

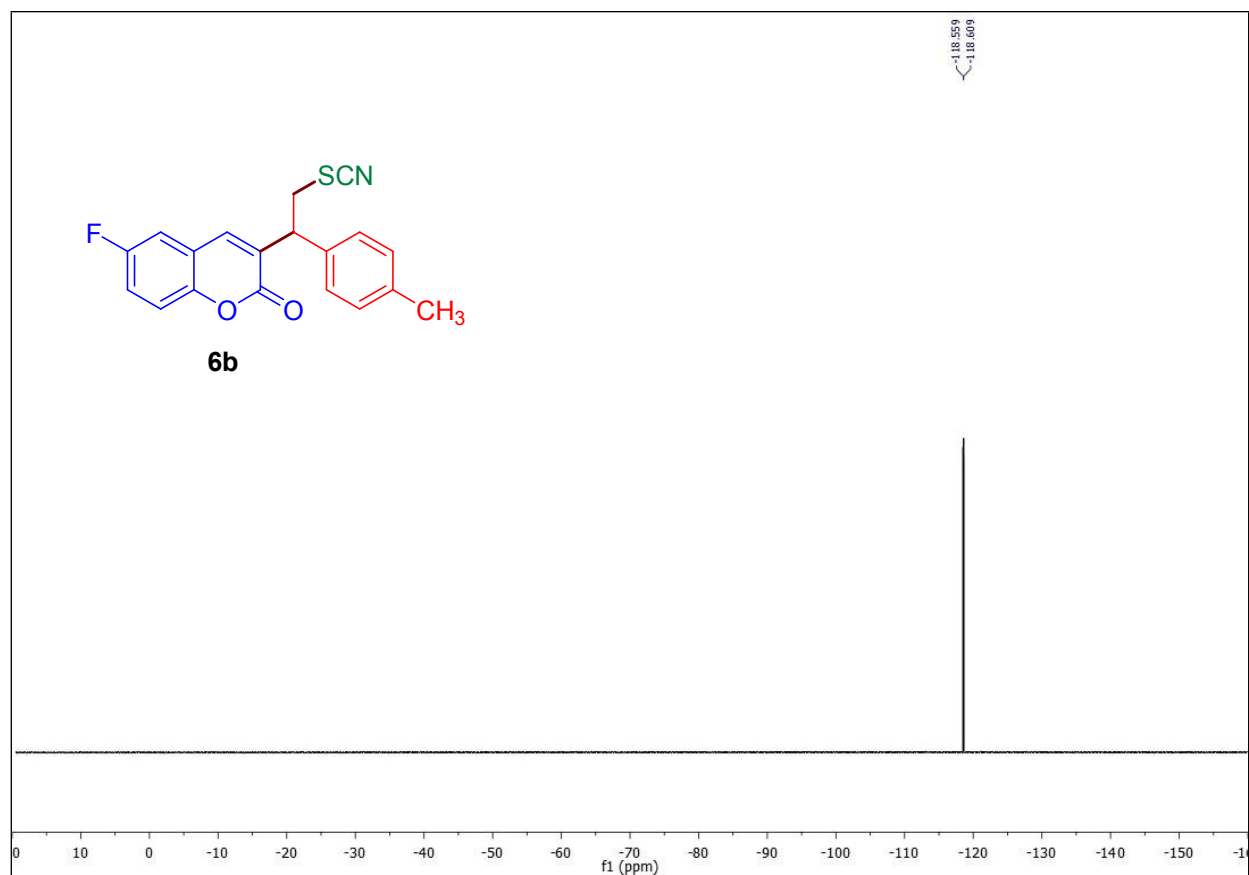


Figure S5. ^{19}F (282 MHz) NMR spectra of **6b** in CD_2Cl_2 .

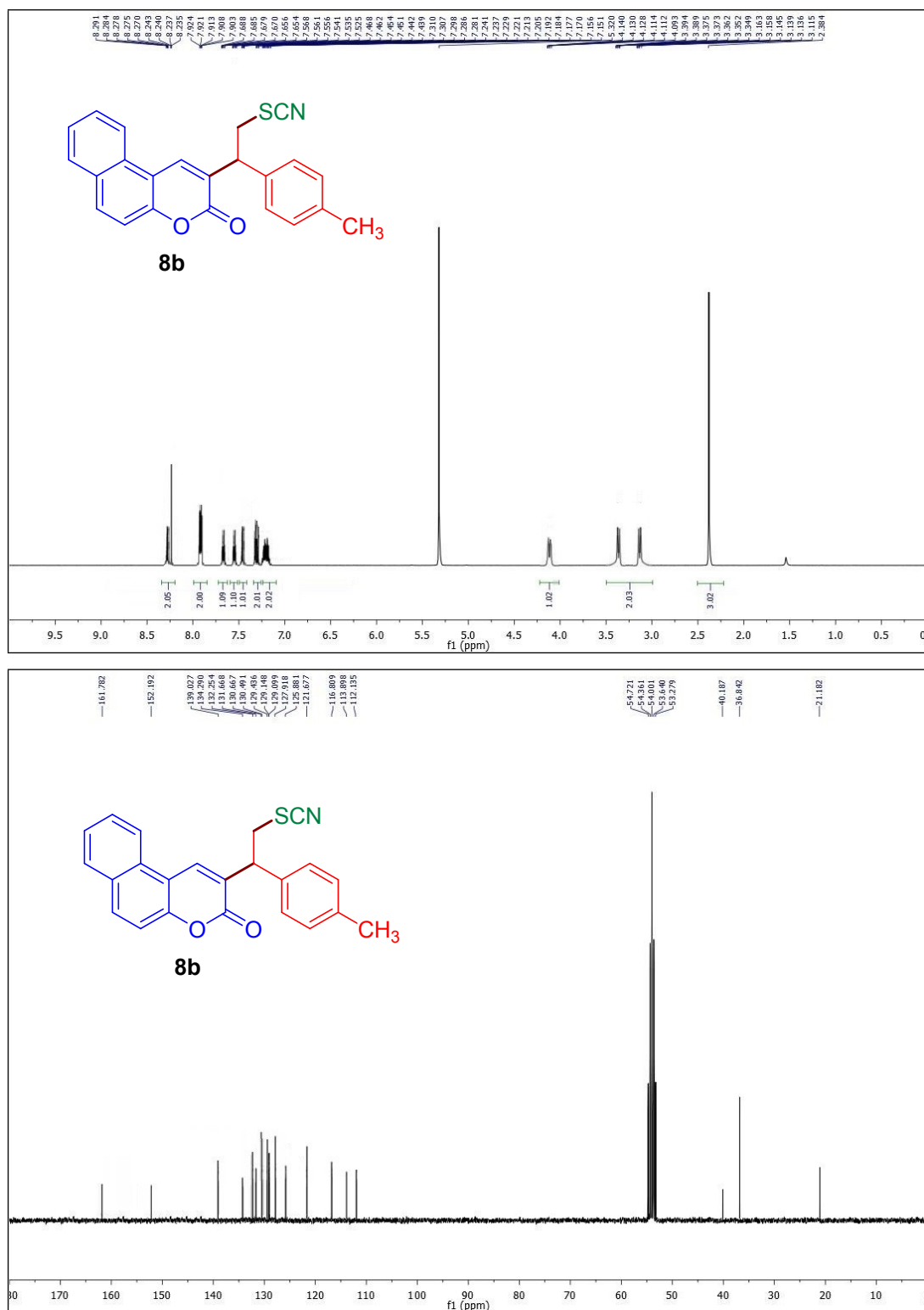


Figure S6. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **8b** in CD₂Cl₂.

