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Synthesis of Tetraaryl- and Tetraalkenylpyrazines by Suzuki-Miyaura Reactions of Tetrachloropyrazine

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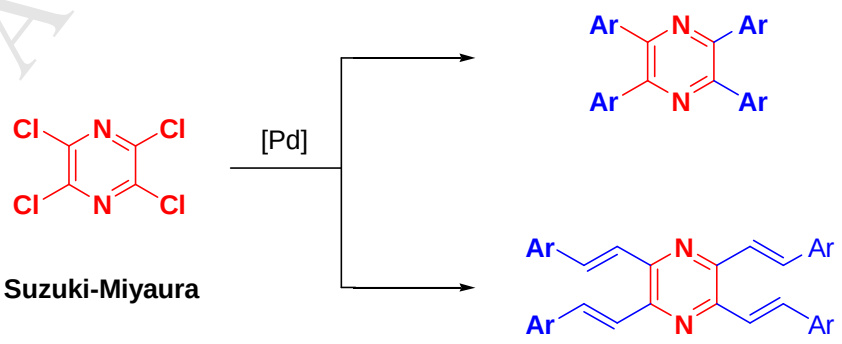
Abstract: The first Suzuki-Miyaura reactions of tetrachloropyrazine allowed for a new and convenient approach to synthesize a variety of tetraarylpyrazines and tetraalkenylpyrazines which were isolated in good to excellent yields. The products show strong fluorescence with good quantum yields. The emission wavelength depends on the substitution pattern which suggests an electronic interaction of the aryl groups with the pyrazine moiety.

Key words: pyrazines; Suzuki-Miyaura reaction; heterocycles; palladium; catalysis

Graphical Abstract



Introduction

Pyrazines are of considerable pharmacological interest and are found in several natural products.[1] A range of aryl substituted pyrazines have been reported to show activity as anti-platelet aggregants,[2] antihyperglycemics,[3] regulators of estrogen receptors (ER),[4] cannabinoid receptor 1 (CB1) antagonists,[5] COX-2 inhibitors,[6] and sphingosine-1-phosphate (S1P) agonists.[7] In addition, di-, tri- and tetraarylpyrazines are useful materials for diagnostic imaging in medical applications, due to their absorption and emission properties.[8]

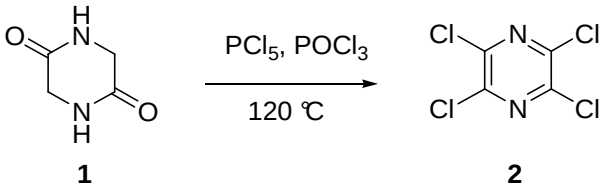
Previous studies on tetraalkenylpyrazines and other analogous cross-shaped alkenyl derivatives were focused on their electro-optical properties.[9] In particular, tetraalkenylpyrazines show interesting two-photon absorption properties and are used as selective sensors for the detection of thrombin.[10]

Tetraarylated pyrazines have been previously prepared by reaction of α-hydroxyketones with ammonium acetate,[11] by reaction of 2-nitrooxiranes with ammonia,[12] by cyclizations of *N,N'*-dibenzylidene derivatives,[13] and by dimerization of azirines.[14] These procedures have disadvantages, such as the availability of the starting materials, low yields, or requirement of the use of high pressure. In recent years, palladium-catalyzed Suzuki-Miyaura-,[15] Sonogashira-,[16] Heck-,[17] and Stille[18] reactions of dichloropyrazines have been reported. Suzuki-Miyaura reactions of tetrahalopyrazines have, to the best of our knowledge, not been previously reported.[19] Herein, we report, for the first time, an efficient protocol for tetrafold Suzuki-Miyaura reactions of tetrachloropyrazine. These reactions provide a new approach to symmetrical tetraarylpyrazines. In addition, the starting material is readily available. Our procedure is more convenient and higher yielding than previously reported methods. In addition, we report the Suzuki-Miyaura reactions of tetrachloropyrazine with alkenylboronates, which offers an easy and straightforward access to tetraalkenylpyrazines. A thorough optimization of the conditions and application of modern catalysts and ligands allowed the preparation of a broad variety of target molecules in high yields and using small amounts of catalyst. Some tetraalkenylpyrazines have been previously synthesized from tetramethylpyrazine and the appropriate aldehydes under basic conditions.[9g,9h,9i,10] However, our protocol based on the Suzuki reaction is advantageous in terms of yield, selectivity, scope and mildness of the conditions. In addition, we report that the tetraalkenylpyrazines prepared

exhibit fluorescence properties with high quantum yields. The emission wavelength depends on the substitution pattern which suggests an electronic interaction of the aryl groups with the pyrazine moiety.

Results and Discussion

Tetrachloropyrazine **2** was prepared according to the procedure reported by Fleischauer *et. al* (Scheme 1).[20]

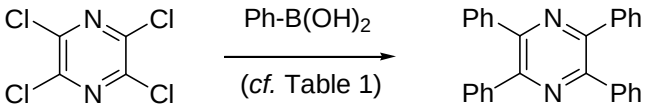


1 **2**

Scheme 1. Synthesis of tetrachloropyrazine **2**.

To evaluate the best catalyst system for the tetrafold arylation we tested various catalysts in the Suzuki-Miyaura reaction of **2** with phenylboronic acid (Scheme 2). The application of standard conditions, i.e. $Pd(PPh_3)_4$ (5 mol%) as the catalyst, toluene as the solvent and potassium phosphate as the base, gave tetraphenylpyrazine **3a** in 83% yield (Table 1, entry 1). The yield could be improved to more than 90% when the reaction was carried out using $Pd(OAc)_2$ (5 mol%) in the presence of bulky monodentate phosphine ligands, such as S-Phos,[21] Cata*CX*ium A,[22] or tricyclohexylphosphine ($P(Cy)_3$) (Figure 1). Product **3a** was isolated in 97% yield when $Pd(OAc)_2$ (5 mol%) in the presence of $P(Cy)_3$ (10 mol%) was employed (entry 4). It is important to note that the amounts of catalyst and ligand could be reduced to 0.25 mol% and 0.5 mol% without any decrease of the yield, respectively (entries 7-10). Further reduction of the catalyst loading (0.1 mol% of catalyst and 0.2 mol% of ligand) resulted in a slight decrease of the yield (88%, entry 11). The reaction mixture was stirred for 18 h at 100 °C. A decrease of the yield to 82% was observed when the reaction time was shortened to 10 h (entry 12). An excess of base and of phenylboronic acid was employed (8.0

equiv.). The yields only slightly dropped when the amounts of the reagents were reduced to 6.0 or 5.0 equiv. (entries 5 and 6).



2 **3a**

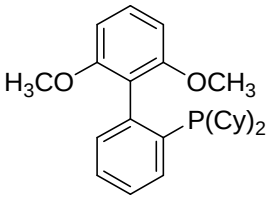
Scheme 2. Optimization of the synthesis of **3a**.

Table 1. Optimization of the synthesis of **3a**.

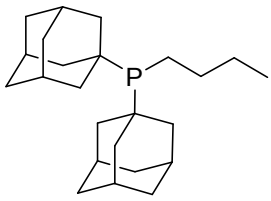
Entry	Catalyst	K_3PO_4/Ph-B(OH)$_2$ [equiv.]	Time [h]	Yield [a] [%]
1	$Pd(PPh_3)_4$ (5 mol%)	8/8	18	83
2	$Pd(OAc)_2$ (5 mol%) S-Phos (10 mol%)	8/8	18	96
3	$Pd(OAc)_2$ (5 mol%) Cata*CX*ium A (10 mol%)	8/8	18	92
4	$Pd(OAc)_2$ (5 mol%) $P(Cy)_3$ (10 mol%)	8/8	18	97
5	$Pd(OAc)_2$ (5 mol%) $P(Cy)_3$ (10 mol%)	5/5	18	86
6	$Pd(OAc)_2$ (5 mol%) $P(Cy)_3$ (10 mol%)	6/6	18	90
7	$Pd(OAc)_2$ (3 mol%) $P(Cy)_3$ (6 mol%)	8/8	18	96
8	$Pd(OAc)_2$ (1 mol%) $P(Cy)_3$ (2 mol%)	8/8	18	97
9	$Pd(OAc)_2$ (0.5 mol%) $P(Cy)_3$ (1 mol%)	8/8	18	96
10	$Pd(OAc)_2$ (0.25 mol%) $P(Cy)_3$ (0.5 mol%)	8/8	18	97
11	$Pd(OAc)_2$ (0.1 mol%)	8/8	18	88

	$P(Cy)_3$ (0.2 mol%)			
12	$Pd(OAc)_2$ (0.25 mol%) $P(Cy)_3$ (0.5 mol%)	8/8	10	82

[a] Yields of isolated products; *conditions*: catalyst (see Table), **2**, phenylboronic acid, K_3PO_4, toluene, 100 °C, 18 h.



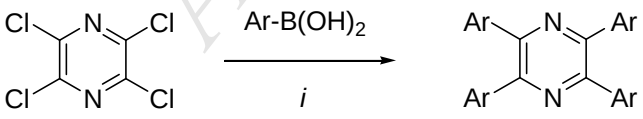
S-Phos



Cata*CX*ium A

Figure 1. Structures of S-Phos and Cata*CX*ium A.

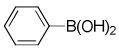
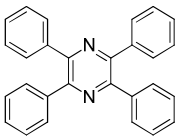
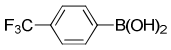
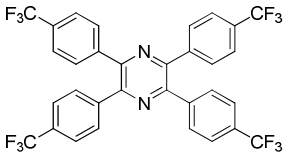
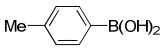
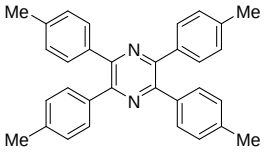
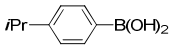
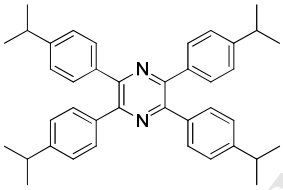
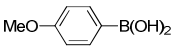
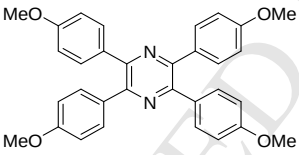
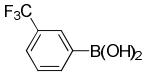
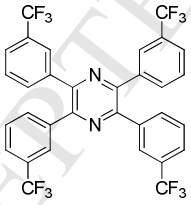
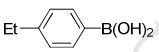
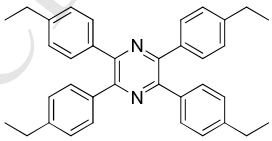
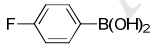
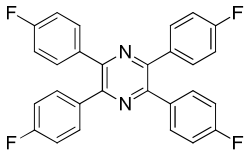
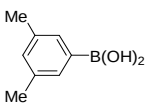
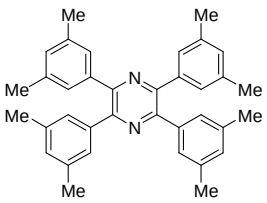
Having efficient reaction conditions in hand (Table 1, entry 10), we studied the preparative scope of the reaction (Scheme 3, Table 2). The Suzuki-Miyaura reaction of **2** with various arylboronic acids afforded tetraarylpyrazines **3a-j** in very good to excellent yields. The reactions were carried out using 0.25 mol% of $Pd(OAc)_2$ and 0.5 mol% of $P(Cy)_3$. In case of **3k-p**, the catalyst loading had to be increased to 2 mol% of $Pd(OAc)_2$ and 4 mol% of $P(Cy)_3$ in order to achieve good yields. Both electron-poor and -rich arylboronic acids were successfully employed in the reaction and gave equally good yields. In addition, a vinyl group was tolerated (product **3l**). The syntheses of **3a**,[12,23] **3c**,[24] and **3e**[5,12] have been previously reported. However, spectroscopic data were reported only for compounds **3a** and **3e**.

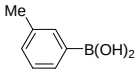
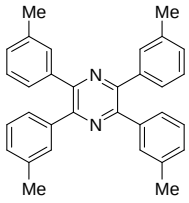
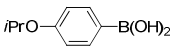
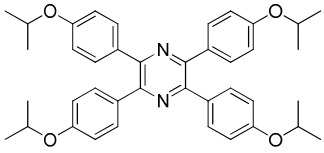
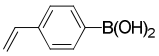
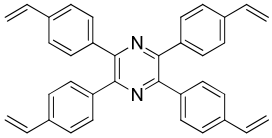
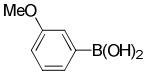
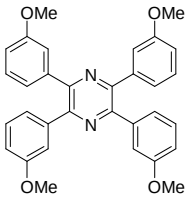
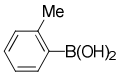
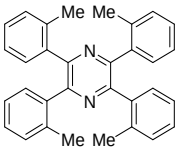
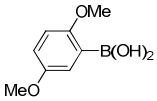
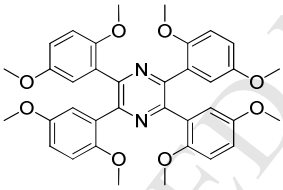
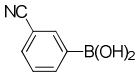
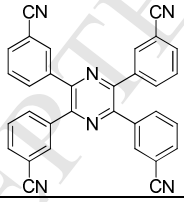


2 **3a-p**

Scheme 3. Synthesis of **3a-p**; *i*: **2**, Ar-$B(OH)_2$ (8 equiv.), K_3PO_4 (8 equiv.), toluene, 100 °C, 18 h, for **3a-j**: $Pd(OAc)_2$ (0.25 mol%), $P(Cy)_3$ (0.5 mol%), for **3k-p**: $Pd(OAc)_2$ (2 mol%), $P(Cy)_3$ (4 mol%).

Table 2. Synthesis of **3a-p**.

3	Ar-$B(OH)_2$	Product	Yield [%][a]
a			97
b			85
c			93
d			96
e			90
f			96
g			87
h			99
i			81

j			94
k			92
l			76
m			99
n			99
o			74
p			50

[a] Yields of isolated products.

The molecular structure of **3b** was independently confirmed by X-ray crystal structure analysis. The aryl substituents were proven to be twisted out from the plane of the pyrazine ring by 32-50° in a propeller-like arrangement (Figure 2). Due to the twisted conformation of the peripheral substituents, tetraarylpyrazines can be used as solid-state luminogens[11b] owing their aggregation-induced emission (AIE)[25] characteristics.

Next, we studied the application of styrylboronic acid which gives access to tetraalkenylpyrazines. Surprisingly, the developed reaction conditions discussed above gave only low yields for the desired product. However, changing to the more bulky Cata*CX*ium A

ligand and using 1,4-dioxane as solvent gave the desired tetrastyrylpyrazine **4a** in quantitative yield.[26]

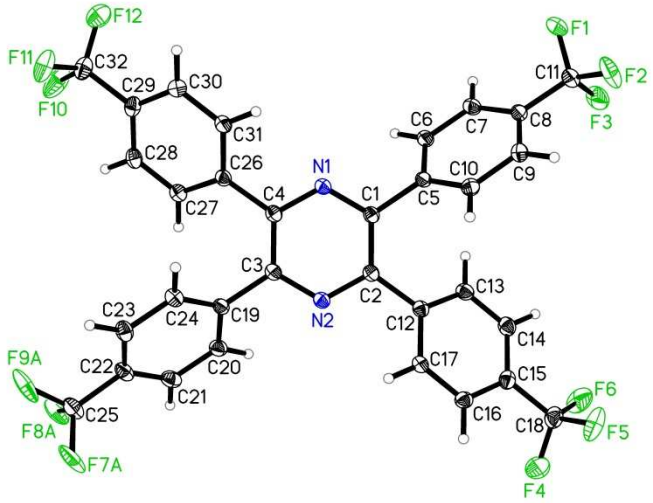
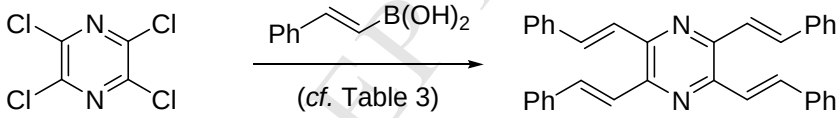


Figure 2. ORTEP diagram of **3b**. Displacement ellipsoids are drawn at the 30% probability level.

Further studies were devoted to the reduction of the catalyst loading. Using 1-2 mol% of palladium-catalyst, the product could be isolated in almost quantitative yield. However, the yield dropped to 60% when only 0.25 mol% of $Pd(dba)_2$ was employed. Thus, we employed 2 mol% of $Pd(dba)_2$ and 4 mol% of the Cata*CX*ium A ligand for elaboration of the substrate scope.



2 **4a**

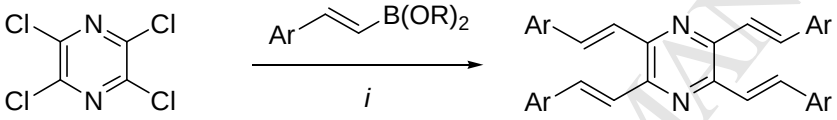
Scheme 4. Optimization of the synthesis of **4a**.

Table 3. Optimization of the synthesis of **4a**.

Entry	Catalyst	Yield [a] [%]
1	$Pd(OAc)_2$ (2 mol%) $P(Cy)_3$ (4 mol%)	12 [b]
2	$Pd(dba)_2$ (5 mol%) Cata*CX*ium A (10 mol%)	99

3	$Pd(dba)_2$ (4 mol%) Cata*CX*ium A (8 mol%)	98
4	$Pd(dba)_2$ (2 mol%) Cata*CX*ium A (4 mol%)	97
5	$Pd(dba)_2$ (1 mol%) Cata*CX*ium A (2 mol%)	95
6	$Pd(dba)_2$ (0.25 mol%) Cata*CX*ium A (0.5 mol%)	60

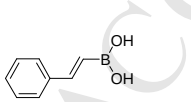
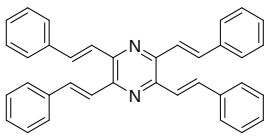
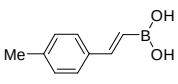
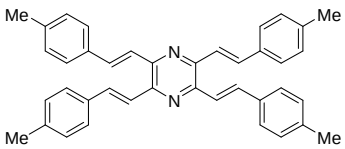
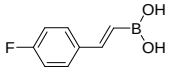
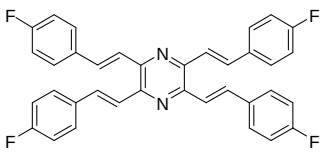
[a] Yields of isolated products; *conditions*: catalyst (see Table), **2**, styrylboronic acid (8 equiv.), K_3PO_4 (8 equiv.), 1,4-dioxane, 100 °C, 20 h. [b] *conditions:* same as for the synthesis of **3k-p** (Scheme 3).

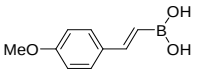
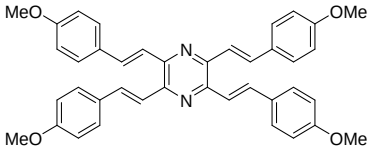
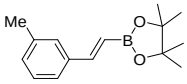
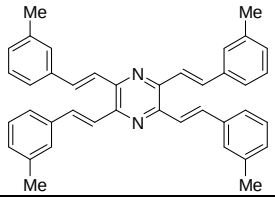


2 **4a-e**

Scheme 5. Synthesis of **4a-e**; *i*: $Pd(dba)_2$ (2 mol%), Cata*CX*ium A (4 mol%), **2**, styrylboronic acid or -pinacol ester (8 equiv.), K_3PO_4 (8 equiv), 1,4-dioxane, 100 °C, 20 h.

Table 4. Synthesis of **4a-e**.

4	Coupling partner	Product	Yield [%][a]
a			97
b			95
c			99

d			93
e			70

[a] Yields of isolated products.

All products were isolated in good to excellent yields. Styrylboronic acids containing donating methyl- or methoxy-groups in *para* position gave slightly diminished yields (table 4, compounds **4b** and **4d**), while the substitution with the strongly electronegative fluorine gave quantitative yield of the desired product (compound **4c**). A methyl group located in 3-position (compound **4e**) resulted in a decreased yield of 70 %.

UV/Vis and Fluorescence Properties

As tetraalkenylpyrazines are known to show interesting photophysical properties [9d,9g,9i,10] we decided to investigate the steady-state UV/Vis- and fluorescence properties of compounds **4a**, **4c** and **4d** (Figure 3). For the measurement of the optical properties it has to be considered that solutions of all studied compounds undergo photochemical reactions in solution even under exposition to daylight for some time. These reactions include for instance *E/Z*-isomerisations, cyclizations or polymerisations and are quite common for such alkenylderivatives.[27] All three absorption spectra consist of three conspicuous transitions in the range of 323nm – 459 nm (Table 5). Compound **4d**, containing a donating methoxy-group, shows a bathochromic shift, while the UV/Vis-spectra of compounds **4a** and **4c** show almost no difference between each other. The same trend is also observed in the fluorescence spectra of these compounds. Tetraalkenylderivative **4d** is bathochromically shifted with an emission maximum at 522 nm while compounds **4a** and **4c** show emission maxima at 498 nm and 497 nm, respectively. The bathochromic effect can be explained by the push-pull substitution pattern of **4d**. This result suggests an electronic interaction of the aryl groups with the pyrazine moiety. All three emission spectra possess at longer wavelengths a shoulder, due to a vibrational progression. We determined the quantum yields of the synthesized compounds

using quinine bisulfate as standard (Table 5). All compounds show good quantum yields between 0.55-0.61. The substitution pattern of the tetrastyrylpyrazines has only a marginal influence on the quantum yield. The fluorine and also the donating methoxy-group gave slightly increased quantum yields as compared to compound **4a**. Since the magnitude of the Stoke shifts is rather low and the quantum yields are quite high, significant intramolecular charge transfer contributions can be ruled out.

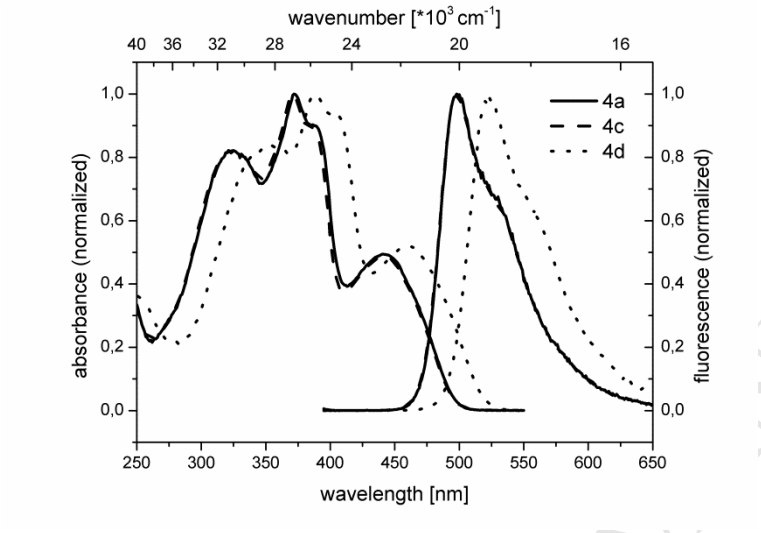


Figure 3. Normalized absorption and corrected emission spectra of compounds **4a**, **4c** and **4d**.

Table 3. UV/Vis absorption and fluorescence data for compounds **4a**, **4c**, **4d** in dichloromethane. For the measurement of the fluorescence quantum yields a solution of quinine bisulfate in 0.05 M H_2SO_4 ($\boldsymbol{\phi_f}$ = 0.52)[28] was applied as standard.

compd	$\lambda_{abs}(\varepsilon_{abs})$ [nm] ([10^4 $M^{-1}cm^{-1}$])	$\tilde{\nu}_{Stokes}$ [cm^{-1}]	λ_{max}^{fluo} [nm]	ϕ_{fluo} Quantum yield
4a	323 (4.35) 373 (5.02) 441 (2.63)	2600	498	0.55
4c	324 (4.45) 371 (5.46) 441 (2.66)	2560	497	0.57
4d	353 (5.05) 388 (6.02) 459 (3.15)	2630	522	0.61

Conclusion

In conclusion, we synthesized various tetraarylpyrazines using the Suzuki-Miyaura reaction. After a thorough optimization the products were isolated in good to quantitative yields using only 0.25 mol% of the palladium catalyst. Furthermore, we synthesized tetrastyrylpyrazines in high yields by application of a modified protocol. Tetrastyrylpyrazines are promising substrates for photonic applications due to their high fluorescence quantum yields. So far, we have not been able to realize the selective reaction of tetrachloropyrazine with one or two equivalents of the boronic acids as the reactions result in the formation of complex mixtures. However, this project is topic of ongoing studies in our laboratories.

