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Strong Electron Acceptor Properties of 3′(Pentafluorophenyl)isoxazolo[4′,5′:1,2][60]fullerene Derivatives

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Abstract: Investigations on the synthesis and electrochemical behaviour of a new class of acceptor substituted isoxazolofullerenes is described. The influence of distance and orientation of pentafluorophenyl substituents on cyclic voltammetry is discussed. The strong acceptor effect of **1c** could be due to a through space interaction of a pentafluoro-phenyl substituent with the [60]fullerene surface.

Introduction

Fullerenes are well known to be electron acceptors.[1] The ability of [60]fullerene to accept up to six electrons reversibly has been confirmed chemically [2] and via cyclovoltammetric experiments.[3] Some fullerene derivatives have been reported where electronegative atoms [4] or strong electron withdrawing groups [5] were directly connected to the fullerene core in order to enhance the reduction potentials compared to the unsubstituted [60]fullerene. C_{60} was also used to increase the electron affinity of sustituents in fullerene adducts.[6] Periconjugative effects have been used to improve the electron acceptor ability of fullerene derivatives.[7] In fulleropyrrolidinium salts the positive charge leads to a shift of the redox potentials towards positive values compared with the neutral fulleropyrrolidines.[8] By cyclovoltammetry investigations of isoxazolofullerenes with various substituents no significant effect could be observed compared to unsubstituted fullerenes.[9]

In this communication we investigated the influence of pentafluoro-phenyl substituents with strong electron accepting properties to isoxazolo[60]fullerenes. Variation of distance and orientation of the acceptor group to the fullerene moiety have been examined. Therefore we synthesized the fullerene derivatives **1a-c** (Scheme 1).

Results and Discussion

Several [2+3] cycloaddition reaction of nitrile oxides[9,10] or trimethylsilylnitronates[11] to [60] and [70]fullerenes yielding isoxazolo-fullerenes have been synthesized. **1d** was described in an earlier publication [9a] and is used as a reference compound due to the unsubstituted phenyl ring. The new isoxazolo-fullerenes **1a-c** were formed via a convenient synthetic method. The oximes **2** were chlorinated with *N*-chlorosuccinimide (NCS) and subsequently in situ dehydrochlorinated forming the reactive nitrile oxides. The 1,3-dipole reagents react in a [2+3] cycloaddition with the [60]fullerene. Oxime **2a** have been described in the literature and the new oximes **2b** and **2c** were obtained from the corresponding aldehydes (Scheme 2).

