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Highly stereoselective synthesis of *N*-substituted π-conjugated phthalimides

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ABSTRACT

A new regio- and stereoselective synthesis of (*E*)-*N*-(2-arylvinyl)phthalimides as well as phthalimide-containing (*E*,*E*)-buta-1,3-dienes and (*E*)-but-1-en-3-ynes has been developed. The one-pot ruthenium-catalyzed silylative coupling/iododesilylation sequence provides (*E*)-*N*-(2-iodovinyl)phthalimide **1**, which undergoes palladium-catalyzed Suzuki–Miyaura or Sonogashira cross-coupling to afford stereodefined highly π-conjugated phthalimides and functionalized dienimides containing phthalimide groups.

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1. Introduction

Enamides and their derivatives are versatile building blocks in organic synthesis, especially for enantioselective hydrogenation and for stereoselective C–C and C–N bond formation reactions.[1]

Isoindole-1,3-diones, commonly known as phthalimides, are key structural units in a variety of biologically important compounds. Several fungicides,[2] metabolic drugs,[3] and functional materials[4] contain alkenyl-substituted phthalimides as key structural elements. A number of transition metal-catalyzed approaches for the selective synthesis of *N*-alkenyl-substituted phthalimides have recently emerged. Among them, protocols based on the ruthenium-catalyzed addition of phthalimide to terminal alkynes,[5] copper-catalyzed N-vinylation of phthalimide by alkenyl halides,[6] alkenyl boronic acids[7] or potassium alkenyltrifluoroborate,[8] and palladium-catalyzed oxidative amination of alkenes[9] stand out for their synthetic versatility and efficiency. *N*-Styrylphthalimides have also been obtained via palladium-catalyzed Heck arylation of *N*-vinylphthalimide with aryl halides, however, the main drawback found for this reaction is the control of α- and β-regioselectivity.[10] Recently, a regioselective protocol for the synthesis of (*E*)-*N*-styrylphthalimides based on Heck arylation of *N*-vinylphthalimide in the presence of oxime-derived palladacycles has been developed.[10e]

Dienamides and related compounds are important Diels–Alder partners that have been used for the preparation of polycyclic systems, including natural products.[11] Despite their synthetic utility and biological potential, the synthetic routes available for the stereoselective preparation of dienamides are limited.[12] Thus, acyclic *N*-(1,3-butadienyl)amides have been made by olefination of *N*-formyl imides,[13] ruthenium-catalyzed co-oligomerization of *N*-vinylamides with alkynes,[14] titanium-mediated coupling of ynamides with alkynes[15] or cobalt-mediated hydroaminative coupling of diynes with amides.[16] α,γ-Dienamide esters have also been obtained by stereospecific palladium-catalyzed Suzuki–Miyaura cross-coupling of β-bromoenamide esters with vinyl boronic acids.[17] Nevertheless, to the best of our knowledge, no examples of a general method for the synthesis of stereodefined (*E*,*E*)-1,3-dienes containing *N*-substituted phthalimide groups have been given so far.[18]

β-Iodoenamides are synthetically versatile variants of enamides, which offer rapid access to β-metalated enamides that can serve as acyl anion equivalents or can be involved in transition metal-catalyzed reactions. In addition, stereodefined iodoenamides are excellent candidates for use as coupling partners in palladium-catalyzed cross-coupling reactions allowing regio- and stereoselective construction of complex enamide and dienamide derivatives. Despite this versatility, there are only a few examples of synthetic application of iodoenamides, presumably because of difficulties in their synthesis.[19] Smith and co-workers applied (*Z*)-β-iodovinyl butyramide as a Stille coupling partner in the synthesis of the (*Z*,*E*)-dienamide unit of the marine natural product Lituarine C.[20] Isomeric iodoenamides have been shown to be versatile reagents in Sonogashira couplings to yield enynamides.[19b,21]

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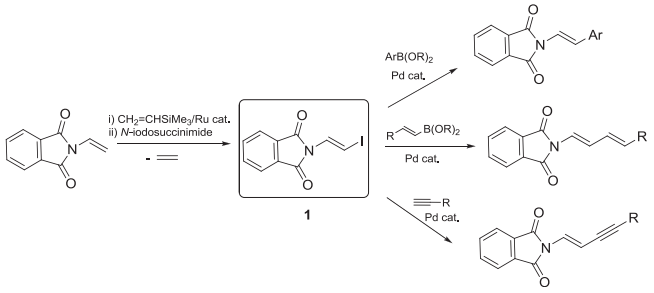
Heterocyclic iodoenamides have also been applied in palladium-catalyzed Suzuki–Miyaura[22] and Sonogashira[23] couplings.

A flexible, one-pot, and stereoselective procedure for the synthesis of iodoenamide building blocks would greatly improve current approaches to the synthesis of enamide-containing natural products and pharmaceutically relevant heterocyclic systems.

(*E*)-*N*-(2-Iodovinyl)phthalimide would offer a synthetically versatile variant of *N*-vinylphthalimide, which could be used as a coupling partner in palladium-catalyzed cross-coupling reactions allowing regio- and stereoselective construction of complex (*E*)-*N*-(2-arylvinyl)phthalimides as well as (*E*,*E*)-*N*-(buta-1,3-dien-1-yl) phthalimides and (*E*)-*N*-(but-1-en-3-yl)phthalimides.

In this paper we report the one-pot synthesis of a new building block—(*E*)-*N*-(2-iodovinyl)phthalimide **1** ((*E*)-2-(2-iodovinyl)-isoindoline-1,3-dione) from *N*-vinylphthalimide by a silylative coupling–iododesilylation sequence and its application in the palladium-catalyzed Suzuki–Miyaura and Sonogashira cross-coupling reactions to yield *N*-substituted highly π-conjugated phthalimide derivatives (Scheme 1).



Scheme 1. New synthetic strategy to highly π-conjugated *N*-substituted phthalimides.

