Electronic Supplementary Information

Persulfate-nitrogen doped graphene mixture as an oxidant for the synthesis of 3-nitro-4-aryl-2H-chromen-2-ones from aryl alkynoate esters and nitrite

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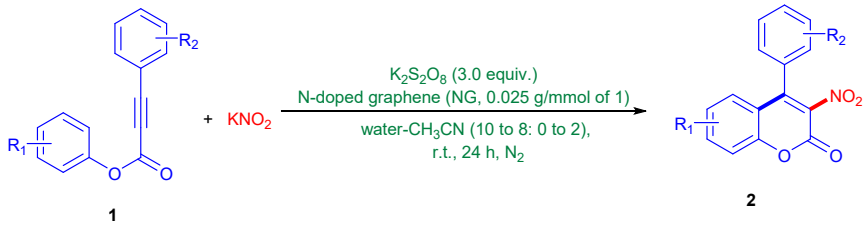
Experimental Section

General Aspects

Unless otherwise noted, all the reactions were performed at 25 °C. All chemicals, reagents and precursors were purchased from commercial sources with the best quality and they were used without further purification. All carbonaceous materials were purchased from commercial sources with the best quality and dried at 60 °C under vacuum before use. All solvents were dried over 3 Å/4 Å a molecular sieve, distilled and de-aerated prior to use.[1] Double-distilled water was used for all purposes. All reactions were carried out in a nitrogen gas atmosphere. 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 at 356 nm lights. All NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer in DCM-d_2 as a solvent. 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 designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets 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. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer.

General procedure for the synthesis of 3-nitro-4-aryl-2H-chromen-2-ones from aryl alkynoate esters and nitrite



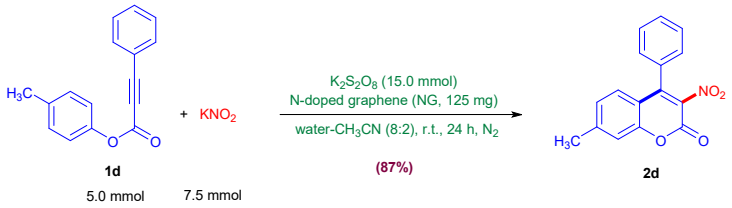
Aryl alkynoate ester (**1**, 1.0 mmol, 1.0 equiv.), KNO_2 (128 mg, 1.5 mmol, 1.5 equiv.), $K_2S_2O_8$ (811 mg, 3.0 mmol, 3.0 equiv.) and N-doped graphene (NG, 0.025 g/ mmol of aryl alkynoate ester) were charged to an oven-dried Schlenk-tube equipped with a magnetic stir bar. To this mixture, H_2O-CH_3CN (8:2, v/v mL, 18 mL) was added. The tube was then sealed with a glass stopper, and a N_2-gas inlet/outlet was given by a side-neck. The resulting mixture was vigorously

stirred at 25 °C in a nitrogen gas environment. After the completion (24 h, as indicated by disappearance of precursor as determined by TLC), the organic matter (product) was completely precipitated by adding NaCl (3.0 g) followed by cooling to 5 °C. Filtration was used to isolate the precipitates, which were then washed with excess of water to remove any water-soluble contaminants. In many cases, the ultimate purification was accomplished by recrystallization at low temperatures (vide infra). Spectroscopic examination and a comparison with authentic sample spectra were used to establish the product's identity and purity.

General procedure for the isolation of pure products (2) by recrystallization

The acquired product precipitates were placed fully into a glass beaker and then dissolved using a minimum amount of ethanol at room temperature. The resulting suspension was filtered to eliminate all carbonaceous materials, and the clear yellow filtrate solution was diluted with water and stored overnight at 8-10 °C. After that, the pure product was collected by filtration (using a G5-crucible) and dried under vacuum for overnight.

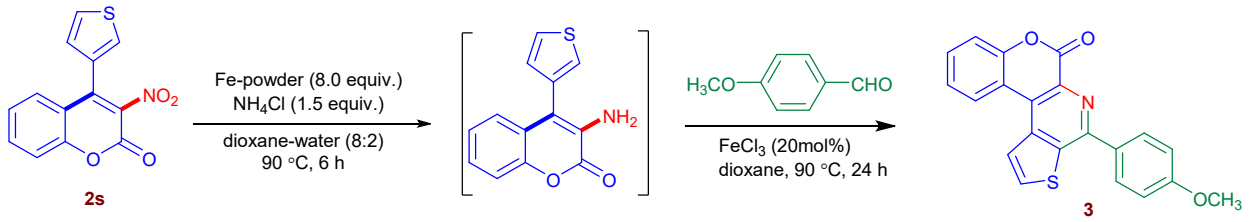
Procedure for the large-scale synthesis of 2d



1d 5.0 mmol 7.5 mmol **2d**

An oven-dried round bottom flask equipped with a magnetic stir bar was charged with *p*-tolyl 3-phenylpropiolate (**1d**, 1.18 g, 5.0 mmol, 1.0 equiv.), KNO_2 (638 mg, 7.5 mmol, 1.5 equiv.), $K_2S_2O_8$ (4.05 g, 15.0 mmol, 3.0 equiv.) and N-doped graphene (NG, 125 mg). To this mixture, H_2O-CH_3CN (8:2, v/v mL, 85 mL) was added. The tube was then sealed with a glass stopper, and a N_2-gas inlet/outlet was given by a side-neck. The resulting mixture was vigorously stirred at 25 °C in a nitrogen gas environment. After 24 h, the organic matter (product) was completely precipitated by adding solid NaCl followed by cooling to 5 °C. The precipitates were isolated by filtration, and then rinsed with excess water to eliminate any water-soluble contaminants. Following that, the pure product **2d** as a yellow solid in 87% (1.25 g) yield was obtained by recrystallization using the general recrystallization procedure described above.

Procedure for synthesis of compound 3 from 3-nitro-4-(thiophen-3-yl)-2H-chromen-2-one (2s) a representative of 3-nitrocoumarins



2s 3

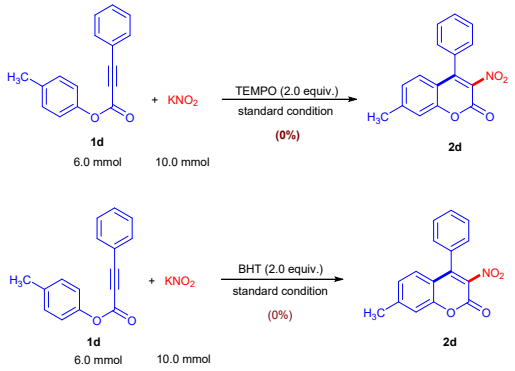
To an oven dried Schlenk-tube charged with a magnetic stirring bar, 3-nitro-4-(thiophen-3-yl)-2H-chromen-2-one (**2s**, 137 mg, 0.5 mmol, 1.0 equiv) was taken and dissolved in dioxane-H_2O (8:2, v/v mL, 10 mL) mixture. Fe powder (224 mg, 4.0 mmol, 8.0 equiv) and NH_4Cl (40 mg, 0.75 mmol, 1.5 equiv) were then added to it, and the mixture was stirred at 90 °C. After 6 h, the reaction mixture was cooled to room temperature and volatiles were totally evaporated to dryness under reduced pressure and then vacuum dried. As such, the crude reaction mixture was treated with 4-anisaldehyde (102 mg, 91 µl, 0.75 mmol, 1.5 equiv) in the presence of $FeCl_3$ (16 mg, 20 mol%) as a catalyst and dioxane (10 mL) as a solvent. The resulting solution was then stirred for 24 h at 90 °C in a nitrogen gas atmosphere. Afterwards, the volatiles were evaporated under reduced pressure and then admixed with aqueous NaCl solution (20 mL). The organic matters are extracted with ethyl acetate, dried over Na_2SO_4 and evaporated under reduced pressure to yield a pale-yellow gummy-solid, which was purified by a column chromatography using a mixture of ethyl acetate and hexane as eluent to provide the expected product **3** as a pale-yellow solid in 66% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz)[2]: δ 8.54 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 5.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 5.6 Hz, 1H), 7.47-7.61 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 156.8, 155.1, 150.2, 146.3, 135.9, 135.1, 129.7, 129.0, 126.2, 125.8, 125.6, 121.3, 119.9, 119.6, 113.4, 113.1, 109.5, 50.8.

Procedure for NG isolation and recycle

An oven-dried round bottom flask equipped with a magnetic stir bar was charged with *p*-tolyl 3-phenylpropiolate (**1d**, 1.18 g, 5.0 mmol, 1.0 equiv.), KNO_2 (638 mg, 7.5 mmol, 1.5 equiv.), $K_2S_2O_8$ (4.05 g, 15.0 mmol, 3.0 equiv.) and N-doped graphene (NG, 125 mg). To this mixture, H_2O-CH_3CN (8:2, v/v mL, 85 mL) was added. The tube was then sealed with a glass stopper, and a N_2-gas inlet/outlet was given by a side-neck. The resulting mixture was vigorously stirred

at 25 °C in a nitrogen gas environment. After 24 h, the organic matter (product) was completely precipitated by adding solid NaCl followed by cooling to 5 °C. The precipitates were isolated by filtration, and then rinsed with excess water to eliminate any water-soluble contaminants. The acquired precipitates were placed fully into a glass beaker and then dissolved using a minimum amount of ethanol at room temperature. The insoluble NG was easily recovered by a simple filtration, washed with excess ethanol and dried under vacuum. Afterwards, the recovered NG was employed for **2d** synthesis again. The process was repeated up to four times.

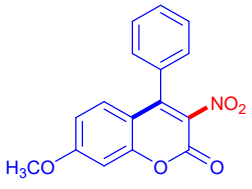
Procedure for control experiments



TEMPO (2 equiv., 2,2,6,6-tetramethyl-1-piperidinyloxy) was added to the standard reaction conditions. Resultant mixture was stirred under nitrogen gas atmosphere at 25 °C for 24 h. Afterwards, TLC and NMR measurements were performed on the reaction mixture, which revealed that there was no product **2d**.

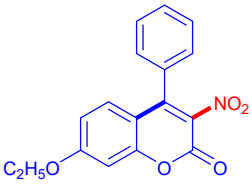
BHT (2 equiv. butyl-hydroxytoluene) was added to the standard reaction conditions. Resultant mixture was stirred under nitrogen gas atmosphere at 25 °C for 24 h. Following that, TLC and NMR tests were performed on the reaction mixture, which revealed that there was no product **2d**.

Experimental characterization data for products



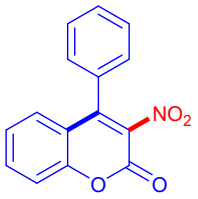
2a

7-Methoxy-3-nitro-4-phenyl-2H-chromen-2-one (2a)[3]: Synthesized from **1a** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 50% aqueous ethanol solution. Obtained 265 mg, 89% Yield. Yellow solid. R_f = 0.2 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3316, 3122, 3016, 1738, 1617, 1541, 1463, 1020, 765. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.53-7.50 (m, 3H), 7.38-7.34 (m, 2H), 7.17 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 2.2 Hz, 1H), 6.87 (dd, J = 8.6, 2.2 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 164.7, 155.2, 154.1, 148.0, 134.6, 130.8, 130.3, 129.5, 129.3, 128.1, 114.2, 111.2, 101.3, 56.4. HRMS (ESI) calcd for $C_{16}H_{11}NO_5$ $[M+H]^+$ 298.0715, found 298.0721.



