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Diversifying the superbase-catalyzed C=N bond ethynylation: triaryl-1-pyrrolines and triaryl-1*H*-pyrroles from *N*-benzyl aldimines and arylacetylenes

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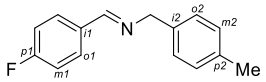
1. General information

^{1}H (400.1 MHz), ^{13}C (100.6 MHz), and ^{15}N (40.5 MHz) NMR spectra were recorded on a Bruker AV400 instrument in $CDCl_3$. The assignment of signals in the ^{1}H NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The ^{1}H and ^{13}C chemical shifts (δ) were referenced to hexamethyldisiloxane (0.05 ppm and 2.0 respectively). The chemical shifts were recorded in ppm. Coupling constants (*J*) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet). The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment. The ^{15}N chemical shifts were referenced to CH_3NO_2. IR spectra were taken with FT-IR. Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium foil sheets (eluent: hexane/ethyl acetate= 10:1 or 1:1) and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel, 70-230 mesh, pore size 60 Å (eluent: hexane/diethyl ether).

2. Starting materials

Imines **1** were synthesized by published procedures from ketones and amines in the presence of PCl_5.[S1] Physical-chemical characteristics of imines **1a-d** were identical to the literature data.[S2] Ketones, amines, acetylenes and all other chemicals and solvents are commercially available and were used without further purification.

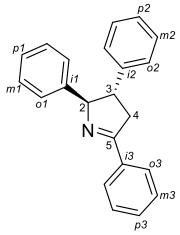
((*E*)-1-(4-Fluorophenyl)-*N*-(4-methylbenzyl)methanimine (**1e**).



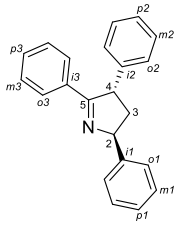
Compound **1e** was prepared from 4-fluorobenzaldehyde (20 mmol, 2.482 g) and *p*-tolylmethanamine (20 mmol, 2.424 g) and was isolated as light yellow crystal (3.364 g, 74% yield). Elemental analysis calcd (%) for $C_{15}H_{14}FN$ (227.28): C, 79.27; H, 6.21; F, 8.36; N, 6.16; found: C, 79.53; H, 6.17; F, 8.27; N, 6.03. ^{1}H NMR: δ 8.35 (s, 1H, C<u>H</u>=N), 7.88 – 7.64 (m, 2H, H^{o1}), 7.27–7.20 (m, 2H, H^{o2}), 7.20–7.14 (m, 2H, H^{m2}), 7.15–7.05 (m, 2H, H^{m1}), 4.78 (s, 2H, N-CH_2), 2.36 (s, 3H, *p2*-<u>Me</u>). ^{13}C NMR: δ 164.37 (d, ^{1}J = 250.6 Hz, C^{p1}), 160.21 (CH=N), 136.68, 136.22 (C^{i2,p2}), 132.63 (d, ^{4}J = 2.2 Hz, C^{i1}), 130.20 (d, ^{3}J = 8.6 Hz, C^{o1}), 129.29, 128.04 (C^{o2,m2}), 115.70 (d, ^{2}J = 21.8 Hz, C^{m1}), 64.78 (N-CH_2), 21.17 (Me). IR (film, ν/cm^{-1}): 3048, 3025, 2921, 2851, 2817, 1646, 1599, 1510, 1438, 1415, 1374, 1337, 1295, 1231, 1152, 1097, 1043, 909, 838, 804, 733.

3. Synthesis of pyrrolines 3 *(typical procedure 1)*.
A mixture of imine **1** (2 mmol), arylacetylene **2** (2 mmol) and Bu^{t}OK (0.4 mmol, 0.045 g) in DMSO (6 ml) was stirred at 60 ^{o}C (oil bath) for 15 min. The reaction mixture was diluted with solution of K_2CO_3 (0.4 g) in H_2O (10 ml) and extracted with Et_2O (7 × 2 ml). The organic extract was washed with H_2O (3 × 2 ml) and dried over K_2CO_3 for 1 h. Et_2O was evaporated under reduced pressure. A mixture of pyrrolines **3** and **3'** was isolated by column chromatography [SiO_2, eluent: ethyl acetate/hexane = 1:10 (for **3a,b,d-g,i,j**); eluent: ethyl acetate/hexane = 1:1 (for **3c**,**h,k**)].

Following the typical procedure 1, **3a**+**3'a** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2a** (2 mmol, 0.204 g) and was isolated as a colourless oil (0.268 g, 45% total yield). (2*R**,3*S**)-2,3,5-triphenyl-3,4-dihydro-2*H*-pyrrole (**3'a**, major tautomer). Pure **3'a** was isolated from as a colorless solid (0.208 g, 35% yield) by recrystallization (from hexane) of the crude product. M. p. = 90-93 °C. Elemental analysis calcd (%) for $C_{22}H_{19}N$ (297.15): C, 88.85; H, 6.44; N, 4.71; found: C, 88.69; H, 6.52; N, 4.79. R_f = 0.35 (hexane – diethyl ether = 3:1).



^{1}H NMR: δ 7.99-7.93 (m, 2H, H^{o3}), 7.49-7.40 (m, 3H, H^{o3,p3}), 7.37-7.14 (m, 10H, H$_{Ph}$), 5.31 (d, ^3J 6.7 Hz, 1H, H^2), 3.62 (dd, ^2J 17.0 Hz, ^3J 9.4 Hz, 1H, H^4), 3.42 (ddd, ^3J = 9.4 Hz, ^3J = 7.6 Hz, ^3J 6.7 Hz, 1H, H^3), 3.20 (dd, ^2J 17.0 Hz, ^3J 7.6 Hz, 1H, H^4) ppm. ^{13}C NMR: δ 172.5 (C^5), 143.8, 143.5 (C^{i1,i2}), 134.3 (C^{i3}), 130.9 (C^{p3}), 128.9, 128.7, 128.6, 128.1, 127.4, 127.1, 126.8, 126.6 (15C, C$_{Ph}$), 84.4 (C^2), 53.3 (C^3), 44.9 (C^4) ppm. IR (film): ν_{max} 3061, 3030, 2917, 2858, 1612, 1576, 1494, 1450, 1338, 1304, 1267, 1179, 1077, 1048, 1027, 910, 758, 734, 698 cm^{-1}. MS (EI), m/z (%): 297.25 [M]$^{+\cdot}$. Calc. for $C_{22}H_{19}N$, m/z: 297.15.
(2*S**,4*S**)-2,4,5-Triphenyl-3,4-dihydro-2*H*-pyrrole (**3a**, minor isomer) was isolated as light brown oil (0.036 g, 6% yield) by second column chromatography of crude product (SiO_2, eluent: ethyl acetate/hexane = 1:20). Elemental analysis calcd (%) for $C_{22}H_{19}N$ (297.15): C, 88.85; H, 6.44; N, 4.71; found: C, 89.11; H, 6.32; N, 4.57. R_f = 0.36 (hexane – diethyl ether = 3:1).

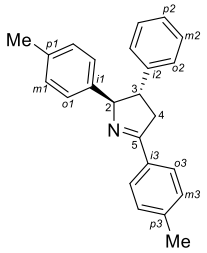


^{1}H NMR: δ 7.87-7.82 (m, 2H, H^{o3}), 7.36-7.32 (m, 1H, H^{p3}), 7.35-7.30 (m, 4H, H^{o1,m1}), 7.29-7.21 (m, 4H, H^{m2,m3}), 7.27-7.23 (m, 1H, H^{p1}), 7.22-7.18 (m, 1H, H^{p2}), 7.21-7.16 (m, 1H, H^{o2}), 5.39 (m, 1H, H^2), 4.70 (m, 1H, H^4), 2.49 (m, 1H), 2.39 (m, 1H) [H^3] ppm. ^{13}C NMR: δ 174.6 (C^5), 144.4 (C^{i1}), 141.7 (C^{i2}), 133.8 (C^{i3}), 130.6 (C^{p3}), 129.2 (C^{m3}), 128.8 (C^{o3}), 128.7 (C^{m1}), 128.5 (C^{m2}), 127.5 (Co^2), 127.1 (C^{p1}), 126.9 (C^{p2}), 126.8 (C^{o1}), 74.4 (C^2), 55.2 (C^4), 44.6 (C^3) ppm. IR (film): ν_{max} 3104, 3082, 3060, 3028, 3004, 2937, 2916, 2867, 1616, 1605, 1574, 1494, 1449, 1337, 1266, 1178, 1144, 1077, 1048, 1026 cm^{-1}. MS (EI), m/z (%): 297.25 [M]$^{+\cdot}$. Calc. for $C_{22}H_{19}N$, m/z: 297.15.

Following the typical procedure 1, **3b**+**3'b** tautomeric mixture was prepared from **1b** (2 mmol, 0.447 g) and **2a** (2 mmol, 0.204 g) and was isolated as a colourless oil (0.332 g, 51% total yield). The content of minor tautomer **3b** was 20%. Elemental analysis calcd (%) for $C_{24}H_{23}N$ (325.46):

C, 88.57; H, 7.12; N, 4.30; found: C, 88.69; H, 7.05; N, 4.26. R_f = 0.42 (hexane/diethyl ether = 3:1).

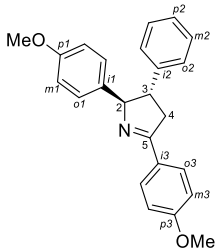
(2*R**,3*S**)-3-Phenyl-2,5-di-*p*-tolyl-3,4-dihydro-2*H*-pyrrole (**3'b**, major tautomer).



^{1}H NMR: δ 7.97-7.91 (m, 2H, H^{o3}), 7.41-7.24 (m, 7H), 7.21-7.05 (m, 4H) [H$_{Ar}$], 5.35 (ddd, ^3J 6.6 Hz, ^4J 2.0 Hz, ^4J 1.9 Hz, 1H, H^2), 3.68 (dd, ^2J 17.0 Hz, ^3J 9.3 Hz, 1H, H^4), 3.48 (dd, ^3J 9.3 Hz, ^3J 7.4 Hz, ^3J 6.6 Hz, 1H, H^3), 3.25 (ddd, ^2J 17.0 Hz, ^3J 7.4 Hz, 1H, H^4), 2.48 (s, 3H), 2.38 (s, 3H) [*p1-Me*, *p3-Me*]. ^{13}C NMR: δ 172.0 (C^5), 143.9, 141.0, 140.6, 136.4, 131.5, 129.2, 129.1, 128.7, 127.9, 127.2, 126.6, 126.4 (18C, C$_{Ar}$), 84.0 (C^2), 53.2 (C^3), 44.7 (C^4), 21.5, 21.1 (2C, *p1-Me*, *p3-Me*). IR (film, ν/cm^{-1}): 3055, 3028, 2919, 2865, 1611, 1567, 1512, 1496, 1451, 1411, 1336, 1299, 1266, 1182, 1111, 1051, 1023, 909, 814, 757, 732, 702. MS (EI), m/z (%): 325.25 [M]$^{+\cdot}$. Calc. for $C_{24}H_{23}N$, m/z: 325.46.

Following the typical procedure[1], **3c**+**3'c** tautomeric mixture was prepared from **1c** (2 mmol, 0.511 g) and **2a** (2 mmol, 0.204 g) and was isolated as a colourless oil (0.393 g, 55% total yield). The content of minor tautomer **3c** was 18%. Elemental analysis calcd (%) for $C_{24}H_{23}NO_2$ (325.46): C, 80.64; H, 6.49; N, 3.92; found: C, 80.71; H, 6.33; N, 3.88. R_f = 0.11 (hexane/diethyl ether = 3:1).

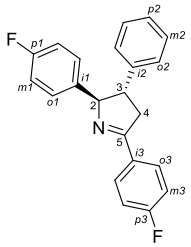
(2*R**,3*S**)-2,5-Bis(4-methoxyphenyl)-3-phenyl-3,4-dihydro-2*H*-pyrrole (**3'c**, major tautomer).



^{1}H NMR: δ 8.04-7.86 (m, 2H, H^{o3}), 7.31-7.24 (m, 3H), 7.19-7.14 (m, 2H), 7.11-7.05 (m, 2H), 6.98-6.91 (m, 2H), 6.83-6.78 (m, 2H) [H$_{Ar}$], 5.21 (ddd, ^3J 6.6 Hz, ^4J 2.0 Hz, ^4J 1.9 Hz, 1H, H^2), 3.82 (s, 3H), 3.74 (s, 3H) [*p1*-O*Me*, *p3*-O*Me*], 3.58 (dd, ^2J 16.9 Hz, ^3J 9.3 Hz, 1H, H^4), 3.37 (ddd, ^3J 9.3 Hz, ^3J 7.7 Hz, ^3J 7.0 Hz, 1H, H^3), 3.15 (dd, ^2J 16.9 Hz, ^3J 7.7 Hz, 1H, H^4). ^{13}C NMR: δ 171.1 (C^5), 161.5, 158.5 (C^{p1,p3}), 143.5, 135.7 (C^{i1,i2}), 129.4, 128.6, 127.5, 127.1 (8C$_{Ar}$), 126.9, 126.4 (C^{p2,i3}), 113.7, 113.6 (C^{m1,m3}), 83.4 (C^2), 55.1, 54.9 (*p1*-OMe, *p3*-OMe), 53.4 (C^3), 44.3 (C^4). IR (film, ν/cm^{-1}): 3061, 3029, 3003, 2955, 2935, 2907, 2836, 1607, 1574, 1511, 1459, 1420, 1336, 1304, 1249, 1175, 1110, 1032, 910, 834, 759, 732, 702. MS (EI), m/z (%): 357.15 [M]$^{+\cdot}$. Calc. for $C_{24}H_{23}NO_2$, m/z: 357.17.

Following the typical procedure 1, **3d**+**3'd** tautomeric mixture was prepared from **1d** (2 mmol, 0.463 g) and **2a** (2 mmol, 0.204 g) and was isolated as a colourless oil (0.141 g, 21% total yield). The content of minor tautomer **3d** was 11%. Elemental analysis calcd (%) for $C_{22}H_{17}F_2N$ (333.38): C, 79.26; H, 5.14; F, 11.40; N, 4.20; found: C, 79.38; H, 5.02; F, 11.36; N, 4.24. R_f = 0.37 (hexane/diethyl ether = 3:1).

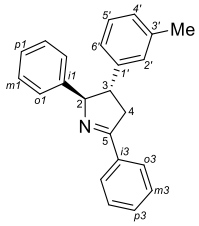
(2*R**,3*S**)-2,5-Bis(4-fluorophenyl)-3-phenyl-3,4-dihydro-2*H*-pyrrole (**3'd**, major tautomer).



^{1}H NMR: δ 8.16-7.81 (m, 2H, H^{o3}), 7.46-7.12 (m, 8H), 7.11-6.93 (m, 3H) [H$_{Ar}$], 5.30 (ddd, ^3J 7.4 Hz, ^4J 2.2 Hz, ^4J 2.0 Hz, 1H, H^2), 3.66 (dd, ^2J 16.9 Hz, ^3J 9.2 Hz, 1H, H^4), 3.51-3.34 (m, 1H, H^3), 3.24 (dd, ^2J 16.9 Hz, ^3J 8.2 Hz, 1H, H^4). ^{13}C NMR: δ 171.4 (C^5), 164.6 (d, ^1J 251.3 Hz), 162.1 (d, ^1J 244.6 Hz) [C^{p1,p3}], 143.0 (C^{i2}), 139.2 (d, ^4J 3.3 Hz), 130.5 (d, ^4J 3.2 Hz) [C^{i1,i3}], 130.1 (d, ^3J 8.6 Hz, C^{o1}), 129.0 (C^{m2}), 128.1 (d, ^3J 8.0 Hz, C^{o3}), 127.4 (C^{o2}), 126.9 (C^{p2}), 115.7 (d, ^2J 21.7 Hz), 115.3 (d, ^2J 21.2 Hz) [C^{m1,m3}], 83.5 (C^2), 53.8 (C^3), 44.8 (C^4). IR (film, ν/cm^{-1}): 3062, 3031, 2914, 2862, 1603, 1508, 1452, 1411, 1336, 1264, 1227, 1156, 1096, 1051, 1013, 839, 758, 733, 701. MS (EI), m/z (%): 333.10 [M]$^{+\cdot}$. Calc. for $C_{23}H_{20}FN$, m/z: 333.13.

Following the typical procedure 1, **3e**+**3'e** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2b** (2 mmol, 0.232 g) and was isolated as a colourless oil (0.280 g, 45% total yield). The content of minor tautomer **3e** was 18%. Elemental analysis calcd (%) for $C_{23}H_{21}N$ (311.43): C, 88.71; H, 6.80; N, 4.50; found: C, 88.63; H, 6.94; N, 4.43. R_f = 0.34 (hexane/diethyl ether = 3:1).

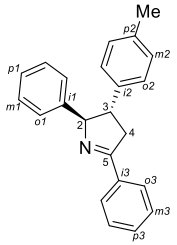
(2*R**,3*S**)-2,5-Diphenyl-3-(*m*-tolyl)-3,4-dihydro-2*H*-pyrrole (**3'e**, major tautomer).



^{1}H NMR: δ 8.02-7.92 (m, 2H, H^{o3}), 7.50-7.41 (m, 3H), 7.41-7.12 (m, 7H), 7.07-6.91 (m, 3H) [H$_{Ar}$], 5.33 (d, ^3J 6.5 Hz, 1H, H^2), 3.62 (dd, ^2J 17.1 Hz, ^3J 9.3 Hz, 1H, H^4), 3.45-3.32 (m, 1H, H^3), 3.20 (dd, ^2J 17.1 Hz, ^3J 7.3 Hz, 1H, H^4), 2.31 (s, 3H, *3'-Me*). ^{13}C NMR: δ 172.3 (C5), 143.7, 143.6 (C$^{i1,1'}$), 138.3, 134.2 (C$^{i3,3'}$), 130.8 (C^{p3}), 128.7, 128.5, 128.4, 127.9, 127.4, 127.0, 126.4, 124.3 (13C$_{Ar}$), 84.2 (C^2), 53.1 (C^3), 44.9 (C^4), 21.5 (*3'-Me*). IR (film, ν/cm^{-1}): 3057, 3028, 2919, 2860, 1609, 1577, 1491, 1448, 1338, 1266, 1176, 10751048, 1027, 784, 761, 697. MS (EI), m/z (%): 311.25 [M]$^{+\cdot}$. Calc. for $C_{23}H_{21}N$, m/z: 311.17.

Following the typical procedure 1, **3f**+**3'f** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2c** (2 mmol, 0.232 g) and was isolated as a colourless oil (0.298 g, 48% total yield). The content of minor tautomer **3f** was 17%. Elemental analysis calcd (%) for $C_{23}H_{21}N$ (311.43): C, 88.71; H, 6.80; N, 4.50; found: C, 88.65; H, 6.89; N, 4.46. R_f = 0.37 (hexane/diethyl ether = 3:1).

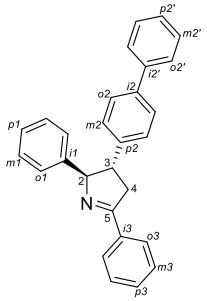
(2*R**,3*S**)-2,5-Diphenyl-3-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**3'f**, major tautomer).



^{1}H NMR: δ 8.07-7.93 (m, 2H, H^{o3}), 7.48-7.41 (m, 3H), 7.34-7.20 (m, 3H), 7.18-7.15 (m, 2H), 7.13-7.05 (m, 4H) [H$_{Ar}$], 5.29 (d, ^3J = 7.0 Hz, 1H, H^2), 3.61 (dd, ^2J 17.1 Hz, ^3J 9.4 Hz, 1H, H^4), 3.40 (ddd, ^3J 9.4 Hz, ^3J 7.7 Hz, ^3J 7.0 Hz, 1H, H^3), 3.18 (dd, ^2J 17.1 Hz, ^3J 7.7 Hz, 1H, H^4), 2.32 (s, 3H, *p2-Me*). ^{13}C NMR: δ 172.4 (C^5), 143.4, 140.4 (C^{i1,i2}), 136.0, 134.1 (C^{i3,p2}), 130.8 (C^{p3}), 129.4, 128.5, 128.4, 127.9, 127.1, 126.9, 126.4 (13C$_{Ar}$), 84.1 (C^2), 52.9 (C^3), 44.7 (C^4), 21.0 (*p2-Me*). IR (film, ν/cm^{-1}): 3057, 3027, 2919, 2865, 1612, 1575, 1513, 1494, 1448, 1338, 1266, 1179, 1048, 1027, 807, 785, 761, 696. MS (EI), m/z (%): 311.20 [M]$^{+\cdot}$. Calc. for $C_{23}H_{21}N$, m/z: 311.17.

Following the typical procedure 1, **3g**+**3'g** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2d** (2 mmol, 0.356 g) and was isolated as a light yellow oil (0.306 g, 41% total yield). The content of minor tautomer **3g** was 17%. Elemental analysis calcd (%) for $C_{28}H_{23}N$ (373.50): C, 90.04; H, 6.21; N, 3.75; found: C, 90.21; H, 6.18; N, 3.61. R_f = 0.31 (hexane/diethyl ether = 3:1).

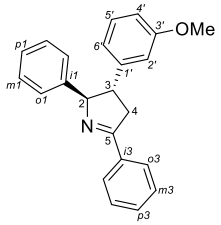
(2*R**,3*S**)-3-([1,1'-Biphenyl]-4-yl)-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole (**3'g**, major tautomer).



^{1}H NMR: δ 8.06-7.90 (m, 2H, H^{o3}), 7.59-7.39 (m, 10H), 7.34-7.17 (m, 7H) [H$_{Ar}$], 5.35 (d, ^3J 6.7 Hz, 1H, H^2), 3.66 (dd, ^2J 17.1 Hz, ^3J 9.4 Hz, 1H, H^4), 3.47 (ddd, ^3J 9.4 Hz, ^3J 7.6 Hz, ^3J 6.7 Hz, 1H, H^3), 3.25 (dd, ^2J 17.1 Hz, ^3J 7.6 Hz, 1H, H^4). ^{13}C NMR: δ 172.7 (C^5), 143.3, 142.6, 140.7, 139.6, 134.0 (5C, C$^{i1,i2,i2',i3,p2}$), 131.1 (C^{p3}), 128.9, 128.7, 128.6, 128.1, 127.8, 127.5, 127.3, 127.2, 127.0, 126.5 (18C$_{Ar}$), 84.1 (C^2), 52.9 (C^3), 44.8 (C^4). IR (film, ν/cm^{-1}): 3079, 3058, 3028, 2919, 2853, 1614, 1604, 1574, 1520, 1488, 1449, 1408, 1338, 1267, 1218, 1179, 1156, 1113, 1076, 1048, 1026, 1006, 832. MS (EI), m/z (%): 373.25 [M]$^{+\cdot}$. Calc. for $C_{28}H_{23}N$, m/z: 373.18.

Following the typical procedure 1, **3h**+**3'h** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2e** (2 mmol, 0.264 g) and was isolated as a colourless oil (0.138 g, 21% total yield). The content of minor tautomer **3h** was 17%. Elemental analysis calcd (%) for $C_{23}H_{21}NO$ (327.43): C, 84.37; H, 6.46; N, 4.28; found: C, 84.48; H, 6.17; N, 4.11. R_f = 0.63 (hexane/ethyl acetate = 20:1).

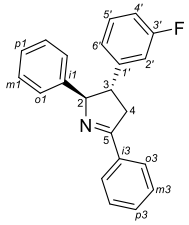
(2*R**,3*S**)-3-(3-Methoxyphenyl)-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole (**3'h**, major tautomer).



^{1}H NMR: δ 7.99-7.91 (m, 2H, H*o3*), 7.46-7.39 (m, 2H), 7.34-7.15 (m, 7H), 6.81-6.71 (m, 3H) [H$_{Ar}$], 5.32 (d, ^3J 6.7 Hz, 1H, H^2), 3.73 (s, 3H, *3'*-O*Me*), 3.60 (dd, ^2J 17.1 Hz, ^3J 9.2 Hz, 1H, H^4), 3.39 (ddd, ^3J 9.2 Hz, ^3J 7.6 Hz, ^3J 6.7 Hz, 1H, H^3), 3.19 (dd, ^2J 17.1 Hz, ^3J 7.6 Hz, 1H, H^4). ^{13}C NMR: δ 172.4 (C^5), 160.0 (C$^{3'}$), 145.5, 143.6, 134.3 (C$^{i1,i3,1'}$), 130.9 (C^{p3}), 129.9 (C$^{5'}$), 128.6, 128.5, 128.0, 127.1, 126.6 (9C$_{Ar}$), 119.7 (C$^{6'}$), 113.2, 111.9 (C$^{2',4'}$), 84.2 (C^2), 55.3 (*3'*-O*Me*), 53.3 (C^3), 44.8 (C^4). IR (film, ν/cm^{-1}): 3081, 3058, 3028, 3002, 2948, 2931, 2920, 2852, 2835, 1645, 1605, 1583, 1489, 1449, 1340, 1288, 1262, 1157, 1076, 1048, 1028, 844, 779, 762, 697. MS (EI), m/z (%): 327.25 [M]$^{+\cdot}$. Calc. for $C_{23}H_{21}NO$, m/z: 327.16.

Following the typical procedure 1, **3i**+**3'i** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2f** (2 mmol, 0.240 g) and was isolated as a light yellow oil (0.226 g, 36% total yield). The content of minor tautomer **3i** was 12%. Elemental analysis calcd (%) for $C_{22}H_{18}FN$ (315.39): C, 83.78; H, 5.75; F, 6.02; N, 4.44; found: C, 83.96; H, 5.72; F, 5.91; N, 4.41. R_f = 0.25 (hexane/diethyl ether = 3:1).

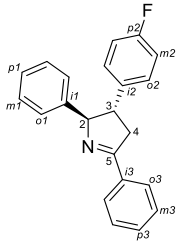
(2*R**,3*S**)-3-(3-Fluorophenyl)-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole (**3'i**, major tautomer).



^{1}H NMR: δ 8.13-7.88 (m, 2H, H^{o3}), 7.56-7.42 (m, 3H), 7.39-7.20 (m, 4H), 7.18-7.13 (m, 2H), 7.05-6.56 (m, 3H) [H$_{Ar}$], 5.29 (d, ^3J 6.8 Hz, 1H, H^2), 3.64 (dd, ^2J 17.1 Hz, ^3J 9.4 Hz, 1H, H^4), 3.43 (ddd, ^3J 9.4 Hz, ^3J 7.6 Hz, ^3J 6.8 Hz, 1H, H^3), 3.19 (dd, ^2J 17.1 Hz, ^3J 7.6 Hz, 1H, H^4). ^{13}C NMR: δ 172.2 (C^5), 163.0 (d, ^1J 246.3 Hz, C$^{3'}$), 146.2 (d, ^3J 7.0 Hz, C$^{1'}$), 143.1 (C^{i1}), 134.0 (C^{i3}), 130.9 (C^{p3}), 130.23 (d, ^3J 8.3 Hz, C$^{5'}$), 128.6, 128.5, 128.0, 127.2, 126.4 (9C$_{Ar}$), 123.0 (d, ^4J 2.9 Hz, C$^{6'}$), 114.1 (d, ^2J 21.4 Hz), 113.5 (d, ^2J 21.1 Hz) [C$^{2',4'}$], 84.1 (C^2), 53.0 (d, ^4J 1.8 Hz, C^3), 44.6 (C^4). IR (film, ν/cm^{-1}): 3060, 3031, 2919, 2858, 1614, 1587, 1489, 1449, 1339, 1254, 1144, 1076, 1048, 1027, 784, 761, 695. MS (EI), m/z (%): 315.15 [M]$^{+\cdot}$. Calc. for $C_{22}H_{18}FN$, m/z: 315.14.

Following the typical procedure 1, **3j**+**3'j** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2g** (2 mmol, 0.240 g) and was isolated as a light yellow solid (0.229 g, 36% total yield). The content of minor tautomer **3j** was 17%. Elemental analysis calcd (%) for $C_{22}H_{18}FN$ (315.39): C, 83.78; H, 5.75; F, 6.02; N, 4.44; found: C, 83.64; H, 5.81; F, 5.96; N, 4.59. R_f = 0.33 (hexane/diethyl ether = 3:1).

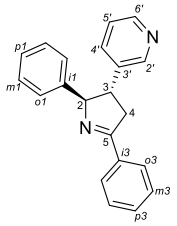
(2*R**,3*S**)-3-(4-Fluorophenyl)-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole (**3'j**, major tautomer).



^{1}H NMR: δ 8.04-7.83 (m, 2H, H^{o3}), 7.59-7.40 (m, 3H), 7.35-7.20 (m, 3H), 7.19-7.11 (m, 4H), 7.03-6.92 (m, 2H) [H$_{Ar}$], 5.26 (d, ^3J 5.3 Hz, 1H, H^2), 3.64 (dd, ^2J 17.1 Hz, ^3J 9.3 Hz, 1H, H^4), 3.42 (ddd, ^3J 9.3 Hz, ^3J 7.8 Hz, ^3J 5.3 Hz, 1H, H^3), 3.17 (dd, ^2J 17.1 Hz, ^3J 7.8 Hz, 1H, H^4). ^{13}C NMR: δ 172.5 (C^5), 161.8 (d, ^1J 244.9 Hz, C^{p2}), 143.3 (C^{i1}), 139.3 (d, ^4J 3.3 Hz, C^{i2}), 134.2 (C^{i3}), 131.0 (C^{p3}), 128.8 (d, ^3J 7.9 Hz, C^{o2}), 128.7, 128.6, 128.0, 127.2, 126.5 (9C$_{Ar}$), 115.7 (d, ^2J 21.2 Hz, C^{m2}), 84.4 (C^2), 52.7 (C^3), 44.8 (C^4). IR (film, ν/cm^{-1}): 3059, 3031, 2915, 2864, 1610, 1509, 1448, 1338, 1225, 1159, 1097, 1048, 1026, 829, 760, 696. MS (EI), m/z (%): 315.20 [M]$^{+\cdot}$. Calc. for $C_{22}H_{18}FN$, m/z: 315.14.

Following the typical procedure 1, **3k**+**3'k** tautomeric mixture was prepared from **1a** (2 mmol, 0.391 g) and **2h** (2 mmol, 0.206 g) and was isolated as a light yellow oil (0.149 g, 25% total yield). The content of minor tautomer **3k** was 17%. Elemental analysis calcd (%) for $C_{21}H_{18}N_2$ (298.15): C, 84.53; H, 6.08; N, 9.39; found: C, 84.72; H, 5.95; N, 9.33. R_f = 0.26 (hexane/ethyl acetate = 5:1).

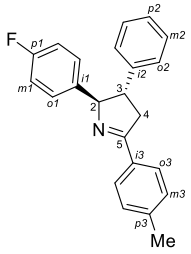
3-((2*R**,3*S**)-2,5-Diphenyl-3,4-dihydro-2*H*-pyrrol-3-yl)pyridine (**3'k**).



