Synthesis S. Chow et al. Paper

Efficient Approaches for the Synthesis of Diverse α-Diazo Amides

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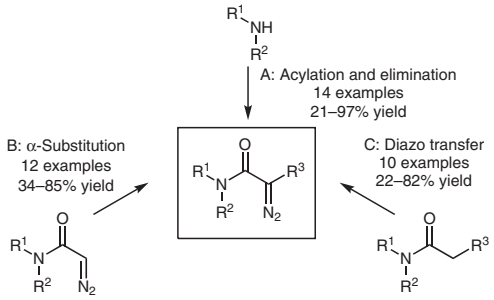

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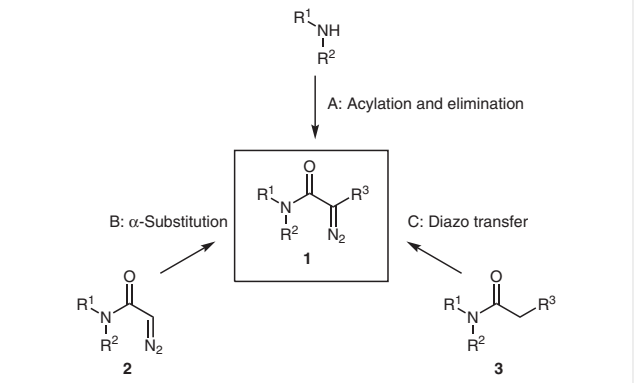
Abstract Metal-catalysed carbenoid chemistry can be exploited for the synthesis of diverse ranges of small molecules from α-diazo carbonyl compounds. In this paper, three synthetic approaches to α-diazo amides are described, and their scope and limitations are determined. On the basis of these synthetic studies, recommendations are provided to assist the selection of the most appropriate approach for specific classes of product. The availability of practical and efficient syntheses of diverse α-diazo acetamides is expected to facilitate the discovery of many different classes of bioactive small molecules.

Key words diazo compounds, molecular diversity, carbenoid chemistry

Metal-catalysed carbenoid chemistry can enable the synthesis of many different classes of small molecule.[1] The diversity of the possible products stems from the many different patterns of reactivity that are possible, and the scope for both inter- and intramolecular reactions. The diverse patterns of possible reactivity include insertion into C–H, O–H and N–H bonds, cyclopropanation and ylide formation; some of these processes also enable subsequent chemistry such as cycloaddition or rearrangement reactions.[2–4] Crucially, judicious choice of catalyst can provide control over stereochemistry, chemoselectivity (e.g., a particular C–H bond in a complex substrate) and reaction fate (e.g., which mode of reactivity is favoured).[5–10] The diversity of possible reaction outcomes can enable the parallel discovery of diverse bioactive chemotypes.[11,12]

We therefore investigated a suite of methods for the synthesis of α-diazo amides and some related compounds. These methods would ideally enable the efficient synthesis of structurally diverse diazo compounds from readily available substrates without the need for purification of any intermediates. Overall, the developed methods would ideally be complementary, and enable the efficient synthesis of a wide range of substrates.

We envisaged three general synthetic approaches to α-diazo amides **1** (Scheme 1): acylation with an appropriate reagent followed by elimination (Approach A); α-substitution of α-diazo acetamides **2** (Approach B); and diazo transfer (Approach C). Here, we describe the development and demonstrate the scope and limitations of practical methods for the synthesis of α-diazo amides (and some related compounds) from readily available starting materials.



Scheme 1 Overview of synthetic approaches to α-diazo amides

Approach A: Synthesis by Acylation and Elimination

We developed a one-pot synthesis of α-diazo amides from readily available amines that was based on an established synthesis of α-diazoacetic esters.[13,14] Glyoxylic acid (**4a**) and phenylglyoxylic acid (**4b**) were initially converted into the corresponding toluenesulfonyl hydrazones **5**. Subsequent treatment with thionyl chloride in toluene at 90 °C gave the corresponding acid chlorides **6** that were used without purification (Scheme 2). The acid chlorides **6a** and **6b** were orange and yellow amorphous solids respectively,

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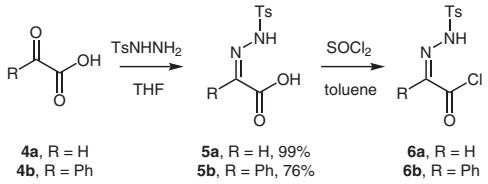


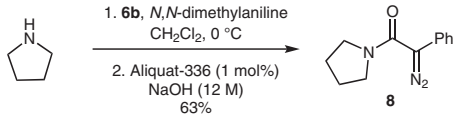
Scheme 2 Synthesis of the acid chlorides **6** that were used without purification

and were stored *in vacuo* at room temperature for a maximum of 12 hours prior to use.

The acid chloride **6a** was exploited in the synthesis of α-diazo acetamides. Accordingly, a solution of the acid chloride **6a** in dichloromethane at 0 °C was treated with the requisite amine and *N*,*N*-dimethylaniline under a nitrogen atmosphere; after 2 hours, triethylamine was added to induce elimination to yield the corresponding α-diazo acetamide (Scheme 3). Although DBU has been used in syntheses of related products,[15] we found triethylamine enabled more facile product purification.

The approach enabled the synthesis of a wide range of α-diazo acetamides. In particular, a primary amine (→ **2a**), secondary amines (→ **2b**–**g**) and anilines/hetarylamines (→ **2h**–**m**) were successful as substrates. In the case of sterically hindered secondary amines, prolonged coupling and/or elimination was necessary to yield the corresponding α-diazo acetamides (e.g., **2f**). The α-diazo acetamides **2a**–**m** were stored at –20 °C; under these conditions, the α-diazo acetamide **2h**, for example, was spectroscopically identical after storage for more than a year.

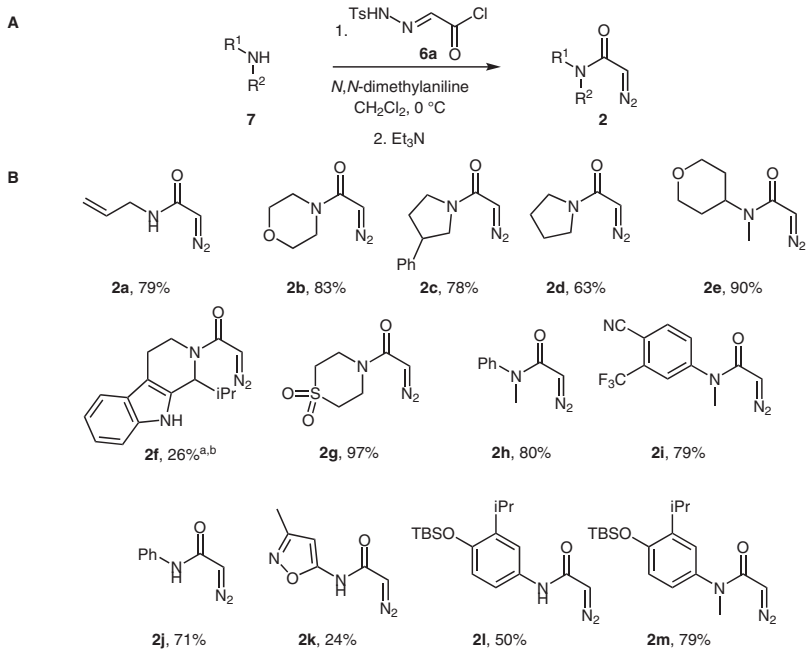
The acid chloride **6b** was exploited in the synthesis of an α-diazo α-phenyl acetamide (Scheme 4). After coupling with pyrrolidine (3.3 equiv) in the presence of *N*,*N*-dimethylaniline, elimination was induced by treatment with a 12 M aqueous solution of sodium hydroxide and the phase-transfer catalyst trioctylmethylammonium chloride (Aliquat® 336; 1 mol%). We had investigated the use of trimethylamine and DBU in the elimination step with little success, even at elevated temperature, before arriving at these optimal conditions.[16] We demonstrated that, with pyrrolidine, good yields of the corresponding α-diazo α-phenyl acetamide **8** could be obtained.



Scheme 4 One-pot synthesis of a α-diazo α-phenyl acetamide **8**

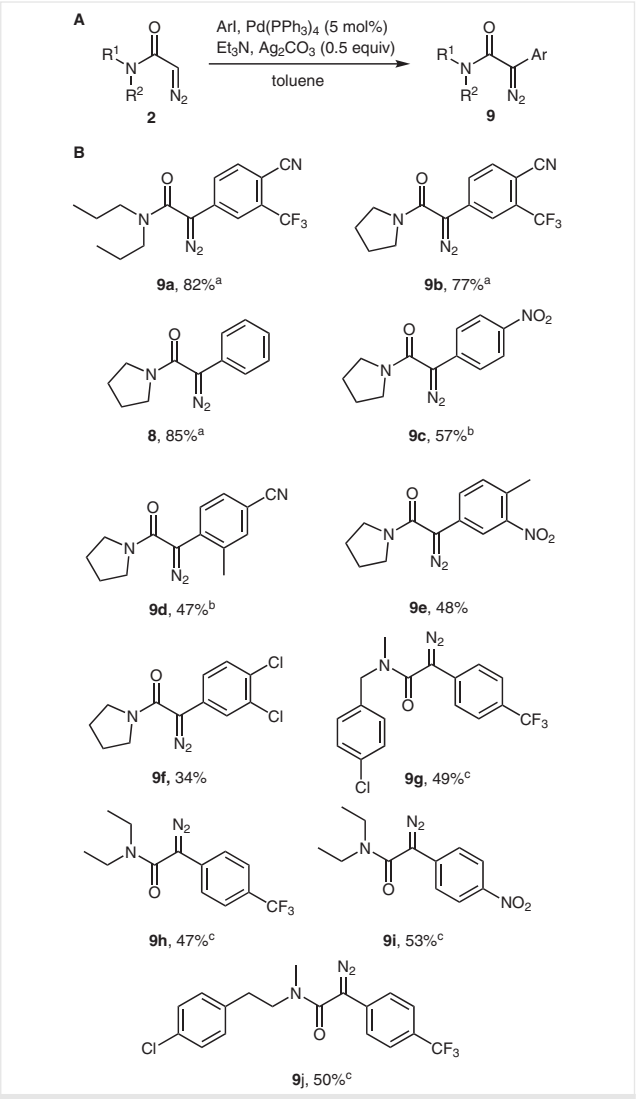
Approach B: Synthesis by α-Arylation of the Corresponding α-Diazo Acetamide

We have also developed a method for the α-arylation of α-diazo acetamides **2** (Scheme 5).[17] The beneficial effect of Ag_2CO_3 was found following a limited additive screen, and is in line with previous studies involving related substrates.[17b] In each case, $Pd(PPh_3)_4$ (5 mol%) and Ag_2CO_3 (0.5 equiv) were placed in oven-dried glassware under a nitro-



Scheme 3 One-pot synthesis of α-diazo acetamides. Panel A: General synthetic scheme. Panel B: Structures of the α-diazo acetamides prepared. [a] A prolonged reaction (24 h) between the amine and the acid chloride was required. [b] A prolonged reaction time (48 h) for the elimination was required.

