

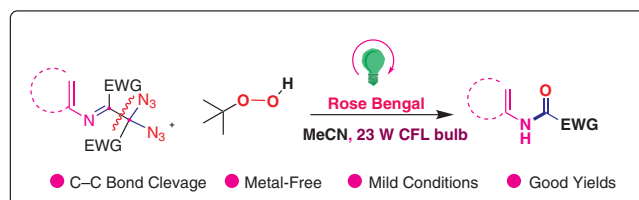
Visible-Light-Mediated Photocatalytic Oxidative C–C Bond Cleavage of Geminal Diazides: An Approach to Oxamates

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Dedicated to all covid-19 warriors



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Abstract Photoredox catalysis has received great attention in both academia and industry and remarkable progress has been made over the past decade. Now, it has been shown that a visible-light-mediated oxidative C–C bond cleavage of geminal diazides can be induced by organic dye catalysis for the synthesis of oxamates. A mechanistic study, confirmed by control experiments, indicates that this proceeds through single-electron transfer (SET). This methodology can be applied to convert a wide array of geminal diazides into oxamates.

Key words photoredox, oxamates, C–C cleavage

Visible-light photoredox catalysis is a fast-growing research area in recent decades.¹ However, despite the mildness of conditions, the photocatalysts are usually expensive and so organic dyes present an alternative for sustainable photoredox catalysis. Rose bengal is a versatile and inexpensive organic dye, attractive for use in photoredox catalysis,² and the use of organic dyes as photocatalysts in organic synthesis has emerged.³ However, transformations involving C–C bond cleavage remain challenging owing to the high C–C bond-dissociation energy.⁴ Despite the stoichiometric reactions of C–C triple-bond cleavage that have been studied thoroughly,⁵ catalytic reactions have been rarely achieved except for the metathesis of alkynes. Regardless of the progress in C–C bond cleavages, successful examples are still limited and employ expensive catalysts such as rhodium, ruthenium, and palladium.⁶ Therefore, is a demand for

exploring new types of C–C bond transformations using organic dyes as catalysts.⁷

Numerous scientific endeavours have been focusing on target methodologies.⁸ Among oxidative C–C bond-cleavage procedures with common active oxidants such as hypervalent iodine reagents, organic peroxides are extensively used. Recently, Chen et al. reported metal-free C–C bond cleavage of α -azido ketones leading to the synthesis of α -keto-thioamides and amides.⁹

Recently, a renaissance in photoredox methodology in organic synthesis transformations has been experienced.^{10,11} For instance, oxidative C–C bond cleavage of aldehydes via visible-light photoredox catalysis was reported by Xia et al. However, the need for intense sources of visible light imposes restrictions on the scalability of such photochemical reactions and selectivity remains difficult.¹² Hence, exploration to accomplish C–C bond cleavage of geminal diazides under mild reaction is attractive.

Rose bengal is an organic dye, much employed due to its ability to enable electron-transfer processes in visible-light-mediated photochemical synthetic applications in the formation and cleavage of C–C and C–X bonds.¹³ The application of organic dyes to visible-light-induced synthetic transformations is an active field in organic chemistry.¹⁴ Inspired by previous reports,^{15,16} herein, we report a metal-free synthesis of oxamates via oxidative cleavage of geminal diazides in the presence of Rose Bengal and TBHP in decane.

Our initial attempts were directed towards visible-light-mediated C–C bond cleavage of geminal diazide **1a** as a model substrate in the presence 4 equiv of aqueous tertiary butyl hydroperoxide (aq TBHP) as the oxidizing agent and 3 mol% Rose Bengal in DMF. The reaction was carried out at room temperature under irradiation with a standard 23 W bulb to afford the desired ethyl 2-oxo-2-(phenylamino) ace-

