Functionalisation of 2-(1-Naphthyl)-5-phenyl-1,3,4-oxadiazole with Alkoxysilanes

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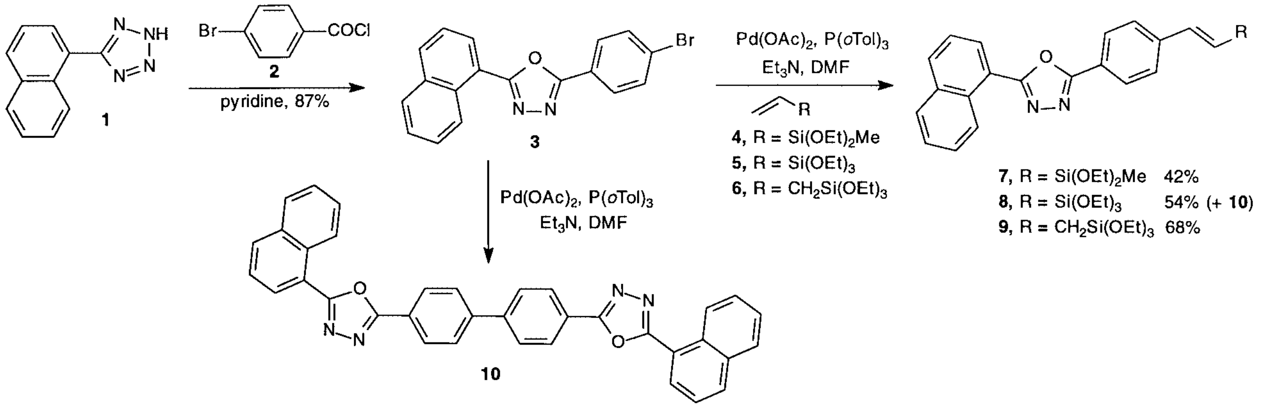
Abstract: A short route for the synthesis of 2,5-diaryl-1,3,4-oxadiazoles with rigid connections to alkoxysilanes **7**, **8**, **9** via Heck reaction of the bromo compound **3** with vinylalkoxysilanes **4**, **5**, **6**, and also via palladium-catalysed vinylation to the styrene **11** and cross-metathesis with vinyl silanes is described. An extension of the conjugated system to **14** is possible with silyl-substituted styrene **13**.

Key words: Heck reaction, heterocycles, metathesis, silicon, materials science

Organodi- and trialkoxysilanes hydrolyse to reactive silanols condensing to oligomers or three-dimensional siloxane networks with covalently linked organic groups. The mild conditions of this process allow the synthesis of organic-inorganic hybrid materials and coatings with a variety of potential applications depending on the organic moiety. Aromatic hydrocarbons with extended π-systems have been directly coupled with alkoxysilanes[1–3] and recently, some electro-optically active molecules were linked to aminopropyltrialkoxysilanes[4–6] and converted to hybrid materials. 2,5-Diaryl-1,3,4-oxadiazoles are widely used as additives in liquid and plastic scintillators[7] and as hole blocking/electron transporting materials in organic light emitting diodes.[8] Small molecules like 5-(4-*tert*-butylphenyl)-2-(4-diphenyl)-1,3,4-oxadiazole are applied as vacuum-deposited layers, however, the stability of these films is only moderate.[9] Polymers for these applications include those units in the main chain[10–13] or as side chains.[14–16] In this paper, we report the synthesis of naphthyl-oxadiazolylstyrenes and -stilbene with alkoxysilane units, compounds which can be useful for UV absorbing or luminescent coatings and also for curable electron transport layers in electro-optical devices.

