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Supporting Information

for

Hydrazides in the reaction with hydroxypyrrolines: less nucleophilicity – more diversity

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Experimental methods, compound characterization data, and copies of ^{1}H and ^{13}C NMR spectra

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General information

All chemicals and solvents were purchased from commercial sources and used without further purification. Commercial acetonitrile was dried with 4 Å MS before use. The starting 5-hydroxy-Δ^1-pyrrolines **1a–e** were prepared by a literature method.[1] Thin layer chromatography was carried out on Merck silica gel 60 F_{254} precoated aluminum foil sheets and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel (SiO_2), 70–230 mesh, pore size 60 Å, eluent – hexane/diethyl ether 1:1 (v/v). NMR spectra were recorded from solutions in $CDCl_3$ or DMSO-d_6 on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C). Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.27 and δ_C 77.10 for $CDCl_3$, δ_H 2.50 and δ_C 39.50 for DMSO-d_6, was used as a reference. Coupling constants (J) are reported in hertz (Hz). The multiplicity abbreviations used are: s singlet, d doublet, dd doublet of doublet, t triplet, q quartet, m multiplet, br broad signal. Signals were assigned through analysis of 2D COSY, NOESY, HMBC, and HSQC experiments, if required. High-resolution mass spectra were recorded from acetonitrile solutions with 0.1% HFBA on HPLC Agilent 1200/Agilent 6210 TOF instrument equipped with an electrospray ionization (ESI) source. Melting points (uncorrected) were measured on a digital melting point apparatus Electrothermal IA 9200.

[1] a) D. A. Shabalin, M. Yu. Dvorko, E. Yu. Schmidt, I. A. Ushakov, B. A. Trofimov, *Tetrahedron* **2016**, *72*, 6661-6667; b) D. A. Shabalin, M. Yu. Dvorko, E. Yu. Schmidt, N. I. Protsuk, B. A. Trofimov, *Tetrahedron Lett.* **2016**, *57*, 3156-3159.

General procedure for the synthesis of 1,4,5,6-tetrahydropyridazines 3

A mixture of 5-hydroxy-Δ^1-hydroxypyrroline **1** (0.5 mmol), hydrazide **2** (1.0 mmol), acetonitrile (3 mL), and trifluoroacetic acid (4 μL, 0.05 mmol, 10 mol %) was placed in a 10-mL round-bottomed flask with a stirring bar, equipped with reflux condenser, and heated for 3 h at 80 °C (silicon oil bath). The residue after solvent evaporation was treated with diethyl ether or diethyl ether/hexane 1:1 (v/v) mixture to afford after filtration the desired 1,4,5,6-tetrahydropyridazine **3** as a powder.

N'-(2-Benzoyl-5,5-dimethyl-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)benzohydrazide (**3aa**). Following the general procedure, **3aa** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1.0 mmol); **3aa** was isolated as a white powder (199 mg, 93% yield), mp 162-164 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ = 10.02 (d, *J* = 5.8 Hz, 1H, NH), 7.80 (d, *J* = 7.5 Hz, 2H, Ph), 7.55-7.52 (m, 3H, Ph), 7.47-7.45 (m, 2H, Ph), 7.35-7.31 (m, 8H, Ph), 5.97-5.95 (m, 1H, NH), 5.86 (dd, *J* = 6.2 Hz, *J* = 4.5 Hz, 1H, CH), 2.29 (dd, *J* = 14.4 Hz, *J* = 4.5 Hz, 1H, CH_2), 2.08 (dd, *J* = 14.4 Hz, *J* = 6.2 Hz, 1H, CH_2), 1.43 (s, 3H, Me), 1.16 (s, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 172.0, 166.5, 158.4, 137.1, 134.9, 132.7, 131.8, 130.5, 130.0, 128.7, 128.4, 128.1, 128.0, 127.4, 127.1, 66.9, 39.1, 32.0, 28.3, 27.6. HRMS (ESI-TOF) calcd for $[C_{26}H_{26}N_4O_2+H]^+$ 427.2134, found 427.2137.

N'-(5,5-Dimethyl-2-(4-nitrobenzoyl)-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)-4-nitrobenzohydrazide (**3ac**). Following the general procedure, **3ac** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and 4-nitrobenzohydrazide (**2c**, 181 mg, 1.0 mmol); **3ac** was isolated as a white powder (222 mg, 86% yield), mp 201-203 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ = 10.44 (d, *J* = 5.7 Hz, 1H, NH), 8.32 (d, *J* = 8.8 Hz, 2H, Ar), 8.20 (d, *J* = 8.6 Hz, 2H, Ar), 8.06 (d, *J* = 8.8 Hz, 2H, Ar), 7.80 (d, *J* = 8.6 Hz, 2H, Ar), 7.33-7.29 (m, 5H, Ph), 6.06 (m, 1H, NH), 5.95 (dd, *J* = 5.2 Hz, *J* = 3.8 Hz, 1H, CH), 2.32 (dd, *J* = 14.3 Hz, *J* = 3.8 Hz, 1H, CH_2), 2.12 (dd, *J* = 14.3 Hz, *J* = 5.2 Hz, 1H, CH_2), 1.47 (s, 3H, Me), 1.13 (s, 3H, Me). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 168.6, 165.0, 159.6, 149.0, 147.6, 142.5, 139.1, 137.1, 129.9, 128.8, 128.2, 128.0, 127.9, 123.5, 122.5, 62.8, 36.7, 31.5, 28.2, 27.6. HRMS (ESI-TOF) calcd for $[C_{26}H_{24}N_6O_6+H]^+$ 517.1836, found 517.1835.

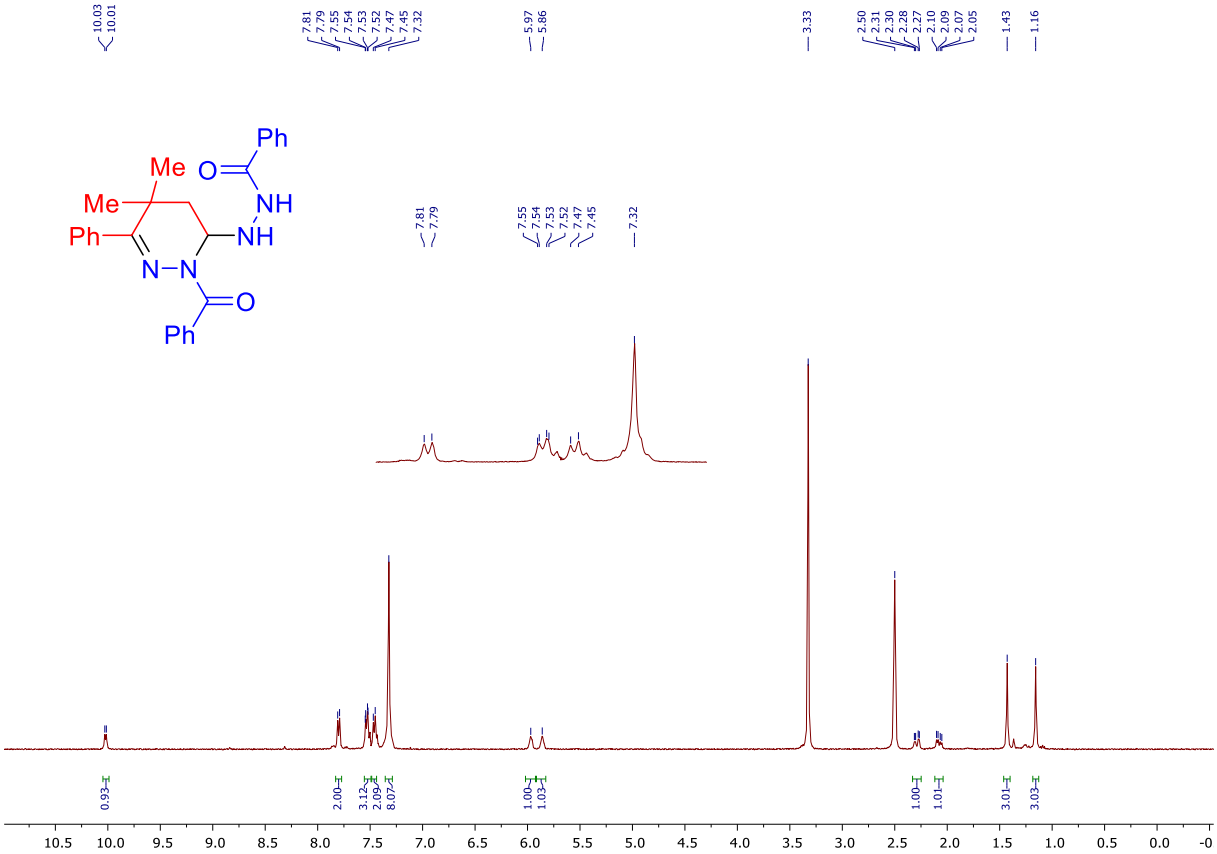
N'-(2-Isonicotinoyl-5,5-dimethyl-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)isonicotinohydrazide (**3af**). Following the general procedure, **3af** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and isonicotinohydrazide (**2f**,

137 mg, 1.0 mmol); **3af** was isolated as a white powder (128 mg, 60% yield), mp 154-156 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ = 10.38 (d, *J* = 4.6 Hz, 1H, NH), 8.73 (d, *J* = 5.6 Hz, 2H, Py), 8.58 (d, *J* = 5.1 Hz, 2H, Py), 7.73 (d, *J* = 5.6 Hz, 2H, Py), 7.46 (d, *J* = 5.1 Hz, 2H, Py), 7.33-7.31 (m, 5H, Ph), 6.02 (m, 1H, NH), 5.91 (dd, *J* = 5.2 Hz, *J* = 3.6 Hz, 1H, CH), 2.29 (dd, *J* = 14.3 Hz, *J* = 3.6 Hz, 1H, CH_2), 2.08 (dd, *J* = 14.3 Hz, *J* = 5.2 Hz, 1H, CH_2), 1.47 (s, 3H, Me), 1.11 (s, 3H, Me). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 168.5, 165.0, 159.4, 150.1, 149.0, 143.8, 140.5, 137.1, 128.3, 127.9, 127.9, 122.5, 121.4, 62.6, 36.7, 31.4, 28.3, 27.7. HRMS (ESI-TOF) calcd for $[C_{24}H_{24}N_6O_2+H]^+$ 429.2039, found 429.2041.

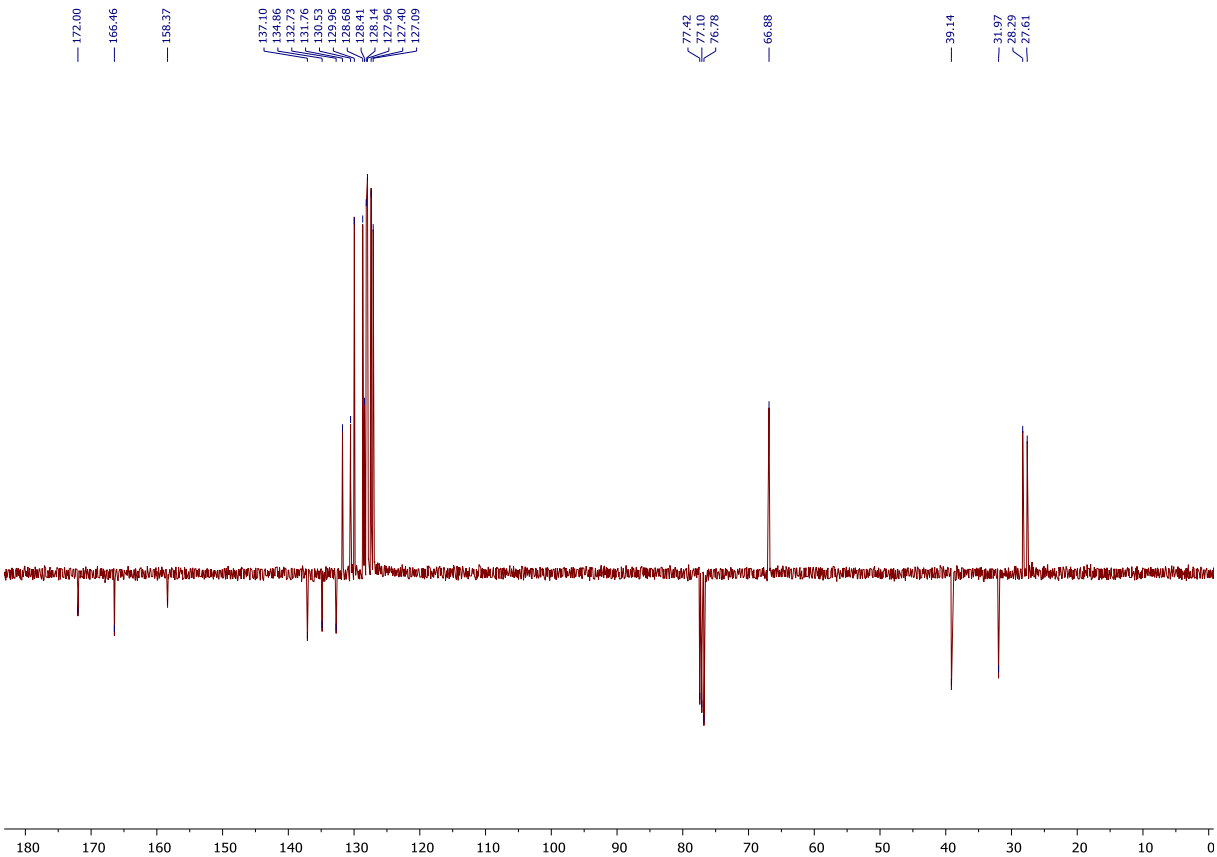
N'-(2-Benzoyl-5,5-dimethyl-6-(p-tolyl)-2,3,4,5-tetrahydropyridazin-3-yl)benzohydrazide (**3ba**). Following the general procedure, **3ba** was prepared from 3,3-dimethyl-5-hydroxy-2-(*p*-tolyl)-Δ^1-pyrroline (**1b**, 102 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1 mmol); **3ba** was isolated as a cream powder (127 mg, 58% yield), mp 134-136 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 5.9 Hz, 1H, NH), 7.82 (d, *J* = 7.6 Hz, 2H, Ph), 7.72 (d, *J* = 8.0 Hz, 2H, Ph), 7.52-7.48 (m, 1H, Ph), 7.44-7.41 (m, 2H, Ph), 7.39-7.36 (m, 1H, Ph), 7.33-7.30 (m, 2H, Ph), 7.26 (d, *J* = 7.8 Hz, 2H, Ar), 7.10 (d, *J* = 7.8 Hz, 2H, Ar), 5.60 (t, *J* = 5.8 Hz, 1H, CH), 2.33 (s, 3H, Me), 2.24-2.22 (m, 2H, CH_2), 1.48 (s, 3H, Me), 1.28 (s, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 172.0, 166.5, 158.5, 138.3, 135.0, 134.3, 132.8, 131.7, 130.5, 130.0, 128.7, 128.7, 128.1, 127.4, 127.1, 66.9, 39.2, 32.0, 28.3, 27.6, 21.2. HRMS (ESI-TOF) calcd for$[C_{27}H_{28}N_4O_2+H]^+$ 441.2291, found 441.2291.

