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Lewis-Acid-Promoted Arylation Reaction: Synthesis of Dihydrobenzofuran Derivatives from Aryltriazenes

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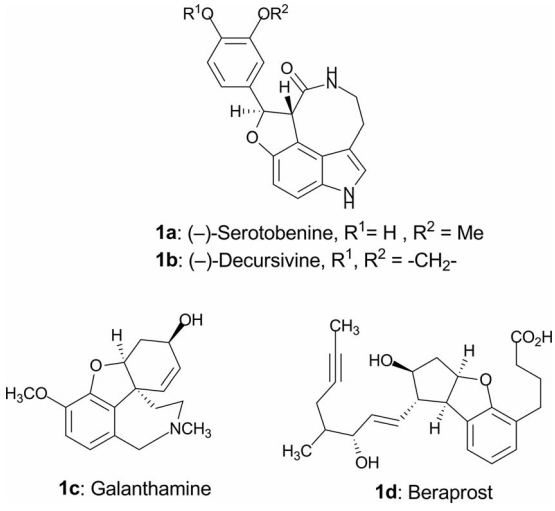
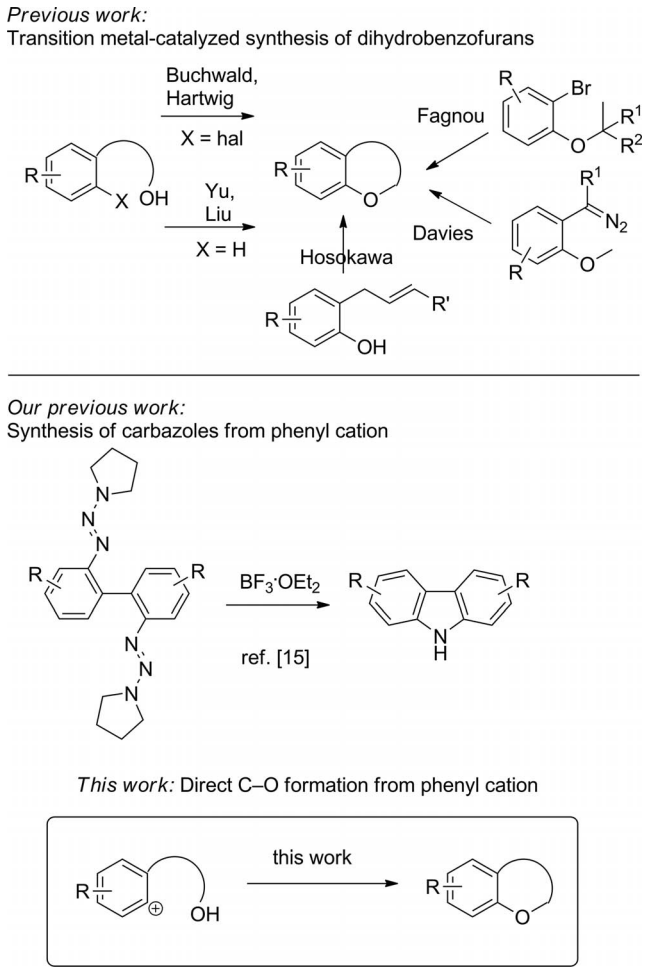
A Lewis-acid-promoted approach to the synthesis of highly functionalized dihydrobenzofuran derivatives was developed. A diverse range of functional groups are tolerated in this type of reaction. The reaction mechanism investigation indicates that the highly reactive phenyl cation intermediate is probably involved in this process. The chirality of substrate is retained under the reaction conditions.

Introduction

Dihydrobenzofuran rings are common structural motifs in many natural and pharmaceutical products, such as (–)-serotobenine (**1a**, Scheme 1), (–)decursivine (**1b**),[1] galanthamine (**1c**),[2,8] and beraprost (**1d**),[3] most of which show strong biological activity. Hence, effective methods for the synthesis of dihydrobenzofurans have been developed over the past decades (Scheme 2).[4] The transition-metal-catalyzed synthesis of dihydrobenzofurans has proved to be a robust method. The formation of C–O bonds[5] using Pd as catalyst was developed by Buchwald and Hartwig.[6] The intramolecular Heck reaction,[7] which was used in the total synthesis of galanthamine (**1b**),[8] is another good method



Scheme 1. Natural and pharmaceutical products containing a dihydrobenzofuran moiety.



Scheme 2. Strategies for the synthesis of dihydrobenzofurans and related compounds.

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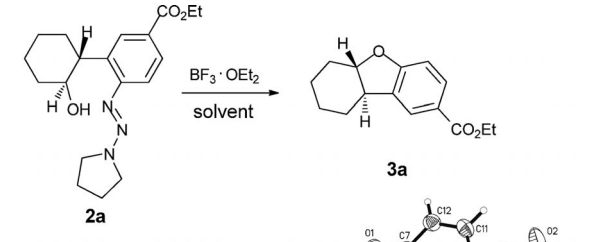
to synthesize dihydrobenzofuran cores. Intramolecular oxidative cyclization of *ortho*allyl phenol,[9] intramolecular alkane arylation,[10] hydroxy-directed C–H activation/C–O cyclization,[11] and carbenoid C–H insertion[12] also provide efficient methods to synthesize dihydrobenzofurans (Scheme 2).

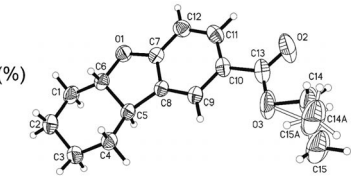
It is very important to find efficient ways to construct heterocyclic compounds.[13] The direct nucleophilic substitution of a phenyl cation is an efficient and straightforward method for arylation, but the instability of phenyl cation[14] limits its applicability. Recently, we have focused our interest on the generation of reactive phenyl cations and their application in the synthesis of heterocyclic compounds such as unsymmetrical and highly functionalized carbazoles and dibenzofurans.[15] In this paper, we describe a Lewis-acid-promoted protocol for the synthesis of dihydrobenzofurans from aryl triazenes.[16]

Results and Discussion

Initially, we treated triazene alcohol **2a** with $BF_3{\cdot}OEt_2$ in different solvents (Scheme 3), and we found that the cyclization reaction occurred in both polar and non-polar solvents. When the reaction was carried out in dichloromethane, the desired cyclization product (i.e., **3a**) was formed in the highest yield of 76%. The structure of **3a** was confirmed by X-ray analysis (Scheme 3).[17]



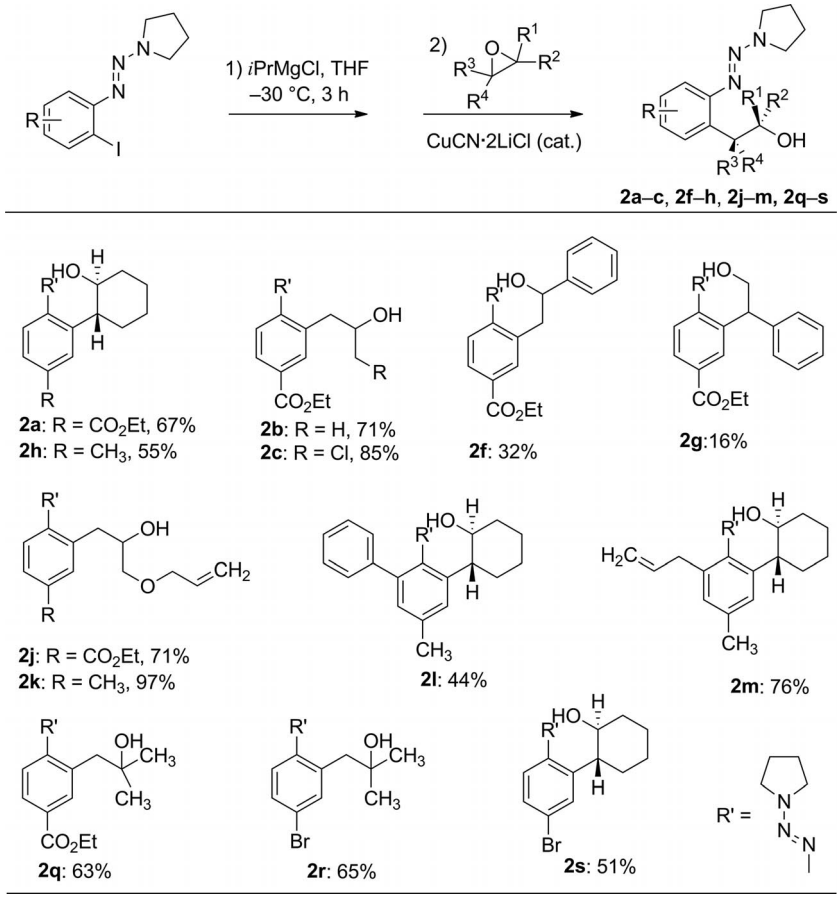
Entry	Solvent	Yield (%)
1	dichloromethane	76
2	tetrahydrofuran	25
3	dimethylformamide	54
4	ethanol	72
5	acetonitrile	44



crystal structure of **3a**

Scheme 3. Screening of different solvents for the cyclization reaction of **2a**, and X-ray crystal structure of **3a**.

Triazene alcohol derivatives were prepared from the corresponding iodoaryltriazenes. The iodoaryltriazenes were transformed into the corresponding Grignard reagents



Scheme 4. Synthesis of triazene alcohols from iodoaryltriazenes by metal–halogen exchange. Isolated yields after flash chromatography are shown.

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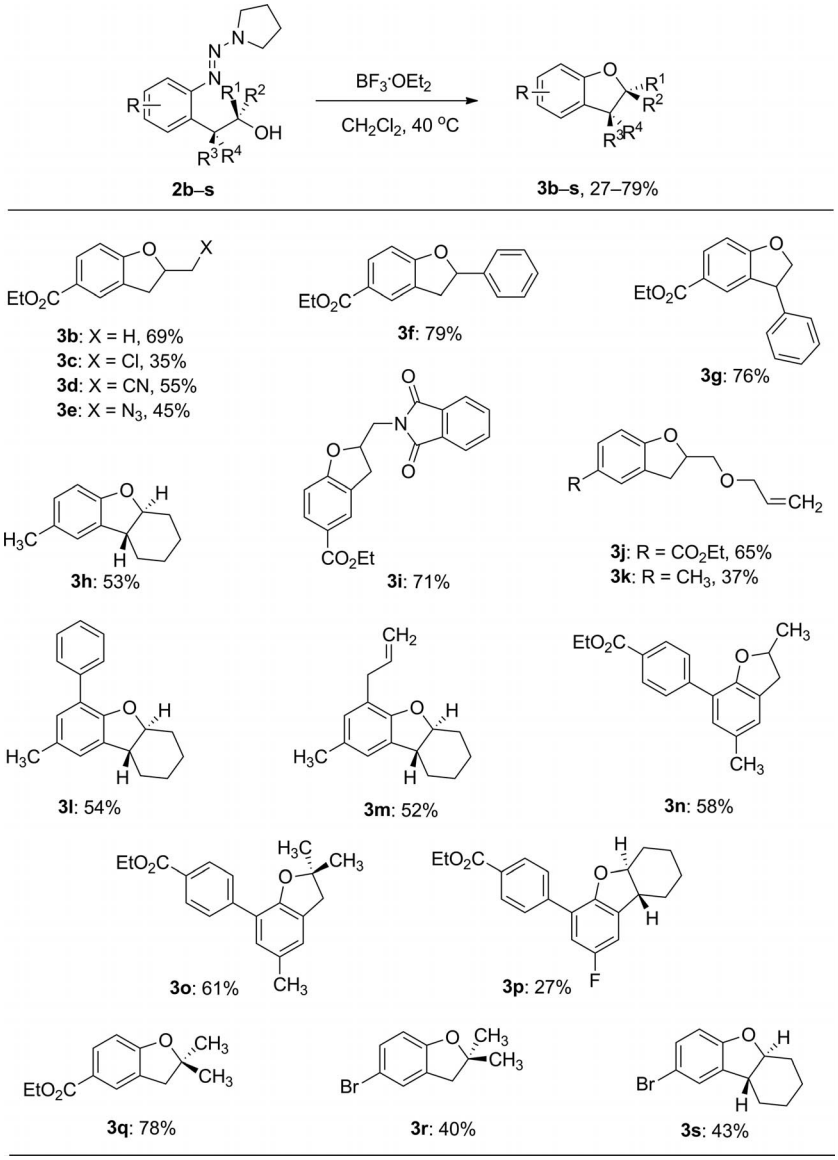
smoothly by metal–halogen exchange with *i*PrMgCl.[18] The reaction of these Grignard reagents with epoxides[19] provided the triazene alcohol derivatives in moderate to good yields, and a variety of examples are shown in Scheme 4.