Acknowledgements

Financial support by the Volkswagenstiftung is gratefully acknowledged. We thank Mr. Wolfgang Breitsprecher for the measurements of the fluorescence spectra.

Experimental Section

General. All reactions were carried out under argon atmosphere. All chemicals are commercially available and were used without further purification. Column chromatography was performed using Merck Silicagel 60 (0.043 - 0.06 mm). NMR data were recorded on Bruker ARX 300, Bruker ARX 400 and Fourier 300 spectrometers. ^{13}C and ^{1}H NMR spectra were referenced to signals of deuterated solvent and residual protonated solvent, respectively. Peak characterization: s = singlet, d = doublet, t = triplet, pt = pseudo triplet, q = quartet, sept = septet, m = multiplet, bs = broad singlet, dd = doublet of doublet. Infrared Spectra were recorded on Nicolet 550 FT – IR spectrometer with ATR sampling technique for solids as well as liquids. Signal characterization: w = weak, m = medium, s = strong. Gas chromatography-mass analyses were carried out on Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column using helium carrier gas. ESI HR-MS measurements were performed on an Agilent 1969A TOF mass spectrometer. For High Resolution MS (HRMS) Finnigan MAT 95 XP was used. Only the measurements with an average deviation from the theoretical mass of ± 2mDa were accounted as correct. Elemental analyses (EA) were performed with a LecoMikroanalysator - TrueSpec CHNS Micro. Melting points were determined on a Micro-Hot-Stage GalenTM III Cambridge Instruments, and are not corrected. X-ray crystal structure data were collected on a STOE IPDS II diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package. [29] [30] Absorption spectra were measured on an Analytik Jena Specord 50 or Perkin-

Elmer UV/Vis spectrometer Lambda2. The fluorescence spectra were recorded with a Fluoromax-4 Spectrofluorometer (Horiba Scientific). For the absorption spectra dichloromethane was used as solvent and a concentration of 5×10^{-6} M was applied for the quantitative determination of the molar extinction coefficient. A solution of quinine sulphate in 0.05 M sulphuric acid was applied as standard for the measurement of the fluorescence quantum yields ($\varphi_f = 0.52$).[28] Samples and standard were measured in air-equilibrated solutions and exhibited an absorbance of ~ 0.1 at the excitation wavelength.

General Procedures and Experimental Data

Synthesis of tetraarylpyrazines

Prior to all, solutions of $Pd(OAc)_2$ and $P(Cy)_3$ were prepared in dried and argon filled Schlenk tubes (both 0.0125 mmol, 5 mol%) using 1 mL of extra dry THF and toluene, respectively. Solutions were stirred at room temperature for 10 min.

To an argon-flushed glass pressure tube 50 µL of $Pd(OAc)_2$ solution (0.000625 mmol, 0.25 mol%) was added (In cases of compounds **3k-p**, 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$ were used). After the removal of THF via evacuation of pressure tube, 100µL of earlier prepared solution of $P(Cy)_3$ (0.00125 mmol, 0.5 mol%), **2** (54 mg, 0.25 mmol), the appropriate arylboronic acid (2 mmol, 8.0 equiv.) and K_3PO_4 (2 mmol, 8.0 equiv.) were added, followed by the injection of dry toluene (3.5 mL). The tube was closed with a teflon screw cap and the reaction mixture was stirred at 100 °C for 18 hours. Subsequently, the mixture was cooled down to room temperature and diluted with water and dichloromethane. The aqueous layer was extracted three times with dichloromethane. Combined organic layers were dried over Na_2SO_4 and filtered. Unless otherwise noted, solvent was evaporated and the residue was purified by column chromatography on silica gel using mixture of hexane and dichloromethane as eluent.

2,3,5,6-Tetraphenylpyrazine (3a):

According to the general procedure, compound **3a** was isolated as a white solid (93 mg, 97 %); mp. = 248 – 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 - 7.34 (m, 12H), 7.60 - 7.66 (m, 8H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.2 (CH), 128.5 (CH), 129.8 (CH), 138.4 (C), 148.4 (C). MS (EI, 70 eV): m/z (%) = 384 (M^+, 100), 305 (7), 178 (44), 152 (8), 103 (10). HRMS (ESI): calcd. for $C_{28}H_{21}N_2$ ($[M+H]^+$): 385.16993; found: 385.17036. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3038 (w), 1389 (m), 1170 (m), 1104 (m), 1011 (m), 762 (s), 692 (s), 536 (s).

2,3,5,6-Tetrakis(4-(trifluoromethyl)phenyl)pyrazine (3b):

According to the general procedure, compound **3b** was isolated as a white solid (139 mg, 85 %); mp. = 265 – 266 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, 8H, ^{3}J = 8.2 Hz), 7.74 (d, 8H, ^{3}J = 8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.8 (q, $^{1}J_{C–F}$ = 272.3 Hz, CF_3), 125.5 (q, $^{3}J_{C–F}$ = 3.8 Hz, CH), 130.1 (CH), 131.3 (q, $^{2}J_{C–F}$ = 32.6 Hz, C), 140.8 (C), 147.9 (C).^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.3 (s, 12F, CF_3). MS (EI, 70 eV): m/z (%) = 656 (M^+, 100), 637 (15), 587 (14), 314 (77), 295 (15), 264 (10), 225 (7), 171 (7). HRMS (ESI): calcd. For $C_{32}H_{17}F_{12}N_2$([M+H]$^+$): 657.11946; found: 657.1192. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1322 (s), 1167 (m), 1105 (s), 1011 (m), 849 (s), 631 (m), 535 (m). EA: calcd. for $C_{32}H_{16}F_{12}N_2$ (656.46): C, 58.55; H, 2.46; N, 4.27; found: C, 57.92; H, 2.32; N, 4.23.

2,3,5,6-Tetra-*p*-tolylpyrazine (3c):

According to the general procedure, compound **3c** was isolated as a white solid (103 mg, 93 %); mp. = 284 – 286 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 12H, CH_3), 7.09 - 7.13 (m, 8H), 7.52 - 7.56 (m, 8H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 128.9 (CH), 129.6 (CH), 135.8 (C), 138.3 (C), 147.7 (C). MS (EI, 70 eV): m/z (%) = 440 (M^+, 100), 425 (10), 206 (19), 189 (8). HRMS (ESI): calcd. for $C_{32}H_{29}N_2$ ([M+H]$^+$): 441.23253; found: 441.23245. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2917 (w), 1385 (s), 1172 (m), 1096 (m), 1009 (m), 820 (s), 728 (s), 626 (m), 530 (s), 513 (s).

2,3,5,6-Tetrakis(4-isopropylphenyl)pyrazine (3d):

According to the general procedure, compound **3d** was isolated as yellowish-white solid (133 mg, 96 %); mp. = 279 – 281 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (d, 24H, ^{3}J = 6.9 Hz, CH_3), 2.90 (sept, 4H, ^{3}J = 6.9 Hz, C$H_{i\text{-Pr}}$), 7.13 - 7.17 (m, 8H), 7.56 - 7.60 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8 (CH_3), 33.8 (*C*H$_{i\text{-Pr}}$), 126.2 (CH), 129.7 (CH), 136.1 (C), 147.5 (C), 149.2 (C). MS (EI, 70 eV): m/z (%) = 552 (M^+, 100), 537 (11), 509 (7). HRMS (ESI): calcd. for $C_{40}H_{45}N_2$ ([M+H]$^+$): 553.35773; found: 553.35861. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2959 (m), 2926 (w), 2866 (w), 1388 (s), 1181 (m), 1098 (m), 1006 (m), 839 (s), 632 (m), 552 (s).

2,3,5,6-Tetrakis(4-methoxyphenyl)pyrazine (3e):

According to the general procedure, compound **3e** was isolated as a light brown solid (113 mg, 90 %); mp. = 278 – 280 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 12H, OCH_3), 6.81 - 6.86 (m, 8H), 7.56 - 7.61 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 113.6 (CH), 131.0 (CH), 131.2 (C), 146.8 (C), 159.8 (C). MS (EI, 70 eV): m/z (%) = 504 (M^+, 100), 252 (12), 238 (15), 223 (34), 195 (10), 152 (12), 133 (11). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2O_4$: 504.20436; found: 504.20469. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2926 (w), 2834 (w), 1602 (s), 1573 (m), 1511 (s), 1418 (m), 1381 (s), 1295 (s), 1244 (s), 1164 (s), 1027 (s), 830 (s), 796 (s), 740 (m), 529 (s).

2,3,5,6-Tetrakis(3-(trifluoromethyl)phenyl)pyrazine (3f):

According to the general procedure, compound **3f** was isolated as a white solid (157 mg, 96 %); mp. = 165 – 167 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (pt, 4H, ^{3}J = 7.8 Hz), 7.65 (d, 4H, ^{3}J = 7.8 Hz), 7.75 (d, 4H, ^{3}J = 7.8 Hz), 7.86 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.6 (q, $^{1}J_{C–F}$ = 271.9 Hz, CF_3), 125.9 (q, $^{3}J_{C–F}$ = 3.6 Hz, CH), 126.7 (q, $^{3}J_{C–F}$ = 3.8 Hz, CH), 129.1 (CH), 131.1 (q, $^{2}J_{C–F}$ = 32.6 Hz, C), 133.0 (CH), 138.0 (C), 148.1 (C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.5 (s, 12F, CF_3). MS (EI, 70 eV): m/z (%) = 656 (M^+, 100), 637 (12), 314 (99), 295 (10), 264 (7), 225 (11), 171 (17). HRMS (EI, 70 eV): calcd. for $C_{32}H_{16}F_{12}N_2$: 656.11164; found: 656.11102. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1323 (s), 1280 (m), 1164 (s), 1127 (s), 1069 (s), 908 (m), 801 (m), 700 (s). EA: calcd. for $C_{32}H_{16}F_{12}N_2$ (656.46): C, 58.55; H, 2.46; N, 4.27; found: C, 58.85; H, 2.28; N, 4.35.

2,3,5,6-Tetrakis(4-ethylphenyl)pyrazine (3g):

According to the general procedure, compound **3g** was isolated as a white solid (108 mg, 87 %); mp. = 235 – 236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, 12H, ^{3}J = 7.5 Hz, CH_3), 2.65 (q, 8H, ^{3}J = 7.5 Hz, CH_2), 7.12 - 7.14 (m, 8H), 7.55 - 7.59 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 28.6 (CH_2), 127.7 (CH), 129.7 (CH), 136.0 (C), 144.6 (C), 147.6 (C). MS (EI, 70 eV): m/z (%) = 496 (M^+, 100), 467 (12), 219 (28), 204 (14), 116 (11). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2$: 496.28730; found: 496.28760. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2961 (m), 2929 (w), 2870 (w), 1387 (s), 1180 (s), 1097 (m), 1007 (m), 632 (m), 536 (m). EA: calcd. for $C_{36}H_{36}N_2$ (496.68): C, 87.05; H, 7.31; N, 5.64; found: C, 86.96; H, 7.31; N, 5.63.

2,3,5,6-Tetrakis(4-fluorophenyl)pyrazine (3h):

According to the general procedure, compound **3h** was isolated as a white solid (113 mg, 99 %); mp. = 233 – 234 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 - 7.05 (m, 8H), 7.54 - 7.61 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.4 (d, $^{2}J_{C–F}$ = 21.8 Hz, CH), 131.6 (d, $^{3}J_{C-F}$ = 8.3 Hz, CH), 134.0 (d, $^{4}J_{C-F}$ = 3.2 Hz, C), 147.3 (C), 163.1 (d, $^{1}J_{C–F}$ = 250.1 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.7 (s, 4F, CF). MS (EI, 70 eV): m/z (%) = 456 (M^+, 100), 359 (6), 214 (36). HRMS (EI, 70 eV): calcd. for $C_{28}H_{16}F_4N_2$: 456.12441; found: 456.12366.IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1602 (s), 1510 (s), 1415 (m), 1384 (s), 1226 (s), 1152 (s), 1108 (m), 1011 (m), 839 (s), 735 (m), 617 (m), 526 (s). EA: calcd. for $C_{28}H_{16}F_4N_2$ (456.43): C, 73.68; H, 3.53; N, 6.14; found: C, 73.64; H, 3.33; N, 6.09.

2,3,5,6-Tetrakis(3,5-dimethylphenyl)pyrazine (3i):

According to the general procedure, compound **3i** was isolated as a white solid (101 mg, 81 %); mp. = 275 – 277 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 24H, CH_3), 6.94 (bs, 4H),

7.19 (bs, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 127.6 (CH), 129.9 (CH), 137.3 (C), 138.5 (C), 148.8 (C). MS (EI, 70 eV): m/z (%) = 496 (M^+, 100), 248 (10), 133 (22). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2$: 496.28730; found: 496.28686. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3025 (w), 2912 (m), 2855 (w), 1600 (m), 1391 (s), 1374 (s), 1187 (m), 1154 (m), 855 (s), 843 (s), 691 (s), 424 (m). EA: calcd. for $C_{36}H_{36}N_2$ (496.68): C, 87.05; H, 7.31; N, 5.64; found: C, 86.89; H, 7.44; N, 5.39.

2,3,5,6-Tetra-*m*-tolylpyrazine (3j):

According to the general procedure, compound **3j** was isolated as a white solid (104 mg, 94 %); mp. = 153 – 154 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 12H, CH_3), 7.13 - 7.16 (m, 8H), 7.28 - 7.32 (m, 4H), 7.55 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 127.0 (CH), 127.8 (CH), 129.2 (CH), 130.4 (CH), 137.8 (C), 138.5 (C), 148.6 (C). MS (EI, 70 eV): m/z (%) = 440 (M^+, 100), 425 (12), 384 (26), 258 (16), 206 (11), 102 (17), 69 (13), 57 (13). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2$: 440.22470; found: 440.22433. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3034 (w), 2915 (w), 1371 (m), 1167 (m), 847 (m), 778 (s), 704 (s), 471 (s), 447 (m). EA: calcd. for $C_{32}H_{28}N_2$ (440.58): C, 87.24; H, 6.41; N, 6.36; found: C, 87.30; H, 6.36; N, 6.32.

2,3,5,6-Tetrakis(4-isopropoxyphenyl)pyrazine (3k):

In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3k** was isolated as a white solid (142 mg, 92 %); mp. = 241 – 243 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, 24H, ^3J = 6.1 Hz, CH_3), 4.55 (sept, 4H, ^3J = 6.1 Hz, C$H_{i\text{-Pr}}$), 6.79 - 6.82 (m, 8H), 7.55 - 7.59 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (CH_3), 69.7 (CH$_{i\text{-Pr}}$), 115.3 (CH), 131.0 (CH), 131.0 (C), 146.7 (C), 158.1 (C). MS (EI, 70 eV): m/z (%) = 616 (M^+, 100), 574 (13), 447 (37), 224 (12), 210 (16), 57 (14), 43 (14). HRMS (EI, 70 eV): calcd. for $C_{40}H_{44}N_2O_4$: 616.32956; found: 616.32852. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2974 (m), 2923 (w), 1603 (s), 1510 (s), 1382 (s), 1287 (m), 1240 (s), 1163 (s), 1116 (s), 948 (s), 834 (s), 742 (m), 742 (m), 623 (m), 536 (s).

2,3,5,6-Tetrakis(4-vinylphenyl)pyrazine (3l):

In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3l** was isolated as a yellowish-white solid (93 mg, 76 %); mp. > 375 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.27 (dd, 4H, $^3J_{cis}$ = 10.9 Hz, $^2J_{gem}$ = 0.7 Hz, CH=CH_{cis}-H), 5.77 (dd, 4H, $^3J_{trans}$ = 17.5 Hz, $^2J_{gem}$ = 0.7 Hz, CH=CH-H_{trans}), 6.71 (dd, 4H, $^3J_{trans}$ = 17.5 Hz, $^3J_{cis}$ = 10.9 Hz, CH=CH_2), 7.34 - 7.38 (m, 8H), 7.60 - 7.64 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 114.5 (CH), 126.1 (CH), 130.0 (CH), 136.3 (CH), 137.7 (C), 137.8 (C), 147.5 (C). MS (EI, 70 eV): m/z (%) = 488 (M^+, 100), 461 (4), 230 (17), 202 (5), 71 (4). HRMS (EI, 70 eV): calcd. for $C_{36}H_{28}N_2$: 488.22470; found: 488.22447. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2950 (w), 2917 (w), 2851 (w), 1627 (m), 1388 (s), 1174 (m), 1101 (m), 987 (s), 901 (s), 845 (s), 534 (s).

2,3,5,6-Tetrakis(3-methoxyphenyl)pyrazine (3m):

In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3m** was isolated as a light brown solid (125 mg, 99 %); mp. = 170 – 172 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 12H, OCH_3), 6.85 - 6.89 (m, 4H), 7.15 - 7.22 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 114.8 (2 x CH), 122.4 (CH), 129.2 (CH), 139.6 (C), 148.2 (C), 159.2 (C). MS (EI, 70 eV): m/z (%) = 504 (M^+, 100), 262 (12), 207 (9), 188 (16), 145 (14), 117 (10), 73 (10). 60 (12), 43 (15). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2O_4$: 504.20436; found: 504.20339. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3006 (w), 2921 (m), 2853 (w), 1578 (s), 1424 (m), 1377 (s), 1290 (m), 1229 (s), 1028 (s), 775 (s), 719 (s). EA: calcd. for $C_{32}H_{28}N_2O_4$ (504.58): C, 76.17; H, 5.59; N, 5.55; found: C, 76.49; H, 5.50; N, 5.42.

2,3,5,6-Tetra-*o*-tolylpyrazine (3n):

In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3n** was isolated as a white solid (109 mg, 99 %); mp. = 252 – 254 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 12H, CH_3), 6.99 - 7.06 (m, 4H), 7.08 - 7.15 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1 (CH_3), 125.2 (CH), 128.2 (CH), 130.2 (CH), 130.4 (CH), 136.2 (C), 137.7 (C), 151.6 (C). MS (EI, 70 eV): m/z (%) = 440 (M^+, 100), 425 (60), 349 (16), 205 (12), 73 (16), 60 (17), 43 (14). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2$: 440.22470; found: 440.22351. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3016 (w), 2921 (w), 2852 (w), 1382 (s), 1081 (m), 1016 (m), 757 (s), 723 (s), 460 (s). EA: calcd. for $C_{32}H_{28}N_2$ (440.58): C, 87.24; H, 6.41; N, 6.36; found: C, 87.47; H, 6.69; N, 6.20.

2,3,5,6-Tetrakis(2,5-dimethoxyphenyl)pyrazine (3o):

Reaction was made according to the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$. After combined organic layers were dried over sodium sulphate, filtered and solvent was removed, compound **3o** was isolated as a white solid by recrystallization of crude mixture from warm dichloromethane (116 mg, 74 %); mp. = 260 – 262 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36 (s, 12H, OCH_3), 3.70 (s, 12H, OCH_3), 6.64 (d, 4H, ^3J = 8.9 Hz), 6.77 (dd, 4H, ^3J = 8.9 Hz, ^4J = 3.0 Hz), 7.05 (d, ^4J = 3.0 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 55.8 (OCH_3), 111.9 (CH), 115.3 (CH), 116.6 (CH), 129.4 (C), 149.4 (C), 150.8 (C), 153.3 (C). MS (EI, 70 eV): m/z (%) = 624 (M^+, 100), 609 (45), 593 (71), 579 (12), 487 (23), 312 (11), 60 (10). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2O_8$: 624.24662; found: 624.24559. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3002 (w), 2960 (w), 2833 (w), 1499 (s), 1447 (m), 1424 (s), 1275 (s), 1229 (s), 1079 (m), 1042 (s), 1016 (s), 873 (m), 802 (s). EA: calcd. for $C_{36}H_{36}N_2O_8$ (624.68): C, 69.22; H, 5.81; N, 4.48; found: C, 69.58; H, 5.74; N, 4.66.

2,3,5,6-Tetrakis(3-cyanophenyl)pyrazine (3p):

In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3p** was isolated as a white solid (61 mg, 50 %); mp. = 296 – 297 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (pt, 4H, ^3J = 7.8 Hz), 7.70 - 7.76 (m, 8H), 7.96 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 113.4 (C), 117.9 (C), 129.6 (CH), 133.1 (CH), 133.2 (CH), 133.8 (CH), 138.0 (C), 147.2 (C). MS (EI, 70 eV): m/z (%) = 484 (M^+, 100), 380 (7), 355 (5), 228 (38), 201 (8), 60 (5), 44 (5). HRMS (EI, 70 eV): calcd. for $C_{32}H_{16}N_6$: 484.14310; found: 484.14195. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 2953 (w), 2227 (m), 1371 (m), 1164 (m), 917 (m), 799 (s), 697 (s), 515 (m).

Synthesis of tetraalkenylpyrazines

An argon-flushed glass pressure tube was charged with $Pd(dba)_2$ (0.005 mmol, 2 mol%), Cata*CX*ium A (0.01 mmol, 4 mol%), **2** (54.4 mg, 0.25 mmol), the appropriate alkenylboronic acid or pinacol ester (2 mmol, 8.0 eq.), K_3PO_4 (2 mmol, 8.0 eq.) and anhydrous 1,4-dioxane (4 mL). The tube was sealed with a teflon cap and the reaction mixture was stirred at 100 °C for 20 hours. Resulting mixture was cooled down to room temperature, diluted with water and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was evaporated. After, the crude residue was purified by column chromatography on silica gel using mixture of hexane and dichloromethane as eluent. Gained solids in the end, were washed with cold hexane to give pure orange-coloured products.

2,3,5,6-Tetra((*E*)-styryl)pyrazine (4a):

According to the general procedure, compound **4a** was isolated as an orange solid (119 mg, 97 %); mp. = 258 – 259 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 - 7.35 (m, 4H, CH), 7.39 - 7.43 (m, 8H, CH), 7.54 (d, 4H, ^3J = 15.5 Hz, C*H*=CH), 7.66 - 7.68 (m, 8H, CH), 7.96 (d, 4H, ^3J = 15.5 Hz, CH=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.2 (*C*H=CH), 127.4, 128.6, 128.8 (CH), 135.9 (CH=*C*H), 136.8, 145.2 (C). MS (EI, 70 eV): m/z (%) = 488 (M^+, 100), 411 (63), 397 (34), 320 (14), 167 (10), 115 (11), 91 (16). HRMS (EI, 70 eV): calcd. for $C_{36}H_{28}N_2$: 488.22470; found: 488.22372. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3019 (w), 1622 (m), 1493 (m), 1381 (m), 1165 (s), 955 (s), 740 (s), 685 (s), 588 (s), 457 (s). EA: calcd. for $C_{36}H_{28}N_2$ (488.62): C, 88.49; H, 5.78; N, 5.73; found: C, 88.64; H, 5.54; N, 5.71.

2,3,5,6-Tetrakis((*E*)-4-methylstyryl)pyrazine (4b):

According to the general procedure, compound **4b** was isolated as an orange solid (129 mg, 95 %); mp. = 292 – 294 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 12H, CH_3), 7.21 (d, 8H, ^3J = 7.9 Hz, CH), 7.48 (d, 4H, ^3J = 15.5 Hz, C*H*=CH), 7.55 (d, 8H, ^3J = 7.9 Hz, CH), 7.91 (d, 4H, ^3J = 15.5 Hz, CH=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 121.3 (*C*H=CH), 127.3, 129.4 (CH), 134.2 (C), 135.5 (CH=*C*H), 138.6, 145.1 (C). MS (EI, 70 eV): m/z (%) = 544 (M^+, 100), 453 (35), 439 (28), 287 (13), 195 (21), 119 (14), 105 (19), 44 (17), 36 (10). HRMS (EI, 70 eV): calcd. for $C_{40}H_{36}N_2$:

544.28730; found: 544.28748. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2913 (w), 1622 (m), 1508 (m), 1382 (m), 1165 (s), 956 (s), 797 (s), 474 (s). EA: calcd. for $C_{40}H_{36}N_2$ (544.73): C, 88.20; H, 6.66; N, 5.14; found: C, 88.05; H, 6.61; N, 5.07.

