Supporting Information

Modular Synthesis of Alkylarylazo Compounds via Iron(III)-Catalyzed Olefin Hydroamination

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Contents

General Information S2
Scopes of aryldiazo sulfones S3
Synthesis and Characterization of 1 S3
General Procedure for Synthesis of alkylarylazo compounds 3 or 4 S4
Characterization of Products 3 and 4 S5-S19
Derivation of isoindolinone 4j to 5 and 6 S19-S20
References S20
1H and 13C NMR spectra of all the products S21-S67
Research on stability of compound 3-3 in different solvents S68-S69
**General Information:**

$^1$H NMR and $^{13}$C NMR spectra were recorded on BRUKER AVANCE III 600 spectrometer. (CD$_3$)$_2$CO and CDCl$_3$ were used as solvent. Chemical shifts were referenced relative to residual solvent signal ((CD$_3$)$_2$CO, $^1$H NMR: $\delta$ 2.05 ppm, $^{13}$C NMR: $\delta$ 29.92 ppm; CDCl$_3$: $^1$H NMR: $\delta$ 7.26 ppm, $^{13}$C NMR: $\delta$ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants ($J$) are reported in Hertz (Hz). HRMS were performed on AB Sciex LC 30A-Triple TOF 4600 apparatus (ESI). Melting points were measured with micro melting point apparatus.

Unless otherwise noted, Alkenes 2 obtained from commercial suppliers were used directly without further purification. Aryldiazo sulfones 1 was prepared in our own way based on literature.$^1$
Scopes of aryldiazo sulfones

Synthesis and Characterization of 1:

To the phenylhydrazine (10 mmol, 2.0 equiv.) was added EtOH (20 mL), and the solution was cooled to 0 °C. 4-methylbenzenesulfonyl chloride (5 mmol, 1.0 equiv.) was added over 10 min. Afterwards, the solution was warmed to RT and kept for 1 h. Then it was concentrated and the solid was washed with water and ethanol, respectively. The dry product 1' was obtained with a yield about 65%, which was used directly in the next step.
To a 100 mL flask charged with the above substituted benzoquinone (2 mmol) was added anhydrous DCM (30 mL), copper sulfate (0.6 mmol, 0.3 equiv) and potassium carbonate (4 mmol, 2.0 equiv). The solution was kept vigorously stirring at room temperature for 3 h under air. Then it was concentrated and the residue was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as eluent to give aryldiazo sulfones 1 (about 70% yield).

For selected characterization of substrates 1, see:

![Diagram of aryldiazo sulfones 1](image)

**(E)-1-(2,6-dichlorophenyl)-2-tosylidazene (1r).** Yellow solid; m.p. 50-52 °C; $^1$H NMR (CDCl$_3$, 600MHz) $\delta$ 7.72 (d, $J$ = 8.4 Hz, 2H), 7.67 (d, $J$ = 7.8 Hz, 2H), 7.54 (d, $J$ = 7.8 Hz, 2H), 7.28 (d, $J$ = 7.8 Hz, 2H), 3.91 (t, $J$ = 6.0 Hz, 2H), 2.42 (s, 3H), 2.10 (t, $J$ = 7.8 Hz, 2H), 1.37 (s, 6H); $^{13}$C NMR (CDCl$_3$, 150MHz) $\delta$ 150.8, 143.4, 137.8, 137.4, 129.7, 127.6, 127.1, 122.6, 70.9, 59.8, 43.5, 25.3, 21.2; HRMS (ESI) (m/z): calcld for C$_{13}$H$_{10}$Cl$_2$N$_2$O$_2$SNa$^+$ ([M+Na]$^+$), 350.9732; found 350.9716.

**General Procedure for Synthesis of alkylarylazo compounds 3 or 4:**

![Diagram of general procedure](image)

To a 25-mL tube equipped with a magnetic stir bar, 1a (52 mg, 0.2 mmol, 1.0 equiv.), olefin 2 (0.4 mmol), KHCO$_3$ (10 mg, 0.2 mmol, 1.0 equiv.), Fe(acac)$_3$ (14 mg, 20 mol %), PhSiH$_3$ (48 µL, 0.4 mmol, 2.0 equiv.), MeOH (80 µL, 2 mmol, 10.0 equiv.), THF (super dry, 2.0 mL) were added under N$_2$ atmosphere. The sealed tube was stirred at room temperature for 5 h. The solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica was added to the flask, and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on a silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as the
eluent to give alkylazo compounds products 3.

\[
\begin{align*}
\text{Br} & \quad \text{N=N-Ts} \\
\text{1n} & + \quad \text{MeOH (0.8 mL)} \\
\text{THF (super dry, 6.0 mL)} & \quad \text{MeOH (10 eq)} \\
\text{PhSiH}_3 (2.0 \text{ eq}) & \quad \text{MeOH (10 eq)} \\
\text{Fe(acac)}_3 (20 \text{ mol %}) & \quad \text{THF, rt, 5 h} \\
\text{KHCO}_3 (1.0 \text{ eq}) & \\
\text{N=N-} & \\
\text{OH} & \\
\text{4j} &
\end{align*}
\]

To a 25 mL tube equipped with a magnetic stir bar, 1n (680 mg, 2 mmol, 1.0 equiv.), olefin 2-5 (350 µL, 4 mmol, 2.0 equiv.), KHCO₃ (100 mg, 2 mmol, 1.0 equiv.), Fe(acac)₃ (140 mg, 20 mol %), PhSiH₃ (0.48 mL, 0.4 mmol, 2.0 equiv.), MeOH (0.8 mL, 2 mmol, 10.0 equiv.), THF (super dry, 6.0 mL) were added under N₂ atmosphere. The sealed tube was stirred at room temperature for 5 h. The solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica was added to the flask, and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on a silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as the eluent to give isoindolinone products 4j with the yield of 68% (0.37 g).

