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Synthesis and Characterization of Oxadisilole-Fused 1*H*-Benzo[*f*]indazoles and 1*H*-Naphtho[2,3-*f*]indazoles

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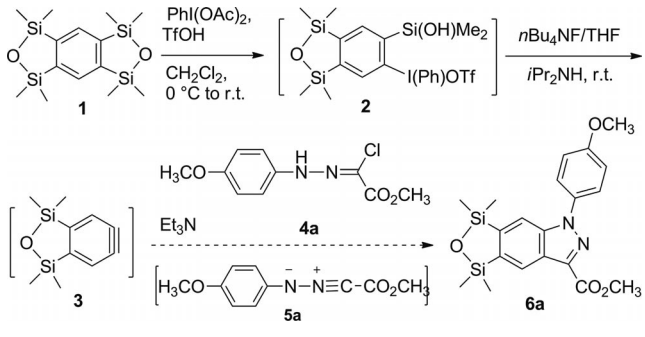
Oxadisilole-fused 1*H*-benzo[*f*]- and 1*H*-naphtho[2,3-*f*]-indazoles have been synthesized by the 1,3-dipolar cycloaddition reactions of benzo- or naphtho-oxabicycloalkenes with nitrile imines generated in situ from *N*-arylhydrazonoyl chlorides followed by deoxygenation and aromatization. The photophysical, redox and thermal properties of these compounds have been characterized. Some of the indazoles show potential as deep-blue emitters for OLED applications as a result of their high fluorescence quantum yields and good thermal stabilities.

Introduction

1,3-Dipolar cycloaddition reactions have received considerable attention because they have been shown to be an efficient synthetic tool for the preparation of a wide variety of heterocyclic compounds.[1] Nitrile imines are versatile 1,3-dipoles that undergo cycloaddition reactions with a wide range of alkenes,[2] alkynes,[3] C=N[4] and C=S compounds[5] and benzyne,[6] allowing the construction of substituted pyrazole, indazole and other azo heterocycles. Pyrazoles[7] and indazoles[8] exhibit diverse bioactivities and pharmacological activities, including anti-HIV, Rho-kinase inhibition, anti-fertility, anti-arthritic, anti-inflammatory, and contraceptive activities. Meanwhile, the use of pyrazole derivatives such as dipyrazolopyridines or pyrazoloquinolines as efficient blue or green light-emitting materials in multi-layer OLEDs has been reported.[9] Various methods for the synthesis of the 1*H*-indazole (benzopyrazole) core have been developed.[10] Recently, several methodologies have been reported that involve aryne intermediates in [3+2] cycloaddition reactions with diazo compounds[6b,11] and in situ generated nitrile imines.[6] Most benzynes are commonly accessed in situ by fluoride-promoted *ortho* elimination of *o*-(trimethylsilyl)aryl triflates.[6,11] The formation of the benzyne of benzoxadisilole by phenyliodination with *o*-bis(trimethylsilyl)benzene has also been reported by Kitamura and Yamane.[12]

Recently, we became interested in the chemistry of arynes generated from benzobis(oxadisilole), benzotris(oxadisilole) and 2,3-naphthoxadisilole under very mild conditions. We reported the synthesis of oxadisilole-fused benzo[*d*]isoxazoline, benzotriazole and benzisoxazole derivatives as well as the naphtho[2,3-*d*]isoxazoline, naphthotriazole and naphthisoxazole derivatives by the 1,3-dipolar cycloaddition of nitrones, azides and nitrile oxides to arynes generated from benzobis(oxadisilole) and 2,3-naphthoxadisilole, respectively, under very mild conditions.[13] On the other hand, our attempt to synthesize **6a** by the 1,3-dipolar cycloaddition reaction of oxadisilole-fused benzyne **3** with nitrile imine **5a** was in vain (Scheme 1), likely because of the problem of simultaneous in situ generation of reactive nitrile imine **5a** from *N*-arylhydrazonoyl chloride **4a** and benzyne **3** moieties derived from benzobis(oxadisilole) **1**. In this contribution we report our findings on the synthesis of oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e** and 1*H*-naphtho-[2,3-*f*]indazoles **15a**–**e** by 1,3-dipolar cycloaddition reactions of oxabicyclic alkenes **7** and **13**, respectively, with ni-



Scheme 1. Synthesis of oxadisilole-fused 1*H*-indazole **6a** proved not to be feasible.

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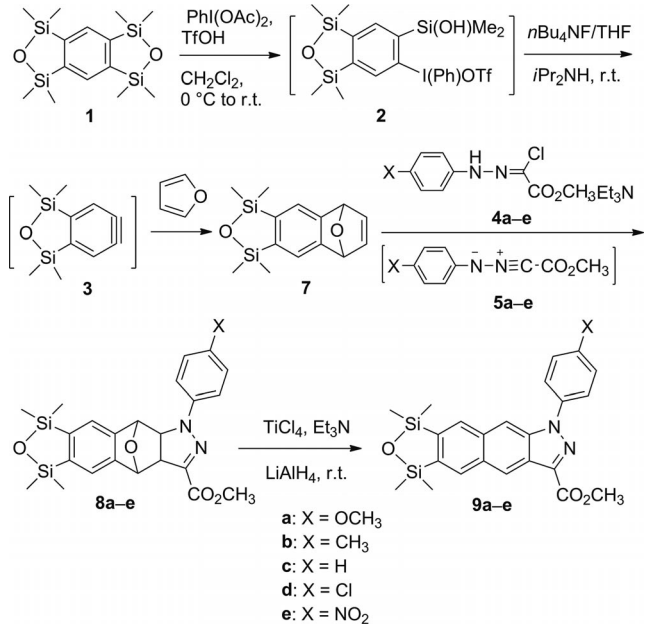
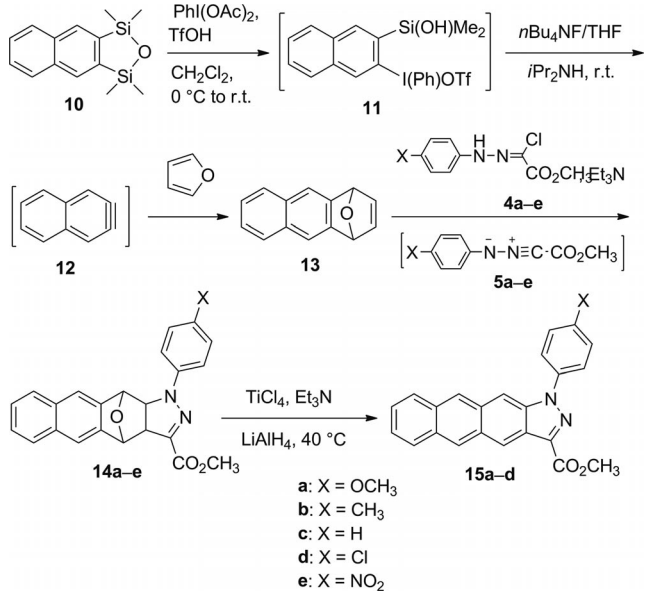
trile imines **5a**–**e** followed by deoxygenation and aromatization. The oxabicyclic alkenes **7** and **13** are the furan cycloadducts of benzyne **3** and naphthyne **12** generated from benzobis(oxadisilole) **1** and 2,3-naphthoxadisilole **10**, respectively (see Schemes 2 and 3).[14] The nitrile imine dipoles **5a**–**e** were generated by treating *N*-arylhydrazonoyl chlorides **4a**–**e** with base.[6] The deoxygenation protocol depicted in Schemes 2 and 3 leads to the linear polycyclic aromatic skeletons. The previously unknown compounds **9a**–**e** and **15a**–**d** were characterized.