2,3,5,6-Tetrakis((*E*)-4-fluorostyryl)pyrazine (4c):

According to the general procedure, compound **4c** was isolated as an orange solid (139 mg, 99 %); mp. = 284 – 286 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.25 - 7.33 (m, 8H, CH), 7.88 (d, 4H, ^3J = 15.5 Hz, C*H*=CH), 7.97 - 8.05 (m, 12H, CH, CH=C*H*). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 115.8 (d, $^2J_{C–F}$ = 21.6 Hz, CH), 121.9 (*C*H=CH), 130.2 (d, $^3J_{C-F}$ = 8.3 Hz, CH), 133.3 (d, $^4J_{C-F}$ = 3.2 Hz, C), 134.5 (CH=*C*H), 144.8 (C), 162.5 (d, $^1J_{C–F}$ = 246.2 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.6 (s, 4F, CF). MS (EI, 70 eV): m/z (%) = 560 (M^+, 100), 465 (38), 451 (19), 356 (10), 109 (16), 69 (11), 44 (13). HRMS (ESI): calcd. for $C_{36}H_{24}F_4N_2$ ($[M+H]^+$): 561.19484; found: 561.19421. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1590 (m), 1503 (s), 1415 (m), 1226 (s), 1153 (s), 1091 (m), 964 (s), 813 (s), 529 (s), 479 (s). EA: calcd. for $C_{36}H_{24}F_4N_2$ (560.58): C, 77.13; H, 4.32; N, 5.00; found: C, 77.44; H, 4.42; N, 4.99.

2,3,5,6-Tetrakis((*E*)-4-methoxystyryl)pyrazine (4d):

According to the general procedure, compound **4d** was isolated as an orange solid (142 mg, 93 %); mp. = 229 – 230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 12H, OCH_3), 6.93 (d, 8H, ^3J = 8.5 Hz, CH), 7.35 (d, 4H, ^3J = 15.5 Hz, C*H*=CH), 7.58 (d, 8H, ^3J = 8.5 Hz, CH), 7.85 (d, 4H, ^3J = 15.5 Hz, CH=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.1(CH), 120.2 (*C*H=CH), 128.7 (CH), 129.8 (C), 134.7 (CH=*C*H), 144.9, 159.9 (C). MS (EI, 70 eV): m/z (%) = 608 (M^+, 100), 501 (34), 487 (18), 227 (18), 121 (74). HRMS (ESI): calcd. for $C_{40}H_{36}N_2O_4$ ($[M+H]^+$): 609.27478; found: 609.27537. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3007 (w), 2929 (w), 2834 (w), 1602 (s), 1573 (m), 1508 (s), 1420 (m), 1245 (s), 1162 (s), 1028 (s), 965 (s), 810 (s), 561 (s).

2,3,5,6-Tetrakis((*E*)-3-methylstyryl)pyrazine (4e):

According to the general procedure, compound **4e** was isolated as an orange solid (96 mg, 70 %); mp. = 200 – 202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 12H, CH_3), 7.16 (d, 4H, ^3J = 7.5 Hz, CH), 7.28 - 7.33 (m, 4H, CH), 7.44 - 7.50 (m, 12H, CH, C*H*=CH), 7.90 (d, 4H, ^3J = 15.5 Hz, CH=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 122.0 (*C*H=CH), 124.5, 128.2, 128.6, 129.4 (CH), 135.8 (CH=*C*H), 136.8, 138.3, 145.2 (C). MS (EI, 70 eV): m/z (%) = 544 (M^+, 100), 453 (43), 439 (27), 195 (12), 119 (10), 105 (15), 44 (12). HRMS (ESI): calcd. for $C_{40}H_{36}N_2$ ($[M+H]^+$): 545.29513; found: 545.29509. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2913 (w), 1623 (m), 1597 (m), 1371 (m), 1232 (m), 1156 (m), 962 (s), 766 (s), 685 (s), 431 (s). EA: calcd. for $C_{40}H_{36}N_2$ (544.73): C, 88.20; H, 6.66; N, 5.14; found: C, 87.99; H, 6.64; N, 5.15.

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Supporting Information

Synthesis of Tetraaryl- and Tetraalkenylpyrazines by Suzuki-Miyaura Reactions of Tetrachloropyrazine

Andranik Petrosyan, Peter Ehlers, Sebastian Reimann, Tariel V. Ghochikyan, Ashot S. Saghyan, Anke Spannenberg, Stefan Lochbrunner, Peter Langer

Contents

1. General Remarks

All reactions were carried out under argon atmosphere. All chemicals are commercially available and were used without further purification.

Column chromatography was performed using Merck Silicagel 60 (0.043 - 0.06 mm).

NMR data were recorded on Bruker ARX 300, Bruker ARX 400 and Fourier 300 spectrometers. ^{13}C and ^{1}H NMR spectra were referenced to signals of deuterated solvent and residual protonated solvent, respectively. Peak characterization: s = singlet, d = doublet, t = triplet, pt = pseudo triplet, q = quartet, sept = septet, m = multiplet, bs = broad singlet, dd = doublet of doublet.

Infrared Spectra were recorded on Nicolet 550 FT – IR spectrometer with ATR sampling technique for solids as well as liquids. Signal characterization: w = weak, m = medium, s = strong.

Gas chromatography-mass analyses were carried out on Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column using helium carrier gas.

ESI HR-MS measurements were performed on an Agilent 1969A TOF mass spectrometer. For High Resolution MS (HRMS) Finnigan MAT 95 XP was used. Only the measurements with an average deviation from the theoretical mass of ± 2mDa were accounted as correct.

Elemental analyses (EA) were performed with a LecoMikroanalysator - TrueSpec CHNS Micro.

Melting points were determined on a Micro-Hot-Stage GalenTM III Cambridge Instruments, and are not corrected.

X-ray crystal structure data were collected on a STOE IPDS II diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[1]

Absorption spectra were measured on an Analytik Jena Specord 50 or Perkin-Elmer UV/Vis spectrometer Lambda2. The fluorescence spectra were recorded with a Fluoromax-4 Spectrofluorometer (Horiba Scientific). For the absorption spectra dichloromethane was used as solvent and a concentration of 5×10^{-6} M was applied for the quantitative determination of

[1] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.

the molar extinction coefficient. A solution of quinine sulphate in 0.05 M sulphuric acid was applied as standard for the measurement of the fluorescence quantum yields ($\varphi_f = 0.52$).[2] Sample and standard were excited with an absorbance of ~ 0.1 in air-equilibrated solution.

[2] Meech, S. R., Phillips, D. *J. Photochem.***1983**, *23*, 193-217

2. General Procedures and Experimental Data

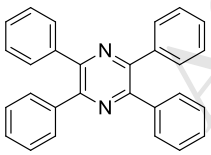
Synthesis of tetraarylpyrazines

Prior to all, solutions of $Pd(OAc)_2$ and $P(Cy)_3$ were prepared in dried and argon filled Schlenk tubes (both 0.0125 mmol, 5 mol%) using 1 mL of extra dry THF and toluene, respectively. Solutions were stirred at room temperature for 10 min.

To an argon-flushed glass pressure tube 50 µL of $Pd(OAc)_2$ solution (0.000625 mmol, 0.25 mol%) was added[3]. After the removal of THF via evacuation of pressure tube, 100µL of earlier prepared solution of $P(Cy)_3$ (0.00125 mmol, 0.5 mol%), **2** (54 mg, 0.25 mmol), the appropriate arylboronic acid (2 mmol, 8.0 equiv.) and K_3PO_4 (2 mmol, 8.0 equiv.) were added, followed by the injection of dry toluene (3.5 mL). The tube was closed with a teflon screw cap and the reaction mixture was stirred at 100 °C for 18 hours. Subsequently, the mixture was cooled down to room temperature and diluted with water and dichloromethane. The aqueous layer was extracted three times with dichloromethane. Combined organic layers were dried over Na_2SO_4 and filtered. Unless otherwise noted, solvent was evaporated and the residue was purified by column chromatography on silica gel using mixture of hexane and dichloromethane as eluent.

2,3,5,6-Tetraphenylpyrazine (3a):

According to the general procedure, compound **3a** was isolated as a white solid (93 mg, 97 %); mp. = 248 – 250 °C.

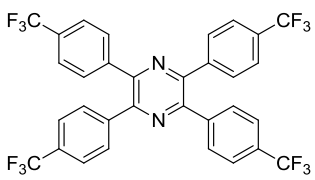


^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 - 7.34 (m, 12H), 7.60 - 7.66 (m, 8H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.2 (CH), 128.5 (CH), 129.8 (CH), 138.4 (C), 148.4 (C). MS (EI, 70 eV): m/z (%) = 384 (M^+, 100), 305 (7), 178 (44), 152 (8), 103 (10). HRMS (ESI): calcd. for $C_{28}H_{21}N_2$ ($[M+H]^+$): 385.16993; found: 385.17036. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3038 (w), 1389 (m), 1170 (m), 1104 (m), 1011 (m), 762 (s), 692 (s), 536 (s).

[3] In cases of compounds **3k-p**, 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$ were used.

2,3,5,6-Tetrakis(4-(trifluoromethyl)phenyl)pyrazine (3b):

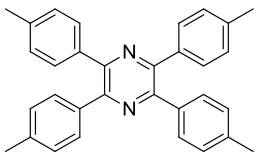
According to the general procedure, compound **3b** was isolated as a white solid (139 mg, 85 %); mp. = 265 – 266 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, 8H, ^{3}J = 8.2 Hz), 7.74 (d, 8H, ^{3}J = 8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.8 (q, $^{1}J_{C–F}$ = 272.3 Hz, CF_3), 125.5 (q, $^{3}J_{C–F}$ = 3.8 Hz, CH), 130.1 (CH), 131.3 (q, $^{2}J_{C–F}$ = 32.6 Hz, C), 140.8 (C), 147.9 (C).^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.3 (s, 12F, CF_3). MS (EI, 70 eV): m/z (%) = 656 (M^+, 100), 637 (15), 587 (14), 314 (77), 295 (15), 264 (10), 225 (7), 171 (7). HRMS (ESI): calcd. for $C_{32}H_{17}F_{12}N_2$([M+H]$^+$): 657.11946; found: 657.1192. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1322 (s), 1167 (m), 1105 (s), 1011 (m), 849 (s), 631 (m), 535 (m). EA: calcd. for $C_{32}H_{16}F_{12}N_2$ (656.46): C, 58.55; H, 2.46; N, 4.27; found: C, 57.92; H, 2.32; N, 4.23.

2,3,5,6-Tetra-*p*-tolylpyrazine (3c):

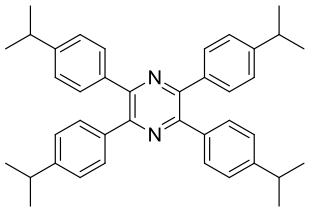
According to the general procedure, compound **3c** was isolated as a white solid (103 mg, 93 %); mp. = 284 – 286 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 12H, CH_3), 7.09 - 7.13 (m, 8H), 7.52 - 7.56 (m, 8H).^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 128.9 (CH), 129.6 (CH), 135.8 (C), 138.3 (C), 147.7 (C). MS (EI, 70 eV): m/z (%) = 440 (M^+, 100), 425 (10), 206 (19), 189 (8). HRMS (ESI): calcd. for $C_{32}H_{29}N_2$ ([M+H]$^+$): 441.23253; found: 441.23245. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2917 (w), 1385 (s), 1172 (m), 1096 (m), 1009 (m), 820 (s), 728 (s), 626 (m), 530 (s), 513 (s).

2,3,5,6-Tetrakis(4-isopropylphenyl)pyrazine (3d):

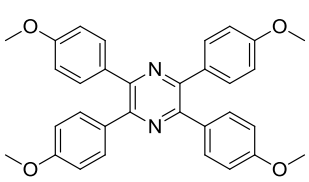
According to the general procedure, compound **3d** was isolated as yellowish-white solid (133 mg, 96 %); mp. = 279 – 281 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (d, 24H, ^{3}J = 6.9 Hz, CH_3), 2.90 (sept, 4H, ^{3}J = 6.9 Hz, C$H_{i\text{-Pr}}$), 7.13 - 7.17 (m, 8H), 7.56 - 7.60 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8 (CH_3), 33.8 (*C* $H_{i\text{-Pr}}$), 126.2 (CH), 129.7 (CH), 136.1 (C), 147.5 (C), 149.2 (C). MS (EI, 70 eV): m/z (%) = 552 (M^+, 100), 537 (11), 509 (7). HRMS (ESI): calcd. for $C_{40}H_{45}N_2$ ($[M+H]^+$): 553.35773; found: 553.35861. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2959 (m), 2926 (w), 2866 (w), 1388 (s), 1181 (m), 1098 (m), 1006 (m), 839 (s), 632 (m), 552 (s).

2,3,5,6-Tetrakis(4-methoxyphenyl)pyrazine (3e):

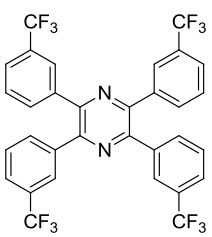
According to the general procedure, compound **3e** was isolated as a light brown solid (113 mg, 90 %); mp. = 278 – 280 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 12H, OCH_3), 6.81 - 6.86 (m, 8H), 7.56 - 7.61 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 113.6 (CH), 131.0 (CH), 131.2 (C), 146.8 (C), 159.8 (C). MS (EI, 70 eV): m/z (%) = 504 (M^+, 100), 252 (12), 238 (15), 223 (34), 195 (10), 152 (12), 133 (11). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2O_4$: 504.20436; found: 504.20469. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2926 (w), 2834 (w), 1602 (s), 1573 (m), 1511 (s), 1418 (m), 1381 (s), 1295 (s), 1244 (s), 1164 (s), 1027 (s), 830 (s), 796 (s), 740 (m), 529 (s).

2,3,5,6-Tetrakis(3-(trifluoromethyl)phenyl)pyrazine (3f):

According to the general procedure, compound **3f** was isolated as a white solid (157 mg, 96 %); mp. = 165 – 167 °C.

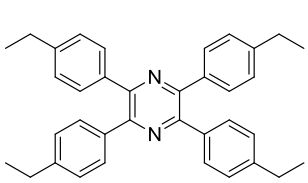


^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (pt, 4H, ^{3}J = 7.8 Hz), 7.65 (d, 4H, ^{3}J = 7.8 Hz), 7.75 (d, 4H, ^{3}J = 7.8 Hz), 7.86 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.6 (q, $^{1}J_{C–F}$ = 271.9 Hz, CF_3), 125.9 (q, $^{3}J_{C–F}$ = 3.6 Hz, CH), 126.7 (q, $^{3}J_{C–F}$ = 3.8 Hz, CH), 129.1 (CH), 131.1 (q, $^{2}J_{C–F}$ = 32.6 Hz, C), 133.0 (CH), 138.0 (C), 148.1 (C).

^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.5 (s, 12F, CF_3). MS (EI, 70 eV): m/z (%) = 656 (M^+, 100), 637 (12), 314 (99), 295 (10), 264 (7), 225 (11), 171 (17). HRMS (EI, 70 eV): calcd. for $C_{32}H_{16}F_{12}N_2$: 656.11164; found: 656.11102. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1323 (s), 1280 (m), 1164 (s), 1127 (s), 1069 (s), 908 (m), 801 (m), 700 (s). EA: calcd. for $C_{32}H_{16}F_{12}N_2$ (656.46): C, 58.55; H, 2.46; N, 4.27; found: C, 58.85; H, 2.28; N, 4.35.

2,3,5,6-Tetrakis(4-ethylphenyl)pyrazine (3g):

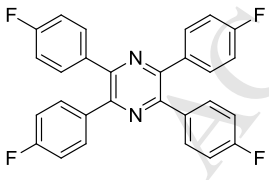
According to the general procedure, compound **3g** was isolated as a white solid (108 mg, 87 %); mp. = 235 – 236 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, 12H, ^3J = 7.5 Hz, CH_3), 2.65 (q, 8H, ^3J = 7.5 Hz, CH_2), 7.12 - 7.14 (m, 8H), 7.55 - 7.59 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 28.6 (CH_2), 127.7 (CH), 129.7 (CH), 136.0 (C), 144.6 (C), 147.6 (C). MS (EI, 70 eV): m/z (%) = 496 (M^+, 100), 467 (12), 219 (28), 204 (14), 116 (11). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2$: 496.28730; found: 496.28760. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2961 (m), 2929 (w), 2870 (w), 1387 (s), 1180 (s), 1097 (m), 1007 (m), 632 (m), 536 (m). EA: calcd. for $C_{36}H_{36}N_2$ (496.68): C, 87.05; H, 7.31; N, 5.64; found: C, 86.96; H, 7.31; N, 5.63.

2,3,5,6-Tetrakis(4-fluorophenyl)pyrazine (3h):

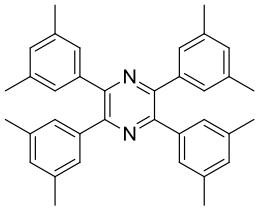
According to the general procedure, compound **3h** was isolated as a white solid (113 mg, 99 %); mp. = 233 – 234 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 - 7.05 (m, 8H), 7.54 - 7.61 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.4 (d, $^2J_{C–F}$ = 21.8 Hz, CH), 131.6 (d, $^3J_{C-F}$ = 8.3 Hz, CH), 134.0 (d, $^4J_{C-F}$ = 3.2 Hz, C), 147.3 (C), 163.1 (d, $^1J_{C–F}$ = 250.1 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.7 (s, 4F, CF). MS (EI, 70 eV): m/z (%) = 456 (M^+, 100), 359 (6), 214 (36). HRMS (EI, 70 eV): calcd. for $C_{28}H_{16}F_4N_2$: 456.12441; found: 456.12366.IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1602 (s), 1510 (s), 1415 (m), 1384 (s), 1226 (s), 1152 (s), 1108 (m), 1011 (m), 839 (s), 735 (m), 617 (m), 526 (s). EA: calcd. for $C_{28}H_{16}F_4N_2$ (456.43): C, 73.68; H, 3.53; N, 6.14; found: C, 73.64; H, 3.33; N, 6.09.

2,3,5,6-Tetrakis(3,5-dimethylphenyl)pyrazine (3i):

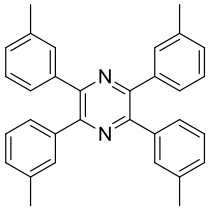
According to the general procedure, compound **3i** was isolated as a white solid (101 mg, 81 %); mp. = 275 – 277 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 24H, CH_3), 6.94 (bs, 4H), 7.19 (bs, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 127.6 (CH), 129.9 (CH), 137.3 (C), 138.5 (C), 148.8 (C). MS (EI, 70 eV): m/z (%) = 496 (M^+, 100), 248 (10), 133 (22). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2$: 496.28730; found: 496.28686. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3025 (w), 2912 (m), 2855 (w), 1600 (m), 1391 (s), 1374 (s), 1187 (m), 1154 (m), 855 (s), 843 (s), 691 (s), 424 (m). EA: calcd. for $C_{36}H_{36}N_2$ (496.68): C, 87.05; H, 7.31; N, 5.64; found: C, 86.89; H, 7.44; N, 5.39.

2,3,5,6-Tetra-*m*-tolylpyrazine (3j):

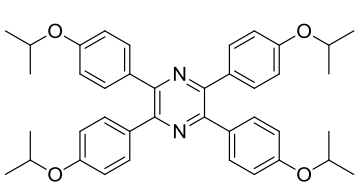
According to the general procedure, compound **3j** was isolated as a white solid (104 mg, 94 %); mp. = 153 – 154 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 12H, CH_3), 7.13 - 7.16 (m, 8H), 7.28 - 7.32 (m, 4H), 7.55 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 127.0 (CH), 127.8 (CH), 129.2 (CH), 130.4 (CH), 137.8 (C), 138.5 (C), 148.6 (C). MS (EI, 70 eV): m/z (%) = 440 (M^+, 100), 425 (12), 384 (26), 258 (16), 206 (11), 102 (17), 69 (13), 57 (13). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2$: 440.22470; found: 440.22433. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3034 (w), 2915 (w), 1371 (m), 1167 (m), 847 (m), 778 (s), 704 (s), 471 (s), 447 (m). EA: calcd. for $C_{32}H_{28}N_2$ (440.58): C, 87.24; H, 6.41; N, 6.36; found: C, 87.30; H, 6.36; N, 6.32.

2,3,5,6-Tetrakis(4-isopropoxyphenyl)pyrazine (3k):

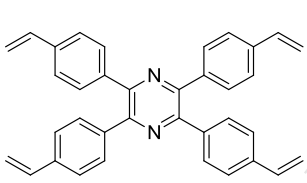
In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3k** was isolated as a white solid (142 mg, 92 %); mp. = 241 – 243 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, 24H, ^3J = 6.1 Hz, CH_3), 4.55 (sept, 4H, ^3J = 6.1 Hz, C$H_{i\text{-Pr}}$), 6.79 - 6.82 (m, 8H), 7.55 - 7.59 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (CH_3), 69.7 (*C* $H_{i\text{-Pr}}$), 115.3 (CH), 131.0 (CH), 131.0 (C), 146.7 (C), 158.1 (C). MS (EI, 70 eV): m/z (%) = 616 (M^+, 100), 574 (13), 447 (37), 224 (12), 210 (16), 57 (14), 43 (14). HRMS (EI, 70 eV): calcd. for $C_{40}H_{44}N_2O_4$: 616.32956; found: 616.32852. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2974 (m), 2923 (w), 1603 (s), 1510 (s), 1382 (s), 1287 (m), 1240 (s), 1163 (s), 1116 (s), 948 (s), 834 (s), 742 (m), 742 (m), 623 (m), 536 (s).

2,3,5,6-Tetrakis(4-vinylphenyl)pyrazine (3l):

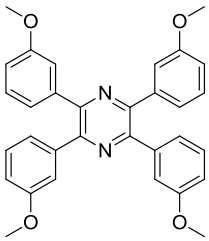
In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3l** was isolated as a yellowish-white solid (93 mg, 76 %); mp. > 375 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.27 (dd, 4H, $^3J_{cis}$ = 10.9 Hz, $^2J_{gem}$ = 0.7 Hz, CH=CH_{cis}-H), 5.77 (dd, 4H, $^3J_{trans}$ = 17.5 Hz, $^2J_{gem}$ = 0.7 Hz, CH=CH-H_{trans}), 6.71 (dd, 4H, $^3J_{trans}$ = 17.5 Hz, $^3J_{cis}$ = 10.9 Hz, C*H*=CH_2), 7.34 - 7.38 (m, 8H), 7.60 - 7.64 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 114.5 (CH), 126.1 (CH), 130.0 (CH), 136.3 (CH), 137.7 (C), 137.8 (C), 147.5 (C). MS (EI, 70 eV): m/z (%) = 488 (M^+, 100), 461 (4), 230 (17), 202 (5), 71 (4). HRMS (EI, 70 eV): calcd. for $C_{36}H_{28}N_2$: 488.22470; found: 488.22447. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2950 (w), 2917 (w), 2851 (w), 1627 (m), 1388 (s), 1174 (m), 1101 (m), 987 (s), 901 (s), 845 (s), 534 (s).

2,3,5,6-Tetrakis(3-methoxyphenyl)pyrazine (3m):

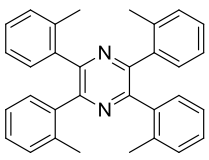
In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3m** was isolated as a light brown solid (125 mg, 99 %); mp. = 170 – 172 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 12H, OCH_3), 6.85 - 6.89 (m, 4H), 7.15 - 7.22 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 114.8 (2 x CH), 122.4 (CH), 129.2 (CH), 139.6 (C), 148.2 (C), 159.2 (C). MS (EI, 70 eV): m/z (%) = 504 (M^+, 100), 262 (12), 207 (9), 188 (16), 145 (14), 117 (10), 73 (10). 60 (12), 43 (15). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2O_4$: 504.20436; found: 504.20339. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3006 (w), 2921 (m), 2853 (w), 1578 (s), 1424 (m), 1377 (s), 1290 (m), 1229 (s), 1028 (s), 775 (s), 719 (s). EA: calcd. for $C_{32}H_{28}N_2O_4$ (504.58): C, 76.17; H, 5.59; N, 5.55; found: C, 76.49; H, 5.50; N, 5.42.