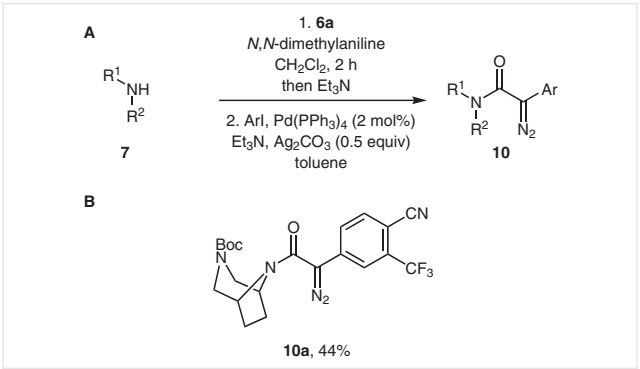
gen atmosphere, and anhydrous toluene, the aryl halide (1 equiv), triethylamine and a solution of the α-diazo acetamide **2** (1.3 equiv) in anhydrous toluene were added sequentially. The reactions were stirred at room temperature, generally for 4 hours.



Scheme 5 Palladium-catalysed synthesis of α-aryl α-diazo acetamides. Panel A: General synthetic scheme. Panel B: The prepared α-aryl α-diazo acetamides. [a] Prepared by method B2 (see the Supporting Information), with a 1:1 stoichiometry of diazo compound to aryl iodide. [b] Prepared from the corresponding aryl bromide. [c] Prepared from the α-diazo acetamides described in the Supporting Information.

The demonstrated scope of the method is shown in Scheme 5 (Panel B). Couplings were successful with a wide range of aryl iodides including iodobenzene (→ **8**) and electron-deficient substrates (e.g., → **9a**, **9b** and **9e–i**); it was found that the coupling proceeded most rapidly with electron-deficient substrates. Couplings with 5-iodoindole and 4-iodoanisole showed slow conversion by TLC and, despite extended (48 h) reaction times, product purification was difficult due to the poor conversions. In addition, couplings with aryl bromides were successful with electron-deficient substrates (e.g., → **9c** and **9d**); however, there was no evidence of conversion by TLC with bromobenzene, 1-bromo-3-methoxybenzene, 1-bromo-4-methoxybenzene and 3-bromopyridine, even with extended reaction times.

We also developed a procedure in which the synthesis of the α-diazo acetamide was telescoped with subsequent α-arylation (Scheme 6). The telescoped procedure was successful with a bridged secondary amine as a substrate (→ **10a**).

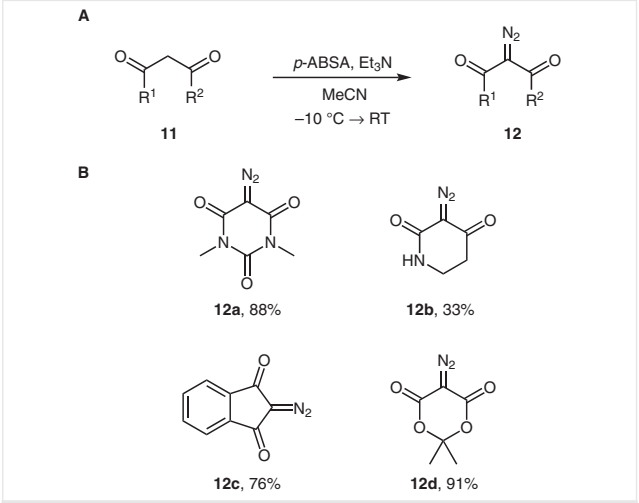


Scheme 6 Telescoped synthesis of α-aryl α-diazo acetamides from amines and a lactam. Panel A: General synthetic scheme. Panel B: An example of an α-aryl α-diazo acetamide prepared by this route.

Approach C: Synthesis by Diazo Transfer

The synthesis of α-diazo carbonyl compounds by diazo transfer has been demonstrated with a range of substrate classes.[18,19] We initially adopted this approach with cyclic 1,3-dicarbonyl compounds (Scheme 7). In our preliminary studies, we had found that the use of triethylamine as the base, rather than DBU, enabled more facile product purification. Accordingly, triethylamine (1.2 equiv) was added dropwise to a solution of the appropriate 1,3-dicarbonyl compound and 4-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.5 equiv) in anhydrous acetonitrile at –10 °C, and the reaction then stirred at room temperature. Under these optimal conditions, diazo transfer was rapid and was accompanied by precipitation of 4-acetamidobenzenesulfonamide.[20] Efficient diazo transfer was observed with a range of 1,3-dicarbonyl compounds including 1,3-dimethylbarbituric acid (→ **12a**), a β-keto lactam (→ **12b**), a 1,3-diketone (→ **12c**) and Meldrum's acid (→ **12d**).

We also investigated the diazo transfer reactions of acyclic β-keto amides (Scheme 8). A range of structurally diverse β-keto amide derivatives was prepared by reaction of the appropriate nitrogen nucleophile with 2,2,6-trimethyl-1,3-dioxin-4-one (1.1 equiv) under microwave irradiation (110 °C, max 200 W, max 300 psi) for 1.5–2 hours.[21] Our previous experience[11,12] had shown that it was possible to telescope the acylation step with a subsequent diazo trans-



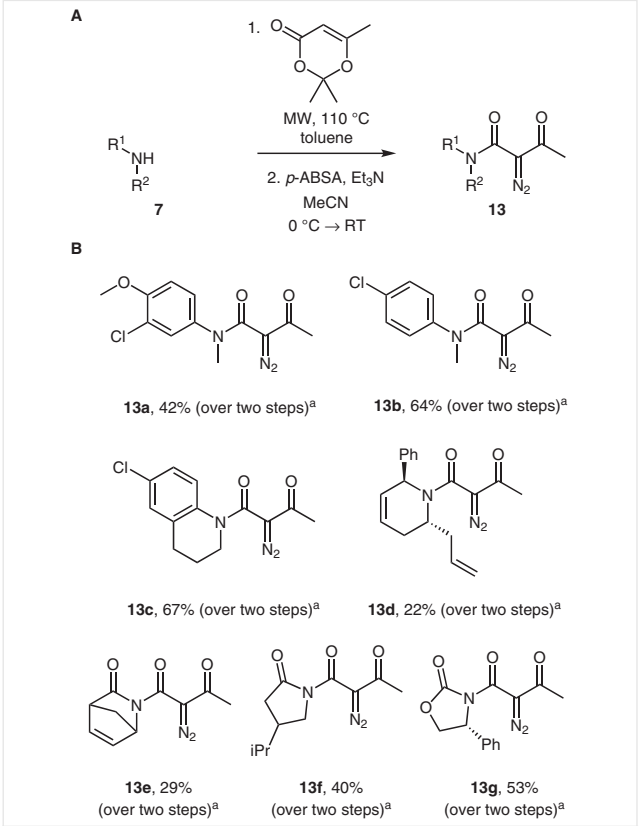
Scheme 7 Diazo transfer with cyclic 1,3-dicarbonyl substrates

fer reaction. Accordingly, treatment of the crude acylation products and *p*-ABSA with triethylamine at 0 °C resulted in smooth diazo transfer. Significantly extended reaction times (20–24 h) were required to yield the diazo products **13d**, **13f** and **13g**. Remarkably, the approach was successful with a wide range of nitrogen nucleophiles including anilines (→ **13a–c**), a secondary amine (→ **13d**), lactams (→ **13e** and **13f**) and an oxazolidinone (→ **13g**).

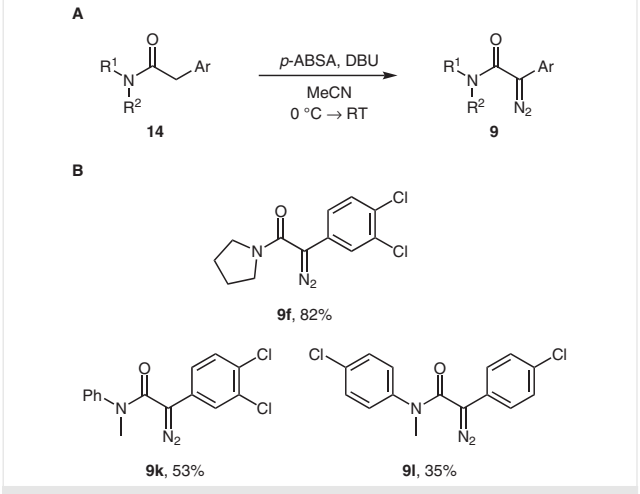
The synthesis of α-aryl α-diazo acetamides **9** by diazo transfer was also investigated (Scheme 9). Although similar α-aryl α-diazo acetamides **9** had previously been prepared using diphenyl phosphoryl azide (DPPA) and LDA,[22] we recognised the advantages of *p*-ABSA in terms of both safety and ease of product purification. We found DBU to be an effective base for the transformation. Accordingly, DBU (2 equiv) was added dropwise to a solution of the appropriate α-aryl acetamide and *p*-ABSA (1.1 equiv); the reactions were then allowed to warm to room temperature over 4 hours. The method was successful with α-aryl acetamides derived from both anilines (→ **9k** and **9l**) and a secondary amine (→ **9f**).

