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. ^{1}H, and ^{13}C NMRspectra were recorded on Bruker DRX-400 Avance spectrometer at 400 and 100 MH_Z,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) ($\bar{\upsilon}$max, cm^{-1}): 3333 (NH), 1731, 1713 (C=O). Calcd. for ($C_{20}H_{17}ClN_2O_4$): C, 62.42; H, 4.45; N, 7.28%. Found: C, 62.33; H, 4.52; N, 7.35%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.85(3 H, s), 3.75(3 H, s), 6.60 (2 H, t $^{3}J_{HH}$ = 8 H_Z), 7.00 (1 H, t, $^{3}J_{HH}$ = 8 H_Z), 7.19 (1 H, S, Pyr-H), 7.26 (2 H, t, $^{3}J_{HH}$ = 8 H_Z), 7.38 (4 H, m), 7.80(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ = 51.6, 52.0 (aliphathic 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) ($\bar{\upsilon}$max, cm^{-1}): 3335 (NH), 1715 (C=O).Calcd. for ($C_{20}H_{17}BrN_2O_4$): C, 55.96; H, 3.99; N, 6.53%. Found: C, 55.85; H, 4.01; N, 6.60%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.75 (3 H, s), 3.84 (3 H, s), 6.60 (2 H, d, $^{3}J_{HH}$ = 8 H_Z), 7.00 (1 H, t $^{3}J_{HH}$ = 8 H_Z), 7.19 (1 H, S, Pyr-H), 7.26 (1 H, t, $^{3}J_{HH}$ = 8 H_Z), 7.33 (2 H, d, $^{3}J_{HH}$ = 8 H_Z), 7.52(2 H, d, t $^{3}J_{HH}$ = 8 H_Z), 7.79 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ = 52.1, 52.5 (aliphathic 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) ($\bar{\upsilon}$max, cm^{-1}): 3321 (NH), 1717 (C=O). Calcd. for ($C_{20}H_{17}N_3O_6$): C, 60.76; H, 4.33; N, 10.63%. Found: C, 60.83; H, 4.21; N, 10.52% ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.77 (3 H, s), 3.87 (3 H, s), 6.61 (2 H, d, $^{3}J_{HH}$ = 8 H_Z), 7.01 (1 H, t $^{3}J_{HH}$ = 8 H_Z), 7.25 (1 H, S, Pyr-H), 7.28 (1 H, t, $^{3}J_{HH}$ = 8 H_Z), 7.61 (2 H, d, $^{3}J_{HH}$ = 8 H_Z), 7.81 (1 H, s, NH PhNH), 8.26 (2 H, d, t $^{3}J_{HH}$ = 8 H_Z), ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ = 52.2, 52.6 (aliphathic 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) ($\bar{\upsilon}$max, cm-1): 3263 (NH), 1716 (C=O).Calcd. for ($C_{20}H_{18}N_2O_4$): C, 68.56; H, 5.18; N, 8.00%.Found: C, 68.64; H, 5.06; N, 8.19%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.76(3 H, s), 3.85(3 H, s), 6.61 (2 H, t $^{3}J_{HH}$ = 8 H_Z), 6.99 (1 H, t $^{3}J_{HH}$ = 8 H_Z), 7.28 (1 H, S, Pyr-H), 7.31 (1 H, t $^{3}J_{HH}$ = 8 H_Z), 7.41 (2 H, t, $^{3}J_{HH}$ = 8 H_Z), 7.47(2 H, d, t $^{3}J_{HH}$ = 8 H_Z), 7.47(2 H, d $^{3}J_{HH}$ = 8 H_Z), 7.80(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ =21.08, 29.7, 52.0, 52.5 (aliphathic 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) ($\bar{\upsilon}$max, cm^{-1}): 3380 (NH), 1720, 1699 (C=O). Calcd. for ($C_{26}H_{29}BrN_2O_4$): C, 60.82; H, 5.69; N, 5.46%. Found: C, 60.71; H, 5.81; N, 5.58%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (9 H, s), 1.45 (9 H, s), 6.67 (2 H, d, $^3J_{HH}$ = 8 H_Z), 6.98 (1 H, t $^3J_{HH}$ = 8 H_Z), 7.25 (2H, t, $^3J_{HH}$ = 8 H_Z), 7.28 (1 H, S, Pyr-H), 7.32 (2 H, d, $^3J_{HH}$ = 8 H_Z), 7.51 (2 H, t, $^3J_{HH}$ = 8 H_Z), 7.70 (1 H, s, NH PhNH, t $^3J_{HH}$ = 8 H_Z). ^{13}C NMR ($CDCl_3$, 100 MH_Z): 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) ($\bar{\upsilon}$max, cm^{-1}): 3280 (NH), 1720, 1699 (C=O). Calcd. for ($C_{26}H_{29}ClN_2O_4$): C, 60.82; H, 5.69; N, 5.46%. Found: C, 60.94; H, 5.53; N, 5.32%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (9 H, s,), 1.45 (9 H, s), 6.59 (2 H, d, $^3J_{HH}$ = 8 H_Z), 6.59 (2 H, d, $^3J_{HH}$ = 8 H_Z), 6.98 (1 H, t, $^3J_{HH}$ = 8 H_Z), 7.25 (1 H, d, $^3J_{HH}$ = 8 H_Z), 7.28 (1 H, s, Pyr-H), 7.36 (3 H, d, t $^3J_{HH}$ = 8 H_Z), 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) ($\bar{\upsilon}$max, cm^{-1}): 3328 (NH), 1709 (C=O). Calcd. for ($C_{22}H_{21}BrN_2O_4$): C, 57.78; H, 4.63; N, 6.13%. Found: C, 57.62; H, 4.77; N, 6.26%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.21 (3 H, t, $^3J_{HH}$ = 8 H_Z), 1.31 (3 H, t, $^3J_{HH}$ = 8 H_Z), 4.22 (2 H, q, $^3J_{HH}$ = 8 H_Z), 4.32 (2 H, q, $^3J_{HH}$ = 8 H_Z), 6.62 (2 H, d, $^3J_{HH}$ = 8 H_Z, arom), 7.00 (1 H, t, $^3J_{HH}$ = 8 H_Z, arom), 7.18 (1 H, S, Pyr-H)), 7.27(1 H, t, $^3J_{HH}$ = 8 H_Z, arom), 7.39(4 H, m, arom), 7.81(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): 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) ($\bar{\upsilon}$max, cm^{-1}): 3328 (NH), 1709 (C=O). Calcd. for ($C_{22}H_{21}ClN_2O_4$): C, 57.78; H, 4.63; N, 6.13%. Found: C, 57.67; H, 4.76; N, 6.27%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (3 H, t, $^3J_{HH}$ = 8 H_Z), 1.31 (3 H, t, $^3J_{HH}$ = 8 H_Z), 4.22 (2 H, q $^3J_{HH}$ = 8 H_Z), 4.32 (2 H, q $^3J_{HH}$ = 8 H_Z), 6.62 (2 H, d, $^3J_{HH}$ = 8 H_Z, arom), 7.00 (1 H, t, $^3J_{HH}$ = 8 H_Z, arom), 7.18 (1 H, S, Pyr-H)), 7.27(1 H, t, $^3J_{HH}$ = 8 H_Z, arom), 7.39(4 H, m, arom), 7.81(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): 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) ($\bar{\upsilon}$max, cm^{-1}): 3304 (NH), 1720 (C=O). Calcd. for ($C_{26}H_{24}N_2O_4$): C, 72.88; H, 5.65; N, 6.54%.Found: C, 73.02; H, 5.51; N, 6.43% ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (3 H, t, $^3J_{HH}$ = 8 H_Z), 1.31 (3 H, t, $^3J_{HH}$ = 8 H_Z), 4.24 (2 H, q $^3J_{HH}$ = 8 H_Z), 4.35 (2 H, q $^3J_{HH}$ = 8 H_Z), 6.67 (2 H, d, $^3J_{HH}$ = 8 H_Z, arom), 7.01 (1 H, t, $^3J_{HH}$ = 8 H_Z, arom), 7.29 (2 H, t, $^3J_{HH}$ = 8 H_Z, 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 MH_Z): 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) ($\bar{\upsilon}$max, cm^{-1}): 3320 (NH), 1725, 1705 (C=O). Calcd. for ($C_{27}H_{32}N_2O_4$): C, 72.30; H, 7.19; N, 6.25;%. Found: C, 72.15; H, 7.33; N, 6.38;%. ^{1}H 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, $^3J_{HH}$ = 8 H_Z), 6.98 (1 H, t $^3J_{HH}$ = 8 $_{HZ}$), 7.02 (1 H, S, Pyr-H), 7.20 (2H, d, $^3J_{HH}$ = 8 H_Z), 7.26(2H, m), 7.35 (2 H, d, $^3J_{HH}$ = 8 H_Z), 7.73 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): 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) (ῡmax, cm^{-1}): 3310(NH), 1717 (C=O). Calcd. for ($C_{21}H_{20}N_2O_4$): C, 69.22; H, 5.53; N, 7.69%. Found: C, 69.37; H, 5.40; N, 7.56%. ^{1}H 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, $^3J_{HH}$ = 8 H_Z), 7.00 (1 H, t $^3J_{HH}$ = 8 H_Z), 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 $^3J_{HH}$ = 8 H_Z), 7.81 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ = 21.2, 52.0, 52.5 (aliphathic 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) (ῡmax, cm^{-1}): 3286 (NH), 1723 (C=O). Calcd. for ($C_{24}H_{20}N_2O_4$): C, 71.99; H, 5.03; N, 7.00%. Found: C, 71.85; H, 5.17; N, 7.13%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.79 (3 H, s), 3.87 (3 H, s), 3.88, 6.66 (2 H, d, $^3J_{HH}$ = 8 H_Z), 7.00 (1 H, t $^3J_{HH}$ = 8 H_Z), 7.29 (3 H, t $^3J_{HH}$ = 8 H_Z), 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 MH_Z): δ = 52.1, 52.5 (aliphathic 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.

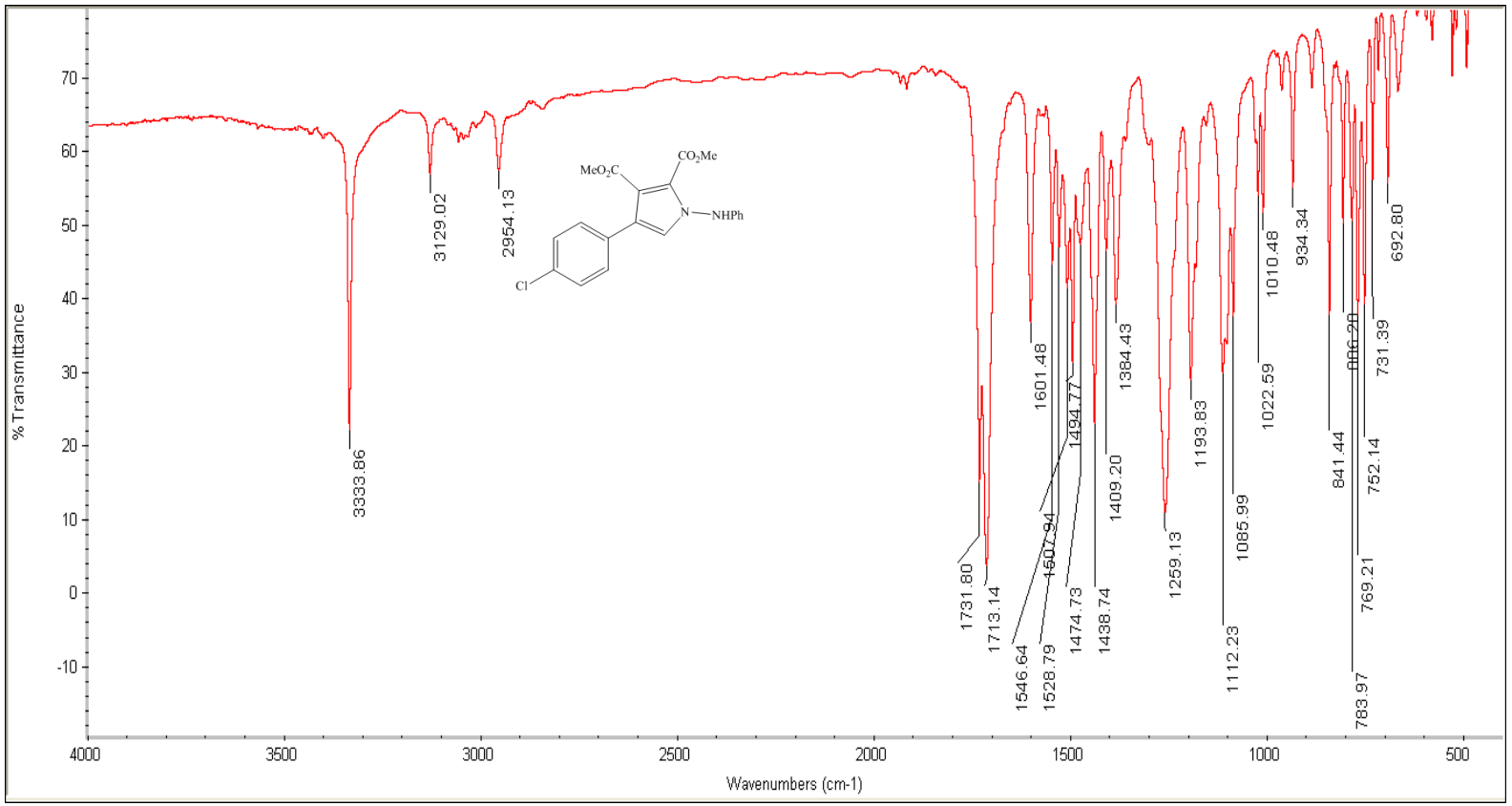


Figure S1. IR specctrum (KBr) (ῡmax, cm^{-1}) of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4a).**

