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MICROWAVE-ASSISTED SELECTIVE SYNTHESIS OF 2*H*-INDAZOLES VIA DOUBLE SONOGASHIRA COUPLING OF 3,4-DIODO-PYRAZOLES AND BERGMAN–MASAMUNE CYCLOAROMATIZATION

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Abstract – The microwave-assisted double Sonogashira coupling of 3,4-diiodo-1-trityl and 1-phenylpyrazole with terminal acetylene took only three minutes. Dialkynylpyrazoles, the coupling products, were heated at 240 °C in the presence of 1,4-cyclohexadiene to obtain 2*H*-2-trityl and 2-phenylindazoles, respectively. This synthetic route to 2*H*-indazole, which was achieved via cyclization to form the 6-membered ring of dialkynylpyrazole, is a novel procedure.

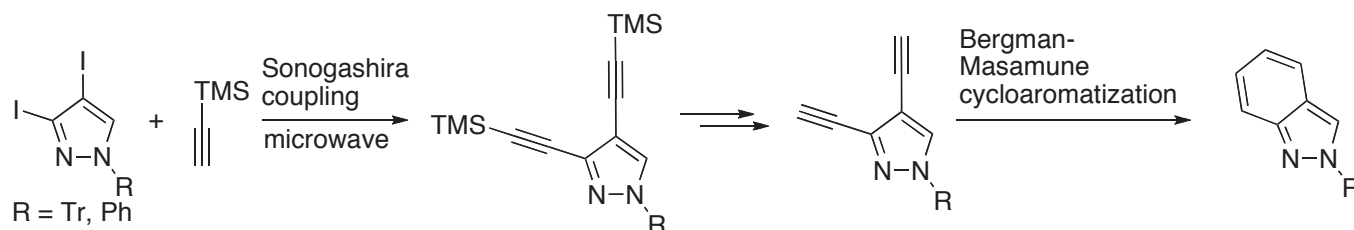
INTRODUCTION

Pyrazoles and indazoles are important molecules in organic synthesis because they serve as the structural framework for large biologically active compounds, such as HIV-1 protease inhibitor,¹ COX-2 inhibitor,² dopamine receptor agonist,³ cisplatin-like metal complexes,⁴ and others.⁵ Generally, substituted pyrazoles are synthesized by the condensation of 1,3-dicarbonyl compounds and hydrazine or the 1,3-dipolar cycloaddition reaction of diazomethane with acetylene.⁶ 4-Substituted pyrazoles are synthesized by the condensation of a malonaldehyde derivative and hydrazine; however, the synthesis of 4-substituted pyrazoles requires multiple steps.⁷ We have recently reported the synthesis of 4-arylpyrazoles via the Kumada coupling of 4-bromo-1-tritylpyrazole, which can be easily prepared from commercially available pyrazole, and an aryl Grignard reagent.⁸ Although a great number of cross-coupling reactions of heterocycles using palladium catalysts have been reported, there is little work on the synthesis via coupling of a 4-substituted pyrazole.⁹ Microwave irradiation, which is frequently used for

palladium-catalyzed cross-coupling reactions, is a powerful tool in synthetic chemistry and its ability to shorten reaction times, increase reaction yields, and promote reactions that are otherwise unsuccessful under conventional hood conditions is the property that medicinal chemists are looking for to optimize routine procedures.¹⁰

Whereas substituted indazoles are generally prepared as *1H*- and *2H*-indazole mixtures by the *N*-alkylation or *N*-arylation of indazole, only a handful of studies of the syntheses of *2H*-indazoles involve the regioselective cyclization of a five-membered ring.¹¹

In this paper, we describe the synthesis of alkynylpyrazoles as invaluable intermediates and the effect of microwave irradiation on the double Sonogashira coupling of 3,4-diiodo-1-tritylpyrazole. We also describe the regioselective synthesis of *2H*-indazole via the Bergman-Masamune cycloaromatization of dialkynylpyrazoles, which has not been reported so far (Scheme 1). An *ab initio* study of the strategy for indazoles has been reported.¹²



Scheme 1. A strategy for *2H*-indazole via Bergmann-Masamune cycloaromatization through microwave-assisted double Sonogashira coupling

