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New method for *in situ* generation of enolate-iminium 1,4-dipoles for [4 + 2] and [4 + 1] dipolar heterocycloaddition reactions†

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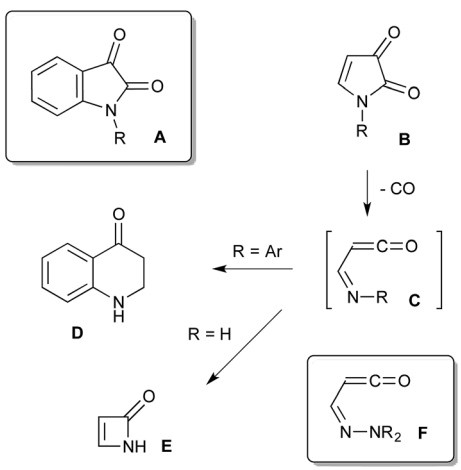
Generation of hydrazoylketenes by thermal decomposition of *N*-(diphenylenamino)pyrrolediones is accompanied by 5-*exo*-*trig* ring closure to furnish a zwitterionic dihydropyrazolone species. In contrast to Lisowskaya's earlier report, we established that in most cycloaddition reactions such dihydropyrazolones react as 1,4-dipoles. This reactivity pattern was demonstrated in several [4 + 4]-homodimerizations and in a series of [4 + 2] and [4 + 1] cycloaddition reactions with various dipolarophiles.

Introduction

2,3-Dihydro-2,3-pyrroldiones (**B**),[1] being monocyclic analogs of isatines (**A**),[2] can also be viewed as vinylogous lactams with a highly electrophilic conjugate double bond moiety. This unusual feature determines their very rich chemistry involving an array of addition and cyclo-condensation reactions allowing for expeditious assembly of various pyrrole-based scaffolds.[3,4] In addition, it is well documented that thermolysis of *N*-substituted pyrrolediones leads to decarbonylation to afford imidoylketenes (**C**) (Scheme 1).[5] The chemical behavior of the generated ketenes generally depends on the nature of the substituent at N-1. Thus, thermolysis of non-substituted and *N*-alkyl-substituted pyrroldiones (**A**, R = H, Alk) normally does not provide any distinct isolable products due to facile decomposition and polymerization of the corresponding ketenes. However, Wentrup reported detection of azetidinones **E** (or their cyclic dimers) under FVP conditions.[6] The reaction of *N*-aryl-substituted pyrrolediones (**A**, R = Ar) is typically accompanied by intramolecular C–H acylation of ketenes to provide 4-quinolones (**D**) (Scheme 1).[7] In the frame of our continuous studies on the transformations of imidoylketenes,[8,9] we became interested in the possibility of generating related hydrazoylketenes **F** and investigating their following transformations (Scheme 1). Herein we wish to report our progress in this area.



Scheme 1

Results and discussion

In 2004 Lisowskaya reported reactions of 2-(hydrazinyl)-4-oxobut-2-enoates **1** with oxalyl chloride.[10] It was proposed that *N*-(diphenylenamino)pyrroledione **2** initially formed under these conditions experienced facile CO-extrusion at elevated temperatures. Then, the resulting hydrazonoketene **3** undergoes further 5-*exo*-*trig* ring closure to provide a zwitterionic dihydropyrazolone species, which can be represented by two resonance forms **4** and **5**. Lisowskaya suggested that form **5** is a chief contributor, which renders it reactive as a 1,3-CNN-dipole. This proposal was supported by isolation of *tert*-butyl-substituted dimeric [3 + 3]-adduct **6c** (Scheme 2), the structure of which was unambiguously proved by X-ray crystallography.[10] By

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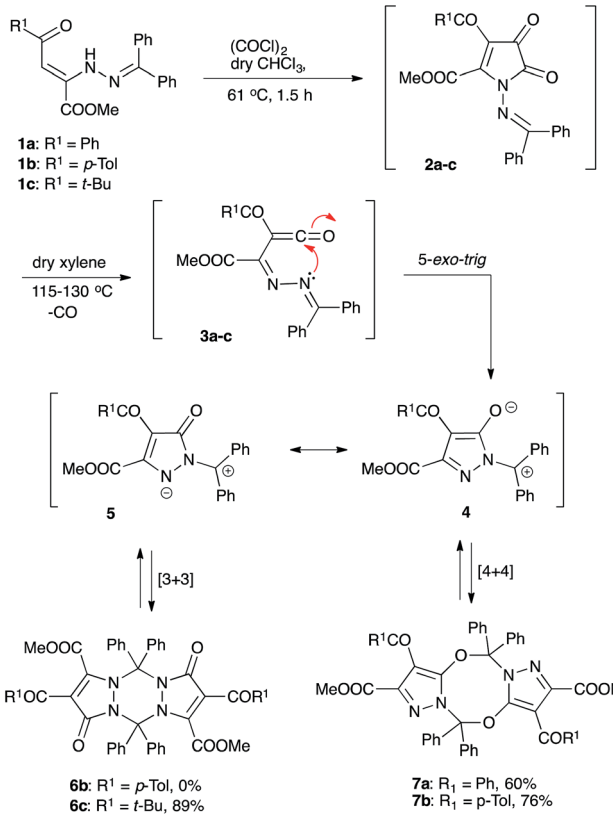


Scheme 2

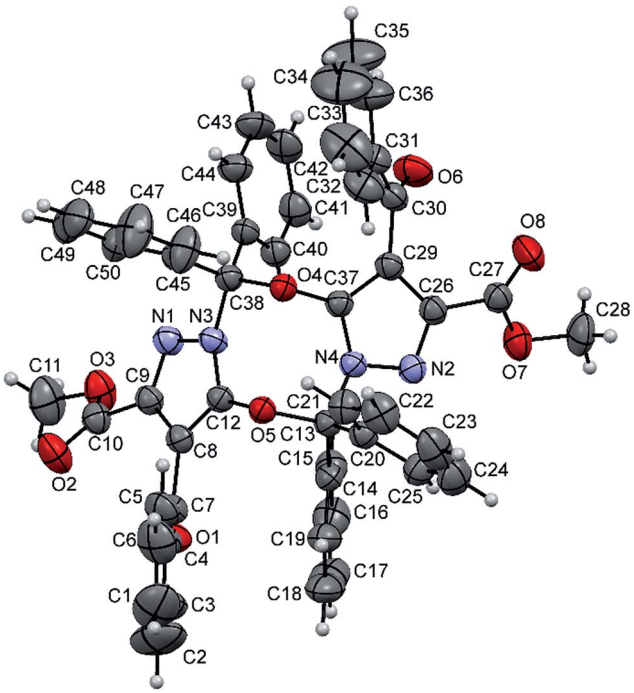
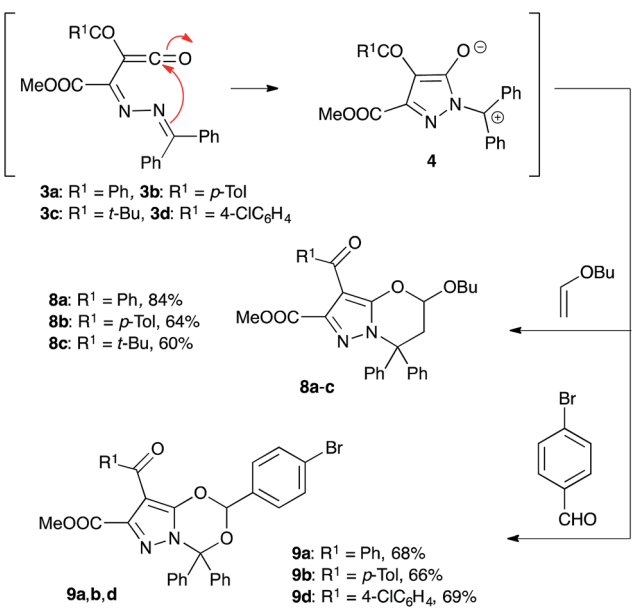