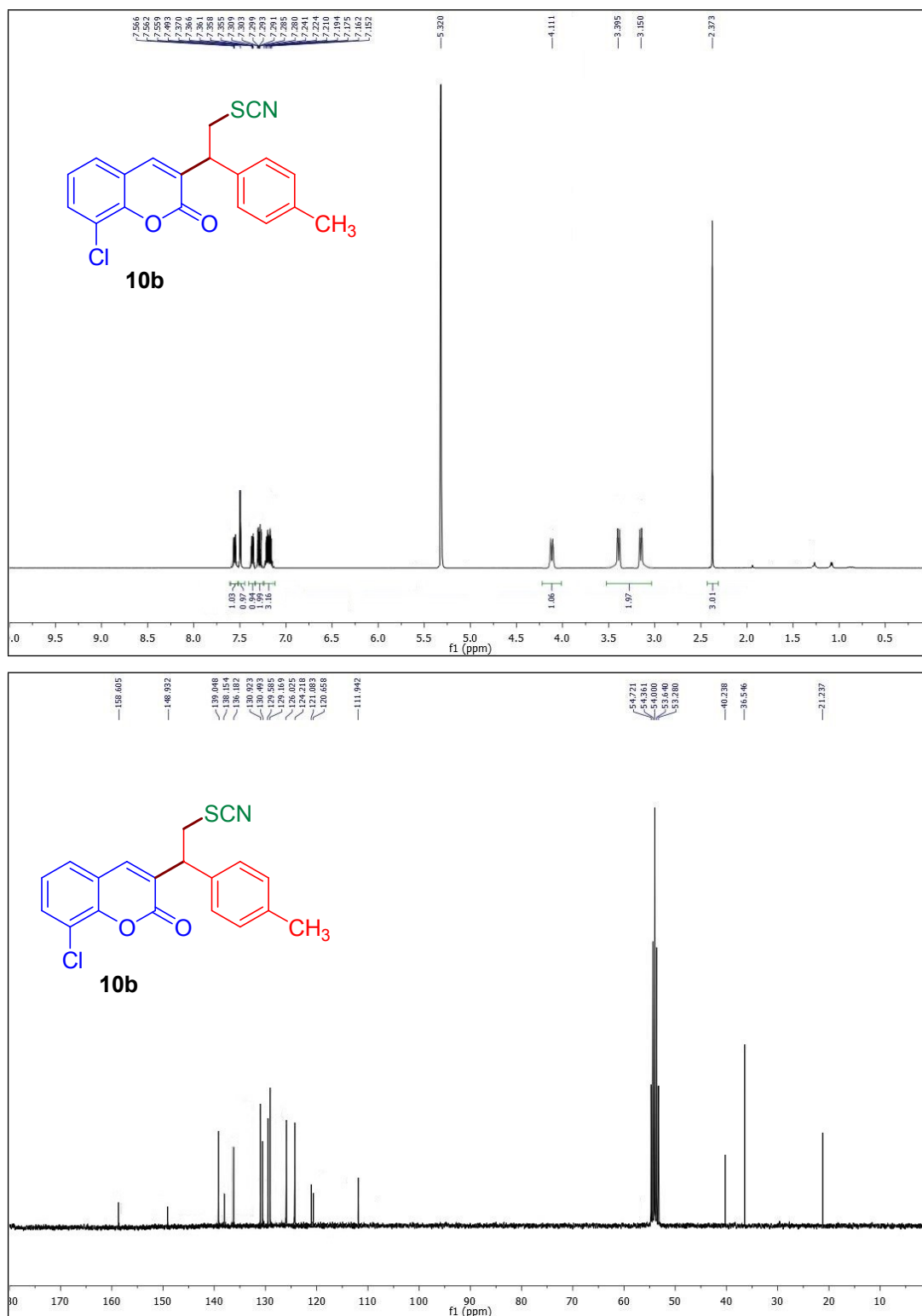


Figure S7. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **10b** in CD₂Cl₂.

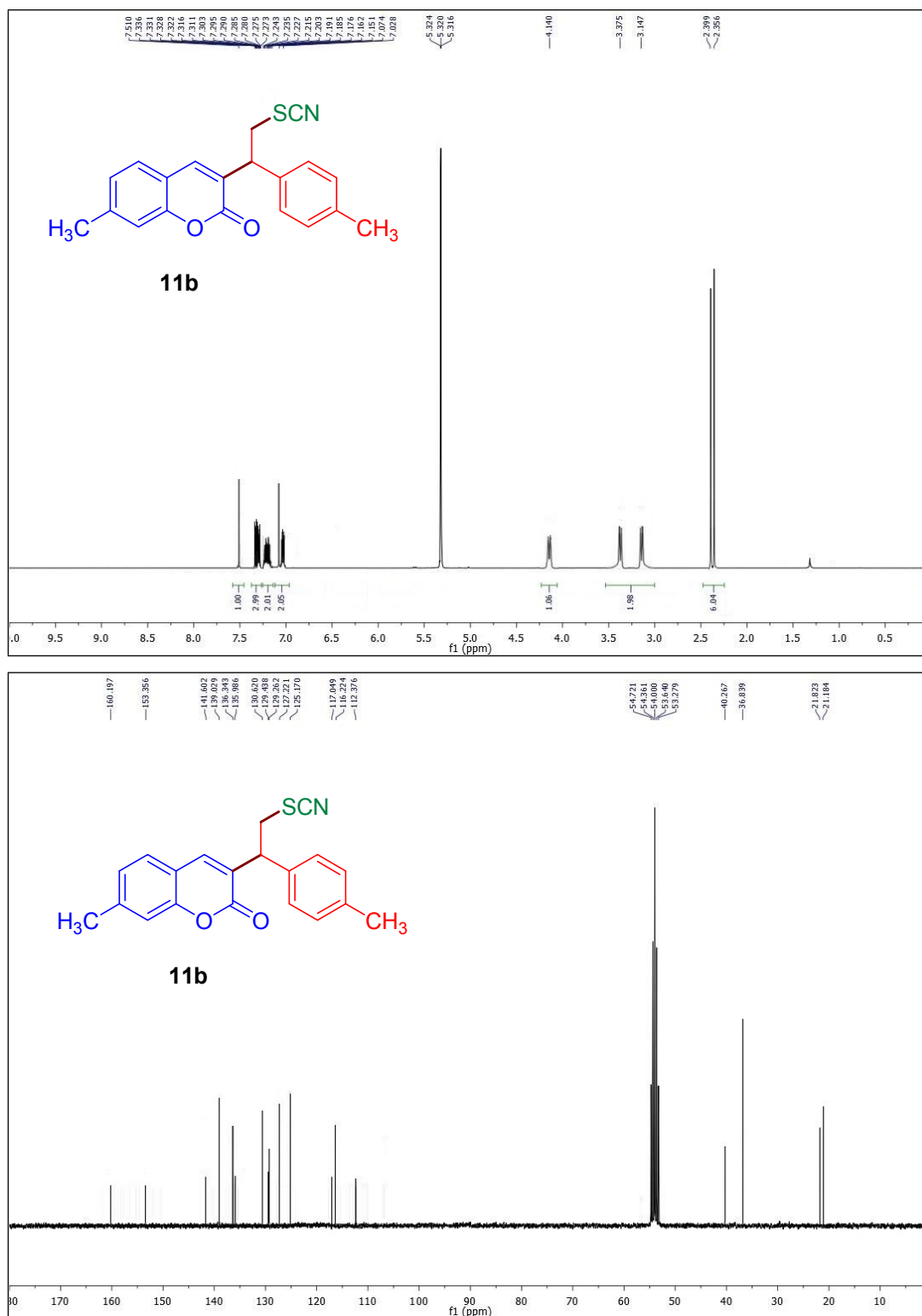


Figure S8. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **11b** in CD₂Cl₂.

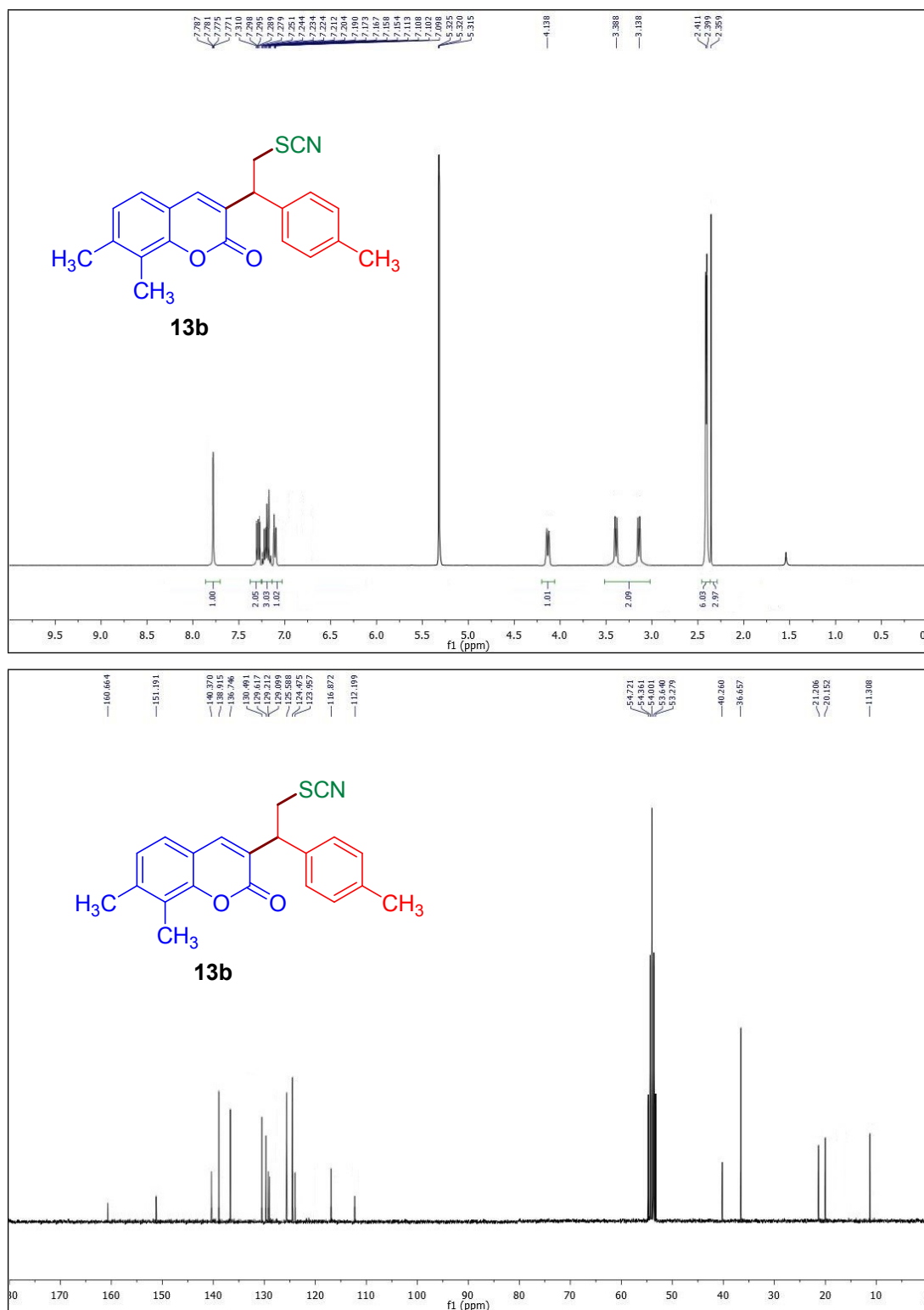


Figure S9. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **13b** in CD₂Cl₂.

