Unexpected isocyanide-based cascade cycloaddition reaction with methyleneindolinone

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Supporting Information

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1 General Information:

The NMR spectra were recorded on Bruker AC – 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) with $CDCl_3$ as the solvent and TMS as internal reference. ^{1}H NMR spectral data were reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz). ^{13}C NMR spectral data were reported in terms of the chemical shift. The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Low-resolution mass spectra were obtained on a Shimadzu LCMS-2010EV spectrometer in ESI mode and reported as m/z. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on a X-4 digital melting point apparatus without correction. Chemical yields referred to pure isolated product. Purification of products was accomplished by column chromatography packed with silica gel. Unless otherwise stated, all reagents were commercially purchased and used without further purification. Aromatic isocyanides **1** were prepared from the corresponding anilines according to the method disclosed by Ugi with a slight modification.[1] Substrate arenacylideneoxindoles **2** or **4** were synthesized according to procedures reported previously.[2-5]

2 General Procedure

2.1 General Procedure for the Formation of Product 3

2,6-dimethylphenyl isocyanide **1a** (1.2 mmol) and arenacylideneoxindoles **2** (1.0 mmol) were placed in 10 mL THF in a flask, then $BF_3{\cdot}Et_2O$ (0.4 mmol) was added to this mixture. The reaction mixture was stirred under reflux for several hours and the progress was monitored using TLC detection. After completion of present reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel [silica: 200-300; eluant: petroleum ether/ethyl acetate] to afford the desired product **3**.

2.2 General Procedure for the Formation of 5

2,6-dimethylphenyl isocyanide **1a** (1.2 mmol) and arenacylideneoxindoles **4** (1.0 mmol) were placed in 10 mL THF in a flask, then then $BF_3{\cdot}Et_2O$ (0.4 mmol) was added to this mixture. The reaction mixture was stirred under reflux for several hours and the progress was monitored using TLC detection. After completion of present reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel [silica: 200-300; eluant: petroleum ether/ethyl acetate] to afford the desired product **5**.

References:

[1] a) I. Ugi, R. Meyr, *Organic Syntheses* **1973**, *Coll. Vol. 5*, 1060-1062. b) R. Obrecht, R. Herrmann, I. Ugi, *Synthesis* **1985**, 400-402.

[2] a) B. M. Trost, Y. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 14548-14549. b) R. Shintani, M. Inoue, T. Hayashi, *Angew. Chem. Int. Ed.* **2006**, *45*, 3353-3356.

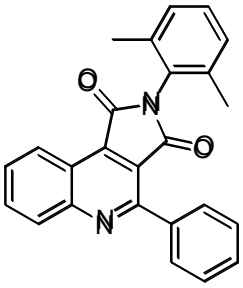
[3] a) C. Marti, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 11505-11515. b) J. M. Ellis, L. E. Overman, H. R. Tanner, J. Wang, *J. Org. Chem.* **2008**, *73*, 9151–9154.

[4] H. Lv, X.-Y. Chen, L.-H. Sun, S. Ye, *J. Org. Chem.* **2010**, *75*, 6973-6976.

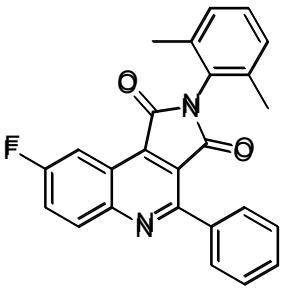
[5] H. J. Lindwall, J. S. Maclennan, *J. Am. Chem. Soc.* **1932**, *54*, 4739-4744.

3 Characterization Data

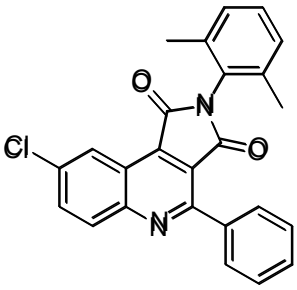
Spectroscopic Data of All Compounds



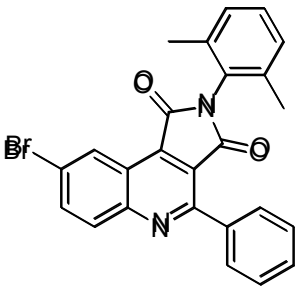
(3a): yellow solid: m. p. 260-262 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm)= 9.01 (dt, 1H, *J* = 8.5, 0.5 Hz), 8.33 (d, 1H, *J* = 8.5 Hz), 8.07-8.05 (m, 2H), 7.97 (ddd, 1H, *J* = 8.5, 6.0, 1.5 Hz), 7.80 (ddd, 1H, *J* = 8.5, 6.0, 1.0 Hz), 7.57-7.54 (m, 3H), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.23 (s, 6H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 167.0, 166.6, 155.5, 152.0, 137.4, 137.0, 136.6, 133.3, 130.4, 130.3, 130.2, 129.8, 129.7, 129.6, 128.6, 128.2, 125.3, 121.1, 121.0, 18.3. HRMS: Calcd for $C_{25}H_{19}N_2O_2$ $[M+H]^+$ 379.1447, Found 379.1440.



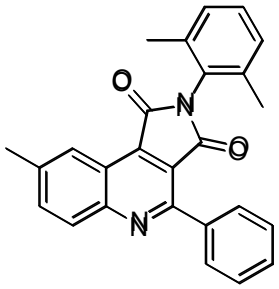
(3b): yellow solid: m. p. 222-224 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) =8.62 (dd, 1H, *J* = 8.5, 2.5 Hz), 8.33 (dd, 1H, *J* = 9.5, 5.0 Hz), 8.05-8.03 (m, 2H), 7.75-7.71 (ddd, 1H, *J* = 9.5, 8.0, 3.0 Hz), 7.56-7.53 (m, 3H), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.22 (s, 6H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 166.8, 166.3, 162.6 (d, $^{1}J_{C\text{-}F}$ = 252.5 Hz), 154.8, 149.3, 137.0, 136.3, 132.9 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 130.3 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 129.8, 129.4, 128.7, 128.3, 124.0 (d, $^{2}J_{C\text{-}F}$ = 26.3 Hz), 121.8, 121.7, 121.6, 108.9, 108.7, 18.3. HRMS: Calcd for $C_{25}H_{18}FN_2O_2$ $[M+H]^+$ 397.1352, Found 397.1345.



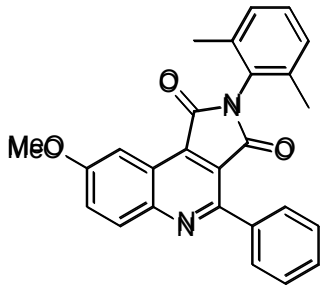
(3c): yellow solid: m. p. 237-239 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$):δ (ppm) = 8.99 (d, 1H, *J* = 2.0 Hz), 8.25 (d, 1H, *J* = 9.5 Hz), 8.06-8.04 (m, 2H), 7.88 (dd, 1H, *J* = 9.0, 2.5 Hz), 7.56-7.55 (m, 3H), 7.31 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.23 (s, 3H) 2.22 (s, 3H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 166.6, 166.2, 155.6, 150.3, 136.9, 136.5, 136.3, 136.2, 134.3, 131.7, 130.5, 130.3, 129.8, 129.4, 128.7, 128.3, 124.0, 121.7, 121.4, 18.3. HRMS: Calcd for $C_{25}H_{18}ClN_2O_2$ $[M+H]^+$ 413.1057, Found 413.1063.



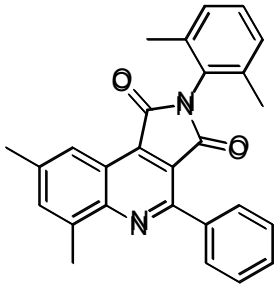
(3d): yellow solid: m. p. 273-275 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 9.17 (d, 1H, *J* = 2.0 Hz), 8.17 (d, 1H, *J* = 9.5 Hz), 8.06-8.01 (m, 3H), 7.55 (t, 3H, *J* = 3.0 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.6 Hz), 2.22 (s, 6H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 166.6, 166.2, 155.8, 150.5, 136.9, 136.8, 136.4, 136.2, 131.7, 130.5, 130.4, 129.8, 129.4, 128.7, 128.3, 127.4, 124.6, 121.8, 121.6, 18.3. HRMS: Calcd for $C_{25}H_{18}BrN_2O_2$ $[M+H]^+$ 457.0552, Found 457.0552.



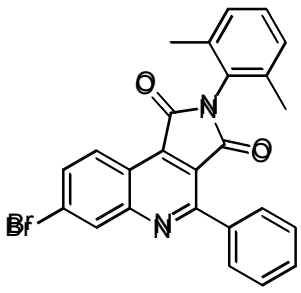
(3e): yellow solid: m. p. 225-227 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.77 (s, 1H), 8.21 (d, 1H, *J* = 8.5 Hz), 8.04-8.02 (m, 2H), 7.80 (dd, 1H, *J* = 8.5, 2.0 Hz), 7.55-7.53 (m, 3H), 7.29 (t, 1H, *J*= 7.5 Hz), 7.20 (d, 2H, *J* = 8.0 Hz), 2.65 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 166.7, 154.5, 150.9, 140.6, 137.0, 136.7, 136.5, 135.8, 130.3, 130.1, 130.0, 129.7, 129.6, 128.6, 128.2, 123.8, 121.2, 121.0, 22.2, 18.3. HRMS: Calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1603, Found 393.1594.



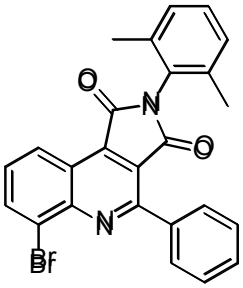
(3f): yellow solid: m. p. 206-208 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.26-8.24 (m, 1H), 8.20 (dd, 1H, *J* = 9.5, 2.0 Hz), 8.03-8.02 (m, 2H), 7.60 (dd, 1H, *J* = 9.5, 3.0 Hz), 7.52 (dd, 3H, *J* = 7.0, 2.5 Hz), 7.31-7.27 (m, 1H), 7.21-7.19 (m, 2H), 4.03 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.6, 166.7, 160.6, 152.7, 148.9, 137.0, 136.7, 135.1, 131.7, 130.2, 129.9, 129.7, 128.6, 128.2, 127.1, 122.6, 121.0, 101.6, 56.1, 18.3. HRMS: Calcd for $C_{26}H_{21}N_2O_3$ $[M+H]^+$ 409.1552, Found 409.1537.



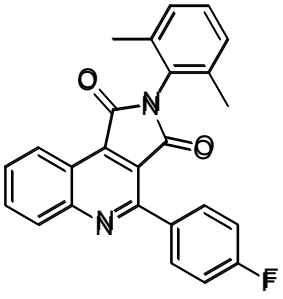
(3g): yellow solid: m. p. 210-211 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.63 (s, 1H), 8.14 (dd, 2H, *J* = 7.5, 2.0 Hz), 7.64 (s, 1H), 7.54-7.53 (m, 3H), 7.29 (t, 1H, *J* = 7.5 Hz), 7.20 (d, 2H, *J* = 7.5 Hz), 2.88 (s, 3H), 2.60 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.5, 167.0, 152.8, 150.0, 140.4, 138.1, 137.2, 137.1, 136.5, 135.6, 130.6, 130.0, 129.8, 129.6, 128.6, 128.1, 121.6, 121.3, 120.6, 22.2, 18.4, 18.3. HRMS: Calcd for $C_{27}H_{23}N_2O_2$ $[M+H]^+$ 407.1760, Found 407.1738.



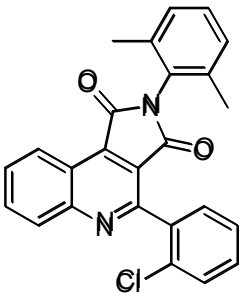
(3h): yellow solid: m. p. 306-308 °C. ^{1}H NMR (500 MHz, $CDCl_3$):δ (ppm) = 8.86 (d, 1H, *J* = 9.0 Hz), 8.53 (s, 1H), 8.04-8.03 (m, 2H), 7.87 (dd, 1H, *J* = 9.0, 1.5 Hz), 7.55-7.54 (m, 3H), 7.30 (t, 1H, *J* = 7.5 Hz), 7.20 (d, 2H, *J* = 7.5 Hz), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.7, 166.3, 156.6, 152.3, 137.8, 137.0, 136.2, 133.4, 132.6, 130.6, 130.4, 129.9, 129.4, 128.7, 128.5, 128.3, 126.5,121.1, 119.6, 18.3. HRMS: Calcd for $C_{25}H_{18}BrN_2O_2$ $[M+H]^+$ 457.0552, Found 457.0535.



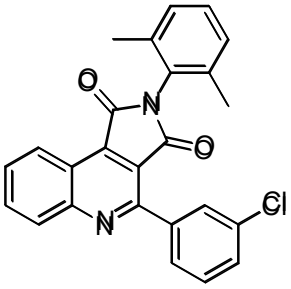
(3i): yellow solid: m. p. 218-220 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.00 (dd, 1H, *J* = 8.0, 1.0 Hz), 8.28 (dd, 1H, *J* = 7.5, 1.0 Hz), 8.24-8.22 (m, 2H), 7.62 (t, 1H, *J* = 8.0 Hz), 7.57-7.56 (m, 3H), 7.31 (t, 1H, *J* = 7.5 Hz), 7.22 (d, 2H, *J* = 7.5 Hz), 2.23 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.5, 166.2, 155.7, 148.6, 138.2, 136.9, 136.7, 136.2, 130.9, 130.7, 130.1, 129.8, 129.5, 128.7, 128.3, 126.1, 125.0, 122.3, 121.8, 18.3. HRMS: Calcd for $C_{25}H_{18}BrN_2O_2$ $[M+H]^+$ 457.0552, Found 457.0546.



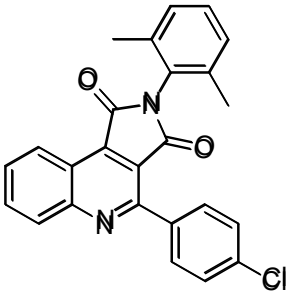
(**5a**): yellow solid: m. p. 211-212 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 9.00 (dd, 1H, *J* = 8.5, 1.0 Hz), 8.30 (d, 1H, *J* = 8.5 Hz), 8.11-8.07 (m, 2H), 7.97 (ddd, 1H, *J* = 8.5, 6.0, 1.5 Hz), 7.80 (ddd, 1H, *J* = 8.5, 6.0, 1.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.25-7.20 (m, 4H), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.0, 166.7, 164.3 (d, $^{1}J_{C\text{-}F}$ = 248.8 Hz), 154.3, 152.0, 137.5, 137.0, 133.4, 132.7 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 132.5(d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 130.2, 129.9, 129.8, 129.5, 128.7, 125.3, 120.9 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 115.4, 115.2, 18.3. HRMS: Calcd for $C_{25}H_{18}FN_2O_2$ $[M+H]^+$ 397.1352, Found 397.1362.



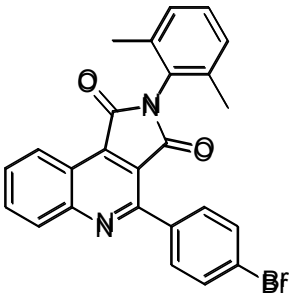
(**5b**): yellow solid: m. p. 228-230°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.01 (d, 1H, *J* = 8.0 Hz), 8.36 (dd, 1H, *J* = 8.5, 0.5 Hz), 8.01-7.98 (m, 1H), 7.86 (t, 1H, *J* = 7.5 Hz), 7.68-7.65 (m, 1H), 7.54-7.51 (m, 1H), 7.49-7.45 (m, 2H), 7.28 (d, 1H, *J* = 7.0 Hz), 7.19 (d, 2H, *J* = 7.5 Hz), 2.22 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.0, 165.9, 152.9, 151.9, 137.0, 136.2, 136.1, 133.7, 133.2, 130.9, 130.8, 130.4, 130.3, 129.7, 129.6, 129.5, 128.6, 127.2, 125.4, 122.8, 121.5, 18.2. HRMS: Calcd for $C_{25}H_{18}ClN_2O_2$ $[M+H]^+$ 413.1057, Found 413.1079.



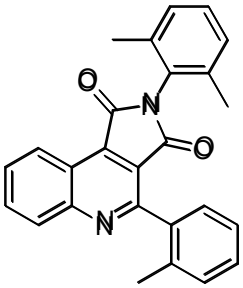
(5c): yellow solid: m. p. 188-190 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.00 (d, 1H, *J* = 8.0 Hz), 8.32 (d, 1H, *J* = 8.5 Hz), 8.07 (s, 1H), 8.00-7.97 (m, 1H), 7.94 (d, 1H, *J* = 7.5 Hz), 7.84-7.81 (m, 1H), 7.52-7.49 (m, 1H), 7.46 (t, 1H, *J* = 7.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.9, 166.5, 153.8, 152.0, 138.3, 137.5, 137.0, 134.4, 133.5, 130.4, 130.3, 130.2, 130.1, 129.9, 129.5, 129.4, 128.8, 128.7, 125.4, 121.2, 121.0, 18.3. HRMS: Calcd for $C_{25}H_{18}ClN_2O_2$ $[M+H]^+$ 413.1057, Found 413.1064.



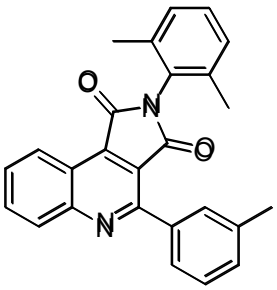
(5d): yellow solid: m. p. 225-227 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 8.99 (d, 1H, *J* = 8.0 Hz), 8.30 (d, 1H, *J* = 8.5 Hz), 8.02 (d, 2H, *J* = 8.5 Hz), 7.98 (t, 1H, *J* = 7.5 Hz), 7.81 (t, 1H, *J* = 8.5 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.0, 166.6, 154.1, 152.0, 137.5, 137.0, 136.7, 135.1, 133.5, 131.8, 130.3, 130.1, 129.8, 129.5, 128.7, 128.5, 125.4, 121.1, 120.9, 18.3. HRMS: Calcd for $C_{25}H_{18}ClN_2O_2$ $[M+H]^+$ 413.1057, Found 413.1042.



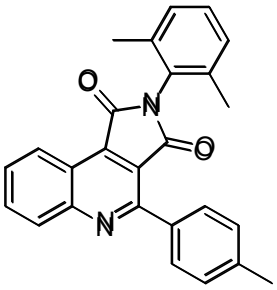
(**5e**): yellow solid: m. p. 242-244 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.00 (d, 1H, *J* = 8.5 Hz), 8.31 (d, 1H, *J* = 9.0 Hz), 7.99-7.96 (m, 3H), 7.81 (t, 1H, *J* = 8.0 Hz), 7.67 (d, 2H, *J* = 8.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.9, 166.6, 154.2, 152.0, 137.5, 137.0, 135.5, 133.5, 132.0, 131.5, 130.3, 130.1, 129.8, 129.5, 128.7, 125.4, 125.1, 121.1, 120.9, 18.3. HRMS: Calcd for $C_{25}H_{18}BrN_2O_2$ $[M+H]^+$ 457.0552, Found 457.0555.



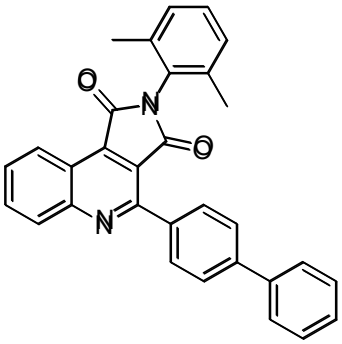
(**5f**): yellow solid: m. p. 149-151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.01 (d, 1H, *J* = 8.5 Hz), 8.33 (d, 1H, *J* = 8.5 Hz), 7.98 (t, 1H, *J* = 7.5 Hz), 7.84 (t, 1H, *J* = 7.5 Hz), 7.49-7.47 (m, 1H), 7.42 (d, 1H, *J* = 7.5 Hz),7.36-7.34 (m, 2H), 7.27 (t, 1H, *J* = 7.5 Hz), 7.18 (d, 2H, *J* = 7.5 Hz), 2.30 (s, 3H), 2.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.1, 166.2, 156.0, 152.0, 136.9, 136.6, 136.5, 133.2, 130.5, 130.4, 130.0, 129.8, 129.7, 129.6, 128.6, 125.8, 125.3, 122.1, 121.2, 20.0, 18.3. HRMS: Calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1603, Found 393.1593.



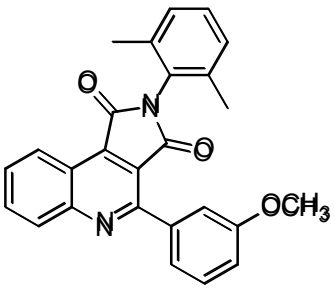
(**5g**): yellow solid: m. p. 229-230 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.01 (d, 1H, *J* = 8.0 Hz), 8.33 (d, 1H, *J* = 8.5 Hz), 7.97 (ddd, 1H, *J* = 8.5, 7.0, 1.5 Hz), 7.87 (s, 1H), 7.83 (d, 1H, *J* = 7.5 Hz), 7.80 (ddd, 1H, *J* = 8.5, 7.0, 1.0 Hz), 7.45-7.42 (m, 1H), 7.36 (d, 1H, *J* = 7.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.49 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.1, 166.6, 155.7,152.0, 138.0, 137.4, 137.0, 136.5, 133.3, 131.0, 130.7, 130.3, 129.8, 129.7, 129.6, 128.7, 128.1, 127.7, 125.3, 121.1, 121.0, 21.6, 18.3. HRMS: Calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1603, Found 393.1609.



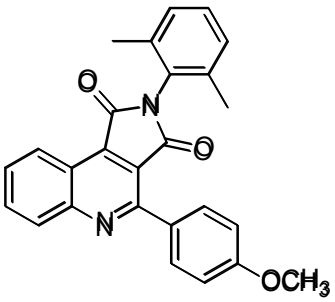
(**5h**): yellow solid: m. p. 259-261°C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 8.99 (d, 1H, *J* = 8.5 Hz), 8.31 (d, 1H, *J* = 8.5 Hz), 7.98-7.94 (m, 3H), 7.78 (t, 1H, *J* = 8.0 Hz), 7.36 (d, 2H, *J* = 7.5 Hz), 7.29 (t, 1H, *J* = 7.5 Hz), 7.20 (d, 2H, *J* = 7.5 Hz), 2.46 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 167.1, 166.7, 155.5, 152.1, 140.5, 137.4, 137.0, 133.9, 133.2, 130.3, 129.7, 129.6, 129.0, 128.6, 125.3, 121.0, 21.6, 18.3. HRMS: Calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1603, Found 393.1596.



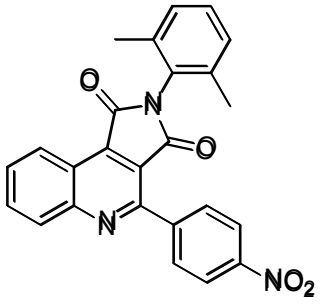
(**5i**): yellow solid: m. p. 238-240°C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 9.01 (d, 1H, *J* = 8.5 Hz), 8.34 (d, 1H, *J* = 8.5 Hz), 8.16 (d, 2H, *J* = 8.0 Hz), 7.98 (t, 1H, *J* = 8.0 Hz), 7.82-7.77 (m, 3H), 7.68 (d, 2H, *J* = 7.5 Hz), 7.48 (t, 2H, *J* = 7.5 Hz), 7.39 (t, 1H, *J* = 7.5 Hz), 7.31 (t, 1H, *J* = 7.5 Hz), 7.22 (d, 2H, *J* = 7.5 Hz), 2.24 (s, 6H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 167.1, 166.8, 155.1, 152.1, 143.1, 140.8, 137.5, 137.0, 135.6, 133.4, 130.9, 130.3, 129.9, 129.8, 129.6, 129.0, 128.7, 127.8, 127.4, 127.1, 125.4, 121.1, 18.3. HRMS: Calcd for $C_{31}H_{23}N_2O_2$ $[M+H]^+$ 455.1760, Found 455.1731.



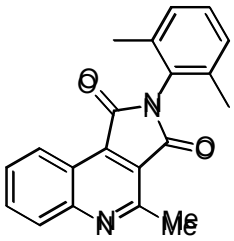
(**5j**): yellow solid: m. p. 215-217 °C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 9.01 (dd, 1H, *J* = 8.5, 0.5 Hz), 8.33 (d, 1H, *J* = 8.5 Hz), 7.97 (ddd, 1H, *J* = 8.5, 7.0, 1.5 Hz), 7.80 (td, 1H, *J* = 7.5, 1.0 Hz), 7.65-7.63 (m, 2H), 7.46 (t, 1H, *J* = 8.0 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 7.09 (dt, 1H, *J* = 8.5, 1.5 Hz), 3.91 (s, 3H), 2.23 (s, 6H).^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 167.0, 166.5, 159.5, 155.2, 151.9, 137.8, 137.4, 137.0, 133.3, 130.3, 129.9, 129.7, 129.6, 129.2, 128.6, 125.3, 122.9, 121.1, 121.0, 116.2, 115.6, 55.5, 18.3. HRMS: Calcd for $C_{26}H_{21}N_3O_3$ $[M+H]^+$ 409.1552, Found 409.1552.



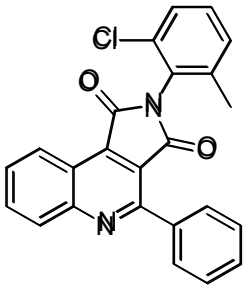
(**5k**): yellow solid: m. p. 168-170 °C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 8.97 (d, 1H, *J* = 8.0 Hz), 8.28 (d, 1H, *J* = 8.5 Hz), 8.06 (d, 2H, *J* = 8.5Hz), 7.94 (t, 1H, *J* = 7.5 Hz), 7.76 (t, 1H, *J*= 7.5 Hz), 7.29 (t, 1H, *J*= 7.5 Hz), 7.20 (d, 2H, *J* = 7.5 Hz), 7.06 (d, 2H, *J* = 8.5 Hz), 3.89 (s, 3H), 2.21(s, 6H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 167.2, 166.9, 161.5, 155.1, 152.1, 137.5, 137.0, 133.3, 132.1, 130.1, 129.7, 129.6, 129.5, 129.2, 128.7, 125.3, 120.8, 120.7, 113.7, 55.6, 18.3. HRMS: Calcd for $C_{26}H_{21}N_3O_3$ $[M+H]^+$ 409.1552, Found 409.1546.



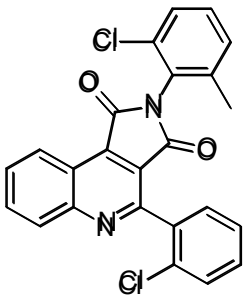
(**5l**): yellow solid: m. p. 198-199°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.03 (d, 1H, *J* = 7.5 Hz), 8.38 (dd, 2H, *J* = 7.0, 2.0 Hz), 8.34 (d, 1H, *J* = 8.5 Hz), 8.26-8.24 (m, 2H), 8.03 (ddd, 1H, *J* = 8.5, 7.0, 1.5 Hz), 7.87 (ddd, 1H, *J* = 8.5, 7.0, 1.0 Hz), 7.31 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.7,166.4, 152.7, 152.0, 148.9, 142.6, 137.6, 136.9, 133.8, 131.5, 130.8, 130.5, 129.9, 129.3, 128.8, 125.4, 123.3, 121.4, 121.1, 18.3. HRMS: Calcd for $C_{25}H_{18}N_3O_4$ $[M+H]^+$ 424.1297, Found 424.1292.