N'-(3-Benzoyl-1-phenyl-2,3-diazaspiro[5.5]undec-1-en-4-yl)benzohydrazide (**3da**). Following the general procedure, **3da** was prepared from 1-phenyl-2-azaspiro[4.5]dec-1-en-3-ol (**1d**, 115 mg, 0.5 mmol) and benzohydrazide (**2a** ,136 mg, 1.0 mmol); **3da** was isolated as a cream powder (132 mg, 57% yield), mp 177-178 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.42 (br s, 1H, NH), 7.81 (d, *J* = 7.5 Hz, 2H, Ph), 7.71 (d, *J* = 7.5 Hz, 2H, Ph), 7.51-7.49 (m, 1H, Ph), 7.45-7.41 (m, 2H, Ph), 7.32-7.27 (m, 8H, Ph), 5.69 (br s, 1H, NH), 5.60 (t, *J* = 6.3 Hz, 1H, CH), 2.47-2.45 (m, 2H, CH_2), 1.86-1.82 (m, 1H, Cy), 1.73-1.59 (m, 8H, Cy), 1.21-1.16 (m, 1H, Cy). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.4, 166.5, 161.2, 136.9, 134.7, 132.7, 131.6, 130.4, 129.9, 128.5, 128.5, 128.1, 127.7, 127.2, 127.1, 66.6, 36.0, 33.6, 33.4, 31.1, 25.4, 21.0, 20.5. HRMS (ESI-TOF) calcd for$[C_{29}H_{30}N_4O_2+H]^+$ 467.2447, found 467.2452.

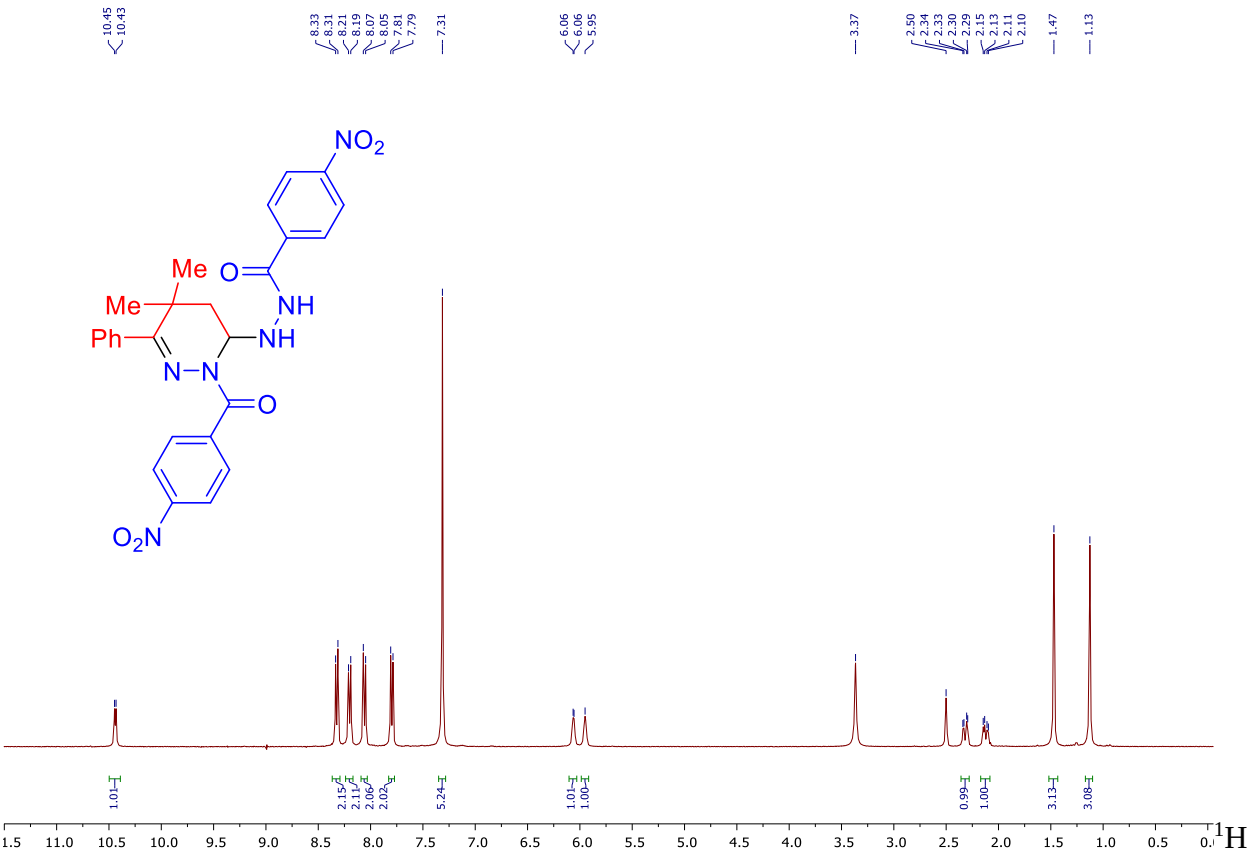
^{1}H and ^{13}C NMR spectra of 1,4,5,6-tetrahydropyridazines 3



^{1}H NMR spectrum of **3aa** (400.1 MHz, DMSO-d_6)



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



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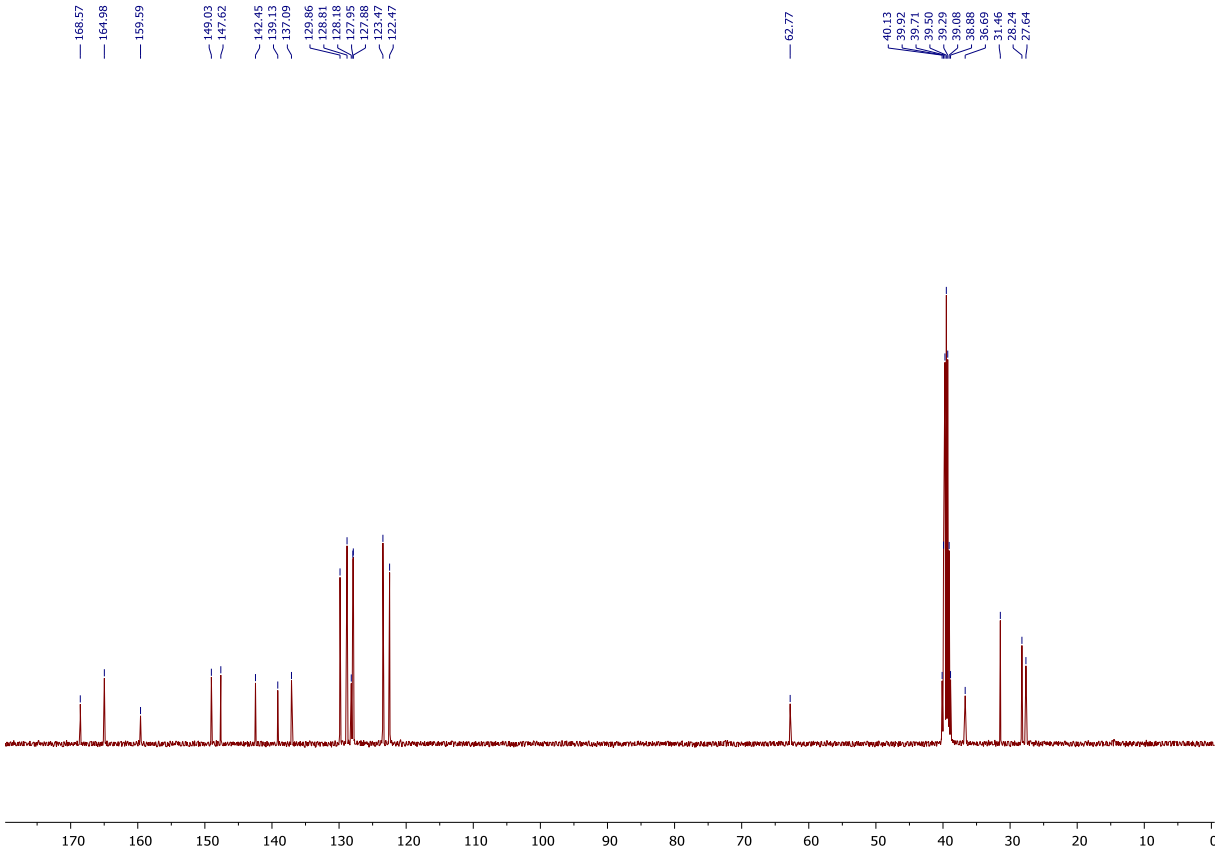
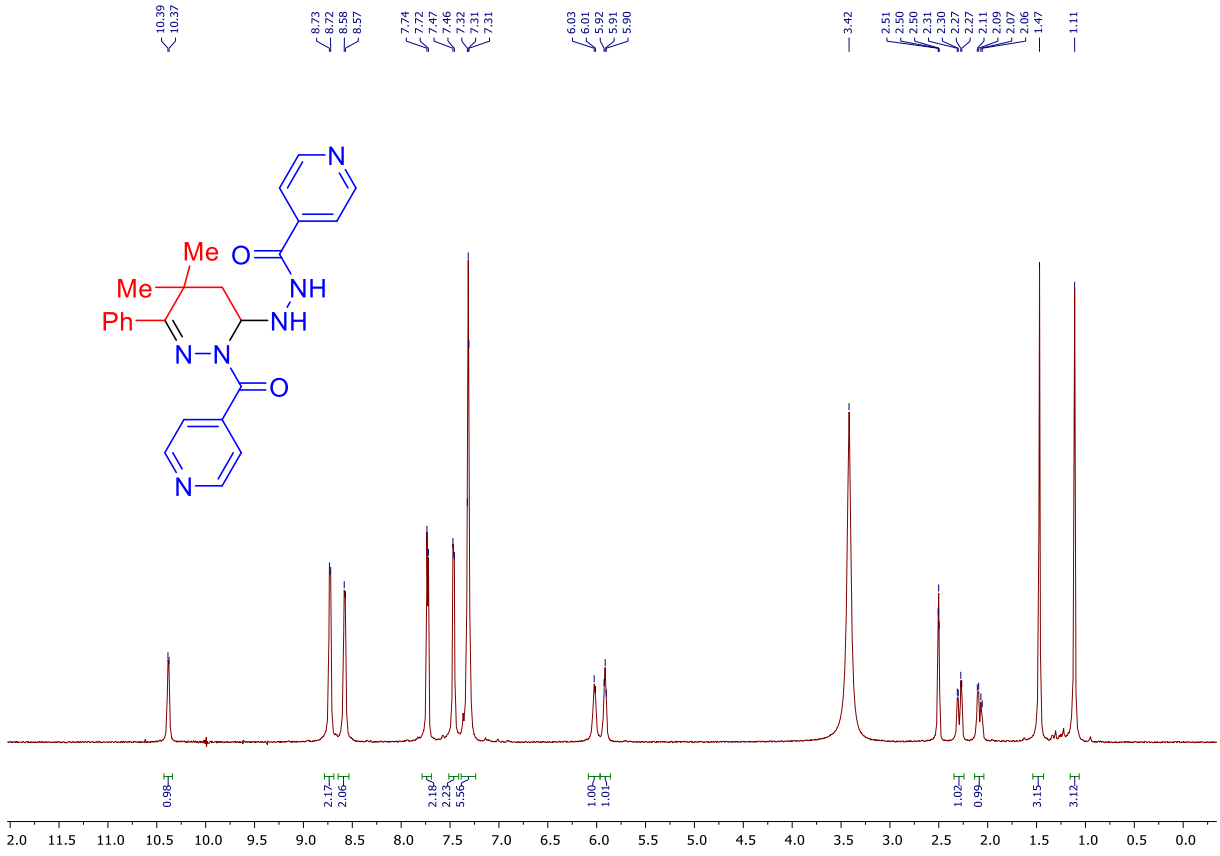


^{13}C NMR spectrum of **3ac** (100.6 MHz, DMSO-d_6)



