Supporting information

for

An access to 6-arylpyrrolo[2,3-*d*]pyrimidines *via* palladium-catalyzed direct C-H arylation reaction

by

Jelena Dodonova and Sigitas Tumkevičius*

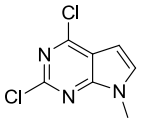
Vilnius University, Department of Organic Chemistry, Naugarduko 24, LT-03225 Vilnius, Lithuania

sigitas.tumkevicius@chf.vu.lt

General Methods

Reagents were purchased directly from commercial suppliers; solvents were purified by known procedures. Thin layer chromatography was performed using TLC-aluminum sheets with silica gel (Merck 60 F254). Visualization was accomplished by UV light. Column chromatography was performed using Silica gel 60 (0.040-0.063 mm) (Merck). NMR spectra were recorded on a Bruker Ascend 400 (400 MHz and 100 MHz, respectively). ^{1}H NMR and ^{13}C NMR spectra were referenced to residual solvent peaks. Signal multiplicities in the ^{13}C spectra were assigned by APT and HSQC experiments. Melting points were determined in open capillaries with a digital melting point IA9100 series apparatus (ThermoFischer Scientific) and were not corrected. High Resolution Mass Spectrometry (HRMS) analyses were carried out on a quadrupole, time-of-flight mass spectrometer (microTOF-Q II, Bruker Daltonik GmbH, Bremen, Germany) or on Dual-ESI Q-TOF 6520 (Agilent Technologies) mass spectrometer.

2,4-Dichloro-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine

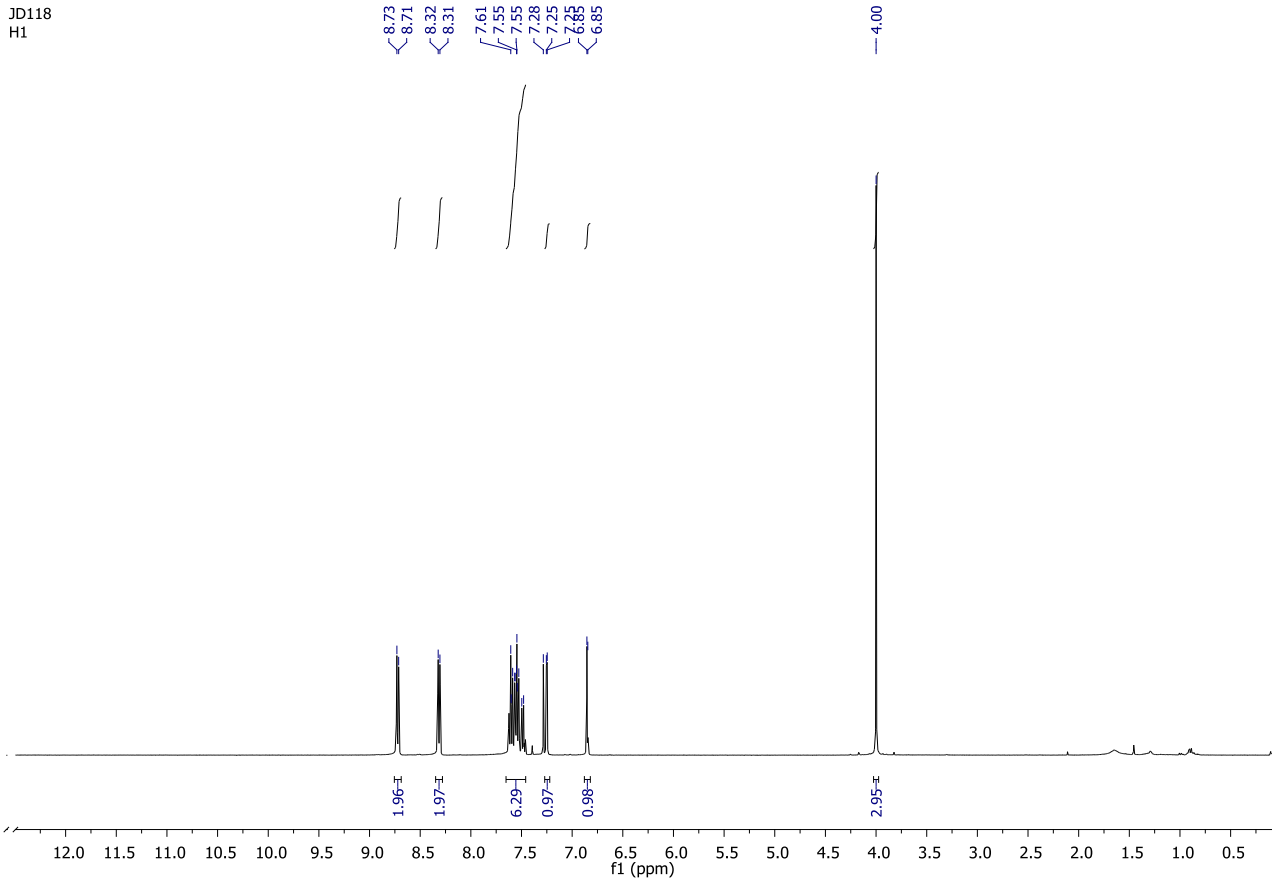


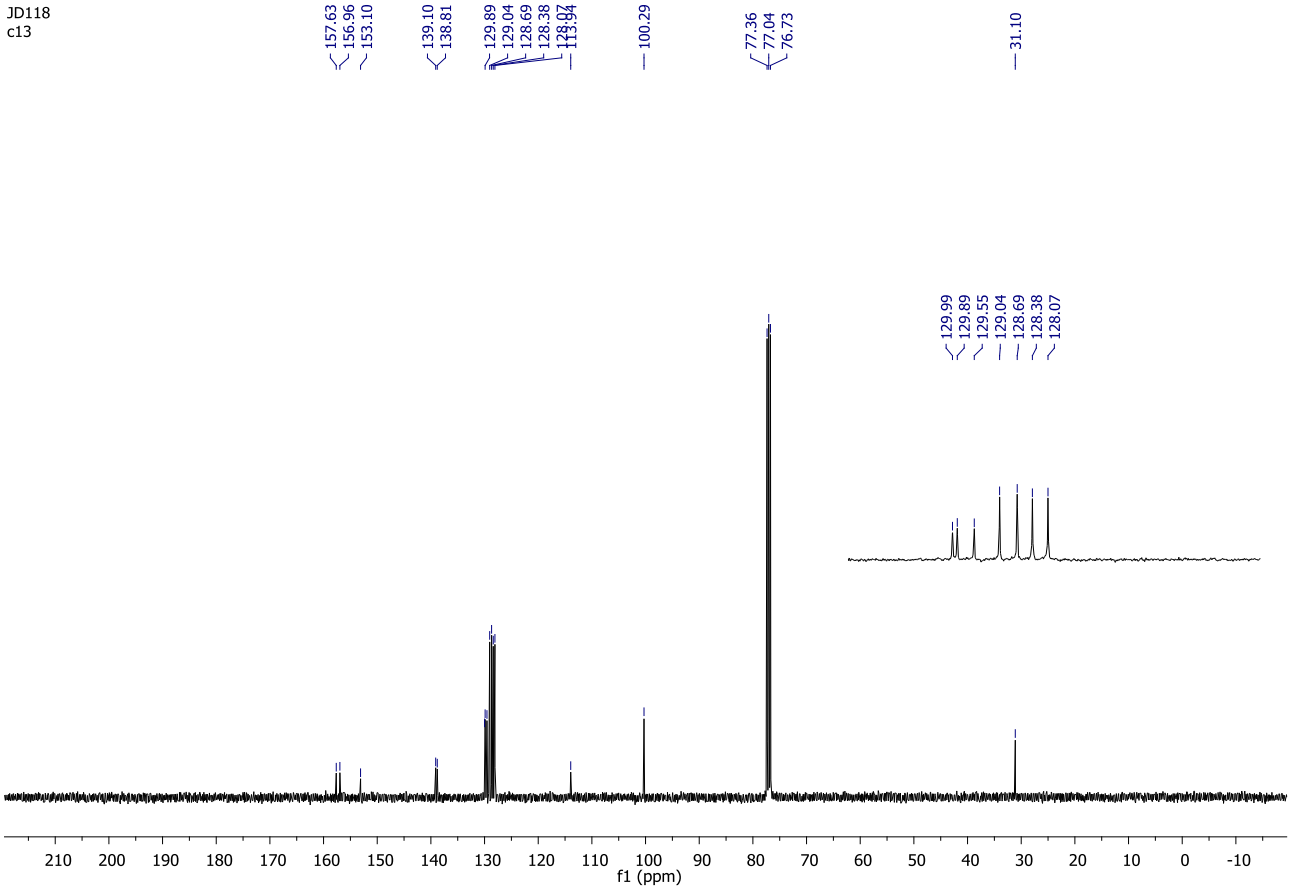
A solution of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine[1] (2 g, 10.6 mmol) in dry THF (20 ml) was cooled to 0 °C. Once cool, 60% NaH (510 mg, 21.3 mmol) in oil was added slowly. The reaction mixture was allowed to stir until the evolution of hydrogen was complete. Iodomethane (2.26 g, 0.99 ml, 16.0 mmol) was then added and the reaction was allowed to slowly come to room temperature. The reaction mixture was stirred overnight and poured into ice water. The obtained solution was extracted with chloroform (3×25 mL), organic layer was dried over Na_2SO_4, chloroform removed by distillation under reduced pressure and residue was purified by column chromatography using chloroform as an eluent to give 2,4-dichloro-7-methylpyrrolo[2,3-*d*]pyrimidine (1.6 g, 74%) as a colourless solid, mp 151-152.7 °C. Lit.[1] mp 151 °C. All spectra matched literature values.[1]

^{1}H NMR (400 MHz, $CDCl_3$): 3.89 (3H, s, NCH_3), 6.62 [1H, d, J = 4 Hz, 5-H (pp)], 7.22 [1H, d, J = 4 Hz, 6-H (pp)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 31.8, 99.9, 116.3, 130.8, 151.9, 152.2, 152.6 ppm.

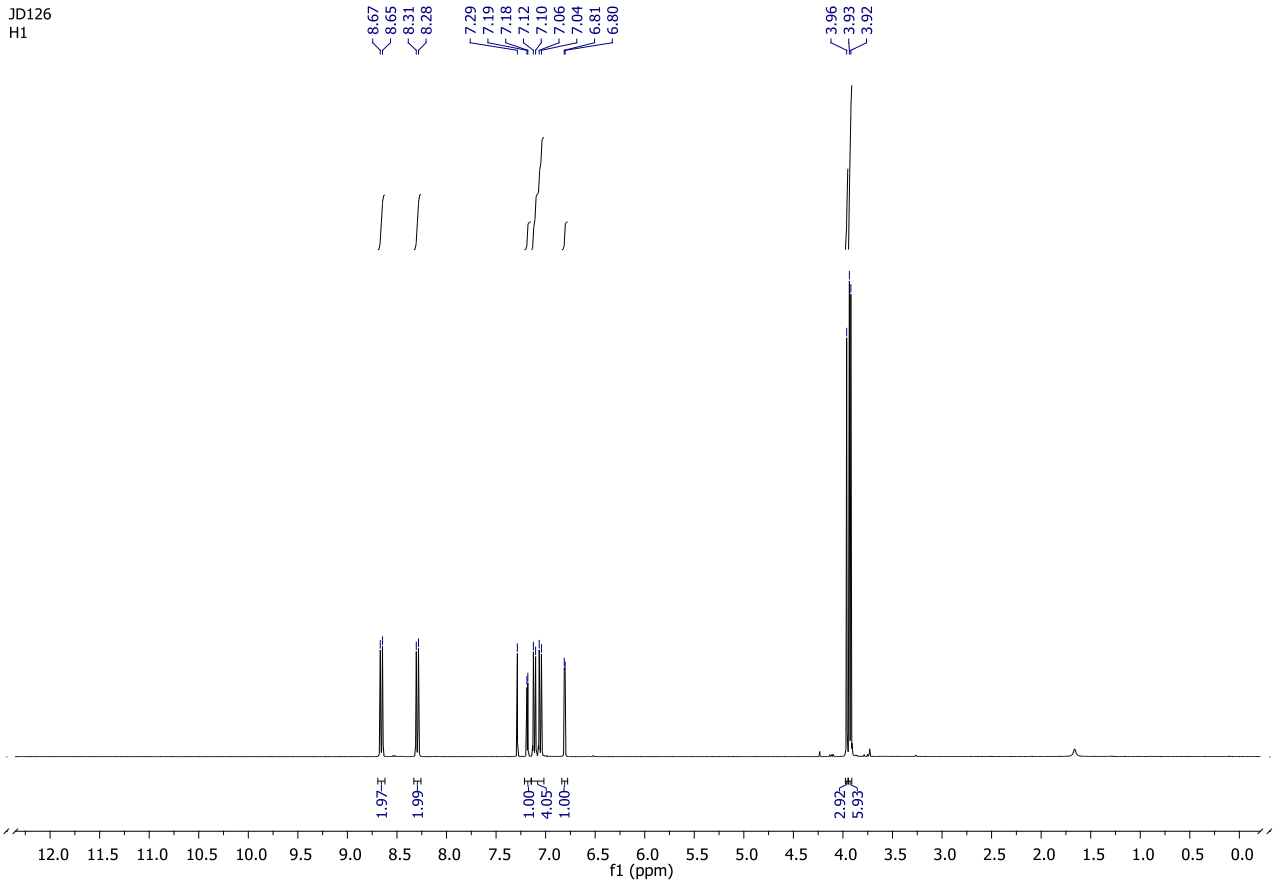
[1] F. Seela, H. Driller, *Liebigs Ann. Chem.* **1984**, 722-733.

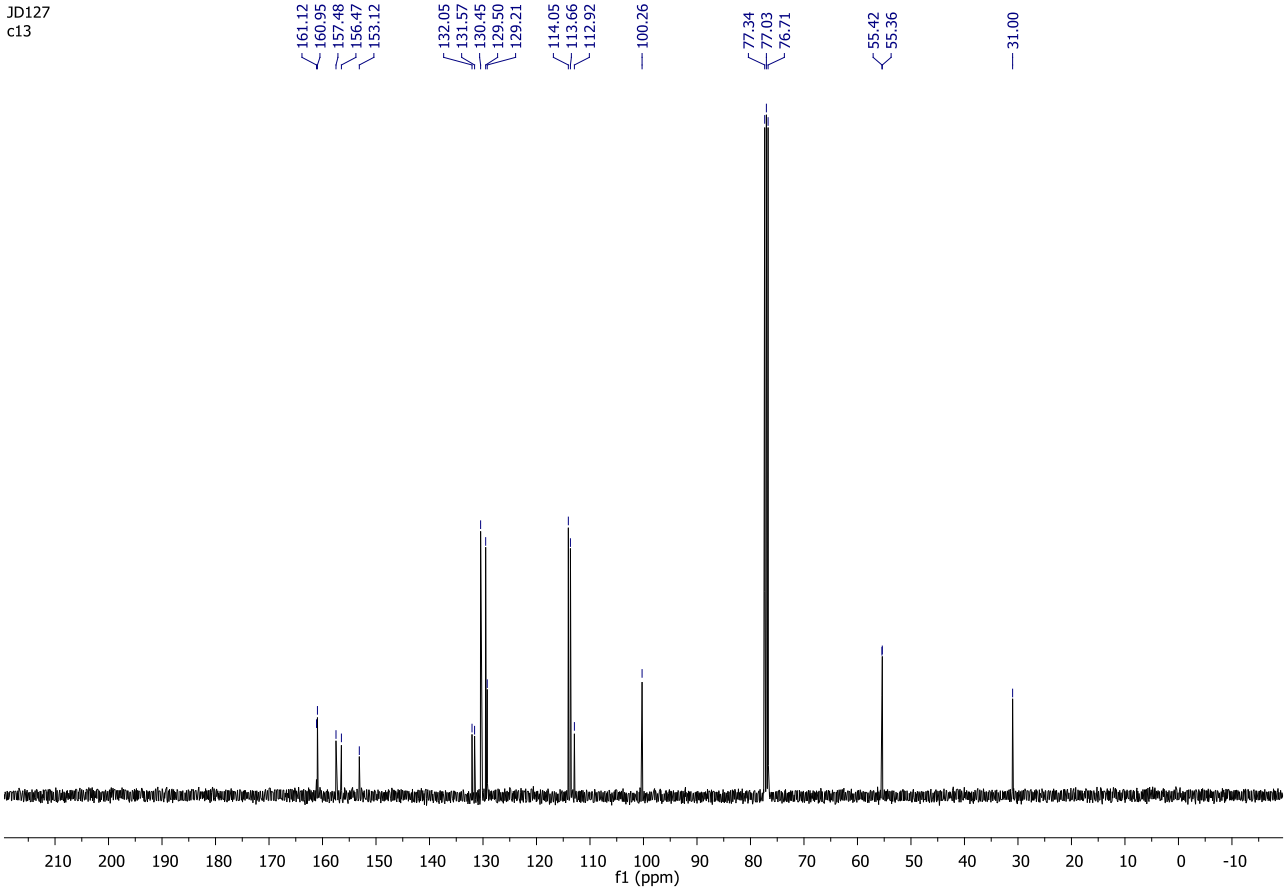
7-Methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (1a). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



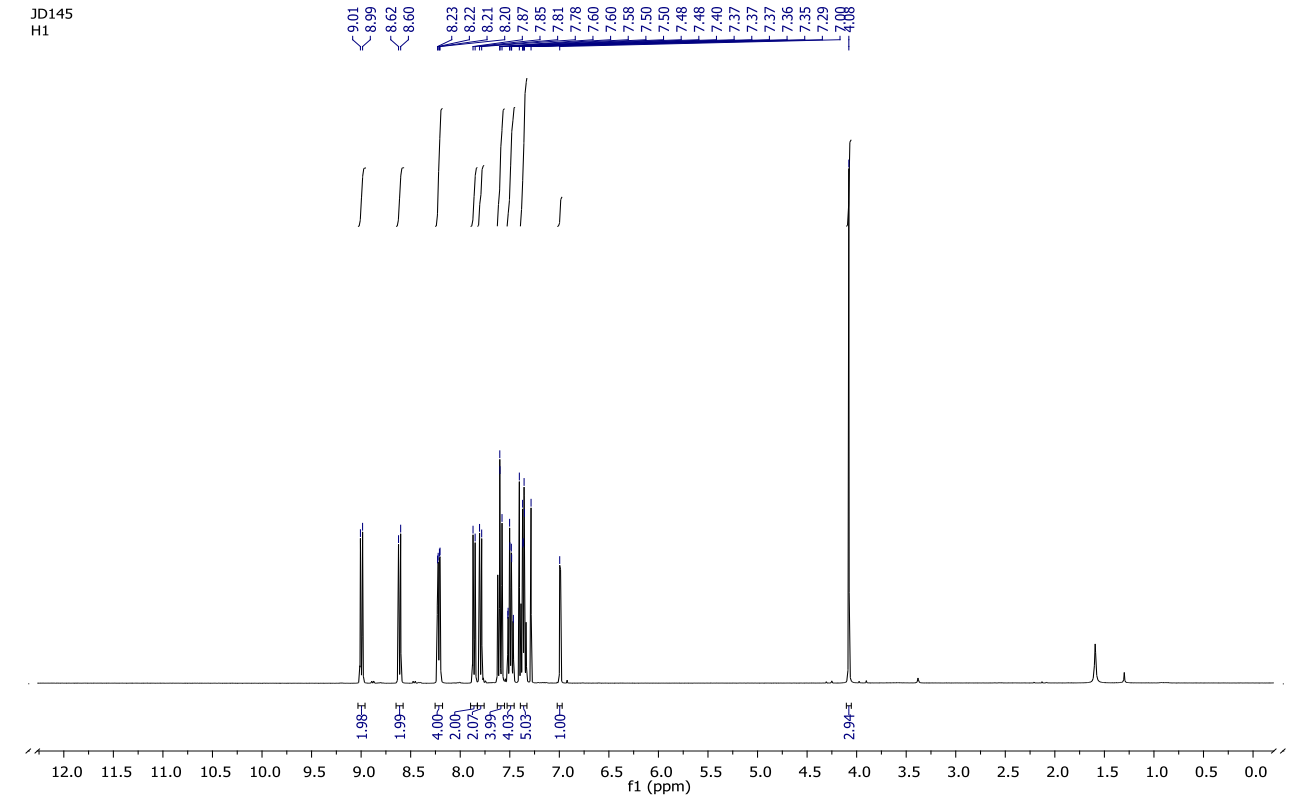


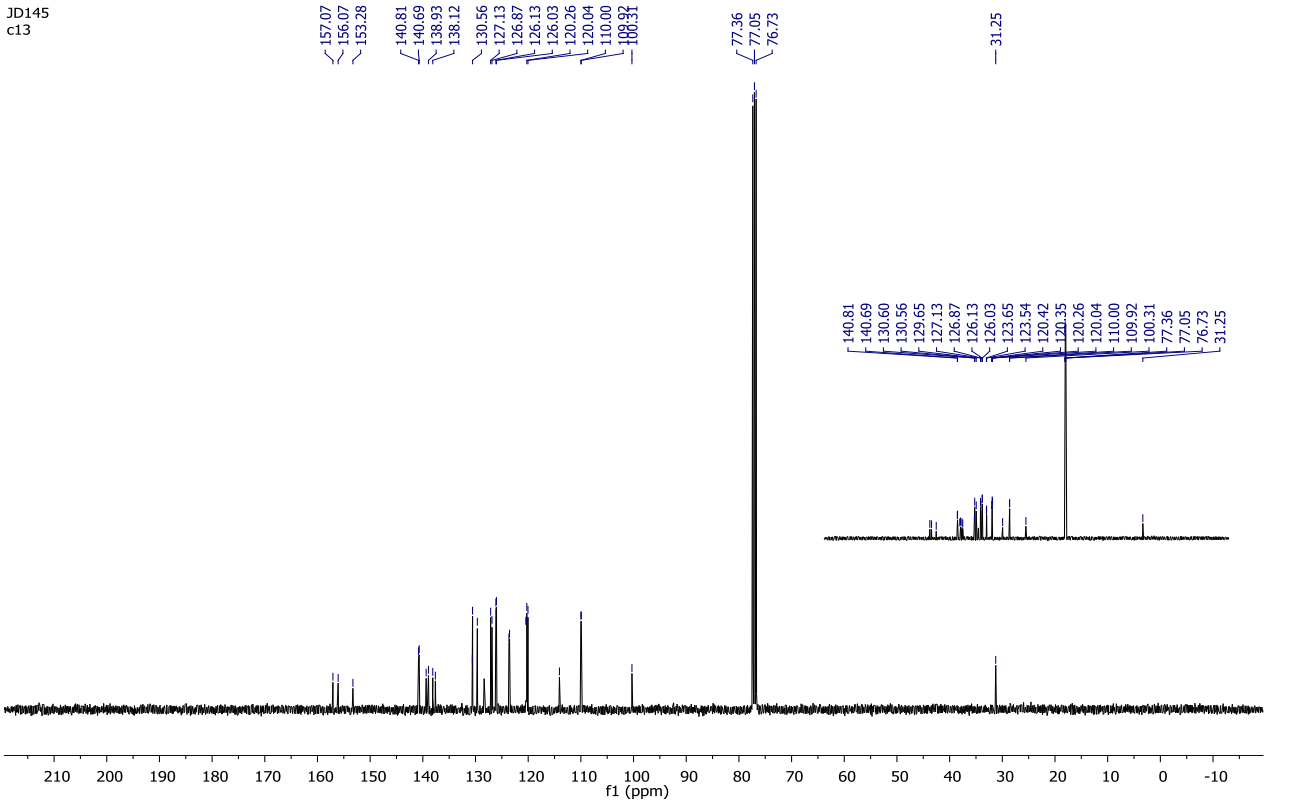
2,4-Di(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (1b). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