Scheme 2. Synthesis of oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e**.



Scheme 3. Synthesis of 1*H*-naphtho[2,3-*f*]indazoles **15a**–**d**.

Results and Discussion

The procedures for the synthesis of the oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e** or 1*H*-naphtho[2,3-*f*]indazoles **15a**–**d** are outlined in Schemes 2 and 3. The oxabicyclic alkenes **7** and **13** were prepared according to our previously reported phenyliodination/fluoride-induced desilylation protocol by trapping the arynes (**3** and **12**) generated from **1** and **10** with furan in yields of 88 and 54%, respectively.[14] The 1,3-dipolar nitrile imines **5a**–**e** are reactive intermediates, commonly generated in situ by the base-induced dehydrodechlorination of *N*-arylhydrazonoyl chlorides **4a**–**e**.[6,11] Compounds **4a**–**e** were prepared according to literature procedures.[6] Oxadisilole-fused benzo-oxabicyclic alkene **7** and naphtho-oxabicyclic alkene **13** reacted with nitrile imines **5a**–**e** by 1,3-dipolar cycloaddition to afford **8a**–**e** and **14a**–**e**, respectively, in good yields. After deoxygenation followed by aromatization, oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e** and 1*H*-naphtho[2,3-*f*]indazoles **15a**–**d**, respectively, were synthesized.

We optimized the procedure by starting with the reaction of oxadisilole-fused benzo-oxabicyclic alkene **7** and nitrile imine **5d** generated in situ from the corresponding **4d** (1.2 equiv.) with triethylamine as base at room temperature in $CHCl_3$ for 24 h. The [3+2] cycloadduct **8d** was obtained in 46% isolated yield (Scheme 2, Table 1, entry 1). By using 2.0 and 3.0 equiv. of **4d** at room temperature for 24 h, **8d** was obtained in yields of 48 and 56%, respectively (Table 1, entries 2 and 3). The [3+2] cycloaddition reaction of **7** with **5d**, obtained from 3.0 and 2.0 equiv. of **4d**, at 50 °C for 24 h improved the yield of product **8d** to 67 and 68%, respectively (Table 1, entries 4 and 5). Shortening the reaction time to 6 h at 50 and 60 °C also gave higher yields of 74 and 71%, respectively (Table 1, entries 6 and 7). Thus, the optimal results were obtained when the reaction between **7** and **5d** was performed with 2.0 equiv. of **4d** in $CHCl_3$ at 50 °C for 6 h (Table 1, entry 6).

Table 1. Optimization of the conditions for the reaction between **7** (1 equiv.) and **5d** generated from **4d** in $CHCl_3$.

Entry	**4d** [equiv.]	*T* [°C]	Time [h]	Yield[a] [%]
1	1.2	r.t.	24	46
2	2.0	r.t.	24	48
3	3.0	r.t.	24	56
4	3.0	50	24	67
5	2.0	50	24	68
6	2.0	50	6	74
7	2.0	60	6	71

[a] Isolated yield.

We then studied the 1,3-dipolar cycloaddition reaction of oxadisilole-fused benzo-oxabicyclic alkene **7** with various nitrile imine dipoles **5a**–**e** generated in situ from the corresponding hydrazonoyl chlorides **4a**–**e** in $CHCl_3$ at 50 °C for 6 h. The cycloadducts **8a**–**e** were obtained in yields of 58–89% (Scheme 2, Table 2, entries 1–5). The results indicate that the cycloaddition reactions of **7** with **5a**–**e** are quite sensitive to the electronic nature (X = OCH_3, CH_3, H, Cl, NO_2) of the substituents on the phenyl rings of **4a**–**e**; the

electron-rich hydrazonoyl chlorides gave higher yields than the electron-deficient compounds. Thus, the stronger the electron-donating nature of the substituent (X = OCH_3; Table 2, entry 1), the higher the isolated yield. In contrast, the stronger the electron-withdrawing nature of the substituent (X = NO_2), the poorer the yield (Table 2, entry 5).

Table 2. Cycloaddition reactions of **7** and **13** (1 equiv.) with **5a**–**e** generated from **4a**–**e** (2 equiv.) in $CHCl_3$ at 50 °C.

Entry	Hydrazonoyl chloride	X	Oxabicyclic alkene	Product	Yield[a] [%]
1	**4a**	OCH_3	**7**	**8a**	89
2	**4b**	CH_3	**7**	**8b**	78
3	**4c**	H	**7**	**8c**	76
4	**4d**	Cl	**7**	**8d**	74
5	**4e**	NO_2	**7**	**8e**	58
6	**4a**	OCH_3	**13**	**14a**	78
7	**4b**	CH_3	**13**	**14b**	89
8	**4c**	H	**13**	**14c**	84
9	**4d**	Cl	**13**	**14d**	67
10	**4e**	NO_2	**13**	**14e**	49

[a] Isolated yield.

We then turned out attention to the 1,3-dipolar cycloaddition reaction of naphtho-oxabicyclic alkene **13** with various nitrile imine dipoles **5a**–**e** generated in situ from the corresponding hydrazonoyl chlorides **4a**–**e** in $CHCl_3$ at 50 °C for 6 h. Both the electron-rich and -deficient dipoles successfully participated in the [3+2] cycloaddition reaction to afford the desired products **14a**–**e** in yields of 49–89% (Scheme 3, Table 2, entries 6–10). Again, a strongly electron-withdrawing substituent (X = NO_2) on the phenyl ring led to a lower yield (Table 2, entry 10).

As outlined in Scheme 2 and Scheme 3, deoxygenation of the cycloadducts **8a**–**e** and **14a**–**e** with $TiCl_4/LiAlH_4/Et_3N$ in CH_2Cl_2 afforded the oxadisilole-fused 1*H*-benzo[*f*]-indazoles **9a**–**e** and 1*H*-naphtho[2,3-*f*]indazoles **15a**–**d**, respectively, under mild conditions.

The deoxygenation/aromatization[14] of cycloadduct **8d** with $TiCl_4/LiAlH_4/Et_3N$ in THF at room temperature for 24 h afforded the oxadisilole-fused 1*H*-benzo[*f*]indazole **9d** in 6% yield (Table 3, entry 1). To tackle the low yield, the reaction conditions were optimized. No product was detected with DME as the solvent (Table 3, entry 2). By changing the solvent to toluene or CH_2Cl_2, the product yield greatly improved to 32 and 67%, respectively (Table 3, entries 3 and 4). When the reaction was performed for 12 or 30 h and the temperature was increased to 40 °C, the desired product **9d** was obtained in yields of 56, 57 and 63%, respectively (Table 3, entries 5–7). Thus, the optimal conditions were the use $TiCl_4/LiAlH_4/Et_3N$ in CH_2Cl_2 at room temperature with a reaction time of 24 h (Table 3, entry 4).

