Unusual Emission Properties of the Selected Organosilicon Compounds Containing Styryl-Carbazole Chromophore. Inversion of the Singlet Excited States

K. Rachuta,[a] M. Bayda,*[a,b] M. Majchrzak,*[a] J. Koput[a] and B. Marciniak[a]

[a]Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89 b, 61-614 Poznan, Poland
[b]Center of Advanced Technologies, Adam Mickiewicz University, Umultowska 89 c, 61-614 Poznan, Poland

Electronic Supplementary Information

Synthetic procedure of carbazole derivatives

Carbazole derivatives were prepared according to the reference 1 with a slight modification consisting in changing the phase-transfer catalyst to catalytically faster tetrabutylammonium fluoride.

***N*-isopropyl-*9H*-carbazole** (**0**) A three-neck round bottom flask equipped with a double-condenser and magnetic stirring bar was charged with carbazole (5 g, 0.03 mol) and acetone (100 mL). The solution was stirred and heated at boiling point. Isopropyl bromide (4.67 mL, 0.51 mol), tetrabutylammonium fluoride (0.53 g, 0.002 mol) and potassium hydroxide (2.67 g, 0.048 mol) were added to the solution. The reaction mixture was stirred for 2 hours. The mixture was cooled to the room temperature and the solvent was evaporated. The residue was dissolved in dichloromethane and extracted with H_2O. The organic part was dried over anhydrous $MgSO_4$ for 8 hours and filtered. The solution was isolated by very quick 'flash' column system (filter G4, SiO_2- 60, Celite®) connected to membrane pump. The excess of solvent was evaporated under vacuum. The residue was stirred with cold ether, filtered and dried under high vacuum pump for 15 minutes. *N*-isopropylcarbazole was obtained with 97% yield (6.06 g) as a white solid. The reaction progress was monitored by TLC, GC and GCMS analysis. The product **0** was confirmed by spectroscopic methods.
Analytic data: ^{1}H NMR (300 MHz, $CDCl_3$; δ(ppm)): 1.76 (d, 6H, J_{HH} = 6.9 Hz), 5.04 (m, 1H), 7.24 (d, 2H, J_{HH} = 7.5 Hz), 7.28 (t, 2H), 7.58 (d, 2H, J_{HH} = 9 Hz), 8.17 (d, 2H, J_{HH} = 7.8 Hz). MS (EI) (m/z (relat. int. %)): 209.6 (100) ($M^{+\cdot}$), 208.0 (13.0), 207.6 (5.7), 194.7 (38), 193.0 (10.2). Melting point: mp. 120°C.

3-bromo-*N*-isopropyl-*9H*-carbazole (**3**) A DMF (6 mL) solution of *N*-Bromosuccinimide (2.55 g, 0.014 mol) was added dropwise very slowly to a solution of *N*-isopropylcarbazole (3 g, 0.014 mol) in dichloromethane (38 mL) at 14-15°C. Then the mixture was warmed at room temperature and stirred for 8 hours. The reaction progress was controlled by GC and GCMS analysis. The crude mixture was extracted with H_2O (three times) and dried over anhydrous $MgSO_4$ for 12h and filtered. The organic part was isolated by very quick 'flash' column system (filter G4, SiO_2 - 60, Celite®) connected to membrane pump. The excess of

organic solvent was evaporated and dried under vacuum for 15 minutes. The final product **3** was isolated as a yellowish solid. The yield was over 98% (4.10 g).

Analytic data: ^{1}H NMR (300 MHz, $CDCl_3$; δ(ppm)): 1.73 (d, 6H, J_{HH} = 7.3 Hz), 4.99 (m, 1H), 7.23-7.59 (m, 5H), 8.09 (d, 1H, J_{HH} = 7.7 Hz), 8.26 (s, 1H). MS (EI) (m/z (relat. int. %)): 289.3 (39.0) ($M^{+\cdot}$), 288.3 (9.0), 287.0 (36.0), 275.2 (17.5), 274.1 (100), 273.2 (18), 272.2 (90), 193.2 (34.5), 192.3 (8.9), 166.2 (14.9). MS (FAB, m/z (%) (M^+, 100): 288.2. Melting point: mp. 88°C.

