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Efficient Synthesis of 1,1'-(2,2-diphenylethene-1,1-diyl) Bis(1H-indole) by the Reaction of (2,2-difluoroethene-1,1-diyl) Dibenzene) with Indole Derivatives

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We report a convenient two-step methodology for the synthesis of 1,1'-(2,2-diphenylethene-1,1-diyl) bis(1H-indole). The cross-coupling reaction of 2,2-difluoro-1-iodoethenyl tosylate with 4 equiv of boronic acid in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ and K_3PO_4 resulted in the formation of symmetrical di-coupling products ((2,2-difluoroethene-1,1-diyl) dibenzene) in high yields. The symmetrical products of the (diphenylethene-1,1-diyl) bis(1H-indole) were obtained in high yield by the reaction of the di-coupling product ((2,2-difluoroethene-1,1-diyl) dibenzene) with 2 equiv. of indole derivatives in the presence of base.

Keywords: Boronic acid, catalysis, cross-coupling, iodoethnyl tosylate, gem-difluoroethene, palladium, indole

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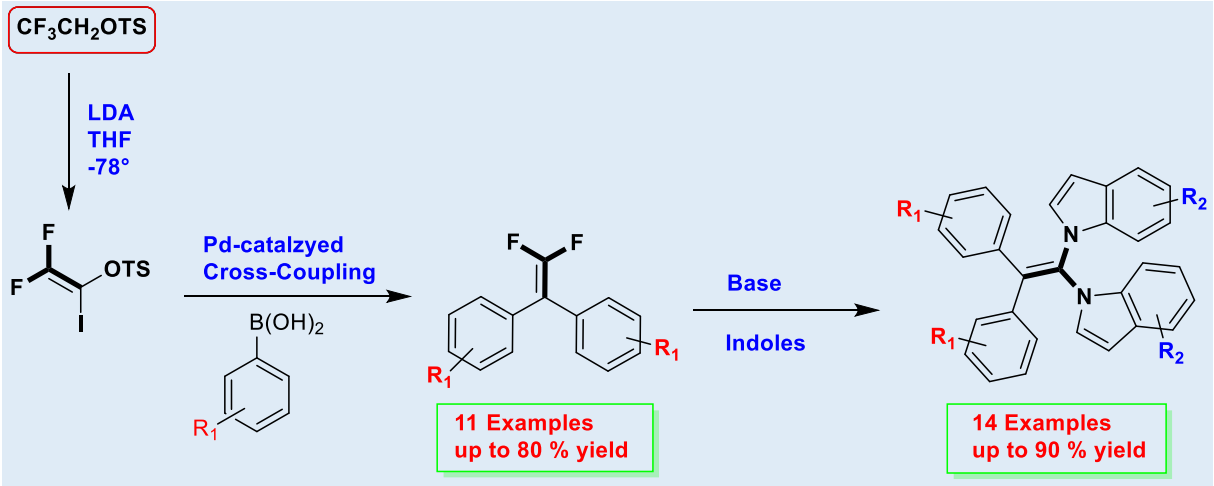
Graphical Abstract



The ubiquity of fluorinated organic molecules has been highlighted in organic chemistry and pharmaceuticals [1-4]. Successful incorporation of fluorine-containing structural motifs into bioactive compounds typically alters their biological and physicochemical properties, such as metabolic stability, lipophilicity, and potency [5-8]. Among numerous fluorine-containing compounds, gem-difluoroethene is an important structural motif found in many biologically active compounds, such as γ-aminobutyric acid aminotransferase inhibitors, mechanism-based enzyme inhibitors, antiepileptic drug candidates, and anticancer agents [9]. One of the most important classes of gem-difluoroethenes is 1,1-diaryl-2,2-difluoroethenes, which have the potential to be used for a wide range of purposes [10-12]. The synthesis of this compound has received much attention from synthetic organofluorine chemists in recent years because of their unique chemical reactivities toward nucleophiles to produce monofluorinated organic compounds [13-20]. Although numerous methods for the preparation of 2,2-disubstitutedbenzene-1,1-difluoroethenes have been reported in the previous literature [21-30], a consecutive cross-coupling reaction of a proper precursor such as a 1,1-difluoroethenylidene species bearing a metal functional group, a halogen substituent, or a tosylate group at the vinyl carbon will provide a concise and efficient method for the synthesis of 2,2-disubstitutedbenzene-1,1-difluoroethenes. The cross-coupling reactions of 2,2-difluoroethenyl tosylate appear to be promising approaches toward such 1,1-difluoro-1-alkene compounds because this tosylate

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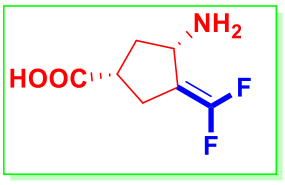
is readily attained from 2,2,2-trifluoroethanol, which has been widely employed as a solvent in organic synthesis [31-32].

The second step, including the reaction of indole derivatives with gem-Difluoroehtene in an unprecedentedly reported pathway to form novel fluorinated indole derivatives, and herein we report a facile synthesis of novel diphenylethene-containing indole derivatives, and we believe that our method will help medicinal chemists discover and rapidly construct a series of diphenylethene-containing indole derivatives.

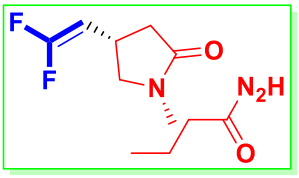
RESULTS AND DISCUSSION

Although the chemistry of the 2,2-difluoroethenylidene species as a building block has been well established in recent years, 2,2-difluoro-1-iodoethenyl tosylate 2 was previously prepared from the easily synthesized starting material 2 from the reaction of 2,2,2-trifluoroethyl tosylate 1, which is commercially available, with 2 equiv of LDA in THF at −78 °C, followed by treatment with 1 equiv of iodine (Scheme 1) [33].

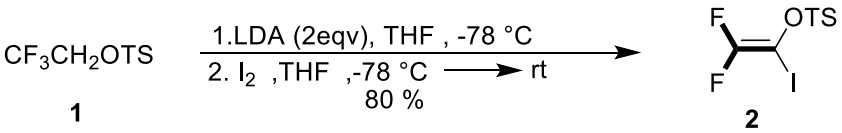
The Suzuki-Miyaura cross-coupling reaction required an additional optimization (Table 1). Table 1 shows the influence of different catalysts, bases, solvents, and temperatures. Initially tested the reaction was tested with pd2dba3 and K3PO4 in toluene at 90 °C these conditions delivered 4a, albeit, in only 15 % using of Pd(OAc) and KF in methanol at 45°C increased the yield to 30 % the replacing of methanol by ethanol and the KF by K3PO4 and reduce the temperature to room temperature deliver the product in 69 %. No product at all could be isolated when DMF was employed as a solvent.



γ-aminobutyric acid aminotransferase inhibitor

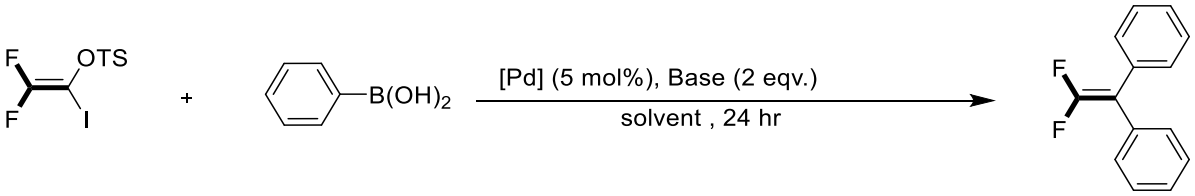


Seletracetam antiepileptic drug candidate



Scheme 1. Preparation of 2,2-difluoro-1-iodoethenyl tosylate 2.

Table 1. Optimization of the synthesis of 1,1-diaryl-2,2-difluoroethenes 4a.



2 **3** **4a**

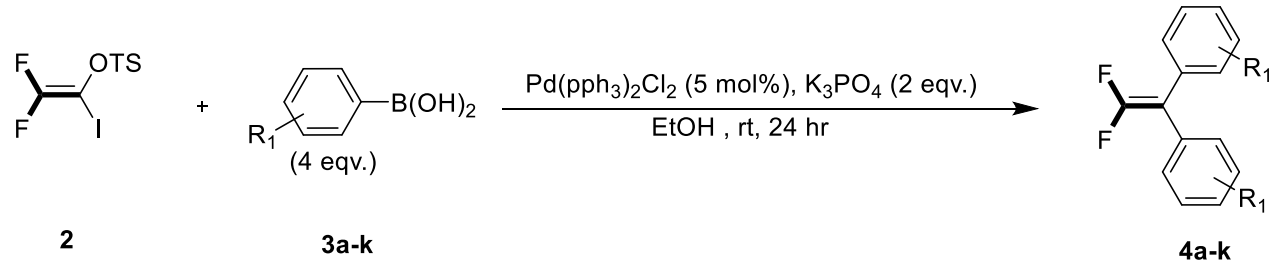
Entry	Base	Solvent	T [°C]	Catalyst	T [h]	Yield[a] (%)
1	K_3PO_4	Toluene	90	Pd_2dba_3	24	15
2	KF	DMF	120	$Pd(PPh_3)_4$	24	traces
3	KF	MeOH	45	$Pd(OAc)_2$	24	30
4	**K_3PO_4**	**EtOH**	**rt**	**$Pd(PPh_3)_2Cl_2$**	**24**	**69**
5	K_3PO_4	EtOH	40	$Pd(PPh_3)_2Cl_2$	24	45
6	Cs_2CO_3	EtOH	rt	$Pd(OAc)_2$	24	25

Conditions: i: 2 (1.0 eq.), phenylboronic acid (4.0 eq.), Pd $(PPh_3)_2Cl_2$ (5 mol%), K_3PO_4 (2.0 eq.), EtOH, rt, 24 h, a) isolated yield.