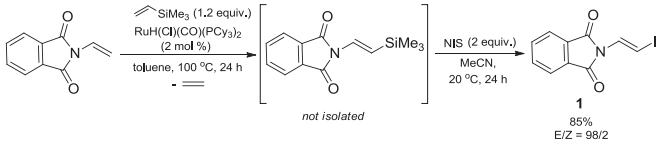
In the past two decades, we have developed the silylative coupling of olefins with vinyl-substituted organosilicon compounds occurring in the presence of complexes containing initially or generating in situ M–H and M–Si bonds.[24] The silylative coupling, in combination with subsequent desilylation reactions, such as Hiyama cross-coupling and halodesilylation, appears to be a valuable step to provide highly conjugated π-electron compounds, such as stilbenes, aryl-substituted polyenes, or styryl halides.[24b]

As we have previously reported, the silylative coupling of *N*-vinylamides with vinylsilanes catalyzed by a ruthenium–hydride complex occurred stereoselectively to give (*E*)-*N*-(2-silylvinyl)amides in good yields.[25] On the basis of our recent results on the highly stereoselective one-pot synthesis of (*E*)-β-arylvinyl halides from functionalized terminal alkenes,[26] we envisaged that the ruthenium-catalyzed *E*-selective silylative coupling[25] of commercially available and inexpensive *N*-vinylphthalimide with trimethylvinylsilane followed by *N*-iodosuccinimide-mediated iododesilylation[27] could be a valuable synthetic method for the one-pot conversion of *N*-vinylphthalimide into (*E*)-*N*-(2-iodovinyl)phthalimide **1**. The resulting iodide could be used as a coupling partner for the stereoselective synthesis of imide-functionalized alkenes, dienes, and enynes.

2. Results and discussion

The silylative coupling reaction of *N*-vinylphthalimide and trimethylvinylsilane (1.2 equiv) was conducted following the original procedure ($RuHCl(CO)(PCy_3)_2$ catalyst (2 mol %), toluene, 24 h, 100 °C, sealed ampoule under Ar atmosphere)[25] to give exclusively (*E*)-*N*-(2-trimethylsilylvinyl)phthalimide (GC yield 97%). Treatment of (*E*)-*N*-(2-trimethylsilylvinyl)-phthalimide with 2 equiv of *N*-iodosuccinimide (NIS) in acetonitrile at room temperature allowed isolation of stereochemically pure (*E*)-*N*-(2-iodovinyl)phthalimide **1** in 89% yield. To the best of our knowledge, this is the first iododesilylation process disclosed for β-silylenimides.[28] Thus, by sequencing the highly *E*-selective silylative coupling of *N*-vinylphthalimide with a stereospecific iododesilylation, the stereochemical fidelity of the product is preserved. During the course of our experiments, we have found that molecular iodine (1.2 equiv) in CH_2Cl_2 could also be employed for the iododesilylation of (*E*)-*N*-(2-trimethylsilylvinyl)phthalimide at room temperature. However, it seemed to be less effective than NIS and gave the product with moderate yield and selectivity (GC yield 68%, *E*/*Z*=7/3). In contrast, when iodine monochloride ICl (1 equiv) in CH_2Cl_2 was applied, no iododesilylation product was detected and decomposition of (*E*)-*N*-(2-trimethylsilylvinyl)phthalimide was observed.

After several attempts we have found that iododesilylation of (*E*)-*N*-(2-trimethylsilylvinyl)phthalimide occurs efficiently also when a 4/1 mixture of acetonitrile and toluene is employed as the solvent without affecting either the reaction yield or stereoselectivity. This result prompted us to attempt the iododesilylation step in one pot with silylative coupling without further purification of the (*E*)-*N*-(2-trimethylsilylvinyl)-phthalimide intermediate (Scheme 2).



Scheme 2. One-pot synthesis of key precursor—(*E*)-*N*-(2-iodovinyl)-phthalimide **1**.

In a typical procedure, *N*-vinylphthalimide, trimethylvinylsilane (1/1.2 molar ratio) and $RuHCl(CO)(PCy_3)_2$ catalyst (2 mol %) were dissolved in dry toluene (0.5 M concentration) and heated under an Ar atmosphere in a Schlenk bomb flask fitted with a plug valve at 100 °C for 24 h. Next, after cooling the reaction mixture to room temperature, a 4-fold volume excess of acetonitrile and 2 equiv of solid *N*-iodosuccinimide were added. Treatment of the silylative coupling product with NIS caused iododesilylation in a stereospecific manner, giving (*E*)-*N*-(2-iodovinyl)phthalimide **1** in high geometrical purity (*E*/*Z*=98/2) within 24 h. The reaction was quenched with aqueous $Na_2S_2O_3$, extracted with hexane, and concentrated to dryness. Column chromatography of the resulting product (silica gel, eluent: hexane/ethyl acetate 50/2) afforded pure compound **1** in 85% overall yield. The *E*-configuration of carbon–carbon double bond in **1** was determined on the basis of the ^1H and ^{13}C NMR spectra. Moreover, compound **1** proved to be a solid and yielded a crystal amenable to X-ray structure determination (Fig. 1).[29]

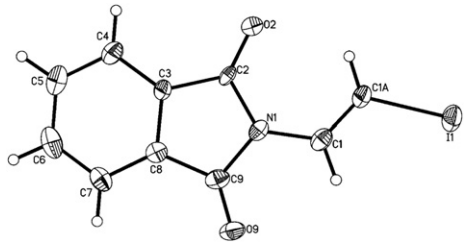


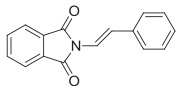
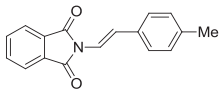
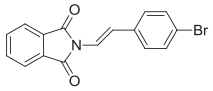
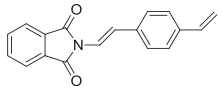
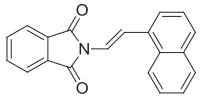
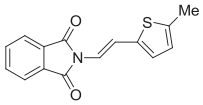
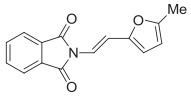
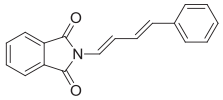
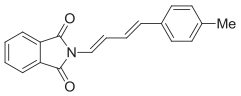
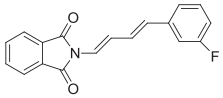
Fig. 1. Perspective view of the molecule **1** (CCDC-707362). Ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

This approach to (*E*)-*N*-(2-iodovinyl)phthalimide **1** provides a very useful synthesis of various β-substituted vinylphthalimides via elaboration of the resulting iodide functionality into other substituents by using palladium-catalyzed cross-coupling processes. Thus, to demonstrate the synthetic usefulness of **1**, we investigated palladium-catalyzed Suzuki–Miyaura and Sonogashira coupling reactions.