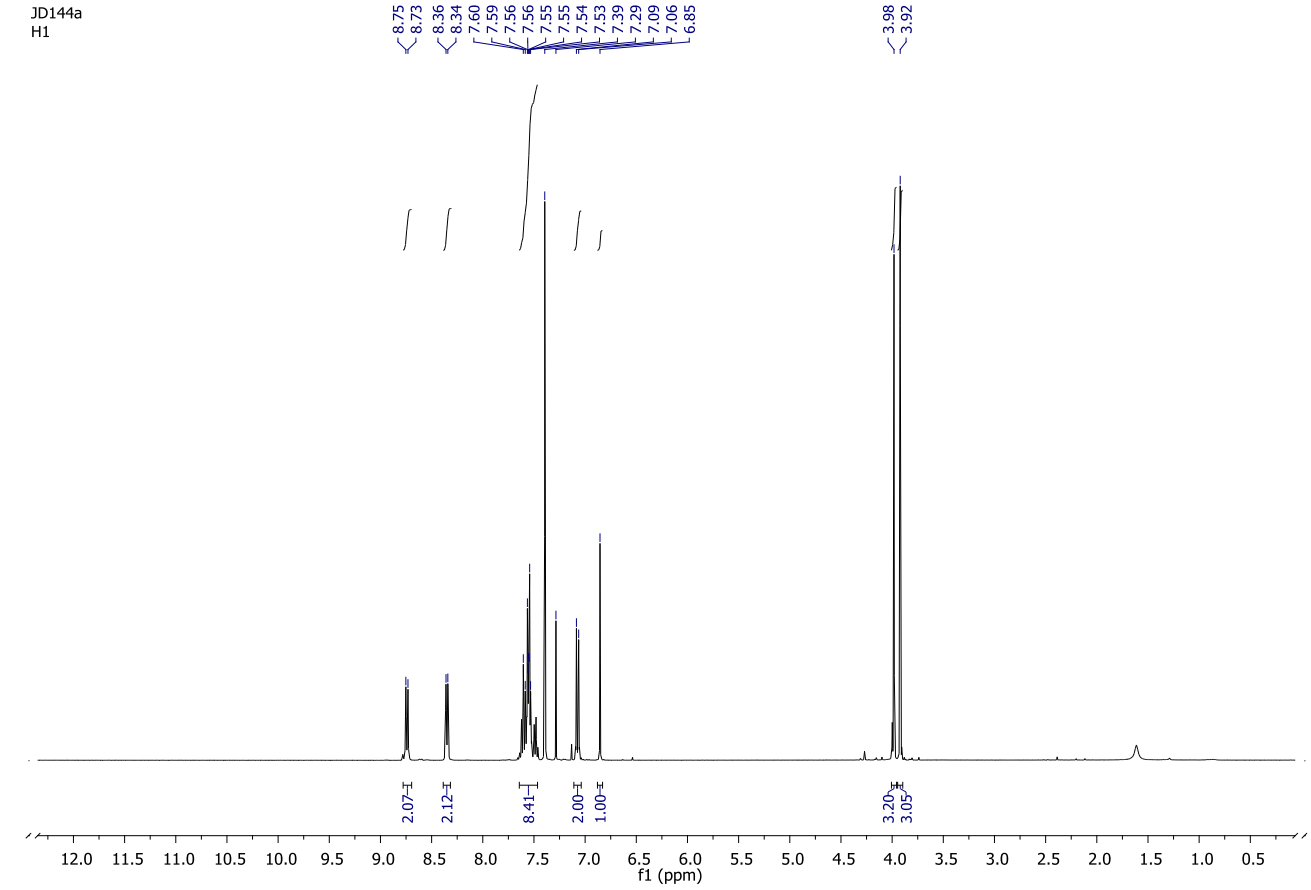


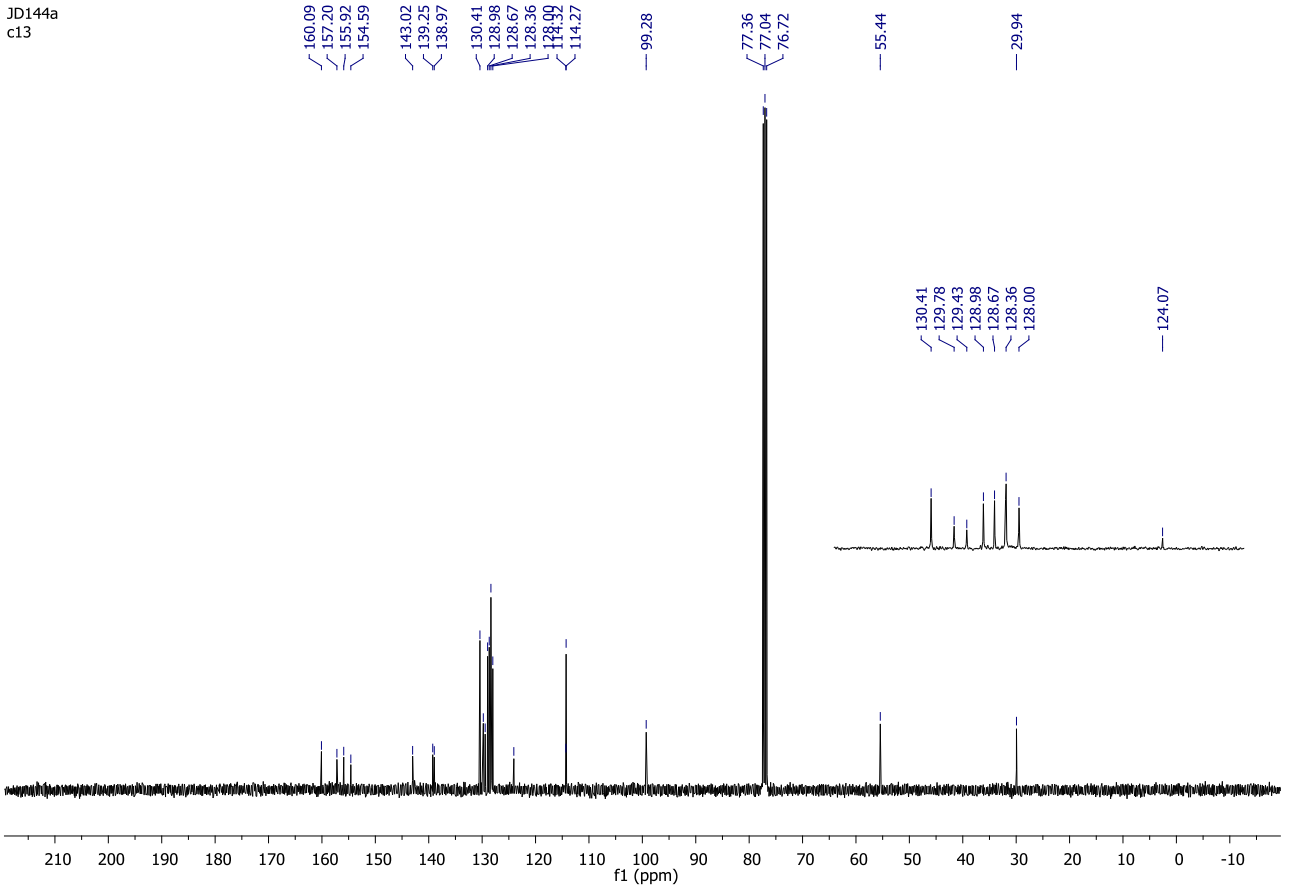
2,4-Di[4-(9*H*-carbazol-9-yl)phenyl]-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (1c). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).

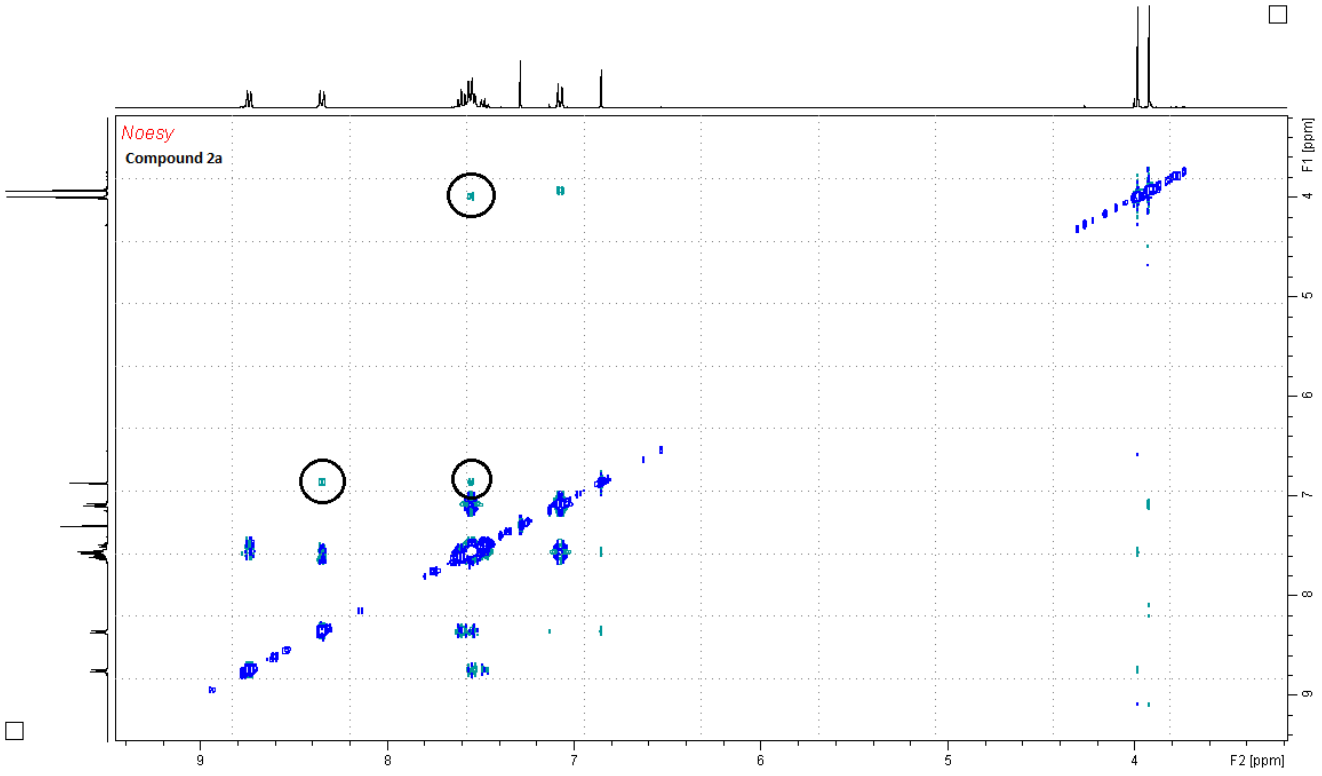




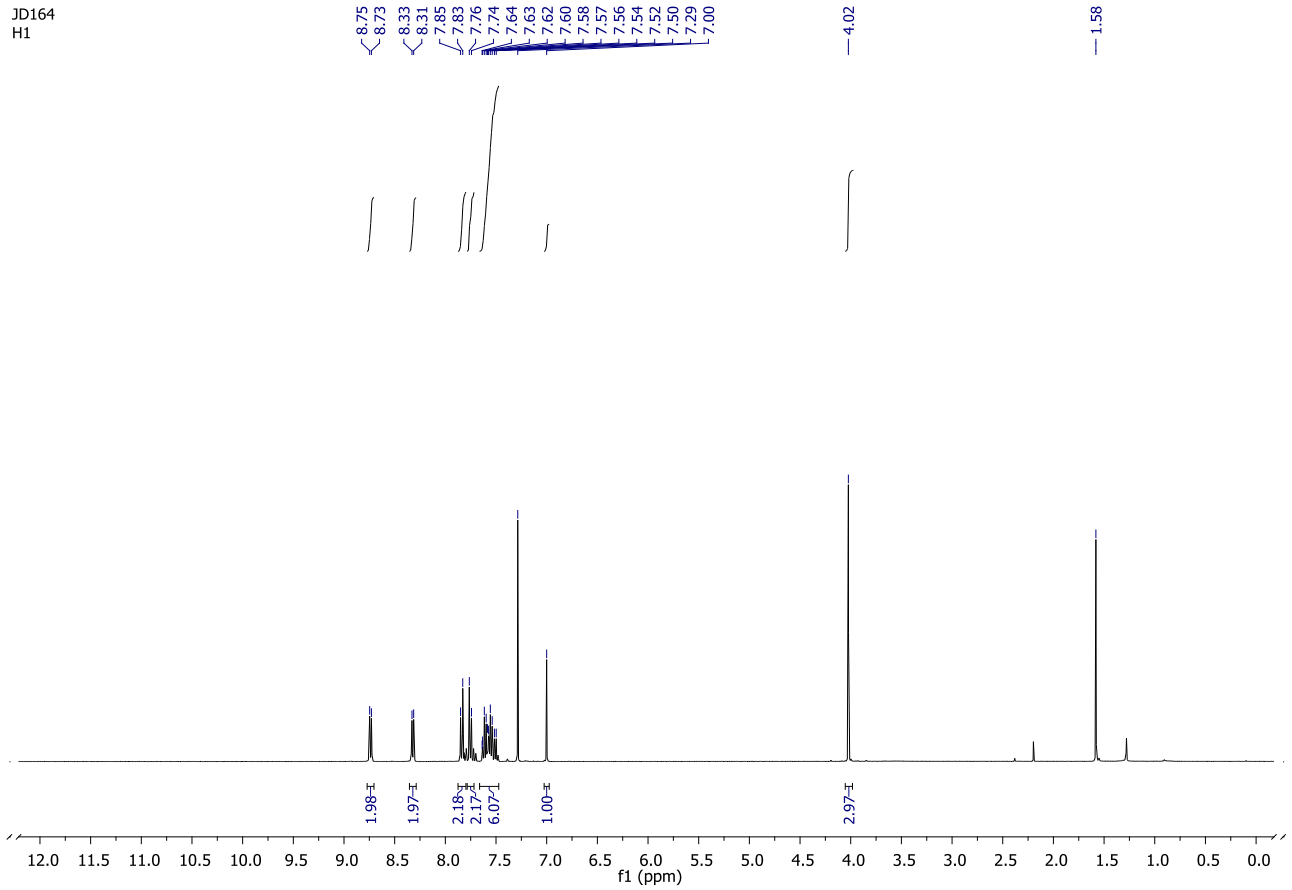
6-(4-Methoxyphenyl)-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2a). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).

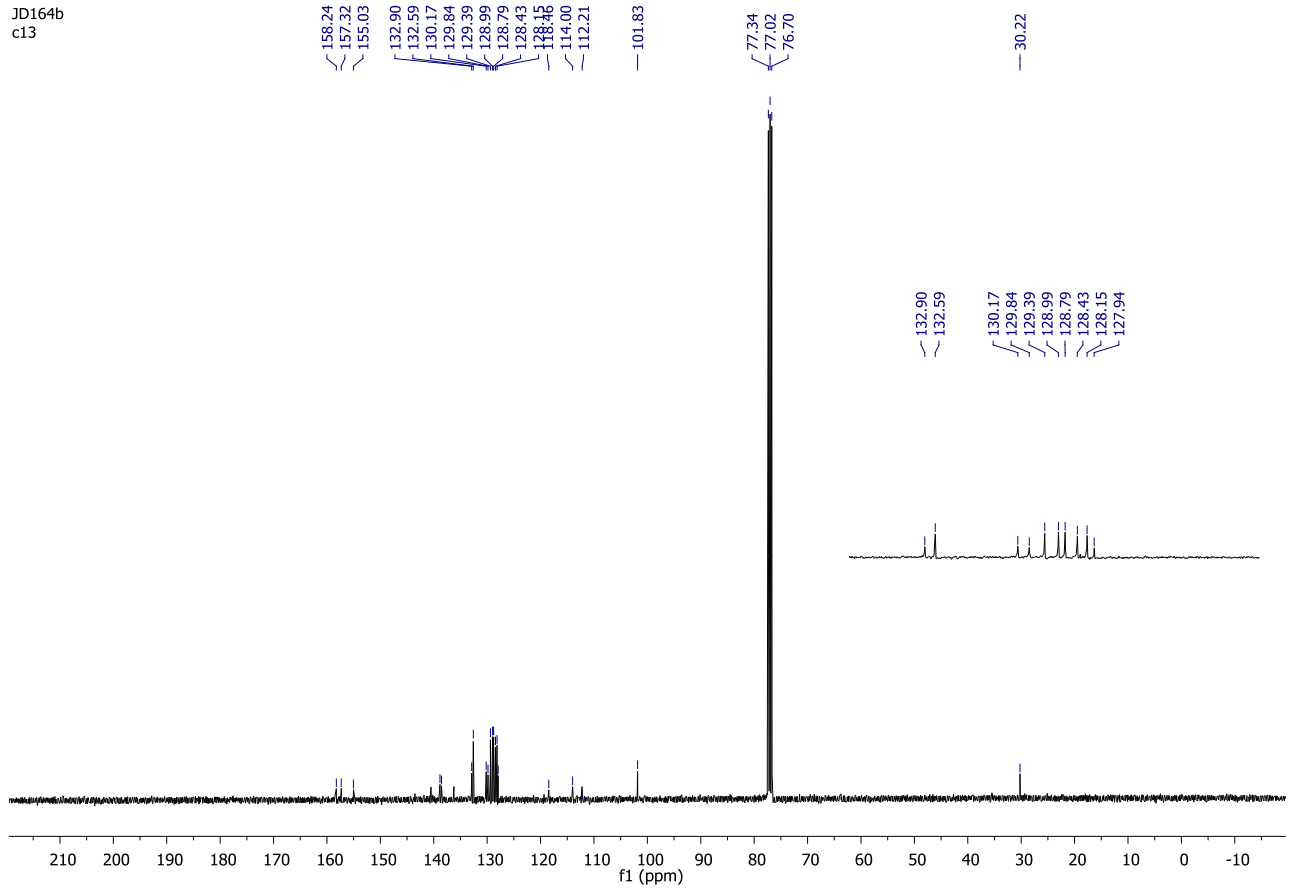




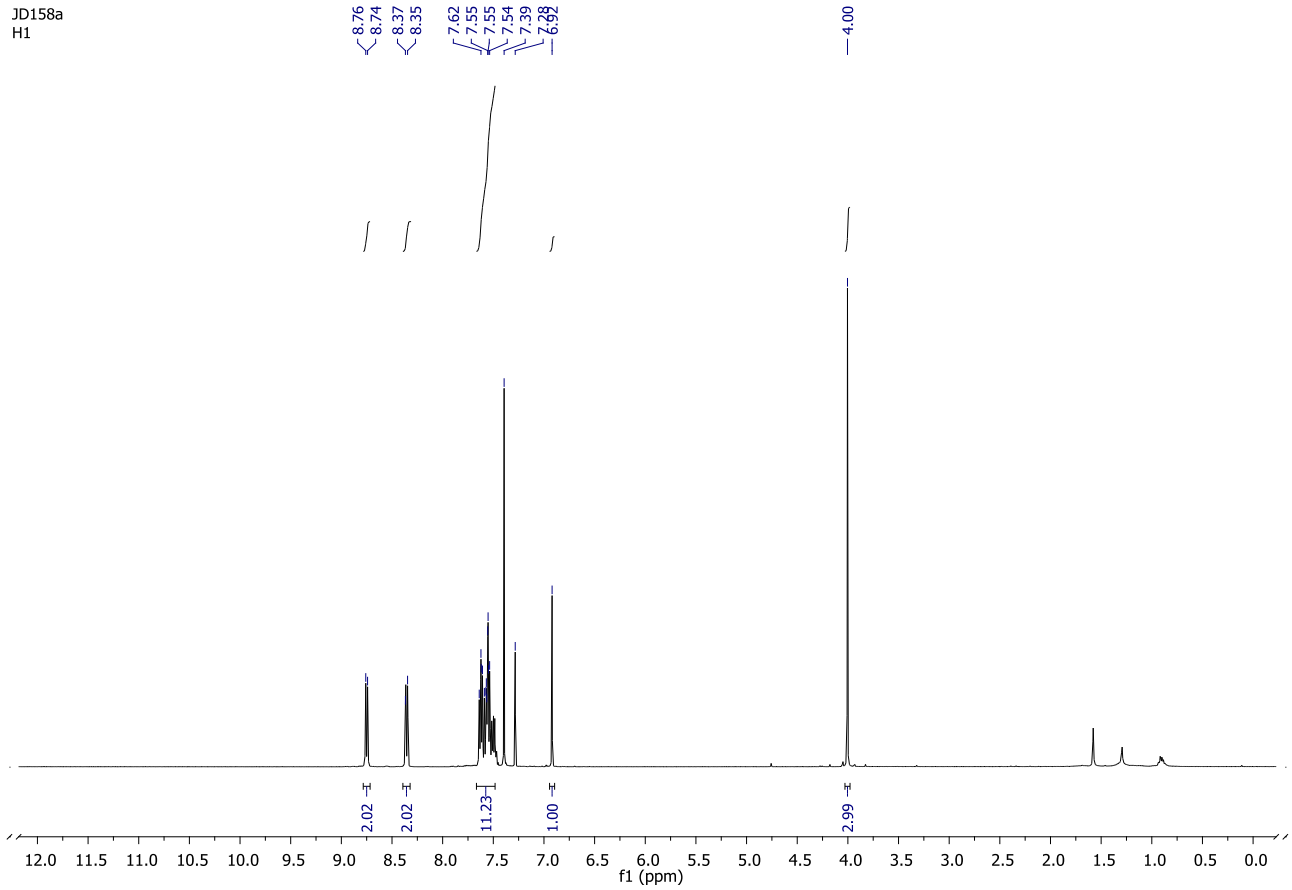

Noesy
Compound 2a
F1 [ppm]
F2 [ppm]
9
8
7
6
5
4

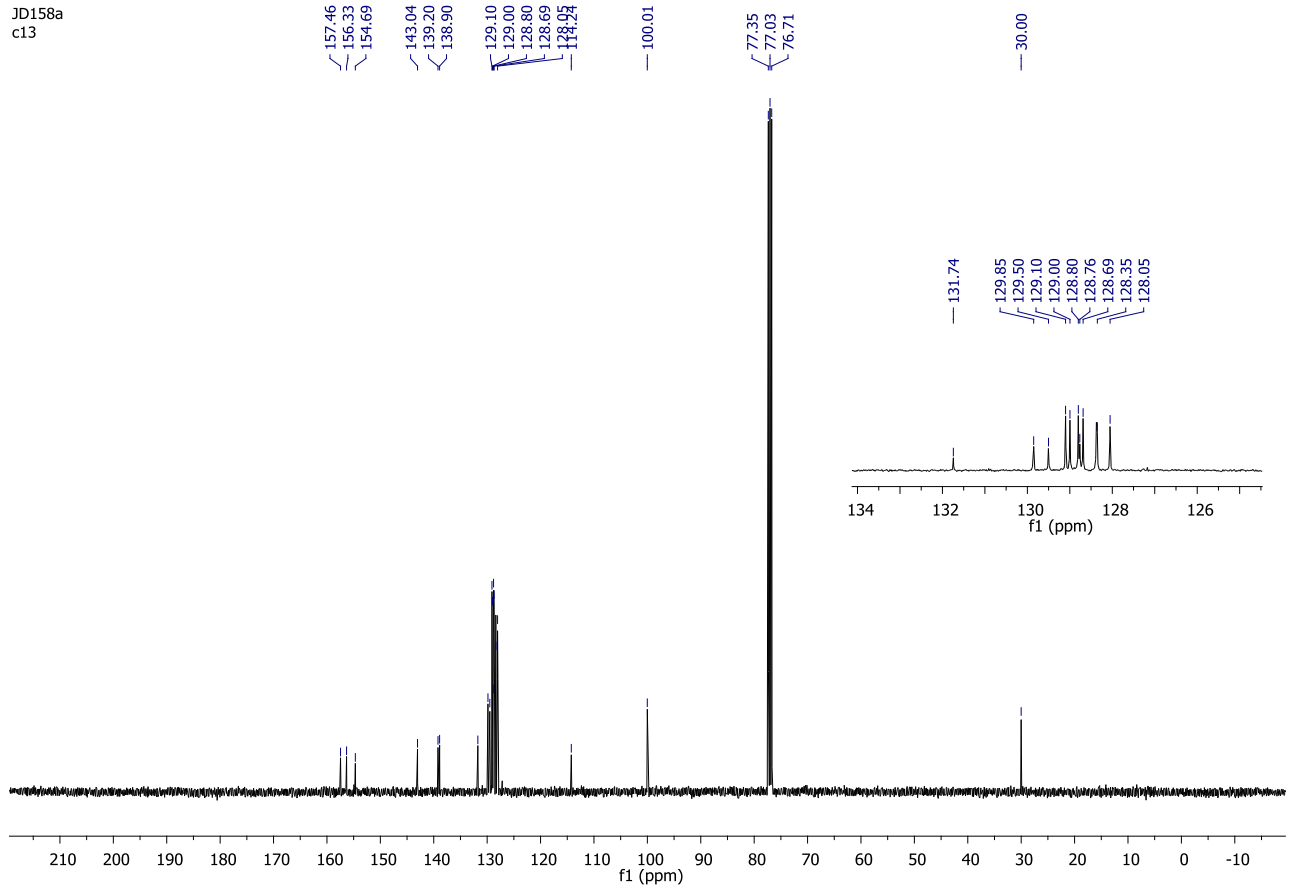
6-(4-Cyanophenyl)-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2b). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