^{1}H NMR: δ 8.64-8.30 (m, 2H, H$^{2',6'}$), 7.99-7.92 (m, 2H, H^{o3}), 7.60-7.50 (m, 1H, H$^{4'}$), 7.50-7.41 (m, 3H), 7.35-7.21 (m, 4H), 7.20-7.10 (m, 2H) [H$_{Ar}$], 5.29 (d, ^3J 6.9 Hz, 1H, H^2), 3.67 (dd, ^2J 17.0 Hz, ^3J 9.3 Hz, 1H, H^4), 3.45 (ddd, ^3J 9.3 Hz, ^3J 7.7 Hz, ^3J 6.9 Hz, 1H, H^3), 3.20 (dd, ^2J 17.0 Hz, ^3J 7.7 Hz, 1H, H^4). ^{13}C NMR: δ 172.3 (C^5), 149.2, 148.3 (C$^{2',6'}$), 142.7, 138.9, 134.4, 133.9 (C$^{i1,i3,3',4'}$), 131.1 (C^{p3}), 128.7, 128.0, 127.4, 126.5 (9C$_{Ar}$), 123.8 (C$^{5'}$), 84.1 (C^2), 50.7 (C^3), 44.4 (C^4). IR (film, ν/cm^{-1}): 3082, 3058, 3029, 3001, 2920, 2855, 1685, 1614, 1574, 1494, 1480, 1449, 1424, 1338, 1302, 1267, 1179, 1048, 1026, 915, 804, 761, 715, 696. MS (EI), m/z (%): 298.25 [M]$^{+\cdot}$. Calc. for $C_{21}H_{18}N_2$, m/z: 298.15.

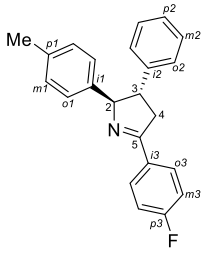
Following the typical procedure 1, **3'l**+**4'l** mixture was obtained from **1e** (2 mmol, 0.455 g) and **2a** (2 mmol, 0.204 g). Isomers **3'l** and **4'l** were separated by column chromatography (SiO_2, eluent: ethyl acetate/hexane = 1:20).

(2*R**,3*S**)-2-(4-Fluorophenyl)-3-phenyl-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**3'l**).



3'l was isolated as a light yellow oil (0.112 g, 17% yield). Elemental analysis calcd (%) for $C_{23}H_{20}FN$ (329.16): C, 83.86; H, 6.12; F, 5.77; N, 4.25; found: C, 83.92; H, 6.23; F, 5.72; N, 4.13. R_f = 0.36 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 7.85-7.83 (m, 2H, H^{o3}), 7.32-7.27 (m, 2H, H^{m2}), 7.26 -7.22 (m, 2H, H^{m3}), 7.25-7.21 (m, 1H, H^{p2}), 7.20-7.15 (m, 2H, H^{o2}), 7.12-7.07 (m, 2H, H^{o1}), 6.97-6.93 (m, 2H, H^{m1}), 5.25 (d, ^3J 7.5 Hz, 1H, H^2), 3.61 (dd, ^2J 17.2 Hz, ^3J 9.3 Hz, 1H, H^4), 3.34 (ddd, ^3J 9.3 Hz, ^3J 7.8 Hz, ^3J 7.5 Hz, 1H, H^3), 3.19 (dd, ^2J 17.2 Hz, ^3J 7.8 Hz, 1H, H^4), 2.40 (s, 3H, *p3*-Me). ^{13}C NMR: δ 172.6 (C^5), 162.2 (d, ^1J 244.5 Hz, C^{p1}), 143.3 (C^{i2}), 141.4 (C^{p3}), 139.4 (d, ^4J 3.0 Hz, C^{i1}), 131.5 (C^{i3}), 129.4 (Cm^3), 129.0 (Cm^2), 128.12 (d, ^3J 7.9 Hz, C^{o1}), 128.1 (C^{o3}), 127.4 (Co^2), 126.9 (C^{p2}), 115.3 (d, ^2J 21.3 Hz, C^{m1}), 83.6 (C^2), 53.8 (C^3), 44.9 (C^4), 21.7 (*p3-Me*). ^{15}N NMR: δ -61.5. IR (film, ν/cm^{-1}): 3057, 3030, 2920, 2856, 1607, 1565, 1508, 1454, 1436, 1337, 1263, 1224, 1156, 1051, 1020, 818, 757, 732, 701. MS (EI), m/z (%): 329.20 [M]$^{+\cdot}$. Calc. for $C_{23}H_{20}FN$, m/z: 329.16.

(2*R**,3S*)-5-(4-Fluorophenyl)-3-phenyl-2-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**4'l**).



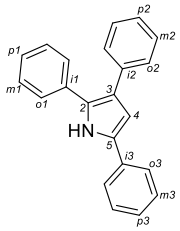
4'l was isolated as a light yellow oil (0.119 g, 18% yield). Elemental analysis calcd (%) for $C_{23}H_{20}FN$ (329.16): C, 83.86; H, 6.12; F, 5.77; N, 4.25; found: C, 83.98; H, 6.25; F, 5.64; N, 4.13. R_f = 0.35 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 8.00-7.91 (m, 2H, H^{o3}), 7.33-7.26 (m, 3H, H^{m2,p2}), 7.20-7.17 (m, 2H, H^{o1}), 7.13-7.09 (m, 2H, H^{m3}), 7.11-7.09 (m, 2H, H^{o1}), 7.05-7.02 (m, 2H, H^{o1}), 5.27 (d, ^3J 6.8 Hz, 1H, H^2), 3.60 (dd, ^2J 17.0 Hz, ^3J 9.3 Hz, 1H, H^4), 3.42 (ddd, ^3J

9.3 Hz, ^3J 7.6 Hz, ^3J 6.8 Hz, 1H, H^3), 3.17 (dd, ^2J 17.0 Hz, ^3J 7.6 Hz, 1H, H^4), 2.31 (s, 3H, *p1-Me*). ^{13}C NMR: δ 171.2 (C^5), 164.6 (d, ^1J 251.2 Hz, C^{p3}), 143.7 (C^{i2}), 140.4 (C^{i1}), 136.8 (C^{p1}), 130.2 (d, ^3J 8.7 Hz, C^{o3}), 129.3, 128.9 (4C$_{Ar}$), 127.4 (C^{i3}), 127.4 (C^{o1}), 126.8 (C^{p2}), 126.5 (2C, C$_{Ar}$), 115.7 (d, ^2J 21.9 Hz, C^{m3}), 84.2 (C^2), 53.38 (C^3), 44.9 (C^4), 21.3 (*p1-Me*). ^{15}N NMR: δ -57.7. IR (film, ν/cm^{-1}): 3058, 3028, 2920, 2856, 1604, 1509, 1454, 1335, 1231, 1157, 1100, 1052, 1020, 910, 840, 811, 758, 733, 701. MS (EI), m/z (%): 329.20 [M]$^{+\cdot}$. Calc. for $C_{23}H_{20}FN$, m/z: 329.16.

4. Synthesis of 1*H*-pyrroles 5 (*typical procedure 2*).

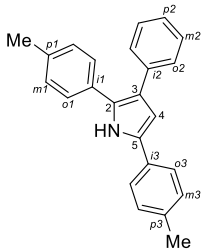
A mixture of imine **1** (2 mmol), arylacetylene **2** (2 mmol) and Bu^{t}OK (0.4 mmol, 0.045 g) in DMSO (6 ml) was stirred at 60 °C (oil bath) for 15 min. Then, chloranil (2 mmol, 0.492 g) was added, and the reaction mixture was stirred at 60 °C for 1 h. The reaction mixture was diluted with H_2O (50 ml) and extracted with Et_2O (7 × 10 ml). The organic extract was washed with H_2O (3 × 10 ml) and dried over $MgSO_4$ for 1 h. Et_2O was evaporated under reduced pressure, and the pure 1*H*-pyrrole **5** was obtained by column chromatography [SiO_2, eluent: ethyl acetate/hexane = 1:10 (for **5a-d**); eluent: ethyl acetate/hexane = 1:1 (for **5k**)].

2,3,5-Triphenyl-1*H*-pyrrole (**5a**).



Following the procedure 2, **5a** was prepared from **1a** (2 mmol, 0.391 g) and **2a** (2 mmol, 0.204 g). **5a** was isolated as a colourless solid (0.331 g, 56% yield). M. p. = 134-135 °C. Elemental analysis calcd (%) for $C_{22}H_{17}N$ (295.39): C, 89.46; H, 5.80; N, 4.74; found: C, 89.38; H, 5.88; N, 4.74. R_f = 0.45 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 8.36 (br. s, 1H, NH), 7.55-7.49 (m, 2H), 7.42-7.33 (m, 6H), 7.33-7.15 (m, 7H) [H$_{Ph}$], 6.67 (s, 1H, H^4). ^{13}C NMR: δ 136.5, 133.2, 132.3, 129.4 (C^{2,5,i1,i2,i3}), 129.1, 128.8, 128.5, 128.4, 127.6 (10C$_{Ph}$), 127.1, 126.6, 126.0 (C^{p1,p2,p3}), 123.9 (C^3), 123.9 (C^{o3}), 108.7 (C^4). The NMR data were in accordance with the literature.[S3] IR (film, ν/cm^{-1}): 3429, 3058, 3024, 2955, 2922, 2853, 1605, 1588, 1504, 1486, 1452, 1286, 1262, 1231, 1217, 1179, 1072, 1054, 1029, 955, 909, 812, 759, 697. MS (EI), m/z (%): 295.35 [M]$^{+\cdot}$. Calc. for $C_{22}H_{17}N$, m/z: 295.15.

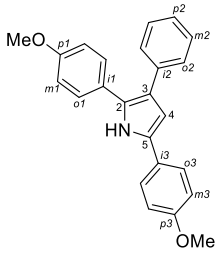
3-Phenyl-2,5-di-*p*-tolyl-1*H*-pyrrole (**5b**).



Following the typical procedure 2, **5b** was prepared from **1b** (2 mmol, 0.447 g) and **2a** (2 mmol, 0.204 g). **5b** was isolated as a colourless solid (0.395 g, 61% yield). M. p. = 135-136 °C. Elemental analysis calcd (%) for $C_{24}H_{21}N$ (323.17): C, 89.12; H, 6.54; N, 4.33; found: C, 89.07; H, 6.62; N, 4.31. R_f = 0.45 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 8.35 (br. s, 1H, NH), 7.52-7.39 (m, 4H, H^{o1,o3}), 7.35-7.26 (m, 4H, H^{o2,m2}), 7.25-7.19 (m, 3H), 7.19-7.07 (m, 2H) [H^{m1,m3,p2}], 6.67 (s, 1H, H^4), 2.39 (s, 3H), 2.38 (s, 3H) [*p1-Me*, *p3-Me*]. ^{13}C NMR: δ 136.8, 136.7 (C^{p1,p3}), 136.3, 132.2, 130.4 (C^{i1,i2,i3}), 129.74, 129.67, 129.5, 129.2, 128.5, 128.4, 127.5, 125.9, 123.8 (14C, C^{2,5}, C$_{Ar}$), 123.4 (C^3), 108.1 (C^4), 21.3, 21.3 (*p1-Me*, *p3-Me*). IR (film, ν/cm^{-1}): 3454, 3429, 3059, 3035, 2921, 2852, 1601, 1572, 1532, 1511, 496, 1470, 1443, 1287, 1260, 1231,

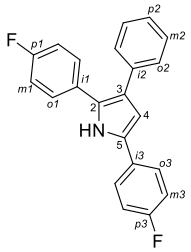
1178, 1158, 1097, 1072, 1052, 956, 909, 836, 813, 765, 733, 700. MS (EI), m/z (%): 323.30 $[M]^{+\cdot}$. Calc. for $C_{24}H_{21}N$, m/z: 323.17.

2,5-Bis(4-methoxyphenyl)-3-phenyl-1*H*-pyrrole (**5c**).



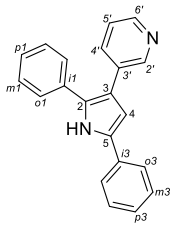
Following the typical procedure 2, **5c** was prepared from **1c** (2 mmol, 0.511 g) and **2a** (2 mmol, 0.204 g). **5c** was isolated as a colourless solid (0.462 g, 65% yield). M. p. = 132-133 °C. Elemental analysis calcd (%) for $C_{23}H_{21}NO_2$ (355.44): C, 81.10; H, 5.96; N, 3.94; found: C, 81.25; H, 5.84; N, 3.85. R_f = 0.12 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 8.24 (br. s, 1H, NH), 7.53-7.44 (m, 2H), 7.44-7.37 (m, 2H) [$H^{o1,o3}$], 7.36-7.30 (m, 2H, H^{o2}), 7.33-7.25 (m, 2H, H^{m2}), 7.24-7.16 (m, 1H, H^{p2}), 7.00-6.92 (m, 2H), 6.91-6.84 (m, 2H) [$H^{m1,m3}$], 6.60 (s, 1H, H^4), 3.85 (s, 1H), 3.83 (s, 1H) [*p1*-O*Me*, *p3*-O*Me*]. ^{13}C NMR: δ 158.8, 158.5 ($C^{p1,p3}$), 136.7, 131.9 ($C^{5,i2}$), 129.0, 128.8, 128.4, 126.0, 125.8, 125.5, 125.3 (11C, $C^{2,i1,i3}$, C_{Ar}), 122.9 (C^3), 114.5, 114.3 ($C^{m1,m3}$), 107.3 (C^4), 55.4, 55.34 (*p1*-O*Me*, *p3*-O*Me*). IR (film, ν/cm^{-1}): 3428, 3058, 3027, 3002, 2957, 2934, 2836, 1603, 1588, 1534, 1512, 1497, 1463, 1441, 1303, 1293, 1276, 1247, 1177, 1110, 1073, 1053, 1031, 956, 9009, 832, 800, 765, 732, 700. MS (EI), m/z (%): 355.40 $[M]^{+\cdot}$. Calc. for $C_{23}H_{21}NO_2$, m/z: 355.16.

2,5-Bis(4-fluorophenyl)-3-phenyl-1*H*-pyrrole (**5d**).



Following the typical procedure 2, **5d** was prepared from **1d** (2 mmol, 0.463 g) and **2a** (2 mmol, 0.204 g). **5d** was isolated as a slightly green oil (0.225 g, 34% yield). Elemental analysis calcd (%) for $C_{23}H_{21}F_2N$ (331.37): C, 79.74; H, 4.56; F, 11.47; N, 4.23; found: C, 79.87; H, 4.72; F, 11.15; N, 4.26. R_f = 0.38 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 8.27 (br. s, 1H, NH), 7.57-7.48 (m, 2H), 7.42-7.29 (m, 6H) [H_{Ar}], 7.28-7.20 (m, 1H, H^{p2}), 7.17-7.09 (m, 2H), 7.08 – 6.99 (m, 2H) [$H^{m3,m1}$], 6.64 (s, 1H, H^4). ^{13}C NMR: δ 162.1 (d, ^1J 246.9 Hz), 161.8 (d, ^1J 246.2 Hz) [$C^{p1,p3}$], 136.2, 131.6 ($C^{5,i1}$), 129.3 (d, ^4J 3.4 Hz), 128.7 (d, ^4J 3.2 Hz) [$C^{i1,i3}$], 128.6, 128.4 ($C^{o2,m2}$), 128.5 (C^2), 126.2 (C^{p2}), 129.4 (d, ^3J 7.9 Hz), 125.6 (d, ^3J 7.9 Hz) [$C^{o1,o3}$], 123.9 (C^3), 116.1 (d, ^2J 21.1 Hz), 115.9 (d, ^2J 21.1 Hz) [$C^{m1,m3}$], 108.5 (C^4). IR (film, ν/cm^{-1}): 3454, 3429, 3059, 3035, 2621, 2852, 1601, 1572, 1532, 1511, 1496, 1470, 1443, 1260, 1231, 1158, 1097, 1072, 1014, 956, 909, 836, 813, 765, 733, 700. MS (EI), m/z (%): 331.25 $[M]^{+\cdot}$. Calc. for $C_{23}H_{21}F_2N$, m/z: 331.12.

3-(2,5-Diphenyl-1*H*-pyrrol-3-yl)pyridine (**5k**)



Following the typical procedure 2, **5k** was prepared from **1a** (2 mmol, 0.391 g) and **2h** (2 mmol, 0.206 g). **5k** was isolated as a colourless solid (0.166 g, 28% yield). M. p. = 181-183 °C. Elemental analysis calcd (%) for $C_{21}H_{16}N_2$ (296.37): C, 85.11; H, 5.44; N, 9.45; found: C, 84.98; H, 5.51; N, 9.51. R_f = 0.25 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 9.02 (br. s, 1H, NH), 8.60 (d, ^4J 2.3 Hz, 1H, H$^{4'}$), 8.37 (dd, ^3J 4.8 Hz, ^4J 1.7 Hz, 1H, H$^{6'}$), 7.61 (ddd, ^3J 7.9 Hz, ^4J 2.3 Hz, ^4J 1.7 Hz, 1H, H$^{4'')}$, 7.58-7.50 (m, 2H), 7.43-7.20 (m, 8H) [H$_{Ph}$], 7.14 (dd, ^3J 7.9 Hz, ^3J 4.8 Hz, 1H, H$^{5'}$), 6.66 (s, 1H, H^4). ^{13}C NMR: δ 149.3, 147.0 (C$^{2',6'}$), 135.5 (C$^{4'}$), 133.0, 132.6, 132.4, 132.1, 130.4 (C$^{2,5,3',i1,i3}$), 129.1, 129.0, 127.8 (6C$_{Ph}$), 127.5, 126.9 (C^{p1,p3}), 124.1 (C^{o3}), 123.3 (C$^{5'}$), 119.9 (C^3), 108.1 (C^4). The NMR data were in accordance with the literature.[S3] IR (film, ν/cm^{-1}): 3435, 3203, 3137, 3094, 3060, 3025, 2968, 2919, 2875, 2853, 2766, 1609, 1595, 1567, 1487, 1465, 1411, 1299, 1275, 1241, 1196, 1178, 1104, 1073, 1027, 957, 908, 803, 764, 732, 698. MS (EI), m/z (%):296.15 [M]$^{+\cdot}$. Calc. for $C_{21}H_{16}N_2$, m/z: 296.13.

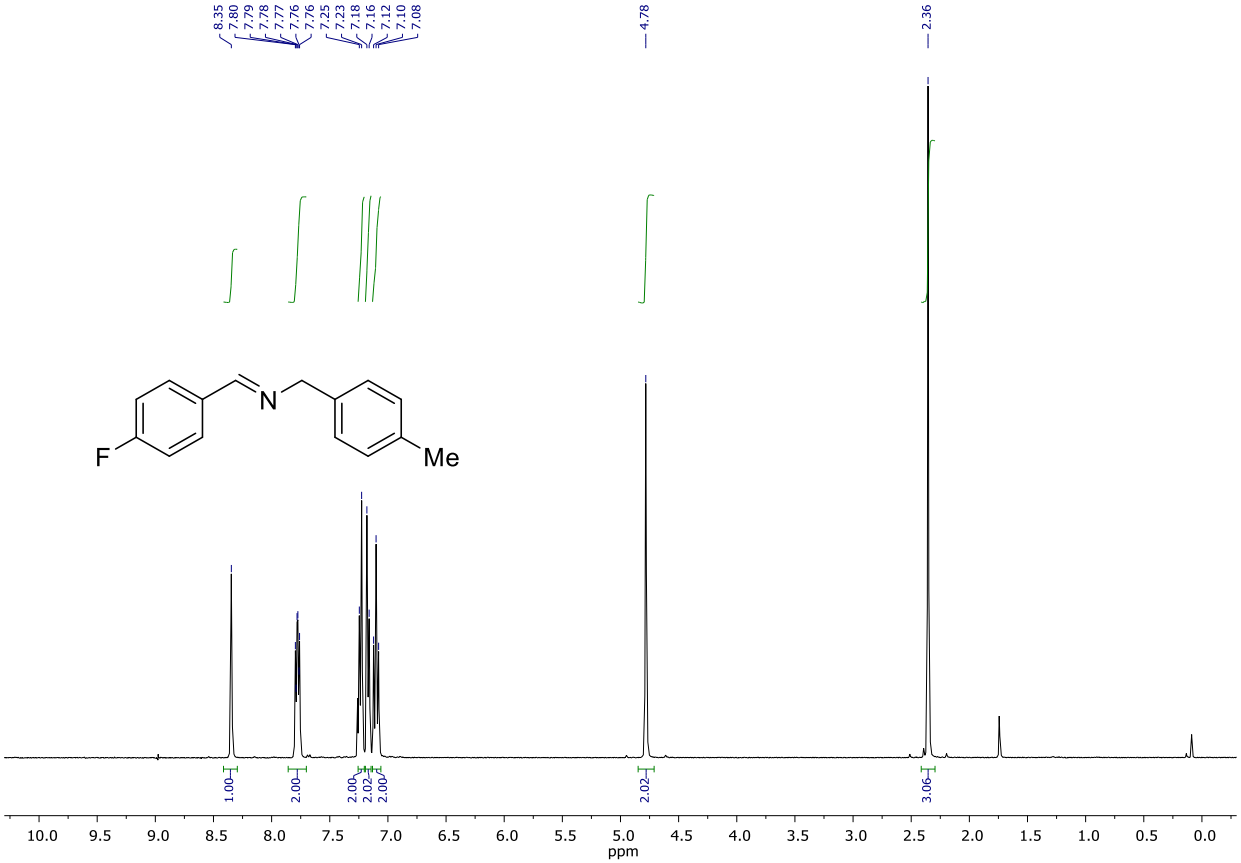
References

S1. D. Y. Curtin, E. J. Grubbs and C. G. McCart, *J. Am. Chem. Soc.*, 1966, **88**, 2775.

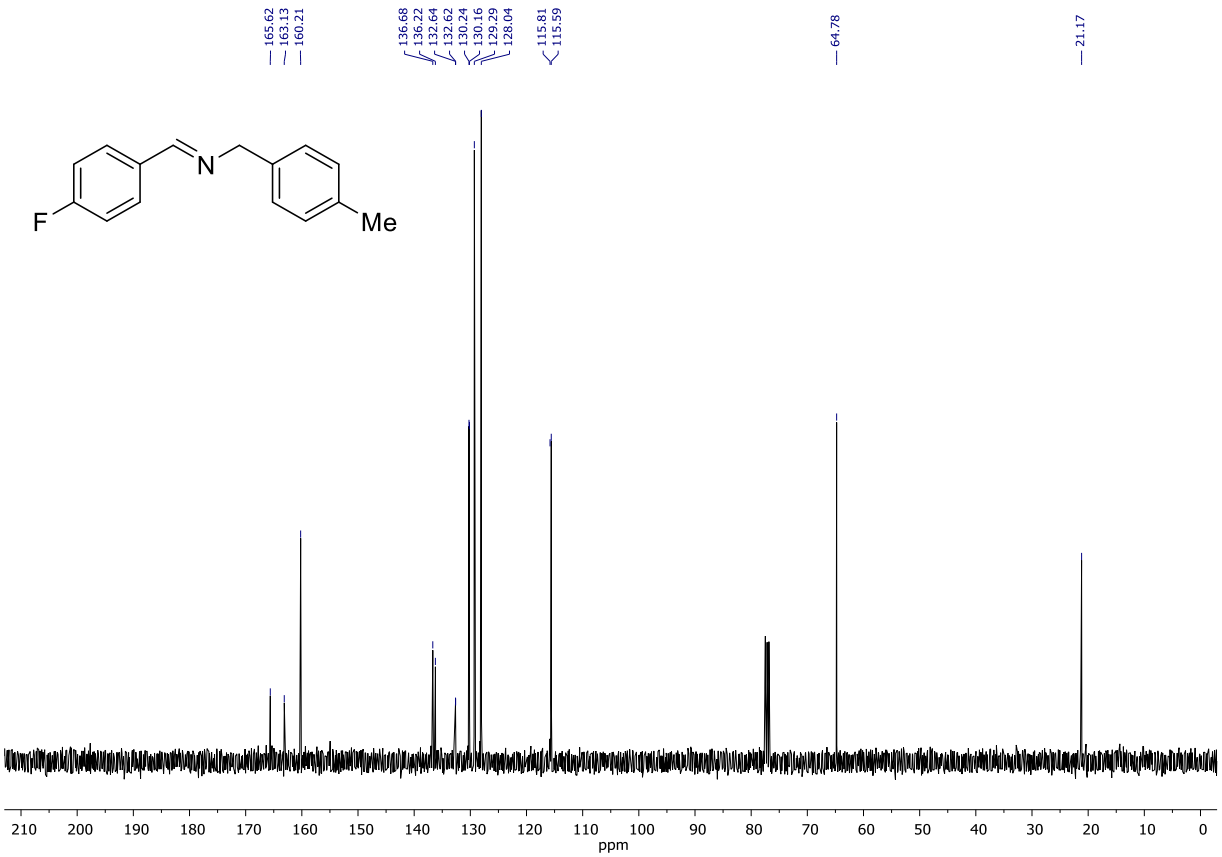
S2. (*a*) K. Singh, A. Kaur, V. S. Mithu and S. Sharma, *J. Org. Chem.*, 2017, **82**, 5285; (*b*) R. Brišar, F. Unglaube, D. Hollmann, H. Jiao and E. Mejía, *J. Org. Chem.*, 2018, **83**, 13481.

S3. M.Yamaguchi, S. Fujiwara and R. Manabe, *Org. Lett.*, 2019, **21**, 6972.

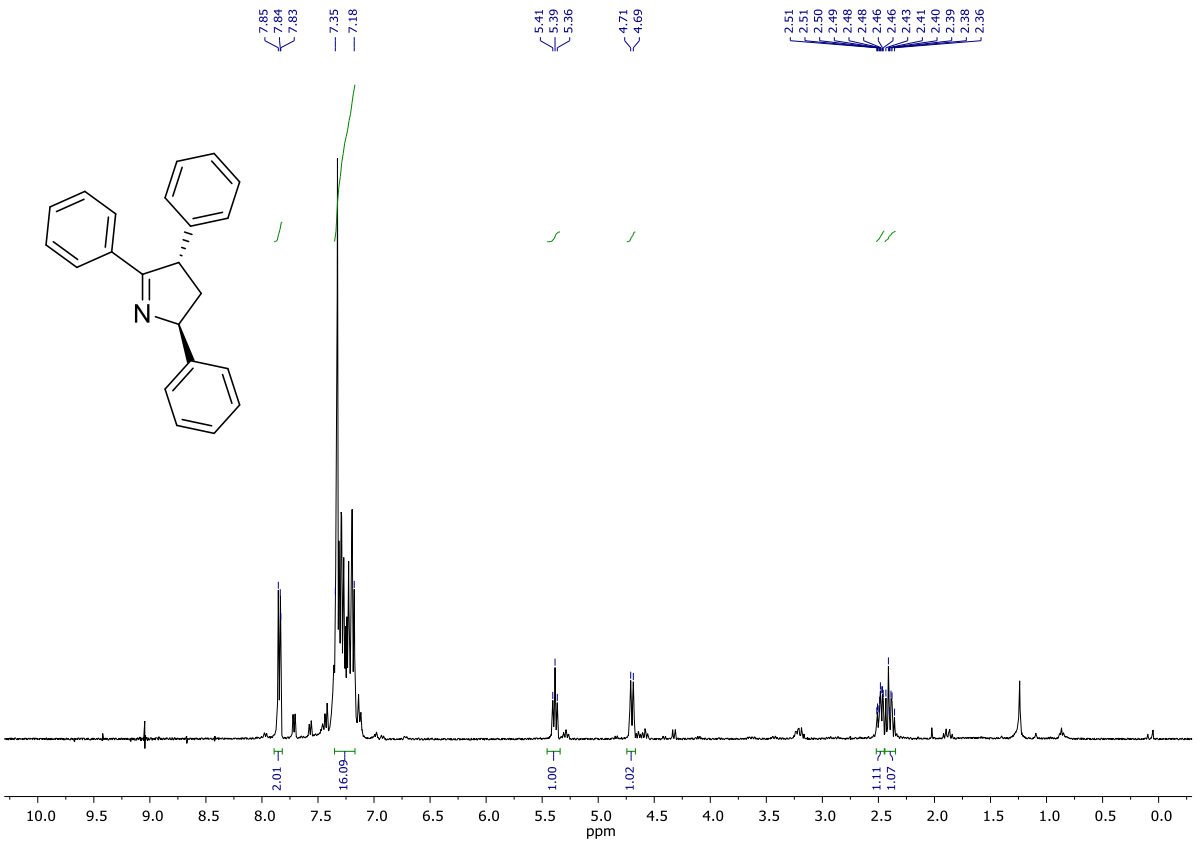
NMR Spectra



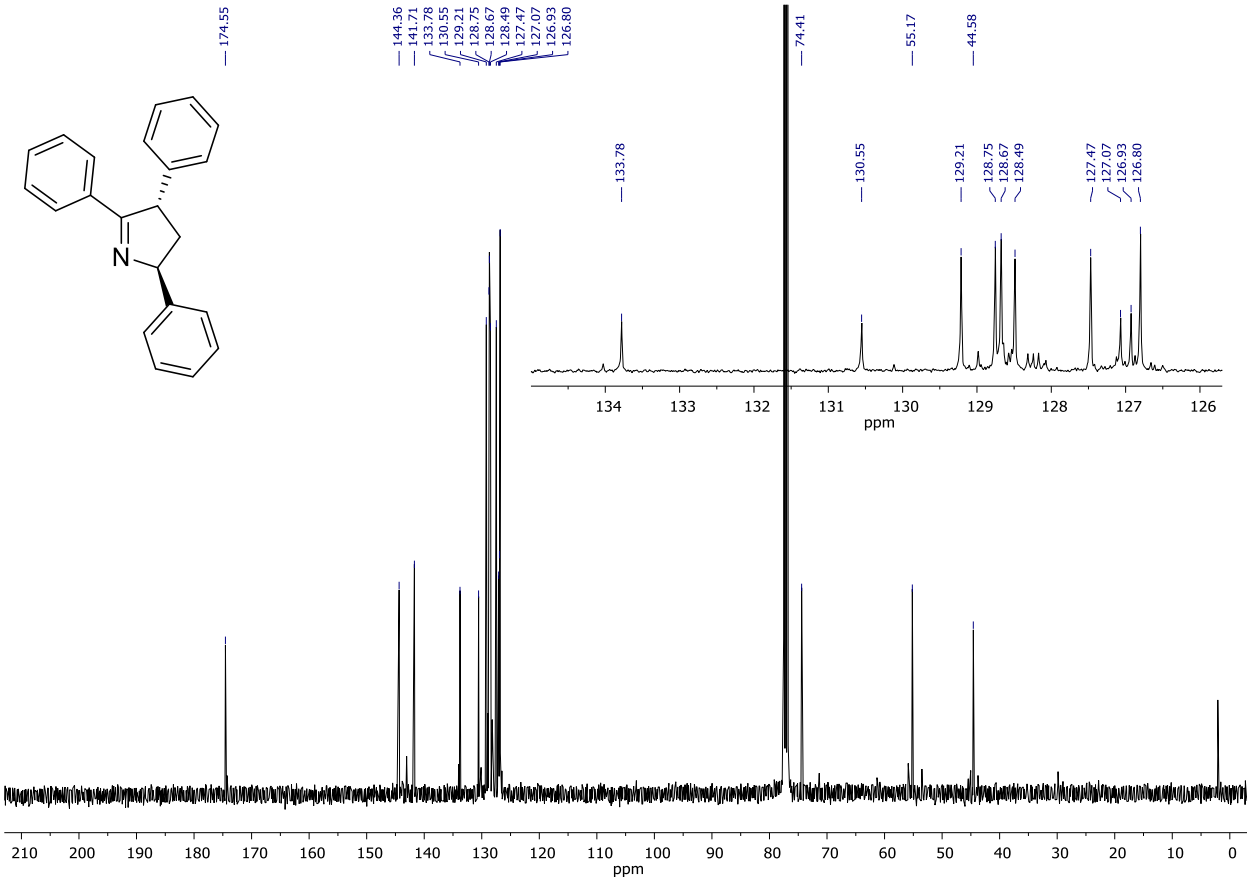
^{1}H NMR spectrum of **1e** (400.1 MHz, $CDCl_3$)