Table 3. Optimization of the synthesis of **9d** by the deoxygenation of **8d** in the presence of $TiCl_4$, Et_3N and $LiAlH_4$.

Entry	Solvent	*T* [°C]	Time [h]	Yield[a] [%]
1	THF	r.t.	24	6
2	DME	r.t.	24	0
3	toluene	r.t.	24	32
4	CH_2Cl_2	r.t.	24	67
5	CH_2Cl_2	r.t.	12	56
6	CH_2Cl_2	r.t.	30	57
7	CH_2Cl_2	40	24	63

[a] Isolated yield.

Having established the optimal reaction conditions, we studied the deoxygenation of **8a**–**e** with $TiCl_4/LiAlH_4/Et_3N$ in CH_2Cl_2 at room temperature for 24 h; oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e** were obtained in yields of 18–67% (Scheme 2, Table 4, entries 1–5). Note that the yield of **9e** (X = NO_2) was rather poor (Table 4, entry 5).

Table 4. Synthesis of **9a**–**e** and **15a**–**d** by the deoxygenation of **8a**–**e** and **14a**–**e** in the presence of $TiCl_4$, Et_3N and $LiAlH_4$ in CH_2Cl_2.[a]

Entry	Cycloadduct	X	Product	Yield[b] [%]
1	**8a**	OCH_3	**9a**	60
2	**8b**	CH_3	**9b**	63
3	**8c**	H	**9c**	47
4	**8d**	Cl	**9d**	67
5	**8e**	NO_2	**9e**	18
6	**14a**	OCH_3	**15a**	43
7	**14b**	CH_3	**15b**	69
8	**14c**	H	**15c**	65
9	**14d**	Cl	**15d**	62

[a] The reactions of **8a**–**e** were performed at room temp. for 24 h and the reactions of **14a**–**e** were performed at 40 °C for 1 h. [b] Isolated yield.

Aromatization by the deoxygenation of **14b** with $TiCl_4/LiAlH_4/Et_3N$ in CH_2Cl_2 at room temperature for 24 h afforded 1*H*-naphtho[2,3-*f*]indazole **15b** in only 6% yield (Scheme 3, Table 5, entry 1). The reaction was optimized and the results are summarized in Table 5. It was found that the deoxygenation of **14b** at 40 °C for 1 h greatly improved the yield of **15b** to 69% (Table 5, entry 5).

Table 5. Optimization of the synthesis of **15d** by the deoxygenation of **14d** in the presence of $TiCl_4$, Et_3N and $LiAlH_4$ in CH_2Cl_2.

Entry	*T* [°C]	Time [h]	Yield[a] [%]
1	r.t.	24	6
2	40	24	14
3	40	5	17
4	40	3	26
5	40	1	69
6	40	0.5	53

[a] Isolated yield.

The same reaction sequence was then applied to the deoxygenation of **14a**–**e** under the optimized conditions of $TiCl_4/LiAlH_4/Et_3N$ in CH_2Cl_2 at 40 °C for 1 h. 1*H*-Naphtho[2,3-*f*]indazoles **15a**–**d** were obtained in yields of 43–69% (Scheme 3, Table 4, entries 6–9). Again, the desired product **15e**, bearing the strongly electron-withdrawing group NO_2, could not be obtained.

The structues of compounds **8a**–**e**, **9a**–**e**, **14a**–**e** and **15a**–**d** were established by ^1H and ^{13}C NMR and IR spectroscopy, MS and elemental analysis; the results were in good agreement with the expected structures.

The absorption spectra of **9a**–**e** and **15a**–**d** were recorded in CH_2Cl_2 and the spectral data are summarized in Table 6. The absorption spectra of **9a**–**e** and **15a**–**d** show the charac-

teristic strong β-band absorption at approximately 268 nm for **9a**–**e** and 277 nm for **15a**–**d**, with the long wavelength absorption bands located between 386 and 400 nm for **9a**–**e** and 484 and 487 nm for **15a**–**d** (Figures 1 and 2). A slight redshift is observed for the absorption maximum of **9a**–**e** compared with **15a**–**d** due to extended conjugation in the latter compounds **15a**–**d**. A substituent effect is also observed in the **9a**–**e** series, with electron-donating and -withdrawing groups (**9a**: X = OCH_3 and **9e**: X = NO_2) producing a slight redshift in the absorption with respect to **9c** (X = H).

Table 6. Summary of optical measurements and thermal properties of **9a**–**e** and **15a**–**d**.

	λ^{abs}_{max}[a][nm] (ε_{max} [10^4 M^{-1} cm^{-1}])	λ^{em}_{max}[a,b] [nm]	Φ_{FL}[c]	T_m [°C]	T_{dec}[d] [°C]
9a	388 (0.90)	466	0.59	188	338
9b	386 (0.88)	449	0.76	171	329
9c	386 (0.87)	446	0.80	167	322
9d	387 (0.99)	448	0.47	192	316
9e	400 (0.54)	523	0.16	204	250
15a	487(0.18)	502	0.39	186	186
15b	485 (0.37)	502	0.46	166	218
15c	484 (0.32)	497	0.45	171	201
15d	484 (0.58)	499	0.48	206	342

[a] Measured in CH_2Cl_2. [b] Excited at the absorption maximum. [c] Norharman in 0.1 M H_2SO_4 ($\Phi_{330\sim390}$ = 0.58) was used as a standard for the oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e** and coumarin 6 in ethanol (Φ_{420} = 0.78) was used as a standard for 1*H*-naphtho[2,3-*f*]indazoles **15a**–**d**. [d] Determined by thermal gravimetric analysis at a heating rate of 10 °C min^{-1} under N_2.

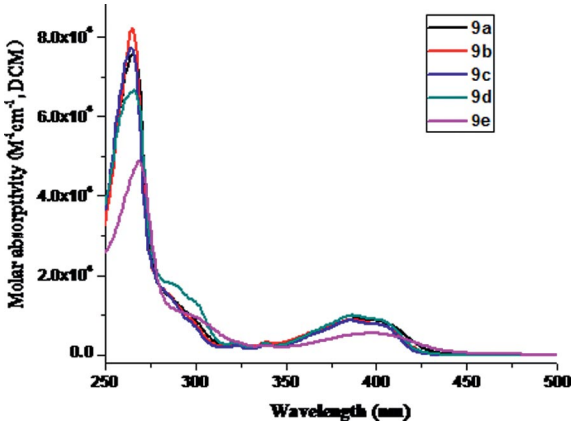


Figure 1. Absorption spectra of **9a**–**e** in CH_2Cl_2.