Preparation and characterization of 3-(4-vinylphenyl)-*N*-isopropyl-9H-carbazole (**2**):

The title olefin was prepared according to the reference 1 with a slight modification which consisted in changing the concentration of final mixture and using smaller amount of palladium catalyst **Pd**.

A three-neck bottom flask connected to a condenser and magnetic stirring bar was charged under argon with **3** (0.000650 mol) and 4-vinylphenylboronic acid (0.000683, 5 mol% excess based on **3**), toluene (6.5 mL, 0.1M), ethanol (1.33 mL), palladium complex [Pd(η^2-dba)(P(*o*-tol)$_3$] (**Pd**) (3 mg, 3.28 x 10^{-6} mol) and potassium carbonate (1.95 mL, 2M aqua solution). The reaction mixture was stirred and heated in an oil bath at 85°C for 2-4 hours. The molar ratio of the reactants was as follows: [Br-substrate]:[boronic acid]:[palladium complex] - 1:1.05:4x10^{-3}. The reaction progress was monitored by TLC, GC and GCMS analysis. The mixture was isolated by very quick 'flash' column system (filter G3, SiO_2 - 60, Celite®) connected to membrane pump, next extracted from DCM/H_2O and dried over anhydrous $MgSO_4$ for 8h and filtered again. After that, the excess of solvent was evaporated under vacuum. The final products were filtered off and dried under vacuum for 20 minutes. The final product **2** was isolated as a yellowish solid at 20^{o}C. The yield was very high 97% (196 mg). NMR spectroscopic analysis confirmed the formation of the expected product.

Analytic data: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76 (d, 6H, J_{HH} = 6.9 Hz), 5.03 (m, 1H), 5.28 (d, 1H, J_{HH} = 10.8 Hz), 5.82 (d, 1H, J_{HH} = 16.8 Hz), 6.79 (dd, 1H, (C), J_{HH} = 17.7 Hz), 7.19 (t, 1H), 7.46 (t, 1H, 7.53 (d, 2H, J_{HH} = 8.1 Hz), 7.56 (d, 1H, J_{HH} = 4.3 Hz), 7.6 (s, 1H), 7.69 (d, 2H, J_{HH} = 8.5 Hz), 8.15 (d, 1H, J_{HH} = 7.8 Hz), 8.14 (d, 1H, J_{HH} = 1.5 Hz), 8.34 (d, 1H, J_{HH} = 1.2 Hz). MS (EI) (m/z (relat. int. %)): 312.2 (24.8) ($M^{+\cdot}$), 311.4 (100), 297.8 (11.6), 296.8 (66.4), 268.8 (7.0), 267.8 (4.8). MS (FAB, m/z (%) (M^+, 100): 311.

General synthesis procedure of trimethylsilyl-substituted-carbazole 3-(4-((*E*)-2(trimethylsilyl)vinyl)phenyl)-*N*-isopropyl-9H-carbazole *(1a)*

The title olefins were prepared according to the reference 1 with a slight modification which consisted in changing the concentration of final mixture, smaller amount of vinylsilane and short time.