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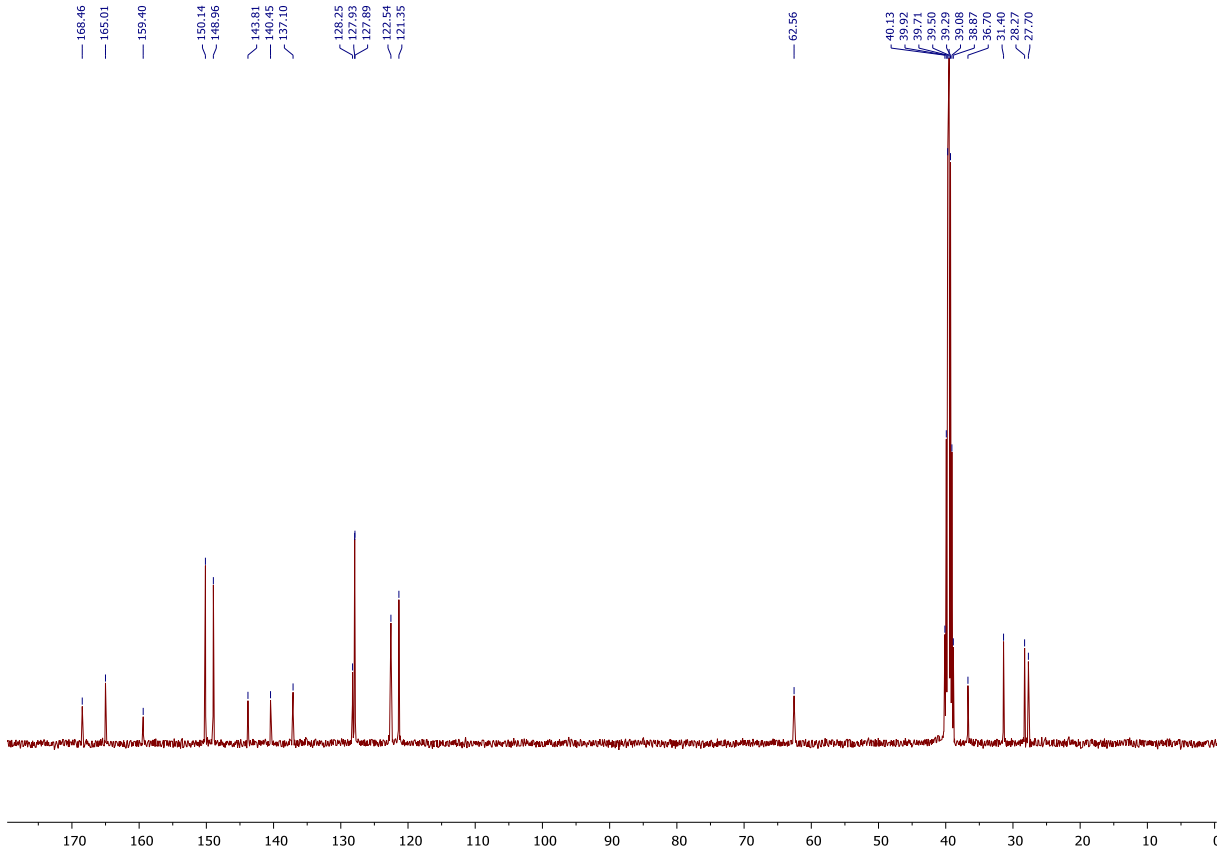
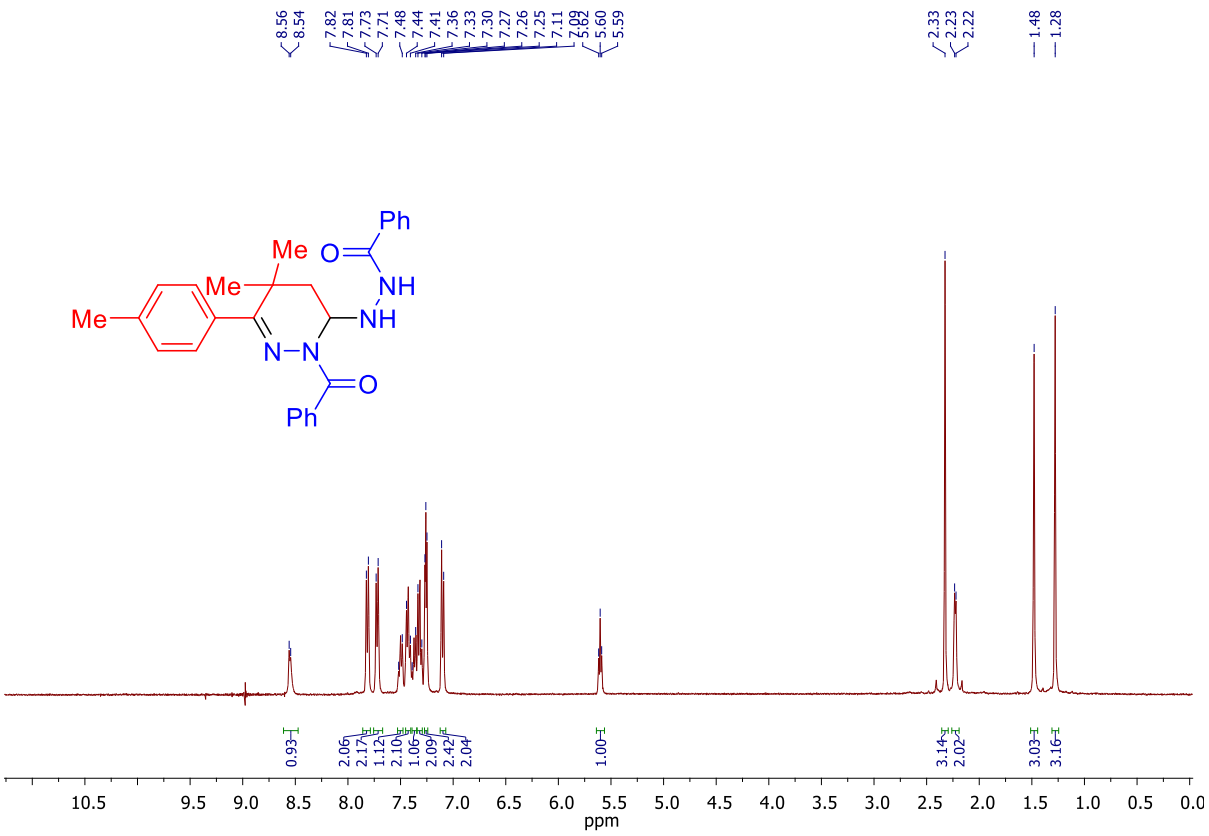
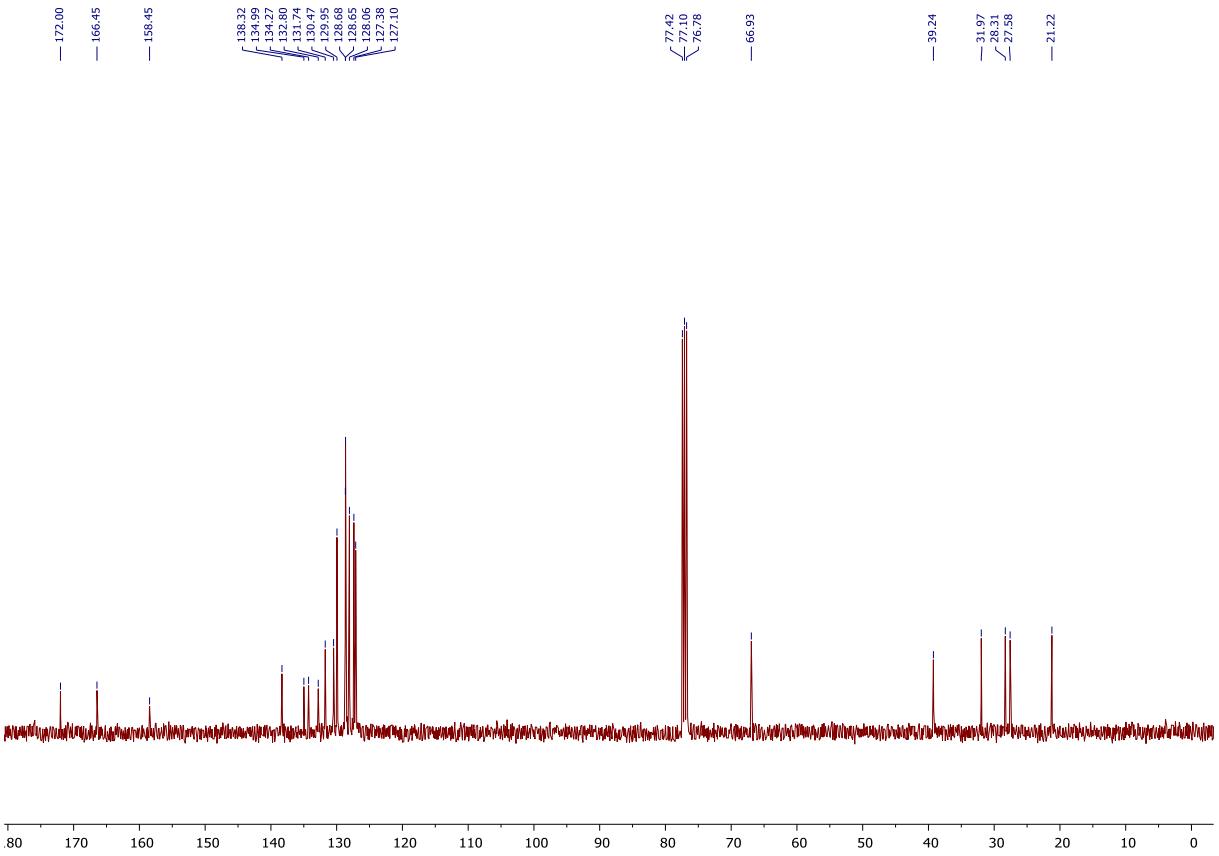


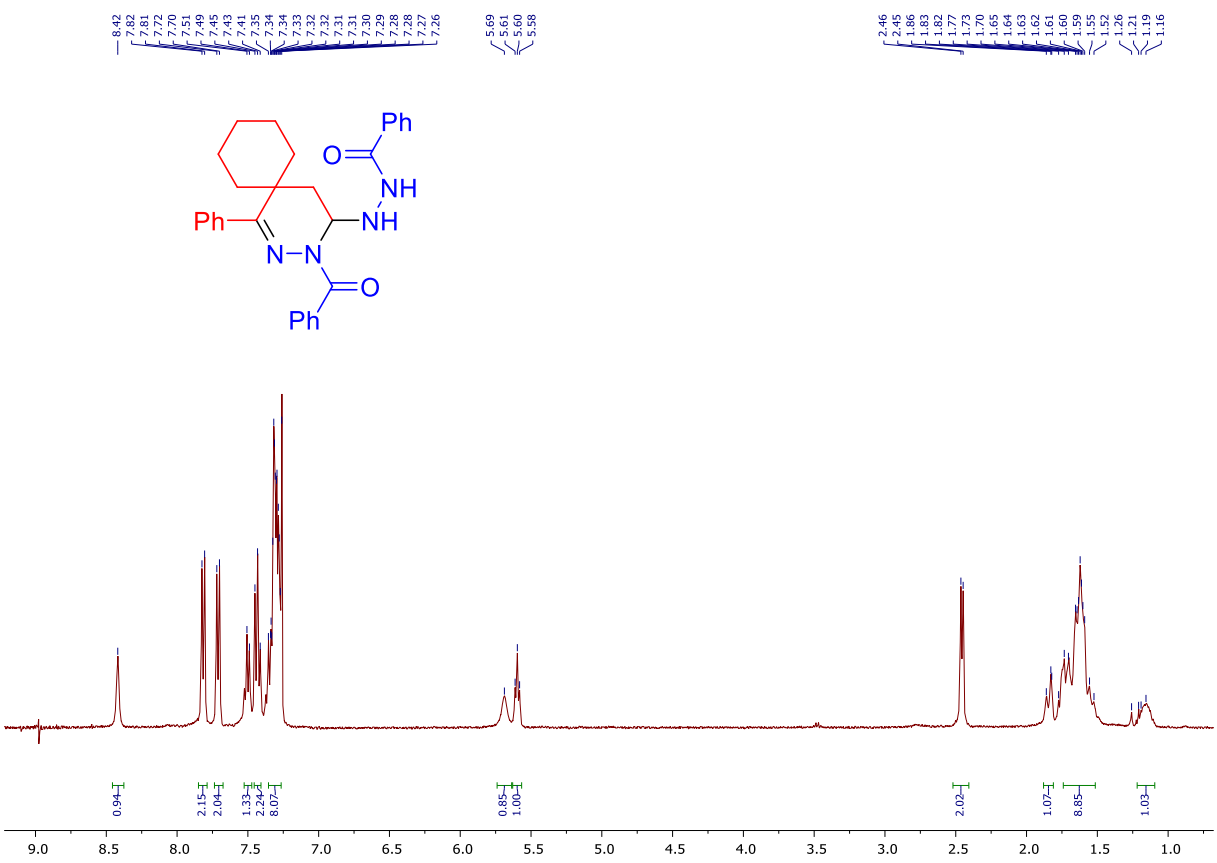
^{13}C NMR spectrum of **3af** (100.6 MHz, DMSO-d_6)



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



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



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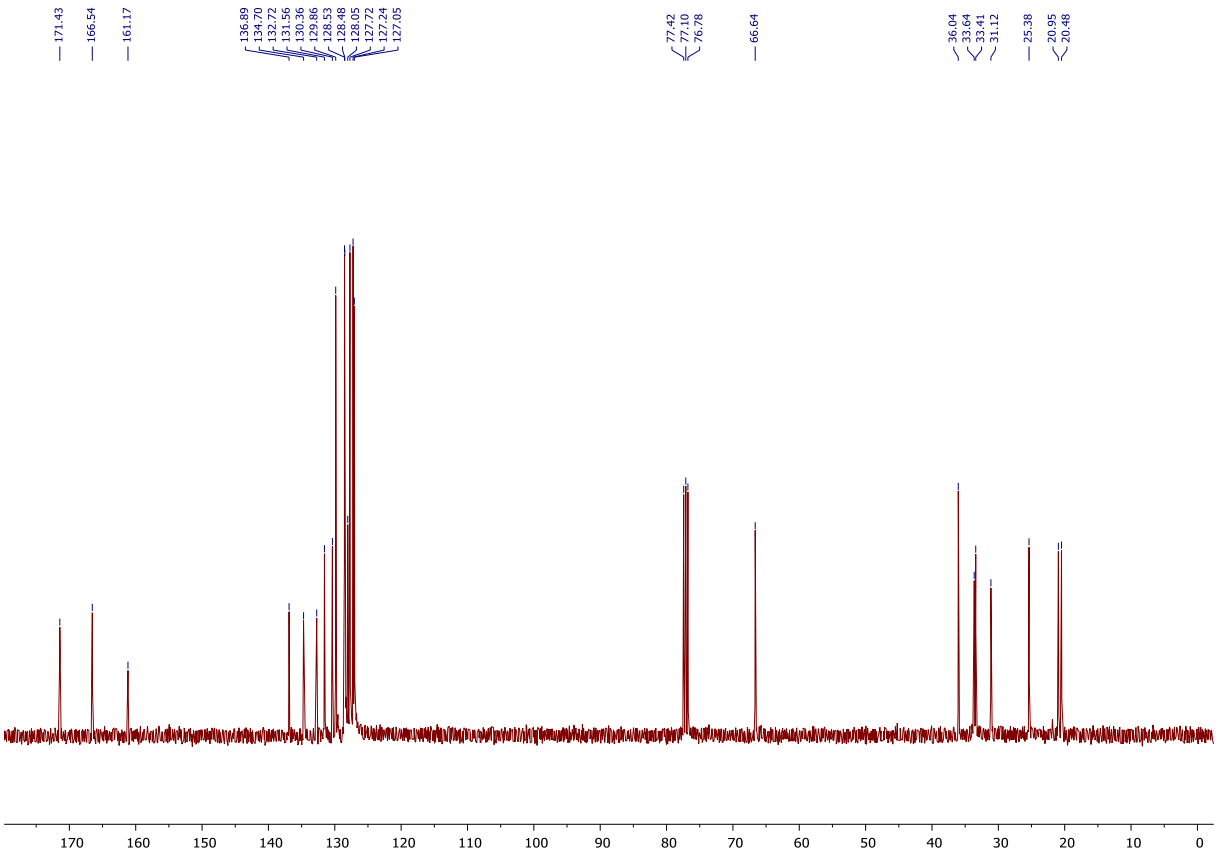


^{13}C NMR spectrum of **3da** (100.6 MHz, $CDCl_3$)

General procedure for the synthesis of 1,4-dihydropyridazines 4 and tricycle 5

A mixture of 5-hydroxy-Δ^1-hydroxypyrroline **1** (0.5 mmol), hydrazide **2** (1.0 mmol), acetonitrile (3 mL), and trifluoroacetic acid (4 μL, 0.05 mmol, 10 mol %) was placed in a 10-mL round-bottomed flask with a stirring bar, equipped with reflux condenser, and heated for 3 h at 80 °C (silicon oil bath). Then, trifluoroacetic acid (54 μL, 0.7 mmol, 140 mol %) was added and the reaction mixture additionally heated for 3 h at 80 °C (silicon oil bath). The residue after solvent evaporation was neutralized with Et_3N (210 μL, 1.5 mmol) and purified by column chromatography on silica to afford the desired 1,4-dihydropyridazine **4** or tricycle **5**.

(4,4-Dimethyl-3-phenylpyridazin-1(4H)-yl)(phenyl)methanone (**4aa**). Following the general procedure, **4aa** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1.0 mmol); **4aa** was isolated as a white powder (107 mg, 74% yield), mp 96-98 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.83-7.80 (m, 2H, Ph), 7.55 (d, *J* = 7.9 Hz, 1H, CH), 7.48-7.46 (m, 2H, Ph), 7.40-7.32 (m, 6H, Ph), 5.13 (d, *J* = 7.9 Hz, 1H, CH), 1.35 (s, 6H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.9, 156.1, 136.7, 133.9, 130.8, 130.2, 128.7, 128.7, 127.9, 127.4, 120.1, 116.2, 33.2, 29.3. HRMS (ESI-TOF) calcd for $[C_{19}H_{18}N_2O+H]^+$ 291.1497, found 291.1499.

(4,4-Dimethyl-3-phenylpyridazin-1(4H)-yl)(p-tolyl)methanone (**4ab**). Following the general procedure, **4ab** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and 4-methylbenzohydrazide (**2b**, 150 mg, 1.0 mmol); **4ab** was isolated as a cream powder (105 mg, 69% yield), mp 111-113 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 7.8 Hz, 2H, Ar), 7.52 (d, *J* = 8.0 Hz, 1H, CH), 7.47-7.45 (m, 2H, Ph), 7.37-7.32 (m, 3H, Ph), 7.14 (d, *J* = 7.8 Hz, 2H, Ar), 5.11 (d, *J* = 8.0 Hz, 1H, CH), 2.34 (s, 3H, Me), 1.33 (s, 6H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.8, 156.0, 141.3, 136.9, 130.9, 130.6, 128.8, 128.7, 128.2, 128.0, 120.3, 116.0, 33.2, 29.4, 21.6. HRMS (ESI-TOF) calcd for $[C_{20}H_{20}N_2O+H]^+$ 305.1654, found 305.1654.