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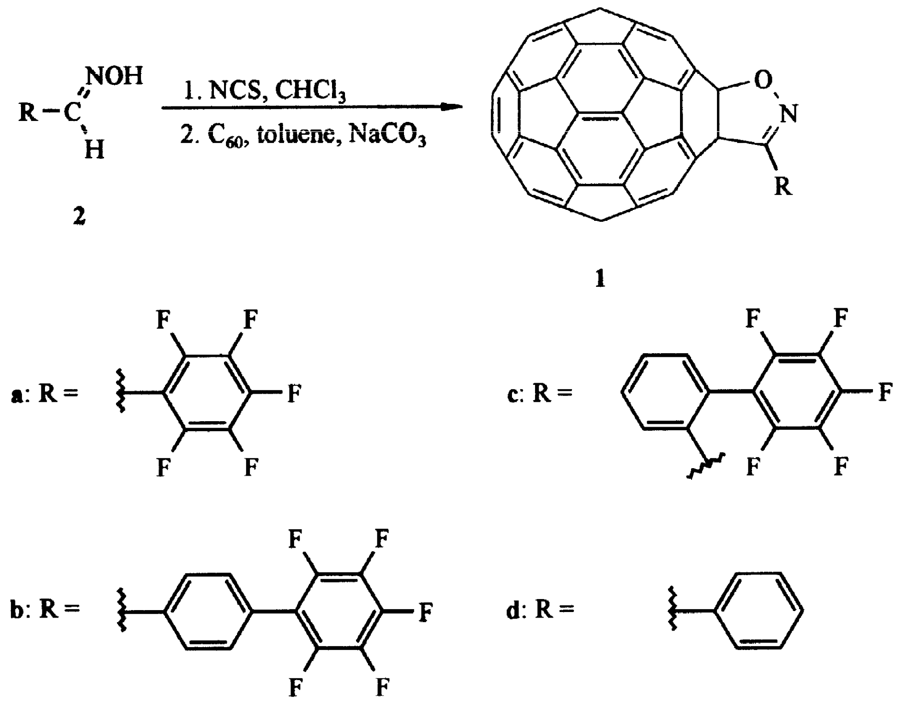
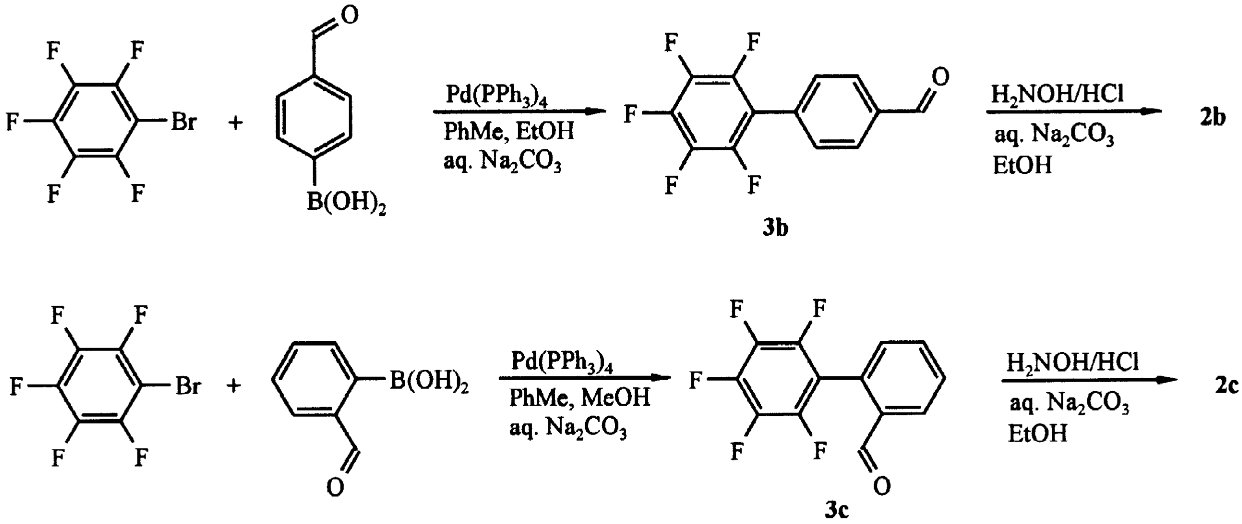


Scheme 1



Scheme 2

3b and **3c** were synthesized via the Suzuki cross coupling reaction using 4-formylphenyl-boronic acid and 2-formylphenyl-boronic acid, respectively. The remarkable coupling reaction substitutes selectively the more reactive bromine in the polyhalogenated aromatic system by a formyl-phenyl system. The reaction is a useful method to build up functionalized biphenyl systems.

All new compounds have been characterized by IR, UV-VIS, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy and high resolution mass spectrometry or elemental analysis respectively. For all cycloadducts **1** the expected reduced number of carbon signals in the fullerene region proofs mirror symmetry. This leads to the conclusion that the addition of the nitrile oxide took place at the [6,6]bond in the[60]fullerene.

Investigations about the redox behaviour of the isoxazolofullerenes **1a-d** were carried out by cyclic voltammetry. Figure 1 shows the cyclovoltammogram of compound **1a** within the redox range 0.40 to –2.40 V.