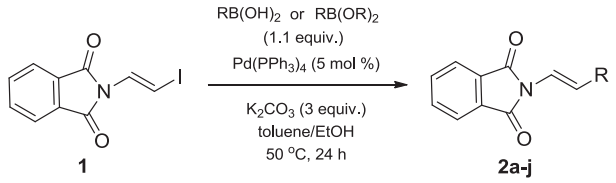
The cross-coupling reactions of **1** with aryl boronic acids were carried out under standard biphasic reaction conditions[30] (toluene (0.1 M), aqueous K_2CO_3 (3 equiv, 2 M), and ethanol (15 equiv)). Suzuki–Miyaura coupling of **1** with selected aryl boronic acids (Table 1, entries 1–5) and heteroaryl boronic acid pinacol esters (Table 1, entries 6–7) proceeded smoothly at 50 °C in the presence of $Pd(PPh_3)_4$ catalyst (5 mol %) to give the corresponding (*E*)-*N*-(2-arylvinyl)phthalimides **2a**–**g** within 24 h in good yields (61–90%). As the boronic acids were used in slight excess (1.1 equiv), the formation of by-products—symmetrical biphenyl derivatives was observed (5–10%) in the reaction mixture, however, they could be separated by column chromatography. In an effort to explore the scope of the method, we have screened the coupling of **1** with *para*-substituted aryl boronic acids as well as heteroaryl boronic acid esters containing thienyl- and furyl-groups. Under these conditions, boronic acid coupling partners bearing functional groups, such as –Me, –Br, and $-CH{=}CH_2$, reacted successfully to give the corresponding (*E*)-*N*-(2-arylvinyl)phthalimides in high yields (Table 1), irrespective of the substituent electronic character. In most cases, the *E*-double bond geometry was strongly favored, with approximately 95/5 to 99/1 *E*/*Z* ratio (for arylvinyl derivatives) and 92/8 to 94/6 ratio (for heteroaryl derivatives) as measured by ^1H NMR spectroscopy. The optimal conditions established for the reaction of compound **1** with aryl boronic acids were also applied to (*E*)-arylvinyl boronic acids, providing good yields (72–90%) of the desired (*E*,*E*)-buta-1,3-dienylphthalimide derivatives (**2h**–**j**). Thus, the coupling reactions were performed in a toluene/ethanol mixture using $Pd(PPh_3)_4$ (5 mol %) as catalyst, in the presence of a 2 M aqueous solution of K_2CO_3 (3 equiv) at 50 °C (Scheme 3).

It is worth noting that the Suzuki–Miyaura coupling processes proceeded in a highly stereoselective manner to yield products containing (*E*,*E*)-dienes as predominant products (isomeric purity over 90%), however, partial isomerization leading to small amounts of the respective (*E*,*Z*)-isomers was also detected using the GC–MS method (Table 1). In all cases, trace amounts of by-products—(*E*,*E*)-1,4-diarylbuta-1,3-dienes formed by competitive *homo*-coupling of

Table 1
Synthesis of (*E*)-*N*-(2-arylvinyl)phthalimides and (*E*,*E*)-*N*-(buta-1,3-dien-1-yl)phthalimides

Entry	Compound	R	Product structure	Isomeric purity[a]	Yield[b] (%)
1	**2a**	Ph		95/5 (*E*/*Z*)	90
2	**2b**	4-MeC_6H_4		96/4 (*E*/*Z*)	85
3	**2c**	4-BrC_6H_4		95/5 (*E*/*Z*)	76
4	**2d**	4-$CH_2{=}CHC_6H_4$		99/1 (*E*/*Z*)	79
5	**2e**	1-Naphthyl		99/1 (*E*/*Z*)	75
6	**2f**	5-Methylthienyl		92/8 (*E*/*Z*)	82
7	**2g**	5-Methylfuryl		94/6 (*E*/*Z*)	61
8	**2h**	(*E*)-PhCH=CH		93/7 (*E*,*E*)/(*E*/*Z*)	90
9	**2i**	(*E*)-4-$MeC_6H_4CH{=}CH$		90/10 (*E*,*E*)/(*E*,*Z*)	85
10	**2j**	(*E*)-3-$FC_6H_4CH{=}CH$		92/8 (*E*,*E*)/(*E*,*Z*)	72

[a] Determined by GC–MS.
[b] Isolated yields.



Scheme 3. Suzuki–Miyaura coupling of (*E*)-*N*-(2-iodovinyl)phthalimide **1** with aryl boronic acids and (*E*)-arylvinyl boronic acids.

the arylvinyl boronic acids (used in slight excess) were observed, however, they can be separated by column chromatography.

Compounds **2a**–**j** were isolated and spectroscopically characterized.[29] The *E*-configuration of the double bonds of (*E*)-2-(4-methylstyryl)isoindoline-1,3-dione **2b** (Fig. 2), 2-((*E*,*E*)-4-phenylbuta-1,3-dien-1-yl)isoindoline-1,3-dione **2h** (Fig. 3), and 2-((*E*,*E*)-4-(3-fluorophenyl)buta-1,3-dien-1-yl)isoindoline-1,3-dione **2j** (Fig. 4) was further confirmed by single-crystal X-ray diffraction analysis.[29]

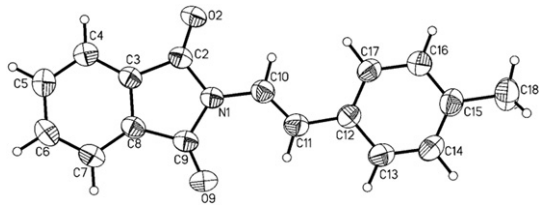


Fig. 2. Perspective view of the molecule **2b** (CCDC-832076). Ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

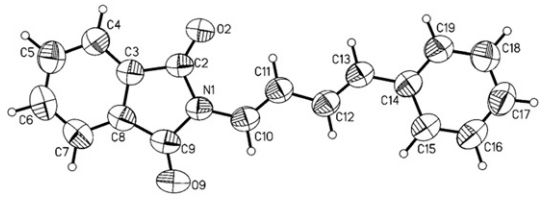


Fig. 3. Perspective view of the molecule **2h** (CCDC-832079). Ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