Table 2 summarizes the products of the Suzuki-Miyaura cross-coupling reaction starting from 4a-k using our optimized reaction conditions. A variety of different arylboronic acids were successfully employed to achieve a broad substitution pattern. 3-methoxy boronic acid gave the highest yield (product 4i). While the employment of 3,5-dimethylarylboronic acid (product 4h) resulted in decreased yields. In general, the yield of products was very satisfying, which clearly indicates the activity of the synthesis method.

The second step of our work includes the reaction of 1,1-diaryl-2,2-difluoroethenes 4a-k with indole derivatives 5a-d to synthesize the finally novel compounds 1,1'-(2,2-diphenylethene-1,1-diyl) bis(1H-indole) 6a-n. The reactions were carried out by using K2PO4 (4 equiv.), indoles (2 equiv.), and DMF as a solvent at 120 °C for 12 hr. During the optimization of the reaction conditions (Table 2), it proved to be important to carry out the reaction at 120 °C rather than at 140 °C to improve the yield. The reactions proceeded very well, and very good yields were obtained for the products.

Table 2. Synthesis of 1,1-diaryl-2,2-difluoroethenes 4a-k.



2 **3a-k** **4a-k**

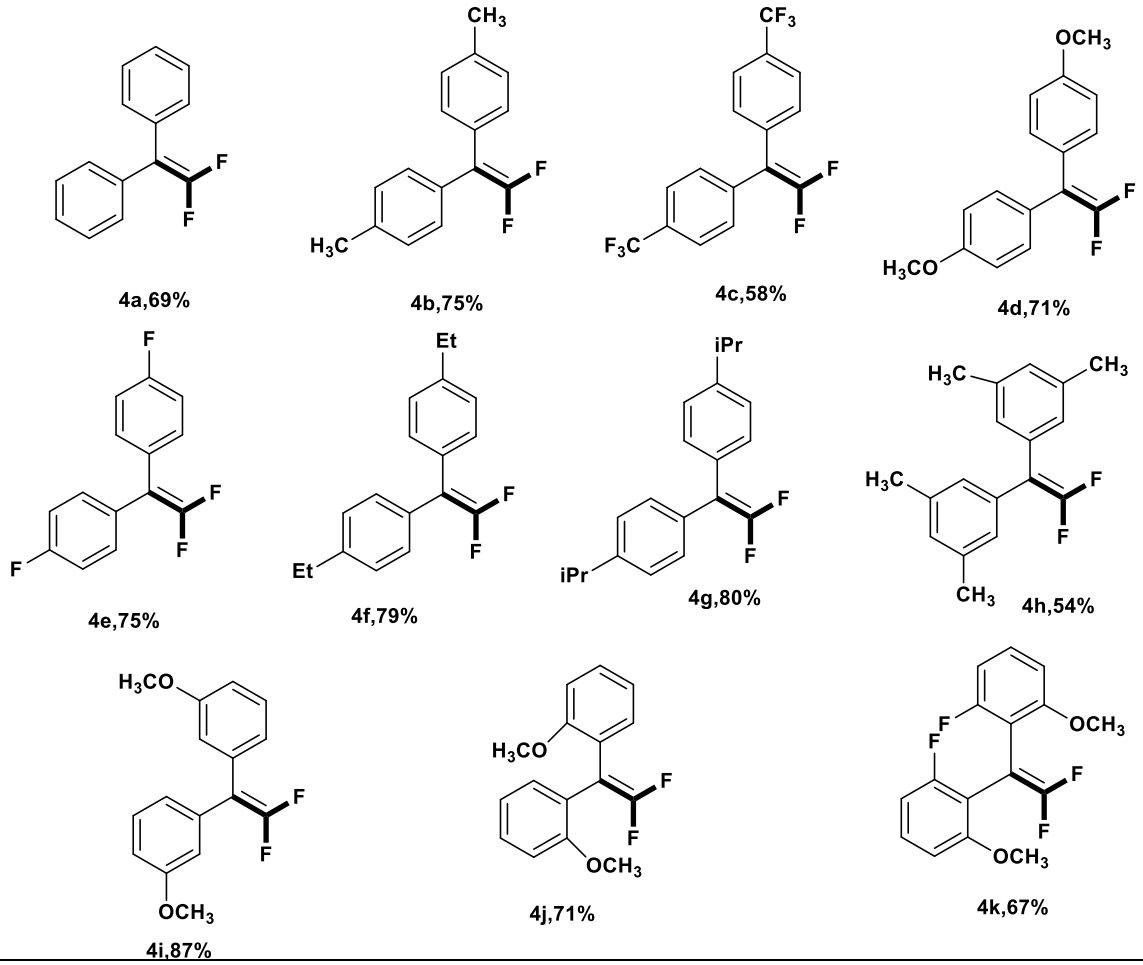
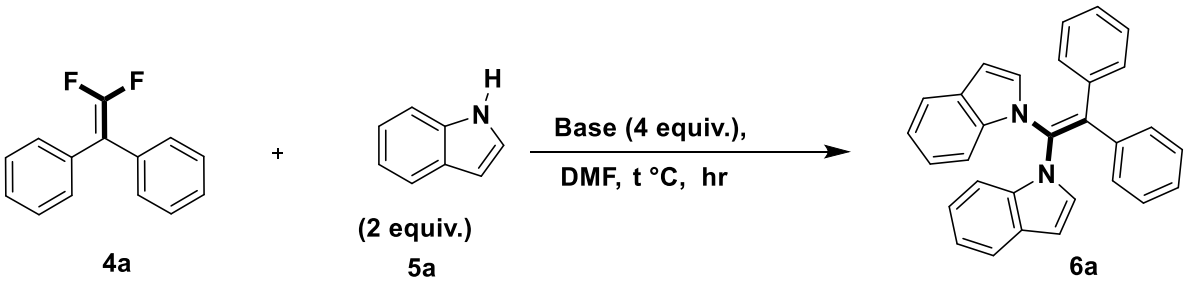


Table 3. Optimization of the synthesis of 1,1'-(2,2-diphenylethene-1,1-diyl) bis(1H-indole).



Entry	Base (equiv.)	Solvent	T [°C]	Tim,h	Yield[a] (%)
1	K_3PO_4 (4)	DMF	100	20	70
2	**K_3PO_4 (4)**	**DMF**	**120**	**12**	**90**
3	K_3PO_4 (4)	DMF	120	12	89
4	K_2CO_3 (4)	DMF	120	12	12
5	K_3PO_4 (4)	DMF	120	20	94
6	K_3PO_4 (4)	DMF	130	12	91
7	K_3PO_4 (4)	DMF	140	12	78

Conditions: i: Condition: K_3PO_4 (4.0 eq.), DMF, 120 °C, 24 h; [a)] isolated yields.

Table 4 summarizes the products of the reaction of indole derivatives with gem- Difluoroehtene using our optimized reaction conditions. Four types of indole derivatives have been successfully employed (5a-d) (R2H, 5-F, 5-OCH3, 5-CN) to achieve a broad substitution pattern.