The generality of the BF_3·OEt_2-promoted cyclization is shown in Scheme 5. A variety of secondary alcohols were cyclized to form the corresponding dihydrobenzofurans in moderate to good yields (**3b**–**f**, **3h**–**n**, and **3s**). Functional groups such as alkenyl (**3j**, **3k**, and **3m**), ester (**3b**–**g**, **3i**, **3j**, **3n**–**q**, and **3t**–**v**), cyano (**3d**), and azido (**3e**), were tolerated in this BF_3·OEt_2-promoted process. The secondary alcohols bearing αsubstituents such as chloride, cyano, *N*-phthalimido, and even azido, afforded the corresponding dihydrobenzofurans (i.e., **3c**–**e** and **3i**) in moderate to good yields. Steric hindrance near to the reaction center (as in the formation of **3l**–**o**) did not decrease the yields of the corresponding dihydrobenzofurans. However, electron-withdrawing groups such as fluoro decreased the yield (to 27% for **3p**). Under these mild reaction conditions, the tertiary alcohols gave the desired dihydrobenzofurans successfully in 40–78% yields (**3o**, **3q**, and **3r**). Substrates **2r** and **2s** bearing bromide on the aromatic ring afforded bromodihydrobenzofurans **3r** and **3s** in 40 and 43% yields, respectively.

This method could be extended to the synthesis of compounds containing sixmembered rings. Primary alcohol **2t** and secondary alcohols **2u** and **2v** all provided the desired 6*H*dibenzo[*b*,*d*]pyran derivatives (i.e., **3t**–**v**) in 44–57% yields (Scheme 6).

We next turned our attention to the cyclization of optically active triazene alcohols to determine whether the optical purity was retained under these reaction conditions. As



Scheme 5. Synthesis of functionalized dihydrobenzofurans. All reactions were carried out with triazene alcohol (0.5 mmol), BF_3·OEt_2 (1.0 mmol) in CH_2Cl_2 (20 mL) at 40 °C for 4 h, except for the synthesis of **3r**, which was carried out for 24 h. Isolated yields after flash chromatography are shown.

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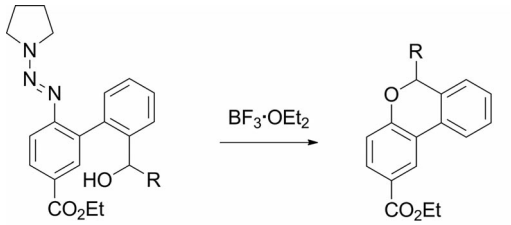
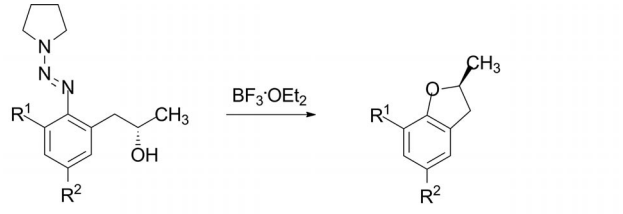


2t: R = H
2u: R = Et
2v: R = *i*Pr

3t: R = H, 48%
3u: R = Et, 57%
3v: R = *i*Pr, 44%

Scheme 6. Synthesis of compounds containing sixmembered rings from triazene alcohols.

shown in Scheme 7, the chirality of optically active triazene alcohols (*S*)**4a** and (*S*)**4b** was retained during the course of cyclization sequence.

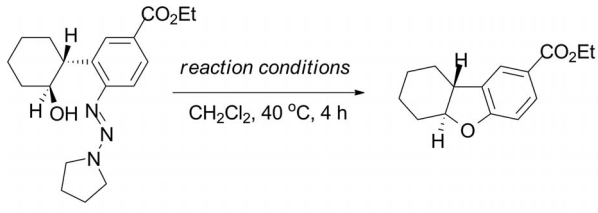


(s)-**4a**: R^1 = H, R^2 = CO_2Et
ee = 99 %
(s)-**4b**: R^1 = *p*-COOEtPh, R^2 = CH_3
ee = 99 %

(s)-**5a**: R^1 = H, R^2 = CO_2Et,
yield: 59 %, *ee* = 96 %
(s)-**5b**: R^1 = *p*-COOEtPh, R^2 = CH_3
yield: 62%, *ee* = 98 %

Scheme 7. Cyclization of optically active triazene alcohols.

In this reaction, the initial interaction between the terminal nitrogen atom of the triazene and the Lewis acid generates a complex, decomposes to form aryl cations and aryl radicals.[20] In order to probe the reaction mechanism, a radical-inhibition test was performed for the standard reaction conditions. When radical scavengers, such as butylated hydroxytoluene (BHT), 2,2,6,6-tetramethylpiperidinooxy (TEMPO), or 1,1-diphenylethylene, were added to reactions, the yields of the reactions were not affected (Scheme 8). These results suggest that the reaction does not go via aryl radical intermediates. The triazene may initially form a diazonium salt in the presence of the Lewis acid,



Reaction conditions and yields

1. with BF_3·OEt_2 (2.0 equiv.), 76 %
2. with BF_3·OEt_2 (2.0 equiv.) and BHT (1.0 equiv.), 69 %
3. with BF_3·OEt_2 (2.0 equiv.) and TEMPO (1.0 equiv.), 72 %
4. with BF_3·OEt_2 (2.0 equiv.) and 1,1-diphenylethylene (1.0 equiv.), 76 %

Scheme 8. Reaction results in the presence of radical inhibitors.

and then decompose to generate an aryl cation, which can cyclize onto the hydroxy group.

Conclusions

In summary, we have developed a Lewis-acid-promoted approach to the synthesis of highly functionalized dihydrobenzofurans in moderate to good yields. These reactions were carried out under mild reaction conditions with good tolerance of a variety of functional groups. Mechanistic investigations indicated that a highly reactive phenyl cation intermediate is probably involved in the reaction. Further investigations of the reaction mechanism and synthetic applications are underway.

Experimental Section

General Methods: THF was dried with sodium and distilled freshly before use. CH_2Cl_2 was dried with CaH_2 and distilled freshly before use. DMF was dried with CaH_2 and distilled under reduced pressure. Other materials and solvents were purchased from commercial suppliers and used without additional purification. NMR spectra were recorded on Bruker Avance spectrometers operating for ^1H NMR at 400 or 500 MHz, and for ^{13}C NMR at 100 or 125 MHz. Chemical shifts were calibrated using residual $CHCl_3$ (δ = 7.26 ppm) for ^1H NMR, and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR. Mass spectroscopy data of the products were collected with an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization. Infrared spectra were recorded with a Bruker ATR-FTIR spectrometer. Melting points were measured with a WRS-1A digital point apparatus.

Typical Procedure for the Synthesis of Aryltriazenes: Aniline (10 mmol, 1.0 equiv.) was dissolved in CH_3CN (10 mL) at room temperature, and then concentrated hydrochloric acid (4 mL, 50 mmol, 5.0 equiv.) was added. The resulting solution was stirred and cooled to –10 °C. After 15 min, a solution of $NaNO_2$ (10.5 mmol, 1.05 equiv.) in cold water (10 mL) was added dropwise. The resulting solution of the diazonium salt was stirred for 30 min and then added to a solution of pyrrolidine (11.0 mmol, 1.1 equiv.) and K_2CO_3 (25.0 mmol, 2.5 equiv.) in CH_3CN/H_2O (1:2, 30 mL), which was previously cooled to –10 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. After completion of the reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate (3 × 15 mL). The organic extracts were dried with Na_2SO_4, filtered, concentrated under reduced pressure, and purified by silica gel chromatography (eluent: hexanes/EtOAc, 50:1).

General Procedure for the Preparation of Triazene Alcohol Derivatives 2a–2c, 2f–2h, 2j, 2k and 2q–2s: In a dry and N_2-flushed 50 mL Schlenk tube, ethyl 3-iodo-4-(pyrrolidin-1-yldiazenyl)benzoate (1.49 g, 4.0 mmol, 1.0 equiv.) was dissolved in dry THF (4.0 mL). *i*PrMgCl (0.984 M in THF, 4.90 mL, 4.80 mmol, 1.2 equiv.) was then added dropwise at –30 °C. After 3 h, a complete conversion into the corresponding Grignard reagent was observed, as indicated by TLC and GC analysis. A CuCN·2LiCl solution (1.0 M in THF, 0.2 mL, 0.2 mmol, 0.05 equiv.) and 7-oxabicyclo[4.1.0]heptane (628 mg, 6.4 mmol, 1.6 equiv.) were added slowly to the resulting reaction mixture. Then the reaction mixture was slowly warmed to room temperature and stirred for 4 h before the addition of saturated aqueous NH_4Cl solution. The resulting reaction was

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quenched by saturated aqueous NH_4Cl solution (5 mL), extracted with ethyl acetate (3 × 10 mL). The organic layers were dried with Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash chromatography on silica gel (hexanes/EtOAc, 5:1) to afford **2a** (0.926 g, 67%) as a yellow solid.

Ethyl 3-(2-Hydroxycyclohexyl)-4-[(*E*)-pyrrolidin-1-yldiazenyl]benzoate (2a): Yellow solid, m.p. 101–103 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (s, 1 H, ArH), 7.86 (d, J = 8.0 Hz, 1 H, ArH), 7.42 (d, J = 8.0 Hz, 1 H, ArH), 4.36 (q, J = 6.8 Hz, 2 H, CH_3CH_2O), 3.98 (br., 2 H, CH_2N), 3.51–3.75 (m, 3 H, CH_2N and OH), 3.20–3.40 (m, 2 H, C*H*OH and ArC*H*), 2.18–2.20 (m, 1 H), 1.95–2.07 (m, 4 H, 2 CH_2CH_2N), 1.74–1.84 (m, 4 H, 2 CH_2), 1.30–1.44 (m, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 152.8, 137.2, 128.6, 128.4, 127.1, 116.5, 75.3, 60.7, 51.3, 47.0, 45.6, 36.4, 31.7, 26.3, 25.1, 23.9, 23.5, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3664, 2979, 2902, 1700, 1599, 1402, 1247, 1071 cm^{-1}. MS (EI): *m*/*z* (%) = 345 (3) $[M]^+$, 300 (13), 272 (12), 261 (65), 218 (32), 201 (17), 179 (100). HRMS (EI-TOF): calcd. for $C_{19}H_{27}N_3O_3$ $[M]^+$ 345.2052; found 345.2054.

Ethyl 3-(2-Hydroxypropyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (2b): Yield 871 mg, 71%, red solid, m.p. 76–77 °C. R_f = 0.15 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.88 (m, 2 H, ArH), 7.48 (d, J = 8.4 Hz, 1 H, ArH), 4.76 (s, 1 H, OH), 4.35 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 4.05–4.15 (m, 1 H, C*H*OH), 3.92–4.02 (m, 2 H, CH_2N), 3.56–3.72 (m, 2 H, CH_2N), 2.98–3.03 (m, 2 H, $ArCH_2$), 2.00–2.08 (m, 4 H, 2 CH_2CH_2N), 1.39 (t, J = 7.2 Hz, 3 H, CH_3CH_2), 1.22 (d, J = 6.0 Hz, 3 H, CH_3CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 152.5, 133.12, 133.07, 128.8, 126.8, 116.4, 69.4, 60.7, 51.6, 47.2, 41.9, 23.9, 23.6, 23.5, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2978, 2902, 1686, 1398, 1255, 1053 cm^{-1}. MS (EI): *m*/*z* (%) = 305 (6) $[M]^+$, 260 (20), 235 (9), 221 (38), 179 (100). HRMS (EI-TOF): calcd. for $C_{16}H_{23}N_3O_3$ $[M]^+$ 305.1739; found 305.1747.

