Electronic Supplementary Information

Ni(0)-Cu(I): A powerful combo catalyst for simultaneous coupling and cleavage of C-N bond with cyclization to valuable amide-based pyrroles and 4-pyridones

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1. **Materials and methods**

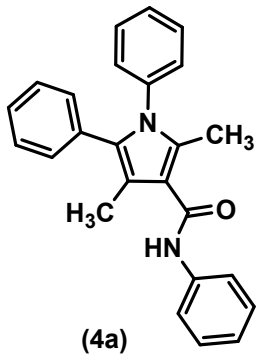
All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether (boiling range 60-80 ºC) were distilled before use. Toluene was dried using sodium wires. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer in thin film. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer.

2. General procedure for synthesis of pentasubstituted pyrroles

Acetoacetanilide derivative (2.0 mmol) and 1-aryl-2-propyn-1-ol derivative (1.0 mmol) were added in dry toluene (15 mL) in presence of bis(1,5-cyclooctadiene)nickel(0) (7 mol%, 21 mg), CuI (10 mol%, 19 mg) and cyclopentadiene (dimer) (0.3 mmol, 40 mg) and refluxed for 7-11 h in the inert condition under nitrogen atmosphere. The reaction was monitored by thin layer chromatography (TLC). The post-reaction mixture was filtered through cellite and filtrate was concentrated in a rotary evaporator through removal of toluene. The reduced mass was extracted with EtOAc (2x15 mL), and the combined organic layer was washed with water (3x10 mL) and brine (1x10 mL). It was dried over anhydrous Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. The crude product was purified by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (10%, v/v) as an eluent, which afforded the corresponding pentasubtituted pyrroles (**4a-4l**).

3. Characterization data of pentasubstituted pyrroles (4a-4k)

3.1. 2,4-Dimthyl-*N*,1,5-triphenyl-1*H*-pyrrole-3-carboxamide (4a)

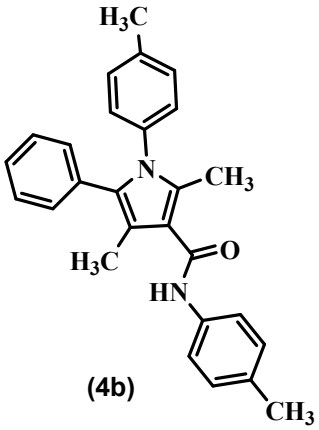


(4a)

Yield: 62% (228 mg).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 (3H, s), 2.43 (3H, s), 6.78 (2H, d, *J* = 6.6), 6.89-6.92 (3H, m), 7.02-7.17 (5H, m), 7.17-7.23 (5H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 11.7, 12.4, 117.0, 123.5, 125.6, 126.4, 127.0, 127.1, 128.0, 128.4, 129.0, 130.7, 131.2, 131.4, 132.8, 135,2, 136.0, 137.6, 165.8.
FT-IR (neat, cm^{-1}): 1169, 1263, 1331, 1460, 1530, 1588, 2928, 3388.
HR-MS (*m*/*z*) for $C_{25}H_{23}N_2O$ (M+H): Calculated 367.1810, found 367.1808.

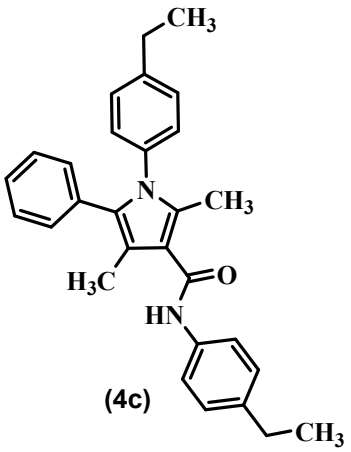
3.2. 2,4-Dimethyl-5-phenyl-*N*,1-di-4-totyl-1*H*-pyrrole-3-carboxamide (4b)



(4b)

Yield: 66% (262 mg).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (3H, s), 2.24 (3H, s), 2.40 (3H, s), 2.44 (3H, s), 6.98 (4H, s), 7.15 (2H, d, *J* = 8.1 Hz), 7.31 (2H,d, *J* = 8.1 Hz)7.42-7.49 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 12.5, 20.7, 21.1, 114.1, 119.1, 119.3, 126.4, 127.3, 128.0, 128.8, 129.1, 130.0, 131.0, 132.5, 135.1, 135.5, 136.1, 138.5, 163.9.
FT-IR (neat, cm^{-1}): 1069, 1173, 1401, 1530, 1638, 2922, 3398.
HR-MS (*m*/*z*) for $C_{27}H_{27}N_2O$ (M+H): Calculated 395.2123, found 395.2126.

3.3. *N*,1-Bis(4-ethylphenyl)-2,4-dimethyl-5-phenyl-1*H*-pyrrole-3-carboxamide (4c)

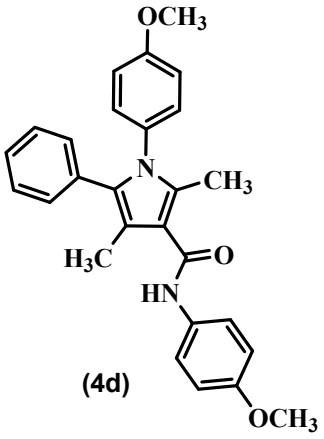


(4c)

Yield: 68% (287 mg).
Characteristic: Pale yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, t, *J* = 7.5 Hz), 1.34 (3H, t, *J* = 7.2Hz), 1.92 (3H, s), 2.43 (3H, s), 2.56 (2H, q, *J* = 7.2 Hz), 2.74 (2H, t, *J* = 7.5 Hz), 7.02 (4H, d, *J* = 4.8 Hz), 7.19-7.22 (2H, m), 7.35 (2H, d, *J* = 8.4 Hz), 7.41-7.49 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 12.5, 15.2, 15.6, 28.2, 28.5, 114.0, 119.2, 126.4, 127.3, 127.9, 128.0, 128.4, 128.7, 128.8, 131.0, 135.3, 135.6, 136.3, 139.0, 144.7, 163.9.

FT-IR (neat, cm^{-1}): 1156, 1315, 1408, 1514, 1650, 2926, 3399.
HR-MS (*m*/*z*) for $C_{29}H_{31}N_2O$ (M+H): Calculated 423.2436, found 423.2440.

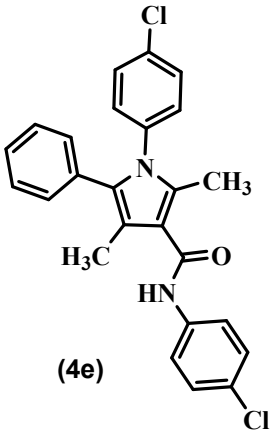
3.4. *N*,1-Bis(4-methoxyphenyl)-2,4-dimethyl-5-phenyl-1*H*-pyrrole-3-carboxamide (4d)



(4d)

Yield: 80% (341 mg).
Characteristic: yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (3H, s), 2.39 (3H, s), 3.73 (3H, s), 3.84 (3H, s), 6.74 (2H, d, *J* = 9Hz), 6.91 (1H, s), 7.00-7.03 (4H, m), 7.20 (2H, d, *J* = 9Hz), 7.36-7.49 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 12.4, 55.4, 55.5, 113.9, 114.5, 119.2, 120.8, 126.6, 127.2, 128.8, 129.2, 130.4, 130.9, 131.9, 135.2, 135.6, 155.6, 159.5, 163.9.
FT-IR (Neat, cm^{-1}): 1029, 1171, 1247, 1510, 1650, 2852, 2923, 3406.
HR-MS (*m*/*z*) for $C_{27}H_{27}N_2O_3$ (M+H):Calculated 427.2022, found 427.2020.

3.5. *N*,1-Bis(4-chlorophenyl)-2,4-dimethyl-5-phenyl-1*H*-pyrrole-3-carboxamide (4e)

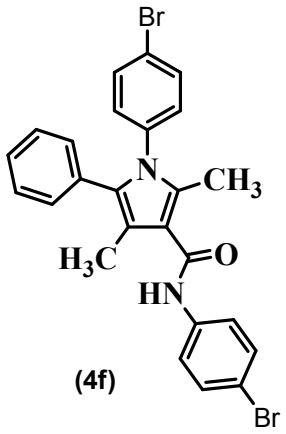


(4e)

Yield: 72% (312 mg).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (3H,s), 2.40 (3H,s), 7.02 (2H, d, *J* = 6.0 Hz), 7.13 (2H, d, *J* = 6.0 Hz), 7.21-7.24 (3H, m), 7.40-7.52 (6H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 12.5, 114.2, 119.7, 120.2, 126.4, 127.6, 127.9, 128.6, 129.0, 129.5, 129.7, 130.9, 134.7, 135.1, 135.4, 136.1, 137.1, 163.7.

FT-IR (neat, cm^{-1}): 1240, 1289, 1308, 1402, 1493, 1592, 1660, 2923, 3399.
HR-MS (*m*/*z*) for $C_{25}H_{21}Cl_2N_2O$ (M+H): Calculated 435.1031, found 435.1034 (One of the major peaks).

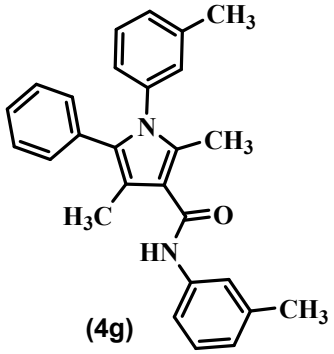
3.6. *N*,1-Bis(4-bromophenyl)-2,4-dimethyl-5-phenyl-1*H*-pyrrole-3-carboxamide (4f)



(4f)

Yield: 68% (407 mg).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.97 (3H,s), 2.23 (3H,s), 6.49 (2H, d, *J* = 2.1Hz), 6.95 (4H, d, *J* = 8,7Hz), 7.35-7.53 (3H, m), 7.53-7.57 (4H, m).
^{3}C NMR (75 MHz, $CDCl_3$): δ 11.0, 12.5, 114.3, 119.4, 120.5, 125.6, 126.3, 127.4, 128.2, 128.4, 128.9, 129.3, 130.1, 137.0, 137.2, 137.4, 138.8, 139.1, 163.9.
FT-IR (Neat, cm^{-1}): 1250, 1389, 1448, 1492, 1593, 1652, 1660, 2920, 3359.
HR-MS (*m*/*z*) for $C_{25}H_{21}Br_2N_2O$ (M+H): Calculated 523.0021, found 523.0026 (One of the major peaks).

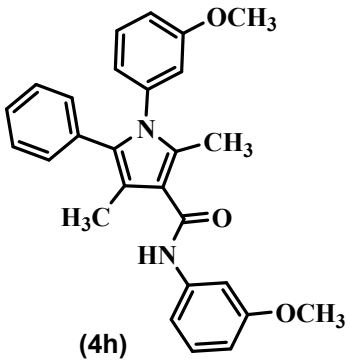
3.7. 2,4-Dimethyl-5-phenyl-*N*,1-di-3-tolyl-1*H*-pyrrole-3-carboxamide (4g)



(4g)

Yield: 64% (252 mg).
Characteristic:Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.98 (3H, s), 2.26 (3H, s), 2.36 (3H, s), 2.42 (3H, s), 6.90-7.02 (3H, m), 7.20-7.25 (2H, t, *J* = 8.1Hz), 7.28-7.57 (4H, m), 7.58-7.60 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.4, 12.6, 20.4, 22.3, 115.5, 117.6, 124.2, 125.9, 126.7, 127.2, 127.4, 128.3, 128.7, 128.8, 129.1, 129.3, 130.8, 131.0, 131.4, 132.4, 135.5, 136.2, 137.4, 164.9.
FT-IR (Neat, cm^{-1}): 1070, 1163, 1471, 1540, 1649, 2952, 3398.
HR-MS (*m*/*z*) for $C_{27}H_{27}N_2O$ (M+H): Calculated 395.2123, found 395.2126.