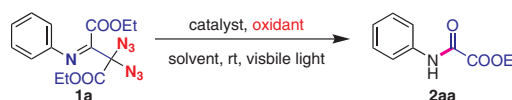
tate (**2aa**) with 31% yield (Table 1, entry 1) and, in the presence of H₂O₂ as the oxidizing agent in MeCN, the yield improved to 58% (Table 1, entry 2). We screened other oxidants (Table 1, entries 3–6) and this resulted in TBHP in decane was found to be a potential oxidant system (84%, Table 1, entry 4). Subsequently, we screened a range of organic dyes and photocatalysts such as Eosin-Y, riboflavin, rhodamine B, Ru(bpy)₃Cl₂, azure-B, and methylene blue. Among these, Ru(bpy)₃Cl₂ and Rose Bengal were found to be the most efficient catalysts for C–C bond cleavage (Table 1, entries 4 and 10). Next, the reactions with different amounts of Rose Bengal catalyst were screened (Table 1, entries 12–14), and 0.03 equiv was found to be optimum, furnishing oxamate **2aa** in 83% yield with 0.03 equiv of Rose Bengal, 4 equiv of TBHP in decane using a 23 W CFL bulb as light source in MeCN solvent (Table 1, entry 12). The reaction did not proceed in the absence of photocatalyst or visible light, indicating that both components are crucial for this reaction (entries 15, 16). Furthermore, we performed the reaction under sunlight instead of using a 23 W bulb and this gave a 21% of yield (entry 17). We performed the reaction with 11 W and 34 W irradiation, but this did not improve the yield (entries 18, 19). Use of bases such as DIPEA and Cs₂CO₃ was also not advantageous (entries 20, 21). Among solvents examined in (entries 22–25), MeCN showed that is the most suitable solvent (entry 12) for these conditions.

After optimization of the reaction conditions, we investigated the substrate scope of geminal diazides **1** (Scheme 1). Those with aromatic rings possessing electron-donating groups provided their corresponding oxamate derivatives **2aa**, **2ba**, **2ca**, **2da**, and **2ab** in good yields. Those with electron-withdrawing groups such as halogen and nitro substituents reacted well, providing the corresponding products **2ae**, **2af**, **2ag**, **2ah**, **2ia**, **2bb**, **2cb**, **2ja**, and **2db** in moderate to good yields. Unfortunately, aliphatic amine-substituted geminal diazides were found to afford the corresponding oxamates in very low yields (**2af**, **2ag**, and **2ah**). With a substituent at the β-position of the α,α-diazo β-iminoester under the optimized conditions, this failed to furnish the desired products **2ac**, **2ad**, and **2ae**.

To gain insight into a possible mechanism of C–C bond cleavage, we performed several control experiments (Scheme 2). We knew from the optimization studies (Table 1, entries 15, 16) that reaction did not occur in the absence of light and the desired product was not observed in the absence of TBHP in decane (Scheme 2). In addition, the standard reaction was performed in the presence of TEMPO (2.0 equiv). In this case, we did not detect any radical intermediates.

On the basis of the above results, observations and literature reports,^{17–19} a plausible mechanism can be proposed for the C–C bond cleavage of α,α-diazo β-iminoesters to ox-

Table 1 Optimization of Reaction Conditions^a



Entry	Catalyst	Oxidant	Solvent	Yield (%) ^b
1	Rose Bengal	aq TBHP	DMF	31
2	Rose Bengal	H ₂ O ₂	MeCN	58
3	Rose Bengal	O ₂ balloon	MeCN	49
4	Rose Bengal	TBHP in decane	MeCN	84
5	Rose Bengal	DTBP	MeCN	trace
6	Rose Bengal	TBP	MeCN	16
7	Eosin Y	TBHP in decane	MeCN	46
8	riboflavin	TBHP in decane	MeCN	38
9	rhodamine	TBHP in decane	MeCN	41
10	Ru(bpy) ₃ Cl ₂	TBHP in decane	MeCN	71
11	methylene blue	TBHP in decane	MeCN	68
12	Rose Bengal	TBHP in decane	MeCN	83
13	Rose Bengal	TBHP in decane	MeCN	70
14	azure-B	TBHP in decane	MeCN	66
15	–	TBHP in decane	MeCN	nd
16	Rose Bengal	TBHP in decane	MeCN	trace ^c
17	Rose Bengal	TBHP in decane	MeCN	21 ^d
18	Rose Bengal	TBHP in decane	MeCN	68 ^e
19	Rose Bengal	TBHP in decane	MeCN	76 ^f
20	Rose Bengal	TBHP in decane	MeCN	84 ^g
21	Rose Bengal	TBHP in decane	MeCN	83 ^h
22	Rose Bengal	TBHP in decane	DCE	71
23	Rose Bengal	TBHP in decane	DMSO	17
24	Rose Bengal	TBHP in decane	DCM	39
25	Rose Bengal	TBHP in decane	PhMe	46