Ethyl 3-(3-Chloro-2-hydroxypropyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (2c): Yield 2.904 g, 85%. yellow solid, m.p. 68–70 °C. R_f = 0.15 (hexanes/EtOAc, 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s, 1 H, ArH), 7.88 (dd, J = 8.0, J = 2.0 Hz, 1 H, ArH), 7.49 (d, J = 9.0 Hz, 1 H, ArH), 5.51 (d, J = 4.0 Hz, 1 H, CH*OH*), 4.35 (q, J = 7.0 Hz, 2 H, CH_3CH_2O), 4.08–4.15 (m, 1 H, C*H*OH), 3.99 (t, J = 6.5 Hz, 2 H, CH_2N), 3.60–3.70 (m, 2 H, CH_2N), 3.46–3.54 (m, 2 H, CH_2Cl), 3.11–3.22 (m, 2 H, CH_2CHOH), 2.00–2.14 (m, 4 H, 2 CH_2CH_2N), 1.39 (t, J = 7.3 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 152.5, 133.0, 131.4, 129.2, 127.0, 116.5, 72.9, 60.8, 51.8, 48.7, 47.3, 36.8, 23.8, 23.5, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3672, 2983, 2902, 1699, 1603, 1403, 1314, 1254, 1071, 899, 734 cm^{-1}. MS (EI): *m*/*z* (%) = 341 (2) [M, $Cl^{37}]^+$, 339 (5) [M, $Cl^{35}]^+$, 303 (7), 294 (8), 269 (8), 195 (25), 179 (100). HRMS (EI-TOF): calcd. for $C_{16}H_{22}ClN_3O_3$ $[M]^+$ 339.1350; found 339.1354.

Ethyl 3-(3-Cyano-2-hydroxypropyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (2d): NaCN (588 mg, 12 mmol, 2 equiv.) and KI (100 mg, 0.6 mmol, 0.1 equiv.) were added to a solution of triazene alcohol **2c** (2.04 g, 6 mmol, 1.0 equiv.) in DMF (50 mL). The reaction mixture was stirred vigorously at 105 °C for 2.5 h before it was allowed to cool to room temperature. Water was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The organic extracts were washed with H_2O and brine, dried with Na_2SO_4, and concentrated in vacuo. After flash chromatography (eluent: hexanes/EtOAc, 5:1), pure product **2d** (1.657 g, 84%) was obtained as a yellow solid, m.p. 111–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, J = 8.8, J = 1.6 Hz, 1 H, ArH), 7.87 (s, 1 H, ArH), 7.49 (d, J = 8.4 Hz, 1 H, ArH), 5.85 (d, J = 3.6 Hz, 1 H, CHO*H*), 4.35 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 4.18–4.27 (m, 1 H, C*H*OH), 3.99 (t, J = 6.6 Hz, 2 H, CH_2N), 3.55–3.76 (m, 2 H, CH_2N), 3.18–3.28 (m, 1 H), 3.03–3.13 (m, 1 H), 2.53 (dq, J = 16.3, J = 5.7 Hz, 2 H, CH_2CHOH), 1.98–2.17 (m, 4 H, 2 CH_2CH_2N), 1.38 (t, J = 7.2 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 152.4, 132.8, 130.7, 129.5, 127.0, 117.8, 116.6, 69.2, 60.8, 51.9, 47.4, 38.8, 26.1, 23.8, 23.5, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2980, 2902, 1684, 1400, 1251, 1054, 895 cm^{-1}. MS (EI): *m*/*z* (%) = 330 (21) $[M]^+$, 285 (16), 260 (20), 246 (8), 232 (3), 204 (6), 186 (100). HRMS (EI-TOF): calcd. for $C_{17}H_{22}N_4O_3$ $[M]^+$ 330.1692; found 330.1696.

Ethyl 3-(3-Azido-2-hydroxypropyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (2e): NaN_3 (975 mg, 15 mmol, 3.0 equiv.) and KI (83 mg, 0.5 mmol, 0.1 equiv.) were added to a solution of triazene alcohol **2c** (1.70 g, 5 mmol, 1.0 equiv.) in DMF (50 mL). The reaction mixture was stirred vigorously at 160 °C for 60 h before it was allowed to cool to room temperature. Water was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The organic extracts were washed with H_2O and brine, dried with Na_2SO_4, filtered, concentrated in vacuo. After flash chromatography (eluent: hexanes/EtOAc, 5:1), pure product **2e** (1.006 g, 58%) was obtained as a yellow solid, m.p. 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, J = 8.4, J = 2.0 Hz, 1 H, ArH), 7.85 (d, J = 2.0 Hz, 1 H, ArH), 7.49 (d, J = 8.4 Hz, 1 H, ArH), 5.48 (d, J = 3.6 Hz, 1 H, CHO*H*), 4.35 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 4.04–4.13 (m, 1 H, C*H*OH), 3.99 (t, J = 6.6 Hz, 2 H, CH_2N), 3.55–3.74 (m, 2 H, CH_2N), 3.32–3.36 (m, 1 H), 3.12–3.18 (m, 1 H), 2.97–3.01 (m, 1 H), 1.98–2.16 (m, 4 H, 2 CH_2CH_2N), 1.38 (t, J = 7.0 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 152.4, 132.9, 131.8, 129.1, 126.9, 116.5, 72.5, 60.8, 56.5, 51.8, 47.3, 37.4, 23.8, 23.5, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3672, 2981, 2902, 2105, 1705, 1395, 1253, 1056, 901 cm^{-1}. MS (EI): *m*/*z* (%) = 346 (16) $[M]^+$, 304 (53), 290 (22), 276 (22), 262 (13), 206 (11), 192 (11), 174 (14), 164 (24), 147 (36), 119 (59), 103 (22), 91 (100). HRMS (EI-TOF): calcd. for $C_{16}H_{22}N_6O_3$ $[M]^+$ 346.1753; found 346.1755.

Ethyl 3-(2-Hydroxy-2-phenylethyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (2f): Yield 476 mg, 32%. yellow solid, m.p. 141–144 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (dd, J = 8.5, J = 2.0 Hz, 1 H, ArH), 7.79 (d, J = 2.0 Hz, 1 H, ArH), 7.52 (d, J = 8.5 Hz, 1 H, ArH), 7.41 (d, J = 7.5 Hz, 2 H, ArH), 7.34 (t, J = 7.5 Hz, 2 H, ArH), 7.24 (d, J = 7.0 Hz, 1 H, ArH), 5.38 (d, J = 3.0 Hz, 1 H, OH), 5.00–5.08 (m, 1 H, C*H*OH), 4.35 (q, J = 3.0 Hz, 2 H, CH_3CH_2), 3.98–4.05 (m, 2 H, CH_2N), 3.71–3.81 (m, 2 H, CH_2N), 3.26–3.35 (m, 1 H), 3.17 (dd, J = 14.0, J = 2.5 Hz, 1 H), 2.03–2.20 (m, 4 H, 2 CH_2CH_2N), 1.38 (t, J = 7.0 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 152.6, 145.2, 133.0, 132.8, 129.0, 128.2, 127.0, 126.9, 125.6, 116.4, 76.0, 60.7, 51.8, 47.3, 43.0, 23.9, 23.6, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3672, 2979, 2902, 1700, 1395, 1256, 1053 cm^{-1}. MS (EI): *m*/*z* (%) = 367 (2) $[M]^+$, 350 (2), 294 (22), 283 (100), 261 (42), 232 (54), 223 (62), 178 (91). HRMS (EI-TOF): calcd. for $C_{21}H_{25}N_3O_3$ $[M]^+$ 367.1896; found 367.1900.

Ethyl 3-(2-Hydroxy-1-phenylethyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (2g): Yield 233 mg, 16%. red solid, m.p. 106–109 °C. R_f = 0.15 (hexanes/EtOAc, 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, J = 1.5 Hz, 1 H, ArH), 7.87 (dd, J = 8.3, J = 1.8 Hz, 1 H, ArH), 7.49 (d, J = 8.5 Hz, 1 H, ArH), 7.28 (d, J = 4.5 Hz, 4 H, ArH), 7.19 (br., 1 H, ArH), 4.98 (t, J = 7.0 Hz, 1 H, CH), 4.33 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 4.18–4.30 (m, 2 H, CH_2OH), 3.93 (br., 2 H, CH_2N), 3.59 (br., 2 H, CH_2N), 2.76 (br., 1 H, OH), 2.03 (m, 4 H, 2 CH_2CH_2N), 1.37 (t, J = 7.3 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 152.3, 141.7, 135.6, 130.0,

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128.7, 128.4, 128.3, 126.7, 126.2, 116.5, 66.1, 60.7, 51.2, 47.9, 46.9, 23.8, 23.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3672, 2978, 2902, 1684, 1394, 1254, 1059 cm^{-1}. MS (EI): *m/z* (%) = 367 (4) $[M]^+$, 349 (21), 322 (15), 283 (12), 265 (25), 223 (46), 179 (92), 165 (100). HRMS (EI-TOF): calcd. for $C_{21}H_{25}N_3O_3$ $[M]^+$ 367.1896; found 367.1894.

***trans*-2-{5-Methyl-2-[(*E*)-pyrrolidin-1-yldiazenyl]phenyl}cyclohexanol (2h):** Yield 634 mg, 55%. red oil. R_f = 0.2 (hexanes/EtOAc, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 1 H, ArH), 7.12 (s, 1 H, ArH), 7.00 (d, *J* = 8.0 Hz, 1 H, ArH), 3.80 (br., 4 H, 2 CH_2N), 3.62–3.69 (m, 2 H), 3.17–3.27 (m, 1 H), 2.34 (s, 3 H, CH_3), 2.15–2.20 (m, 1 H), 2.05 (br. s, 4 H), 1.70–1.85 (m, 4 H), 1.27–1.43 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 136.8, 135.2, 127.6, 127.4, 116.7, 75.5, 45.5, 36.4, 31.6, 26.3, 25.2, 23.7, 21.2 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2979, 2903, 1404, 1252, 1055, 893 cm^{-1}. MS (EI): *m/z* (%) = 287 (13) $[M]^+$, 203 (80), 160 (28), 121 (100), 105 (47), 91 (36). HRMS (EI-TOF): calcd. for $C_{17}H_{25}N_3O$ $[M]^+$ 287.1998; found 287.1988.

Ethyl 3-[3-(1,3-Dioxoisoindolin-2-yl)-2-hydroxypropyl]-4-(pyrrolidin-1-yldiazenyl)benzoate (2i): KI (9.96 g, 60 mmol, 10 equiv.) was added to a solution of triazene alcohol **2c** (2.04 g, 6 mmol, 1.0 equiv.) in acetone (45 mL). The reaction mixture was stirred vigorously at reflux for 72 h. The solvent was then removed in vacuo, and the residue was dissolved in water and extracted with ethyl acetate. The organic extracts were washed with aqueous $Na_2S_2O_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo. Ethyl 3-(2-hydroxy-3-iodopropyl)-4-(pyrrolidin-1-yldiazenyl) benzoate (2.107 g, 81%) was obtained after flash column chromatography (eluent: hexanes/EtOAc, 5:1).