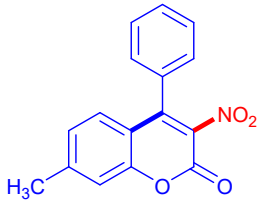
2b

7-Ethoxy-3-nitro-4-phenyl-2H-chromen-2-one (2b)[3]: Synthesized from **1b** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 50% aqueous ethanol solution. Obtained 290 mg, 93% Yield. Yellow solid. R_f = 0.2 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3291, 2926, 2856, 1741, 1611, 1541, 1423. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58-7.51 (m, 3H), 7.36-7.33 (m, 2H), 7.18 (d, J = 9.0 Hz, 1H), 6.90 (d, J = 2.4 Hz, 1H), 6.85 (dd, J = 8.6, 2.4 Hz, 1H), 4.13 (q, J = 7.4 Hz, 2H), 1.49 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 164.5, 155.1, 154.1, 148.2, 134.4, 130.8, 130.4, 129.6, 129.3, 128.1, 114.8, 110.9, 101.5, 64.7, 14.5. HRMS (ESI) calcd for $C_{17}H_{13}NO_5$ $[M+H]^+$ 312.0872, found 312.0879.



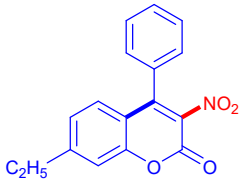
2c

3-Nitro-4-phenyl-2H-chromen-2-one (2c)[4]: Synthesized from **1c** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 244 mg, 91% Yield. Yellow solid. R_f = 0.4 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3045, 2932, 2854, 1742, 1604, 1541, 1421, 763. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.71-7.68 (m, 1H), 7.55-7.47 (m, 4H), 7.39-7.31 (m, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.5, 153.1, 147.2, 136.9, 134.2, 130.9, 129.4, 128.9, 128.2, 125.7, 118.1, 117.5, 115.3. HRMS (ESI) calcd for $C_{15}H_9NO_4$ $[M+H]^+$ 268.0610, found 268.0617.



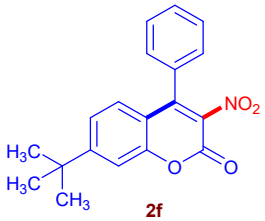
2d

7-Methyl-3-nitro-4-phenyl-2H-chromen-2-one (2d)[3]: Synthesized from **1d** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 249 mg, 88% Yield. Yellow solid. R_f = 0.3 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3064, 3035, 2997, 1736, 1617, 1541, 1462, 744. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58-7.53 (m, 3H), 7.39-7.36 (m, 2H), 7.29 (s, 1H), 7.18 (d, J = 8.2 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.7, 153.2, 147.4, 146.2, 136.3, 130.8, 129.4, 129.2, 129.0, 128.1, 126.9, 117.8, 115.5, 22.1. HRMS (ESI) calcd for $C_{16}H_{11}NO_4$ $[M+H]^+$ 282.0766, found 282.0764.



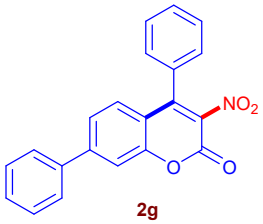
2e

7-Ethyl-3-nitro-4-phenyl-2H-chromen-2-one (2e)[3]: Synthesized from **1e** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 258 mg, 87% Yield. Yellow solid. R_f = 0.3 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3053, 2929, 2854, 1737, 1613, 1541, 1422, 846, 761. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58-7.52 (m, 3H), 7.39-7.35 (m, 2H), 7.31 (d, J = 1.0 Hz, 1H), 7.22 (d, J = 8.2 Hz, 1H), 7.17-7.14 (m, 1H), 2.78 (q, J = 7.8 Hz, 2H), 1.30 (t, J = 7.8 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.8, 153.2, 152.4, 147.4, 136.2, 130.8, 129.4, 129.2, 129.2, 128.1, 125.9, 116.4, 115.6, 29.2, 15.2. HRMS (ESI) calcd for $C_{17}H_{13}NO_4$ $[M+H]^+$ 296.0923, found 296.0929.



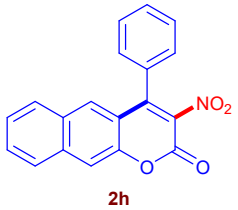
2f

7-(*tert*-butyl)-3-nitro-4-phenyl-2H-chromen-2-one (2f)[3]: Synthesized from **1f** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 289 mg, 89% Yield. Yellow solid. R_f = 0.3 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3052, 2930, 2852, 1736, 1635, 1542, 1456, 842, 757. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.55-7.50 (m, 3H), 7.46 (d, J = 1.8 Hz, 1H), 7.38-7.32 (m, 3H), 7.21 (d, J = 8.2 H, 1H), 1.37 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.3, 153.8, 153.2, 147.3, 136.1, 130.8, 129.4, 129.2, 128.8, 128.1, 123.4, 115.3, 114.5, 35.6, 31.1. HRMS (ESI) calcd for $C_{19}H_{17}NO_4$ $[M+H]^+$ 324.1236, found 324.1241.



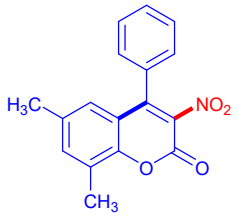
2g

3-Nitro-4,7-diphenyl-2H-chromen-2-one (2g)[3]: Synthesized from **1g** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 269 mg, 78% Yield. Yellow solid. R_f = 0.23 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) ν 3122, 3045, 2993, 2932, 2853, 1738, 1617, 1544, 1422, 872, 762. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.70 (s, 1H), 7.65 (d, J = 7.0 Hz, 2H), 7.59-7.46 (m, 7H), 7.41 (d, J = 4.6 Hz, 2H), 7.35 (d, J = 8.0 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.8, 153.5, 147.8, 147.3, 138.4, 130.9, 129.8 129.5, 129.4, 129.3, 129.2, 129.1, 128.1, 127.6, 124.5, 116.7, 115.4. HRMS (ESI) calcd for $C_{21}H_{13}NO_4$ $[M+H]^+$ 344.0923, found 344.0919.



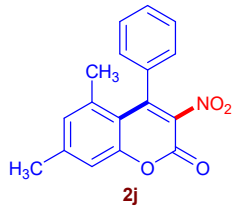
2h

3-Nitro-4-phenyl-2H-benzo[g]chromen-2-one (2h)[3]: Synthesized from **1h** according to the general procedure. The precipitate obtained was purified by following a general recrystallization procedure in 30% aqueous ethanol solution. Obtained 268 mg, 84% Yield. Yellow solid. R_f = 0.21 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) ν 3211, 3116, 3013, 2987, 2894, 1743, 1637, 1544, 1466, 851, 749. ^1H NMR (300 MHz, CD_2Cl_2) δ 8.61-8.56 (m, 1H), 7.91 (dd, J = 6.2, 2.4 Hz, 1H), 7.78-7.71 (m, 2H), 7.66 (d, J = 8.6 Hz, 1H), 7.60-7.57 (m, 3H), 7.45-7.41 (m, 2H), 7.22 (d, J = 8.6 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.4, 151.1, 148.5, 136.4, 135.8, 130.9, 130.4, 129.6, 129.4, 128.3, 128.1, 125.6, 123.2, 123.0, 122.9, 113.2. HRMS (ESI) calcd for $C_{19}H_{11}NO_4$ $[M+H]^+$ 318.0766, found 318.0772.



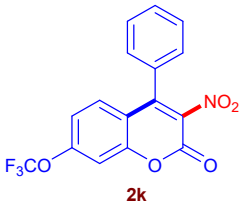
2i

6,8-Dimethyl-3-nitro-4-phenyl-2H-chromen-2-one (2i): Synthesized from **1i** according to the general procedure. However, instead of 24 h specified in the general synthetic procedure, the reaction was carried out for 48 hours. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 204 mg, 69% Yield. Yellow solid. R_f = 0.2 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3067, 3036, 2998, 1739, 1613, 1543, 1422. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.65-7.56 (m, 3H), 7.31 (dd, J = 7.6, 1.4 Hz, 2H), 7.26 (s, 1H), 6.68 (s, 1H), 2.49 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 160.7, 154.8, 149.5, 135.1, 133.8, 133.3, 129.8, 129.4, 127.8, 126.2, 125.3, 116.7, 115.6, 20.9, 17.6. HRMS (ESI) calcd for $C_{17}H_{13}NO_4$ $[M+H]^+$ 296.0923, found 296.0930.



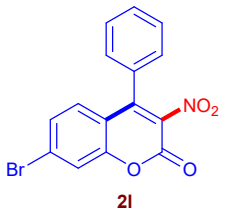
2j

5,7-Dimethyl-3-nitro-4-phenyl-2H-chromen-2-one (2j): Synthesized from **1j** according to the general procedure. However, instead of 24 h specified in the general synthetic procedure, the reaction was carried out for 48 hours. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 15 mg, 5% Yield. Yellow solid. R_f = 0.2 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3129, 3066, 3038, 2999, 1738, 1619, 1541, 1464, 921, 817, 744. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.57-7.54 (m, 3H), 7.32 (s, 1H), 7.24-7.21 (m, 2H), 6.68 (s, 1H), 2.47 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 166.1, 159.7, 150.5, 136.6, 134.4, 133.6, 129.3, 128.6, 128.2, 126.5, 126.3, 119.9, 112.6, 20.9, 15.5. HRMS (ESI) calcd for $C_{17}H_{13}NO_4$ $[M+H]^+$ 296.0923, found 296.0927.



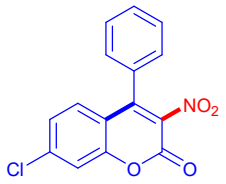
2k

3-Nitro-4-phenyl-7-(trifluoromethoxy)-2H-chromen-2-one (2k): Synthesized from **1k** according to the general procedure. The crude reaction mixture was purified by chromatography on a silica gel. Obtained 257 mg, 73% Yield. Yellow wax. R_f = 0.14 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3051, 2987, 1743, 1637, 1544, 1466, 1312, 1160, 1015. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.67-7.61 (m, 3H), 7.33-7.29 (m, 3H), 7.21 (d, J = 8.8 Hz, 1H), 7.13-7.10 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.7, 156.5, 154.3, 152.6, 132.7, 130.5, 130.3, 129.3, 127.8, 120.3 (q, J = 258 Hz), 118.2, 117.1, 109.1, 107.9. ^{19}F NMR (CD_2Cl_2) δ -58.9. HRMS (ESI) calcd for $C_{16}H_8NO_5F_3$ $[M+H]^+$ 352.0433, found 352.0439.



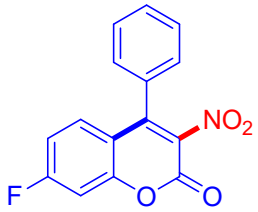
2l

7-Bromo-3-nitro-4-phenyl-2H-chromen-2-one (2l)[3]: Synthesized from **1l** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 30% aqueous ethanol solution. Obtained 297 mg, 86% Yield. Yellow solid. R_f = 0.4 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3066, 2914, 1748, 1616, 1595, 1547, 1456, 1015, 765. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.68 (s, 1H), 7.58-7.54 (m, 3H), 7.46-7.42 (m, 1H), 7.38 (d, J = 7.2 Hz, 2H), 7.17 (d, J = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.1, 152.9, 146.7, 136.6, 131.3, 130.2, 129.6, 129.3, 128.8, 128.5 128.1, 120.9, 117.2. HRMS (ESI) calcd for $C_{15}H_8BrNO_4$ $[M+H]^+$ 345.9715, found 345.9721.



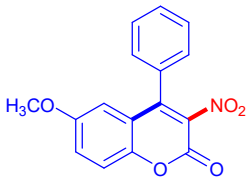
2m

7-Chloro-3-nitro-4-phenyl-2H-chromen-2-one (2m)[3]: Synthesized from **1m** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 224 mg, 74% Yield. Yellow solid. R_f = 0.4 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3069, 2922, 1742, 1639, 1541, 1463, 756. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.61-7.56 (m, 3H), 7.51 (d, J = 1.6 Hz, 1H), 7.38 (d, J = 7.2 Hz, 2H), 7.29 (dd, J = 8.4, 1.6 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.2, 153.0, 146.8, 140.7, 131.3, 130.2, 129.6, 128.6, 128.1, 126.5, 117.9, 116.6. HRMS (ESI) calcd for $C_{15}H_8ClNO_4$ $[M+H]^+$ 302.0220, found 302.0224.