α-Diazo amides have diverse reactivity that can be harnessed in the synthesis of a wide range of molecular scaffolds. Indeed, we have previously exploited metal-catalysed reactions of α-diazo amides in the activity-directed synthesis of diverse androgen receptor agonists. The scope of three synthetic approaches has been determined, and a summary of our recommendations for which approach is most suitable for specific classes of product is provided in Figure 1.

We demonstrated that Approach A (synthesis by acylation with an acid chloride **6** and subsequent elimination) enables the synthesis of a wide range of α-diazo acetamides. The value of the approach is likely to be extremely high because of the very wide availability of primary amine, secondary amine and aniline substrates.



Scheme 8 Synthesis of α-diazo β-keto amides by diazo transfer. Panel A: General synthetic scheme. Panel B: The prepared α-diazo β-keto amides. [a] Telescoped yield.



Scheme 9 Synthesis of α-aryl α-diazo acetamides by diazo transfer. Panel A: General synthetic scheme. Panel B: The prepared α-aryl α-diazo acetamides.

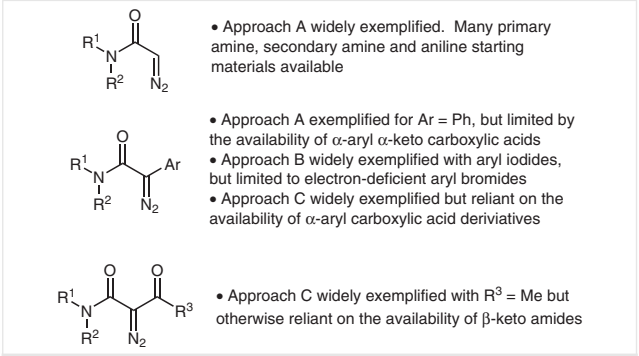


Figure 1 Scope of the approaches for the synthesis of α-diazo amides. Approach A: Synthesis by acylation and elimination. Approach B: Synthesis by α-arylation of the corresponding α-diazo acetamide. Approach C: Synthesis by diazo transfer.

All three of the approaches can enable the synthesis of α-aryl α-diazo amides. The poor availability of α-aryl α-keto carboxylic acids means that Approach A is likely to be most useful for the synthesis of phenyl-substituted analogues. Approach B (synthesis by Pd-catalysed α-arylation of α-diazo acetamides), on the other hand, enables the introduction of a very broad range of (het)aryl substituents. However, although many aryl iodides are competent substrates, the scope of the approach is less broad with (more generally available) aryl bromides. Finally, Approach C (synthesis by diazo transfer) is successful with a range of α-aryl acetamides and enables the synthesis of a wide range of α-diazo β-keto amides. The approach is particularly valuable for α-diazo β-keto butanamides because the required substrates may be easily prepared by acylation of the appropriate nitrogen nucleophile (including amines, anilines, lactams and oxazolidinones).

Overall, the availability of practical and efficient approaches for the synthesis of α-diazo acetamides is expected to facilitate the discovery of diverse bioactive small molecules.

CAUTION! Diazo compounds are potentially explosive and must be handled with care. For concentration of material under reduced pressure, a maximum water bath temperature of 40 °C was used. Contact with metal was avoided during syntheses. No problems were encountered during our synthetic studies on the scales that are described below.

Details regarding the syntheses and structures of precursors S1–11 can be found in the Supporting Information. All non-aqueous reactions were carried out under an atmosphere of nitrogen unless otherwise stated and water-sensitive reactions were performed in anhydrous solvents (obtained from a PureSolv MD5 Purification System) in oven-dried glassware and cooled under nitrogen before use. All other solvents and reagents were of analytical grade and used as supplied. Ether refers to diethyl ether and petrol refers to petroleum spirit (bp 40–60 °C) unless otherwise stated. Solvents were removed under reduced pressure using an IKA RV 10 rotary evaporator. General procedures B2 and C3 are included in the Supporting Information. Flash column chromatography was carried out using silica gel 60 (35–70 μm particles) supplied by Merck. Thin-layer chromatography was carried out using commercially available pre-coated aluminium plates (Merck silica gel 60 F254). A UV lamp (λ_{max} = 254 nm) and $KMnO_4$ were used for visualisation. Infrared spectra were recorded on a Bruker Alpha ATR FR-IR spectrophotometer; absorptions are reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were collected on Bruker Avance 500, Bruker DPX500, DPX400 or DPX300 spectrometers using an internal deuterium lock. NMR spectra were recorded at 300 K unless otherwise stated. Chemical shifts are quoted in parts per million down field of trimethylsilane and coupling constants (*J*) are given in Hz. High-resolution mass spectrometry (HRMS) was performed using electrospray ionisation on a Bruker MaXis Impact spectrometer.

Synthesis of Diazo Compounds Using Acid Chloride Reagents; General Procedure A

Toluenesulfonyl hydrazone **5a** or **5b** (1 equiv) was dissolved in anhydrous toluene (25 mL) and purged with N_2 for 5 min. Thionyl chloride (2 equiv) was added dropwise at RT and the solution was stirred vigorously and slowly heated to 90 °C over 30 min. After 4 h, the reaction mixture was cooled to RT, the solvent was removed under reduced pressure and the crude product was dried under vacuum.

The crude product (1 equiv) was dissolved in anhydrous CH_2Cl_2 (3 mL/mmol) and cooled to 0 °C. A solution of amine (2 equiv) in CH_2Cl_2 (0.5 mL/mmol) and a separate solution of dimethylaniline (1 equiv) were added slowly under an N_2 atmosphere. The reaction mixture was stirred overnight before Et_3N (5 equiv) was added dropwise over 10 min. The reaction mixture was allowed to return to RT gradually and the solution was stirred overnight. The reaction mixture was washed with aqueous sodium bicarbonate solution and brine solution successively. The organic layer was collected, dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the crude diazo amides **2a–k**, **8**.

Synthesis of Diazo Acetamides; General Procedure B1

The appropriate diazo compound (1.3 equiv) as a solution in dry toluene was added to a stirred suspension of the appropriate aryl iodide (1 equiv), $Pd(PPh_3)_4$ (5 mol%), Ag_2CO_3 (0.5 equiv) and Et_3N (1.3 equiv) in dry toluene under an N_2 atmosphere. The syringe was washed twice with dry toluene and the washings were added to the reaction mixture for a final concentration of 0.25 M. After 4 h, the reaction mixture was filtered through a silica plug (2 × Ø2 cm) eluting with EtOAc (2 × 10 mL). The filtrate was concentrated under reduced pressure and the crude residue was purified by flash column chromatography to yield compounds **9c–j**.

Synthesis of Diazo Compounds by Diazo Transfer; General Procedure C1

A solution of dicarbonyl compound (1 equiv) and *p*-ABSA (1.5 equiv) in anhydrous MeCN was cooled to –10 °C. Et_3N (1.2 equiv) was added dropwise over 5–10 min and the mixture was stirred at RT under a N_2 atmosphere. After 0.5–1 h (when a solid precipitated out of solution and the starting material had been consumed according to TLC), the solvent was removed under reduced pressure and the crude residue was dissolved in Et_2O (30 mL/mmol), filtered and the resulting solid rinsed with CH_2Cl_2 (30 mL/mmol). The filtrate was concentrated and purified by flash column chromatography to yield compounds **12a–d**.

Synthesis of Diazo Compounds by Acylation Followed by Diazo Transfer; General Procedure C2

2,2,6-Trimethyl-4*H*-1,3-dioxin-4-one (1.1 equiv) was added to a solution of aniline **7** (1 equiv) in toluene and the mixture was reacted under microwave irradiation (110 °C, max 200 W, max 300 psi). After 1.5–2 h, the solvent was removed under reduced pressure. *p*-ABSA (1.5 equiv) was added followed by anhydrous MeCN and the solution was cooled to 0 °C. Et_3N (1.2 equiv) was added dropwise over 5–10 min and the mixture was stirred at RT under an N_2 atmosphere. After 4 h, the solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography to yield compounds **13a–g**.

2-(4-Methylbenzenesulfonamido)imino Acetic Acid (5a)

Glyoxylic acid (0.08 mol, 7.4 g) and *p*-toluenesulfonylhydrazide (0.05 mol, 10.0 g) were dissolved in THF (70 mL) and the mixture stirred vigorously at RT for 24 h. The solvent was removed under reduced pressure and the resulting residue was triturated with cold water. The solid was air-dried for two days to attain the crude product, which was recrystallised in EtOAc to afford pure product **5a** as a white amorphous solid (12.80 g, 99%).

IR (neat): 3170, 2892, 1695, 1595 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 11.01 (s, 1 H, OH), 7.82 (d, *J* = 8.0 Hz, 2 H, phenyl 3-H, 5-H), 7.43 (d, *J* = 8.0 Hz, 2 H, phenyl 2-H, 6-H), 7.32 (s, 1 H, 2-H), 2.42 (s, 3 H, Me).

^{13}C NMR (100 MHz, acetone-d_6): δ = 206.3, 163.8, 145.3, 137.3, 130.6, 128.5, 21.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_{10}N_2O_4SNa$: 265.0254; found: 265.0252.

2-Diazo-*N*-(prop-2-en-1-yl)acetamide (2a)

By employing general procedure A, the reaction of **6a** (3 mmol, 780 mg) with allylamine (6 mmol, 448 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2a** as a yellow oil (298 mg, 79%).