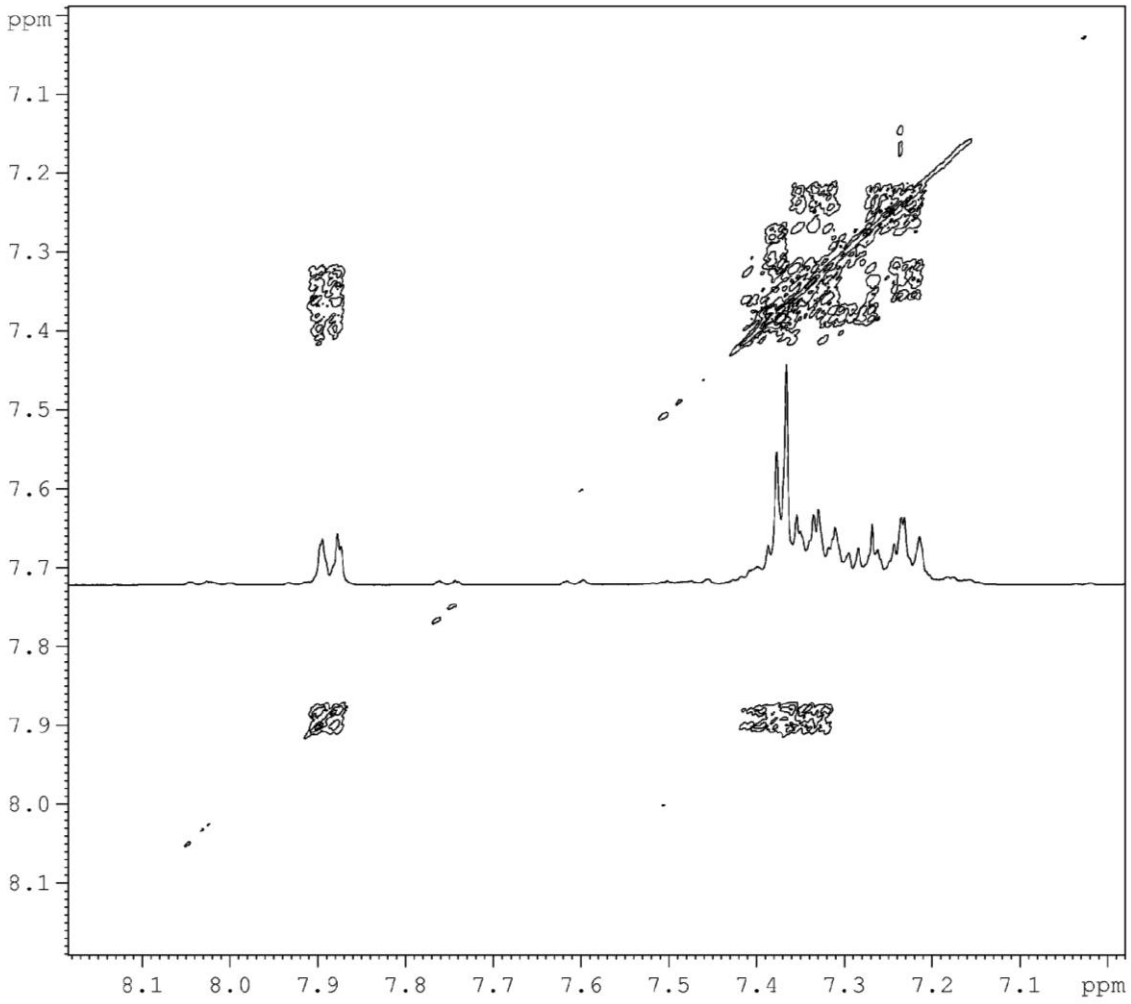
^{13}C NMR spectrum of **1e** (100.6 MHz, $CDCl_3$)



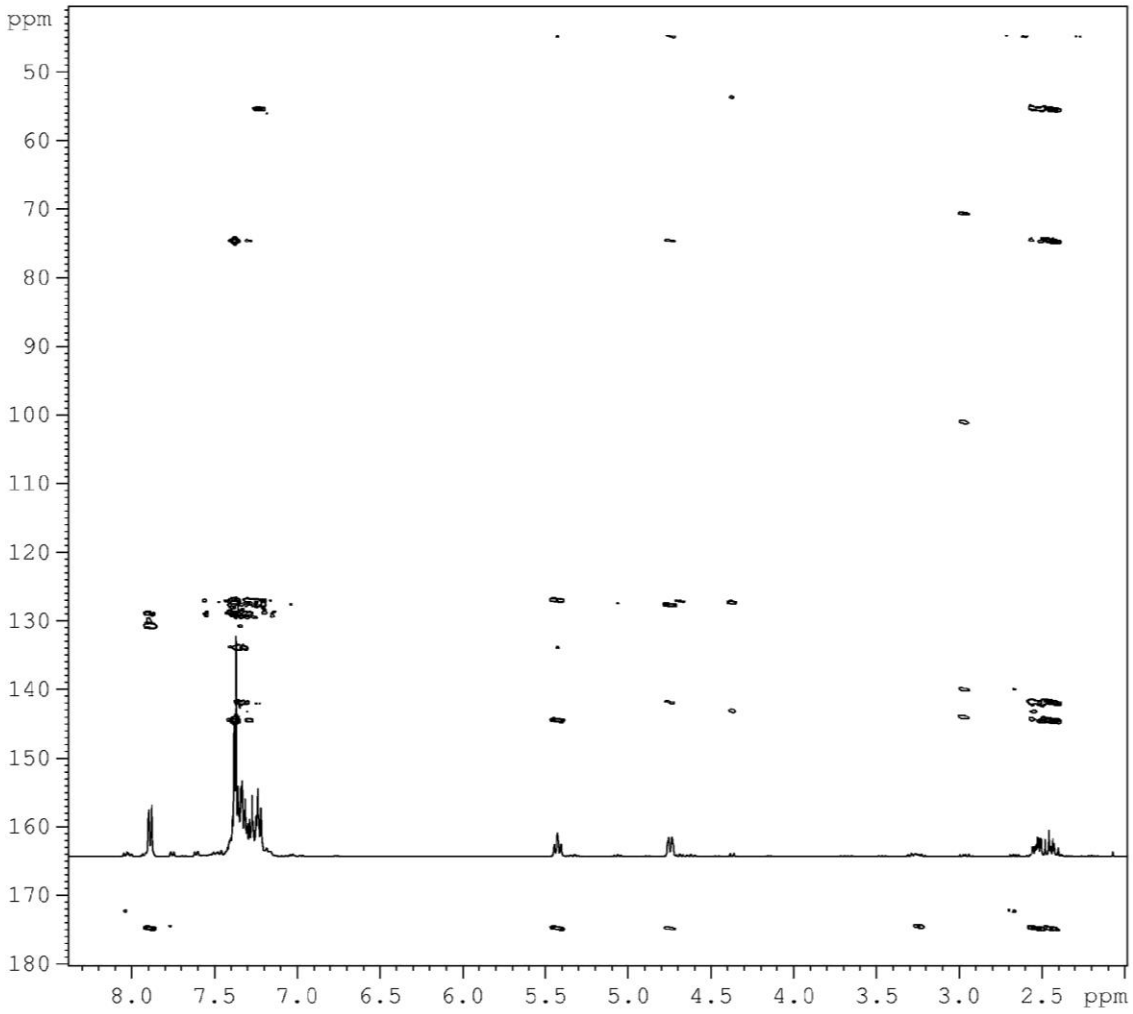
^{1}H NMR spectrum of **3a** (400.1 MHz, $CDCl_3$)



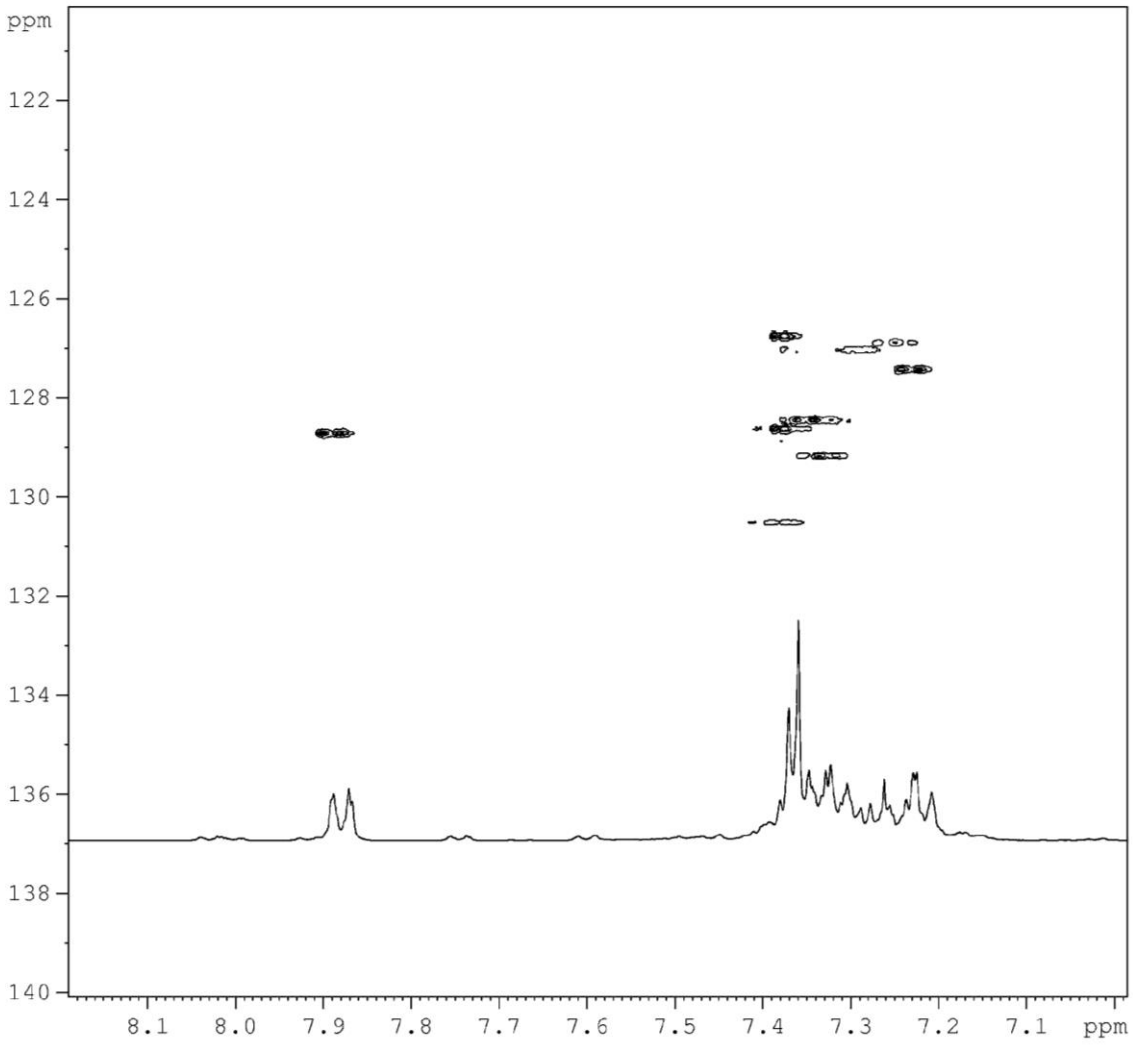
^{13}C NMR spectrum of **3a** (100.6 MHz, $CDCl_3$)



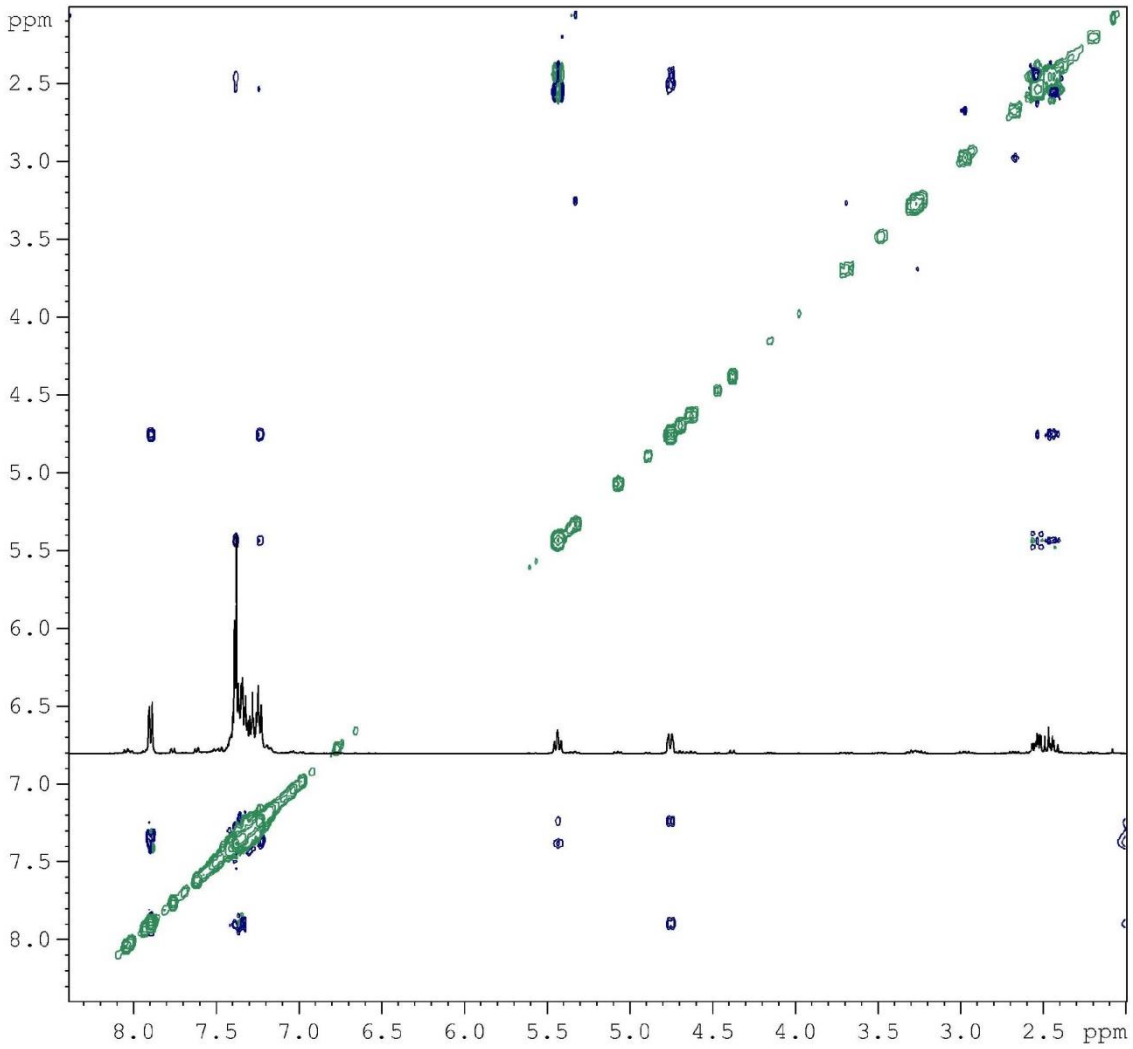
COSY spectrum of **3a** (aromatic region**)** (400.1 MHz, $CDCl_3$)



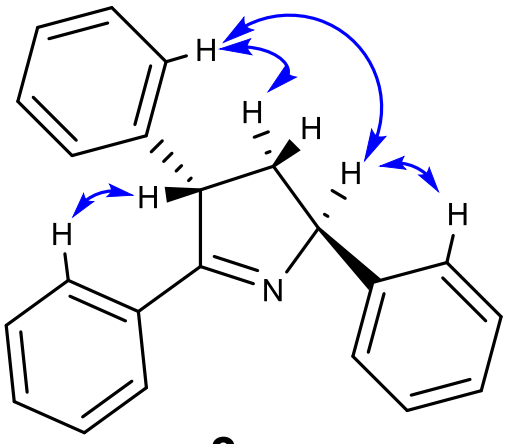
2D ^{1}H-^{13}C HMBC spectrum of **3a**



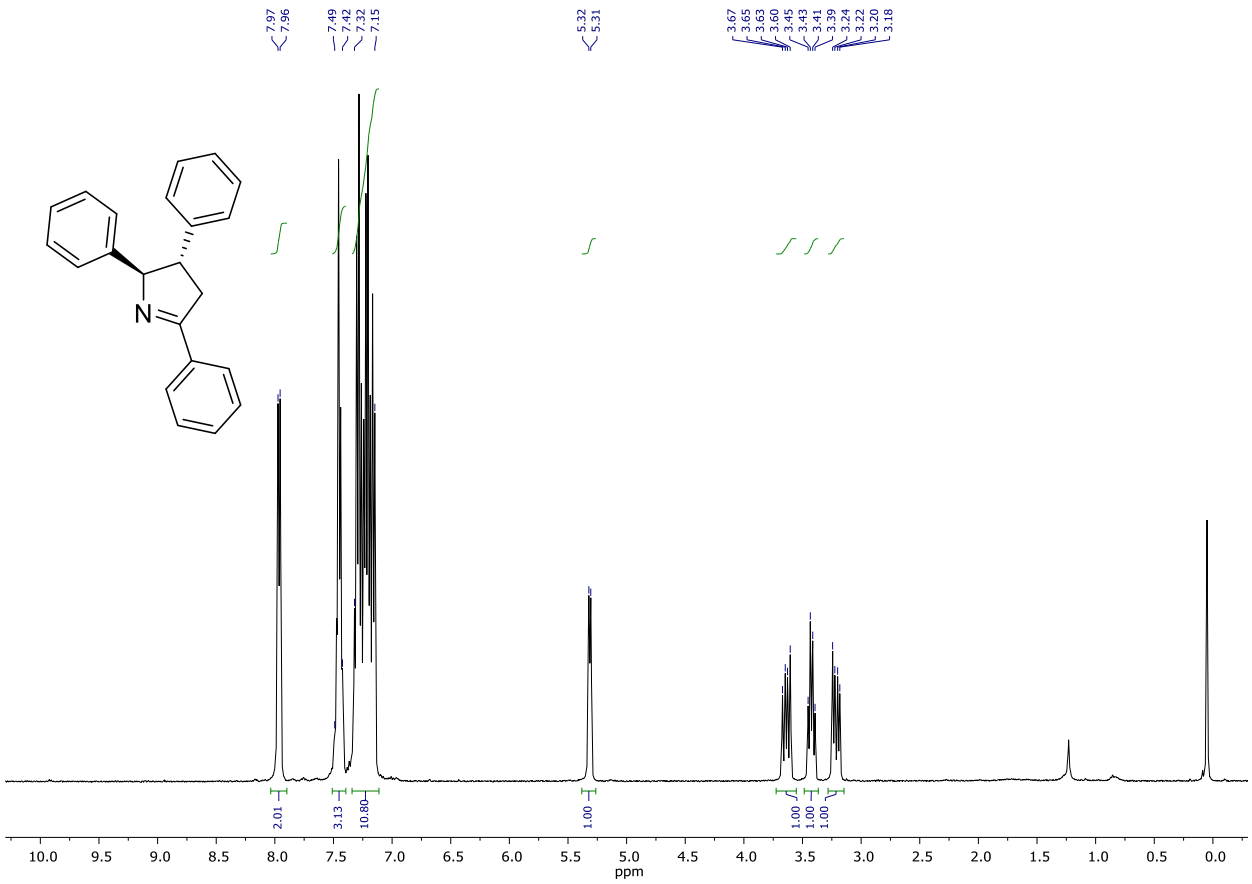
2D ^{1}H-^{13}C HSQC spectrum of **3a** (aromatic region**)**



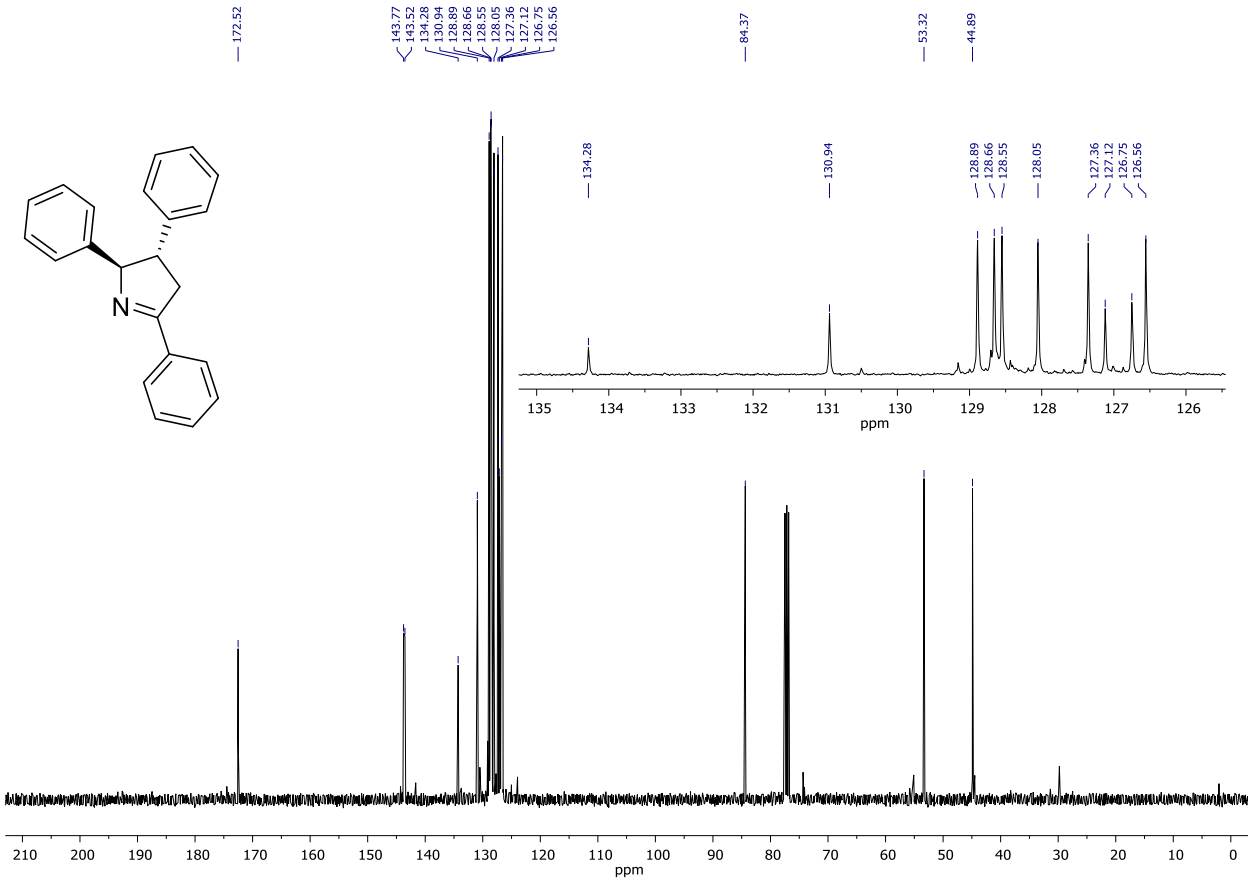
2D NOESY spectrum of **3a** (400.1 MHz, $CDCl_3$)



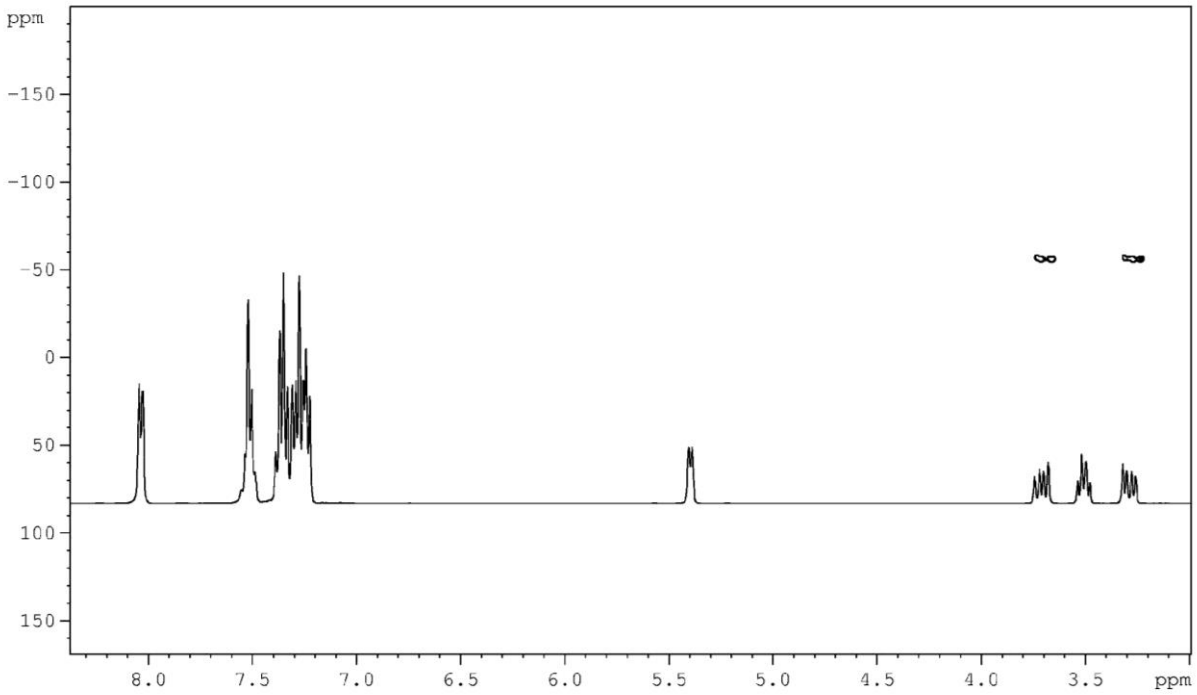
3a



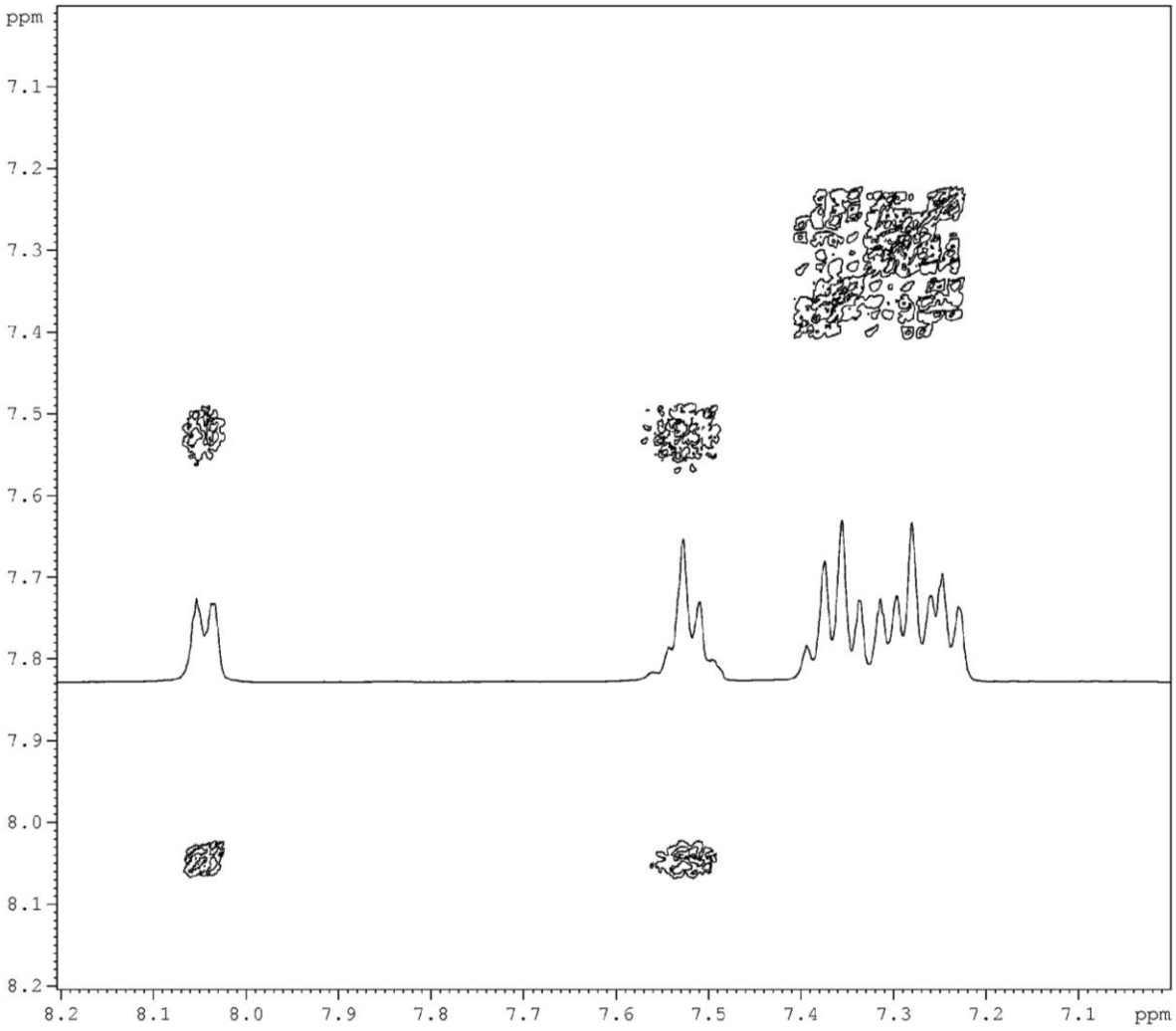
^{1}H NMR spectrum of **3'a** (400.1 MHz, $CDCl_3$)



