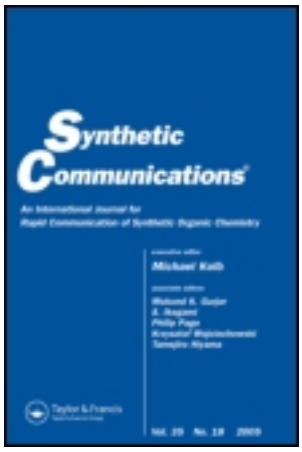

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THE PREPARATION OF 3-(2-PHENYLETHENYL)-1H-PYRAZOLES FROM DILITHIATED (3E)-4-PHENYL-3-BUTEN-2-ONE HYDRAZONES

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THE PREPARATION OF 3-(2-PHENYLETHENYL)-1*H*-PYRAZOLES FROM DILITHIATED (3*E*)-4-PHENYL-3-BUTEN-2-ONE HYDRAZONES

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ABSTRACT

The phenyl-, carbomethoxy-, and carboethoxy-hydrazones of (3*E*)-4-phenyl-3-buten-2-one [benzalacetone] were treated with excess lithium diisopropylamide, and the resulting 1,4-dianions were condensed with several aromatic esters, followed by acid cyclization of *C*-acylated intermediates, to afford substituted 3-(2-phenylethenyl)-1*H*-pyrazoles [3-styryl-pyrazoles].

The preparation and uses of substituted 1*H*-pyrazoles and related materials are well-documented with regard to their biological potential, their use in other syntheses, and in numerous studies, including dye stuffs (1–7). A favored traditional preparation of these compounds involves the condensation/cyclization of symmetrical or unsymmetrical β-diketones with hydrazines. The latter β-diketones

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usually afford a mixture of isomeric pyrazoles that would require additional separation, normally by chromatographic techniques. Also, only a limited number of unsymmetrical β-diketones are commercially available. Another well-known synthesis is the regioselective preparation of unsymmetrical pyrazoles by the 1,3-dipolar addition of nitrilimines to alkynes. This preparative method does not appear to be readily adaptable to the preparation of 3-styryl-pyrazoles (1–7), which is the focus of this report.

In a series of earlier investigations, we prepared unsymmetrical 3,5-disubstituted 1*H*-pyrazoles from a variety of *C*(α),*N*-hydrazones and aromatic esters or anhydrides (8–19). For example, the *C*(α),*N*-phenylhydrazones or *C*(α),*N*-carboalkoxy hydrazones of ketones, such as acetophenone, were dilithiated with lithium diisopropylamide (LDA), and the resulting 1,4-dianion intermediates were regioselectively condensed with a variety of substituted benzoate esters to afford *C*-acylated intermediates that were not isolated, but cyclized immediately with aqueous acid to give the targeted pyrazoles. In each instance, only one isomeric pyrazole resulted, because the atoms making up the five-membered pyrazole ring were in place in the *C*-acylation intermediate prior to cyclization. While many of these studies have involved the utilization of acetophenones and related carbonyl compounds for making hydrazones, fewer all aliphatic ketones, and no examples of α,β-unsaturated ketones, such as benzalacetone, have been used.

There are only a few reports concerning the preparations and uses of 3-styryl-pyrazoles, and only 1,5-diphenyl-3-(2-phenylethenyl)-1*H*-pyrazole, **5,** made in this study, is known (20–24). It has been [a] prepared by the reaction of (β-arylacryloyl)-oxiranes with phenylhydrazine, or [b] used in electric circuit boards impregnated with a fluorescent brightener for optical examination, or [c] made by oxidative dehydrogenation of 4,5-dihydro-1*H*-pyrazoles with cobalt(II) and oxygen, or [d] used in electrochemical reduction reactions, or also [e] used in effect of nonlinear photochemical transformations on light generation in allowed transitions of complex organic molecules, and [f] made as a part of additional oxidative studies using manganese dioxide.