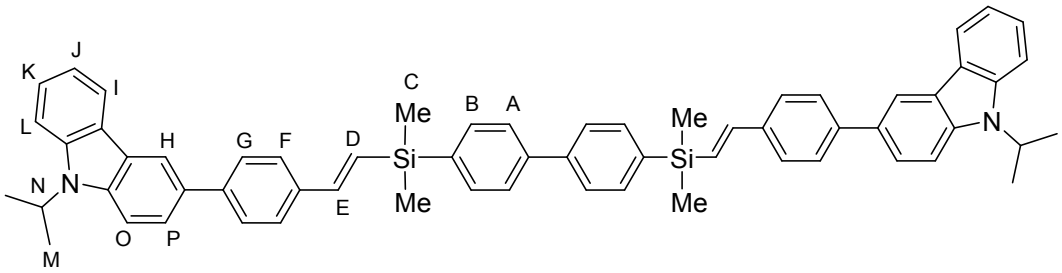
The Schlenk reactor equipped with magnetic stirring bar was charged under argon with monostyryl-carbazole derivative **2** ($3.21x10^{-4}$ mol) and trimethylvinylsilane ($6.42x10^{-4}$ mol), toluene (0.75 M solution, calculated per styrylcarbazole) and [Ru(CO)H(Cl)(PCy_3)$_2$] (**Ru**) complex. The solution was stirred and heated in an oil bath at 90°C for 10h. The molar ratio of the reactants was as follows: [olefin]:[trimethylvinylsilane]:[Ru-H] = $1:2:5x10^{-3}$. The reaction was monitored by GC and GCMS analysis. The mixture was isolated by very quick 'flash' column system (filter G4, SiO_2 - 60, Celite®) connected to membrane pump. Next extracted from DCM/H_2O (three times) and dried over anhydrous $MgSO_4$ for 8h. Afterwards the excess of solvent was evaporated under vacuum. Silyl-carbazole derivatives were purified by repeated precipitation from DCM/hexane system and isolated by column chromatography (SiO_2, Celite®, sand) with hexane/dichloromethane (1:40) mixture as an eluent (R_f = 0.40). The final product **1a** was dried under vacuum. It was isolated as a yellowish solid at 20°C. The isolated yield was very high 96% (118 mg). NMR spectroscopic analysis confirmed the formation of the expected product.

Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.74 (d, 6H, J_{HH} = 7.1 Hz), 5.02 (m, 1H), 6.53 (d, 2H, J_{HH} = 19.6 Hz), 6.95 (d, 2H, J_{HH} = 19.2 Hz), 7.2-7.7 (m, 4H), 7.54 (d, 2H, J_{HH} = 8.2 Hz), 7.59 (s, 1H), 7.69 (d, 2H, J_{HH} = 6.1 Hz), 8.17 (d, 1H, J_{HH} = 8.0 Hz), 8.32 (d, 1H, J_{HH} = 1.6 Hz. ^{29}Si NMR (99 MHz, $CDCl_3$): δ -6.27. MS (EI) (m/z (relat. int. %)): 384.5 (34.5) ($M^{+\cdot}$), 383.5 (100), 370.8 (9.8), 369.9 (27.2), 369 (50.4), 73.2 (3.8), 59.1 (3.46). MS (FAB, m/z (%) (M+, 100): 383. HRMS (m/z) calcd. for $C_{26}H_{29}NSi$: 383.20693, found 383.20689. Melting point: mp. 127°C. UV-Vis: ε_{max}= 30 700 $M^{-1}cm^{-1}$ (ACN), ε_{max}= 36 600 $M^{-1}cm^{-1}$ (hex);