Characterization of Products 3 and 4:

**(E)-2-methyl-2-(phenyldiazenyl)propan-1-ol (3-1):** 36 mg, 68% yield; Oil; \(^1\)H NMR (Acetone-d⁶, 600 MHz) \(\delta\) 7.72-7.67 (m, 2H), 7.54-7.47 (m, 3H), 3.84 (t, \(J = 4.8\) Hz, 2H), 1.30 (s, 6H); \(^{13}\)C NMR (Acetone-d⁶, 150 MHz) \(\delta\) 153.2, 131.2, 129.9, 122.9, 72.4, 69.6, 22.1; HRMS (ESI) \((m/z)\): calcd for C\(_{10}\)H\(_{15}\)N\(_2\)O\(^{+}\)([M+H]⁺), 179.1179; found 179.1165.

![3-1](image)

**2-(phenyldiazenyl)propan-1-ol (3-2):** 19 mg, 58% yield; Oil; \(^1\)H NMR (Acetone-d⁶, 600 MHz) \(\delta\) 7.68 (dd, \(J_1 = 8.4\) Hz, \(J_2 = 1.8\) Hz, 2H), 7.51-7.47 (m, 3H), 4.08 -4.04 (m, 1H), 3.92-3.84 (m, 3H), 1.29 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR...
(Acetone-d$_6$, 150 MHz) δ 153.1, 131.3, 129.9, 123.1, 75.9, 65.8, 15.5; HRMS (ESI) (m/z): calcd for C$_9$H$_{13}$N$_2$O$^+([M+H]^+)$, 165.1022; found 165.1108.

(S,E)-3-(phenyldiazenyl)butan-1-ol (3-3): 23 mg, 65% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) δ 7.68-7.63 (m, 2H), 7.48-7.42 (m, 3H), 4.03-3.96 (m, 1H), 3.74-3.68 (m, 2H), 2.19-2.14 (m, 1H), 2.06-2.02 (m, 1H), 1.40 (d, J = 6.6 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 152.0, 130.7, 129.2, 122.3, 70.6, 60.0, 38.0, 19.0; HRMS (ESI) (m/z): calcd for C$_{10}$H$_{15}$N$_2$O$^+([M+H]^+)$, 179.1179; found 179.1171.

(S,E)-2-methyl-3-(phenyldiazenyl)butan-2-ol (3-4): 25 mg, 60% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) δ 7.71-7.67 (m, 2H), 7.52-7.46 (m, 3H), 3.70 (s, 1H), 3.61 (q, J = 7.2 Hz, 1H), 1.31 (s, 3H), 1.30-1.24 (m, 6H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) δ 153.3, 131.3, 130.0, 123.1, 82.3, 72.2, 27.7, 26.6, 14.4; HRMS (ESI) (m/z): calcd for C$_{11}$H$_{17}$N$_2$O$^+([M+H]^+)$, 193.1335; found 193.1324.

(E)-3-methyl-3-(phenyldiazenyl)butan-1-ol (3-5): 29 mg, 75% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) δ 7.65-7.61 (m, 2H), 7.47-7.42 (m, 3H), 3.88 (t, J = 6.0 Hz, 2H), 2.06 (t, J = 6.0 Hz, 2H), 1.34 (s, 6H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 152.0, 130.6, 129.2, 122.1, 71.0, 59.8, 43.5, 29.8, 25.3; HRMS (ESI) (m/z): calcd for C$_{11}$H$_{17}$N$_2$O$^+([M+H]^+)$, 193.1335; found 193.1322.

(S)-3,7-dimethyl-7-(phenyldiazenyl)octan-1-ol (3-6): 37 mg, 70% yield; Oil; $^1$H
NMR (Acetone-d$_6$, 600 MHz) $\delta$ 7.70-7.63 (m, 2H), 7.53-7.45 (m, 3H), 3.61-3.53 (m, 2H), 3.41 (t, $J = 6.0$ Hz, 1H), 1.83-1.71 (m, 2H), 1.59-1.50 (m, 2H), 1.34-1.26 (m, 9H), 1.23-1.08 (m, 2H), 0.86 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) $\delta$ 153.2, 131.0, 130.0, 122.7, 60.6, 41.9, 41.0, 38.7, 30.2, 25.2, 25.1, 22.2, 20.0; HRMS (ESI) ($m/z$): calcd for C$_{16}$H$_{27}$N$_2$O$^+$([M+H]$^+$), 263.2118; found 263.2120.

(E)-(1-(phenyldiazenyl)cyclohexyl)methanol (3-7): 29 mg, 67% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) $\delta$ 7.70-7.67 (m, 2H), 7.52-7.46 (m, 3H), 3.71 (d, $J = 6.0$ Hz, 2H), 3.67-3.63 (m, 1H), 1.78-1.72 (m, 2H), 1.59-1.54 (m, 2H), 1.52-1.45 (m, 4H), 1.29 (d, $J = 9.0$ Hz, 2H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) $\delta$ 153.3, 131.1, 129.9, 122.8, 74.2, 67.6, 31.8, 26.7, 22.9; HRMS (ESI) ($m/z$): calcd for C$_{13}$H$_{19}$N$_2$O$^+$([M+H]$^+$), 219.1492; found 219.1472.

(E)-1-(1-methylcyclohexyl)-2-phenyldiazene (3-8): 20 mg, 50% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.65 (d, $J = 7.2$ Hz, 2H), 7.45 (t, $J = 7.2$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 1.61-1.53 (m, 6H), 1.49 (d, $J = 5.4$ Hz, 2H), 1.26 (s, 1H), 1.19 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 152.8, 130.0, 129.0, 121.9, 69.6, 36.4, 26.1, 22.7; HRMS (ESI) ($m/z$): calcd for C$_{13}$H$_{19}$N$_2$Na$^+$([M+Na]$^+$), 233.1049; found 233.1036.

