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Cobalt(III)-Catalyzed C−H Activation: Azo Directed Selective 1,4-Addition of *Ortho* C−H Bond to Maleimides

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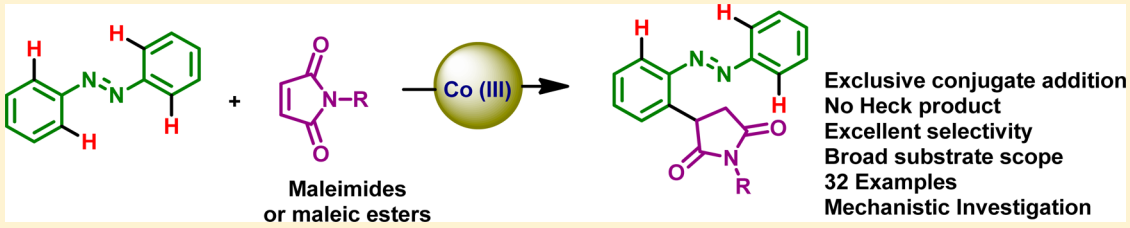
Supporting Information



ABSTRACT: Highly selective azo directed 1,4-addition of an *ortho* C−H bond to maleimides has been developed using Co(III) catalyst. This reaction furnishes 3-arylated succinimide derivatives in good yields with excellent selectivity. This protocol exhibits a broad substrate scope and is compatible with symmetrical and unsymmetrical azobenzene derivatives, with maleimides and maleate esters. Preliminary deuterium incorporation studies have been performed to understand the mechanism of the reaction.

INTRODUCTION

Transition-metal-catalyzed C−H bond activation using a directing group strategy is a well explored area using Pd,[1] Ru,[2] and Rh catalysts.[3,4] Most of the Cp*M-catalyzed C−H activation reactions employ Cu additive ($Cu(OAc)_2 \cdot H_2O$) and acid additives (AcOH) in either stoichiometric or super-stoichiometric amounts.[2−4] In this direction, high-valent Co-catalyzed C−H activation is coming to the forefront as Co is less expensive and naturally abundant and Co complexes are air-stable and are synthesized easily.[5] On the environmental point of view, Cp*Co(III)-catalyzed reactions require only a catalytic amount of acetate source, which results in reducing the amount of additives. In 2013, Kanai and Matsunaga employed high-valent cationic Co(III) complexes in the C−H activation reactions.[6,7] Further developments of cobalt(III)-catalyzed C−H functionalization reactions have been achieved by the groups of Ellman,[8] Chang,[9] Ackermann,[10] Glorius,[11] Daugulis,[12] and others.[13] At the same time, Co(II)-catalyzed C−H activation reactions are reported by using bidendate directing groups.[14] Aromatic azo compounds are widely used as industrial dyes and find applications in material research and are used as protein probes.[15,16] The past few years have witnessed the Pd-,[17] Rh-,[18,19] Ru-,[20a] and Re[20b,c]-catalyzed functionalization of azobenzene derivatives. To the best of our knowledge, there are only a few reports on the functionalization of azobenzene using Co(III) catalyst.[21] Thus, cationic Co(III)-catalyzed synthesis of indazoles from azobenzenes, and annulation of azobenzene using diphenylacetylene, are recently reported by Ellman[8a] and Cheng.[21] Recently, we have reported Ru-catalyzed conjugate addition of indoles,[22a] acetophenones,[22b] benzamides and acetanilides[22c] with maleimide (Scheme 1). After this report,[22] maleimide has been widely used as coupling partner in C−H activation reactions (Scheme 1).[23] One of the reasons for using maleimide is that the succinimide moiety is found in many natural products and pharmaceutically active compounds,[24] and the succinimide ring can be easily reduced to pyrrolidine, which can also be cleaved into useful functional groups.[25] In pursuit of our efforts,[26] in this paper, we disclose a Co(III)-catalyzed 1,4-addition of maleimides using azobenzene as a directing group.

RESULTS AND DISCUSSION

Optimization of Reaction Conditions. The optimization study was initiated by reacting (*E*)-1,2-di-*p*-tolyldiazene (**1a**, 0.2 mmol) with *N*-ethylmaleimide (**2a**, 0.4 mmol), [Cp*Co(CO)-I_2] (10 mol %), $AgSbF_6$ (20 mol %), and AgOAc (2 equiv) in DCE at 120 °C, which led to the formation of monoactivated product **3aa** in 12% yield (NMR yield) and diactivated product (**3aa′**) in a trace amount (entry 1, Table 1). Decreasing the amount of AgOAc to 20 mol % led to a dramatic increase in the formation of **3aa** to 61%, whereas the formation of diactivated product **3aa′** was observed in 25% yield (entry 2). This reaction clearly indicates that a catalytic amount of additive (acetate source) is essential for this reaction. Further investigation revealed that additives such as CsOAc, NaOAc, and KOAc were useful and furnished the desired product **3aa** in 53, 68, and 60% yields, respectively (entries 3−5), whereas the reaction of **1a** with **2a** in the presence of acid additives such as PivOH and AcOH also furnished the desired product **3aa** in 68% and 65% yields, respectively (entries 6 and 7). Using 1.5 equiv of **1a** and 1 equiv of **2a** furnished **3aa** in 70% (entry 8). Further, the reaction using 2 equiv of **1a** and 1 equiv of **2a** enhanced the yield of **3aa** to 75% (entry 9). Finally, the optimal

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Scheme 1. Comparison of Previous Works with This Work

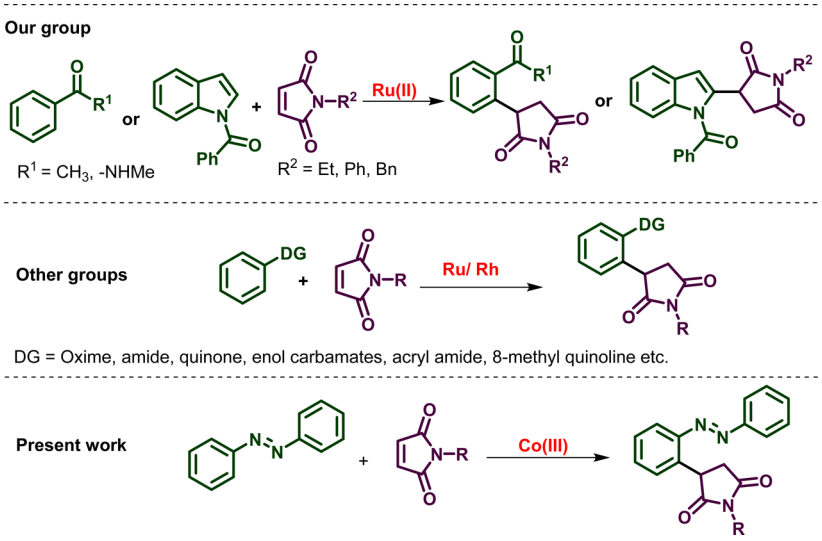
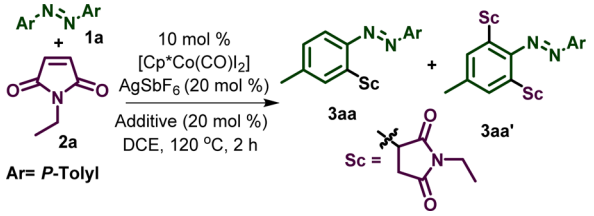


Table 1. Optimization of Reaction Conditions[a]



entry	**1a** (equiv)	**2a** (equiv)	Co (mol%)	additive (20 mol%)	NMR yield (%)[b]	
					3aa	**3aa'**
1	1	2	10	AgOAc (2 equiv)	12	trace
2	1	2	10	AgOAc	61	25
3	1	2	10	CsOAc	53	22
4	1	2	10	NaOAc	68	25
5	1	2	10	KOAc	60	33
6	1	2	10	Piv-OH	68	15
7	1	2	10	AcOH	65	10
8	1.5	1	10	NaOAc	70	20
9	2	1	10	NaOAc	75	15
10	**2**	**1**	**5**	**NaOAc**	**89**[c]	**5**
11	2	1	2.5	NaOAc	80	12
12	2	1	5	NaOAc	67	18[d]
13	2	1	5	NaOAc	40	10[e]
14	2	**1**	none	NaOAc	nd	nd
15	2	1	5	NaOAc	nd	nd[f]
16	2	1	5	none	nd	nd
17	2	1	Rh	$Cu(OAc)_2{\cdot}H_2O$	trace	nd[g]
18	2	1	Rh	AcOH	77	trace[h]
19	2	1	Ru	$Cu(OAc)_2{\cdot}H_2O$	nd	nd[i]

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), $[Cp^*Co(CO)I_2]$ (10 mol %), $[AgSbF_6]$ (20 mol %), additive (20 mol %), solvent (2 mL), at 120 °C for 2 h. [b]^1H NMR yield (using terephthalaldehyde as an internal standard). [c]Isolated yield. [d]Reaction was performed at 100 °C. [e]10 mol % of $AgSbF_6$. [f]Absence of $AgSbF_6$. [g]$[Cp^*RhCl_2]_2$ (2.5 mol %) instead of Co catalyst, $AgSbF_6$ (10 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (1 equiv). [h]$[Cp^*RhCl_2]_2$ (2.5 mol %) instead of Co catalyst, $AgSbF_6$ (10 mol %), and AcOH (2 equiv). [i]$[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %) instead of Co catalyst, $AgSbF_6$ (20 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv), and AcOH (10 equiv). nd = not detected.

