Reactions of Morita–Baylis–Hillman Acetates with Huisgen Zwitterions: A Novel Strategy for the Synthesis of β-Amino Acid Derivatives

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Abstract: The reaction of Huisgen Zwitterion with Morita–Baylis–Hillman acetates afforded β-amino acid derivatives.

Key words: Huisgen zwitterion, Morita–Baylis–Hillman acetate, β-amino acid

Although Huisgen zwitterion[1] was known for nearly four decades, its synthetic potential remained largely unexploited except in some notable reactions like Mitsunobu Reaction.[2] In view of our longstanding interest in zwitterion chemistry,[3] recently we have explored the reactivity of Huisgen zwitterion towards various substrates like aldehydes, ketones, chalcones, diaryl 1,2-diones, quinones, isatins, and allenes.[4–6] In this context it was of interest to examine the reactivity of Huisgen zwitterion towards Morita–Baylis–Hillman (MBH) adducts,[7,8] which are unique substrates of great synthetic potential incorporating three manipulatable groups, namely, a hydroxy group, a double bond, and an electron-withdrawing group. In this paper, we describe the results of our investigations on the reaction of Huisgen zwitterion with MBH acetates.

The present studies were initiated by treating methyl 2-[(4-chlorophenyl)acetyloxymethyl]acrylate (**1a**) with diisopropyl azodicarboxylate and triphenylphosphine in THF at room temperature for 2 hours. The reaction afforded two products, namely, diisopropyl *N*-acetyl-*N*′-[3-(4-chlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (**3a**) and diisopropyl *N*-[3-(4-chlorophenyl)-2-(methoxycarbonyl) allyl]hydrazine-1,2-dicarboxylate (**4a**) in 46% and 51% yield, respectively (Scheme 1).

The structure elucidation of **3a** and **4a** was accomplished by usual spectroscopic analysis. The ^{1}H NMR spectrum of the compound **3a** showed singlet resonance signals at δ = 2.35 and 3.81 due to CH_3CO group and CH_3OCO groups. The NCH_2 group was discernable at δ = 4.14–4.73 as a multiplet. In the ^{13}C NMR spectrum the three ester carbonyl groups were present at δ = 169.4, 167.4 and 154.7 and that of the keto carbonyl group appeared at δ = 152.7, supporting the IR absorption observed in the region 1750–1700 and 1631 cm^{-1}. All other signals were also in good agreement with the proposed structure. The structure and stereochemistry of the compound was unambiguously established by single crystal X-ray analysis (Figure 1) of a representative compound, **3g**.

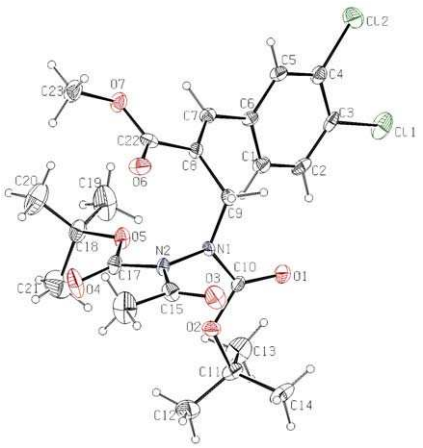
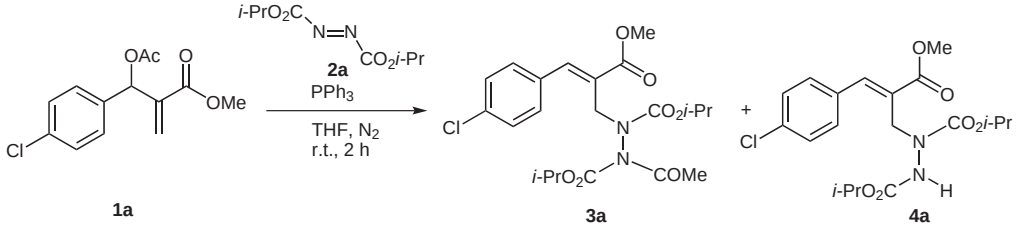


Figure 1 Single crystal X-ray structure of di-*tert*-butyl *N*-acetyl-*N*′-[3-(3,4-dichlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (**3g**)



Scheme 1 Reaction of Huisgen zwitterion with MBH acetate

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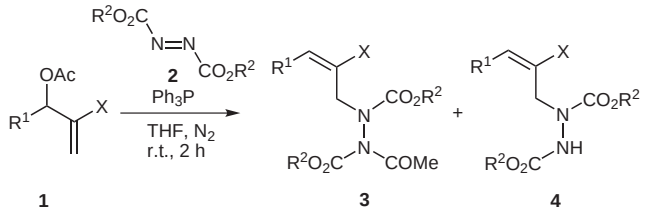
Table 1 Hydrazine-1,2-dicarboxylates **3** and **4** Prepared



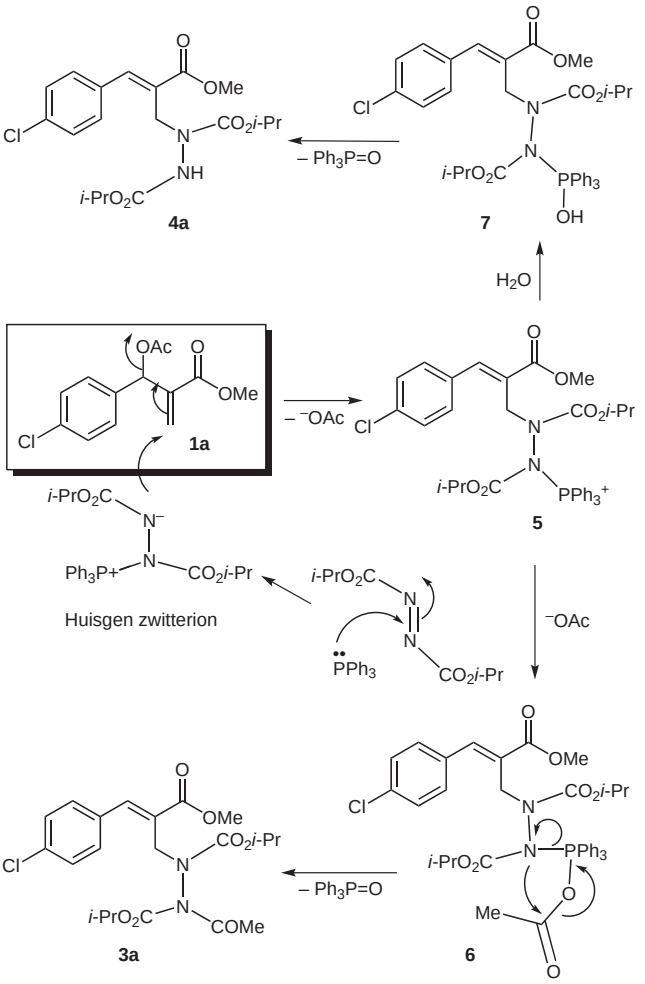
1 3 4

3, **4**	R^1	R^2	X	Yield (%)	
				3	**4**
a	4-ClC_6H_4	*i*-Pr	CO_2Me	46	51
b	4-$CF_3C_6H_4$	Et	CO_2Me	57	41
c	3-ClC_6H_4	Et	CO_2Me	38	49
d	Ph	*i*-Pr	CO_2Me	35	56
e	Ph	*i*-Pr	CN	57	37
f	4-FC_6H_4	*t*-Bu	CO_2Me	37	46
g	3,4-$Cl_2C_6H_3$	*t*-Bu	CO_2Me	58	30
h	Ph	Et	CO_2Me	35	49
i	4-MeC_6H_4	*i*-Pr	CO_2Me	40	36
j	4-BrC_6H_4	*i*-Pr	CO_2Me	54	40

The IR spectrum of the compound **4a** showed strong absorptions at 3308 and 1703–1722 cm^{-1} due to NH group and the ester carbonyl groups, respectively. The ^1H NMR showed singlets at δ = 4.5 and 6.71 due to NCH_2 and NH groups. In the ^{13}C NMR spectrum signals due to the ester carbonyl groups were discernable at δ = 155.5, 156.3, and 167.7. Other signals were also in good agreement with the proposed structure.

The mechanism of the reaction may be rationalized by invoking an S_N2' process, involving the Huisgen zwitterion and the Morita–Baylis–Hillman acetate (Scheme 2). Evidently, the first step of the reaction is the formation of Huisgen zwitterion by the addition of triphenylphosphine to diisopropyl azodicarboxylate. The S_N2' displacement of the acetate from **1a** induced by Huisgen zwitterion would lead to the formation of the cationic intermediate **5**. The attack of the acetate on **5** followed by rearrangement and the elimination of Ph_3PO, would result in the formation of diisopropyl *N*-acetyl-*N*′-[3-(4-chlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (**3a**). Similarly by the addition of hydroxy anion to **5**, an intermediate **7** is formed, and the latter on elimination of triphenylphosphine oxide would deliver diisopropyl *N*-[3-(4-chlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (**4a**).

As disclosed inTable 1, the reaction was found to be general with various Morita–Baylis–Hillman acetates and Huisgen zwitterions.



Scheme 2 Mechanistic rationale for the formation of hydrazine-1,2-dicarboxylates **3a** and **4a**

In conclusion, herein we have reported a facile C–N bond-forming reaction, which incidentally constitutes the first example of the participation of Huisgen zwitterions in an S_N2' reaction.

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 MHz (^1H) and 75 MHz (^{13}C) respectively on a Bruker Avance DPX-300 MHz NMR spectrometer. Chemical shifts are reported (δ) relative to TMS (^1H) and $CDCl_3$ (^{13}C) as the internal standards. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra were recorded under EI/HRMS (at 5000 resolution) or FAB^+/HRMS using Jeol JMS 600H mass spectrometer. IR spectra were recorded on Nicolet Impact 400D FT-IR spectrophotometer. Commercial grade solvents were distilled prior to use.

Reactions of Morita–Baylis–Hillman Acetates with Huisgen Zwitterions; General Procedure

The Morita–Baylis–Hillman acetate **1** (1 equiv) dissolved in THF (5 mL) was treated with the respective azodicarboxylate **2** (1.2 equiv) and Ph_3P (1.2 equiv) at r.t. for 2 h under N_2. The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography using silica gel (60–120 mesh) and hexane–EtOAc.

Diisopropyl *N*-Acetyl-*N′*-[3-(4-chlorophenyl)-2(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3a)
Yield: 46%.

IR (KBr): 2983, 1750–1700, 1631, 1582 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.18–1.34 (m, 12 H), 2.35 (s, 3 H), 3.81 (s, 3 H), 4.24–4.73 (m, 2 H), 4.88–5.00 (m, 2 H), 7.26–7.38 (m, 4 H), 7.83 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3, 21.6, 21.7, 22.1, 25.1, 42.8, 51.5, 70.2, 71.7, 126.7, 127.1, 128.8, 130.9, 132.8, 135.5, 140.4, 143.5, 152.7, 154.2, 167.4, 169.4.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{27}ClN_2O_7$: 454.1507; found: 454.0291.

Diisopropyl *N′*-[3-(4-Chlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4a)
Yield: 51%.

IR (KBr): 3309, 2983, 1722–1703 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.14–1.25 (m, 12 H), 3.74 (s, 3 H), 4.5 (s, 2 H), 4.77– 4.92 (m, 2 H), 6.71 (s, 1 H), 7.13–7.28 (m, 4 H), 7.72 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.6, 21.9 45.5, 51.7, 69.4, 70.1, 128.3, 128.7, 129.7, 130.7, 133.5, 135.1, 142.3, 155.5, 156.3, 167.7.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{25}ClN_2O_6$: 412.1401; found: 412.1396.

Diethyl *N*-Acetyl-*N′*-[3-(4-trifluoromethylphenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3b)
Yield: 57%.

IR (KBr): 1715 (br), 1242, 1103 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.17–1.25 (m, 6 H), 2.35 (s, 3 H), 3.82 (s, 3 H), 4.10–4.16 (m, 4 H), 4.53–4.74 (m, 2 H), 7.38 (m, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.89 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.9, 14.1, 14.4, 25.1, 43.1, 52.3, 62.7, 63.6, 124.9, 125.4, 128.7, 128.9, 129.7, 131.2, 137.9, 142.9, 153.1, 154.5, 167.3, 169.3.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{23}F_3N_2O_7$: 460.1456; found: 454.1457.

Diethyl *N′*-[3-(4-Trifluoromethylphenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4b)
Yield: 41%.

IR (KBr): 3421, 2999, 1755–1697 (br), 1263 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.30 (m, 6 H), 3.84 (s, 3 H), 4.11–4.23 (m, 4 H), 4.57 (s, 2 H), 6.78 (s, 1 H), 7.54 (m, 2 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.87 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.9, 14.1, 14.4, 25.1, 43.1, 52.3, 62.7, 63.6, 124.9, 125.4, 128.7, 128.9, 129.7, 131.2, 137.9, 142.9, 153.1, 154.5, 167.3, 169.5.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{12}F_3N_2O_6$: 418.1461; found: 418.1463.

Diethyl *N*-Acetyl-*N′*-[3-(3-chlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3c)
Yield: 38%.

IR (KBr): 1713, 1240 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.17–1.27 (m, 6 H), 2.36 (s, 3 H), 3.80 (s, 3 H), 4.11–4.24 (m, 4 H), 4.34–4.74 (m, 2 H), 7.06–7.46 (m, 4 H), 7.55 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.0, 14.5, 14.6, 25.2, 43.9, 125.9, 126.5, 130.4, 131.5, 131.9, 143.8, 144.0, 153.2, 154.7, 162.2, 167.8, 169.5.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{23}ClN_2O_7$: 426.1217; found: 426.1219.

Diethyl *N′*-[3-(3-Chlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4c)
Yield: 49%.

IR (KBr): 3424, 2983, 1759–1699 (br), 1487 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.16–1.29 (m, 6 H), 3.74 (s, 3 H), 4.03–4.15 (m, 4 H), 4.52 (s, 2 H), 6.72 (s, 1 H), 7.00–7.33 (m, 4 H), 7.75 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.2, 14.5, 46.7, 52.2, 61.9, 62.5, 115.6, 126.9, 130.5, 131.5, 142.8, 155.9, 162.0, 164.0.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{21}ClN_2O_6$: 384.1107; found: 384.1111.

Diisopropyl *N*-Acetyl-*N′*-[3-phenyl-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3d)
Yield: 35%.

IR (KBr): 1712, 1249 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.16–1.28 (m, 12 H), 2.30 (s, 3 H), 3.81 (s, 3 H), 4.53–4.80 (m, 4 H), 4.87–4.99 (m, 2 H), 7.38 (m, 5 H), 7.90 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.1, 21.5, 21.9, 25.0, 52.0, 70.0, 70.4, 71.5, 128.5, 129.1, 129.4, 129.5, 145.0, 152.7, 154.1, 167.7, 169.3.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{28}N_2O_7$: 420.1910; found: 420.1907.

Diisopropyl *N′*-[3-Phenyl-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4d)
Yield: 56%.

IR (KBr): 3211, 2991, 1753–1698 (br) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.20–1.32 (m, 12 H), 4.11 (s, 3 H), 4.62 (s, 2 H), 4.92–4.98 (m, 2 H), 6.62 (s, 1 H), 7.37 (s, 5 H), 7.86 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.7, 21.8, 21.9, 43.3, 52.0, 70.0, 70.2, 70.3, 128.9, 129.3, 134.4, 155.6, 156.4, 166.5.

LRMS-FAB: *m*/*z* calcd for $C_{19}H_{26}ClN_2O_6$ $(M + H)^+$: 379.18; found: 379.20.

Diisopropyl *N*-Acetyl-*N′*-[(3-phenyl-2-cyano)allyl]hydrazine-1,2-dicarboxylate (3e)
Yield: 57%.

IR (KBr): 3037, 2218, 1762–1703 (br), 1361 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.19–1.33 (m, 12 H), 2.56 (s, 3 H), 4.95–5.04 (m, 2 H), 7.40–7.42 (m, 5 H), 7.77 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3, 21.6, 25.1, 45.7, 53.1, 70.5, 72.1, 106.2, 109.9, 117.9, 119.4, 128.7, 129.8, 130.6, 132.6, 146.1, 147.8, 152.4, 153.3, 154.0, 169.7.

LRMS (+FAB): *m*/*z* calcd for $C_{20}H_{23}ClN_3O_5$ $(M + H)^+$: 388.18; found: 388.21.

Diisopropyl *N*-[(3-Phenyl-2-cyano)allyl]hydrazine-1,2-dicarboxylate (4e)
Yield: 37%.

IR (KBr): 3413, 2988, 2216, 1752–1715 (br), 1481, 1381 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.33 (m, 12 H), 4.43–4.53 (m, 2 H), 4.89–5.05 (m, 2 H), 6.89 (s, 1 H), 7.41–7.75 (m, 5 H), 7.76 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.6, 21.9, 52.5, 69.7, 69.9, 106.5, 128.8, 128.9, 130.5, 132.9, 154.8, 156.4.

LRMS-FAB: *m*/*z* calcd for $C_{18}H_{23}N_3O_4$ $(M + H)^+$: 346.17; found: 346.20.

Di-*tert*-butyl *N*-Acetyl-*N*′-[3-(4-fluorophenyl)-2-(methoxycarbonyl)allyl]hydrazene-1,2-dicarboxylate (3f)
Yield: 32%.

IR (KBr): 1741 (br), 1379, 1240, 1103 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41–1.50 (m, 18 H), 2.30 (s, 3 H), 3.81 (s, 3 H), 4.48–4.70 (m, 2 H), 7.06–7.4 7 (m, 4 H), 7.84 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 25.3, 25.4, 27.7, 28.0, 28.2, 29.4, 30.8, 42.1, 43.6, 51.5, 52.1, 115.8, 126.7, 130.7, 131.9, 143.6, 153.2, 164.2, 167.9, 169.9.

LRMS-FAB: *m*/*z* calcd for $C_{23}H_{31}FN_2O_7$ $(M + H)^+$: 467.21; found: 467.22.

Di-*tert*-butyl *N*′-[3-(4-Fluorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4f)
Yield: 46%

IR (KBr): 2985, 1750, 1379, 1242, 1105 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42–1.46 (m, 18 H), 3.81 (s, 3 H), 4.57 (s, 2 H), 6.36 (s, 1 H), 7.02–7.42 (m, 4 H), 7.79 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.1, 29.1, 30.7, 31.7, 52.0, 81.2, 115.4, 115.7, 127.3, 131.5, 139.0, 142.3, 155.0, 161.3, 167.9.

LRMS-FAB: *m*/*z* calcd for $C_{21}H_{29}FN_2O_6$ $(M + H)^+$: 425.20; found: 425.21.

Di-*tert*-butyl *N*-Acetyl-*N*′-[3-(3,4-dichlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3g)
Yield: 58%.

IR (KBr): 3037, 2985, 1762, 1745, 1703, 1382, 1286, 1240 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43–1.51 (m, 18 H), 2.36 (s, 3 H), 3.82 (s, 3 H), 4.45–4.63 (m, 2 H), 7.29 (d, *J* = 9 Hz, 1 H), 7.45 (d, *J* = 9 Hz, 1 H), 7.60 (s, 1 H), 7.75 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.7, 25.3, 26.9, 27.7, 27.8, 42.2, 52.3, 81.5, 83.8, 128.0, 129.0, 130.5, 131.6, 138.7, 142.2, 151.7, 153.2, 167.2, 169.9.

LRMS-FAB calcd for $C_{23}H_{30}Cl_2N_2O_7$ $(M + H)^+$: 517.14; found: 517.15.