(S,E)-1-phenyl-2-(1-phenylethyl)diazene (3-9): 22 mg, 52% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) $\delta$ 7.74-7.67 (m, 2H), 7.54-7.46 (m, 5H), 7.40 (t, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 1H), 4.92 (q, $J = 6.6$ Hz, 1H), 1.66 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) $\delta$ 153.0, 142.8, 131.6, 130.0, 129.5, 128.4, 128.4, 123.2, 77.9, 21.24; HRMS (ESI) ($m/z$): calcd for C$_{14}$H$_{14}$N$_2$Na$^+$([M+Na]$^+$), 233.1049; found 233.1036.
(E)-1-((1S,2S,4R)-bicyclo[2.2.1]heptan-2-yl)-2-phenyldiazene (3-10): 22 mg, 55% yield; Oil; $^1$H NMR (Acetone-$d^6$, 600 MHz) $\delta$ 7.68-7.62 (m, 2H), 7.50-7.44 (m, 3H), 3.76 (dd, $J_1 = 7.8$ Hz, $J_2 = 3.0$ Hz, 1H), 2.44 (s, 1H), 2.39 (d, $J = 4.2$ Hz, 1H), 1.97-1.93 (m, 1H), 1.86-1.82 (m, 1H), 1.66-1.58 (m, 3H), 1.36-1.29 (m, 3H); $^{13}$C NMR (Acetone-$d^6$, 150 MHz) $\delta$ 153.1, 131.2, 129.9, 122.9, 81.0, 43.6, 37.2, 36.6, 36.5, 29.9, 27.4; HRMS (ESI) ($m/z$): calcd for C$_{13}$H$_{17}$N$_2$+$^{[M+H]^+}$, 201.1386; found 201.1378.

(S,E)-1-(1-(4-methoxyphenyl)propan-2-yl)-2-phenyldiazene (3-11): 30 mg, 60% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.63 (d, $J = 7.2$ Hz, 2H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 4.02 (dd, $J_1 = 13.8$ Hz, $J_2 = 6.6$ Hz, 1H), 3.78 (s, 3H), 3.19 (dd, $J_1 = 13.8$ Hz, $J_2 = 7.2$ Hz, 1H), 2.98 (dd, $J_1 = 13.8$ Hz, $J_2 = 6.6$ Hz, 1H), 1.35 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 158.2, 152.3, 130.8, 130.6, 130.4, 129.1, 122.2, 113.9, 74.8, 55.4, 40.8, 18.5; HRMS (ESI) ($m/z$): calcd for C$_{16}$H$_{19}$N$_2$O+$^{[M+H]^+}$, 255.1492; found 255.1486.

(S,E)-1-(2-(phenyldiazeny1)propyl)-1H-indole (3-12): 30 mg, 57% yield; Oil; $^1$H NMR (Acetone-$d^6$, 600 MHz) $\delta$ 7.58-7.55 (m, 2H), 7.51-7.44 (m, 5H), 7.22 (d, $J = 3.6$ Hz, 1H), 7.12 (t, $J = 7.8$ Hz, 1H), 6.99 (t, $J = 7.8$ Hz, 1H), 6.37 (d, $J = 3.6$ Hz, 1H), 4.82 (dd, $J_1 = 15.0$ Hz, $J_2 = 8.4$ Hz, 1H), 4.64 (dd, $J_1 = 14.4$ Hz, $J_2 = 4.2$ Hz, 1H), 4.27-4.20 (m, 1H), 1.40 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (Acetone-$d^6$, 150 MHz) $\delta$ 152.9, 137.4, 131.6, 129.9, 129.7, 129.6, 123.1, 122.1, 121.4, 120.0, 110.8, 101.8, 73.8, 50.8, 16.8; HRMS (ESI) ($m/z$): calcd for C$_{17}$H$_{18}$N$_3$+$^{[M+H]^+}$, 264.1495; found
(E)-1-(2-methyl-4-phenylbutan-2-yl)-2-phenyldiazene (3-13): 31 mg, 61% yield; Oil; $^1$H NMR (Acetone-$d_6$, 600 MHz) $\delta$ 7.70 (d, $J = 8.4$ Hz, 2H), 7.54-7.49 (m, 2H), 7.49-7.45 (m, 1H), 7.26 (t, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 7.2$ Hz, 2H), 7.15 (t, $J = 7.8$ Hz, 1H), 2.66-2.60 (m, 2H), 2.14-2.08 (m, 2H), 1.36 (s, 6H); $^{13}$C NMR (Acetone-$d_6$, 150 MHz) $\delta$ 153.2, 143.7, 131.2, 130.0, 129.3, 129.2, 126.6, 122.8, 70.5, 43.8, 31.3, 25.14; HRMS (ESI) ($m/z$): calcd for $C_{17}H_{21}N_2^+([M+H]^+)$, 253.1699; found 253.1688.

(7S)-2-methyl-7-((E)-phenyldiazenyl)octan-3-ol (3-14): 33 mg, 66% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.65 (d, $J = 7.2$ Hz, 2H), 7.48-7.36 (m, 3H), 3.85-3.67 (m, 1H), 3.35 (s, 1H), 2.03-1.92 (m, 1H), 1.83-1.70 (m, 1H), 1.66-1.59 (m, 1H), 1.54-1.44 (m, 2H), 1.43-1.32 (m, 5H), 0.93-0.84 (m, 6H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 152.2, 130.4, 129.1, 122.3, 76.7, 73.4, 35.4, 34.2, 33.6, 22.9, 19.1, 19.0, 17.2; HRMS (ESI) ($m/z$): calcd for $C_{15}H_{25}N_2O^+([M+H]^+)$, 249.1961; found 249.1952.