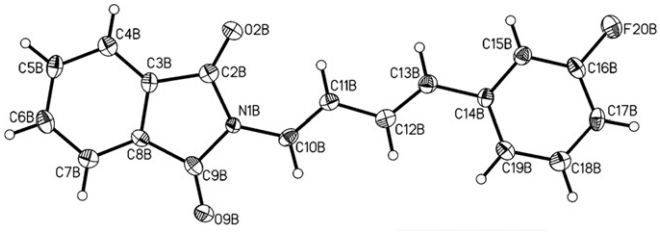
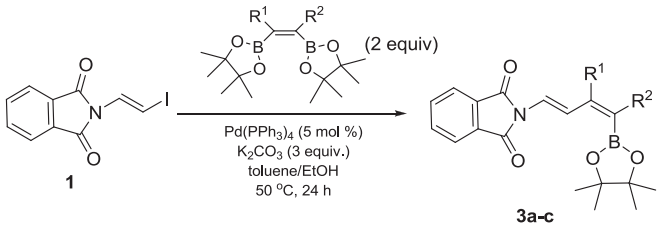


Fig. 4. Perspective view of the molecule **2j** (CCDC-742617). Ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

As an extension to the present study we have found that compound **1** can be also used in the synthesis of functionalized tetrasubstituted buta-1,3-dienes containing a phthalimide group (Scheme 4). Suzuki–Miyaura cross-coupling of **1** with 2 equiv of ethylenediboronic acid bis(pinacol) esters (substituted (*Z*)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenes) performed under optimal conditions established for the reaction of **1** with aryl boronic acid pinacol esters ($Pd(PPh_3)_4$ catalyst (5 mol %), toluene (0.05 M), aqueous K_2CO_3 (3 equiv, 2 M), and ethanol (15 equiv)) provides monophthalimido-substituted buta-1,3-dienes containing boryl groups (Table 2) in good yield (69–85%). Only trace amounts of bis(phthalimido)-substituted products (trienes containing two phthalimide units) have been observed under the given conditions. Stereodefined products **3a**–**c** can be used as a lynchpin reagents for further catalytic transformations.



Scheme 4. Suzuki–Miyaura coupling of **1** with ethylenediboronic acid bis(pinacol) esters.

Table 2
Synthesis of tetrasubstituted buta-1,3-dienes

Compound	R^1	R^2	*E*/*Z*[a]	Yield (%)[b]
3a	Ph	Ph	99/1	85
3b	H	*n*-Bu	99/1	69
3c	COOMe	*n*-Bu	99/1	81

[a] Configuration of PhthNCH=CH– double bond determined by ^{1}H NMR spectroscopy.
[b] Isolated yield.

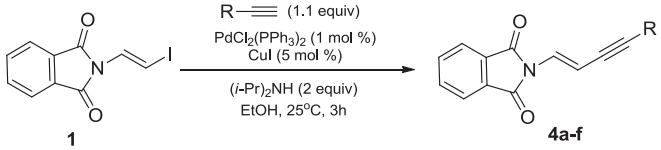
Finally, we decided to evaluate the utility of β-iodoenimide **1** in palladium-catalyzed Sonogashira coupling[31] with the aim of obtaining new enyne building blocks containing phthalimide units. Sonogashira coupling of **1** with selected alkynes (Table 3) proceeded smoothly at room temperature in the presence of a $PdCl_2(PPh_3)_2$/CuI catalytic system to give the corresponding (*E*)-*N*-(but-1-en-3-yn-1-yl)phthalimides **4a**–**f** in good yields (60–84%). As the terminal alkynes were used in excess, formation of by-products—symmetrical 1,3-diynes were observed (5–10%) in the reaction mixture, however, they can be separated by column

Table 3
Synthesis of (*E*)-*N*-(but-1-en-3-yn-1-yl)phthalimides

Entry	R	Product structure	*E*/*Z*[a]	Yield[b] (%)
1	Ph	**4a**	94/6	83
2	1-Naphthyl	**4b**	99/1	84
3	$SiMe_3$	**4c**	98/2	70
4	$C_6H_{10}(OSiMe_3)$	**4d**	94/6	82
5	*n*-C_6H_{13}	**4e**	97/3	75
6	4-$C_6H_4(BO_2C_6H_{12})$	**4f**	99/1	60

[a] Determined by GC–MS.
[b] Isolated yields.

chromatography. In an effort to explore the scope of the method, we have screened the coupling of **1** with alkyl-, aryl-, and trimethylsilyl-substituted acetylenes (Table 3). All the reactions were stereospecific and in most cases, the (*E*)-double bond geometry was strongly favored, with approximately 94/6–99/1 *E*/*Z* ratio as measured by ^{1}H NMR spectroscopy (Scheme 5).



Scheme 5. Sonogashira coupling of **1** with terminal alkynes.

The structural assignment of the enyne **4a**—(*E*)-2-(4-phenylbut-1-en-3-yn-1-yl)isoindoline-1,3-dione was confirmed by X-ray crystallography.[29] The configuration around the double bond in **4a** is (*E*)-, as is evident from the value of the N–C=C–C torsion angles: 179.93(13)° (Fig. 5).

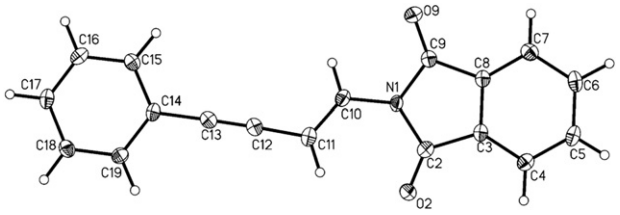


Fig. 5. Perspective view of the molecule **4a** (CCDC-790990). Ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

3. Conclusions

In conclusion, the one-pot ruthenium-catalyzed silylative coupling of *N*-vinylphthalimide with trimethylvinylsilane followed by NIS-mediated iododesilylation provides facile entry to (*E*)-*N*-(2-iodovinyl)phthalimide, which is a versatile building block shown to undergo subsequent palladium-catalyzed Suzuki–Miyaura and Sonogashira coupling reactions en route to β-functionalized *N*-vinylphthalimides and new stereodefined phthalimide-containing di- and tetrasubstituted buta-1,3-dienes. Further results on the application of this strategy to the synthesis of highly π-conjugated triene systems will be reported in due course.