The photoluminescence spectra of **9a**–**e** and **15a**–**d** in CH_2Cl_2 show moderate-to-strong deep-blue to green emission with maxima in the range of 446–523 nm (Figures 3 and 4, Table 6). A similar substituent effect was also found for the emission maximum in **9a**–**e**, that is, the emission maximum shifts to a longer wavelength for derivatives substituted with an electron-donating or -withdrawing group (i.e., X = OCH_3 or NO_2) relative to that of **9c** (X = H), which allows the color emission of this series to be tuned. The fluorescence quantum yields (Φ) measured in CH_2Cl_2 by using norharman as the reference for **9a**–**e** and coumarin 6 as the reference for **15a**–**d** are in the range of 47–80%

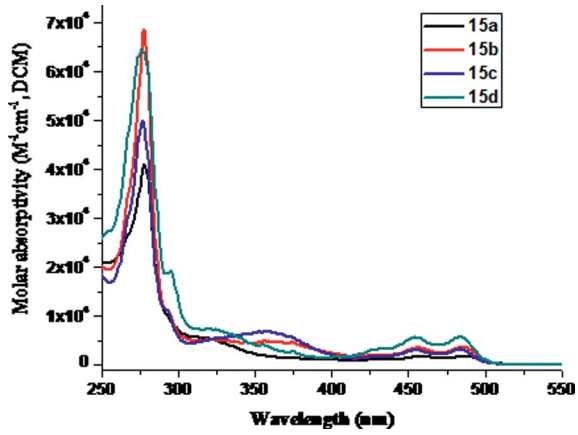


Figure 2. Absorption spectra of **15a**–**d** in CH_2Cl_2.

for **9a**–**d** (with a value of 16% for **9e**) and 39–48% for **15a**–**d**, respectively. Thus, molecules **9a**–**d** show potential as deep-blue emitters for organic light-emitting diode (OLED) applications. In addition, the thermal properties of these two series were determined by differential scanning calorim-

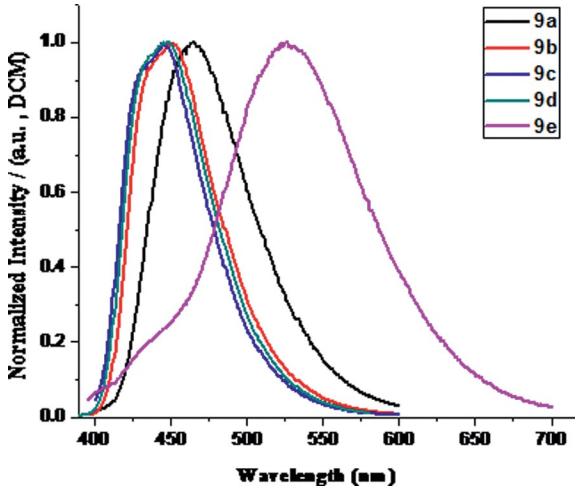


Figure 3. Emission spectra of **9a**–**e** in CH_2Cl_2.

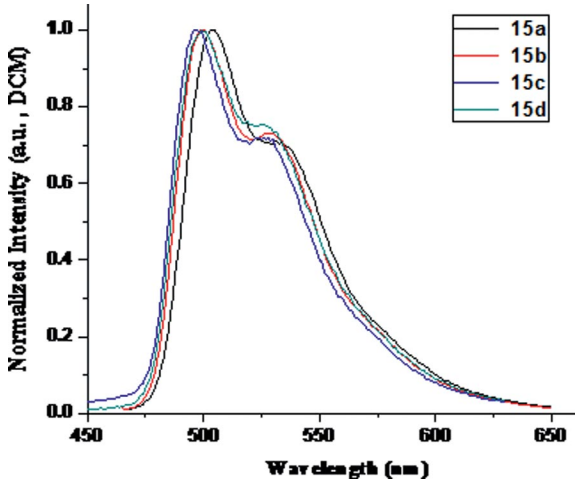


Figure 4. Emission spectra of **15a**–**d** in CH_2Cl_2.

etry (DSC) and thermal gravimetric analysis (TGA) analyses. In general, they show good thermal stability, particularly **9a**–**d**, over 300 °C and high melting points ranging from 166 to 206 °C.

The redox properties as well as the HOMO (highest-occupied molecular orbital) and LUMO (lowest-unoccupied molecular orbital) energy levels of **9a**–**e** and **15a**–**d** are tabulated in Table 7. The redox properties of **9a**–**e** and **15a**–**d** were studied by cyclic voltammetry in a three-electrode cell in CH_2Cl_2 with 0.1 M of Bu_4NPF_6 as the supporting electrolyte. All of the potentials reported are referenced to Fc/Fc^+ as standard. In contrast to the optical properties, the substituent on the 1-aryl ring has an insignificant effect on the oxidation potential (E_{ox}), which lies in the range of 1.28–1.41 V for **9a**–**d** (with 0.09 V for **9e**) and 0.97–1.01 V for **15a**–**d**. The HOMO energy values were calculated by the equation of Janietz or Schmidt,[15,16a] and the LUMO energy levels were obtained by subtraction of the optical band gap from the HOMO. Molecules within the same series, that is, **9a**–**e** or **15a**–**d**, show similar HOMO energies. In addition, the band gaps within the same series are also very similar, with the exception of **9e**, which has a smaller band gap due to a larger redshift in the absorption spectrum.

Table 7. Oxidation potentials and HOMO and LUMO energy levels of **9a**–**e** and **15a**–**d**.

	E_{ox}[a] [V]	HOMO[b] [eV]	Band gap[c] [eV]	LUMO[d] [eV]
9a	1.28	–5.59	2.89	–2.70
9b	1.34	–5.65	2.92	–2.73
9c	1.37	–5.68	2.94	–2.74
9d	1.41	–5.72	2.93	–2.79
9e	0.90	–5.21	2.81	–2.40
15a	0.97	–5.28	2.45	–2.83
15b	0.98	–5.29	2.47	–2.82
15c	1.01	–5.32	2.48	–2.84
15d	1.01	–5.32	2.47	–2.85

[a] E_{ox} was estimated by CV in CH_2Cl_2 with a platinum disk as the working electrode, a platinum wire as the counter electrode and SCE as the reference electrode with an agar salt bridge connecting the compound solution and ferrocene as an external standard, and 0.1 M $TBAPF_6$ at a scan rate of 100 mV/s, $E_{1/2}(Fc/Fc^+)$ = 0.49 V vs. SCE, calculated with ferrocene (4.8 eV vs. vacuum). [b] HOMO = E_{ox} – [$E_{1/2}$ (Fc/Fc^+)] + 4.8. [c] Estimated from the absorption edge in CH_2Cl_2. [d] LUMO = HOMO + Optical band gap.

Conclusions

Two previously unknown series of oxadisilole-fused 1*H*-benzo[*f*]indazoles **9a**–**e** and 1*H*-naphtho[2,3-*f*]indazoles **15a**–**d** have been synthesized, respectively, by the 1,3-dipolar cycloaddition reactions of oxabicyclic alkenes **7** and **13** with nitrile imines **5a**–**e** generated in situ from *N*-arylhydrazonoyl chlorides **4a**–**e** followed by deoxygenation/aromatization under mild conditions. The photophysical, redox and thermal properties of the oxadisilole-fused 1*H*-benzo[*f*]- and 1*H*-naphtho[2,3-*f*]indazoles have been characterized. Compounds **9a**–**d** show potential as deep-blue emitters for OLED applications because of their high fluorescence quantum yields and thermal stabilities.