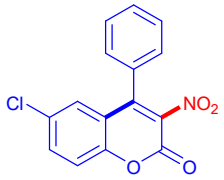
2n

7-Fluoro-3-nitro-4-phenyl-2H-chromen-2-one (2n)[3]: Synthesized from **1n** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 50% aqueous ethanol solution. Obtained 206 mg, 72% Yield. Yellow solid. R_f = 0.36 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3098, 2987, 2906, 1751, 1617, 1542, 1458, 816, 764. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.61-7.56 (m, 3H), 7.38 (d, J = 7.2 Hz, 2H), 7.33-7.28 (m, 1H), 7.20 (dd, J = 8.4, 2.2 Hz, 1H), 7.08-7.06 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 165.8 (d, J = 256.9 Hz), 154.2, 154.3, 153.1, 147.0, 131.4 (d, J = 11.2 Hz), 131.2, 129.6, 128.8, 128.1, 114.9 (d, J = 3.1 Hz), 114.2 (d, J = 23.2 Hz), 105.4 (d, J = 25.6 Hz). ^{19}F NMR (CD_2Cl_2) δ -113.6. HRMS (ESI) calcd for $C_{15}H_8FNO_4$ $[M+H]^+$ 286.0516, found 286.0511.



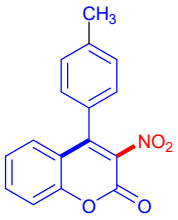
2o

6-Methoxy-3-nitro-4-phenyl-2H-chromen-2-one (2o)[3]: Synthesized from **1o** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 50% aqueous ethanol solution. Obtained 260 mg, 87% Yield. Yellow solid. R_f = 0.2 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3318, 3121, 3014, 1735, 1632, 1571, 1544, 1423, 756. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58-7.53 (m, 3H), 7.41-7.37 (m, 3H), 7.27-7.24 (m, 1H), 6.69 (d, J = 3.0 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.8, 153.5, 147.2, 146.9, 137.1, 131.0, 129.3, 129.0, 128.1, 121.6, 118.7, 118.5, 111.4, 56.2. HRMS (ESI) calcd for $C_{16}H_{11}NO_5$ $[M+H]^+$ 298.0715, found 298.0719.



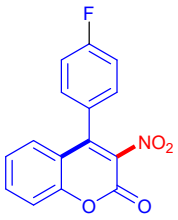
2p

6-Chloro-3-nitro-4-phenyl-2H-chromen-2-one (2p): Synthesized from **1p** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 251 mg, 83% Yield. Yellow solid. R_f = 0.4 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3107, 3052, 2927, 1746, 1623, 1547, 1424, 874, 756. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.78-7.73 (m, 2H), 7.59-7.55 (m, 3H), 7.38-7.34 (m, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.8, 151.7, 146.1, 137.2, 137.1, 131.4, 131.2, 129.7, 128.1, 128.0, 119.6, 119.3, 118.5. HRMS (ESI) calcd for $C_{15}H_8ClNO_4$ $[M+H]^+$ 302.0220, found 302.0227.



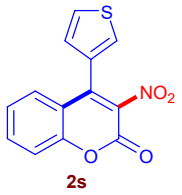
2q

3-Nitro-4-(*p*-tolyl)-2H-chromen-2-one (2q)[3]: Synthesized from **1q** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 40% aqueous ethanol solution. Obtained 260 mg, 92% Yield. Pale-yellow solid. R_f = 0.3 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 3116, 3021, 2988, 1742, 1638, 1546, 1467, 757. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.71-7.65 (m, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.37-7.32 (m, 4H), 7.30-7.27 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.6, 152.9, 147.3, 141.5, 136.6, 134.2, 130.1, 129.3, 128.1, 125.9, 125.5, 118.2, 117.4, 21.7. HRMS (ESI) calcd for $C_{16}H_{11}NO_4$ $[M+H]^+$ 282.0766, found 282.0762.



2r

4-(4-Fluorophenyl)-3-nitro-2H-chromen-2-one (2r)[3]: Synthesized from **1r** according to the general procedure. The precipitate obtained was purified by following the general recrystallization procedure in 50% aqueous ethanol solution. Obtained 232 mg, 81% Yield. Yellow solid. R_f = 0.3 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 2976, 2865, 1748, 1599, 1548, 1422, 749. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.73 (t, J = 7.4 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.40-7.32 (m, 3H), 7.29-7.24 (m, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 164.0 (d, J = 250.6 Hz), 153.2, 153.1, 146.2, 137.0, 134.6, 130.3 (d, J = 8.4 Hz), 129.1, 125.6, 124.7 (d, J = 3.4 Hz), 117.8, 117.6, 116.7 (d, J = 21.8 Hz). HRMS (ESI) calcd for $C_{15}H_8FNO_4$ $[M+H]^+$ 286.0516, found 286.0513.



2s

3-Nitro-4-(thiophen-3-yl)-2H-chromen-2-one (2s)[2]: Synthesized from **1s** according to the general procedure. The crude reaction mixture was purified by chromatography on a silica gel. Obtained 233 mg, 85% Yield. Yellow oil. R_f = 0.3 in 9:1 hexane-ethyl acetate mixture. IR (KBr, cm^{-1}) *v* 2974, 1742, 1606, 1545, 1424, 765. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.57-7.51 (m, 2H), 7.40-7.36 (m, 1H), 7.31-7.25 (m, 2H), 7.20-7.17 (m, 1H), 7.14-7.11 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.3, 152.4, 146.5, 133.2, 131.6, 129.1, 128.0, 127.6, 127.3, 124.4, 122.6, 120.7, 116.5. HRMS (ESI) calcd for $C_{13}H_7SNO_4$ $[M+H]^+$ 274.0174, found 274.0170.

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2 T. U. Kumar, Y. Bobde, S. Pulya, K. Rangan, B. Ghosh and A. Bhattacharya, *ChemistrySelect* 2019, **4**, 10726-10730.

3 S. Sau and P. Mal, *Chem. Commun.*, 2021, **57**, 9228-9231.

4 W. Liu, Y. Zhang and H. Guo, *J. Org. Chem.*, 2018, **83**, 10518-10524.

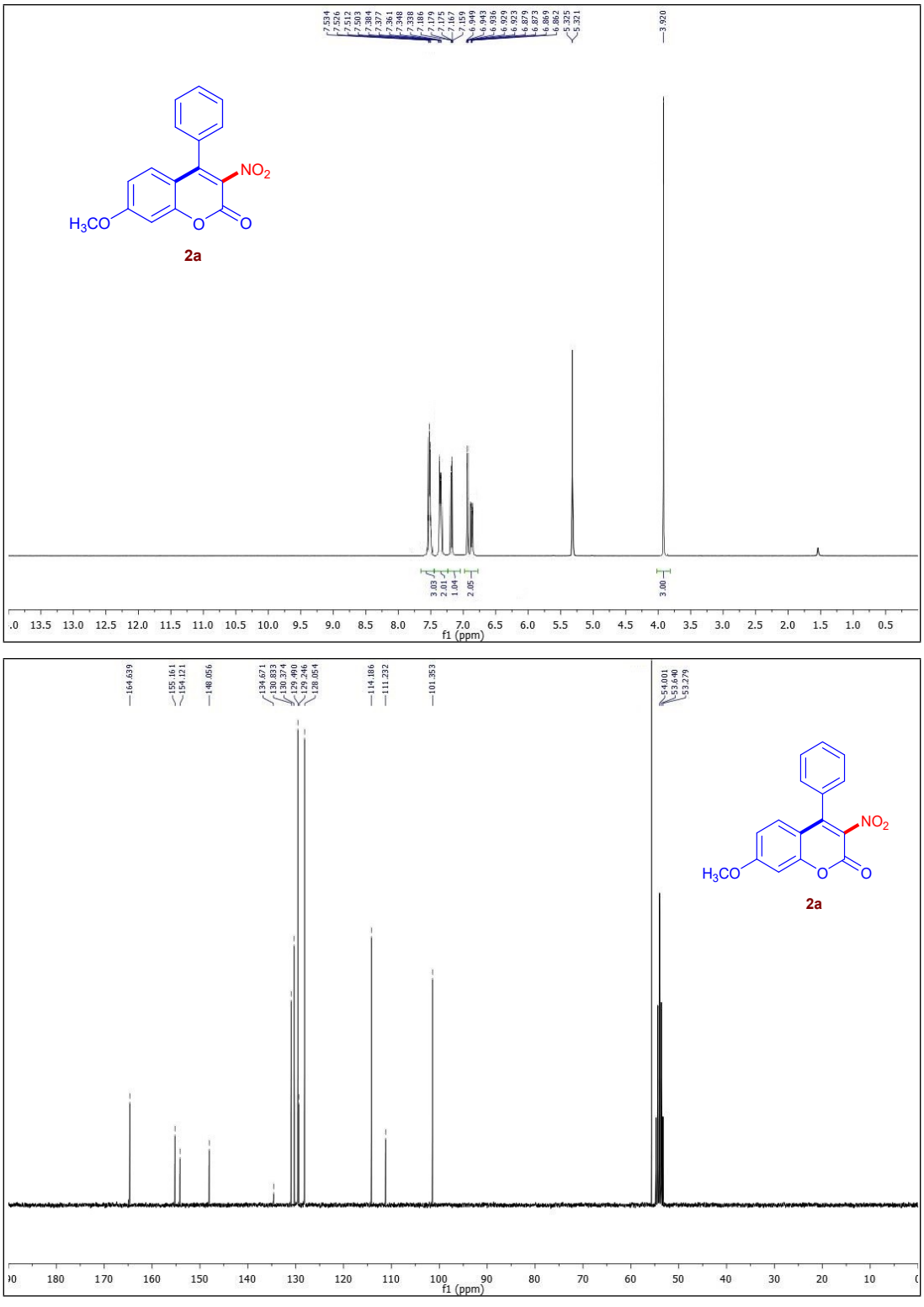

Figure S1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a** in CD_2Cl_2.