(7S)-1-phenyl-7-((E)-phenyldiazenyl)octan-3-ol (3-15): 43 mg, 70% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.68 (d, $J = 7.2$ Hz, 2H), 7.49-7.43 (m, 3H), 7.29 (t, $J = 7.8$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 3H), 3.85-3.69 (m, 1H), 3.65-3.59 (m, 1H), 2.82-2.75 (m, 1H), 2.69-2.63 (m, 1H), 2.05-1.90 (m, 1H), 1.80-1.70 (m, 3H), 1.60-1.45 (m, 4H), 1.37 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 152.2, 142.2, 130.4, 129.1, 128.5, 125.9, 122.3, 73.3, 71.3, 39.1, 37.5, 35.3, 32.1, 22.4, 19.1; HRMS (ESI) ($m/z$): calcd for $C_{20}H_{26}N_2ONa^+([M+Na]^+)$, 333.1937; found 333.1923.
(E)-1-(furan-2-yI)-5-(phenyldiazenyl)hexan-1-ol (3-16): 28 mg, 51% yield; Oil; $^1$H NMR (Acetone-$d^6$, 600 MHz) $\delta$ 7.67 (d, $J = 7.2$ Hz, 2H), 7.54-7.48 (m, 3H), 7.44-7.41 (m, 1H), 6.35-6.31 (m, 1H), 6.24-6.21 (m, 1H), 4.66-4.61 (m, 1H), 4.28 (dd, $J_1 = 5.4$ Hz, $J_2 = 2.4$ Hz, 1H), 3.76 (dd, $J_1 = 13.2$ Hz, $J_2 = 6.6$ Hz, 1H), 2.00-1.95 (m, 1H), 1.87-1.77 (m, 3H), 1.49-1.43 (m, 1H), 1.38-1.34 (m, 1H), 1.32 (d, $J = 6.0$ Hz, 3H); $^{13}$C NMR (Acetone-$d^6$, 150 MHz) $\delta$ 159.3, 153.1, 142.3, 131.2, 130.0, 123.0, 110.8, 106.0, 73.8, 67.7, 36.7, 35.8, 23.1, 19.2; HRMS (ESI) ($m/z$): calcd for C$_{16}$H$_{21}$N$_2$O$_2$+([M+H]$^+$), 273.1598; found 273.1605.

(E)-1-((1-benzyloxy)-2-methylpropan-2-yl)-2-phenyldiazene (3-17): 34 mg, 67% yield; Oil; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.69 (d, $J = 7.8$ Hz, 2H), 7.50-7.43 (m, 3H), 7.36-7.33 (m, 4H), 7.32-7.29 (m, 1H), 4.58 (s, 2H), 3.79 (s, 2H), 1.37 (s, 6H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 168.2, 152.2, 134.1, 132.1, 130.6, 129.0, 123.4, 122.4, 117.9, 71.1, 41.8, 40.2, 16.8; HRMS (ESI) ($m/z$): calcd for C$_{17}$H$_{21}$N$_2$O$^+$([M+H]$^+$), 269.1648; found 269.1636.

(S,E)-3-(phenyldiazenyl)butanenitrile (3-18): 15 mg, 43% yield; Oil; $^1$H NMR (Acetone-$d^6$, 600 MHz) $\delta$ 7.76-7.70 (m, 2H), 7.58-7.50 (m, 3H), 4.23-4.14 (m, 1H), 3.08-2.98 (m, 2H), 1.47 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (Acetone-$d^6$, 150 MHz) $\delta$ 152.6, 132.1, 130.1, 123.2, 68.7, 22.8, 18.3; HRMS (ESI) ($m/z$): calcd for C$_{10}$H$_{11}$N$_3$Na$^+$(M+Na)$^+$, 196.0845; found 196.0831.
(S,E)-1-(1-(2-bromophenoxy)propan-2-yl)-2-phenyldiazene (3-19): 39 mg, 62% yield; Oil; \(^1^H\) NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.69 (dd, \(J_1 = 8.4\) Hz, \(J_2 = 1.8\) Hz, 3H), 7.51 (dd, \(J_1 = 7.2\) Hz, \(J_2 = 1.8\) Hz, 2H), 7.48-7.43 (m, 4H), 4.38-4.27 (m, 3H), 1.50 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 155.3, 152.3, 133.5, 130.7, 129.1, 128.5, 122.4, 122.3, 114.0, 112.7, 71.8, 71.6, 15.7; HRMS (ESI) (m/z): calcd for C\(_{15}\)H\(_{16}\)BrN\(_2\)O\(^-\)([M+H]\(^+\)), 319.0441; found 319.0422.

(S,E)-1-(1-(2-bromo-6-chlorophenyl)propan-2-yl)-2-phenyldiazene (3-20): 39 mg, 58% yield; Oil; \(^1^H\) NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.65 (d, \(J = 7.2\) Hz, 2H), 7.49 (d, \(J = 7.8\) Hz, 2H), 7.45-7.39 (m, 3H), 6.90 (t, \(J = 7.8\) Hz, 1H), 4.28 (dd, \(J_1 = 12.6\) Hz, \(J_2 = 6.0\) Hz, 1H), 3.67 (dd, \(J_1 = 13.8\) Hz, \(J_2 = 7.8\) Hz, 1H), 3.49 (dd, \(J_1 = 13.8\) Hz, \(J_2 = 7.8\) Hz, 1H), 1.49 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 152.2, 138.2, 132.5, 130.4, 129.0, 129.0, 126.2, 122.5, 72.5, 41.6, 18.9; HRMS (ESI) (m/z): calcd for C\(_{15}\)H\(_{15}\)BrN\(_2\)O\(^-\)([M+H]\(^+\)), 380.9597; found 380.9599.

(S,E)-2-(2-(phenyldiazenyl)propyl)isoindoline-1,3-dione (3-21): 25 mg, 43% yield; Oil; \(^1^H\) NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.79 (dd, \(J_1 = 5.4\) Hz, \(J_2 = 3.0\) Hz, 2H), 7.67 (dd, \(J_1 = 5.4\) Hz, \(J_2 = 3.0\) Hz, 2H), 7.56 (dd, \(J_1 = 8.4\) Hz, \(J_2 = 1.8\) Hz, 2H), 7.41-7.37 (m, 3H), 4.31-4.29 (m, 1H), 4.21-4.15 (m, 1H), 3.98 (dd, \(J_1 = 13.8\) Hz, \(J_2 = 4.8\) Hz, 1H), 1.47 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 168.2, 152.2, 134.1, 132.1,
130.6, 129.0, 123.4, 122.4, 71.1, 41.8, 16.8; HRMS (ESI) (m/z): calcd for C_{17}H_{15}N_{3}O_{2}Na^+([M+Na]^+), 316.1056; found 316.1042.