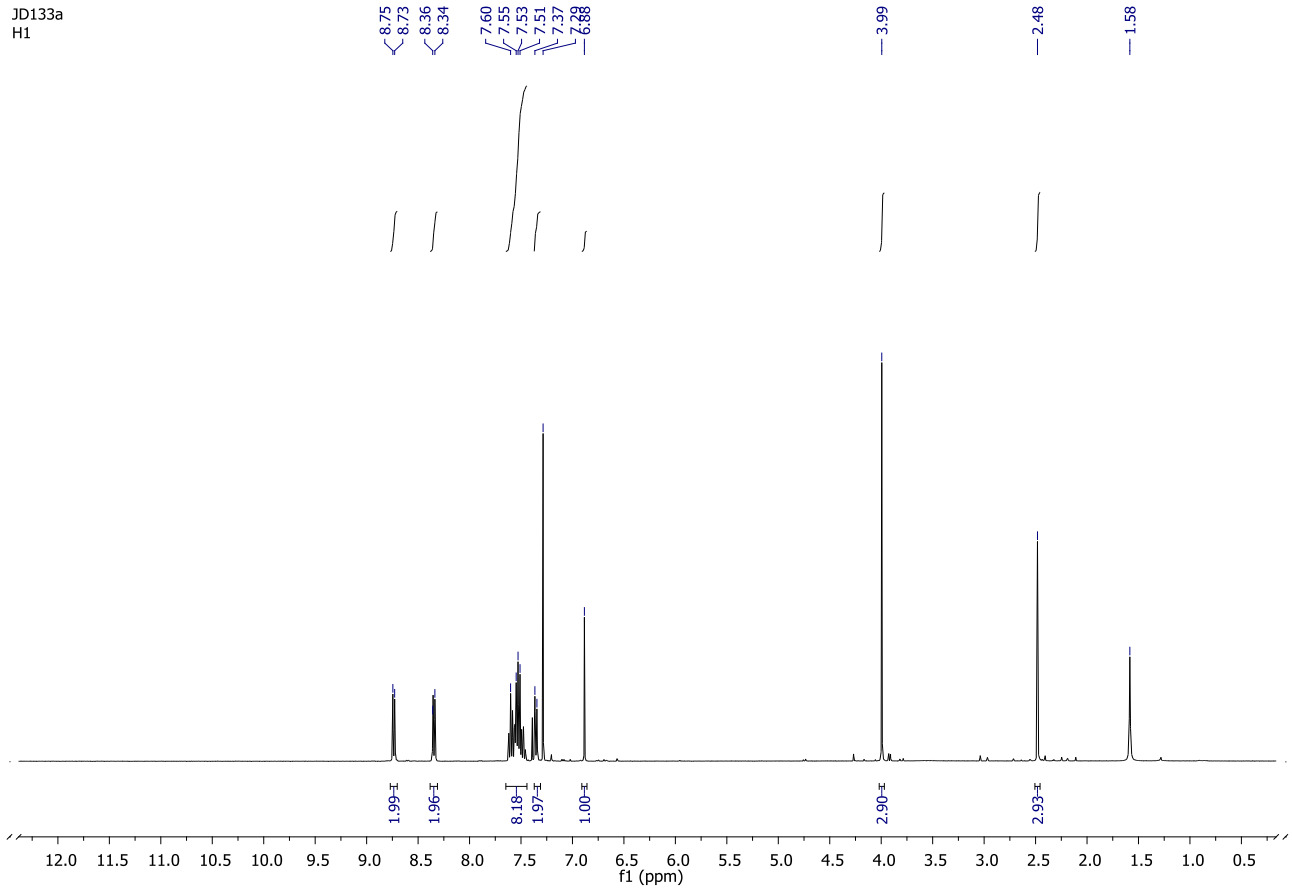


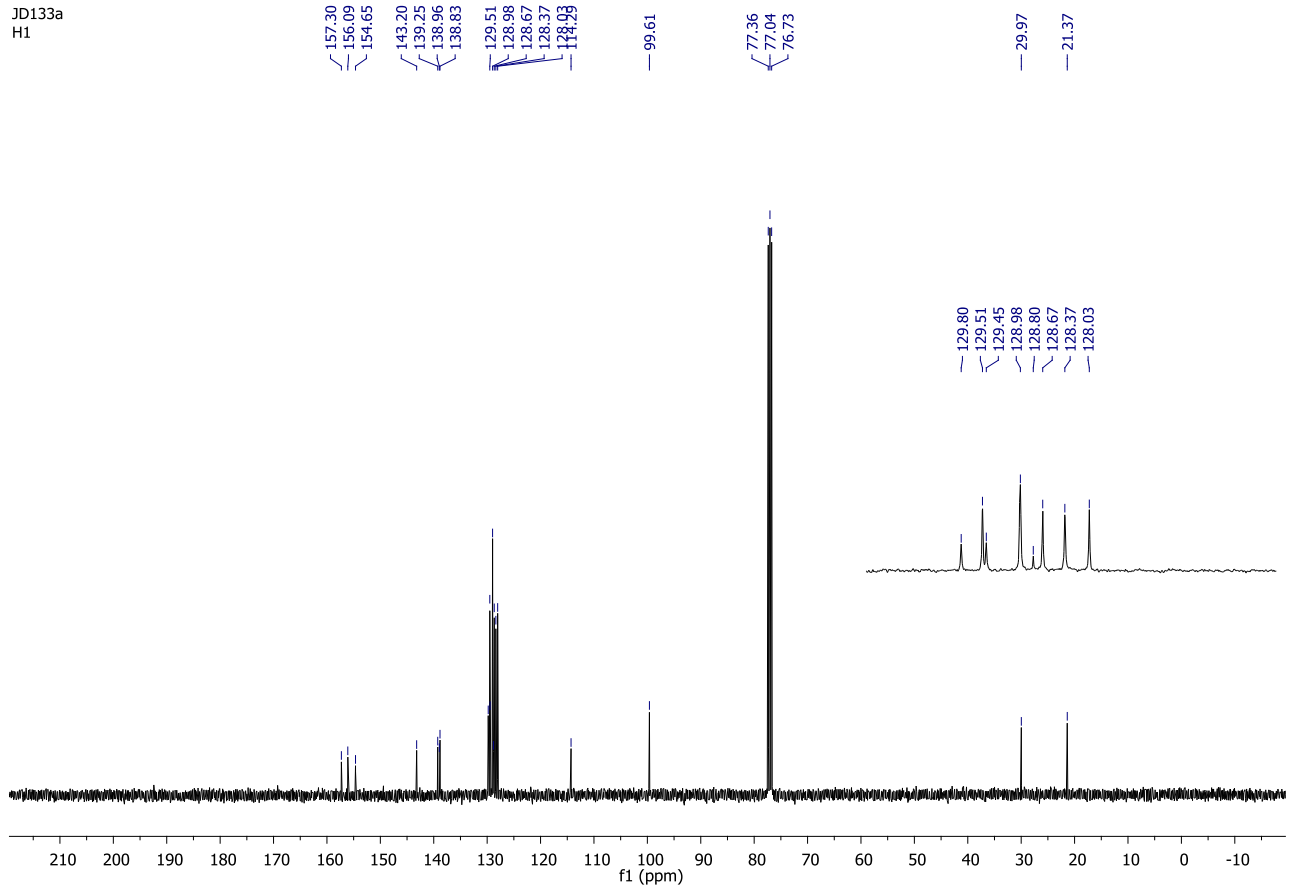
7-Methyl-2,4,6-triphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2c). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



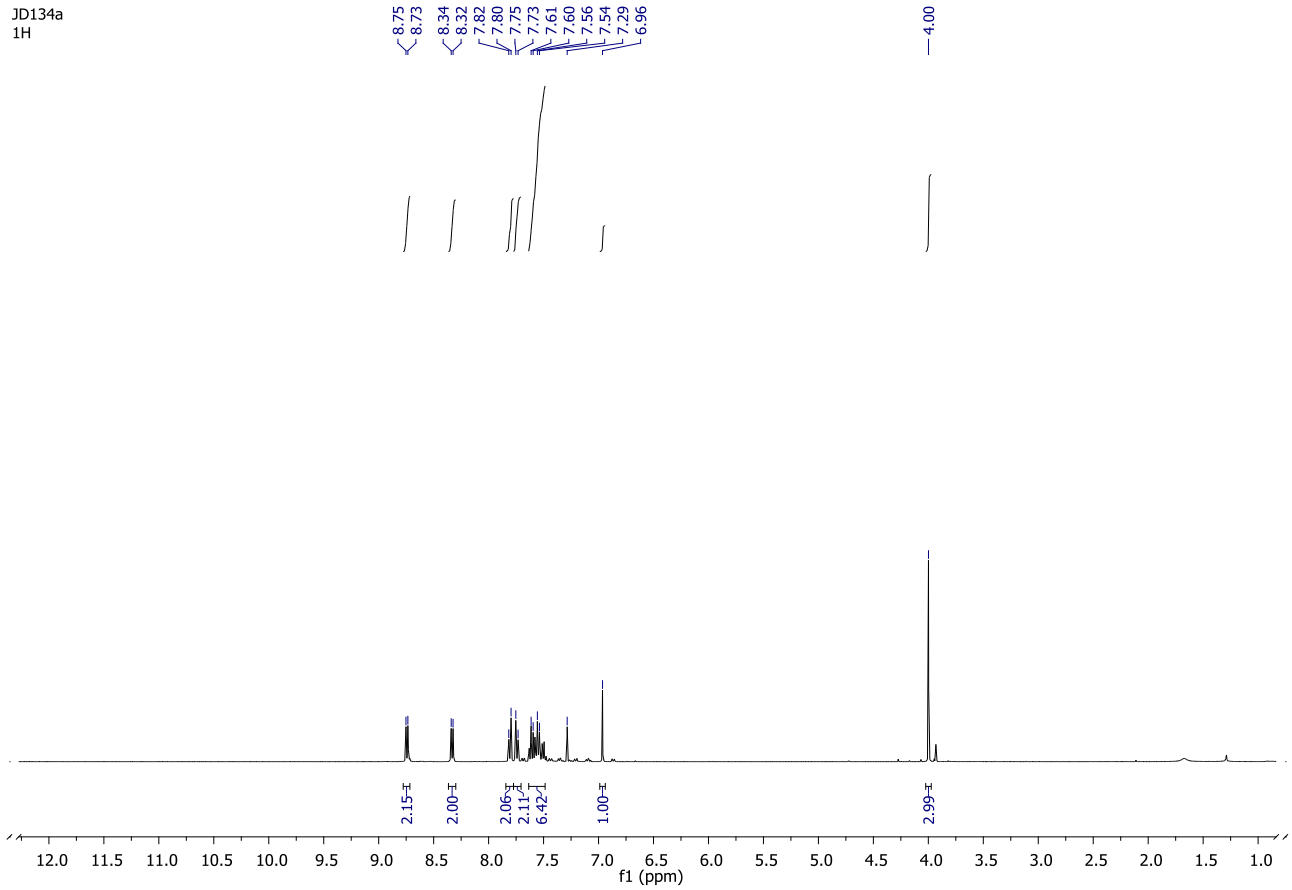


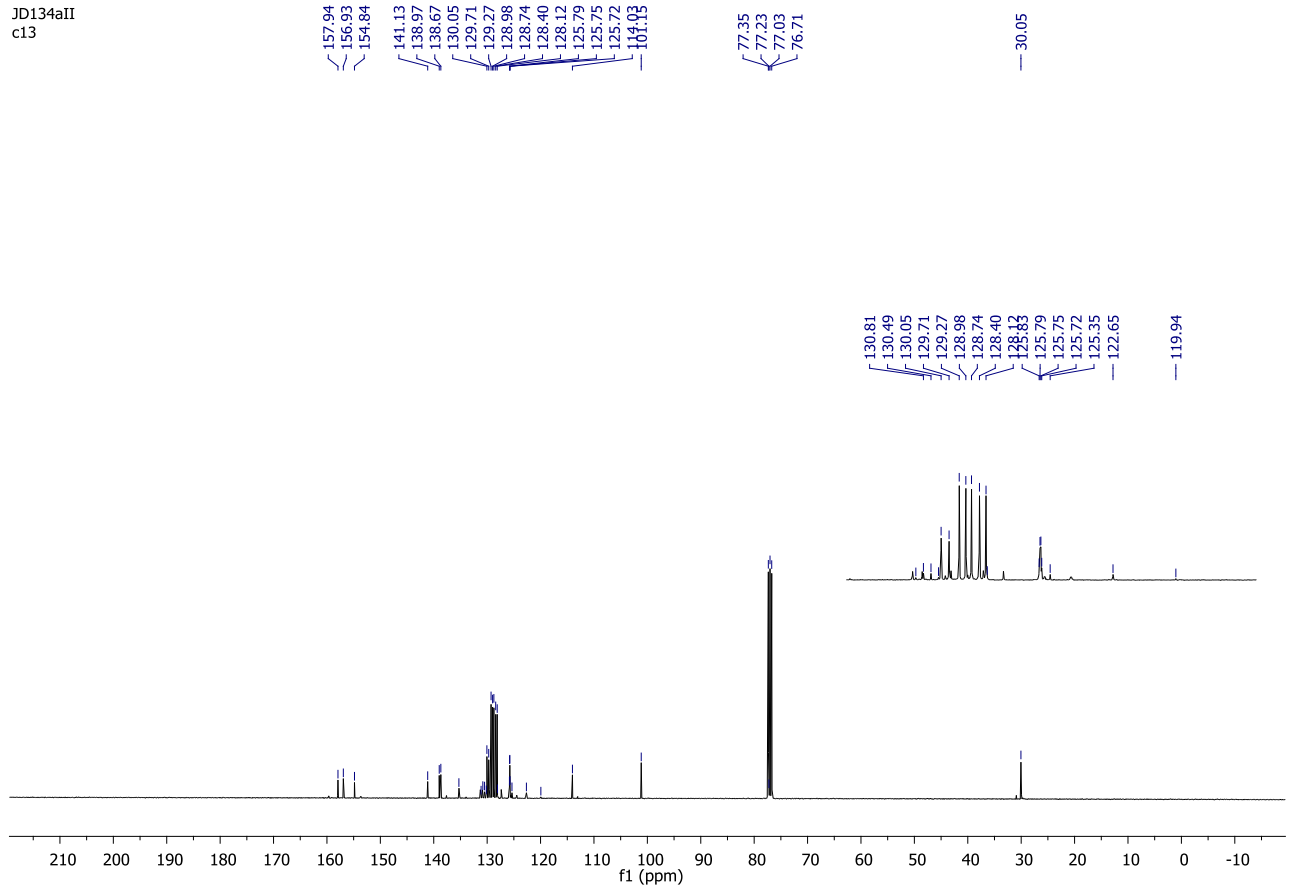
7-Methyl-6-(4-methylphenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2d). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



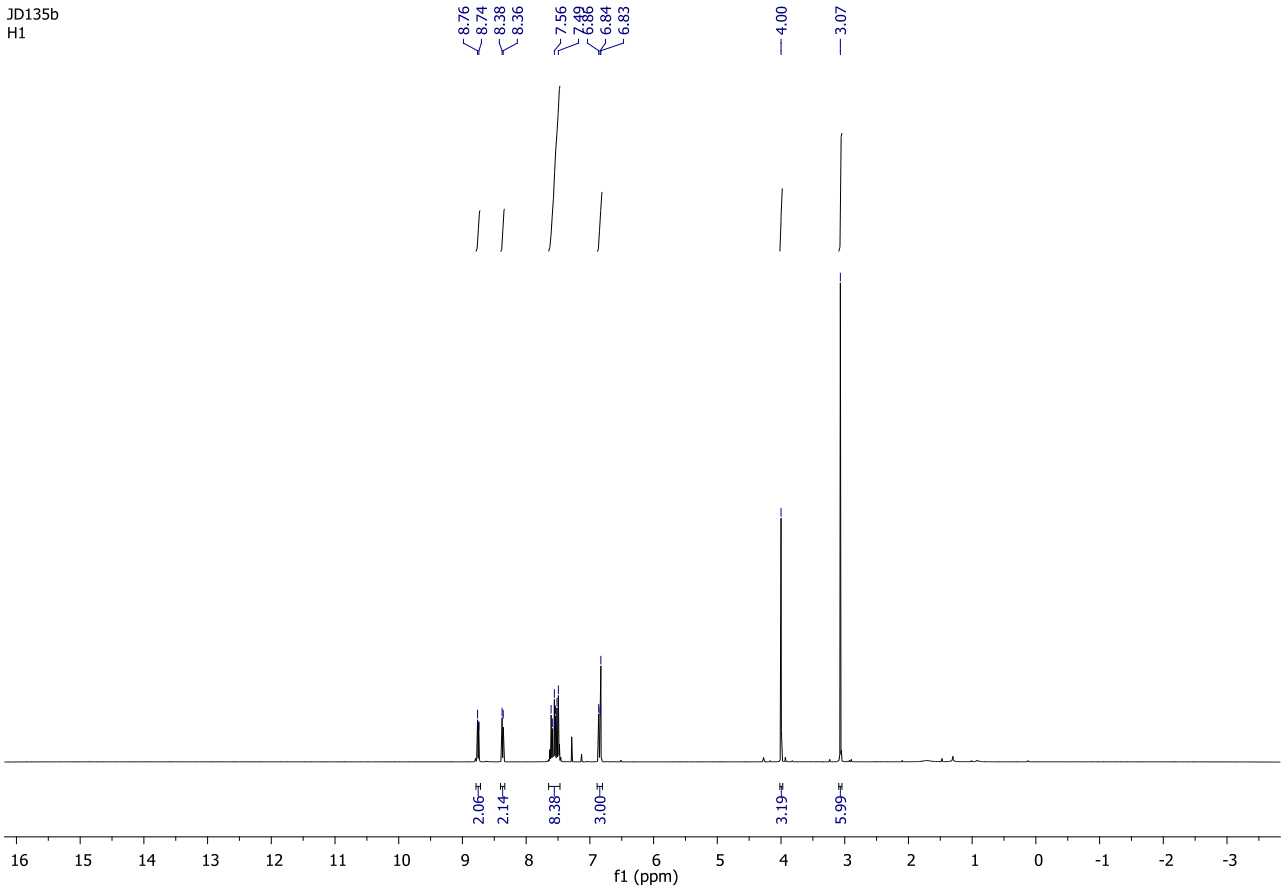


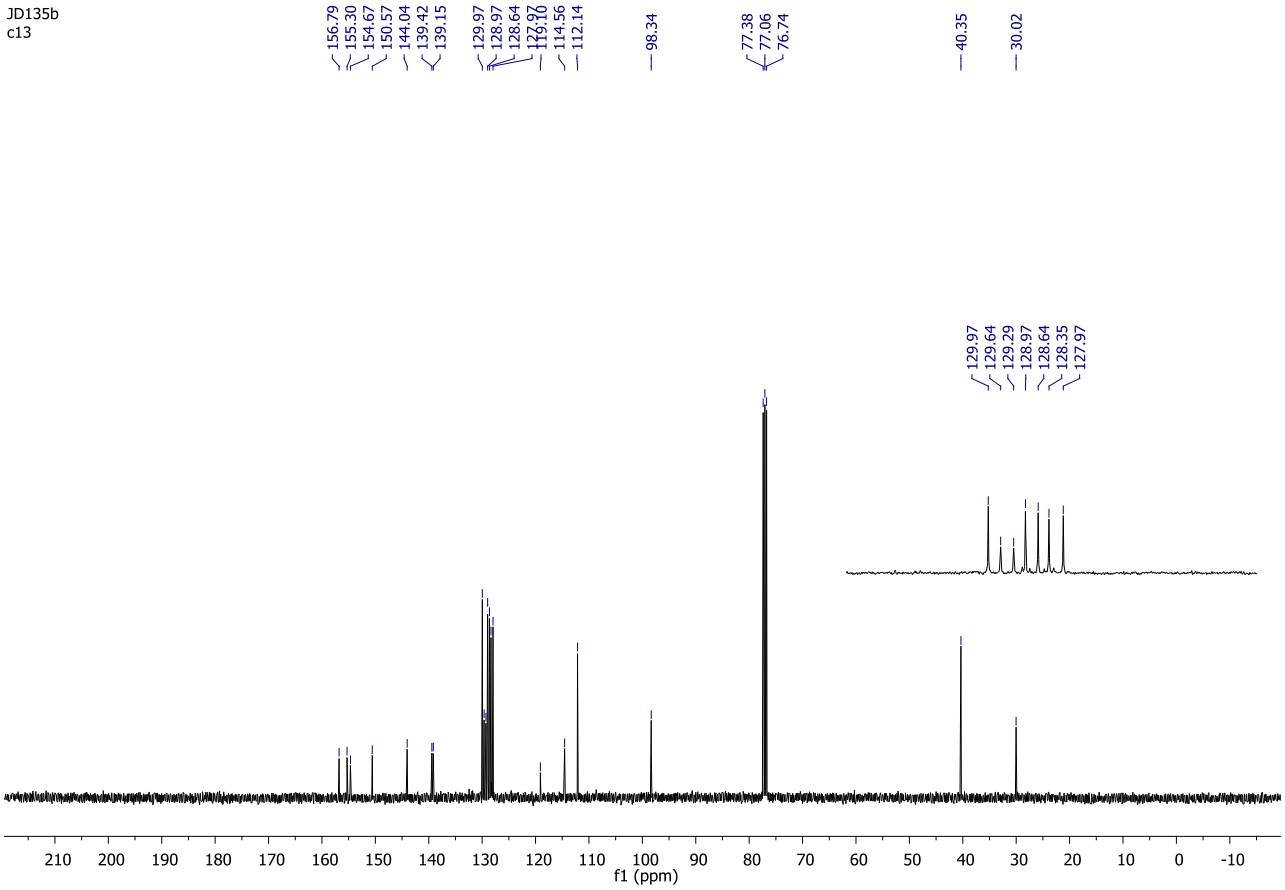
6-(4-Trifluoromethylphenyl)-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2e). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