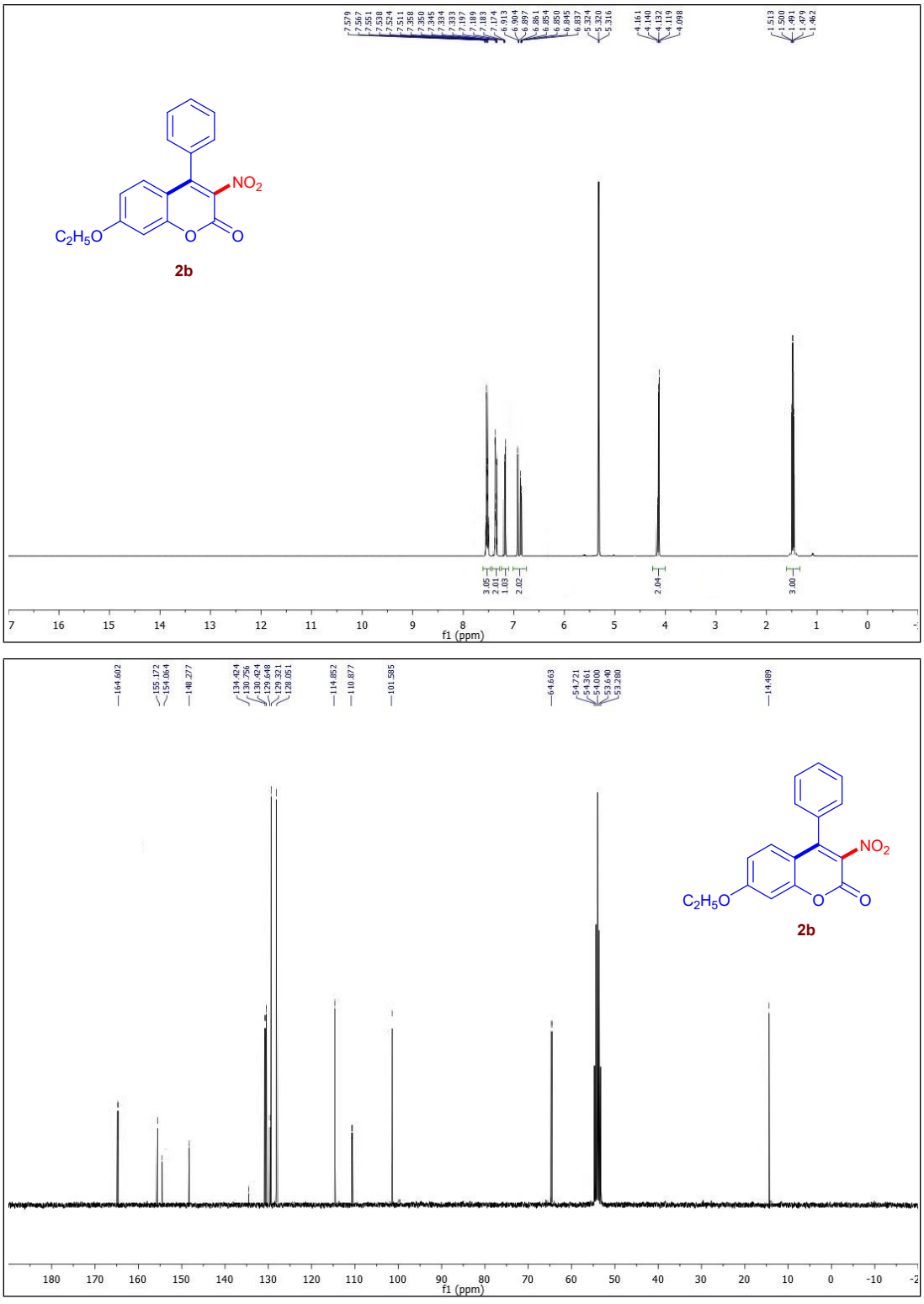

Figure S2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2b** in CD_2Cl_2.

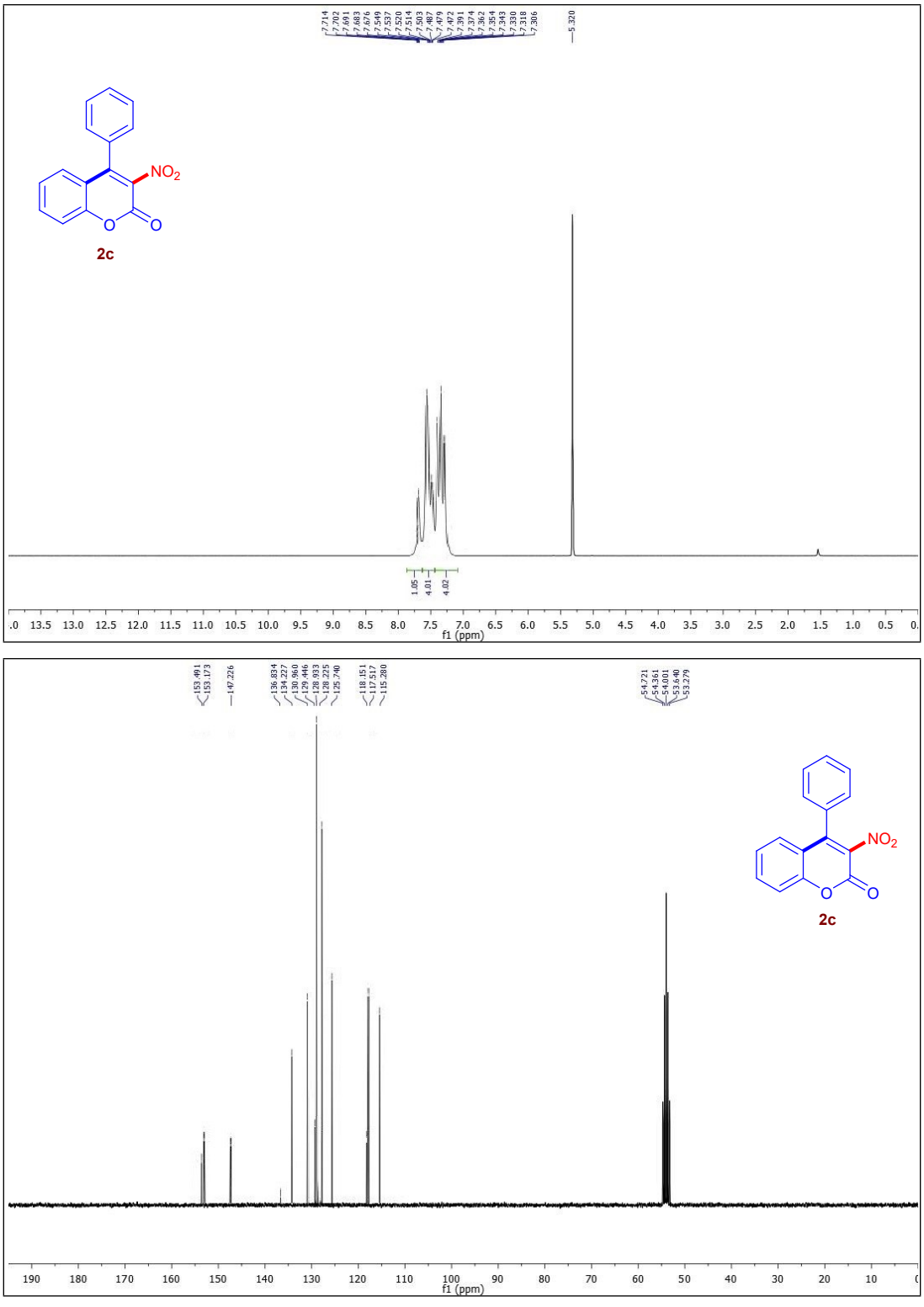

Figure S3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2c** in CD_2Cl_2.

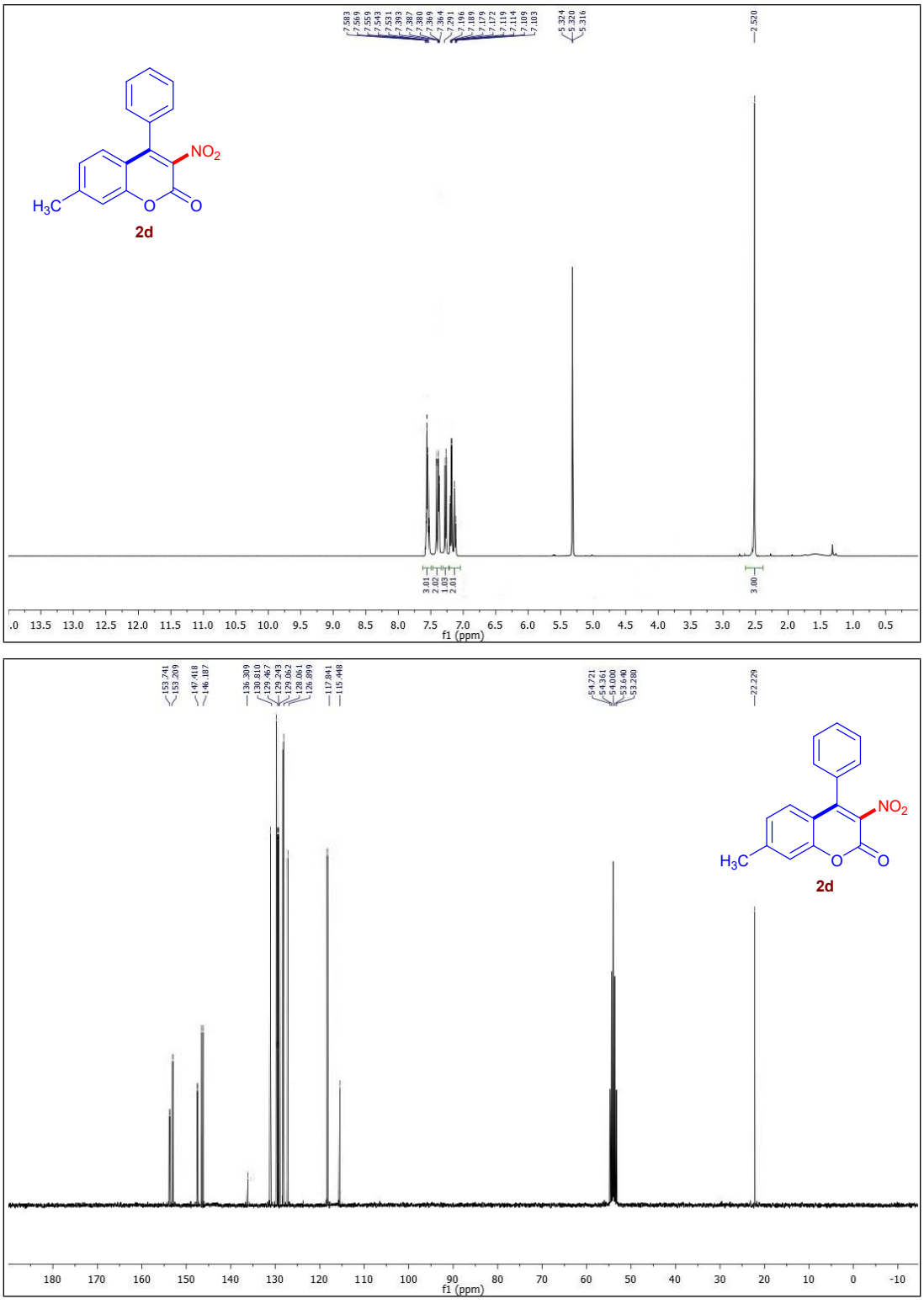

Figure S4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2d** in CD_2Cl_2.

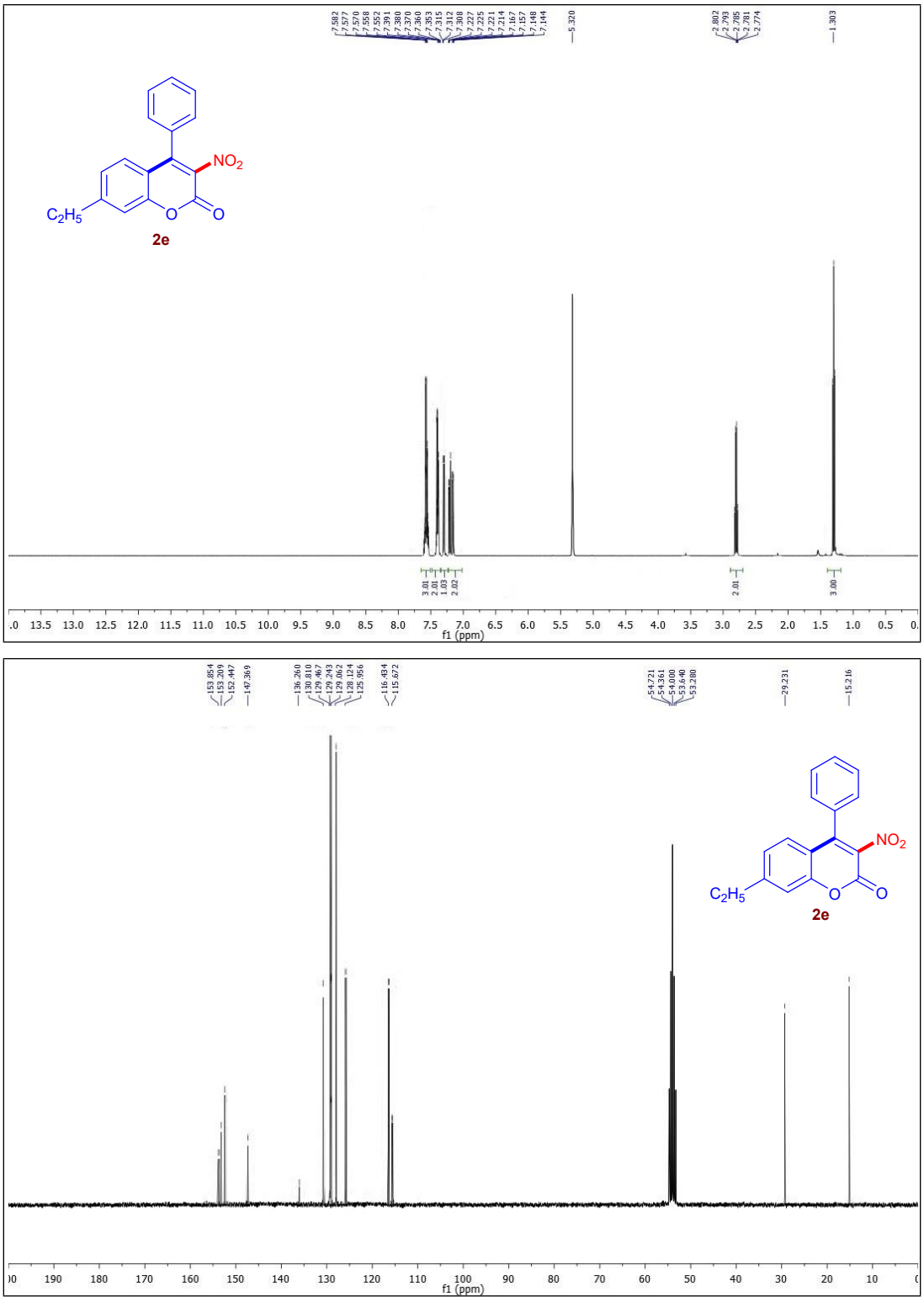

Figure S5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2e** in CD_2Cl_2.