Fig. 1 ORTEP drawing of **7a** (CCDC #1457141) showing 50% probability amplitude displacement ellipsoids.

analogy, the same structure was putatively assigned to *p*-tolyl-substituted analog **6b** (Scheme 2), for which an isolated yield of 67% was reported.[10] We were very puzzled by this finding, since we felt that an alternative resonance form **4** – hosting an anionic charge on the more electronegative oxygen atom and strongly benefiting from aromatic stabilization of heterocyclic ring – should be more favored. If so, it could be able to react as a 1,4-dipole of unusual CNCO-type, which should open new avenues for expeditious assembly of heterocyclic scaffolds. Keeping this issue in mind, we decided to revisit this topic. In accordance with Lisowskaya's protocol, hydrazonoketenes were generated bearing phenyl (**3a**), *p*-tolyl (**3b**), and *tert*-butyl (**3c**) substituents. We confirmed that the reaction of the *tert*-butyl substituted starting material indeed led to the formation of [3 + 3]-cycloadduct, dipyrazolotetrazine **6c**, in 89% yield (Scheme 2). However, the reactivities of aryl-substituted derivatives were drastically different. Thus, in contrast to Lisowskaya's report, no [3 + 3]-cyclodimer **6b** was formed. Instead, bis-pyrazolodioxadiazocine **7b**—the product of [4 + 4]-cyclodimerization—was afforded in high yield resulting from the reactivity of 1,4-dipolar resonance form **4**. Similarly, in the reaction of phenyl-substituted ketene **3a**, [4 + 4]-cycloadduct **7a** was obtained, whose structure was proved by X-ray crystallography (CCDC #1457141, Fig. 1).

Inspired by these interesting initial results, we decided to elaborate on the development of various synthetic schemes utilizing the cycloaddition of this unusual 1,4-dipole. To this end, we performed the generation of ketenes **3a–c** in the presence of vinyl butyl ether, targeting products of [4 + 2] dipolar cycloaddition. Gratifyingly, these reactions proceeded smoothly and corresponding pyrazolooxazines **8a–c** were formed in good yields and with perfect regioselectivities (Scheme 3). Expectedly, the anionic terminus of the dipole attacks the more electropositive carbon atom of the enol ether, affording an exocyclic acetal moiety (Scheme 3). Interestingly, *tert*-butyl substituted

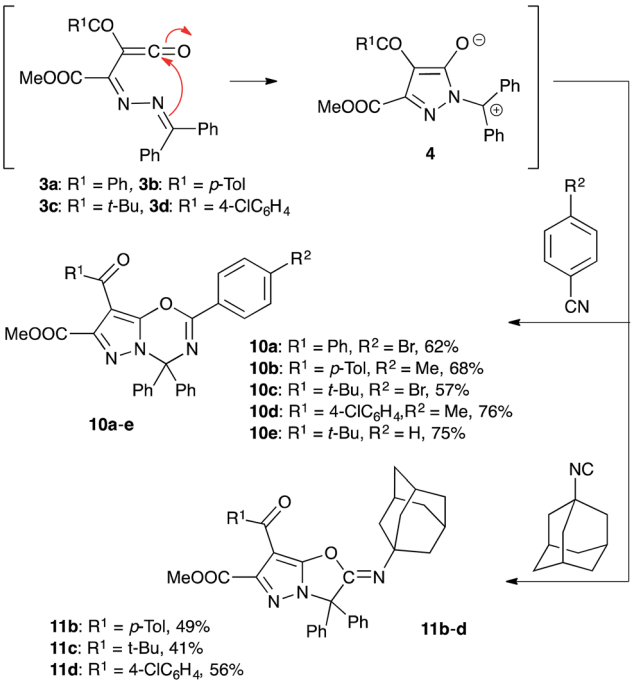


Scheme 3

ketene **3c** also reacted as a 1,4-dipole in this case, and the formation of a new oxazinane ring was confirmed by X-ray crystallography (CCDC #1457144, Fig. 2). Next, we decided to investigate the reactivity of these dipoles with electron-deficient dipolarophiles, such as aldehydes and nitriles. Ketenes **3a**, **b**, **d** were generated in the presence of *p*-bromobenzaldehyde to afford the corresponding pyrazolodioxazines **9a**, **b**, **d** in good yields (Scheme 3). Again, the regiochemistry of this [4 + 2]-cycloaddition process was perfect, in which the anionic oxygen formed a bond with the carbonyl carbon bearing a partial positive charge, furnishing cyclic acetal scaffolds (Scheme 3). Reaction in the presence of benzonitriles also proceeded uneventfully, providing the corresponding pyrazolooxadiazines in good yields (Scheme 4). Formation of cyclic adducts in the described transformations with aldehydes and nitriles was proved by X-ray crystal structures of products **9a** (CCDC #1457142, Fig. 3) and **10a** (CCDC #1457143, Fig. 4), respectively.

In an attempt to develop a related cascade transformation involving the [4 + 1]-cycloaddition pattern, we tested the interaction with isocyanides. As expected, this reaction was very facile and proceeded much faster than [4 + 2]-cycloadditions involving other dipolarophiles discussed above. The corresponding cycloadducts, pyrazolooxazoles **11b–d**, were afforded in medium yields (Scheme 4). Formation of a five-membered ring in **11d** was confirmed by single-crystal X-ray crystallography (CCDC #1457145, Fig. 5).

