

Supplementary Material

A direct phosphine-mediated synthesis of polyfunctionalized 1-aminopyrroles from arylglyoxals, phenylhydrazine and acetylene diesters

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Materials and characterization techniques

All the utilized arylglyoxals were prepared by the SeO₂-oxidation of the related aryl methylketones on the basis of the reported procedure and used as their monohydrates.¹ Elemental analyses were performed using a Heraeus CHN-O-Rapidanalyzer. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ¹H, and ¹³C NMR spectra were recorded on Bruker DRX-400 Avance spectrometer at 400 and 100 MHz, respectively. The chemicals used in this work purchased from Merck and were used without further purification.

General procedure for the synthesis of compounds 4a-m. A mixture of dialkyl acetylenedicarboxylate (1 mmol) in dichloromethane (3 mL) was added drop wise to a magnetically stirred solution of triphenylphosphine (1 mmol) and phenylhydrazine (1 mmol) in dichloromethane (10 mL). The reaction mixture was then stirred for 1 min. Arylglyoxal (1 mmol) was added, and the reaction mixture was stirred for more 10 hs at room temperature. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–hexane mixture as eluent.

Dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4a). Yield: 80%; white solid; m.p. 134-136 °C. IR (KBr) ($\bar{\nu}_{\max}$, cm⁻¹): 3333 (NH), 1731, 1713 (C=O). Calcd. for (C₂₀H₁₇ClN₂O₄): C, 62.42; H, 4.45; N, 7.28%. Found: C, 62.33; H, 4.52; N, 7.35%. ¹H NMR (CDCl₃, 400 MHz): δ = 3.85 (3 H, s), 3.75 (3 H, s), 6.60 (2 H, t, ³J_{HH} = 8 Hz), 7.00 (1 H, t, ³J_{HH} = 8 Hz), 7.19 (1 H, s, Pyr-H), 7.26 (2 H, t, ³J_{HH} = 8 Hz), 7.38 (4 H, m), 7.80 (1 H, s, NH PhNH). ¹³C NMR (CDCl₃, 100 MHz): δ = 51.6, 52.0 (aliphatic carbon), 113.0, 119.0, 120.0, 120.1, 122.1, 125.5, 126.3, 126.4, 128.3, 128.4, 130.8, 132.7, 147.2 (aromatic carbons), 165.5, 169.6 (C=O).

Dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4b). Yield: 83%; white solid; m.p. 150-153 °C. IR (KBr) ($\bar{\nu}_{\max}$, cm⁻¹): 3335 (NH), 1715 (C=O). Calcd. for (C₂₀H₁₇BrN₂O₄): C, 55.96; H, 3.99; N, 6.53%. Found: C, 55.85; H, 4.01; N, 6.60%. ¹H NMR (CDCl₃, 400 MHz): δ = 3.75 (3 H, s), 3.84 (3 H, s), 6.60 (2 H, d, ³J_{HH} = 8 Hz), 7.00 (1 H, t, ³J_{HH} = 8 Hz), 7.19 (1 H, s, Pyr-H), 7.26 (1 H, t, ³J_{HH} = 8 Hz), 7.33 (2 H, d, ³J_{HH} = 8 Hz), 7.52 (2 H, d, t ³J_{HH} = 8 Hz), 7.79 (1 H, s, NH PhNH). ¹³C NMR (CDCl₃, 100 MHz): δ = 52.1, 52.5 (aliphatic carbon), 113.7, 120.7, 121.3, 122.6, 123.1, 125.9, 127.5, 128.8, 129.2, 129.4, 131.1, 147.1 (aromatic carbons), 160.1, 166.1 (C=O).

Dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate (4c). Yield: 82%; white solid; m.p. 165-167 °C. IR (KBr) ($\bar{\nu}_{\max}$, cm⁻¹): 3321 (NH), 1717 (C=O). Calcd. for (C₂₀H₁₇N₃O₆): C, 60.76; H, 4.33; N, 10.63%. Found: C, 60.83; H, 4.21; N, 10.52%. ¹H NMR (CDCl₃, 400 MHz): δ = 3.77 (3 H, s), 3.87 (3 H, s), 6.61 (2 H, d, ³J_{HH} = 8 Hz), 7.01 (1 H, t, ³J_{HH} = 8 Hz), 7.25 (1 H, s, Pyr-H), 7.28 (1 H, t, ³J_{HH} = 8 Hz), 7.61 (2 H, d, ³J_{HH} = 8 Hz), 7.81 (1 H, s, NH PhNH), 8.26 (2 H, d, t ³J_{HH} = 8 Hz), ¹³C NMR (CDCl₃, 100 MHz): δ = 52.2, 52.6 (aliphatic carbon), 113.8, 119.6, 120.5, 121.0, 122.8, 124.9, 126.6, 128.1, 129.5, 139.6, 146.7, 147.4 (aromatic carbons), 159.9, 165.6 (C=O).

Dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4d). Yield: 87%; white solid; m.p. 153-155 °C. IR (KBr) ($\bar{\nu}_{\max}$, cm⁻¹): 3263 (NH), 1716 (C=O). Calcd. for (C₂₀H₁₈N₂O₄): C, 68.56; H, 5.18; N, 8.00%. Found: C, 68.64; H, 5.06; N, 8.19%. ¹H NMR (CDCl₃, 400 MHz): δ = 3.76 (3 H, s), 3.85 (3 H, s), 6.61 (2 H, t ³J_{HH} = 8 Hz), 6.99 (1 H, t ³J_{HH} = 8 Hz), 7.28 (1 H, s, Pyr-H), 7.31 (1 H, t ³J_{HH} = 8 Hz), 7.41 (2 H, t, ³J_{HH} = 8 Hz), 7.47 (2 H, d, t ³J_{HH} = 8 Hz), 7.47 (2 H, d, ³J_{HH} = 8 Hz), 7.80 (1 H, s, NH PhNH). ¹³C NMR (CDCl₃, 100 MHz): δ = 21.08, 29.7, 52.0, 52.5 (aliphatic carbon), 113.7, 119.7, 120.8, 121.7, 122.5, 123.1, 126.1, 127.2, 127.5, 128.9, 129.4, 132.8, 147.9 (aromatic carbons), 160.1, 166.3 (C=O).

Di-*t*-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4e). Yield: 75%; White solid m.p. 90-93°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3380 (NH), 1720, 1699 (C=O). Calcd. for ($\text{C}_{26}\text{H}_{29}\text{BrN}_2\text{O}_4$): C, 60.82; H, 5.69; N, 5.46%. Found: C, 60.71; H, 5.81; N, 5.58%. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.39 (9 H, s), 1.45 (9 H, s), 6.67 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 6.98 (1 H, t, $^3J_{\text{HH}} = 8$ Hz), 7.25 (2H, t, $^3J_{\text{HH}} = 8$ Hz), 7.28 (1 H, s, Pyr-H), 7.32 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 7.51 (2 H, t, $^3J_{\text{HH}} = 8$ Hz), 7.70 (1 H, s, NH PhNH, t $^3J_{\text{HH}} = 8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 27.4, 81.2, 82.1 (aliphathic carbon), 131.3, 113.3, 120.3, 120.4, 120.6, 121.9, 124.0, 128.8, 129.6, 130.7, 147.9 (aromatic carbons), 158.7, 163.3 (C=O).

Di-*t*-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4f). Yield: 70%; White solid m.p. 111-113°C; m.p. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3280 (NH), 1720, 1699 (C=O). Calcd. for ($\text{C}_{26}\text{H}_{29}\text{ClN}_2\text{O}_4$): C, 60.82; H, 5.69; N, 5.46%. Found: C, 60.94; H, 5.53; N, 5.32%. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.39 (9 H, s,), 1.45 (9 H, s), 6.59 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 6.59 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 6.98 (1 H, t, $^3J_{\text{HH}} = 8$ Hz), 7.25 (1 H, d, $^3J_{\text{HH}} = 8$ Hz), 7.28 (1 H, s, Pyr-H), 7.36 (3 H, d, t $^3J_{\text{HH}} = 8$ Hz), 7.70 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 27.4, 81.2, 82.1 (aliphathic carbon), 131.3, 113.3, 120.3, 120.4, 120.6, 121.9, 124.0, 128.8, 129.6, 130.7, 147.9 (aromatic carbons), 158.7, 163.3 (C=O).

Diethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4g). Yield: 86%; white solid; m.p. 153-155°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3328 (NH), 1709 (C=O). Calcd. for ($\text{C}_{22}\text{H}_{21}\text{BrN}_2\text{O}_4$): C, 57.78; H, 4.63; N, 6.13%. Found: C, 57.62; H, 4.77; N, 6.26%. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.21 (3 H, t, $^3J_{\text{HH}} = 8$ Hz), 1.31 (3 H, t, $^3J_{\text{HH}} = 8$ Hz), 4.22 (2 H, q, $^3J_{\text{HH}} = 8$ Hz), 4.32 (2 H, q, $^3J_{\text{HH}} = 8$ Hz), 6.62 (2 H, d, $^3J_{\text{HH}} = 8$ Hz, arom), 7.00 (1 H, t, $^3J_{\text{HH}} = 8$ Hz, arom), 7.18 (1 H, s, Pyr-H), 7.27 (1 H, t, $^3J_{\text{HH}} = 8$ Hz, arom), 7.39 (4 H, m, arom), 7.81 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 13.9, 14.0, 61.1, 61.6 (aliphathic carbon), 113.8, 120.2, 120.5, 120.8, 121.2, 122.6, 125.7, 129.3, 129.4, 131.96, 147.8 (aromatic carbons), 159.7, 165.6 (C=O).

Diethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4h). Yield: 85%; white solid; m.p. 153-155°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3328 (NH), 1709 (C=O). Calcd. for ($\text{C}_{22}\text{H}_{21}\text{ClN}_2\text{O}_4$): C, 57.78; H, 4.63; N, 6.13%. Found: C, 57.67; H, 4.76; N, 6.27%. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.23 (3 H, t, $^3J_{\text{HH}} = 8$ Hz), 1.31 (3 H, t, $^3J_{\text{HH}} = 8$ Hz), 4.22 (2 H, q, $^3J_{\text{HH}} = 8$ Hz), 4.32 (2 H, q, $^3J_{\text{HH}} = 8$ Hz), 6.62 (2 H, d, $^3J_{\text{HH}} = 8$ Hz, arom), 7.00 (1 H, t, $^3J_{\text{HH}} = 8$ Hz, arom), 7.18 (1 H, s, Pyr-H), 7.27 (1 H, t, $^3J_{\text{HH}} = 8$ Hz, arom), 7.39 (4 H, m, arom), 7.81 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 13.9, 14.2, 61.3, 61.8 (aliphathic carbon), 114.0, 120.2, 120.5, 120.9, 121.2, 122.6, 126.1, 129.7, 129.9, 131.96, 147.8 (aromatic carbons), 159.7, 165.6 (C=O).

Diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4i). Yield: 80%; white solid; m.p. 97-99°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3304 (NH), 1720 (C=O). Calcd. for ($\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4$): C, 72.88; H, 5.65; N, 6.54%. Found: C, 73.02; H, 5.51; N, 6.43%. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.25 (3 H, t, $^3J_{\text{HH}} = 8$ Hz), 1.31 (3 H, t, $^3J_{\text{HH}} = 8$ Hz), 4.24 (2 H, q, $^3J_{\text{HH}} = 8$ Hz), 4.35 (2 H, q, $^3J_{\text{HH}} = 8$ Hz), 6.67 (2 H, d, $^3J_{\text{HH}} = 8$ Hz, arom), 7.01 (1 H, t, $^3J_{\text{HH}} = 8$ Hz, arom), 7.29 (2 H, t, $^3J_{\text{HH}} = 8$ Hz, arom), 7.48-7.54 (2 H, m), 7.60-7.63 (1 H, m, arom), 7.85-7.89 (3H, m, naph, py), 7.95 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 13.9, 14.1, 61.0 (aliphathic carbon), 113.8, 119.9, 121.3, 121.5, 125.9, 126.0, 126.1, 126.3, 127.6, 127.9, 128.2, 129.4, 130.4, 132.4, 133.5, 148.0 (aromatic carbons), 165.9 (C=O).

Di-*tert*-butyl 1-(phenylamino)-4-(*p*-tolyl)-1H-pyrrole-2,3-dicarboxylate (4j). Yield: 75%; White solid m.p. 142-144°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3320 (NH), 1725, 1705 (C=O). Calcd. for ($\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_4$): C, 72.30; H, 7.19; N, 6.25%. Found: C, 72.15; H, 7.33; N, 6.38%. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.40 (9 H, s), 1.45 (9 H, s), 2.40 (1H, s, CH_3), 6.61 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 6.98 (1 H, t, $^3J_{\text{HH}} = 8$ Hz), 7.02 (1 H, s, Pyr-H), 7.20 (2H, d, $^3J_{\text{HH}} = 8$ Hz), 7.26 (2H, m), 7.35 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 7.73 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 27.4 (aliphathic carbon), 81.2, 82.1, 131.3, 113.3, 120.3, 120.4, 120.6, 121.9, 124.0, 128.8, 129.6, 130.7, 147.9 (aromatic carbons), 159.4, 164.2 (C=O).

Dimethyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (4k). Yield: 83%; white solid;m.p. 105°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3310(NH), 1717 (C=O). Calcd. for ($\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4$): C, 69.22; H, 5.53; N, 7.69%. Found: C, 69.37; H, 5.40; N, 7.56%. ^1H NMR (CDCl_3 , 400 MHz): δ = 2.40 (3 H, s), 3.67 (3 H, s), 3.88 (3H, s), 6.62 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 7.00 (1 H, t $^3J_{\text{HH}} = 8$ Hz), 7.20 (1 H, s, Pyr-H), 7.21-7.24 (2 H, m), 7.26-7.28 (2 H, m), 7.35(2 H, d, t $^3J_{\text{HH}} = 8$ Hz), 7.81 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 21.2, 52.0, 52.5 (aliphatic carbon), 113.7, 119.5, 120.7, 121.7, 122.5, 126.0, 127.4, 129.4, 129.8, 137.0, 147.9 (aromatic carbons), 160.2, 166.4(C=O).

Dimethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4i). Yield: 75%; white solid;m.p. 119°C. IR (KBr) ($\bar{\nu}_{\max}$, cm^{-1}): 3286 (NH), 1723 (C=O). Calcd. for ($\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4$): C, 71.99; H, 5.03; N, 7.00%. Found: C, 71.85; H, 5.17; N, 7.13%. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.79 (3 H, s), 3.87 (3 H, s), 3.88, 6.66 (2 H, d, $^3J_{\text{HH}} = 8$ Hz), 7.00 (1 H, t $^3J_{\text{HH}} = 8$ Hz), 7.29 (3 H, t $^3J_{\text{HH}} = 8$ Hz), 7.48-7.55 (2 H, m), 7.56-7.61 (1 H, m), 7.86-7.90 (4 H, m, arom, Pyr-H), 7.94 (1 H, s, NH PhNH). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 52.1, 52.5 (aliphatic carbon), 113.8, 119.8, 121.0, 121.7, 122.6, 125.9, 126.0, 126.3, 126.4, 127.6, 128.0, 128.3, 129.4, 130.3, 132.5, 133.5, 147.9 (aromatic carbons), 160.2, 166.4(C=O).

References

1. Riley, H. A.; Gray, A. R. *Organic Syntheses*. **1943**, 2, 509.

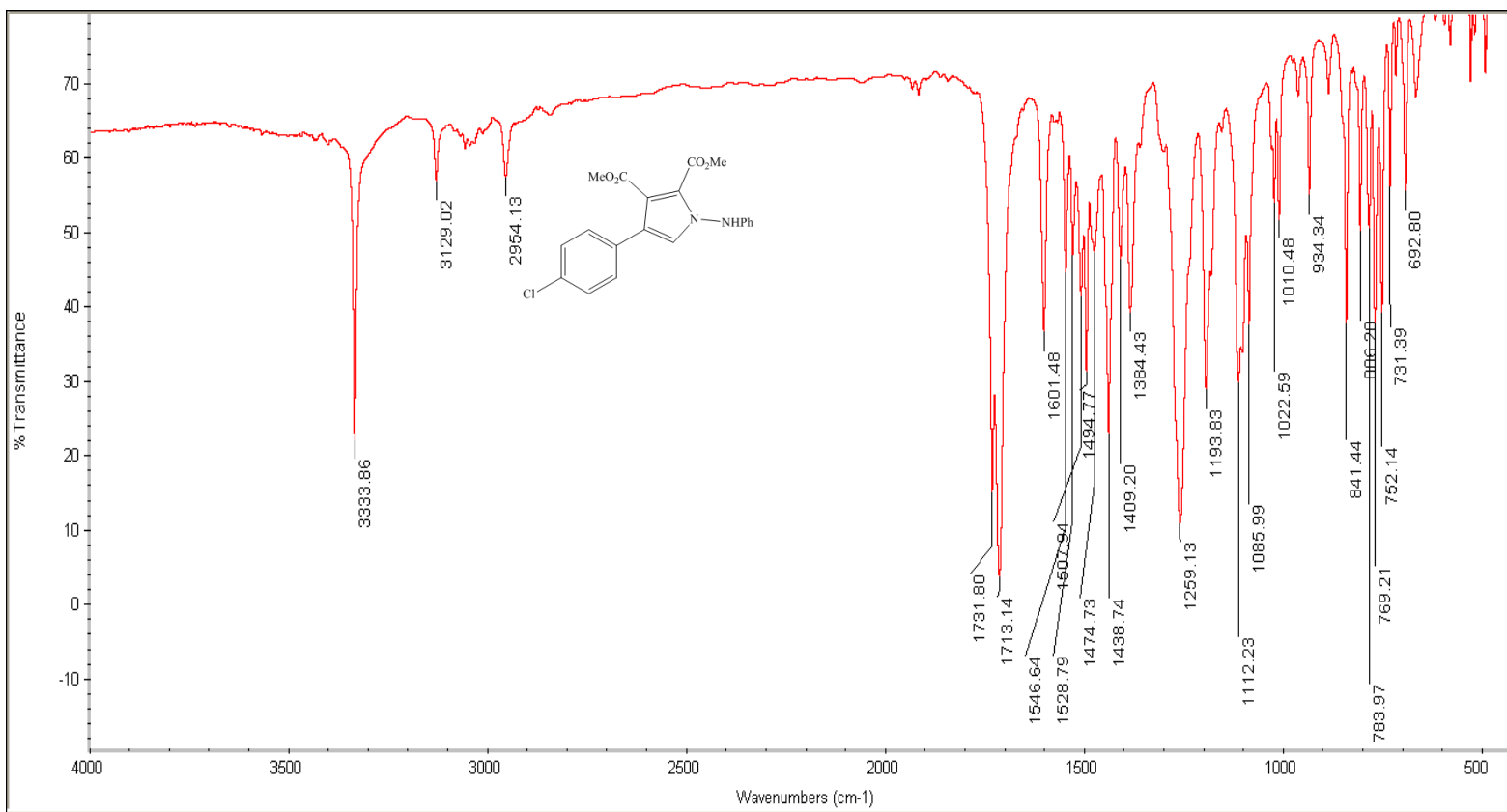


Figure S1. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4a**).