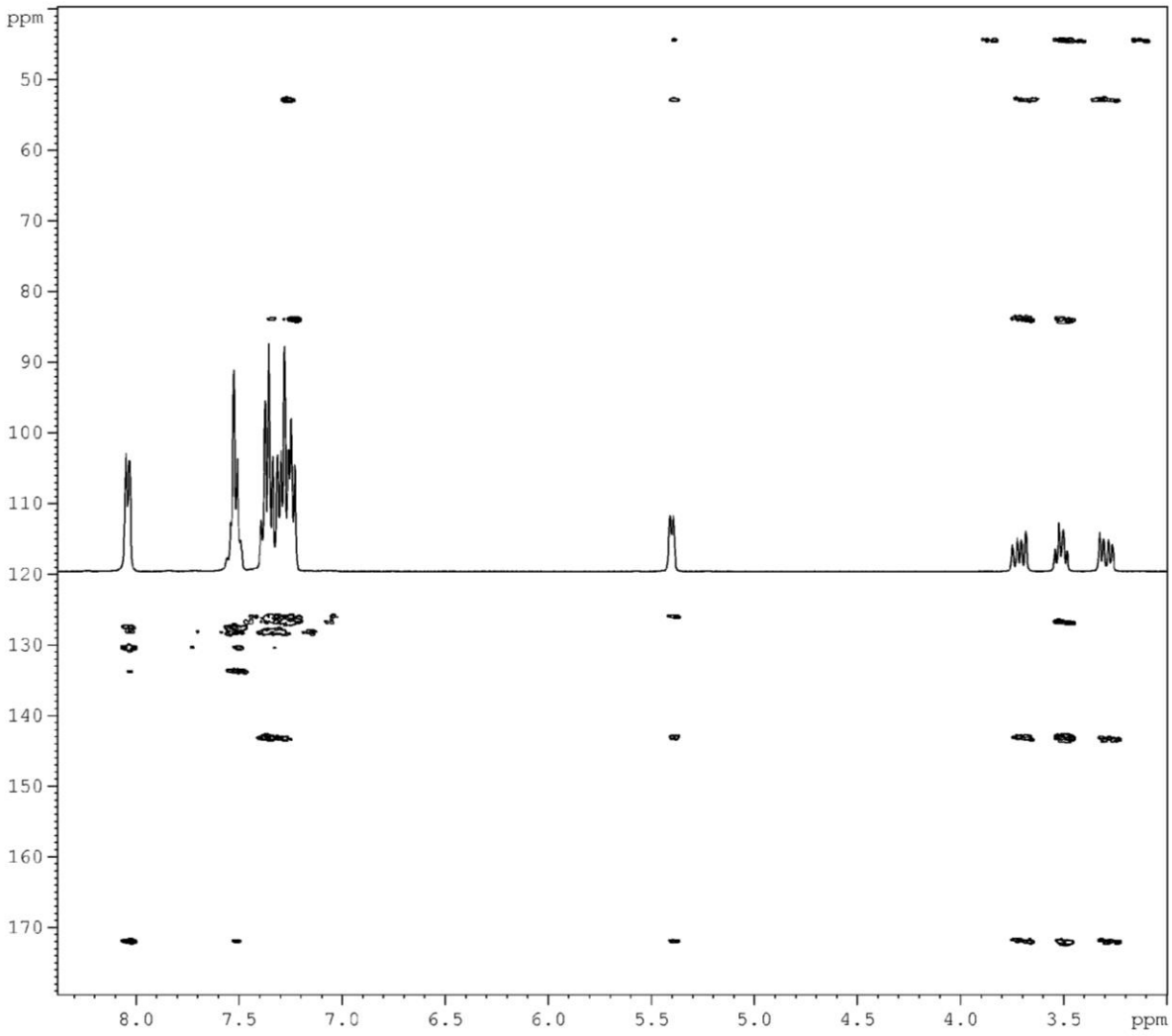
^{13}C NMR spectrum of **3'a** (100.6 MHz, $CDCl_3$)



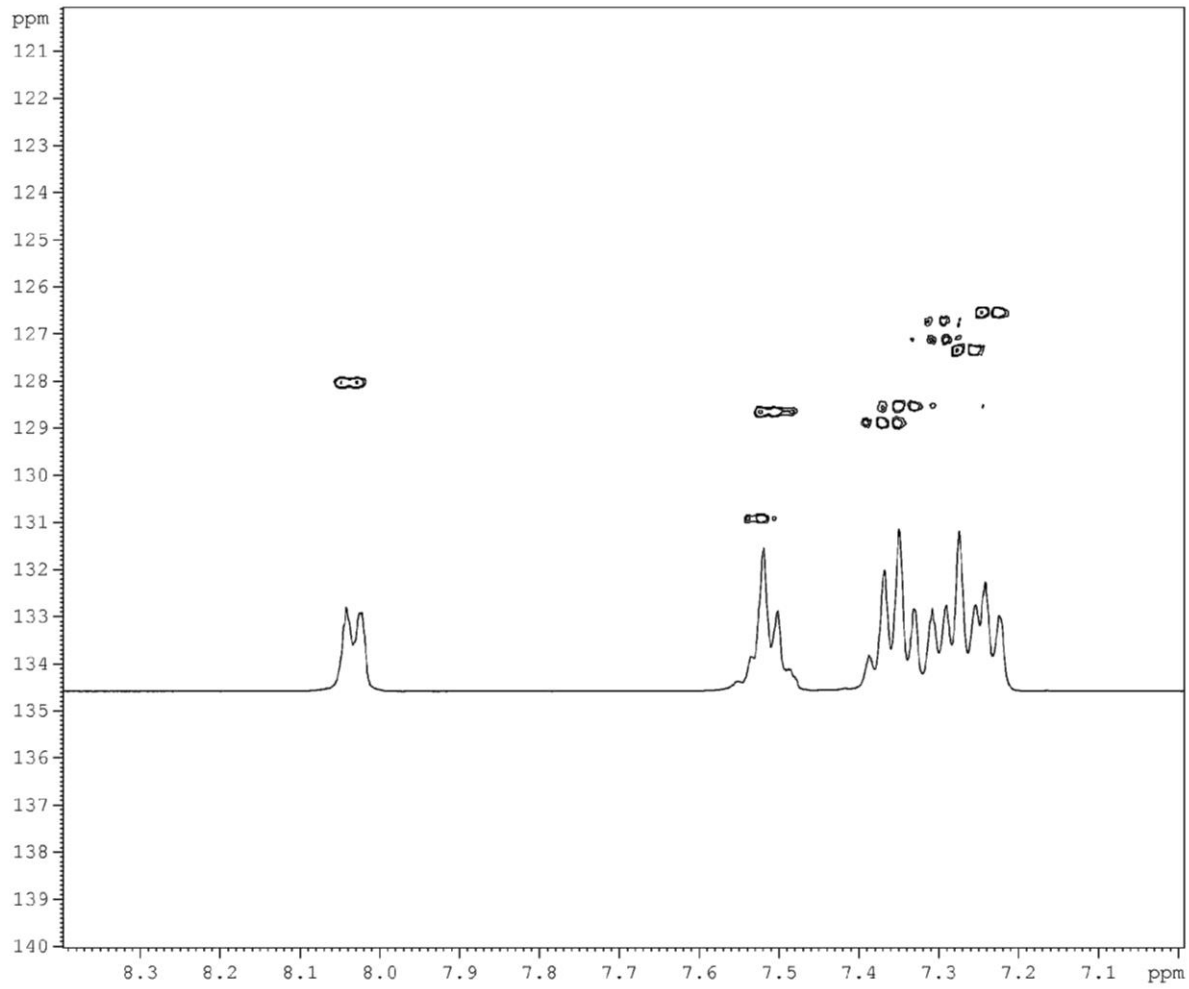
2D ^{1}H-^{15}N HMBC spectrum of **3'a**



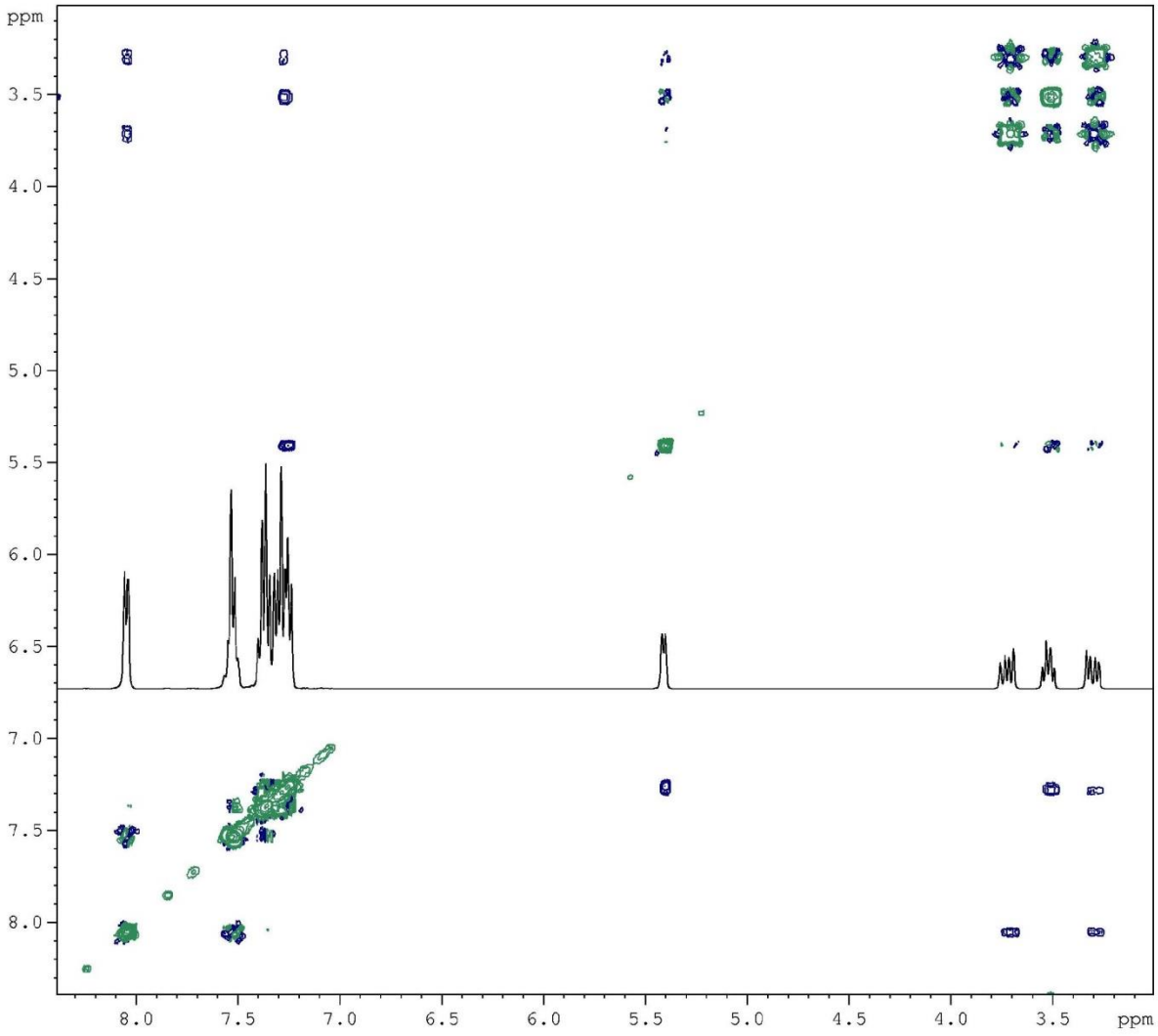
2D COSY spectrum of **3'a** (aromatic region) (400.1 MHz, $CDCl_3$)



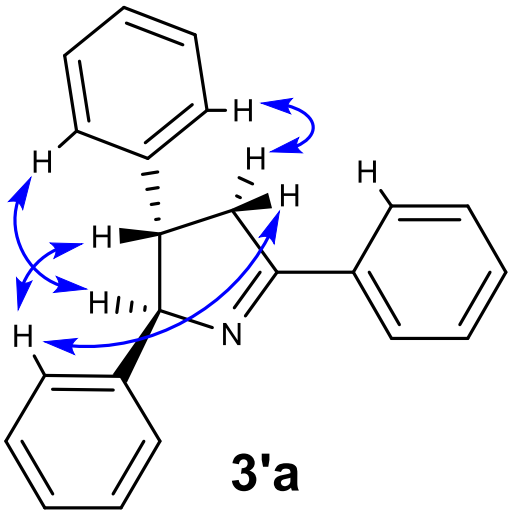
2D ^{1}H-^{13}C HMBC spectrum of **3'a**



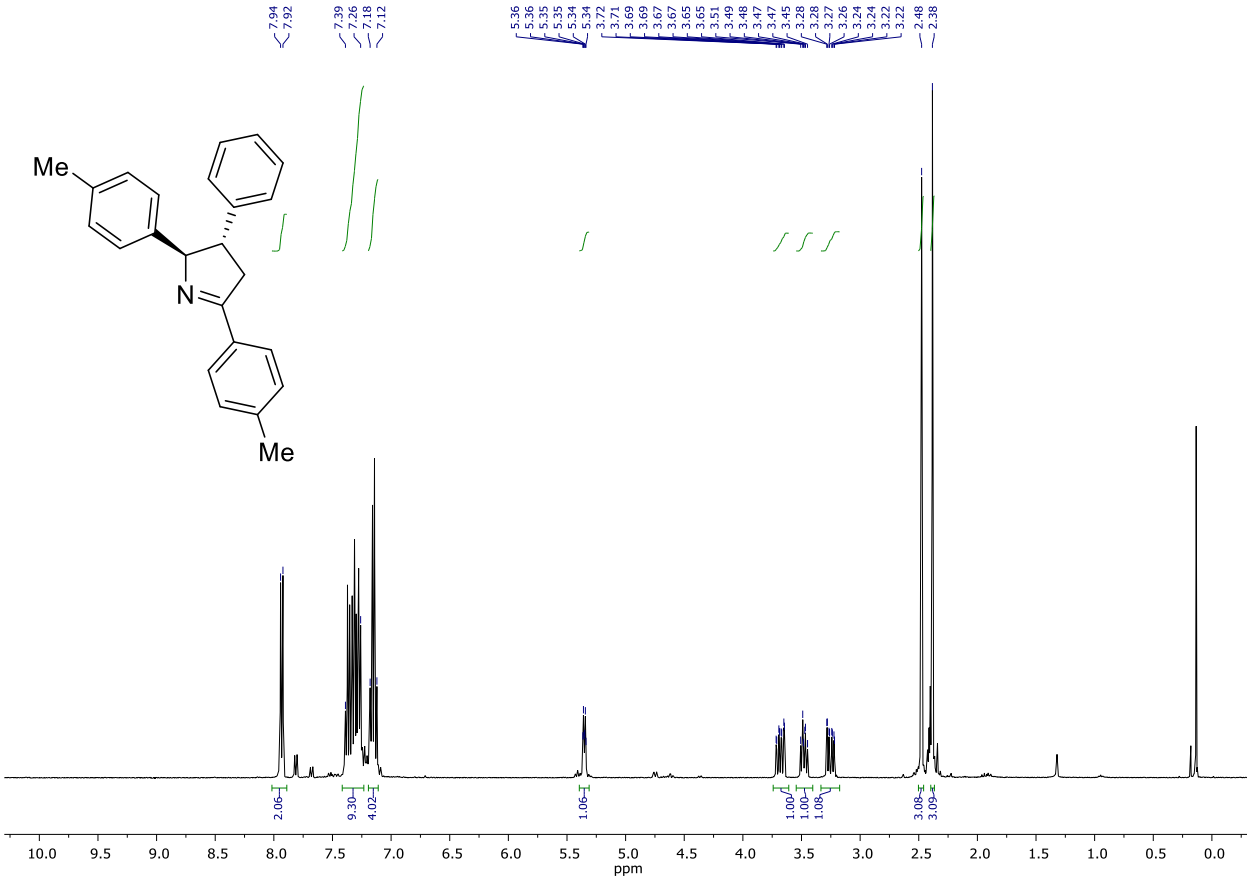
2D ^{1}H-^{13}C HSQC spectrum of **3'a** (aromatic region**)**



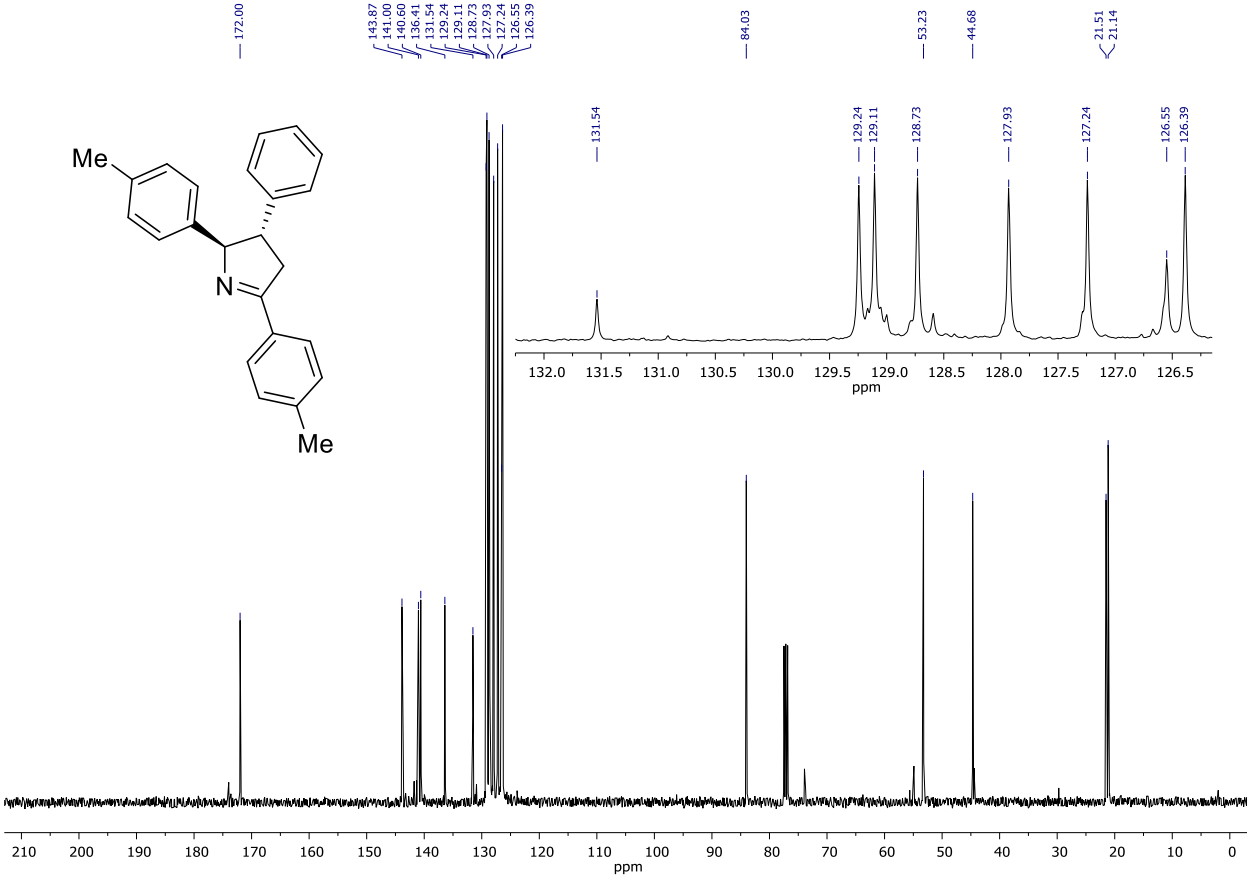
2D NOESY spectrum of **3'a** (400.1 MHz, $CDCl_3$)



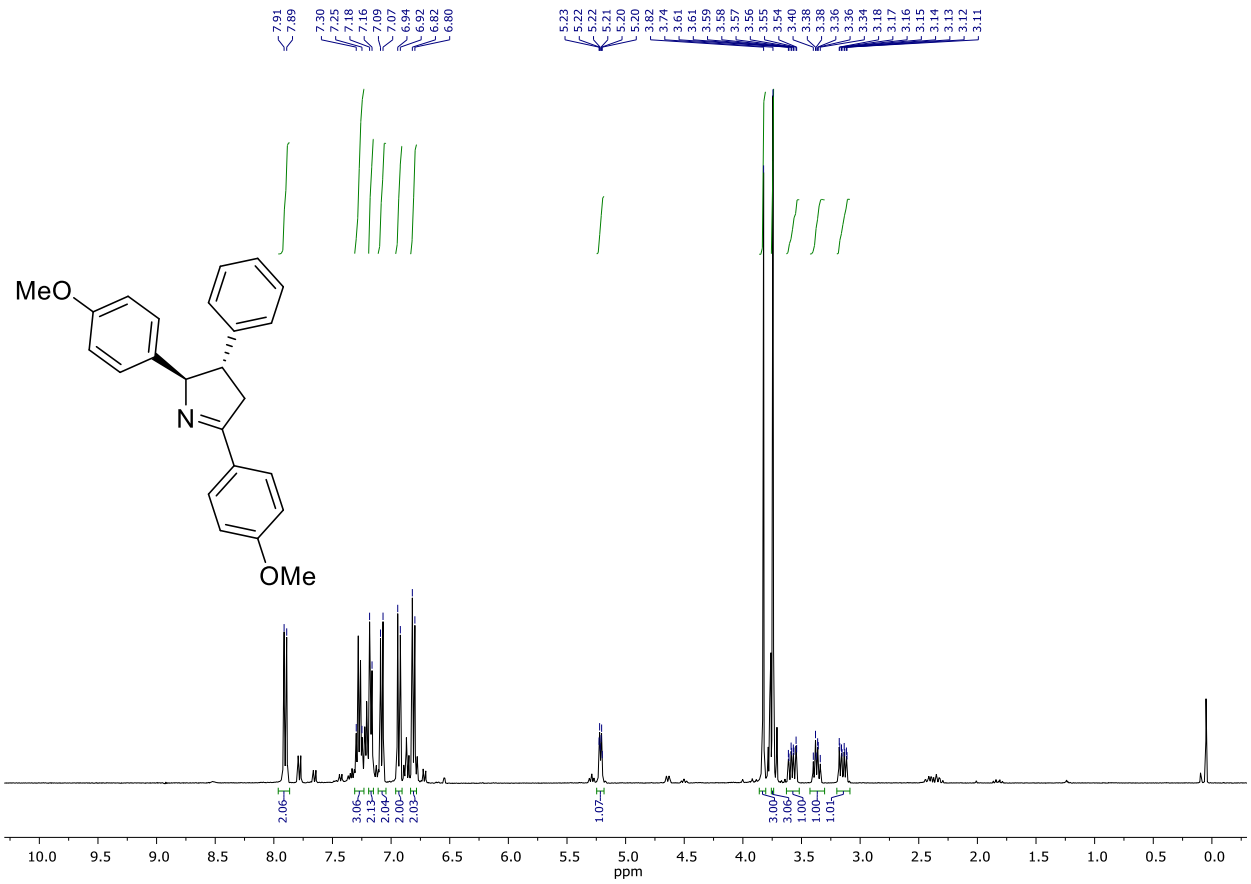
3'a



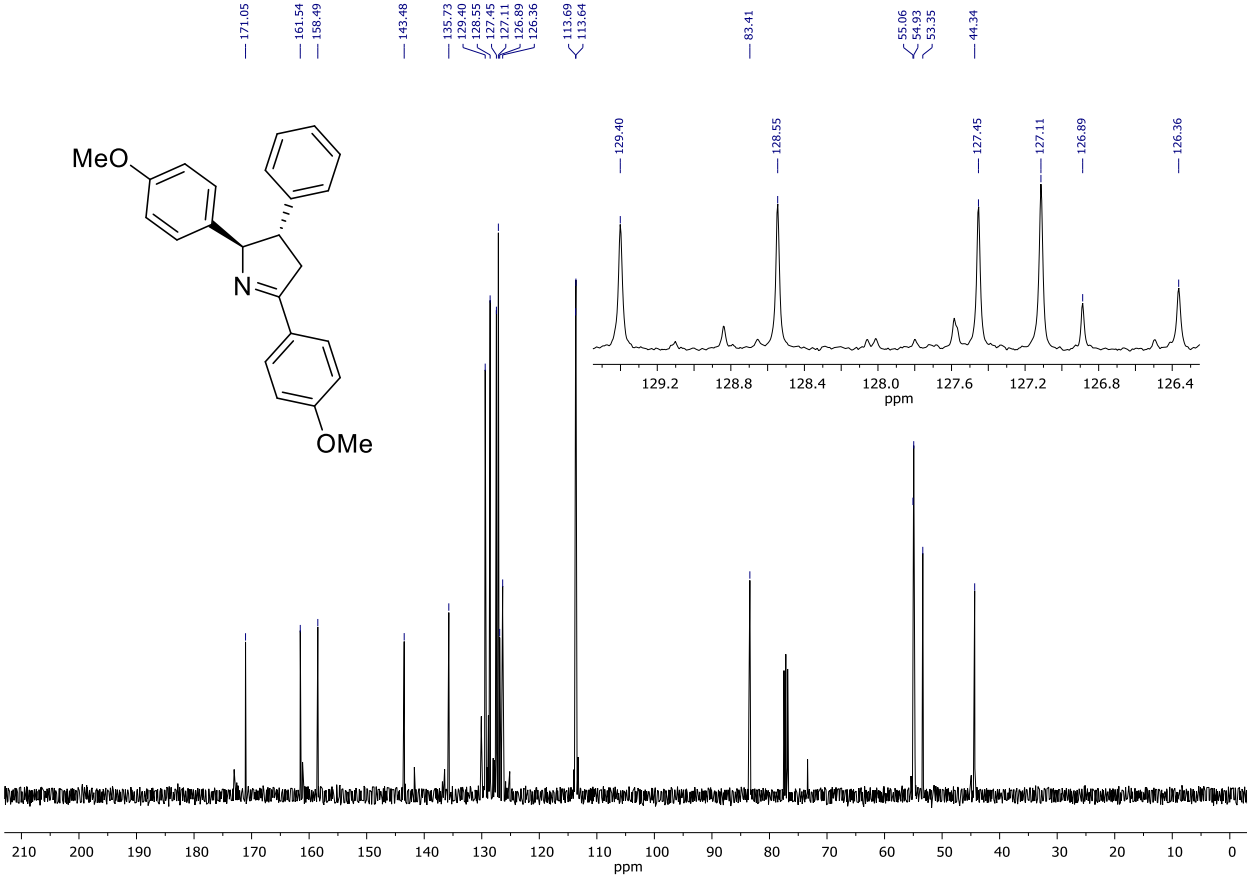
^{1}H NMR spectrum of **3b**+**3'b** tautomeric mixture (400.1 MHz, $CDCl_3$)



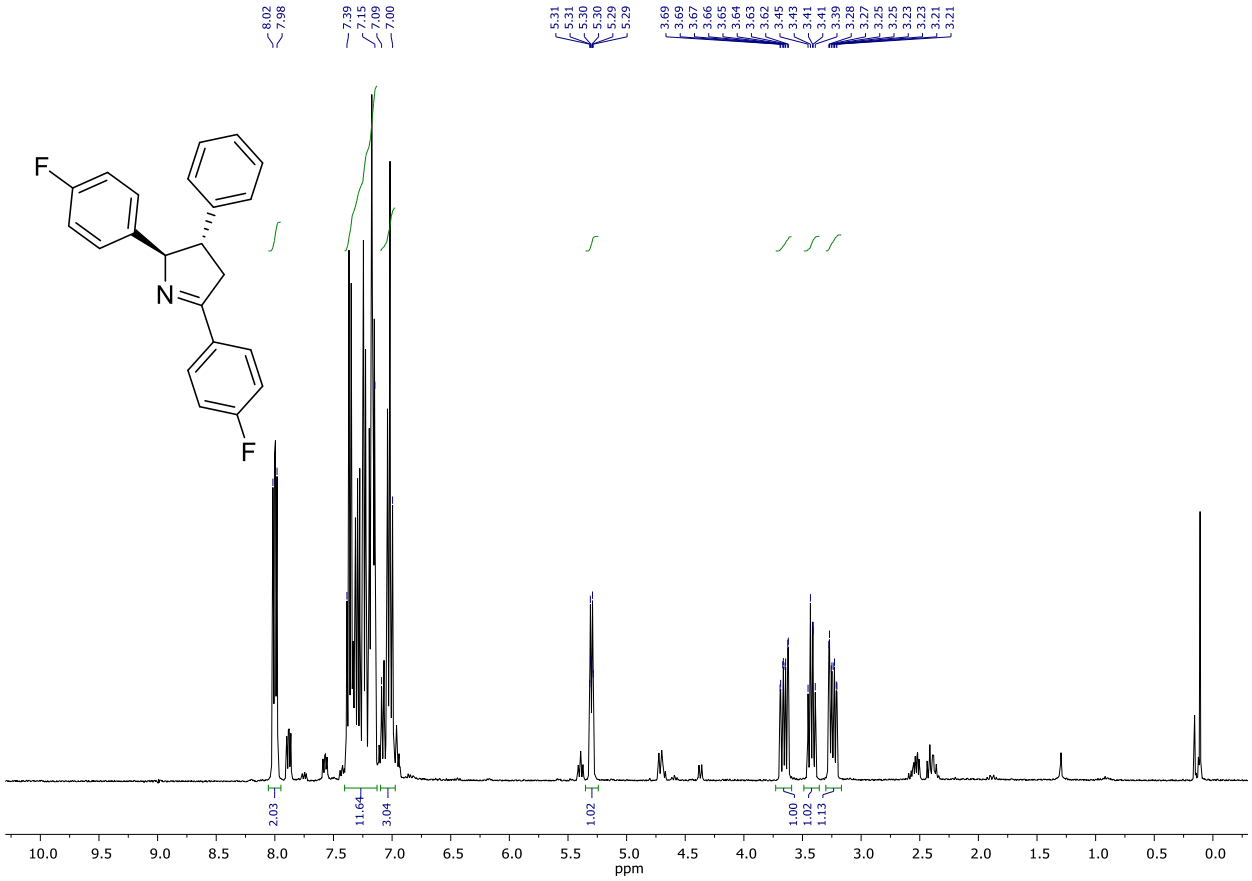
^{13}C NMR spectrum of **3b**+**3'b** tautomeric mixture (100.6 MHz, $CDCl_3$)



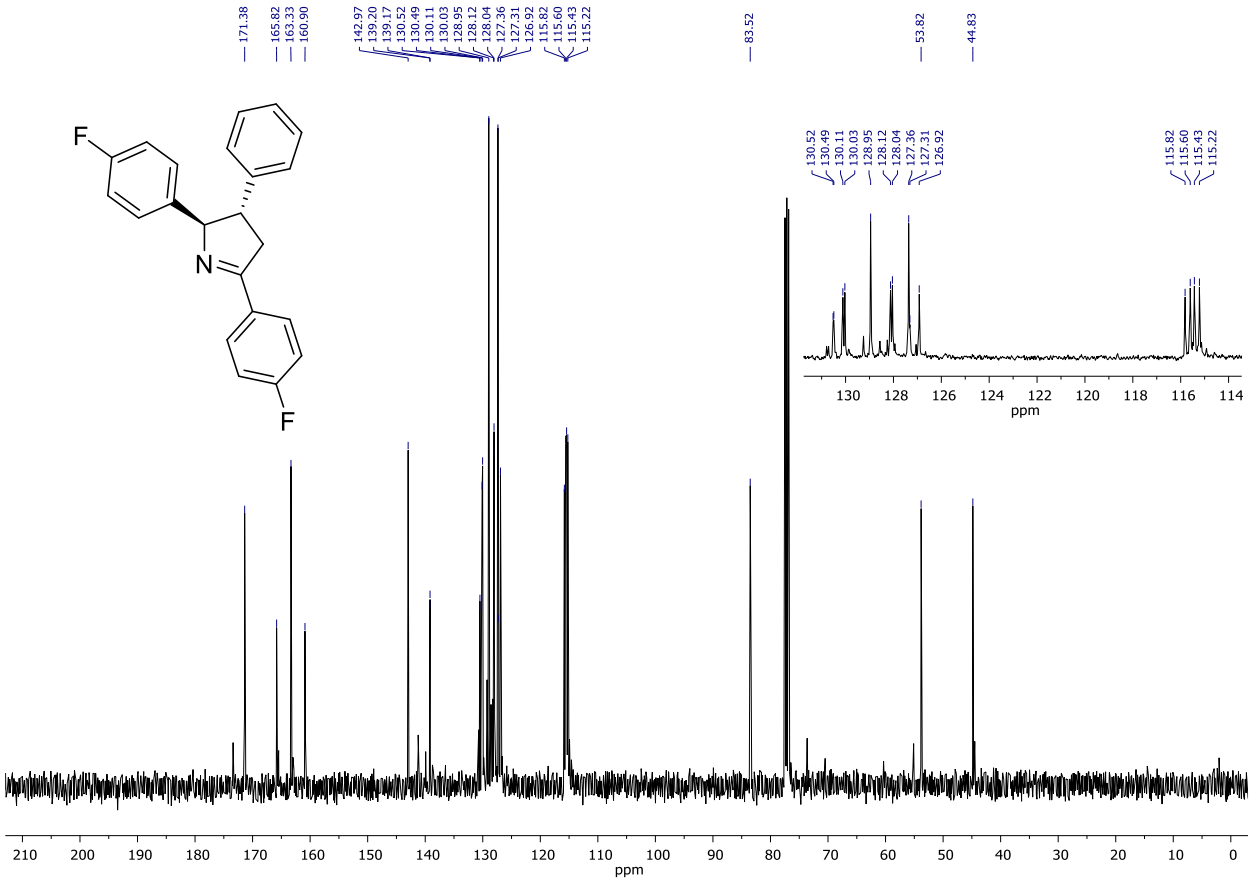
^{1}H NMR spectrum of **3c**+**3'c** tautomeric mixture (400.1 MHz, $CDCl_3$)