EXPERIMENTAL SECTION

General Information

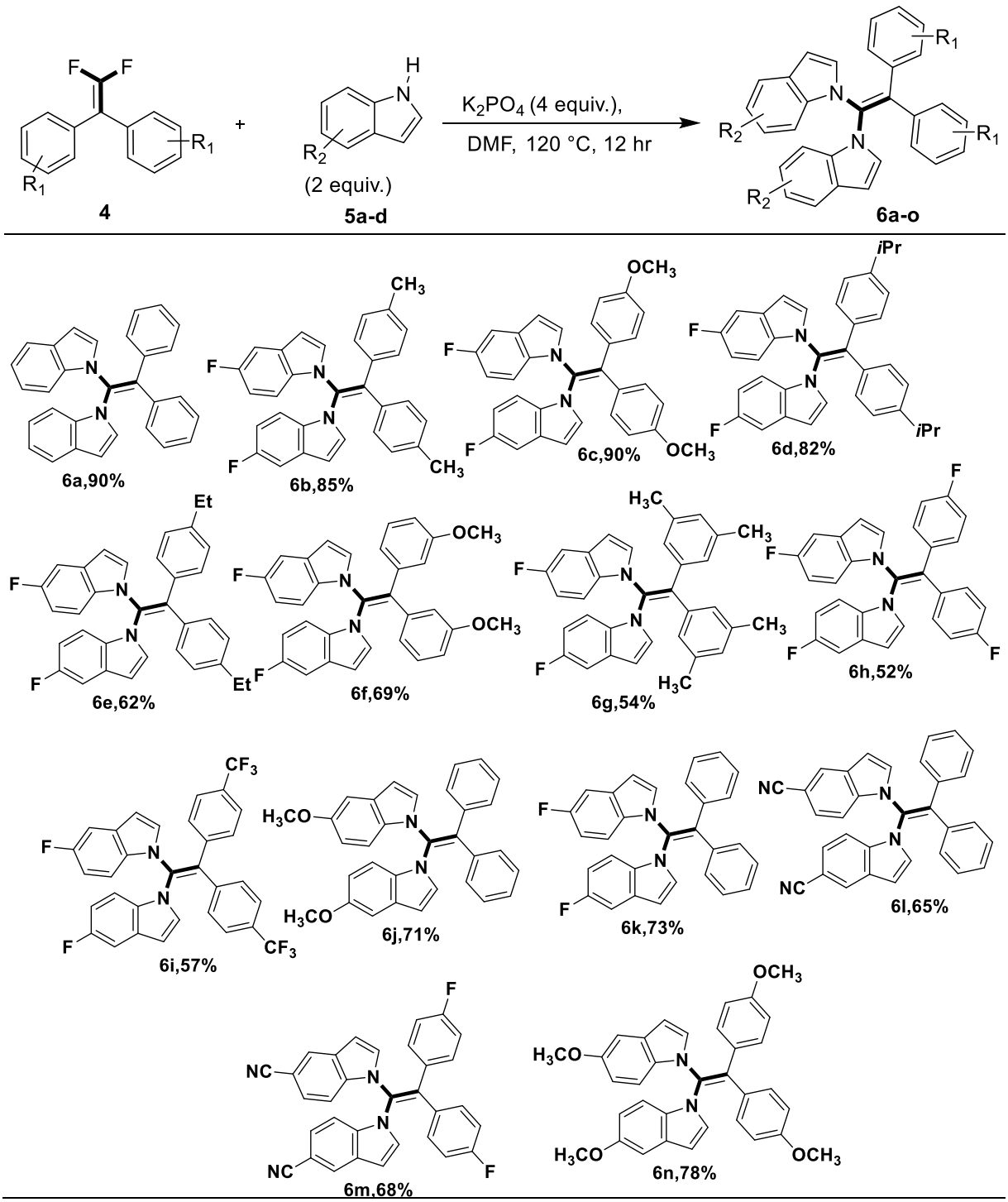
The nuclear magnetic resonance spectra ($^1H/^{13}C/^{19}F$ NMR) were recorded on a Bruker AVANCE 300 III, 250 II, or 500 spectrometers. Analysed chemical shifts δ are referenced to residual solvents signals of the deuterated solvents $CDCl_3$ (δ = 7.26 ppm/77.2 ppm), DMSO-d_6 (δ = 2.50 ppm/39.5 ppm), or TFA-d (δ = 11.50 ppm/164.2 ppm). Multiplicities due to spin-spin correlation are reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, m = multiplet, and further described through their coupling constants J. Infrared spectra (IR) were measured as attenuated total reflection (ATR) experiments with a Nicolet 380 FT-IR spectrometer. The signals have been characterized through their wave numbers ṽ, and their corresponding absorption as very strong (vs), strong (s), medium (m), weak (w).

EXPERIMENTAL SECTION

General procedure for the synthesis of 2,2-difluoro-1-iodoethenyl p-toluene sulfonate (2)

A 250 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, septum, and adaptor connected to an argon source was charged with **1** 2,2,2-trifluoroethyl p-toluene sulfonate (3 g, 11.8 mmol) and 11 mL of dry THF. LDA (2.0 M solution, 13.0 mL, 26.0 mmol) was added dropwise to a stirred solution at −78 °C. After the addition was completed, the solution was stirred −78 °C for 30 min, and then iodine (3 g, 11.8 mmol) was added slowly to the stirred solution. The mixture was allowed to warm to room temperature over 2 h, then quenched with aqueous ammonium chloride (50 mL), the solution was extracted with ether (100 mL × 2), washed with 5% KF and brine, dried over anhydrous Na_2SO_4, and the residue was purified by column chromatography (silica gel, heptane/EtOAc) **2** [25].

Table 4. Synthesis of 1,1'-(2,2-diphenylethene-1,1-diyl) bis(1H-indole)6a-n.



2,2-difluoro-1-iodoethenyl p-toluene sulfonate (2): Was isolated as a yellow oil. (1.2697 g, 3,537 mmol, 90 %). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 2.40 (3H, s, CH_3), 7.32 (2H, d, *J* = 8.2 Hz, ArH), 7.76 (2H, d, *J* = 8.3 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.84 (CH_3), 57.43 (dd, $J_{F,C}$ = 56, 25 Hz, CF_2), 57.63 , 57.90, 58.10 (C), 128.39, 130.15, 152.90, 157.58 (CH),^{19}F NMR (471, MHz): δ = -93.62, -78.31 (CF). IR (KBr, cm^{-1}): ν = 2936 (w), 2833 (w), 2964 (w), 1596 (w), 1572 (s), 1475 (s), 1409 (m), 1370 (m), 1340 (m), 1230 (s), 1201(s), 1116 (s),1028 (s), 851 (m),770 (m). GC-MS (EI, 70 eV): *m/z* (%) = 360 ([M]$^+$, 100), 184 (11), 183 (77), 106 (10), 105 (54), 78 (11), 77 (73), 51 (23). HRMS (EI,

70 eV) calcd for $C_9H_7F_2O_3IS$ ([M]$^+$): 359.91232, found: 359.91192.

General procedure for the synthesis of (2,2-difluoroethene-1,1-diyl) dibenzene(4a-k): In a glass pressure tube, a solution of **2** (70 mg, 0.194 mmol), K_3PO_4 (82 mg, 0.389 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol %, 0.010 mmol), and arylboronic acid (94 mg, 0.778 mmol)) In EtOH (8 mL) was stirred at room temperature for 24 h. under an argon atmosphere and then quenched with water. The reaction mixture was extracted with ethyl acetate (10 mL × 2), washed with 5% KF and brine. The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in a vacuum. The residue was purified by column chromatography (silica gel, heptane/EtOAc) and obtained as a colorless oil in 69 % yield.

(2,2-difluoroethene-1,1-diyl) dibenzene(4a): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3a**) (94 mg, 0.778 mmol,) and EtOH (8 mL), (**4a**) was isolated as colorless oil (29 mg, 69 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.07 – 7.29 (6H, m, ArH), 7.34 (2H, t, J =7.4 Hz, ArH), 7.48 (2H, d, J = 0.8 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 57.43 (dd, $J_{F,C}$ = 56, 25 Hz, CF_2), 57.63 , 57.90, 58.10, 128.39, 128.95, 129.79, 129.82, 129.85 (CH), 130.15, 152.90, 157.58 (C), ^{19}F NMR (282, MHz): δ = -87.74 (CF). IR (KBr, cm^{-1}): 3047 (w), 2853 (w), 2596 (w), 2417 (w), 2326 (w), 2050(w), 1891(w), 1594 (w) , 1487 (w), 1392 (w), 1318 (s), 1228 (s) . GC-MS (EI v = eV): *m/z* (%) = 216 ([M]$^+$, 100), 215 (38), 214 (19), 196 (20), 165 (75), 166 (27), 164 (11), 83 (12). HRMS (EI, 70 eV) calcd for $C_{14}H_{10}F_2$ ([M]$^+$): 216.07451, found: 216.07391.

4,4'-(2,2-difluoroethene-1,1-diyl) bis(methylbenzene) (4b): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3b**) (105 mg, 0.778 mmol) and EtOH (8 mL), (**4b**) was isolated as colorless oil (36 mg, 75 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.29 (6H, d, J =10.2 Hz, 3xCH_3), 7.07 (4H, s, ArH), 7.16 (2H, d, J = 8.6 Hz, ArH), 7.39 (2H, s, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.17 (2xCH_3), 29.72 (C), 95.84 (dd, $J_{F,C}$ = 46, 27 Hz, CF_2), 126.81, 129.07 129.43, 129.45(C), 129.50, 131.52, 136.69, 137.27, 138.30, 153.26, 153.61(CH) ,^{19}F NMR (282, MHz): δ = -88.70 (CF). IR (KBr, cm^{-1}): v = 2959 (m), 2926 (m), 2868 (m), 1493 (m), 1399 (m), 1370 (w), 1316 (w), 1271 (w), 1182 (w), 1137 (w), 1048 (m), 1003 (m), 962 (m), 813 (m), 764 (m). GC-MS (EI, 70 eV): *m/z* (%) = 244 ([M]$^+$, 100), 229 (28), 228 (11), 214 (26), 193 (17), 179 (11), 178 (17). HRMS (EI, 70 eV) calcd for $C_{16}H_{14}F_2$ ([M]$^+$): 244.10636, found: 214.10657.