During this investigation, several benzalacetone hydrazones **2a–c** were deprotonated with excess LDA, and the resulting dilithiated intermediates **3a–c** were condensed at the carbanion center with a variety of substituted benzoate esters, such as methyl benzoate [for **5** and **9**], methyl 4-*tert*-butylbenzoate [for **13**], (lithiated) methyl 4-hydroxybenzoate [for **8** and **11**], methyl 4-methoxybenzoate [for **6**, **10** and **12**], or methyl 3,4,5-trimethoxybenzoate [for **7**]. After acid cyclization of **4** with 3 *N* hydrochloric acid, the desired 3-styryl-pyrazoles **5–13** were isolated in 38–93% yield. Styryl-pyrazoles, **6–13**, prepared in the current study, are new, and the one that has been reported earlier (**5**), had excellent agreement when comparing melting points [this study, mp 138°–139°C; lit. (24) mp 139°C].

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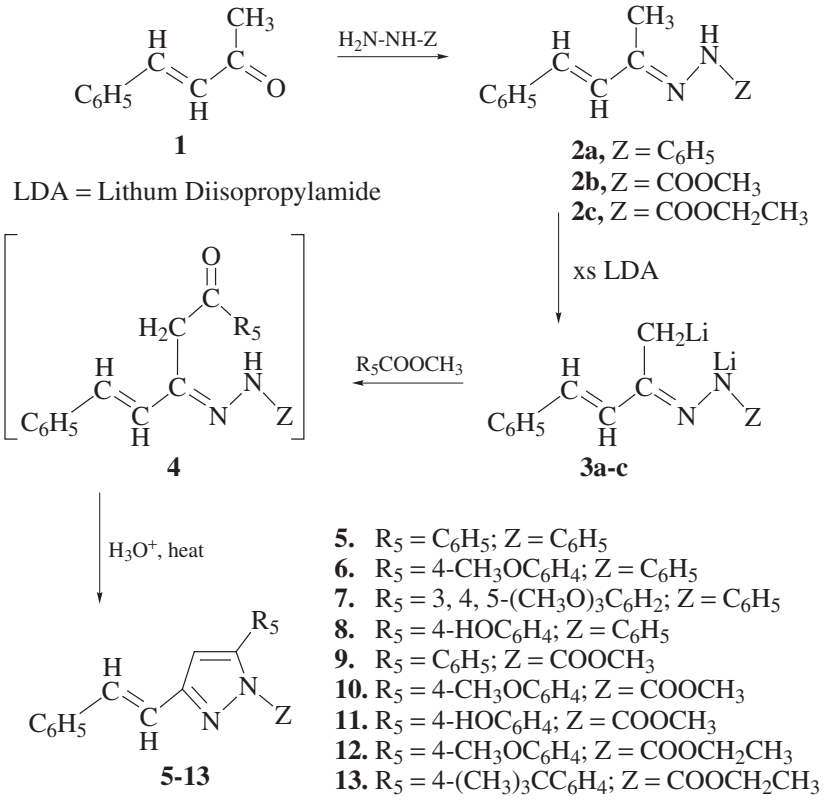

5. $R_5 = C_6H_5$; $Z = C_6H_5$
6. $R_5 = 4\text{-}CH_3OC_6H_4$; $Z = C_6H_5$
7. $R_5 = 3, 4, 5\text{-}(CH_3O)_3C_6H_2$; $Z = C_6H_5$
8. $R_5 = 4\text{-}HOC_6H_4$; $Z = C_6H_5$
9. $R_5 = C_6H_5$; $Z = COOCH_3$
10. $R_5 = 4\text{-}CH_3OC_6H_4$; $Z = COOCH_3$
11. $R_5 = 4\text{-}HOC_6H_4$; $Z = COOCH_3$
12. $R_5 = 4\text{-}CH_3OC_6H_4$; $Z = COOCH_2CH_3$
13. $R_5 = 4\text{-}(CH_3)_3CC_6H_4$; $Z = COOCH_2CH_3$