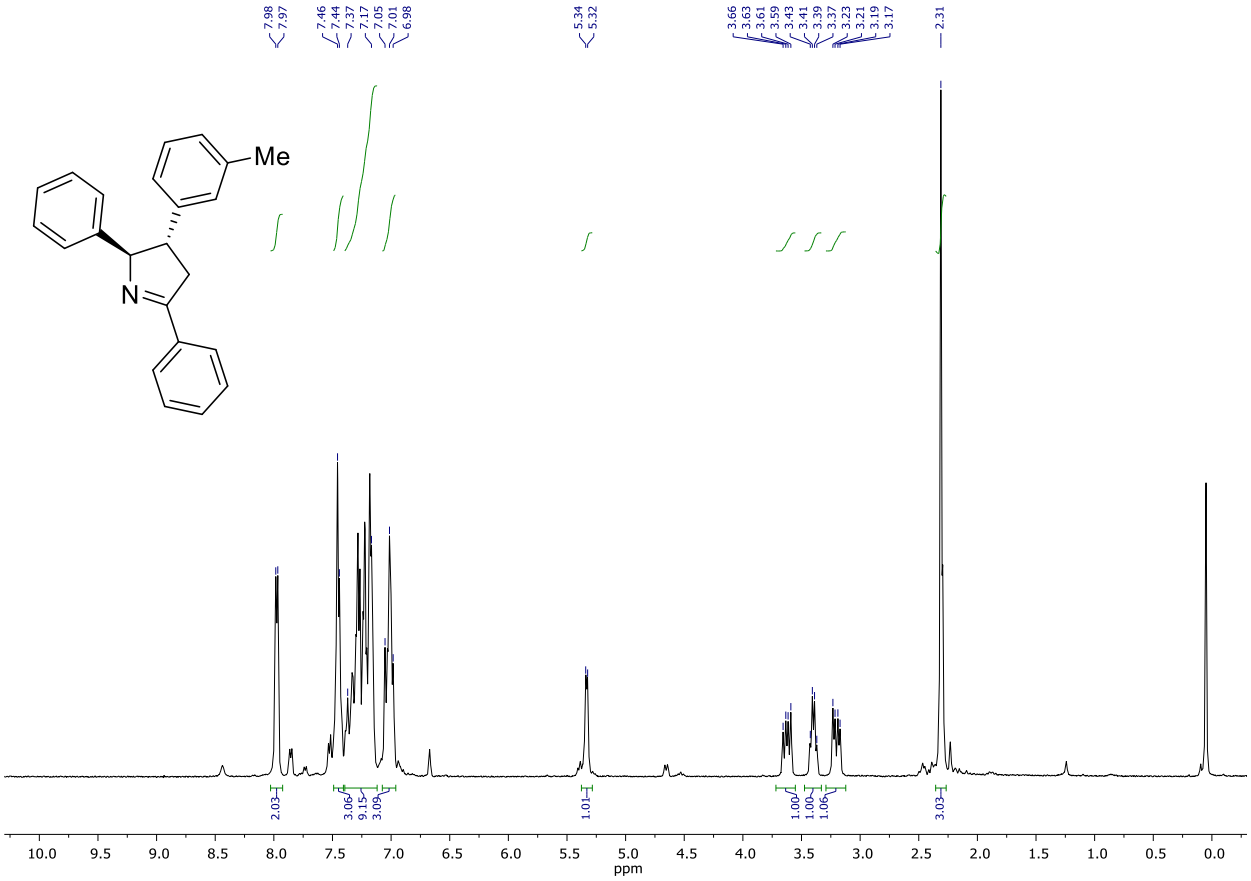
^{13}C NMR spectrum of **3c**+**3'c** tautomeric mixture (100.6 MHz, $CDCl_3$)



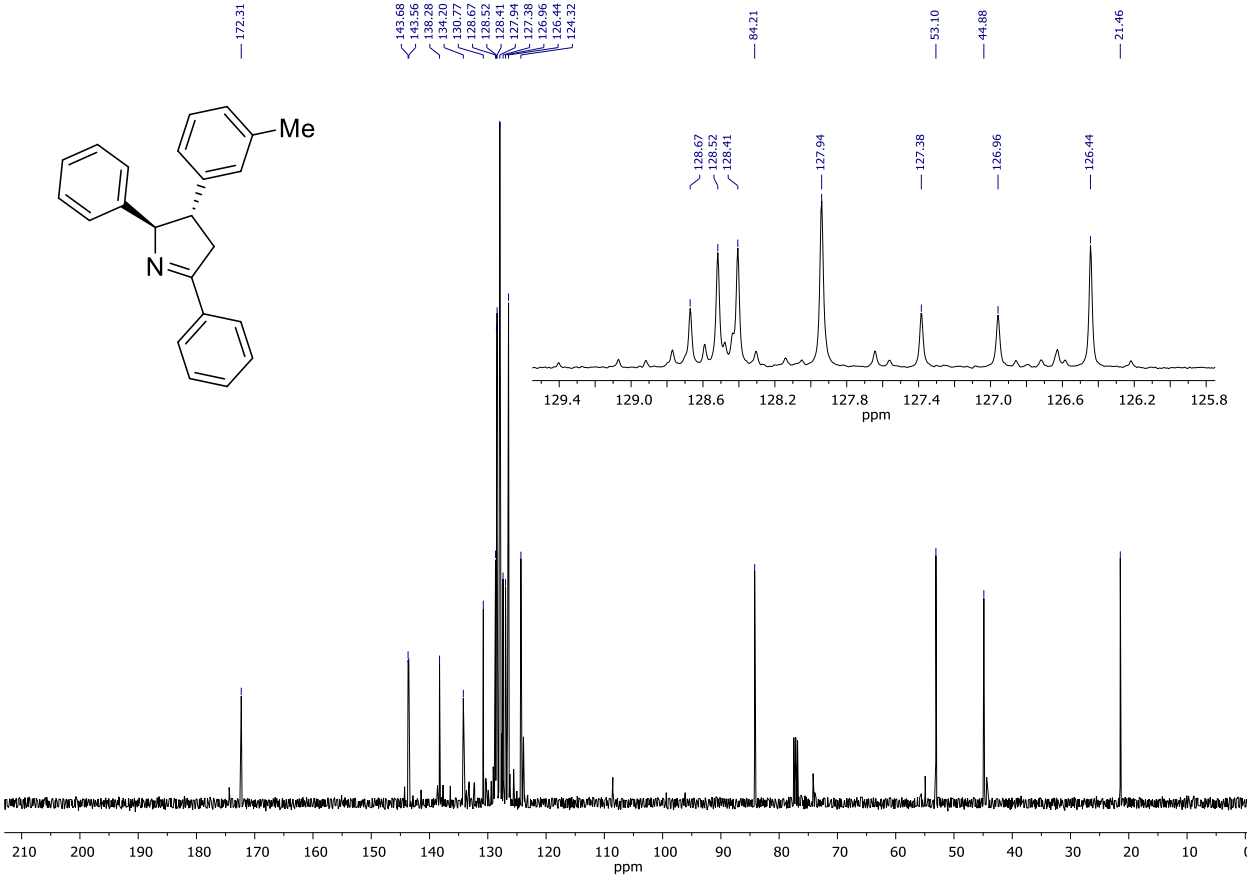
^{1}H NMR spectrum of **3d**+**3'd** tautomeric mixture (400.1 MHz, $CDCl_3$)



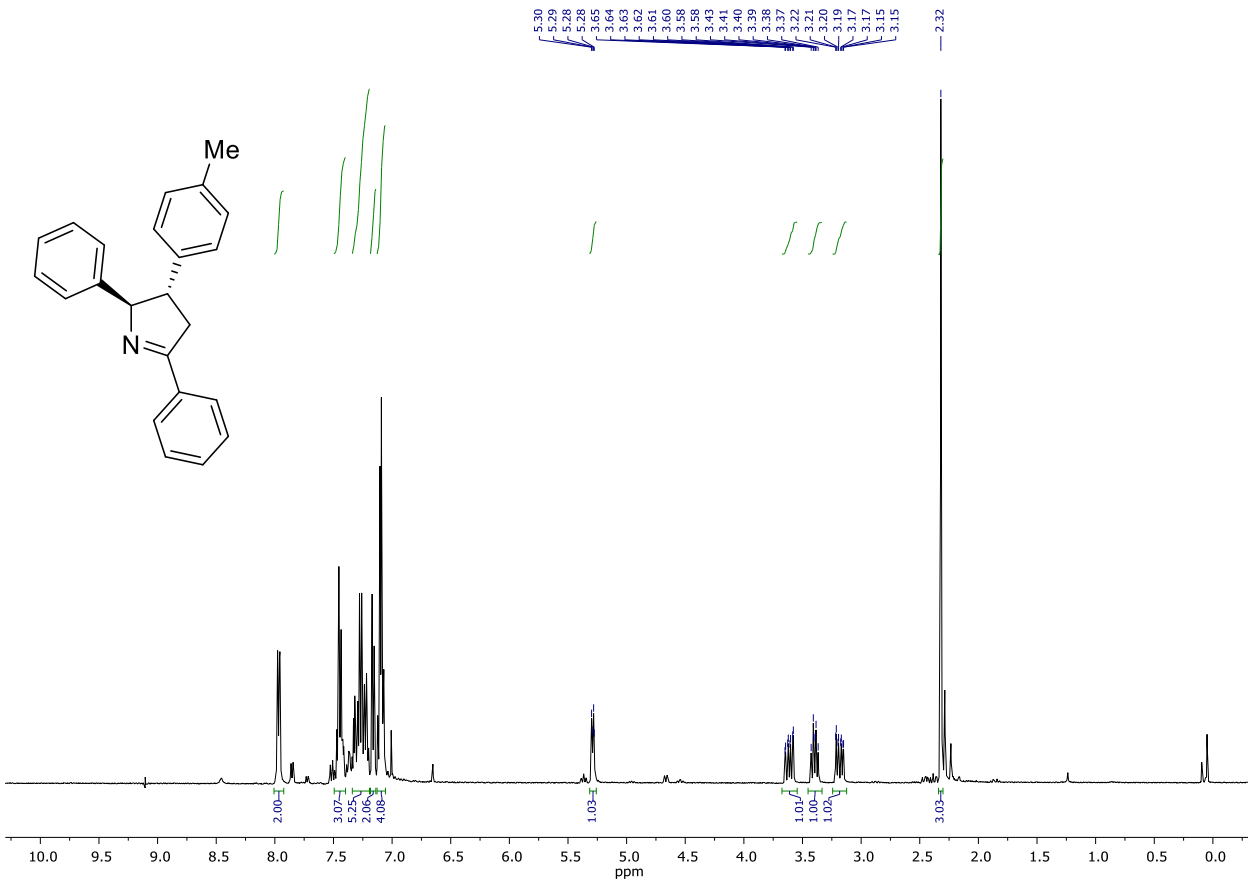
^{13}C NMR spectrum of **3d**+**3'd** tautomeric mixture (100.6 MHz, $CDCl_3$)



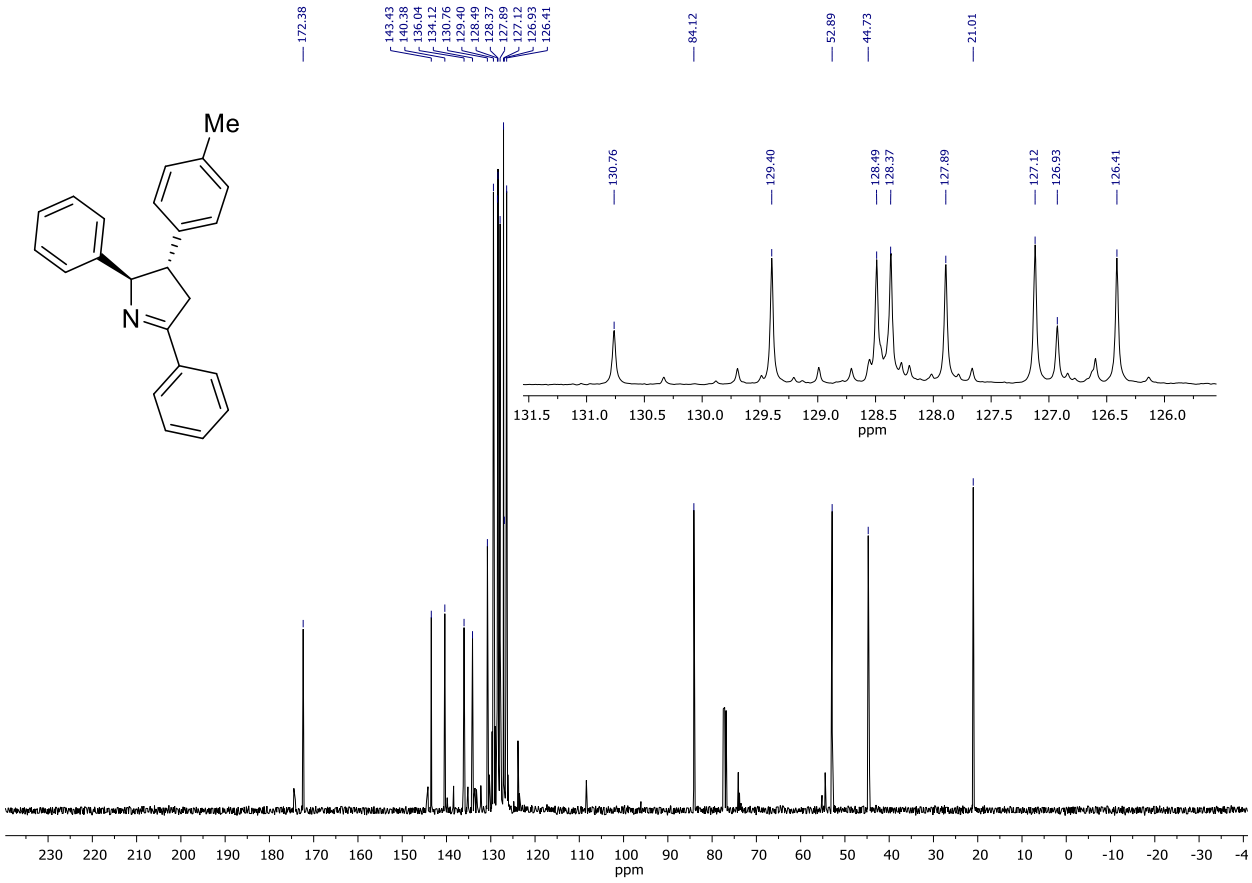
^{1}H NMR spectrum of **3e**+**3'e** tautomeric mixture (400.1 MHz, $CDCl_3$)



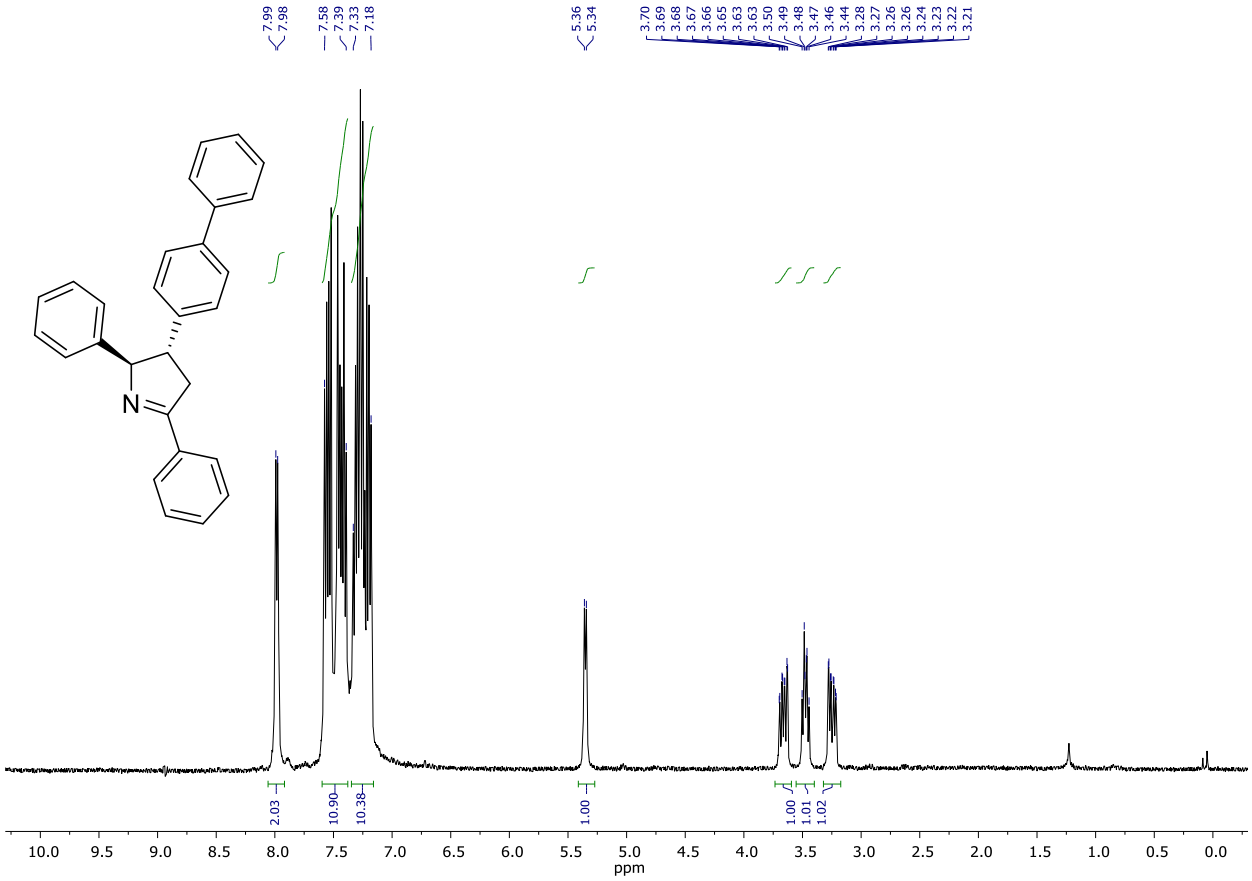
^{13}C NMR spectrum of **3e**+**3'e** tautomeric mixture (100.6 MHz, $CDCl_3$)



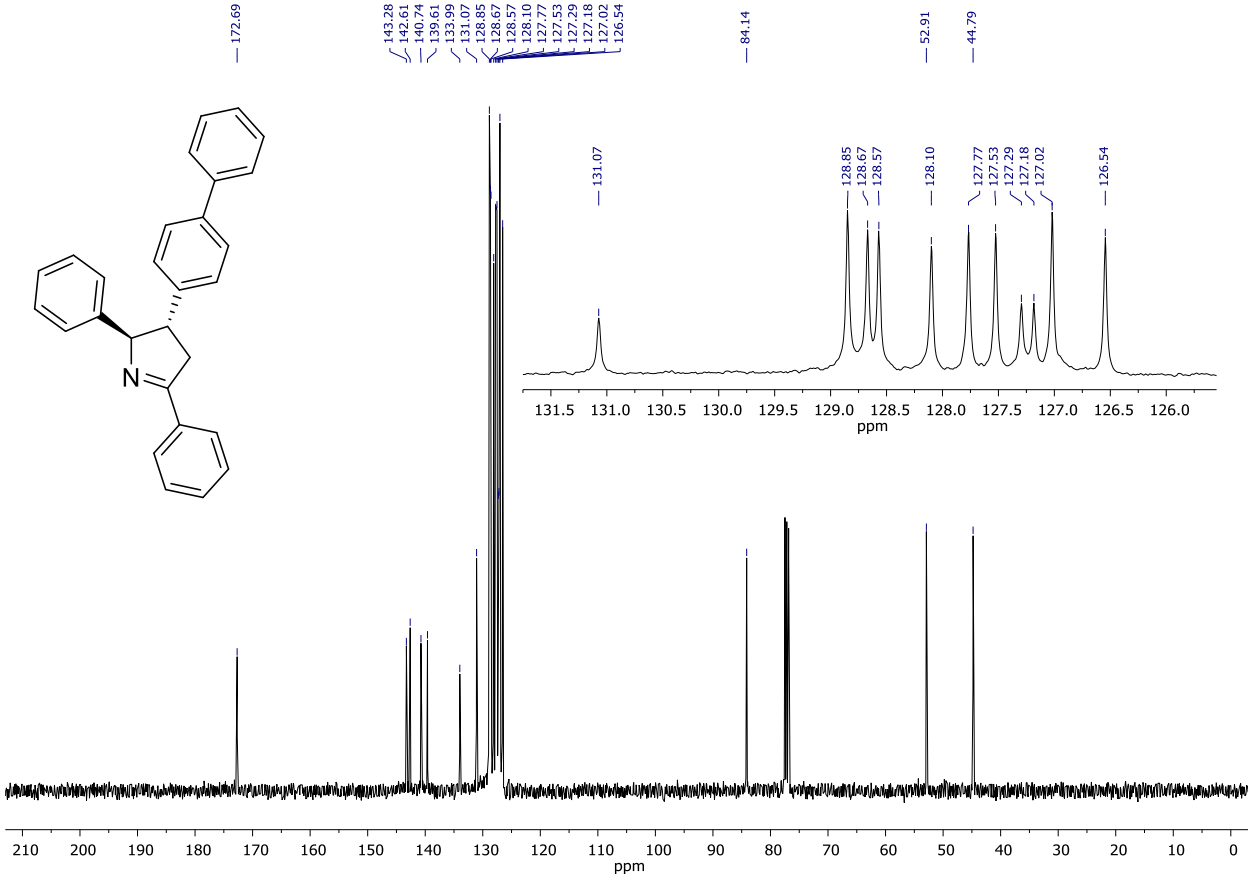
^{1}H NMR spectrum of **3f**+**3'f** tautomeric mixture (400.1 MHz, $CDCl_3$)



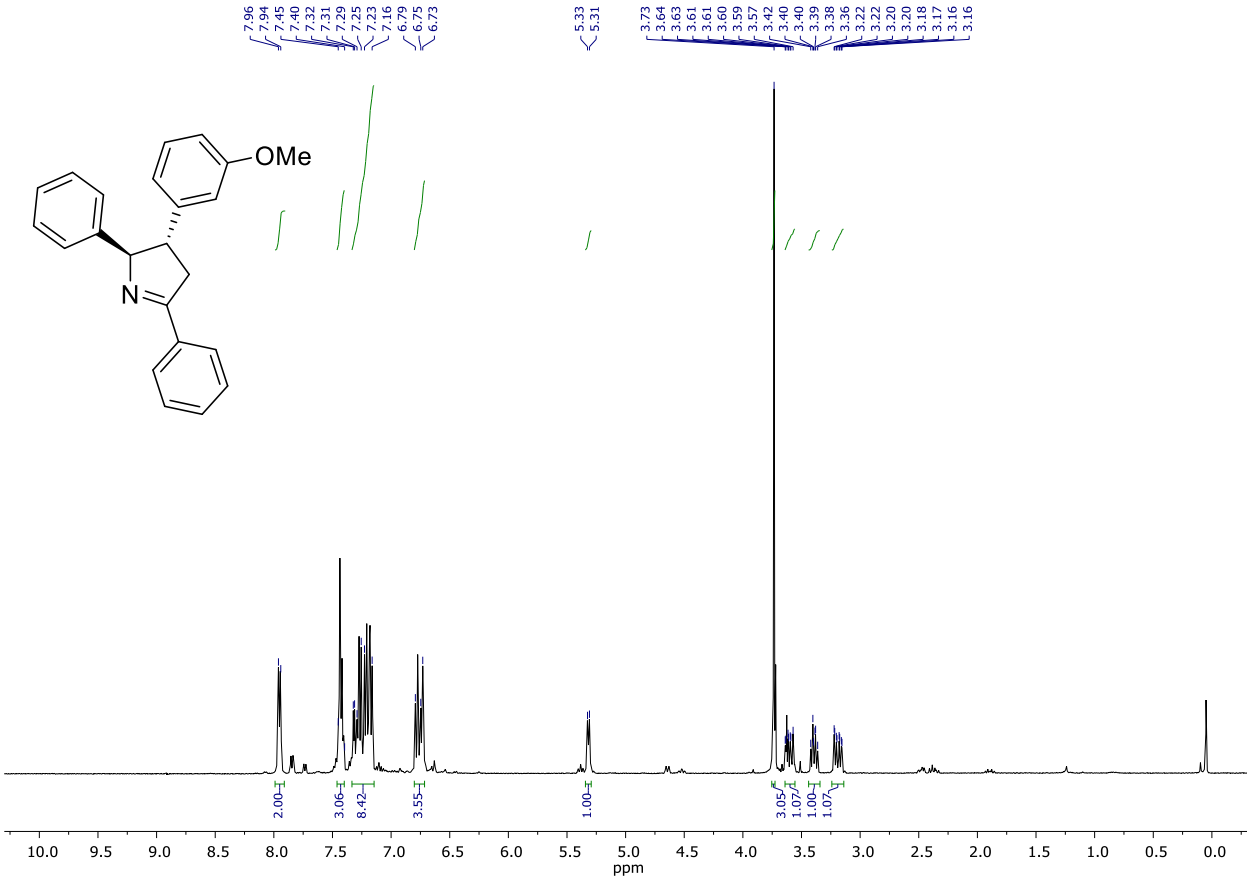
^{13}C NMR spectrum of **3f**+**3'f** tautomeric mixture (100.6 MHz, $CDCl_3$)



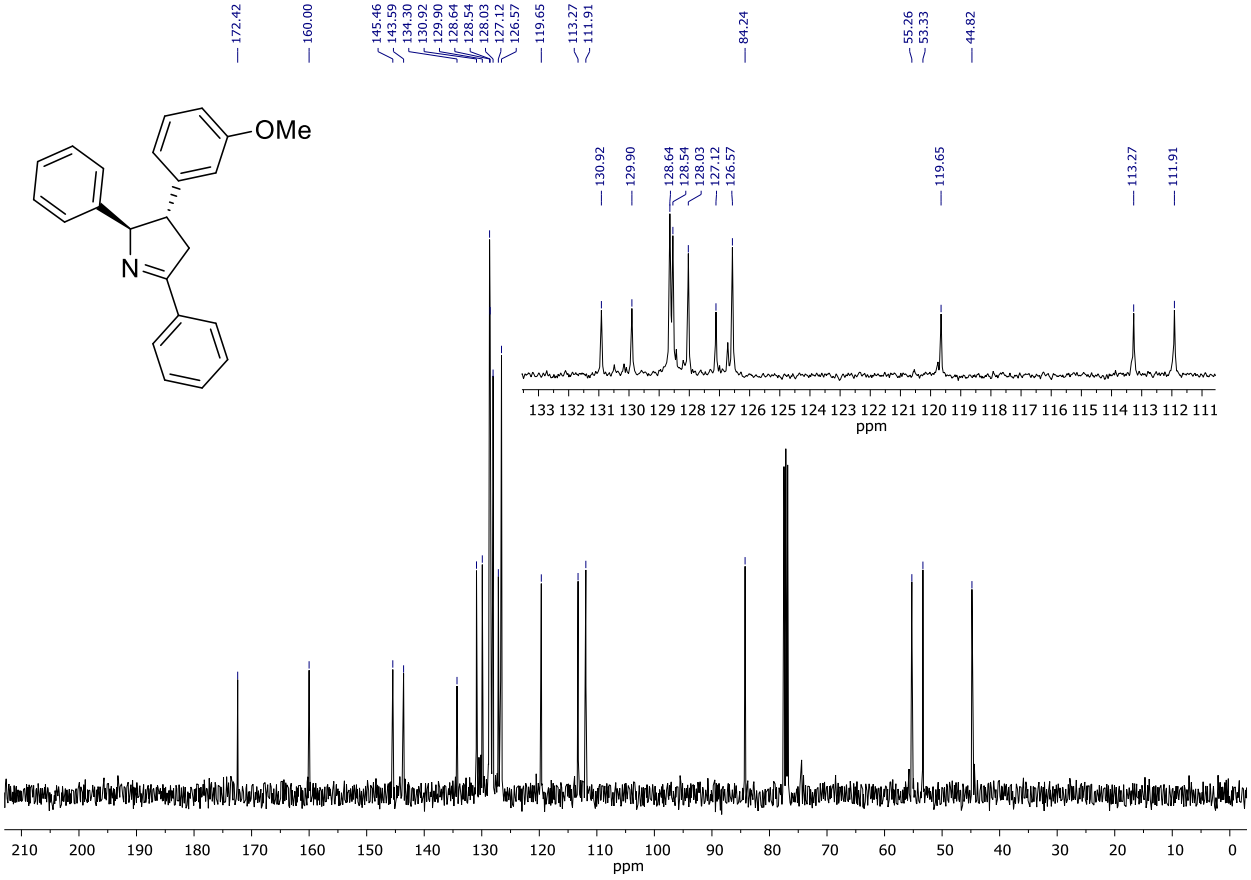
^{1}H NMR spectrum of **3'g** (400.1 MHz, $CDCl_3$)