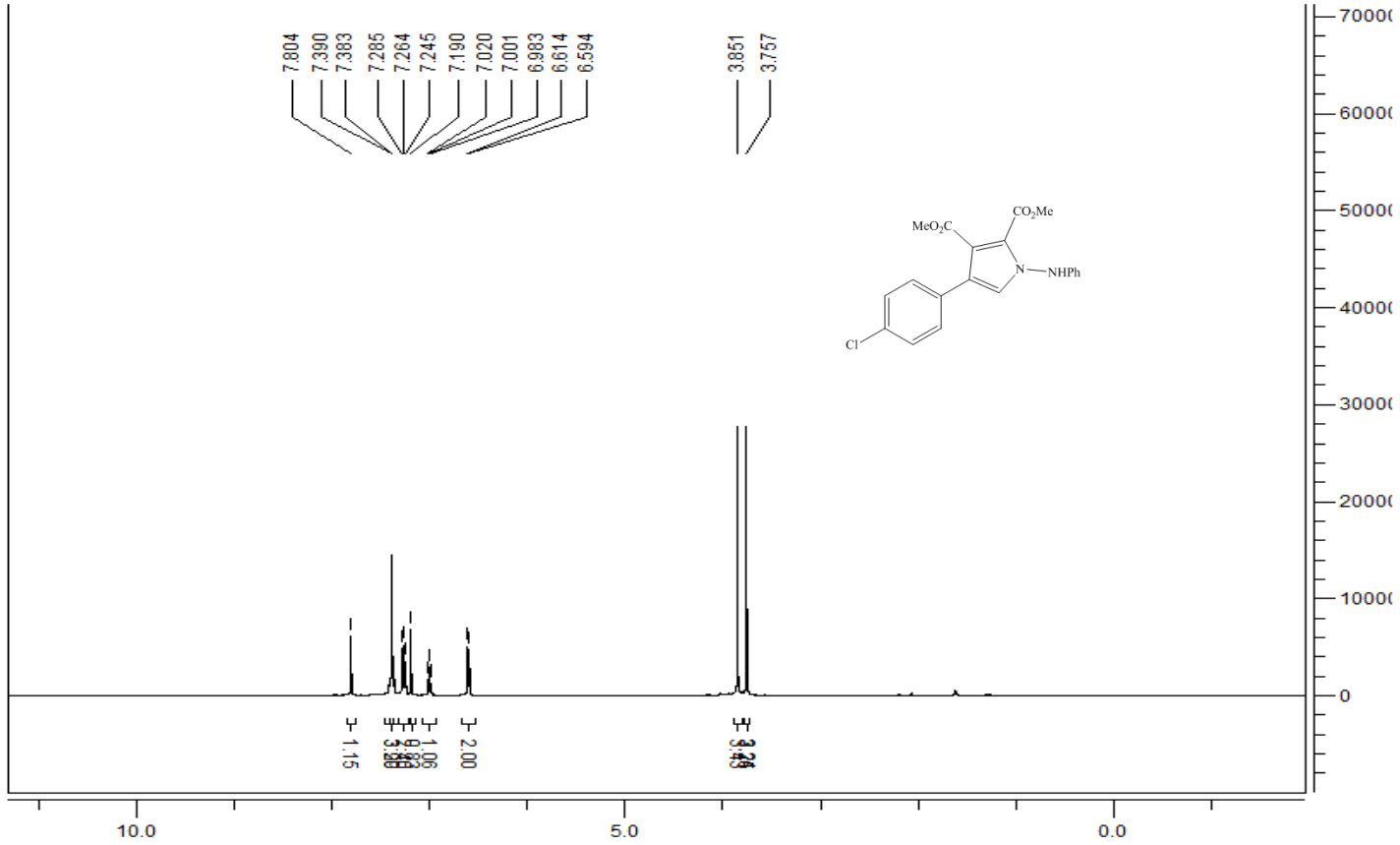


Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4a).**

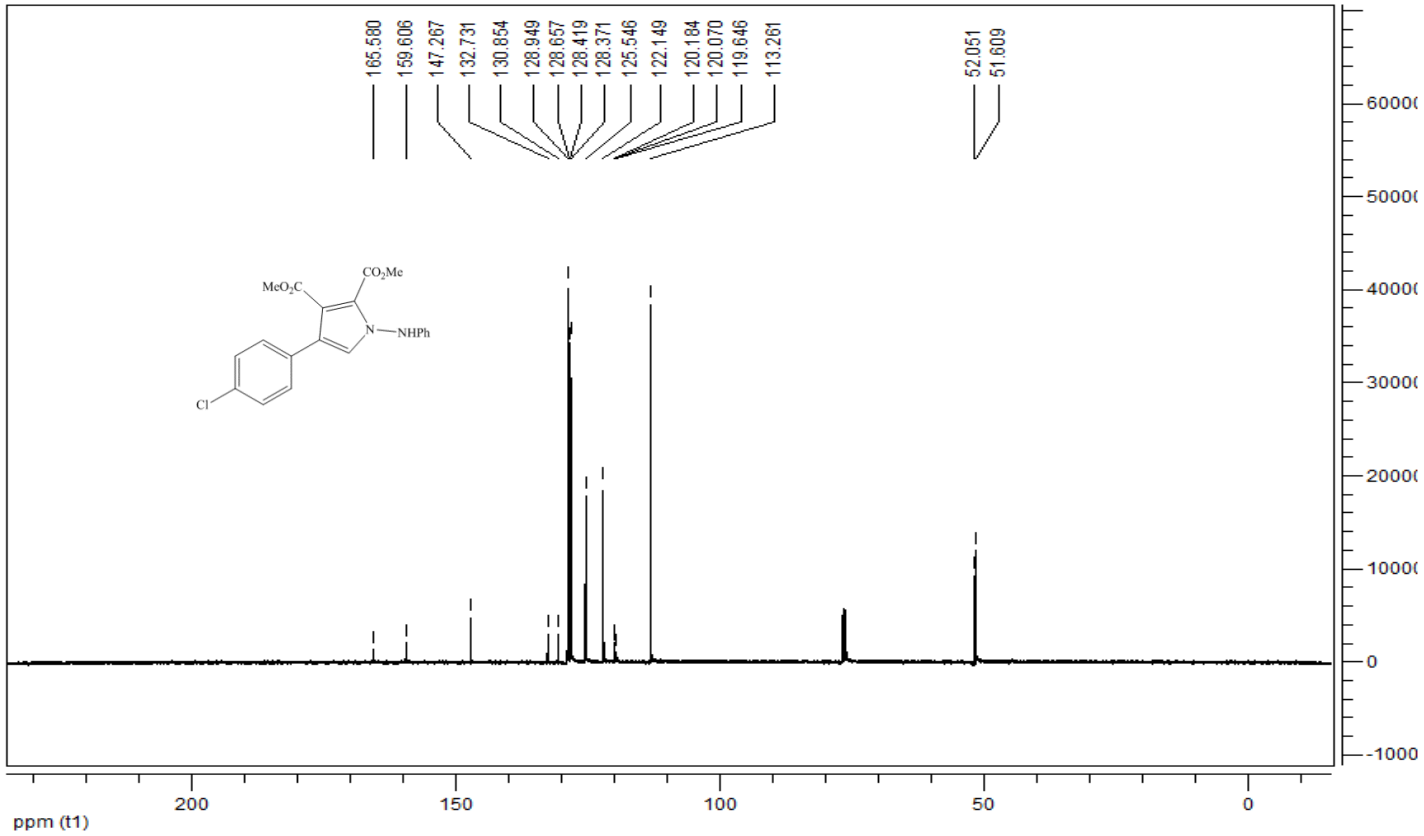
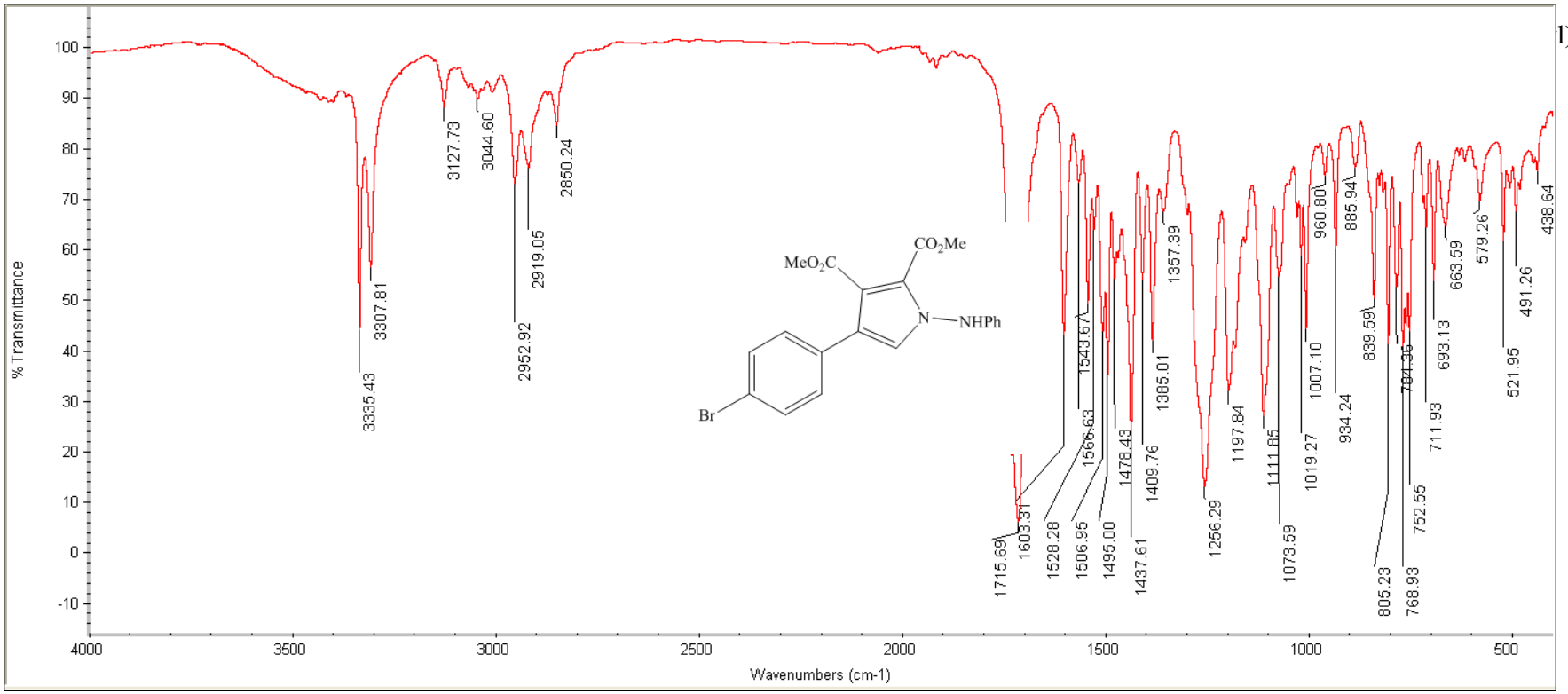


Figure S3. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4a).**

l)ethanone(**4b)**



Figures S4. IR specctrum (KBr) (ῡmax, cm^{-1}) of dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate**(4b).**