The synthesis of the title compounds required the construction of the 1,3,4-oxadiazole and the connection of the aromatic unit and the alkoxysilane. Due to the sensitivity of the latter towards acids and hydrolysis, the former was prepared first. Besides, the cyclocondensation of acyl hydrazides,[17] the acylation of tetrazoles and thermal ring transformation (Huisgen reaction)[18] is a general method for the synthesis of 1,3,4-oxadiazoles. Tetrazole **1**[19] and the acid chloride **2** were transformed to **3** – a unit well known for its high electron affinity and good electron transport capability.[15] A bromine atom on the phenyl ring of **3** serves as reactive site for the coupling of the chromophore to the vinyl silanes. The connection of the aromatic unit **3** with the commercially available ethoxysilanes **4**–**6** was performed via Heck reactions with palladium(II)acetate and tris(2-methylphenyl)phosphine as catalyst using anhydrous DMF as solvent (Scheme 1). Among the different silanes **4**–**6** applied, allyltriethoxysilane **6** gave the best results in the Heck reaction: 68% of **9** (115 °C, 3 hours). Comparable conditions were used for **4** (120 °C, 2 hours) and **5** (120 °C, 5 hours) to yield 42% of **7** and 54% of **8**, respectively. In contrast to the reactions of **4** and **6** with **3**, the more sluggish reaction of **5** to **8** was accompanied by the competitive formation of small amounts of diphenyl **10**[21] as a by-product. In a separate



Scheme 1 Synthesis of alkoxysilane-substituted diaryloxadiazoles

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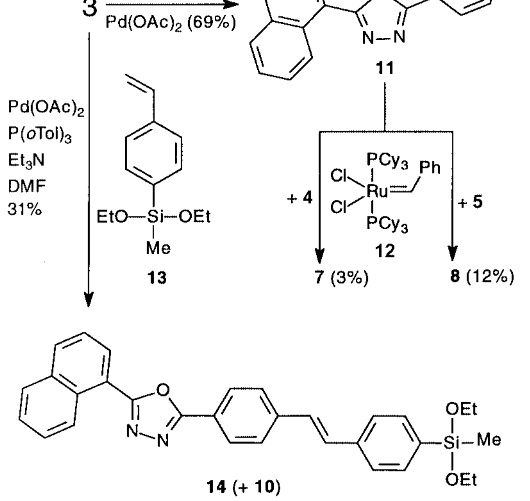
experiment under the same conditions but in the absence of vinylsilanes, **10** was formed from **3** in an Ullmann-type reaction.[22] Prolonged reaction times (5 hours) in the transformation of **3** and **4** to **7** gave rise to a secondary reaction; the fission of the vinyl-silicon bond of **7** to yield styrene **11**.

Vinyl silanes were proven reactive substrates[23] in cross-metathesis reactions. The ruthenium-catalysed cross-metathesis was investigated as an alternative route to alkoxysilyl-substituted chromophores. A styrene carrying an 1,3,4-oxadiazole was prepared by Prasad et al.[24] in three steps via Wittig reaction and used for the synthesis of multi-branched structures. Starting from **3**, a Pd-catalysed vinylation with compressed ethene[25,26] led to styrene **11** in 69% yield (Scheme 2). This was subjected to cross-metathesis reactions with **5**[23] and Grubbs catalyst[27] [Cl$_2$(PCy$_3$)$_2$Ru=CHPh] **12** under continuous removal of ethene by a gentle flow of dry and oxygen-free nitrogen. After a short time, the very clean reaction of **11** and **5** stopped (only **5**, **8,** and **11** could be detected by mass spectroscopy) and neither additional catalyst nor elevated temperature nor sonication was suitable to promote the conversion. Work-up by chromatography gave **8** in 12% yield and 83% of unchanged **11**; while the reaction of **4** with **11** generated only traces of **7**.



Scheme 2 Alkoxysilyl-substituted diaryloxadiazoles via Heck reactions and cross-metathesis

A further extension of the conjugated system of **7**–**9** will alter the optical and electrical properties of the chromophore. 1,3,4-Oxadiazoles are strong activating groups for methyl arenes in the Siegrist synthesis of stilbenes,[28] but the reaction conditions are not suitable for the sensitive alkoxysilanes, and alkoxysilyl-substituted benzaldehydes or aniles are not available. A Heck reaction with styrene **13** was successful for the preparation of a compound with an additional phenylene unit separating the alkoxysilyl and vinyl groups (Scheme 2). Silane **13**[20] was prepared from 4-bromostyrene and triethoxymethylsilane in a Barbier–Grignard reaction. The Pd-catalysed coupling of **3** and **13** yielded stilbene **14** (31%), again accompanied by the formation of diphenyl **10**.