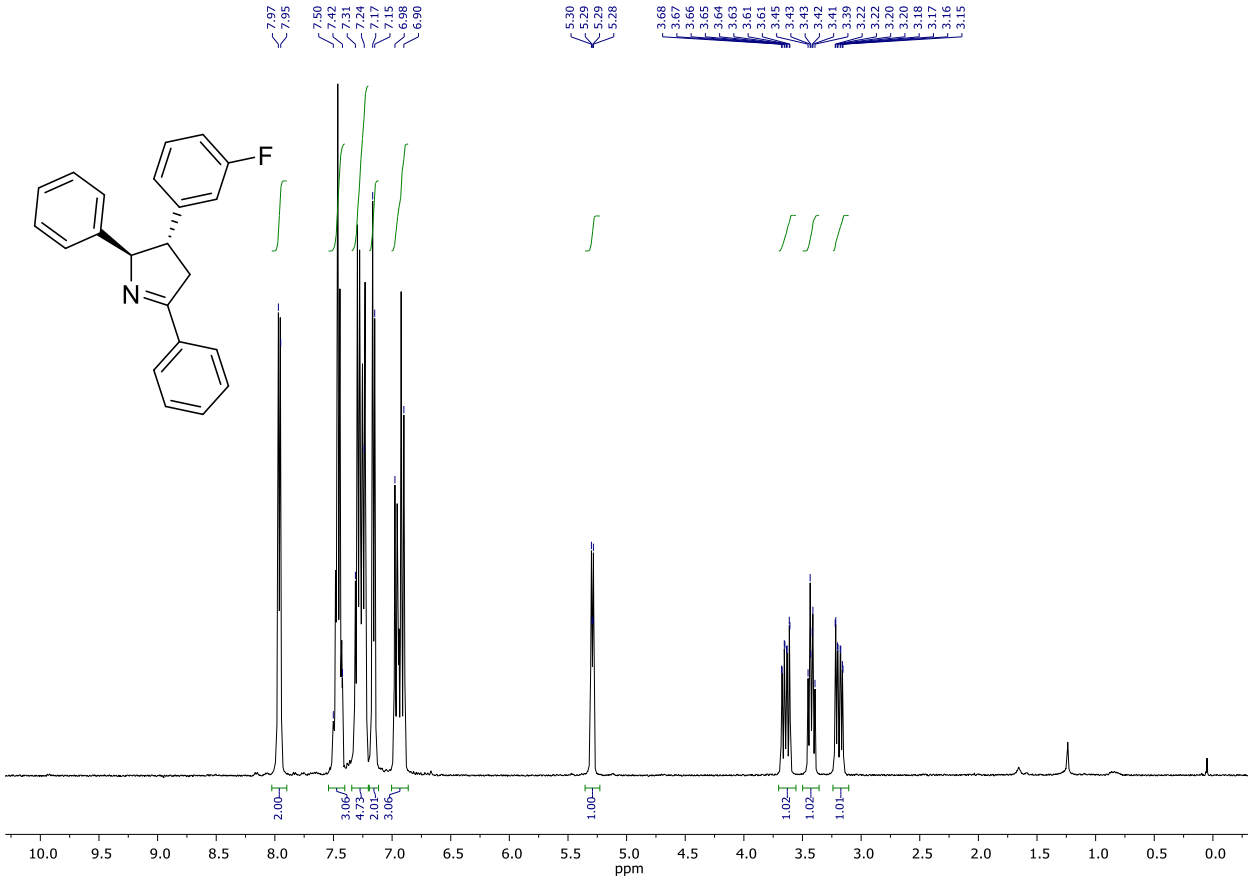
^{13}C NMR spectrum of **3'g** (100.6 MHz, $CDCl_3$)



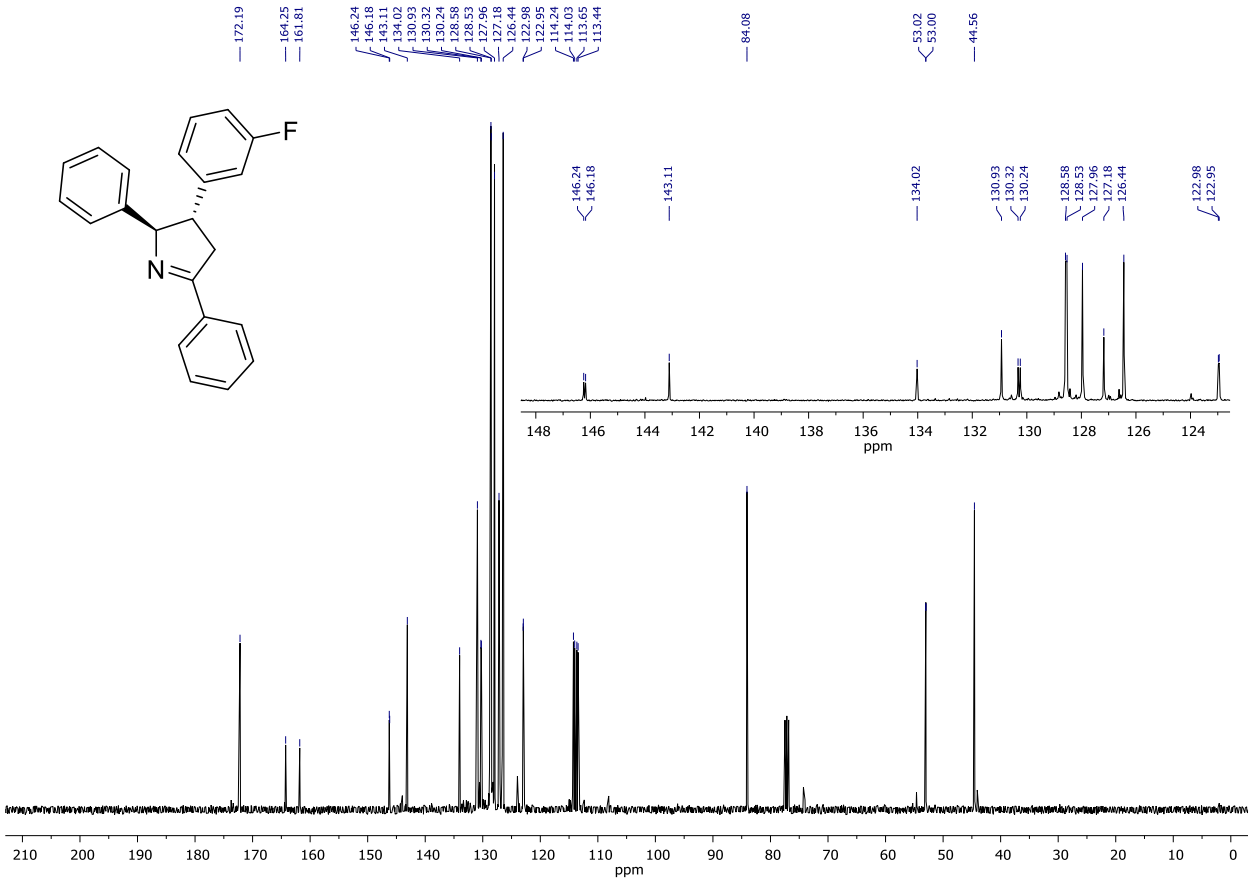
^{1}H NMR spectrum of **3h**+**3'h** tautomeric mixture (400.1 MHz, $CDCl_3$)



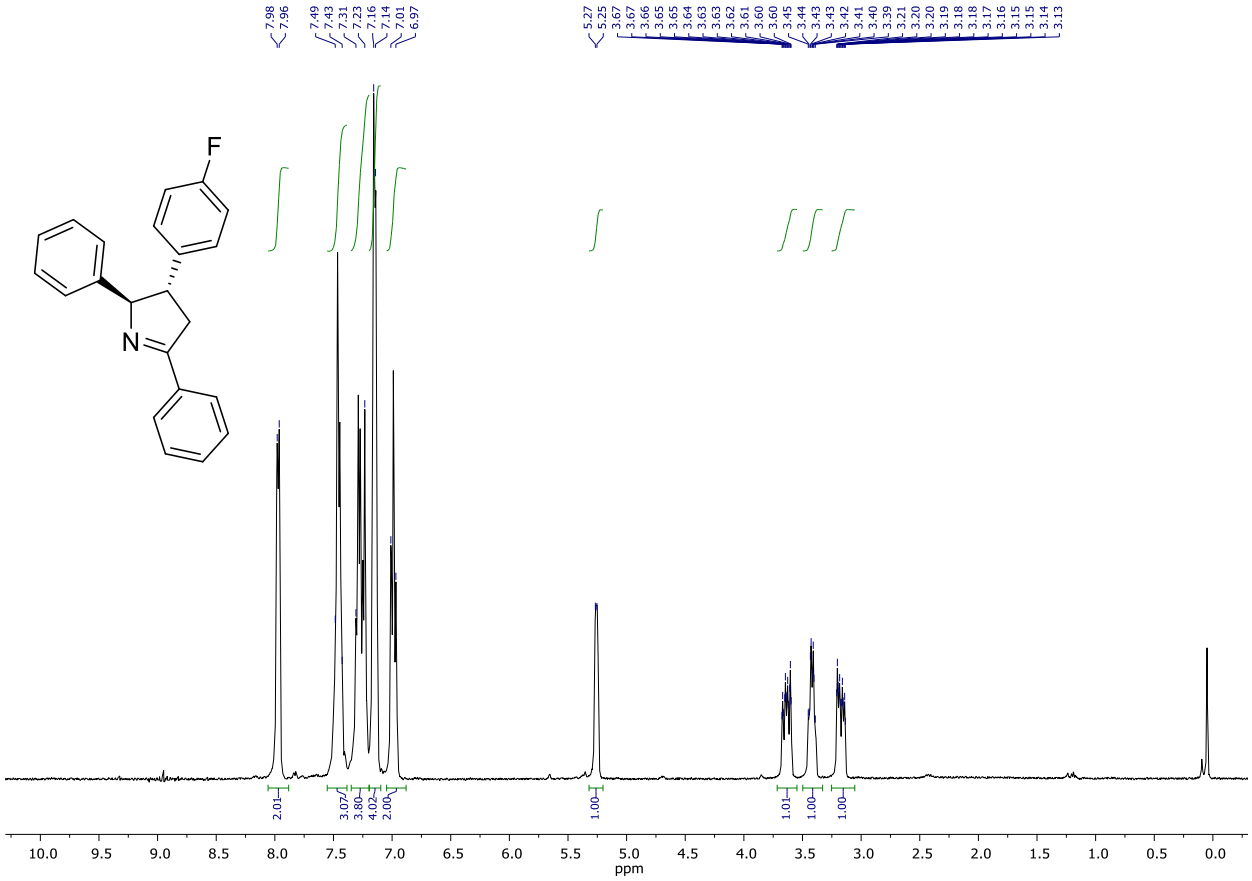
^{13}C NMR spectrum of **3h**+**3'h** tautomeric mixture (100.6 MHz, $CDCl_3$)



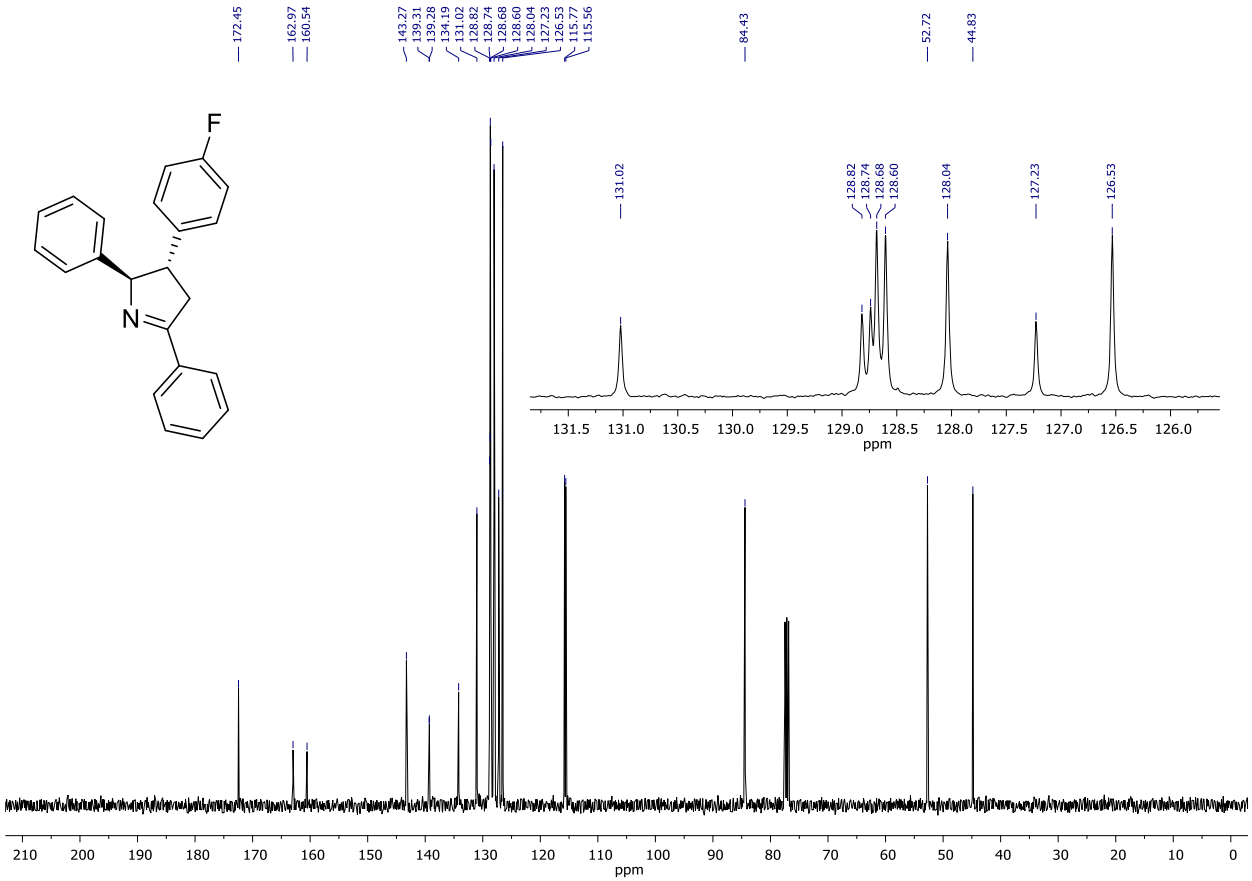
^{1}H NMR spectrum of **3'i** (400.1 MHz, $CDCl_3$)



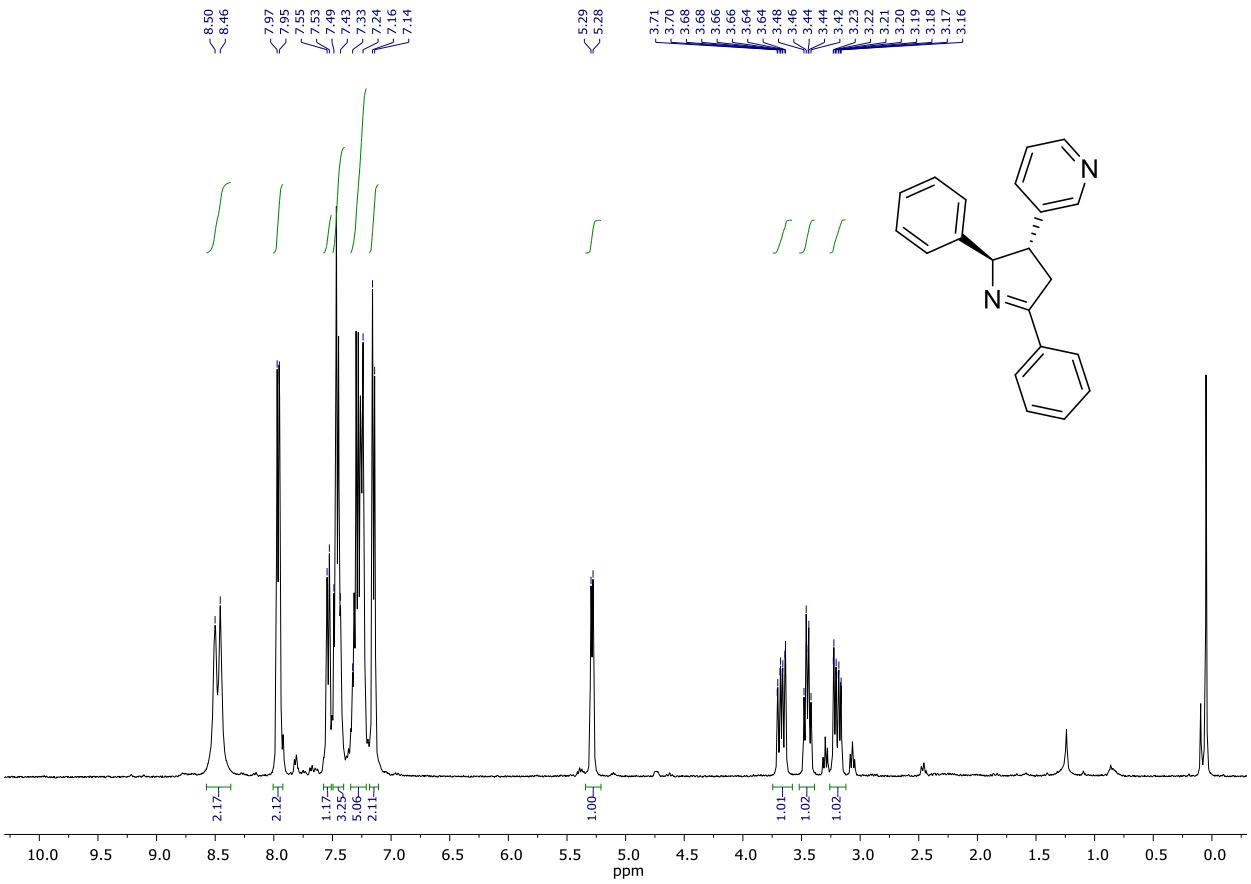
^{13}C NMR spectrum of **3'i** (100.6 MHz, $CDCl_3$)



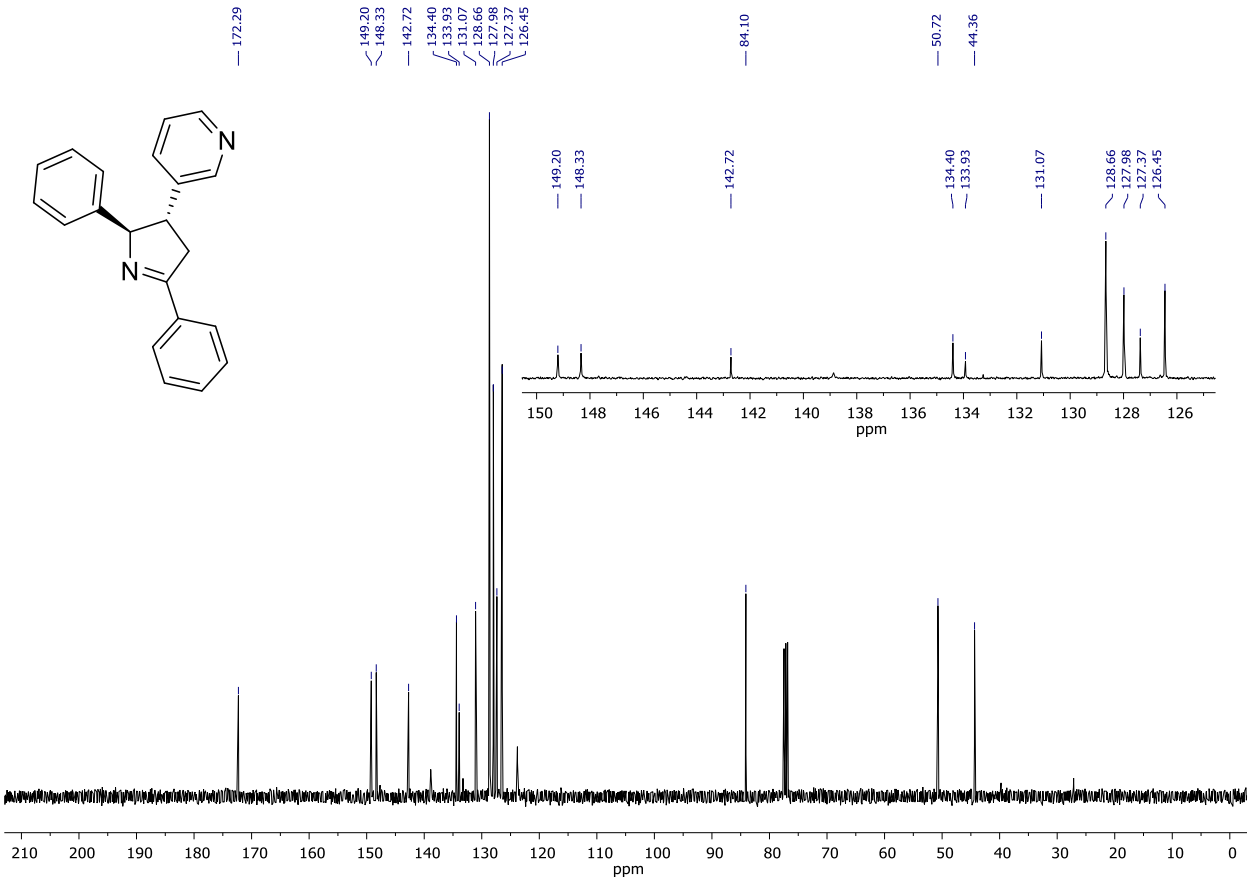
^{1}H NMR spectrum of **3'j** (400.1 MHz, $CDCl_3$)



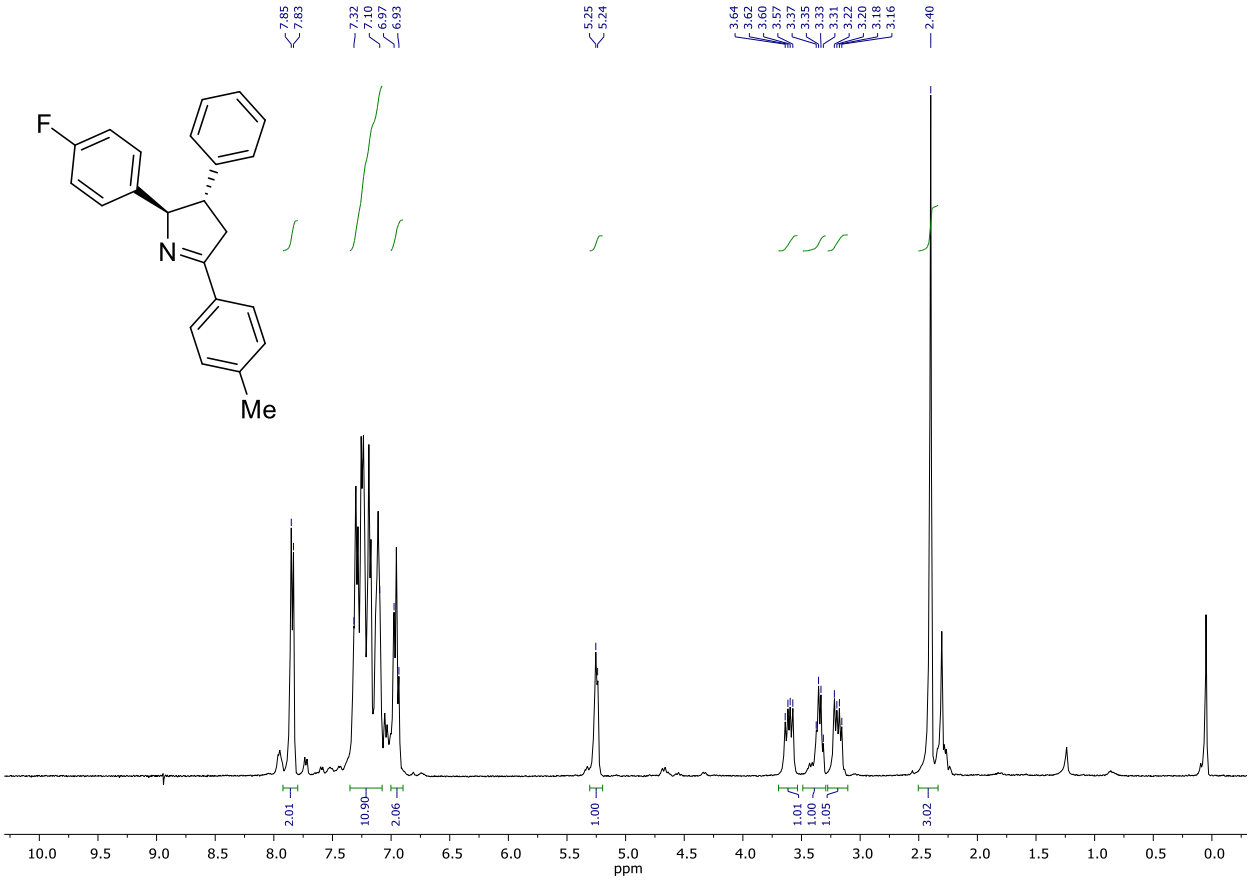
^{13}C NMR spectrum of **3'j** (100.6 MHz, $CDCl_3$)



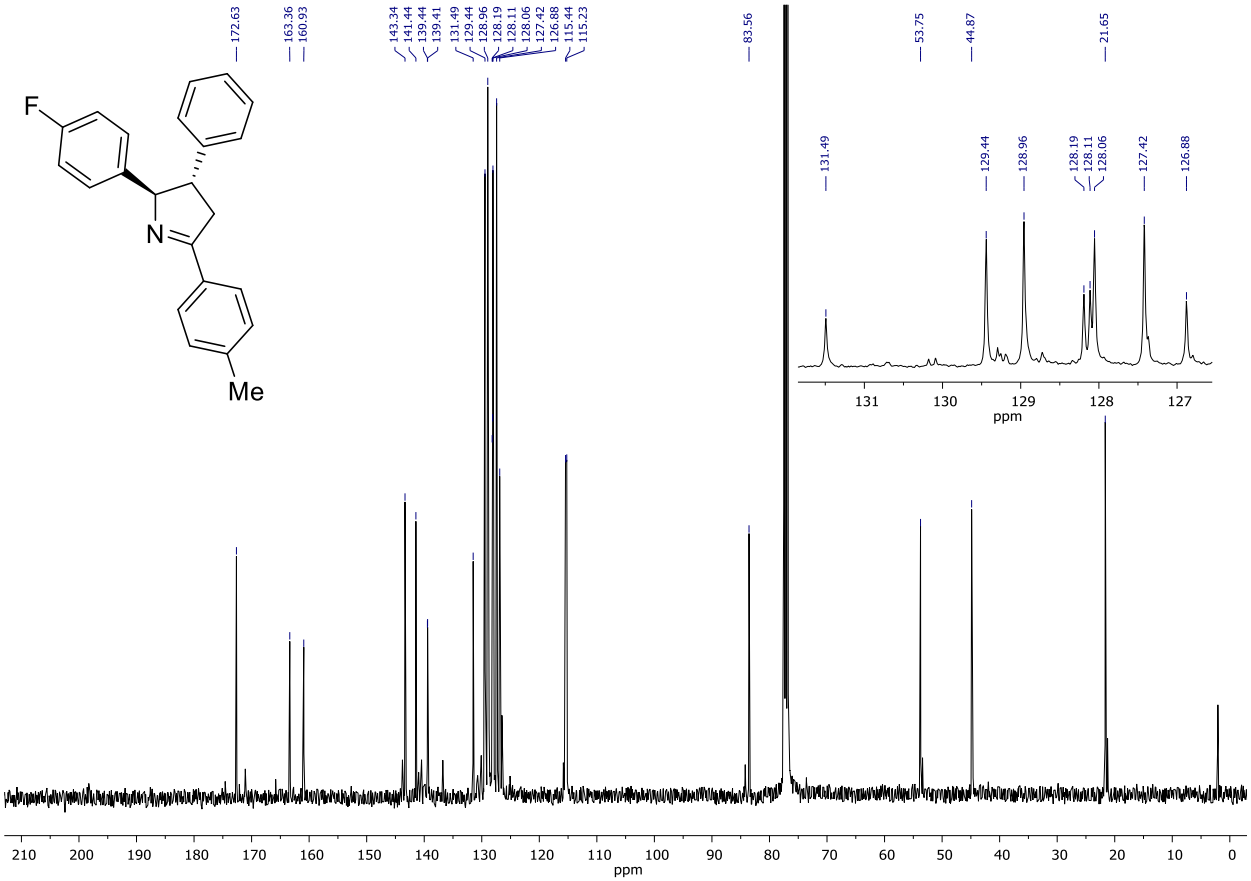
^{1}H NMR spectrum of **3k**+**3'k** tautomeric mixture (400.1 MHz, $CDCl_3$)



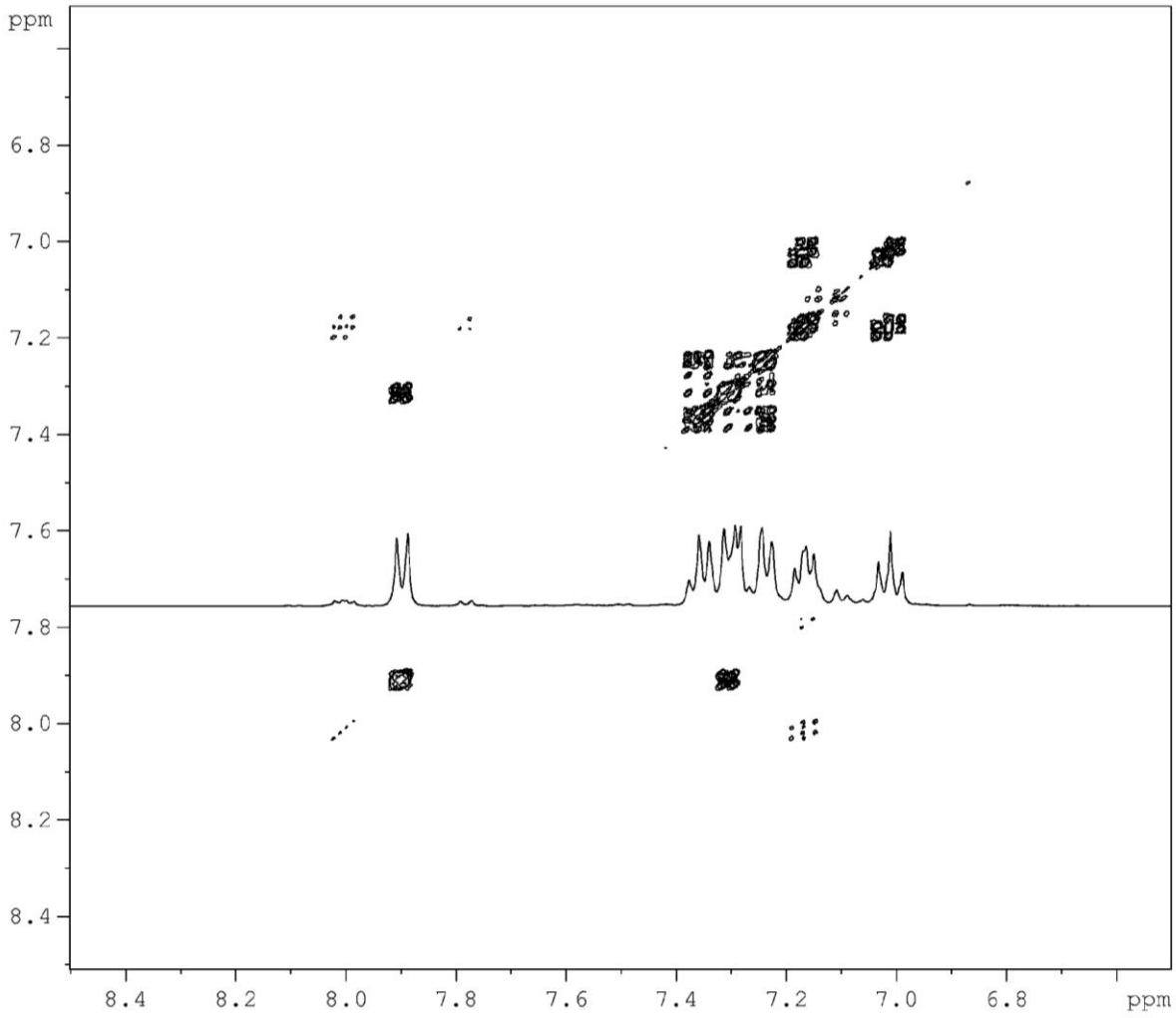
^{13}C NMR spectrum of **3k**+**3'k** tautomeric mixture (100.6 MHz, $CDCl_3$)