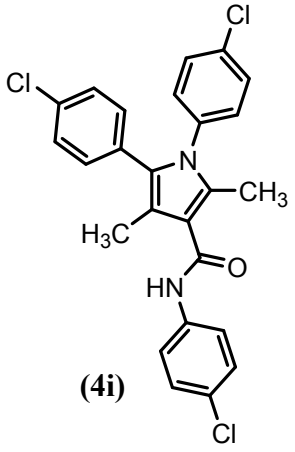
3.8. *N*,1-Bis(3-methoxyphenyl)-2,4-dimethyl-5-phenyl-1*H*-pyrrole-3-carboxamide (4h)



(4h)

Yield: 82% (349 mg).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (3H, s), 2.43 (3H, s), 3.73 (3H, s), 3.85 (3H, s), 6.46-6.54 (2H, m), 6.85 (1H, d, *J* = 9Hz), 6.91 (1H, d, *J* = 9Hz), 6.99-7.09 (4H, m), 7.39-7.45 (6H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.0, 12.5, 55.2, 55.5, 104.5, 109.3, 11.3, 114.0, 114.1, 114.3, 119.4, 120.5, 126.4, 127.4, 128.5, 128.6, 128.9, 129.3, 130.1, 131.0, 135.2, 135.4, 138.8, 139.9, 159.9, 160.4, 164.0.
FT-IR (neat, cm^{-1}): 1034,1157,1384, 1491, 1661,1737, 2836, 2921, 3064,3403.
HR-MS (*m*/*z*) for $C_{27}H_{27}N_2O_3$ (M+H): Calculated 427.2022, found 427.2026.

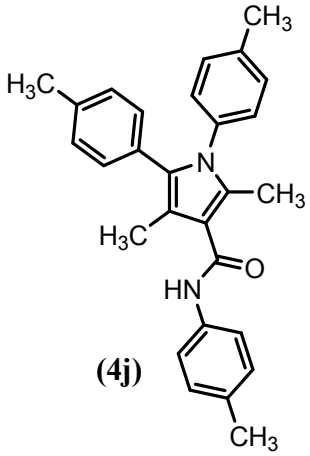
3.9. *N*,1,5-*tris*(4-Chlorophenyl)-2,4-dimethyl-1*H*-pyrrole-3-carboxamide (4i)



(4i)

Yield: 70% (328 mg).
Characteristic: colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (3H, s), 2.44 (3H, s), 7.21-7.30 (4H, m), 7.44-7.49 (2H, m), 7.55-7.65 (3H, m), 7.74-7.81 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ. 11.5, 12.8, 119.1, 124.3, 126.2, 127.7, 128.2, 128.6, 129.8, 131.5, 132.2, 133.4, 133.7, 136.5, 137.8, 141.2, 166.3.
FT-IR (Neat, cm^{-1}):. 1097, 1160, 1365, 1390, 1589, 1660, 3030, 3478.
HR-MS (*m*/*z*) for $C_{25}H_{20}Cl_3N_2O$ (M+H): Calculated 469.0641 found 468.06456 (One of the major peaks).

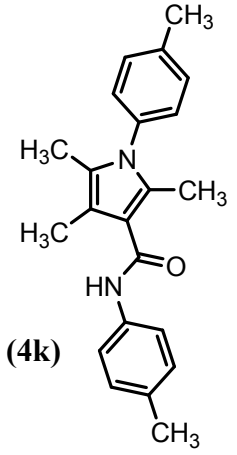
3.10. 2,4-dimethyl-*N*,1,5-trip-tolyl-1*H*-pyrrole-3-carboxamide (4j)



(4j)

Yield: 55% (225 mg)
Characteristic: yellow oil
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (3H, s), 2.26 (3H, s), 2.35 (3H, s), 2.40 (3H, s), 2.46 (3H, s), 7.04-7.21 (6H, m), 7.38-7.54 (4H, m), 7.85 (2H, d, J = 6.6 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 12.2, 21.1, 22.1, 22.5, 119.3, 124.6, 127.8,128.3, 128.4, 128.5, 129.9, 129.99, 131.5, 131.7, 132.3, 133.0, 133.5, 137.6, 141.2, 142.7, 163.9.
FT-IR (neat, cm^{-1}): 1069, 1243, 1351, 1560, 1659, 2878, 3399
HR-MS (*m*/*z*) for $C_{28}H_{28}N_2O$: Calculated 408.2206, found 409.2283 $(M+H)^+$.

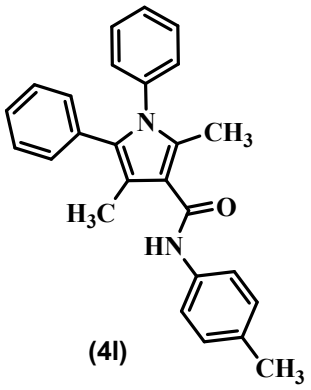
3.11. 2,4,5-trimethyl-*N*,1-dip-tolyl-1*H*-pyrrole-3-carboxamide (4k)



(4k)

Yield: 44% (145 mg)
Characteristic: Yellow oil
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.91 (3H, s), 2.22 (3H, s), 2.25 (3H, s), 2.41 (3H, s), 2.48 (3H, s), 7.11-7.27 (4H, m), 7.37 (2H, d, J = 8.1 Hz), 7.62 (2H, d, J = 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 11.2, 12.2, 12.8, 20.9, 22.2, 117.5, 119.9, 120.3, 123.0, 124.9, 125.2, 126.1, 126.4, 127.4, 128.1, 131.7, 131.8, 135.0, 166.3.
FT-IR (neat, cm^{-1}): 1169, 1283, 1541, 1590, 1638, 2957, 3380.
HR-MS (*m*/*z*) for $C_{22}H_{24}N_2O$: Calculated 332.1910, found 333.1970 $(M+H)^+$.

3.12. **2,4-dimethyl-1,5-diphenyl-*N*-*p*-tolyl-1*H*-pyrrole-3-carboxamide (4l)**



(4l)

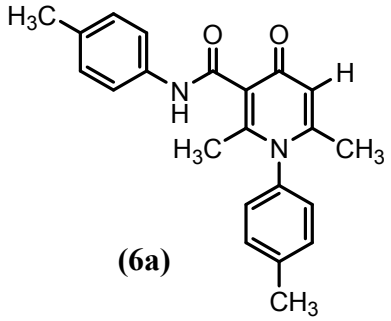
Yield: 15% (57 mg).
Characteristic: Pale yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.91 (3H,s), 2.25 (3H,s), 2.41 (3H,s), 6.99-7.04 (2H, s), 7.08-7.16 (2H, m), 7.18-7.27 (4H, m), 7.29-7.45 (3H, m), 7.46-7.55 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ. 11.1, 12.5, 20.73, 119.1, 119.4, 123.1, 126.3, 126.4, 127.3, 127.4, 128.0, 128.3, 128.5, 128.6, 128.8, 128.9, 129.1, 129.4, 131.0, 132.6, 135.0, 135.2, 135.4, 136,1, 137.8, 163.9.
FT-IR (Neat, cm^{-1}):. 1058, 1115, 1298, 1334, 1512, 1640, 2956, 3399.
HR-MS (*m*/*z*) for $C_{26}H_{25}N_2O$ (M+H): Calculated 381.1967, found 381.1969.

4. General procedure for synthesis of 4-pyridones

Acetoacetanilide derivative (2.0 mmol) was added in dry toluene (15 mL) containing bis(1,5-cyclooctadiene)nickel(0) (7 mol%, 21 mg), CuI (10mol%, 19 mg) and 2-methylfuran (0.3 mmol, 25 mg) and refluxed for 3.5-5 h in the inert condition under nitrogen atmosphere using a glove box. The reaction was monitored by thin layer chromatography (TLC). The post-reaction mixture was filtered through a sintered funnel and the filtrate was concentrated in rotary evaporator to remove toluene. The reduced mass was extracted with EtOAc (2x15 mL), and the combined organic layer was washed with water (3x10 mL) and brine (1x10 mL). It was dried over activated Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. The crude product was purified by column chromatography using silica gel (60-120 mesh) and ethyl acetate-petroleum ether (25%, v/v) as an eluent. The synthesized subtituted pyridones (**6a-6i**) were characterized by means of NMR (^{1}H and ^{13}C), FT-IR and mass (HR-MS) spectral analyses and measuring melting points.

5. Characterization of the compounds synthesized following the above general procedure for the formation of substituted pyridone derivatives (6a-6i)

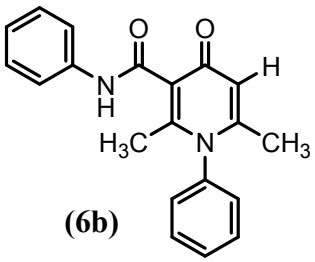
5.1. 2,6-Dimethyl-4-oxo-*N*,1-di-4-totyl-1,4-dihydropyridine-3-carboxamide (6a)[1]



(6a)

Yield: 81% (280 mg).
Characteristic: Colorless crystalline solid.
m.p.: 242-243 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.94 (3H, s), 2.33 (3H, s), 2.40 (3H, s), 2.52 (3H, s), 6.54 (1H, s), 7.07-7.15 (4H, m), 7.37 (2H, d, *J*=8.1 Hz), 7.60 (2H, d, *J*=8.4 Hz), 12.51 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ. 20.7, 20.8, 21.1, 21.7, 118.7, 119.2, 120.7, 127.4, 129.2, 129.4, 130.9, 133.1, 136.4, 137.0, 140.2, 156.3, 164.0, 177.7.
FT-IR (KBr, cm^{-1}):. 1155, 1215, 1388, 1474, 1572, 1680, 3056, 3419
HR-MS (*m*/*z*) for $C_{22}H_{22}N_2O_2$: Calculated 346.1681, found 346.1682

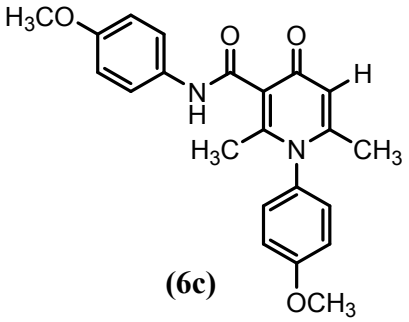
5.2. 2,6-Dimethyl-4-oxo-*N*,1-diphenyl-1,4-dihydropyridine-3-carboxamide (6b)[1]



(6b)

Yield: 74% (235 mg).
Characteristic: Colorless crystalline solid.
m.p.: 201-213 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (3H, s), 2.49 (3H, s), 6.49 (1H, s), 7.02-7.07 (2H, m), 7.17-7.19 (2H, m), 7.20-7.32 (2H, m), 7.53-7.55 (2H, m), 7.58-7.70 (2H, m), 12.66 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ. 20.8, 21.7, 118.8, 120.7, 123.6, 127.7, 128.7, 130.0, 130.4, 139.0, 139.5, 148.5, 156.2, 164.2, 177.9.
FT-IR (KBr, cm^{-1}):. 1090, 1215, 1399, 1484, 1592, 1675, 2656, 3369.
HR-MS (*m*/*z*) for $C_{20}H_{18}N_2O_2$: Calculated 318.1368, found 318.1371.

