Supporting Information

PIDA-Promoted metal-free [3 + 2] heteroannulation of β-ketothioamides with 4-hydroxy coumarins: chemo-/regioselective access to furo[3,2-c]chromen-4-ones at room temperature

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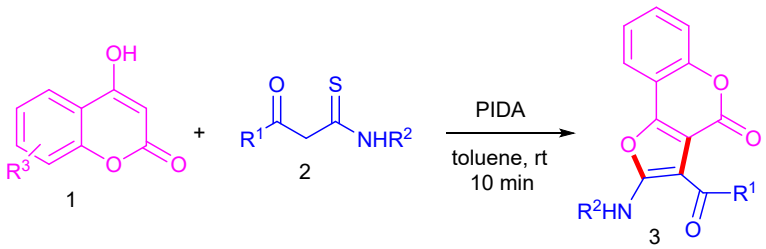
1. General Information. The commercially available solvents and reagents were used as received without any further purification. The β-ketothioamides were synthesized by the reported procedure.[1] Toluene was purchased from Merck. PIDA and Coumarins were purchased from Sigma Aldrich. All the reactions were monitored by analytical thin layer chromatography (TLC) using Merck pre-coated aluminium sheets, and visualized by a UV lamp. Flash column chromatography was performed on silica gel (230-400 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL 500 FT-NMR spectrometer operating at 500 and 125 MHz, respectively. Chemical shifts (δ) for ^{1}H and $^{13}C\{^{1}H\}$ NMR are given in parts per million (ppm) using the residual solvent peaks as a reference relative to tetramethylsilane (TMS). Coupling constant (J) values are reported in Hertz (Hz). High-resolution mass spectra (HRMS, m/z) were recorded in EI or ESI mode, on Sciex X500R QTOF instrument. All the reactions were carried out using a single-neck round bottom (25 mL) borosilicate flask. Melting points have been determined with Büchi B-540 melting point apparatus and are uncorrected. IUPAC names were obtained using the ChemDraw (version 19.1) software.

1. X. M. Zeng, C. Y. Meng, J. X. Bao, D. C. Xu, J. W. Xie and W. D. Zhu, *J. Org. Chem*., 2015, **80**, 11521-11528.

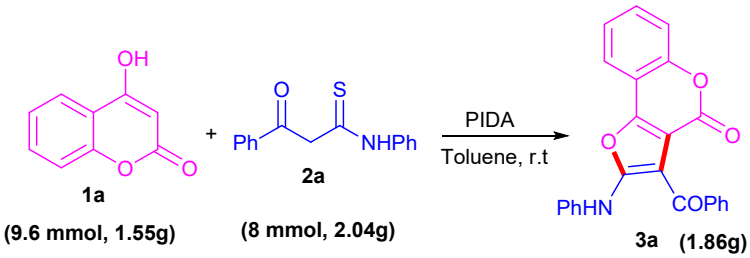
2. General Experimental Procedure for the Synthesis of Compounds 3.



4-Hydroxycoumarins **1** (0.3 mmol), β-ketothioamides **2** (0.25 mmol) and PIDA (1.5 equiv.) were added into a 25 mL oven-dried single neck round bottom flask followed by addition of 2.0 mL of toluene. The reaction mixture was allowed to stir at room temperature for 10 min in an open atmosphere. After completion of the reaction (monitored by TLC), the reaction was quenched with

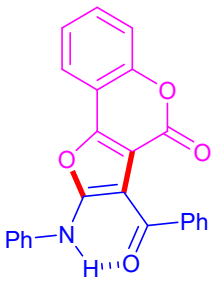
water (10 mL) followed by extraction with ethyl acetate (15 mL) and water (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by silica gel column chromatography to give the pure product **3** (20:1 hexane/ethyl acetate). The isolated product was dried under a vacuum and then the analytical studies were performed.

3. Scale-up Synthesis of Compounds 3a



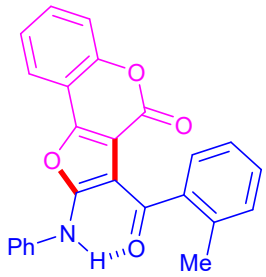
4-Hydroxycoumarin **1a** (9.6 mmol, 1.55 g), β-ketothioamide **2a** (8.0 mmol, 2.04 g) and PIDA (12.0 mmol, 3.86 g) were added into a 100 mL oven-dried single neck round bottom flask followed by addition of 10.0 mL of toluene. The reaction mixture was allowed to stir at room temperature for 20 min in an open atmosphere. After completion of the reaction (monitored by TLC), the reaction was quenched with water (50 mL) followed by extraction with ethyl acetate (2×30 mL) and water (2×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by silica gel column chromatography to give the pure product **3a** (1.86 g, 61%).

4. Characterization data of compounds 3a-3zd

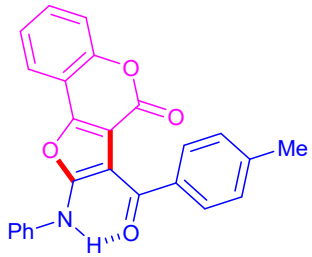


3-benzoyl-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3a**)**:** Isolated yield (61 mg, 64%); Brown solid crystal; mp. 170-172 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.69 (s, 1H), 7.85 (d, J = 10.0 Hz, 1H), 7.73-7.71 (m, 2H), 7.58-7.46 (m, 8H),

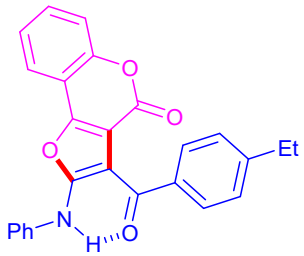
7.42-7.36 (m, 2H), 7.23-7.21 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 190.6, 161.2, 156.0, 152.1, 149.8, 140.0, 136.9, 132.0, 130.3, 129.8, 128.7, 127.8, 124.8, 124.6, 120.2, 119.8, 117.1, 111.8, 108.4, 95.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{24}H_{15}NO_4$, 382.1074, found 382.1068.



3-(2-methylbenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3b**)**:** Isolated yield (64 mg, 65%); Yellow solid powder; mp. 252-254 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.06 (s, 1H), 7.82-7.81 (m, 1H), 7.57-7.56 (m, 2H), 7.50-7.45 (m, 3H), 7.39 (t, J = 7.5 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.21 (m, 2H), 2.43 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 193.0, 161.0, 155.5, 152.1, 149.7, 140.9, 136.7, 135.4, 130.5, 130.2, 130.0, 129.8, 127.4, 125.1, 125.0, 124.5, 120.1, 120.0, 117.0, 111.8, 108.2, 97.2, 19.7; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{17}NO_4$, 396.1230, found 396.1228.

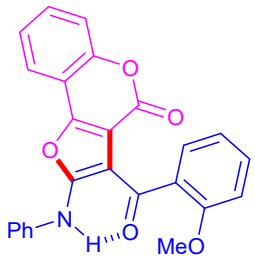


3-(4-methylbenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3c**)**:** Isolated yield (65 mg, 66%); yellow solid powder; mp. 262-264 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.61 (s, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.64 (d, J = 5.0 Hz, 2H), 7.52-7.44 (m, 6H), 7.41 (d, J = 10.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.25 (s, 1H), 7.21 (t, J = 7.5 Hz, 1H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 190.3, 161.0, 156.2, 152.1, 149.8, 142.7, 137.2, 137.1, 130.2, 129.8, 129.0, 128.6, 124.7, 124.6, 120.2, 119.7, 117.1, 111.9, 108.6, 96.0, 21.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{17}NO_4$, 396.1230, found 396.1238.

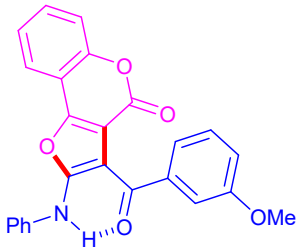


3-(4-ethylbenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3d**)**:** Isolated yield (70 mg, 68%); Brown solid crystal; mp. 183-185 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.61 (s, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.65 (d, J = 10.0 Hz, 2H), 7.50-7.48 (m, 3H), 7.45-7.43 (m, 2H), 7.38 (d, J = 5.0 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.27-7.25 (m, 2H), 7.19 (t, J = 7.5 Hz, 1H), 2.73 (q, J = 8.3 Hz, 2H), 1.28 (t, J = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 190.2, 161.0, 156.1, 152.0, 149.7, 148.8, 137.4, 137.0, 130.2, 129.8, 129.1, 127.3,

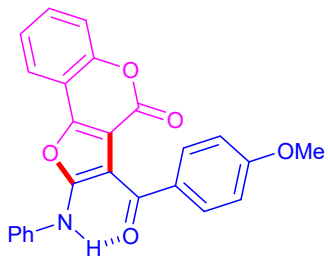
124.7, 124.6, 120.2, 119.6, 117.0, 111.9, 108.6, 96.0, 29.1, 15.2; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{26}H_{19}NO_4$, 410.1387, found 410.1389.



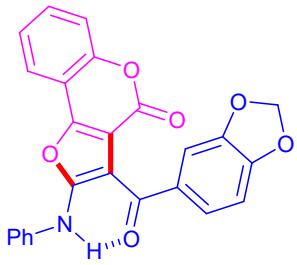
3-(2-methoxybenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3e**)**:** Isolated yield (66 mg, 64%); Yellow solid powder; mp. 212-214 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.17 (s, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.51-7.45 (m, 5H), 7.37-7.33 (m, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 10.0 Hz, 1H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.5, 160.9, 157.8, 156.0, 151.9, 149.3, 136.9, 132.2, 130.6, 130.0, 129.7, 129.2, 124.7, 124.5, 120.3, 120.1, 119.9, 116.9, 111.9, 110.7, 108.8, 98.2, 55.2; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{17}NO_5$, 412.1179, found 412.1179.



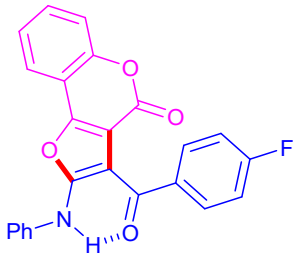
3-(3-methoxybenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3f**)**:** Isolated yield (60 mg, 58%); Yellow solid powder; mp. 202-204 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 1H), 7.82 (d, J = 5.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 3H), 7.46-7.43 (m, 2H), 7.39-7.31 (m, 4H), 7.24 (d, J = 5.0 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.09-7.07 (m, 1H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.3, 161.2, 159.3, 156.0, 152.2, 149.9, 141.2, 136.9, 130.3, 129.8, 128.8, 124.9, 124.6, 121.5, 120.2, 119.8, 118.3, 117.1, 113.4, 111.8, 108.5, 96.0, 55.5; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{17}NO_5$, 434.0999, found 434.1011.



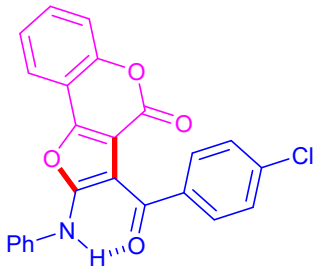
3-(4-methoxybenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3g**)**:** Isolated yield (68 mg, 66%); Brown solid crystal; mp. 111-113 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.55 (s, 1H), 7.86 (d, J = 5.0 Hz, 1H), 7.75-7.74 (m, 2H), 7.50 (t, J = 7.5 Hz, 3H), 7.47-7.42 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 10.0 Hz, 2H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.2, 163.1, 160.9, 156.3, 152.1, 149.8, 137.2, 132.4, 131.3, 130.2, 129.8, 124.6, 124.6, 120.3, 119.6, 117.1, 113.2, 111.9, 108.7, 96.0, 55.5; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{25}H_{17}NO_5$, 434.0999, found 434.1013.



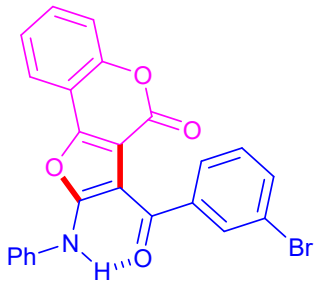
3-(benzo[d][1,3]dioxole-5-carbonyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3h**)**:** Isolated yield (74 mg, 70%); Brown solid crystal; mp. 185-187 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.84 (d, J = 5.0 Hz, 1H), 7.51-7.48 (m, 3H), 7.45 (t, J = 7.5 Hz, 2H), 7.41 (d, J = 10.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 5.0 Hz, 1H), 7.24 (s, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 10.0 Hz, 1H),6.05 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 188.8, 160.9, 156.2, 152.1, 151.2, 149.8, 147.5, 137.0, 134.1, 130.2, 129.8, 125.1, 124.7, 124.6, 120.2, 119.6, 117.1, 111.8, 109.02, 108.6, 107.5, 101.7, 95.9; HRMS (ESI-TOF, [M + Na]$^+$): Calcd for $C_{25}H_{15}NO_6$, 448.0792, found 448.0800.



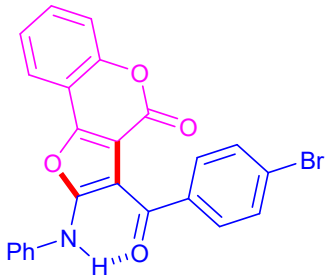
3-(4-fluorobenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3i**)**:** Isolated yield (52 mg, 52%); Yellow solid crystal; mp. 188-190 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.65 (s, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.74-7.72 (m, 2H), 7.52-7.50 (m, 3H), 7.48-7.45 (m, 2H), 7.42 (d, J = 5.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 5.0 Hz, 1H), 7.12 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.0, 166.2, 164.2, 161.3, 156.2, 152.1, 150.0, 136.8, 136.2, 131.3, 131.2, 130.4, 129.8, 124.9, 124.7, 120.3, 119.9, 117.1, 115.1, 114.9, 111.8, 108.3, 95.8; HRMS (ESI-TOF, [M + H]$^+$): Calcd for $C_{24}H_{14}FNO_4$, 400.0980, found 400.0992.



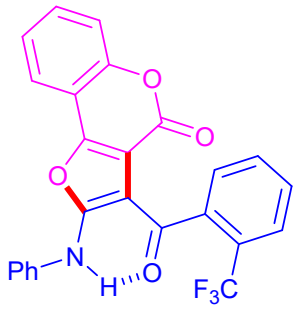
3-(4-chlorobenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3j**)**:** Isolated yield (57 mg, 55%); Yellow solid crystal; mp. 210-212 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.68 (s, 1H), 7.84 (d, J = 10.0 Hz, 1H), 7.65 (d, J = 10.0 Hz, 2H), 7.53-7.51 (m, 2H), 7.47 (t, J = 7.5 Hz, 3H), 7.42 (d, J = 10.0 Hz, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 10.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.2, 161.4, 156.2, 152.2, 150.0, 138.3, 138.2, 136.8, 130.5, 130.2, 129.9, 128.2, 125.1, 124.7, 120.3, 119.9, 117.2, 111.8, 108.3, 95.8; HRMS (ESI-TOF, [M + Na]$^+$): Calcd for $C_{24}H_{14}ClNO_4$, 438.0504, found 438.0516.



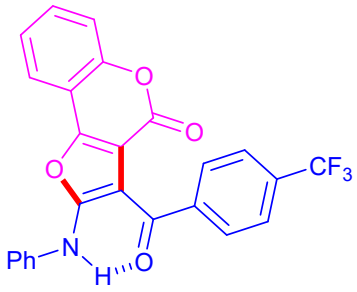
3-(3-bromobenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3k**)**:** Isolated yield (63 mg, 55%); Yellow solid powder; mp. 255-257 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.72 (s, 1H), 7.85-7.84 (m, 2H), 7.68-7.67 (m, 1H), 7.61-7.60 (m, 1H), 7.54-7.47 (m, 5H), 7.43-7.42 (m, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.23 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 188.9, 161.5, 156.0, 152.2, 150.1, 141.8, 136.6, 134.7, 131.6, 130.5, 129.9, 129.3, 127.3, 125.2, 124.7, 122.0, 120.3, 120.0, 117.2, 111.7, 108.1, 95.7; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{24}H_{14}BrNO_4$, 460.0179, found 460.0203.



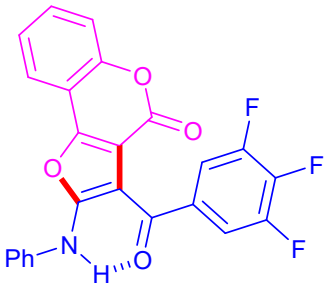
3-(4-bromobenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3l**)**:** Isolated yield (68 mg, 59%); Brown solid powder; mp. 93-95 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.69 (s, 1H), 7.84 (d, J = 10.0 Hz, 1H), 7.58 (s, 3H), 7.53-7.46 (m, 5H), 7.43-7.36 (m, 3H), 7.24-7.22 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.3, 161.4, 156.2, 152.1, 150.0, 138.7, 136.7, 131.1, 130.5, 130.3, 129.9, 129.1, 126.8, 125.1, 124.7, 120.3, 119.9, 117.1, 111.7, 108.2, 95.7; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{24}H_{14}BrNO_4$, 460.0179, found 460.0209.



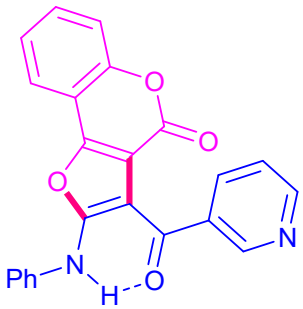
2-(phenylamino)-3-(2-(trifluoromethyl)benzoyl)-4H-furo[3,2-c]chromen-4-one (**3m**)**:** Isolated yield (56 mg, 50%); Yellow solid powder; mp. 185-187 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.02 (s, 1H), 7.81-7.77 (m, 2H), 7.59-7.57 (m, 4H), 7.51-7.45 (m, 3H), 7.41 (s, 1H), 7.36-7.32 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.9, 161.1, 155.6, 152.1, 149.8, 140.0, 136.4, 131.3, 130.4, 129.9, 129.5, 127.6, 127.4, 127.1, 126.3, 126.3, 125.4, 125.3, 124.6, 120.3, 120.2, 117.1, 111.7, 107.9, 96.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{14}F_3NO_4$, 450.0948, found 450.0963.



2-(phenylamino)-3-(4-(trifluoromethyl)benzoyl)-4H-furo[3,2-c]chromen-4-one (**3n**)**:** Isolated yield (58 mg, 52%); White solid powder, mp. 245-247 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.77 (s, 1H), 7.83 (d, J = 10.0 Hz, 1H), 7.77 (d, J = 5.0 Hz, 2H), 7.70 (d, J = 5.0 Hz, 2H), 7.52 (t, J = 5.0 Hz, 3H), 7.49-7.46 (m, 2H), 7.40 (d, J = 10.0 Hz, 1H), 7.36 (d, J = 10.0 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.3, 161.6, 156.1, 152.2, 150.1, 143.2, 136.5, 133.3, 133.0, 130.6, 129.9, 128.8, 125.3, 124.9, 124.8, 120.3, 120.1, 117.2, 111.7, 108.0, 95.8; HRMS (ESI-TOF, [M + H]$^+$): Calcd for $C_{25}H_{14}F_3NO_4$, 450.0948, found 450.0968.

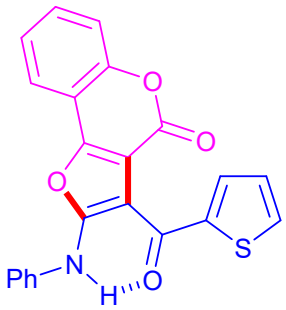


2-(phenylamino)-3-(3,4,5-trifluorobenzoyl)-4H-furo[3,2-c]chromen-4-one (**3o**)**:** Isolated yield (52 mg, 48%); Brown solid crystal; mp. 172-174 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.63 (s, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.56-7.48 (m, 5H), 7.45-7.43 (m, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 5.0 Hz, 2H), 7.28 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 186.7, 161.7, 156.1, 152.2, 150.4, 136.4, 135.7, 130.8, 129.9, 129.2, 125.5, 125.1, 124.9, 120.4, 120.2, 117.2, 113.3, 113.3, 113.2, 113.1, 111.6, 107.8, 95.3; HRMS (ESI-TOF, [M + Na]$^+$): Calcd for $C_{24}H_{12}F_3NO_4$, 436.0791, found 436.0799.

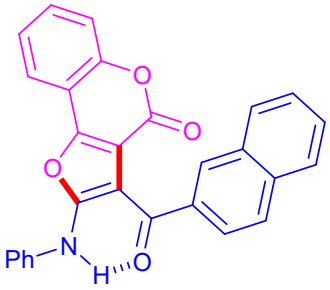


3-nicotinoyl-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3p**)**:** Isolated yield (48 mg, 50%); Brown solid; mp. 92-94 °C. Isolation: hexane/ethyl acetate (5/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.86 (s, 1H), 8.93 (s, 1H), 8.78 (s, 1H), 8.11 (d, J = 10.0 Hz, 1H), 7.90 (d, J = 5.0 Hz, 1H), 7.81(d, J = 10.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.51-7.48 (m, 3H), 7.40-7.35 (m, 2H), 7.29-7.27 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 187.9, 161.6, 156.2, 152.1, 151.7, 150.2, 149.3, 136.4,

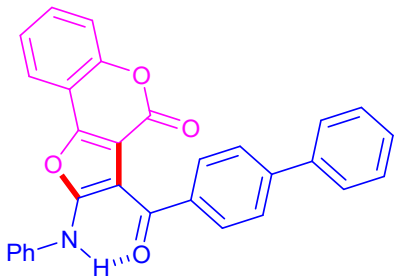
136.2, 135.9, 130.6, 129.9, 125.3, 124.8, 123.0, 120.3, 120.1, 117.1, 111.6, 107.9, 95.8; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{23}H_{14}N_2O_4$, 383.1026, found 383.1032.



2-(phenylamino)-3-(thiophene-2-carbonyl)-4H-furo[3,2-c]chromen-4-one (**3q**)**:** Isolated yield (63 mg, 65%); Brown solid crystal; mp. 180-182 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.38 (s, 1H), 7.85 (d, J = 10.0 Hz, 1H), 7.68 (d, J = 5.0 Hz, 1H), 7.58 (d, J = 5.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.49-7.46 (m, 3H), 7.45-7.43 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 5.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 181.2, 160.9, 156.4, 152.1, 150.3, 143.7, 137.0, 133.9, 133.0, 130.4, 129.8, 127.5, 124.8, 124.7, 120.3, 119.7, 117.1, 111.8, 108.2, 95.8; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{22}H_{13}NO_4S$, 410.0457, found 410.0462.

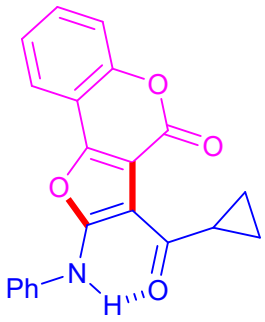


3-(2-naphthoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3r**)**:** Isolated yield (67 mg, 62%); Brown solid crystal; mp. 215-217 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.74 (s, 1H), 8.22 (s, 1H), 7.92-7.86 (m, 4H), 7.83 (d, J = 10.0 Hz, 1H), 7.58-7.54 (m, 3H), 7.52-7.46 (m, 4H), 7.42-7.37 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.4, 161.2, 156.1, 152.1, 149.9, 137.2, 136.9, 135.3, 132.4, 130.3, 130.1, 129.8, 129.5, 128.0, 127.8, 127.7, 126.5, 125.1, 124.8, 124.7, 120.3, 119.8, 117.1, 111.9, 108.6, 96.2; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{28}H_{17}NO_4$, 452.1050, found 452.1063.

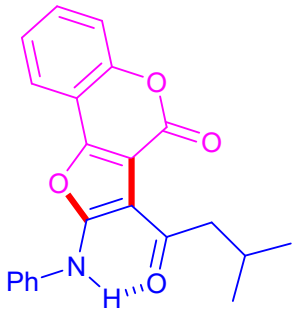


3-([1,1'-biphenyl]-4-carbonyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3s**)**:** Isolated yield (78 mg, 68%); Yellow solid powder; mp. 210-212 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.70 (s, 1H), 7.85 (d, J = 10.0 Hz, 1H), 7.82-7.80 (m, 2H),

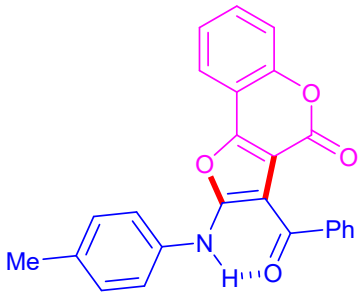
7.69-7.66 (m, 4H), 7.52 (t, J = 10.0 Hz, 3H), 7.49-7.44 (m, 4H), 7.42-7.41 (m, 1H), 7.37 (t, J = 7.5, 2H), 7.23 (t, J = 7.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 189.9, 161.2, 156.2, 152.1, 149.9, 144.7, 140.5, 138.6, 136.9, 130.3, 129.8, 129.5, 128.9, 127.9, 127.4, 126.5, 124.8, 124.6, 120.3, 119.8, 117.1, 111.8, 108.5, 96.0; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{30}H_{19}NO_4$, 459.1465, found 459.1443.



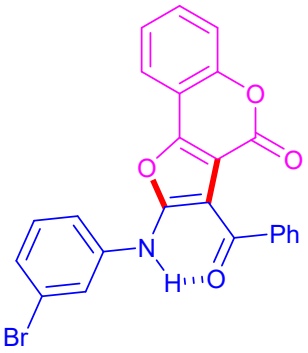
3-(cyclopropanecarbonyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3t**)**:** Isolated yield (47 mg, 55%); Yellow solid crystal; mp. 178-180 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.21 (s, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.53-7.42 (m, 6H), 7.37 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 3.88 -3.83 (m, 1H), 1.25-1.23 (m, 2H), 1.10-1.08 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 196.9, 160.0, 157.7, 151.8, 149.7, 137.0, 130.2, 129.7, 124.8, 124.6, 120.2, 119.7, 117.0, 111.9, 108.5, 97.0, 19.5, 12.3; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{21}H_{15}NO_4$, 368.0893, found 368.0900.



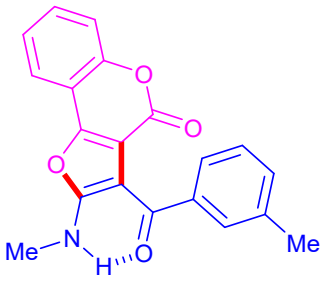
3-(3-methylbutanoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3u**)**:** Isolated yield (52 mg, 58%); Yellow solid crystal; mp. 170-172 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.19 (s, 1H), 7.81 (d, J = 10.0 Hz, 1H), 7.52-7.49 (m, 3H), 7.45 (t, J = 7.5 Hz, 3H), 7.36 (t, J = 5.0 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 3.21 (d, J = 5.0 Hz, 2H), 2.27-2.19 (m, 1H), 1.04 (d, J = 5.0 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 197.6, 160.6, 157.3, 151.9, 149.5, 137.0, 130.1, 129.7, 124.7, 120.2, 119.8, 117.0, 111.9, 108.2, 96.6, 50.9, 26.6, 22.7; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{22}H_{19}NO_4$, 362.1387, found 362.1397.



