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Simple access toward 3-halo- and 3-nitro-pyrazolo[1,5-*a*]pyrimidines through a one-pot sequence

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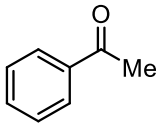
SUPPORTING INFORMATION

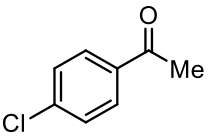
Content:

1. Overview of substrates numbering

Acetophenones



1a



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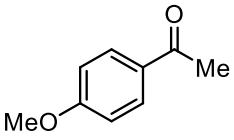

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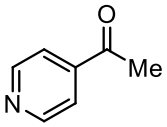

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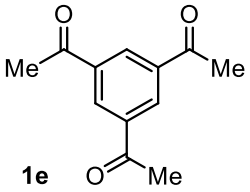

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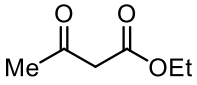

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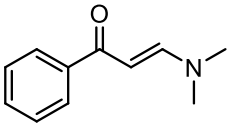
β-Enaminones



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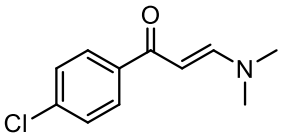

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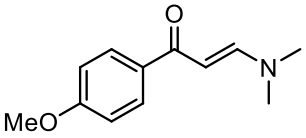

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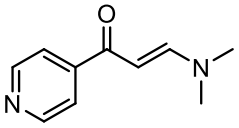

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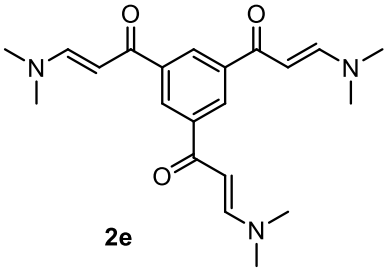

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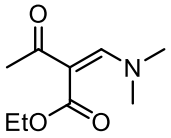
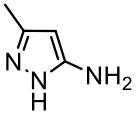


2f

NH-5-Aminopyrazoles



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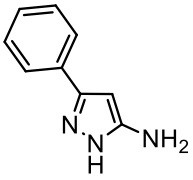

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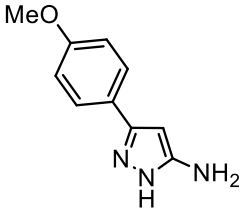

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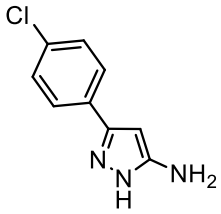

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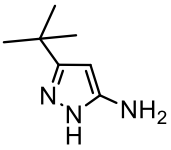

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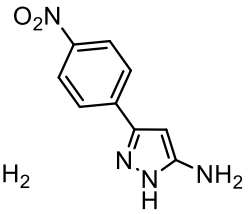


3f

2. Experimental procedures and characterization data

2.1 General information

All reagents were purchased from commercial sources and used without further purification, unless otherwise noted. All starting materials were weighed and handled in air at room temperature. The reactions were monitored by TLC visualized by UV lamp (254 or 365 nm) and/or with *p*-anisaldehyde and H_2SO_4 in EtOH. Flash chromatography was performed on silica gel (230-400 mesh). Reactions under microwave irradiation were performed in oven-dried 10.0 mL (or 35 mL) sealable Pyrex tubes equipped with a Teflon coated stirring bar (obtained from CEM). All reactions under microwave irradiation (ν = 2.45 GHz) were performed in a focused microwave reactor (300 W CEM Discover® SP). NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) at 298 K using tetramethylsilane (0 ppm) as the internal reference. NMR spectroscopic data were recorded in $CDCl_3$ or [D_6]DMSO using as internal standards the residual non-deuteriated signal for ^{1}H NMR and the deuteriated solvent signal for ^{13}C NMR spectroscopy. DEPT spectra were used for the assignment of carbon signals. Chemical shifts (δ) are given in ppm and coupling constants (J) are given in Hz. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Melting points were collected using a capillary melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded using a Q-TOF spectrometer via electrospray ionization (ESI). Crystallographic data were recorded on a diffractometer using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Structures were solved by direct methods in SHELXS-97.[1] Non-commercially available *NH*-5-aminopyrazoles (**3**) were prepared using known procedures.[2,3]

2.2 General procedures

*General procedure for the synthesis of β-enaminones **2a–f***. A 35 mL sealable (Teflon screw cap) oven-dried tubular reaction vessel was charged with the corresponding methyl ketone **1** (8.0 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (DMF–DMA, 12.0 mmol), and the resulting mixture was subjected to microwave irradiation under solvent-free conditions at 160 °C for 15 min, after which the reaction mixture was cooled to 55 °C with an air flow. The excess of DMF–DMA was removed under reduced pressure and the resulting clean crude product was used without further purification.[4]

*General procedure for the synthesis of 2,7-disustituted pyrazolo[1,5-a]pyrimidines **4a–r***. A mixture of *β*-enaminone **2** (0.50 mmol) and *NH*-5-aminopyrazole (**3**, 0.50 mmol) was irradiated with microwaves under solvent-free conditions at 180 °C for 2 min in a sealed tube containing a Teflon-coated magnetic stirring bar. The resulting reaction mixture was cooled to 55 °C by airflow, and the precipitated product formed upon the addition of cold EtOH/H_2O (1:1, 1.0 mL) was filtered off, washed and dried to give the pure product **4**.

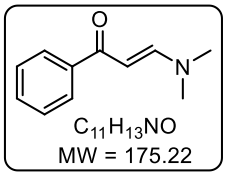
*General procedure for the synthesis of 3-halopyrazolo[1,5-a]pyrimidines **5a–i***. A mixture of *β*-enaminone **2** (0.50 mmol) and *NH*-5-aminopyrazole (**3**, 0.50 mmol) was irradiated with microwaves under solvent-free conditions at 180 °C for 2 min in a sealed tube containing a Teflon-coated magnetic stirring bar. After cooling, anhydrous 1,2-dichloroethane (2.0 mL) and *N*-halosuccinimide (0.50 mmol) was added into the tube, after which the reaction mixture was stirred at 25 °C for 20 min. The resulting reaction mixture was concentrated under reduced pressure, and the residue was directly purified by flash chromatography on silica gel (eluent: CH_2Cl_2) to afford the halogenated product **5**.

*General procedure for the synthesis of 3-nitropyrazolo[1,5-a]pyrimidines **6a–d***. A mixture of *β*-enaminone **2** (0.50 mmol) and *NH*-5-aminopyrazole (**3**, 0.50 mmol) was irradiated with microwaves under solvent-free conditions at 180 °C for 2 min in a sealed tube containing a Teflon-coated magnetic stirring bar. After cooling, nitric acid (2.0 mmol) and sulfuric acid (1.0 mmol) was carefully added into the tube, after which the reaction mixture was irradiated with microwaves at 60 °C for 10 min. The resulting reaction mixture was cooled to 55 °C by airflow, and the pH of the solution was maintained at 7 by adding an aqueous solution of sodium hydroxide (10%). The product of the reaction was extracted with dichloromethane (2 x 5.0 mL) and the combined organic layers were washed with brine (2 x 5.0 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (eluent: CH_2Cl_2) to afford the nitro derivative **6**.

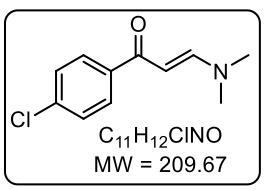
*General procedure for the synthesis of 3-phenylethynylpyrazolo[1,5-a]pyrimidines **7a–b***. A 10 mL sealable (Teflon screw cap) oven-dried tubular reaction vessel was charged with 3-iodopyrazolo[1,5-*a*]pyrimidine **5** (0.25 mmol), 10% Pd/C (11 mg, 0.01 mmol), PPh_3 (10 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol) and Et_3N (167 μL, 1.2 mmol) in water (2.0 mL), and the yellow suspension was stirred for 30 min under argon. The phenylacetylene (49 μL, 0.38 mmol) was injected and the mixture was subjected to microwave irradiation at 80 °C for 1 h. After the reaction was cooled to 55 °C by airflow, the reaction mixture was filtered through a Celite pad and washed with ethyl acetate (5.0 mL). The filtrate was collected and extracted with ethyl acetate (3 x 5.0 mL). The combined organic layers were washed with brine (2 x 5.0 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using *n*-pentane/CH_2Cl_2 (1:1) as eluent to provide the desired product **7**.

*General procedure for the synthesis of pyrazolo[1,5-a]pyrimidin-3-amines **8a–b***. A solution of 3-nitropyrazolo[1,5-*a*]pyrimidine **6** (0.50 mmol) and 10% Pd/C (5 wt % of substrate) in EtOH (5.0 mL) was vigorously stirred at 25 °C for 3 h under an H_2 atmosphere at ambient pressure. The resulting reaction mixture was filtered through a Celite pad and washed with EtOH (2 x 5.0 mL). The filtrate was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: CH_2Cl_2) to afford the desired product **8**.

2.3 Characterization data

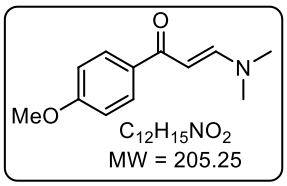


*(E)-3-(Dimethylamino)-1-phenylprop-2-en-1-one **2a***. Following the general procedure at 160 °C for 15 min for the reaction with acetophenone (**1a**, 971 μL, 8.32 mmol) and DMF–DMA (1661 μL, 12.5 mmol), the *β*-enaminone **2a** was obtained as a yellow solid (1413 mg, 97%). Mp 95–96 °C (amorphous) (Lit.[5] 95 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92 (s, 3H), 3.11 (s, 3H), 5.71 (d, J = 12.4 Hz, 1H), 7.38–7.46 (m, 3H), 7.80 (d, J = 12.4 Hz, 1H), 7.89 (d, J = 8.2 Hz 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 37.2 (CH_3), 44.9 (CH_3), 92.2 (CH), 127.4 (CH), 128.1 (CH), 130.8 (CH), 140.5 (C), 154.2 (CH), 188.6 (C) ppm. HRMS (ESI+): calcd. for $C_{11}H_{14}NO^+$ 176.1075 [M + H]$^+$; found 176.1080. These NMR data matched previously reported data.[5]

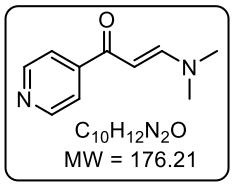


*(E)-1-(4-Chlorophenyl)-3-(dimethylamino)prop-2-en-1-one **2b***. Following the general procedure at 160 °C for 15 min for the reaction with 4-chloroacetophenone (**1b**, 1088 μL, 8.39 mmol) and DMF–DMA (1674 μL, 12.6 mmol), the *β*-enaminone **2b** was obtained as a yellow solid (1724 mg, 98%). Mp 88–89 °C

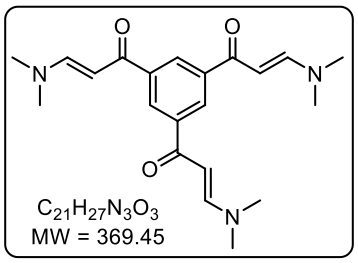
(amorphous) (Lit.[5] 88 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90 (s, 3H), 3.12 (s, 3H), 5.63 (d, J = 12.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 12.5 Hz, 1H), 7.82 (d, J = 8.5 Hz, 2H) ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 37.2 (CH_3), 45.4 (CH_3), 91.6 (CH), 128.2 (CH), 128.8 (CH), 136.8 (C), 138.7 (C), 154.4 (CH), 187.0 (C) ppm. HRMS (ESI+): calcd. for $C_{11}H_{13}ClNO^+$ 210.0686 $[M + H]^+$; found 210.0691. These NMR data matched previously reported data.[5]



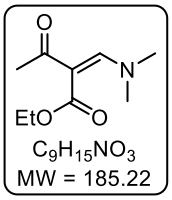
(E)-3-(Dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one ***2c***. Following the general procedure at 160 °C for 15 min for the reaction with 4-methoxyacetophenone (**1c**, 1137 μL, 8.25 mmol) and DMF–DMA (1647 μL, 12.4 mmol), the β-enaminone **2c** was obtained as a yellow solid (1609 mg, 95%). Mp 97 °C (amorphous) (Lit.[6] 95 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.99 (br s, 6H), 3.82 (s, 3H), 5.68 (d, J = 12.3 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 12.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 37.2 (CH_3), 44.9 (CH_3), 55.2 (CH_3), 91.6 (CH), 113.2 (CH), 129.3 (CH), 133.0 (C), 153.7 (CH), 161.8 (C), 187.3 (C) ppm. HRMS (ESI+): calcd. for $C_{12}H_{16}NO_2^+$ 206.1181 $[M + H]^+$; found 206.1183. These NMR data matched previously reported data.[6]



(E)-3-(Dimethylamino)-1-(pyridin-4-yl)prop-2-en-1-one ***2d***. Following the general procedure at 160 °C for 15 min for the reaction with 4-acetylpyridine (**1d**, 930 μL, 8.41 mmol) and DMF–DMA (1674 μL, 12.6 mmol), the β-enaminone **2d** was obtained as a brown solid (1437 mg, 97%). Mp 111 °C (amorphous) (Lit.[7] 111–113 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 3H), 3.13 (s, 3H), 5.60 (d, J = 12.1 Hz, 1H), 7.62 (d, J = 6.1 Hz, 2H), 7.79 (d, J = 12.0 Hz, 1H), 8.63 (d, J = 6.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 37.2 (CH_3), 45.1 (CH_3), 91.6 (CH), 121.1 (CH), 147.1 (C), 149.9 (CH), 155.1 (CH), 186.4 (C) ppm. HRMS (ESI+): calcd. for $C_{10}H_{13}N_2O^+$ 177.1028 $[M + H]^+$; found 177.1033. These NMR data matched previously reported data.[7]

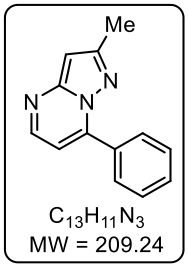


(2E,2'E,2''E)-1,1',1''-(Benzene-1,3,5-triyl)tris(3-(dimethylamino)prop-2-en-1-one) ***2e***. Following the general procedure at 160 °C for 15 min for the reaction with 1,3,5-triacetylbenzene (**1e**, 615 mg, 3.01 mmol) and DMF–DMA (1793 μL, 13.5 mmol), the β-enaminone **2e** was obtained as an orange solid (1068 mg, 96%). Mp 248 °C (amorphous) (Lit.[8] 250 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.94 (s, 9H), 3.14 (s, 9H), 5.85 (d, J = 12.2 Hz, 3H), 7.82 (d, J = 12.2 Hz, 3H), 8.52 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 37.4 (CH_3), 45.1 (CH_3), 92.4 (CH), 128.9 (CH), 140.3 (C), 154.6 (CH), 187.9 (C) ppm. HRMS (ESI+): calcd. for $C_{21}H_{28}N_3O_3^+$ 370.2131 $[M + H]^+$; found 370.2135. These NMR data matched previously reported data.[8]

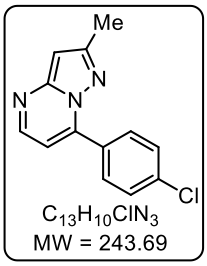


(E)-Ethyl 2-(dimethylaminomethylene)-3-oxobutanoate ***2f***. Following the general procedure at 160 °C for 15 min for the reaction with ethyl acetoacetate (**1f**, 490 μL, 3.84 mmol) and DMF–DMA (765 μL, 5.76 mmol), the β-enaminone **2f** was obtained as an orange oil (668 mg, 94%). (Lit.[9] orange oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.8 Hz, 3H), 2.30 (s, 3H), 2.88 (br s, 3H), 3.12 (br s, 3H), 4.20 (q, J = 7.7 Hz, 2H), 7.66 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 29.4 (CH_3), 36.4 (CH_3),

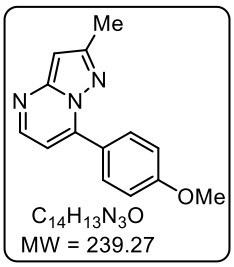
42.8 (CH_3), 60.0 (CH_2), 102.8 (C), 156.7 (CH), 168.2 (C), 195.3 (C) ppm. HRMS (ESI+): calcd. for $C_9H_{16}NO_3^+$ 186.1130 $[M + H]^+$; found 186.1137. These NMR data matched previously reported data.[9]



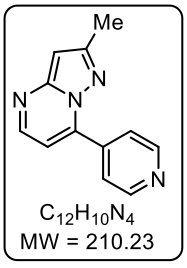
*2-Methyl-7-phenylpyrazolo[1,5-a]pyrimidine **4a***. The general procedure at 180 °C for 2 min with **2a** (88 mg, 0.50 mmol) and **3a** (48 mg, 0.50 mmol) afforded product **4a** as a white solid (99 mg, 95%). Mp 123 °C (amorphous) (Lit.[10] 125 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3H), 6.55 (s, 1H), 6.78 (d, J = 4.4 Hz, 1H), 7.53–7.55 (m, 3H), 8.04–8.06 (m, 2H), 8.42 (d, J = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 15.2 (CH_3), 96.7 (CH), 106.9 (CH), 129.0 (CH), 129.6 (CH), 131.3 (CH), 131.7 (C), 146.5 (C), 149.0 (CH), 151.1 (C), 155.4 (C) ppm. HRMS (ESI+): calcd. for $C_{13}H_{12}N_3^+$ 210.1031 $[M + H]^+$; found 210.1029. These NMR data matched previously reported data.[10]



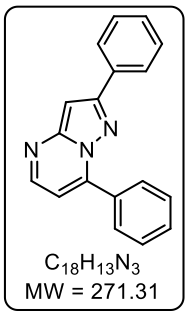
*7-(4-Chlorophenyl)-2-methylpyrazolo[1,5-a]pyrimidine **4b***. The general procedure at 180 °C for 2 min with **2b** (115 mg, 0.55 mmol) and **3a** (54 mg, 0.55 mmol) afforded product **4b** as a yellow solid (121 mg, 90%). Mp 146–147 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3H), 6.57 (s, 1H), 6.78 (d, J = 4.4 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 8.44 (d, J = 4.4 Hz, 1H) ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ =14.7 (CH_3), 96.4 (CH), 106.2 (CH), 128.9 (CH), 129.6 (C), 130.5 (CH), 137.1 (C), 144.9 (C), 148.4 (CH), 150.5 (C), 155.1 (C) ppm. HRMS (ESI+): calcd. for $C_{13}H_{11}ClN_3^+$ 244.0642 $[M + H]^+$; found 244.0644.



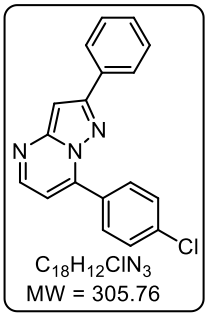
*7-(4-Methoxyphenyl)-2-methylpyrazolo[1,5-a]pyrimidine **4c***. The general procedure at 180 °C for 2 min with **2c** (107 mg, 0.52 mmol) and **3a** (50 mg, 0.52 mmol) afforded product **4c** as a yellow solid (119 mg, 96%). Mp 128 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H), 3.90 (s, 3H), 6.53 (s, 1H), 6.76–6.78 (m, 1H), 7.07 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 8.39–8.41 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.8 (CH_3), 55.4 (CH_3), 96.1 (CH), 105.7 (CH), 114.0 (CH), 123.4 (C), 130.9 (CH), 145.9 (C), 148.5 (CH), 150.8 (C), 154.8 (C), 161.7 (C) ppm. HRMS (ESI+): calcd. for $C_{14}H_{14}N_3O^+$ 240.1137 $[M + H]^+$; found 240.1137.



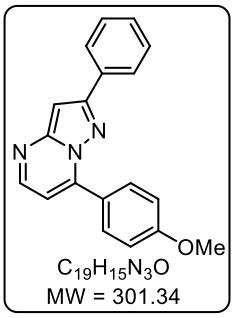
*2-Methyl-7-(pyridin-4-yl)pyrazolo[1,5-a]pyrimidine **4d***. The general procedure at 180 °C for 2 min with **2d** (90 mg, 0.51 mmol) and **3a** (50 mg, 0.51 mmol) afforded product **4d** as a yellow solid (92 mg, 86%). Mp 178–179 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3H), 6.60 (s, 1H), 6.85 (d, J = 4.4 Hz, 1H), 7.97 (d, J = 4.6 Hz, 2H), 8.48 (d, J = 4.4 Hz, 1H), 8.83 (d, J = 4.6 Hz, 2H) ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ =14.7 (CH_3), 96.9 (CH), 106.7 (CH), 123.0 (CH), 138.6 (C), 143.1 (C), 148.4 (CH), 150.4 (CH), 150.5 (C), 155.4 (C) ppm. HRMS (ESI+): calcd. for $C_{12}H_{11}N_4^+$ 211.0984 $[M + H]^+$; found 211.0984.



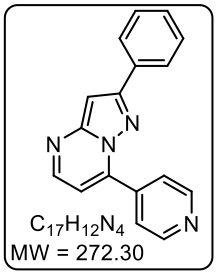
*2,7-Diphenylpyrazolo[1,5-a]pyrimidine **4e***. The general procedure at 180 °C for 2 min with **2a** (89 mg, 0.51 mmol) and **3b** (81 mg, 0.51 mmol) afforded product **4e** as a yellow solid (127 mg, 92%). Mp 152 °C (amorphous) (Lit.[10] 157 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (d, *J* = 4.2 Hz, 1H), 7.09 (s, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.58–7.59 (m, 3H), 8.03 (d, *J* = 7.3 Hz, 2H), 8.18–8.20 (m, 2H), 8.48 (d, *J* = 4.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 93.6 (CH), 107.1 (CH), 126.6 (CH), 128.5 (CH), 128.7 (CH), 128.9 (CH), 129.4 (CH), 131.0 (CH), 131.0 (C), 132.9 (C), 146.3 (C), 148.9 (CH), 151.1 (C), 155.8 (C) ppm. HRMS (ESI+): calcd. for $C_{18}H_{14}N_3^+$ 272.1188 $[M + H]^+$; found 272.1195. These NMR data matched previously reported data.[10]



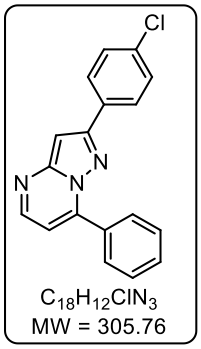
*7-(4-Chlorophenyl)-2-phenylpyrazolo[1,5-a]pyrimidine **4f***. The general procedure at 180 °C for 2 min with **2b** (113 mg, 0.54 mmol) and **3b** (86 mg, 0.54 mmol) afforded product **4f** as a yellow solid (145 mg, 88%). Mp 142 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (d, *J* = 4.6 Hz, 1H), 7.07 (s, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 7.4 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 2H), 8.46 (d, *J* = 4.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 93.8 (CH), 106.9 (CH), 126.6 (CH), 128.7 (CH), 128.8 (CH), 129.0 (CH), 129.3 (C), 130.7 (CH), 132.7 (C), 137.1 (C), 145.0 (C), 148.8 (CH), 151.1 (C), 155.9 (C) ppm. HRMS (ESI+): calcd. for $C_{18}H_{13}ClN_3^+$ 306.0798 $[M + H]^+$; found 306.0799.



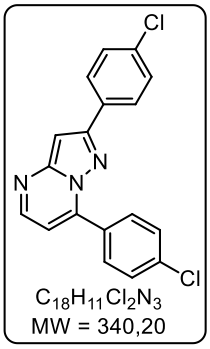
*7-(4-Methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyrimidine **4g***. The general procedure at 180 °C for 2 min with **2c** (103 mg, 0.50 mmol) and **3b** (80 mg, 0.50 mmol) afforded product **4g** as a yellow solid (137 mg, 91%). Mp 150 °C (amorphous) (Lit.[11] 140 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 6.85 (d, *J* = 4.4 Hz, 1H), 7.04 (s, 1H), 7.08 (d, *J* = 8.9 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.1 Hz, 2H), 8.02 (d, *J* = 7.1 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 8.43 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_3), 93.4 (CH), 106.2 (CH), 113.9 (CH), 123.2 (C), 126.6 (CH), 128.6 (CH), 128.9 (CH), 131.2 (CH), 133.0 (C), 146.0 (C), 148.8 (CH), 151.3 (C), 155.6 (C), 161.8 (C) ppm. HRMS (ESI+): calcd. for $C_{19}H_{16}N_3O^+$ 302.1293 $[M + H]^+$; found 302.1301. These NMR data matched previously reported data.[11]



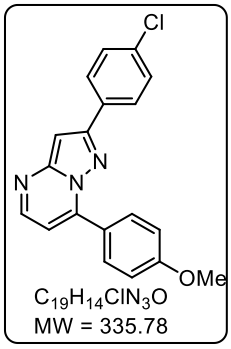
*2-Phenyl-7-(pyridin-4-yl)pyrazolo[1,5-a]pyrimidine **4h***. The general procedure at 180 °C for 2 min with **2d** (88 mg, 0.50 mmol) and **3b** (80 mg, 0.50 mmol) afforded product **4h** as a yellow solid (120 mg, 88%). Mp 126 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (d, *J* = 4.3 Hz, 1H), 7.11 (s, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 8.00 (d, *J* = 7.3 Hz, 2H), 8.10 (d, *J* = 4.6 Hz, 2H), 8.54 (d, *J* = 4.3 Hz, 1H), 8.90 (br s, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 94.2 (CH), 107.3 (CH), 123.2 (CH), 126.6 (CH), 128.8 (CH), 129.2 (CH), 132.5 (C), 138.4 (C), 143.4 (C), 148.8 (CH), 150.3 (CH), 151.0 (C), 156.2 (C) ppm. HRMS (ESI+): calcd. for $C_{17}H_{13}N_4^+$ 273.1140 $[M + H]^+$; found 273.1149.



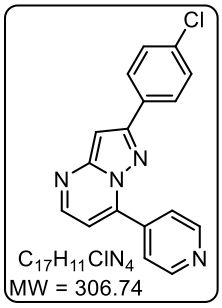
2-(4-Chlorophenyl)-7-phenylpyrazolo[1,5-a]pyrimidine ***4i***. The general procedure at 180 °C for 2 min with **2a** (88 mg, 0.50 mmol) and **3d** (96 mg, 0.50 mmol) afforded product **4i** as a yellow solid (144 mg, 94%). Mp 154 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (d, J = 4.4 Hz, 1H), 7.03 (s, 1H), 7.40 (d, J = 8.6 Hz, 2H), 7.57–7.60 (m, 3H), 7.93 (d, J = 8.6 Hz, 2H), 8.14–8.16 (m, 2H), 8.50 (d, J = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 93.6 (CH), 107.3 (CH), 127.8 (CH), 128.5 (CH), 128.9 (CH), 129.4 (CH), 130.9 (C), 131.1 (CH), 131.4 (C), 134.8 (C), 146.4 (C), 149.1 (CH), 151.2 (C), 154.6 (C) ppm. HRMS (ESI+): calcd. for $C_{18}H_{13}ClN_3^+$ 306.0798 $[M + H]^+$; found 306.0794.



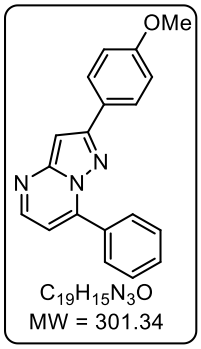
2,7-bis(4-Chlorophenyl)pyrazolo[1,5-a]pyrimidine ***4j***. The general procedure at 180 °C for 2 min with **2b** (113 mg, 0.54 mmol) and **3d** (100 mg, 0.52 mmol) afforded product **4j** as a yellow solid (163 mg, 92%). Mp 176 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (d, J = 4.3 Hz, 1H), 7.04 (s, 1H), 7.42 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.7 Hz, 2H), 8.50 (d, J = 4.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 93.8 (CH), 107.1 (CH), 127.8 (CH), 128.9 (CH), 129.0 (CH), 129.2 (C), 130.7 (CH), 131.2 (C), 134.9 (C), 137.3 (C), 145.1 (C), 149.0 (CH), 151.1 (C), 154.7 (C) ppm. HRMS (ESI+): calcd. for $C_{18}H_{12}Cl_2N_3^+$ 340.0408 $[M + H]^+$; found 340.0410.



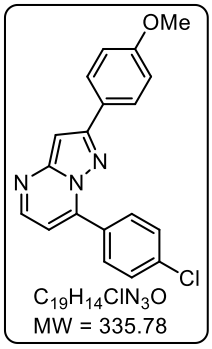
2-(4-Chlorophenyl)-7-(4-methoxyphenyl)pyrazolo[1,5-a]pyrimidine ***4k.*** The general procedure at 180 °C for 2 min with **2c** (113 mg, 0.55 mmol) and **3d** (104 mg, 0.54 mmol) afforded product **4k** as a yellow solid (163 mg, 90%). Mp 177–178 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.87 (d, J = 4.5 Hz, 1H), 7.00 (s, 1H), 7.09 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 8.19 (d, J = 8.9 Hz, 2H), 8.45 (d, J = 4.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_3), 93.4 (CH), 106.5 (CH), 114.0 (CH), 123.0 (C), 127.8 (CH), 128.8 (CH), 131.1 (CH), 131.5 (C), 134.7 (C), 146.1 (C), 149.0 (CH), 151.3 (C), 154.4 (C), 161.8 (C) ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}ClN_3O^+$ 336.0904 $[M + H]^+$; found 336.0900.



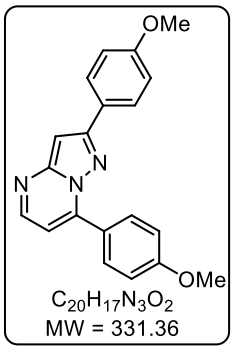
2-(4-Chlorophenyl)-7-(pyridin-4-yl)pyrazolo[1,5-a]pyrimidine ***4l***. The general procedure at 180 °C for 2 min with **2d** (97 mg, 0.55 mmol) and **3d** (108 mg, 0.56 mmol) afforded product **4l** as a yellow solid (143 mg, 85%). Mp 210 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, J = 4.3 Hz, 1H), 7.08 (s, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H), 8.07 (d, J = 4.9 Hz, 2H), 8.56 (d, J = 4.3 Hz, 1H), 8.90 (d, J = 5.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 94.2 (CH), 107.6 (CH), 123.1 (CH), 127.9 (CH), 129.0 (CH), 131.1 (C), 135.2 (C), 138.4 (C), 143.5 (C), 149.0 (CH), 150.4 (CH), 151.1 (C), 155.1 (C) ppm. HRMS (ESI+): calcd. for $C_{17}H_{12}ClN_4^+$ 307.0750 $[M + H]^+$; found 307.0748.



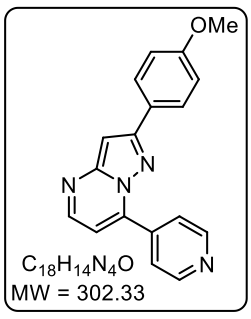
2-(4-Methoxyphenyl)-7-phenylpyrazolo[1,5-a]pyrimidine ***4m***. The general procedure at 180 °C for 2 min with **2a** (89 mg, 0.51 mmol) and **3c** (98 mg, 0.52 mmol) afforded product **4m** as a white solid (144 mg, 94%). Mp 145 °C (amorphous) (Lit.[12] 138–140 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3H), 6.84 (d, *J* = 4.4 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.98 (s, 1H), 7.55–7.58 (m, 3H), 7.94 (d, *J* = 9.0 Hz, 2H), 8.16–8.18 (m, 2H), 8.44 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 92.9 (CH), 106.8 (CH), 114.1 (CH), 125.6 (C), 127.9 (CH), 128.5 (CH), 129.4 (CH), 130.9 (CH), 131.1 (C), 146.1 (C), 148.8 (CH), 151.2 (C), 155.7 (C), 160.3 (C) ppm. HRMS (ESI+): calcd. for $C_{19}H_{16}N_3O^+$ 302.1293 $[M + H]^+$; found 302.1292. These NMR data matched previously reported data.[12]



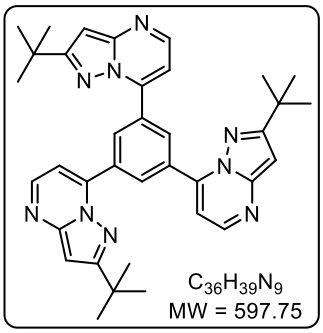
7-(4-Chlorophenyl)-2-(4-methoxyphenyl)pyrazolo[1,5-a]pyrimidine ***4n***. The general procedure at 180 °C for 2 min with **2b** (115 mg, 0.55 mmol) and **3c** (102 mg, 0.54 mmol) afforded product **4n** as a yellow solid (169 mg, 93%). Mp 164 °C (amorphous) (Lit.[12] 158–159 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3H), 6.83 (d, *J* = 4.4 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.99 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 8.45 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 93.1 (CH), 106.6 (CH), 114.1 (CH), 125.4 (C), 127.9 (CH), 128.8 (CH), 129.5 (C), 130.7 (CH), 137.1 (C), 144.9 (C), 148.7 (CH), 151.2 (C), 155.8 (C), 160.4 (C) ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}ClN_3O^+$ 336.0904 $[M + H]^+$; found 336.0906. These NMR data matched previously reported data.[12]



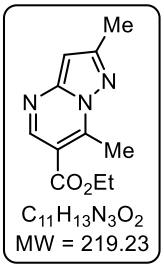
2,7-bis(4-Methoxyphenyl)pyrazolo[1,5-a]pyrimidine ***4o***. The general procedure at 180 °C for 2 min with **2c** (103 mg, 0.50 mmol) and **3c** (95 mg, 0.50 mmol) afforded product **4o** as a yellow solid (161 mg, 97%). Mp 165–166 °C (amorphous) (Lit.[12] 150–151 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 3.92 (s, 3H), 6.84 (d, *J* = 4.4 Hz, 1H), 6.97–7.00 (m, 3H), 7.09 (d, *J* = 8.9 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 8.43 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 55.4 (CH_3), 92.6 (CH), 105.9 (CH), 113.9 (CH), 114.1 (CH), 123.3 (C), 125.7 (C), 127.9 (CH), 131.2 (CH), 146.0 (C), 148.6 (CH), 151.2 (C), 155.6 (C), 160.3 (C), 161.8 (C) ppm. HRMS (ESI+): calcd. for $C_{20}H_{18}N_3O_2^+$ 332.1399 $[M + H]^+$; found 332.1408. These NMR data matched previously reported data.[12]



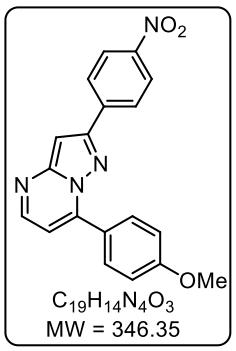
2-(4-Methoxyphenyl)-7-(pyridin-4-yl)pyrazolo[1,5-a]pyrimidine ***4p***. The general procedure at 180 °C for 2 min with **2d** (88 mg, 0.50 mmol) and **3c** (93 mg, 0.49 mmol) afforded product **4p** as a yellow solid (132 mg, 89%). Mp 154–155 °C (amorphous) (Lit.[12] 132–134 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 6.92 (d, *J* = 4.3 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 6.2 Hz, 2H), 8.50 (d, *J* = 4.3 Hz, 1H), 8.87 (d, *J* = 6.1 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 93.4 (CH), 107.0 (CH), 114.2 (CH), 123.1 (CH), 125.1 (C), 127.9 (CH), 138.6 (C), 143.1 (C), 148.6 (CH), 150.3 (CH), 151.1 (C), 156.1 (C), 160.5 (C) ppm. HRMS (ESI+): calcd. for $C_{18}H_{15}N_4O^+$ 303.1246 $[M + H]^+$; found 303.1255. These NMR data matched previously reported data.[12]



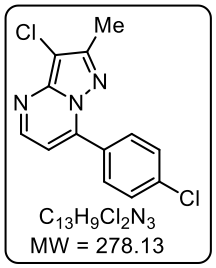
1,3,5-tris(2-(tert-Butyl)pyrazolo[1,5-a]pyrimidin-7-yl)benzene ***4q***. The general procedure at 180 °C for 2 min with **2e** (196 mg, 0.53 mmol) and **3e** (224 mg, 1.61 mmol) afforded product **4q** as a yellow solid (291 mg, 92%). Mp > 300 °C (amorphous). Recrystallization of **4q** from methanol afforded crystalline yellow prisms suitable for X-ray diffraction analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 27H), 6.71 (s, 3H), 7.14 (d, J = 4.4 Hz, 3H), 8.53 (d, J = 4.3 Hz, 3H), 9.48 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 30.5 (CH_3), 33.0 (C), 93.5 (CH), 106.3 (CH), 131.6 (C), 132.6 (CH), 144.3 (C), 148.3 (CH), 150.4 (C), 167.9 (C) ppm. HRMS (ESI+): calcd. for $C_{36}H_{40}N_9^+$ 598.3407 [M + H]$^+$; found 598.3401.



