Synthesis of Indenyl Triazenes by Rhodium-Catalyzed Annulation Reactions

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Abstract. The synthesis of vinyl triazenes by metal-catalyzed processes is attractive, but only few examples have been described so far. Here, we describe Rh-catalyzed [3+2] annulation reactions of arylboronic acid derivatives and alkynyl triazenes. These reactions provide access to functionalized indenyl triazenes. The regioselectivity of the annulations is mostly high, but strongly dependent on the substituents on the alkyne. The triazene group in the products can be cleaved under acidic condition. In contrast to what has been reported for other vinyl triazenes, rearrangements are observed instead of direct substitution reactions.

Introduction

1-Aryl triazenes are popular compounds in synthetic chemistry because: a) they are easy to synthesize and handle, b) they are stable under neutral and basic conditions, and c) the triazene groups can be replaced by numerous other functions under acidic conditions.[1] 1-Vinyl triazenes share the two latter characteristics with aryl triazenes. Notably, they can be used as vinyl cation surrogates, enabling electrophilic vinylation reactions (Scheme 1a).[2–8] However, synthetic access to vinyl triazenes is still limited. The first procedures described in the literature were based on the coupling of vinyl Grignard reagents with azides (Scheme 1b).[2,3] However, this method was found to have a limited scope.[4] We have recently published a modified version of the Grignard/azide route, which involves an intramolecular alkylation step.[5] This procedure has a broader scope, but limitations were still encountered.[9] Instead of azides, it is possible to use aminodiazotates for the coupling with vinyl Grignard reagents, but only few examples have been reported so far.[6] A fundamental problem of all these methods is the reliance on Grignard reagents, which implies a reduced compatibility with functional groups.
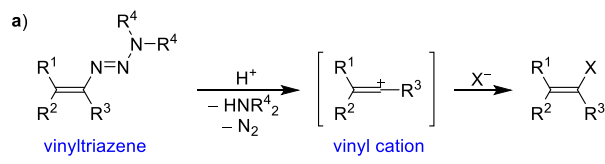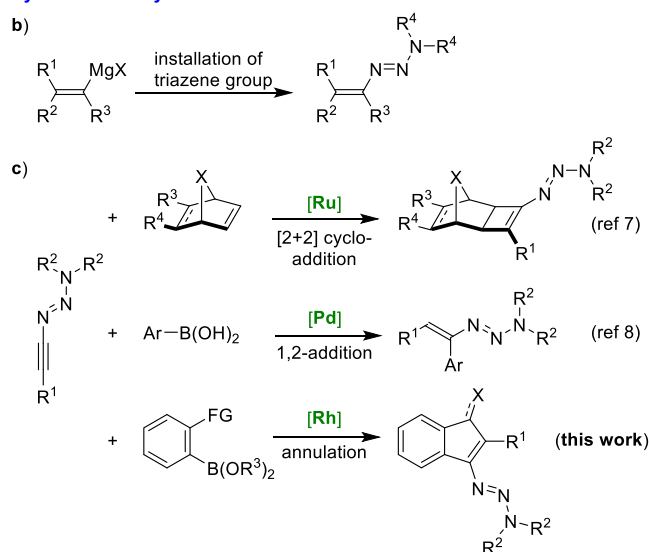
Scheme 1. Under acidic conditions, vinyl triazenes show a vinyl cation-like reactivity (a). The synthesis of vinyl triazenes can be accomplished starting from vinyl Grignard reagents (b), or from alkynyl triazenes (c).

An interesting alternative for synthesizing vinyl triazenes are metal-catalyzed addition reactions to alkynyl triazenes (Scheme 1c).[7,8,10] In collaboration with the Cramer group, we have shown that polycyclic vinyl triazenes can be prepared by Ru-catalyzed [2+2] cycloaddition reactions of alkynyl triazenes and bicyclic alkenes.[7] Furthermore, we have demonstrated that Pd-catalyzed addition reactions are well suited to prepare a range of vinyl triazenes.[8] Below, we report that indenyl triazenes are accessible by Rh-catalyzed annulation reactions of alkynyl triazenes with arylboronic acid derivatives. The reactions are compatible with a range of functional groups such as aldehydes, ketones, and esters, and triazene cleavage-reactions can be used for further structural diversifications.

Results and Discussion

The indene subunit can be found in many bioactive compounds, and numerous procedures for synthesizing substituted indenes have been reported in the literature.[11] Indenyl triazenes appeared to be a worthwhile synthetic target because the triazene group itself can potentially trigger bioactivity.[12] Furthermore, we anticipated that acid-induced cleavage reactions could allow further structural modifications of the indene scaffold.

Indenes can be synthesized by Rh-catalyzed [3+2] annulation reactions of functionalized arylboronic acids and alkynes.[13,14] The reactions are typically performed with Rh^I complexes such as [RhCl(cod)]$_2$ (cod = 1,5-cyclooctadiene) as catalyst precursor under basic conditions. We hypothesized that this methodology might be suited for the synthesis of indenyl triazenes. However, we also anticipated potential problems, such as insertion of the low-oxidation-state metal into the C–N bond of the triazene (as postulated for reactions of aryl triazenes with Pd complexes),[15] or attenuated catalytic activity due to the presence of a metal-binding triazene function.[16]

We started our investigations by performing reactions between 2-formylphenylboronic acid and 1-(3,3-dimethylbutynyl)-3,3-diisopropyl triazene in 1,4-dioxane/water (4:1). In analogy to published procedures,[14] we have used [RhCl(cod)]$_2$ as catalyst precursor (3 mol%) and KOH as base. A brief screening of reaction conditions revealed that a clean annulation reaction can be induced by microwave heating to 100 °C for 30 min. Indenol **1a** was isolated with good regioselectivity (8:1) in 90% yield (Table 1, entry 1).

Six other alkynyl triazenes were used as substrates for the coupling with 2-formylphenylboronic acid, providing the indenols **1b–g** in yields between 34% and 72%. Two regioisomers **A** and **B** are possible (Table 1), and an attribution was established by correlation NMR spectroscopy (HMBC). The results were corroborated by crystallographic analyses of the main isomers of **1a** and **1k**.[17]

The regioselectivity is strongly influenced by the substituents on the alkyne, with size apparently being a key factor. Notably, a complete change in regioselectivity was observed when the substituent attached to the alkyne was changed from a large *tert*-butyl group to a methyl, *n*-butyl or cyclopentyl group (entry 1 vs. entry 5–7).

Table 1. Rh-catalyzed reaction of 2-formyl- and 2-acetylphenylboronic acids with alkynyl triazenes.[a]
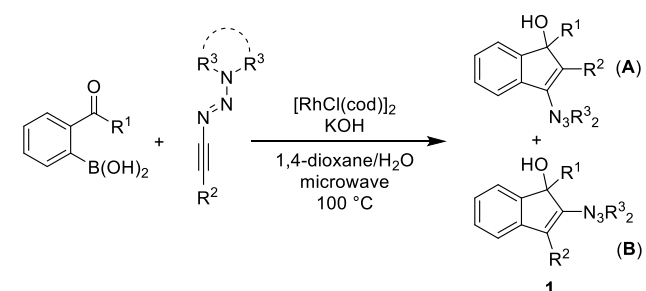
	Prod.	R^1	R^2	R^3	A:B[b]	Yield [%][d]
1	**1a**	H	*t*Bu	*i*Pr	8:1	90
2	**1b**	H	*t*Bu	(CH$_2$)$_4$	4:1	34
3	**1c**	H	*t*Bu	(CH$_2$)$_5$	> 20:1[c]	67
4	**1d**	H	Ph	*i*Pr	> 20:1[c]	48
5	**1e**	H	Me	Cy	< 1:20[c]	64
6	**1f**	H	*n*Bu	*i*Pr	< 1:20[c]	44
7	**1g**	H	*c*Pent	*i*Pr	< 1:20[c]	61
8	**1h**	Me	Ph	*i*Pr	6:1	60
9	**1i**	Me	*t*Bu	*i*Pr	> 20:1[c]	60
10	**1j**	Me	Me	*i*Pr	< 1:20[c]	46
11	**1k**	Me	Me	Cy	< 1:20[c]	54

a) Reaction conditions: boronic acid (1.2 eq.), alkynyl triazene (1 eq.), [RhCl(cod)]$_2$ (3–4 mol%), KOH (0.3–0.5 eq.), 1,4-dioxane/H$_2$O (4:1), microwave, 100 °C, 15–45 min. b) Isomer ratio of the product as determined by ^{1}H NMR. c) Ratio of the separated isomers. d) Isolated yield.
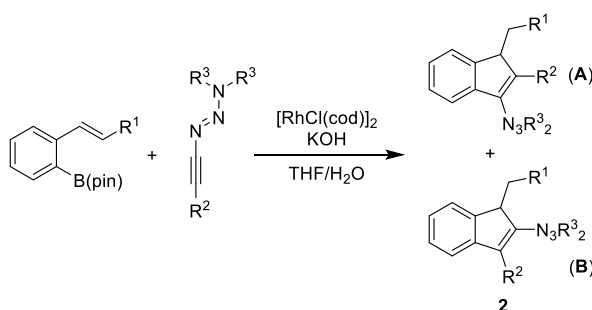
Subsequently, we have investigated reactions with 2-acetylphenylboronic acid. Using similar conditions as described before, we were able to prepare indenols **1h–k** in yields between 46% and 60% (Table 1). The regioselectivity was again strongly influenced by the substituents on the triazene (entry 9 vs. entry 10).

A plausible mechanism[13] for these reactions involves the formation of an arylrhodium complex from the arylboronic acid, followed by insertion of the alkyne into the carbon-rhodium bond. The resulting styrylrhodium complex adds to the carbonyl group of the acyl or acetyl substituent to give an alkoxyrhodium complex. The products are then formed by protonolysis. With regard to regioselectivity, one should note that alkynyl triazenes show a very polarized triple bond.[18] From an electronic point of view, the carborhodation step is expected to favor isomer **A**. In fact, this kind of selectivity was observed exclusively for reactions involving a carbopalladation step.[8] For reactions with alkynes having a methyl, *n*-butyl or cyclopentyl group

next to the triple bond, electronic effects are apparently overruled. Aside from steric considerations, it is possible that mechanistic differences are at play. All 1-alkynyltriazenes leading to isomer **B** bear a proton next to the triple bond, which could allow for a different mechanistic pathway favoring isomer **B**.