The alkoxysilanes **7**, **8**, and **9** are fairly stable towards hydrolysis and can be purified by chromatography using silica gel, on the condition that the crude product is separated from the solvents and salts of the reaction mixture. These impurities particularly promote the hydrolysis of the diethoxymethyl compound **14**, resulting in a mixture of oligomeric siloxanes.

We have described a brief synthesis of 2,5-diaryl-1,3,4-oxadiazoles with rigid connections to ethoxysilyl groups (**7**–**9**, **14**) by the Heck reactions of the 4-bromophenyl substituted heterocycle **3** and the vinyl-substituted silanes **4**–**6**, and **13**. The reactivity of the vinyl compounds is strongly controlled by the silane, with ethene and allylsilane **6** giving the best results, followed by **5** which is superior to **4** and **13**. In case of **5**, a catalytic Ullmann coupling to biaryl **13** was observed. Due to the ethoxysilyl moieties, **7**–**9** and **14** are interesting as conjugated systems with high electron affinity for the preparation of polysiloxanes and organic-inorganic hybrid materials for applications like coatings or electro-optical devices.[4,5]

IR spectra: Beckman Acculab 4. NMR spectra: CDCl$_3$, Bruker AC 200 and AM 400. Chemical shifts are reported in ppm and referenced to the solvent as internal standard. Mass spectra: 70 eV, Varian MAT 711 (EI), MAT 95 (FD). The elemental analyses were performed at the microanalytical laboratory of the Chemical Institute of the Johannes Gutenberg–Universität, Mainz, Germany. Mps are uncorrected. Chemicals were used as received; solvents were dried according to standard procedures and distilled. DMF was stirred with CaH$_2$ for 5 h at 120 °C, distilled in vacuum and stored over activated molecular sieves.

2-(4-Bromophenyl)-5-(1-naphthyl)-1,3,4-oxadiazole (3)

A mixture of tetrazole **1** (6.5 g, 0.033 mol) and anhyd pyridine (35 mL) was stirred and 4-bromobenzoyl chloride **2** (8.0 g, 0.036 mol) was added in portions of 1 g. The mixture warmed up, N$_2$ was evolved, and finally a solid separated. After the gas evolution ceased, the mixture was heated to 100 °C for 1.5 h and poured into MeOH (70 mL). H$_2$O (30 mL) was added and the solid was isolated by filtration and recrystallised from toluene. Yield: 10.1 g (87%), slightly brownish crystals, mp 140 °C.

IR (KBr): $\nu = 3025$, 1590, 1520, 1470, 1397, 1240, 1087, 1070, 1002, 830, 800, 765 cm^{-1}.

^{1}H NMR (CDCl$_3$): $\delta = 7.55$ (m, 2H, 3-H, 6-H, naph), 7.68 (d, 2H, $J = 8.5$ Hz, 3-H, 5-H, ph), 7.70 (m, 1H, 7-H, naph), 7.92 (d, 1H, $J = 8.2$ Hz, 5-H, naph), 8.04 (d, 3H, $J = 8.5$ Hz, 2-H, 6-H, ph; 4H, naph), 8.24 (d, 1H, $J = 7.4$ Hz, 2-H, naph), 9.25 (d, 1H, $J = 8.8$ Hz, 8-H, naph).

^{13}C NMR (CDCl$_3$): $\delta = 120.0$, 122.6, 126.3, 129.8, 133.6 (C$_q$), 124.6 (C-3, naph), 126.0 (C-8, naph), 126.6 (C-6, naph), 128.0 (C-7, naph), 128.1 (C-2, C-6 ph), 128.5 (C-5, naph), 132.2 (C-3, C-5, ph), 132.5 (C-4, naph), 163.1, 164.5 (C-2, C-5, oxd).