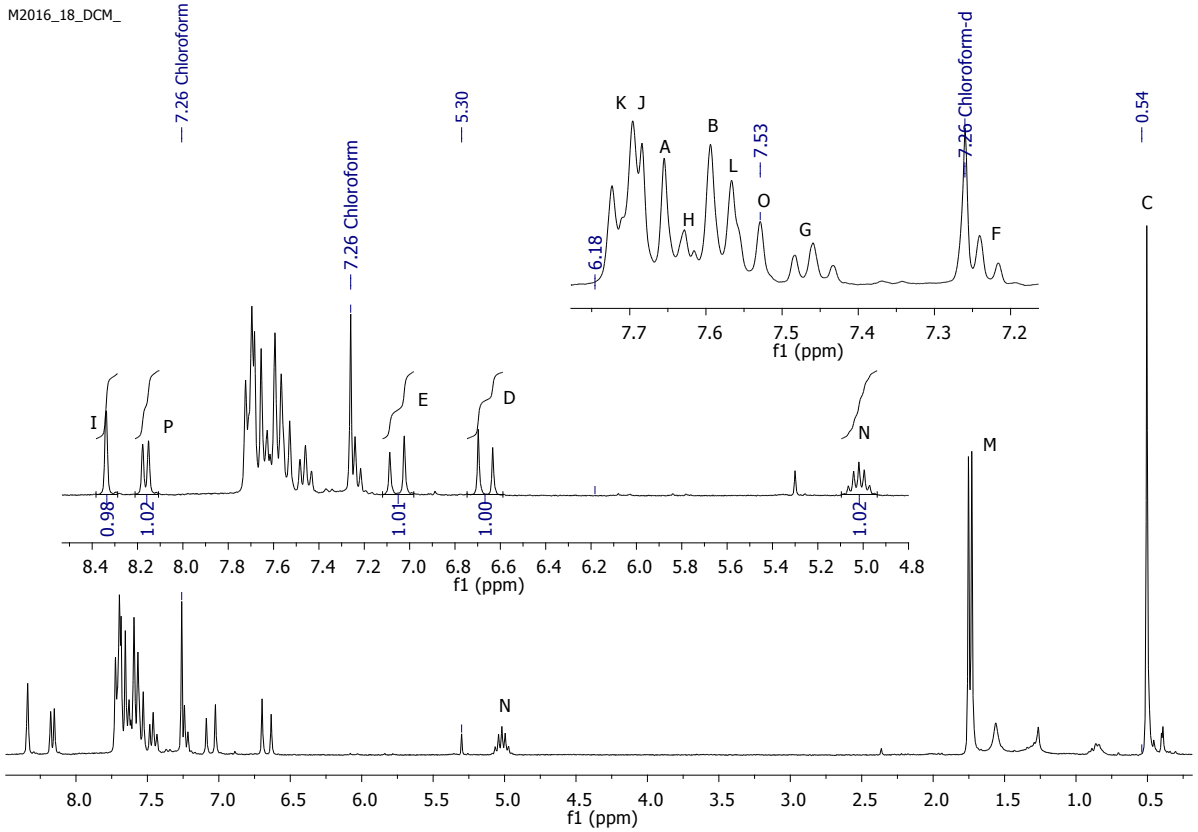
General synthesis procedure of disubstituted-organo-silicon carbazole 4,4'-bis(((E)-4-((*N*-isopropyl-9H-carbazol-3-yl)styryl)dimethylsilyl)biphenyl (1)

A two-neck bottom flask connected to a condenser and magnetic stirring bar was charged under argon with monostyryl-carbazole derivative **2** (110 mg, $3.55x10^{-4}$ mol), bissilyl-derivative **1b** (56.4 mg, $1.75x10^{-4}$ mol), toluene (0.5 M solution, calculated per styrylcarbazole) and [Ru(CO)H(Cl)(PCy_3)$_2$] (**Ru**) complex (0.5 %mol). The solution was stirred and heated in an oil bath at 90°C for 24h. The molar ratio of the reactants was as follows: [olefin]:[vinylsilane]:[Ru-H] = $2.02:1:1x10^{-2}$. The conversion of substrates was monitored by GCMS analysis. The mixture was isolated by very quick 'flash' column system (filter G4, SiO_2 - 60, Celite®) connected to membrane pump. Next extracted from DCM/H_2O (three times) and dried over anhydrous $MgSO_4$ for 6h. Then, the excess of solvent was evaporated under vacuum. Moreover, the product was purified by repeated precipitation from DCM/hexane cool system. The final product was filtered off and dried under vacuum. In addition, to increase the purity of the product the crude fraction was isolated by column chromatography (SiO_2, Celite®, sand) with hexane/chloroform (1:30) mixture as an eluent (R_f = 0.45). The compound **1** was isolated as a yellowish solid at 20°C with high yield 91% (141 mg). NMR spectroscopic analysis confirmed the formation of the expected products.