Potassium 1,3-dioxoisoindolin-2-ide (1.11 g, 6 mmol, 2.0 equiv.) was added to a solution of ethyl 3-(2-hydroxy-3-iodopropyl)-4-(pyrrolidin-1-yldiazenyl)benzoate (1.293 g, 3 mmol, 1.0 equiv.) in dry DMF (6 mL). The reaction mixture was stirred vigorously at 100 °C for 8 h. After cooling, water was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The organic layers were washed with H_2O and brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. After flash chromatography (eluent: hexanes/EtOAc, 5:1), pure product **2i** (1.309 g, 97%) was obtained as a yellow solid . m.p.137–139 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.90 (m, 2 H, ArH), 7.79–7.84 (m, 2 H, ArH), 7.65–7.72 (m, 2 H, ArH), 7.48 (d, *J* = 9.0 Hz, 1 H, ArH), 4.81 (d, *J* = 4.6 Hz, 1 H, CHO*H*), 4.33 (q, *J* = 7.3 Hz, 2 H, CH_2O), 4.25–4.29 (m, 1 H, C*H*OH), 3.90–4.02 (m, 2 H, CH_2CH_2N), 3.70–3.82 (m, 2 H, CH_2N), 3.50–3.68 (m, 2 H, CH_2CH_2N), 3.02–3.15 (m, 2 H, CH_2), 1.95–2.10 (m, 4 H, 2 CH_2CH_2N), 1.37 (t, *J* = 7.0 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.5, 166.5, 152.5, 133.8, 132.9, 132.1, 131.7, 129.1, 126.8, 123.2, 116.3, 70.5, 60.7, 51.6, 47.2, 44.3, 38.0, 23.8, 23.5, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2980, 2902, 1697, 1385, 1253, 1072, 875 cm^{-1}. MS (EI): *m/z* (%) = 450 (2) $[M]^+$, 405 (19), 377 (14), 366 (14), 352 (40), 321 (16), 306 (100), 290 (19), 262 (19), 232 (7), 206 (100), 190 (14), 179 (44), 160 (100). HRMS (EI-TOF): calcd. for $C_{24}H_{26}N_4O_5$ $[M]^+$ 450.1903; found 450.1901.

Ethyl 3-[3-(Allyloxy)-2-hydroxypropyl]-4-(pyrrolidin-1-yldiazenyl)-benzoate (2j): Yield 1.03 g, 71%. red solid, m.p. 67–70 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1 H, ArH), 7.85 (dd, *J* = 8.4, *J* = 2.0 Hz, 1 H, ArH), 7.46 (d, *J* = 8.4 Hz, 1 H, ArH), 5.86–5.98 (m, 1 H, CH=), 5.26 (dd, *J* = 17.2, *J* = 1.6 Hz, 1 H), 5.15 (dd, *J* = 10.2, *J* = 1.8 Hz, 1 H), 4.84 (d, *J* = 3.2 Hz, 1 H, C*H*OH), 4.33 (q, *J* = 7.2 Hz, 2 H, CH_3CH_2O), 4.04–4.15 (m, 1 H, OH), 3.87–4.04 (m, 4 H), 3.53–3.71 (m, 2 H), 3.37–3.45 (m, 1 H), 3.29–3.37 (m, 1 H), 3.08 (d, *J* = 5.6 Hz, 2 H), 1.90–2.13 (m, 4 H, CH_2CH_2N), 1.37 (t, *J* = 7.2 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 152.5, 134.7, 133.0, 132.3, 128.8, 126.7, 116.9, 116.3, 73.8, 72.2, 71.6, 60.6, 51.5, 47.1, 36.6, 23.8, 23.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2980, 2902, 1708, 1396, 1253, 1073 cm^{-1}. MS (EI): *m/z* (%) = 361 (6) $[M]^+$, 316 (30), 290 (38), 277 (38), 260 (12), 232 (5), 217 (21), 206 (99), 191 (26), 177 (54), 163 (22), 147 (100). HRMS (EI-TOF): calcd. for $C_{19}H_{27}N_3O_4$ $[M]^+$ 361.2002; found 361.2008.

1-(Allyloxy)-3-[5-methyl-2-(pyrrolidin-1-yldiazenyl)phenyl]propan-2-ol (2k): Yield 1.177 g, 97%. red oil. R_f = 0.2 (hexanes/EtOAc, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.8 Hz, 1 H, ArH), 7.00 (br., 2 H, ArH), 5.88–6.00 (m, 1 H, CH=), 5.27 (d, *J* = 17.2 Hz, 1 H), 5.23 (s, 1 H), 5.17 (d, *J* = 10.8 Hz, 1 H), 4.04–4.13 (m, 1 H), 4.01 (t, *J* = 4.8 Hz, 2 H), 3.50–3.95 (br., 4 H, 2 CH_2CH_2N), 3.40–3.47 (m, 1 H), 3.32–3.39 (m, 1 H), 2.98–3.05 (m, 2 H), 2.30 (s, 3 H, CH_3), 1.98 (m, 4 H, 2 CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 134.9, 134.8, 132.4, 132.1, 127.9, 116.7, 116.4, 74.0, 72.1, 71.8, 36.8, 23.7, 20.8 ppm. IR (thin film): $\tilde{\nu}$ = 3665, 2976, 2903, 1405, 1317, 1258, 1219, 1073, 819 cm^{-1}. MS (EI): *m/z* (%) = 303 (20) $[M]^+$, 279 (23), 233 (23), 219 (53), 176 (24), 161 (94), 145 (55), 133 (71), 121 (90), 105 (100). HRMS (EI-TOF): calcd. for $C_{17}H_{25}N_3O_2$ $[M]^+$ 303.1947; found 303.1955.

1-{[3-Iodo-5-methyl-(1,1′-biphenyl)-2-yl]diazenyl}pyrrolidine (1l): A dry and N_2-flushed 50 mL Schlenk tube, equipped with a magnetic stirrer and a septum was charged with [(2,6-diiodo-4-methylphenyl) pyrrolidin-1-yl]diazene (3.024 g, 6.86 mmol, 1.0 equiv.) in dry THF (6 mL). *i*PrMgCl (0.984 M in THF, 8.4 mL, 8.30 mmol, 1.2 equiv.) was then added dropwise at –30 °C. After 2 h, complete conversion to the corresponding Grignard reagent was observed, as indicated by TLC. $ZnBr_2$ (1.0 M in THF, 9.0 mL, 9 mmol, 1.3 equiv.) was added. The reaction mixture was allowed to warm slowly to room temperature over 0.5 h. Then iodobenzene (0.8 mL, 7.09 mmol, 1.03 equiv.) and $Pd(PPh_3)_4$ (162 mg, 0.14 mmol, 0.02 equiv.) were added. The reaction mixture was stirred at room temperature for 12 h, before being quenched by H_2O. The resulting mixture was extracted with ethyl acetate. The organic layers were dried with Na_2SO_4, and concentrated in vacuo. Purification by flash chromatography on silica gel (hexanes/EtOAc, 50:1) gave **1l** (1.62 g, 61%) as a yellow solid, m.p. 110–111 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1 H, ArH), 7.21–7.30 (m, 5 H, ArH), 7.11 (s, 1 H, ArH), 3.54 (t, *J* = 6.0 Hz, 4 H, 2 CH_2N), 2.33 (s, 3 H, CH_3), 1.91 (br., 4 H, 2 CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 140.6, 138.6, 136.1, 135.1, 131.9, 129.9, 127.5, 126.1, 94.0, 23.8, 20.3 ppm. IR (thin film): $\tilde{\nu}$ = 2974, 2888, 1408, 1319, 1254, 1221, 1054 cm^{-1}. MS (EI): *m/z* (%) = 391 (15) $[M]^+$, 321 (26), 293 (42), 180 (11), 166 (100). HRMS (EI-TOF): calcd. for $C_{17}H_{18}IN_3$ $[M]^+$ 391.0545; found 391.0544.

***trans*-2-{5-Methyl-2-[(*E*)-pyrrolidin-1-yldiazenyl]-(1,1′-biphenyl)-3-yl}cyclohexanol (2l):** Yield 634 mg, 44%. red oil. R_f = 0.2 (hexanes/EtOAc, 5:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.28 (m, 4 H, ArH), 7.17–7.20 (m, 1 H, ArH), 7.14 (d, *J* = 2.5 Hz, 1 H, ArH), 7.01 (d, *J* = 1.5 Hz, 1 H, ArH), 3.71 (br., 1 H, OH), 3.60–3.66 (m, 1 H), 3.40–3.49 (m, 4 H), 2.83–2.89 (m, 1 H), 2.36 (s, 3 H, CH_3), 2.16–2.20 (m, 1 H), 1.88 (br., 4 H, 2 CH_2CH_2N), 1.72–1.86 (m, 3 H), 1.56–1.67 (m, 1 H), 1.21–1.43 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.0, 141.5, 136.2, 134.88, 134.84, 130.2, 129.7, 127.3, 126.5, 125.7, 75.4, 48.7, 45.7, 36.4, 32.7, 29.6, 26.2, 25.1, 23.7, 21.2 ppm. IR (thin film): $\tilde{\nu}$ = 3342, 2920, 2849, 1427, 1339, 1214, 1066, 701 cm^{-1}. MS (EI): *m/z* (%) = 363 (2) $[M]^+$, 307 (4), 293 (4), 279 (37), 264 (46), 249 (9), 235 (10), 221 (20), 209 (16), 197 (100). HRMS (EI-TOF): calcd. for $C_{23}H_{29}N_3O$ $[M]^+$ 363.2311; found 363.2316.

1-[(2-Allyl-6-iodo-4-methylphenyl)diazenyl]pyrrolidine (1m): A dry and N_2-flushed 50 mL Schlenk tube, equipped with a magnetic stir-

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rer and a septum was charged with [(2,6-diiodo-4-methylphenyl) pyrrolidin-1-yl]diazene (6.615 g, 15 mmol, 1.0 equiv.) in dry THF (15 mL). *i*PrMgCl (0.984 M in THF, 18.3 mL, 18 mmol, 1.2 equiv.) was then added dropwise at –30 °C. After 3 h, complete conversion into the corresponding Grignard reagent was observed, as indicated by TLC. CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 0.05 equiv.) and allyl bromide (1.8 mL, 19.5 mmol, 1.3 equiv.) were added slowly to the resulting reaction mixture. Then the reaction mixture was allowed to warm slowly to room temperature, and stirred for 2 h before the addition of saturated aqueous NH_4Cl solution. The resulting mixture was extracted with ethyl acetate. The organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexanes/EtOAc, 50:1) gave **1m** (4.48 g, 84%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1 H, ArH), 6.97 (s, 1 H, ArH), 5.84–5.94 (m, 1 H, CH=), 5.00–5.04 (m, 2 H, CH_2=), 3.81 (br., 4 H, 2 CH_2N), 3.33 (d, J = 6.4 Hz, 2 H, CH_2), 2.26 (s, 3 H, CH_3), 2.05 (s, 4 H, 2 CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 137.4, 137.2, 135.9, 132.5, 130.9, 115.4, 93.3, 36.6, 23.7, 20.2 ppm. IR (thin film): $\tilde{\nu}$ = 3665, 2974, 2904, 1636, 1596, 1417, 1321, 1257, 1216, 1054 cm^{-1}. MS (EI): *m*/*z* (%) = 355 (5) $[M]^+$, 285 (19), 130 (100). HRMS (EI-TOF): calcd. for $C_{17}H_{18}IN_3$ $[M]^+$ 355.0545; found 355.0555.

***trans*-2-{3-Allyl-5-methyl-2-[(*E*)-pyrrolidin-1-yldiazenyl]phenyl} cyclohexanol (2m):** Yield 993 mg, 76%, red oil. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.02 (s, 1 H, ArH), 6.88 (s, 1 H, ArH), 5.88–5.96 (m, 1 H, CH=), 4.97–5.03 (m, 2 H, CH_2=), 3.77 (br., 4 H, 2 CH_2N), 3.57 (dt, J = 10.3, J = 4.3 Hz, 2 H), 3.33 (d, J = 5.2 Hz, 2 H), 2.75 (m, 1 H), 2.30 (s, 3 H, CH_3), 2.15–2.18 (m, 1 H), 2.05 (t, J = 6.5 Hz, 4 H, 2 CH_2CH_2N), 1.70–1.80 (m, 3 H), 1.52–1.59 (m, 1 H), 1.19–1.41 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 138.0, 135.5, 134.8, 132.1, 128.7, 125.4, 114.9, 75.3, 36.6, 36.4, 32.8, 26.2, 25.1, 23.8, 21.2 ppm. IR (thin film): $\tilde{\nu}$ = 3664, 2978, 2903, 1406, 1252, 1069, 895 cm^{-1}. MS (EI): *m*/*z* (%) = 327 (3) $[M]^+$, 271 (3), 257 (6), 243 (40), 228 (6), 200 (16), 185 (18), 161 (100), 143 (35), 128 (26). HRMS (EI-TOF): calcd. for $C_{20}H_{29}N_3O$ $[M]^+$ 327.2311; found 327.2307.