Di-*tert*-butyl *N*′-[3-(3,4-Dichlorophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4g)
Yield: 30%.

IR (KBr): 3415, 2975, 1751, 1741, 1712, 1481, 1381, 1250, 1105 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 18 H), 3.82 (s, 3 H), 4.54 (s, 2 H), 6.4 (s, 1 H), 7.44 (d, *J* = 9 Hz, 2 H), 7.52 (s, 1 H), 7.71 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.2, 19.4, 20.9, 22.6, 28.1, 52.2, 81.0, 129.3, 130.5, 131.2, 132.8, 134.5, 140.7, 154.8, 161.3, 170.8.

LRMS-FAB: *m*/*z* calcd for $C_{21}H_{28}Cl_2N_2O_6$ $(M + H)^+$: 475.13; found: 475.02.

Diisopropyl *N*-Acetyl-*N*′-[3-(4-methylphenyl)-2(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3i)
Yield: 40%.

IR (KBr): 3314, 2982, 1739–1723, 1634, 1109 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12–1.44 (m, 12 H), 2.30 (s, 3 H), 2.37 (s, 3 H), 3.80 (s, 3 H), 4.52–4.80 (m, 2 H), 4.75–4.99 (m, 2 H), 7.15–7.32 (m, 4 H), 7.87 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2, 21.4, 21.6, 21.9, 46.3, 51.9, 69.3, 69.7, 69.9, 126.1, 128.3, 128.8, 129.2, 129.5, 131.5, 139.2, 143.8, 155.6, 156.3, 168.1.

LRMS-FAB: *m*/*z* calcd for $C_{22}H_{30}N_2O_7$ $(M + H)^+$: 435.21; found: 435.37.

Diisopropyl *N*′-[3-(4-Methylphenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4i)
Yield: 36%.

IR (KBr): 3309, 2983, 1730–1703 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20–1.35 (m, 12 H), 2.36 (m, 3 H), 3.80 (s, 3 H), 4.64 (s, 2 H), 4.82–5.00 (m, 2 H), 6.71 (s, 1 H), 7.12–7.31 (m, 4 H), 7.84 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2, 21.4, 21.9, 29.6, 46.3, 51.9, 69.4, 69.7, 70.0, 72.4, 126.1, 128.4, 128.9, 129.5, 131.5, 139.2, 143.8, 155.6, 168.1.

LRMS-FAB: *m*/*z* calcd for $C_{20}H_{28}N_2O_6$ $(M + H)^+$: 391.18; found: 391.97

Diisopropyl *N*-Acetyl-*N*′-[3-(4-bromophenyl)-2(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (3k)
Yield: 54%.

IR (KBr): 3334, 2983, 1788–1711, 1634, 1587 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14–1.33 (m, 12 H), 2.36 (s, 3 H), 3.81 (s, 3 H), 4.52–4.62 (m, 2 H), 4.90–4.96 (m, 2 H), 7.15–7.55 (m, 4 H), 7.81 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3, 21.6, 21.8, 22.0, 25.3, 29.7, 42.8, 51.7, 70.8, 71.7, 123.8, 126.8, 130.2, 133.4, 140.5, 143.7, 152.7, 154.2, 167.7, 169.5.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{27}ClN_2O_7$: 499.1002; found: 499.1010.

Diisopropyl *N*′-[3-(4-Bromophenyl)-2-(methoxycarbonyl)allyl]hydrazine-1,2-dicarboxylate (4k)
Yield: 40%.

IR (KBr): 3310, 2983, 1730–1703 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21–1.36 (m, 12 H), 3.81 (s, 3 H), 4.57 (s, 2 H), 4.86–4.99 (m, 2 H), 6.72 (s, 1 H), 7.29–7.52 (m, 4 H), 7.77 (s, 1 H).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.7, 21.9, 46.1, 51.7, 69.5, 70.6, 128.4, 128.8, 129.8, 131.0, 133.7, 135.3, 142.4, 155.8, 156.4, 167.8.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{25}BrN_2O_6$: 457.0896; found: 457.0912.

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