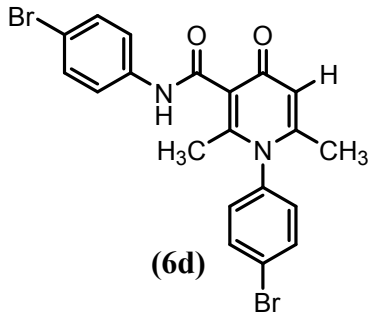
5.3. *N*,1-Bis(4-methoxyphenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamide (6c)[1]



(6c)

Yield: 82% (309 mg).
Characteristic: Colorless crystalline solid.
m.p.: 212-213 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85 (3H, s), 2.44 (3H, s), 3.71 (3H, s), 3.80 (3H, s), 6.41 (1H, s), 6.77-6.81 (2H, m), 6.94-7.04 (4H, m), 7.52-7.56 (2H, m), 12.47 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 21.7, 55.4, 55.6, 113.9,115.3, 118.7, 118.9, 122.1, 128.7, 132.2, 148.9, 155.8, 156.6, 160.2, 163.9, 177.9.
FT-IR (Neat, cm^{-1}):. 1158, 1225, 1378, 1474, 1519, 1679, 2996, 3369
HR-MS (*m*/*z*) for $C_{22}H_{22}N_2O_4$: Calculated 378.1580, found 378.1585.

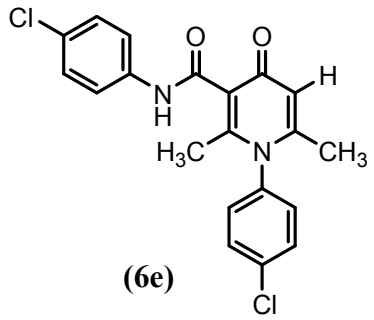
5.4 . *N*,1-bis(4-bromophenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamide(6d)



(6d)

Yield: 78% (371 mg).
Characteristic: Colorless crystalline solid.
m.p.: 231-233 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.84 (3H, s), 2.43 (3H, s), 6.42 (1H, s), 7.00-7.05 (2H, m), 7.32-7.38 (2H, m), 7.50-7.55 (2H, m), 7.63-7.66 (2H, m), 12.71 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ.20.7, 21.7, 116.0, 118.6, 119.0, 122.1, 124.3, 129.3, 131.6, 133.7, 138.0, 138.4, 148.1, 156.2, 163.9, 177.8.
FT-IR (KBr, cm^{-1}):. 1034, 1235, 1348, 1454, 1572, 1660, 2346, 3289.
HR-MS (*m*/*z*) for $C_{20}H_{16}Br_2N_2O_2$: Calculated 473.9579, found 473.9576 (One of the major peaks).

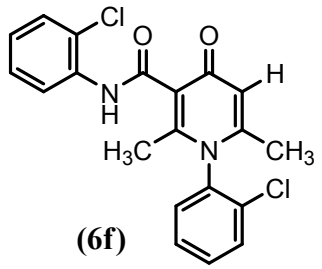
5.5. *N*,1-Bis(4-chlorophenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamide(6e)[1]



(6e)

Yield: 77% (298 mg).
Characteristic: Colorless crystalline solid.
m.p.: 269-270 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (3H, s), 2.49 (3H, s), 6.49, (1H, s), 7.22 (2H, d, *J* = 8.4 Hz), 7.29 (2H , d, *J* = 8.4 Hz), 7.59 (2H , d, *J* = 8.8 Hz), 7.68 (2H , d, *J*= 8.8 Hz), 12.92 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 21.5, 119.6, 119.4, 121.4, 127.3, 128.3, 129.4, 131.7, 135.3, 138.6, 138.8, 149.3, 157.2, 165.0, 178.8.
FT-IR (KBr, cm^{-1}):. 1238, 1235, 1358, 1464, 1592, 1690, 2896, 3349.
HR-MS (*m*/*z*) for $C_{20}H_{16}Cl_2N_2O_2$: Calculated 386.0589, found 386.0593 (One of the major peaks).

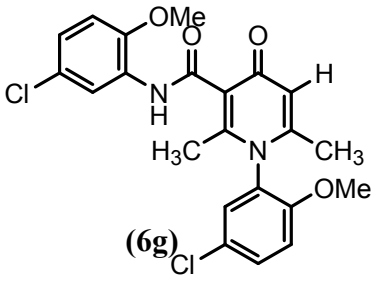
5.6. *N*,1-Bis(2-chlorophenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamide (6f)[1]



(6f)

Yield: 75% (290 mg).
Characteristic: Colorless crystalline solid.
m.p.: 185-186 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (3H, s), 2.52 (3H, s), 6.59 (1H, s), 7.00-7.05 (1H, m), 7.27-8.48 (1H, m), 7.40 (dd, *J* = 2.0, 5.6 Hz, 1H), 7.47 (dd, *J* = 1.2, 6.8 Hz, 1H), 7.50−7.55 (m, 2H), 7.67 (dd, *J* = 2.0, 6.0 Hz, 1H), 8.29 (dd, *J* = 1.2, 6.8 Hz, 1H), 13.06 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4, 21.2, 118.6, 119.3, 123.6, 124.5, 124.7, 127.0, 127.8, 129.6, 129.8, 132.6, 133.6, 137.3, 139.1, 149.1, 155.5, 163.3, 179.1.
FT-IR (KBr, cm^{-1}):. 1239, 1239, 1363, 1474, 1584, 1680, 2856, 3369.
HR-MS (*m*/*z*) for $C_{20}H_{16}Cl_2N_2O_2$: Calculated 386.0589, found 386.0594 (One of the major peaks).

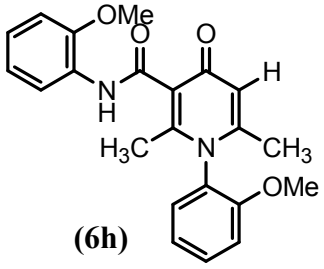
5.7. *N*,1-Bis(5-chlorophenyl-2methoxyphenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamide (6g)[1]



(6g)

Yield: 74% (165 mg).
Characteristic: Colorless crystalline solid.
m.p.: 215-216 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (3H, s), 2.52 (3H, s), 3.83 (3H, s), 3.96 (3H, s), 6.55 (1H, s), 6.82 (1H, d, J = 8.8 Hz), 7.00 (1H, dd, *J* = 2.4, 6.4 Hz), 7.05 (1H, d, J = 9.2 Hz), 7.20 (1H, d, J = 2.4 Hz), 7.50 (1H, dd, *J* = 2.4, 6.4 Hz), 8.61 (1H, d, J = 2.4 Hz), 12.98 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 20.8, 56.2, 56.3, 110.7, 113.3, 118.9, 120.4, 122.5, 125.4, 126.2, 128.5, 128.8, 129.8, 131.6, 147.8, 148.4, 153.1, 156.5, 164.1, 178.1.
FT-IR (KBr, cm^{-1}): 1025, 1136, 1179, 1424, 1499, 1736, 1680, 2946, 3509.
HR-MS (*m*/*z*) for $C_{22}H_{20}Cl_2N_2O_2$: Calculated 446.0800, found 446.0803 (One of the major peaks).

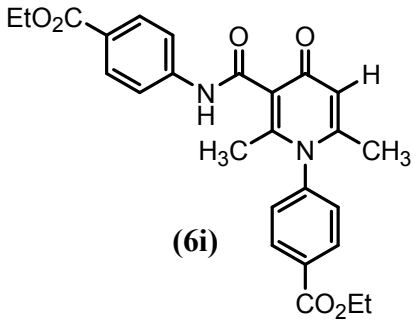
5.8. *N*,1-Bis(2-methoxyphenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamide (6h)[1]



(6h)

Yield: 81% (154 mg).
Characteristic: Colorless crystalline solid.
m.p.: 240-242 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.86 (3H, s), 2.47 (3H, s), 3.80 (3H, s), 3.96 (3H, s), 6.51 (1H, s), 6.95-6.90 (2H, m), 7.10-7.13 (4H, m), 7.48-7.50 (1H, m), 8.51 (1H, d, J = 7.6 Hz), 12.75 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 20.9, 55.8, 55.9, 110.2, 112.4, 118.7, 119.3, 120.6, 120.8, 121.6, 123.2, 128.0, 128.8, 128.9, 131.6, 148.8, 149.3, 154.3, 156.5, 164.3, 178.0.
FT-IR (KBr, cm^{-1}): 1020, 1124, 1276, 1345, 1461, 1599, 1668, 2966, 3629.
HR-MS (*m*/*z*) for $C_{22}H_{22}N_2O_4$: Calculated 378.1580, found 378.1582.

5.9. Ethyl 4-(1-(ethoxycarbonyl)phenyl)-2,6-dimethyl-4-oxo-1,4-dihydropyridine-3-carboxamidobenzoate (6i)[1]



(6i)

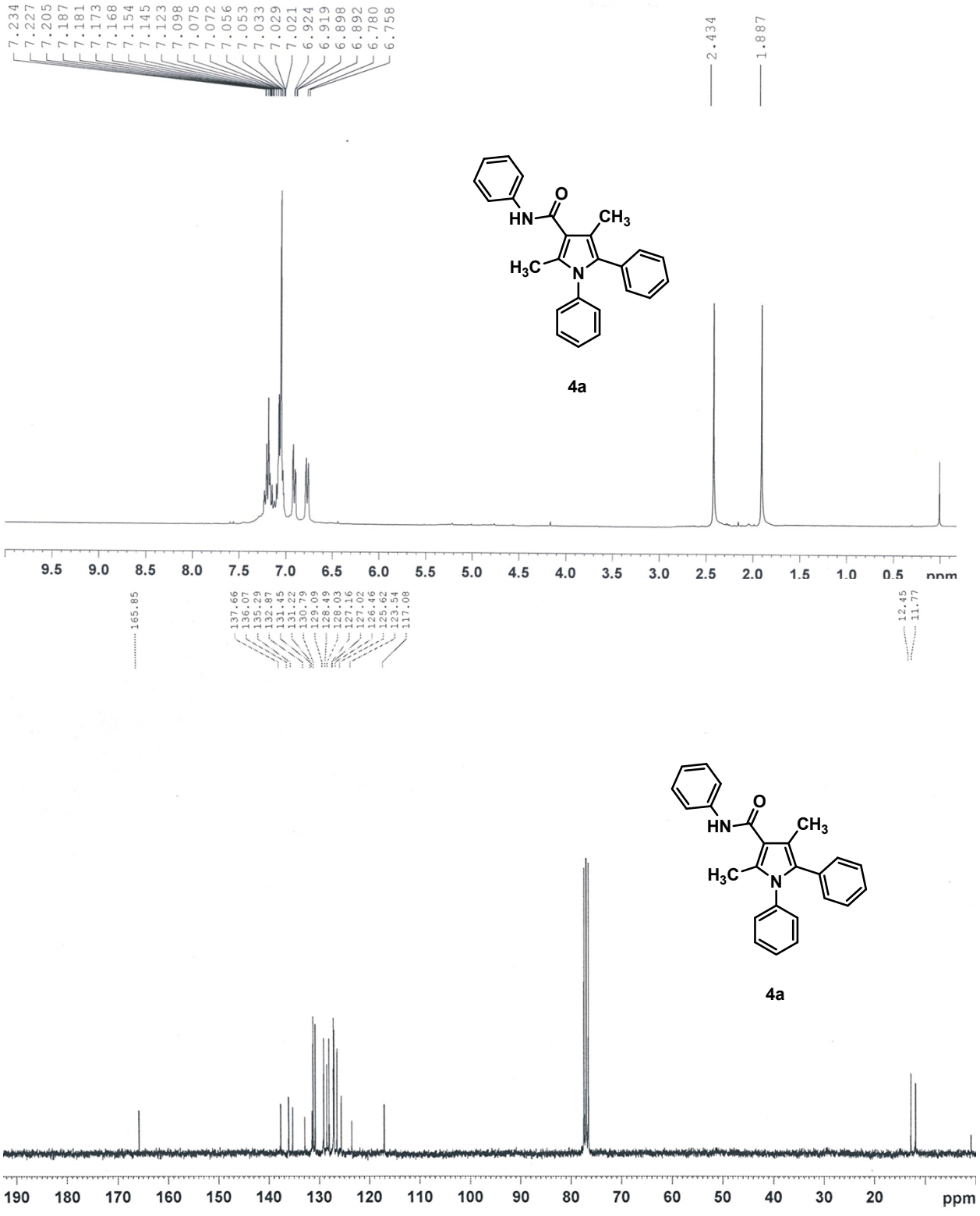
Yield: 79% (183 mg).
Characteristic: Colorless crystalline solid.
m.p.: 180-181 ºC
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (3H, t, J = 7.2 Hz), 1.44 (3H, t, J = 7.2 Hz), 1.92 (3H, s), 2.52 (3H, s), 4.34 (2H, q, J = 7.2 Hz), 4.45 (2H, q, J = 7.2 Hz),6.52 (1H, s), 7.35 (2H, d, J = 8.4 Hz), 7.78 (2H, d, J = 8.8 Hz), 8.00 (2H, d, *J* = 8.8 Hz), 8.28 (2H, d, J = 8.4 Hz), 13.14 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 20.9, 21.8, 60.6, 61.8, 118.4, 119.2, 119.6, 125.1, 128.0, 130.0, 131.8, 132.3, 143.0, 143.1, 148.1, 156.4, 164.3, 164.8, 166.5, 178.0.
FT-IR (KBr, cm^{-1}): 1042, 1199, 1444, 1521, 1677, 2400, 3060, 3665.
HR-MS (*m*/*z*) for $C_{26}H_{26}N_2O_6$: Calculated 462.1791, found 462.1789.