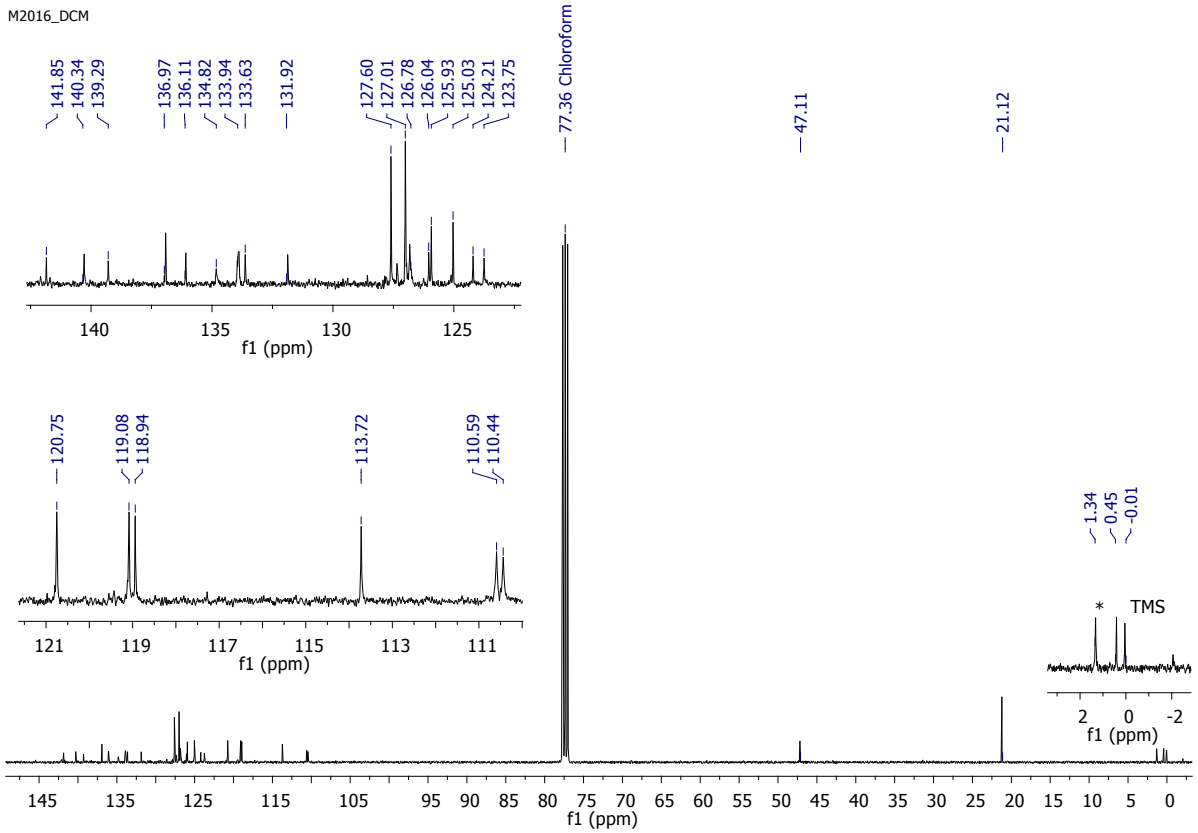
Analytic data: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.51 (s, 12H, (C)), 1.75 (d, 12H, J_{HH} = 6.9 Hz, (M)), 5.02 (m, 2H, (N)), 6.66 (d, 2H, J_{HH} = 18.9 Hz, (D)), 7.05 (d, 2H, J_{HH} = 19.2 Hz, (E)), 7. 22 (d, 4H, J_{HH} = 7.5 Hz, (F)), 7.47 (d, 4H, J_{HH} = 7.4 Hz, (G)), 7.53 (s, 2H, (O)), 7.57 (s, 2H, (L)), 7.59 (s, 4H, (B)), 7.63 (s, 2H, (H)), 7.66 (s, 4H, (A)), 7.68-7.72 (m, 4H, (K, J)) 8.16 (d, 2H, J_{HH} = 7.5 Hz, (P)), 8.34 (d, 2H, J_{HH} = 5.1 Hz, (I)). ^{13}C NMR (300 MHz, $CDCl_3$): δ 0.5, 21.1, 47.1, 110.4, 110.6, 113.7, 118.9, 119.1, 120.8, 123.8, 124.2, 125.0, 125.9, 126.0, 126.8, 127.0, 127.6, 131.9, 133.6, 133.9, 134.8, 136.1, 136.9, 139.3, 140.3, 141.9. ^{29}Si NMR (75 MHz, $CDCl_3$): δ -6.04. MS (FAB, m/z (%) (M+, 100): 889. Elemental analyses calcd. for $C_{62}H_{60}N_2Si_2$: C 83.73, H 6.80, N 3.15; found C 83.22, H 6.76, N 3.11.