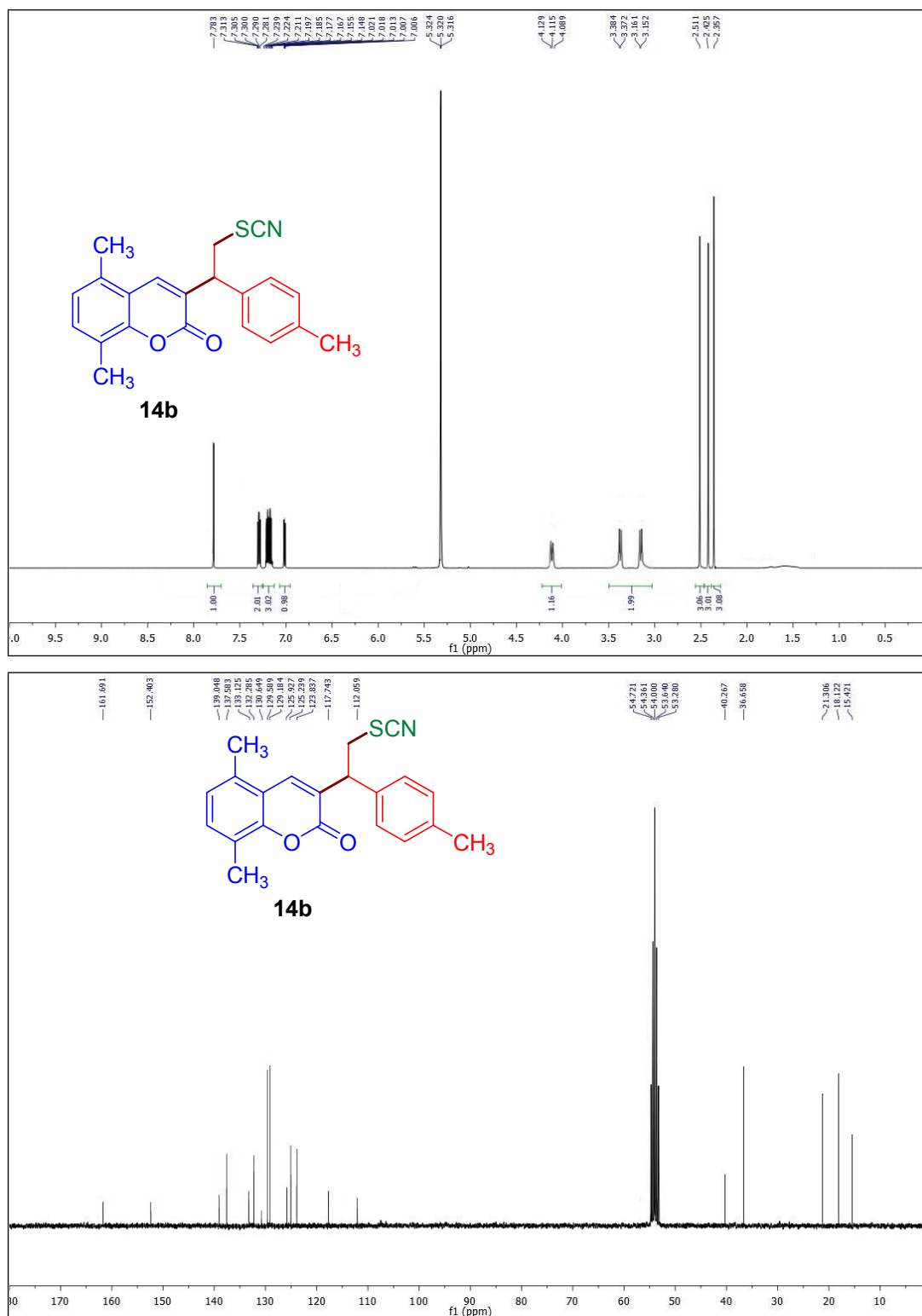


Figure S10. ^1H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **14b** in CD_2Cl_2 .

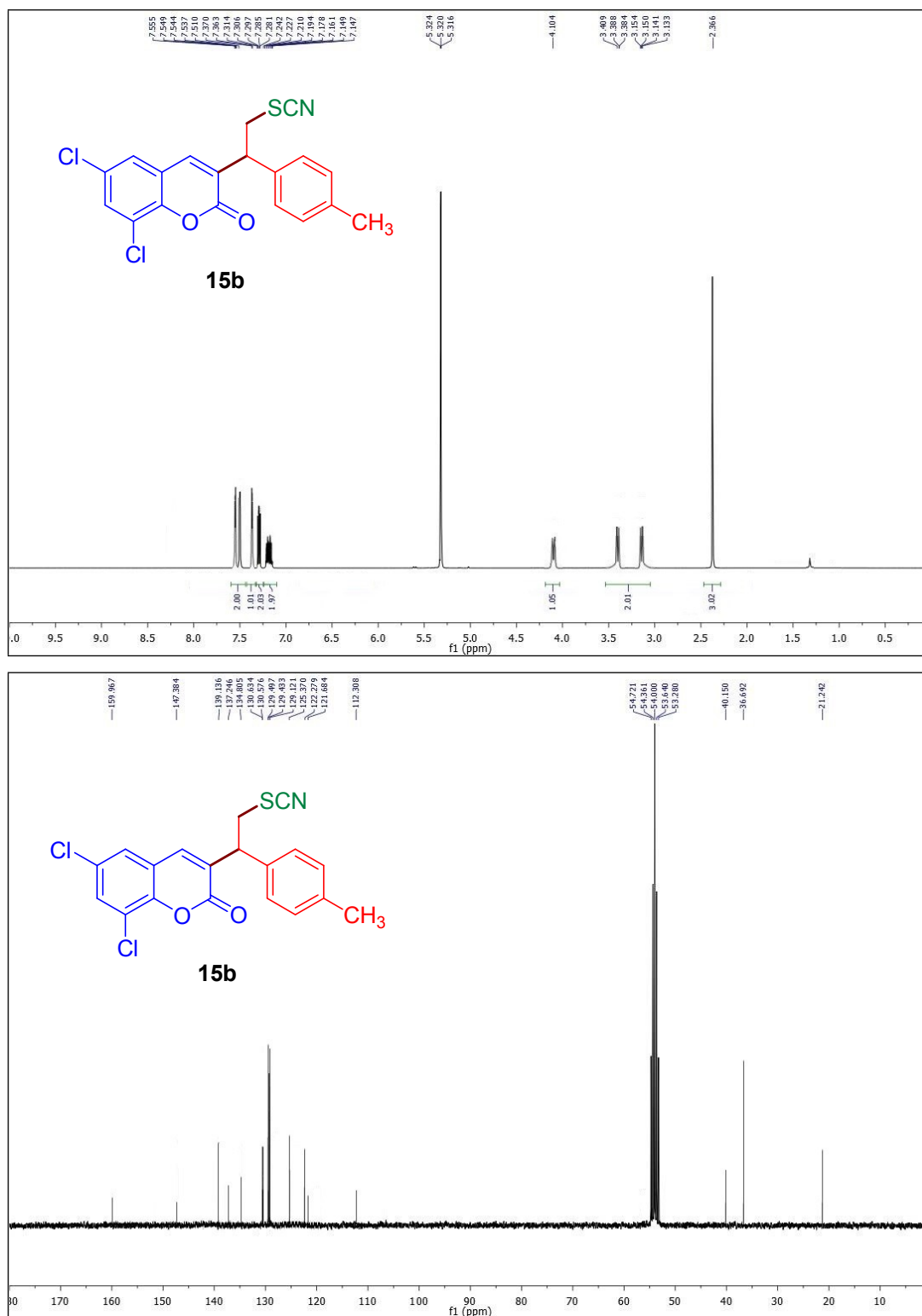


Figure S11. ^1H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **15b** in CD_2Cl_2 .