(E)-N-(4-(phenyldiazenyl)pentyl)benzenesulfonamide (3-22): 48 mg, 73% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) δ 7.88-7.81 (m, 3H), 7.64-7.63 (m, 2H), 7.61-7.59 (m, 1H), 7.57-7.54 (m, 2H), 7.52-7.46 (m, 3H), 2.96-2.92 (m, 3H), 1.94-1.89 (m, 1H), 1.78-1.73 (m, 1H), 1.50-1.44 (m, 2H), 1.26 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) δ 153.0, 142.1, 133.1, 131.3, 130.0, 129.9, 127.7, 123.0, 73.3, 43.9, 33.0, 27.2, 19.2; HRMS (ESI) (m/z): calcd for C$_{17}$H$_{22}$N$_3$O$_2$S$^+([M+H]^+), 332.1427; found 332.1411.

(S,E)-4-(phenyldiazenyl)pentyl 4-methylbenzenesulfonate (3-23): 45 mg, 62% yield; Yellow Solid; $^1$H NMR (CDCl$_3$, 600 MHz) δ 7.79 (d, $J = 8.4$ Hz, 2H), 7.68-7.65 (m, 2H), 7.50-7.45 (m, 3H), 7.33 (d, $J = 8.4$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.73-3.67 (m, 1H), 2.45 (s, 3H), 1.95-1.89 (m, 1H), 1.72-1.66 (m, 4H), 1.33 (d, $J = 6.6$ Hz, 4H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 152.0, 134.3, 130.6, 129.2, 128.0, 122.1, 71.0, 59.8, 43.5, 29.8, 25.3; HRMS (ESI) (m/z): calcd for C$_{19}$H$_{25}$N$_2$O$_3$S$^+([M+H]^+), 361.1580; found 361.1375.

(S,E)-N-phenyl-4-(phenyldiazenyl)pentanamide (3-24): 34 mg, 60% yield; Yellow Solid; $^1$H NMR (Acetone-d$_6$, 600 MHz) δ 9.16 (s, 1H), 7.68-7.63 (m, 4H), 7.53-7.45 (m, 3H), 7.26 (t, $J = 7.8$ Hz, 2H), 7.03 (t, $J = 7.2$ Hz 1H), 3.85-3.78 (m, 1H), 2.40 (t, $J = 7.8$ Hz, 2H), 232-2.25 (m, 1H), 2.21-2.15 (m, 1H), 1.35 (d, $J = 6.0$ Hz, 3H); $^{13}$C
NMR (Acetone-\textit{d}^6, 150 MHz) $\delta$ 171.4, 153.0, 140.5, 131.4, 130.0, 129.5, 124.0, 123.1, 120.0, 73.2, 34.3, 31.5, 19.2; HRMS (ESI) (m/z): calcd for C_{17}H_{26}N_{3}O^{+}([M+H]^+), 282.1601; found 282.1584.

(S,E)-N,N-diethyl-4-(phenyldiazenyl)pentanamide (3-25): 33 mg, 64% yield; Oil; $^1$H NMR (Acetone-\textit{d}^6, 600 MHz) $\delta$ 7.70-7.65 (m, 2H), 7.55-7.45 (m, 3H), 3.82-3.77 (m, 1H), 3.33-3.27 (m, 4H), 2.35-2.27 (m, 2H), 2.23-2.17 (m, 1H), 2.13-2.06 (m, 1H), 1.33 (d, $J = 6.6$ Hz, 3H), 1.09-1.01 (m 6H); $^{13}$C NMR (Acetone-\textit{d}^6, 150 MHz) $\delta$ 171.3, 153.1, 131.3, 130.0, 123.0, 73.1, 42.4, 40.6, 31.5, 19.3, 14.7, 13.5; HRMS (ESI) (m/z): calcd for C_{15}H_{24}N_{3}O^{+}([M+H]^+), 262.1914; found 262.1904.

Benzyl (S,E)-4-(phenyldiazenyl)pentanoate (3-26): 40 mg, 68% yield; Oil; $^1$H NMR (Acetone-\textit{d}^6, 600 MHz) $\delta$ 7.69-7.65 (m, 2H), 7.53-7.44 (m, 4H), 7.36 (d, $J = 4.8$ Hz, 4H), 5.08 (q, $J = 12.5$ Hz, 2H), 3.84-3.76 (m, 1H), 2.44-2.40 (m, 2H), 2.26-2.22 (m, 1H), 2.14-2.08 (m, 1H), 1.33 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (Acetone-\textit{d}^6, 150 MHz) $\delta$ 173.3, 153.0, 137.6, 131.5, 130.0, 129.3, 128.9, 128.9, 123.0, 72.8, 66.5, 31.4, 31.0, 19.0; HRMS (ESI) (m/z): calcd for C_{18}H_{24}N_{2}O_{2}^{+}([M+H]^+), 297.1598; found 297.1587.

(E)-3-methyl-3-(phenyldiazenyl)butyl benzoate (3-27): 30 mg, 50% yield; Oil; $^1$H NMR (Acetone-\textit{d}^6, 600 MHz) $\delta$ 7.99-7.92 (m, 2H), 7.71-7.66 (m, 2H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.51-7.42 (m, 5H), 4.45 (t, $J = 7.2$ Hz, 2H), 2.34 (t, $J = 6.6$ Hz, 2H), 1.40 (s, 6H); $^{13}$C NMR (Acetone-\textit{d}^6, 150 MHz) $\delta$ 166.7, 153.0, 133.8, 131.3, 130.2, 130.0,
129.4, 122.9, 69.8, 62.3, 39.8, 25.5; HRMS (ESI) (m/z): calcd for C_{18}H_{21}N_{2}O_{2}^{+}([M+H]^{+}), 297.1598; found 297.1585.