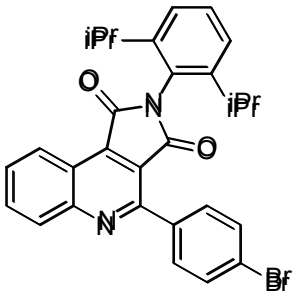
(**5m**): yellow solid: m. p. 165-166°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.86 (d, 1H, *J* = 8.5 Hz), 8.18 (d, 1H, *J* = 8.5 Hz), 7.91 (td, 1H, *J* = 7.0, 1.5 Hz), 7.74 (t, 1H, *J* = 7.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 3.11 (s, 3H), 2.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.5, 167.3, 155.5, 151.9, 137.1, 136.0, 133.0, 129.7, 129.5, 129.4, 129.2, 128.7, 125.3, 122.0, 120.9, 22.4, 18.3. HRMS: Calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290, Found 317.1281.



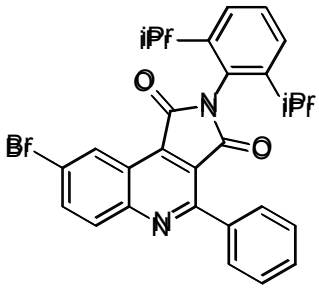
(**6a**): yellow solid: m. p. 264-266 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.99 (d, 1H, *J* = 8.0 Hz), 8.32 (d, 1H, *J* = 8.5 Hz), 8.05-8.03 (m, 2H), 7.98 (ddd, 1H, *J* = 8.5, 7.0, 1.5 Hz), 7.81 (ddd, 1H, *J* = 8.5, 7.0, 1.0 Hz), 7.55-7.54 (m, 3H), 7.42 (d, 1H, *J* = 8.0 Hz), 7.35 (t, 1H, *J* = 8.0 Hz), 7.28 (d, 1H, *J* = 7.5 Hz), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.5, 166.0, 155.6, 152.1, 139.9, 137.4, 136.6, 133.9, 133.4, 130.8, 130.4, 130.3, 129.9, 129.5, 128.5, 128.3, 127.8, 125.4, 121.1, 18.6. HRMS: Calcd for $C_{24}H_{16}ClN_2O_2$ $[M+H]^+$ 399.0900, Found 399.0883.



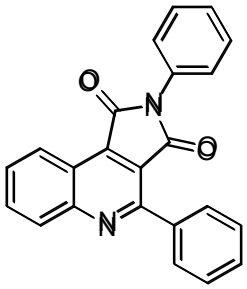
(**6b**): yellow solid: m. p. 183-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.99 (d, 1H, *J* = 8.0 Hz), 8.35 (d, 1H, *J* = 8.5 Hz), 8.0 (td, 1H, *J* = 7.0, 1.5 Hz), 7.88-7.84 (m, 1H), 7.66-7.64 (m, 1H), 7.54-7.51 (m, 1H), 7.47-7.45 (m, 2H), 7.39 (d, 1H, *J* = 8.0 Hz), 7.32 (t, 1H, *J* = 7.5 Hz), 7.26 (d, 1H, *J* = 7.5 Hz), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.4, 165.2, 153.0, 151.9, 139.8, 136.2, 136.1, 133.8, 133.7, 133.3, 130.9, 130.8, 130.7, 130.4, 130.3, 129.6, 129.4, 128.4, 127.8, 127.2, 125.4, 122.7, 121.5, 18.6. HRMS: Calcd for $C_{24}H_{15}Cl_2N_2O_2$ $[M+H]^+$ 433.0511, Found 433.0503.



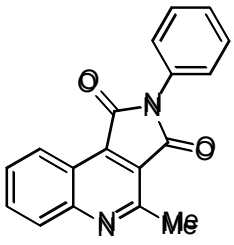
(**6c**): yellow solid: m. p. 238-240 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 9.01 (d, 1H, *J* = 8.5 Hz), 8.31 (d, 1H, J = 8.5 Hz), 8.00-7.95 (m, 3H), 7.83-7.80 (m, 1H), 7.67 (d, 2H, *J* = 8.5 Hz),7.49 (t, 1H, *J* = 8.0 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 2.78 (heptet, 2H, *J* = 7.0 Hz), 1.19 (dd, 12H, *J* = 10.0, 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 167.9, 167.5, 154.2, 152.0, 147.5, 137.5, 135.6, 133.5, 132.0, 131.5, 130.6, 130.3, 130.0, 126.6, 125.6, 125.1, 124.2, 121.2, 120.9, 29.6, 24.2, 24.1. HRMS: Calcd for $C_{29}H_{26}BrN_2O_2$ $[M+H]^+$ 513.1178, Found 513.1169.



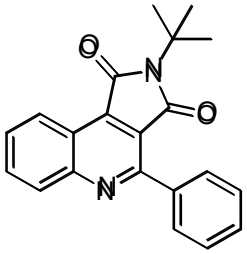
(**6d**): yellow solid: m. p. 258-260 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 9.19 (s, 1H), 8.20 (d, 1H, *J* = 9.0 Hz), 8.04 (t, 3H, *J* = 9.0 Hz), 7.55-7.49 (m, 4H), 7.33 (d, 2H, *J* = 8.0 Hz), 2.81-2.78 (m, 2H), 1.21 (dd, 12H, J = 12.0, 7.0 Hz). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 167.6, 167.1, 155.7, 150.5, 147.4, 136.8, 136.4, 136.3, 131.7, 130.6, 130.5, 130.4, 128.3, 127.5, 126.5, 124.6, 124.2, 121.8, 121.6, 29.6, 24.2, 24.1. HRMS: Calcd for $C_{29}H_{26}BrN_2O_2$ $[M+H]^+$ 513.1178, Found 513.1179.



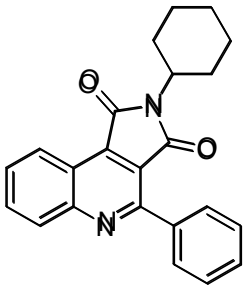
(**6e**): yellow solid: m. p. 241-242 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 8.98 (d, 1H, *J* = 8.5 Hz), 8.29 (d, 1H, *J* = 8.5 Hz), 8.01-7.93 (m, 3H), 7.78 (t, 1H, *J* = 7.0 Hz), 7.55-7.42 (m, 8H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 167.1, 166.6, 155.5, 151.9, 137.2, 136.7, 133.3, 131.4, 130.3, 130.2, 130.2, 129.9, 129.3, 128.5, 128.2, 126.9, 125.2, 121.0, 120.8. HRMS: Calcd for $C_{23}H_{15}N_2O_2$ $[M+H]^+$ 351.1134, Found 351.1151.



(**6f**): yellow solid: m. p. 170-172 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) = 8.79 (d, 1H, *J* = 8.0 Hz), 8.12 (d, 1H, *J* = 8.5 Hz), 7.89-7.86 (m, 1H), 7.69 (t, 3H, *J* = 7.5 Hz), 7.55-7.42 (m, 5H), 3.06 (s, 3H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ (ppm) = 167.5, 167.3, 155.4, 151.7, 135.7, 132.9, 131.4, 129.4, 129.3, 129.2, 128.4, 126.7, 125.1, 121.6, 120.7, 22.3. HRMS: Calcd for $C_{18}H_{13}N_2O_2$ $[M+H]^+$ 289.0977, Found 289.0962.



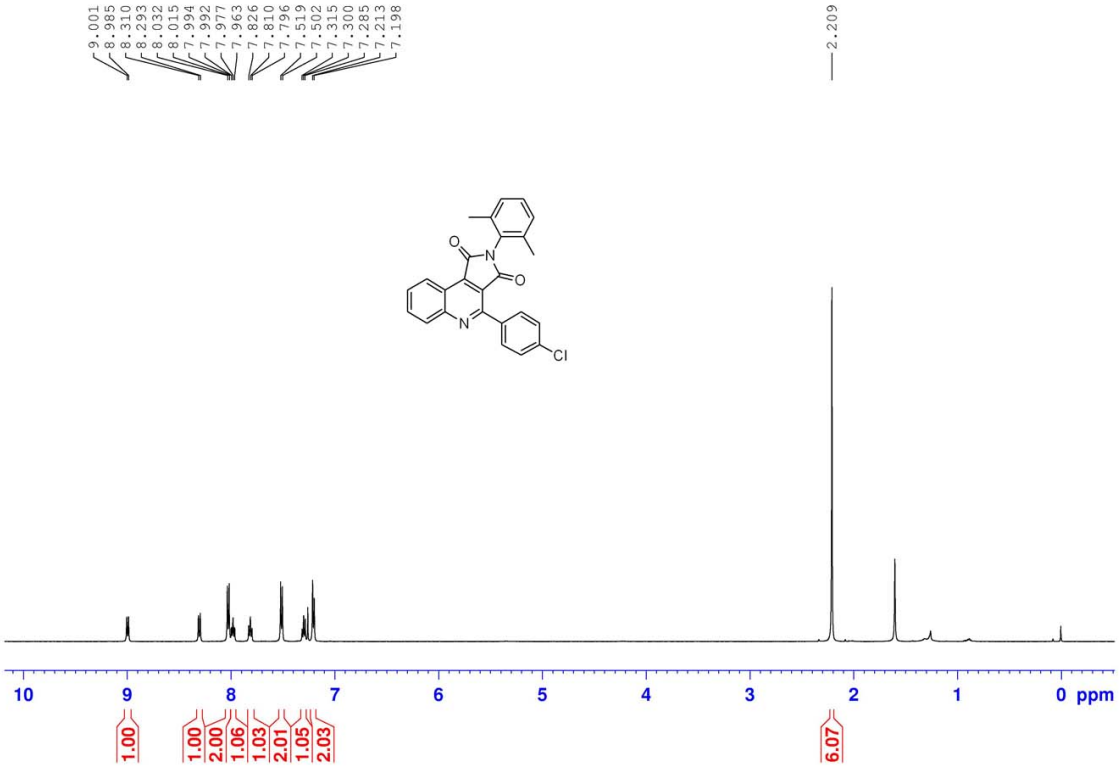
(**6g**): yellow solid: m. p. 151-152°C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 8.95 (d, 1H, *J* = 8.5 Hz), 8.24 (d, 1H, *J* = 8.5 Hz), 7.92-7.87 (m, 3H), 7.75-7.72 (m, 1H), 7.57-7.53 (m, 3H), 1.73 (s, 9H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 169.5, 168.8, 155.1, 151.5, 137.1, 137.0, 132.7, 130.2, 130.1, 129.9, 129.5, 128.2, 125.1, 121.3, 120.8, 58.6, 29.3. HRMS: Calcd for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 331.1447, Found 331.1424.

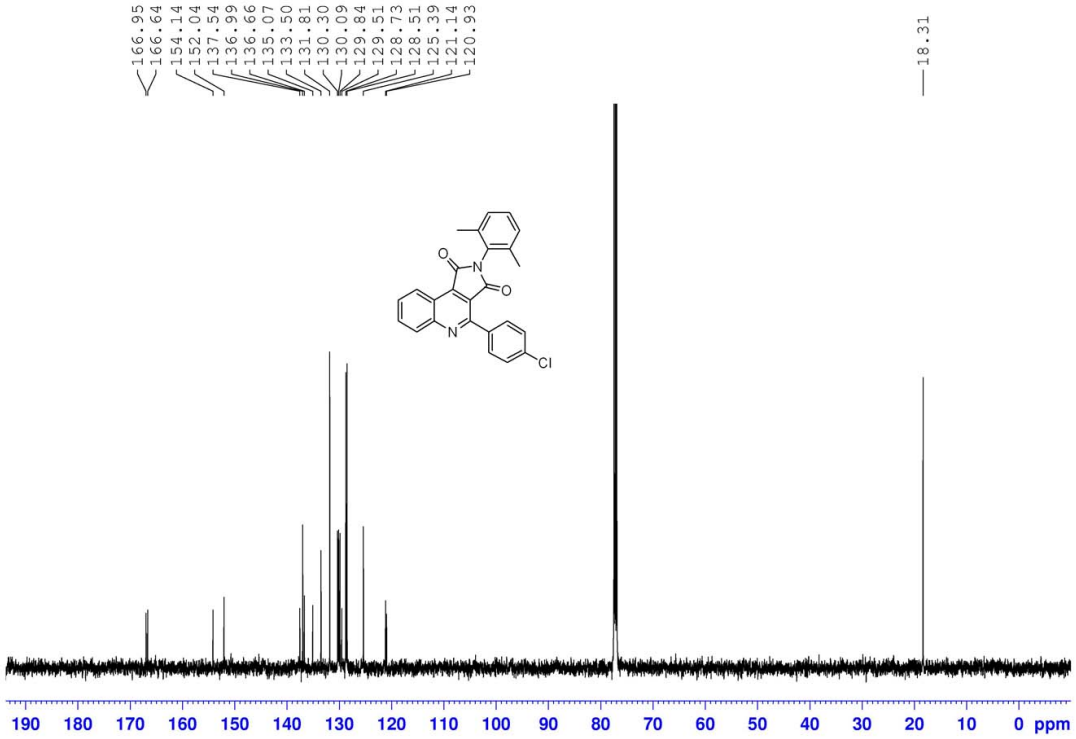


(**6h**): yellow solid: m. p. 163-164°C. ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) = 8.91 (dt, 1H, *J* = 8.5, 0.5 Hz), 8.23 (d, 1H, *J* = 8.5 Hz), 7.96-7.86 (m, 3H), 7.74-7.71 (m, 1H), 7.57-7.53 (m, 3H), 4.20-4.14 (m, 1H), 2.29-2.20 (m, 2H), 1.90-1.69 (m, 5H), 1.42-1.25 (m, 3H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ (ppm) = 168.2, 167.7, 155.1, 151.6, 137.3, 136.8, 132.8, 130.2, 130.1, 130.0, 129.5, 128.1, 125.0, 121.1, 120.9, 51.4, 30.0, 26.2, 25.2. HRMS: Calcd for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ 357.1603, Found 357.1574.

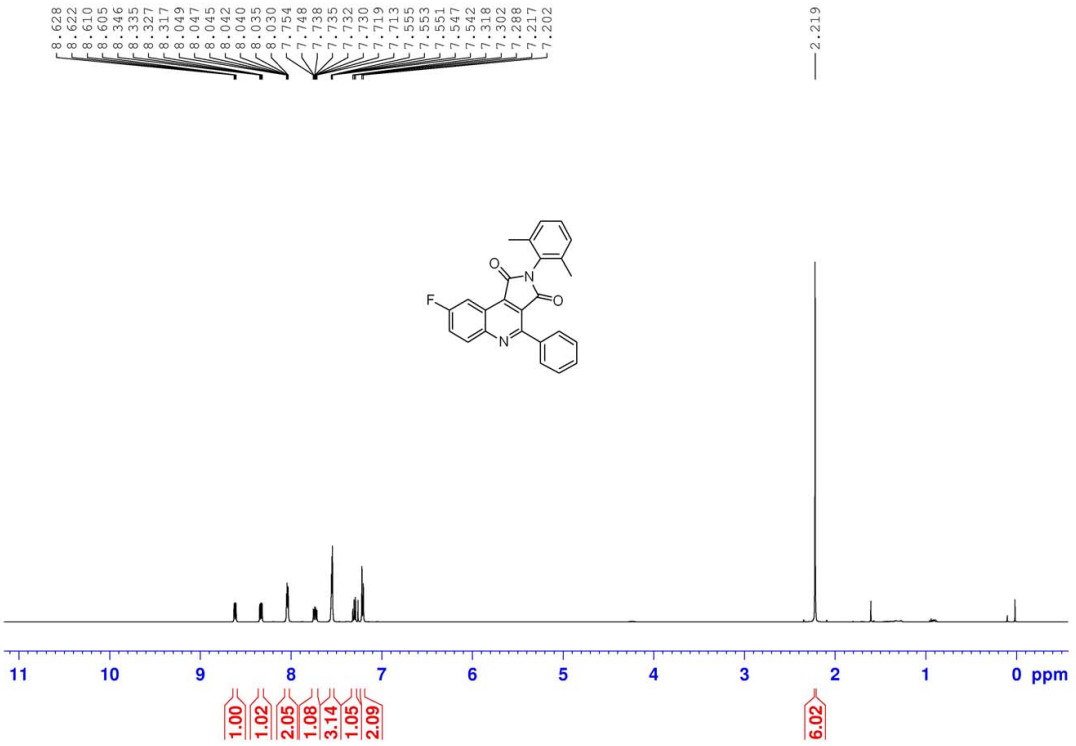
4 ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

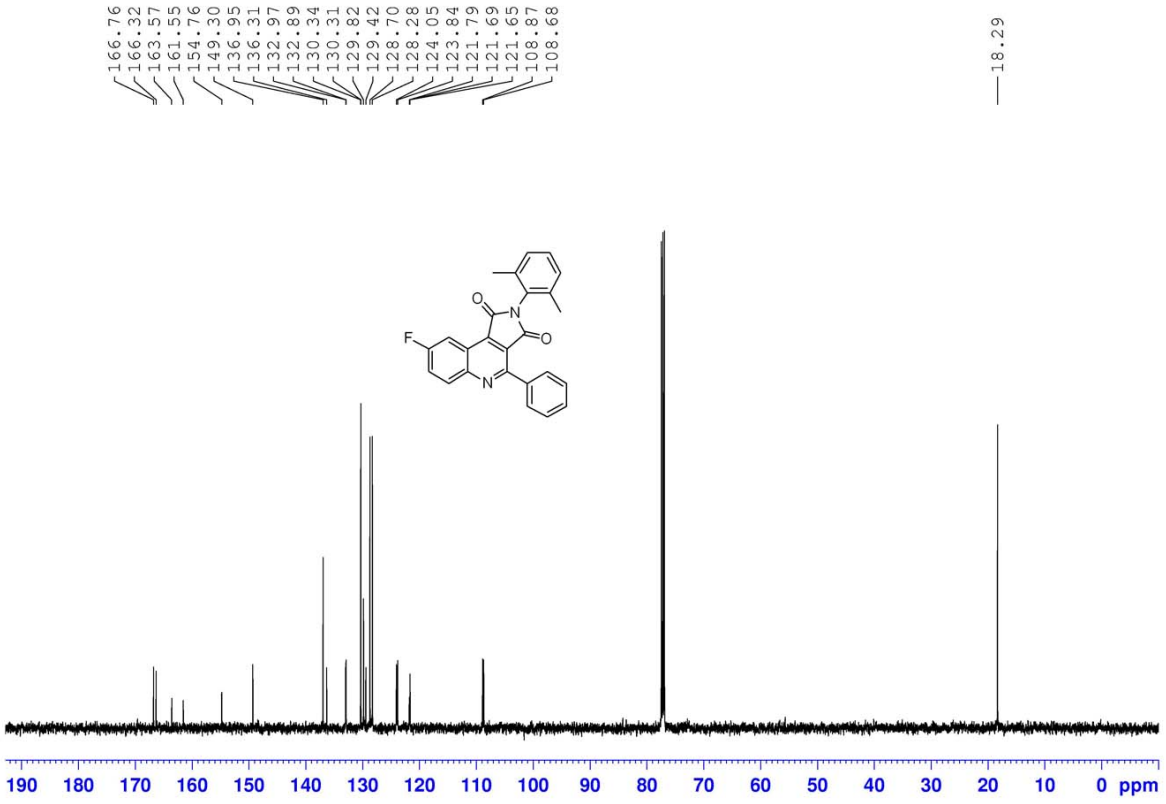
Compound **3a**



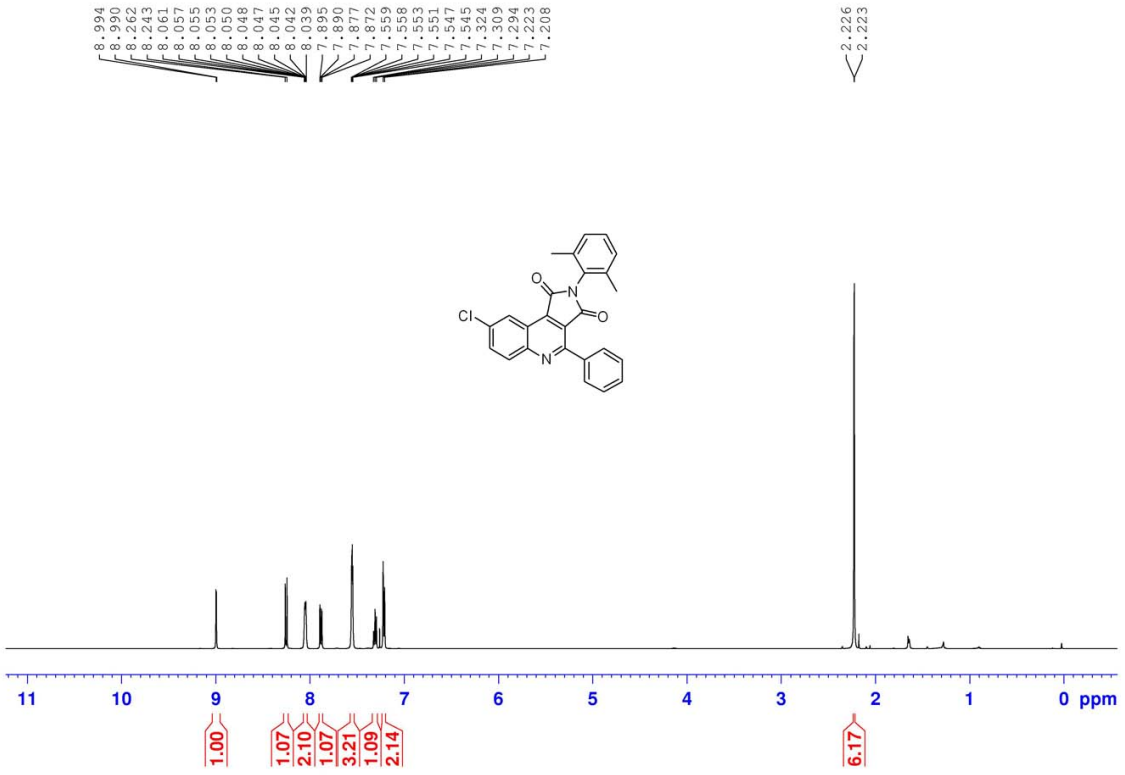

166.95
166.64
154.14
152.04
137.54
136.99
136.66
135.07
133.50
131.81
130.30
130.09
129.84
129.51
128.73
128.51
125.39
121.14
120.93
18.31
O
N
O
N
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

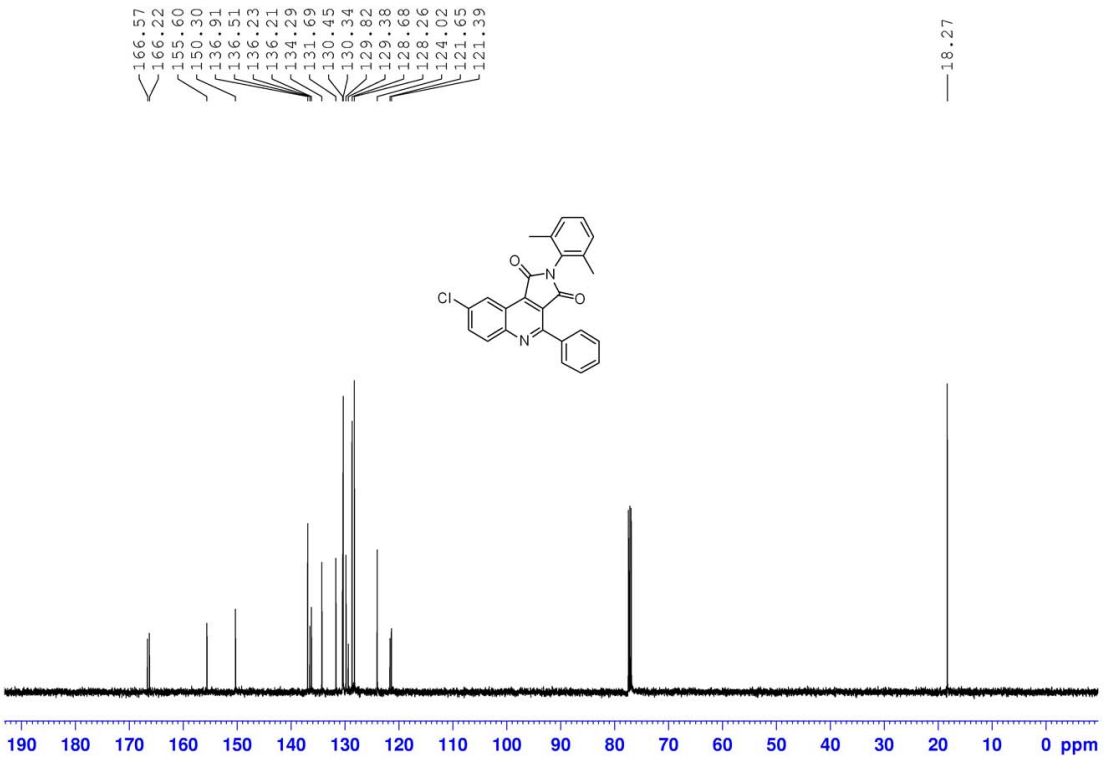
Compound **3b**


8.628
8.622
8.610
8.605
8.346
8.335
8.327
8.317
8.049
8.047
8.045
8.042
8.040
8.035
8.030
7.754
7.748
7.738
7.735
7.732
7.730
7.719
7.713
7.555
7.553
7.551
7.547
7.542
7.318
7.302
7.288
7.217
7.202
2.219
O
N
O
F
N
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
2.05
1.08
3.14
1.05
2.09
6.02

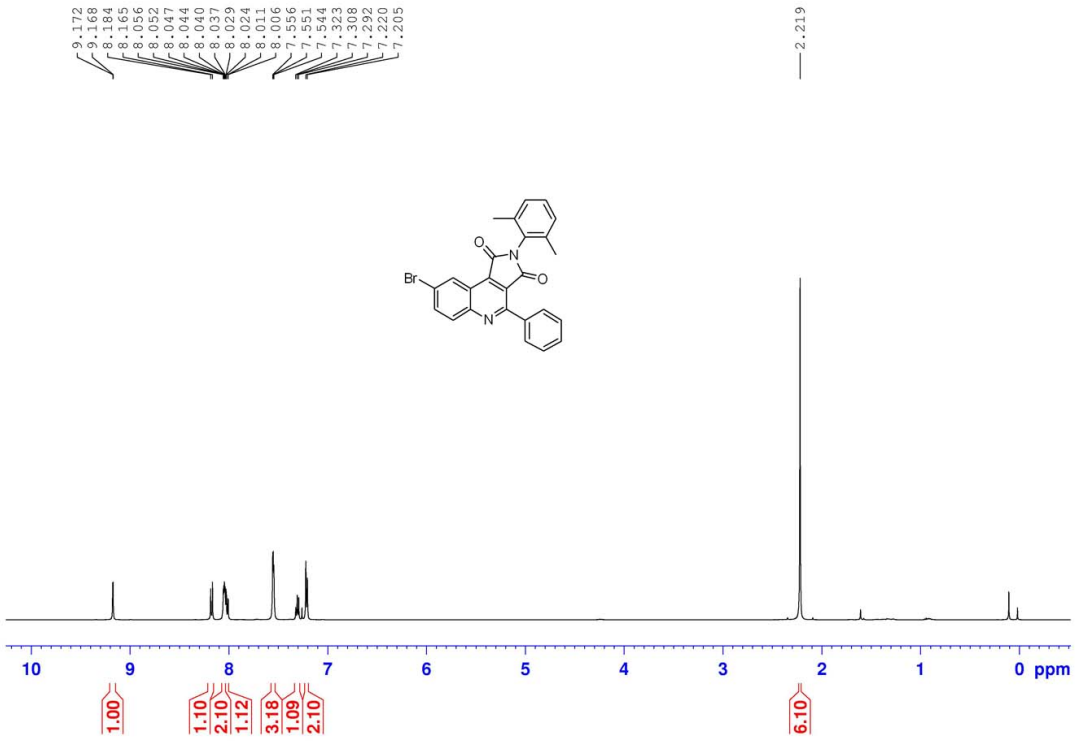

166.76
166.32
163.57
161.55
154.76
149.30
136.95
136.31
132.97
132.89
130.34
130.31
129.82
129.42
128.70
128.28
124.05
123.84
121.79
121.69
121.65
108.87
108.68
18.29
O
N
O
F
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