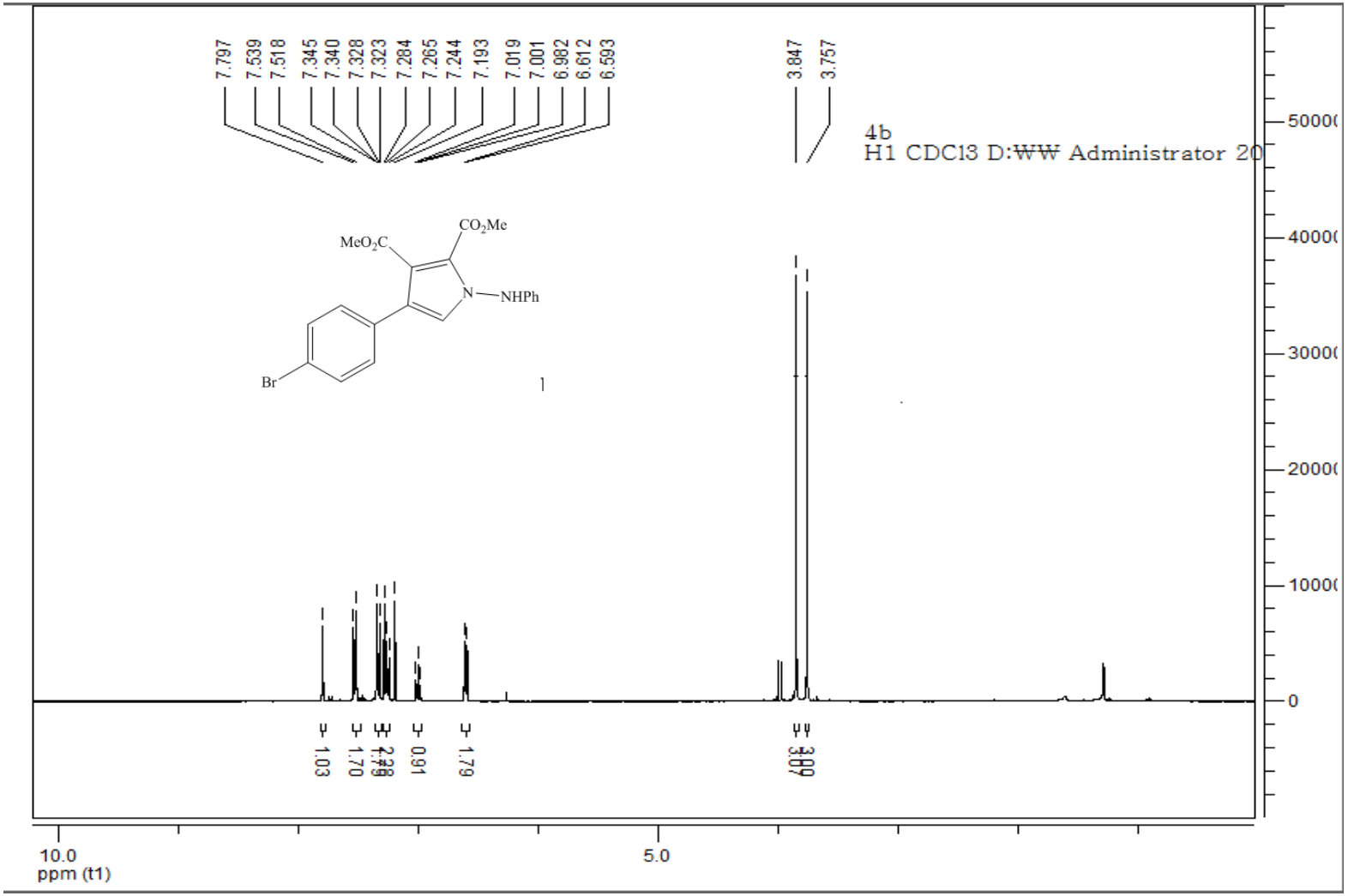


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4b).**

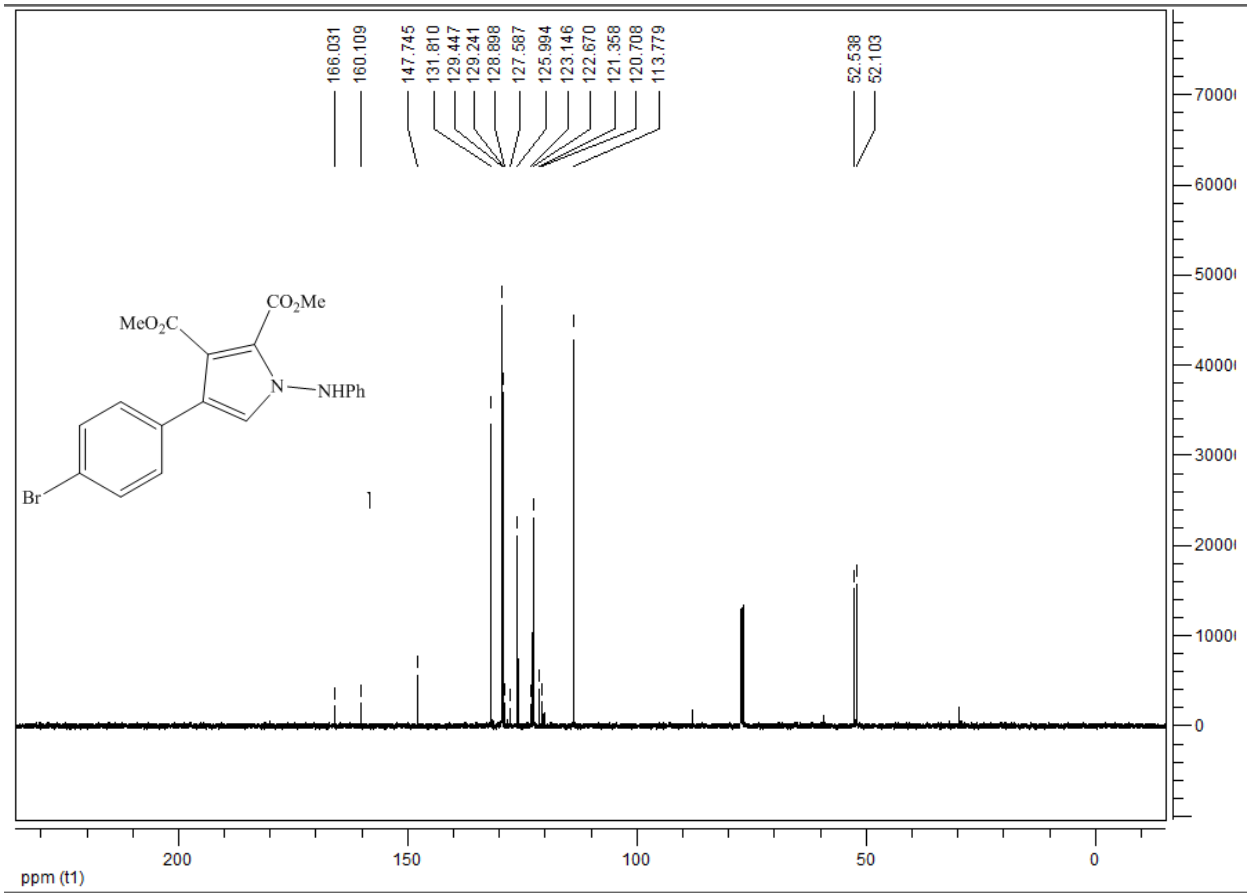


Figure S6. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4b).**

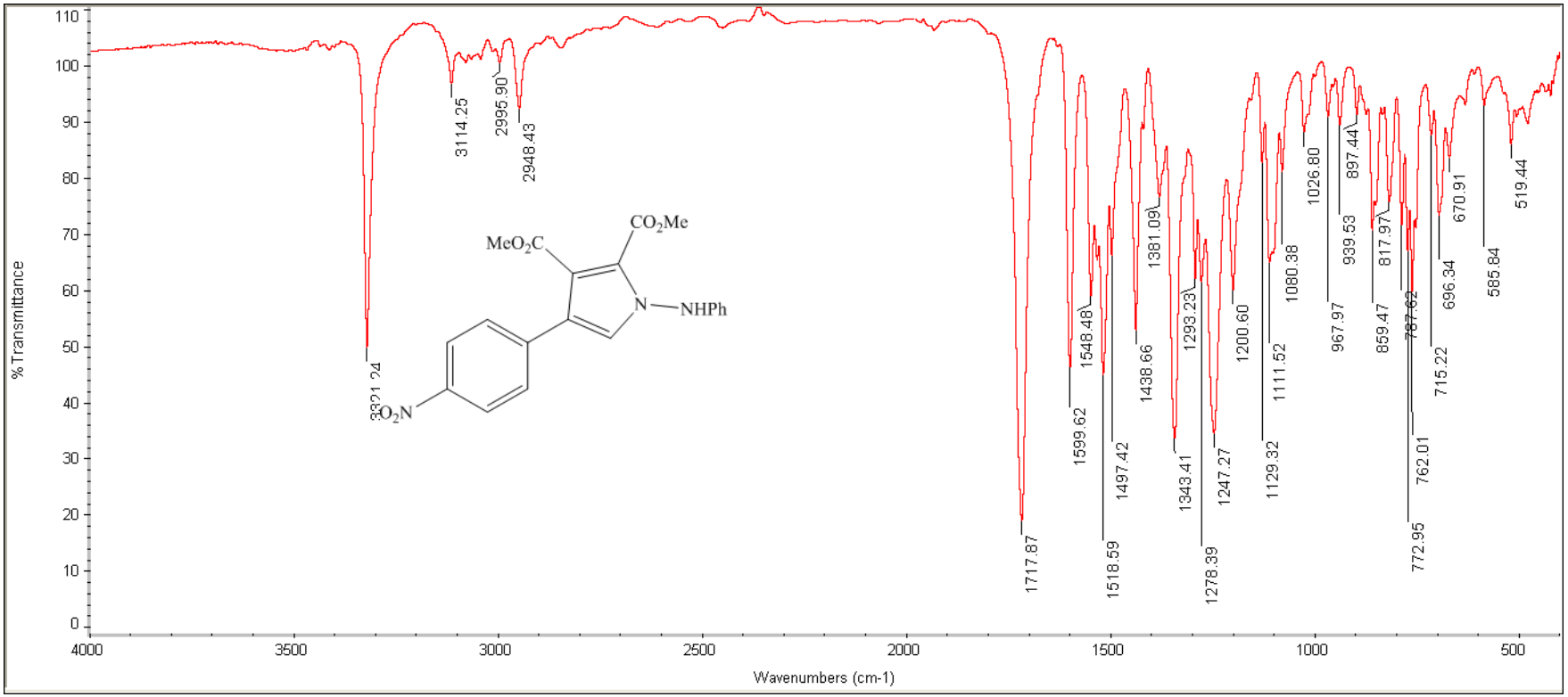


Figure S7. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate **(4c).**

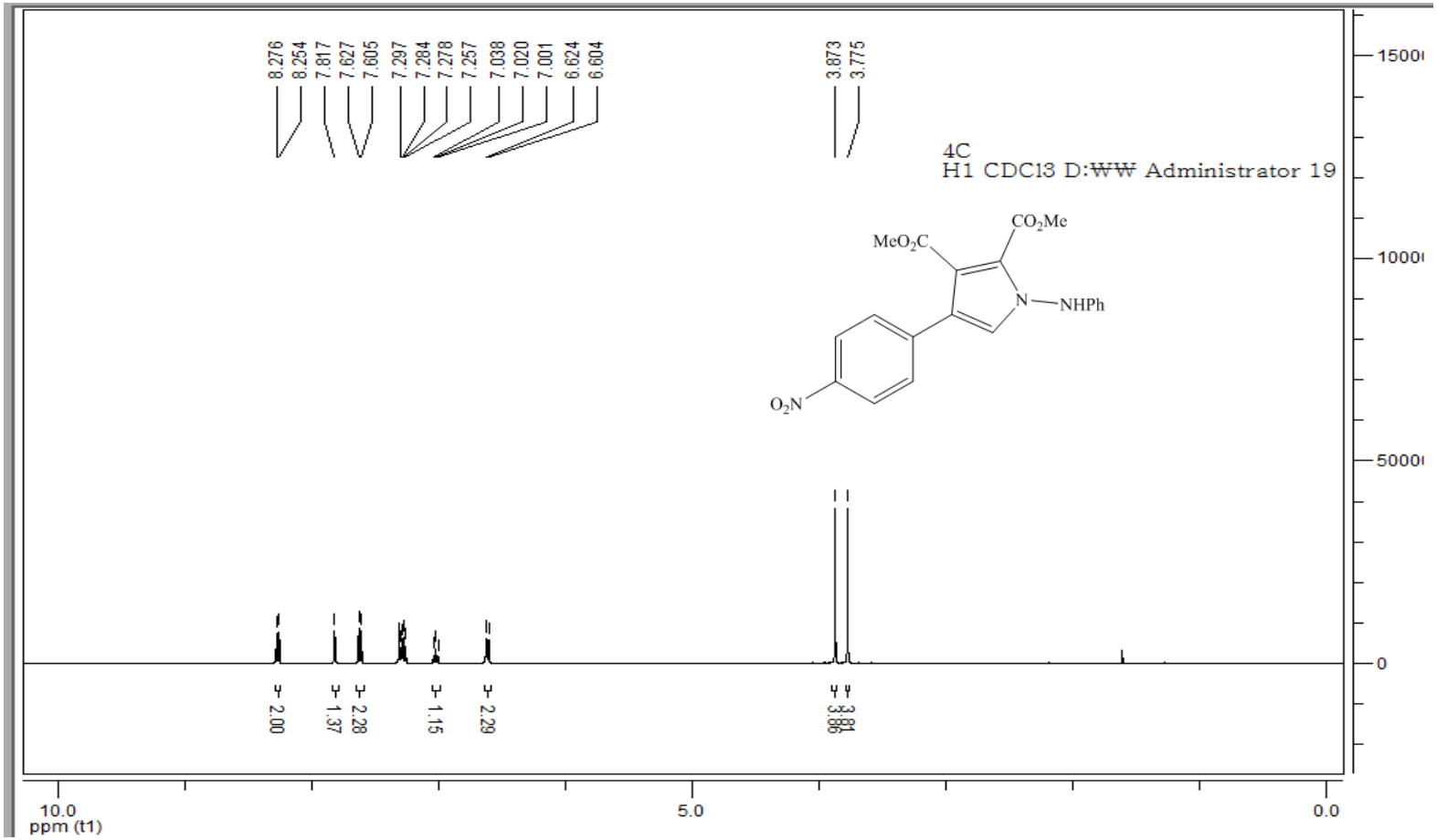


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate **(4c).**

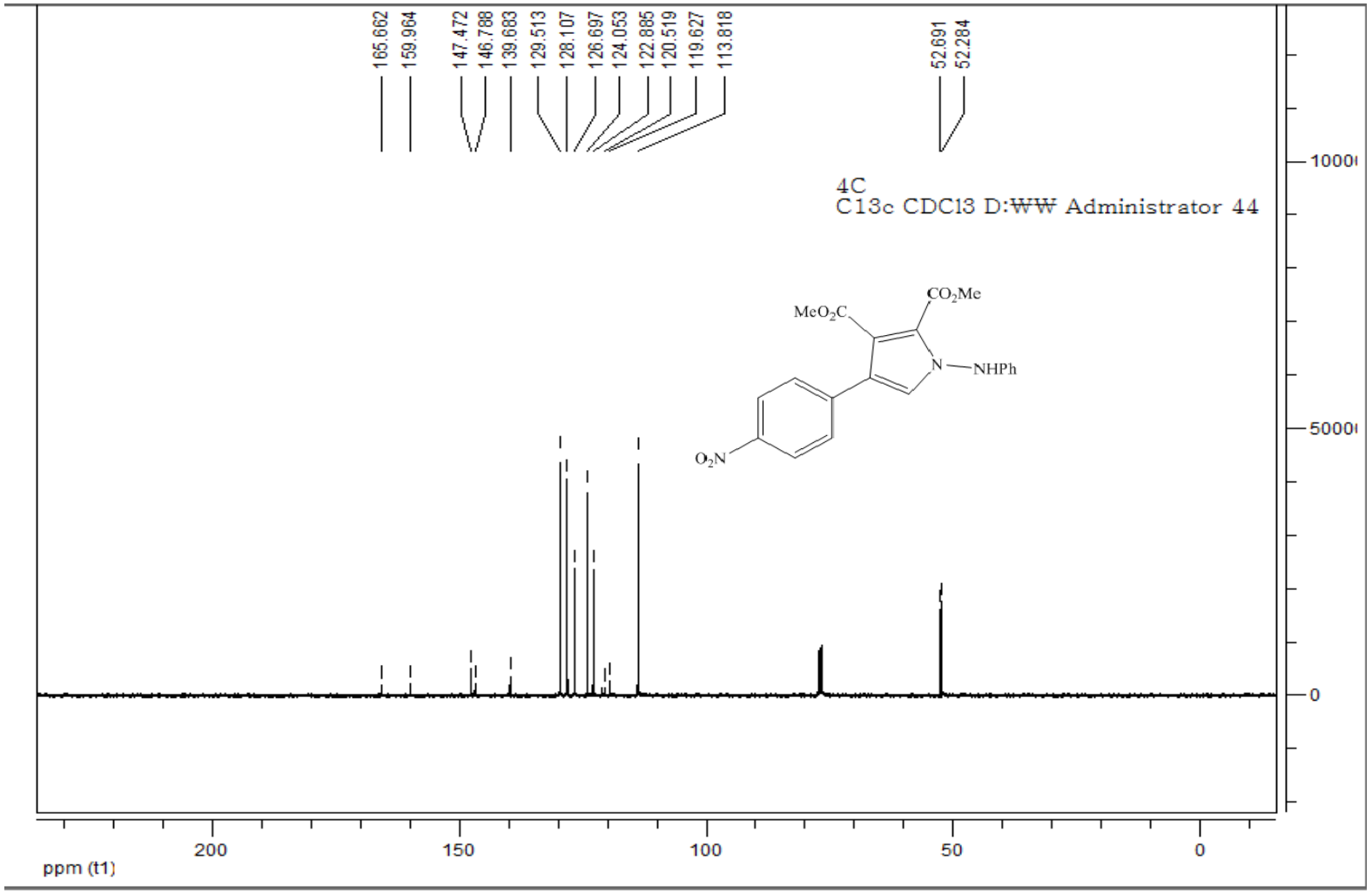


Figure S9. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of dimethyl 1-methyl-5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate **(4c).**

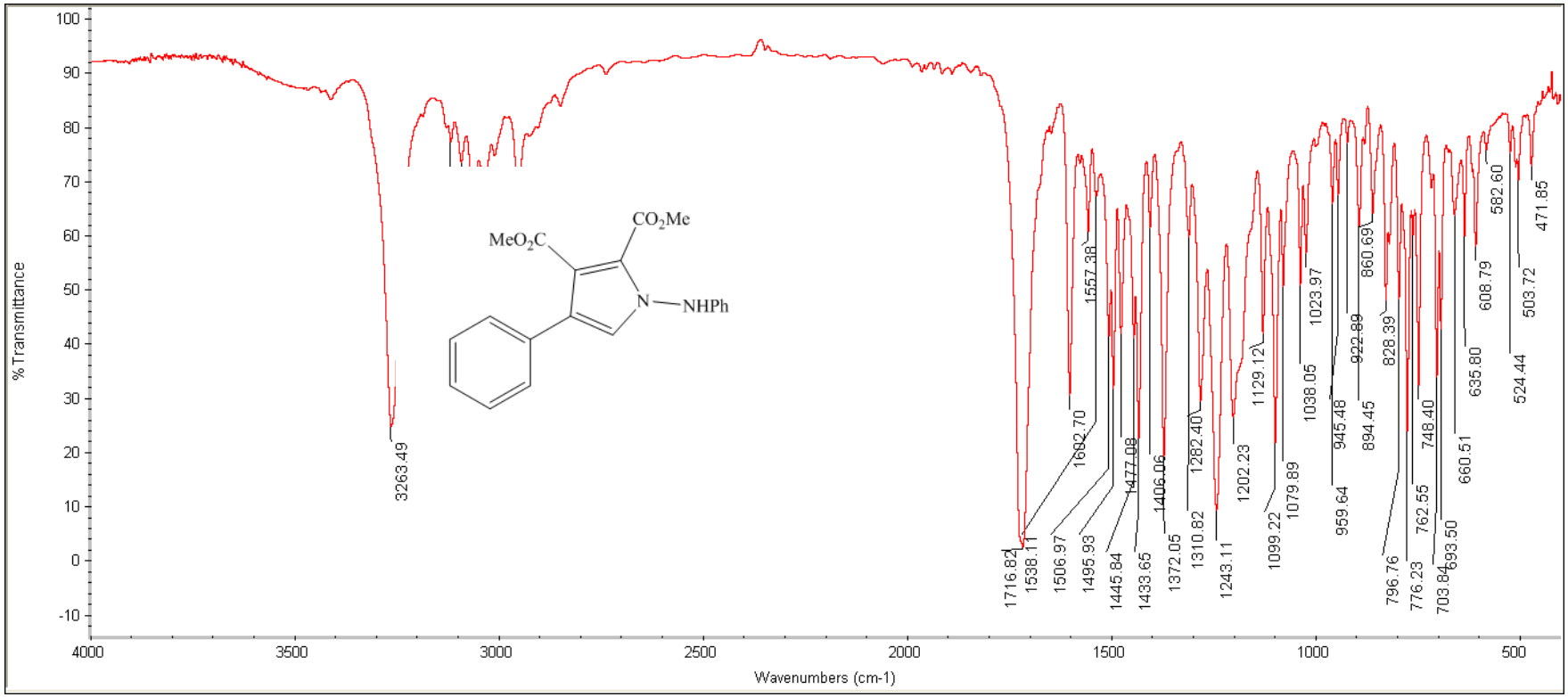


Figure S10. IR specctrum (KBr) (ῡmax, cm^{-1}) of dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4d).**