2,3,5,6-Tetra-*o*-tolylpyrazine (3n):

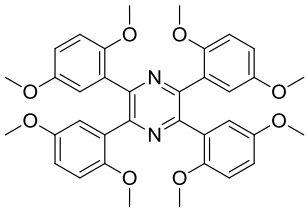
In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3n** was isolated as a white solid (109 mg, 99 %); mp. = 252 – 254 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 12H, CH_3), 6.99 - 7.06 (m, 4H), 7.08 - 7.15 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1 (CH_3), 125.2 (CH), 128.2 (CH), 130.2 (CH), 130.4 (CH), 136.2 (C), 137.7 (C), 151.6 (C). MS (EI, 70 eV): m/z (%) = 440 (M^+, 100), 425 (60), 349 (16), 205 (12), 73 (16), 60 (17), 43 (14). HRMS (EI, 70 eV): calcd. for $C_{32}H_{28}N_2$: 440.22470; found: 440.22351. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3016 (w), 2921 (w), 2852 (w), 1382 (s), 1081 (m), 1016 (m), 757 (s), 723 (s), 460 (s). EA: calcd. for $C_{32}H_{28}N_2$ (440.58): C, 87.24; H, 6.41; N, 6.36; found: C, 87.47; H, 6.69; N, 6.20.

2,3,5,6-Tetrakis(2,5-dimethoxyphenyl)pyrazine (3o):

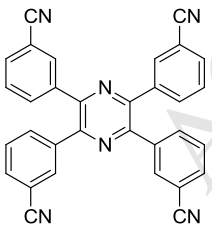
Reaction was made according to the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$. After combined organic layers were dried over sodium sulphate, filtered and solvent was removed, compound **3o** was isolated as a white solid by recrystallization of crude mixture from warm dichloromethane. (116 mg, 74 %); mp. = 260 – 262 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36 (s, 12H, OCH_3), 3.70 (s, 12H, OCH_3), 6.64 (d, 4H, ^3J = 8.9 Hz), 6.77 (dd, 4H, ^3J = 8.9 Hz, ^4J = 3.0 Hz), 7.05 (d, ^4J = 3.0 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 55.8 (OCH_3), 111.9 (CH), 115.3 (CH), 116.6 (CH), 129.4 (C), 149.4 (C), 150.8 (C), 153.3 (C). MS (EI, 70 eV): m/z (%) = 624 (M^+, 100), 609 (45), 593 (71), 579 (12), 487 (23), 312 (11), 60 (10). HRMS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2O_8$: 624.24662; found: 624.24559. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3002 (w), 2960 (w), 2833 (w), 1499 (s), 1447 (m), 1424 (s), 1275 (s), 1229 (s), 1079 (m), 1042 (s), 1016 (s), 873 (m), 802 (s). EA: calcd. for $C_{36}H_{36}N_2O_8$ (624.68): C, 69.22; H, 5.81; N, 4.48; found: C, 69.58; H, 5.74; N, 4.66.

2,3,5,6-Tetrakis(3-cyanophenyl)pyrazine (3p):

In agreement with the general procedure, but with 2 mol% (1.1 mg) of $Pd(OAc)_2$ and 4 mol% (2.8mg) of $P(Cy)_3$, compound **3p** was isolated as a white solid (61 mg, 50 %); mp. = 296 – 297 °C.



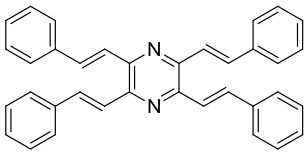
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (pt, 4H, ^3J = 7.8 Hz), 7.70 - 7.76 (m, 8H), 7.96 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 113.4 (C), 117.9 (C), 129.6 (CH), 133.1 (CH), 133.2 (CH), 133.8 (CH), 138.0 (C), 147.2 (C). MS (EI, 70 eV): m/z (%) = 484 (M^+, 100), 380 (7), 355 (5), 228 (38), 201 (8), 60 (5), 44 (5). HRMS (EI, 70 eV): calcd. for $C_{32}H_{16}N_6$: 484.14310; found: 484.14195. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 2953 (w), 2227 (m), 1371 (m), 1164 (m), 917 (m), 799 (s), 697 (s), 515 (m).

Synthesis of tetraalkenylpyrazines

An argon-flushed glass pressure tube was charged with $Pd(dba)_2$ (0.005 mmol, 2 mol%), Cata*CX*ium A (0.01 mmol, 4 mol%), **2** (54.4 mg, 0.25 mmol), the appropriate alkenylboronic acid or pinacol ester (2 mmol, 8.0 eq.), K_3PO_4 (2 mmol, 8.0 eq.) and anhydrous 1,4-dioxane (4 mL). The tube was sealed with a teflon cap and the reaction mixture was stirred at 100 °C for 20 hours. Resulting mixture was cooled down to room temperature, diluted with water and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was evaporated. After, the crude residue was purified by column chromatography on silica gel using mixture of hexane and dichloromethane as eluent. Gained solids in the end, were washed with cold hexane to give pure orange-coloured products.

2,3,5,6-Tetra((*E*)-styryl)pyrazine (4a):

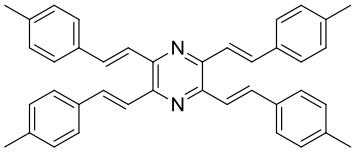
According to the general procedure, compound **4a** was isolated as an orange solid (119 mg, 97 %); mp. = 258 – 259 °C.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 - 7.35 (m, 4H, CH), 7.39 - 7.43 (m, 8H, CH), 7.54 (d, 4H, ^3J = 15.5 Hz, C*H*=CH), 7.66 - 7.68 (m, 8H, CH), 7.96 (d, 4H, ^3J = 15.5 Hz, CH=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.2 (*C*H=CH), 127.4, 128.6, 128.8 (CH), 135.9 (CH=*C*H), 136.8, 145.2 (C). MS (EI, 70 eV): m/z (%) = 488 (M^+, 100), 411 (63), 397 (34), 320 (14), 167 (10), 115 (11), 91 (16). HRMS (EI, 70 eV): calcd. for $C_{36}H_{28}N_2$: 488.22470; found: 488.22372. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3019 (w), 1622 (m), 1493 (m), 1381 (m), 1165 (s), 955 (s), 740 (s), 685 (s), 588 (s), 457 (s). EA: calcd. for $C_{36}H_{28}N_2$ (488.62): C, 88.49; H, 5.78; N, 5.73; found: C, 88.64; H, 5.54; N, 5.71.

2,3,5,6-Tetrakis((*E*)-4-methylstyryl)pyrazine (4b):

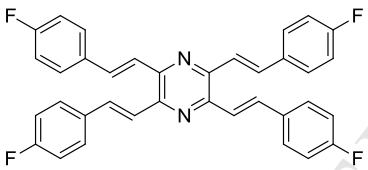
According to the general procedure, compound **4b** was isolated as an orange solid (129 mg, 95 %); mp. = 292 – 294 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 12H, CH_3), 7.21 (d, 8H, ^{3}J = 7.9 Hz, CH), 7.48 (d, 4H, ^{3}J = 15.5 Hz, C*H*=CH), 7.55 (d, 8H, ^{3}J = 7.9 Hz, CH), 7.91 (d, 4H, ^{3}J = 15.5 Hz, CH=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 121.3 (*C*H=CH), 127.3, 129.4 (CH), 134.2 (C), 135.5 (CH=*C*H), 138.6, 145.1 (C). MS (EI, 70 eV): m/z (%) = 544 (M^+, 100), 453 (35), 439 (28), 287 (13), 195 (21), 119 (14), 105 (19), 44 (17), 36 (10). HRMS (EI, 70 eV): calcd. for $C_{40}H_{36}N_2$: 544.28730; found: 544.28748. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2913 (w), 1622 (m), 1508 (m), 1382 (m), 1165 (s), 956 (s), 797 (s), 474 (s). EA: calcd. for $C_{40}H_{36}N_2$ (544.73): C, 88.20; H, 6.66; N, 5.14; found: C, 88.05; H, 6.61; N, 5.07.

2,3,5,6-Tetrakis((*E*)-4-fluorostyryl)pyrazine (4c):

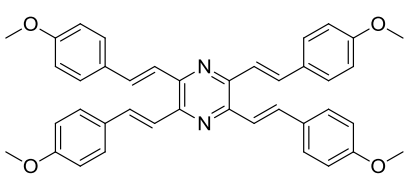
According to the general procedure, compound **4c** was isolated as an orange solid (139 mg, 99 %); mp. = 284 – 286 °C.



^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.25 - 7.33 (m, 8H, CH), 7.88 (d, 4H, ^{3}J = 15.5 Hz, C*H*=CH), 7.97 - 8.05 (m, 12H, CH, CH=C*H*). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 115.8 (d, $^{2}J_{C–F}$ = 21.6 Hz, CH), 121.9 (*C*H=CH), 130.2 (d, $^{3}J_{C-F}$ = 8.3 Hz, CH), 133.3 (d, $^{4}J_{C-F}$ = 3.2 Hz, C), 134.5 (CH=*C*H), 144.8 (C), 162.5 (d, $^{1}J_{C–F}$ = 246.2 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.6 (s, 4F, CF). MS (EI, 70 eV): m/z (%) = 560 (M^+, 100), 465 (38), 451 (19), 356 (10), 109 (16), 69 (11), 44 (13). HRMS (ESI): calcd. for $C_{36}H_{24}F_4N_2$ ($[M+H]^+$): 561.19484; found: 561.19421. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1590 (m), 1503 (s), 1415 (m), 1226 (s), 1153 (s), 1091 (m), 964 (s), 813 (s), 529 (s), 479 (s). EA: calcd. for $C_{36}H_{24}F_4N_2$ (560.58): C, 77.13; H, 4.32; N, 5.00; found: C, 77.44; H, 4.42; N, 4.99.

2,3,5,6-Tetrakis((*E*)-4-methoxystyryl)pyrazine (4d):

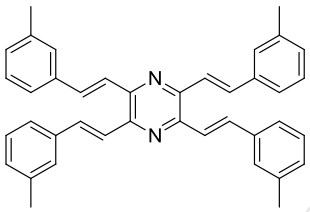
According to the general procedure, compound **4d** was isolated as an orange solid (142 mg, 93 %); mp. = 229 – 230 °C.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 12H, OCH_3), 6.93 (d, 8H, ^{3}J = 8.5 Hz, CH), 7.35 (d, 4H, ^{3}J = 15.5 Hz, C*H*=CH), 7.58 (d, 8H, ^{3}J = 8.5 Hz, CH), 7.85 (d, 4H, ^{3}J = 15.5 Hz, CH=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.1(CH), 120.2 (*C*H=CH), 128.7 (CH), 129.8 (C), 134.7 (CH=*C*H), 144.9, 159.9 (C). MS (EI, 70 eV): m/z (%) = 608 (M^+, 100), 501 (34), 487 (18), 227 (18), 121 (74). HRMS (ESI): calcd. for $C_{40}H_{36}N_2O_4$ ($[M+H]^+$): 609.27478; found: 609.27537. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3007 (w), 2929 (w), 2834 (w), 1602 (s), 1573 (m), 1508 (s), 1420 (m), 1245 (s), 1162 (s), 1028 (s), 965 (s), 810 (s), 561 (s).

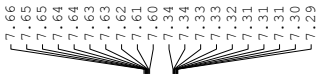
2,3,5,6-Tetrakis((*E*)-3-methylstyryl)pyrazine (4e):

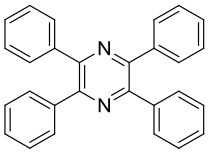
According to the general procedure, compound **4e** was isolated as an orange solid (96 mg, 70 %); mp. = 200 – 202 °C.

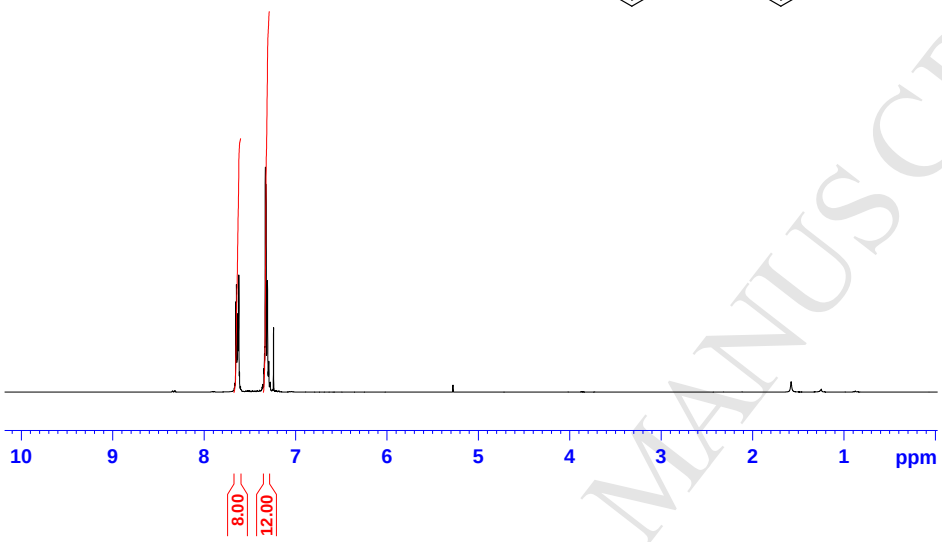


^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 12H, CH_3), 7.16 (d, 4H, ^{3}J = 7.5 Hz, CH), 7.28 - 7.33 (m, 4H, CH), 7.44 - 7.50 (m, 12H, CH, C*H*=CH), 7.90 (d, 4H, ^{3}J = 15.5 Hz, CH=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 122.0 (*C*H=CH), 124.5, 128.2, 128.6, 129.4 (CH), 135.8 (CH=*C*H), 136.8, 138.3, 145.2 (C). MS (EI, 70 eV): m/z (%) = 544 (M^+, 100), 453 (43), 439 (27), 195 (12), 119 (10), 105 (15), 44 (12). HRMS (ESI): calcd. for $C_{40}H_{36}N_2$ ($[M+H]^+$): 545.29513; found: 545.29509. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2913 (w), 1623 (m), 1597 (m), 1371 (m), 1232 (m), 1156 (m), 962 (s), 766 (s), 685 (s), 431 (s). EA: calcd. for $C_{40}H_{36}N_2$ (544.73): C, 88.20; H, 6.66; N, 5.14; found: C, 87.99; H, 6.64; N, 5.15.

3. ^{1}H- and ^{13}C-NMR spectra







BRUKER

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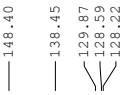

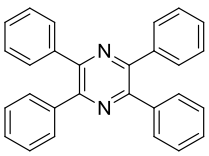

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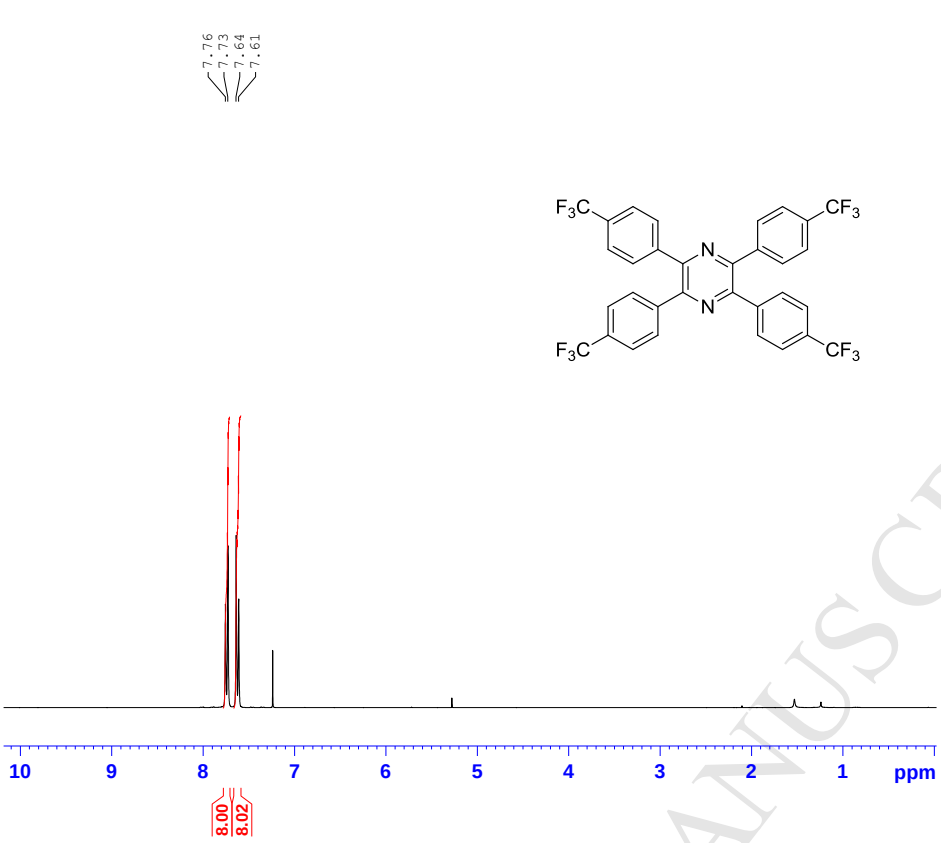
INSTRUM              AV300
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              21097.047 Hz
FIDRES               0.643831 Hz
AQ                0.7766016 sec
RG                   32768
DW                  23.700 usec
DE                   6.00 usec
TE                  296.9 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                      1
SFO1          75.4771825 MHz
NUC1                   13C
P1                   9.60 usec
PLW1          -1.00000000 W
SFO2          300.1312005 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2              100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                   32768
SF            75.4677540 MHz
WDW                     EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

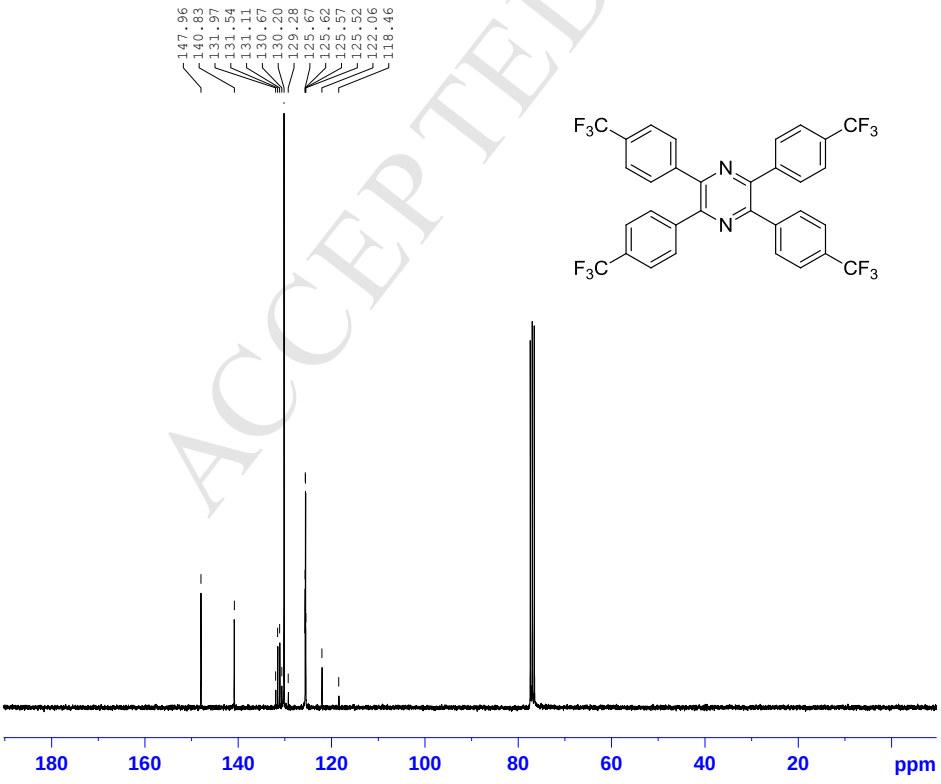



```
Current Data Parameters
NAME                  AP-147
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120809
Time                  22.56
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    296.2 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1        0 dB
SFO1           300.1318534 MHz

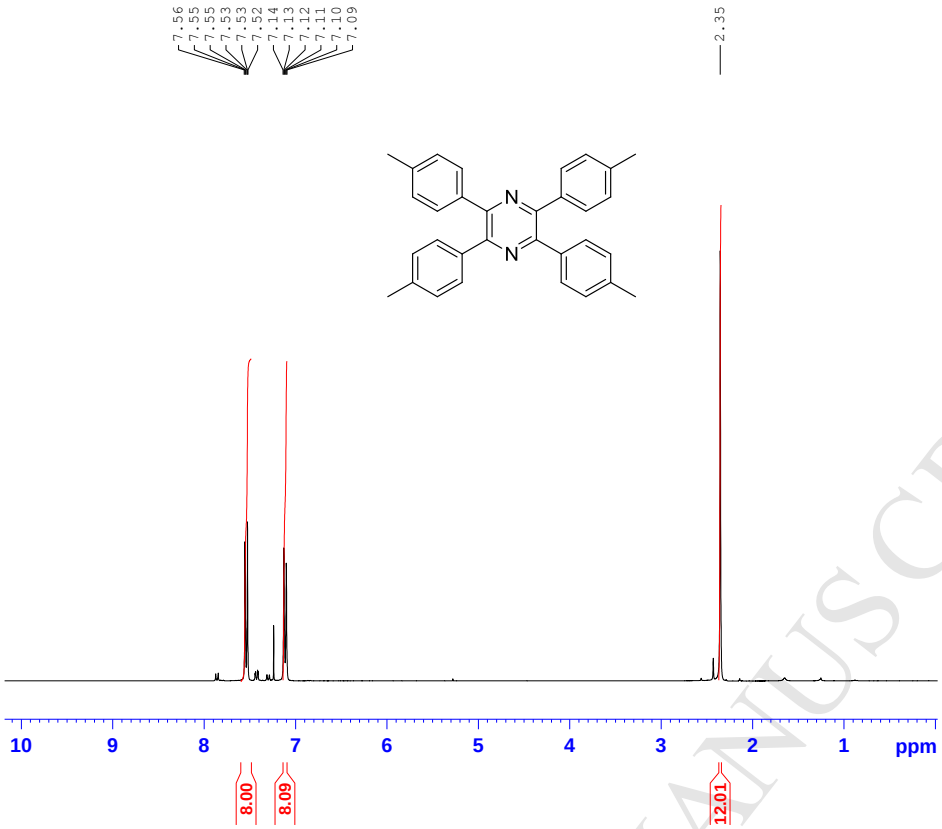
F2 - Processing parameters
SI                    32768
SF             300.1300215 MHz
WDW                      EM
SSB        0
LB                     0.10 Hz
GB         0
PC                     1.00
```




```
Current Data Parameters
NAME                  AP-147
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120814
Time                  13.13
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    32768
SOLVENT               CDCl3
NS                     2000
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                    32768
DW                    23.700 usec
DE                     6.00 usec
TE                    296.4 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1
SFO1           75.4771825 MHz
NUC1                      13C
P1                     9.60 usec
PLW1              -1.00000000 W
SFO2           300.1312005 MHz
NUC2                      1H
CPDPRG[2           waltz16
PCPD2                100.00 usec
PLW2              -1.00000000 W
PLW12             -1.00000000 W
PLW13             -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4677522 MHz
WDW                      EM
SSB        0
LB                     1.00 Hz
GB         0
PC                     1.40
```