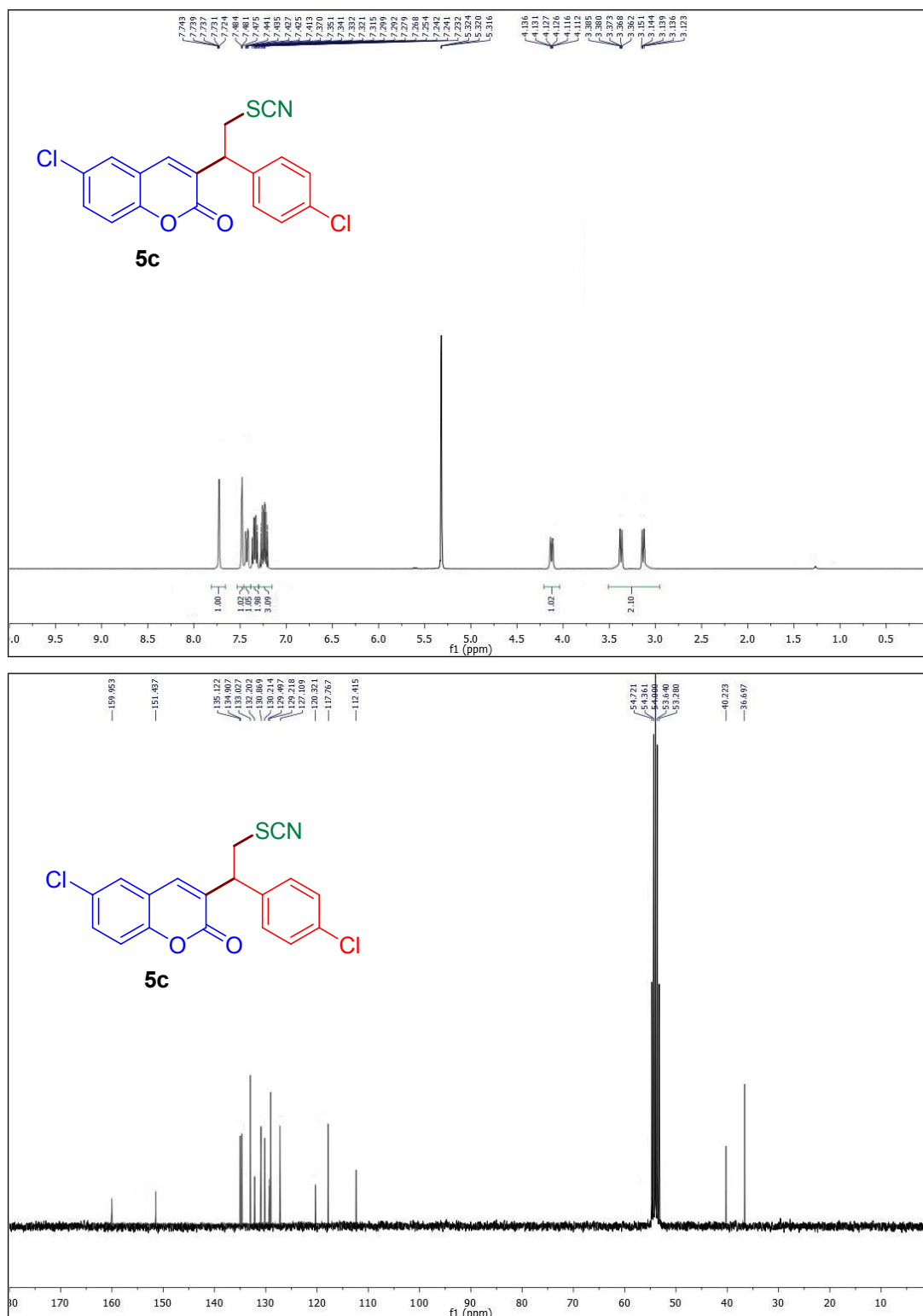


Figure S12. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **5c** in CD₂Cl₂.

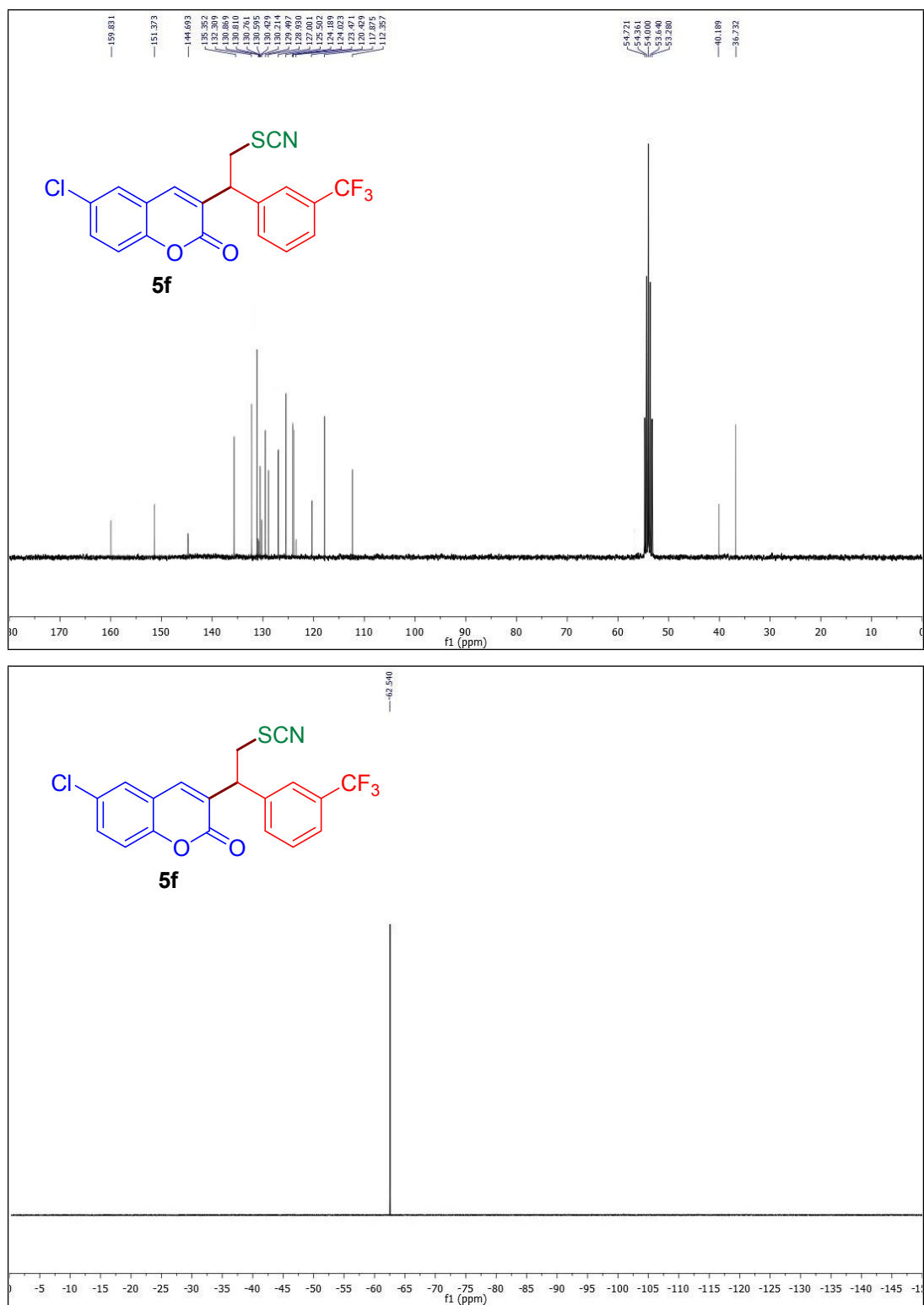


Figure S13. ^{13}C (top, 75 MHz) and ^{19}F (bottom, 282 MHz) NMR spectra of **5f** in CD_2Cl_2 .