EXPERIMENTAL

Melting points were obtained with a Mel-Temp II melting point apparatus in open capillary tubes and are uncorrected. Fourier Transform IR spectra were obtained with a Nicolet Impact 410 FT-IR; paraffin oil mulls. Proton and ^{13}C NMR spectra were obtained with a Varian Associates Mercury Oxford 300 MHz nuclear magnetic resonance spectrometer, and chemical shifts were recorded in δ ppm downfield from an internal tetramethylsilane (TMS) standard. Combustion analyses for C, H, and N were performed by Quantitative Technologies, Inc., P.O. Box 470, Whitehouse, NJ 08888. The THF was distilled from sodium (benzophenone ketyl as an indicator of dryness) prior to use, and additional chemicals were obtained from Aldrich Chemical Co.

Infrared spectra displayed alkene absorptions from 1639–1646 cm^{-1} in all products **5–13** and a carboalkoxy carbonyl in products **9–13** from 1756–1763 cm^{-1}

was noted. The phenolic OH absorptions in **8** and **11** were poorly defined and recorded as shoulders in the region *ca.* 3200 cm^{-1}. The ^1H NMR spectra displayed pyrazole C_4-H proton absorptions that were upfield and distinguishable from aromatic protons, and recorded as singlets from δ 6.60–6.88 ppm. The conjugation of the styryl group with the heteroaromatic pyrazole ring placed the *trans* styryl proton absorptions with the aromatic protons. By comparison, the styryl protons in the new carboalkoxyhydrazone starting materials **2b–c**, not having this conjugation, were displayed as two well-defined doublets upfield from the phenyl protons at δ 6.86 or 6.85 and 7.03 or 7.05 ppm. The phenolic protons were sharply defined and noted at δ 9.77 ppm in **8** and δ 9.76 ppm in **11**. Other routine proton absorptions were recorded as expected. Carbon-13 NMR spectra for **5–13** gave the expected number of carbon absorptions for each compound. The C-4 carbon absorptions of the pyrazole ring were assigned in an analogous fashion to the C_4-H of the proton resonance spectra, where the chemical shifts were noted between δ 104.6–108.7 ppm, and they were upfield from the regular aromatic carbon and vinyl carbon resonance absorptions.

This is a strong-base synthetic method, with a detailed experimental procedure, and it is a convenient method for the preparation of a particular 3-(2-phenylethenyl)-1*H*-pyrazole. All of the spectral data are consistent with the structural assignments made for each compound **5–13**. The yields of these products may not be optimal, especially for a particular compound, but the current general procedure readily affords multi-gram quantities of pure products resulting from recrystallization from common solvents, which are in sufficient amounts for a variety of uses. The experimental procedure is straightforward so that someone not necessarily familiar with strong base procedures can be successful with the reactions, and the experimental set-up is not elaborate.

General Procedure for Preparation of Benzalacetone Hydrazones 2a–c

Benzalacetone phenylhydrazone **2a** has been reported (25), and carbomethoxy- and carboethoxy-hydrazones **2b** and **2c** are new. These materials were made by a 1:1 condensation of benzalacetone **1** with the substituted hydrazine following a minor modification of a documented procedure (26). In a typical reaction, 0.100 mole of **1** was mixed with 0.105 mole [5% excess] of methyl hydrazincarboxylate or ethyl hydrazincarboxylate, dissolved in 200 mL of methanol or ethanol. Glacial acetic acid (1 mL) was added, and the solution was heated gently in a fume hood using an open beaker or Erlenmeyer flask for approximately 45 min until the volume was reduced to 100 mL. Upon cooling crystallization occurred, and the mixture was filtered on a Buchner funnel. On occasion a few crystals of ice had to be added to induce crystallization. Further reduction in volume of the original filtrate usually afforded a second crop of product.