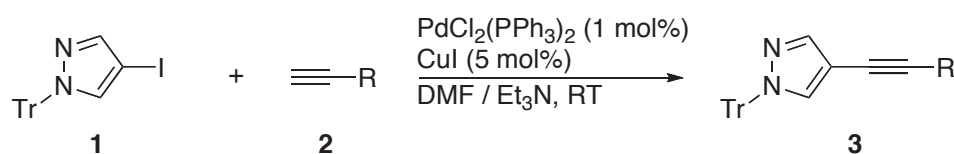
RESULTS AND DISCUSSION

The Sonogashira coupling of 4-iodo-1-tritylpyrazole (**1**) with propargyl alcohol (**2a**) in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI as cocatalyst furnished the corresponding 4-alkynylpyrazole **3** in good yield (Table 1). When 1 mol% each of $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI was used for the coupling reaction, a long reaction time was required (entry 3). The reactions of phenyl acetylene (**2d**) and *p*-fluorophenyl acetylene (**2e**) gave coupled products in excellent yields. In contrast, the reaction of *p*-methoxy phenylacetylene (**2f**) was slow because of the low acidity of the terminal acetylene (entries 6 – 8).

Then, 3,4-diiodo-1-tritylpyrazole (**4**) and **2a** reacted under same conditions as those specified in Table 1 to produce dialkynylpyrazole (**5a**) in moderate yield (Table 2). Increasing the catalyst load gave **5** in good yield; however, the reaction time was approximately 5 days under a conventional hood (entries 2 and 3). Since diiodopyrazoles are very inactive than mono-iodopyrazoles for Sonogashira coupling, the reaction condition is drastic changed. To shorten the reaction time for dialkynylation, microwave-assisted Sonogashira coupling was attempted. It is known that the microwave-assisted cross-coupling reaction with palladium complexes reduces the reaction time dramatically.¹⁰ In our case, **5** was obtained after only

three minutes under microwave conditions in good yields (entries 4 and 7). When the catalyst loading was reduced, the starting material was recovered (entry 5). Microwave irradiation for seven minutes accompanied by detritylation reduced the product yield (entry 6). It is known that the dialkynylpyrazoles are obtained from condensation of (*Z*)-enediynes compounds and diazomethane, and then cyclization.¹³ Our double Sonogashira coupling method is proceeded for very short time and with easier operation than that route.

Table 1. Sonogashira coupling of 4-iodo-1-tritylpyrazole and various terminal acetylenes^a



entry	terminal acetylenes	PdCl ₂ (PPh ₃) ₂ , CuI (mol%)	time (h)	yield (%) ^b
1	$\text{C}\equiv\text{C-CH}_2\text{OH}$ (2a)	5, 5	2	99
2	2a	1, 5	2	95
3	2a	1, 1	14.5	83
4	$\text{C}\equiv\text{C-TMS}$ (2b)	1, 5	2	96
5	$\text{C}\equiv\text{C-(CH}_2)_5\text{CH}_3$ (2c)	1, 5	13	90
6	$\text{C}\equiv\text{C-C}_6\text{H}_5$ (2d)	1, 5	2.5	86
7	$\text{C}\equiv\text{C-C}_6\text{H}_4\text{-F}$ (2e)	1, 5	2	99
8	$\text{C}\equiv\text{C-C}_6\text{H}_4\text{-OMe}$ (2f)	1, 5	2	45

^a Reagent and conditions: **1**, alkyne **2** (5 equiv), PdCl₂(PPh₃)₂, CuI, solvent, RT: room temperature. ^b isolated yield.

Silylacetylene **5b** and **7**, which were prepared by the microwave-assisted double Sonogashira coupling, were used as starting materials for 2*H*-indazole synthesis, respectively (Scheme 2). The desilylation of **5b** and **7** with TBAF proceeded in quantitative yields. Terminal acetylene **8** and **9** were heated at 240 °C for 0.5 h in the presence of an excess amount of 1,4-cyclohexadiene to give Bergman-Masamune cycloaromatization products **10** and **11** in 20% and 40% yields, respectively.