4,4'-(2,2-difluoroethene-1,1-diyl) bis ((trifluoromethyl) benzene)(4c): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3c**) (147 mg, 0.778 mmol) and EtOH (8 mL), (**4c**) was isolated as colorless oil (40 mg, 58 %).^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.23 (2H, d, J = 8.1 Hz, ArH), 7.56 (6H, d, J = 5.9 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ= 122.18, 122.37 (dd, $J_{F,C}$ = 69.14 Hz, CF_2), 125.51, 125.56 (d, $J_{F,C}$ = 246.9 Hz, CF_3), 125.61, 125.66 (dd, $J_{F,C}$ = 246.0 Hz, CF_3), 125.85, 125.90, 125.96, 126.00, 127.59, 129.88 129.93, 129.97 (CH), 130.12 (d, $J_{F,C}$ = 19.12 Hz, C), 130.56 (d, $J_{F,C}$ = 16.34 Hz, C), 137.28, 143.24 (C),^{19}F NMR (282, MHz): δ = -84.68 ($ArCF_3$), -62.86 (CF). IR (KBr, cm^{-1}): v = 3368 (m), 3047 (w), 2925 (w), 2856 (w), 2464 (w), 2398 (w), 2025(w), 1891(w), 1586 (m), 1487 (m), 1487 (m), 1392 (m), 1318 (w), 1228 (s), 1156 (m), 1108 (m), 1009 (m), 1005 (m). GC-MS (EI, 70 eV): *m/z* (%) = 352 ([M]$^+$, 100), 333 (25), 332 (13), 283 (25), 282 (19), 263 (19), 233 (33), 232 (10), 214 (47). HRMS (EI, 70 eV) calcd for $C_{16}H_8F_8$ ([M]$^+$): 352.04928, found: 352.04869.

4,4'-(2,2-difluoroethene-1,1-diyl) bis(methoxybenzene) (4d): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3d**) (118 mg, 0.778 mmol) and EtOH (8 mL), (**4d**) was isolated as colorless oil (38 mg, 71 %).^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.76 (6H, s, 2xOCH_3), 6.88 (4H, d, J = 8.9 Hz,ArH), 7.40 (4H, d, J = 8.9 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 54.28 (2xOCH_3), 94.43 (dd, $J_{F,C}$ = 76.01 Hz, CF_2), 112.77, 113.14, 125.75, 126.69, 127.38 (C), 129.02, 129.63, 129.67, 130.23, 132.45, 145.06, 148.56, 152.43 (CH) ,^{19}F NMR (282, MHz): δ = -89.80 (CF). IR (KBr, cm^{-1}): v = 2050 (w), 1969 (w), 1891 (w), 1592 (w), 1487 (s), 1392 (m), 1320 (w), 1228 (s), 1156 (m), 1108 (m), 1013 (m), 1003 (m) , 818 (s), 764 (m), 692 (m). GC-MS (EI, 70 eV): *m/z* (%) = 276 ([M]$^+$, 100), 274 (28), 226 (10), 225 (27), 210 (17), 201 (12). HRMS (EI, 70 eV) calcd for $C_{16}H_{14}O_2F_2$ ([M]$^+$): 276.09564, found: 276.09633.

4,4'-(2,2-difluoroethene-1,1-diyl) bis(fluorobenzene) (4e): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3e**) (94 mg, 0.778 mmol,) and EtOH (8 mL), (**4e**) was isolated as colorless oil (34 mg, 70 %).^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 7.04 (4H, t, J = 8.6 Hz, ArH), 7.41 (4H, dd, J = 5.3, 8.7 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ 77.44, 115.39 (dd, $J_{F,C}$ = 72.13 Hz, CF_2), 115.54, 115.68, 115.75 (CH), 115.82 (d, $J_{F,C}$ = 68.10 Hz, CF), 127.02, 127.25 (CH), 128.40 (d, $J_{F,C}$ = 62.11 Hz, CF), 128.52, 128.63, 128.74 (CH), 128.82, 136.38 (C),^{19}F NMR (282, MHz): δ = -115.76 (ArF), -87.92 (F). IR (KBr, cm^{-1}): v = (:::) 3109 (w), 2961 (w), 2866 (w), 2223 (w), 1815 (w), 1739 (w), 1640 (w), 1607, 1508 (m), 1156 (w), 1201 (w), 1116 (w),1467 (w), 1415 (w), 1345 (w), 1320 (w). GC-MS (EI, 70 eV): *m/z* (%) = 252 ([M]$^+$, 100), 232 (25), 202 (13), 201 (20), 181 (19), 175 (10), 107 (12), 105 (17), 98 (10), 87 (12), 75 (38), 74 (12), 70 (16), 62 (10), 57 (33), 51 (38), 50 (18), 33 (14), 31 (24). HRMS (EI, 70 eV) calcd for $C_{14}H_8F_4$ ([M]$^+$): 252.05566, found: 252.05546.

4,4'-(2,2-difluoroethene-1,1-diyl) bis(ethylbenzene) (4f): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3f**) (116 mg, 0.778 mmol,) and EtOH (8 mL), (**4f**) was isolated as colorless oil (42 mg, 79 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 1.19 (6H, t, J=7.6 Hz,

2xCH_3), 2.53 – 2.66 (4H, m, 2xCH_2), 7.17 (4H, d, *J*=8.5 Hz, ArH), 7.42 (4H, d, *J*=8.3 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 15.61 (2xCH_3), 28.54 (2xCH_2), 126.88, 126.96, 127.87, 128.26 (d, $J_{F,C}$ = 69.11 Hz, CF_2), 128.73 (C), 129.46, 129.56, 131.66, 136.71, 138.36, 138.62, 143.08, 143.47 (CH),^{19}F NMR (282, MHz): δ = -88.57 (CF). IR (KBr, cm^{-1}): ν = 3323 (m), 3109 (w), 2924 (w), 2853 (w), 2221 (w), 1739 (s), 1607 (m), 1574 (w), 1508 (w), 1467 (m), 1415 (m), 1345 (m), 1320 (m), 1250 (m), 1219 (m). GC-MS (EI, 70 eV): *m/z* (%) = 272 ([M]$^+$, 100), 258 (15), 257 (89), 243 (10), 227 (12), 121 (14), 105 (10). HRMS (EI, 70 eV) calcd for $C_{18}H_{18}F_2$ ([M]$^+$): 272.13711, found: 272.13687.

4,4'-(2,2-difluoroethene-1,1-diyl) bis(isopropylbenzene) (4g): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3g**) (127 mg, 0.778 mmol,) and EtOH (8 mL), (**4g**) was isolated as colorless oil (47 mg, 80 %).^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 1.53 (12H, d, *J* = 6.9 Hz, 4xCH_3), 3.17 (2H, p, *J* = 6.6 Hz, 2xCH), 7.52 (4H, d, *J* = 8.1 Hz, ArH), 7.76 (4H, d, *J* = 8.2 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 24.25 (4xCH_3), 34.01 (2xCH), 112.2 (dd, $J_{F,C}$ = 74.11 Hz, CF_2), 126.61, 127.16, 127.29, 128.91, 129.76, 132.09, 134.11 (C), 135.59, 136.59, 136.72, 138.95, 139.33, 147.79 (CH),^{19}F NMR (282, MHz): δ = -88.52 (CF). IR (KBr, cm^{-1}): ν = 2917 (w), 2861 (w), 2598 (w), 2431 (w), 2050 (w), 1978 (w), 1891 (w), 1592 (w), 1485 (m), 1156 (s), 1108 (m), 1103 (s), 818 (m), 803 (m), 700 (m). GC-MS (EI, 70 eV): *m/z* (%) = 300 ([M]$^+$, 74), 286 (21), 285 (100), 220 (10), 215 (15), 203 (14), 202 (18), 191 (10), 165 (24), 152 (16), 146 (16), 127 (10), 116 (25), 104 (35), 91 (11), 79 (10), 51 (20). HRMS (EI, 70 eV) calcd for $C_{20}H_{22}F_2$ ([M]$^+$): 300.16841, found: 300.16841.