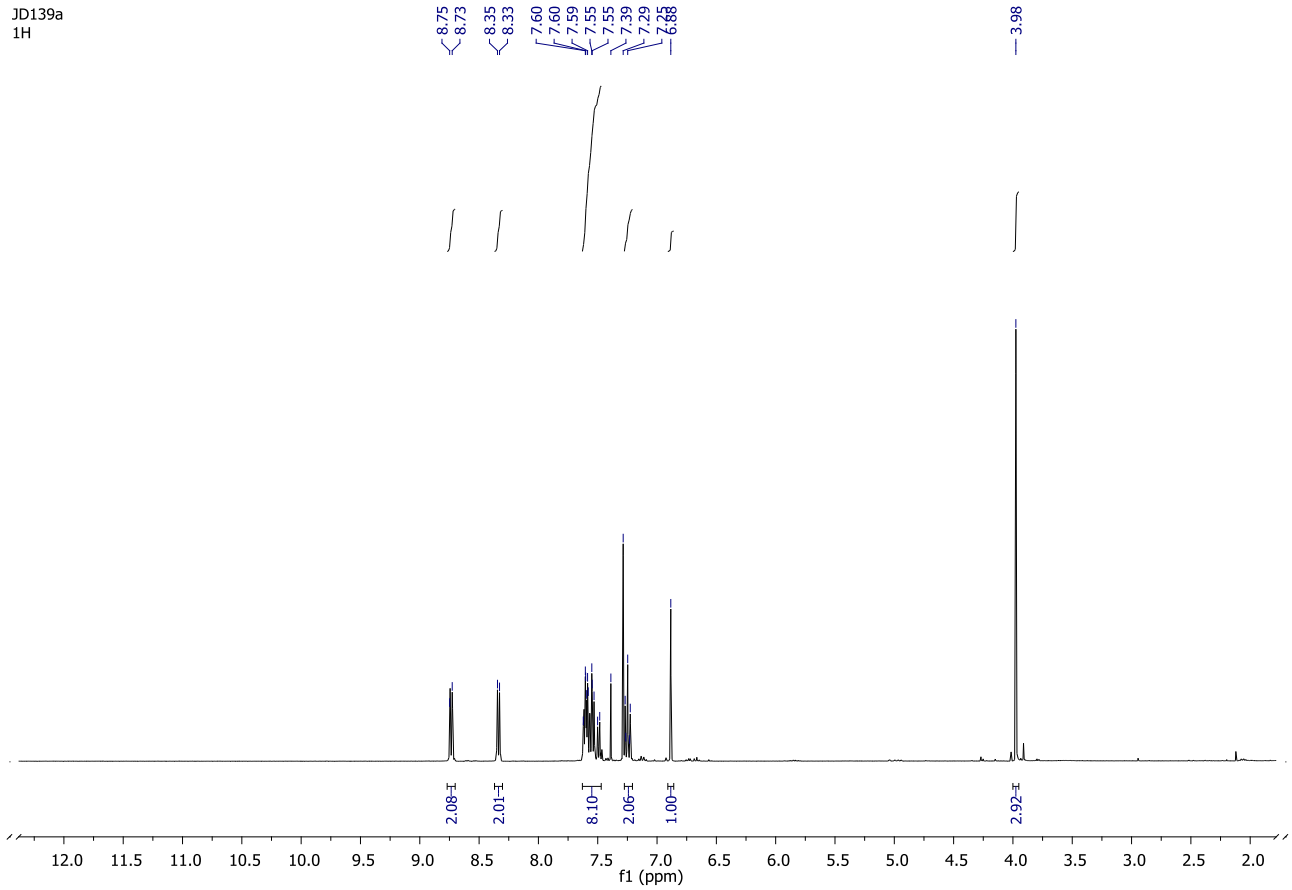


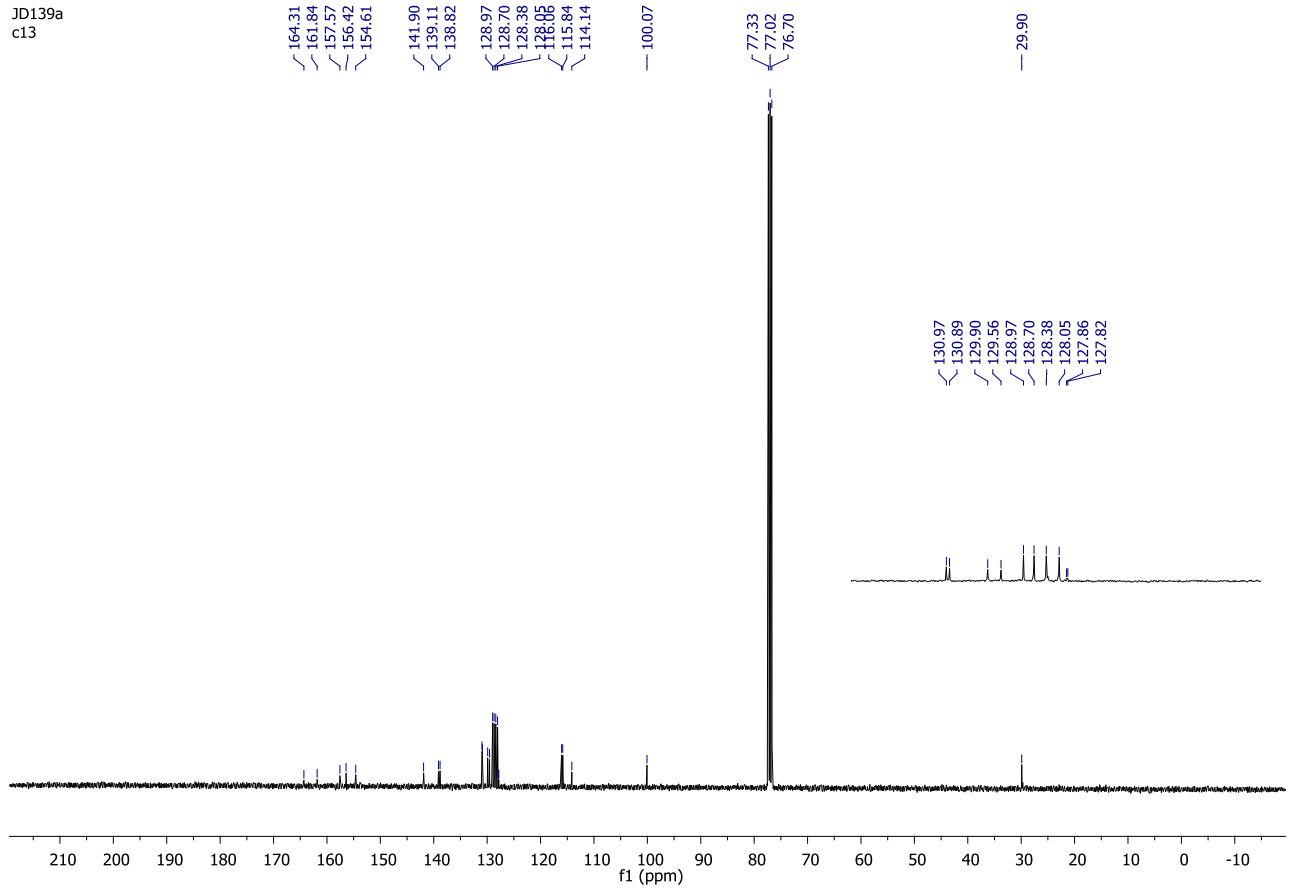
6-[4-(Dimethylamino)phenyl)-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2f). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



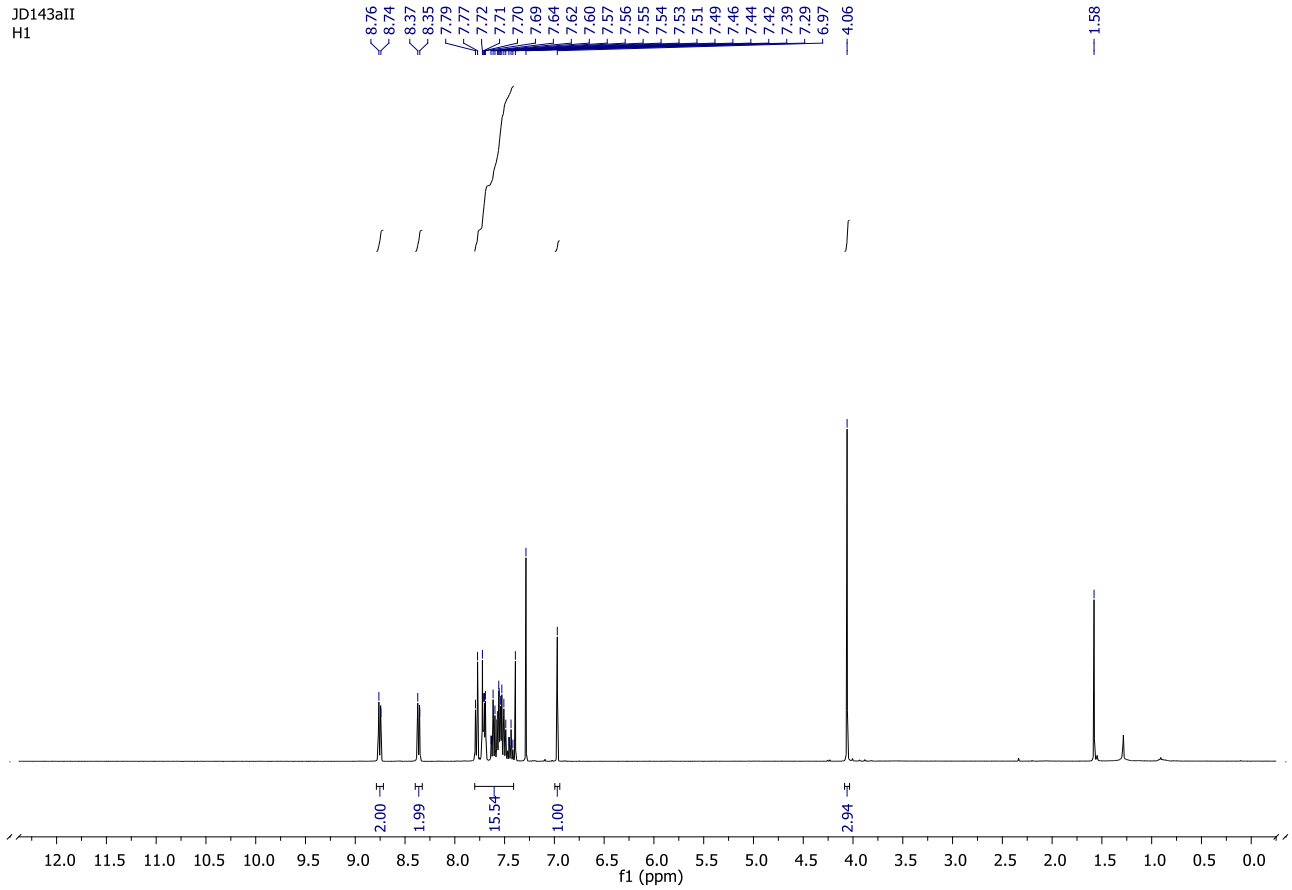


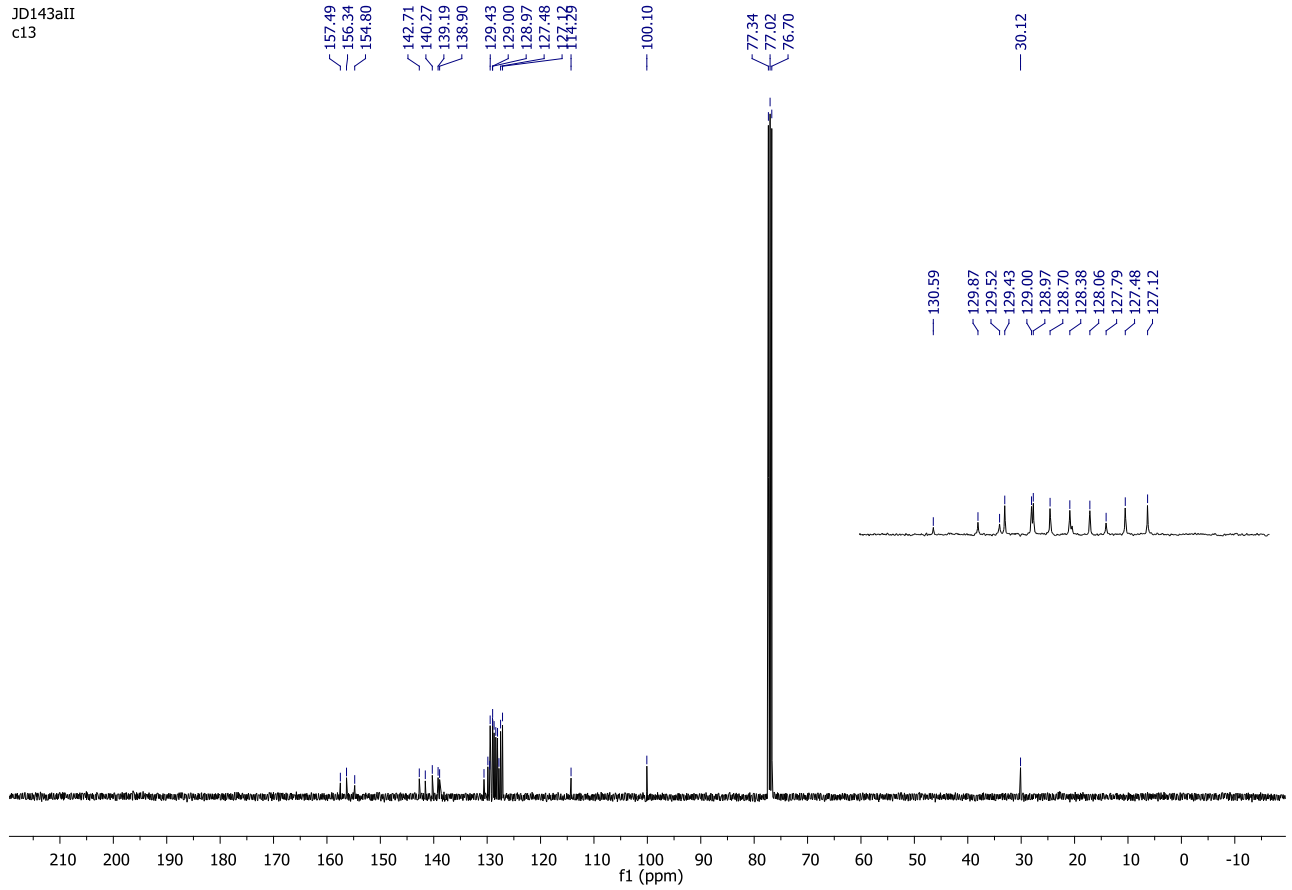
6-(4-Fluorophenyl)-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2g). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



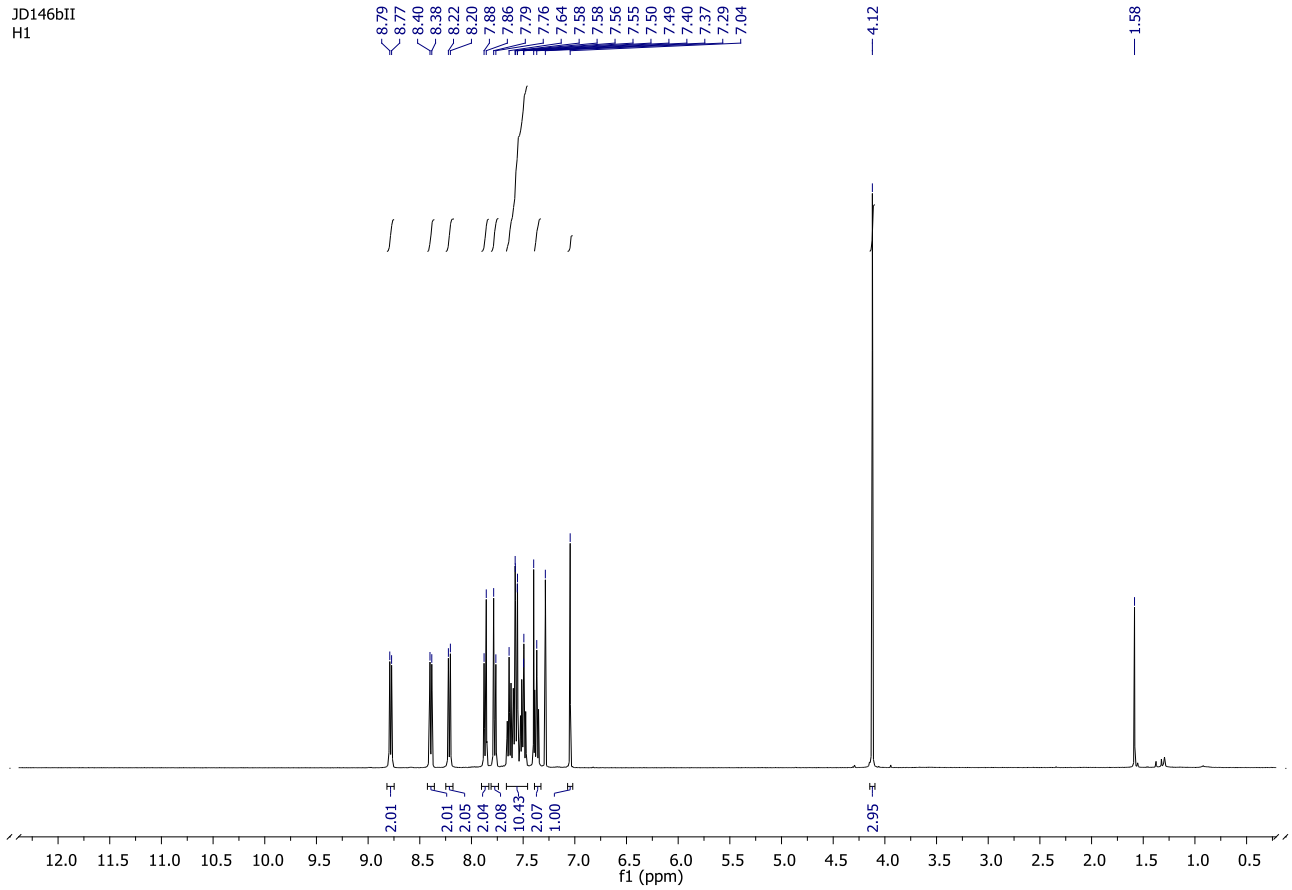


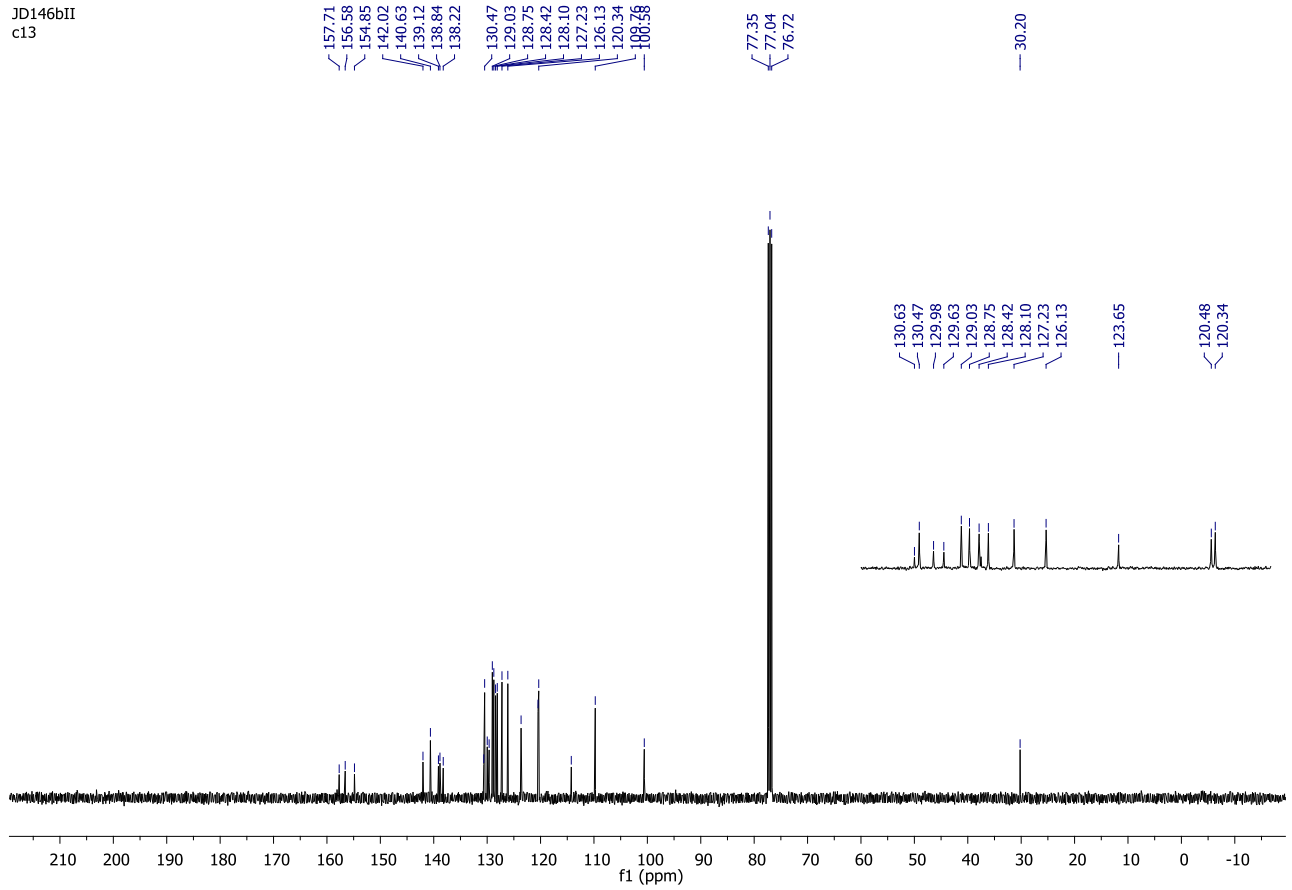
6-(Biphenyl-4-yl)-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2h). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



