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1,8-二氮杂双环[5.4.0]十一碳-7-烯(DBU)驱动的双分子硝基烷烃对重氮化合物的亲核加成反应: 多官能化腙和四氢哒嗪化合物的合成

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摘要 以重氮化合物作为有效的端氮亲电试剂, 成功实现了 1,8-二氮杂双环[5.4.0]十一碳-7-烯(DBU)驱动的两分子硝基烷烃对重氮化合物分子间的亲核加成反应. 该反应从易得的起始原料出发, 提供了两种在温和反应条件下一步构建含有硝基烷烃基本结构单元的官能化腙和四氢哒嗪类化合物的新方法. 该反应涉及连续的分子间亲核加成/消除/分子间 Aza-Henry 反应/分子内环化反应过程, 一步产生两个或三个相邻的立体中心.

关键词 重氮化合物; 端氮亲电试剂; 硝基烷烃; 腙; 四氢哒嗪

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-Promoted Nucleophilic Addition of Two Molecules of Nitroalkanes to Diazo Compounds: Synthesis of Highly Functionalized Hydrazones and Tetrahydropyridazines

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Abstract A 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-promoted intermolecular addition reaction two molecules of nitroalkanes to diazo compounds has been developed, in which diazo compounds sereve as the efficient N-terminal electrophiles. The reaction provides two new and highly efficient methods for the construction of functionalized hydrazones and tetrahydropyridazines bearing the structure feature of nitroalkanes from readily available starting materials. The reaction involves a sequential intermolecular nucleophilic addition/elimination/intermolecular Aza-Henry reaction/intramolecular cyclization procedure where two or three adjacent stereocenters are created simultaneously in one-pot manner.

Keywords diazo compound; N-terminal electrophile; nitroalkane; hydrazone; tetrahydropyridazine

1 Introduction

The hydrazone skeleton is a privileged structure frequently present in a wide range of bioactive molecules.[1] Furthermore, hydrazone derivatives are also employed as valuable and versatile building blocks participating in a variety of useful transformations such as radical reactions, cycloadditions and transition-metalcatalyzed reactions.[2] On the other hand, nitroalkanes represent an important class of useful molecules in organic synthesis.[3] Not only the nitro group can be converted into a range of other functionalities, but nitroalkanes also participate in the generation of new C—C bonds mainly via Michael, Henry, nitro-Mannich, and transition-metal-catalyzed allylation and arylation reactions.[3-4] As a consequence, combination of these two structural features within a single framework gives novel nitroalkane featured hydrazones, which is likely to be more important intermediates for organic synthesis. Although various methods for the synthesis of hydrazones[5] and nitroalkanes[6] have been developed, to the best of our

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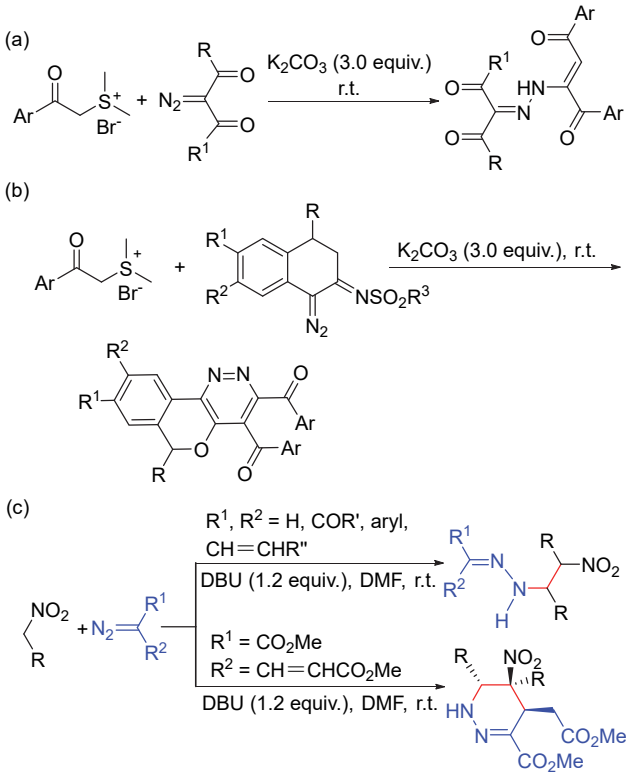
knowledge, the method for synthesis of hydrazones bearing the structure feature of nitroalkanes has never been reported.

Diazo compounds are highly useful building blocks that have been extensively applied in organic chemistry.[7] In contrast to the vast majority of studies focused on the metal carbene precursors,[8] 1,3-dipoles,[9] and C-nucleophiles,[10] the utility of the electrophilic nature for the terminal nitrogen of diazo compounds has scarcely been explored.[11-15] Recently, our group[12] and other groups[13] independently reported the intermolecular nucleophilic addition of one molecule of active methylene compounds to diazo compound as the N-terminal electrophiles. In 2019, Xu and co-workers[14] reported a based-promoted intermolecular nucleophilic addition of two molecules of dimethylsulfonium ylides to *α*-diazo-*β*-ketoesters/ketones to produce the corresponding functionalized hydrazones (Scheme 1, a). Very recently, the intermolecular domino cyclization of two dimethylsulfonium ylides with 4-diazoisochoman-3-imines as *N*-terminal electrophiles was developed for the synthesis of functionalized isochromeno[4,3-*c*]pyridazines by Wang and co-workers[15] (Scheme 1, b). As part of our research on carbon-carbon and carbon-nitrogen bond-forming reactions,[12,16] herein we reported a 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)-promoted intermolecular nucleophilic addition of two molecules of nitroalkanes to diazo compounds (Scheme 1, c). The reaction works with a broad range of various diazo compounds and provides two new and highly efficient methods for the construction of various functionalized hydrazones and tetrahydropyridazines



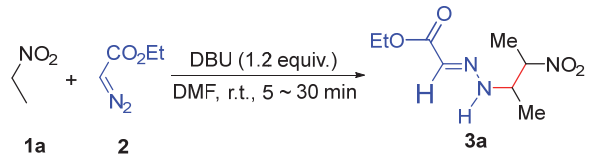
Scheme 1 Nucleophilic addition of two molecules of active methylene compounds to diazo compounds

bearing the structure feature of nitroalkanes where up to three adjacent stereocenters are created simultaneously in one-pot manner under rather mild conditions (Scheme 1, c).

2 Results and discussion

Initially, the model reaction of nitroethane (**1a**) with ethyl diazoacetate (EDA, **2a**) was examined to optimize the reaction conditions (Table 1). It was found that the reaction of **1a** (0.4 mmol) with EDA (**2a**, 0.2 mmol) proceeded very rapidly at room temperature in the presence of DBU (1.2 equiv.) to give (*E*)-hydrazone **3a** in 80% yield (Entry 3). The yield of **3a** increased up to 92% by raising the ratio of **1a**/**2a** to 4∶1 under otherwise identical conditions as above (Entry 5). Decreasing the amount of DBU and the ratio of **1a**/**2a** led to lower yields of **3a** (Entries 1, 2 and 4). In addition, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) was also an efficient catalyst although affording **3a** in relatively lower yield (Entry 7). However, other bases, such as triethylamine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and Cs_2CO_3 were entirely ineffective (Entries 8～10). Among the solvents tested, *N*,*N*-dimethylformamide (DMF) turned out to be the best choice. Other solvents, such as dimethyl sulfoxide (DMSO), acetonitrile, tetrahydrofuran (THF) and 1,2-dichloroethane (DCE) gave lower yields (Entries 11～14).