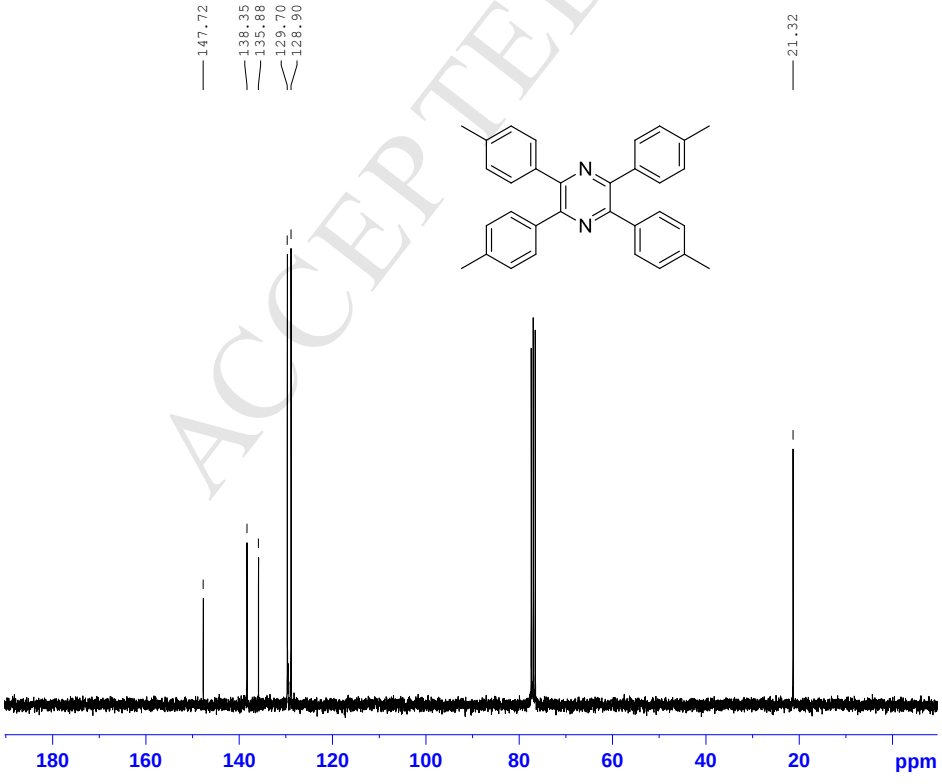


Current Data Parameters
NAME AP-148
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120809
Time 20.04
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542079 sec
RG 322.5
DW 81.000 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0 dB
SFO1 300.1318534 MHz

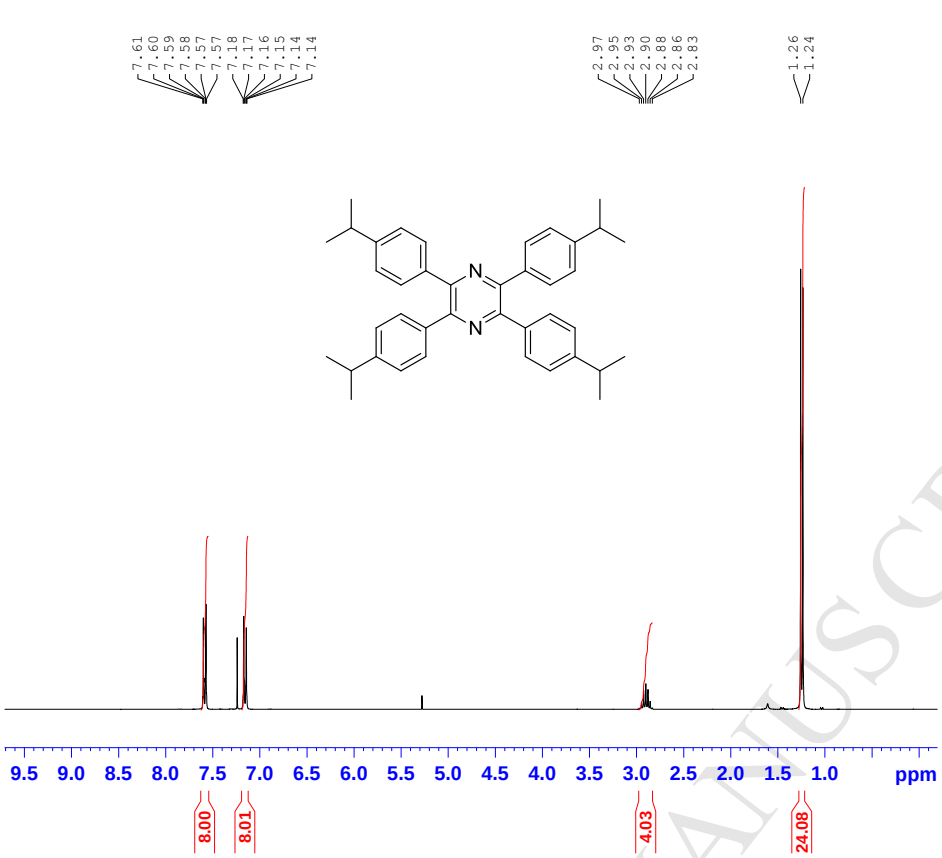
F2 - Processing parameters
SI 32768
SF 300.1300214 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AP-148
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120809
Time 22.39
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 21097.047 Hz
FIDRES 0.643831 Hz
AQ 0.7766016 sec
RG 32768
DW 23.700 usec
DE 6.00 usec
TE 296.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4771825 MHz
NUC1 13C
P1 9.60 usec
PLW1 -1.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 75.4677541 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



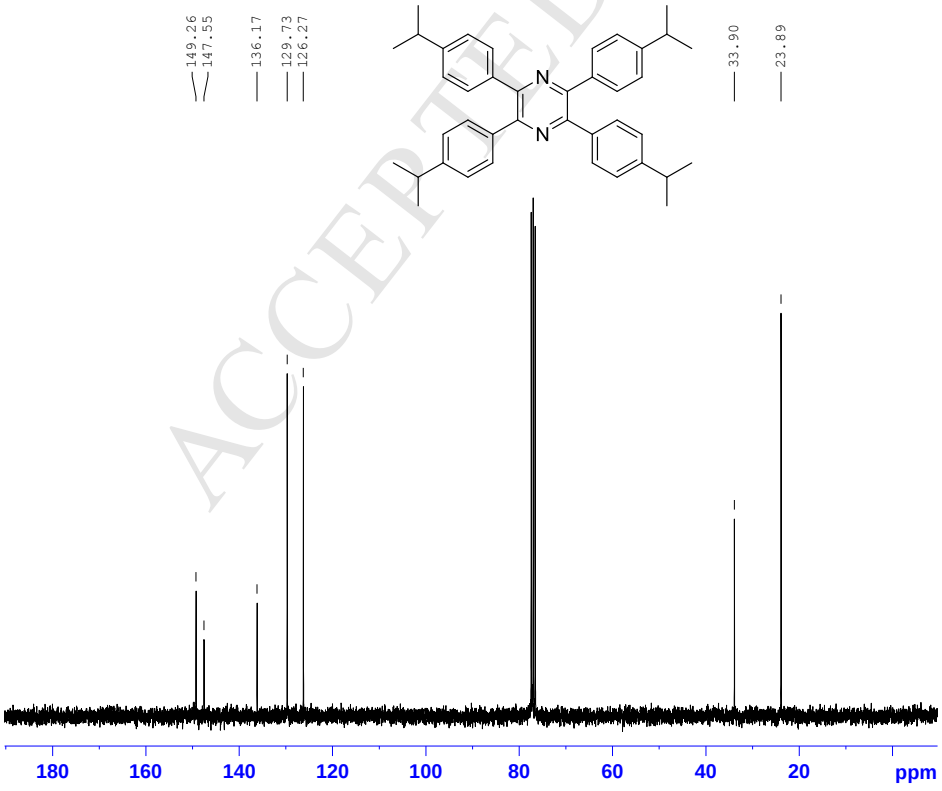
BRUKER

```
Current Data Parameters
NAME                  AP-149
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120809
Time                  23.27
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    296.3 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.00 usec
PL1        0 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF             300.1300214 MHz
WDW                      EM
SSB        0
LB                     0.10 Hz
GB         0
PC                     1.00
```

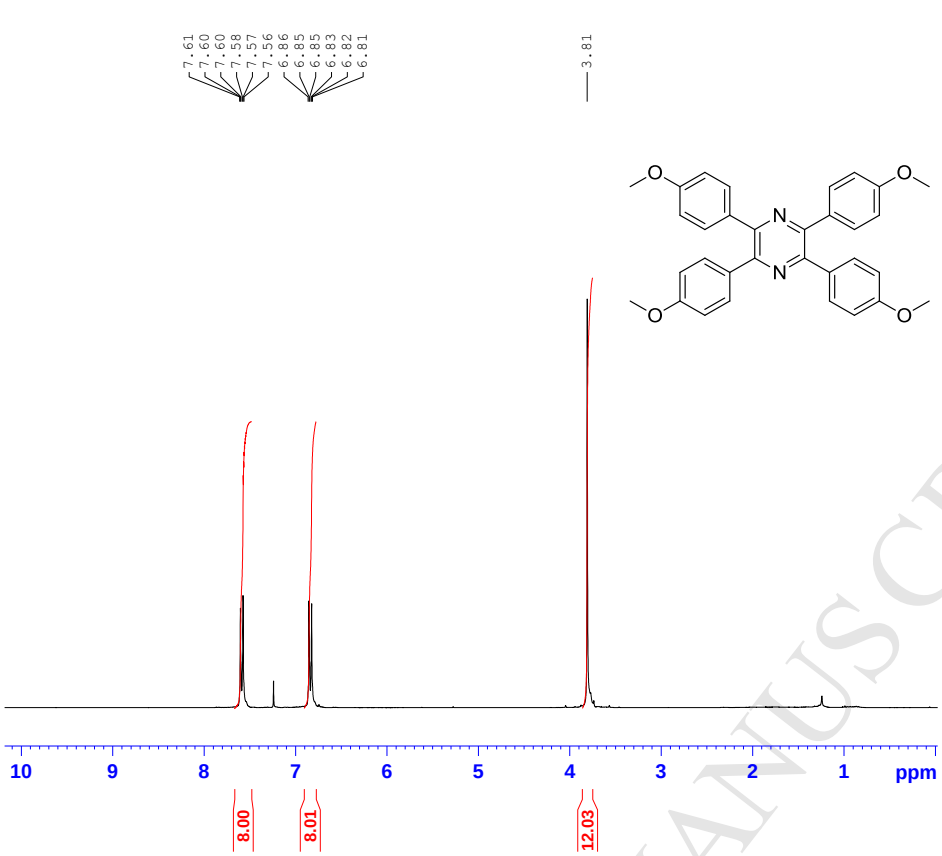


BRUKER

```
Current Data Parameters
NAME                  AP-149
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120809
Time                  23.40
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                    32768
DW                    23.700 usec
DE                     6.00 usec
TE                    296.8 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1
SFO1           75.4771825 MHz
NUC1                    13C
P1                     9.60 usec
PLW1          -1.00000000 W
SFO2          300.1312005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4677528 MHz
WDW                      EM
SSB        0
LB                     1.00 Hz
GB         0
PC                     1.40
```

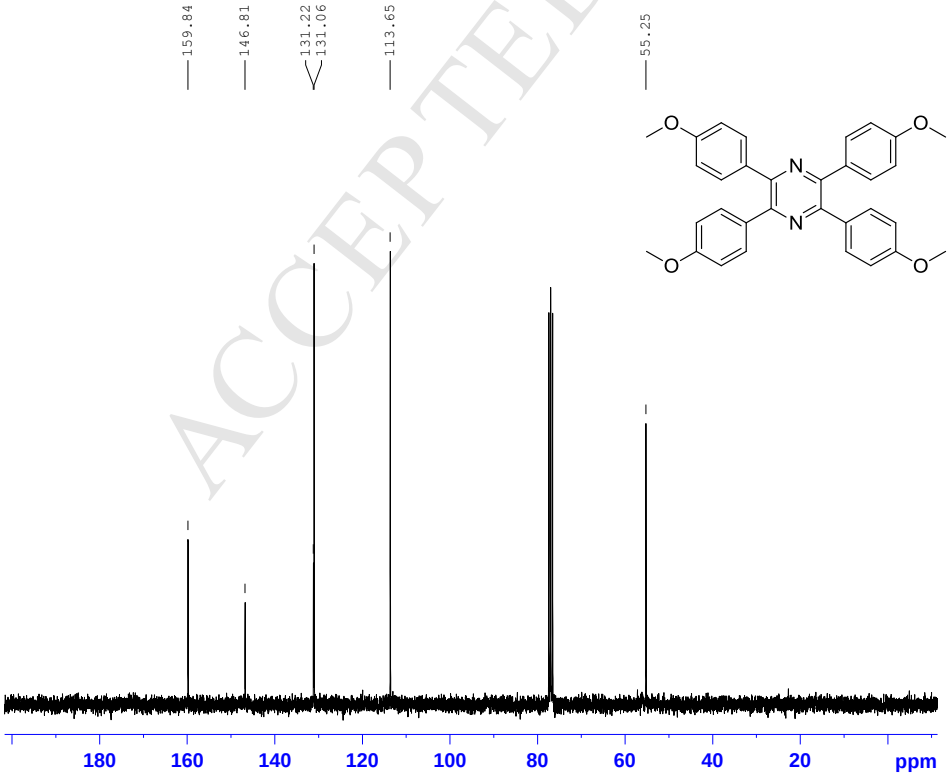



```
Current Data Parameters
NAME                  AP-151
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120816
Time                   4.01
INSTRUM              AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    295.6 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.00 usec
PL1        0 dB
SFO1           300.1318534 MHz

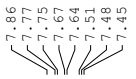
F2 - Processing parameters
SI                    32768
SF             300.1300216 MHz
WDW                      EM
SSB          0
LB                     0.10 Hz
GB           0
PC                     1.00
```

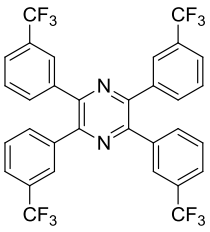


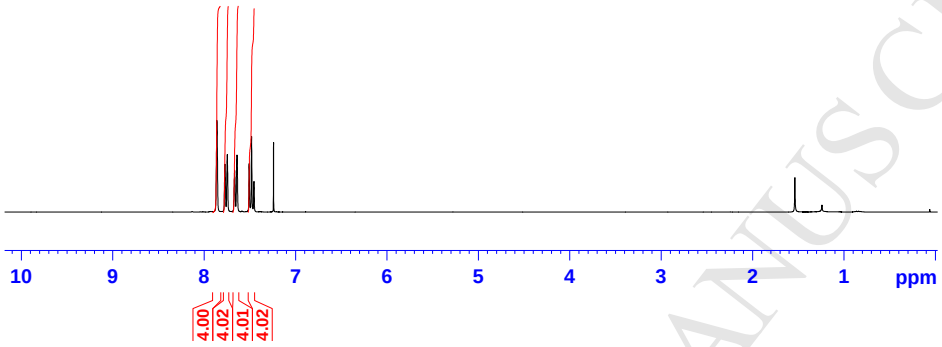

```
Current Data Parameters
NAME                  AP-151
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120816
Time                   4.14
INSTRUM              AV300
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                     32768
DW                    23.700 usec
DE                     6.00 usec
TE                    296.1 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1
SFO1           75.4771825 MHz
NUC1                     13C
P1                     9.60 usec
PLW1          -1.00000000 W
SFO2          300.1312005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4677541 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```





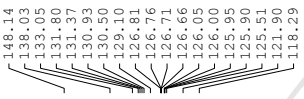


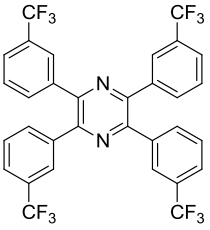
Current Data Parameters
NAME AP-155
EXPNO 10
PROCNO 1

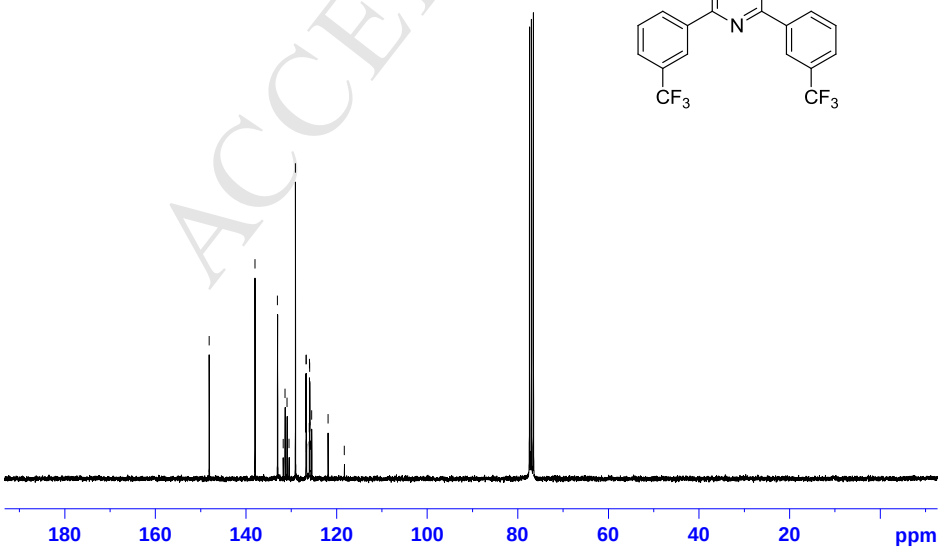
F2 - Acquisition Parameters
Date_ 20120817
Time 21.36
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542079 sec
RG 322.5
DW 81.000 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300214 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



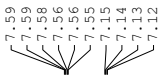


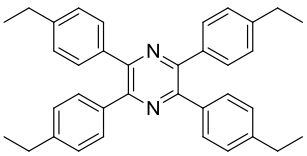


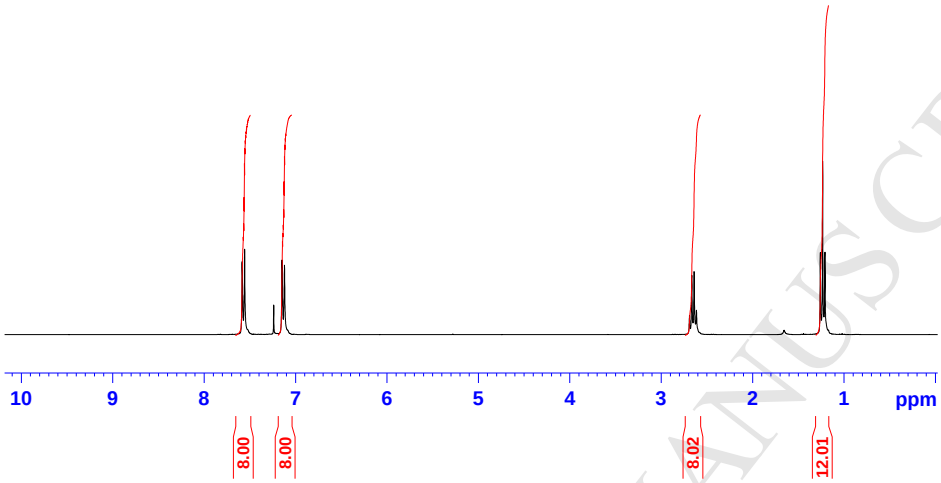
Current Data Parameters
NAME AP-155
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120817
Time 23.58
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3000
DS 4
SWH 21097.047 Hz
FIDRES 0.643831 Hz
AQ 0.7766016 sec
RG 32768
DW 23.700 usec
DE 6.00 usec
TE 296.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4771825 MHz
NUC1 13C
P1 9.60 usec
PLW1 -1.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 75.4677522 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





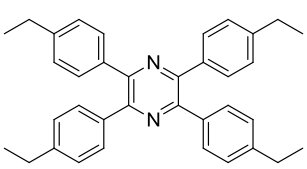



```
Current Data Parameters
NAME                  AP-156
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20120816
Time                    4.31
INSTRUM                AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    295.6 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 usec
PL1        0 dB
SFO1           300.1318534 MHz

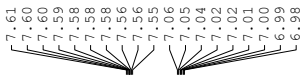
F2 - Processing parameters
SI                    32768
SF             300.1300215 MHz
WDW                      EM
SSB        0
LB                     0.10 Hz
GB         0
PC                     1.00
```

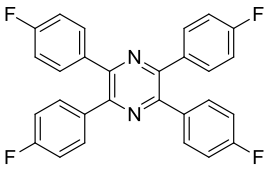


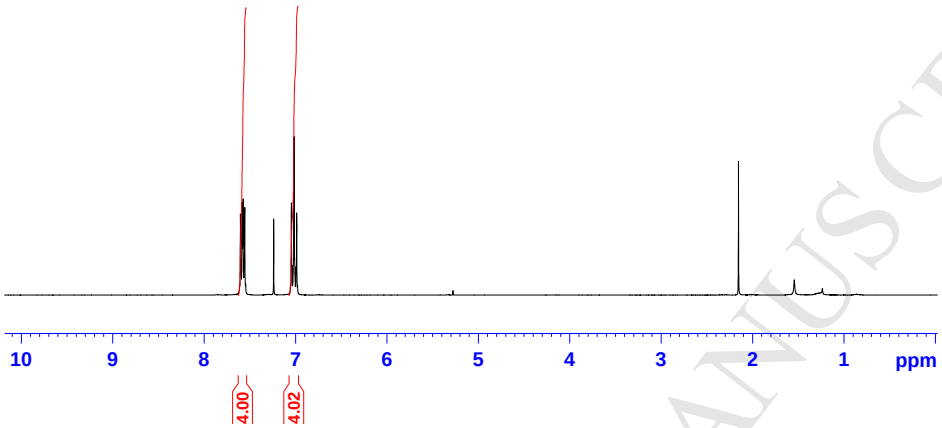