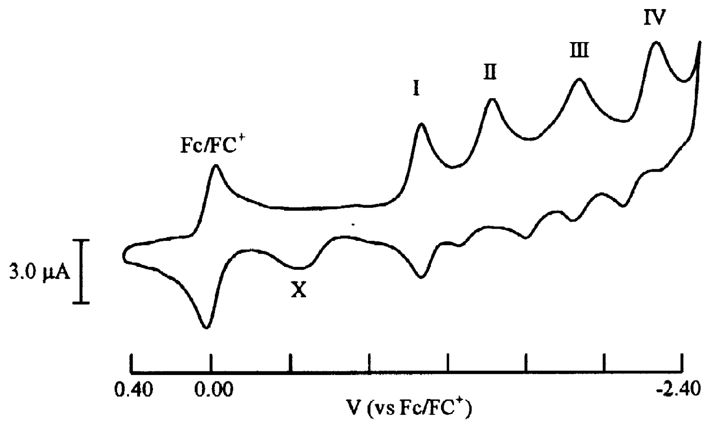


Figure 1:Cyclic voltammogram of **1a** at 50 mV/s

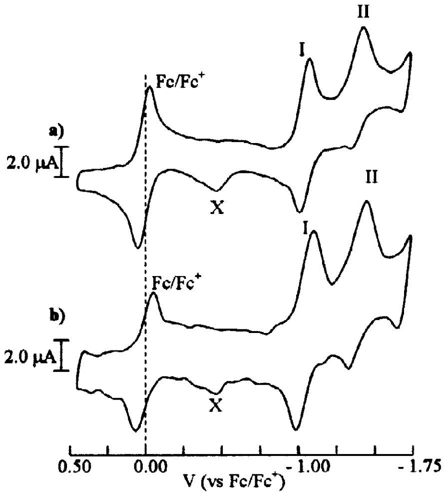


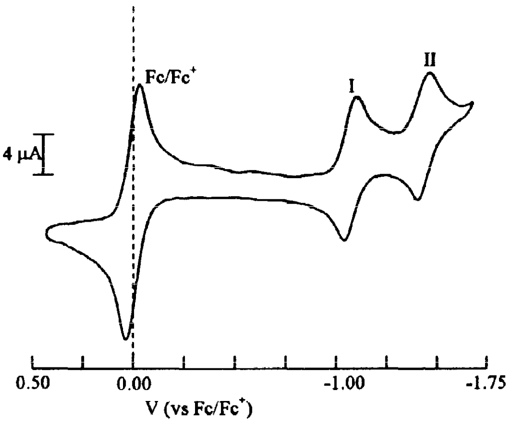
Figure 2: Cyclic voltammograms of **1a** at a) 100 mV/s and b) 200 mV/s

The first redox couple appears reversibly but the second and subsequent redox pairs are irreversible due to chemical processes leading to different species. Figure 2 presents the electrochemical properties of derivative **1a** within the redox range down to – 1.75 V at different scan rates. Increase of the sweep rate leads to a more reversible second redox couple due to the appearance of the corresponding second anodic half-wave. To the same degree of this increase the irreversible redoxpotential X disappears noticeably. This behaviour leads to the conclusion that irreversible chemical steps occur forming new species. We assume an irreversible electrochemical ring opening reaction of the heterocycle probably due to a N-O bond cleavage. Interestingly for the compounds **1b-d** the second redox couple in the range down to –1.75 V is reversible even at low scan rates (50 mV/s) (Figure 3 and 4).

Obviously the strong electron withdrawing effect of the direct connection of the pentafluoro-phenyl substituent with the heterocycle in compound **1a** enhances the reductive ring opening reaction of the isoxazolinering.

If the reduction range is extended up to more negative potentials than –1.75 V, irreversible processes are also observed for the derivatives **1b-d**. For this reason we only regard the first two redox couples to discuss the influence of the pentafluoro-phenyl acceptors to the fullerene system.

Investigations of Suzuki et al.[13] about the influence of directly attached groups to [60]fullerenes led to the conclusions that saturation of a double bond shifts the reduction potential to more negative values compared with the pristine C_{60}.



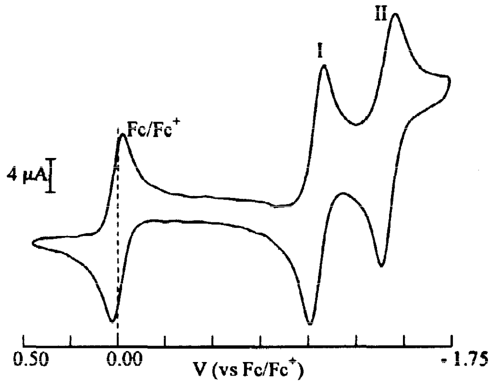


Figure 3: Cyclovoltammogram of **1b** at 50 mV/s

Figure 4: Cyclovoltammogram of **1c** at 50 mV/s

In contrast an addition of a nitrile oxide leading to a fused isoxazoline ring at a [6,6] double bond of the [60]fullerene shifts the potentials towards positive values (Table 1). The redox value for the first reduction of the reference compound **1d** is shifted about 40 mV to higher potentials compared to the naked C_{60} (Diagram 1). Obviously the isoxazoline heterocycle has a strong electron accepting effect on the redox behaviour of the fullerene core.