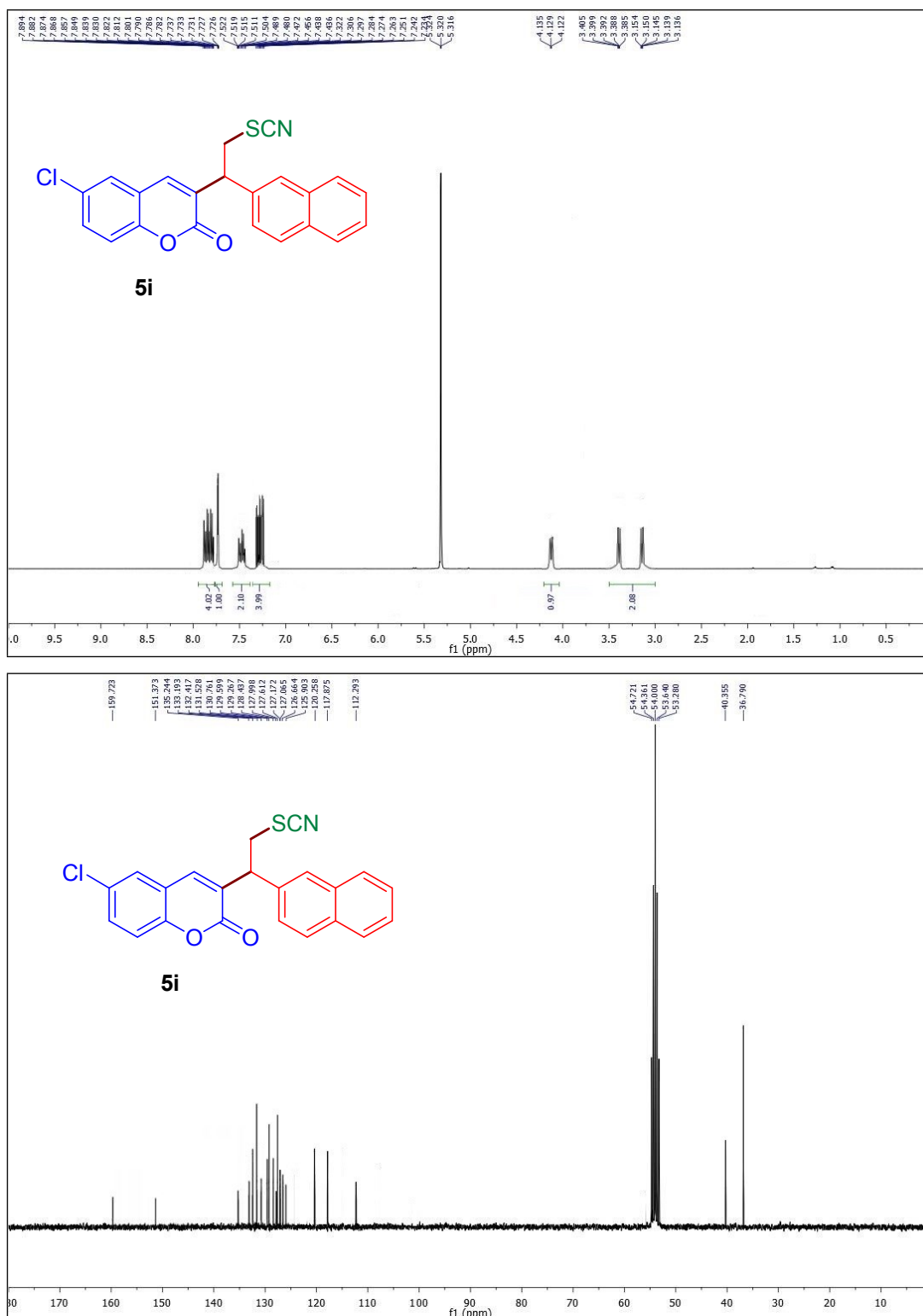


Figure S14. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **5i** in CD₂Cl₂.

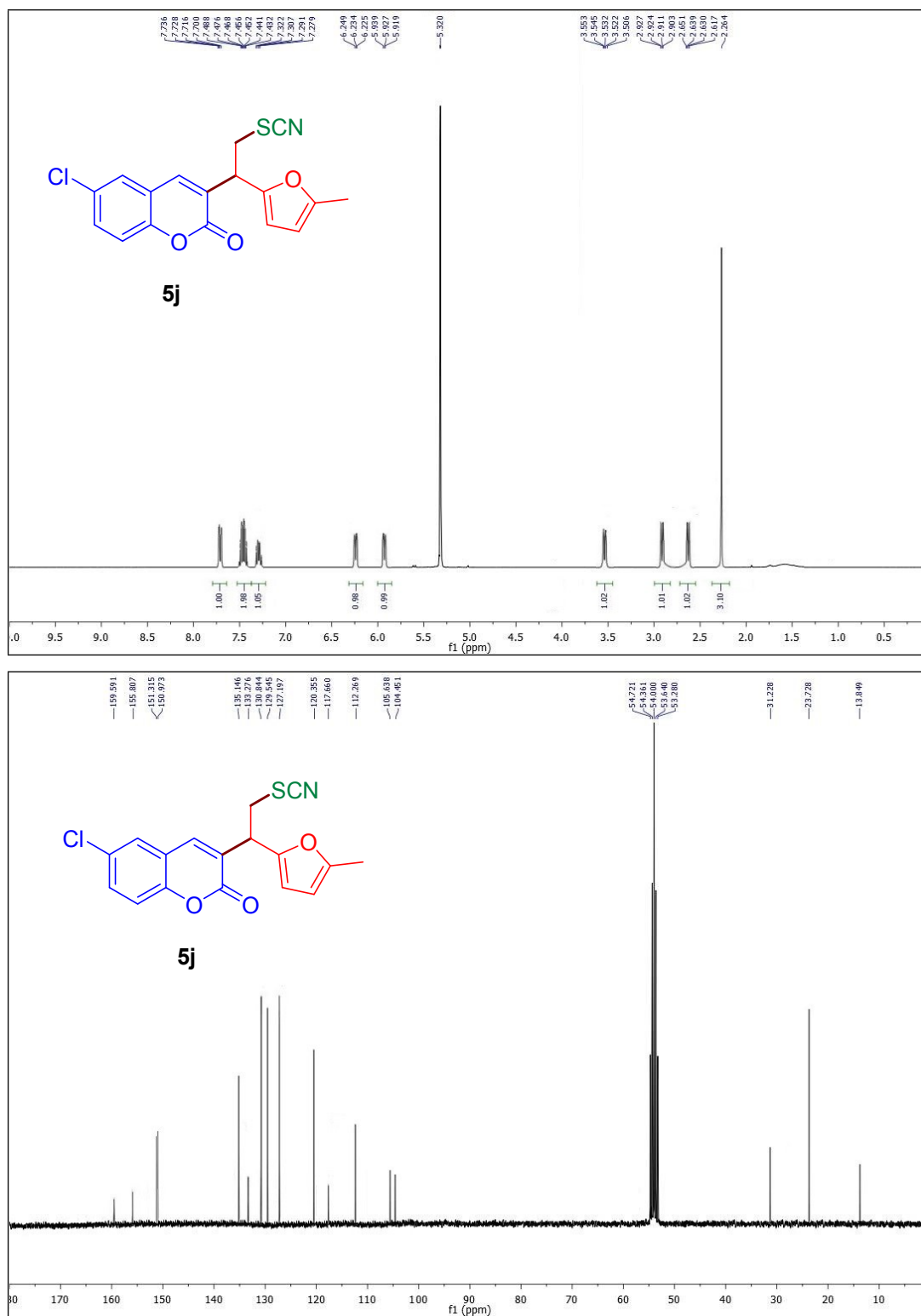


Figure S15. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **5j** in CD₂Cl₂.

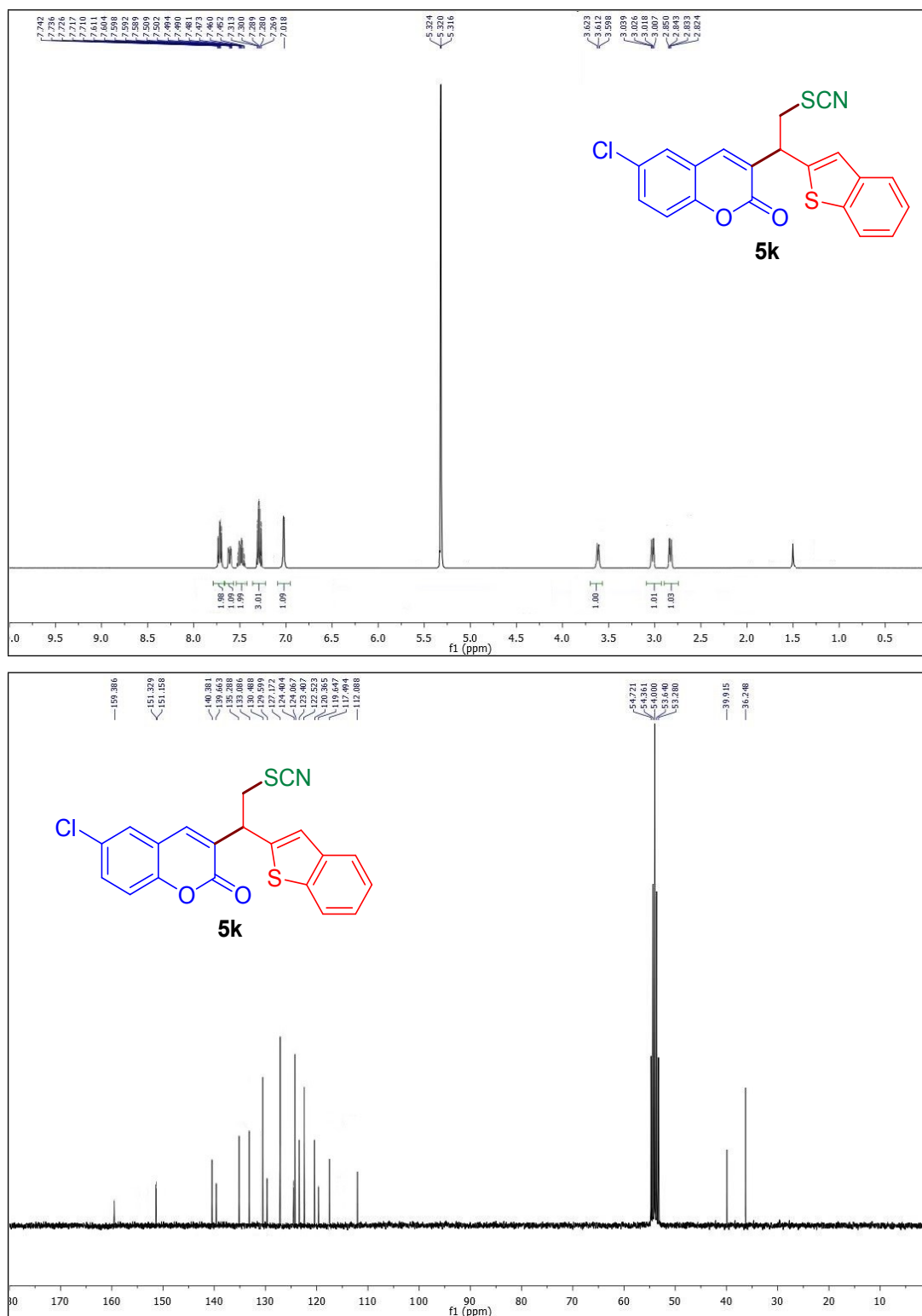


Figure S16. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **5k** in CD₂Cl₂.