1-[3-Iodo-5-methyl-2-(pyrrolidin-1-yldiazenyl)phenyl]propan-2-ol (1n): A dry and N_2-flushed 50 mL Schlenk tube, equipped with a magnetic stirrer and a septum was charged with [(2,6-diiodo-4-methylphenyl)pyrrolidin-1-yl]diazene (2.205 g, 5 mmol, 1.0 equiv.) in dry THF (5 mL). *i*PrMgCl (1.15 M in THF, 4.8 mL, 5.5 mmol, 1.1 equiv.) was then added dropwise at –30 °C. After 2.5 h, complete conversion into the corresponding Grignard reagent was observed, as indicated by TLC and GC analysis. A CuCN·2LiCl solution (1.0 M in THF, 0.25 mL, 0.25 mmol, 0.05 equiv.) and 2-methyloxirane (0.56 mL, 8 mmol, 1.6 equiv.) were added slowly to the resulting reaction mixture. Then the reaction mixture was slowly allowed to warm to room temperature, and stirred for 4 h before the addition of saturated aqueous NH_4Cl solution. The resulting mixture was extracted with ethyl acetate. The organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. After silica gel chromatography (eluent: hexanes/EtOAc, 5:1), pure product **1n** (1.208 g, 62%) was obtained as a red solid, m.p. 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1 H, ArH), 6.96 (s, 1 H, ArH), 3.63–4.03 (m, 5 H), 2.62–2.75 (m, 2 H), 2.25 (s, 3 H, CH_3), 2.00–2.14 (m, 4 H, 2 CH_2CH_2N), 1.19 (d, J = 6.4 Hz, 3 H, CH_3CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 138.4, 136.2, 132.3, 131.9, 92.6, 68.8, 50.9, 46.8, 46.7, 41.9, 23.7, 23.6, 20.2 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2972, 2904, 1412, 1316, 1257, 1226, 1052 cm^{-1}. MS (EI): *m*/*z* (%) = 374 (14) $[M]^+$, 303 (26), 289 (34), 247 (100). HRMS (EI-TOF): calcd. for $C_{14}H_{20}IN_3O$ $[M]^+$ 373.0651; found 373.0653.

Ethyl 3′-(2-Hydroxypropyl)-5′-methyl-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-4-carboxylate (2n): [4-(Ethoxycarbonyl)phenyl]boronic acid (640 mg, 3.3 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (87 mg, 0.075 mmol, 0.025 equiv.), Cs_2CO_3 (1.956 g, 6.0 mmol, 2 equiv.) were added to a solution of iodotriazene alcohol **1n** (1.16 g, 3.0 mmol, 1.0 equiv.) in dioxane (8 mL) and H_2O (2 mL) in a screw-cap vial. The vial was flushed with N_2, sealed, and heated at 100 °C for 12 h while stirring. After cooling, the solution was diluted with ethyl acetate and washed with water. The combined organic extracts were washed with water and brine, and dried with Na_2SO_4. After silica gel chromatography (eluent: hexanes/EtOAc, 5:1), pure product **2n** (913 mg, 77%) was obtained as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.0 Hz, 2 H, ArH), 7.29 (d, J = 8.0 Hz, 2 H, ArH), 7.01 (s, 1 H, ArH), 7.03 (s, 1 H, ArH), 4.62 (s, 1 H, C*H*OH), 4.37 (q, J = 7.1 Hz, 2 H, CH_2O), 4.10 (br., 1 H, OH), 3.30–3.50 (m, 4 H, 2 CH_2N), 2.75–2.90 (m, 2 H, CH_2CH), 2.34 (s, 3 H, CH_3), 1.74–2.20 (m, 4 H, 2 CH_2CH_2N), 1.40 (t, J = 7.2 Hz, 3 H, CH_3CH$_2$), 1.25 (d, J = 6.4 Hz, 3 H, CH_3CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 146.9, 145.6, 134.7, 133.7, 132.9, 131.7, 130.0, 129.9, 128.7, 127.6, 69.2, 60.8, 41.8, 23.7, 23.6, 20.8, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3672, 2974, 2903, 1711, 1606, 1414, 1268, 1073, 857 cm^{-1}. MS (EI): *m*/*z* (%) = 395 (17) $[M]^+$, 350 (18), 325 (13), 311 (64), 296 (19), 279 (13), 269 (28), 251 (100). HRMS (EI-TOF): calcd. for $C_{23}H_{29}N_3O_3$ $[M]^+$ 395.2209; found 395.2208.

Ethyl 3′-(2-Hydroxy-2-methylpropyl)-5′-methyl-2′-(pyrrolidin-1-yldiazenyl)[1,1′-biphenyl]-4-carboxylate (2o): Compound **2o** was prepared from 2,2-dimethyloxirane and [(2,6-diiodo-4-methylphenyl)-pyrrolidin-1-yl]diazene according to the procedure for the preparation of **2n**. Yield 954 mg, 78%, yellow solid, m.p. 84–86 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.0 Hz, 2 H, ArH), 7.25 (d, J = 8.0 Hz, 2 H, ArH), 6.98 (d, J = 7.2 Hz, 2 H, ArH), 5.80 (s, 1 H, OH), 4.37 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 3.38 (br., 4 H, 2 CH_2N), 2.89 (s, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 1.60–2.00 (m, 4 H, 2 CH_2CH_2N), 1.40 (t, J = 7.2 Hz, 3 H, CH_3CH$_2$), 1.27 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 147.2, 145.5, 134.5, 133.4, 132.8, 130.3, 129.8, 128.8, 127.4, 71.3, 60.8, 45.9, 30.3, 23.6, 20.9, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3665, 2976, 1713, 1407, 1054 cm^{-1}. MS (EI): *m*/*z* (%) = 409 (29) $[M]^+$, 392 (8), 293 (84), 265 (100), 197 (86). HRMS (EI-TOF): calcd. for $C_{24}H_{31}N_3O_3$ $[M]^+$ 409.2365; found 409.2362.

Ethyl 5′-Fluoro-3′-[(1R,2S)-2-hydroxycyclohexyl]-2′-[(*E*)-pyrrolidin-1-yldiazenyl][1,1′-biphenyl]-4-carboxylate (2p): Triazene alcohol **2p** was prepared from [(2,6-dibromo-4-fluorophenyl)pyrrolidin-1-yl]-diazene according to the procedure for the preparation of **2m**. Yield 972 mg, 74%, brown solid, m.p. 117–119 °C. R_f = 0.3 (hexanes/EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.0 Hz, 2 H, ArH), 7.31 (d, J = 8.4 Hz, 2 H, ArH), 7.07 (dd, J = 10.0, J = 2.4 Hz, 1 H, ArH), 6.90 (dd, J = 8.8, J = 2.4 Hz, 1 H, ArH), 4.38 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.55–3.70 (m, 2 H), 3.35–3.55 (m, 4 H), 2.91 (t, J = 10.2 Hz, 1 H), 2.18 (d, J = 12.0 Hz, 1 H), 1.65–2.10 (m, 7 H), 1.53–1.56 (m, 1 H), 1.39 (t, J = 7.2 Hz, 3 H), 1.15–1.47 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 160.4 (d, $J_{C,F}$ = 242.0 Hz), 145.4, 144.6 (d, $J_{C,F}$ = 3.0 Hz), 139.3 (d, $J_{C,F}$ = 6.7 Hz), 135.5 (d, $J_{C,F}$ = 7.6 Hz), 129.9, 128.8, 128.2, 115.2 (d, $J_{C,F}$ = 23.0 Hz), 113.1 (d, $J_{C,F}$ = 22.1 Hz), 75.3, 60.9, 45.8, 36.5, 32.5, 26.0, 25.0, 23.6, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2979, 2902, 1690, 1407, 1257, 1070, 863 cm^{-1}. MS (EI): *m*/*z* (%) = 440 (24) $[M]^+$, 422 (2), 394 (4), 369 (12), 355 (54), 338 (7), 323 (3), 312 (19), 295 (9), 273 (100), 257 (11). HRMS (EI-TOF): calcd. for $C_{25}H_{30}FN_3O_3$ $[M]^+$ 439.2271; found 439.2265.

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Ethyl 3-(2-Hydroxy-2-methylpropyl)-4-(pyrrolidin-1-yldiazenyl)-benzoate (2q): Compound **2q** was prepared from ethyl 3-iodo-4-(pyrrolidin-1-yldiazenyl) benzoate by treatment with 2,2-dimethyloxirane according to the procedure for the preparation of compound **2a**. Yield 804 mg, 63%, red solid, m.p. 79–80 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.4 Hz, 1 H, ArH), 7.80 (s, 1 H, ArH), 7.50 (d, J = 8.4 Hz, 1 H, ArH), 5.70 (s, 1 H, OH), 4.36 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.99 (br., 2 H, CH_2N), 3.63 (br., 2 H, CH_2N), 3.04 (s, 2 H, CH_2), 2.03–2.09 (m, 4 H, 2 CH_2CH_2N), 1.39 (t, J = 7.0 Hz, 3 H, CH_3CH_2), 1.23 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 152.6, 134.1, 132.6, 128.8, 126.7, 116.5, 71.6, 60.7, 51.8, 47.3, 46.2, 30.1, 23.8, 23.5, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3666, 2973, 2903, 1702, 1600, 1399, 1314, 1258, 1072 cm^{-1}. MS (EI): *m*/*z* (%) = 319 (6) $[M]^+$, 302 (3), 274 (10), 261 (32), 249 (13), 232 (30), 179 (100). HRMS (EI-TOF): calcd. for $C_{17}H_{25}N_3O_3$ $[M]^+$ 319.1896; found 319.1899.

1-[5-Bromo-2-(pyrrolidin-1-yldiazenyl)phenyl]-2-methylpropan-2-ol (2r): Compound **2r** was prepared from 1-[(4-bromo-2-iodophenyl)-diazenyl]pyrrolidine by treatment with 2,2-dimethyloxirane according to the procedure for the preparation of compound **2a**. Yield 850 mg, 65%, yellow solid, m.p. 110–112 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.40 (m, 3 H, ArH), 5.70 (s, 1 H, OH), 3.94 (br., 2 H, CH_2N), 3.58 (br., 2 H, CH_2N), 2.95 (s, 2 H, CH_2), 2.04 (br., 4 H, 2 CH_2CH_2N), 1.22 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 134.9, 134.8, 130.1, 118.3, 118.2, 71.5, 51.5, 47.1, 46.0, 30.1, 23.8, 23.6 ppm. IR: $\tilde{\nu}$ = 3669, 2971, 1392, 1311, 1072 cm^{-1}. MS (EI): *m*/*z* (%) = 327 (8) [M, $Br^{81}]^+$, 325 (8) [M, $Br^{79}]^+$, 267 (9), 257 (20), 199 (12), 187 (72), 171 (25), 130 (100). HRMS (EI-TOF): calcd. for $C_{14}H_{20}BrN_3O$ $[M]^+$ 325.0790; found 325.0797.