5,5'-(2,2-difluoroethene-1,1-diyl) bis(1,3-dimethylbenzene) (4h): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3h**) (116 mg, 0.778 mmol,) and EtOH (8 mL), (**4h**) was isolated as colorless oil (29 mg, 54 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.69 (12H, d, *J*=27.8 Hz, 4xCH_3), 7.29 (5H, d, *J*=4.1 Hz, ArH), 7.60 (1H, s, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.47 (2xCH_3), 21.63 (2xCH_3), 96.62 (d, $J_{F,C}$ = 17.90 Hz, CF_2), 125.48, 127.76, 129.07, 129.07 (CH), 138.11, 138.34 (C), 129,58, 141.91, 145.83, 150.23, 150.61 (CH), 154.10, 157.97 (C),^{19}F NMR (282, MHz): δ = -87.89 (CF). IR (KBr, cm^{-1}): ν = 3052 (m), 3039 (m), 1941 (w), 1849 (w), 1720 (w), 1591(s), 1523 (s), 1470 (s), 1427 (w), 1300 (m), 1168 (m), 1078 (m), 1042 (m), 1020 (m), 903 (m). GC-MS (EI, 70 eV): *m/z* (%) = 272 ([M]$^+$, 100), 257 (22), 242 (25), 221 (10), 207 (10). HRMS (EI, 70 eV) calcd for $C_{18}H_{18}F_2$ ([M]$^+$): 272.13711, found: 272.13736.

3,3'-(2,2-difluoroethene-1,1-diyl) bis(methoxybenzene) (4i): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3i**) (118 mg, 0.778 mmol,) and EtOH (8 mL), (**4i**) was isolated as colorless oil (47 mg, 87 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.92 (6H, d, *J*=44.7 Hz, 2xOCH_3), 7.04 (4H, dd, *J*=7.8, 27.6 Hz, ArH), 7.31 – 7.44 (3H, m, ArH), 7.50 (1H, t, *J*=7.9 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 55.17 (1xOCH_3), 55.24 (1xOCH_3), 96.23 (d, $J_{F,C}$ = 18.11 Hz, CF_2), 101.33 (d, $J_{F,C}$ = 18.11 Hz, C), 101.44, 112.92, 113.17, 115.66 (CH), 119.81, 122.22 (C), 129,58, 129.95, 135.62, 142.78 (CH), 159.82, 160.21 (C),^{19}F NMR (282, MHz): δ = -86.76 (CF). IR (KBr, cm^{-1}): ν = 3057 (m), 3033 (m), 1943 (w), 1846 (w), 1747 (w), 1596 (m), 1568 (m), 1475 (m), 1428 (s), 1343 (m), 1170 (m), 1090 (m), 1040 (m), 1003 (m), 902 (m), 725 (m). GC-MS (EI, 70 eV): *m/z* (%) = 276 ([M]$^+$, 100), 245 (26), 230 (10), 214 (12), 213 (13), 201 (24), 189 (11), 188 (14), 183 (12), 139 (12), 63 (11), 39 (12). HRMS (EI, 70 eV) calcd for $C_{16}H_{14}O_2F_2$ ([M]$^+$): 276.09564, found: 276.09490.

2,2'-(2,2-difluoroethene-1,1-diyl) bis(methoxybenzene) (4j): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3j**) (118 mg, 0.778 mmol,) and EtOH (8 mL), (**4j**) was isolated as colorless oil (38 mg, 71 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.66 (6H, s, 2xOCH_3), 6.85 – 6.94 (4H, m, ArH), 7.13 – 7.26 (4H, m, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 55.74 (2xOCH_3), 99.23 (d, $J_{F,C}$ = 20.10 Hz, CF_2), 111.33 (d, $J_{F,C}$ = 32.13 Hz, C), 120.41, 127.92, 128.47, 129.02 (CH), 146.15, 146.25 (C), 130.85, 131.16, 131.54, 132.26 (CH), 159.82, 160.21 (C),^{19}F NMR (282, MHz): δ = -86.62 (CF). IR (KBr, cm^{-1}): ν = 3086 (w), 3057 (w), 3031 (m), 2924 (m), 2804 (m), 1943 (w), 1877 (w), 1813 (w), 1794 (w), 1747 (w), 1662 (w), 1596 (s), 1568 (s), 1475 (m), 1428 (m), 1343 (m), 1254 (m), 1170 (m), 1110 (m), 1081 (m), 1040 (m), 902 (s). GC-MS (EI, 70 eV): *m/z* (%) = 276 ([M]$^+$, 100), 261 (17), 241(29), 221 (16), 193 (10), 183 (27), 165 (41), 91 (14). HRMS (EI, 70 eV) calcd for $C_{16}H_{14}O_2F_2$ ([M]$^+$): 276.09564, found: 276.09575.

2,2'-(2,2-difluoroethene-1,1-diyl)bis(4-fluoro-1-methoxybenzene)(4k): Starting with (**2**) (70 mg, 0.194 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol- %, 0.010 mmol), K_3PO_4 (82 mg, 0.389 mmol), (**3k**) (132 mg, 0.778 mmol) and EtOH (8 mL), (**4k**) was isolated as colorless oil (40 mg, 67 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.65 (6H, s, 2xOCH_3), 6.69 – 6.77 (2H, m, ArH), 7.29 (2H, d, *J* = 8.0 Hz, ArH), 7.73 (2H, d, *J* = 8.4 Hz, ArH), ^{13}C NMR (126 MHz, $CDCl_3$) δ = 56.27 (2xOCH_3), 100.38, 100.58 (d, $J_{F,C}$ = 59.10 Hz, CF_2), , 101.17, 101.38, 112.23, 112.35, 115.09, 115.39 (CH), 117.81, 117.84, 118.09 (d, $J_{F,C}$ = 17.11 Hz, C), 118.12, 118.15 (d, $J_{F,C}$ = 15.12 Hz, C), 124.35, (C),^{19}F NMR (282, MHz): δ = -124.13 (ArF), -85.22 (F). IR (KBr, cm^{-1}): ν =3068 (w), 3047 (w), 2856 (w), 2398 (w), 2050 (w), 1891 (w), 1759 (w), 1697 (w) , 1594 (m), 1487 (m), 1395 (m), 1320 (m), 1228 (s), 1156 (m), 1108 (m), 1013 (m), 956 (s), 941 (s). GC-MS (EI, 70 eV): *m/z* (%) = 312 ([M]$^+$, 89), 277 (46), 257 (43), 253 (10), 237 (12), 235 (25), 229 (17), 219 (42), 217(18), 216 (25), 204 (19), 202 (16), 199 (11), 188 (22), 175 (18), 168 (10), 109 (20), 99 (10), 81 (12), 57 (21), 33 (11), 29 (11). HRMS (EI,

70 eV) calcd for $C_{16}H_{12}O_2F_4$ ([M]$^+$): 312.07679, found: 312.07663.

General procedure for the synthesis of 1,1'-(2,2-diphenylethene-1,1-diyl) bis(1H-indole) (6a-n): In a glass pressure tube to (0.5 mmol, 108.0 mg, 1 equiv.) of compound **4** were added (1.0 mmol, 135.1 g, 2 equiv.) of **5**, (2 mmol, 424.5 mg, 4 equiv.) of K_3PO_4 and DMF (8-10 mL). Reaction was stirred at 120 °C for 12 h. After cooling to room temperature reaction was quenched with H_2O, aqueous phase was extracted with EtOAc (3 times). The combined organic layers were washed with brine and dried over (Na_2SO_4), filtered and concentrated under reduced pressure. The synthesized compound **6** was purified by column chromatography (silica gel, heptane/EtOAc). The final product was obtained as a colorless, thick oil in 90% yield.

1,1'-(2,2-diphenylethene-1,1-diyl)bis(1H-indole)(6a): Starting with (**4a**) (108 mg, 0.5 mmol), (117 mg, 1 mmol) (**5a**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6a**) was isolated as colorless, thick oil (185 mg, 90 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ= 6.35 (dd, *J* = 0.8, 3.4 Hz, 2H, ArH), 6.62 – 6.67 (m, 2H, NCH), 6.80 (dd, *J* = 1.2, 7.1 Hz, 2H, CH), 6.83 – 6.87 (m, 3H, ArH), 6.87 – 6.94 (m, 7H, ArH), 6.95 – 7.01 (m, 7H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 105.45, 105,78, 111.24 (C), 111.25, 120.94, 121.07, 122.98, 128.27, 128.29. 128.33, 128.39, 129.11 (CH),129.26, 129.37, 129.39, 129.67, 135.93, 139.37, 139.76 (C). IR (KBr, cm^{-1}): *v* = 3052 (w), 3043 (w), 2921 (w), 2893 (w), 2486 (w), 2563 (w), 2396 (w), 2325 (w), 2212 (w), 2150 (w), 1997 (w), 1893 (w), 1758 (w), 1725 (s), 1678 (s), 1632 (m), 1591 (m), 1328 (m), 1322 (m), 1229 (m), 1155 (m), 1109 (m), 1011 (m), 1007 (m) , 819 (s), 804 (s). GC-MS (EI, 70 eV): *m/z* (%) = 411 ([M]$^+$, 50), 410 (100), 295 (35), 294 (99), 293 (19), 292 (17), 291 (14), 217 (14), 205 (12), 199 (15). HRMS (EI, 70 eV) calcd for $C_{30}H_{22}N_2$ ([M]$^+$): 411.18611 found: 410.18790.