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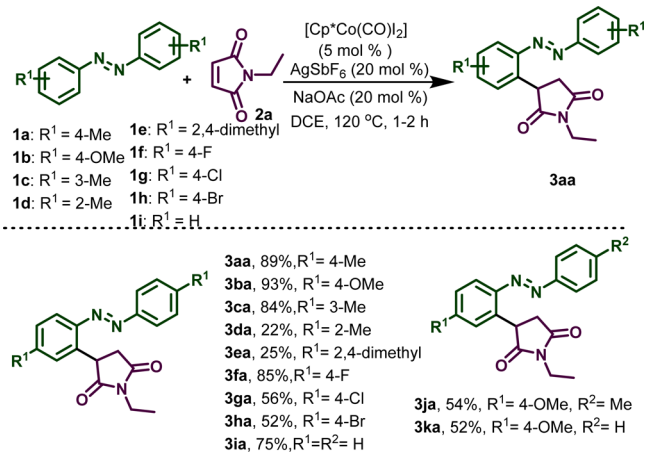
reaction condition was achieved using 2 equiv of **1a**, 1 equiv of **2a**, and 5 mol % of cobalt catalyst, which furnished **3aa** in 89% yield (entry 10). Further reactions of **1a** with **2a** by decreasing the catalyst loading to 2.5 mol % or increasing the reaction temperature to 100 °C were not useful (entries 11 and 12). Performing the reaction with 10 mol % of $AgSbF_6$, the yield of the product **3aa** has dropped to 40% (entry 13). Reactions in the absence of $[Cp^*Co(CO)I_2]$ or $AgSbF_6$ or base did not furnish the expected product **3aa** (entries 14−16). Further, this reaction was investigated using Rh(III) and Ru(II)-catalysts. Thus, the reaction of **1a** with **2a** in the presence of Rh(III) catalyst and $Cu(OAc)_2{\cdot}H_2O$ (1 equiv) furnished only a trace amount of **3aa** (entry 17), whereas, with the reaction in the presence of 2 equiv of AcOH, the product **3aa** was obtained in 77% yield (entry 18). Using Ru(II) catalyst in the presence of $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv) and AcOH (10 equiv) did not furnish the expected product (entry 19). Further investigation has been continued using Co(III) catalyst, as Co(III) catalysts are less expensive than Rh(III) catalysts.

The scope of the 1,4-addition reaction of maleimides has been explored using various symmetrical and unsymmetrical azobenzene derivatives (Scheme 2). Thus, 4-methyl, 4-

Scheme 2. Substrate Scope for Azobenzene Derivatives[a,b]

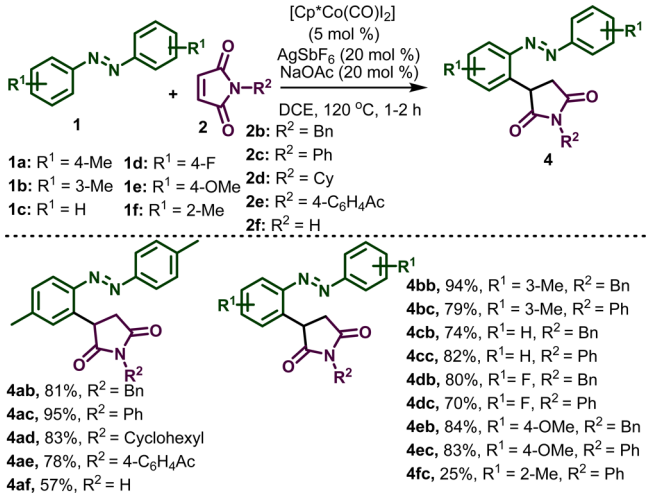


[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), $[Cp^*Co(CO)I_2]$ (5 mol %), $AgSbF_6$ (20 mol %), NaOAc (20 mol %), solvent (2 mL), at 120 °C for 1−2 h. [b]Isolated yields.

methoxy, and 3-methyl substituted azobenzenes **1a**, **1b**, and **1c** reacted smoothly with *N*-ethylmaleimide **2a** under the optimal conditions, affording the corresponding 1,4-addition products **3aa**, **3ba**, and **3ca**, respectively, in good to excellent yields (89, 93, and 84%, respectively). C-2 substituted azobenzene derivatives such as 2-methyl- and 2,4-dimethylazobenzene furnished the corresponding products **3da** and **3ea** in low yields (22% and 25%, respectively). Halo-substituted azobenzene derivatives such as 4-fluoro azobenzene, 4-chloro azobenzene, and 4-bromo azobenzene afforded the desired products **3fa**, **3ga**, and **3ha** in good to moderate yields (85, 56, and 52%, respectively). Similarly, azobenzene **1i** reacted smoothly with **2a**, furnishing the corresponding 1,4-addition product **3ia** in 75% yield. The reactions of unsymmetrical azobenzenes such as (*E*)-1-(4-methoxyphenyl)-2-(*p*-tolyl)-diazenes and (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene are noteworthy. In these two examples, selective 1,4-addition occurred at the electron-rich aryl ring, providing the corresponding products **3ja** and **3ka** in moderate yields (54% and 52%, respectively).

Next, the scope of the reaction with a variety of azobenzene derivatives with different maleimide derivatives (Scheme 3) has

Scheme 3. Substrate Scope for Azobenzene and Maleimide Derivatives[a,b]



[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), $[Cp^*Co(CO)I_2]$ (5 mol %), $AgSbF_6$ (20 mol %), NaOAc (20 mol %), DCE (2 mL), at 120 °C for 1−2 h. [b]Isolated yields

been explored. Thus, we examined the reactions of a variety of *N*-protected maleimides with different azobenzene derivatives. Thus, *N*-benzylmaleimide **2b**, *N*-phenylmaleimide **2c**, *N*-cyclohexylmaleimide **2d**, 1-(4-acetylphenyl)maleimide **2e**, and unprotected maleimide **2f** reacted well with (*E*)-1,2-di-*p*-tolyldiazene **1a**, furnishing the corresponding 1,4-addition products **4ab**, **4ac**, **4ad**, **4ae**, and **4af**, respectively, in good yields (81, 95, 83, 78, and 57%, respectively). Similarly, the reaction of (*E*)-1,2-di-*m*-tolyldiazene **1b** with 1-(4-benzyl)-maleimide **2b** and *N*-phenylmaleimide **2c** furnished the 1,4-addition products **4bb** and **4bc** in 94% and 79% yields, respectively. As expected, the azocompounds **1c**, **1d**, and **1e** underwent a facile reaction with maleimides **2b** and **2c**, furnishing the corresponding 1,4-addition products **4cb**, **4cc**, **4db**, **4dc**, **4eb**, and **4ec** in good to excellent yields. As expected, the reaction of 2-methyl azobenzene with *N*-phenylmaleimide furnished the product **4fc** in low yield (25%), which may be attributed to the steric factors.

The scope of the reaction was further extended by reacting diazo derivatives with the esters of maleic acids (Scheme 4). Thus, dimethyl maleate **5a** and dibutyl maleate **5b** reacted smoothly with azobenzene derivatives (**1a**, **1b**, **1c**, **1d**, and **1e**), affording the corresponding 1,4-addition products **6aa**, **6ab**, **6ca**, **6db**, **6ea**, **6eb**, and **6ba** in 75, 75, 68, 76, 72, 74, and 93% yields, respectively (Scheme 4).