(4,4-Dimethyl-3-phenylpyridazin-1(4H)-yl)(4-nitrophenyl)methanone (**4ac**). Following the general procedure, **4ac** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and 4-nitrobenzohydrazide (**2c**, 181 mg, 1.0 mmol); **4ac** was isolated as a yellow powder (73 mg, 44% yield), mp 100-102 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.8 Hz, 2H, Ar), 7.89 (d, *J* = 8.8 Hz, 2H, Ar), 7.50 (d, *J* = 8.1 Hz, 1H, CH), 7.40-7.33 (m, 5H, Ph), 5.20 (d, *J* = 8.1 Hz, 1H, CH), 1.34 (s, 6H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ =

166.0, 157.6, 148.8, 140.1, 136.3, 131.0, 129.1, 128.5, 128.2, 122.7, 119.3, 117.4, 33.5, 29.4. HRMS (ESI-TOF) calcd for $[C_{19}H_{17}N_3O_3+H]^+$ 336.1348, found 336.1349.

1-(4,4-Dimethyl-3-phenylpyridazin-1(4H)-yl)ethan-1-one (**4ag**). Following the general procedure, **4ag** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and acetohydrazide (**2g**, 74 mg, 1.0 mmol); **4ag** was isolated as a light-yellow powder (62 mg, 54% yield), mp 42-44 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.51-7.48 (m, 2H, Ph), 7.41-7.38 (m, 3H, Ph), 7.34 (d, *J* = 8.1 Hz, 1H, CH), 4.97 (d, *J* = 8.1, Hz, 1H, CH), 2.36 (s, 3H, Me), 1.28 (s, 6H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.4, 156.0, 137.1, 128.7, 128.7, 128.0, 118.8, 114.9, 33.0, 29.5, 21.2. HRMS (ESI-TOF) calcd for $[C_{14}H_{16}N_2O+H]^+$ 229.1341, found 229.1340.

(4,4-Dimethyl-3-(p-tolyl)pyridazin-1(4H)-yl)(phenyl)methanone (**4ba**). Following the general procedure, **4ba** was prepared from 3,3-dimethyl-5-hydroxy-2-(*p*-tolyl)-Δ^1-pyrroline (**1b**, 102 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1.0 mmol); **4ba** was isolated as a white powder (78 mg, 51% yield), mp 129-131 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.1 Hz, 2H, Ph), 7.53 (d, *J* = 8.0 Hz, 1H, CH), 7.42-7.33 (m, 3H, Ph, 2H, Ar), 7.14 (d, *J* = 7.8 Hz, 2H, Ar), 5.12 (d, *J* = 8.0 Hz, 1H, CH), 2.35 (s, 3H, Me), 1.35 (s, 6H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 167.9, 156.0, 138.7, 134.0, 133.9, 130.8, 130.3, 128.7, 128.6, 127.4, 120.0, 116.4, 33.2, 29.4, 21.2. HRMS (ESI-TOF) calcd for $[C_{20}H_{20}N_2O+H]^+$ 305.1654, found 305.1654.

(3-(Furan-2-yl)-4,4-dimethylpyridazin-1(4H)-yl)(phenyl)methanone (**4ca**). Following the general procedure, **4ca** was prepared from 3,3-dimethyl-2-(2-furyl)-5-hydroxy-Δ^1-pyrroline (**1c**, 90 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1.0 mmol); **4ca** was isolated as an yellow oil (28 mg, 20% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.82-7.80 (m, 2H, Ph), 7.47-7.39 (m, 1H, CH, 1H, Fur, 3H, Ph), 6.60 (d, *J* = 3.4 Hz, 1H, Fur), 6.39 (dd, *J* = 3.4 Hz, *J* = 1.7 Hz, 1H, Fur), 5.08 (d, *J* = 8.4 Hz, 1H, CH), 1.49 (s, 6H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.5, 152.1, 145.8, 142.9, 133.8, 130.9, 130.4, 127.4, 118.3, 117.1, 111.5, 111.2, 32.0, 29.7. HRMS (ESI-TOF) calcd for $[C_{17}H_{16}N_2O_2+H]^+$ 281.1290, found 281.1291.

Phenyl(1-phenyl-2,3-diazaspiro[5.5]undeca-1,4-dien-3-yl)methanone (**4da**). Following the general procedure, **4da** was prepared from 1-phenyl-2-azaspiro[4.5]dec-1-en-3-ol (**1d**, 115 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1.0 mmol); **4da** was isolated as a white powder (83 mg, 50% yield), mp 143-145 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.6 Hz, 2H, Ph), 7.61 (d, *J* = 7.9 Hz, 1H, CH), 7.40-7.32 (m, 8H, Ph), 5.63 (d, *J* = 7.9 Hz, 1H, CH), 1.74-

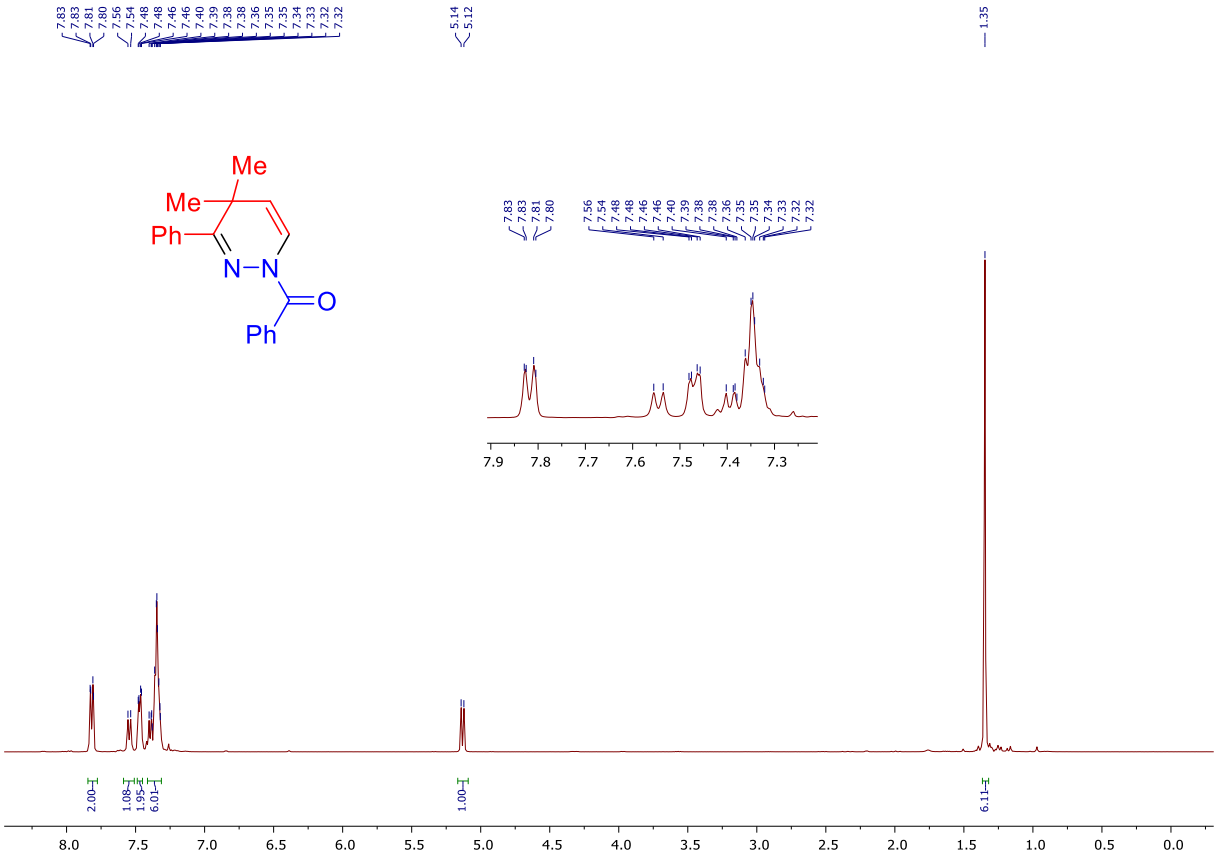
1.56 (m, 9H, Cy), 1.17-1.14 (m, 1H, Cy). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 168.2, 157.9, 136.5, 133.9, 130.9, 130.3, 128.9, 128.4, 127.9, 127.5, 121.5, 111.6, 38.2, 35.1, 25.5, 20.7. HRMS (ESI-TOF) calcd for $[C_{22}H_{22}N_2O+H]^+$ 331.1810, found 331.1810.

Phenyl(1-(p-tolyl)-2,3-diazaspiro[5.5]undeca-1,4-dien-3-yl)methanone (**4ea**). Following the general procedure, **4ea** was prepared from 1-phenyl-2-azaspiro[4.5]dec-1-en-3-ol (**1e**, 122 mg, 0.5 mmol) and benzohydrazide (**2a**, 136 mg, 1.0 mmol); **4ea** was isolated as a beige powder (65 mg, 38% yield), mp 150-152 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.79-7.77 (m, 2H, Ph), 7.59 (d, *J* = 7.9 Hz, 1H, CH), 7.41-7.31 (m, 3H, Ph), 7.24 (d, *J* = 7.9 Hz, 2H, Ar), 7.14 (d, *J* = 7.9 Hz, 2H, Ar), 5.61 (d, *J* = 7.9 Hz, 1H, CH), 2.35 (s, 3H, Me), 1.72-1.55 (m, 9H, Cy), 1.21-1.10 (m, 1H, Cy). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 168.2, 157.9, 138.3, 134.0, 133.6, 130.9, 130.3, 128.9, 128.6, 127.5, 121.5, 111.6, 38.2, 35.1, 25.5, 21.3, 20.8. HRMS (ESI-TOF) calcd for $[C_{23}H_{24}N_2O+H]^+$ 345.1967, found 345.1968.

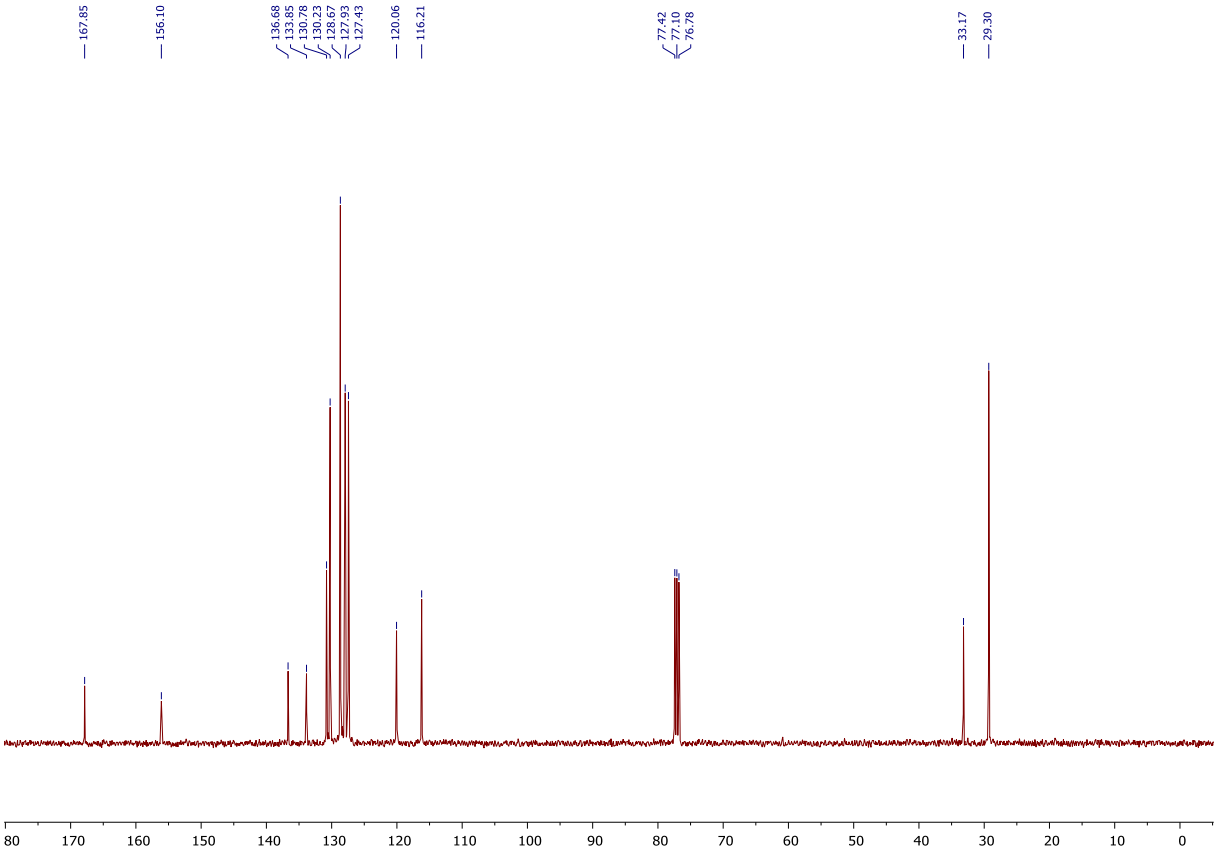
3,3-Dimethyl-2-phenyl-4,4a-dihydro-3H,10H-benzo[e]pyridazino[6,1-b][1,3]oxazin-10-one (**5ad**). Following the general procedure, **5ad** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and 2-hydroxybenzohydrazide (**2d**, 152 mg, 1.0 mmol); **5ad** was isolated as a beige powder (81 mg, 53% yield), mp 110-112 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.7 Hz, 1H, Ar), 7.49-7.45 (m, 1H, Ar), 7.42-7.39 (m, 2H, Ph), 7.33-7.31 (m, 3H, Ph), 7.16-7.13 (m, 1H, Ar), 6.99 (d, *J* = 8.2 Hz, 1H, Ar), 5.68 (dd, *J* = 8.2 Hz, *J* = 6.8 Hz, 1H, CH), 2.25-2.23 (m, 2H, CH_2), 1.39 (s, 3H, Me), 1.19 (s, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 160.8, 158.8, 157.0, 136.4, 134.5, 129.3, 128.7, 128.4, 128.0, 123.2, 118.9, 116.3, 82.1, 39.5, 34.2, 27.6, 27.0. HRMS (ESI-TOF) calcd for $[C_{19}H_{18}N_2O_2+H]^+$ 307.1447, found 307.1446.

3,3-Dimethyl-2-phenyl-3,4,4a,5-tetrahydro-10H-pyridazino[6,1-b]quinazolin-10-one (**5ae**). Following the general procedure, **5ae** was prepared from 3,3-dimethyl-5-hydroxy-2-phenyl-Δ^1-pyrroline (**1a**, 95 mg, 0.5 mmol) and 2-aminobenzohydrazide (**2e**, 151 mg, 1.0 mmol); **5ae** was isolated as a beige powder (43 mg, 28% yield), mp 242-244 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.9 Hz, 1H, Ar), 7.42-7.39 (m, 2H, Ph), 7.33-7.28 (m, 1H, Ar, 3H, Ph), 6.94-6.90 (m, 1H, Ar), 6.72 (d, *J* = 8.1 Hz, 1H, Ar), 5.16 (dd, *J* = 11.0 Hz, *J* = 4.1 Hz, 1H, CH), 4.73 (br s, 1H, NH), 2.13-1.99 (m, 2H, CH_2), 1.38 (s, 3H, Me), 1.12 (s, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 160.5, 159.1, 146.8, 137.1, 133.7, 129.8, 128.7, 128.4, 128.0, 120.2, 117.4, 114.9, 63.6, 40.9, 33.2, 28.2, 28.0. HRMS (ESI-TOF) calcd for $[C_{19}H_{19}N_3O+H]^+$ 306.1606, found 306.1607.