(1S,2R)-2-{5-Bromo-2-[(*E*)-pyrrolidin-1-yldiazenyl]phenyl}cyclohexanol (2s): Compound **2s** was prepared from 1-[(4-bromo-2-iodophenyl)diazenyl]pyrrolidine by treatment with 7-oxabicyclo[4.1.0]-heptane according to the procedure of compound **2a**. Yield 722 mg, 51%, brown solid, m.p. 110–112 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 1 H, ArH), 7.25–7.34 (m, 2 H, ArH), 3.55–4.05 (m, 5 H), 3.45 (br., 1 H), 3.20–3.30 (m, 1 H), 2.15–2.25 (m, 1 H), 2.00–2.14 (m, 4 H, 2 CH_2CH_2N), 1.75–1.90 (m, 3 H), 1.60–1.70 (m, 1 H), 1.23–1.50 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 139.4, 129.74, 129.69, 119.0, 118.4, 75.4, 45.4, 36.5, 31.6, 26.2, 25.1, 23.7 ppm. IR (thin film): $\tilde{\nu}$ = 3665, 2977, 1392, 1059 cm^{-1}. MS (EI): *m*/*z* (%) = 353 (5) [M, $Br^{81}]^+$, 351 (5) [M, $Br^{79}]^+$, 267 (41), 187 (100). HRMS (EI-TOF): calcd. for $C_{16}H_{22}BrN_3O$ $[M]^+$ 351.0946; found 351.0939.

Ethyl 2′-(Hydroxymethyl)-6-(pyrrolidin-1-yldiazenyl)[1,1′-biphenyl]-3-carboxylate (2t): [5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)-phenyl]boronic acid (961 mg, 3.3 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (87 mg, 0.075 mmol, 0.025 equiv.), and Cs_2CO_3 (1.956 g, 6.0 mmol, 2.0 equiv.) were added to a solution of (2-bromophenyl)methanol (561 mg, 3.0 mmol, 1.0 equiv.) in dioxane (8 mL) and H_2O (2 mL) in a screw-cap vial. The vial was flushed with N_2, sealed, and heated at 100 °C for 12 h while stirring. After cooling, the solution was diluted with ethyl acetate and washed with water. The combined organic extracts were washed with water and brine, and dried with Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (eluent: hexanes/EtOAc, 5:1) to give pure compound **2t** (360 mg, 34%) as a yellow solid, m.p.112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (dd, J = 8.4, J = 2.0 Hz, 1 H, ArH), 7.88 (d, J = 2.0 Hz, 1 H, ArH), 7.40–7.51 (m, 2 H, ArH), 7.27–7.40 (m, 2 H, ArH), 7.15 (dd, J = 7.4, J = 1.4 Hz, 1 H, ArH), 4.44–4.54 (m, 2 H), 4.27–4.40 (m, 3 H, CH_2O and OH), 3.80–3.96 (br., 2 H, CH_2N), 3.28 (br., 2 H, CH_2N), 1.93 (br., 4 H, 2 CH_2CH_2N), 1.37 (t, J = 7.2 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 152.6, 139.2, 138.9, 135.4, 132.2, 130.3, 129.8, 129.3, 127.9, 127.7, 126.8, 117.8, 64.6, 60.7, 51.6, 46.9, 23.6, 23.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2979, 2902, 1696, 1397, 1233, 1052 cm^{-1}. MS (EI): *m*/*z* (%) = 353 (6) $[M]^+$, 308 (22), 283 (9), 269 (31), 252 (56), 225 (17), 209 (100), 193 (10), 182 (72), 165 (100), 152 (62). HRMS (EI-TOF): calcd. for $C_{20}H_{23}N_3O_3$ $[M]^+$ 353.1739; found 353.1733.

Ethyl 2′-(1-Hydroxypropyl)-6-(pyrrolidin-1-yldiazenyl)[1,1′-biphenyl]-3-carboxylate (2u): Compound **2u** was prepared from 1-(2-bromophenyl)propan-1-ol by treatment with [5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl]boronic acid according to the procedure for the synthesis of compound **2t**. Yield 273 mg, 24%, red oil. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.4 Hz, 1 H, ArH), 7.88 (s, 1 H, ArH), 7.54 (d, J = 8.0 Hz, 1 H, ArH), 7.38–7.47 (m, 2 H, ArH), 7.30 (t, J = 7.6 Hz, 1 H, ArH), 7.11 (d, J = 7.2 Hz, 1 H, ArH), 4.65 (s, 1 H, OH), 4.45 (t, J = 7.2 Hz, 1 H, $CHCH_2$), 4.36 (q, J = 6.9 Hz, 2 H, CH_3CH_2O), 3.87 (br., 2 H, CH_2N), 3.27 (br., 2 H, CH_2N), 1.91–1.97 (m, 4 H, 2 CH_2CH_2N), 1.73–1.78 (m, 2 H, CH_2CH_3), 1.38 (t, J = 7.0 Hz, 3 H, CH_3CH_2O), 0.82 (t, J = 7.4 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 152.7, 141.8, 139.4, 135.7, 132.2, 130.2, 129.7, 128.0, 127.2, 126.9, 124.9, 117.8, 72.4, 60.8, 51.6, 46.8, 27.8, 23.6, 23.5, 14.3, 10.6 ppm. IR (thin film): $\tilde{\nu}$ = 3664, 2973, 2904, 1710, 1599, 1394, 1303, 1234, 1051 cm^{-1}. MS (EI): *m*/*z* (%) = 382 (8) $[M + H]^+$, 364 (66), 268 (100), 252 (26). HRMS (EI-TOF): calcd. for $C_{22}H_{27}N_3O_3$ $[M]^+$ 381.2052; found 381.2050.

Ethyl 2′-(1-Hydroxy-2-methylpropyl)-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (2v): Compound **2v** was prepared from 1-(2-bromophenyl)-2-methylpropan-1-ol by treatment with [5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl]boronic acid according to the procedure for the preparation of compound **2t**. Yield 371 mg, 31%, yellow solid, m.p. 63–65 °C. R_f = 0.2 (hexanes/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.4 Hz, 1 H, ArH), 7.88 (s, 1 H, ArH), 7.52 (d, J = 8.0 Hz, 1 H, ArH), 7.36–7.46 (m, 2 H, ArH), 7.25–7.30 (m, 2 H, ArH), 7.10 (d, J = 6.8 Hz, 1 H, ArH), 4.36 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 4.06 (d, J = 10.0 Hz, 1 H, CHO*H*), 3.86 (br., 2 H, CH_2N), 3.25 (br., 2 H, CH_2N), 2.15–2.20 [m, 1 H, $(CH_3)_2CH$], 1.90 (br., 4 H, 2 CH_2CH_2N), 1.38 (t, J = 7.0 Hz, 3 H, CH_3CH_2O), 1.33 (d, J = 7.2 Hz, 1 H), 1.03 (d, J = 6.0 Hz, 3 H, CH_3CH), 0.58 (d, J = 6.4 Hz, 3 H, CH_3CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 152.7, 141.7, 139.5, 135.9, 132.0 (2 C), 130.0, 129.6, 128.0, 127.0, 125.4, 117.7, 60.8, 51.6, 46.8, 32.1, 23.6, 23.5, 23.4, 19.8, 19.3, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3665, 2977, 2902, 1709, 1404, 1232, 1054 cm^{-1}. MS (EI): *m*/*z* (%) = 396 (2) $[M + H]^+$, 352 (15) $[M - i\text{Pr}]^+$, 322 (16), 311 (10), 277 (12), 268 (100), 262 (44), 251 (65), 225 (57), 183 (57). HRMS (EI-TOF): calcd. for $C_{23}H_{29}N_3O_3$ $[M]^+$ 395.2209; found 395.2215.

General Procedure for the Synthesis of Compounds 3a–3v: $BF_3{\cdot}OEt_2$ (0.13 mL, 1 mmol, 2.0 equiv.) was slowly added to a solution of triazene alcohol **2a**–**2v** (0.5 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) at room temperature, and stirring was continued at 40 °C for 4 h, before the reaction mixture was cooled and the reaction was quenched by a 5% aqueous solution of $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2. The organic extracts were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc, 50:1).

Ethyl 5a,6,7,8,9,9a-Hexahydrodibenzo[*b*,*d*]furan-2-carboxylate (3a): Yield 94 mg, 76%, white solid, m.p. 63–64 °C. ^{1}H NMR (400 MHz,

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$CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 1 H, ArH), 7.79 (s, 1 H, ArH), 6.83 (d, J = 8.8 Hz, 1 H, ArH), 4.33 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.86–3.93 (m, 1 H, OCH), 2.75–2.85 (m, 1 H, CH), 2.31–2.40 (m, 2 H), 1.94–1.98 (m, 1 H), 1.77–1.88 (m, 2 H), 1.41–1.46 (m, 3 H), 1.36 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 164.1, 132.2, 130.7, 124.0, 123.1, 109.5, 91.4, 60.5, 48.0, 30.5, 26.9, 25.3, 24.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2981, 2939, 2903, 1707, 1610, 1244, 1073, 1014 cm^{-1}. MS (EI): m/z (%) = 246 (100) $[M]^+$, 201 (50), 173 (35), 145 (31), 115 (23), 67 (24). HRMS (EI-TOF): calcd. for $C_{15}H_{18}O_3$ $[M]^+$ 246.1256; found 246.1258.

Ethyl 2-Methyl-2,3-dihydrobenzofuran-5-carboxylate (3b): Yield 71 mg, 69%, pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85–7.88 (m, 2 H, ArH), 6.75 (d, J = 8.5 Hz, 1 H, ArH), 4.98–5.03 (m, 1 H, $CHCH_3$), 4.33 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.20–3.40 (m, 1 H), 2.78–2.86 (m, 1 H), 1.48 (d, J = 6.0 Hz, 3 H, CH_3CH), 1.37 (t, J = 7.3 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 163.5, 131.0, 127.3, 126.7, 122.8, 108.9, 80.8, 60.5, 36.4, 21.7, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 2978, 2904, 1707, 1610, 1485, 1443, 1384, 1265, 1167, 1081 cm^{-1}. MS (EI): m/z (%) = 206 (95) $[M]^+$, 191 (12), 178 (44), 161 (100), 133 (36), 77 (28). HRMS (EI-TOF): calcd. for $C_{12}H_{14}O_3$ $[M]^+$ 206.0943; found 206.0948.

Ethyl 2-(Chloromethyl)-2,3-dihydrobenzofuran-5-carboxylate (3c): Yield 42 mg, 35%, white solid, m.p. 41–43 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86–7.92 (m, 2 H, ArH), 6.80 (d, J = 8.0 Hz, 1 H, ArH), 5.04–5.12 (m, 1 H, $CHCH_2Cl$), 4.33 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.66–3.78 (m, 2 H, CH_2Cl), 3.34–3.41 (m, 1 H), 3.12–3.20 (m, 1 H), 1.37 (t, J = 7.3 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.3, 163.0, 131.1, 126.7, 126.1, 123.5, 109.1, 82.4, 60.6, 45.9, 32.7, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2980, 2902, 1694, 1613, 1438, 1267, 1242, 1079, 767 cm^{-1}. MS (EI): m/z (%) = 242 (23) [M, $Cl^{37}]^+$, 240 (67) [M, $Cl^{35}]^+$, 225 (7), 212 (23), 195 (100), 191 (26). HRMS (EI-TOF): calcd. for $C_{12}H_{13}ClO_3$ $[M]^+$ 240.0553; found 240.0554.

Ethyl 2-(Cyanomethyl)-2,3-dihydrobenzofuran-5-carboxylate (3d): Yield 64 mg, 55%, pink solid, m.p. 58–61 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86–7.92 (m, 2 H, ArH), 6.82 (d, J = 8.5 Hz, 1 H, ArH), 5.05–5.15 (m, 1 H, $CHCH_2CN$), 4.32 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.45–3.51 (m, 1 H), 3.07 (dd, J = 16.3, J = 6.3 Hz, 1 H), 2.80 (d, J = 6.5 Hz, 2 H, $CHCH_2CN$), 1.36 (t, J = 3.5 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 162.2, 131.3, 126.8, 125.3, 123.9, 116.0, 109.4, 78.1, 60.7, 34.2, 24.3, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2979, 2903, 2252, 1698, 1611, 1398, 1267, 1071, 768 cm^{-1}. MS (EI): m/z (%) = 231 (90) $[M]^+$, 216 (11), 203 (30), 191 (8), 186 (100). HRMS (EI-TOF): calcd. for $C_{13}H_{13}NO_3$ $[M]^+$ 231.0895; found 231.0889.