After successful synthesis of 3-arylated succinimide derivatives, a scaling-up experiment has been performed to demonstrate the efficacy of these reactions (Scheme 5, eq 1). Hence, the reaction of *N*-ethyl maleimide **2a** (4 mmol, 500 mg) with **1a** under optimal reaction conditions afforded the corresponding product **3aa** in 74% yield. Further, to demonstrate the utility of the 1,4-addition product, cyclization of 1,4-addition product (**3aa**) has been undertaken. Thus, the reaction of **3aa** in the presence of Zn and NH_4COOH afforded

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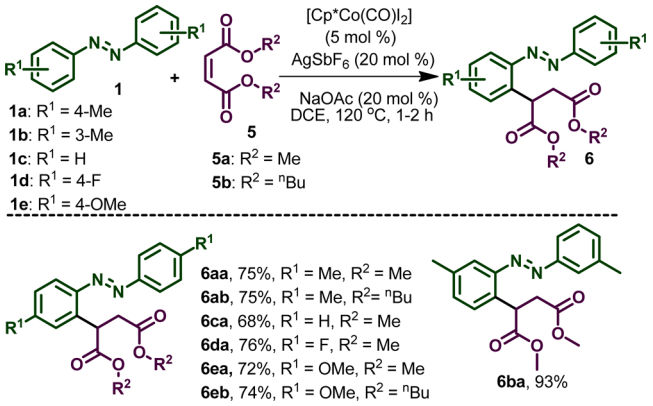
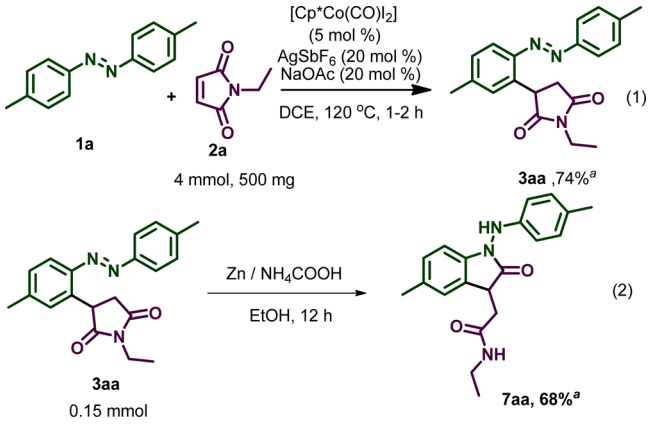
Scheme 4. Substrate Scope for Azobenzene and Maleate Derivatives[a,b]



[a]Reaction conditions: **1** (0.4 mmol), **5** (0.2 mmol), [Cp*Co(CO)I_2] (5 mol %), $AgSbF_6$ (20 mol %), NaOAc (20 mol %), DCE (2 mL), at 120 °C for 1−2 h. [b]Isolated yields.

Scheme 5. Scale-Up Reaction and Synthetic Transformation[a]

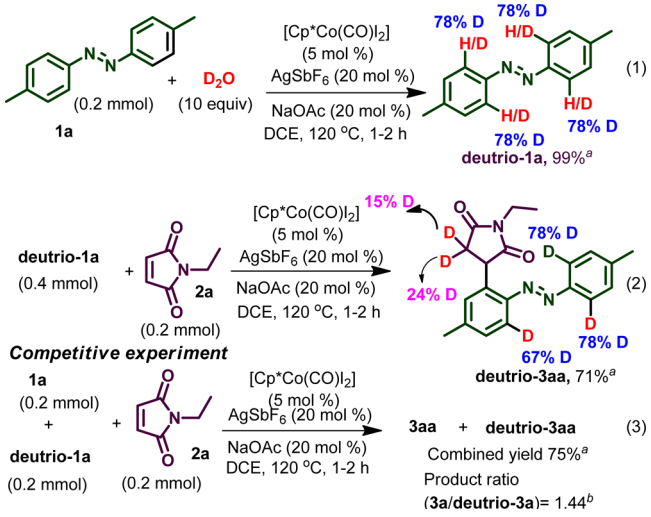


[a]Isolated yields.

the expected cyclic product 1-amino oxindole derivative **7aa** in 68% yield (Scheme 5, eq 2).[27,19f]

To gain insight of the reaction mechanism, a few control experiments were performed (Scheme 6). 4-Methyl azobenzene was reacted with 10 equiv of D_2O under optimal reaction conditions. This reaction led to 78% deuterium incorporation at the *ortho* carbons of azobenzene (Scheme 6, eq 1). It is noteworthy that this deuterium exchange experiment indicates that the C−H activation step may be reversible. When **deutrio-1a** and *N*-ethylmaleimide **2a** were subjected to 1,4-addition reaction under standard reaction conditions, 15% and 24% of deuterium transfer was observed at the C-4 of the succinimide ring (Scheme 6, eq 2). This experiment clearly indicates that the *ortho*-proton of azobenzene is transferred to the C-4 position of the succinimide ring, thereby leading to the corresponding 1,4-addition product through a cobaltocycle intermediate. Finally, the competitive reaction between azobenzene **1a** and **deutrio-1a** with **2a** (in same vessel) furnished a mixture **3aa** and **deutrio-3aa** in a ratio of 1.44:1 in 75% yield (Scheme 6, eq 3), suggesting that the C−H activation step may not be involved in the rate-determining step.

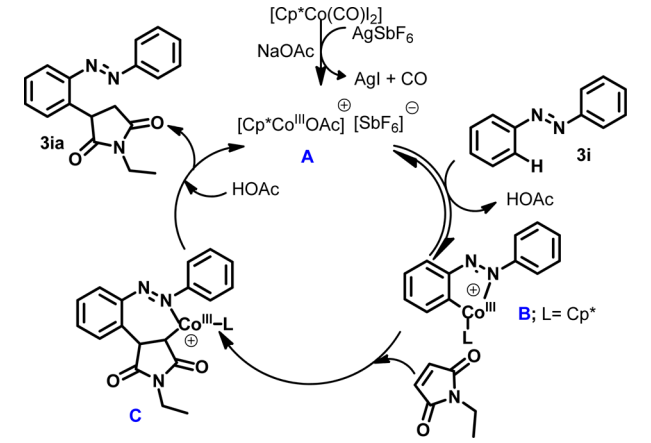
Scheme 6. Preliminary Mechanistic Investigation



[a]Isolated yields. [b]Determined by ^1H NMR

On the basis of these preliminary mechanistic investigation and literature precedence,[6−13] a tentative mechanism has been depicted in Scheme 7. The reaction of [Cp*Co(CO)I_2] with

Scheme 7. Proposed Mechanism



$AgSbF_6$ and NaOAc generates a cationic species of Co(III) (**A**) with dissociation of CO. After the formation of the catalytically active species **A**, C−H metalation takes place, forming a cobaltocycle **B** and AcOH. Following the insertion of alkene to the cobaltocycle, a 7-membered intermediate **C** will be formed, which cannot undergo *β*-hydride elimination, due to unavailability of the *syn*-periplanar *β*-hydrogen atom. Subsequently, protodemetalation allows regeneration of the active species **A** along with the desired product **3ia**.

CONCLUSION

In conclusion, we have developed a novel and efficient cobalt(III)-catalyzed functionalization of azobenzene with maleimides using an azo group as a directing group to obtain 3-arylated succinimides. This protocol has been applied to a wide range of substrates, and the deuterium incorporation studies have been conducted to understand the reaction mechanism.

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EXPERIMENTAL SECTION

General Information. All reactions were carried out using distilled solvents. Reactions were monitored by using precoated silica TLC plates. Mass spectra were recorded on EI, and ESI (TOF) modes. NMR spectra were recorded in 400 MHz spectrometers in $CDCl_3$, DMSO-d_6, tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard for ^{1}H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$, δ = 77.00 ppm and DMSO-d_6, δ = 39.52 ppm) was used as internal standard for ^{13}C NMR. Column chromatography was carried out on silica gel 230−400 mesh or 100−200 mesh (Merck), and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from commercial suppliers were used without further purification. All azobenzene[28a] derivatives and cobalt catalyst[28b] were prepared according to a reported literature procedure. All unsymmetrical azobenzenes were synthesized by diazotisation[28c] of phenol and amines, followed by methylation.[28d]

Experimental Section. *(a) Typical Experimental Procedure.* In an 8 mL screw cap reaction vial, azobenzene (0.4 mmol), maleimide derivative or maleate (0.2 mmol), cobalt catalyst (4.76 mg, 5 mol %), NaOAc (3.28 mg, 20 mol %), and $AgSbF_6$ (13.7 mg, 20 mol %) were added, followed by the addition of DCE (2 mL). This vial was sealed with a screw cap and placed in a preheated metal block at 120 °C, and the reaction mixture was stirred at the same temperature. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using a EtOAc/hexane or DCM/hexane mixture.

*(b) Typical Experimental Procedure for Diactivated Product (**3aa′**).* In an 8 mL screw cap reaction vial, 4-methylazobenzene (42 mg, 0.2 mmol), *N*-ethylmaleimide (50 mg, 0.4 mmol), cobalt catalyst (9.52 mg, 10 mol %), KOAc (3.9 mg, 20 mol %), and $AgSbF_6$ (13.7 mg, 20 mol %) were added, followed by the addition of DCE (2 mL). This vial was sealed with a screw cap and placed in a preheated metal block at 120 °C, and the reaction mixture was stirred at the same temperature. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using EtOAc/hexane.