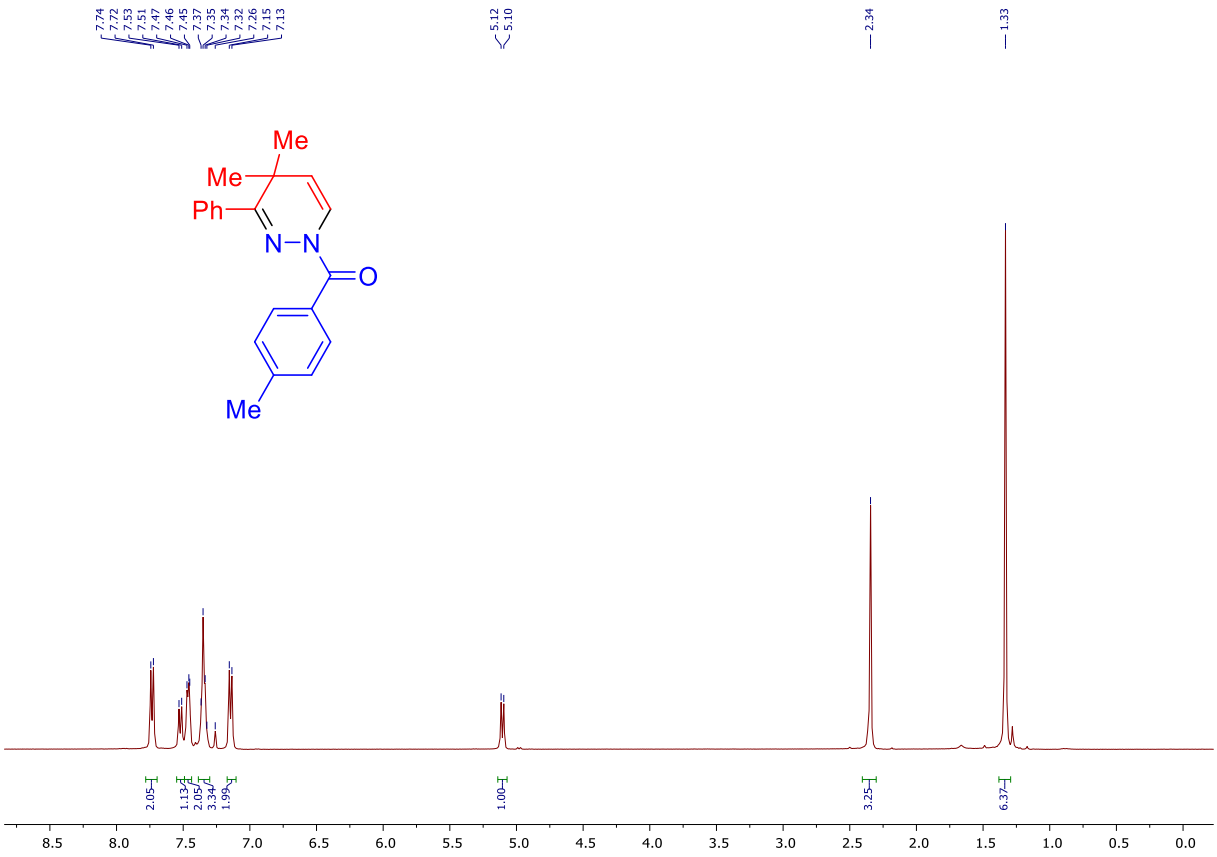
^{1}H and ^{13}C NMR Spectra of 1,4-Dihydropyridazines 4 and Tricycles 5



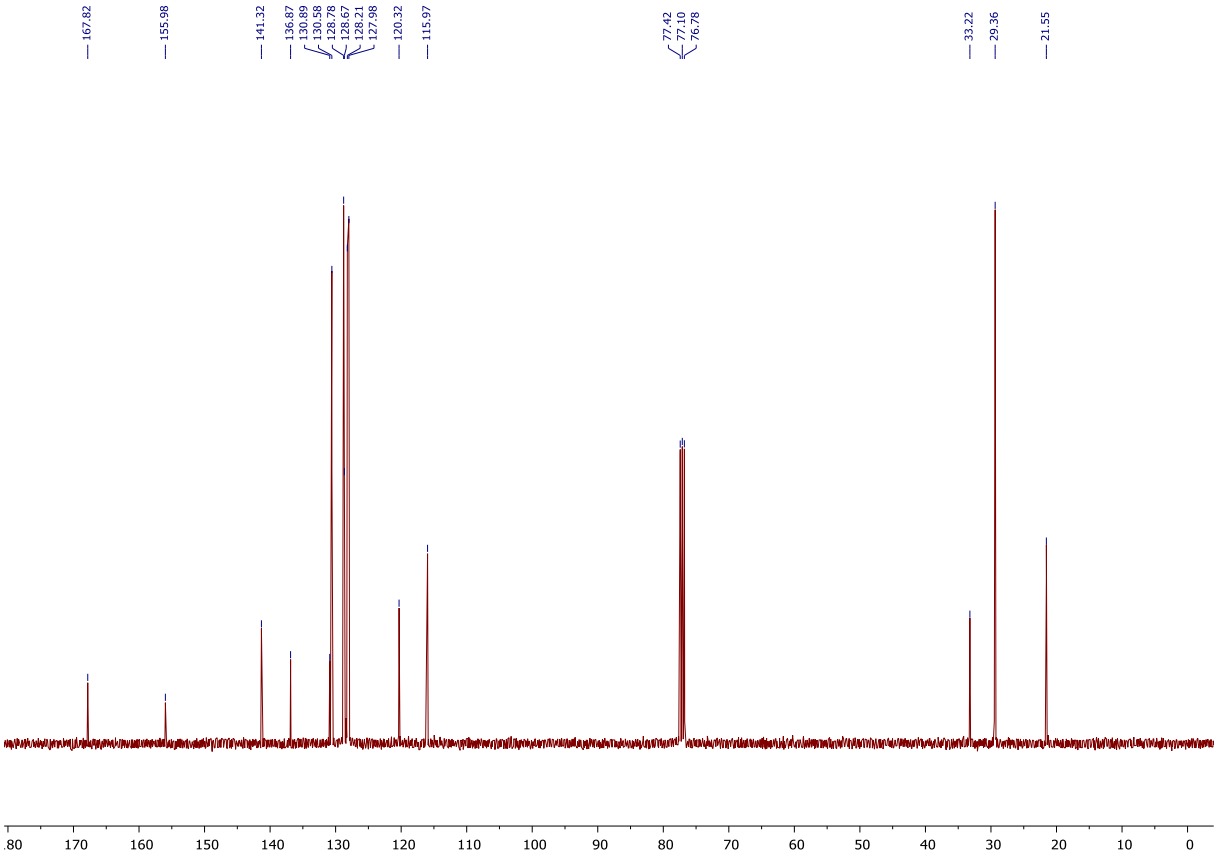
^{1}H NMR spectrum of **4aa** (400.1 MHz, $CDCl_3$)



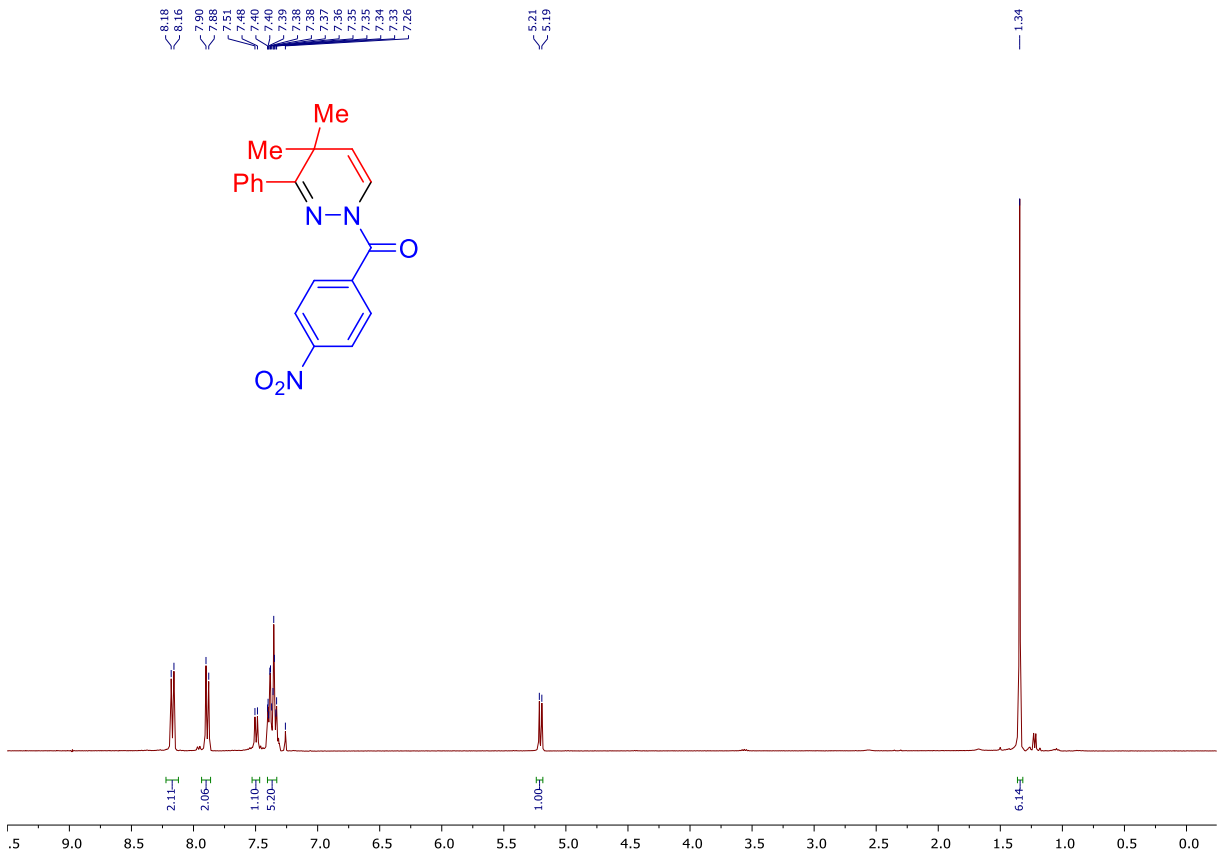
^{13}C NMR Spectrum of **4aa** (100.6 MHz, $CDCl_3$)



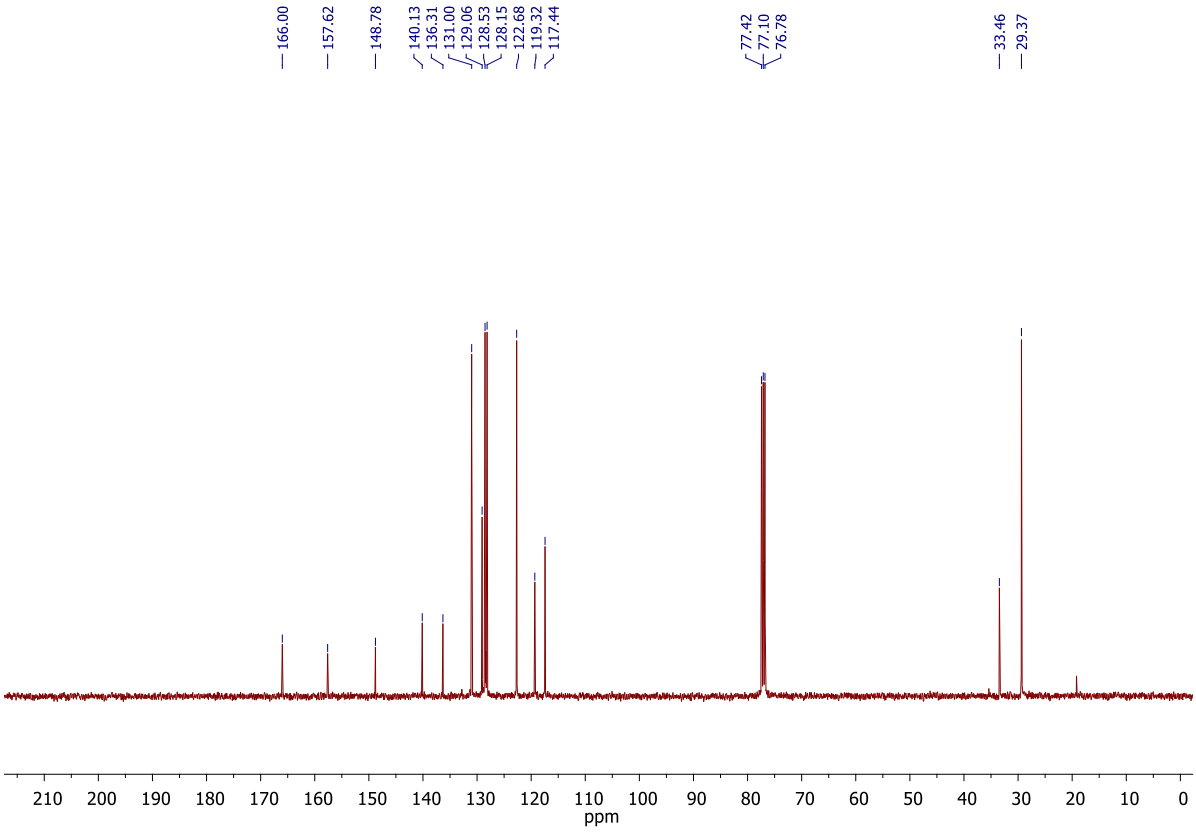
^{1}H NMR spectrum of **4ab** (400.1 MHz, $CDCl_3$)