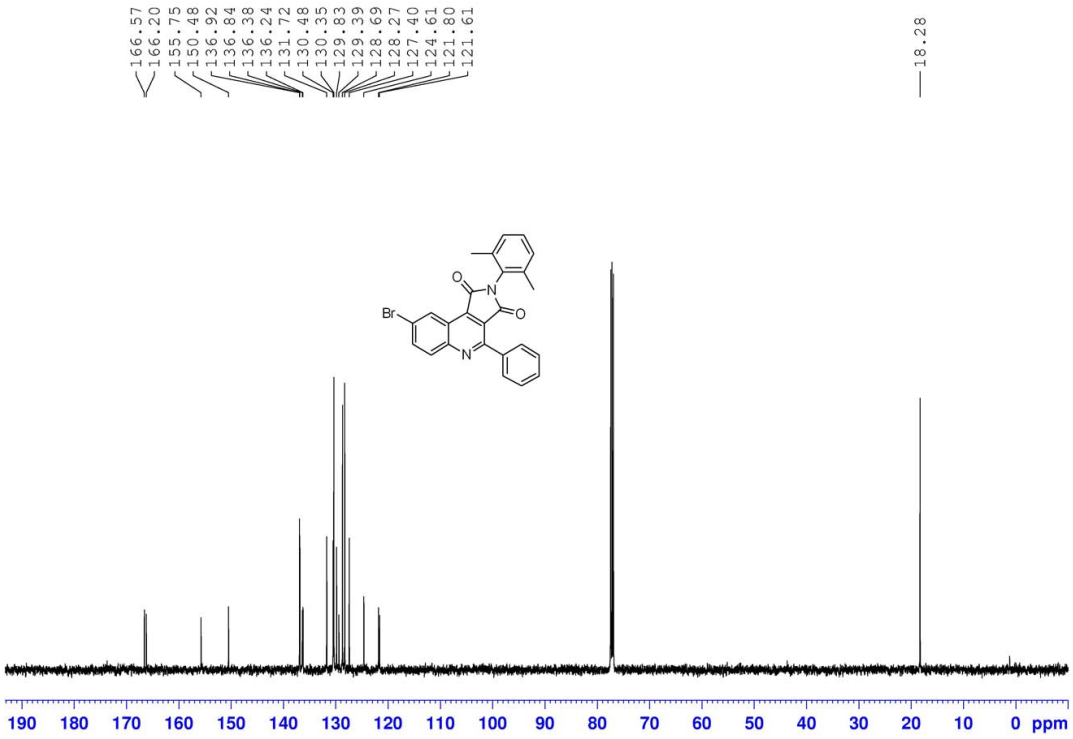
Compound **3c**


8.994
8.990
8.262
8.243
8.061
8.057
8.055
8.053
8.050
8.048
8.047
8.045
8.042
8.039
7.895
7.890
7.877
7.872
7.559
7.558
7.553
7.551
7.547
7.545
7.324
7.309
7.294
7.223
7.208
2.226
2.223
O
N
O
Cl
N
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.07
2.10
1.07
3.21
1.09
2.14
6.17

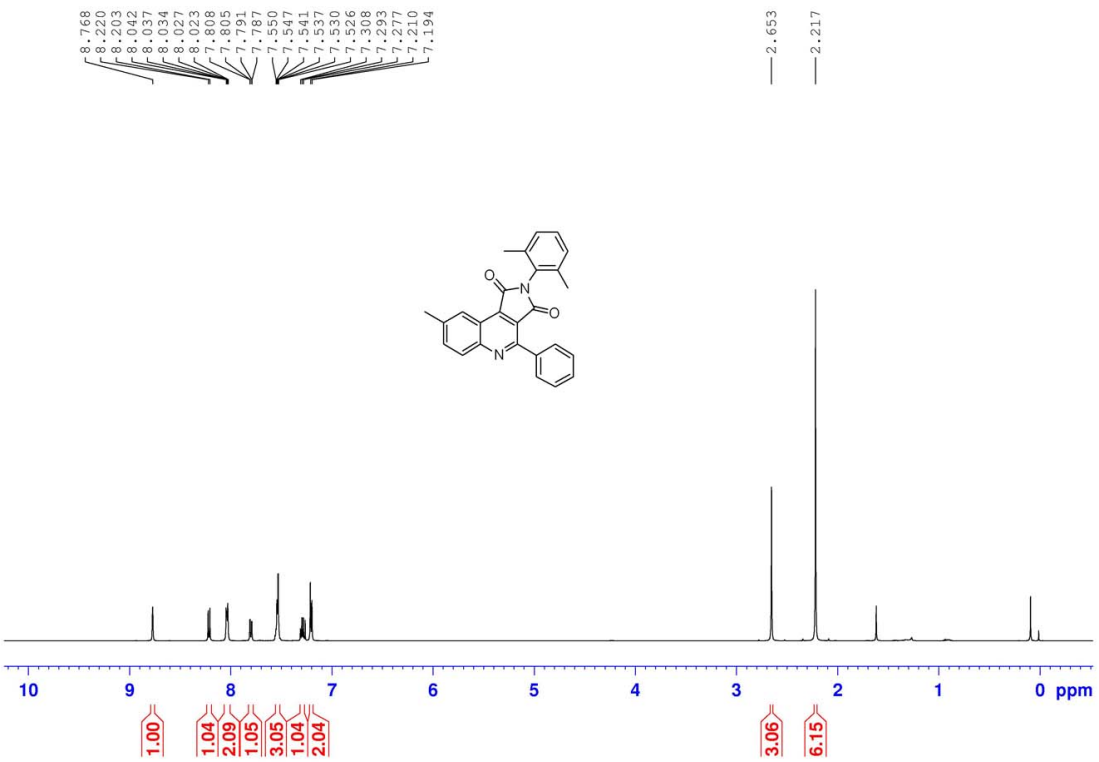

166.57
166.22
155.60
150.30
136.91
136.51
136.23
136.21
134.29
131.69
130.45
130.34
129.82
129.38
128.68
128.26
124.02
121.65
121.39
18.27
Cl
O
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

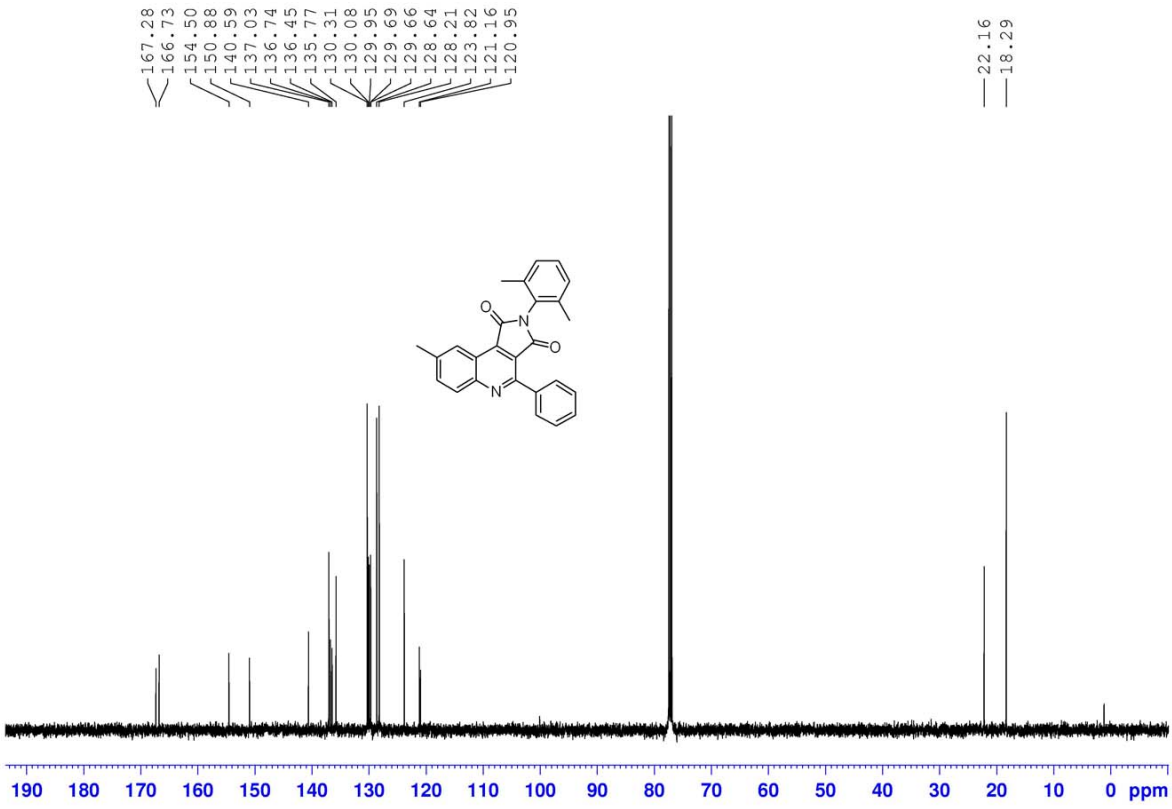
Compound **3d**


9.172
9.168
8.184
8.165
8.056
8.052
8.047
8.044
8.040
8.037
8.029
8.024
8.011
8.006
7.556
7.551
7.544
7.323
7.308
7.292
7.220
7.205
2.219
Br
O
N
O
N
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.10
2.10
1.12
3.18
1.09
2.10
6.10

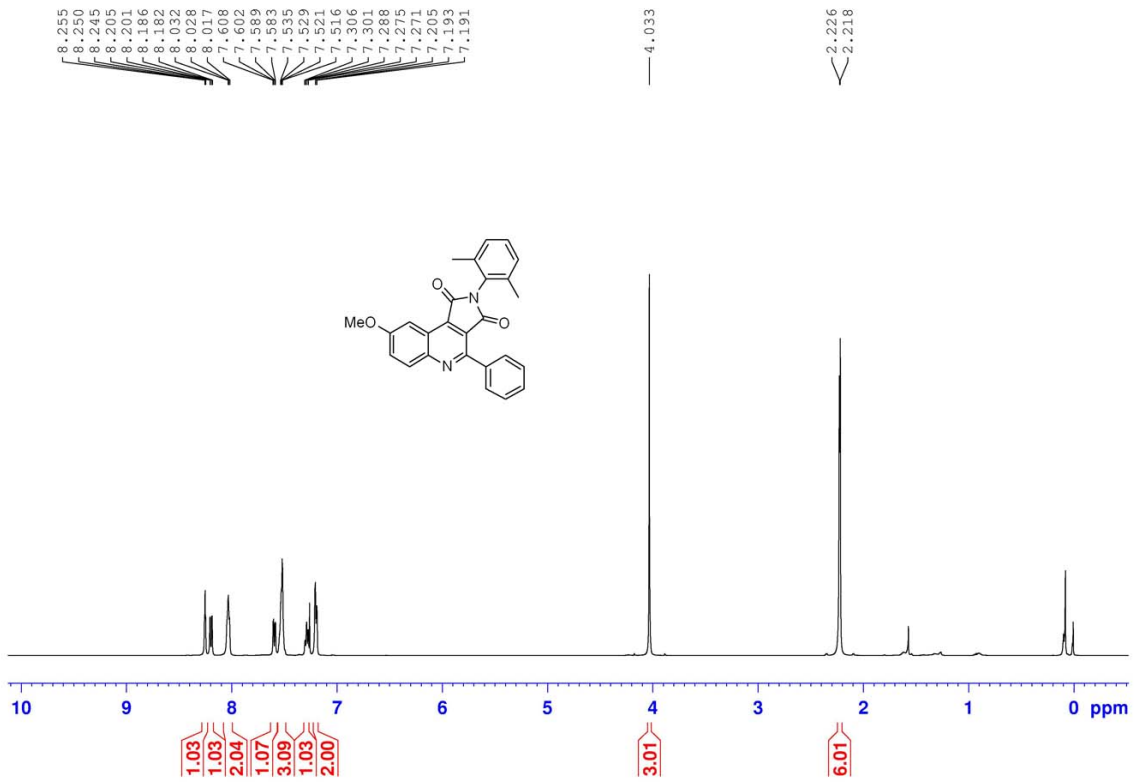

166.57
166.20
155.75
150.48
136.92
136.84
136.38
136.24
131.72
130.48
130.35
129.83
129.39
128.69
128.27
127.40
124.61
121.80
121.61
18.28
O
N
O
Br
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

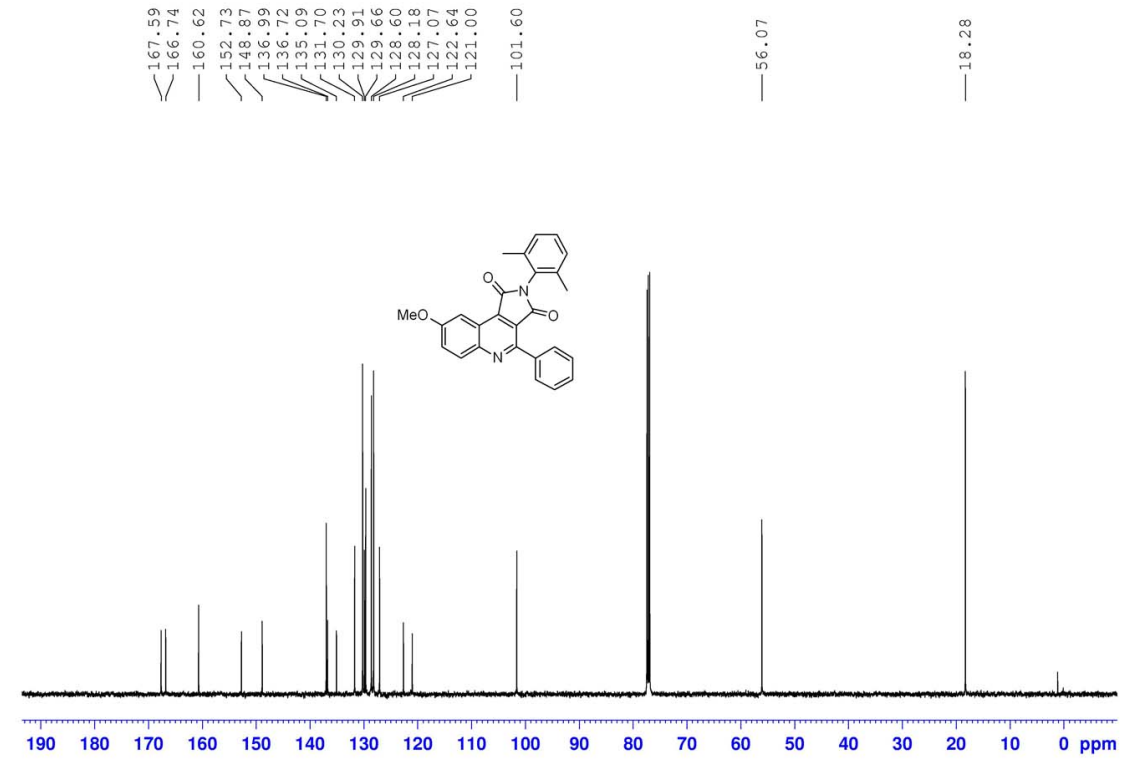
Compound **3e**


8.768
8.220
8.203
8.042
8.037
8.034
8.027
8.023
7.808
7.805
7.791
7.787
7.550
7.547
7.541
7.537
7.530
7.526
7.308
7.293
7.277
7.210
7.194
2.653
2.217
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.04
2.09
1.05
3.05
1.04
2.04
3.06
6.15

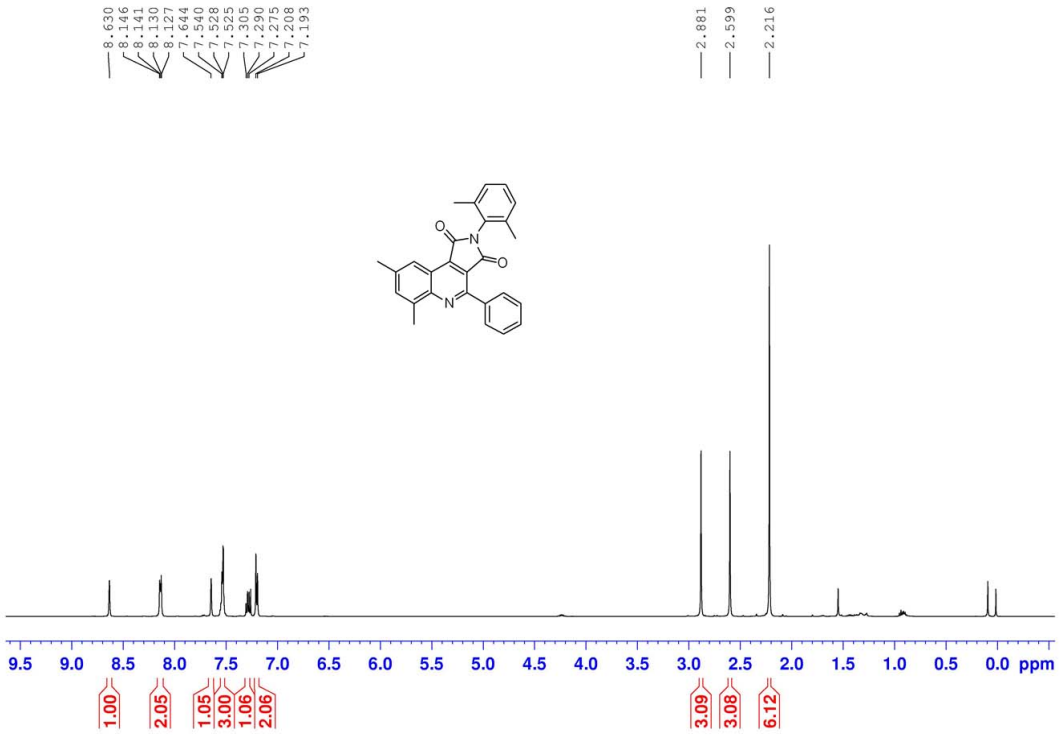

167.28
166.73
154.50
150.88
140.59
137.03
136.74
136.45
135.77
130.31
130.08
129.95
129.69
129.66
128.64
128.21
123.82
121.16
120.95
22.16
18.29
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

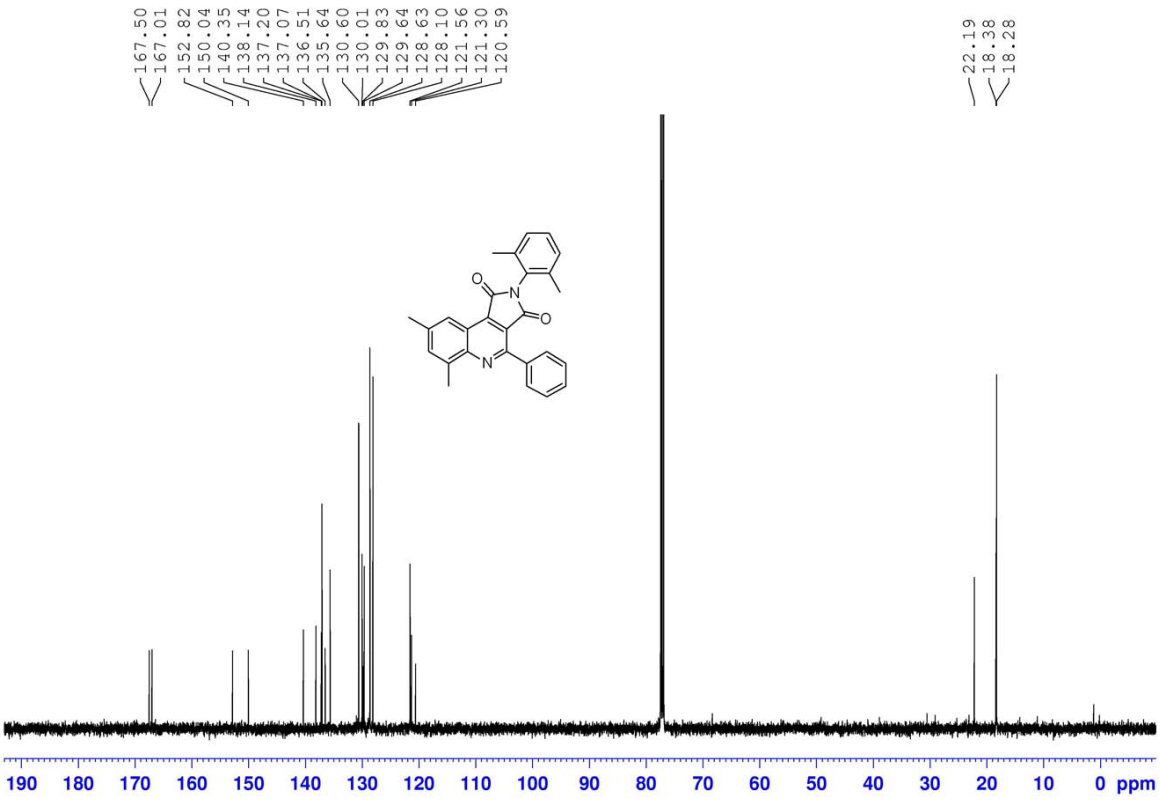
Compound **3f**


8.255
8.250
8.245
8.205
8.201
8.186
8.182
8.032
8.028
8.017
7.608
7.602
7.589
7.583
7.535
7.529
7.521
7.516
7.306
7.301
7.288
7.275
7.271
7.205
7.193
7.191
4.033
2.226
2.218
MeO
O
N
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
1.03
2.04
1.07
3.09
1.03
2.00
3.01
6.01

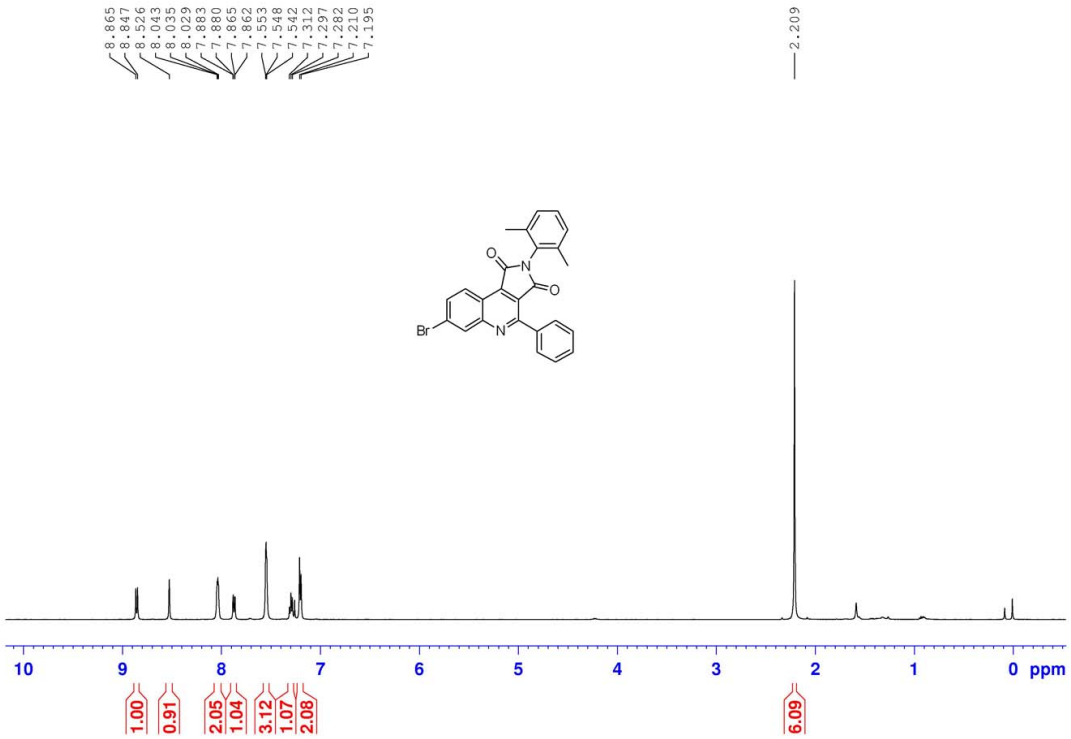

167.59
166.74
160.62
152.73
148.87
136.99
136.72
135.09
131.70
130.23
129.91
129.66
128.60
128.18
127.07
122.64
121.00
101.60
56.07
18.28
MeO
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

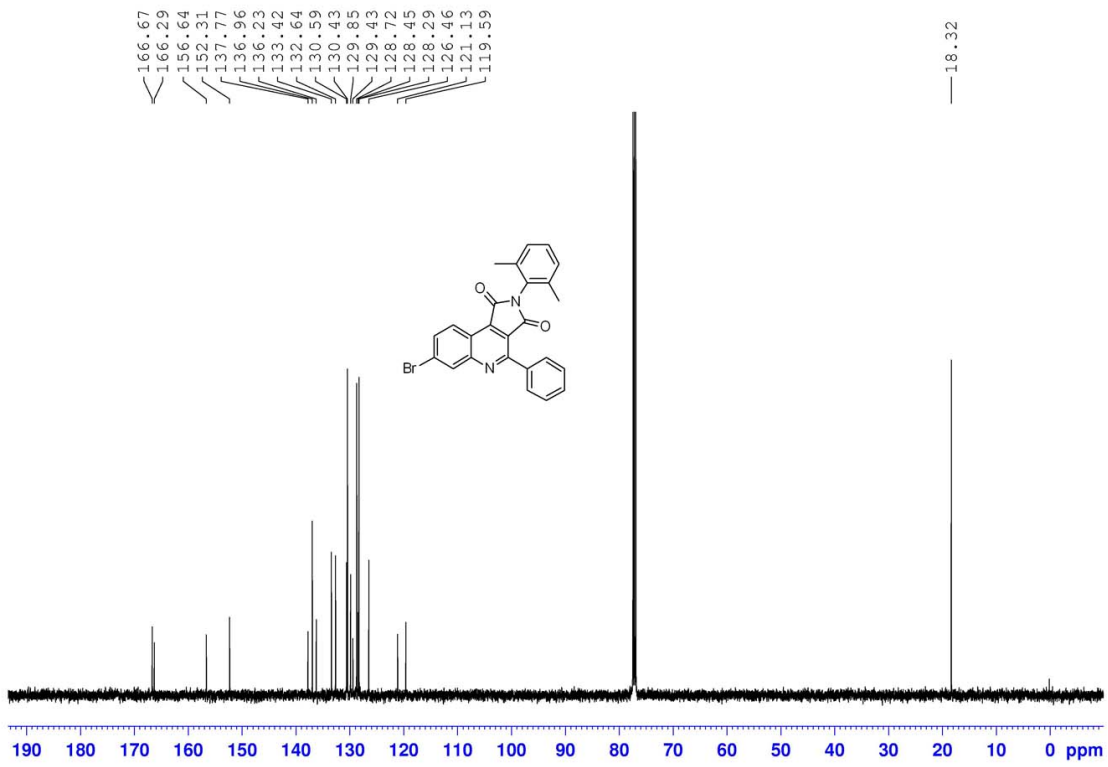
Compound **3g**


8.630
8.146
8.141
8.130
8.127
7.644
7.540
7.528
7.525
7.305
7.290
7.275
7.208
7.193
2.881
2.599
2.216
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.05
1.05
3.00
1.06
2.06
3.09
3.08
6.12