4. Experimental section

4.1. Synthesis of (*E*)-*N*-(2-iodovinyl)phthalimide (1)

A mixture consisting of *N*-vinylphthalimide (2.0 g, 11.5 mmol), vinyltrimethylsilane (2.03 mL, 13.8 mmol), $RuHCl(CO)(PCy_3)_2$ (0.167 g, 0.23 mmol), and 23 mL of dry toluene was placed under an argon atmosphere in a 150 mL Schlenk bomb flask fitted with a plug valve and heated at 100 °C for 24 h to complete the reaction (GC analysis). Next, after cooling the reaction mixture to room temperature, 92 mL of acetonitrile and *N*-iodosuccinimide (5.18 g, 23.0 mmol) were added and the mixture was stirred for 24 h at room temperature. After this time the solvents were evaporated and the reaction mixture was quenched with aqueous $Na_2S_2O_3$, extracted with hexane, and concentrated to dryness. The final product was purified by column chromatography on silica gel, eluting with *n*-hexane/EtOAc (50/2). R_f (4% EtOAc/hexane)=0.48; Yield: 85%. Pale yellow crystals, mp 121–122 °C; IR, ν_{max} (KBr)=3110, 2964, 1718, 1612, 1466, 1377, 1262, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.40 (d, 1H, *J*=15.0 Hz), 7.30–7.24 (m, 2H), 7.07–6.99 (m, 2H), 6.76 (dd, 1H, *J*=15.0, 0.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=164.2, 160.9, 143.6, 133.9, 133.8, 127.6, 127.5, 115.8, 115.5. 76.1; MS (EI) *m*/*z*=299 (M^+, 25%), 172 (100), 144 (10), 127 (12), 116 (22), 104 (25), 89 (20), 76 (24). HRMS (*m*/*z*)=298.9455, calcd for $C_{10}H_6INO_2$: 298.9443.

4.2. Representative procedure for the Suzuki–Miyaura cross-coupling of 1 with boronic acids or boronic acid pinacol esters

To a solution of $Pd(PPh_3)_4$ (0.017 mmol, 19.3 mg), (*E*)-*N*-(2-iodovinyl)phthalimide (0.334 mmol, 100 mg), and 0.337 mmol of boronic acid (for the synthesis of compounds **2a**–**e** and **2h**–**j**) or boronic acid pinacol ester (for compounds **2f**,**g**) in toluene (3.3 mL, 0.1 M) an aqueous K_2CO_3 (1 mmol, 0.5 mL, 2 M) and ethanol (5 mmol, 230 mg, 0.29 mL) were added. The reaction mixture was stirred at 50 °C under an argon atmosphere for 24 h. The organic layer was concentrated and the crude product was preloaded onto silica. Products were purified by silica gel chromatography, eluting with EtOAc in *n*-hexane—0–50%.

*4.2.1. (E)-2-Styrylisoindoline-1,3-dione (**2a**).*[10e] Pale yellow solid, mp 188–189 °C; R_f (50% EtOAc/hexane)=0.42; IR, ν_{max} (KBr)=3025, 2952, 1714, 1639, 1466, 1581, 1382, 1108 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=7.92–7.88 (m, 2H), 7.80–7.74 (m, 2H), 7.65 (d, 1H, *J*=15.6 Hz), 7.50–7.46 (m, 2H), 7.39–7.33 (m, 3H); 7.29–7.23 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.5, 135.9, 134.6, 131.7, 128.7, 127.6, 126.2, 123.7, 120.2, 117.6. MS (EI) *m*/*z*=249 (M^+, 100%), 232 (22), 220 (25), 204 (40), 165 (15), 128 (24), 102 (38), 104 (34), 76 (57), 50 (53); HRMS (*m*/*z*)=249.0793, calcd for $C_{16}H_{11}NO_2$: 249.0790.

*4.2.2. (E)-2-(4-Methylstyryl)isoindoline-1,3-dione (**2b**).*[10e] Yellow solid, mp 174 °C; R_f (50% EtOAc/hexane)=0.46; IR, ν_{max} (KBr)=3070, 3012, 2850, 1716, 1649, 1465, 1382, 1082 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=7.91–7.87 (m, 2H), 7.77–7.74 (m, 2H), 7.62 (d, 1H, *J*=15.1 Hz), 7.37 (d, 2H, *J*=8.1 Hz), 7.32 (d, 1H, *J*=15.1 Hz), 7.16 (d, 2H, *J*=8.1 Hz), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.5, 137.6, 134.5, 133.1, 131.7, 129.4, 126.1, 123.6, 120.3, 116.8, 21.2; MS (EI) *m*/*z*=263 (M^+, 15%), 183 (10), 167 (12), 149 (20), 128 (22), 99 (35), 83 (38), 57 (40). HRMS (*m*/*z*)=263.0941, calcd for $C_{17}H_{13}NO_2$: 263.0946.

*4.2.3. (E)-2-(4-Bromostyryl)isoindoline-1,3-dione (**2c**).* Yellow solid, mp 173–174 °C; R_f (50% EtOAc/hexane)=0.48; IR, ν_{max} (KBr)=3069, 1713, 1636, 1465, 1383, 1083 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=7.92–7.87 (m, 2H), 7.80–7.74 (m, 2H), 7.60 (d, 1H, *J*=15.1 Hz), 7.49–7.43 (m, 2H), 7.38–7.29 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.3, 135.2, 134.6, 131.8, 131.7, 131.6, 127.8, 127.7, 125.0, 123.7, 118.9, 118.1; MS (EI) *m*/*z*=329 ($[M+2]^+$ 100%), 327 (90), 282 (10), 248 (15), 204 (14), 186 (65), 104 (33), 76 (58), 50 (50), 28 (40); HRMS (*m*/*z*)=326.9903, calcd for $C_{16}H_{10}^{79}BrNO_2$: 326.9895.