Next, we examined reactions with arylboronate esters featuring α,β-unsaturated carbonyl substituents.[14a,f] THF/water (20:1) was found to be a suitable solvent system for these reactions. As catalyst precursor, we have used once more [RhCl(cod)]$_2$. Annulation reactions with alkynyl triazenes gave the desired indene derivatives in moderate to good yields (Table 2). The reaction is compatible with boronate esters having aldehyde (entries 1–3), ketone (entries 4–6), and ester groups (entries 7 and 8). The regioselectivity of the reaction was again strongly influenced by the substituents on the triazene. Alkynes with large *tert*-butyl or mesityl groups were found to favor isomer **A** with the triazene group in 3-position. A reversed selectivity was observed for alkynes with methyl substituents. For **2b**, the preferential formation of isomer **B** was confirmed by a single crystal X-ray analysis.[17]

**Table 2.** Rh-catalyzed reaction of functionalized boronate esters with alkynyl triazenes.[a]

Entry	Prod.	R^1	R^2	R^3	**A:B**[b]	Yield [%][d]
1	**2a**	COH	*t*Bu	*i*Pr	9:1[c]	67
2	**2b**	COH	Me	Cy	< 1:20	69
3	**2c**	COH	Mes	*i*Pr	6:1	59[e]
4	**2d**	COMe	Ph	*i*Pr	1:1	80
5	**2e**	COMe	*t*Bu	*i*Pr	2:1	81
6	**2f**	COMe	Me	Cy	< 1:20[c]	66
7	**2g**	CO$_2$Me	*t*Bu	*i*Pr	6:1	68
8	**2h**	CO$_2$Me	Me	Cy	< 1:20	55[f]

a) Reaction conditions: boronate ester (1.2 eq.), alkynyl triazene (1 eq.), [RhCl(cod)]$_2$ (3–5 mol%), KOH (0.3 eq.), THF/H$_2$O (2.5–5 vol% H$_2$O), 0 °C (0–7 h) then RT (0–6.5 h). b) Isomer ratio of the product as determined by ^{1}H NMR. c) Ratio of the separated isomers. d) Isolated yield. e) 80 °C (15 min). f) 0 °C, then RT (overnight), then 50 °C (6 h)

Annulation reactions of 2-cyanophenylboronic acid and alkynes are known to give indenones.[14e] We have examined a corresponding reaction with 1-(3,3-dimethylbutynyl)-3,3-diisopropyl triazene (Scheme 2). Surprisingly, we isolated ketimine **3** instead of an

indenone, even though the reaction was performed in the presence of water under harsh conditions (100 °C, 2 d). The presence of a C=NH group instead of a keto group was corroborated by a ^{1}H NMR signal at 10.1 ppm, and by a crystallographic analysis of the adduct **3** x HCl.[17] The low susceptibility of the imine to hydrolyze can be attributed to the presence of an electron-donating triazene group, which reduces the electrophilicity of the imine carbon.
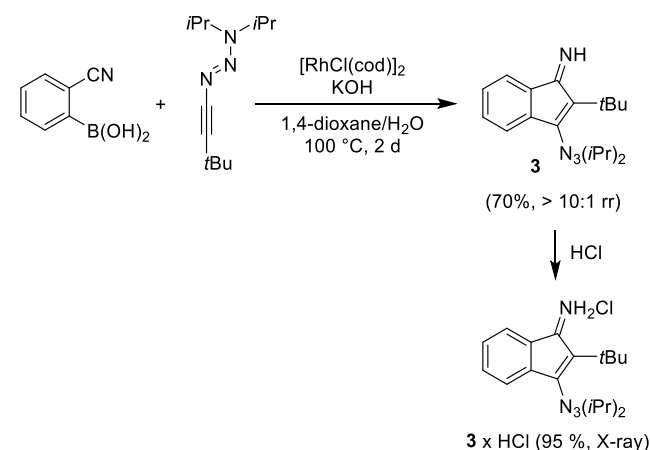
Scheme 2. Synthesis of ketimine **3**. Conditions: boronic acid (4 eq.), alkynyl triazene (1 eq.), [RhCl(cod)]$_2$ (3 mol%), KOH (2 eq.), 1,4-dioxane/H$_2$O (40:1), 100 °C (48 h)

As discussed in the introduction, triazenes can be cleaved under acidic conditions. In the case of 1-aryl triazenes, the addition of acid leads to formation of aryldiazonium compounds, which can be used for subsequent synthetic transformations.[1] In the case 1-vinyl triazenes, the corresponding vinyl diazonium compounds are more reactive and prone to loose dinitrogen.[19] For indenyl triazenes, nitrogen loss would result in the formation of high-energy cyclic vinyl cations,[20] and alternative decomposition pathways might be favored. Indeed, when indenyl triazenes were subjected to strong acids, rearranged products were formed as opposed to addition products to hypothetical vinyl cations (Scheme 3).
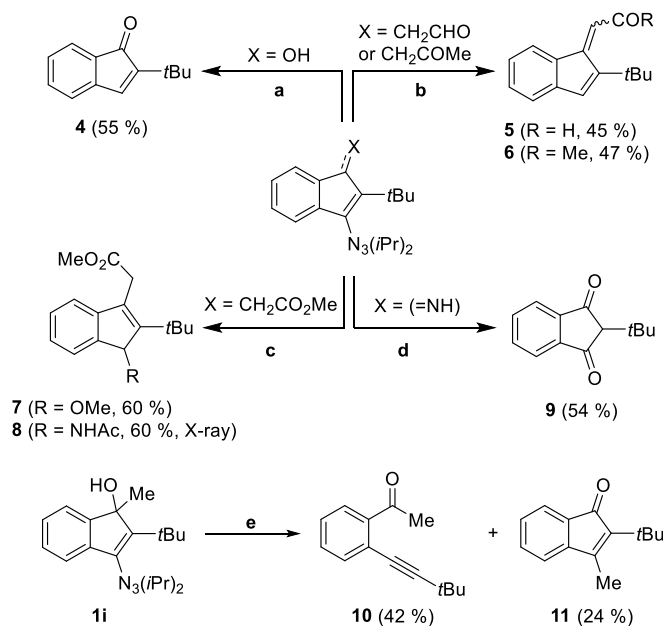
The addition of trifluoroacetic acid (TFA) to a solution of triazene **1a** in diethyl ether resulted in the formation of indenone **4**, which could be isolated in 55% yield. A similar reactivity (triazene cleavage plus deprotonation) was observed for reactions of **2a** and **2e** with TFA, which gave the 1-methylene-1*H*-indene derivatives **5** and **6**. An exchange of the triazene function against a methoxy or an acetamide group (via a Ritter-type reaction) was found for mixtures of **2g** and HBF$_4$ in methanol or acetonitrile (**7** and **8**). However, the substitution went along with a rearrangement of the double bond, as evidenced by NMR spectroscopy and by a crystallographic analysis of **8**.

Triazene cleavage of ketimine **3** required forcing conditions, because the imine group is more basic than the triazene (as evidenced by isolation of **3** x HCl). When a solution of **3** in THF/water (5:1) was heated with an excess of HCl to 60 °C, we observed the complete hydrolysis to 1,3-indandione derivative **9** (Scheme 3).

The reactions leading to **4–6** show that substitution of the triazene group by nucleophiles is disfavored in the presence of acidic protons. Compound **1i** does not feature acidic protons, and we thus attempted a displacement of the triazene by fluoride using HF·pyridine.[7,10a] However, as main products of the reaction, we observed alkyne **10** along with minor amounts of indenone **11** (Scheme 3).
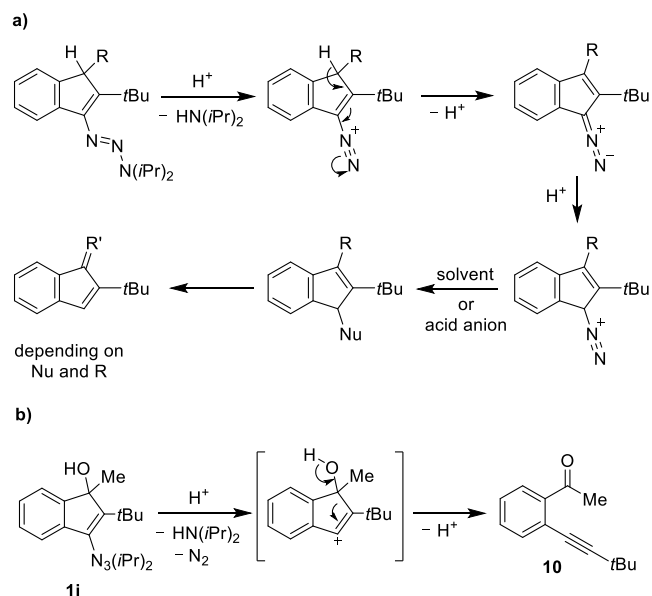
For cleavage reactions with triazenes having a hydrogen atom in 1-position, we propose the following tentative mechanism: The addition of a strong acid results in rupture of the N1–N2 bond of the triazene group and formation of a vinyl diazonium compound (Scheme 4a). Instead of N$_2$, a proton is lost to give a diazo compound. It is worth noting that there is literature precedence for the formation of diazo compounds from triazenes.[21] Acid-induced substitution of the diazo group by HNu then gives indenes with a rearranged double bond (e.g. **7** or **8**), or elimination products (e.g. **4–6**). The latter likely form via a TFA adduct (Nu = CF$_3$CO$_2$). In fact, for reactions leading to **5**, we have been able to characterize the intermediate TFA adduct by NMR spectroscopy.

For reactions with **1i**, the formation of a diazo compound is not possible (no H atom in position 1). In this case, the reaction might proceed via a shot-lived vinyl cation, which undergoes a ring-opening reaction to give alkyne **10** (Scheme 4b).

Conclusion

Vinyl triazenes are commonly prepared from vinyl Grignard reagents.[2–6] We have recently introduced a complementary approach, namely metal-catalyzed addition reactions to alkynyl triazenes. In continuation of studies about Ru- and Pd-catalyzed reactions,[7,8] we have now shown that substituted indenyl triazenes are accessible by Rh-catalyzed [3+2] annulation reactions. As substrates, we have employed arylboronic acid derivatives with aldehyde, ketone, ester or cyano groups. The regioselectivity of the reaction was mostly high, and strongly dependent on the substituent at the alkyne. The addition of acids allows cleavage of the triazene group in the products. This cleavage does not result in direct substitution of the triazene by

nucleophiles, as observed for other vinyl triazenes. Instead, we observed substrate-specific rearrangements. Nevertheless, it is possible to use these cleavage reactions to prepare structurally complex indenes, as exemplified by the synthesis of compounds **5–8**.

Experimental Section

For experimental details and X-ray data, see Supporting Information.

General Information

The syntheses of the alkynyl triazenes as well as of compounds **1a-c**, and **1e** were carried out under an atmosphere of dry nitrogen resp. nitrous oxide (purity: 99.999%, Messer Schweiz AG) using standard Schlenk and glovebox techniques in oven-dried glassware. Other reactions were carried out under ambient atmosphere unless indicated otherwise. Reagents and solvents were purchased from abcr, Acros, Apollo Scientific, Fluorochem Sigma Aldrich or TCI. Chemicals were used as obtained from the suppliers. Dry solvents were obtained using a solvent purification system with an aluminum oxide column (Innovative Technologies). Flash column chromatography was performed with Silicycle silica gel 60 (0.040–0.063 μm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualized under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. For the purification of acid-sensitive compounds, silicagel 230–400 mesh particle size (100 g) was deactivated prior to use by adding DCM containing 5 vol% triethylamine (300 mL), removal of the solvent under reduced pressure, and drying of the silica at RT under oil pump vacuum overnight. NMR spectra were recorded on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe, Bruker DRX600 (600 MHz) and Bruker AvanceII (800 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm), and CD$_3$CN (quint, 1.94 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad or combinations of those. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker AV400 spectrometer. Chemical shifts are reported in ppm relative to CDCl$_3$ (77.16 ppm), and CD$_3$CN (1.32 ppm). Fluorine-19 nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker AV400 spectrometer and were not referenced. High resolution mass are given in *m/z*. Electrospray–ionization (ESI) HRMS data were acquired on a Xevo G2-S QTOF (Waters) or an Agilent LC-MS TOF operated in the positive ionization mode. Data from the Lock–Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo–ionization (APPI) HRMS measurements were done on a LTQ–Orbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. Data were processed using the XCalibur v2.2 software. Atmospheric-pressure chemical ionization (APCI) HRMS data were acquired on a Xevo G2-S QTOF (Waters) operated in the positive ionization mode. Data were processed using MassLynx 4.1 software. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). The X-ray analyses were performed by Dr. R. Scopelliti and Dr. F. Fadaei-Tirani at the EPF Lausanne.