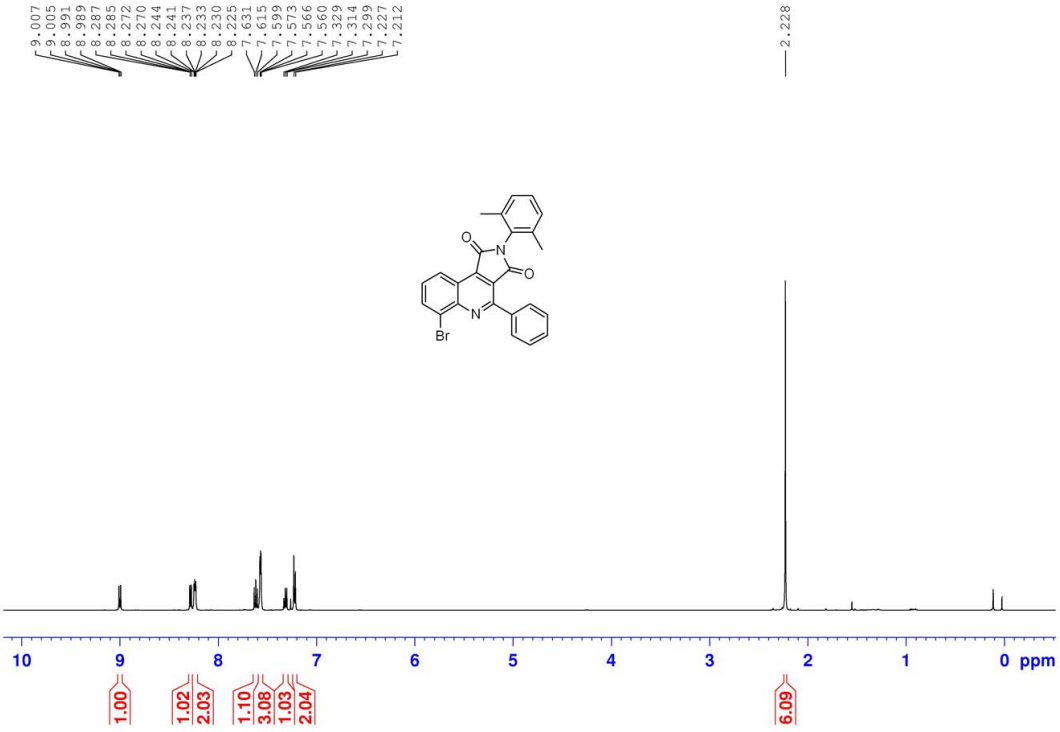

167.50
167.01
152.82
150.04
140.35
138.14
137.20
137.07
136.51
135.64
130.60
130.01
129.83
129.64
128.63
128.10
121.56
121.30
120.59
22.19
18.38
18.28
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

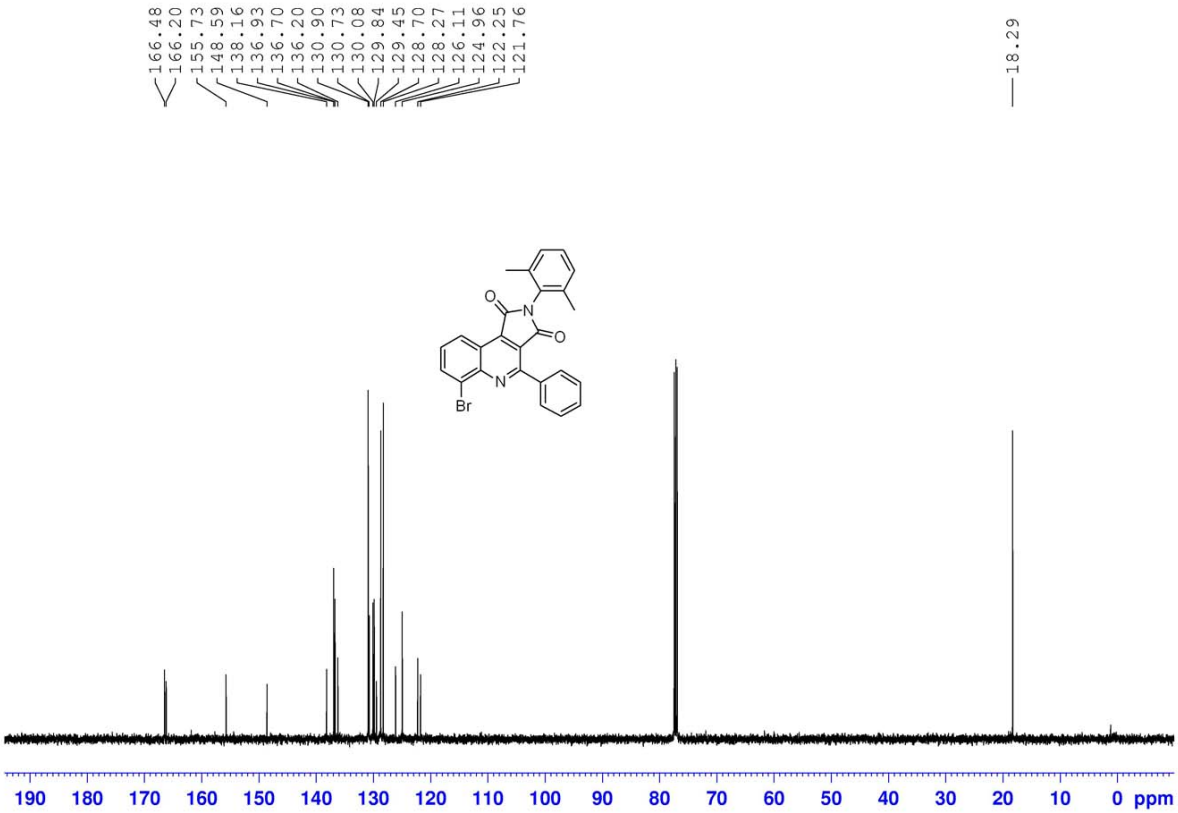
Compound **3h**


8.865
8.847
8.526
8.043
8.035
8.029
7.883
7.880
7.865
7.862
7.553
7.548
7.542
7.312
7.297
7.282
7.210
7.195
2.209
Br
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.91
2.05
1.04
3.12
1.07
2.08
6.09

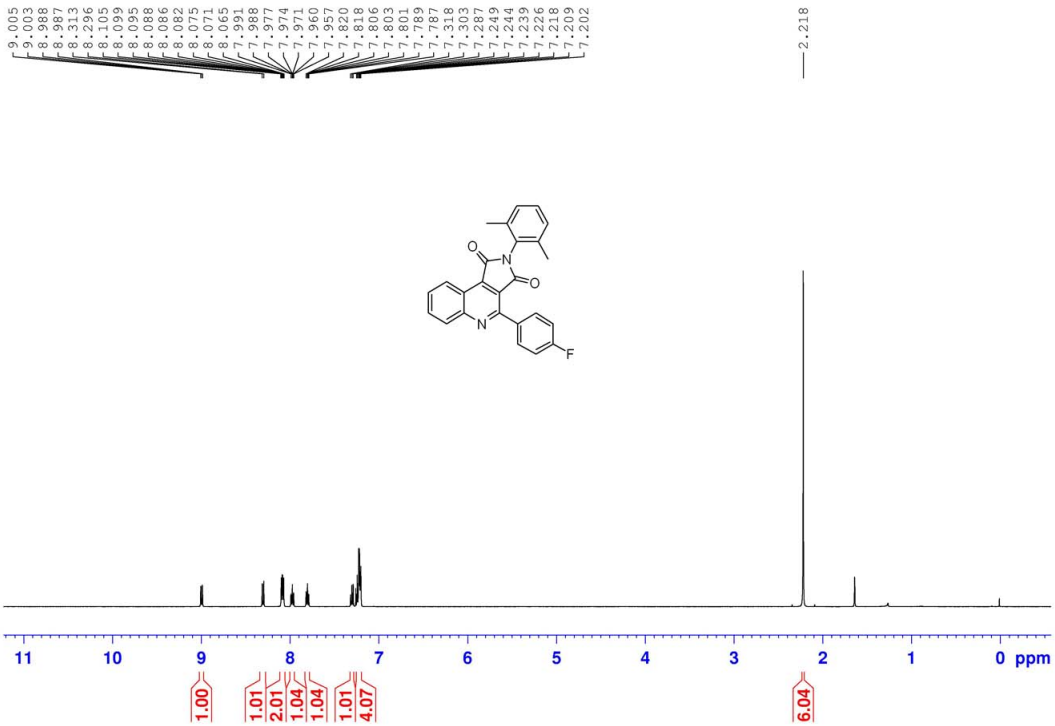

166.67
166.29
156.64
152.31
137.77
136.96
136.23
133.42
132.64
130.59
130.43
129.85
129.43
128.72
128.45
128.29
126.46
121.13
119.59
18.32
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

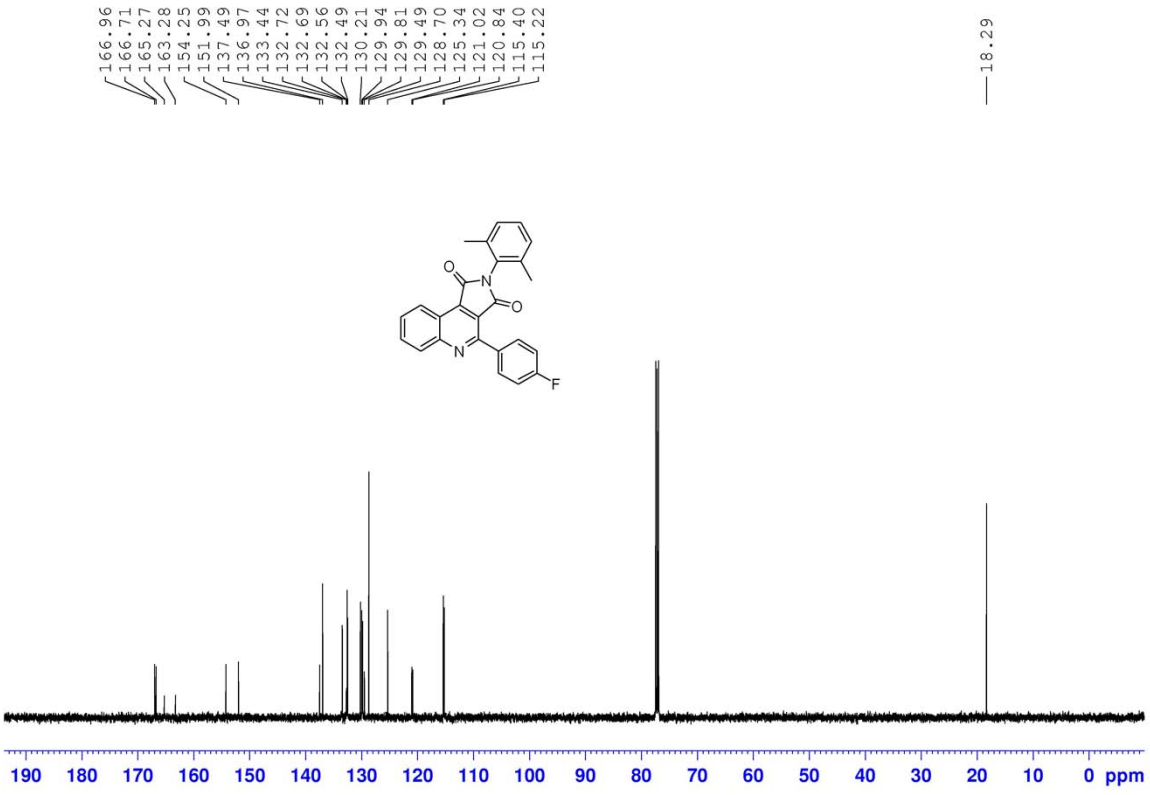
Compound **3i**


9.007
9.005
8.991
8.989
8.287
8.285
8.272
8.270
8.244
8.241
8.237
8.233
8.230
8.225
7.631
7.615
7.599
7.573
7.566
7.560
7.329
7.314
7.299
7.227
7.212
2.228
O
N
O
N
Br
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.02
2.03
1.10
3.08
1.03
2.04
6.09

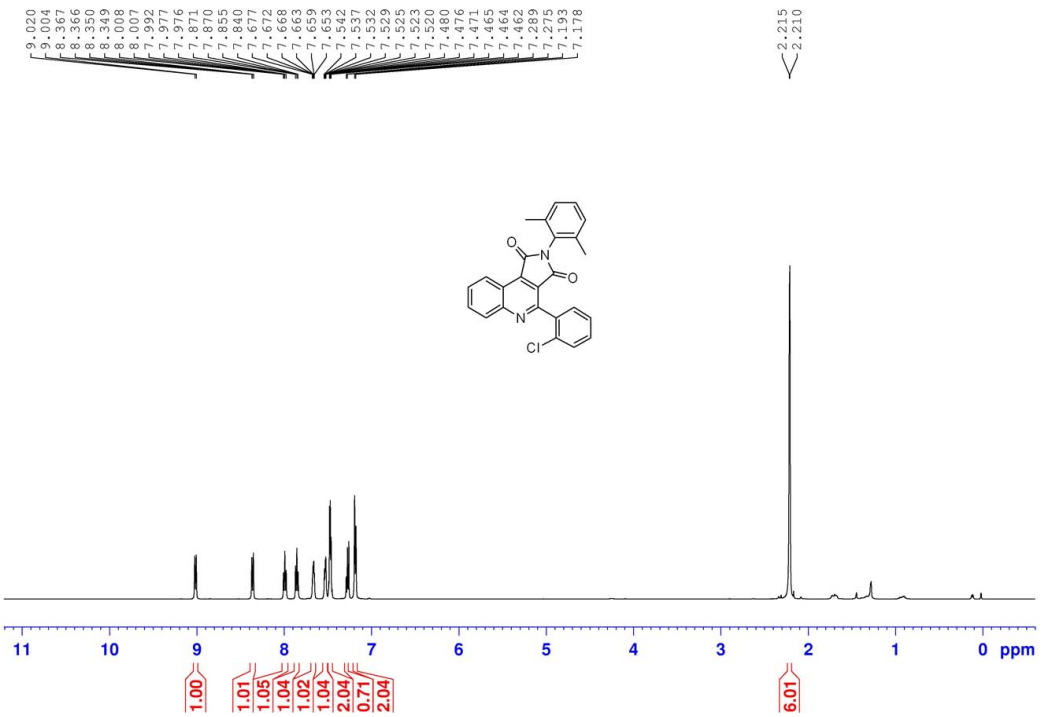

166.48
166.20
155.73
148.59
138.16
136.93
136.70
136.20
130.90
130.73
130.08
129.84
129.45
128.70
128.27
126.11
124.96
122.25
121.76
18.29
O
N
O
N
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

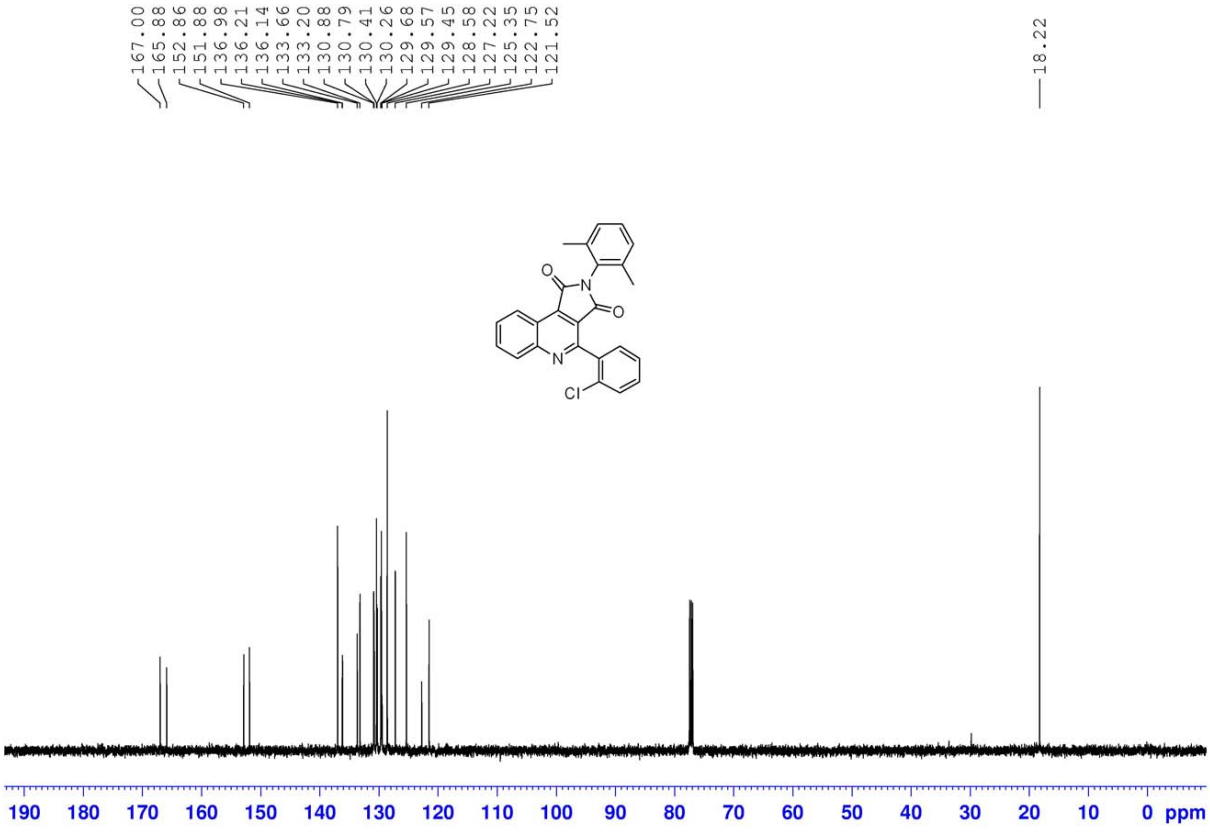
Compound **5a**


9.005
9.003
8.988
8.987
8.313
8.296
8.105
8.099
8.095
8.088
8.086
8.082
8.075
8.071
8.065
7.991
7.988
7.977
7.974
7.971
7.960
7.957
7.820
7.818
7.806
7.803
7.801
7.789
7.787
7.318
7.303
7.287
7.249
7.244
7.239
7.226
7.218
7.209
7.202
2.218
O
N
O
N
F
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
2.01
1.04
1.04
1.01
4.07
6.04

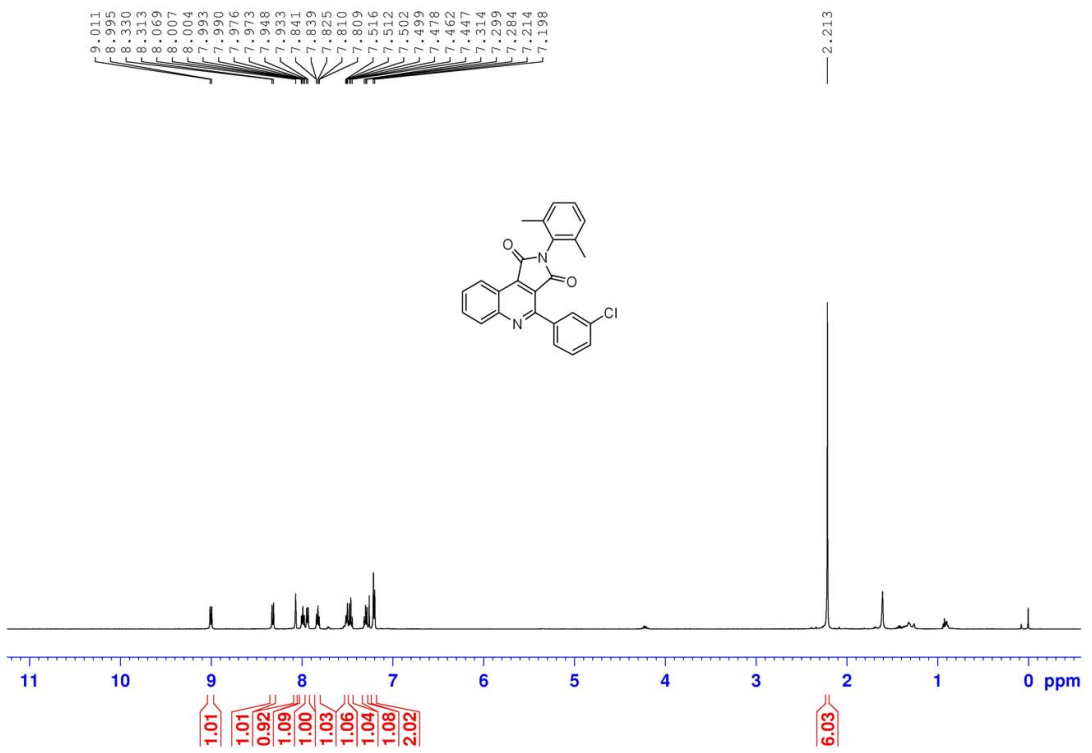

166.96
166.71
165.27
163.28
154.25
151.99
137.49
136.97
133.44
132.72
132.69
132.56
132.49
130.21
129.94
129.81
129.49
128.70
125.34
121.02
120.84
115.40
115.22
18.29
O
N
O
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

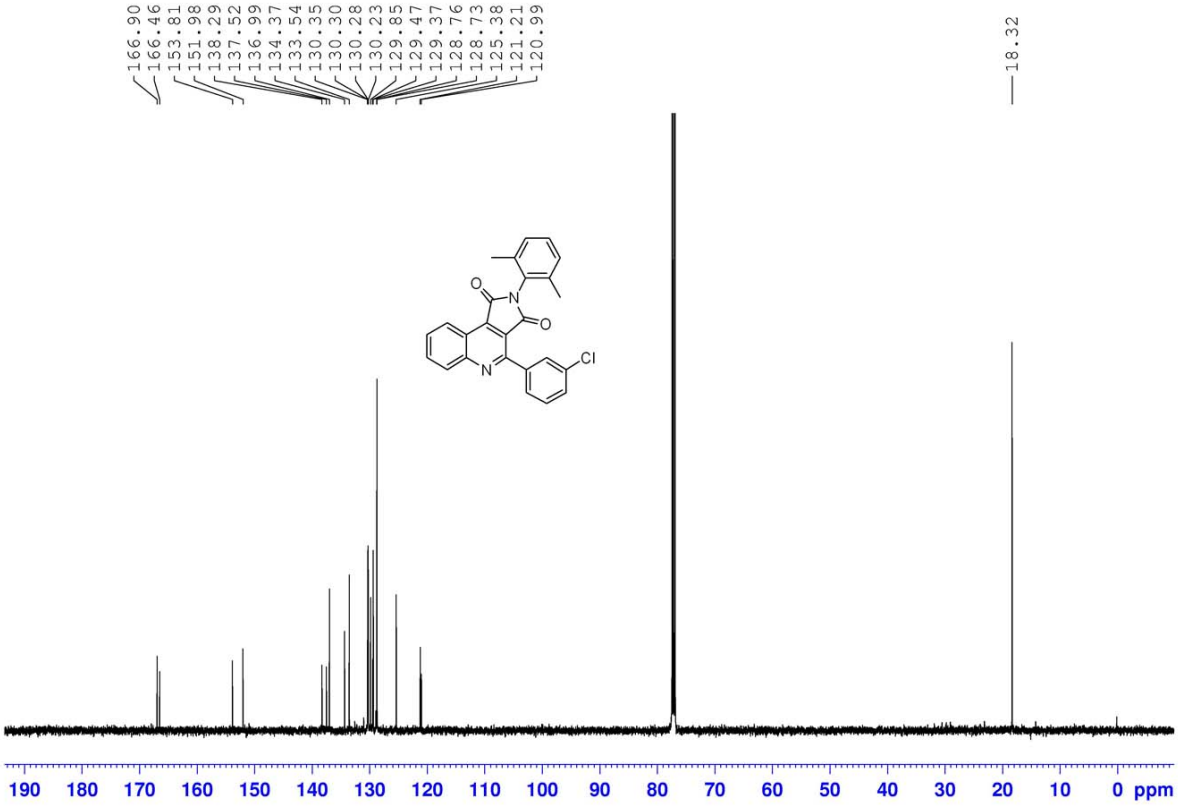
Compound **5b**


9.020
9.004
8.367
8.366
8.350
8.349
8.008
8.007
7.992
7.977
7.976
7.871
7.870
7.855
7.840
7.677
7.672
7.668
7.663
7.659
7.653
7.542
7.537
7.532
7.529
7.525
7.523
7.520
7.480
7.476
7.471
7.465
7.464
7.462
7.289
7.275
7.193
7.178
2.215
2.210
O
N
O
N
Cl
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
1.05
1.04
1.02
1.04
2.04
0.71
2.04
6.01

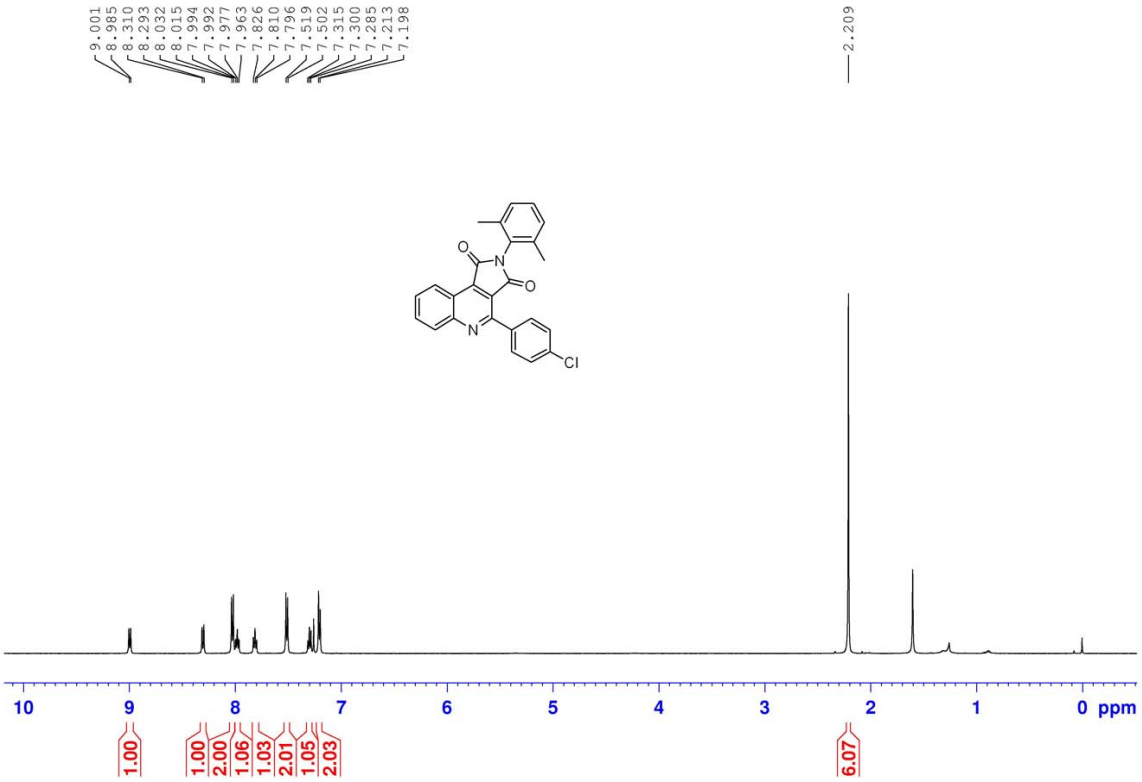

167.00
165.88
152.86
151.88
136.98
136.21
136.14
133.66
133.20
130.88
130.79
130.41
130.26
129.68
129.57
129.45
128.58
127.22
125.35
122.75
121.52
18.22
O
N
O
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