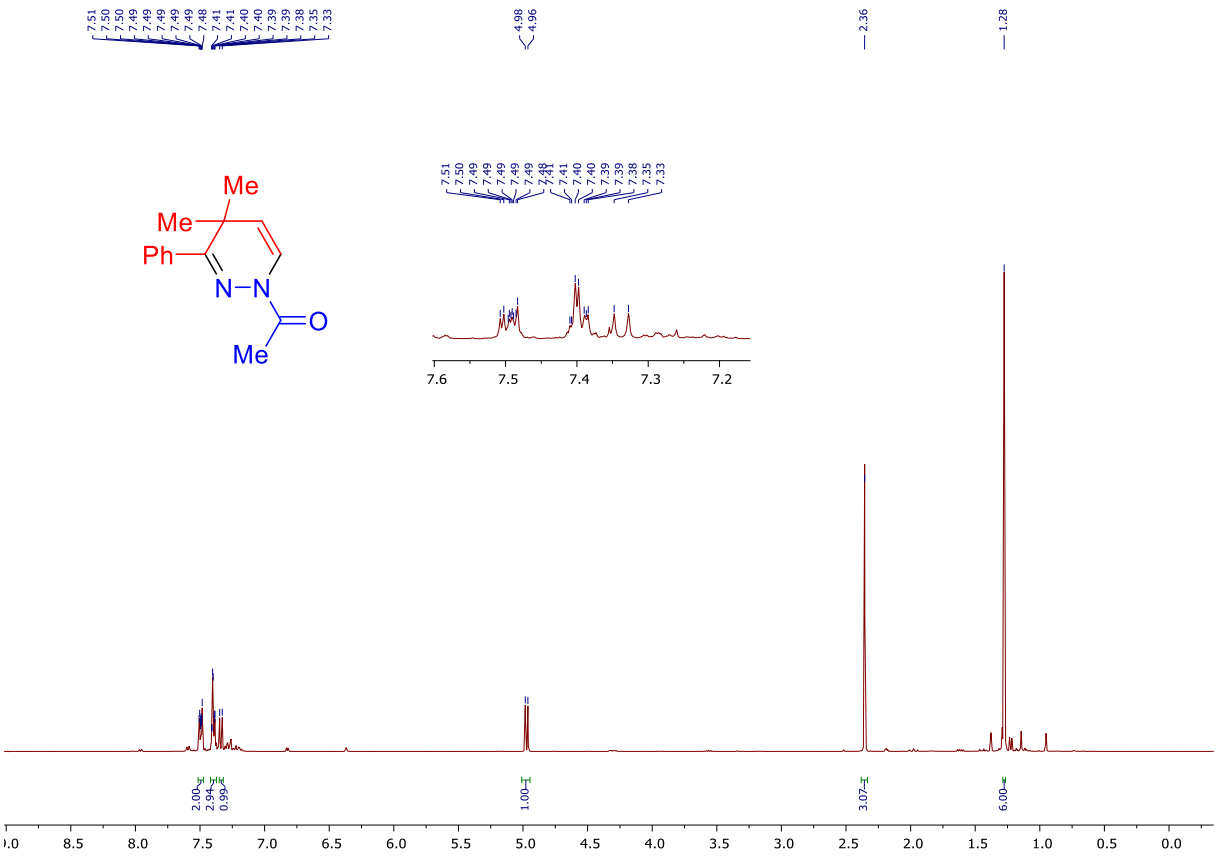
^{13}C NMR spectrum of **4ab** (100.6 MHz, $CDCl_3$)



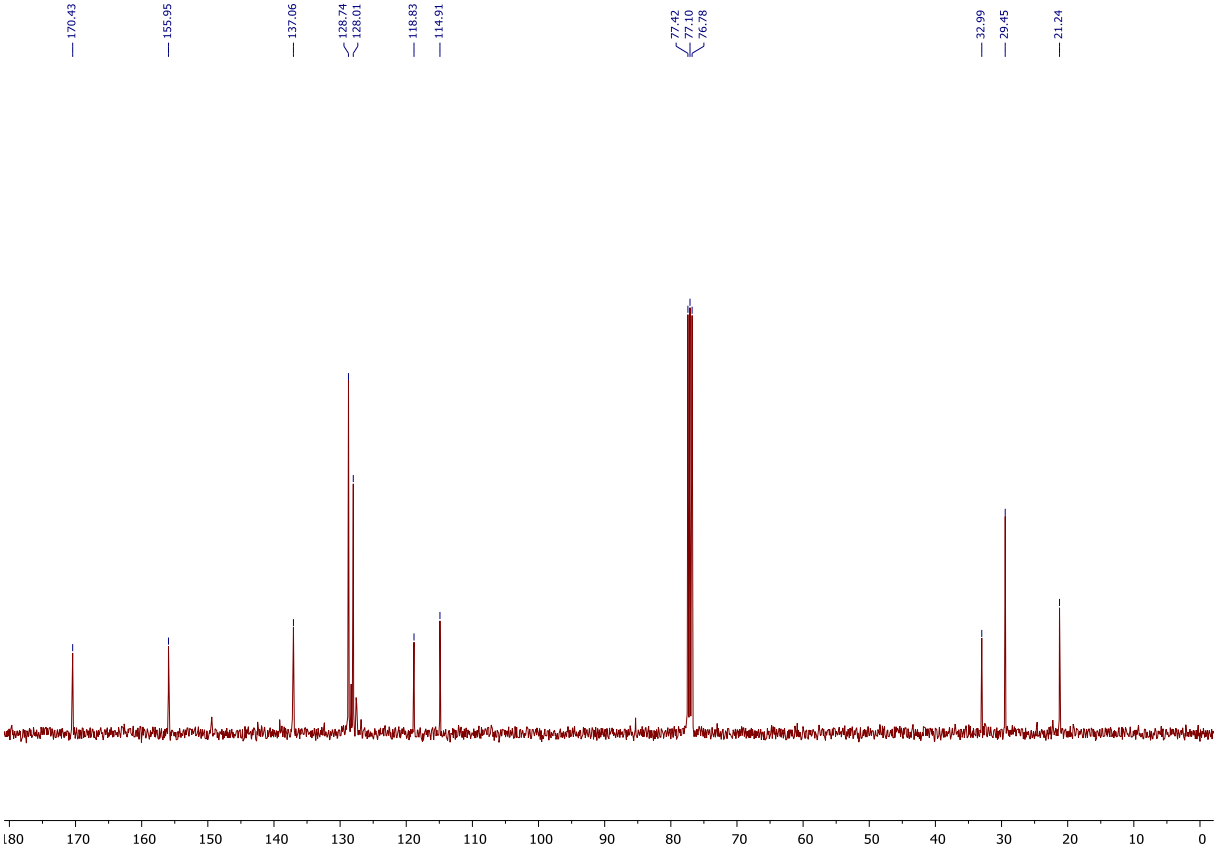
^{1}H NMR spectrum of **4ac** (400.1 MHz, $CDCl_3$)



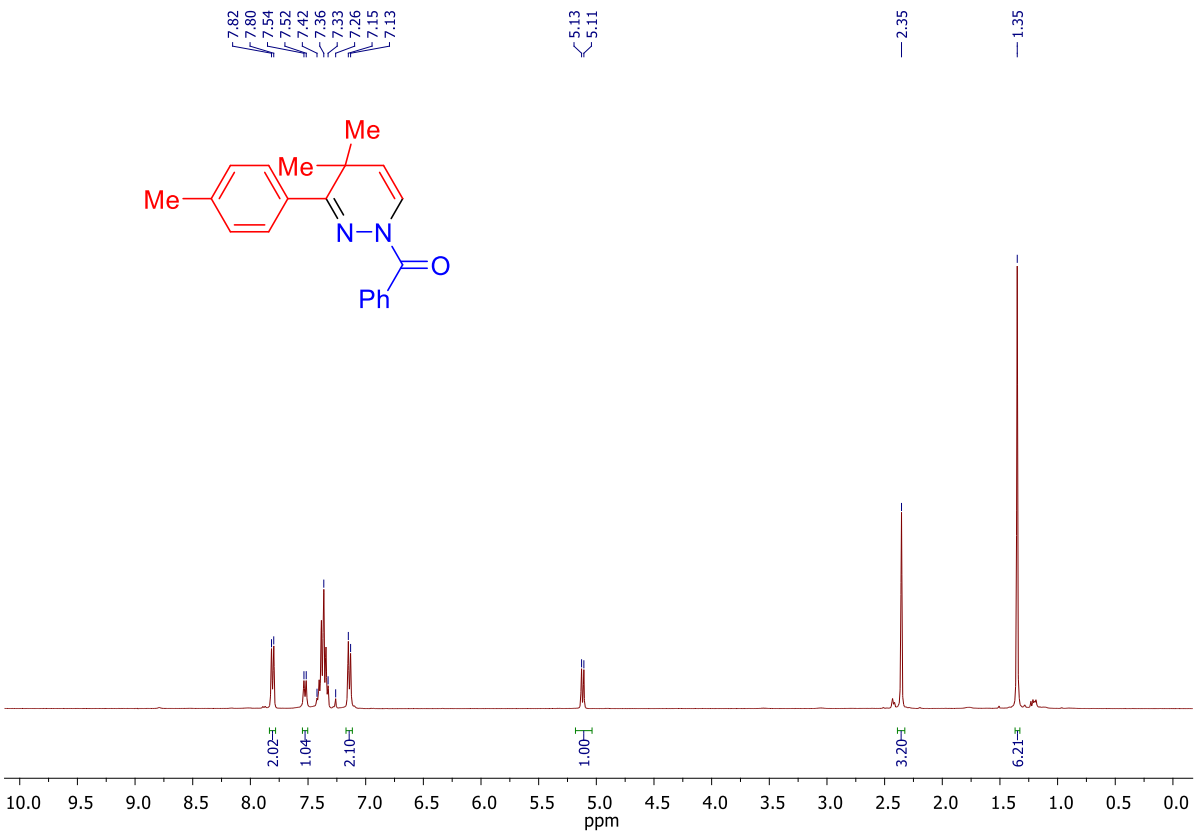
^{13}C NMR Spectrum of **4ac** (100.6 MHz, $CDCl_3$)



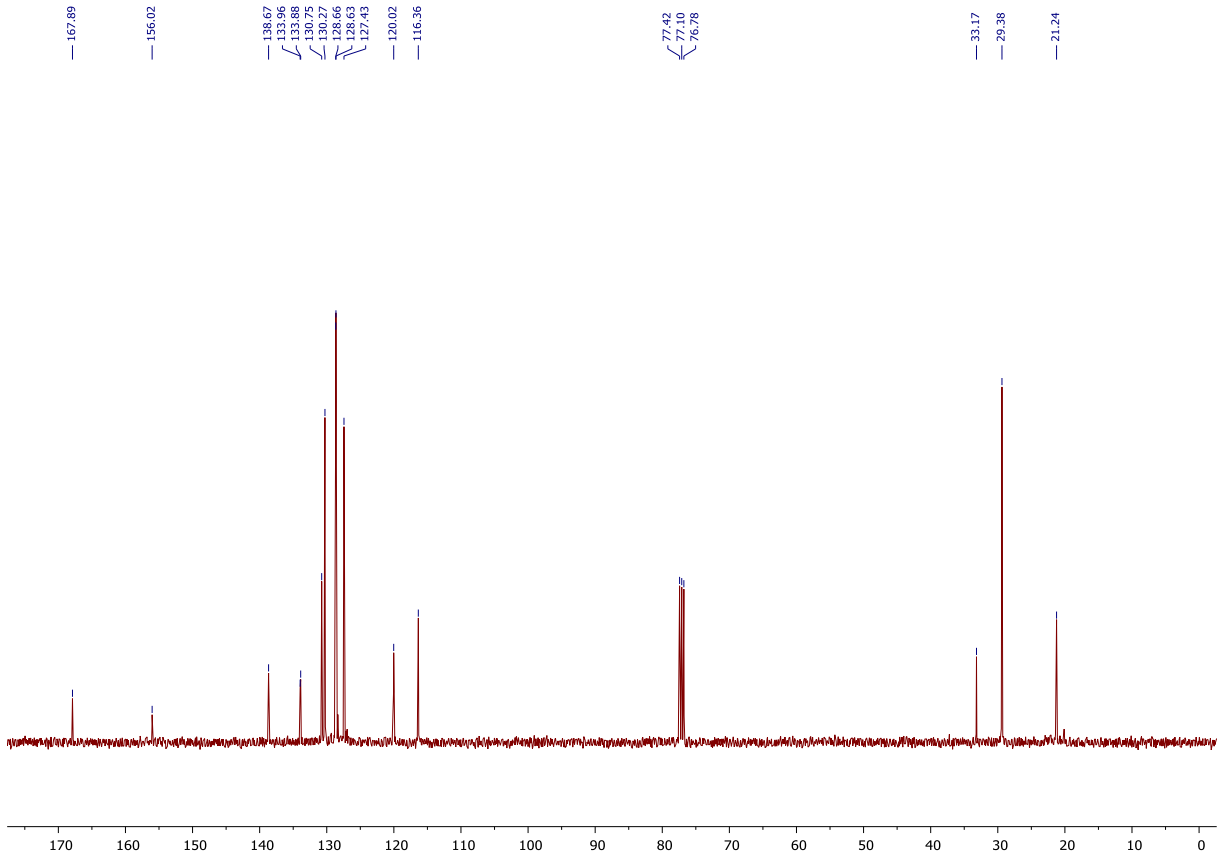
^{1}H NMR spectrum of **4ag** (400.1 MHz, $CDCl_3$)



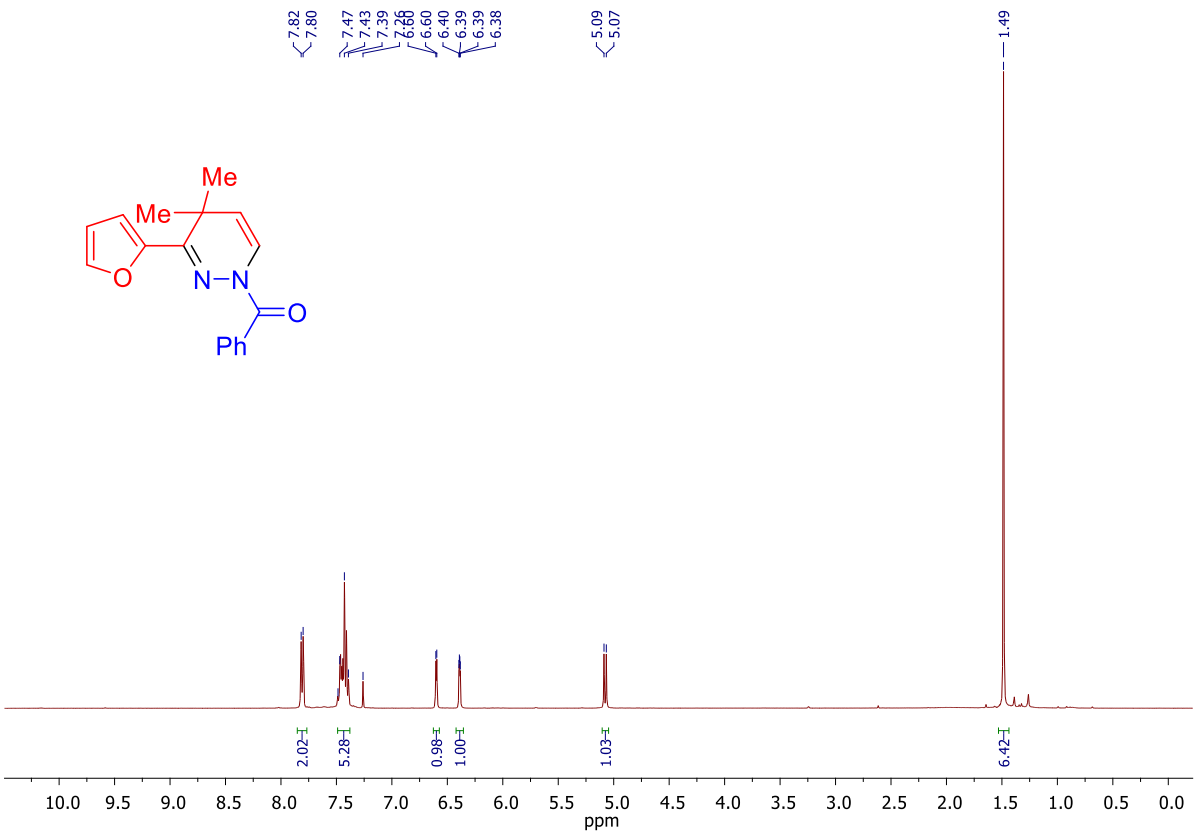
^{13}C NMR spectrum of **4ag** (100.6 MHz, $CDCl_3$)



