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Guanidinium iodide/urea hydrogen peroxide-catalyzed azidation of β-dicarbonyl compounds with trimethylsilyl azide

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ABSTRACT

We present an efficient synthesis of α-azido-β-dicarbonyl compounds from β-dicarbonyl compounds and trimethylsilyl azide, catalyzed by guanidinium hypoiodite. The reaction can be run in air at ambient temperature (up to 40 °C) and is not sensitive to moisture. The substrate scope is broad, including cyclic and linear β-dicarbonyl compounds, and the α-azide products are obtained in 55%–99% yield.

1. Introduction

In recent years, oxidative bond-forming reactions with I^-/IO^- catalytic systems have drawn considerable attention.[1] Since hypoiodite (represented by IOX or IO^-) is easily generated in situ from iodine or iodide with oxidants under mild conditions, this system has been used in a variety of oxidative coupling reactions as an environmentally benign process.[2–5] In these catalytic systems, the powerful oxidizing abilities of hypoiodites enable bond-forming reactions between nucleophiles without the need for pre-functionalization. Among reactive nucleophiles, azide anions and α-carbons of carbonyl compounds are an attractive combination to generate synthetically useful α-azido carbonyl compounds, which are useful in multistep synthesis as amino acid precursors, or as precursors for cycloaddition with alkynes, i.e., Huisgen reaction.[6–8] However, only two methods have been reported for hypoiodite-catalyzed oxidative azidation (Scheme 1).[8] In 2012, Kirsch and co-workers reported the reaction of nucleophilic sodium azide and β-dicarbonyl compounds to generate C–N bonds in the presence of a catalytic amount of sodium iodide and a stoichiometric amount of IBX-SO_3K as the terminal oxidant (Scheme 1-1).[8a] Although this reaction is applicable to a wide range of β-dicarbonyl compounds, formation of by-products from IBX-SO_3K remains an issue. More recently, Prabhu and co-workers reported hypoiodite-catalyzed azidation of β-dicarbonyl compounds based on a hypoiodite catalytic system of tetrabutylammonium iodide and a stoichiometric amount of *tert*-butyl hydroperoxide under heating (Scheme 1-2).[8b] On the other hand, our group has recently reported triazabicyclodecene hypoiodite (TBD·IOH) catalysis for oxidative α-nitroalkylation of β-ketoamides under mild conditions,[5a] and we considered that a similar approach might be applicable for oxidative α-azidation of β-dicarbonyl compounds. In this paper, we describe an operationally simple and environmentally friendly method for the synthesis of α-azido-β-dicarbonyl compounds based on an oxidative coupling strategy utilizing a guanidinium hypoiodite catalytic system (Scheme 1-3).

2. Results and discussion

Initially, we investigated the reactivity of guanidinium iodides in the oxidative azidation of β-keto ester **1a**, derived from 1-indanone, and trimethylsilyl azide ($TMSN_3$) (1.1 equiv) in the presence of

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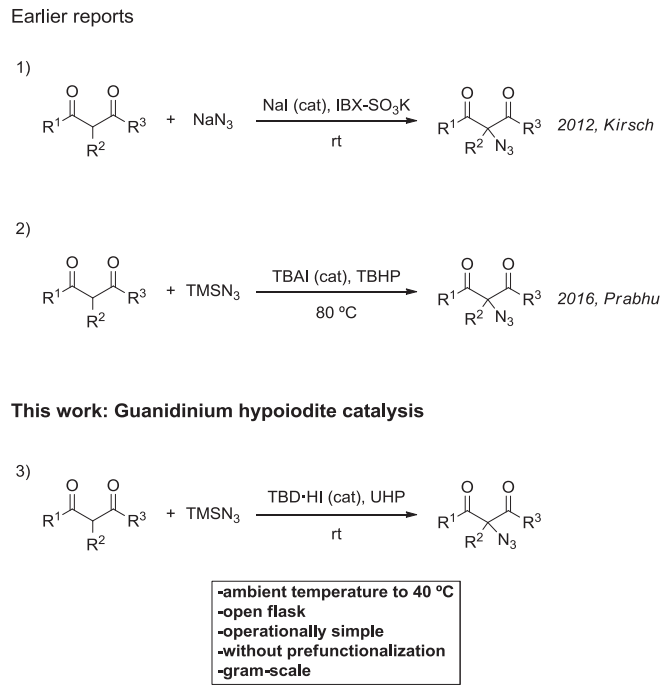
0040-4020/

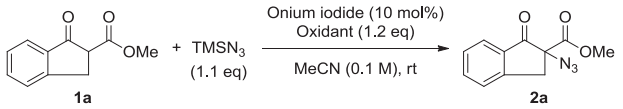


Scheme 1. α-Azidation of β-dicarbonyl compounds.

hydrogen peroxide (30%, 1.2 equiv) in acetonitrile (Table 1). As shown in entry 1, azide **2a** was obtained in 94% yield by using the cyclic guanidinium salt triazabicyclodecene hydroiodide (TBD·HI). On the other hand, the yield of **2a** dropped to 71% when tetramethylguanidinium iodide (TMG·HI) was used (entry 2). To compare the reactivity of onium iodides, tetrabutylammonium iodide and pyridinium iodide (Py·HI) were also examined and these catalysts were found to be less effective for the reaction (66% and 32% yields of **2a**, respectively; entries 3, 4). Next, various oxidants were tested in the presence of TBD·HI (entries 5–7). In the case of urea hydrogen peroxide (UHP), the yield of **2a** was increased to 96% (entry 7). With sodium azide as an alternative azide anion source, the yield of **2a** was only 52% (entry 8). Since the hydrochloric acid salt of TBD, i.e., TBD·HCl, did not catalyze the reaction at all, iodine anion is mandatory for the reaction (entry 9). It is noteworthy that this reaction did not proceed with a stoichiometric amount of trivalent iodine reagent iodobenzene diacetate (PIDA) or [bis(trifluoroacetoxy)indo]benzene (PIFA) (entries 10, 11).

Among the conditions we examined, the combination of TBD·HI and UHP, i.e., entry 7, gave the best result. Thus, we next investigated the scope of the reaction under the optimized conditions. As summarized in Table 2, all of the tested indanone-derived β-keto esters were converted into the corresponding azide products **2b**–**l** in high yields (75%–99%). A bulky substituent at the ester group did not decrease the yield: **2b**–**d** were obtained in 90%–98% yields. Electron-donating and electron-withdrawing groups as well as disubstitution on the aromatic group were also tolerated, affording products in 75%–95% yields (**2e**–**2i**). Substrates with methyl substitution on the aromatic group gave the corresponding products **2j**–**2l** in high yields (95%–99%). Indanone-derived β-keto amides **1m**–**1o**, including Weinreb amide **1n**, also gave the corresponding products in high yields (92%–95%). Noteworthy, the reaction of Weinreb amide **1n** was easily scaled-up to 2 g-scale. Moreover, the reactions of various non-fused β-dicarbonyl compounds **1q**–**1s** proceeded smoothly, generating the corresponding compounds **2q**–**2s** in moderate to high yields (70%–92%). Acyclic β-dicarbonyl compounds also provided corresponding azides **2t** and **2u** in 55% and 85% yields, respectively.

Table 1
Optimization of the reaction[a]



Entry	Onium iodide	Oxidant	Time (h)	Yield of **2a** (%)[b]
1	TBD·HI	H_2O_2[c]	1	94
2	TMG·HI	H_2O_2[c]	2.5	71
3	nBu$_4$NI	H_2O_2[c]	3	66
4	Py·HI	H_2O_2[c]	3	32
5	TBD·HI	CHP	1.5	88
6	TBD·HI	TBHP[d]	3.5	74
7	TBD·HI	UHP	1	96
8[e]	TBD·HI	UHP	2	52
9	TBD·HCl	UHP	1	0
10	PIDA[f]	—	1	0
11	PIFA[f]	—	1	0

Py·HI=pyridinium iodide, TMG·HI=tetramethylguanidinium iodide, TBD·HI=triazabicyclodecene hydroiodide, TBHP=*tert*-butyl hydroperoxide, CHP=cumene hydroperoxide, UHP=urea hydrogen peroxide.

[a] Reaction conditions: β-keto ester **1a** (0.1 mmol), $TMSN_3$ (0.11 mmol), onium iodide (0.01 mmol), oxidant (0.12 mmol), MeCN (1.0 mL), under air, at room temperature.

[b] Isolated yield.

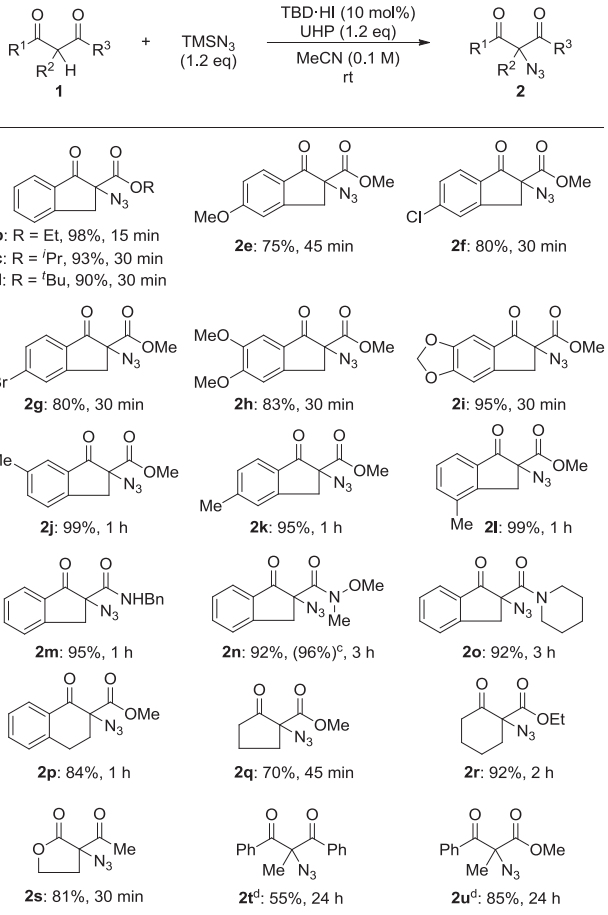
[c] 30% H_2O_2 was used.

[d] 70% TBHP in H_2O was used.

[e] NaN_3 (1.1 equiv) was used instead of $TMSN_3$.

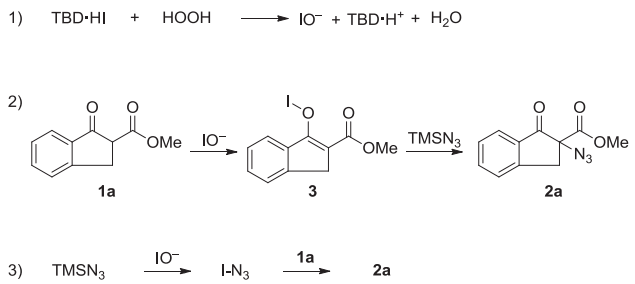
[f] A stoichiometric amount of trivalent iodine reagent (0.12 mmol) was used.

Table 2
Scope of the azidation of 1,3-dicarbonyl compounds[a,b]



[a] Reaction conditions: β-dicarbonyl compound (0.1 mmol), $TMSN_3$ (0.11 mmol), TBD·HI (0.01 mmol), UHP (0.12 mmol), MeCN (1 mL), in air, at room temperature. [b] Isolated yield. [c] 2.30 g (9.12 mmol) scale. [d] $TMSN_3$ (0.22 mmol), TBD·HI (0.02 mmol), UHP (0.24 mmol) at 40 °C.

The mechanism of this reaction was examined (Scheme 2). Firstly, hypoiodite IO^- should be generated by reaction of I^- with urea hydrogen peroxide (Scheme 2-1).[2g] This hypoiodite species would react with β-ketoester **1a** to form iodoenolate **3**,[2a] followed by nucleophilic azidation with trimethylsilyl azide (Scheme 2-2). It is also possible that the hypoiodite species reacts first with trimethylsilyl azide to form iodine azide, followed by nucleophilic reaction with β-ketoester **1a** (Scheme 2-3). It is noteworthy that, under the optimized conditions (Table 1, entry 9), addition of a radical scavenger such as dibutylhydroxytoluene (BHT) did not affect the azidation reaction of **1a**, since **2a** was still obtained in 98% yield. Thus, a radical mechanism is ruled out.



Scheme 2. Proposed mechanism of the azidation reaction.

3. Conclusion

In conclusion, we have developed a method for synthesis of α-azido-β-dicarbonyl compounds based on oxidative azidation of β-dicarbonyl compounds in the presence of hypoiodite generated from UHP as an oxidant and a catalytic amount of TBD·HI. A wide range of β-dicarbonyl compounds is available for the reaction under these conditions. This direct and simple oxidative catalytic reaction is expected to be a powerful and practically useful approach to obtain α-azido-substituted β-dicarbonyl compounds.

4. Experimental section

4.1. General remarks

Flash chromatography was performed using silica gel 60 (spherical, particle size 0.040–0.100 mm; Kanto Co., Inc., Japan). ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX300, ECA/ECX400 instruments. Chemical shifts in chloroform-d was reported in the scale relative to chloroform-d (^{1}H NMR; δ=7.26 ppm, ^{13}C NMR; δ=77.0 ppm) as an internal reference. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ ppm). IR spectra were measured on JASCO FT/IR-420 spectrometer. Mass spectra were recorded on JEOL JMS-T100X spectrometer.

4.2. Synthesis of β-dicarbonyl compounds 1

*4.2.1. N-Methoxy-N-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxamide (**1n**).* To a stirred solution of 1-indanone (1.47 g, 11.2 mmol) and *N*-methoxy-*N*-methyl-1*H*-imidazole-1-carboxamide (5.20 g, 33.5 mmol) in THF (110 mL), was added NaH (4.48 g, 112 mmol) at ambient temperature under N_2 atmosphere. The reaction mixture was then heated to 60 °C. After stirring for 30 min, the reaction mixture was cooled to 0 °C and water was added. The water layer was extracted with ethyl acetate (×3), the combined organic layer was washed with brine, dried over $MgSO_4$. After removing solvent under reduced pressure, the residue was purified by flash column chromatography (*n*-hexane/ethyl acetate=1:1) to afford title compound **1n** as a white solid (2.35 g, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J*=7.5 Hz, 1H), 7.59 (td, *J*=7.5, 0.9 Hz, 1H), 7.48 (d, *J*=7.5 Hz, 1H), 7.36 (t, *J*=7.5 Hz, 1H), 4.28 (dd, *J*=8.4, 3.9 Hz, 1H), 3.46 (dd, *J*=17.1, 3.9 Hz, 1H), 3.32 (dd, *J*=17.1, 8.4 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 170.2, 154.2, 135.5, 135.0, 127.5, 126.4, 124.3, 61.6, 50.1, 32.2, 30.6; FTIR (neat) 3019, 2360, 1716, 1654, 1216, 755, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_{13}N_1Na_1O_3$ 242.0793, found 242.0799.

*4.2.2. 2-(Piperidine-1-carbonyl)-2,3-dihydro-1H-inden-1-one (**1o**).* To a suspension of activated MS4Å (600 mg) in toluene (10 mL) was added β-ketoester **1a** (380 mg, 2.00 mmol) and piperidine (397 μL, 4.00 mmol) under N_2 atmosphere. The resulting mixture was heated at 70 °C for 20 h. The reaction mixture was then cooled to ambient temperature, and filtered through a pad of Celite, and the filtrates were concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 9:1 to 2:1 as eluent) to give title compound **1o** as a white solid (400 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J*=7.5 Hz, 1H), 7.58 (td, *J*=7.5, 1.2 Hz, 1H), 7.49 (d, *J*=7.5 Hz, 1H), 7.34 (t, *J*=7.5 Hz, 1H), 4.93 (dd, *J*=7.5, 3.6 Hz, 1H), 3.88–3.80 (m, 1H), 3.80 (dd, *J*=17.4, 3.6 Hz, 1H), 3.80–3.68 (m, 1H), 3.66–3.53 (m, 1H), 3.53–3.40 (m, 1H), 3.28 (dd, *J*=17.4, 7.5 Hz, 1H), 1.95–1.50 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 166.0, 154.6, 135.4, 135.1, 127.4, 126.4, 124.2, 50.4, 47.6, 43.6, 30.6, 26.5, 25.6, 24.5; FTIR (neat) 3019, 2360, 1216, 750, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{15}H_{17}N_1Na_1O_2$ 266.1157, found 266.1196.

4.3. Synthesis of α-azido-β-dicarbonyl compounds

General procedure for α-azidation of β-dicarbonyl compounds.

*4.3.1. Methyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2a**).* To a stirred solution of β-dicarbonyl compound **1a** (19.0 mg, 0.100 mmol) in acetonitrile (1.0 mL) was added TBD·HI (2.7 mg, 0.01 mmol), $TMSN_3$ (14.5 μL, 0.11 mmol) and UHP (11.3 mg, 0.12 mmol) at ambient temperature. After stirring for 1 h at this temperature, the reaction was quenched with a 10% aqueous solution of $Na_2S_2O_3$. The aqueous layer was extracted with ethyl acetate (×2) and the combined organic layer was washed with brine and then dried over $MgSO_4$. After removing solvent under reduced pressure, the residue was purified by flash column chromatography (*n*-hexane/ethyl acetate=5:1) to afford α-azido-β-dicarbonyl compound **2a** (22.2 mg, 96% yield). NMR data correspond to the reported values.[7c] (Detail of the reaction conditions was shown in Table 2).

*4.3.2. Isopropyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2c**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1c** (93% yield, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J*=7.2 Hz, 1H), 7.68 (t, *J*=7.2 Hz, 1H), 7.48–7.43 (m, 2H), 5.13 (dq, *J*=6.0, 6.0 Hz, 1H), 3.65 (d, *J*=17.6 Hz, 1H), 3.02 (d, *J*=17.6 Hz, 1H), 1.26 (d, *J*=6.0 Hz, 3H), 1.24 (d, *J*=6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 168.0, 152.1, 136.3, 133.0, 128.3, 126.4, 125.6, 71.1, 70.1, 38.4, 21.6, 21.5; FTIR (neat) 3020, 2116, 1744, 1718, 1216, 756, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{13}H_{13}N_3Na_1O_3$ 282.0855, found 282.0846.

*4.3.3. Methyl 2-azido-5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2f**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1f** (80% yield, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J*=8.4 Hz, 1H), 7.47 (d, *J*=1.2 Hz, 1H), 7.44 (dd, *J*=8.4, 1.2 Hz, 1H), 3.81 (s, 3H),

3.65 (d, *J*=17.7 Hz, 1H), 3.01 (d, *J*=17.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 168.5, 153.4, 143.2, 131.4, 129.3, 126.7, 126.6, 70.1, 53.7, 38.1; FTIR (neat) 3446, 3020, 2115, 1755, 1721, 1600, 1216, 769, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{11}H_8Cl_1N_3Na_1O_3$ 288.0152, found 288.0145.

*4.3.4. Methyl 2-azido-5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2g**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1g** (80% yield, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J*=8.4 Hz, 1H), 7.66 (s, 1H), 7.60 (d, *J*=8.4 Hz, 1H), 3.81 (s, 3H), 3.65 (d, *J*=17.7 Hz, 1H), 3.02 (d, *J*=17.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 168.5, 153.4, 132.2, 131.8, 129.8, 126.7, 70.0, 53.7, 38.1; FTIR (neat) 2114, 1755, 1721, 1595, 1263, 1179, 1058, 909 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{11}H_8{}^{81}Br_1N_3Na_1O_3$ 333.9626 and $C_{11}H_8{}^{79}Br_1N_3Na_1O_3$ 331.9647, found 333.9604 and 331.9617.

*4.3.5. Methyl 2-azido-5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2h**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1h** (83% yield, pale yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.60 (s, 1H), 4.39 (s, 3H), 4.32 (s, 3H), 4.21 (s, 3H), 3.98 (d, *J*=17.6 Hz, 1H), 3.34 (d, *J*=17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 169.2, 157.0, 150.2, 147.9, 125.6, 107.1, 105.4, 70.6, 56.4, 56.2, 53.5, 38.2; FTIR (neat) 3022, 2112, 1749, 1707, 1592, 1505, 1464, 1439, 1320, 1275, 1133, 1104, 1051, 749, 668 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{13}H_{13}N_3Na_1O_5$ 314.0753, found 314.0768.

*4.3.6. Methyl 6-azido-5-oxo-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole-6-carboxylate (**2i**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1i** (95% yield, pale yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 1H), 6.82 (s, 1H), 6.11 (s, 2H), 3.80 (s, 3H), 3.54 (d, *J*=17.1 Hz, 1H), 2.89 (d, *J*=17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 169.0, 155.8, 150.2, 149.1, 127.3, 105.5, 103.5, 102.8, 70.6, 53.5, 38.3; FTIR (neat) 3020, 2360, 2112, 1749, 1713, 1473, 1319, 1268, 1216, 1040, 759, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_9N_3Na_1O_5$ 298.0440, found 298.0452.

*4.3.7. Methyl 2-azido-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2j**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1j** (99% yield, pale yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.50 (d, *J*=7.8 Hz, 1H), 7.35 (d, *J*=7.8 Hz, 1H), 3.79 (s, 3H), 3.66 (d, *J*=17.4 Hz, 1H), 2.98 (d, *J*=17.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 169.0, 149.4, 138.6, 137.8, 133.1, 126.1, 125.4, 70.5, 53.5, 38.1, 21.0; FTIR (neat) 3019, 2121, 1752, 1718, 1495, 1435, 1216, 1051, 753, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_{11}N_3Na_1O_3$ 268.0698, found 268.0652.

*4.3.8. Methyl 2-azido-5-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2k**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1k** (95% yield, yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J*=8.1 Hz, 1H), 7.27 (s, 1H), 7.25 (d, *J*=8.1 Hz, 1H), 3.79 (s, 3H), 3.62 (d, *J*=17.7 Hz, 1H), 2.98 (d, *J*=17.7 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 169.1, 152.5, 148.2, 130.6, 129.7, 126.7, 125.4, 70.3, 53.5, 38.3, 22.3; FTIR (neat) 3021, 2122, 1752, 1719, 1270, 1217, 758, 668 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_{11}N_3Na_1O_3$ 268.0698, found 268.0687.

*4.3.9. Methyl 2-azido-4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2l**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1l** (99% yield, pale yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J*=7.5 Hz, 1H), 7.49 (d, *J*=7.5 Hz, 1H), 7.37 (t, *J*=7.5 Hz, 1H), 3.81 (s, 3H), 3.56 (d, *J*=17.1 Hz, 1H), 2.92 (d, *J*=17.1 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 169.0, 151.0, 137.0, 135.8, 132.7, 128.6, 123.0, 70.0, 53.5, 37.5, 17.7; FTIR (neat) 3020, 2112, 1752, 1718, 1609, 1437, 1330, 1216, 1052, 752, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_{11}N_3Na_1O_3$ 268.0698, found 268.0686.

*4.3.10. 2-Azido-N-benzyl-1-oxo-2,3-dihydro-1H-indene-2-carboxamide (**2m**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1m** (95% yield, pale yellow solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J*=7.8 Hz, 1H), 7.70 (t, *J*=7.2 Hz, 1H), 7.52 (d, *J*=7.5 Hz, 1H), 7.45 (t, *J*=7.8 Hz, 1H), 7.39–7.27 (m, 5H), 7.10 (br, 1H), 4.51 (dd, *J*=15.0, 6.0 Hz, 1H), 4.45 (dd, *J*=15.0, 6.0 Hz, 1H), 4.05 (d, *J*=17.1 Hz, 1H), 3.26 (d, *J*=17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 166.2, 152.4, 137.2, 136.7, 133.3, 128.8, 128.4, 127.7, 127.6, 126.4, 125.4, 72.7, 44.0, 37.6; FTIR (neat) 3019, 2115, 1724, 1678, 1608, 1528, 1216, 759, 668 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{17}H_{14}N_4Na_1O_2$ 329.1014, found 329.1058.

*4.3.11. 2-Azido-N-methoxy-N-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxamide (**2n**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1n** (92% yield, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J*=7.2 Hz, 1H), 7.66 (t, *J*=7.2 Hz, 1H), 7.45 (t, *J*=7.2 Hz, 1H), 7.44 (d, *J*=7.2 Hz, 1H), 3.44 (d, *J*=17.1 Hz, 1H), 3.25 (s, 3H), 3.23 (s, 3H), 3.05 (d, *J*=17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 168.8, 150.8, 135.7, 133.6, 128.1, 126.4, 125.1, 71.6, 59.8, 38.4, 32.9; FTIR (neat) 2924, 2116, 1717, 1671, 1457, 986, 691 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_{12}N_4Na_1O_3$ 283.0807, found 283.0805.

*4.3.12. 2-Azido-2-(piperidine-1-carbonyl)-2,3-dihydro-1H-inden-1-one (**2o**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1o** (92% yield, white solid). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J*=7.6 Hz, 1H), 7.65 (td, *J*=7.6, 1.2 Hz, 1H), 7.44 (t, *J*=7.6 Hz, 1H), 3.75–3.25 (m, 4H), 3.47 (d, *J*=17.1 Hz, 1H), 3.14 (d, *J*=17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 165.7, 150.0, 136.0, 133.7, 128.5, 126.4, 125.5, 71.7, 38.6, 25.8, 24.4; FTIR (neat) 3015, 2944, 2861, 2107, 1724, 1636, 1443, 1216, 908, 759, 667 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{15}H_{16}N_4Na_1O_2$ 307.1171, found 307.1136.

*4.3.13. Methyl 2-azido-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2p**).* The title compound was synthesized according to the general procedure from β-dicarbonyl compound **1p** (84% yield, brown oil). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J*=7.8 Hz, 1H), 7.55 (t, *J*=7.5 Hz, 1H), 7.37 (t, *J*=7.5 Hz, 1H), 7.27 (d, *J*=7.5 Hz, 1H), 3.85 (s, 3H), 3.15 (ddd, *J*=16.8, 9.6, 4.8 Hz, 1H), 2.93 (dt, *J*=16.8, 4.8 Hz, 1H), 2.62 (ddd, *J*=14.8, 9.6, 4.8 Hz, 1H), 2.22 (dt, *J*=14.8, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 169.1, 143.4, 134.6, 129.9, 128.7, 128.6, 127.3, 70.9, 53.3, 31.4, 24.8; FTIR (neat) 3020, 2111, 1750, 1683, 1602, 1436, 1304, 1216, 1072, 754, 669 cm^{-1}; HRMS (ESI, M+Na) calcd for $C_{12}H_{11}N_3NaO_3$ 268.0698, found 268.0691.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.07.015.

References and notes

1. For reviews, see: (a) Uyanik, M.; Ishihara, K. *ChemCatChem* **2012**, *4*, 177; (b) *Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds*; Zhdankin, V. V., Ed.; John Wiley & Sons: Chichester, 2013; (c) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, 5769; (d) Wu, X. F.; Gong, J. L.; Qi, X. *Org. Biomol. Chem.* **2014**, *12*, 5807; (e) Liu, D.; Lei, A. *Chem.—Asian J.* **2015**, *10*, 806.
2. For selected example of C–O bond-forming reactions at α-positions of carbonyls, see: (a) Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K. *Science* **2010**, *328*, 1376; (b) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331 *Angew. Chem.* **2011**, *123*, 5443; (c) Wei, W.; Wang, Y.; Yin, J.; Xue, J.; Li, Y. *Org. Lett.* **2012**, *14*, 1158; (d) Wei, L.; Xue, J.; Liu, H.; Wang, W.; Li, Y. *Org. Lett.* **2012**, *14*, 5302; (e) Guo, S.; Yu, J. T.; Dai, Q.; Yang, H.; Cheng, J. *Chem. Commun.* **2014**, *50*, 6240; (f) Boominathan, S. S. K.; Hu, W. P.; Senadi, G. C.; Vandavasi, J. K.; Wang, J. J. *Chem. Commun.* **2014**, *50*, 6726; (g) Uyanik, M.; Hayashi, H.; Ishihara, K. *Science* **2014**, *345*, 291 Benzylic position, see; (h) Huang, J.; Li, L. T.; Li, H. Y.; Husan, E.; Wang, P.; Wang, B. *Chem. Commun.* **2012**, *48*, 10204; (i) Niu, L.; Yang, H.; Yang, D.; Fu, H. *Adv. Synth. Catal.* **2012**, *354*, 2211; (j) Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* **2013**, *49*, 3031; (k) Liu, L.; Yun, L.; Wang, Z.; Fu, X.; Yan, C. H. *Tetrahedron Lett.* **2013**, *54*, 5383 Other examples, see; (l) Chen, L.; Shi, E.; Liu, Z.; Chen, S.; Wei, W.; Li, H.; Xu, K.; Wan, X. *Chem.—Eur. J.* **2011**, *17*, 4085; (m) Xue, Q.; Xie, J.; Xu, P.; Hu, K.; Cheng, Y.; Zhu, C. *ACS Catal.* **2013**, *3*, 1365; (n) Yu, H.; Shen, J. *Org. Lett.* **2014**, *16*, 3204; (o) Xu, W.; Nachtsheim, B. *Org. Lett.* **2015**, *17*, 1585.