Synthesis of starting materials

Non-commercial boronic esters were synthesized according to literature procedures by Mantuso and Lautens.[22] All spectra were in good agreement with the reported data. Most of the 1-alkynyltriazenes used in this study have already been reported, and they were prepared as described in the literature.[6,7,10a,23] For 1-((3,3-dimethylbut-1-yn-1-yl)diazenyl)pyrrolidine and 3,3-diisopropyl-1-(mesitylethynyl)triaz-1-ene, the synthetic method was adapted from a published procedure.[6]

General procedure for the synthesis of the triazenes 1a–1k

[RhCl(cod)]$_2$ (3–4 mol%), KOH (0.3–0.5 eq.) and the respective 1-alkynyl triazene (1.0 eq.) were dissolved in 1,4-dioxane/water (4:1, 0.1 M) and stirred for 5 min at RT. 2-Formylphenylboronic acid (72 mg, 0.48 mmol, 1.2 eq.) was added, the reaction flask was sealed and heated at 100 °C in the microwave for 15–45 min. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic phases were dried over MgSO$_4$ and the solvent was removed under vacuum. The product was purified by column chromatography on deactivated silica.

3-(*tert*-Butyl)-2-(3,3-diisopropyltriaz-1-en-1-yl)-1*H*-inden-1-ol (1a)

Dark-red oil (107 mg, 0.34 mmol, 90%, 8:1 rr). **^{1}H NMR** (400 MHz, CDCl$_3$, 275 K): δ (ppm) = 8.03–7.85 (m, 1H, CH$_{ar}$), 7.55–7.40 (m, 1H, CH$_{ar}$), 7.32–7.13 (m, 2H, CH$_{ar}$), 5.39–5.24 (m, 1H, CH$_{iPr}$), 5.23–5.13 (m, 1H, C*H*OH), 4.15–3.94 (m, 1H, CH$_{iPr}$), 1.74–1.62 (m, 1H, CHO*H*), 1.52–1.47 (m, 9H, CH$_{3\,tBu}$), 1.46–1.20 (m, 12H, CH$_{3\,iPr}$). The shift of the OH-proton is consistent with literature reports for indenols.[24] **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 145.0 (br, C$_{q\,ar}$ + C$_{sp2}$-N$_3$iPr$_2$), 143.8 (C$_{sp2}$-*t*Bu), 140.0 (C$_{q\,ar}$), 128.0 (CH$_{ar}$), 125.6 (CH$_{ar}$), 123.4 (CH$_{ar}$), 123.0 (CH$_{ar}$), 76.4 (COH), 48.1 (CH$_{iPr}$), 45.3 (CH$_{iPr}$), 33.9 (C$_{q\,tBu}$), 30.8 (CH$_{3\,tBu}$), 24.2 (CH$_{3\,iPr}$), 24.0 (CH$_{3\,iPr}$), 19.6 (CH$_{3\,iPr}$), 19.5 (CH$_{3\,iPr}$). **IR** (neat): ν = 3284 (w), 2976 (w), 2914 (w), 2858 (w), 1699 (w), 1604 (w), 1464 (m), 1408 (m), 1402 (s), 1346 (m), 1313 (m), 1234 (s), 1206 (m), 1150 (s), 1094 (m), 999 (m), 926 (w), 893 (m), 770 (w), 742 (s) cm^{-1}. **HRMS (ESI–TOF)**: Calculated (MH+) 316.2389; Found 316.2390.

2-(*tert*-Butyl)-3-(pyrrolidin-1-yldiazenyl)-1*H*-inden-1-ol (1b)

Red solid (39 mg, 0.14 mmol, 34 %). **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 7.85 (dd, J = 7.1, 1.2 Hz, 1H, CH$_{ar}$), 7.46 – 7.43 (m, 1H, CH$_{ar}$), 7.21 (td, J = 7.5, 1.4 Hz, 1H, CH$_{ar}$), 7.16 (td, J = 7.3, 1.3 Hz, 1H, CH$_{ar}$), 5.19 (d, J = 10.1 Hz, 1H, C*H*OH), 3.81 (br, 4 H, NCH$_2$), 2.05 (td, J = 7.0, 5.6, 3.4 Hz, 4H, (CH$_2$)$_2$), 1.47 (s, 9HCH$_{3\,tBu}$), 1.37 (d, J = 10.2 Hz, 1H, CHO*H*). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 144.95 (C$_q$), 144.80 (C$_q$), 144.63 (C$_q$), 140.01 (C$_q$), 127.95 (CH$_{ar}$), 125.62 (CH$_{ar}$), 123.22 (CH$_{ar}$), 122.80 (CH$_{ar}$), 76.48 (CHOH), 33.95 (C$_{q\,tBu}$), 30.53 (CH$_{3\,tBu}$). **IR** (neat): ν = 3385 (w), 2951 (m), 2871 (m), 1679 (w), 1604 (w), 1457 (w), 1411 (s), 1308 (s), 1126 (m), 1026 (w), 912 (w), 744 (m), 731 (m). **HRMS (ESI/QTOF)**: Calculated (MH+) 286.1914; Found 286.1911.

2-(*tert*-Butyl)-3-(piperidin-1-yldiazenyl)-1*H*-inden-1-ol (1c)

Yellow-orange solid (80 mg, 0.27 mmol, 67 %). **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 7.91 – 7.77 (m, 1H, CH$_{ar}$), 7.49 – 7.40 (m, 1H, CH$_{ar}$), 7.21 (td, J = 7.5, 1.6 Hz, 1H, CH$_{ar}$), 7.17 (td, J = 7.3, 1.5 Hz, 1H, CH$_{ar}$), 5.20 (d, J = 9.5 Hz, 1H, C*H*OH), 3.78 (m, 4H, NCH$_2$), 1.80 – 1.64 (m, 6H, (CH$_2$)$_3$), 1.46 (s, 9H, CH$_{3\,tBu}$), 1.39 (d, J = 10.2 Hz, 1H, CHO*H*). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 145.98 (C$_{sp2}$-N), 144.99 (C$_{sp2}$-*t*Bu), 144.45 (C$_{q\,ar}$), 139.99 (C$_{q\,ar}$), 128.12 (CH$_{ar}$), 125.87 (CH$_{ar}$), 123.34 (CH$_{ar}$), 123.02 (CH$_{ar}$), 76.61 (CHOH), 34.17 (C$_{q\,tBu}$), 30.95 (CH$_{3\,tBu}$), 25.45 (CH$_2$), 24.59 (CH$_2$). **IR** (neat): ν = 3368 (w), 2941 (s), 2857 (m), 1428 (s), 1353 (s), 1320 (m), 1182 (s), 1105 (s), 1013 (m), 906 (m), 742 (s). **HRMS (ESI/QTOF)**: Calculated (MH+) 300.2070; Found 300.2065.

2-(3,3-Diisopropyltriaz-1-en-1-yl)-3-phenyl-1*H*-inden-1-ol (1d)

Dark-red solid (61 mg, 0.18 mmol, 48%). **¹H NMR** (400 MHz, CDCl₃, 275 K): δ (ppm) = 8.10–7.93 (m, 3H, CH$_{ar}$), 7.57 (d, J = 6.9 Hz, 1H, CH$_{ar}$), 7.36 (d, J = 6.9 Hz, 2H, CH$_{ar}$), 7.32–7.06 (m, 3H, CH$_{ar}$), 5.62 (d, J = 9.0 Hz, 1H, C*H*OH), 5.44–5.20 (m, 1H, CH$_{iPr}$),)4.13–3.95 (m, 1H, CH$_{iPr}$), 1.68 (d, J = 9.0 Hz, 1H, CHO*H*), 1.46–1.35 (m, 6H, CH₃ $_{iPr}$), 1.36–1.17 (m, 6H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 146.4 (C$_{sp2}$), 145.1 (C$_{ar}$), 139.5 (C$_{ar}$), 135.1 (C$_{ar}$), 129.6 (C$_{ar}$), 128.4 (C$_{sp2}$), 128.2 (C$_{ar}$), 126.6 (C$_{ar}$), 126.5 (C$_{ar}$), 124.2 (C$_{ar}$), 123.6 (C$_{ar}$), 75.1 (CHOH), 49.1 (CH$_{iPr}$), 46.2 (CH$_{iPr}$), 24.2 (CH₃ $_{iPr}$), 23.9 (CH₃ $_{iPr}$), 19.6 (CH₃ $_{iPr}$), 19.4 (CH₃ $_{iPr}$). **IR** (neat): ν = 3050 (w), 2975 (w), 2931 (w), 2875 (w), 1719 (m), 1600 (m), 1463 (m), 1396 (s), 1381 (s), 1341 (m), 1255 (s), 1148 (m), 1098 (m), 1068 (m), 1006 (m), 856 (w), 754 (m) cm⁻¹. **HRMS (ESI–TOF)**: Calculated (MH+) 336.2073; Found 336.2076.

2-(3,3-Dicyclohexyltriaz-1-en-1-yl)-3-methyl-1*H*-inden-1-ol (1e)

Yellow solid (45.8 mg, 0.130 mmol, 64%). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.44 (d, J = 7.2 Hz, 1H, CH$_{ar}$), 7.31–7.25 (m, 1H, CH$_{ar}$), 7.17 (d, J = 7.4 Hz, 1H, CH$_{ar}$), 7.16 (td, J = 7.3, 1.1 Hz, 1H, CH$_{ar}$), 5.46 (s, 1H, C*H*OH), 4.96 (s, 1H, CH$_{Cy}$), 3.49 (s, 1H, CH$_{Cy}$), 3.33 (d, J = 1.9 Hz, 1H, OH), 2.19 (d, J = 1.4 Hz, 3H, CH₃) , 1.95–1.12 (m, 20H, CH₂ $_{Cy}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 152.2 (C$_{sp2}$-N₃Cy₂), 145.1 (C$_{q\ ar}$), 141.5 (C$_{q\ ar}$), 128.5 (CH$_{ar}$), 127.5 (C$_{sp2}$-Me), 125.5 (CH$_{ar}$), 123.2 (CH$_{ar}$), 118.6 (CH$_{ar}$), 73.8 (CHOH), 34.8 (br, CH₂ $_{Cy}$), 30.0 (br, CH₂ $_{Cy}$), 26.1 (br, CH₂ $_{Cy}$), 9.4 (CH₃). The NCH signals were not detected due to broadening. Based on HSQC spectroscopy, they are estimated to appear at 54 and 58 ppm, respectively. **IR** (neat): ν = 3357 (w), 2928 (m), 2850 (m), 2850 (m), 1602 (w), 1454 (w), 1394 (s), 1334 (m), 1320 (m), 1255 (s), 1213 (m), 1180 (m), 1142 (m), 1090 (m), 1012 (s), 798 (m), 758 (s), 728 (s) cm⁻¹. **HRMS (ESI/QTOF)**: Calculated (MH+) 354.2540; Found 354.2540.