Scaling-Up Experiment (Experimental Procedure). In a 50 mL pressure tube, 4-methylazobenzene (1.68g, 8 mmol), 4-methylazobenzene (500 mg, 4 mmol), cobalt catalyst (95.2 mg, 5 mol %), NaOAc (65.6 mg, 20 mol %), and $AgSbF_6$ (274 mg, 20 mol %) were added, followed by the addition of DCE (20 mL). This pressure tube was heated at 120 °C, and the reaction mixture was stirred at the same temperature. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using an EtOAc/hexane mixture.

*(E)-1-Ethyl-3-(5-methyl-2-(p-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**3aa**).* Yellow solid; Yield − (59.6 mg, 89%); mp: 123−125 °C; R_f (30% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1697,1602, 1222, 1120; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.12 (t, *J* = 7.20 Hz, 3 H) 2.41 (s, 6 H) 2.94 (dd, *J* = 18.19, 5.81 Hz, 1 H) 3.23 (dd, *J* = 18.19, 9.60 Hz, 1 H) 3.50−3.68 (m, 2 H) 4.36 (dd, *J* = 9.47, 5.68 Hz, 1 H) 7.17 (s, 1 H) 7.21 (d, *J* = 8.34 Hz, 1 H) 7.26 (d, *J* = 8.34 Hz, 2 H) 7.56 (d, *J* = 8.08 Hz, 2 H) 7.68 (d, *J* = 8.34 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.0, 21.4, 21.5, 34.1, 38.6, 44.9, 116.2, 122.8, 129.6, 129.7, 131.6, 137.0, 141.8, 141.9, 147.6, 150.7, 176.4, 178.5 ; HRESI-MS (*m*/*z*): Calculated for $C_{20}H_{21}N_3O_2Na$ (M + Na): 358.1531, found 358.1530.

*(E)-3,3′-(5-Methyl-2-(p-tolyldiazenyl)-1,3-phenylene)bis(1-ethylpyrrolidine-2,5-dione) (**3aa′**).* Orange solid; Yield − (30.3 mg, 33%); mp: 184−186 °C; R_f (30% EtOAc/Hexane) 0.2; Prepared as shown in experimental procedure (b). IR (KBr, cm^{-1}): 1693,1601, 1219, 1120; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.04 (t, *J* = 7.20 Hz, 3 H) 1.15 (t, *J* = 7.20 Hz, 3 H) 2.40 (s, 6 H) 2.85 (dd, *J* = 18.4, 5.76 Hz, 1 H) 2.95 (dd, *J* = 18.4, 5.4 Hz, 1 H) 3.18−3.25 (m, 2 H) 3.49−3.61 (m, 4 H) 4.35−4.39 (m, 2 H) 7.15−7.17 (m, 3 H) 7.22−7.26 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.8, 13.0, 21.4 (2 C), 34.0 (2 C), 38.3, 38.6, 44.6, 44.8, 115.9, 116.1, 129.5, 131.6, 137.5, 142.6, 142.7, 147.9, 176.4 (2 C), 178.1 (2 C); HRESI-MS (*m*/*z*): Calculated for $C_{26}H_{28}N_4O_4Na$ (M + Na): 483.2008, found 483.2006.

*(E)-1-Ethyl-3-(5-methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)-pyrrolidine-2,5-dione (**3ba**).* Yellow solid; Yield − (68.3 mg, 93%); mp: 120−122 °C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1768, 1693, 1593, 1500; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm1.13 (t, *J* = 7.07 Hz, 3 H) 2.97 (dd, *J* = 18.06, 5.68 Hz, 1 H) 3.23 (dd, *J* = 18.19, 9.60 Hz, 1 H) 3.52−3.66 (m, 2 H) 3.86 (s, 3 H) 3.87 (s, 3 H) 4.34 (dd, *J* = 9.47, 5.68 Hz, 1 H) 6.86−6.96 (m, 4 H) 7.62 (d, *J* = 8.84 Hz, 2 H) 7.78 (d, *J* = 9.09 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.0, 34.1, 38.5, 45.2, 55.5, 55.6, 114.2, 114.2, 115.8, 118.0, 124.5, 138.5, 143.9, 147.0, 161.6, 161.9, 176.4, 178.2; HRESI-MS (*m*/*z*): Calculated for $C_{20}H_{21}N_3O_4Na$ (M + Na): 390.1430, found 390.1430.

*(E)-1-Ethyl-3-(4-methyl-2-(m-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**3ca**).* Red semisolid; Yield − (56 mg, 84%); R_f (30% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1772, 1701, 1602; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm1.07 (t, *J* = 7.20 Hz, 4 H) 2.38 (s, 3 H) 2.41 (s, 3 H) 2.93 (dd, *J* = 18.19, 5.81 Hz, 1 H) 3.22 (dd, *J* = 17.94, 9.60 Hz, 1 H) 3.47−3.61 (m, 2 H) 4.35 (dd, *J* = 9.60, 5.81 Hz, 1 H) 7.25−7.26 (m, 3 H) 7.35 (t, *J* = 7.58 Hz, 1 H) 7.44 (s, 1 H) 7.46 (d, *J* = 7.83 Hz, 1 H) 7.55 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.9, 21.1, 21.2, 34.0, 38.6, 44.6, 116.6, 120.8, 122.7, 128.9, 130.8, 132.1, 132.2, 134.4, 139.0, 139.0, 132.3, 149.4, 152.7, 176.4, 178.5; HRESI-MS (*m*/*z*): Calculated for $C_{20}H_{21}N_3O_2Na$ (M + Na): 358.1531, found 358.1530.

*(E)-1-Ethyl-3-(3-methyl-2-(o-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**3da**).* Red solid; Yield − (15 mg, 22%); mp: 149−150 °C; R_f (30% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1701, 1602, 1226, 1124; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.02 (t, *J* = 7.20 Hz, 3 H) 2.42 (s, 3 H) 2.64 (s, 3 H) 2.91 (dd, *J* = 18.06, 5.94 Hz, 1 H) 3.15 (dd, *J* = 18.19, 9.60 Hz, 1 H) 3.39 (q, *J* = 7.33 Hz, 2 H) 4.26 (dd, *J* = 9.35, 5.81 Hz, 1 H) 7.18−7.38 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.8, 17.7, 20.8, 33.9, 38.2, 45.0, 114.7, 126.4, 128.4, 129.3 130.1, 131.4, 131.5, 132.4,134.6, 138.4, 149.5, 151.0, 176.2, 178.2. ; HRESI-MS (*m*/*z*): Calculated for $C_{20}H_{21}N_3O_2Na$ (M + Na): 358.1531, found 358.1529.

*(E)-3-(2-((2,4-Dimethylphenyl)diazenyl)-3,5-dimethylphenyl)-1-ethylpyrrolidine-2,5-dione (**3ea**).* Red solid; Yield − (18 mg, 25%); mp: 128−130 °C; R_f (50% DCM/Hexane) 0.2; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1695, 1602, 1224; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.05 (t, *J* = 7.20 Hz, 3 H) 2.36 (s, 6 H) 2.40 (s, 3 H) 2.59 (s, 3 H) 2.89 (dd, *J* = 18.06, 5.94 Hz, 1 H) 3.13 (dd, *J* = 18.06, 9.47 Hz, 1 H) 3.44 (q, *J* = 7.33 Hz, 2 H) 4.23 (dd, *J* = 9.47, 5.94 Hz, 1 H) 6.99−7.01 (m, 2 H) 7.06 (s, 1 H) 7.11−7.13 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.9, 17.7, 21.1, 21.2, 21.3, 33.9, 38.3, 45.2, 114.4, 127.1, 129.2, 130.0, 131.9, 133.2, 135.1, 138.3, 139.4, 141.7, 147.2, 149.2, 176.3, 178.3; HRESI-MS (*m*/*z*): Calculated for $C_{22}H_{25}N_3O_2Na$ (M + Na): 386.1844, found 386.1847.