(S,E)-1-(4-methoxyphenyl)-5-(phenyldiazenyl)hexan-1-one (3-28): 36 mg, 58% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) $\delta$ 7.98-7.93 (m, 2H), 7.72-7.63 (m, 2H), 7.53-7.45 (m, 3H), 7.01-6.96 (m, 2H), 3.87 (s, 3H), 3.83-3.78 (m, 1H), 3.04-2.95 (m, 2H), 2.04-1.96 (m, 1H), 1.86-1.80 (m, 1H), 1.73-1.65 (m, 2H), 1.33 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) $\delta$ 198.5, 164.4, 131.3, 131.1, 131.1, 130.0, 123.0, 114.6, 73.7, 56.0, 38.4, 35.5, 22.0, 19.2; HRMS (ESI) (m/z): calcd for C_{19}H_{23}N_{2}O_{2}^{+}([M+H]^{+}), 311.1754; found 311.1740.

(S,E)-2-(2-(phenyldiazenyl)propyl)aniline (3-29): 29 mg, 58% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) $\delta$ 7.66-7.59 (m, 2H), 7.50-7.44 (m, 3H), 6.98 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 6.93-6.88 (m, 1H), 6.66 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.54-6.52 (m, 1H), 4.13-4.07 (m, 1H), 3.18 (dd, $J_1 = 13.8$ Hz, $J_2 = 7.8$ Hz, 1H), 2.98 (dd, $J_1 = 13.8$ Hz, $J_2 = 6.0$ Hz, 1H), 1.36 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) $\delta$ 153.0, 147.1, 131.9, 131.3, 130.0, 128.1, 123.5, 123.0, 118.0, 116.3, 73.5, 37.8, 19.2; HRMS (ESI) (m/z): calcd for C_{15}H_{18}N_{3}^{+}([M+H]^{+}), 240.1495; found 240.1484.

(E)-3-methyl-4-(phenyldiazenyl)-1-(p-tolyl)pyrrolidine (3-30): 39 mg, 70% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) $\delta$ 7.74-7.68 (m, 2H), 7.55-7.47 (m, 3H), 7.02-7.96 (m, 2H), 4.33-4.24 (m, 1H), 4.15-4.06 (m, 1H), 3.50-3.43 (m, 2 H), 3.35-3.30 (m, 1H), 3.11-3.06 (m, 1H), 3.01-2.95 (m, 1H), 2.67-2.60 (m, 1H), 2.20 (s,
3H), 1.17 (d, J = 7.2 Hz, 3H); HRMS (ESI) (m/z): calcd for C_{19}H_{24}N_{3}^{+}([M+H]^{+}), 294.1965; found 294.1965.

(E)-3-methyl-3-(o-tolyl diazenyl)butan-1-ol (4a): 30 mg, 73% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) δ 7.34-7.31 (m, 2H), 7.25-7.21 (m, 2H), 3.69-3.65 (m, 2H), 3.52 (t, J = 4.8 Hz, 1H), 2.55 (s, 3H), 2.10-2.01 (m, 2H), 1.31 (s, 6H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) δ 151.3, 136.7, 131.8, 130.9, 127.3, 116.4, 70.7, 58.9, 44.3, 25.6, 17.3; HRMS (ESI) (m/z): calcd for C$_{12}$H$_{19}$N$_2$O$^+$([M+H]$^+$), 207.1492; found 207.1484.

(E)-3-((2-fluorophenyl)diazenyl)-3-methylbutan-1-ol (4b): 33 mg, 78% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) δ 7.52-7.48 (m, 1H), 7.45-7.39 (m, 1H), 7.34-7.30 (m, 1H), 7.26-7.22 (m, 1H), 3.67-3.63 (m, 2H), 3.49 (t, J = 4.8 Hz, 1H), 2.07-0.03 (m, 2H), 1.31 (s, 6H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) δ 160.6, 158.9 (d, J = 7.5 Hz), 132.9, 125.5 (d, J = 3.0 Hz), 119.1, 117.7 (d, J = 17.5 Hz), 71.3, 58.8, 44.2, 25.4; HRMS (ESI) (m/z): calcd for C$_{11}$H$_{16}$FN$_2$O$^+$([M+H]$^+$), 211.1241; found 211.1234.

(E)-3-((2-chlorophenyl)diazenyl)-3-methylbutan-1-ol (4c): 28 mg, 63% yield; Oil; $^1$H NMR (Acetone-d$_6$, 600 MHz) δ 7.56 (dd, J$_f$ = 7.8 Hz, J$_s$ = 1.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.40-7.37 (m 1H), 7.32 (dd, J$_f$ = 7.8 Hz, J$_s$ = 1.8 Hz, 1H), 3.66 (m, 2H), 3.52 (t, J = 5.4 Hz, 1H), 2.08-2.02 (m, 2H), 1.33 (s, 6H); $^{13}$C NMR (Acetone-d$_6$, 150 MHz) δ 149.5, 133.4, 132.0, 131.2, 128.7, 118.9, 71.6, 58.8, 44.1, 25.5; HRMS (ESI) (m/z): calcd for C$_{11}$H$_{16}$ClN$_2$O$^+$([M+H]$^+$), 227.0946; found 227.0936.
(E)-3-methyl-3-(m-tolyl diazenyl)butan-1-ol (4d): 23mg, 55% yield; Oil; $^1$H NMR (Acetone-\textit{d}$_6$, 600 MHz) $\delta$ 7.72 (d, $J = 9.0$ Hz, 2H), 7.63 (d, $J = 8.4$ Hz, 2H), 3.67-3.64 (m, 2H), 3.51 (t, $J = 4.8$ Hz, 1H), 2.05 (m, 2H), 1.31 (s, 6H); $^{13}$C NMR (Acetone-\textit{d}$_6$, 150 MHz) $\delta$ 152.0, 133.2, 124.8, 124.7, 70.5, 58.8, 44.2, 25.4; HRMS (ESI) (m/z): calcd for C$_{12}$H$_{19}$N$_2$O$^+$([M+H]$^+$), 207.1492; found 207.1484.