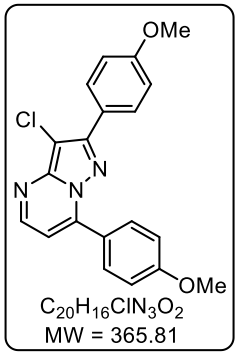
Ethyl 2,7-dimethylpyrazolo[1,5-a]pyrimidine-6-carboxylate ***4r***. The general procedure at 180 °C for 2 min with **2f** (94 mg, 0.51 mmol) and **3a** (50 mg, 0.51 mmol) afforded product **4r** as a white solid (99 mg, 89%). Mp 106–107 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.1 Hz, 3H), 2.52 (s, 3H), 3.15 (s, 3H), 4.40 (q, J = 7.1 Hz, 2H), 6.50 (s, 1H), 8.87 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 14.8 (CH_3), 15.0 (CH_3), 61.3 (CH_2), 97.6 (CH), 109.7 (C), 149.3 (C), 149.6 (CH), 150.8 (C), 157.2 (C), 164.9 (C) ppm. HRMS (ESI+): calcd. for $C_{11}H_{14}N_3O_2^+$ 220.1086 [M + H]$^+$; found 220.1083.



7-(4-Methoxyphenyl)-2-(4-nitrophenyl)pyrazolo[1,5-a]pyrimidine ***4s***. The general procedure at 180 °C for 2 min with **2c** (105 mg, 0.51 mmol) and **3f** (103 mg, 0.50 mmol) afforded product **4s** as a yellow solid (151 mg, 87%). Mp 261-262 °C (amorphous). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.89 (s, 3H), 7.18 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 4.2 Hz, 1H), 7.46 (s, 1H), 8.27 (m, 6H), 8.58 (d, J = 4.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 55.3 (CH_3), 94.8 (CH), 107.8 (CH), 114.1 (CH), 122.4 (C), 124.2 (CH), 127.1 (CH), 131.3 (CH), 138.9 (C), 145.3 (C), 147.5 (C), 150.1 (CH), 150.9 (C), 152.2 (C), 161.6 (C) ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}N_4O_3^+$ 347.1144 [M + H]$^+$; found 347.1152.

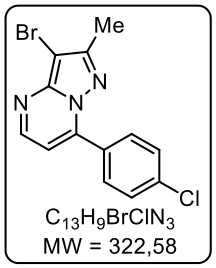


3-Chloro-7-(4-chlorophenyl)-2-methylpyrazolo[1,5-a]pyrimidine ***5a***. Following the general procedure, the reaction between *β*-enaminone **2b** (115 mg, 0.55 mmol), *NH*-5-aminopyrazole **3a** (54 mg, 0.55 mmol) and *N*-chlorosuccinimide (73 mg, 0.55 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5a** as a yellow solid (138 mg, 90%). Mp 199 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 3H), 6.84 (d, J = 4.4 Hz, 1H), 7.54 (d, J = 8.6 Hz, 2H), 8.00 (d, J = 8.6 Hz, 2H), 8.51 (d, J = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 12.4 (CH_3), 99.4 (C), 107.1 (CH), 128.6 (C), 129.1 (CH), 130.6 (CH), 137.5 (C), 145.3 (C), 145.4 (C), 149.2 (CH), 151.8 (C) ppm. HRMS (ESI+): calcd. for $C_{13}H_{10}Cl_2N_3^+$ 278.0252 [M + H]$^+$; found 278.0252.

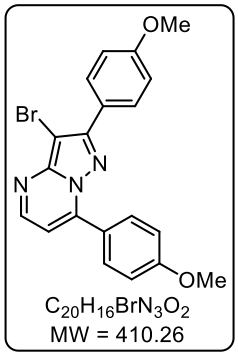


3-Chloro-2,7-bis(4-methoxyphenyl)pyrazolo[1,5-a]pyrimidine ***5b***. Following the general procedure, the reaction between *β*-enaminone **2c** (105 mg, 0.51 mmol), *NH*-5-aminopyrazole **3c** (94 mg, 0.50 mmol) and *N*-chlorosuccinimide (67 mg, 0.50 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5b** as a yellow solid (174 mg, 95%). Mp 126 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s,

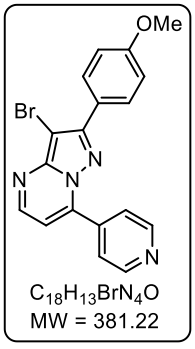
3H), 3.90 (s, 3H), 6.90 (d, J = 4.4 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 8.11 (d, J = 9.0 Hz, 2H), 8.17 (d, J = 9.0 Hz, 2H), 8.50 (d, J = 4.4 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 55.4 (CH_3), 97.0 (C), 106.9 (CH), 113.9 (CH), 114.0 (CH), 122.3 (C), 124.1 (C), 129.5 (CH), 131.2 (CH), 146.2 (C), 146.6 (C), 149.2 (CH), 150.6 (C), 160.4 (C), 162.0 (C) ppm. HRMS (ESI+): calcd. for $C_{20}H_{17}ClN_3O_2^+$ 366.1009 $[M + H]^+$; found 366.1018.



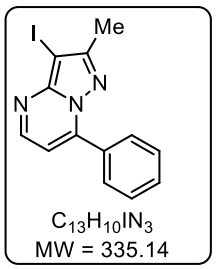
3-Bromo-7-(4-chlorophenyl)-2-methylpyrazolo[1,5-a]pyrimidine ***5c***. Following the general procedure, the reaction between β-enaminone **2b** (103 mg, 0.49 mmol), *NH*-5-aminopyrazole **3a** (49 mg, 0.50 mmol) and *N*-bromosuccinimide (89 mg, 0.50 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5c** as a yellow solid (152 mg, 96%). Mp 168 °C (amorphous). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 6.76 (d, J = 4.4 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 8.6 Hz, 2H), 8.44 (d, J = 4.4 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.3 (CH_3), 85.3 (C), 107.2 (CH), 128.6 (C), 129.0 (CH), 130.6 (CH), 137.5 (C), 145.5 (C), 146.8 (C), 149.5 (CH), 153.4 (C) ppm. HRMS (ESI+): calcd. for $C_{13}H_{10}BrClN_3^+$ 321.9747 $[M + H]^+$; found 321.9751.



3-Bromo-2,7-bis(4-methoxyphenyl)pyrazolo[1,5-a]pyrimidine ***5d***. Following the general procedure, the reaction between β-enaminone **2c** (119 mg, 0.58 mmol), *NH*-5-aminopyrazole **3c** (110 mg, 0.58 mmol) and *N*-bromosuccinimide (105 mg, 0.59 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5d** as a yellow solid (221 mg, 93%). Mp 130 °C (amorphous). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3H), 3.90 (s, 3H), 6.92 (d, J = 3.7 Hz, 1H), 7.01 (d, J = 8.9 Hz, 2H), 7.07 (d, J = 8.9 Hz, 2H), 8.10 (d, J = 8.9 Hz, 2H), 8.17 (d, J = 8.9 Hz, 2H), 8.53 (d, J = 3.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 55.4 (CH_3), 82.3 (C), 106.9 (CH), 113.8 (CH), 114.0 (CH), 122.2 (C), 124.4 (C), 129.7 (CH), 131.2 (CH), 146.4 (C), 147.7 (C), 149.5 (CH), 152.2 (C), 160.3 (C), 162.0 (C) ppm. HRMS (ESI+): calcd. for $C_{20}H_{17}BrN_3O_2^+$ 410.0504 $[M + H]^+$; found 410.0503.

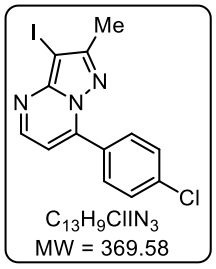


3-Bromo-2-(4-methoxyphenyl)-7-(pyridin-4-yl)pyrazolo[1,5-a]pyrimidine ***5e***. Following the general procedure, the reaction between β-enaminone **2d** (104 mg, 0.59 mmol), *NH*-5-aminopyrazole **3c** (113 mg, 0.60 mmol) and *N*-bromosuccinimide (107 mg, 0.60 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5e** as a yellow solid (200 mg, 89%). Mp 149 °C (amorphous). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 7.00–7.03 (m, 3H), 8.05–8.08 (m, 4H), 8.61 (d, J = 4.3 Hz, 1H), 8.86 (d, J = 5.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 83.5 (C), 108.2 (CH), 114.0 (CH), 123.2 (CH), 123.8 (C), 129.7 (CH), 138.0 (C), 143.4 (C), 147.6 (C), 149.4 (CH), 149.9 (CH), 152.8 (C), 160.6 (C) ppm. HRMS (ESI+): calcd. for $C_{18}H_{14}BrN_4O^+$ 381.0351 $[M + H]^+$; found 381.0360.

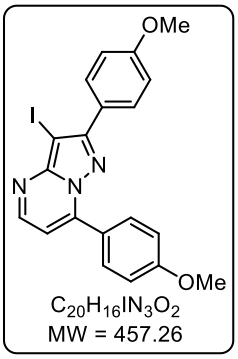


3-Iodo-2-methyl-7-phenylpyrazolo[1,5-a]pyrimidine ***5f***. Following the general procedure, the reaction between β-enaminone **2a** (88 mg, 0.50 mmol), *NH*-5-aminopyrazole **3a** (49 mg, 0.50 mmol) and *N*-iodosuccinimide (115 mg, 0.51 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5f** as a yellow solid (159 mg, 95%). Mp 115–116 °C (amorphous). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H), 6.88 (d, J = 4.3 Hz, 1H), 7.55–7.60 (m, 3H), 8.01–8.03 (m, 2H), 8.55 (d, J = 4.3 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 15.2 (CH_3), 52.8 (C), 107.6 (CH),

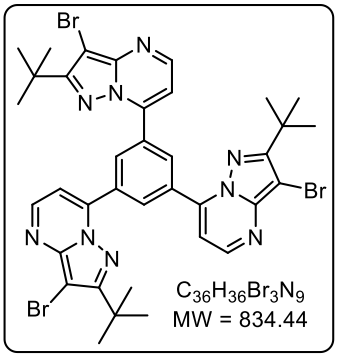
128.7 (CH), 129.2 (CH), 130.3 (C), 131.2 (CH), 146.9 (C), 149.5 (C), 149.9 (CH), 156.4 (C) ppm. HRMS (ESI+): calcd. for $C_{13}H_{11}IN_3^+$ 335.9998 $[M + H]^+$; found 336.0005.



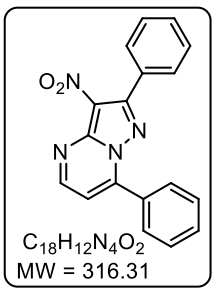
7-(4-Chlorophenyl)-3-iodo-2-methylpyrazolo[1,5-a]pyrimidine ***5g***. Following the general procedure, the reaction between *β*-enaminone **2b** (109 mg, 0.52 mmol), *NH*-5-aminopyrazole **3a** (51 mg, 0.53 mmol) and *N*-iodosuccinimide (119 mg, 0.53 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5g** as a pale green solid (179 mg, 93%). Mp 157 °C (amorphous). Recrystallization of **5g** from methanol afforded crystalline pale green prisms suitable for X-ray diffraction analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H), 6.85 (d, J = 4.3 Hz, 1H), 7.54 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 8.54 (d, J = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 15.2 (CH_3), 53.1 (C), 107.4 (CH), 128.7 (C), 129.0 (CH), 130.6 (CH), 137.5 (C), 145.7 (C), 149.6 (C), 149.8 (CH), 156.6 (C) ppm. HRMS (ESI+): calcd. for $C_{13}H_{10}ClIN_3^+$ 369.9608 $[M + H]^+$; found 369.9602.



3-Iodo-2,7-bis(4-methoxyphenyl)pyrazolo[1,5-a]pyrimidine ***5h***. Following the general procedure, the reaction between *β*-enaminone **2c** (101 mg, 0.49 mmol), *NH*-5-aminopyrazole **3c** (94 mg, 0.50 mmol) and *N*-iodosuccinimide (112 mg, 0.50 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5h** as a yellow solid (204 mg, 91%). Mp 134 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3H), 3.90 (s, 3H), 6.92 (d, J = 4.4 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 9.0 Hz, 2H), 8.55 (d, J = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 49.5 (C), 55.3 (CH_3), 55.5 (CH_3), 107.2 (CH), 113.8 (CH), 114.1 (CH), 122.4 (C), 125.2 (C), 130.1 (CH), 131.2 (CH), 146.6 (C), 149.9 (CH), 150.5 (C), 155.3 (C), 160.4 (C), 162.0 (C) ppm. HRMS (ESI+): calcd. for $C_{20}H_{17}IN_3O_2^+$ 458.0365 $[M + H]^+$; found 458.0372.

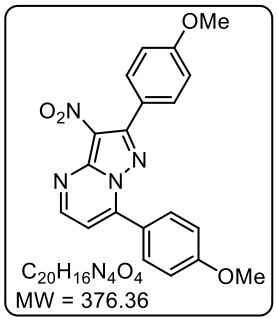


1,3,5-tris(3-Bromo-2-(tert-butyl)pyrazolo[1,5-a]pyrimidin-7-yl)benzene ***5i***. Following the general procedure, the reaction between *β*-enaminone **2e** (129 mg, 0.35 mmol), *NH*-5-aminopyrazole **3e** (153 mg, 1.10 mmol) and *N*-bromosuccinimide (198 mg, 1.11 mmol) in 2.0 mL of 1,2-dichloroethane afforded compound **5i** as a yellow solid (263 mg, 90%). Mp 255 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 27H), 7.24 (d, J = 4.3 Hz, 3H), 8.65 (d, J = 4.3 Hz, 3H), 9.46 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 28.6 (CH_3), 34.0 (C), 82.9 (C), 107.2 (CH), 130.8 (C), 132.8 (CH), 144.2 (C), 147.5 (C), 149.5 (CH), 161.9 (C) ppm. HRMS (ESI+): calcd. for $C_{36}H_{37}Br_3N_9^+$ 832.0722 $[M + H]^+$; found 832.0730.

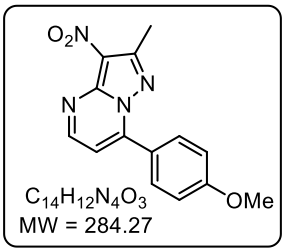


3-Nitro-2,7-diphenylpyrazolo[1,5-a]pyrimidine ***6a***. Following the general procedure, the reaction between *β*-enaminone **2a** (86 mg, 0.49 mmol), *NH*-5-aminopyrazole **3b** (81 mg, 0.51 mmol), nitric acid (84 μL, 2.0 mmol) and sulfuric acid (54 μL, 1.0 mmol) afforded compound **6a** as a yellow solid (135 mg, 87%). Mp 206–207 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 4.4 Hz, 1H), 7.46–7.53 (m, 3H), 7.58–7.63 (m, 3H), 7.80 (d, J = 7.7 Hz, 2H), 8.08 (d, J = 7.3 Hz, 2H), 8.96 (d, J = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 110.9 (CH), 120.9 (C), 128.2 (CH),

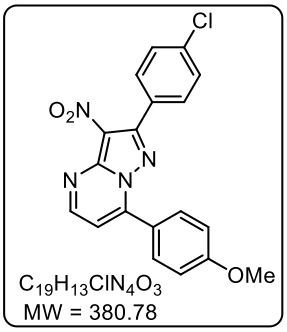
128.9 (CH), 129.0 (C), 129.8 (CH), 129.9 (CH), 130.1 (CH), 130.1 (C), 132.1 (CH), 145.6 (C), 148.1 (C), 153.4 (C), 154.3 (CH) ppm. HRMS (ESI+): calcd. for $C_{18}H_{13}N_4O_2^+$ 317.1039 $[M + H]^+$; found 317.1041.



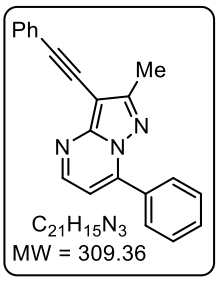
2,7-bis(4-Methoxyphenyl)-3-nitropyrazolo[1,5-a]pyrimidine ***6b***. Following the general procedure, the reaction between *β*-enaminone **2c** (103 mg, 0.50 mmol), *NH*-5-aminopyrazole **3c** (94 mg, 0.50 mmol), nitric acid (84 μL, 1.0 mmol) and sulfuric acid (54 μL, 1.0 mmol) afforded compound **6b** as a yellow solid (167 mg, 89%). Mp 152 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3H), 3.91 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 9.1 Hz, 2H), 7.23 (d, *J* = 4.6 Hz, 1H), 7.80 (d, *J* = 9.1 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 8.87 (d, *J* = 4.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 55.5 (CH_3), 109.9 (CH), 113.7 (CH), 114.4 (CH), 120.6 (C), 121.1 (C), 122.5 (C), 131.4 (CH), 131.8 (CH), 145.9 (C), 147.6 (C), 153.0 (C), 153.9 (CH), 161.2 (C), 162.7 (C) ppm. HRMS (ESI+): calcd. for $C_{20}H_{17}N_4O_4^+$ 377.1250 $[M + H]^+$; found 377.1245.



7-(4-Methoxyphenyl)-2-methyl-3-nitropyrazolo[1,5-a]pyrimidine ***6c*****.** Following the general procedure, the reaction between *β*-enaminone **2c** (103 mg, 0.50 mmol), *NH*-5-aminopyrazole **3a** (48 mg, 0.50 mmol), nitric acid (84 μL, 2.0 mmol) and sulfuric acid (54 μL, 1.0 mmol) afforded compound **6c** as a yellow solid (124 mg, 87%). Mp 242 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (s, 3H), 3.93 (s, 3H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 4.1 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.87 (d, *J* = 4.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.4 (CH_3), 55.6 (CH_3), 109.8 (CH), 114.4 (CH), 121.1 (C), 131.7 (CH), 145.3 (C), 147.8 (C), 154.0 (C), 162.8 (C) ppm. HRMS (ESI+): calcd. for $C_{14}H_{13}N_4O_4^+$ 285.0988 $[M + H]^+$; found 285.0997.

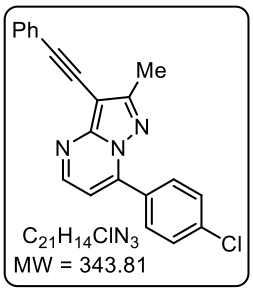


2-(4-Chlorophenyl)-7-(4-methoxyphenyl)-3-nitropyrazolo[1,5-a]pyrimidine ***6d***. Following the general procedure, the reaction between *β*-enaminone **2c** (103 mg, 0.50 mmol), *NH*-5-aminopyrazole **3c** (96 mg, 0.50 mmol), nitric acid (84 μL, 2.0 mmol) and sulfuric acid (54 μL, 1.0 mmol) afforded compound **6d** as a yellow solid (149 mg, 78%). Mp 196-198 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 4.7 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 8.92 (d, *J* = 4.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.6 (CH_3), 110.2 (CH), 114.5 (CH), 120.9 (C), 128.5 (CH), 128.8 (C), 131.2 (CH), 131.8 (CH), 136.4 (C), 145.8 (C), 147.9 (C), 152.2 (C), 154.3 (CH), 162.9 (C) ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}ClN_4O_4^+$ 381.0754 $[M + H]^+$; found 381.0765.

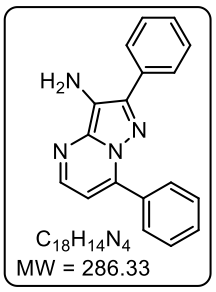


2-Methyl-7-phenyl-3-(phenylethynyl)pyrazolo[1,5-a]pyrimidine ***7a***. Following the general procedure, the reaction between 3-iodopyrazolo[1,5-*a*]pyrimidine **5f** (84 mg, 0.25 mmol), 10% Pd/C (11 mg, 0.01 mmol), PPh_3 (10 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (167 μL, 1.20 mmol) and phenylacetylene (42 μL, 0.38 mmol) in 2.0 mL of water afforded compound **7a** as a yellow solid (58 mg, 75% yield). Mp 156–157 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3H), 6.89 (d, *J* = 4.3 Hz, 1H), 7.31–7.37 (m, 3H), 7.55–7.62 (m, 5H), 8.04–8.06 (m, 2H), 8.56 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 13.7 (CH_3), 79.6 (C), 93.3

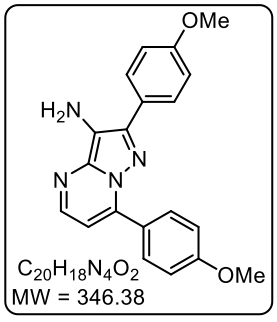
(C), 94.7 (C), 107.7 (CH), 123.8 (C), 127.8 (CH), 128.1 (CH), 128.7 (CH), 129.2 (CH), 130.5 (C), 131.2 (CH), 131.5 (CH), 146.8 (C), 149.8 (CH), 150.1 (C), 157.2 (C) ppm. HRMS (ESI+): calcd. for $C_{21}H_{16}N_3^+$ 310.1344 $[M + H]^+$; found 310.1340.



7-(4-Chlorophenyl)-2-methyl-3-(phenylethynyl)pyrazolo[1,5-a]pyrimidine ***7b***. Following the general procedure, the reaction between 3-iodopyrazolo[1,5-*a*]pyrimidine **5g** (92 mg, 0.25 mmol), 10% Pd/C (11 mg, 0.01 mmol), PPh_3 (10 mg, 0.04 mmol), CuI (4.0 mg, 0.02 mmol), Et_3N (167 μL, 1.20 mmol) and phenylacetylene (42 μL, 0.38 mmol) in 2.0 mL of water afforded compound **7b** as a yellow solid (52 mg, 60% yield). Mp 169 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3H), 6.88 (d, *J* = 4.4 Hz, 1H), 7.32–7.38 (m, 3H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.58 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 13.7 (CH_3), 79.4 (C), 93.6 (C), 94.9 (C), 107.6 (CH), 123.7 (C), 127.9 (CH), 128.2 (CH), 128.9 (C), 129.0 (CH), 130.6 (CH), 131.5 (CH), 137.5 (C), 145.6 (C), 149.7 (CH), 150.1 (C), 157.4 (C) ppm. HRMS (ESI+): calcd. for $C_{21}H_{15}ClN_3^+$ 344.0955 $[M + H]^+$; found 344.0953.



2,7-Diphenylpyrazolo[1,5-a]pyrimidin-3-amine ***8a***. Following the general procedure, the reaction of 3-nitro-2,7-diphenylpyrazolo[1,5-*a*]pyrimidine (**6a**, 161 mg, 0.51 mmol) and 10% Pd/C (8 mg) in 5.0 mL of EtOH at 25 °C for 3 h afforded compound **8a** as an orange solid (134 mg, 92%). Mp 159–160 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (br s, 2H), 6.77 (d, *J* = 4.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.54–7.57 (m, 3H), 8.01–8.04 (m, 2H), 8.16–8.19 (m, 2H), 8.31 (d, *J* = 4.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 106.6 (CH), 116.1 (C), 127.4 (CH), 128.1 (CH), 128.5 (CH), 128.7 (CH), 129.2 (CH), 130.9 (CH), 131.0 (C), 133.2 (C), 140.6 (C), 143.8 (C), 145.3 (C), 145.5 (CH) ppm. HRMS (ESI+): calcd. for $C_{18}H_{15}N_4^+$ 287.1297 $[M + H]^+$; found 287.1304.



2,7-bis(4-Methoxyphenyl)pyrazolo[1,5-a]pyrimidin-3-amine ***8b***. Following the general procedure, the reaction of 2,7-*bis*(4-methoxyphenyl)-3-nitropyrazolo[1,5-*a*]pyrimidine (**6b**, 188 mg, 0.50 mmol) and 10% Pd/C (10 mg) in 5.0 mL of EtOH at 25 °C for 3 h afforded compound **8b** as an orange solid (156 mg, 90%). Mp 160 °C (amorphous). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.54 (br s, 2H), 3.86 (s, 3H), 3.90 (s, 3H), 6.72 (d, *J* = 4.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 4.3 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 55.4 (CH_3), 105.4 (CH), 113.9 (CH), 114.2 (CH), 115.1 (C), 123.2 (C), 125.9 (C), 128.6 (CH), 130.9 (CH), 140.9 (C), 143.9 (C), 145.0 (C), 145.5 (CH), 159.5 (C), 161.6 (C) ppm. HRMS (ESI+): calcd. for $C_{20}H_{19}N_4O_2^+$ 347.1508 $[M + H]^+$; found 347.1510.

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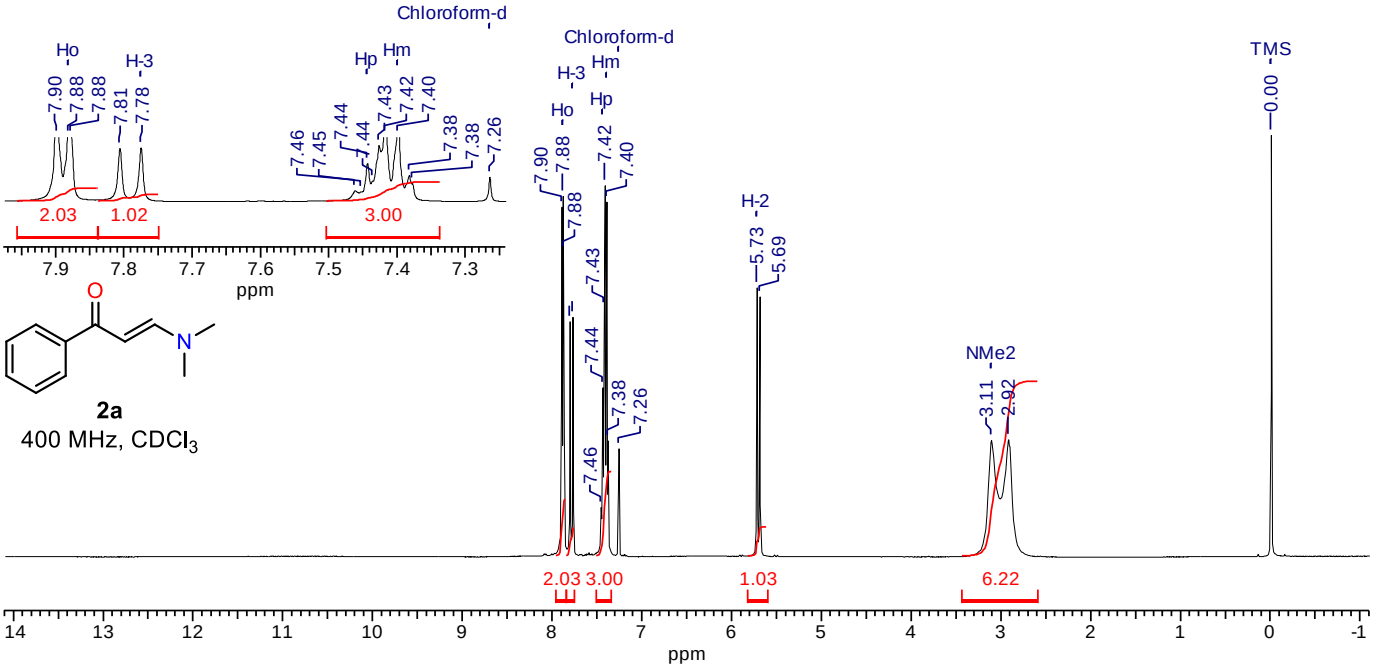
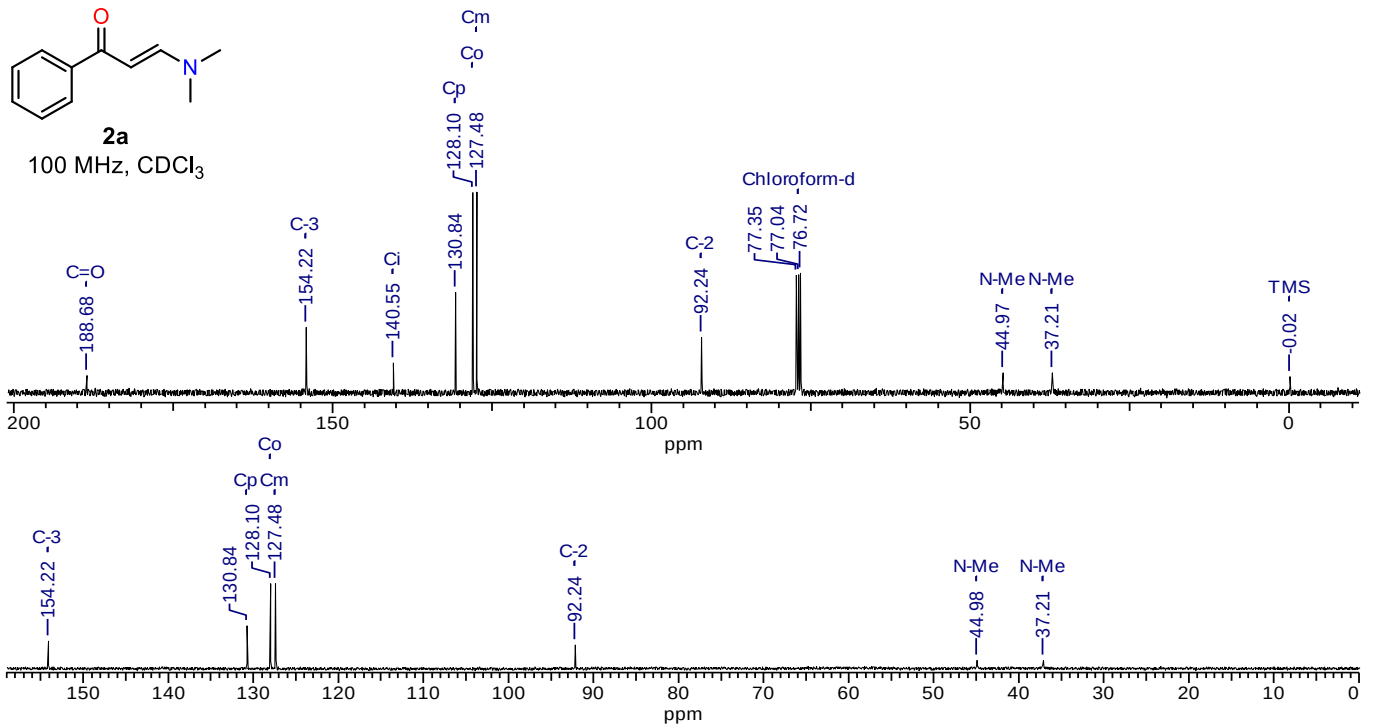
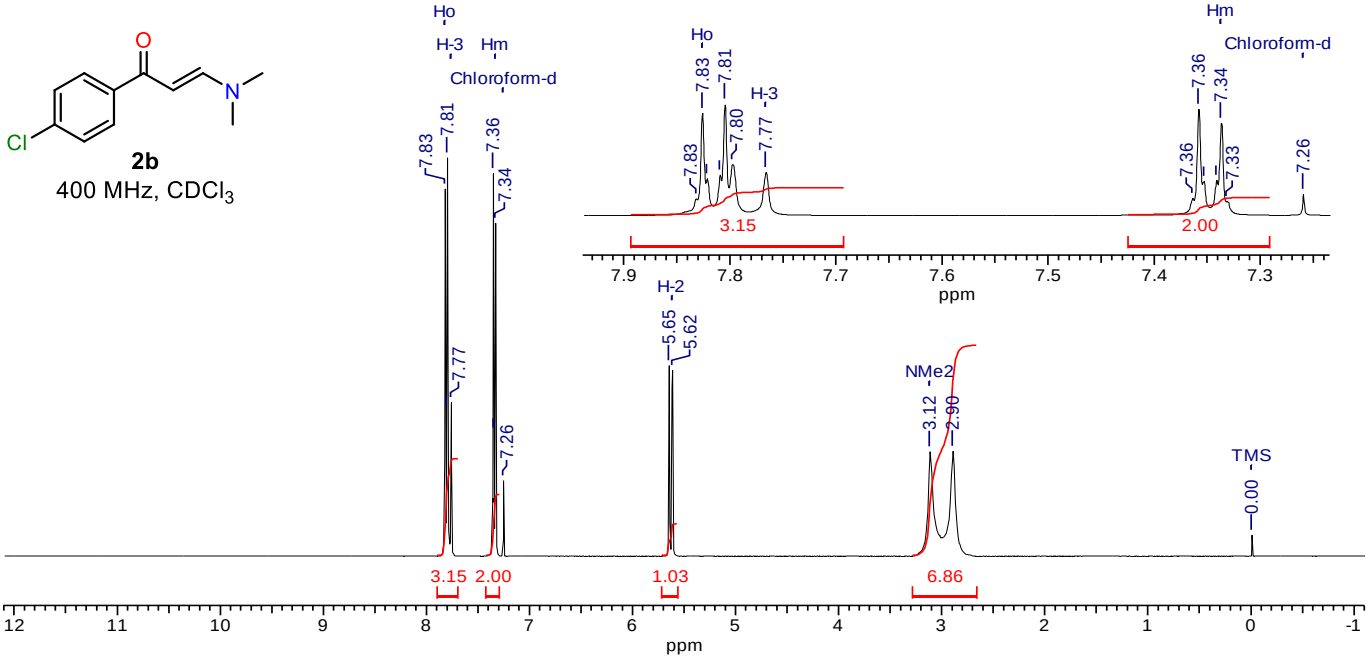
3. Copies of NMR spectra

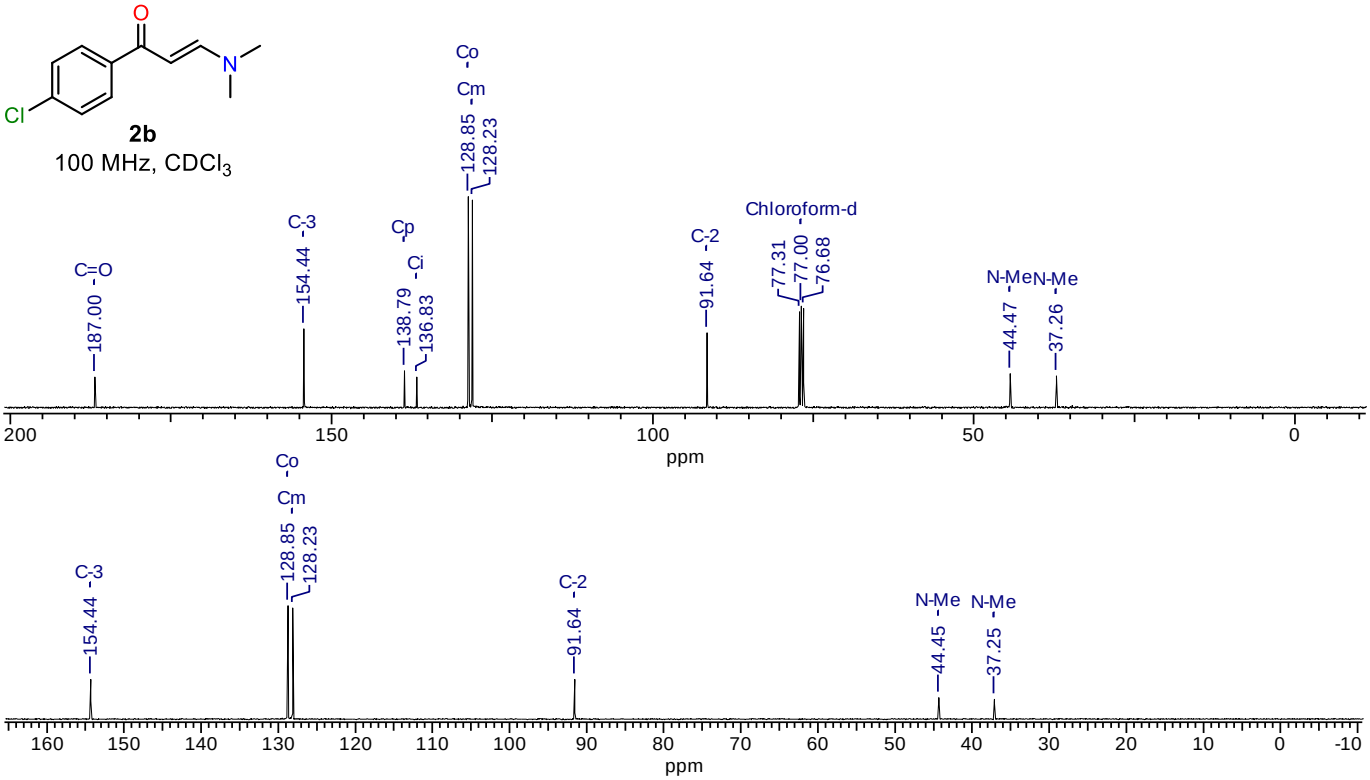
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a**