*4.2.4. (E)-2-(4-Vinylstyryl)isoindoline-1,3-dione (**2d**).* White solid, mp 180–181 °C; R_f (50% EtOAc/hexane)=0.50; IR, ν_{max} (KBr)=3077, 3043, 2985, 2922, 2851, 1912, 1720, 1646, 1509, 1465, 1381, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=7.92–7.89 (m, 2H), 7.78–7.75 (m, 2H), 7.64 (d, 1H, *J*=15.1 Hz), 7.46–7.34 (m, 5H), 6.72 (dd, 1H, *J*=17.5, 10.9 Hz), 5.76 (dd, 1H, *J*=17.5, 1.0 Hz), 5.25 (dd, 1H, *J*=10.9, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.9, 136.9, 136.4, 135.5, 134.5, 131.7, 126.6, 126.3, 123.7, 119.8, 117.5, 113.8; MS (EI) *m*/*z*=276 ($[M+1]^+$ 25%), 275 (100), 128 (25), 76 (14), 50 (10); HRMS (*m*/*z*)=275.0938, calcd for $C_{18}H_{13}NO_2$: 275.0946.

*4.2.5. (E)-2-(2-(Naphthalen-1-yl)vinyl)isoindoline-1,3-dione (**2e**).* White solid, mp 148–149 °C; R_f (50% EtOAc/hexane)=0.52; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=8.42 (d, 1H, *J*=14.9 Hz), 8.19 (d, 1H, *J*=7.9 Hz), 7.95–7.46 (m, 10H), 7.36 (d, 1H, *J*=14.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.5, 134.6, 133.7, 133.6, 131.7, 131.4, 128.5, 128.1, 126.2, 125.9, 125.7, 124.0, 123.7, 123.2, 119.5, 117. 8; MS (EI) *m*/

z=299 (M^+, 50%), 152 (100), 104 (12), 76 (20), 50 (14); HRMS (m/z)= 299.0924, calcd for $C_{20}H_{13}NO_2$: 299.0946.

*4.2.6. (E)-2-(2-(5-Methylthiophen-2-yl)vinyl)isoindoline-1,3-dione (**2f**).* White solid, mp 159–160 °C; R_f (50% EtOAc/hexane)=0.43; IR, ν_{max} (KBr)=3093, 3045, 2955, 2925, 2854, 1718, 1609, 1466, 1381, 1225, 1099, 1086 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ=7.90–7.87 (m, 2H), 7.76–7.67 (m, 3H), 7.12 (d, 1H, J=14.9 Hz), 6.86 (d, 1H, J=3.3 Hz), 6.65–6.63 (m, 1H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.3, 139.1, 138.1, 134.4, 131.7, 126.6, 125.7, 123.6, 115.8, 114.7, 15.6; MS (EI) m/z=270 ($[M+1]^+$ 20%), 269 (100), 122 (30), 121 (18), 76 (13), 50 (20); HRMS (m/z)=269.0494, calcd for $C_{15}H_{11}NO_2S$: 269.0501.

*4.2.7. (E)-2-(2-(5-Methylfuran-2-yl)vinyl)isoindoline-1,3-dione (**2g**).* Pale yellow oil; R_f (50% EtOAc/hexane)=0.44; IR, ν_{max} (KBr)= 3090, 3065, 2956, 2919, 2850, 1722, 1538, 1463, 1385, 1293, 1209, 1101, 1087 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.89–7.86 (m, 2H), 7.76–7.72 (m, 2H), 7.40 (d, 1H, J=14.7 Hz), 7.27 (d, 1H, J=14.7 Hz), 6.21 (d, 1H, J=3.2 Hz), 5.98 (dd, 1H, J=3.2, 0.9 Hz), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=166.7, 152.2, 135.4, 134.4, 131.7, 123.6, 114.9, 110.3, 109.2, 107.6, 13.7; MS (EI) m/z=254 ($[M+1]^+$ 20%), 253 (100), 210 (16), 106 (20), 76 (10), 50 (20); HRMS (m/z)=253.0732, calcd for $C_{15}H_{11}NO_3$: 253.0739.

*4.2.8. 2-((1E,3E)-4-Phenylbuta-1,3-dien-1-yl)isoindoline-1,3-dione (**2h**).* Pale yellow needles, mp 119–120 °C; R_f (50% EtOAc/hexane)= 0.45; ^1H NMR (300 MHz, $CDCl_3$): δ=7.90–7.86 (m, 2H), 7.78–7.74 (m, 2H), 7.48–7.23 (m, 6H), 6.98 (d, 1H, J=14.4 Hz), 6.86–6.78 (dd, 1H, J=10.4, 15.6 Hz), 6.70 (d, 1H, J=15.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.3, 134.5, 133.1, 131.7, 128.6, 127.6, 127.0, 126.3, 123.8, 123.6, 120.9, 120.2; MS (EI) m/z=275 (M^+, 18%), 129 (12), 128 (100), 115 (13), 104 (10), 77 (10), 76 (10), 50 (15); HRMS (m/z)=275.0941, calcd for $C_{18}H_{13}NO_2$: 275.0946.

*4.2.9. 2-((1E,3E)-4-(p-Tolyl)buta-1,3-dien-1-yl)isoindoline-1,3-dione (**2i**).* Yellow solid, mp 125–126 °C; R_f (50% EtOAc/hexane)=0.45; IR, ν_{max} (KBr)=3049, 3022, 2963, 2853, 1731, 1605, 1509, 1412, 1261, 1182, 1096 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.89–7.85 (m, 2H), 7.79–7.73 (m, 2H), 7.46–7.23 (m, 3H), 7.15–7.08 (m, 2H), 6.98 (d, 1H, J=14.5 Hz), 6.82–6.73 (dd, 1H, J=10.4, 15.6 Hz), 6.65 (d, 1H, J=15.6 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.2, 137.5, 134.5, 133.1, 131.7, 129.4, 129.3, 126.2, 126.0, 123.6, 121.2, 119.7, 21.3; MS (EI) m/z=289 (M^+, 16%), 143 (13), 142 (100), 141 (20), 115 (15), 104 (8), 76 (7), 50 (15); HRMS (m/z)=289.1111, calcd for $C_{19}H_{15}NO_2$: 289.1103.

