Supporting Information

for

A toolbox of molecular photoswitches to modulate the CXCR3 chemokine receptor with light

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Computational methods

The small molecules were built and optimized using MOE (Molecular Operating Environment, version 2016.0802). A conformational analysis using the stochastic search method (default settings) was performed to obtain the ideal conformation of the azobenzene moieties (taken from the global energy minimum conformation). The potential of the azobenzene atoms was fixed to ensure an optimal conformation throughout molecular superpositions. The three-dimensional structures of 1e and the azobenzene analogues (trans- and cis-2a) were superposed using the flexible alignment module, using volume as the similarity term (weight 3). Other settings were used as default. For the superposition of trans-2a with 1e, the alignment with the lowest alignment score S of −75.5234 was selected, which is the sum of the average strain energy U (95.8843 kcal/mol) and the similarity score F (−171.4077) values. The same procedure was used with 1e and cis-2a, leading to the best alignment with S, U and F values of −197.7601, 95.3657 kcal/mol and −293.1258, respectively.
Photochemistry procedures

The photochemistry procedures are the same or similar to those published previously by us [1].

UV–vis spectra were obtained using a Thermo-scientific Evolution 201 PC spectrophotometer. Fits of UV–vis spectroscopy data were generated using GraphPad Prism 6 or 7 software. Illumination was executed using a Sutter instruments Lambda LS with a 300 Watt full-spectrum lamp connected to a Sutter instruments Lambda 10-3 optical filter changer equipped with 494 ± 9 nm, 460 ± 5 nm, 434 ± 9 nm and 360 ± 20 nm filters. The light intensity is 0.77 mW/mm² for the 360 ± 20 nm filter, 0.57 mW/mm² for the 434 ± 9 nm filter, 0.26 mW/mm² for the 460 ± 5 nm filter and 0.77 mW/mm² for the 494 ± 9 nm filter as measured using a Thorlabs PM16-401 power meter. For the determination of UV–vis spectra, the cis-to-trans thermal relaxation or the cis-to-trans back isomerisation, illuminations were performed in Hellma Suprasil™ quartz 114-QS cuvettes with a 360 nm, 434 nm, 460 nm or 494 nm filter during 2 min. Samples were 25 µM in PBS buffer + 1% DMSO.

Selected cis-to-trans thermal relaxations were performed in the dark at 10 µM PSS360 in HEPES solution with 1% DMSO, either by prolonged measuring at 25 ºC (4d, 6f) [1] or by an Arrhenius extrapolation method from measurements at higher temperatures (6e, Figure S3) [2].

Illuminations for pharmacological experiments were performed in cylindrical clear glass vials with a volume of 150 µL during 30 min with a 360-nm filter. Samples were 1.0 mM in a mixture of 68 vol % TRIS binding buffer and 32 vol % DMSO, or 1.0 mM in a mixture of 68 vol % HEPES binding buffer and 32 vol % DMSO (for [35S]-GTPγS binding experiments). For compounds 6e,g,h, irradiation was performed at 3.16 mM in 100 % DMSO and subsequent dilution adapted accordingly. The photoisomerization and photostability was monitored by LC-PDA for all the samples. The typical distance between light source and vial or cuvette was 2 cm.
Figure S1. (A) UV–vis absorption spectra of compounds as trans- or as PSS-forms after irradiation with various different wavelengths. (B) Overlay of UV–vis absorption spectra of PSS360 forms of 6b, 4d, 6d and 6e (having substituent Y = F, Cl, Br and I respectively) and 6f, 6g and 6h (having Y = OMe, O-iPr and SMe, respectively).
Figure S2. Monitoring of photoisomerisation over time of 4d (10 mM in DMSO-$_d_6$) from trans to PSS cis ($\lambda = 360$ nm) and from PSS cis to PSS trans ($\lambda = 434$ nm) as followed by $^1$H NMR spectroscopy (integration of $\alpha$-ammonium-methylene protons) and LC-PDA-MS analysis (integration at 276 nm).
Figure S3. Arrhenius plot for 6e measured at a concentration of 10 μM in HEPES buffer with 1% DMSO-
$^d_6$. The value provided in the main text is an extrapolation of the linear fit presented in this plot. The
$R^2$ value for linear fit was over 0.999.
Pharmacology procedures

The pharmacology procedures are the same or similar to those published previously by us [1].

Cell culture and transfection: Human embryonic kidney 293T (HEK293T) cells were cultured at 37 °C and 5% CO₂ in Dulbecco's modified Eagle's medium (Thermo Scientific, Waltham, MA, USA) supplemented with 10% fetal bovine serum (Bodinco, Alkmaar, The Netherlands), 50 IU/mL penicillin and 50 µg/mL streptomycin (Thermo Scientific). Cells were transfected using linear polyethyleneimine (PEI) with a molecular weight of 25 kDa (Polysciences, Warrington, PA, USA). Briefly, 1 µg cDNA encoding human CXCR3 (isoform A) and 4 µg empty vector pcDEF3 (a gift from Dr. Langer, Robert Wood Johnson Medical School, Piscataway, NJ, USA) was diluted in a total volume of 250 µL NaCl solution (150 mM). Next, 30 µg PEI diluted in a total volume of 250 µL NaCl solution was added to the DNA solution, mixed and incubated for 20 min at 22 °C. The DNA/PEI mixture was subsequently added to the medium of adherent HEK293T cells.

Membrane preparation: Membranes were prepared as previously described [3]. In brief, 48 h post-transfection, CXCR3-expressing HEK293T cells were collected in phosphate buffered saline (PBS). Then, cells were subsequently centrifuged at 1500xg for 10 min at 4 °C and washed with PBS. The cell pellet was resuspended in ice-cold membrane buffer (15 mM Tris, pH 7.5, 1 mM EGTA, 0.3 mM EDTA and 2 mM MgCl₂) and homogenized using a Teflon-glass potter. Next, the membranes were frozen in liquid N₂ and thawed twice and subsequently centrifuged at 40.000xg for 25 min at 4°C. The pellet was resuspended in Tris-sucreose buffer (20 mM Tris, pH 7.4, 250 mM sucrose) and further homogenized through a 23G needle. Aliquots were quickly frozen in liquid nitrogen and stored at −80 °C.

[^H]-VUF11211 binding assay: [^H]-VUF11211 binding was performed as previously described [3]. In brief, CXCR3 membranes were incubated in black 96-well plates with increasing concentrations photoswitchable ligand and 1 nM [^H]VUF11211 (PerkinElmer Life Sciences, Boston, MA, USA, 38.4 Ci/mmol) in binding buffer (50 mM Tris-HCl, pH 7.4, 100 mM NaCl, 0.1% (w/v) Tween80, 0.1% (w/v) BSA fraction V) for 2 h at 25 °C (shaking at 600 rpm and protected from light). After incubation, the membranes were harvested by rapid filtration and washing with ice-cold wash buffer (50 mM Tris-HCl, pH 7.4, 0.5 M NaCl) over 96-well GF/C filter plates (PerkinElmer) that were presoaked in 0.5% w/v BSA/H₂O. The GF/C plates were dried and scintillation liquid was added to determine bound radioactivity with a MicroBeta scintillation counter (PerkinElmer).

[^S]-GTPyS binding assay: [^S]-GTPyS binding was performed as previously described [4]. Briefly, 5 µg/well CXCR3-membranes were incubated in a black 96-well plate with indicated concentrations of photoswitchable ligand and 300 pM [^S]GTP NPD-3079S (PerkinElmer, 1250 Ci/mmol) in assay buffer (50 mM HEPES, 10 mM MgCl₂, and 100 mM NaCl, pH 7.2), supplemented with 3 µM GDP (Sigma-Aldrich) and 5 µg/well saponin for 1 h at 25 °C (shaking at 600 rpm and protected from light). Next, the CXCR3 membranes were harvested by rapid filtration through Unifilter GF/B plates (PerkinElmer) using ice-cold washing buffer (50 mM Tris-HCl, pH 7.4, 5 mM MgCl₂) and scintillation liquid was added after drying the GF/B plates. [^S]GTPyS membrane binding was determined using a Microbeta scintillation counter (PerkinElmer) and the response was normalized to that of the endogenous agonist CXCL11 (PeproTech, Rocky Hill, NJ, USA) to determine the relative efficacy of the photoswitchable ligands (α value).

Data analysis: GraphPad Prism 6, 7 or 8 software (GraphPad Software, San Diego) was used for plotting radioligand displacement curves and sigmoidal concentration-response curves and to
determine IC$_{50}$ and pEC$_{50}$ values, respectively, by nonlinear regression. The IC$_{50}$ values were converted to $K_i$ values using the method of Cheng and Prusoff [5]. Statistical analyses were performed using Graphpad Prism 6, 7 or 8 software.
Figure S4. Full functional dose-response curves for compounds 3e, 4d, 6b and 6d-h in trans (turquoise) or PSS360 (magenta) form. Dose-response curves for compounds 3e, 4d, 6b, 6d and 6f have been published by us before [1].
Synthesis methods and procedures

Unless mentioned otherwise, all reactions were performed under N₂ atmosphere. All chemicals and solvents were obtained from commercial suppliers (primarily Sigma-Aldrich, Acros Organics, Fluorochem and Combi-Blocks) and used without purification. DCM, DMF, THF and Et₂O were dried by passing through a PureSolv solvent purification system. Triethylamine (TEA) was dried over alumina. Compounds 2–6 were synthesized according the procedures detailed below. Compound 6i and 7 were synthesized as reported previously [1,6]. Reactions were monitored by thin layer chromatography (Merck Silicagel 60 F254) by visualization under 254 nm lamp or under natural light conditions (for colored compounds). Flash column chromatography was performed with SNAP KP-Sil 50 µm (Biotage) or GraceResolv (Büchi) cartridges on Isolera One with UV–vis detection (Biotage).

Nuclear magnetic resonance (NMR) spectra were determined with a Bruker Avance 500 Ultrashield or a Bruker Avance 600 Ultrashield plus spectrometer. Chemical shifts are reported in parts per million (ppm) against the reference compound using the signal of the residual non-deuterated solvent (CDCl₃ δ = 7.26 ppm (¹H), δ = 77.16 ppm (¹³C)). NMR spectra were processed using MestreNova 10.0.2 software. The peak multiplicities are defined as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; ddd, doublet of doublets of doublets; d, doublet of triplets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; tt, triplet of triplets; br, broad signal; m, multiplet; app, apparent.

Purity determination was performed with Liquid Chromatography using a Shimadzu LC-20AD liquid chromatography pump system with a Shimadzu SPDM20A photodiode array detector and MS detection with a Shimadzu LC-MS-2010EV mass spectrometer operating in both positive and negative ionization mode. A Waters XBridge C18 column 5 µm 4.6 × 50 mm was used at 40 °C. The mobile phase used was a mixture of A = water + 0.1% HCO₂H and B = acetonitrile (MeCN) + 0.1% HCO₂H. The eluent program used is as follows: flow rate: 1.0 mL/min, start 95% A in a linear gradient to 10% A over 4.5 min, hold 1.5 min at 10% A, in 0.5 min in a linear gradient to 95% A, hold 1.5 min at 95% A, total runtime: 8.0 min. Compound purities were calculated as the percentage peak area of the analyzed compound by UV detection at 254 nm. All chemistry and analyses of photosensitive compounds were carried out under dimmed or red light. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF mass spectrometer using ESI in positive ion mode (HRMS).

General synthetic procedures

Many general synthetic procedures are the same or similar to those published previously by us [1].

**General synthetic procedure A for compounds 9a–c, 13f–h, 14e and 16b,d–h:** In a round-bottom flask, compound 7 (1.0–1.3 equiv) and 8a–c, 26f–h, 27 or 28b,d–h (1.0 equiv) were dissolved in DCE. TEA (1.1–1.6 equiv) was added. The solution was stirred at rt for 30 min. Subsequently, NaBH(OAc)₃ (1.6 equiv) was added and the solution was stirred from 6 to 16 h at rt. After that, aq. Na₂CO₃ (2 M) was added and the resulting mixture was stirred for 10 min. DCM was added. The layers were separated and the aqueous layer was extracted twice with DCM. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give a residue, which was purified with automated flash chromatography (cHex/EtOAc + 1% TEA) to give compounds 9a–c, 13f–h, 14e and 16b,d–h as a colourless/orange oil with high purity.

**General synthetic procedure B for compounds 10a–c:** In a round bottom flask, a mixture of compound 9a–c (1.0 equiv) and SnCl₂·2H₂O (5 equiv) in EtOH was stirred for 2 h at 75 °C. Subsequently, the mixture was filtered through Celite and washed with DCM. The resulting solution was washed twice with aq. Na₂CO₃ (2 M), dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give
compounds 10a–c as yellow oils, which were used without further purification.

**General synthetic procedure C for compounds 12a–e, 13a–e, 14a–d, 14f–i and 15b,c**: A solution of Oxone™ (3.0 equiv) in water (4 vol) was added to a solution of the corresponding aniline (1.5 equiv) in DCM (1 vol). The resulting mixture was stirred vigorously at rt during 2 h. Water was added and the layers were separated. The green organic layer was washed with aq. HCl (1 M), water and brine. The resulting green nitrosobenzene solution was used directly by mixing with the corresponding aniline (1.0 equiv). For the preparation of compound 12a and 13a, the commercially available nitrosobenzene (11a) was directly used (1.5 equiv) dissolved in DCM. Two drops of AcOH were added and the resulting solution was left stirring for 1–5 d protected from light. Subsequently, the solvents were removed in vacuo and the resulting dark residue was purified with automated flash chromatography (cHex/DCM/EtOAc + 1% TEA) to give compounds 12a–e, 13a–e, 14a–d, 14f–i and 15b,c as an orange/red oil with high purity.

**General synthetic procedure D for compounds 2a–e, 3a–h, 4a–6, 5b,c, 6b and 6d–i**: In a round-bottom flask, the tertiary amine precursor 12a–e, 13a–h, 14a–6, 15b,c, 16b and 16d–i (1.0 equiv) was dissolved in DCM. The flask was closed with a septum and protected from light. Excess Mel (20 equiv) was added to the solution via a syringe. The reaction mixture was stirred at rt in the dark during 6–72 h. The reaction mixture was cooled in an ice bath, and MTBE (3 vol equiv with respect to DCM) was added slowly. This induced precipitation of the salt, which was filtered and washed with a precooled solution of DCM/MTBE (1:3). This delivered the product 2a–e, 3a–h, 4a–6, 5b,c, 6b and 6d–i as an orange solid with high purity.

**General synthetic procedure E for compounds 18a–d**: A solution of Oxone™ (2.0 equiv) in water (4 vol) was added to a solution of the corresponding aniline 17a–d (1.0 equiv) in DCM (1 vol). The resulting mixture was stirred vigorously at rt during 2 h. Water was added and the layers were separated. The green organic layer was washed with aq. HCl (1 M), water and brine, dried over Na2SO4 and concentrated to give the corresponding nitrosocompound 18a–d, which was used without further purification.

**General synthetic procedure F for compounds 20f–h, 21, 22b and 22d**: The corresponding nitrosocompound 18a–d (1.1–1.5 equiv) and the corresponding aniline 19a–d (1.0 equiv) were dissolved in AcOH. The mixture was stirred at 100 °C for 16–20 h protected from light. Subsequently, the solvents were removed in vacuo and the resulting dark residue was purified with automated flash chromatography (cHex/DCM) to give compound 20f–h, 21, 22b or 22d as an orange/red solid with high purity.

**General synthetic procedure G for compounds 23f–g, 24, 25b and 25d**: The corresponding azobenzoates 20f–g, 21, 22b or 22d (1.0 equiv) were dissolved in THF. DIBAL-H (3–4 equiv, 1.0 M in THF) was added slowly at 0–5 °C. The reaction mixture was warmed slowly to rt and stirred for 2–4 h. After that, the reaction was quenched with satd. aq. NH4Cl. Aq. Rochelle Salt (10%) and EtOAc were added and the resulting mixture was stirred at room temperature 1–2 h. The layers were separated. The organic phase was washed with brine, dried over MgSO4, filtered and the solvent was removed in vacuo. The resulting residue (orange/red oil) corresponded to the expected products with high purity (23g, 25b, 25c) or were purified with automated flash chromatography (cHex/DCM) to give alcohols (23f, 24) as an orange/red oil with high purity.

**General synthetic procedure H for compounds 26f–h, 27, 28b and 28d**: The corresponding alcohols
23f-g, 24, 25b or 25d (1.0 equiv) and Dess Martin periodinane (1.0 equiv) were dissolved in DCM. The resulting red solution was stirred for 1–2 h at rt. After that, satd. aq. NaHCO₃ and EtOAc were added and the layers were separated. The organic layer was washed with satd. aq. NaHCO₃ (twice), water and brine, dried over MgSO₄ and concentrated in vacuo. The residue obtained was purified with automated flash chromatography (cHex/DCM or cHex/EtOAc) to give benzaldehyde 23f-g, 24, 25b or 25d as an orange/red oil with high purity.