6. References

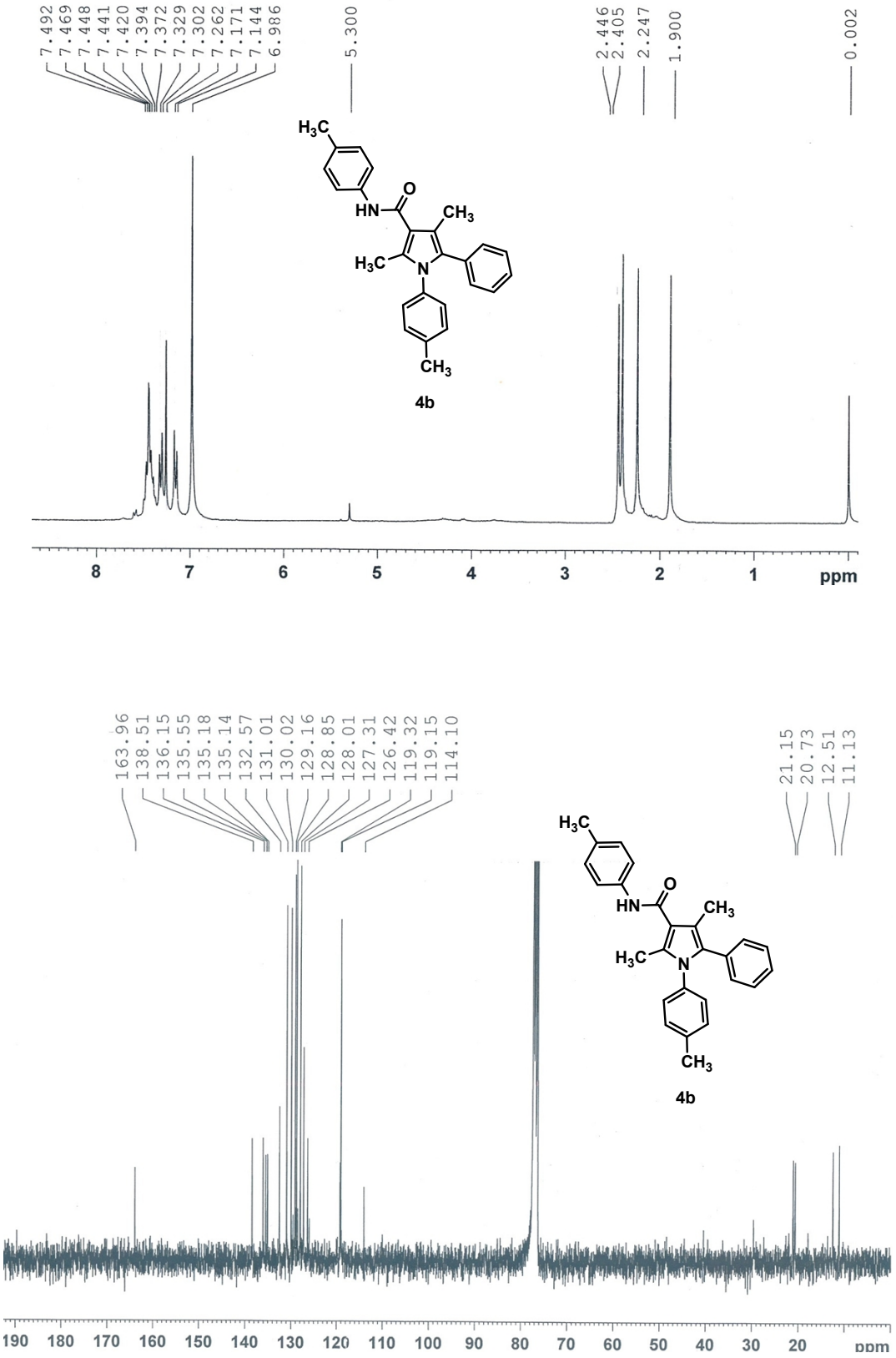
1. Z. Zhang, S. Fang, Q. Liu and G. Zhang, *J. Org. Chem.,* 2012, **77**, 7665;

7. ^{1}H and ^{13}C-NMR spectra of the compounds (4a-4l)

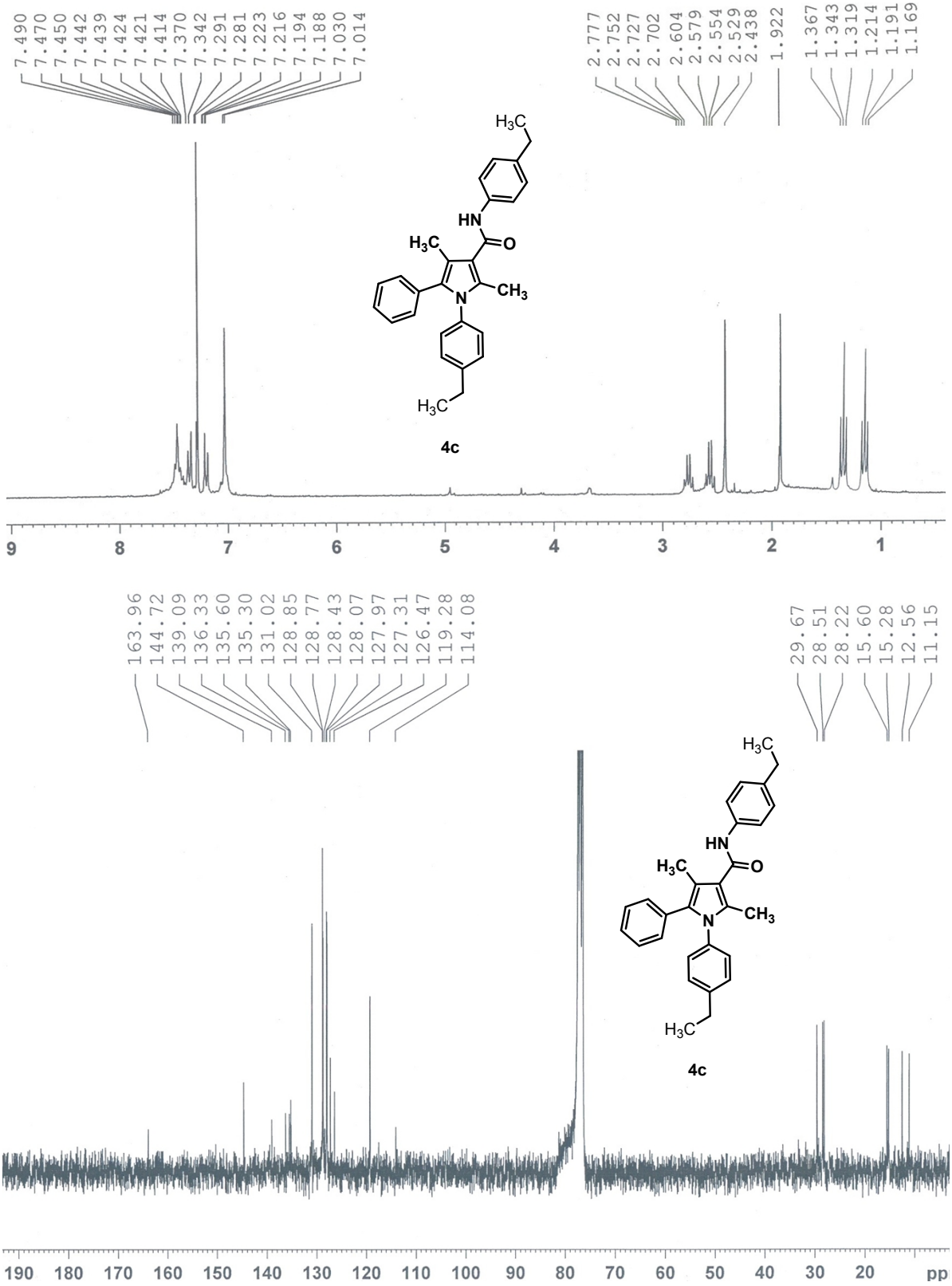
SI Figure 1: ^{1}H and ^{13}C-NMR spectra of compound **4a**