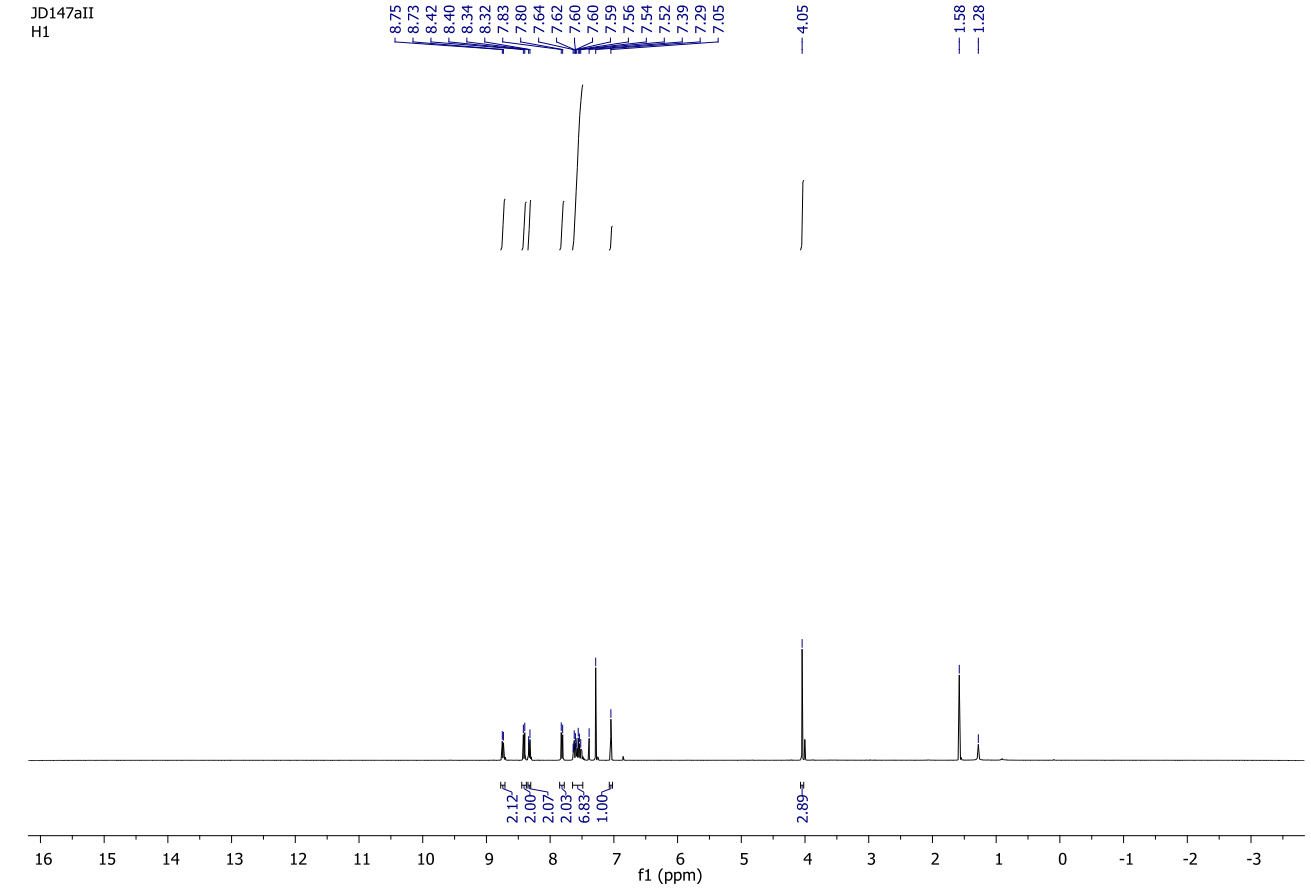


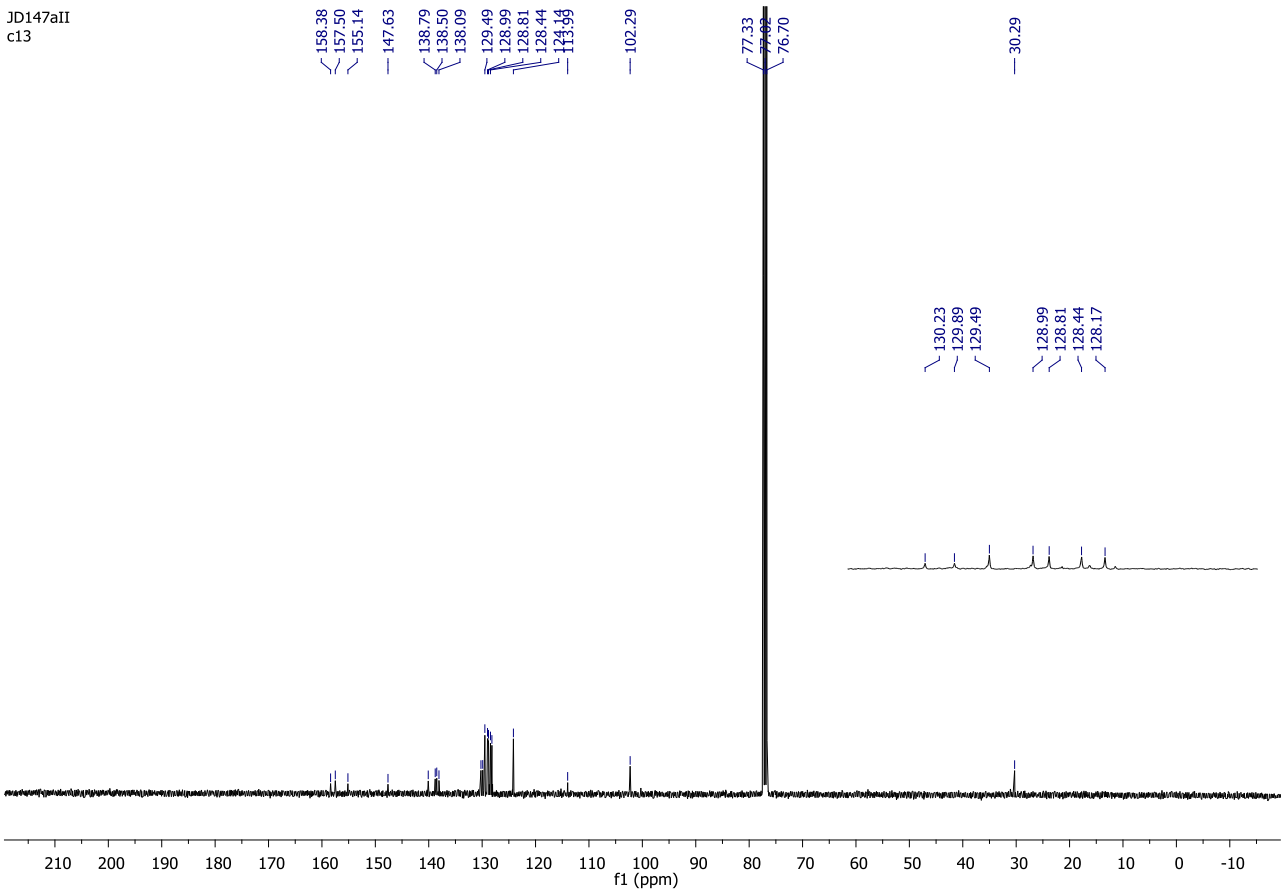
6-[4-(9*H*-carbazol-9-yl)phenyl]-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2i). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



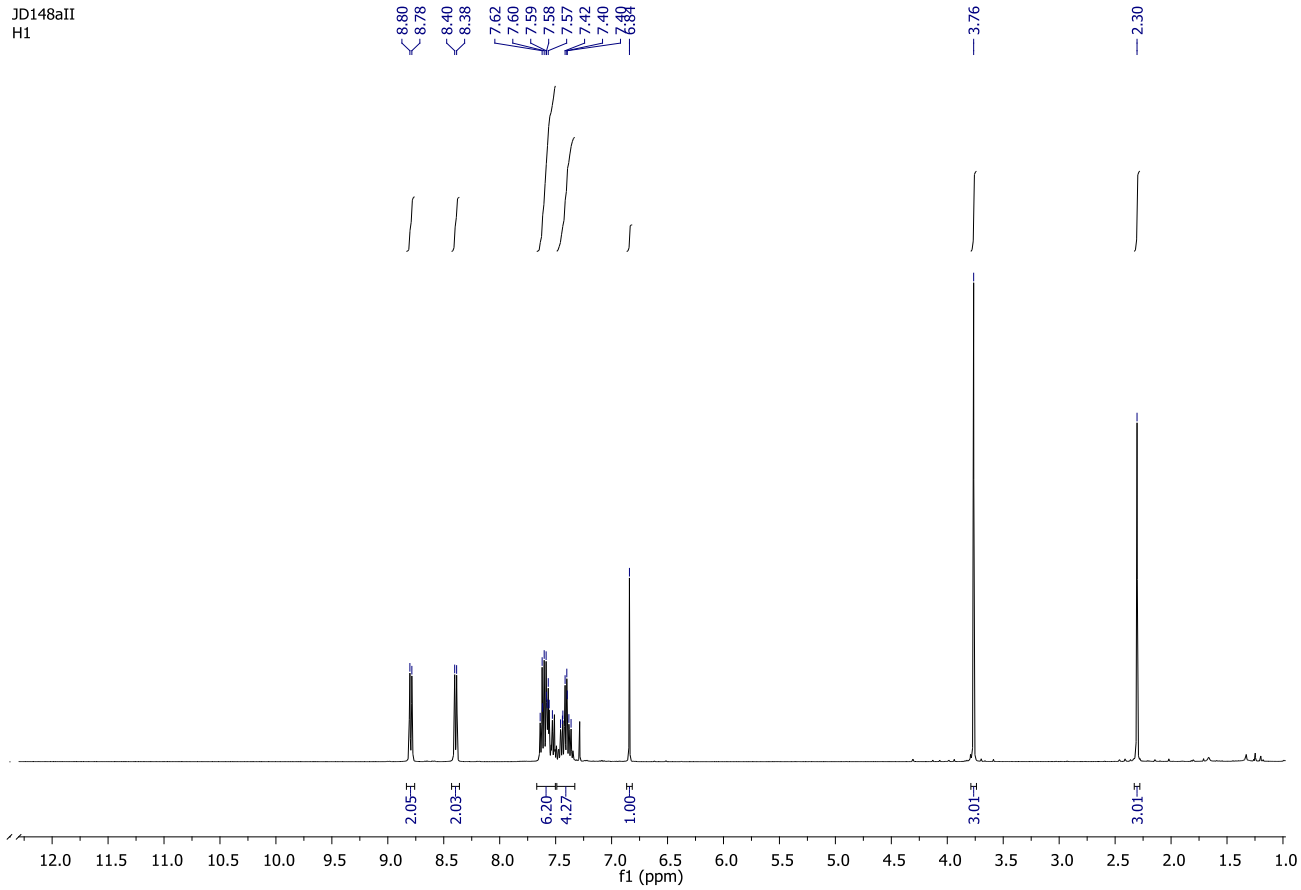


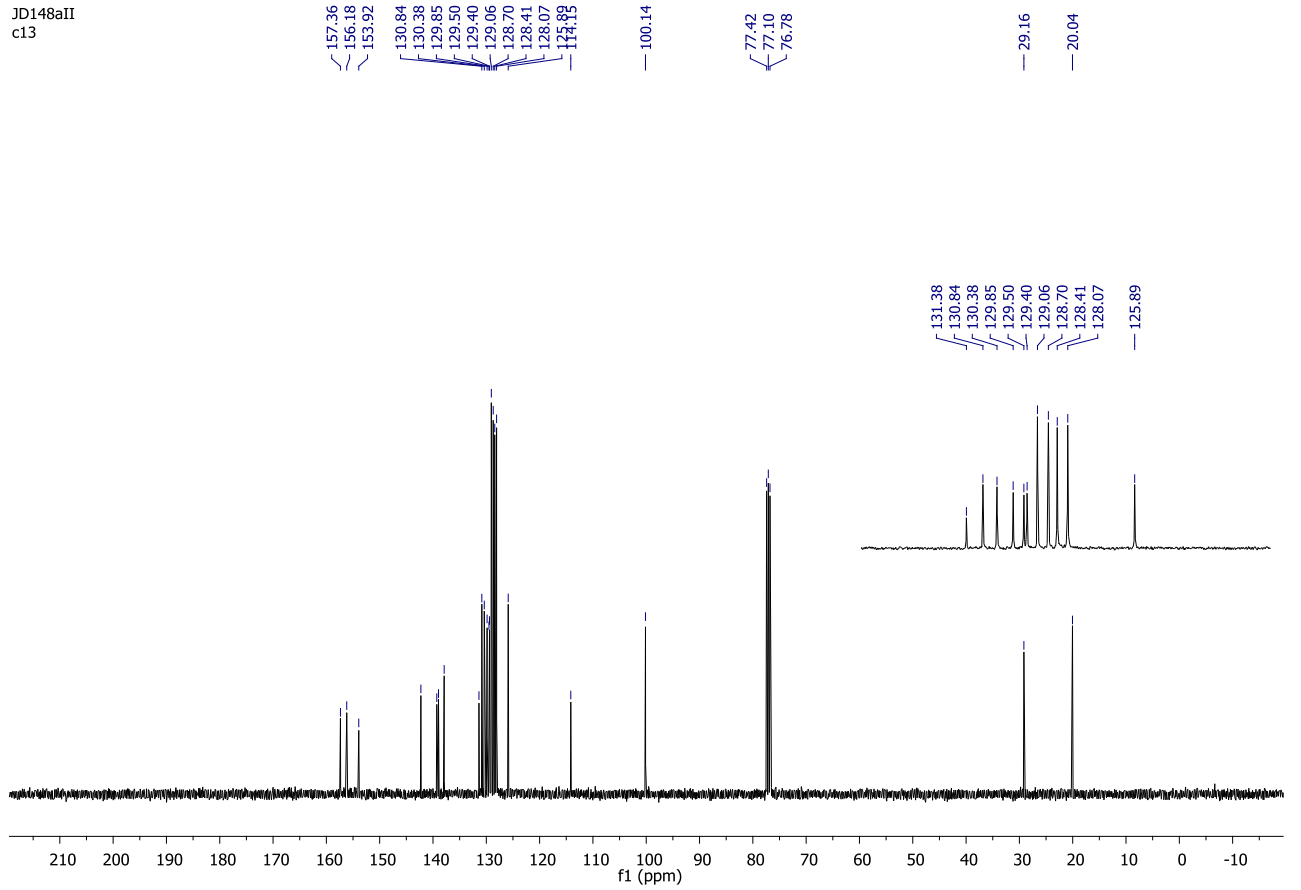
7-Methyl-6-(4-nitrophenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2j). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



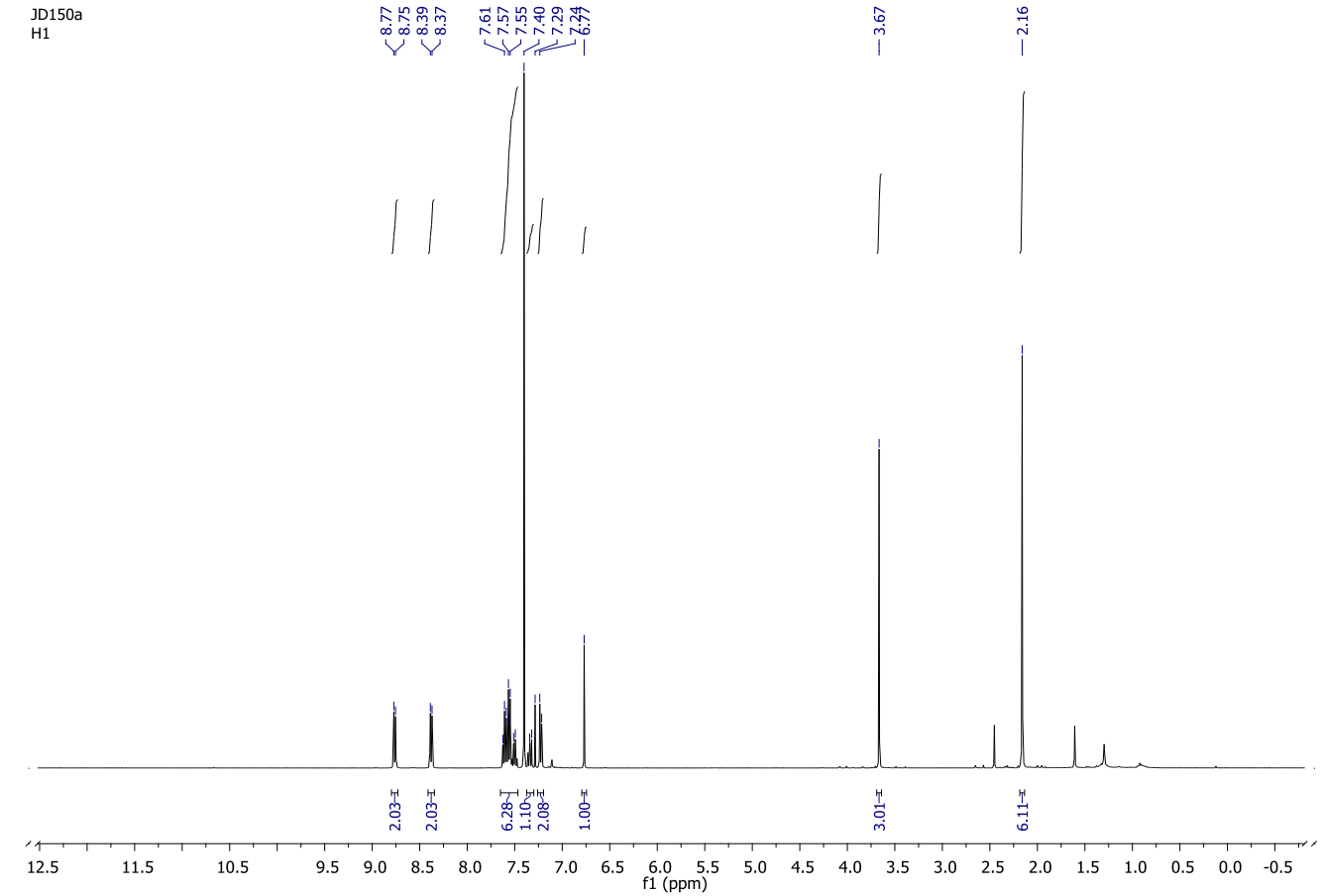


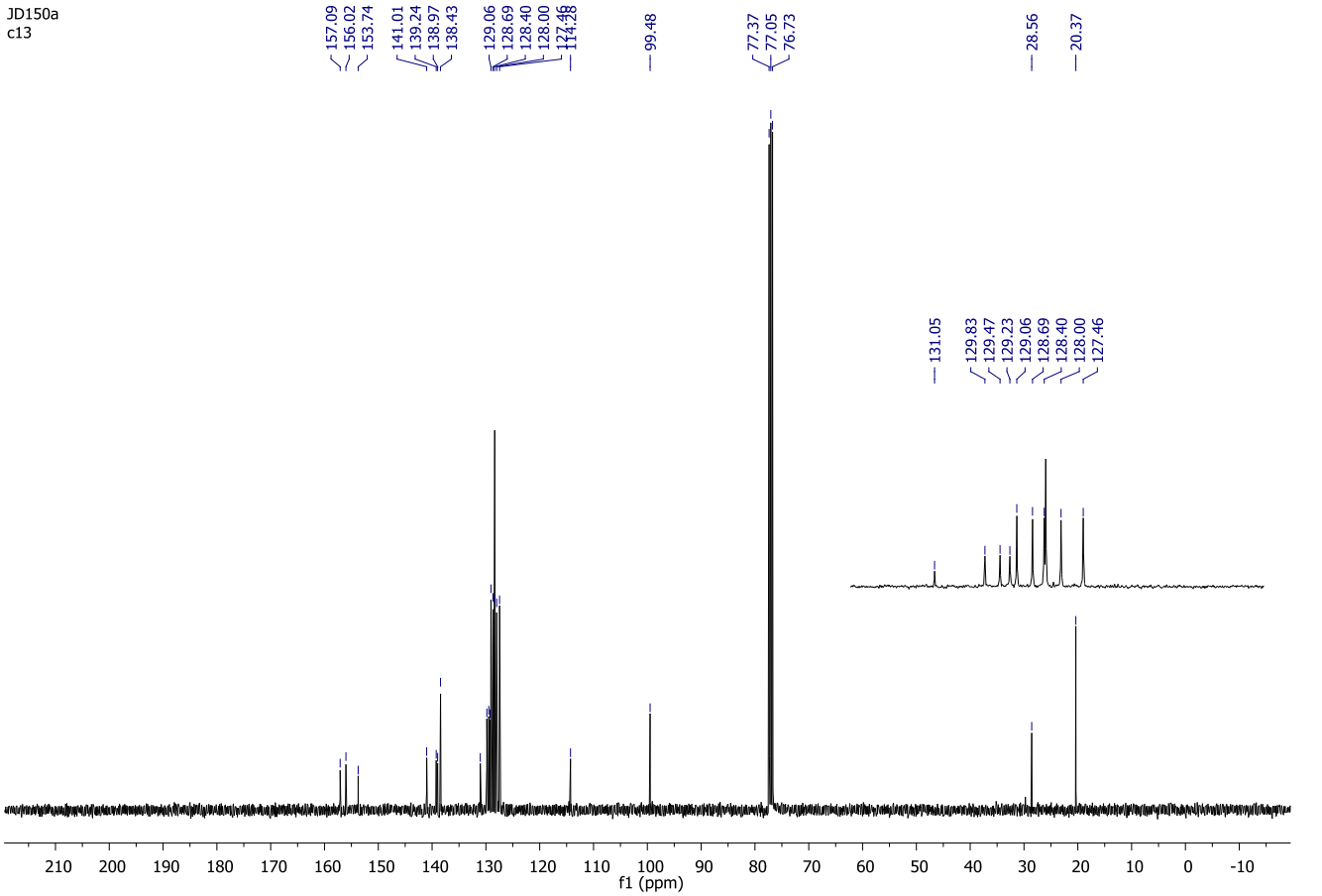
7-Methyl-6-(2-methylphenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2k). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