Table 1 Optimization of reaction conditions[a]



1a 2 3a

Entry	Base (equiv.)	1a∶2a	Solvent	*t*/min	Yield[b]/%	*dr*
1	DBU (0.5)	2∶1	DMF	20	60	1/1
2	DBU (0.8)	2∶1	DMF	20	75	1/1
3	DBU (1.2)	2∶1	DMF	10	80	1/1
4	DBU (1.2)	3∶1	DMF	8	86	1/1
5	DBU (1.2)	4∶1	DMF	5	92	1/1
6	DBU (1.2)	4∶1	DMF	20	75	1/1.1[c]
7	DBN (1.2)	4∶1	DMF	10	88	1/1
8	Et_3N (1.2)	4∶1	DMF	40	—	—
9	TMEDA (1.2)	4∶1	DMF	40	—	—
10	K_2CO_3 (1.2)	4∶1	DMF	40	—	—
11	DBU (1.2)	4∶1	DMSO	5	80	1/1
12	DBU (1.2)	4∶1	MeCN	60	71	1/1
13	DBU (1.2)	4∶1	THF	60	65	1/1.1
14	DBU (1.2)	4∶1	DCE	60	50	1/1.1

[a] Reaction conditions: **1a** (0.4～0.8 mmol), **2a** (0.2 mmol), base (0.10～0.24 mmol), solvent (1.0 mL), at room temperature for 5～60 min. [b] Isolated yield. [c] The reaction was performed at 0 ℃.

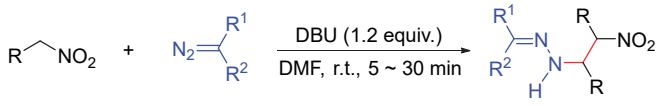
With the optimal conditions in hand, the scope of this domino reaction was examined with respect to the diazo compounds and nitroalkanes, and the results are shown in Table 2. The domino reaction showed broad tolerance for various diazo compounds. All selected *α*-diazocarbonyl compounds **2b**～**2f** bearing alkoxy carbonyl groups reacted

rapidly with nitroethane (**1a**) to give the corresponding (*E*)-hydrazones **3a**～**3f** in good to high yields within 30 min. The exclusive (*E*)-selectivity can be rationalized by the less steric repulsion between the hydrogen atom and the *N*-alkyl substituent, and the (*E*)-configuration of **3b** was further determined by X-ray crystallography.[17] In addition, when *α*-diazocarbonyl compounds **2g**～**2j** bearing aroyl groups (with either an electron-donating or electron-withdrawing group on the benzene ring) were employed as the N-terminal electrophile, the desired (*Z*)-hydrazones **3g**～**3j** were produced as main products in high yields. Notably, even in the case of *α*,*α*-disubstituted diazocarbonyl compounds **2k**～**2q**, the addition reaction also worked well, yielding the desired hydrazones **3k**～**3q** in good to high yields. The predominant or exclusive (*Z*)-selectivity of **3g**～**3j** and **3l**～**3q** can be explained by intramolecular hydrogen bonding, which was confirmed by ^{1}H NMR spectroscopy. More importantly, diaryldiazomethanes **2r**～**2t** also underwent the addition reaction with **1a** to give the desired hydrazones **3r**～**3t** in good to high yields. Besides nitroethane, 1-nitropropane (**1b**) and (nitromethyl)benzene (**1c**) also smoothly underwent this transformation, the corresponding (*E*)-products **3u** and **3v** were generated in 92% and 55% yields, respectively (Table 2).

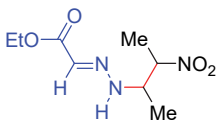
On the basis of the above experimental results together with the consideration of the structural feature of products **3**, we reasoned that the tetrahydropyridazines **4** could be constructed via the intramolecular cyclization of hydrazone intermediate generated *in situ* from the addition reaction of two molecules of nitroalkanes **1** to alkenyldiazoacetate **2w** under suitable reaction conditions. As expected, the desired tetrahydropyridazines **4a** and **4b** were obtained in 85% and 86% yields from **1a** or **1b** with **2w** under the optimized reaction conditions, respectively (Scheme 2).[18] According to ^{1}H NMR and ^{13}C NMR of **4a** and **4b**, the domino reaction proceeded with excellent diastereoselectivity and simultaneously set three adjacent stereocenters. Undoubtedly, the above reaction not only demonstrated the wide scope for diazo compounds, but also provided a simple and efficient one-step access to tetrahydropyridazine derivatives.[19]

In addition, we found that the domino addition reaction of 1-nitropropane (**1b**) with EDA (**2a**) is easy to scale-up. A gram-scale reaction of 3.56 g of **1b** and 1.14 g of **2a** was carried out for 2 h under otherwise identical conditions as

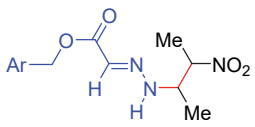
Table 2 DBU-Mediated nucleophilic addition reaction of nitroethanes **1** with diazo compounds[a,b,c]



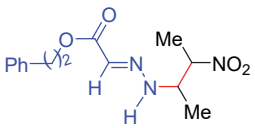
1 **2** **3a ~ 3v**



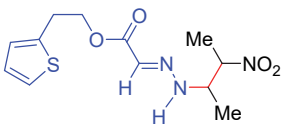
3a, 92%, *dr* 1/1



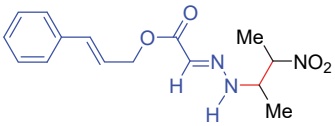
3b, Ar = C_6H_4Cl-*p*, 71%, *dr* 1.2/1
3c, Ar = C_6H_4OMe-*p*, 57%, *dr* 1/1



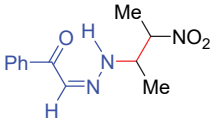
3d, 67%, *dr* 1.5/1



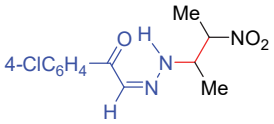
3e, 63%, *dr* 0.73/1



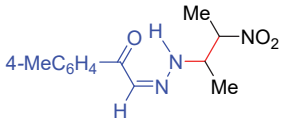
3f, 83%, *dr* 1/1



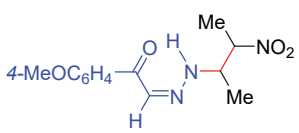
3g, 85%, *dr* 1/1
Z:*E* 8:1



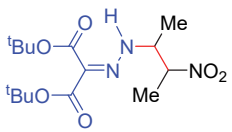
3h, 87%, *dr* 1/1
Z:*E* 7:1



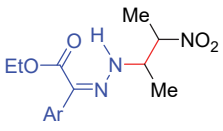
3i, 72%, *dr* 1/1
Z:*E* 4:1



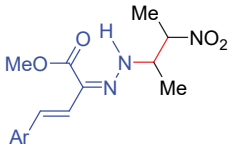
3j, 55%, *dr* 1/1
Z:*E* 7:1



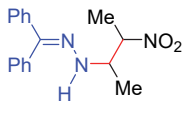
3k, 83%, *dr* 1/1



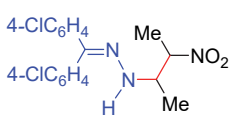
3l, Ar = Ph, 70%, *dr* 1/1
3m, Ar = C_6H_4Cl-*p*, 73%, *dr* 0.86/1
3n, Ar = C_6H_4Br-*p*, 67%, *dr* 1/1