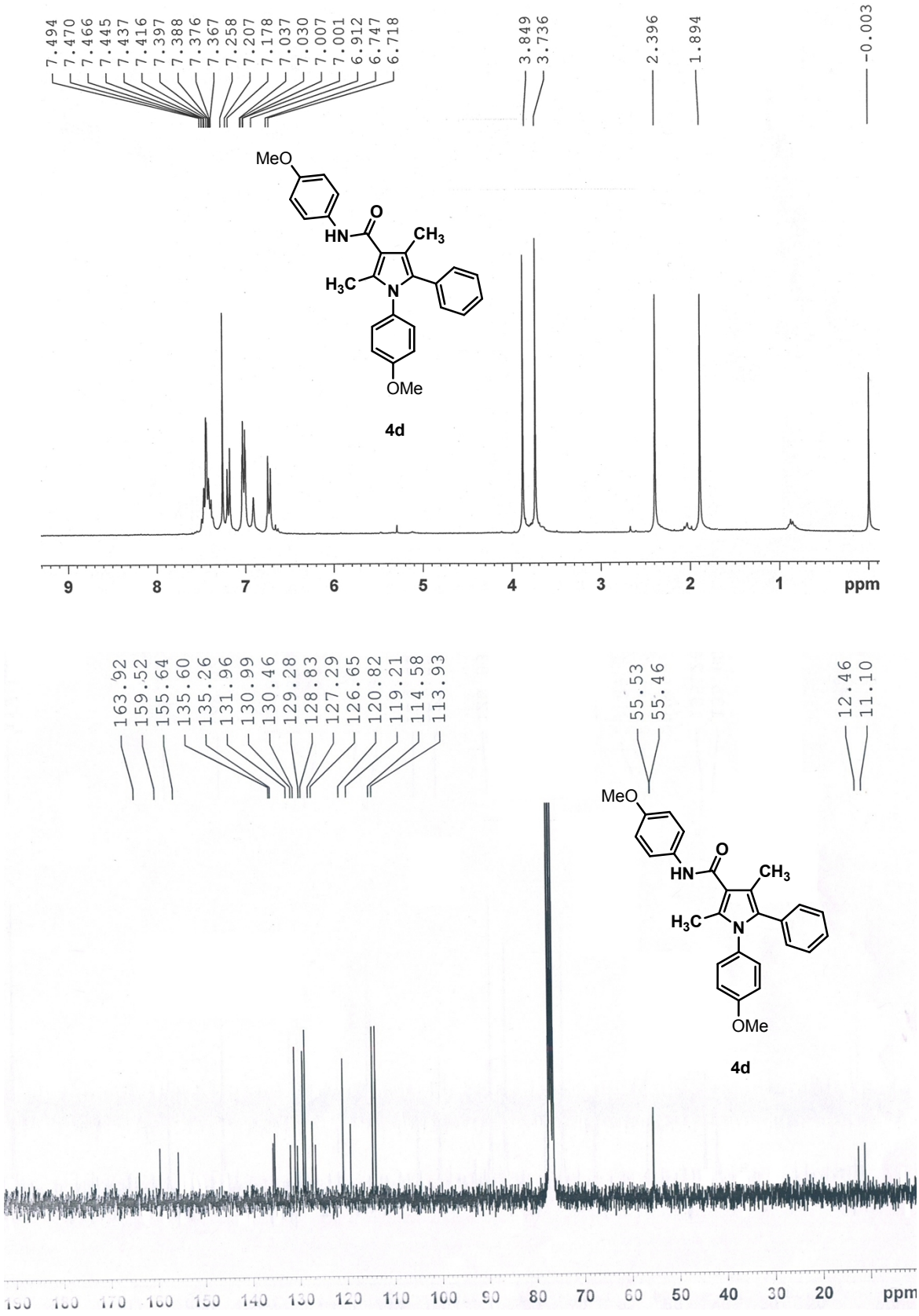
SI Figure 2: ^{1}H and ^{13}C-NMR spectra of compound **4b**



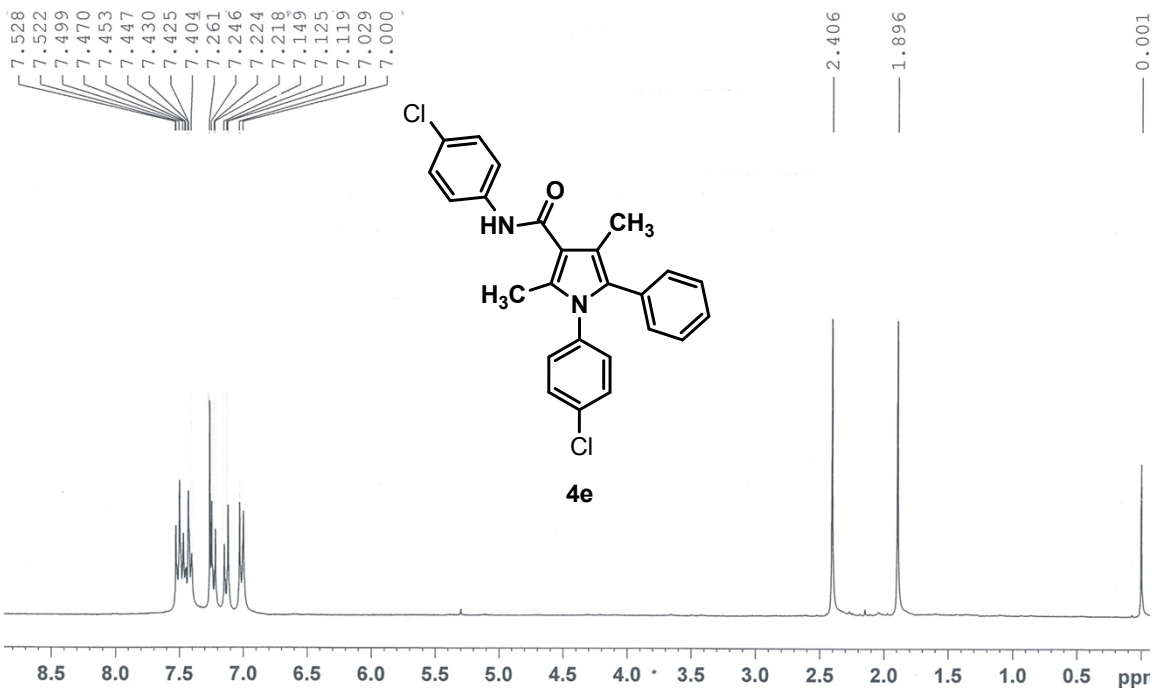
SI Figure 3: ^{1}H and ^{13}C-NMR spectra of compound **4c**