2-Butyl-3-(3,3-diisopropyltriaz-1-en-1-yl)-1*H*-inden-1-ol (1f)

Red oil (56 mg, 0.18 mmol, 44%). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.45 (d, J = 7.2 Hz, 1H, CH$_{ar}$), 7.29 – 7.23 (m, 1H, CH$_{ar}$), 7.21 (d, J = 7.3 Hz, 1H, CH$_{ar}$), 7.15 (td, J = 7.3, 1.3 Hz, 1H, CH$_{ar}$), 5.46 (d, J = 1.9 Hz, 1H, C*H*OH), 5.15 (s, 1H, CH$_{iPr}$), 4.01 (s, 1H, CH$_{iPr}$), 3.30 (d, J = 2.0 Hz, 1H, CHO*H*), 2.79 – 2.61 (m, 2H, CH₂ $_{nBu}$), 1.73 – 1.56 (m, 2H, CH₂ $_{nBu}$), 1.45 – 1.21 (m, 14H, CH₂ $_{nBu}$ + CH₃ $_{iPr}$), 0.93 (t, J = 7.3 Hz, 3H, CH₃ $_{nBu}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 152.2 (C$_{sp2}$-N₃iPr₂), 144.4 (C$_{q\ ar}$), 141.8 (C$_{q\ ar}$), 132.2 (C$_{sp2}$-nBu), 128.4 (CH$_{ar}$), 125.3 (CH$_{ar}$), 123.4 (CH$_{ar}$), 119.0 (CH$_{ar}$), 73.7 (CHOH), 30.7 (CH₂ $_{nBu}$), 24.0 (CH₂ $_{nBu}$), 22.8 (CH₂ $_{nBu}$), 14.1 (CH₃ $_{nBu}$). The NCH and the CH₃ $_{iPr}$ signals were not detected due to broadening. Based on HSQC spectroscopy, the CH₃ $_{iPr}$ signals are estimated to appear at 19 and 24 ppm respectively. **IR** (neat): ν = 3544 (w), 2971 (m), 2958 (m), 2930 (m), 2871 (w), 2859 (w), 1606 (w), 1461 (m), 1401 (s), 1245 (s), 1205 (m), 1149 (s), 1032 (m), 731 (m). **HRMS (ESI/QTOF)**: Calculated (MH+) 316.2383; Found 316.2388.

3-Cyclopentyl-2-(3,3-diisopropyltriaz-1-en-1-yl)-1*H*-inden-1-ol (1g)

Red highly viscous oil (81 mg, 0.25 mmol, 61 %). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.46 (d, J = 7.2 Hz, 1H, CH$_{ar}$), 7.31 – 7.22 (m, 2H, CH$_{ar}$), 7.15 (td, J = 6.9, 2.1 Hz, 1H, CH$_{ar}$), 5.46 (d, J = 1.9 Hz, 1H, C*H*OH), 5.15 (s, 1H, CH$_{iPr}$), 4.01 (s, 1H, CH$_{iPr}$), 3.46 (p, J = 9.0 Hz, 1H, CH$_{cPent}$), 3.35 (d, J = 2.0 Hz, 1H CHO*H*), 2.12 – 1.99 (m, 2H, CH₂ $_{cPent}$), 1.98 – 1.81 (m, 4H, CH₂ $_{cPent}$), 1.78 – 1.64 (m, 2H, CH₂ $_{cPent}$), 1.49 – 1.16 (m, 12H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 151.7 (C$_{sp2}$-N₃iPr₂), 143.9 (C$_{q\ ar}$), 142.2 (C$_{q\ ar}$), 135.1 (C$_{sp2}$-cPent), 128.4 (CH$_{ar}$), 125.4 (CH$_{ar}$),

123.7 (CH$_{ar}$), 120.2 (CH$_{ar}$), 73.9 (CHOH), 49.0 (CH$_{iPr}$), 46.6 (CH$_{iPr}$), 36.9 (CH$_{cPent}$), 31.6 (CH₂ $_{cPent}$), 31.5 (CH₂ $_{cPent}$), 27.0 (CH₂ $_{cPent}$), 26.9 (CH₂ $_{cPent}$), 24.1 (CH₃ $_{iPr}$), 19.7 (CH₃ $_{iPr}$). **IR** (neat): ν = 2956 (m), 2868 (w), 2076 (w), 1601 (w), 1461 (m), 1400 (s), 1380 (s), 1365 (m), 1332 (m), 1244 (s), 1206 (m), 1149 (s), 1031 (m), 767 (m), 732 (s). **HRMS (ESI/QTOF)**: Calculated (MH+) 328.2383; Found 328.2387.

3-(3,3-Diisopropyltriaz-1-en-1-yl)-1-methyl-2-phenyl-1*H*-inden-1-ol (1h)

Yellow solid (60 mg, 0.174 mmol, 40%, major isomer) and as an oil (30 mg, 0.086 mmol, 20%, 1.4:1 rr). The data for the major isomer are reported. **¹H NMR** (400 MHz, CDCl₃ 298 K): δ (ppm) = 8.22–8.09 (m, 2H, CH$_{ar}$), 8.08–7.98 (m, 1H, CH$_{ar}$), 7.62–7.43 (m, 1H, CH$_{ar}$), 7.43–7.33 (m, 2H, CH$_{ar}$), 7.32–7.19 (m, 3H, CH$_{ar}$), 5.39–5.14 (m, 1H, CH$_{iPr}$), 4.20–3.97 (m, 1H, CH$_{iPr}$), 1.99 (s, 1H, OH), 1.67 (s, 3H, CH₃ $_{tBu}$), 1.53–1.37 (m, 6H, CH₃ $_{iPr}$), 1.36–1.19 (m, 6H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃) δ 150.5 (C$_{sp2}$), 145.2 (C$_{ar}$), 138.1 (C$_{ar}$), 135.6 (C$_{ar}$), 135.2 (C$_{ar}$), 129.9 (C$_{sp2}$), 128.2 (C$_{ar}$), 127.6 (CH$_{ar}$), 126.8 (CH$_{ar}$), 126.6 (CH$_{ar}$), 124.1 (CH$_{ar}$), 121.5 (CH$_{ar}$), 81.6 (CHOH), 49.0 (CH$_{iPr}$), 45.9 (CH$_{iPr}$), 24.6 (CH₃), 19.7 (CH₃ $_{iPr}$), 19.5 (br, CH₃ $_{iPr}$). An unknown impurity shows a peak at 8.2 ppm in the ¹³C NMR spectrum. **IR** (neat): ν = 3362 (w), 2976 (m), 2937 (w), 2864 (w), 1598 (w), 1453 (w), 1402 (s), 1380 (m), 1358 (m), 1279 (w), 1234 (s), 1156 (s), 1094 (s), 1022 (m), 910 (w), 842 (m), 753 (s), 691 (s) cm⁻¹. **HRMS (ESI–TOF)**: Calculated (MH+) 350.2227; Found 350.2231.

2-(*tert*-Butyl)-3-(3,3-diisopropyltriaz-1-en-1-yl)-1-methyl-1*H*-inden-1-ol (1i)

Yellow solids (major: 102 mg, 0.311 mmol, 58%, minor: 3.5 mg, 11 μmol, 2 %,).). The data for the major isomer are reported. **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.90–7.78 (m, 1H, CH$_{ar}$), 7.42–7.33 (m, 1H, CH$_{ar}$), 7.24–7.13 (m, 2H, CH$_{ar}$), 5.49–5.07 (m, 1H, CH$_{iPr}$), 4.24–3.78 (m, 1H, CH$_{iPr}$), 1.77 (s, 3H, CH₃), 1.63 (s, 1H, OH), 1.51 (s, 9H, CH₃ $_{tBu}$), 1.46–1.24 (m, 12H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 151.1 (C$_{q\ ar}$), 146.5 (C$_{sp2}$-tBu), 144.2 (C$_{sp2}$-N₃iPr₂), 138.3 (C$_{q\ ar}$), 127.7 (CH$_{ar}$), 125.9 (CH$_{ar}$), 123.4 (CH$_{ar}$), 120.7 (CH$_{ar}$), 82.8 (*C*(CH₃)OH), 34.9 (C$_{q\ tBu}$), 31.4 (CH₃ $_{tBu}$), 25.9 (CH₃). **IR** (neat): ν = 3317 (w), 2973 (m), 2948 (w), 2870 (w), 1601 (w), 1455 (w), 1415 (s), 1396 (m), 1363 (m), 1345 (m), 1307 (m), 1238 (s), 1224 (s), 1151 (s), 1120 (m), 1078 (s), 1040 (s), 1023 (s), 927 (m), 874 (m), 802 (m), 760 (s), 711 (s) cm⁻¹. **HRMS (ESI/QTOF):** Calculated (MH+) 330.2540; Found 330.2540.

2-(3,3-Diisopropyltriaz-1-en-1-yl)-1,3-dimethyl-1*H*-inden-1-ol (1j)

Yellow, highly viscous oil that crystalizes upon storage at –20 °C (33.1 mg, 0.115 mmol, 46%). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.42–7.37 (m, 1H, CH$_{ar}$), 7.32–7.25 (m, 1H, CH$_{ar}$), 7.23–7.15 (m, 2H, CH$_{ar}$), 5.30 (s, 1H, CH$_{iPr}$), 4.02 (s, 1H, CH$_{iPr}$), 3.60 (s, 1H, OH), 2.19 (s, 3H, C$_{sp2}$-*CH*₃), 1.66 (s, 3H, C(OH)*CH*₃), 1.51–1.16 (m, 12H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 153.3 (C$_{sp2}$-N₃iPr₂), 147.1 (C$_{q\ ar}$), 143.5 (C$_{q\ ar}$ or C$_{sp2}$-Me), 128.3 (CH$_{ar}$), 126.6 (C$_{q\ ar}$ or C$_{sp2}$-Me), 125.8 (CH$_{ar}$), 121.2 (CH$_{ar}$), 118.9 (CH$_{ar}$), 80.3 (C(OH)Me), 48.6 (br, CH$_{iPr}$), 45.7 (br, CH$_{iPr}$), 26.9 (C(OH)*CH*₃), 23.8 (CH₃ $_{iPr}$), 19.5 (CH₃ $_{iPr}$), 9.4 (C$_{sp2}$-*CH*₃). **IR** (neat): ν = 3542 (w), 3529 (w), 3055 (w), 2970 (w), 2927 (w), 2866 (w), 1605 (w), 1462 (w), 1397 (s), 1375 (m), 1316 (m), 1251 (s), 1209 (s), 1152 (s), 1089 (s), 1025 (s), 1014 (s), 933 (m), 748 (s) cm⁻¹. **HRMS (ESI/QTOF)**: Calculated (MH+) 288.2070; Found 288.2070.