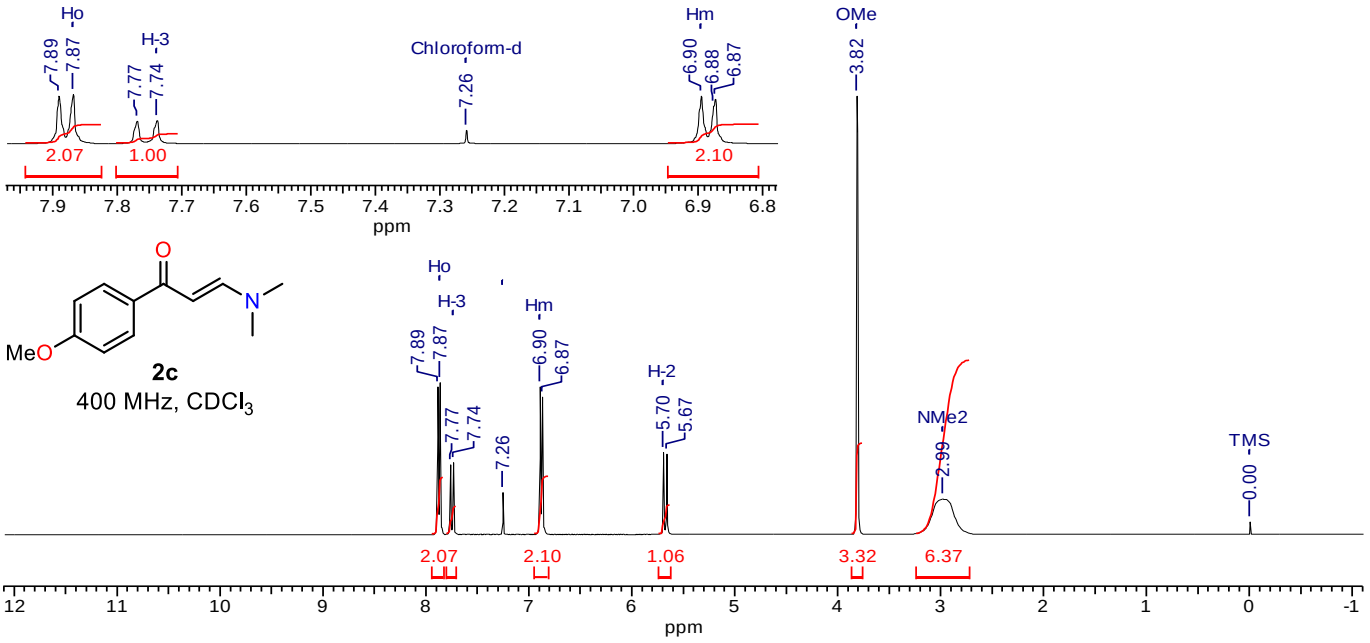


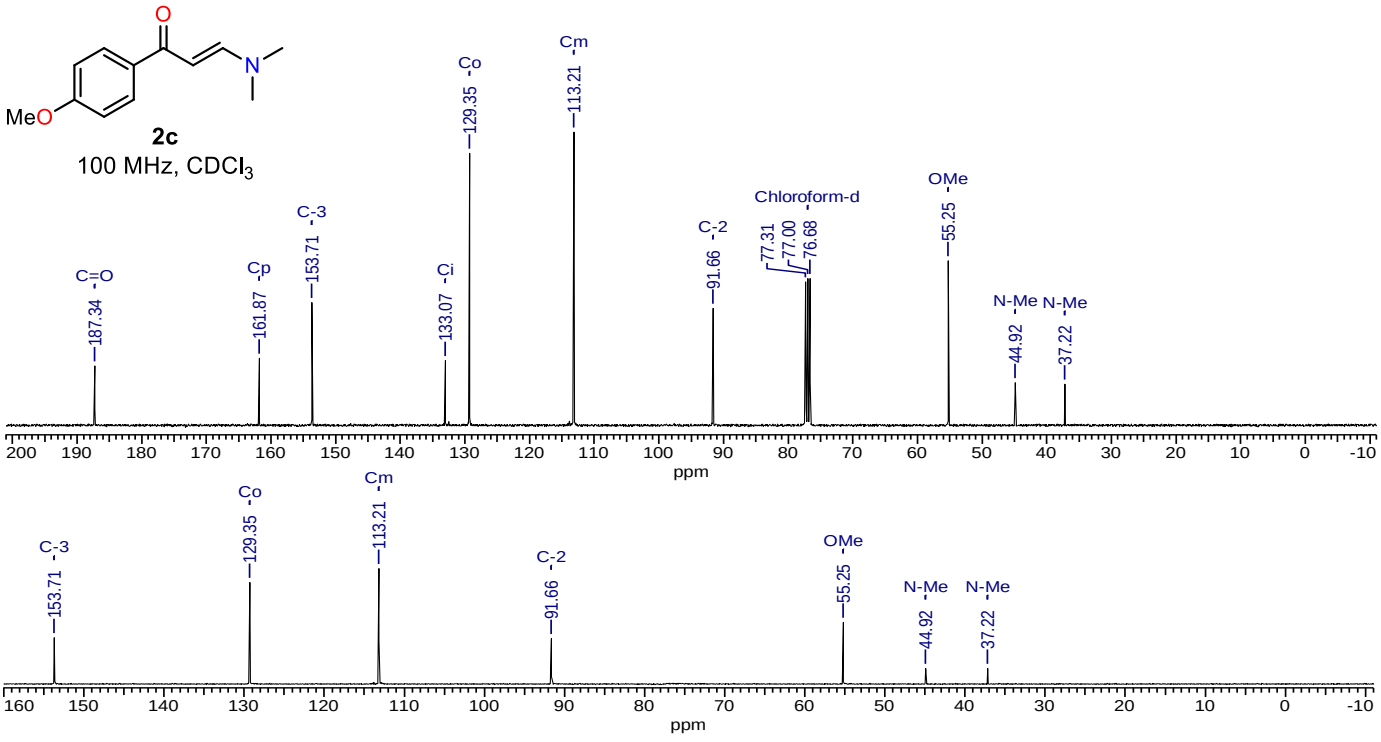
^{1}H and ^{13}C{^{1}H} NMR spectra of (*E*)-1-(4-chlorophenyl)-3-(dimethylamino)prop-2-en-1-one **2b**



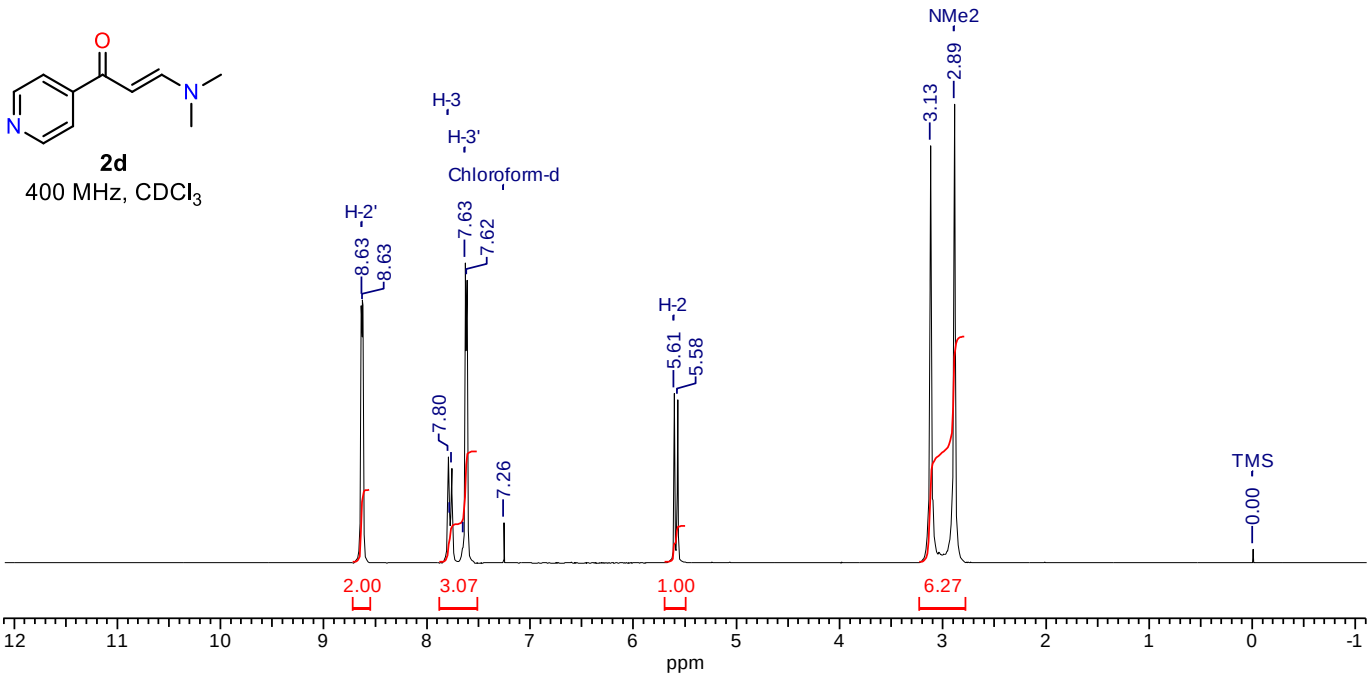


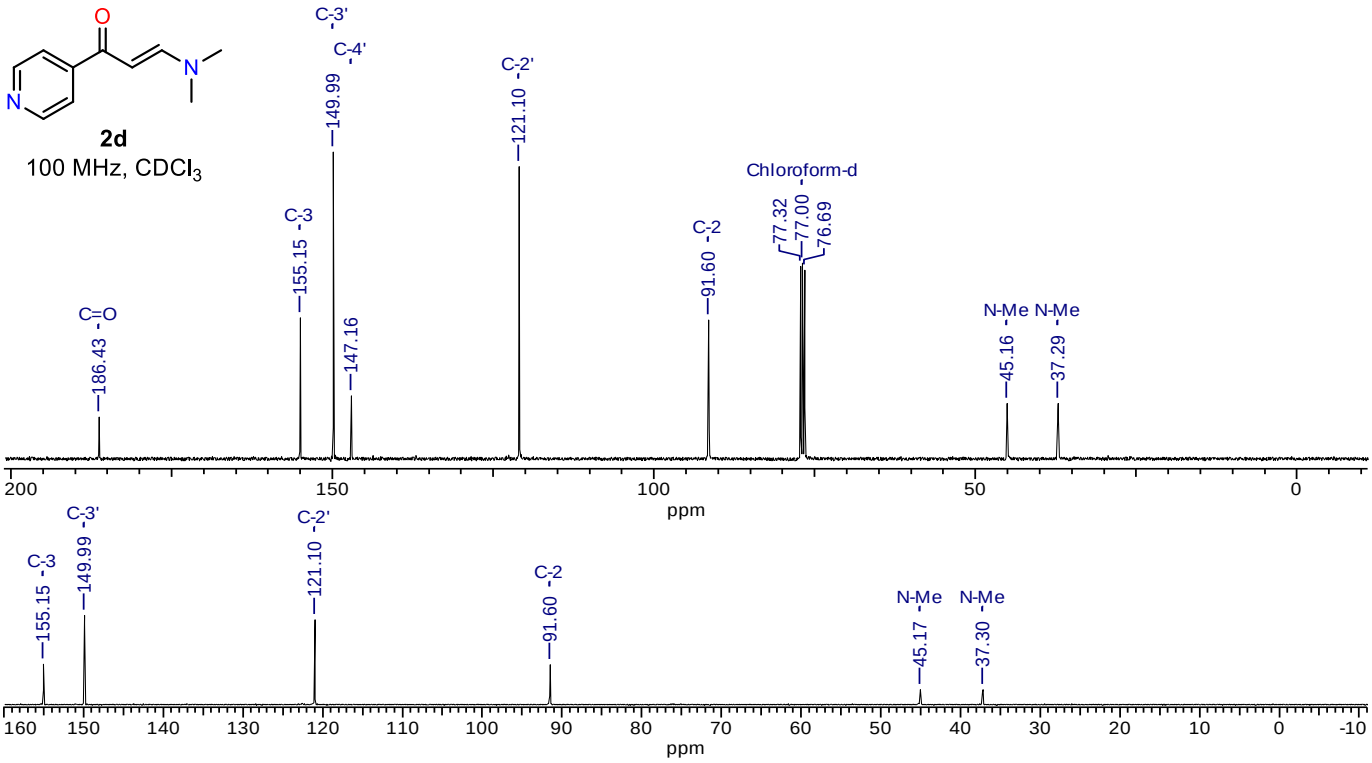
^{1}H and ^{13}C{^{1}H} NMR spectra of (*E*)-3-(dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one **2c**



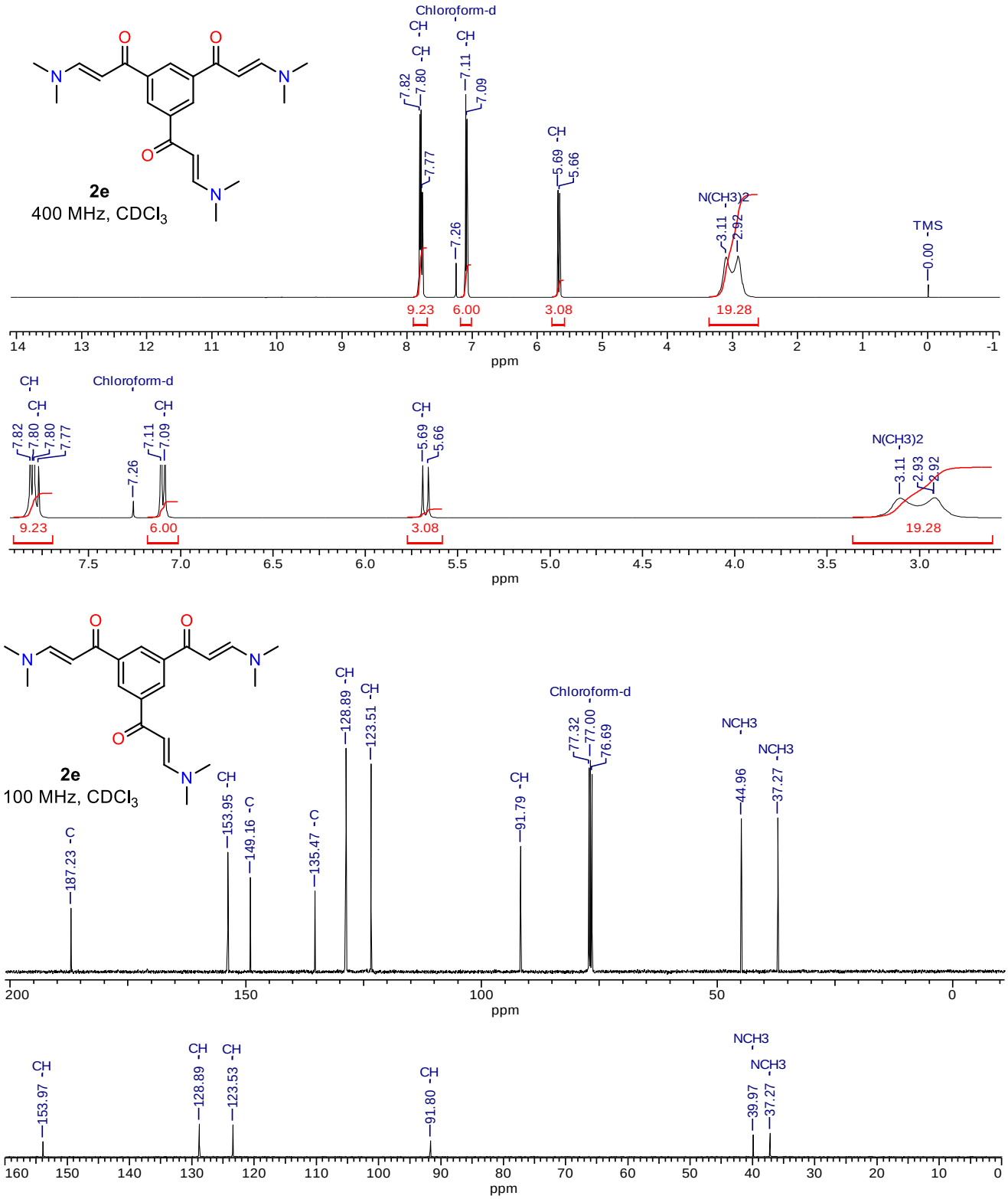


^{1}H and ^{13}C{^{1}H} NMR spectra of (*E*)-3-(dimethylamino)-1-(pyridin-4-yl)prop-2-en-1-one **2d**

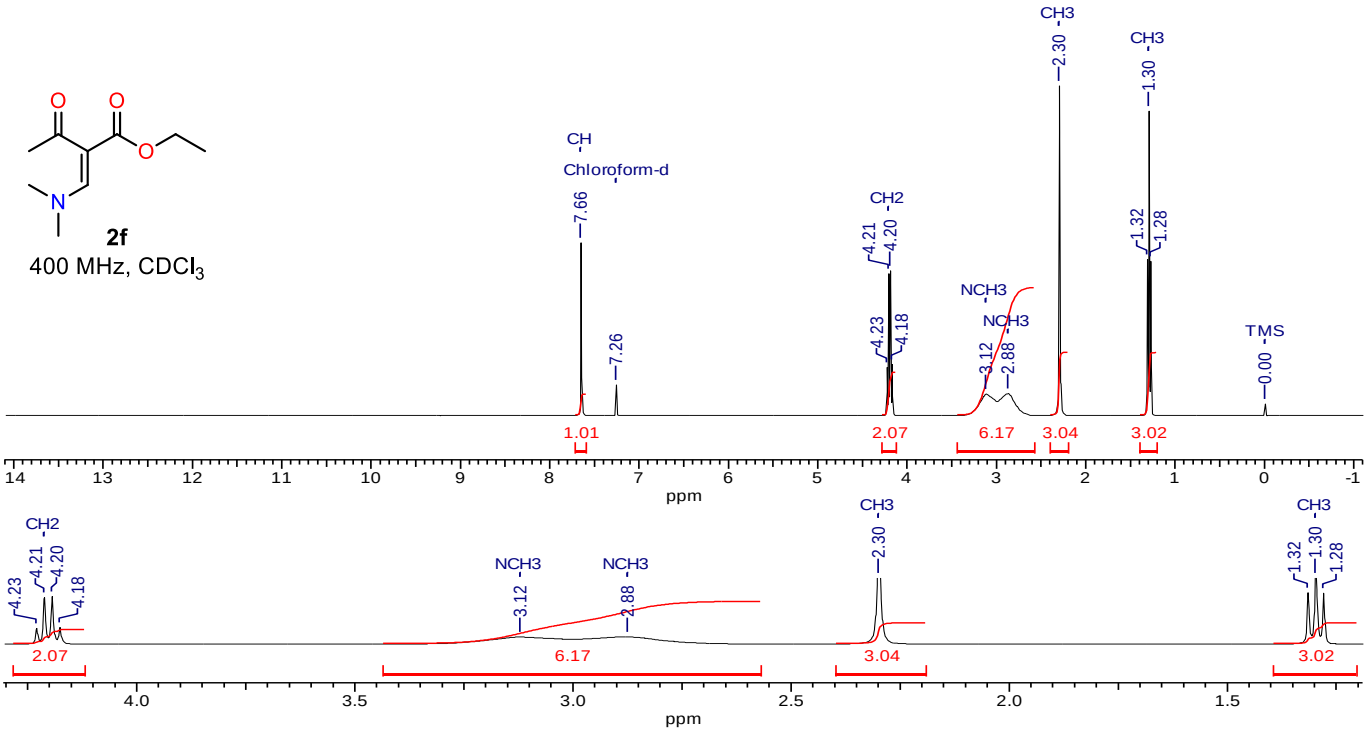


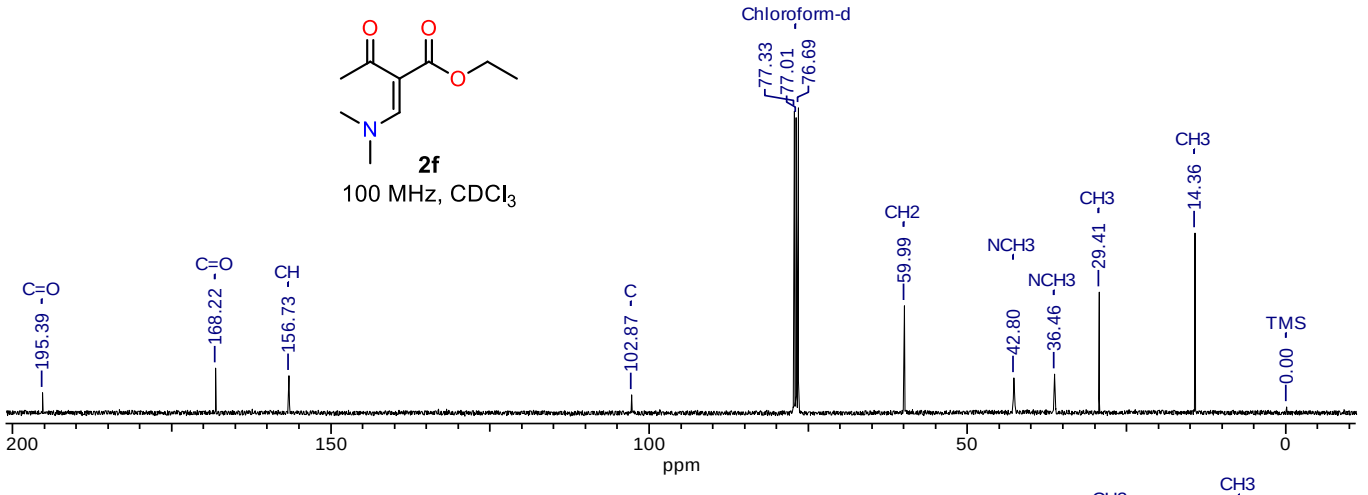


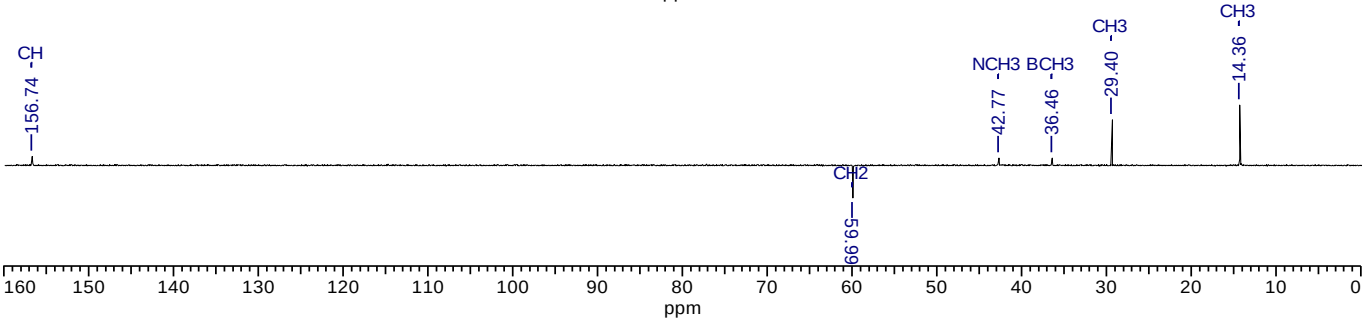
^{1}H and ^{13}C{^{1}H} NMR spectra of (2*E*,2'*E*,2"*E*)-1,1',1"-(benzene-1,3,5-triyl)*tris*(3-(dimethylamino)prop-2-en-1-one) **2e**



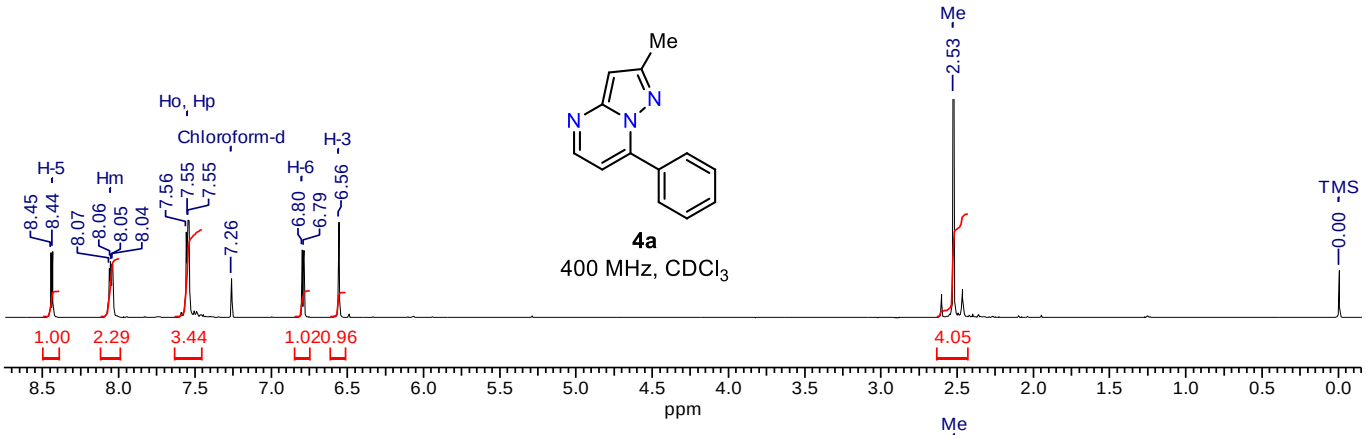
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of (*E*)-ethyl 2-(dimethylaminomethylene)-3-oxobutanoate **2f**

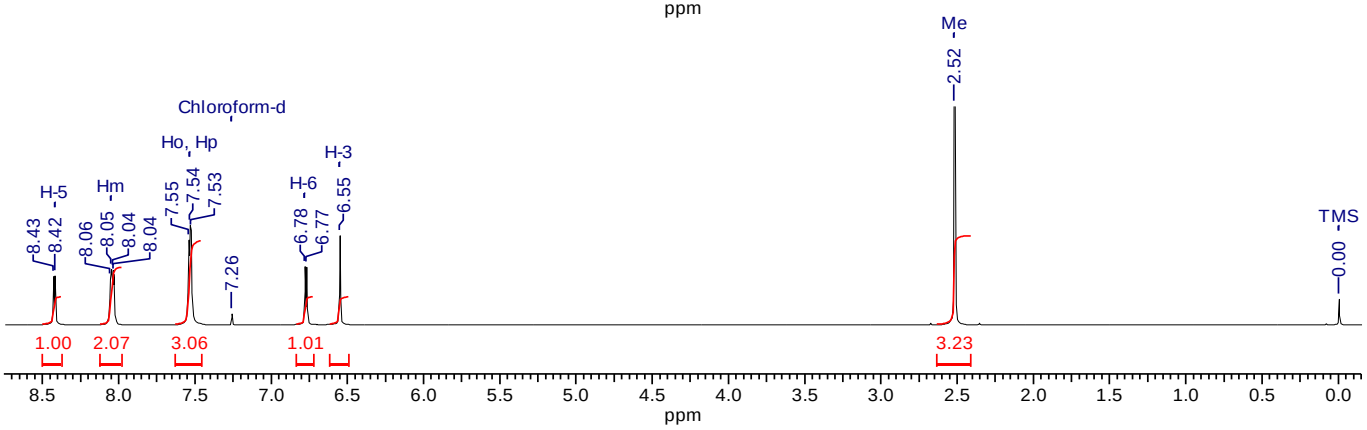


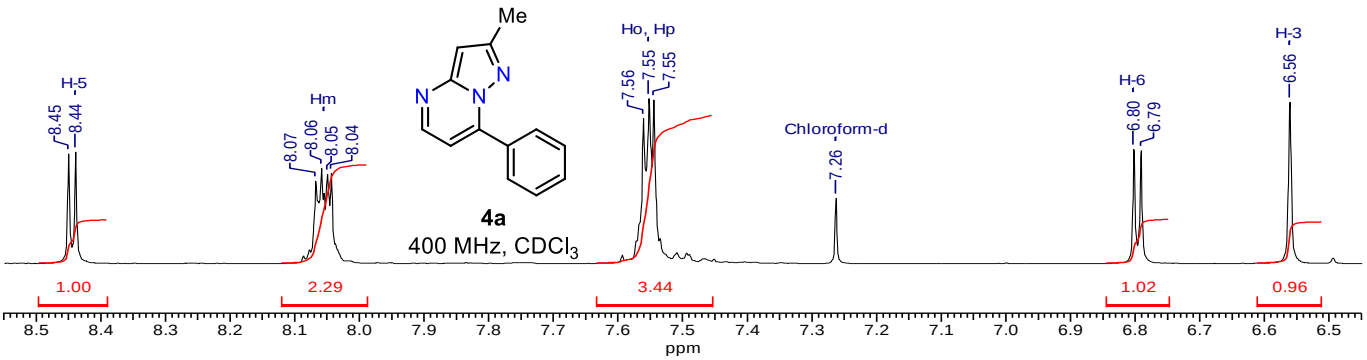


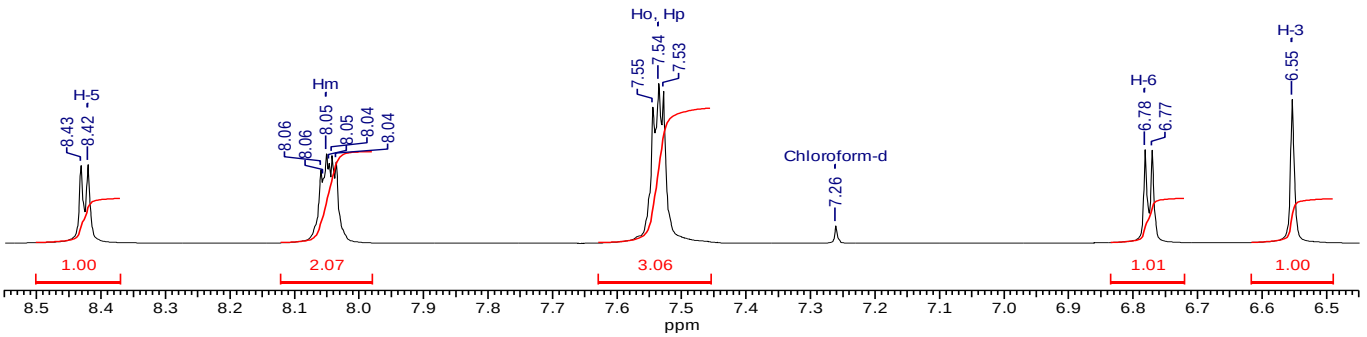


^{1}H NMR spectrum for the crude product **4a** *vs* ^{1}H NMR spectrum for 2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine **4a** after purification by simple recrystallization.