**Detailed synthetic procedures and characterisation of compounds**

![Scheme S1](image)

**Scheme S1**: Synthetic strategies for compounds 2a–e, 3a–e, 4a–d, 4f–i and 5b,c. GSP = General Synthetic Procedure.

1-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methyl-N-(4-nitrobenzyl)methanamine (9a): The general synthetic procedure A was used with ammonium salt 7 (2.00 g, 9.9 mmol), TEA (1.5 mL, 10.8 mmol) and 4-nitrobenzaldehyde (8a) (1.42 g, 9.4 mmol) in DCE (50 mL) to give the nitrocompound 9a as a colourless oil (2.74 g, 97%). ¹H NMR (600 MHz, CDCl₃) δ 8.15 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 5.47–5.38 (m, 1H), 3.59 (d, J = 14.3 Hz, 1H), 3.44 (d, J = 14.2 Hz, 1H), 2.92 (app. dq, J = 13.1, 1.8 Hz, 1H), 2.84 (app. dq, J = 13.0, 1.3 Hz, 1H), 2.40 (dt, J = 8.6, 5.6 Hz, 1H), 2.33–2.18 (m, 3H), 2.12 (s, 3H), 2.12–2.05 (m, 1H), 1.29 (s, 3H), 1.11 (d, J = 8.6 Hz, 1H), 0.81 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 148.11, 147.07, 146.13, 129.29, 123.53, 120.35, 63.87, 60.84, 44.34, 42.78, 41.00, 38.06, 31.91, 31.48, 26.40, 21.21. HPLC-PDA-MS: RT = 3.34 min, 99.1% (254 nm), PDA λ max = 262 nm, MS (m/z) [M+H]⁺ 301.15.

1-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methyl-N-(3-nitrobenzyl)methanamine
(9b): The synthesis and characterization of this compound have been published by us [1].

\[ N-(2\text{-Chloro-5-nitrobenzyl})-1-((1R,5S)-6,6\text{-dimethylbicyclo[3.1.1]hept-2-en-2-yl})-N\text{-methyl methanamine (9c):} \]

The synthesis and characterization of this compound have been published by us [1].

\[ 4-(((1R,5S)-6,6\text{-Dimethylbicyclo[3.1.1]hept-2-en-2-yl})\text{-methyl})(\text{methyl})\text{amino}methyl)aniline (10a): \]

The general synthetic procedure B was used with nitrocompound 9a (1.36 g, 4.5 mmol) and SnCl\textsubscript{2}\cdot2H\textsubscript{2}O (5.10 g, 22.6 mmol) in EtOH (23 mL) to give the aniline 10a as a yellow oil (1.23 g, quant.). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta \) 7.08 (d, 2H), 6.64 (d, \( J = 8.3 \) Hz, 2H), 5.46 – 5.36 (m, 1H), 3.60 (br, 2H), 3.43 (d, \( J = 12.9 \) Hz, 1H), 3.26 (d, \( J = 13.0 \) Hz, 1H), 2.90 (app. dd, \( J = 13.1, 1.9 \) Hz, 1H), 2.79 (app. dd, \( J = 13.1, 1.4 \) Hz, 1H), 2.41 (dt, \( J = 8.6, 5.6 \) Hz, 1H), 2.32 – 2.17 (m, 3H), 2.11 (s, 4H), 1.32 – 1.25 (m, 3H), 1.16 (d, \( J = 8.6 \) Hz, 1H), 0.85 (s, 3H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \( \delta \) 146.52, 145.22, 130.20, 129.41, 119.80, 115.03, 63.53, 61.26, 44.36, 42.43, 41.06, 38.04, 31.98, 31.52, 26.42, 21.25. HPLC-PDA-MS: RT = 3.34 min, 99.1% (254 nm), PDA \( \lambda_{\text{max}} \) = 248, 280 nm, MS (m/z) \text{[M+H]}^+ = 271.20.

\[ 3-(((1R,5S)-6,6\text{-Dimethylbicyclo[3.1.1]hept-2-en-2-yl})\text{-methyl})(\text{methyl})\text{amino}methyl)aniline (10b): \]

The synthesis and characterization of this compound have been published by us [1].

\[ 4\text{-Chloro-}3-(((1R,5S)-6,6\text{-dimethylbicyclo[3.1.1]hept-2-en-2-yl})\text{-methyl})(\text{methyl})\text{amino}methyl)aniline (10c): \]

The synthesis and characterization of this compound have been published by us [1].

\[ 1-((1R,5S)-6,6\text{-Dimethylbicyclo[3.1.1]hept-2-en-2-yl})-N\text{-methyl-N-}(4-(\text{E-phenyldiazenyl})benzyl) methanamine (12a): \]

The general synthetic procedure C was used with nitrosobenzene (11a) (45 mg, 0.42 mmol) and the aniline 10a (103 mg, 0.38 mmol) in DCM (2 mL) to give the azocompound 12a as an orange oil (70 mg, 51%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.91 (d, \( J = 7.1 \) Hz, 2H), 7.87 (d, \( J = 8.3 \) Hz, 2H), 7.52 (t, \( J = 7.4 \) Hz, 2H), 7.49 – 7.43 (m, 3H), 5.44 (br, 1H), 3.61 (d, \( J = 13.6 \) Hz, 1H), 3.44 (d, \( J = 13.6 \) Hz, 1H), 2.96 (d, \( J = 13.1 \) Hz, 1H), 2.86 (d, \( J = 13.0 \) Hz, 1H), 2.43 (dt, \( J = 8.5, 5.6 \) Hz, 1H), 2.39 – 2.20 (m, 3H),
2.17 (s, 3H), 2.14 – 2.06 (m, 1H), 1.31 (s, 3H), 1.16 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 152.84, 151.87, 146.40, 143.38, 130.95, 129.63, 129.21, 122.90, 122.85, 120.13, 63.81, 61.39, 44.35, 42.78, 41.03, 38.11, 31.99, 31.54, 26.43, 21.27. HPLC-PDA-MS: RT = 4.64 min, 96.9% (254 nm), PDA λmax = 320 nm, MS (m/z) [M+H]+ 360.25.

**N-(4-[(E)-(2-Chlorophenyl)diazenyl]benzyl)-1-[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-N-methylmethanamine (12b):** The general synthetic procedure C was used with 2-chloroaniline (125 µL, 1.19 mmol) in DCM (3.6 mL) and Oxone® (1.49 g, 2.4 mmol) in water (14.4 mL), to form the corresponding nitrosocompound 11b, and the aniline 10a (166 mg, 0.61 mmol) in DCM (7 mL) to give the azocompound 12b as an orange oil (167 mg, 69%). 1H NMR (500 MHz, CDCl3) δ 7.93 (d, J = 8.0 Hz, 2H), 7.69 (dd, J = 7.9, 1.6 Hz, 1H), 7.56 (dd, J = 7.9, 1.3 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.39 (td, J = 7.6, 1.7 Hz, 1H), 7.34 (td, J = 7.5, 1.4 Hz, 1H), 5.44 (br, 1H), 3.61 (d, J = 13.7 Hz, 1H), 3.44 (d, J = 12.7 Hz, 1H), 2.96 (d, J = 13.0 Hz, 1H), 2.86 (d, J = 12.1 Hz, 1H), 2.43 (dt, J = 8.5, 5.6 Hz, 1H), 2.38 – 2.20 (m, 3H), 2.17 (s, 3H), 2.14 – 2.05 (m, 1H), 1.31 (s, 3H), 1.16 (d, J = 8.6 Hz, 1H), 0.84 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 152.02, 148.93, 146.47, 144.19, 135.27, 131.61, 130.79, 129.66, 127.42, 123.39, 120.11, 117.73, 63.83, 61.40, 44.36, 42.81, 41.03, 38.12, 31.99, 31.56, 26.43, 21.28. HPLC-PDA-MS: RT = 4.80 min, 89.9% (254 nm), PDA λmax = 323 nm, MS (m/z) [M+H]+ 394.20.

**N-(4-[(E)-(3-Chlorophenyl)diazenyl]benzyl)-1-[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-N-methylmethanamine (12c):** The general synthetic procedure C was used with 3-chloroaniline (37 µL, 0.35 mmol) in DCM (2.0 mL) and Oxone® (424 mg, 0.69 mmol) in water (4.0 mL), to form the corresponding nitrosocompound 11c, and the aniline 10a (70 mg, 0.26 mmol) in DCM (3 mL) to give the azocompound 12c as an orange oil (65 mg, 64%). 1H NMR (600 MHz, CDCl3) δ 7.89 (t, J = 1.9 Hz, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.82 (dt, J = 7.4, 1.7 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.46 – 7.41 (m, 2H), 5.46 – 5.42 (m, 1H), 3.60 (d, J = 13.7 Hz, 1H), 3.44 (d, J = 13.7 Hz, 1H), 2.96 (dd, J = 13.0, 2.0 Hz, 1H), 2.86 (d, J = 13.0 Hz, 1H), 2.43 (dt, J = 8.6, 5.6 Hz, 1H), 2.36 – 2.28 (m, 2H), 2.24 (app. dd, J = 17.6, 3.5 Hz, 1H), 2.17 (s, 3H), 2.14 – 2.09 (m, 1H), 1.31 (s, 3H), 1.16 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 153.69, 151.60, 146.41, 144.10, 135.24, 130.62, 130.23, 129.63, 123.07, 122.44, 121.84, 120.13, 63.87, 61.41, 44.41, 42.81, 41.08, 38.11, 31.99, 31.55, 26.46, 21.28. HPLC-PDA-MS: RT = 5.04 min, 97.0% (254 nm), PDA λmax = 319 nm, MS (m/z) [M+H]+ 394.20.

**N-(4-[(E)-(4-Chlorophenyl)diazenyl]benzyl)-1-[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-N-methylmethanamine (12d):** The general synthetic procedure C was used with 4-chloroaniline (152 mg, 1.19 mmol) in DCM (3.6 mL) and Oxone® (1.50 g, 2.4 mmol) in water (14.4 mL), to form the
corresponding nitrosocompound 11d, and the aniline 10a (162 mg, 0.60 mmol) in DCM (7 mL) to give
the azocompound 12d as an orange oil (102 mg, 43%). 1H NMR (500 MHz, CDCl3) δ 7.86 (d, J = 8.6 Hz, 4H), 7.48 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 7.5 Hz, 2H), 5.44 (br, 1H), 3.60 (d, J = 13.7 Hz, 1H), 3.44 (d, J = 13.7 Hz, 1H), 2.95 (d, J = 13.1 Hz, 1H), 2.85 (d, J = 13.0 Hz, 1H), 2.43 (dt, J = 8.0, 5.6 Hz, 1H), 2.37 – 2.20 (m, 3H), 2.16 (s, 3H), 2.14 – 2.07 (m, 1H), 1.31 (s, 3H), 1.16 (d, J = 8.4 Hz, 1H), 0.85 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 151.40, 150.91, 146.15, 143.56, 136.54, 129.38, 129.19, 123.92, 122.68, 119.86, 63.60, 61.14, 44.08, 42.57, 40.78, 37.85, 31.73, 31.28, 26.18, 21.02. HPLC-PDA-MS: RT = 4.87 min, 94.9% (254 nm), PDA λmax = 326 nm, MS (m/z) [M+H]⁺ 394.20.

1-(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methyl-N-(3-(6-(2-Bromophenyl)diazenyl)benzyl)methanamine (13a): The general synthetic procedure C was used with nitrosobenzene (11a) (47 mg, 0.44 mmol) and the aniline 10b (107 mg, 0.40 mmol) in DCM (2 mL) to give the azocompound 13a as an orange oil (95 mg, 67%). 1H NMR (500 MHz, CDCl3) δ 7.84 – 7.75 (m, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.50 – 7.44 (m, 3H), 5.45 (br, 1H), 3.63 (d, J = 13.4 Hz, 1H), 3.48 (d, J = 13.3 Hz, 1H), 2.98 (app. dd, J = 13.0, 2.0 Hz, 1H), 2.88 (d, J = 13.0 Hz, 1H), 2.44 (dt, J = 8.6, 5.6 Hz, 1H), 2.36 (td, J = 5.7, 1.4 Hz, 1H), 2.28 (app. q, J = 17.7 Hz, 2H), 2.18 (s, 3H), 2.15 – 2.06 (m, 1H), 1.32 (s, 3H), 1.18 (d, J = 8.5 Hz, 1H), 0.86 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 152.81, 152.78, 146.42, 141.08, 131.69, 131.03, 129.21, 129.02, 123.33, 122.94, 121.63, 120.07, 63.83, 61.40, 44.34, 42.72, 41.04, 38.10, 32.00, 31.54, 26.44, 21.28. HPLC-PDA-MS: RT = 4.66 min, 96.1% (254 nm), PDA λmax = 318 nm, MS (m/z) [M+H]⁺ 360.20.
**N-(3-((E)-(2-Chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (13b):** The general synthetic procedure C was used with 2-chloroaniline (63 µL, 0.60 mmol) in DCM (1.8 mL) and Oxone® (0.74 g, 1.2 mmol) in water (7.1 mL), to form the corresponding nitrosocompound 11b, and the aniline 10b (80 mg, 0.30 mmol) in DCM (1.5 mL) to give the azocompound 13b as an orange oil (91 mg, 78%). 1H NMR (600 MHz, CDCl₃) δ 7.92 (t, J = 1.7 Hz, 1H), 7.85 (dd, J = 7.9, 1.7 Hz, 1H), 7.70 (dd, J = 7.9, 1.7 Hz, 1H), 7.56 (dd, J = 7.9, 1.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.39 (td, J = 7.6, 1.8 Hz, 1H), 7.35 (td, J = 7.6, 1.5 Hz, 1H), 5.45 (br, 1H), 3.64 (d, J = 13.4 Hz, 1H), 3.48 (d, J = 13.4 Hz, 1H), 2.98 (app. dd, J = 13.1, 2.0 Hz, 1H), 2.88 (d, J = 13.1 Hz, 1H), 2.44 (dt, J = 8.6, 5.6 Hz, 1H), 2.36 (td, J = 5.7, 1.4 Hz, 1H), 2.31 (app. d, J = 17.6 Hz, 1H), 2.25 (app. dd, J = 17.5, 2.8 Hz, 1H), 2.18 (s, 3H), 2.15 – 2.08 (m, 1H), 1.31 (s, 3H), 1.17 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H). 13C NMR (151 MHz, CDCl₃) δ 152.97, 148.95, 146.46, 141.24, 135.35, 132.23, 131.66, 130.80, 129.07, 127.40, 124.02, 121.92, 120.08, 117.74, 63.87, 61.33, 44.38, 42.71, 41.09, 38.11, 32.01, 31.56, 26.46, 21.29. HPLC-PDA-MS: RT = 4.84 min, 94.0% (254 nm), PDA λ max = 312 nm, MS (m/z) [M+H]+ 394.20.

**N-(3-((E)-(3-Chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (13c):** The general synthetic procedure C was used with 3-chloroaniline (37 µL, 0.60 mmol) in DCM (2.0 mL) and Oxone® (424 mg, 0.69 mmol) in water (4.0 mL), to form the corresponding nitrosocompound 11c, and the aniline 10b (70 mg, 0.26 mmol) in DCM (3 mL) to give the azocompound 13c as an orange oil (72 mg, 71%). 1H NMR (500 MHz, CDCl₃) δ 7.90 (t, J = 1.9 Hz, 1H), 7.86 (s, 1H), 7.84 (dt, J = 7.2, 1.9 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.51 – 7.41 (m, 4H), 5.45 (br, 1H), 3.63 (d, J = 13.4 Hz, 1H), 3.48 (d, J = 13.4 Hz, 1H), 2.98 (d, J = 13.1 Hz, 1H), 2.88 (d, J = 13.1 Hz, 1H), 2.44 (dt, J = 8.5, 5.6 Hz, 1H), 2.35 (td, J = 5.8, 1.4 Hz, 1H), 2.28 (app. q, J = 19.0, 18.5 Hz, 2H), 2.18 (s, 3H), 2.15 – 2.07 (m, 1H), 1.31 (s, 3H), 1.17 (d, J = 8.5 Hz, 1H), 0.85 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 153.61, 152.51, 146.38, 141.25, 135.24, 132.22, 130.74, 130.26, 129.11, 123.45, 122.51, 121.90, 121.86, 120.10, 63.82, 61.33, 44.35, 42.72, 41.03, 38.11, 32.00, 31.55, 26.44, 21.28. HPLC-PDA-MS: RT = 4.99 min, 97.0% (254 nm), PDA λ max = 317 nm, MS (m/z) [M+H]+ 394.20.

**N-(3-((E)-(4-Chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (13d):** The general synthetic procedure C was used with 4-chloroaniline (152 mg, 1.19 mmol) in DCM (3.6 mL) and Oxone® (1.50 g, 2.4 mmol) in water (14.4 mL), to form the corresponding nitrosocompound 11d, and the aniline 10b (166 mg, 0.61 mmol) in DCM (7 mL) to give the azocompound 13d as an orange oil (79 mg, 33%). 1H NMR (500 MHz, CDCl₃) δ 7.88 (d, J = 8.6 Hz,
2H), 7.85 (s, 1H), 7.79 (td, J = 4.8, 4.2, 2.0 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.48 – 7.42 (m, 2H), 5.45 (br, 1H), 3.62 (d, J = 13.4 Hz, 1H), 3.47 (d, J = 13.4 Hz, 1H), 2.97 (d, J = 13.1 Hz, 1H), 2.87 (d, J = 13.1 Hz, 1H), 2.43 (dt, J = 8.4, 5.6 Hz, 1H), 2.35 (t, J = 5.9 Hz, 1H), 2.26 (app. q, J = 18.6, 17.8 Hz, 2H), 2.17 (s, 3H), 2.14 – 2.06 (m, 1H), 1.31 (s, 3H), 1.17 (d, J = 8.7 Hz, 1H), 0.85 (s, 3H).