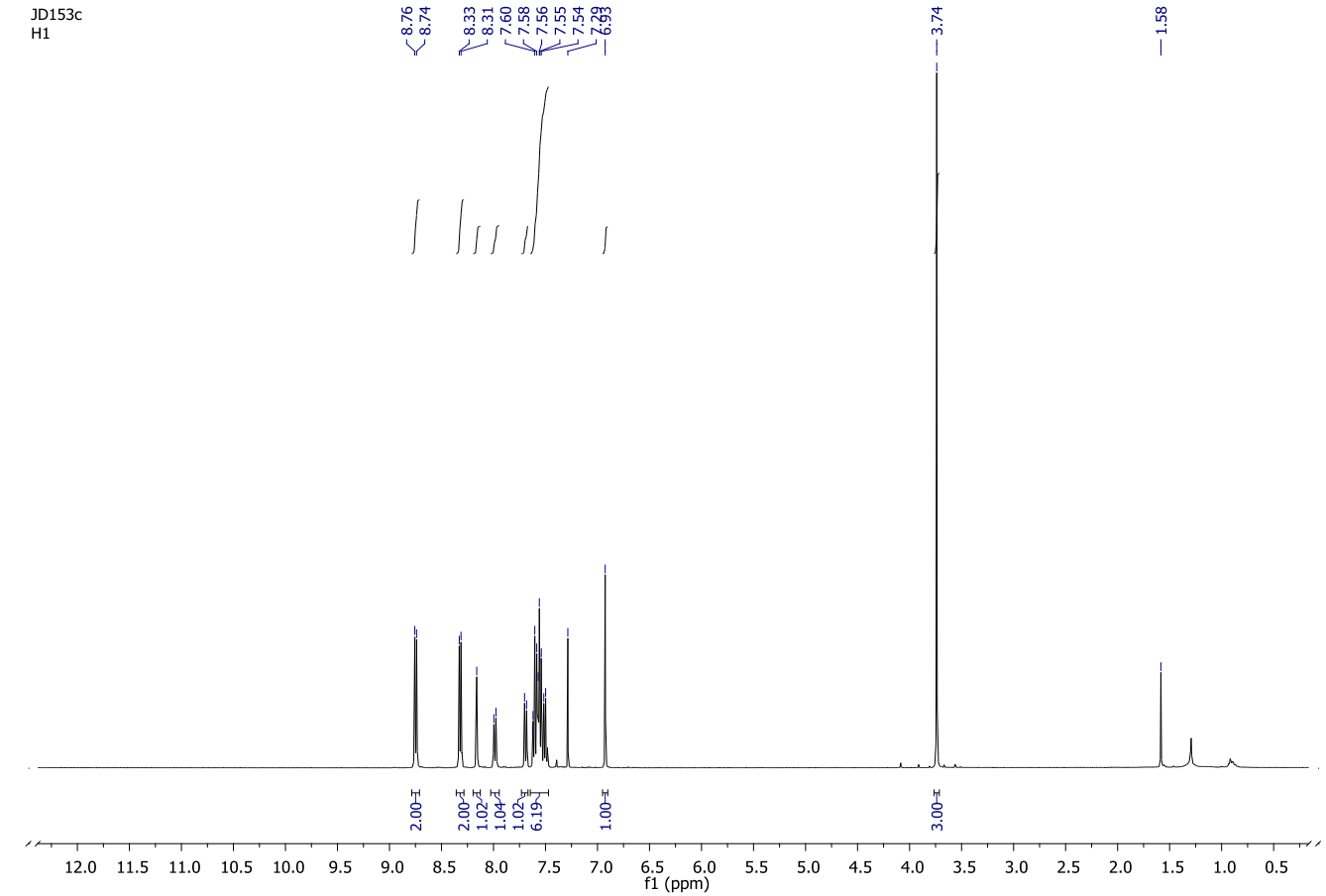


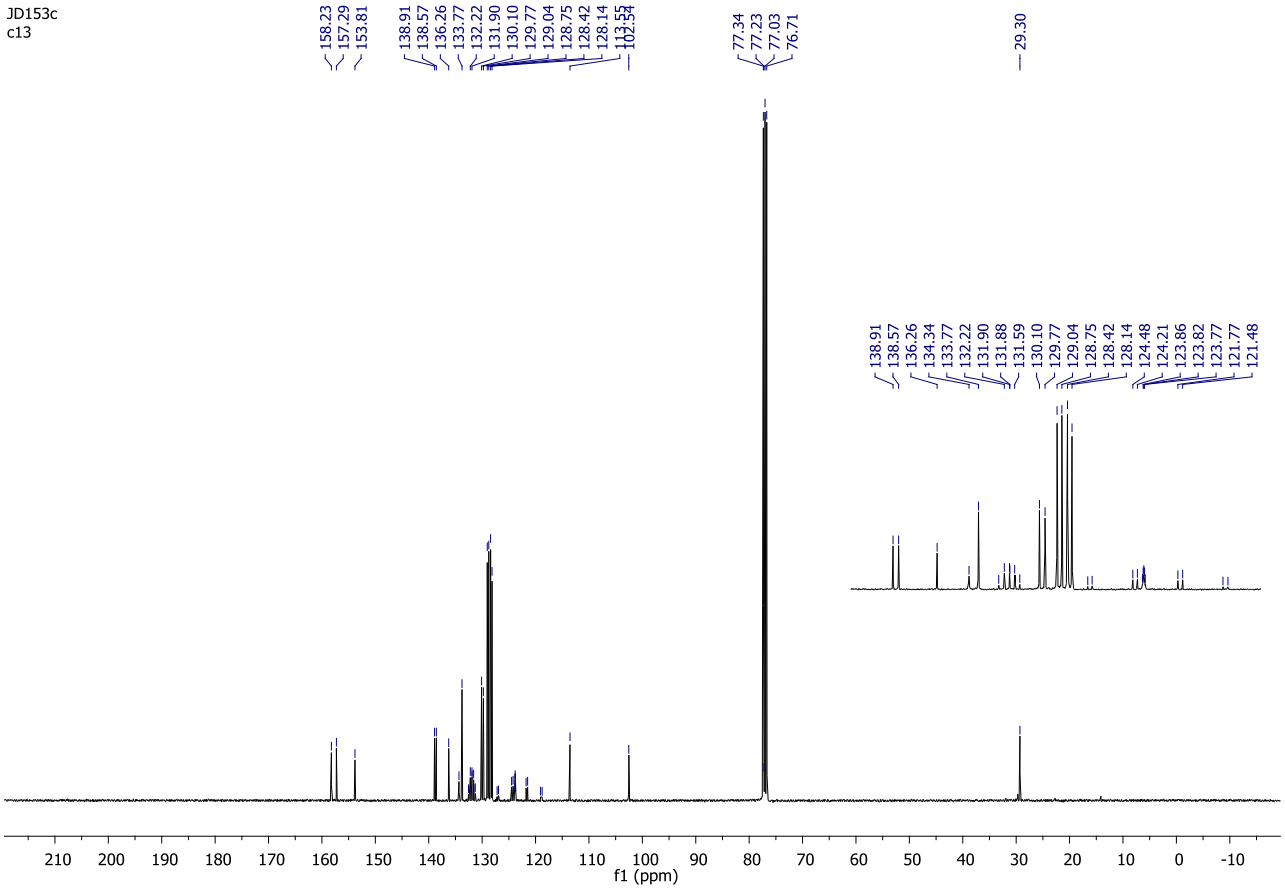
7-Methyl-6-(2,6-dimethylphenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2l). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



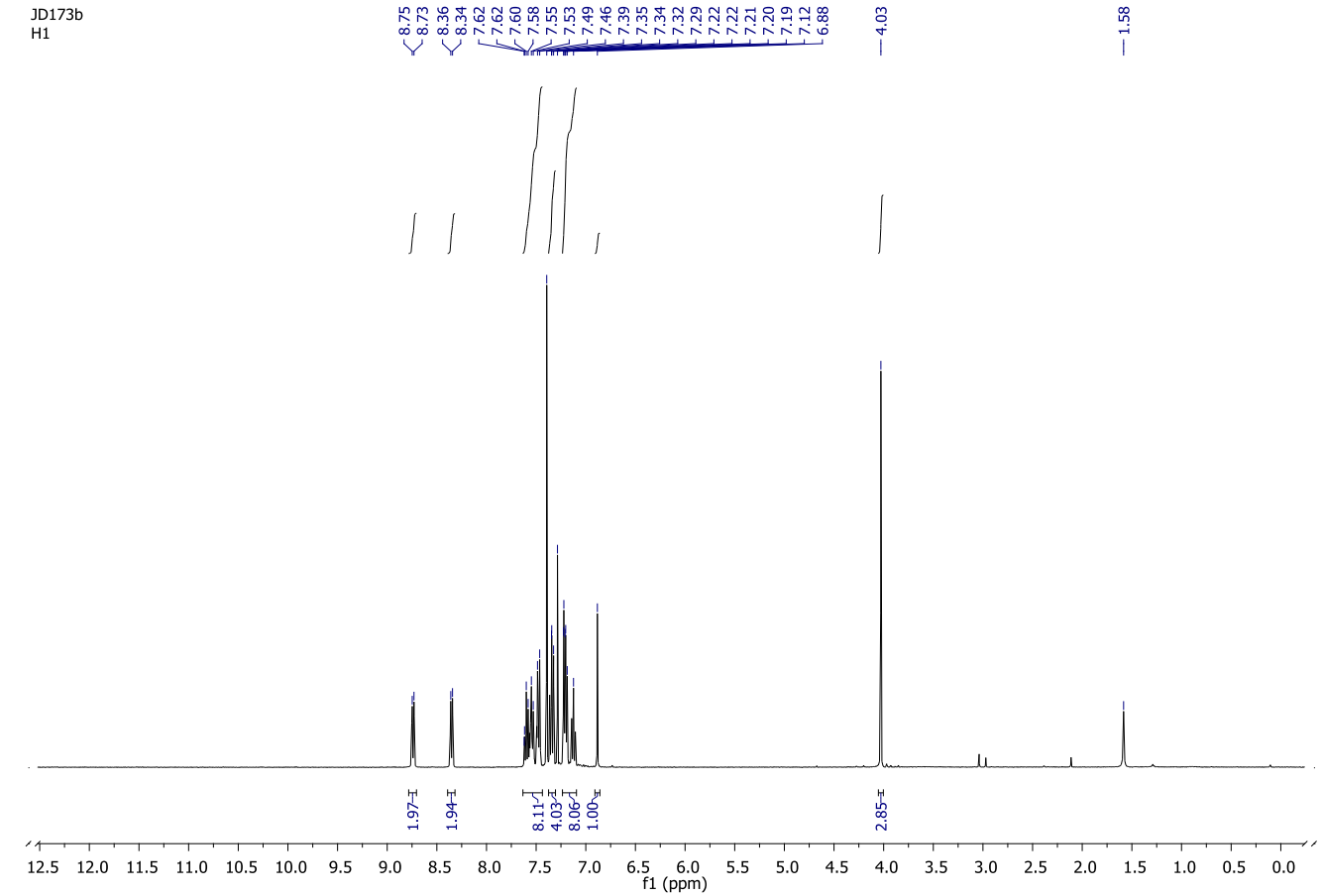


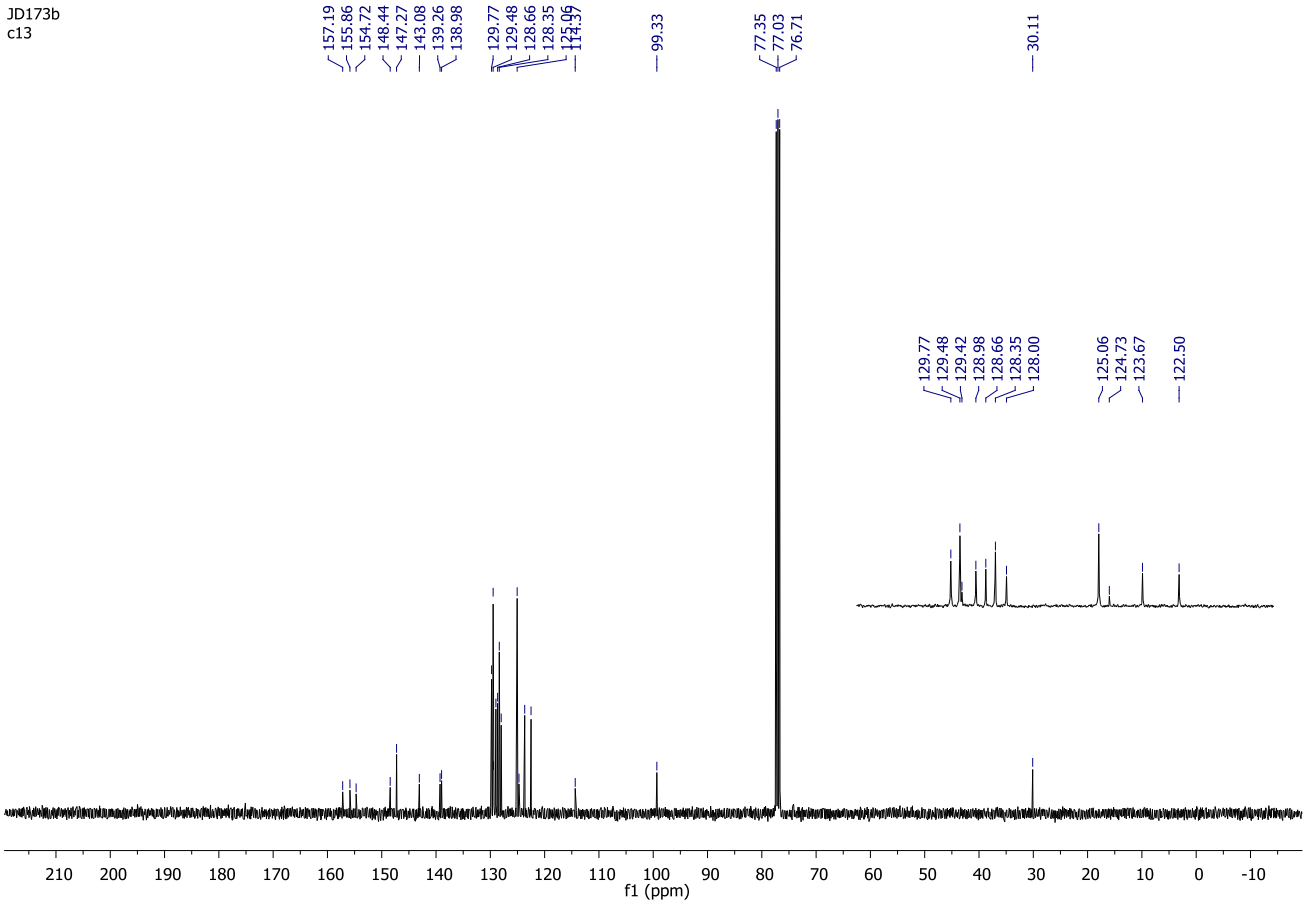
6-[2,4-Di(trifluoromethyl)phenyl]-7-methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2m). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



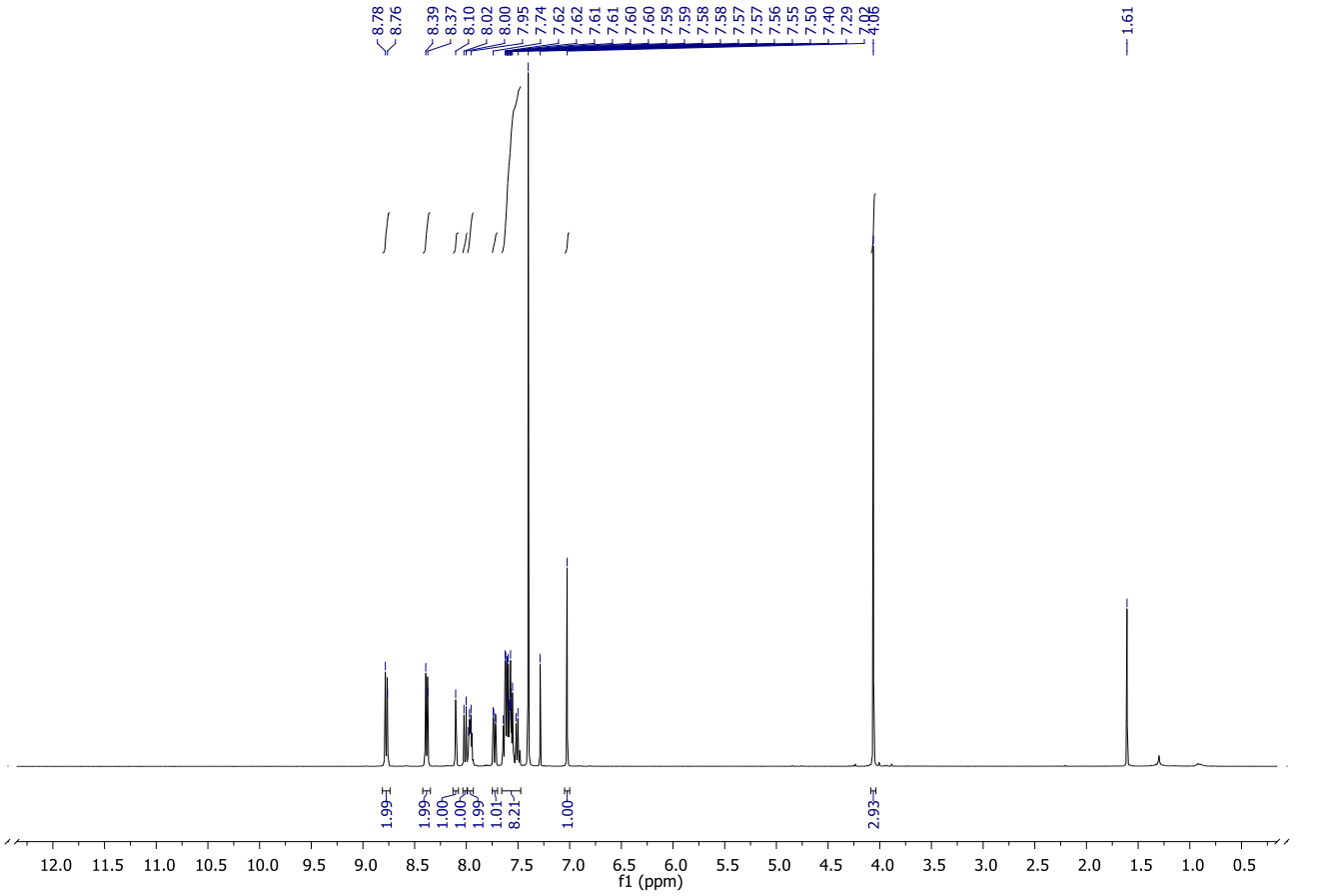


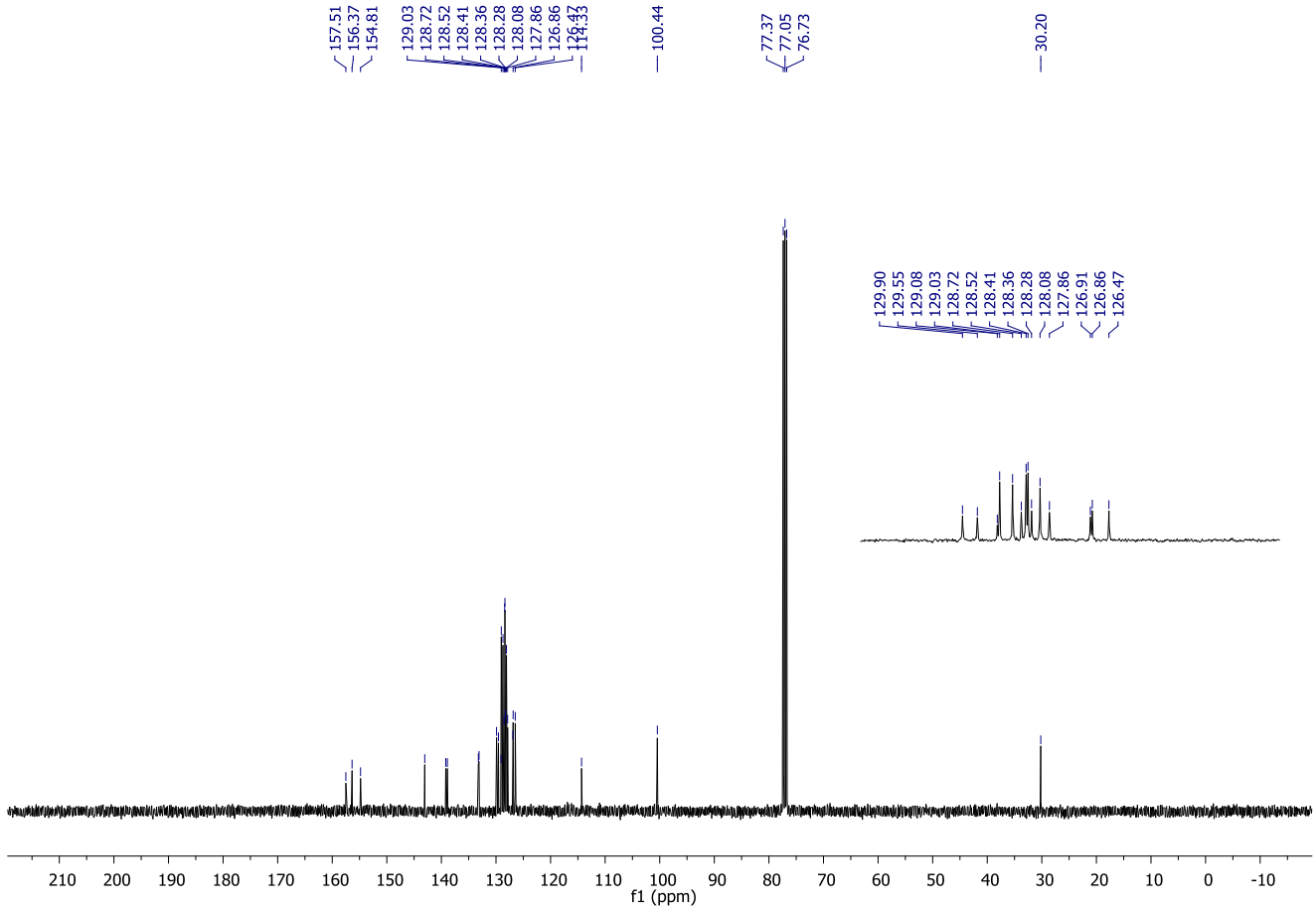
7-Methyl-6-[(4-diphenylamino)phenyl]-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2n). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



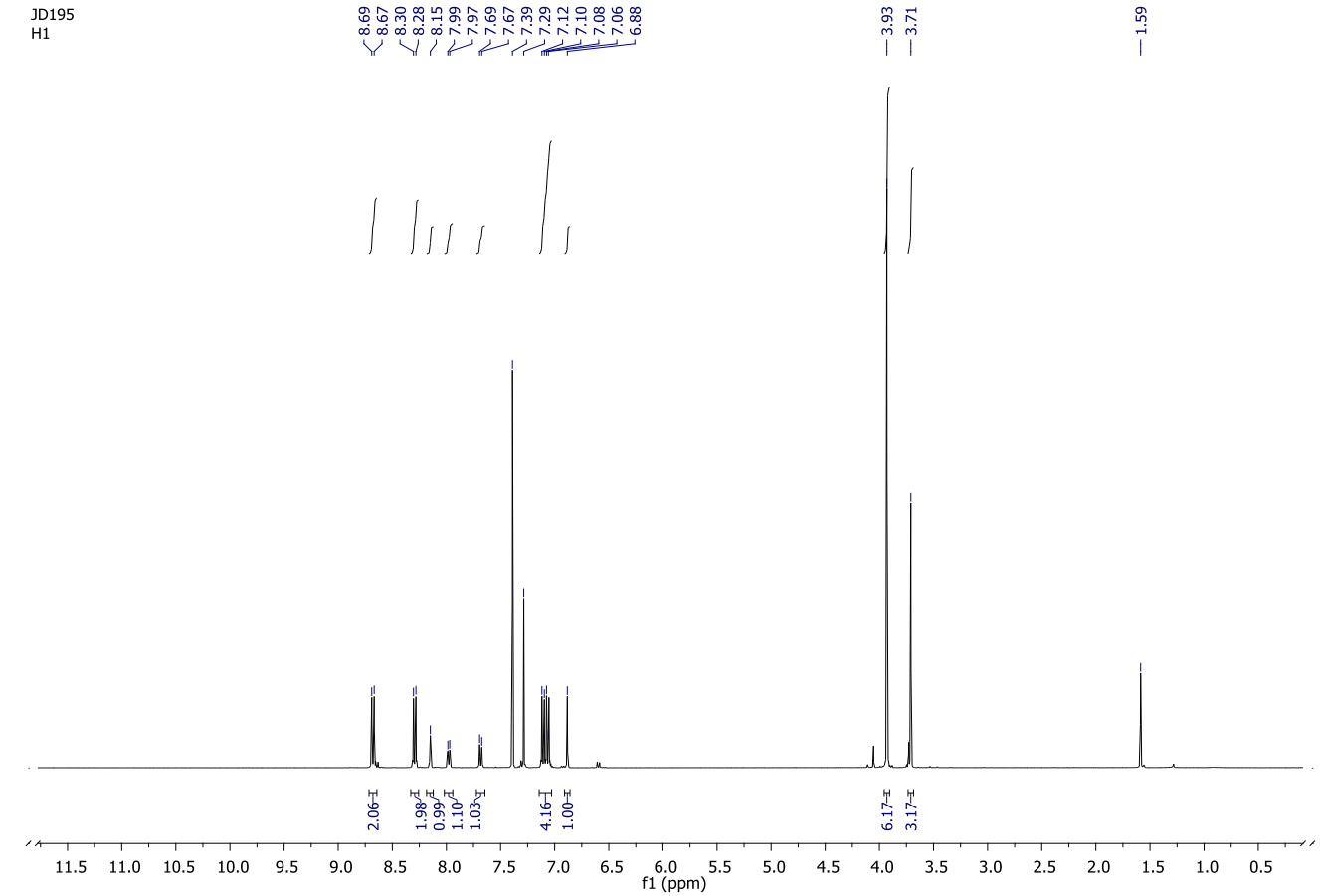


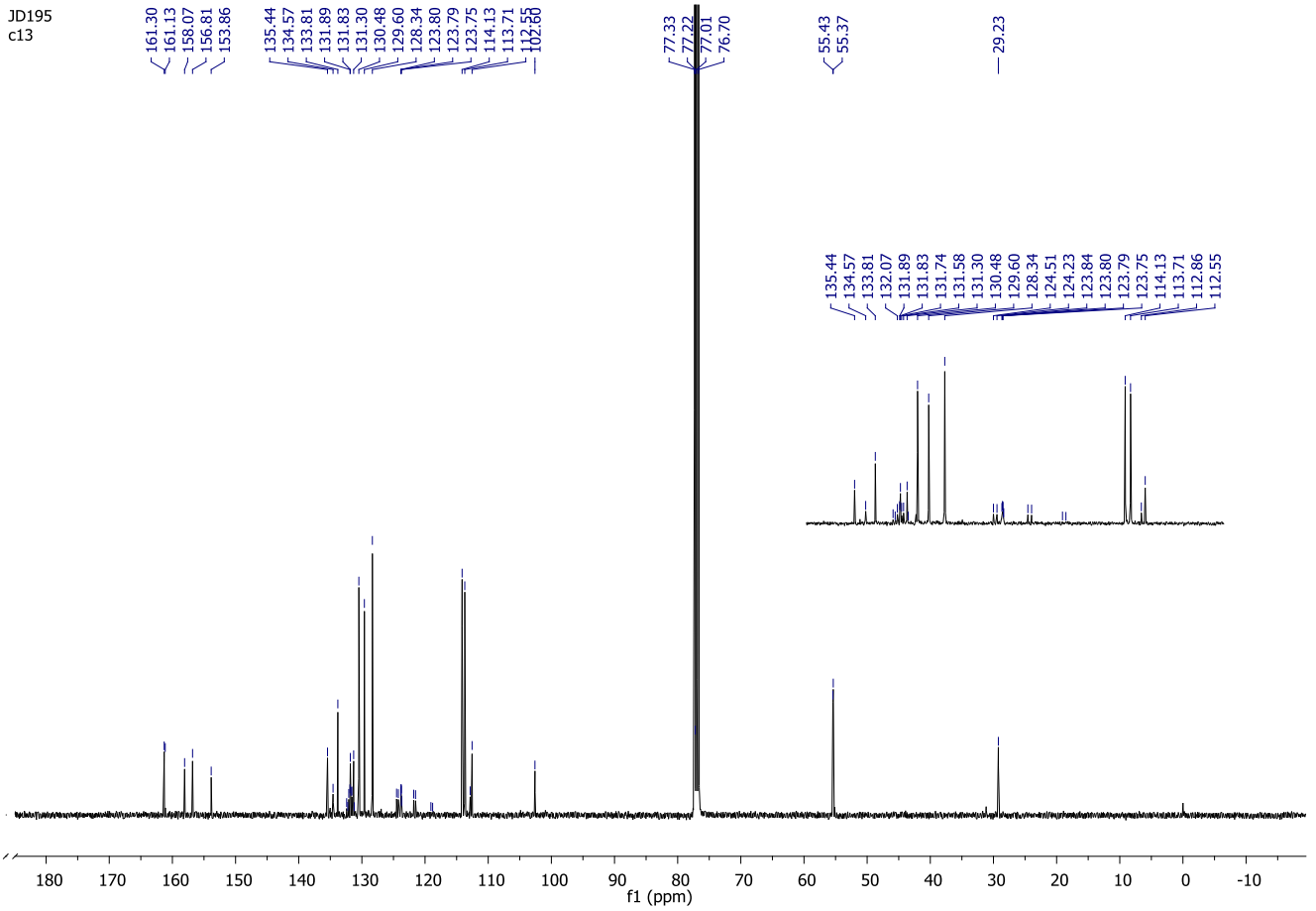
7-Methyl-6-(naphthalen-2-yl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2o). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).