R_f = 0.40 (Et_2O).

IR (film): 3291, 3089, 2925, 2103, 1618, 1542 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 6.91 (br s, 1 H, NH), 5.85 (ddt, *J* = 17.2, 10.6, 5.4 Hz, 1 H, propenyl 2-H), 5.72 (s, 1 H, diazo acetamide 2-H1), 5.16 (dq, *J* = 17.2, 1.6 Hz, 1 H, propenyl 3-H_{trans}), 5.04 (dq, *J* = 10.3, 1.6 Hz, 1 H, propenyl 3-H_{cis}), 3.86 (tt, *J* = 5.7, 1.6 Hz, 2 H, propenyl 1-H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 165.7, 136.4, 115.5, 46.8, 42.5.

HRMS (ESI): *m*/*z* [2 M + Na]$^+$ calcd for $C_{10}H_{14}N_6O_2Na$: 273.1076; found: 273.1069.

2-Diazo-1-(morpholin-4-yl)ethan-1-one (2b)

By employing general procedure A, the reaction of **6a** (1.5 mmol, 390 mg) and morpholine (3 mmol, 260 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2d** as a yellow oil (193 mg, 83%).

R_f = 0.24 (Et_2O).

IR (film): 3056, 2973, 2036, 1647, 1488 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 5.34 (s, 1 H, diazo acetamide 2-H1), 3.48–3.18 (app br m, 4 H, morpholine 2-H_{AB}, 6-H_{AB}), 1.99–1.74 (m , 4 H, morpholine 3-H_{AB}, 5-H_{AB}).

^{13}C NMR (75 MHz, acetone-d_6): δ = 164.0, 46.4, 26.5, 25.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_6H_{10}N_3O_2$: 156.0773; found: 156.0768.

2-Diazo-1-(3-phenylpyrrolidin-1-yl)ethan-1-one (2c)

By employing general procedure A, the reaction of **6a** (3.4 mmol, 884 mg) and 3-phenylpyrrolidine (6.8 mmol, 1.0 g) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2 for three column volumes and then CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2c** as a bright orange oil (574 mg, 78%).

R_f = 0.32 (Et_2O).

IR (CH_2Cl_2): 2095, 1600, 1417, 1166 cm^{-1}.

^1H NMR (500 MHz, CD_2Cl_2): δ = 7.33 (dd, *J* = 8.0, 7.0 Hz, 2 H), 7.26 (m, 3 H), 4.89 (s, 1 H), 4.02–3.81 (m, 1 H), 3.61–3.23 (m, 4 H), 2.35–2.29 (m, 1 H), 2.07–2.01 (m, 1 H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ (rotamers A/B) = 163.8 (A/B), 141.4 (B), 141.1 (A), 129.9 (B), 129.8 (A), 128.7 (A/B), 127.14 (A/B), 52.5 (A/B), 52.3 (A/B), 46.2 (A), 45.8 (B), 44.6 (A), 42.9 (B), 33.4 (A), 33.1 (B).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{14}N_3O$: 216.1137; found: 216.1127.

2-Diazo-1-(pyrrolidin-1-yl)ethan-1-one (2d)

By employing general procedure A, the reaction of **6a** (1.5 mmol, 390 mg) and pyrrolidine (3 mmol, 246 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2f** as a yellow oil (132 mg, 63%).

R_f = 0.20 (Et_2O).

IR (neat): 3063, 2974, 2875, 2096, 1594, 1425 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.80 (s, 1 H, diazo acetamide 2-H), 3.52 (app br s, 2 H, pyr 2-H_A, 5-H_A), 3.20 (app br s, 2 H, pyr 2-H_B, 5-H_B), 1.94 (app br s, 2 H, pyr 3-H_A, 4-H_A), 1.87 (app br s, 2 H, pyr 3-H_B, 4-H_B).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 63.2, 45.5, 17.8, 14.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_6H_9N_3ONa$: 162.0643; found: 162.0638.

2-Diazo-*N*-methyl-*N*-(oxan-4-yl)acetamide (2e)

By employing general procedure A, the reaction of **6a** (4.3 mmol, 1.12 g) and *N*-methyl-*N*-tetrahydro-2*H*-pyran-4-ylamine (4.3 mmol, 495 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) for 3 column volumes an then Et_2O to afford the diazo acetamide **2h** as a bright orange oil (708 mg, 90%).

R_f = 0.10 (Et_2O).

IR (CH_2Cl_2): 2098, 1600, 1410, 1256, 1144, 1086 cm^{-1}.

^1H NMR (500 MHz, CD_2Cl_2): δ = 5.01 (s, 1 H), 3.98 (d, *J* = 4.6 Hz, 1 H), 3.96 (d, *J* = 4.6 Hz, 1 H), 3.44 (t, *J* = 11.4 Hz, 2 H), 2.70 (s, 3 H), 1.77–1.73 (m, 3 H), 1.55–1.52 (m, 2 H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ (rotamers A/B) = 165.9 (A/B), 130.0 (A), 126.6 (B), 104.6 (A/B), 67.8 (A/B), 46.8 (A/B), 30.7 (A/B).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_8H_{13}N_3O_2Na$: 206.0905; found: 206.0892.

2-Diazo-1-(1-isopropyl-1*H*,3*H*,4*H*,9*H*-pyrido[3,4-*b*]indol-2-yl)ethan-1-one (2f)

By employing general procedure A, the reaction of **6a** (6.2 mmol, 1.61 g) and 1-isopropyl-1*H*,2*H*,3*H*,4*H*,9*H*-pyrido[3,4-*b*]indole (12.4 mmol, 2.66 g) gave a crude material that was purified by flash column chromatography eluting with CH_2Cl_2–MeOH (99:1) to give the diazo acetamide **2f** as a yellow amorphous solid (0.457 g, 26%).

R_f = 0.39 (CH_2Cl_2–MeOH, 99:1).

IR (film): 3194, 2967, 2103, 1580, 1467, 1428, 1349 cm^{-1}.

^1H NMR (300 MHz, CD_2Cl_2): δ = 7.48 (d, *J* = 7.5 Hz, 1 H, ind 5-H), 7.36 (d, *J* = 7.5 Hz, 1 H, ind 8-H), 7.21–7.08 (m, 2 H, ind 6-H, 7-H), 5.58 (d, *J* = 14.4 Hz, 1 H, ind 1-H), 5.25 (s, 1 H, 2-H), 3.50 (br m, 2 H, ind 3-H), 2.84–2.69 (m, 2 H, ind 4-H), 2.14 (dt, *J* = 14.4, 6.7, 6.7 Hz, 1 H, iPr H), 1.15 (d, *J* = 6.7 Hz, 3 H, iPr H[a]), 0.99 (d, *J* = 6.7 Hz, 3 H, iPr H[b]); iPr = isopropyl, ind = indolyl.

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 166.1, 136.7, 134.7, 127.1, 121.9, 119.5, 118.2, 111.6, 107.7, 56.2, 47.1, 41.2, 33.7, 22.3, 20.2, 20.1.

HRMS (ESI): *m*/*z* [M – N_2]$^+$ calcd for $C_{16}H_{18}N_2O$: 254.1414; found: 254.1486.

2-Diazo-1-(1,1-dioxidothiomorpholino)ethan-1-one (2g)

By employing general procedure A, the reaction of **6a** (1.5 mmol, 390 mg) and thiomorpholine-1,1-dioxide (3 mmol, 405 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2g** as a yellow solid (295 mg, 97%).

R_f = 0.34 (pentane–Et_2O, 1:1).

^1H NMR (400 MHz, acetone-d_6): δ = 5.88 (s, 1 H, diazo acetamide 2-H), 3.95–3.87 (m, 4 H, 2-H_{AB}, 6-H_{AB}), 3.12–3.08 (m, 4 H, 3-H_{AB}, 5-H_{AB}).

^{13}C NMR (100 MHz, acetone-d_6): δ = 165.6, 52.42, 46.9, 43.2 cm^{-1}.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_6H_9N_3O_3SNa$: 226.0262; found: 226.0255.

2-Diazo-*N*-methyl-*N*-phenylacetamide (2h)

By employing general procedure A, the reaction of **6a** (3 mmol, 780 mg) and *N*-methylaniline (6 mmol, 650 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2h** as an orange oil (419 mg, 80%).

R_f = 0.45 (pentane–Et_2O, 1:1).

IR (neat): 3118, 3061, 2934, 2101, 1621 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 7.48–7.28 (m, 2 H, Ar 3-H, 5-H), 7.28–7.18 (m, 1 H, Ar 4-H), 7.20–7.16 (m, 2 H, Ar 2-H, 6-H), 4.81 (s, 1 H, diazo acetamide 2-H), 3.12 (s, 3 H, *N*Me).

^{13}C NMR (100 MHz, acetone-d_6): δ = 165.7, 144.4, 130.5, 128.4, 128.2, 47.4, 37.1.

The spectroscopic data match with the literature.[15b]

***N*-[4-Cyano-3-(trifluoromethyl)phenyl]-2-diazo-*N*-methylacetamide (2i)**

By employing general procedure A, the reaction of **6a** (1 mmol, 260 mg) and *N*-methyl-4-cyano-3-trifluoromethylaniline (2 mmol, 400 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2i** as a yellow solid (212 mg, 79%).

R_f = 0.43 (Et_2O).

IR (neat): 3091, 2231, 2108, 1605, 1377 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.11 (d, *J* = 8.4 Hz, 1 H, Ar 5-H), 8.05 (d, *J* = 2.0 Hz, 1 H, Ar 2-H), 7.89 (dd, *J* = 8.4, 2.0 Hz, 1 H, Ar 6-H), 5.56 (s, 1 H, diazo acetamide 2-H), 3.40 (s, 3 H, *N*Me).