MS (EI): $m/z = 350.4$ (51) Br-pattern [M$^+$], 183 (22) Br-pattern [C$_6$H$_4$BrCO$^+$], 155 (100) [C$_{10}$H$_7$CO$^+$], 127 (69) [C$_{10}$H$_7$$^+$].

2-(1-Naphthyl)-5-(4-vinylphenyl)-1,3,4-oxadiazole (11)

A solution of **3** (1.0 g, 2.8 mmol), Pd(OAc)$_2$ (40 mg, 0.18 mmol), tris-*o*-tolylphosphine (160 mg, 0.53 mmol) and Et$_3$N (0.6 g, 0.60

mmol) in anhyd DMF (30 mL) was placed in an autoclave, purged with N_2, and stirred under ethene (30 bar) for 40 h at 100 °C. The cooled mixture was diluted with H_2O (100 mL), extracted with $CHCl_3$ (3 × 50 mL), and the combined organic solutions were washed with H_2O (3 × 100 mL), and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether–EtOAc, 5:1). Yield: 0.58 g (69%), slightly yellowish crystals, mp 134 °C.

IR (KBr): ν = 3070, 3040, 2990, 2910, 1615, 1600, 1565, 1520, 1485, 1400, 1242, 1090, 1070, 1008, 980, 925, 900, 842, 820, 770, 715, 696, 655 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 5.39 (d, 1H, *J* = 10.7 Hz, vin), 5.87 (d, 1H, *J* = 17.5 Hz, vin), 6.77 (dd, 1H, *J* = 17.5, 10.7 Hz, vin), 7.59 (m, 3H, ph, naph), 7.71 (2 × t, 2 × 1H, *J* = 8.5 Hz, naph), 8.15 (d, 2H, *J* = 8.0 Hz, ph), 7.93, 8.05, 8.26, 9.28 (4 d, 4 × 4 × 1H *J* = 8.4 Hz, 2-H, 4-H, 5-H, 8-H, naph).

^{13}C NMR ($CDCl_3$): δ = 116.4, 124.9, 126.3, 126.8, 126.9 (2C), 127.9 (2C), 128.2, 128.4, 128.7, 132.6, 135.9 (CH), 120.5, 123.0, 130.1, 133.9, 140.9 (C_q), 167.5, (oxd) (1 signal of the heterocycle is missing).

MS (EI): *m/z* = 298 (46) [M^+], 241 (77), 215 (100).

2-{4-[Diethoxy(methyl)silyl]ethenylphenyl}-5-(1-naphthyl)-1,3,4-oxadiazole (7)

Prepared from **3** and **4** according to the procedure (a) described for **8**. The reaction time was 2 h. The crude product was purified by column chromatography (silica gel, $CHCl_3$–petroleum ether, 3:1). Yield: 250 mg (42%) as a slowly crystallising yellowish oil, mp 98 °C.

The cross metathesis of **11** and **4**, according to procedure (b) described for **8**, yielded <3% of **7.**

IR (neat): ν = 3040, 2960, 2915, 1600, 1565, 1535, 1520, 1500, 1480, 1430, 1405, 1380, 1320, 1290, 1250, 1210, 1195, 1160, 1097, 1070, 1005, 802, 760, 735 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.30 (s, 3H, Si-CH_3), 1.26 (t, 6H, *J* = 7.0 Hz, CH_3), 3.85 (q, 4H, *J* = 7.0 Hz, OCH_2), 6.45 (d, 1H, *J* = 19.6 Hz, vin), 7.15 (d, 1H, *J* = 19.6 Hz, vin), 7.52–7.78 (m, 5H, ph, naph), 7.93 (d, 1H, *J* = 8.0 Hz, naph), 8.05 (d, 1H, *J* = 8.0 Hz, naph), 8.16 (d, 2H, *J* = 8.0 Hz, 2-H, 6-H, ph), 8.26 (dd, 1H, *J* = 8.0, 1 Hz, naph), 9.27 (d, 1H, *J* = 8.8 Hz, naph).