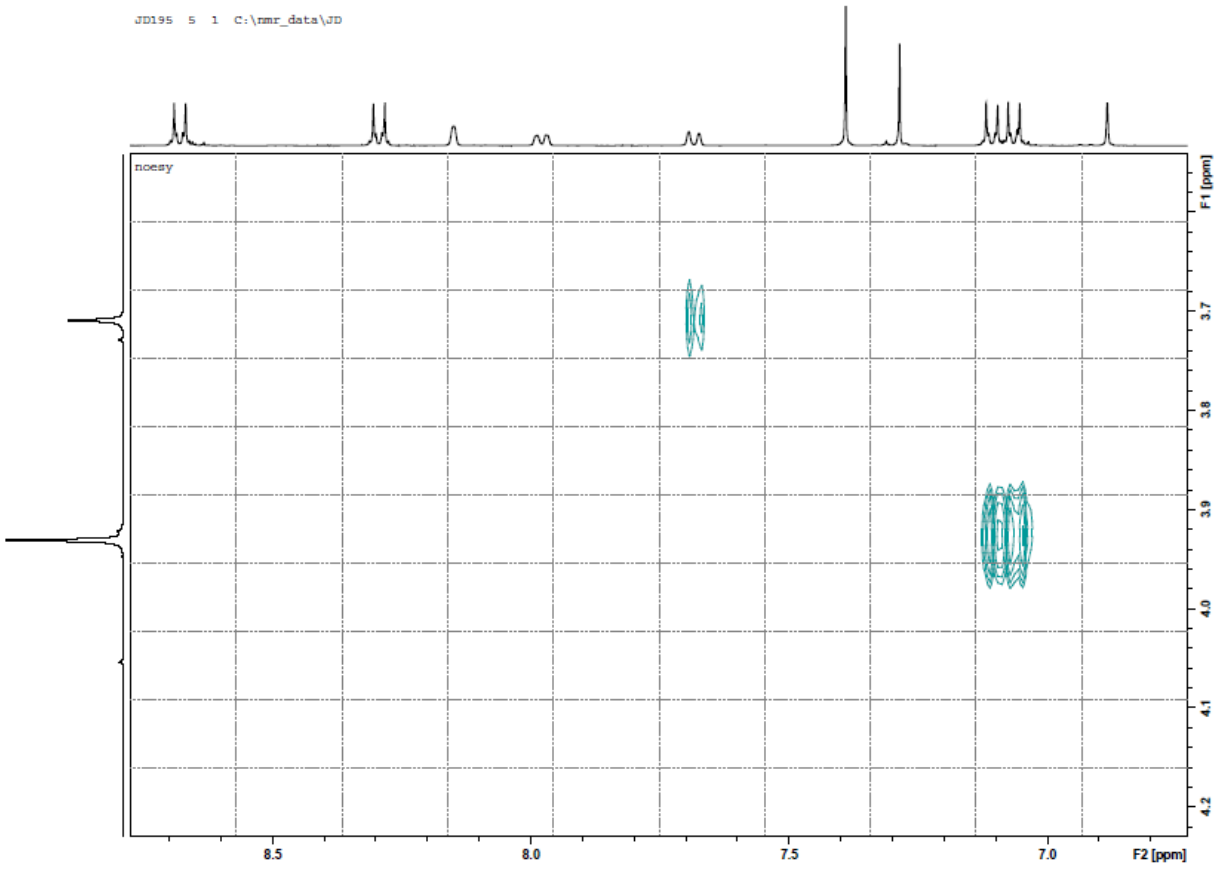




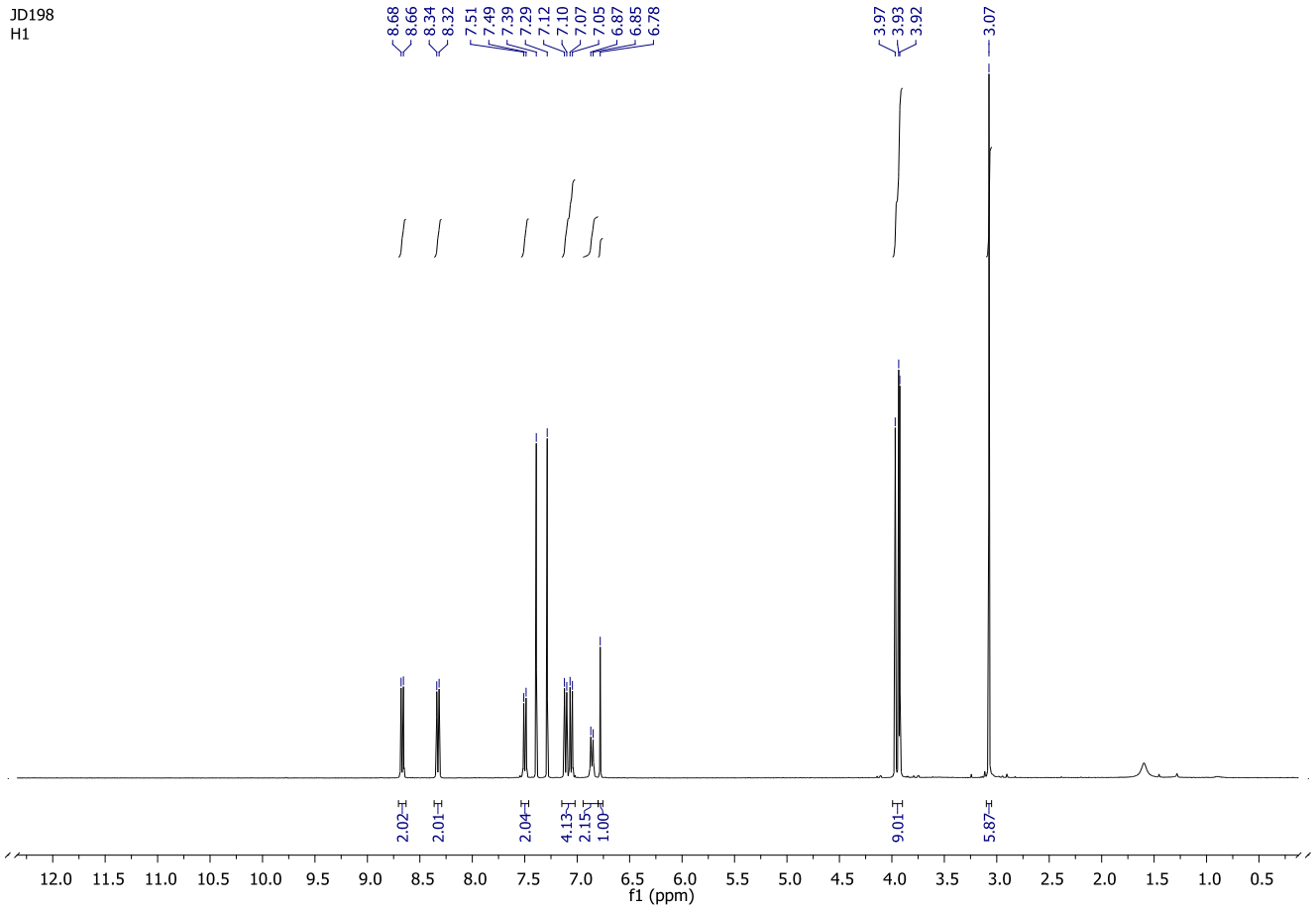
6-(2,4-Di(trifluoromethyl)phenyl)-2,4-di(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2p). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).

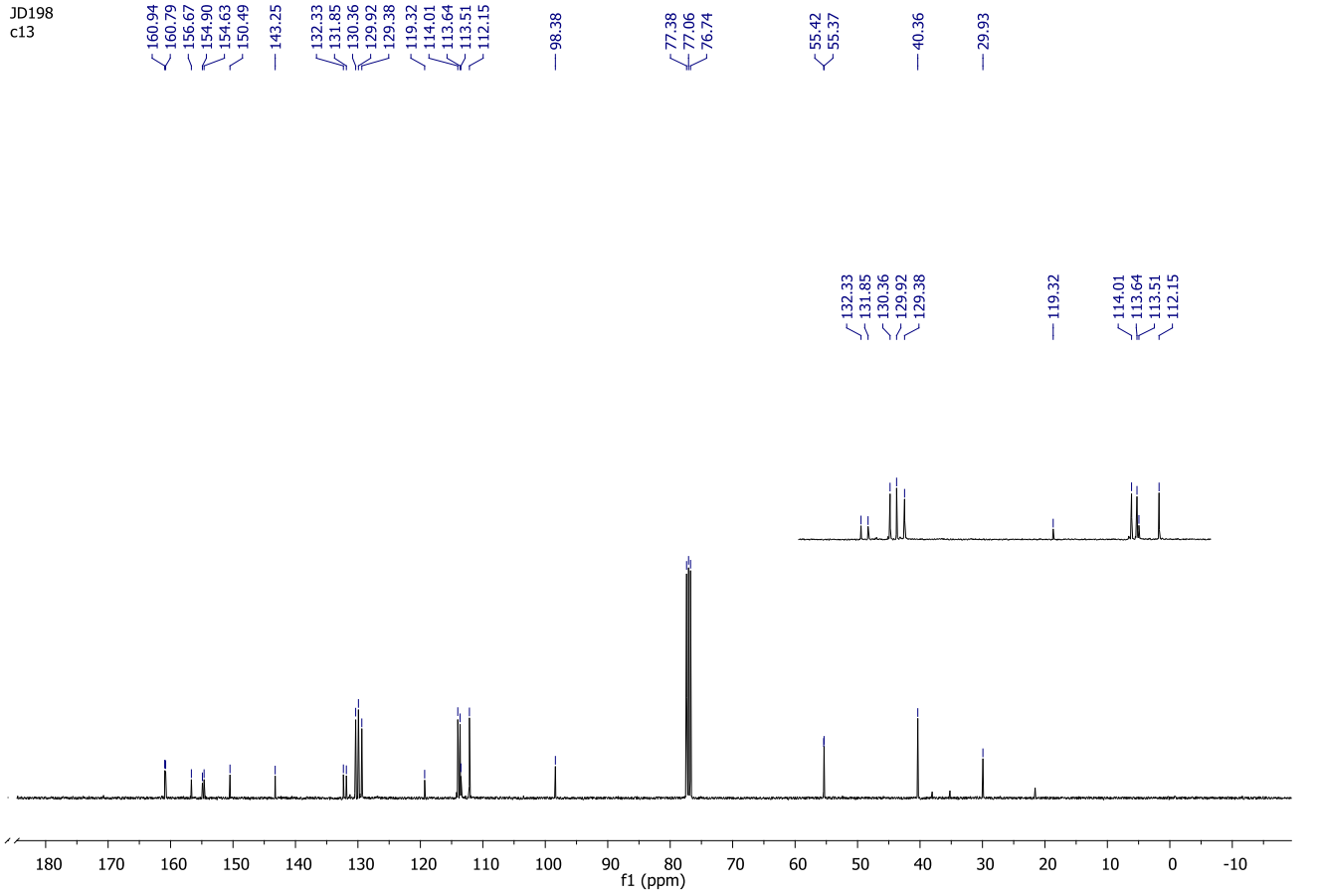


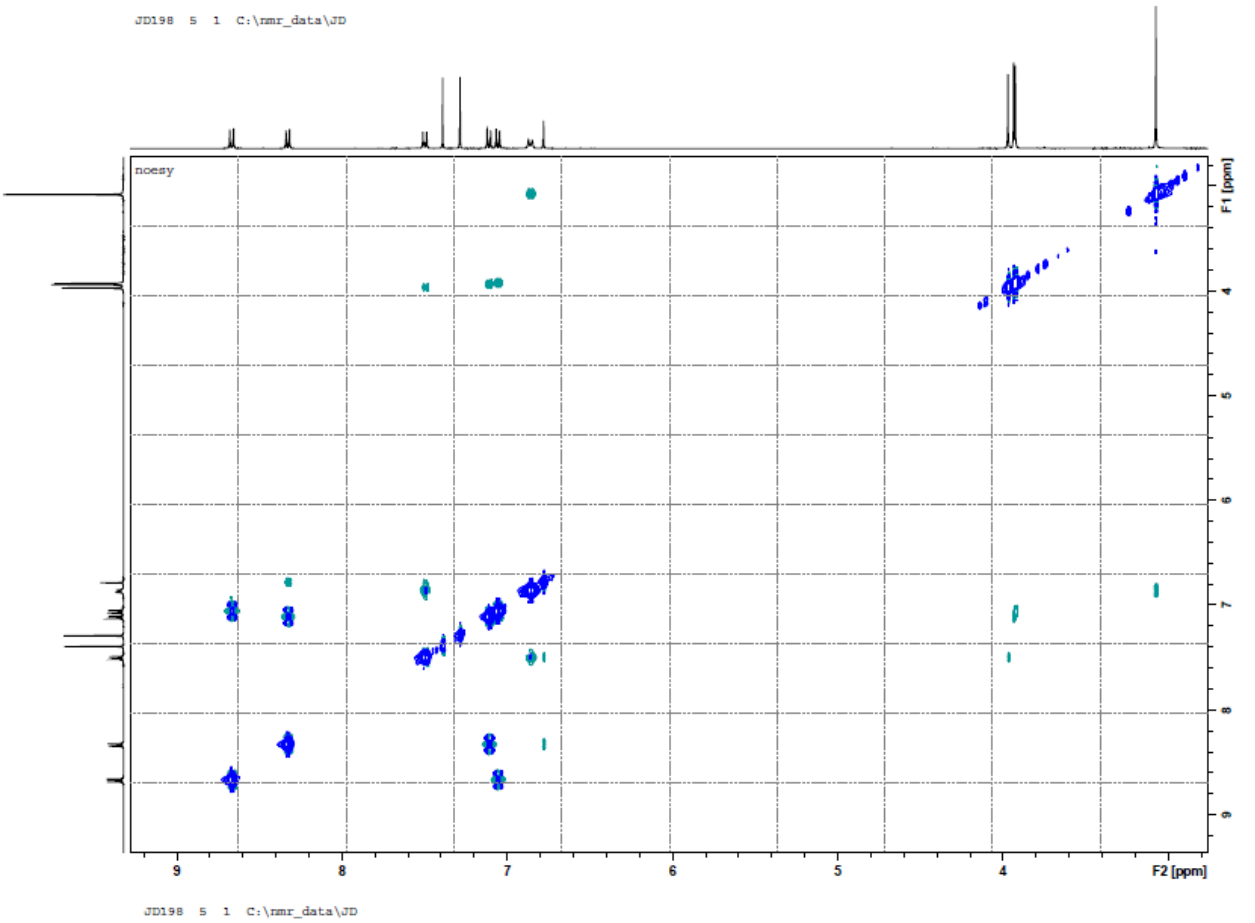


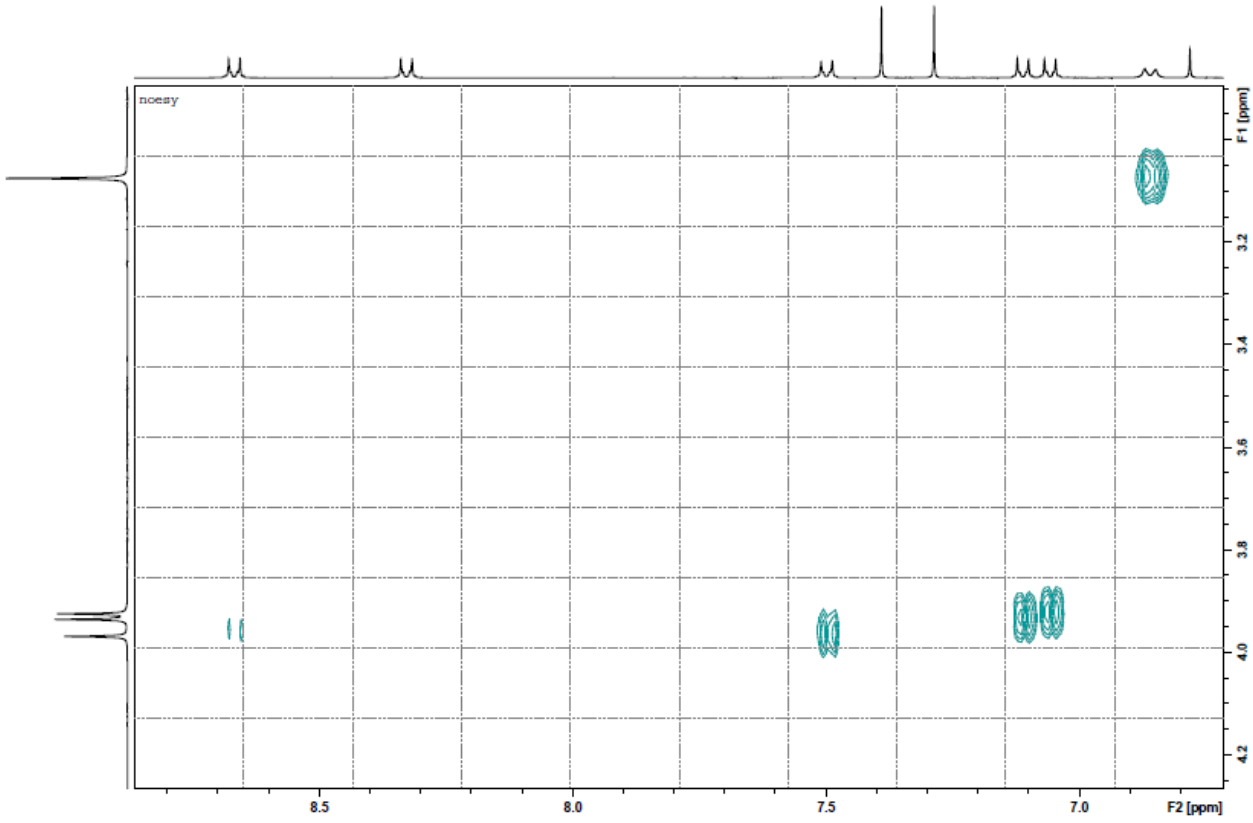

JD195 5 1 C:\nmr_data\JD
noesy
F1 [ppm]
3.7
3.8
3.9
4.0
4.1
4.2
8.5
8.0
7.5
7.0
F2 [ppm]

6-[4-(Dimethylamino)phenyl)- 2,4-di(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2q). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).