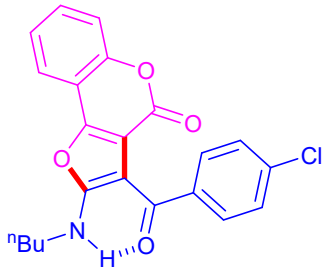
3-benzoyl-2-(p-tolylamino)-4H-furo[3,2-c]chromen-4-one (**3v**)**:** Isolated yield (64 mg, 65%); Brown solid crystal; mp. 182-184 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 1H), 7.80 (d, J = 10.0 Hz, 1H), 7.70 (d, J = 5.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.49-7.43 (m, 4H), 7.40-7.37 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (s, 1H), 2.39 (s, 3H);^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.4, 161.4, 156.1, 152.0, 149.7, 140.1, 134.8, 134.2, 131.9, 130.3, 130.1, 128.7, 127.8, 124.6, 120.2, 120.0, 117.0, 111.8, 108.5, 95.6, 21.0; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{17}NO_4$, 396.1230, found 396.1232.



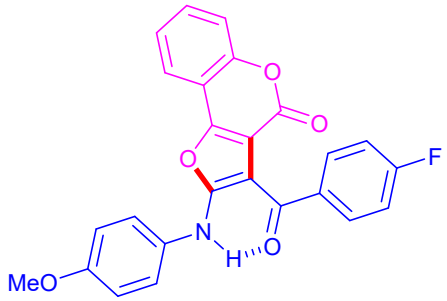
3-benzoyl-2-((3-bromophenyl)amino)-4H-furo[3,2-c]chromen-4-one (**3w**)**:** Isolated yield (57 mg, 50%); Yellow solid crystal; mp. 214-216 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.62 (s, 1H), 7.84 (d, J = 10.0 Hz, 1H), 7.76 (s, 1H), 7.71 (d, J = 10.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 10.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.43-7.39 (m, 3H), 7.33-7.31 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.8, 160.5, 156.0, 152.2, 150.1, 139.7, 138.3, 132.3, 131.1, 130.5, 128.8, 127.9, 127.6, 124.8, 123.4, 122.5, 120.3, 118.2, 117.2, 111.7, 108.4, 96.6; HRMS (ESI-TOF, $[M + Na^+]$): Calcd for $C_{24}H_{14}BrNO_4$, 481.9998, found 482.0009.



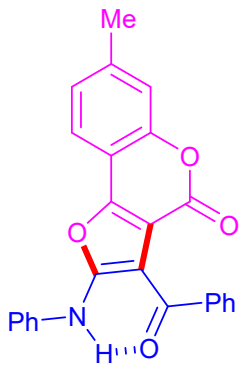
2-(methylamino)-3-(3-methylbenzoyl)-4H-furo[3,2-c]chromen-4-one (**3x**)**:** Isolated yield (50 mg, 60%); Yellow solid powder; mp. 215-217 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.80-7.78 (m, 1H), 7.47-7.44 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.29 (m, 3H), 3.31 (s, 3H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.2, 166.0, 156.2, 151.8, 149.2, 140.4, 137.3, 132.3, 129.7, 129.0, 127.5, 125.9, 124.4, 120.0, 117.0, 112.1, 109.1, 93.9, 28.8, 21.5; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{20}H_{15}NO_4$, 334.1074, found 334.1083.



2-(butylamino)-3-(4-chlorobenzoyl)-4H-furo[3,2-c]chromen-4-one (**3y**)**:** Isolated yield (65 mg, 66%); Yellow solid crystal; mp. 194-196 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.78 (d, J = 5.0 Hz, 1H), 7.58 (d, J = 5.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.39-7.37 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 3.66 (q, J = 6.6 Hz, 2H), 1.79-1.73 (m, 2H), 1.55-1.47 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 188.4, 165.7, 156.3, 151.9, 149.4, 138.9, 137.5, 130.0, 129.9, 127.9, 124.5, 120.1, 117.0, 112.0, 108.8, 93.4, 42.4, 31.9, 20.0, 13.7; HRMS (ESI-TOF, [M + Na]$^+$): Calcd for $C_{22}H_{18}ClNO_4$, 418.0817, found 418.0819.

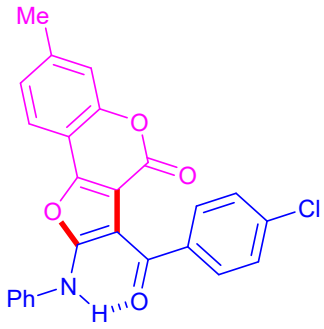


3-(4-fluorobenzoyl)-2-((4-methoxyphenyl)amino)-4H-furo[3,2-c]chromen-4-one (**3z**)**:** Isolated yield (71 mg, 66%); Brown solid crystal; mp. 170-172 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.58 (s, 1H), 7.79 (d, J = 5.0 Hz, 1H), 7.73-7.70 (m, 2H), 7.50-7.47 (m, 1H), 7.43 (d, J = 10.0 Hz, 2H), 7.40 (d, J = 10.0 Hz, 1H), 7.36-7.33 (m, 1H), 7.11 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 10.0 Hz, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 188.8, 166.1, 164.1, 161.8, 157.2, 156.2, 152.0, 149.7, 136.3, 131.2, 131.1, 130.2, 129.6, 124.6, 122.0, 120.2, 117.0, 115.0, 114.8, 111.8, 108.4, 95.0, 55.7; HRMS (ESI-TOF, [M + H]$^+$): Calcd for $C_{25}H_{16}FNO_5$, 430.1085, found 430.1097.

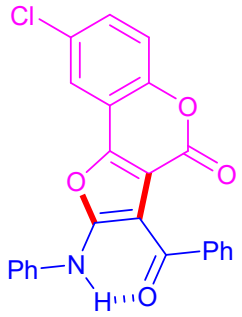


3-benzoyl-7-methyl-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3za**)**:** Isolated yield (73 mg, 74%); Yellow solid powder; mp. 210-212 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.70 (s, 1H), 7.72 (d, J = 5.0 Hz, 3H), 7.56 (t, J = 7.5 Hz, 1H), 7.53-7.51 (m, 2H), 7.48-7.44 (m, 4H), 7.23-7.20 (m, 2H), 7.18 (d, J =10.0 Hz, 1H), 2.47 (s, 3H); ^{13}C{^{1}H}

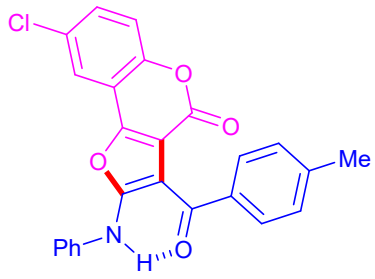
NMR (125 MHz, $CDCl_3$): δ 190.6, 161.0, 156.3, 152.3, 150.3, 141.5, 140.1, 137.0, 131.9, 129.8, 128.7, 127.8, 125.8, 124.7, 119.9, 119.8, 117.3, 109.3, 107.5, 95.9, 21.9.; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{25}H_{17}NO_4$, 396.1230, found 396.1226.



3-(4-chlorobenzoyl)-7-methyl-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3zb**)**:** Isolated yield (67 mg, 62%); Yellow solid powder; mp. 215-217 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 10.69 (s, 1H), 7.72 (d, J = 5.0 Hz, 1H), 7.65 (d, J = 5.0 Hz, 2H), 7.52-7.51 (m, 2H), 7.48-7.45 (m, 2H), 7.42 (d, J = 10.0 Hz, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 5.0 Hz, 1H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.1, 161.2, 156.4, 152.4, 150.5, 141.7, 138.4, 138.1, 136.8, 130.2, 129.8, 128.1, 125.9, 124.9, 120.0, 119.9, 117.3, 109.2, 107.2, 95.7, 22.0; HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{25}H_{16}ClNO_4$, 430.0841, found 430.0848.



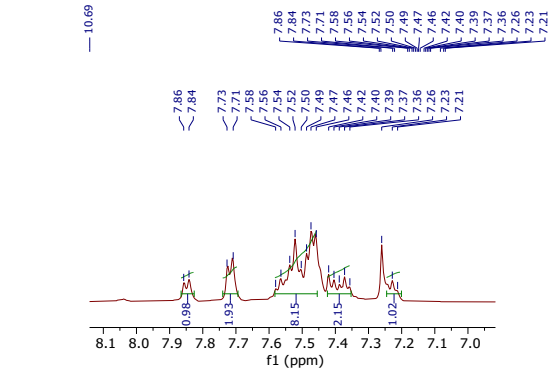
3-benzoyl-8-chloro-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3zc**)**:** Isolated yield (66 mg, 64%); Brown solid crystal; mp. 180-182 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 10.68 (s, 1H), 7.78 (s, 1H), 7.70 (d, J = 10.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.51-7.49 (m, 4H), 7.47-7.44 (m, 3H), 7.43-7.42 (m, 1H), 7.35-7.33 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 190.6, 161.4, 155.5, 150.3, 148.3, 139.9, 136.6, 132.1, 130.2, 130.1, 129.9, 128.7, 127.9, 125.1, 120.0, 119.6, 118.5, 112.9, 109.4, 96.0; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{24}H_{14}ClNO_4$, 416.0684, found 416.0682.

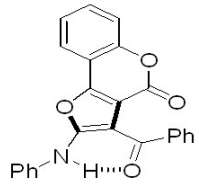


8-chloro-3-(4-methylbenzoyl)-2-(phenylamino)-4H-furo[3,2-c]chromen-4-one (**3zd**)**:** Isolated yield (77 mg, 72%); Brown solid crystal; mp. 192-194 °C. Isolation: hexane/ethyl acetate (20/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.61 (s, 1H), 7.78-7.77 (m, 1H), 7.62 (d, J = 10.0 Hz, 2H), 7.50-7.47 (m, 5H), 7.44-7.42 (m, 1H), 7.36-7.34 (m, 1H), 7.25-7.22 (m, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.2, 161.2, 155.6, 150.3, 148.2, 142.9, 137.1, 136.8, 130.2, 130.1, 129.9, 128.9, 128.6, 125.0, 119.8, 119.6, 118.5, 113.0, 109.5, 96.0, 21.9; HRMS (ESI-TOF, [M + Na]$^{+}$): Calcd for $C_{25}H_{16}ClNO_4$, 430.0841, found 430.0851.

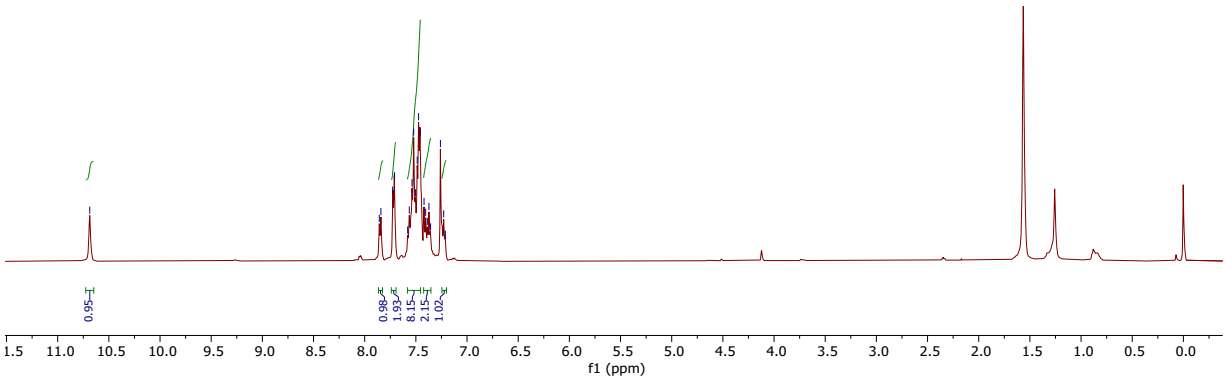
5. Copies of ^{1}H and ^{13}C NMR Spectra

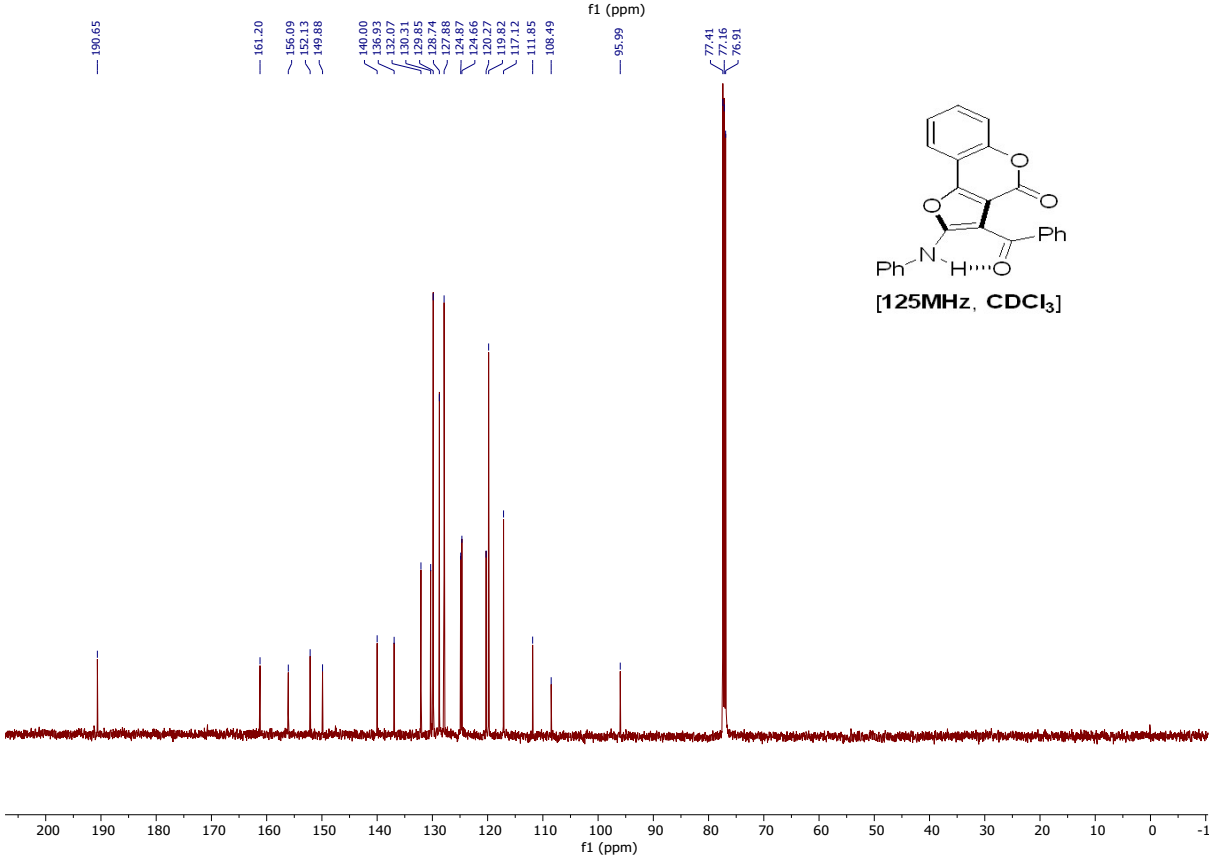
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3a





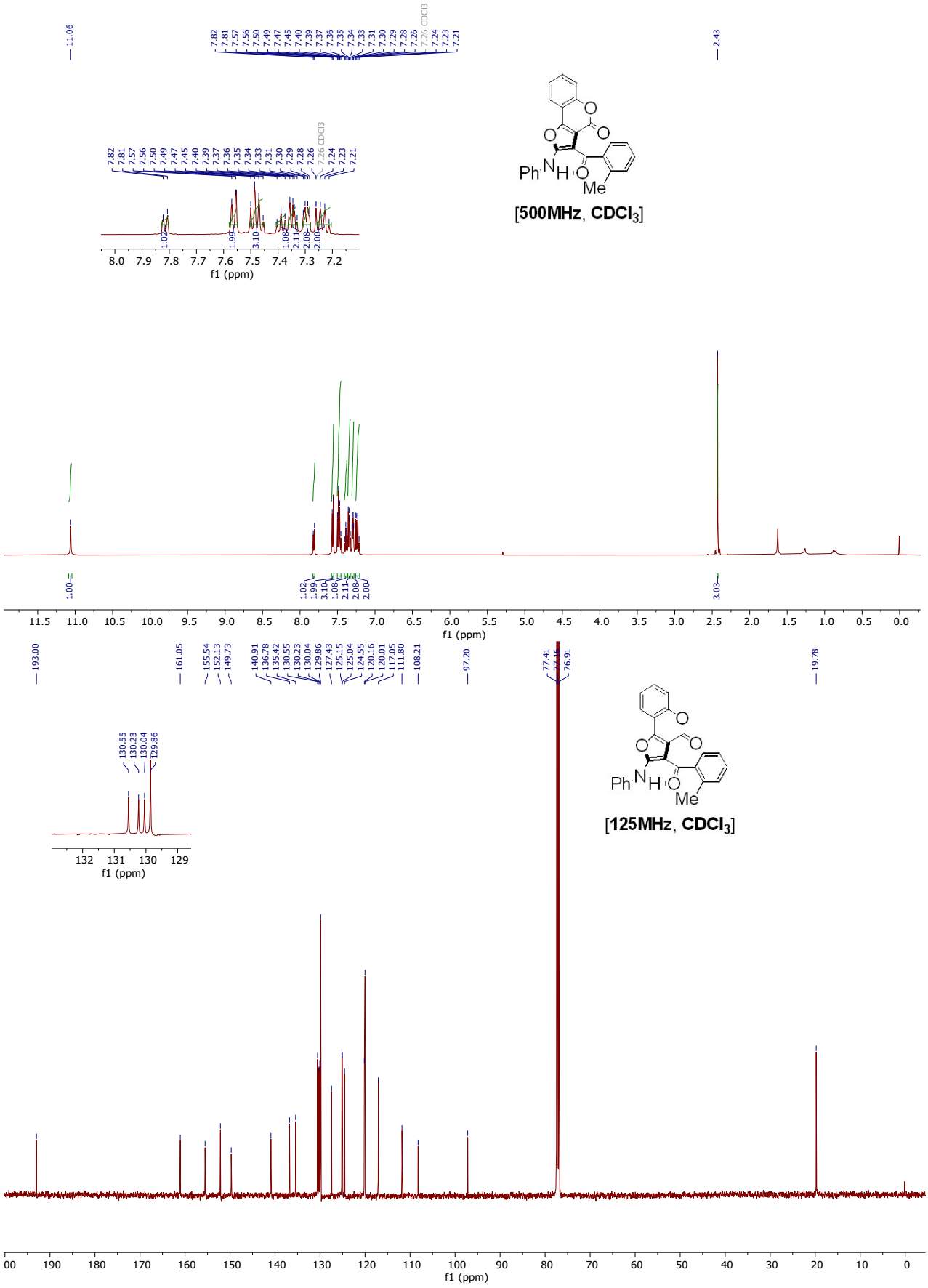
[500MHz, $CDCl_3$]



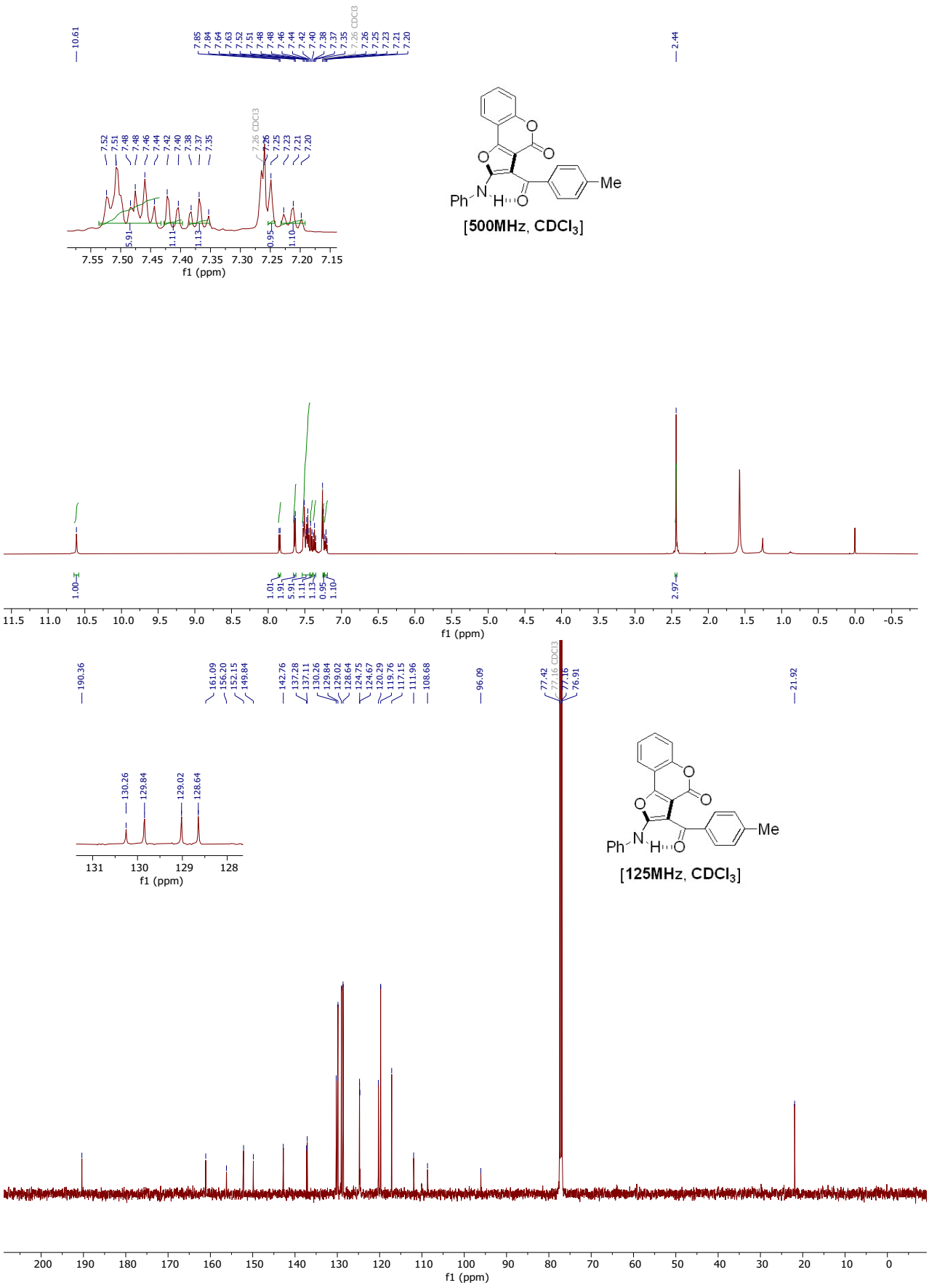


[125MHz, $CDCl_3$]

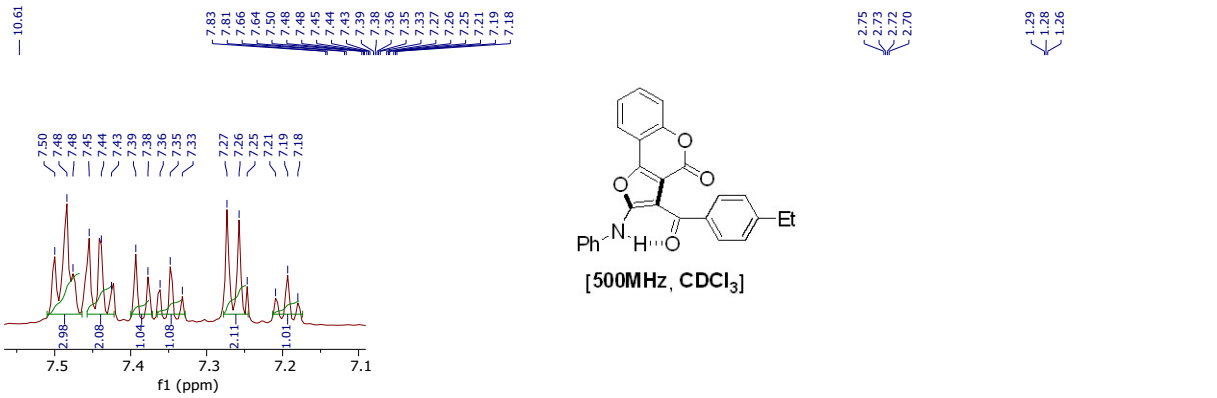
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3b

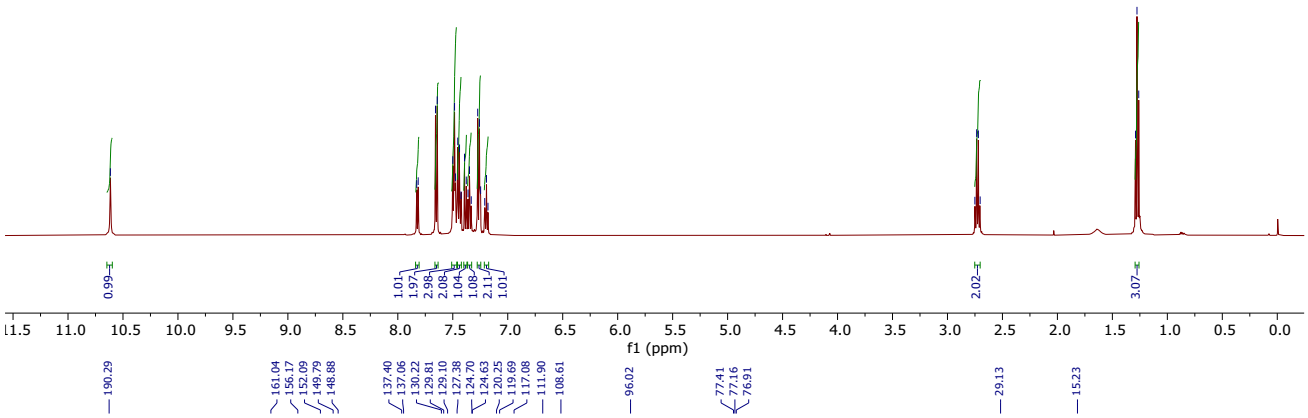


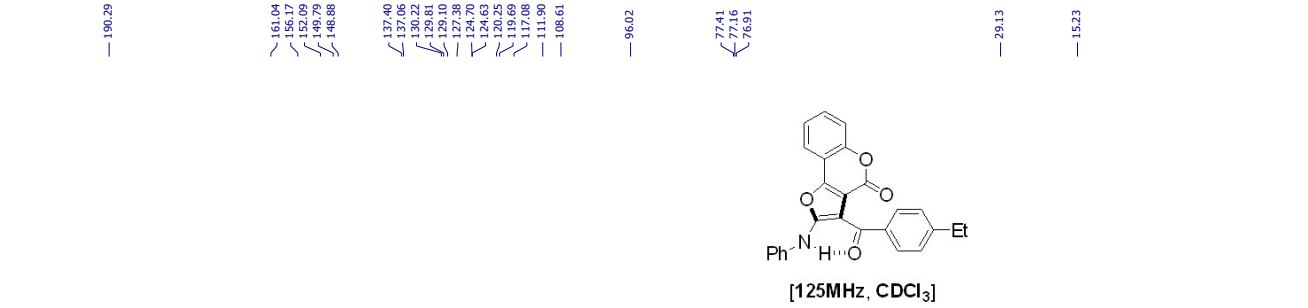
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3c