(E)-3-((3-methoxyphenyl)diazenyl)-3-methylbutan-1-ol (4e): 24 mg, 55% yield; Oil; $^1$H NMR (Acetone-\textit{d}$_6$, 600 MHz) $\delta$ 7.42 (t, $J = 7.8$ Hz, 1H), 7.32-7.26 (m, 1H), 7.21 (t, $J = 2.4$ Hz, 1H), 7.08-7.02 (m, 1H), 3.86 (s, 3H), 3.67 (t, $J = 7.2$ Hz, 2H), 2.07-2.03 (m, 2H), 1.31 (s, 6H); $^{13}$C NMR (Acetone-\textit{d}$_6$, 150 MHz) $\delta$ 165.6, 163.9, 125.0, 125.0, 116.8, 116.6, 70.1, 58.9, 44.3, 25.4; HRMS (ESI) (m/z): calcd for C$_{12}$H$_{19}$N$_2$O$_2$+$^+$([M+H]$^+$), 223.1441; found 223.1432.

(E)-3-methyl-3-(p-tolyl diazenyl)butan-1-ol (4f): 26 mg, 63% yield; Oil; $^1$H NMR (Acetone-\textit{d}$_6$, 600 MHz) $\delta$ 7.59 (d, $J = 3.6$ Hz, 2H), 7.33 (d, $J = 7.8$ Hz, 2H), 3.68 (t, $J = 7.2$ Hz, 2H), 2.40 (s, 3H), 2.09-2.02 (m, 2H), 1.31 (s, 6H); $^{13}$C NMR (Acetone-\textit{d}$_6$, 150 MHz) $\delta$ 151.2, 141.4, 130.5, 122.8, 69.8, 58.9, 44.4, 25.5, 21.3; HRMS (ESI) (m/z): calcd for C$_{12}$H$_{19}$N$_2$O$^+$([M+H]$^+$), 207.1492; found 207.1483.
(E)-3-((4-methoxyphenyl)diazenyl)-3-methylbutan-1-ol (4g): 70% yield; Oil; \(^1\)H NMR (Acetone-d\(^6\), 600 MHz) \(\delta\) 7.69-7.64 (m, 2H), 7.07-7.01 (m, 2H), 3.86 (s, 3H), 3.66 (t, \(J = 7.2\) Hz, 2H), 2.02 (t, \(J = 7.2\) Hz, 2H), 1.28 (s, 6H); \(^13\)C NMR (Acetone-d\(^6\), 150 MHz) \(\delta\) 162.6, 147.1, 124.5, 115.0, 69.4, 59.0, 56.0, 44.5, 25.6; HRMS (ESI) (m/z): calcd for C\(_{12}\)H\(_{19}\)N\(_2\)O\(_2\)^+([M+H]^+), 223.1441; found 223.1429.

![4g](image)

(E)-3-((4-fluorophenyl)diazenyl)-3-methylbutan-1-ol (4h): 24 mg, 58% yield; Oil; \(^1\)H NMR (Acetone, 600 MHz) \(\delta\) 7.79-7.72 (m, 2H), 7.31-7.26 (m, 2H), 3.66 (t, \(J = 6.6\) Hz, 2H), 2.08-2.02 (m, 3H), 1.31 (s, 6H); \(^13\)C NMR (Acetone-d\(^6\), 150 MHz) \(\delta\) 165.6, 163.9, 149.7 (d, \(J =3.0\) Hz), 125.0 (d, \(J =9.0\) Hz), 116.8, 116.6, 70.1, 58.9, 44.3, 25.4 (d, \(J =3.0\) Hz); HRMS (ESI) (m/z): calcd for C\(_{11}\)H\(_{16}\)FN\(_2\)O\(_2\)^+([M+H]^+), 211.1241; found 211.1232.

![4h](image)

(E)-3-((4-chlorophenyl)diazenyl)-3-methylbutan-1-ol (4i): 35 mg, 60% yield; Oil; \(^1\)H NMR (Acetone-d\(^6\), 600 MHz) \(\delta\) 7.71-7.67 (m, 2H), 7.58-7.52 (m, 2H), 3.67-3.63 (m, 2H), 3.50 (t, \(J =5.4\) Hz, 1H), 2.07-2.02 (m, 2H), 1.31 (s, 6H); \(^13\)C NMR (Acetone-d\(^6\), 150 MHz) \(\delta\) 151.7, 136.5, 130.1, 124.4, 70.5, 58.8, 44.3, 25.4; HRMS (ESI) (m/z): calcd for C\(_{11}\)H\(_{16}\)ClN\(_2\)O\(_2\)^+([M+H]^+), 227.0946; found 227.0938.

![4i](image)

(E)-3-((4-bromophenyl)diazenyl)-3-methylbutan-1-ol (4j): 35 mg, 65% yield; Oil; \(^1\)H NMR (Acetone-d\(^6\), 600 MHz) \(\delta\) 7.71 (d, \(J =9.0\) Hz, 2H), 7.62 (d, \(J =9.0\) Hz, 2H), 3.67-3.64 (m, 2H), 3.53 (t, \(J =4.8\) Hz, 1H), 2.07-2.04 (m, 2H), 1.31 (s, 6H); \(^13\)C NMR (Acetone-d\(^6\), 150 MHz) \(\delta\) 152.0, 138.4, 133.2, 124.7, 70.5, 58.8, 44.2, 25.4; HRMS
(ESI) (m/z): calcd for C₁₁H₁₆BrN₂O⁺([M+H]⁺), 271.0441; found 271.0432.