Ethyl 2-(Azidomethyl)-2,3-dihydrobenzofuran-5-carboxylate (3e): Yield 56 mg, 45%, red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.92 (m, 2 H, ArH), 6.82 (d, J = 8.0 Hz, 1 H, ArH), 4.95–5.08 (m, 1 H, $CHCH_2N_3$), 4.33 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.52–3.60 (m, 1 H), 3.43–3.52 (m, 1 H), 3.30–3.40 (m, 1 H), 3.00–3.08 (m, 1 H), 1.37 (t, J = 7.2 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 162.5, 130.9, 126.4, 125.9, 123.2, 108.9, 81.9, 60.3, 54.0, 31.7, 14.0 ppm. IR (thin film): $\tilde{\nu}$ = 2981, 2099, 1705, 1610, 1487, 1440, 1266, 1241, 1164, 1111, 1019, 767 cm^{-1}. MS (EI): m/z (%) = 247 (53) $[M]^+$, 218 (5), 202 (39), 190 (100), 175 (20), 162 (45), 145 (73), 129 (7), 119 (60), 91 (100). HRMS (EI-TOF): calcd. for $C_{12}H_{13}N_3O_3$ $[M]^+$ 247.0957; found 247.0954.

Ethyl 2-Phenyl-2,3-dihydrobenzofuran-5-carboxylate (3f): Yield 106 mg, 79%, pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, J = 9.0 Hz, 1 H, ArH), 7.90 (s, 1 H, ArH), 7.30–7.45 (m, 5 H, ArH), 6.88 (d, J = 9.0 Hz, 1 H, ArH), 5.84 (t, J = 8.8 Hz, 1 H, ArOCHPh), 4.35 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.65–3.70 (m, 1 H), 3.20–3.30 (m, 1 H), 1.38 (t, J = 7.0 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.4, 163.6, 141.2, 131.2, 128.7, 128.3, 126.9, 126.6, 125.7, 123.3, 109.0, 85.2, 60.6, 37.6, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 2979, 2903, 1707, 1609, 1485, 1443, 1394, 1261, 1165, 1077 cm^{-1}. MS (EI): m/z (%) = 268 (100) $[M]^+$, 223 (63), 253 (4), 240 (7), 194 (17), 165 (30), 152 (16). HRMS (EI-TOF): calcd. for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099; found 268.1101.

Ethyl 3-Phenyl-2,3-dihydrobenzofuran-5-carboxylate (3g): Yield 102 mg, 76%, yellow solid, m.p. 57–59 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.3 Hz, 1 H, ArH), 7.72 (s, 1 H, ArH), 7.32–7.35 (m, 2 H, ArH), 7.24–7.30 (m, 1 H, ArH), 7.17–7.22 (m, 2 H, ArH), 6.90 (d, J = 8.0 Hz, 1 H, ArH), 4.99 (t, J = 9.3 Hz, 1 H, ArCH), 4.69 (t, J = 8.5 Hz, 1 H), 4.50–4.54 (m, 1 H), 4.23–4.33 (m, 2 H, CH_3CH_2O), 1.34 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.3, 164.1, 142.2, 131.4, 131.0, 128.9, 127.7, 127.3, 127.1, 123.5, 109.3, 80.1, 60.6, 47.8, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2979, 2902, 1707, 1603, 1458, 1395, 1248, 1075 cm^{-1}. MS (EI): m/z (%) = 268 (100) $[M^+]$, 253 (2), 239 (9), 223 (66), 195 (20), 165 (28), 152 (15). HRMS (EI-TOF): calcd. for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099; found 268.1100.

***trans*-8-Methyl-1,2,3,4,4a,9b-hexahydrodibenzo[*b*,*d*]furan (3h):** Yield 50 mg, 53%, white solid, m.p. 73–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90–6.95 (m, 2 H, ArH), 6.75 (d, J = 7.6 Hz, 1 H, ArH), 3.83 (dt, J = 12.0, J = 3.6 Hz, 1 H, ArOCH), 2.70–2.82 (m, 1 H, ArCH), 2.32–2.36 (m, 2 H), 2.30 (s, 3 H, $ArCH_3$), 1.94–1.99 (m, 1 H), 1.76–1.88 (m, 2 H), 1.34–1.47 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.0, 132.1, 130.0, 127.8, 123.1, 109.5, 90.6, 48.6, 30.7, 27.2, 25.5, 24.5, 20.9 ppm. IR (thin film): $\tilde{\nu}$ = 2978, 2904, 1452, 1400, 1228, 1055, 891, 812 cm^{-1}. MS (EI): m/z (%) = 188 (100) $[M]^+$, 173 (31), 159 (42), 145 (76), 121 (45). HRMS (EI-TOF): calcd. for $C_{13}H_{16}O$ $[M]^+$ 188.1201; found 188.1199.

Ethyl 2-[(1,3-Dioxoisoindolin-2-yl)methyl]-2,3-dihydrobenzofuran-5-carboxylate (3i): Yield 125 mg, 71%, white solid, m.p. 118–120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85–7.90 (m, 4 H, ArH), 7.71–7.76 (m, 2 H, ArH), 6.75 (d, J = 9.5 Hz, 1 H, ArH), 5.15–5.23 (m, 1 H, ArOCH), 4.31 (q, J = 7.3 Hz, 2 H, CH_3CH_2O), 4.03 (dd, J = 14.3, J = 7.8 Hz, 1 H), 3.83 (dd, J = 14.0, J = 5.0 Hz, 1 H), 3.36 (dd, J = 16.3, J = 9.3 Hz, 1 H), 3.04 (dd, J = 16.3, J = 6.3 Hz, 1 H), 1.35 (t, J = 7.3 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.1, 166.3, 162.8, 134.1, 131.8, 131.2, 126.7, 126.1, 123.4, 109.4, 80.6, 60.5, 41.7, 32.5, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2981, 2902, 1708, 1392, 1242, 1055, 838, 709 cm^{-1}. MS (EI): m/z (%) = 351 (70) $[M]^+$, 306 (51), 277 (45), 259 (1), 204 (100), 191 (52). HRMS (EI-TOF): calcd. for $C_{21}H_{17}NO_5$ $[M]^+$ 351.1107; found 351.1104.

Ethyl 2-[(Allyloxy)methyl]-2,3-dihydrobenzofuran-5-carboxylate (3j): Yield 85 mg, 65%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.90 (m, 2 H, ArH), 6.78 (d, J = 8.5 Hz, 1 H, ArH), 5.84–5.93 (m, 1 H, CH=), 5.26 (d, J = 17.5 Hz, 1 H), 5.18 (d, J = 10.0 Hz, 1 H), 4.99–5.06 (m, 1 H, OCH), 4.31 (q, J = 7.0 Hz, 2 H, CH_3CH_2O), 4.00–4.10 (m, 2 H), 3.58–3.69 (m, 2 H), 3.23–3.32 (m, 1 H), 2.98–3.06 (m, 1 H), 1.35 (t, J = 7.0 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.4, 163.4, 134.2, 130.9, 126.7, 126.6, 122.9, 117.5, 109.0, 82.7, 72.4, 71.8, 60.5, 31.3, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2980, 2903, 1706, 1610, 1487, 1264, 1165, 1084, 768 cm^{-1}. MS (EI): m/z (%) = 262 (73) $[M]^+$, 217 (39), 204 (100), 191 (38), 175 (27). HRMS (EI-TOF): calcd. for $C_{15}H_{18}O_4$ $[M]^+$ 262.1205; found 262.1201.

2-[(Allyloxy)methyl]-5-methyl-2,3-dihydrobenzofuran (3k): Yield 38 mg, 37%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (s,

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1 H, ArH), 6.91 (d, J = 8.0 Hz, 1 H, ArH), 6.71 (d, J = 8.0 Hz, 1 H, ArH), 5.86–6.00 (m, 1 H, CH=), 5.30 (dd, J = 17.0, J = 1.4 Hz, 1 H), 5.21 (d, J = 10.0 Hz, 1 H), 4.90–5.00 (m, 1 H, OCH), 4.02–4.16 (m, 2 H), 3.56–3.72 (m, 2 H), 3.18–3.28 (m, 1 H), 2.90–3.02 (m, 1 H), 2.28 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 134.5, 129.6, 128.2, 126.2, 125.5, 117.4, 109.0, 81.4, 72.4, 72.1, 32.2, 20.7 ppm. IR (thin film): $\tilde{\nu}$ = 2978, 2903, 1489, 1451, 1404, 1246, 1072, 922, 807 cm^{-1}. MS (EI): m/z (%) = 204 (100) $[M]^+$, 163 (13), 145 (100), 133 (100), 115 (22), 105 (100). HRMS (EI-TOF): calcd. for $C_{13}H_{16}O_2$ $[M]^+$ 204.1150; found 204.1151.

***trans*-8-Methyl-6-phenyl-1,2,3,4,4a,9b-hexahydrodibenzo[*b*,*d*]furan (3l):** Yield 71 mg, 54%, red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (dd, J = 8.5, J = 1.5 Hz, 2 H, ArH), 7.43 (t, J = 7.8 Hz, 2 H, ArH), 7.29–7.33 (m, 1 H, ArH), 7.12 (s, 1 H, ArH), 6.93 (s, 1 H, ArH), 3.85–3.91 (m, 1 H, OCH), 2.80–2.85 (m, 1 H, ArC*H*), 2.37 (s, 3 H, CH_3), 2.31–2.36 (m, 2 H), 1.95–2.02 (m, 1 H), 1.80–1.92 (m, 2 H), 1.37–1.50 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.4, 137.4, 133.0, 130.4, 128.4, 128.3, 127.8, 126.9, 123.5, 122.2, 90.6, 48.6, 30.8, 27.3, 25.5, 24.6, 20.9 ppm. IR (thin film): $\tilde{\nu}$ = 2978, 2906, 1499, 1450, 1388, 1251, 1197, 1073 cm^{-1}. MS (EI): m/z (%) = 264 (100) $[M]^+$, 249 (13), 235 (15), 221 (30), 197 (26). HRMS (EI-TOF): calcd. for $C_{19}H_{20}O$ $[M]^+$ 264.1514; found 264.1519.

***trans*-6-Allyl-8-methyl-1,2,3,4,4a,9b-hexahydrodibenzo[*b*,*d*]furan (3m):** Yield 59 mg, 52%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 1 H, ArH), 6.78 (s, 1 H, ArH), 5.96–6.06 (m, 1 H, CH=), 5.05–5.13 (m, 2 H, CH_2=), 3.78–3.84 (m, 1 H, OCH), 3.35 (dd, J = 6.6, J = 1.4 Hz, 2 H, CH_2CH=), 2.76 (t, J = 12.0 Hz, 1 H), 2.30–2.36 (m, 2 H), 2.29 (s, 3 H, CH_3), 1.95–1.98 (m, 1 H), 1.80–1.88 (m, 2 H), 1.35–1.46 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0, 136.6, 131.8, 130.0, 128.3, 121.7, 120.9, 115.5, 90.4, 48.8, 33.7, 30.8, 27.3, 25.5, 24.6, 20.9 ppm. IR (thin film): $\tilde{\nu}$ = 2975, 2933, 1451, 1388, 1254, 1213, 1055, 858, 832 cm^{-1}. MS (EI): m/z (%) = 228 (100) $[M]^+$, 213 (21), 199 (22), 185 (34), 161 (33). HRMS (EI-TOF): calcd. for $C_{16}H_{20}O$ $[M]^+$ 228.1514; found 228.1521.