It should be emphasized that in all the tested transformations, zwitterionic intermediates reacted as 1,4-dipoles **4**. At the same time, formation of [3 + 3]-dimeric adduct **6c** could be potentially explained by thermodynamic control. Indeed, this might be the case, if dimerization reactions are reversible and **6c** is thermodynamically more favored than the alternative [4 + 4] adduct **7c**. To check this hypothesis, we heated 4 + 4 dimers **6** in the interval of 140 to 220 °C with or without solvents. Unfortunately, at such high temperatures in the absence of dipolarophiles most of the material decomposed with the formation of polymeric resins, and we failed to



Scheme 4

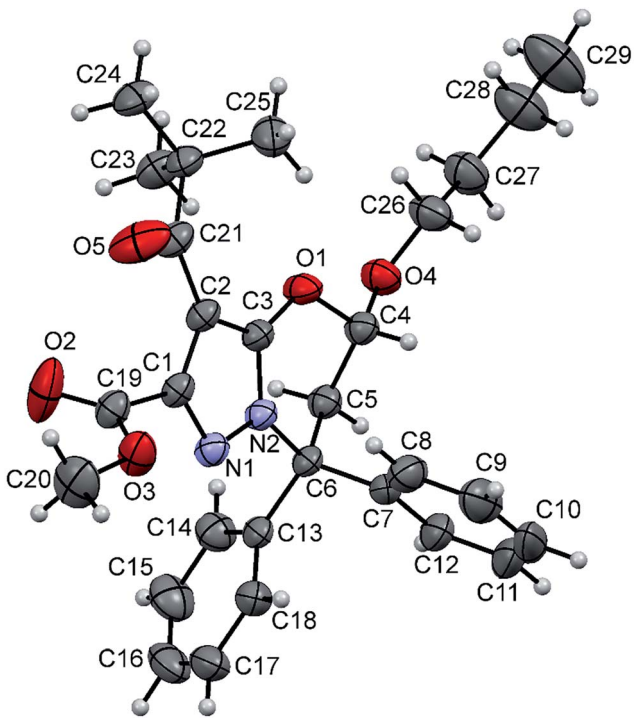


Fig. 2 ORTEP drawing of **8c** (CCDC #1457144) showing 50% probability amplitude displacement ellipsoids.

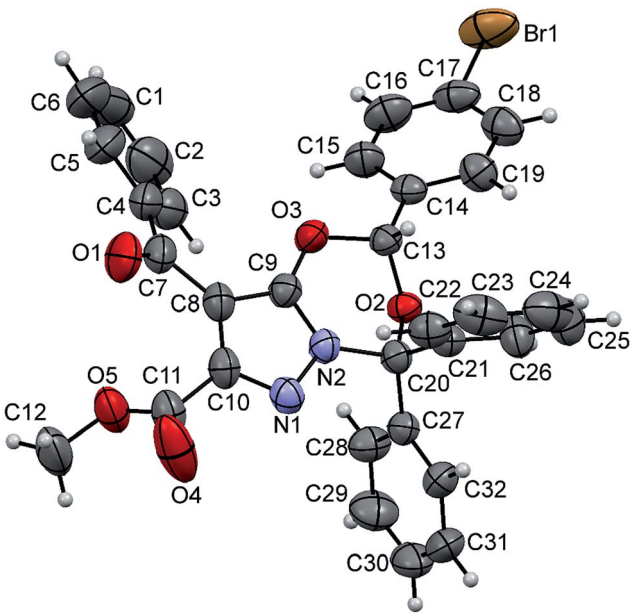


Fig. 3 ORTEP drawing of **9a** (CCDC #1457142) showing 50% probability amplitude displacement ellipsoids.

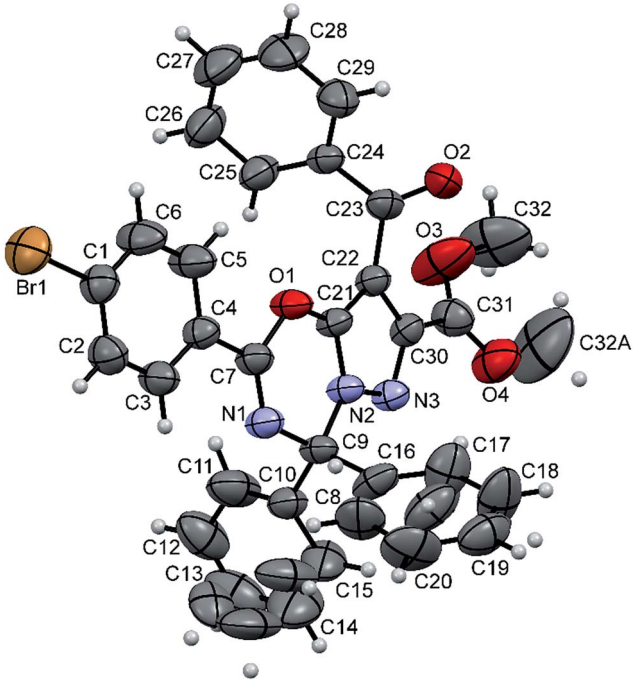


Fig. 4 ORTEP drawing of **10a** (CCDC #1457143) showing 50% probability amplitude displacement ellipsoids. Phenyl groups C10–C15 and C8, C16–C20 show librational and rotational disorder, respectively.

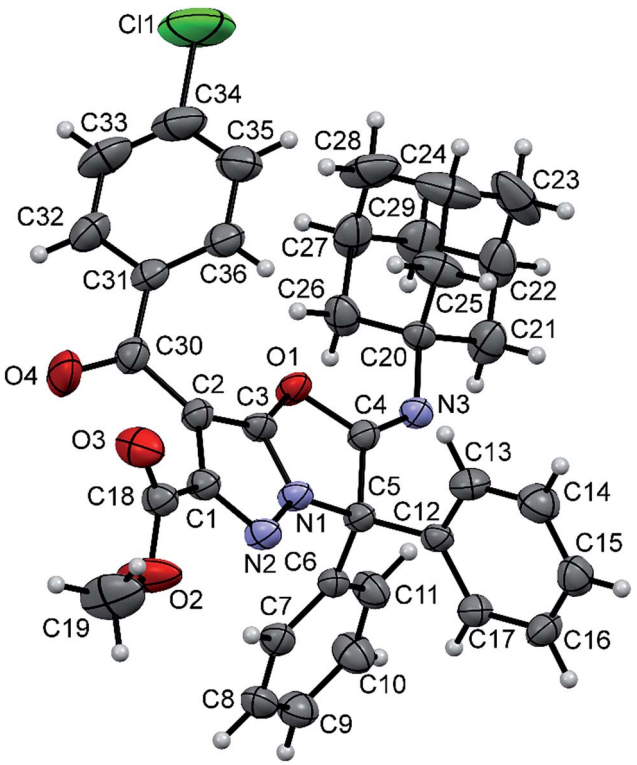


Fig. 5 ORTEP drawing of **11d** (CCDC #1457145) showing 50% probability amplitude displacement ellipsoids.

detect any [3 + 3]-adducts in the reaction mixtures. However we noticed that short-term heating of the colorless solution of [4 + 4]-adducts **6** (or [3 + 3]-adducts **7** alike) in xylene at temperatures exceeding their decomposition point (110–140 °C) leads in both cases to the formation of navy-blue solution of monomeric zwitterions **4**, which can be easily intercepted by appropriate dipolarophiles. Thus, addition of 1-isocyanoadamantane to a solution of [4 + 4]-dimeric compound **7b** stirred in xylene at 140 °C led to the formation of [4 + 1]-cross adduct **11b**, which was isolated in 32% yield. Similarly, [4 + 1]-cross adduct **11c** was afforded in a yield of 67% by melting a neat mixture of [3 + 3]-dimer **6c** with the same isocyanide.