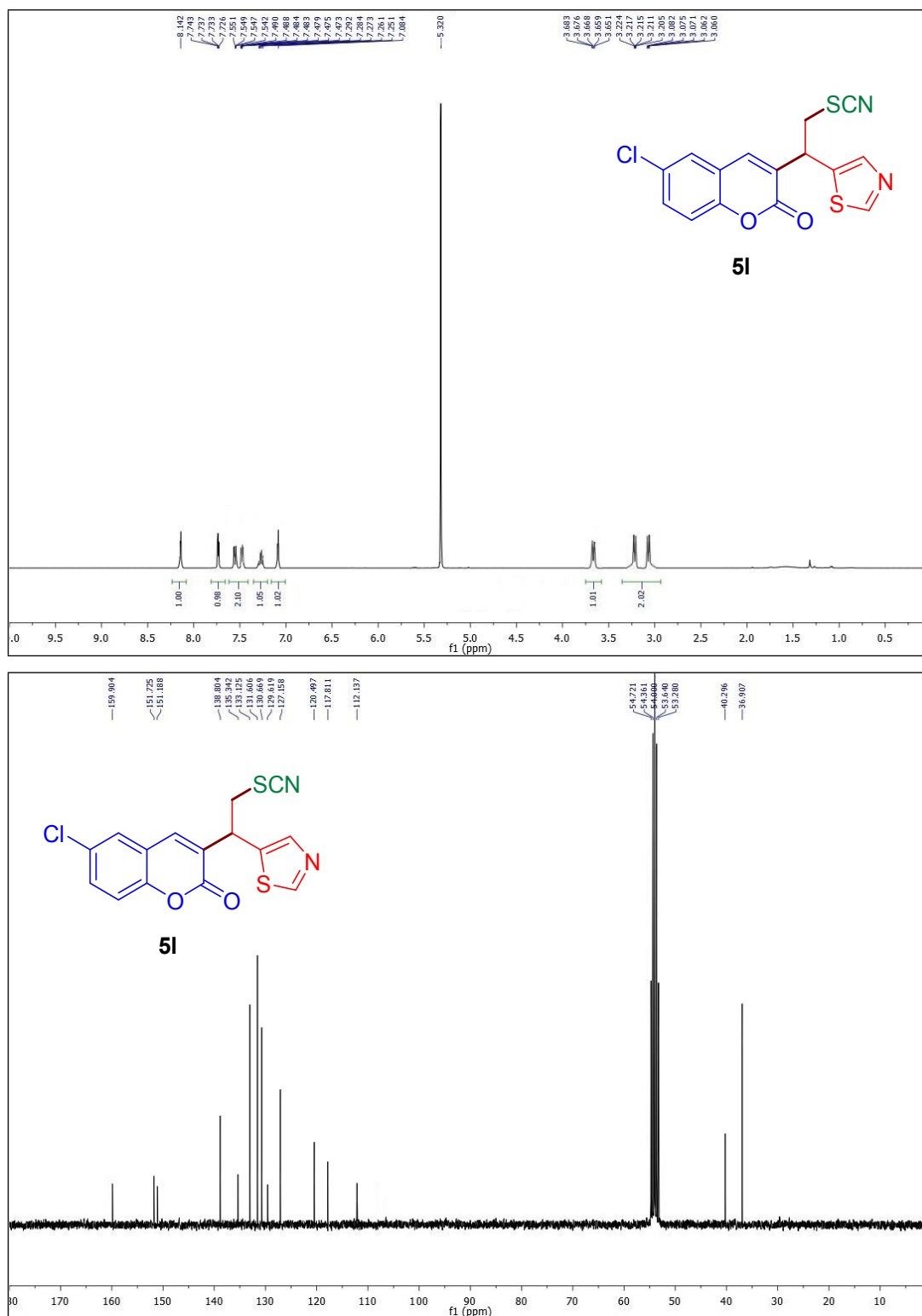


Figure S17. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **5I** in CD₂Cl₂.

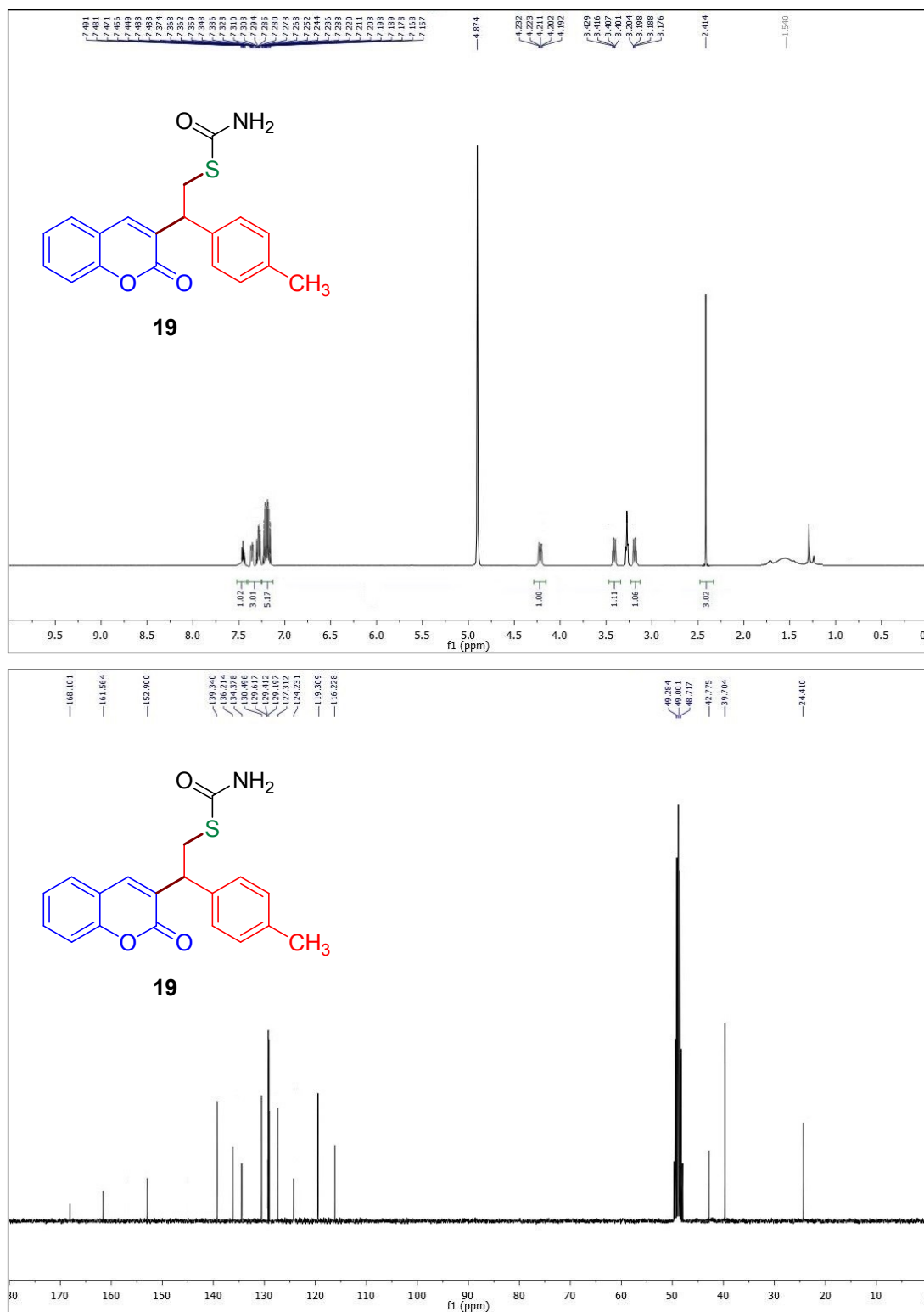


Figure S18. ^1H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **19** in CD_3OD .