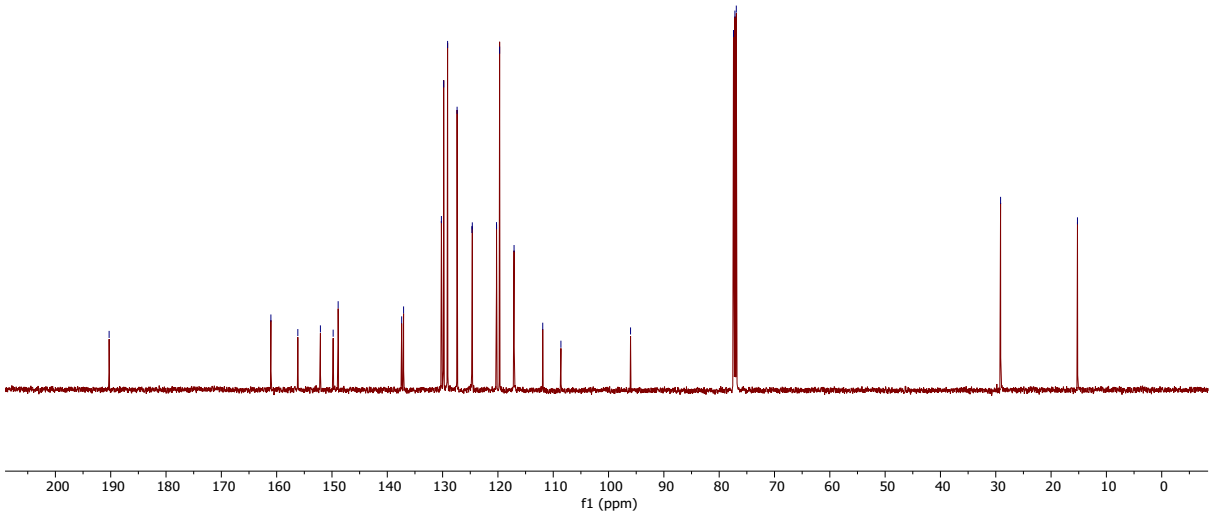


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3d

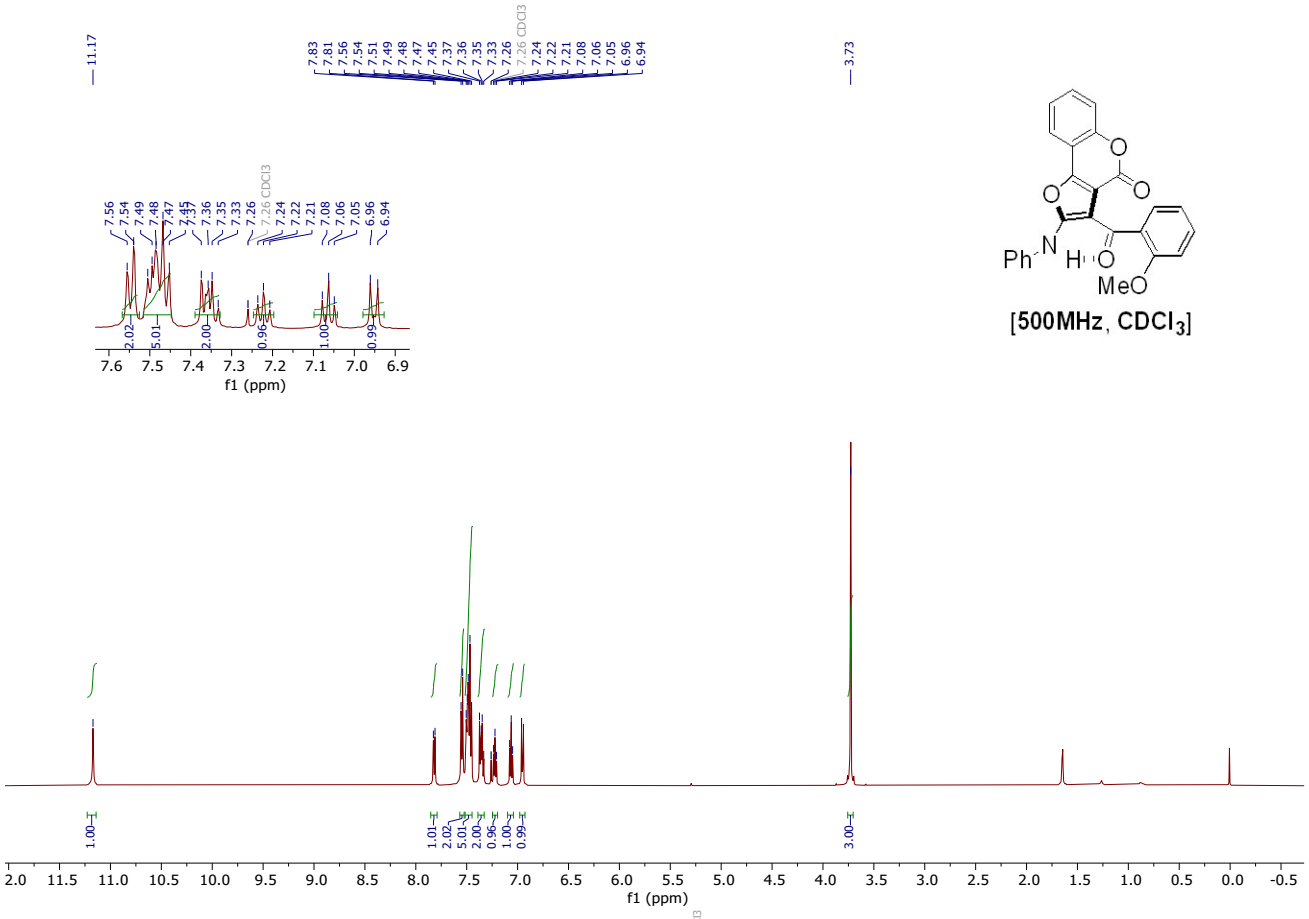


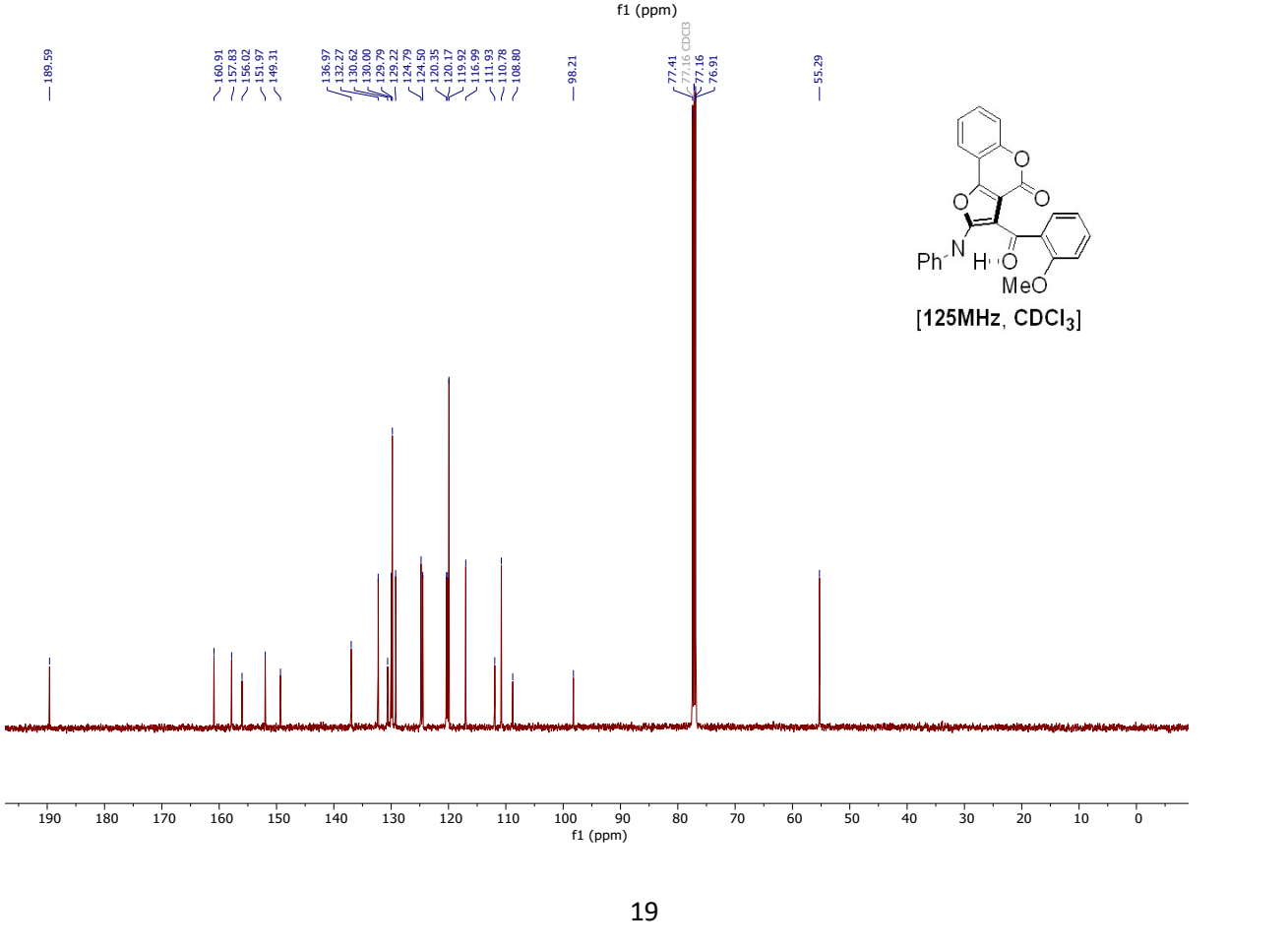




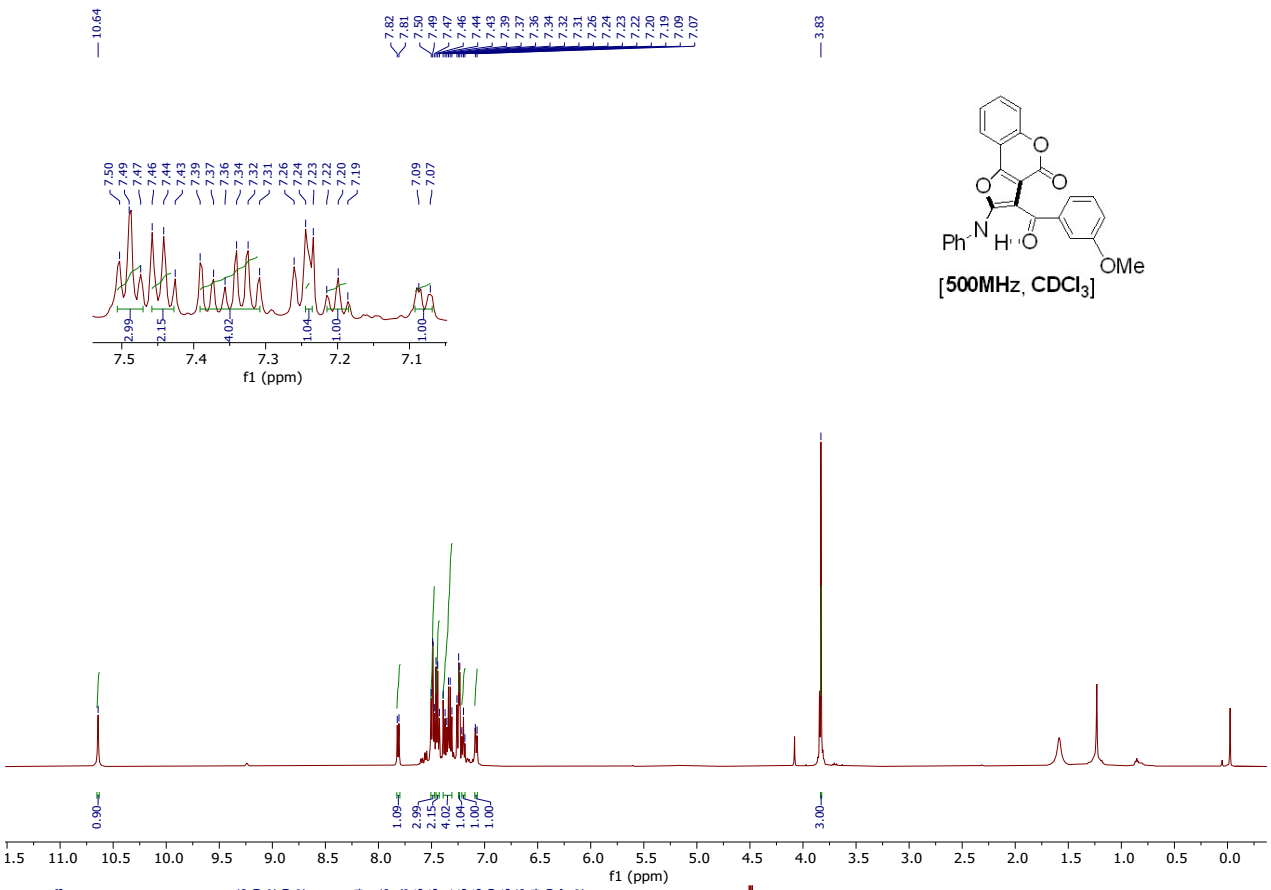


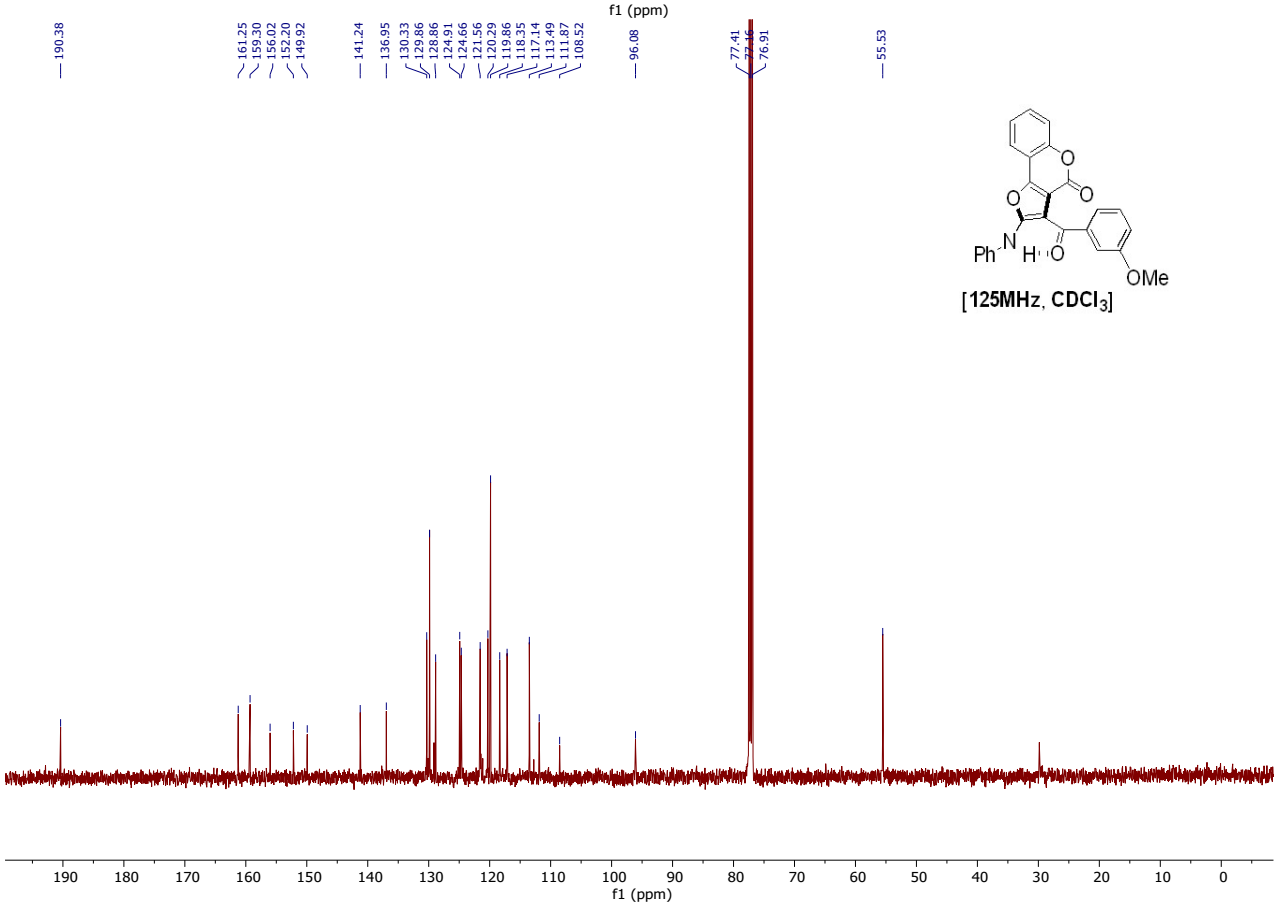
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3e



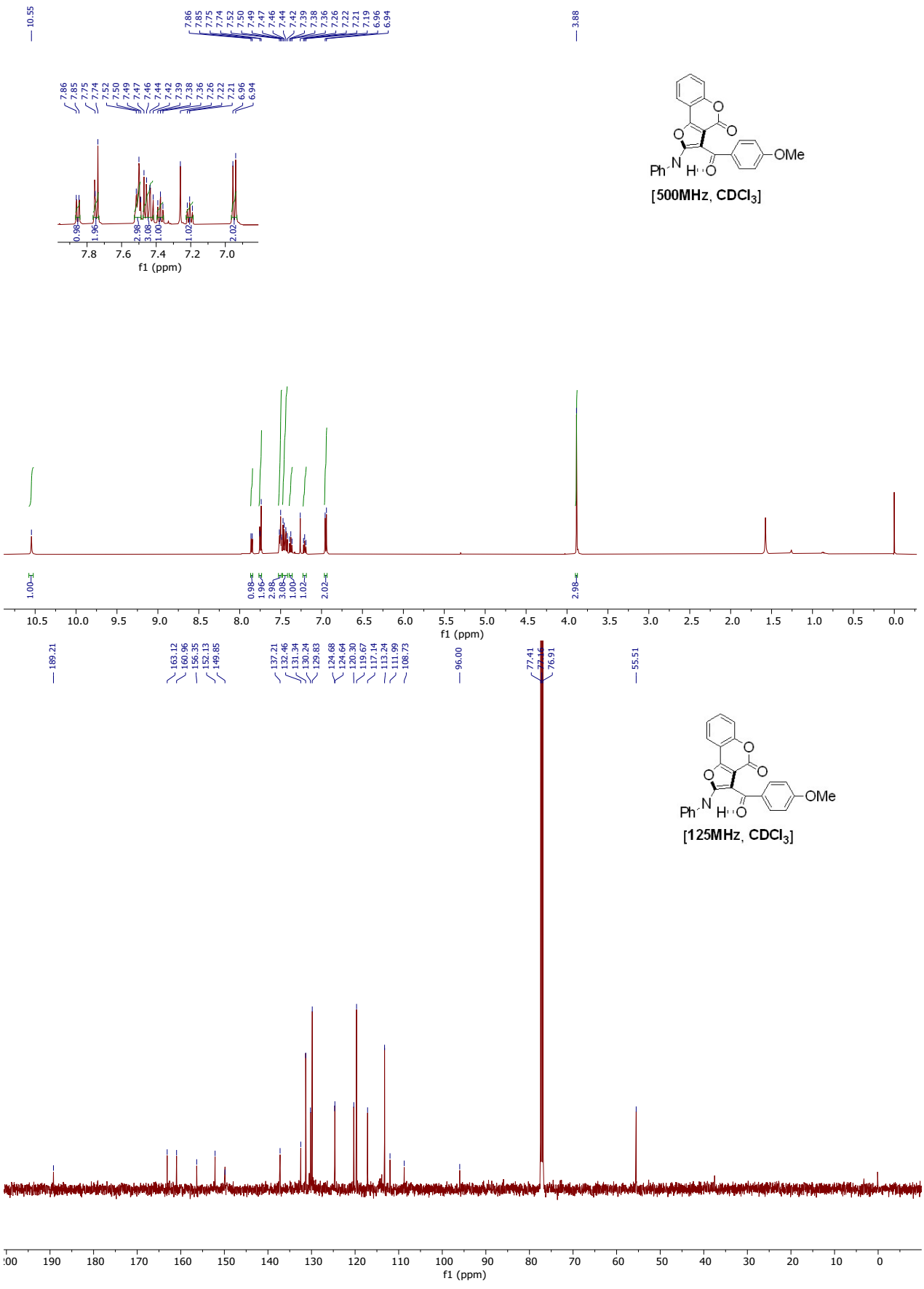


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3f

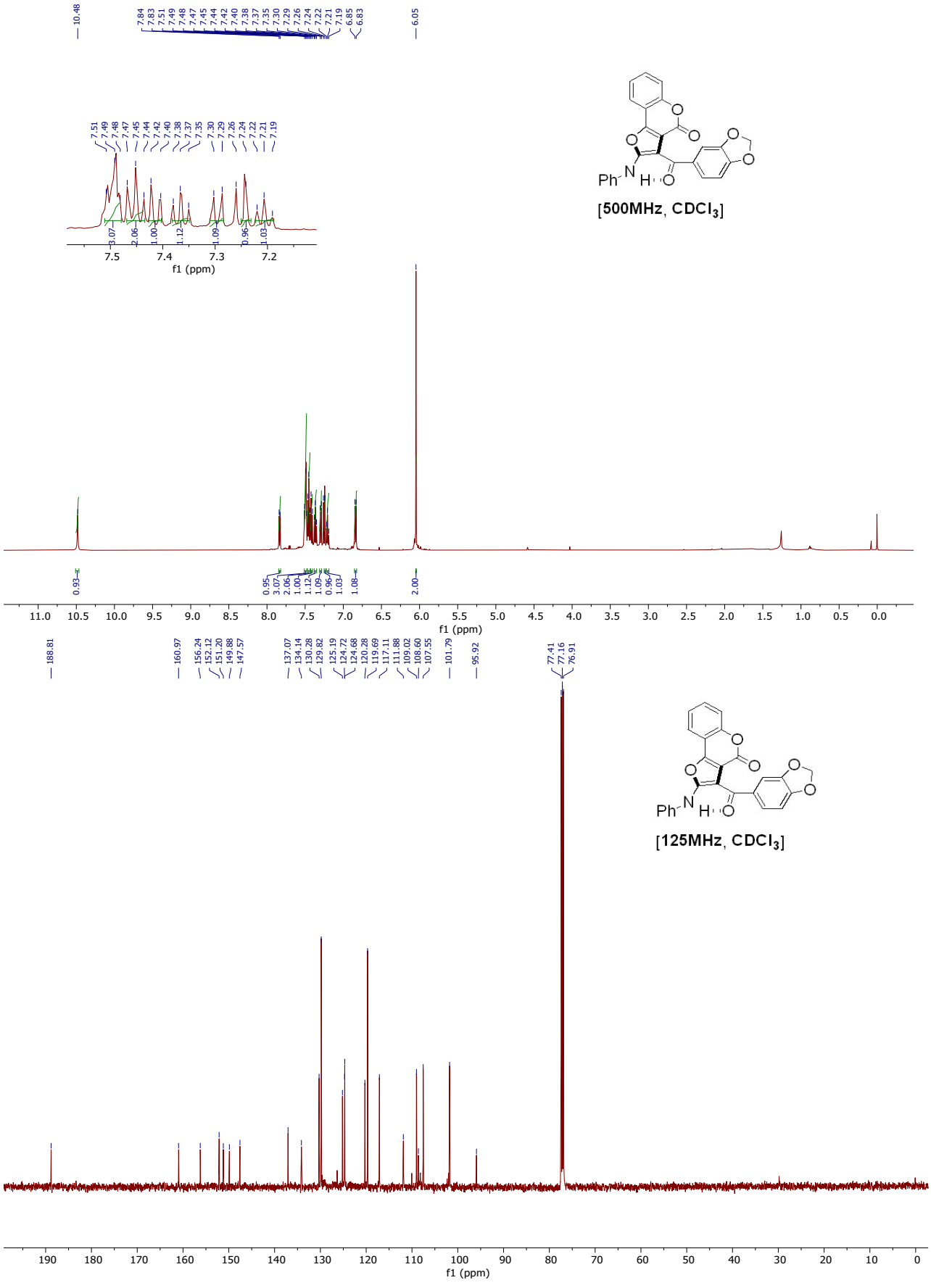




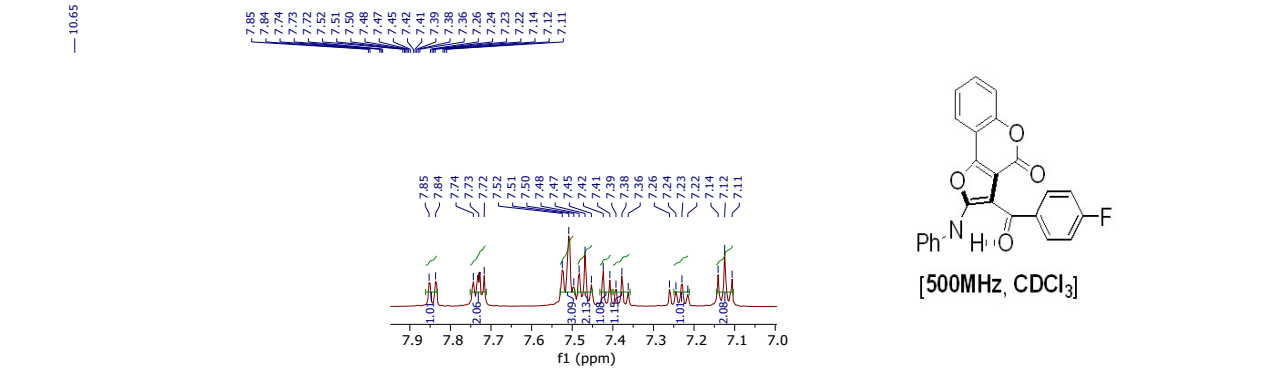
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3g