13C NMR (126 MHz, CDCl3) δ 152.60, 151.14, 146.42, 141.22, 131.98, 129.46, 129.08, 124.23, 123.34, 121.77, 120.08, 63.83, 61.36, 44.34, 42.73, 41.03, 38.11, 32.00, 31.55, 26.44, 21.28.

HPLC-PDA-MS: RT = 4.87 min, 98.4% (254 nm), PDA λmax = 234 nm, MS (m/z) [M+H]+ 394.20.

N-(3-((E)-(2-Bromophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (13e): The synthesis and characterization of this compound have been published by us [1].

N-(2-Chloro-5-((E)-phenyldiazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14a): The general synthetic procedure C was used with nitrosobenzene (11a) (111 mg, 1.04 mmol) and the aniline 10c (155 mg, 0.51 mmol) in DCM (5.5 mL) to give the azocompound 14a as an orange oil (118 mg, 59%). 1H NMR (500 MHz, CDCl3) δ 8.08 (s, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.3 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.47 – 7.41 (m, 2H), 5.43 (br, 1H), 3.67 (d, J = 14.6 Hz, 1H), 3.00 (d, J = 13.1 Hz, 1H), 2.92 (d, J = 13.1 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.34 (t, J = 5.8 Hz, 1H), 2.11 – 2.01 (m, 1H), 1.26 (s, 3H), 1.13 (d, J = 10.1 Hz, 1H), 0.80 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 152.67, 151.28, 146.39, 138.51, 136.68, 131.24, 130.09, 129.23, 125.69, 123.02, 121.52, 120.06, 64.03, 58.22, 44.37, 42.89, 41.00, 38.09, 32.00, 31.55, 26.44, 21.24. HPLC-PDA-MS: RT = 4.87 min, 82.6% (254 nm), PDA λmax = 324 nm, MS (m/z) [M+H]+ 394.20.

N-(2-Chloro-5-((E)-(2-fluorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14b): The general synthetic procedure C was used with 2-fluoroaniline (97 µL, 1.0 mmol) in DCM (2.7 mL) and Oxone® (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosocompound 11f, and the aniline 10c (153 mg, 0.50 mmol) in DCM (5.5 mL) to give the azocompound 14b as an orange oil (102 mg, 49%). 1H NMR (600 MHz, CDCl3) δ 8.14 (d, J = 2.4 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.50 – 7.43 (m, 2H), 7.32 – 7.25 (m, 1H), 7.23 (t, J = 7.7 Hz, 1H), 5.53 – 5.39 (m, 1H), 3.70 (d, J = 14.6 Hz, 1H), 3.60 (d, J = 14.6 Hz, 1H), 3.03 (d, J = 13.2 Hz, 1H), 2.95 (d,
J = 13.1 Hz, 1H), 2.42 (dt, J = 8.6, 5.6 Hz, 1H), 2.36 (t, J = 5.2 Hz, 1H), 2.31 (app. d, J = 17.6 Hz, 1H), 2.28 – 2.18 (m, 4H), 2.13 – 2.06 (m, 1H), 1.29 (d, J = 8.6 Hz, 1H), 0.83 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 161.15, 159.44, 151.52, 146.43, 140.78, 140.74, 138.66, 137.21, 132.76, 132.70, 130.16, 126.44, 124.44, 124.41, 121.35, 120.10, 117.88, 117.31, 117.17, 64.06, 58.17, 44.43, 42.88, 41.06, 38.09, 31.99, 31.57, 26.38, 21.24. HPLC-PDA-MS: RT = 4.82 min, 90.6% (254 nm), PDA λmax = 327 nm, MS (m/z) [M+H]+ 412.20.

N-(2-Chloro-5-((E)-(2-chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14c): The general synthetic procedure C was used with 2-chloroaniline (105 µL, 1.0 mmol) in DCM (2.7 mL) and Oxone® (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosocompound 11b, and the aniline 10c (153 mg, 0.50 mmol) in DCM (5.5 mL) to give the azocompound 14c as an orange oil (125 mg, 58%). 1H NMR (600 MHz, CDCl3) δ 8.16 (s, 1H), 7.78 (dd, J = 8.5, 2.4 Hz, 1H), 7.71 (dd, J = 8.0, 1.7 Hz, 1H), 7.56 (dd, J = 8.0, 1.3 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.40 (td, J = 7.6, 1.7 Hz, 1H), 7.35 (td, J = 8.0, 1.3 Hz, 1H), 5.47 (br, 1H), 3.71 (d, J = 14.6 Hz, 1H), 3.60 (d, J = 14.6 Hz, 1H), 3.04 (d, J = 13.2 Hz, 1H), 2.96 (d, J = 13.1 Hz, 1H), 2.41 (dt, J = 8.5, 5.6 Hz, 1H), 2.39 – 2.34 (m, 1H), 2.31 (app. d, J = 17.3 Hz, 1H), 2.27 – 2.20 (m, 4H), 2.12 – 2.06 (m, 1H), 1.28 (s, 3H), 1.15 (d, J = 8.6 Hz, 1H), 0.83 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 151.51, 148.79, 146.44, 138.73, 135.62, 64.14, 58.13, 38.11, 32.01, 31.57. δ. HPLC-PDA-MS: RT = 5.08 min, 76.2% (254 nm), PDA λmax = 326 nm, MS (m/z) [M+H]+ 428.20.

N-(5-((E)-(2-Bromophenyl)diazenyl)-2-chlorobenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14d): The synthesis and characterization of this compound have been published by us[1].

N-(2-Chloro-5-((E)-o-tolyl diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14f): The general synthetic procedure C was used with o-toluidine (107 µL, 1.00 mmol) in DCM (2.7 mL) and Oxone® (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosocompound 11g, and the aniline 10c (151 mg, 0.50 mmol) in DCM (5.5 mL) to give the azocompound 14f as an orange oil (47 mg, 23%). 1H NMR (600 MHz, CDCl3) δ 8.10 (d, J = 2.4 Hz, 1H), 7.72 (dd, J = 8.4, 2.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 5.46 (br, 1H), 3.70 (d, J = 14.6 Hz, 1H), 3.60 (d, J = 14.6 Hz, 1H), 3.04 (d, J = 13.2 Hz, 1H),
2.96 (d, J = 13.1 Hz, 1H), 2.74 (s, 3H), 2.41 (dt, J = 8.5, 5.6 Hz, 1H), 2.36 (t, J = 5.4 Hz, 1H), 2.30 (app. d, J = 17.9 Hz, 1H), 2.27 – 2.18 (m, 4H), 2.14 – 2.05 (m, 1H), 1.28 (s, 3H), 1.15 (d, J = 8.5 Hz, 1H), 0.83 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 151.72, 150.79, 146.49, 138.54, 138.39, 136.46, 131.42, 131.20, 130.04, 126.58, 125.62, 121.67, 120.02, 115.55, 64.17, 58.21, 44.39, 42.82, 41.07, 38.11, 31.99, 31.56, 26.43, 21.23, 17.70. HPLC-PDA-MS: RT = 5.15 min, 97.8% (254 nm), PDA \(\lambda_{\text{max}}\) = 325 nm, MS (m/z) [M+H]\(^+\) 408.25.

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\text{N-}[2\text{-Chloro-5-}((E)-(2\text{-trifluoromethyl})\text{phenyl})\text{diazenyl}][\text{benzyl}]\text{-}[1\text{(1R,SS)}-6,6\text{-dimethylbicyclo [3.1.1]hept-2-en-2-yl}]\text{-N-methylmethanamine (14g): The general synthetic procedure C was used with 2-(trifluoromethyl)aniline (126 \(\mu\)L, 1.00 mmol) in DCM (2.7 mL) and Oxone\(^*\) (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosos compound 11h, and the aniline 10c (155 mg, 0.51 mmol) in DCM (5.5 mL) to give the azocompound 14g as an orange oil (116 mg, 49%).} \]

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^{1}H\text{ NMR (500 MHz, CDCl}_{3}\text{) }\delta\text{ 8.18 (s, 1H), 7.89 – 7.80 (m, 2H), 7.76 (d, J = 8.5 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 5.47 (br, 1H), 3.70 (d, J = 14.8 Hz, 1H), 3.60 (d, J = 14.8 Hz, 1H), 3.06 (d, J = 13.2 Hz, 1H), 2.97 (d, J = 13.1 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.37 (t, J = 5.9 Hz, 1H), 2.34 – 2.16 (m, 5H), 2.13 – 2.05 (m, 1H), 1.28 (s, 3H), 1.14 (d, J = 8.4 Hz, 1H), 0.82 (s, 3H).} \]

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^{13}C\text{ NMR (126 MHz, CDCl}_{3}\text{) }\delta\text{ 157.15, 154.53, 146.45, 138.80, 137.61, 132.69, 130.63, 130.26, 129.09, 128.84, 128.59, 128.34, 127.37, 126.89, 126.78, 126.74, 126.70, 126.65, 125.20, 123.02, 121.46, 120.84, 120.08, 116.29, 64.24, 58.07, 44.26, 42.74, 41.02, 38.09, 31.95, 31.55, 26.34, 21.20.} \]

HPLC-PDA-MS: RT = 5.15 min, 92.8% (256 nm), PDA \(\lambda_{\text{max}}\) = 324 nm, MS (m/z) [M+H]\(^+\) 462.20.

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\text{N-}[2\text{-Chloro-5-}((E)-(2\text{-methoxyphenyl})\text{diazenyl}][\text{benzyl}]\text{-}[1\text{(1R,SS)}-6,6\text{-dimethylbicyclo [3.1.1]hept-2-en-2-yl}]\text{-N-methylmethanamine (14h): The general synthetic procedure C was used with 2-methoxyaniline (113 \(\mu\)L, 1.00 mmol) in DCM (2.7 mL) and Oxone\(^*\) (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosos compound 11i, and the aniline 10c (159 mg, 0.52 mmol) in DCM (5.5 mL) to give the azocompound 14h as an orange oil (88 mg, 40%).} \]

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^{1}H\text{ NMR (500 MHz, CDCl}_{3}\text{) }\delta\text{ 8.08 (t, J = 2.1 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.10 (d, J = 8.3 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 5.46 (s, 1H), 3.70 (d, J = 14.4 Hz, 1H), 3.59 (d, J = 14.3 Hz, 1H), 3.03 (d, J = 13.2 Hz, 1H), 2.94 (d, J = 13.1 Hz, 1H), 2.40 (app. qd, J = 6.5, 5.7, 3.6 Hz, 1H), 2.34 (t, J = 6.0 Hz, 1H), 2.33 – 2.17 (m, 5H), 2.14 – 2.04 (m, 1H), 1.28 (s, 3H), 1.15 (d, J = 8.5 Hz, 1H), 0.82 (s, 3H).} \]

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^{13}C\text{ NMR (126 MHz, CDCl}_{3}\text{) }\delta\text{ 157.15, 151.83, 146.39, 142.28, 138.33, 136.54, 132.77, 130.07, 127.21, 120.90, 120.37, 120.04, 117.08, 112.85, 64.09, 58.23, 56.44, 44.34, 42.77, 40.99, 38.07, 31.99, 31.54, 26.38, 21.21.} \]

HPLC-PDA-MS: RT = 4.63 min, 98.0% (254 nm), PDA \(\lambda_{\text{max}}\) = 324, 363 nm, MS (m/z) [M+H]\(^+\) 424.25.
**N-(2-Chloro-5-((E)-(2-(trifloromethoxy)phenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14i):** The general synthetic procedure C was used with 2-(trifloromethoxy)aniline (136 µL, 1.00 mmol) in DCM (2.7 mL) and Oxone® (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosocompound 11j, and the aniline 10c (153 mg, 0.50 mmol) in DCM (5.5 mL) to give the azocompound 14i as an orange oil (152 mg, 63%). ^1H NMR (600 MHz, CDCl₃) δ 8.15 (d, J = 2.0 Hz, 1H), 7.79 (dd, J = 8.1, 1.7 Hz, 1H), 7.75 (dd, J = 8.5, 2.4 Hz, 1H), 7.52 (dd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.44 (dt, J = 8.2, 1.4 Hz, 1H), 7.41 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 5.46 (br, 1H), 3.70 (d, J = 14.6 Hz, 1H), 3.60 (d, J = 14.7 Hz, 1H), 3.05 (d, J = 13.1 Hz, 1H), 2.96 (d, J = 13.2 Hz, 1H), 2.40 (dt, J = 8.6, 5.6 Hz, 1H), 2.34 (t, J = 5.3 Hz, 1H), 2.30 (app. d, J = 17.7 Hz, 1H), 2.27 – 2.18 (m, 4H), 2.13 – 2.05 (m, 1H), 1.27 (s, 3H), 1.14 (d, J = 8.6 Hz, 1H), 0.82 (s, 3H). ^13C NMR (151 MHz, CDCl₃) δ 151.51, 147.00, 146.42, 145.12, 138.74, 137.48, 132.12, 130.23, 127.69, 126.95, 123.34, 123.20, 121.04, 120.05, 119.93, 118.22, 117.63, 64.19, 58.13, 44.38, 42.79, 41.06, 38.09, 31.96, 31.56, 26.37, 21.20.

HPLC-PDA-MS: RT = 5.24 min, 87.8% (254 nm), PDA λ max = 324 nm, MS (m/z) [M+H]^+ 478.25.

**N-(5-((E)-(3-Bromophenyl)diazenyl)-2-chlorobenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (15b):** The general synthetic procedure C was used with 3-bromoaniline (109 µL, 1.00 mmol) in DCM (2.7 mL) and Oxone® (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosocompound 11k, and the aniline 10c (153 mg, 0.50 mmol) in DCM (5.5 mL) to give the azocompound 15b as an orange oil (161 mg, 68%). ^1H NMR (300 MHz, CDCl₃) δ 8.12 (d, J = 2.4 Hz, 1H), 8.06 (t, J = 1.9 Hz, 1H), 7.88 (ddd, J = 8.0, 1.6, 0.9 Hz, 1H), 7.73 (ddd, J = 8.5, 2.4 Hz, 1H), 7.60 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 5.46 (br, 1H), 3.70 (d, J = 14.8 Hz, 1H), 3.57 (s, 1H), 3.03 (d, J = 12.5 Hz, 1H), 2.94 (d, J = 13.1 Hz, 1H), 2.48 – 2.19 (m, 7H), 2.16 – 2.03 (m, 1H), 1.30 (s, 3H), 1.15 (d, J = 8.3 Hz, 1H), 0.83 (s, 3H). ^13C NMR (126 MHz, CDCl₃) δ 153.54, 150.98, 146.35, 138.71, 137.26, 133.82, 130.60, 130.18, 125.73, 124.79, 123.27, 123.15, 121.74, 120.09, 64.01, 58.19, 44.39, 42.94, 40.99, 38.11, 32.00, 31.55, 26.46, 21.25. HPLC-PDA-MS: RT = 5.26 min, 96% (254 nm), PDA λ max = 324 nm, MS (m/z) [M+H]^+ 474.15.

**N-(5-((E)-(4-Bromophenyl)diazenyl)-2-chlorobenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (15c):** The general synthetic procedure C was used with 4-
bromoaniline (109 µL, 1.00 mmol) in DCM (2.7 mL) and Oxone® (1.26 g, 2.1 mmol) in water (10.7 mL), to form the corresponding nitrosocompound 11, and the aniline 10c (153 mg, 0.50 mmol) in DCM (5.5 mL) to give the azocompound 15c as an orange oil (165 mg, 70%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 8.10 (s, 1\text{H}), 7.80 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.65 (d, J = 8.3 \text{ Hz}, 2\text{H}), 7.46 (d, J = 8.5 \text{ Hz}, 1\text{H}), 5.46 (br, 1\text{H}), 3.69 (d, J = 14.6 \text{ Hz}, 1\text{H}), 3.60 (d, J = 14.7 \text{ Hz}, 1\text{H}), 3.02 (d, J = 13.2 \text{ Hz}, 1\text{H}), 2.95 (d, J = 13.2 \text{ Hz}, 1\text{H}), 2.40 (dt, J = 8.5, 5.6 \text{ Hz}, 1\text{H}), 2.35 (t, J = 5.7 \text{ Hz}, 1\text{H}), 2.31 (app. d, J = 17.8 \text{ Hz}, 1\text{H}), 2.28 – 2.21 (m, 4\text{H}), 2.14 – 2.05 (m, 1\text{H}), 1.29 (s, 3\text{H}), 1.15 (d, J = 8.6 \text{ Hz}, 1\text{H}), 0.83 (s, 3\text{H}). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 151.42, 151.15, 146.38, 138.70, 137.04, 132.49, 130.16, 125.66, 125.63, 124.53, 121.65, 120.07, 64.01, 58.22, 44.45, 42.93, 41.04, 35.17, 26.47, 21.25.