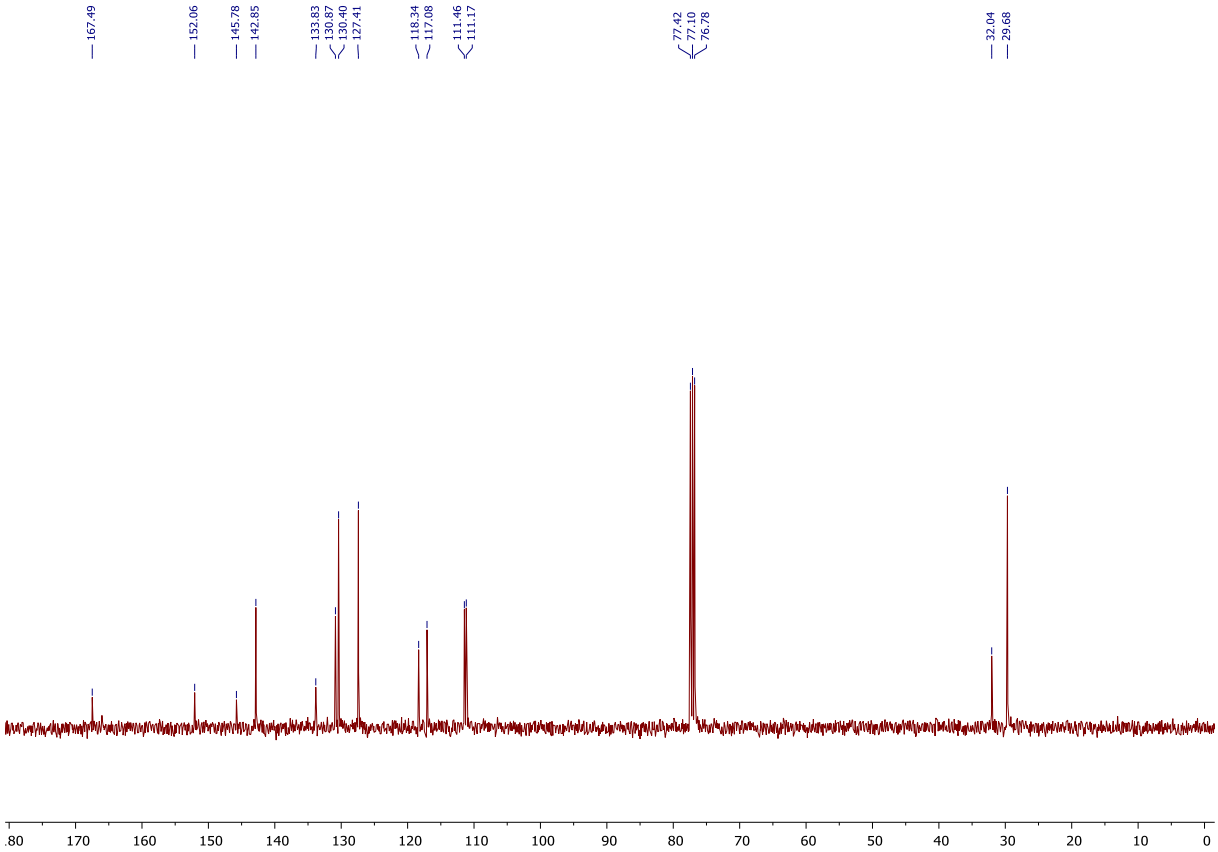
^{1}H NMR spectrum of **4ba** (400.1 MHz, $CDCl_3$)



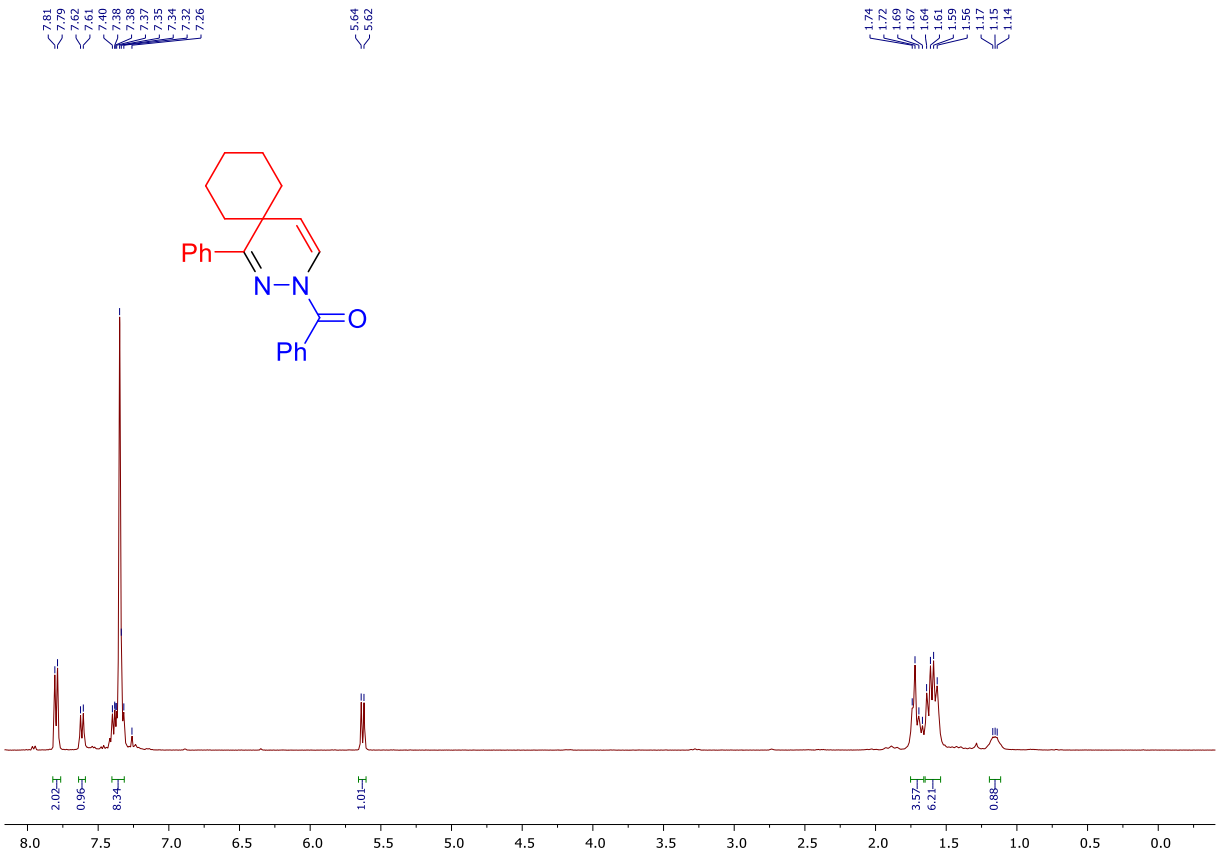
^{13}C NMR spectrum of **4ba** (100.6 MHz, $CDCl_3$)



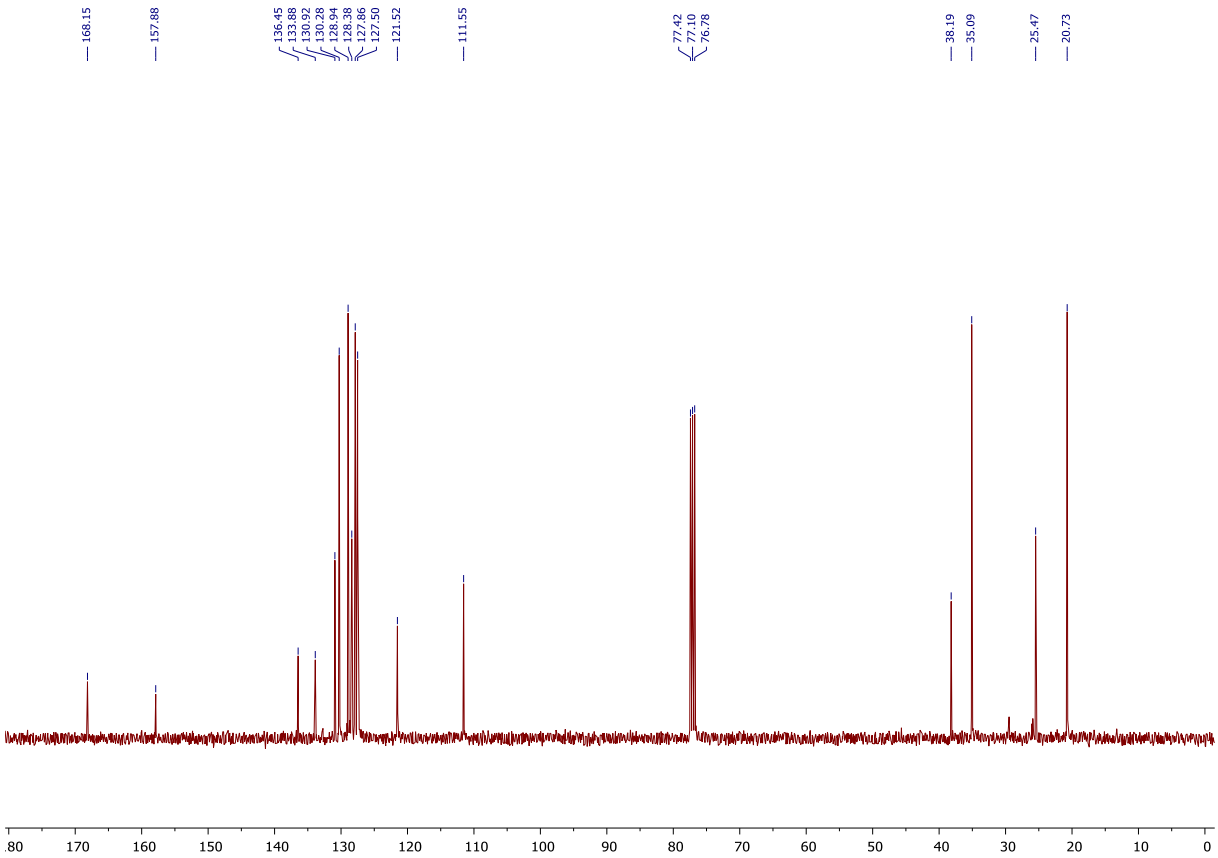
^{1}H NMR spectrum of **4ca** (400.1 MHz, $CDCl_3$)



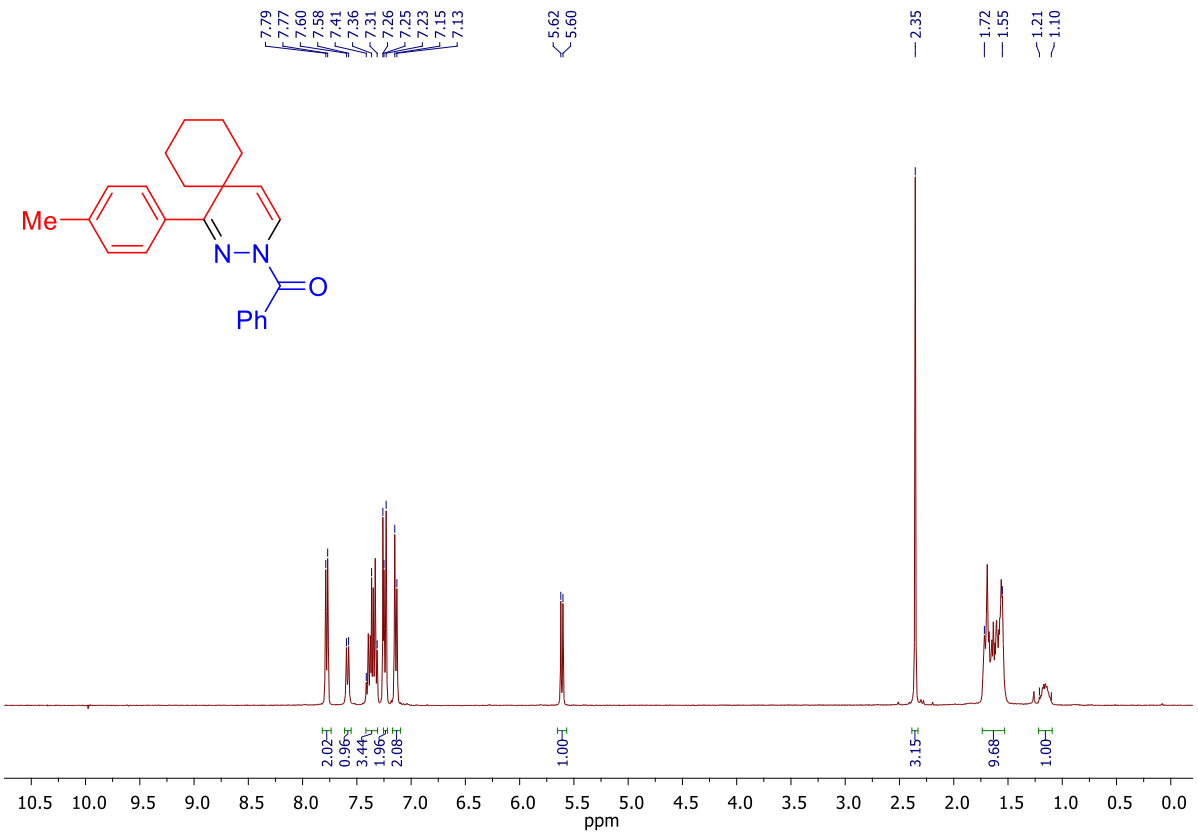
^{13}C NMR spectrum of **4ca** (100.6 MHz, $CDCl_3$)



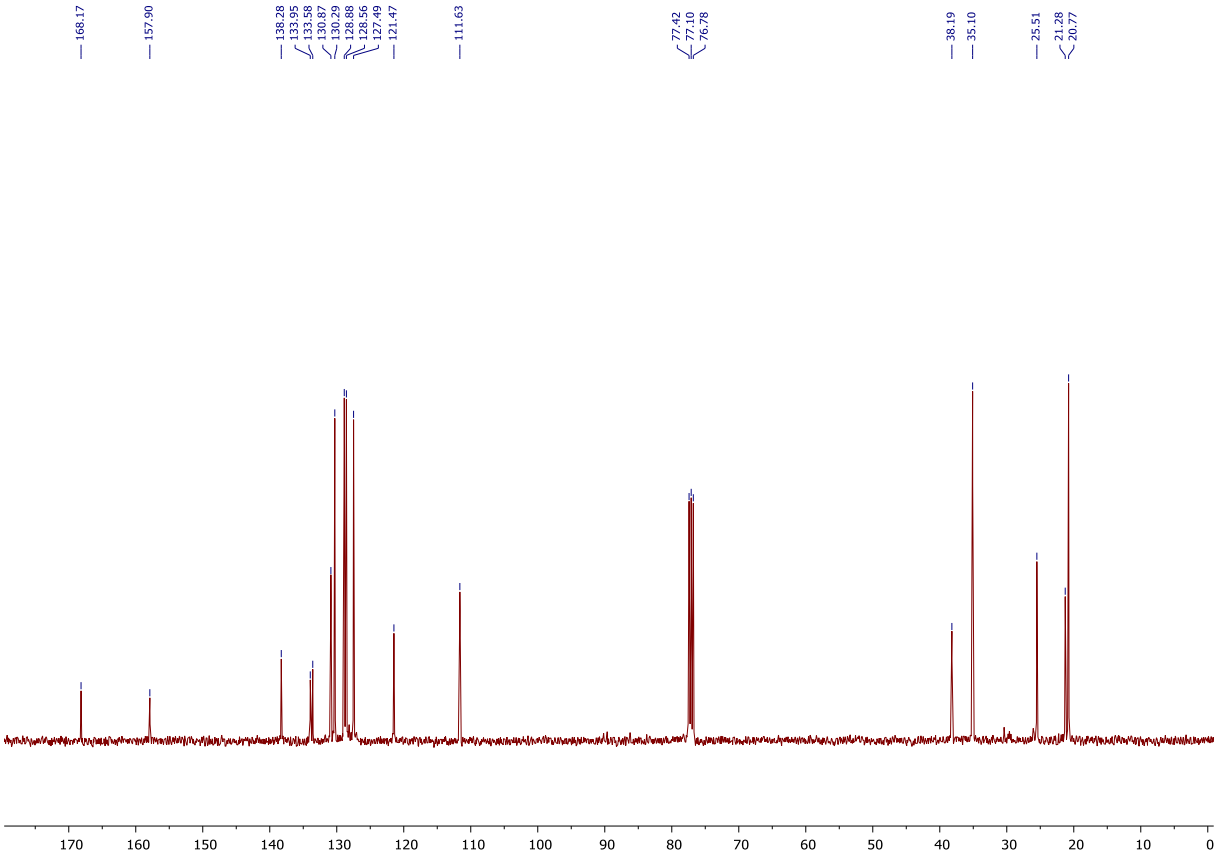
^{1}H NMR spectrum of **4da** (400.1 MHz, $CDCl_3$)