*4.2.10. 2-((1E,3E)-4-(3-Fluorophenyl)buta-1,3-dien-1-yl)isoindoline-1,3-dione (**2j**).* Yellow needles, mp 139–140 °C; R_f (50% EtOAc/ hexane)=0.48; IR, ν_{max} (KBr)=3016, 1715, 1650, 1608, 1581, 1383 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.90–7.86 (m, 2H), 7.78–7.74 (m, 2H), 7.42 (dd, 1H, J=14.4, 10.6 Hz), 7.32–7.09 (m, 2H), 6.99 (d, 1H, J=14.5 Hz), 6.95–6.89 (m, 3H), 6.65 (dd, 1H, J=15.7, 10.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.1, 162.8 (d, J ($^{13}C-^{19}F$)= 245.3 Hz), 139.6 (d), 134.6, 131.7 (d), 130.0 (d), 128.6 (d), 123.6 (d), 122.2 (d, J ($^{13}C-^{19}F$)=2.4 Hz), 120.3 (d), 114.3 (d, J ($^{13}C-^{19}F$)= 21.7 Hz), 112.5 (d, J ($^{13}C-^{19}F$)=21.7 Hz); ^{19}F NMR ($CDCl_3$, 282.3 MHz): δ=−113.93 (td, J=9.7, 6.1 Hz); MS (EI) m/z=293 (M^+, 15%), 147 (12), 146 (100), 133 (14), 104 (17), 76 (26), 50 (16); HRMS (m/z)=293.0858, calcd for $C_{18}H_{12}FNO_2$: 293.0852.

4.3. Representative procedure for the Suzuki–Miyaura cross-coupling of 1 with ethylene-diboronic acid bis(pinacol) esters

To a solution of $Pd(PPh_3)_4$ (0.0167 mmol, 19.3 mg), (*E*)-*N*-(2-iodovinyl)phthalimide **1** (0.334 mmol, 100 g), and the appropriate ethylenediboronic acid bis(pinacol) ester (0.668 mmol) in toluene (6.6 mL, 0.05 M) were added aqueous K_2CO_3 (1 mmol, 0.5 mL, 2 M) and ethanol (5 mmol, 230 mg, 0.29 mL). The reaction mixture was stirred at 50 °C under argon atmosphere for 24 h. The organic layer was concentrated and the crude product was preloaded onto silica. Products **3a**–**c** were purified by silica gel chromatography, eluting with EtOAc in *n*-hexane—0–50%.

*4.3.1. 2-((1E,3Z)-3,4-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)isoindoline-1,3-dione (**3a**).* Yellow solid, mp 172–173 °C; R_f (50% EtOAc/hexane)=0.58; IR, ν_{max} (KBr)=3114, 3097, 3077, 2982, 2928, 2854, 1781, 1723, 1626, 1547, 1441, 1372, 1298, 1212, 1099, 1086 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ=8.26 (d, 1H, J=14.6 Hz), 7.87–7.84 (m, 2H), 7.73–7.71 (m, 2H), 7.19–7.15 (m, 2H), 7.06–6.98 (m, 2H), 6.92–6.89 (m, 6H), 6.58 (d, 1H, J=14.6 Hz), 1.42 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.0, 149.7, 141.2, 138.2, 134.4, 131.7, 130.4, 129.4, 127.9, 127.3, 126.9, 125.5, 123.6, 123.3, 122.6, 84.1, 24.8; MS (EI) m/z=477 (M^+, 2%), 366 (25), 365 (100), 104 (44), 76 (25); HRMS (m/z)=477.2104, calcd for $C_{30}H_{28}BNO_4$: 477.2111.

*4.3.2. 2-((1E,3E)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) octa-1,3-dien-1-yl)isoindoline-1,3-dione (**3b**).* Pale yellow solid, mp 192–193 °C; R_f (50% EtOAc/hexane)=0.56; IR, ν_{max} (KBr)=2994, 2979, 2931, 2873, 1721, 1618, 1468, 1332, 1273, 1222, 1142, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ=8.02 (dd, 1H, J=14.5, 11.6 Hz), 7.88–7.85 (m, 2H), 7.74–7.70 (m, 2H), 6.85 (d, 1H, J=14.5 Hz), 6.56 (d, 1H, J=11.6 Hz), 2.22 (t, 2H, J=6.9 Hz), 1.42–1.25 (m, 16H), 0.91–0.85 (t, 3H, J=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=166.2, 141.5, 134.4, 131.8, 123.5, 120.9, 120.7, 83.9, 36.6, 32.3, 29.7, 24.8, 22.5, 14.1; MS (EI) m/z=381 (M^+, 25%), 338 (32), 274 (50), 252 (15), 238 (100), 237 (36), 208 (31), 192 (28), 148 (20), 130 (50), 83 (48), 76 (18), 54 (25); HRMS (m/z)=381.2132, calcd for $C_{22}H_{28}NO_4B$: 381.2112.

*4.3.3. (Z)-Methyl 2-((E)-2-(1,3-dioxoisoindolin-2-yl)vinyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (**3c**).* Yellow oil; R_f (50% EtOAc/hexane)=0.45; ^1H NMR ($CDCl_3$, 300 MHz) δ=8.13 (d, 1H, J=15.2 Hz), 7.88–7.85 (m, 2H), 7.75–7.71 (m, 2H), 6.76 (d, 1H, J=15.2 Hz), 3.87 (s, 3H), 2.18–2.11 (m, 2H), 1.36 (s, 6H), 1.27 (s, 6H), 1.30–1.25 (m, 4H), 0.90–0.85 (t, 3H, J=6.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=169.0, 165.9, 142.4, 134.4, 131.6, 123.6, 119.9, 117.6, 83.9, 51.7, 33.8, 31.7, 30.9, 29.4, 24.7, 24.6, 22.4, 13.9; MS (EI) m/z=439 (M^+, 5%), 421 (30), 394 (20), 353 (78), 339 (100), 294 (40), 250 (48), 238 (32), 163 (28), 147 (12), 130 (40), 119 (30), 105 (20), 76 (15), 55 (20). HRMS (m/z)=439.2151, calcd for $C_{24}H_{30}BNO_6$: 439.2166.

4.4. Representative procedure for the Sonogashira coupling of 1 with terminal alkynes

$PdCl_2(PPh_3)_2$ (3.5 mg, 5.0 μmol, 1 mol %) and CuI (4.8 mg, 25 μmol) were mixed with EtOH (2 mL) in a glass vial equipped with a screw cap. Diisopropylamine (140 μL, 1.0 mmol) was added and the vial was flushed with argon. (*E*)-*N*-(2-Iodovinyl)phthalimide **1** (150 mg, 0.50 mmol) and the appropriate acetylene (0.55 mmol 1.1 equiv) were added and the mixture was stirred for 3 h. After the reaction was completed (GC–MS analysis) the volatiles were evaporated under vacuum and the crude product was chromatographed on silica gel (eluent: EtOAc in *n*-hexane 0–50%) to afford the analytically pure products.