Compound	$E_{1,\text{red.}}$	$E_{2,\text{red.}}$
C_{60}	-1.12	-1.47
1a*	-1.05	-1.40
1b	-1.08	-1.44
1c	-1.05	-1.42
1d	-1.08	-1.43

Table 1. $E_{1/2}$ values (V vs Fc/Fc$^+$) of the redox couples of C_{60} and compounds **1a-d**, detected by CV (scan rate 50 mV/s; *200 mV/s) in 1,2-dichlorobenzene (0.1 mol/L $(n\text{-}Bu)_4NPF_6$) at room temperature. Errors are estimated at ±10 mV. $E_{1/2} = (E^{an}_{peak} + E^{cat}_{peak})/2$.

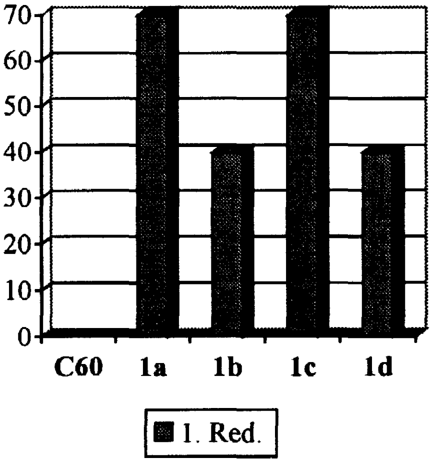


Diagram 1. Deviation of the redox potentials from derivatives **1a-d** to [60]fullerene in mV.

Direct linkage of a pentafluoro-phenyl substituent to the isoxazoline ring in compound **1a** shifts the redox potential even more to positive values (70 mV compared to C_{60}) leading to powerful electron accepting fullerene system. The strong inductive effect of the pentafluoro-phenyl to the heterocycle could be a reason for the easily performed reductive ring opening reaction. Insertion of a *p*-phenylene spacer between the isoxazoline ring and the acceptor group in derivative **1b** does not change the redox system significantly compared to the reference system **1d**. Obviously the distance between pentafluoro-phenyl acceptor group and fullerene is too large. On the other hand leads the insertion of a *o*-phenylene spacer in compound **1c** to an enhancement of the acceptor ability of the fullerene system. With a difference of 70 mV is the effect as strong as in derivative **1a** with the difference that in **1c** the reduction of the fullerene system does not easily lead to irreversible processes due to a N-O bond cleavage in the heterocycle. We assume that the *o*-phenylene spacer forces a geometry in which the pentafluoro-phenyl addent comes close to the fullerene surface. Therefore we propose a through space interaction rather than a through bond mechanism.

We are continuing our investigations into the concept of through space interactions.

Experimental Section

Instrumentation

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AC 300 and DRX 300 spectrometers. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane. UV-VIS spectra werde taken on a Hewlett Packard HP 8452 A Diode Array spectrophotometer. FT-IR spectra were recorded on a Bruker IFS 66 spectrophotometer and mass spectra were obtained on a VG-ZAB-2F (electron impact), on a JOEL JMS-700 (FAB) and on a Bruker Biflex-(MALDI-TOF; negative mode, matrix: 9-nitro-anthracene). Melting points were determined with a Büchi apparatus and are uncorrected. Cyclic votammograms were taken on a HEKA potentiostat/galvanostat, model 285/IEC using the program HEKA.POT (Vers. 3.01; HEKA Electronic).

Materials

[60]Fullerene was extracted from fullerene containing carbon soot using a literature procedure.[14] Tetra-*n*-butyl-ammonium hexafluoro-phosphate was purchased from Fluka. 1,2-Dichloro-benzene (spectrophotometric grade, Aldrich) was treated with neutral alumina (dried under vacuum at 250 °C) before use. All other reagents were used as purchased from Fluka and the pentafluoro-benzaldoxime **2a** was prepared by a literature procedures.[12]

General procedure for the synthesis of the isoxazolo-fullerenes 1a-c

277.5 μmol of the aromatic oxime was solved in 40 ml of chloroform and cooled with an ice bath to 5 °C. To this solution 74.2 mg (555.0 μmol; 2 eq.) of *N*-chlorosuccinimide (NCS) and 10 μl of pyridine was added. The reaction mixture was stirred for 3 h at 5 °C and afterwards given to a suspension of 200 mg (277.5 μmol) of C_{60} solved in 200 ml of toluene and 23 mg of Na_2CO_3 solved in 5 ml of water. The mixture was stirred for one day and subsequently washed five times with water. The organic solvent was evaporated in vacuo and the remaining residue was purified by chromatography (eluant: CS_2).