^{13}C NMR (101 MHz, acetone-d_6): δ = 166.4, 148.9, 137.0, 130.4, 125.2, 125.1, 116.0, 48.7, 36.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_8F_3N_4O$: 269.0690; found: 269.0619.

The spectroscopic data match with the literature.[12]

2-Diazo-*N*-phenylacetamide (2j)

By employing general procedure A, the reaction of **6a** (3 mmol, 780 mg) and aniline (6 mmol, 545 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2j** as an orange solid (682 mg, 71%).

R_f = 0.52 (CH_2Cl_2–Et_2O, 9:1).

IR (CH_2Cl_2): 3085, 2093 (diazo), 1631, 1600, 1548, 1442, 1369.

^1H NMR (400 MHz, acetone-d_6): δ = 8.88 (s, 1 H, acetamide NH), 7.62–7.58 (m, 2 H, Ar 3-H, 5-H), 7.30–7.24 (m, 2 H, Ar 2-H, 6-H), 7.04–6.99 (m, 1 H, Ar 4-H), 5.40 (s, 1 H, diazo acetamide 2-H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 164.4, 140.7, 129.6, 123.7, 119.7, 119.6, 48.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_8H_8N_3O$: 162.0667; found: 162.0655.

The spectroscopic data match with the literature.[23]

2-Diazo-*N*-(3-methylisoxazol-5-yl)acetamide (2k)

By employing general procedure A, the reaction of **6a** (4.3 mmol, 1.12 g) and 5-amino-3-methylisoxazole (4.3 mmol, 422 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **2k** as a bright orange oil (170 mg, 24%).

R_f = 0.49 (Et_2O).

IR (CH_2Cl_2): 3205, 2109 (diazo), 1648, 1551, 1381, 1364, 1197, 1155 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 10.17 (s, 1 H, acetamide NH), 6.13 (s, 1 H, isoxazol 4-H), 5.99 (s, 1 H, diazo acetamide 2-H), 2.19 (s, 3 H, methyl 3-H).

^{13}C NMR (125 MHz, acetone-d_6): δ (rotamers A/B) = 162.7 (A), 162.6 (B), 162.2 (A), 162.1 (B), 161.6 (A/B), 88.7 (A), 88.6 (B), 49.3 (A/B), 11.6 (A/B).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_6H_6N_4O_2Na$: 189.0388; found: 189.0379.

***N*-{4-[(*tert*-Butyldimethylsilyl)oxy]-3-(propan-2-yl)phenyl}-2-diazoacetamide (2l)**

By employing general procedure A1, the reaction of **6a** (2.7 mmol, 700 mg) and aniline **S3** (500 mg, 1.9 mmol) gave a crude material that was purified by column chromatography eluting with pentane–Et_2O (1:1) to yield the diazo acetamide **2l** as a yellow solid (333 mg, 50%).

R_f = 0.2 (pentane–Et_2O, 1:1).

IR (film): 3279, 3085, 2959, 2929, 2886, 2858, 2101, 1622, 1602, 1550, 1490, 1471 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.72 (br s, 1 H, NH), 7.42 (d, *J* = 2.6 Hz, 1 H, 2-H), 7.37 (dd, *J* = 8.6, 2.6 Hz, 1 H, 6-H), 6.77 (d, *J* = 8.6 Hz, 1 H, 5-H), 5.36 (s, 1 H, diazo acetamide 2-H), 3.33 (sept, *J* = 6.9 Hz, 1 H, propan-2-yl 2-H), 1.18 (d, *J* = 6.9 Hz, 6 H propan-2-yl 1-H, 3-H), 1.04 (s, 9 H, *tert*-butyl-H), 0.25 (s, 6 H, dimethyl-H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 164.1, 149.2, 139.8, 134.7, 119.3, 118.4, 118.3, 48.4, 27.5, 26.3, 23.3, 19.0, –3.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{28}N_3O_2Si$: 334.1951; found: 334.1949.

N-{4-[(*tert*-Butyldimethylsilyl)oxy]-3-(propan-2-yl)phenyl}-2-diazo-*N*-methylacetamide (2m)

By employing general procedure A1, the reaction of **6a** (2.7 mmol, 700 mg) and aniline **S4** (1.8 mmol, 500 mg) gave a crude material that was purified by column chromatography eluting with pentane–Et_2O (8:2) to yield the diazo acetamide **2m** as a yellow solid (500 mg, 79%).

R_f = 0.4 (pentane–Et_2O, 8:2).

IR (film): 3280, 3085, 2959, 2930, 2859, 2101, 1622, 1602, 1549, 1491 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.15 (d, *J* = 2.7 Hz, 1 H, 2-H), 7.00 (dd, *J* = 8.5, 2.7 Hz, 1 H, 6-H), 6.91 (d, *J* = 8.5 Hz, 1 H, 5-H), 4.77 (s, 1 H, diazo acetamide 2-H), 3.35 (sept, *J* = 6.9 Hz, 1 H, propan-2-yl 2-H), 3.21 (s, 3 H, methyl-H), 1.21 (d, *J* = 6.9 Hz, 6 H, propan-2-yl 1-H, 3-H), 1.05 (s, 9 H, *tert*-butyl-H), 0.29 (s, 6 H, dimethyl-H).

^{13}C NMR (126 MHz, acetone-d_6): δ = 166.0, 153.0, 141.3, 137.8, 126.4, 126.4, 120.0, 47.3, 37.4, 27.7, 26.3, 23.2, 19.0, –3.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{30}N_3O_2Si$: 348.2107; found: 348.2112.

2-Diazo-2-phenyl-1-(pyrrolidin-1-yl)ethan-1-one (8)

By employing general procedure A, the reaction of **6b** (1.5 mmol, 500 mg) and pyrrolidine (3 mmol, 250 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **8** as a yellow oil (274 mg, 63%).

R_f = 0.34 (pentane–Et_2O, 1:1).

IR (neat): 2925, 2101, 1646 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.99–7.95 (m, 2 H, Ar 2-H, 6-H), 7.74 (tt, *J* = 7.2, 1.2 Hz, 1 H, Ar 4-H), 7.61 (app t, *J* = 7.2 Hz, 2 H, Ar 3-H, 5-H), 3.77–3.71 (m, 4 H, pyr 2-H_{AB}, 5-H_{AB}), 3.63–3.60 (m, 2 H, pyr 3-H_{AB}), 3.39–3.37 (m, 2 H, pyr 4-H_{AB}).

^{13}C NMR (101 MHz, acetone-d_6): δ = 165.2, 134.7, 129.4, 129.1, 128.6, 127.3, 66.4, 66.2, 46.0, 41.2.

2-[4-Cyano-3-(trifluoromethyl)phenyl]-2-diazo-*N*,*N*-dipropylacetamide (9a)

By employing general procedure B2 (1 mmol scale), the reaction of **S11** (1 mmol, 169 mg) and 4-iodo-2-(trifluoromethyl)benzonitrile (1 mmol, 297 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (19:1) to yield the diazo acetamide **9a** as a red solid (277 mg, 82%).

R_f = 0.52 (pentane–Et_2O, 1:1).

IR (neat): 2960, 2937, 2878, 2228, 2068, 1632, 1434 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 8.00 (d, *J* = 8.4 Hz, 1 H, Ar 5-H), 7.86 (d, *J* = 1.9 Hz, 1 H, Ar 2-H), 7.68 (dd, *J* = 8.4, 2.0 Hz, 1 H, Ar 6-H), 3.43–3.35 (m, 4 H, Pr 1-H), 1.65 (sext, *J* = 7.4 Hz, 4 H, Pr 2-H), 0.89 (t, *J* = 7.4 Hz, 6 H, Pr 3-H); Pr = propyl.

^{13}C NMR (101 MHz, acetone-d_6): 162.3, 137.2, 136.1, 132.9 (q, $^2J_{CF}$ = 32 Hz), 127.1, 123.0 (q, $^1J_{CF}$ = 222 Hz), 121.0, 116.4, 105.0, 49.8, 21.3, 11.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{18}F_3N_4O$: 339.1433; found: 339.1423

4-[1-Diazo-2-oxo-2-(pyrrolidin-1-yl)ethyl]-2-(trifluoromethyl)benzonitrile (9b)

By employing general procedure B2 (0.5 mmol scale), the reaction of **2d** (0.5 mmol, 70mg) and 4-iodo-2-(trifluoromethyl)benzonitrile (0.5 mmol, 149 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **9b** as a red solid (119 mg, 77%).

R_f = 0.33 (Et_2O).

IR (neat): 2899, 2848, 2193, 2045, 1675, 1390 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): 8.09 (d, *J* = 2.0 Hz, 1 H, Ar 3-H), 7.99 (d, *J* = 8.4 Hz, 1 H, Ar 6-H), 7.77 (dd, *J* = 8.4, 2.0 Hz, 1 H, Ar 5-H), 3.54–3.50 (m, 4 H, 2-H_{AB}, 5-H_{AB}), 2.00–1.81 (m, 4 H, 3-H_{AB}, 4-H_{AB}).

^{13}C NMR (101 MHz, acetone-d_6): δ = 161.5, 136.9, 135.9, 132.5, 127.2, 125.5, 122.3, 121.9, 116.5, 105.0, 48.3, 25.9 (1 signal missing).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}F_3N_4ONa$: 331.0783; found: 331.0776.

2-Diazo-2-(4-nitrophenyl)-1-(pyrrolidin-1-yl)ethan-1-one (9c)

By employing general procedure B1 (1.53 mmol scale), the reaction of **2d** (2 mmol, 280 mg) and 4-iodo-1-nitrobenzene (1.53 mmol, 310 mg) gave a crude material that was purified using column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **9c** as a dark orange solid (226 mg, 57%).

R_f = 0.6 (CH_2Cl_2–Et_2O, 9:1).

IR (neat): 2062, 1625, 1525, 1391, 1346, 1235, 1170, 826 cm^{-1}.