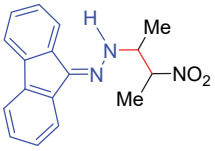
3o, Ar = C_6H_5, 81%, *dr* 1/1
3p, Ar = C_6H_4Cl-*p*, 66%, *dr* 1.2/1
3q, Ar = C_6H_4OMe-*p*, 87%, *dr* 1.2/1



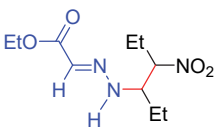
3r, 50%, *dr* 8/1



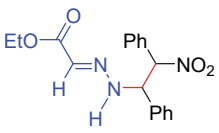
3s, 55%, *dr* 3/1



3t, 92%, *dr* 1.2/1

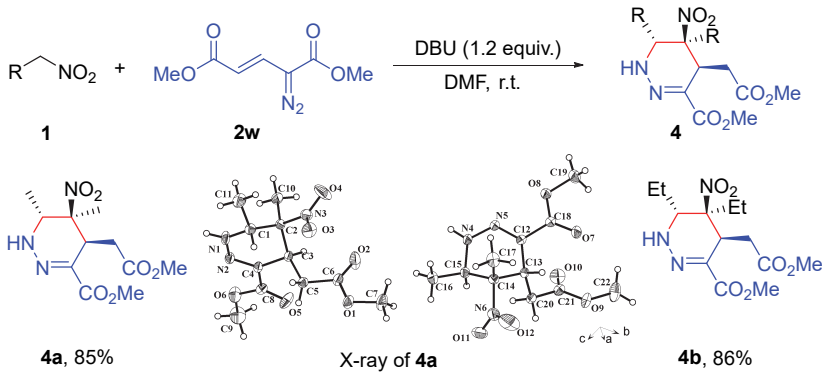


3u, 92%, *dr* 1/1



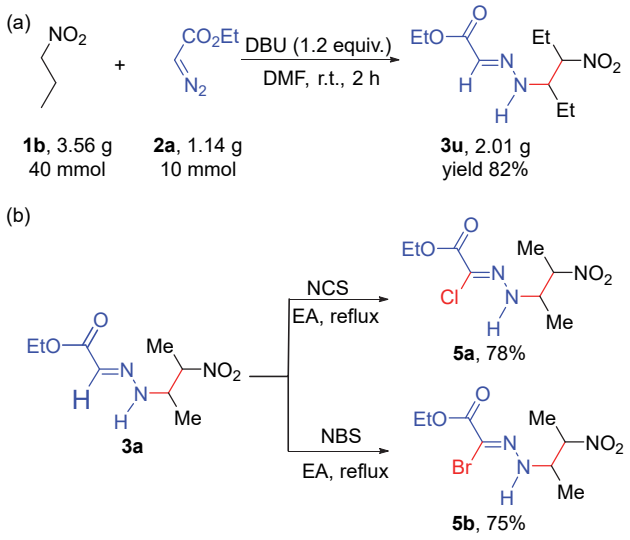
3v, 55%, *dr* 3/1

[a] Reaction conditions: **1** (0.8 mmol), **2** (0.2 mmol), DBU (0.24 mmol), DMF (1.0 mL), at room temperature, 5～30 min. [b] Isolated yield. [c] Diastereomeric ratios were determined by the ^{1}H NMR spectra of **3**.



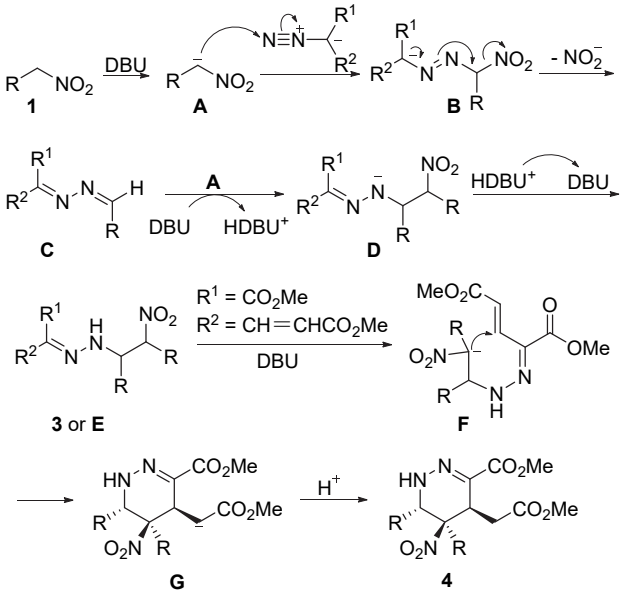
Scheme 2 DBU-Mediated domino cyclization of nitroethanes **1** with alkenyldiazoacetate **2w**

above, furnishing 2.01 g of the desired product **3u** in 82% yield (Scheme 3, a). In addition, the further transformation of product **3** was investigated. It was found that the halogenation reaction of **3a** (0.2 mmol) with *N*-chlorosuccinimide (NCS, 0.6 mmol) or *N*-bromosuccinimide (NBS, 0.6 mmol) in ethyl acetate under reflux condition for 3 h could easily proceed to give the halogenated hydrazones **5a** and **5b** in 78% and 75% yields, respectively (Scheme 3, b).



Scheme 3 Scale-up synthesis of **3u** and transformation of **3a**

On the basis of the above experimental results together with related reports,[11-14] a possible mechanism for the formation of **3** and **4** is proposed in Scheme 4. Initially, the intermediate **A**, generated by the deprotonation of nitroalkanes **1** in the presence of DBU, attacks the terminal nitrogen of diazo compounds **2** to generate intermediate **B**, which eliminates a nitrous acid under basic conditions to generate intermediate **C**. Subsequently, intermediate **C** was trapped by the second molecule of intermediate **A** to give intermediate **D**, followed by the protonation to produce products **3** (Scheme 4). When alkenyldiazoacetate **2w** was employed as the N-terminal electrophile, the intermediate **E** undergoes a deprotonation to form intermediate **F**, which undergoes an intramolecular Michael addition to produce intermediate **G**, followed by the protonation to give the tetrahydropyridazines **4** (Scheme 4).



Scheme 4 Proposed mechanisms for the formation of **3** and **4**

3 Conclusions

In conclusion, a DBU-promoted intermolecular addition reaction two molecules of nitroalkanes to diazo compound was developed, in which diazo compounds sereved as the efficient N-terminal electrophiles. The reaction provides two new and highly efficient methods for the construction of functionalized hydrazones and tetrahydropyridazines bearing the structure feature of nitroalkanes. The transformation involves a sequential intermolecular nucleophilic addition/elimination/intermolecular Aza-Henry reaction/intramolecular cyclization procedure where up to three adjacent stereocenters are created simultaneously in one-pot manner. These reactions feature readily available starting materials, mild conditions, one-pot procedure, broad substrate scope, and good functional group tolerance. Further work on the applications of diazo compound is currently under investigation in our laboratory.

4 Experimental section

4.1 General information

All reagents were commercial and used without further purification. Chromatography was carried on flash silica gel or aluminium oxide (200～300 mesh). All reactions were monitored by thin-layer chromatography (TLC), which was performed on percolated aluminum sheets of silica gel 60 (F254). Melting points were tested in an X-4A instrument without correcting temperature. Unless noted, the ^{1}H NMR spectra were recorded at 400, 500 or 600 MHz in $CDCl_3$ or DMSO-d_6, and the ^{13}C NMR spectra were recorded at 101, 126 or 151 MHz in $CDCl_3$ with TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

4.2 General procedures for the preparation of **3**

Taking synthesis of **3a** as example, to a solution of **1a** (0.8 mmol, 57.2 μL) and ethyl diazoacetate (EDA, **2a**) (0.2 mmol, 21.0 μL) in DMF (1.0 mL) was added DBU in one portion (0.24 mmol, 35.8 μL). The reaction mixture was stirred at room temperature for 5 min. After **2a** was consumed (monitored by TLC), the reaction mixture was poured into brine (30 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by aluminium oxide, basic (200～300 mesh) chromatography (acetone/petroleum ether, V∶V=1∶50) to give **3a** (40.0 mg, 92%) as a yellow liquid.

Ethyl (*E*)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)-acetate (**3a**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow liquid (40.0 mg, 92%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.00 (s, 1H), 6.95 (d, J=6.1 Hz, 1H), 4.85～4.80 (m, 1H), 4.30～4.26 (m, 2H), 4.09～4.04 (m, 1H), 1.61～1.56 (m, 3H), 1.35～1.30 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.98, 126.17, 85.92, 60.60, 57.44, 15.83, 15.14, 14.16; HRMS (ESI-TOF) calcd for $C_8H_{15}N_3O_4Na$ $[M+Na]^+$ 240.0955, found 240.0948. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.97 (s, 1H), 6.90 (d, J=6.9 Hz, 1H), 4.80～4.76 (m, 1H), 4.26～4.23 (m, 2H), 4.02～3.97 (m, 1H), 1.56～1.54 (m, 3H), 1.30～1.23 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.92, 125.39, 85.38, 60.53, 56.82, 15.62, 15.14, 13.89; HRMS (ESI-TOF) calcd for $C_8H_{15}N_3O_4Na$ $[M+Na]^+$ 240.0955, found 240.0948.

4-Chlorobenzyl (*E*)-2-(2-(3-nitrobutan-2-yl)hydrazine-ylidene)acetate (**3b**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1.2∶1; yellow solid (44.6 mg, 71%). **Isomer 1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (d, J=7.5 Hz, 4H), 7.00 (s, 1H), 6.98～6.95 (m, 1H), 5.20 (s, 2H), 4.81～4.77 (m, 1H), 4.06～4.00 (m, 1H), 1.56～1.53 (m, 3H), 1.27 (d, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.68, 134.32, 133.99, 129.60, 128.58, 125.22, 85.99, 65.39, 57.47, 15.96, 15.00; HRMS (ESI-TOF) calcd for $C_{13}H_{16}ClN_3O_4Na$ $[M+Na]^+$ 336.0722, found 336.0724. **Isomer 2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (d, J=7.5 Hz, 4H), 6.99 (s, 1H), 6.94～6.93 (m, 1H), 5.19 (s, 2H), 4.76～4.73 (m, 1H), 4.00～3.95 (m, 1H), 1.53～1.50 (m, 3H), 1.23 (d, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.62, 134.27, 133.96, 129.56, 128.58, 124.47, 85.32, 65.32, 56.95, 15.83, 13.86; HRMS (ESI-TOF) calcd for $C_{13}H_{16}ClN_3O_4Na$ $[M+Na]^+$ 336.0722, found 336.0724.

4-Methoxybenzyl (*E*)-2-(2-(3-nitrobutan-2-yl)hydra-zineylidene)acetate (**3c**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow solid (35.3 mg, 57%). **Isomer 1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25 (s, 1H), 7.24 (s, 1H), 6.91～6.82 (m, 4H), 5.09 (s, 2H), 4.71～4.67 (m, 1H), 3.96～3.90 (m, 1H), 3.71 (s, 3H), 1.46～1.43 (m, 3H), 1.16 (d, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.84, 159.51, 130.13, 127.84, 125.69, 113.77, 85.88, 66.08, 57.43, 55.13, 15.86, 15.10; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_3O_5Na$ $[M+Na]^+$ 332.1217, found 332.1222. **Isomer 2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25 (s, 1H), 7.23 (s, 1H), 6.81～6.75 (m, 4H), 5.08 (s, 2H), 4.66～4.64 (m, 1H), 3.89～3.85 (m, 1H), 3.71 (s, 3H), 1.43～1.42 (m, 3H), 1.12 (d, J=6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.78, 159.49, 130.10, 127.80, 124.89, 113.77, 85.33, 66.01, 56.84, 55.13, 15.68, 13.82; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_3O_5Na$ $[M+Na]^+$ 332.1217, found 332.1222.

Benzyl (*E*)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)-acetate (**3d**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1.5∶1; yellow liquid (39.3 mg, 67%). **Isomer 1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31～7.28 (m, 2H), 7.24～7.21 (m, 3H), 7.02 (d, J=6.0 Hz, 1H), 6.95 (s, 1H), 4.82～4.75 (m, 1H), 4.44～4.38 (m, 2H), 4.08～3.99 (m, 1H), 3.00～2.98 (m, 2H), 1.53～1.52 (m, 3H), 1.25 (d, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.86, 137.52, 128.75, 126.35, 125.46, 124.82, 85.85, 64.91, 57.35, 34.90, 15.69, 15.00; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 316.1268, found 316.1257. **Isomer 2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28～7.26 (m, 2H), 7.21～7.18 (m, 3H), 6.99 (d, J=6.5 Hz, 1H), 6.92 (s, 1H), 4.75～4.70 (m, 1H), 4.38～4.34 (m, 2H), 3.99～3.89 (m, 1H), 2.98～2.95 (m, 2H), 1.52～1.50 (m, 3H), 1.22 (d, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.82, 137.49, 128.27, 126.35, 125.46, 124.82, 85.38, 64.86, 56.83, 34.90, 15.54, 13.98; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 316.1268, found 316.1257.

2-(Thiophen-2-yl)ethyl (*E*)-2-(2-(3-nitrobutan-2-yl)-hydrazineylidene)acetate (**3e**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 0.73∶1; yellow liquid (37.7 mg, 63%). **Isomer 1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.16 (s, 1H), 7.00～6.95 (m, 2H), 6.88 (s, 1H), 6.83 (d, J=6.1 Hz, 1H), 4.84～4.80 (m, 1H), 4.45～4.43 (m, 2H), 4.08～4.01 (m, 1H), 3.23～3.21 (m, 2H), 1.58～1.56 (m, 3H), 1.30 (d, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.70, 139.65, 126.81, 125.88, 125.02, 123.95, 86.08, 64.79, 57.56, 29.22, 16.09, 15.16; HRMS (ESI-TOF) calcd for $C_{12}H_{17}N_3O_4SNa$ $[M+Na]^+$ 322.0832, found 322.0829. **Isomer 2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.15 (s, 1H), 6.95～6.90 (m, 2H), 6.88 (s, 1H),

6.78 (d, J=6.8 Hz, 1H), 4.80～4.75 (m, 1H), 4.43～4.38 (m, 2H), 4.00～3.95 (m, 1H), 3.21～3.18 (m, 2H), 1.56～1.53 (m, 3H), 1.25 (d, J=6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.63, 139.61, 126.81, 125.55, 125.02, 123.95, 85.36, 64.72, 56.98, 29.22, 15.91, 13.87; HRMS (ESI-TOF) calcd for $C_{12}H_{17}N_3O_4SNa$ [M + Na]$^+$ 322.0832, found 322.0829.

Cinnamyl (*E*)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)-acetate (**3f**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow solid (50.7 mg, 83%). **Isomer 1**: ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.05 (d, J=2.2 Hz, 1H), 7.47 (s, 2H), 7.34 (t, J=7.5 Hz, 2H), 7.26 (t, J=7.3 Hz, 1H), 7.00 (s, 1H), 6.71 (s, 1H), 6.42～6.39 (m, 1H), 4.84～4.81 (m, 1H), 4.77 (s, 2H), 4.10～4.03 (m, 1H), 1.44 (d, J=3.7 Hz, 3H), 1.17 (d, J=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.74, 136.03, 128.48, 126.51, 125.81, 122.88, 85.99, 85.34, 65.21, 57.50, 15.97, 15.12, 13.80; HRMS (ESI-TOF) calcd for $C_{15}H_{19}N_3O_4Na$ [M+Na]$^+$ 328.1268, found 328.1257. **Isomer 2**: ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.03 (d, J=2.1 Hz, 1H), 7.45 (s, 2H), 7.34 (t, J=7.5 Hz, 2H), 7.26 (t, J=7.3 Hz, 1H), 6.99 (s, 1H), 6.67 (s, 1H), 6.39～6.35 (m, 1H), 4.81～4.78 (m, 1H), 4.76 (s, 2H), 4.00～3.93 (m, 1H), 1.42 (d, J=3.7 Hz, 3H), 1.14 (d, J=6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.67, 134.40, 127.98, 126.51, 124.87, 122.88, 85.92, 85.26, 65.13, 56.90, 15.81, 15.12, 13.77; HRMS (ESI-TOF) calcd for $C_{15}H_{19}N_3O_4Na$ [M + Na]$^+$ 328.1268, found 328.1257.

(*Z*)-2-(2-(3-Nitrobutan-2-yl)hydrazineylidene)-1-phenylethan-1-one (**3g**) and (*E*)-2-(2-(3-nnitrobutan-2-yl)hydrazineylidene)-1-phenylethan-1-one (**3g'**): According to the ^{1}H NMR, the ratio of *Z*/*E* (**3g**/**3g'**) was approximately 8∶1; according to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow liquid (42.4 mg, 85%). **Isomer 1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.64 (s, 1H), 7.83～7.82 (m, 2H), 7.50～7.44 (m, 2H), 7.38～7.35 (m, 2H), 4.78～4.70 (m, 1H), 4.08～4.04 (m, 1H), 1.46 (d, J=6.8 Hz, 3H), 1.26 (t, J=7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 185.79, 137.01, 132.53, 128.57, 127.81, 121.89, 86.07, 58.59, 15.61, 15.30; HRMS (ESI-TOF) calcd for $C_{12}H_{15}N_3O_3Na$ [M + Na]$^+$ 272.1006, found 272.1010. **Isomer 2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.64 (s, 1H), 7.82～7.79 (m, 2H), 7.44～7.41 (m, 2H), 7.35～7.30 (m, 2H), 4.68～4.60 (m, 1H), 4.04～4.98 (m, 1H), 1.46 (d, J=6.8 Hz, 3H), 1.26 (t, J=7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 185.75, 136.98, 132.48, 128.54, 127.73, 121.77, 85.91, 57.20, 15.50, 15.30; HRMS (ESI-TOF) calcd for $C_{12}H_{15}N_3O_3Na$ [M+Na]$^+$ 272.1006, found 272.1010.

(*Z*)-1-(4-Chlorophenyl)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)ethan-1-one (**3h**) and (*E*)-1-(4-chlorophenyl)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)ethan-1-one (**3h'**): According to the ^{1}H NMR, the ratio of *Z*/*E* (**3h**/**3h'**) was approximately 7∶1 and the diastereomeric ratios were approximately 1∶1; yellow liquid (49.4 mg, 87%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.77～12.74 (m, 1H), 7.89～7.86 (m, 2H), 7.50 (s, 1H), 7.45～7.43 (m, 2H), 4.88～4.82 (m, 1H), 4.22～4.15 (m, 1H), 1.59 (d, J=3.4 Hz, 3H), 1.38 (t, J=7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 184.43, 138.99, 135.42, 131.15, 129.21, 121.49, 86.13, 58.90, 16.19, 15.49; HRMS (ESI-TOF) calcd for $C_{12}H_{14}ClN_3O_3Na$ [M + Na]$^+$ 306.0616, found 306.0612. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.77～12.74 (m, 1H), 7.86～7.84 (m, 2H), 7.49 (s, 1H), 7.43～7.41 (m, 2H), 4.77～4.71 (m, 1H), 4.15～4.11 (m, 1H), 1.58 (d, J=3.3 Hz, 3H), 1.38 (t, J=7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 184.38, 138.93, 135.39, 131.09, 128.16, 121.36, 85.91, 58.74, 57.37, 15.65, 14.68; HRMS (ESI-TOF) calcd for $C_{12}H_{14}ClN_3O_3Na$ [M + Na]$^+$ 306.0616, found 306.0612.

(*Z*)-2-(2-(3-Nitrobutan-2-yl)hydrazineylidene)-1-(*p*-tolyl)ethan-1-one (**3i**) and (*E*)-2-(2-(3-nitrobutan-2-yl)-hydrazineylidene)-1-(*p*-tolyl)ethan-1-one (**3i'**): According to the ^{1}H NMR, the ratio of *Z*/*E* (**3i**/**3i'**) was approximately 4∶1 and the diastereomeric ratios were approximately 1∶1; yellow liquid (37.9 mg, 72%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.71 (s, 1H), 7.86～7.83 (m, 2H), 7.53 (s, 1H), 7.28～7.25 (m, 2H), 4.86～4.81 (m, 1H), 4.18～4.14 (m, 1H), 2.40 (s, 3H), 1.59～1.56 (m, 3H), 1.37 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 185.65, 143.44, 134.47, 129.32, 127.88, 121.99, 86.09, 58.75, 21.48, 15.71, 15.25; HRMS (ESI-TOF) calcd for $C_{13}H_{17}N_3O_3Na$ [M+Na]$^+$ 286.1162, found 286.1166. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.71 (s, 1H), 7.83～7.79 (m, 2H), 7.52 (s, 1H), 7.25～7.22 (m, 2H), 4.77～4.71 (m, 1H), 4.14～4.10 (m, 1H), 2.40 (s, 3H), 1.56～1.53 (m, 3H), 1.35 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 185.60, 143.37, 134.44, 129.29, 127.88, 121.87, 86.00, 58.55, 21.48, 15.48, 14.70; HRMS (ESI-TOF) calcd for $C_{13}H_{17}N_3O_3Na$ [M+Na]$^+$ 286.1162, found 286.1166.

(*Z*)-1-(4-Methoxyphenyl)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)ethan-1-one (**3j**) and (*E*)-1-(4-methoxyphenyl)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)ethan-1-one (**3j'**): According to the ^{1}H NMR, the ratio of *Z*/*E* (**3j**/**3j'**) was approximately 7∶1 and the diastereomeric ratios were approximately 1∶1; yellow solid (30.7 mg, 55%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.65 (s, 1H), 7.98～7.93 (m, 2H), 7.52 (s, 1H), 6.97～6.95 (m, 2H), 4.87～4.80 (m, 1H), 4.16～4.13 (m, 1H), 3.88 (s, 3H), 1.58 (d, J=3.2 Hz, 3H), 1.37 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 184.90, 163.30, 130.16, 122.02, 113.99, 86.16, 58.83, 55.44, 15.89, 15.24; HRMS (ESI-TOF) calcd for $C_{13}H_{17}N_3O_4Na$ [M + Na]$^+$ 302.1111, found 302.1118. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.65 (s, 1H), 7.93～7.90 (m, 2H), 7.51 (s, 1H), 6.95～6.93 (m, 2H), 4.75～4.70 (m, 1H), 4.13～4.10 (m, 1H), 3.87 (s, 3H), 1.57 (d, J=3.2 Hz, 3H), 1.35 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 184.85, 163.26, 130.16, 121.89, 113.97, 86.16, 58.56 , 55.44, 15.52, 14.92; HRMS (ESI-TOF) calcd for $C_{13}H_{17}N_3O_4Na$ [M+Na]$^+$ 302.1111, found 302.1118.

Di-*tert*-butyl 2-(2-(3-nitrobutan-2-yl)hydrazineylidene)-malonate (**3k**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow liquid (57.3 mg, 83%). **Isomer 1**: ^{1}HNMR (600 MHz, $CDCl_3$) δ: 10.70～10.68 (m, 1H), 4.85～4.77 (m, 1H), 4.18～4.10 (m,

1H), 1.58～1.57 (m, 3H), 1.55～1.52 (m, 18H), 1.35～1.34 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.13, 162.12, 123.66, 85.87, 82.55, 81.22, 58.87, 28.10, 15.68, 15.27; HRMS (ESI-TOF) calcd for $C_{15}H_{27}N_3O_6Na$ $[M+Na]^+$ 368.1792, found 368.1790. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.66～10.65 (m, 1H), 4.77～4.72 (m, 1H), 4.10～4.03 (m, 1H), 1.57～1.56 (m, 3H), 1.52～1.51 (m, 18H), 1.34～1.32 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.09, 162.12, 123.53, 85.87, 82.50, 81.17, 58.44, 28.00, 15.41, 14.95; HRMS (ESI-TOF) calcd for $C_{15}H_{27}N_3O_6Na$ $[M+Na]^+$ 368.1792, found 368.1790.

Ethyl (*Z*)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)-2-phenylacetate (**3l**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow liquid (41.1 mg, 70%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.51 (d, J=4.8 Hz, 1H), 7.52～7.51 (m, 2H), 7.32 (t, J=7.5 Hz, 2H), 7.29～7.26 (m, 1H), 4.88～4.82 (m, 1H), 4.32～4.28 (m, 2H), 4.13～4.10 (m, 1H), 1.55 (d, J=2.2 Hz, 3H), 1.35～1.31 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.25, 136.51, 128.17, 127.68, 127.21, 86.29, 60.66, 58.42, 15.71, 15.47, 14.78, 14.03; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 316.1268, found 316.1278. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.48 (d, J=5.2 Hz, 1H), 7.50～7.49 (m, 2H), 7.32 (t, J=7.5 Hz, 2H), 7.26～7.23 (m, 1H), 4.82～4.72 (m, 1H), 4.28～4.25 (m, 2H), 4.10～4.07 (m, 1H), 1.54 (d, J=2.2 Hz, 3H), 1.31～1.28 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.24, 136.43, 128.14, 127.65, 127.16, 86.07, 60.61, 58.14, 15.71, 15.36, 14.78, 14.03; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 316.1268, found 316.1278.

Ethyl (*Z*)-2-(4-chlorophenyl)-2-(2-(3-nitrobutan-2-yl)-hydrazineylidene)acetate (**3m**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 0.86∶1; yellow liquid (47.9 mg, 73%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ:10.59 (d, J=5.2 Hz, 1H), 7.46 (d, J=7.5 Hz, 2H) 7.29 (t, J=7.5 Hz, 2H), 4.89～4.80 (m, 1H),4.32～4.29 (m, 2H), 4.16～4.12 (m, 1H), 1.56 (d, J=4.0 Hz, 3H), 1.36～1.33 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.02, 135.02, 133.00, 129.46, 127.83, 126.63, 86.38, 60.81, 58.48,15.84, 15.58, 14.54; HRMS (ESI-TOF) calcd for $C_{14}H_{18}ClN_3O_4Na$ $[M+Na]^+$ 350.0878, found 350.0886. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.56 (d, J=5.4 Hz, 1H), 7.45 (d, J=7.5 Hz, 2H), 7.28 (d, J=7.5 Hz, 2H), 4.77～4.71 (m, 1H), 4.29～4.26 (m, 2H), 4.10～4.07 (m,1H), 1.55 (d, J=4.0 Hz, 3H), 1.33～1.29 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 162.99, 134.93, 132.94, 129.42, 127.80, 126.44, 85.98, 60.77, 58.27, 15.84, 15.47, 14.04; HRMS (ESI-TOF) calcd for $C_{14}H_{18}ClN_3O_4Na$ $[M+Na]^+$ 350.0878, found 350.0886.

Ethyl (*Z*)-2-(4-bromophenyl)-2-(2-(3-nitrobutan-2-yl)-hydrazineylidene)acetate (**3n**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; colorless liquid (49.9 mg, 67%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.61 (d, J=5.2 Hz, 1H), 7.50～7.42 (m, 4H), 4.84～4.80 (m, 1H), 4.32～4.29 (m, 2H), 4.16～4.11 (m, 1H), 1.58～1.55 (m, 3H), 1.36～1.33 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 162.96, 135.47, 130.77, 129.76, 126.62, 121.22, 86.35, 60.80, 58.46, 15.83, 15.58, 14.53; HRMS (ESI-TOF) calcd for $C_{14}H_{18}BrN_3O_4Na$ $[M+Na]^+$ 394.0373, found 394.0377. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.58 (d, J=5.4 Hz, 1H), 7.40～7.38 (m, 4H), 4.76～4.70 (m, 1H), 4.29～4.25 (m, 2H), 4.11～4.06 (m, 1H), 1.55～1.53 (m, 3H), 1.32～1.29 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 162.94, 135.38, 130.74, 129.73, 126.44, 121.16, 85.95, 60.76, 58.26, 15.84, 15.47, 14.03; HRMS (ESI-TOF) calcd for $C_{14}H_{18}BrN_3O_4Na$ $[M+Na]^+$ 394.0373, found 394.0377.

Methyl (2*Z*,3*E*)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)-4-phenylbut-3-enoate (**3o**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow solid (49.5 mg, 81%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.59 (d, J=4.9 Hz, 1H) 7.45 (s, 2H), 7.30 (t, J=7.6 Hz, 2H), 7.20 (t, J=7.1 Hz, 1H), 7.05～7.02 (m, 1H), 6.98 (s, 1H), 4.86～4.81 (m, 1H), 4.13～4.11 (m, 1H), 3.81 (s, 3H), 1.54 (s, 3H), 1.34 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.53, 137.49, 128.43, 127.54, 127.23, 126.35, 125.47, 122.72, 86.27, 58.50, 51.39, 15.59, 15.25; HRMS (ESI-TOF) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1268, found 328.1271. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.56 (d, J=5.3 Hz, 1H), 7.44 (s, 2H), 7.30 (t, J=7.6 Hz, 2H), 7.20 (t, J=7.1 Hz, 1H), 7.02～7.99 (m, 1H), 6.96 (s, 1H), 4.81～4.70 (m, 1H), 4.11～4.06 (m, 1H), 3.81 (s, 3H), 1.53 (s, 3H), 1.32 (d, J=7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.53, 137.44, 128.43, 127.44, 127.19, 126.33, 125.34, 122.63, 86.10, 58.25, 51.37, 15.48, 14.67; HRMS (ESI-TOF) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1268, found 328.1271.

Methyl (2*Z*,3*E*)-4-(4-chlorophenyl)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)but-3-enoate (**3p**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1.2∶1; yellow liquid (44.9 mg, 66%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.64 (d, J=5.3 Hz, 1H), 7.37 (s, 2H), 7.26 (s, 2H), 6.96～6.94 (m, 2H), 4.86～4.82 (m, 1H), 4.16～4.13 (m, 1H), 3.82 (s, 3H), 1.55 (d, J=2.5 Hz, 3H), 1.35 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.41, 136.06, 132.57, 128.51, 127.47, 126.01, 125.08, 123.31, 86.27, 58.50, 51.39, 15.61, 15.32; HRMS (ESI-TOF) calcd for $C_{15}H_{18}ClN_3O_4Na$ $[M+Na]^+$ 362.0878, found 362.0880. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.61 (d, J=5.5 Hz, 1H), 7.35 (s, 2H), 7.25 (s, 2H), 6.94～6.90 (m, 2H), 4.76～4.71 (m, 1H), 4.13～4.09 (m, 1H), 3.81 (s, 3H), 1.54 (d, J=2.4 Hz, 3H), 1.33 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.41, 136.02, 132.53, 128.51, 127.45, 125.91, 124.96, 123.20, 86.01, 58.31, 51.37, 15.45, 14.48; HRMS (ESI-TOF) calcd for $C_{15}H_{18}ClN_3O_4Na$ $[M+Na]^+$ 362.0878, found 362.0880.

Methyl (2*Z*,3*E*)-4-(4-methoxyphenyl)-2-(2-(3-nitrobutan-2-yl)hydrazineylidene)but-3-enoate (**3q**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1.2∶1; yellow liquid (58.4 mg, 87%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.48 (d, J=5.3 Hz, 1H), 7.40 (s, 2H), 6.98 (d, J=7.4 Hz, 1H), 6.87～6.86 (m, 2H), 6.83 (s, 1H), 4.87～4.83 (m, 1H), 4.15～4.11 (m, 1H), 3.83 (s, 3H),

3.80 (s, 3H), 1.56 (d, J=3.7 Hz, 3H), 1.35 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.60, 159.07, 130.32, 127.63, 127.32, 125.93, 120.67, 113.93, 86.28, 58.52, 55.17, 51.41, 15.57, 15.17; HRMS (ESI-TOF) calcd for $C_{16}H_{21}N_3O_5Na$ $[M+Na]^+$ 358.1373, found 358.1372. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.46 (d, J=5.5 Hz, 1H), 7.38 (s, 2H), 6.95 (d, J=7.4 Hz, 1H), 6.86～6.84 (m, 2H), 6.82 (s, 1H), 4.76～4.71 (m, 1H), 4.11～4.06 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 1.55 (d, J=3.7 Hz, 3H), 1.33 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.60, 159.05, 130.28, 127.61, 127.23, 125.78, 120.58, 113.93, 86.20, 58.21, 55.17, 51.40, 15.57, 14.83; HRMS (ESI-TOF) calcd for $C_{16}H_{21}N_3O_5Na$ $[M+Na]^+$ 358.1373, found 358.1372.

1-(Diphenylmethylene)-2-(3-nitrobutan-2-yl)hydrazine (**3r**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 8∶1; yellow liquid (29.7 mg, 50%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55～7.51 (m, 2H), 7.48～7.47 (m, 3H), 7.30～7.25 (m, 5H), 5.43 (d, J=7.2 Hz, 1H), 4.97～4.87 (m, 1H), 3.95～3.87 (m, 1H), 1.55～1.52 (m, 3H), 1.16 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.94, 138.27, 133.15, 129.45, 128.74, 128.09, 126.33, 85.60, 58.26, 15.16, 14.61; HRMS (ESI-TOF) calcd for $C_{17}H_{20}N_3O_2$ $[M+H]^+$ 298.1550, found 298.1559. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.60～7.57 (m, 2H), 7.47～7.44 (m, 3H), 7.25～7.22 (m, 5H), 5.39 (d, J=5.3 Hz, 1H), 4.87～4.84 (m, 1H), 3.87～3.83 (m, 1H), 1.52～1.51 (m, 3H), 1.23 (d, J=6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.23, 137.58, 132.38, 130.03, 128.95, 128.24, 126.30, 86.57, 57.44, 15.73, 15.43; HRMS (ESI-TOF) calcd for $C_{17}H_{20}N_3O_2$ $[M+H]^+$ 298.1550, found 298.1559.

1-(Bis(4-chlorophenyl)methylene)-2-(3-nitrobutan-2-yl)hydrazine (**3s**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 3∶1; yellow liquid (40.3 mg, 55%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52～7.48 (m, 2H), 7.35～7.32 (m, 2H), 7.24～7.15 (m, 4H), 5.43～5.40 (m, 1H), 4.86～4.80 (m, 1H), 3.88～3.80 (m, 1H), 1.53 (d, J=6.8 Hz, 3H), 1.25 (d, J=6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 143.50, 136.50, 135.20, 133.84, 131.27, 129.95, 128.28, 127.36, 86.80, 57.57, 15.99, 14.79; HRMS (ESI-TOF) calcd for $C_{17}H_{18}Cl_2N_3O_2$ $[M+H]^+$ 366.0771, found 366.0775. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48～7.45 (m, 2H), 7.36～7.35 (m, 2H), 7.27～7.24 (m, 4H), 5.43～5.40 (m, 1H), 4.88～4.86 (m, 1H), 3.92～3.90 (m, 1H), 1.53 (d, J=6.8 Hz, 3H), 1.15 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 144.29, 136.44, 135.24, 133.98, 130.87, 130.23, 128.72, 127.39, 85.39, 58.26, 15.82, 14.33; HRMS (ESI-TOF) calcd for $C_{17}H_{18}Cl_2N_3O_2$ $[M+H]^+$ 366.0771, found 366.0775.

1-(9*H*-Fluoren-9-ylidene)-2-(3-nitrobutan-2-yl)hydrazine (**3t**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1.2∶1; yellow liquid (54.3 mg, 92%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.64～7.60 (m, 2H), 7.53 (t, J=6.4 Hz, 1H), 7.44 (t, J=5.3 Hz, 1H), 7.21 (d, J=7.4 Hz, 1H), 7.16～7.14 (m, 3H), 6.64 (d, J=6.2 Hz, 1H), 4.80～4.76 (m, 1H), 3.91～3.87 (m, 1H), 1.41 (t, J=6.6 Hz, 3H), 1.18 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.39, 140.99, 138.01, 129.98, 128.06, 124.64, 120.32, 119.36, 86.39, 58.83, 16.11, 14.88; HRMS (ESI-TOF) calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1386. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.60～7.56 (m, 2H), 7.53 (t, J=6.4 Hz, 1H), 7.44 (t, J=5.3 Hz, 1H), 7.19 (d, J=7.5 Hz, 1H), 7.14～7.12 (m, 3H), 6.57 (d, J=5.6 Hz, 1H), 4.76～4.72 (m, 1H), 3.87～3.82 (m, 1H), 1.41 (t, J=6.6 Hz, 3H), 1.18 (d, J=6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 141.94, 140.88, 137.89, 129.93, 127.95, 124.54, 120.45, 119.33, 85.58, 58.31, 15.60, 14.65; HRMS (ESI-TOF) calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1386.

Ethyl (*E*)-2-(2-(4-nitrohexan-3-yl)hydrazineylidene)-acetate (**3u**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 1∶1; yellow liquid (45.1 mg, 92%). **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.41～7.33 (m, 1H), 7.07～7.03 (m, 1H), 4.72～4.67 (m, 1H), 4.31～4.25 (m, 2H), 3.84～3.77 (m, 1H), 2.15～2.05 (m, 2H), 1.71～1.63 (m, 2H), 1.35～1.31 (m, 3H), 1.15～0.98 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 164.14, 124.76, 92.44, 62.52, 60.20, 23.94, 23.27, 22.29, 13.96, 10.27; HRMS (ESI-TOF) calcd for $C_{10}H_{19}N_3O_4Na$ $[M+Na]^+$ 268.1268, found 268.1270. **Isomer 2**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.33～7.29 (m, 1H), 7.03～6.99 (m, 1H), 4.67～4.60 (m, 1H), 4.25～4.19 (m, 2H), 3.77～3.71 (m, 1H), 2.05～1.82 (m, 2H), 1.63～1.49 (m, 2H), 1.31～1.28 (m, 3H), 0.98～0.93 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 164.09, 124.10, 92.12, 61.92, 60.20, 23.73, 23.27, 22.24, 13.96, 9.89; HRMS (ESI-TOF) calcd for $C_{10}H_{19}N_3O_4Na$ $[M+Na]^+$ 268.1268, found 268.1270.

Ethyl (*E*)-2-(2-(2-nitro-1,2-diphenylethyl)hydrazineylidene)acetate (**3v**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 3∶1; yellow liquid (37.6 mg, 55%). **Isomer 1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (t, J=8.1 Hz, 2H), 7.33～7.23 (m, 6H), 7.17 (s, 4H), 6.86 (s, 1H), 6.11 (d, J=10.2 Hz, 1H), 5.47 (dd, J=10.2, 5.4 Hz, 1H), 4.26～4.22 (m, 2H), 1.32～1.27 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.77, 135.29, 131.23, 129.93, 129.15, 128.82, 128.49, 128.19, 127.75, 126.54, 93.06, 64.98, 60.71, 14.22; HRMS (ESI-TOF) calcd for $C_{18}H_{19}N_3O_4Na$ $[M+Na]^+$ 364.1268, found 364.1241. **Isomer 2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62～7.59 (m, 2H), 7.39～7.33 (m, 6H), 7.17 (s, 4H), 6.63 (s, 1H), 6.06 (d, J=10.3 Hz, 1H), 5.38 (dd, J=10.3, 4.6 Hz, 1H), 4.22～4.18 (m, 2H), 1.27～1.24 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.77, 135.98, 131.40, 130.44, 129.09, 128.78, 128.52, 128.19, 127.57, 125.88, 93.57, 64.06, 60.66, 14.22; HRMS (ESI-TOF) calcd for $C_{18}H_{19}N_3O_4Na$ $[M+Na]^+$ 364.1268, found 364.1241.

4.3 General procedures for the preparation of **4**

Taking synthesis of **4a** as example, to a solution of **1a** (0.8 mmol, 57.2 μL) and alkenyldiazoacetate (**2w**, 0.2 mmol, 36.8 mg) in DMF (1.0 mL) was added DBU in one portion (0.24 mmol, 35.8 μL). The reaction mixture was stirred at room temperature for 1 h. After **2w** was consumed

(monitored by TLC), the reaction mixture was poured into brine (30 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by aluminium oxide, basic (200～300 mesh) chromatography (acetone/petroleum ether, V∶V=3∶50) to give **4a** (48.8 mg, 85%) as a white solid. Compound **4b** was synthesized using the same way.

Methyl (4*R**,5*S**,6*R**)-4-(2-methoxy-2-oxoethyl)-5,6-dimethyl-5-nitro-1,4,5,6-tetrahydropyrid-azine-3-carboxylate (**4a**): White solid (48.8 mg, 85%); m.p. 153～154 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.28～7.19 (m, 1H), 3.97 (s, 1H), 3.76～3.73 (m, 3H), 3.63～3.57 (m, 4H), 2.52～2.45 (m, 2H), 1.37 (s, 3H), 1.19～1.17 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.27, 164.06, 129.18, 85.09, 52.11, 51.83, 49.02, 39.86, 36.18, 18.21, 12.76; HRMS (ESI-TOF) calcd for $C_{11}H_{17}N_3O_6Na$ $[M+Na]^+$ 310.1010, found 310.1015.

Methyl (4*R**,5*S**,6*R**)-5,6-diethyl-4-(2-methoxy-2-oxoethyl)-5-nitro-1,4,5,6-tetrahydropyrid-azine-3-carboxylate (**4b**): Yellow liquid (54.2 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.80～6.78 (m, 1H), 3.99～3.96 (m, 1H), 3.82 (s, 3H), 3.80 (d, J=9.1 Hz, 1H), 3.67 (s, 3H), 2.63～2.51 (m, 2H), 2.05～1.95 (m, 1H), 1.75～1.65 (m, 1H), 1.56～1.43 (m, 2H), 1.15～1.10 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.56, 163.94, 130.31, 87.67, 56.67, 52.29, 51.95, 36.07, 35.65, 24.82, 21.24, 11.14, 8.45; HRMS (ESI-TOF): calcd for $C_{13}H_{21}N_3O_6Na$ $[M+Na]^+$ 338.1323, found 338.1324.

4.4 General procedures for the preparation of 5

A sealed tube equipped with a magnetic stir bar was charged with **3a** (0.2 mmol, 43.4 mg) in ethyl acetate (2.0 mL), then NBS or NCS (0.6 mmol) was added. The reaction mixture was stirred under reflux conditions for 3 h. The reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with DCM (10 mL×3). The combined organic extracts were dried over anhydrous $NaSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel column chromatography (EtOAc/petroleum ether, V∶V=1∶50) to afford product **5** as a yellow liquid.

(*Z*)-Ethyl 2-chloro-2-(2-(3-nitrobutan-2-yl)hydrazono)-acetate (**5a**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 10∶1; yellow liquid (39.3 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.63 (d, J=5.5 Hz, 1H), 4.75～4.70 (m, 1H), 4.26 (q, J=7.1 Hz, 2H), 4.05 (q, J=6.6 Hz, 1H), 1.51 (d, J=6.9 Hz, 3H), 1.29 (t, J=7.3 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 159.38, 116.11, 86.30, 62.64, 57.29, 16.40, 15.91, 14.20; HRMS (ESI-TOF) calcd for $C_8H_{14}ClN_3NaO_4$ $[M+Na]^+$ 274.0565, found 274.0564.

(*Z*)-Ethyl 2-bromo-2-(2-(3-nitrobutan-2-yl)hydr-azono)-acetate (**5b**): According to the ^{1}H NMR, the diastereomeric ratios were approximately 10∶1; yellow liquid (44.2 mg, 75%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.72 (d, J=5.6 Hz, 1H), 4.75～4.71 (m, 1H), 4.28～4.25 (m, 2H), 4.11～4.06 (m, 1H), 1.51 (d, J=6.9 Hz, 3H), 1.29 (d, J=7.0 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 159.36, 109.37, 86.32, 62.85, 57.14, 16.41, 15.92, 14.22; HRMS (ESI-TOF) calcd for $C_8H_{14}BrN_3NaO_4$ $[M+Na]^+$ 318.0060, found 318.0065.

Supporting Information The detailed procedure for the synthesis of **3**～**5**, X-ray structure of **3b** and **4a**, and ^{1}H NMR and ^{13}C NMR spectra of compounds **3**～**5**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

References and notes

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