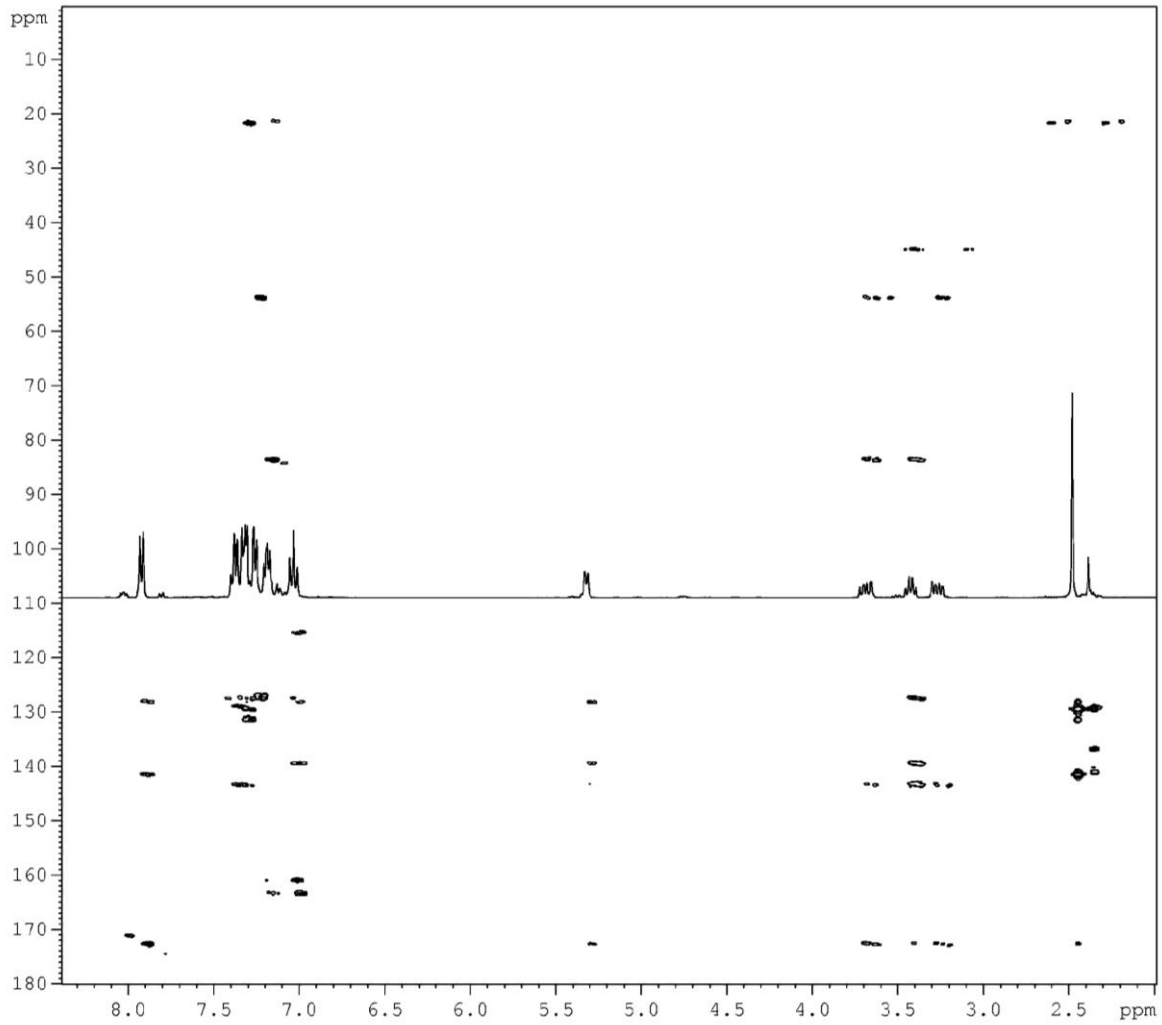
^{1}H NMR spectrum of **3l**+**3'l** tautomeric mixture (400.1 MHz, $CDCl_3$)



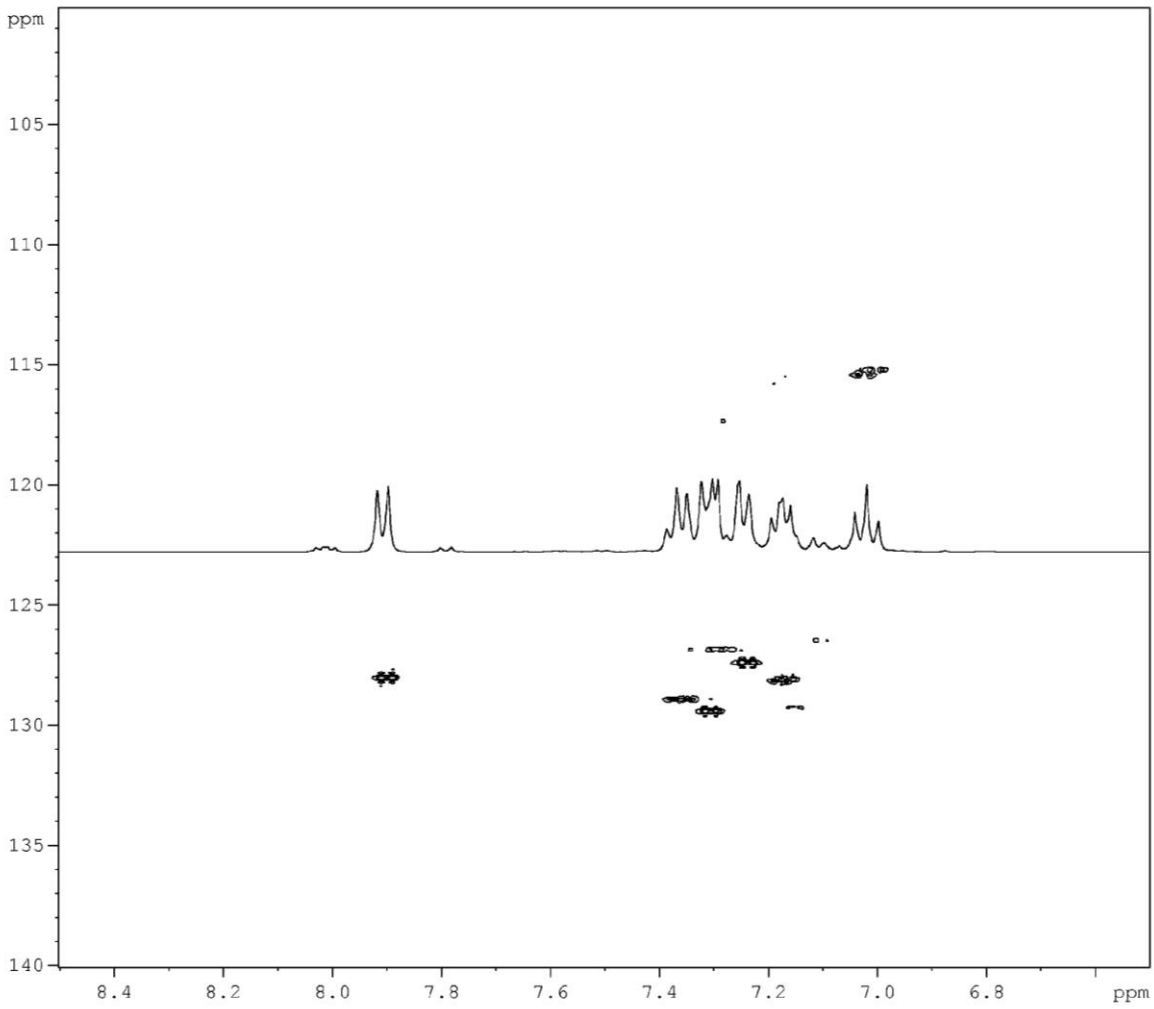
^{13}C NMR spectrum of **3l**+**3'l** tautomeric mixture (100.6 MHz, $CDCl_3$)



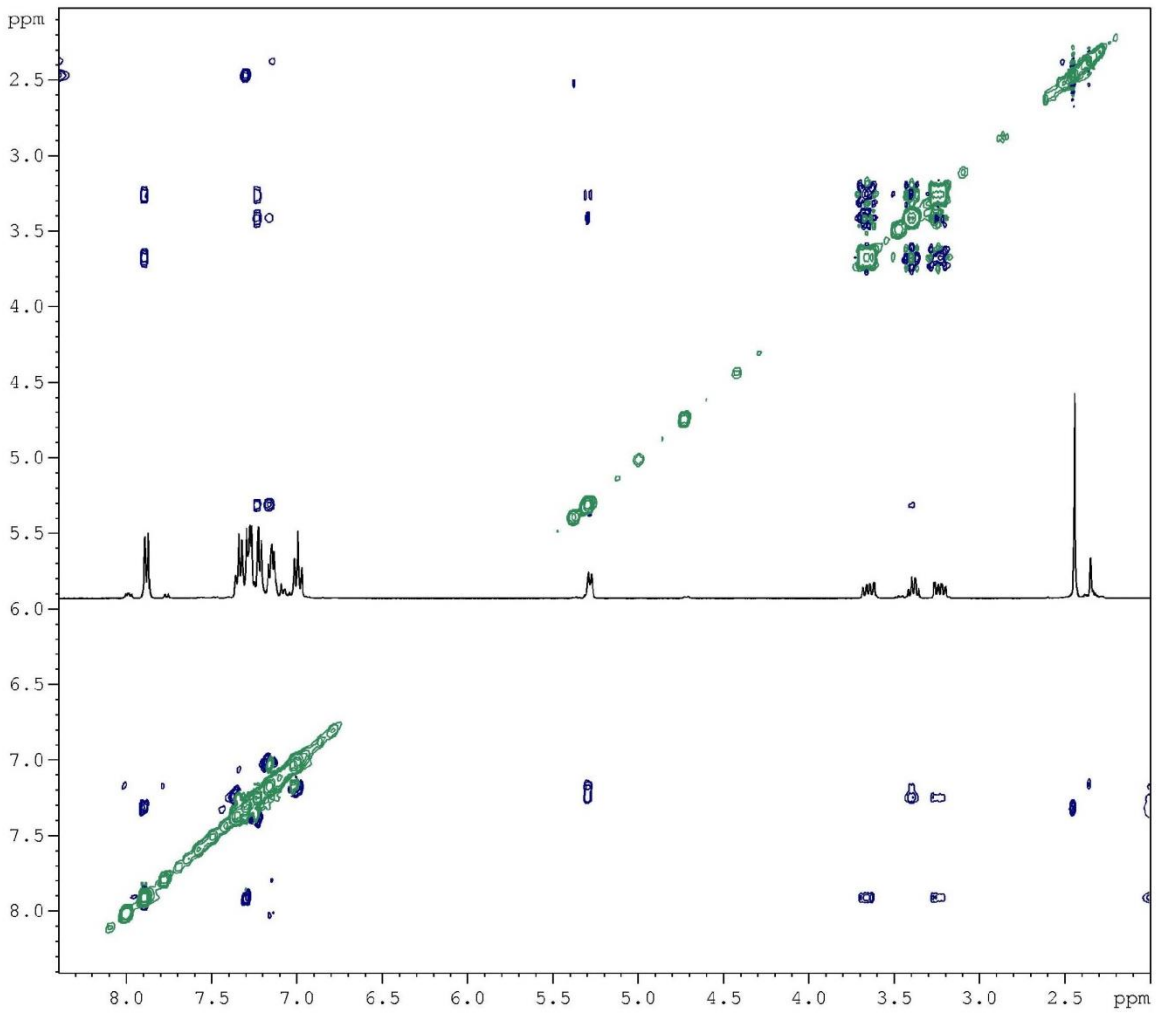
2D COSY spectrum of **3'l** (aromatic region**)** (400.1 MHz, $CDCl_3$)



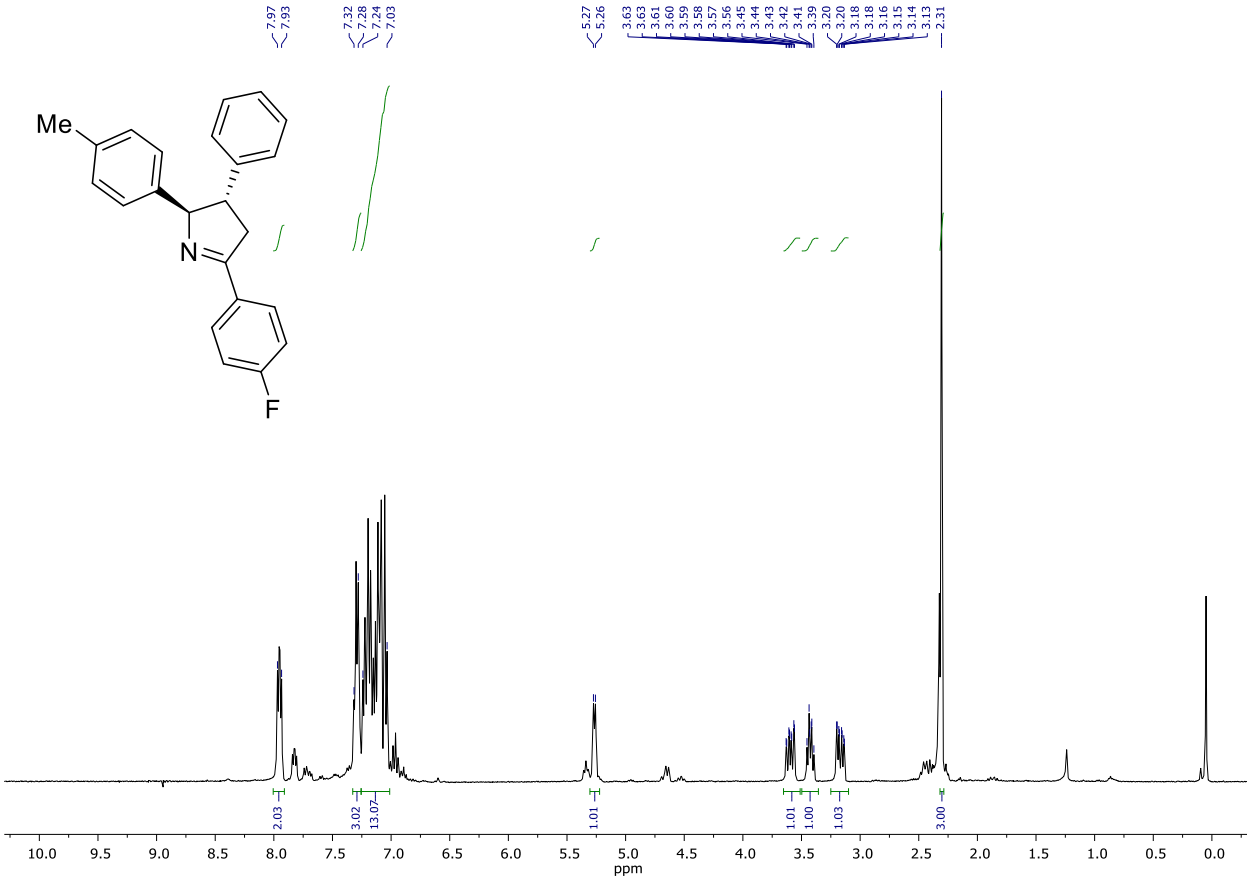
2D ^{1}H-^{13}C HMBC spectrum of **3'l**



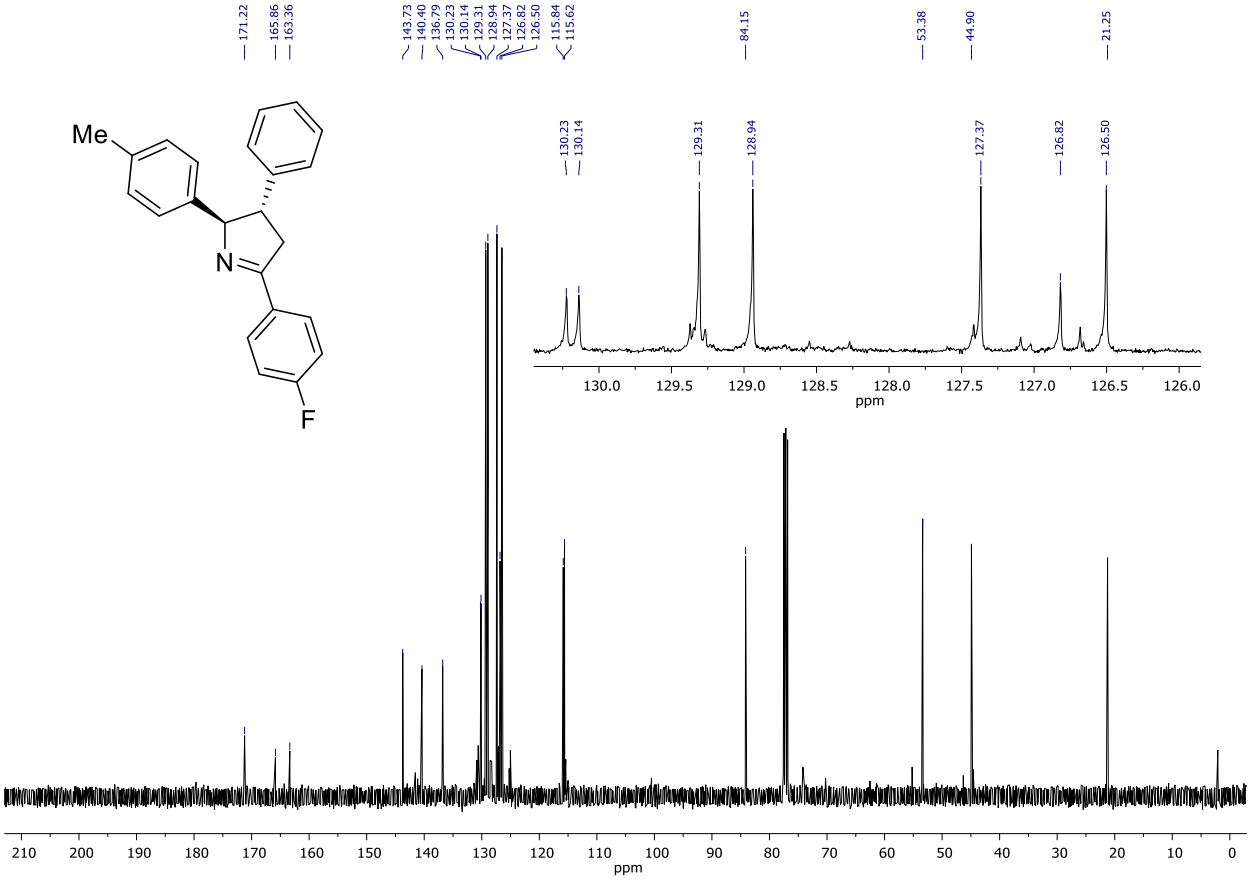
2D ^{1}H-^{13}C HSQC spectrum of **3'l** (aromatic region**)**



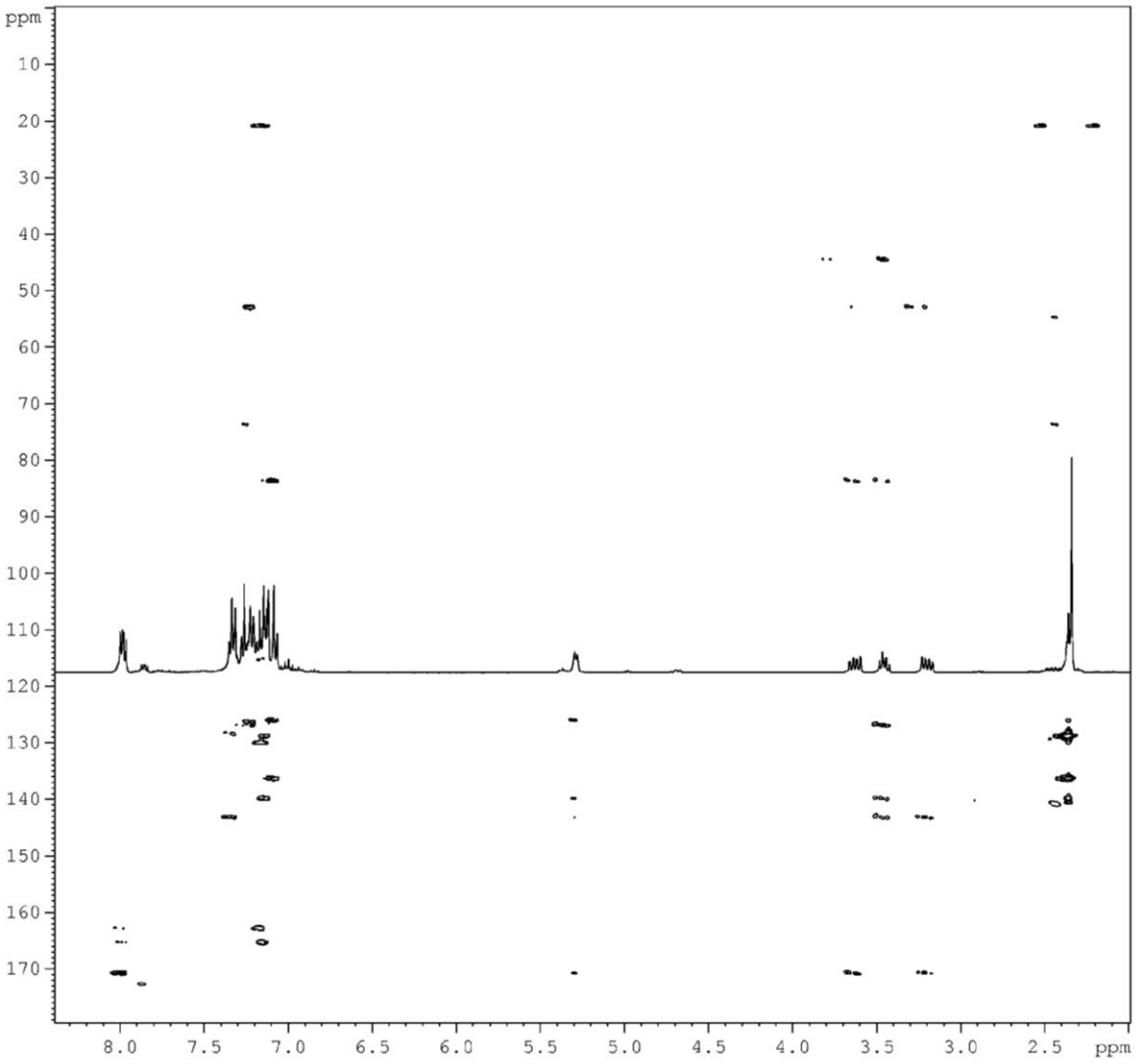
2D NOESY spectrum of **3'l** (400.1 MHz, $CDCl_3$)



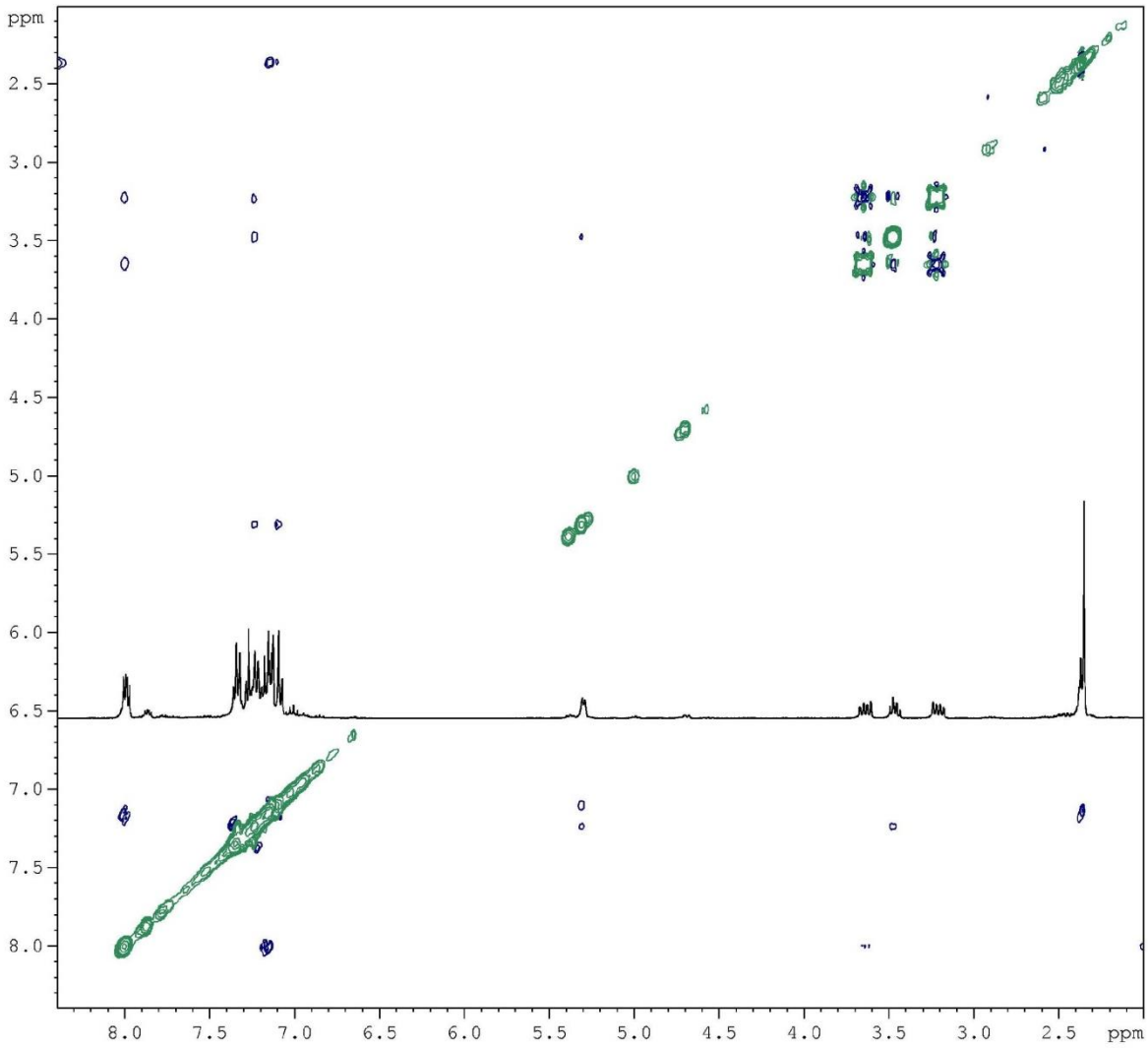
^{1}H NMR spectrum of **4l**+**4'l** tautomeric mixture (400.1 MHz, $CDCl_3$)



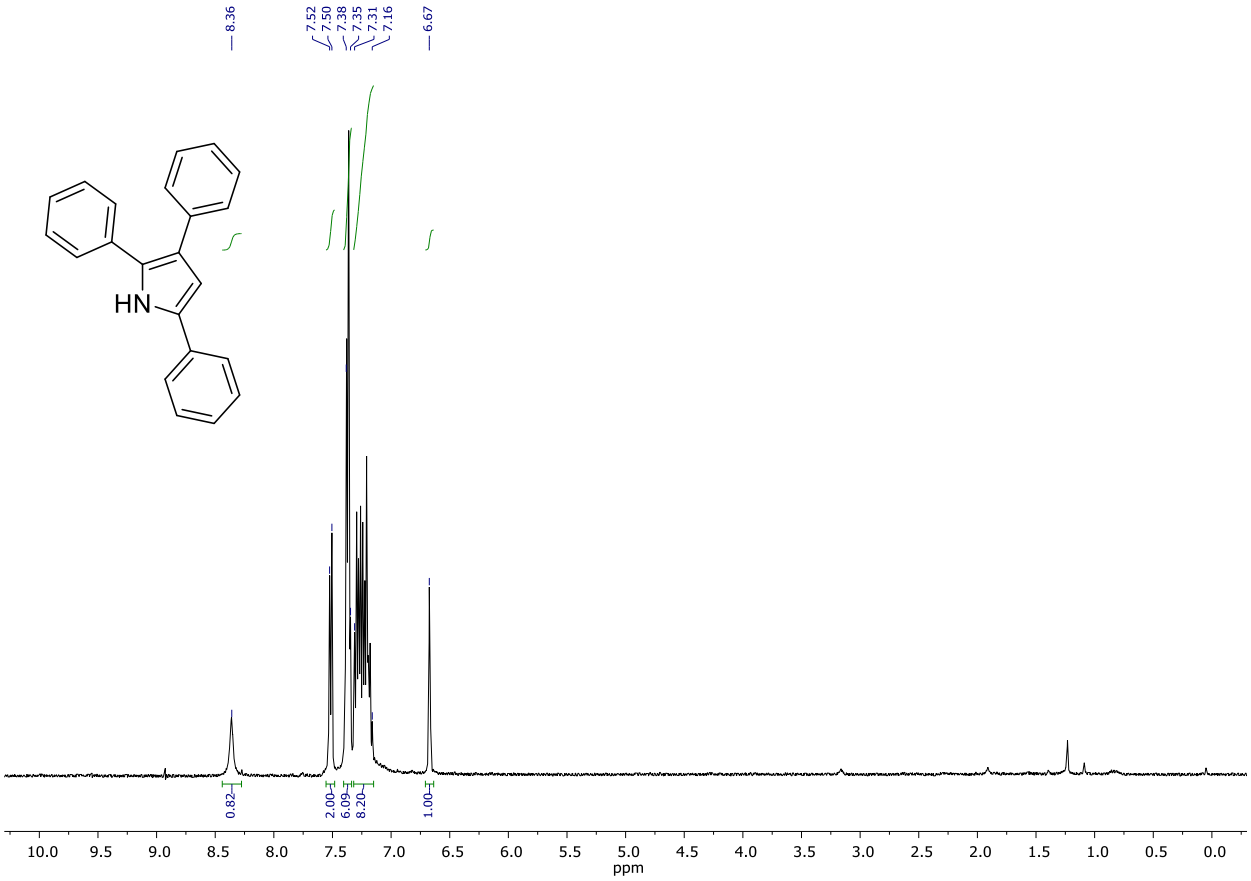
^{13}C NMR spectrum of **4l**+**4'l** tautomeric mixture (100.6 MHz, $CDCl_3$)