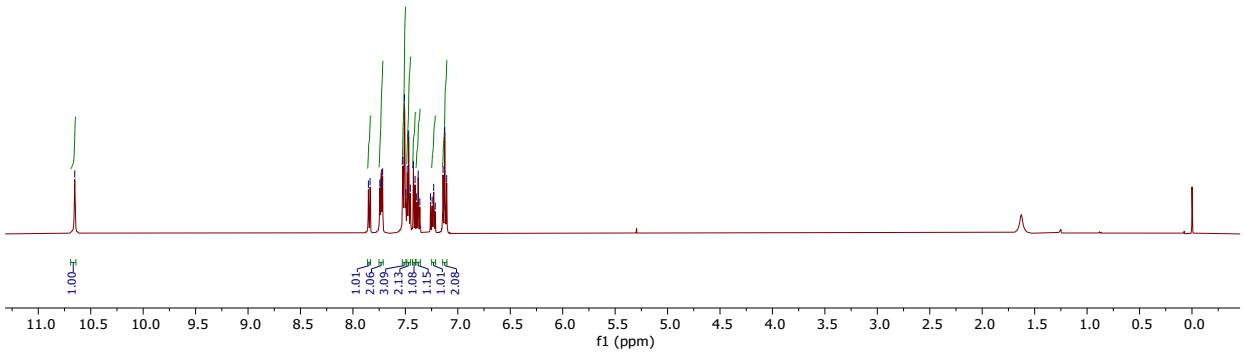


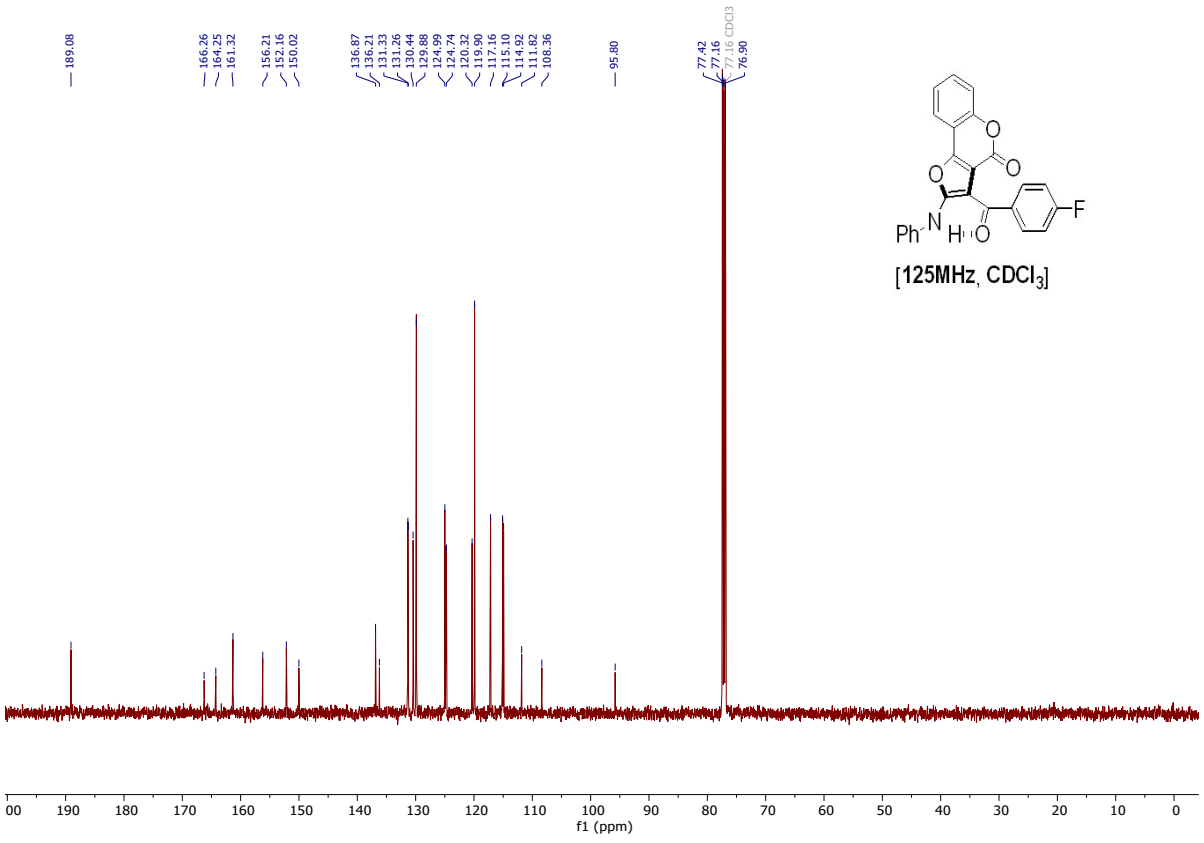
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3h



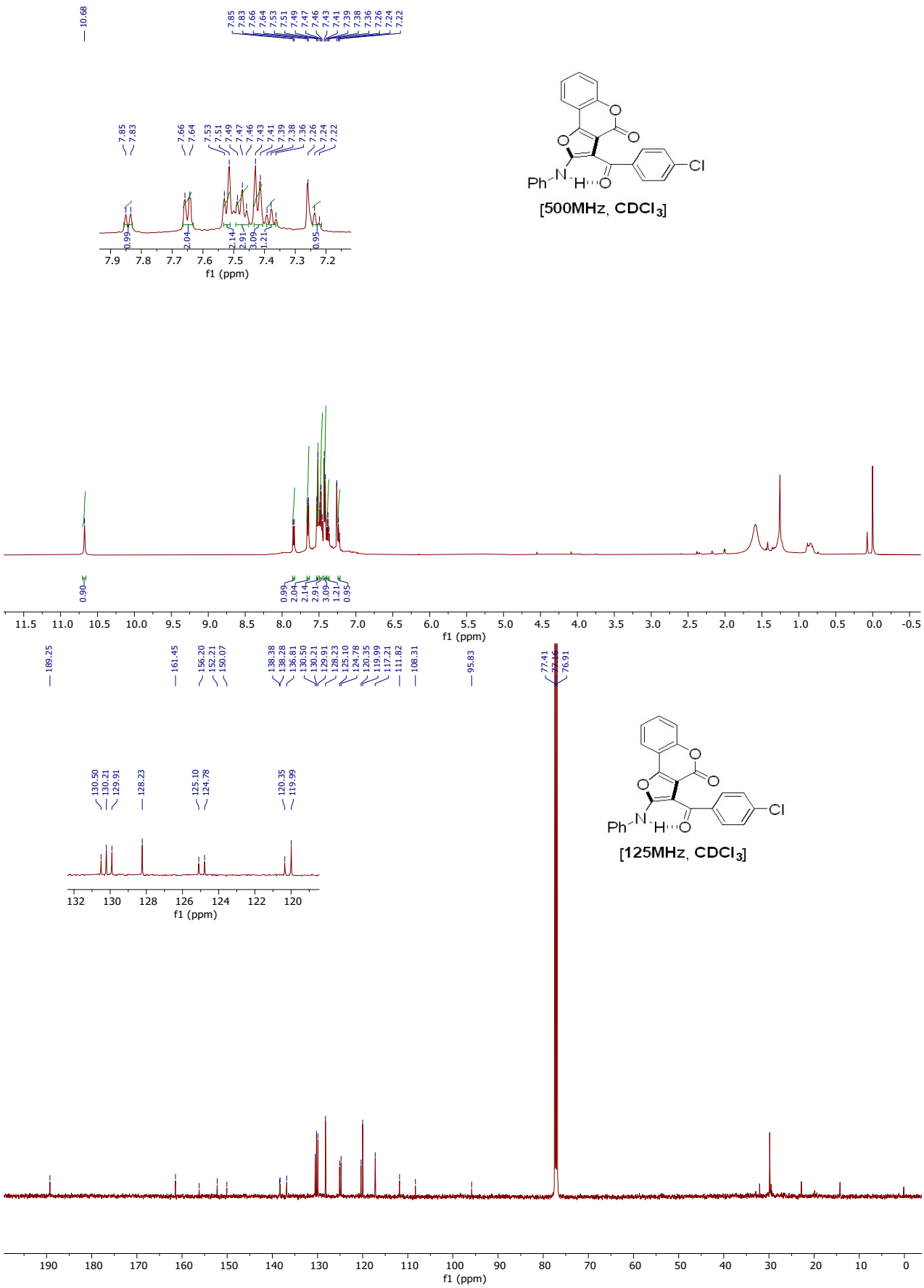
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3i



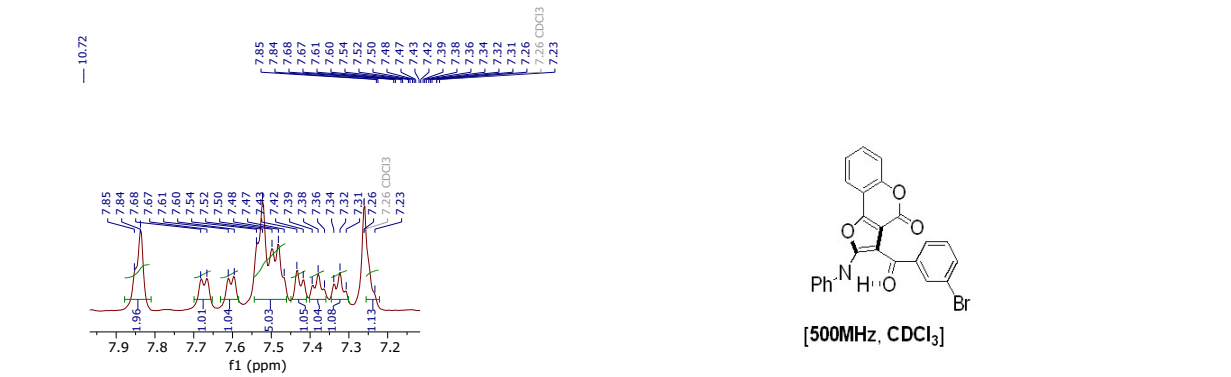


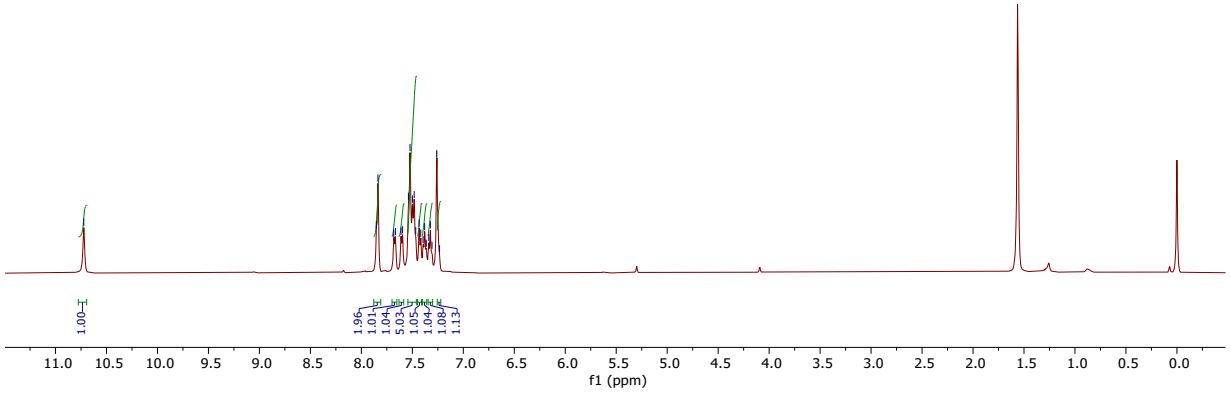


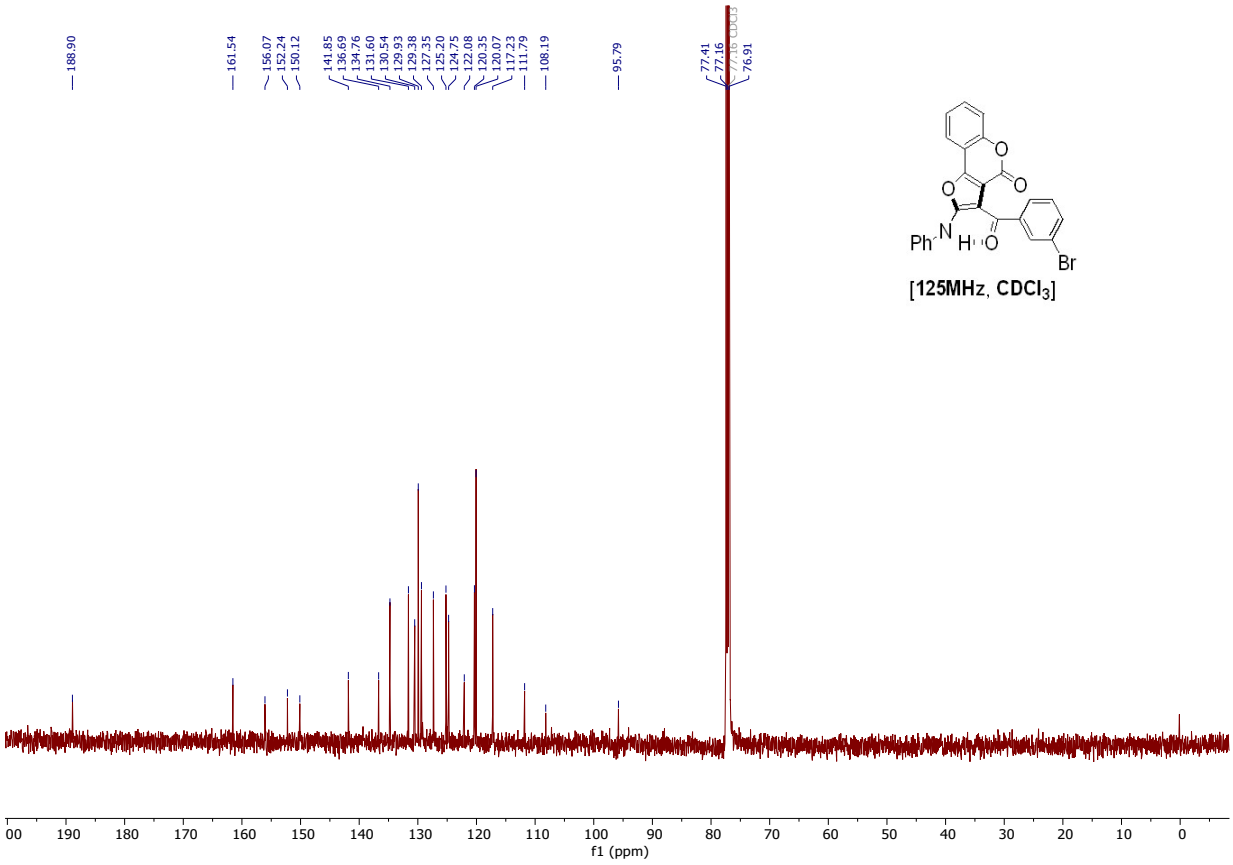
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3j



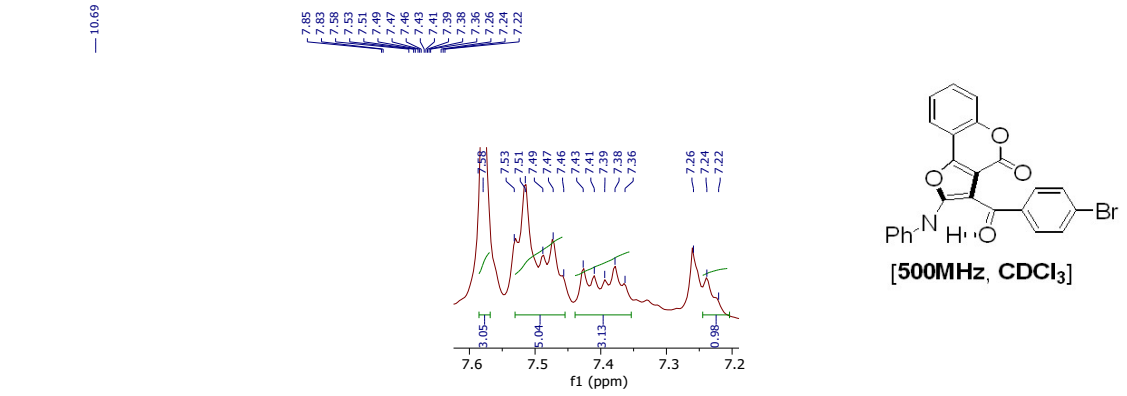
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3k

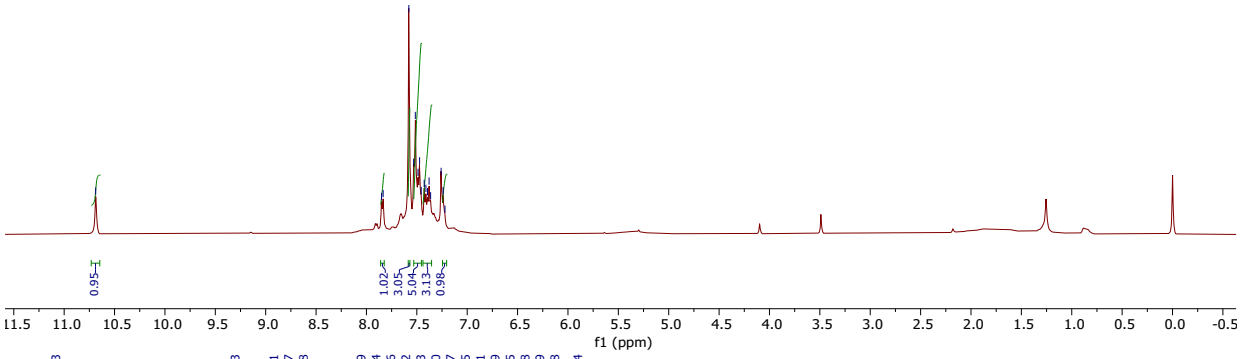


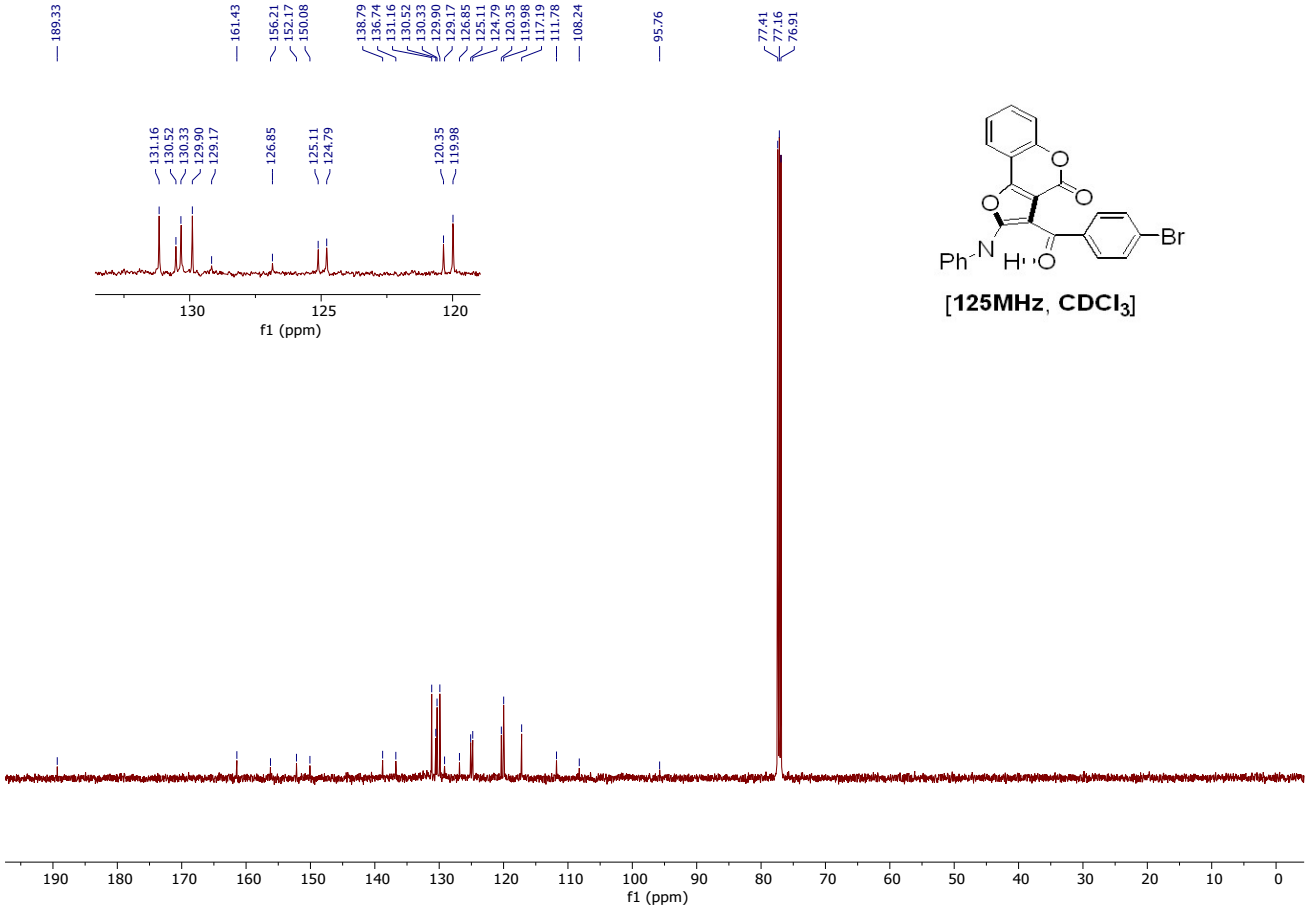




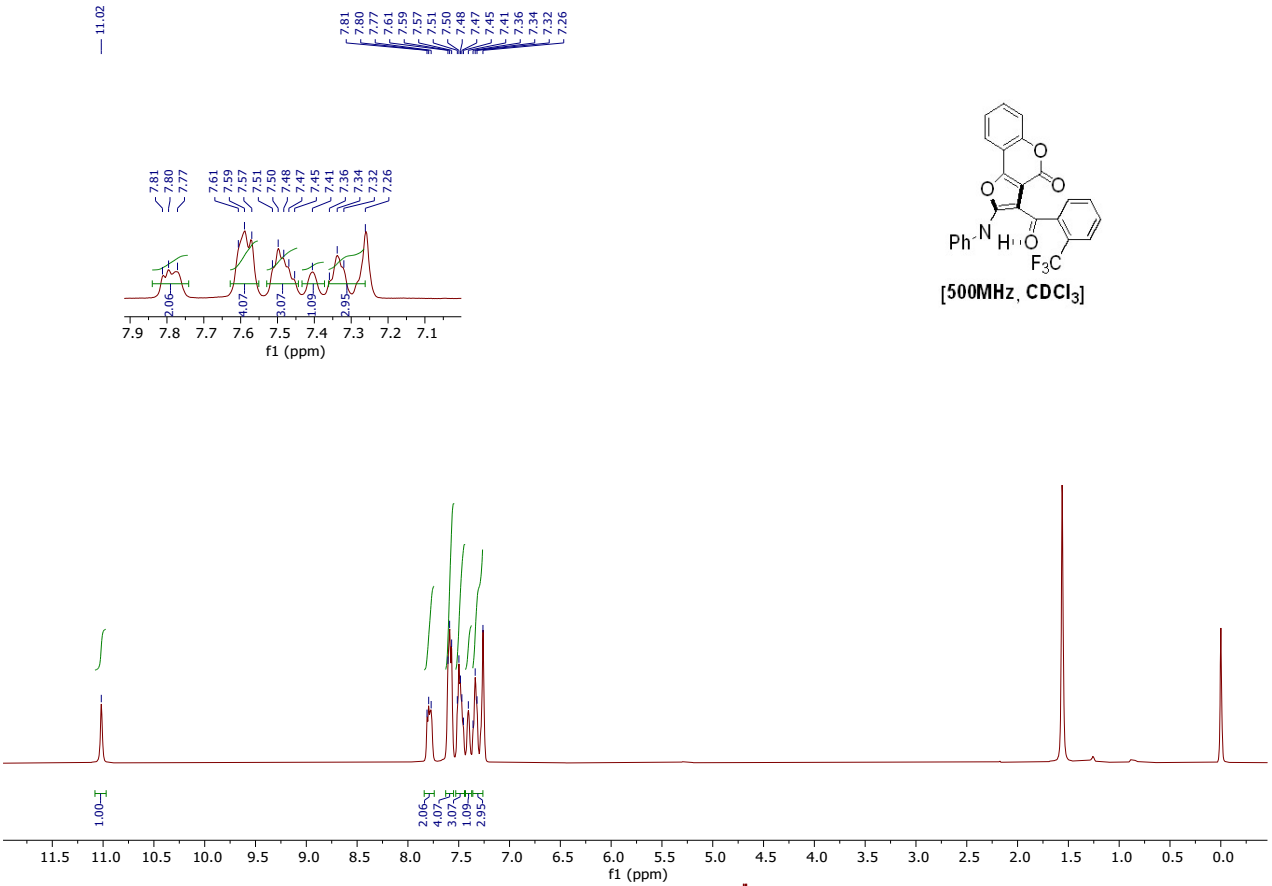
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3l