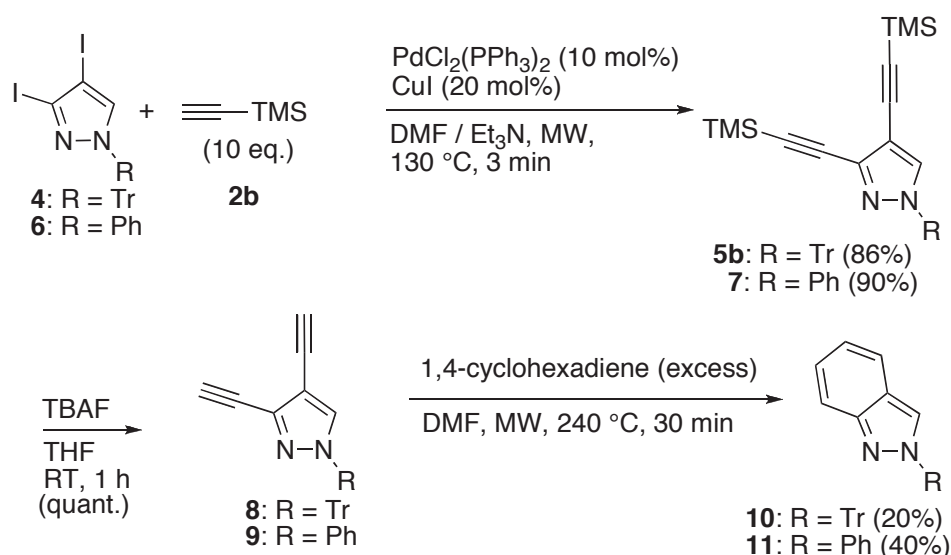
In conclusion, the microwave-assisted double Sonogashira coupling of 3,4-diiodo-1-tritylpyrazole (**4**) required only three minutes and 2*H*-indazoles **10** and **11** were obtained from dialkynylpyrazoles (**5**). This synthetic route to 2*H*-indazole, which was achieved by cyclization to form a 6-membered ring of

dialkynylpyrazole, is a novel procedure. Known synthetic routes to 2*H*-indazoles involve cyclization to form 5-membered rings. In the future, we will attempt to prepare various dialkynylpyrazoles and multi-fused heterocyclic compounds by microwave-assisted tandem radical cyclization of substituted dialkynylpyrazoles.

Table 2. Microwave assisted double Sonogashira coupling of 3,4-diiodo-1-tritylpyrazole^a

entry	alkyne (eq.)	PdCl ₂ (PPh ₃) ₂ , CuI (mol%)	temp. (°C), Time	yield (%) ^d
1	2a , 10	1, 5	70, 15 h	54
2	2a , 2.4	10, 20	RT ^b , 124 h	84
3	2b , 10	10, 20	RT ^b , 125 h	93
4	2a , 10	10, 20	MW ^c , 130, 3 min.	82
5	2a , 10	1, 2	MW ^c , 130, 3 min.	15
6	2a , 10	10, 20	MW ^c , 130, 7 min.	62
7	2b , 10	10, 20	MW ^c , 130, 3 min.	86

^a Reagent and conditions: **1**, alkyne **2**, Pd cat., CuI, solvent. ^b RT: room temperature. ^c MW: microwave. ^d Isolated yield.



Scheme 2. The synthesis of 2-trityl-2*H*-indazole and 2-phenyl-2*H*-indazole via Bergman-Masamune cycloaromatization

EXPERIMENTAL

Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Kishida chemical, nacalai tesque, Wako pure chemicals and TCI) and were used without further purification. A microwave-assisted Sonogashira coupling was took place by Biotage Initiator as a microwave synthesizer with sealed reaction vessels. IR spectra were obtained with a JEOL FT/IR-680 Plus spectrometer. HRMS was determined with a Hitachi 4000H or a JEOL JMS-700 (2) mass spectrometer. NMR spectra were recorded at 27 °C on Varian UNITY INOVA-500, Gemini-2000, and XL-300 spectrometers in CDCl₃ with tetramethylsilane (TMS) as internal standard. Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Liquid column chromatography was conducted over silica gel (SiliCycle, SilaFlash F60, 40-63 μm). Analytical TLC was performed on precoated Merck aluminum sheets (DC-Alufohlen Kieselgel 60 F₂₅₄), and compounds were detected by spraying an ethanol solution of phosphomolybdic acid, followed by heating.

A representative procedure for the microwave-assisted double Sonogashira coupling (Table 2, entry 4): CuI (38 mg, 0.2 mmol) and PdCl₂(PPh₃)₂ (70 mg, 0.1 mmol) were added to an Et₃N (10 mL) and DMF (5 mL) solution of **4** (0.56 g, 1.0 mmol) and propargyl alcohol (0.6 mL, 10.0 mmol) and the mixture was heated by microwave at 130 °C for 3 min. The mixture was poured into saturated aqueous NH₄Cl solution and extracted with EtOAc, and the organic layer was washed with 10% HCl solution and dried over MgSO₄. The crude product was concentrated under vacuum and purified via silica gel column chromatography (hexane/EtOAc = 1:2) to give 0.34 g (82%) of **5a**.