*4.4.1. (E)-2-(4-Phenylbut-1-en-3-yn-1-yl)isoindoline-1,3-dione (**4a**).* Pale yellow solid, mp 114–115 °C; R_f (50% EtOAc/hexane)= 0.42; IR, ν_{max} (KBr)=3074, 3054, 2990, 2924, 2853, 2198, 1781, 1725, 1628, 1593, 1491, 1466, 1382, 1261, 1106 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ=7.88–7.85 (m, 2H), 7.75–7.71 (m, 2H), 7.44–7.41 (m, 2H), 7.31–7.27 (m, 4H), 6.94 (d, 1H, J=14.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=165.8, 134.8, 131.5, 131.4, 128.3, 128.2, 127.8, 123.9, 123.2, 100.2, 92.1, 86.5; MS (EI) m/z=273 (M^+, 100%), 189 (10), 130 (10),

126 (20), 114 (12), 104 (10), 76 (15) 50 (20); HRMS calcd for $C_{18}H_{11}NO_2$: 273.0790, found: 273.0798.

*4.4.2. (E)-2-(4-(Naphthalen-1-yl)but-1-en-3-yn-1-yl)isoindoline-1,3-dione (**4b**).* Pale yellow solid, mp 196 °C; R_f (50% EtOAc/hexane)=0.43; IR, ν_{max} (KBr)=3054, 2959, 2929, 2873, 2859, 2137, 1727, 1581, 1503, 1462, 1390, 1287, 1267, 1122, 1073 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ=8.36 (m, 1H), 7.94–7.77 (m, 4H), 7.71–7.37 (m, 7H), 7.13 (d, 1H, J=14.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=165.8, 134.8, 133.2, 133.1, 131.5, 130.3, 128.7, 128.3, 127.8, 126.8, 126.4, 126.2, 125.3, 123.9, 120.9, 100.4, 91.4, 90.3; MS (EI) m/z=323 (M^+, 100%), 176 (15), 76 (10), 50 (5); HRMS calcd for $C_{22}H_{13}NO_2$: 323.0946, found: 323.0947.

*4.4.3. (E)-2-(4-(Trimethylsilyl)but-1-en-3-yn-1-yl)isoindoline-1,3-dione (**4c**).* Pale yellow solid, mp 121–122 °C; R_f (50% EtOAc/hexane)=0.40; ^1H NMR ($CDCl_3$, 300 MHz) δ=7.90–7.87 (m, 2H), 7.78–7.75 (m, 2H), 7.23 (d, 1H, J=15.4 Hz), 6.76 (d, 1H, J=15.4 Hz), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=165.7, 134.8, 131.5, 128.9, 123.9, 101.9, 99.9, 97.4, −0.1; MS (EI) m/z=269 (M^+, 25%), 254 (100), 227 (20), 102 (5), 50 (5); HRMS calcd for $C_{15}H_{15}NO_2Si$: 269.0872, found: 269.0862.

*4.4.4. (E)-2-(4-(1-(Trimethylsiloxy)cyclohexyl)but-1-en-3-yn-1-yl) isoindoline-1,3-dione (**4d**).* Pale yellow solid, mp 101–102 °C; R_f (50% EtOAc/hexane)=0.49; ^1H NMR ($CDCl_3$, 300 MHz) δ=7.90–7.88 (m, 2H), 7.78–7.74 (m, 2H), 7.13 (d, 1H, J=14.8 Hz), 6.80 (d, 1H, J=14.8 Hz), 1.95–1.25 (m, 10H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=165.8, 134.8, 131.4, 127.5, 123.9, 100.1, 96.3, 82.2, 77.2, 70.5, 41.2, 30.9, 25.2, 23.2, 2.0; MS (EI) m/z=367 (M^+, 10%), 352 (45), 338 (15), 324 (100), 278 (15), 207 (25); HRMS calcd for $C_{21}H_{25}NSiO_3$: 367.1604, found: 367.1588.

*4.4.5. (E)-2-(Dec-1-en-3-yn-1-yl)isoindoline-1,3-dione (**4e**).* Pale yellow solid, mp 184 °C; R_f (50% EtOAc/hexane)=0.42; ^1H NMR ($CDCl_3$, 300 MHz) δ=7.89–7.86 (m, 2H), 7.77–7.73 (m, 2H), 7.10 (d, 1H, J=14.9 Hz), 6.76–7.69 (ddd, 1H, J=14.9, 2.2, 2.2 Hz), 2.37–2.32 (m, 2H), 1.58–1.51 (m, 2H), 1.44–1.36 (m, 2H), 1.31–1.25 (m, 4H), 0.92–0.83 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=165.9, 134.6, 131.5, 126.9, 123.7, 101.2, 93.5, 77.5, 31.4, 29.7, 28.7, 22.5, 19.6, 14.1; MS (EI) m/z=281 (M^+, 20%), 252 (25), 239 (50), 212 (100), 182 (20), 134 (75); HRMS calcd for $C_{18}H_{19}NO_2$: 281.1416, found: 281.1427.

*4.4.6. (E)-2-(4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)but-1-en-3-yn-1-yl)isoindoline-1,3-dione (**4f**).* Yellow solid, mp 171–172 °C; R_f (50% EtOAc/hexane)=0.47; ^1H NMR ($CDCl_3$, 300 MHz) δ=7.92–7.89 (m, 2H), 7.79–7.75 (m, 4H), 7.47–7.44 (m, 2H), 7.29 (d, 1H, J=14.9 Hz), 6.98 (d, 1H, J=14.9 Hz), 1.35 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=165.8, 134.8, 134.6, 131.5, 130.6, 128.1, 125.9, 123.9, 100.1, 92.3, 87.9, 83.9, 29.7, 24.9; MS (EI) m/z=399 (M^+, 100%), 384 (10), 313 (17), 299 (15), 104 (5), 76 (6), 50 (4); HRMS calcd for $C_{24}H_{22}BNO_4$: 399.1642, found: 399.1629.

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Supplementary data

NMR spectra of all compounds and crystallographic data for compounds **1**, **2b**, **2h**, **2j**, and **4a**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.03.012.

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