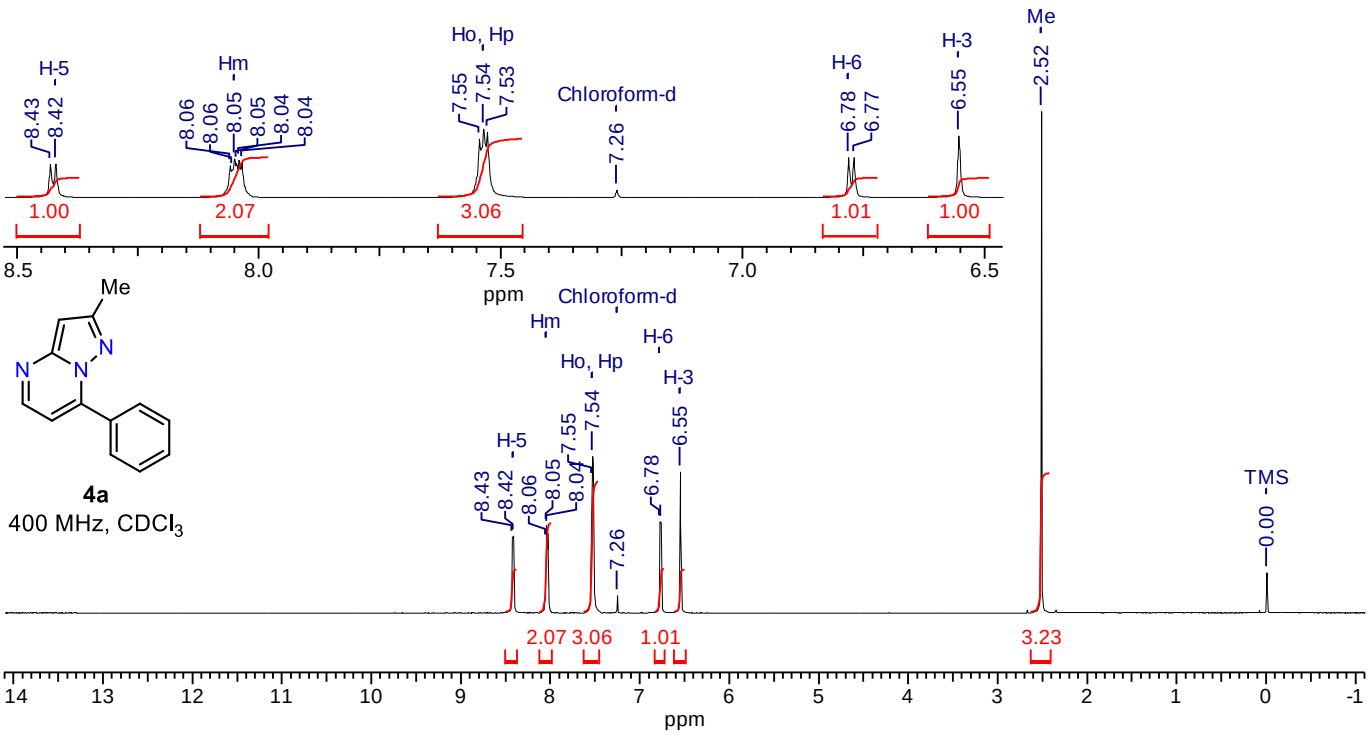


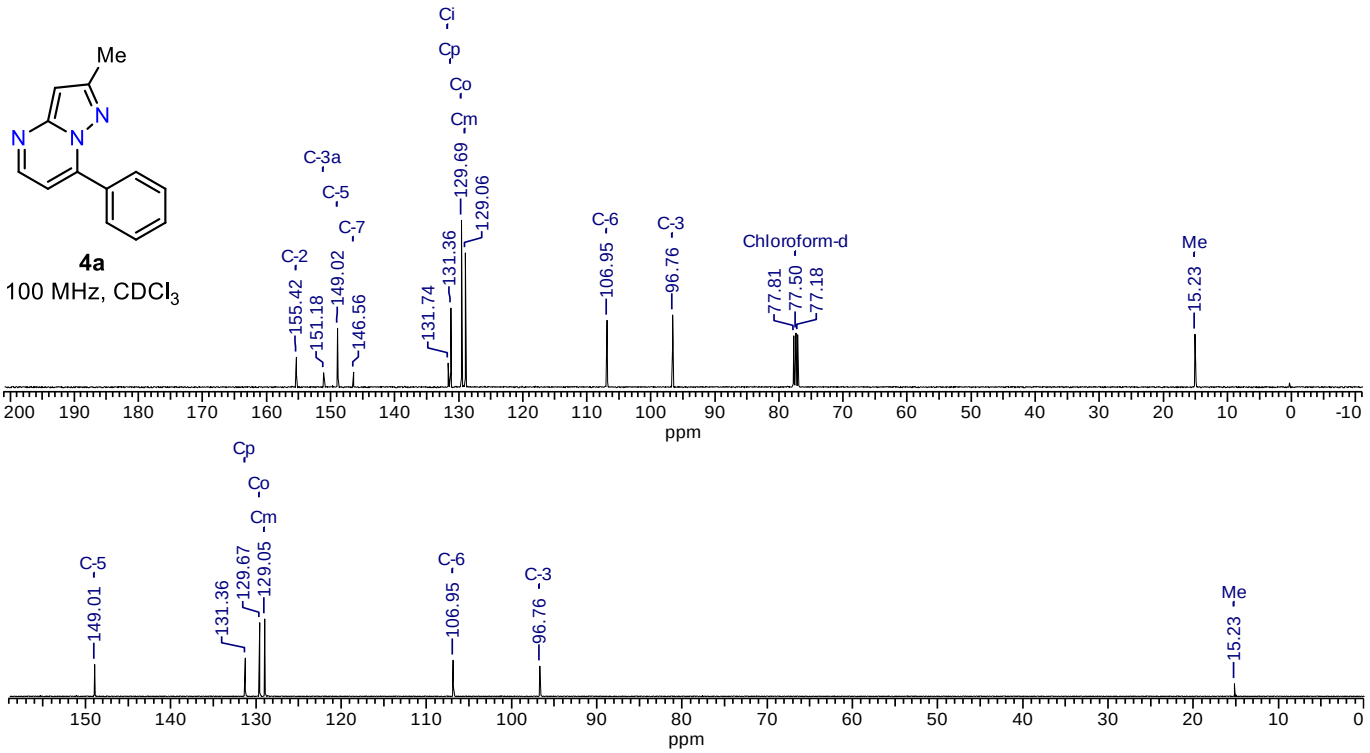




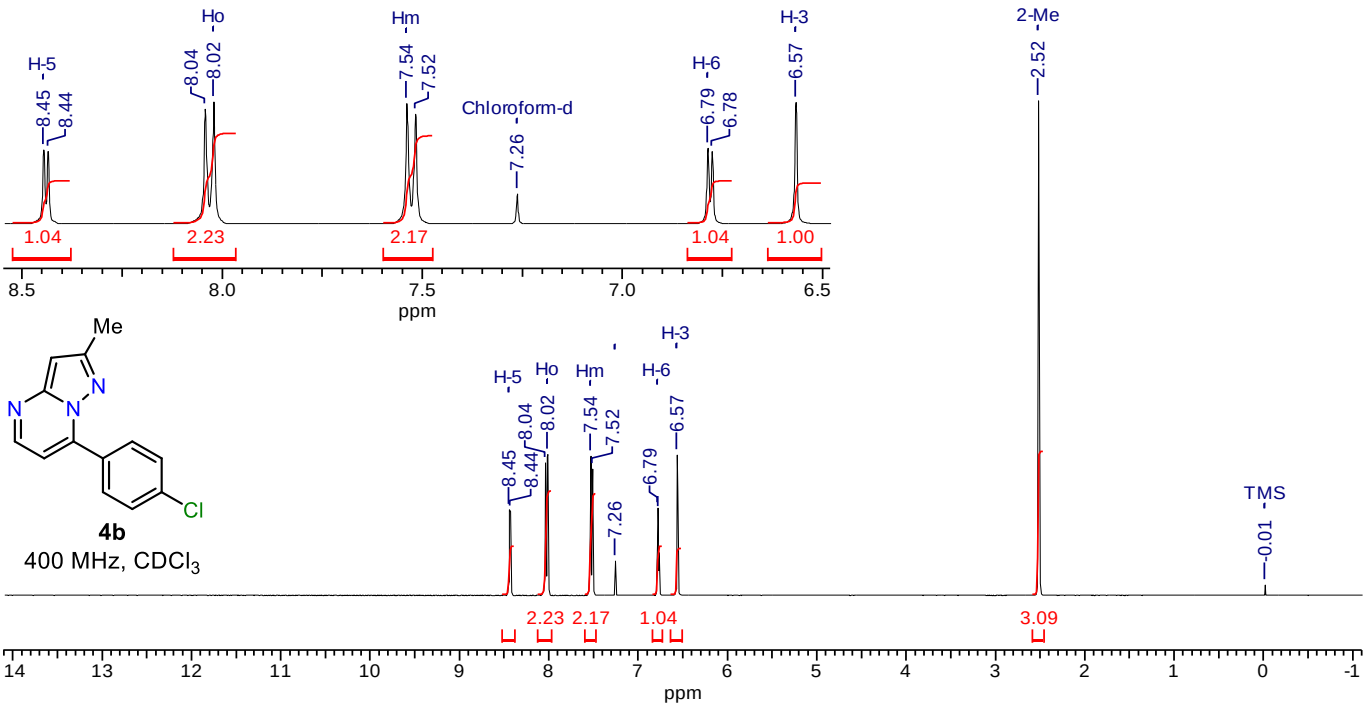


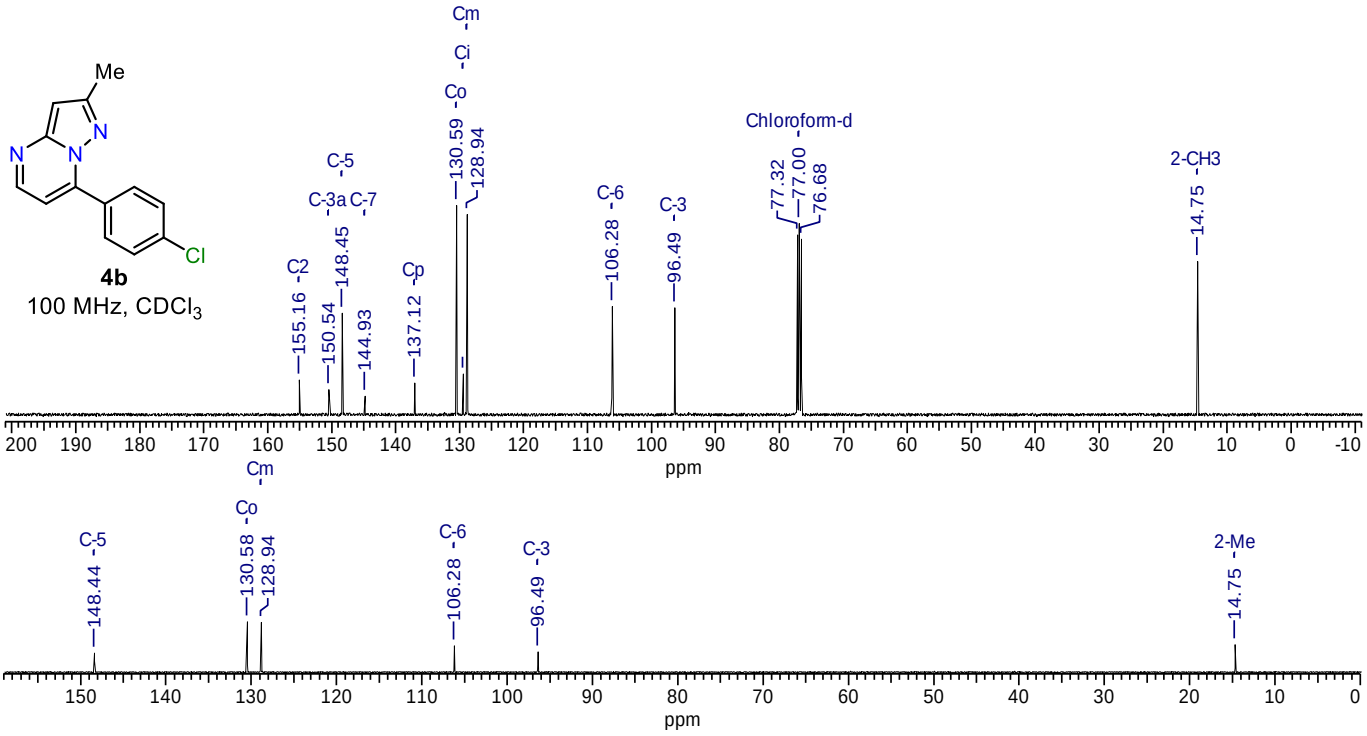
^{1}H and ^{13}C{^{1}H} NMR spectra of 2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine **4a**



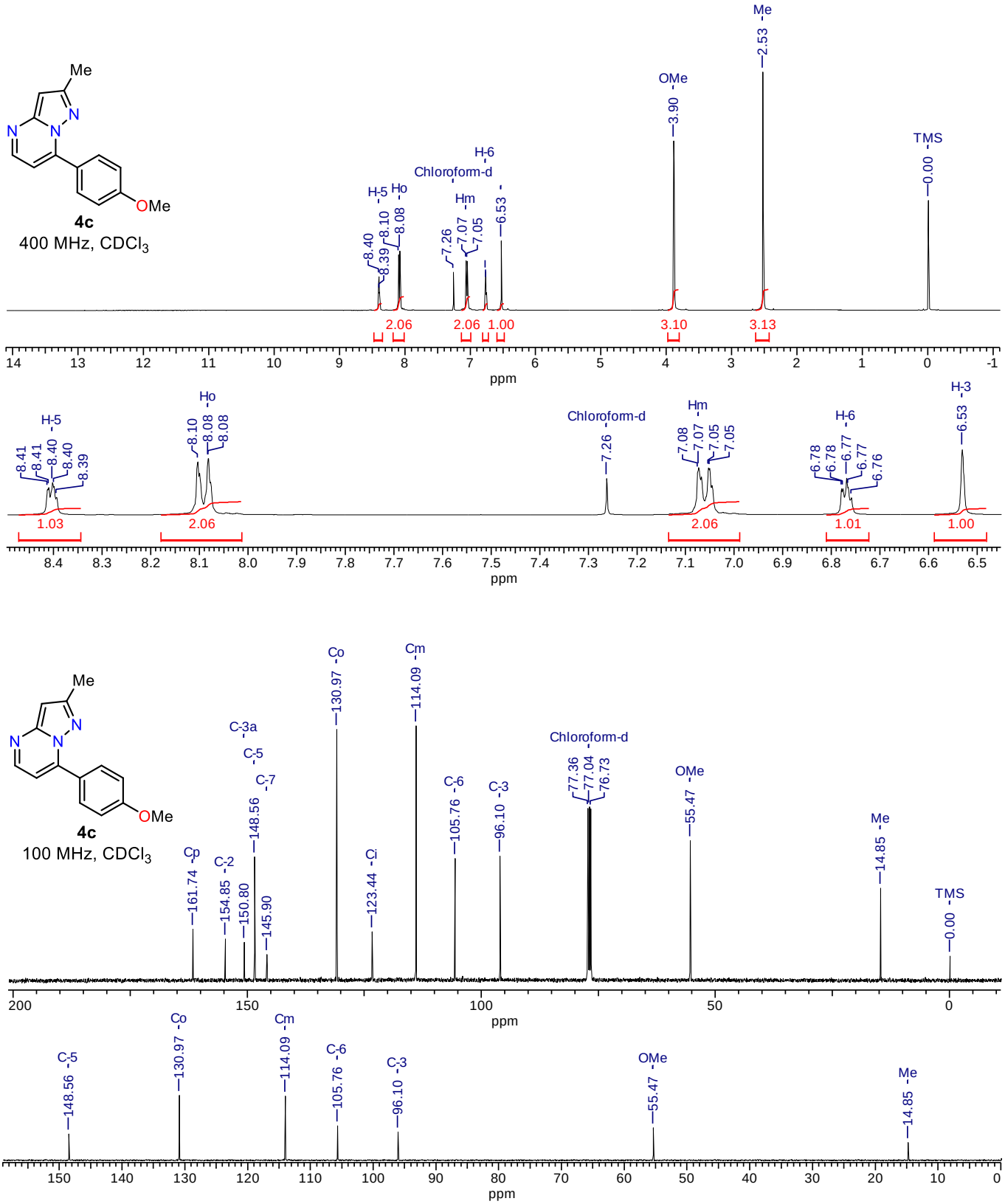


^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-chlorophenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine **4b**

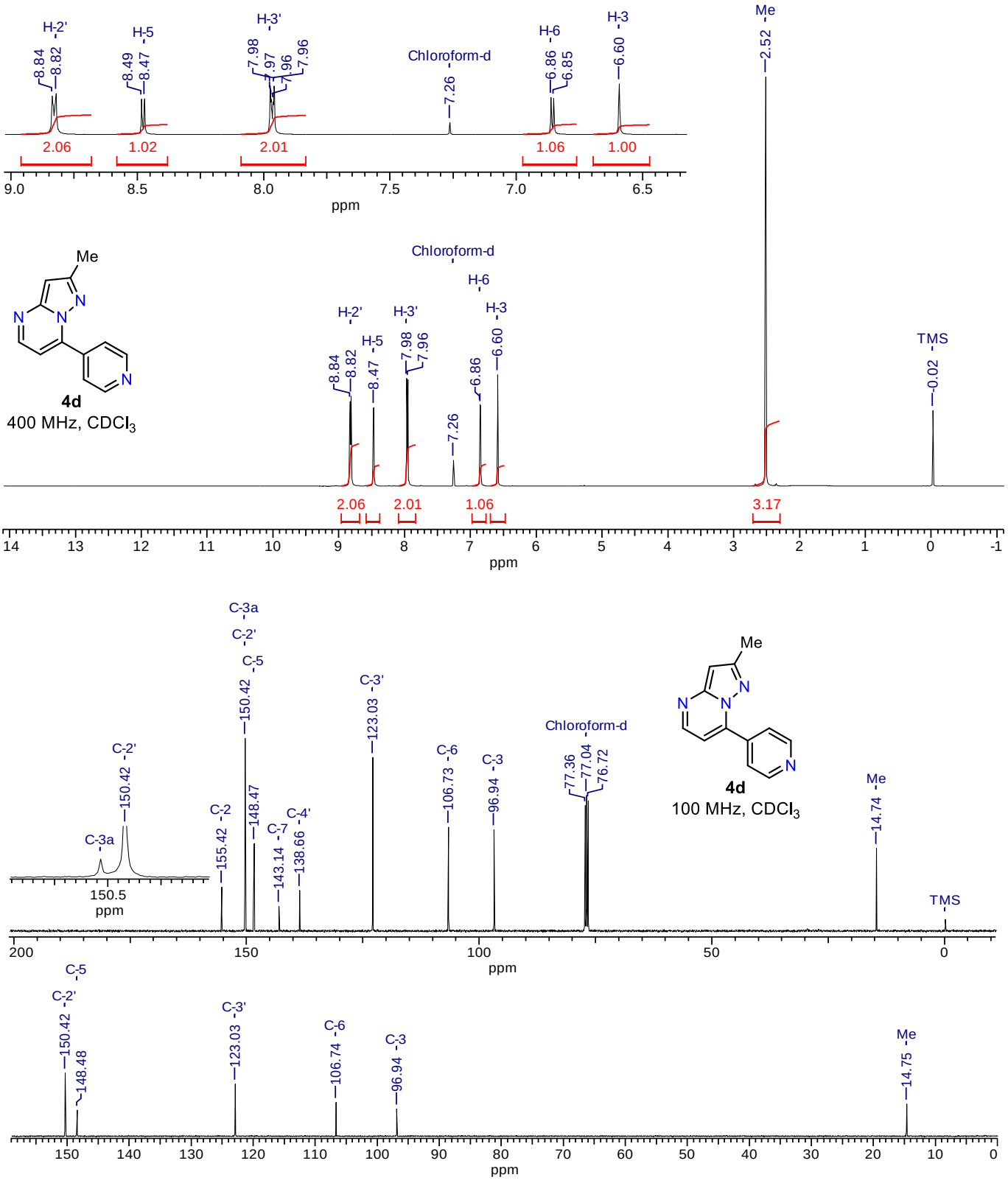




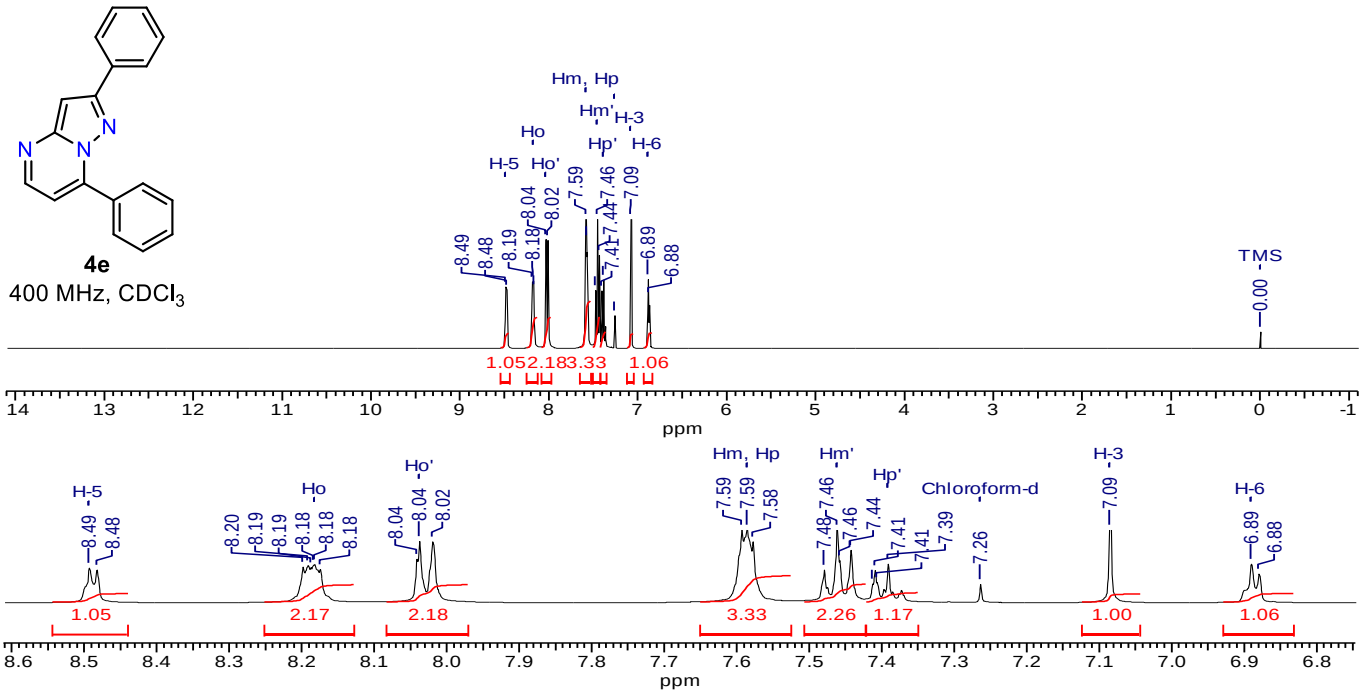
^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-methoxyphenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine **4c**

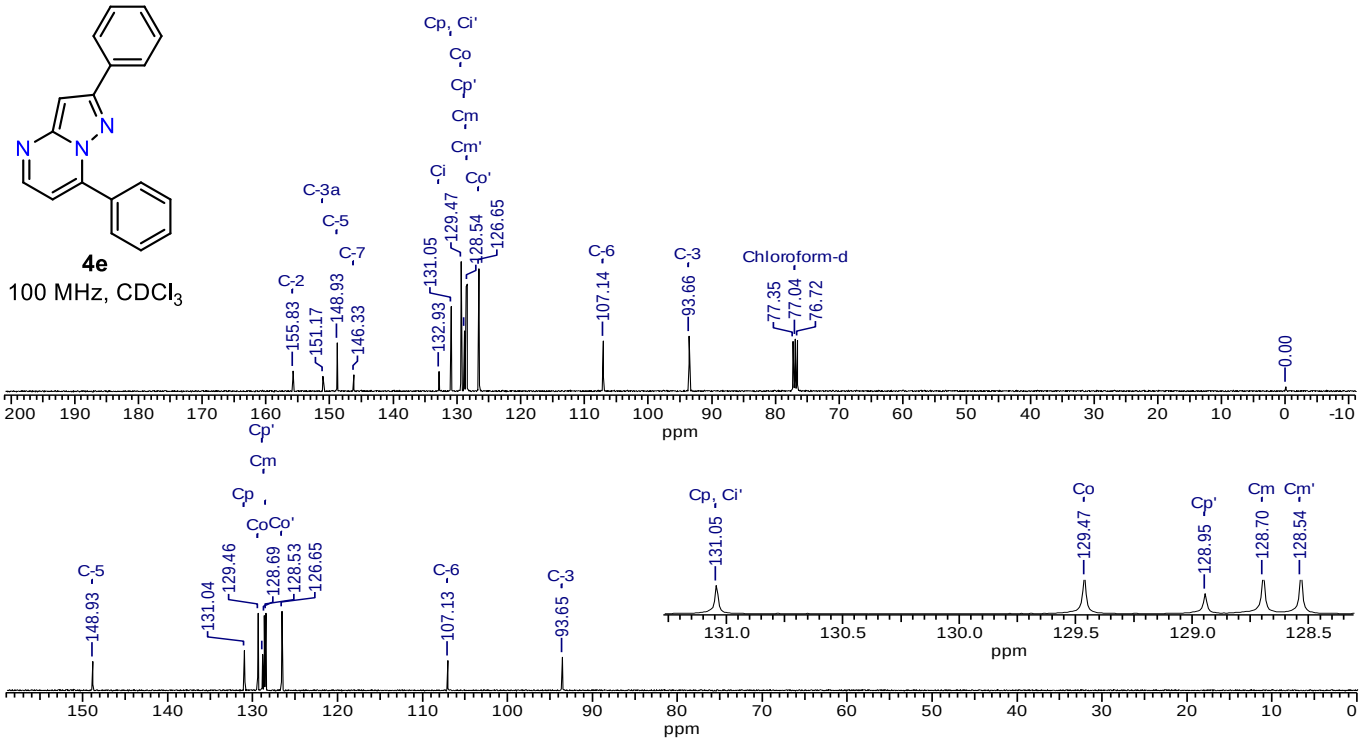


^{1}H and ^{13}C{^{1}H} NMR spectra of 2-methyl-7-(pyridin-4-yl)pyrazolo[1,5-*a*]pyrimidine **4d**

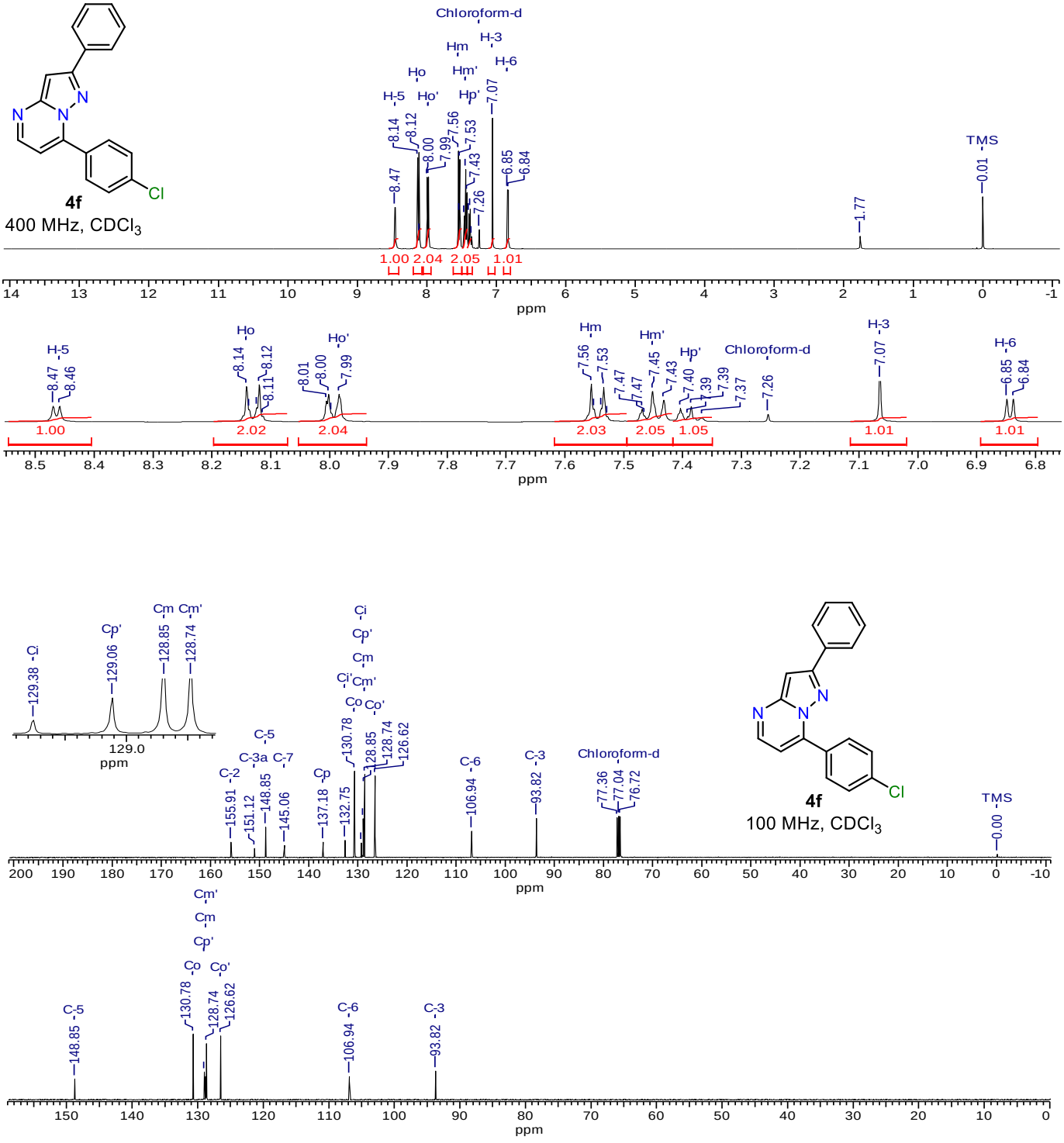


^{1}H and ^{13}C{^{1}H} NMR spectra of 2,7-diphenylpyrazolo[1,5-*a*]pyrimidine **4e**

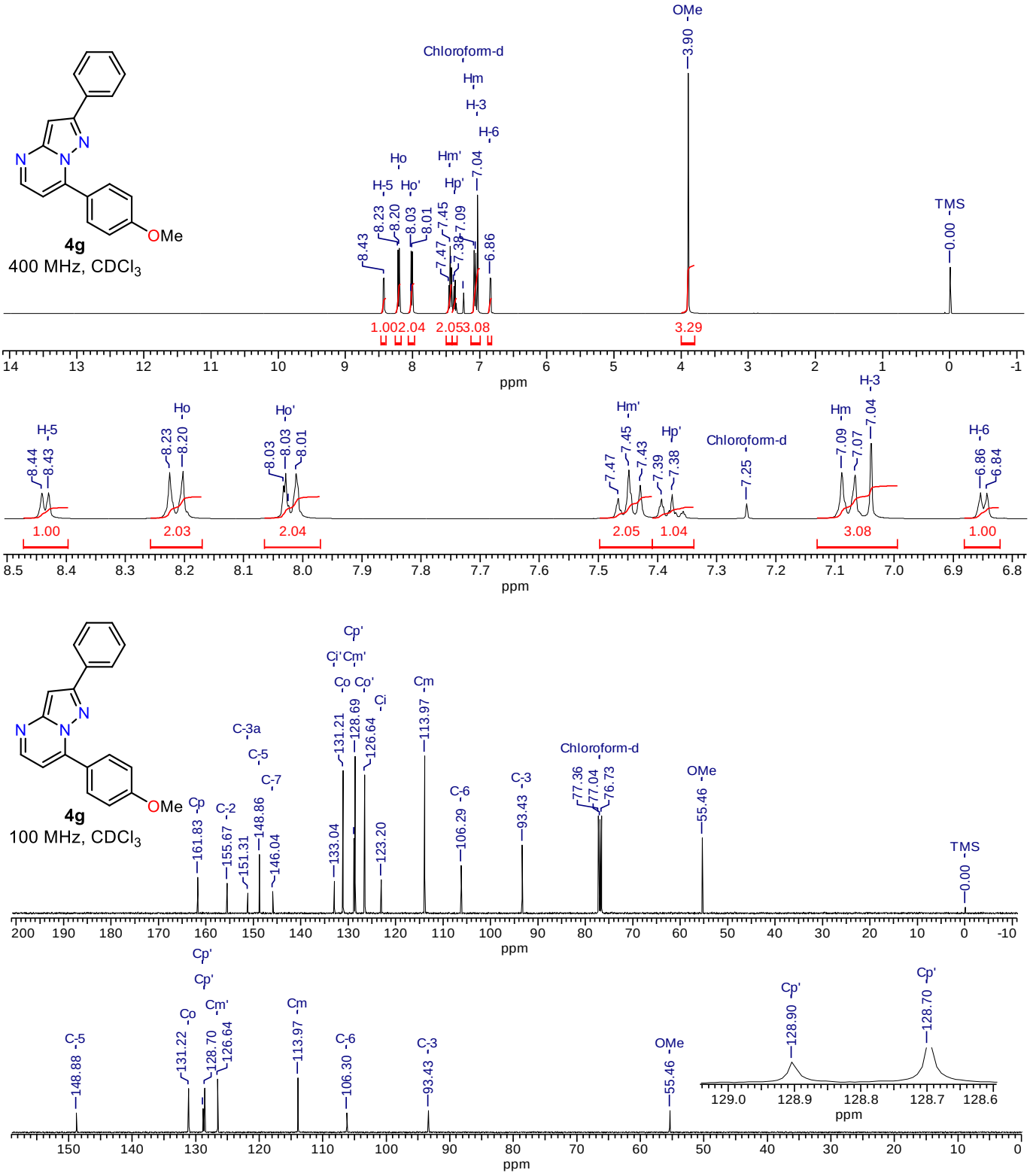




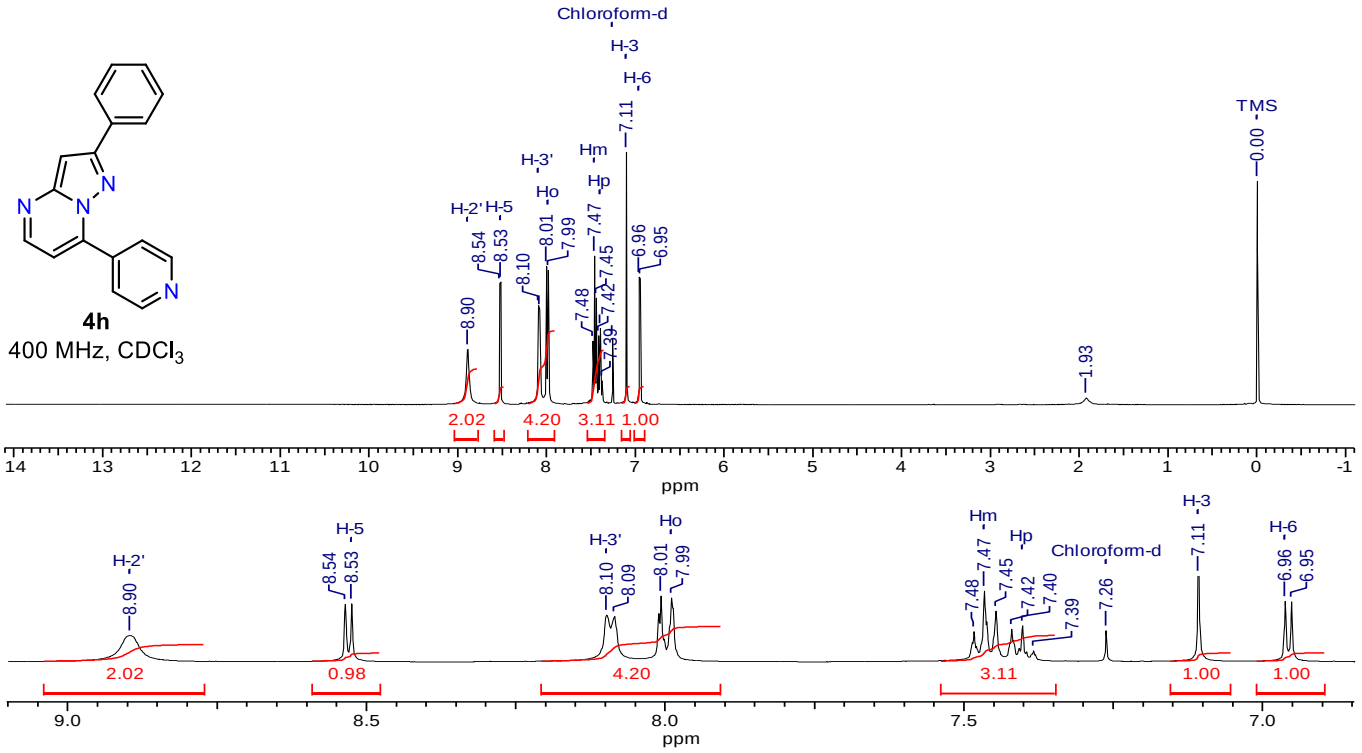
^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-chlorophenyl)-2-phenylpyrazolo[1,5-*a*]pyrimidine **4f**

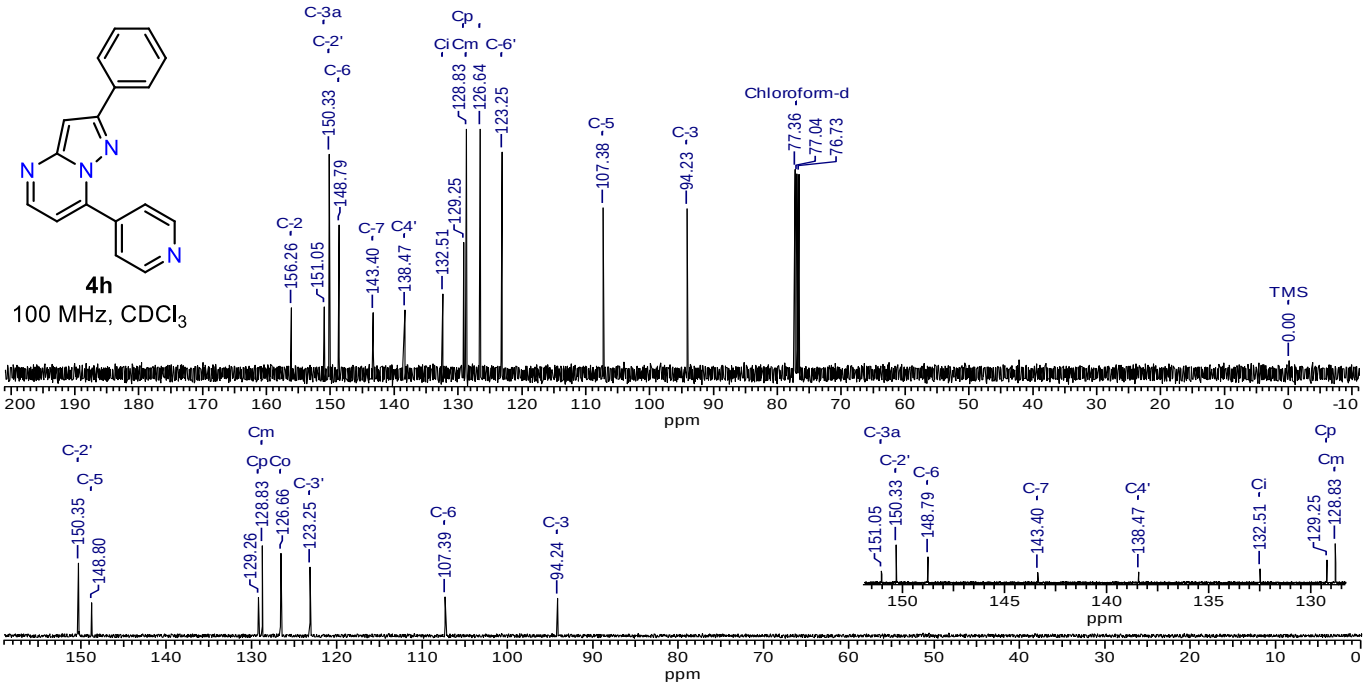


^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-methoxyphenyl)-2-phenylpyrazolo[1,5-*a*]pyrimidine **4g**