3'-(2,3,4,5,6-Pentafluoro-phenyl)-isoxazolo[4',5':1,2][60]fullerene (1a). Yield 60.4 mg (23%) of brown crystals. ^{19}F NMR (282 MHz, CDCl$_3$) δ -139.44 (m, 2F), -151.50 (m, 1F), -162.67 (m, 2F). ^{13}C NMR (125 MHz, CDCl$_3$) δ 79.53 (1C, sp^3), 93.89 (1C, sp^3) 137.01 (2C), 137.03 (2C), 140.24 (2C), 140.85 (2C), 141.78 (2C), 142.04 (2C), 142.20 (2C), 142.34 (2C), 142.40 (2C), 142.46 (2C), 142.72 (2C), 142.84 (2C), 142.87 (2C), 142.99 (2C), 143.01 (2C), 144.05 (2C), 144.30 (2C), 144.61 (2C), 144.70 (2C), 145.22 (2C), 145.25 (2C), 145.27 (2C), 145.29 (CN), 145.74 (2C), 145.97 (2C), 146.09 (2C), 146.35 (2C), 146.43 (4C), 147.37 (1C), 147.93 (1C). The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. FT-IR(KBr) cm^{-1} 1520 (m), 1501 (s), 1440 (w, C$_{60}$), 1187 (w, C$_{60}$), 1074 (m), 992 (m), 804 (m), 769 (m), 575 (w, C$_{60}$), 527 (s, C$_{60}$). UV-VIS (CHCl$_3$): λ_{max}(lg ε) nm 232 (4.86), 256 (4.97), 316 (4.46). MS (MALDI-TOF, negativ-mode): m/z 929 (M$^-$), 720 (C$_{60}$-). HR-FAB-MS: m/z: 928.985 (M$^+$, calcd. 928,990).

3'-[4-(2,3,4,5,6-Pentafluoro-biphenyl)]-isoxazolo[4',5':1,2][60]fullerene (1b). Yield 79 mg (28%) of brown crystals. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.64 (d, ^{3}J=8.4 Hz, 2H), 8.38 (d, ^{3}J=8.4 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 80.75 (1C, sp^3), 97.38 (1C, sp^3), 128.85 (arom.), 129.08 (arom.), 130.03 (arom.), 130.92 (arom.), 136.77 (2C), 137.20 (2C), 140.36 (2C), 140.44 (2C), 141.75 (2C), 142.04 (2C), 142.32 (4C), 142.49 (2C), 142.51 (2C), 142.91 (4C), 143.03 (2C), 144.11 (2C), 144.16 (2C), 144.34 (2C), 144.43 (2C), 144.73 (2C), 145.20 (2C), 145.30 (2C), 145.42 (2C), 145.69 (2C), 145.71 (2C), 146.01 (2C), 146.07 (2C), 146.31 (2C), 146.34 (2C), 146.46 (2C), 147.35 (1C), 147.85 (1C), 153.20 (CN). The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. ^{19}F NMR (282 MHz, CDCl$_3$) δ -142.37 (m, 2F), -153.79 (m, 1F), -161.06 (m, 2F). FT-IR(KBr) cm^{-1} 1650 (w, C=N), 1492 (s), 1428 (w, C$_{60}$), 1066 (m), 988 (s), 849 (s), 730 (m), 527 (s, C$_{60}$). UV-VIS (CHCl$_3$) λ_{max}(lg ε) nm 230 (4.74), 256 (4.93), 316 (4.39). MS (MALDI-TOF, negative-mode): m/z 1006 (M$^-$), 720 (C$_{60}$-). HR-FAB-MS: m/z 1005.029 (M$^+$, calcd. 1005.021).