```
Current Data Parameters
NAME                  AP-156
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_               20120816
Time                    4.45
INSTRUM                AV300
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                     32768
DW                    23.700 usec
DE                     6.00 usec
TE                    296.1 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1
SFO1           75.4771825 MHz
NUC1                    13C
P1                     9.60 usec
PLW1          -1.00000000 W
SFO2          300.1312005 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4677535 MHz
WDW                      EM
SSB        0
LB                     1.00 Hz
GB         0
PC                     1.40
```





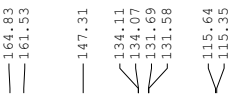


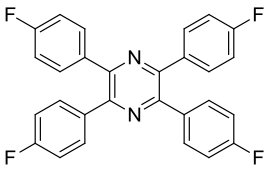
Current Data Parameters
NAME AP-161
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120818
Time 0.23
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542079 sec
RG 456.1
DW 81.000 usec
DE 6.00 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300214 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

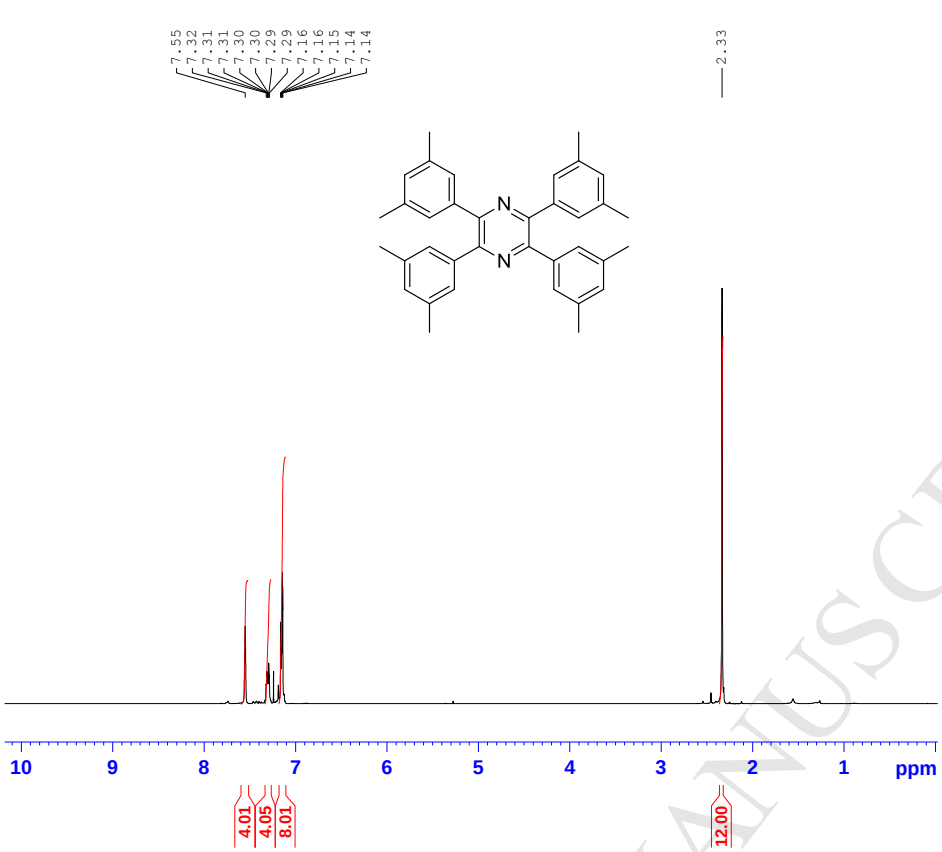




Current Data Parameters
NAME AP-161
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120818
Time 2.47
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3000
DS 4
SWH 21097.047 Hz
FIDRES 0.643831 Hz
AQ 0.7766016 sec
RG 32768
DW 23.700 usec
DE 6.00 usec
TE 296.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4771825 MHz
NUC1 13C
P1 9.60 usec
PLW1 -1.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 75.4677528 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

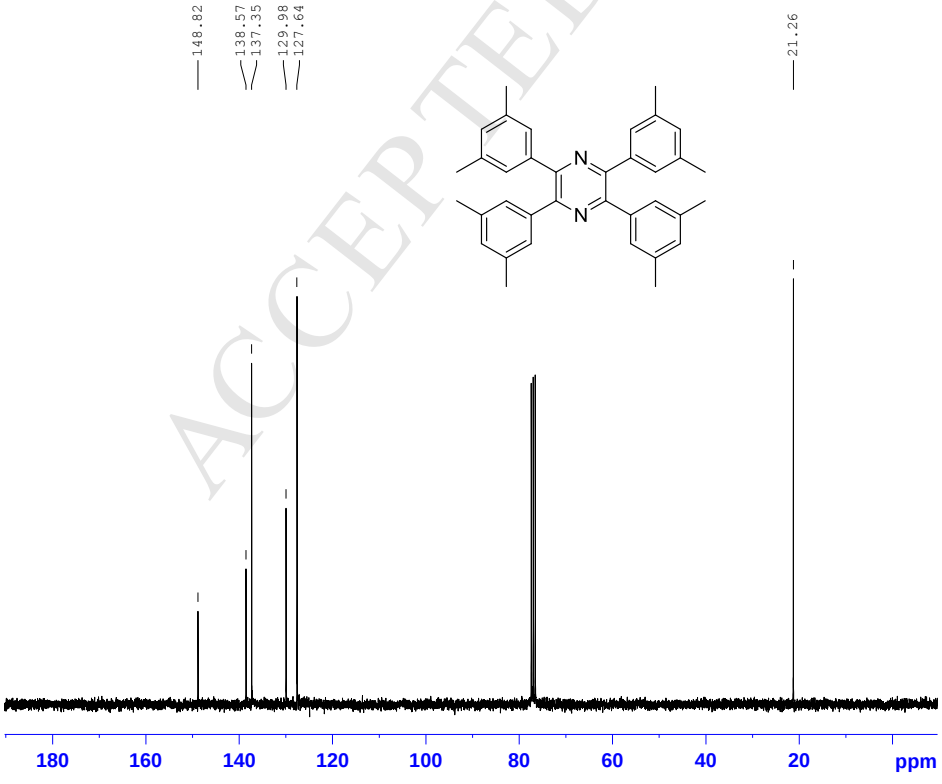


Current Data Parameters
NAME AP-167
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120823
Time 0.53
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542079 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0 dB
SFO1 300.1318534 MHz

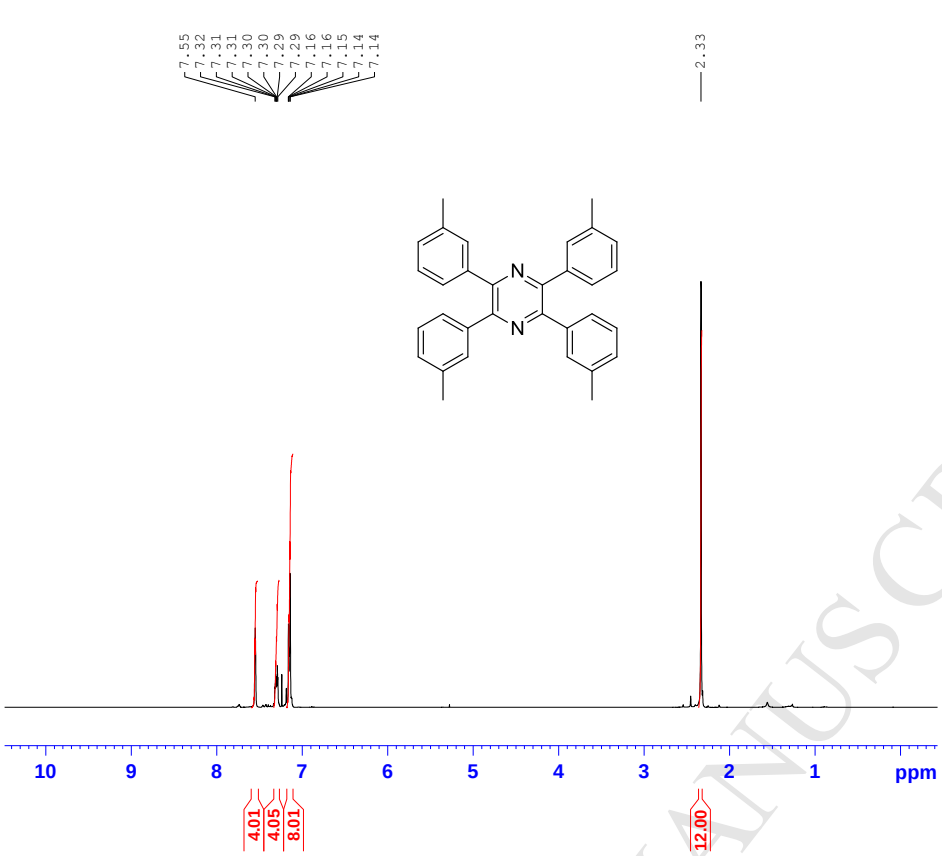
F2 - Processing parameters
SI 32768
SF 300.1300214 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AP-166
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120821
Time 0.59
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 21097.047 Hz
FIDRES 0.643831 Hz
AQ 0.7766016 sec
RG 32768
DW 23.700 usec
DE 6.00 usec
TE 297.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4771825 MHz
NUC1 13C
P1 9.60 usec
PLW1 -1.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 75.4677541 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

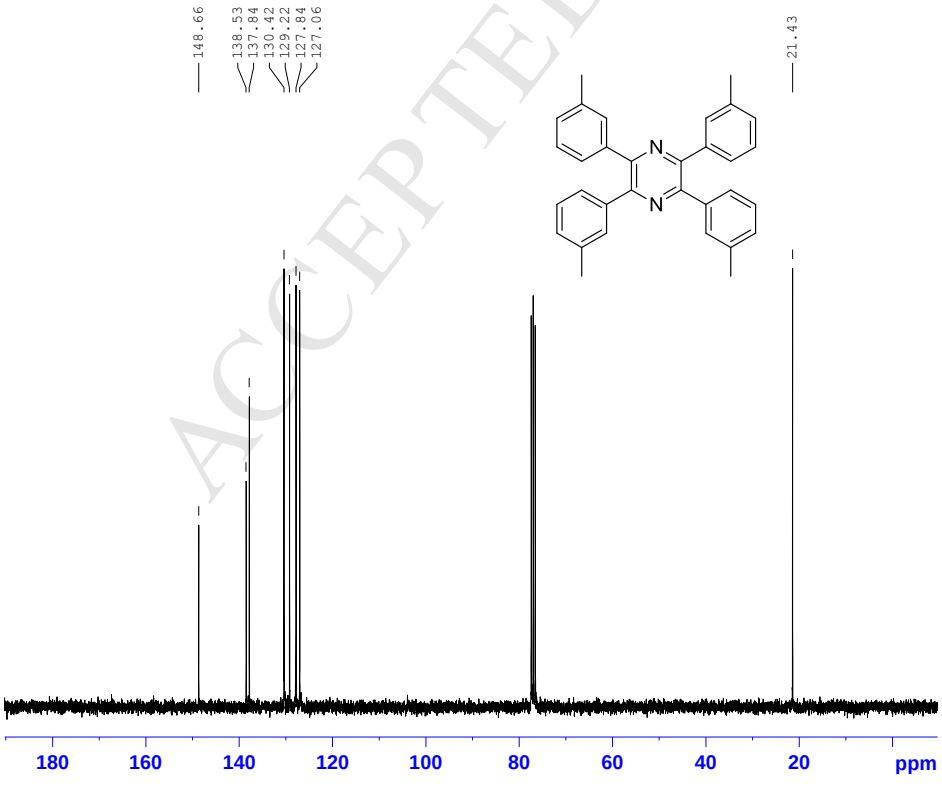


Current Data Parameters
NAME AP-167
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120823
Time 0.53
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542079 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0 dB
SFO1 300.1318534 MHz

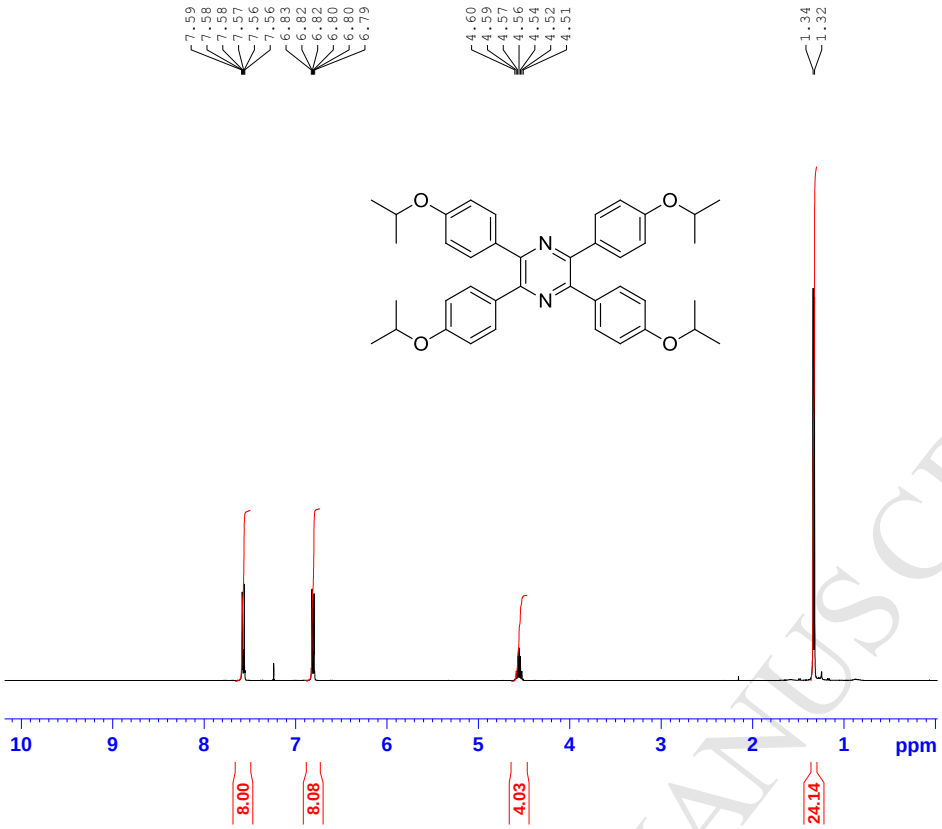
F2 - Processing parameters
SI 32768
SF 300.1300214 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AP-167
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120823
Time 1.06
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 21097.047 Hz
FIDRES 0.643831 Hz
AQ 0.7766016 sec
RG 32768
DW 23.700 usec
DE 6.00 usec
TE 297.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4771825 MHz
NUC1 13C
P1 9.60 usec
PLW1 -1.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 75.4677554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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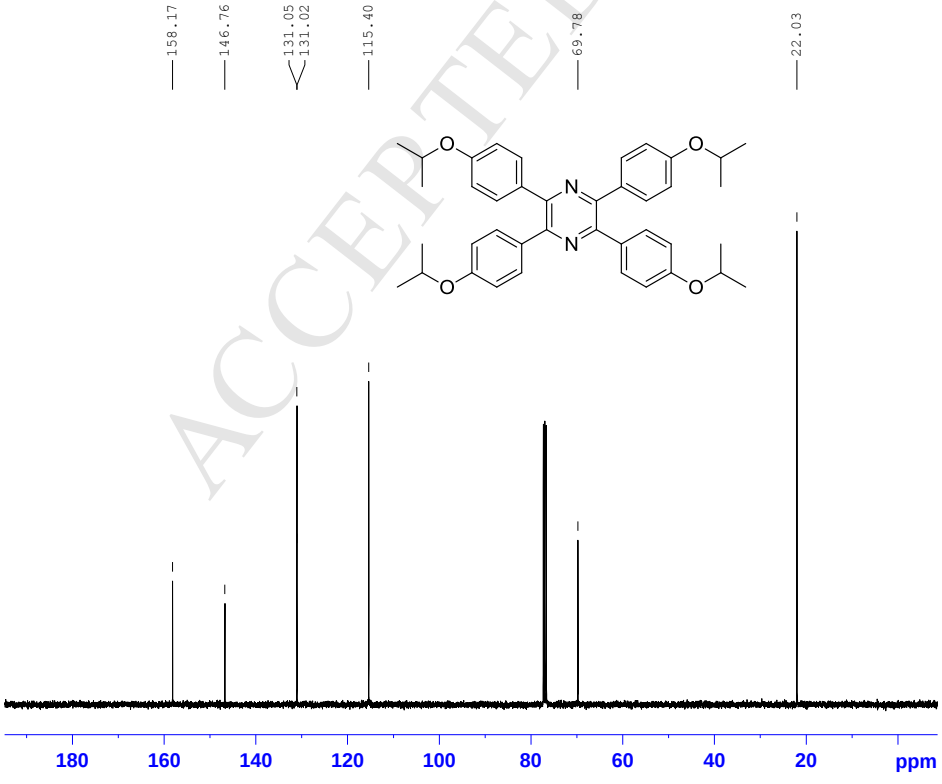
```
Current Data Parameters
NAME                  AP-244
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121127
Time                  16.27
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 2.0447233 sec
RG                    161.3
DW                   62.400 usec
DE                    6.00 usec
TE                   297.0 K
D1                1.50000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.10 usec
PL1                    -1.00 dB
PL1W           12.26963711 W
SFO1           400.1324000 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300292 MHz
WDW                      EM
SSB          0
LB                     0.10 Hz
GB           0
PC                     1.00
```



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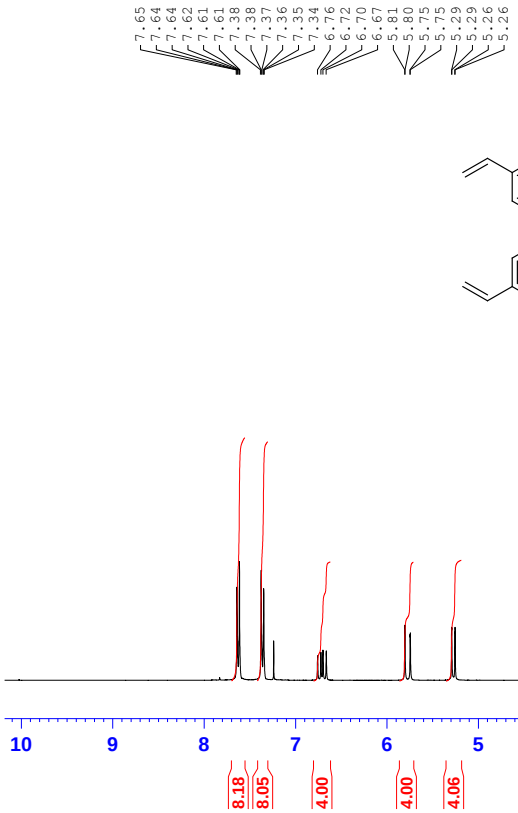
```
Current Data Parameters
NAME                  AP-244
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121127
Time                  16.42
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               29940.119 Hz
FIDRES             0.456850 Hz
AQ                 1.0944512 sec
RG                    1290.2
DW                   16.700 usec
DE                    6.00 usec
TE                   297.0 K
D1                1.70000005 sec
d11               0.03000000 sec
DELTA             1.60000002 sec
TD0                        1
SFO1           100.6260690 MHz
NUC1                     13C
P1                    10.00 usec
PLW1          -1.00000000 W
SFO2           400.1318000 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             100.6127752 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.00
```



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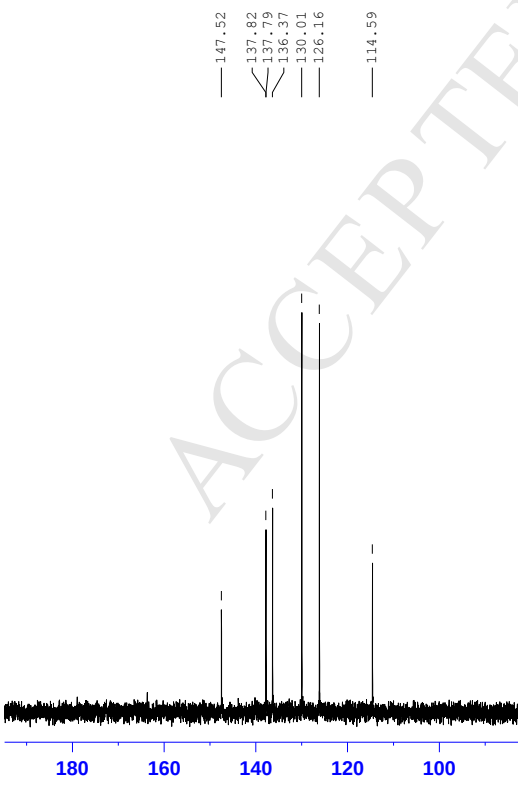
```
Current Data Parameters
NAME                  AP-245
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121130
Time                   2.51
INSTRUM              AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    294.2 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.00 usec
PL1        0 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF             300.1300214 MHz
WDW                      EM
SSB          0
LB                     0.10 Hz
GB           0
PC                     1.00
```

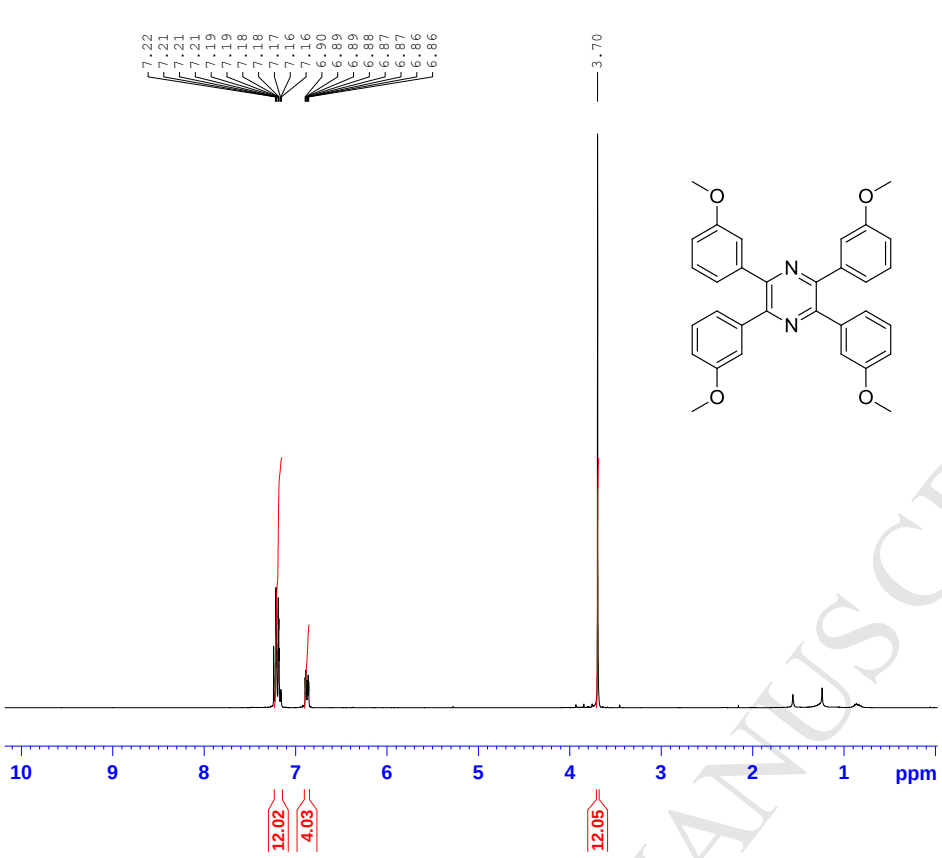


BRUKER

```
Current Data Parameters
NAME                  AP-245
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121130
Time                   3.06
INSTRUM              AV300
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                     32768
DW                    23.700 usec
DE                     6.00 usec
TE                    294.7 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1
SFO1           75.4771825 MHz
NUC1                     13C
P1                     9.60 usec
PLW1           -1.00000000 W
SFO2          300.1312005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4677535 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

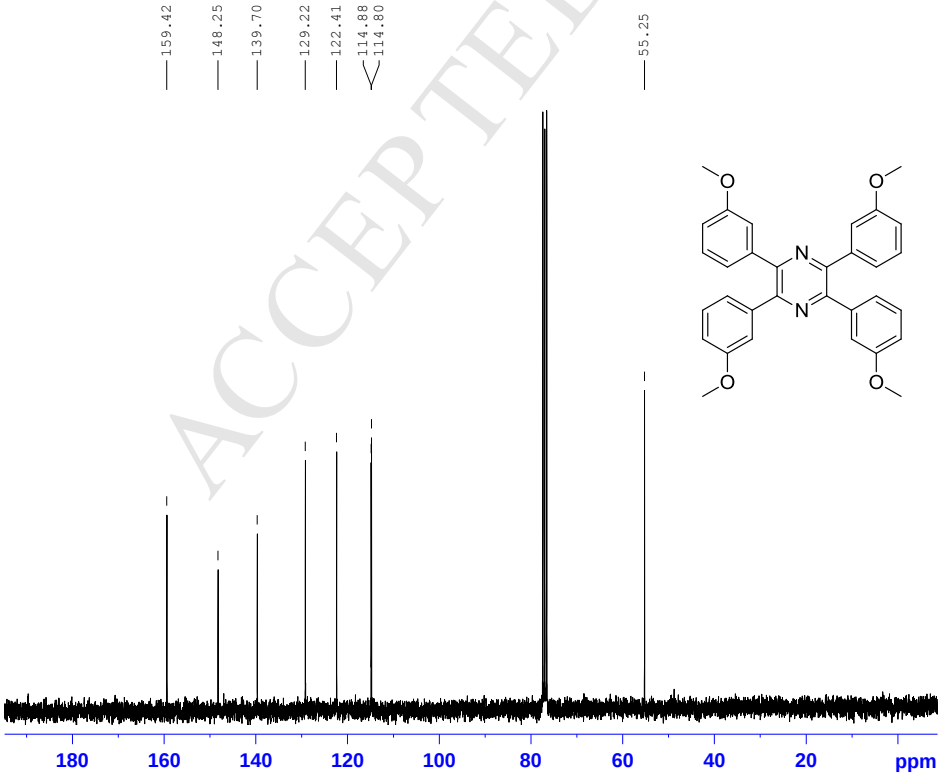


Current Data Parameters
NAME AP-247
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121128
Time 22.47
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542079 sec
RG 322.5
DW 81.000 usec
DE 6.00 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0 dB
SFO1 300.1318534 MHz