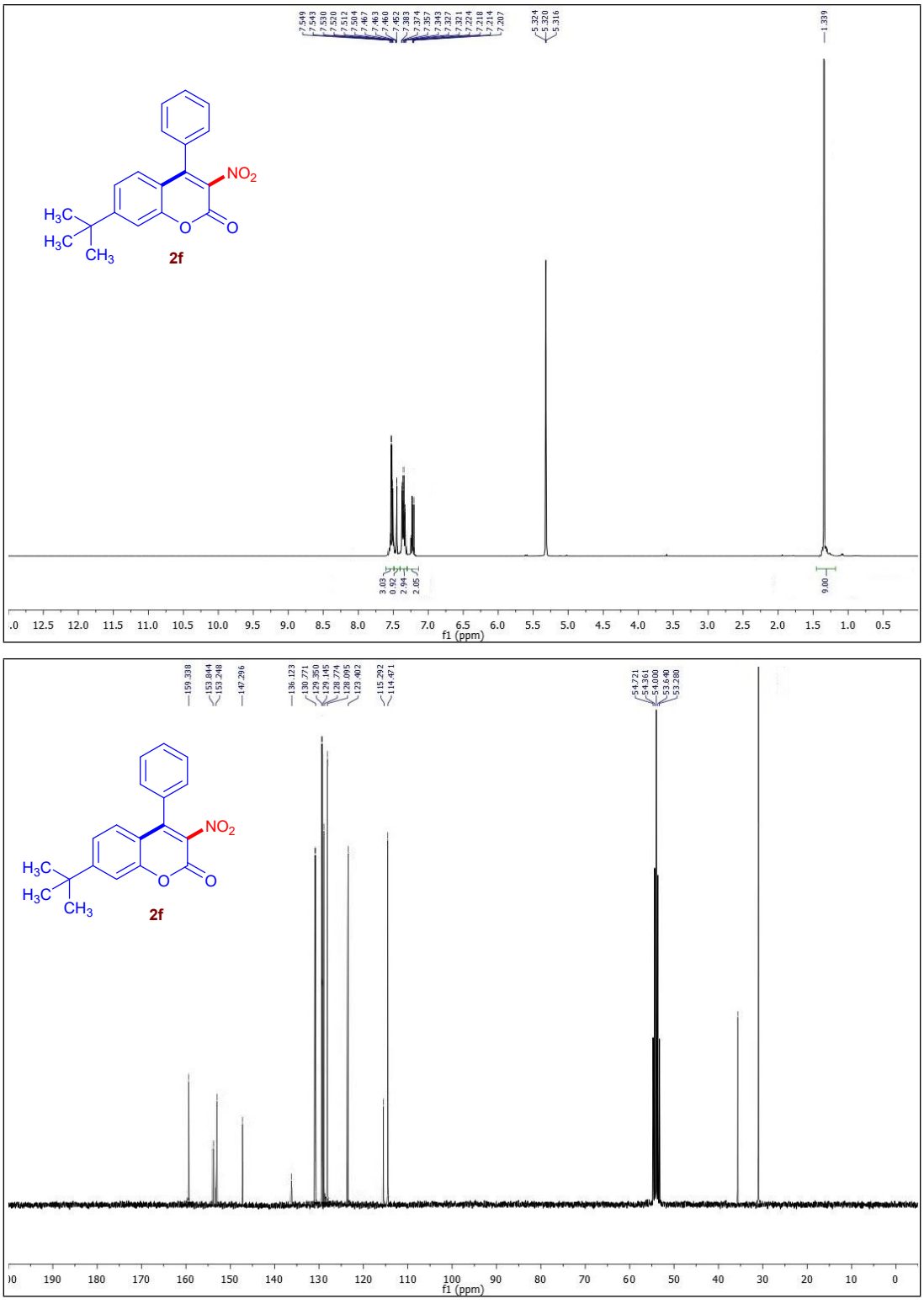

Figure S6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2f** in CD_2Cl_2.

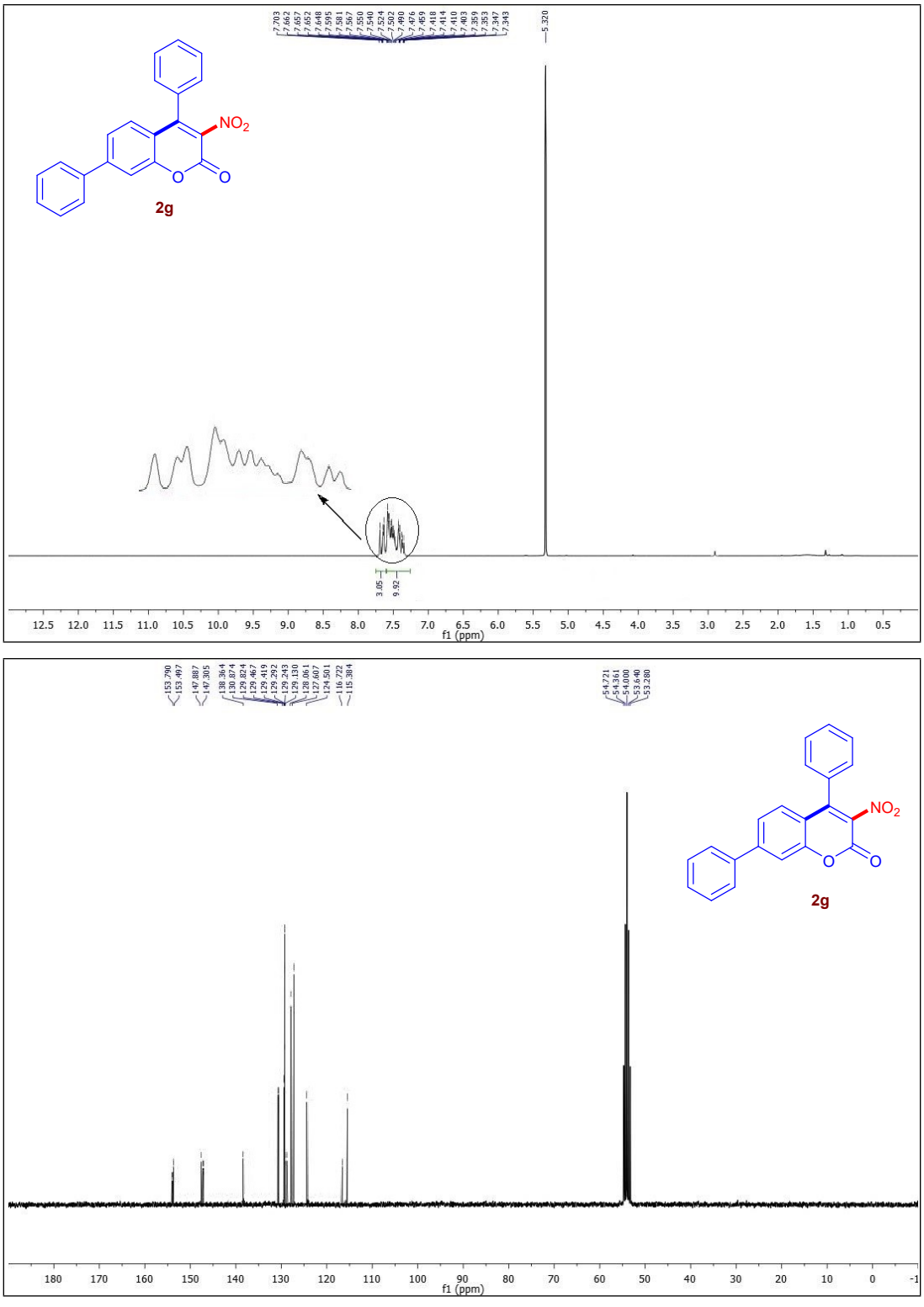

Figure S7. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2g** in CD_2Cl_2.

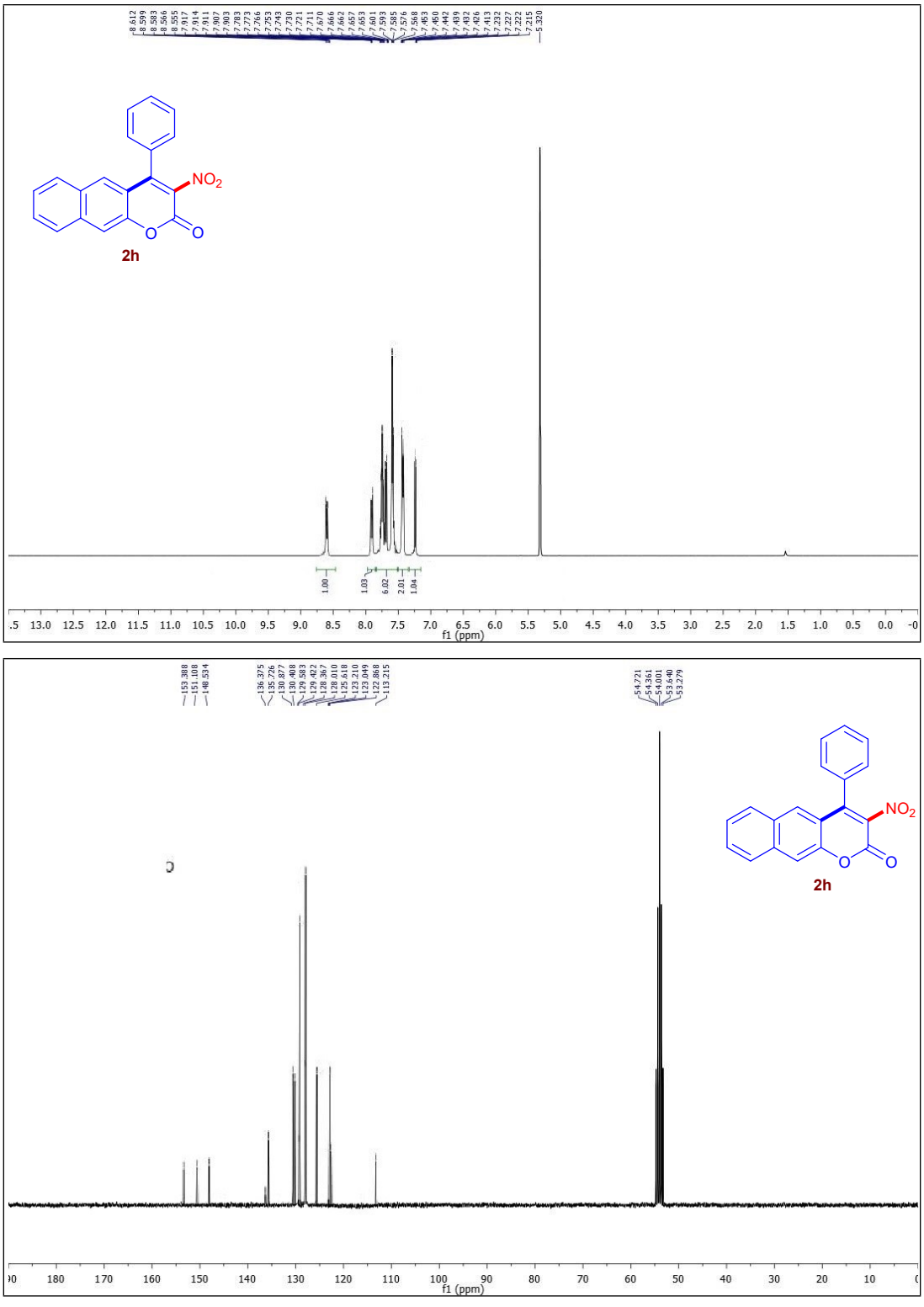

Figure S8. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2h** in CD_2Cl_2.