*(E)-1-Ethyl-3-(5-fluoro-2-((4-fluorophenyl)diazenyl)phenyl)-pyrrolidine-2,5-dione (**3fa**).* Red solid; Yield − (58 mg, 85%); mp: 141−143 °C; R_f (20% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1774, 1695, 1589, 1496, 1234; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.10 (t, *J* = 7.20 Hz, 4 H) 2.93 (dd, *J* = 18.19, 5.81 Hz, 1 H) 3.25 (dd, *J* = 18.19, 9.60 Hz, 1 H) 3.49−3.62 (m, 2 H) 4.42 (dd, *J* = 9.73, 5.68 Hz, 1 H) 7.08−7.17 (m, 4 H) 7.66 (dd, *J* = 8.72, 5.18 Hz, 2 H) 7.79 (dd, *J* = 8.46, 5.68 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm12.9, 34.2, 38.3, 44.5, 116.1 (d, *J* = 23 Hz), 116.2 (d, *J* = 23 Hz), 117.6 (d, *J* = 23 Hz), 118.6 (d, *J* = 9 Hz), 124.9 (d, *J* = 9 Hz), 139.5 (d, *J* = 9 Hz), 146.0, 148.9, 164.3 (d, *J* = 252 Hz), 164.6 (d, *J* = 252 Hz), 175.9, 177.6; HRESI-MS (*m*/*z*): Calculated for $C_{18}H_{15}F_2N_3O_2Na$ (M + Na): 366.1030, found 366.1030.

*(E)-3-(5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl)-1-ethylpyrrolidine-2,5-dione (**3ga**).* Brown solid; Yield − (42 mg, 56%); mp:

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166−168 °C; R_f (50% DCM/Hexane) 0.2; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1697, 1581, 1400; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.13 (t, J = 7.20 Hz, 3 H) 2.92 (dd, J = 18.19, 5.81 Hz, 1 H) 3.26 (dd, J = 18.19, 9.60 Hz, 1 H) 3.51−3.64 (m, 2 H) 4.40 (dd, J = 9.60, 5.81 Hz, 1 H) 7.39−7.41 (m, 2 H) 7.46 (d, J = 8.84 Hz, 2 H) 7.61 (d, J = 8.59 Hz, 2 H) 7.73 (d, J = 8.84 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.9, 34.2, 38.2, 44.4, 117.8, 124.2, 129.2, 129.4, 130.9, 137.7, 137.8, 138.7, 147.8, 150.7, 175.7, 177.5; HRESI-MS (m/z): Calculated for $C_{18}H_{15}Cl_2N_3O_2Na$ (M + Na): 398.0439, found 398.0437.

*(E)-3-(5-Bromo-2-((4-bromophenyl)diazenyl)phenyl)-1-ethylpyrrolidine-2,5-dione (**3ha**).* Brown solid; Yield − (48 mg, 52%); mp: 185−187 °C; R_f (20% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1697, 1637, 1573, 1400; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.12 (t, J = 7.20 Hz, 3 H) 2.92 (dd, J = 18.19, 5.56 Hz, 1 H) 3.26 (dd, J = 18.19, 9.85 Hz, 1 H) 3.50−3.64 (m, 2 H) 4.38 (dd, J = 9.60, 5.56 Hz, 1 H) 7.53−7.58 (m, 4 H) 7.61−7.67 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.0, 34.2, 38.2, 44.4, 117.9, 124.4, 126.3, 126.4, 132.2, 132.5, 133.9, 139.0, 148.2, 151.1, 175.8, 175.5; HRESI-MS (m/z): Calculated for $C_{18}H_{15}Br_2N_3O_2Na$ (M + Na): 485.9429, found 485.9430.

*(E)-1-Ethyl-3-(2-(phenyldiazenyl)phenyl)pyrrolidine-2,5-dione (**3ia**).* Red semisolid; Yield − (46 mg, 75%); R_f (30% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1770, 1699, 1587; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.10 (t, J = 7.07 Hz, 3 H) 2.97 (dd, J = 18.19, 5.81 Hz, 1 H) 3.26 (dd, J = 18.06, 9.47 Hz, 1 H) 3.50−3.63 (m, 2 H) 4.45 (dd, J = 9.47, 5.68 Hz, 1 H) 7.37−7.51 (m, 6 H) 7.67−7.69 (m, 2 H) 7.77 (dd, J = 7.96, 1.72 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.9, 34.1, 38.5, 44.8, 116.4, 122.9, 128.9, 129.1, 130.9, 131.4, 131.6, 137.2, 149.5, 152.6, 176.2, 178.2; HRESI-MS (m/z): Calculated for $C_{18}H_{17}N_3O_2Na$ (M + Na): 330.1218, found 330.1217.

*(E)-1-Ethyl-3-(5-methoxy-2-(p-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**3ja**).* Brown solid; Yield − (38 mg, 54%); mp: 122−124 °C; R_f (30% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1402, 1494, 1599, 1700, 1722; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.14 (t, J = 7.20 Hz, 3 H) 2.42 (s, 3H) 2.98 (dd, J = 18.16, 5.8 Hz, 1 H) 3.26 (dd, J = 18.12, 9.56 Hz, 1 H) 3.54−3.67 (m, 2 H) 3.90 (s, 3 H) 4.37 (dd, J = 9.52, 5.76 Hz, 1 H) 6.89 (d, J = 2.8 Hz, 1 H) 6.94 (dd, J = 8.96, 2.76 Hz, 1 H) 7.27 (d, J = 8.24 Hz, 2 H) 7.55 (d, J = 8.32 Hz, 2 H) 7.83 (d, J = 8.96 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.9, 21.4, 34.1, 38.5, 45.1, 55.6, 114.2, 115.8, 118.0, 122.6, 139.0, 141.3, 143.8, 150.7, 161.9, 176.2, 178.1; HRESI-MS (m/z): Calculated for $C_{20}H_{21}N_3O_3Na$ (M + Na): 374.1481, found 374.1483.

*(E)-1-Ethyl-3-(5-methoxy-2-(phenyldiazenyl)phenyl)pyrrolidine-2,5-dione (**3ka**).* Red semisolid; Yield − (35 mg, 52%); R_f (30% EtOAc/Hexane) 0.3; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1224, 1254, 1599, 1699; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.10 (t, J = 7.12 Hz, 3 H), 2.98 (dd, J = 18.12, 5.76 Hz, 1 H) 3.26 (dd, J = 18.12, 9.56 Hz, 1 H) 3.53−3.64 (m, 2 H) 3.89 (s, 3 H) 4.38 (dd, J = 9.4, 5.84 Hz, 1 H) 6.88 (s, J = 2.36 Hz, 1 H) 6.94 (d, J = 8.8 Hz, 2.4 Hz, 1H) 7.42−7.47 (m, 3 H) 7.62 (d, J = 7.04 Hz, 2 H) 7.83 (d, J = 8.96 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 12.9, 34.1, 38.5, 45.1, 55.6, 114.2, 115.8, 118.1, 122.6, 129.0, 130.7, 139.4, 143.7, 152.6, 162.6, 176.2, 178.1; HRESI-MS (m/z): Calculated for $C_{19}H_{19}N_3O_3Na$ (M + Na): 360.1324, found 360.1327.

*(E)-1-Benzyl-3-(5-methyl-2-(p-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**4ab**).* Yellow solid; Yield − (64 mg, 81%); mp: 133−135 °C; R$_f$ (30% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1774, 1703, 1602, 1394; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.38 (s, 3 H) 2.41 (s, 3 H) 2.97 (dd, J = 18.44, 5.56 Hz, 1 H) 3.23 (dd, J = 18.19, 9.60 Hz, 1 H) 4.41 (dd, J = 9.47, 5.68 Hz, 1 H) 4.62 (d, J = 13.89 Hz, 1 H) 4.73 (d, J = 13.89 Hz, 1 H) 7.01 (s, 1 H) 7.19−7.28 (m, 6 H) 7.41−7.42 (m, 2 H) 7.54 (d, J = 7.83 Hz, 2 H) 7.69 (d, J = 8.08 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 21.4, 21.5, 38.6, 42.8, 44.7, 116.2, 122.8, 127.9, 128.6, 129.0, 129.7, 131.3, 135.9, 137.1, 141.9, 142.0, 147.6, 150.7, 176.1, 178.4; HRESI-MS (m/z): Calculated for $C_{25}H_{23}N_3O_2Na$ (M + Na): 420.1688, found 420.1687.

*(E)-3-(5-Methyl-2-(p-tolyldiazenyl)phenyl)-1-phenylpyrrolidine-2,5-dione (**4ac**).* Yellow solid; Yield − (73 mg, 95%); mp: 187−189 °C; R_f (30% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1707, 1598, 1496, 1381, 1159; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.37 (s, 3 H) 2.44 (s, 3 H) 3.14 (dd, J = 18.19, 6.06 Hz, 1 H) 3.41 (dd, J = 18.19, 9.85 Hz, 1 H) 4.48 (dd, J = 9.73, 6.19 Hz, 1 H) 7.18 (t, J = 7.58 Hz, 4 H) 7.24−7.26 (m, 2 H) 7.32−7.40 (m, 3 H) 7.58 (d, J = 8.34 Hz, 2 H) 7.73 (d, J = 8.08 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 21.4, 21.5, 38.7, 45.5, 116.4, 122.9, 126.4, 128.3, 128.9, 129.8, 129.9, 132.0, 132.1, 136.9, 141.9, 142.0, 147.6, 150.8, 175.4, 177.4; HRESI-MS (m/z): Calculated for $C_{24}H_{21}N_3O_2Na$ (M + Na): 406.1531, found 406.1533.