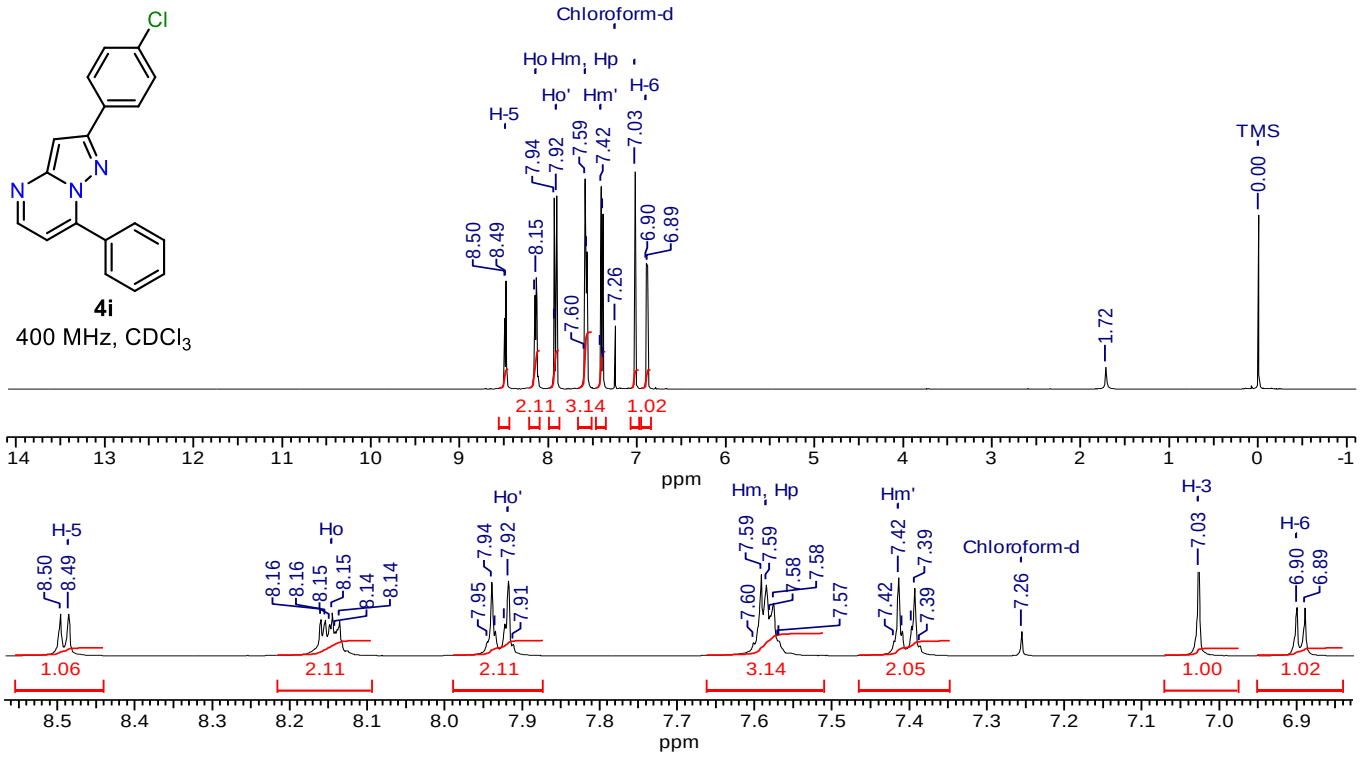


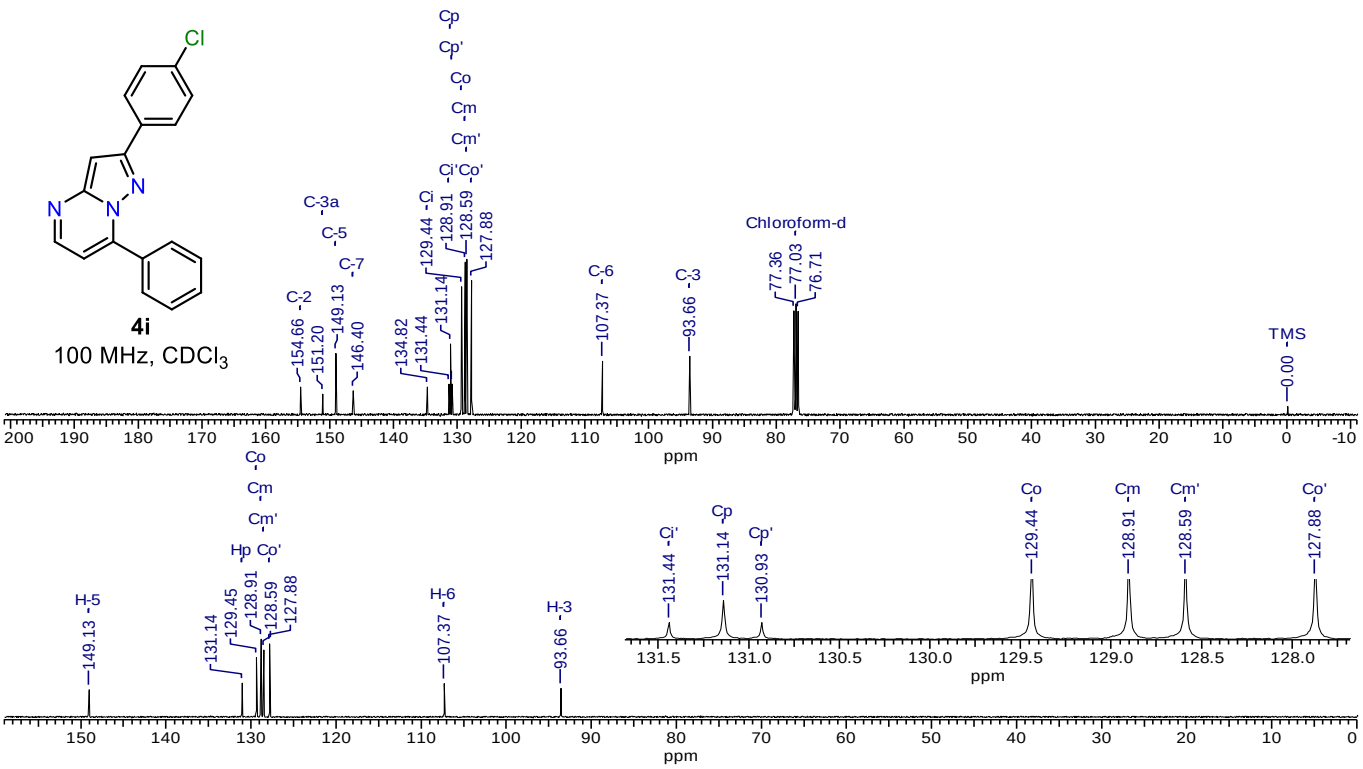
^{1}H and ^{13}C{^{1}H} NMR spectra of 2-phenyl-7-(pyridin-4-yl)pyrazolo[1,5-*a*]pyrimidine **4h**



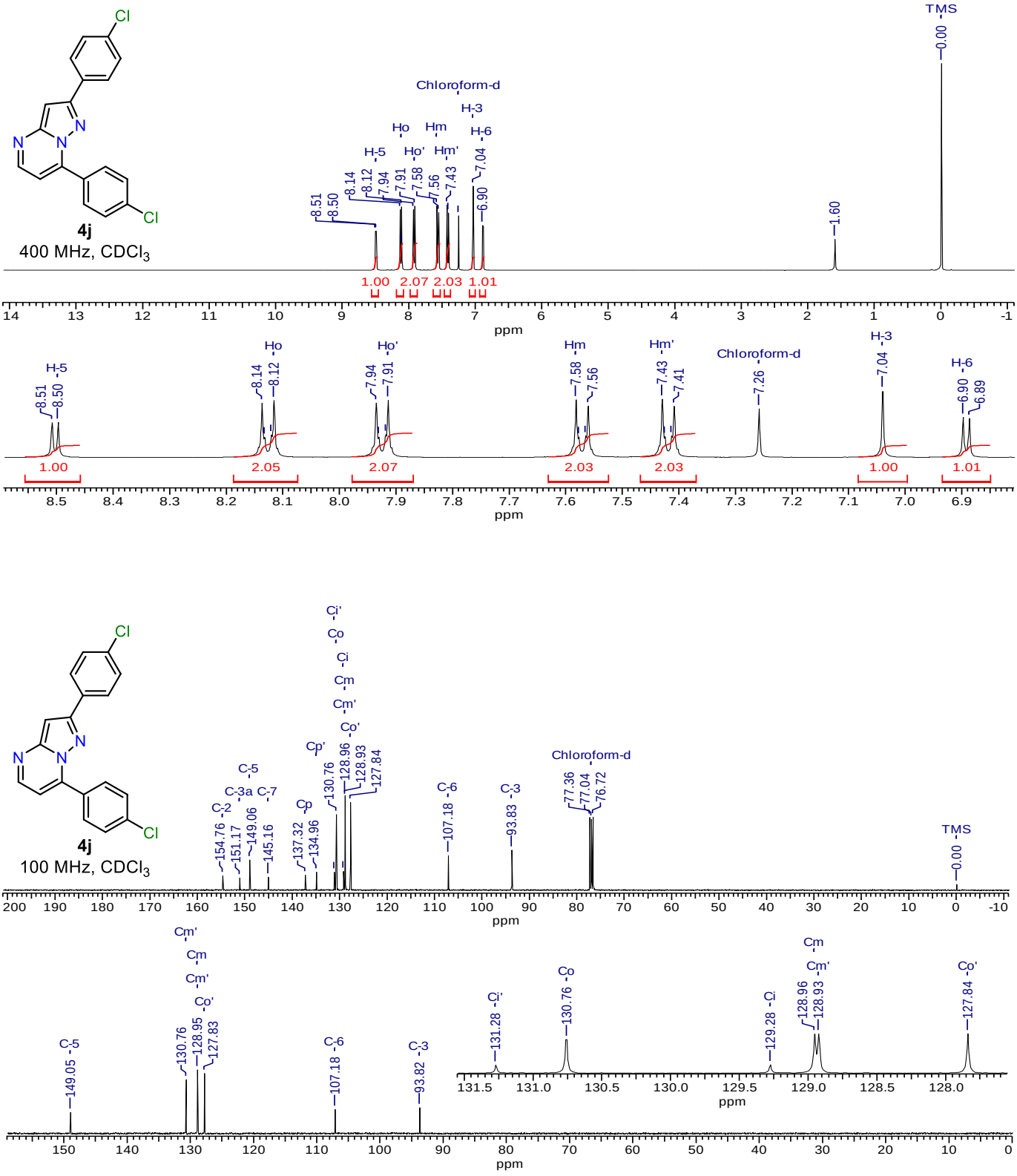


^{1}H and ^{13}C{^{1}H} NMR spectra of 2-(4-chlorophenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine **4i**

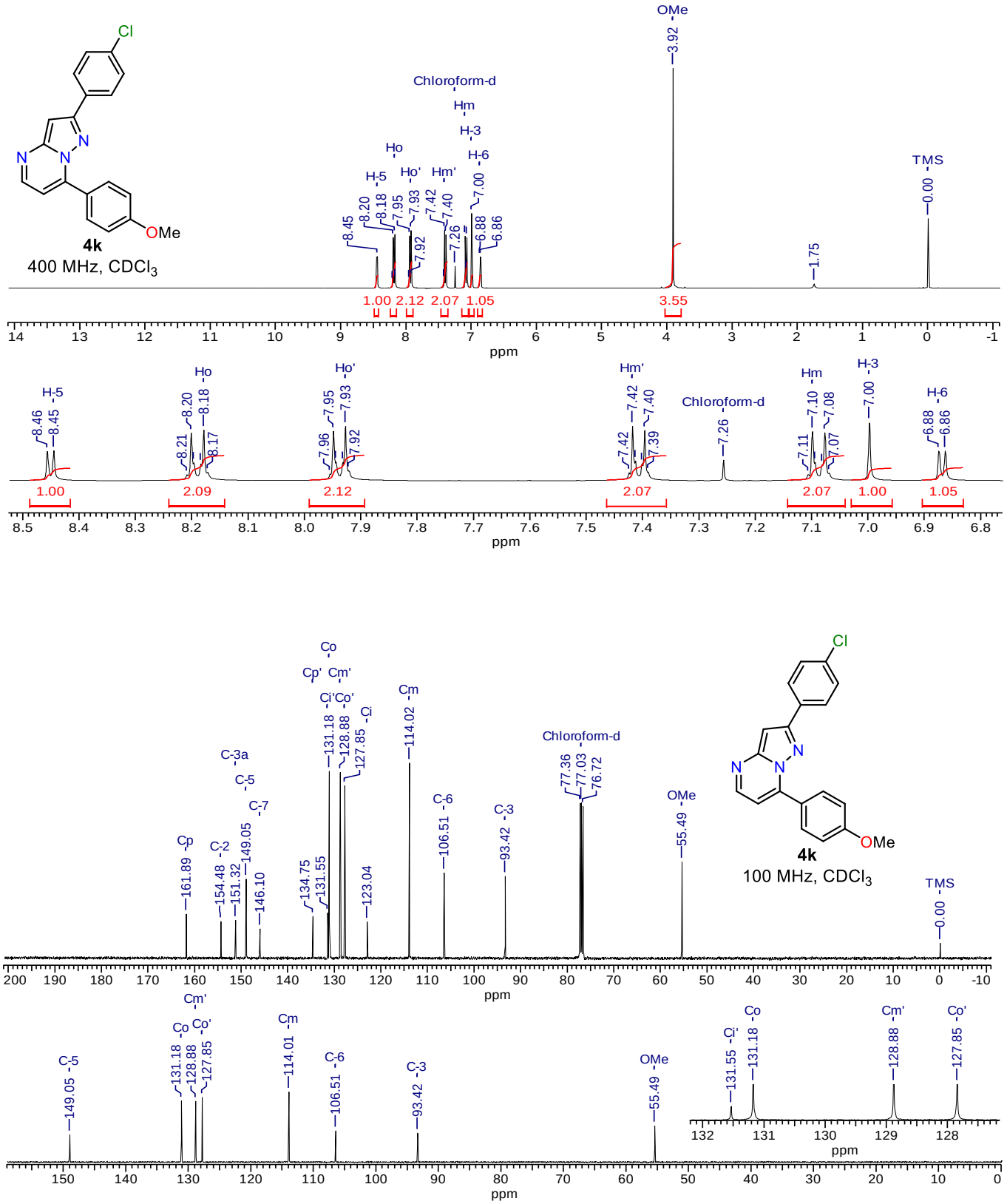




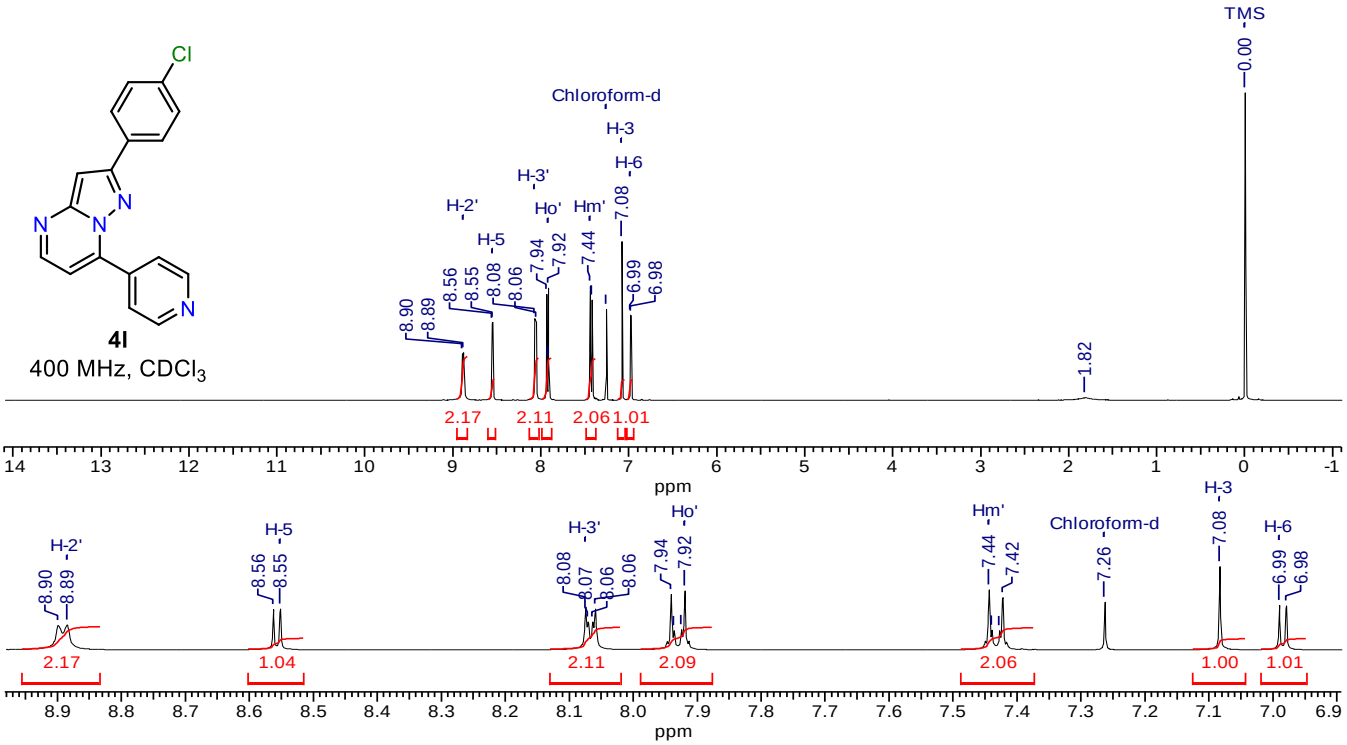
^{1}H and ^{13}C{^{1}H} NMR spectra of 2,7-*bis*(4-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine **4j**

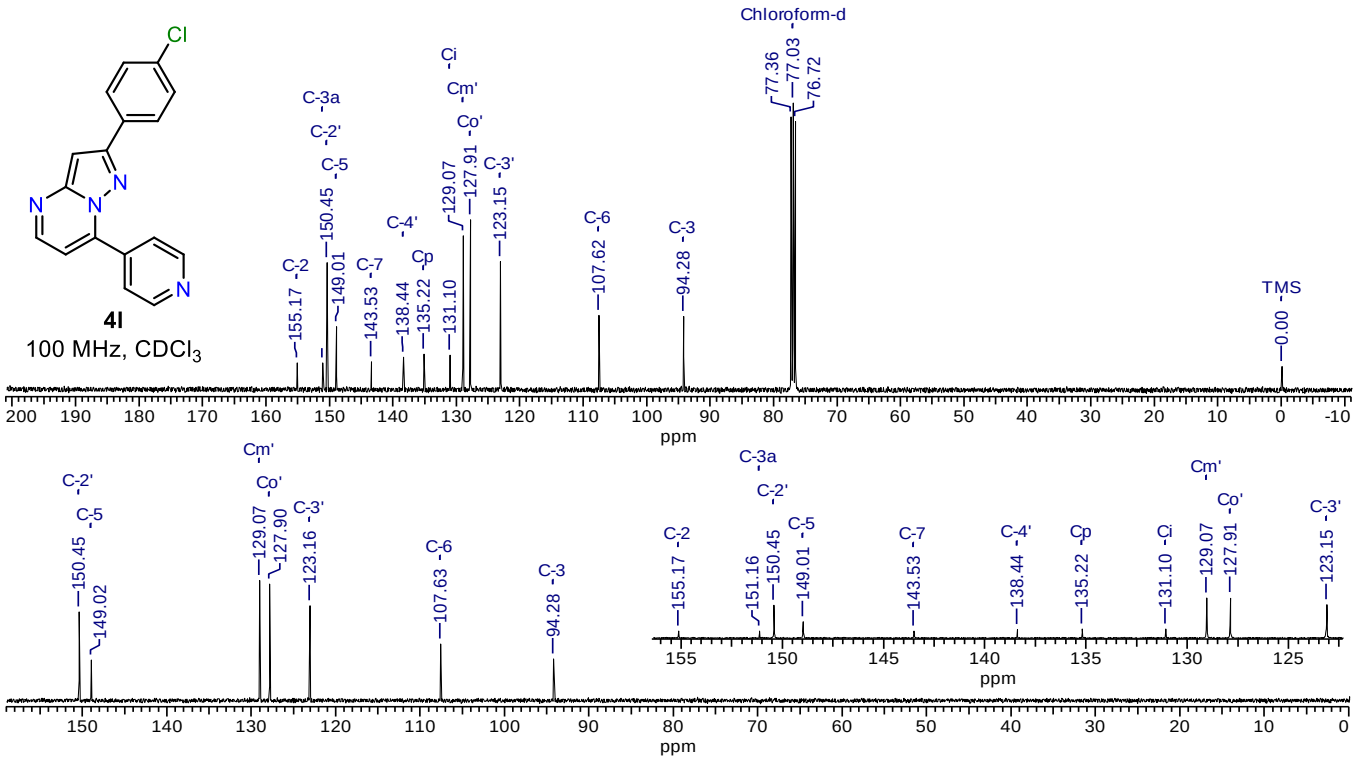


^{1}H and ^{13}C{^{1}H} NMR spectra of 2-(4-chlorophenyl)-7-(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine **4k**

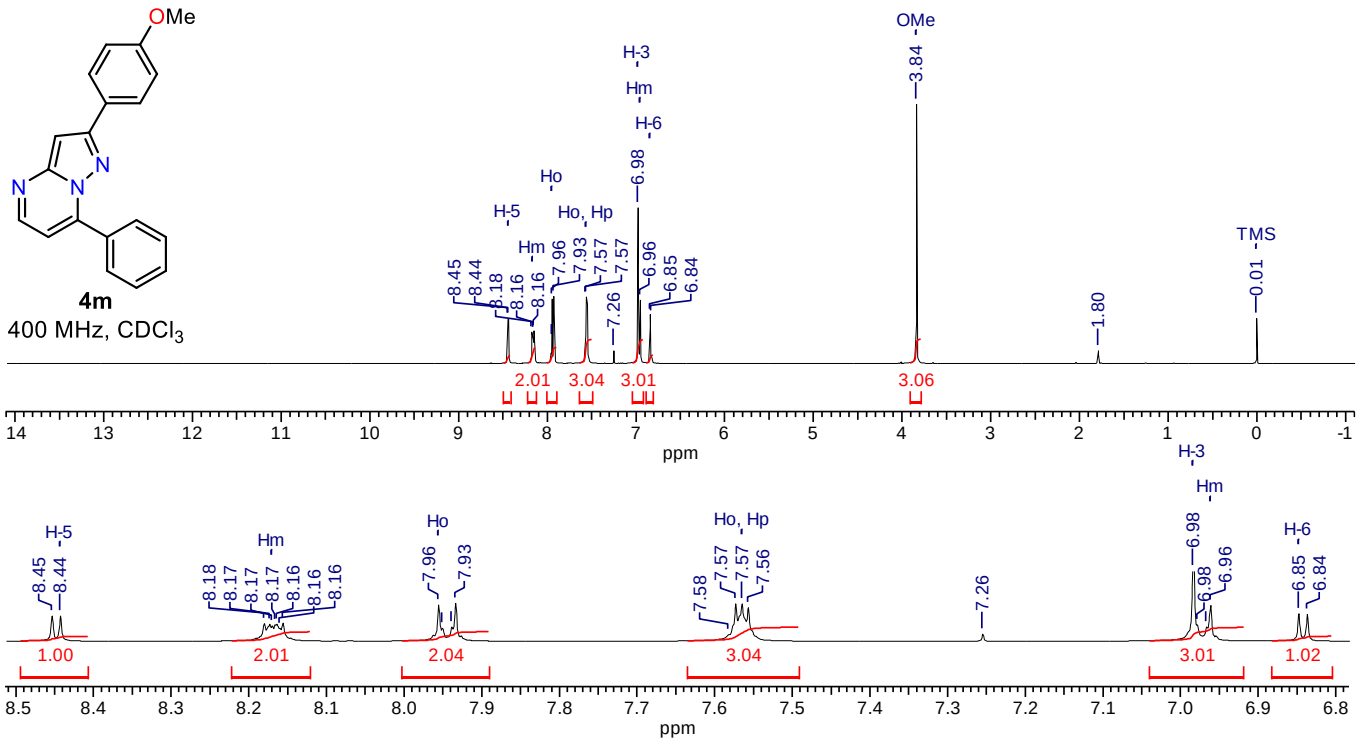


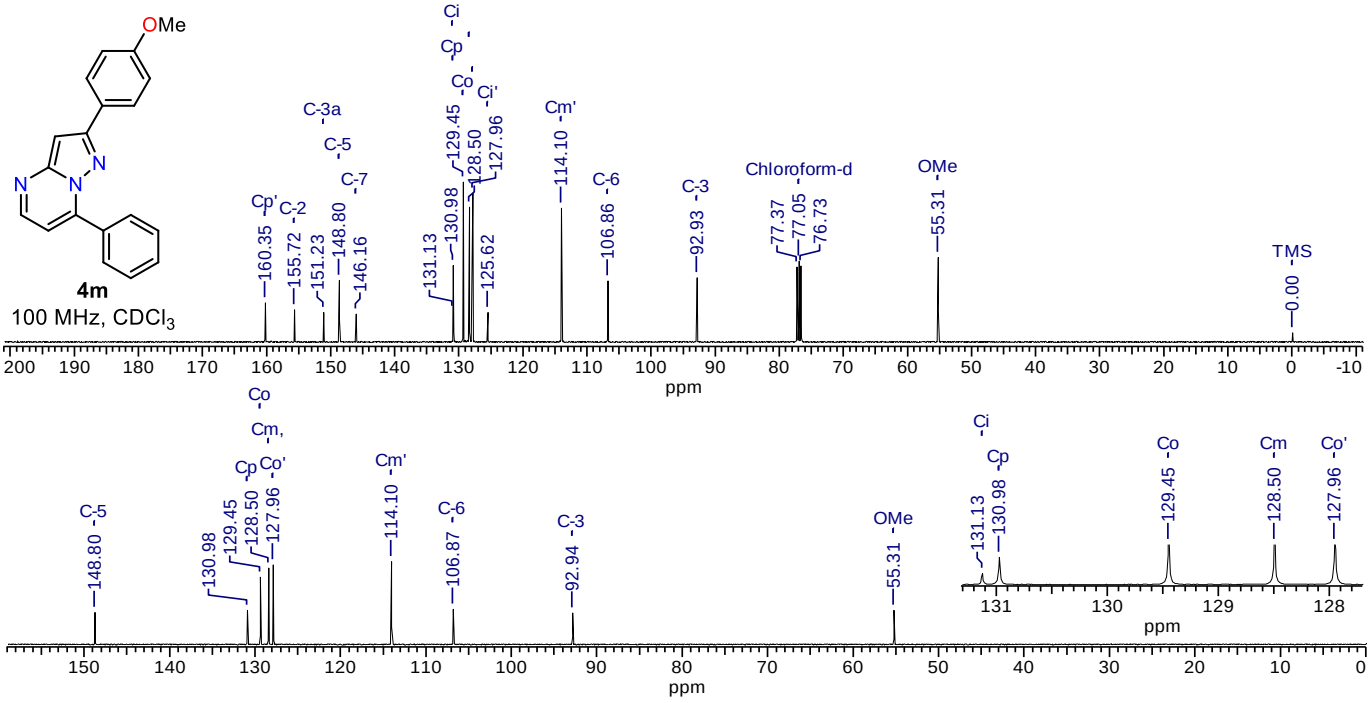
^{1}H and ^{13}C{^{1}H} NMR spectra of 2-(4-chlorophenyl)-7-(pyridin-4-yl)pyrazolo[1,5-*a*]pyrimidine **4l**



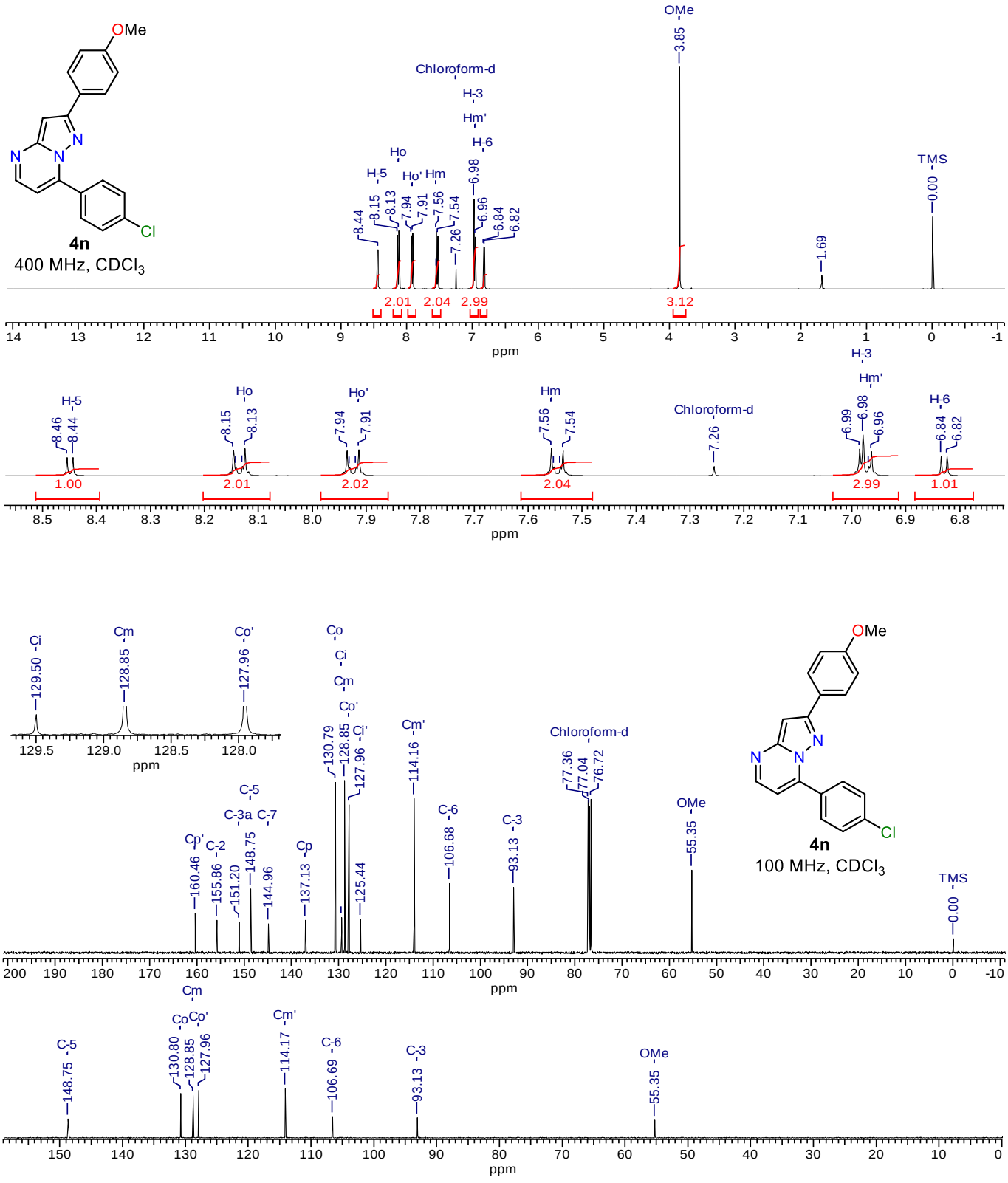


^{1}H and ^{13}C{^{1}H} NMR spectra of 2-(4-methoxyphenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine **4m**

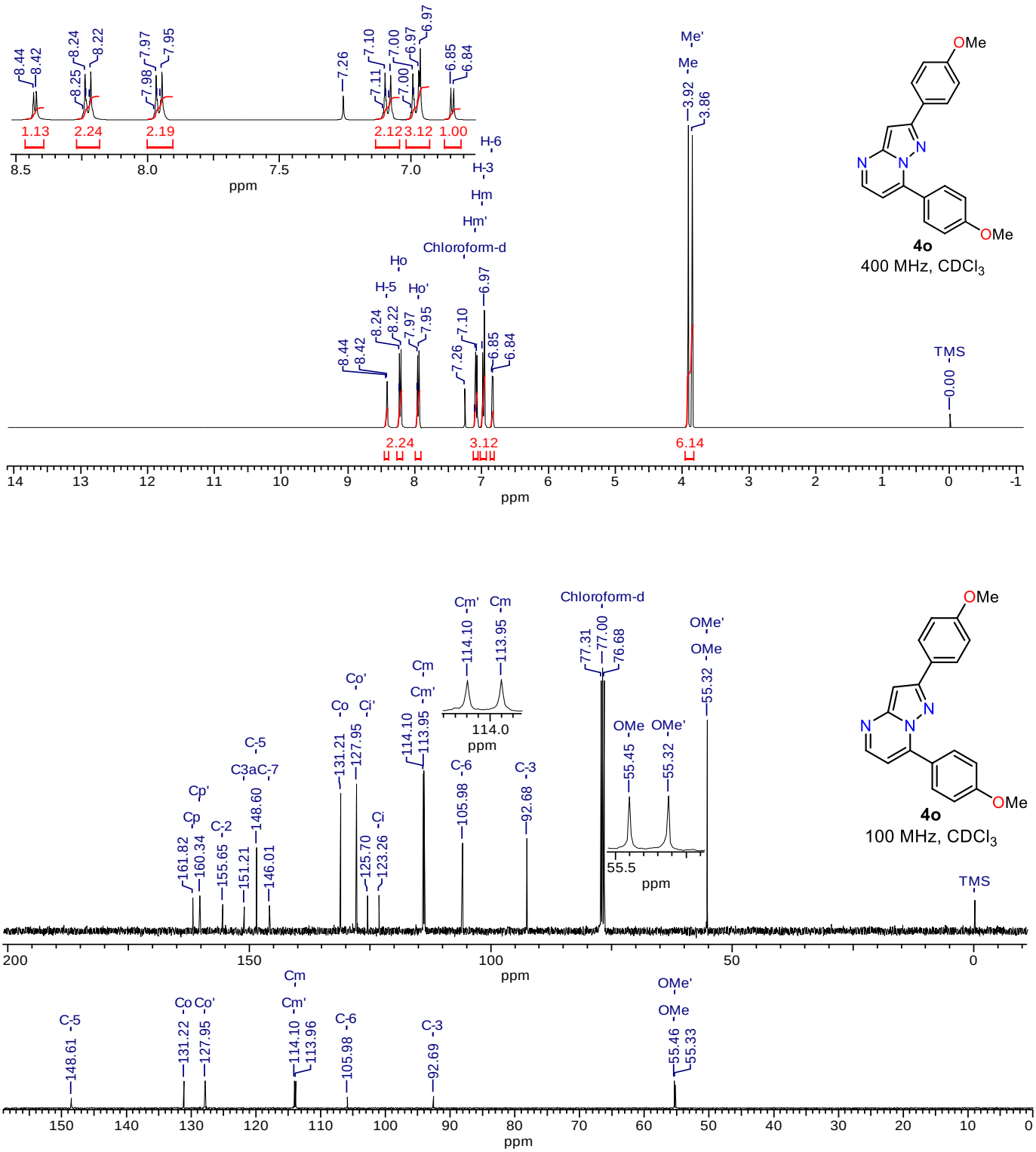




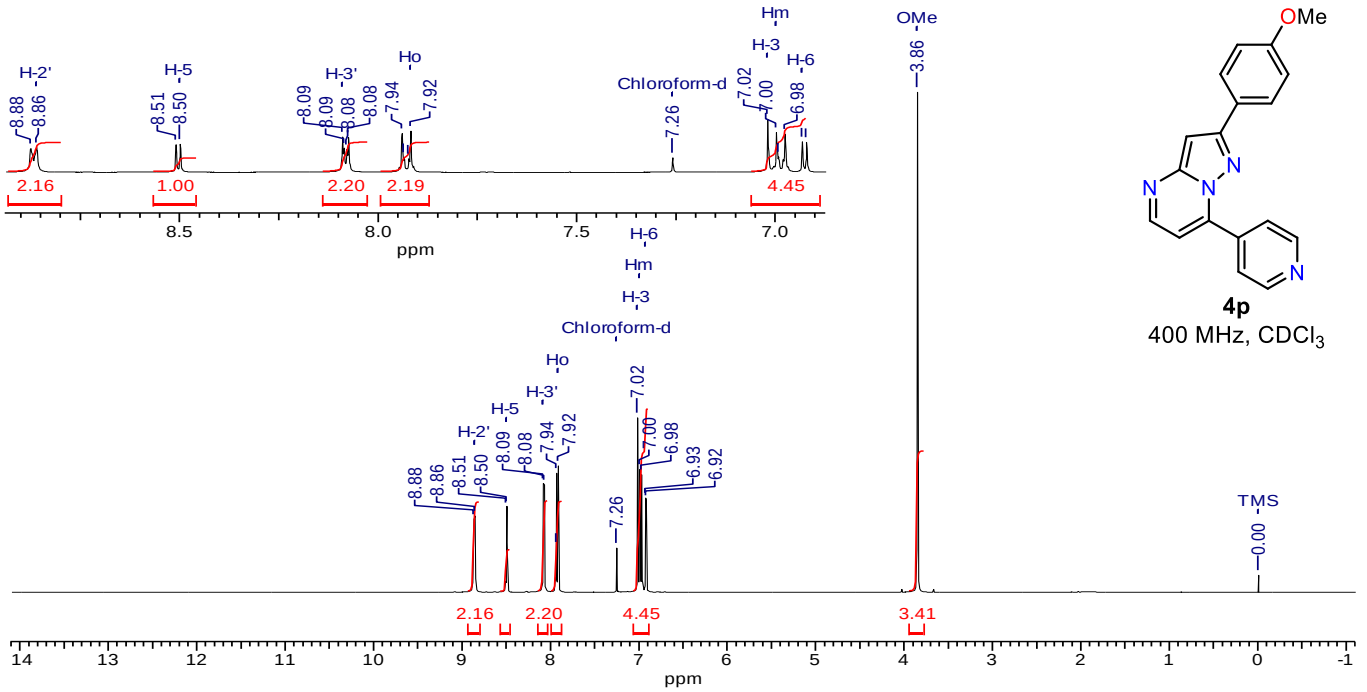
^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-chlorophenyl)-2-(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine **4n**