3'-[2-(2,3,4,5,6-Pentafluoro-biphenyl)]-isoxazolo[4',5':1,2][60]fullerene (1c). Yield 50 mg (18%) of brown crystals. ^{1}H NMR (300 MHz, CS$_2$: CDCl$_3$ [1:1]) δ 7.52-7.55 (m, 1H), 7.68-7.71 (m, 2H), 8.15-8.18 (m, 1H). ^{13}C NMR (75 MHz, CS$_2$: CDCl$_3$ [1:1]) δ 79.27 (1C, sp^3), 100.16 (1C, sp^3), 127.66 (arom.), 129.36 (arom.), 129.96 (arom.), 130.16 (arom.), 130.61 (arom.), 132.49 (arom.), 136.36 (2C), 136.47 (2C), 140.32 (2C), 140.41 (2C), 141.78 (2C), 142.16 (2C), 142.19 (2C), 142.28 (2C), 142.48 (2C), 142.50 (2C), 142.88 (2C), 142.90 (2C), 143.03 (2C), 144.04 (2C), 144.12 (4C), 144.40 (2C), 144.69 (2C), 145.20 (2C), 145.26 (2C), 145.37 (2C), 145.47 (2C), 145.67 (2C), 145.98 (2C), 146.04 (2C), 146.31 (4C), 146.45 (2C), 147.32 (1C), 147.82 (1C), 151.86 (CN). The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. ^{19}F NMR (282 MHz, CDCl$_3$) δ -137.56 (m, 2F), -153.13 (m, 1F), -161.06 (m, 2F). FT-IR(KBr) cm^{-1} 1499 (m), 1066 (m), 990 (s), 853 (m), 772 (m), 761 (m), 527 (s, C$_{60}$). UV-VIS (CHCl$_3$): λ_{max}(lg ε) nm 220 (4.77), 224 (4.85), 232 (5.00), 256 (5.12), 316 (4.65). MS (MALDI-TOF, negative-mode): m/z 1006 (M$^-$), 720 (C$_{60}$-). HR-FAB-MS: m/z 1005.029 (M$^+$, calcd. 1005.021).

2',3',4',5',6'-Pentafluoro-biphenyl-4-carbaldehyde (3b). A solution of 0.26 ml (0.51 g; 2.04 mmol) of bromo-pentafluoro-benzene, 311 mg (2.04 mmol) of 4-formylphenyl-boronic acid, 70 mg (60.6 mmol) of tetrakis-(triphenylphosphin)-palladium, 10 ml of ethanol and 20 ml of toluene was stirred under an argon atmosphere. To this solution an aqueous solution of 10 ml 2 M Na$_2$CO$_3$ was added. The suspension was stirred for 24 h at 80 °C and afterwards the reaction mixture was washed three times with water. The organic solvent was removed in vacuo and the residue was purified by flash chromatography (eluant: chloroform) yielding 350 mg (63%) of colourless crystals. Mp 78 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 10.08 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 129.84, 130.94, 132.41, 136.67, 191.39. The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. ^{19}F NMR (282 MHz, CDCl$_3$) δ -143.18 (m, 2F), -154.06 (m, 1F), -161.85 (m, 2F). FT-IR (KBr) cm^{-1} 1707 (s), 1534 (s), 1510 (m) 1488 (s), 1072 (m), 989 (s), 836 (m), 821 (m). UV-VIS (CHCl$_3$) λ_{max} nm (lg ε) = 264 (4.31). MS: m/z 272 (M$^+$), 244 (M$^+$-CO), 243 (M$^+$-CHO). HR-MS: m/z 272.026 (M$^+$, calcd. 272.026). Anal. Calcd for $C_{13}H_5F_5O$ (272.18): C 57.36; H 1.85. Found: C 57.37; H 1.90.

2',3',4',5',6'-Pentafluoro-biphenyl-2-carbaldehyde (3c). A solution of 0.52 ml (1.01 g; 4.08 mmol) of bromopentafluorobenzene, 612 mg (4.08 mmol) of 2-formyl-phenyl-boronic acid, 100 mg (86.5 μmol) of tetrakis-(triphenylphosphin)-palladium, 10 ml of methanol and 40 ml of toluene was stirred under an argon atmosphere. To this solution an aqueous solution of 20 ml of 2 M Na_2CO_3 was added. The suspension was stirred for 48 hours at 60 °C and afterwards the reaction mixture was washed three times with water. The organic solvent was removed in vacuo and the residue was purified by flash chromatography (eluant: chloroform) yielding 850 mg (76%) of colourless crystals. Mp 48 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, ^3J=7.9 Hz, 1H), 7.70-7.76 (m, 2H) 8.05 (dd, ^3J=7.0 Hz, ^4J=2.2 Hz, 1H), 9.95 (s, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.21, 130.25, 131.83, 132.25, 133.98, 134.32, 190.39 (CHO). The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. ^{19}F NMR (282 MHz, $CDCl_3$) δ -162.42 (m, 2F), -154.44 (m, 1F), -141.41 (m, 2F). FT-IR(KBr) cm^{-1} 1706 (s, C=O), 1573 (m), 1531 (m) 1491 (s), 696 (s).). UV-VIS ($CHCl_3$) λ_{max} nm (lg ε) 266 (4.14). MS: m/z 272 (M^+). HR-MS: m/z 272.026 (M^+, calcd. 272.026). Anal. Calcd for $C_{13}H_5F_5O$ (272.18): C 57.36; H 1.85. Found: C 57.26; H 2.00.