^a Reaction conditions: **1a** (1 mmol), solvent (2 mL), room temperature, 23 W visible-light bulb, for 24–48 h.

^b Isolated yields.

^c Reaction performed in the dark.

^d Reaction carried out under sunlight.

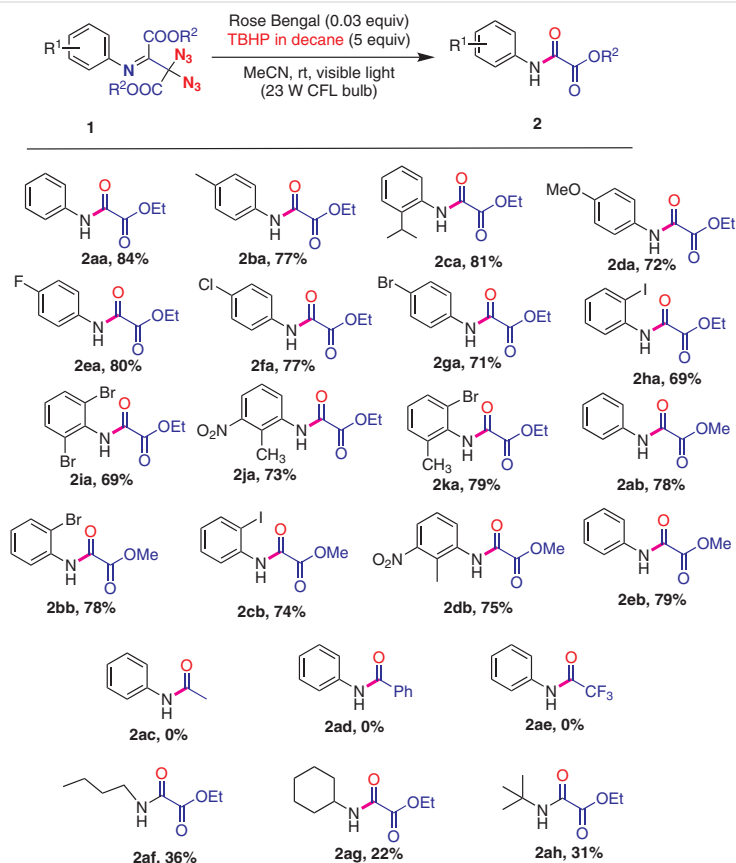
^e Reaction carried out under 11 W visible-light bulb.

^f Reaction carried out under 34 W visible-light bulb.

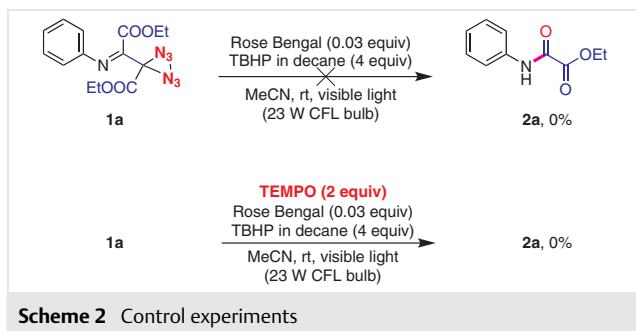
^g DIPEA (1.0 equiv).