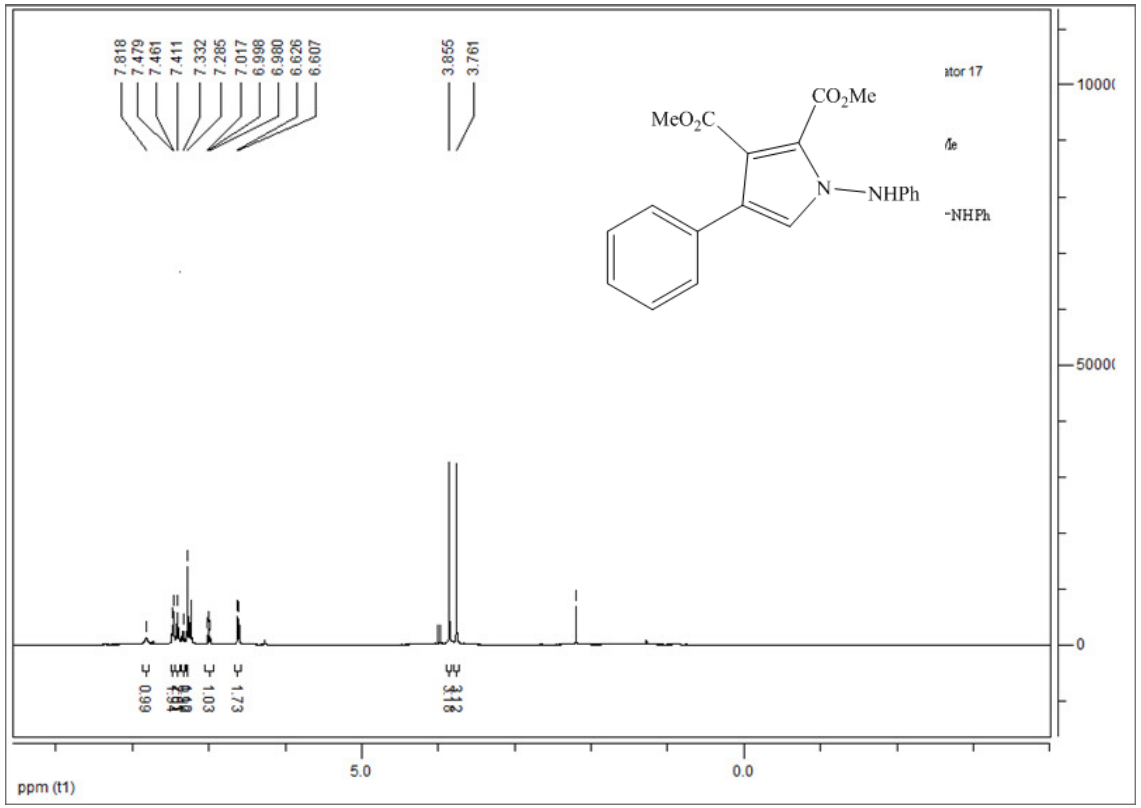


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4d).**

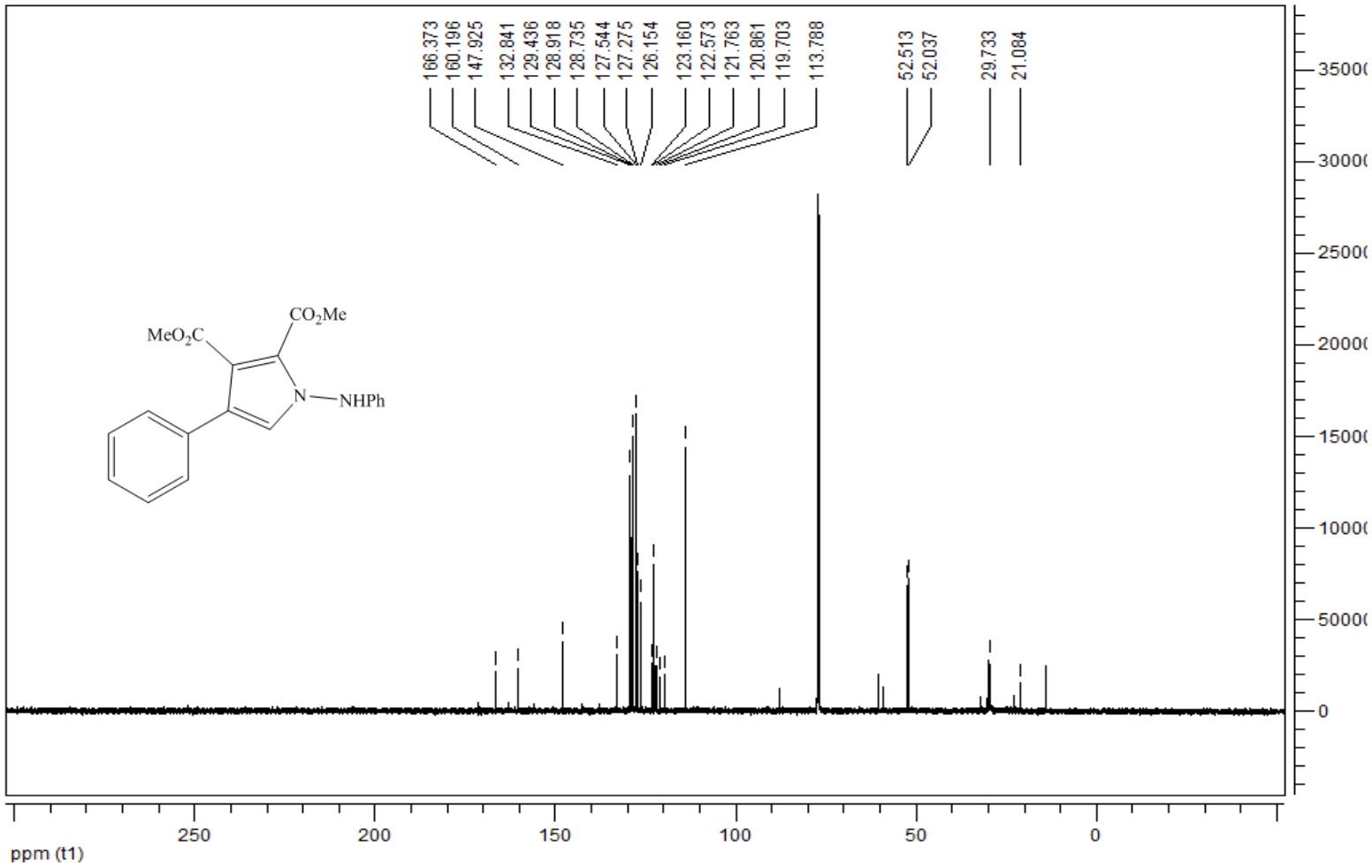


Figure S12. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4d).**

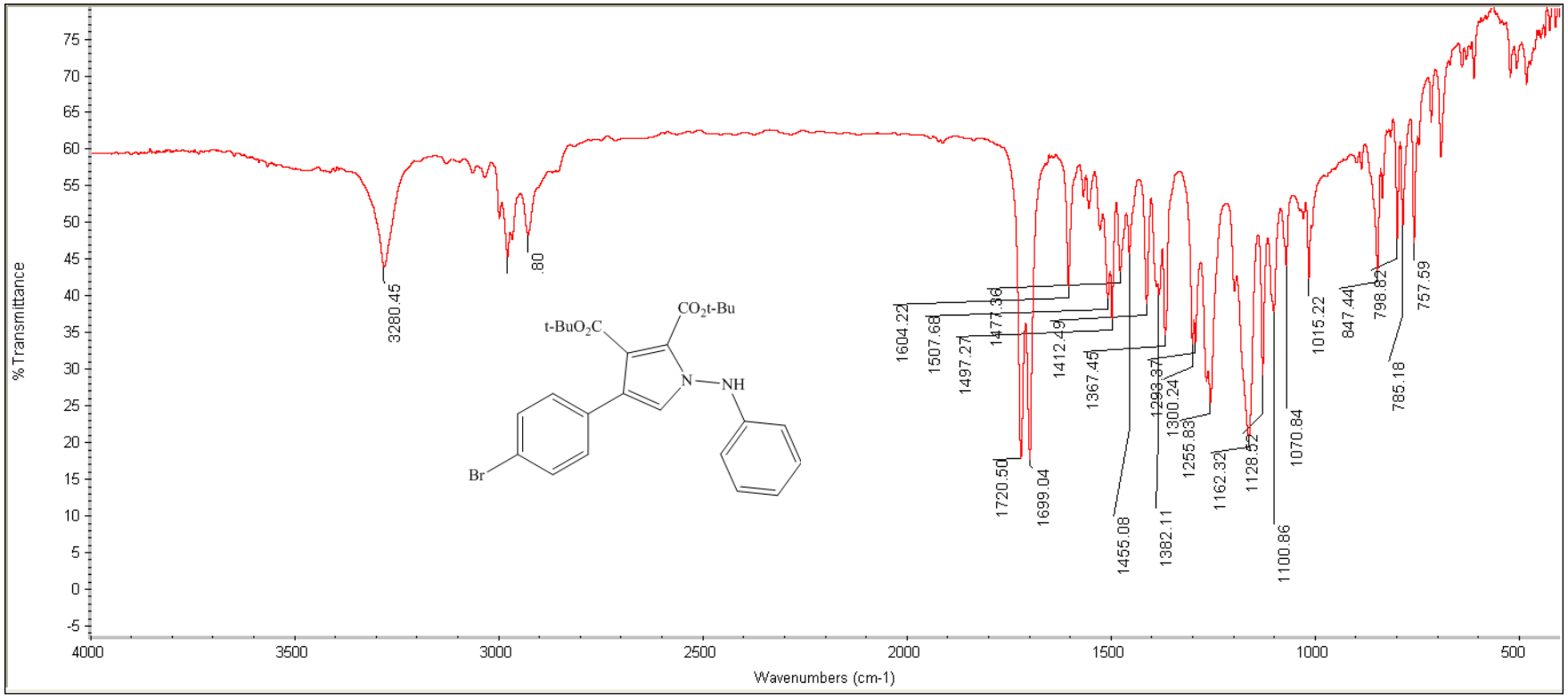


Figure S13. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of di-tert-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4e).**

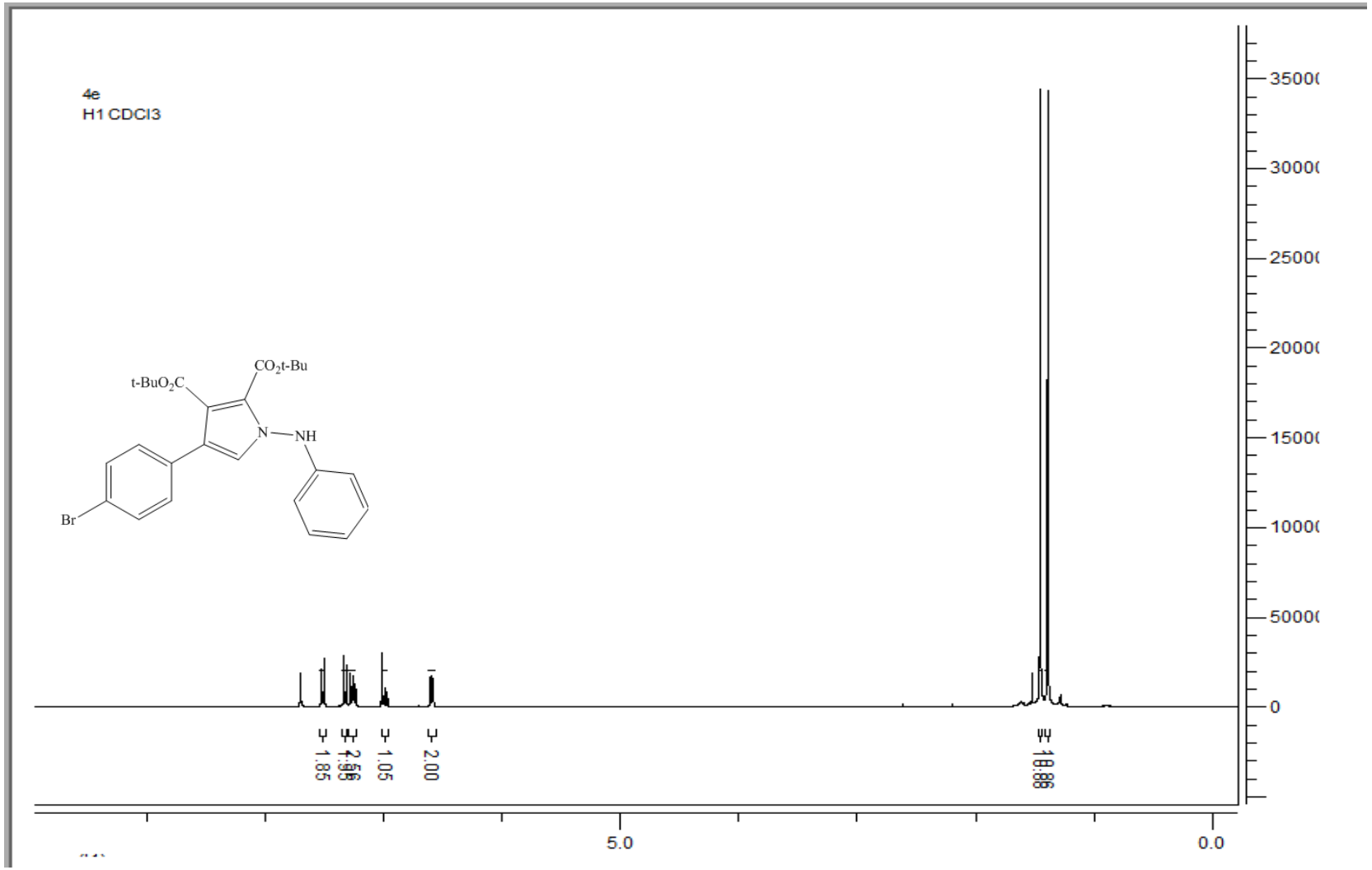


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) ofdi-tert-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4e).**

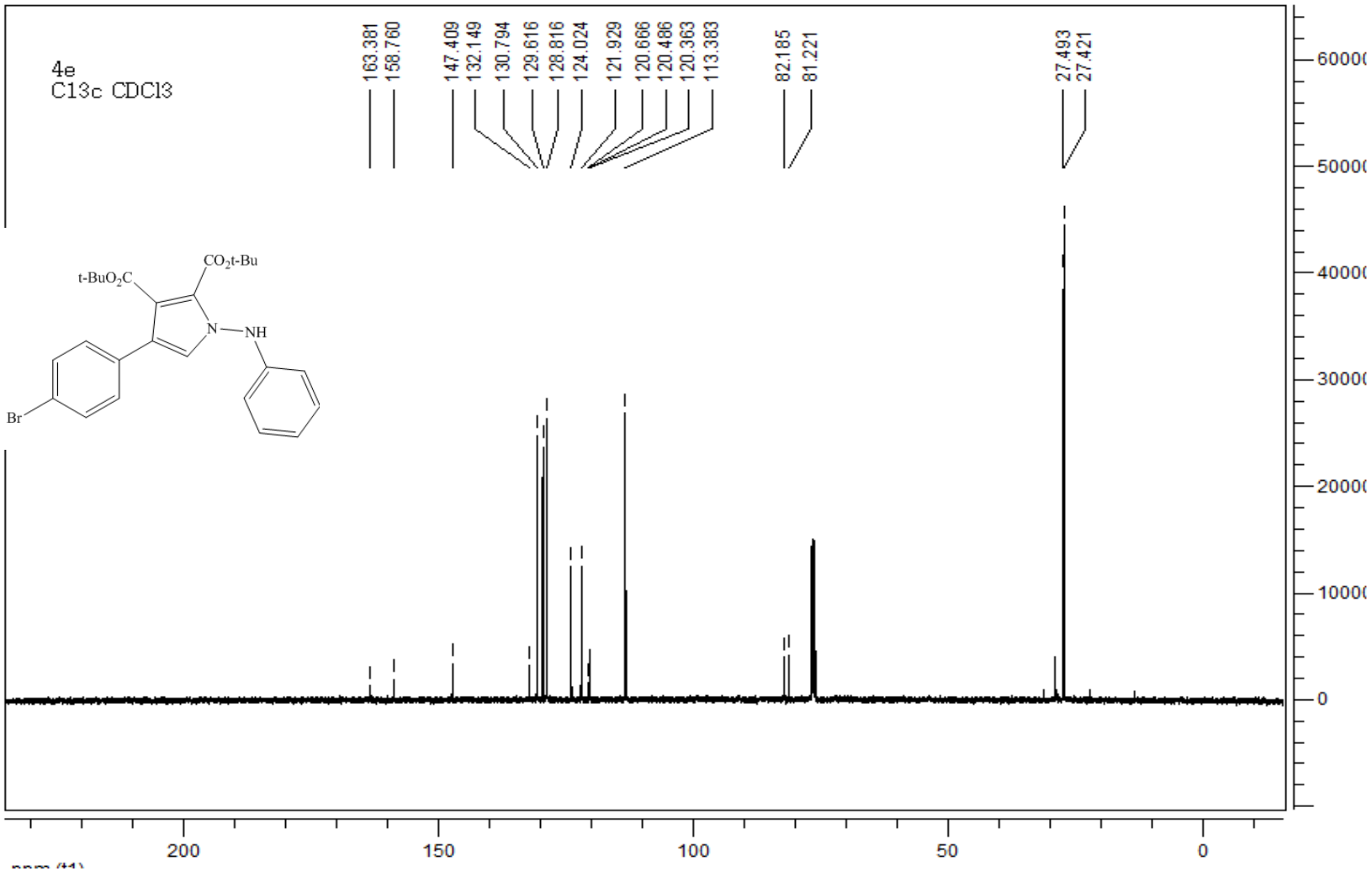


Figure S15.[13]CNMR spectrum ($CDCl_3$, 100MHz) ofdi-tert-butyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4e).**

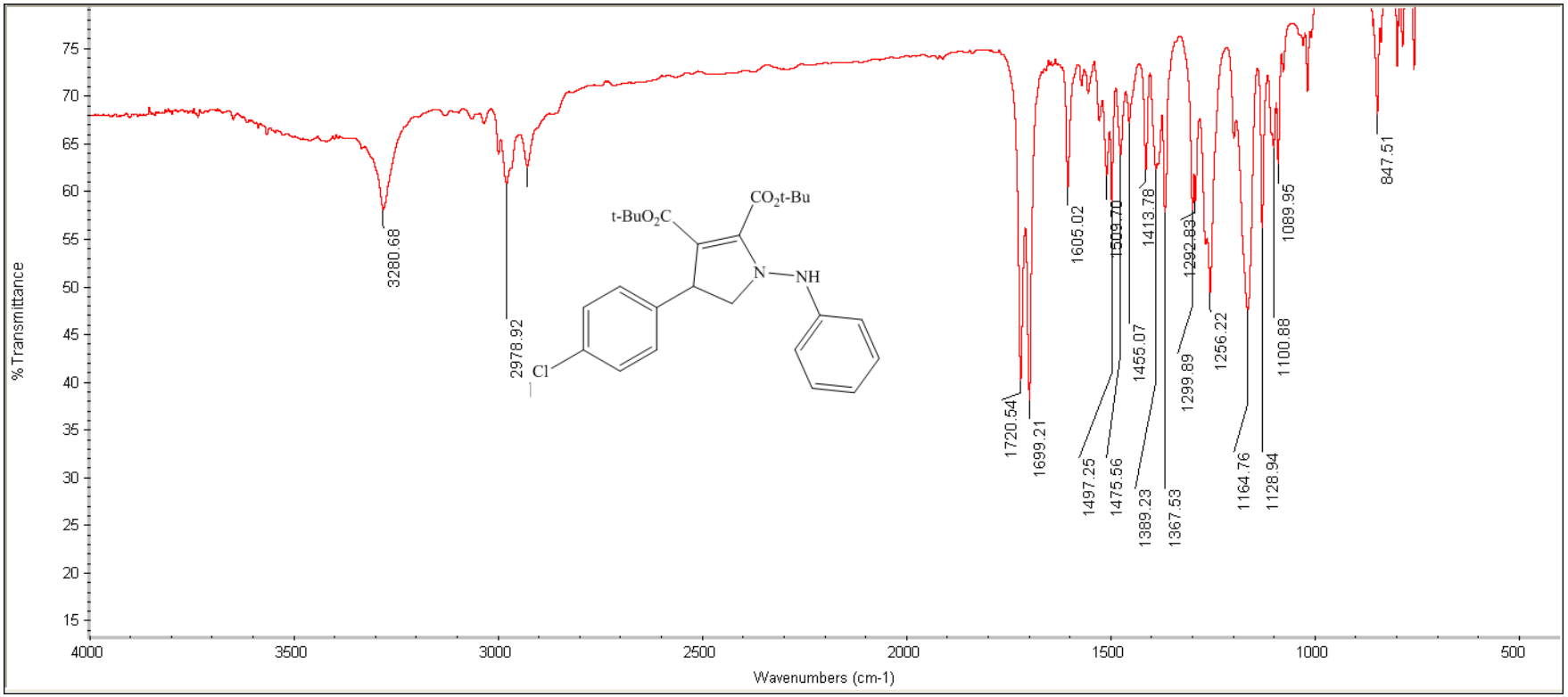


Figure S16. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of di-tert-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4f).**

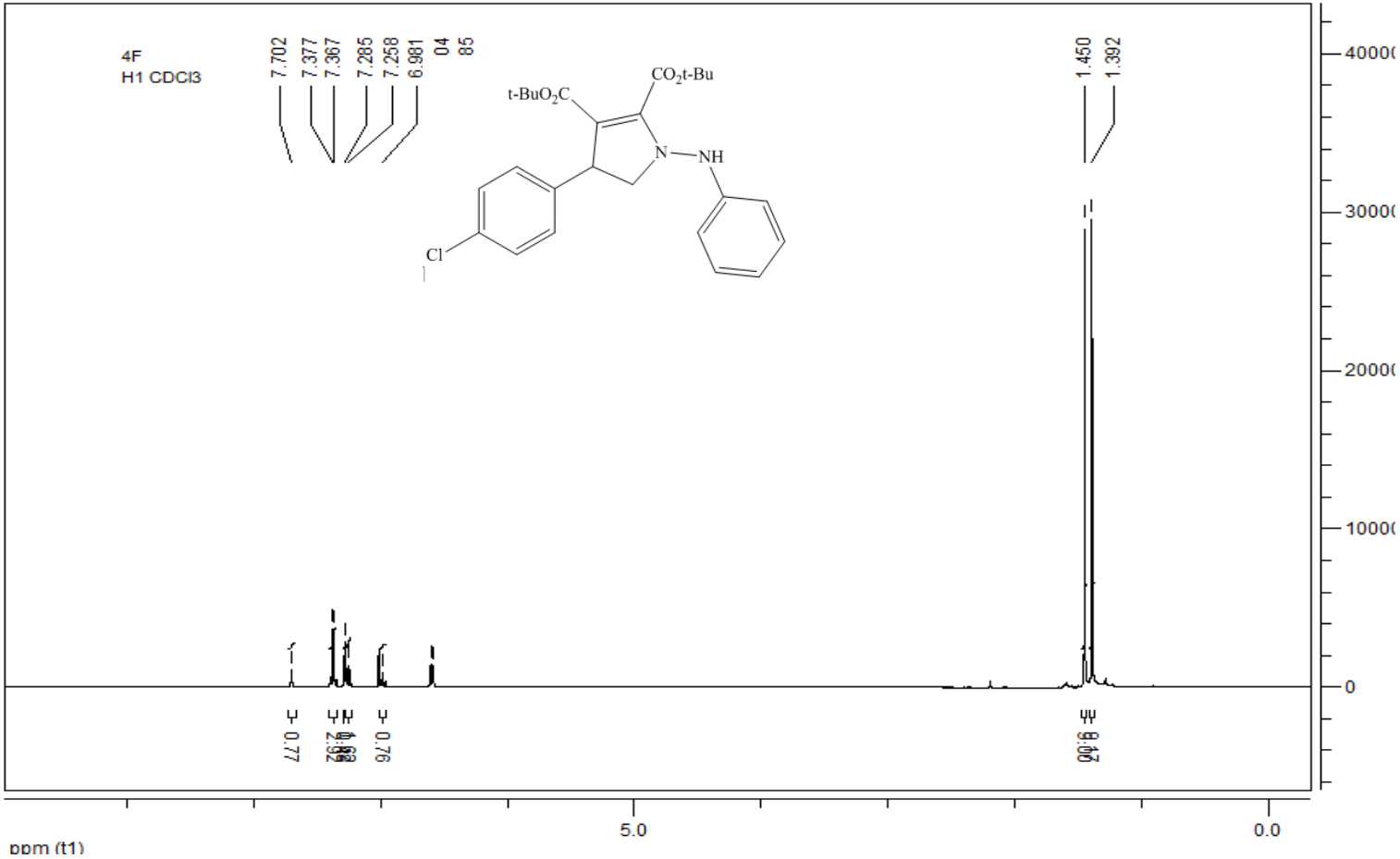


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) ofdi-tert-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4f).**