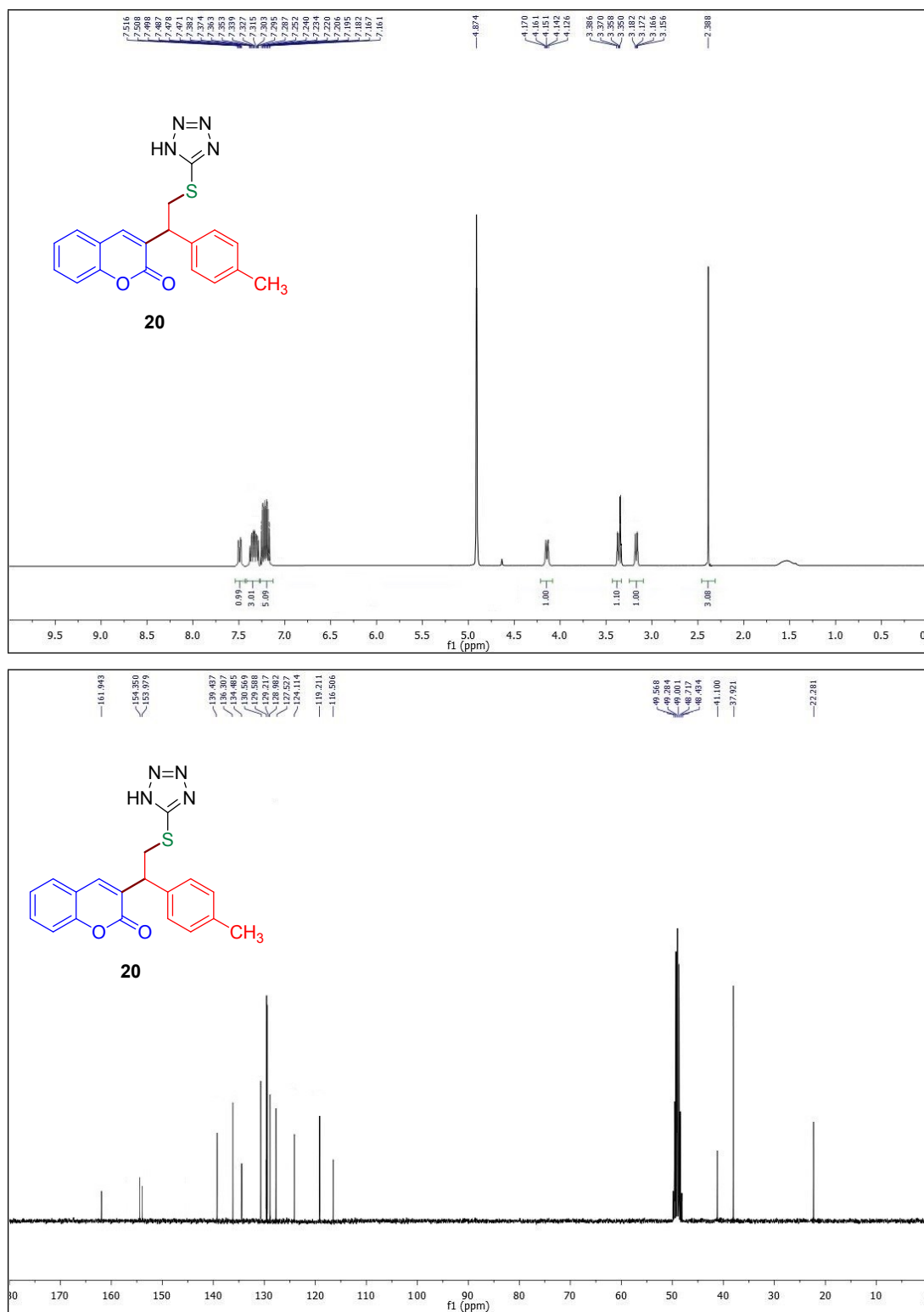


Figure S19. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **20** in CD₃OD.

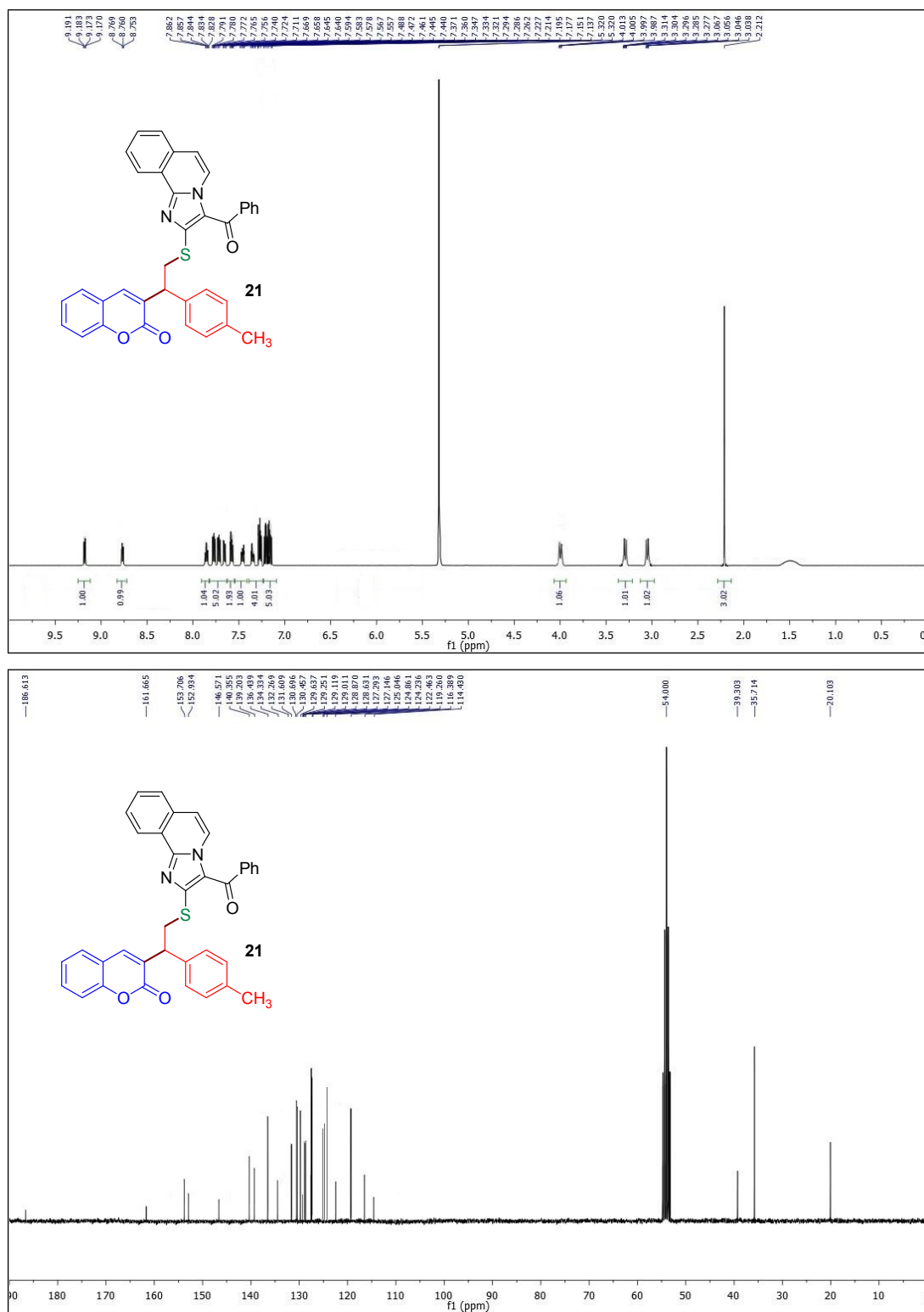


Figure S20. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **21** in CD₂Cl₂.

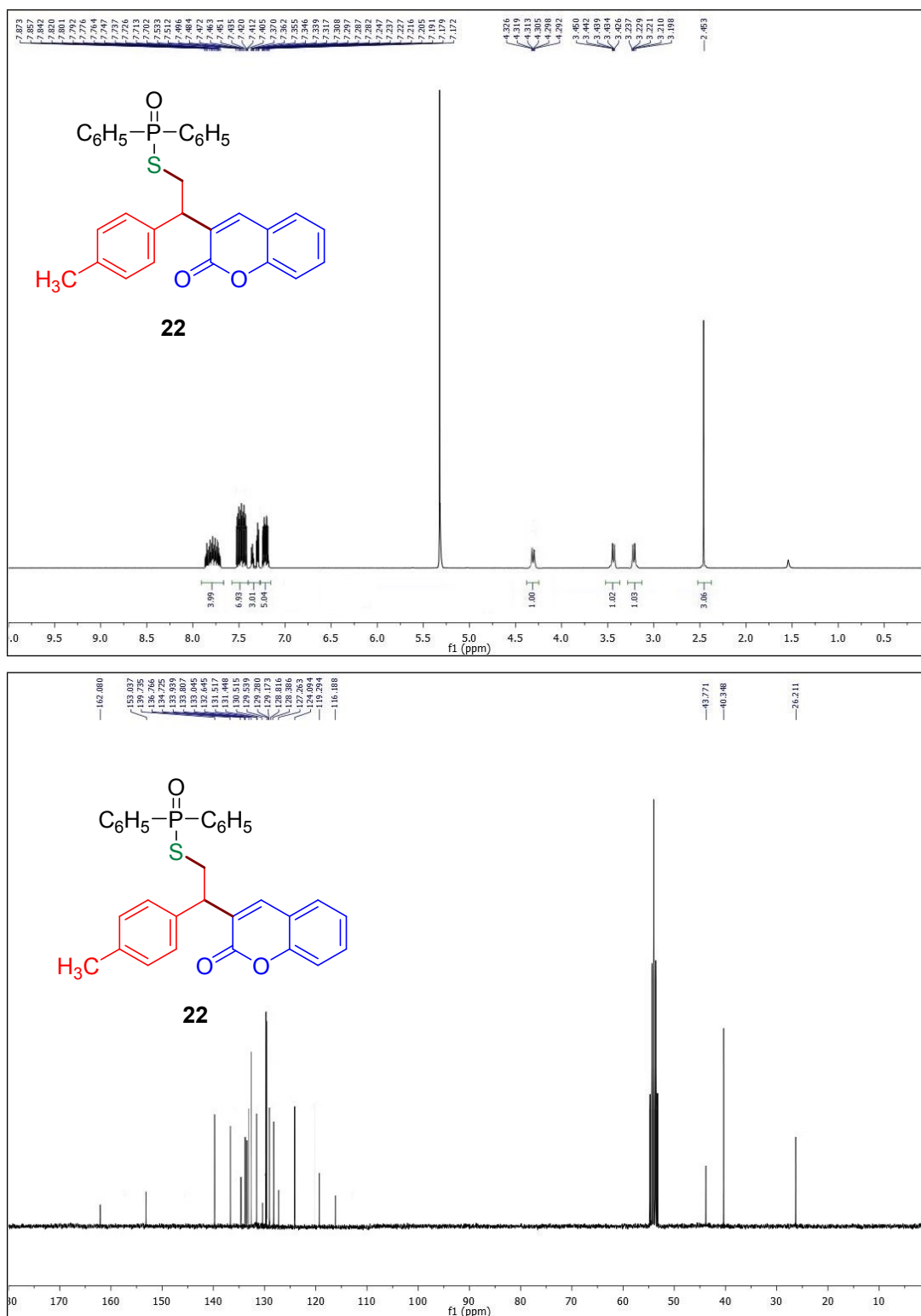


Figure S21. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **22** in CD₂Cl₂.