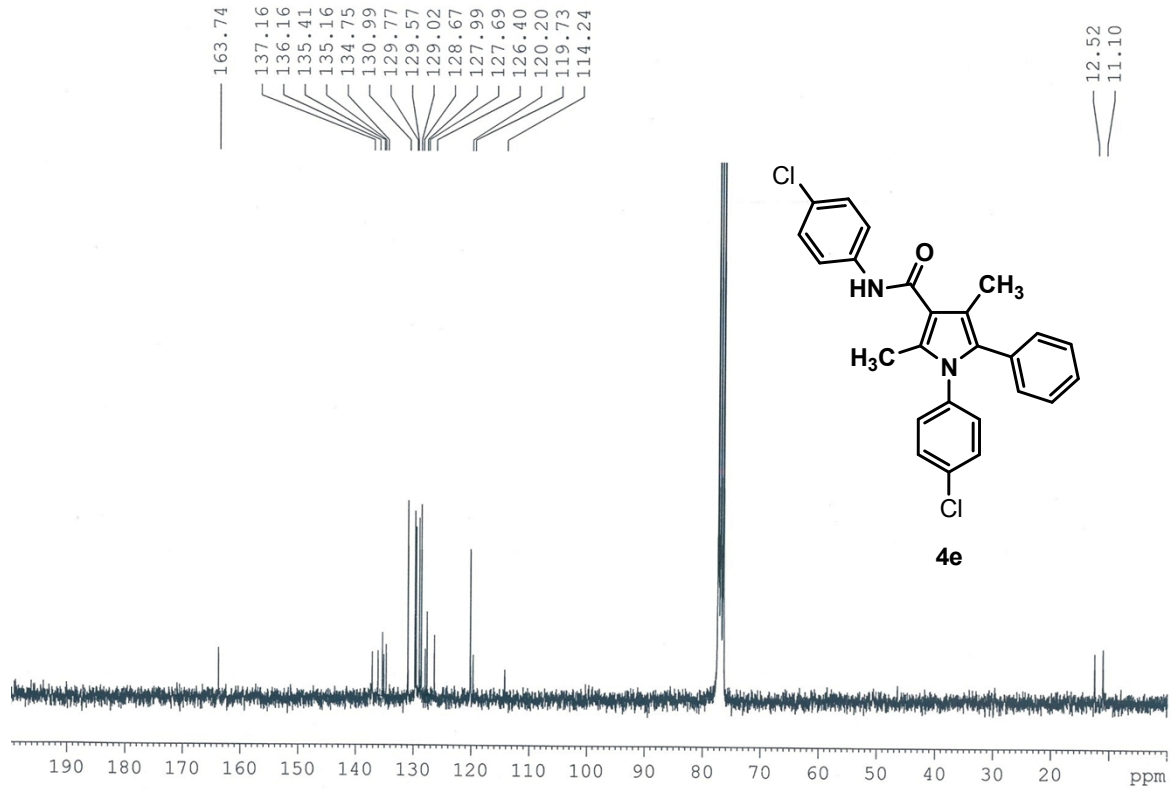


SI Figure 4: ^{1}H and ^{13}C-NMR spectra of compound **4d**

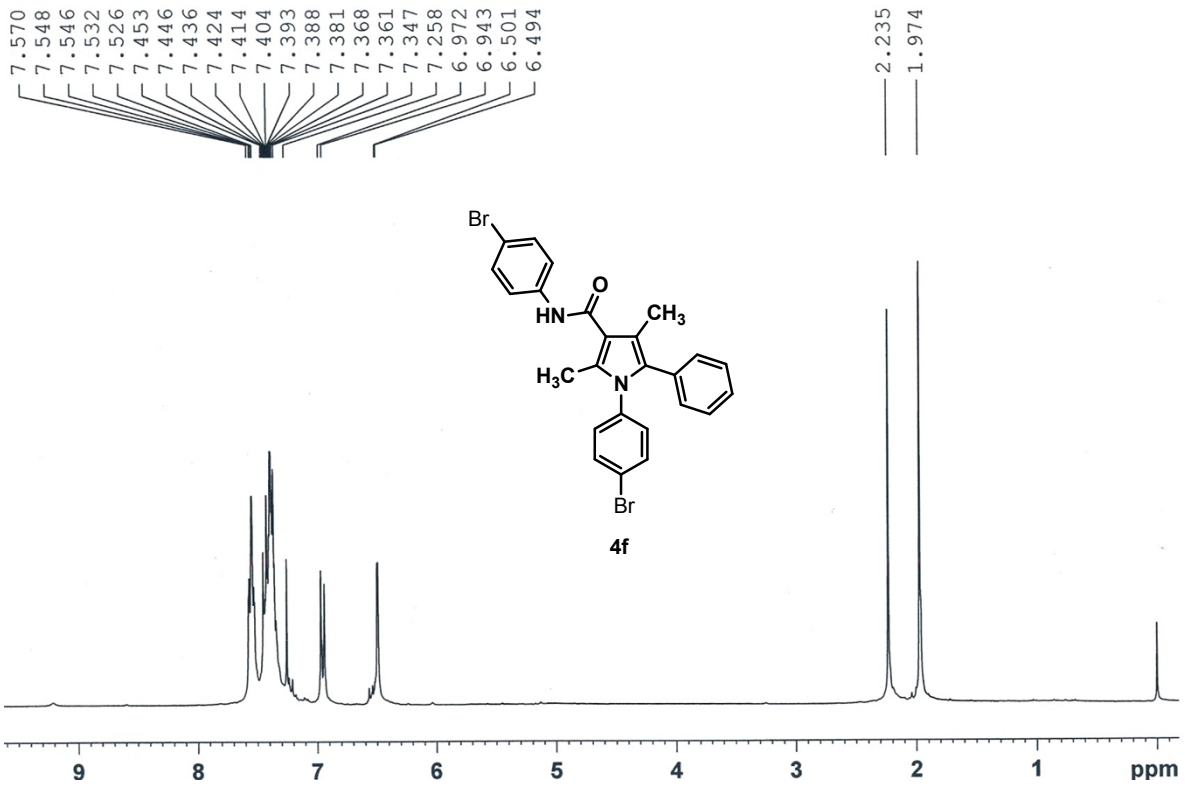


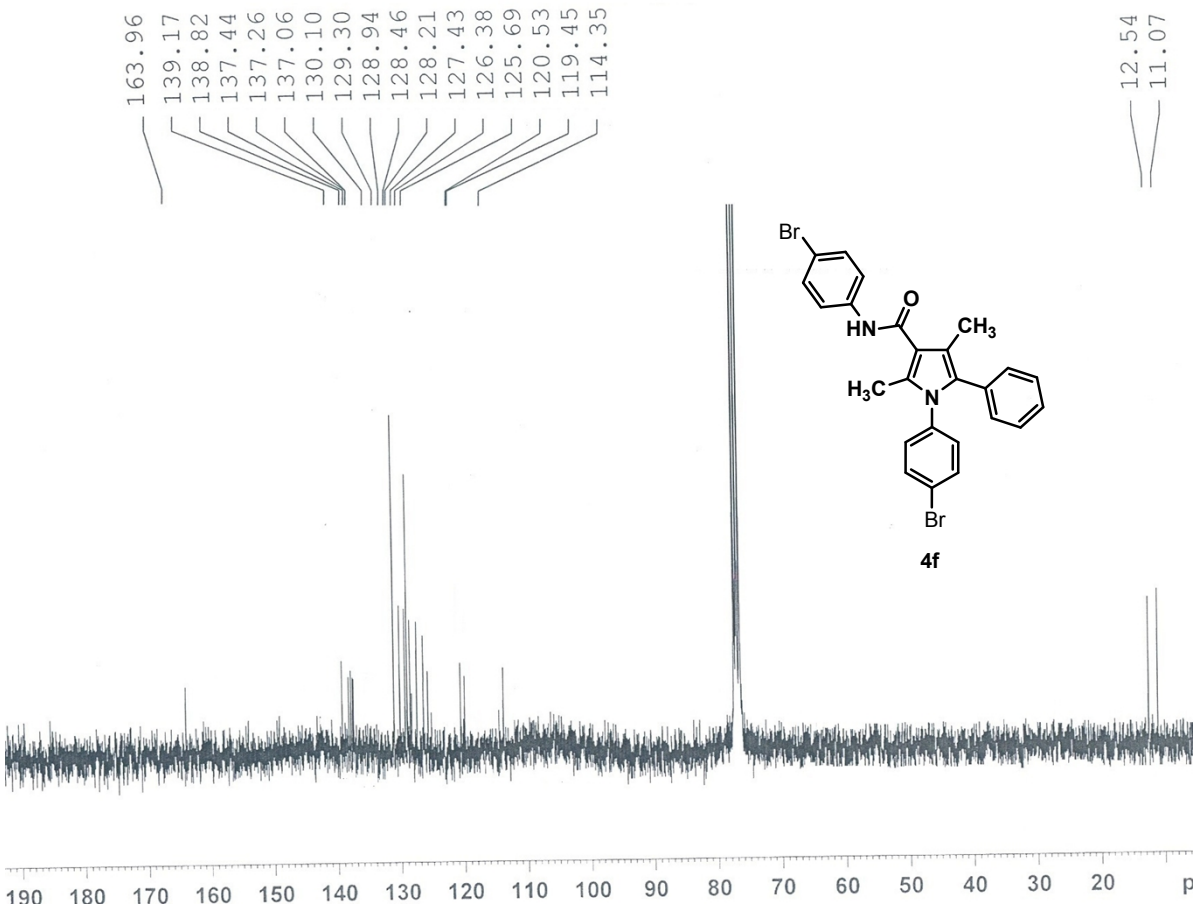
SI Figure 5: ^{1}H and ^{13}C-NMR spectra of compound **4e**