Conclusions

It was confirmed, that the generation of hydrazonoketenes **3** by thermal decomposition of *N*-(diphenylenamino)pyrrolediones **2** is accompanied by 5-*exo*-*trig* ring closure to furnish zwitterionic dihydropyrazolone species. Lisowskaya, who previously investigated this reaction, suggested that these species have predominantly azomethine-iminium form **5** and react as 1,3-dipoles. In contrast to her report, we established that in most reactions such dihydropyrazolones have predominantly enolate-iminium form **4** and react as 1,4-dipoles. This reactivity pattern was demonstrated in several [4 + 4]-homodimerizations and in a series of [4 + 2] and [4 + 1] cycloaddition reactions with various dipolarophiles.

Experimental part

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD spectrometer (400 or 100 MHz, respectively) in $CDCl_3$ using TMS (δ_H = 0.00 ppm), HMDSO (δ_H = 0.07 ppm) or the residual solvent peak (δ_H = 7.26 ppm, δ_C = 77.16 ppm) as internal standards. FT-IR spectra were recorded for mulls in mineral oil employing Perkin Elmer Spectrum Two spectrometer. The mass spectra were recorded on an Waters UPLC-MS instrument equipped with an ESI MS Xevo TQD detector. Combustion elemental analysis (CHN) was performed on a Perkin Elmer 2400 Series II Analyzer. Melting points were measured with Mettler Toledo MP70 Melting Point System. Anhydrous toluene was obtained by heating at reflux with molten sodium followed by distillation in under an atmosphere of dry nitrogen. Anhydrous chloroform was obtained by heating at reflux with phosphorus pentoxide followed by distillation in under an atmosphere of dry nitrogen. Reaction progress and purity of isolated compounds were monitored by TLC (Merck, Silica gel 60 F254), eluting with toluene/EtOAc mixtures. All reagents and solvents were purchased from commercial vendors and used as received. X-ray structural analysis of compounds **7a**, **8c**, **9a**, **10a**, and **11d** were performed on an Xcalibur Ruby diffractometer using Mo X-ray source (MoKα 0.71073 Å), scanning at 295(2) K. The structures were solved by the SHELXS software and refined by full-matrix least-squares on all F^2 data using SHELXL-97 (ref. 11) in conjunction with the WinGX graphical

user interface.[12] Full crystallographic data are deposited at the Cambridge Crystallographic Data Center (CCDC #1457141 (**7a**), #1457144 (**8c**), #1457142 (**9a**), #1457143 (**10a**), #1457145 (**11d**)).

Methyl (*Z*)-2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-phenylbut-2-enoate (1a) (typical procedure)

To a solution of methyl 2,4-dioxo-4-phenylbutanoate (4.12 g, 20 mmol, 1.0 equiv.) in toluene (20 mL) were added benzophenone hydrazone (3.93 g, 20 mmol, 1.0 equiv.) and acetic acid (114 μL, 120 mg, 2 mmol, 10 mol%). The reaction mixture was refluxed for 2 h in a flask equipped with a Dean–Stark adaptor. The solution was cooled down to RT, the formed precipitate was filtered and purified by crystallization from ethanol, affording the titled compound as yellowish crystals in 93% yield (7.14 g, 18.6 mmol); mp 158–160 °C (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.73 (s, 1H), 7.84–7.79 (m, 2H), 7.71–7.61 (m, 3H), 7.58–7.54 (m, 2H), 7.48–7.31 (m, 8H), 6.02 (s, 1H), 4.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 164.6, 153.1, 151.7, 138.8, 137.1, 132.2, 131.9, 130.2, 129.9 (2C), 129.8, 128.5 (2C), 128.4 (4C), 127.8 (2C), 127.6 (2C), 91.8, 52.9; FT IR (cm^{-1}): 3056, 1737, 1619, 1608, 1582, 1554, 1506.

Methyl (*Z*)-2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-(*p*-tolyl)but-2-enoate (1b)

This compound was prepared according to typical procedure listed for **1a** employing methyl 2,4-dioxo-4-(*p*-tolyl)butanoate (4.40 g, 20 mmol, 1.0 equiv.) and isolated as yellowish crystals in 90% yield (7.16 g, 18.0 mmol); mp 145–147 °C (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ [12.71 (s) & 6.02 (s) & 4.54 (s), $\sum$2H], [7.86 (d, J = 8.3 Hz) & 7.72 (d, J = 8.2 Hz), $\sum$2H], [7.70–7.53 (m) & 7.46–7.31 (m), $\sum$10H], [7.22 (d, J = 8.0 Hz) & 7.18 (d, J = 8.0 Hz), $\sum$2H], [4.04 (s) & 3.83 (s), $\sum$3H], [2.39 (s) & 2.37 (s), $\sum$3H]. ^{13}C NMR (100 MHz, $CDCl_3$) δ major: 190.2, 164.7, 152.7, 151.4, 142.5, 137.2, 136.2, 132.2, 130.1, 129.9 (2C), 129.7, 129.1 (2C), 128.5 (2C), 128.4 (2C), 127.8 (2C), 127.7 (2C), 91.8, 52.9, 21.6; minor: 194.5, 164.8, 162.1, 151.8, 144.3, 137.7, 134.3, 134.1, 130.7 (2C), 130.4, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.2 (2C), 127.9 (2C), 52.9, 39.0, 21.7; FT IR (cm^{-1}): 3057, 1738, 1610, 1575, 1554, 1515.

Methyl (*Z*)-2-(2-(diphenylmethylene)hydrazinyl)-5,5-dimethyl-4-oxohex-2-enoate (1c)

This compound was prepared according to typical procedure listed for **1a** employing methyl 5,5-dimethyl-2,4-dioxohexanoate (3.72 g, 20 mmol, 1.0 equiv.) and isolated as yellowish crystals in 89% yield (6.50 g, 17.8 mmol); mp 150–152 °C (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (s, 1H), 7.65–7.55 (m, 3H), 7.52–7.47 (m, 2H), 7.37–7.28 (m, 5H), 5.48 (s, 1H), 3.98 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 165.0, 151.7, 150.8, 137.4, 132.2, 130.1, 129.8 (2C), 129.5, 128.6 (2C), 128.3 (2C), 127.7 (2C), 91.0, 52.8, 42.7, 27.3 (3C); FT IR (cm^{-1}): 3057, 1739, 1616, 1584, 1557, 1504.

Methyl (*Z*)-4-(4-chlorophenyl)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxobut-2-enoate (1d)

This compound was prepared according to typical procedure listed for **1a** employing methyl 4-(4-chlorophenyl)-2,4-dioxobutanoate (4.81 g, 20 mmol, 1.0 equiv.) and isolated as yellowish crystals in 92% yield (7.70 g, 18.4 mmol); mp 165–167 °C (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ [12.73 (s) & 5.96 (s) & 4.51 (s), $\sum$2H], [7.90–7.85 (m) & 7.77–7.72 (m), $\sum$2H], [7.70–7.53 (m) & 7.32–7.46 (m), $\sum$12H], [4.04 (s) & 3.83 (s), $\sum$3H]. ^{13}C NMR (100 MHz, $CDCl_3$) δ major: 188.9, 164.4, 153.5, 152.0, 138.1, 137.1, 136.9, 132.1, 130.2, 129.9 (2C), 129.9, 129.0 (2C), 128.6 (2C), 128.4 (2C), 128.4 (2C), 127.8 (2C), 91.3, 52.9; minor: 193.8, 164.7, 162.5, 151.5, 139.9, 137.5, 134.9, 134.2, 130.6 (2C), 130.0, 129.8 (2C), 129.5 (2C), 129.0 (2C), 128.2 (2C), 127.9 (2C), 53.0, 38.94; FT IR (cm^{-1}): 3056, 1737, 1609, 1594, 1576, 1550, 1505.