^h Cs₂CO₃ (1.0 equiv).

amates via visible-light photoredox catalysis as illustrated in Scheme 3. The photoexcited state Rose Bengal (RB*) can undergo oxidative quenching by the geminal diazide intermediate **1a**, resulting in (RB^{•-}) and radical cation **II**. The Rose Bengal radical anion, upon transfer of an electron to *t*-BuOOH, provides the tertiary butoxide radical and a hydroxide anion and completes the photoredox cycle by regeneration of Rose Bengal. On the other hand, radical cation **II** can undergo further fragmentation giving nitrilium ion

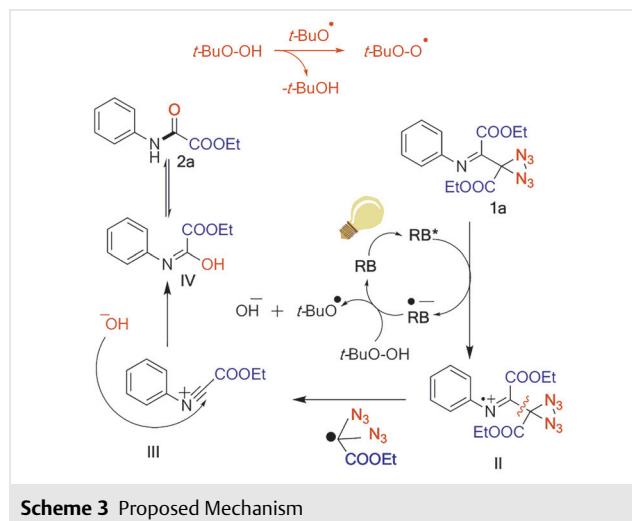


Scheme 1 Substrate scope with respect to geminal diazides. *Reagents and conditions:* **1a** (1.0 mmol), Rose Bengal (3 mol%), TBHP in decane (4.0 equiv), MeCN (1.5 mL), 23 W CFL lightbulb, rt, for 24–48 h. Isolated yields after silica gel column chromatography.



intermediate **III**. This intermediate can react with OH^- to form oxygenated intermediate **IV**, which would further undergo keto–enol tautomerism to give the desired product **2a**.

In conclusion, a straightforward strategy for generating oxamates by the C–C bond cleavage of geminal diazides has been developed. The important features of this procedure are mild conditions, high yields, operational simplicity, and atom economy.



General Procedure (GP-I) for the Synthesis of Oxamate Derivatives (2aa–ah)

In a screw-capped vial (Fischer Disposable Borosilicate Glass Tube, tube volume 25 mL), containing **1** (**1aa–ah**, 1.0 mmol) and Rose Bengal (0.03 equiv), followed by addition of TBHP in decane (4.0 equiv), MeCN (1.5 mL) was added slowly, and the reaction mixture was stirred under visible light (23 W CFL bulb). The progress of the reaction was monitored by TLC until completion (24–48 h). After completion of reaction, the reaction mixture was concentrated *in vacuo* and purified by column chromatography (silica gel; petroleum ether/ethyl acetate = 9.4:0.6) as eluents to yield the desired oxamates **2aa–ah**.

General Procedure (GP-II) for the Synthesis of Geminal Diazides¹⁸

Compounds **1aa–ah** were prepared according to our recently developed method.¹⁸ The amine (1 mmol) was taken in a dried 10 mL round-bottom flask, and the alkyne (1 mmol) was added slowly in DCE (0.5 mL), and the reaction mixture was stirred (if required) at room temperature for 10 min to 3 h. After the formation of the hydroamination product (confirmed by TLC), DCE (0.25 M, based on hypervalent iodine), tetrabutylammonium bromide (TBAB, 2 mmol) and NaN₃ (4 mmol) were added, followed by addition of phenyl iodo(III)diacetate (PIDA, 3 mmol) portion-wise over 30 min. The progress of the reaction was monitored by TLC until the reaction was complete (4–14 h). The reaction mixture was quenched by addition of saturated aqueous NaHCO₃, extracted with ethyl acetate, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified through a silica gel column using petroleum ether/ethyl acetate (9.8:0.2) as eluent.