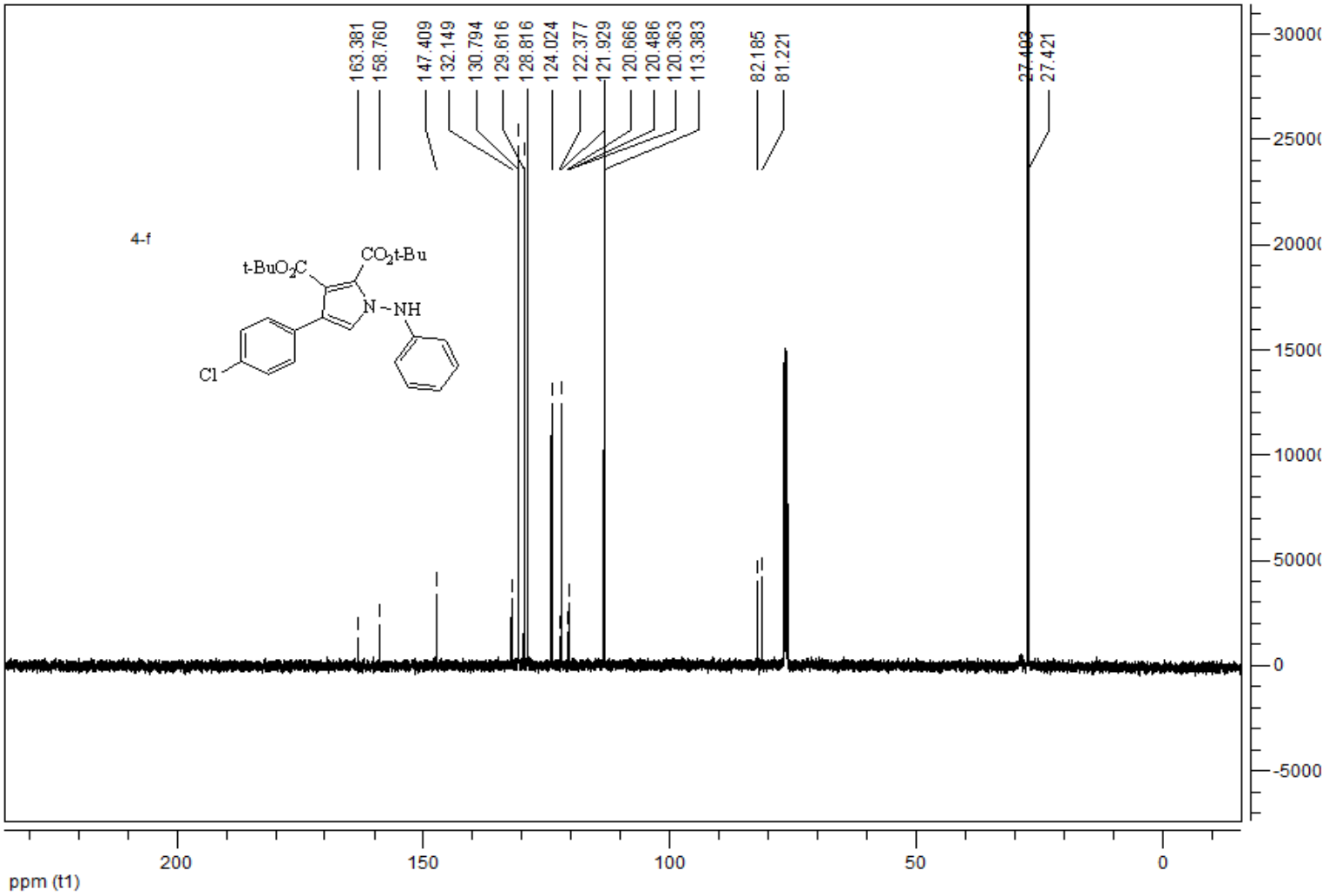


Figure S18.[13]CNMR spectrum ($CDCl_3$, 100MHz) of di-tert-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate**.**

(4f)

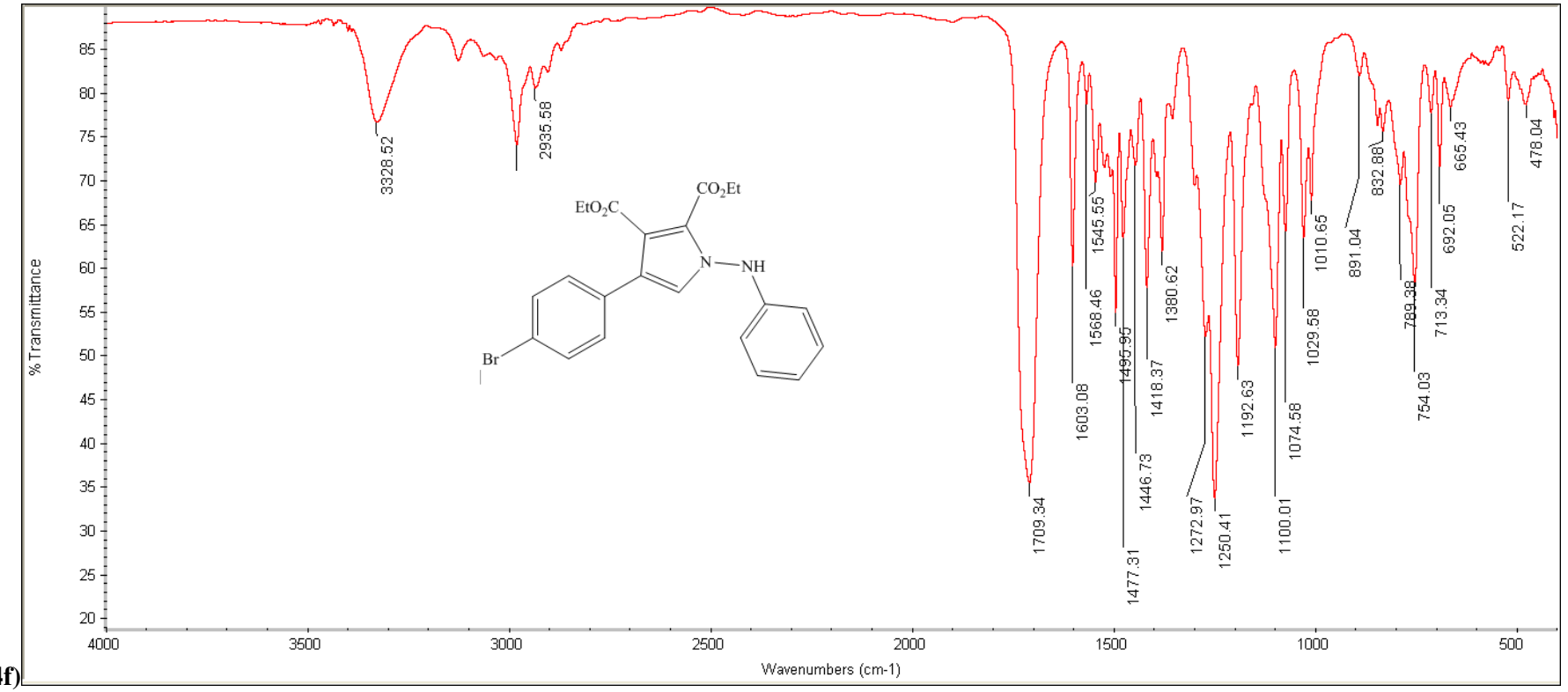


Figure S19. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of diethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4g).**

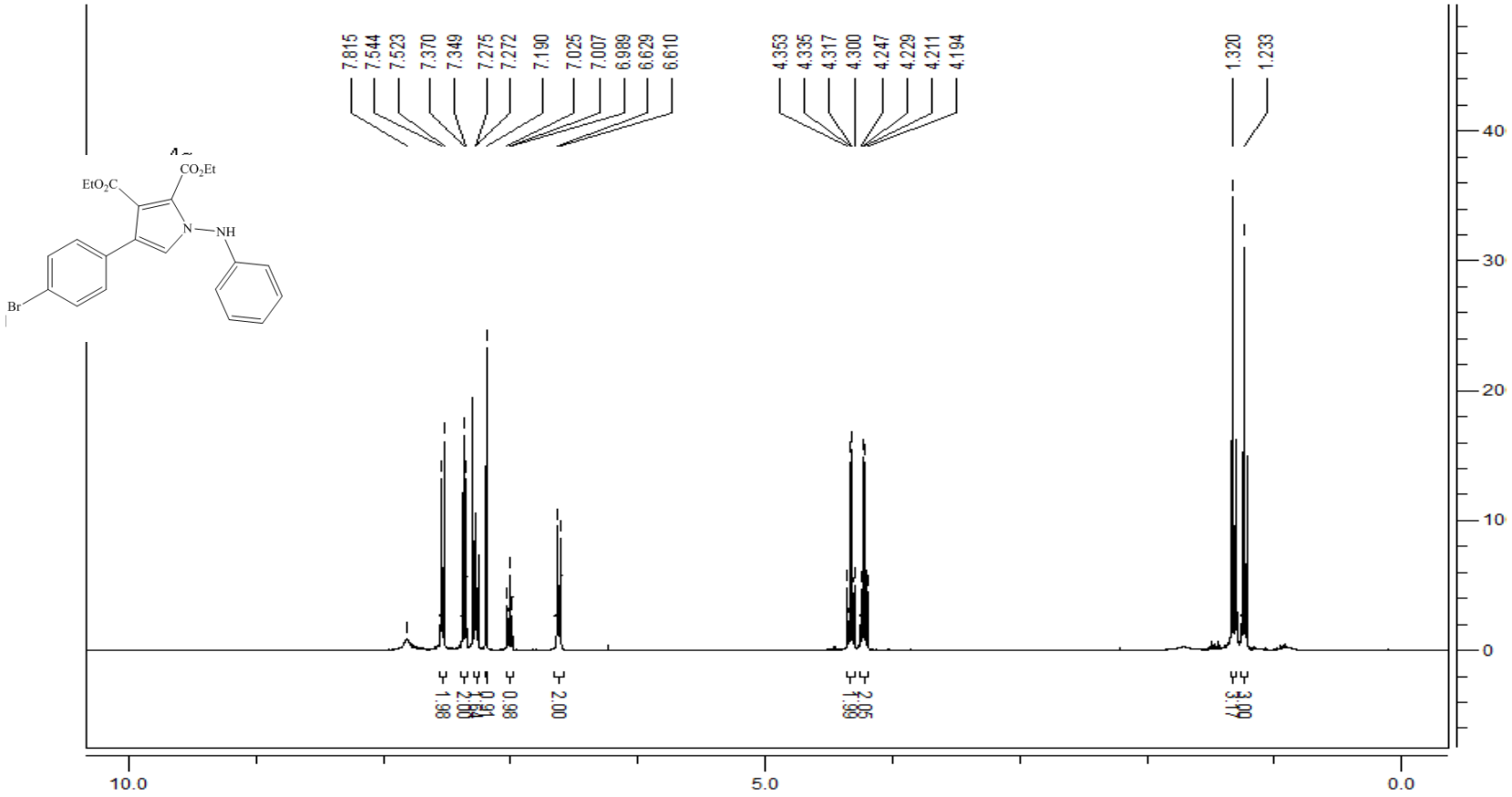


Figure S20[1]H NMR spectrum ($CDCl_3$, 400 MHz) ofdiethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4g).**

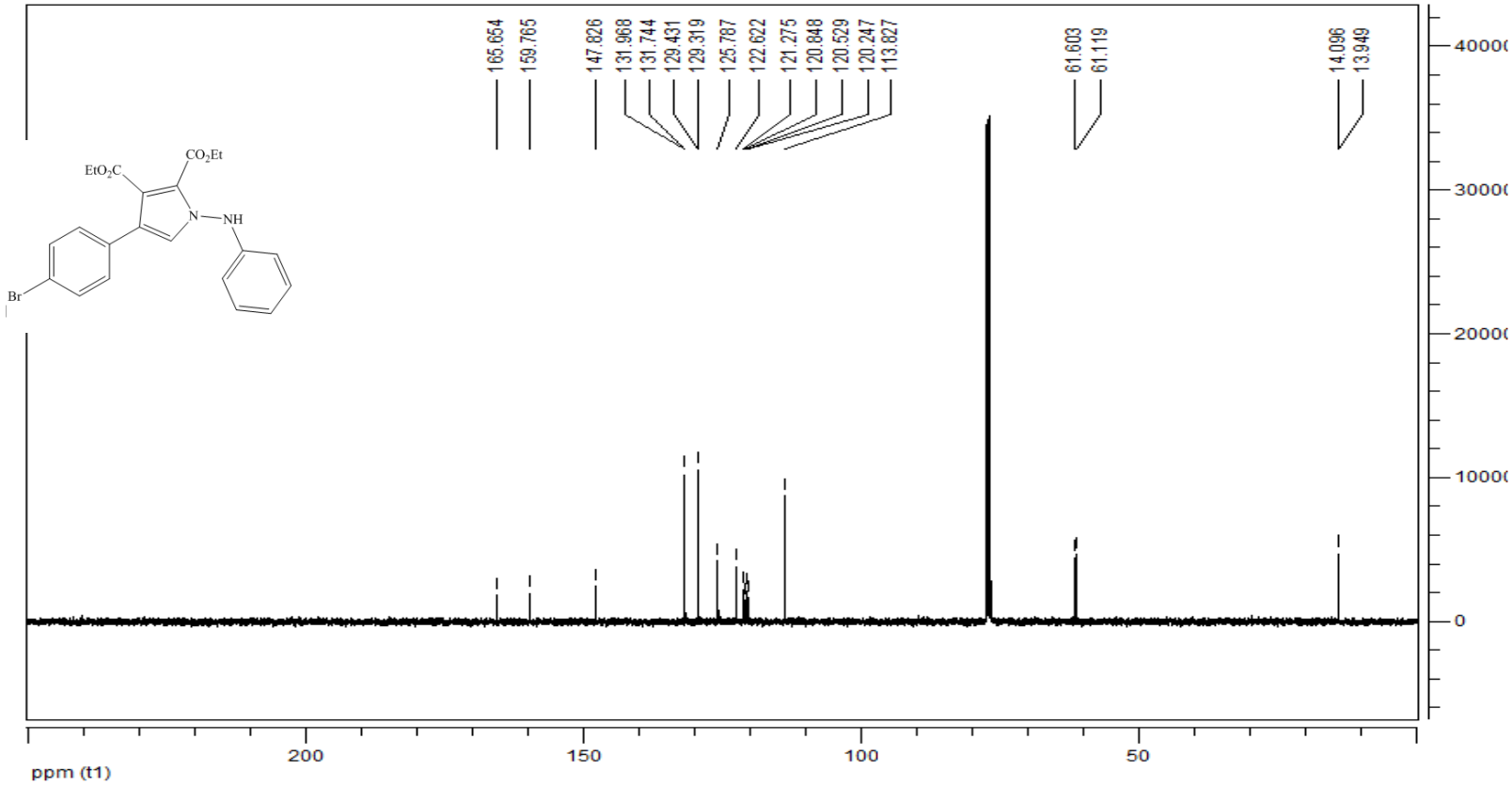


Figure S21. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of diethyl 5-(4-bromophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4g).**