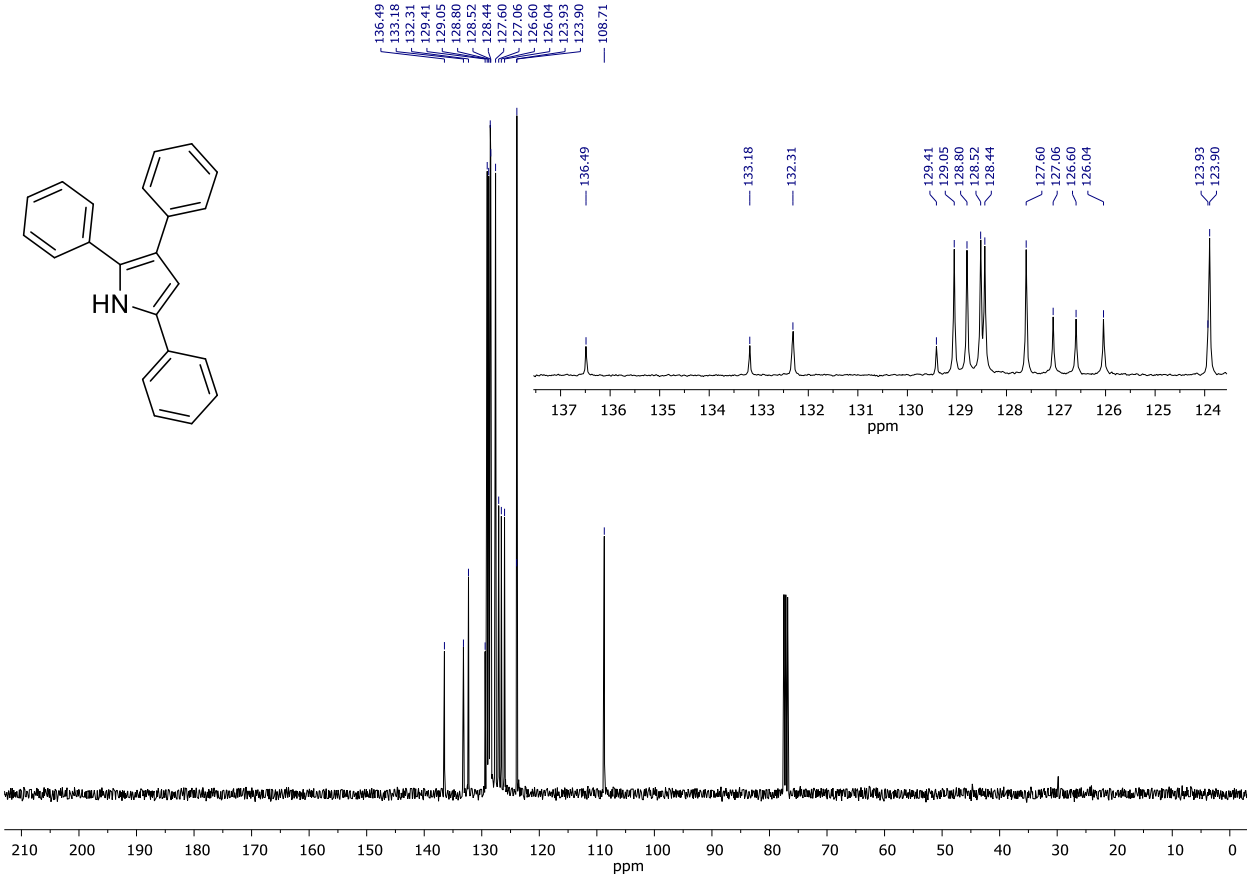
2D ^{1}H-^{13}C HMBC spectrum of **4'l**



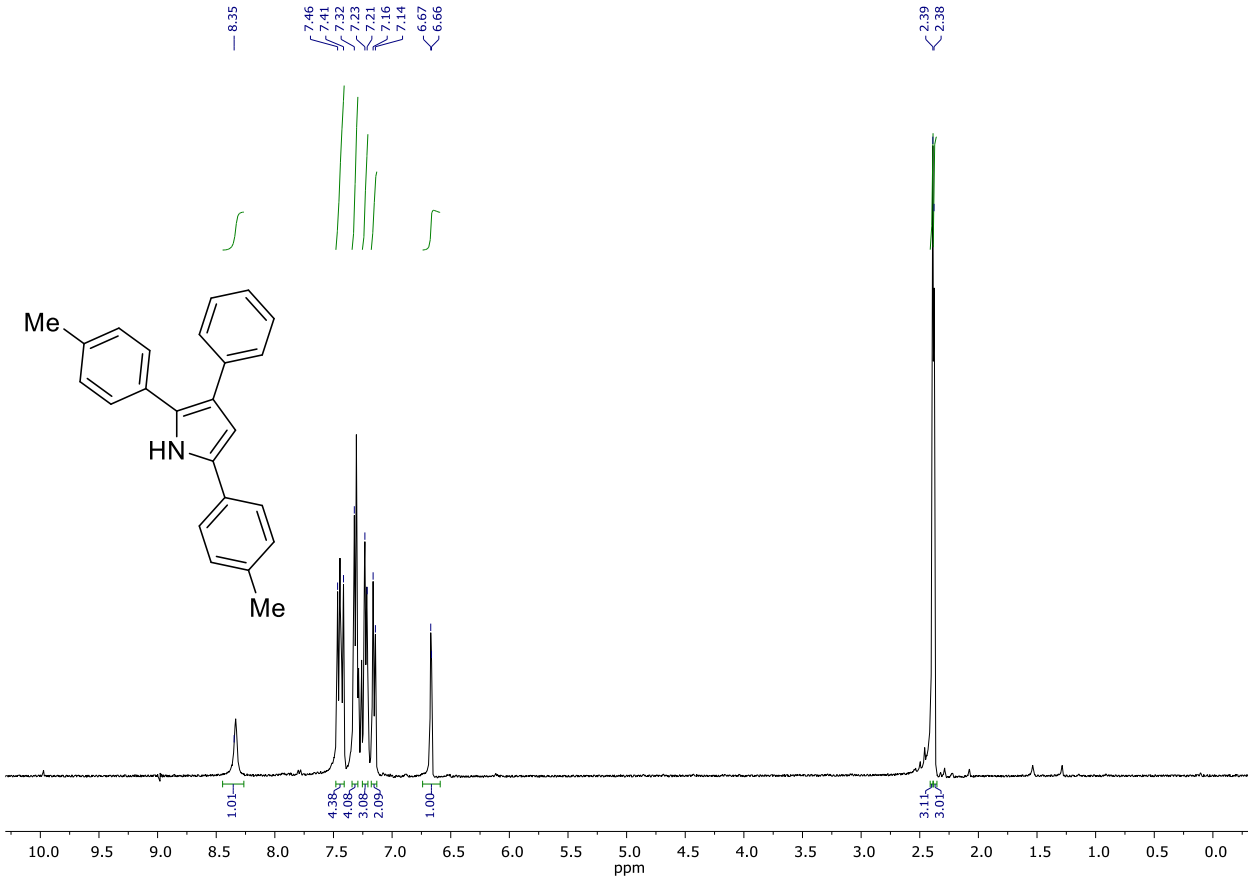
2D NOESY spectrum of **4'l** (400.1 MHz, $CDCl_3$)



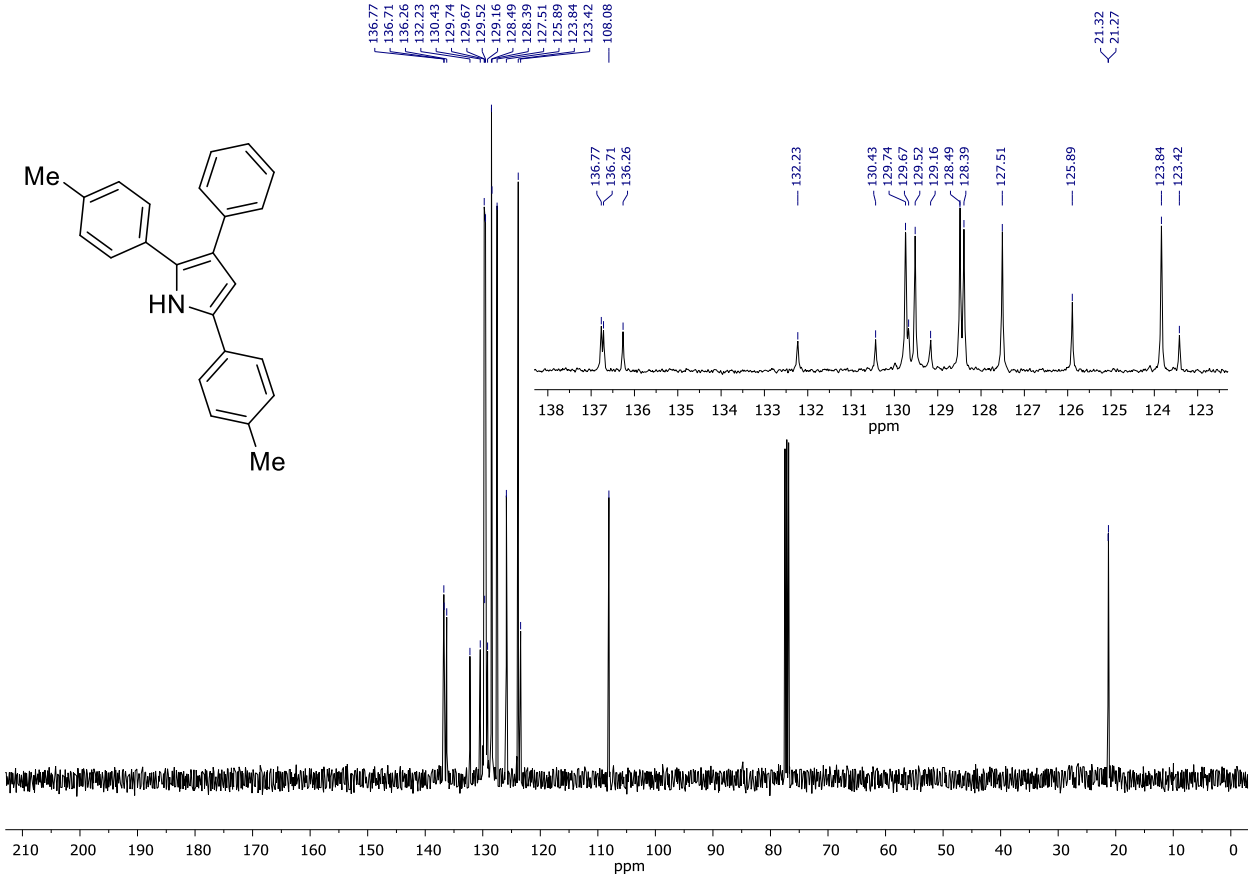
^{1}H NMR spectrum of **5a** (400.1 MHz, $CDCl_3$)



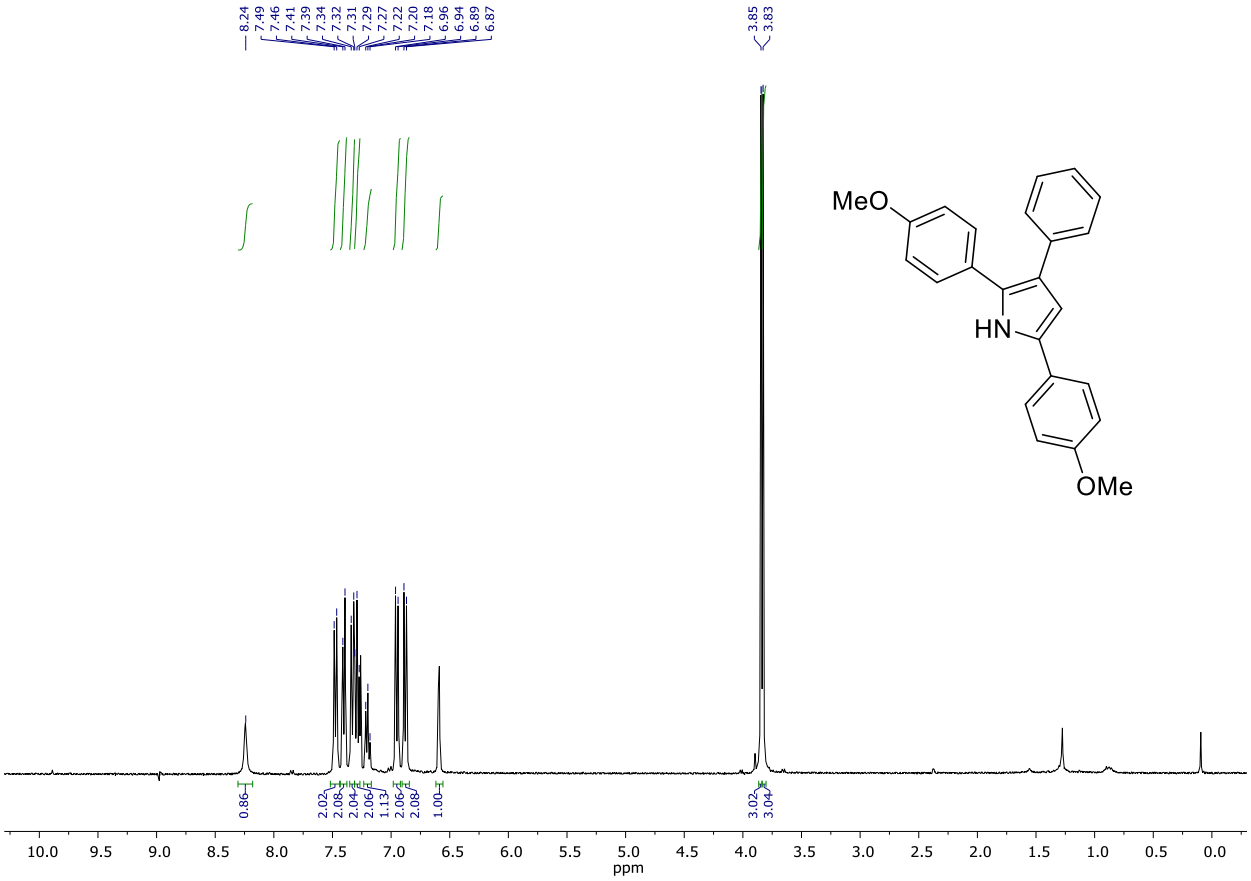
^{13}C NMR spectrum of **5a** (100.6 MHz, $CDCl_3$)



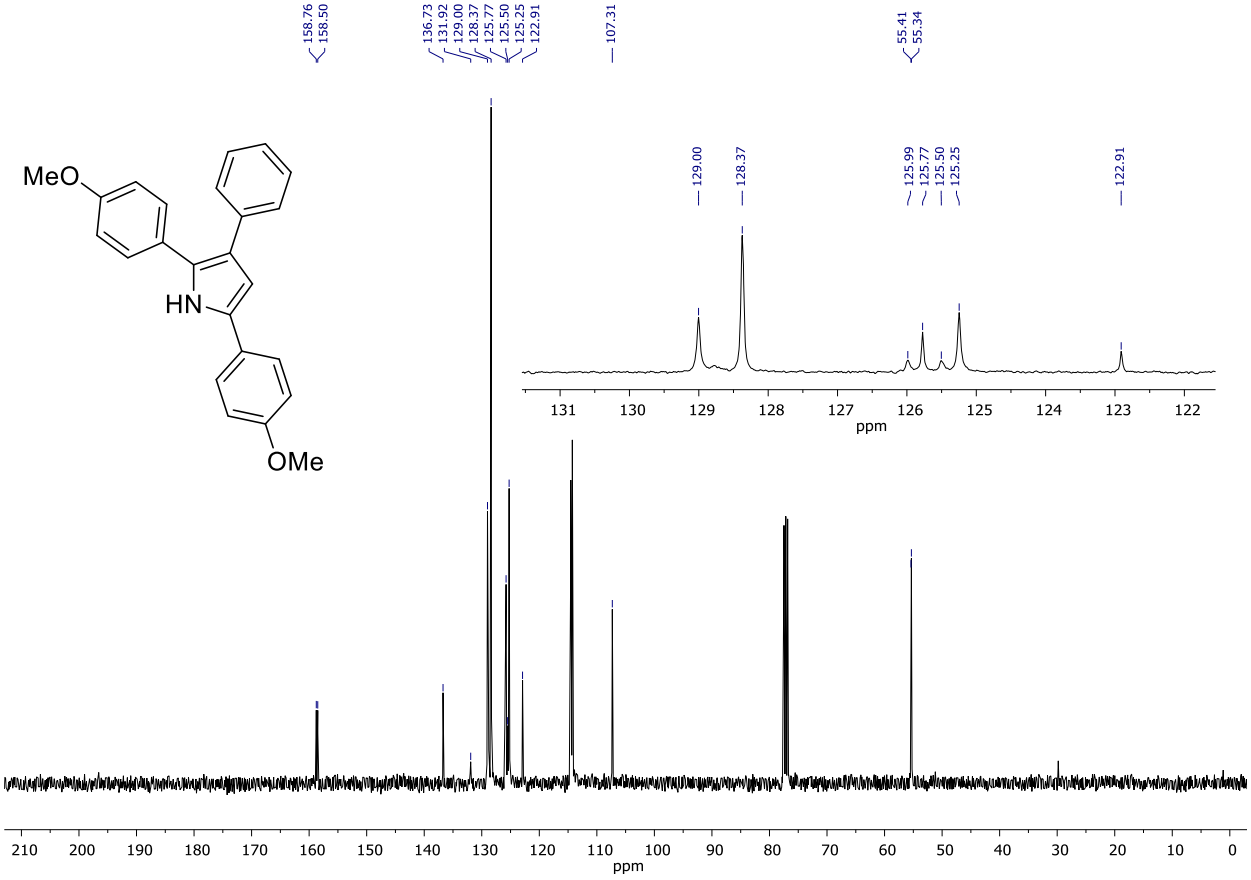
^{1}H NMR spectrum of **5b** (400.1 MHz, $CDCl_3$)



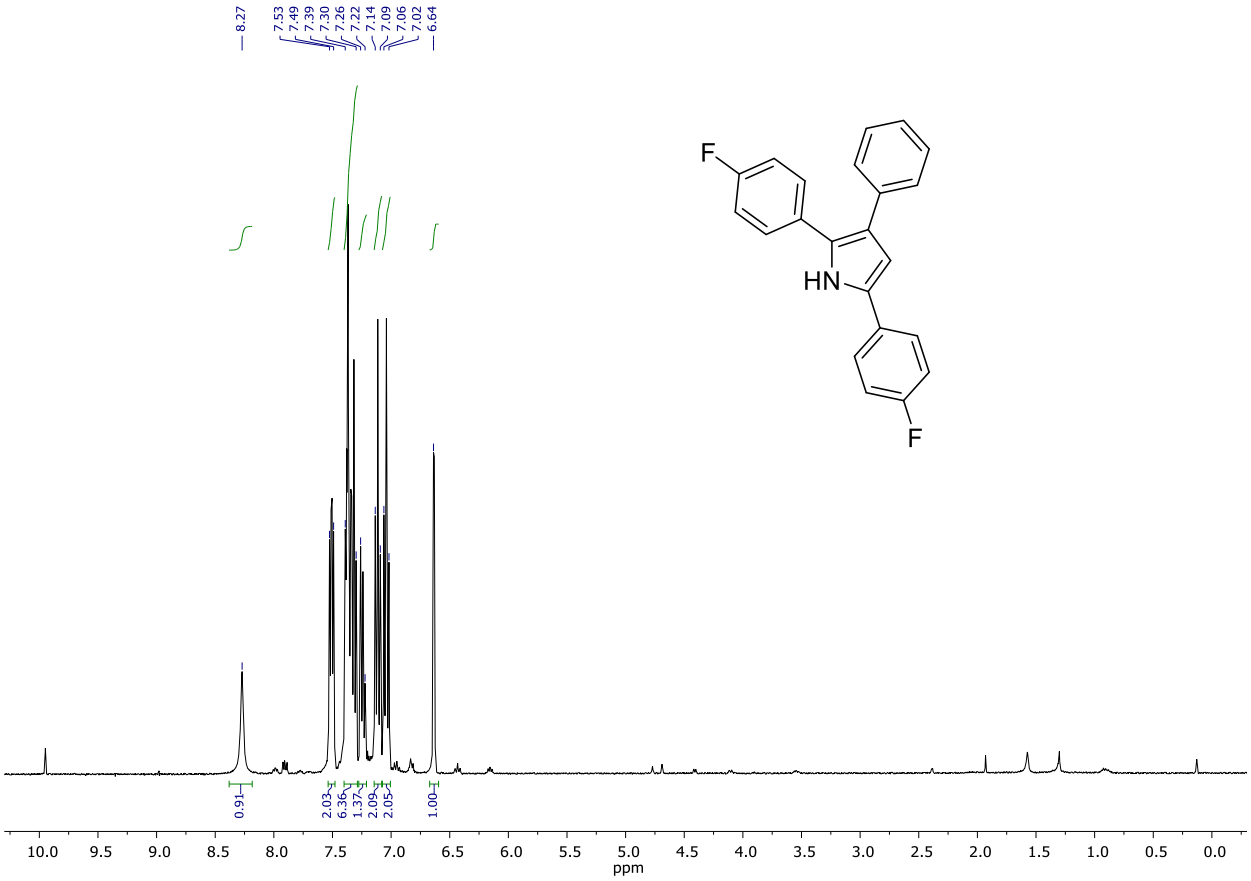
^{13}C NMR spectrum of **5b** (100.6 MHz, $CDCl_3$)



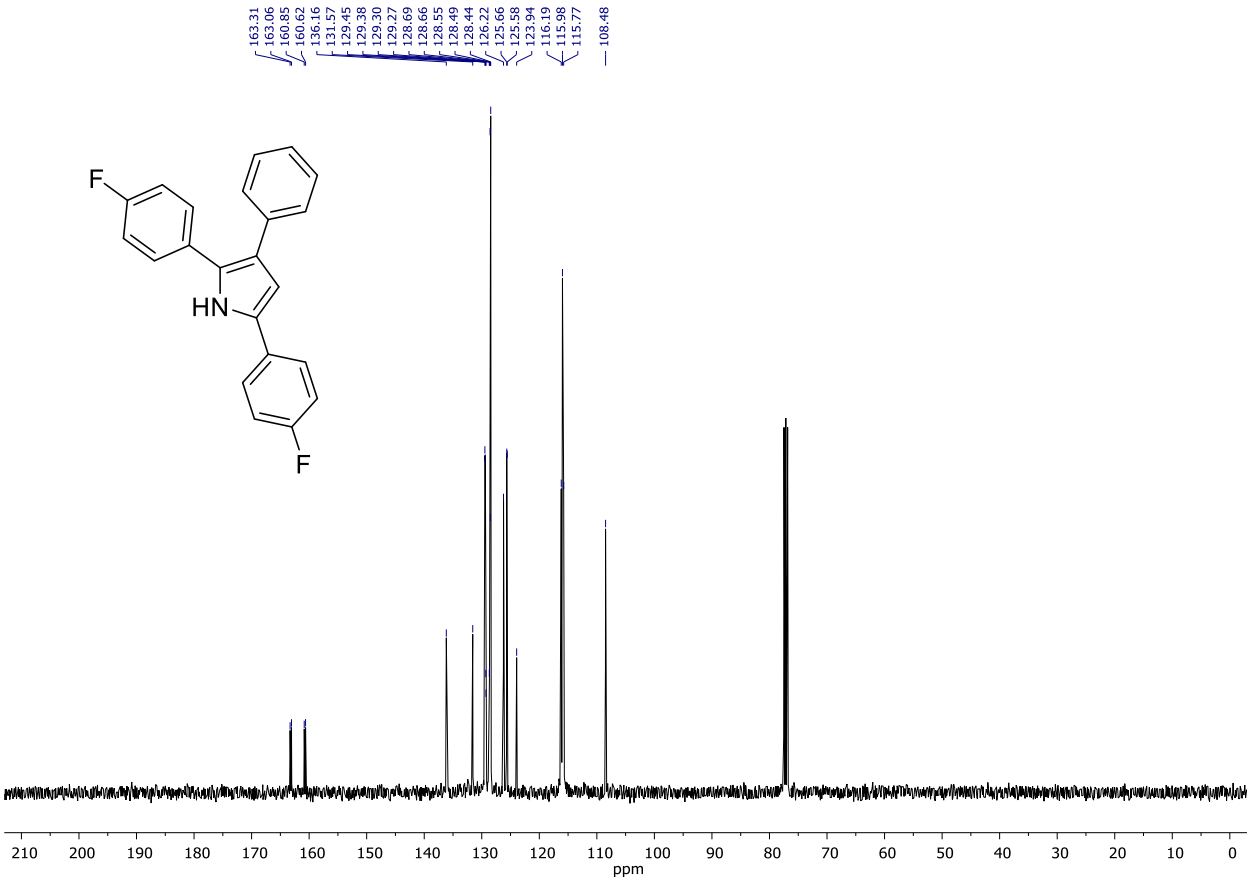
^{1}H NMR spectrum of **5c** (400.1 MHz, $CDCl_3$)



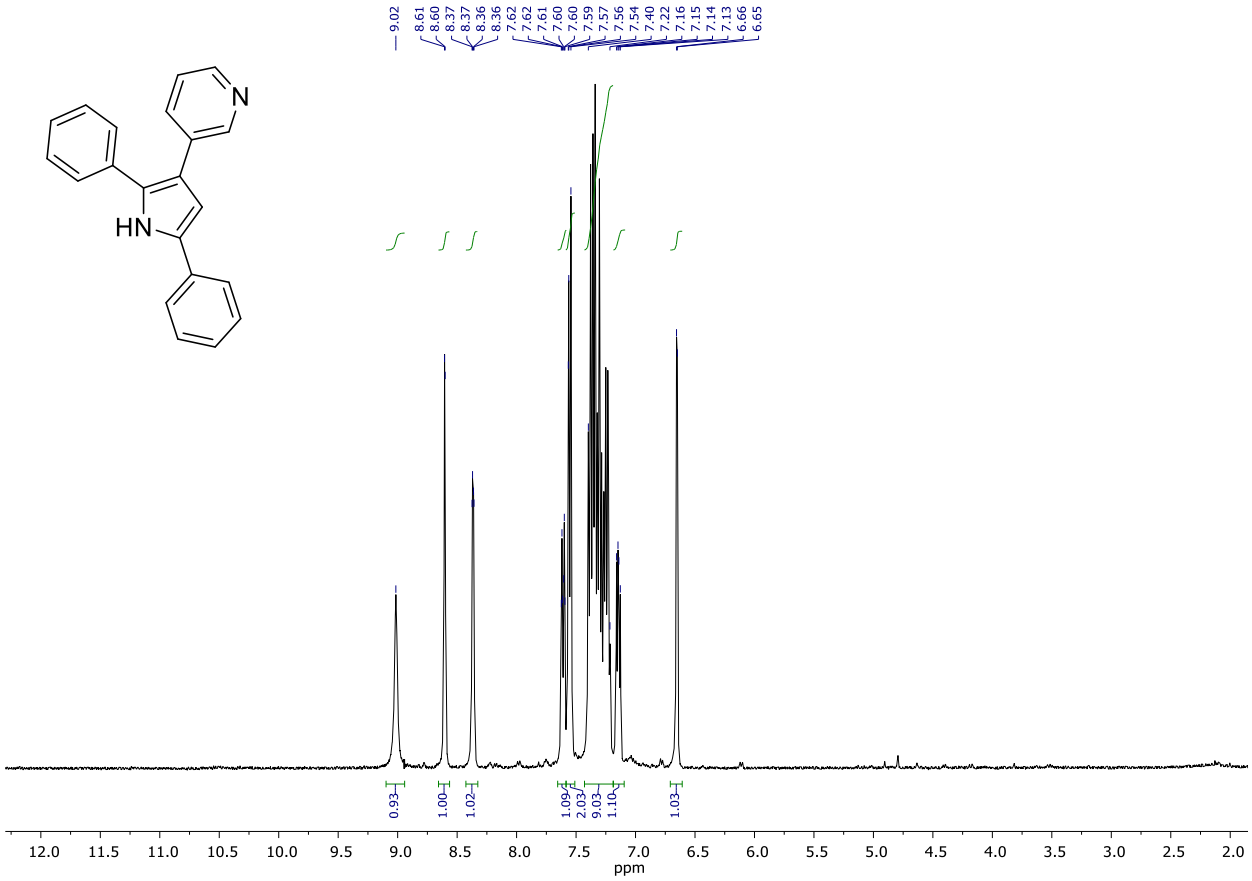
^{13}C NMR spectrum of **5c** (100.6 MHz, $CDCl_3$)



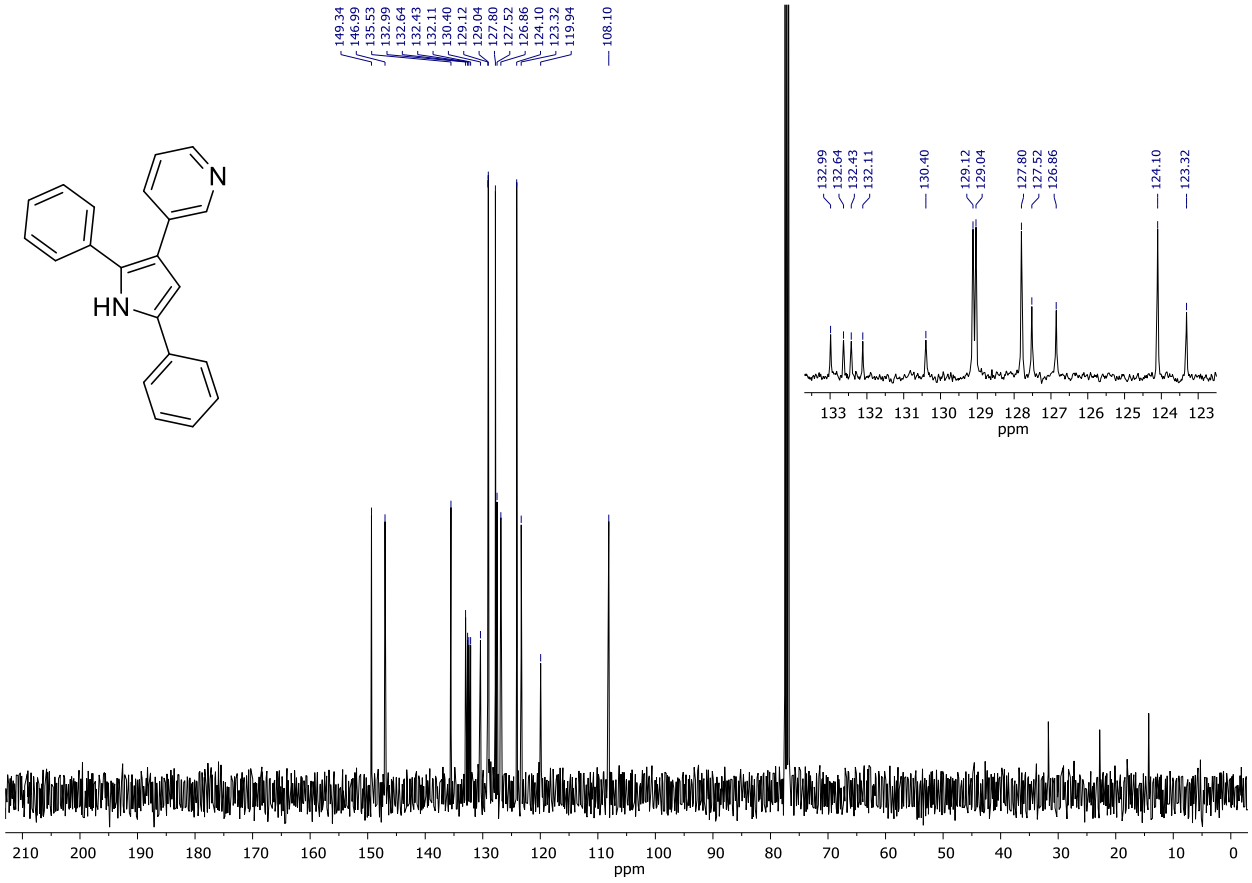
^{1}H NMR spectrum of **5d** (400.1 MHz, $CDCl_3$)



^{13}C NMR spectrum of **5d** (100.6 MHz, $CDCl_3$)



^{1}H NMR spectrum of **5k** (400.1 MHz, $CDCl_3$)



^{13}C NMR spectrum of **5k** (100.6 MHz, $CDCl_3$)