Ethyl 2-Oxo-2-(phenylamino) Acetate (2aa)

Yield 81 mg (84%); white solid; mp 72–73 °C.

IR (MIR-ATR, 4000–600 cm⁻¹): ν_{\max} = 3310.26, 2924.82, 1690.15, 1599.09, 1535.45, 1495.52, 1444.16, 1279.76, 1172.21, 1158.45, 1013.90, 754.28, 692.46.

¹H NMR (CDCl₃, 400 MHz): δ = 8.93 (br s, 1 H), 7.69–7.55 (m, 2 H), 7.41–7.32 (m, 2 H), 7.26–7.12 (m, 1 H), 4.48–4.37 (m, 2 H), 1.42 (t, J = 7.3 Hz, 3 H).

¹³C NMR (CDCl₃, 100 MHz): 161.0, 136.4, 129.2, 125.5, 119.9, 77.4, 77.1, 76.7, 63.7, 14.0.

HRMS (ESI+): m/z calcd for C₁₀H₁₀NaN₂O₅ [M + Na]⁺: 261.0825; found: 261.0482.

Ethyl 2-Oxo-2-(*p*-tolylamino) Acetate (2ba)

Yield 61 mg (77%); white solid; mp 69–71 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.85 (br s, 1 H), 7.52 (d, J = 8.3 Hz, 2 H), 7.17 (d, J = 8.3 Hz, 3 H), 4.41 (d, J = 7.3 Hz, 2 H), 2.33 (s, 4 H), 1.42 (t, J = 7.1 Hz, 4 H).

¹³C NMR (CDCl₃, 100 MHz): 161.1, 153.8, 135.3, 133.8, 129.7, 119.8, 77.4, 77.1, 76.7, 63.7, 21.0, 14.0.

Ethyl 2-[(2-Isopropylphenyl)amino]-2-oxoacetate (2ca)

Yield 70 mg (81%); white solid; mp 111–113 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.95 (br s, 1 H), 7.95 (dd, J = 1.7, 7.6 Hz, 1 H), 7.35–7.15 (m, 3 H), 4.44 (q, J = 7.3 Hz, 2 H), 3.12–2.96 (m, 1 H), 1.45 (t, J = 7.3 Hz, 3 H), 1.31–1.23 (m, 6 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.3, 154.2, 139.4, 132.8, 126.7, 126.5, 125.8, 122.8, 77.4, 77.0, 76.7, 63.8, 28.1, 22.9, 14.0.

Ethyl 2-[(4-Methoxyphenyl)amino]-2-oxoacetate (2da)

Yield 61 mg (72%); white solid; mp 112–113 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.81 (br s, 1 H), 7.62–7.50 (m, 2 H), 7.01–6.85 (m, 2 H), 4.41 (q, J = 6.8 Hz, 2 H), 3.84–3.77 (m, 3 H), 1.43 (t, J = 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.2, 157.2, 153.7, 129.5, 121.4, 114.4, 63.7, 55.5, 14.0.

Ethyl 2-[(2-Fluorophenyl)amino]-2-oxoacetate (2ea)

Yield 79 mg (80%); brown solid; mp 93–95 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 9.10 (br s, 1 H), 8.44–8.29 (m, 1 H), 7.23–7.09 (m, 3 H), 3.99 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.9, 153.6, 151.4, 125.9, 125.9, 124.8, 124.8, 121.5, 115.2, 115.0, 77.3, 77.0, 76.7, 54.1.