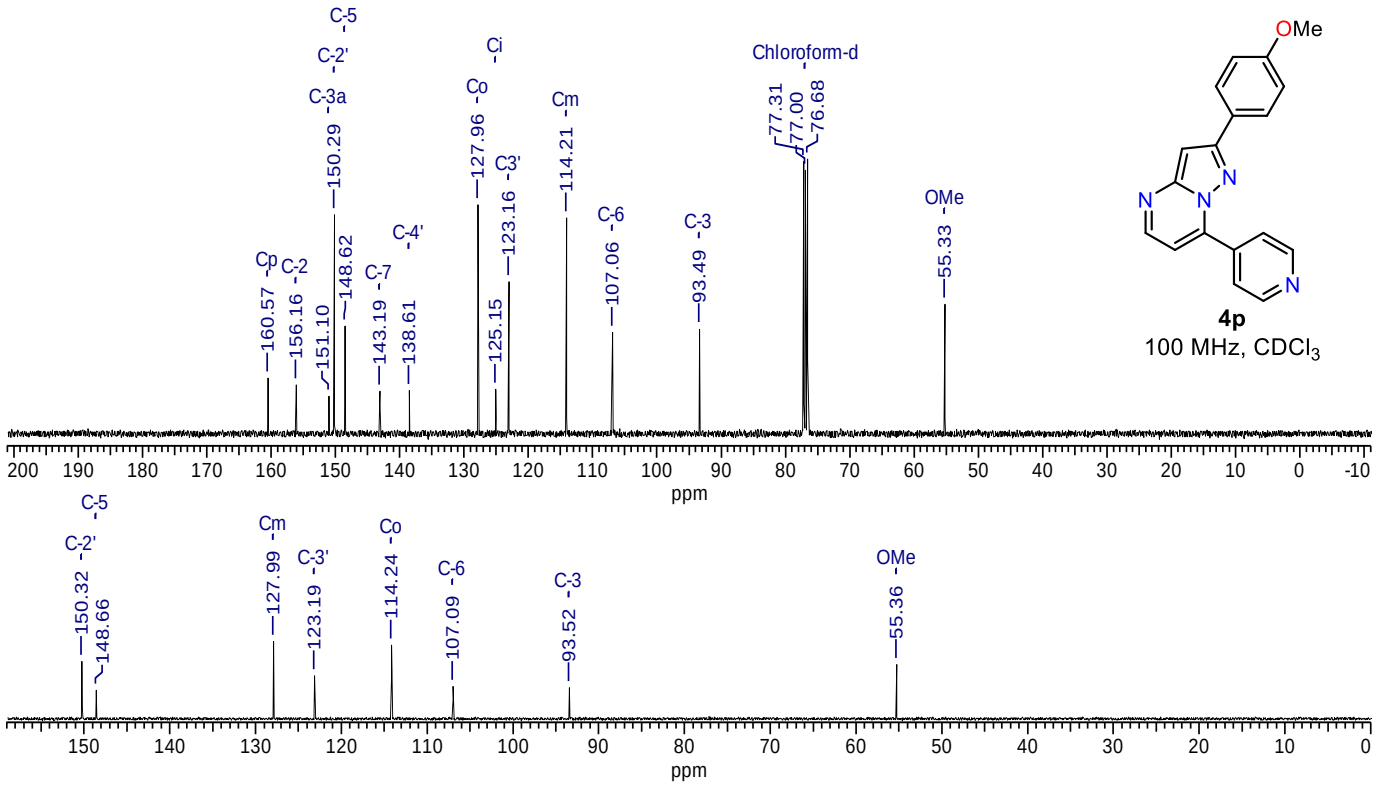


^{1}H and ^{13}C{^{1}H} NMR spectra of 2,7-*bis*(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine **4o**

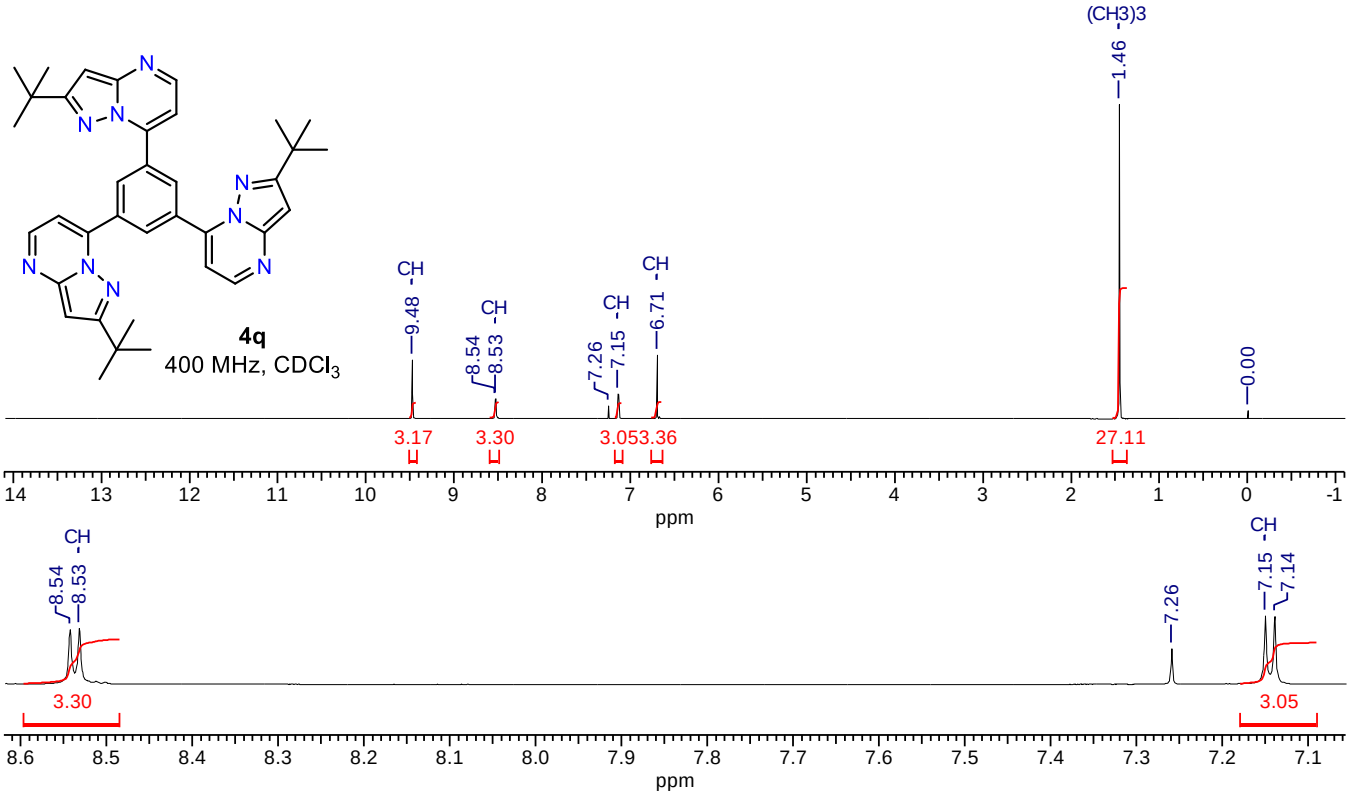


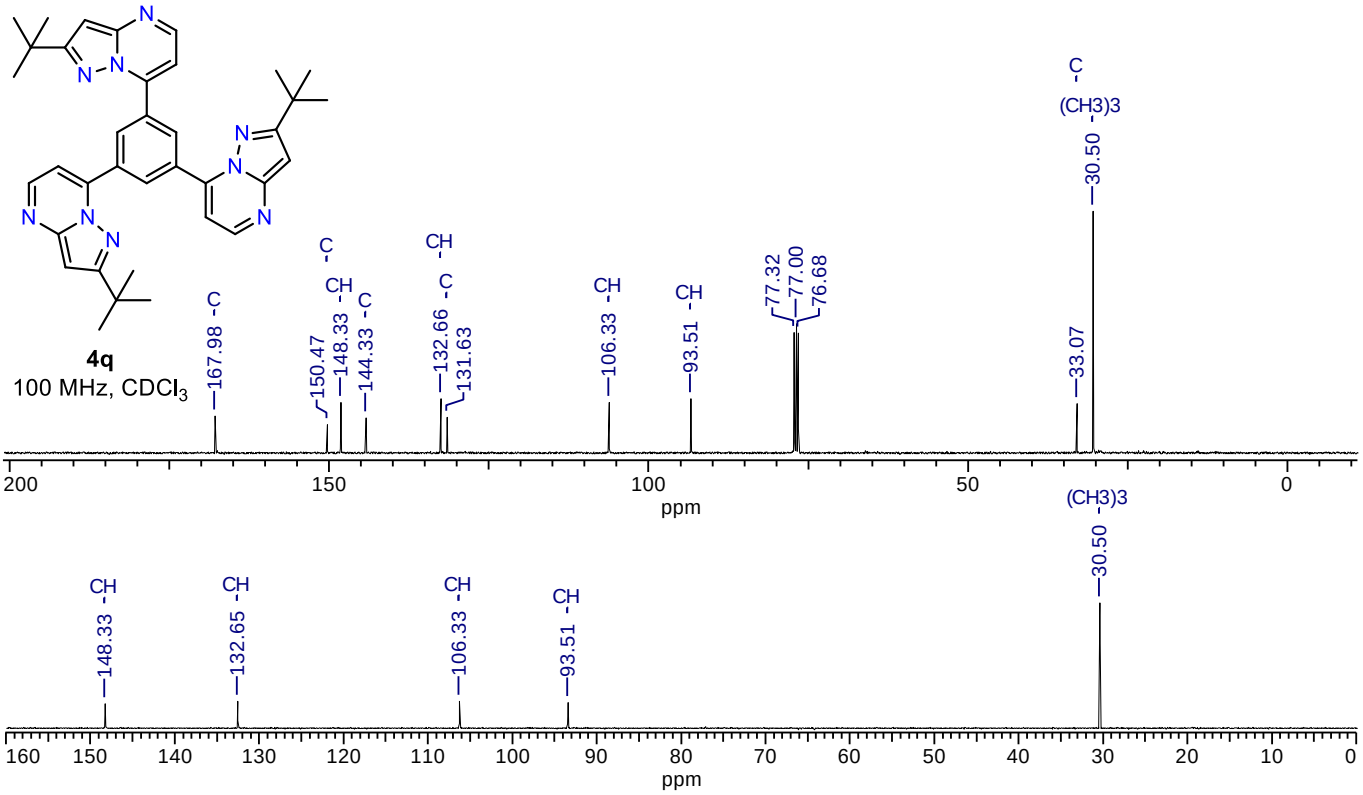
^{1}H and ^{13}C{^{1}H} NMR spectra of 2-(4-methoxyphenyl)-7-(pyridin-4-yl)pyrazolo[1,5-*a*]pyrimidine **4p**



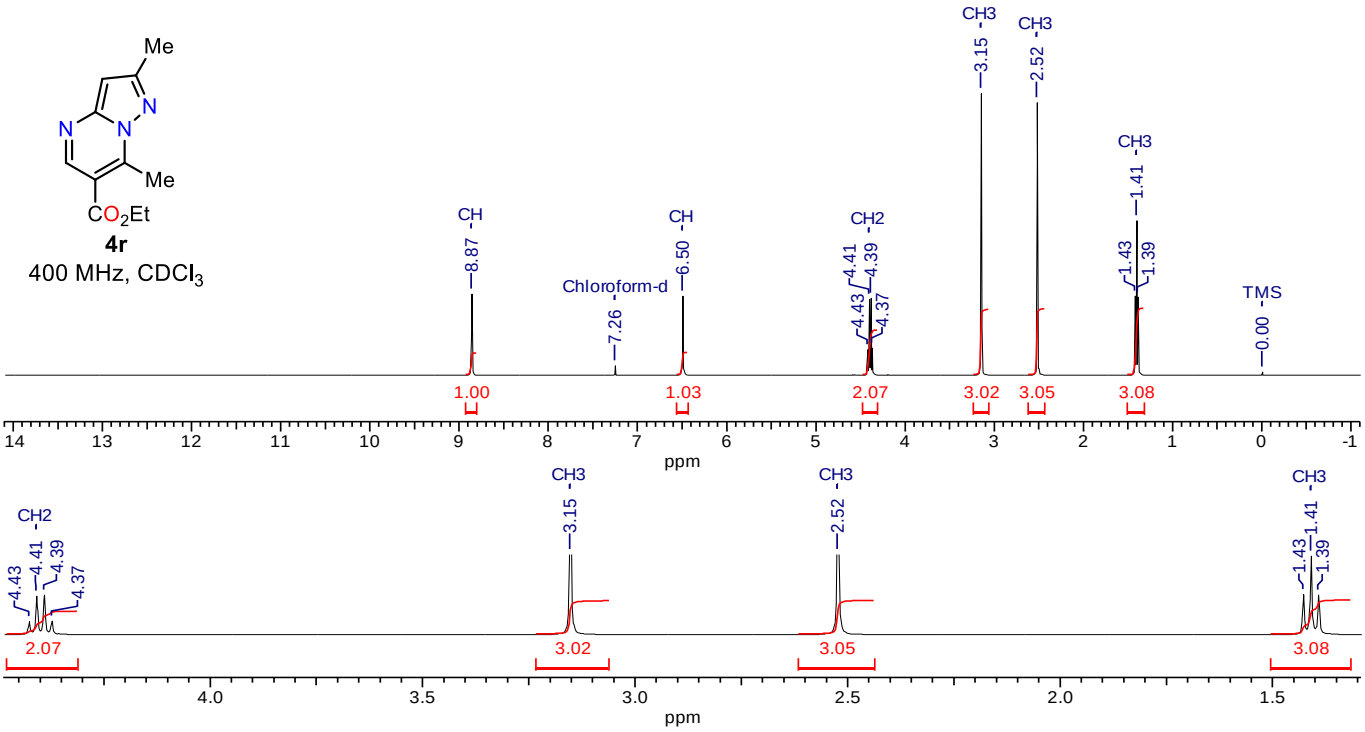


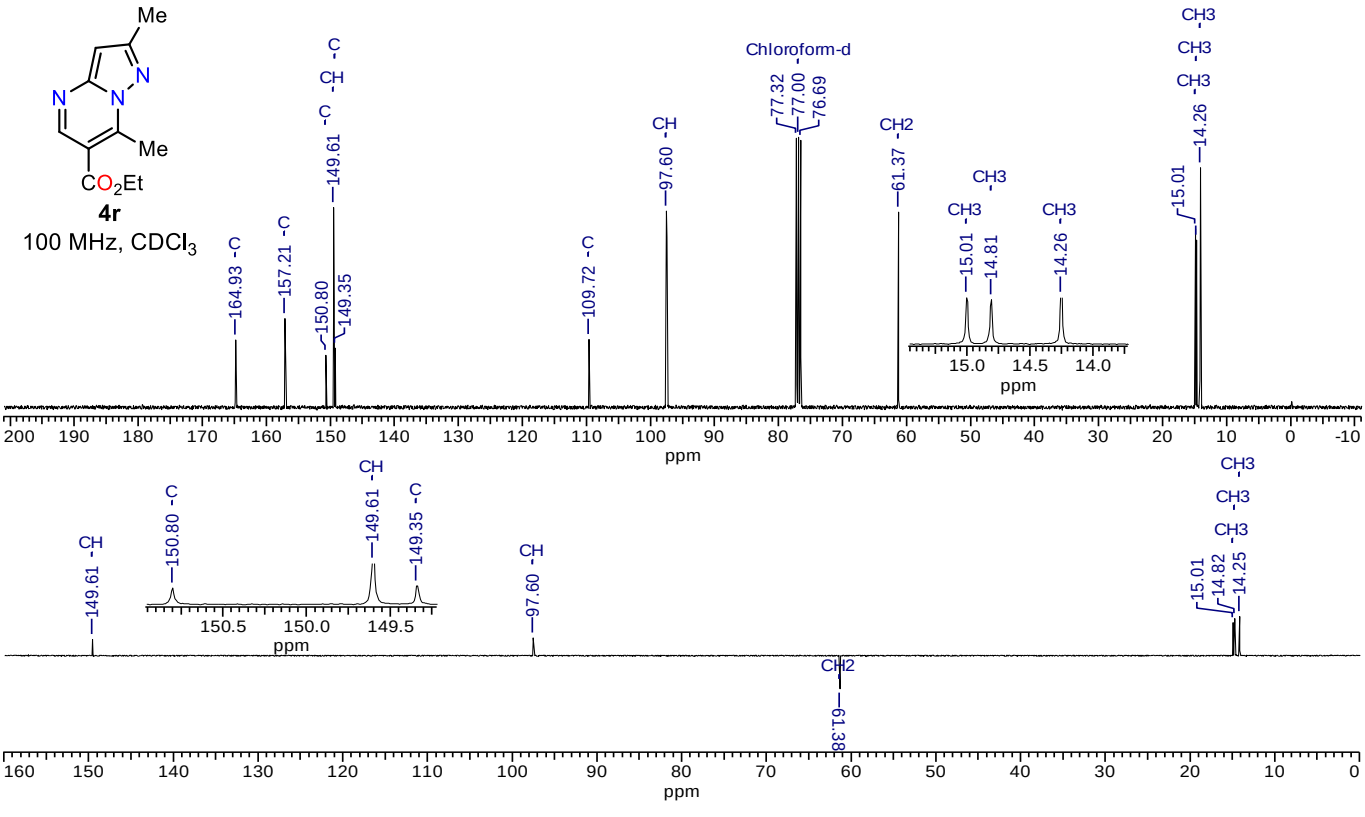
^{1}H and ^{13}C{^{1}H} NMR spectra of 1,3,5-*tris*(2-(*tert*-butyl)pyrazolo[1,5-*a*]pyrimidin-7-yl)benzene **4q**



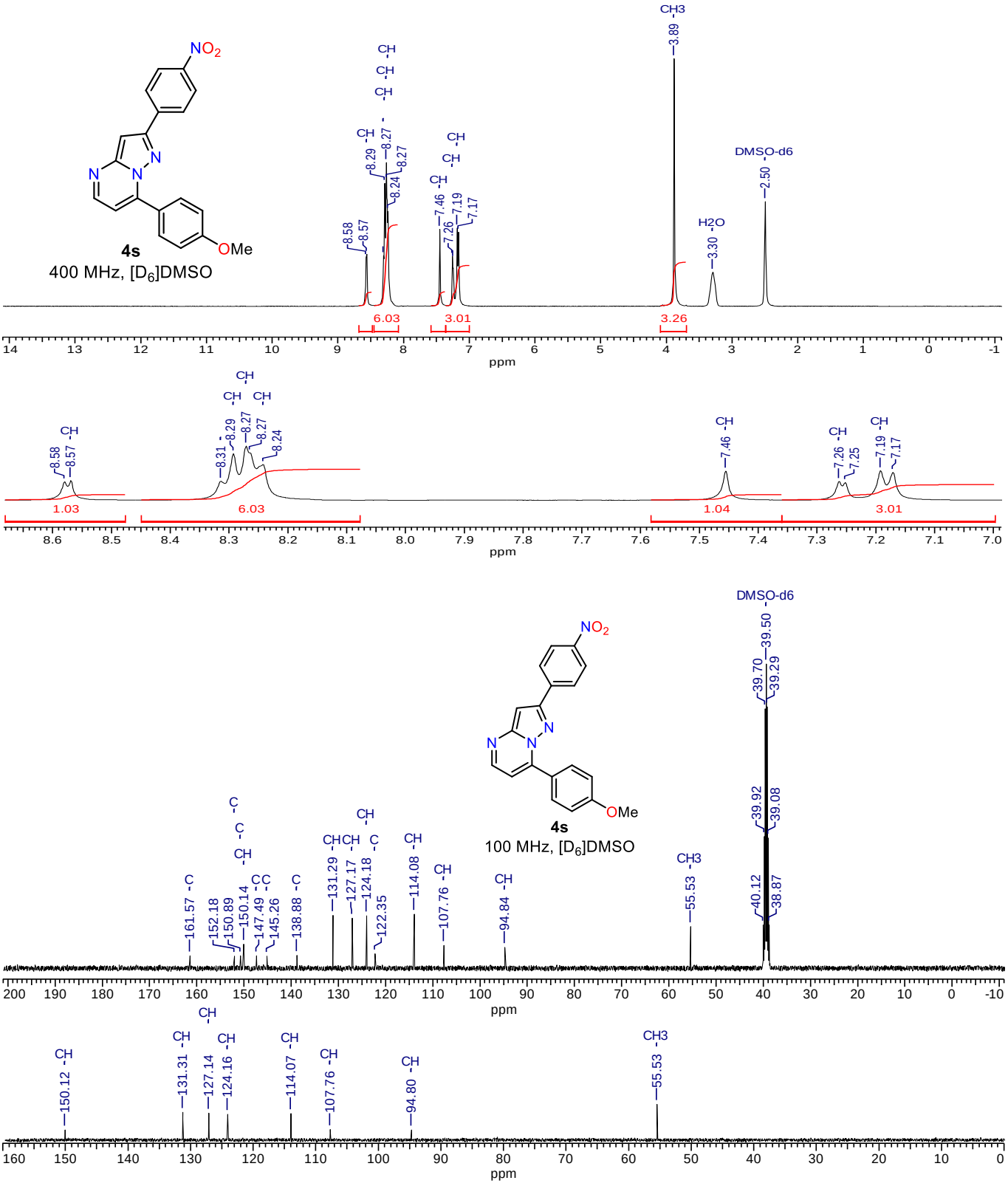


^{1}H and ^{13}C{^{1}H} NMR spectra of ethyl 2,7-dimethylpyrazolo[1,5-*a*]pyrimidine-6-carboxylate **4r**

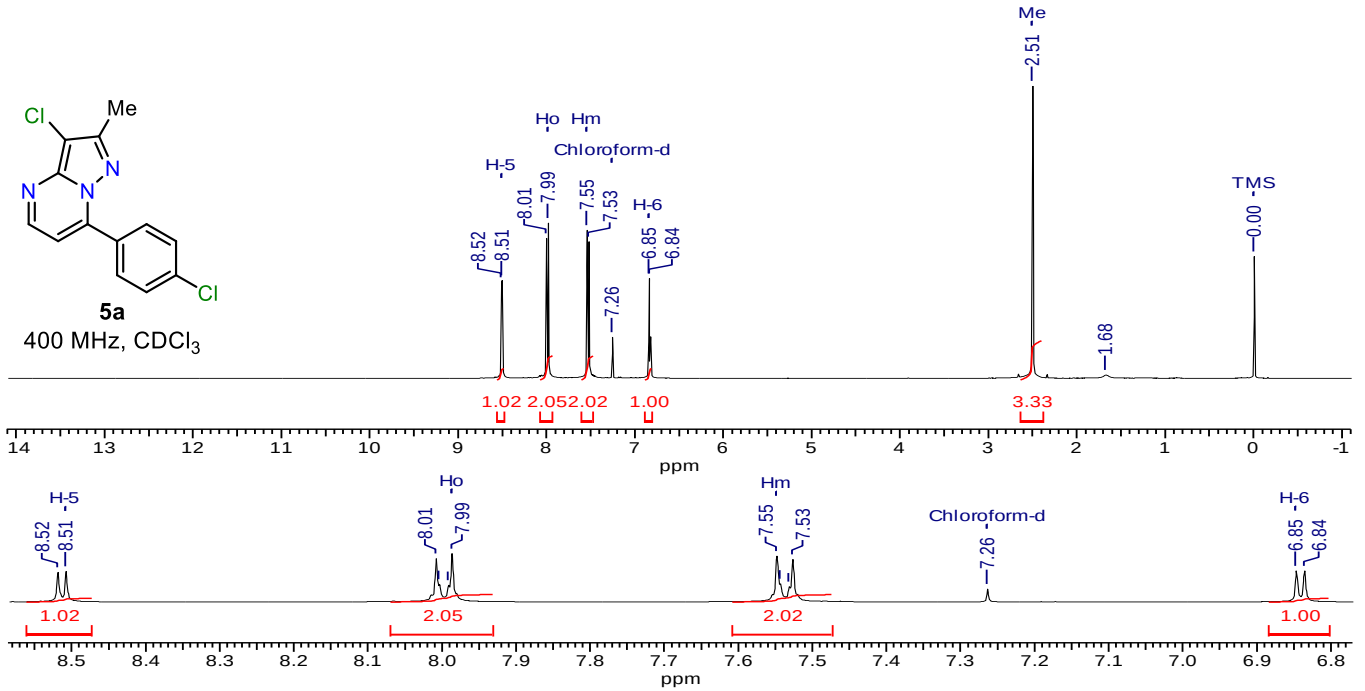


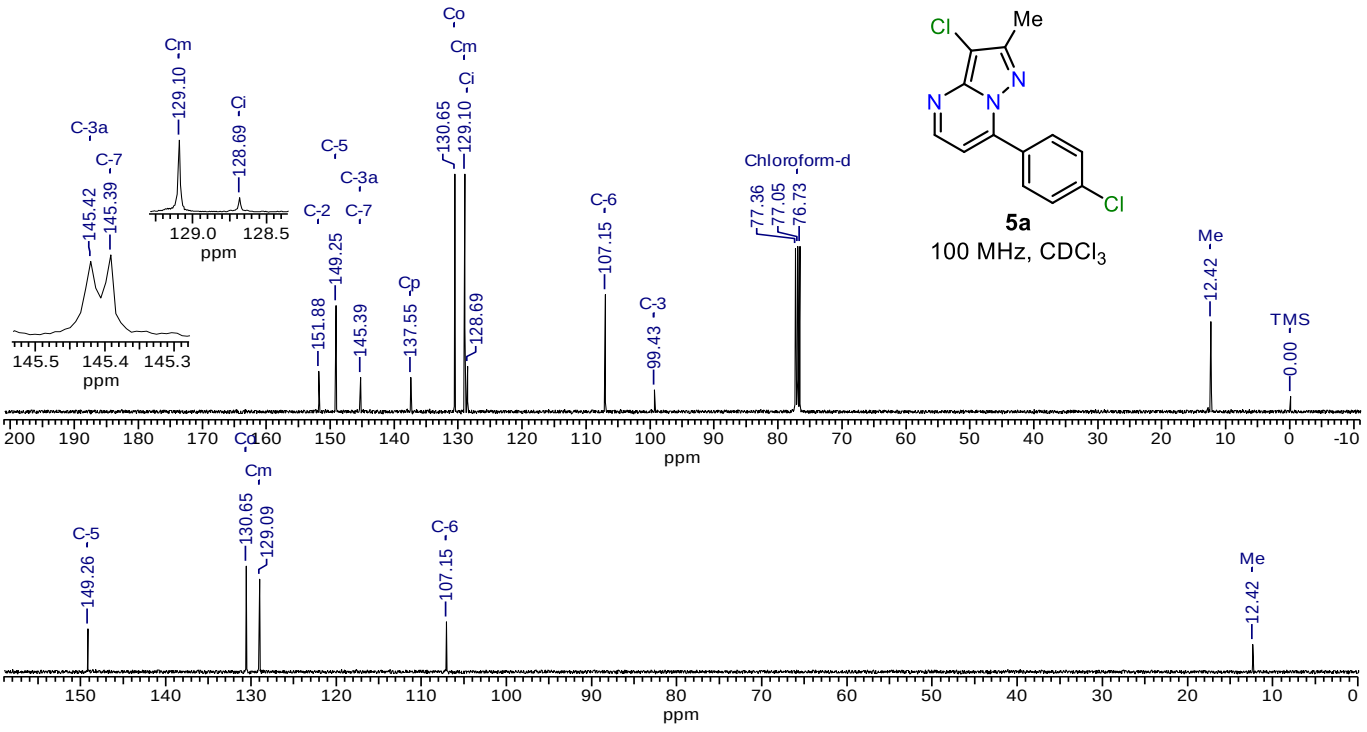


^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-methoxyphenyl)-2-(4-nitrophenyl)pyrazolo[1,5-*a*]pyrimidine **4s**

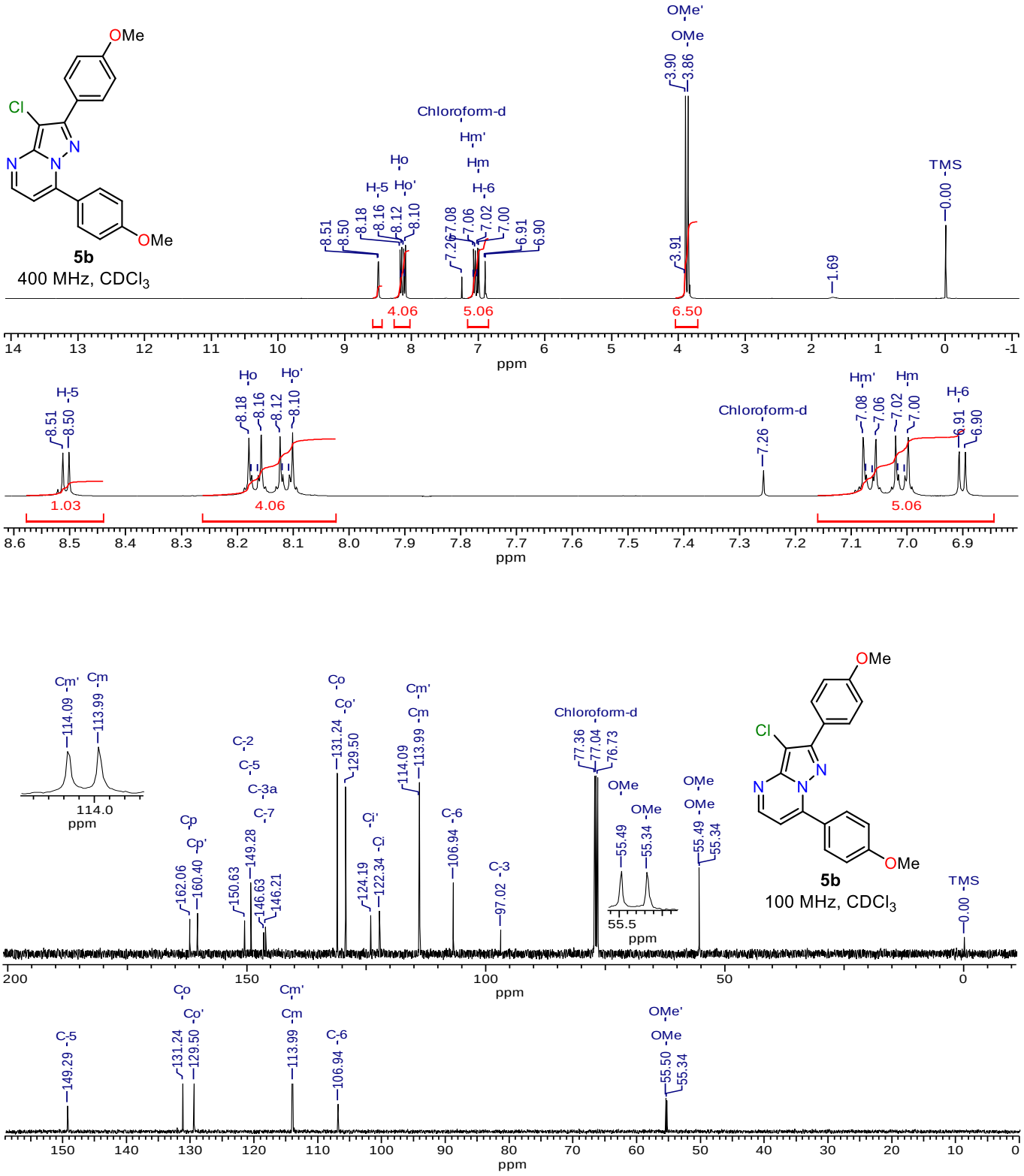


^{1}H and ^{13}C{^{1}H} NMR spectra of 3-chloro-7-(4-chlorophenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine **5a**

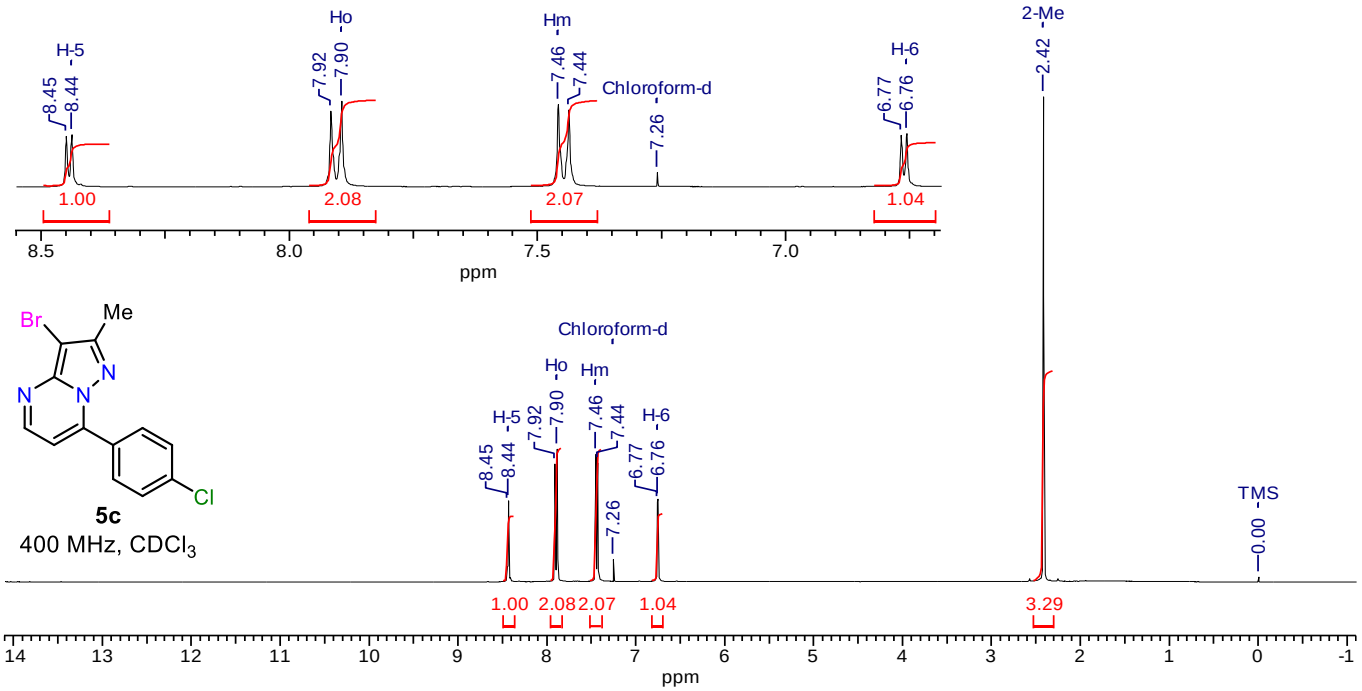


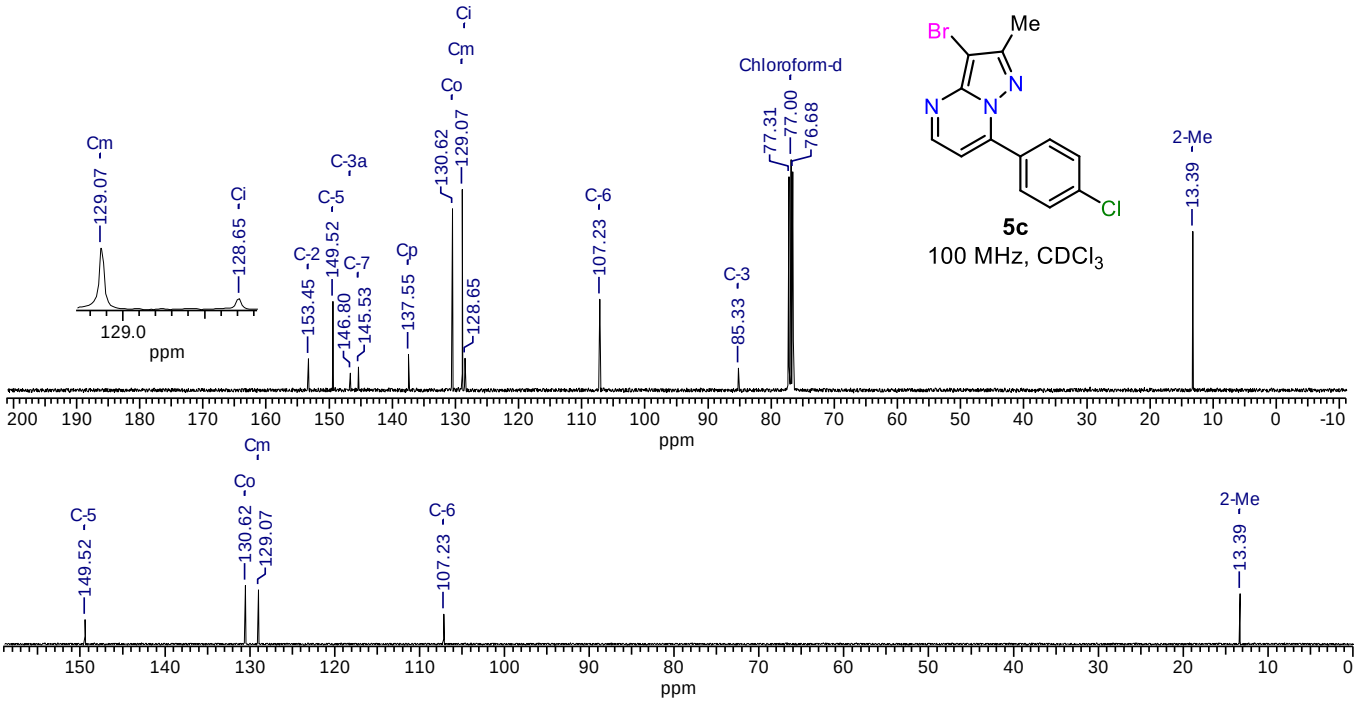


^{1}H and ^{13}C{^{1}H} NMR spectra of 3-chloro-2,7-*bis*(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine **5b**