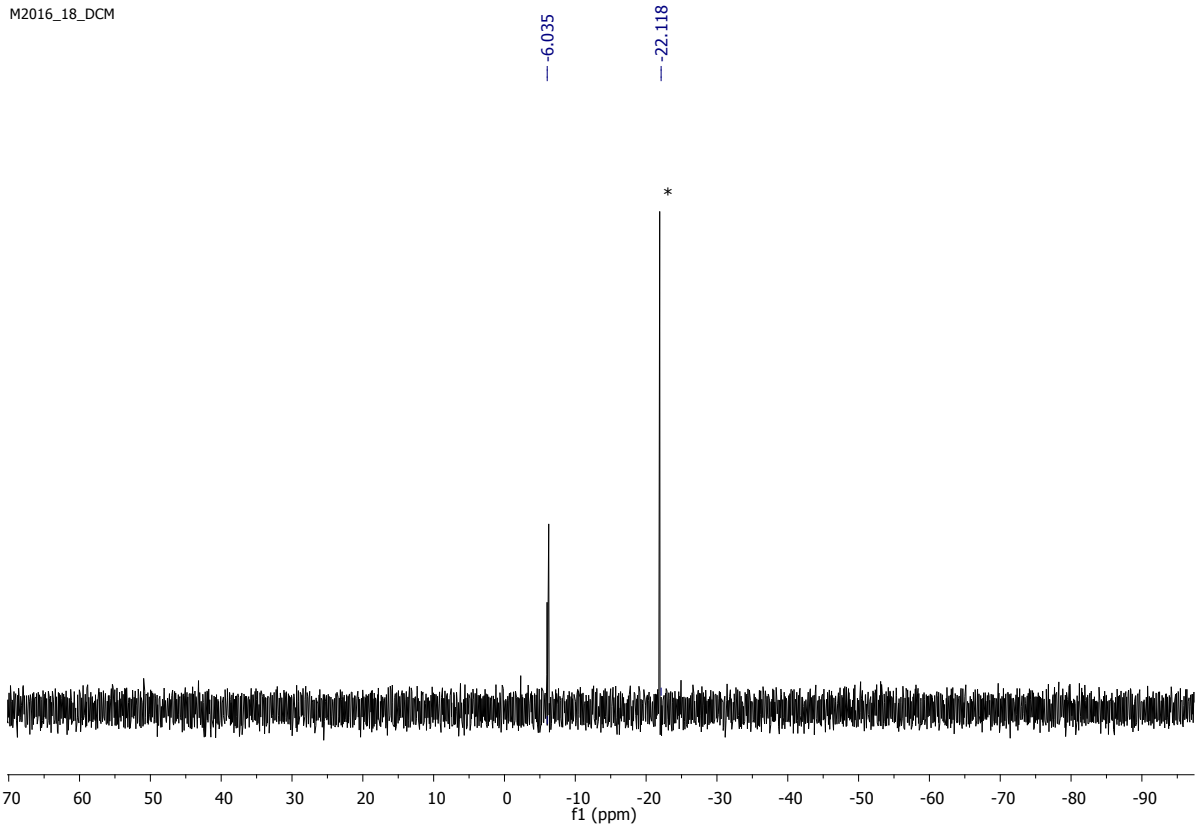
NMR spectra



Compound **1** - ^{1}H NMR in $CDCl_3$



Compound **1** - ^{13}C NMR in $CDCl_3$



Compound **1** - ^{29}Si NMR in $CDCl_3$

Signals marked * are due to silicon grease.

References

1. M. Majchrzak, M. Grzelak, B. Marciniec, *Org. Biomol. Chem.,* **2016**, *14*, 9406–9415.