Ethyl 2-[(4-Chlorophenyl)amino]-2-oxoacetate (2fa)

Yield 64 mg (77%); brown solid; mp 146–148 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 9.11 (br s, 1 H), 8.36 (s, 1 H), 7.19–7.10 (m, 3 H), 4.46–4.41 (m, 2 H), 1.43 (t, J = 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.4, 153.9, 151.4, 125.8, 125.7, 124.8, 124.8, 121.4, 115.2, 115.0, 77.4, 77.1, 76.7, 63.8, 14.0, 14.0.

Ethyl 2-[(4-Bromophenyl)amino]-2-oxoacetate (2ga)

Yield 66 mg (71%); yellow solid; mp 135–137 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.91 (br s, 1 H), 7.64–7.45 (m, 4 H), 4.48–4.31 (m, 2 H), 1.43 (tt, J = 1.5, 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.7, 153.9, 137.6, 130.5, 128.6, 122.8, 118.4, 77.4, 77.0, 76.7, 63.9, 14.0.

Ethyl 2-[(2-Iodophenyl)amino]-2-oxoacetate (2ha)

Yield 66 mg (69%); brown solid; mp 123–125 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 9.34 (br s, 1 H), 8.32 (d, J = 6.8 Hz, 1 H), 7.80 (d, J = 6.4 Hz, 1 H), 7.40–7.30 (m, 1 H), 6.93–6.85 (m, 1 H), 4.47–4.35 (m, 3 H), 1.45–1.39 (m, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.5, 154.0, 139.1, 137.0, 129.5, 127.0, 121.3, 89.6, 77.4, 77.1, 76.7, 63.9, 14.0.

Ethyl 2-[(2,6-Dibromophenyl)amino]-2-oxoacetate (2ia)

Yield 48 mg (69%); yellow solid; mp 113–115 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 9.47 (br s, 1 H), 8.62 (br s, 1 H), 7.45–7.37 (m, 1 H), 7.19 (d, J = 8.3 Hz, 1 H), 4.50–4.37 (m, 2 H), 1.44 (t, J = 7.1 Hz, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.2, 153.9, 135.5, 133.4, 129.3, 124.1, 122.2, 112.2, 77.4, 77.0, 76.7, 64.1, 14.0.

Ethyl 2-[(2-Methyl-3-nitrophenyl)amino]-2-oxoacetate (2ja)

Yield 62 mg (73%); yellow solid; mp 111–113 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.97 (br s, 1 H), 8.22 (d, J = 8.3 Hz, 1 H), 7.69 (d, J = 8.3 Hz, 1 H), 7.40 (t, J = 8.1 Hz, 1 H), 4.46 (q, J = 7.3 Hz, 2 H), 2.45 (s, 3 H), 1.45 (t, J = 7.3 Hz, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.7, 154.3, 135.9, 127.2, 126.4, 121.5, 77.3, 77.0, 76.7, 64.2, 14.0, 13.3.

Ethyl 2-[(2-Bromo-6-methylphenyl)amino]-2-oxoacetate (2ka)

Yield 61 mg (79%); yellow liquid.

¹H NMR (CDCl₃, 400 MHz): δ = 9.42 (br s, 1 H), 8.27 (d, *J* = 8.31 Hz, 1 H), 7.33–7.43 (m, 1 H), 7.09–7.18 (m, 1 H), 4.43 (q, *J* = 6.85 Hz, 2 H), 2.31 (s, 3 H), 1.42–1.49 (m, 2 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.5, 153.7, 136.6, 132.8, 132.6, 131.9, 129.2, 129.0, 121.2, 115.8, 113.6, 63.8, 20.7, 20.1, 14.0.

Methyl 2-Oxo-2-(phenylamino)acetate (2ab)

Yield 76 mg (78%); white solid; mp 111–113 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.91 (br s, 1 H), 7.88 (d, *J* = 7.83 Hz, 2 H), 7.40 (t, *J* = 7.82 Hz, 2 H), 7.21–7.18 (m, 1 H), 3.98 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.4, 153.6, 136.2, 129.2, 125.5, 119.9, 54.0.