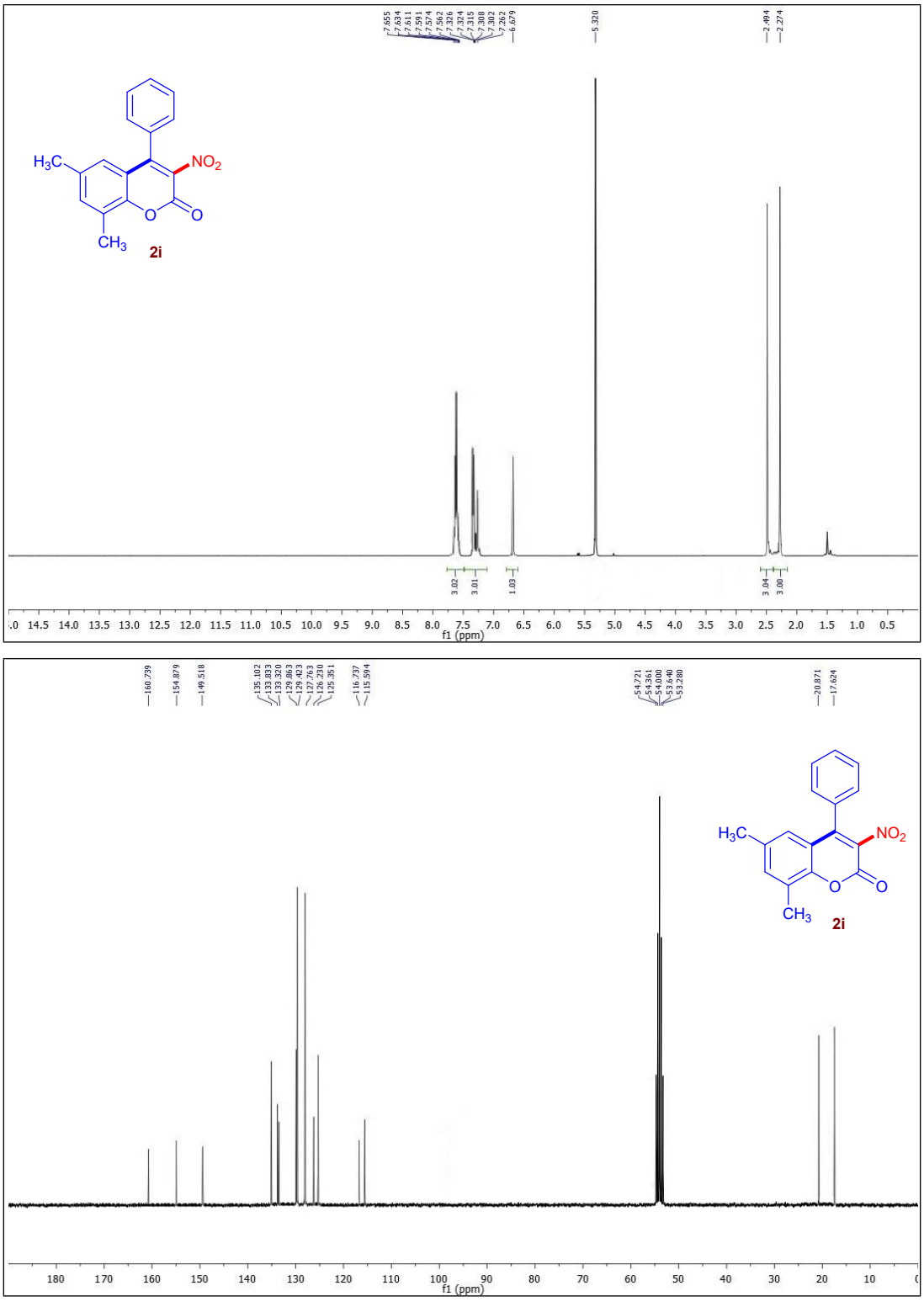

Figure S9. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2i** in CD_2Cl_2.

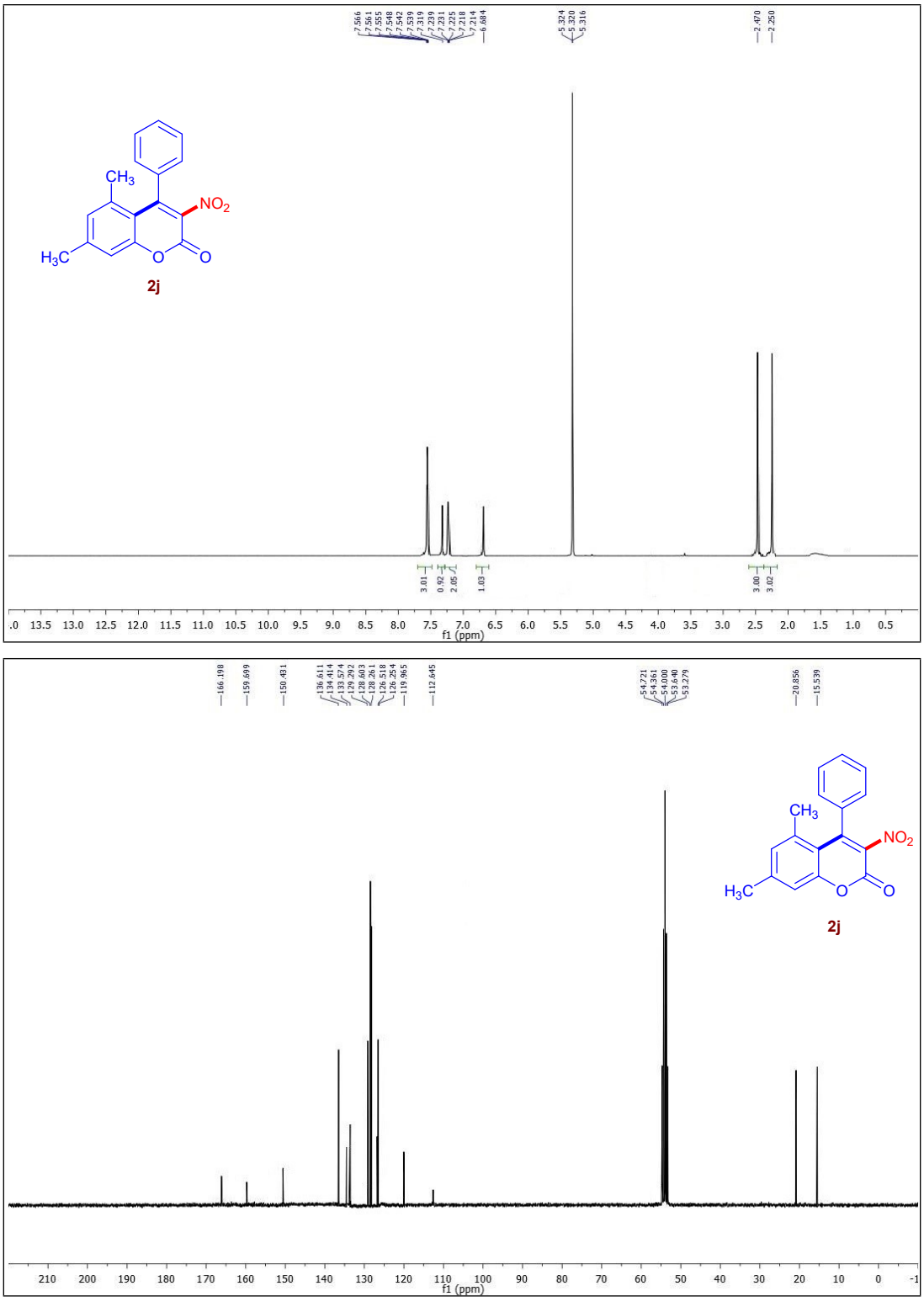

Figure S10. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2j** in CD_2Cl_2.

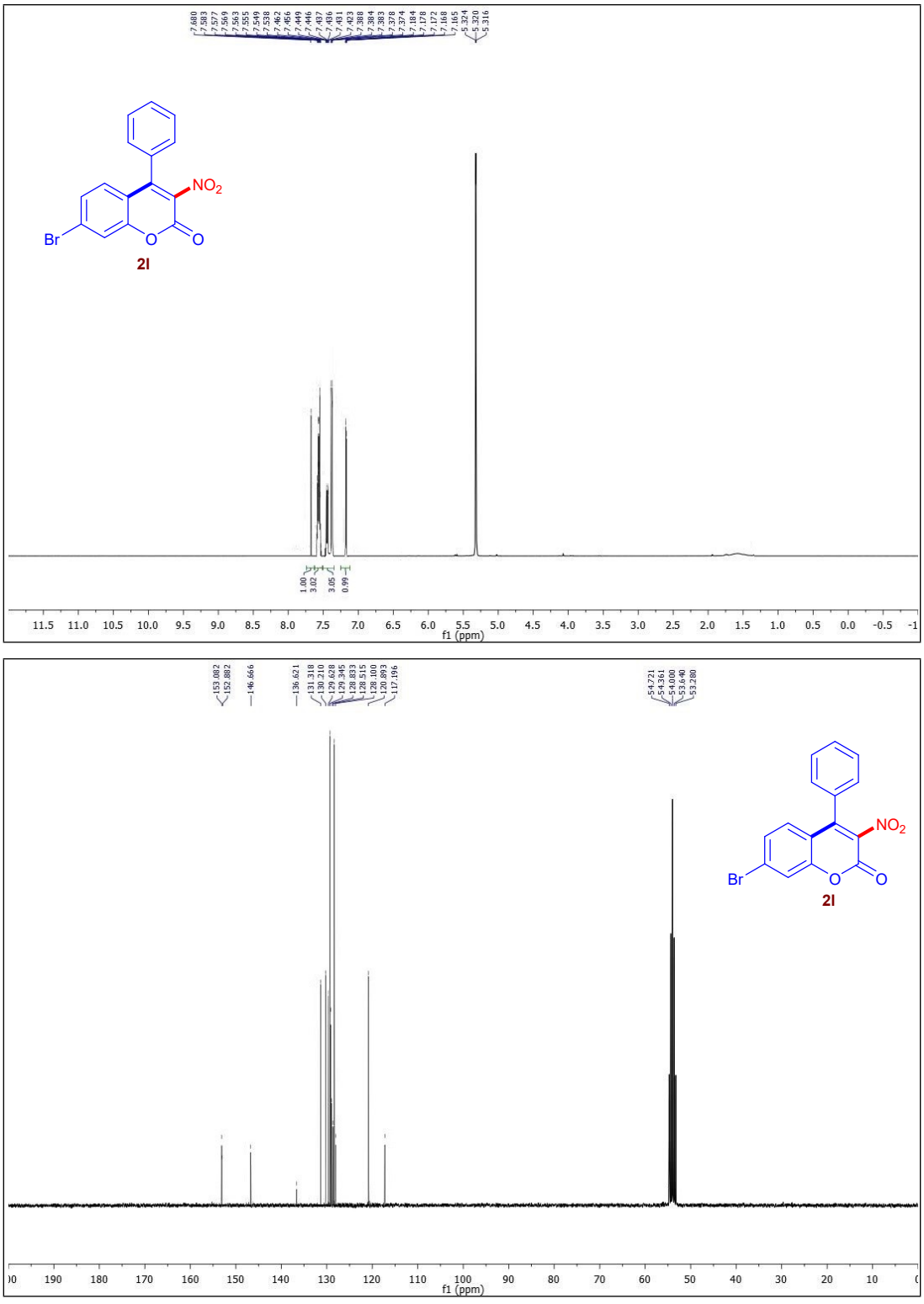

Figure S11. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2l** in CD_2Cl_2.