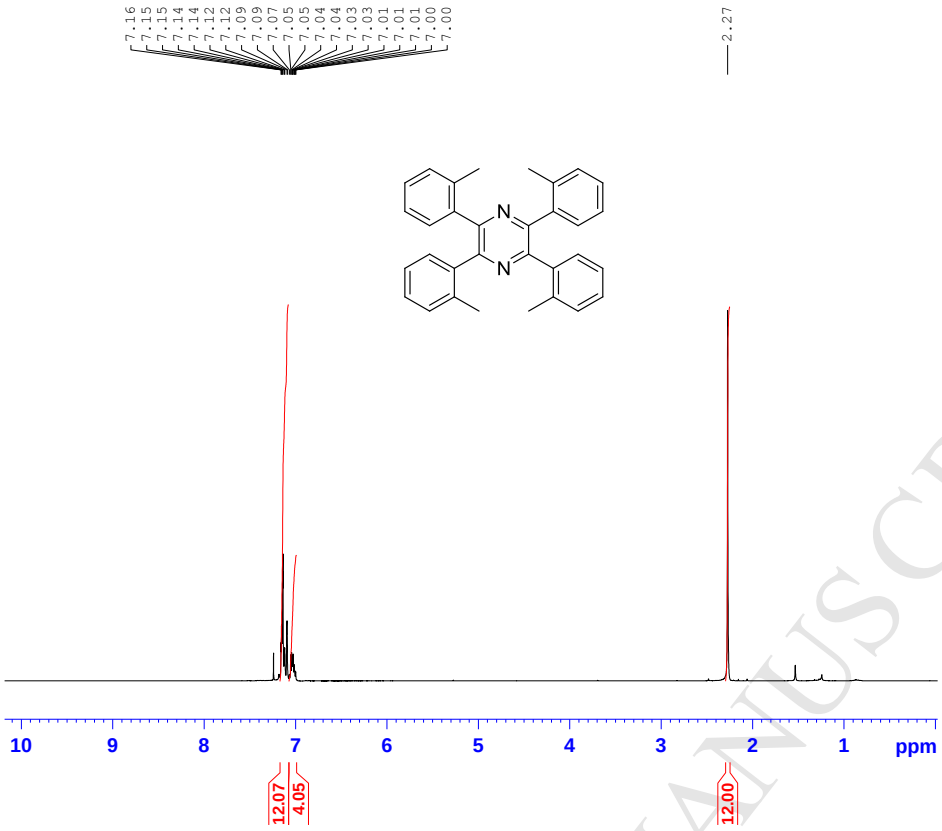
F2 - Processing parameters
SI 32768
SF 300.1300214 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AP-247
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121128
Time 23.01
INSTRUM AV300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 21097.047 Hz
FIDRES 0.643831 Hz
AQ 0.7766016 sec
RG 32768
DW 23.700 usec
DE 6.00 usec
TE 294.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4771825 MHz
NUC1 13C
P1 9.60 usec
PLW1 -1.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 75.4677537 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

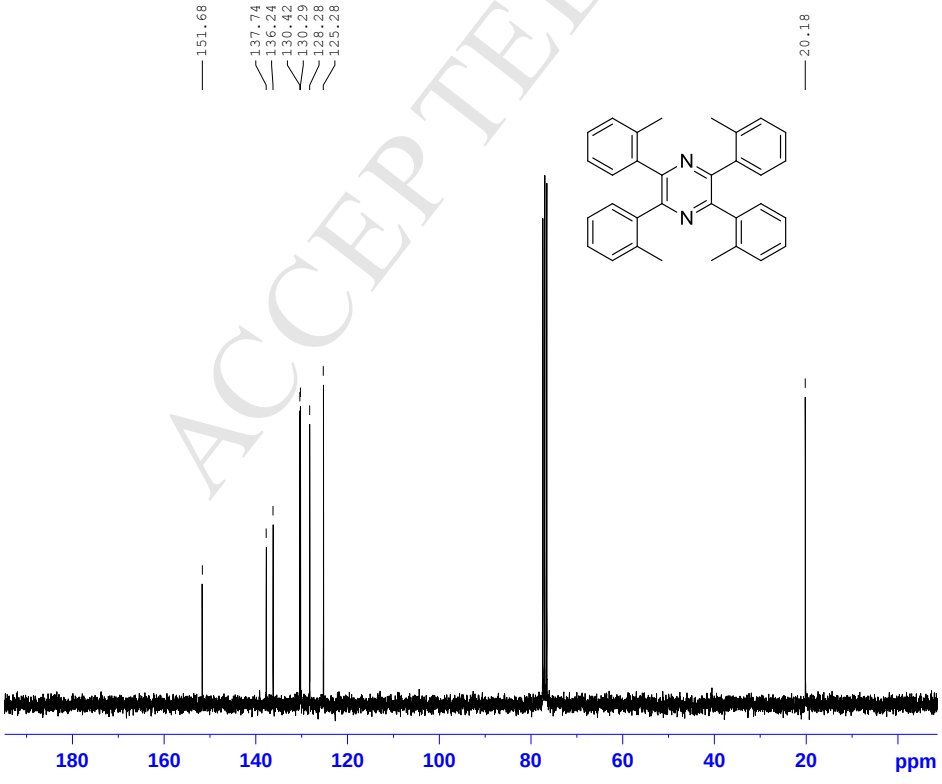



```
Current Data Parameters
NAME                  AP-248
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121127
Time                  18.58
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    294.6 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1       0 dB
SFO1           300.1318534 MHz

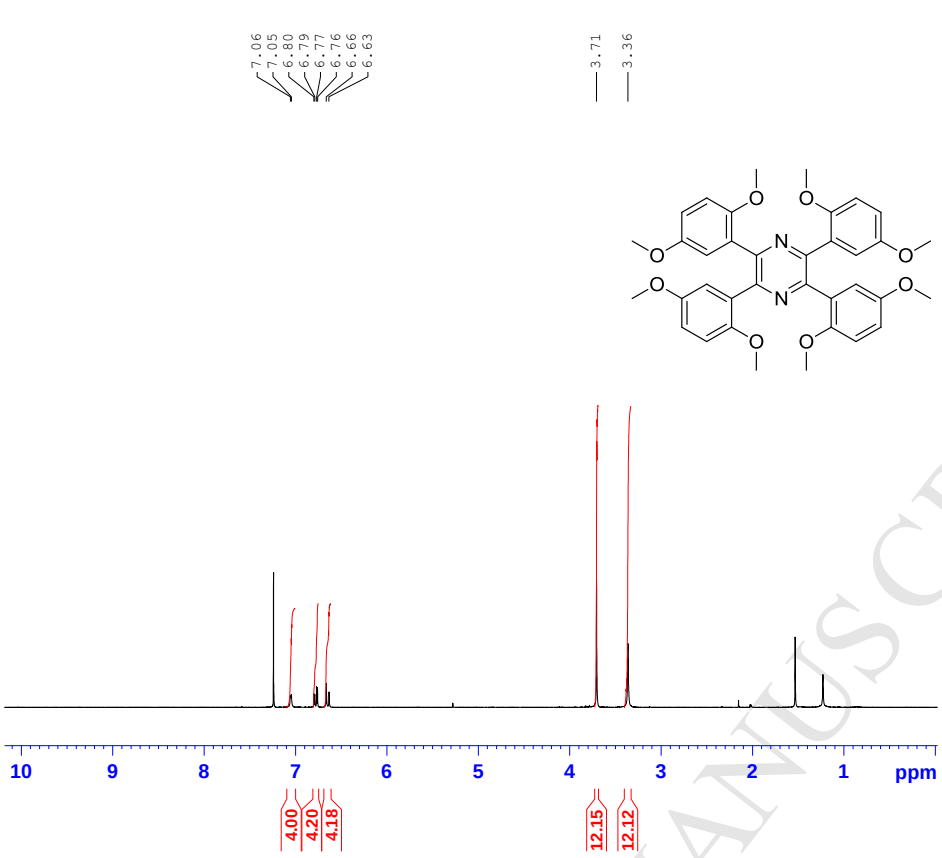
F2 - Processing parameters
SI                    32768
SF             300.1300214 MHz
WDW                      EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     1.00
```




```
Current Data Parameters
NAME                  AP-248
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121127
Time                  19.12
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                     32768
DW                    23.700 usec
DE                     6.00 usec
TE                    295.1 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1
SFO1           75.4771825 MHz
NUC1                      13C
P1                     9.60 usec
PLW1          -1.00000000 W
SFO2           300.1312005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4677541 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

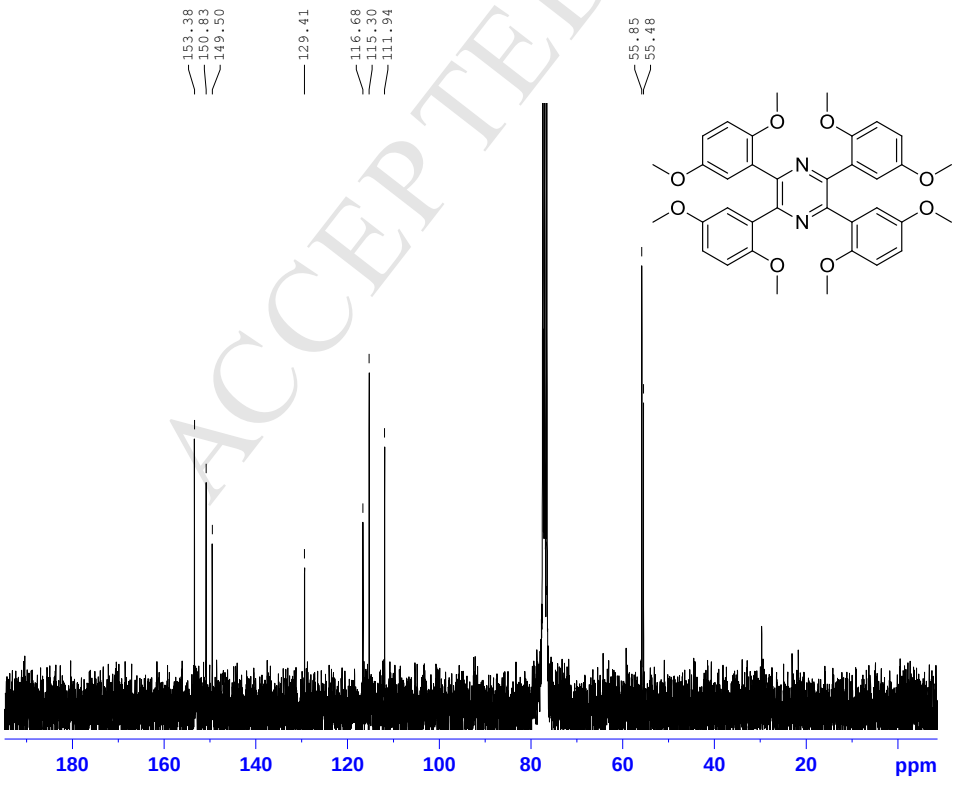



```
Current Data Parameters
NAME                  AP-250-
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20121130
Time                    3.17
INSTRUM                AV300
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        32
DS                         4
SWH                 6172.839 Hz
FIDRES              0.188380 Hz
AQ                  2.6542079 sec
RG                      812.7
DW                     81.000 usec
DE                      6.00 usec
TE                     294.2 K
D1                  1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1       0 dB
SFO1          300.1318534 MHz

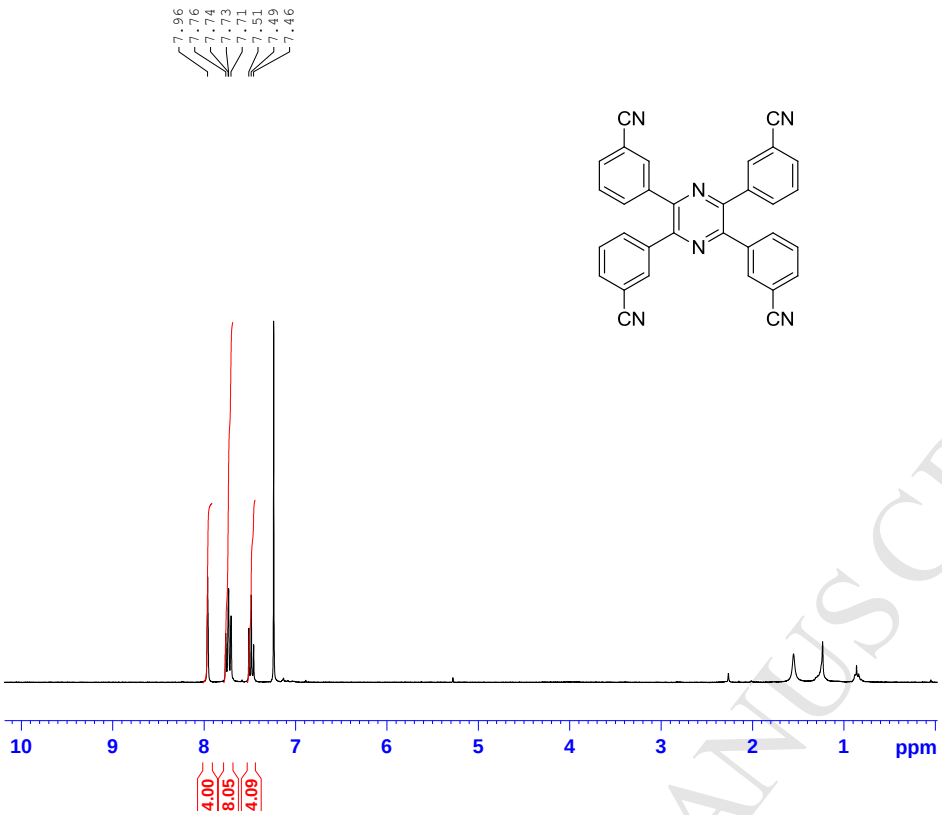
F2 - Processing parameters
SI                     32768
SF                300.1300214 MHz
WDW                       EM
SSB       0
LB                      0.10 Hz
GB        0
PC                      1.00
```




```
Current Data Parameters
NAME                  AP-250-
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20121130
Time                    7.14
INSTRUM                AV300
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                     32768
SOLVENT                CDCl3
NS                      5000
DS                         4
SWH                21097.047 Hz
FIDRES              0.643831 Hz
AQ                  0.7766016 sec
RG                     32768
DW                     23.700 usec
DE                      6.00 usec
TE                     294.8 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                        1
SFO1           75.4771825 MHz
NUC1                      13C
P1                      9.60 usec
PLW1          -1.00000000 W
SFO2          300.1312005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                     32768
SF                75.4677527 MHz
WDW                       EM
SSB       0
LB                      1.00 Hz
GB        0
PC                      1.40
```



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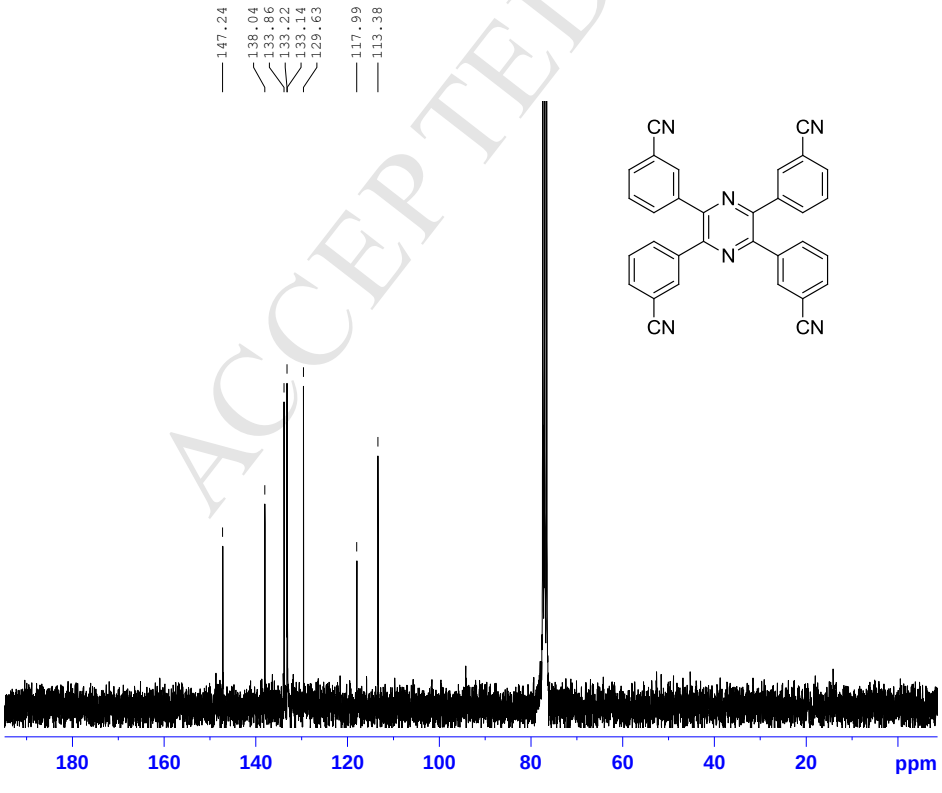
```
Current Data Parameters
NAME                  AP-251
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121210
Time                  12.15
INSTRUM           FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       48
DS                        2
SWH                6103.516 Hz
FIDRES             0.093132 Hz
AQ                 5.3687091 sec
RG                    283.33
DW                    81.920 usec
DE                     6.50 usec
TE                    300.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              300.2018539 MHz
NUC1                      1H
P1                     11.00 usec
PLW1              16.00000000 W

F2 - Processing parameters
SI                        65536
SF                300.2000101 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



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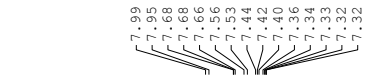
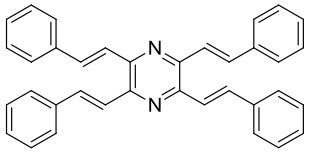
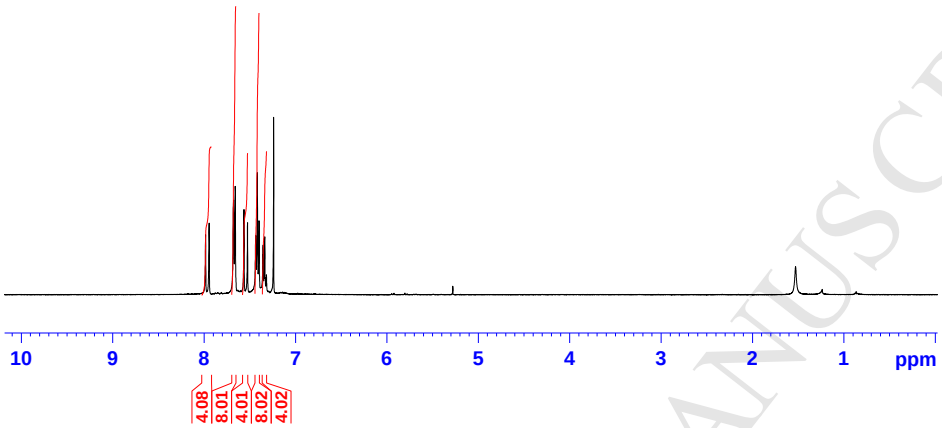
```
Current Data Parameters
NAME                  AP-251
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121212
Time                   5.06
INSTRUM                AV300
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    32768
SOLVENT               CDCl3
NS                     4000
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                    32768
DW                    23.700 usec
DE                     6.00 usec
TE                    293.6 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1
SFO1              75.4771825 MHz
NUC1                      13C
P1                     9.60 usec
PLW1              -1.00000000 W
SFO2              300.1312005 MHz
NUC2                      1H
CPDPRG[2               waltz16
PCPD2                100.00 usec
PLW2              -1.00000000 W
PLW12             -1.00000000 W
PLW13             -1.00000000 W

F2 - Processing parameters
SI                        32768
SF                75.4677530 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```





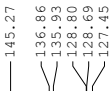


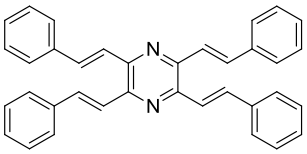
Current Data Parameters
NAME AP-413
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130628
Time 10.51
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 645.1
DW 62.400 usec
DE 6.00 usec
TE 297.0 K
D1 1.50000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.20 usec
PL1 -2.00 dB
PL1W 15.44655800 W
SFO1 400.1324000 MHz

F2 - Processing parameters
SI 32768
SF 400.1300292 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

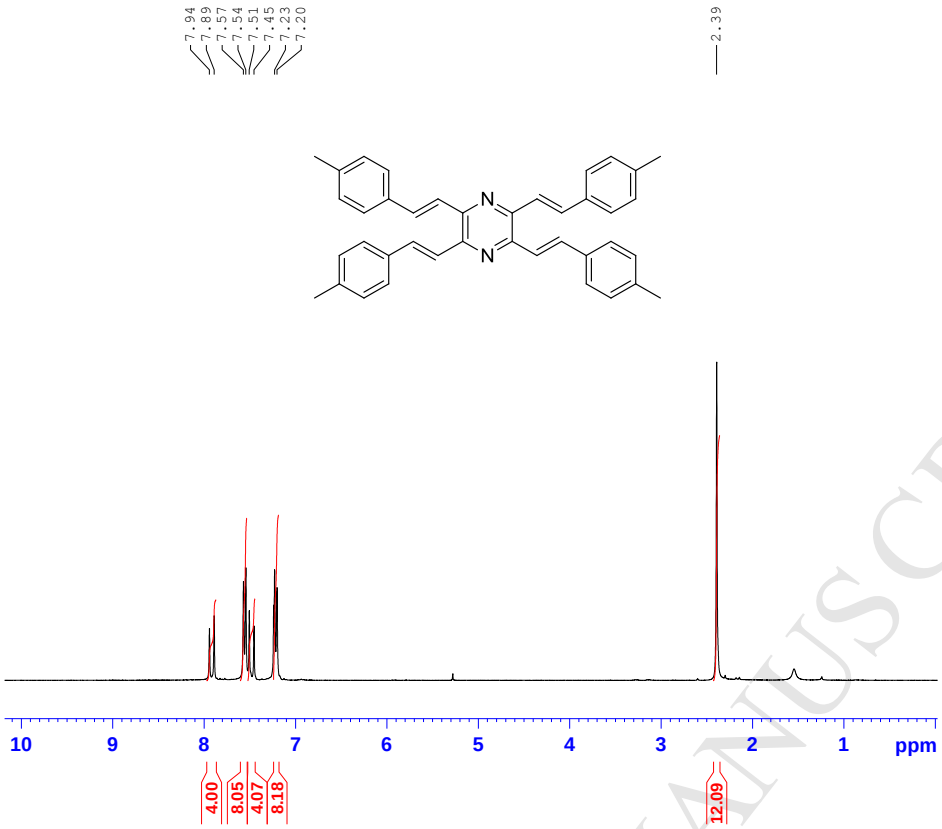




Current Data Parameters
NAME AP-413
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130628
Time 11.20
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 29940.119 Hz
FIDRES 0.456850 Hz
AQ 1.0944512 sec
RG 1625.5
DW 16.700 usec
DE 6.00 usec
TE 297.0 K
D1 1.70000005 sec
d11 0.03000000 sec
DELTA 1.60000002 sec
TD0 1
SFO1 100.6260690 MHz
NUC1 13C
P1 10.00 usec
PLW1 -1.00000000 W
SFO2 400.1318000 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 100.6127734 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



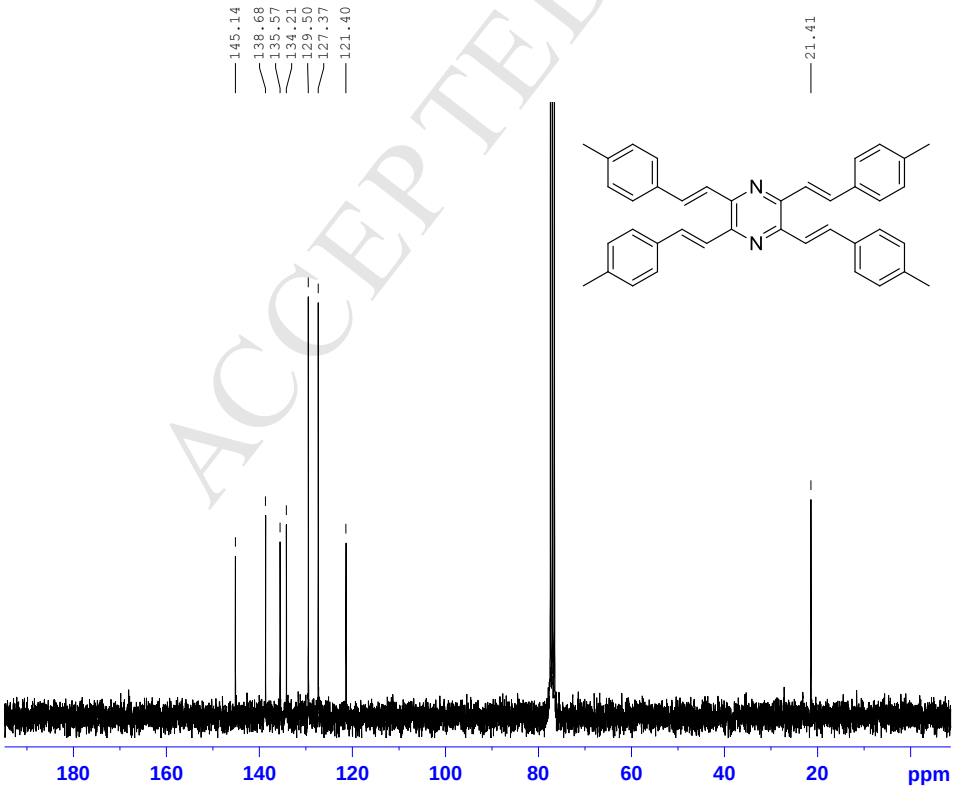
BRUKER