1,1'-(2,2-di-p-tolylethene-1,1-diyl)bis(5-fluoro-1H-indole)(6b): Starting with (**4b**) (122 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6b**) was isolated as colorless, thick oil (201 mg, 85 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.13 (s, 6H, 2xCH_3), 6.32 (d, *J* = 3.3 Hz, 2H, NCH), 6.47 – 6.62 (m, 4H, ArH), 6.78 (q, *J* = 8.3 Hz, 8H, ArH), 6.89 (d, *J* = 3.4 Hz, 2H, CH), 7.00 – 7.13 (m, 2H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.22 (2xCH_3), 105.13, 105.19 (d, $J_{F,C}$ = 48.11 Hz, CF), 105.89, 106.20, 127.62 (d, $J_{F,C}$ = 60.16 Hz, CF), 128.88, 129.08, 129.12, 129.21, 129.39, 129.42, 129.56, 130.00 (CH), 132.33, 136.52, 137.46 (C).^{19}F NMR (282 MHz): δ = -123.80 (2xArF) . IR (KBr, cm^{-1}): *v* = 3111 (w), 3025 (w), 2919 (w), 1912 (w), 1860 (w), 1720 (w), 1615 (m), 1605 (m), 1582 (w), 1463 (w), 1463 (s), 1444 (s), 1395 (m), 1343 (m), 1320 (m), 1273 (m), 1246 (m), 1230 (m), 1211 (m), 1168 (s), 1139 (m), 1127 (m), 1050 (m), 1022 (m), 949 (m), 861 (m). GC-MS (EI, 70 eV): *m/z* (%) = 474 ([M]$^+$, 100), 341 (18), 340 (70), 325 (16), 324 (12), 310 (10), 309 (12), 155 (20), 137 (12), 109 (21). HRMS (EI, 70 eV) calcd for $C_{32}H_{24}F_2N_2$ ([M]$^+$): 474.1907 found: 473.9876.

1,1'-(2,2-bis(4-methoxyphenyl)ethene-1,1-diyl)bis(5-fluoro-1H-indole)(6c): Starting with (**4d**) (138 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6c**) was isolated as colorless, thick oil (227 mg, 90 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.65 (s, 6H, 2xOCH_3), 6.35 (dd, *J* = 0.7, 3.4 Hz, 2H, NCH), 6.50 – 6.65 (m, 8H, ArH), 6.77 – 6.86 (m, 4H,ArH), 6.92 (d, *J* = 3.4 Hz, 2H, CH), 7.08 (dd, *J* = 2.3, 9.1 Hz, 2H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 55.14 (2xOCH_3), 105.01, 105.02 (d, $J_{F,C}$ = 59.10 Hz, CF), 105.04, 105.09 (d, $J_{F,C}$ = 59.10 Hz, CF), 105.82, 106.13, 111.28, 111.54, 111.67, 113.76, 128.39, 129.33, 129.47, 130.66, 131.67 (CH), 132.22, 158.94. (d, $J_{F,C}$ = 15.12 Hz, C), 124.35 (C),^{19}F NMR (282, MHz): δ = -123.30 (2xArF). IR (KBr, cm^{-1}): *v* = 3132 (w), 3111 (w), 3077 (w), 3068 (w), 3047 (w), 2987 (w), 2938 (w), 2837 (w), 1934 (w), 1852 (w), 1726 (w), 1592 (w), 1595 (s), 1498 (s), 1495 (s), 1452 (s), 1442 (m), 1392 (m), 1335 (m), 1316 (m), 1283 (m), 1250 (m), 956 (s), 941 (s). GC-MS (EI, 70 eV): *m/z* (%) = 507 ([M]$^+$, 34), 506 (100), 373 (11), 372 (46), 341 (10), 235 (25), 328 (12), 238 (11), 223 (34), 195 (14), 152 (12), 134 (22), 107 (20). HRMS (EI, 70 eV) calcd for $C_{32}H_{24}F_2N_2O_2$ ([M]$^+$): 507.1884 found: 507.1876.

1,1'-(2,2-bis(4-isopropylphenyl)ethene-1,1-diyl) bis(5-fluoro-1H-indole)(6d): Starting with (**4g**) (150 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6d**) was isolated as colorless, thick oil (217 mg, 82 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 1.07 (s, 6H, 2xOCH_3), 1.10 (s, 6H, 2x2OCH_3), 2.71 (p, *J* = 6.9 Hz, 2H, 2xCH), 6.34 (dd, *J* = 0.6, 3.4 Hz, 2H. NCH), 6.46 – 6.64 (m, 4H, ArH), 6.76 – 6.82 (m, 4H, ArH), 6.84 – 6.93 (m, 6H, ArH), 7.07 (dd, *J* = 2.2, 9.3 Hz, 2H, CH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 22.73 (2xCH_3), 28.68 (2xCH_3), 32.66 (2xCH), 103.99, 104.04, (d, $J_{F,C}$ = 55.10 Hz, CF) 104.71, 105.02, 109.80, 110.14, 110.62, 110.75,125.27, 126.57, 127.73, 128.34 (CH), 128.99 (d, $J_{F,C}$ = 38.17 Hz, CF), 131.22, 135.65, 147.27, 158.95. (C).^{19}F NMR (282, MHz): δ = -123.41 (2xArF) . IR (KBr, cm^{-1}): *v* = 3115 (w), 3023 (w), 2919 (w), 1917 (w), 1868 (w), 1725 (w), 1615 (m), 1611 (m), 1573(w), 1463 (w), 1462 (s), 1444 (s), 1398 (m), 1344 (m), 1320 (m), 1277 (m), 1246 (m), 1231 (m), 1291 (m), 1168 (s), 1159 (m), 1137 (m), 1053 (m), 1022 (m), 940 (m), 861 (m), 845 (m). GC-MS (EI, 70 eV): *m/z* (%) =530 ([M]$^+$, 100), 335 (10), 338 (9), 325 (16), 310 (10), 136 (15), 135 (38), 134 (39), 108 (11), 107 (24), 104 (11), 43 (100), 41 (17). HRMS (EI, 70 eV) calcd for $C_{36}H_{22}F_2N_2$ ([M]$^+$): 530.25281 found: 530.25259.

1,1'-(2,2-bis(4-ethylphenyl)ethene-1,1-diyl)bis(5-fluoro-1H-indole)(6e): Starting with (**4f**) (136 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6e**) was isolated as colorless, thick oil (156 mg, 62 %). ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 1.05 (t, *J* = 7.6 Hz, 6H, 2xCH_3), 2.44 (q,

J = 7.6 Hz, 4H, 2xCH_2), 6.31 (dd, *J* = 0.6, 3.4 Hz, 2H, NCH), 6.45 – 6.55 (m, 3H, ArH), 6.59 (dd, *J* = 2.4, 8.9 Hz, 1H, ArH), 6.73 – 6.86 (m, 8H, ArH), 6.89 (d, *J* = 3.4 Hz, 2H, CH), 7.04 (dd, *J* = 2.2, 9.5 Hz, 2H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.10 (2xCH_3), 27.40 (2xCH_2), 104.01, 104.08, 104.72, 105.09 (d, $J_{F,C}$ = 45.10 Hz, CF), 109.82, 110.23, 110.56, 110.71, 126.55, 126.73 (d, $J_{F,C}$ = 35.10 Hz, CF), 127.77, 128.35, 128.48, 128.94, 131.22 (CH), 135.60, 142.62 (C).^{19}F NMR (282, MHz): δ = -123.20 (2xArF) . IR (KBr, cm^{-1}): ν = 3011 (w), 3025 (w), 2965 (w), 2926 (m), 2872 (w), 2853 (w), 1910 (w), 1860 (w), 1735 (w), 1710 (w), 1609 (m), 1576 (w), 1460 (w), 1444 (w), 1388 (w), 1388 (s), 1341 (s), 1327 (m), 1275 (m), 1248 (m), 1228 (m), 12309 (m), 1168 (m), 1137 (m), 1127 (m), 1112 (s), 1096 (s), 1057 (s). GC-MS (EI, 70 eV): *m/z* (%) =502 ($[M]^+$, 100), 369 (14), 368 (50), 325 (16), 339 (27), 338 (10), 324 (12), 310 (10), 309 (16), 209 (10). HRMS (EI, 70 eV) calcd for $C_{36}H_{22}F_2N_2$ ($[M]^+$): 530.25281 found: 530.25259.