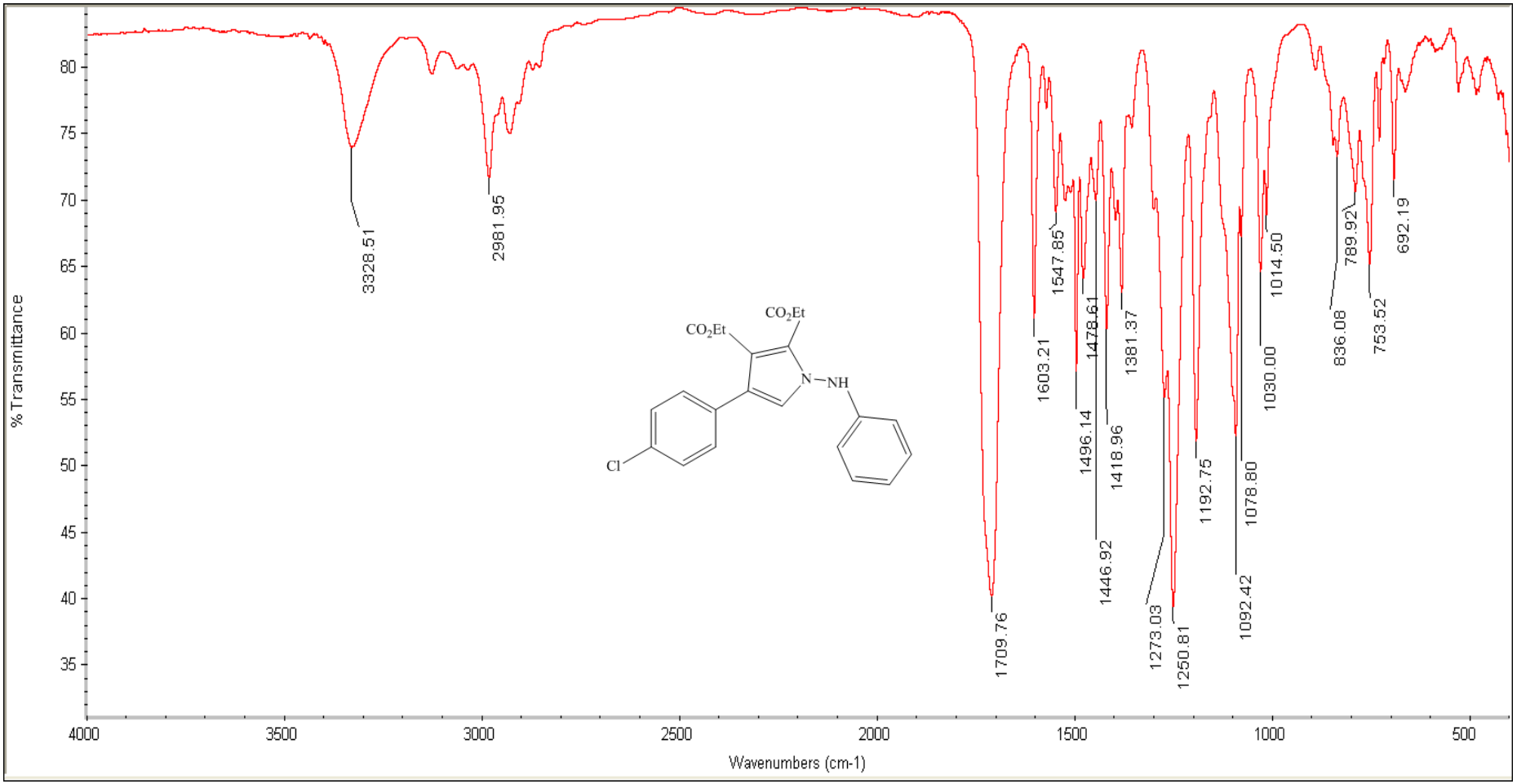


Figure S22. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of diethyl 4-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate **(4h).**

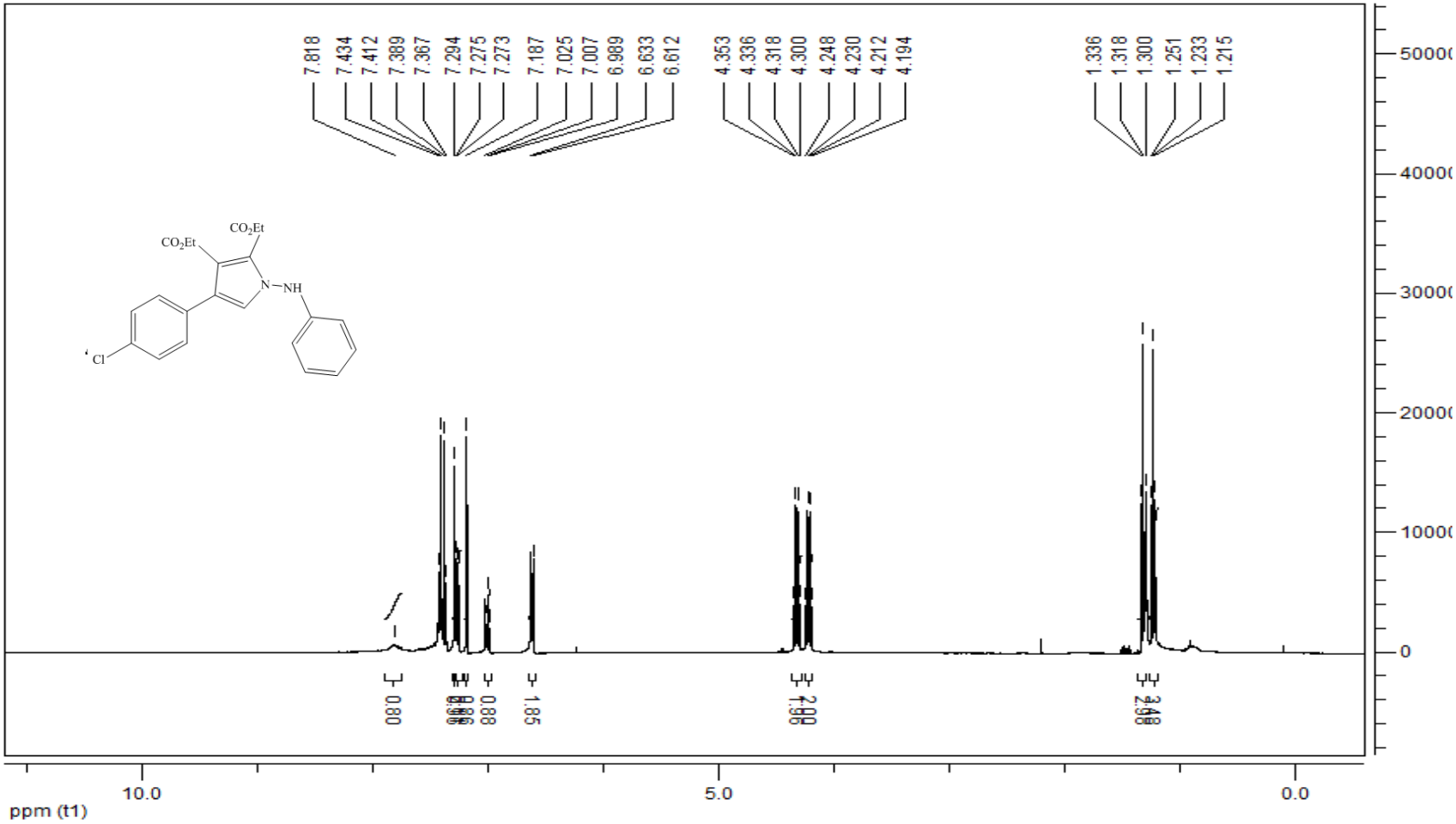
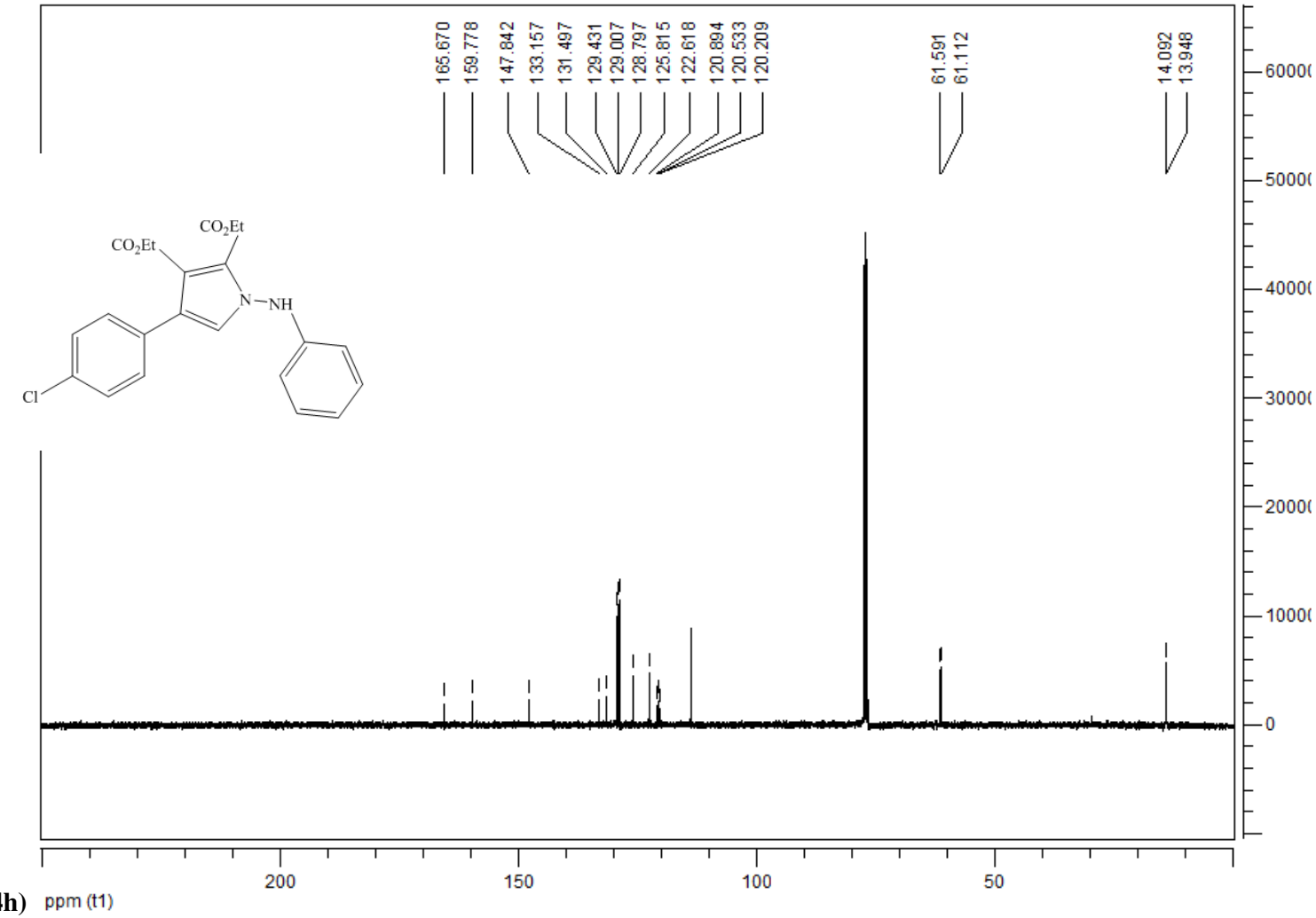
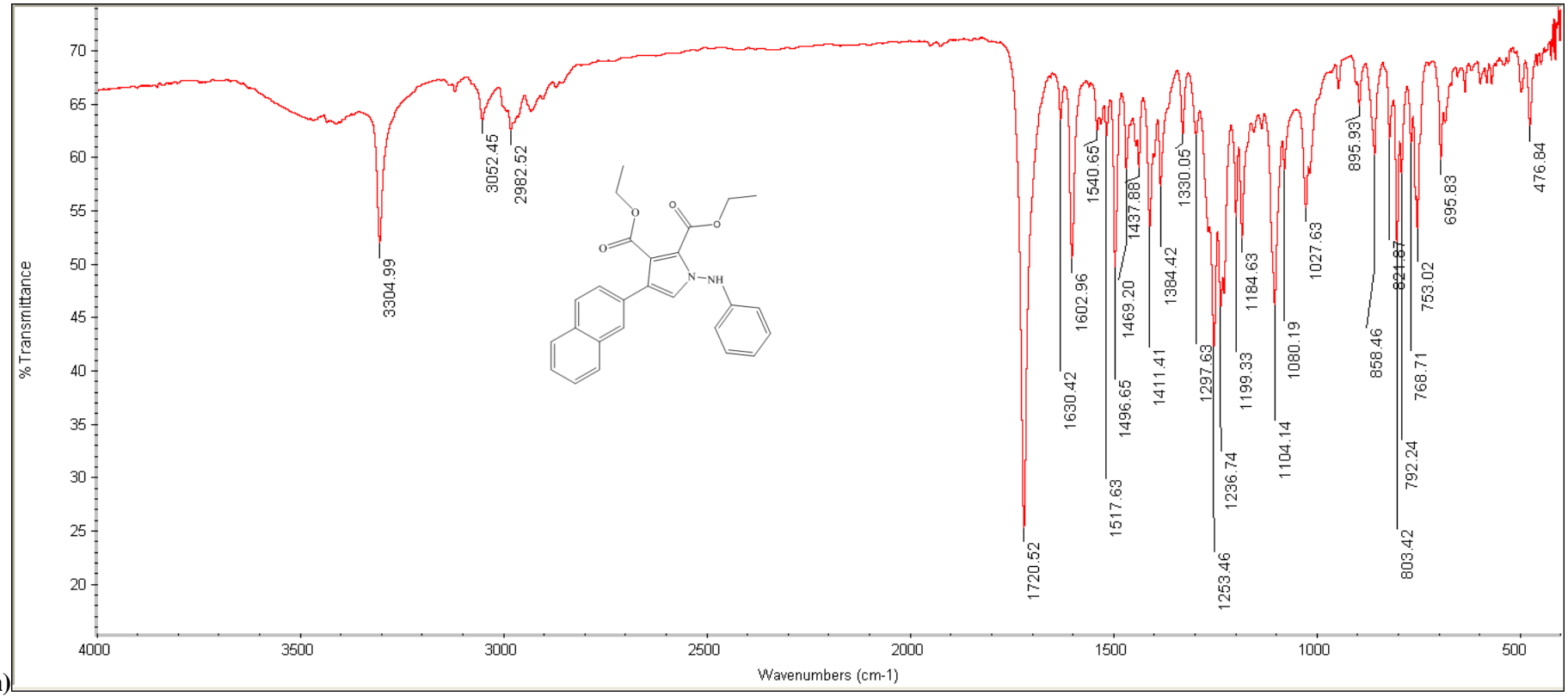


Figure S23 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of diethyl 4-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.



(4h)

Figure S24.[13]CNMRspectrum ($CDCl_3$, 100MHz) of diethyl 4-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.



(4h)

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

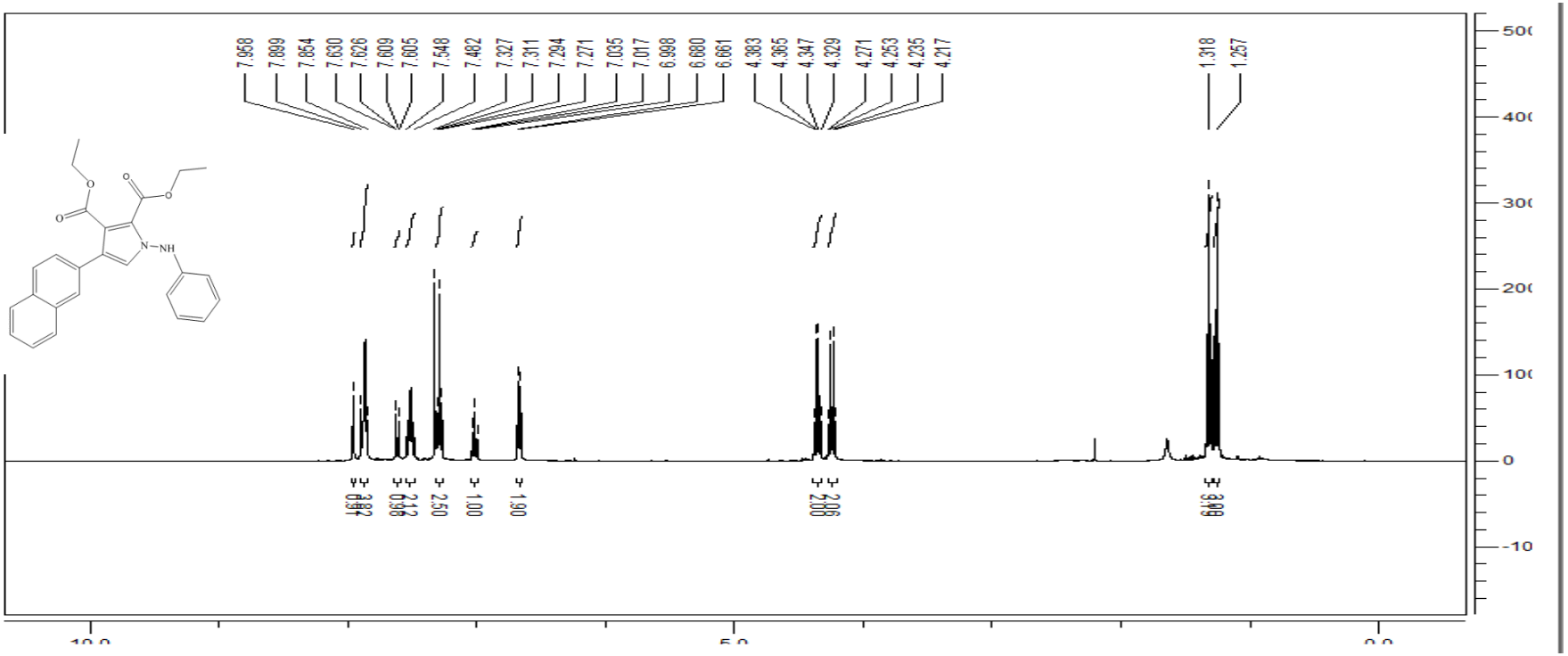


Figure S26 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4i).