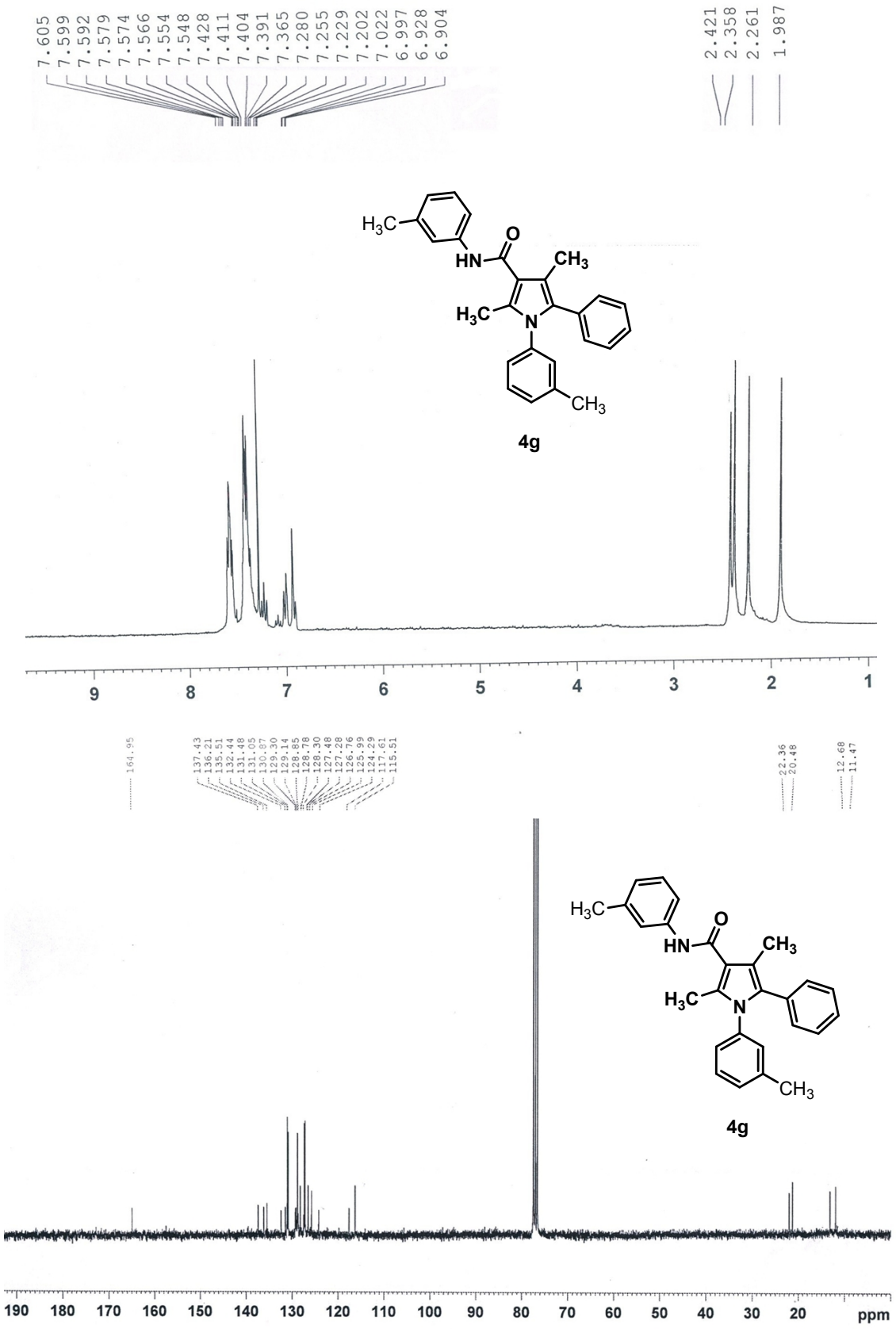


SI Figure 6: ^{1}H and ^{13}C-NMR spectra of compound **4f**

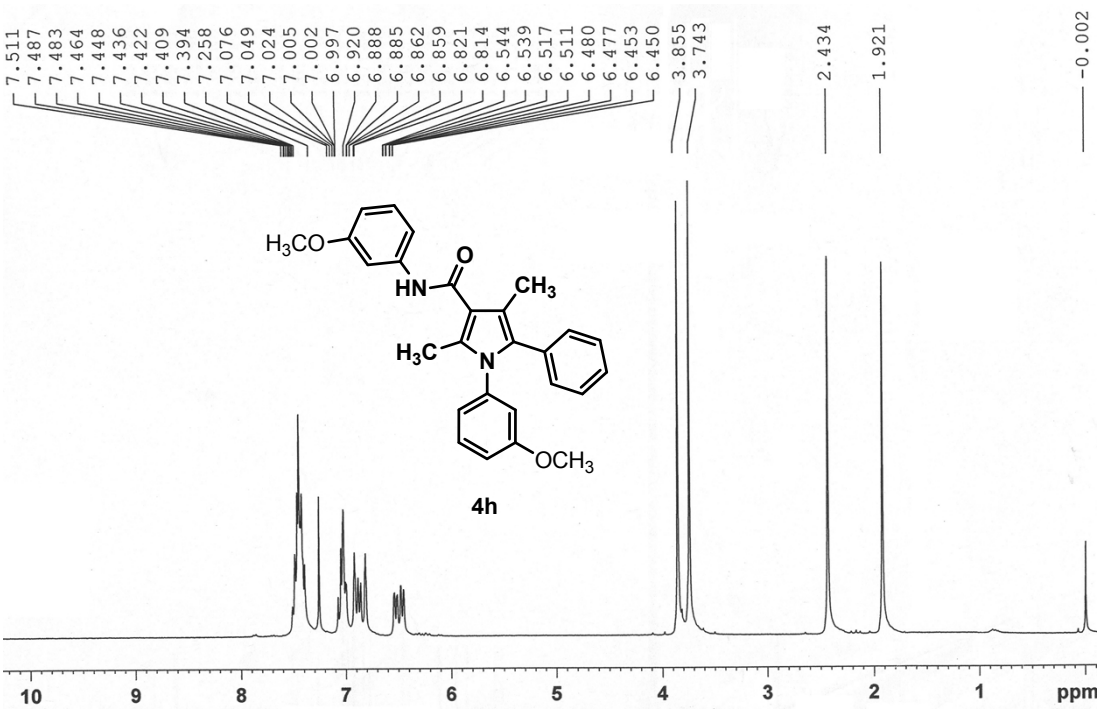


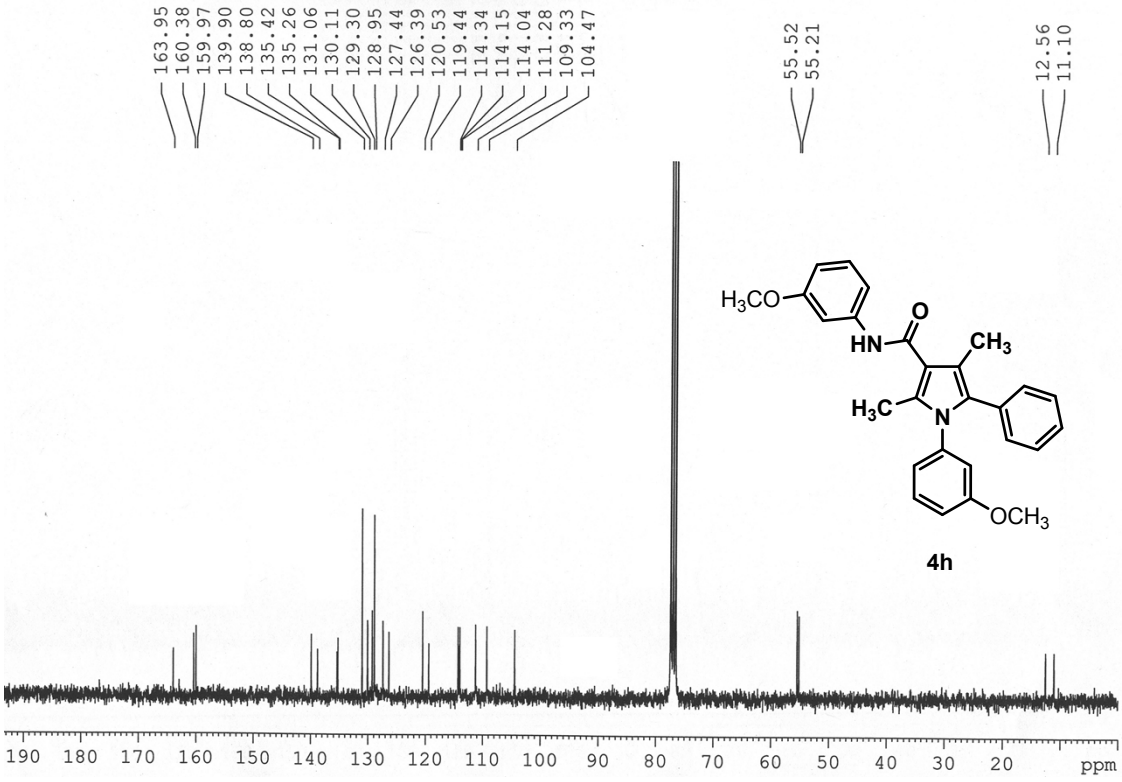


SI Figure 7: ^{1}H and ^{13}C-NMR spectra of compound **4g**

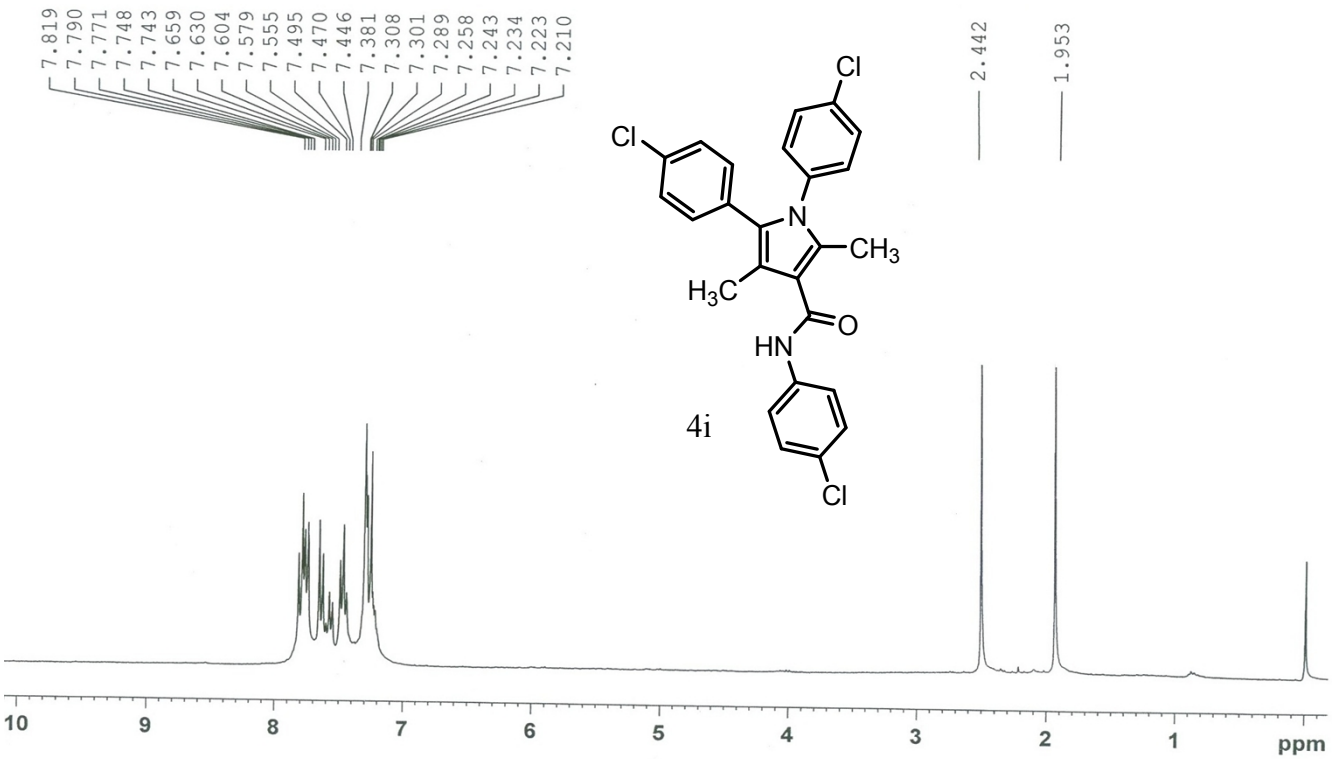


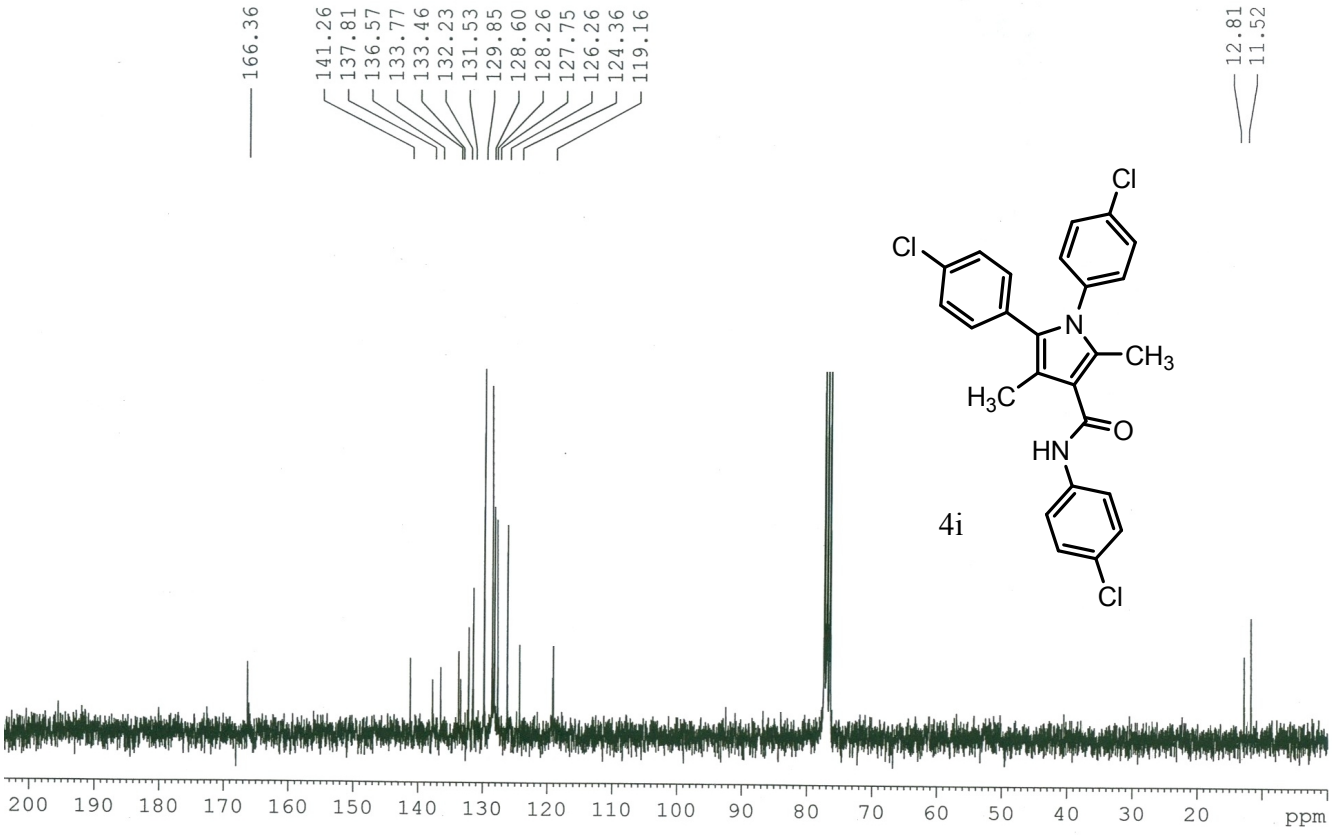
SI Figure 8: ^{1}H and ^{13}C-NMR spectra of compound **4h**