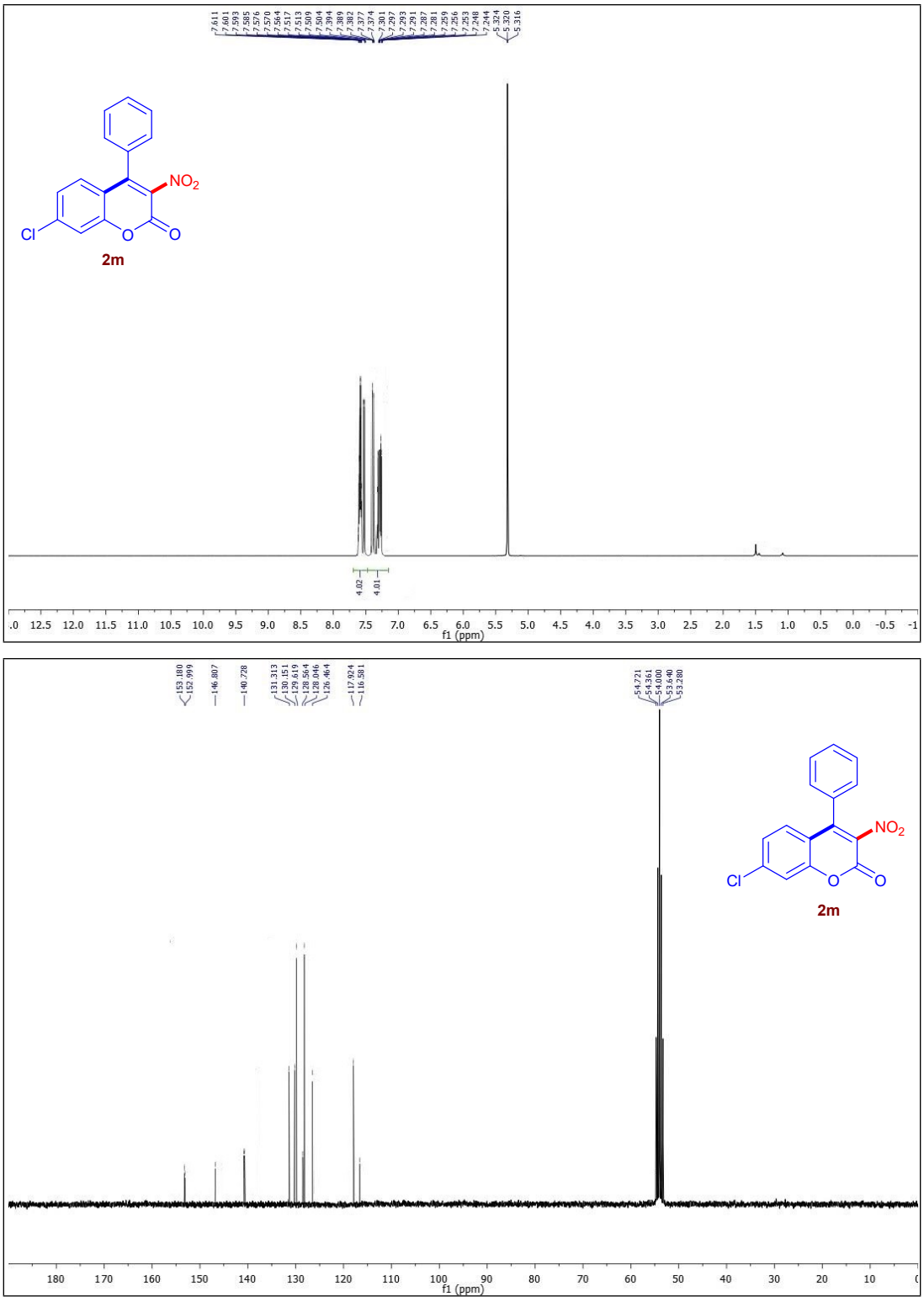

Figure S12. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2m** in CD_2Cl_2.

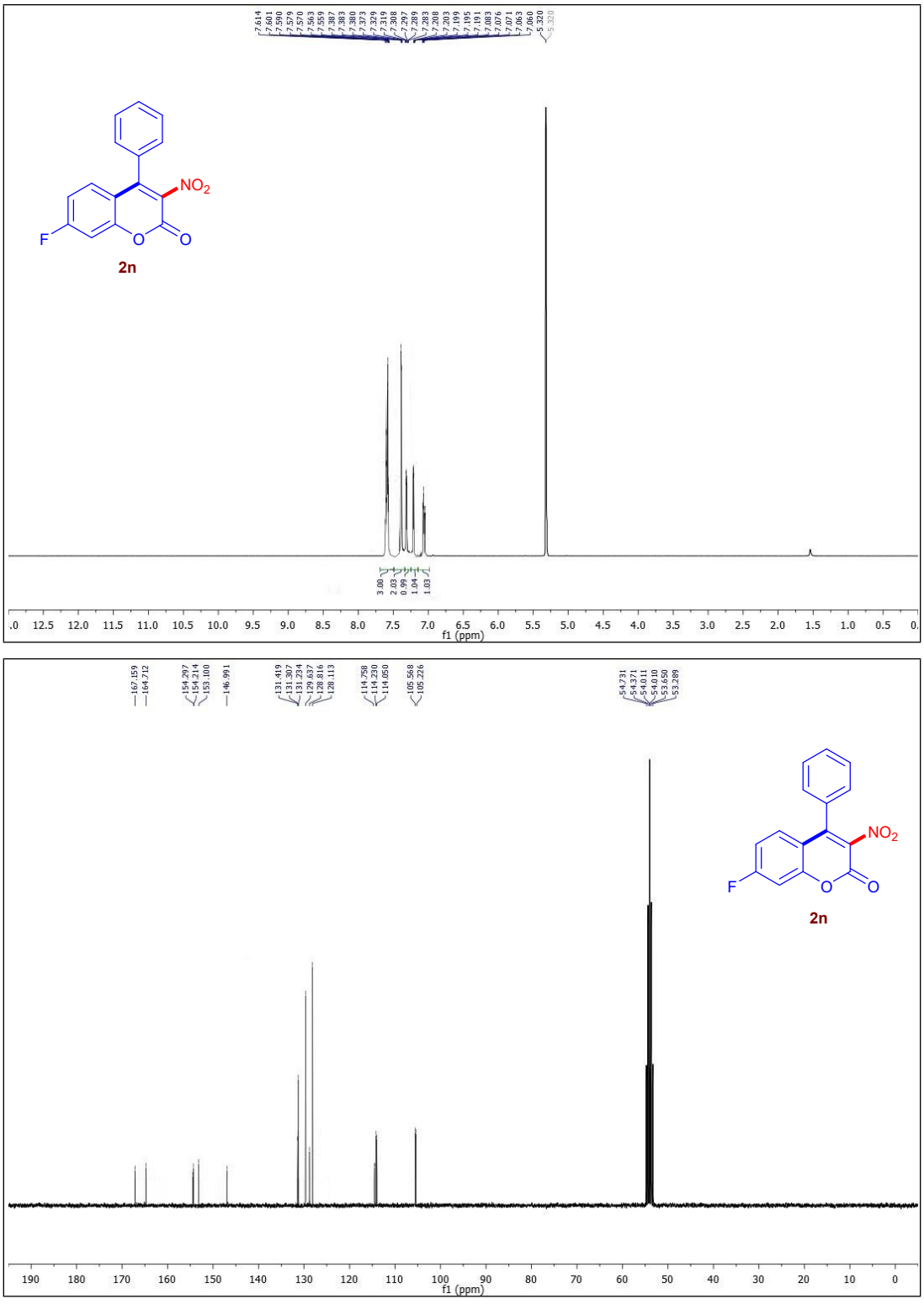

Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2n** in CD_2Cl_2.

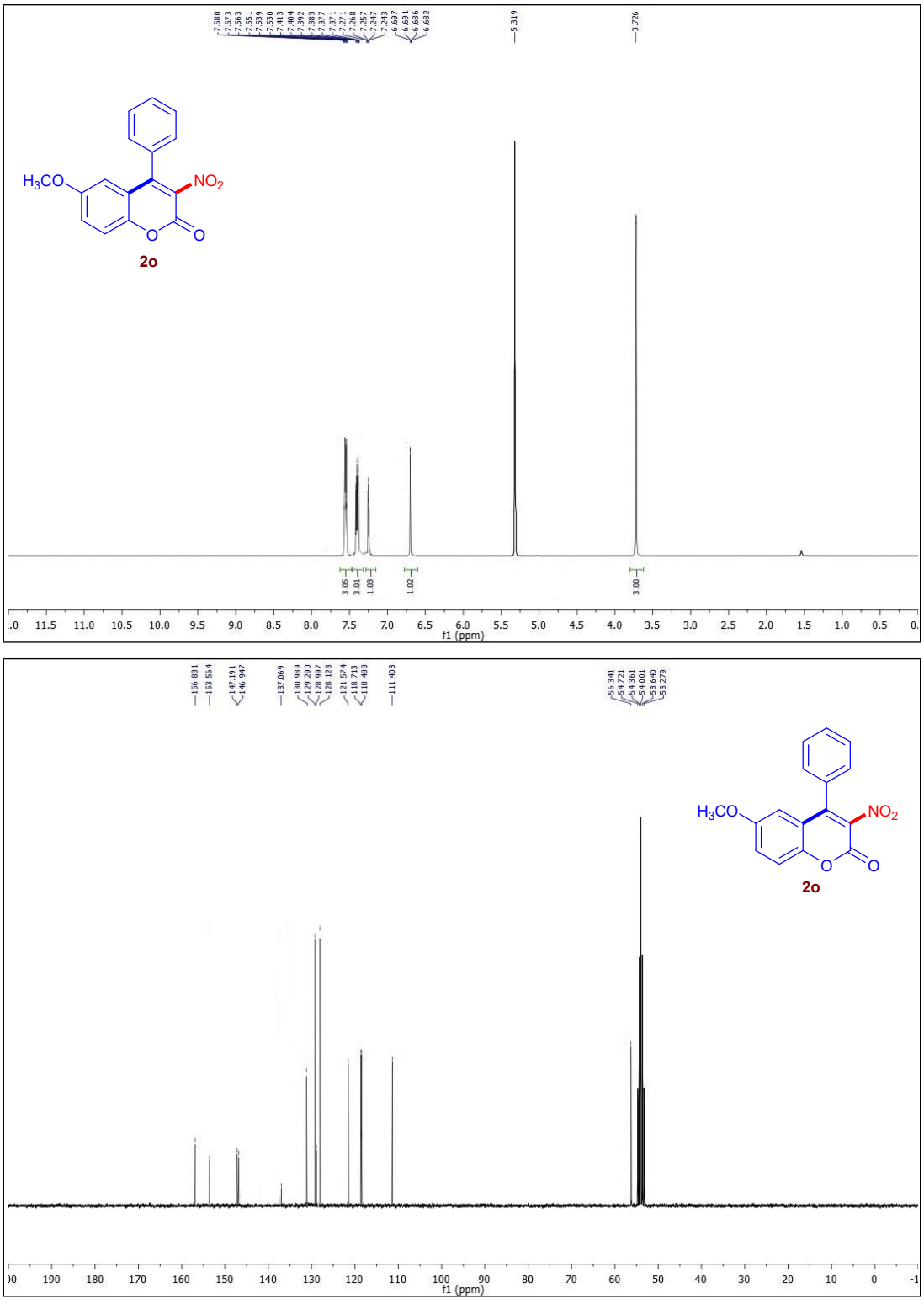

Figure S14. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2o** in CD_2Cl_2.