Experimental Section

General Methods: Purification was effected by silica gel column chromatography (200–300 mesh silica gel) using mixtures of reagent-grade EtOAc/petroleum ether (PE, 60–80 °C) as eluents. NMR spectra were recorded with a Bruker DRX-500 NMR spectrometer at 500 MHz for ^1H and at 125 MHz for ^{13}C with $CDCl_3$ as solvent. Chemical shifts are reported in ppm on the δ scale relative to the residual resonance of $CHCl_3$ (δ = 7.26 ppm for ^1H and 77.16 ppm for the central peak of the triplet in ^{13}C). Coupling constants (J) are reported in Hz. IR spectra were recorded with an FTIR spectrometer in KBr discs. Low-resolution mass spectra were recorded with an Agilent spectrometer in EI or API-ES mode. High-resolution mass spectra were recorded with a Waters Micromass GCT instrument. Element analyses were performed at the Shanghai University. The fluorescence quantum yields in solution were determined by the dilution method using norharman ($\Phi_{330-390}$ = 0.58) or coumarin 6 (Φ_{420} = 0.78) as standard. Thermal stabilities were determined by thermal gravimetric analysis with a heating rate of 10 °C min^{-1} under N_2.

Synthesis of Cycloadducts 8a–e and 14a–e: Triethylamine (0.12 mL, 4.0 mmol in 6 mL chloroform) was added by means of a syringe to a stirred mixture of compound **7** or **13** (1.0 mmol) and hydrazonoyl chlorides **4a**–**e** (2.0 mmol) in chloroform (12 mL) at 50 °C under N_2. The reaction mixture was stirred at 50 °C for 6 h and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 5–10% EtOAc in PE (60–80 °C) as the eluent to afford cycloadducts **8a**–**e** and **14a**–**e**.

Methyl 1-(4-Methoxyphenyl)-6,7-[oxybis(dimethylsilanediyl)]-3a,4,9,9a-tetrahydro-4,9-epoxy-1*H*-benzo[*f*]indazole-3-carboxylate (8a): Yield 427 mg, 89%; yellow solid; m.p. 120–121 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.346 (s, 3 H, SiMe), 0.351 (s, 3 H, SiMe), 0.39 (s, 3 H, SiMe), 0.41 (s, 3 H, SiMe), 3.82 (s, 3 H, OMe), 3.91 (d, J = 9.0 Hz, 1 H, C*H*-C=), 3.92 (s, 3 H, OMe), 4.70 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.72 (s, 1 H, C*H*-O), 5.73 (s, 1 H, C*H*-O), 6.93 (d, J = 9.0 Hz, 2 H, Ar-H), 7.23 (d, J = 9.0 Hz, 2 H, Ar-H), 7.59 (s, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.07, 1.15, 1.18, 1.3, 52.3, 55.5, 55.8, 69.8, 83.1, 83.5, 114.9, 115.0, 115.6, 122.5, 135.6, 135.7, 143.4, 146.3, 148.2, 148.9, 155.2, 163.4 ppm. IR (KBr): $\tilde{\nu}$ = 3436, 2954, 1697, 1512, 1449, 1250, 932, 792 cm^{-1}. MS (API-ES): m/z (%) = 503.1 (35) [M + Na]$^+$, 233.1 (100). $C_{24}H_{28}N_2O_5Si_2$ (480.67): calcd. C 59.97, H 5.87, N 5.83; found C 59.65, H 6.25, N 5.49.

Methyl 1-(4-Methylphenyl)-6,7-[oxybis(dimethylsilanediyl)]-3a,4,9,9a-tetrhydro-4,9-epoxy-1*H*-benzo[*f*]indazole-3-carboxylate (8b): Yield 362 mg, 78%; yellow solid; m.p. 152–153 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.36 (s, 6 H, $SiMe_2$), 0.40 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe), 2.34 (s, 3 H, Me), 3.91 (d, J = 9.5 Hz, 1 H, C*H*-C=), 3.93 (s, 3 H, OMe), 4.71 (d, J = 9.5 Hz, 1 H, C*H*-N), 5.74 (s, 1 H, C*H*-O), 5.75 (s, 1 H, C*H*-O), 7.17–7.21 (m, 4 H, Ar-H), 7.60 (s, 1 H, Ar-H), 7.61 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.05, 1.14, 1.16, 1.3, 20.8, 52.3, 55.5, 69.4, 83.0, 83.5, 114.1, 122.5, 122.6, 130.1, 131.4, 136.2, 139.3, 143.4, 146.3, 148.2, 148.9, 163.4 ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2955, 1710, 1518, 1447, 1261, 933, 792 cm^{-1}. MS (API-ES): m/z (%) = 487.0 (31) [M + Na]$^+$, 217.1 (100). $C_{24}H_{28}N_2O_4Si_2$ (464.67): calcd. C 62.06, H 6.07, N 6.03; found C 61.96, H 5.88, N 5.87.

Methyl 1-Phenyl-6,7-[oxybis(dimethylsilanediyl)]-3a,4,9,9a-tetrahydro-4,9-epoxy-1*H*-benzo[*f*]indazole-3-carboxylate (8c): Yield 342 mg, 76%; yellow solid; m.p. 107–108 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.359 (s, 3 H, SiMe), 0.360 (s, 3 H, SiMe), 0.40 (s, 3

H, SiMe), 0.42 (s, 3 H, SiMe), 3.92 (d, J = 9.0 Hz, 1 H, C*H*-C=), 3.93 (s, 3 H, OMe), 4.73 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.75 (s, 1 H, C*H*-O), 5.76 (s, 1 H, C*H*-O), 7.03 (t, J = 7.0 Hz, 1 H, Ar-H), 7.28–7.31 (m, 2 H, Ar-H), 7.36–7.40 (m, 2 H, Ar-H), 7.60 (s, 1 H, Ar-H), 7.62 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.05, 1.14, 1.16, 1.23, 52.3, 55.6, 69.3, 83.0, 83.5, 114.1, 121.9, 122.5, 122.6, 129.6, 137.0, 141.6, 143.3, 146.2, 148.3, 148.9, 163.3 ppm. IR (KBr): $\tilde{\nu}$ = 3436, 2954, 1699, 1502, 1448, 1257, 931, 792 cm^{-1}. MS (API-ES): m/z (%) = 473.0 (59) [M + Na]$^+$, 203.1 (100). $C_{23}H_{26}N_2O_4Si_2$ (450.64): calcd. C 61.30, H 5.82, N 6.22; found C 61.47, H 6.29, N 5.84.

Methyl 1-(4-Chlorophenyl)-6,7-[oxybis(dimethylsilanediyl)]-3a,4,9,9a-tetrahydro-4,9-epoxy-benzo[*f*]indazole-3-carboxylate (8d): Yield 359 mg, 74%; yellow solid; m.p. 146–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.35 (s, 6 H, $SiMe_2$), 0.39 (s, 3 H, SiMe), 0.41 (s, 3 H, SiMe), 3.92 (d, J = 9.0 Hz, 1 H, C*H*-C=), 3.93 (s, 3 H, OMe), 4.67 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.70 (s, 1 H, C*H*-O), 5.75 (s, 1 H, C*H*-O), 7.20 (J = 9.0 Hz, 2 H, Ar-H), 7.31–7.33 (m, 2 H, Ar-H), 7.60 (s, 1 H, Ar-H), 7.61 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.1, 1.15, 1.24, 52.5, 55.9, 69.3, 82.9, 83.3, 115.2, 122.56, 122.61, 126.9, 129.6, 137.7, 140.3, 143.1, 146.1, 148.4, 149.1, 163.1 ppm. IR (KBr): $\tilde{\nu}$ = 3443, 2953, 1731, 1549, 1495, 1239, 929, 790 cm^{-1}. MS (API-ES): m/z (%) = 507.0 (100) [M + Na]$^+$. $C_{23}H_{25}ClN_2O_4Si_2$ (485.09): calcd. C 56.95, H 5.19, N 5.78; found C 56.55, H 5.24. N 5.74.