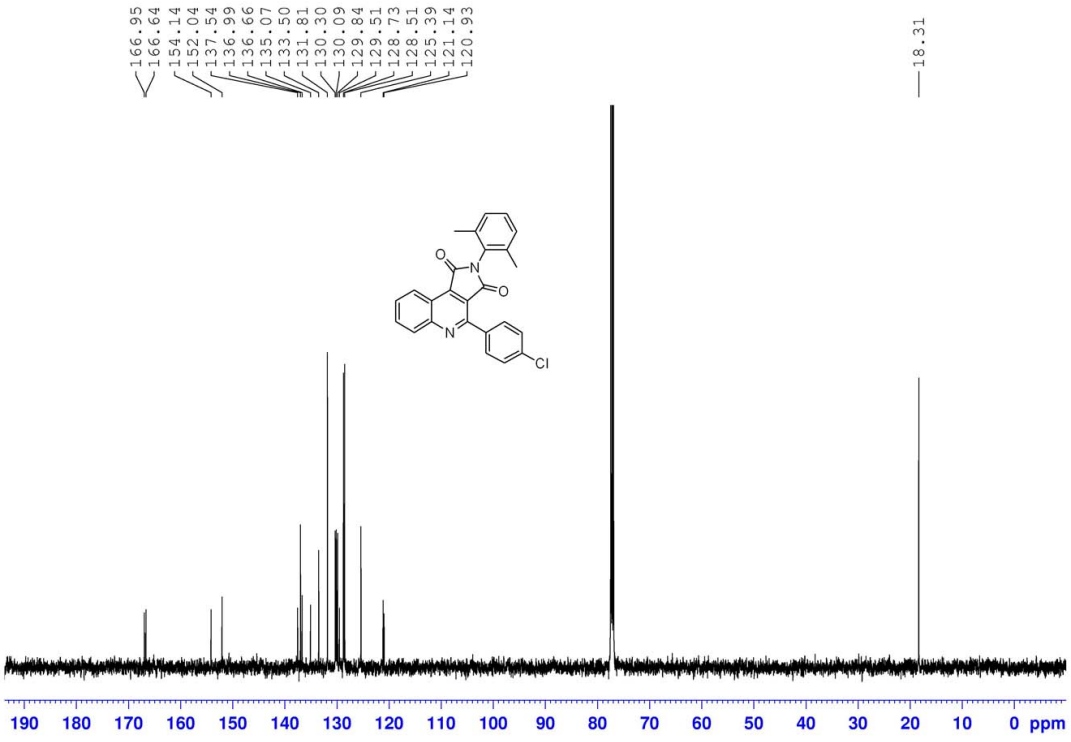
Compound **5c**


9.011
8.995
8.330
8.313
8.069
8.007
8.004
7.993
7.990
7.976
7.973
7.948
7.933
7.841
7.839
7.825
7.810
7.809
7.516
7.512
7.502
7.499
7.478
7.462
7.447
7.314
7.299
7.284
7.214
7.198
2.213
Cl
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.01 1.01 0.92 1.09 1.00 1.03 1.06 1.04 1.08 2.02
6.03

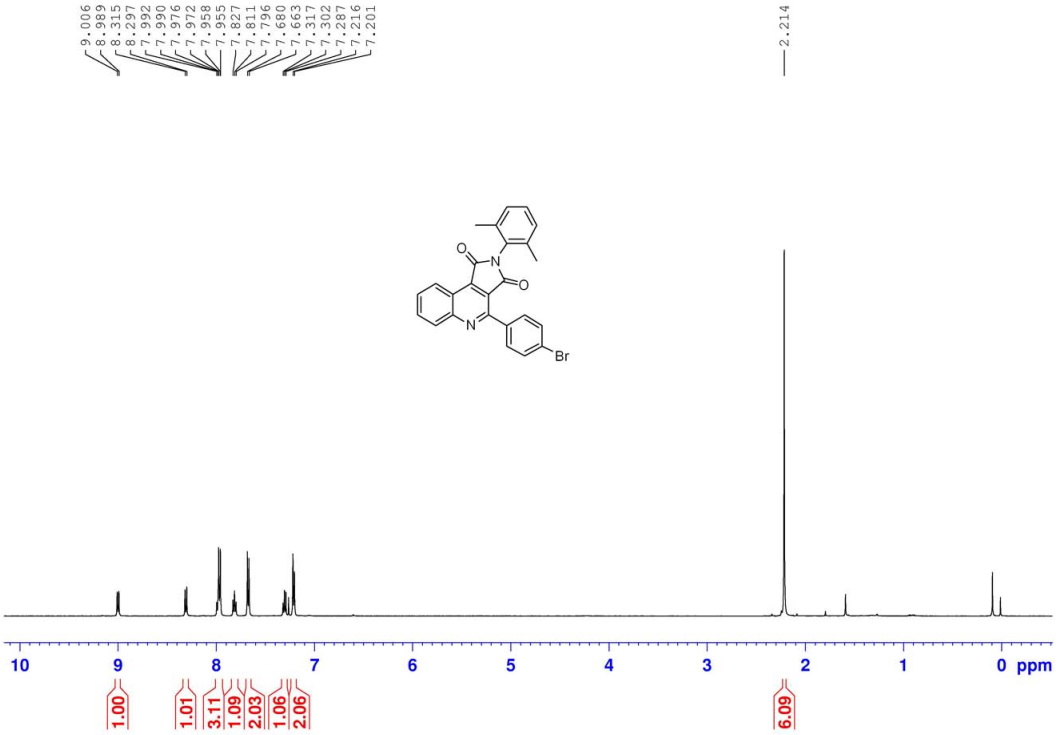

166.90
166.46
153.81
151.98
138.29
137.52
136.99
134.37
133.54
130.35
130.30
130.28
130.23
129.85
129.47
129.37
128.76
128.73
125.38
121.21
120.99
18.32
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

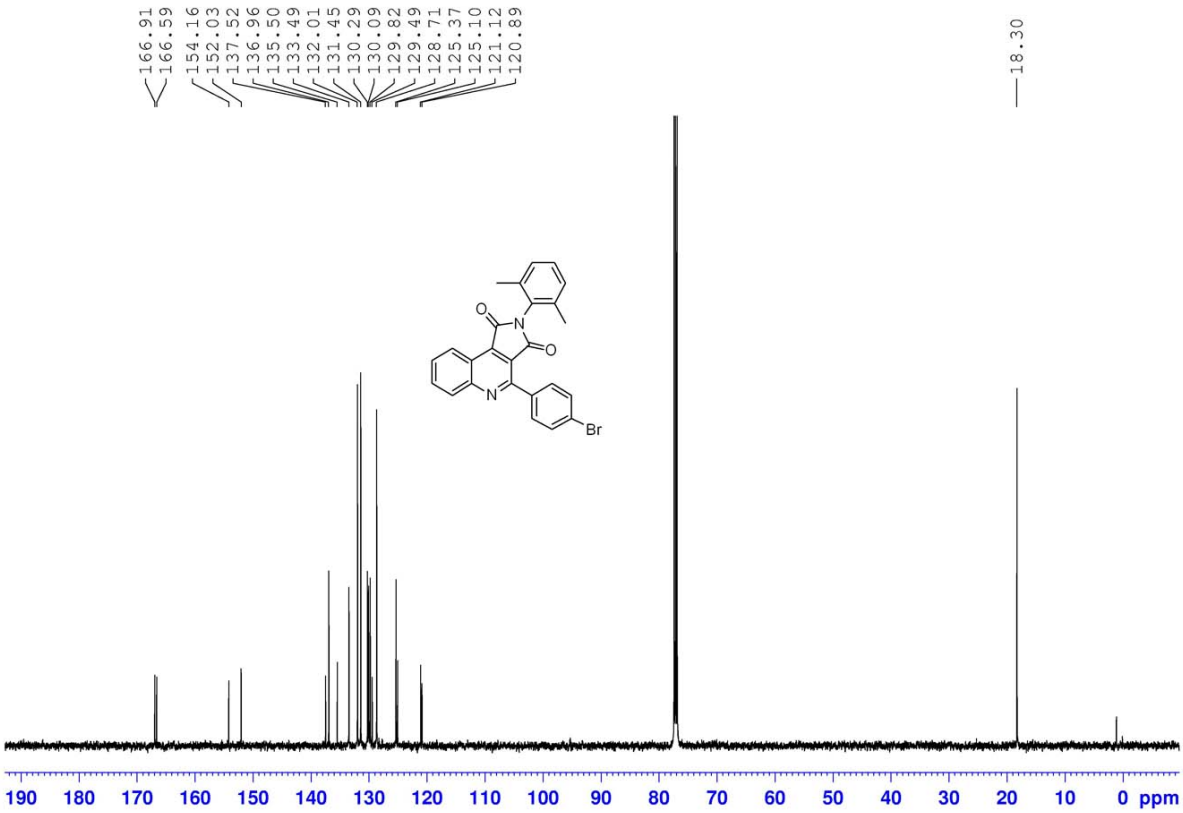
Compound **5d**


9.001
8.985
8.310
8.293
8.032
8.015
7.994
7.992
7.977
7.963
7.826
7.810
7.796
7.519
7.502
7.315
7.300
7.285
7.213
7.198
2.209
O
N
O
N
Cl
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
2.00
1.06
1.03
2.01
1.05
2.03
6.07

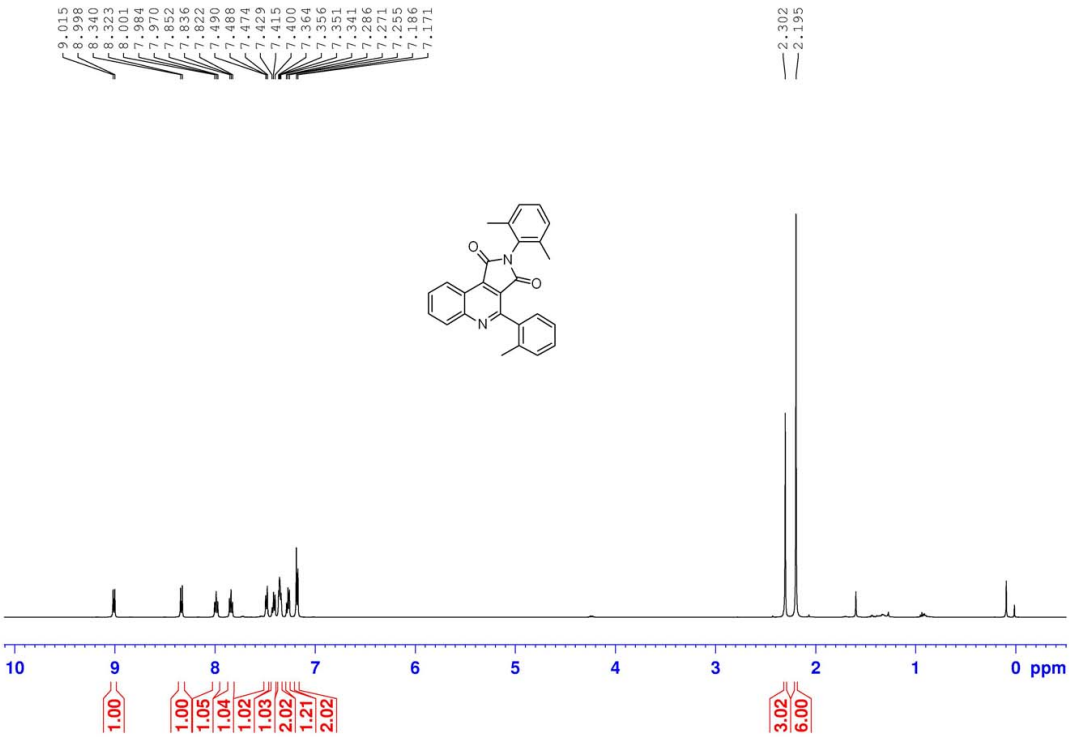

166.95
166.64
154.14
152.04
137.54
136.99
136.66
135.07
133.50
131.81
130.30
130.09
129.84
129.51
128.73
128.51
125.39
121.14
120.93
18.31
O
N
O
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

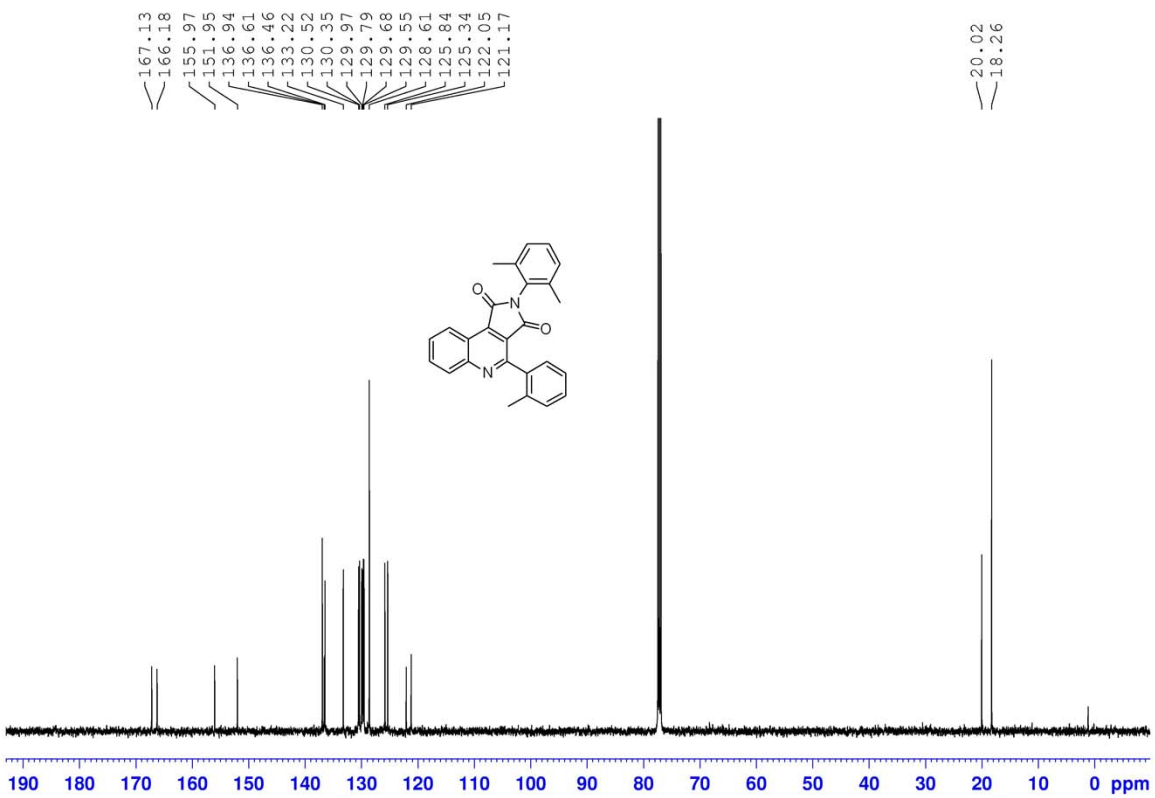
Compound **5e**


9.006
8.989
8.315
8.297
7.992
7.990
7.976
7.972
7.958
7.955
7.827
7.811
7.796
7.680
7.663
7.317
7.302
7.287
7.216
7.201
2.214
O
N
O
N
Br
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
3.11
1.09
2.03
1.06
2.06
6.09

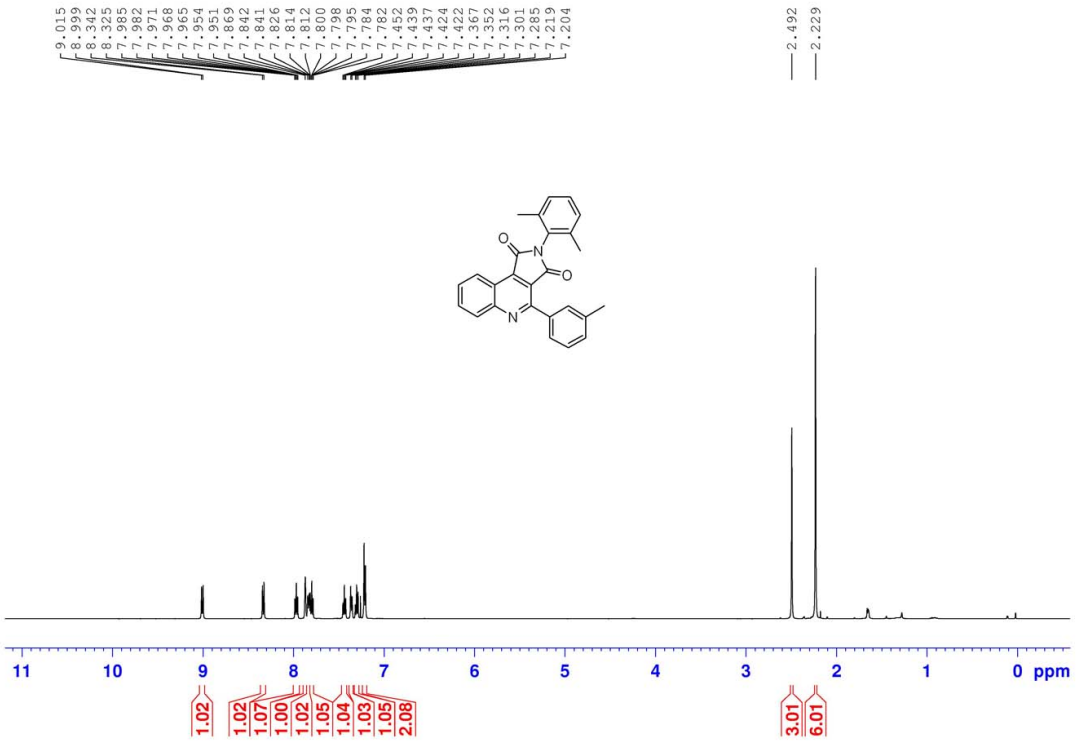

166.91
166.59
154.16
152.03
137.52
136.96
135.50
133.49
132.01
131.45
130.29
130.09
129.82
129.49
128.71
125.37
125.10
121.12
120.89
18.30
O
N
O
N
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

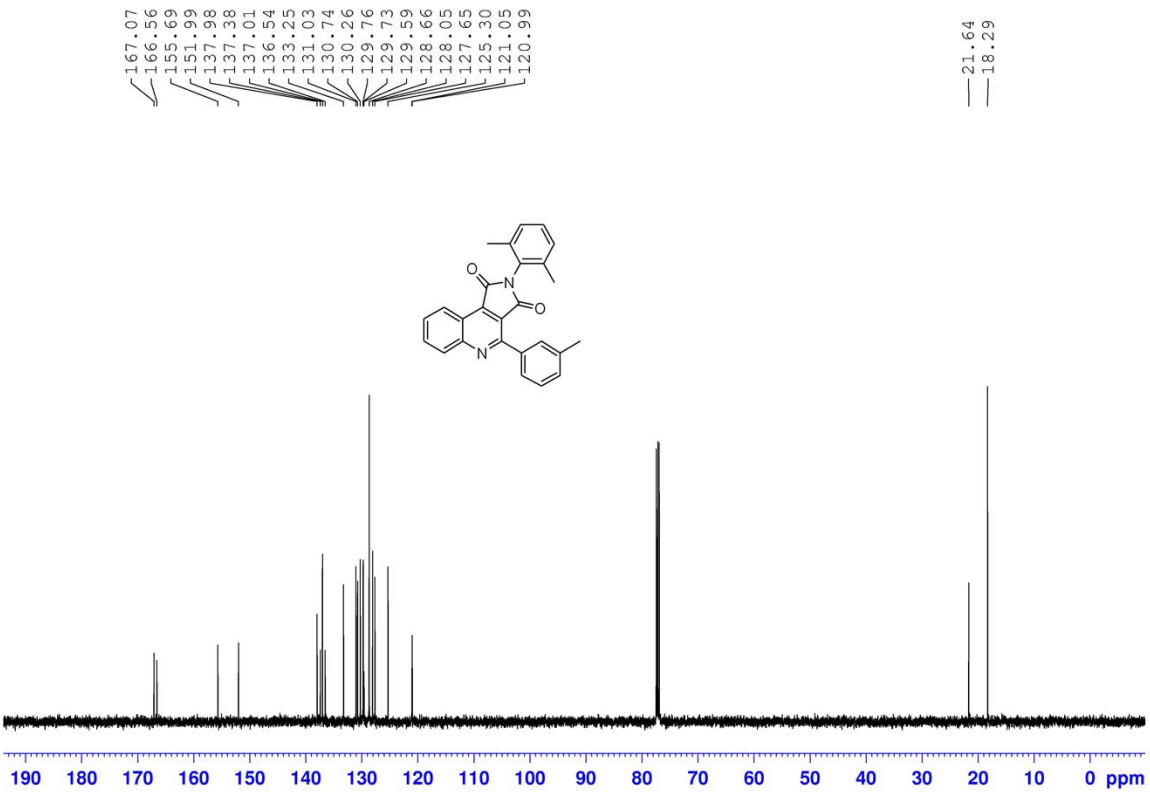
Compound **5f**


9.015
8.998
8.340
8.323
8.001
7.984
7.970
7.852
7.836
7.822
7.490
7.488
7.474
7.429
7.415
7.400
7.364
7.356
7.351
7.341
7.286
7.271
7.255
7.186
7.171
2.302
2.195
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
1.05
1.04
1.02
1.03
2.02
1.21
2.02
3.02
6.00

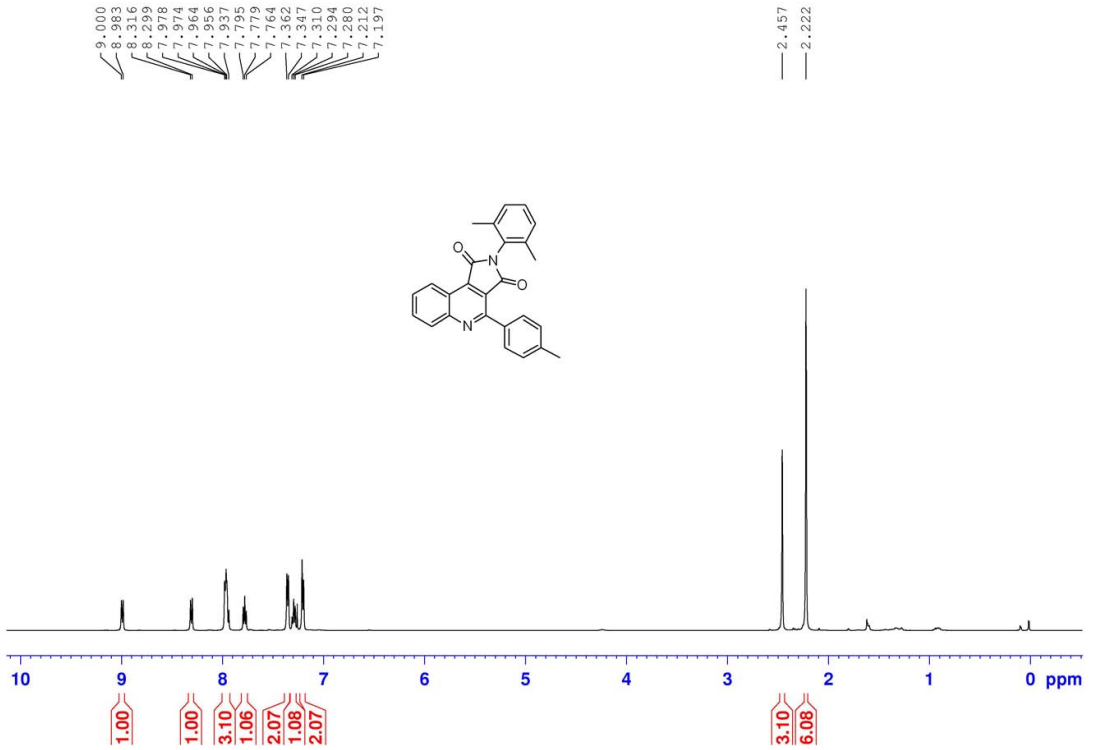

167.13
166.18
155.97
151.95
136.94
136.61
136.46
133.22
130.52
130.35
129.97
129.79
129.68
129.55
128.61
125.84
125.34
122.05
121.17
20.02
18.26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

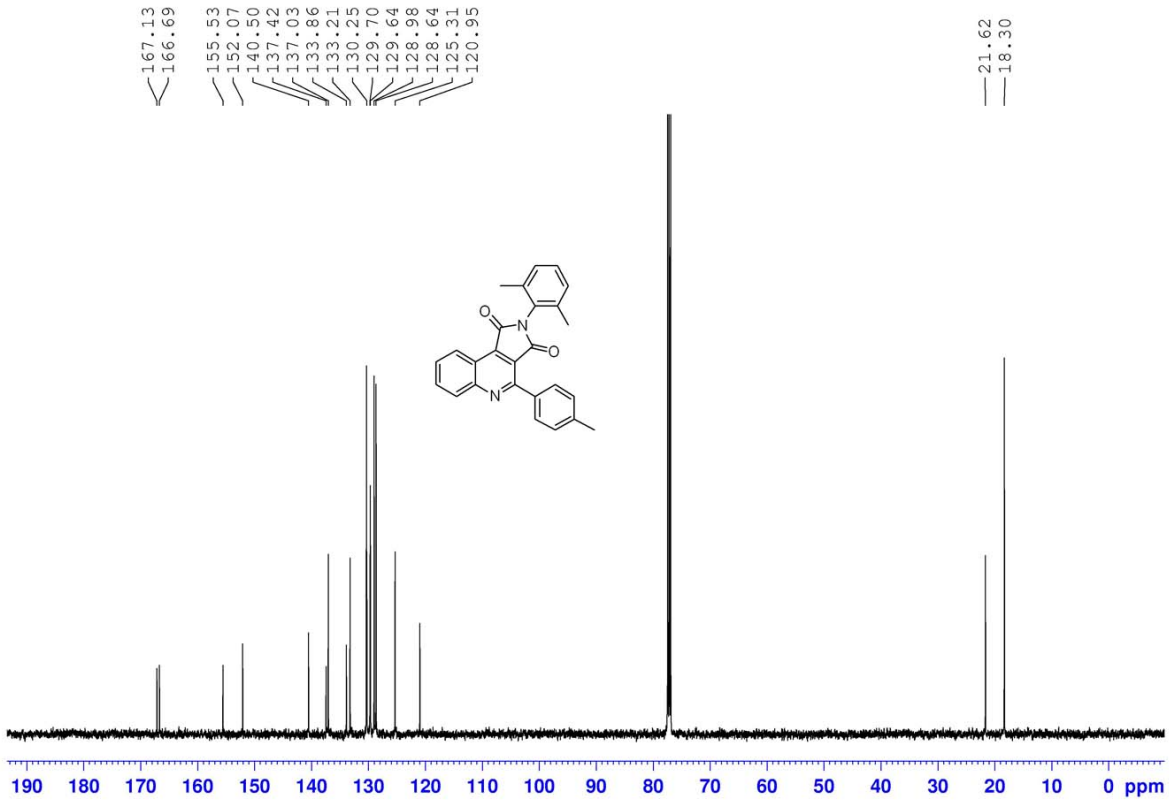
Compound **5g**


9.015
8.999
8.342
8.325
7.985
7.982
7.971
7.968
7.965
7.954
7.951
7.869
7.842
7.841
7.826
7.814
7.812
7.800
7.798
7.795
7.784
7.782
7.452
7.439
7.437
7.424
7.422
7.367
7.352
7.316
7.301
7.285
7.219
7.204
2.492
2.229
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.02 1.02 1.07 1.00 1.02 1.05 1.04 1.03 1.05 2.08
3.01 6.01