Dimethyl 3,9-dibenzoyl-5,5,11,11-tetraphenyl-5*H*,11*H*-dipyrazolo[5,1-*b*:5′,1′-*f*][1,5,3,7]dioxadiazocine-2,8-dicarboxylate (7a) (typical procedure A)

To a stirred solution of methyl (*Z*)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxo-4-phenylbut-2-enoate (384 mg, 1 mmol, 1.0 equiv.) in dry $CHCl_3$ (2 mL), oxalyl chloride (86 μL, 127 mg, 1 mmol, 1.0 equiv.) was added. The reaction mixture was refluxed for 90 min, then *o*-xylene (2 ml) was added. Chloroform was distilled off until the vapor temperature above the mixture reached 130 °C. After refluxing for 10 min the solution was cooled down to RT, diethyl ether (200 μL) was added, and the mixture was set aside for crystallization. Next day, the formed precipitate was filtered off and purified by re-crystallization from acetone, affording the titled compound as colorless crystals in 60% yield (246 mg, 0.3 mmol); mp 110–120 °C (acetone, with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.37 (m, 2H), 7.37–6.95 (m, 28H), 3.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 161.7, 149.1, 144.0, 136.5, 132.9, 129.9, 129.8, 128.3, 127.8, 114.8, 103.2, 52.3; FT IR (cm^{-1}): 1746, 1733, 1666, 1596, 1579, 1547; MS (ESI+): found 843.04; calcd. for $C_{50}H_{36}N_4NaO_8$ $(M + Na)^+$ 843.24; EA (%) calcd. for $C_{50}H_{36}N_4O_8$: C 73.16, H 4.42, N 6.83; found: C 72.97, H 4.23, N 6.95.

Dimethyl 3,9-bis(4-methylbenzoyl)-5,5,11,11-tetraphenyl-5*H*,11*H*-dipyrazolo[5,1-*b*:5′,1′-*f*][1,5,3,7]dioxadiazocine-2,8-dicarboxylate (7b)

This compound was prepared according to the typical procedure A employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-(*p*-tolyl)but-2-enoate (398 mg, 1 mmol, 1.0 equiv.) and isolated as colorless crystals in 76% yield (322 mg, 0.38 mmol); mp 110–111 °C (acetone, with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.11 (m, 24H), 7.05 (d, J = 8.0 Hz, 4H), 3.54 (s, 6H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 161.1, 148.3, 143.3, 143.0, 133.6, 129.3, 129.2, 127.8, 127.6, 114.4, 102.5, 51.6, 21.1; FT IR (cm^{-1}): 1731, 1664, 1602, 1556; MS (ESI+): found 849.41; calcd. for $C_{52}H_{41}N_4O_8$ $(M + H)^+$ 849.29; EA (%) calcd. for $C_{52}H_{40}N_4O_8$: C 73.57, H 4.75, N 6.60; found: C 73.46, H 4.61, N 6.64.

Methyl 3-benzoyl-5-butoxy-7,7-diphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (8a) (typical procedure B)

To a solution of methyl (*Z*)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxo-4-phenylbut-2-enoate (384 mg, 1 mmol, 1.0 equiv.) in $CHCl_3$ (2 mL) was added oxalyl chloride (86 μL, 127 mg, 1 mmol, 1.0 equiv.) in one portion. The reaction mixture was refluxed for 90 min, then *o*-xylene (2 mL) was added, and chloroform was distilled out until the vapor temperature above the mixture reached 120 °C. After that the solution was refluxed for 15 min, butyl vinyl ether (155 μL, 120 mg, 1.2 mmol, 1.2 equiv.) was added, and the reaction mixture was refluxed for additional 20 min. The resulting solution was cooled down to RT, the solvent was evaporated under reduced pressure and the residual solid was triturated with hexanes and recrystallized from acetone to afford the titled compound as colorless crystals in 84% yield (429 mg, 0.84 mmol); mp 122–125 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 2H), 7.55–7.49 (m, 1H), 7.46–7.30 (m, 8H), 7.24–7.19 (m, 2H), 7.15–7.10 (m, 2H), 5.21 (dd, J = 7.5, 2.9 Hz, 1H), 3.64 (dt, J = 9.4, 6.6 Hz, 1H), 3.56 (s, 3H), 3.36 (dt, J = 9.4, 6.6 Hz, 1H), 3.10 (dd, J = 14.6, 7.5 Hz, 1H), 3.04 (dd, J = 14.5, 2.9 Hz, 1H), 1.42–1.33 (m, 2H), 1.22–1.11 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 162.6, 151.7, 143.0, 142.0, 140.9, 139.1, 132.5, 129.2 (2C), 129.0 (2C), 128.5 (2C), 128.4, 128.4, 128.3 (2C), 128.3 (2C), 127.2 (2C), 104.0, 99.8, 69.9, 68.2, 52.1, 41.9, 31.4, 19.0, 13.8; FT IR (cm^{-1}): 1731, 1635, 1598, 1578, 1552, 1500; MS (ESI+): found 511.14; calcd. for $C_{31}H_{31}N_2O_5$ $(M + H)^+$ 511.22; EA (%) calcd. for $C_{31}H_{30}N_2O_5$: C 72.92, H 5.92, N 5.49; found: C 72.80, H 5.75, N 5.38.

Methyl 5-butoxy-3-(4-methylbenzoyl)-7,7-diphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (8b)

This compound was prepared according to typical procedure B employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-(*p*-tolyl)but-2-enoate (398 mg, 1.0 mmol, 1.0 equiv.) and isolated as colorless crystals in 64% yield (336 mg, 0.64 mmol); mp 133–135 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.42–7.28 (m, 6H), 7.22 (d, J = 7.8 Hz, 4H), 7.14–7.09 (m, 2H), 5.20 (dd, J = 7.5, 2.8 Hz, 1H), 3.65 (dt, J = 9.4, 6.6 Hz, 1H), 3.58 (s, 3H), 3.36 (dt, J = 9.4, 6.6 Hz, 1H), 3.09 (dd, J = 14.5, 7.6 Hz, 1H), 3.03 (dd, J = 14.5, 2.8 Hz, 1H), 2.39 (s, 3H), 1.42–1.32 (m, 2H), 1.21–1.10 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 162.0, 150.8, 142.6, 142.2, 141.4, 140.3, 135.8, 128.9 (2C), 128.3 (2C), 128.3 (2C), 127.9 (2C), 127.8, 127.7, 127.7 (2C), 126.6 (2C), 103.6, 99.1, 69.3, 67.5, 51.5, 41.3, 30.8, 21.2, 18.4, 13.1; FT IR (cm^{-1}): 1739, 1646, 1605, 1563; MS (ESI+): found 525.23; calcd. for $C_{32}H_{33}N_2O_5$ $(M + H)^+$ 525.24; EA (%) calcd. for $C_{32}H_{32}N_2O_5$: C 73.26, H 6.15, N 5.34; found: C 73.42, H 6.28, N 5.35.

Methyl 5-butoxy-7,7-diphenyl-3-pivaloyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (8c)

This compound was prepared according to typical procedure B employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-5,5-dimethyl-4-oxohex-2-enoate (364 mg, 1 mmol, 1.0 equiv.) and isolated as colorless crystals in 60% yield (294 mg, 0.60 mmol); mp 137–140 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.27 (m, 6H), 7.21–7.14 (m, 2H), 7.12–7.03 (m, 2H), 5.19 (dd, J = 7.2, 3.6 Hz, 1H), 3.85 (dt, J = 9.3, 6.6 Hz, 1H), 3.79 (s, 3H), 3.48 (dt, J = 9.3, 6.4 Hz, 1H), 3.06 (dd, J = 13.4, 6.3 Hz, 1H), 3.02 (dd, J = 13.5, 2.5 Hz, 1H), 1.56–1.46 (m, 2H), 1.34–1.22 (m, 11H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 163.0, 147.9, 142.1, 142.0, 141.0, 129.0 (2C), 128.6 (2C), 128.4, 128.4, 128.3 (2C), 127.1 (2C), 104.9, 99.9, 70.1, 68.2, 52.3, 44.8, 42.2, 31.5, 26.6 (3C), 19.2, 13.8; FT IR (cm^{-1}): 1739, 1649, 1538; MS (ESI+): found 491.34; calcd. for $C_{29}H_{35}N_2O_5$ $(M + H)^+$ 491.25; EA (%) calcd. for $C_{29}H_{34}N_2O_5$: C 71.00, H 6.99, N 5.71; found: C 70.89, H 6.88, N 5.64.

Methyl 8-benzoyl-2-(4-bromophenyl)-4,4-diphenyl-4*H*-pyrazolo[5,1-*d*][1,3,5]dioxazine-7-carboxylate (9a) (typical procedure C)

To a solution of methyl (*Z*)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxo-4-phenylbut-2-enoate (384 mg, 1.0 mmol, 1.0 equiv.) in $CHCl_3$ (2 mL) was added oxalyl chloride (86 μL, 127 mg, 1.0 mmol, 1.0 equiv.) in one portion. The reaction mixture was refluxed for 90 min, then *o*-xylene (2 mL) was added, and chloroform was distilled out until the vapor temperature above the mixture reached 140 °C. The solution was refluxed for 10 min, 4-bromobenzaldehyde (185 mg, 1 mmol, 1.0 equiv.) was added, and the refluxing was continued for additional 15 min. Then the mixture was cooled down to RT, the solvent was evaporated under reduced pressure, and the residual solid was recrystallized from acetone to afford the titled compound as a colorless crystalline mass in 68% yield (405 mg, 0.68 mmol); mp 167–170 °C (acetone, decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.83 (m, J = 8.5, 1.6 Hz, 2H), 7.57–7.31 (m, 17H), 6.21 (s, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 162.3, 150.6, 142.8, 139.0, 138.7, 138.6, 132.9, 132.8, 132.0 (2C), 130.2, 130.0, 129.3 (2C), 129.1 (2C), 128.6 (2C), 128.4 (2C), 128.4 (2C), 128.1 (2C), 127.3 (2C), 124.7, 104.3, 96.6, 95.6, 52.3; FT IR (cm^{-1}): 1734, 1638, 1603, 1553; MS (ESI+): Found 619.12; calcd. for $C_{32}H_{23}BrN_2NaO_5$ $(M + Na)^+$ 619.07; EA (%) calcd. for $C_{32}H_{23}BrN_2O_5$: C 64.55, H 3.89, N 4.70; found: C 64.61, H 3.78, N 4.67.

Methyl 2-(4-bromophenyl)-8-(4-methylbenzoyl)-4,4-diphenyl-4*H*-pyrazolo[5,1-*d*][1,3,5]dioxazine-7-carboxylate (9b)

This compound was prepared according to typical procedure C, employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-(*p*-tolyl)but-2-enoate (398 mg, 1.0 mmol, 1.0 equiv.), and isolated as colorless crystals in 66% yield (402 mg, 0.66 mmol); mp 187–190 °C (acetone, decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.50–7.31 (m, 12H), 7.23 (d, J = 7.9 Hz, 2H), 6.20 (s, 1H), 3.60 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 162.3, 150.3, 143.8, 142.7, 139.2, 138.8, 136.2, 133.0, 132.0 (2C), 130.2, 130.0, 129.5 (2C), 129.1 (2C), 129.1 (2C), 128.6 (2C), 128.3 (2C), 128.2 (2C), 127.4 (2C), 124.7, 104.5, 96.6, 95.6, 52.2, 21.8; FT IR (cm^{-1}): 1734, 1638, 1603, 1553; MS (ESI+): found 633.03; calcd. for

$C_{33}H_{25}BrN_2NaO_5$ (M + Na)$^+$ 633.08; EA (%) calcd. for $C_{33}H_{25}BrN_2O_5$: C 65.03, H 4.13, N 4.60; found: C 64.77, H 4.29, N 4.56.

Methyl 2-(4-bromophenyl)-8-(4-chlorobenzoyl)-4,4-diphenyl-4*H*-pyrazolo[5,1-*d*][1,3,5]dioxazine-7-carboxylate (9d)

This compound was prepared according to typical procedure C, employing methyl 4-(4-chlorophenyl)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxobut-2-enoate (419 mg, 1.0 mmol, 1.0 equiv.) and isolated as colorless crystals in 69% yield (435 mg, 0.69 mmol); mp 170–172 °C (acetone, decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.57–7.31 (m, 16H), 6.21 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 162.2, 150.6, 142.7, 139.4, 139.0, 138.6, 137.1, 132.7, 132.1 (2C), 130.7 (2C), 130.2, 130.1, 129.2 (2C), 128.8 (2C), 128.6 (2C), 128.4 (2C), 128.1 (2C), 127.3 (2C), 124.9, 104.1, 96.7, 95.8, 52.3; FT IR (cm^{-1}): 1733, 1641, 1588, 1552; MS (ESI+): found 652.98; calcd. for $C_{32}H_{22}BrClN_2NaO_5$ (M + Na)$^+$ 653.03; EA (%) calcd. for $C_{32}H_{22}BrClN_2O_5$: C 61.02, H 3.52, N 4.45; found: C 60.81, H 3.53, N 4.43.

Methyl 8-benzoyl-2-(4-bromophenyl)-4,4-diphenyl-4*H*-pyrazolo[5,1-*b*][1,3,5]oxadiazine-7-carboxylate (10a) (typical procedure D)

To a solution of methyl (*Z*)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxo-4-phenylbut-2-enoate (384 mg, 1.0 mmol, 1.0 equiv.) in $CHCl_3$ (2 mL) was added oxalyl chloride (86 μL, 127 mg, 1.0 mmol, 1.0 equiv.) in one portion. The reaction mixture was refluxed for 90 min, then *o*-xylene (2 mL) was added, and chloroform was distilled out until the temperature of vapors over the mixture reached 140 °C. The solution was refluxed for 10 min, 4-bromobenzonitrile (182 mg, 1.0 mmol, 1.0 equiv.) was added, and the reaction mixture was refluxed for additional 20 min. The resulting solution was cooled down to RT, the solvent was evaporated under reduced pressure and the residual solid was recrystallized from dichloromethane-ethanol mixture (1 : 1), to afford the titled compound as colorless crystals in 62% yield (367 mg, 0.62 mmol); mp 228–230 °C (CH_2Cl_2–EtOH, 1 : 1, decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.84 (m, 2H), 7.81–7.77 (m, 2H), 7.63–7.58 (m, 1H), 7.55–7.34 (m, 14H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 162.0, 145.8, 145.7, 142.4, 141.7 (2C), 138.7, 133.1, 132.1 (2C), 129.8 (2C), 129.2 (2C), 129.0 (2C), 128.7 (2C), 128.5 (4C), 127.9, 127.8, 127.7 (4C), 104.4, 80.7, 52.4; FT IR (cm^{-1}): 1736, 1651, 1596, 1564; MS (ESI+): found 594.03; calcd. for $C_{32}H_{23}BrN_3O_4$ (M + H)$^+$ 594.09; EA (%) calcd. for $C_{32}H_{22}BrN_3O_4$: C 64.88, H 3.74, N 7.09; found: C 64.71, H 3.82, N 7.03.

Methyl 8-(4-methylbenzoyl)-4,4-diphenyl-2-(*p*-tolyl)-4*H*-pyrazolo[5,1-*b*][1,3,5]oxadiazine-7-carboxylate (10b)

This compound was prepared according to typical procedure D employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-(*p*-tolyl)but-2-enoate (398 mg, 1.0 mmol, 1.0 equiv.) and *p*-tolunitrile (117 mg, 1.0 mmol, 1.0 equiv.), and isolated as a colorless crystals in 68% yield (368 mg, 0.68 mmol); mp 165–167 °C (CH_2Cl_2–EtOH, 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.49–7.43 (m, 4H), 7.40–7.32 (m, 6H), 7.29 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 3.65 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 162.2, 146.4, 145.9, 143.9, 143.4, 142.3, 142.1 (2C), 136.2, 129.5 (2C), 129.4 (2C), 129.3 (2C), 128.8 (2C), 128.4 (6C), 127.8 (4C), 126.3, 104.5, 80.5, 52.3, 21.8, 21.7; FT IR (cm^{-1}): 1746, 1667, 1602, 1586, 1574; MS (ESI+): found 542.26; calcd. for $C_{34}H_{28}N_3O_4$ (M + H)$^+$ 542.21; EA (%) calcd. for $C_{34}H_{27}N_3O_4$: C 75.40, H 5.03, N 7.76; found: C 75.21, H 4.87, N 7.73.

Methyl 2-(4-bromophenyl)-4,4-diphenyl-8-pivaloyl-4*H*-pyrazolo[5,1-*b*][1,3,5]oxadiazine-7-carboxylate (10c)

This compound was prepared according to typical procedure D employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-5,5-dimethyl-4-oxohex-2-enoate (364 mg, 1.0 mmol, 1.0 equiv.) and 4-bromobenzonitrile (182 mg, 1 mmol, 1.0 equiv.), and isolated as colorless crystals in 57% yield (326 mg, 0.57 mmol); mp 162–164 °C (CH_2Cl_2–EtOH, 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.91 (m, 2H), 7.64–7.58 (m, 2H), 7.40–7.32 (m, 10H), 3.84 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 162.1, 145.8, 141.9, 141.8 (2C), 140.7, 132.2 (2C), 129.6 (2C), 128.9 (2C), 128.4 (4C), 128.3, 127.7, 127.6 (4C), 105.2, 80.6, 52.5, 45.5, 26.6 (3C); FT IR (cm^{-1}): 1738, 1680, 1657, 1588, 1539; MS (ESI+): found 574.06; calcd. for $C_{30}H_{27}BrN_3O_4$ (M + H)$^+$ 574.12; EA (%) calcd. for $C_{30}H_{26}BrN_3O_4$: C 62.94, H 4.58, N 7.34; found: C 62.81, H 4.40, N 7.29.

Methyl 8-(4-chlorobenzoyl)-4,4-diphenyl-2-(*p*-tolyl)-4*H*-pyrazolo[5,1-*b*][1,3,5]oxadiazine-7-carboxylate (10d)

This compound was prepared according to typical procedure D employing methyl 4-(4-chlorophenyl)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxobut-2-enoate (419 mg, 1.0 mmol, 1.0 equiv.) and *p*-tolunitrile (117 mg, 1.0 mmol, 1.0 equiv.), and isolated as colorless crystals in 76% yield (427 mg, 0.76 mmol); mp 115–117 °C (CH_2Cl_2–EtOH, 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.79 (m, 4H), 7.48–7.33 (m, 12H), 7.20 (d, J = 8.2 Hz, 2H), 3.67 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 162.0, 146.3, 146.1, 143.6, 142.3, 142.0 (2C), 139.5, 137.2, 130.7 (2C), 129.5 (2C), 129.0 (2C), 128.9 (2C), 128.4 (4C), 128.3 (2C), 127.7 (4C), 126.2, 104.1, 80.6, 52.4, 21.7; FT IR (cm^{-1}): 1737, 1673, 1653, 1566; MS (ESI+): found 562.23; calcd. for $C_{33}H_{25}ClN_3O_4$ (M + H)$^+$ 562.15; EA (%) calcd. for $C_{33}H_{24}ClN_3O_4$: C 70.52, H 4.30, N 7.48; found: C 70.36, H 4.27, N 7.32.

Methyl 2,4,4-triphenyl-8-pivaloyl-4*H*-pyrazolo[5,1-*b*][1,3,5] oxadiazine-7-carboxylate (10e)

This compound was prepared according to typical procedure D employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-5,5-dimethyl-4-oxohex-2-enoate (364 mg, 1.0 mmol, 1.0 equiv.) and benzonitrile (102 μL, 103 mg, 1.0 mmol, 1.0 equiv.), and isolated as colorless crystals in 75% yield (370 mg, 0.75 mmol); mp 115–117 °C (CH_2Cl_2–EtOH, 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, J = 8.6, 1.8 Hz, 2H), 7.58–7.53 (m, 1H), 7.50–7.44 (m, 2H), 7.41–7.32 (m, 10H), 3.85 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 162.2, 146.4, 142.1, 142.0 (2C), 140.8, 132.7, 129.3, 128.9 (2C), 128.8 (2C), 128.4 (4C), 128.2 (2C), 127.7

(4C), 105.2, 80.5, 52.5, 45.4, 26.6 (3C); FT IR (cm^{-1}): 1749, 1731, 1682, 1662, 1568, 1545; MS (ESI+): found 494.27; calcd. for $C_{30}H_{28}N_3O_4$ $(M + H)^+$ 494.21; EA (%) calcd. for $C_{30}H_{27}N_3O_4$: C 73.01, H 5.51, N 8.51; found: C 72.89, H 5.35, N 8.43.