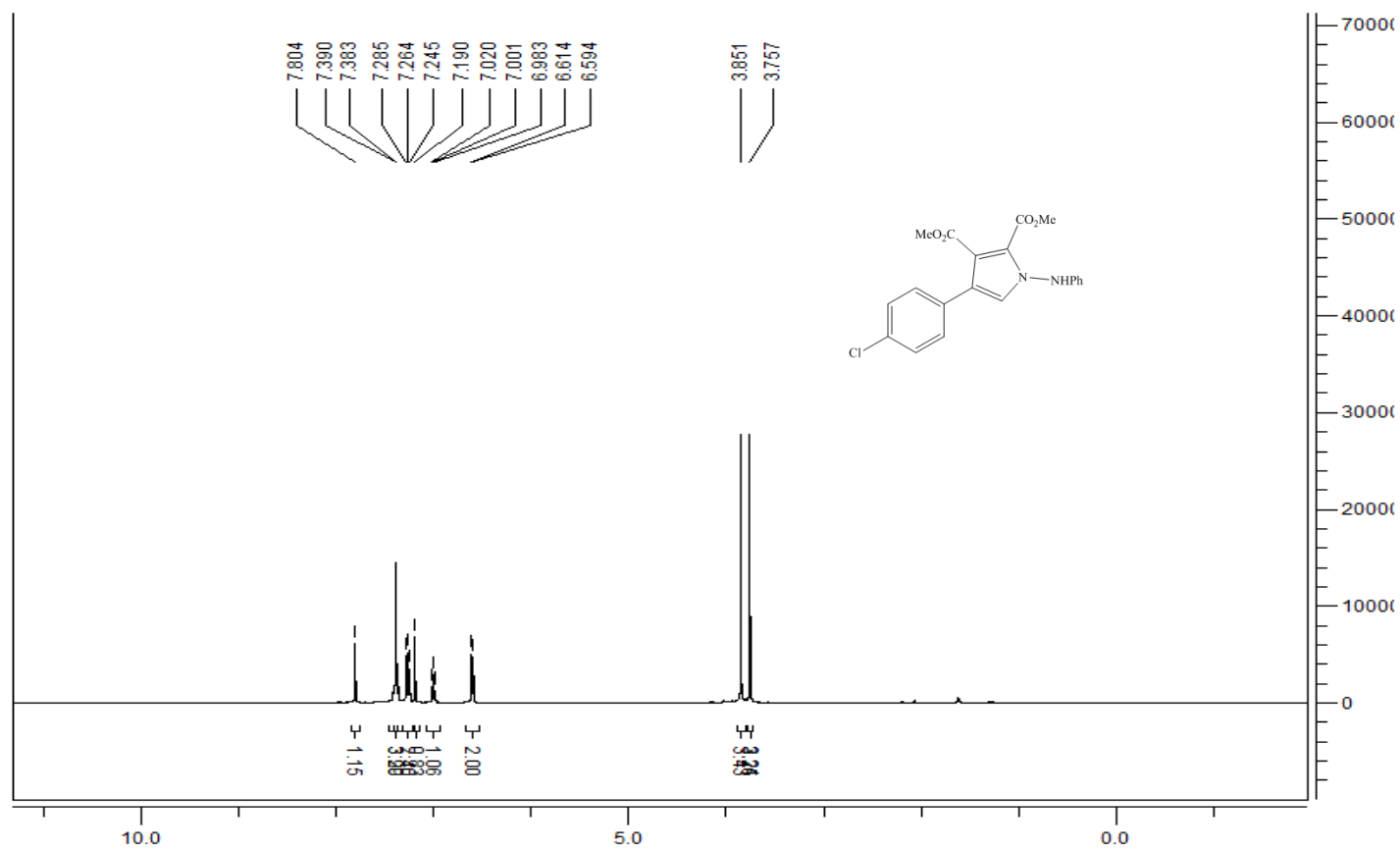


Figure S2. ¹H NMR spectrum (CDCl₃, 400 MHz) of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4a**).

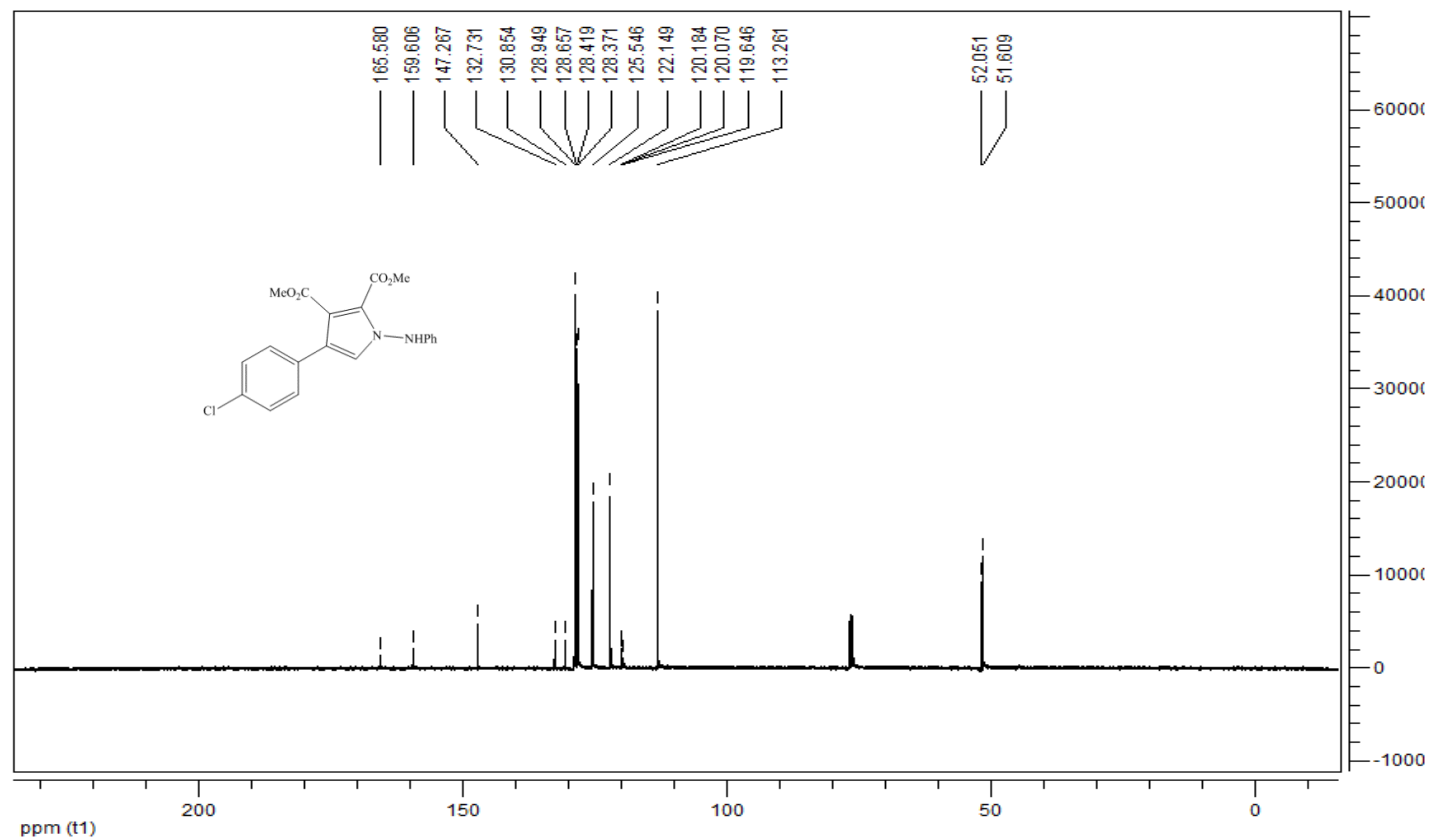
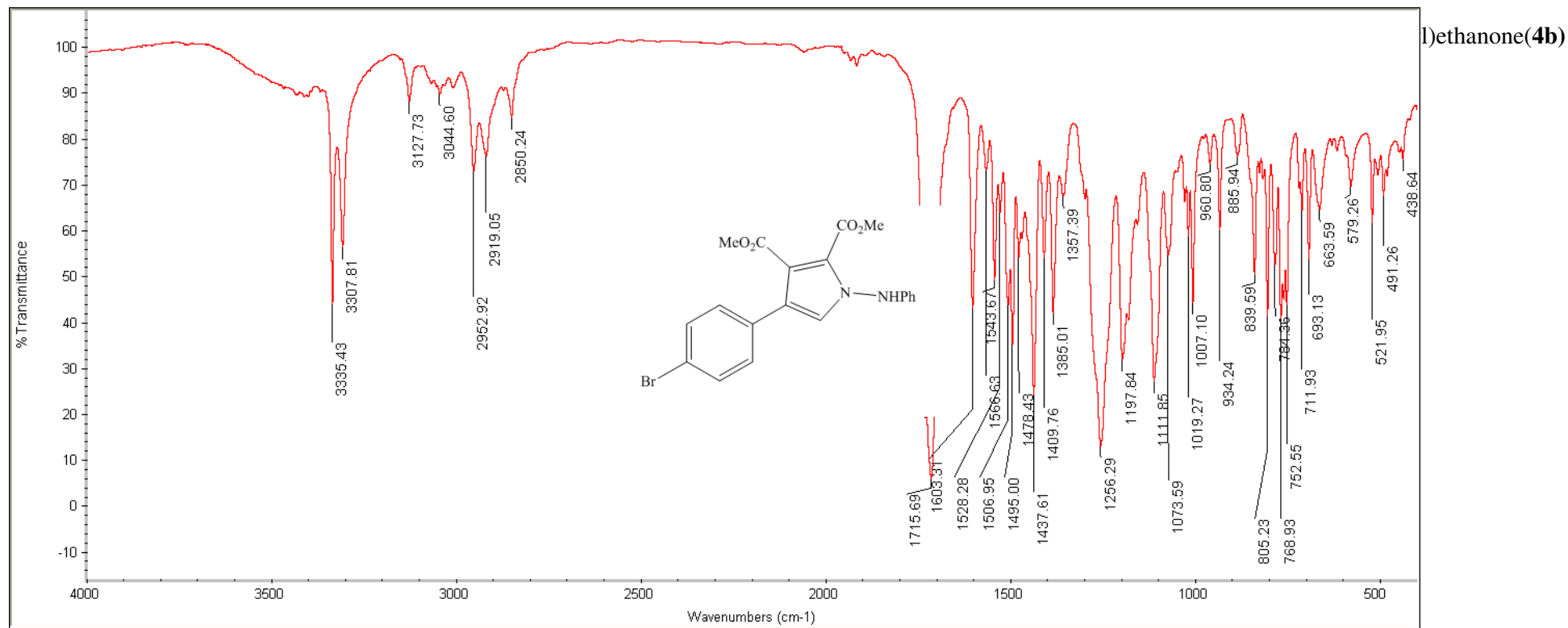


Figure S3. ¹³CNMR spectrum (CDCl₃, 100MHz) of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4a**).



Figures S4. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4b**).

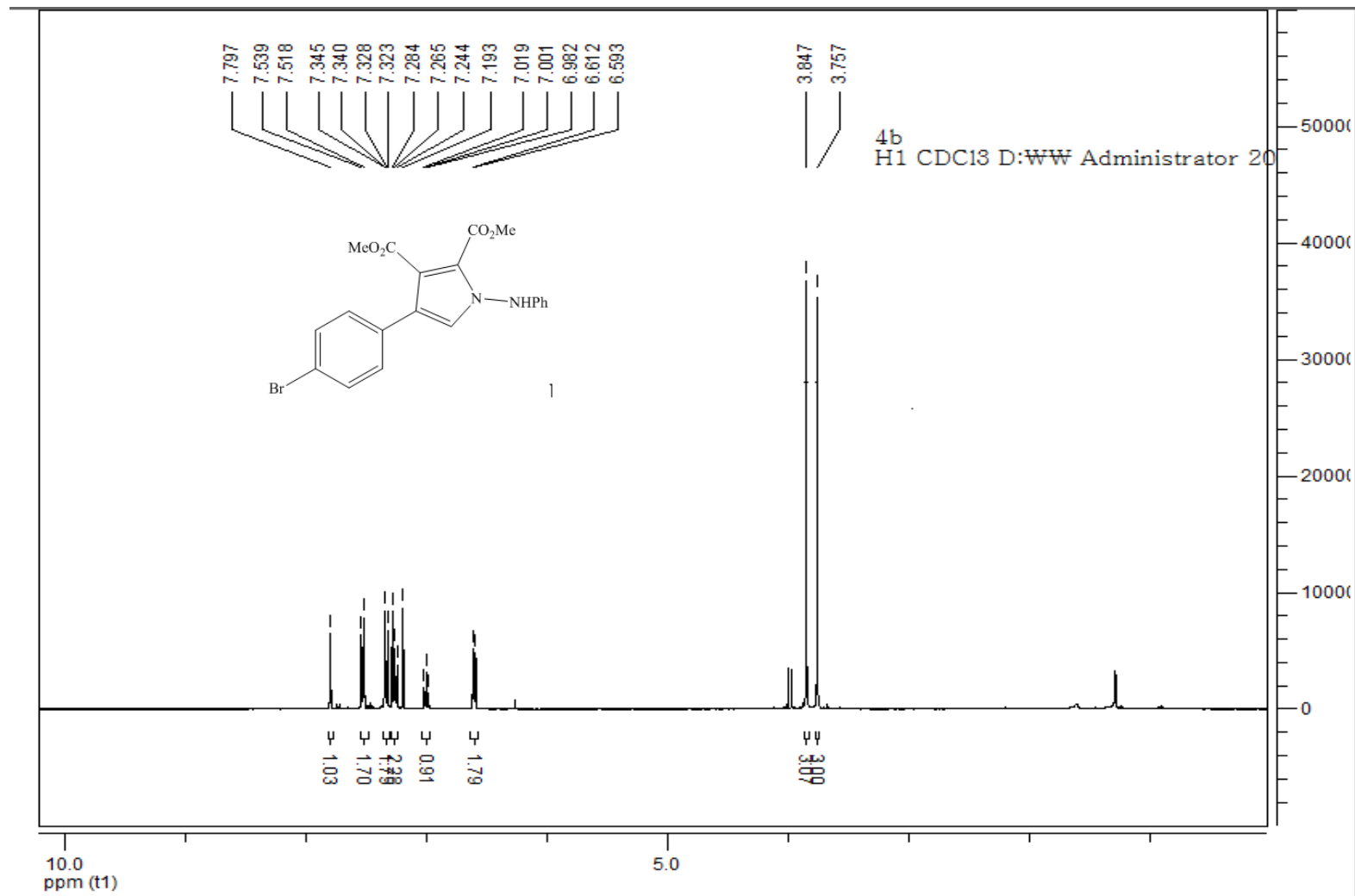


Figure S5. ^1H NMR spectrum (CDCl_3 , 400 MHz) of dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4b**).

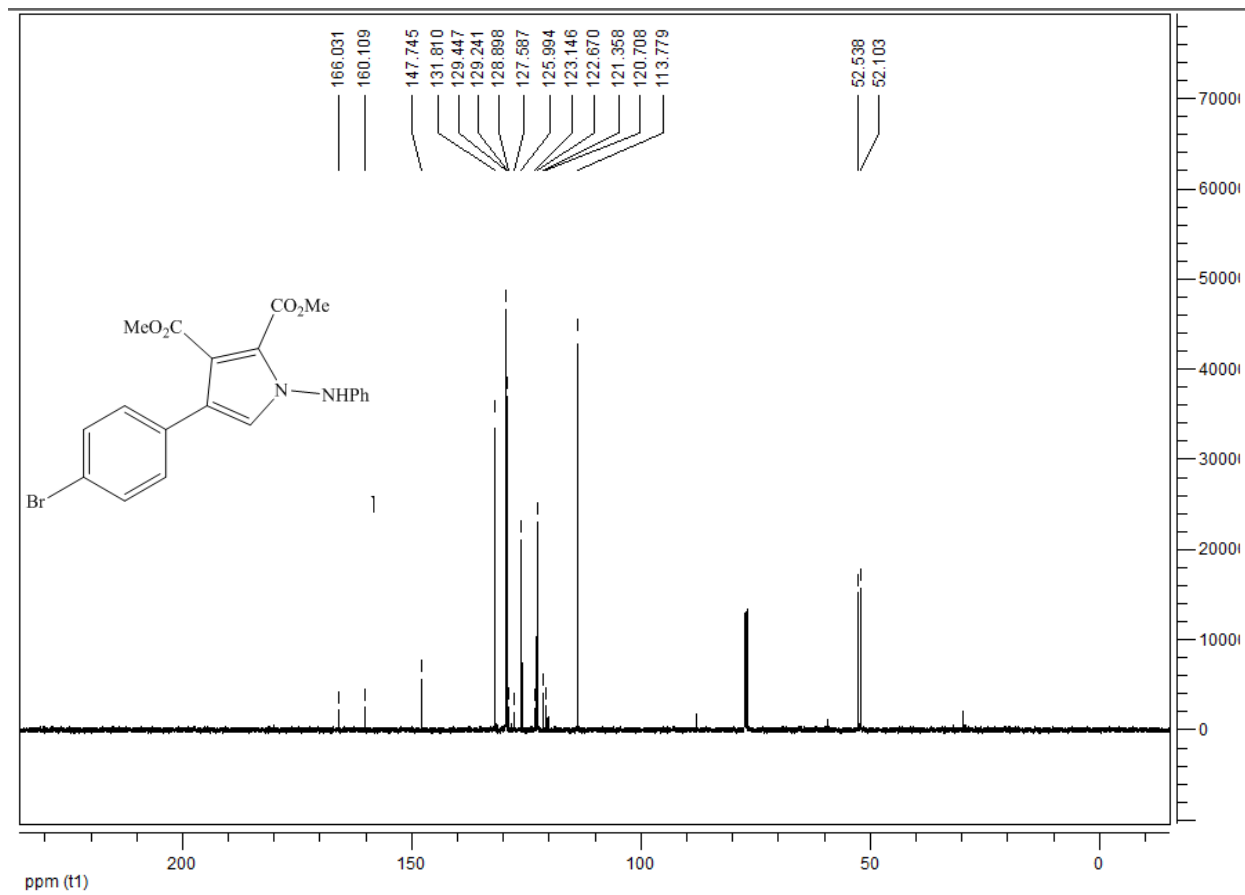


Figure S6. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4b**).