Methyl 1-(4-Nitrophenyl)-6,7-[oxybis(dimethylsilanediyl)]-3a,4,9,9a-tetrahydro-4,9-epoxy-1*H*-benzo[*f*]indazole-3-carboxylate (8e): Yield 287 mg, 58%; yellow solid; m.p. 170–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.359 (s, 3 H, SiMe), 0.363 (s, 3 H, SiMe), 0.39 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe), 3.97 (s, 3 H, OMe), 3.98 (d, J = 9.0 Hz, 1 H, C*H*-C=), 4.73 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.73 (s, 1 H, C*H*-O), 5.78 (s, 1 H, C*H*-O), 7.31 (d, J = 9.0 Hz, 2 H, Ar-H), 7.61 (s, 1 H, Ar-H), 7.65 (s, 1 H, Ar-H), 8.27 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.1, 1.17, 1.23, 52.8, 56.6, 69.0, 82.7, 83.1, 113.3, 122.7, 122.8, 126.1, 141.7, 142.6, 145.8, 146.6, 147.6, 148.8, 149.5, 162.6 ppm. IR (KBr): $\tilde{\nu}$ = 3439, 2956, 1729, 1599, 1336, 930, 792 cm^{-1}. MS (API-ES): m/z = 496.1 (100) [M + H]$^+$. HRMS (MALDI-TOF): calcd. for $C_{23}H_{25}N_3O_6Si_2$ [M + H]$^+$ 496.1368; found 496.1355.

Methyl 1-(4-Methoxyphenyl)-3a,4,11,11a-tetrahydro-4,11-epoxy-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (14a): Yield 312 mg, 78%; yellow solid; m.p. 170–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OMe), 3.94 (d, J = 9.5 Hz, 1 H, C*H*-C=), 3.96 (s, 3 H, OMe), 4.72 (d, J = 9.5 Hz, 1 H, C*H*-N), 5.83 (s, 1 H, C*H*-O), 5.86 (s, 1 H, C*H*-O), 6.96 (d, J = 8.5 Hz, 2 H, Ar-H), 7.25 (d, J = 8.5 Hz, 2 H, Ar-H), 7.51–7.53 (m, 2 H, Ar-H), 7.81–7.87 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.2, 55.7, 56.0, 70.0, 83.0, 83.5, 115.0, 115.5, 118.9, 119.1, 126.5, 126.6, 128.3, 128.5, 133.0, 133.3, 135.5, 135.9, 139.6, 142.3, 155.2, 163.4 ppm. IR (KBr): $\tilde{\nu}$ = 3434, 2948, 1721, 1510, 1239, 1166, 826 cm^{-1}. MS (API-ES): m/z (%) = 423.0 (100) [M + Na]$^+$. HRMS (MALDI-TOF): calcd. for $C_{24}H_{20}N_2O_4Na$ [M + Na]$^+$ 423.1315; found 423.1328.

Methyl 1-(4-Methylphenyl)-3a,4,11,11a-tetrahydro-4,11-epoxy-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (14b): Yield 342 mg, 89%; yellow solid; m.p. 186–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, Me), 3.90 (d, J = 9.0 Hz, 1 H, C*H*-C=), 3.94 (s, 3 H, OMe), 4.68 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.83 (s, 1 H, C*H*-O), 5.86 (s, 1 H, C*H*-O), 7.20 (s, 4 H, Ar-H), 7.51–7.53 (m, 2 H, Ar-H), 7.79 (s, 1 H, Ar-H), 7.81 (s, 1 H, Ar-H), 7.85–7.87 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8, 52.3, 56.0, 69.7, 83.0, 83.5, 114.2, 119.0, 119.2, 126.55, 126.64, 128.4, 128.5, 130.1, 131.5, 133.0, 133.3, 136.4, 139.3, 139.7, 142.3, 163.4 ppm. IR (KBr): $\tilde{\nu}$ = 3443, 2951, 1682, 1510, 1279, 1166, 809 cm^{-1}. MS (API-ES): m/z (%) = 407.1 (100) [M + Na]$^+$. $C_{24}H_{20}N_2O_3$ (384.43): calcd. C 74.98, H 5.24, N 7.29; found C 74.87, H 5.35, N 6.79.

Methyl 1-Phenyl-3a,4,11,11a-tetrahydro-4,11-epoxy-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (14c): Yield 311 mg, 84%; yellow solid; m.p. 190–191 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.94 (d, J = 9.0 Hz, 1 H, C*H*-C=), 3.95 (s, 3 H, OMe), 4.72 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.85 (s, 1 H, C*H*-O), 5.87 (s, 1 H, C*H*-O), 7.04 (t, J = 7.0 Hz, 1 H, Ar-H), 7.30–7.32 (m, 2 H, Ar-H), 7.38–7.42 (m, 2 H, Ar-H), 7.52–7.54 (m, 2 H, Ar-H), 7.81 (s, 1 H, Ar-H), 7.83 (s, 1 H, Ar-H), 7.86–7.87 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.4, 56.2, 69.5, 83.0, 83.5, 114.1, 119.0, 119.2, 121.9, 126.6, 126.7, 128.4, 128.6, 129.6, 133.0, 133.3, 137.2, 139.6, 141.6, 142.3, 163.3 ppm. IR (KBr): $\tilde{\nu}$ = 3441, 2950, 1693, 1503, 1264, 1117, 858, 745 cm^{-1}. MS (API-ES): m/z (%) = 393.1 (100) [M + Na]$^+$. HRMS (MALDI-TOF): calcd. for $C_{23}H_{18}N_2O_3Na$ [M + Na]$^+$ 393.1210; found 393.1222.

Methyl 1-(4-Chlorophenyl)-3a,4,11,11a-tetrahydro-4,11-epoxy-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (14d): Yield 271 mg, 67%; yellow solid; m.p. 168–170 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.91 (d, J = 9.0 Hz, 1 H, C*H*-C=), 3.94 (s, 3 H, OMe), 4.63 (d, J = 9.0 Hz, 1 H, C*H*-N), 5.78 (s, 1 H, C*H*-O), 5.85 (s, 1 H, C*H*-O), 7.20 (d, J = 9.0 Hz, 2 H, Ar-H), 7.33 (d, J = 9.0 Hz, 2 H, Ar-H), 7.51–7.53 (m, 2 H, Ar-H), 7.80 (d, J = 9.0 Hz, 2 H, Ar-H), 7.84–7.86 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.5, 56.4, 69.5, 82.9, 83.2, 115.2, 119.1, 119.3, 126.7, 126.8, 126.9, 128.4, 128.6, 129.6, 133.0, 133.3, 137.8, 139.3, 140.3, 142.1, 163.1 ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2952, 1686, 1496, 1288, 1166, 859 cm^{-1}. MS (API-ES): m/z (%) = 427.0 (100) [M + Na]$^+$. HRMS (MALDI-TOF): calcd. for $C_{23}H_{17}ClN_2O_3Na$ [M + Na]$^+$ 427.0820; found 427.0834.