^{1}H NMR (501 MHz, DMSO-d_6): δ = 7.77–7.74 (app m, *J* = 9.1, 2.0 Hz, 2 H, Ar 3-H, 5-H), 7.14–7.11 (app m, *J* = 9.1, 2.0 Hz, 2 H, Ar 2-H, 6-H), 2.97 (app m, 4 H, pyr 2-H_{ab}, 5-H_{ab}), 1.44–1.39 (m, 4 H, pyr 3-H_{ab}, 4-H_{ab}); pyr = pyrrolidinyl.

^{13}C NMR (126 MHz, DMSO-d_6): δ = 160.93, 144.40, 136.97, 131.52, 130.73, 64.05, 47.88, 25.31.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{12}N_4O_3Na$: 283.0807; found: 283.0800.

4-[1-Diazo-2-oxo-2-(pyrrolidin-1-yl)ethyl]-3-methylbenzonitrile (9d)

By employing general procedure B1 (1 mmol scale), the reaction of **2d** (1.3 mmol, 180 mg) and 4-bromo-3-methylbenzonitrile (1 mmol, 196 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **9d** as a pale yellow solid (119 mg, 47%).

R_f = 0.46 (CH_2Cl_2–Et_2O, 9:1).

IR (neat): 2231, 1685, 1637, 1444, 1220, 1012, 848, 708 cm^{-1}.

^{1}H NMR (501 MHz, acetone-d_6): δ = 7.78 (d, *J* = 8.1 Hz, 1 H, 5-H), 7.66 (app s, 1 H, 2-H), 7.63 (app d, *J* = 8.1 Hz, 1 H, 5-H), 3.42–3.38 (m, 4 H, pyr 2-H_{ab}, 5-H_{ab}), 2.48 (s, 3 H, Me CH_3), 1.85–1.83 (m, 4 H, pyr 3-H_{ab}, 4-H_{ab}); pyr = pyrrolidinyl.

^{13}C NMR (126 MHz, acetone-d_6): δ = 192.8, 164.1, 141.2, 136.4, 135.3, 132.1, 129.7, 117.6, 115.9, 46.4, 45.2, 25.7, 23.6, 19.8.

HRMS (ESI): *m*/*z* [M – N_2]$^+$ calcd for $C_{14}H_{15}N_2O$: 227.1184); found: 227.1177.

2-Diazo-2-(4-methyl-3-nitrophenyl)-1-(pyrrolidin-1-yl)ethan-1-one (9e)

By employing general procedure B1 (0.83 mmol scale), the reaction of **2d** (1.1 mmol, 153 mg) and 4-iodo-1-methyl-2-nitrobenzene (0.83 mmol, 218 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **9e** as an orange solid (118 mg, 48%).

R_f = 0.55 (CH_2Cl_2–Et_2O, 9:1).

IR (neat): 2066, 1627, 1590, 1510, 1393, 1337, 1111, 850, 751 cm^{-1}.

^1H NMR (501 MHz, acetone-d_6): δ = 7.94 (d, J = 2.0 Hz, 1 H, 2-H), 7.37 (dd, J = 8.2, 2.0 Hz, 1 H, 5-H), 7.30 (d, J = 8.2 Hz, 1 H, 6-H), 3.33–3.31 (m, 4 H, pyr 2-H_{ab}, 5-H_{ab}), 2.36 (s, 3 H, Me CH_3), 1.80–1.77 (m, 4 H, pyr 3-H_{ab}, 4-H_{ab}); pyr = pyrrolidinyl.

^{13}C NMR (126 MHz, acetone-d_6): δ = 161.8, 149.8, 133.0, 129.3, 127.9, 119.9, 47.5, 25.1, 18.7.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{14}N_4O_3Na$: 297.0963; found: 297.0960.

2-Diazo-2-(3,4-dichlorophenyl)-1-(pyrrolidin-1-yl)ethan-1-one (9f)

By employing general procedure B1 (1 mmol scale), the reaction of **2d** (1.3 mmol, 180 mg) and 1,2-dichloro-4-iodobenzene (1 mmol, 273 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **9f** as an orange oil (96 mg, 34%).

R_f = 0.51 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 2062, 1626, 1474, 1388, 1338, 1135, 1027, 735 cm^{-1}.

^1H NMR (501 MHz, acetone-d_6): δ = 7.70 (app d, J = 2.2 Hz, 1 H, 5-H), 7.56–7.53 (app m, 1 H, 2-H), 7.32-7.30 (m, 1 H, 6-H), 3.48-3.44 (app m, 4 H, pyr 2-H_{ab}, 5-H_{ab}), 1.95-1.92 (m, 4 H, pyr 3-H_{ab}, 4-H_{ab}); pyr = pyrrolidinyl.

^{13}C NMR (126 MHz, acetone-d_6): δ = 161.7, 132.2, 130.6, 129.4, 127.8, 125.8, 123.7, 54.1, 47.4, 25.1.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{12}H_{11}Cl_2N_3Ona$: 306.0177; found: 306.0170.

***N*-[(4-Chlorophenyl)methyl]-2-diazo-*N*-methyl-2-[4-(trifluoromethyl)phenyl]acetamide (9g)**

By employing general procedure B1 (3 mmol scale), the reaction of **S8** (3.9 mmol, 872 mg) and 4-trifluoromethyliodobenzene (3 mmol, 440 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield aryl diazo acetamide **9g** as a bright orange oil (535 mg, 49%).

R_f = 0.5 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 3096, 2107, 1632, 1208 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 [d, J = 8.4 Hz, 2 H Ar(F) 3-H, 5-H], 7.29–7.25 [m, 4 H, Ar(F) 2-H, 6-H and Ar(Cl) 3-H, 5-H], 7.16 [d, J = 8.5 Hz, 2 H Ar(Cl) 2-H, 6-H], 4.51 (s, 2 H, ArCH_2), 2.80 (s, 3 H, N-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.5, 134.9, 133.8, 131.9, 129.4, 129.1, 126.1 (q, $^3J_{C-F}$ = 4 Hz), 123.9, 62.7 (verified through HMBC), 52.1, 36.1 (2 signals missing).

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{13}ClF_3N_3ONa$: 390.0591; found: 390.0586.

2-Diazo-*N*,*N*-diethyl-2-[4-(trifluoromethyl)phenyl]acetamide (9h)

By employing general procedure B1 (2 mmol scale), the reaction of **S9** (2.6 mmol, 366 mg) and 4-trifluoromethyliodobenzene (2 mmol, 294 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the aryl diazo acetamide **9h** as a bright orange oil (264 mg, 47%).

R_f = 0.45 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 3083, 2111, 1644, 1204 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.4 Hz, 2 H, Ar 3-H, 5-H), 7.24 (d, J = 8.4 Hz, 2 H, Ar 2-H, 6-H), 3.34 (q, J = 7.1 Hz, 4 H, Et 1-H), 1.13 (t, J = 7.1 Hz, 6 H, Et 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6, 132.4, 127.6 (q, $^2J_{C-F}$ = 29 Hz), 125.9 (q, $^3J_{C-F}$ = 4 Hz), 125.5 (q, $^1J_{C-F}$ = 277 Hz), 61.5, 41.9, 13.2 (2 signals missing).

HRMS (ESI): m/z [M + H – N_2]$^+$ calcd for $C_{13}H_{15}F_3NO$: 258.1100; found: 258.1102.

2-Diazo-*N*,*N*-diethyl-2-(4-nitrophenyl)acetamide (9i)

By employing general procedure B1 (2 mmol scale), the reaction of **S9** (2.6 mmol, 366 mg) and 4-nitroiodobenzene (2 mmol, 498 mg) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the aryl diazo acetamide **9i** as a bright orange amorphous solid (277 mg, 53%).

R_f = 0.45 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 3029, 2119, 1659, 1503 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 9.1 Hz, 2 H, Ar 3-H, 5-H), 7.27 (d, J = 9.1 Hz, 2 H, Ar 2-H, 6-H), 3.36 (q, J = 7.1 Hz, 4 H, Et 1-H), 1.16 (t, J = 7.1 Hz, 6 H, Et 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.7, 144.8, 136.3, 124.4, 123.3, 62.2 (verified through HMBC), 42.0, 13.2.

HRMS (ESI): m/z [M + H – N_2]$^+$ calcd for $C_{12}H_{15}N_2O_3$: 235.1077; found: 235.1074.

***N*-[2-(4-Chlorophenyl)ethyl]-2-diazo-*N*-methyl-2-[4-(trifluoromethyl)phenyl]acetamide (9j)**

By employing general procedure B1 (4 mmol scale), the reaction of **S10** (5.2 mmol, 1.23 g) and 4-trifluoromethyliodobenzene (4 mmol, 589 µL) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the aryl diazo acetamide **9j** as a bright orange oil (769 mg, 50%).

R_f = 0.52 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 3087, 2113, 1652, 1199 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 [d, J = 8.3 Hz, 2 H, Ar(F) 3-H, 5-H], 7.20 [d, J = 8.3 Hz, 2 H, Ar(F) 2-H, 6-H], 7.09 [d, J = 8.1 Hz, 2 H, Ar(Cl) 3-H, 5-H], 7.06 [d, J = 8.1 Hz, 2 H, Ar(Cl) 2-H, 6-H], 3.57 (t, J = 7.3 Hz, 2 H, ArCH_2CH_2), 2.86–2.81 (m, 5 H, ArCH_2CH_2 and N-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.4, 136.7, 132.6, 131.9, 130.1, 128.8, 127.6 (q, $^2J_{C-F}$ = 29 Hz), 125.9 (q, $^3J_{C-F}$ = 3 Hz), 123.8, 62.4 (verified through HMBC), 50.7, 36.6, 33.1.