```
Current Data Parameters
NAME                  AP-423
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130712
Time                   8.09
INSTRUM        FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                6103.516 Hz
FIDRES             0.093132 Hz
AQ                 5.3687091 sec
RG                    80.7194
DW                   81.920 usec
DE                    6.50 usec
TE                   299.0 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             300.2018539 MHz
NUC1                     1H
P1                    11.00 usec
PLW1            16.00000000 W

F2 - Processing parameters
SI                    65536
SF               300.2000096 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



BRUKER

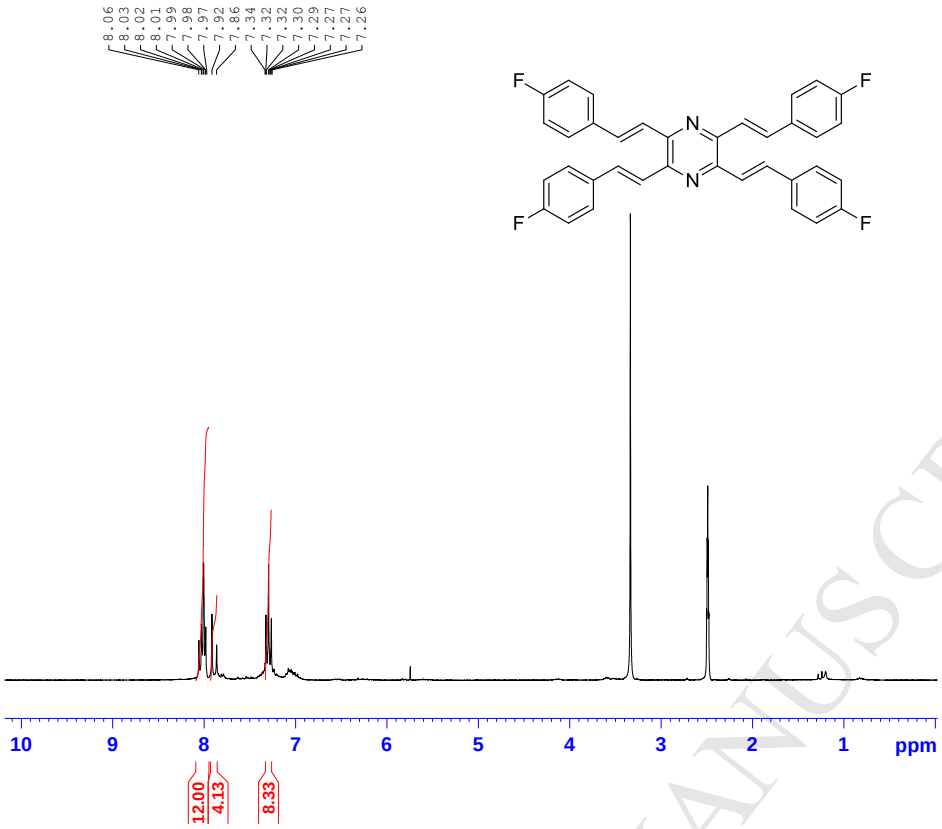
```
Current Data Parameters
NAME                  AP-423
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130712
Time                   8.13
INSTRUM        FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG           zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1000
DS                        4
SWH               24414.063 Hz
FIDRES             0.372529 Hz
AQ                 1.3421773 sec
RG                   501.187
DW                   20.480 usec
DE                    6.50 usec
TE                   299.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
D31                0.00001140 sec
D40                0.02898005 sec
L4                       40
L5                       57
P32                  90.00 usec
TD0                       1

======== CHANNEL f1 ========
SFO1              75.4928982 MHz
NUC1                     13C
P1                    11.40 usec
PLW1            30.00000000 W

======== CHANNEL f2 ========
SFO2             300.2012008 MHz
NUC2                     1H
CPDPRG[2             waltz16
PCPD2                 90.00 usec
PLW2            16.00000000 W
PLW12            0.23901001 W
PLW13            0.19360000 W

F2 - Processing parameters
SI                    32768
SF               75.4853510 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

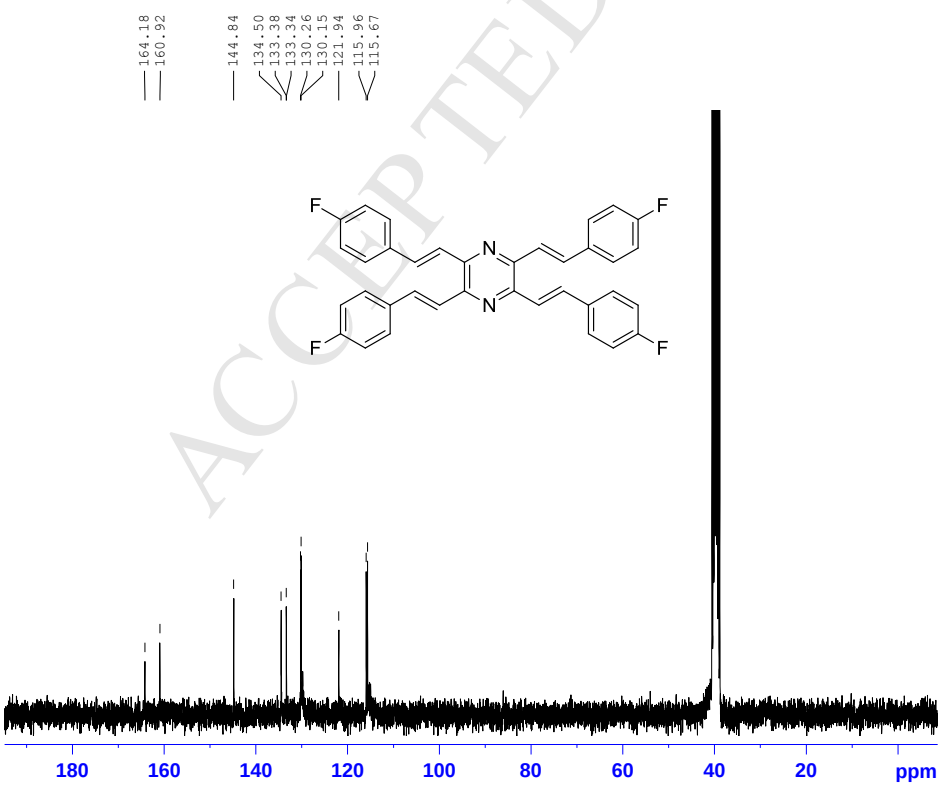



```
Current Data Parameters
NAME                  AP-398
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130618
Time                  22.56
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT  DMSO-d6  --CDCl3--
NS                       32
DS                        4
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542079 sec
RG                     322.5
DW                    81.000 usec
DE                     6.00 usec
TE                    295.5 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1        0 dB
SFO1           300.1318534 MHz

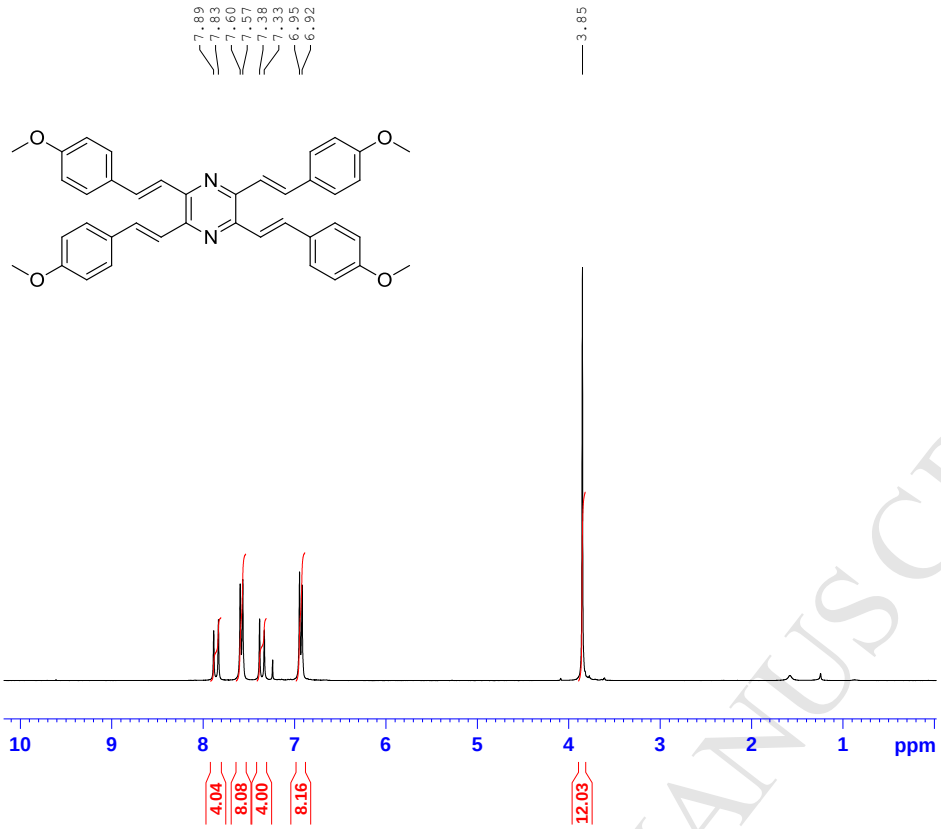
F2 - Processing parameters
SI                    32768
SF             300.1314393 MHz
WDW                      EM
SSB        0
LB                     0.10 Hz
GB         0
PC                     1.00
```




```
Current Data Parameters
NAME                  AP-398
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130619
Time                   1.19
INSTRUM               AV300
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    32768
SOLVENT  DMSO-d6  --CDCl3--
NS                     3000
DS                        4
SWH               21097.047 Hz
FIDRES             0.643831 Hz
AQ                 0.7766016 sec
RG                    32768
DW                   23.700 usec
DE                     6.00 usec
TE                    295.8 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1
SFO1           75.4771825 MHz
NUC1                     13C
P1                     9.60 usec
PLW1          -1.00000000 W
SFO2           300.1312005 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             75.4681302 MHz
WDW                      EM
SSB        0
LB                     1.00 Hz
GB         0
PC                     1.40
```



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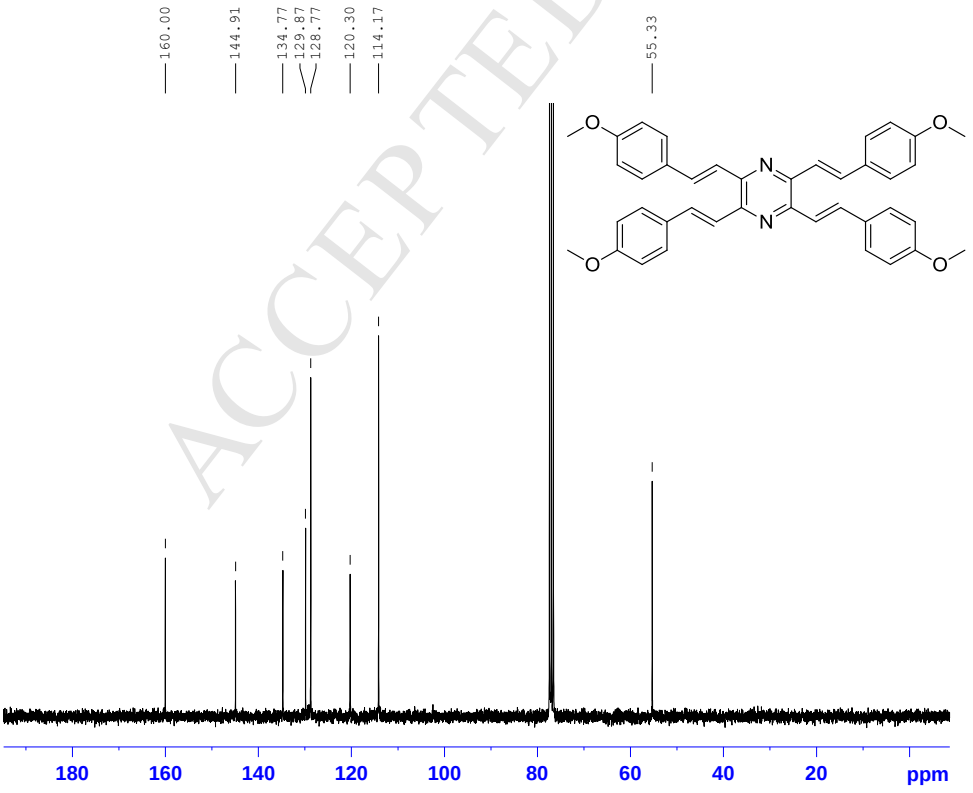
```
Current Data Parameters
NAME                  AP-425
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130715
Time                  16.42
INSTRUM         FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                6103.516 Hz
FIDRES             0.093132 Hz
AQ                 5.3687091 sec
RG                    31.623
DW                    81.920 usec
DE                     6.50 usec
TE                   298.8 K
D1            1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          300.2018539 MHz
NUC1                     1H
P1                    11.00 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                    65536
SF            300.2000095 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



BRUKER

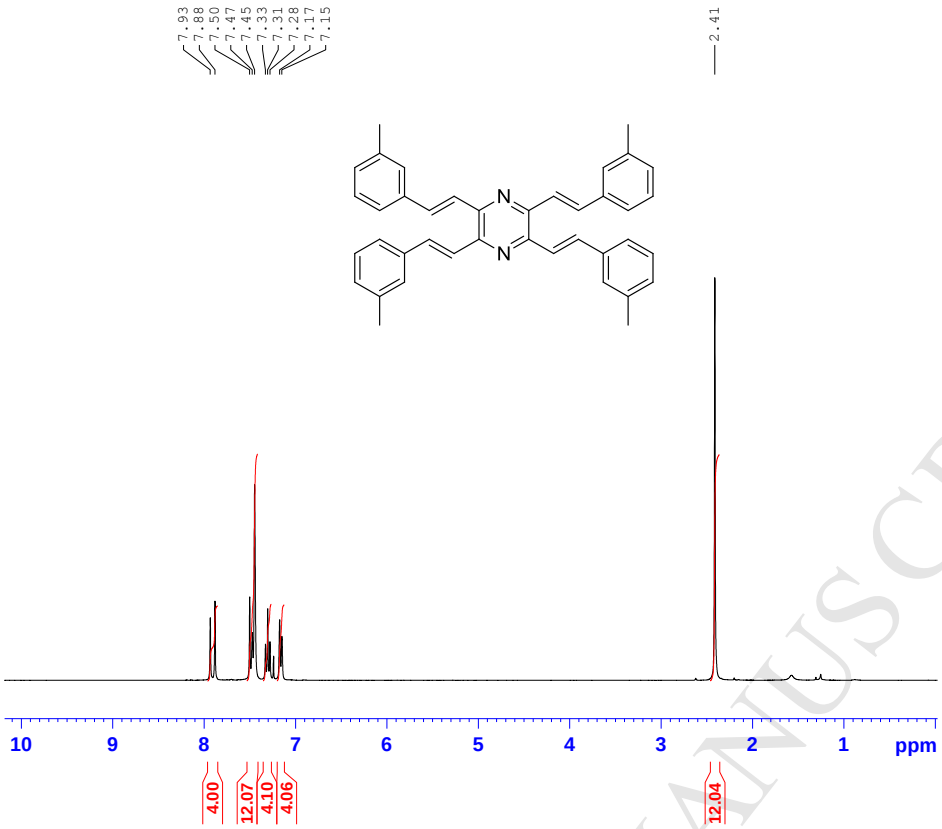
```
Current Data Parameters
NAME                  AP-425
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130715
Time                  16.46
INSTRUM         FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG           zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1000
DS                        4
SWH               24414.063 Hz
FIDRES             0.372529 Hz
AQ                 1.3421773 sec
RG                   501.187
DW                    20.480 usec
DE                     6.50 usec
TE                   298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
D31           0.00001140 sec
D40           0.02898005 sec
L4                       40
L5                       57
P32                   90.00 usec
TD0                       1

======== CHANNEL f1 ========
SFO1          75.4928982 MHz
NUC1                    13C
P1                    11.40 usec
PLW1          30.00000000 W

======== CHANNEL f2 ========
SFO2          300.2012008 MHz
NUC2                     1H
CPDPRG[2           waltz16
PCPD2                 90.00 usec
PLW2          16.00000000 W
PLW12          0.23901001 W
PLW13          0.19360000 W

F2 - Processing parameters
SI                    32768
SF            75.4853525 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

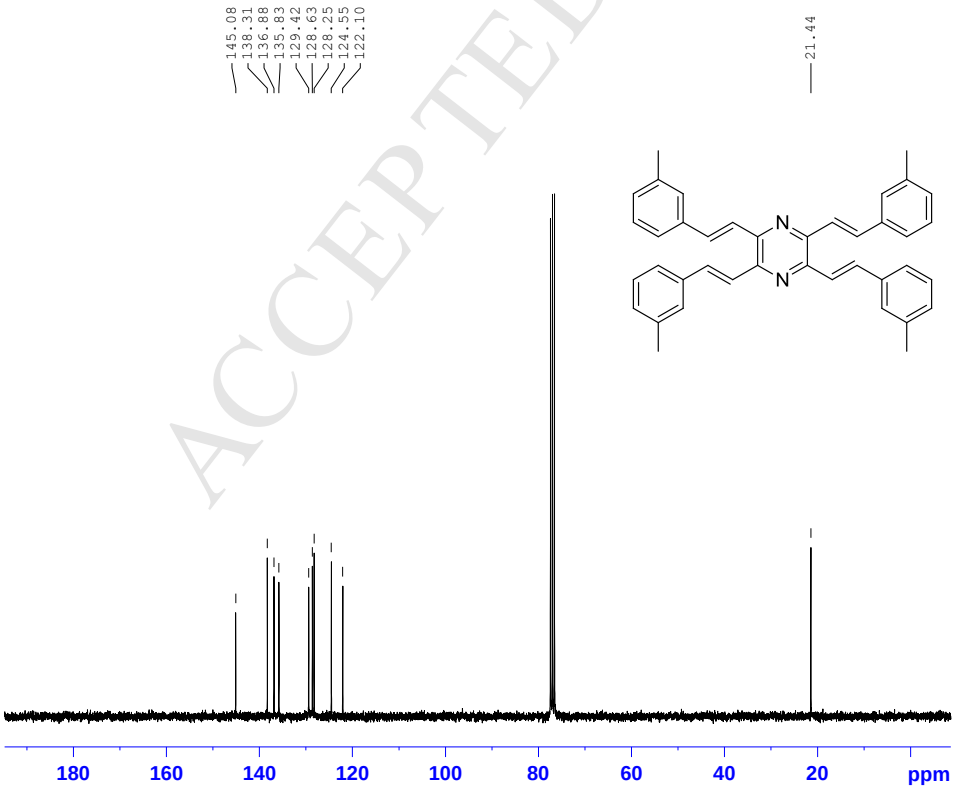



```
Current Data Parameters
NAME                  AP-426
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130717
Time                   9.00
INSTRUM          FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                6103.516 Hz
FIDRES             0.093132 Hz
AQ                 5.3687091 sec
RG                    31.623
DW                   81.920 usec
DE                    6.50 usec
TE                   300.0 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             300.2018539 MHz
NUC1                     1H
P1                    11.00 usec
PLW1            16.00000000 W

F2 - Processing parameters
SI                    65536
SF               300.2000095 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```




```
Current Data Parameters
NAME                  AP-426
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130717
Time                   9.04
INSTRUM          FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG            zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1000
DS                        4
SWH               24414.063 Hz
FIDRES             0.372529 Hz
AQ                 1.3421773 sec
RG                   501.187
DW                   20.480 usec
DE                    6.50 usec
TE                   300.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
D31                0.00001140 sec
D40                0.02898005 sec
L4                       40
L5                       57
P32                  90.00 usec
TD0                       1

======== CHANNEL f1 ========
SFO1             75.4928982 MHz
NUC1                    13C
P1                    11.40 usec
PLW1            30.00000000 W

======== CHANNEL f2 ========
SFO2            300.2012008 MHz
NUC2                     1H
CPDPRG[2             waltz16
PCPD2                 90.00 usec
PLW2            16.00000000 W
PLW12            0.23901001 W
PLW13            0.19360000 W

F2 - Processing parameters
SI                    32768
SF               75.4853524 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

4. Data of Crystal Structure Analysis

Crystal structure of **3b** was deposited at the Cambridge Crystallographic Data Centre. The data have been assigned the following deposition number: CCDC 945041.

Crystal data for **3b**: $C_{32}H_{16}F_{12}N_2$, M = 656.47, monoclinic, a = 11.6303(4), b = 10.9593(2), c = 22.1529(8) Å, β = 102.842(3)°, V = 2752.98(15) Å^3, T = 150(2) K, space group $P2_1/n$, Z = 4, 45142 reflections measured, 6328 independent reflections (R_{int} = 0.0361), final R values ($I > 2\sigma(I)$): R_1 = 0.0420, wR_2 = 0.1122, final R values (all data): R_1 = 0.0666, wR_2 = 0.1184, 443 refined parameters.

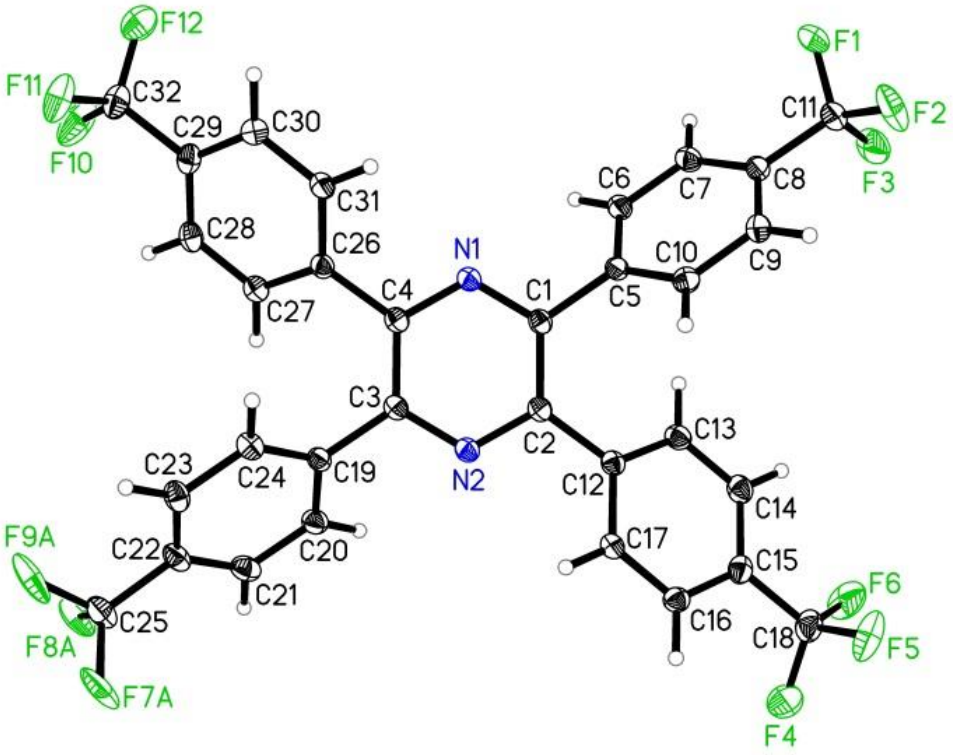


Figure 1. ORTEP diagram of **3b**. Displacement ellipsoids are drawn at the 30% probability level. Angle between the pyrazine plane and the plane defined by C5-C10: 49.9°, angle between the pyrazine plane and the plane defined by C12-C17: 32.0°, angle between the pyrazine plane and the plane defined by C19-C24: 48.9°, angle between the pyrazine plane and the plane defined by C26-C31: 34.8°.