HPLC-PDA-MS: RT = 5.96 min, % (254 nm), PDA \(\lambda_{\text{max}} = 332 \text{ nm}, \text{ MS (m/z) [M+H]}^+ 474.20.

1-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethyl-N-(4-((E)-phenyldiazenyl)benzyl)methanaminium iodide (2a): The general synthetic procedure D was used with the amine 12a (35 mg, 0.10 mmol) and MeI (122 µL, 1.9 mmol) in DCM (2.5 mL) to give the ammonium salt 2a as an orange solid (32 mg, 66%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.03 – 7.76 (m, 6\text{H}), 7.59 – 7.38 (m, 3\text{H}), 6.23 (br, 1\text{H}), 5.27 (s, 2\text{H}), 4.42 (d, J = 12.4 \text{ Hz}, 1\text{H}), 4.26 (d, J = 12.4 \text{ Hz}, 1\text{H}), 3.19 (s, 3\text{H}), 3.15 (s, 3\text{H}), 2.57 – 2.28 (m, 4\text{H}), 2.19 – 2.08 (m, 1\text{H}), 1.28 (s, 3\text{H}), 1.14 (d, J = 8.3 \text{ Hz}, 1\text{H}), 0.83 (s, 3\text{H}). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 153.72, 152.43, 136.94, 136.13, 136.06, 134.55, 132.50, 130.87, 130.23, 127.37, 127.68, 117.49, 68.97, 66.59, 49.13, 48.91, 47.01, 39.70, 38.18, 32.24, 32.06, 26.00, 21.52. HPLC-PDA-MS: RT = 4.54 min, 99.6% (254 nm), PDA \(\lambda_{\text{max}} = 320, 442 \text{ nm}, \text{ MS (m/z) [M]}^+ 374.30. \text{ HRMS (m/z): [M]}^+ \text{ calculated for C}_{25}\text{H}_{32}\text{N}_{3}, 374.2591; \text{ found, 374.2585.}

N-((E)-(2-Chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (2b): The general synthetic procedure D was used with the amine 12b (54 mg, 0.14 mmol) and MeI (171 µL, 2.7 mmol) in DCM (2.5 mL) to give the ammonium salt 2b as an orange solid (62 mg, 84%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.92 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.88 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.62 (dd, J = 8.1, 1.5 \text{ Hz}, 1\text{H}), 7.52 (dd, J = 8.0, 1.2 \text{ Hz}, 1\text{H}), 7.38 (td, J = 7.7, 1.6 \text{ Hz}, 1\text{H}), 7.29 (t, J = 8.1 \text{ Hz}, 1\text{H}), 6.22 (br, 1\text{H}), 5.30 (s, 2\text{H}), 4.41 (d, J = 12.4 \text{ Hz}, 1\text{H}), 4.25 (d, J = 12.4 \text{ Hz}, 1\text{H}), 3.19 (s, 3\text{H}), 3.15 (s, 3\text{H}), 2.49 (dt, J = 9.0, 5.6 \text{ Hz}, 1\text{H}), 2.45 – 2.28 (m, 3\text{H}), 2.21 – 2.08 (m, 1\text{H}), 1.27 (s, 3\text{H}), 1.14 (d, J = 8.9 \text{ Hz}, 1\text{H}), 0.83 (s, 3\text{H}). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 153.72, 148.37, 136.94, 136.09, 134.47, 131.82, 129.63, 129.25, 123.34, 123.25, 68.98, 66.71, 49.13, 48.91, 47.02, 39.70, 38.18, 32.24, 32.06, 26.00, 21.52. HPLC-PDA-MS: RT = 4.66 min, 98.7% (254 nm), PDA \(\lambda_{\text{max}} = 323, 455 \text{ nm}, \text{ MS (m/z) [M]}^+ 408.20. \text{ HRMS (m/z): [M]}^+ \text{ calculated for C}_{25}\text{H}_{31}\text{ClN}_{3}, 408.2202; \text{ found, 408.2202.}
**N-(4-((E)-(3-Chlorophenyl)diazetyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylethanaminium iodide (2c):** The general synthetic procedure D was used with the amine 12c (38 mg, 0.10 mmol) and MeI (121 µL, 1.9 mmol) in DCM (2.5 mL) to give the ammonium salt 2c as an orange solid (47 mg, 91%). ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 4H), 7.81 (t, J = 2.1 Hz, 1H), 7.49 – 7.36 (m, 2H), 6.22 (br, 1H), 5.29 (s, 2H), 4.41 (d, J = 12.4 Hz, 1H), 4.25 (d, J = 12.4 Hz, 1H), 3.18 (s, 3H), 3.15 (s, 3H), 2.50 (dt, J = 9.0, 5.6 Hz, 1H), 2.47 – 2.29 (m, 3H), 2.18 – 2.10 (m, 1H), 1.28 (s, 3H), 1.15 (d, J = 9.0 Hz, 1H), 0.83 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.29, 153.10, 137.00, 136.06, 135.30, 134.55, 131.51, 130.30, 130.17, 123.51, 122.84, 121.98, 69.08, 66.61, 49.14, 48.90, 47.04, 39.71, 38.20, 32.07, 26.00, 21.52. HPLC-PDA-MS: RT = 4.79 min, 99.5% (254 nm), PDA λ max = 319, 447 nm, MS (m/z) [M]⁺ 408.25. HRMS (m/z): [M]⁺ calculated for C₂₅H₃₁ClN₃ 408.2201; found, 408.2198.

**N-(4-((E)-(4-Chlorophenyl)diazetyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylethanaminium iodide (2d):** The general synthetic procedure D was used with the amine 12d (90 mg, 0.23 mmol) and MeI (286 µL, 4.6 mmol) in DCM (4.5 mL) to give the ammonium salt 2d as an orange solid (104 mg, 85%). ¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.81 (m, 4H), 7.78 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 6.22 (br, 1H), 5.31 (s, 2H), 4.40 (d, J = 12.4 Hz, 1H), 4.24 (d, J = 12.4 Hz, 1H), 3.18 (s, 3H), 3.14 (s, 3H), 2.49 (dt, J = 8.7, 5.7 Hz, 1H), 2.46 – 2.27 (m, 3H), 2.20 – 2.09 (m, 1H), 1.28 (s, 3H), 1.14 (d, J = 9.0 Hz, 1H), 0.83 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.39, 150.67, 137.85, 136.94, 136.06, 134.52, 129.92, 129.50, 124.46, 123.38, 68.98, 66.57, 49.11, 48.88, 47.03, 39.70, 38.18, 32.25, 32.06, 26.00, 21.51. HPLC-PDA-MS: RT = 4.80 min, 99.7% (254 nm), PDA λ max = 319, 447 nm, MS (m/z) [M]⁺ 408.20. HRMS (m/z): [M]⁺ calculated for C₂₅H₃₁ClN₃ 408.2201; found, 408.2193.

**N-(4-((E)-(2-Bromophenyl)diazetyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylethanaminium iodide (2e):** The general synthetic procedure D was used with the amine 12e (143 mg, 0.33 mmol) and MeI (408 µL, 6.5 mmol) in DCM (6.0 mL) to give the ammonium salt 2e as an orange solid (147 mg, 78%). ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.71 (dd, J = 7.5, 1.8 Hz, 1H), 7.60 (dd, J = 7.6, 2.1 Hz, 1H), 7.35 – 7.27 (m, 2H), 6.22 (br, 1H), 5.30 (s, 2H), 4.41 (d, J = 12.4 Hz, 1H), 4.24 (d, J = 12.4 Hz, 1H), 3.19 (s, 3H), 3.15 (s, 3H), 2.49 (dt, J = 8.9, 5.6 Hz, 1H), 2.46 – 2.28 (m, 3H), 2.13 (td, J = 5.7, 2.6 Hz, 1H), 1.27 (s, 3H), 1.14 (d, J = 9.0 Hz, 1H), 0.83 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.55, 149.25, 136.94, 136.06, 134.56, 133.94, 132.70, 130.25, 128.07, 126.69, 123.87, 117.69, 68.98, 66.59, 49.14, 48.91, 47.01, 39.69, 38.17, 32.24, 32.05,
1-(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethyl-N-{3-[(E)-phenylidazeyl]benzyl}methanaminium iodide (3a): The general synthetic procedure D was used with the amine 13a (39 mg, 0.11 mmol) and MeI (136 µL, 2.2 mmol) in DCM (2.5 mL) to give the ammonium salt 3a as an orange solid (33 mg, 61%). ¹H NMR (500 MHz, CDCl₃) δ 8.05 (s, 1H), 7.95 (t, J = 6.4 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.55 – 7.45 (m, 3H), 6.25 (br, 1H), 5.24 (s, 2H), 4.47 (d, J = 12.4 Hz, 1H), 4.32 (d, J = 12.3 Hz, 1H), 3.21 (s, 3H), 3.18 (s, 3H), 2.49 (dt, J = 8.3, 5.6 Hz, 1H), 2.46 – 2.28 (m, 3H), 2.19 – 2.09 (m, 1H), 1.28 (s, 3H), 1.14 (d, J = 8.9 Hz, 1H), 0.83 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.79, 152.33, 137.01, 136.09, 135.92, 131.80, 130.33, 129.29, 128.42, 127.97, 124.11, 123.24, 69.13, 66.89, 49.25, 49.02, 47.01, 39.70, 38.17, 32.24, 32.08, 26.00, 21.54. HPLC-PDA-MS: RT = 4.62 min, 99.6% (254 nm), PDA λ_max = 317, 440 nm, MS (m/z) [M]+ 374.20. HRMS (m/z): [M]+ calculated for C_{25}H_{32}N_{3}, 374.2591; found, 374.2581.

N-(3-[(E)-(2-Chlorophenyl)diazenyl]benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (3b): The general synthetic procedure D was used with the amine 13b (61 mg, 0.16 mmol) and MeI (194 µL, 3.1 mmol) in DCM (4.5 mL) to give the ammonium salt 3b as an orange solid (34 mg, 41%). ¹H NMR (500 MHz, CDCl₃) δ 8.09 (t, J = 1.9 Hz, 1H), 7.99 (t, J = 8.2 Hz, 2H), 7.69 (dd, J = 8.0, 1.7 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.55 (dd, J = 8.0, 1.3 Hz, 1H), 7.41 (td, J = 7.6, 1.7 Hz, 1H), 7.34 (td, J = 7.7, 1.4 Hz, 1H), 6.27 (br, 1H), 5.24 (s, 2H), 4.46 (d, J = 12.4 Hz, 1H), 4.30 (d, J = 12.4 Hz, 1H), 3.22 (s, 3H), 3.19 (s, 3H), 2.51 (dt, J = 9.0, 5.6 Hz, 1H), 2.47 – 2.31 (m, 3H), 2.19 – 2.10 (m, 1H), 1.29 (s, 3H), 1.16 (d, J = 9.0 Hz, 1H), 0.85 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 152.94, 148.33, 137.16, 136.48, 136.06, 136.05, 132.59, 130.93, 130.52, 129.03, 128.49, 127.53, 123.92, 117.67, 69.28, 66.85, 47.08, 39.73, 32.28, 32.11, 26.02, 21.56. HPLC-PDA-MS: RT = 4.67 min, 98.6% (254 nm), PDA λ_max = 317, 440 nm, MS (m/z) [M]+ 408.25. HRMS (m/z): [M]+ calculated for C_{25}H_{32}ClN_{3}, 408.2201; found, 408.2202.

N-(3-[(E)-(3-Chlorophenyl)diazenyl]benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (3c): The general synthetic procedure D was used with the amine 13c (52 mg, 0.13 mmol) and MeI (165 µL, 2.64 mmol) in DCM (2.5 mL) to give the ammonium salt 3c as an orange solid (33 mg, 47%). ¹H NMR (500 MHz, CDCl₃) δ 8.06 (s, 1H), 7.95 (t, J = 8.9 Hz, 2H),
7.86 (s, 1H), 7.82 (t, J = 4.3 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 4.6 Hz, 2H), 6.25 (br, 1H), 5.28 (s, 2H), 4.46 (d, J = 12.3 Hz, 1H), 4.31 (d, J = 12.4 Hz, 1H), 3.21 (s, 3H), 3.19 (s, 3H), 2.50 (dt, J = 8.8, 5.8 Hz, 1H), 2.45 – 2.29 (m, 3H), 2.18 – 2.11 (m, 1H), 1.28 (s, 3H), 1.15 (d, J = 8.9 Hz, 1H), 0.83 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 153.05, 152.45, 137.05, 136.40, 136.07, 135.29, 131.47, 130.38, 130.36, 128.56, 128.15, 124.31, 122.85, 122.04, 69.13, 66.77, 49.23, 49.00, 47.02, 39.70, 38.18, 32.25, 32.09, 26.00, 21.55. HPLC-PDA-MS: RT = 4.79 min, 99.5% (254 nm), PDA λmax = 319, 447 nm, MS (m/z) [M]+ 408.25. HRMS (m/z): [M]+ calculated for C25H31ClN3, 408.2201; found, 408.2191.
**N-(3-((E)-(4-Chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (3d):** The general synthetic procedure D was used with the amine **13d** (52 mg, 0.13 mmol) and Mel (165 µL, 2.6 mmol) in DCM (2.5 mL) to give the ammonium salt **3d** as an orange solid (59 mg, 83%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.06 (s, 1H), 7.92 (d, $J = 8.2$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 6.24 (br, 1H), 5.28 (s, 2H), 4.45 (d, $J = 12.3$ Hz, 1H), 4.31 (d, $J = 12.4$ Hz, 1H), 3.20 (s, 3H), 3.18 (s, 3H), 2.49 (dt, $J = 8.8$, 5.6 Hz, 1H), 2.45–2.25 (m, 3H), 2.19–2.09 (m, 1H), 1.27 (s, 3H), 1.14 (d, $J = 9.0$ Hz, 1H), 0.83 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.57, 150.62, 137.76, 137.00, 136.11, 136.07, 130.31, 129.53, 128.52, 128.16, 124.52, 124.11, 69.06, 66.80, 49.20, 48.97, 47.00, 39.69, 38.17, 32.23, 32.07, 26.00, 21.53. HPLC-PDA-MS: RT = 4.78 min, 98.9% (254 nm), PDA $\lambda_{max}$ = 317, 441 nm, MS (m/z) [M]$^+$ 408.25. HRMS (m/z): [M]$^+$ calculated for C$_{25}$H$_{31}$ClN$_3$, 408.2201; found, 408.2186.

**N-(3-((E)-(2-Bromophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (3e):** The synthesis and characterization of this compound have been published by us [1].

**N-(2-Chloro-5-((E)-phenyldiazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4a):** The general synthetic procedure D was used with the amine **14a** (100 mg, 0.25 mmol) and Mel (317 µL, 5.1 mmol) in DCM (5.0 mL) to give the ammonium salt **4a** as an orange solid (100 mg, 74%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.46 (s, 1H), 7.98 – 7.89 (m, 3H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.54 – 7.46 (m, 3H), 6.37 (br, 1H), 5.25 (d, $J = 13.4$ Hz, 1H), 5.19 (d, $J = 13.1$ Hz, 1H), 4.66 (d, $J = 12.4$ Hz, 1H), 4.44 (d, $J = 12.3$ Hz, 1H), 3.25 (s, 6H), 2.62 – 2.51 (m, 1H), 2.51 – 2.32 (m, 3H), 2.21 – 2.11 (m, 1H), 1.31 (s, 3H), 1.23 (d, $J = 8.9$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.17, 151.35, 138.67, 137.66, 136.07, 132.16, 131.87, 131.66, 129.31, 126.48, 124.36, 123.53, 70.40, 49.74, 49.52, 47.16, 39.72, 38.26, 32.34, 32.06, 26.01, 21.54. HPLC-PDA-MS: RT = 4.64 min, 99.2% (254 nm), PDA $\lambda_{max}$ = 231, 324 nm, MS (m/z) [M]$^+$ 408.20. HRMS (m/z): [M]$^+$ calculated for C$_{25}$H$_{31}$ClN$_3$, 408.2201; found, 408.2208.
N-{(2-Chloro-5-((E)-(2-fluorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4b): The general synthetic procedure D was used with the amine 14b (89 mg, 0.22 mmol) and MeI (270 µL, 4.3 mmol) in DCM (4.3 mL) to give the ammonium salt 4b as an orange solid (116 mg, 97%). {^1}H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.79 (t, J = 7.9 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.9 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 6.38 (br, 1H), 5.29 (d, J = 13.2 Hz, 1H), 5.23 (d, J = 13.2 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.45 (d, J = 12.3 Hz, 1H), 3.27 (s, 6H), 2.61 – 2.52 (m, 1H), 2.52 – 2.32 (m, 3H), 2.23 – 2.12 (m, 1H), 1.32 (s, 3H), 1.24 (d, J = 8.9 Hz, 1H), 0.88 (s, 3H). {^{13}}C NMR (126 MHz, CDCl₃) δ 161.63, 159.57, 151.52, 140.26, 140.21, 139.20, 137.72, 136.05, 133.92, 133.85, 131.75, 126.57, 124.64, 124.61, 122.82, 118.01, 117.36, 117.20, 70.41, 63.03, 49.77, 47.19, 39.74, 38.28, 32.35, 32.08, 26.02, 21.56. HPLC-PDA-MS: RT = 4.78 min, 99.1% (254 nm), PDA λ_max = 328 nm, MS (m/z) [M]+ 426.20. HRMS (m/z): [M]+ calculated for C_{25}H_{30}FClN_{3}, 426.2107; found, 426.2100.