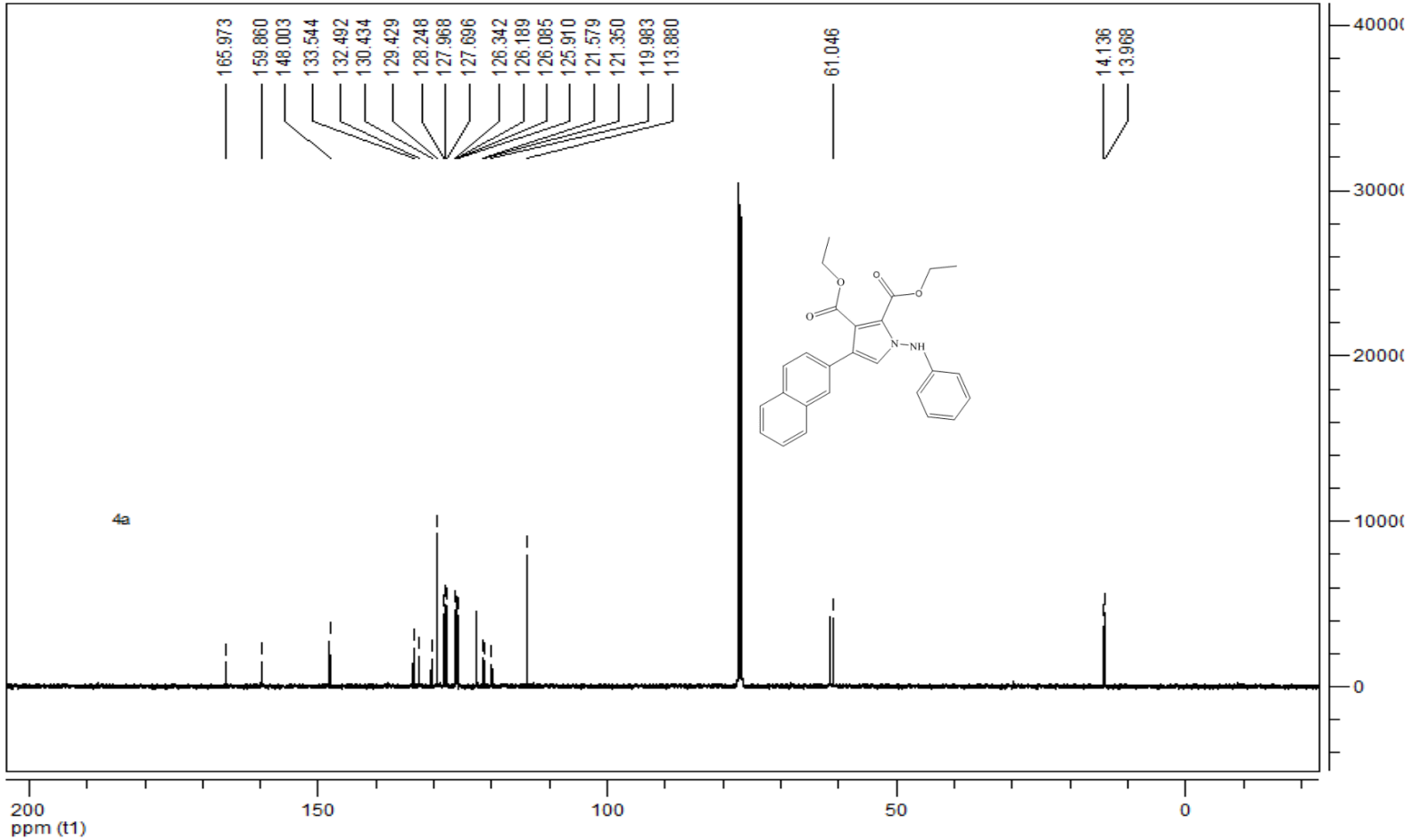


Figure S27. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate.

(4i)

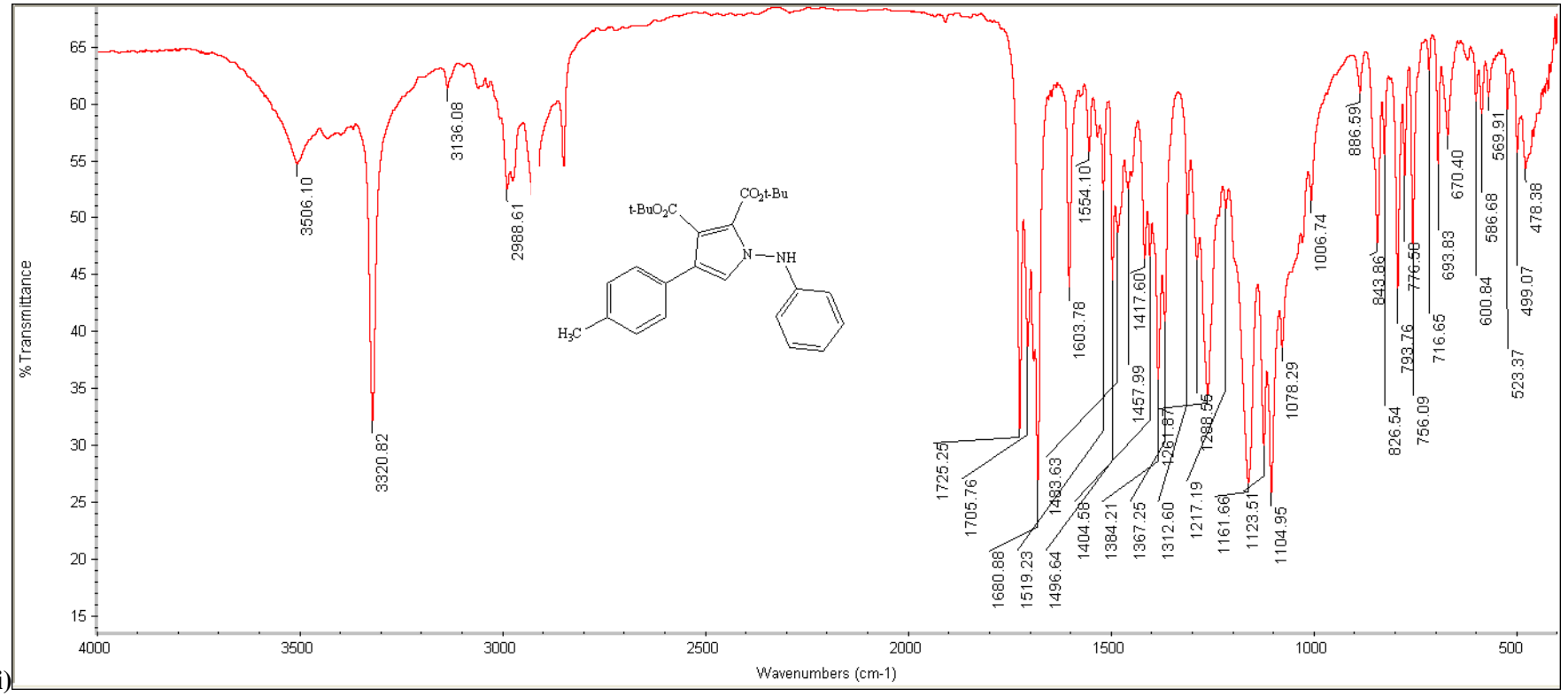


Figure S28. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate **(4j).**

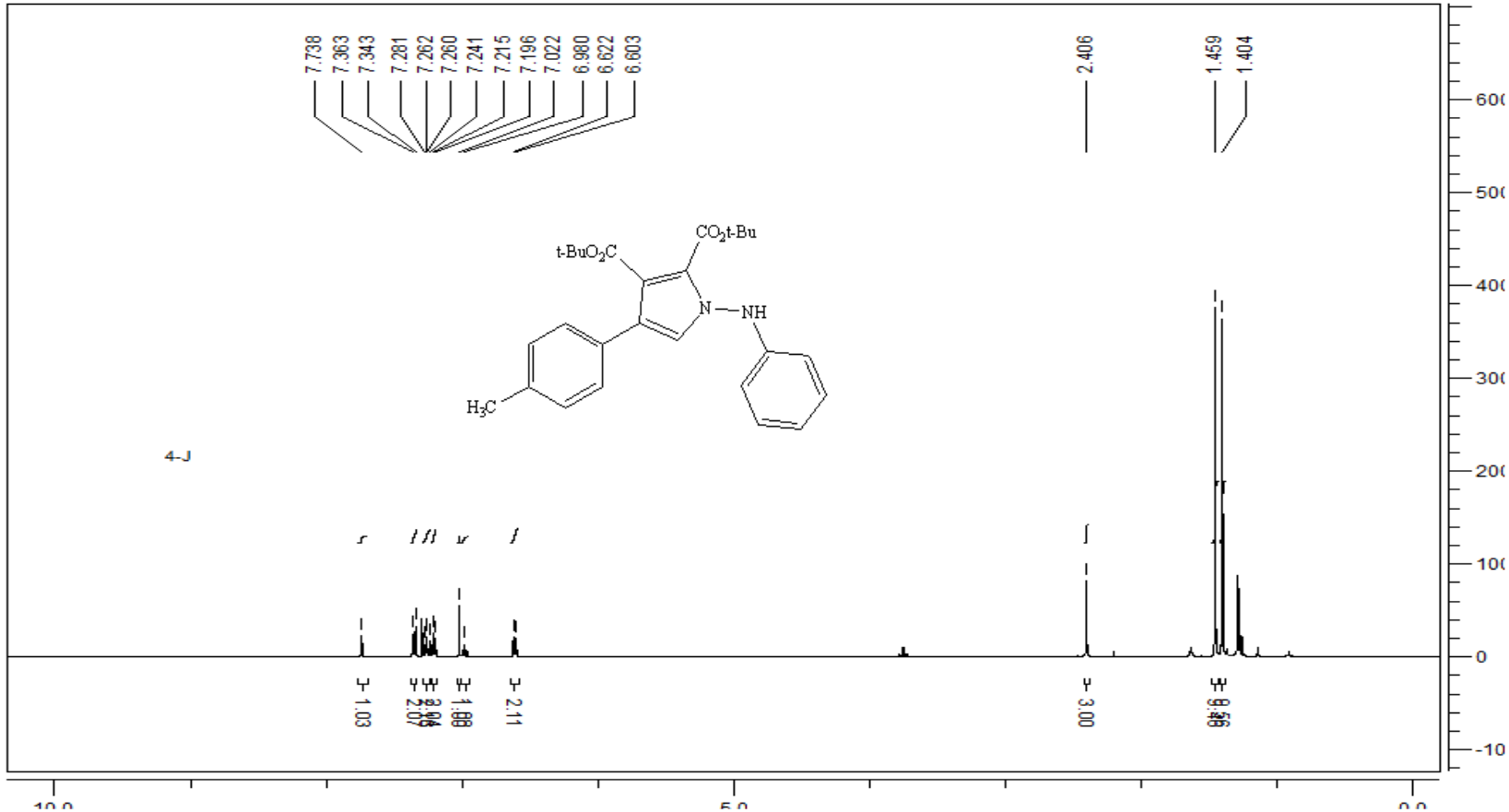
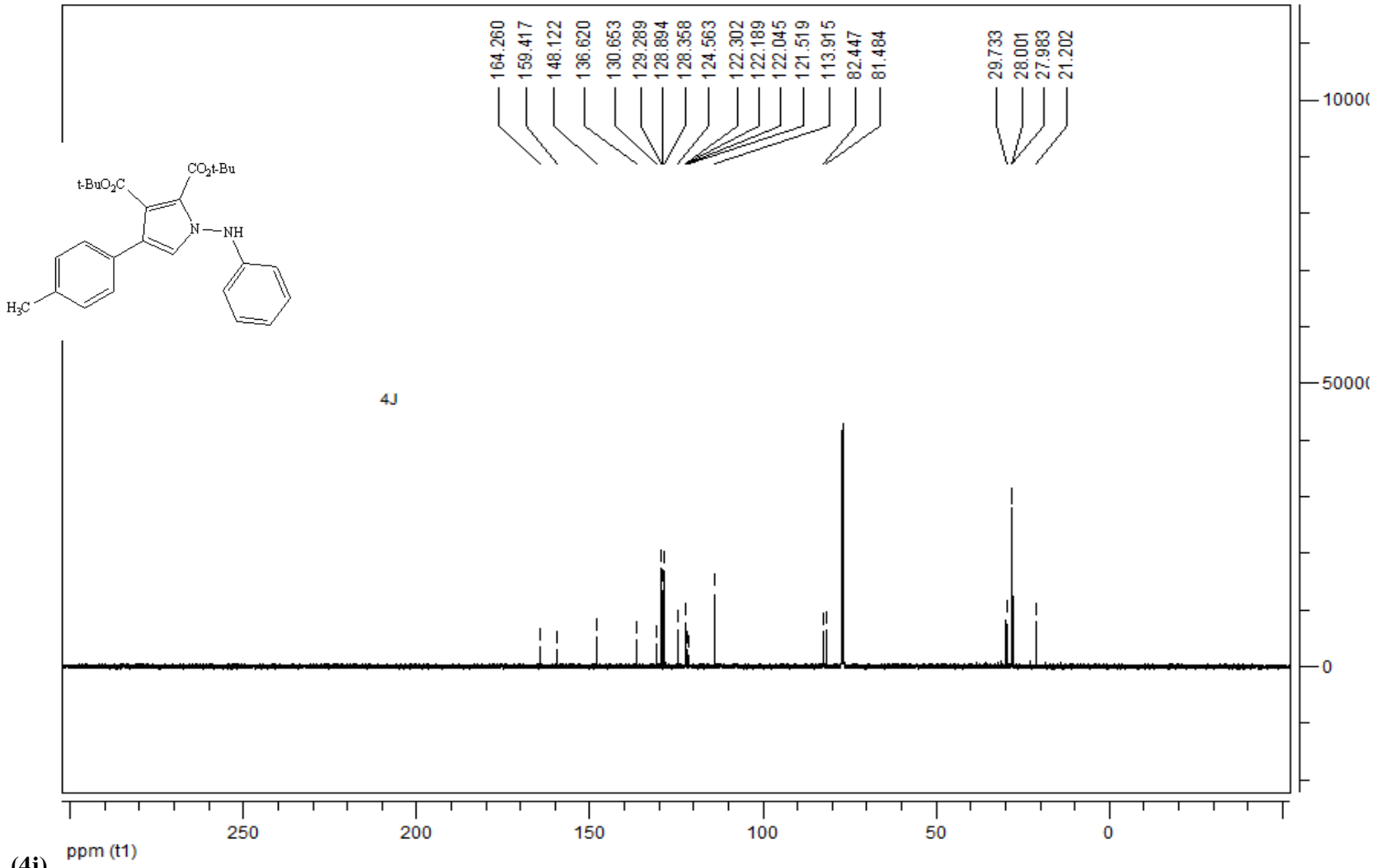


Figure S29 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) ofdi-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate**.**



(4j)

Figure S30. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate **(4j).**

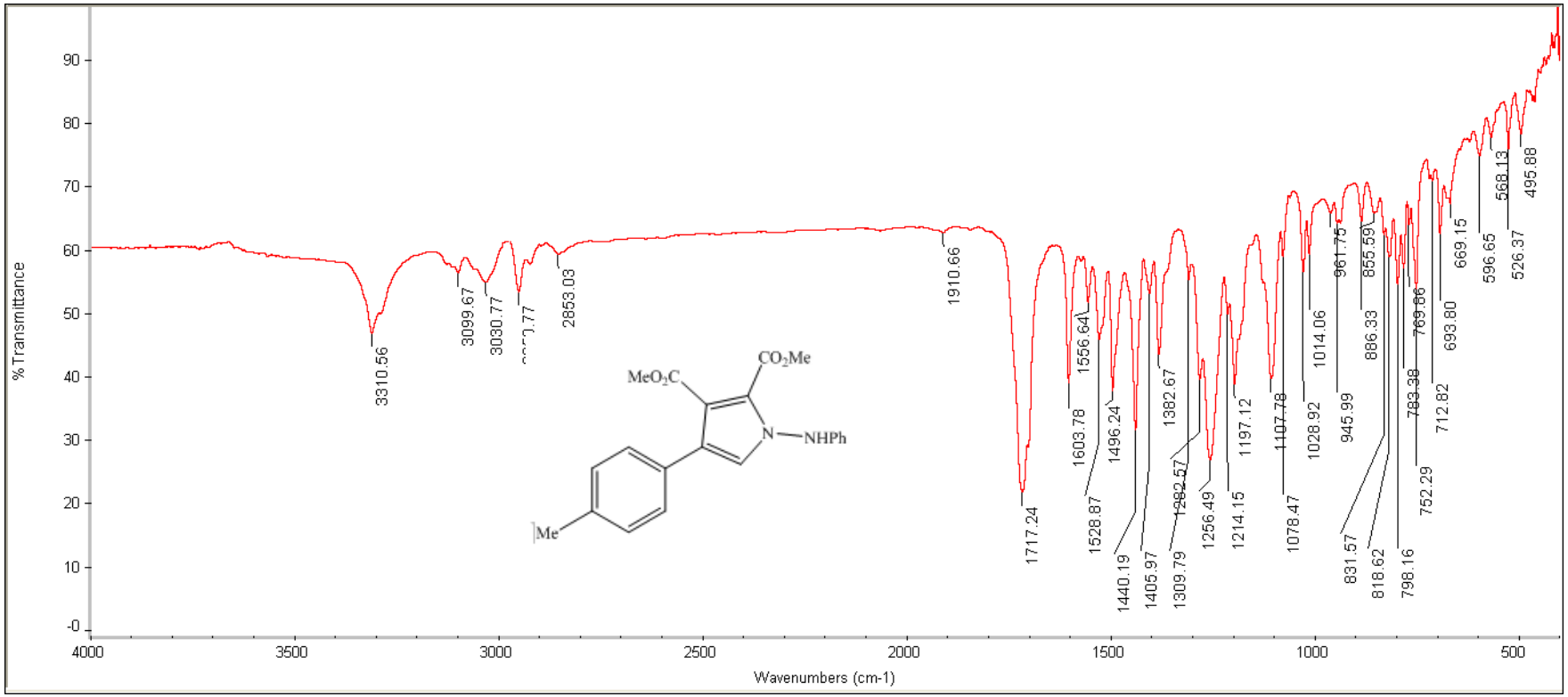


Figure S31. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of dimethyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate **(4k).**