Methyl 1-(4-Nitrophenyl)-3a,4,11,11a-tetrahydro-4,11-epoxy-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (14e): Yield 203 mg, 49% yellow solid; m.p. 211–212 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.99 (s, 3 H, OMe), 4.01 (d, J = 8.5 Hz, 1 H, C*H*-C=), 4.75 (d, J = 8.5 Hz, 1 H, C*H*-N), 5.84 (s, 1 H, C*H*-O), 5.90 (s, 1 H, C*H*-O), 7.34 (d, J = 9.0 Hz, 2 H, Ar-H), 7.55–7.56 (m, 2 H, Ar-H), 7.85 (s, 1 H, Ar-H), 7.89 (s, 3 H, Ar-H), 8.30 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.9, 57.1, 69.2, 82.7, 83.1, 113.3, 119.4, 119.6, 126.2, 126.9, 127.0, 128.5, 128.6, 133.1, 133.4, 138.8, 141.6, 141.7, 141.8, 146.7, 162.6 ppm. IR (KBr): $\tilde{\nu}$ = 3440, 2924, 1594, 1321, 1289, 1110, 844 cm^{-1}. MS (API-ES): m/z (%) = 416.1 (76) [M + H]$^+$, 268.0 (100). HRMS (MALDI-TOF): calcd. for $C_{23}H_{17}N_3O_5$[M + H]$^+$ 416.1237; found 416.1241.

Synthesis of Methyl 1-Aryl-6,7-[oxybis(dimethylsilanediyl)]-1*H*-benzo[*f*]indazole-3-carboxylates 9a–e by the Deoxygenation of 8a–e: $LiAlH_4$ (285 mg, 7.5 mmol) was added to a mixture of **8a**–**e** (0.25 mmol), $TiCl_4$ (15 mL, 15 mmol) and Et_3N (1.05 mL, 7.5 mmol) in dichloromethane (20 mL) at room temp. under N_2. The reaction mixture was stirred at this temperature for 24 h and then poured into iced water (100 mL). The resulting mixture was extracted with CH_2Cl_2 (2 × 30 mL). The organic extract was dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 10–15% EtOAc in PE (60–80 °C) as eluent to afford the products **9a**–**e**.

Methyl 1-(4-Methoxyphenyl)-6,7-[oxybis(dimethylsilanediyl)]-1*H*-benzo[*f*]indazole-3-carboxylate (9a): Yield 69 mg, 60%; yellow solid; m.p. 187–188 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.44 (s, 6 H, $SiMe_2$), 0.46 (s, 6 H, $SiMe_2$), 3.91 (s, 3 H, OMe), 4.13 (s, 3 H, OMe), 7.11 (d, J = 9.0 Hz, 2 H, Ar-H), 7.74 (d, J = 9.0 Hz, 2 H,

Ar-H), 8.13 (s, 1 H, Ar-H), 8.17 (s, 1 H, Ar-H), 8.32 (s, 1 H, Ar-H), 8.92 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.3, 1.4, 52.4, 55.8, 106.9, 114.9, 121.9, 124.7, 125.5, 130.8, 131.6, 132.7, 133.05, 133.14, 136.5, 139.3, 142.1, 144.5, 159.4, 163.2 ppm. IR (KBr): $\tilde{\nu}$ = 3446, 2955, 1737, 1516, 1252, 933, 792 cm^{-1}. MS (EI): *m*/*z* (%) = 462.2 (100) $[M]^+$. HRMS (EI): calcd. for $C_{24}H_{26}N_2O_4Si_2$ $[M]^+$ 462.1431; found 462.1435.

Methyl 1-(4-Methylphenyl)-6,7-[oxybis(dimethylsilanediyl)]-1*H*-benzo[*f*]indazole-3-carboxylate (9b): Yield 70 mg, 63%; yellow solid; m.p. 170–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.45 (s, 6 H, $SiMe_2$), 0.47 (s, 6 H, $SiMe_2$), 2.47 (s, 3 H, Me), 4.13 (s, 3 H, OMe), 7.39 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.73 (d, *J* = 8.0 Hz, 2 H, Ar-H), 8.18 (s, 1 H, Ar-H), 8.20 (s, 1 H, Ar-H), 8.32 (s, 1 H, Ar-H), 8.93 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.3, 1.4, 21.3, 52.4, 107.1, 121.9, 123.6, 124.8, 130.3, 130.8, 131.7, 133.0, 133.1, 136.7, 137.2, 137.9, 138.9, 142.0, 144.4, 163.1 ppm. IR (KBr): $\tilde{\nu}$ = 3455, 2953, 1749, 1518, 1252, 928, 790 cm^{-1}. MS (EI): *m*/*z* (%) = 446.2 (7) $[M]^+$, 191.2 (100). HRMS (EI): calcd. for $C_{24}H_{26}N_2O_3Si_2$ $[M]^+$ 446.1482; found 446.1485.

Methyl 1-Phenyl-6,7-[oxybis(dimethylsilanediyl)]-1*H*-benzo[*f*]indazole-3-carboxylate (9c): Yield 51 mg, 47%; yellow solid; m.p. 166–167 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.45 (s, 6 H, $SiMe_2$), 0.47 (s, 6 H, $SiMe_2$), 4.14 (s, 3 H, OMe), 7.45–7.48 (m, 1 H, Ar-H), 7.59–7.63 (m, 2 H, Ar-H), 7.87–7.89 (m, 2 H, Ar-H), 8.19 (s, 1 H, Ar-H), 8.24 (s, 1 H, Ar-H), 8.32 (s, 1 H, Ar-H), 8.94 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.3, 1.4, 52.4, 107.1, 122.1, 123.7, 124.9, 127.9, 129.8, 130.9, 131.7, 133.0, 133.2, 137.1, 138.9, 139.7, 142.2, 144.6, 163.1 ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2953, 1719, 1505, 1252, 931, 791 cm^{-1}. MS (EI): *m*/*z* (%) = 432.2 (100) $[M]^+$. $C_{23}H_{24}N_2O_3Si_2$ (432.63): calcd. C 63.85, H 5.59, N 6.48; found C 63.55, H 5.638, N 6.275.

Methyl 1-(4-Chlorophenyl)-6,7-[oxybis(dimethylsilanediyl)]-1*H*-benzo[*f*]indazole-3-carboxylate (9d): Yield 78 mg, 67%; yellow solid; m.p. 191–193 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.45 (s, 6 H, $SiMe_2$), 0.47 (s, 6 H, $SiMe_2$), 4.13 (s, 3 H, OMe), 7.56 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.81 (d, *J* = 8.0 Hz, 2 H, Ar-H), 8.18 (s, 1 H, Ar-H), 8.19 (s, 1 H, Ar-H), 8.32 (s, 1 H, Ar-H), 8.93 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.3, 1.4, 52.5, 106.8, 122.3, 124.6, 124.8, 129.9, 130.9, 131.6, 133.0, 133.3, 133.4, 137.4, 138.2, 138.6, 142.5, 144.9, 162.9 ppm. IR (KBr): $\tilde{\nu}$ = 3474, 2956, 1730, 1252, 939, 785 cm^{-1}. MS (EI): *m*/*z* (%) = 466.1 (100) $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{23}N_2O_3Si_2Cl$ $[M]^+$ 466.0936; found 466.0937.