N-{(2-Chloro-5-((E)-(2-chlorophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4c): The general synthetic procedure D was used with the amine 14c (95 mg, 0.22 mmol) and MeI (277 µL, 4.4 mmol) in DCM (4.5 mL) to give the ammonium salt 4c as an orange solid (97 mg, 77%). {^1}H NMR (500 MHz, CDCl₃) δ 8.54 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.9 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 6.38 (br, 1H), 5.29 (d, J = 13.1 Hz, 1H), 5.23 (d, J = 13.1 Hz, 1H), 4.66 (d, J = 12.4 Hz, 1H), 4.44 (d, J = 12.3 Hz, 1H), 3.27 (s, 6H), 2.60 – 2.51 (m, 1H), 2.51 – 2.33 (m, 3H), 2.24 – 2.12 (m, 1H), 1.32 (s, 3H), 1.24 (d, J = 8.8 Hz, 1H), 0.88 (s, 3H). {^{13}}C NMR (126 MHz, CDCl₃) δ 161.46, 159.05, 151.52, 140.26, 140.21, 139.20, 137.72, 136.05, 133.92, 133.85, 131.75, 126.57, 124.64, 124.61, 122.82, 118.01, 117.36, 117.20, 70.41, 63.03, 49.77, 47.19, 39.74, 38.28, 32.35, 32.08, 26.02, 21.56. HPLC-PDA-MS: RT = 4.95 min, 99.5% (254 nm), PDA λ_max = 323, 329 nm, MS (m/z) [M]+ 442.20. HRMS (m/z): [M]+ calculated for C_{25}H_{30}Cl_{2}N_{3}, 442.1811; found, 4421805.

N-{(5-((E)-(2-Bromophenyl)diazenyl)-2-chlorobenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4d, VUF15888): The synthesis and characterization of this compound have been published by us [1].
**N-(2-Chloro-5-((E)-tolyldiazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4f):** The general synthetic procedure D was used with the amine 14f (40 mg, 0.10 mmol) and MeI (123 µL, 2.0 mmol) in DCM (2.0 mL) to give the ammonium salt 4f as an orange solid (22 mg, 41%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.46 (s, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.38 (br, 1H), 5.27 (d, J = 12.5 Hz, 1H), 5.21 (d, J = 13.5 Hz, 1H), 4.68 (d, J = 12.4 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 3.26 – 3.21 (m, 1H), 3.21 (s, 6H), 2.74 (s, 3H), 2.61 – 2.52 (m, 1H), 2.52 – 2.33 (m, 3H), 2.23 – 2.11 (m, 1H), 1.31 (s, 3H), 1.24 (d, J = 8.9 Hz, 1H), 0.87 (s, 3H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 151.75, 150.25, 139.52, 138.41, 137.69, 136.09, 132.24, 131.76, 131.62, 131.58, 126.60, 126.45, 124.54, 115.61, 70.35, 63.05, 49.70, 49.47, 47.18, 39.74, 38.28, 32.35, 32.08, 26.03, 21.56. HPLC-PDA-MS: RT = 4.99 min, 99.7% (254 nm), PDA \(\lambda_{\text{max}}\) = 324 nm, MS (m/z) [M]+ 422.20. HRMS (m/z): [M]+ calculated for C\(_{26}\)H\(_{33}\)ClN\(_3\) 422.2358; found, 422.2359.

**N-(2-Chloro-5-((E)-2-(trifluoromethyl)phenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4g):** The general synthetic procedure D was used with the amine 14g (95 mg, 0.21 mmol) and MeI (257 µL, 4.1 mmol) in DCM (4.0 mL) to give the ammonium salt 4g as an orange solid (109 mg, 88%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.59 (s, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.65 – 7.55 (m, 2H), 6.39 (br, 1H), 5.31 (d, J = 13.2 Hz, 1H), 5.26 (d, J = 13.2 Hz, 1H), 4.68 (d, J = 12.3 Hz, 1H), 4.46 (d, J = 12.3 Hz, 1H), 3.27 (s, 6H), 2.63 – 2.52 (m, 1H), 2.52 – 2.35 (m, 3H), 2.23 – 2.14 (m, 1H), 1.32 (s, 3H), 1.24 (d, J = 8.9 Hz, 1H), 0.88 (s, 3H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 151.33, 148.75, 139.69, 137.78, 136.04, 134.59, 132.92, 131.91, 131.69, 129.54, 129.29, 129.05, 128.80, 127.29, 126.84, 126.80, 126.75, 126.71, 126.64, 125.11, 122.94, 122.71, 120.76, 116.50, 70.39, 63.01, 49.75, 49.52, 47.19, 39.74, 38.29, 32.35, 32.08, 26.02, 21.54. HPLC-PDA-MS: RT = 4.88 min, 99.7% (254 nm), PDA \(\lambda_{\text{max}}\) = 324 nm, MS (m/z) [M]+ 476.25. HRMS (m/z): [M]+ calculated for C\(_{26}\)H\(_{30}\)Cl\(_3\)F\(_3\)N\(_3\) 476.2075; found, 476.2092.

**N-(2-Chloro-5-((E)-(2-methoxyphenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4h):** The general synthetic procedure D was used with amine 14h (70 mg, 0.17 mmol) and MeI (206 µL, 3.3 mmol) in DCM (3.3 mL). Following the general synthetic procedure D the ammonium salt 4h did not precipitate as a solid, but as an oil. MTBE was
decanted and the oil was washed with several portions of MTBE. The product was dried in the vacuum oven to give an orange oil, which corresponded to the expected product 4h with the presence of a 0.44 molar fraction of solvated MTBE (91 mg, 91%). The MTBE solvate could not be removed under high vacuum and temperature and was taken into account when calculating the yield and the concentrations for pharmacological experiments. The product contained 95% of the trans-isomer and 5% of cis-isomer. 1H NMR (600 MHz, CDCl3) δ 8.41 (d, J = 2.3 Hz, 1H), 7.91 (dd, J = 8.6, 2.3 Hz, 1H), 7.71 (dd, J = 8.1, 1.7 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H), 7.48 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.38 (br, J = 3.4 Hz, 1H), 5.23 (d, J = 13.3 Hz, 1H), 5.17 (d, J = 13.3 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.42 (d, J = 12.4 Hz, 1H), 4.03 (s, 3H), 3.25 (s, 6H), 2.55 (dt, J = 8.9, 5.6 Hz, 1H), 2.52 – 2.35 (m, 3H), 2.24 – 2.13 (m, 1H), 1.32 (s, 3H), 0.88 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 157.73, 152.12, 141.84, 138.29, 137.73, 136.07, 133.98, 132.69, 131.67, 126.32, 123.61, 120.99, 117.31, 113.04, 72.91, 70.49, 63.38, 49.77, 49.55, 47.27, 39.80, 38.31, 32.38, 32.09, 27.11, 26.05, 21.57. HPLC-PDA-MS: trans-isomer: RT = 4.48 min, 94.7% (254 nm), PDA λmax = 323, 362 nm, MS (m/z) [M]+ 438.30; cis-isomer: RT = 4.20 min, 4.1% (254 nm), PDA λmax = 434 nm, MS (m/z) [M]+ 438.35. HRMS (m/z): [M]+ calculated for C26H33ClF3N3O, 438.2307; found, 438.2298.

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\text{N-[(2-Chloro-5-((E)-(2-(trifluoromethoxy)phenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (4i):} \]

The general synthetic procedure D was used with the amine 14i (74 mg, 0.16 mmol) and MeI (194 µL, 3.1 mmol) in DCM (3.10mL) to give the ammonium salt 4i as an orange solid (72 mg, 75%). 1H NMR (500 MHz, CDCl3) δ 8.56 (s, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.46 – 7.35 (m, 2H), 6.39 (br, 1H), 5.30 (d, J = 13.1 Hz, 1H), 5.24 (d, J = 13.3 Hz, 1H), 4.69 (d, J = 12.3 Hz, 1H), 4.48 (d, J = 12.4 Hz, 1H), 3.28 (s, 6H), 2.65 – 2.50 (m, 1H), 2.50 – 2.36 (m, 3H), 2.23 – 2.12 (m, 1H), 1.31 (s, 3H), 1.23 (d, J = 8.9 Hz, 1H), 0.87 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 151.43, 147.37, 144.43, 139.56, 137.72, 136.07, 134.50, 133.26, 131.85, 127.88, 126.62, 123.73, 123.19, 122.35, 121.68, 119.63, 117.75, 117.58, 70.32, 62.96, 49.72, 49.50, 47.15, 39.72, 36.28, 32.34, 32.06, 26.00, 21.53. HPLC-PDA-MS: RT = 5.05 min, 99.7% (254 nm), PDA λmax = 325 nm, MS (m/z) [M]+ 492.25. HRMS (m/z): [M]+ calculated for C26H33BrClF3N3O, 492.2019; found, 492.2024.

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\text{N-[(5-((E)-(3-Bromophenyl)diazenyl)-2-chlorobenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (5b):} \]

The general synthetic procedure D was used with the amine 15b (138 mg, 0.29 mmol) and MeI (365 µL, 5.8 mmol) in DCM (6.0 ml) to give the ammonium salt 5b as an orange solid (148 mg, 82%). 1H NMR (500 MHz, CDCl3) δ 8.50 (s, 1H), 8.02 (s, 1H), 7.97 – 7.87 (m, 2H), 7.65 – 7.56 (m, 2H), 7.39 (t, J = 7.7 Hz, 1H), 6.37 (br, 1H), 5.28 (d, J = 13.1 Hz, 1H), 5.22 (d, J = 13.2 Hz, 1H), 4.66 (d, J = 12.3 Hz, 1H), 4.45 (d, J = 12.4 Hz, 1H), 3.26 (s, 6H), 2.63 – 2.50 (m, 1H), 2.50 – 2.31 (m, 3H), 2.22 – 2.10 (m, 1H), 1.31 (s, 3H), 1.23 (d, J = 8.8 Hz, 1H), 0.86 (s, 3H). 13C
NMR (126 MHz, CDCl₃) δ 152.95, 150.97, 139.28, 137.68, 136.07, 134.69, 131.89, 131.74, 130.72, 126.67, 125.09, 124.67, 123.67, 123.25, 70.40, 62.93, 47.15, 39.72, 38.26, 32.34, 32.07, 26.02, 21.55. HPLC-PDA-MS: RT = 4.96 min, 99.7% (254 nm), PDA λmax = 324 nm, MS (m/z) [M]+ 488.20. HRMS (m/z): [M]+ calculated for C₂₅H₃₀BrClN₃, 486.1306; found, 486.1302.

**N-(5-((E)-(4-Bromophenyl)diazenyl)-2-chlorobenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (5c):** The general synthetic procedure D was used with the amine 15c (76 mg, 0.16 mmol) and Mel (201 µL, 3.2 mmol) in DCM (3.3 mL) to give the ammonium salt 5c as an orange solid (58 mg, 59%). ¹H NMR (500 MHz, CDCl₃) δ 8.51 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.67 – 7.58 (m, 3H), 6.36 (br, 1H), 5.28 (d, J = 12.9 Hz, 1H), 5.21 (d, J = 13.2 Hz, 1H), 4.64 (d, J = 12.4 Hz, 1H), 4.44 (d, J = 12.3 Hz, 1H), 3.25 (s, 6H), 2.61 – 2.50 (m, 1H), 2.50 – 2.31 (m, 3H), 2.17 (app. q, J = 4.3, 3.8 Hz, 1H), 1.30 (s, 3H), 1.23 (d, J = 8.9 Hz, 1H), 0.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.14, 150.85, 138.99, 137.66, 136.06, 132.57, 131.97, 131.70, 126.75, 126.62, 125.00, 124.48, 70.35, 62.99, 49.77, 49.53, 47.15, 39.72, 38.26, 32.34, 32.06, 26.01, 21.55. HPLC-PDA-MS: RT = 4.95 min, 97.6% (254 nm), PDA λmax = 233, 333 nm, MS (m/z) [M]+ 488.20. HRMS (m/z): [M]+ calculated for C₂₅H₃₀BrClN₃, 486.1306; found, 486.1304.

**Scheme S2:** Synthetic strategies for compounds 3f-h, 4e, 6b and 6d. (*)Compound 23h was not prepared under the same conditions of the general procedure G. GSP = General Synthetic Procedure.
Methyl 3-nitrosobenzoate (18a): The general synthetic procedure E was used with methyl 3-aminobenzoate (17a) (1.00 g, 6.6 mmol) in DCM (20 mL) and Oxone® (8.3 g, 13.6 mmol) in water (80 mL) to form the corresponding nitrosocompound 18a (1.03 g, 94%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.60 (s, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 4.00 (s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.84, 164.89, 135.84, 131.83, 129.66, 123.90, 122.61, 52.84.

Methyl 2-fluoro-5-nitrosobenzoate (18b): The synthesis and characterization of this compound have been published by us [1].

Methyl 2-chloro-5-nitrosobenzoate (18c): The general synthetic procedure E was used with methyl 5-amino-2-chlorobenzoate (17c) (630 mg, 3.4 mmol) in DCM (10 mL) and Oxone® (4.38 g, 7.1 mmol) in water (40 mL) to form the corresponding nitrosocompound 18c (665 mg, 98%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.54 (d, J = 2.9 Hz, 1H), 7.78 (dd, J = 8.5, 2.2 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 4.02 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.84, 162.46, 141.56, 132.48, 131.26, 125.66, 122.09, 53.15.

Methyl 2-bromo-5-nitrosobenzoate (18d): The synthesis and characterization of this compound have been published by us [1].

Methyl (E)-3-((2-iodophenyl)diazenyl)benzoate (20f): The general synthetic procedure F was used with the nitrosocompound 18a (444 mg, 2.7 mmol) and 2-idoaniline 19a (544 mg, 2.5 mmol) in AcOH (10 mL) to give the azocompound 20f as an orange solid (662 mg, 73%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.64 (t, J = 1.8 Hz, 1H), 8.17 (td, J = 8.3, 7.8, 1.6 Hz, 2H), 8.04 (d, J = 7.9 Hz, 1H), 7.65 (dd, J = 8.0, 1.6 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.18 (td, J = 7.6, 1.6 Hz, 1H), 3.98 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.55, 152.35, 151.25, 140.08, 132.74, 132.36, 131.56, 129.42, 129.06, 126.40, 126.10, 117.47, 103.02, 52.55. HPLC-PDA-MS: RT = 5.77 min, 93% (254 nm), PDA λ$_{max}$ = 321 nm, MS (m/z) [M+H]$^+$ 367.05.
Methyl (E)-3-((3-iodophenyl)diazenyl)benzoate (20g): The general synthetic procedure F was used with the nitrosocompound 18a (280 mg, 1.70 mmol) and 3-iodoaniline 19b (248 mg, 1.13 mmol) in AcOH (11 mL) to give the azocompound 20g as an orange solid (397 mg, 96%). 1H NMR (600 MHz, CDCl3) δ 8.55 (t, J = 1.9 Hz, 1H), 8.27 (t, J = 1.8 Hz, 1H), 8.17 (dt, J = 7.7, 1.4 Hz, 1H), 8.09 (ddd, J = 8.0, 2.0, 1.2 Hz, 1H), 7.93 (ddd, J = 7.9, 1.9, 1.0 Hz, 1H), 7.81 (dt, J = 7.9, 1.3 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 3.97 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 166.53, 153.26, 152.36, 140.07, 132.26, 131.51, 130.88, 130.83, 129.39, 127.26, 124.25, 123.85, 94.71, 52.53. HPLC-PDA-MS: RT = 6.01 min, 99.4 % (254 nm), PDA λmax = 315 nm, MS (m/z) [M+H]+ 366.95.

Methyl (E)-3-((4-iodophenyl)diazenyl)benzoate (20h): The general synthetic procedure F was used with the nitrosocompound 18a (450 mg, 2.7 mmol) and 4-iodoaniline 19c (475 mg, 2.2 mmol) in AcOH (10 mL) to give the azocompound 20h as an orange solid (730 mg, 92%). 1H NMR (600 MHz, CDCl3) δ 8.56 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 3.97 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 166.59, 152.52, 151.85, 138.58, 132.11, 131.51, 129.40, 127.19, 124.73, 124.23, 98.42, 52.54. HPLC-PDA-MS: RT = 5.99 min, 97.8 % (254 nm), PDA λmax = 332 nm, MS (m/z) [M+H]+ 367.00.