2-(3,3-Dicyclohexyltriaz-1-en-1-yl)-1,3-dimethyl-1*H*-inden-1-ol (1k)

Yellow solid (41.0 mg, 0.112 mmol 54%). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.42–7.08 (m, 4H, CH$_{ar}$), 4.98 (s, 1H, CH$_{Cy}$), 3.64 (s, 1H, OH), 3.48 (s, 1H, CH$_{Cy}$), 2.15

(s, 3H, C$_{sp2}$-CH$_3$), 1.63 (s, 3H, C(OH)CH$_3$), 2.01–0.76 (m, 20H, CH$_2$ $_{Cy}$). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 153.3 (C$_{sp2}$-N$_3$Cy$_2$), 147.1 (C$_{q\ ar}$), 143.6 (C$_{q\ ar}$), 128.3 (CH$_{ar}$), 126.3 (C$_{sp2}$-Me), 125.7 (CH$_{ar}$), 121.10 (CH$_{ar}$), 118.8 (CH$_{ar}$), 80.3 (C(OH)CH$_3$), 57.6 (CH$_{Cy}$), 54.0 (CH$_{Cy}$), 34.8 (br, CH$_2$ $_{Cy}$), 30.0 (br, CH$_2$ $_{Cy}$), 26.9 (br, CH$_2$ $_{Cy}$), 26.1 (C(OH)CH$_3$), 9.4 (C$_{sp2}$-CH$_3$). **IR** (neat): v = 3503 (w), 2973 (w), 2924 (m), 2851 (m), 1608 (w), 1444 (m), 1398 (s), 1398 (s), 1379 (s), 1336 (m), 1313 (s), 1253 (m), 1209 (s), 1194 (s), 1086 (m), 1030 (s), 760 (s), 1140 (m), 1014 (m), 1274 (m), 1070 (m), 988 (m), 917 (m), 892 (m) cm^{-1}. **HRMS (nanochip-ESI/LTQ-Orbitrap)**: Calculated (MH+) 368.2696; Found 368.2696.

General procedure for the synthesis of the triazenes 2a–2h

[RhCl(cod)]$_2$ (3–5 mol %), KOH (0.3 eq.) and the respective 1-alkynyl triazene (1 eq.) were dissolved in THF/water (2.5–5 vol% H$_2$O, 0.1 M) and stirred for 5 min at 0 °C. The boronic acid (1.2 eq.) was added and the reaction mixture was stirred at 0 °C for 1 h. Stirring was continued at RT until completion of the reaction. The reaction mixture was filtered over a plug of deactivated silica (NEt$_3$) and the solvent was removed under vacuum. The product was purified by column chromatography on deactivated silica.

2-(2-(*tert*-Butyl)-3-(3,3-diisopropyltriaz-1-en-1-yl)-1*H*-inden-1-yl)acetaldehyde (2a)

Yellow solid (88.2 mg, 0.258 mmol, 60%). **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 9.38 (dd, J = 2.8, 1.4 Hz, 1H, CHO), 7.97 (d, J = 7.7 Hz, 1H, CH$_{ar}$), 7.32 (d, J = 7.4 Hz, 1H, CH$_{ar}$), 7.23 (dd, J = 7.7, 1.3 Hz, 1H, td expected, partially covered by solvent signal, CH$_{ar}$), 7.15 (td, J = 7.4, 1.2 Hz, 1H, CH$_{ar}$), 5.22 (br, 1H, CH$_{iPr}$), 4.09 (dd, J = 7.1, 3.2 Hz, 1H, CHCH$_2$COH), 4.03 (br, 1H, CH$_{iPr}$), 3.17 (ddd, J = 17.4, 3.2, 1.4 Hz, 1H, CH$_2$COH), 2.78 (ddd, J = 17.5, 7.1, 2.8 Hz, 1H, CH$_2$COH), 1.43 (s, 9H, CH$_3$ $_{tBu}$), 1.34 (br, 12H, CH$_3$ $_{iPr}$). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 202.8 (CHO), 146.0 (C$_{q\ ar}$ or C$_{sp2}$-N$_3$iPr$_2$), 145.8 (C$_{q\ ar}$ or C$_{sp2}$-N$_3$iPr$_2$), 144.7 (C$_{sp2}$-tBu), 140.9 (C$_{q\ ar}$), 126.8 (CH$_{ar}$), 125.0 (CH$_{ar}$), 123.4 (CH$_{ar}$), 122.6 (CH$_{ar}$), 46.2 (CH$_2$COH), 43.8 (CHCH$_2$COH), 34.4 (C$_{q\ tBu}$), 31.2 (CH$_3$ $_{tBu}$). **IR** (neat): v = 2973 (m), 2823 (w), 2722 (w), 1718 (s), 1458 (m), 1399 (s), 1344 (m), 1241 (s), 1153 (s), 1127 (m), 1096 (m), 1023 (m), 938 (m), 757 (m), 744 (m) cm^{-1}. **HRMS (nanochip-ESI/LTQ-Orbitrap)**: Calculated (MNa+) 364.2359; Found 364.2358.

2-(3-(*tert*-butyl)-2-(3,3-diisopropyltriaz-1-en-1-yl)-1*H*-inden-1-yl)acetaldehyde (2a')

Yellow solid (9.9 mg, 0.029 mmol, 7%). **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 9.44 (s, 1H, CHO), 7.64 (d, J = 7.8 Hz, 1H, CH$_{ar}$), 7.29 (d, J = 7.3 Hz, 1H, CH$_{ar}$), 7.22 (td, J = 7.6, 1.3 Hz, 1H, CH$_{ar}$), 7.09 (td, J = 7.4, 1.1 Hz, 1H, CH$_{ar}$), 5.12 (s, 1H, CH$_{iPr}$), 4.23 (dd, J = 7.4, 3.5 Hz, 1H, CHCH$_2$COH), 3.97 (s, 1H, CH$_{iPr}$), 2.96 (ddd, J = 17.3, 3.5, 1.9 Hz, 1H, CH$_2$COH), 2.65 (ddd, J = 17.3, 7.4, 2.2 Hz, 1H, CH$_2$COH), 1.56 (s, 9H, CH$_3$ $_{tBu}$), 1.39 – 1.11 (m, 12H, CH$_3$ $_{iPr}$). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 202.92 (CHO), 152.67 (C$_{sp2}$-N$_3$iPr$_2$), 144.97 (C$_{q\ ar}$), 144.82 (C$_{q\ ar}$), 137.69 (C$_{sp2}$-tBu), 126.52 (CH$_{ar}$), 124.11 (CH$_{ar}$), 123.29 (CH$_{ar}$), 122.88 (CH$_{ar}$), 45.84 (CH$_2$COH), 40.66 (CHCH$_2$COH), 35.26 (C$_{q\ tBu}$), 31.40 (CH$_3$ $_{tBu}$). **IR** (neat): v = 2972 (m), 2953 (w), 2930 (w), 2906 (w), 2870 (w), 2191 (w), 1719 (s), 1457 (m), 1397 (s), 1379 (s), 1359 (s), 1243 (s), 1204 (m), 1158 (s), 1143 (s), 1098 (s), 1004 (m), 753 (s). **HRMS (ESI/QTOF)**: Calculated (MH+) 342.2540; Found 342.2536.

2-(2-(3,3-Dicyclohexyltriaz-1-en-1-yl)-3-methyl-1*H*-inden-1-yl)acetaldehyde (2b)

Brown-orange solid (167.9 mg, 0.445 mmol, 69%, > 20:1 rr). **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 9.52 (s, 1H, CHO), 7.33–7.26 (m, 2H, CH$_{ar}$), 7.33–7.23 (m, 3H, CH$_{ar}$), 5.06–4.82 (m, 1H, CH$_{Cy}$), 4.25–4.14 (m, 1H, CHCH$_2$CHO), 3.80–3.37 (m, 1H, CH$_{Cy}$), 3.06 (ddd, J = 17.3, 3.6, 1.9 Hz, 1H, CH$_2$CHO), 2.70 (ddd, J = 17.3, 7.7, 2.2 Hz, 1H, CH$_2$CHO), 2.25 (s, 3H, CH$_3$), 1.93–1.10 (m, 20H, CH$_2$ $_{Cy}$). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 202.7 (CHO), 153.1 (C$_{sp2}$-N$_3$Cy$_2$), 145.9 (C$_{q\ ar}$), 143.9 (C$_{q\ ar}$), 127.4 (C$_{sp2}$-Me), 127.0 (CH$_{ar}$), 124.5 (CH$_{ar}$), 123.0 (CH$_{ar}$), 118.4 (CH$_{ar}$), 57.7 (br, CH$_{Cy}$), 54.4 (br, CH$_{Cy}$), 45.1 (CH$_2$CHO), 40.4 (CHCH$_2$CHO), 34.5 (br, CH$_2$ $_{Cy}$), 34.3 (br, CH$_2$ $_{Cy}$), 30.0 (br, CH$_2$ $_{Cy}$), 29.8 (br, CH$_2$ $_{Cy}$), 26.1 (br, CH$_2$ $_{Cy}$), 9.56 (CH$_3$). **IR** (neat): v = 3065 (w), 3041 (w), 3019 (w), 2930 (s), 2853 (m), 2718 (w), 1723 (s), 1604 (w), 1452 (m), 1399 (s), 1334 (m), 1276 (m), 1255 (m), 1206 (s), 1183 (m), 1140 (m), 1062 (w), 1015 (w), 990 (w), 893 (w), 758 (m) cm^{-1}. **HRMS (nanochip-ESI/LTQ-Orbitrap)**: Calculated (MNa+) 402.2516; Found 402.2520.

2-(3-(3,3-Diisopropyltriaz-1-en-1-yl)-2-mesityl-1*H*-inden-1-yl)acetaldehyde (2c)

Orange oil (45.2 mg, 0.112 mmol, 59%, 6:1 rr). **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 9.68 (t, J = 1.6 Hz, 1H, CHO), 7.92 (d, J = 7.4 Hz, 1H, CH$_{Indenyl}$), 7.39 (d, J = 7.4 Hz, 1H, CH$_{Indenyl}$), 7.34 (td, J = 7.5, 1.2 Hz, 1H, CH$_{Indenyl}$), 7.22 (td, J = 7.5, 1.2 Hz, 1H, CH$_{Indenyl}$), 6.87 (s, 1H, CH$_{Mes}$), 6.86 (s, 1H, CH$_{Mes}$), 4.99 (s, 1H, CH$_{iPr}$), 4.36 (dd, J = 8.4, 5.3 Hz, 1H, CHCH$_2$CHO), 3.89 (s, 1H, CH$_{iPr}$), 2.68 (ddd, J = 17.5, 5.3, 1.5 Hz, 1H, CH$_2$CHO), 2.56 (ddd, J = 17.5, 8.4, 1.8 Hz, 1H, CH$_2$CHO), 2.28 (s, 3H, p-CH$_3$ $_{Mes}$), 2.19 (s, 3H o-CH$_3$ $_{Mes}$), 2.07 (s, 4H o-CH$_3$ $_{Mes}$), 1.34–0.95 (m, 12H, CH$_3$ $_{iPr}$). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 202.0 (CHO), 146.6 (C$_{sp2}$), 146.5 (C$_{sp2}$), 141.5 (C$_{sp2}$), 137.2 (o-C$_{q\ Mes}$), 137.1 (o-C$_{q\ Mes}$), 136.3 (p-C$_{q\ Mes}$), 132.9 (C$_{sp2}$), 132.8 (C$_{sp2}$), 128.3 (CH$_{Mes}$), 128.0 (CH$_{Mes}$), 127.0 (CH$_{Indenyl}$), 125.2 (CH$_{Indenyl}$), 123.4 (CH$_{Indenyl}$), 122.1 (CH$_{Indenyl}$), 45.2 (CH$_2$CHO), 44.5 (CHCH$_2$CHO), 21.2 (p-CH$_3$ $_{Mes}$), 21.0 (o-CH$_3$ $_{Mes}$), 20.9 (o-CH$_3$ $_{Mes}$). **IR** (neat): v = 2971 (m), 2924 (w), 2871 (w), 2821 (w), 2724 (w), 2065 (w), 1721 (s), 1610 (w), 1459 (m), 1400 (s), 1365 (m), 1347 (m), 1240 (s), 1219 (s), 1153 (s), 1125 (m), 1022 (m), 850 (m), 744 (m) cm^{-1}. **HRMS (ESI/QTOF)**: Calculated (MH+) 404.2696; Found 404.2689.

