

Synthesis of Esters by in Situ Formation and Trapping of Diazoalkanes

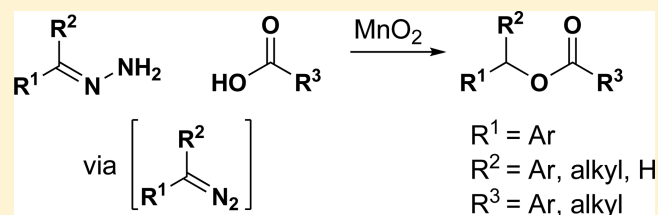
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S Supporting Information

ABSTRACT: A general method has been developed for the in situ formation and trapping of diazoalkanes by carboxylic acids to form esters. The method is applicable to a large variety of carboxylic acids using diazo compounds that are formed from the hydrazones of benzaldehydes and aryl ketones. In situ reaction monitoring with IR spectroscopy (ReactIR) was used to demonstrate that slow addition of the hydrazone to a mixture of oxidant and carboxylic acid avoids the buildup of the diazo compound. This method enables the safe preparation of esters from simple precursors without isolation of diazo compounds.



INTRODUCTION

Diazoalkanes are useful synthetic species that have a broad number of applications due to their ylide reactivity and utility as carbene precursors; however, use of diazoalkanes is hampered by their toxicity and poor thermal stability.^{1,2} Additionally, the difficulty and hazards associated with isolation and storage of diazoalkanes greatly reduces their practicality. Diazoalkanes are typically prepared from a diazo transfer reagent or the base-mediated cleavage of a tosyl hydrazone.³ Diazoalkanes have also been synthesized via the oxidation of their corresponding hydrazones with a variety of transition metals, such as HgO, Ag₂O, CrO₂, Ni₂O₃, KMnO₄-Al₂O₃, MnO₂, and Pb(OAc)₄, as well as organic oxidants, such as TsNIK, TEMPO, and DMSO/oxalyl chloride (Swern conditions).⁴

To bypass the isolation, handling, and/or storage of diazoalkanes, we are interested in developing reactions where these species are consumed at rates that are competitive with their formation in situ. Although MnO₂ has been used for the preparation and isolation of diazo compounds that were used to form esters, there is only one example of doing so in situ so as to avoid handling potentially explosive reagents.⁵ Most reactions of diazoalkanes involve separate steps for the formation and consumption of the species, often in a single pot.⁶ An early example of the formation and simultaneous consumption of a diazoalkane demonstrated that benzophenone hydrazone could be oxidized and used in the esterification of carboxylic acids.⁷ In 2004, Myers and Furrow prepared esters from *N*-TBS hydrazones using (difluoroiodo)benzene and 2-chloropyridine in a one-pot oxidation-esterification sequence.⁸ This transformation was notable in that the formation of azines could be successfully avoided, and the reaction works well for diazoalkanes possessing α -hydrogens that might normally be eliminated. The one liability in the Myers method lies in the use of PhIF₂, which is prepared fresh from concentrated HF.⁹ More

recently, our group reported a one-pot oxidation of hydrazones to diazoalkanes using MnO₂ in the presence of a rhodium(II) catalyst that enables concomitant C–H insertion reactions of the transient carbene.¹⁰ Herein, we present a one-pot synthesis of esters by the rapid capture of diazoalkane compounds formed in situ by the cheap and commercially available oxidant MnO₂. In addition, we use in situ FTIR spectroscopy (ReactIR) to demonstrate that these conditions avoid buildup of the diazoalkane species.

RESULTS AND DISCUSSION

We first attempted to form ester **2** through the oxidation of hydrazone **1** with MnO₂ followed by capture with benzoic acid (Table 1). Benzophenone hydrazone **1** was allowed to stir for 5 min in MnO₂, rapidly oxidizing to the diazo compound, as evident by the formation of a dark pink solution. The carboxylic acid was then added, rapidly consuming the diazoalkane to release a stream of nitrogen bubbles. Our initial result afforded the ester product in 49% yield, which was improved to 72% by using an excess of the hydrazone (Table 1, entries 1–3). Two other polar aprotic solvents, EtOAc and CH₃CN, were also screened, giving no increase in yield (Table 1, entries 4–6). Attempts at reducing the temperature did not cause an increase of yield (Table 1, entry 7), and subzero temperatures reduced the formation of the ester product (Table 1, entries 8 and 9). Lowering the amount of oxidant to 4 equiv also led to a significant reduction in yield (Table 1, entry 10).

Given the beneficial effect of alumina on the esterification reported by Curini,⁷ we explored the use of several mildly basic reagents (Table 1, entries 11–14). Alumina offered no improvement in the reaction (Table 1, entry 11). No product

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Table 1. Optimization Conditions for the Esterification Reaction

entry	hydrazone equiv	solvent	additive	temp (°C)	yield (%)
1	0.83	CH ₂ Cl ₂	none	25	49
2	1.5	CH ₂ Cl ₂	none	25	72
3	1.0	CH ₂ Cl ₂	none	25	68
4	1.2	CH ₂ Cl ₂	none	25	70
5	1.2	CH ₃ CN	none	25	65
6	1.2	EtOAc	none	25	57
7	1.2	CH ₂ Cl ₂	none	0	70
8	1.2	CH ₂ Cl ₂	none	-5	43
9	1.2	CH ₂ Cl ₂	none	-10	42
10 ^a	1.2	CH ₂ Cl ₂	none	25	48
11	1.2	CH ₂ Cl ₂	8 equiv of alumina	25	47
12	1.2	CH ₂ Cl ₂	8 equiv of Na ₂ CO ₃	25	0
13	1.2	CH ₂ Cl ₂	8 equiv of K ₂ HPO ₄	25	28
14	1.2	CH ₂ Cl ₂	8 equiv of KH ₂ PO ₄	25	90
15 ^b	1.2	CH ₂ Cl ₂	8 equiv of KH ₂ PO ₄	25	77

^aWith 4 equiv of MnO₂. ^bHydrazone added dropwise to a solution of acid, buffer, and oxidant.

formation was observed in the presence of Na₂CO₃ (Table 1, entry 12).¹¹ We attribute this result to the deprotonation of the carboxylic acid, which prevents initial protonation of the diazoalkane. The use of less basic reagents was more effective. Addition of K₂HPO₄ enabled the ester product to be formed in 28% yield (Table 1, entry 13), whereas when KH₂PO₄ was employed, an increase in yield to 90% was observed (Table 1, entry 14). Dropwise addition of the hydrazone to the remainder of the reagents was also explored, showing a minor depreciation of yield to 77% (Table 1, entry 15).