(E)-4-((4-hydroxy-2-methylbutan-2-yl)diazenyl)benzonitrile (4k): 27 mg, 62% yield; Oil; ¹H NMR (Acetone-d₆, 600 MHz) δ 7.92 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 3.65-3.62 (m, 2H), 3.54 (t, J = 5.4 Hz, 1H), 2.07-2.02 (m, 3H), 1.31 (s, 6H); ¹³C NMR (Acetone-d₆, 150 MHz) δ 155.3, 134.3, 123.5, 119.0, 114.3, 71.4, 58.7, 44.1, 25.3; HRMS (ESI) (m/z): calcd for C₁₂H₁₆N₃O⁺([M+H]⁺), 218.1288; found 218.2173.

(E)-3-methyl-3-((4-(trifluoromethyl)phenyl)diazenyl)butan-1-ol (4l): 28 mg, 54% yield; Oil; ¹H NMR (Acetone-d₆, 600 MHz) δ 7.87 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 3.68-3.64 (m, 2H), 3.50 (t, J = 5.4 Hz, 1H), 2.10-2.03 (m, 2H), 1.33 (s, 6H); ¹³C NMR (Acetone-d₆, 150 MHz) δ 155.4, 132.0 (q, J = 31.5 Hz), 127.3 (q, J = 4.5 Hz), 125.2 (q, J = 270.0 Hz), 123.4, 71.2, 58.8, 44.2, 25.4; HRMS (ESI) (m/z): calcd for C₁₂H₁₆F₃N₂O⁺([M+H]⁺), 261.1209; found 261.1199.

(E)-3-((3,5-dichlorophenyl)diazenyl)-3-methylbutan-1-ol (4m): 27 mg, 51% yield; Oil; ¹H NMR (Acetone-d₆, 600 MHz) δ 7.61 (d, J = 2.4 Hz, 2H), 7.59 (t, J = 1.8 Hz, 1H), 3.64 (m, 2H), 3.51 (t, J = 5.4 Hz, 1H), 1.32 (s, 6H); ¹³C NMR (Acetone-d₆, 150 MHz) δ 154.6, 136.2, 130.3, 121.7, 71.4, 58.7, 44.1, 25.3; HRMS (ESI) (m/z): calcd for C₁₁H₁₅C₁₂N₂O⁺([M+H]⁺), 261.0556; found 261.0546.
(E)-3-((2,6-dichlorophenyl)diazenyl)-3-methylbutan-1-ol (4n): 31 mg, 60% yield; Oil; $^1$H NMR (Acetone-$d_6$, 600 MHz) $\delta$ 7.51 (d, $J = 1.8$ Hz, 2H), 7.34 (t, $J = 7.8$ Hz, 1H), 3.76-3.70 (m, 2H), 2.13 (t, $J = 7.8$ Hz, 2H), 1.38 (s, 6H); $^{13}$C NMR (Acetone-$d_6$, 150 MHz) $\delta$ 149.5, 130.0, 129.4, 126.0, 125.0, 73.5, 58.8, 43.8, 25.3; HRMS (ESI) (m/z): calcd for C$_{11}$H$_{15}$Cl$_2$N$_2$O$^+$([M+H]$^+$), 261.0556; found 261.0548.

**Derivation of isoindolinone 4j to 5 and 6:**

**Compound (5):** In a 100 mL flask with a stir-bar was charged with 3-((2-(4-bromophenyl)hydrazinyl)-3-methylbutan-1-ol 4j (54.4 mg, 0.2 mmol, 1.0 equiv) and p-tolylboronic acid (30 mg, 0.22 mmol, 1.1 equiv). EtOH (2 mL), H$_2$O (1 mL), Pd(OAc)$_2$ (2.2 mg, 5 mol %) and Na$_2$CO$_3$ (21 mg, 1.0 equiv) were added and the solution was stirred at RT for 12 hours. The solution was filtered by diatomite and most of the EtOH was evaporated. The solution was extracted with ethyl acetate (10 mL * 3). The crude compound was purified by silica gel chromatography (ethyl acetate/petroleum ether, v/v = 1:5 as eluent) to give 5 (45 mg, 80 %) as a white solid, m.p. 87-89 °C, $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.72 (d, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 7.8$ Hz, 2H), 7.54 (d, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 3.91 (t, $J = 6.0$ Hz, 2H), 2.42 (s, 3H), 2.10 (t, $J = 7.8$ Hz, 2H), 1.37 (s, 6H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 150.8, 143.4, 137.8, 137.4, 129.7, 127.6, 127.1, 122.6, 70.9, 59.8, 43.5, 25.3, 21.2; HRMS (ESI) (m/z): calcd for C$_{18}$H$_{23}$N$_2$O$^+$([M+H]$^+$), 283.1805; found 283.1793.
**Compound (6):** To a solution of 3-(2-(4-bromophenyl)hydrazinyl)-3-methylbutan-1-ol 4j (0.2 mmol, 54.4 mg) in ethanol (4 mL) at room temperature, was added hydrazine (1 mL). The solution was heated to 60 °C for 10 hours. The solution was evaporated to give compound 6 in quantitative yield as an oil, which can be transferred to 4j again in solvent under air. \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.58 (d, \(J = 9.0\) Hz, 2H), 7.51 (d, \(J = 8.4\) Hz, 2H), 3.85 (t, \(J = 6.0\) Hz, 2H), 2.06 (t, \(J = 6.0\) Hz, 2H), 1.32 (s, 6H); \(^1\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 150.7, 132.4, 124.9, 123.7, 71.1, 59.7, 43.5, 25.2; HRMS (ESI) (m/z): calcd for C\(_{11}\)H\(_{18}\)BrN\(_2\)O\(^+\) ([M+H]\(^+\)), 273.0597; found 273.0593.

**Reference:**
$^1$H and $^{13}$C NMR spectra of all the products
Research on stability of compound 3-3 in different solvents

We carefully texted the stability of compound 3-3 that has a one hydrogen atom in the α-position on the alkyl part in different solvents (from left to right: acetone, ethyl acetate, THF, DCM, CHCl₃, CDCl₃, MeOH and MeCN). The following figure shows that this class of compounds will go bad quickly in chlorogorm and DCM, while alkylarylazo compounds with no hydrogen atom in the α-position on the alkyl part are very stable in these solvents at room temperature (given no picture).