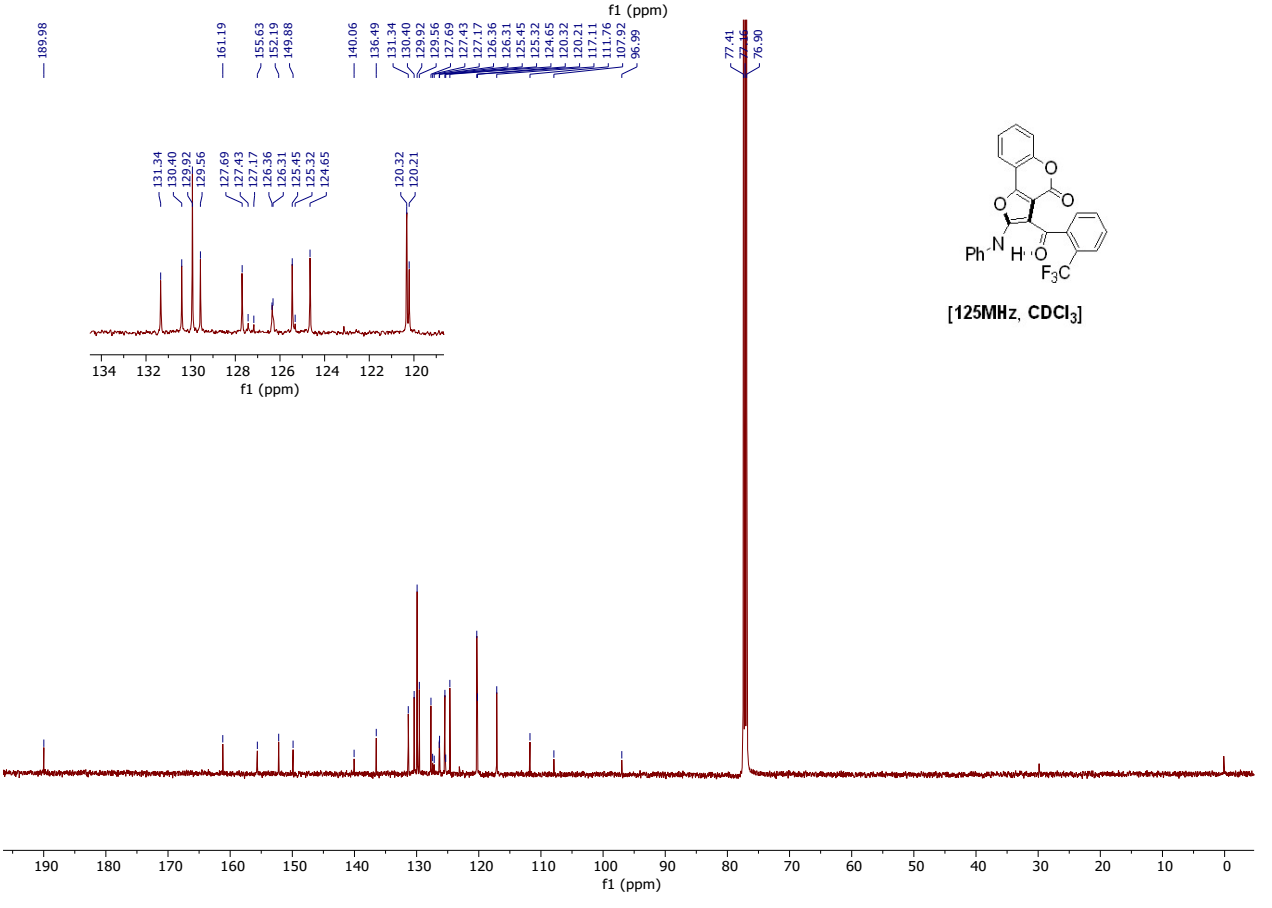




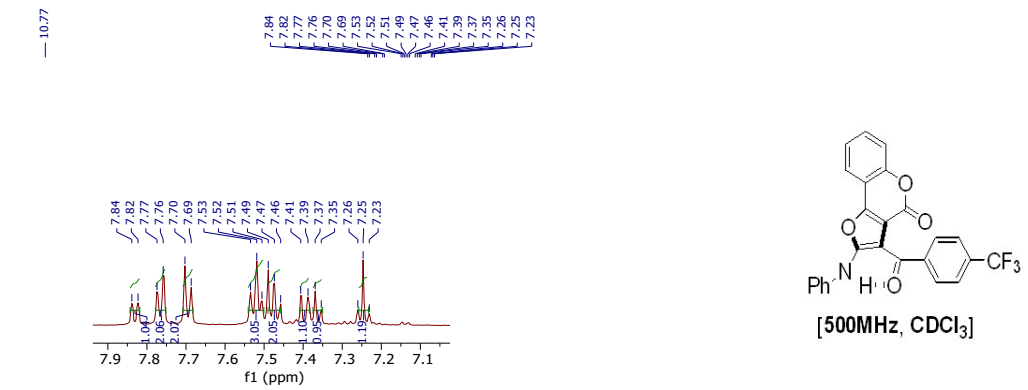


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3m

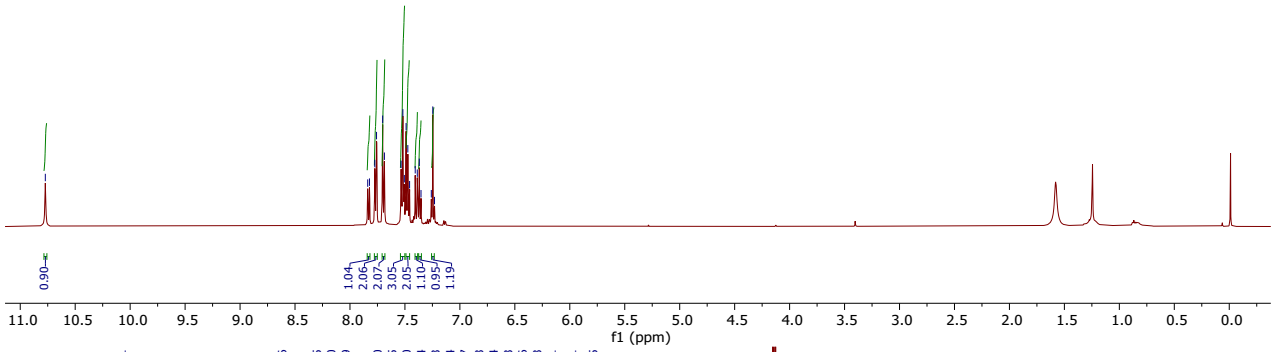


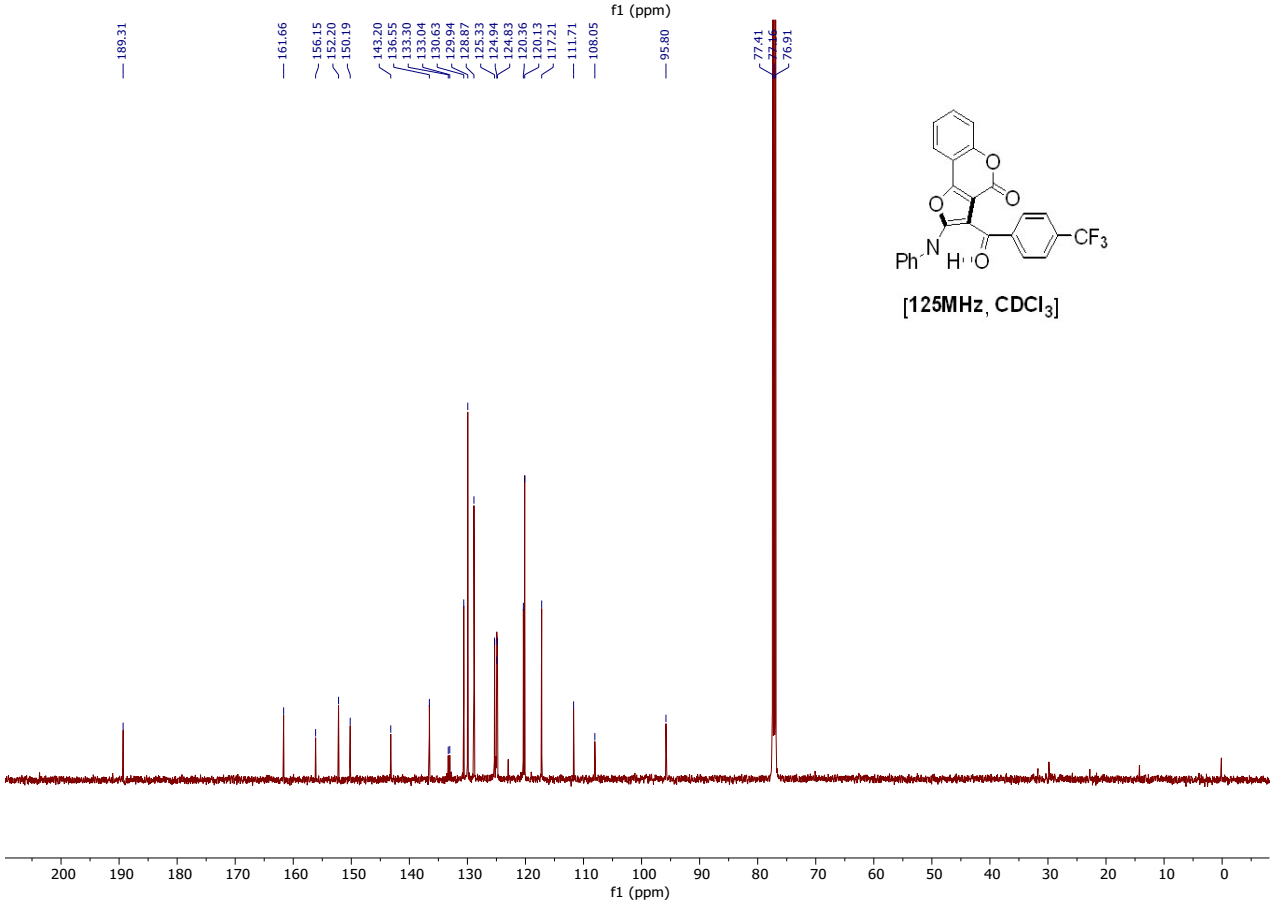


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3n



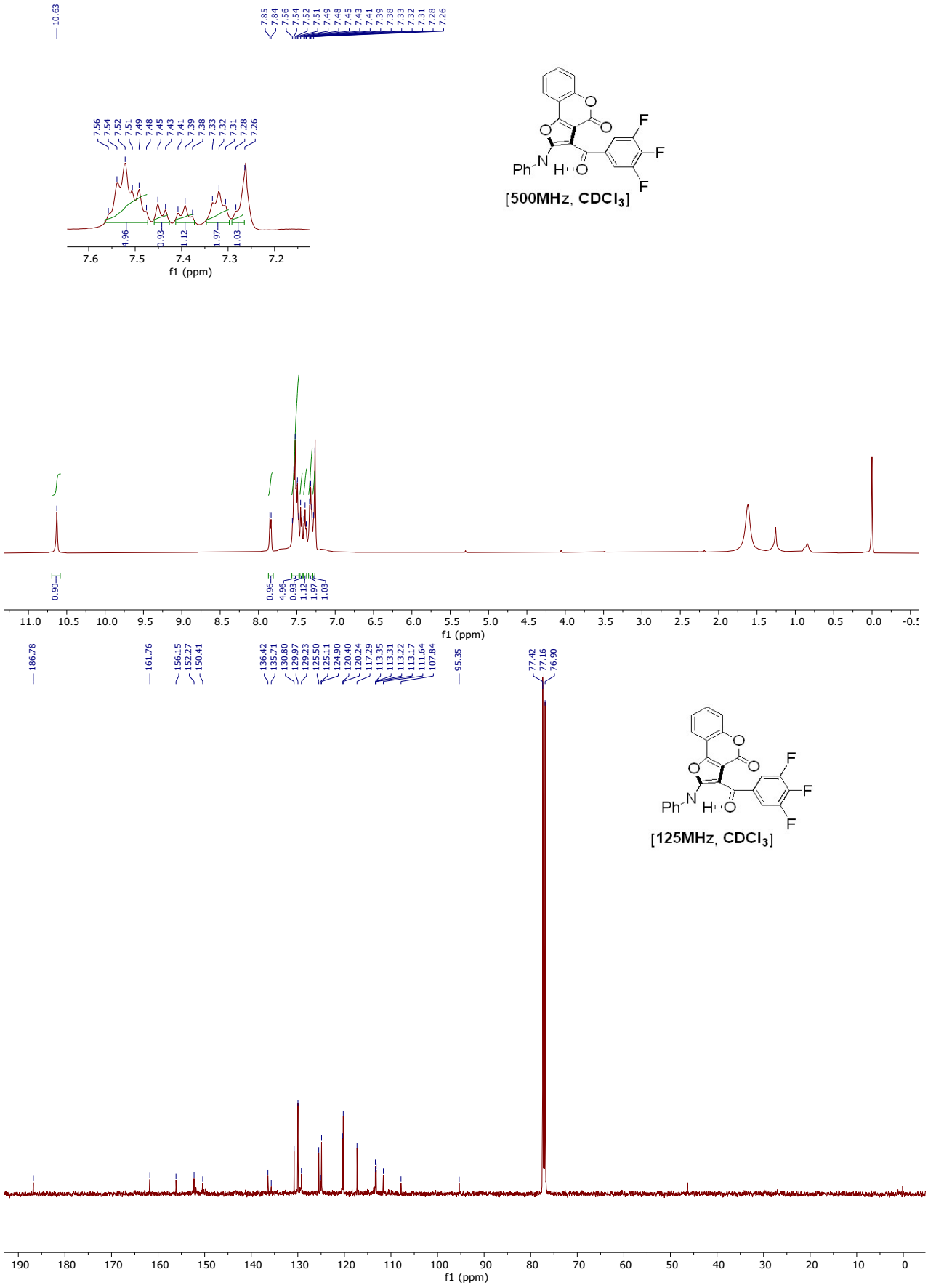
[500MHz, $CDCl_3$]



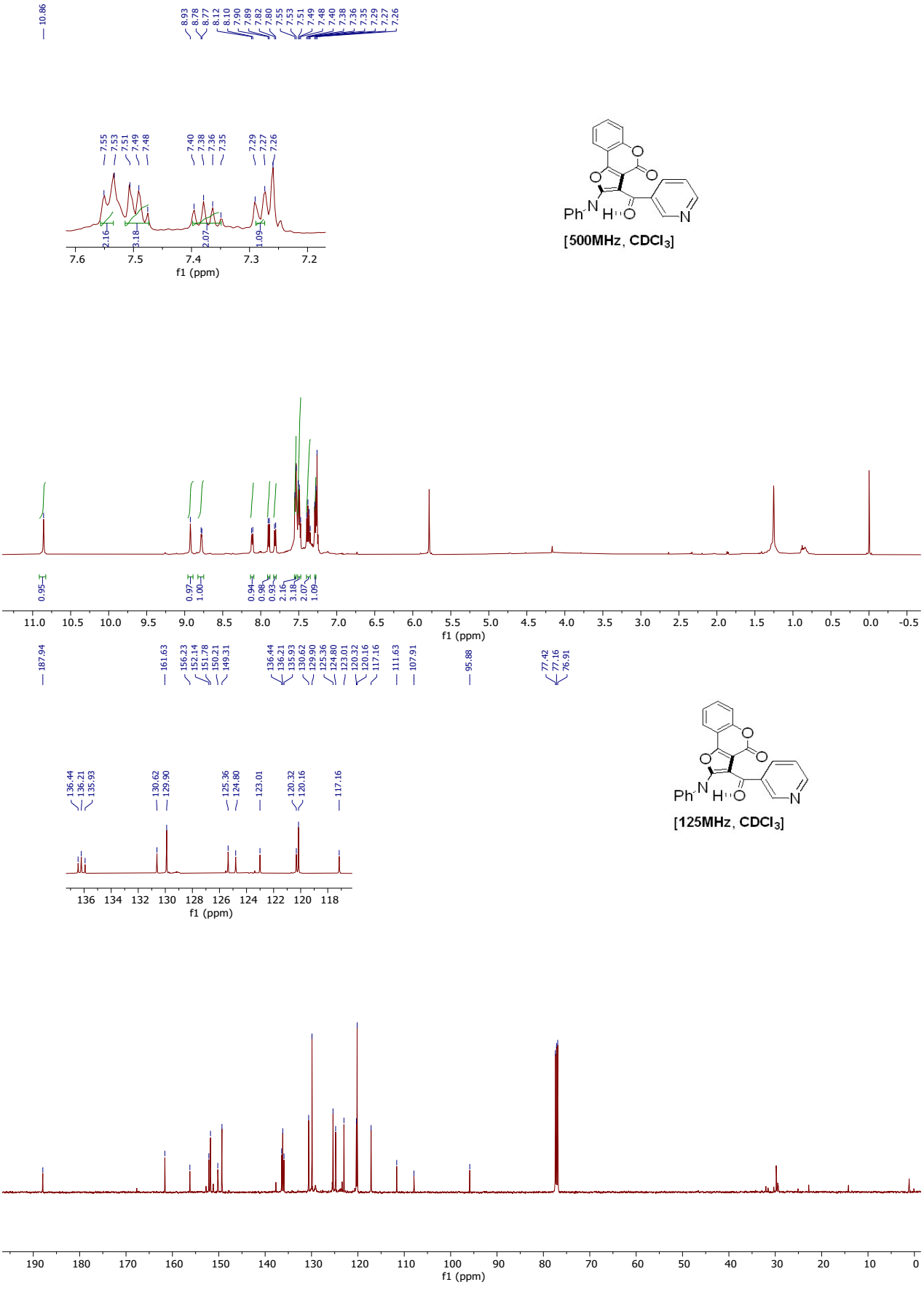


[125MHz, $CDCl_3$]

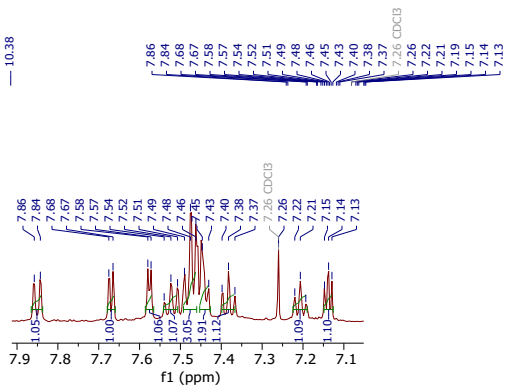
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3o

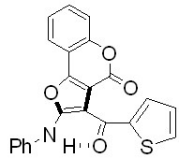


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3p

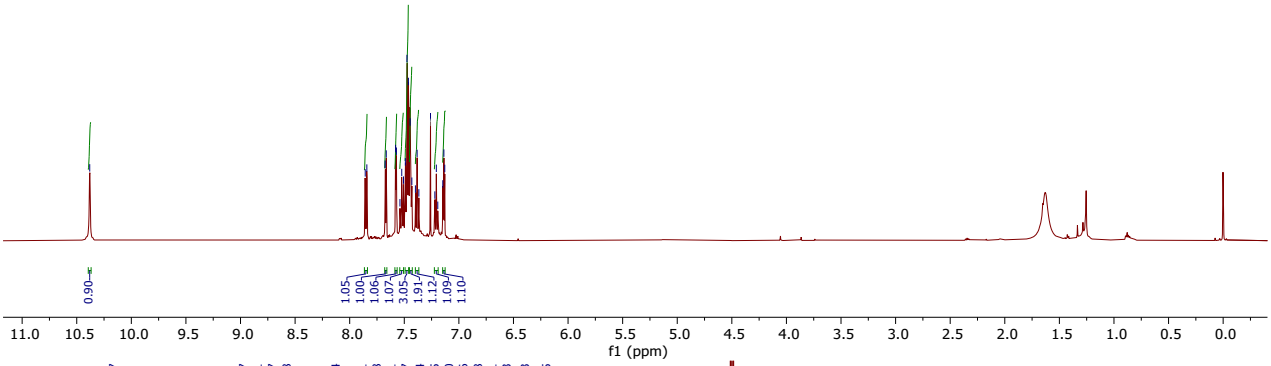


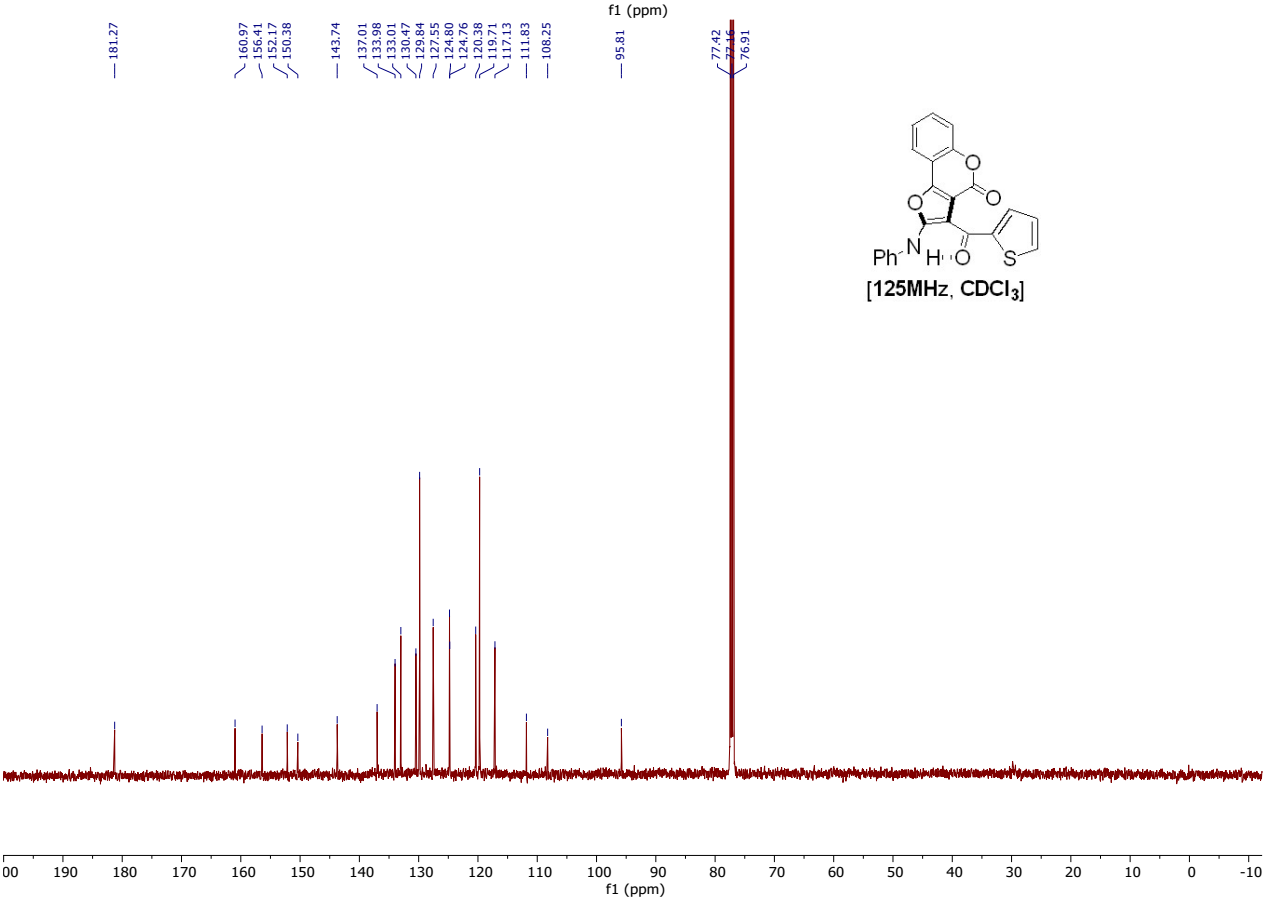
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3q





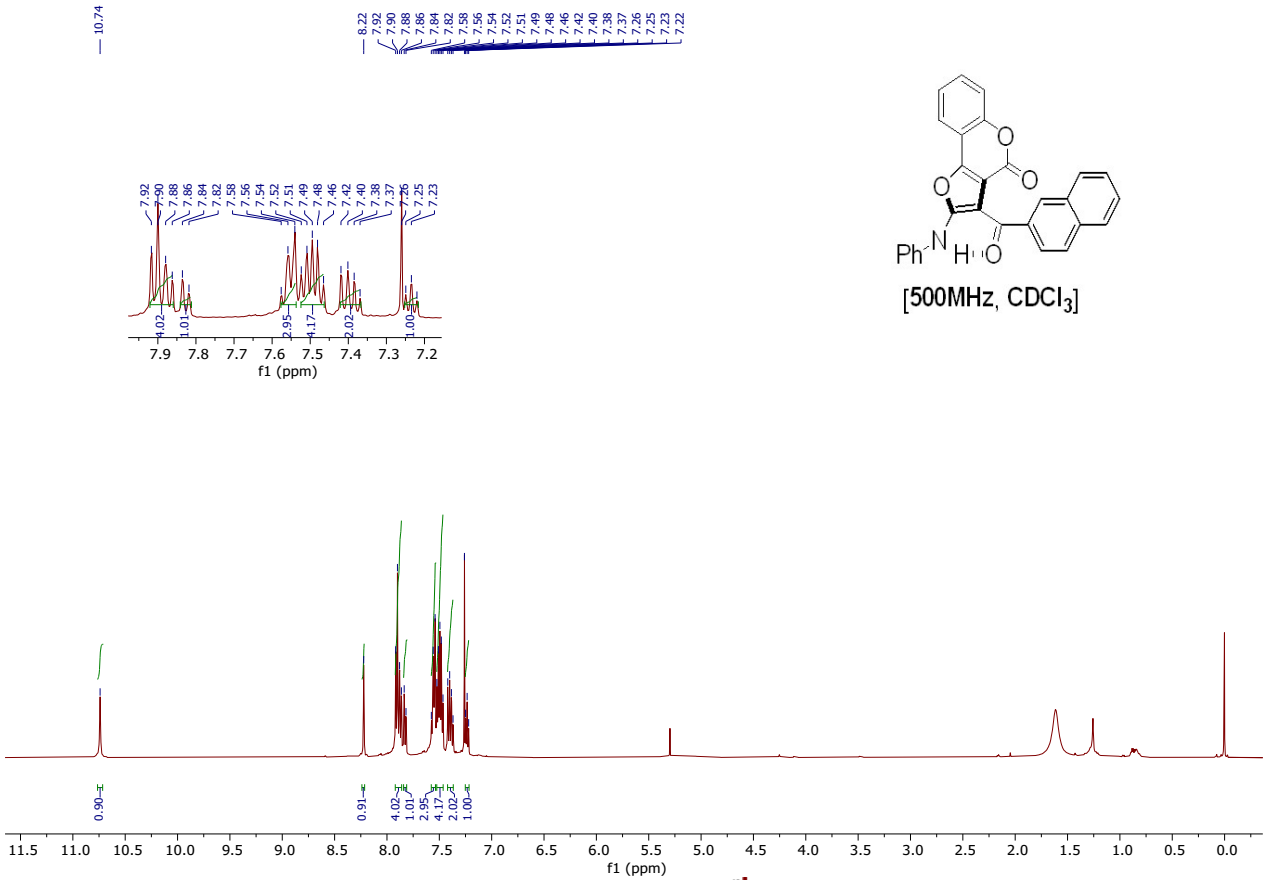
[500MHz, $CDCl_3$]

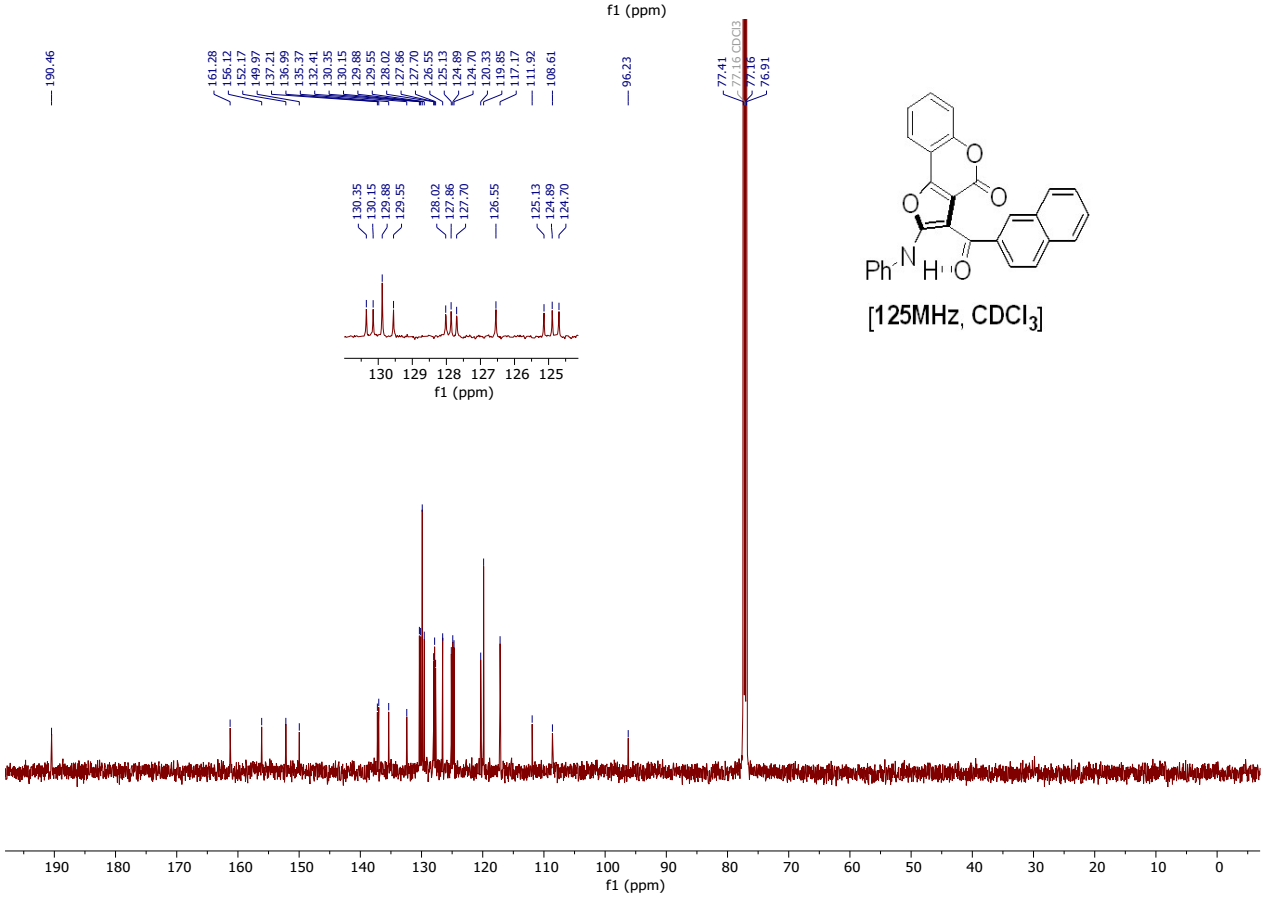




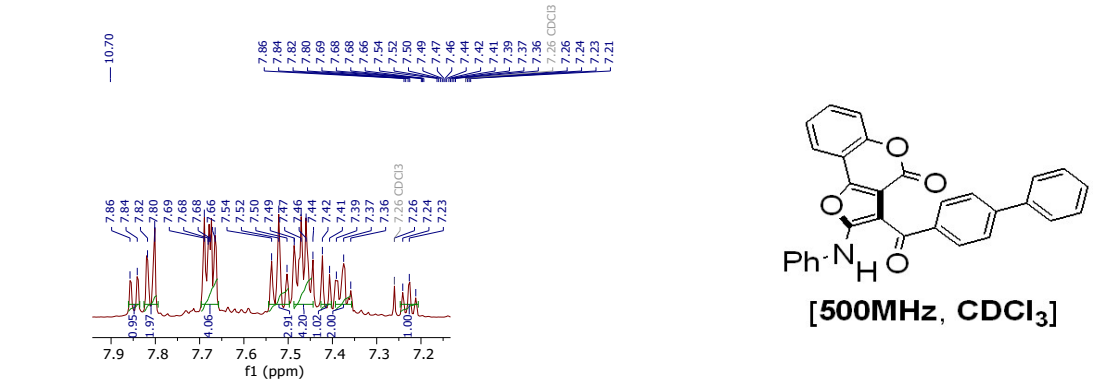
[125MHz, $CDCl_3$]