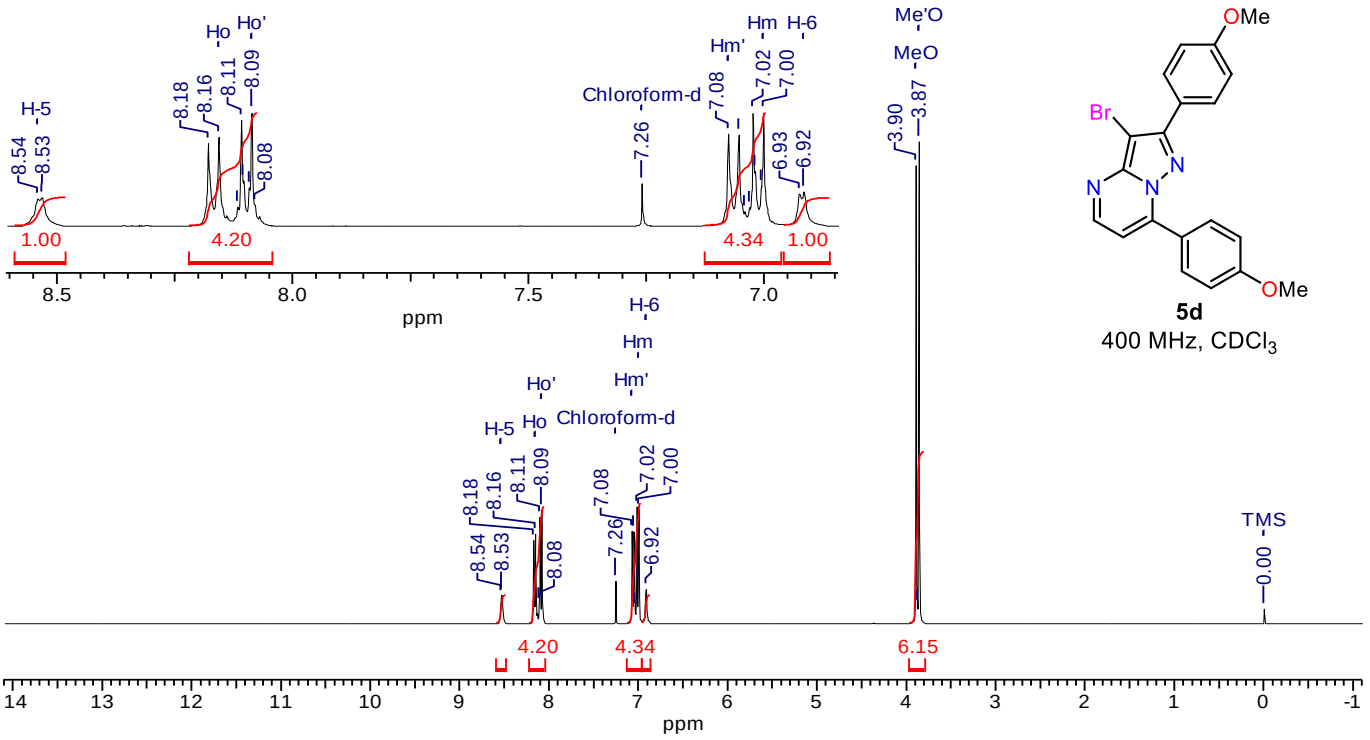


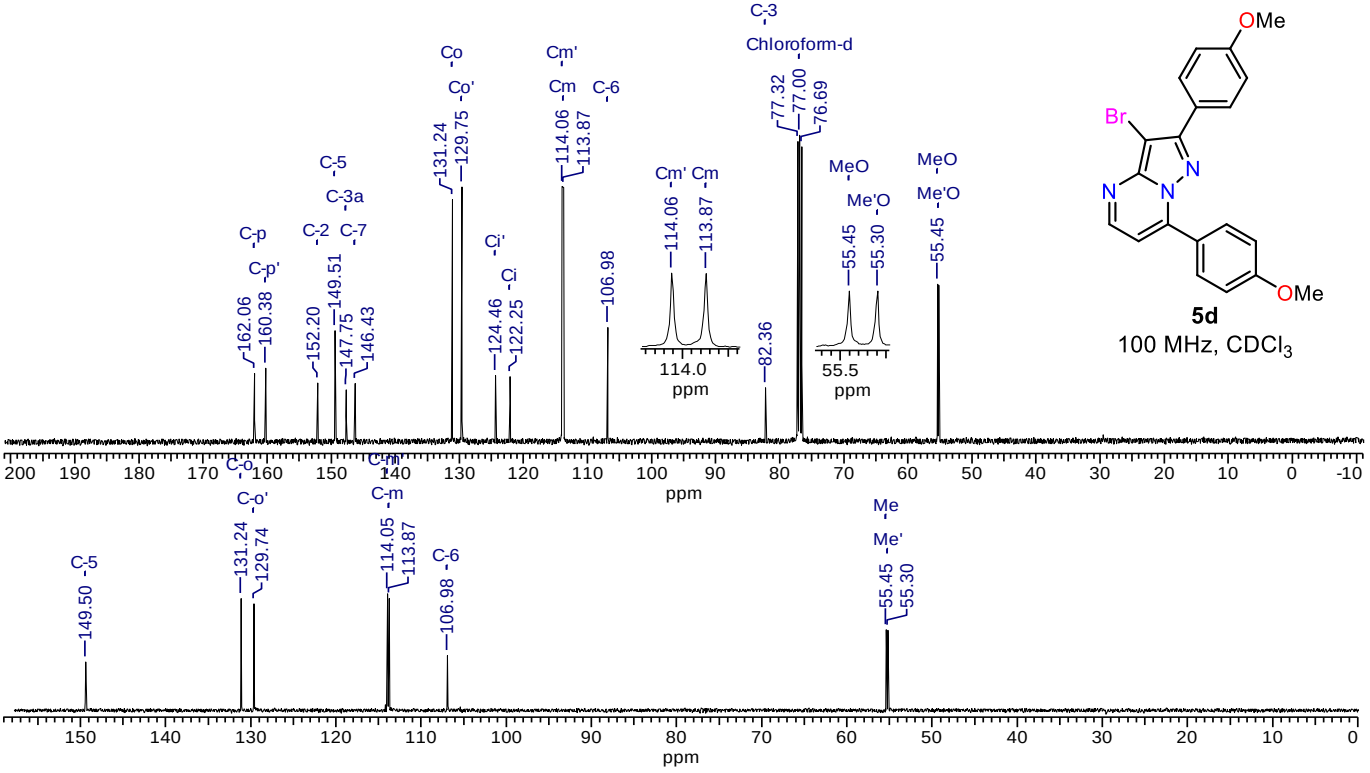
^{1}H and ^{13}C{^{1}H} NMR spectra of 3-bromo-7-(4-chlorophenyl)-2-methylpyrazolo[1,5-*a*]pyrimidine **5c**



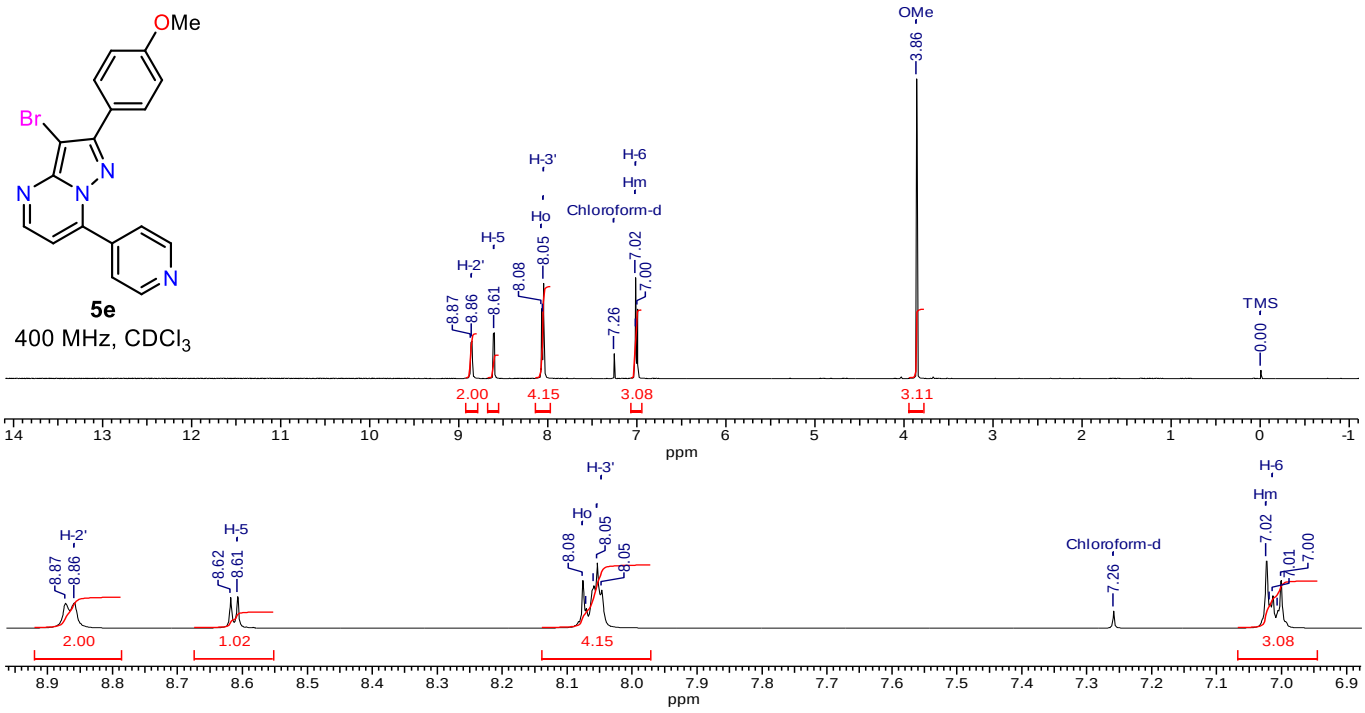


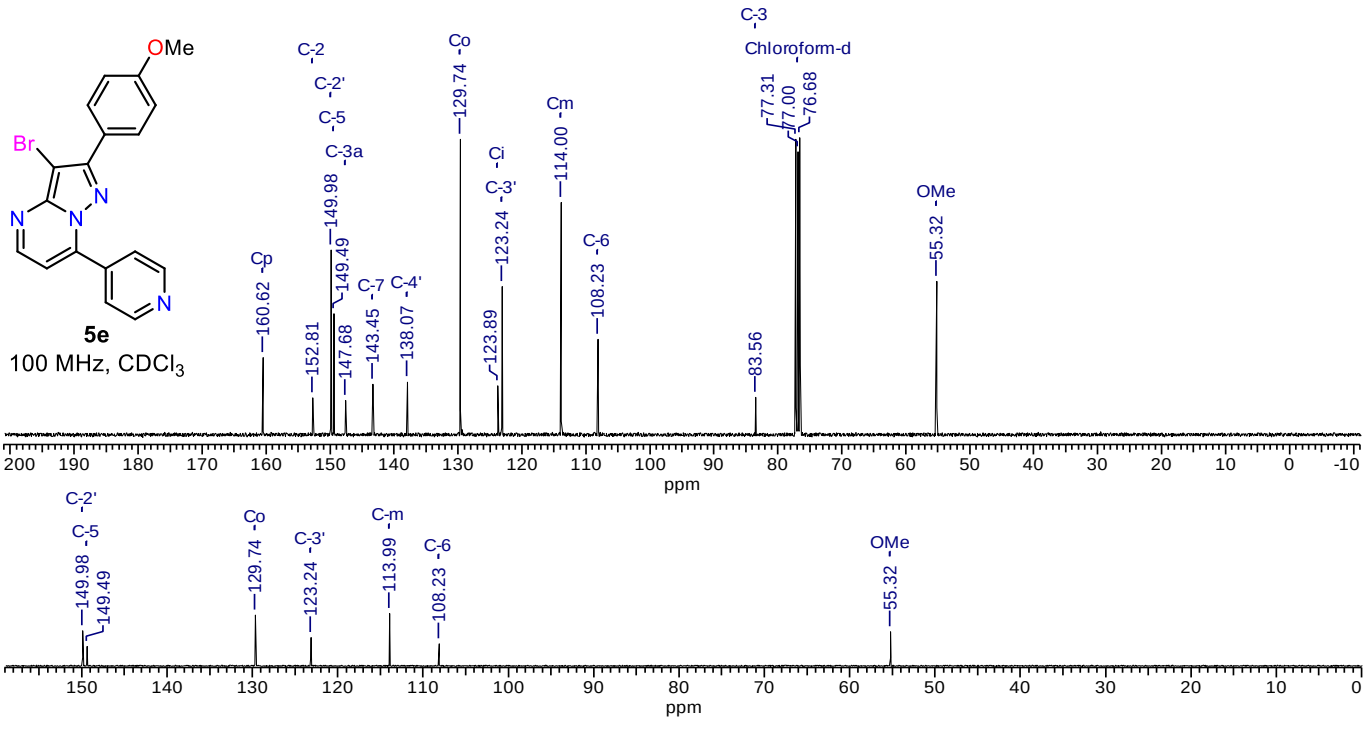
^{1}H and ^{13}C{^{1}H} NMR spectra of 3-bromo-2,7-*bis*(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine **5d**



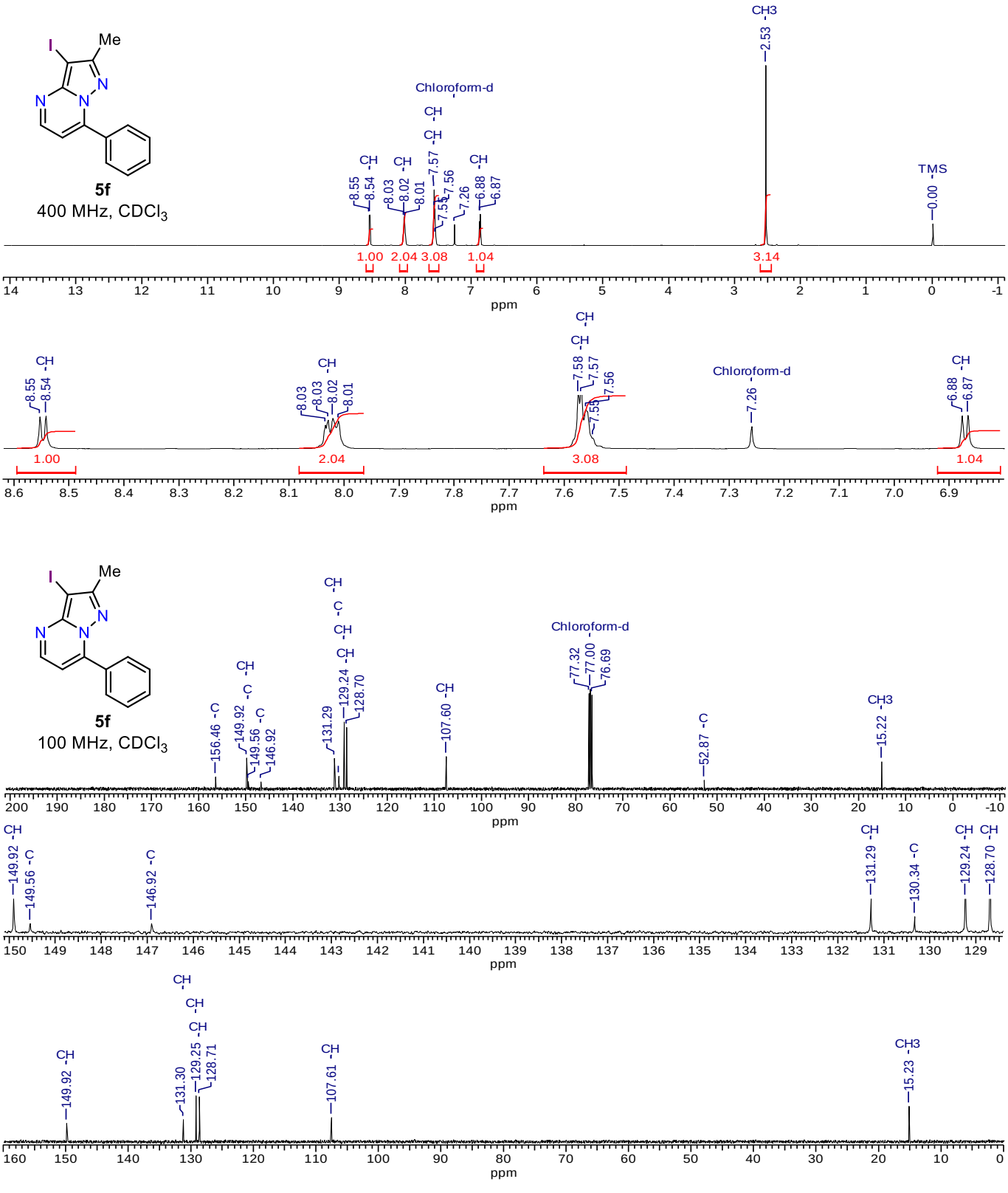


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 3-bromo-2-(4-methoxyphenyl)-7-(pyridin-4-yl)pyrazolo[1,5-*a*]pyrimidine **5e**

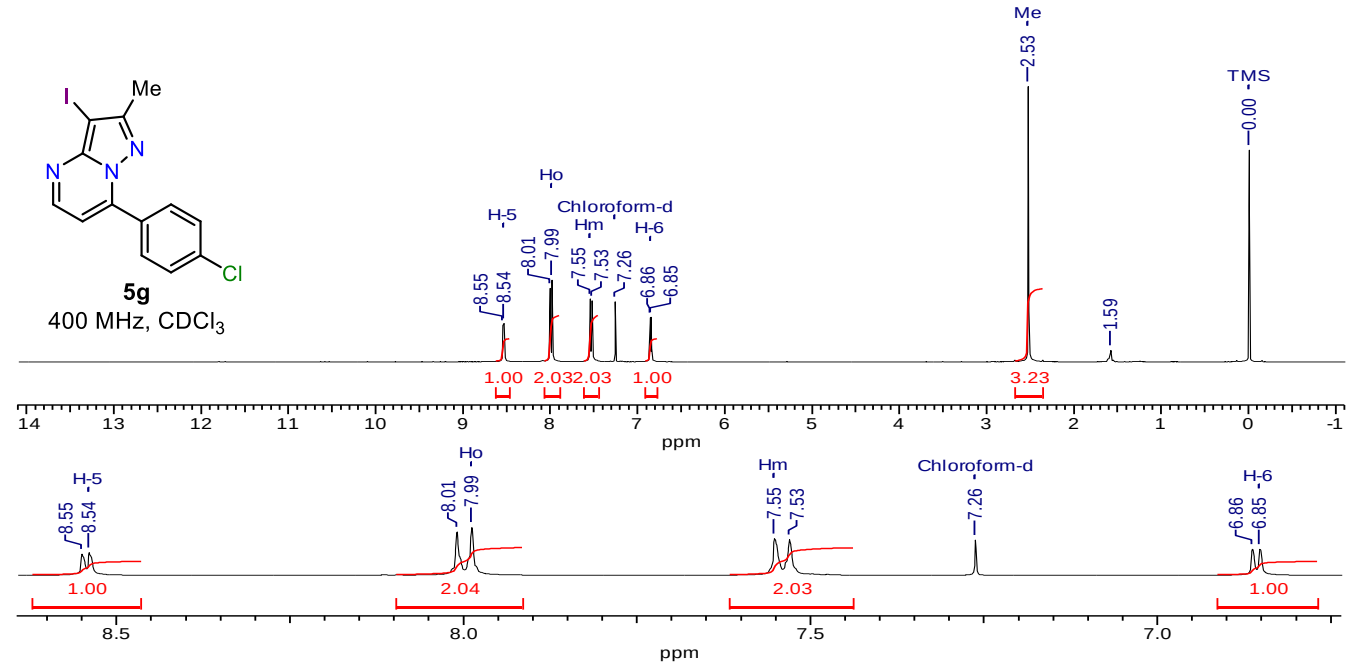


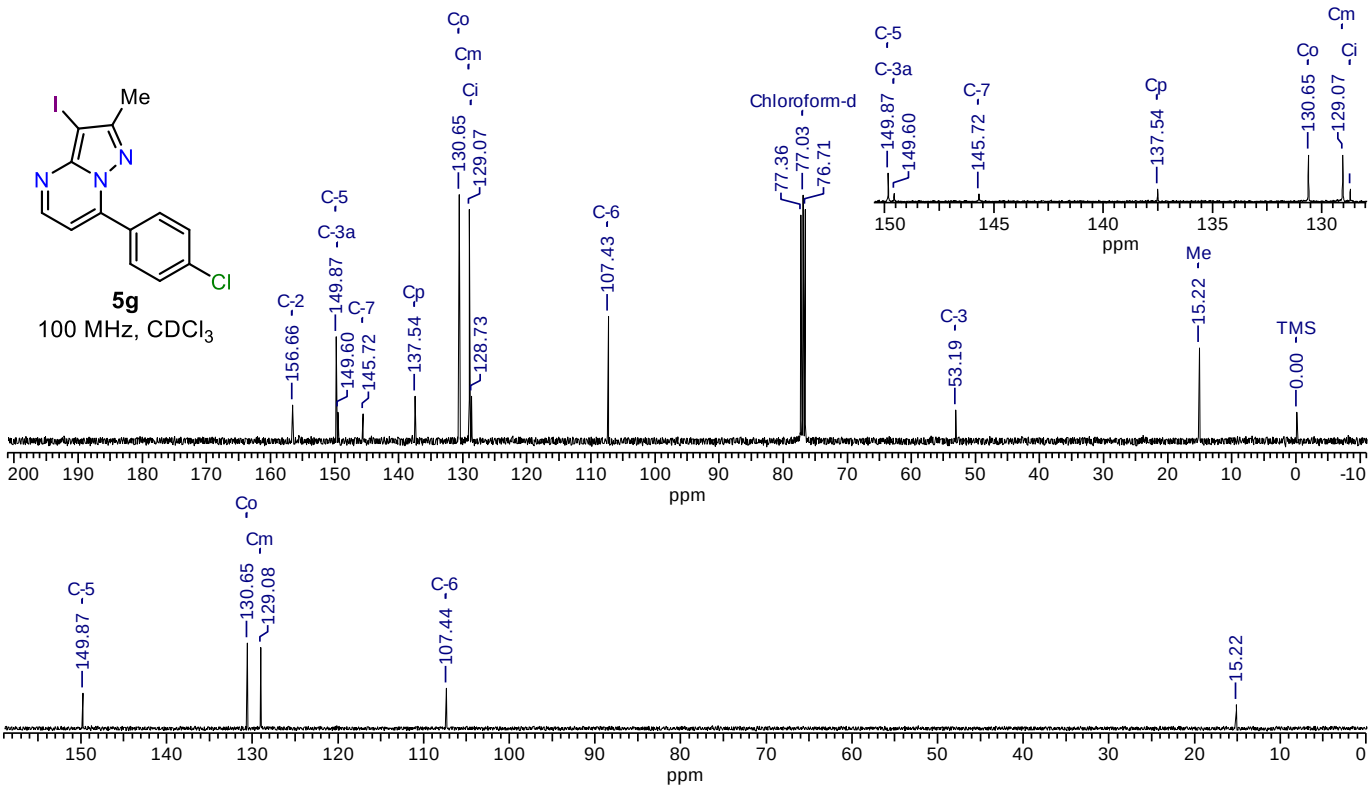


^{1}H and ^{13}C{^{1}H} NMR spectra of 3-iodo-2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine **5f**

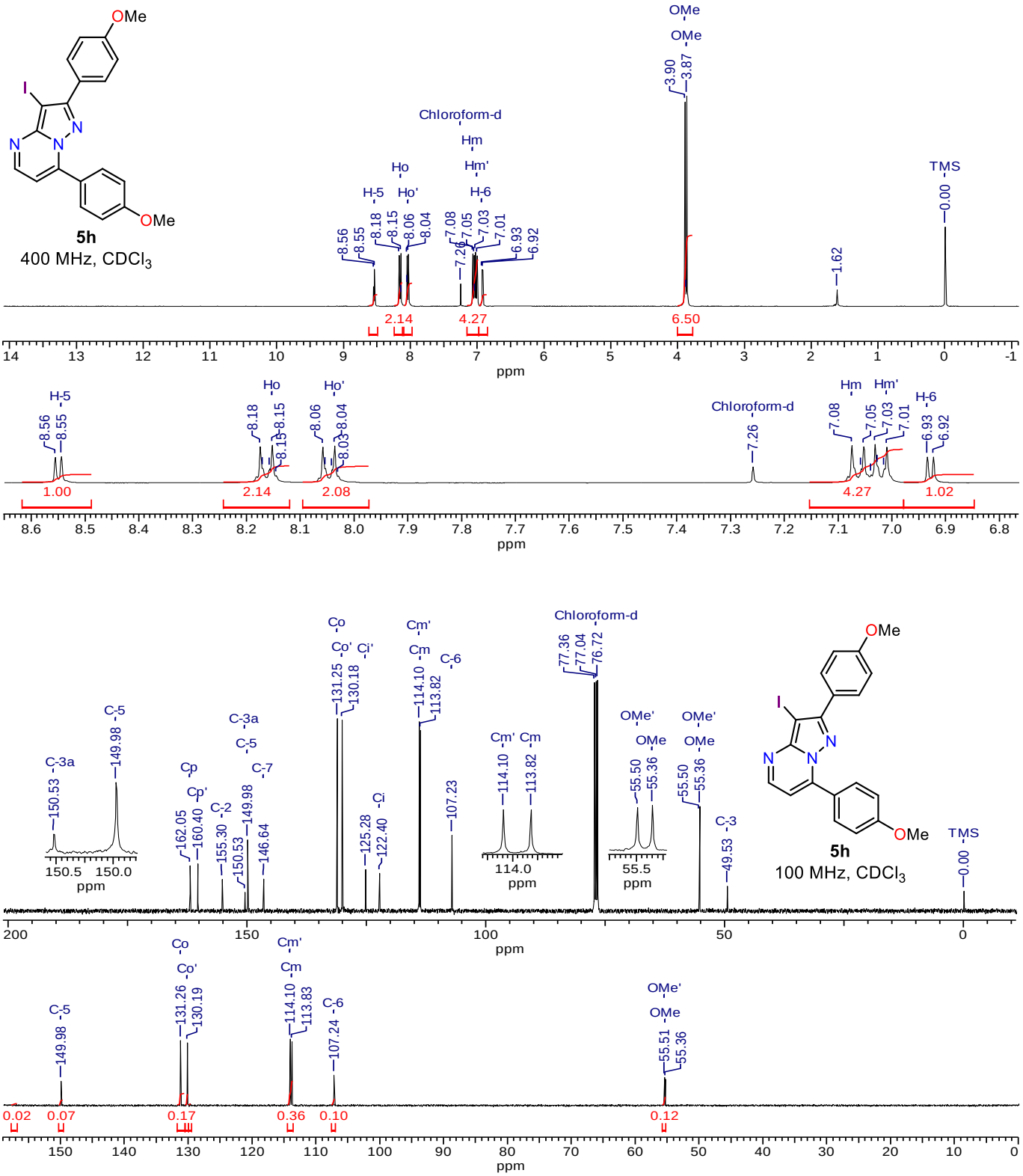


^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-chlorophenyl)-3-iodo-2-methylpyrazolo[1,5-*a*]pyrimidine **5g**

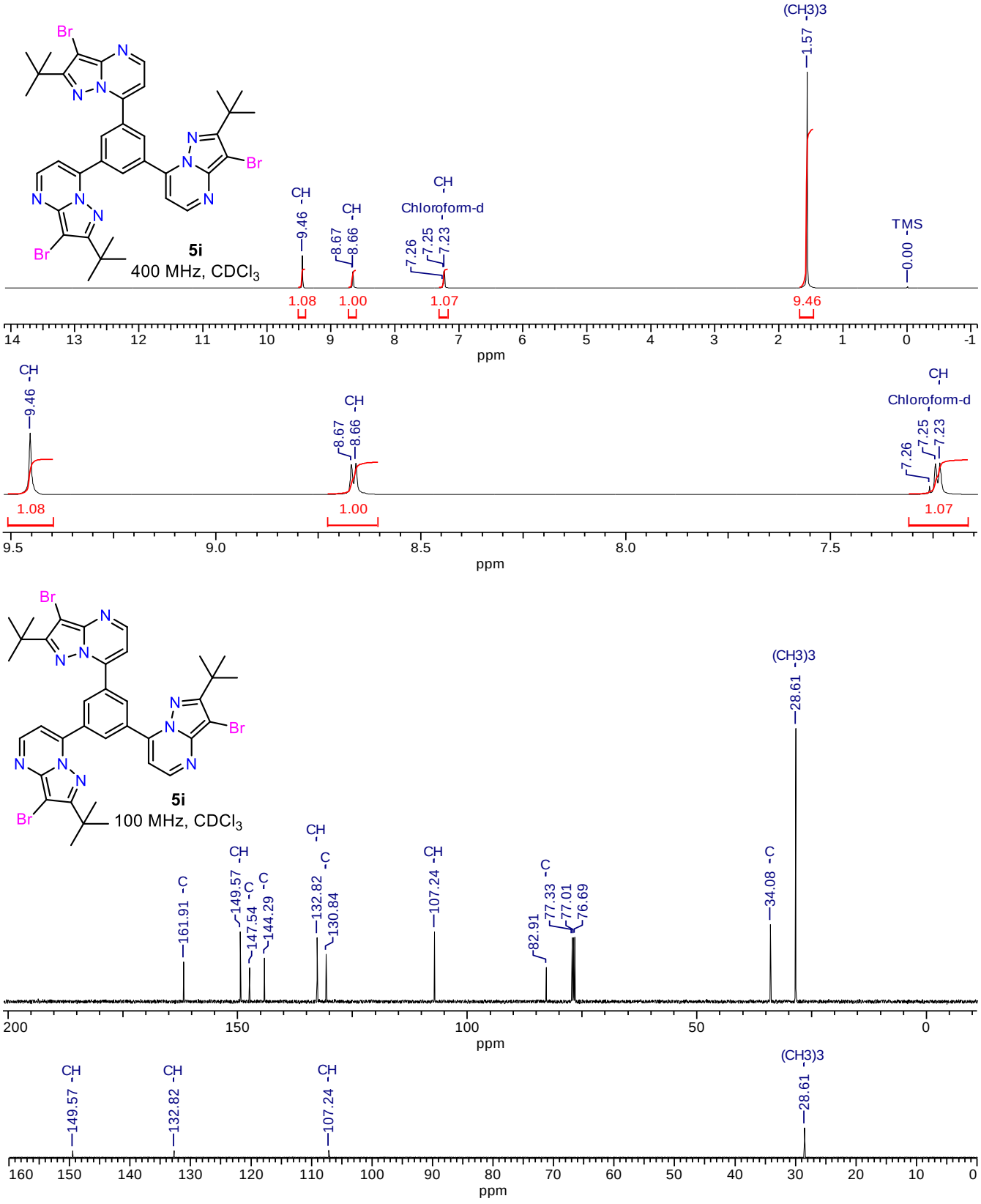




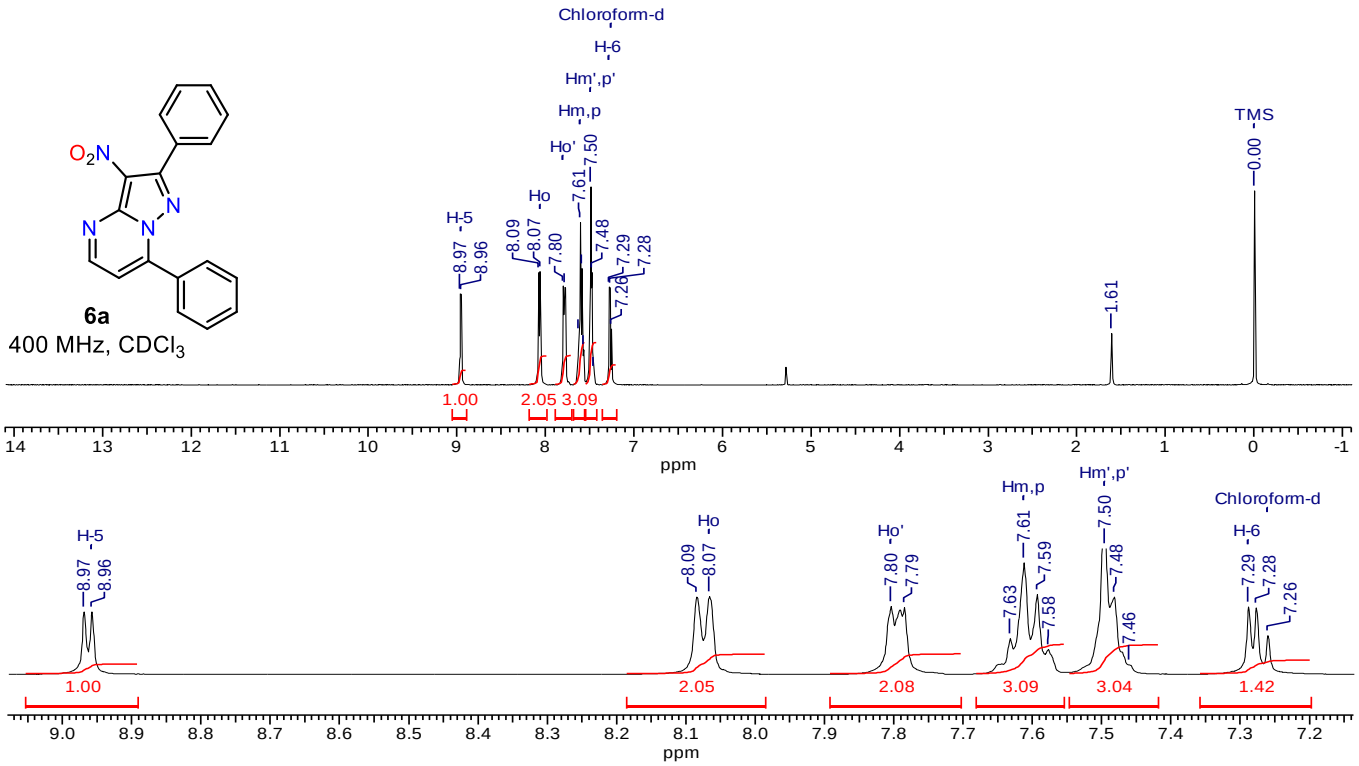
^{1}H and ^{13}C{^{1}H} NMR spectra of 3-iodo-2,7-*bis*(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine **5h**

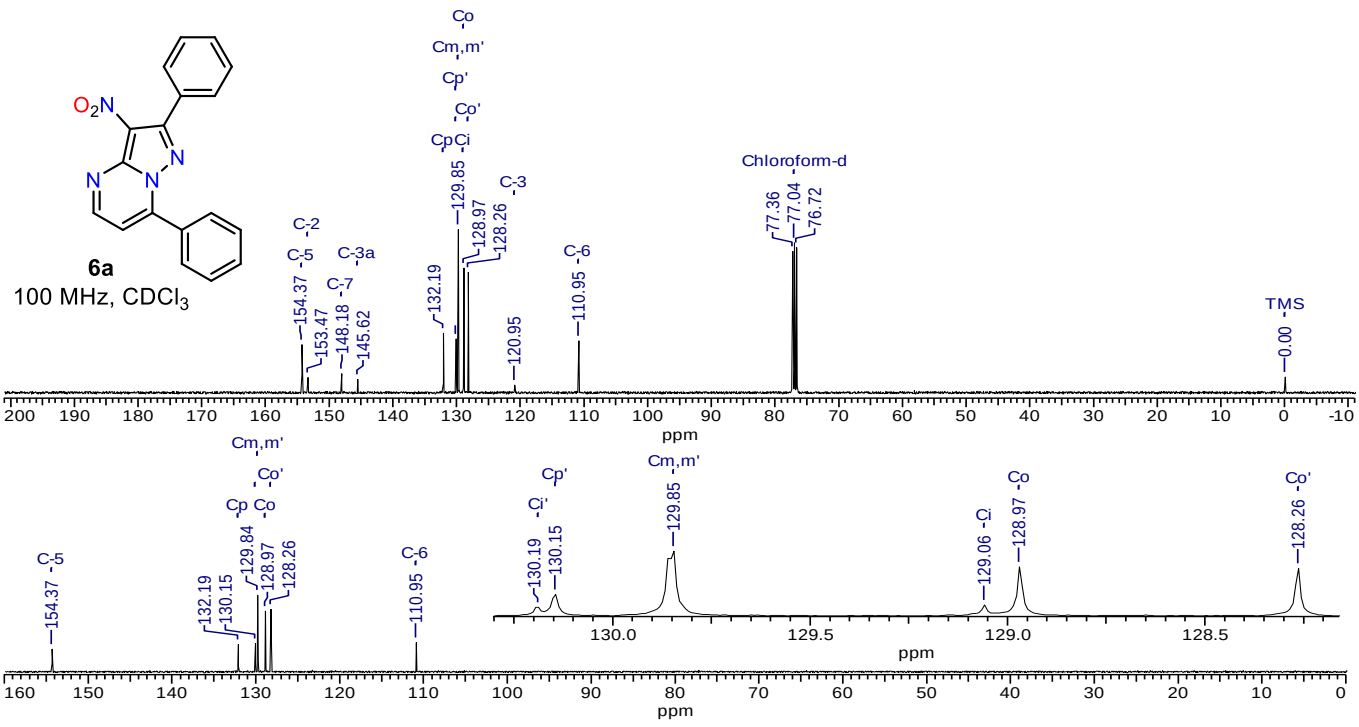


^{1}H and ^{13}C{^{1}H} NMR spectra of 1,3,5-*tris*(3-bromo-2-(*tert*-butyl)pyrazolo[1,5-*a*]pyrimidin-7-yl)benzene **5i**