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[1-(2(*E*)-Phenylethenyl)ethylidene]-hydrazinecarboxylic Acid, Methyl Ester or Benzalacetone Carbomethoxyhydrazone (**2b**)

This compound, 20.1 g (92% yield) mp 163°–164°C (methanol), was prepared from the condensation of **1** and methyl hydrazincarboxylate. IR[5]: 3221, 1732, 1709, 1628 and 1587 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 6.86 (d, 1H, vinyl, J = 16.5 Hz), 7.03 (d, 1H, vinyl, J = 16.5 Hz), and 7.24–7.47 ppm (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ 11.0, 53.4, 127.0, 128.5, 128.8, 128.9, 133.5, 136.2, and 149.8 ppm. *Anal.* calcd. for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.82. Found: C, 65.99; H, 6.47; N, 12.87.

[1-(2(*E*)-Phenylethenyl)ethylidene]-hydrazinecarboxylic Acid, Ethyl Ester or Benzalacetone Carboethoxyhydrazone (**2c**)

This compound, 15.1 g (65% yield) mp 154°–155.5°C (ethanol), was prepared from the condensation of **1** and ethyl hydrazincarboxylate. IR: 3230, 1728, 1709, 1626 and 1579 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H, CH_3), 2.05 (s, 3H, CH_3), 4.33 (q, 2H, CH_2), 6.85 (d, 1H, vinyl, J = 16.5 Hz), 7.05 (d, 1H, vinyl, J = 16.5 Hz), and 7.23–7.47 ppm (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ 10.9, 14.8, 62.3, 126.9, 128.5, 128.8, 129.1, 133.0. *Anal.* calcd. for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94: N, 12.06 Found: C, 67.11; H, 6.98; N, 12.03.

General Procedure for Preparation of 3-(2-Phenylethenyl)-1*H*-pyrazoles 5–13

[0.015 mol scale; hydrazone: LDA: ester- 1:3:1 for **5**–**7**,**9**,**10**,**12**,**13** and 1:4:1 (13) for **8** and **11**]

In a typical reaction sequence, LDA [0.047 mol; 0.063 mol for **8** and **11**] was prepared by the addition of 30 mL [or 39 mL for **8** and **11**] of 1.6 *M n*-butyllithium [0.047 mol; 0.063 mol for **8** and **11**] to a three-neck round-bottom flask (*ca.* 500 mL) equipped with a nitrogen inlet tube, a side-arm addition funnel (*ca.* 125 mL), and a stir bar. The flask was cooled in an ice-water bath and 4.81 g (0.047 mol) [or 6.41 g (0.063 mol) for **8** and **11**] of diisopropylamine, dissolved in 35–50 mL of dry THF (0°C, N_2), was added from the addition funnel at a fast dropwise rate over a period of 5 min. The solution was stirred for an additional 15–20 min and treated *via* the addition funnel with 0.015 mol of benzalacetone, phenylhydrazone **2a**, or carbomethoxyhydrazone **2b**, or carboethoxyhydrazone **2c** dissoved in 50 mL of THF. In order to speed up the solution process, the mixture of **2b** was heated gently before pouring it into the addition funnel. After 45–60 min (0°C, N_2), 0.0158 mol of ester [5% excess] dissolved in 35–45 mL of THF, was added to the dilithiated intermediate, and the solution was stirred for 45–60 min for **5** and **13**, 1–1.5 h

for **6**, **7**, **10**, and **12**, and 2 h for **8** and **11** (0°C, N_2). Finally, 100 mL of 3 *N* HCl was added, and the two-phase mixture was well-stirred and heated under reflux for approximately 45–60 min. At the end of this period, the mixture was poured into a large flask containing ice (*ca.* 100 g), followed by the addition of 100 mL of solvent-grade ether. The mixture was then neutralized with solid sodium bicarbonate and the layers were separated. The aqueous layer was extracted with ether or THF (2 × 75 mL), and the organic fractions were combined, evaporated, and recrystallized.