^{13}C NMR ($CDCl_3$): δ = –4.2 (Si-CH_3), 18.4 (CH_3), 58.5 (OCH_2), 120.5, 123.6, 130.2, 133.9, 141.0 (C_q), 124.9, 125.8, 126.3, 126.8, 127.3 (2C), 128.2, 128.4, 128.7, 132.6, 146.0 (CH), 164.0, 164.6 (C-2, C-5, oxadiazole).

MS (FD): *m/z* = 431 (100) [M^+], 215.7 (5) [M^{2+}].

2-(1-Naphthyl)-5-{4-[(*E*)-2-(triethoxysilyl)ethenyl]phenyl}-1,3,4-oxadiazole (8)

Procedure (a)

$Pd(OAc)_2$ (20 mg, 0.089 mmol) and tris-*o*-tolylphosphine (50 mg, 0.180 mmol) were added to a solution of **3** (0.30 g, 0.89 mmol), Et_3N (0.45 g, 4.45 mmol) and silane **5** (0.17 g, 0.89 mmol) in anhyd DMF (30 mL). The mixture was purged with N_2 and stirred at 120 °C for 5 h. The cooled reaction mixture was stirred with a mixture of cyclohexane and toluene (2:1, 4 × 40 mL) for 1 h, and the combined hydrocarbon solutions were washed with iced water (3 × 50 mL), and dried ($MgSO_4$). Compound **8** was purified by chromatography on silica gel (toluene–EtOAc, 5:1). Yield: 0.22 g (54%) as a slowly crystallising yellowish oil, mp 118 °C.

Procedure (b)

Grubbs catalyst $[Ru(PCy_3)_2(H_5C_6CH)]Cl_2$ (**12,** 2 mg) was added to a solution of **5** (180 mg, 1 mmol) and **11** (300 mg, 1 mmol) in anhyd benzene (8 mL) placed in a 2-necked round bottom flask equipped with an efficient reflux condenser and bubble counter, and a gentle flow of dry and O_2-free N_2 was bubbled through the solution to remove ethene (16 h, ambient temperature). The solvent was stripped off and the residue purified by chromatography. Yield: 55 mg (12%) of **8** and 250 mg (83%) of **11**.

IR (neat): ν = 3040, 2960, 2915, 1595, 1567, 1520, 1483, 1450, 1380, 1290, 1195, 1161, 1097, 1070, 958, 802, 772, 750 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.30 (t, 9H, *J* = 7.0 Hz, CH_3), 3.90 (q, 6H, *J* = 7.0 Hz, OCH_2), 6.35 (d, 1H, *J* = 19.6 Hz, vin), 7.24 (d, 1H, *J* = 19.6 Hz, vin), 7.53–7.73 (m, 5H, ph, naph), 7.95 (d, 1H, *J* = 8.0 Hz, naph), 8.04 (d, 1H, *J* = 8.0 Hz, naph), 8.16 (d, 2H, *J* = 8.0 Hz, 2-H, 6-H, ph), 8.26 (dd, 1H, *J* = 8.0, 1.0 Hz, naph), 9.29 (d, 1H, *J* = 8.4 Hz, naph).

^{13}C NMR ($CDCl_3$): δ = 18.3 (CH_3), 58.7 (OCH_2), 120.5, 123.7, 130.1, 133.9, 140.8 (C_q), 121.1, 124.9, 126.3, 126.8, 127.3 (2C), 127.4 (2C), 128.2, 128.4, 128.7, 132.7, 147.6 (CH), 164.0, 164.6 (C-2, C-5, oxadiazole).

MS (FD): *m/z* = 922 (1) [M_2^+], 461 (100) [M^+], 230.7 (1) [M^{2+}].