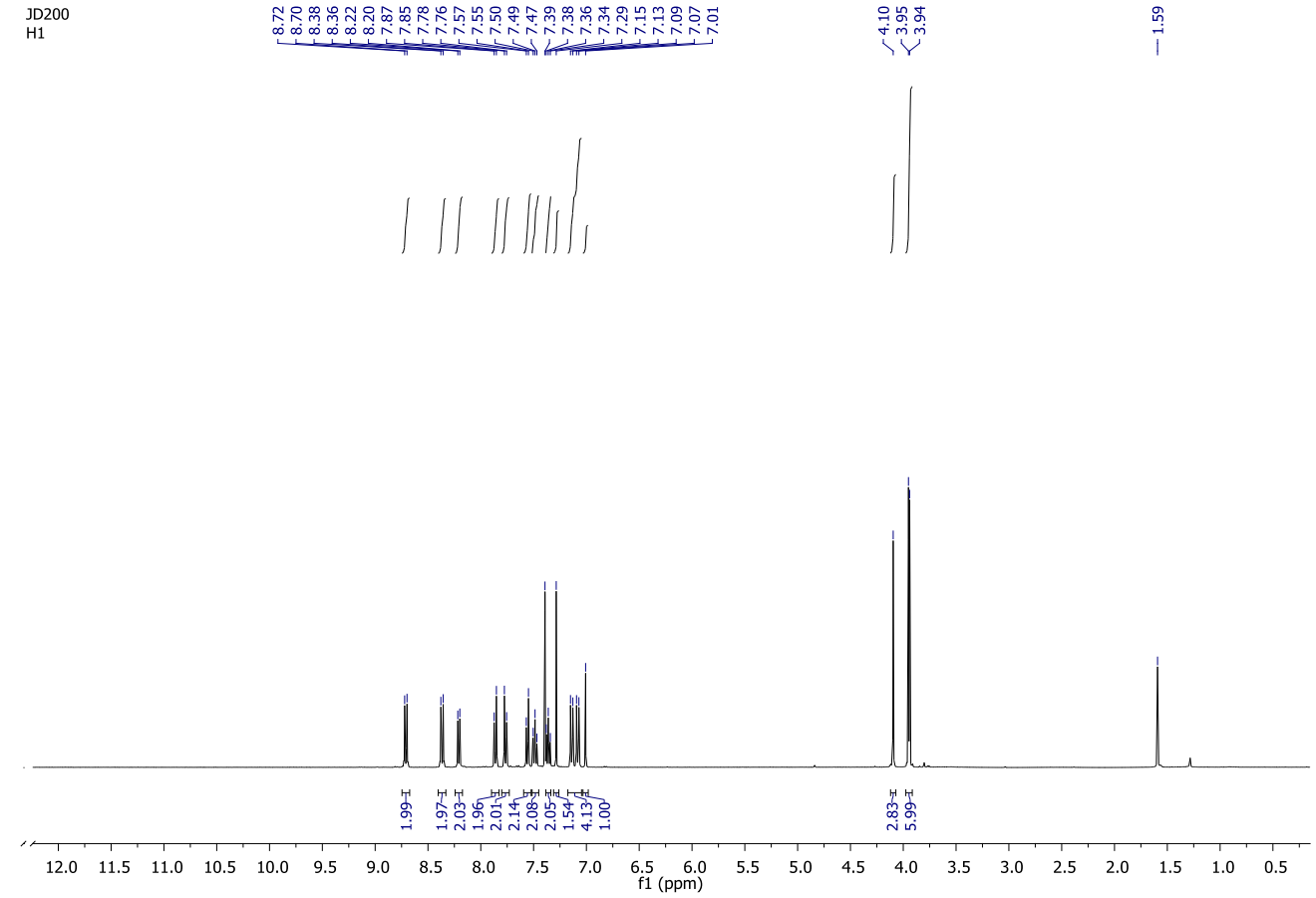


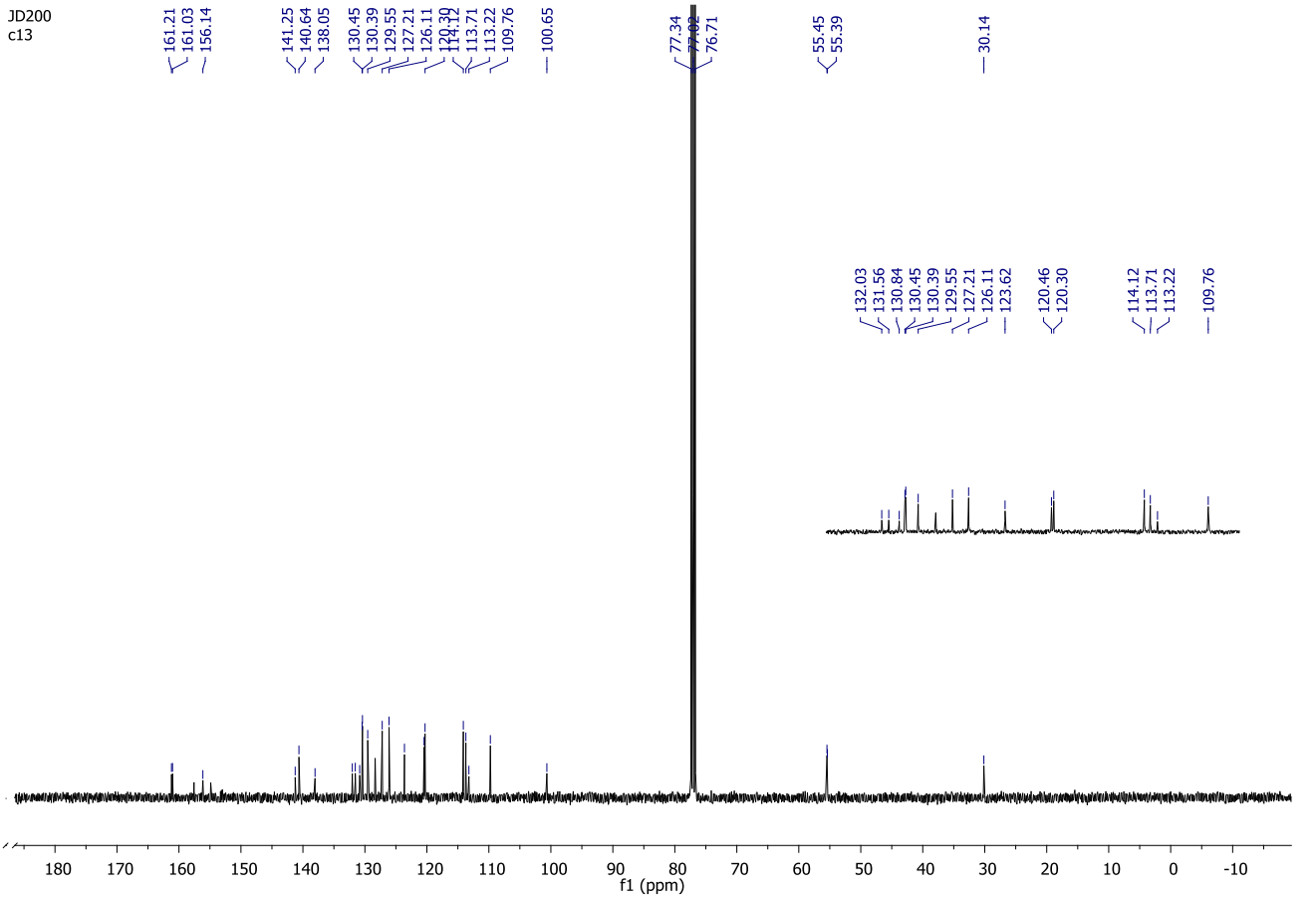



JD198 5 1 C:\nmr_data\JD
noesy
F1 [ppm]
F2 [ppm]
9
8
7
6
5
4

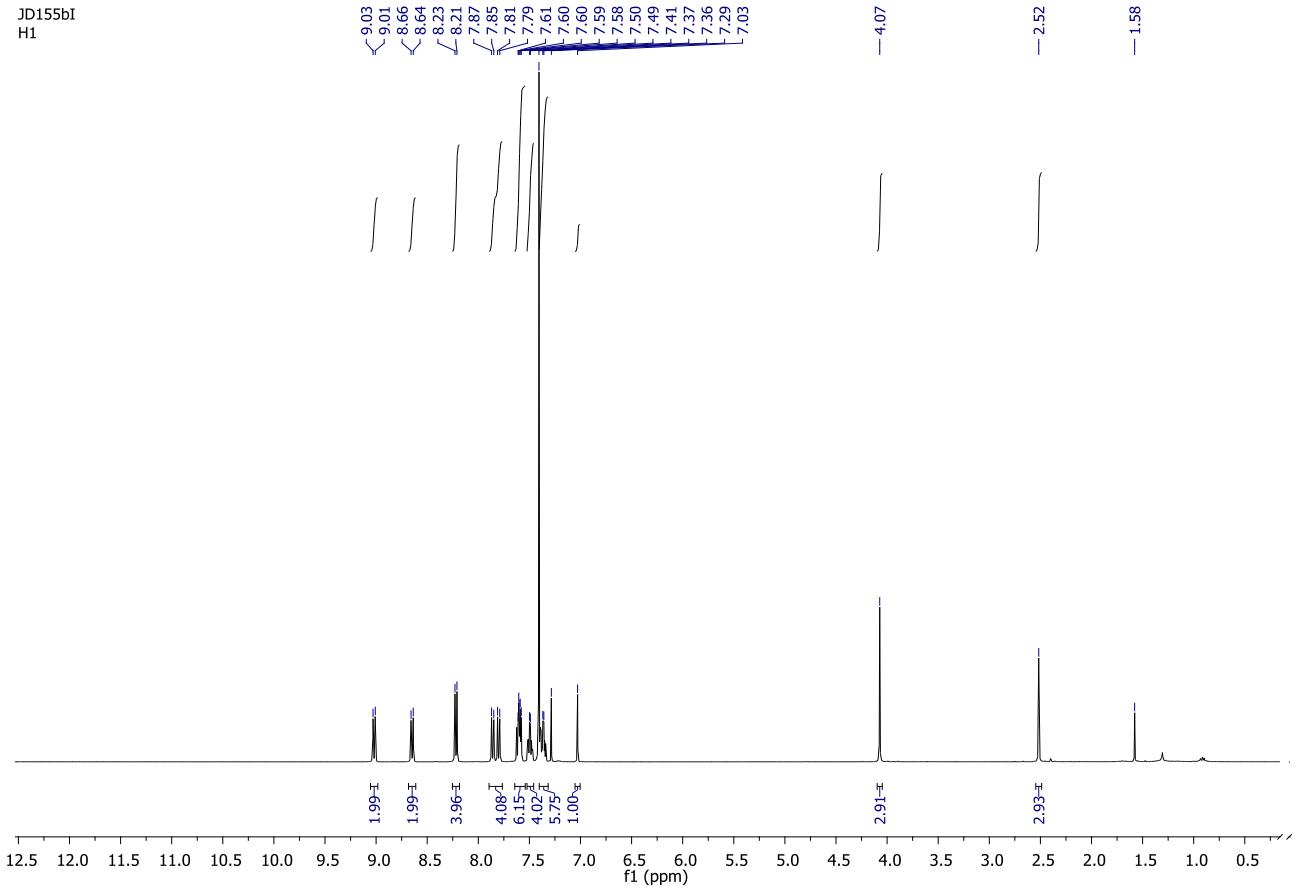

JD198 5 1 C:\nmr_data\JD
noesy
F1 [ppm]
F2 [ppm]
8.5
8.0
7.5
7.0
3.2
3.4
3.6
3.8
4.0
4.2

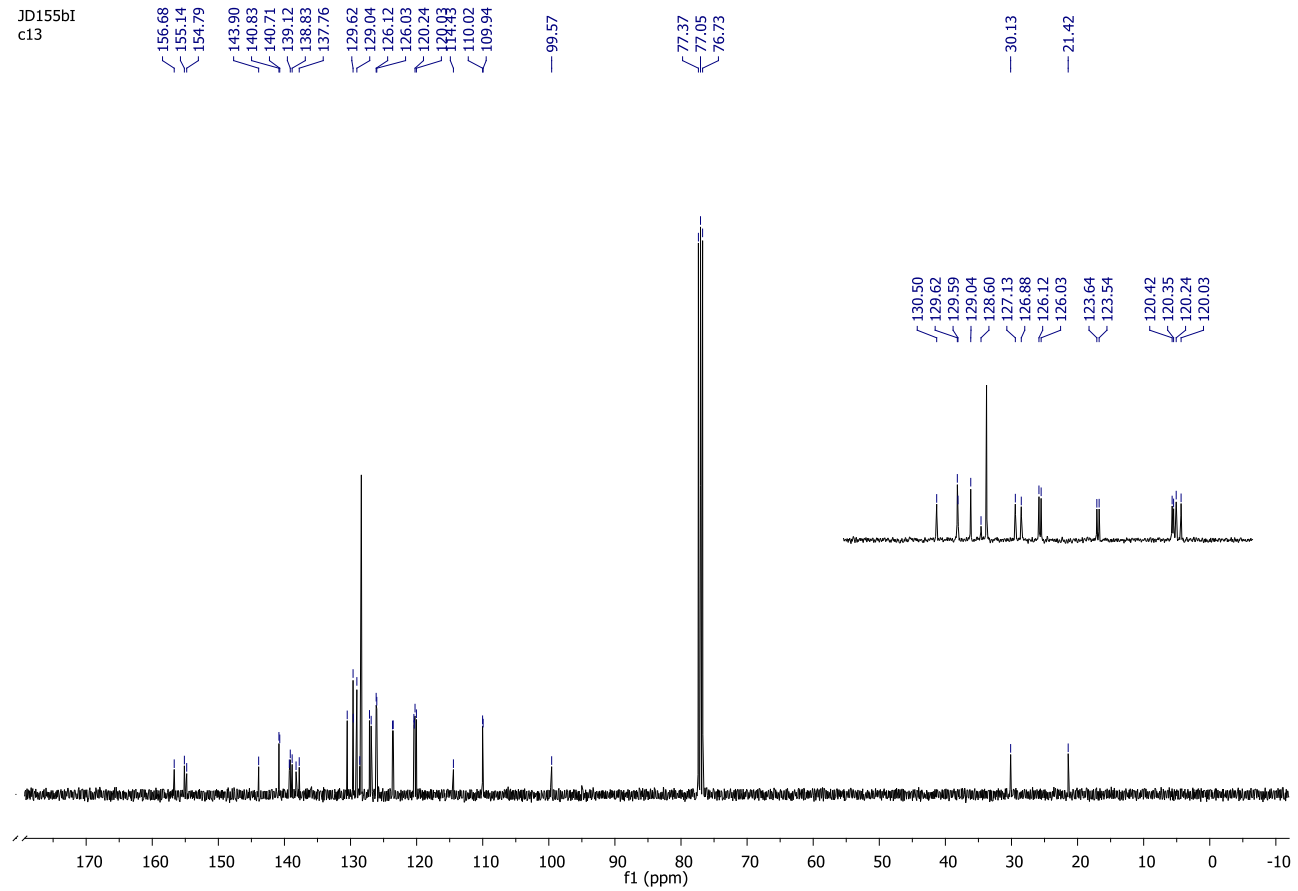
6-[4-(9*H*-carbazol-9-yl)phenyl]- 2,4-di(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2r). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).



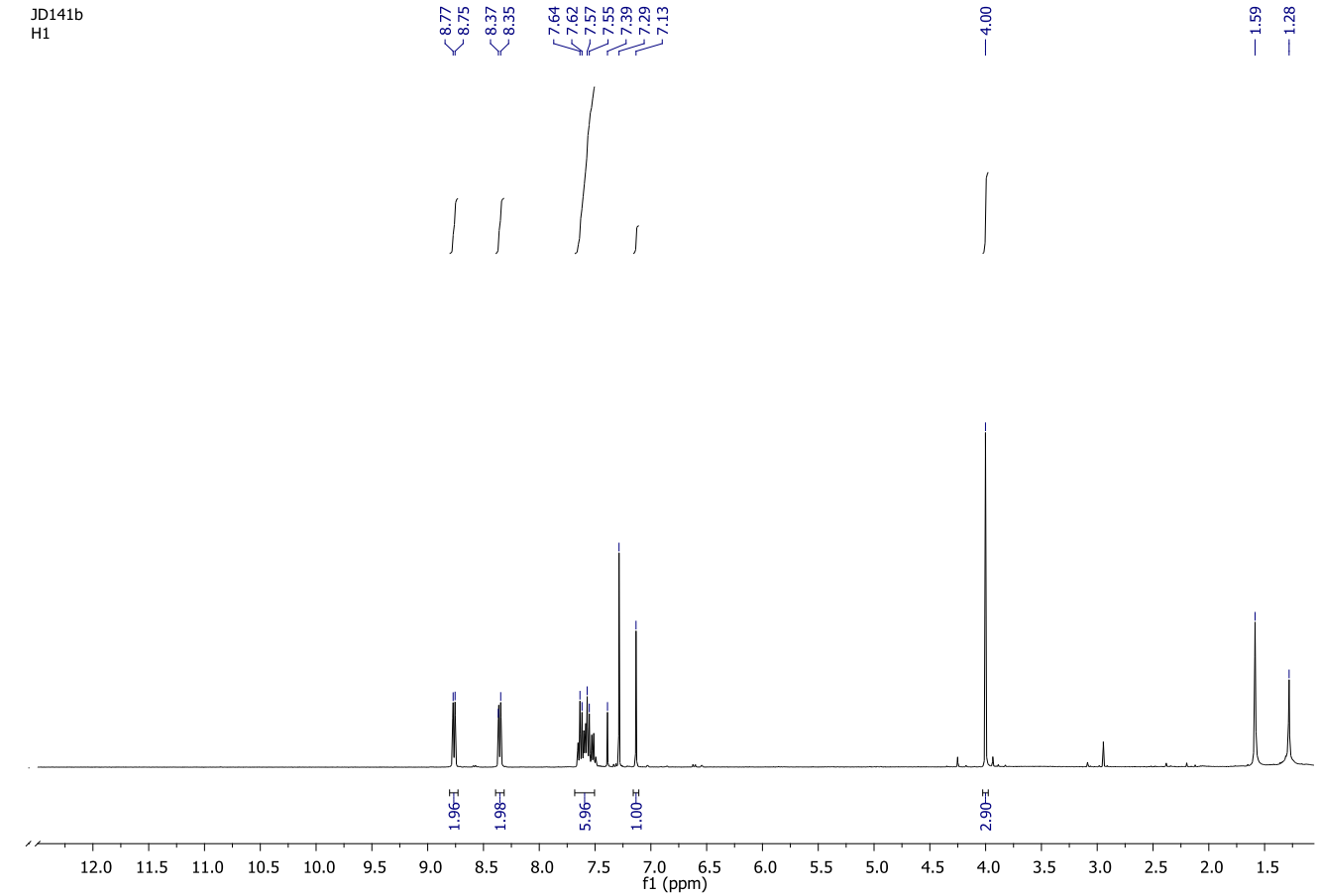


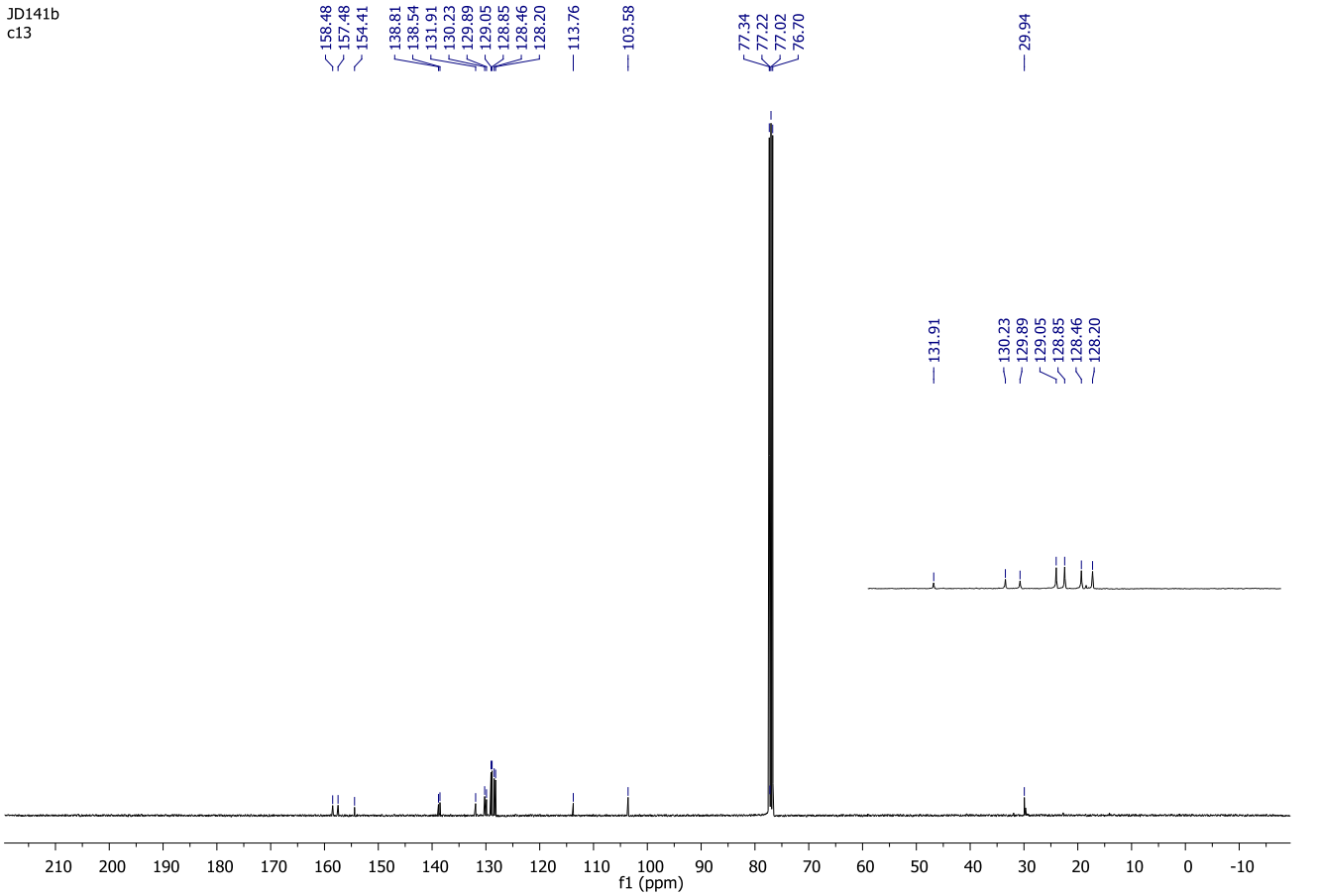
2,4-Di(4-(9*H*-carbazol-9-yl)phenyl)-7-methyl-6-(4-methylphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (2s). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).

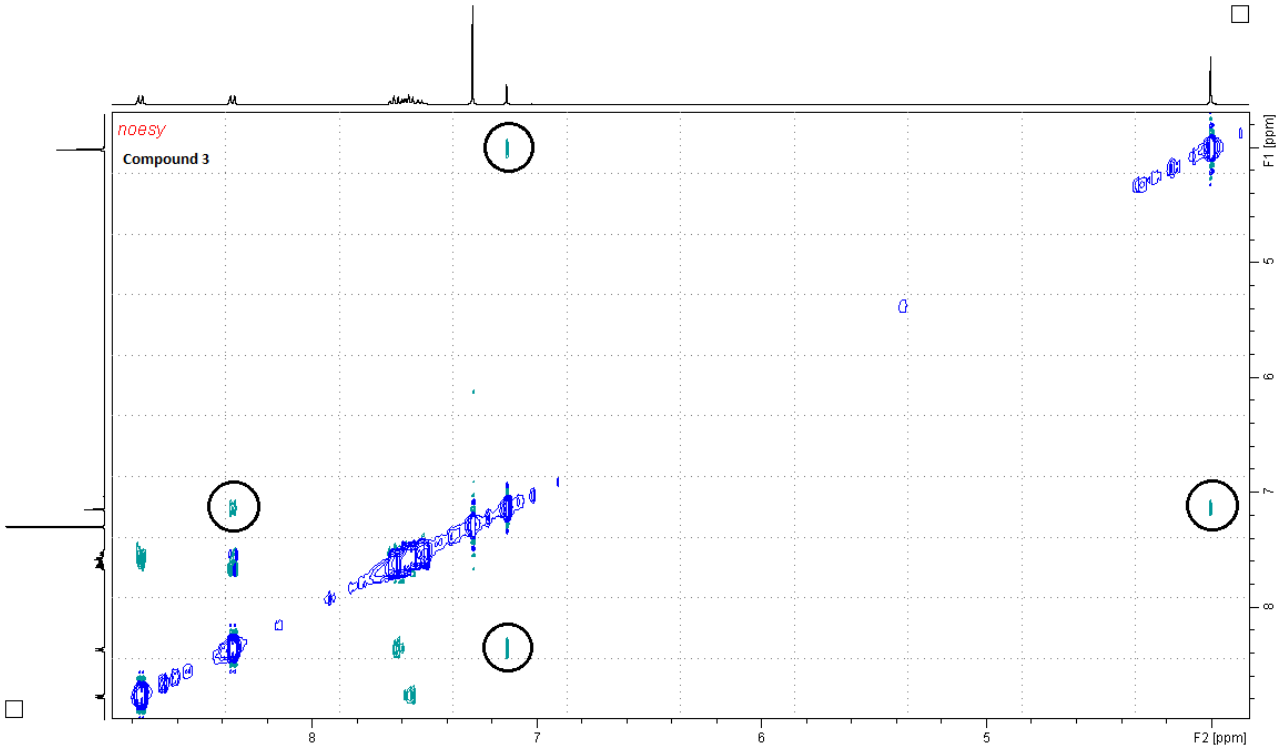




7,7'-Dimethyl-2,2'4,4'-tetraphenyl-7*H*,7'*H*-5,5'bipyrrolo[2,3-*d*]pyrimidine (3). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).






noesy
Compound 3
F1 [ppm]
F2 [ppm]
8
7
6
5

7-Methyl-5,6-di(4-nitrophenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (4). ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$).