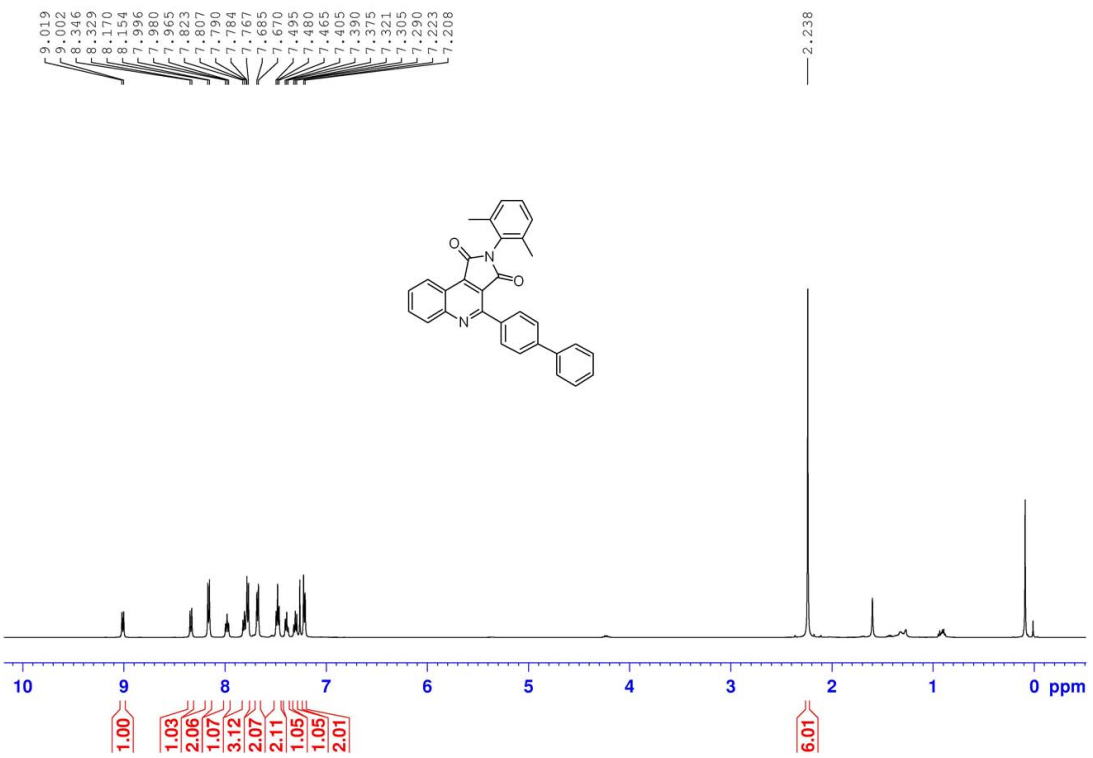

167.07
166.56
155.69
151.99
137.98
137.38
137.01
136.54
133.25
131.03
130.74
130.26
129.76
129.73
129.59
128.66
128.05
127.65
125.30
121.05
120.99
21.64
18.29
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

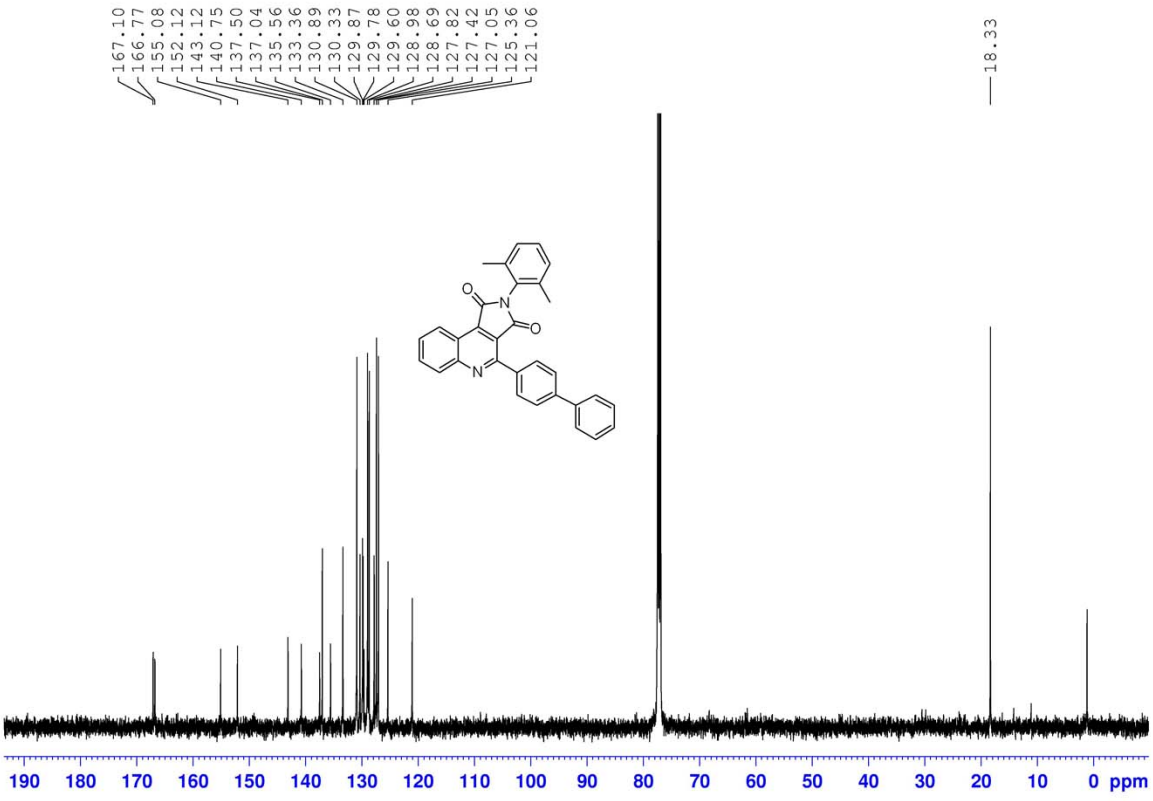
Compound **5h**


9.000
8.983
8.316
8.299
7.978
7.974
7.964
7.956
7.937
7.795
7.779
7.764
7.362
7.347
7.310
7.294
7.280
7.212
7.197
2.457
2.222
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
3.10
1.06
2.07
1.08
2.07
3.10
6.08

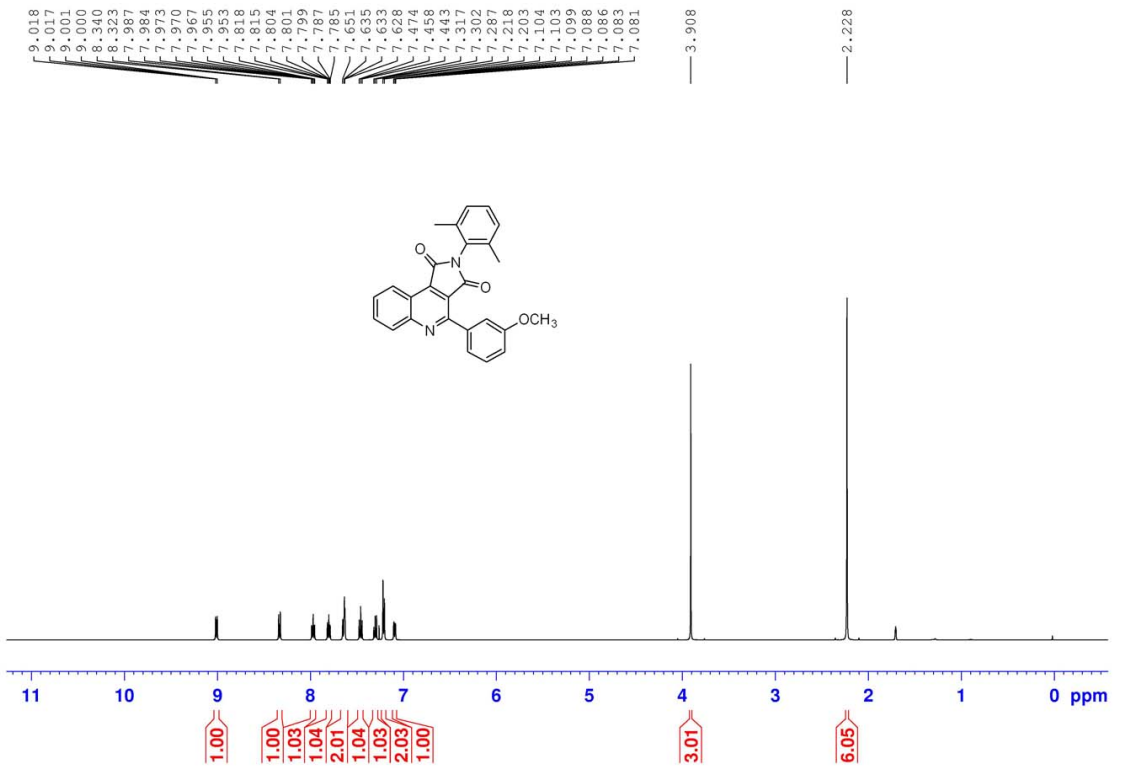

167.13
166.69
155.53
152.07
140.50
137.42
137.03
133.86
133.21
130.25
129.70
129.64
128.98
128.64
125.31
120.95
21.62
18.30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

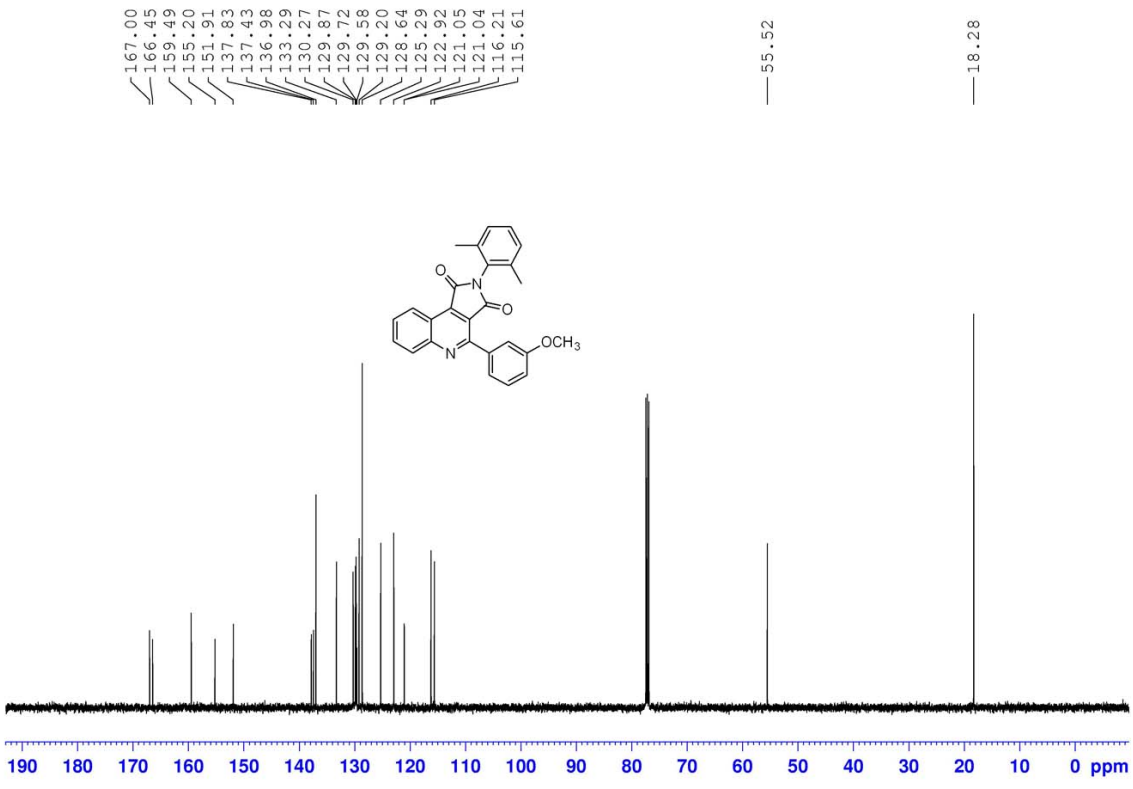
Compound **5i**


9.019
9.002
8.346
8.329
8.170
8.154
7.996
7.980
7.965
7.823
7.807
7.790
7.784
7.767
7.685
7.670
7.495
7.480
7.465
7.405
7.390
7.375
7.321
7.305
7.290
7.223
7.208
2.238
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.03
2.06
1.07
3.12
2.07
2.11
1.05
2.01
6.01

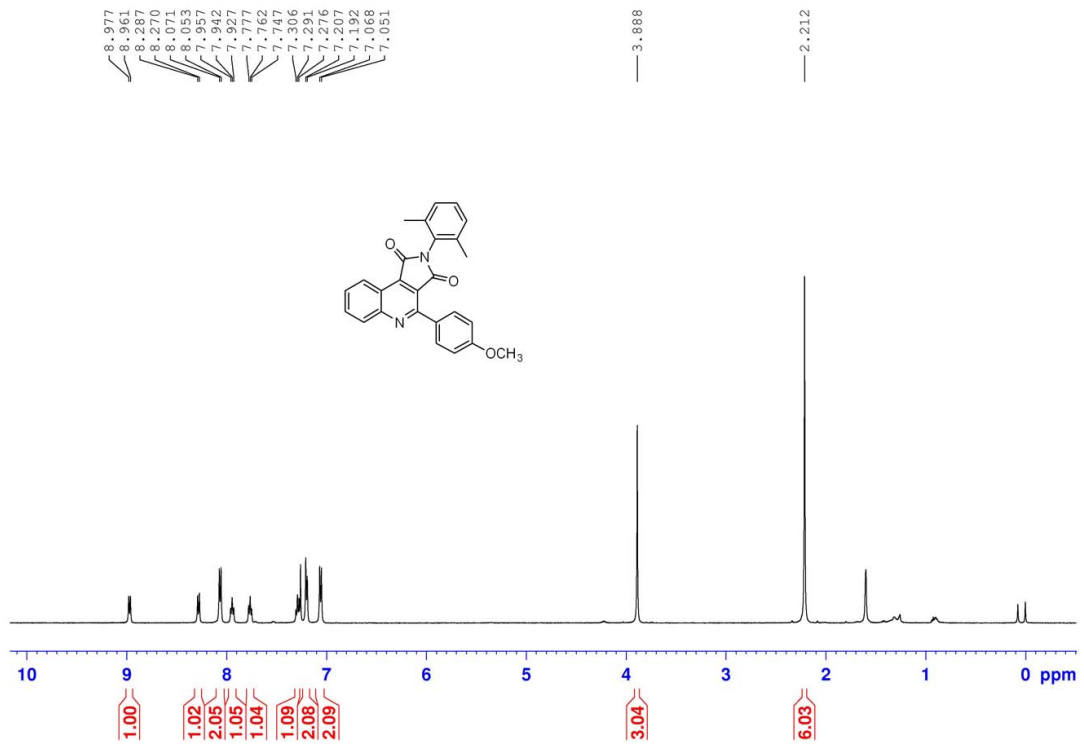

167.10
166.77
155.08
152.12
143.12
140.75
137.50
137.04
135.56
133.36
130.89
130.33
129.87
129.78
129.60
128.98
128.69
127.82
127.42
127.05
125.36
121.06
18.33
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

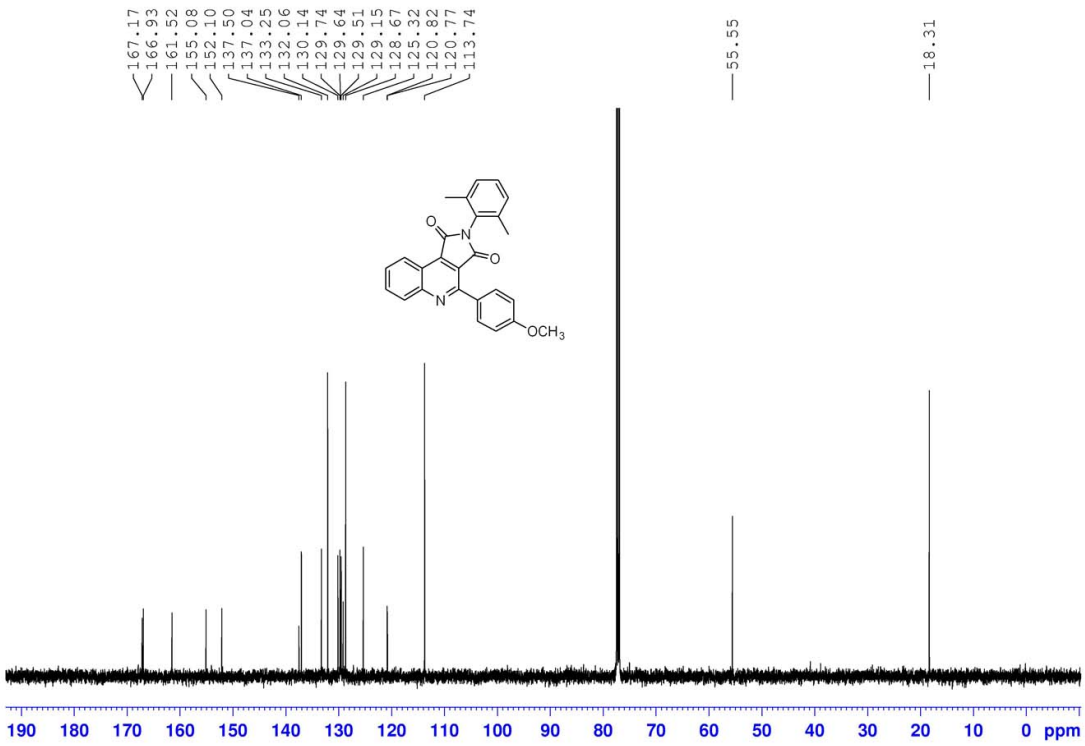
Compound **5j**


9.018
9.017
9.001
9.000
8.340
8.323
7.987
7.984
7.973
7.970
7.967
7.955
7.953
7.818
7.815
7.804
7.801
7.799
7.787
7.785
7.651
7.635
7.633
7.628
7.474
7.458
7.443
7.317
7.302
7.287
7.218
7.203
7.104
7.103
7.099
7.088
7.086
7.083
7.081
3.908
2.228
OCH3
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.00 1.03 1.04 2.01 1.04 1.03 2.03 1.00 3.01 6.05

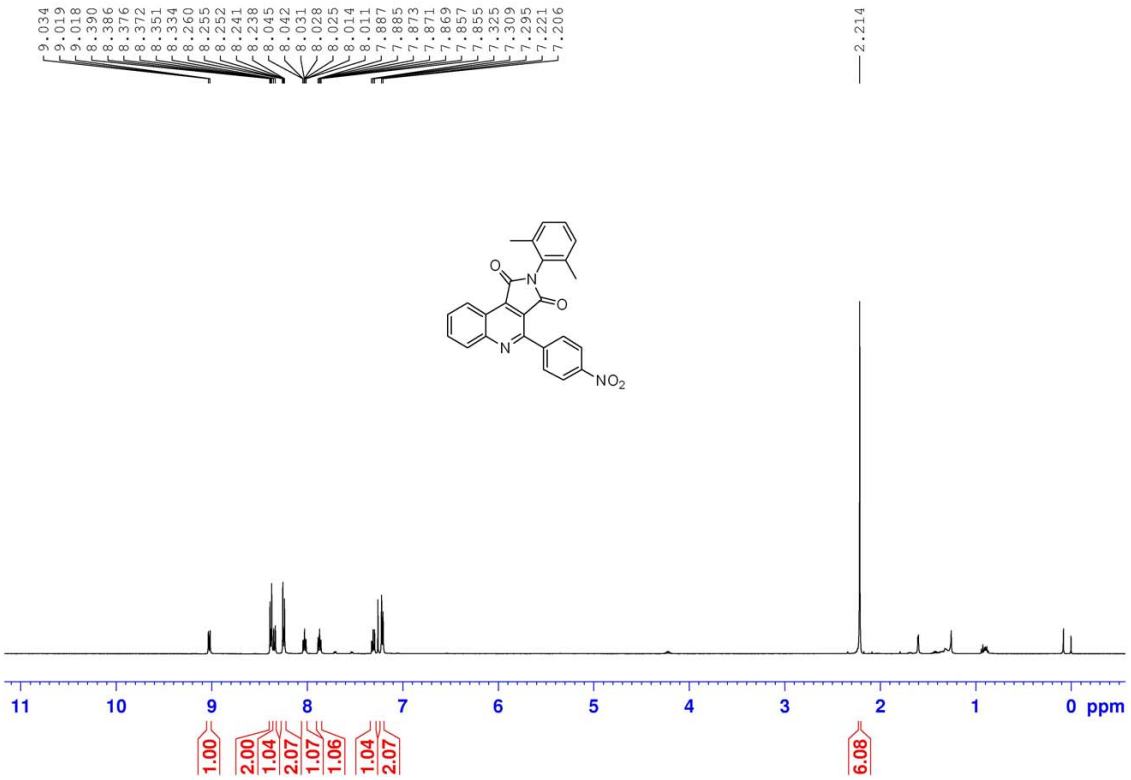

167.00
166.45
159.49
155.20
151.91
137.83
137.43
136.98
133.29
130.27
129.87
129.72
129.58
129.20
128.64
125.29
122.92
121.05
121.04
116.21
115.61
55.52
18.28
OCH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

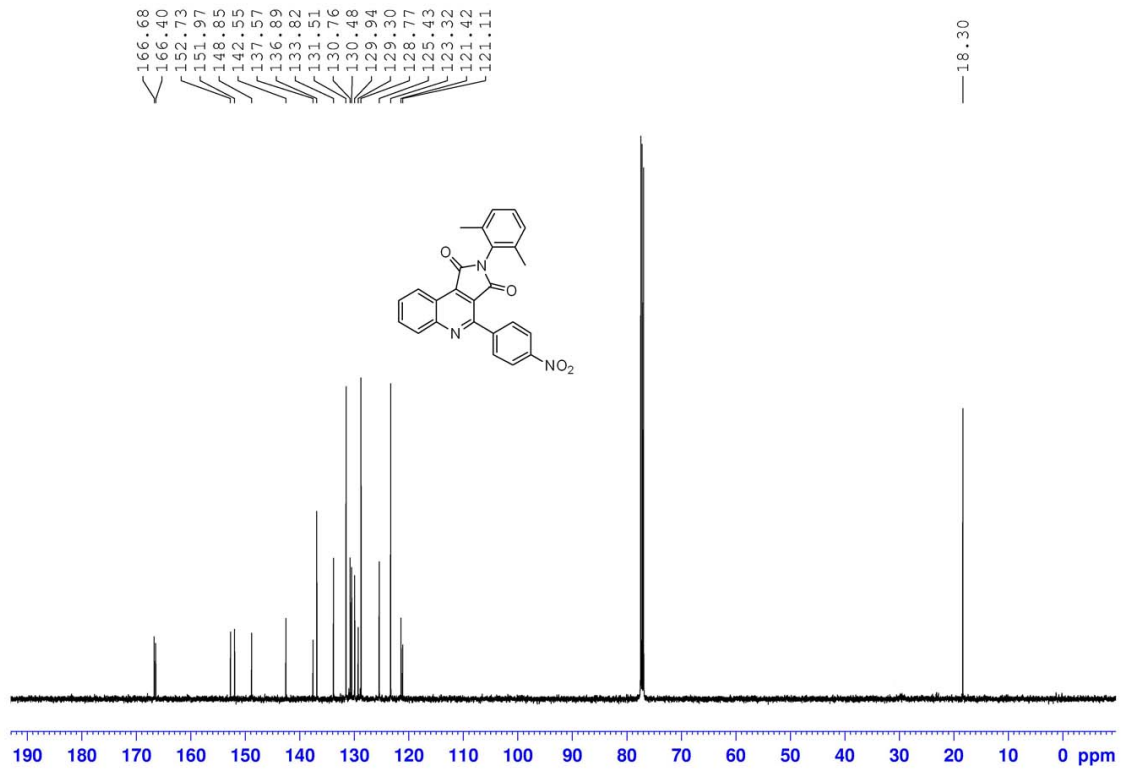
Compound **5k**


8.977
8.961
8.287
8.270
8.071
8.053
7.957
7.942
7.927
7.777
7.762
7.747
7.306
7.291
7.276
7.207
7.192
7.068
7.051
3.888
2.212
OCH3
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
2.05
1.05
1.04
1.09
2.08
2.09
3.04
6.03

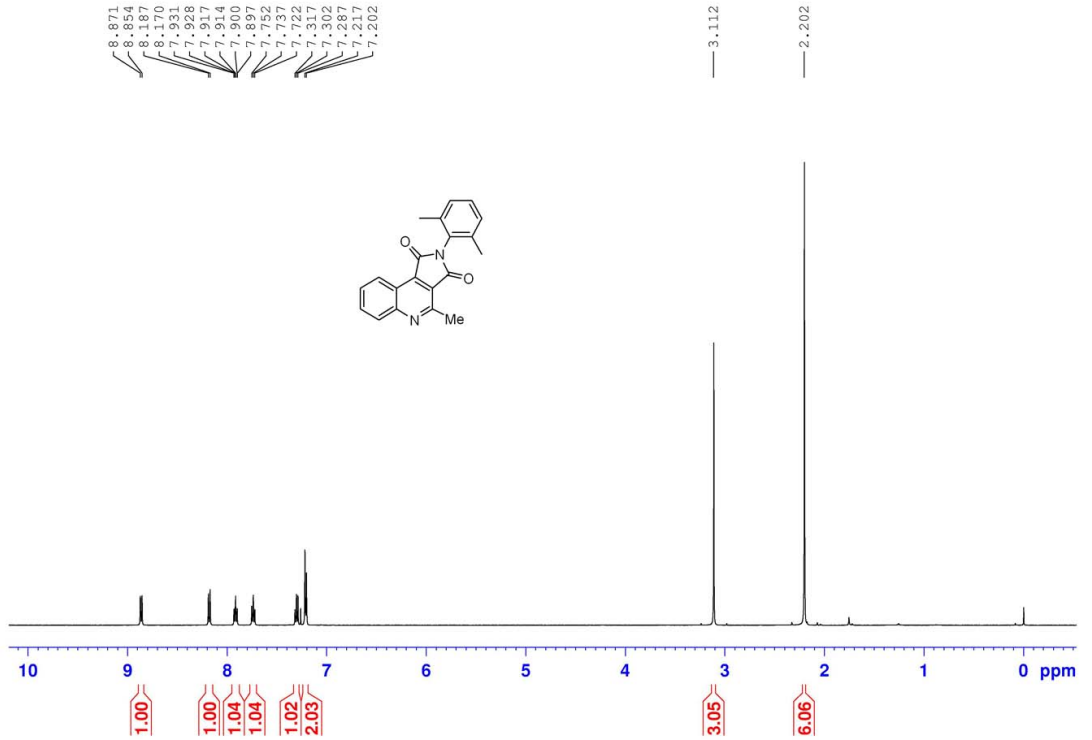

167.17
166.93
161.52
155.08
152.10
137.50
137.04
133.25
132.06
130.14
129.74
129.64
129.51
129.15
128.67
125.32
120.82
120.77
113.74
55.55
18.31
OCH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