Both of the conditions for esterification were applied to a range of carboxylic acids. Benzoic acids containing electron-withdrawing or -donating groups in the para position were found to work well (Table 2, entries 1 and 2). When an additional O–H insertion site was present (Table 2, entry 3), the yield for both procedures dropped significantly. Cinnamic acid and dihydrocinnamic acid worked in high yields (Table 2, entries 4 and 5). Acetic acid and pivalic acid were able to add to convert to their respective esters without KH₂PO₄; however, in the presence of the buffer, the reaction did not proceed (Table 2, entries 6 and 7). *N*-Boc-protected valine and 3-furanoic acid were converted to their corresponding esters in high yields (Table 2, entries 8 and 9).

The substrate scope for different hydrazones was also explored (Table 3). The hydrazones were, in some cases, contaminated with azine that formed during their synthesis. Azine has been known to form from both diazo compounds as well as hydrazone.^{8,12} Benzyl ester formation worked well with both benzyl hydrazone and *p*-methoxy benzyl (PMB) hydrazone (Table 3, entry 2). Upon addition of the carboxylic acid, the reaction evolved N₂ for 30 seconds, indicating that the reaction occurred rapidly. The addition of an electron-withdrawing group caused a decrease in yield (Table 3, entry 3). The more sterically demanding mesityl hydrazone was able

Table 2. Substrate Scope of Acids for the Esterification Reaction

entry	product	R	yield (% method A)	yield (% method B)
1	3a	4-OCH ₃ C ₆ H ₄	84	74
2	3b	4-CNC ₆ H ₄	84	75
3	3c	4-OHC ₆ H ₄	49	30
4	3d	<i>E</i> -C ₆ H ₅ CHCH	85	70
5	3e	C ₆ H ₅ CH ₂ CH ₂	87	68
6	3f	(CH ₃) ₃ C	51 ^a	30 ^a
7	3g	CH ₃	86 ^a	82 ^a
8	3h	<i>N</i> -Boc(Val)	80	28
9	3i	3-furyl	91	73

^aNo KH₂PO₄ was added for these entries.

to react with benzoic acid in high yield but did not work with cyclohexane carboxylic acid (Table 3, entry 4). The esters formed from the hydrazones of α -tetralone, propanoic acid, and acetophenone reacting with benzoic acid were all formed in high yields, showing that the reaction tolerates the presence of α -protons (Table 3, entries 5–7). Cyclohexane carboxylic acid gave poor yield with diphenyl hydrazone; however, it worked well with both benzyl hydrazone and *p*-methoxy benzyl hydrazone (Table 3, entries 8 and 9).

Conducting this reaction on larger scale poses hazards associated with large quantities of the diazo compound. A method that involved the dropwise addition of the hydrazone to the rest of the reagents would provide access to the ester products without buildup of the diazo compound. We investigated whether changing the order of steps could mitigate any buildup of potentially explosive compound. A suspension of the benzoic acid, MnO₂, and K₂HPO₄ in CH₂Cl₂, followed by the dropwise addition of hydrazone, furnished the ester product in 77% yield (Table 1, entry 15).

To prove that we were able to access ester 1 without diazo buildup, we monitored reaction progress with in situ IR spectroscopy (aka ReactIR) using both methods of addition. Although there is at least one case where ReactIR has been used to monitor reactions that employ a diazo-alkane, there are no examples that examine the formation and consumption of these species.¹³ We found that when the hydrazone was added first there was a large diazo peak at 2050 cm⁻¹, and the reaction went to completion in 25 min (Figure 1). Interestingly, when method B was employed, there was no peak corresponding to diazo; however, the reaction took almost 18 h to go to completion, indicating that the rate of diazo formation was slowed (Figure 2).

One final order of addition was investigated by ReactIR. Benzoic acid and benzophenone hydrazone were allowed to stir in solvent and buffer followed by the addition of MnO₂ last (Figure 3). This sequence of addition showed similar initial kinetics as was observed when hydrazone was added last. This indicates that if the hydrazone and acid are allowed to equilibrate, then the oxidation reaction is slow and that dropwise addition of the hydrazone is not necessary to prevent buildup of diphenyldiazomethane. This reaction was conducted

Table 3. Substrate Scope of Hydrazones for the Esterification Reaction

entry	product	R ¹	R ²	R ³	yield (% , method A)	yield (% , method B)
1	5a	C ₆ H ₅	H	C ₆ H ₅	76	80
2	5b	4-OCH ₃ C ₆ H ₄	H	C ₆ H ₅	84	77
3	5c	4-CNC ₆ H ₄	H	C ₆ H ₅	52	45
4	5d	2,4,6-(CH ₃) ₃ C ₆ H ₂	H	C ₆ H ₅	96	92
5	5e	C ₆ H ₅	CH ₂ CH ₂ CH ₃	C ₆ H ₅	99	85
6	5f	C ₆ H ₅	CH ₃	C ₆ H ₅	93	94
7	5g	α -tetralone		C ₆ H ₅	97	84
8	5h	C ₆ H ₅	H	<i>c</i> -C ₆ H ₁₁	95	80
9	5i	4-OCHC ₆ H ₄	H	<i>c</i> -C ₆ H ₁₁	68	21

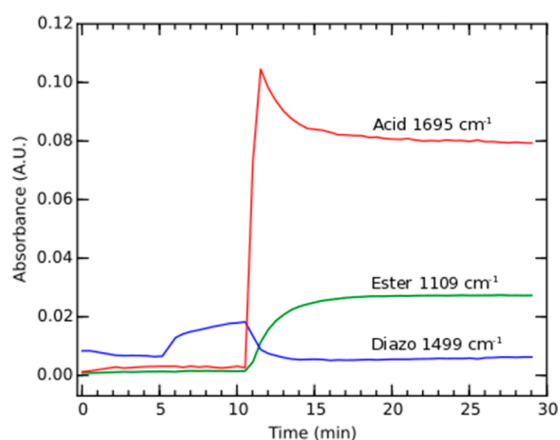


Figure 1. ReactIR data for the “acid last” esterification conditions (Table 1) showing buildup of diphenyldiazomethane (blue), consumption of benzoic acid (red), and appearance of diphenylmethyl benzoate (2, green). Note: the acid carbonyl stretch does not return to baseline because of interference from the ester stretch that appears.