*(E)-1-Cyclohexyl-3-(5-methyl-2-(p-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**4ad**).* Orange solid; Yield − (65 mg, 83%); mp: 139−141 °C; R_f (30% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1603, 1698, 1770; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.15−1.31 (m, 3H) 1.42−1.63 (m, 3H) 1.72−1.77 (m, 2H) 2.03−2.15 (m, 2H) 2.40 (s, 3H) 2.41 (m, 3H) 2.96 (dd, J = 18.18, 5.88 Hz, 1H) 3.17 (dd, J = 18.18, 9.68 Hz, 1H) 3.94−4.02 (m, 1H) 4.42 (dd, J = 9.6, 5.88 Hz, 1H) 7.13 (s, 1H) 7.19−7.21 (m, 1H) 7.26 (d, J = 8.08 Hz, 2H) 7.61 (d, J = 8.24 Hz, 2H) 7.67 (d, J = 8.28 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 21.4, 21.5, 25.0, 25.7, 25.8, 28.5, 28.8, 38.3, 44.2, 51.9, 116.1, 122.8, 129.5, 129.6, 131.0, 137.1, 141.6, 141.9, 147.8, 150.8, 176.7, 178.5; HRESI-MS (m/z): Calculated for $C_{24}H_{27}N_3O_2Na$ (M + Na): 412.2001, found 412.2004.

*(E)-1-(4-Acetylphenyl)-3-(5-methyl-2-(p-tolyldiazenyl)phenyl)-pyrrolidine-2,5-dione (**4ae**).* Yellow solid; Yield − (66 mg, 78%); mp: 137−139 °C; R_f (50% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1156, 1260, 1373, 1597; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.35 (s, 3H) 2.43 (s, 3H) 2.58 (s, 3H) 3.15 (dd, J = 18.32, 6.2 Hz, 1H) 3.42 (dd, J = 18.32, 8.52 Hz, 1H) 4.43 (dd, J = 9.72, 6.16 Hz, 1H) 7.14 (d, J = 8.12 Hz, 2H) 7.24−7.25 (m, 2H) 7.33 (d, J = 8.56 Hz, 2H) 7.53 (d, J = 8.24 Hz, 2H) 7.72−7.74 (m, 1H) 7.94 (d, J = 8.56 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 21.3, 21.4, 26.6, 38.6, 45.6, 116.4, 122.8, 126.2, 128.8, 129.7, 129.9, 132.1, 136.2, 136.6, 141.9, 142.0, 147.5, 150.8, 174.8, 176.9, 197.0; HRESI-MS (m/z): Calculated for $C_{26}H_{23}N_3O_3Na$ (M + Na): 448.1637, found 448.1639.

*(E)-3-(5-Methyl-2-(p-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**4af**).* Yellow semisolid; Yield − (35 mg, 57%); R_f (50% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1172, 1351, 1693, 3176; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.40 (s, 3 H) 2.41 (s, 3 H) 2.94 (dd, J = 18.36, 6.0 Hz, 1 H)3.25 (dd, J = 18.32, 9.72 Hz, 1 H) 4.41 (dd, J = 9.6, 6.0 Hz, 1 H) 7.18 (s, 1H) 7.22−7.27 (m, 3H) 7.61 (d, J = 8.28 Hz, 2H) 7.71 (d, J = 8.2 Hz, 1H) 8.36 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm21.4, 21.5, 39.8, 46.3, 116.3, 122.9, 129.8, 129.8, 131.5, 136.6, 141.9, 142.0, 147.5, 150.8, 176.2, 178.8; HRESI-MS (m/z): Calculated for $C_{18}H_{17}N_3O_2Na$ (M + Na): 330.1218, found 330.1220.

*(E)-1-Benzyl-3-(4-methyl-2-(m-tolyldiazenyl)phenyl)pyrrolidine-2,5-dione (**4bb**).* Red solid; Yield − (67 mg, 94%); mp: 87−89 °C; R_f (30% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1703, 1595, 1392; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.40 (s, 3 H) 2.43 (s, 3 H) 2.93 (dd, J = 18.32, 5.68 Hz, 1 H) 3.23 (dd, J = 18.19, 9.60 Hz, 1 H) 4.40 (dd, J = 9.60, 5.56 Hz, 1 H) 4.59 (d, J = 13.89 Hz, 1 H) 4.70 (d, J = 13.89 Hz, 1 H) 7.20−7.27 (m, 6 H) 7.34−7.39 (m, 3 H) 7.46 (s, 1 H) 7.51 (d, J = 7.83 Hz, 1 H) 7.58 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 21.1, 21.2, 38.6, 42.6, 44.3, 116.5, 120.9, 122.5, 127.8, 128.5, 128.8, 128.9, 130.6, 132.2, 132.2, 134.4, 135.8, 138.9, 139.0, 149.2, 152.5, 176.0, 178.3; HRESI-MS (m/z): Calculated for $C_{25}H_{23}N_3O_2Na$ (M + Na): 420.1688, found 420.1686.

*(E)-3-(4-Methyl-2-(m-tolyldiazenyl)phenyl)-1-phenylpyrrolidine-2,5-dione (**4bc**).* Orange solid; Yield − (50 mg, 79%); mp: 156−158 °C; R_f (30% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1708, 1598, 1498, 1382; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.17 (s, 3 H) 2.43 (s, 3 H) 3.12

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(dd, J = 18.32, 5.94 Hz, 1 H) 3.43 (dd, J = 18.19, 9.85 Hz, 1 H) 4.46 (dd, J = 9.60, 6.06 Hz, 1 H) 7.16 (d, J = 8.34 Hz, 2 H) 7.22 (d, J = 7.2 Hz, 1 H) 7.29−7.38 (m, 6 H) 7.42 (s, 1 H) 7.57 (d, J = 7.83 Hz, 1 H) 7.64 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.8, 21.2 45.2, 116.7, 121.8, 121.9, 126.3, 128.1, 128.8, 128.9, 131.4, 132.1, 132.2, 132.3, 134.5, 139.2, 139.3, 149.2, 152.6, 175.4, 177.4; HRESI-MS (m/z): Calculated for $C_{24}H_{21}N_3O_2Na$ (M + Na): 406.1531, found 406.1531.

(E)-1-Benzyl-3-(2-(phenyldiazenyl)phenyl)pyrrolidine-2,5-dione (**4cb**). Red solid; Yield − (55 mg, 74%); mp: 127−129 °C; R_f (30% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1703, 1589, 1394; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.95 (dd, J = 18.32, 5.68 Hz, 1 H) 3.26 (dd, J = 18.19, 9.60 Hz, 1 H) 4.49 (dd, J = 9.60, 5.56 Hz, 1 H) 4.61 (d, J = 13.89 Hz, 1 H) 4.72 (d, J = 13.89 Hz, 1 H) 7.24−7.29 (m, 3 H) 7.33−7.35 (m, 1 H) 7.40 (d, J = 7.83 Hz, 2 H) 7.42−7.47 (m, 5 H) 7.67 (dd, J = 6.32, 2.78 Hz, 2 H) 7.77−7.80 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.5, 42.7, 44.5, 116.3, 122.8, 127.9, 128.5, 128.9, 129.1, 130.7, 131.4, 131.6, 135.7, 137.2, 149.4, 152.4, 175.9, 178.1 ; HRESI-MS (m/z): Calculated for $C_{23}H_{19}N_3O_2Na$ (M + Na): 392.1375, found 392.1377.

(E)-1-Phenyl-3-(2-(phenyldiazenyl)phenyl)pyrrolidine-2,5-dione (**4cc**). Pale yellow solid; Yield − (59 mg, 82%); mp: 177−179 °C; R_f (30% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1712, 1593, 1496; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.14 (dd, J = 18.32, 6.19 Hz, 1 H) 3.42 (dd, J = 18.32, 9.73 Hz, 1 H) 4.54 (dd, J = 9.60, 6.06 Hz, 1 H) 7.16 (dd, J = 7.76, 1.08 Hz, 2 H) 7.32−7.48 (m, 9 H) 7.70 (dd, J = 8.2, 1.76 Hz, 2 H) 7.83 (dd, J = 8.12, 1.72 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.7, 45.4, 116.5, 123.0, 126.3, 128.3, 128.8, 129.1, 129.2, 131.4, 131.5, 131.6, 132.0, 137.1, 149.4, 152.6, 175.2, 177.2; HRESI-MS (m/z): Calculated for $C_{22}H_{17}N_3O_2Na$ (M + Na): 378.1216, found 378.1219.