1-(3-(3,3-Diisopropyltriaz-1-en-1-yl)-2-phenyl-1*H*-inden-1-yl)propan-2-one (2d)

Orange solid (74.0 mg, 0.197 mmol, 81%, 1:1 rr). The ratio of regioisomers was determined from the NMR spectrum of the crude product before purification (see Supporting Information). A small amount of **2d** could be separated from the other isomer, allowing a simplified characterization. This amount was very small, which is why it was combined with the remaining mixture of regioisomers after completion of the characterization. **^{1}H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 7.70 (dd, J = 8.3, 1.3 Hz, 2H, o-CH$_{Ph}$), 7.47 (d, J = 7.6 Hz, 1H, CH$_{Indenyl}$), 7.46–7.40 (m, 2H, m-CH$_{Ph}$), 7.35 (dd, J = 7.3, 1.1 Hz, 1H, CH$_{Indenyl}$), 7.31 (tt, J = 7.5, 1.2 Hz, 1H, p-CH$_{Ph}$), 7.28–7.19 (m, 1H, CH$_{Indenyl}$), 7.12 (td, J = 7.4, 1.2 Hz, 1H, CH$_{Indenyl}$), 5.22–5.01 (m, 1H, CH$_{iPr}$), 4.50 (dd, J = 9.8, 2.6 Hz, 1H, CHCH$_2$COCH$_3$), 4.08–3.89 (m, 1H, CH$_{iPr}$), 3.23 (dd, J = 17.5, 2.6 Hz, 1H, CH$_2$COCH$_3$), 2.52 (dd, J = 17.4, 9.8 Hz, 1H, CH$_2$COCH$_3$), 2.15 (s, 3H, CH$_2$COCH$_3$), 1.25 (dd, J = 54.3, 7.2 Hz, 12H, CH$_3$ $_{iPr}$). **^{13}C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 207.9 (COCH$_3$), 154.9 (C$_{sp2}$-Ph, 145.3 (C$_{q\ Indenyl}$), 144.1 (C$_{q\ Indenyl}$), 134.8 (C$_{q\ Ph}$), 130.0 (o-CH$_{Ph}$), 129.9 (C$_{sp2}$-N$_3$iPr$_2$), 127.9 (m-CH$_{Ph}$), 126.9 (p-CH$_{Ph}$ or CH$_{Indenyl}$), 126.8 (p-CH$_{Ph}$ or CH$_{Indenyl}$), 124.8 (CH$_{Indenyl}$), 123.7 (CH$_{Indenyl}$), 119.9 (CH$_{Indenyl}$), 49.1 (br, CH$_{iPr}$), 46.8 (CH$_2$COCH$_3$), 46.5 (br, CH$_{iPr}$), 41.3 (CHCH$_2$COCH$_3$), 30.5 (COCH$_3$), 24.0 (br, CH$_3$ $_{iPr}$), 23.6 (br, CH$_3$ $_{iPr}$), 19.7 (br, CH$_3$ $_{iPr}$), 19.6 (br, CH$_3$ $_{iPr}$). **IR** (neat): v = 3061 (w), 3025 (w), 2972 (w), 2931 (w), 2870 (w), 2064 (w), 1714 (m), 1597 (w), 1493 (w), 1456 (m), 1398 (s), 1351 (s), 1242 (s), 1152 (s), 1024 (m), 761 (m), 745 (s) cm^{-1}. **HRMS (ESI/QTOF)**: Calculated (MH+) 376.2383; Found 376.2381.

1-(2-(*tert*-Butyl)-3-(3,3-diisopropyltriaz-1-en-1-yl)-1*H*-inden-1-yl)propan-2-one (2e)

Yellow solid (88.5 mg, 0.249 mmol, 81%, 2:1 rr). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.96 (d, J = 7.6 Hz, 1H, CH$_{ar}$), 7.27–7.16* (m, 3H, CH$_{ar}$), 7.08 (td, J = 7.5, 1.3 Hz, 1H, CH$_{ar}$), 5.13 (s, 1H, CH$_{iPr}$), 4.23 (dd, J = 9.6, 2.3 Hz, 1H, CHCH₂CMeO), 3.95 (s, 1H, CH$_{iPr}$), 3.26 (d, J = 17.7, 2.4 Hz, 1H, CH₂COCH₃), 2.41 (dd, J = 17.6, 9.6 Hz, 1H, CH₂COCH₃), 2.12 (s, 3H, COCH₃), 1.42 (s, 9H, CH₃ $_{tBu}$), 1.46–1.15* (br s, 27H, CH₃ $_{iPr}$). Signals marked with an * correspond to overlapping signals from atoms of both isomers. **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 208.0 (COCH₃), 147.5 (C$_{q\ ar}$), 145.9 (C$_{sp2}$-tBu), 145.0 (C$_{sp2}$-N₃iPr₂ or C$_{q\ ar}$), 140.5 (C$_{sp2}$-N₃iPr₂ or C$_{q\ ar}$), 126.5 (CH$_{ar}$), 124.7 (CH$_{ar}$), 123.1 (CH$_{ar}$), 122.5 (CH$_{ar}$), 47.6 (CH₂COCH₃), 44.2 (CHCH₂COCH₃), 34.3 (C$_{q\ tBu}$), 31.1 (CH₃ $_{tBu}$), 31.0 (COCH₃), 24.2 (br, CH₃ $_{iPr}$), 19.7 (br, CH₃ $_{iPr}$). **IR** (neat): ν = 2972 (m), 2870 (w), 1717 (m), 1599 (w), 1459 (m), 1418 (m), 1397 (s), 1363 (m), 1316 (m), 1297 (w), 1237 (s), 1223 (s), 1150 (s), 1124 (m), 1097 (m), 1024 (m), 962 (w), 930 (w), 896 (w), 873 (w), 811 (w), 771 (m), 745 (s) cm⁻¹. **HRMS (APPI/LTQ-Orbitrap)** Calculated (MH+) 356.2696; Found 356.2705.

1-(2-(3,3-Dicyclohexyltriaz-1-en-1-yl)-3-methyl-1H-inden-1-yl)propan-2-one (2f)

Yellow solid (53.9 mg, 0.137 mmol, 66%). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.25 (m, J = 12.2, 6.0 Hz, 3H, CH$_{ar}$), 7.07 (dq, J = 8.3, 4.1 Hz, 1H, CH$_{ar}$), 5.35–4.68 (m, 1H, CH$_{Cy}$), 4.27 (d, J = 9.8 Hz, 1H, CHCH₂COCH₃), 3.71–3.31 (m, 1H, CH$_{Cy}$), 3.20 (d, J = 17.3, 2.7 Hz, 1H, CH₂C(CH3)O), 2.36 (dd, J = 17.3, 9.9 Hz, 1H, CH₂C(CH3)O), 2.23 (s, 3H, C$_{sp2}$-CH₃), 2.12 (s, 3H, C(CH₃)O), 2.01–0.98 (m, 20H, CH₂ $_{Cy}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 208.1 (COCH₃), 153.9 (C$_{sp2}$-N₃Cy₂), 145.8 (C$_{q\ ar}$), 145.2 (C$_{q\ ar}$), 127.0 (C$_{sp2}$-Me), 126.8 (CH$_{ar}$), 124.4 (CH$_{ar}$), 123.2 (CH$_{ar}$), 118.4 (CH$_{ar}$), 57.6 (CH$_{Cy}$), 54.3 (CH$_{Cy}$), 46.3 (CH₂COCH₃), 41.2 (CHCH₂COCH₃), 34.7 (br, CH₂ $_{Cy}$), 34.4 (br, CH₂ $_{Cy}$), 30.4 (COCH₃), 30.1 (br, CH₂ $_{Cy}$), 26.2 (br, CH₂ $_{Cy}$), 9.6 (C$_{sp2}$-CH₃). **IR** (neat): ν = 2928 (m), 2852 (m), 1718 (m), 1601 (w), 1446 (w), 1398 (s), 1332 (s), 1257 (m), 1202 (s), 1183 (s), 1138 (s), 1100 (m), 1059 (m), 1015 (m), 988 (m), 892 (m), 761 (s), 742 (m), 723 (w) cm⁻¹. **HRMS (APPI/LTQ-Orbitrap)** Calculated (MH+) 394.2853; Found 394.2865.

Methyl 2-(3-(tert-butyl)-2-(3,3-diisopropyltriaz-1-en-1-yl)-1H-inden-1-yl)acetate (2g)

Orange oil (47 mg, 0.13 mmol, 68%, 6:1 rr). The signals of the triazene group are broadened. **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.89 (d, J = 7.7 Hz, 1H, CH$_{ar}$), 7.20 (d, J = 7.2 Hz, 1H, CH$_{ar}$), 7.14 (t, J = 7.5 Hz, 1H, CH$_{ar}$), 7.08–6.98 (m, 1H, CH$_{ar}$), 5.36–4.86 (m, 1H, CH$_{iPr}$), 4.11–3.79 (m, 2H, CH$_{iPr}$ +CH₂CO₂Me), 3.67 (s, 3H, CO₂Me), 3.17 (d, J = 16.1 Hz, 1H, CH₂CO₂Me), 2.07 (dd, J = 16.1, 10.2 Hz, 1H, CH), 1.37 (s, 9H, CH₃ $_{tBu}$), 1.32–1.18 (m, 12H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃, 265K): δ (ppm) = 172.2 (CO₂Me), 145.6 (C$_q$), 144.1 (C$_q$), 143.9 (C$_q$), 139.4 (C$_q$), 125.5 (CH$_{ar}$), 123.5 (CH$_{ar}$), 122.0 (CH$_{ar}$), 121.1 (CH$_{ar}$), 50.6 (OCH₃), 46.6 (br, CH$_{iPr}$), 44.5 (br, CH$_{iPr}$), 44.3 (CH₂C=O), 37.3 (C$_{tBu}$), 33.1 (CHCH₂C=O), 29.9 (CH₃), 22.5 (br, CH₃), 18.5 (br, CH₃). **IR** (neat): ν = 2976 (m), 2914 (m), 1744 (m), 1632 (w), 1464 (m), 1419 (m), 1397 (m), 1363 (m), 1346 (m), 1234 (s), 1156 (s), 1022 (m), 926 (w), 887 (w), 770 (m), 747 (m) cm⁻¹. **HRMS (ESI–TOF)**: Calculated (MH+) 371.2654; Found 371.2651.