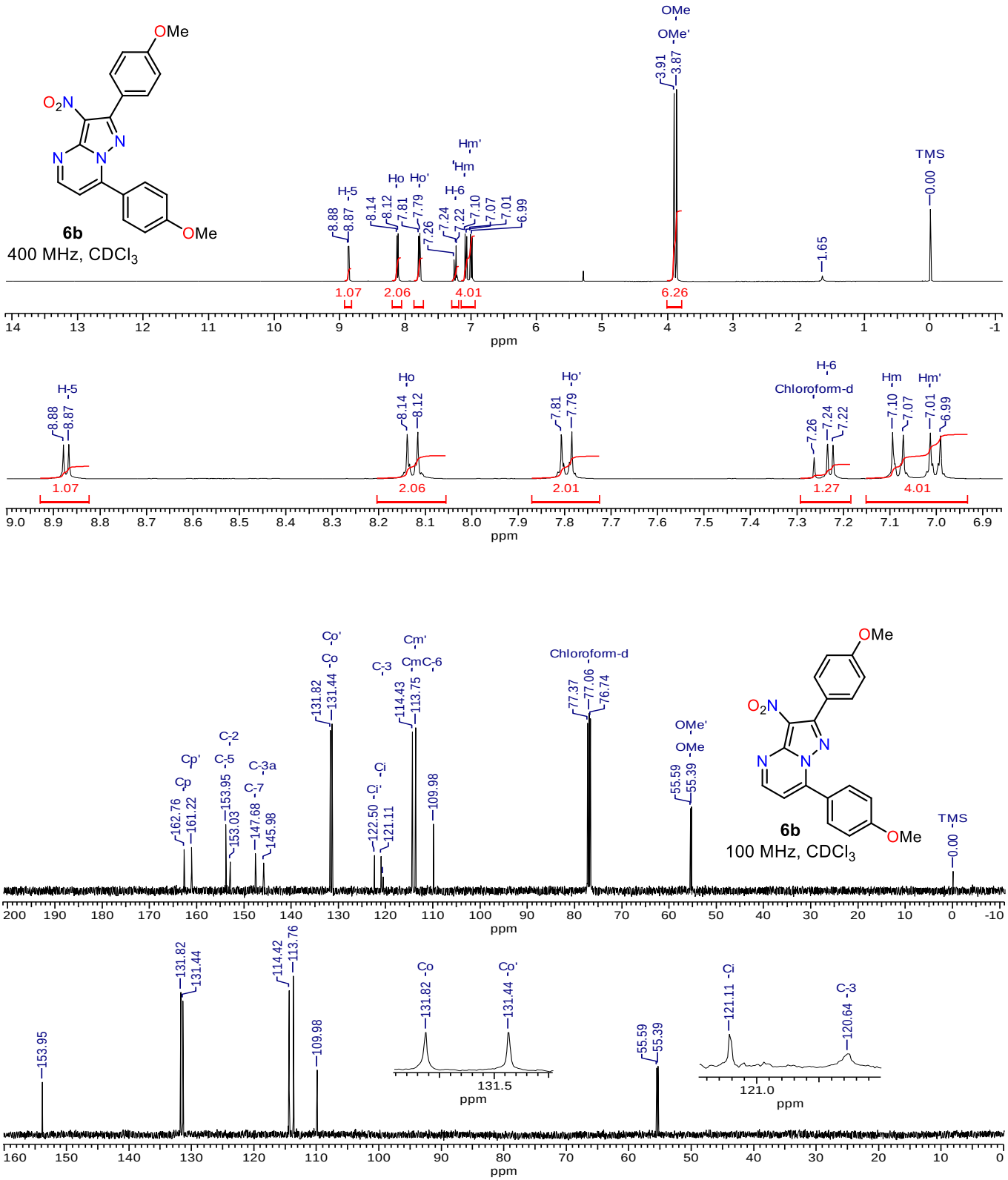


^{1}H and ^{13}C{^{1}H} NMR spectra of 3-nitro-2,7-diphenylpyrazolo[1,5-*a*]pyrimidine **6a**

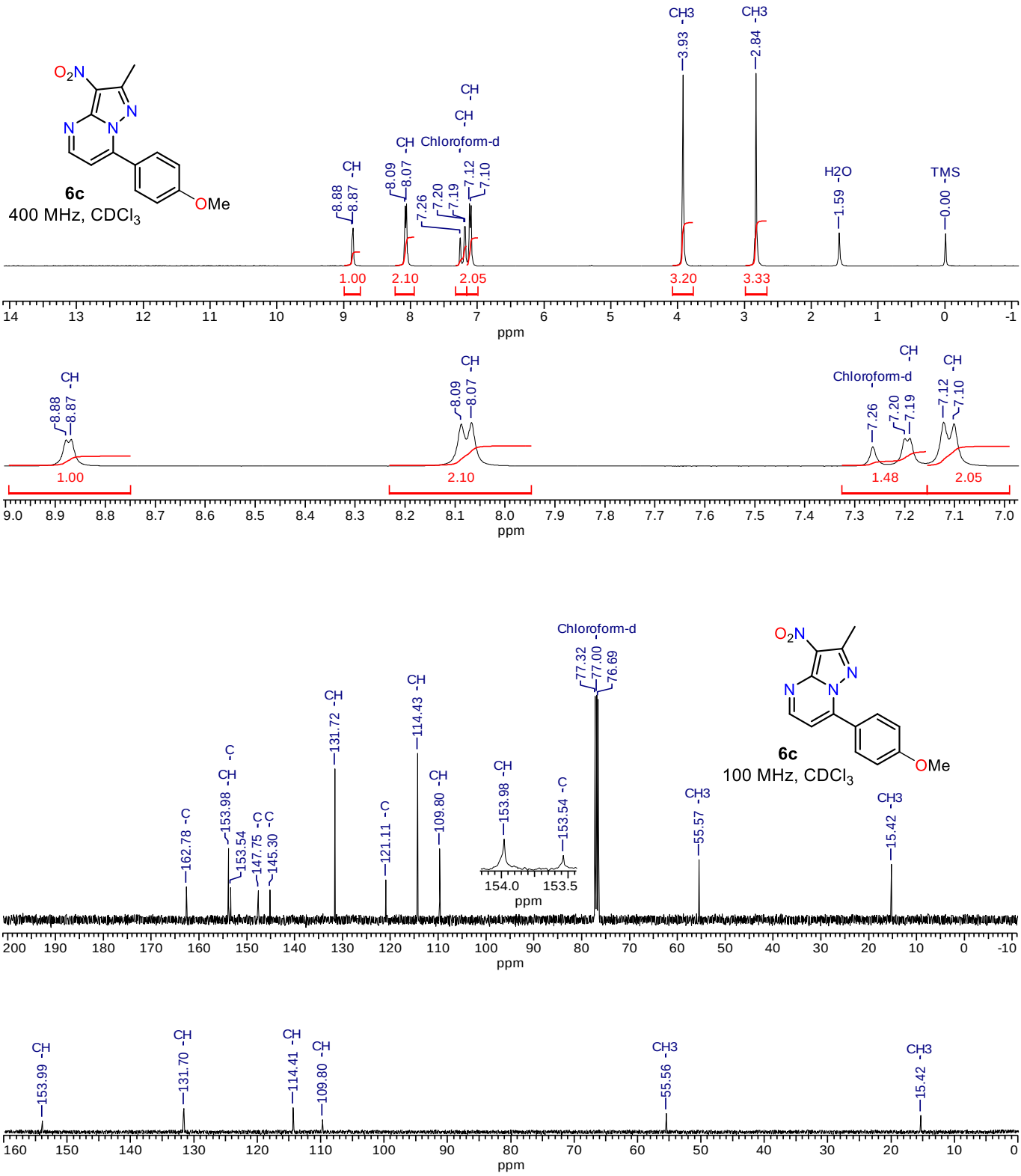




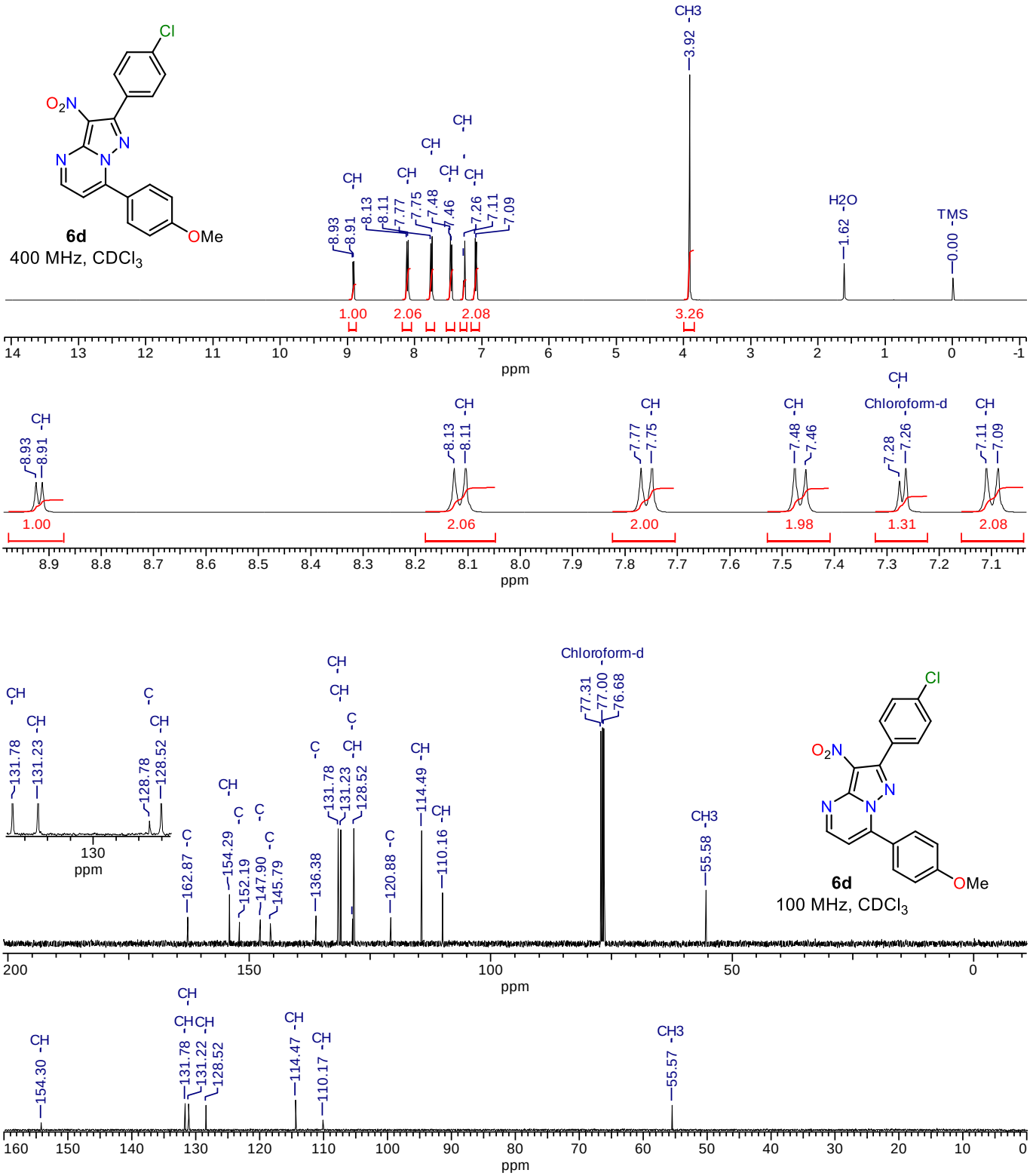
^{1}H and ^{13}C{^{1}H} NMR spectra of 2,7-*bis*(4-methoxyphenyl)-3-nitropyrazolo[1,5-*a*]pyrimidine **6b**



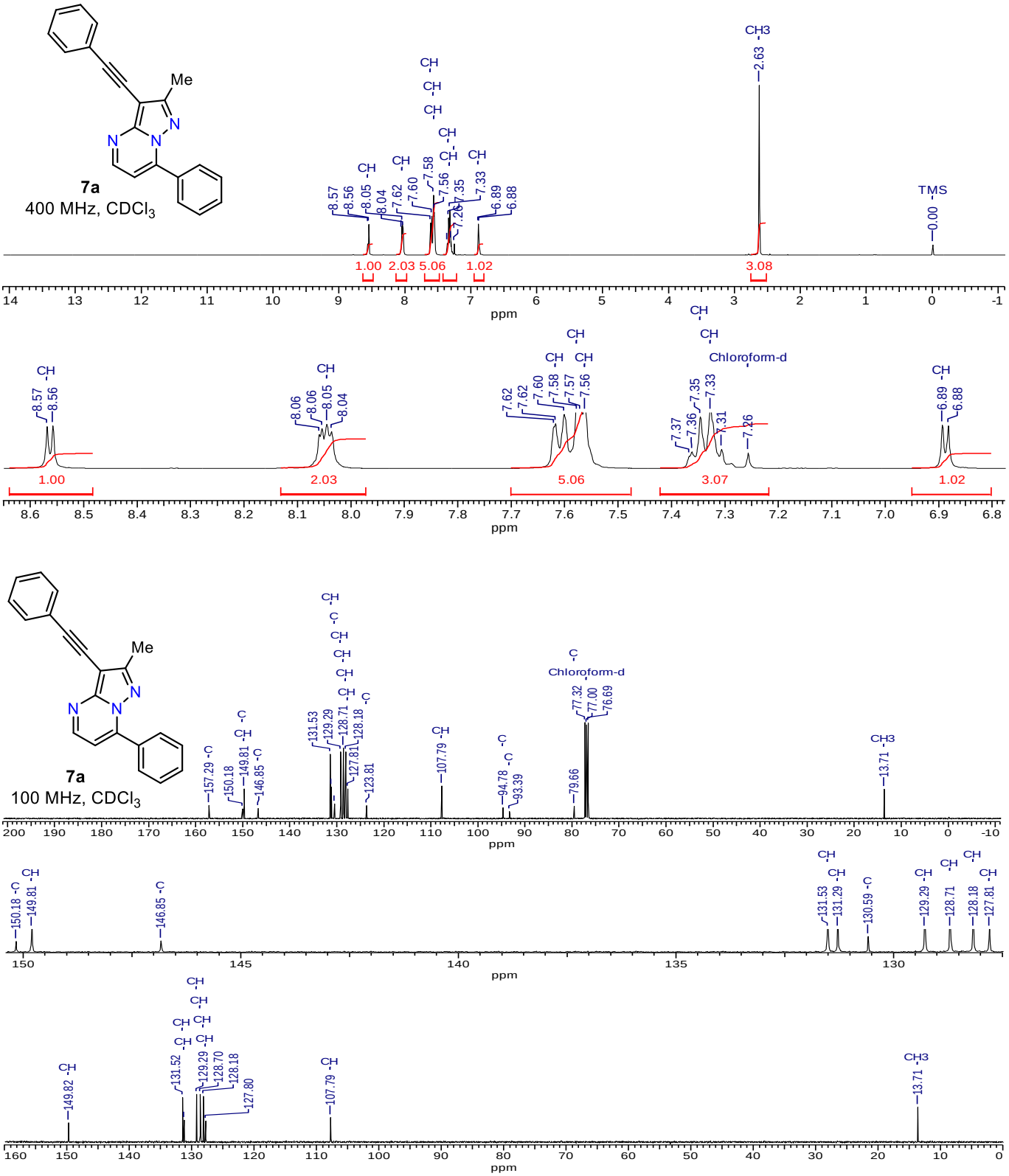
^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-methoxyphenyl)-2-methyl-3-nitropyrazolo[1,5-*a*]pyrimidine **6c**



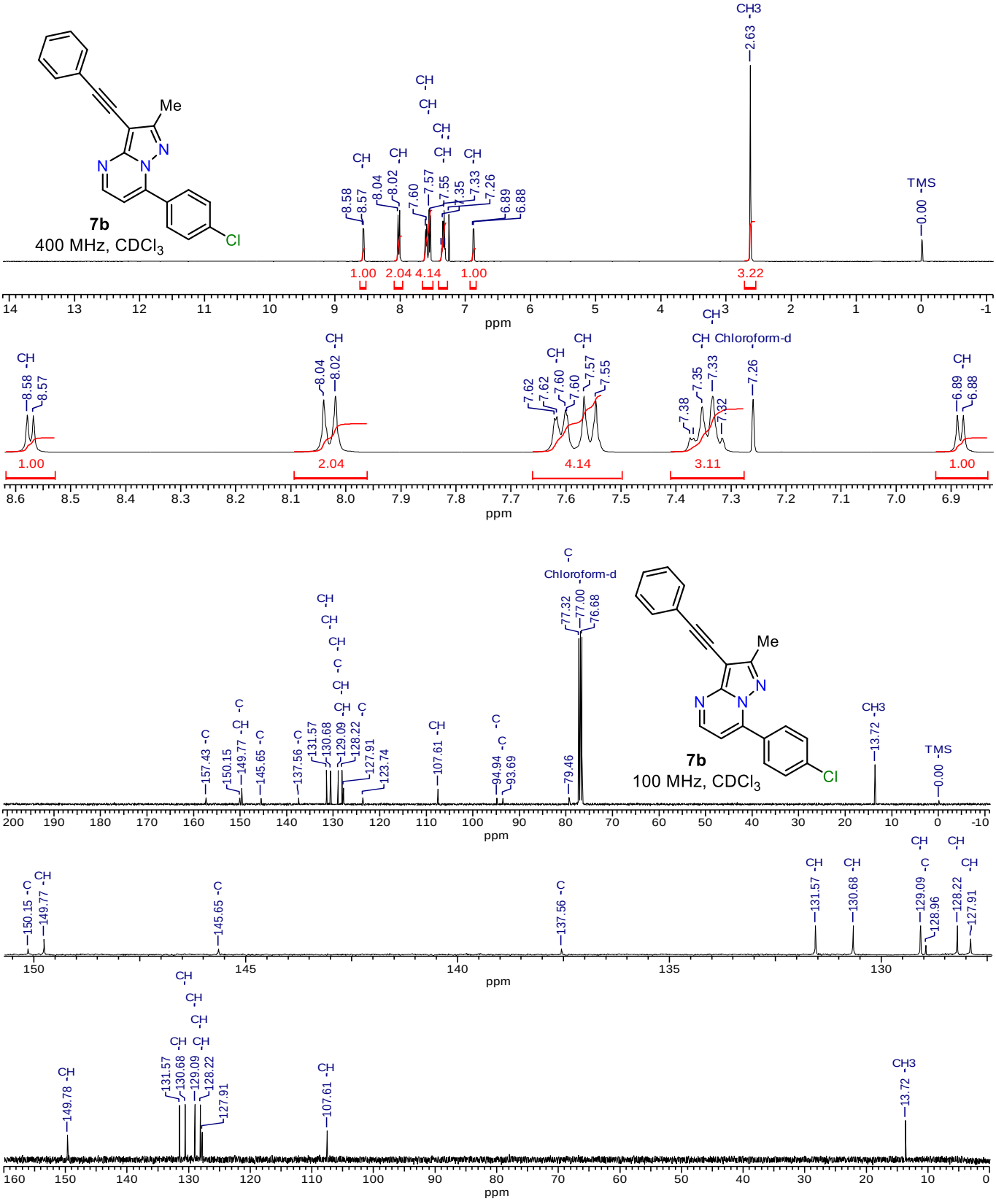
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 2-(4-chlorophenyl)-7-(4-methoxyphenyl)-3-nitropyrazolo[1,5-*a*]pyrimidine **6d**



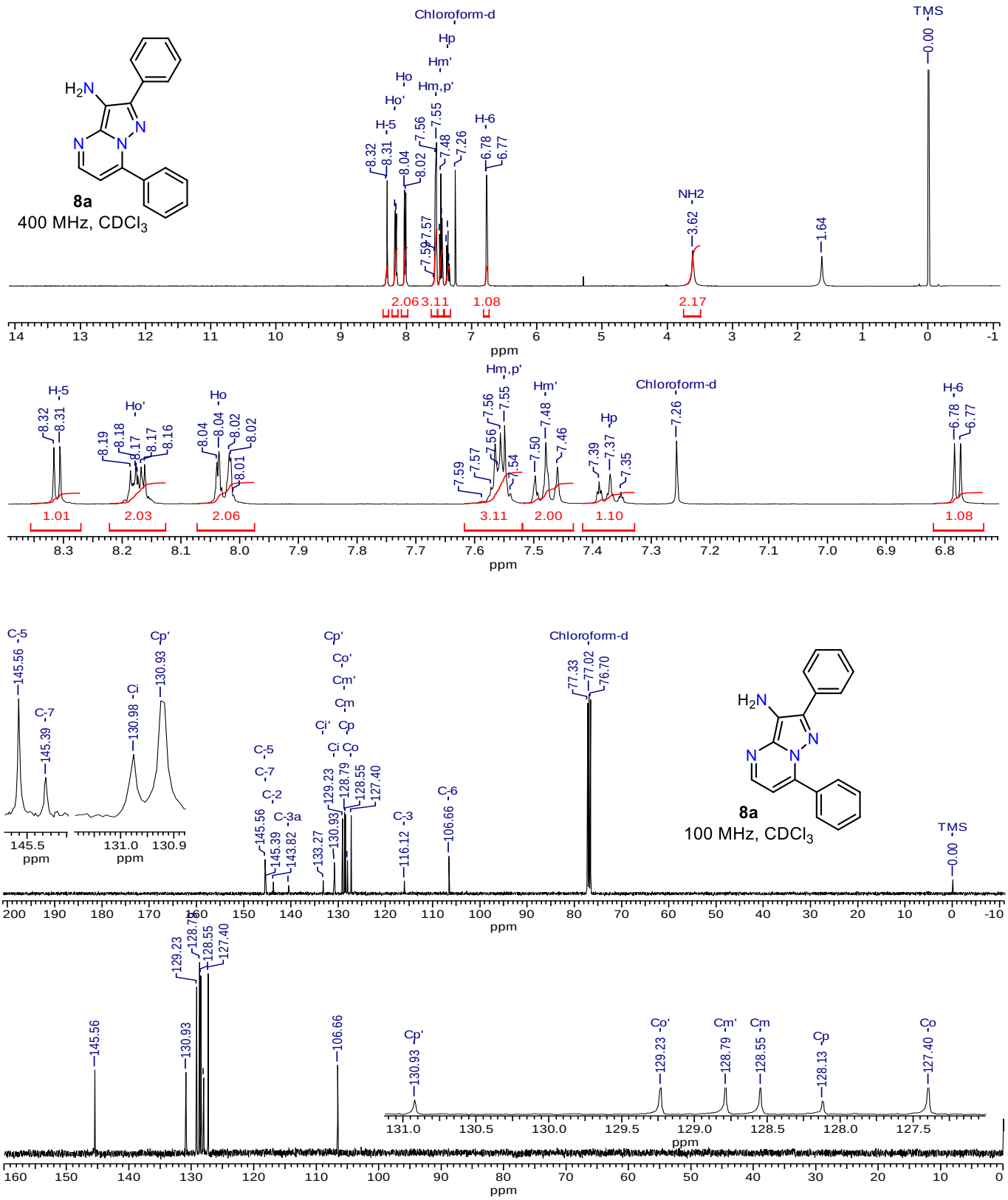
^{1}H and ^{13}C{^{1}H} NMR spectra of 2-methyl-7-phenyl-3-(phenylethynyl)pyrazolo[1,5-*a*]pyrimidine **7a**



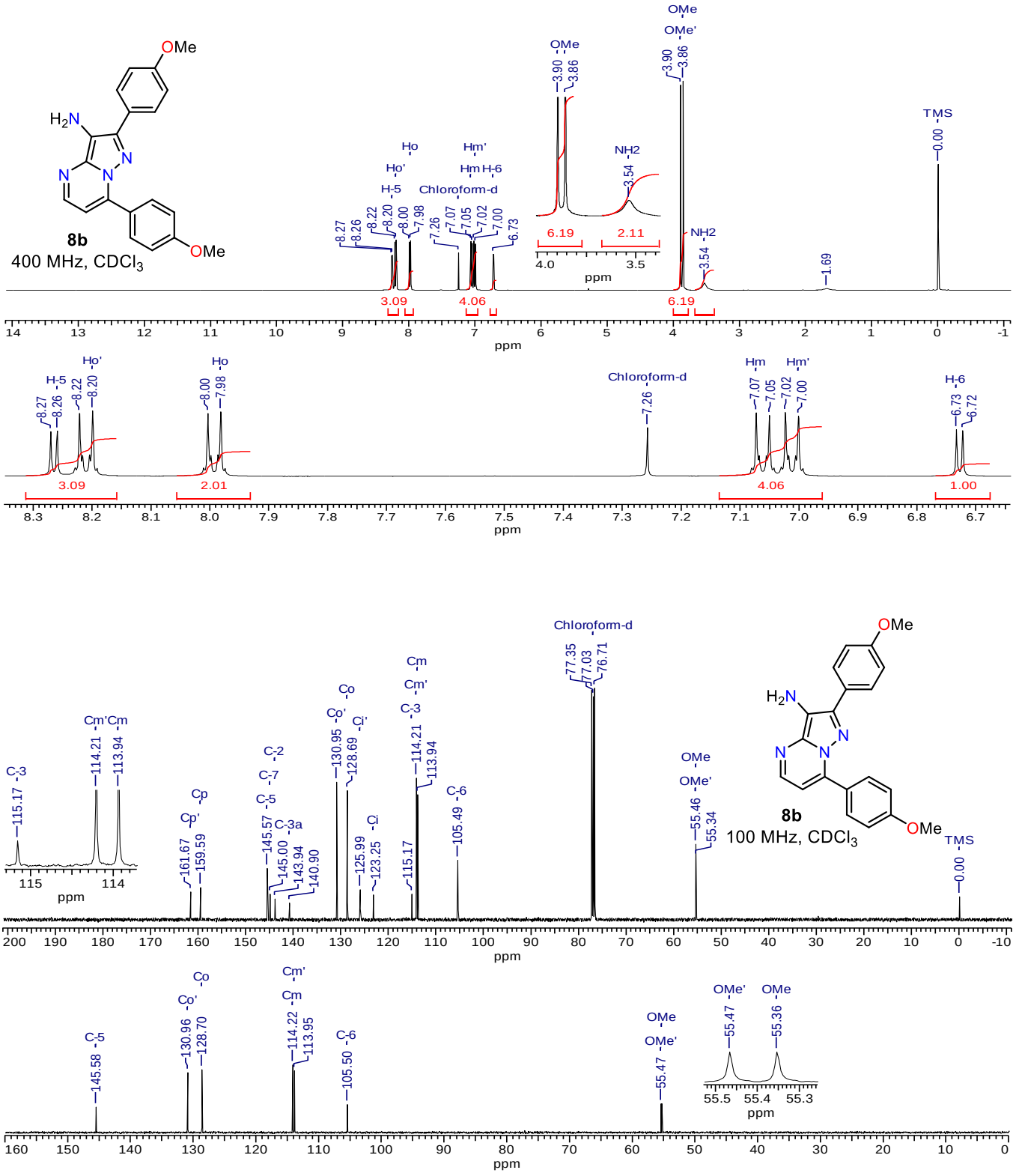
^{1}H and ^{13}C{^{1}H} NMR spectra of 7-(4-chlorophenyl)-2-methyl-3-(phenylethynyl)pyrazolo[1,5-*a*]pyrimidine **7b**



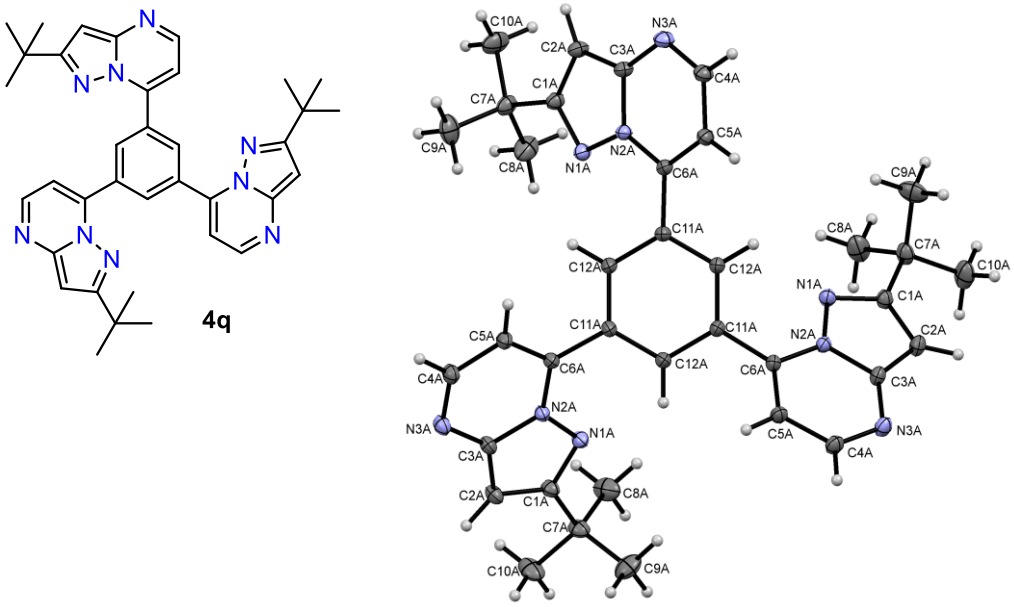
^{1}H and ^{13}C{^{1}H} NMR spectra of 2,7-diphenylpyrazolo[1,5-*a*]pyrimidin-3-amine **8a**



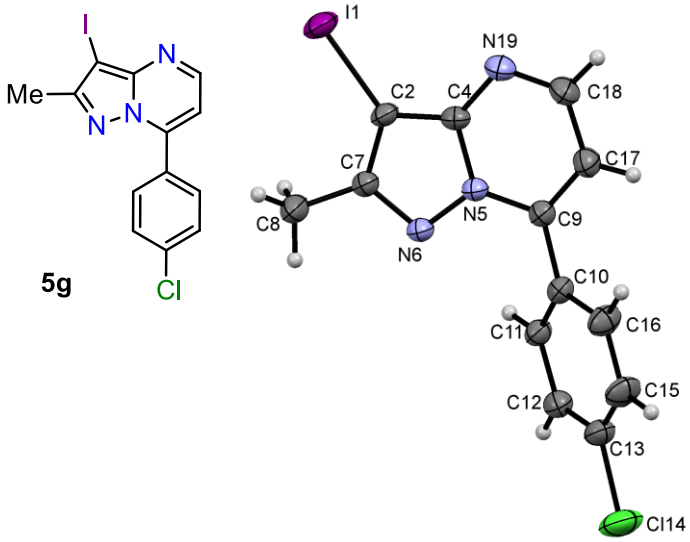
^{1}H and ^{13}C{^{1}H} NMR spectra of 2,7-*bis*(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidin-3-amine **8b**



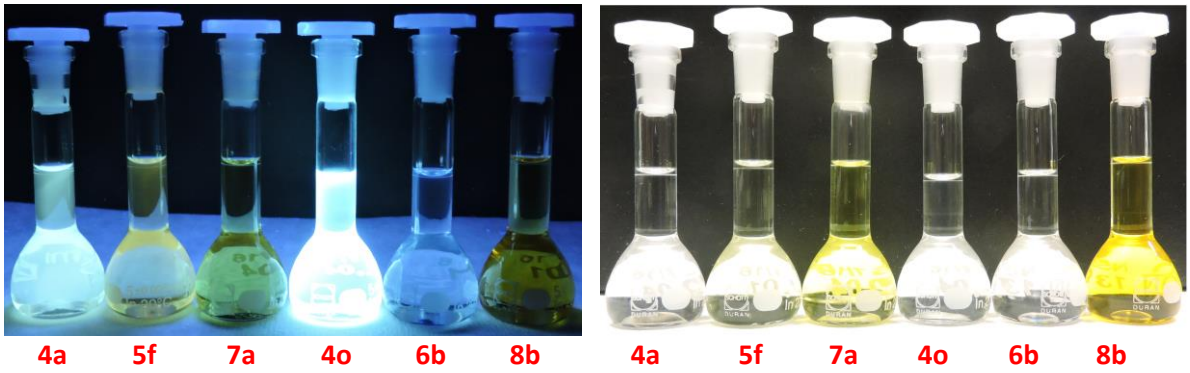
4. Figure 1. ORTEP drawing for structure 4q
Displacement ellipsoids are drawn at the 50% probability level.

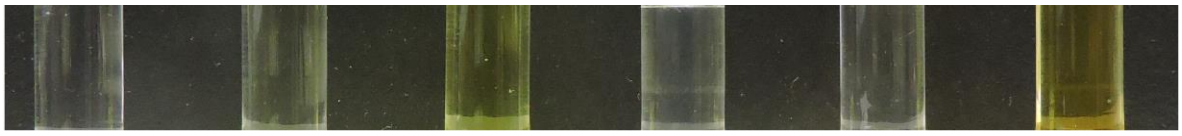


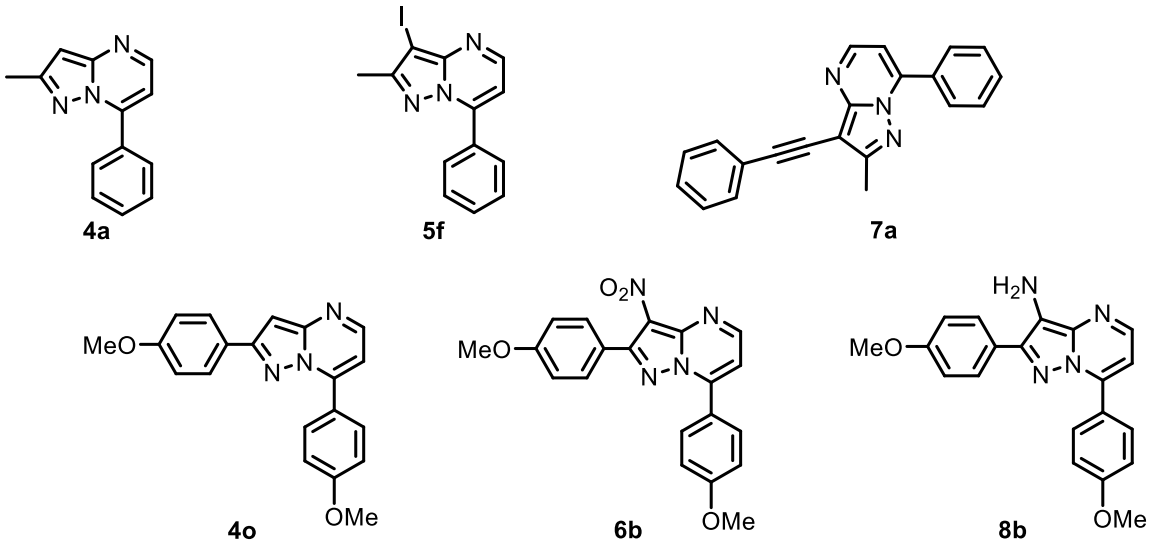
5. Figure 2. ORTEP drawing for structure 5g
Displacement ellipsoids are drawn at the 30% probability level.



6. Image 1. Picture of some representative products







Pictures were taken using 10 μM solutions of each compound (**4a**, **5f**, **7a**, **4o**, **6b**, and **6b**) in CH_2Cl_2. Long wavelengths (λ= 365 nm) and white light were used, respectively.