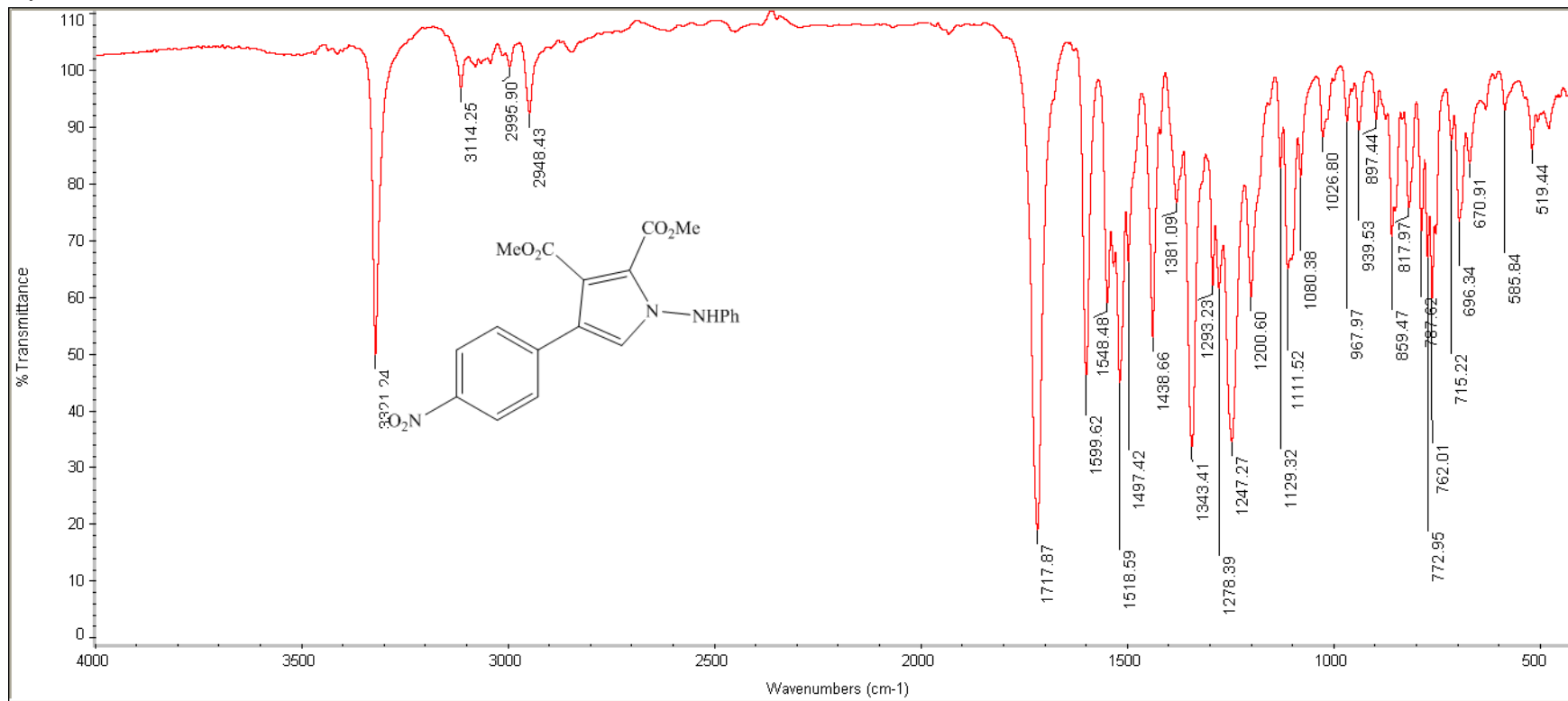


Figure S7. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm^{-1}) of dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate (**4c**).

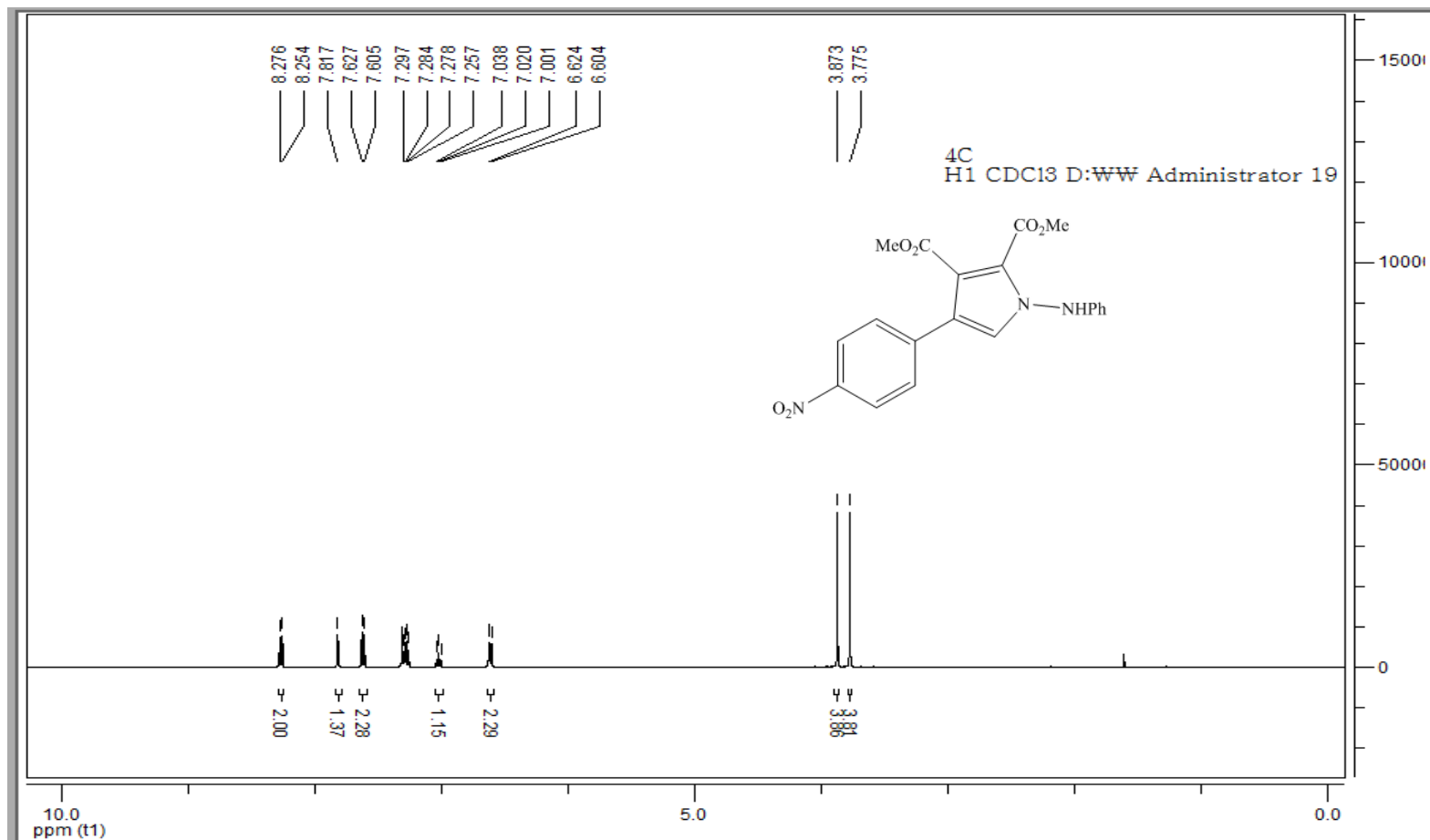


Figure S8. ^1H NMR spectrum (CDCl_3 , 400 MHz) of dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate (**4c**).

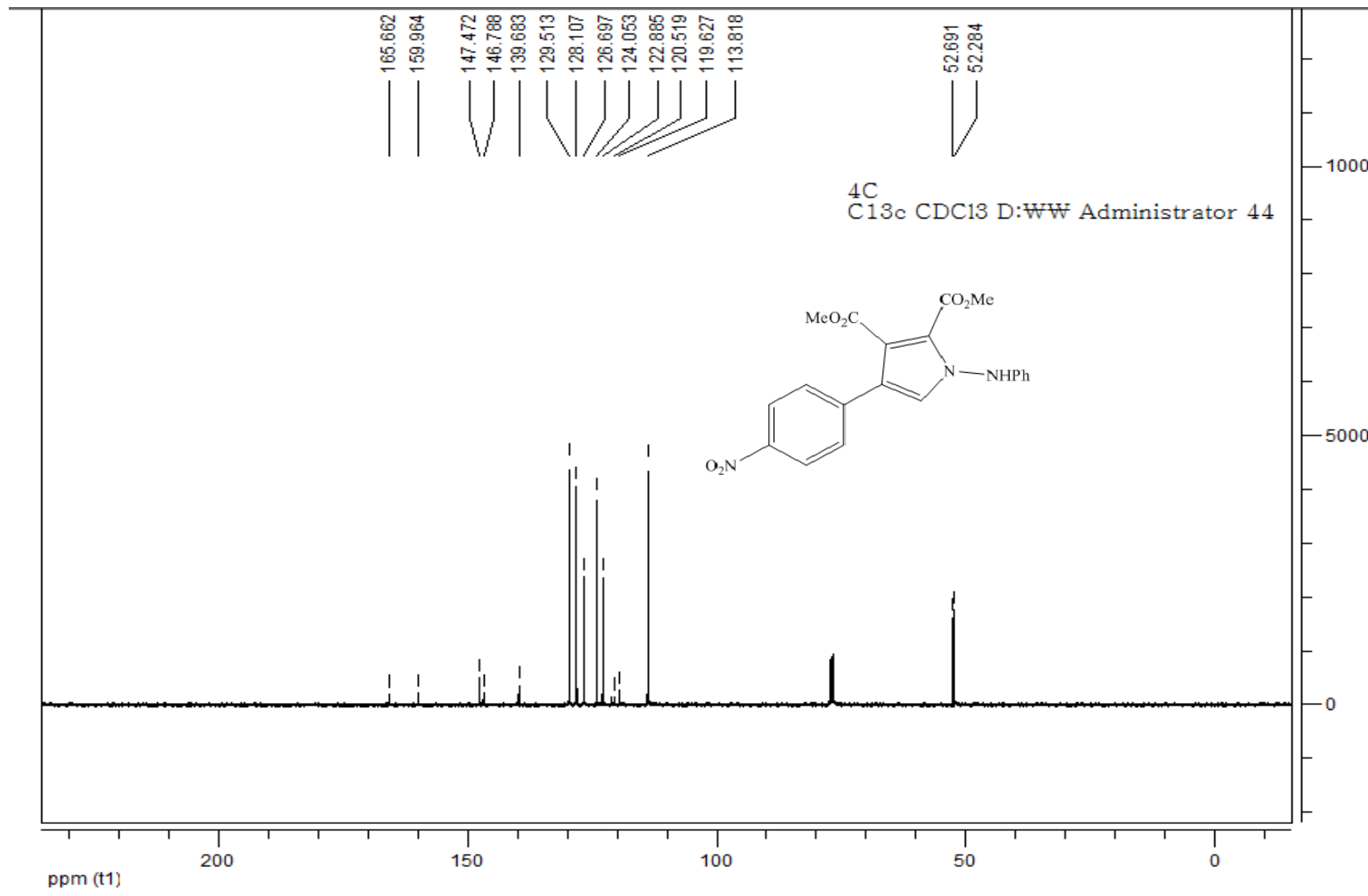


Figure S9. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate (**4c**).

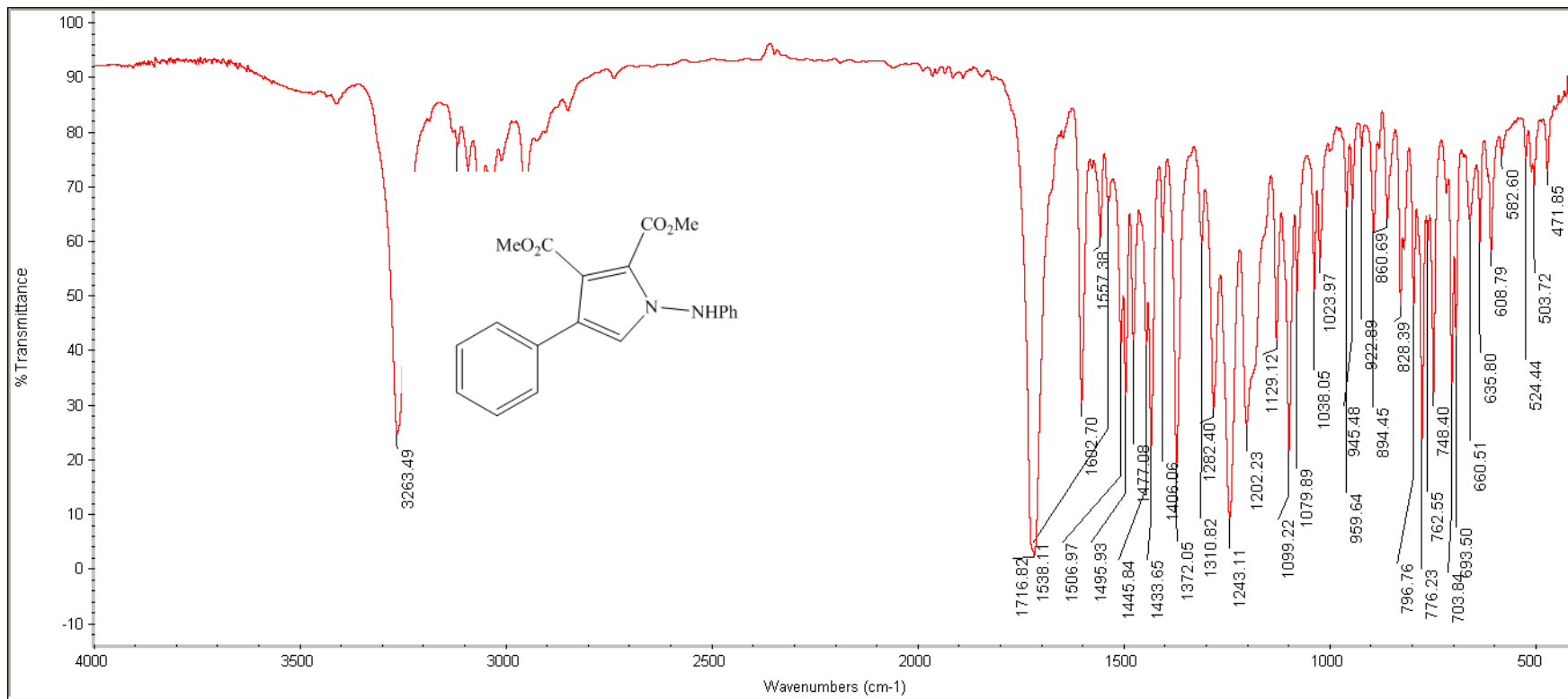


Figure S10. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4d**).

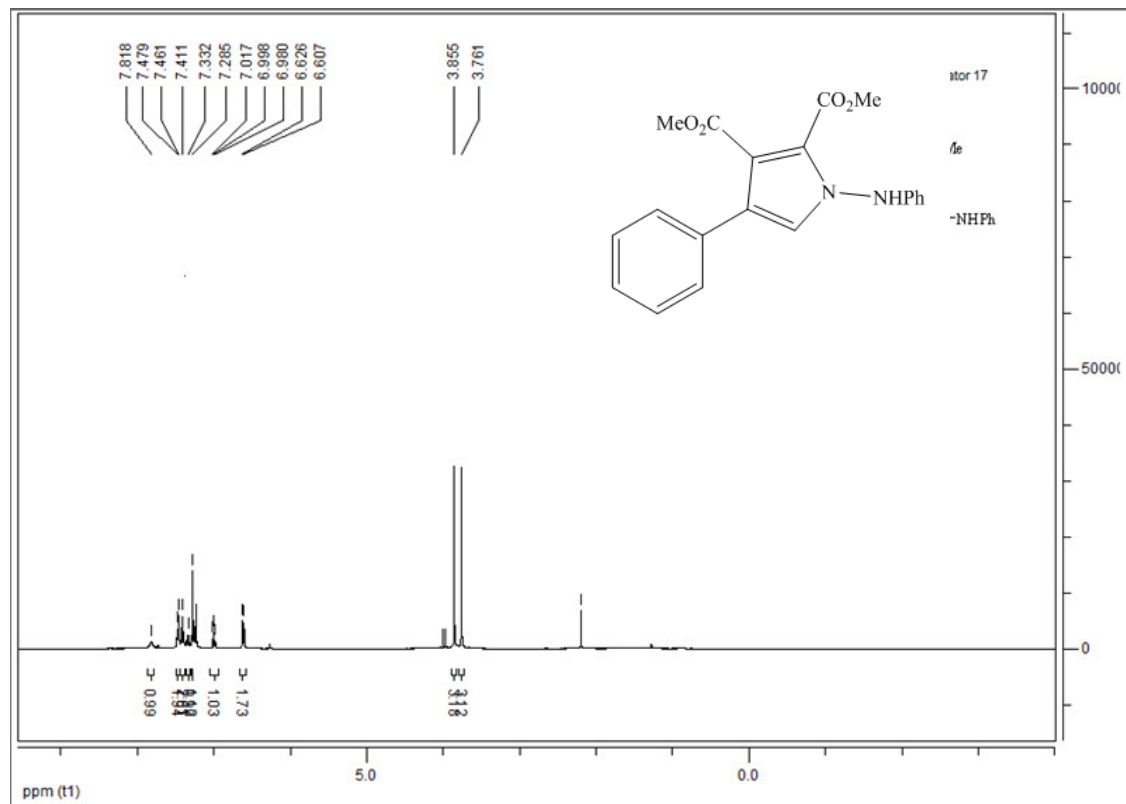


Figure S11. ¹H NMR spectrum (CDCl₃, 400 MHz) of dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4d**).