1,5-Diphenyl-3-(2-phenylethenyl)-1*H*-pyrazole (**5**)

This compound, 3.90 g (81% yield) mp 138°–139°C (ethanol) [lit. (24) mp 139°C], was prepared from 0.0150 mol of **3a** and 0.0158 mol methyl benzoate. IR: 1646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.74 (s, 1H, C_4-H), 7.16–7.39, and 7.52–7.55 ppm (m, 17H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 105.2, 120.7, 125.3, 126.7, 127.6, 127.9, 128.5, 128.7, 128.90, 128.92, 129.1, 130.6, 130.9, 137.3, 140.2, 144.4, and 151.4 ppm.

5-(4-Methoxyphenyl)-1-phenyl-3-(2-phenylethenyl)-1*H*-pyrazole 6

This compound, 4.15g (79% yield) mp 114°–116°C (ethanol), was prepared from 0.0150 mol of **3a** and 0.0158 mol methyl 4-methoxybenzoate. IR: 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3H, $ArOCH_3$), 6.66 (s, 1H, C_4-H), 6.79–6.84, and 7.11–7.53 ppm (m, 16H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 55.4, 104.6, 114.1, 120.7, 122.9, 125.3, 126.6, 127.4, 127.9, 128.8, 129.0, 130.1, 130.7, 137.3, 140.2, 144.2, 151.2, and 159.7 ppm. *Anal.* calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.71; H, 5.66; N, 7.86.

1-Phenyl-3-(2-phenylethenyl)-5-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole (**7**)

This compound, 5.88 g (93% yield) mp 116°–118°C (ethanol), was prepared from 0.0150 mol of **3a** and 0.0158 mol methyl 3,4,5-trimethoxybenzoate. IR: 3628, 3546, 1646, and 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.67 (s, 6H, $ArOCH_3$), 3.86 (s, 3H, $ArOCH_3$), 6.43 (s, 2H, ArH), 6.74 (s, 1H, C_4-H), 7.22–7.38, and 7.52–7.54 ppm (m, 12 H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 56.2, 61.2, 104.6, 106.2, 120.6, 125.7, 125.8, 126.7, 127.8, 128.0, 128.9, 129.2, 131.0, 137.3, 138.3, 140.3, 144.4, 151.4, and 153.4 ppm. *Anal.* calcd. for $C_{26}H_{24}N_2O_3 \cdot 1/2H_2O$: C, 74.09; H, 5.97; N, 6.65. Found: C, 74.26; H, 6.30; N, 6.40.

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5-(4-Hydoxyphenyl)-1-phenyl-3-(2-phenylethenyl)-1*H*-pyrazole (**8**)

This compound, 3.88 g (77% yield) mp 250°–252°C (ethanol/toluene), was prepared from 0.0150 mol of **3a** and 0.0158 mol lithiated methyl 4-hydoxybenzoate. IR: 3181 sh and 1646 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.87 (s, 1H, C_4-H), 6.73–6.77, 7.05–7.38, 7.58, and 7.59 ppm (m, 14H, styryl and ArH) and 9.77 (s, 1H, ArOH); ^{13}C NMR (DMSO-d_6) δ 104.6, 115.4, 120.5, 120.6, 124.9, 126.4, 127.4, 127.8, 128.8, 129.0, 129.9, 130.3, 136.8, 139.9, 144.0, 150.5, and 157.7 ppm. *Anal.* calcd. for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.27; H, 5.51; N, 8.21.

1-Carbomethoxy-5-phenyl-3-(2-phenylethenyl)-1*H*-pyrazole (**9**)

This compound, 2.22 g (49% yield) mp 120°–121°C (ethanol), was prepared from 0.0150 mol of **3b** and 0.0158 mol methyl benzoate. IR: 1762 and 1644 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.96 (s, 3H, OCH_3). 6.65 (s, 1H, C_4-H), and 7.14–7.53 ppm (m, 12H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 54.9, 59.4, 108.8, 119.6, 127.0, 128.1, 128.7, 129.0, 129.2, 130.8, 134.4, 136.4, 148.4, 150.5, and 153.9 ppm. *Anal.* calcd. for $C_{13}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.97; H, 5.22; N, 9.08.