1,1'-(2,2-bis(3-methoxyphenyl)ethene-1,1-diyl)bis(5-fluoro-1H-indole)(6f): Starting with (**4i**) (138 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6f**) was isolated as colorless, thick oil (175 mg, 69 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.25 (s, 6H, 2xOCH_3), 6.31 (d, *J* = 3.4 Hz, 2H, NCH), 6.34 – 6.40 (m, 2H, ArH), 6.45 – 6.51 (m, 2H, CH), 6.56 (dd, *J* = 1.9, 7.6 Hz, 6H, ArH), 6.83 – 6.95 (m, 4H, ArH), 6.98 – 7.08 (m, 2H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 54.96 (2xOCH_3),105.49, 105.55, 105.98 (d, $J_{F,C}$ = 35.12 Hz, CF), 106.29, 111.15, 111.49 (d, $J_{F,C}$ = 85.12 Hz, CF), 111.69, 111.82, 113.95, 114.37, 122.18, 128.71, 128.83, 129.40, 129.60, 129.74 (CH), 129.95, 132.43 (d, $J_{F,C}$ = 75.12 Hz, C), 140.40, 159.54. (C),^{19}F NMR (282, MHz): δ = -122.62 (2xArF). IR (KBr, cm^{-1}): ν = 3132 (w), 3111 (w), 3077 (w), 3068 (w), 3047 (w), 2987 (w), 2938 (w), 2837 (w), 1934 (w), 1852 (w), 1726 (w), 1592 (w), 1595 (s), 1498 (s), 1495 (s), 1452 (s), 1442 (m), 1392 (m), 1335 (m), 1316 (m), 1283 (m), 1250 (m), 956 (s), 941 (s). GC-MS (EI, 70 eV): *m/z* (%) = 507 ($[M]^+$, 46), 506 (100), 373 (16), 372 (77). HRMS (EI, 70 eV) calcd for $C_{32}H_{24}F_2N_2O_2$ ($[M]^+$): 507.1884 found: 507.17977.

1,1'-(2,2-bis(3,5-dimethylphenyl)ethene-1,1-diyl)bis(5-fluoro-1H-indole)(6g): Starting with (**4h**) (136 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6g**) was isolated as colorless, thick oil (136 mg, 54 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.11 (s, 6H, 2xCH_3), 2.52 (s, 6H, 2xCH_3), 6.53 (dd, *J* = 0.8, 3.4 Hz, 2H, NCH), 6.59 – 6.69 (m, 2H, ArH), 6.93 (d, *J* = 27.3 Hz, 2H, CH), 7.00 – 7.18 (m, 3H, ArH), 7.17 – 7.40 (m, 3H, ArH), 7.49 (dd, *J* = 4.4, 8.7 Hz, 3H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 21.22 (2xCH_3), 21.42 (2xCH_3), 105.22, 105.26 (d, $J_{F,C}$ = 45.10 Hz, CF),105.89, 106.20, 111.16, 111.51, 112.35, 112.39, 112.48, 112.52, 127.04 (d, $J_{F,C}$ = 45.10 Hz, CF),127.09, 127.75, 127.80, 129.27, 129.37, 129.41 (CH), 129.44, 129.70, 136.60 (C).^{19}F NMR (282, MHz): δ = -122.66 (2xArF). IR (KBr, cm^{-1}): ν = 3138 (w), 3117 (w), 3000 (w), 2915 (m), 2858 (m), 2746 (w), 1654 (s), 1621 (m), 1596 (m), 1522 (m), 1463 (w), 1446 (s), 1378 (s),1349 (w), 1277 (s), 1211 (s), 1173 (s), 1137 (s), 1102 (s). GC-MS (EI, 70 eV): *m/z* (%) = 502 ($[M]^+$, 100), 346 (12), 339 (10), 325 (16), 312 (14), 156 (15), 144 (30), 134 (46), 109 (11), 108 (28), 103 (10), 43 (99), 44 (17). HRMS (EI, 70 eV) calcd for $C_{34}H_{28}F_2N_2$ ($[M]^+$): 502.22206 found: 502.13457.

1,1'-(2,2-bis(4-fluorophenyl)ethene-1,1-diyl)bis(5-fluoro-1H-indole)(6h): Starting with (**4e**) (126 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6h**) was isolated as colorless, thick oil (125 mg, 52 %). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ= 6.39 (d, *J* = 3.2 Hz, 2H, NCH), 6.66 (d, *J* = 8.3 Hz, 2H, CH), 6.79 – 6.98 (m, 8H, ArH), 6.98 – 7.07 (m, 5H, ArH), 7.42 (d, *J* = 7.8 Hz, 2H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 103.63, 103.69 (d, $J_{F,C}$ = 55.18 Hz, CF), 105.71, 105.76 (d, $J_{F,C}$ = 61.16 Hz, CF), 106.10, 106.42, 110.59, 110.94 (d, $J_{F,C}$ = 34.20 Hz, CF), 111.20, 111.28 (d, $J_{F,C}$ = 88.17 Hz, CF), 111.32, 111.52, 111.62, 115.49, 115.78, 116.00, 124.53, 126.33, 128.22 (CH) 135.04, 135.09, 138.79, 160.12 (C).^{19}F NMR (282, MHz): δ = -124.10, -123.22 (4xArF). IR (KBr, cm^{-1}): ν = 3053 (w), 3043 (w), 2959 (w), 2924 (w), 2853 (w), 1848 (w), 1732 (w), 1625 (w), 1611 (m), 1559 (w), 1520 (w), 1467 (s), 1379 (m), 1318 (s), 1281 (w), 1252 (w), 1232 (w), 1164 (w). GC-MS (EI, 70 eV): *m/z* (%) = 482 ($[M]^+$, 95), 386 (10), 349 (23), 348 (100), 347 (16), 328 (10), 327 (19), 253 (16), 252 (11), 214 (16). HRMS (EI, 70 eV) calcd for $C_{30}H_{20}N_2F_4$ ($[M]^+$): 482.14006 found: 482.140203.

1,1'-(2,2-bis(4-(trifluoromethyl)phenyl)ethene-1,1-diyl)bis(5-fluoro-1H-indole)(6i): Starting with (**4c**) (176 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6i**) was isolated as colorless, thick oil (166 mg, 57 %). ^{1}H-NMR ($CDCl_3$, 250 MHz) δ= 6.27 – 6.50 (m, 4H, ArH), 6.48 – 6.73 (m, 2H, NCH), 6.84 (d, *J* = 3.4 Hz, 2H, CH), 6.96 (d, *J* = 8.1 Hz, 4H, ArH), 7.07 (dd, *J* = 2.4, 9.0 Hz, 2H, ArH), 7.30 (d, *J* = 8.2 Hz, 4H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 105.30, 105.53 (d, $J_{F,C}$ = 34.67 Hz, CF), 105.60, 105.68 (d, $J_{F,C}$ = 34.78 Hz, CF_3), 110.57 (d, $J_{F,C}$ = 55.67 Hz, CF_3), 110.72 (d, $J_{F,C}$ = 64.18 Hz, CF), 110.98 (d, $J_{F,C}$ = 25.78 Hz, C), 123.43 (d, $J_{F,C}$ = 61.16 Hz, C), 124.50, 124.56, 124.62, 124.68, 128.44, 128.73, 128.93, 130.15 (CH), 131.02, 141.49. (C).^{19}F NMR (282 MHz): δ = -121.80 (2xArF), -62.70 (2x$ArCF_3$). IR (KBr, cm^{-1}): ν = 2959 (w), 2924 (w), 2651 (w), 1980 (w), 1887 (w), 1827 (w), 1730 (w), 1625 (w), 1611 (w), 1586 (w), 1522 (w), 1467 (s), 1444 (s), 1397 (m), 1318 (m), 1281 (m), 1252 (m), 1211 (m), 1164 (m), 1127 (m), 1108 (m), 1063 (m), 1015 (m). GC-MS (EI, 70 eV): *m/z* (%) = 582 ($[M]^+$, 58), 449 (26), 379 (14), 378 (11), 309 (10), 303 (11), 134 (11). HRMS (EI, 70 eV) calcd for $C_{32}H_{18}N_2F_8$ ($[M]^+$): 582.13368 found: 582.13346.