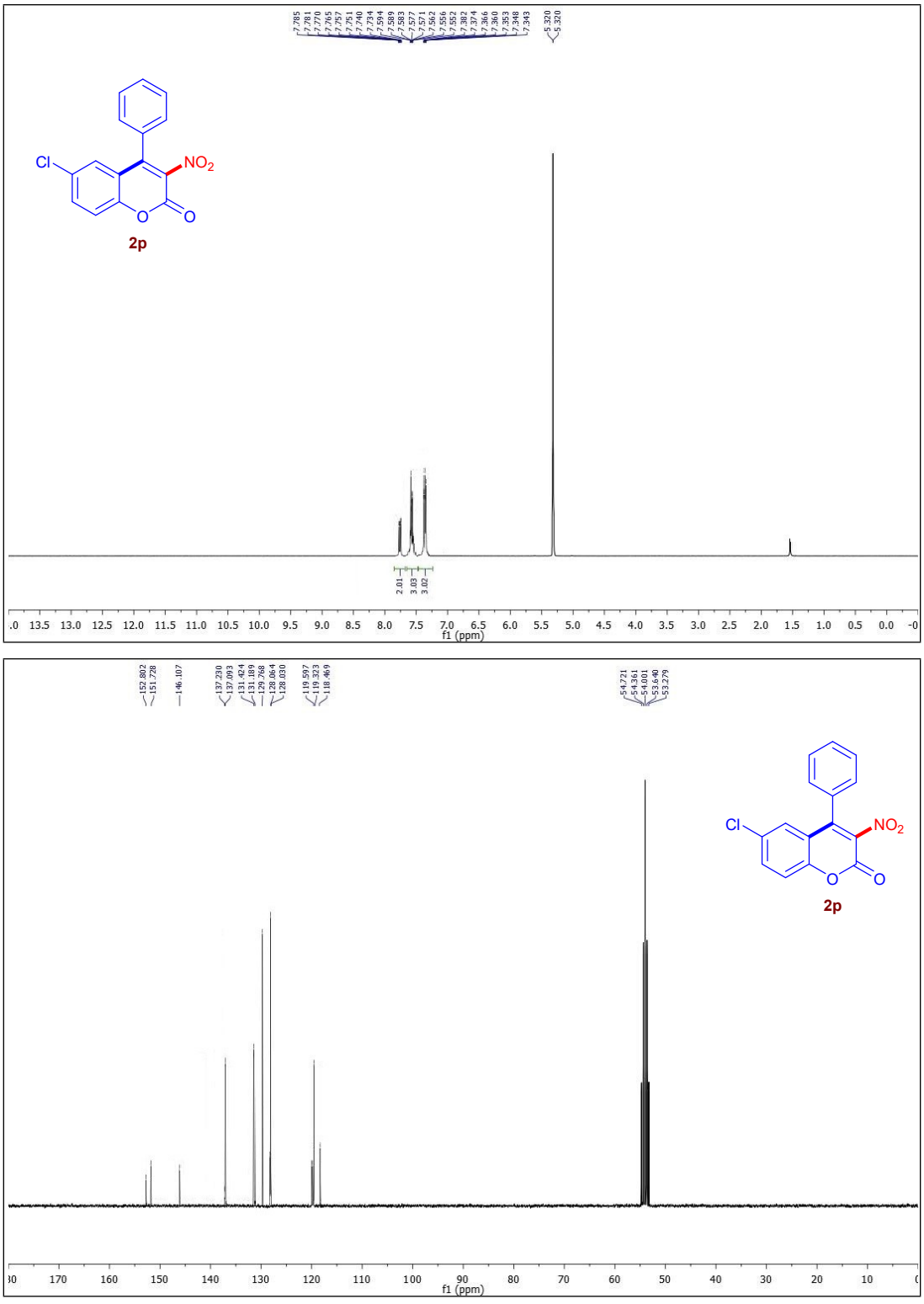

Figure S15. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2p** in CD_2Cl_2.

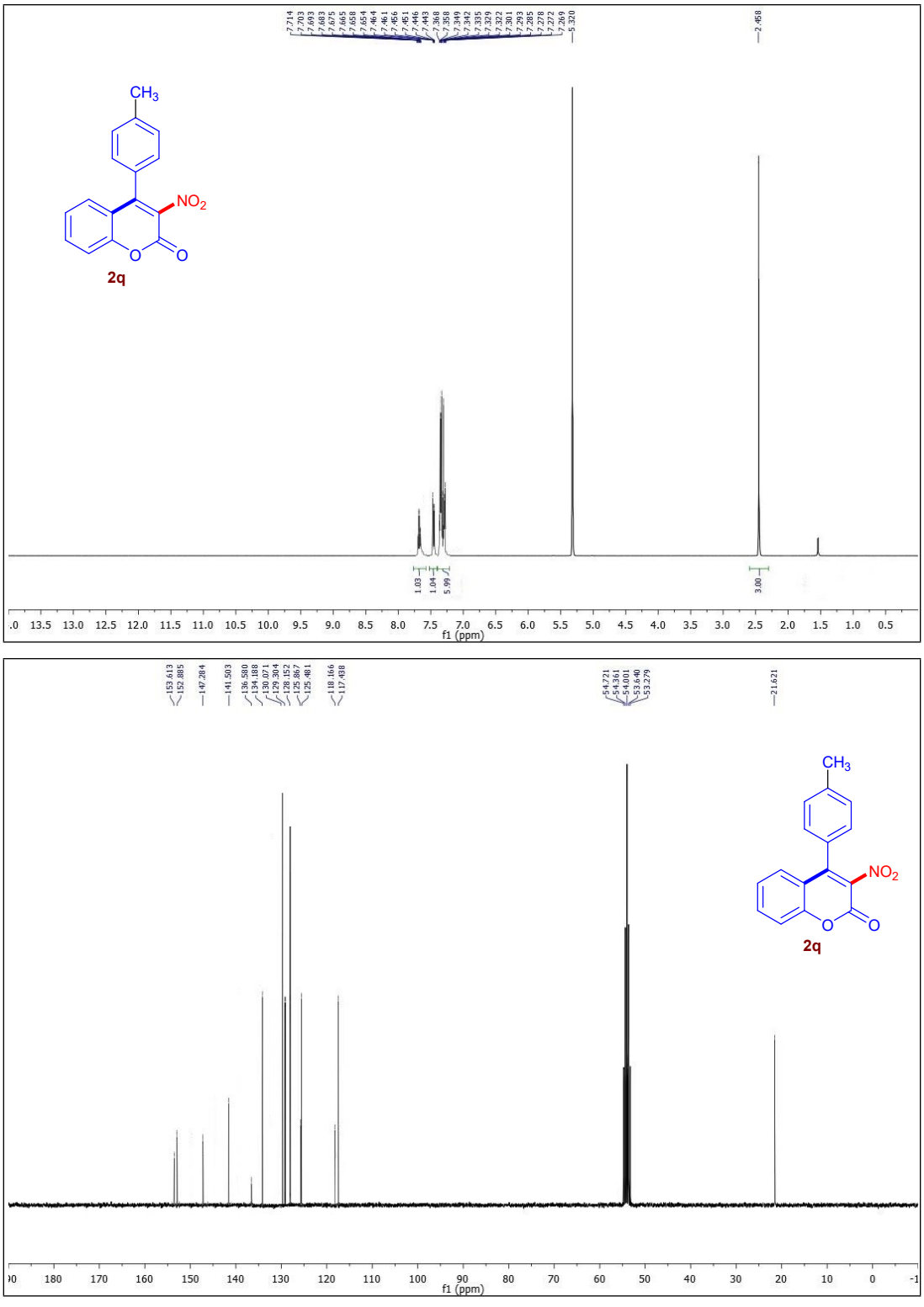

Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2q** in CD_2Cl_2.

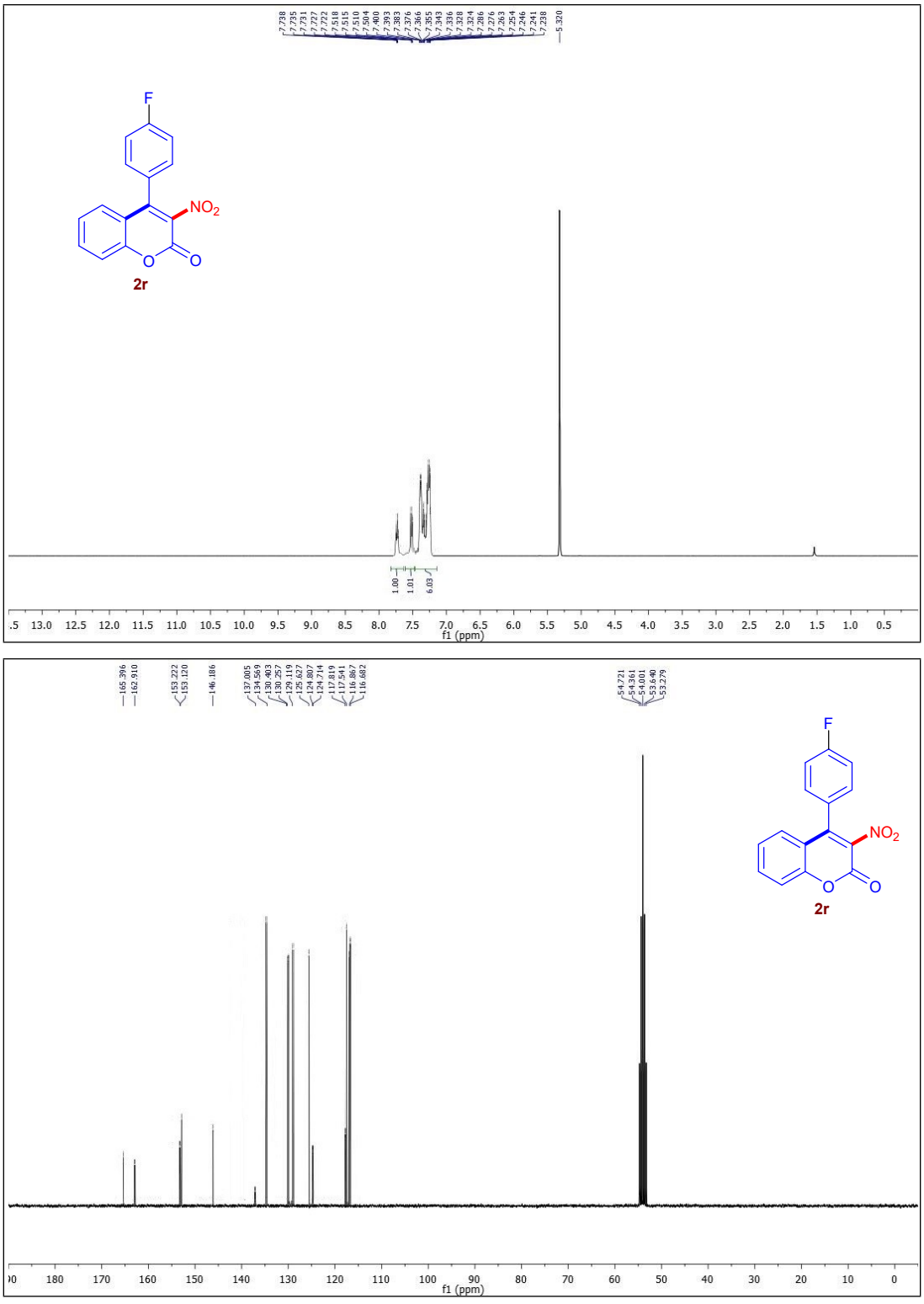

Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2r** in CD_2Cl_2.