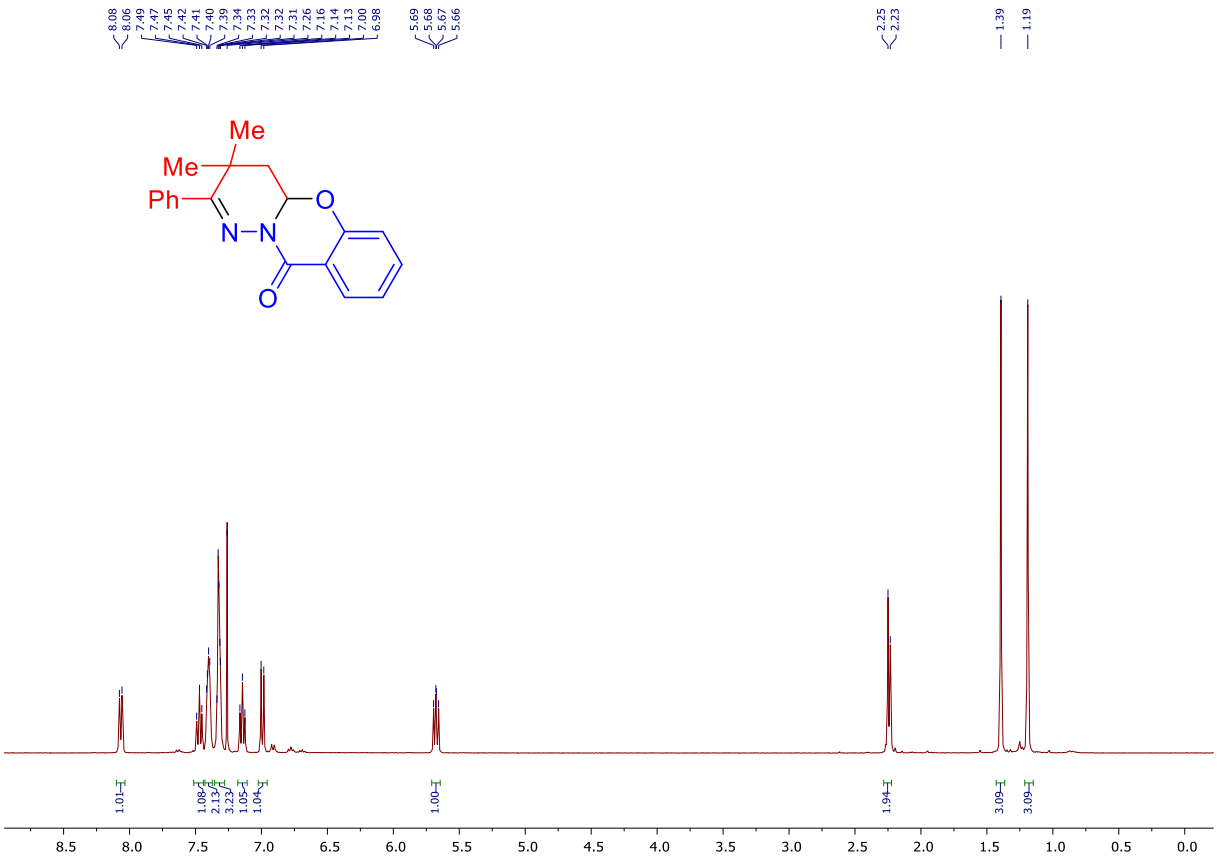
^{13}C NMR spectrum of **4da** (100.6 MHz, $CDCl_3$)



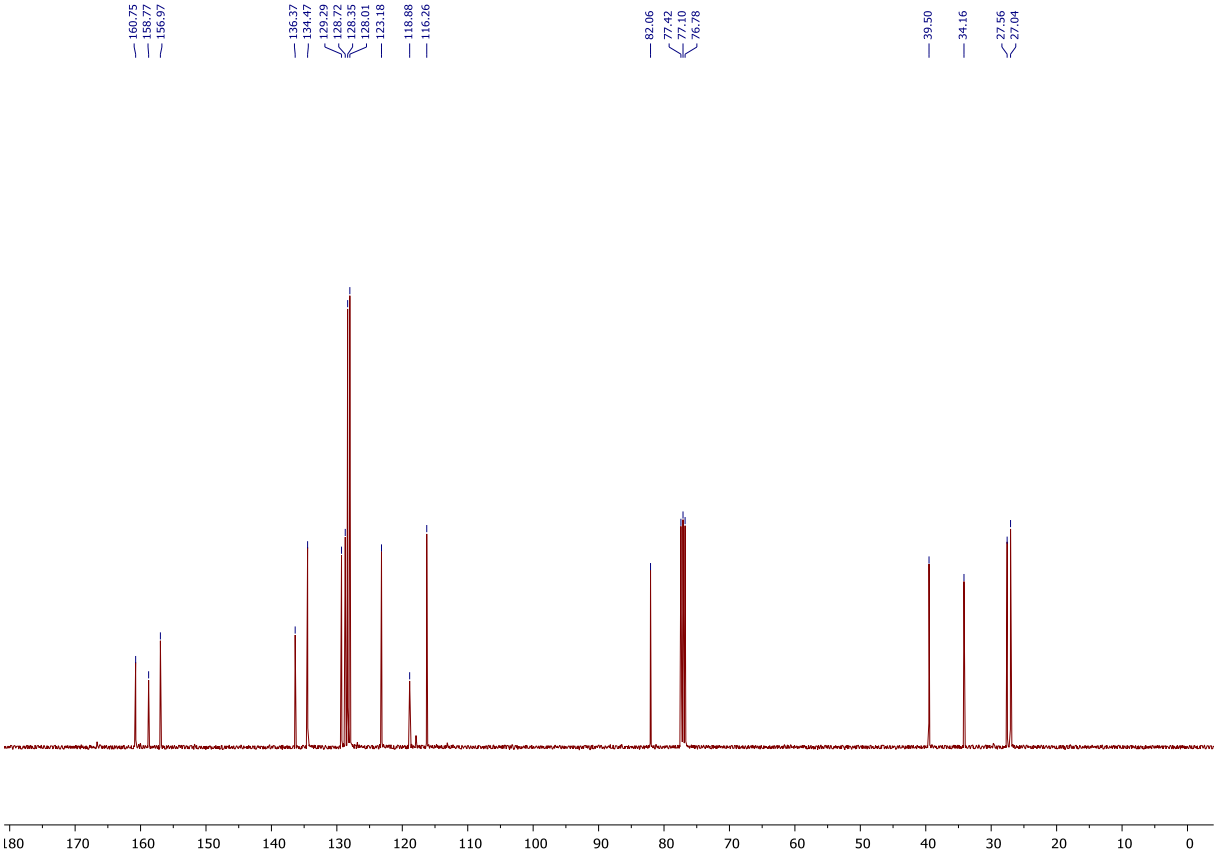
^{1}H NMR spectrum of **4ea** (400.1 MHz, $CDCl_3$)



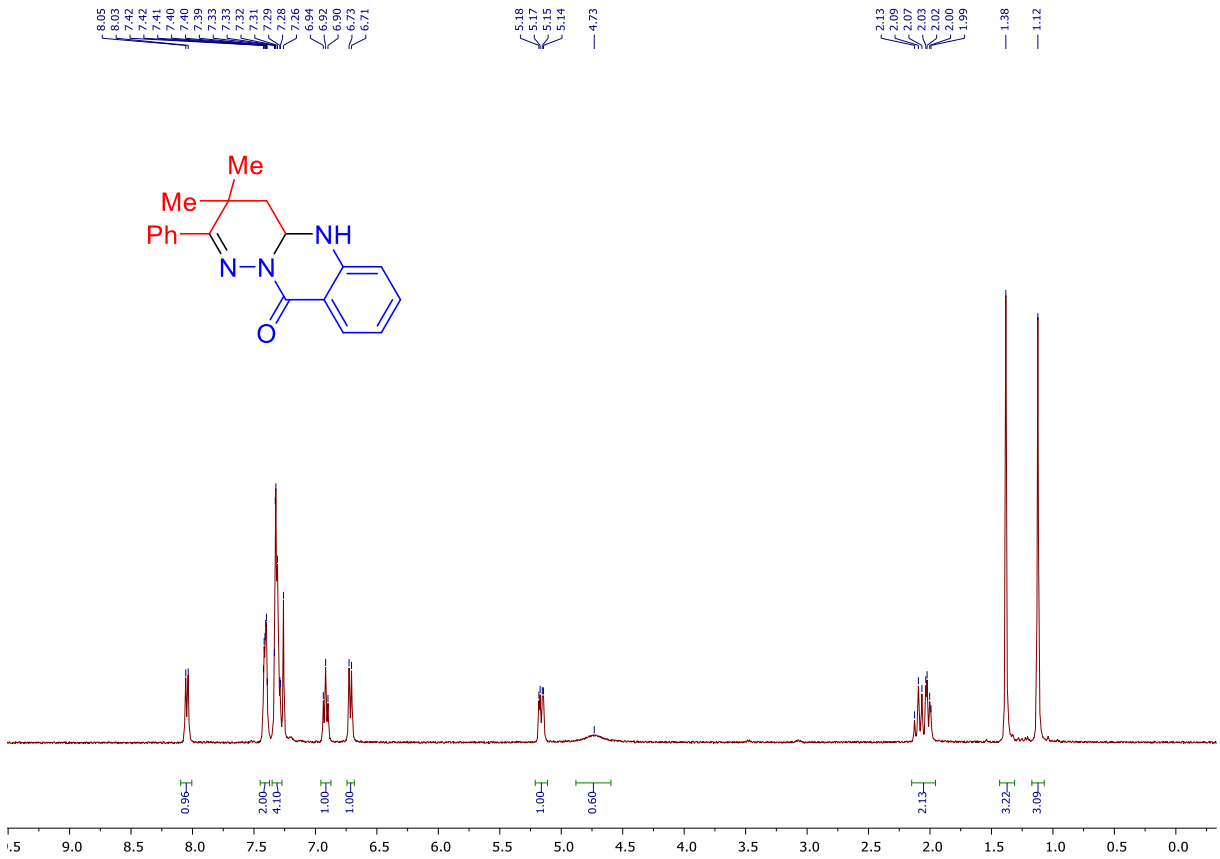
^{13}C NMR spectrum of **4ea** (100.6 MHz, $CDCl_3$)



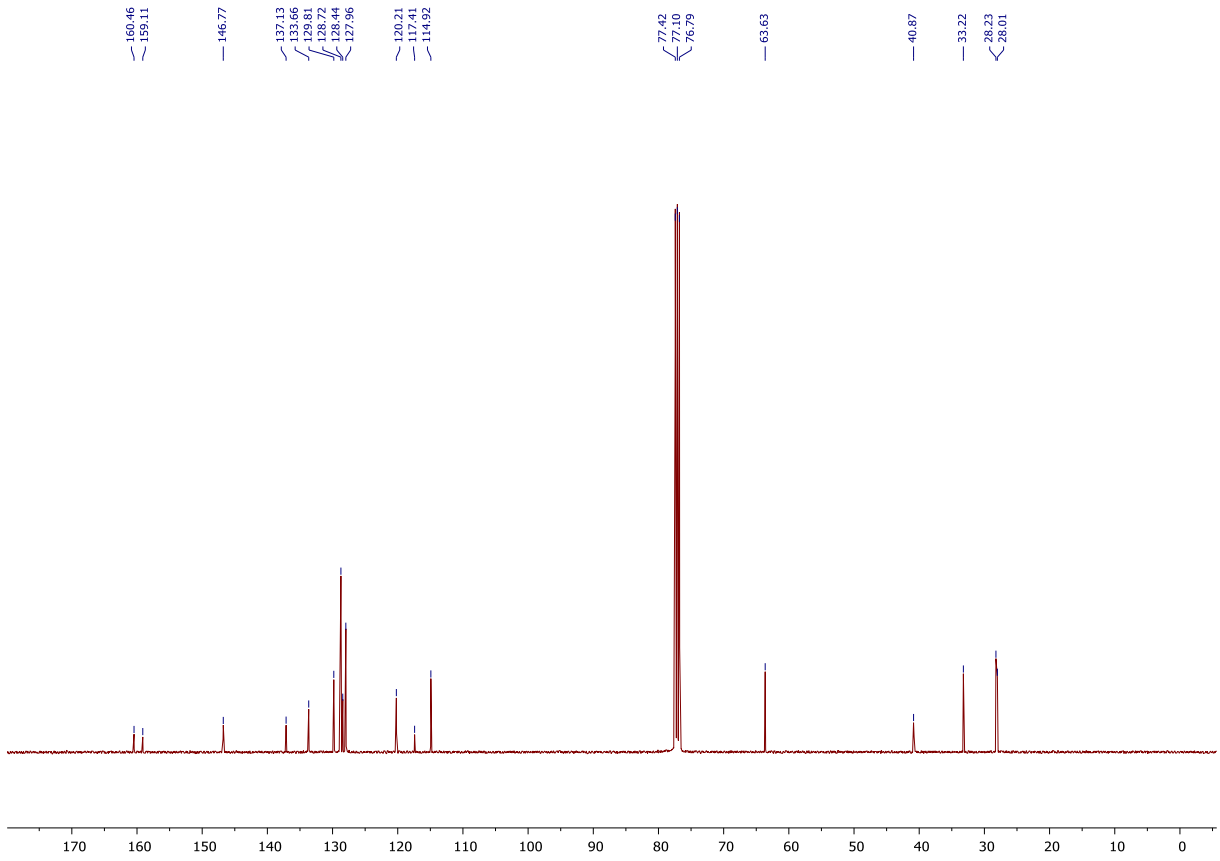
^{1}H NMR spectrum of **5ad** (400.1 MHz, $CDCl_3$)



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



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



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