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{18}H_{16}ClF_3N_3O$: 382.0929; found: 382.0924.

tert-Butyl (1*R*,5*S*)-8-{[4-Cyano-3-(trifluoromethyl)phenyl](diazo)acetyl}-3,8-diazabicyclo[3.2.1]octane-3-carboxylate (10a)

By telescoping general procedures A and B2 (0.25 mmol scale), a crude material was obtained and purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **10a** as a yellow oil (49 mg, 44%).

R_f = 0.10 (Et_2O).

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.91-7.88 (m, 2 H, Ar 5-H, 2-H), 7.69-7.66 (m, 1 H, Ar 6-H), 4.29 (app s, 2 H, 3-H, 6-H), 3.77-3.72 (m, 2 H, 2-H_A, 7-H_A), 3.05-2.85 (m, 2 H, 2-H_B, 7-H_B), 1.83-1.79 (m, 2 H, 4-H_A, 5-H_A), 1.66-1.61 (m, 2 H, 4-H_B, 5-H_B), 1.32 (s, 9 H, *tert*-butyl).

^{13}C NMR (101 MHz, acetone-d_6): δ = 163.3, 156.0, 136.4, 136.2, 127.5, 122.3, 116.4, 105.4, 80.1, 55.4, 27.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{22}F_3N_5O_3Na$: 472.1572; found: 472.1564.

5-Diazo-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (12a)

By employing general procedure C1, to 1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (6.4 mmol, 1.00 g) and *p*-ABSA (9.6 mmol, 2.30 g) in MeCN (0.12 M, 54 mL) was added Et_3N (1.10 mL, 7.68 mmol) dropwise at –10 °C and the resulting mixture was allowed to react at room temperature for 30 min. The crude material was purified by column chromatography eluting with EtOAc–petrol (1:1) to give the diazo compound as a pale yellow amorphous solid (1.025 g, 88%).

R_f = 0.55 (EtOAc–petrol, 1:1).

IR (neat): 2155, 1710, 1638, 1468, 1415, 1372, 1291, 1245, 1066 cm^{-1}.

^{1}H NMR (501 MHz, CD_2Cl_2): δ = 3.27 (s, 6 H, 2 × CH_3).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 158.5, 150.9, 71.9, 28.6.

HRMS (ESI): molecular ion not found.

The spectroscopic data match with the literature.[24]

3-Diazo-2,4-piperidinedione (12b)

By employing general procedure C1, to 2,4-piperidinedione (4.42 mmol, 500 mg) and *p*-ABSA (6.63 mmol, 1.59 g) in MeCN (0.12 M, 37 mL) was added Et_3N (0.73 mL, 5.30 mmol) dropwise at –10 °C and the resulting mixture allowed to react at room temperature for 30 min. The crude material was purified by column chromatography eluting with CH_2Cl_2–MeOH (9:1). The product was further purified by column chromatography eluting with Et_2O to give the diazo compound as a colourless amorphous solid (204 mg, 33%).

R_f = 0.08 (Et_2O).

IR (film): 3183, 3045, 2905, 2150, 1650, 1461, 1416, 1347, 1291, 1039 cm^{-1}.

^{1}H NMR (501 MHz, CD_2Cl_2): δ = 6.96 (s, 1 H, NH), 3.45 (td, *J* = 6.5, 2.8 Hz, 2 H, 6-H), 2.60 (t, *J* = 6.5 Hz, 2 H, 5-H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 188.56, 163.72, 75.41, 37.36, 36.68.

HRMS (ESI): molecular ion not found.

The spectroscopic data match with the literature.[25]

2-Diazoindan-1,3-dione (12c)

By employing general procedure C1, to 1,3-indandione (3.4 mmol, 500 mg) and *p*-ABSA (5.1 mmol, 1.22 g) in MeCN (0.12 M, 30 mL) was added Et_3N (0.57 mL, 4.08 mmol) dropwise at –10 °C and the resulting mixture was allowed to react at room temperature for 1 h. The crude material was purified by column chromatography eluting with CH_2Cl_2 to give the diazo compound as a yellow amorphous solid (446 mg, 76%).

R_f = 0.40 (CH_2Cl_2).

IR (neat): 2119, 1688, 1594, 1350, 1329, 1265, 1188, 738, 709 cm^{-1}.

^{1}H NMR (501 MHz, CD_2Cl_2): δ = 7.84–7.79 (m, 2 H, 4-H, 7-H), 7.78–7.74 (m, 2 H, 5-H, 6-H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 182.39, 137.57, 135.17, 122.88, 70.39.

HRMS (ESI): molecular ion not found.

The spectroscopic data match with the literature.[26]

5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (12d)

By employing general procedure C1, to 2,2-dimethyl-1,3-dioxane-4,6-dione (3.5 mmol, 500 mg) and *p*-ABSA (5.25 mmol, 1.26 g) in MeCN (0.12 M, 30 mL) was added Et_3N (4.20 mmol, 0.58 mL) dropwise at –10 °C and the resulting mixture was allowed to react at room temperature for 30 min. The crude material was purified by column chromatography eluting with CH_2Cl_2 to give the diazo compound as a colourless amorphous solid (541 mg, 91%).

R_f = 0.38 (CH_2Cl_2).

IR (neat): 2175, 1706, 1308, 1296, 1191, 1165, 1026, 977, 905 cm^{-1}.

^{1}H NMR (501 MHz, CD_2Cl_2): δ = 1.76 (s, 6 H, 2 × CH_3).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 158.65, 107.40, 64.39, 26.95.

HRMS (ESI): molecular ion not found.

The spectroscopic data match with the literature.[27]

***N*-(3-Chloro-4-methoxyphenyl)-2-diazo-N-methyl-3-oxobutanamide (13a)**

By employing general procedure C2, 3-chloro-4-methoxy-*N*-methylaniline (3.5 mmol, 600 mg) in toluene (1.4 M, 2.5 mL) and 2,2,6-trimethyl-1,3-dioxin-4-one (3.85 mmol, 510 μL) were reacted under microwave irradiation at 110 °C for 1.5 h. The crude material was purified by column chromatography eluting with CH_2Cl_2–MeOH (98:2) to give the butanamide (840 mg, 94%). By employing general procedure C3, to the butanamide (840 mg, 3.28 mmol) and *p*-ABSA (1.20 g, 4.92 mmol) in MeCN (0.12 M, 28 mL) was added Et_3N (0.55 mL, 3.94 mmol) to give a crude material. Purification by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) gave the diazo compound as a light yellow, low melting solid (412 mg, 45%).

R_f = 0.43 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 3360, 2110, 1642, 1499, 1361, 1265, 1247, 1062, 1020 cm^{-1}.

^{1}H NMR (501 MHz, CD_2Cl_2): δ = 7.27 (d, *J* = 2.6 Hz, 1 H, Ar 2-H), 7.12 (dd, *J* = 8.7, 2.6 Hz, 1 H, Ar 6-H), 6.97 (d, *J* = 8.7 Hz, 1 H, Ar 5-H), 3.91 (s, 3 H, CH_3O), 3.29 (s, 3 H, N-CH_3), 2.44 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 191.6, 161.1, 155.1, 136.5, 128.7, 126.6, 123.7, 113.2, 74.0, 56.8, 38.7, 28.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{12}ClN_3ONa$: 304.0460; found: 304.0456.

***N*-(4-Chlorophenyl)-2-diazo-*N*-methyl-3-oxobutanamide (13b)**

By employing general procedure C2, 4-chloro-*N*-methylaniline (8.3 mmol, 1.00 mL) in toluene (8 mL) and 2,2,6-trimethyl-1,3-dioxin-4-one (12.5 mmol, 1.66 mL) were reacted under microwave irradiation at 110 °C for 30 min. The crude material was then treated with *p*-ABSA (9.1 mmol, 2.20 g) and Et_3N (1.30 mL, 9.1 mmol) and the reaction allowed to warm to room temperature over 16 hours. A white

precipitate formed, which was removed by filtration, and the solvent then removed under reduced pressure to give a dark red oil. Purification by column chromatography eluting with CH_2Cl_2 and then CH_2Cl_2–Et_2O (9:1) gave the diazo compound **13b** as a yellow oil that solidified on standing (1.34 g, 64%).

R_f = 0.10 (CH_2Cl_2).

IR (CH_2Cl_2): 2184 (diazo), 1636, 1590, 1487, 1356 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.7 Hz, 2 H, Ar 3-H, 5-H), 7.14 (d, *J* = 8.7 Hz, 2 H, Ar 2-H, 6-H), 3.34 (s, 3 H, *N*-methyl), 2.46 (s, 3 H, oxobutanamide 4-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 161.1, 157.1, 141.7, 133.9, 130.6, 127.5, 38.6, 28.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{10}ClN_3O_2Na$: 274.0359; found: 274.0350.

1-(6-Chloro-3,4-dihydro-2*H*-quinolin-1-yl)-2-diazobutane-1,3-dione (13c)

By employing general procedure C2, to 6-chloro-1,2,3,4-tetrahydroquinoline (3.0 mmol, 500 mg) in toluene (1 M, 3.00 mL) was added 2,2,6-trimethyl-1,3-dioxin-4-one (3.3 mmol, 440 µL) and the resulting solution was reacted under microwave irradiation at 110 °C for 1.5 h. The crude product was purified by silica gel column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to give the butanamide (744 mg, 99%). By employing general procedure C3, to the butanamide (0.70 g, 2.78 mmol) and *p*-ABSA (1.00 g, 4.17 mmol) in MeCN (0.12 M, 23 mL) was added Et_3N (0.46 mL, 3.34 mmol). After 4 h, the crude material was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to give the diazo compound as a light yellow, low melting solid (439 mg, 57%).

R_f = 0.43 (CH_2Cl_2–Et_2O, 9:1).

IR (film): 2950, 2891, 2107, 1632, 1484, 1345, 1255, 1197, 1170, 1090, 946 cm^{-1}.