1,1'-(2,2-diphenylethene-1,1-diyl)bis(5-methoxy-1H-indole)(6j): Starting with (**4a**) (108 mg, 0.5 mmol), (147 mg, 1 mmol) (**5c**), K_3PO_4 (424 mg, 2 mmol) and

DMF (8-10 mL), (**6j**) was isolated as a colorless, thick oil
(167 mg,71 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.63 (s, 6H, 2xOCH_3), 6.27 (d, *J* = 3.4 Hz, 2H, NCH), 6.48 (s, 4H, AHr), 6.78 – 6.92 (m, 8H, ArH), 6.95 – 7.04 (m, 6H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 55.14 (2xOCH_3), 55.56, 102.87, 105.16, 111.92 (d, $J_{F,C}$ = 58.15 Hz, CF), 112.65, 127.00, 127.32, 128.35, 129.00, 129.29, 129.63 (CH), 129.71 (d, $J_{F,C}$ = 32.23 Hz, CF), 130.96, 139.85, 154.90 (C). IR (KBr, cm^{-1}): *v* = 3068 (w), 3047 (w), 2924 (w), 2853 (w), 2496 (w), 2564 (w), 2398 (w), 2326 (w), 2202 (w), 2050 (w), 1998 (w), 1891 (w), 1759 (w), 1724 (s), 1673 (s), 1634 (m), 1594 (m), 1329 (m), 1320 (m), 1228 (m), 1156 (m), 1108 (m), 1013 (m), 1005 (m), 818 (s), 803 (s). GC-MS (EI, 70 eV): *m/z* (%) = 470 ([M]$^+$, 100), 406 (45), 374 (12), 376 (16), 340 (12), 338 (25), 329 (22), 239 (11), 223 (30), 199 (14), 150 (12), 133 (21), 105 (20), 101 (19). HRMS (EI, 70 eV) calcd for $C_{32}H_{24}N_2O_2$ ([M]$^+$): 470.19888 found: 470.19807.

1,1'-(2,2-diphenylethene-1,1-diyl)bis(5-fluoro-1H-indole)(6k): Starting with (**4a**) (108 mg, 0.5 mmol), (135 mg, 1 mmol) (**5b**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6k**) was isolated as colorless, thick oil (163 mg, 73 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 6.35 (dd, *J* = 0.7, 3.4 Hz, 2H, NCH), 6.48 – 6.65 (m, 4H, ArH), 6.85 – 6.94 (m, 6H, ArH), 6.99 – 7.11 (m, 8H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 105.36, 105.42, 105.93 (d, $J_{F,C}$ = 65.16 Hz, CF), 106.24, 111.06, 111.41, 111.62 (d, $J_{F,C}$ = 45.20 Hz, CF), 111.75 (d, $J_{F,C}$ = 35.10 Hz, C), 128.41(d, $J_{F,C}$ = 55.35 Hz, C), 128.47, 128.54, 129.47, 129.61 (CH), 129.84, 132.23, 139.32 (C).^{19}F NMR (282, MHz): δ = -122.93 (2xArF). IR (KBr, cm^{-1}): *v* = 2959 (w), 2924 (w), 2853 (w), 1860 (w), 1732 (w), 1625 (w), 1611 (w), 1586 (m), 1520 (m), 1467 (s), 1444 (s), 1405 (m), 1379 (m), 1281 (m), 1252 (m), 1120 (s), 1063 (s). GC-MS (EI, 70 eV): *m/z* (%) = 446 ([M]$^+$, 100), 313 (23), 312 (99), 310 (19), 309 (19), 291 (10), 235 (15), 234 (11), 178 (12). HRMS (EI, 70 eV) calcd for $C_{30}H_{20}N_2F_2$ ([M]$^+$): 446.15891 found: 446.15899.

1,1'-(2,2-diphenylethene-1,1-diyl)bis(1H-indole-5-carbonitrile)(6l): Starting with (**4a**) (108 mg, 0.5 mmol), (142 mg, 1 mmol) (**5d**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6l**) was isolated as colorless, thick oil (150 mg, 65 %). ^{1}H-NMR ($CDCl_3$, 250 MHz) δ= 6.44 (d, *J* = 3.4 Hz, 2H, NCH), 6.70 (d, *J* = 8.6 Hz, 2H, CH), 6.87 (dd, *J* = 3.1, 6.5 Hz, 4H, ArH), 6.91 – 7.10 (m, 10H, ArH), 7.69 (s, 2H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 104.66, 106.18 (C), 111.61, 119.97, 126.16, 126.50, 126.57, 128.43, 128.68, 128.78, 129.37 (CH), 130.53, 132.21, 137.15, 138.38 (C). IR (KBr, cm^{-1}): *v* = 3134 (w), 3107 (w), 3041 (w), 3002 (w), 2919 (w), 2851 (w), 2219 (m), 1672 (m), 1607 (w), 1522 (w), 1493 (w), 1463 (w), 1444 (w), 1384 (s), 1320 (s), 1285 (s), 1213 (s), 1191 (w), 1164 (w), 1135 (w), 1092 (w), 1040 (w). GC-MS (EI, 70 eV): *m/z* (%) = 460 ([M]$^+$, 100), 450 (100), 395 (65), 394 (79), 293 (19), 295 (19), 291 (18), 270 (24), 265 (12), 199 (10). HRMS (EI, 70 eV) calcd for $C_{32}H_{20}N_4$ ([M]$^+$): 460.16825 found: 460.16774.

1,1'-(2,2-bis(4-fluorophenyl)ethene-1,1-diyl)bis(1H-indole-5-carbonitrile)(6m): Starting with (**4e**) (126 mg, 0.5 mmol), (142 mg, 1 mmol) (**5d**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6m**) was isolated as colorless, thick oil (169 mg, 68 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ= 6.70 (dd, *J* = 0.8, 3.3 Hz, 2H, NCH), 7.03 – 7.15 (m, 2H, CH), 7.31 – 7.43 (m, 3H, ArH), 7.41 – 7.57 (m, 5H, ArH), 7.58 – 7.68 (m, 2H, ArH), 7.96 (dd, *J* = 0.7, 1.6 Hz, 2H, ArH), 7.98 (dd, *J* = 1.7, 2.6 Hz, 2H, ArH).^{13}C NMR (126 MHz, $CDCl_3$) δ = 103.60, 104.42 (C), 111.43, 115.70 (d, $J_{F,C}$ = 44.67 Hz, CF), 116.10 (d, $J_{F,C}$ = 25.34 Hz, CF), 120.50, 124.90, 125.30, 126.68, 128.45, 128.60 (CH), 128.80, 129.00, 130.34 (d, $J_{F,C}$ = 75.11 Hz, C),, 136.38, 137.50, 137.89 (CH), 139.65, 160.89, 164.76 (C). ^{19}F NMR (282, MHz): δ = -141.80 (2xArF). IR (KBr, cm^{-1}): *v* = 3068 (w), 3047 (w), 2891 (w), 2855 (w), 2856 (w), 2629 (w), 2499 (w), 2417 (w), 2375 (w), 2151 (w), 2050 (w), 1592 (m), 1318 (m), 1226 (m), 1123 (m), 1108 (m), 956 (s), 935 (s), 818 (s). GC-MS (EI, 70 eV): *m/z* (%) = 496 ([M]$^+$, 100), 455 (89), 394 (66), 392 (78), 295 (20), 291 (19), 289 (17), 273 (24), 264 (10), 199 (10). HRMS (EI, 70 eV) calcd for $C_{32}H_{18}F_2N_4$ ([M]$^+$): 496.14995 found 496.14777.

1,1'-(2,2-bis(4-methoxyphenyl)ethene-1,1-diyl) bis(5-methoxy-1H-indole)(6n): Starting with (**4d**) (138 mg, 0.5 mmol), (147 mg, 1 mmol) (**5c**), K_3PO_4 (424 mg, 2 mmol) and DMF (8-10 mL), (**6n**) was isolated as colorless, thick oil (207 mg,78 %). ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 3.60 (s, 6H, 2xOCH_3), 3.65 (s, 6H, 2xOCH_3), 6.29 (d, *J* = 3.3 Hz, 2H, NCH), 6.40 – 6.59 (m, 6H, ArH), 6.66 – 6.93 (m, 9H, ArH), 6.92 – 7.21 (m, 1H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 55.09 (2xOCH_3), 55.54 (2xOCH_3), 102.76, 111.82 (C), 112.50, 113.69, 126.89, 127.43, 129.01, 129.53, 130.75, 130.93 (CH), 132.20, 154.72, 158.68, 124.35 (C). IR (KBr, cm^{-1}): *v* = 3132 (w), 3111 (w), 3077 (w), 3068 (w), 3047 (w), 2987 (w), 2938 (w), 2837 (w), 1934 (w), 1852 (w), 1726 (w), 1592 (w), 1595 (s), 1498 (s), 1495 (s), 1452 (s), 1442 (m), 1392 (m), 1335 (m), 1316 (m), 1283 , 1250 (m), 956 (s), 941 (s). GC-MS (EI, 70 eV): *m/z* (%) = 530 ([M]$^+$, 34), 529 (100), 464 (11), 463 (32), 375 (13), 372 (46), 341 (10), 195 (14), 152 (12), 147 (22), 132 (16), 104 (119, 107 (20), 57 (11), 44 (26), 43 (23). HRMS (EI, 70 eV) calcd for $C_{34}H_{30}N_2O_4$ ([M]$^+$): 530.22001 found: 530.21937.

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