2-(1-Naphthyl)-5-{4-[(1*E*)-3-(triethoxysilyl)-1-propenyl]phenyl}-1,3,4-oxadiazole (9)

$Pd(OAc)_2$ (20 mg, 0.09 mmol), tris-*o*-tolylphosphine (55 mg, 0.18 mmol), and Et_3N (0.43 g, 4.2 mmol) were added to a solution of **3** (0.3 g, 0.85 mmol) and **6** (0.17 g, 0.85 mmol) in anhyd DMF (30 mL) and stirred under N_2 for 3 h at 115 °C. Extraction with toluene-cyclohexane (1:1, 3 × 20 mL), washing with iced water, and drying ($MgSO_4$) was followed by chromatography on silica gel (toluene–EtOAc, 5:1) to yield 270 mg (68%) of a slightly yellow solid, mp 82 °C.

IR (neat): ν = 3040, 2960, 2910, 2870, 1630, 1600, 1550, 1519, 1480, 1380, 1242, 1160, 1060, 955, 860, 802, 770, 740 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.28 (t, 9H, *J* = 7.0 Hz, CH_3), 1.87 (dd, 2H, *J* = 8.0, 1.0 Hz, Si-CH_2), 3.86 (q, 6H, *J* = 7.0 Hz, OCH_2), 6.42 (m, 2H, vin), 7.48 (d, 2H, *J* = 8.0 Hz, ph), 7.53–7.72 (m, 3H, naph), 7.94 (d, 1H, *J* = 8.0 Hz, naph), 8.04 (d, 1H, *J* = 8.0 Hz, naph), 8.11 (d, 2H, *J* = 8.0 Hz, 2-H, 6-H, ph), 8.27 (dd, 1H, *J* = 8.0, 1.0 Hz, naph), 9.28 (d, 1H, *J* = 8.4 Hz, naph).

^{13}C NMR ($CDCl_3$): δ = 7.7 (Si-CH_2), 18.2 (CH_3), 22.7 (CH_2), 40.5 (N-CH_2), 58.4 (OCH_2), 112.1 (2C), 115.0, 120.8, 126.2, 126.6, 127.9, 128.0, 128.3, 128.6, 130.0 (2C), 132.1, 133.8 (CH, C_q, 1 signal superimposed), 151.4 (C-N), 161.5, 164.9 (oxadiazole).

MS (FD): *m/z* = 475 (100) [M^+].

2-(1-Naphthyl)-5{[4′-5(1-naphthyl)-1,3,4-oxadiazol-2-yl][1,1′-biphenyl]-4-yl}-1,3,4-oxadiazole (10)

Procedure (a)

Synthesised according to the procedure described for **8** without adding silane. After stirring for 5 h at 130–135 °C, the cooled mixture was diluted with MeOH (60 mL) and the product was isolated by filtration and washed with MeOH, CH_2Cl_2, and MeOH and dried. Light orange plates with very poor solubility, yield: 153 mg, (6%); mp 317 °C (Lit:[21] mp 319–324 °C).

Procedure (b)

A solution of α-naphthoylchloride (200 mg, 1.1 mmol) and 4,4′-bis(5-tetrazolyl)biphenyl (145 mg, 0.5 mmol) in pyridine (3 mL) was heated to 135 °C for 2 h. The hot mixture was poured into MeOH (10 mL) and diluted with H_2O (10 mL). The greenish solid, isolated by filtration, was recrystallised from toluene. Yield: 155 mg (57%), orange powder. The spectra (IR, ^1H NMR and MS) of the compounds from both sources were identical.

IR (KBr): ν = 1570, 1503, 1470, 1398, 1245, 1185, 1125, 1090, 1070, 1025, 980, 960, 828, 797, 762, 735 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.56–7.76 (m, 6H, naph), 7.88 (d, 4H, J = 8.2 Hz, ph), 7.96 (d, 2H, J = 8.6 Hz, naph), 8.07 (d, 2H, J = 8.3 Hz, naph), 8.28–8.36 (m, 4H, ph + 2H naph), 9.31 (d, 2H, J = 8.3 Hz, 8-H, naph).

MS (FD): m/z = 542.9 (100) [M$^+$], 271.8 (5) [M^{2+}].