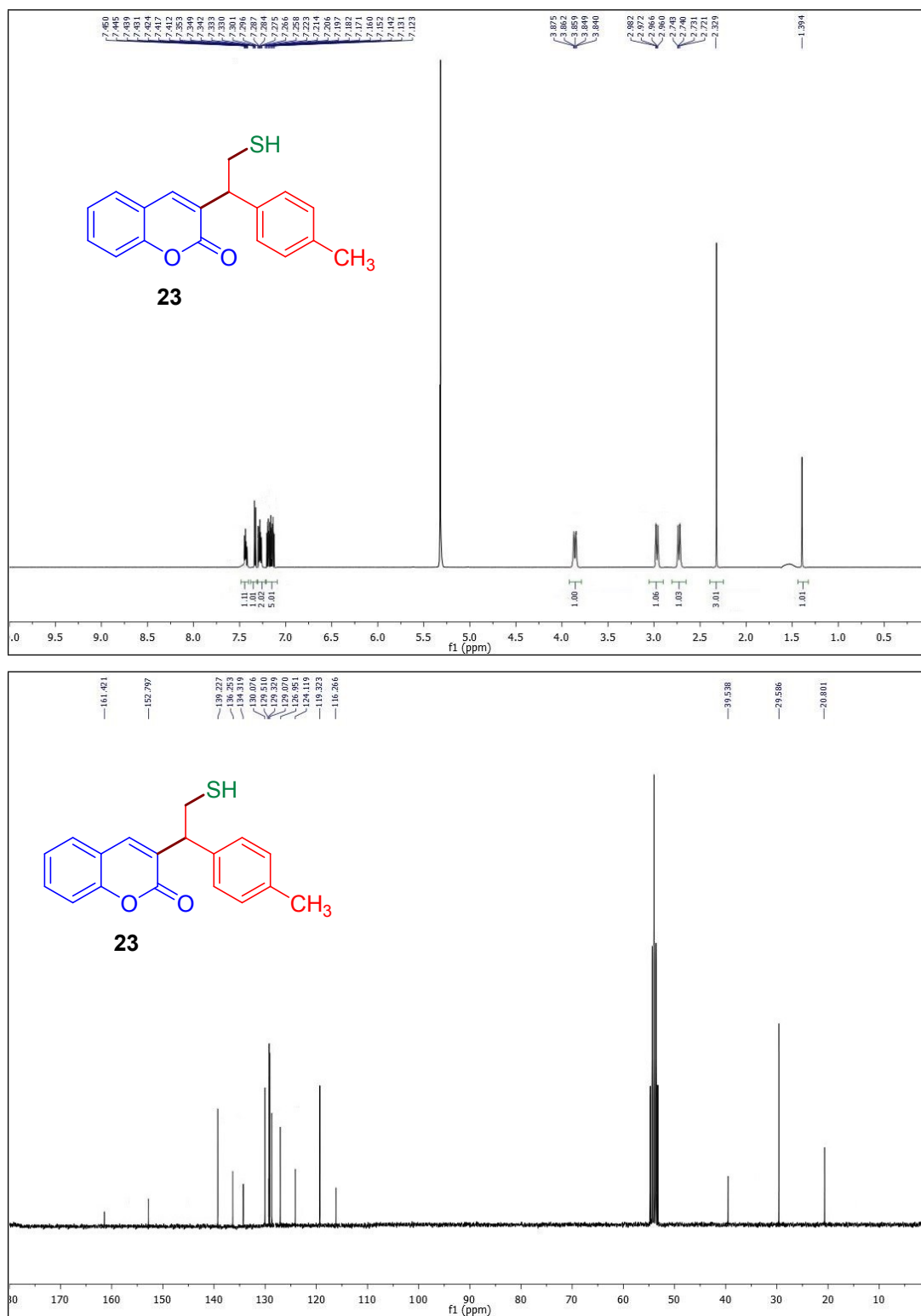


Figure S22. ¹H (top, 300 MHz) and ¹³C (bottom, 75 MHz) NMR spectra of **23** in CD₂Cl₂.

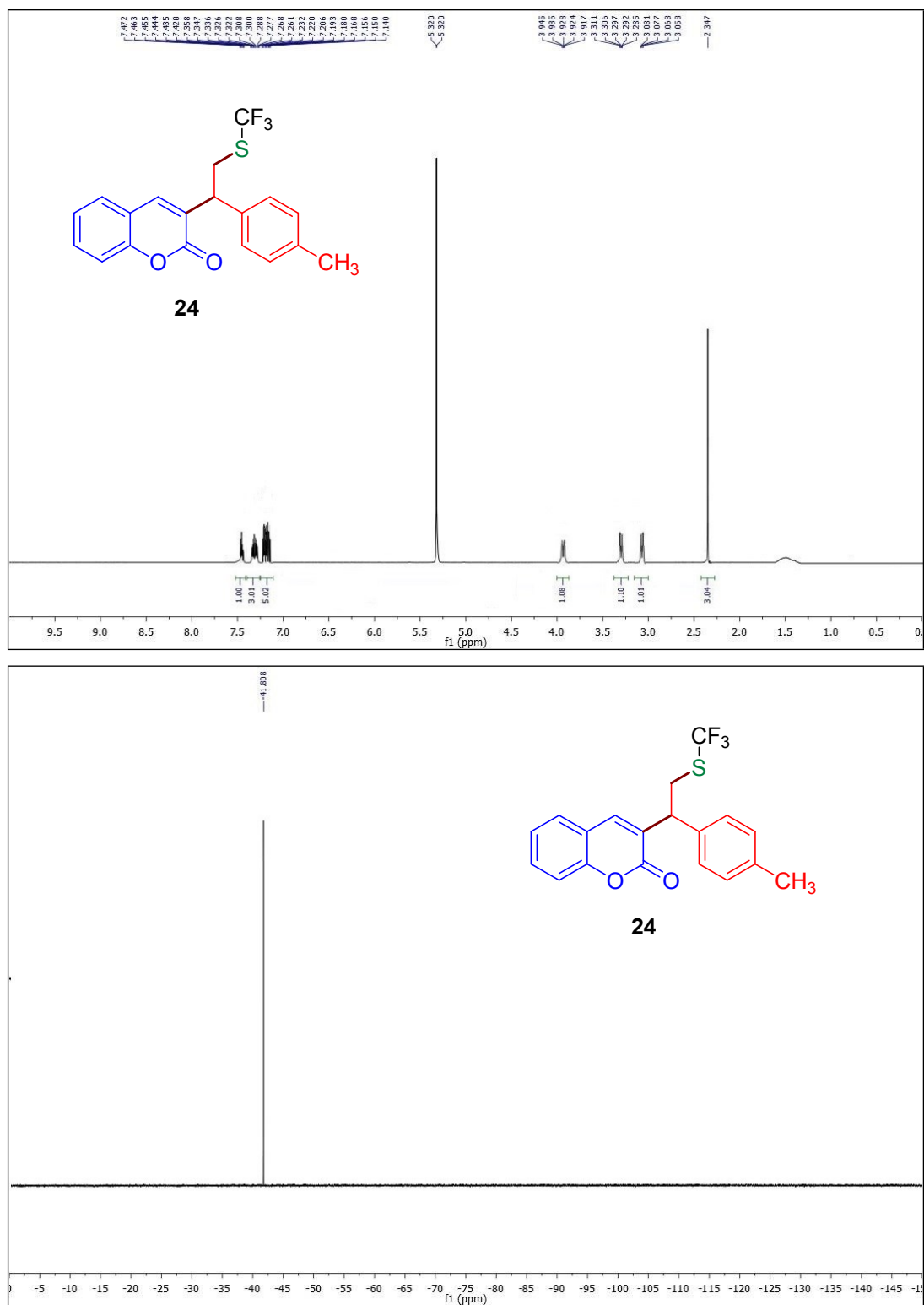


Figure S23. ^1H (top, 300 MHz) and ^{19}F (bottom, 282 MHz) NMR spectra of **24** in CD_2Cl_2 .