Ethyl 4-(2,5-Dimethyl-2,3-dihydrobenzofuran-7-yl)benzoate (3n): Yield 86 mg, 58%, white solid, m.p. 47–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.4 Hz, 2 H, ArH), 7.79 (d, J = 8.4 Hz, 2 H, ArH), 7.12 (s, 1 H, ArH), 7.00 (s, 1 H, ArH), 4.90–5.05 (m, 1 H, ArOC*H*), 4.39 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.33 (dd, J = 15.6, J = 8.8 Hz, 1 H), 2.84 (dd, J = 15.2, J = 7.6 Hz, 1 H), 2.34 (s, 3 H, CH_3), 1.49 (d, J = 6.4 Hz, 3 H CH_3CH), 1.41 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 154.9, 142.1, 130.0, 129.5, 128.6, 128.3, 128.1, 127.9, 125.6, 121.5, 79.7, 60.8, 37.1, 21.8, 20.8, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3671, 2978, 2903, 1702, 1463, 1395, 1259, 1071 cm^{-1}. MS (EI): m/z (%) = 296 (100) $[M]^+$, 281 (3), 268 (7), 251 (19). HRMS (EI-TOF): calcd. for $C_{19}H_{20}O_3$ $[M]^+$ 296.1412; found 296.1407.

Ethyl 4-(2,2,5-Trimethyl-2,3-dihydrobenzofuran-7-yl)benzoate (3o): Yield 95 mg, 61%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.4 Hz, 2 H, ArH), 7.80 (d, J = 8.4 Hz, 2 H, ArH), 7.13 (s, 1 H, ArH), 6.98 (s, 1 H, ArH), 4.40 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 3.03 (s, 2 H, CH_2), 2.34 (s, 3 H, ArCH_3), 1.50 (s, 6 H, 2 CH_3), 1.41 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 154.4, 142.3, 129.6, 129.5, 128.45, 128.40, 128.0, 127.9, 125.7, 121.5, 86.7, 60.8, 42.8, 28.2, 20.8, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2974, 1713, 1608, 1465, 1392, 1369, 1269, 1100, 1022, 853 cm^{-1}. MS (EI): m/z (%) = 310 (100) $[M]^+$, 295 (31), 265 (31), 222 (22), 195 (25). HRMS (EI-TOF): calcd. for $C_{20}H_{22}O_3$ $[M]^+$ 310.1569; found 310.1570.

Ethyl 4-[(5a*S*,9a*R*)-2-Fluoro-5a,6,7,8,9,9a-hexahydrodibenzo[*b*,*d*]-furan-4-]benzoate (3p): Yield 47 mg, 27%, white solid, m.p. 86–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.5 Hz, 2 H, ArH), 7.78 (d, J = 8.5 Hz, 2 H, ArH), 7.03 (dd, J = 10.5, J = 2.0 Hz, 1 H, ArH), 6.84 (dd, J = 6.0, J = 1.0 Hz, 1 H, ArH), 4.39 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.91 (m, 1 H, OCH), 2.83 (t, J = 12.3 Hz, 1 H), 2.25–2.45 (m, 2 H), 1.75–2.05 (m, 3 H), 1.30–1.40 (m, 3 H), 1.41 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.4, 157.9 (d, $J_{C,F}$ = 238.1 Hz), 153.5, 140.7, 134.8 (d, $J_{C,F}$ = 7.5 Hz), 129.7, 129.2, 128.2, 122.9 (d, $J_{C,F}$ = 8.1 Hz), 112.9 (d, $J_{C,F}$ = 23.1 Hz), 109.8 (d, $J_{C,F}$ = 25.5 Hz), 91.1, 60.9, 48.6, 30.7, 27.0, 25.3, 24.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2972, 1707, 1608, 1387, 1267, 1100, 1075, 1021, 794, 778 cm^{-1}. MS (EI): m/z (%) = 340 (100) $[M]^+$, 325 (4), 311 (9), 295 (15). HRMS (EI-TOF): calcd. for $C_{21}H_{21}FO_3$ $[M]^+$ 340.1475; found 340.1479.

Ethyl 2,2-Dimethyl-2,3-dihydrobenzofuran-5-carboxylate (3q): Yield 86 mg, 78%, pink oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.8 Hz, 1 H, ArH), 7.83 (s, 1 H, ArH), 6.72 (d, J = 8.4 Hz, 1 H, ArH), 4.32 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.02 (s, 2 H, CH_2), 1.48 (s, 6 H, 2 CH_3), 1.36 (t, J = 7.2 Hz, 3 H, CH_3CH$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 162.8, 131.0, 127.4, 126.9, 122.5, 109.1, 88.3, 60.5, 42.2, 28.1, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 2975, 1708, 1611, 1486, 1386, 1269, 1094, 873, 768 cm^{-1}. MS (EI): m/z (%) = 220 (100) $[M]^+$, 205 (62), 192 (26), 175 (100), 159 (11), 147 (70), 133 (82). HRMS (EI-TOF): calcd. for $C_{13}H_{16}O_3$ $[M]^+$ 220.1099; found 220.1097.

5-Bromo-2,2-dimethyl-2,3-dihydrobenzofuran (3r): Yield 46 mg, 40%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (s, 1 H, ArH), 7.19 (d, J = 8.8 Hz, 1 H, ArH), 6.60 (d, J = 8.4 Hz, 1 H, ArH), 2.99 (s, 2 H, CH_2), 1.46 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 130.7, 129.6, 128.1, 111.6, 111.0, 87.5, 42.7, 28.1 ppm. IR (thin film): $\tilde{\nu}$ = 2971, 2904, 1392, 1311, 1266, 1227, 1072, 827 cm^{-1}. MS (EI): m/z (%) = 228 (2) [M, $Br^{81}]^+$, 226 (2) [M, $Br^{79}]^+$, 211 (22), 185 (5), 147 (9), 132 (100). HRMS (EI-TOF): calcd. for $C_{10}H_{11}BrO$ $[M]^+$ 225.9993; found 225.9993.

***trans*-8-Bromo-1,2,3,4,4a,9b-hexahydrodibenzo[*b*,*d*]furan (3s):** Yield 55 mg, 43%, white solid, m.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 7.2 Hz, 1 H, ArH), 7.20 (s, 1 H, ArH), 6.71 (d, J = 8.8 Hz, 1 H, ArH), 3.86 (dt, J = 12.8, J = 3.7 Hz, 1 H, OCH), 2.79 (t, J = 12.0 Hz, 1 H, CH), 2.29–2.33 (m, 2 H), 1.95–1.98 (m, 1 H), 1.75–1.88 (m, 2 H), 1.33–1.47 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 134.6, 130.3, 125.7, 112.8, 111.5, 91.0, 48.7, 30.6, 27.0, 25.4, 24.4 ppm. IR (thin film): $\tilde{\nu}$ = 2931, 2860, 1452, 1215, 1176, 1010, 816 cm^{-1}. MS (EI): m/z (%) = 254 (54) [M, $Br^{81}]^+$, 252 (54) [M, $Br^{79}]^+$, 239 (10), 225 (13), 211 (31), 198 (33), 145 (43), 132 (40), 115 (45), 77 (33), 67 (100). HRMS (EI-TOF): calcd. for $C_{12}H_{13}BrO$ $[M]^+$ 252.0150; found 252.0145.

Ethyl 6*H*-Benzo[*c*]chromene-2-carboxylate (3t): Yield 62 mg, 48%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 2.0 Hz, 1 H, ArH), 7.93 (dd, J = 8.4, J = 2.0 Hz, 1 H, ArH), 7.80 (d, J = 7.6 Hz, 1 H, ArH), 7.41 (t, J = 7.6 Hz, 1 H, ArH), 7.29 (t, J = 7.6 Hz, 1 H, ArH), 7.15 (d, J = 8.0 Hz, 1 H, ArH), 7.00 (d, J = 8.8 Hz, 1 H, ArH), 5.18 (s, 2 H, CH_2O), 4.29 (q, J = 6.9 Hz, 2 H, CH_3CH_2O), 1.42 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 158.5, 131.0, 130.7, 129.1, 128.7, 128.2, 125.2, 124.6, 124.3, 122.4, 122.2, 117.3, 68.6, 60.8, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 2979, 2903, 1709, 1610, 1449, 1239, 1102, 1029, 770, 726 cm^{-1}. MS (EI): m/z (%) = 254 (100) $[M]^+$, 239 (2), 225 (46), 209 (55). HRMS (EI-TOF): calcd. for $C_{16}H_{14}O_3$ $[M]^+$ 254.0943; found 254.0940.

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Ethyl 6-Ethyl-6*H*-benzo[*c*]chromene-2-carboxylate (3u): Yield 81 mg, 57%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, ArH), 7.95 (d, J = 8.4 Hz, 1 H, ArH), 7.81 (d, J = 8.0 Hz, 1 H, ArH), 7.40 (t, J = 7.2 Hz, 1 H, ArH), 7.32 (t, J = 7.6 Hz, 1 H, ArH), 7.12 (d, J = 6.8 Hz, 1 H, ArH), 7.01 (d, J = 8.4 Hz, 1 H, ArH), 5.10–5.18 (m, 1 H, C*H*CH_2), 4.40 (q, J = 6.8 Hz, 2 H, CH_3CH_2O), 1.85–1.95 (m, 1 H), 1.70–1.80 (m, 1 H), 1.42 (t, J = 6.8 Hz, 3 H, CH_3CH_2O), 1.04 (t, J = 7.6 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 156.9, 134.2, 131.0, 128.3, 128.1, 128.0, 124.91, 124.87, 123.9, 122.4, 122.1, 117.8, 79.4, 60.8, 28.3, 14.4, 9.9 ppm. IR (thin film): $\tilde{\nu}$ = 2975, 1711, 1241 cm^{-1}. MS (EI): m/z (%) = 282 (2) $[M]^+$, 252 (100), 225 (50). HRMS (EI-TOF): calcd. for $C_{18}H_{18}O_3$ $[M]^+$ 282.1256; found 282.1247.

Ethyl 6-Isopropyl-6*H*-benzo[*c*]chromene-2-carboxylate (3v): Yield 65 mg, 44%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 2.0 Hz, 1 H, ArH), 7.93 (dd, J = 8.4, J = 1.6 Hz, 1 H, ArH), 7.81 (d, J = 8.0 Hz, 1 H, ArH), 7.40 (dt, J = 7.8, J = 1.1 Hz, 1 H, ArH), 7.30 (dt, J = 7.2, J = 0.8 Hz, 1 H, ArH), 7.10 (d, J = 7.2 Hz, 1 H, ArH), 7.00 (d, J = 8.4 Hz, 1 H, ArH), 4.85 (d, J = 7.6 Hz, 1 H, OCH), 4.39 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 1.96–2.05 [m, 1 H, C*H*$(CH_3)_2$], 1.41 (t, J = 7.0 Hz, 3 H, CH_3CH_2O), 1.01 (d, J = 6.4 Hz, 3 H, CH_3CH), 0.89 (d, J = 6.8 Hz, 3 H, CH_3CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 157.2, 132.9, 131.0, 128.31, 128.27, 127.6, 126.3, 124.8, 123.7, 122.4, 122.2, 117.5, 83.6, 60.7, 32.6, 18.8, 18.3, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 2972, 1711, 1609, 1494, 1448, 1367, 1241, 1103, 1002 cm^{-1}. MS (EI): m/z (%) = 296 (7) $[M]^+$, 253 (100), 225 (42), 180 (12), 152 (15). HRMS (EI-TOF): calcd. for $C_{19}H_{20}O_3$ $[M]^+$ 296.1412; found 296.1407.

Supporting Information (see footnote on the first page of this article): experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra for all products, and crystallographic information file (CIF) for compound **3a**.

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[17] CCDC-847960 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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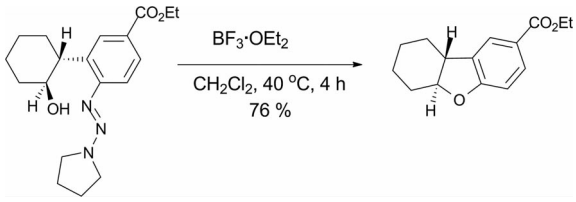

Highly functionalized dihydrobenzofuran derivatives can be prepared from triazene alcohols in the presence of a Lewis acid. The cyclization of optically active triazene alcohols is also discussed in this paper.

Keywords: Synthetic methods / Oxygen heterocycles / Carbocations / Lewis acids / Cyclization

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