3. For selected example of C–N bond-forming reaction at the α-position of carbonyls, see: (a) Zhang, J.; Jiang, J.; Li, Y.; Zhao, Y.; Wan, X. *Org. Lett.* **2013**, *15*, 3222; (b) Lv, Y.; Li, Y.; Xiong, T.; Lu, Y.; Liu, Q.; Zhang, Q. *Chem. Commun.* **2014**, *50*, 2367 Benzylic position, see; (c) Xue, Q.; Xie, J.; Li, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2013**, *49*, 3700 Other examples, see; (d) Froehr, T.; Sindlinger, C. P.; Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *Org. Lett.* **2011**, *13*, 3754; (e) Yoshimura, A.; Middleton, K. R.; Zhu, C.; Nemykin, V. N.; Zhdankin, V. V. *Angew. Chem., Int. Ed.* **2012**, *51*, 8059; (f) Cai, Z. J.; Wang, S. Y.; Ji, S. J. *Org. Lett.* **2013**, *15*, 5226; (g) Wang, R.; Liu, H.; Yue, L.; Zhang, X.; Tan, Q.; Pan, R. *Tetrahedron Lett.* **2014**, *55*, 2233; (h) Zhang, X.; Wang, M.; Li, P.; Wang, L. *Chem. Commun.* **2014**, *50*, 8006.
4. For cycloaddition reactions, see: (a) Wong, Y. C.; Tseng, C. T.; Kao, T. T.; Yeh, Y. C.; Shia, K. S. *Org. Lett.* **2012**, *14*, 6024; (b) Xie, J.; Jiang, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2012**, *48*, 979; (c) Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *J. Org. Chem.* **2013**, *78*, 2751; (d) Yoshimura, A.; Zhu, C.; Middleton, K. R.; Todora, A. D.; Kastern, B. J.; Maskaev, A. V.; Zhdankin, V. V. *Chem. Commun.* **2013**, *49*, 4800; (e) Huang, H. M.; Li, Y. J.; Ye, Q.; Yu, W. B.; Han, L.; Jia, J. H.; Gao, J. R. *J. Org. Chem.* **2014**, *79*, 1084.
5. For C–C bond-forming reaction at the α-position of carbonyls, see: (a) Yasui, K.; Kato, T.; Kojima, K.; Nagasawa, K. *Chem. Commun.* **2015**, *51*, 2290 Benzylic position, see; (b) Rodrìguez, A.; Moran, W. J. *Org. Lett.* **2011**, *13*, 2220; (c) Nobuta, T.; Fujiya, A.; Yamaguchi, T.; Tada, N.; Miura, T.; Itoh, A. *RSC Adv.* **2013**, *3*, 10189; (d) Nobuta, T.; Tada, N.; Fujiya, A.; Kariya, A.; Miura, T.; Itoh, A. *Org. Lett.* **2013**, *15*, 574; (e) Dhineshkumar, J.; Lamani, M.; Alagiri, K.; Prabhu, K. R. *Org. Lett.* **2013**, *15*, 1092 The other example, see; (f) Zhang, C.; Liu, C.; Shao, Y.; Bao, X.; Wan, X. *Chem.—Eur. J.* **2013**, *19*, 17917.
6. Selected reviews, see: (a) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188; (b) *Organic Azides: Syntheses and Applications*; Bräse, S., Banert, K., Eds.; Wiley: Chichester, 2009; (c) Patonay, T.; Kónya, K.; Juhász-Tóth, É. *Chem. Soc. Rev.* **2011**, *40*, 2797.
7. Selected recent examples of α-azidation of β-dicarbonyl compounds, see: (a) Kashinath, D.; Budin, G.; Baati, R.; Meunier, S.; Wagner, A. *Tetrahedron Lett.* **2009**, *50*, 5379; (b) Shibatomi, K.; Soga, Y.; Narayama, A.; Fujisawa, I.; Iwasa, S. *J. Am. Chem. Soc.* **2012**, *134*, 9836; (c) Vita, M. V.; Waser, J. *Org. Lett.* **2013**, *15*, 3246; (d) Deng, Q.-H.; Bleith, T.; Wadepohl, H.; Gade, L. H. *J. Am. Chem. Soc.* **2013**, *135*, 5356; (e) Galligan, M. J.; Akula, R.; Ibrahim, H. *Org. Lett.* **2014**, *16*, 600.
8. (a) Harschneck, T.; Hummel, S.; Kirsch, S. F.; Klahn, P. *Chem.—Eur. J.* **2012**, *18*, 1187; (b) Dhineshkumar, J.; Prabhu, K. R. *Eur. J. Org. Chem.* **2016**, 447.

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