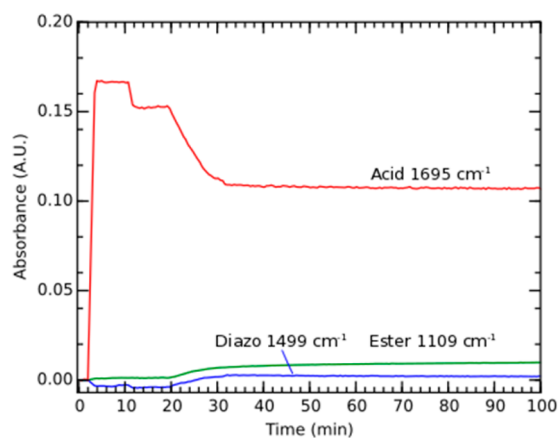


Figure 2. ReactIR data for the “hydrazone last” esterification conditions (Table 1) showing consumption of benzoic acid (red) and appearance of diphenylmethyl benzoate (2, green). Note: MnO₂ was added at 10 min. The benzophenone hydrazone was added starting at 19 min, dropwise, for 10 min.

on preparatory scale (eqs 1 and 2), and yields similar to those of the other two sets of conditions were observed.

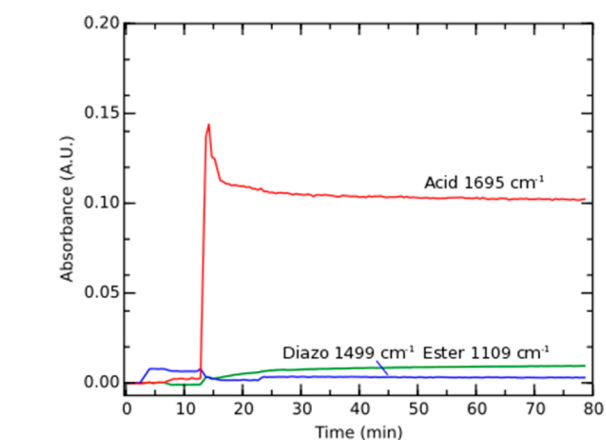
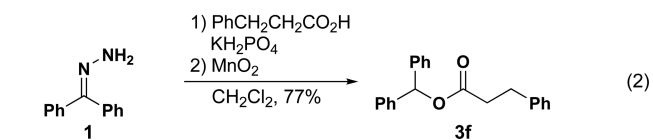
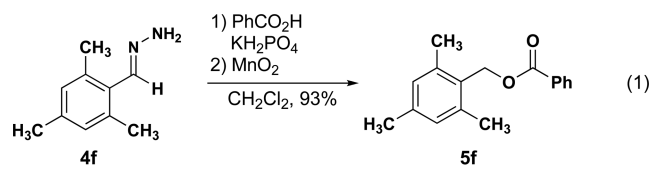
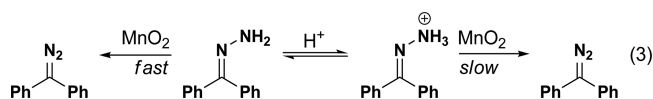


Figure 3. ReactIR data for the “MnO₂ Last” esterification conditions (see Table 1) consumption of benzoic acid (red) and appearance of diphenylmethyl benzoate (2, green). Note: MnO₂ was added at 14 min to a solution of benzophenone hydrazone and benzoic acid.



These results paired with the observation that mildly basic buffer can be beneficial to the reaction suggest that the rate of diazo compound formation and consumption is sensitive to pH (eq 3). When the acid is added last, the diazocompound is



formed quickly and then consumed quickly. With the acid present, it is likely that the hydrazone NH₂ is at least partially protonated and, as a result, slow to oxidize. Furthermore, partial

deprotonation of the carboxylic acid prevents it from reacting with the diazo compound, i.e., by preventing protonation on carbon to form the requisite diazonium species. Although the process is slower and the yields slightly lower (10–20%) on average, the “hydrazone last” procedure is still a useful method of esterification that minimizes the buildup of the diazo compound.

CONCLUSIONS

In summary, a new method has been developed for the facile esterification of acids by in situ oxidation of hydrazones and trapping of the produced diazo compound. The in situ production of diazo compound followed by rapid trapping with acid allows for safe scalability of this reaction following the dropwise protocol, reducing diazo build up.

EXPERIMENTAL SECTION

General Comments. Chemicals were purchased and used without further purification unless otherwise specified. Solvents were purified and dried on a solvent system or purchased anhydrous where required. Reactions were monitored by TLC (Merck) and detected by examination under UV light (254 and 365 nm). Flash column chromatography was performed using silica gel [230–400 mesh (40–63 μm)]. Extracts were concentrated in vacuo using both a rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. ^1H and ^{13}C spectra were measured in CDCl_3 at 300, 400, or 600 MHz and 101 or 151 MHz, respectively. For HRMS analysis, samples were analyzed by flow-injection analysis LTQ Orbitrap XL operated in the centroid mode. Samples were injected into a mixture of 50% CH_3OH and 0.1% formic acid/ H_2O at a flow rate of 200 $\mu\text{l}/\text{min}$. Source parameters were 5 kV spray voltage, capillary temperature of 275 °C, and sheath gas setting of 20. Spectral data were acquired at a resolution setting of 100,000 fwhm with the lockmass feature, which typically results in a mass accuracy of <2 ppm.

General Procedure for Hydrazone Formation. To a solution of anhydrous hydrazine (1.1 mL, 36 mmol) in anhydrous EtOH (25.0 mL) was added the respective ketone (5.0 mmol) dropwise or as a solution in EtOH. After the mixture was allowed to stir overnight, it was poured into water (50 mL) and extracted with CH_2Cl_2 (3 \times 75 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in vacuo (0–10 °C). The hydrazones were taken onto the ester formation reaction without further purification.