Methyl 2-(3-(3,3-dicyclohexyltriaz-1-en-1-yl)-2-methyl-1H-inden-1-yl)acetate (2h)

Orange oil (88 mg, 0.22 mmol, 55%, >20:1). An impurity, which could not be separated, likely the minor isomer, is detected in the ¹H NMR spectrum. The signals of the triazene group are broadened. **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.34–7.28 (m, 1H, CH$_{ar}$), 7.26–7.23 (m, 2H, CH$_{ar}$), 7.16–6.96 (m, 2H, CH$_{ar}$), 5.09–4.85 (m, 1H, CH$_{Cy}$), 4.17 (d, J = 10.2 Hz, 1H,), 3.74 (s, 3H, CO₂Me), 3.54–3.38 (m, 1H, CH$_{Cy}$), 3.19 (dd, J = 15.9, 2.9 Hz, 1H, CHCH₂COOMe), 2.23

(s, 3H, CH₃), 2.10 (dd, J = 15.9, 10.6 Hz, 1H, CHCH₂CO₂Me), 1.87–1.66 (m, 13H, CH₂ $_{Cy}$), 1.46–1.29 (m, 7H, CH₂ $_{Cy}$). **¹³C NMR** (101 MHz, CDCl₃, 265K): δ (ppm) = 173.9 (CO₂Me), 153.6 (C$_q$), 145.9 (C$_q$), 144.7 (C$_q$), 127.0 (CH$_{ar}$), 126.9 (C$_q$), 124.5 (CH$_{ar}$), 123.0 (CH$_{ar}$), 118.5 (CH$_{ar}$), 51.7 (OCH₃), 42.2 (CH₂CO₂Me), 36.8 (CHCH₂CO₂Me), 34.3 (br, CH$_{Cy}$), 30.2 (br, CH$_{Cy}$), 26.3 (br, CH₂ $_{Cy}$), 9.6 (CH₃). **IR** (neat): ν = 2926 (s), 2853 (m), 1734 (m), 1399 (s), 1334 (s), 1254 (s), 1202 (s), 1137 (s), 989 (s), 759 (s) cm⁻¹ **HRMS (ESI–TOF)**: Calculated (MH+) 410.2808; Found 410.2806.

2-(tert-Butyl)-3-(3,3-diisopropyltriaz-1-en-1-yl)-1H-inden-1-imine (3)

[RhCl(cod)]₂ (18 mg, 0.036 mmol, 3 mol%), KOH (90 mg, 1.26 mmol, 2.0 eq.) and 1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (126 mg, 0.6 mmol, 1.0eq.) were dissolved in 1,4-dioxane/water (40:1) and stirred 5 min at RT. 2-Cyanophenylboronic acid (351 mg, 2.4 mmol, 4.0 eq.) was added, the reaction flask was sealed and heated at 100 °C for 48 h. The reaction mixture was diluted with water (4 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic phases were dried over MgSO₄ and the solvent was removed under vacuum. Purification by filtration over a plug of deactivated silica (NEt₃, eluent: DCM) gave the product as mixture of isomers in the form of an orange oil (141 mg, 0.45 mmol, 75%). **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 10.10 (s, 1H, C=NH), 7.75 (d, J = 7.3 Hz, 1H, CH$_{ar}$), 7.48–7.34 (m, 1H, CH$_{ar}$), 7.29–7.07 (m, 2H, CH), 5.34–5.22 (m, 1H, CH$_{iPr}$), 4.07–3.89 (m, 1H, CH$_{iPr}$), 1.50 (s, 9H, CH₃ $_{tBu}$), 1.39 (d, J = 6.1 Hz, 6H, CH₃ $_{iPr}$), 1.19 (d, J = 6.4 Hz, 6H, CH₃ $_{iPr}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 176.2 (C=NH), 154.3 (C$_q$), 139.7 (C$_q$), 130.1 (CH$_{ar}$), 126.6 (CH$_{ar}$), 123.7 (CH$_{ar}$), 118.7 (CH$_{ar}$), 48.9 (CH$_{iPr}$), 46.5 (CH$_{iPr}$), 34.8 (C$_{q\ tBu}$), 31.9 (CH₃ $_{tBu}$), 24.1 (CH₃ $_{iPr}$), 19.6 (CH₃ $_{iPr}$). Two of the quaternary carbons were not detected by ¹³C-NMR. **IR** (neat): ν = 2976 (m), 2897 (m), 1615 (w), 1593 (w), 1537 (w), 1458 (m), 1402 (s), 1363 (m), 1352 (s), 1302 (m), 1246 (s), 1150 (s), 1128 (m), 1083 (s), 1022 (s), 882 (m), 837 (m), 764 (m), 714 (s) cm⁻¹. **HRMS (ESI–TOF)**: Calculated (MH+) 313.2397; Found 313.2392.

2-(tert-Butyl)-1H-inden-1-one (4)

Compound **1a** (31mg, 0.1 mmol, 1.0 eq., mixture of isomers as indicated above) was dissolved in Et₂O (0.5 mL). Trifluoroacetic acid (22.6 µL, 34.2 mg, 0.3mmol, 3.0 eq.) was added and the mixture was stirred at RT for 4 h. The reaction mixture was quenched by NaHCO₃ (sat. aq., 1 mL) and extracted with EtOAc (3 x 1 mL). The combined organic phases were dried over MgSO₄ and the solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 0–100% Et₂O in pentane gave the product in the form of a yellow oil (10 mg, 0.054 mmol, 54%). The spectroscopic data are in good agreement with literature reports.[25] **¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.57–7.42 (m, 3H, CH$_{ar}$), 7.30 (t, J = 7.4 Hz, 1H, CH$_{ar}$), 7.13 (d, J = 7.1 Hz, 1H, CH$_{ar}$), 1.44 (s, 9H, CH₃ $_{tBu}$). **¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 198.1 (C=O) 148.9 (C$_q$), 144.0 (C$_q$), 140.9 (CH), 133.8 (CH), 131.6 (C$_q$), 128.1 (CH), 122.5 (CH), 121.3 (CH), 32.2 (C$_{q\ tBu}$), 29.14 (CH₃ $_{tBu}$). **IR** (neat): ν = 2987 (w), 2897 (w), 1705 (w), 1604 (w), 1397 (w), 1296 (w), 1240 (w), 1050 (w), 910 (s), 719 (s) cm⁻¹. **HRMS (APCI)**: Calculated (MH+) 187.1117; Found 187.1116.

2-(2-(tert-Butyl)-1H-inden-1-ylidene)acetaldehyde (5)

Compound **2a** (50.2 mg, 0.147 mmol, 1 eq.) was dissolved in acetonitrile (2 mL). Trifluoroacetic acid (27.3 µL, 368 µmol, 2.5 eq.) was added and the mixture was stirred at 60 °C for 18.5 h. The mixture was diluted with EtOAc (30 mL), washed with H₂O (2 x 10 mL), NaHCO₃ (sat. aq., 1 x 10 mL) and NaCl (sat. aq. 1 x 10 mL), dried over MgSO₄ and the solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 17–50% DCM in pentane gave the product in the form of an orange solid (14.0 mg, 66.1µmol, 45%). **¹H NMR** (400 MHz, CDCl₃,

298 K): δ (ppm) = 10.79 (d, J = 7.9 Hz, 1H, CHO), 7.68 (d, J = 7.5 Hz, 1H, CH-CHO), 7.25 (td, J = 7.5, 1.0 Hz, 1H, CH$_{ar}$), 7.14–7.06 (m, 2H, CH$_{ar}$), 6.74 (d, J = 7.8 Hz, 1H, CH$_{ar}$), 6.67 (s, 1H, HC=C-tBu), 1.35 (s, 9H, CH$_{3\,t Bu}$). ^{13}C NMR (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 191.2 (C=O), 154.3 (C$_{q\,ar}$), 152.4 (C$_{sp2}$-tBu), 143.2 (C$_{q\,ar}$), 135.2 (C=CH-CHO), 133.8 (HC=C-tBu), 130.6 (CH$_{ar}$), 128.9 (CH-CHO), 126.4 (CH$_{ar}$), 126.0 (CH$_{ar}$), 121.4 (CH$_{ar}$), 33.1 (C$_{q\,tBu}$), 31.3 (CH$_{3\,t Bu}$). **IR** (neat): ν = 3060 (w), 2967 (w), 2957 (w), 2910 (w), 2871 (w), 1712 (w), 1657 (s), 1597 (w), 1479 (w), 1464 (w), 1397 (w), 1368 (w), 1324 (w), 1242 (w), 1170 (w), 1152 (m), 1120 (s), 1083 (m), 1024 (w), 939 (w), 890 (w), 865 (m), 773 (m), 747 (s) cm^{-1}. **HRMS (APPI/LTQ-Orbitrap)** Calculated (M+) 212.1196; Found 212.1205.

1-(2-(tert-Butyl)-1H-inden-1-ylidene)propan-2-one (6)

Compound **2e** (49.5 mg, 0.139 mmol, 1 eq., mixture of isomers as indicated above) was dissolved in acetonitrile (2.4 mL). Trifluoroacetic acid (25.9 µL, 349 µmol, 2.5 eq.) was added and the mixture was heated at 60 °C for 48 h. The reaction was quenched with NaHCO$_3$ (sat. aq., 5 mL) and extracted with EtOAc (3 x 15 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 17–33% DCM in pentane gave the product as an orange oil (14.9 mg, 0.0657 mmol, 47 %). ^{1}**H NMR** (400 MHz, CDCl3, 298 K): δ (ppm) = 8.07–7.97 (m, 1H, CH$_{ar}$), 7.18 (td, J = 7.6, 7.2, 1.0 Hz, 1H, CH$_{ar}$), 7.10–7.02 (m, 2H, CH$_{ar}$), 6.91 (s, 1H, CH(CH$_3$)O), 6.63 (s, 1H, HC=C-tBu), 2.47 (s, 3H, CH$_3$), 1.37 (s, 9H, CH$_{3\,t Bu}$). ^{13}**C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 200.8 (C=O), 151.5 (C$_{sp2}$-tBu), 146.0 (C=CH-COCH$_3$), 143.0 (C$_{q\,ar}$), 134.6 (C$_{q\,ar}$), 132.2 (HC=C-tBu), 130.0 (CH$_{ar}$), 128.0 (CH-COCH$_3$), 126.3 (CH$_{ar}$), 125.5 (CH$_{ar}$), 120.5 (CH$_{ar}$), 33.1 (C$_{q\,tBu}$), 32.2 (COCH$_3$), 31.7 (CH$_{3\,t Bu}$). **IR** (neat): ν = 3068 (w), 2965 (m), 2936 (w), 2909 (w), 2869 (w), 1689 (s), 1610 (m), 1595 (m), 1583 (m), 1457 (s), 1366 (s), 1354 (s), 1289 (w), 1289 (w), 1241 (w), 1195 (s), 1178 (s), 975 (m), 859 (m), 774 (m), 749 (s) cm^{-1}. **HRMS (APPI/LTQ-Orbitrap)**: Calculated (MH+) 171.0804; Found 171.0806.