2′,3′,4′,5′,6′-Pentafluoro-biphenyl-4-carbaldoxime (2b). 500 mg (1.84 mmol) of 2′,3′,4′,5′,6′-pentafluoro-biphenyl-4-carbaldehyde was solved in 40 ml of ethanol and heated under reflux. To the boiling solution 1.27 g (18.4 mmol; 10 eq.) of hydroxylamine-hydrochloride solved in 5 ml of water and neutralized with soda was added. The reaction mixture was heated under reflux for one hour. To the hot solution ice water was given until the product starts precipitating. The oxime crystallized over night and was washed several times with water and finally dried at the air. The solid was purified by sublimation yielding 453 mg (86%) of colourless crystals.Mp 167 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.52 (d, ^3J=8.2 Hz, 2H), 7.74 (d, ^3J=8.2 Hz, 2H), 8.20 (s, 1H, HC=N), 11.48 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ 126.41, 126.72, 130.49, 134.23, 147.49 (C=N). The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.33 (m, 2F), -155.76 (m, 1F), -162.49 (m, 2F). FT-IR(KBr) cm^{-1} 3253 (s, br, OH), 1654 (m, C=N), 1406 (m), 1329 (m), 1073 (s), 989 (s), 938 (m), 850 (m), 832 (m). UV-VIS ($CHCl_3$) λ_{max}(lg ε) nm 272 (4.36). MS: m/z 287 (M^+) 270 (15) (M^+-OH). HR-MS: m/z 287.043 (M^+, calcd. 287.037). Anal. Calcd for $C_{13}H_6F_5NO$ (287.17): C 54.37; H 2.11, N 4.87. Found: C 54.42; H 2.18; N 4.88.

2′,3′,4′,5′,6′-Pentafluoro-biphenyl-2-carbaldoxime (2c). To a 100 ml round bottom flask 500 mg (1.84 mmol) of 2′,3′,4′,5′,6′-pentafluoro-biphenyl-2-carbaldehyde and 40 ml of ethanol was given and heated under reflux. To the boiling solution 1.27 g (18.4 mmol; 10 eq.) hydroxylamine-hydrochloride solved in 5 ml of water and neutralized with soda was added. The reaction mixture was heated under reflux for one hour. To the hot solution ice water was given until the product starts precipitating. The oxime crystallized over night and was washed several times with water and finally dried at the air. The solid was purified by sublimation yielding 249 mg (47 %) of colourless crystals. Mp 89 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.32 (m, 1H), 7.51-7.55 (m, 2H), 7.89-7.97 (m, 1H), 7.97 (s, 1H, HC=N), 8.76 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.52, 127.06, 129.98, 130.06, 131.18, 131.44, 147.88 (C=N). The carbon atoms of the pentafluoro-phenyl-substituent have not been detected due to ^{19}F-^{13}C-coupling. ^{19}F NMR (282 MHz, $CDCl_3$) δ -140.72 (m, 2F), -154.44 (m, 1F), -162.00 (m, 2F). FT-IR(KBr) cm^{-1} 3358 (s, br, OH), 1653 (m, C=N), 1524 (s), 1497 (s), 1450 (m), 1312 (m), 1107 (m), 1062 (s), 991 (s), 970 (s), 847 (m), 664 (m), 633 (m). UV-VIS ($CHCl_3$) λ_{max}(lg ε) nm 232 (4.27), 254 (4.17). MS: m/z 287 (M^+), 270 (M^+-OH), 269 (M^+-H_2O).). Anal. Calcd for $C_{13}H_6F_5NO$ (287.17): C 54.37; H 2.11, N 4.87. Found: C 54.32; H 2.17; N 4.84.

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