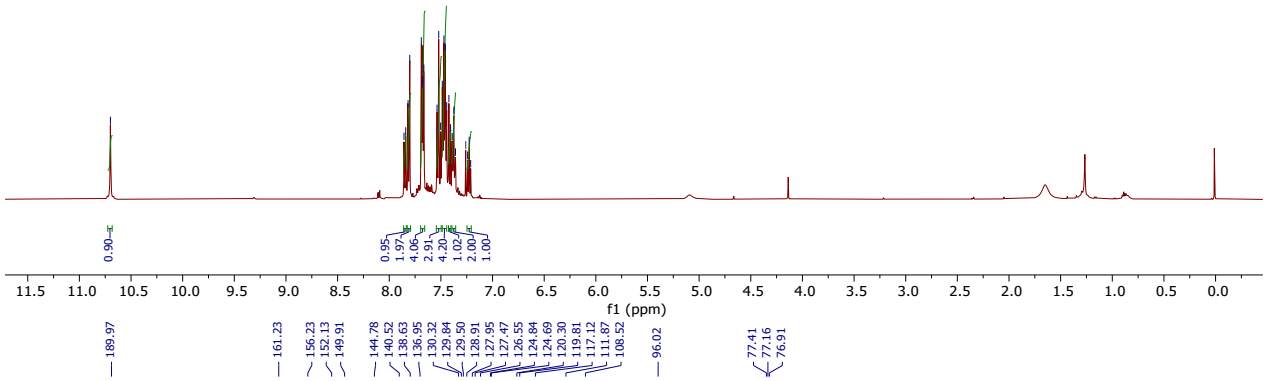
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3r

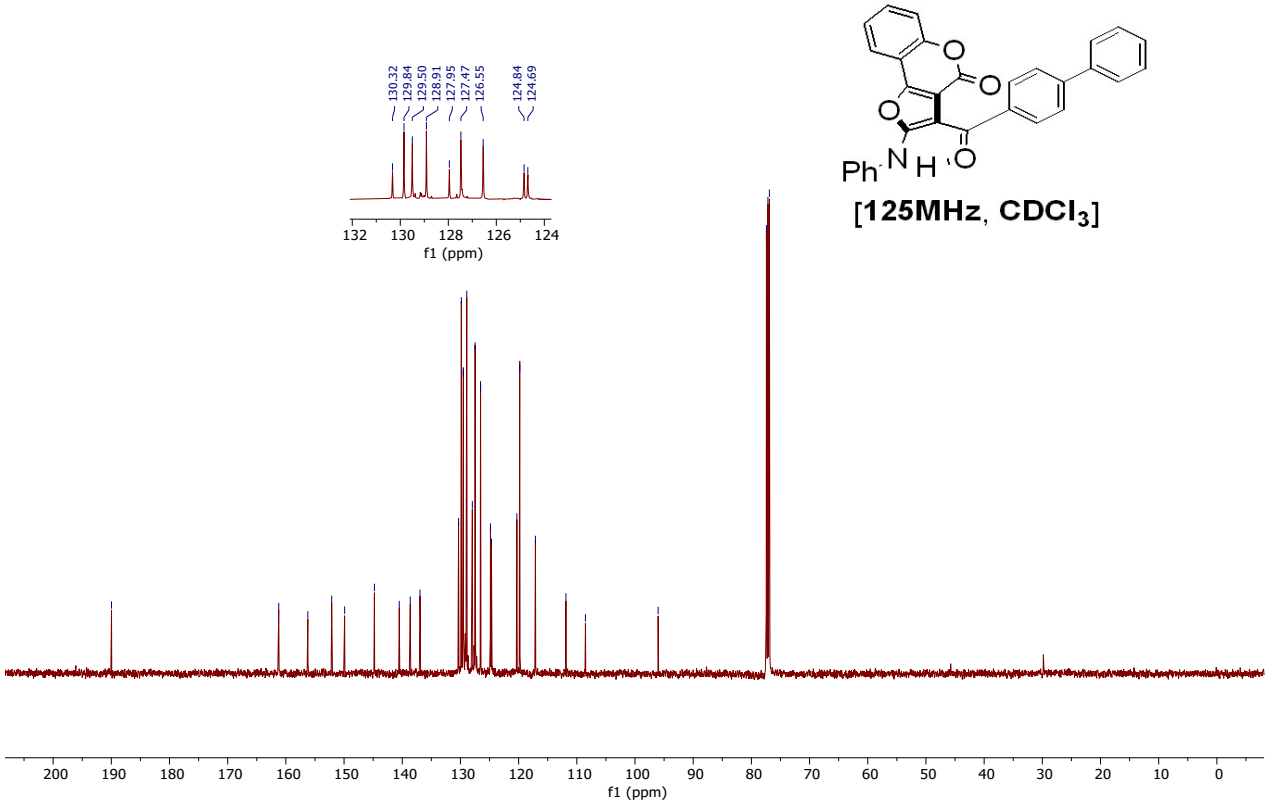




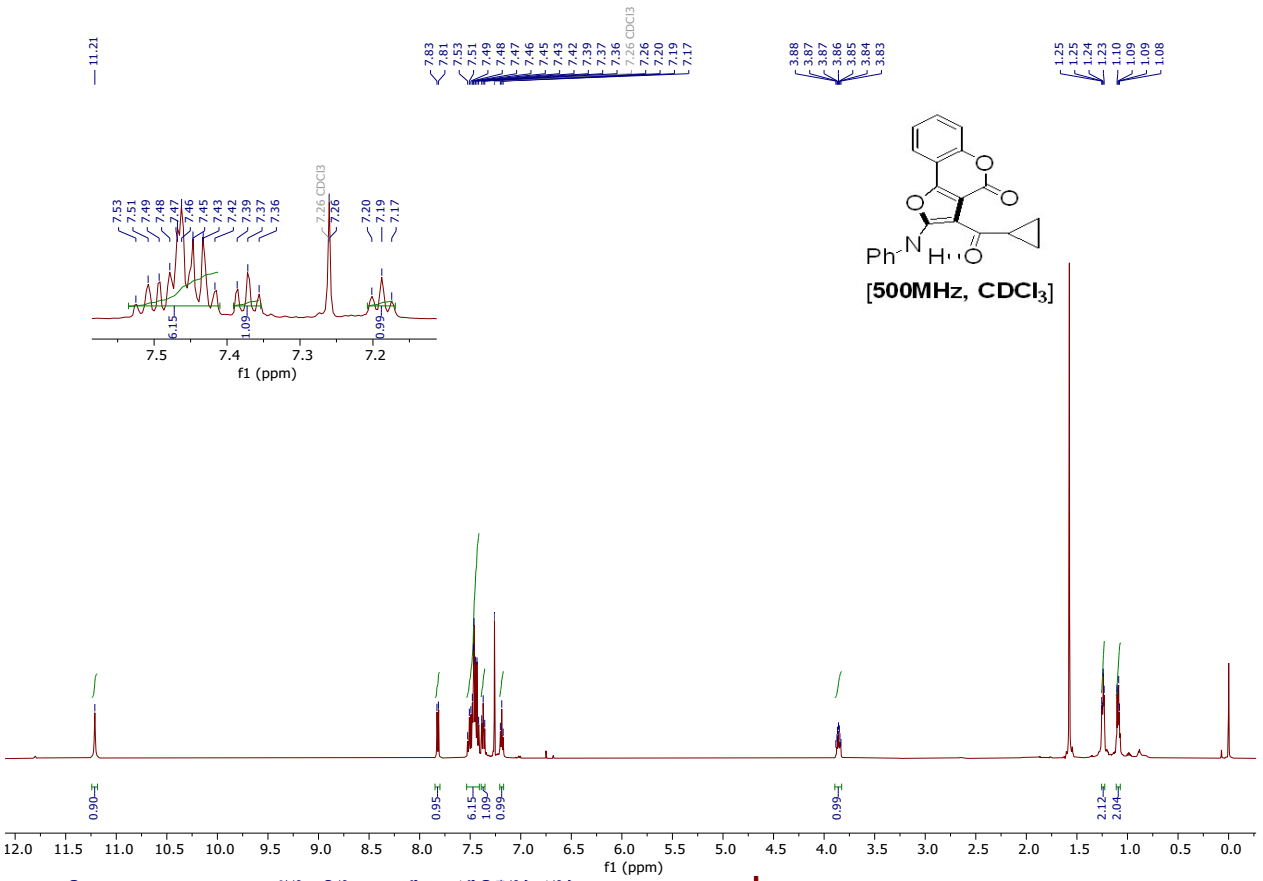
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3s

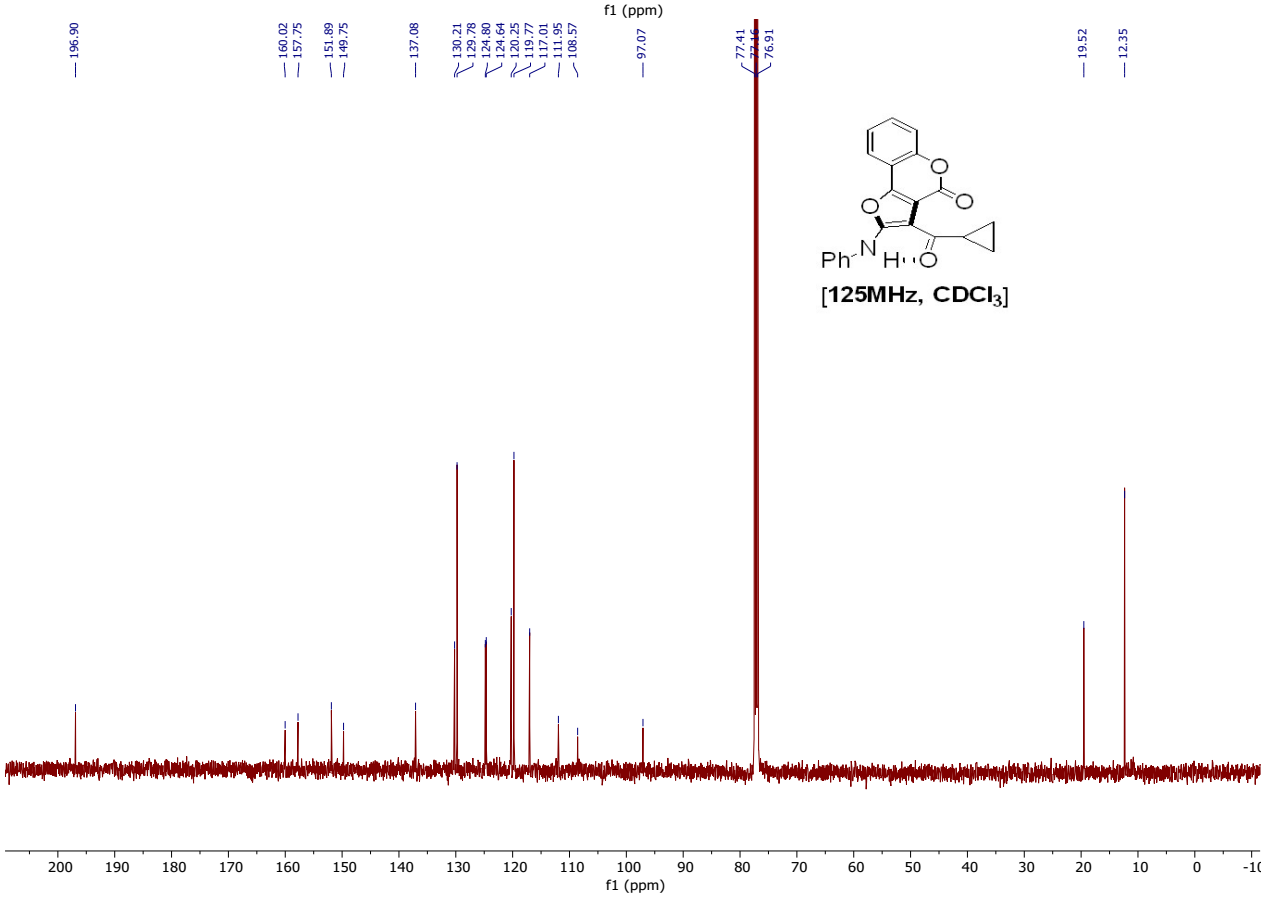




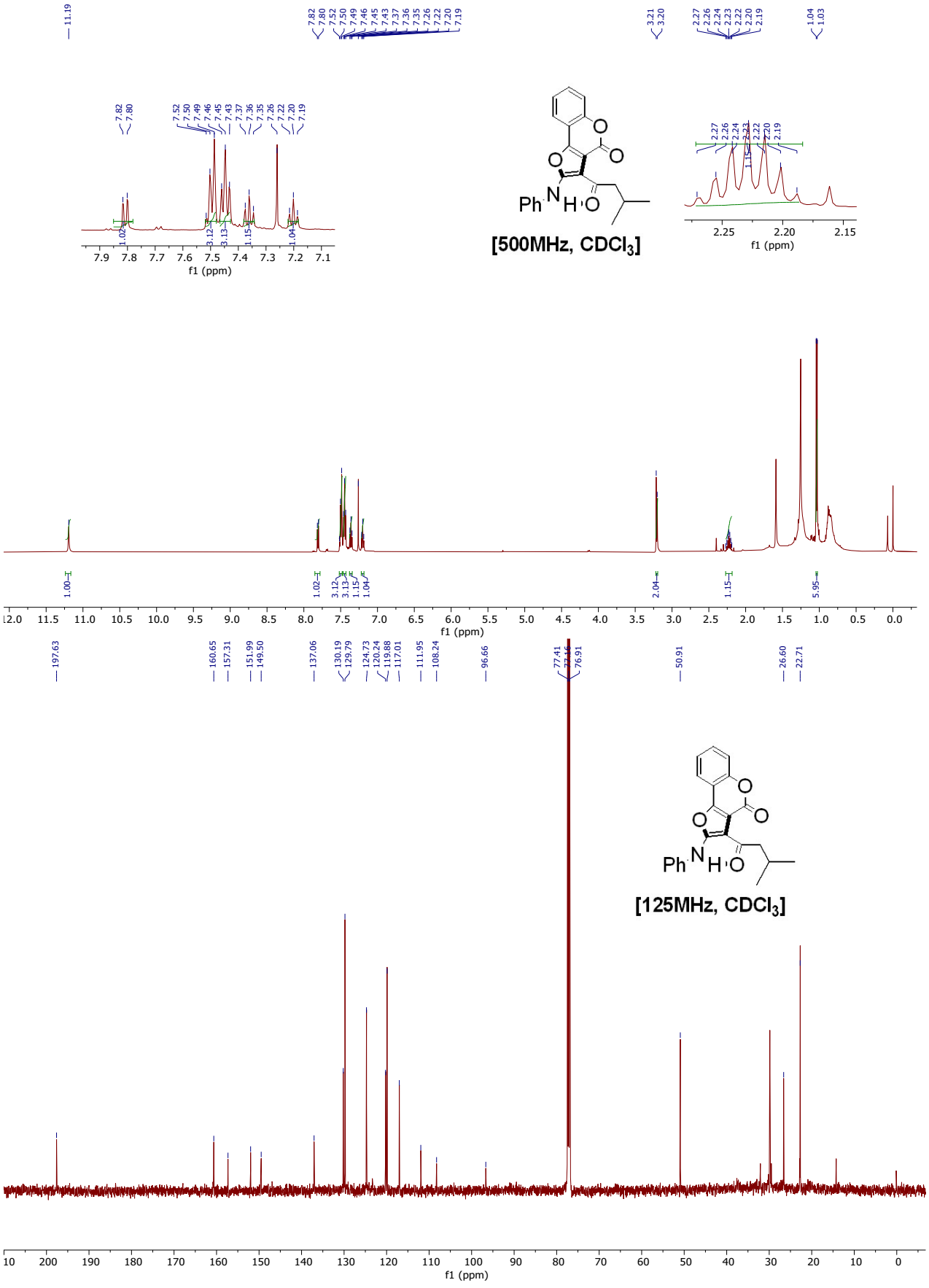


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3t

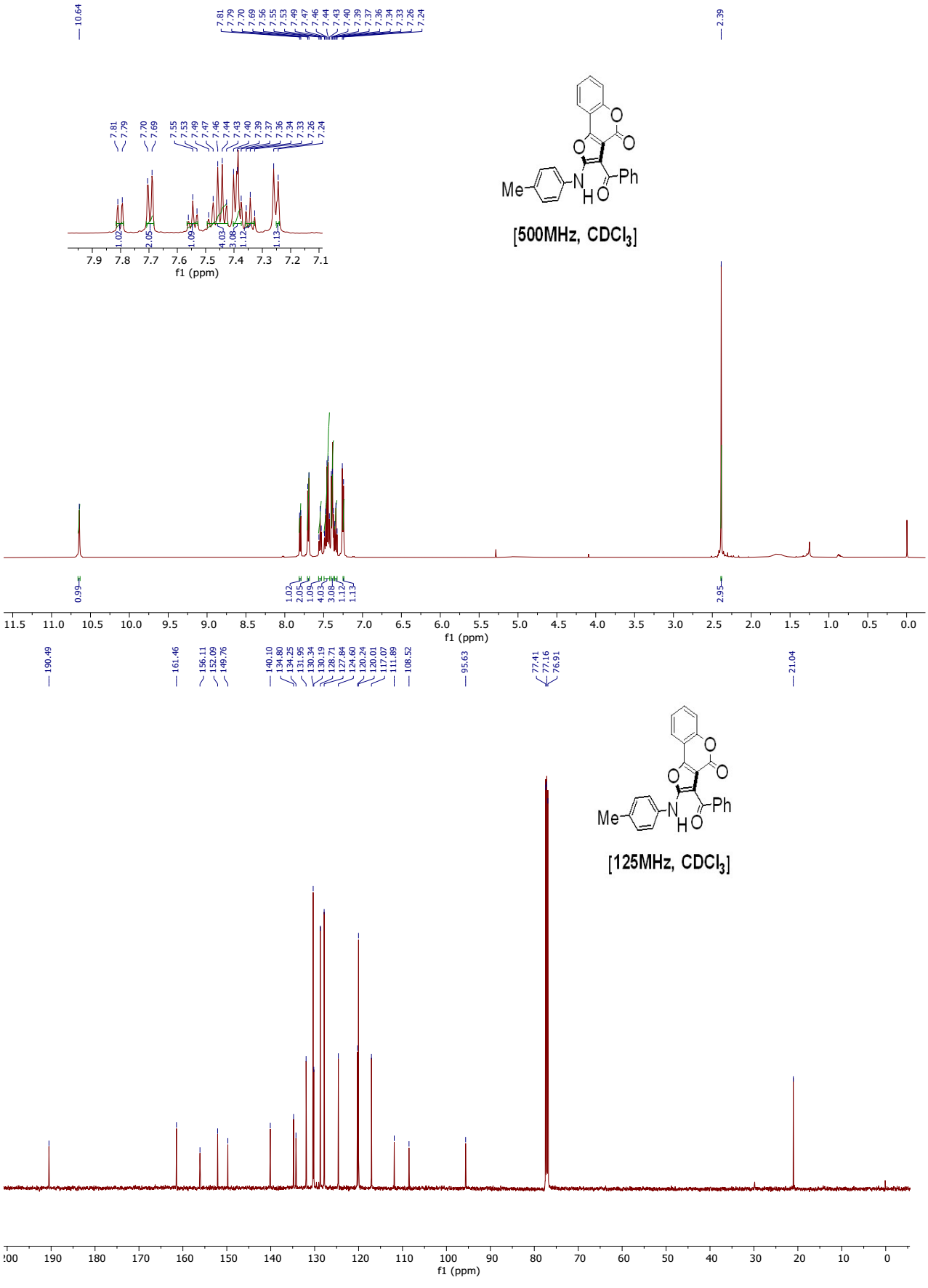




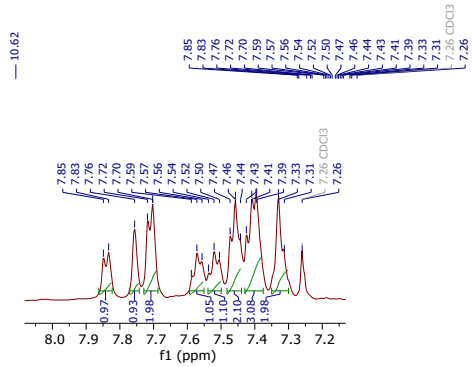
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3u

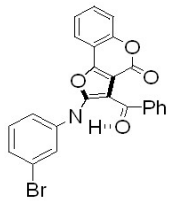


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3v

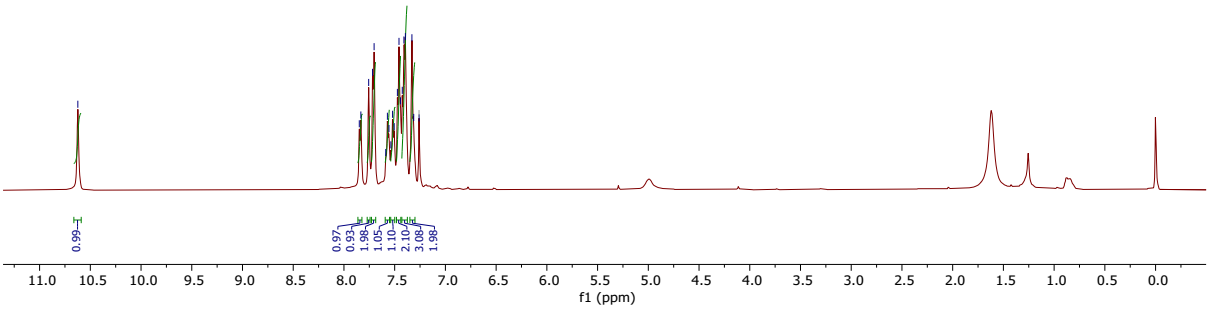


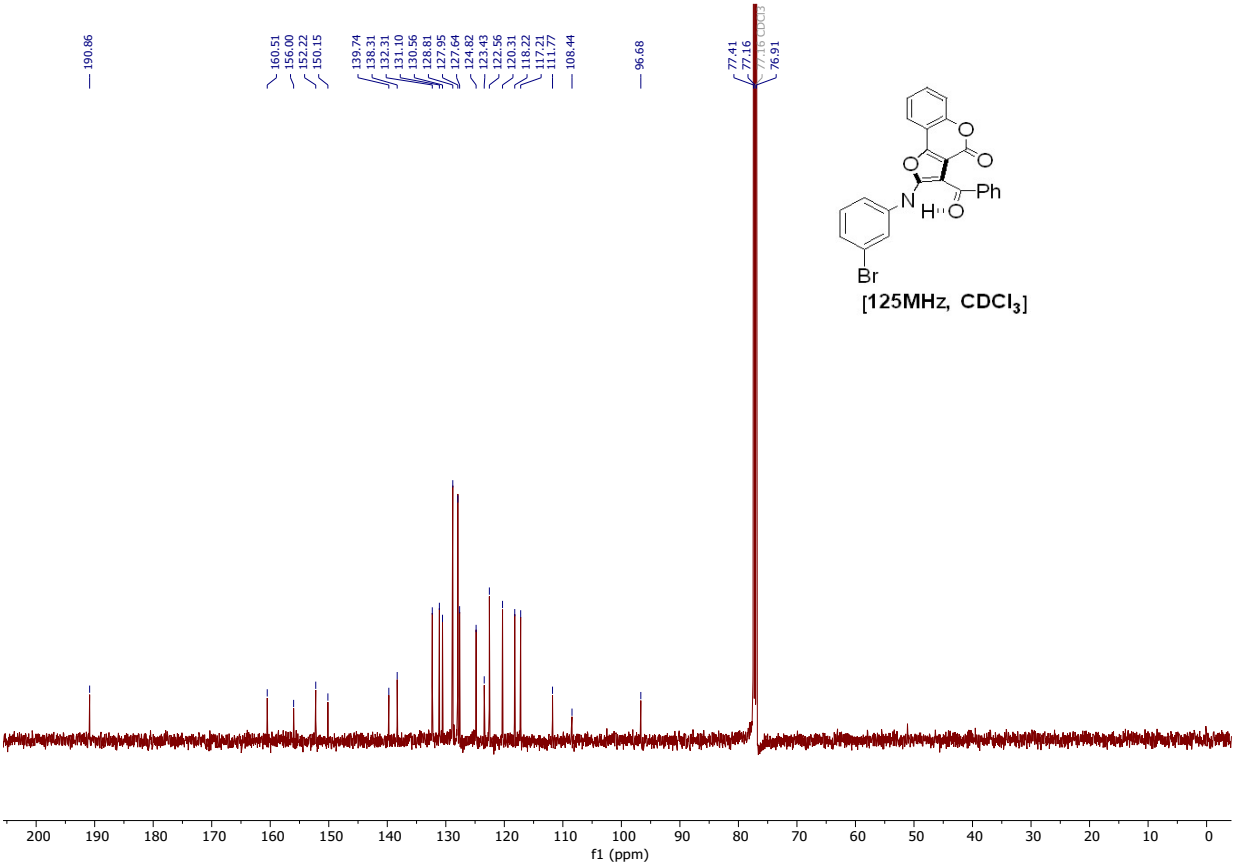
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3w