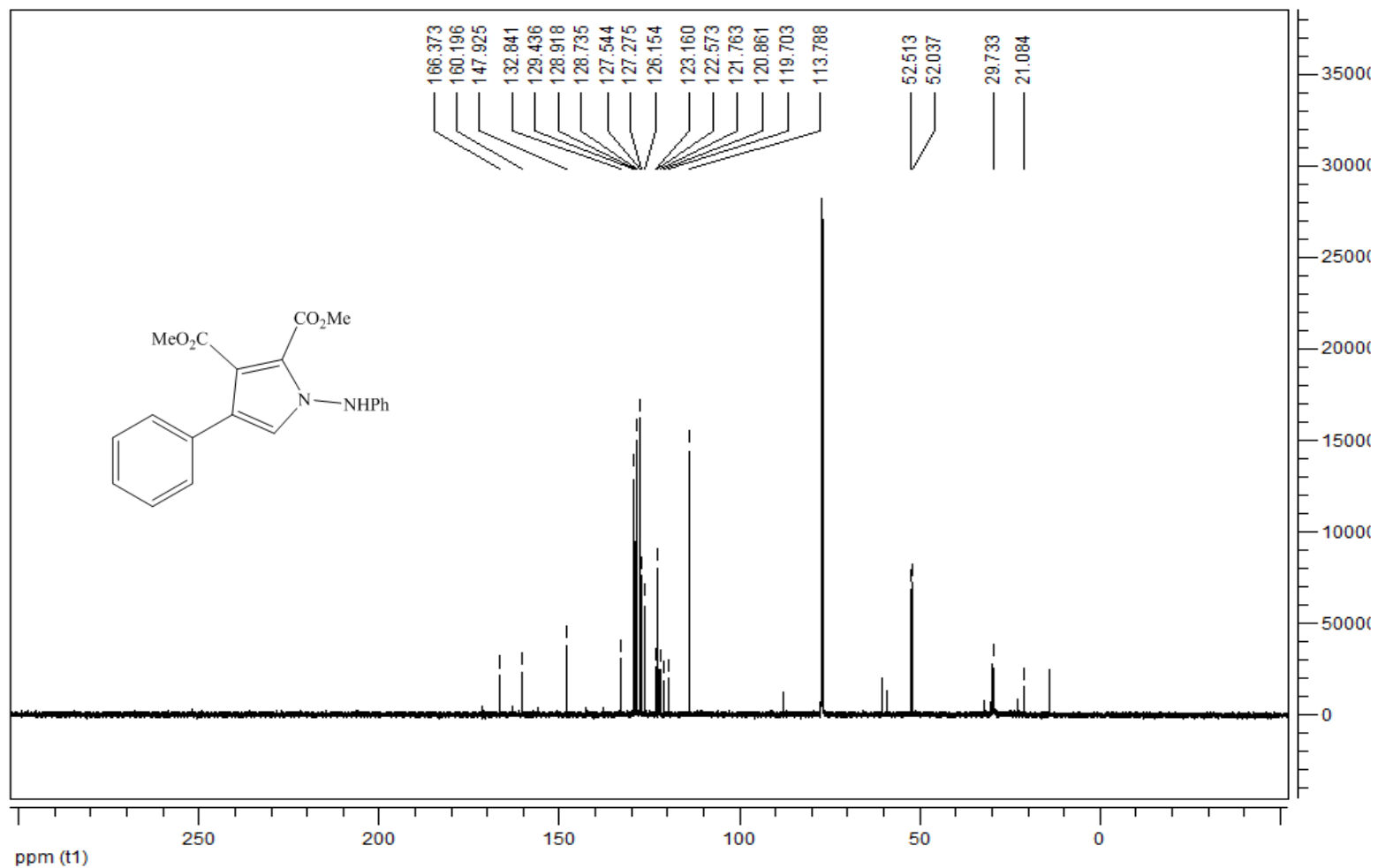


Figure S12. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4d**).

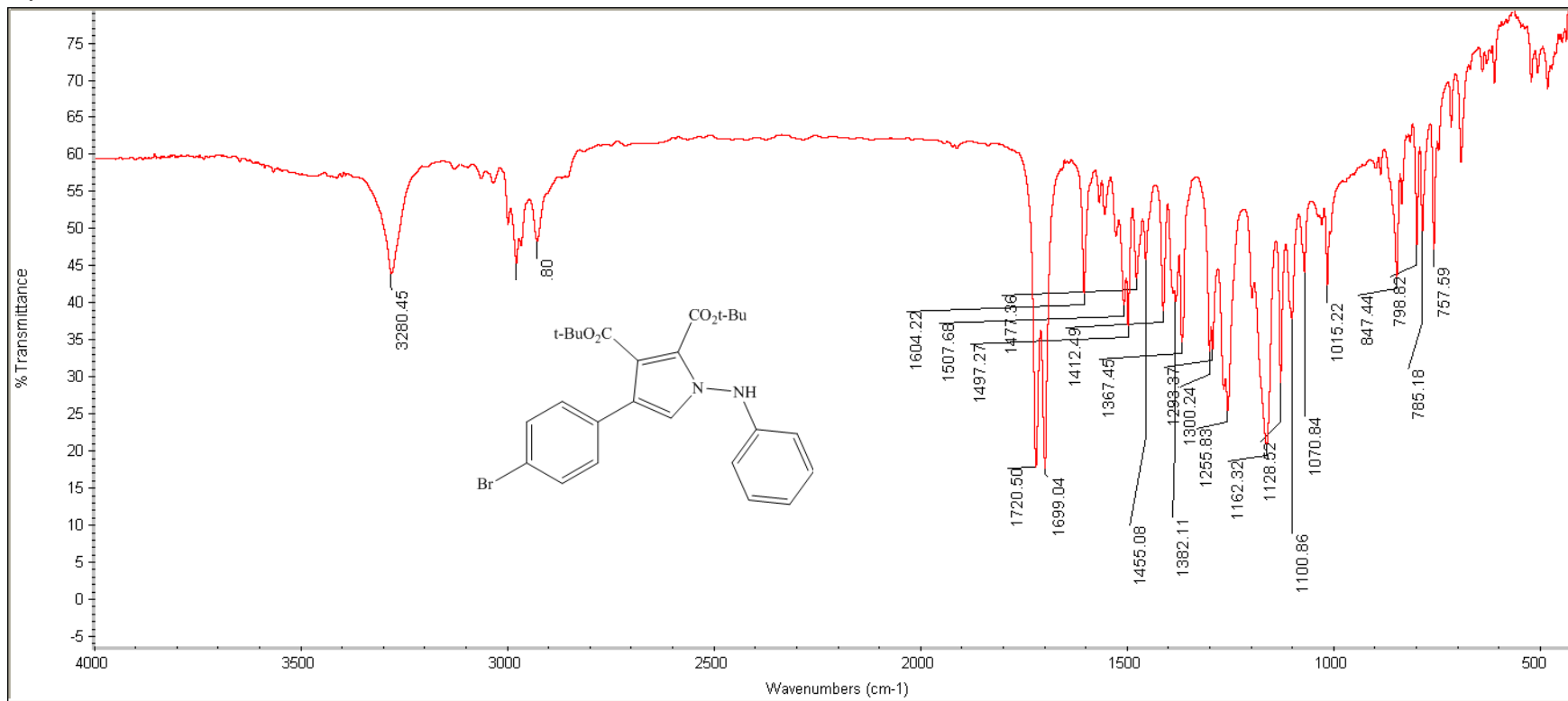


Figure S13. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of di-tert-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4e**).

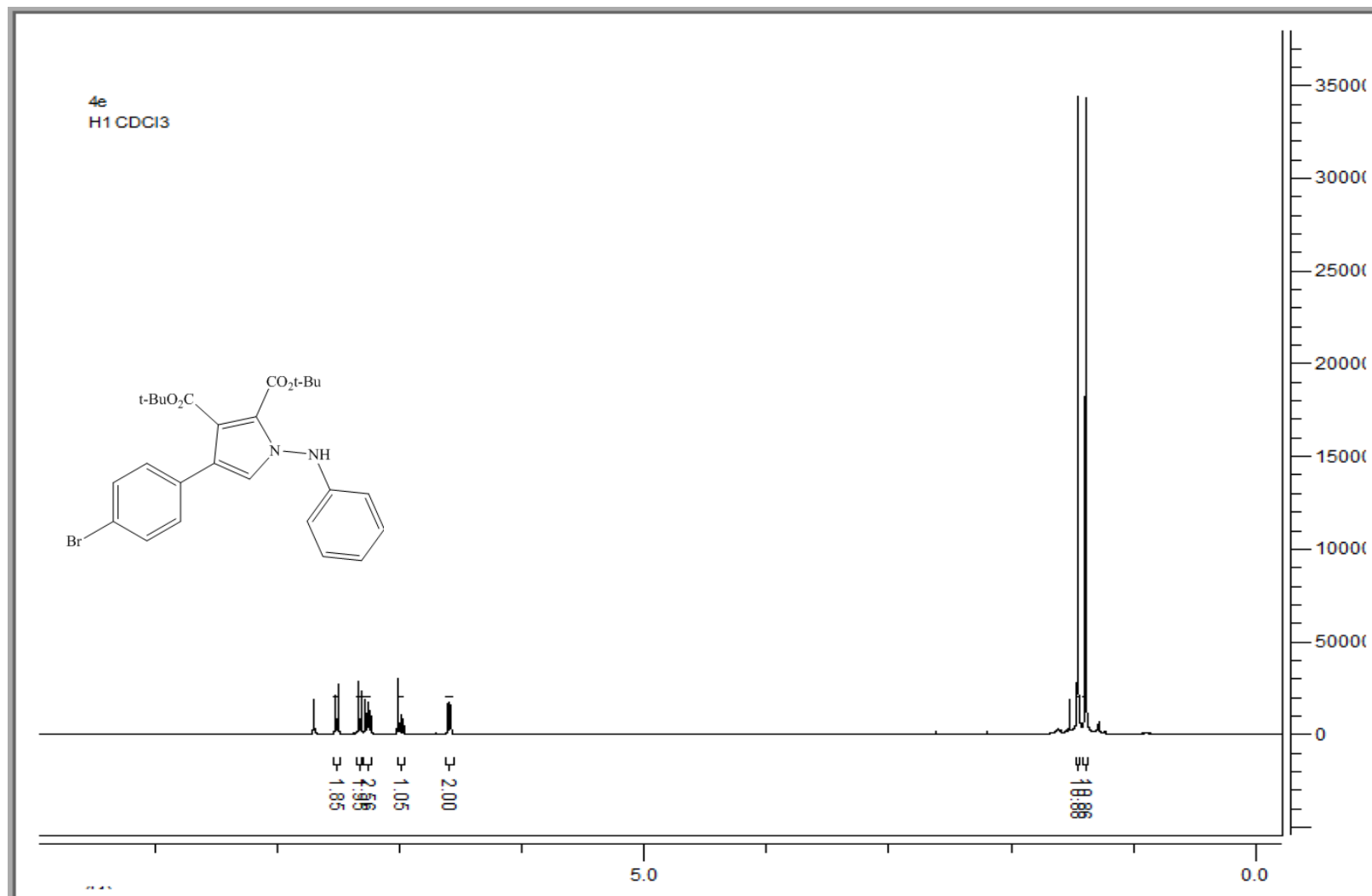


Figure S14. ^1H NMR spectrum (CDCl_3 , 400 MHz) of di-tert-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4e**).

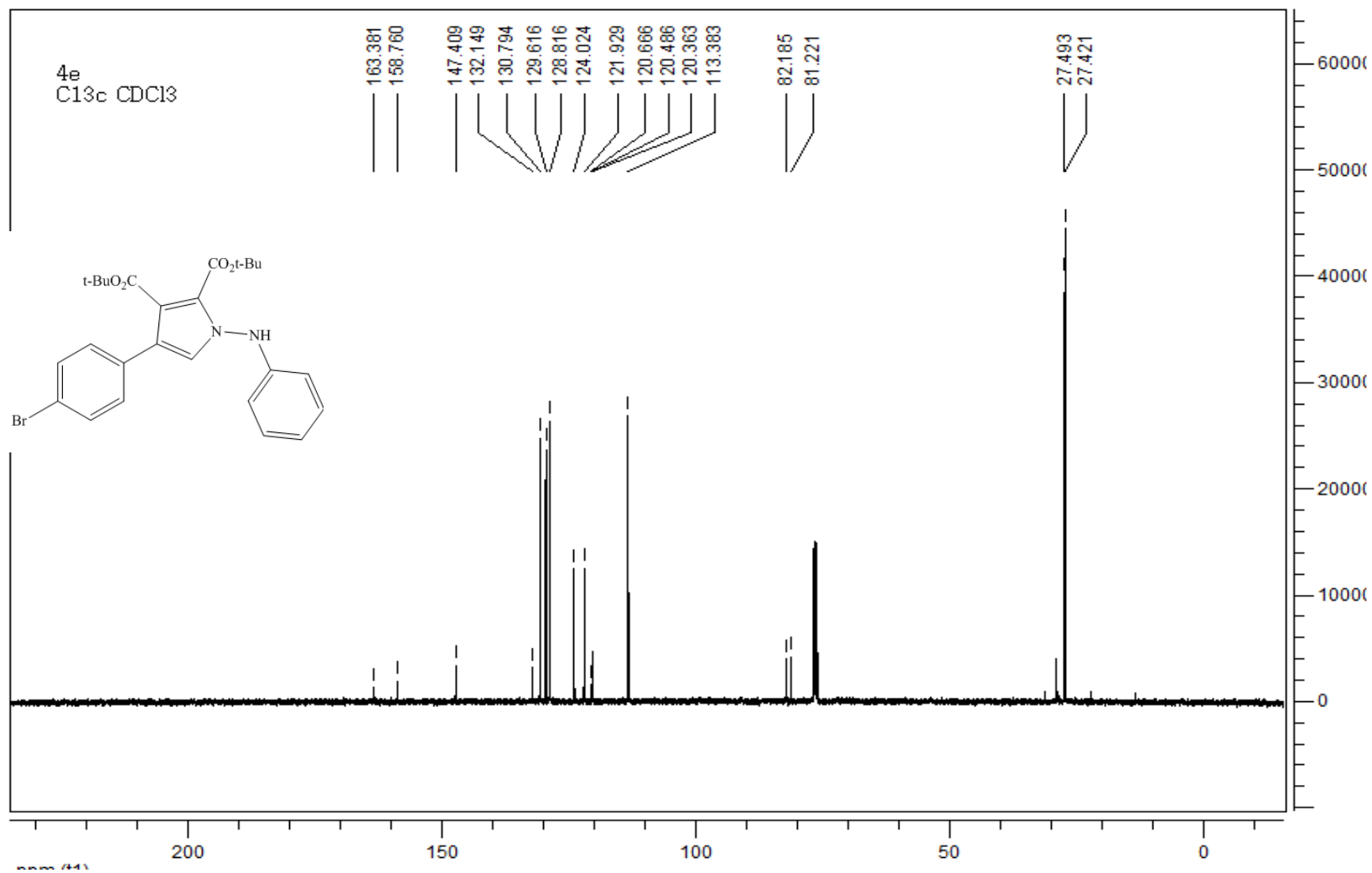


Figure S15. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of di-tert-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4e**).

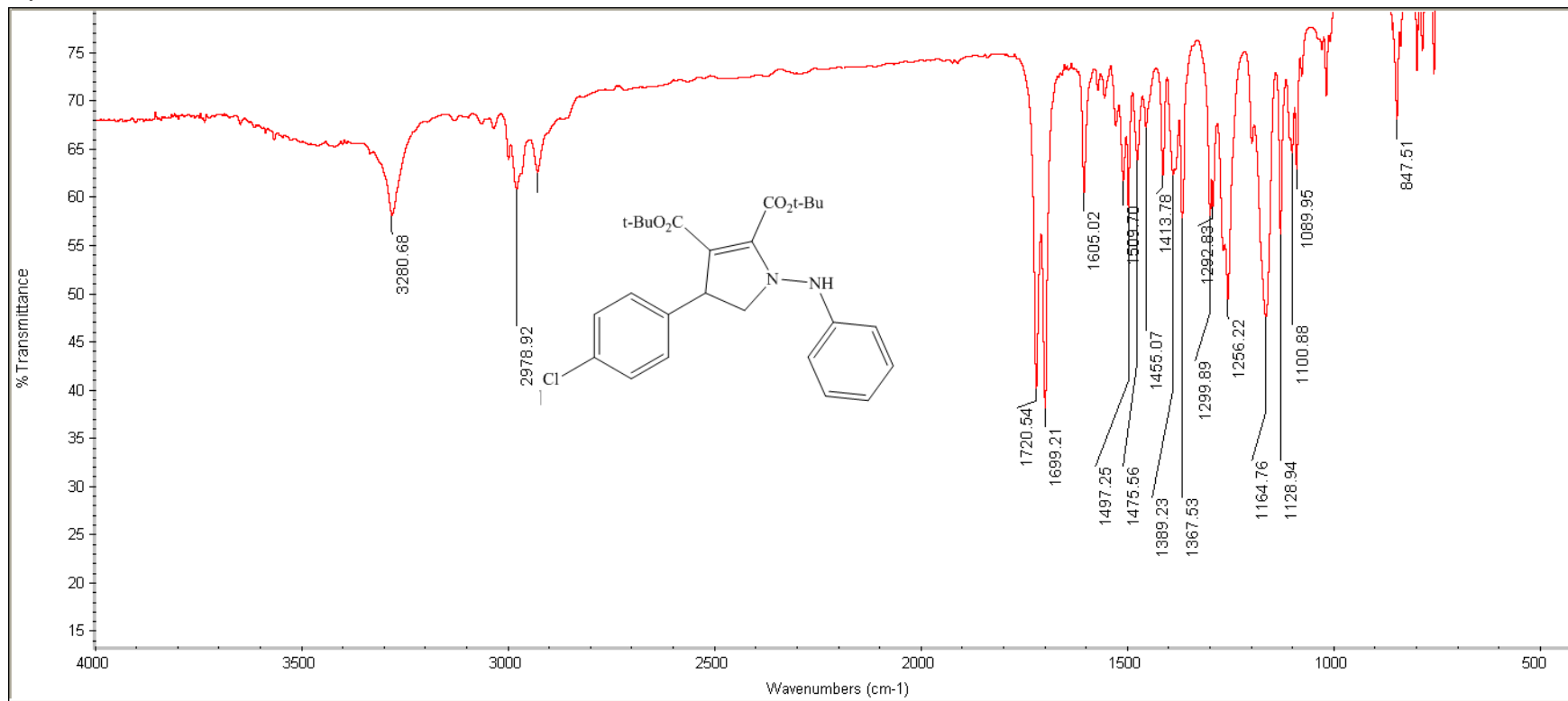


Figure S16. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of di-tert-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4f**).