(E)-1-Benzyl-3-(5-fluoro-2-((4-fluorophenyl)diazenyl)phenyl)-pyrrolidine-2,5-dione (**4db**). Yellow solid; Yield − (65 mg, 80%); mp: 180−182 °C; R_f (30% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1693, 1587, 1492, 1400; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.93 (dd, J = 18.19, 5.56 Hz, 1 H) 3.26 (dd, J = 18.19, 9.60 Hz, 1 H) 4.46 (dd, J = 9.22, 5.68 Hz, 1 H)4.60 (d, J = 13.89 Hz, 1 H) 4.72 (d, J = 13.89 Hz, 1 H) 7.04−7.12 (m, 4 H) 7.24−7.25 (m, 3 H) 7.37−7.38 (m, 2 H) 7.60−7.64 (m, 2 H) 7.81 (dd, J = 8.34, 5.81 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.2, 42.8, 44.4, 116.1 (d, J = 23 Hz), 116.2 (d, J = 23 Hz), 117.5 (d, J = 23 Hz), 118.6 (d, J = 9 Hz), 124.8 (d, J = 9 Hz), 128.0, 128.6, 128.9, 135.5, 139.3 (d, J = 9 Hz), 145.9, 148.8, 164.2 (d, J = 252 Hz), 164.5 (d, J = 252 Hz), 175.5, 177.4; HRESI-MS (m/z): Calculated for $C_{23}H_{17}F_2N_3O_2Na$ (M + Na): 428.1187, found 428.1185.

(E)-3-(5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl)-1-phenyl-pyrrolidine-2,5-dione (**4dc**). Pale yellow solid; Yield − (54 mg, 70%); mp: 202−204 °C; R_f (30% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1707, 1591, 1494, 1386; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.12 (dd, J = 18.32, 6.19 Hz, 1 H) 3.46 (dd, J = 18.44, 9.85 Hz, 1 H) 4.52 (dd, J = 9.85, 6.32 Hz, 1 H) 7.06 (t, J = 8.46 Hz, 2 H) 7.14−7.20 (m, 4 H) 7.35−7.42 (m, 3 H) 7.69 (dd, J = 8.59, 5.31 Hz, 2 H) 7.87 (dd, J = 8.97, 5.43 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.4, 45.1, 116.2 (d, J = 23 Hz), 118.2 (d, J = 23 Hz), 118.8 (d, J = 9 Hz), 125.1 (d, J = 9 Hz), 126.1, 128.5, 128.9, 131.8, 134.2, 139.3 (d, J = 9 Hz), 145.9, 148.9, 164.2 (d, J = 252 Hz), 164.6 (d, J = 252 Hz), 174.8, 176.5; HRESI-MS (m/z): Calculated for $C_{22}H_{15}F_2N_3O_2Na$ (M + Na): 414.1030, found 414.1031.

(E)-1-Benzyl-3-(5-methoxy-2-((4-methoxyphenyl)diazenyl)-phenyl)pyrrolidine-2,5-dione (**4eb**). Yellow solid; Yield − (72 mg, 84%); mp: 178−180 °C; R_f (30% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1701, 1597, 1500, 1396, 1249; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.97 (dd, J = 18.32, 5.68 Hz, 1 H) 3.24 (dd, J = 18.44, 9.60 Hz, 1 H) 3.82 (s, 3 H) 3.87 (s, 3 H) 4.40 (dd, J = 9.47, 5.68 Hz, 1 H) 4.63 (d, J = 14.15 Hz, 1 H) 4.75 (d, J = 13.89 Hz, 1 H) 6.79 (d, J = 2.53 Hz, 1 H) 6.90−6.92 (m, 3 H) 7.24−7.25 (m,3 H) 7.40 (d, J = 6.32 Hz, 2 H) 7.59 (d, J = 8.84 Hz, 2 H) 7.79 (d, J = 9.09 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.5, 42.7, 44.9, 114.2, 114.4, 115.3, 118.0, 124.4, 127.9, 128.5, 128.9, 135.8, 138.5, 143.8, 146.9, 161.6, 161.8, 176.1, 178.1; HRESI-MS (m/z): Calculated for $C_{25}H_{23}N_3O_4Na$ (M + Na): 452.1586, found 452.1586.

(E)-3-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)-1-phenylpyrrolidine-2,5-dione (**4ec**). Orange solid; Yield − (68 mg, 83%); mp: 204−206 °C; R_f (30% EtOAc/Hexane) 0.3; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1707, 1597, 1581, 1498, 1253; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.16 (dd, J = 18.19, 6.06 Hz, 1 H) 3.42 (dd, J = 18.19, 9.85 Hz, 1 H) 3.82 (s, 3 H) 3.89 (s, 3 H) 4.43 (dd, J = 9.73, 6.19 Hz, 1 H) 6.85 (d, J = 9.09 Hz, 2 H) 6.95−6.96 (m, 2 H) 7.22 (d, J = 7.58 Hz, 2 H) 7.32−7.41 (m, 3 H) 7.64 (m, J = 8.84 Hz, 2 H) 7.83−7.86 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.6, 45.7, 55.5, 55.6, 114.2, 114.4, 114.2, 114.4, 116.3, 118.1, 124.6, 126.4, 128.3, 128.8, 132.1, 138.4, 143.8, 146.9, 161.6, 161.9, 175.4, 177.1; HRESI-MS (m/z): Calculated for $C_{24}H_{21}N_3O_4Na$ (M + Na): 438.1430, found 438.1428.

(E)-3-(3-Methyl-2-(o-tolyldiazenyl)phenyl)-1-phenylpyrrolidine-2,5-dione (**4fc**). Brown solid; Yield − (27 mg, 25%); mp: 149−151 °C; R_f (30% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1712,1643, 1498, 1381, 1178; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.45 (s, 3 H) 2.63 (s, 3 H) 3.12 (dd, J = 9.60, 6.4 Hz, 1 H) 3.32 (dd, J = 18, 9.6 Hz, 1 H) 4.41 (dd, J = 18, 6.32 Hz, 1 H) 6.97−6.99 (m, 2 H) 7.07−7.13 (m, 1 H) 7.25−7.36 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 17.8, 21.1, 38.4, 45.6, 115.0, 126.3, 126.7, 128.2, 128.8, 128.9, 129.4, 130.3, 131.4, 131.5, 132.0, 132.7, 134.7, 138.3, 149.4, 151.3, 175.2, 177.1; HRESI-MS (m/z): Calculated for $C_{24}H_{21}N_3O_2Na$ (M + Na): 406.1531, found 406.1530.

(E)-Dimethyl 2-(5-Methyl-2-(p-tolyldiazenyl)phenyl)succinate (**6aa**). Red solid; Yield − (52 mg, 75%); mp: 133−135 °C; R_f (20% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure (a). IR (KBr, cm^{-1}): 1737, 1643, 1602, 1438; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.40 (s, 3 H) 2.42 (s, 3 H) 2.69 (dd, J = 16.67, 5.56 Hz, 1 H) 3.33 (dd, J = 16.80, 8.97 Hz, 1 H) 3.60 (s, 3 H) 3.66 (s, 3 H) 4.86 (dd, J = 8.84, 5.56 Hz, 1 H) 7.17 (d, J = 8.34 Hz, 1 H) 7.22 (s, 1 H) 7.31 (d, J = 8.08 Hz, 2 H) 7.68 (d, J = 8.34 Hz, 1 H) 7.80 (d, J = 8.08 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.6, 45.7, 55.5, 55.6, 114.2, 114.4, 114.2, 114.4, 116.3, 118.1, 124.6, 126.4, 128.3, 128.8, 132.1, 138.4, 143.8, 146.9, 161.6, 161.9, 175.4, 177.1; HRESI-MS (m/z): Calculated for $C_{20}H_{22}N_2O_4Na$ (M + Na): 377.1477, found 377.1475.