Methyl (*Z*)-2-((adamantan-1-yl)imino)-7-(4-methylbenzoyl)-3,3-diphenyl-2,3-dihydropyrazolo[5,1-*b*]oxazole-6-carboxylate (11b) (typical procedure E)

To a solution of methyl 2-(2-(diphenylmethylene)hydrazinyl)-4-oxo-4-(*p*-tolyl)but-2-enoate (398 mg, 1.0 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 mL) was added oxalyl chloride (86 μL, 127 mg, 1 mmol, 1.0 equiv.) in one portion. The reaction mixture was refluxed for 90 min, then *o*-xylene (2 mL) was added, and chloroform was distilled out until the temperature of vapors over the mixture reached 120 °C. The solution was refluxed 15 min, and 1-isocyanoadamantane (161 mg, 1.0 mmol, 1.0 equiv.) was added. The resulting solution was cooled down to RT, the solvent was evaporated under reduced pressure and the residual solid was recrystallized from acetone, affording the titled compound as a colorless crystalline mass in 49% yield (287 mg, 0.49 mmol); mp 205–207 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.74 (m, 2H), 7.51–7.43 (m, 4H), 7.40–7.31 (m, 6H), 7.29–7.24 (m, 2H), 3.79 (s, 3H), 2.41 (s, 3H), 2.02 (br s, 3H), 1.86–1.92 (m, 6H), 1.69–1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 162.4, 152.3, 149.8, 146.9, 143.7, 138.8 (2C), 135.8, 129.5 (2C), 129.2 (2C), 128.9 (2C), 128.7 (4C), 127.7 (4C), 100.2, 72.2, 57.8, 52.6, 42.6 (3C), 36.3 (3C), 29.7 (3C), 21.8; FT IR (cm^{-1}): 1761, 1744, 1652, 1609, 1566; MS (ESI+): found 608.16; calcd. for $C_{37}H_{35}N_3NaO_4$ $(M + Na)^+$ 608.25; EA (%) calcd. for $C_{37}H_{35}N_3O_4$: C 75.88, H 6.02, N 7.17; found: C 75.82, H 5.89, N 7.15.

Methyl (*Z*)-2-((adamantan-1-yl)imino)-3,3-diphenyl-7-pivaloyl-2,3-dihydropyrazolo[5,1-*b*]oxazole-6-carboxylate (11c)

This compound was prepared according to typical procedure E employing methyl 2-(2-(diphenylmethylene)hydrazinyl)-5,5-dimethyl-4-oxohex-2-enoate (**3c**) (364 mg, 1 mmol, 1.0 equiv.) and isolated as colorless crystals in 41% yield (227 mg, 0.41 mmol); mp 173–175 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 4H), 7.37–7.31 (m, 6H), 3.90 (s, 3H), 2.11 (br s, 3H), 2.02 (br d, $J = 2.0$ Hz, 6H), 1.75–1.64 (m, 6H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 163.1, 149.6, 148.7, 147.7, 139.0 (2C), 128.9 (2C), 128.7 (4C), 127.7 (4C), 99.1, 72.1, 57.7, 52.7, 44.3, 42.8 (3C), 36.5 (3C), 29.8 (3C), 26.3 (3C); FT IR (cm^{-1}): 1741, 1677, 1580; MS (ESI+): found 552.17; calcd. for $C_{34}H_{38}N_3O_4$ $(M + H)^+$ 552.29; EA (%) calcd. for $C_{34}H_{37}N_3O_4$: C 74.02, H 6.76, N 7.62; found: C 74.19, H 6.60, N 7.66.

Methyl (*Z*)-2-((adamantan-1-yl)imino)-7-(4-chlorobenzoyl)-3,3-diphenyl-2,3-dihydropyrazolo[5,1-*b*]oxazole-6-carboxylate (11d)

This compound was prepared according to typical procedure E employing methyl 4-(4-chlorophenyl)-2-(2-(diphenylmethylene) hydrazinyl)-4-oxobut-2-enoate (419 mg, 1.0 mmol, 1.0 equiv.) and isolated as a colorless solid in 56% yield (339 mg, 0.56 mmol); mp 203–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.49–7.41 (m, 6H), 7.40–7.32 (m, 6H), 3.81 (s, 3H), 2.04 (br s, 3H), 1.93–1.86 (m, 6H), 1.72–1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 162.2, 152.6, 149.2, 146.8, 139.4, 138.7 (2C), 136.8, 130.6 (2C), 129.0 (2C), 128.8 (2C), 128.7 (4C), 127.6 (4C), 99.8, 72.3, 58.0, 52.7, 42.7 (3C), 36.3 (3C), 29.7 (3C); FT IR (cm^{-1}): 1767, 1736, 1655, 1585, 1564; MS (ESI+): found 606.24; calcd. for $C_{36}H_{33}ClN_3O_4$ $(M + H)^+$ 606.22; EA (%) calcd. for $C_{36}H_{32}ClN_3O_4$: C 71.34, H 5.32, N 6.93; found C 71.16, H 5.19, N 6.87.

Procedure for interception of dipoles generated by decomposition of dimeric adducts

11b. Solution of dimethyl 3,9-bis(4-methylbenzoyl)-5,5,11,11-tetraphenyl-5*H*,11*H*-dipyrazolo[5,1-*b*:5′,1′-*f*][1,5,3,7] dioxadiazocine-2,8-dicarboxylate (**7b**) (424 mg, 0.5 mmol, 1.0 equiv.) in *o*-xylene (8 mL) was stirred at reflux for 10 min, and 1-isocyanoadamantane (161 mg, 1.0 mmol, 2.0 equiv.) was added in one portion. The resulting solution was cooled down to RT and concentrated under reduced pressure. The residual solid was recrystallized from acetone to afford compound **11b** as a colorless crystalline mass in 32% yield (188 mg, 0.32 mmol).

11c. Mixture of dimethyl 1,7-dioxo-5,5,11,11-tetraphenyl-2,8-dipivaloyl-1*H*,5*H*,7*H*,11*H*-dipyrazolo[1,2-*a*:1′,2′-*d*][1,2,4,5] tetrazine-3,9-dicarboxylate (**6c**) (39 mg, 0.05 mmol, 1.0 equiv.) and 1-isocyanoadamantane (16 mg, 0.1 mmol, 2.0 equiv.) was heated at 220 °C in a sealed ampule for 1 min, then cooled down to RT. The crude solid was recrystallized from acetone to afford compound **11c** as a colorless crystalline mass in 67% yield (37 mg, 0.067 mmol).

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