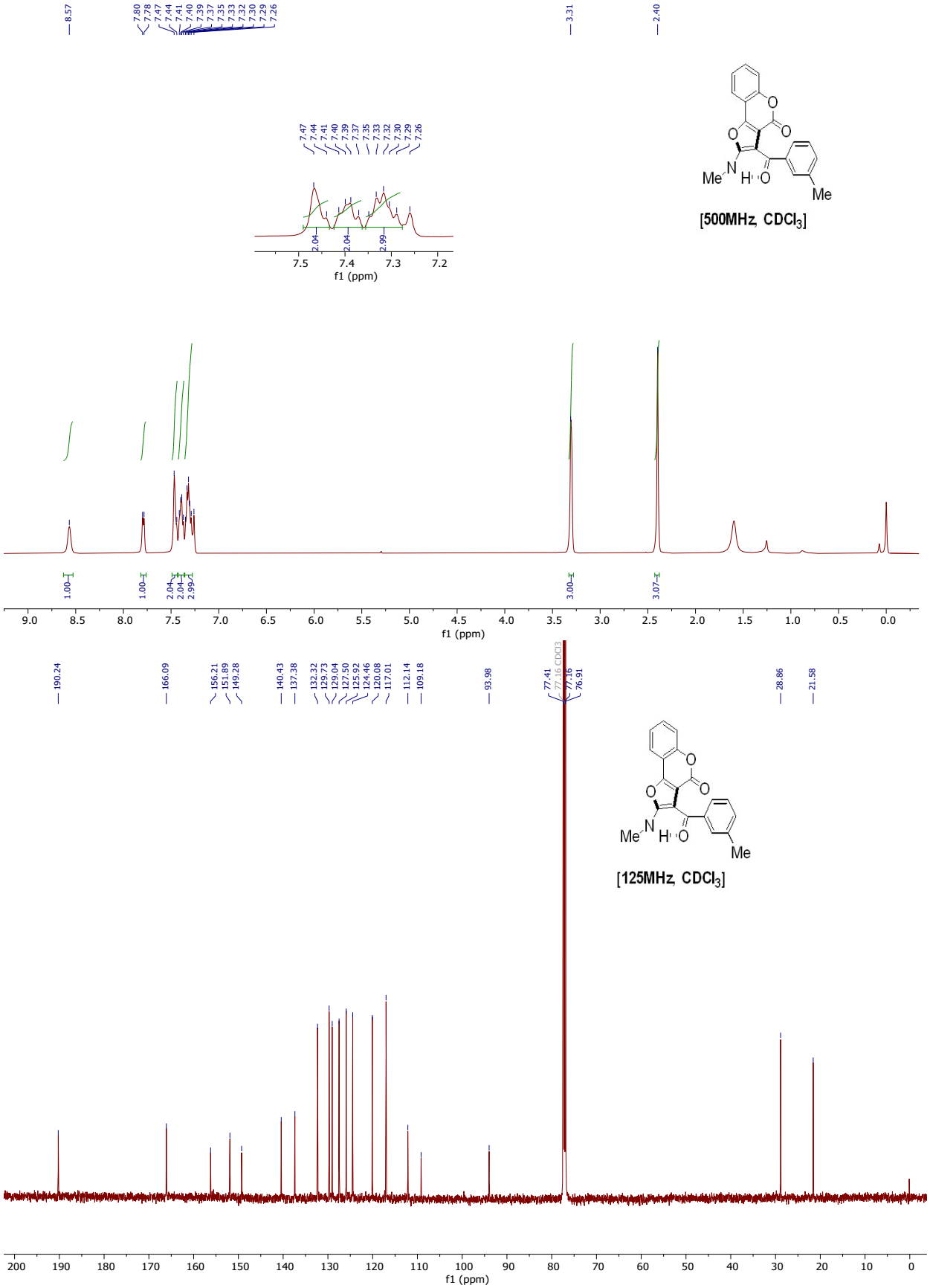
[500MHz, $CDCl_3$]



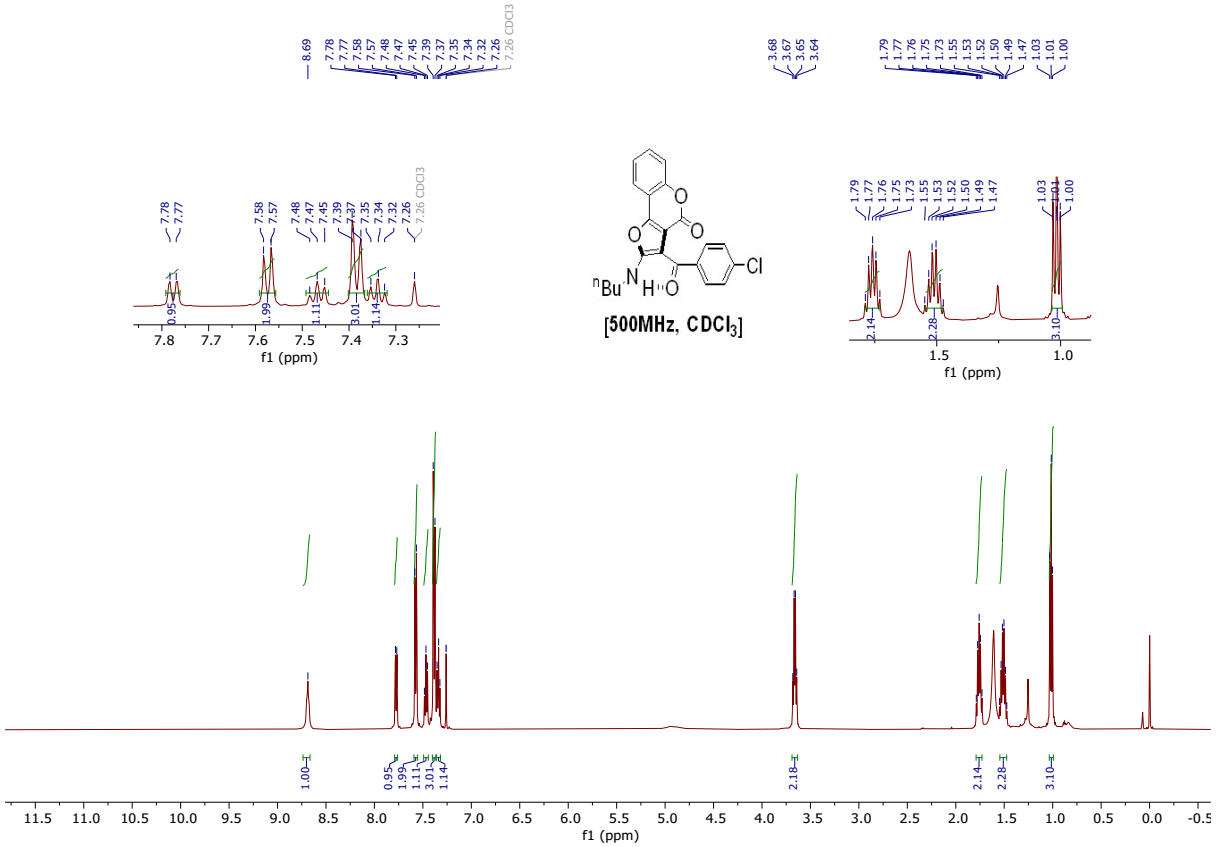


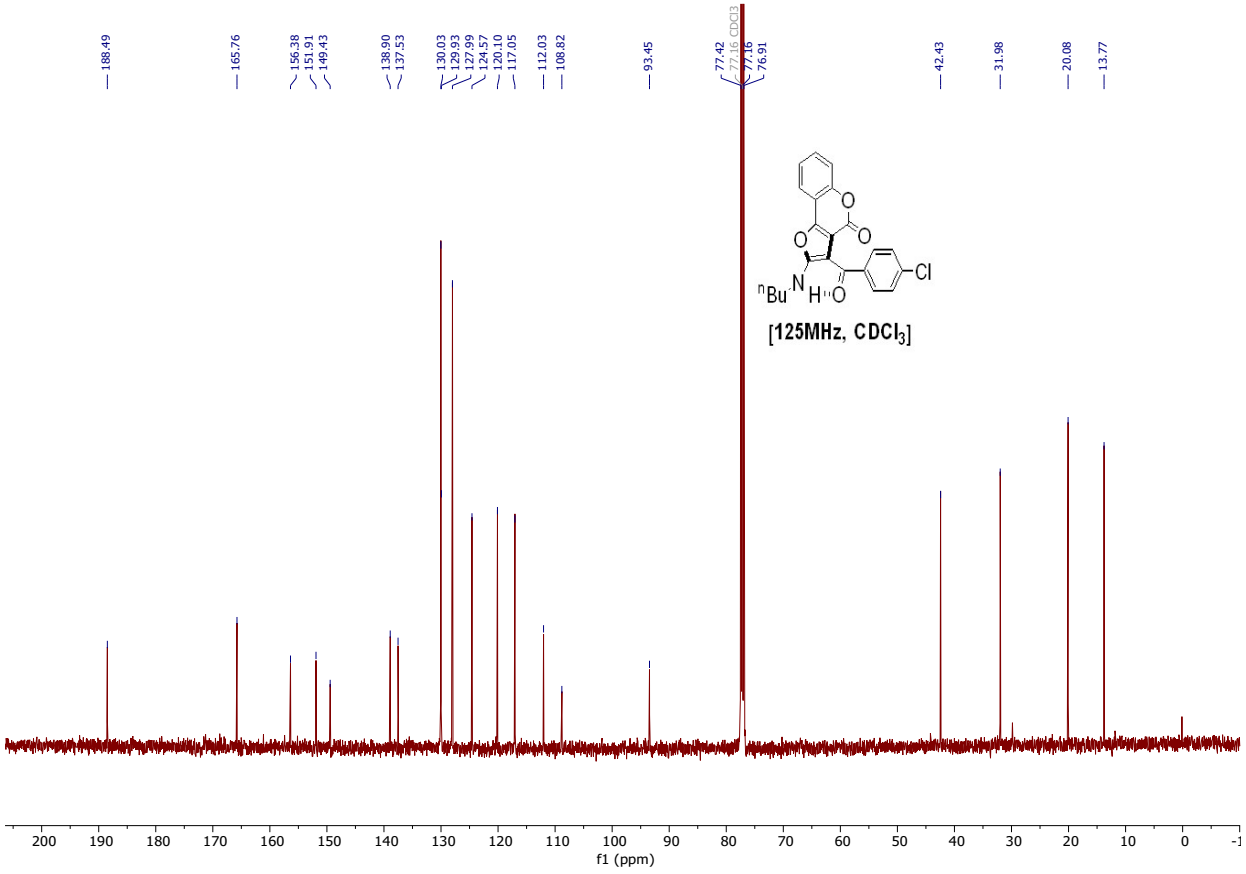
[125MHz, $CDCl_3$]

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3x

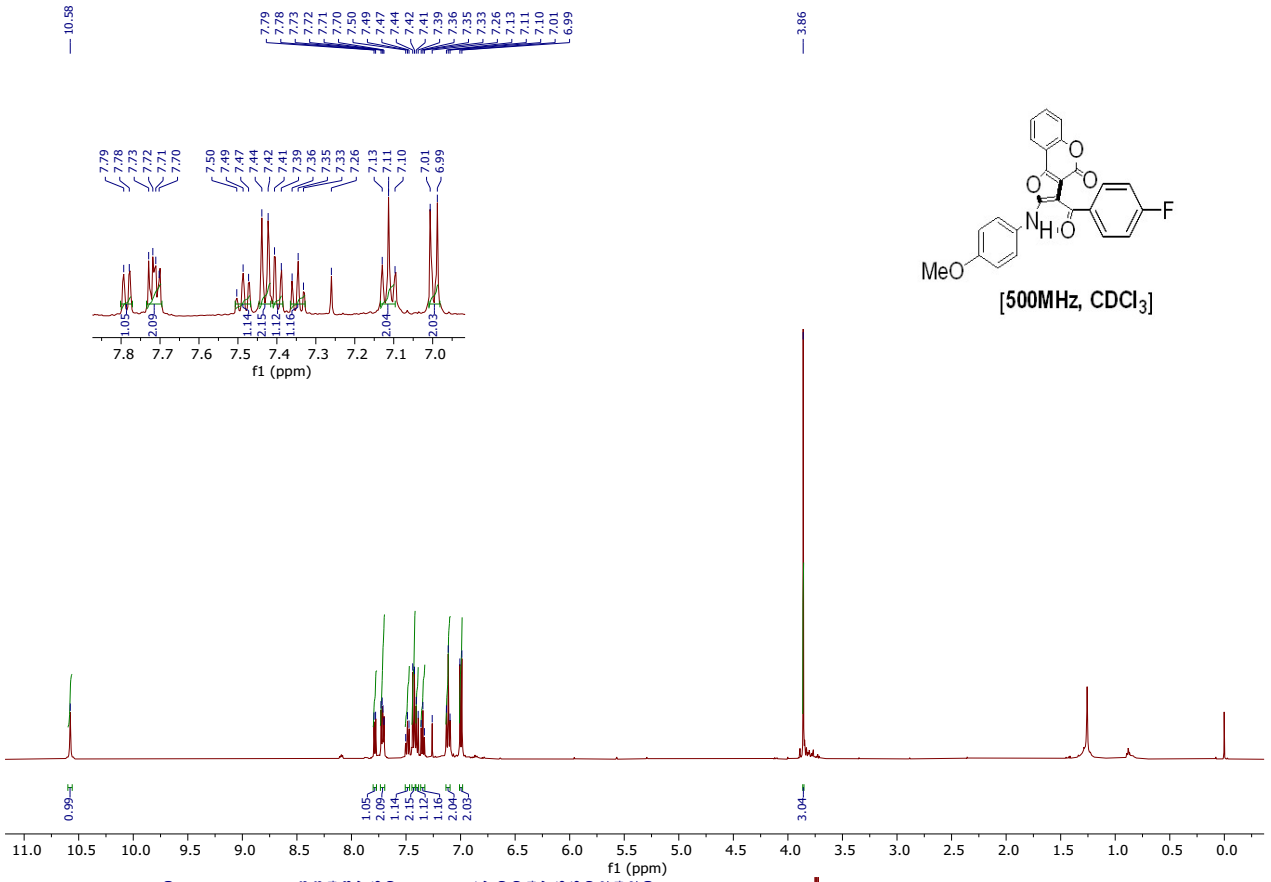


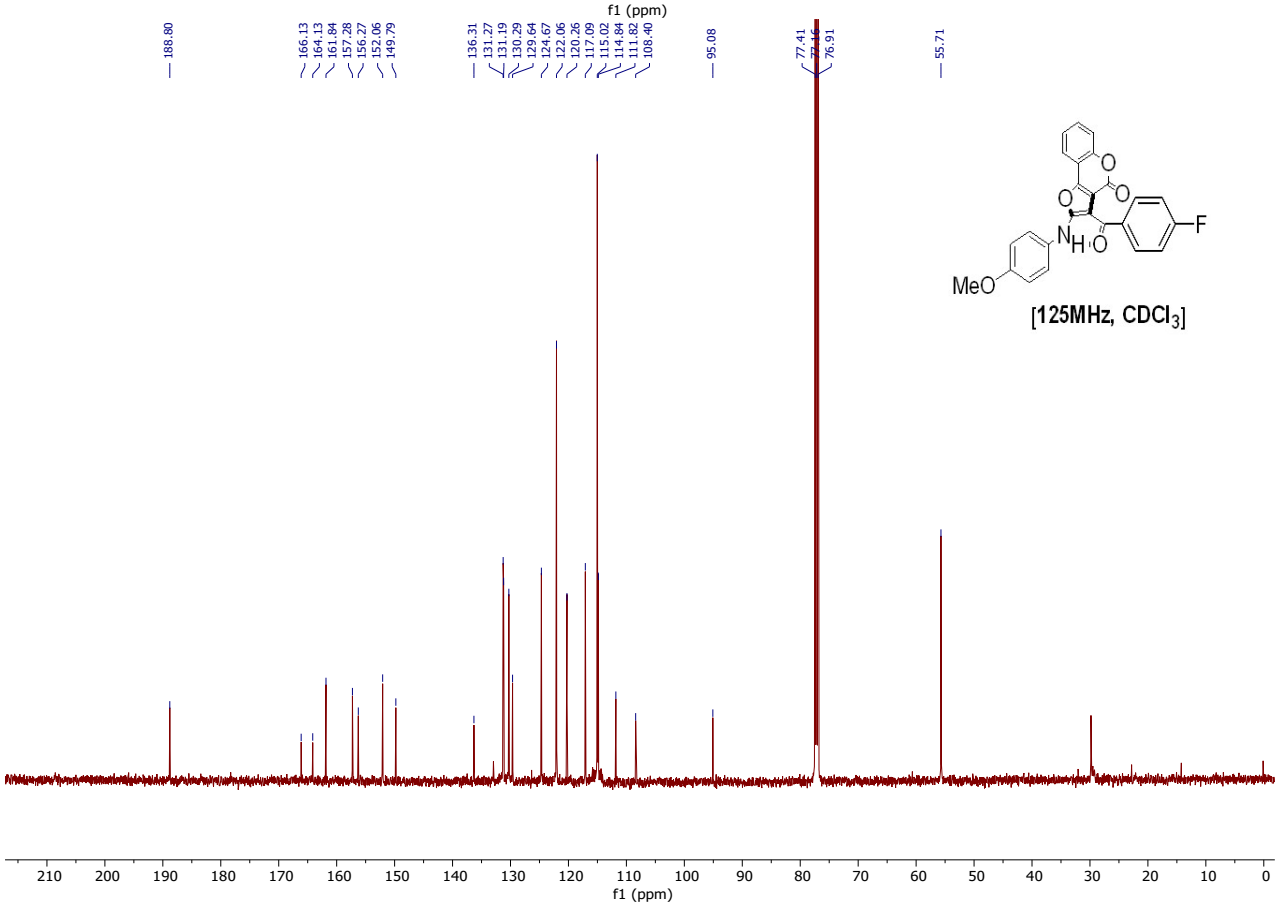
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3y



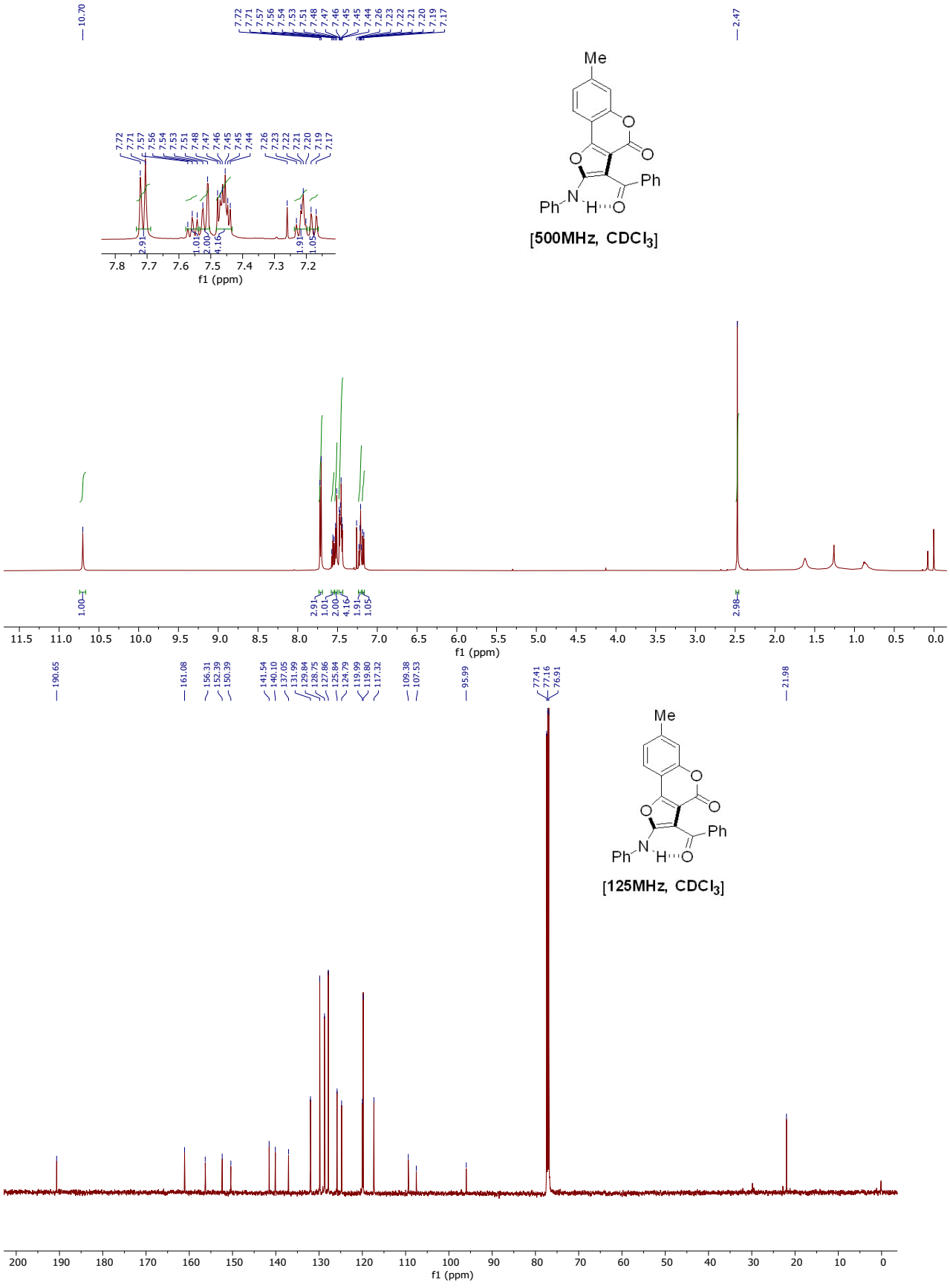


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3z

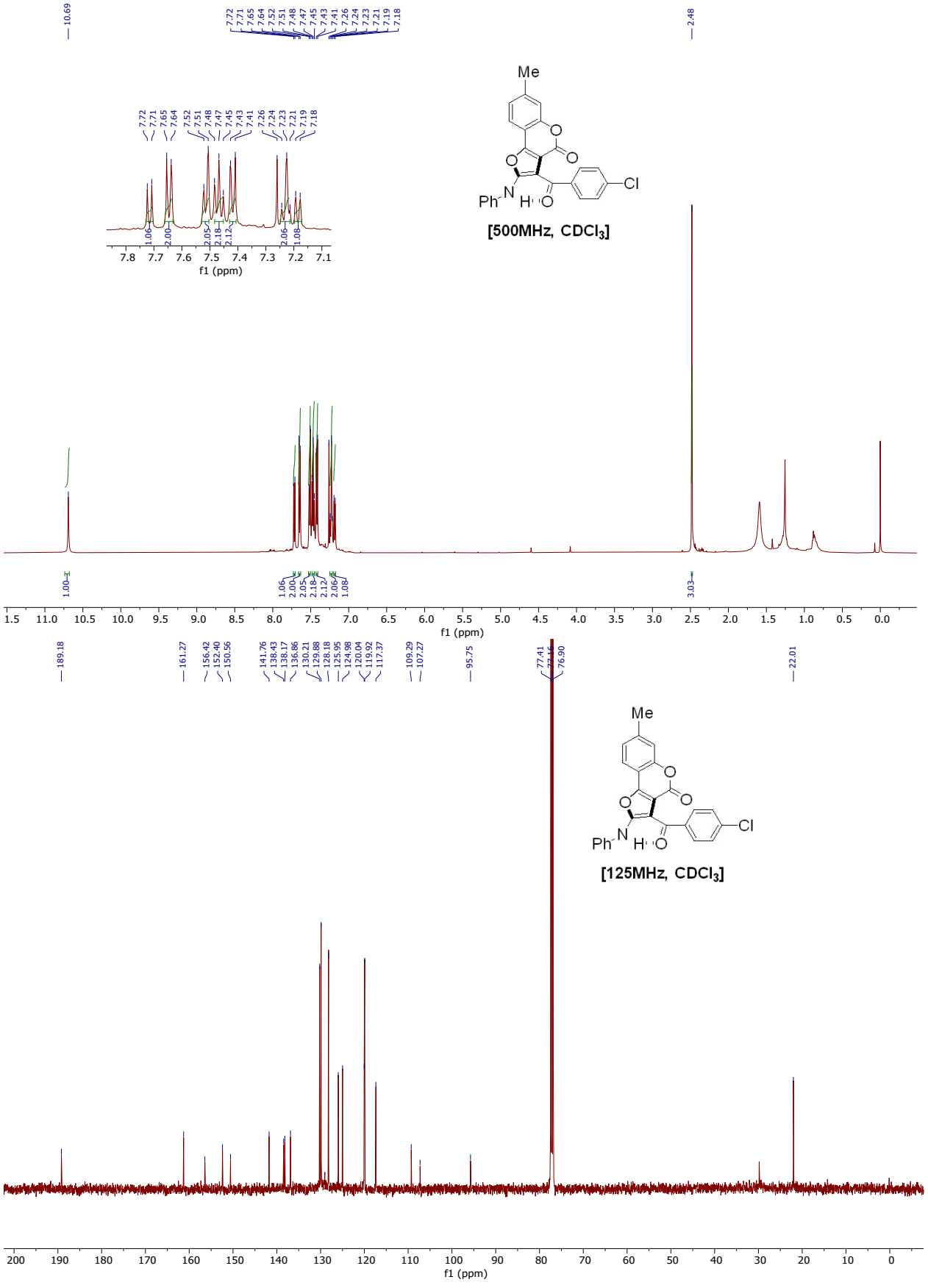




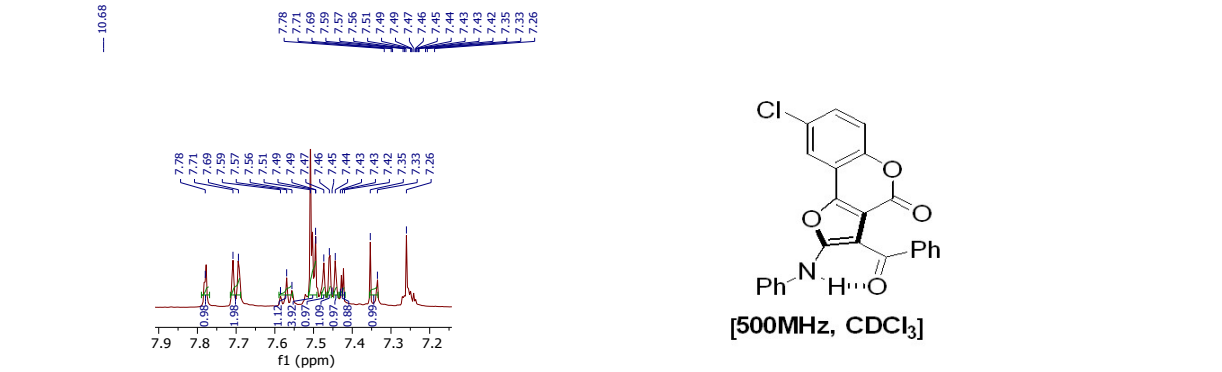
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3za