The synthetic procedure for 2-phenyl-2H-indazole (11) (Scheme 2): CuI (38 mg, 0.2 mmol) and PdCl₂(PPh₃)₂ (70 mg, 0.1 mmol) were added to an Et₃N (10 mL) and DMF (5 mL) solution of **6** (0.56 g, 1.0 mmol) and trimethylsilylacetylene (1.4 mL, 10.0 mmol), and the mixture was heated by microwave at 130 °C for 3 min. The mixture was poured into saturated aqueous NH₄Cl solution and extracted with /EtOAc, and the organic layer was washed with 10% HCl solution and dried over MgSO₄. The crude product was concentrated under vacuum and purified by silica gel column chromatography (hexane/EtOAc = 5:1) to give 0.34 g (90%) of **7**. 1.0 M THF solution of TBAF (1.92 mL, 1.92 mmol) was added to a solution of **7** (0.24 g 0.71 mmol) in THF (30 mL) and the reaction mixture was stirred for 1 h at room temperature. After concentrating under vacuum, the resultant mixture was poured into brine and extracted with EtOAc. The organic layer was dried over MgSO₄ and the crude product was concentrated under vacuum and purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give 0.19 g (99%) of **9**. The reaction mixture of **9** (12 mg, 0.06 mmol) in DMF (0.9 mL) and 1,4-cyclohexadiene (0.3 mL, 5 mmol) was sealed in a reaction vessel and heated by microwave at 240 °C for 0.5 h. The reaction mixture was concentrated under vacuum and the crude product was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give 4.7 mg (40%) of **11**.

4-(3-Hydroxyprop-1-ynyl)-1-tritylpyrazole (3a)

White powder; mp 219 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.68 (brs, 1H, OH), 4.40 (s, 2H, CH_2), 7.10-7.15 (m, 6H, TrH), 7.28-7.33 (m, 9H, TrH), 7.50 (d, $J = 0.4$ Hz, 1H, pyrazole-H), 7.72 (s, $J = 0.4$ Hz, 1H, pyrazole-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 51.8, 77.2, 79.1, 88.1, 101.0, 127.4, 127.5, 129.6, 135.1, 141.7, 142.1; EI-MS m/z 364 (M^+), HRMS m/z 364.1576, Calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}$: 364.1576; IR (ν_{max}) (KBr) 3399 (OH), 3055, 3032, 2233 ($\text{C}\equiv\text{C}$), 1596, 1490, 1445, 1372 cm^{-1} .

4-Trimethylsilylethynyl-1-tritylpyrazole (3b)

White powder; mp 144 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.20 (s, 9H, CH_3Si), 7.09-7.13 (m, 6H, TrH), 7.29-7.31 (m, 9H, TrH), 7.53 (d, $J = 0.7$ Hz, 1H, pyrazole-H), 7.75 (d, $J = 0.7$ Hz, 1H, pyrazole-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 0.5, 79.1, 95.02, 96.34, 101.8, 127.4, 127.5, 129.7, 135.3, 142.1, 142.6; EI-MS m/z 406 (M^+), HRMS m/z 406.1871, Calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{Si}$: 406.1865; IR (ν_{max}) (KBr) 3056, 2165 ($\text{C}\equiv\text{C}$), 1596, 1489, 1445, 1398 (Si-CH_3), 1352 (Si-CH_3) cm^{-1} .

4-Octyn-1-yl-1-tritylpyrazole (3c)

White powder; mp 110 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H, CH_3), 1.26-1.44 (m, 6H, CH_2), 1.56 (quint, $J = 7.3$ Hz, 2H, CH_2), 2.33 (t, $J = 7.1$ Hz, 2H, CH_2), 7.09-7.15 (m, 6H, TrH), 7.29-7.35 (m, 9H, TrH), 7.44 (d, $J = 0.6$ Hz, pyrazole-H), 7.68 (d, $J = 0.6$ Hz, pyrazole-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.5, 19.8, 22.9, 29.0, 29.1, 31.7, 71.4, 78.9, 90.8, 102.3, 127.4, 127.4, 129.7, 134.3, 141.6, 142.3; EI-MS m/z 418 (M^+), HRMS m/z 418.2400, Calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2$: 418.2409; IR (ν_{max}) (KBr) 3032, 3058, 2928, 2856, 2241 ($\text{C}\equiv\text{C}$), 1596, 1486, 1444 cm^{-1} .