Methyl (E)-2-chloro-5-((2-iodophenyl)diazenyl)benzoate (21): The general synthetic procedure F was used with the nitrosocompound 18c (546 mg, 2.7 mmol) and 2-iodoaniline 19a (563 mg, 2.6 mmol) in AcOH (10 mL) to give the azocompound 21 as an orange solid (637 mg, 62%). 1H NMR (600 MHz, CDCl3) δ 8.46 (d, J = 2.4 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 8.02 (dd, J = 8.5, 2.2 Hz, 1H), 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.19 (td, J = 7.6, 1.6 Hz, 1H), 3.99 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 165.59, 151.07, 150.38, 140.16, 136.78, 132.99, 132.19, 130.97, 129.08, 128.01, 125.61, 103.31, 52.85. HPLC-PDA-MS: RT = 5.92 min, 86% (254 nm), PDA λmax = 329 nm, MS (m/z) [M+H]+ 401.00.
**Methyl (E)-5-((2-bromophenyl)diazenyl)-2-fluorobenzoate (22b):** The synthesis and characterization of this compound have been published by us [1].

![Chemical structure of Methyl (E)-5-((2-bromophenyl)diazenyl)-2-fluorobenzoate](image)

**Methyl (E)-2-bromo-5-((2-bromophenyl)diazenyl)benzoate (22d):** The synthesis and characterization of this compound have been published by us [1].

![Chemical structure of Methyl (E)-2-bromo-5-((2-bromophenyl)diazenyl)benzoate](image)

**((E)-3-((2-iodophenyl)diazenyl)phenyl)methanol (23f):** The general synthetic procedure G was used with benzoate 20f (172 mg, 0.40 mmol) and DiBAL-H (1.6 mL, 1.6 mmol) in THF (8 mL) to give the alcohol 23f as an orange oil (102 mg, 76%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.04 (dd, J = 7.9, 1.3 Hz, 1H), 7.99 (br, 1H), 7.96 – 7.88 (m, 1H), 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.43 (ddd, J = 8.2, 7.3, 1.3 Hz, 1H), 7.17 (td, J = 7.6, 1.6 Hz, 1H), 4.83 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 152.67, 151.46, 142.29, 140.01, 132.42, 130.10, 129.57, 129.07, 123.01, 121.95, 117.50, 102.65, 65.10. HPLC-PDA-MS: RT = 4.88 min, 97.9% (254 nm), PDA $\lambda_{max}$ = 324 nm, MS (m/z) [M+H]$^+$ 338.75.

![Chemical structure of ((E)-3-((2-iodophenyl)diazenyl)phenyl)methanol](image)

**((E)-3-((3-iodophenyl)diazenyl)phenyl)methanol (23g):** The general synthetic procedure G was used with benzoate 22g (364 mg, 0.99 mmol) and DiBAL-H (3.0 mL, 3.0 mmol) in THF (20 mL) to give the alcohol 23g as an orange oil (334 mg, 99%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.25 (t, J = 1.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.85 (dt, J = 6.9, 2.1 Hz, 1H), 7.80 (ddd, J = 7.8, 1.7, 1.1 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.27 (t, J = 7.9 Hz, 1H), 4.82 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 153.47, 152.68, 142.27, 139.77, 130.81, 130.75, 129.96, 129.53, 123.75, 123.01, 120.86, 94.71, 65.03. HPLC-PDA-MS: RT = 5.09 min, 98.8% (254 nm), PDA $\lambda_{max}$ = 320 nm, MS (m/z) [M+H]$^+$ 339.05.

![Chemical structure of ((E)-3-((3-iodophenyl)diazenyl)phenyl)methanol](image)
(E)-(3-((4-Iodophenyl)diazenyl)phenyl)methanol (23h): Benzoate 20h (208mg, 0.56 mmol) was dissolved in a mixture of DCM (8 mL) and PhMe (4 mL). DIBAL-H (682 µL, 0.68 mmol, 1.0 M in THF) was added slowly at -78°C and the reaction mixture was stirred for 1 h at -78°C. MeOH (1 mL) was added to quench the reaction. The mixture was slowly warmed to rt. An aqueous Rochelle salt solution (10%, 20 mL) was added and the mixture was stirred for 3 h at rt. Water (30 mL) and DCM (20 mL) were added and the layers were separated. The organic layer was washed with brine (3x20 mL), dried over Na₂SO₄, filtered and evaporated in vacuo to give a residue (orange/red oil) that showed only 50% conversion. The residue was purified with automated flash chromatography (cHex/EtOAc) to give alcohol 23h as an orange/red oil with high purity (86 mg, 45%). 1H NMR (500 MHz, CDCl₃) δ 7.91 (s, 1H), 7.90 – 7.82 (m, 3H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 – 7.48 (m, 2H), 4.81 (s, 2H). 13C NMR (126 MHz, CDCl₃) δ 152.76, 151.97, 142.23, 138.51, 129.82, 129.53, 124.62, 122.95, 120.77, 97.97, 65.04. HPLC-PDA-MS: RT = 5.08 min, 93.4% (254 nm), PDA λmax = 333 nm, MS (m/z) [M+H]+ 338.95.

(E)-(2-Chloro-5-((2-iodophenyl)diazenyl)phenyl)methanol (24): The general synthetic procedure G was used with benzoate 21 (140 mg, 0.28 mmol) and DIBAL-H (1.3 mL, 1.3 mmol) in THF (6 mL) to give the alcohol 24 as an orange oil (88 mg, 81%). 1H NMR (600 MHz, CDCl₃) δ 8.16 (d, J = 2.4 Hz, 1H), 8.04 (dd, J = 7.9, 1.3 Hz, 1H), 7.87 (dd, J = 8.4, 2.4 Hz, 1H), 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.43 (ddd, J = 8.1, 7.2, 1.3 Hz, 1H), 7.18 (td, J = 7.5, 1.6 Hz, 1H), 4.89 (s, 2H). 13C NMR (151 MHz, CDCl₃) δ 151.29, 151.19, 140.09, 139.52, 135.79, 132.65, 129.08, 124.10, 123.23, 117.46, 102.96, 62.80. HPLC-PDA-MS: RT = 5.33 min, 99.1% (254 nm), PDA λmax = 331 nm, MS (m/z) [M+H]+ 373.05.

(E)-(5-((2-Bromophenyl)diazenyl)-2-fluorophenyl)methanol (25b): The synthesis and characterization of this compound have been published by us [1].

(E)-(2-Bromo-5-((2-bromophenyl)diazenyl)phenyl)methanol (25d): The synthesis and characterization of this compound have been published by us [1].
(E)-3-((2-Iodophenyl)diazenyl)benzaldehyde (26f): The general synthetic procedure H was used with alcohol 23f (187 mg, 0.55 mmol) and Dess Martin periodinane (235 mg, 0.55 mmol) in DCM (11 mL) to give benzaldehyde 26f as an orange oil (171 mg, 92%). $^1$H NMR (600 MHz, CDCl$_3$) δ 10.15 (s, 1H), 8.46 (t, J = 1.9 Hz, 1H), 8.25 (ddd, J = 7.9, 2.1, 1.2 Hz, 1H), 8.06 (dd, J = 7.9, 1.2 Hz, 1H), 8.04 (dt, J = 7.6, 1.4 Hz, 2H), 7.71 (t, J = 7.7 Hz, 1H), 7.67 (dd, J = 8.1, 1.6 Hz, 1H), 7.45 (td, J = 7.7, 7.3, 1.3 Hz, 1H), 7.21 (td, J = 7.6, 1.6 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 191.70, 152.74, 151.17, 140.17, 137.56, 132.99, 131.70, 130.12, 129.11, 128.78, 125.41, 117.48, 103.26. HPLC-PDA-MS: RT = 5.49 min, 99.5% (254 nm), PDA $\lambda_{\text{max}}$ = 319 nm, MS (m/z) [M+H]$^+$ 337.10.

(E)-3-((3-Iodophenyl)diazenyl)benzaldehyde (26g): The general synthetic procedure H was used with alcohol 23g (329 mg, 0.97 mmol) and Dess Martin periodinane (413 mg, 0.97 mmol) in DCM (20 mL) to give benzaldehyde 26g as an orange oil (222 mg, 68%). $^1$H NMR (600 MHz, CDCl$_3$) δ 10.14 (s, 1H), 8.40 (t, J = 1.8 Hz, 1H), 8.29 (t, J = 1.8 Hz, 1H), 8.19 (ddd, J = 7.9, 2.0, 1.2 Hz, 1H), 8.03 (dt, J = 7.6, 1.4 Hz, 1H), 7.95 (ddd, J = 7.9, 1.9, 1.0 Hz, 1H), 7.84 (dt, J = 8.0, 1.3 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 191.70, 153.21, 152.80, 140.33, 137.52, 131.71, 130.94, 130.91, 130.10, 129.07, 124.07, 123.97, 94.75. HPLC-PDA-MS: RT = 5.67 min, 91.6% (254 nm), PDA $\lambda_{\text{max}}$ = 319 nm, MS (m/z) [M+H]$^+$ 337.00.

(E)-3-((4-Iodophenyl)diazenyl)benzaldehyde (26h): The general synthetic procedure H was used with alcohol 23h (187 mg, 0.55 mmol) and Dess Martin periodinane (235 mg, 0.55 mmol) in DCM (11 mL) to give benzaldehyde 26h as an orange oil (156 mg, 84%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.14 (s, 1H), 8.40 (s, 1H), 8.19 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 7.9 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) 191.81, 152.89, 151.74, 138.65, 137.47, 131.62, 130.09, 129.02, 124.78, 123.99, 98.78. HPLC-PDA-MS: RT = 5.65 min, 99.6% (254 nm), PDA $\lambda_{\text{max}}$ = 332 nm, MS (m/z) [M+H]$^+$ 337.00.
(E)-2-Chloro-5-((2-iodophenyl)diazenyl)benzaldehyde (27): The general synthetic procedure H was used with alcohol 24 (200 mg, 0.54 mmol) and Dess Martin periodinane (228 mg, 0.54 mmol) in DCM (11 mL) to give benzaldehyde 27 as an orange oil (192 mg, 97%). $^1$H NMR (600 MHz, CDCl$_3$) δ 10.55 (s, 1H), 8.53 (d, J = 2.5 Hz, 1H), 8.13 (dd, J = 8.5, 2.5 Hz, 1H), 8.05 (dd, J = 7.9, 1.3 Hz, 1H), 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.44 (ddd, J = 8.2, 7.3, 1.3 Hz, 1H), 7.21 (td, J = 7.6, 1.6 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 189.10, 150.90, 140.17, 140.09, 133.22, 133.05, 131.66, 128.99, 127.43, 126.07, 117.32, 103.38. HPLC-PDA-MS: RT = 5.91 min, 97.9% (254 nm), PDA λ$_{max}$ = 321 nm, MS (m/z) [M+H]$^+$ 371.10.

(E)-5-((2-Bromophenyl)diazenyl)-2-fluorobenzaldehyde (28b): The synthesis and characterization of this compound have been published by us [1].

(E)-2-Bromo-5-((2-bromophenyl)diazenyl)benzaldehyde (28d): The synthesis and characterization of this compound have been published by us [1].

1-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-((E)-2-iodophenyl)diazenyl)benzyl)-N-methylmethanamine (13f): The general synthetic procedure A was used with ammonium salt 7 (115 mg, 0.57 mmol), TEA (89 µL, 0.64 mmol) and benzaldehyde 26f (153 mg, 0.46 mmol) in DCE (9.0 mL) to give the tertiary amine 13f (213 g, 96%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.03 (d, J = 7.8 Hz, 1H), 7.94 (s, 1H), 7.91 – 7.84 (m, 1H), 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.43 (td, J = 7.7, 1.2 Hz, 1H), 7.16 (td, J = 7.6, 1.6 Hz, 1H), 5.46 (br, 1H), 3.64 (d, J = 13.4 Hz, 1H), 3.48 (d, J = 13.4 Hz, 1H), 2.99 (d, J = 13.6 Hz, 1H), 2.88 (d, J = 13.0 Hz, 1H), 2.44 (dt, J = 8.6, 5.6 Hz, 1H), 2.36 (t, J = 5.2 Hz, 1H), 2.31 (app. d, J = 17.7 Hz, 1H), 2.24 (app. d, J = 17.5 Hz, 1H), 2.16 (s, 3H), 2.15 – 2.07 (m, 1H), 1.31 (s, 3H), 1.17 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 152.53, 151.54, 146.49, 141.29, 139.95, 132.25, 132.21, 129.09, 129.04, 124.55, 121.79, 120.03, 117.49, 102.54, 63.93, 61.39, 44.37, 42.69, 41.11, 38.13, 32.04, 31.57, 26.51, 21.29. HPLC-PDA-MS: RT = 4.81 min, 99.9% (254 nm), PDA λ$_{max}$ = 321 nm, MS (m/z) [M+H]$^+$ 486.25
1-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-(3-((E)-(3-iodophenyl)diazenyl)benzyl)-N-methylmethanamine (13g): The general synthetic procedure A was used with ammonium salt 7 (160 mg, 0.79 mmol), TEA (124 µL, 0.89 mmol) and benzaldehyde 26g (213 mg, 0.63 mmol) in DCE (12.5 mL) to give the tertiary amine 13g (269 mg, 87%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 8.25 (t, J = 1.8 Hz, 1H), 7.91 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.86 (br, 1H), 7.79 (dt, J = 8.3, 1.4 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.26 (t, J = 7.9 Hz, 1H), 5.49 – 5.42 (m, 1H), 3.62 (d, J = 13.4 Hz, 1H), 3.47 (d, J = 13.4 Hz, 1H), 2.97 (d, J = 12.5 Hz, 1H), 2.87 (d, J = 13.1 Hz, 1H), 2.44 (dt, J = 8.6, 5.6 Hz, 1H), 2.35 (t, J = 5.3 Hz, 1H), 2.31 (app. d, J = 17.6 Hz, 1H), 2.24 (app. d, J = 17.9 Hz, 1H), 2.17 (s, 3H), 2.14 – 2.08 (m, 1H), 1.32 (s, 3H), 1.17 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) δ 153.60, 152.52, 146.44, 141.28, 139.55, 132.16, 130.77, 130.08, 128.43, 128.24, 122.85, 120.05, 94.70, 63.84, 61.38, 44.41, 42.74, 41.09, 38.12, 32.02, 31.56, 26.47, 21.29. HPLC-PDA-MS: RT = 4.81 min, 99.9% (254 nm), PDA λ\(_{max}\) = 321 nm, MS (m/z) [M+H\(^+\)] = 486.25

1-((1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-(3-((E)-(4-iodophenyl)diazenyl)benzyl)-N-methylmethanamine (13h): The general synthetic procedure A was used with ammonium salt 4 (110 mg, 0.55 mmol), TEA (100 µL, 0.73 mmol) and benzaldehyde 19h (150 mg, 0.45 mmol) in DCE (10 mL) to give the tertiary amine 13h (192 g, 89%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.91 – 7.83 (m, 3H), 7.82 – 7.76 (m, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.50 – 7.43 (m, 2H), 5.44 (br, 1H), 3.62 (d, J = 13.4 Hz, 1H), 3.47 (d, J = 13.4 Hz, 1H), 2.97 (d, J = 13.1 Hz, 1H), 2.87 (d, J = 13.0 Hz, 1H), 2.50 – 2.39 (m, 1H), 2.39 – 2.20 (m, 3H), 2.17 (s, 3H), 2.15 – 2.08 (m, 1H), 1.31 (s, 3H), 1.17 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H). \(^13\)C NMR (151 MHz, CDCl\(_3\)) δ 153.60, 152.52, 146.44, 141.28, 139.55, 132.16, 130.77, 130.08, 128.43, 128.24, 122.85, 120.05, 94.70, 63.84, 61.38, 44.41, 42.74, 41.09, 38.12, 32.02, 31.56, 26.47, 21.29. HPLC-PDA-MS: RT = 5.64 min, 99.7% (254 nm), PDA λ\(_{max}\) = 333 nm, MS (m/z) [M+H\(^+\)] = 486.15.

N-(2-Chloro-5-((E)-(2-iodophenyl)diazenyl)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (14e): The general synthetic procedure A was used with ammonium salt 7 (116 mg, 0.58 mmol), TEA (90 µL, 0.65 mmol) and benzaldehyde 27 (171 mg, 0.46 mmol) in DCE (9 mL) to give the tertiary amine 14e (199 g, 83%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 8.19 (d, J = 2.4 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.80 (dd, J = 8.5, 2.5 Hz, 1H), 7.64 (dd, J = 8.0, 1.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.43 (td, J = 7.7, 1.2 Hz, 1H), 7.17 (td, J = 7.6, 1.6 Hz, 1H), 5.47 (br, 1H), 3.70 (d, J = 14.7 Hz, 1H), 3.60 (d, J = 14.7 Hz, 1H), 3.06 (d, J = 13.1 Hz, 1H), 2.96 (d, J = 13.1 Hz, 1H), 2.46 – 2.34 (m, 2H), 2.34 –
2.18 (m, 5H), 2.12 – 2.06 (m, 1H), 1.28 (s, 3H), 1.14 (d, J = 8.4 Hz, 1H), 0.82 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 151.36, 151.09, 146.45, 140.02, 138.75, 137.34, 132.45, 130.22, 129.06, 126.80, 121.62, 120.05, 117.44, 102.87, 64.24, 58.19, 44.37, 42.79, 41.08, 38.13, 32.05, 31.58, 26.52, 21.23. HPLC-PDA-MS: RT = 5.13 min, 99.4% (254 nm), PDA λ$_{\text{max}}$ = 329 nm, MS (m/z) [M+H]$^+$ 520.20.