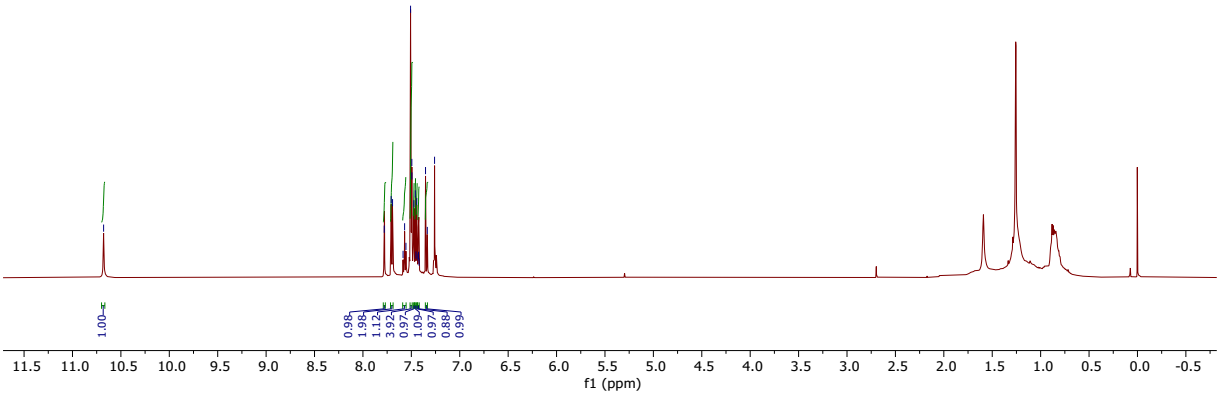


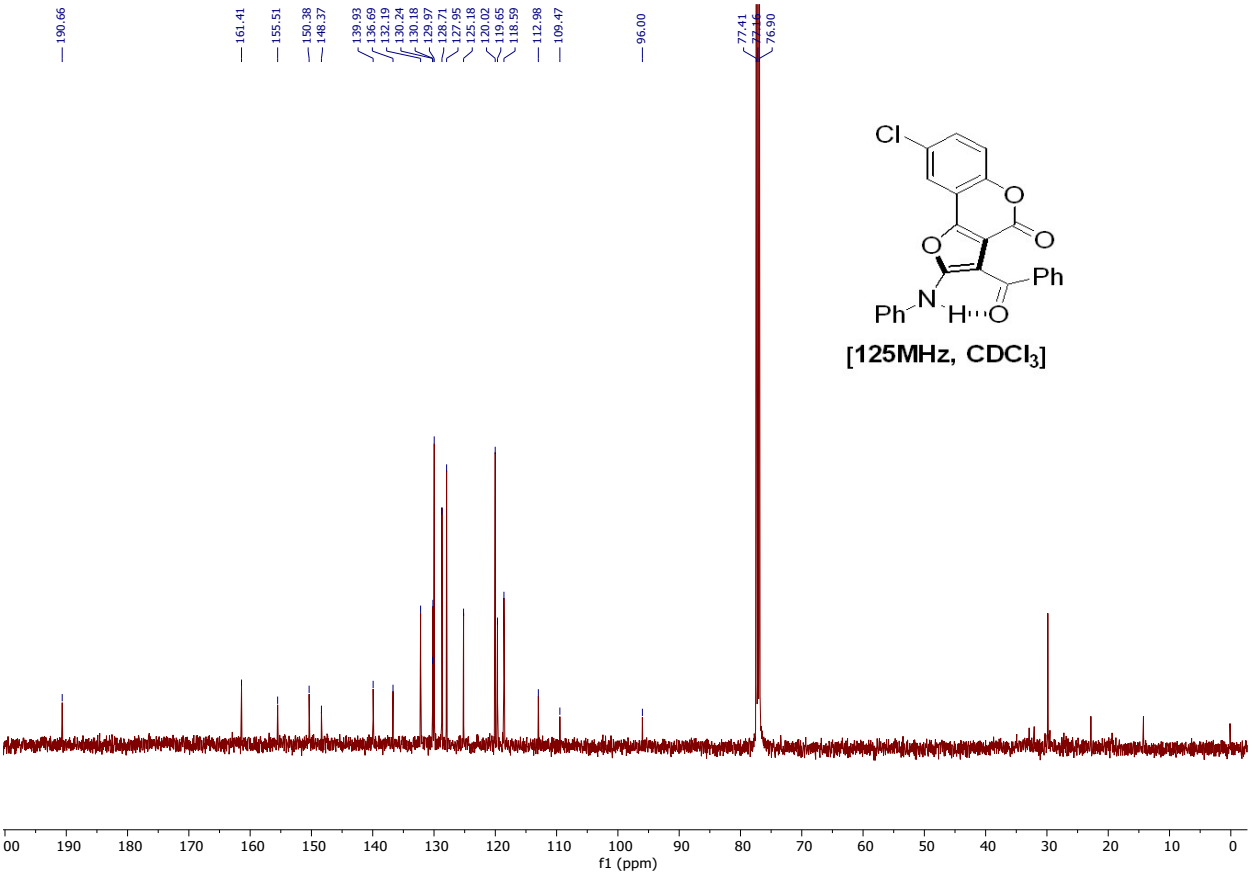
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zb



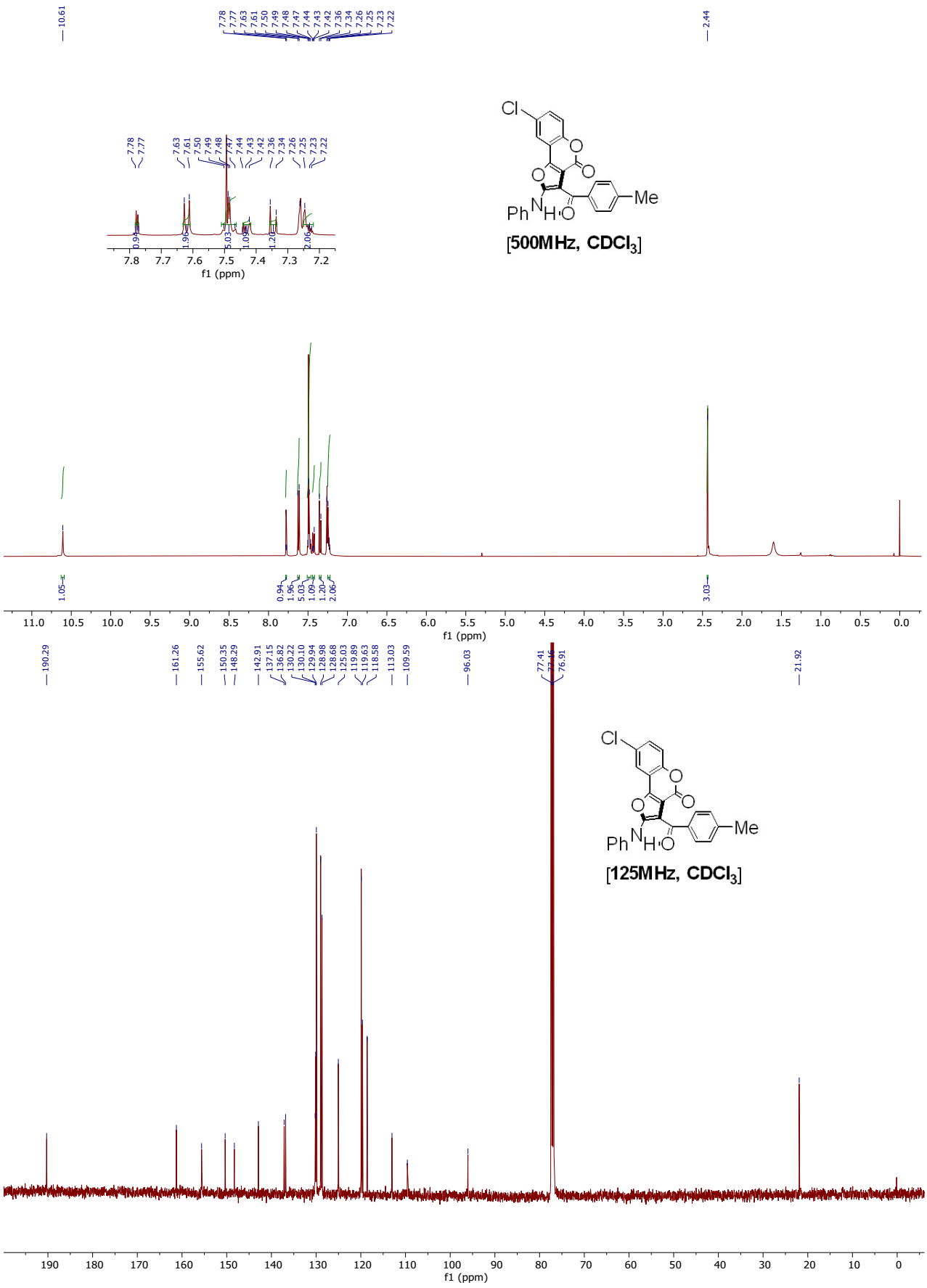
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zc



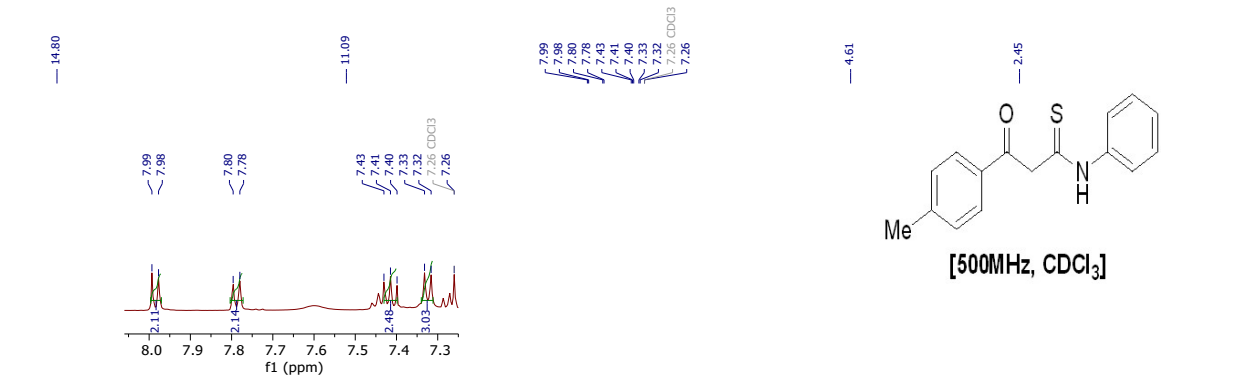




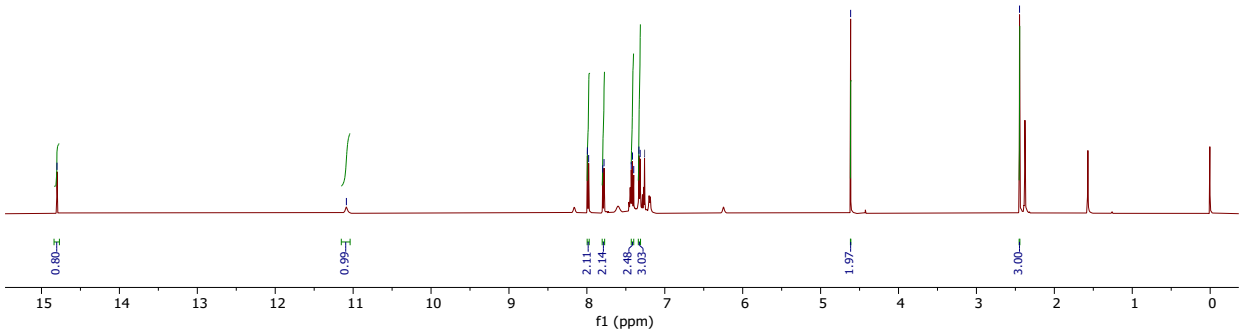
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zd

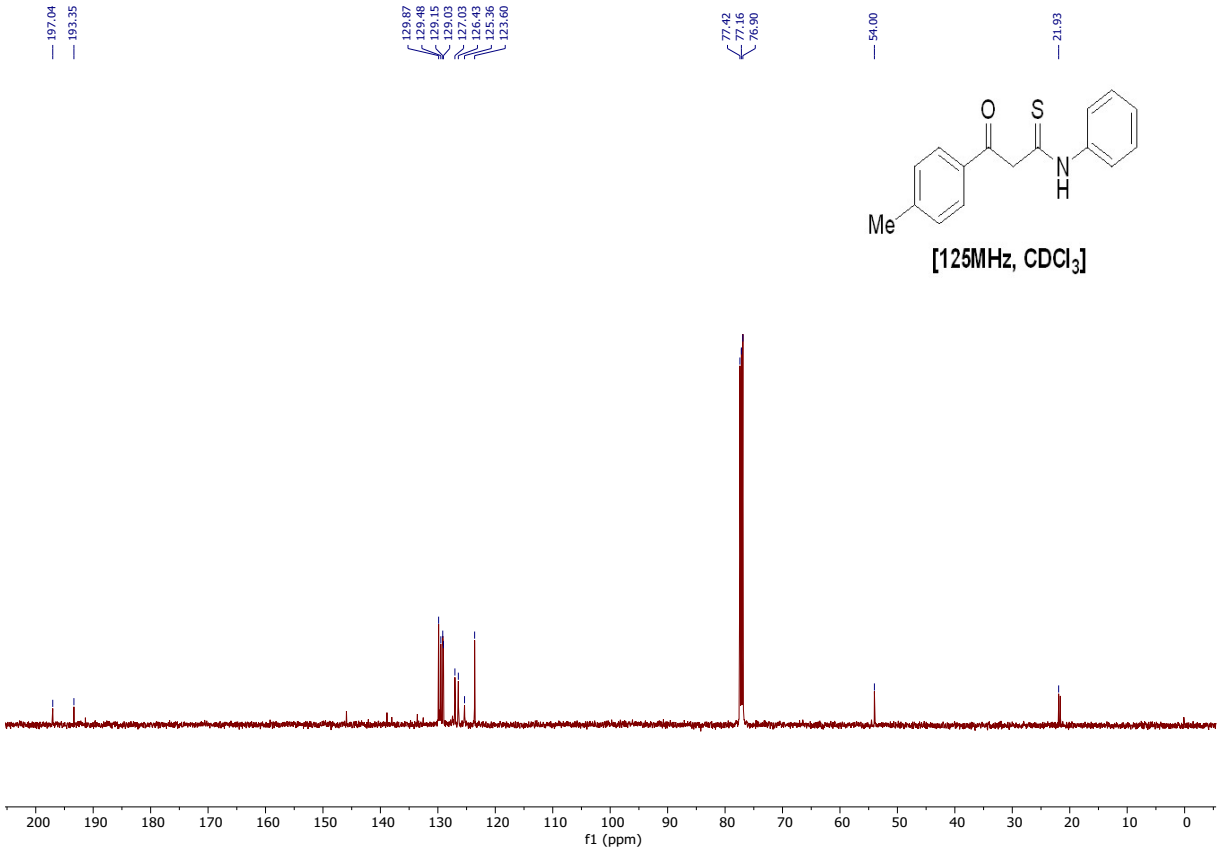


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 2c



[500MHz, $CDCl_3$]





[125MHz, $CDCl_3$]

6. Crystal data and structural refinement

Method for crystals growth of compounds 3a and 3d

For crystallization of the compounds **3a** and **3d,** vacuum-dried pure samples were taken in separate vials and dissolved in 2.0 mL of acetonitrile. The vials were kept at room temperature in dark for slow evaporation. After 6 days, brown solid coloured, cuboidal-shaped crystals were formed, which were further dried for 48 h under high vacuum to remove any solvent residues. The well-dried crystals were picked up and subjected to single crystal XRD study.

6.1 X-Ray Crystallographic Data & ORTEP diagram of 3a (CCDC No. **2298668**)

Bond precision: C-C = 0.0023 A Wavelength=1.54184

Cell: a=20.4669(3) b=8.1277(1) c=21.7889(4)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	3624.56(10)	3624.56(10)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C24 H15 N O4	C24 H15 N O4
Sum formula	C24 H15 N O4	C24 H15 N O4
Mr	381.37	381.37
Dx,g cm-3	1.398	1.398
Z	8	8
Mu (mm-1)	0.785	0.785
F000	1584.0	1584.0
F000'	1589.08	
h,k,lmax	25,10,26	25,10,26
Nref	3557	3536
Tmin,Tmax	0.910,0.962	0.898,1.000
Tmin'	0.855	

Correction method= # Reported T Limits: Tmin=0.898 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 72.047

R(reflections)= 0.0413(2701) wR2(reflections)= 0.1190(3536)
S = 1.038 Npar= 262

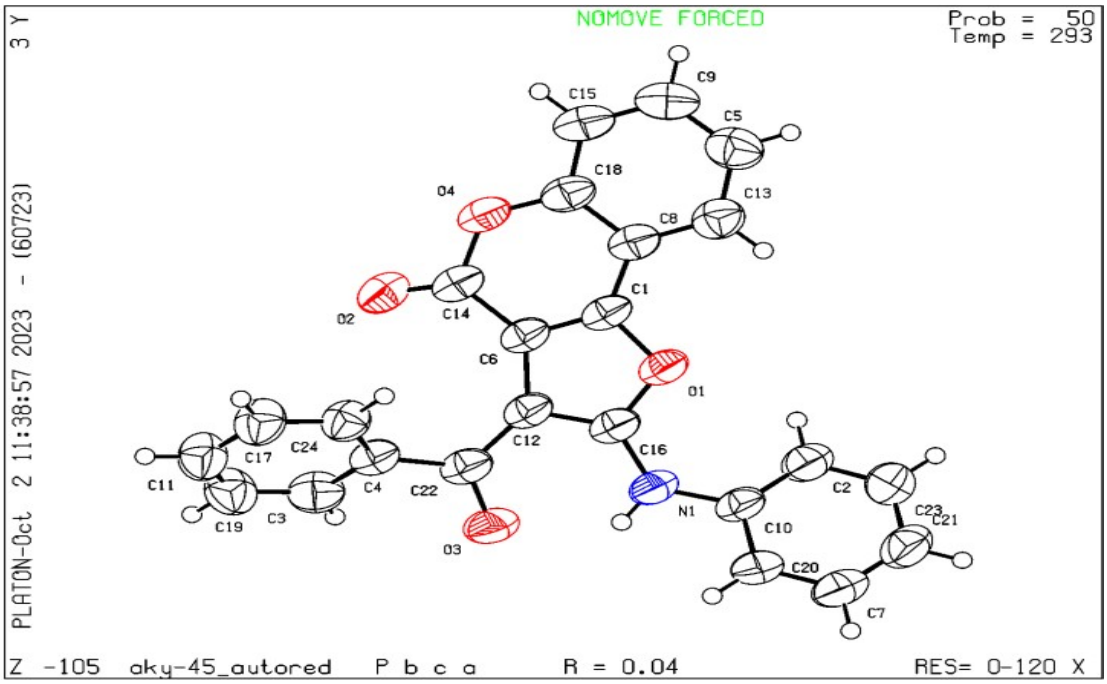


Fig: S1. ORTEP with 50% thermal ellipsoid probability level

6.2 X-Ray Crystallographic Data & ORTEP diagram of 3d (CCDC No. **2298674**)

Bond precision: C-C = 0.0073 A Wavelength=1.54184

Cell: a=11.5055(5) b=22.2353(8) c=8.1847(4)
alpha=90 beta=107.478(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1997.21(16)	1997.21(16)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H19 N O4	C26 H19 N O4
Sum formula	C26 H19 N O4	C26 H19 N O4
Mr	409.42	409.42
Dx,g cm-3	1.362	1.362
Z	4	4
Mu (mm-1)	0.749	0.749
F000	856.0	856.0
F000'	858.68	
h,k,lmax	14,27,10	14,27,10
Nref	3933	3910
Tmin,Tmax	0.835,0.993	0.776,1.000
Tmin'	0.688	

Correction method= # Reported T Limits: Tmin=0.776 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 72.272

R(reflections)= 0.0970(1951) wR2(reflections)= 0.3435(3910)

S = 1.015 Npar= 281

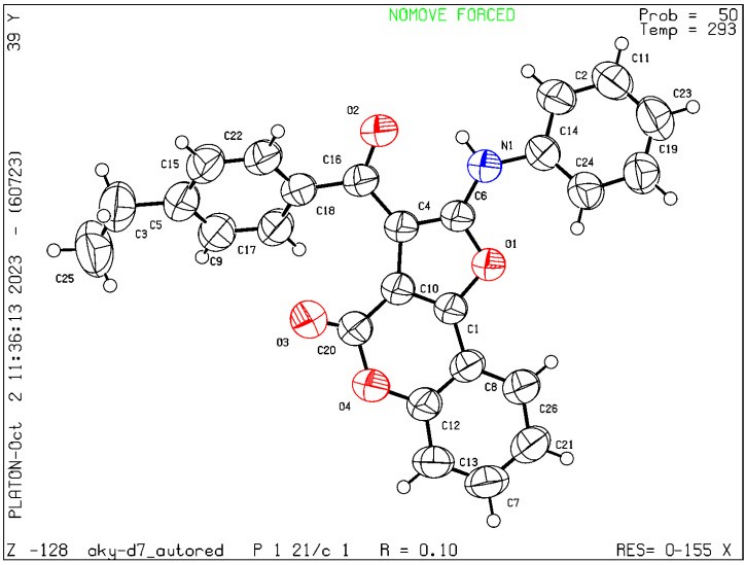


Fig: S2. ORTEP with 50% thermal ellipsoid probability level

7. HRMS spectra of reaction mixture

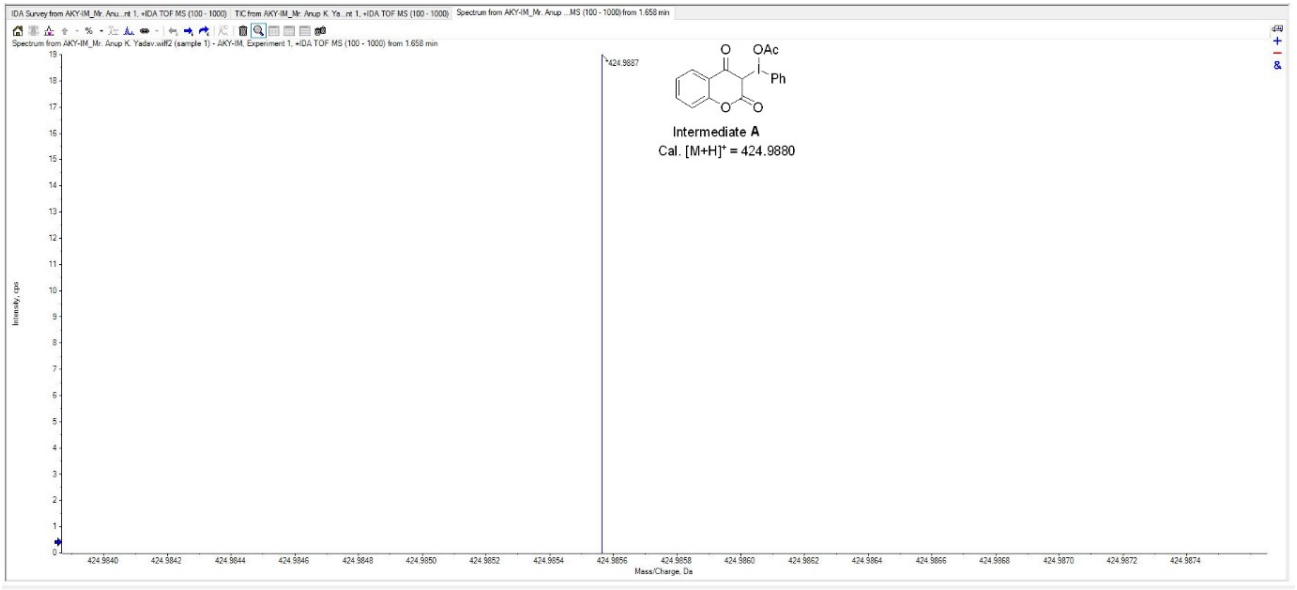


Fig: S3. HRMS spectra of reaction mixture containing intermediate **A** peak

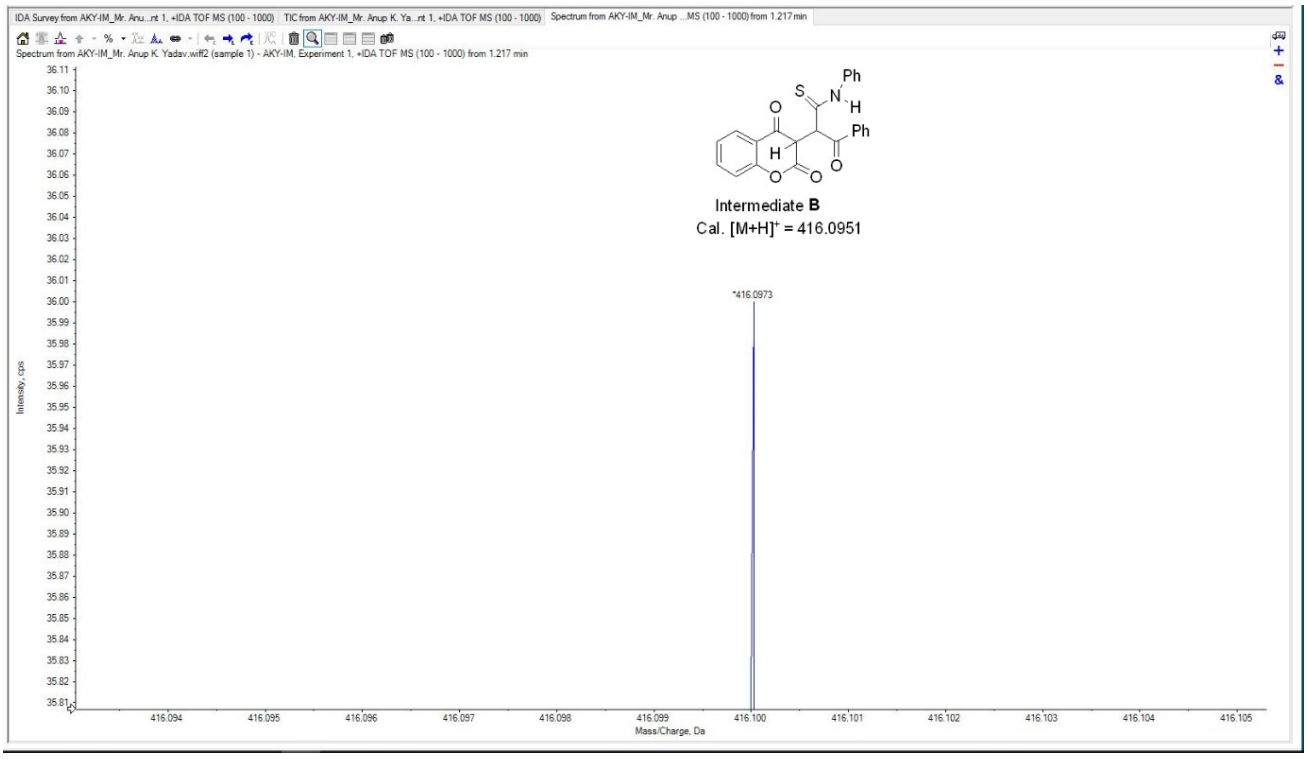


Fig: S4. HRMS spectra of reaction mixture containing intermediate **B** peak

8. AAS data of compound 2c

Sample 089				
Conc	-0.009	-0.009	-0.013	0.0118
%RSD	20.2	0.0	>100	8.6
Mean Abs	-0.0007	-0.0009	-0.0004	0.0038

SpectrAA Report. **10:25 17-04-2024**

Sample 090				
Conc	-0.021	0.005	0.019	0.0111
%RSD	55.9	0.0	36.4	10.0
Mean Abs	-0.0018	0.0005	0.0006	0.0036
	Cu	Mn	Fe	Zn
Sample ID	mg/L	mg/L	mg/L	mg/L
Sample 091				
Conc	-0.020	0.002	-0.028	0.0135
%RSD	47.2	0.0	>100	8.5
Mean Abs	-0.0017	0.0002	-0.0010	0.0044
Sample 092				
Conc	-0.009	-0.009	0.059	0.0254
%RSD	18.4	0.0	22.9	3.7
Mean Abs	-0.0008	-0.0008	0.0020	0.0082
Sample 093				
Conc	-0.002	0.000	-0.016	0.0623
%RSD	13.6	0.0	>100	1.5
Mean Abs	-0.0001	0.0000	-0.0005	0.0201

Table: S1. AAS data of compound **2c**, sample no. 089-091 = Blank (only 1,4-dioxane), sample no. 092-093 = compound **2c** in 1,4-dioxane.

The AAS data of one of the starting materials **2c** were observed via Agilent Technologies 200 series AA 240FS AA from the above AAS data, it is evident there was no metal (Cu, Mn, Fe, Zn) residue involved during the course of the reaction.