General Procedure A for Ester Formation (Acid Last). To a solution of hydrazone (1.2 equiv) in anhydrous CH_2Cl_2 (0.1 M) was added MnO_2 (8 equiv), KH_2PO_4 (8 equiv), and finally the respective acid (1 equiv). After 3–16 h, the reaction mixture was filtered through a plug of silica and washed with EtOAc. The resultant filtrate was concentrated in vacuo and purified by flash column chromatography to yield the desired ester.

General Procedure B for Ester Formation (Dropwise Addition of Hydrazone). A solution of acid (1 equiv), MnO_2 (8 equiv), and KH_2PO_4 (8 equiv) in CH_2Cl_2 (0.1 M) was added dropwise over 5 min to a solution of hydrazone (1.2 mmol) in CH_2Cl_2 (1.0 mL). After 12–16 h, the reaction mixture was filtered through a plug of silica and washed with EtOAc. The resultant filtrate was concentrated in vacuo and purified by flash column chromatography to yield the desired ester.

Benzophenone Hydrazone (1). Hydrazone 1 was recrystallized in CH_3OH from the commercially available material.

Benzylidenehydrazine (4a). Hydrazone 4a (977 mg, 80%) was synthesized according to the general hydrazone procedure using benzaldehyde (1.0 mL, 10 mmol), hydrazine (1.1 mL, 36 mmol), and EtOH (25.0 mL). ^1H NMR (600 MHz, CDCl_3) δ 7.75 (s, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.32–7.27 (m, 1H), 5.53 (s, 2H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁴

(4-Methoxybenzylidene)hydrazine (4b). Hydrazone 4b was synthesized according to the general hydrazone procedure using *p*-anisaldehyde (0.30 mL, 2.5 mmol), hydrazine (0.55 mL, 18 mmol), and EtOH (12.5 mL). ^1H NMR (600 MHz, CDCl_3) δ 7.71 (s, 1H), 7.48 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.40 (s, 2H), 3.81 (s, 3H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁴

4-(Hydrazonomethyl)benzotrile (4c). Hydrazone 4c was synthesized according to the general hydrazone procedure using *p*-cyanobenzaldehyde (330 mg, 10 mmol), hydrazine (1.3 mL, 43 mmol), and EtOH (25.0 mL). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (s, 1H), 7.61 (s, 4H), 5.87 (s, 2H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁷

(E)-(2,4,6-Trimethylbenzylidene)hydrazine (4d). Hydrazone 4d was synthesized according to the general hydrazone procedure using mesitylaldehyde (0.74 mL, 5.0 mmol), hydrazine (1.1 mL, 36 mmol), and EtOH (25.0 mL). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1H), 6.84 (s, 2H), 5.47 (s, 2H), 2.37 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.4, 137.9, 137.2, 129.6, 21.3; mp 85–89 °C. IR (neat): ν_{max} 3365, 2914, 1611, 1380, 1030 cm^{-1} ; AMM (ESI) m/z calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}_2\text{Na}^+$ [$M + \text{H}$] $^+$ 163.1230, found 163.1227.

(3,4-Dihydronaphthalen-1(2H)-ylidene)hydrazine (4e). Hydrazone 4e (645 mg, 87%) was synthesized according to the general hydrazone procedure using propiophenone (0.66 mL, 5.0 mmol), hydrazine (1.1 mL, 36 mmol), and EtOH (25.0 mL). ^1H NMR (600 MHz, CDCl_3) δ 7.65 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 5.42 (s, 2H), 2.65 (q, J = 7.7 Hz, 2H), 1.18 (t, J = 7.7 Hz, 3H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁶

(1-Phenylethylidene)hydrazine (4f). Hydrazone 4f (251 mg, 37%) was synthesized according to the general hydrazone procedure using acetophenone (0.58 mL, 5.0 mmol), hydrazine (1.1 mL, 36 mmol), and EtOH (25.0 mL). ^1H NMR (600 MHz, CDCl_3) δ 7.65 (d, J = 7.7 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 5.35 (s, 2H), 2.14 (s, 3H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁵

3,4-Dihydronaphthalen-1(2H)-ylidene)hydrazine (4g). Hydrazone 4g (801 mg, 93%) was synthesized according to the general hydrazone procedure using α -tetralone (1.0 mL, 5.0 mmol), hydrazine (1.1 mL, 36 mmol), and EtOH (25.0 mL). ^1H NMR (600 MHz, CDCl_3) δ 7.95–7.94 (m, 1H), 7.21–7.18 (m, 2H), 7.12–7.10 (m, 1H), 5.30 (s, 2H), 2.73 (t, J = 6.3, 2H), 2.49 (t, J = 6.6 Hz, 2H), 1.96–1.92 (m, 2H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁵

Benzhydryl Benzoate (2). Ester 2 was synthesized according to general ester formation procedure A using MnO_2 (253 mg, 2.90 mmol), KH_2PO_4 (395 mg, 2.90 mmol), hydrazone 1 (86 mg, 0.44 mmol), benzoic acid (44 mg, 0.36 mmol), and CH_2Cl_2 (3.6 mL). The crude product was purified by flash column chromatography (40:60 toluene/hexanes) affording ester 2 (92 mg, 90%) as a white solid. Procedure B using MnO_2 (291 mg, 3.34 mmol), KH_2PO_4 (455 mg, 3.34 mmol), hydrazone 1 (98 mg, 0.50 mmol), benzoic acid (51 mg, 0.42 mmol), and CH_2Cl_2 (4.2 mL) followed by flash column chromatography as above afforded ester 2 (93 mg, 77%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (dd, J = 7.9, 2.9 Hz, 6H), 7.40 (t, J = 7.5 Hz, 4H), 7.33 (t, J = 7.3 Hz, 2H), 7.18 (s, 1H). Proton NMR data of the crude material was consistent with the reported literature values.¹⁸

Benzhydryl 4-Methoxybenzoate (3a). Ester 3a was synthesized according to general ester formation procedure A using MnO_2 (256 mg, 2.94 mmol), KH_2PO_4 (396 mg, 2.91 mmol), hydrazone 1 (87 mg, 0.44 mmol), *p*-methoxybenzoic acid (55 mg, 0.36 mmol), and CH_2Cl_2 (3.7 mL). The crude product was purified by flash column chromatography (50:50 toluene/hexanes) affording ester 3a (98 mg, 84%) as a white solid. Procedure B using MnO_2 (769 mg, 8.82 mmol), KH_2PO_4 (1200 mg, 8.82 mmol), hydrazone 1 (262 mg, 1.33 mmol), *p*-methoxybenzoic acid (166 mg, 1.09 mmol), and CH_2Cl_2 (11.0 mL) followed by flash column chromatography as above afforded ester 3a (256 mg, 74%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.6 Hz, 4H), 7.33 (t, J = 7.6 Hz, 4H),

7.26 (t, $J = 7.4$ Hz, 2H), 7.10 (s, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.4, 163.7, 140.6, 131.9, 128.7, 128.0, 127.2, 122.7, 113.8, 77.2, 55.5; mp 95.7–99.1 °C. IR (neat): ν_{max} 2846, 1690, 1583, 1255 cm^{-1} ; AMM (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3\text{Na}^+$ [$M + \text{Na}$] $^+$ 341.1153, found 341.1147.

Benzhydryl 4-Cyanobenzoate (3b). Ester **3b** was synthesized according to general ester formation procedure A using MnO_2 (236 mg, 2.71 mmol), KH_2PO_4 (369 mg, 2.71 mmol), hydrazone **1** (80 mg, 0.41 mmol), *p*-cyanobenzoic acid (50 mg, 0.34 mmol), and CH_2Cl_2 (3.4 mL). The crude product was purified by flash column chromatography (8:92 EtOAc/hexanes) affording ester **3b** (89 mg, 84%) as a white solid. Procedure B using MnO_2 (253 mg, 2.91 mmol), KH_2PO_4 (400 mg, 2.94 mmol), hydrazone **1** (87 mg, 0.44 mmol), *p*-cyanobenzoic acid (54 mg, 0.37 mmol), and CH_2Cl_2 (3.7 mL) followed by flash column chromatography as above afforded ester **3b** (87 mg, 75%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.42 (s, 4H), 7.38 (t, $J = 7.5$ Hz, 4H), 7.35–7.29 (t, $J = 7.3$, 2H), 7.14 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 164.2, 139.8, 134.2, 132.5, 130.5, 128.9, 128.5, 127.3, 118.1, 116.8, 78.6; mp 87–88 °C. IR (neat): ν_{max} 2230, 1717, 1258 cm^{-1} ; AMM (ESI) m/z calcd for $\text{C}_{21}\text{H}_{15}\text{O}_2\text{NNa}^+$ [$M + \text{Na}$] $^+$ 336.1000, found 336.1008.

Benzhydryl 4-Hydroxybenzoate (3c). Ester **3c** was synthesized according to general ester formation procedure A using MnO_2 (244 mg, 2.81 mmol), KH_2PO_4 (382 mg, 2.81 mmol), hydrazone **1** (83 mg, 0.42 mmol), *p*-hydroxybenzoic acid (48 mg, 0.35 mmol), and CH_2Cl_2 (3.5 mL). The crude product was purified by flash column chromatography (30:70 EtOAc/hexanes) affording ester **3c** (51 mg, 49%) as an amorphous solid. Procedure B using MnO_2 (276 mg, 3.17 mmol), KH_2PO_4 (432 mg, 3.17 mmol), hydrazone **1** (94 mg, 0.48 mmol), *p*-hydroxybenzoic acid (55 mg, 0.40 mmol), and CH_2Cl_2 (4.0 mL) followed by flash column as above afforded ester **3c** (37 mg, 30%) as an amorphous solid. ^1H NMR (600 MHz, CDCl_3) δ 8.04 (d, $J = 9.0$ Hz, 2H), 7.43 (d, $J = 7.2$ Hz, 4H), 7.34 (t, $J = 7.7$ Hz, 4H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.08 (s, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 5.55 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.2, 160.8, 140.4, 132.4, 128.8, 128.2, 127.3, 122.3, 115.6, 77.7. IR (neat): ν_{max} 3311, 1725, 1165 cm^{-1} ; AMM (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{O}_3\text{Na}^+$ [$M + \text{Na}$] $^+$ 327.0997, found 327.0993.

Benzhydryl Cinnamate (3d). Ester **3d** was synthesized according to general ester formation procedure A using MnO_2 (274 mg, 3.15 mmol), KH_2PO_4 (410 mg, 3.01 mmol), hydrazone **1** (88 mg, 0.45 mmol), trans-cinnamic acid (56 mg, 0.38 mmol), and CH_2Cl_2 (3.8 mL). The crude product was purified by flash column chromatography (30:70 to 50:50 toluene/hexanes) affording ester **3d** (100 mg, 85%) as a white solid. Procedure B using MnO_2 (267 mg, 3.07 mmol), KH_2PO_4 (413 mg, 3.03 mmol), hydrazone **1** (89 mg, 0.45 mmol), trans-cinnamic acid (56 mg, 0.38 mmol), and CH_2Cl_2 (3.8 mL) followed by flash column chromatography as above afforded ester **3d** (83 mg, 70%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 15.9$ Hz, 1H), 7.57 (m, 2H), 7.36–7.33 (m, 11H), 7.27 (m, 2H), 7.09 (s, 1H), 6.62 (d, $J = 16.0$ Hz, 1H). Proton NMR data of the product were consistent with the reported literature values.¹⁹

Benzhydryl 3-Phenylpropanoate (3e). Ester **3e** was synthesized according to general ester formation procedure A using MnO_2 (261 mg, 3.00 mmol), KH_2PO_4 (406 mg, 2.98 mmol), hydrazone **1** (86 mg, 0.44 mmol), phenylpropanoic acid (58 mg, 0.38 mmol), and CH_2Cl_2 (3.8 mL). The crude product was purified by flash column chromatography (50:50 toluene/hexanes) affording ester **3e** (106 mg, 87%) as a white solid. Procedure B using MnO_2 (249 mg, 2.86 mmol), KH_2PO_4 (398 mg, 2.93 mmol), hydrazone **1** (90 mg, 0.46 mmol), phenylpropanoic acid (56 mg, 0.38 mmol), and CH_2Cl_2 (3.8 mL) followed by flash column chromatography as above afforded ester **3e** (81 mg, 68%) as a white solid. Ester **3e** was also synthesized by a third method, MnO_2 last. MnO_2 (901 mg, 10.4 mmol) was added to a suspension of hydrocinnamic acid, (122 mg, 1.24 mmol), KH_2PO_4 (1350 mg, 9.92 mmol), and hydrazone **1** (292 mg, 1.49 mmol) in CH_2Cl_2 (12 mL). The crude product was filtered through silica and purified by flash column chromatography (50:50 toluene/hexanes) affording ester **3e** (199 mg, 77%) as a white solid. ^1H NMR (600

MHz, CDCl_3) δ 7.33–7.21 (m, 12H), 7.20–7.13 (m, 3H), 6.88 (s, 1H), 2.97 (t, $J = 7.8$ Hz, 2H), 2.74 (t, $J = 7.8$ Hz, 2H). Proton NMR data of the product were consistent with the reported literature values.²⁰

benzhydryl pivalate (3f). Ester **3f** was synthesized according to the modified general ester formation procedure A using MnO_2 (1.75 g, 20.0 mmol), hydrazone **1** (589 mg, 3.0 mmol), pivalic acid (267 mg, 2.50 mmol), and CH_2Cl_2 (25.0 mL). The crude product was purified by flash column chromatography (20:80 CH_2Cl_2 /hexanes) affording ester **3f** (359 mg, 51%) as a white solid. Procedure B using MnO_2 (1.72 g, 19.3 mmol), hydrazone **1** (582 mg, 2.97 mmol), pivalic acid (252 mg, 2.47 mmol), and CH_2Cl_2 (24.7 mL) followed by flash column chromatography as above afforded ester **3f** (199 mg, 30%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.35–7.29 (m, 8H), 7.27–7.23 (m, 2H), 6.82 (s, 1H), 1.25 (s, 9H). Proton NMR data of the product were consistent with the reported literature values.²¹

Benzhydryl Acetate (3g). Ester **3g** was synthesized according to the modified general ester formation procedure A using MnO_2 (306 mg, 3.52 mmol), hydrazone **1** (103 mg, 0.530 mmol), acetic acid (28 μL , 0.42 mmol), and CH_2Cl_2 (4.2 mL). The crude product was purified by flash column chromatography (4:96 EtOAc/hexanes) affording ester **3g** (82 mg, 86%) as a white solid. Procedure B using MnO_2 (306 mg, 3.52 mmol), hydrazone **1** (103 mg, 0.530 mmol), acetic acid (28 μL , 0.42 mmol), and CH_2Cl_2 (4.2 mL) followed by flash column chromatography as above afforded ester **3g** (81 mg, 82%) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.39–7.35 (m, 8H), 7.32–7.30 (m, 2H), 6.88 (s, 1H), 2.15 (s, 3H). Proton NMR data of the product were consistent with the reported literature values.¹⁹

Benzhydryl (tert-Butoxycarbonyl)valinate (3h). Ester **3h** was synthesized according to general ester formation procedure A using MnO_2 (256 mg, 2.94 mmol), KH_2PO_4 (400 mg, 2.94 mmol), hydrazone **1** (87 mg, 0.44 mmol), Boc-val-OH (80 mg, 0.37 mmol), and CH_2Cl_2 (3.7 mL). The crude product was purified by flash column chromatography (10:90 EtOAc/hexanes) affording ester **3h** (113 mg, 80%) as a white solid. Procedure B using MnO_2 (256 mg, 2.94 mmol), KH_2PO_4 (409 mg, 2.94 mmol), hydrazone **1** (87 mg, 0.44 mmol), Boc-val-OH (80 mg, 0.37 mmol), and CH_2Cl_2 (3.7 mL) followed by flash column chromatography as above afforded ester **3h** (41 mg, 28%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 7.34–7.32 (m, 8H), 7.29–7.27 (m, 2H), 6.90 (s, 1H), 5.02 (d, $J = 9.3$ Hz, 1H), 4.36 (dd, $J = 9.1$, 4.5 Hz, 1H), 2.22–2.19 (m, 1H), 1.43 (s, 9H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.76 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.5, 155.7, 139.7, 128.5, 128.1, 128.0, 127.3, 127.0, 79.7, 77.8, 58.5, 31.3, 28.3, 19.1, 17.2. IR (neat): ν_{max} 3378, 1732, 1705, 1490, 1260 cm^{-1} ; mp 110–112 °C. AMM (ESI) m/z calcd for $\text{C}_{23}\text{H}_{29}\text{O}_4\text{NNa}^+$ [$M + \text{Na}$] $^+$ 406.1994, found 406.1998.

Benzhydryl Furan-3-carboxylate (3i). Ester **3i** was synthesized according to general ester formation procedure A using MnO_2 (103 mg, 1.19 mmol), KH_2PO_4 (162 mg, 1.19 mmol), hydrazone **1** (35 mg, 0.18 mmol), furanoic acid (17 mg, 0.15 mmol), and CH_2Cl_2 (1.5 mL). The crude product was purified by flash column chromatography (10:90 EtOAc/hexanes) affording ester **3i** (38 mg, 91%) as a white solid. Procedure B using MnO_2 (181 mg, 2.08 mmol), KH_2PO_4 (283 mg, 2.08 mmol), hydrazone **1** (61 mg, 0.31 mmol), furanoic acid (29 mg, 0.26 mmol), and CH_2Cl_2 (2.6 mL) followed by flash column chromatography as above afforded ester **3i** (53 mg, 73%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.12 (s, 1H), 7.45 (s, 1H), 7.40 (d, $J = 7.3$ Hz, 4H), 7.36 (t, $J = 7.5$ Hz, 4H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.07 (s, 1H), 6.82 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.3, 148.2, 144.0, 140.3, 128.8, 128.2, 127.3, 119.6, 110.1, 77.1. IR (neat): ν_{max} 1710, 1299, 1136 cm^{-1} ; mp 98–100 °C. AMM (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{Na}^+$ [$M + \text{Na}$] $^+$ 301.0841, found 301.0838.

Benzyl Benzoate (5a). Ester **5a** was synthesized according to general ester formation procedure A using MnO_2 (225 mg, 2.59 mmol), KH_2PO_4 (353 mg, 2.59 mmol), hydrazone **4a** (47 mg, 0.39 mmol), benzoic acid (39 mg, 0.32 mmol), and CH_2Cl_2 (3.2 mL). The crude product was purified by flash column chromatography (7:93 EtOAc/hexanes) affording ester **5a** (52 mg, 76%) as a yellow oil. Procedure B using MnO_2 (234 mg, 2.69 mmol), KH_2PO_4 (366 mg, 2.69 mmol), hydrazone **4a** (48 mg, 0.40 mmol), benzoic acid (41 mg,

0.34 mmol), and CH_2Cl_2 (3.4 mL) followed by flash column chromatography as above afforded ester **5a** (71 mg, 80%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, $J = 7.9$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.44–7.40 (m, 4H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.3$ Hz, 1H), 5.39 (s, 2H). Proton NMR data of the product were consistent with the reported literature values.¹⁸

4-Methoxybenzyl Benzoate (5b). Ester **5b** was synthesized according to general ester formation procedure A using MnO_2 (227 mg, 2.61 mmol), KH_2PO_4 (355 mg, 2.61 mmol), hydrazone **4b** (59 mg, 0.39 mmol), benzoic acid (40 mg, 0.33 mmol), and CH_2Cl_2 (3.3 mL). The crude product was purified by flash column chromatography (7:93 EtOAc/hexanes) affording ester **5b** (66 mg, 84%) as a clear oil. Procedure B using MnO_2 (232 mg, 2.66 mmol), KH_2PO_4 (363 mg, 2.66 mmol), hydrazone **4b** (60 mg, 0.40 mmol), benzoic acid (41 mg, 0.33 mmol), and CH_2Cl_2 (3.3 mL) followed by flash column chromatography as above afforded ester **5b** (63 mg, 77%) as a clear oil. ^1H NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 8.7$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.47–7.36 (m, 4H), 6.93 (d, $J = 8.7$ Hz, 2H), 5.31 (s, 2H), 3.82 (s, 3H). Proton NMR data of the product were consistent with the reported literature values.²²

4-Cyanobenzyl Benzoate (5c). Ester **5c** was synthesized according to general ester formation procedure A using MnO_2 (216 mg, 2.48 mmol), KH_2PO_4 (338 mg, 2.48 mmol), hydrazone **4c** (54 mg, 0.37 mmol), benzoic acid (37 mg, 0.30 mmol), and CH_2Cl_2 (3.0 mL). The crude product was purified by flash column chromatography (10:90 EtOAc/hexanes) affording ester **5c** (37 mg, 52%) as a white solid. Procedure B using MnO_2 (207 mg, 2.38 mmol), KH_2PO_4 (324 mg, 2.38 mmol), hydrazone **4c** (52 mg, 0.36 mmol), benzoic acid (36 mg, 0.30 mmol), and CH_2Cl_2 (3.0 mL) followed by flash column chromatography as above afforded ester **5c** (32 mg, 45%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.47 (t, $J = 7.7$ Hz, 2H), 5.42 (s, 2H). Proton NMR data of the product were consistent with the reported literature values.¹⁸

2,4,6-Trimethylbenzyl Benzoate (5d). Ester **5d** was synthesized according to general ester formation procedure A using MnO_2 (160 mg, 1.84 mmol), KH_2PO_4 (250 mg, 1.84 mmol), hydrazone **4d** (45 mg, 0.28 mmol), benzoic acid (27 mg, 0.23 mmol), and CH_2Cl_2 (2.3 mL). The crude product was purified by flash column chromatography (3:97 EtOAc/hexanes) affording ester **5d** (57 mg, 96%) as a white solid. Procedure B using MnO_2 (216 mg, 2.48 mmol), KH_2PO_4 (338 mg, 2.48 mmol), hydrazone **4d** (60 mg, 0.37 mmol), benzoic acid (37 mg, 0.31 mmol), and CH_2Cl_2 (3.1 mL) followed by flash column chromatography as above afforded ester **5d** (73 mg, 92%) as a white solid. Ester **5d** was also synthesized by a third method, MnO_2 last. MnO_2 (682 mg, 7.84 mmol) was added to a suspension of benzoic acid, (121 mg, 0.980 mmol), KH_2PO_4 (1067 mg, 7.840 mmol), and hydrazone **4d** (191 mg, 1.18 mmol) in CH_2Cl_2 (10 mL). The crude product was filtered through silica and purified by flash column chromatography (40:60 toluene/hexanes) affording ester **5d** (249 mg, 93%) as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.00 (d, $J = 7.8$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 6.90 (s, 2H), 5.41 (s, 2H), 2.41 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.9, 138.6, 138.5, 133.0, 130.4, 129.8, 129.2, 128.5, 61.8, 21.2, 19.8. IR (neat): ν_{max} 1725, 1451, 1165 cm^{-1} ; mp 65–67 °C. AMM (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{Na}^+$ [$M + \text{Na}$] $^+$ 277.1205, found 277.1210.

1-Phenylpropyl Benzoate (5e). Ester **5e** was synthesized according to general ester formation procedure A using MnO_2 (237 mg, 2.72 mmol), KH_2PO_4 (370 mg, 2.72 mmol), hydrazone **4e** (61 mg, 0.41 mmol), benzoic acid (41 mg, 0.34 mmol), and CH_2Cl_2 (3.4 mL). The crude product was purified by flash column chromatography (3:97 EtOAc/hexanes) affording ester **5e** (81 mg, 99%) as a yellow oil. Procedure B using MnO_2 (251 mg, 2.88 mmol), KH_2PO_4 (392 mg, 2.88 mmol), hydrazone **4e** (64 mg, 0.43 mmol), benzoic acid (44 mg, 0.36 mmol), and CH_2Cl_2 (3.6 mL) followed by flash column chromatography as above afforded ester **5e** (73 mg, 85%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, $J = 7.9$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.29 (t, $J = 7.3$ Hz, 1H), 5.93 (t, $J = 6.8$ Hz, 1H), 2.09 (dd, $J = 14.7, 7.4, 7.4$ Hz, 1H),

1.97 (dd, $J = 14.7, 7.4, 7.4$ Hz, 1H), 0.98 (t, $J = 7.4$ Hz, 3H). Proton NMR data of the product were consistent with the reported literature values.²⁵

1-Phenylethyl Benzoate (5f). Ester **5f** was synthesized according to general ester formation procedure A using MnO_2 (318 mg, 3.66 mmol), KH_2PO_4 (498 mg, 3.66 mmol), hydrazone **4f** (74 mg, 0.54 mmol), benzoic acid (56 mg, 0.46 mmol), and CH_2Cl_2 (4.0 mL). The crude product was purified by flash column chromatography (4:96 EtOAc/hexanes) affording ester **5f** (96 mg, 93%) as a yellow oil. Procedure B using MnO_2 (256 mg, 2.94 mmol), KH_2PO_4 (400 mg, 2.94 mmol), hydrazone **4f** (55 mg, 0.45 mmol), benzoic acid (45 mg, 0.37 mmol), and CH_2Cl_2 (3.7 mL) followed by flash column chromatography afforded ester **5f** (79 mg, 94%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.14 (d, $J = 7.1$ Hz, 2H), 7.58–7.56 (t, $J = 7.4$ Hz, 1H), 7.48 (m, 4H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 6.20 (q, $J = 6.6$ Hz, 1H), 1.72 (d, $J = 6.6$ Hz, 3H). Proton NMR data of the product were consistent with the reported literature values.²⁶

1,2,3,4-Tetrahydronaphthalen-1-yl Benzoate (5g). Ester **5g** was synthesized according to general ester formation procedure A using MnO_2 (210 mg, 2.41 mmol), KH_2PO_4 (329 mg, 2.41 mmol), hydrazone **4g** (58 mg, 0.36 mmol), benzoic acid (36 mg, 0.30 mmol), and CH_2Cl_2 (3.0 mL). The crude product was purified by flash column chromatography (0:100 to 2:98 EtOAc/hexanes) affording ester **5g** (72 mg, 97%) as a yellow oil. Procedure B using MnO_2 (247 mg, 2.84 mmol), KH_2PO_4 (387 mg, 2.84 mmol), hydrazone **4g** (68 mg, 0.43 mmol), benzoic acid (43 mg, 0.36 mmol), and CH_2Cl_2 (3.6 mL) followed by flash column chromatography as above afforded ester **5i** (75 mg, 84%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.40 (d, $J = 7.7$ Hz, 1H), 7.27 (t, $J = 7.4$ Hz, 1H), 7.20 (t, $J = 8.3$ Hz, 2H), 6.30 (t, $J = 4.8$ Hz, 1H), 2.93–2.89 (m, 1H), 2.90–2.74 (m, 2H), 2.13–2.03 (m, 2H), 1.99–1.82 (m, 1H). Proton NMR data of the product were consistent with the reported literature values.²⁵

Benzyl Cyclohexanecarboxylate (5h). Ester **5h** was synthesized according to general ester formation procedure A using MnO_2 (188 mg, 2.16 mmol), KH_2PO_4 (294 mg, 2.16 mmol), hydrazone **4a** (40 mg, 0.33 mmol), cyclohexane carboxylic acid (35 mg, 0.27 mmol), and CH_2Cl_2 (2.7 mL). The crude product was purified by flash column chromatography (5:95 EtOAc/hexanes) affording ester **5h** (56 mg, 95%) as a clear oil. The final product contained up to 17% of the azine byproduct resulting from hydrazone condensation; ^1H NMR (600 MHz, CDCl_3) δ 8.69 (d, $J = 1.3$ Hz, 2H), 7.86–7.83 (m, 4H), 7.34–7.31 (m, 6H). Procedure B using MnO_2 (226 mg, 2.60 mmol), KH_2PO_4 (354 mg, 2.60 mmol), hydrazone **4a** (77 mg, 0.39 mmol), cyclohexane carboxylic acid (42 mg, 0.33 mmol), and CH_2Cl_2 (3.3 mL) followed by flash column chromatography as above afforded ester **5h** (56 mg, 80%) as a clear oil. ^1H NMR (600 MHz, CDCl_3) δ 7.37–7.28 (m, 5H), 5.10 (s, 2H), 2.35 (tt, $J = 11.7, 3.0$ Hz, 1H), 1.96–1.90 (m, 2H), 1.75 (m, 2H), 1.66–1.60 (m, 2H), 1.46 (m, 2H), 1.32–1.18 (m, 2H). Proton NMR data of the product were consistent with the reported literature values.²³

4-Methoxybenzyl Cyclohexanecarboxylate (5i). Ester **5i** was synthesized according to general ester formation procedure A using MnO_2 (341 mg, 3.92 mmol), KH_2PO_4 (533 mg, 3.92 mmol), hydrazone **4b** (111 mg, 0.740 mmol), cyclohexane carboxylic acid (63 mg, 0.49 mmol), and CH_2Cl_2 (4.9 mL). The crude product was purified by flash column chromatography (10:90 EtOAc/hexanes) affording ester **5i** (83 mg, 68%) as a clear oil. Procedure B using MnO_2 (331 mg, 3.58 mmol), KH_2PO_4 (487 mg, 3.58 mmol), hydrazone **4b** (102 mg, 0.670 mmol), cyclohexane carboxylic acid (57 mg, 0.45 mmol), and CH_2Cl_2 (4.5 mL) followed by flash column chromatography as above afforded ester **5i** (23 mg, 21%) as a clear oil. ^1H NMR (600 MHz, CDCl_3) δ 7.27 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 5.03 (s, 2H), 3.79 (s, 3H), 2.31 (tt, $J = 11.3, 3.6$ Hz, 1H), 1.90 (dd, $J = 12.4, 3.6$ Hz, 2H), 1.76–1.71 (m, 2H), 1.64–1.61 (m, 1H), 1.48–1.39 (m, 2H), 1.31–1.18 (m, 3H). Proton NMR data of the product were consistent with the reported literature values.²⁴

■ ASSOCIATED CONTENT**■ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00408.

¹H and ¹³C NMR spectra of new compounds, ¹H of known compounds, and ReactIR experimentals and data (PDF)

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Notes

The authors declare no competing financial interest.

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