$N$-[(E)-(2-Bromophenyl)diazene]-2-fluorobenzyl)-1-{(1$R,5S$)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-$N$-methylmethanamine (16b): The synthesis and characterization of this compound have been published by us [1].

$N$-[(E)-(2-Bromophenyl)diazene]benzyl)-1-{(1$R,5S$)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-$N$-methylmethanamine (16d): The synthesis and characterization of this compound have been published by us [1].

$N$-[(E)-(2-Iodophenyl)diazene]benzyl)-1-{(1$R,5S$)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-$N,N$-dimethylmethanaminium iodide (3f): The general synthetic procedure D was used with the amine 13f (176 mg, 0.36 mmol) and Mel (453 µL, 7.3 mmol) in DCM (7.0 mL) to give the ammonium salt 3f as an orange solid (215 mg, 95%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.10 (t, J = 1.9 Hz, 1H), 8.04 (dd, J = 8.3, 1.5 Hz, 1H), 7.99 (dt, J = 7.6, 1.4 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.41 (ddd, J = 8.1, 7.2, 1.0 Hz, 1H), 7.18 (td, J = 7.6, 1.6 Hz, 1H), 6.28 (br, 1H), 5.27 (s, 2H), 4.49 (d, J = 12.4 Hz, 1H), 4.32 (d, J = 12.4 Hz, 1H), 3.22 (s, 3H), 3.19 (s, 3H), 2.52 (dt, J = 9.0, 5.6 Hz, 1H), 2.47 – 2.32 (m, 3H), 2.19 – 2.13 (m, 1H), 1.30 (s, 3H), 1.15 (s, 1H), 0.86 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 152.42, 150.71, 139.92, 137.06, 136.31, 135.97, 132.97, 130.42, 129.00, 128.38, 124.76, 117.28, 103.77, 69.20, 66.77, 49.20, 48.94, 47.01, 39.66, 38.12, 32.19, 32.01, 25.93, 21.50. HPLC-PDA-MS: RT = 4.75 min, 99.6% (254 nm), PDA λ$_{\text{max}}$ = 322 nm, MS (m/z) [M]$^+$ calculated for C$_{25}$H$_{31}$IN$_3$, 500.1557; found, 500.1547.

1-{(1$R,5S$)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]-$N$-[(E)-(3-Iodophenyl)diazene]benzyl)-$N,N$-dimethylmethanaminium iodide (3g): The general synthetic procedure D was used with the amine 13g (260 mg, 0.54 mmol) and Mel (670 µL, 10.7 mmol) in DCM (11.0 mL) to give the ammonium salt
3g as an orange solid (305 mg, 91%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.22 (s, 1H), 8.04 (s, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 6.26 (br, 1H), 5.28 (s, 2H), 4.48 (d, J = 12.4 Hz, 1H), 4.32 (d, J = 12.4 Hz, 1H), 3.21 (s, 3H), 3.19 (s, 3H), 2.51 (dt, J = 9.0, 5.6 Hz, 1H), 2.47 – 2.32 (m, 3H), 2.20 – 2.08 (m, 1H), 1.30 (s, 3H), 1.16 (d, J = 9.0 Hz, 1H), 0.85 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 153.06, 152.50, 140.34, 137.15, 136.41, 136.09, 130.92, 130.88, 128.53, 128.04, 124.45, 124.00, 94.73, 69.30, 66.89, 49.31, 49.07, 47.13, 39.78, 38.24, 32.30, 32.13, 26.05, 21.58. HPLC-PDA-MS: RT = 4.58 min, 99.9% (254 nm), PDA $\lambda_{max}$ = 317, nm, MS (m/z) [M]$^+$ 500.25. HRMS (m/z): [M]$^+$ calculated for C$_{25}$H$_{31}$IN$_3$, 500.1557; found, 500.1541.

$N$-[(3-[(E)-(4-Iodophenyl)diazenyl)benzyl]-1-[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-$N,N$-dimethylmethanaminium iodide (3h): The general synthetic procedure D was used with the amine 13h (112 mg, 0.23 mmol) and MeI (289 µL, 4.6 mmol) in DCM (4.5 mL) to give the ammonium salt 3h as an orange solid (141 mg, 97%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.05 (t, J = 1.9 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 6.26 (br, 1H), 5.27 (s, 2H), 4.46 (d, J = 12.5 Hz, 1H), 4.30 (d, J = 12.4 Hz, 1H), 3.20 (s, 3H), 3.18 (s, 3H), 2.52 (dt, J = 8.9, 5.6 Hz, 1H), 2.47 – 2.31 (m, 3H), 2.20 – 2.12 (m, 1H), 1.30 (s, 3H), 1.16 (d, J = 9.0 Hz, 1H), 0.85 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 152.66, 151.64, 138.61, 137.16, 136.20, 136.07, 130.42, 128.48, 128.00, 124.82, 124.41, 98.87, 69.32, 66.98, 49.31, 49.07, 47.14, 39.78, 38.24, 32.31, 32.14, 26.05, 21.58. HPLC-PDA-MS: RT = 4.99 min, 100% (254 nm), PDA $\lambda_{max}$ = 333, nm, MS (m/z) [M]$^+$ 500.20. HRMS (m/z): [M]$^+$ calculated for C$_{25}$H$_{31}$IN$_3$, 500.1557; found, 500.1542.

$N$-[(5-[(E)-(2-Iodophenyl)diazenyl)-2-chlorobenzyl]-1-[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-$N,N$-dimethylmethanaminium iodide (4e): The general synthetic procedure D was used with the amine 14e (195 mg, 0.38 mmol) and MeI (469 µL, 7.5 mmol) in DCM (7.5 mL) to give the ammonium salt 4e as an orange solid (203 mg, 82%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.53 (d, J = 2.3 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.39 (br, 1H), 5.30 (d, J = 13.2 Hz, 1H), 5.24 (d, J = 13.2 Hz, 1H), 4.69 (d, J = 12.4 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 3.27 (s, 6H), 2.65 – 2.52 (m, 1H), 2.52 – 2.35 (m, 3H), 2.25 – 2.14 (m, 1H), 1.33 (s, 3H), 1.24 (d, J = 8.9 Hz, 1H), 0.88 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 152.66, 151.64, 138.61, 137.16, 136.20, 136.07, 130.42, 128.48, 128.00, 124.82, 124.41, 98.87, 69.32, 66.98, 49.31, 49.07, 47.14, 39.78, 38.24, 32.31, 32.14, 26.05, 21.58. HPLC-PDA-MS: RT = 4.99 min, 100% (254 nm), PDA $\lambda_{max}$ = 333, nm, MS (m/z) [M]$^+$ 504.20. HRMS (m/z): [M]$^+$ calculated for C$_{25}$H$_{30}$ClIN$_3$, 534.1167; found, 534.1175.
\[ N-\{(E)-(2-\text{Bromophenyl})\text{diazenyl})-2-\text{fluorobenzyl}\}-1-\{(1R,5S)-6,6-\text{dimethylbicyclo}[3.1.1]\text{hept}-2-\text{en}-2-\text{yl})\}-N,N-\text{dimethylmethanaminium iodide (6b)}: \] The synthesis and characterization of this compound have been published by us [1].

\[ N-\{(E)-(2-\text{Bromophenyl})\text{diazenyl})-2-\text{bromobenzyl}\}-1-\{(1R,5S)-6,6-\text{dimethylbicyclo}[3.1.1]\text{hept}-2-\text{en}-2-\text{yl})\}-N,N-\text{dimethylmethanaminium iodide (6d)}: \] The synthesis and characterization of this compound have been published by us [1].

\[ \text{Scheme S3: Synthetic strategy for compound 6e. GSP=General Synthetic Procedure.} \]
(E)-2-Amino-5-((2-bromophenyl)diazenyl)benzaldehyde (30): A solution of phtalimide (195 mg, 1.32 mmol), benzaldehyde 28b (271 mg, 0.88 mmol) and K$_2$CO$_3$ (244 mg, 1.77 mmol) in DMF (6.5 mL) was heated in the microwave at 65 °C for 3 h. Water (30 mL) was added and the mixture was allowed to cool to room temperature. Slightly acidic water (50 mL) and DCM (50 mL) were added. The layers were separated. The organic layer was washed with slightly acidic brine (3 × 30 mL), dried over Na$_2$SO$_4$ and concentrated to give a red solid. The solid was dissolved in AcOH (50 mL). The mixture was heated to reflux for 1 h. Around 30 mL of the solvent were removed in vacuo and water was added slowly to induce precipitation. The suspension was heated to reflux to re-dissolve the solids and slowly cooled to 0 °C to crystallize the product. The crystals were filtered and washed with cold water (3 × 5 mL). The crystalline red solid was purified with automated flash chromatography (cHex/EtOAc) to give compound 30 (179 mg, 67%) as a red solid. $^1$H NMR (600 MHz, CDCl$_3$) δ 10.01 (s, 1H), 8.21 (d, J = 2.3 Hz, 1H), 8.06 (dd, J = 8.9, 2.3 Hz, 1H), 7.73 (dd, J = 8.0, 1.3 Hz, 1H), 7.66 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 8.9 Hz, 1H), 6.62 (br, J = 8.9 Hz, 2H).

(E)-5-((2-Bromophenyl)diazenyl)-2-iodobenzaldehyde (28e): To a solution of pTsOH·H$_2$O (0.139 g, 0.730 mmol) in MeCN (6 mL) was added amine 30 (74 mg, 0.243 mmol). The suspension of ammonium salt was cooled to 10-15 °C and to this was added gradually a solution of NaNO$_2$ (34 mg, 0.487 mmol) and KI (101 mg, 0.61 mmol) in water (0.9 mL). The reaction mixture was stirred for 10 min while allowed to warm to rt, after which it was stirred for 2 h. Water (10 mL) and satd. aq. NaHCO$_3$ were added (until pH = 9-10), followed by aq. Na$_2$S$_2$O$_3$ (1 M, 5 mL). The precipitate was filtered and purified with automated flash chromatography (cHex/DCM) to give compound 28e (13 mg, 13%) as an orange solid. $^1$H NMR (600 MHz, CDCl$_3$) δ 10.16 (s, 1H), 8.44 (d, J = 2.5 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.86 (dd, J = 8.4, 2.5 Hz, 1H), 7.77 (dd, J = 7.8, 1.4 Hz, 1H), 7.70 (dd, J = 7.9, 1.7 Hz, 1H), 7.40 (td, J = 7.6, 1.4 Hz, 1H), 7.36 (td, J = 7.6, 1.7 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 93.91, 152.54, 149.76, 144.15, 134.95, 133.80, 131.24, 128.40, 128.12, 125.18, 118.14, 117.88, 116.98. HPLC-PDA-MS: RT = 5.05 min, 98.2% (254 nm), PDA λ$_{max}$ = 375 nm, MS (m/z) [M+H]$^+$ 304.05, 306.00.
N-[5-[(E)-(2-Bromophenyl)diazenyl]-2-iodobenzyl]-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (16e): The general synthetic procedure A was used with ammonium salt 7 (20 mg, 0.10 mmol), TEA (14 µL, 0.10 mmol), benzaldehyde 28e (33 mg, 0.08 mmol) and NaBH(OAc)₃ (27 mg, 0.13 mmol) in DCE (1.6 mL) to give the tertiary amine 16e (24 mg, 54%) as an orange oil.

1H NMR (600 MHz, CDCl₃) δ 8.11 (br, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 8.0, 1.3 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 6.4 Hz, 1H), 7.42 (td, J = 7.6, 1.3 Hz, 1H), 7.35 (td, J = 7.6, 1.7 Hz, 1H), 5.51 (br, 1H), 3.62 (s, 2H), 3.16 – 2.87 (m, 2H), 2.49 – 2.37 (m, 2H), 2.37 – 2.22 (m, 5H), 2.17 – 2.08 (m, 1H), 1.31 (s, 3H), 1.16 (d, J = 8.3 Hz, 1H), 0.85 (s, 3H).

13C NMR (151 MHz, CDCl₃) δ 52.75, 149.68, 140.93, 140.26, 133.94, 132.24, 128.13, 126.13, 124.42, 121.83, 117.91, 109.53, 104.28, 61.28, 59.03, 44.47, 42.64, 41.01, 38.13, 32.01, 31.60, 26.44, 21.27, 21.27.

HPLC-PDA-MS: RT = 5.50 min, 97.7% (254 nm), PDA λ max = 338 nm, MS (m/z) [M+H]+ 564.05, 566.15.

N-[5-[(E)-(2-Bromophenyl)diazenyl]-2-iodobenzyl]-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N,N-dimethylmethanaminium iodide (6e, VUF16620): The general synthetic procedure D was used with the amine 16e (24 mg, 0.04 mmol) and MeI (53 µL, 0.85 mmol) in DCM (0.9 mL) to give the ammonium salt 6e as an orange solid (14.3 mg, 57%).

1H NMR δ 8.50 (d, J = 2.4 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 7.2 Hz, 2H), 7.69 (dd, J = 8.6, 2.3 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 6.40 (br, 1H), 5.31 (d, J = 13.5 Hz, 1H), 5.28 (d, J = 13.7 Hz, 1H), 4.71 (d, J = 12.5 Hz, 1H), 4.41 (d, J = 12.4 Hz, 1H), 3.31 (s, 3H), 3.28 (s, 3H), 2.63 – 2.53 (m, 1H), 2.53 – 2.35 (m, 3H), 2.24 – 2.16 (m, 1H), 1.37 – 1.28 (m, 4H), 0.88 (s, 3H).

13C NMR (151 MHz, CDCl₃) δ 152.74, 149.09, 142.23, 137.88, 135.96, 134.04, 133.27, 132.43, 131.94, 128.31, 127.10, 123.51, 118.51, 107.86, 70.72, 69.42, 50.06, 49.68, 47.32, 39.83, 38.41, 32.44, 32.14, 26.05, 21.58.HPLC-PDA-MS: trans-6e RT = 4.89 min, 96.8% (254 nm), PDA λ max = 337 nm, MS (m/z) [M]+ 578.10, 570.10; cis-6e RT = 4.62 min, 2.1% (254 nm), PDA λ max = 293, 240 nm, MS (m/z) [M]+ 578.10, 570.10. HRMS (m/z): [M]+ calculated for C₂₅H₁₀BrI₂N₅, 578.0662; found, 578.0661.
**Scheme S4**: Synthetic strategies for compounds 6f-h. GSP = General Synthetic Procedure.

**(E)-5-((2-Bromophenyl)diazene)-2-methoxybenzaldehyde (28f)**: The synthesis and characterization of this compound have been published by us [1], but here we report an alternative procedure. NaOMe (30% in MeOH, 50 µL, 0.27 mmol) was added to a solution of fluoride 28b (66 mg, 0.22 mmol) in anhydrous MeOH (4.5 mL). The mixture was heated in the MW at 65 °C for 60 min. The product partially crystallised. Water (4.5 mL) was added. The resulting suspension was filtered and washed with water (3 x 4.5 mL) to give an orange solid which was dried in the oven overnight. This afforded compound 28f as an orange solid (62 mg, 90%), which was used without further purification. 

1^H NMR (600 MHz, CDCl₃) δ 10.53 (s, 1H), 8.48 (d, J = 2.6 Hz, 1H), 8.22 (dd, J = 8.9, 2.6 Hz, 1H), 7.75 (dd, J = 8.0, 1.3 Hz, 1H), 7.67 (dd, J = 8.0, 1.7 Hz, 1H), 7.39 (td, J = 7.6, 1.3 Hz, 1H), 7.31 (td, J = 7.6, 1.7 Hz, 1H), 7.15 (d, J = 8.9 Hz, 1H), 4.05 (s, 3H). 1^3C NMR (151 MHz, CDCl₃) δ 189.27, 164.00, 149.59, 146.71, 133.92, 131.99, 129.33, 128.14, 125.85, 125.84, 125.24, 117.90, 112.41, 56.40. HPLC-PDA-MS: RT = 5.32 min, 99.0% (254 nm), PDA λ_max = 338 nm, MS (m/z) [M+H]^+ 319.00, 321.05.