Methyl 2-[(2-Bromophenyl)amino]-2-oxoacetate (2bb)

Yield 74 mg (78%); white solid; mp 111–112 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 7.61 (dd, *J* = 1.2, 8.1 Hz, 1 H), 7.27 (s, 1 H), 7.06 (d, *J* = 1.5 Hz, 1 H), 6.71 (dd, *J* = 1.5, 7.8 Hz, 1 H), 4.00–3.93 (m, 3 H), 3.62 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 164.7, 160.3, 155.2, 146.4, 133.1, 127.8, 127.1, 118.6, 113.8, 54.4.

Methyl 2-[(2-Iodophenyl)amino]-2-oxoacetate (2cb)

Yield 71 mg (74%); brown solid; mp 116–118 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 7.61 (dd, *J* = 1.2, 8.1 Hz, 1 H), 7.27 (s, 1 H), 7.06 (d, *J* = 1.5 Hz, 1 H), 6.71 (dd, *J* = 1.5, 7.8 Hz, 1 H), 4.00–3.93 (m, 3 H), 3.62 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 164.7, 160.3, 155.2, 146.4, 133.1, 127.8, 127.1, 118.6, 113.8, 54.4.

Methyl 2-[(2-Methyl-3-nitrophenyl)amino]-2-oxoacetate (2db)

Yield 62 mg (75%); yellow solid; mp 126–128 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 8.94 (br s, 1 H), 8.22 (d, *J* = 8.3 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 7.44–7.37 (m, 1 H), 4.02 (s, 3 H), 2.45 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.1, 154.0, 151.2, 135.8, 127.3, 126.5, 124.0, 121.7, 54.4, 13.3.

Methyl 2-[(2-Fluorophenyl)amino]-2-oxoacetate (2eb)

Yield 71 mg (79%); white solid; mp 128–131 °C.

¹H NMR (CDCl₃, 400 MHz): δ = 9.01 (br s, 1 H), 8.39 (t, *J* = 7.58 Hz, 1 H), 7.14–7.17 (m, 3 H), 3.99 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.3, 158.8, 153.6, 132.3, 121.7, 116.1, 54.1.

Ethyl 2-(Butylamino)-2-oxoacetate (2af)

Yield 36 mg (36%); brown liquid.

¹H NMR (CDCl₃, 400 MHz): δ = 7.15 (br s, 1 H), 4.32 (q, *J* = 7.3 Hz, 3 H), 3.33–3.27 (m, 2 H), 1.54–1.43 (m, 2 H), 1.42–1.30 (m, 7 H), 0.93–0.86 (m, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.9, 156.6, 77.4, 77.1, 76.7, 63.1, 39.6, 31.1, 20.0, 14.0, 13.6.

Ethyl 2-(Cyclohexylamino)-2-oxoacetate (2ag)

Yield 20 mg (22%); brown liquid.

¹H NMR (CDCl₃, 400 MHz): δ = 1.16–1.30 (m, 4 H), 1.37–1.41 (m, 3 H), 1.57–1.69 (m, 1 H), 1.74 (dt, *J* = 13.08, 3.73 Hz, 3 H), 1.91–1.97 (m, 2 H), 3.73–3.86 (m, 1 H), 4.35 (q, *J* = 7.34 Hz, 2 H), 7.00 (br s, 1 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 14.0, 24.6, 25.3, 32.6, 48.8, 63.2, 155.6, 161.1.

Ethyl 2-(tert-Butylamino)-2-oxoacetate (2ah)

Yield 28 mg (31%).

¹H NMR (CDCl₃, 400 MHz): δ = 7.26 (br s, 1 H), 4.31 (br s, 3 H), 1.40 (br s, 2 H), 1.26 (s, 4 H), 1.30 (s, 3 H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.3, 155.6, 77.4, 77.1, 76.7, 63.1, 63.1, 51.9, 30.7, 28.2, 28.2, 27.7, 26.4, 14.1, 13.9, 13.8.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0040-1706048>.

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