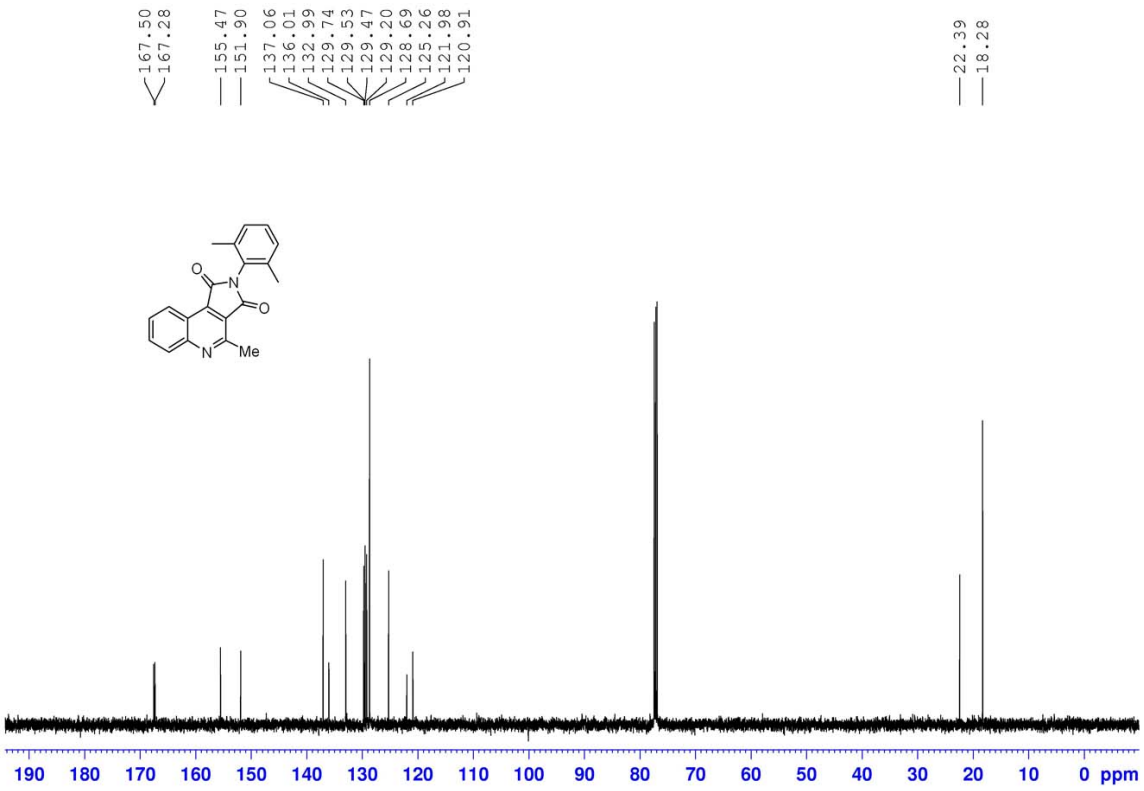
Compound **5l**


9.034
9.019
9.018
8.390
8.386
8.376
8.372
8.351
8.334
8.260
8.255
8.252
8.241
8.238
8.045
8.042
8.031
8.028
8.025
8.014
8.011
7.887
7.885
7.873
7.871
7.869
7.857
7.855
7.325
7.309
7.295
7.221
7.206
2.214
O
N
O
N
NO2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 2.00 1.04 2.07 1.07 1.06 1.04 2.07 6.08

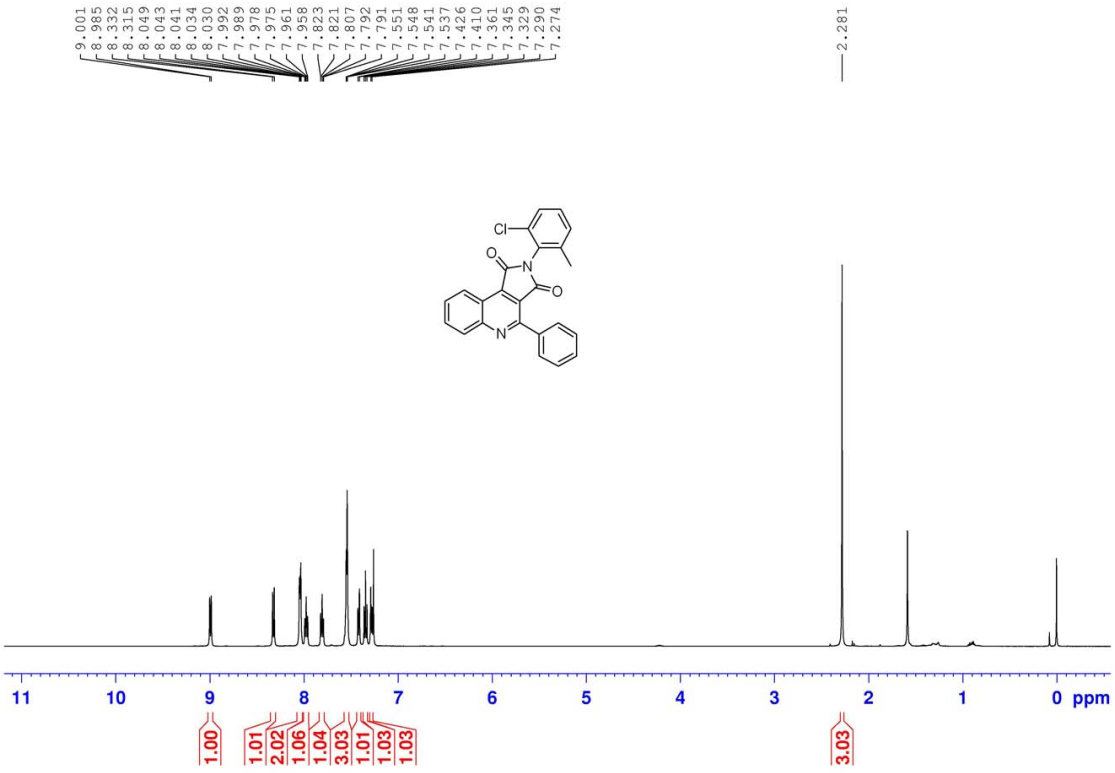

166.68
166.40
152.73
151.97
148.85
142.55
137.57
136.89
133.82
131.51
130.76
130.48
129.94
129.30
128.77
125.43
123.32
121.42
121.11
18.30
O
N
O
N
NO2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

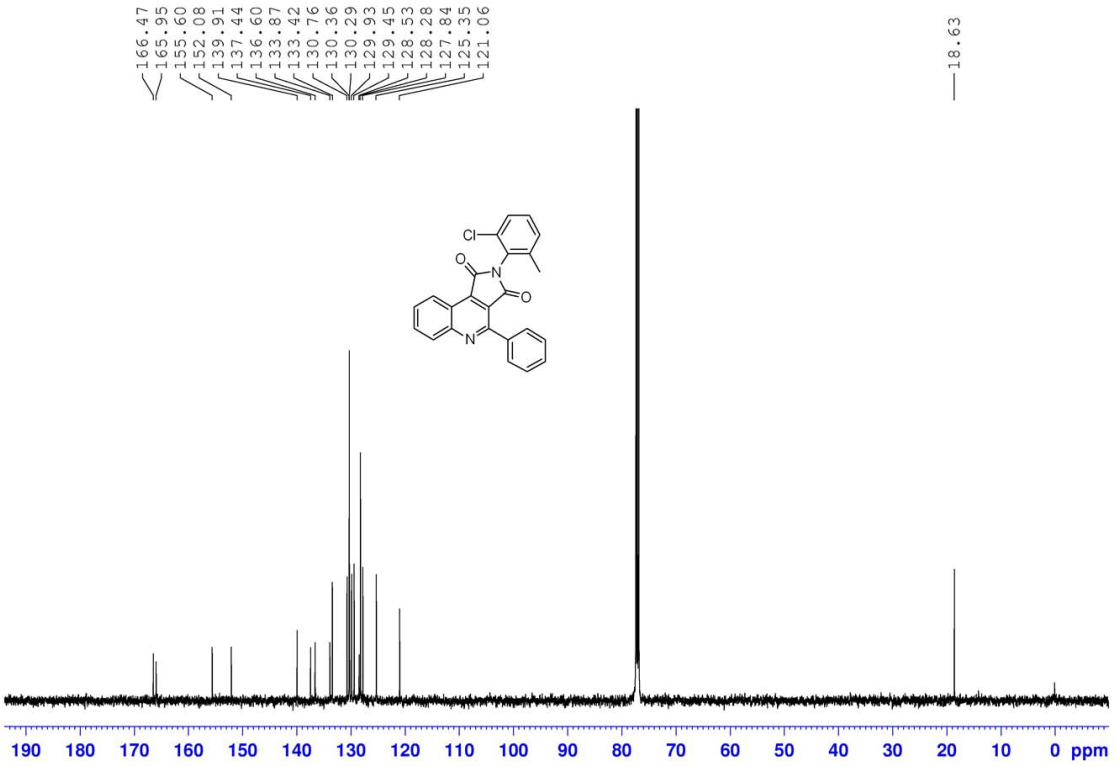
Compound **5m**


8.871
8.854
8.187
8.170
7.931
7.928
7.917
7.914
7.900
7.897
7.752
7.737
7.722
7.317
7.302
7.287
7.217
7.202
3.112
2.202
Me
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
1.04
1.04
1.02
2.03
3.05
6.06

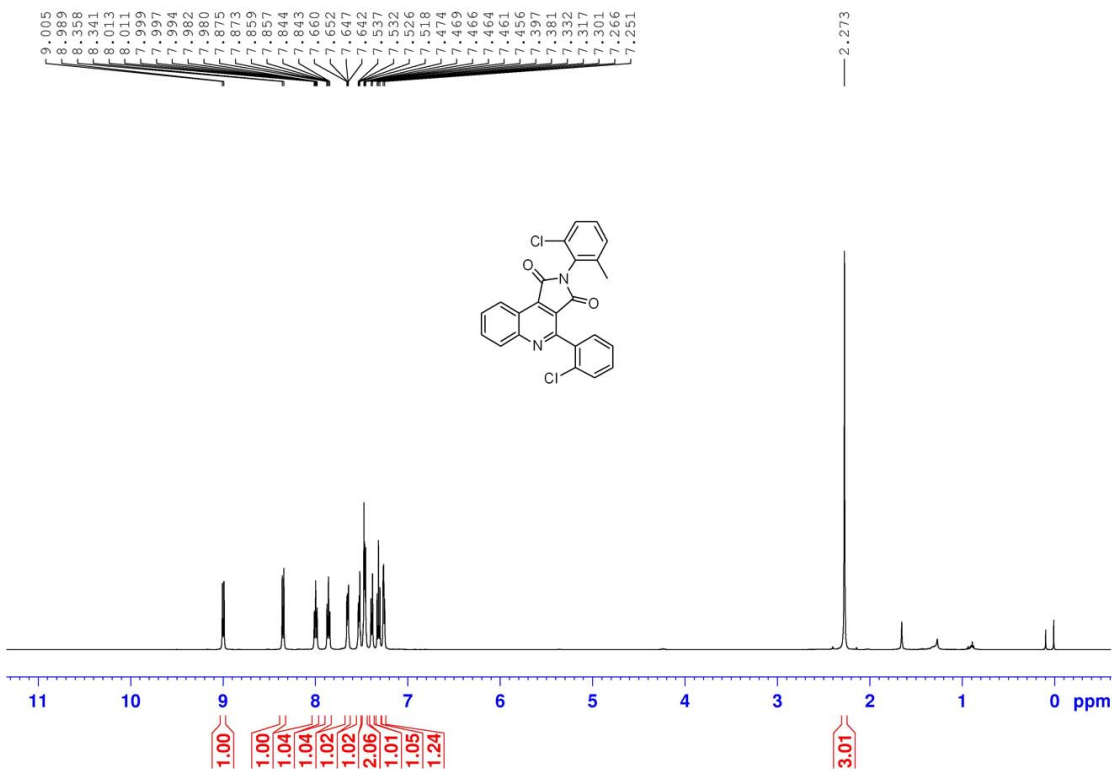

167.50
167.28
155.47
151.90
137.06
136.01
132.99
129.74
129.53
129.47
129.20
128.69
125.26
121.98
120.91
22.39
18.28
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

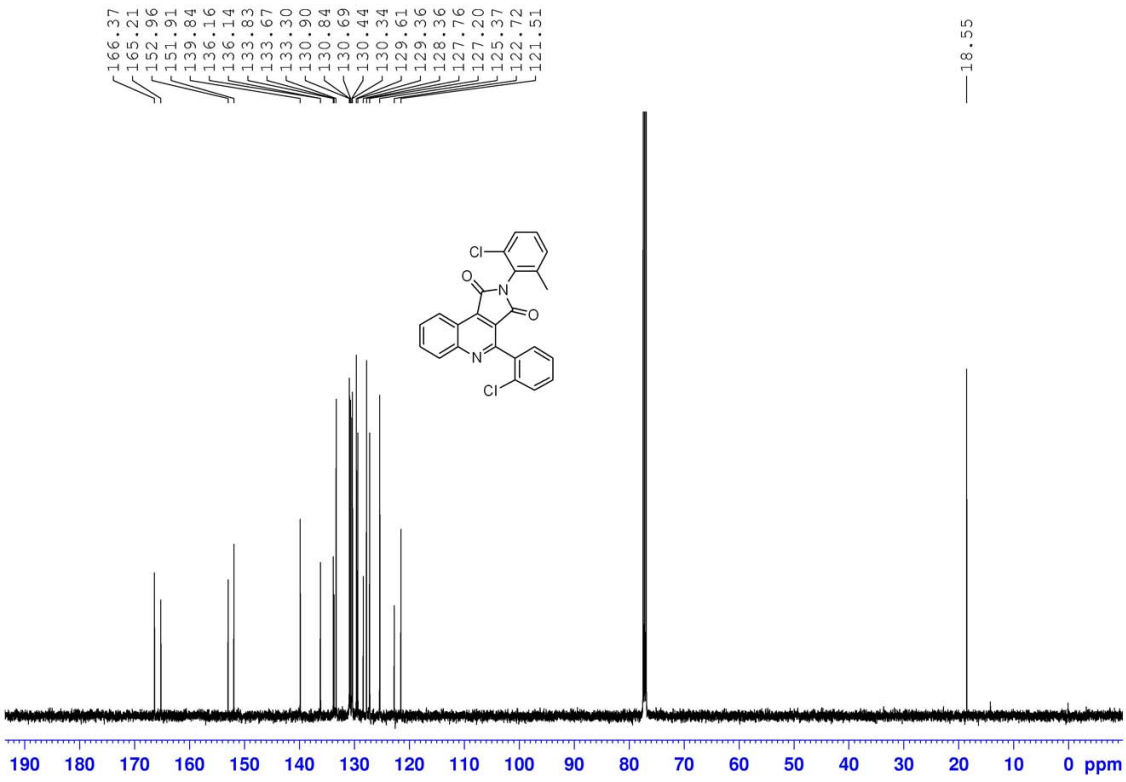
Compound **6a**


9.001
8.985
8.332
8.315
8.049
8.043
8.041
8.034
8.030
7.992
7.989
7.978
7.975
7.961
7.958
7.823
7.821
7.807
7.792
7.791
7.551
7.548
7.541
7.537
7.426
7.410
7.361
7.345
7.329
7.290
7.274
2.281
Cl
O
N
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
2.02
1.06
1.04
3.03
1.01
1.03
1.03
3.03

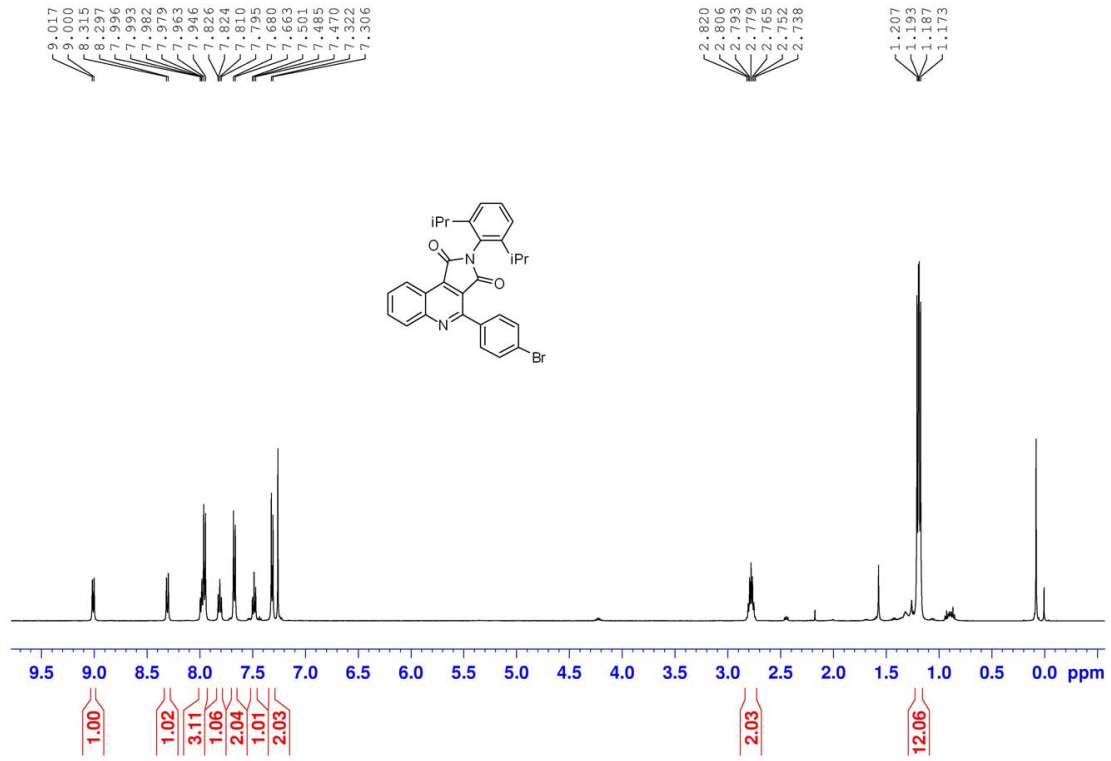

166.47
165.95
155.60
152.08
139.91
137.44
136.60
133.87
133.42
130.76
130.36
130.29
129.93
129.45
128.53
128.28
127.84
125.35
121.06
18.63
Cl
O
N
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

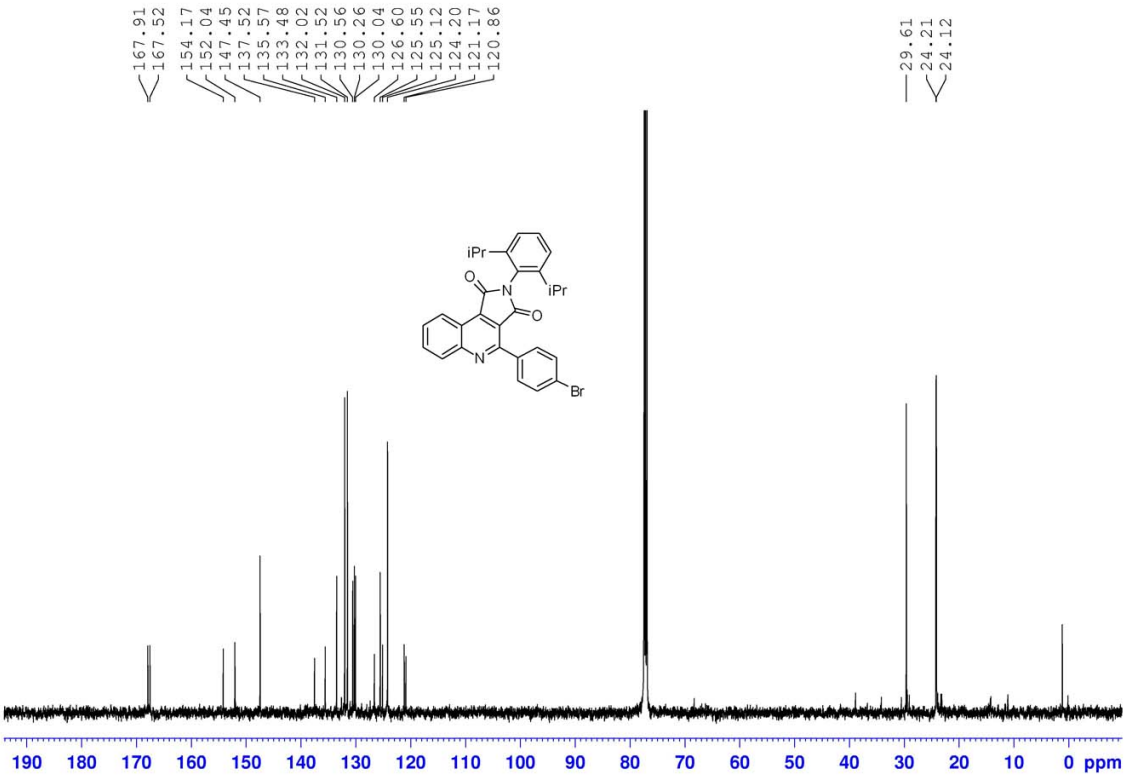
Compound **6b**


9.005
8.989
8.358
8.341
8.013
8.011
7.999
7.997
7.994
7.982
7.980
7.875
7.873
7.859
7.857
7.844
7.843
7.660
7.652
7.647
7.642
7.537
7.532
7.526
7.518
7.474
7.469
7.466
7.464
7.461
7.456
7.397
7.381
7.332
7.317
7.301
7.266
7.251
2.273
Cl
O
N
O
N
Cl
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
1.04
1.04
1.02
1.02
2.06
1.01
1.05
1.24
3.01

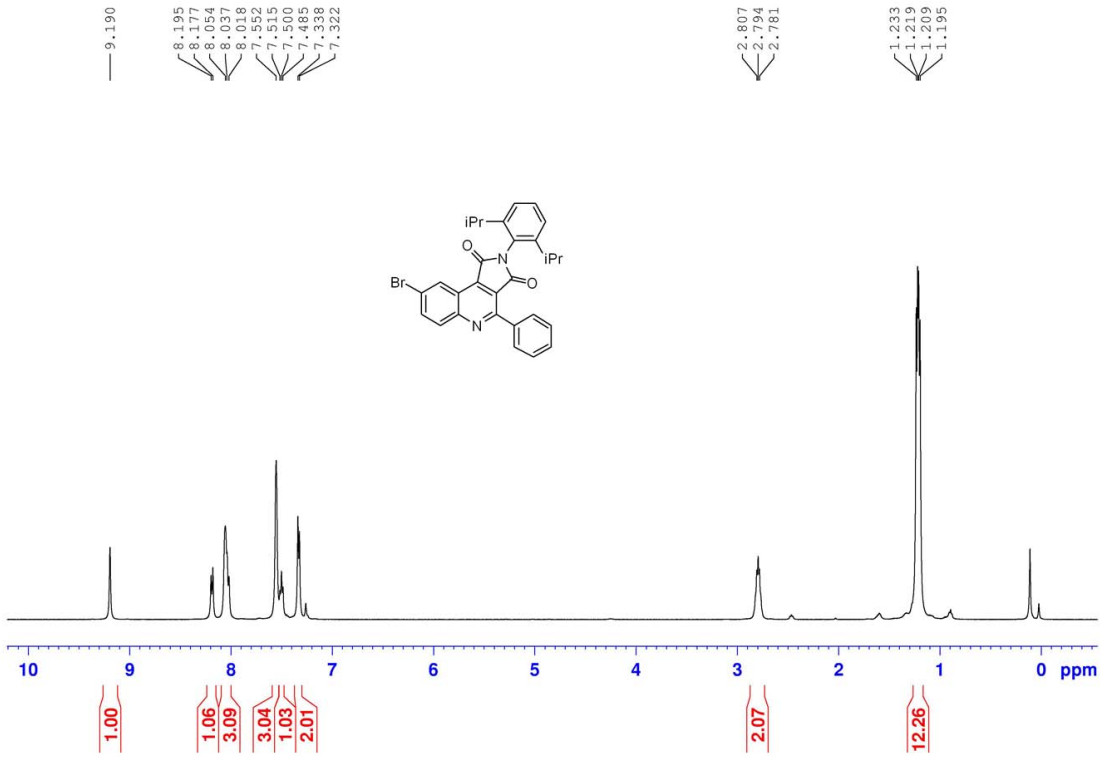

166.37
165.21
152.96
151.91
139.84
136.16
136.14
133.83
133.67
133.30
130.90
130.84
130.69
130.44
130.34
129.61
129.36
128.36
127.76
127.20
125.37
122.72
121.51
18.55
Cl
O
N
O
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

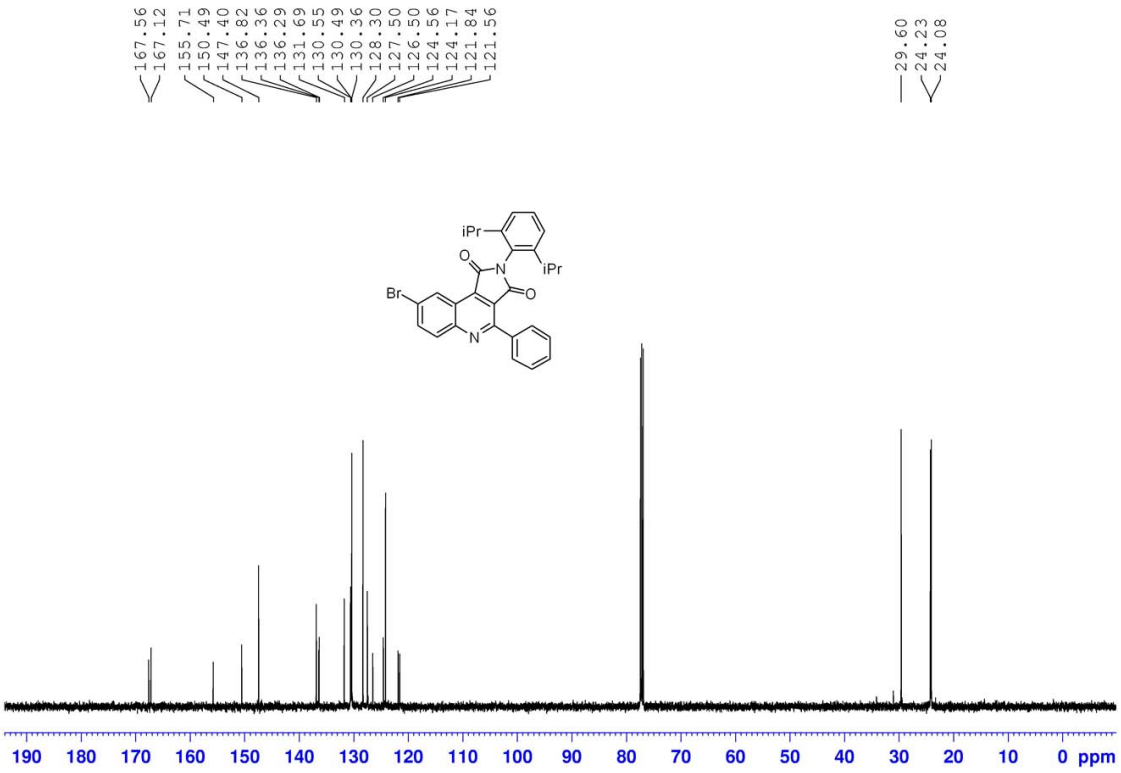
Compound **6c**


9.017
9.000
8.315
8.297
7.996
7.993
7.982
7.979
7.963
7.946
7.826
7.824
7.810
7.795
7.680
7.663
7.501
7.485
7.470
7.322
7.306
2.820
2.806
2.793
2.779
2.765
2.752
2.738
1.207
1.193
1.187
1.173
iPr
iPr
O
N
O
N
Br
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
3.11
1.06
2.04
1.01
2.03
2.03
12.06