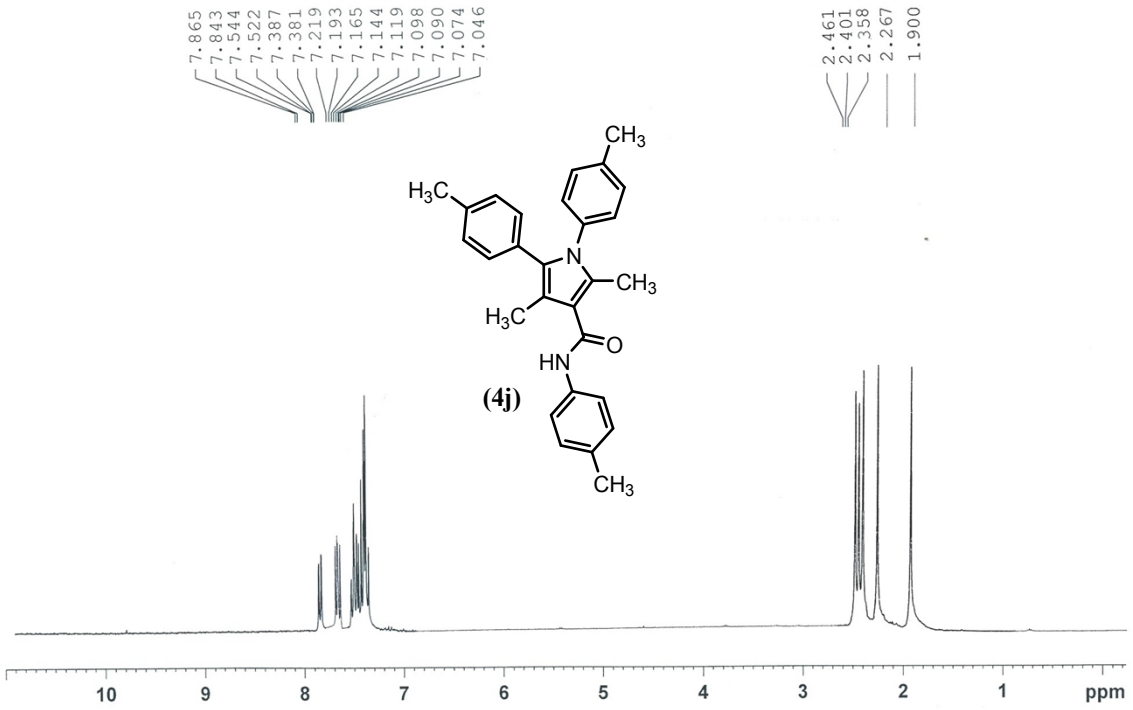


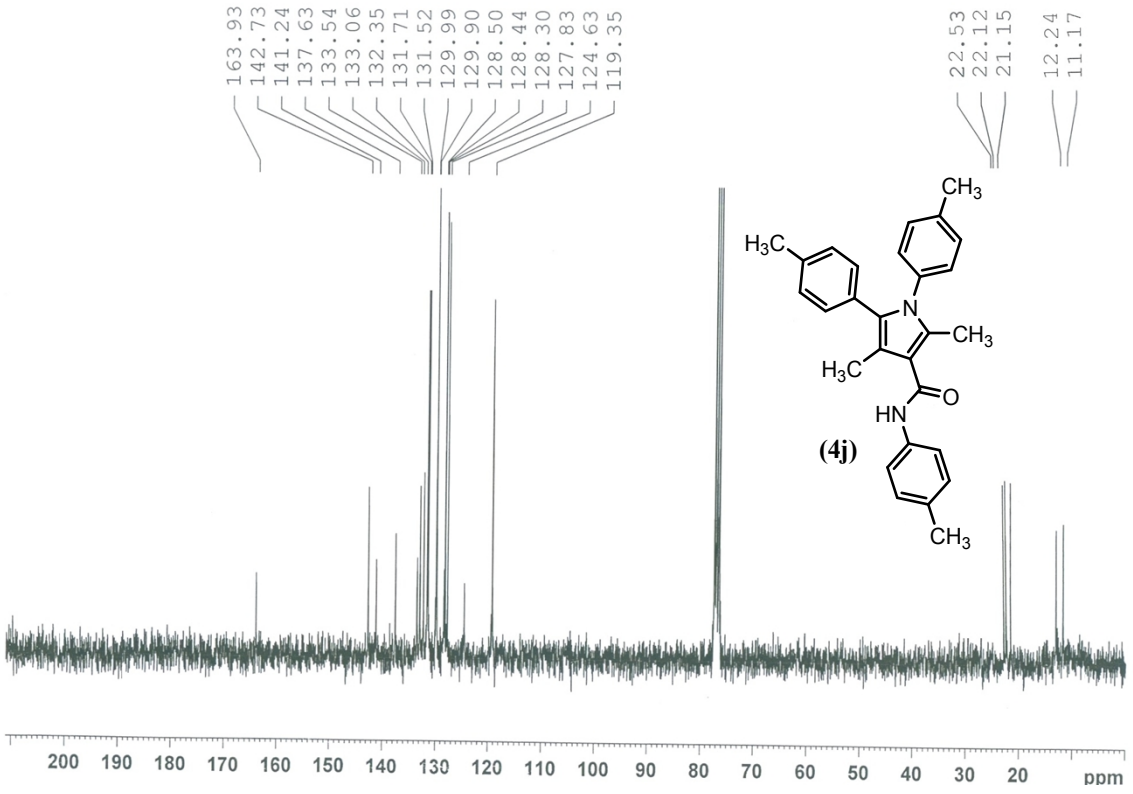
SI Figure 9: ^{1}H and ^{13}C-NMR spectra of compound **4i**



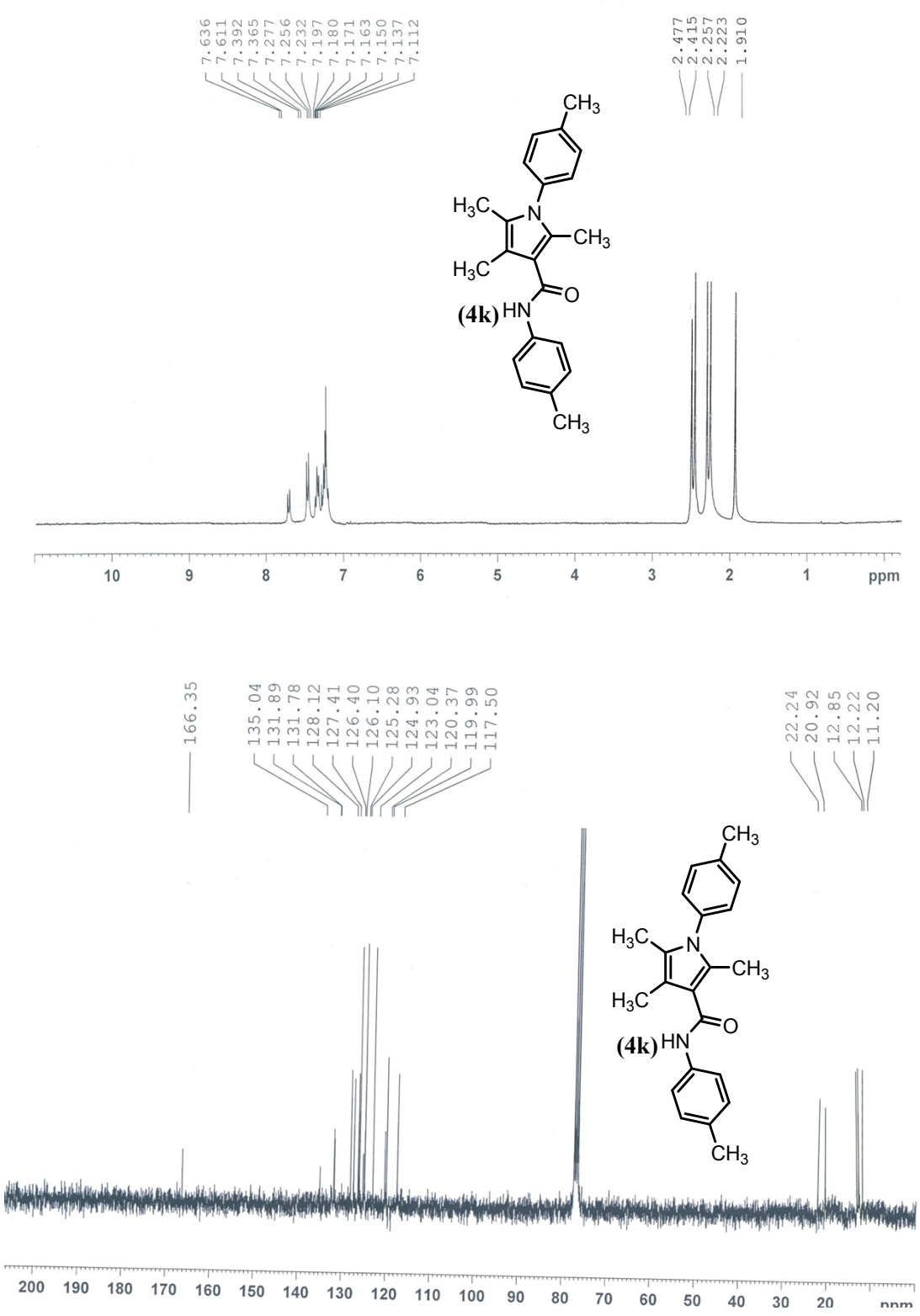


SI Figure 10: ^{1}H and ^{13}C-NMR spectra of compound **4j**

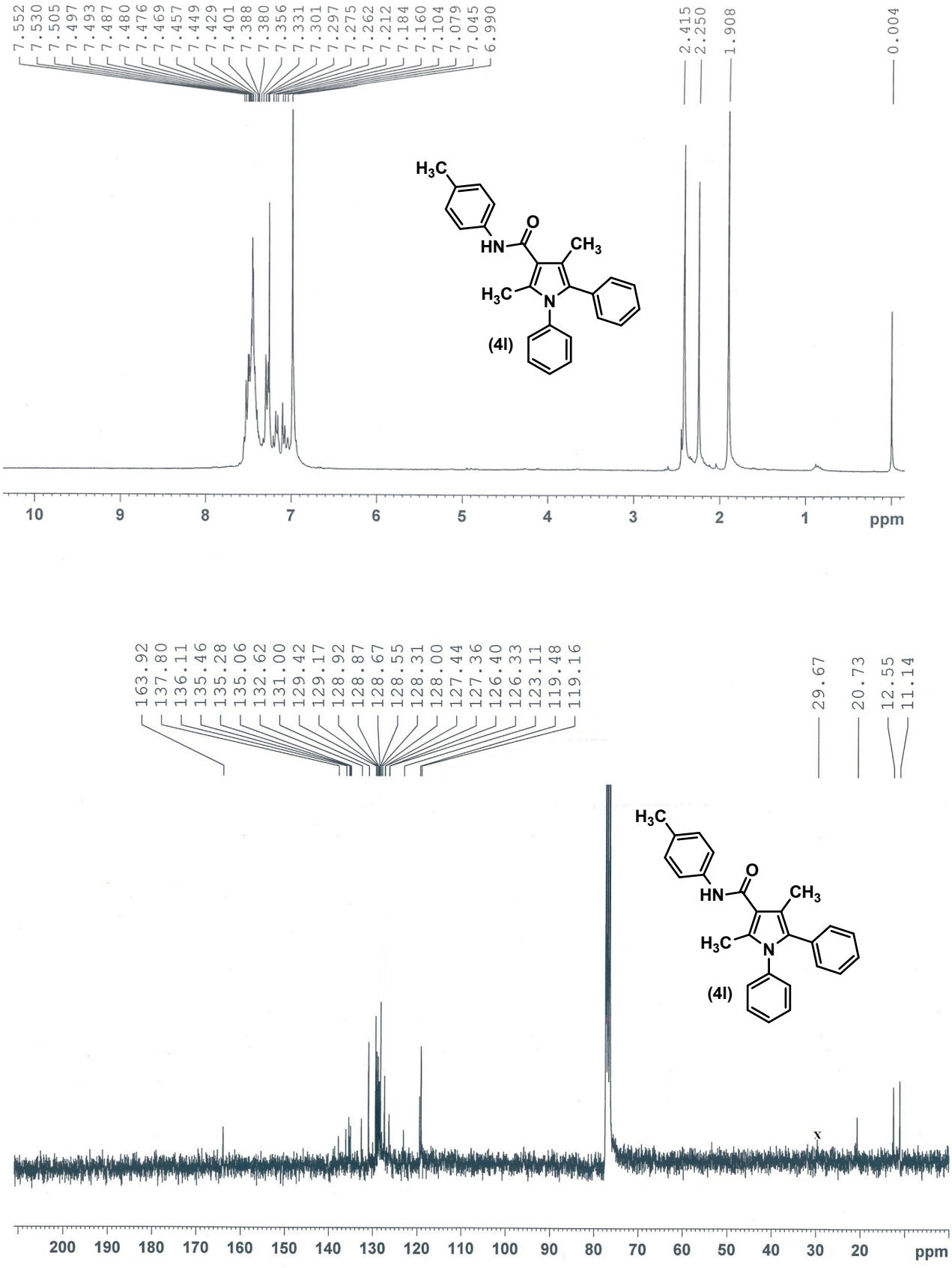

7.865
7.843
7.544
7.522
7.387
7.381
7.219
7.193
7.165
7.144
7.119
7.098
7.090
7.074
7.046
2.461
2.401
2.358
2.267
1.900
CH3
H3C
N
CH3
H3C
O
HN
CH3
(4j)
10
9
8
7
6
5
4
3
2
1
ppm


163.93
142.73
141.24
137.63
133.54
133.06
132.35
131.71
131.52
129.99
129.90
128.50
128.44
128.30
127.83
124.63
119.35
22.53
22.12
21.15
12.24
11.17
CH3
H3C
N
CH3
H3C
O
HN
(4j)
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

SI Figure 11: ^{1}H and ^{13}C-NMR spectra of compound **4k**



SI Figure 12: ^{1}H and ^{13}C-NMR spectra of compound **4l**



7. ^{1}H and ^{13}C-NMR spectra of the compounds (6d)

SI Figure 11: ^{1}H and ^{13}C-NMR spectra of compound **6d**