1-Carbomethoxy-5-(4-methoxyphenyl-3-(2-phenylethenyl)-1*H*-pyrazole (**10**)

This compound, 2.96 g(59% yield) mp 165°–167°C (methanol), was prepared from 0.0150 mol of **3b** and 0.0158 mol methyl 4-methoxybenzoate. IR: 1758 and 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.60 (s, 1H, C_4-H), 6.92–6.97, 7.13–7.40, and 7.48–7.52 ppm (m, 11H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 54.9, 55.4, 108.4, 113.5, 119.7, 122.9, 126.9, 128.6, 128.9, 130.6, 134.2, 136.4, 148.3, 150.6, and 160.3 ppm. *Anal.* calcd. for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.98; H, 5.41, 8.26.

1-Carbomethoxy-5-(4-hydoxyphenyl-3-(2-phenylethenyl)-1*H*-pyrazole (**11**)

This compound, 2.46 g (51% yield) mp 192°–194°C (ethanol), was prepared from 0.0150 mol of **3b** and 0.0158 mol lithiated methyl 4-hydroxybenzoate. IR: 3202 sh., 1756 and 1646 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.83 (s, 3H, OCH_3), 6.88 (s, 1H, C_4-H), 6.79–6.81, 7.15–7.39, 7.53–7.62 (m, 11H, styryl and ArH) and 9.76 ppm (s, 1H, ArOH); ^{13}C NMR (DMSO-d_6) δ 54.3, 108.1, 114.7, 119.4, 120.9, 126.8, 128.4, 128.8, 130.4, 133.7, 136.2, 147.7, 150.1, 152.9, and 158.0 ppm. *Anal.* calcd. for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 70.93; H, 5.21; N, 8.58.

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1-Carboethoxy-5-(4-methoxyphenyl-3-(2-phenylethenyl)-1*H*-pyrazole (**12**)

This compound, 2.55 g (49% yield) mp 162°–163°C (ethanol), was prepared from 0.0150 mol of **3c** and 0.0158 mol methyl 4-methoxybenzoate. IR: 1763 and 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.42 (q, 2H, OCH_2), 6.60 (s, 1H, C_4-H), 6.92–6.97, 7.13–7.40, and 7.48–7.52 ppm (m, 11H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 55.5, 64.5, 108.4, 113.5, 119.9, 123.3, 126.9, 128.6, 129.0, 130.6, 134.1, 136.5, 148.2, 150.1, 153.7, and 160.3 ppm. *Anal.* calcd. for $C_{21}H_20N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.32; H, 5.80; N, 7.99.

1-Carboethoxy-5-(4-(1,1-dimethylethyl)-phenyl)-3-(2-phenylethenyl)-1*H*-pyrazole (**13**)

This compound, 2.13 g (38% yield) mp 128°–129°C (ethanol), was prepared from 0.0150 mol of **3c** and 0.0158 mol methyl 4-*tert*-butylbenzoate. IR: 1763 and 1646 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, 3H, CH_3), 1.36 (s, 9H, $C(CH_3)_3$), 4.41 (q, 2H, OCH_2), 6.63 (s, 1H, C_4-H), and 7.13–7.53 ppm (m, 11H, styryl and ArH); ^{13}C NMR ($CDCl_3$) δ 14.3, 31.5, 35.0, 64.5, 108.7, 120.0, 125.0, 127.0, 128.1, 128.7, 129.0, 134.12, 136.6, 148.4, 150.1, 152.3, and 153.8 ppm. *Anal.* calcd. for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.79; H 7.10; N, 7.44.

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