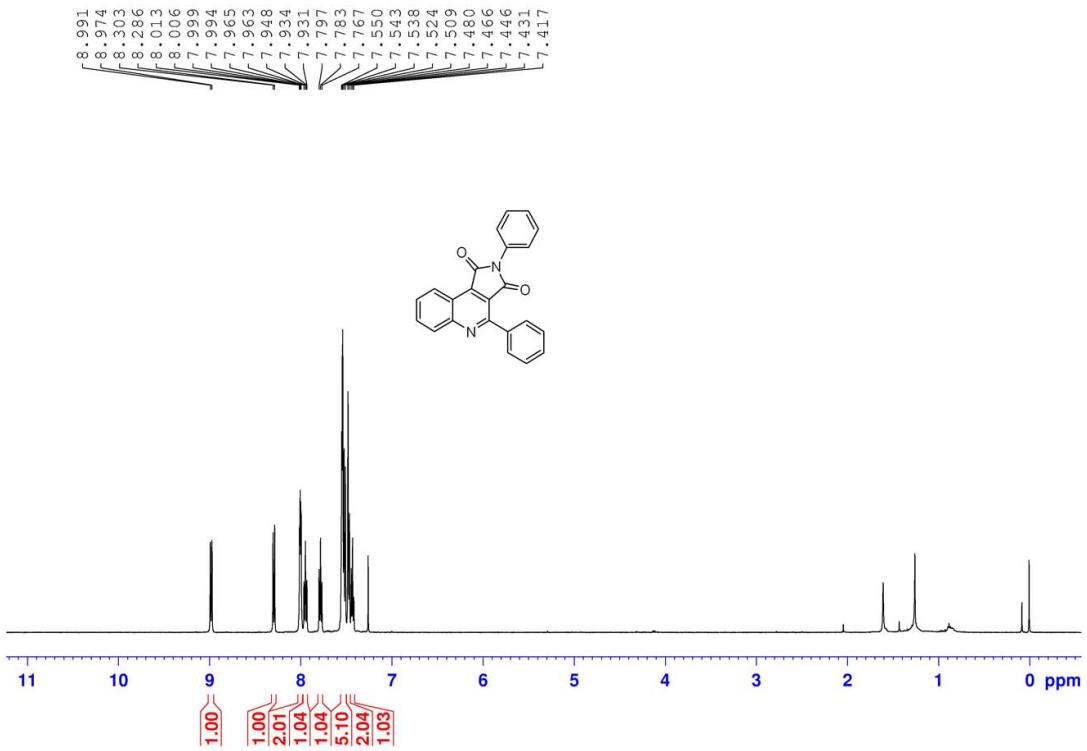

167.91
167.52
154.17
152.04
147.45
137.52
135.57
133.48
132.02
131.52
130.56
130.26
130.04
126.60
125.55
125.12
124.20
121.17
120.86
29.61
24.21
24.12
iPr
iPr
O
N
O
N
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

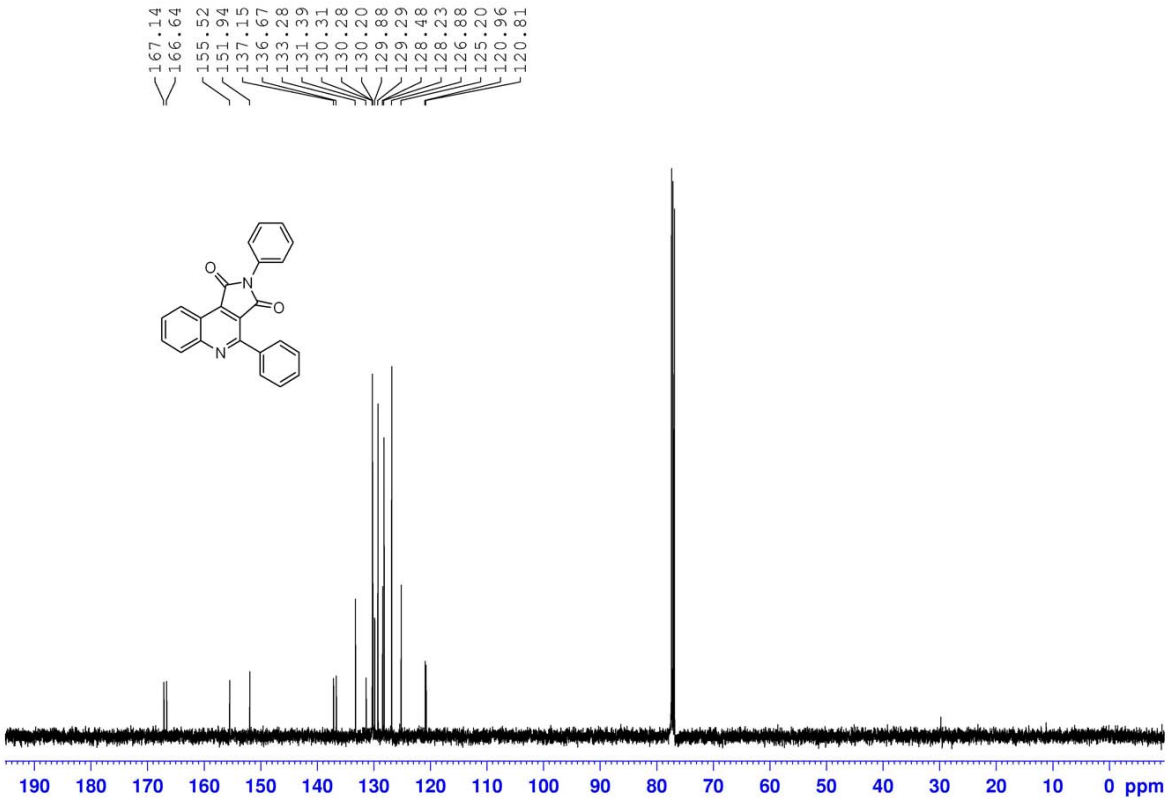
Compound **6d**


9.190
8.195
8.177
8.054
8.037
8.018
7.552
7.515
7.500
7.485
7.338
7.322
2.807
2.794
2.781
1.233
1.219
1.209
1.195
iPr
iPr
Br
O
N
O
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.06
3.09
3.04
1.03
2.01
2.07
12.26

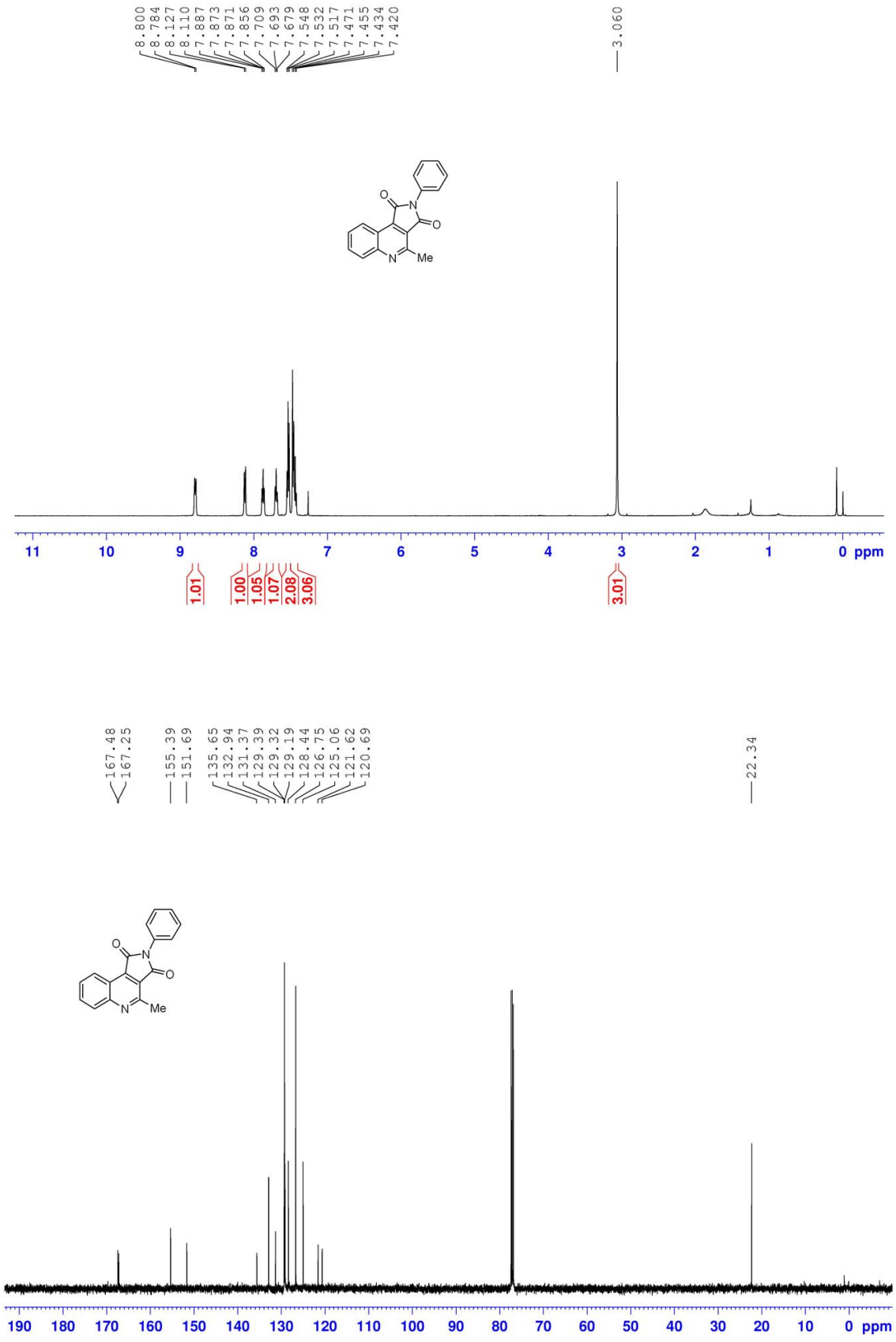

167.56
167.12
155.71
150.49
147.40
136.82
136.36
136.29
131.69
130.55
130.49
130.36
128.30
127.50
126.50
124.56
124.17
121.84
121.56
29.60
24.23
24.08
iPr
iPr
Br
O
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

Compound **6e**

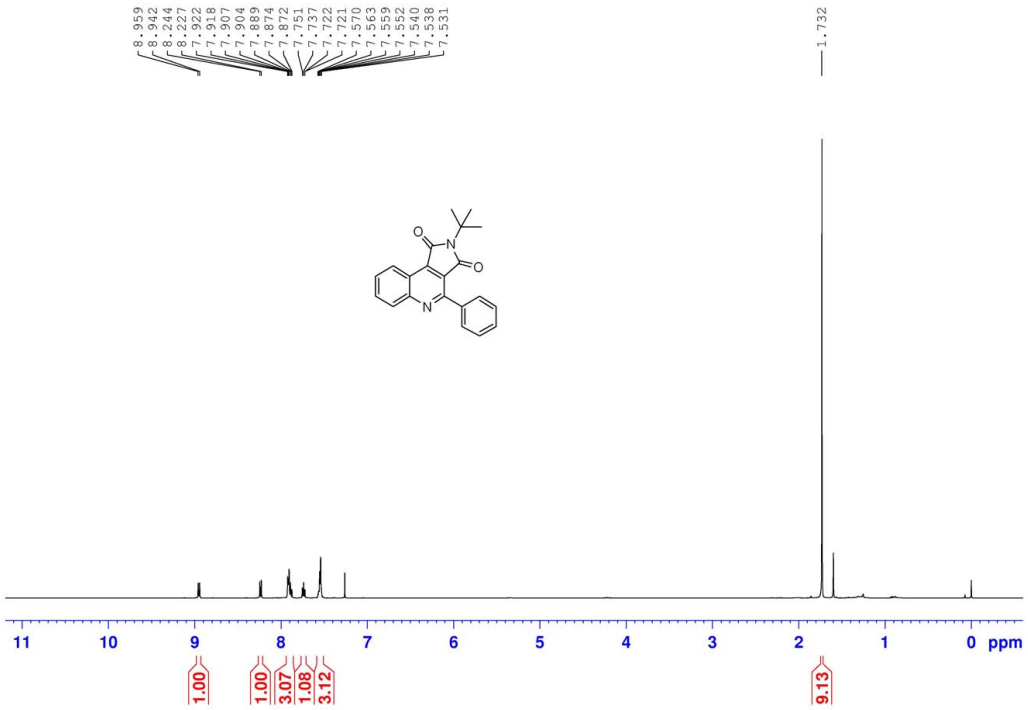

8.991
8.974
8.303
8.286
8.013
8.006
7.999
7.994
7.965
7.963
7.948
7.934
7.931
7.797
7.783
7.767
7.550
7.543
7.538
7.524
7.509
7.480
7.466
7.446
7.431
7.417
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.00 2.01 1.04 1.04 5.10 2.04 1.03

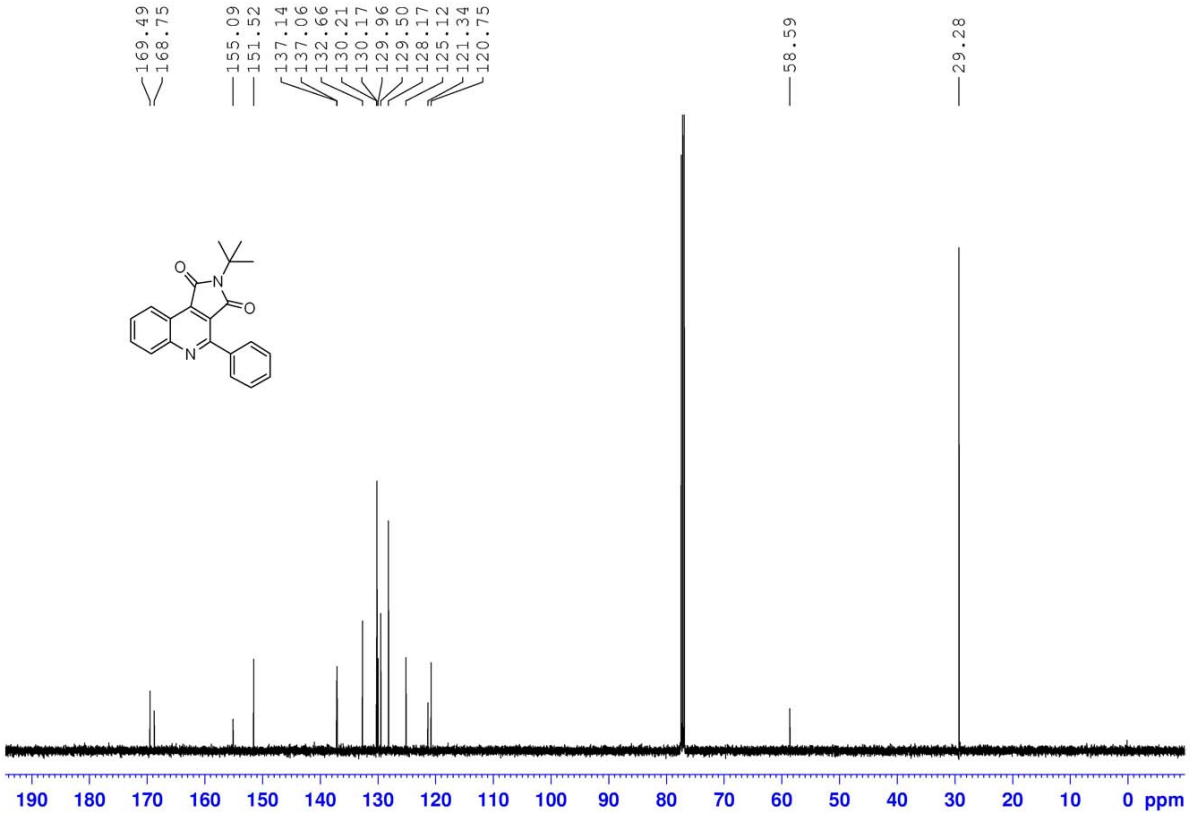

167.14
166.64
155.52
151.94
137.15
136.67
133.28
131.39
130.31
130.28
130.20
129.88
129.29
128.48
128.23
126.88
125.20
120.96
120.81
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Compound **6f**

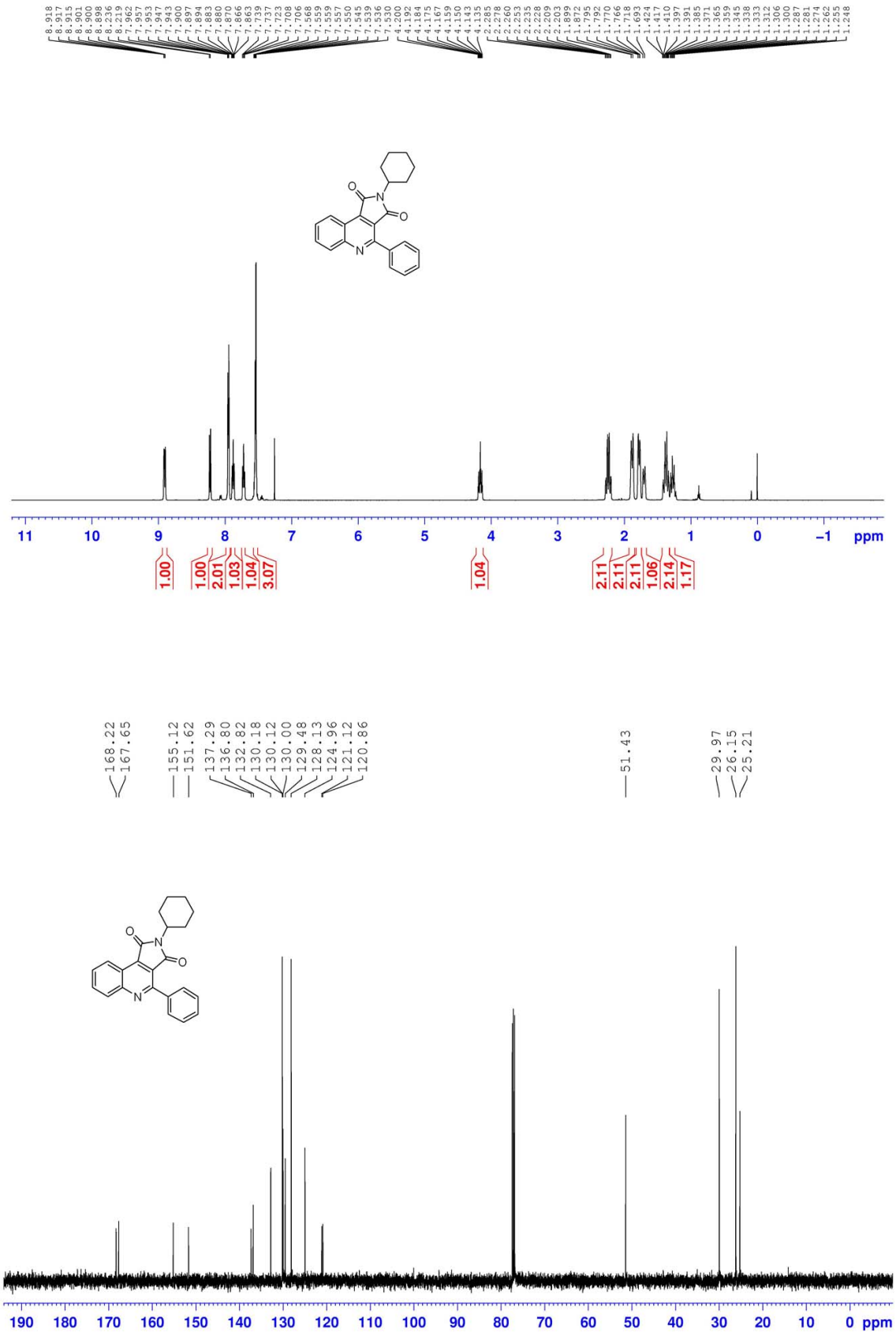

8.800
8.784
8.127
8.110
7.887
7.873
7.871
7.856
7.709
7.693
7.679
7.548
7.532
7.517
7.471
7.455
7.434
7.420
3.060
O
N
O
N
Me
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
1.00
1.05
1.07
2.08
3.06
3.01
167.48
167.25
155.39
151.69
135.65
132.94
131.37
129.39
129.32
129.19
128.44
126.75
125.06
121.62
120.69
22.34
O
N
O
N
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Compound **6g**


8.959
8.942
8.244
8.227
7.922
7.918
7.907
7.904
7.889
7.874
7.872
7.751
7.737
7.722
7.721
7.570
7.563
7.559
7.552
7.540
7.538
7.531
1.732
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
3.07
1.08
3.12
9.13


169.49
168.75
155.09
151.52
137.14
137.06
132.66
130.21
130.17
129.96
129.50
128.17
125.12
121.34
120.75
58.59
29.28
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

Compound **6h**



5 Crystal Structure of Compound 3a

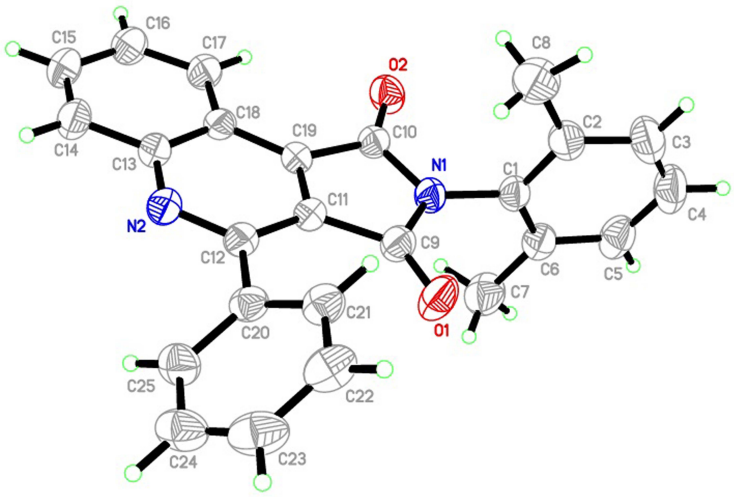


Figure 1 Single Crystal X-Ray structure for **3a**

Table 1 Crystal data and structure refinement for **3a**

Empirical formula	C25 H18 N2 O2
Formula weight	378.41
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.5501(17) Å alpha = 90°. b = 13.4406(17) Å beta = 98.124(2) °. c = 10.7332(13) Å gamma = 90°.
Volume	1935.1(4) Å ^{3}
Z, Calculated density	4, 1.299 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	792
Crystal size	0.10 x 0.07 x 0.03 mm
Theta range for data collection	2.14 to 25.05°
Limiting indices	-16<=h<=13, -15<=k<=16, -10<=l<=12
Reflections collected / unique	9883 / 3420 [R(int) = 0.0412]
Completeness to theta = 25.05	99.9 %
Absorption correction	None
Max. and min. transmission	0.9975 and 0.9917
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3420 / 0 / 265
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1349
R indices (all data)	R1 = 0.0988, wR2 = 0.1655
Extinction coefficient	0.0058(11)

6 Crystal Structure of Compound 3f

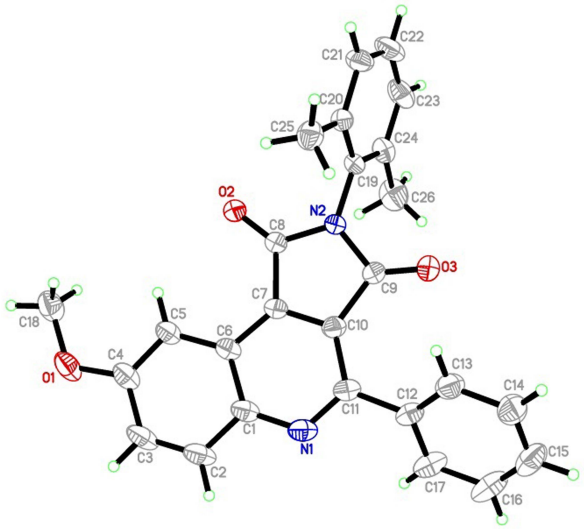


Figure 2 Single Crystal X-Ray structure for **3f**

Table 2 Crystal data and structure refinement for **3f**

Empirical formula	C26 H20 N2 O3
Formula weight	408.44
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.5140(9) Å alpha = 90°.
	b = 13.6267(14) Å beta = 100.8290(10) °.
	c = 18.6805(19) Å gamma = 90°.
Volume	2128.7(4) Å ^{3}
Z, Calculated density	4, 1.274 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F(000)	856
Crystal size	0.24 x 0.20 x 0.12 mm
Theta range for data collection	1.86 to 25.05°
Limiting indices	-10<=h<=7, -15<=k<=16, -22<=l<=21
Reflections collected / unique	10805 / 3761 [R(int) = 0.0180]
Completeness to theta = 25.05	99.8 %
Absorption correction	None
Max. and min. transmission	0.9900 and 0.9801
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3761 / 0 / 284
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1002
R indices (all data)	R1 = 0.0546, wR2 = 0.1102
Extinction coefficient	0.0045(7)
Largest diff. peak and hole	0.162 and -0.142 e. Å $^{-3}$

7 Crystal Structure of Compound 5b

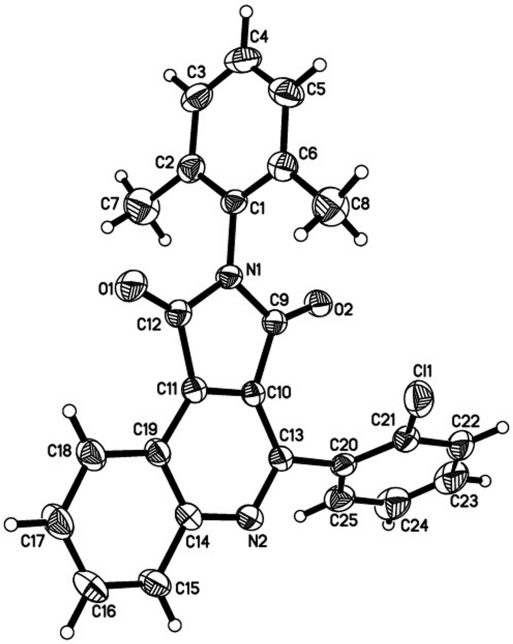


Figure 3 Single Crystal X-Ray structure for **5b**

Table 3 Crystal data and structure refinement for **5b**

Empirical formula	C25 H17 Cl N2 O2
Formula weight	412.86
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 15.341(3) Å alpha = 90°.
	b = 8.1615(13) Å beta = 105.999(2) °.
	c = 17.193(3) Å gamma = 90°.
Volume	2069.3(6) Å ^{3}
Z, Calculated density	4, 1.325 Mg/m^3
Absorption coefficient	0.209 mm^{-1}
F(000)	856
Crystal size	0.21 x 0.13 x 0.05 mm
Theta range for data collection	2.09 to 25.05°
Limiting indices	-18<=h<=14, -8<=k<=9, -20<=l<=20
Reflections collected / unique	10331 / 3663 [R(int) = 0.0223]
Completeness to theta = 25.05	99.7 %
Absorption correction	None
Max. and min. transmission	0.9896 and 0.9575
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3663 / 0 / 273
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1012
R indices (all data)	R1 = 0.0584, wR2 = 0.1106

Largest diff. peak and hole	0.154 and -0.225 e. Å $^{-3}$