4-Phenylethynyl-1-tritylpyrazole (3d)

White powder; mp 212 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.14-7.19 (m, 6H, TrH), 7.29-7.34 (m, 12H, Ph and Tr), 7.59 (s, 1H, pyrazole-H), 7.82 (s, 1H, pyrazole-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 79.1, 80.8, 90.0, 101.8, 123.0, 127.4, 127.48, 127.53, 127.9, 129.7, 130.8, 134.7, 141.6, 142.1; EI-MS m/z 410 (M^+), HRMS m/z 410.1780, Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_2$: 410.1783; IR (ν_{max}) (KBr) 3059, 3032, 2224 ($\text{C}\equiv\text{C}$), 1595, 1489, 1445 cm^{-1} .

4-(4-Fluorophenyl)ethynyl-1-tritylpyrazole (3e)

White powder; mp 220 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.00 (dd, $J = 8.7, 8.7$ Hz, 2H, ArH), 7.12-7.18 (m, 6H, TrH), 7.28-7.35 (m, 9H, TrH), 7.41 (dd, $J = 5.4, J = 8.7$ Hz, 2H, ArH), 7.59 (s, 1H, pyrazole-H), 7.81 (s, 1H, pyrazole-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 79.1, 80.5, 89.0, 101.6, 115.3 (d, $^2J_{\text{C-F}} = 21.6$ Hz), 119.1 (d, $^4J_{\text{C-F}} = 3.4$ Hz), 127.4, 127.5, 129.7, 132.7 (d, $^3J_{\text{C-F}} = 8.0$ Hz), 134.7, 141.6, 142.1, 161.6 (d, $^1J_{\text{C-F}} = 245.2$ Hz); EI-MS m/z 428 (M^+), HRMS m/z 428.1692, Calcd for $\text{C}_{30}\text{H}_{21}\text{FN}_2$: 428.1689; IR (ν_{max}) (KBr) 3058, 3033, 2224 ($\text{C}\equiv\text{C}$), 1599, 1503, 1445, 1227 (C-F) cm^{-1} .

4-(4-Methoxyphenylethynyl)-1-tritylpyrazole (3f)

White powder; mp 201 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 3.80 (s, 3H, OCH_3), 6.83 (d, $J = 8.9$ Hz, 2H, ArH), 7.13-7.33 (m, 15H, TrH), 7.37 (d, $J = 8.9$ Hz, 2H, Ar-H), 7.56 (s, 1H, pyrazole-H), 7.79 (s, 1H,

pyrazole-H); ^{13}C -NMR (75 MHz, CDCl_3) δ 55.4, 79.0, 79.3, 89.8, 102.0, 113.7, 115.1, 127.4, 127.5, 129.7, 132.3, 134.5, 141.5, 142.2, 158.7; EI-MS m/z 440 (M^+), HRMS m/z 440.1891, Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}$: 440.1889; IR (ν_{max}) (KBr) 3068, 2022, 1466, 1445, 1251, 1033 cm^{-1} .

3,4-Bis(3-hydroxyprop-1-ynyl)-1-tritylpyrazole (5a)

White powder; mp 203 °C; ^1H -NMR (200 MHz, CDCl_3) δ 2.10 (br t, $J = 5.6$ Hz, 1H, CH_2OH), 2.24 (brt, $J = 5.6$ Hz, 1H, CH_2OH), 4.45 (d, $J = 5.6$ Hz, 2H, CH_2OH), 4.45 (d, $J = 5.6$ Hz, CH_2OH), 7.07-7.13 (m, 6H, TrH), 7.28-7.34 (m, 9H, TrH), 7.43 (s, 1H, pyrazole-H); ^{13}C -NMR (75 MHz, CDCl_3) δ 51.7, 51.8, 76.0, 77.2, 79.8, 90.6, 90.9, 104.9, 127.5, 127.7, 129.6, 135.2, 136.4, 141.6; EI-MS m/z 418 (M^+), HRMS m/z 418.1685, Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2$: 418.1681; IR (ν_{max}) (KBr) 3304 (OH), 3056, 3033, 2234 ($\text{C}\equiv\text{C}$), 1596, 1492, 1446 cm^{-1} .

3,4-Bis(trimethylsilyl)ethynyl-1-tritylpyrazole (5b)

Yellow powder; mp 196 °C; ^1H -NMR (300 MHz, CDCl_3) δ 0.22 (s, 9H, TMS), 0.24 (s, 9H, TMS), 7.08-7.11 (m, 6H, TrH), 7.26-7.30 (m, 9H, TrH), 7.43 (s, 1H, pyrazole-H); ^{13}C -NMR (75 MHz, CDCl_3) δ -0.2, -0.1, 79.7, 95.1, 95.5, 98.0, 99.0, 106.5, 127.9, 127.9, 130.1, 135.2, 138.2, 142.2; EI-MS m/z 502 (M^+), HRMS m/z 502.2260, Calcd for $\text{C}_{32}\text{H}_{34}\text{N}_2\text{Si}_2$: 502.2261; IR (ν_{max}) (KBr) 2160, 1249 cm^{-1} .