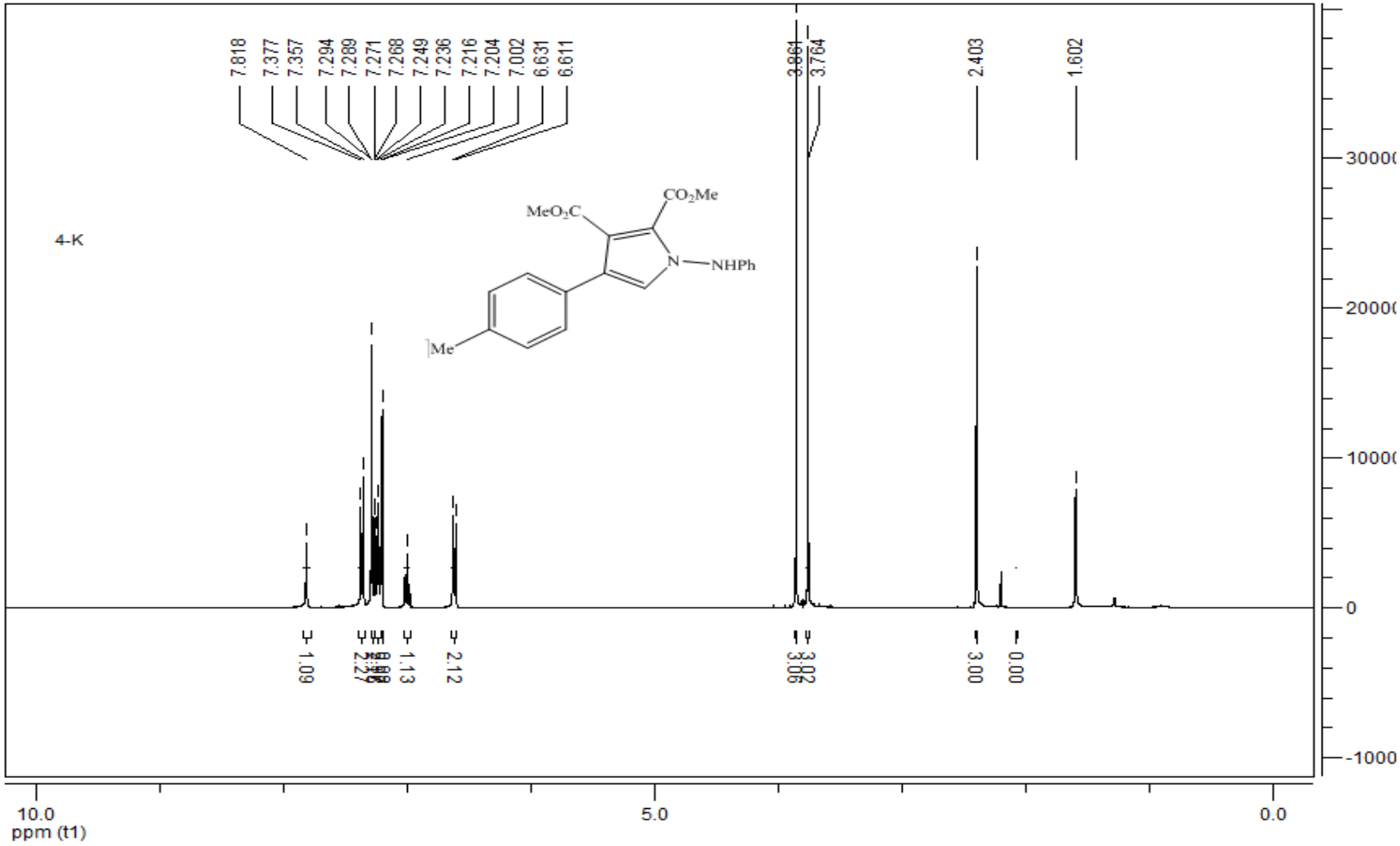
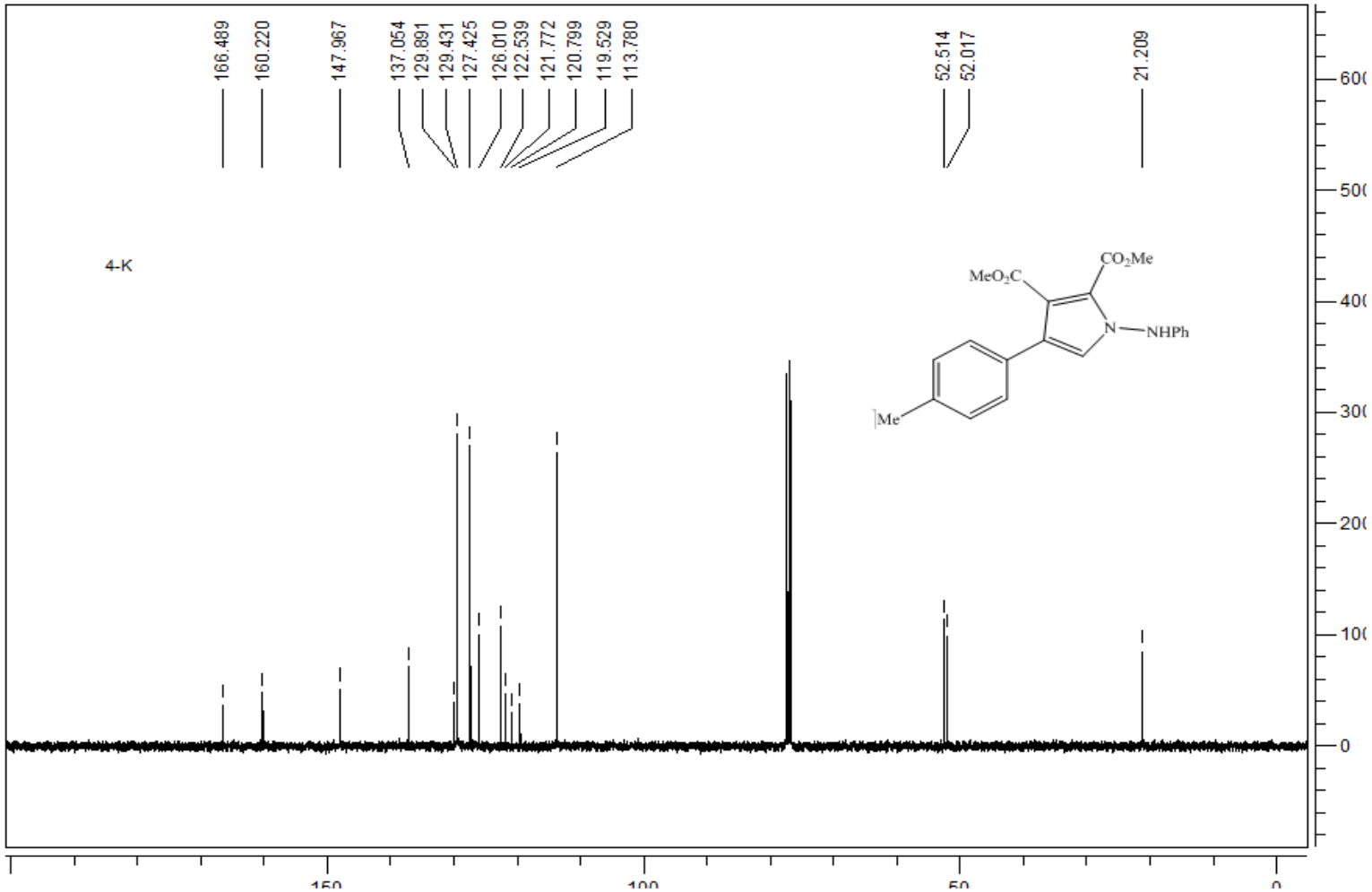


Figure S32[1]H NMR spectrum ($CDCl_3$, 400 MHz) of dimethyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate.



(4k)

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

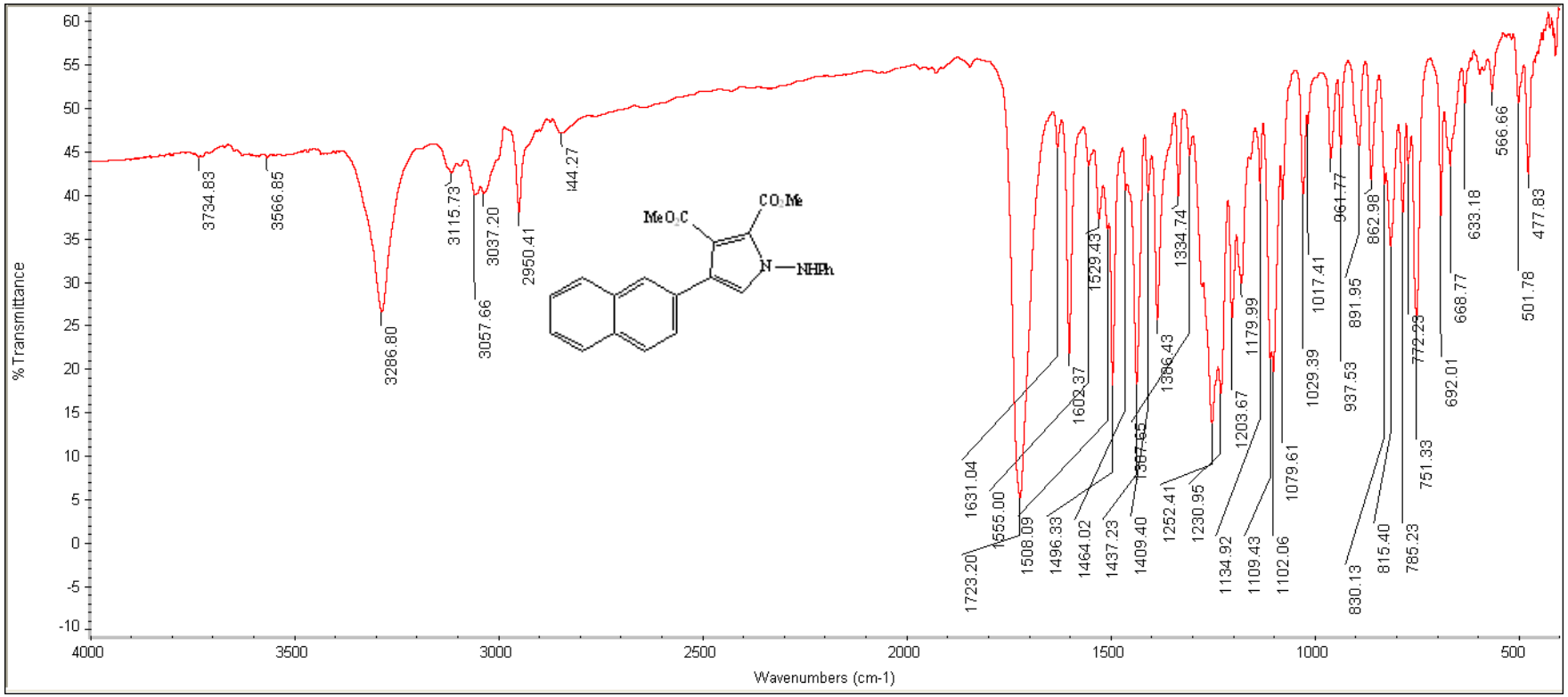


Figure S34. IR specctrum (KBr) ($\bar{\upsilon}$max, cm^{-1}) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate **(4l).**

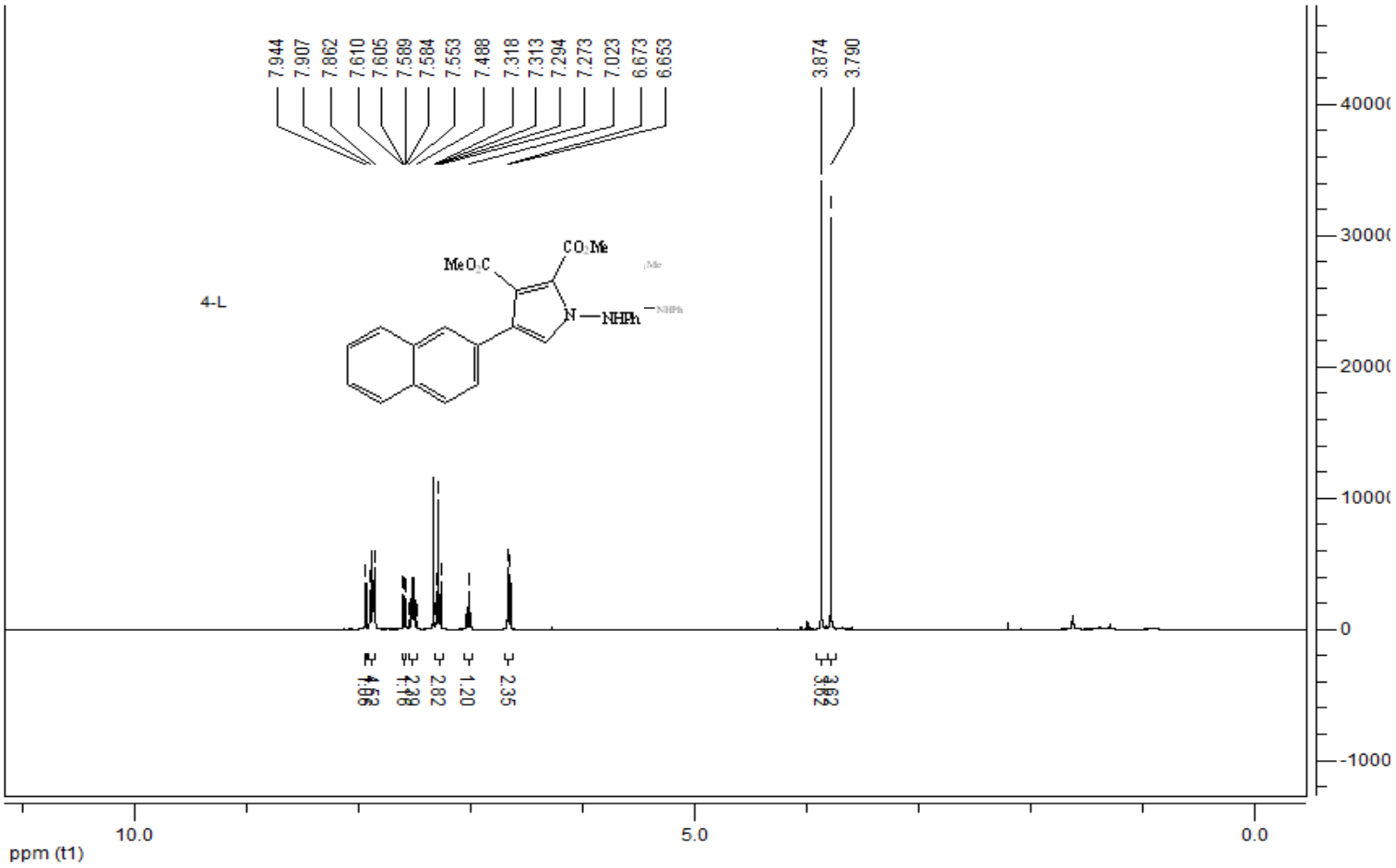


Figure S35[1]H NMR spectrum ($CDCl_3$, 400 MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate **(4l).**

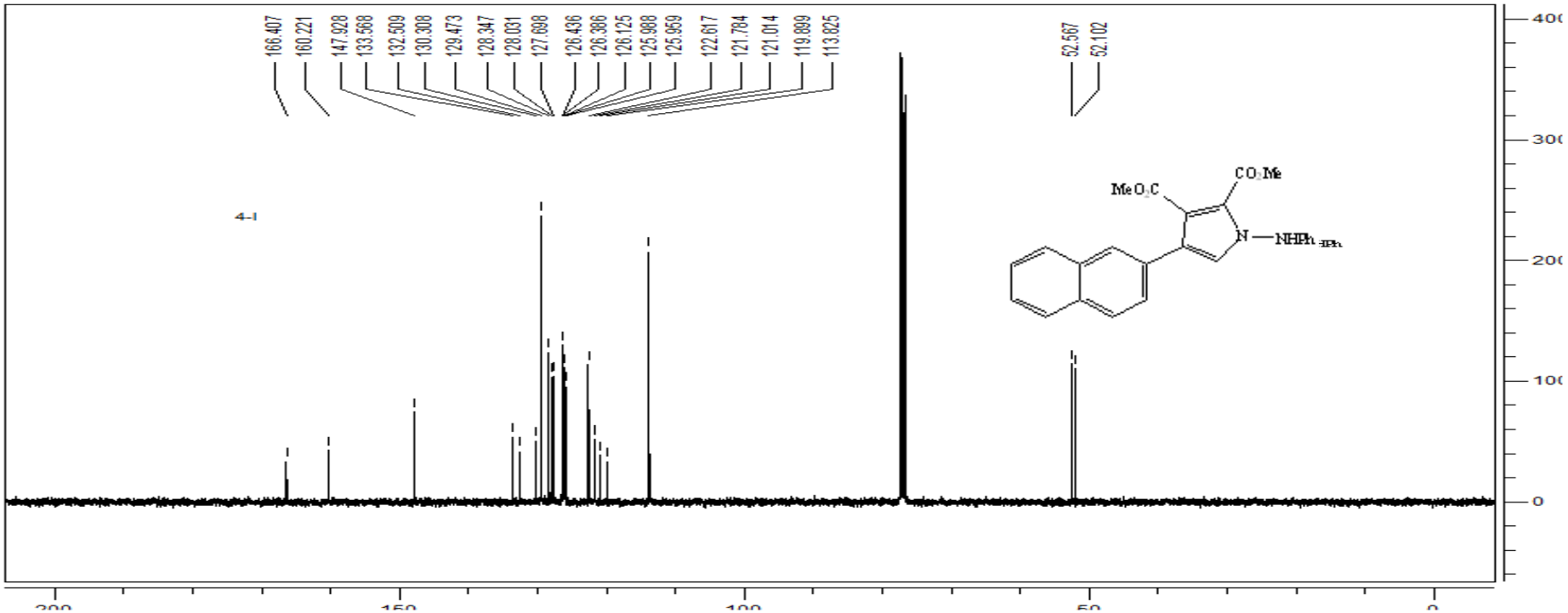


Figure S36. ^{13}CNMR spectrum ($CDCl_3$, 100MHz) of di-tert-butyl 1-(phenylamino)-4-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate **(4l).**