Methyl 1-(4-Nitrophenyl)-6,7-[oxybis(dimethylsilanediyl)]-1*H*-benzo[*f*]indazole-3-carboxylate (9e): Yield 22 mg, 18%; yellow solid; m.p. 203–205 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.43 (s, 6 H, $SiMe_2$), 0.46 (s, 6 H, $SiMe_2$), 4.12 (s, 3 H, OMe), 6.86 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.57 (d, *J* = 8.5 Hz, 2 H, Ar-H), 8.10 (s, 1 H, Ar-H), 8.15 (s, 1 H, Ar-H), 8.31 (s, 1 H, Ar-H), 8.91 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.3, 1.4, 52.4, 107.0, 115.6, 121.8, 124.6, 125.6, 130.7, 130.8, 131.7, 133.0, 133.1, 136.0, 139.4, 141.9, 144.2, 146.6, 163.3 ppm. IR (KBr): $\tilde{\nu}$ = 3455, 3360, 2955, 1720, 1521, 932, 793 cm^{-1}. MS (EI): *m*/*z* (%) = 477.3 (1) $[M]^+$, 447.2 (100). HRMS (EI): calcd. for $C_{23}H_{23}N_3O_5Si_2$ $[M]^+$ 477.1176; found 477.1178.

Synthesis of Methyl 1-Aryl-1*H*-naphtho[2,3-*f*]indazole-3-carboxylates 15a–d by the Deoxygenation of 14a–d: $LiAlH_4$ (285 mg, 7.5 mmol) was added to a mixture of **14a**–**e** (0.25 mmol), $TiCl_4$ (15 mL, 15 mmol) and Et_3N (1.05 mL, 7.5 mmol) in dichloromethane (20 mL) at 40 °C under N_2 and the mixture was stirred at this temperature for 1 h. After cooling to room temperature, the mixture was poured into iced water (100 mL) and the resulting mixture was extracted with CH_2Cl_2 (2 × 230 mL). The organic extract was dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 10–15% EtOAc in PE (60–80 °C) as the eluent to afford the products **15a**–**d**.

Methyl 1-(4-Methoxyphenyl)-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (15a): Yield 41 mg, 43%; yellow solid; m.p. 185–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OMe), 4.14 (s, 3 H, OMe), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.40 (s, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H), 7.93 (d, *J* = 7.0 Hz, 1 H, Ar-H), 7.99 (d, *J* = 7.0 Hz, 1 H, Ar-H), 8.28 (s, 1 H, Ar-H), 8.53 (s, 1 H, Ar-H), 8.73 (s, 1 H, Ar-H), 9.13 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.5, 55.8, 105.5, 114.9, 121.9, 124.9, 125.1, 125.4, 125.9, 126.0, 128.0, 128.2, 128.5, 129.3, 131.1, 132.4, 132.9, 136.3, 138.8, 159.2, 163.2 ppm. IR (KBr): $\tilde{\nu}$ = 3443, 2923, 1715, 1516, 1255, 834, 797 cm^{-1}. MS (API-ES): *m*/*z* (%) = 382.2 (100) $[M]^+$. HRMS (EI): calcd. for $C_{24}H_{18}N_2O_3$ $[M]^+$ 382.1317; found 382.1314.

Methyl 1-(4-Methylphenyl)-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (15b): Yield 63 mg, 69%; yellow solid; m.p. 165–166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, Me), 4.15 (s, 3 H, OMe), 7.39–7.43 (m, 4 H, Ar-H), 7.77 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.94 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.99–8.01 (m, 1 H, Ar-H), 8.36 (s, 1 H, Ar-H), 8.55 (s, 1 H, Ar-H), 8.74 (s, 1 H, Ar-H), 9.15 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4, 52.5, 105.7, 122.0, 123.6, 125.1, 125.2, 125.95, 126.04, 128.0, 128.2, 128.5, 129.3, 130.3, 131.1, 132.4, 136.6, 137.4, 137.8, 138.5, 163.2 ppm. IR (KBr): $\tilde{\nu}$ = 3443, 2956, 2924, 2854, 1716, 1517, 1261, 819 cm^{-1}. MS (API-ES): *m*/*z* (%) = 366.2 (2) $[M]^+$, 57.2 (100). HRMS (EI): calcd. for $C_{24}H_{18}N_2O_2$ $[M]^+$ 366.1368; found 366.1372.

Methyl 1-Phenyl-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (15c): Yield 57 mg, 65%; yellow solid; m.p. 170–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.14 (s, 3 H, OMe), 7.37–7.42 (m, 2 H, Ar-H), 7.45–7.48 (m, 1 H, Ar-H), 7.60–7.64 (m, 2 H, Ar-H), 7.88–7.98 (m, 4 H, Ar-H), 8.33 (s, 1 H, Ar-H), 8.51 (s, 1 H, Ar-H), 8.68 (s, 1 H, Ar-H), 9.09 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.5, 105.6, 122.0, 123.5, 125.1, 125.2, 125.95, 126.01, 127.7, 128.0, 128.2, 128.5, 129.2, 129.8, 131.06, 131.09, 132.4, 136.9, 138.2, 139.9, 163.1 ppm. IR (KBr): $\tilde{\nu}$ = 3451, 2957, 2925, 2854, 1716, 1504, 1262, 804 cm^{-1}. MS (API-ES): *m*/*z* (%) = 352.2 (100) $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{16}N_2O_2$ $[M]^+$ 352.1212; found 352.1215.

Methyl 1-(4-Chlorophenyl)-1*H*-naphtho[2,3-*f*]indazole-3-carboxylate (15d): Yield 60 mg, 62%; yellow solid; m.p. 205–206 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.16 (s, 3 H, OMe), 7.41–7.44 (m, 2 H, Ar-H), 7.60 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.86 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.96 (d, *J* = 8.0 Hz, 1 H, Ar-H), 8.01 (d, *J* = 8.0 Hz, 1 H, Ar-H), 8.35 (s, 1 H, Ar-H), 8.57 (s, 1 H, Ar-H), 8.75 (s, 1 H, Ar-H), 9.15 (s, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.6, 105.4, 122.3, 124.4, 124.9, 125.3, 126.0, 126.1, 128.0, 128.2, 128.5, 129.2, 129.9, 131.0, 131.2, 132.5, 133.1, 137.3, 138.0, 138.4, 162.9 ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2960, 2919, 2850, 1721, 1500, 1261, 800 cm^{-1}. MS (EI): *m*/*z* (%) = 386.2 (100) $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{15}N_2O_2Cl$ $[M]^+$ 386.0822; found 386.0818.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds **8a**–**e**, **9a**–**e**, **14a**–**e** and **15a**–**d**.

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