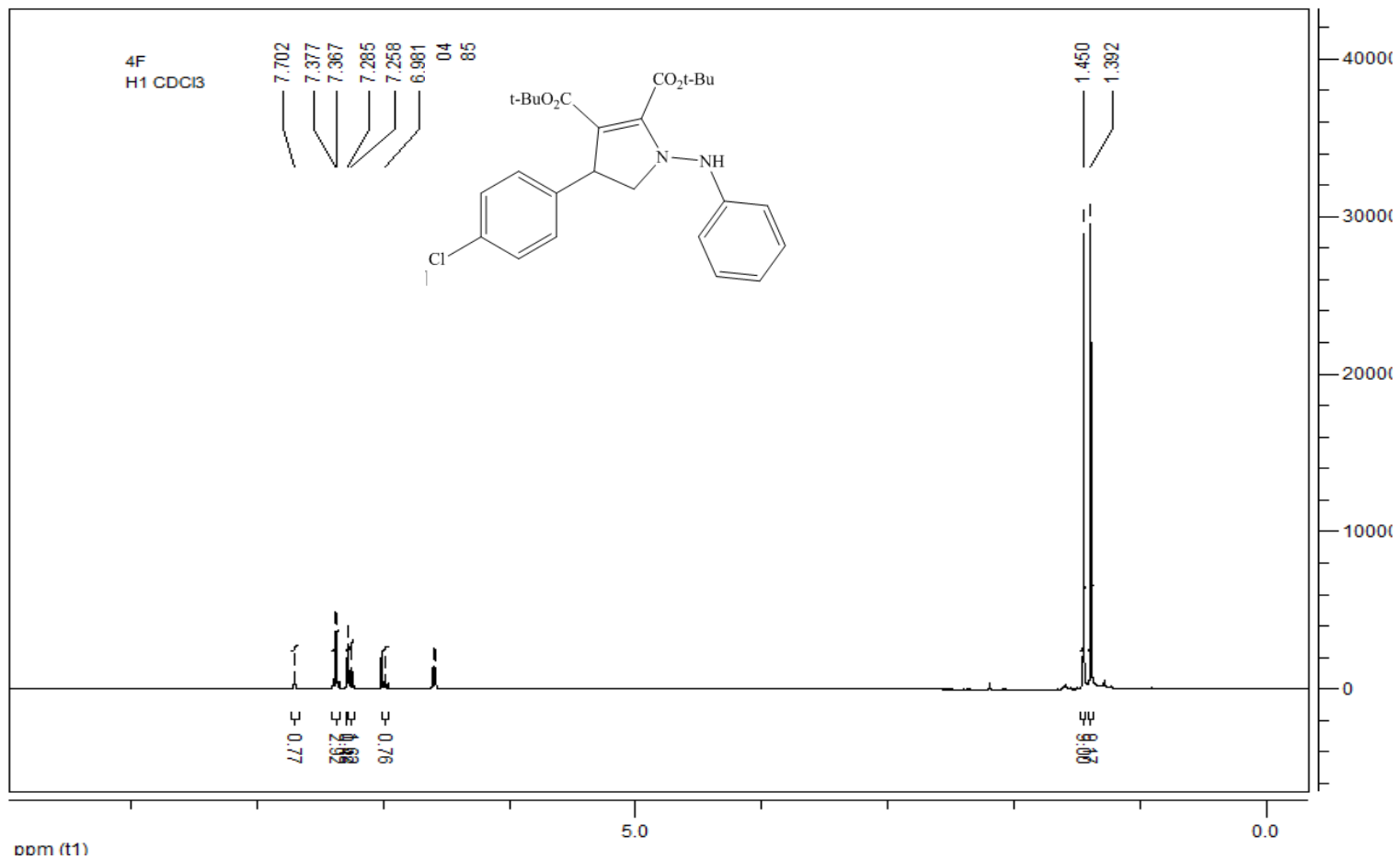


Figure S17. ¹H NMR spectrum (CDCl₃, 400 MHz) of di-tert-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4f**).

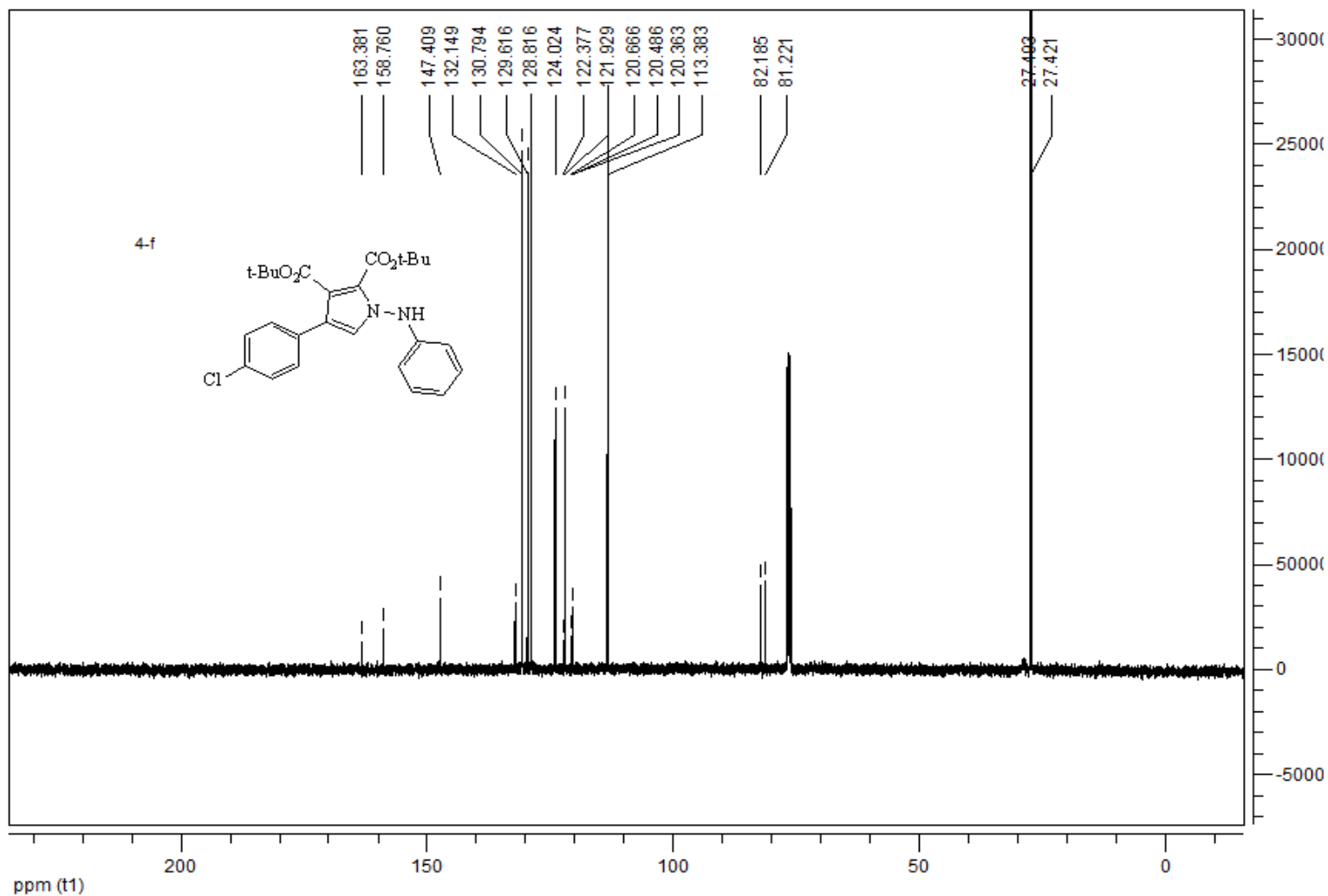


Figure S18. ¹³C NMR spectrum (CDCl₃, 100MHz) of di-tert-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.

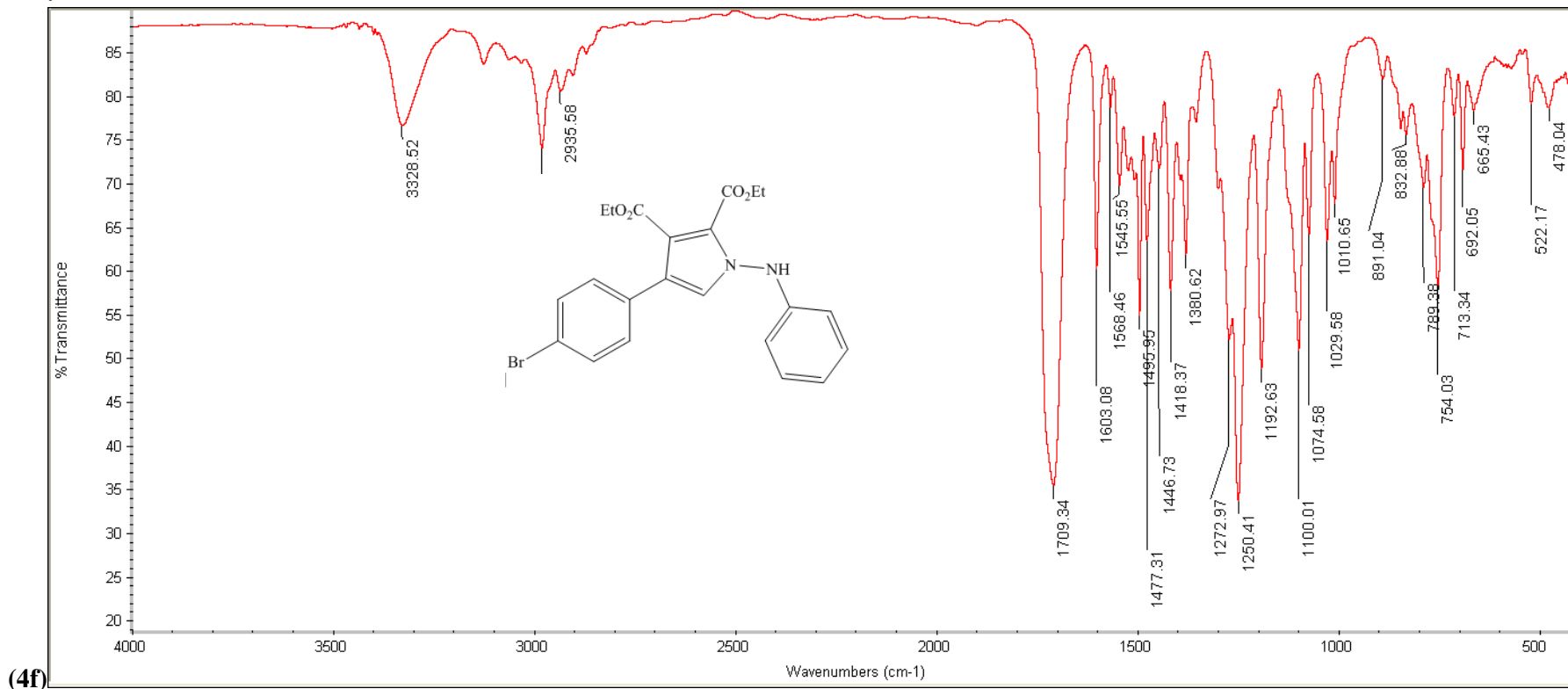


Figure S19. IR spectrum (KBr) ($\bar{\nu}_{\text{max}}$, cm⁻¹) of diethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4g**).

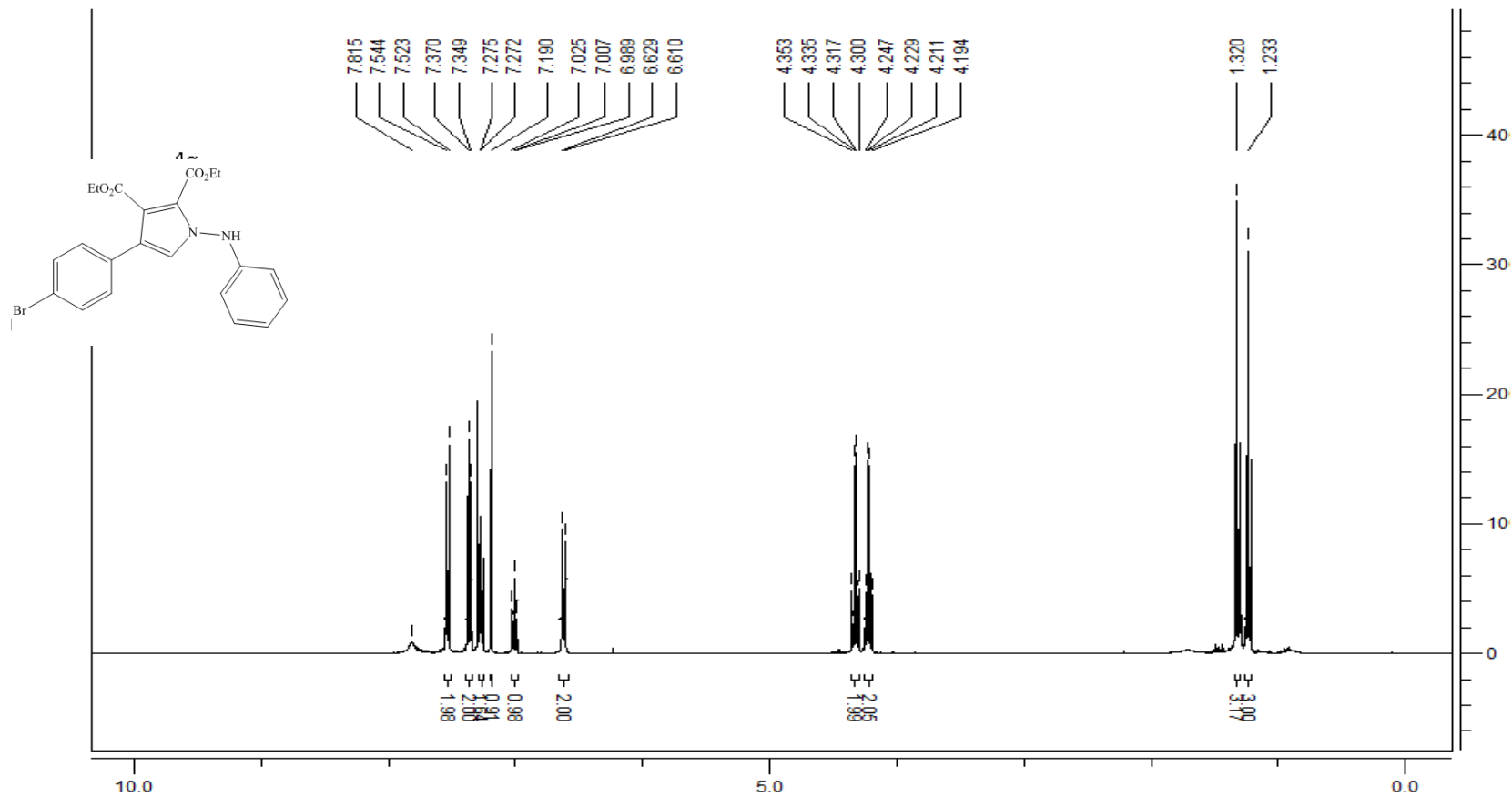


Figure S20 ¹H NMR spectrum (CDCl₃, 400 MHz) of diethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4g**).

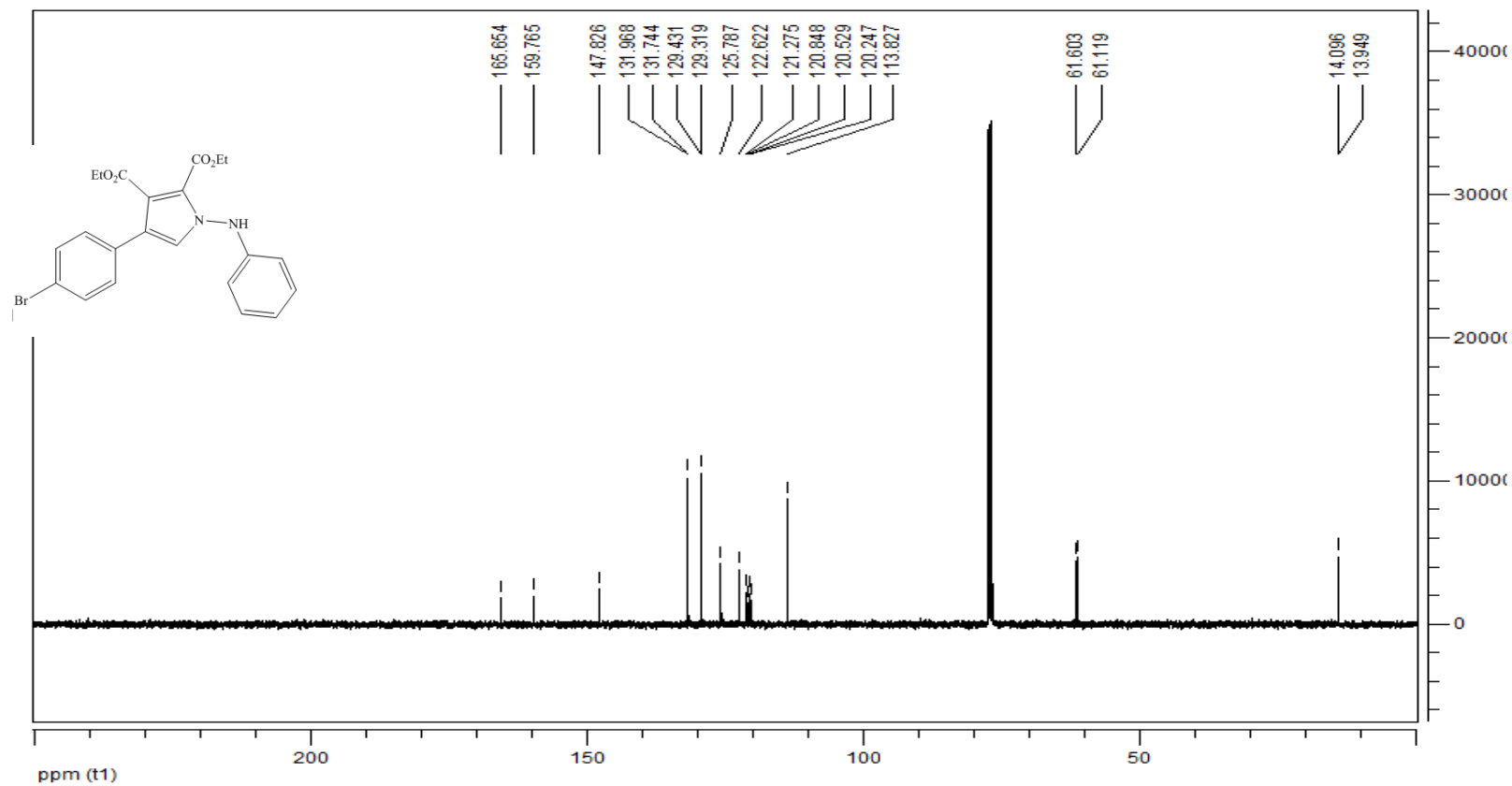


Figure S21. ¹³C NMR spectrum (CDCl₃, 100MHz) of diethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4g**).