^1H NMR (501 MHz, methanol-d_4): δ = 7.32 (d, *J* = 8.6 Hz, 1 H, qui 5-H), 7.25 (d, *J* = 2.5 Hz, 1 H, qui 8-H), 7.17 (dd, *J* = 8.6, 2.5 Hz, 1 H, qui 7-H), 3.75 (t, *J* = 6.5 Hz, 2 H, qui 2-H), 2.74 (t, *J* = 6.5 Hz, 2 H, qui 4-H), 2.32 (s, 3 H, CH_3), 1.98 (quin, *J* = 6.5 Hz, 2 H, qui 3-H); qui = quinolinyl.

^{13}C NMR (126 MHz, methanol-d_4): δ = 191.1, 162.5, 138.4, 135.8, 131.7, 129.7, 127.9, 124.9, 77.4, 45.9, 27.6, 27.4, 24.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{12}ClN_3O_2Na$: 300.0511; found: 300.0508.

2-Diazo-1-[(2*R*,6*S*)-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridin-1-yl]butane-1,3-dione (13d)

By employing general procedure C2 and (2*R*,6*S*)-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridine (996 mg, 5 mmol), the diazo transfer was performed for 24 h followed by purification by column chromatography eluting with CH_2Cl_2 to give the diazo compound **13d** as a yellow oil (0.339 g, 22%).

R_f = 0.14 (CH_2Cl_2).

IR (film): 3033, 2114, 1697, 1655, 1611, 1493, 1449 cm^{-1}.

^1H NMR (501 MHz, acetone-d_6): δ = 7.33 (d, *J* = 7.9 Hz, 2 H, Ph 2-H, 6-H), 7.27 (app t, *J* = 7.9 Hz, 2 H, Ph 3-H, 5-H), 7.17 (app t, *J* = 7.9 Hz, 1 H, Ph 4-H), 5.87 (ddt, *J* = 17.1, 10.1, 7.4 Hz, 1 H, allyl 2-H), 5.76 (dd, *J* = 10.0, 2.3 Hz, 1 H, py 5-H), 5.69 (dt, *J* = 10.0, 3.0 Hz, 1 H, py 4-H), 5.21 (d, *J* = 2.3 Hz, 1 H, py 6-H), 5.14 (d, *J* = 17.1 Hz, 1 H, allyl 3-H_{trans}), 5.09 (dd, *J* = 10.1, 2.0 Hz, 1 H, allyl 3-H_{cis}), 4.29–4.28 (m, 1 H, py 2-H), 2.83–2.79 (m, 1 H, allyl 1-H_a), 2.63–2.60 (m, 1 H, py 3-H_a), 2.36–2.33 (m, 1 H, py 3-H_b), 2.24–2.21 (m, 1 H, allyl 1-H_b), 2.21 (s, 3 H, butane 4-H); py = pyridinyl.

^{13}C NMR (75 MHz, acetone-d_6): δ = 189.0, 164.0, 144.0, 136.4, 130.2, 129.2, 127.5, 127.5, 121.4, 118.5, 76.1, 58.3, 54.8, 38.8, 29.4, 27.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{19}N_3O_2Na$: 332.1370; found: 332.1369.

2-Diazo-1-{3-oxo-2-azabicyclo[2.2.1]hept-5-en-2-yl}butane-1,3-dione (13e)

By employing general procedure C2 and 2-azabicyclo[2,2,1]hept-5-en-3-one (500 mg, 4.6 mmol), the diazo transfer was performed for 24 h, followed by purification by column chromatography eluting with petrol–EtOAc (7:3) to give the diazo compound **13e** as a yellow oil (0.29 g, 29%).

R_f = 0.27 (petrol–EtOAc, 7:3).

IR (film): 2955, 2139, 1745, 1651, 1302 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.91 (dd, *J* = 5.2, 2.3 Hz, 1 H, 5-H), 6.48 (dd, *J* = 5.2, 3.3 Hz, 1 H, 6-H), 4.83–4.82 (m, 1 H, 4-H), 3.39–3.38 (m, 1 H, 1-H), 2.30 (s, 3 H, CH_3), 2.21 (dt, *J* = 8.8, 1.4 Hz, 1 H, 7-H_a), 2.11 (dt, *J* = 8.8, 1.3 Hz, 1 H, 7-H_b).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 189.8, 175.6, 160.3, 140.6, 136.1, 62.2, 53.7, 53.0, 28.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_9N_3O_3Na$: 242.0538; found: 242.0535.

2-Diazo-1-(4-isopropyl-2-oxopyrrolidin-1-yl)butane-1,3-dione (13f)

By employing general procedure C2 and 4-isopropylpyrrolidin-2-one (500 mg, 3.93 mmol), the diazo transfer was performed for 24 h followed by purification by column chromatography eluting with CH_2Cl_2–MeOH (99:1) to give the diazo compound **13f** as a yellow amorphous solid (0.376 g, 40%).

R_f = 0.24 (CH_2Cl_2–MeOH, 99:1).

IR (film): 2962, 2133, 1732, 1650, 1316, 1204 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 3.89 (dd, *J* = 10.8, 7.8 Hz, 1 H, pyr 5-H_a), 3.51 (dd, *J* = 10.8, 9.2 Hz, 1 H, pyr 5-H_b), 2.64 (dd, *J* = 17.4, 8.3 Hz, 1 H, pyr 3-H_a), 2.42 (dd, *J* = 17.4, 8.3 Hz, 1 H, pyr 3-H_b), 2.39 (s, 3 H, butane 4-H), 2.14 (td, *J* = 17.4, 8.3 Hz, 1 H, pyr 4-H), 1.68–1.64 (m, 1 H, iPr H), 0.96 (d, *J* = 6.7 Hz, 6 H, iPr H); pyr = pyrrolidinyl, iPr = isopropyl.

^{13}C NMR (101 MHz, acetone-d_6): δ = 190.2, 174.5, 160.6, 79.2, 51.0, 38.8, 38.1, 32.6, 28.6, 20.7, 20.3.

HRMS (ESI): *m*/*z* [M – N_2 + Na]$^+$ calcd for $C_{11}H_{15}NO_3Na$: 232.0944; found: 232.0942.

2-Diazo-1-[(4*S*)-2-oxo-4-phenyl-1,3-oxazolidin-3-yl]butane-1,3-dione (13g)

By employing general procedure C2 and (4*S*)-4-phenyl-1,3-oxazolidin-2-one (1.5 g, 9.2 mmol), the diazo transfer was performed for 24 h followed by purification by column chromatography eluting with CH_2Cl_2 to give the diazo compound **13g** as a white amorphous solid (1.280 g, 53%).

R_f = 0.17 (CH_2Cl_2).

IR (film): 3058, 2136, 1775, 1656, 1308, 1207 cm^{-1}.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.44–7.38 (m, 5 H, Ph 2-H, 3-H, 4-H, 5-H, 6-H), 5.59 (t, *J* = 8.8 Hz, 1 H, ox 4-H), 4.77 (app t, *J* = 8.8 Hz, 1 H, ox 5-H_a), 4.25 (app t, *J* = 8.8 Hz, 1 H, ox 5-H_b), 2.37 (s, 3 H, butane 4-H); ox = oxazolidinyl.

^{13}C NMR (101 MHz, CD_2Cl_2): δ = 189.7, 160.0, 153.6, 137.3, 129.6, 129.5, 127.1, 80.0, 70.8, 59.2, 28.8.

HRMS (ESI): *m*/*z* [M – N_2 + Na]$^+$ calcd for $C_{13}H_{11}NO_4Na$: 268.0580; found: 268.0577.

2-Diazo-2-(3,4-dichlorophenyl)-*N*-methyl-*N*-phenylacetamide (9k)

By employing general procedure C3 (1 mmol scale), the reaction of 2-(3,4-dichlorophenyl)-*N*-methyl-*N*-phenylacetamide (293 mg, 1 mmol) and *p*-ABSA (264 mg, 1.1 mmol) gave a crude material that was purified by column chromatography eluting with CH_2Cl_2–Et_2O (9:1) to yield the diazo acetamide **9k** as an orange oil (252 mg, 53%).

R_f = 0.67 (pentane–Et_2O, 1:1).

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.63 (d, *J* = 2.3 Hz, 1 H, Ar 2-H), 7.48 (d, *J* = 8.5 Hz, 1 H, Ar 5-H), 7.44–7.39 (m, 2 H, Ph 3-H, 5-H), 7.35–7.33 (m, 2 H, Ph 2-H, 6-H), 7.30-7.26 (m, 1 H, Ph 4-H), 7.18 (dd, *J* = 8.5, 2.3 Hz, 1 H, Ar 6-H), 3.38 (s, 3 H, NMe).

^{13}C NMR (101 MHz, acetone-d_6): δ = 164.2, 145.0, 132.9, 131.4, 130.8, 130.1, 128.9, 127.7, 127.0, 126.6, 124.6, 112.7, 38.7.

HRMS (ESI): *m*/*z* [M – N_2 + H]$^+$ calcd for $C_{15}H_{12}Cl_2NO$: 292.0296; found: 292.0277.

N,2-Bis(4-chlorophenyl)-2-diazo-*N*-methylacetamide (9l)

By employing general procedure C3, the reaction of *N*,2-bis(4-chlorophenyl)-*N*-methylacetamide (300 mg, 1.0 mmol) and *p*-ABSA (269 mg, 1.1 mmol) gave a viscous orange oil that was purified by flash column chromatography eluting with pentane–Et_2O (9:1) to give the diazo compound **9l** as an orange oil (114 mg, 35%).

R_f = 0.14 (pentane/Et_2O, 1:1).

IR (CH_2Cl_2): 2066 (diazo), 1635, 1490, 1313 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.42–7.30 (m, 8 H, Ar), 3.36 (s, 3 H, *N*-methylacetamide).

^{13}C NMR (101 MHz, acetone-d_6): δ = 164.9, 144.2, 132.7, 131.7, 130.8, 130.0, 129.7, 128.3, 127.7, 127.2, 38.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{11}Cl_2N_3O$: 342.0177; found: 342.0165.

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