(E)-Dibutyl 2-(5-Methyl-2-(p-tolyldiazenyl)phenyl)succinate (**6ab**). Red liquid; Yield − (65 mg, 75%); R_f (5% EtOAc/Hexane) 0.3; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1157, 1459, 1603, 1734; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.72 (t, J = 7.32 Hz, 3 H) 0.89 (t, J = 7.40 Hz, 3 H) 1.13 (q, J = 7.28 Hz, 2 H) 1.32 (q, J = 7.48 Hz, 2 H) 1.38−1.44 (m, 2 H) 1.52−1.59 (m, 2 H) 2.39 (s, 3 H), 2.43 (s, 3 H) 2.70 (dd, J = 16.4, 5.6 Hz, 1 H) 3.32 (dd, J = 16.8, 8.8 Hz, 1 H) 3.96−4.08 (m, 4 H) 4.86 (t, J = 7.2 Hz, 1 H) 7.16 (d, J = 8.12 Hz, 1 H) 7.22 (s, 1 H) 7.30 (d, J = 7.80 Hz, 2 H) 7.67 (d, J = 8.2 Hz, 1 H) 7.80 (d, J = 7.88 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.5, 13.7, 18.8, 19.0, 21.5, 30.4, 30.5, 38.5, 43.7, 64.5, 64.9, 115.4, 123.2, 128.9, 129.7, 130.2, 138.6, 141.5, 141.6, 147.2, 150.9, 170.9, 173.4; HRESI-MS (m/z): Calculated for $C_{26}H_{34}N_2O_4Na$ (M + Na): 461.2416, found 461.2413.

(E)-Dimethyl 2-(2-(Phenyldiazenyl)phenyl)succinate (**6ca**). Red semisolid; Yield − (49 mg, 68%); R_f (20% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1735, 1603, 1436; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.72 (dd, J = 16.67, 5.81 Hz, 1 H) 3.35 (dd, J = 16.67, 8.84 Hz, 1 H) 3.60 (s, 3 H) 3.66 (s, 3 H) 4.92 (dd, J = 8.59, 5.81 Hz, 1 H) 7.37−7.55 (m, 6 H) 7.77 (d, J = 7.83 Hz, 1 H) 7.92 (d, J = 8.08 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.3, 43.6, 51.8, 52.3, 115.7, 123.4, 128.3, 129.2, 129.8, 131.3, 131.5, 138.5, 149.1, 152.7, 172.2, 173.7; HRESI-MS (m/z): Calculated for $C_{18}H_{18}N_2O_4Na$ (M + Na): 349.1164, found 349.1165.

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*(E)-Dimethyl 2-(5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl)-succinate (**6da**).* Red semisolid; Yield − (55 mg, 76%); R_f (10% EtOAc/Hexane) 0.3; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1737, 1591, 1494, 1232; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.72 (dd, J = 16.80, 5.94 Hz, 1 H) 3.33 (dd, J = 16.80, 8.46 Hz, 1 H) 3.61 (s, 3 H) 3.68 (s, 3 H) 4.89 (dd, J = 8.21, 6.19 Hz, 1 H) 7.05−7.10 (m, 1 H) 7.16−7.27 (m, 3 H) 7.81 (dd, J = 8.84, 5.56 Hz, 1 H) 7.91 (dd, J = 8.21, 5.43 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.0, 43.4, 51.9, 52.4, 115.5 (d, J = 23 Hz), 116.2 (d, J = 23 Hz), 116.5 (d, J = 23 Hz), 117.8 (d, J = 9 Hz), 125.4 (d, J = 9 Hz), 141.0 (d, J = 9 Hz), 145.4 (d, J = 3 Hz), 149.1 (d, J = 3 Hz), 164.3 (d, J = 252 Hz), 164.5 (d, J = 252 Hz), 171.8, 173.1; HRESI-MS (m/z): Calculated for $C_{18}H_{16}F_2N_2O_4Na$ (M + Na): 385.0976, found 385.0974.

*(E)-Dimethyl 2-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)-phenyl)succinate (**6ea**).* Red semisolid; Yield − (56 mg, 72%); R_f (10% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1732, 1598, 1502, 1436; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.70 (dd, J = 16.80, 5.68 Hz, 1 H) 3.34 (dd, J = 16.67, 8.84 Hz, 1 H) 3.60 (s, 3 H) 3.68 (s, 3 H) 3.87 (s, 3 H) 3.88 (s, 3 H) 4.83 (dd, J = 8.84, 5.56 Hz, 1 H) 6.87−6.92 (m, 2 H) 7.01 (d, J = 9.09 Hz, 2 H) 7.79 (d, J = 8.84 Hz, 1 H) 7.85 (m, J = 8.84 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 38.3, 43.9, 51.8, 52.3, 55.5, 55.5, 114.1, 114.2, 114.2, 117.2, 124.9, 140.2, 143.3, 147.3, 161.6, 161.7, 172.3, 173.7; HRESI-MS (m/z): Calculated for $C_{20}H_{22}N_2O_6Na$ (M + Na): 409.1376, found 409.1377.

*(E)-Dibutyl 2-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)-succinate (**6eb**).* Red liquid; Yield − (70 mg, 74%); R_f (10% EtOAc/Hexane) 0.3; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1252, 1499, 1598, 1732; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.72 (t, J = 7.2 Hz, 3 H) 0.89 (t, J = 7.6 Hz, 3 H) 1.08−1.17 (m, 2 H) 1.32 (q, J = 7.6 Hz, 2 H) 1.37−1.45 (m, 2 H) 1.56 (q, J = 7.48 Hz, 2 H) 2.71 (dd, J = 16.64, 5.8 Hz, 1 H) 3.33 (dd, J = 16.6, 8.68 Hz, 1 H) 3.87 (s, 3 H) 3.89 (s, 3 H) 3.96−4.09 (m, 4 H) 4.83 (dd, J = 8.24, 6.0 Hz, 1 H) 6.86−6.92 (m, 2 H) 7.00 (d, J = 8.8 Hz, 2 H) 7.78 (d, J = 8.8 Hz, 1 H) 7.83 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.5, 13.7, 18.8, 19.0, 30.4, 30.5, 38.5, 44.1, 55.1, 64.5, 64.9, 114.0, 114.1, 114.2, 117.0, 124.9, 140.5, 143.3, 161.6, 161.7, 171.9, 173.3; HRESI-MS (m/z): Calculated for $C_{26}H_{34}N_2O_6Na$ (M + Na): 493.2315, found 493.2318.

*(E)-Dimethyl 2-(4-Methyl-2-(m-tolyldiazenyl)phenyl)succinate (**6ba**).* Red semisolid; Yield − (66 mg, 93%); R_f (20% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure (a). IR (Neat, cm^{-1}): 1737, 1604, 1435; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.40 (s, 3 H) 2.47 (s, 3 H) 2.70 (dd, J = 16.67, 5.81 Hz, 1 H) 3.32 (dd, J = 16.80, 8.72 Hz, 1 H) 3.60 (s, 3 H) 3.65 (s, 3 H) 4.88 (dd, J = 8.59, 6.06 Hz, 1 H) 7.25−7.33 (m, 3 H) 7.41 (t, J = 7.71 Hz, 1 H) 7.55 (s, 1 H) 7.70 (d, J = 8.08 Hz, 1 H) 7.74 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 21.1, 21.3, 38.3, 43.1, 51.7, 52.2, 115.9, 120.0, 124.3, 128.9, 129.5, 132.0, 132.2, 135.6, 138.2, 139.0, 148.9, 152.8, 172.2, 173.8; HRESI-MS (m/z): Calculated for $C_{20}H_{22}N_2O_4Na$ (M + Na): 377.1477, found 377.1477.

*N-Ethyl-2-(5-methyl-2-oxo-1-(p-tolylamino)indolin-3-yl)acetamide (**7aa**).* White semisolid; Yield − (34 mg, 68%); R_f (50% EtOAc/Hexane) 0.2; Prepared according to literature procedure.[27,19f] IR (KBr, cm^{-1}): 1652, 1714, 2316, 2857, 2925, 3403; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.10 (t, J = 7.2 Hz, 3 H) 2.24 (s, 3 H) 2.32 (s, 3 H) 2.58 (dd, J = 15.2, 7.2 Hz, 1 H) 2.88 (dd, J = 15.2, 5.6 Hz, 1 H) 3.23−3.31 (m, 2 H) 3.92 (t, J = 6.8 Hz, 1 H) 6.35 (s, 1 H) 6.54 (s, 1H) 6.66 (d, J = 8.4 Hz, 2H) 6.83 (d, J = 8.0 Hz, 1H) 6.99 (d, J = 8.0 Hz, 2 H) 7.02 (d, J = 7.6 Hz, 1H) 7.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 14.6, 20.5, 21.1, 34.6, 37.0, 41.2, 108.6, 113.6, 125.2, 126.0, 128.7, 129.7, 131.0, 132.9, 140.7, 143.4, 169.6, 176.4; HRESI-MS (m/z): Calculated for $C_{20}H_{23}N_3O_2Na$ (M + Na): 360.1688, found 360.1683.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01094.

The optimization data, and ^1H and ^{13}C NMR spectral data of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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