Diethoxy(methyl)(4-vinylphenyl)silane (13)

Mg turnings (2.7 g, 0.11 mol) were added to a magnetically stirred solution of 4-bromostyrene (18.3 g, 0.10 mol) and triethoxymethylsilane (52 g, 0.3 mol) in anhyd THF (200 mL) and heated under N$_2$ to reflux until the Mg was mostly dissolved (8 h). THF (150 mL) was distilled off, the residue was cooled to ambient temperature, and anhyd petroleum ether (40–70, 300 mL) was added. After 2 h, the liquid layer was separated and the solvents were evaporated under normal pressure, residual triethoxymethylsilane at 20 mbar. *tert*-Butylhydroquinone (0.2 g) was added and the product was distilled under vacuum. Yield: 9.6 g (41%); bp 70 °C (0.07 mbar). Severe loss of product occurred during distillation due to polymerisation.

IR (neat): ν = 3050, 2965, 2920, 2870, 1622, 1590, 1538, 1478, 1435, 1378, 1256, 1165, 1100, 1060, 950, 805, 760 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.34 (s, 3H, Si-CH$_3$), 1.22 (t, 6H, J = 6.5 Hz, CH$_3$), 3.80 (q, 4H, J = 6.3 Hz, OCH$_2$), 5.26 (d, 1H, J = 11.2 Hz, vin), 5.78 (d, 1H, J = 17.6 Hz, vin), 6.71 (dd, 1H, J = 10.8, 17.6 Hz, vin), 7.40 (d, 2H, J = 7.8 Hz, ph), 7.58 (d, 2H, J = 7.8 Hz, ph).

^{13}C NMR (CDCl$_3$): δ = –0.2 (Si-CH$_3$), 18.4 (CH$_3$), 58.5 (OCH$_2$), 114.4 (CH$_2$ vin), 125.6, 133.5, 136.8 (CH), 134.0 (C$_q$) (1 C$_q$ superimposed).

MS (FD): m/z = 236.6 (100) [M$^+$].

2-[4-((*E*)-2-{4-[Diethoxy(methyl)silyl]phenyl}ethenyl)phenyl]-5-(1-naphthyl)-1,3,4-oxadiazole (14)

Synthesised from **3** (220 mg, 0.62 mmol) and **13** (150 mg, 0.62 mmol) according to the procedure described for **8**. Purification by chromatography on silica gel (petroleum ether-toluene, 1:5), followed with EtOAc eluted **14**. Yield: 100 mg (31%) of a slightly yellow solid; mp 158 °C.

IR (CDCl$_3$): ν = 3025, 2950, 2860, 1592, 1572, 1535, 1520, 1478, 1411, 1385, 1258, 1160, 1112, 1065, 1008, 950, 860, 833, 800, 770, 740, 720 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.36 (s, 3H, Si-CH$_3$), 1.27 (t, 6H, J = 7.0 Hz, CH$_3$), 3.82 (q, 4H, J = 7.0 Hz, OCH$_2$), 7.22 (m, 2H), 7.52–7.70 (m, 9H, ph, vin, naph), 7.94 (d, 1H, J = 7.8 Hz, naph), 8.05 (d, 1H, J = 7.8 Hz, naph), 8.18 (d, 2H, J = 8.3 Hz, ph), 8.18 (d, 1H, J = 7.2 Hz, naph), 9.29 (d, 1H, J = 8.3 Hz, naph).

^{13}C NMR (CDCl$_3$): δ = –4.2 (Si-CH$_3$), 18.2 (CH$_3$), 58.5 (OCH$_2$), 120.6, 122.7, 124.8, 126.1 (2C), 126.2, 126.7, 127.0 (2C), 127.3 (2C), 128.1, 128.1, 128.3, 128.6, 130.1, 131.0, 132.5, 133.9, 134.4 (2C), 135.1, 138.1, 140.7(CH, C$_q$), 164.0, 164.5 (C-2, C-5, oxd).

MS (FD): m/z = 507.2 (100) [M$^+$].

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