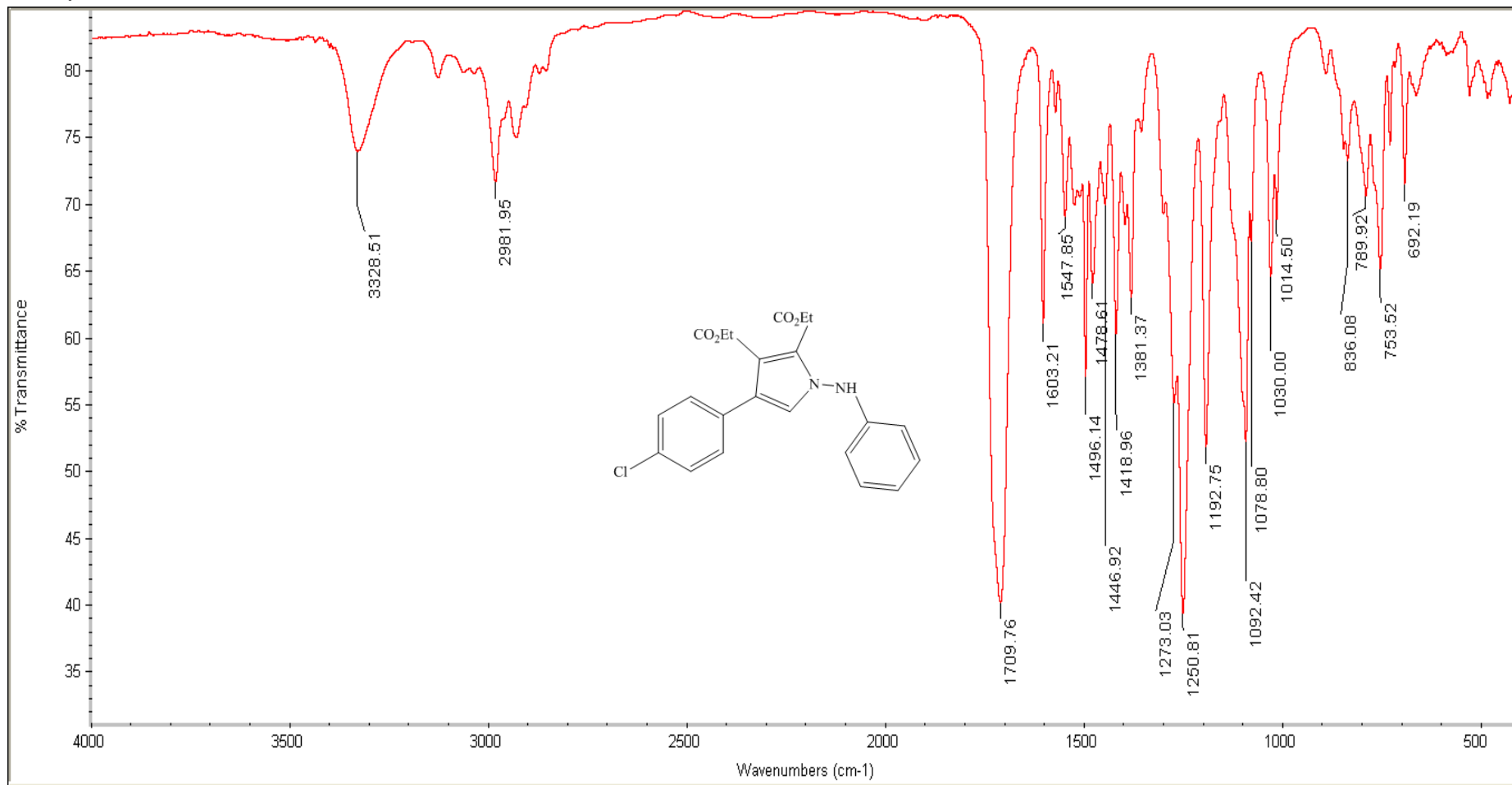


Figure S22. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of diethyl 4-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4h**).

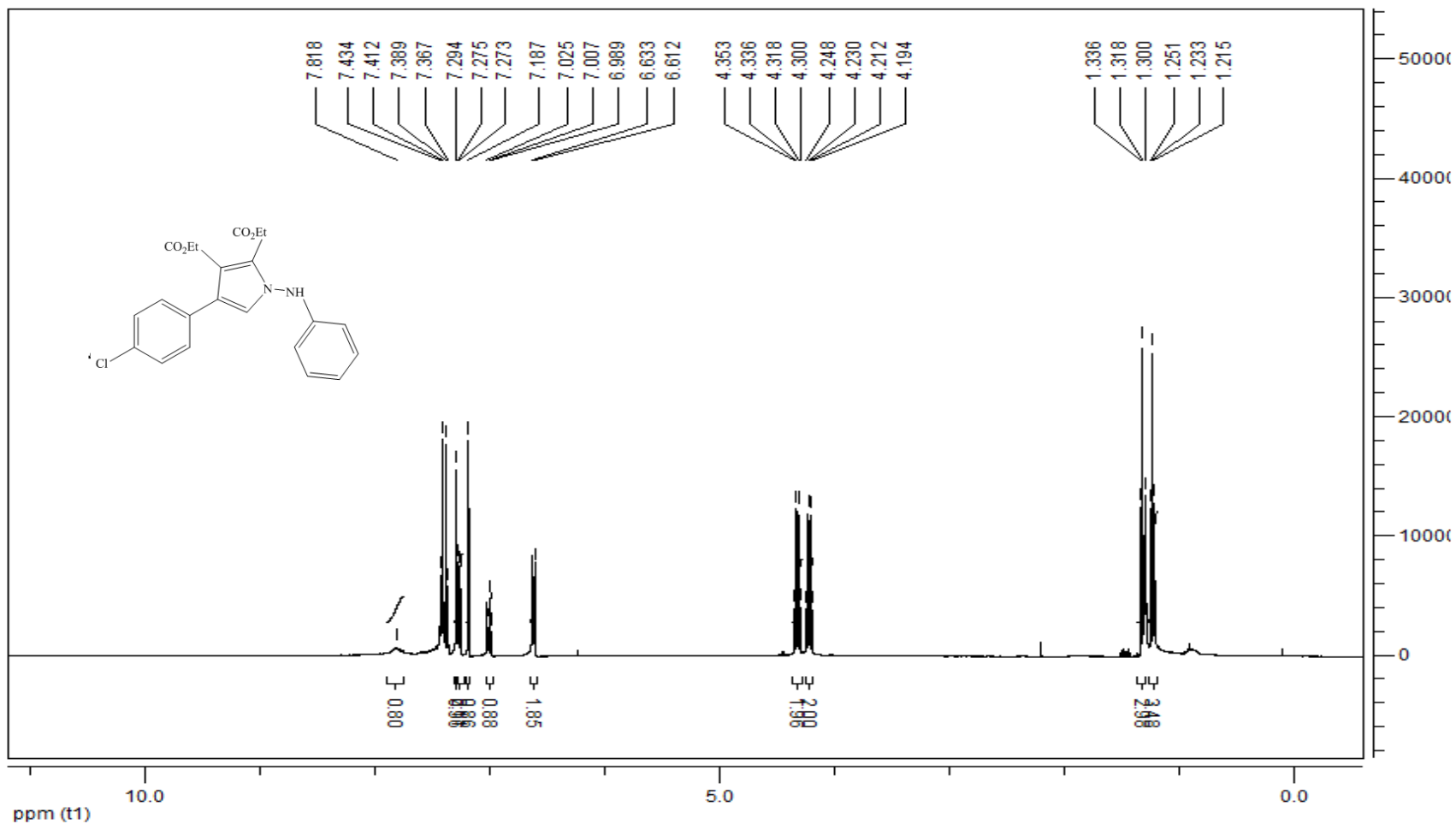


Figure S23 ¹H NMR spectrum (CDCl₃, 400 MHz) of diethyl 4-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.

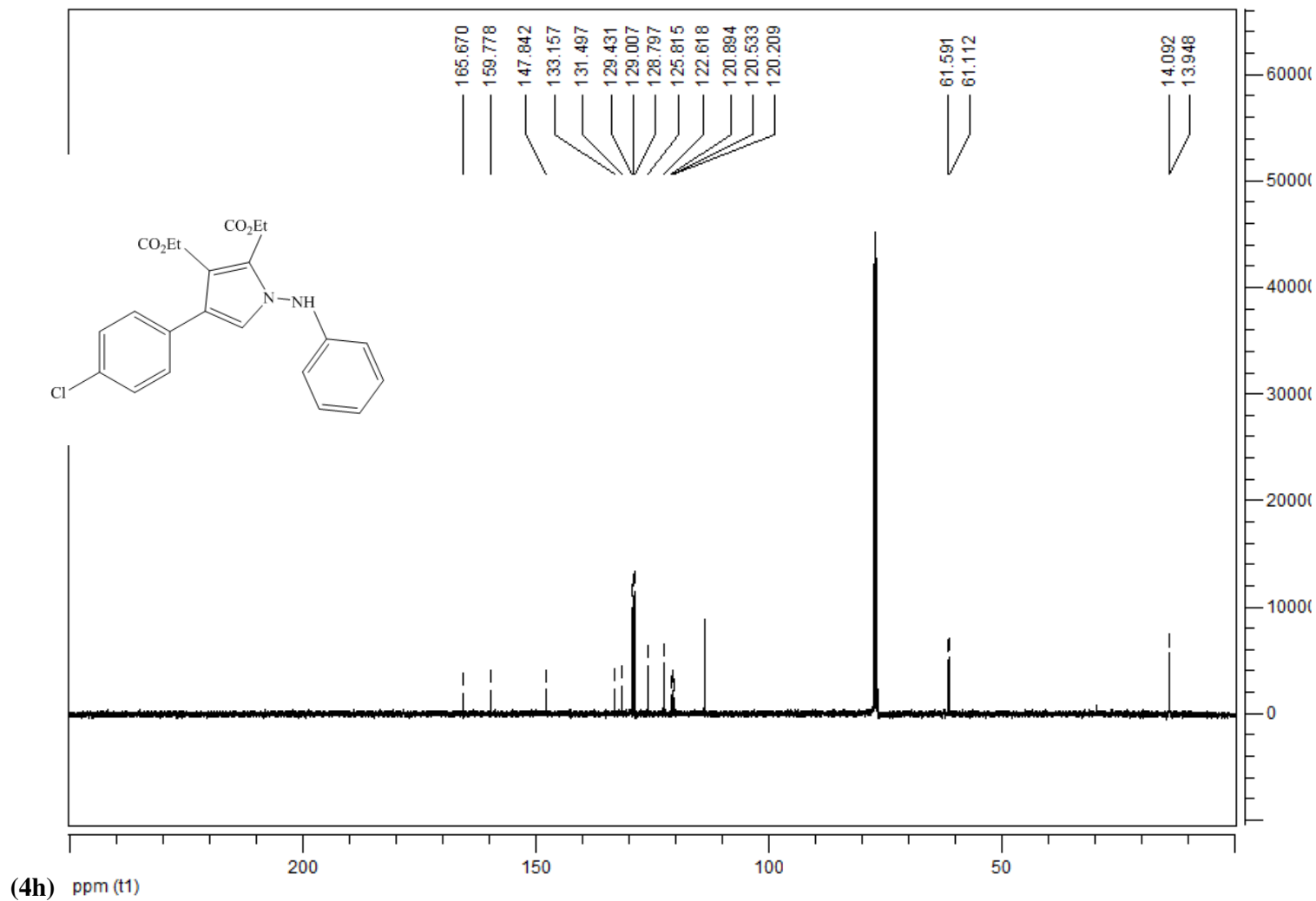


Figure S24. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of diethyl 4-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.

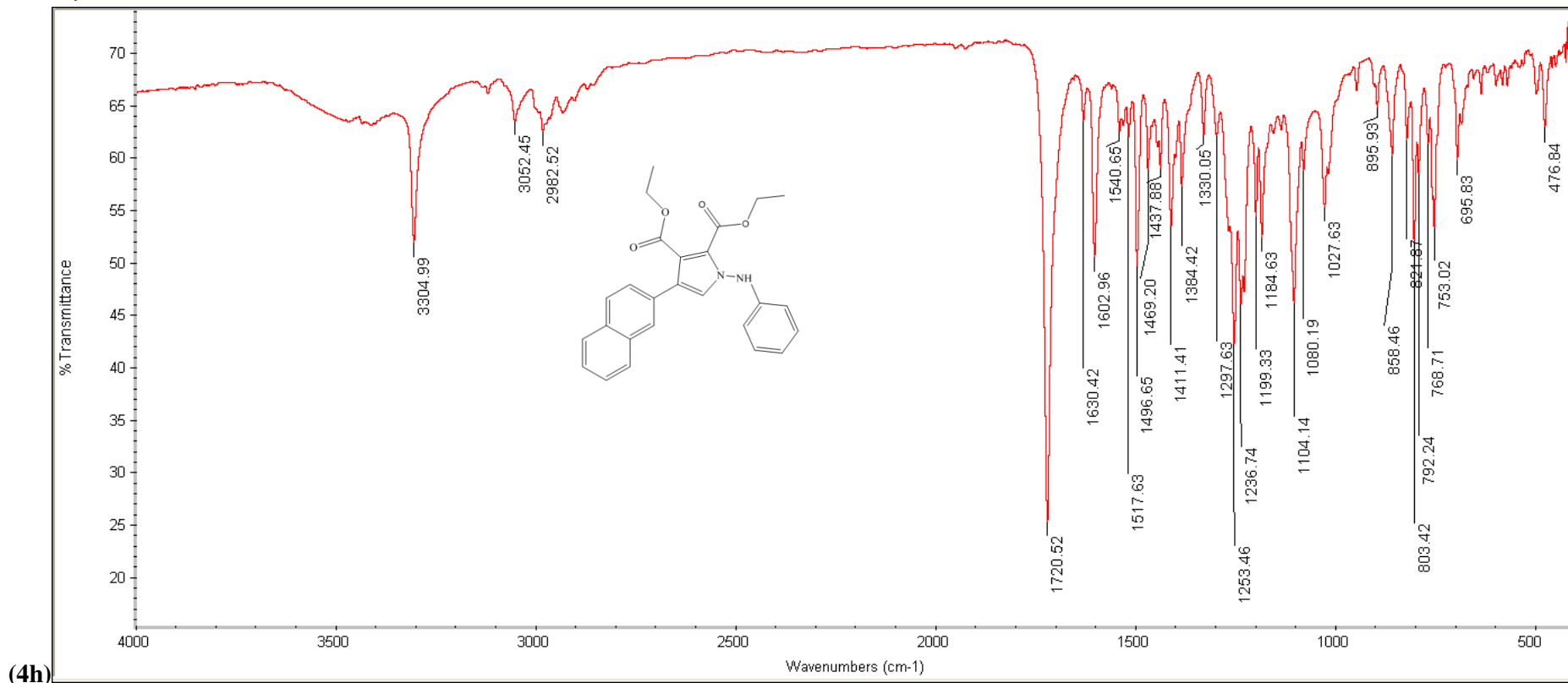


Figure S25. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4i**).

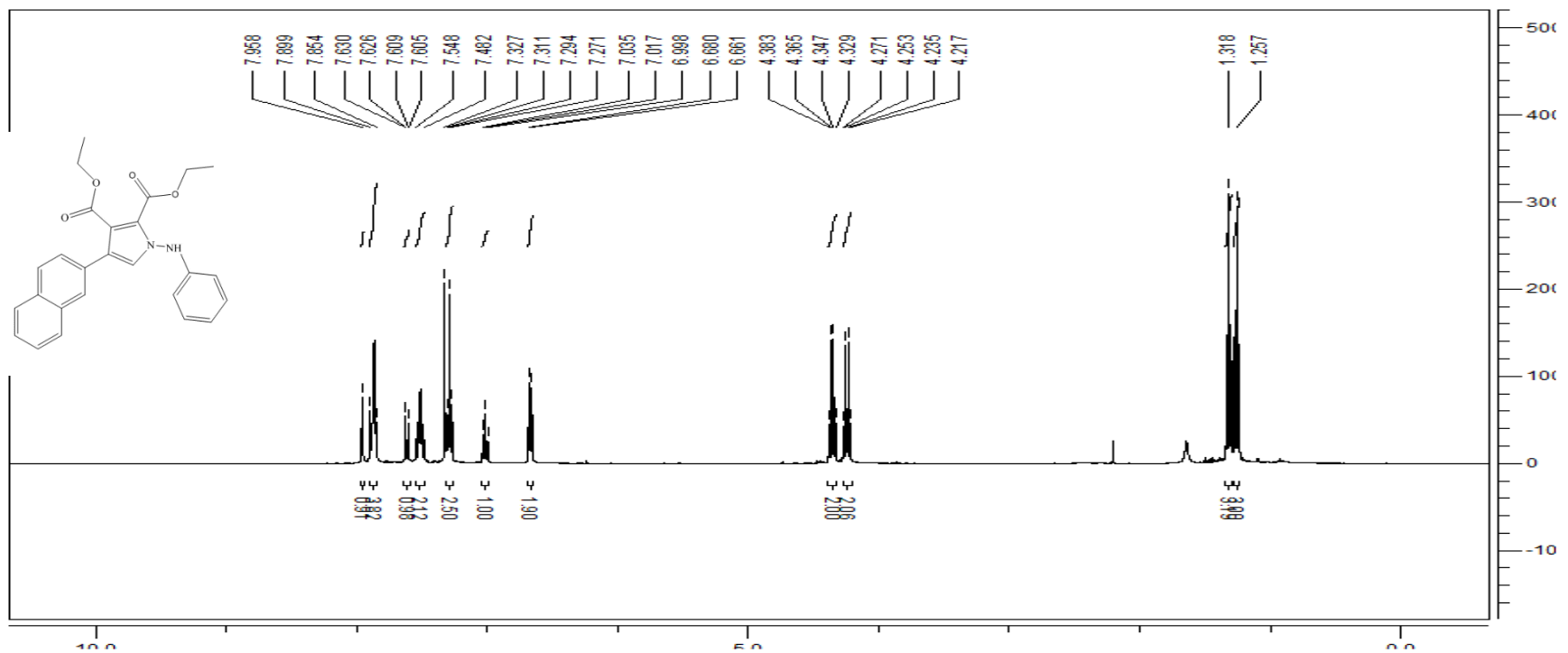


Figure S26 ¹H NMR spectrum (CDCl₃, 400 MHz) of diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4i).

