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SUPPORTING INFORMATION

Synthesis and Photophysical Properties of 2-Azolyl-6-piperidinylpurines

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Experimental procedures for compounds 2, 8, 14, 15 and 16.

2-Hydroxyethyl 3,3,3-triphenylpropanoate (2). To a solution of compound **6**[26] (5.00 g, 16.56 mmol, 1.0 eq.) in dry DCM (60 mL) a drop of dry DMF was added, followed by dropwise addition of oxalyl chloride (3.80 mL, ρ = 1.48 g/cm^3, 43.87 mmol, 2.7 eq.), then the reaction mixture was stirred at 20 °C for 2 h. It was then twice evaporated and dissolved in dry DCM (20 mL). The DCM solution was slowly added to ethylene glycol (4.60 mL, ρ = 1.11 g/cm^3, 82.78 mmol, 5.0 eq.) and Et_3N (4.58 mL, ρ = 0.73 g/cm^3, 33.11 mmol, 2.0 eq.) mixture in dry DCM (10 mL) and stirred at 20 °C for 12 h. Then the reaction mixture was washed with H_2O (3×10 mL) and brine (10 mL), dried over anh. Na_2SO_4 and evaporated. Silica gel column chromatography (DCMl/MeCN, gradient 0-20%) provided product **2** as a colorless oil. Yield 3.19 g, (56%). R_f = 0.60 (DCM/MeCN = 10:1). HPLC: t_R = 6.51 min.

2-Chloro-6-(piperidin-1-yl)-9-(tetrahydro-2*H*-pyran-2-yl)-9*H*-purine (8). To a solution of compound **7** (2.0 g, 7.33 mmol, 1.0 eq.) in EtOH (10 mL) piperidine (2.17 mL, ρ = 0.86 g/cm^3, 22.0 mmol, 3.0 eq.) was added and the reaction mixture was stirred at 80 °C for 30 min. Then the reaction mixture was evaporated and suspended in H_2O (30 mL) and kept at 0 °C for 4 h. The precipitate was then filtered, washed with water (3×30 mL) and dried under vacuum to give product **8** as a colorless solid. Yield 2.24 g (95%). R_f = 0.38 (DCM/MeCN = 20:1). HPLC: t_R = 6.94 min.

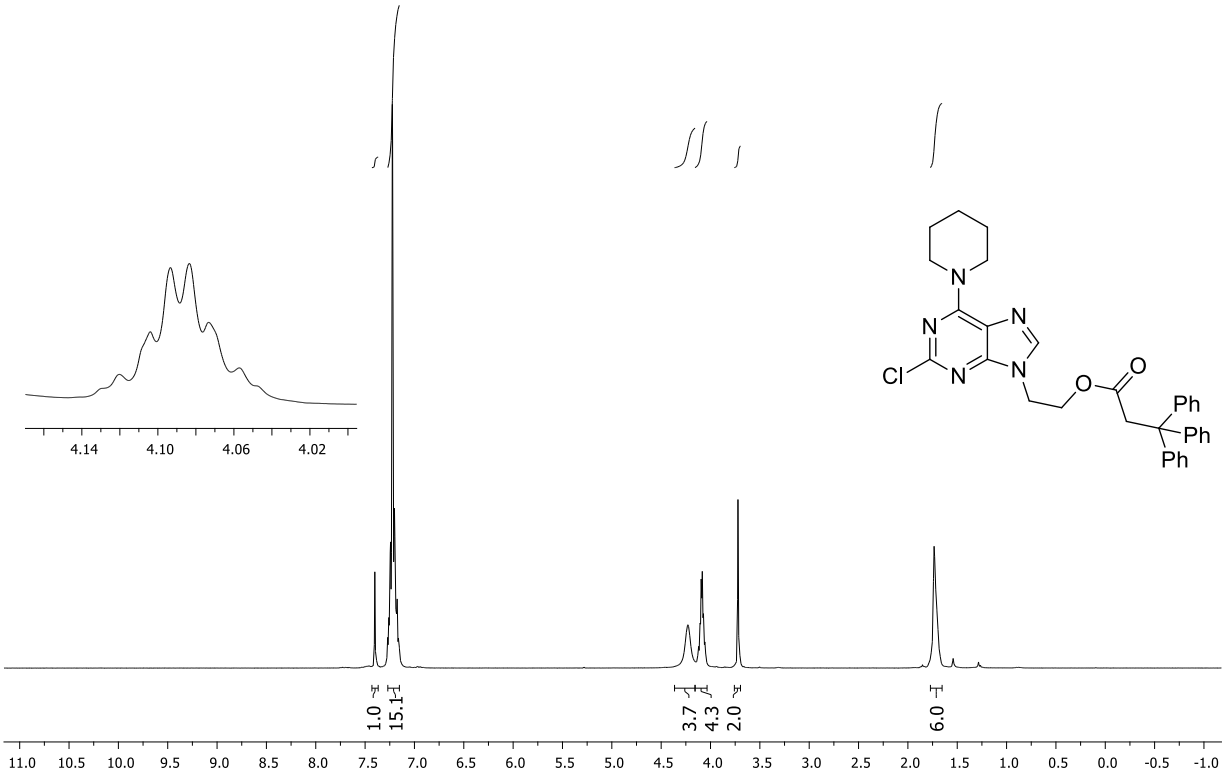
2,6-Diazido-9*H*-purine (14). A solution of 2,6-dichloropurine (2.0 g, 10.6 mmol) in ethanol (15 mL) was heated up to 80 °C, then a solution of sodium azide (2.75 g, 42.3 mmol) in water (8 mL) was added. The resulting mixture was intensively stirred for 15 min at 80 °C, followed by cooling at 0 °C for 1 h. The precipitate was filtered and washed with cold water (2×10 mL). Recrystallization from EtOH (20 mL) provided product **15** as a colorless solid. Yield 1.65 g (77%). mp = 170–190 °C (Degrades) (EtOH). R_f = 0.65 (DCM/MeOH = 10:1). HPLC: t_R = 3.18 min.

2-Azido-6-(piperidin-1-yl)-9*H*-purine (15). To a suspension of compound **14** (2.46 g, 12.18 mmol, 1.0 eq.) in water (10 mL) piperidine (4 mL) was added and the reaction mixture was stirred at 100 °C for 2.5 h. Then the reaction mixture was cooled to room temperature and AcOH was added until pH of the solution reached 7. The mixture was kept in the fridge for 3 h. Precipitate was filtered and washed with cold EtOH (30 mL). Recrystallization from EtOH (75 mL) provided product **15** as a colorless solid. Yield 2.03 g (53%). mp = 215–217 °C (Degrades) (EtOH).

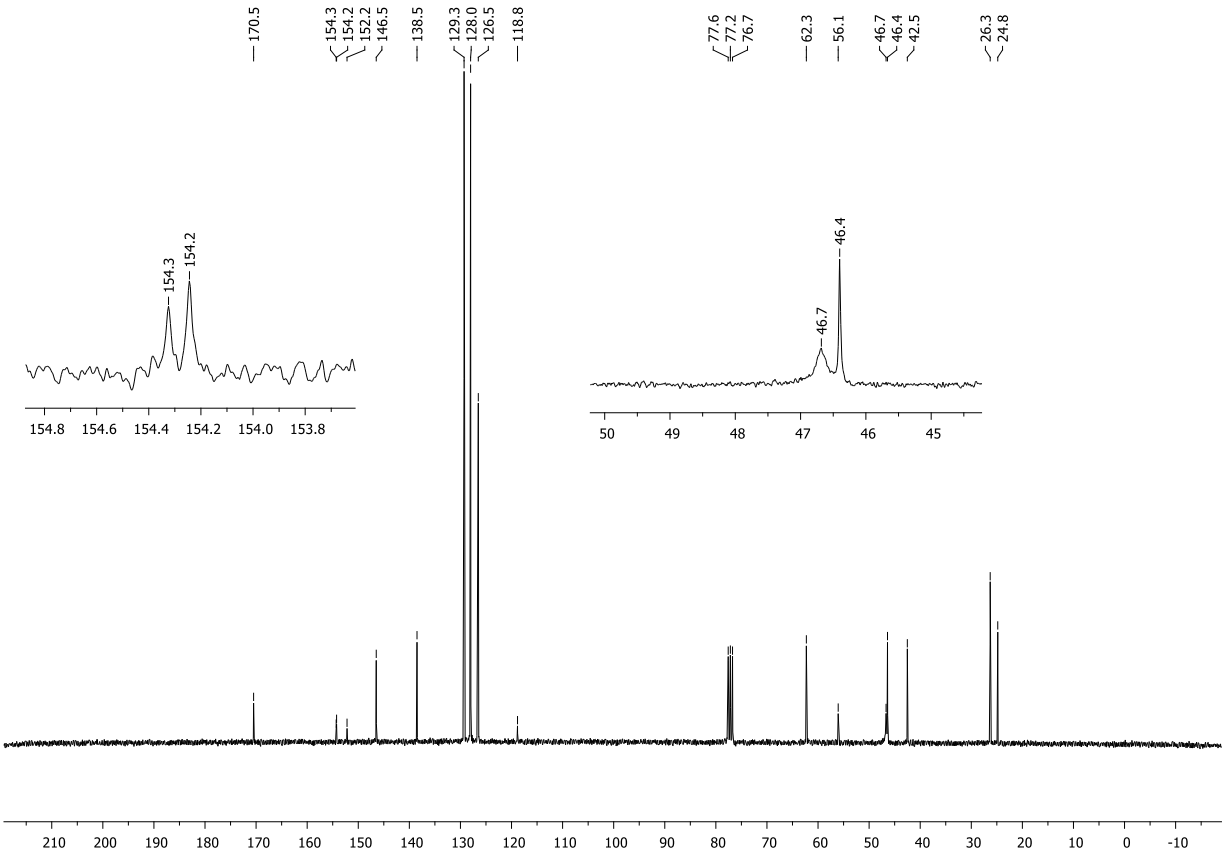
6-(Piperidin-1-yl)-9*H*-purin-2-amine (16). To a suspension of compound **15** (2.0 g, 8.20 mmol, 1.0 eq.) in a mixture of THF (30 mL) and EtOH (30 mL) Pd/C 3% (0.4 g, 20 w%) was added and under vigorous stirring H_2 was bubbled through for 15 min, followed by stirring for 1 h under H_2 atmosphere at 20 °C. Then the reaction mixture was filtered through celite and evaporated to give product **16** as a colorless solid. Yield 1.72 g (96%). R_f = 0.40 (DCM/MeOH = 10:1). HPLC: t_R = 3.37 min.

Copies of ^{1}H and ^{13}C-NMR spectra

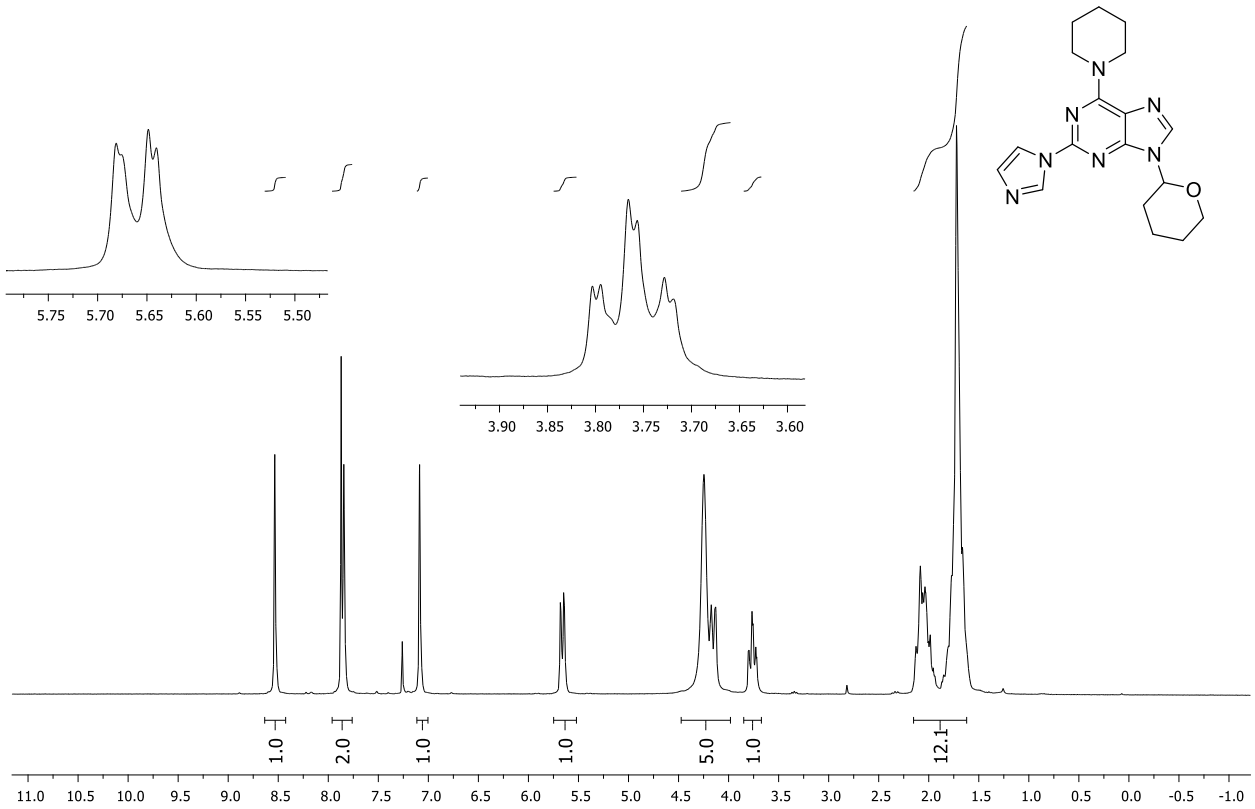
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 4:



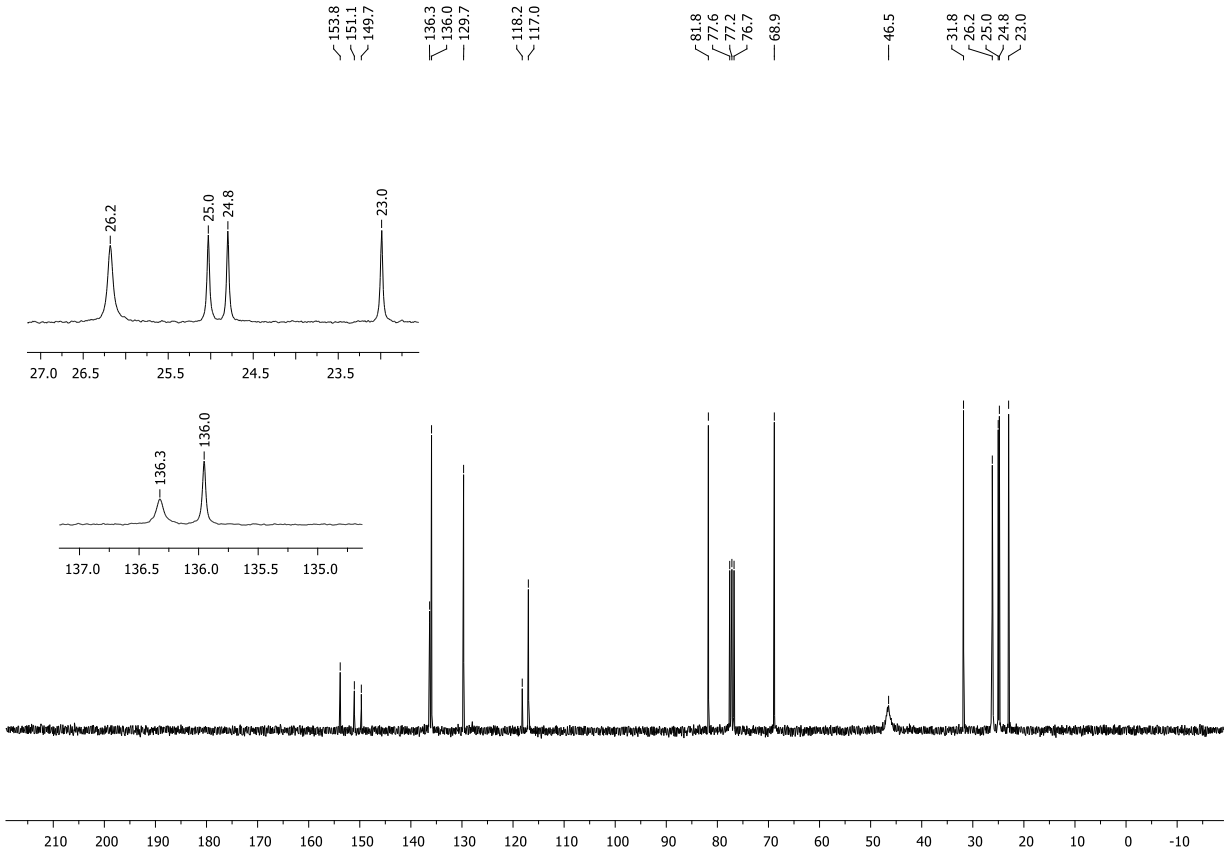
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 4:



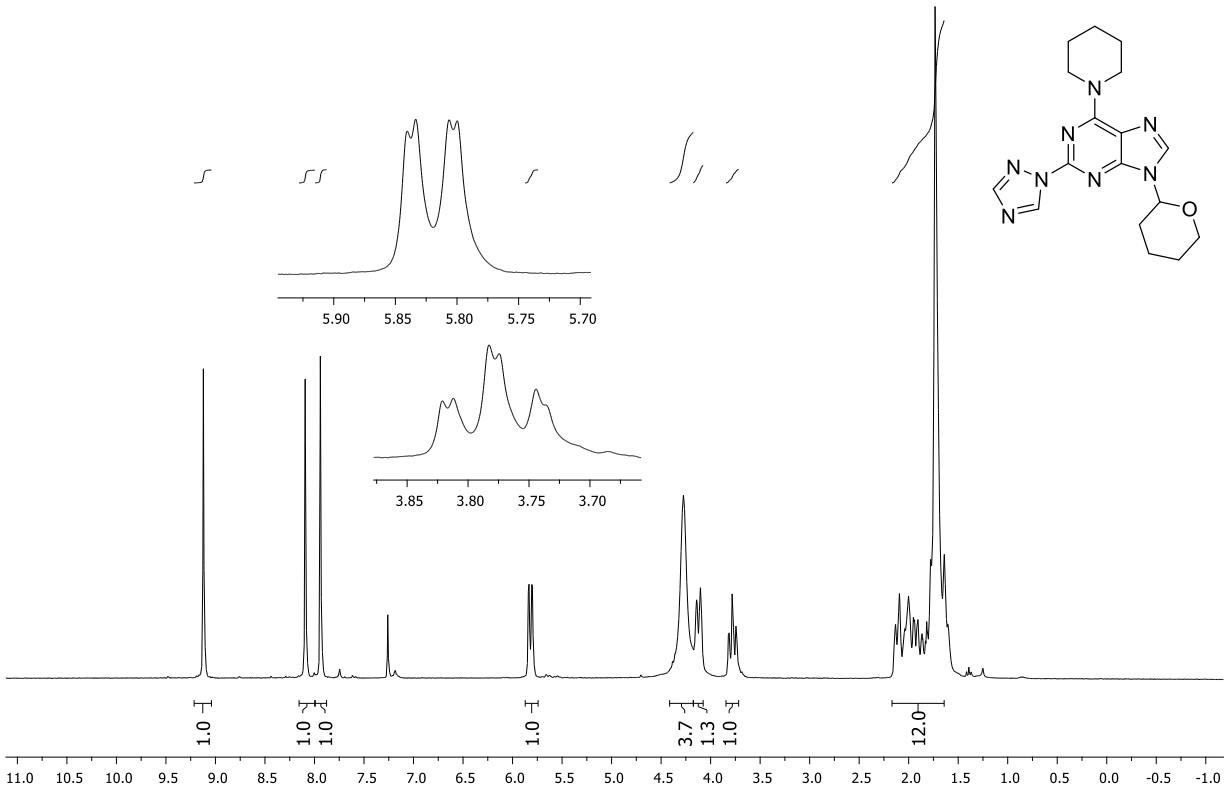
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 9a:



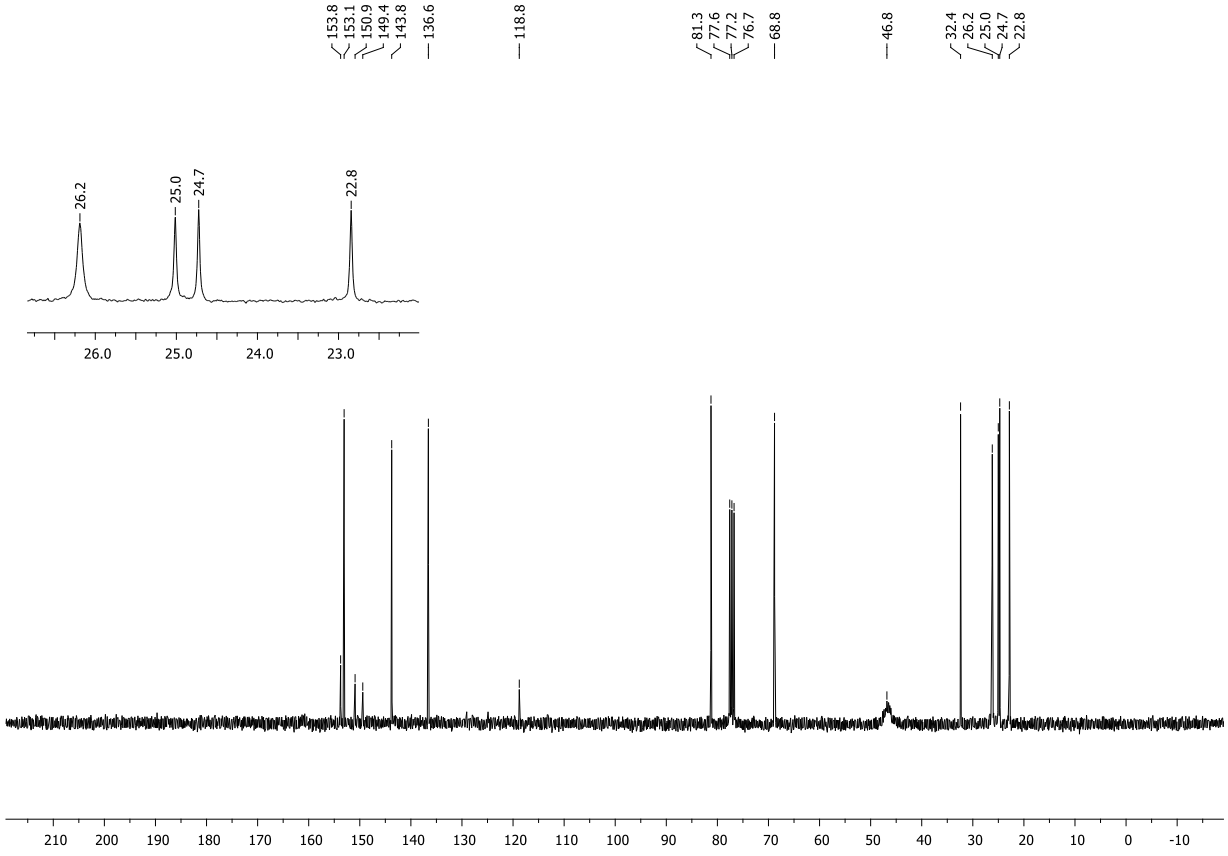
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 9a:



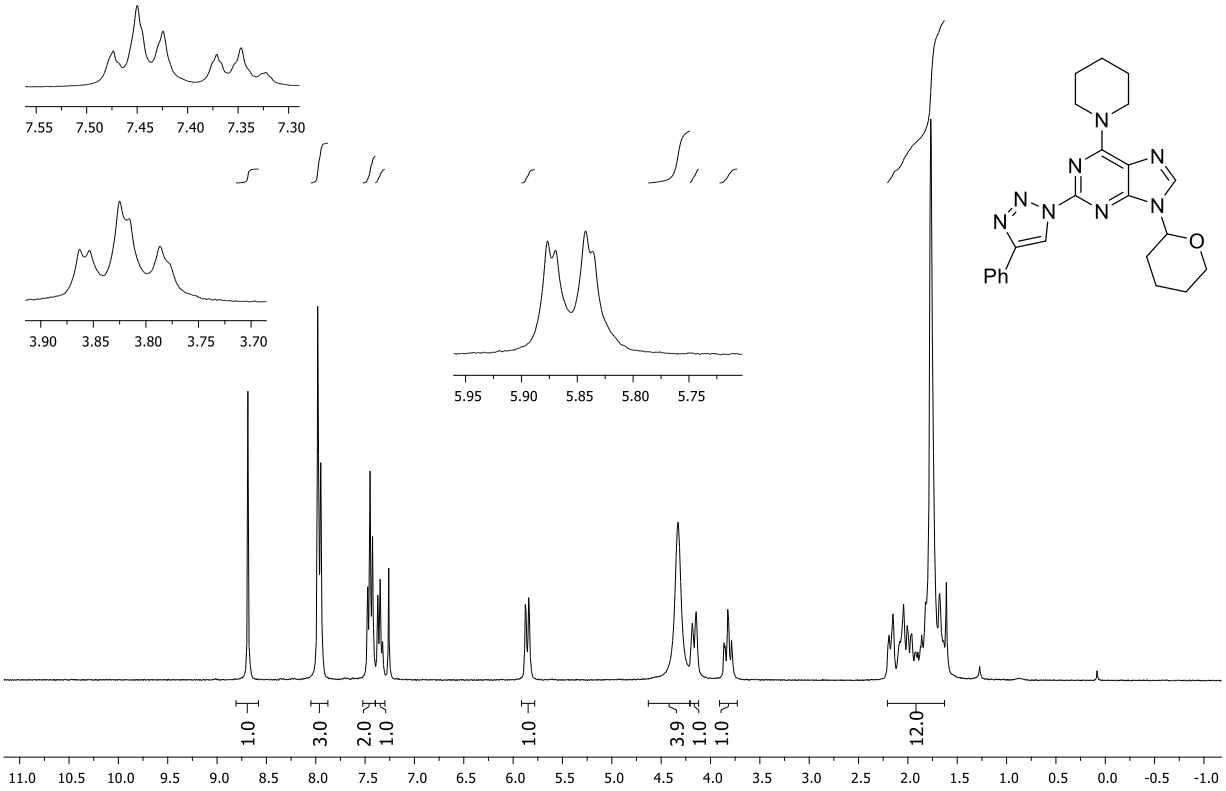
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 9b:



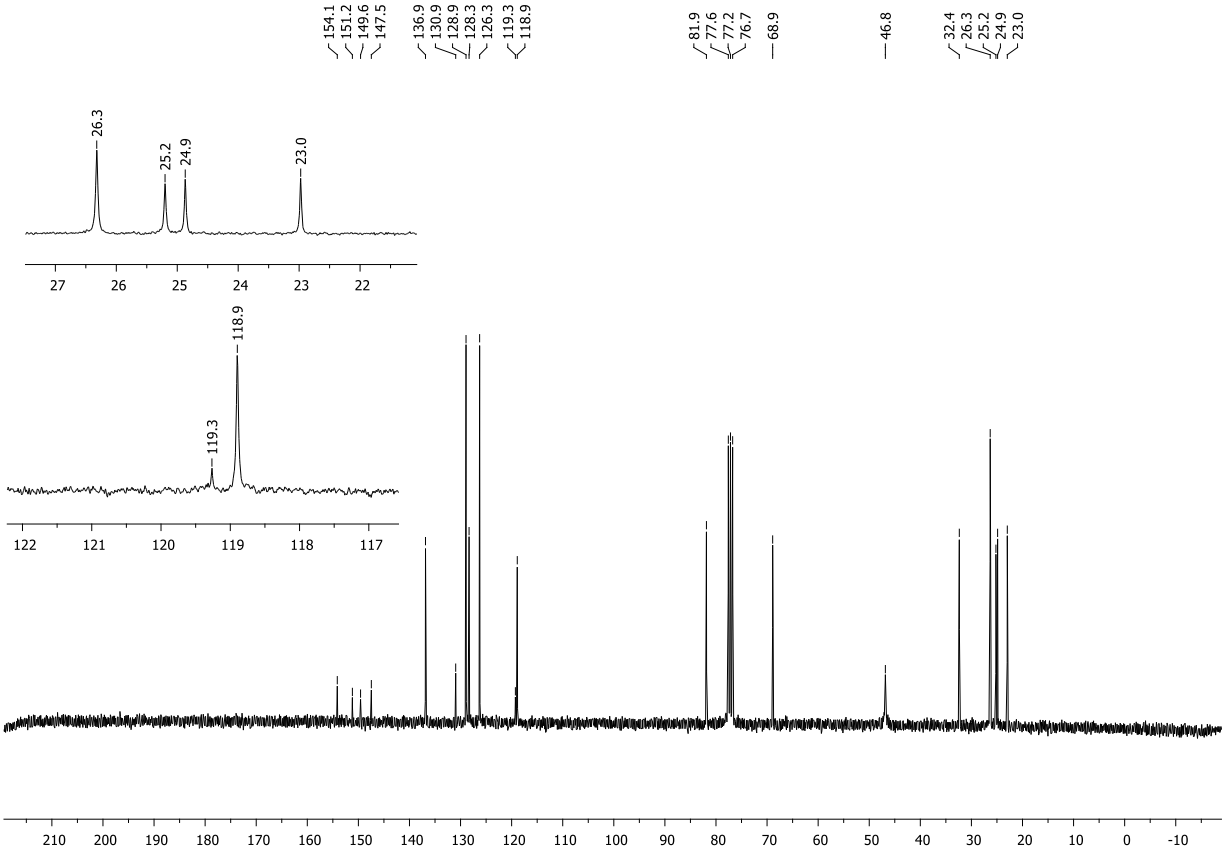
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 9b:



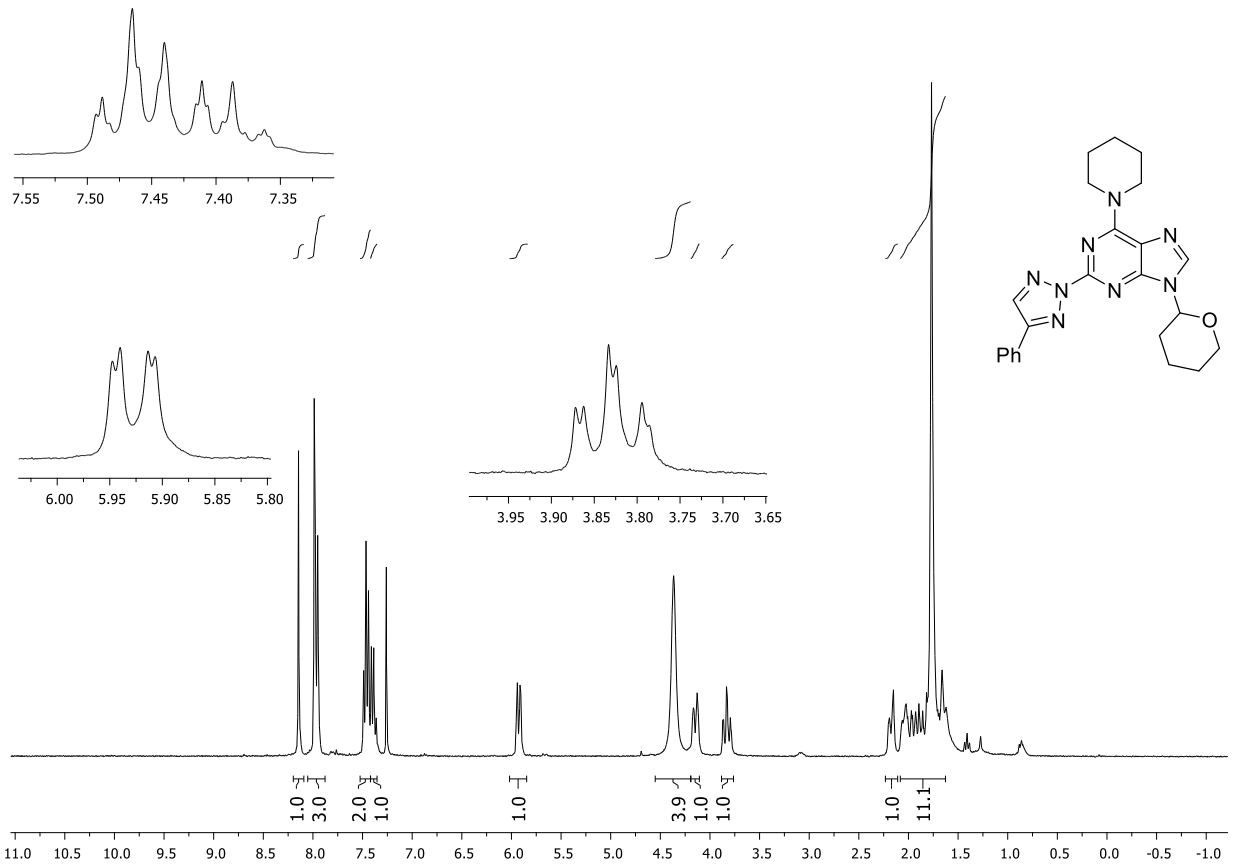
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 9c:



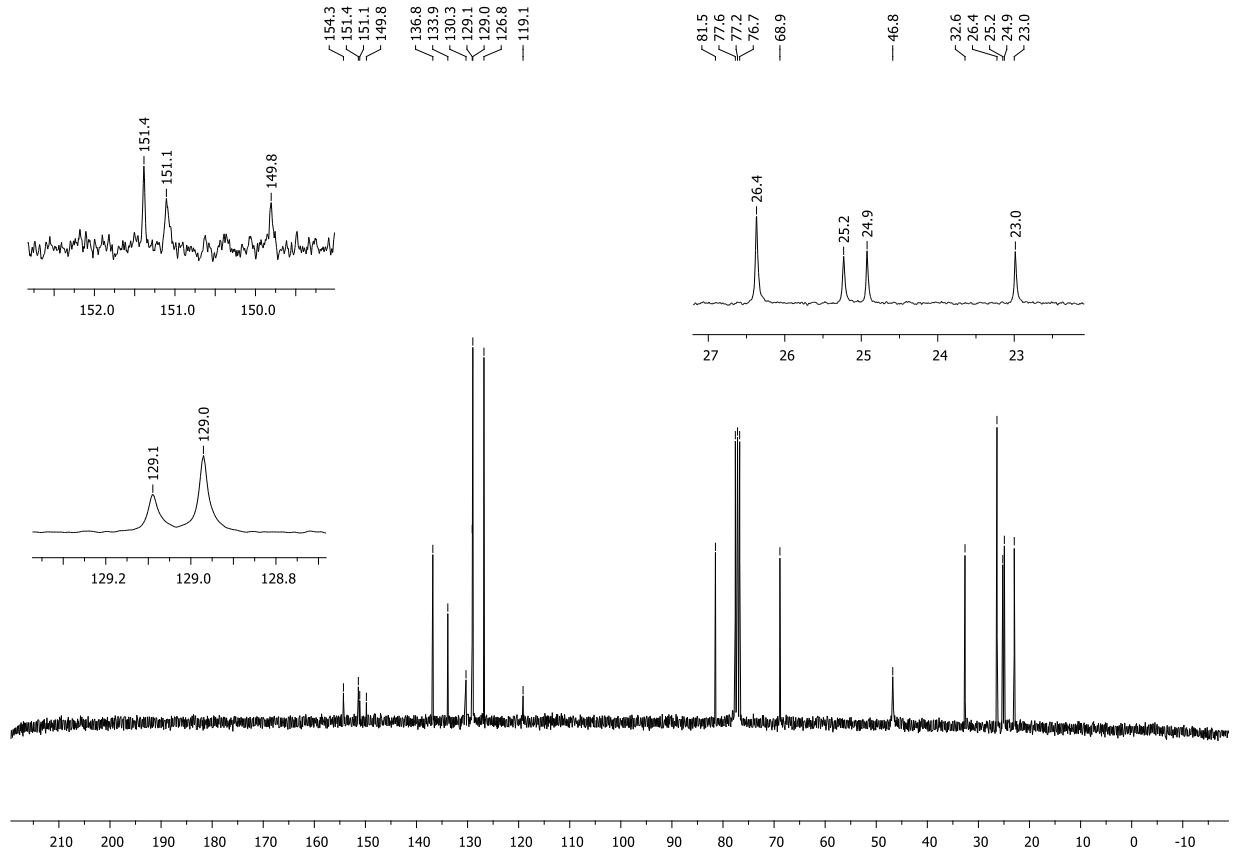
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 9c:



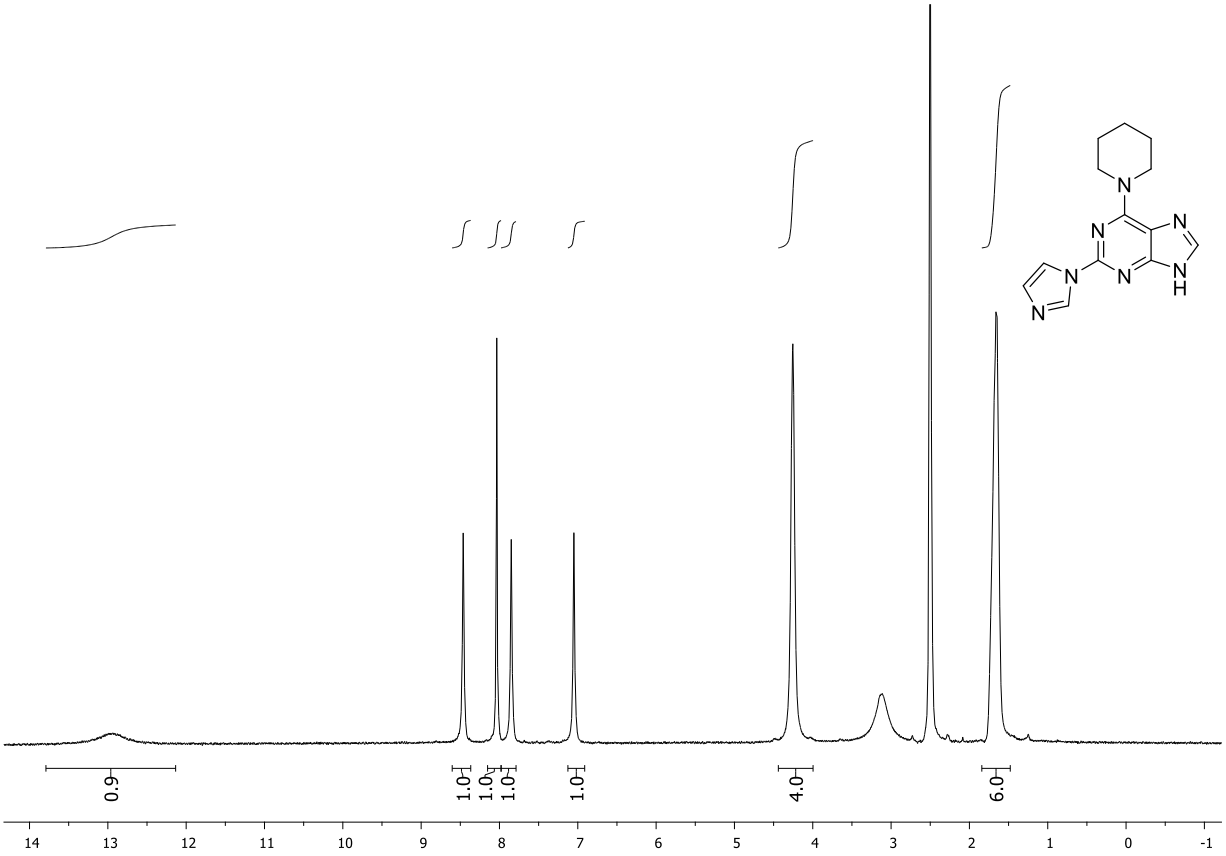
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 9d:



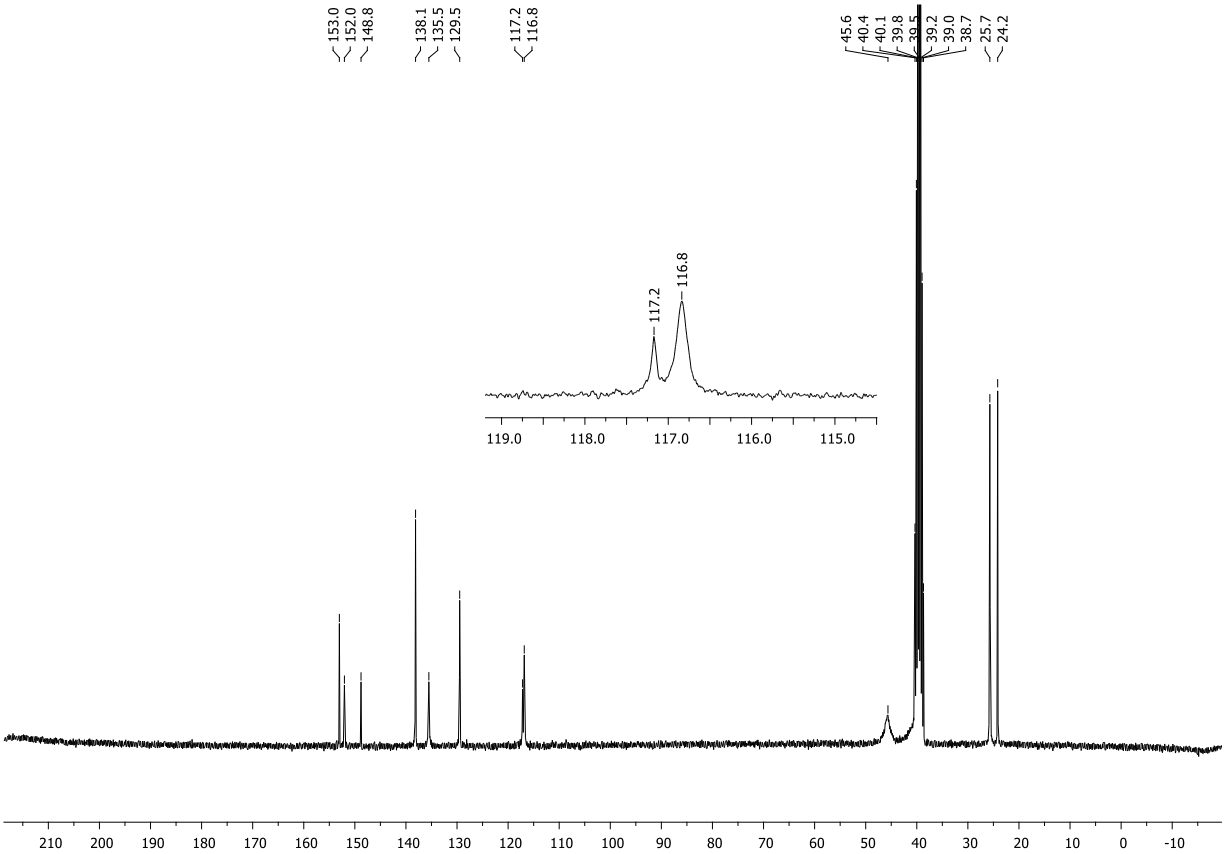
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 9d:



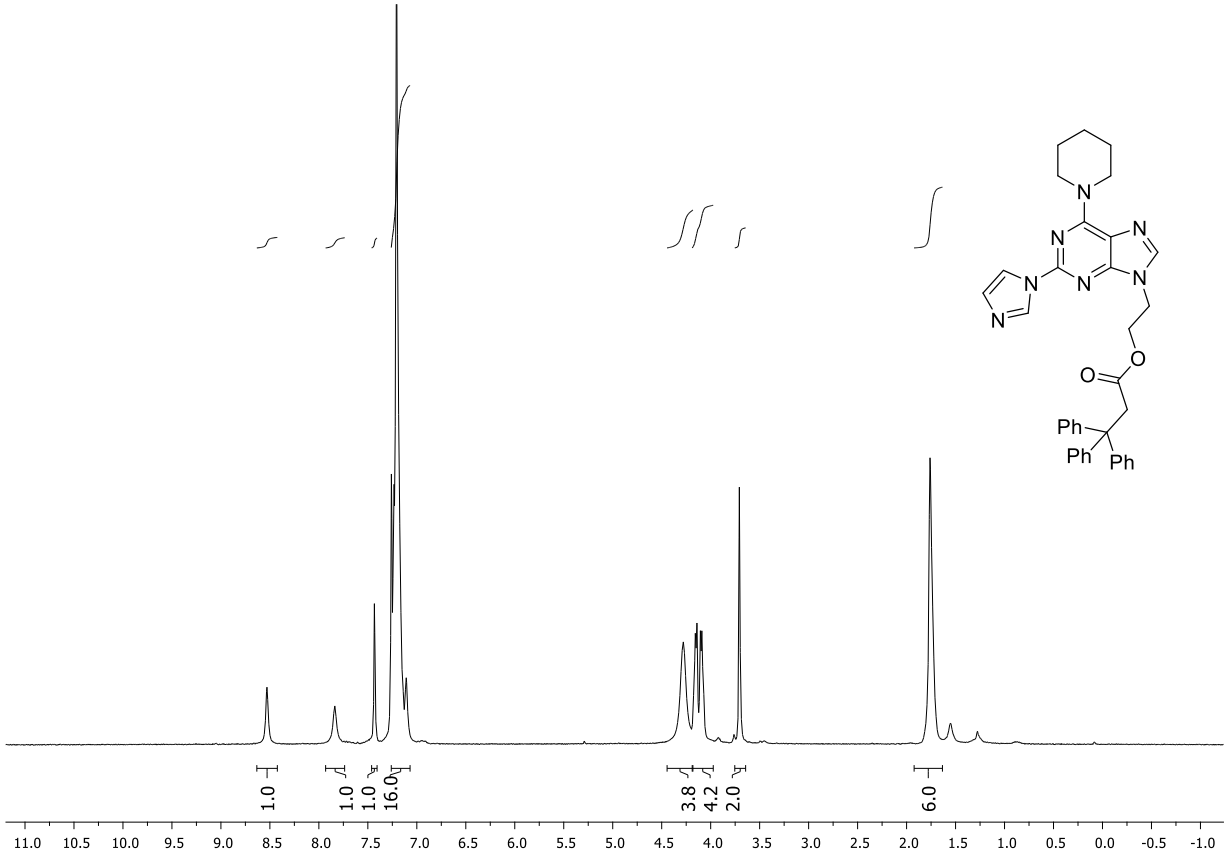
^{1}H-NMR (300 MHz, DMSO-d_6, 60 °C) spectrum of compound 10a:



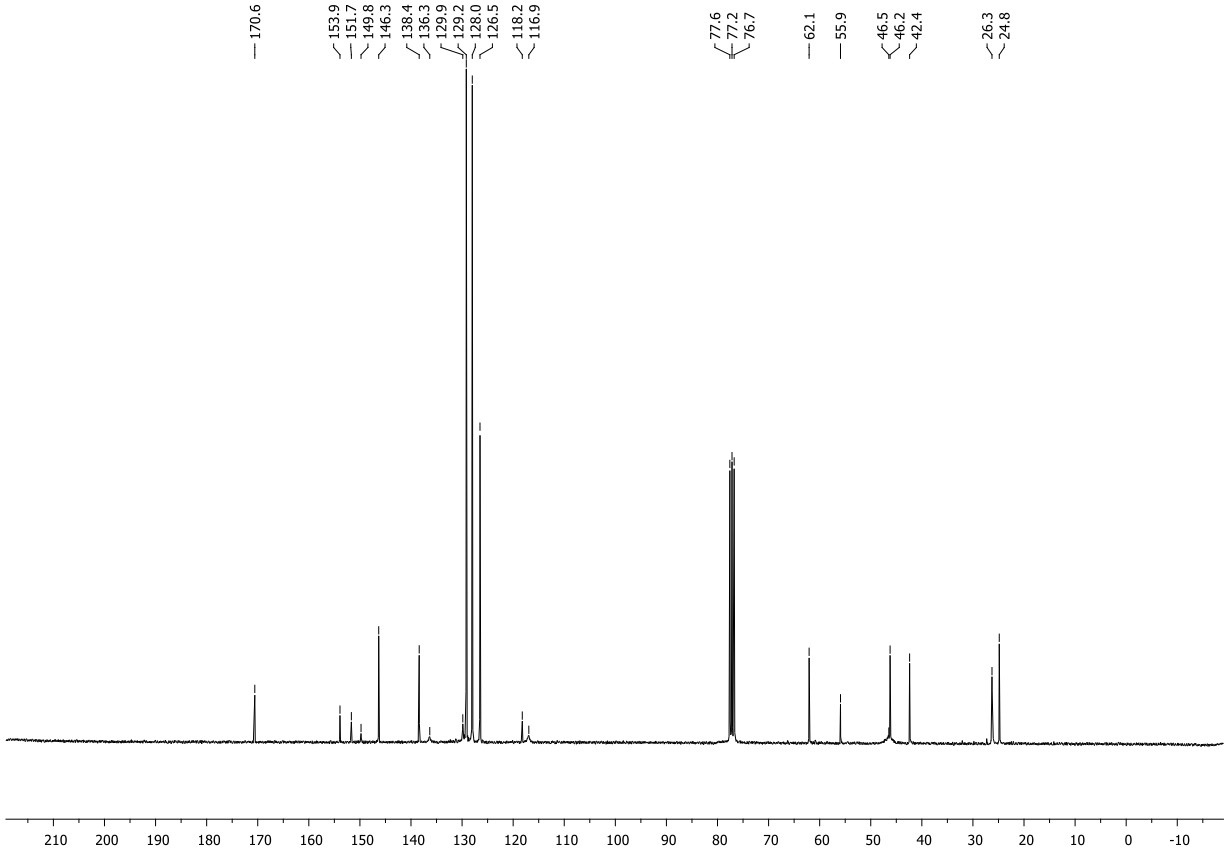
^{13}C-NMR (75.5 MHz, DMSO-d_6, 60 °C) spectrum of compound 10a:



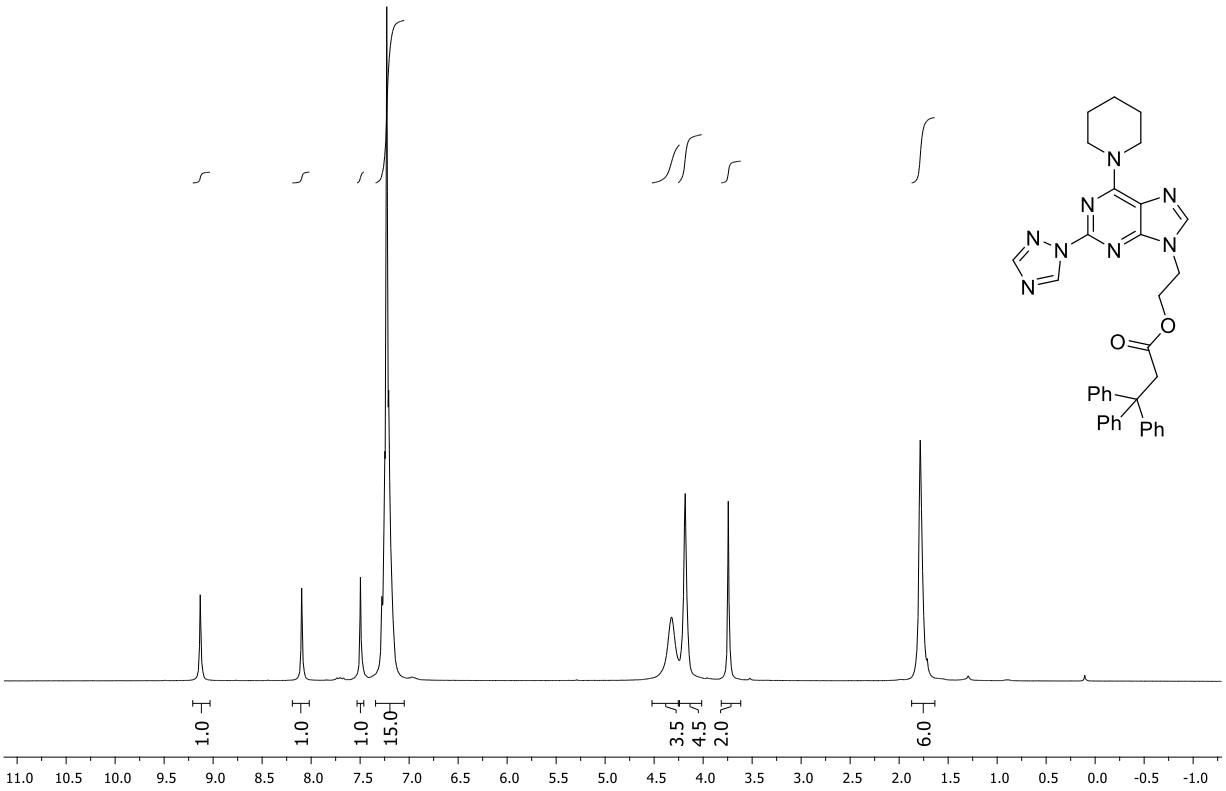
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 11a:



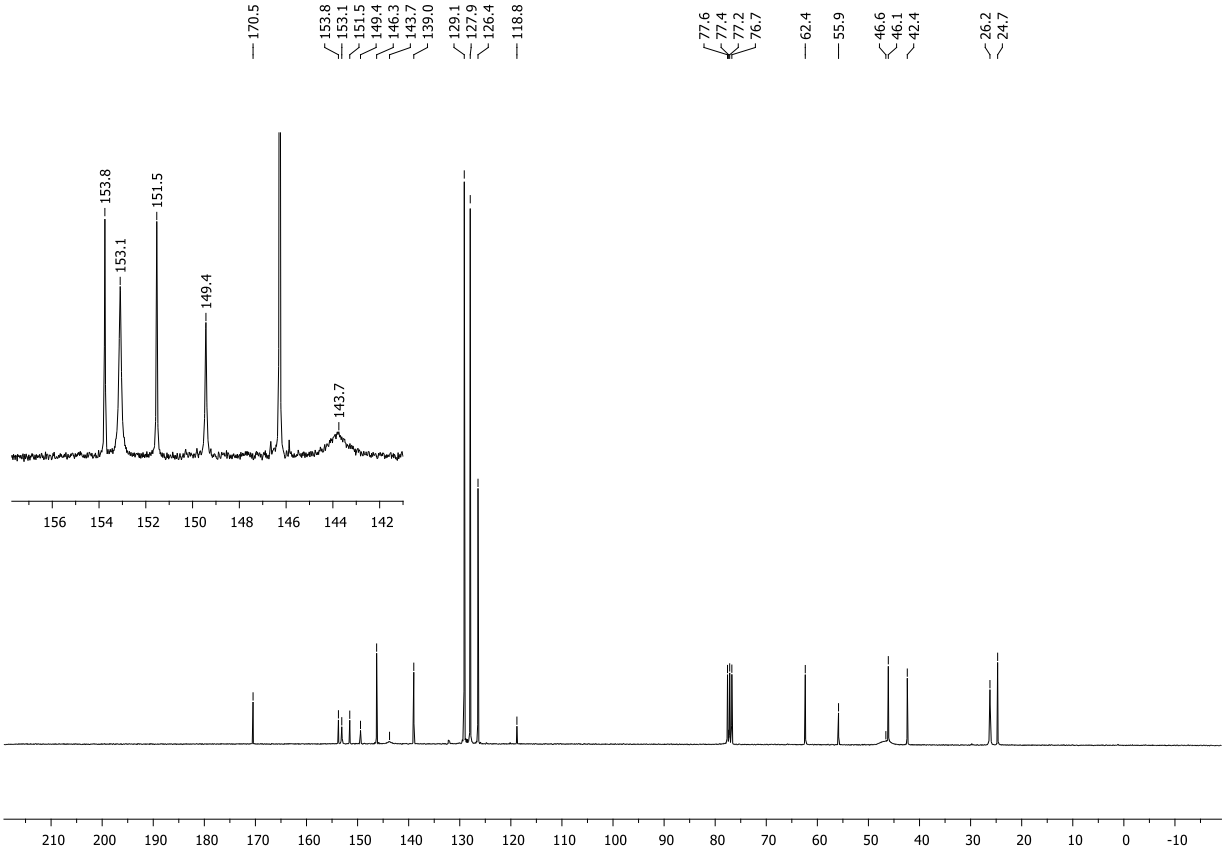
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 11a:



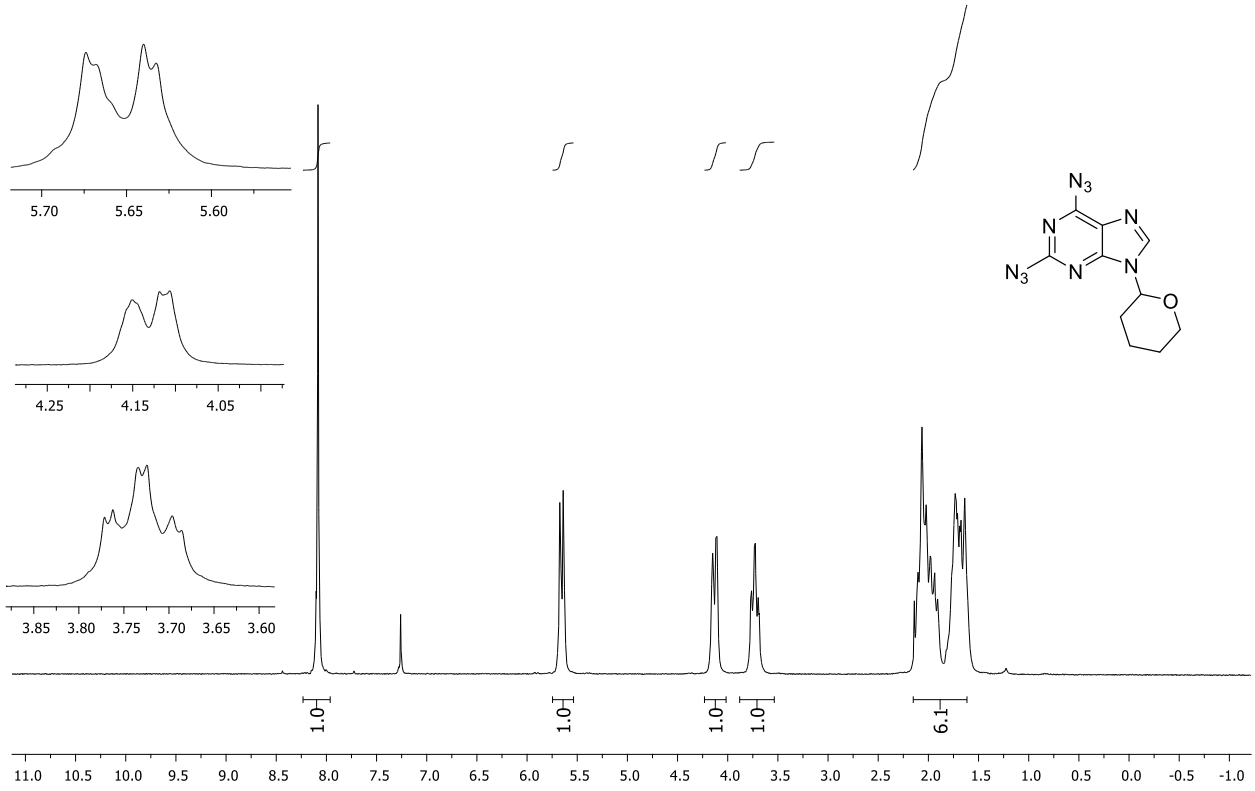
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 11b:



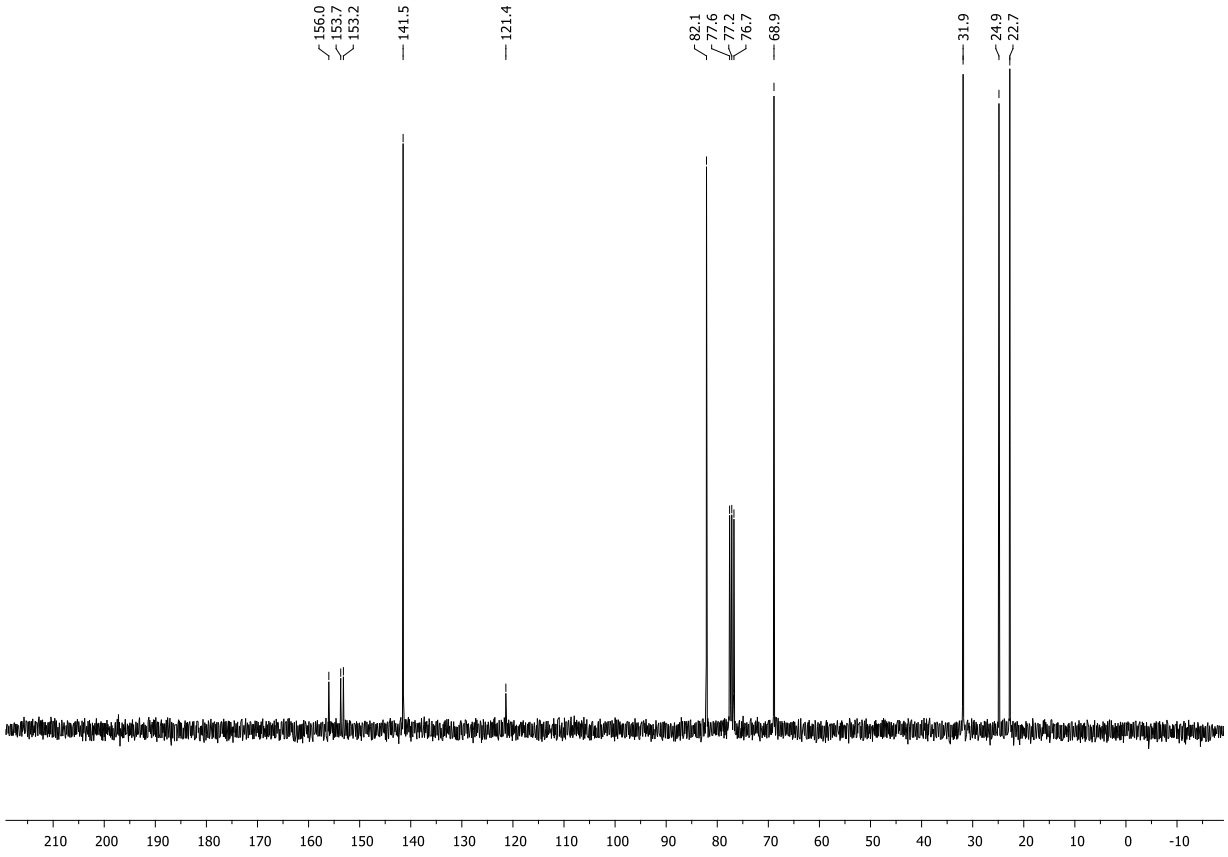
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 11b:



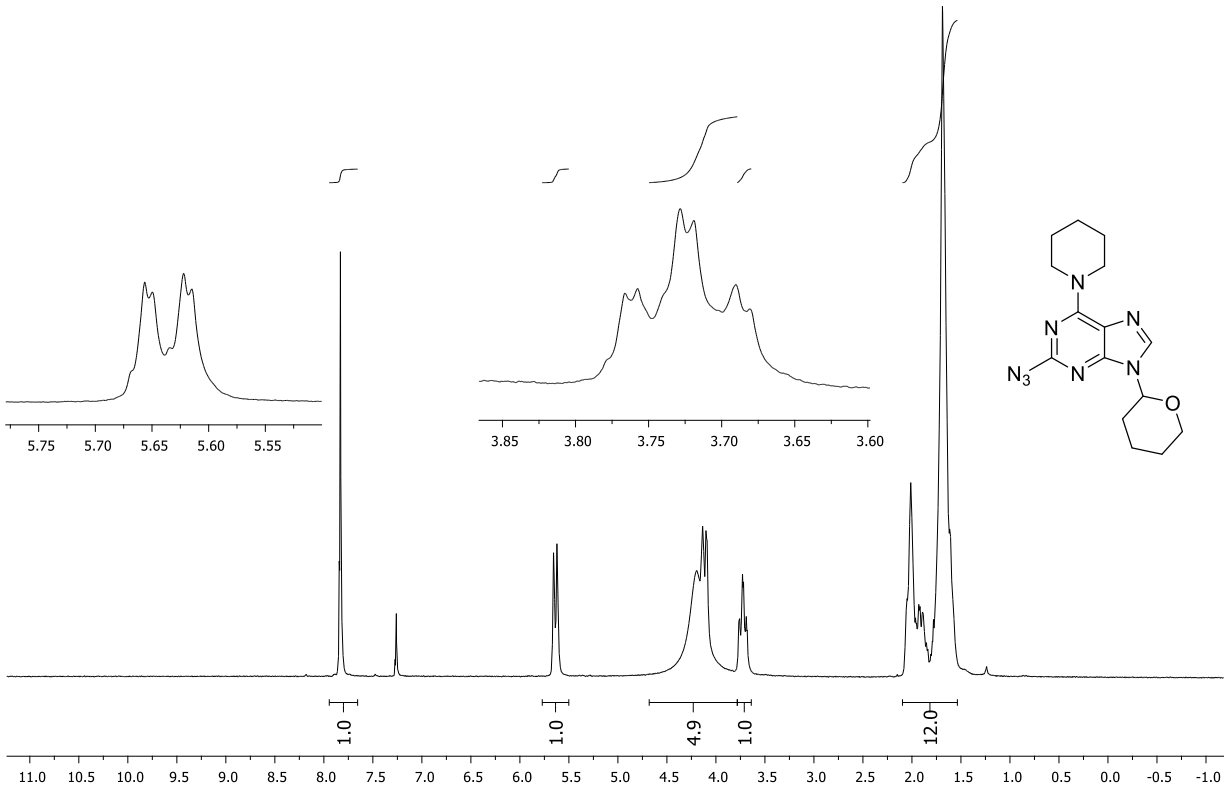
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound 12:



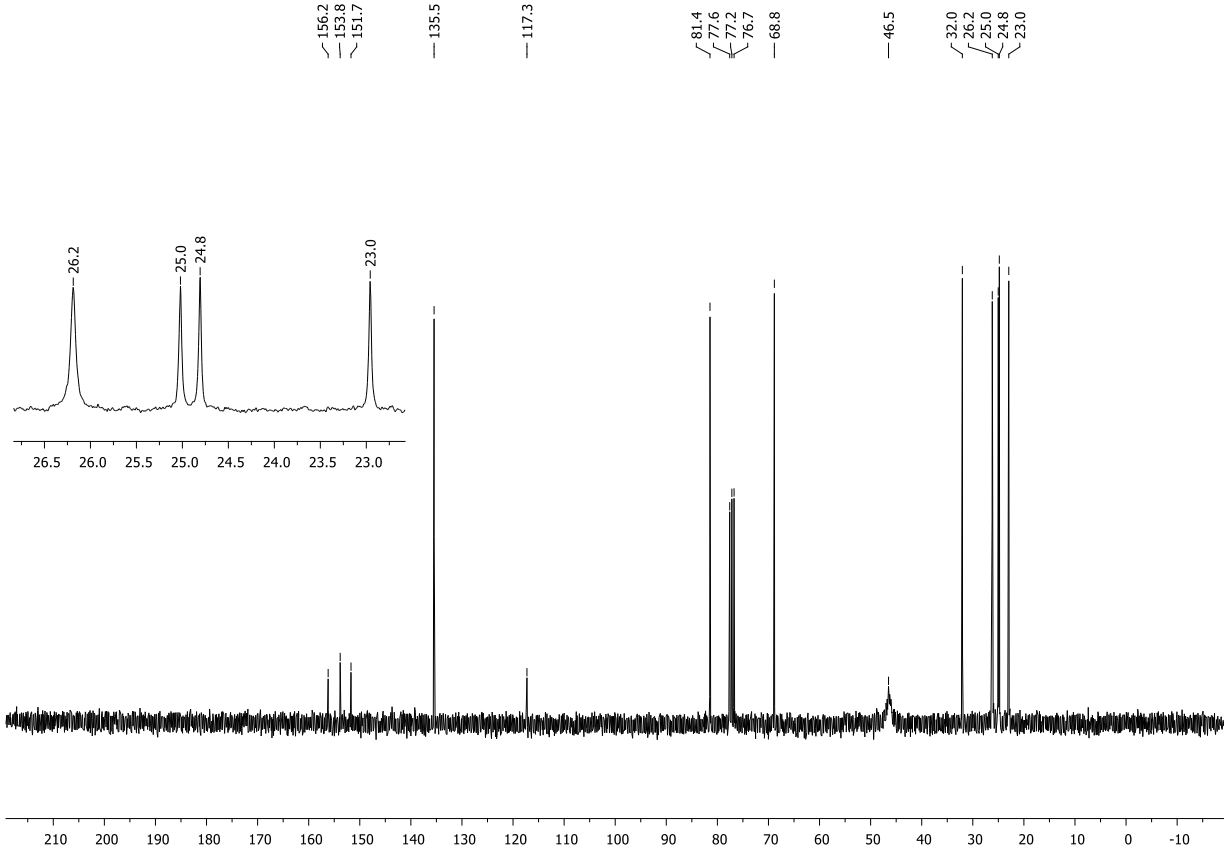
^{13}C-NMR (75.5 MHz, $CDCl_3$) spectrum of compound 12:



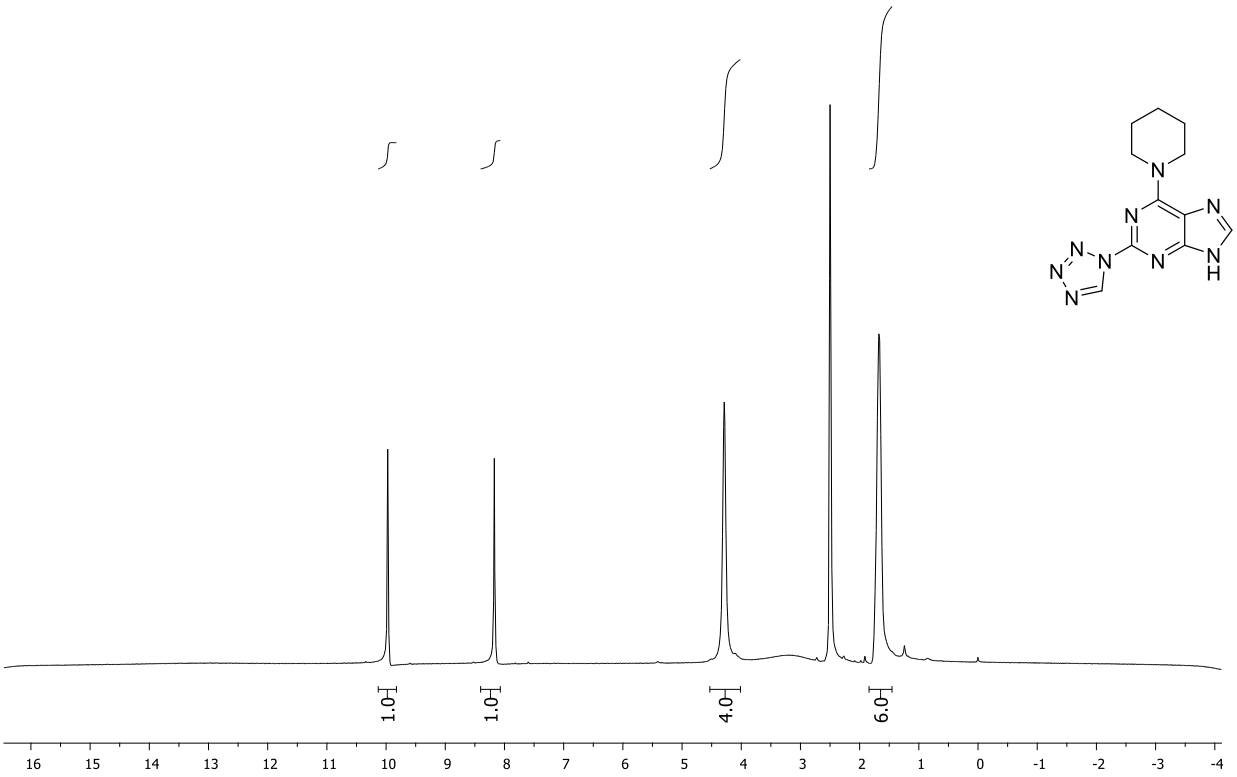
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 13:



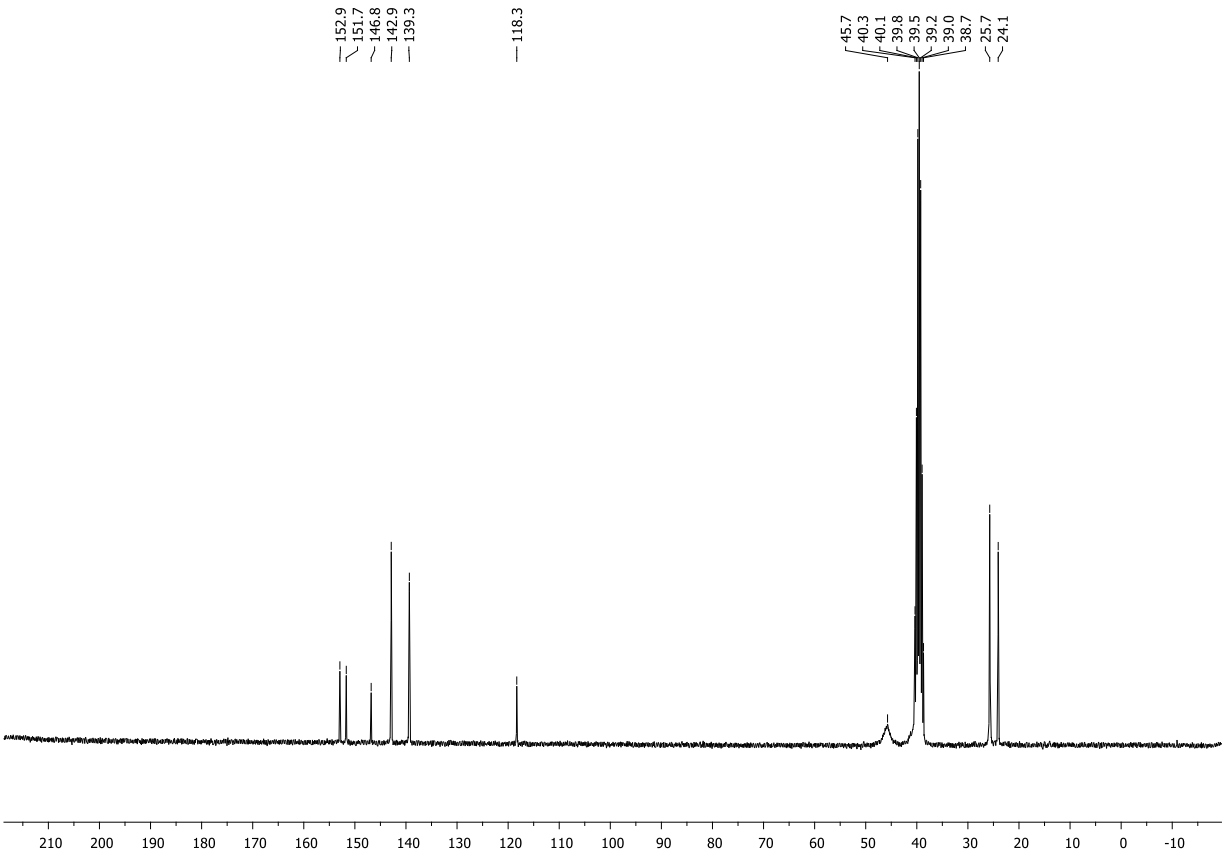
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 13:



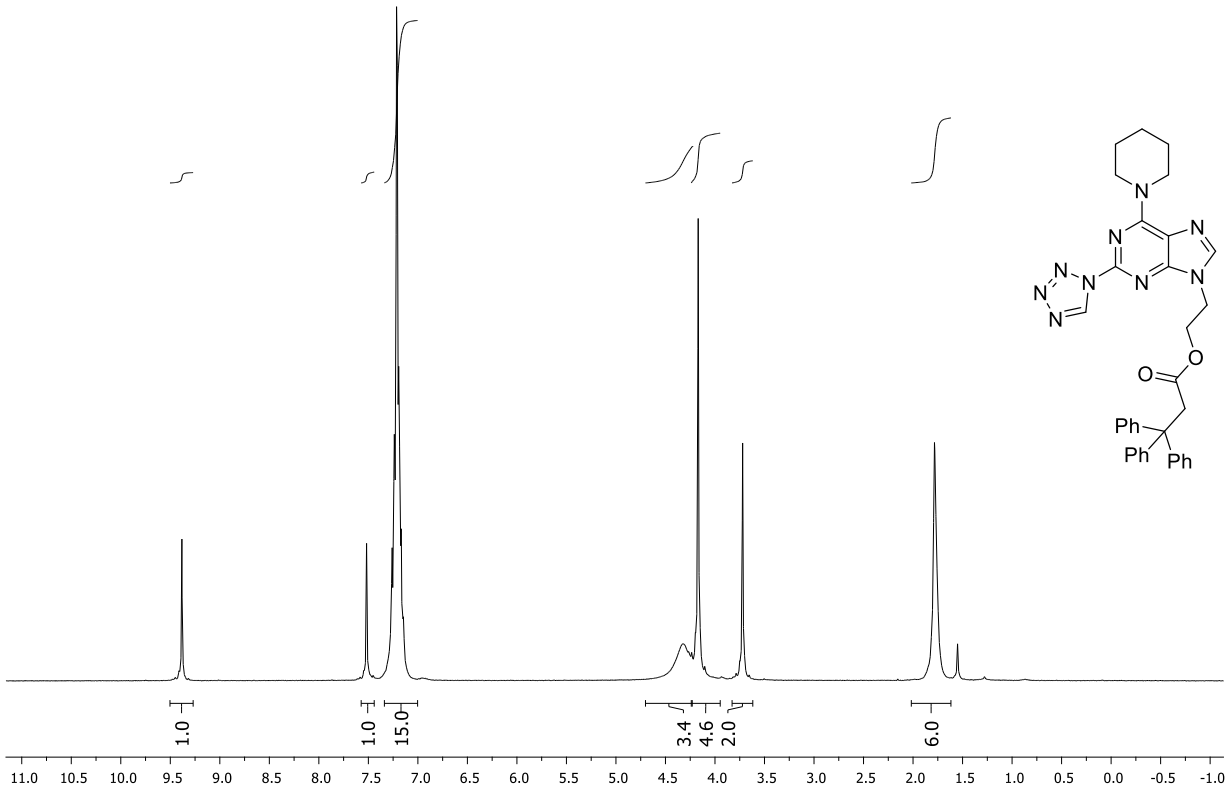
^{1}H-NMR (300 MHz, DMSO-d_6, 60 °C) spectrum of compound 17:



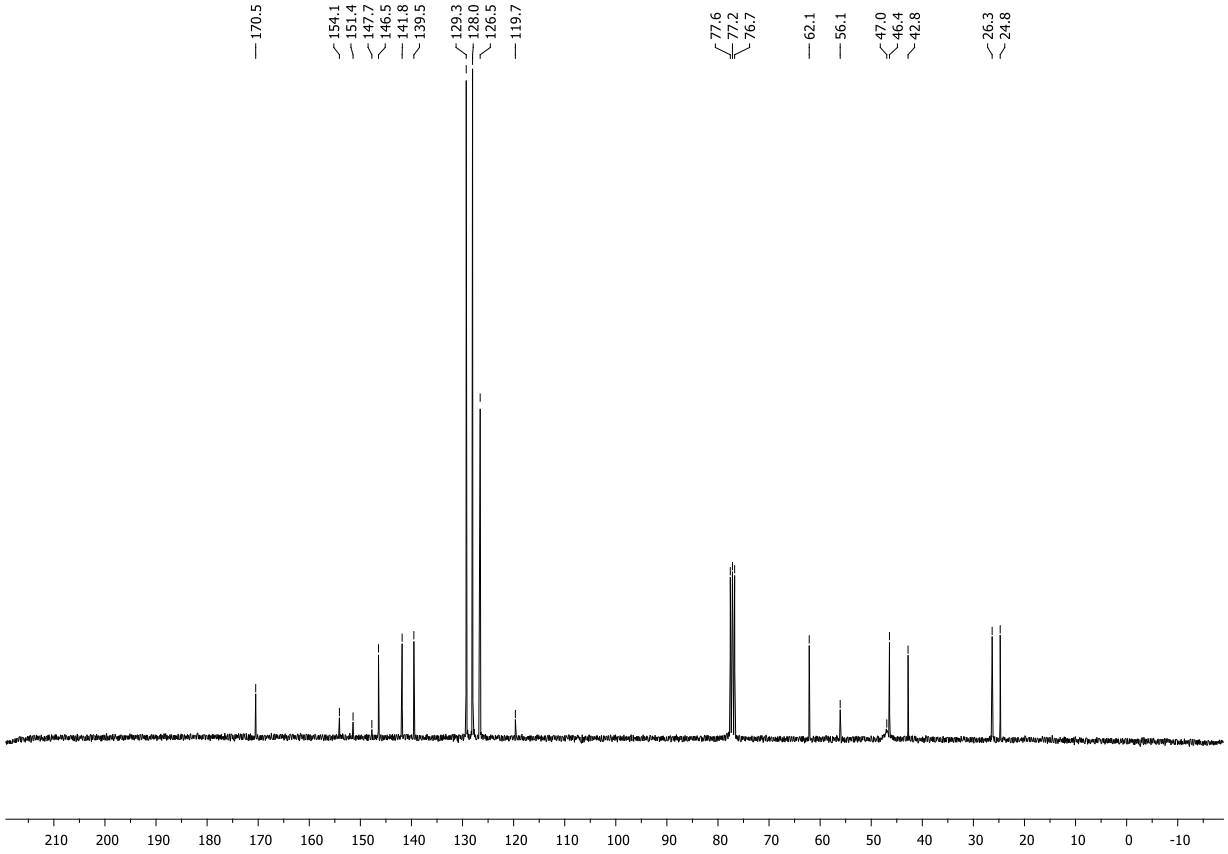
^{13}C-NMR (75.5 MHz, DMSO-d_6, 60 °C) spectrum of compound 17:



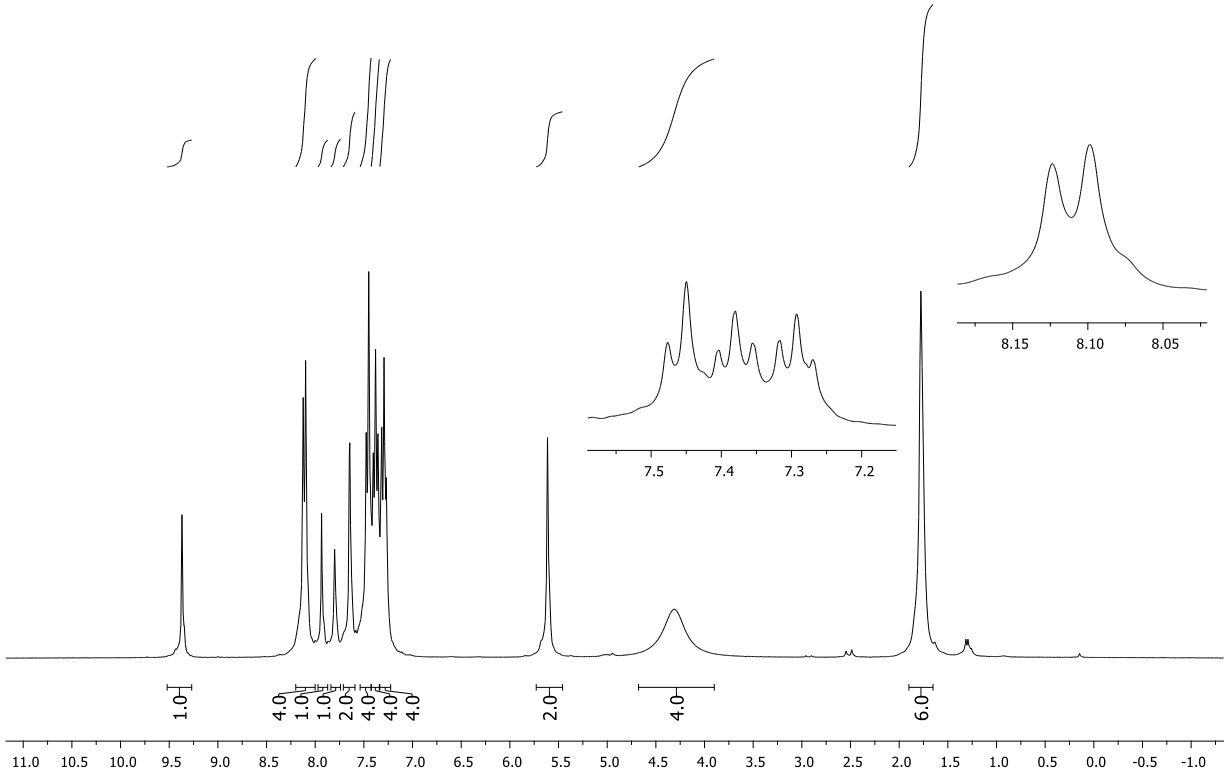
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 18a:



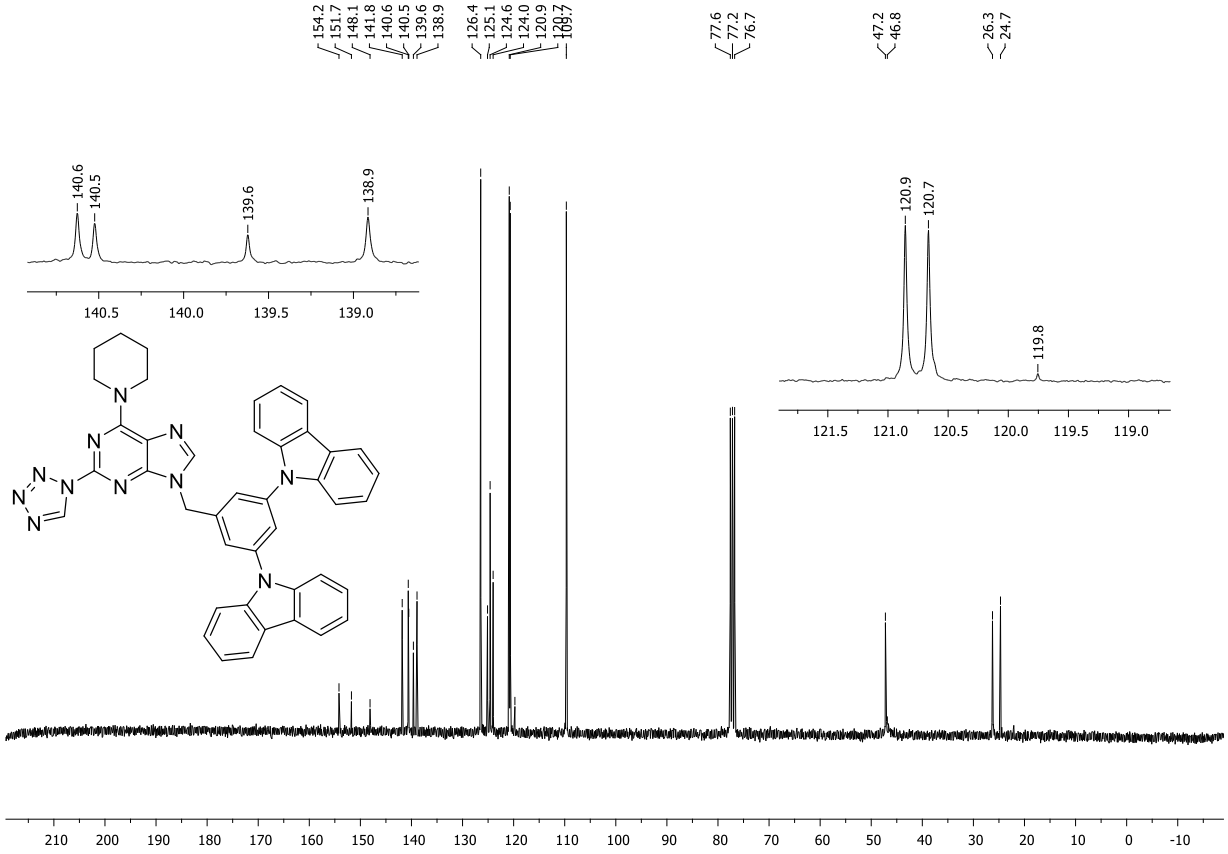
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 18a:



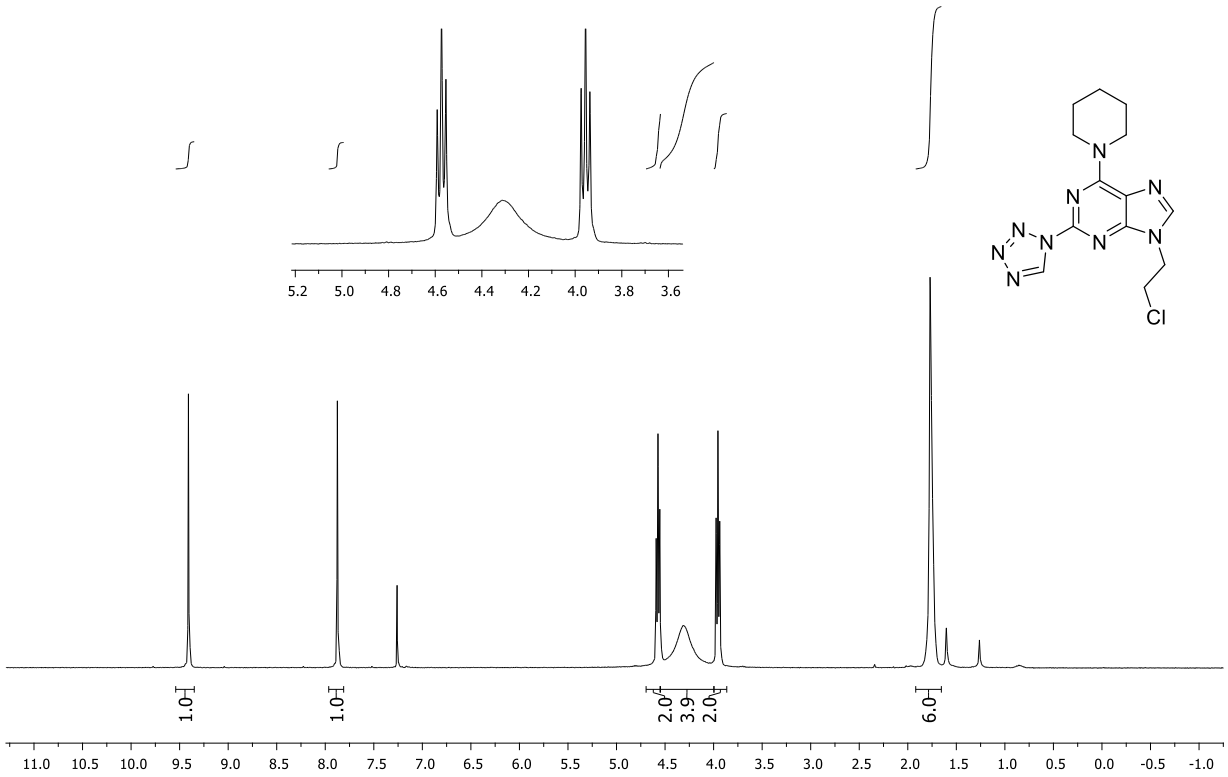
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 18b:



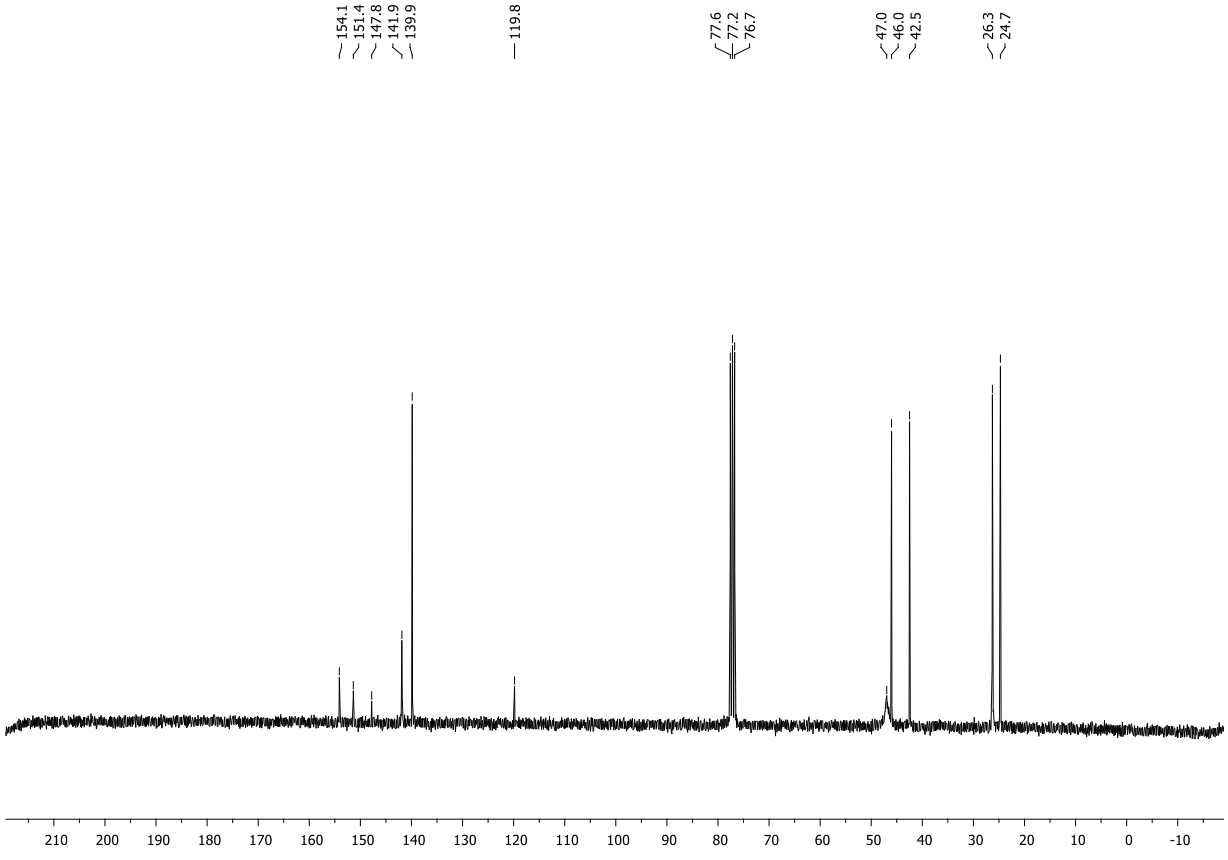
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 18b:



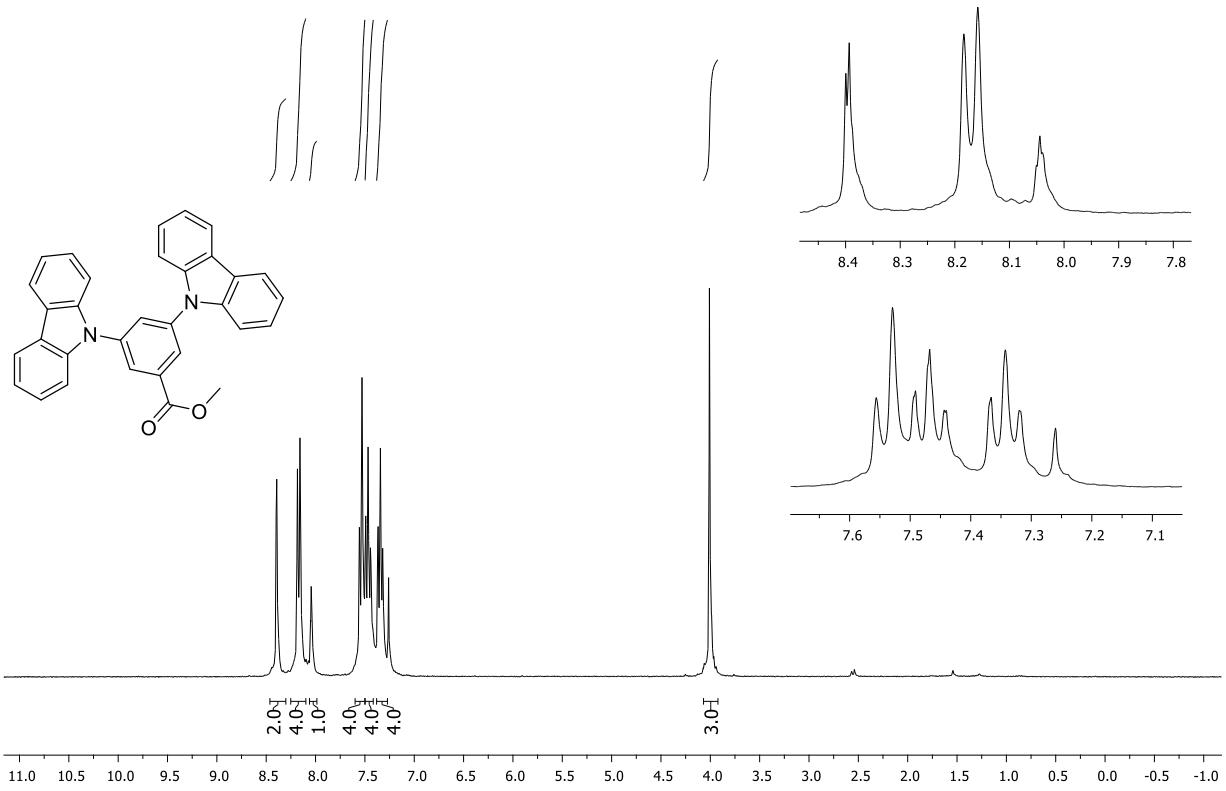
^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C) spectrum of compound 18c:



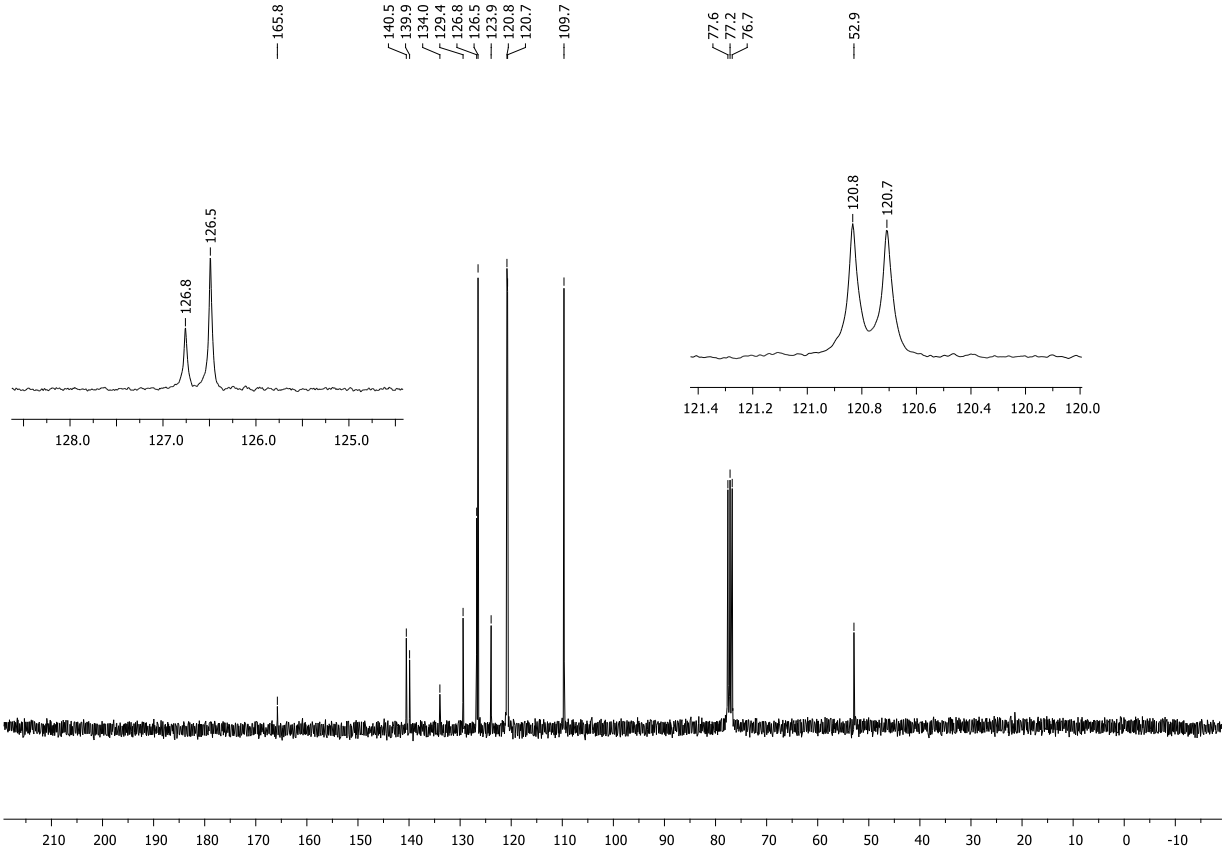
^{13}C-NMR (75.5 MHz, $CDCl_3$, 50 °C) spectrum of compound 18c:



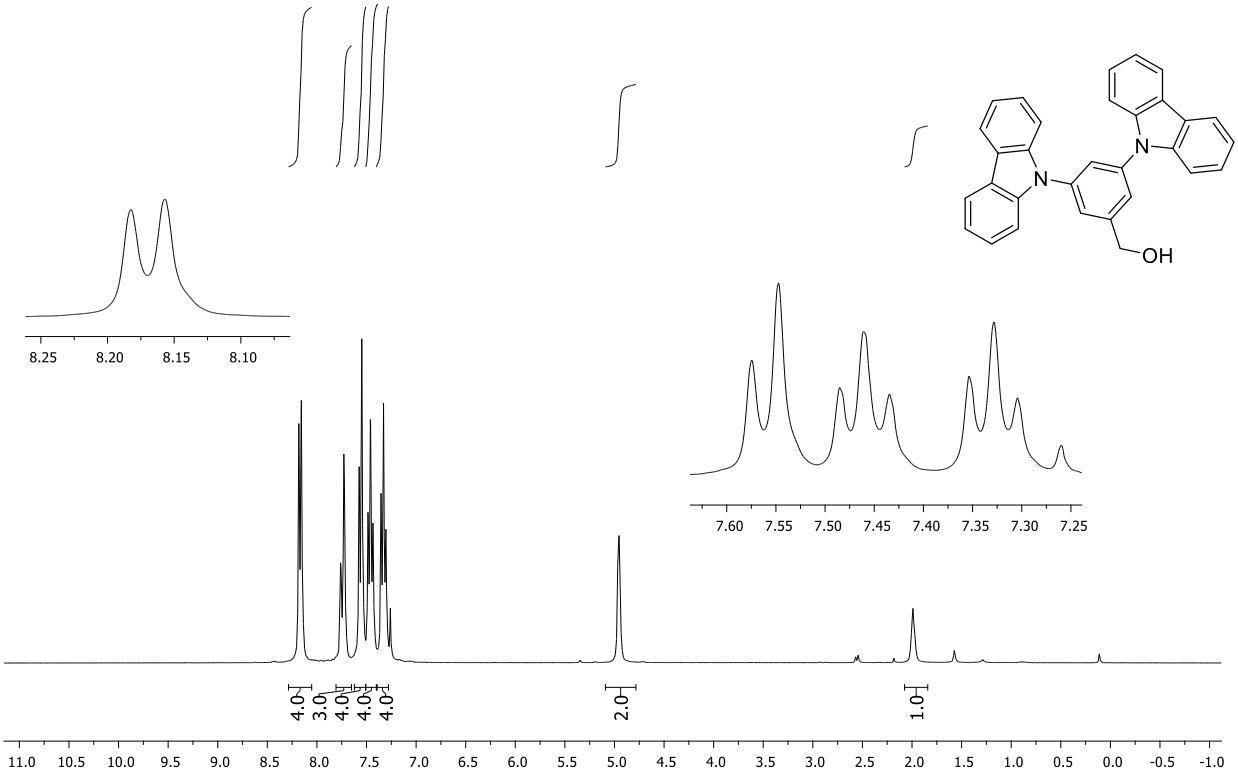
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound 20:



^{13}C-NMR (75.5 MHz, $CDCl_3$) spectrum of compound 20:



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound 21:



^{13}C-NMR (75.5 MHz, $CDCl_3$) spectrum of compound 21: