

Reaction of Huisgen Zwitterion with Diaryl Ketones Leading to the Facile Synthesis of Mono- and Bis(alkoxycarbonyl)hydrazones

Vijay Nair,* Smitha C. Mathew, Akkattu T. Biju, Eringathodi Suresh

Organic Chemistry Section, National Institute for Interdisciplinary Science and Technology (Formerly Regional Research Laboratory), CSIR, Trivandrum 695 019, India

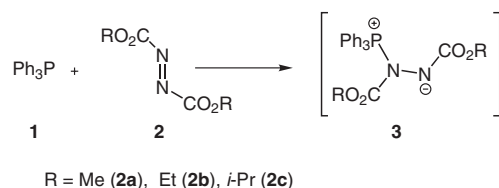
Fax +91(471)2491712; E-mail: vijaynair_2001@yahoo.com

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Abstract: The Huisgen zwitterion, generated from triphenylphosphine and dialkyl azodicarboxylates, afforded upon reaction with diaryl ketones both mono- and bis(alkoxycarbonyl)hydrazones, depending on the reaction conditions.

Key words: Huisgen zwitterion, diaryl ketones, azo compounds, esters, hydrazones

The reaction of electrophiles with zwitterions generated from phosphines and activated carbon–carbon multiple bonds has emerged as an efficient synthetic strategy for the construction of carbon–carbon and carbon–heteroatom bonds.¹ Although the zwitterion formed by the addition of triphenylphosphine to dialkyl azodicarboxylate, commonly known as the Huisgen zwitterion (Scheme 1),² has found extensive use as the pivotal intermediate in the well-known Mitsunobu reaction,³ its general application in organic synthesis was unexplored.

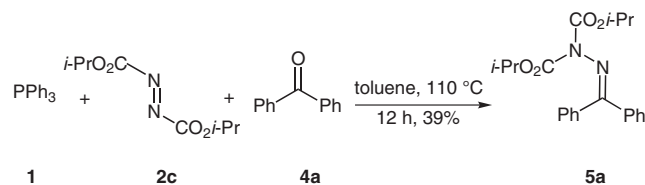


Scheme 1 Huisgen zwitterion

In 2005, Lee and co-workers reported the reaction of Huisgen zwitterion with aliphatic aldehydes and α -keto esters⁴ leading to the synthesis of bisadducts and oxadiazolines; synthesis of hydrazones from salicylaldehydes⁵ and using Huisgen zwitterion was reported elsewhere. Contemporaneous studies from our laboratory have demonstrated that this zwitterionic species can be used efficiently for the synthesis of a variety of novel heterocycles, e.g. dihydrobenzoxadiazole derivatives from *o*-benzoquinones,^{6a} functionalized pyrazoles from allenic esters,^{6b} pyrazolopyridazines from dienones,^{6c} and acyclic monohydrazones from diaryl-1,2-diones.^{6d} Reaction of Huisgen zwitterion with carbonyl compounds possessing an α -hydrogen atom resulted in the formation of vinylhydrazine derivatives.^{4,7} However, there has not been any attempt to

intercept the zwitterion **3** with non-enolizable ketones. In this context and as part of our general interest in the chemistry of zwitterions,^{1c,8} we undertook a detailed study of the reactivity of Huisgen zwitterion towards diaryl ketones and the results are presented in this paper.

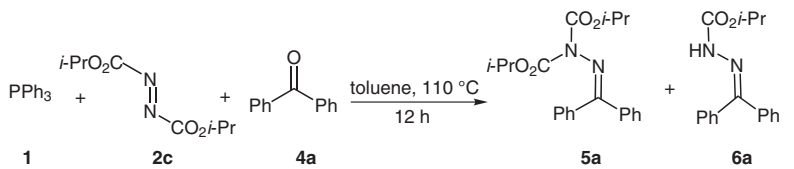
In the initial experiment, a toluene solution of benzophenone (**4a**; 1 equiv) was refluxed with diisopropyl azodicarboxylate (**2c**; 1 equiv) and triphenylphosphine (**1**; 1 equiv) for 12 hours. The reaction afforded the bis(isopropoxycarbonyl)hydrazone derivative **5a** in 39% yield as the sole product (Scheme 2; Table 1, entry 1).



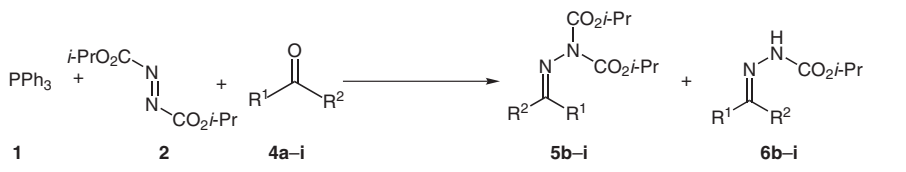
Scheme 2 Reaction of the triphenylphosphine–diisopropyl azodicarboxylate zwitterion with benzophenone, with use of equimolar quantities of starting materials

Since more than half of the starting material remained unchanged, the reaction was repeated, and 1.5 equivalents of the phosphine–azodicarboxylate zwitterion was used (Table 1, entry 2). Complete consumption of the starting material occurred, and the bis(isopropoxycarbonyl)hydrazone derivative **5a** was obtained in 75% yield. In addition to the bis(isopropoxycarbonyl)hydrazone derivative **5a**, a minor amount of the mono(isopropoxycarbonyl)hydrazone **6a** also formed (Table 1). Interestingly, when the stoichiometry of the phosphine–azodicarboxylate zwitterion was increased (from 1.5 equiv to 4 equiv), the mono(isopropoxycarbonyl)hydrazone derivative **6a** became the major product and the bis(isopropoxycarbonyl)hydrazone derivative **5a** formed in a minor amount only (Table 1, entries 2–6).

Even at the higher stoichiometry of the triphenylphosphine–diisopropyl azodicarboxylate zwitterion, a minor amount of bis(isopropoxycarbonyl)hydrazone **5a** formed along with mono(isopropoxycarbonyl)hydrazone **6a**. In the case of unsymmetrically substituted diaryl ketones **4**, the mono(isopropoxycarbonyl)hydrazone **6** formed as an inseparable mixture of regioisomers in an approximately 1:1 ratio. The reaction was found to be general with respect to various substituted diaryl ketones. The results are

Table 1 Effect of the Stoichiometry of the Starting Materials on the Reaction of the Triphenylphosphine–Diisopropyl Azodicarboxylate Zwitterion with Benzophenone


Entry	Equiv of 1 ^a	Equiv of 2c ^a	Yield of 5a (%)	Yield of 6a (%)
1	1	1	39	—
2	1.5	1.5	75	15
3	2	2	50	35
4	2.5	2.5	16	82
5	3	3	14	84
6	4	4	14	84

^a The number of equivalents of **1** and **2c** are relative to that of **4a** (1 equiv).**Table 2** Reaction of 1.5 Equivalents Triphenylphosphine–Diisopropyl Azodicarboxylate Zwitterion with Various Diaryl Ketones^a


Entry	R ¹	R ²	Product 5	Yield (%)	Product 6	Yield (%)
1	4-PhC ₆ H ₄	4-PhC ₆ H ₄	5b	88	6b	—
2	4-ClC ₆ H ₄	4-ClC ₆ H ₄	5c	96	6c	—
3	4-Tol	4-Tol	5d	39	6d	39
4	4- <i>t</i> -BuC ₆ H ₄	4- <i>t</i> -BuC ₆ H ₄	5e	40	6e	26
5	4-Tol	Ph	5f	44	6f	43
6	3-Tol	Ph	5g	56	6g	28
7	3,4-Me ₂ C ₆ H ₃	Ph	5h	35	6h	28
8	PMP	Ph	5i	39	6i	38

^a Reagents and conditions: DIAD (**2c**; 1.5 equiv), PPh₃ (**1**; 1.5 equiv), **4** (1 equiv), toluene, 110 °C, 12 h.

summarized in Table 2 (use of 1.5 equiv PPh₃–DIAD zwitterion) and Table 3 (use of 2.5 equiv PPh₃–DIAD zwitterion).

The products were structurally characterized by spectroscopic analysis. The IR spectrum of compound **5b** showed the ester carbonyl absorptions at 1744 and 1726 cm^{−1}; the structure was further confirmed by the ¹³C NMR spectrum, in which the carbonyl carbon was discernible at δ = 175.8. The methine and methyl protons of the isopropyl group resonated as multiplets at δ = 5.01–4.97 and 1.33–1.24 ppm, respectively. Finally, the structure of **5b** was established unequivocally by single-crystal X-ray analysis (Figure 1).⁹

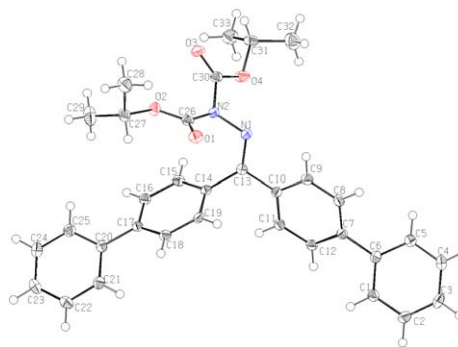
**Figure 1** Single-crystal X-ray crystallographic structure of compound **5b**

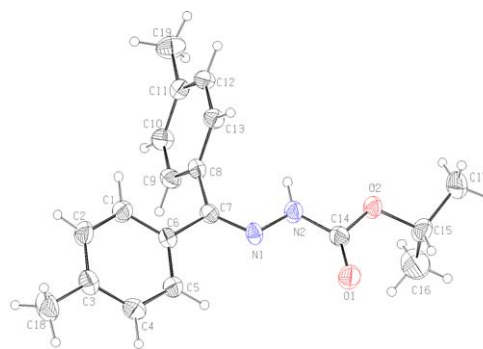
Table 3 Reaction of 2.5 Equivalents Triphenylphosphine–Diisopropyl Azodicarboxylate Zwitterion with Various Diaryl Ketones^a

Entry	R ¹	R ²	Product 5	Yield (%)	Product 6	Yield (%)
1	4-PhC ₆ H ₄	4-PhC ₆ H ₄	5b	82	6b	16
2	4-Tol	4-Tol	5d	24	6d	65
3	4- <i>t</i> -BuC ₆ H ₄	4- <i>t</i> -BuC ₆ H ₄	5e	22	6e	40
4	4-Tol	Ph	5f	18	6f	80
5	3-Tol	Ph	5g	24	6g	56
6	3,4-Me ₂ C ₆ H ₃	Ph	5h	18	6h	80
7	PMP	Ph	5i	32	6i	63

^a Reagents and conditions: DIAD (**2c**; 2.5 equiv), PPh₃ (**1**; 2.5 equiv), **4** (1 equiv), toluene, 110 °C, 12 h.

The structure of mono(isopropoxycarbonyl)hydrazone **6d** was assigned on the basis of spectroscopic data. The IR spectrum of the compound showed an absorption at 3352 cm⁻¹ indicating the presence of the NH functionality. The ester carbonyl absorption was visible at 1747 cm⁻¹. In the ¹H NMR spectrum, the NH proton resonated as a singlet at δ = 7.71 ppm (exchangeable by D₂O). The methyl protons resonated as singlets at δ = 2.45 and 2.34 ppm, respectively. The methine proton of the isopropyl group appeared as a multiplet at δ = 5.08–4.99 ppm. The ester carbonyl carbon was discernible at δ = 151.2 ppm in the ¹³C NMR spectrum. The structure was established unambiguously by single-crystal X-ray analysis (Figure 2).¹⁰

Analogous results were obtained when diethyl- and di-*tert*-butyl-substituted azodicarboxylates were used in place of diisopropyl azodicarboxylate. The results are summarized in Table 4. It may be noted that hydrazones make up a versatile class of chemical intermediates capa-

**Figure 2** Single-crystal X-ray crystallographic structure of compound **6d**

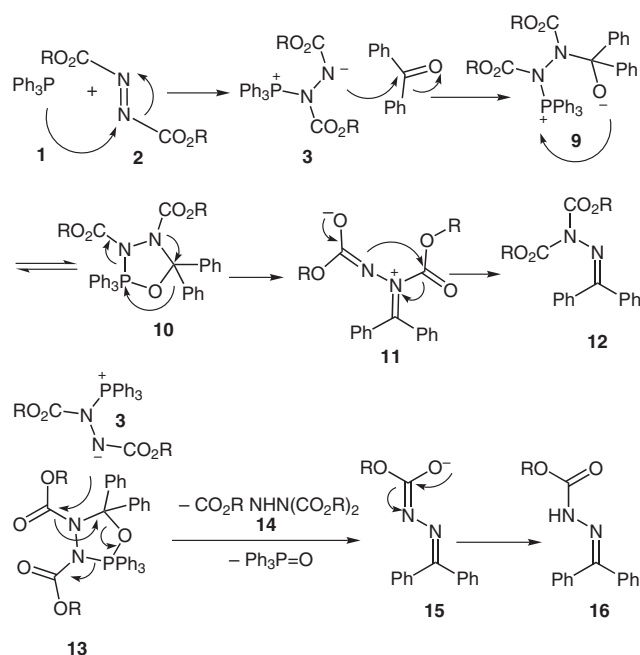
ble of acting as both electrophiles and nucleophiles.¹¹ These are useful precursors for the synthesis of heterocycles such as pyrazoles and oxadiazoles.¹²

Table 4 Reactions of the Triphenylphosphine–Diethyl or Di-*tert*-Butyl Azodicarboxylate Zwitterion with Various Diaryl Ketones^a

Entry	R	R ¹	R ²	Product 7	Yield (%)	Product 8	Yield (%)
1	Et	Ph	Ph	7a	40	8a	57
2	Et	4-PhC ₆ H ₄	4-PhC ₆ H ₄	7b	18	8b	81
3	Et	4-ClC ₆ H ₄	4-ClC ₆ H ₄	7c	–	8c	85
4	Et	4- <i>t</i> -BuC ₆ H ₄	4- <i>t</i> -BuC ₆ H ₄	7d	20	8d	60
5	<i>t</i> -Bu	4- <i>t</i> -BuC ₆ H ₄	4- <i>t</i> -BuC ₆ H ₄	7e	30	8e	55

^a Reagents and conditions: **2** (2.5 equiv), PPh₃ (**1**; 2.5 equiv), **4** (1 equiv), toluene, 110 °C, 12 h.

A mechanistic rationalization for the formation of the products can be outlined as follows (Scheme 3). The zwitterion **3** generated from triphenylphosphine and the dialkyl azodicarboxylate initially adds to the carbonyl group to form the tetrahedral intermediate **9**, which cyclizes to form **10** (Scheme 3). The latter can undergo two types of rearrangement. Elimination of one molecule of phosphine oxide followed by a nitrogen-to-nitrogen migration of the alkoxycarbonyl group will afford the bis(alkoxycarbonyl)hydrazone product **12** (Scheme 3). When excess zwitterion is present in the reaction medium, it can attack the relatively less hindered ester group on the nitrogen atom, thereby making the phosphine oxide elimination more facile and thus leading to the formation of the mono(alkoxycarbonyl)hydrazone **14**. The attack of the excess zwitterion occurs at the intermediate stage, i.e. before the elimination of triphenylphosphine oxide, not after the formation of bis(alkoxycarbonyl)hydrazone. This conclusion is drawn from the fact that the bis(alkoxycarbonyl)hydrazone derivative remains unchanged when it is subjected to toluene reflux in the presence of triphenylphosphine and dialkyl azodicarboxylate for 12 hours.



Scheme 3 Proposed reaction mechanism

In summary, we have examined the general reaction of various symmetrically and unsymmetrically substituted diaryl ketones with the nitrogen nucleophile derived from triphenylphosphine and an azodicarboxylate. By variation of the concentration of the phosphine–azodicarboxylate zwitterion, the reactivity could be tuned, and thereby selective synthesis of mono(alkoxycarbonyl)hydrazone and bis(alkoxycarbonyl)hydrazone derivatives could be achieved.

All reactions were carried out in oven-dried glassware under argon atmosphere. Progress of the reactions was monitored by TLC (visualization by exposure to UV light or I_2), while purification was effected by silica gel column chromatography (100–200 mesh). ^1H (300 MHz) and ^{13}C (75 MHz) NMR data of samples in CDCl_3 were collected at r.t. on a Bruker Avance DPX-300 MHz NMR spectrometer. IR spectra were recorded on a Bomem MB Series FT-IR spectrophotometer. Melting points were recorded on a Büchi melting point apparatus and are uncorrected. HRMS (EI, at 5000 resolution) was carried out on a JEOL JMS 600H mass spectrometer.

Bis(alkoxycarbonyl)hydrazones **5** and **7** and Mono(alkoxycarbonyl)hydrazones **6** and **8**; General Procedure

The appropriate dialkyl azodicarboxylate **2** (0.76 mmol) was added to a stirred soln of the appropriate diaryl ketone **4** (0.51 mmol) in toluene (5 mL), and the mixture was stirred under reflux. Ph_3P (199 mg, 0.76 mmol) in toluene (2 mL) was added dropwise to the refluxing soln, and the reaction mixture was kept stirring under reflux for 12 h. It was then cooled and the solvent was removed under reduced pressure on a rotary evaporator. The residue was subjected to column chromatography (silica gel, hexanes–EtOAc, 85:15); this afforded the bis(alkoxycarbonyl)- and mono(alkoxycarbonyl)hydrazone derivatives **5–8**.

Diisopropyl 2-(Diphenylmethylene)hydrazine-1,1-dicarboxylate (**5a**)

Colorless viscous liquid; yield: 141 mg (75%).

IR (film): 3014, 2987, 1778, 1737, 1610, 1517, 1473, 1377, 1263, 1211, 1095, 927, 786 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.65 (d, J = 7.2 Hz, 2 H), 7.48–7.47 (m, 2 H), 7.39–7.36 (m, 4 H), 7.27–7.21 (m, 2 H), 4.97–4.89 (m, 2 H), 1.28–1.20 (m, 12 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 176.4, 150.9, 144.8, 136.7, 134.5, 132.2, 129.9, 129.7, 129.5, 128.0, 127.9, 124.2, 115.4, 112.4, 70.9, 29.6, 21.7.

HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4$ [M^+]: 368.1503; found: 368.1518.

Isopropyl 2-(Diphenylmethylene)hydrazinecarboxylate (**6a**)

White solid; yield: 120 mg (82%); mp 91–93 °C.

IR (KBr): 3334, 3018, 2937, 1805, 1734, 1485, 1448, 1377, 1321, 1276, 1207, 1114, 1103, 1026, 920, 844, 788 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.71 (s, 1 H), 7.59–7.55 (m, 5 H), 7.32–7.26 (m, 5 H), 5.07–5.01 (m, 1 H), 1.36–1.21 (m, 6 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 157.9, 149.2, 148.6, 137.1, 132.0, 129.8, 129.6, 128.4, 128.2, 127.5, 71.8, 21.6.

HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$ [M^+]: 282.1736; found: 282.1739.

Diisopropyl 2-[Bis(1,1'-biphenyl-4-yl)methylene]hydrazine-1,1-dicarboxylate (**5b**)

Colorless crystalline solid; yield: 233 mg (88%); mp 175–178 °C.

IR (KBr): 2976, 1744, 1726, 1699, 1593, 1487, 1376, 1286, 1235, 1180, 1113, 1095, 1044, 1006, 909, 842, 769, 731, 693, 613 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.80 (d, J = 8.1 Hz, 2 H), 7.66–7.61 (m, 8 H), 7.49–7.35 (m, 8 H), 5.01–4.97 (m, 2 H), 1.33–1.24 (m, 12 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 175.8, 150.9, 144.3, 142.4, 140.2, 135.6, 133.4, 130.6, 130.1, 128.9, 128.6, 128.4, 127.9, 127.1, 127.0, 126.9, 126.8, 72.0, 71.1, 22.1, 21.8, 21.7, 21.6.

HRMS (EI): m/z calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2\text{O}_4$ [M^+]: 520.2362; found: 520.2361.

Isopropyl 2-[Bis(1,1'-biphenyl-4-yl)methylene]hydrazinecarboxylate (6b)

Colorless crystalline solid; yield: 181 mg (82%); mp 157–159 °C.

IR (KBr): 3346, 3030, 2974, 1749, 1712, 1606, 1489, 1394, 1323, 1301, 1207, 1111, 1064, 1014, 933, 854, 763, 736, 700, 495 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.80 (m, 3 H), 7.71–7.65 (m, 4 H), 7.59–7.31 (m, 12 H), 5.09–5.06 (m, 1 H), 1.36–1.27 (m, 6 H).¹³C NMR (75 MHz, CDCl₃): δ = 150.0, 142.7, 142.1, 140.4, 139.9, 136.0, 130.7, 128.9, 128.8, 128.4, 128.0, 127.5, 127.1, 127.0, 126.8, 72.1, 22.1, 21.7.HRMS (EI): *m/z* calcd for C₂₉H₂₆N₂O₂ [M⁺]: 434.1994; found: 434.1941.**Diisopropyl 2-[Bis(4-chlorophenyl)methylene]hydrazine-1,1-dicarboxylate (5c)**

Colorless crystalline solid; yield: 205 mg (96%); mp 91–93 °C.

IR (KBr): 2983, 1745, 1726, 1691, 1585, 1487, 1462, 1382, 1342, 1282, 1253, 1176, 1093, 833, 761 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.59 (d, *J* = 8.6 Hz, 2 H), 7.41–7.33 (m, 4 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 4.96–4.88 (m, 2 H), 1.23–1.21 (m, 12 H).¹³C NMR (75 MHz, CDCl₃): δ = 173.6, 150.5, 137.8, 135.7, 134.5, 132.2, 130.5, 130.0, 129.7, 129.3, 128.4, 128.2, 71.1, 21.8, 21.5.HRMS (EI): *m/z* calcd for C₂₁H₂₂Cl₂N₂O₄ [M⁺]: 436.0957; found: 436.0956.**Diisopropyl 2-[Bis(4-tolyl)methylene]hydrazine-1,1-dicarboxylate (5d)**

Colorless viscous liquid; yield: 77 mg (39%).

IR (film): 2983, 2929, 1743, 1714, 1593, 1506, 1454, 1377, 1344, 1282, 1255, 1180, 1138, 1093, 910, 827, 767 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.54 (d, *J* = 8.1 Hz, 2 H), 7.18–7.08 (m, 6 H), 4.97–4.89 (m, 2 H), 2.38 (s, 6 H), 1.25–1.21 (m, 12 H).¹³C NMR (75 MHz, CDCl₃): δ = 176.6, 150.7, 141.6, 139.3, 134.2, 131.7, 129.5, 128.8, 128.6, 127.9, 71.9, 70.7, 21.7, 21.5, 21.4, 21.3, 20.9.HRMS (EI): *m/z* calcd for C₂₃H₂₈N₂O₄ [M⁺]: 396.2049; found: 396.2023.**Isopropyl 2-[Bis(4-tolyl)methylene]hydrazinecarboxylate (6d)**

White solid; yield: 100 mg (65%); mp 122–124 °C.

IR (KBr): 3352, 2980, 1747, 1610, 1485, 1406, 1379, 1323, 1222, 1178, 1105, 1064, 970, 824, 768, 497 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.71 (s, 1 H), 7.45 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.15–7.07 (m, 4 H), 5.08–4.99 (m, 1 H), 2.45 (s, 3 H), 2.34 (s, 3 H), 1.36–1.19 (m, 6 H).¹³C NMR (75 MHz, CDCl₃): δ = 151.2, 139.5, 134.5, 131.4, 128.8, 128.3, 127.5, 69.3, 22.7, 21.7, 21.6, 21.4.HRMS (EI): *m/z* calcd for C₁₉H₂₂N₂O₂ [M⁺]: 310.1681; found: 310.1675.**Diisopropyl 2-[Bis(4-*tert*-butylphenyl)methylene]hydrazine-1,1-dicarboxylate (5e)**

White solid; yield: 98 mg (40%); mp 76–78 °C.

IR (KBr): 2976, 2960, 1745, 1465, 1355, 1259, 1182, 1143, 1097, 910, 840 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.58 (d, *J* = 8.4 Hz, 2 H), 7.40–7.36 (m, 4 H), 7.15 (d, *J* = 8.3 Hz, 2 H), 4.96–4.92 (m, 2 H), 1.34 (s, 18 H), 1.22–1.19 (m, 12 H).¹³C NMR (75 MHz, CDCl₃): δ = 176.3, 154.6, 152.4, 150.8, 134.3, 131.7, 129.4, 127.9, 125.1, 71.1, 70.8, 34.9, 34.8, 31.3, 21.8, 21.6, 20.9.HRMS (EI): *m/z* calcd for C₂₉H₄₀N₂O₄ [M⁺]: 480.2988; found: 480.2870.**Isopropyl 2-[Bis(4-*tert*-butylphenyl)methylene]hydrazinecarboxylate (6e)**

White solid; yield: 72 mg (40%); mp 176–178 °C.

IR (KBr): 3261, 2958, 1747, 1720, 1492, 1367, 1226, 1109, 1056, 1020, 939, 829, 769 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.77 (s, 1 H), 7.55 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8.3 Hz, 2 H), 5.10–5.02 (m, 1 H), 1.39 (s, 9 H), 1.30 (s, 15 H).¹³C NMR (75 MHz, CDCl₃): δ = 152.6, 134.7, 129.2, 128.2, 127.4, 126.5, 125.0, 69.4, 34.9, 31.4, 31.3, 29.7, 22.1.HRMS (EI): *m/z* calcd for C₂₅H₃₄N₂O₂ [M⁺]: 394.2620; found: 394.2635.**Diisopropyl (2*Z*)-2-[Phenyl(4-tolyl)methylene]hydrazine-1,1-dicarboxylate (5f)**

Colorless viscous liquid; yield: 86 mg (44%).

IR (film): 3018, 2985, 1765, 1517, 1471, 1423, 1379, 1276, 1220, 1209, 1093, 927, 788, 727, 669, 624 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.65 (d, *J* = 8.1 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 2 H), 7.4–7.36 (m, 2 H), 7.24–7.18 (m, 3 H), 7.12 (d, *J* = 8.1 Hz, 1 H), 5.01–4.91 (m, 2 H), 2.39 (s, 3 H), 1.22 (d, *J* = 6.3 Hz, 12 H).¹³C NMR (75 MHz, CDCl₃): δ = 176.4, 150.7, 139.7, 134.5, 132.2, 130.4, 129.6, 128.9, 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 72.1, 70.9, 22.1, 21.8, 21.6, 21.5.HRMS (EI): *m/z* calcd for C₂₂H₂₆N₂O₄ [M⁺]: 382.1893; found: 382.1893.**Isopropyl (2*Z*)- and (2*E*)-2-[Phenyl(4-tolyl)methylene]hydrazinecarboxylate (6f)**

Colorless viscous liquid; yield: 120 mg (80%).

IR (film): 3352, 2981, 1745, 1608, 1487, 1379, 1323, 1217, 1107, 1064, 920, 825, 771, 698 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.76 (s, 2 H), 7.58–7.53 (m, 6 H), 7.45 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.30–7.24 (m, 4 H), 7.16–7.08 (m, 4 H), 5.08–5.00 (m, 2 H), 2.45 (s, 3 H), 2.38 (s, 3 H), 1.29–1.23 (m, 12 H).¹³C NMR (75 MHz, CDCl₃): δ = 152.1, 151.9, 139.6, 139.4, 137.2, 134.3, 132.2, 132.0, 130.4, 129.7, 129.6, 129.3, 128.9, 128.8, 128.4, 128.3, 128.1, 127.5, 127.4, 71.7, 69.4, 22.0, 21.7, 21.6, 20.9.HRMS (EI): *m/z* calcd for C₁₈H₂₀N₂O₂ [M⁺]: 296.1525; found: 296.1522.**Diisopropyl (2*Z*)-2-[Phenyl(3-tolyl)methylene]hydrazine-1,1'-dicarboxylate (5g)**

Colorless viscous liquid; yield: 109 mg (56%).

IR (film): 3020, 2983, 1768, 1739, 1517, 1473, 1423, 1379, 1274, 1209, 1093, 1045, 927, 844, 748, 669 cm⁻¹.¹H NMR (300 MHz, CDCl₃): δ = 7.66 (d, *J* = 7.2 Hz, 2 H), 7.57 (s, 1 H), 7.49–7.46 (m, 1 H), 7.41–7.36 (m, 3 H), 7.30–7.21 (m, 2 H), 5.13–5.01 (m, 2 H), 2.36 (s, 3 H), 1.31–1.29 (m, 12 H).¹³C NMR (75 MHz, CDCl₃): δ = 176.9, 149.9, 137.8, 137.5, 136.7, 134.5, 131.3, 129.7, 128.2, 127.9, 127.8, 126.9, 124.8, 72.2, 70.9, 21.9, 21.8, 21.7, 21.3.

HRMS (EI): m/z calcd for $C_{22}H_{26}N_2O_4$ [M^+]: 382.1893; found: 382.1924.

Isopropyl (2Z)- and (2E)-2-[Phenyl(3-tolyl)methylene]hydrazinecarboxylate (6g)

Colorless viscous liquid; yield: 84 mg (56%).

IR (film): 3321, 3018, 1737, 1600, 1521, 1423, 1222, 927, 771, 667 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (br s, 2 H), 7.58–7.44 (m, 7 H), 7.32–7.24 (m, 7 H), 7.16–7.13 (m, 2 H), 7.06–7.04 (m, 2 H), 5.12–5.00 (m, 2 H), 2.42 (s, 3 H), 2.32 (s, 3 H), 1.36–1.25 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 148.5, 139.5, 137.6, 137.1, 136.9, 132.2, 131.9, 130.4, 130.2, 129.7, 129.6, 129.2, 128.7, 128.4, 128.1, 127.9, 127.8, 127.5, 125.3, 124.9, 71.6, 69.4, 22.0, 21.7, 21.4.

HRMS (EI): m/z calcd for $C_{18}H_{20}N_2O_2$ [M^+]: 296.1525; found: 296.1539.

Diisopropyl (2Z)-2-[(3,4-Dimethylphenyl)(phenyl)methylene]hydrazine-1,1-dicarboxylate (5h)

Colorless viscous liquid; yield: 70 mg (35%).

IR (film): 3014, 2987, 1778, 1737, 1610, 1517, 1473, 1377, 1263, 1211, 1095, 928, 786 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 1 H), 7.53–7.45 (m, 2 H), 7.39–7.34 (m, 2 H), 7.22–7.19 (m, 1 H), 7.14–7.09 (m, 1 H), 6.95–6.93 (m, 1 H), 4.99–4.91 (m, 2 H), 2.28 (s, 3 H), 2.23 (s, 3 H), 1.24–1.21 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.3, 150.7, 140.6, 138.1, 136.2, 134.7, 131.3, 130.3, 129.9, 129.6, 129.5, 129.3, 128.8, 128.1, 128.0, 127.9, 127.4, 125.4, 125.3, 72.1, 70.9, 21.9, 21.8, 21.6, 20.0.

HRMS (EI): m/z calcd for $C_{23}H_{28}N_2O_4$ [M^+]: 396.2049; found: 396.2061.

Isopropyl (2Z)- and (2E)-2-[(3,4-Dimethylphenyl)(phenyl)methylene]hydrazinecarboxylate (6h)

White solid; yield: 125 mg (80%); mp 96–98 °C.

IR (KBr): 3358, 2980, 1747, 1489, 1448, 1379, 1321, 1273, 1219, 1180, 1141, 1107, 1068, 924, 823, 771, 704, 501 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.70 (s, 1 H), 7.61–7.46 (m, 6 H), 7.31–7.18 (m, 7 H), 7.06–6.97 (m, 3 H), 5.13–5.00 (m, 2 H), 2.33 (d, J = 10.4 Hz, 6 H), 2.23 (d, J = 4.7 Hz, 6 H), 1.42–1.21 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.9, 151.1, 138.2, 138.1, 137.2, 136.2, 134.6, 132.2, 130.7, 129.6, 129.5, 129.3, 129.1, 128.3, 127.9, 127.4, 125.6, 125.3, 71.6, 69.2, 21.6, 21.5, 19.8, 19.6, 19.5.

HRMS (EI): m/z calcd for $C_{19}H_{22}N_2O_2$ [M^+]: 310.1681; found: 310.1645.

Diisopropyl (2Z)-2-[(4-Methoxyphenyl)(phenyl)methylene]hydrazine-1,1-dicarboxylate (5i)

Colorless viscous liquid; yield: 79 mg (39%).

IR (KBr): 3018, 1737, 1606, 1510, 1489, 1467, 1375, 1263, 1226, 1095, 1033, 927, 779, 667 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.59 (m, 2 H), 7.39–7.35 (m, 2 H), 7.23–7.16 (m, 2 H), 6.91–6.79 (m, 3 H), 5.07–4.99 (m, 2 H), 3.82 (s, 3 H), 1.37–1.30 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 150.7, 144.8, 137.2, 134.7, 131.2, 129.8, 129.6, 129.2, 128.1, 127.9, 127.8, 113.5, 70.8, 69.9, 55.2, 21.8, 21.7, 21.6.

HRMS (EI): m/z calcd for $C_{22}H_{26}N_2O_5$ [M^+]: 398.1842; found: 398.1833.

Diisopropyl (2Z)- and (2E)-2-[(4-Methoxyphenyl)(phenyl)methylene]hydrazinecarboxylate (6i)

White crystalline solid; yield: 100 mg (63%); mp 60–62 °C.

IR (KBr): 3354, 3290, 2981, 2935, 1739, 1606, 1487, 1377, 1261, 1219, 1176, 1106, 1055, 1029, 918, 837, 781, 766, 702, 580 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1 H), 7.65 (s, 1 H), 7.60–7.50 (m, 6 H), 7.32–7.18 (m, 8 H), 7.07 (d, J = 8.7 Hz, 2 H), 6.83 (d, J = 8.9 Hz, 2 H), 5.11–5.02 (m, 2 H), 3.89 (s, 3 H), 3.80 (s, 3 H), 1.30–1.26 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 160.4, 149.9, 137.4, 129.8, 129.6, 129.2, 128.9, 128.4, 128.0, 127.6, 72.0, 69.3, 55.2, 55.1, 22.0, 21.9, 21.7, 21.6.

HRMS (EI): m/z calcd for $C_{18}H_{20}N_2O_3$ [M^+]: 312.1474; found: 312.1440.

Diethyl 2-(Diphenylmethylene)hydrazine-1,1'-dicarboxylate (7a)

White solid; yield: 69 mg (40%); mp 67–69 °C.

IR (KBr): 3018, 2980, 1774, 1741, 1521, 1475, 1423, 1371, 1265, 1209, 1105, 1045, 927, 848, 740, 667 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.64 (m, 2 H), 7.42–7.38 (m, 6 H), 7.23–7.19 (m, 2 H), 4.39–4.26 (m, 4 H), 1.39–1.29 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.6, 150.8, 136.5, 134.3, 131.4, 129.9, 129.5, 128.2, 127.7, 127.4, 66.3, 63.9, 62.9, 14.4, 14.1, 13.8.

HRMS (EI): m/z calcd for $C_{19}H_{20}N_2O_4$ [M^+]: 340.1423; found: 340.1434.

Ethyl 2-(Diphenylmethylene)hydrazinecarboxylate (8a)

White solid; yield: 76 mg (57%); mp 93–95 °C.

IR (KBr): 3350, 2981, 1747, 1506, 1492, 1444, 1325, 1219, 1068, 1028, 765, 698 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.76 (s, 1 H), 7.59–7.56 (m, 5 H), 7.36–7.26 (m, 5 H), 4.28–4.26 (m, 2 H), 1.32 (br s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 136.9, 131.9, 129.7, 128.4, 128.1, 127.5, 118.2, 61.8, 14.5.

HRMS (EI): m/z calcd for $C_{16}H_{16}N_2O_2$ [M^+]: 268.1212; found: 268.1187.

Diethyl 2-[Bis(1,1'-biphenyl-4-yl)methylene]hydrazine-1,1'-dicarboxylate (7b)

Colorless viscous liquid; yield: 44 mg (18%).

IR (film): 3018, 2983, 1770, 1517, 1473, 1419, 1373, 1276, 1209, 1103, 1043, 927, 848, 752, 669 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.74 (m, 2 H), 7.63–7.54 (m, 8 H), 7.45–7.27 (m, 8 H), 4.19–4.16 (m, 4 H), 1.24–1.20 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.0, 150.4, 144.4, 142.4, 140.0, 135.3, 133.1, 129.9, 128.9, 128.7, 128.3, 127.8, 127.7, 126.9, 126.7, 63.9, 62.9, 14.3, 13.9.

HRMS (EI): m/z calcd for $C_{31}H_{28}N_2O_4$ [M^+]: 492.2049; found: 492.2046.