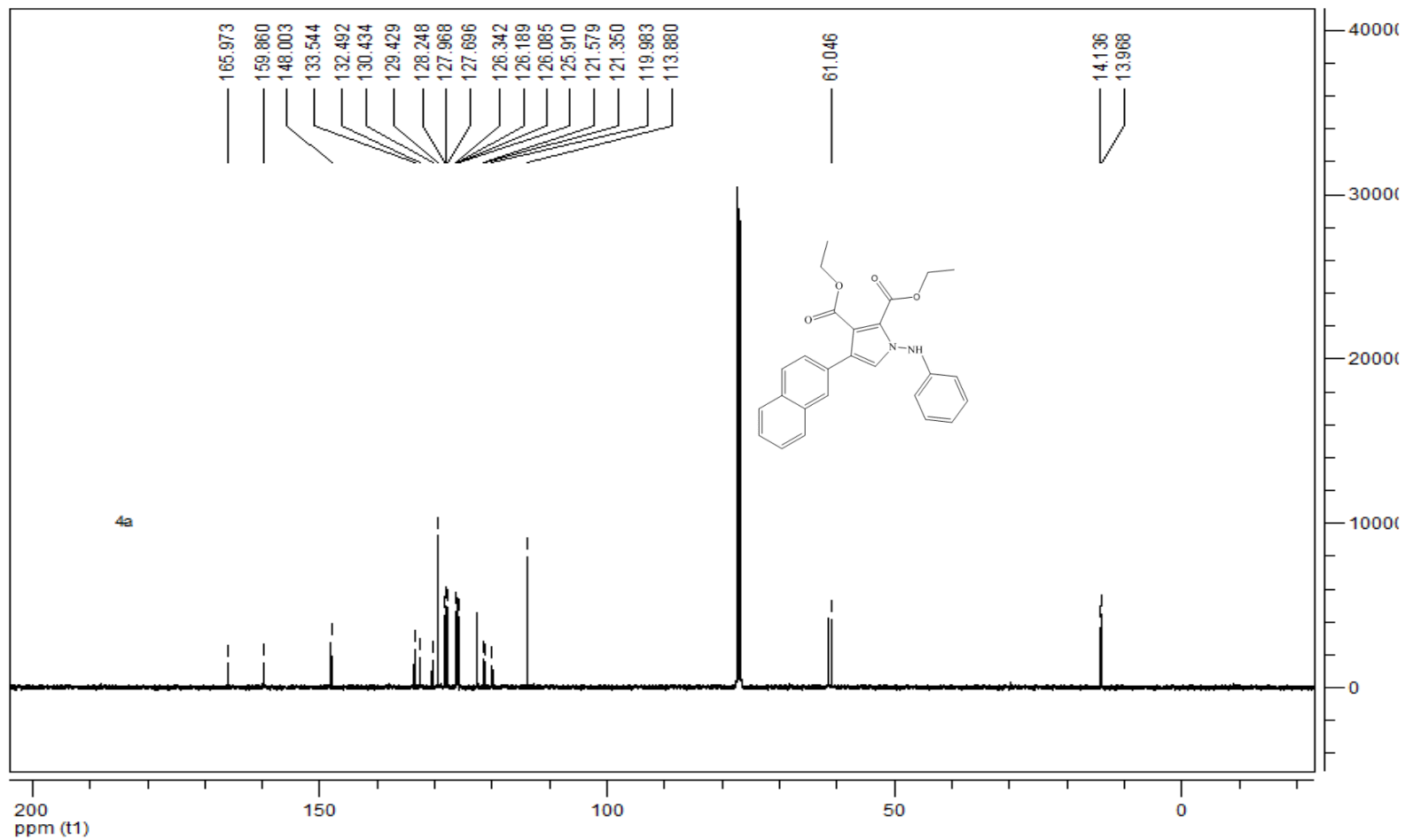


Figure S27. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.

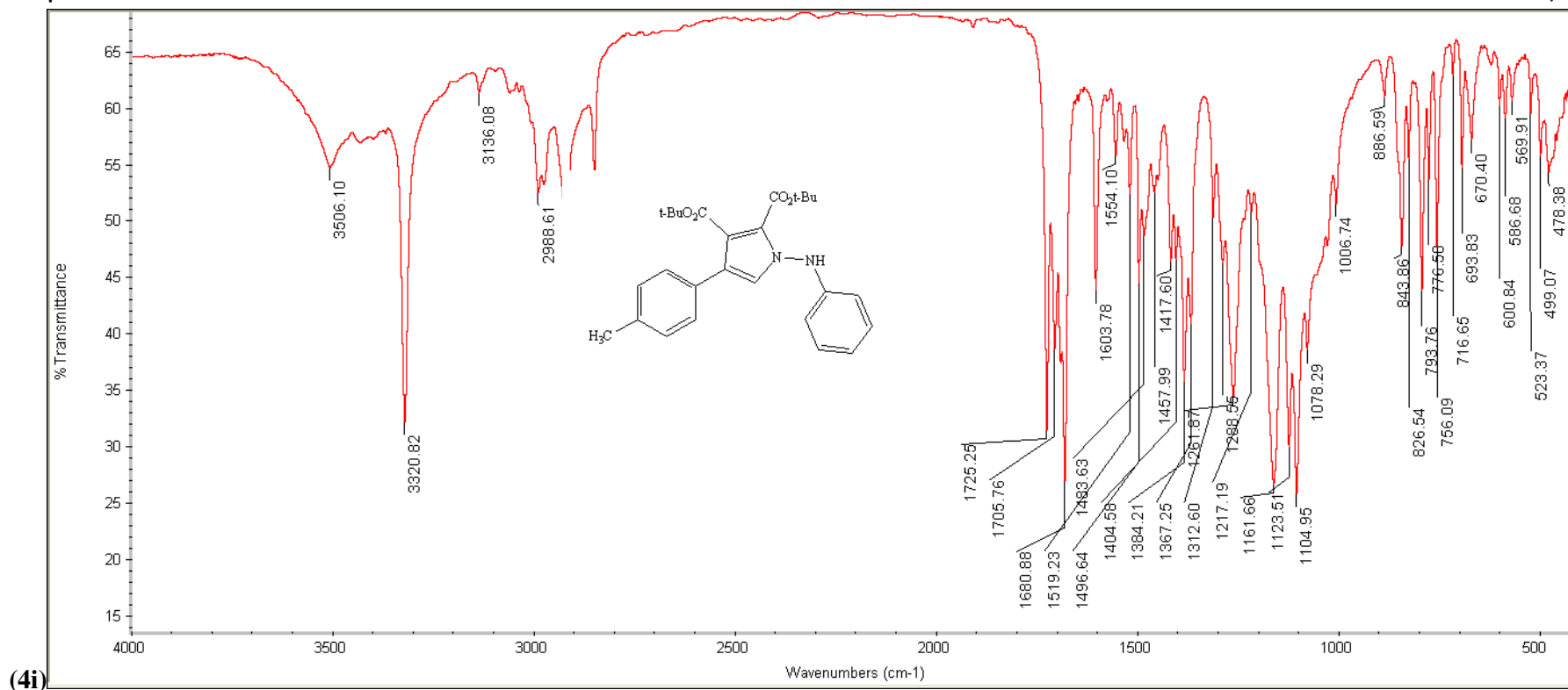


Figure S28. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (4j).

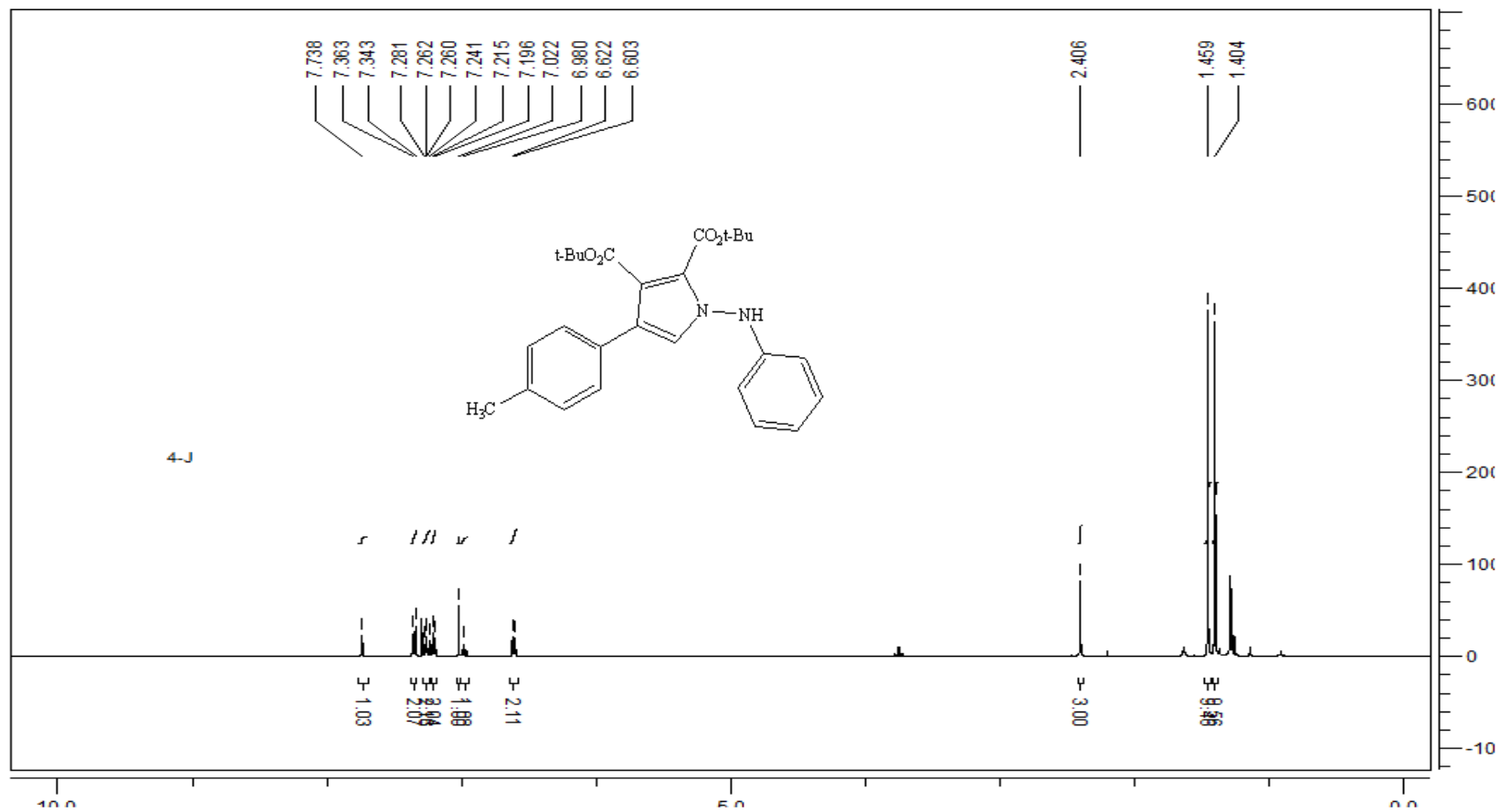


Figure S₂₉ ¹H NMR spectrum (CDCl₃, 400 MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate.

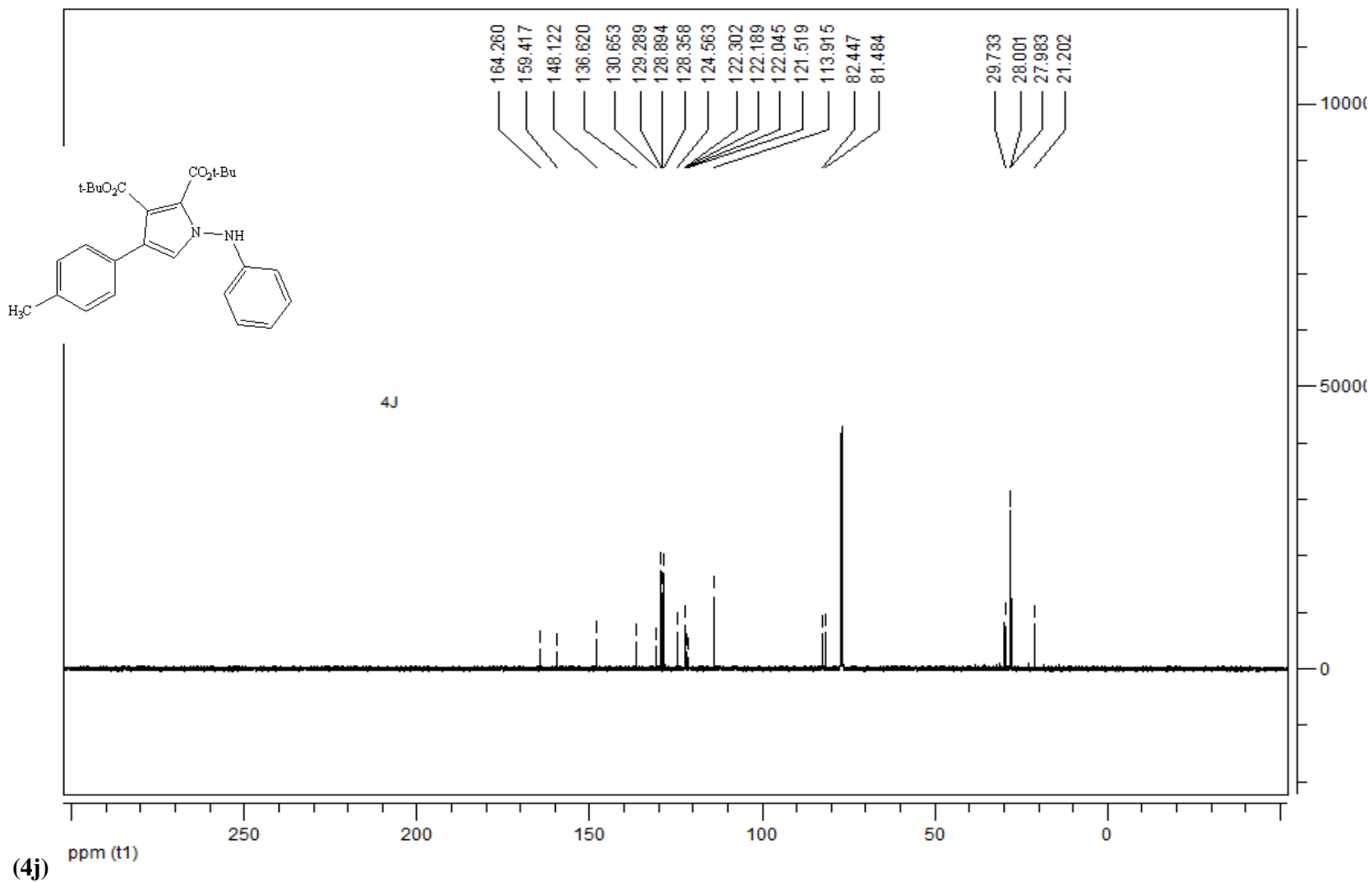


Figure S30. ¹³CNMR spectrum (CDCl₃, 100MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (**4j**).

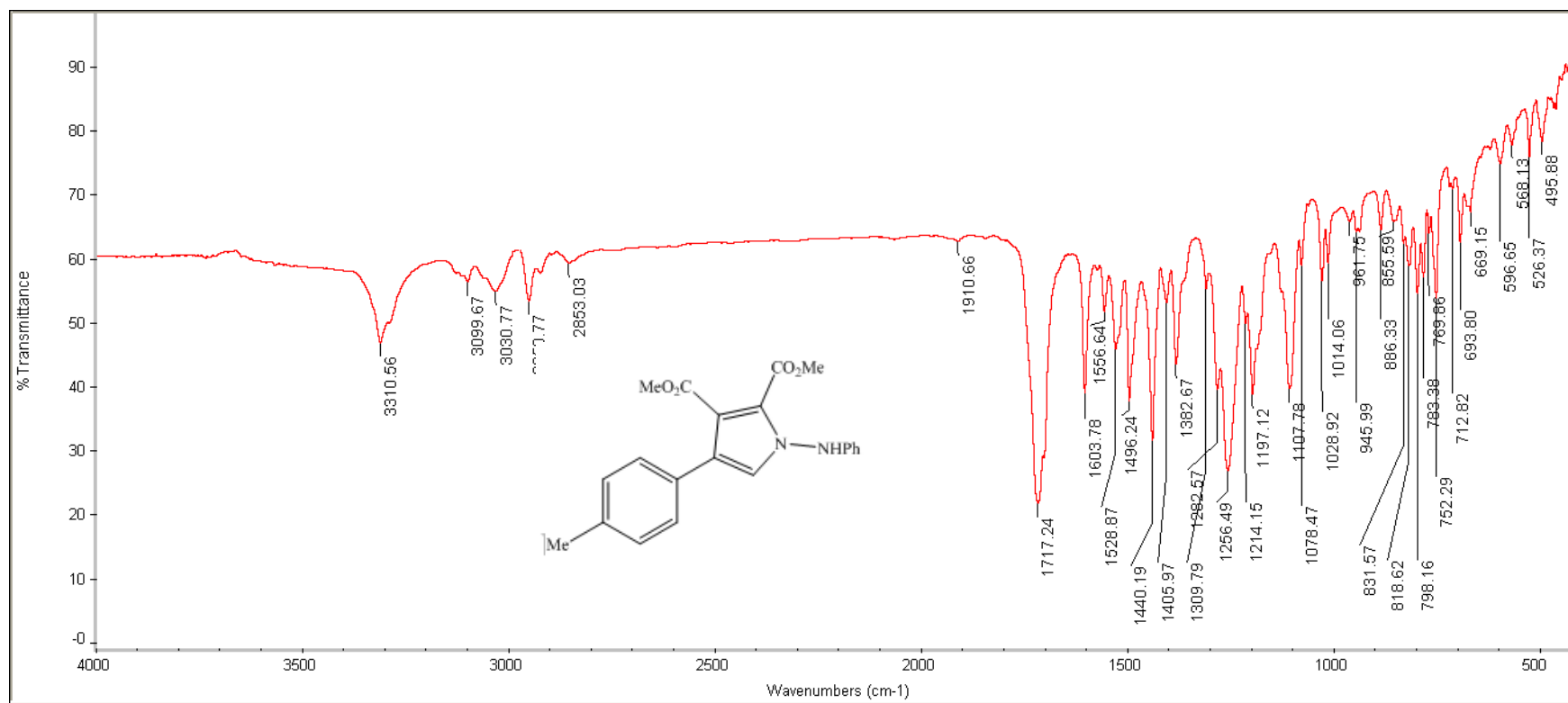


Figure S31. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of dimethyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (**4k**).