Methyl 2-(2-(*tert*-butyl)-1-methoxy-1*H*-inden-3-yl)acetate (7)

Compound **2g** (37 mg, 0.1 mmol, 1.0 eq., mixture of isomers as indicated above) was dissolved in methanol (2 mL). HBF$_4$ in Et$_2$O (40 µL, 7.5 M, 0.3 mmol, 3.0 eq.) was added and the reaction mixture was stirred at 40 °C for 2 days. The reaction mixture was quenched with K$_2$CO$_3$ (69 mg, 0.5 mmol, 5.0 eq.), filtered and the solvent was removed under vacuum. Purification by flash column chromatography on silica with 50% Et$_2$O in pentane gave the product in the form of a yellow oil (23 mg, 7.8 mmol, 60%). ^{1}**H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 7.33 (d, J = 7.2 Hz, 1H, CH$_{ar}$), 7.24–7.15 (m, 1H, CH$_{ar}$), 7.12–6.99 (m, 2H, CH$_{ar}$), 5.16–5.01 (m, 1H, CH), 3.68–3.64 (m, 2H, CH$_2$), 3.61 (s, 3H, COOMe), 2.97 (s, 3H, OMe), 1.30 (s, 9H, CH$_3$). ^{13}**C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 171.3 (CO$_2$Me), 151.6 (C$_q$), 145.2 (C$_q$), 140.8 (C$_q$), 132.0 (C$_q$), 128.5 (CH$_{ar}$), 125.5 (CH$_{ar}$), 123.4 (CH$_{ar}$), 118.5 (CH$_{ar}$), 84.1 (CHOMe), 52.3 (OCH$_3$), 51.2 (OCH$_3$), 34.0 (CH$_2$), 32.9 (C$_{q\,tBu}$), 30.8 (CH$_{3\,t Bu}$). **IR** (neat): ν = 2970 (m), 2903 (w), 1727 (w), 1470 (w), 1391 (w), 1369 (w), 1246 (w), 1195 (m), 1167 (m), 1066 (m), 910 (s), 725 (s) cm^{-1}. **HRMS (ESI–TOF)**: Calculated (MNa+) 298.1468; Found 298.1467.

Methyl 2-(1-acetamido-2-(*tert*-butyl)-1*H*-inden-3-yl)acetate (8)

Compound **2g** (48 mg, 0.13 mmol, 1.0 eq., mixture of isomers as indicated above) was dissolved in wet acetonitrile (2 mL). HBF$_4$ in Et$_2$O (40 µL, 7.5 M, 0.3 mmol, 3.0 eq.) was added and the reaction mixture was stirred at 40 °C for 2 days. The reaction mixture was quenched with K$_2$CO$_3$ (69 mg, 0.5 mmol, 3.8 eq.), filtered and the solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 60–100% EtOAc in pentane gave

the product in the form of a white solid (23 mg, 7.8 mmol, 60 %). Crystals suitable for X-ray diffraction were grown by layering a saturated solution of **8** in CH$_2$Cl$_2$ with pentane. ^{1}**H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 7.30–7.25 (m, 1H, CH$_{ar}$), 7.22–7.15 (m, 1H, CH$_{ar}$), 7.10–7.04 (m, 2H, CH$_{ar}$), 5.89 (d, J = 9.9 Hz, 1H, CHNH), 5.43 (d, J = 9.6 Hz, 1H, CHNH), 3.83–3.66 (m, 5H, CH$_2$+CO$_2$CH$_3$), 2.04 (s, 3H, CH$_3$C=O), 1.33 (s, 9H, CH$_3$). ^{13}**C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 170.2 (CO$_2$Me), 168.8 (NHC=O), 150.8 (C$_q$), 143.4 (C$_q$), 142.6 (C$_q$), 130.8 (C$_q$), 127.0 (CH$_{ar}$), 124.8 (CH$_{ar}$), 121.8 (CH$_{ar}$), 117.4 (CH$_{ar}$), 56.8 (CHNH), 51.1 (CH$_2$), 33.0 (CHNH), 31.7 (C$_{q\,tBu}$), 30.0 (CH$_{3\,tBu}$), 22.6 (OCH$_3$). **IR** (neat): ν = 3239 (w), 3049 (w), 2959 (m), 2914 (w), 1733 (w), 1643 (s), 1542 (s), 1470 (m), 1430 (s), 1369 (s), 1318 (m), 1302 (m), 1268 (m), 1212 (m), 1201 (s), 1162 (s), 999 (m), 971 (m), 792 (w), 758 (s) cm^{-1}. **HRMS (ESI–TOF)**: Calculated (MNa+) 324.1586; Found 324.1576.

2-(tert-Butyl)-1*H*-indene-1,3(2*H*)-dione (9)

Compound **3** (20 mg, 64 µmol, 1.0 eq., mixture of isomers as indicated above) was dissolved in 5:1 THF/water (1.2 mL). HCl (0.054 mL, 7 M aq., 0.384 mmol, 6.0 eq.) was added. The solution turned purple (Color characteristic of the protonated form of **3**). The reaction mixture was stirred at 60 °C overnight. The color faded and the reaction mixture was quenched with NaHCO$_3$ (sat. aq., 2 mL) and extracted with EtOAc (3 x 2 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was removed under vacuum Purification by flash column chromatography on silica with a gradient of 0–10% Et$_2$O in pentane gave the product in the form of a colorless oil (7 mg, 0.032 mmol, 54%). The spectroscopic data are in agreement with literature reports.[26] ^{1}**H NMR** (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 7.94 (dd, J = 5.6, 3.1 Hz, 2H, CH$_{ar}$), 7.81 (dd, J = 5.7, 3.1 Hz, 2H, CH$_{ar}$), 2.65 (s, 1H, CH-tBu), 1.12 (s, 9H, CH$_{3\,t Bu}$). ^{13}**C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 201.0 (C=O), 143.3 (C$_{q\,ar}$), 135.6 (CH$_{ar}$), 122.9 (CH$_{ar}$), 62.2 (CH-tBu), 36.3 (C$_{q\,tBu}$), 28.5 (CH$_{3\,t Bu}$). **IR** (neat): ν = 2973 (m), 2930 (m), 2902 (m), 1740 (w), 1708 (w), 1681 (m), 1463 (m), 1404 (m), 1369 (m), 1311 (s), 1250 (s), 1186 (m), 1153 (m), 1125 (m), 1087 (s), 1026 (s), 894 (m), 857 (w), 768 (m), 754 (m), 726 (s) cm^{-1}. **HRMS (APPI/LTQ-Orbitrap)**: Calculated (MH+) 203.1067; Found 203.1071.

1-(2-(3,3-Dimethylbut-1-yn-1-yl)phenyl)ethan-1-one (10) and 2-(tert-Butyl)-3-methyl-1*H*-inden-1-one (11)

A Falcon tube was charged with compound **1f** (30.9 mg, 93.8 µmol, 1 eq.). A mixture of *n*-pentane (1.8 mL) and tetrahydrofuran (200 µL) was added and the mixture was homogenized by sonication. Hydrogen fluoride pyridine (70 % HF, 60.9 µL, 2.34 mmol, 25 eq.) was added and the mixture was heated to 30 °C for 1 h. The reaction was quenched with calcium gluconate (1.01 g, 2.34 mmol, 25 eq.). The resulting slurry was filtered and rinsed with EtOAc (40 mL). The solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 3–4% Et$_2$O in pentane gave **10** (7.9 mg, 0.039 mmol, 42%) in the form of a faint purple liquid and **11** (4.6 mg, 0.023 mmol, 24%) in the form of a yellow solid. The spectroscopic data are in agreement with literature reports.[27] **10**: ^{1}**H NMR** (400 MHz, CDCl3, 298 K): δ (ppm) = 7.66 (dd, J = 7.8, 1.5 Hz, 1H, CH$_{ar}$), 7.47 (dd, J = 7.7, 1.4 Hz, 1H, CH$_{ar}$), 7.39 (td, J = 7.5, 1.5 Hz, 1H, CH$_{ar}$), 7.32 (td, J = 7.6, 1.4 Hz, 1H, CH$_{ar}$), 2.74 (s, 3H, CH$_3$), 1.33 (s, 9H, CH$_{3\,t Bu}$). ^{13}**C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 201.5 (C=O), 141.2 (C$_{q\,ar}$-C$_{sp}$), 134.0 (CH$_{ar}$), 131.2 (CH$_{ar}$), 128.4 (CH$_{ar}$), 127.7 (CH$_{ar}$), 122.6 (C$_{q\,ar}$-C=O), 104.8 (C$_{sp}$-C$_{q\,ar}$), 78.6 (C$_{sp}$-tBu), 30.8 (CH$_{3\,t Bu}$), 30.4 (CH$_3$), 28.4 (C$_{q\,t Bu}$). **IR** (neat): ν = 2968 (m), 2927 (w), 2869 (w), 2235 (w), 1684 (s), 1594 (w), 1473 (m), 1441 (w), 1357 (m), 1278 (m), 1234 (m), 1201 (w), 1010 (w), 963 (m), 801 (m), 760 (s) cm^{-1}. **HRMS (ESI/QTOF)** Calculated (MH+) 201.1274; Found 201.1276. **11**: ^{1}**H NMR** (400 MHz, CDCl3, 298 K): δ (ppm) = 7.36 – 7.29 (m, 2H, CH$_{ar}$), 7.16 (td, J = 7.2, 0.9 Hz, 1H, CH$_{ar}$), 7.05 (d, J = 7.5 Hz, 1H, CH$_{ar}$), 2.29 (s, 3H, CH$_3$) 1.36 (s, 9H, CH$_{3\,t Bu}$). ^{13}**C NMR** (101 MHz, CDCl$_3$, 298 K): δ (ppm) = 198.7 (C=O), 151.2 (C$_{sp2}$-Me), 147.0 (C$_{q\,ar}$), 140.3 (C$_{sp2}$-tBu), 133.3

(CH$_{ar}$), 130.7 (C$_{q\,ar}$), 128.2 (CH$_{ar}$), 121.3 (CH$_{ar}$), 118.5 (CH$_{ar}$), 34.0 (C$_{q\,tBu}$), 30.6 (CH$_{3\,tBu}$), 13.3 (CH$_3$). **IR** (neat): $v = 2955$ (m), 2918 (w), 2868 (w), 1701 (s), 1605 (m), 1457 (m), 1312 (m), 1184 (w), 1126 (w), 1083 (w), 997 (w), 881 (w), 755 (s), 718 (m) cm^{-1}. **HRMS (ESI/QTOF)** Calculated (MH+) 201.1274; Found 201.1276.

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Synthesis of Indenyl Triazenes by Rhodium-Catalyzed Annulation Reactions

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X = NH, OH, CH$_2$CHO, CH$_2$COMe, CH$_2$CO$_2$Me