Ethyl 2-[Bis(1,1'-biphenyl-4-yl)methylene]hydrazinecarboxylate (8b)

Colorless viscous liquid; yield: 173 mg (81%).

IR (KBr): 3346, 3030, 2974, 1749, 1712, 1606, 1489, 1394, 1323, 1301, 1207, 1111, 1064, 1014, 933, 854, 763, 736, 700, 495 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 1 H), 7.81–7.78 (m, 2 H), 7.71–7.64 (m, 4 H), 7.60–7.31 (m, 12 H), 4.34–4.29 (m, 2 H), 1.35–1.30 (m, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 150.4, 142.5, 142.0, 140.2, 139.7, 135.8, 130.4, 128.9, 128.8, 127.9, 126.9, 126.7, 63.9, 14.1.

HRMS (EI): m/z calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$ [M^+]: 420.1838; found: 420.1847.

Ethyl 2-[Bis(4-chlorophenyl)methylene]hydrazinecarboxylate (8c)

White crystalline solid; yield: 144 mg (85%); mp 157–159 °C.

IR (KBr): 3230, 2987, 1749, 1693, 1602, 1485, 1452, 1377, 1334, 1298, 1170, 1122, 1014, 831, 771, 690 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.69 (s, 1 H), 7.57 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.5 Hz, 2 H), 7.28 (d, J = 11.3 Hz, 2 H), 7.21 (d, J = 11.3 Hz, 2 H), 4.28–4.25 (m, 2 H), 1.32–1.25 (m, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 153.1, 148.5, 136.2, 135.6, 135.1, 130.6, 130.2, 129.8, 128.5, 128.4, 61.9, 14.4.

HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2$ [M^+]: 336.0432; found: 336.0435.

Diethyl 2-[Bis(4-tert-butylphenyl)methylene]hydrazine-1,1'-dicarboxylate (7d)

White solid; yield: 46 mg (20%); mp 147–149 °C.

IR (KBr): 3018, 2968, 1780, 1735, 1614, 1502, 1473, 1371, 1267, 1207, 1105, 1047, 927, 842, 766, 669 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.59 (d, J = 8.5 Hz, 2 H), 7.39 (d, J = 8.5 Hz, 4 H), 7.13 (d, J = 8.4 Hz, 2 H), 4.22–4.13 (m, 4 H), 1.33–1.31 (m, 18 H), 1.26–1.20 (m, 6 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 176.6, 154.8, 152.4, 151.0, 133.9, 131.5, 129.4, 125.1, 63.7, 62.8, 34.7, 31.2, 31.1, 14.2, 14.1.

HRMS (EI): m/z calcd for $\text{C}_{27}\text{H}_{36}\text{N}_2\text{O}_4$ [M^+]: 452.2519; found: 452.2517.

Ethyl 2-[Bis(4-tert-butylphenyl)methylene]hydrazinecarboxylate (8d)

White solid; yield: 116 mg (60%); mp 144–146 °C.

IR (KBr): 3290, 2960, 2902, 1751, 1724, 1496, 1400, 1363, 1321, 1267, 1230, 1064, 835 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.79 (s, 1 H), 7.56–7.48 (m, 4 H), 7.31 (d, J = 8.6 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 4.28–4.25 (m, 2 H), 1.42–1.37 (m, 9 H), 1.30 (s, 12 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 152.6, 151.2, 134.5, 130.0, 129.1, 128.1, 127.4, 126.5, 125.8, 124.9, 61.7, 34.9, 31.3, 31.2, 14.6.

HRMS (EI): m/z calcd for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2$ [M^+]: 380.2464; found: 380.2396.

Di-tert-butyl 2-[Bis(4-tert-butylphenyl)methylene]hydrazine-1,1'-dicarboxylate (7e)

White solid; yield: 78 mg (30%); mp 117–119 °C.

IR (KBr): 2960, 2868, 1747, 1724, 1606, 1504, 1456, 1396, 1365, 1328, 1274, 1251, 1159, 1118, 854, 771, 686 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.55 (d, J = 8.4 Hz, 2 H), 7.39–7.35 (m, 4 H), 7.19 (d, J = 8.3 Hz, 2 H), 1.39 (br s, 18 H), 1.34–1.33 (m, 18 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 174.5, 152.2, 149.7, 134.3, 131.6, 129.8, 129.1, 127.9, 124.9, 124.8, 82.3, 34.8, 34.6, 34.5, 31.1, 31.0, 28.1, 27.9, 27.8.

HRMS (EI): m/z calcd for $\text{C}_{31}\text{H}_{44}\text{N}_2\text{O}_4$ [M^+]: 508.3301; found: 508.3300.

tert-Butyl 2-[Bis(4-tert-butylphenyl)methylene]hydrazinecarboxylate (8e)

White solid; yield: 118 mg (55%); mp 189–191 °C.

IR (film): 3261, 2960, 1745, 1714, 1487, 1363, 1240, 1163, 1114, 1060, 877, 850, 831, 567 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.68 (s, 1 H), 7.54 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.5 Hz, 2 H), 7.29 (d, J = 8.5 Hz, 2 H), 7.18 (d, J = 8.2 Hz, 2 H), 1.42–1.39 (m, 9 H), 1.29–1.28 (m, 18 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 152.5, 134.7, 129.3, 128.2, 127.3, 126.5, 124.9, 81.1, 34.9, 31.4, 31.3, 28.4.

HRMS (EI): m/z calcd for $\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}_2$ [M^+]: 408.2777; found: 408.2768.

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