3,4-Bis(trimethylsilyl)ethynyl-1-phenylpyrazole (7)

Yellow powder; 90 °C; ^1H -NMR (300 MHz, CDCl_3) δ 0.27 (s, 9H, CH_3Si), 0.29 (s, 9H, CH_3Si), 7.31(t, $J = 7.68$ Hz, 1H, PhH), 7.44 (dd, $J = 7.7$ and 7.5 Hz, 2H, PhH), 7.65 (d, $J = 7.50$ Hz, 2H, PhH), 7.97 (s, 1H, pyrazole-H); ^{13}C -NMR (75 MHz, CDCl_3) δ -0.3, -0.1, 94.3, 94.8, 99.1, 100.0, 109.5, 119.5, 127.3, 129.1, 129.5, 139.0, 139.3; EI-MS m/z 336 (M^+), HRMS m/z 336.1480, Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{Si}_2$: 336.1478; IR (ν_{max}) (KBr) 2166, 1252 cm^{-1} .

3,4-Diethynyl-1-tritylpyrazole (8)

Yellow powder; 190 °C; ^1H -NMR (300 MHz, CDCl_3) δ 3.16 (s, 1H, $\text{C}\equiv\text{CH}$), 3.25 (s, 1H, $\text{C}\equiv\text{CH}$), 7.10-7.13 (m, 6H, TrH), 7.29-7.33 (m, 9H, TrH), 7.48 (s, 1H, pyrazole-H); ^{13}C -NMR (75 MHz, CDCl_3) δ 73.9, 74.9, 79.9, 80.9, 105.1, 127.9, 128.0, 130.1, 136.0, 136.9, 142.1; EI-MS m/z 358 (M^+), HRMS m/z 358.1470, Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_2$: 358.1471; IR (ν_{max}) (KBr) 3307, 3280, 2122 cm^{-1} .

3,4-Diethynyl-1-phenylpyrazole (9)

Yellow liquid; ^1H -NMR (300 MHz, CDCl_3) δ 3.27 (s, 1H, $\text{C}\equiv\text{CH}$), 3.36 (s, 1H, $\text{C}\equiv\text{CH}$), 7.36 (tt, $J = 1.4$ and 7.3 Hz, 1H, PhH), 7.47 (dd, $J = 7.3$ and 8.4, 2H, PhH), 7.68 (dd, $J = 1.4$, 8.4 Hz, 2H, PhH), 8.04 (s, 1H, pyrazole-H); ^{13}C -NMR (75 MHz, CDCl_3) δ 73.1, 74.3, 81.6, 108.1, 119.3, 127.5, 129.4, 130.0, 138.0, 138.8; EI-MS m/z 192 (M^+), HRMS m/z 192.0686, Calcd for $\text{C}_{13}\text{H}_8\text{N}_2$: 192.0687; IR (ν_{max}) (neat) 3293, 2118 cm^{-1} .

2-Trityl-2H-indazole (10)¹⁴

^1H -NMR (300 MHz, CDCl_3) δ 7.06 (t, 1H, indazole-5), 7.12-7.33 (m, 16H, TrH and indazole-H), 7.59 (d,

1H, $J_{4,5} = 8.4$ Hz, indazole-H), 7.74 (d, 1H, $J_{6,7} = 9.0$ Hz, indazole-H), 7.90 (s, 1H, indazole-H).

2-Phenyl-2H-indazole (11)^{11a}

White powder; ¹H-NMR (300 MHz, CDCl₃) δ 7.11 (t, 1H, $J = 7.5$ Hz, ArH), 7.32 (t, 1H, $J = 7.7$ Hz, ArH), 7.45 (t, 1H, $J = 7.4$ Hz, ArH), 7.60 (t, 2H, $J = 7.8$ Hz, ArH), 7.72 (d, 1H, $J = 8.4$ Hz, ArH), 7.77 (d, 1H, $J = 8.4$ Hz, ArH), 8.10 (d, 2H, $J = 8.1$ Hz, ArH), 9.11 (s, 1H, H-3); EI-MS m/z 194 (M^+).

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