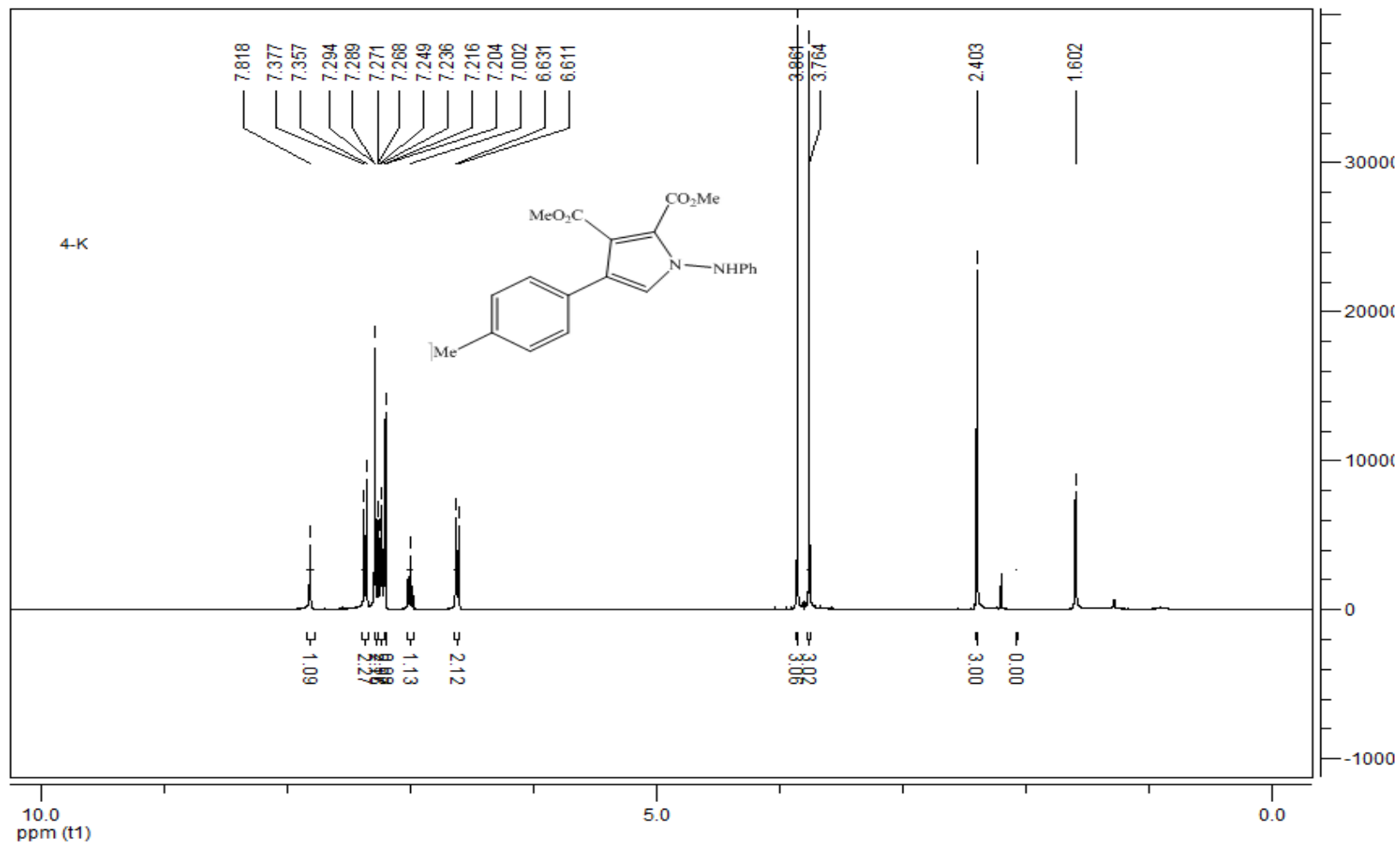
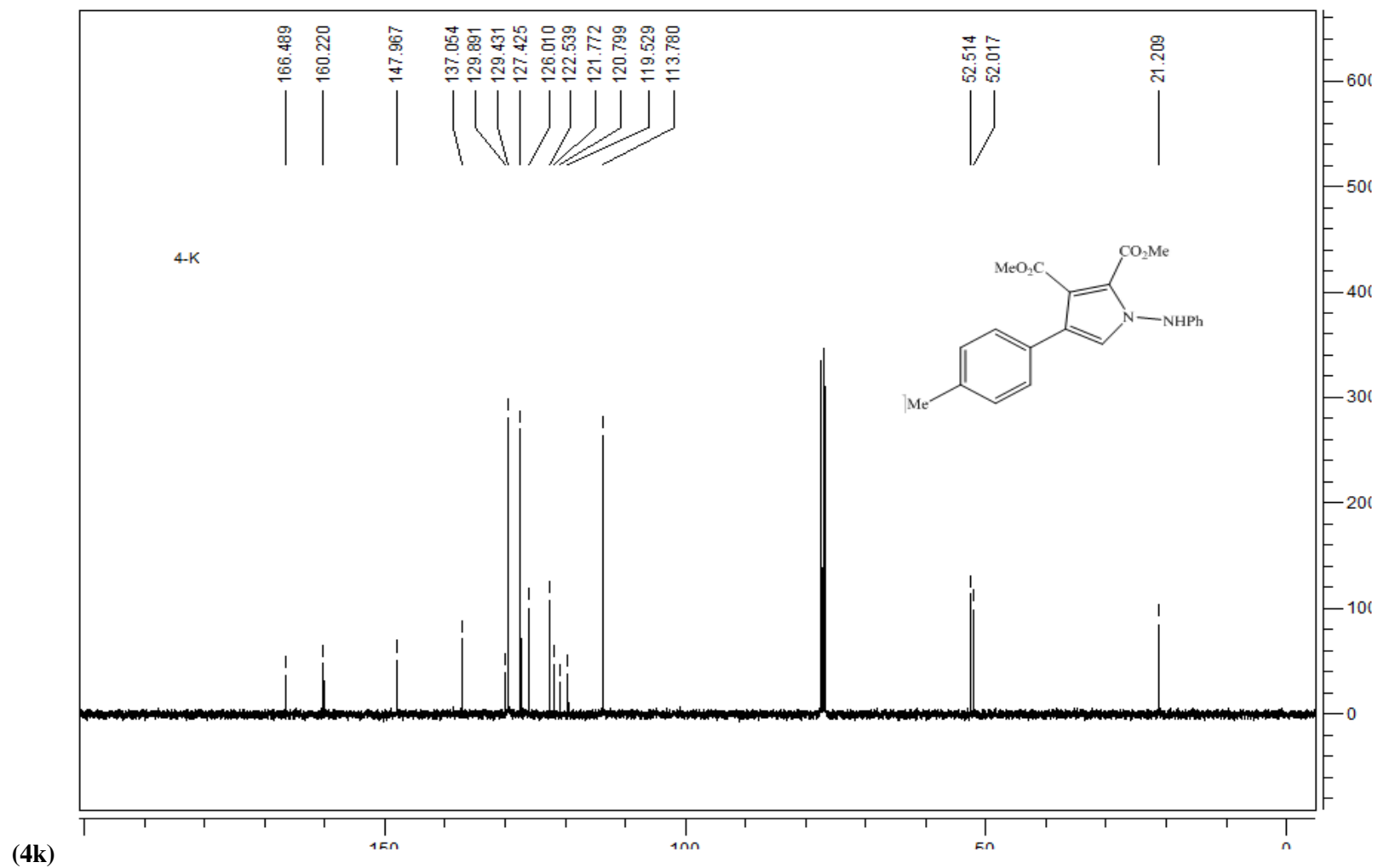


Figure S32 ^1H NMR spectrum (CDCl_3 , 400 MHz) of dimethyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate.



FigureS33. ^{13}C NMR spectrum (CDCl_3 , 100MHz) of dimethyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (**4k**).

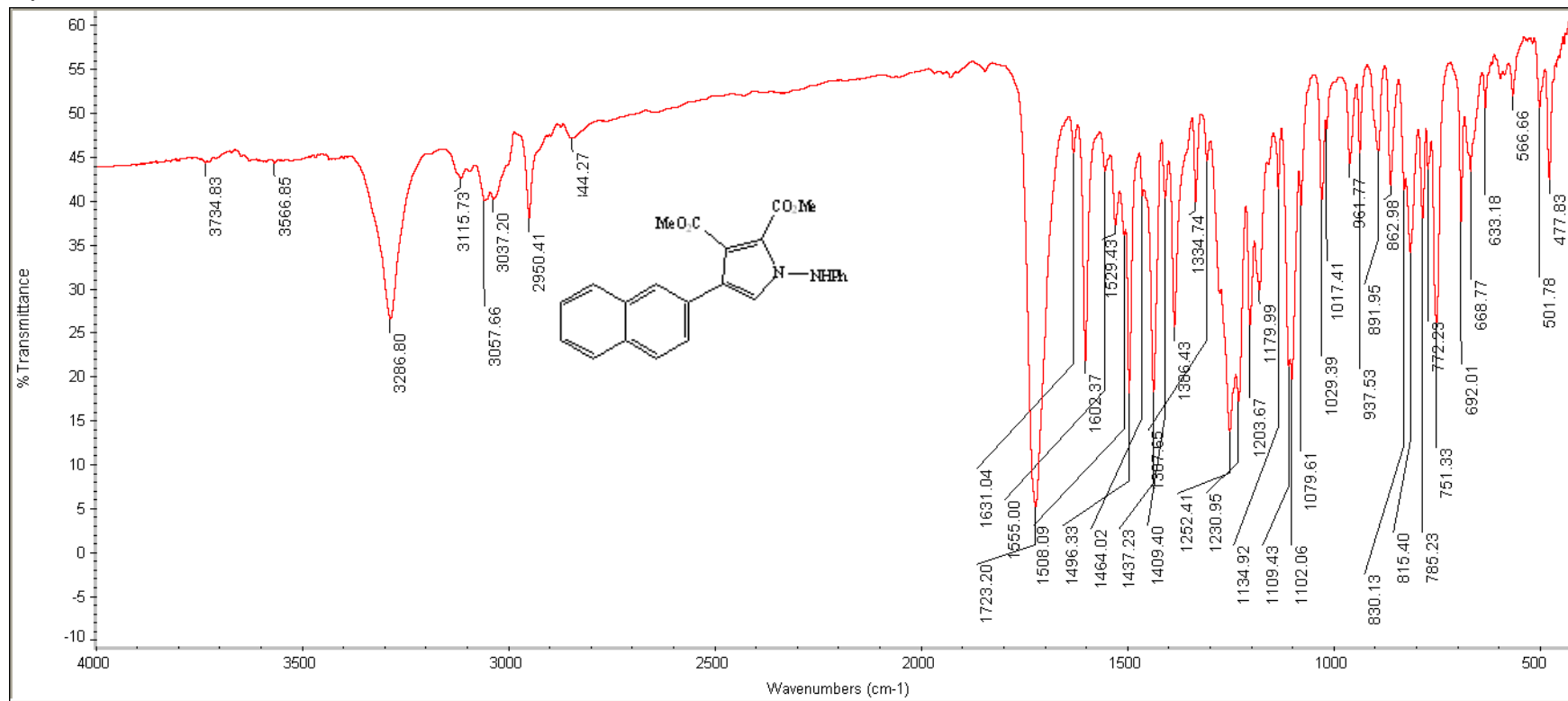


Figure S34. IR spectrum (KBr) ($\bar{\nu}_{\max}$, cm⁻¹) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (**4l**).

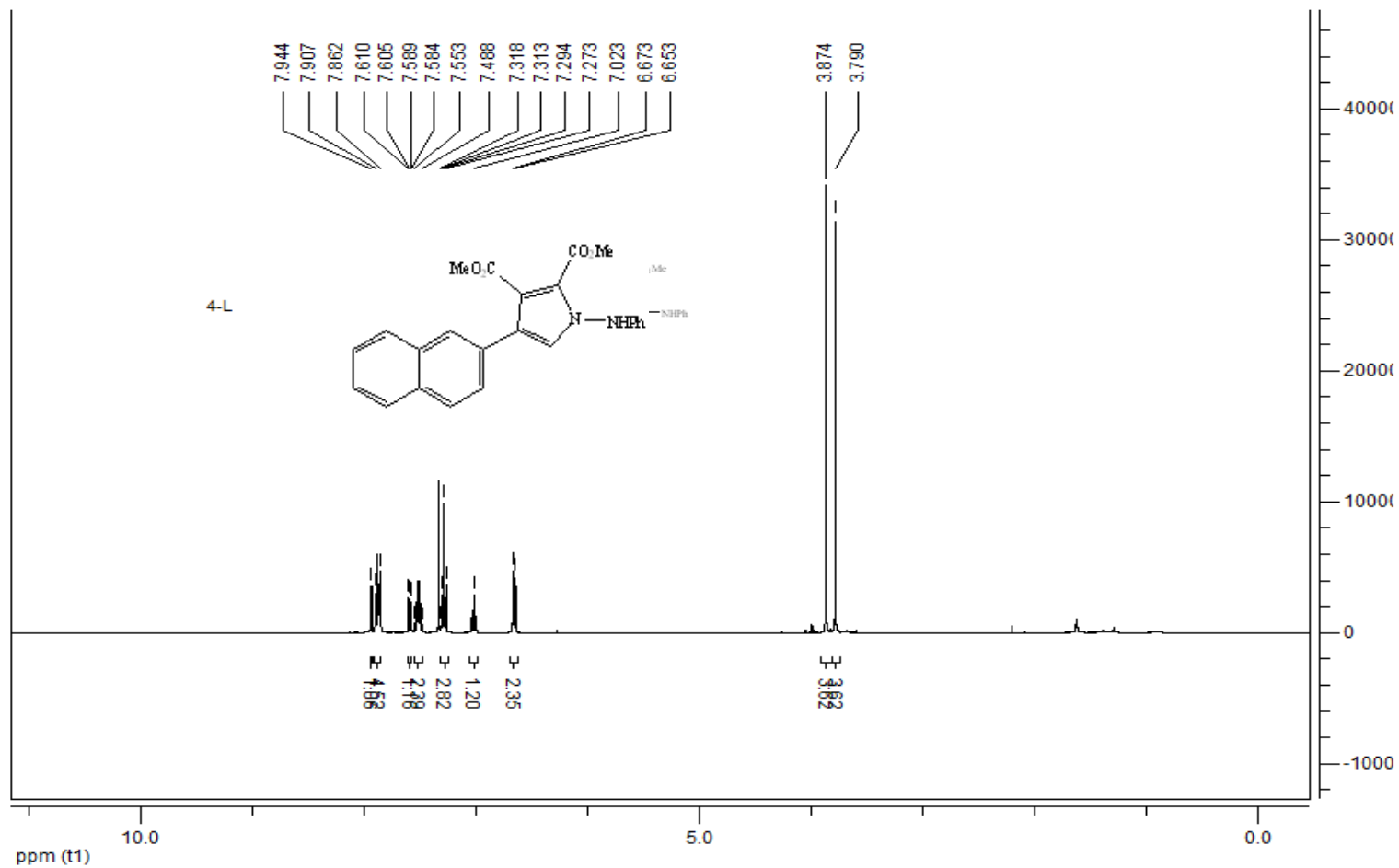


Figure S35 ^1H NMR spectrum (CDCl_3 , 400 MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (**4I**).

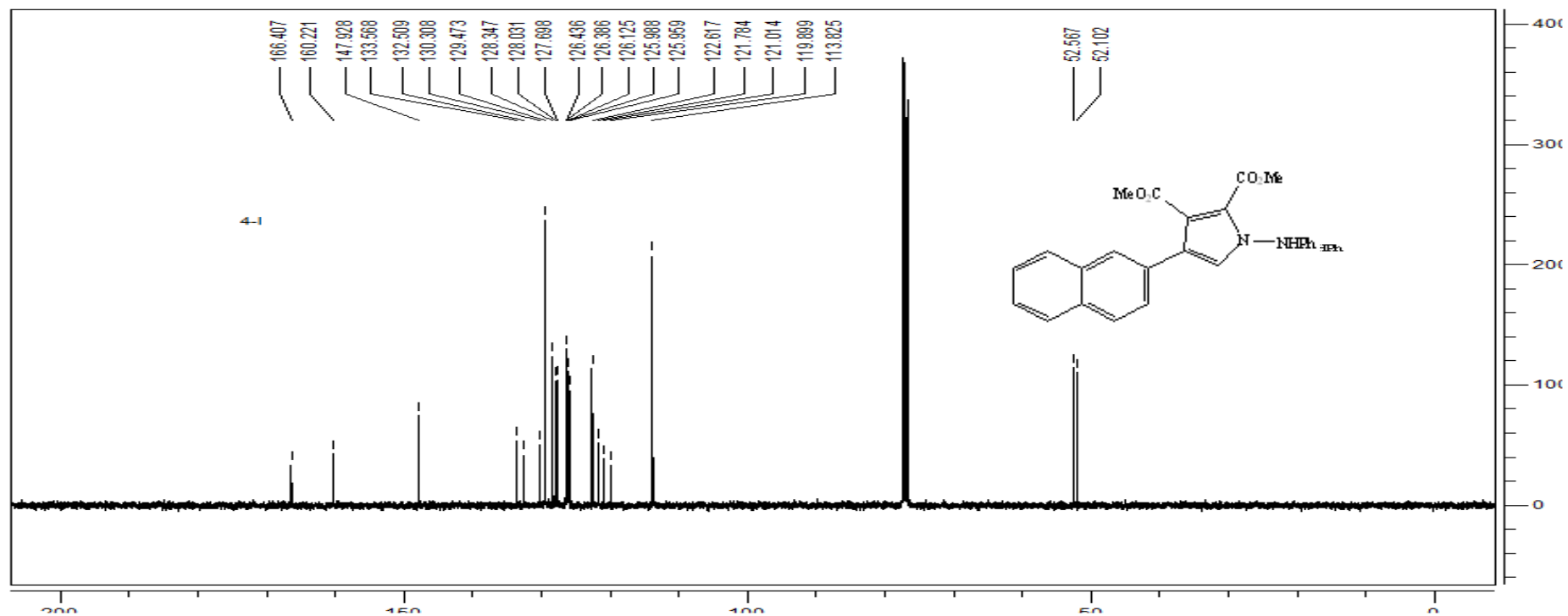


Figure S36. ¹³CNMR spectrum (CDCl₃, 100MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (**4l**).