**(E)-1-(5-((E)-(2-Bromophenyl)diazene)-2-isopropoxyphenyl)-N-(tert-butyl)methanimine (31)**: A solution of benzaldehyde 28b (650 mg, 2.1 mmol) and tert-butylamine (227 µL, 2.2 mmol) in PhMe was heated to reflux with a Dean-Stark system for 20 h. The solvent was removed in vacuo to give an
orange solid that corresponds to 31 (755 mg, 99%) which was used as such in further reactions. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.68 (dd, \(J = 6.8, 2.6\) Hz, 1H), 8.61 (s, 1H), 7.98 (ddd, \(J = 8.7, 4.9, 2.6\) Hz, 1H), 7.75 (dd, \(J = 7.9, 1.3\) Hz, 1H), 7.67 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.42 – 7.36 (m, 1H), 7.32 (td, \(J = 7.6, 1.7\) Hz, 1H), 7.21 (t, \(J = 9.3\) Hz, 1H), 1.34 (s, 9H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 164.77, 163.06, 149.61, 149.33, 149.31, 147.92, 147.90, 133.92, 132.13, 128.24, 126.22, 126.19, 125.92, 125.73, 125.66, 123.68, 123.61, 117.94, 116.91, 116.75, 58.35, 29.78.

HPLC-PDA-MS: RT = 5.43 min, >99 % (254 nm), PDA \(\lambda_{\text{max}}\) = 320 nm, MS (m/z) \([\text{M+H}]^+\) 306.95, 308.95, hydrolysis product (aldehyde) observed in MS.

\((E)-5-[(2-\text{Bromophenyl})\text{diazenyl}]-2-\text{isopropoxybenzaldehyde (28g)}\): Anhydrous 2-PrOH (40 \(\mu\)L, 0.53 mmol) was added to a suspension of NaH (13 mg, 0.53 mmol) in anhydrous DMSO (1.5 mL). It was stirred for 30 min. Fluoride 31 (181 mg, 0.50 mmol) was added. The dark blue mixture was heated to 100 °C for 1 h, during which the colour turned to dark red. The reaction mixture was poured into water (40 mL) and extraction with EtOAc (3 \(\times\) 20 mL) was performed. The combined organic layers were washed with brine, dried over MgSO\(_4\), filtered and concentrated in vacuo to give a pink oil. This residue containing intermediate 32 was dissolved in THF (5 mL). Water (1.5 mL) and AcOH (100 \(\mu\)L) were added. The mixture was stirred for 16 h at rt. The solvent was removed in vacuo and the obtained residue was redissolved in EtOAc/water 3:2 (50 mL). The layers were separated. The organic phase was washed with brine, dried over MgSO\(_4\), filtered and concentrated in vacuo to give a residue that was purified with automated flash chromatography (cHex/DCM) to give 28g as an orange solid (138 mg, 79%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 10.54 (s, 1H), 8.47 (d, \(J = 2.6\) Hz, 1H), 8.17 (dd, \(J = 9.0, 2.6\) Hz, 1H), 7.74 (dd, \(J = 7.9, 1.3\) Hz, 1H), 7.66 (dd, \(J = 8.1, 1.6\) Hz, 1H), 7.38 (ddd, \(J = 8.0, 7.2, 1.4\) Hz, 1H), 7.30 (ddd, \(J = 8.0, 7.2, 1.7\) Hz, 1H), 7.12 (d, \(J = 9.0\) Hz, 1H), 4.81 (hept, \(J = 6.1\) Hz, 1H), 1.47 (d, \(J = 6.1\) Hz, 6H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 189.55, 162.89, 149.60, 146.32, 133.87, 131.89, 128.73, 128.12, 126.05, 125.84, 125.78, 117.90, 114.29, 71.94, 22.12. HPLC-PDA-MS: RT = 5.84 min, 94.4 % (254 nm), PDA \(\lambda_{\text{max}}\) = 341 nm, MS (m/z) \([\text{M+H}]^+\) 347.00, 349.00.

\((E)-5-[(2-\text{Bromophenyl})\text{diazenyl}]-2-\text{(methylthio)benzaldehyde (28h)}\): A solution of fluoride 28b (76 mg, 0.25 mmol) and NaSMe (18 mg, 0.25 mmol) in DMF (3 mL) was heated in the MW at 65 °C for 30 min. Water (6 mL) was added. The suspension was filtered. The solid was washed with water (3 \(\times\) 3 mL) and dried in the oven overnight to give 28h as an orange solid (73 mg, 88%), which was used as such for further reactions. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 10.30 (s, 1H), 8.41 (s, 1H), 8.14 (d, \(J = 2.6\) Hz, 1H), 8.07 (d, \(J = 7.7\) Hz, 1H), 7.76 (d, \(J = 7.9\) Hz, 1H), 7.70 (d, \(J = 8.0\) Hz, 1H), 7.46 (d, \(J = 8.6\) Hz, 1H), 7.40 (t, \(J = 7.7\) Hz, 1H), 7.33 (t, \(J = 7.7\) Hz, 1H), 2.58 (s, 3H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 191.13, 149.53, 149.29, 147.83, 134.01, 132.91, 132.35, 129.93, 128.17, 127.25, 126.19, 125.33, 117.85, 15.45. HPLC-PDA-MS: RT = 5.51 min, 92.1 % (254 nm), PDA \(\lambda_{\text{max}}\) = 353 nm, MS (m/z) \([\text{M+H}]^+\) 334.90, 337.05.
**N-(5-((E)-(2-Bromophenyl)diazene)-2-methoxybenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (16f):** The synthesis and characterization of this compound have been published by us [1].

**N-(5-((E)-(2-Bromophenyl)diazene)-2-isopropoxybenzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (16g):** The general synthetic procedure A was used with ammonium salt 7 (94 mg, 0.47 mmol), TEA (68 µL, 0.49 mmol), benzaldehyde 28g (130 mg, 0.37 mmol) and NaBH(OAc)_3 (127 mg, 0.60 mmol) in DCE (7.5 mL) to give the tertiary amine 16g (172 mg, 93%) as an orange oil. ^1_H NMR (600 MHz, CDCl_3) δ 8.10 (d, J = 2.5 Hz, 1H), 7.86 (dd, J = 8.8, 2.5 Hz, 1H), 7.73 (dd, J = 8.0, 1.3 Hz, 1H), 7.65 (dd, J = 8.0, 1.6 Hz, 1H), 7.37 (td, J = 7.6, 1.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.96 (d, J = 8.8 Hz, 1H), 5.46 (br, 1H), 4.67 (hept, J = 6.0 Hz, 1H), 3.60 (d, J = 14.2 Hz, 1H), 3.55 (d, J = 14.4 Hz, 1H), 3.02 (d, J = 14.1 Hz, 1H), 2.92 (d, J = 13.2 Hz, 1H), 2.42 (dt, J = 8.6, 5.6 Hz, 1H), 2.37 (t, J = 5.7 Hz, 1H), 2.31 (app. d, J = 17.6 Hz, 1H), 2.23 (app. d, J = 17.0 Hz, 2H), 2.20 (s, 3H), 2.15 – 2.05 (m, 1H), 1.39 (d, J = 5.7 Hz, 6H), 1.29 (s, 3H), 1.16 (d, J = 8.5 Hz, 1H), 0.84 (s, 3H). ^13_C NMR (151 MHz, CDCl_3) δ 159.38, 150.09, 146.74, 133.70, 131.10, 129.52, 128.06, 126.51, 125.18, 123.36, 119.59, 117.95, 112.57, 100.13, 70.64, 64.00, 54.81, 44.35, 42.61, 41.13, 38.11, 32.04, 31.58, 26.47, 22.27, 21.25. HPLC-PDA-MS: RT = 5.46 min, 89.9% (254 nm), PDA λ_max = 352 nm, MS (m/z) [M+H]^+ 496.30, 498.35.

**N-(5-((E)-(2-Bromophenyl)diazene)-2-(methylthio)benzyl)-1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-N-methylmethanamine (16h):** The general synthetic procedure A was used with ammonium salt 7 (72 mg, 0.36 mmol), TEA (56 µL, 0.40 mmol), benzaldehyde 28h (96 mg, 0.29 mmol) and NaBH(OAc)_3 (97 mg, 0.46 mmol) in DCE (5.7 mL) to give the tertiary amine 16h (117 mg, 84%) as an orange oil. ^1_H NMR (600 MHz, CDCl_3) δ 8.11 (br, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 8.0, 1.3 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.57 (dd, J = 6.4 Hz, 1H), 7.42 (td, J = 7.6, 1.3 Hz, 1H), 7.35 (td, J = 7.6, 1.7 Hz, 1H), 5.51 (br, 1H), 3.62 (s, 2H), 3.16 – 2.87 (m, 2H), 2.49 – 2.37 (m, 2H), 2.37 – 2.22 (m, 5H), 2.17 – 2.08 (m, 1H), 1.31 (s, 3H), 1.16 (d, J = 8.3 Hz, 1H), 0.85 (s, 3H). ^13_C NMR (151 MHz, CDCl_3) δ 52.75, 149.68, 140.93, 140.26, 133.94, 132.24, 128.13, 126.13, 124.42, 121.83, 117.91, 109.53, 104.28, 61.28, 59.03, 44.47, 42.64, 41.01, 38.13, 32.01, 31.60, 26.44, 21.27, 21.27. HPLC-PDA-MS: RT = 5.14 min, 98.8% (254 nm), PDA λ_max = 367 nm, MS (m/z) [M+H]^+ 484.20, 486.20.
N-(5-{[(E)-2-Bromophenyl]diazenyl}-2-methoxybenzyl)-1-{[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]}-N,N-dimethylmethanaminium iodide (6f, VUF16216): The synthesis and characterization of this compound have been published by us [1].

N-(5-{[(E)-2-Bromophenyl]diazenyl}-2-isopropoxybenzyl)-1-{[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]}-N,N-dimethylmethanaminium iodide (6g): The general synthetic procedure D was used with the amine 16g (153 mg, 0.31 mmol) and MeI (385 µL, 6.2 mmol) in DCM (6.0 mL) to give the ammonium salt 6g as an orange solid (171 mg, 87%). ¹H NMR δ 8.29 (d, J = 2.4 Hz, 1H), 8.07 (dd, J = 9.0, 2.4 Hz, 1H), 7.73 (dd, J = 8.0, 1.3 Hz, 1H), 7.70 (dd, J = 8.1, 1.6 Hz, 1H), 7.39 (td, J = 7.6, 1.3 Hz, 1H), 7.31 (td, J = 7.6, 1.7 Hz, 1H), 7.10 (d, J = 9.0 Hz, 1H), 6.38 (br, 1H), 4.88 (s, 2H), 4.79 (p, J = 6.1 Hz, 1H), 4.60 (d, J = 12.5 Hz, 1H), 4.35 (d, J = 12.5 Hz, 1H), 3.21 (s, 3H), 3.20 (s, 3H), 2.55 (dt, J = 8.9, 5.6 Hz, 1H), 2.51 – 2.36 (m, 3H), 2.23 – 2.16 (m, 1H), 1.43 (d, J = 6.0 Hz, 6H), 1.33 (s, 3H), 1.25 (d, J = 8.8 Hz, 1H), 0.89 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 158.62, 148.34, 145.44, 136.16, 135.37, 132.84, 132.53, 131.19, 127.22, 125.06, 124.15, 117.07, 115.79, 112.67, 70.93, 69.29, 61.00, 48.76, 48.69, 46.29, 38.84, 37.30, 31.36, 31.12, 25.07, 21.27, 20.60. HPLC-PDA-MS: trans-6g RT = 5.32 min, 98.6% (254 nm), PDA λₘₐₓ = 352 nm, MS (m/z) [M]+ 510.30, 512.30; cis-6g RT = 4.84 min, 1.0% (254 nm), PDA λₘₐₓ = 309, 429 nm, MS (m/z) [M]+ 510.35, 512.35. HRMS (m/z): [M]+ calculated for C₂₈H₂₇BrN₃O, 510.2115; found, 510.2121.

N-(5-{[(E)-2-Bromophenyl]diazenyl}-2-(methylthio)benzyl)-1-{[(1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]}-N,N-dimethylmethanaminium iodide (6h): The general synthetic procedure D was used with the amine 16h (104 mg, 0.22 mmol) and MeI (268 µL, 4.3 mmol) in DCM (4.5 mL) to give the ammonium salt 6h as an orange solid (115 mg, 86%). ¹H NMR δ 8.33 (d, J = 2.2 Hz, 1H), 8.01 (dd, J = 8.6, 2.1 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.7 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 6.37 (br, 1H), 5.15 (d, J = 13.4 Hz, 1H), 5.08 (d, J = 13.5 Hz, 1H), 4.63 (d, J = 12.4 Hz, 1H), 4.38 (d, J = 12.4 Hz, 1H), 3.24 (d, J = 6.3 Hz, 6H), 2.58 (s, 3H), 2.57 – 2.52 (m, 1H), 2.50 – 2.36 (m, 3H), 2.20 – 2.14 (m, 1H), 1.32 (s, 3H), 1.29 (d, J = 8.9 Hz, 1H), 0.88 (s, 3H). ¹³C NMR (151 MHz,
CDCl$_3$ $\delta$ 150.06, 149.24, 145.90, 137.53, 136.15, 133.91, 132.67, 132.56, 128.23, 127.58, 126.61, 125.97, 123.00, 118.05, 70.54, 64.02, 49.89, 49.64, 47.29, 39.81, 38.32, 32.37, 32.05, 26.05, 21.56, 16.81. HPLC-PDA-MS: RT = 4.95 min, 99.2% (254 nm), PDA $\lambda_{\text{max}}$ = 367 nm, MS (m/z) [M]$^+$ 498.30, 500.25. HRMS (m/z): [M]$^+$ calculated for C$_{26}$H$_{33}$BrN$_3$S, 498.1565; found, 498.1573.
NMR Spectra

Compound 4d (VUF15888). Analytical data for this compound has been published by us before [1].

1H NMR (500 MHz, Chlороформ-d5) δ 8.52 (d, J = 1.9 Hz, 3H), 7.90 (dd, J = 6.6, 2.2 Hz, 1H), 7.71 (dd, J = 7.8, 1.7 Hz, 1H), 7.31 (dd, J = 7.8, 1.9 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.18 (dd, J = 7.6, 1.7 Hz, 1H), 7.14 (dd, J = 7.6, 1.9 Hz, 1H), 6.91 (s, 1H), 5.79 (s, 1H), 1.72 (d, J = 13.2 Hz, 1H), 0.67 (s, 1H), 1.12 (s, 3H), 1.02 (d, J = 9.2 Hz, 3H), 0.46 (q, 2H).

13C NMR (125 MHz, CDCl3) δ 152.25, 148.06, 139.08, 137.67, 136.18, 135.97, 134.95, 132.79, 128.24, 127.90, 126.65, 125.48, 118.04, 106.01, 62.23, 40.72, 40.03, 41.14, 30.72, 36.25, 32.34, 52.68, 26.64, 22.55.
Compound 6e (VUF16620).

$^1$H NMR (600 MHz, Chloroform-$d_5$) δ 8.50 (d, J = 2.4 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 6.4 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 6.40 (t, J = 5.1 Hz, 1H), 5.28 (s, 3H), 4.71 (d, J = 12.5 Hz, 1H), 4.40 (d, J = 12.4 Hz, 1H), 3.31 (s, 3H), 3.09 (s, 3H), 2.83 – 2.75 (m, 1H), 2.51 – 2.53 (m, 1H), 2.34 – 2.36 (m, 1H), 1.77 – 1.78 (m, 1H), 0.98 (s, 3H).

$^1$C NMR (150 MHz, CDCl$_3$) δ 152.74, 149.01, 142.21, 137.88, 135.96, 134.54, 133.27, 132.43, 131.94, 128.31, 127.10, 123.51, 118.11, 107.86, 70.72, 69.42, 50.68, 47.32, 39.83, 30.41, 32.44, 32.14, 26.05, 21.58.
Compound 6f (VUF16216). Analytical data for this compound has been published by us before [1].

\[ ^1H{\text{NMR}} \ (600 \text{ MHz, Chloroform-d)} \ 8.24 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.9 Hz, 1H), 6.35 (hept, 1H), 4.99 (d, J = 12.9 Hz, 1H), 4.59 (d, J = 12.8 Hz, 1H), 4.34 (d, J = 12.3 Hz, 1H), 4.37 (d, J = 12.5 Hz, 1H), 3.98 (s, 3H), 3.19 (s, 3H), 3.17 (s, 3H), 2.65 - 2.49 (m, 12H), 2.49 - 2.36 (m, 3H), 2.24 - 2.10 (m, 1H), 1.31 (s, 3H), 1.26 (s, J = 7.8 Hz, 1H), 0.99 (s, 3H).

\[ ^13C{\text{NMR}} \ (151 \text{ MHz, CDCl}_3) \ \text{d} \ 161.26, 140.29, 146.76, 137.20, 135.35, 133.05, 132.60, 128.22, 128.21, 126.68, 126.78, 117.88, 116.34, 113.28, 70.03, 64.71, 56.72, 54.05, 54.30, 87.23, 50.91, 50.13, 82.21, 82.21, 32.11, 26.10, 21.35.

S50
LC-PDA-MS chromatograms

Compound 4d (VUF15888). The iodide counter ion is visible at 0.8 min. Analytical data for this compound has been published by us before [1].
Compound 6e (VUF16620). The iodide counter ion is visible at 0.8 min. A trace of cis isomer is visible at 4.62 min.
 Compound 6f (VUF16216). The iodide counter ion is visible at 0.8 min. Analytical data for this compound has been published by us before [1].

### Table 1: PDA Multi 1 / 254nm 4nm

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