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ORIGINAL PAPER

Application of 7-amino coumarins for the synthesis of novel and thermally stable water-insoluble azo-coumarin dyes

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Abstract In this work, a series of novel azo-coumarin dyes were successfully synthesized by the diazotization of 7-amino coumarins followed by coupling with phenol derivatives. The diazotization and subsequent azo-coupling generated the related azo dyes at 0–5 °C in short reaction times with a simple experimental procedure. The spectral analysis of the resulted compounds was confirmed the proposed structures. By this development, the scope of heterocyclic compounds was increased.

Keywords Novel azo-coumarin · Diazotization · 7-Amino coumarins · Phenol derivatives · Simple experimental procedure

Introduction

Azo dyes represent the single largest chemical class of industrial colorants. They are synthesized from heterocyclic compounds and have attracted much attention for their bright and strong color shades ranging from yellow to greenish blue on synthetic and natural fabrics [1–4].

About 3000 azo dyes are known and are currently in use worldwide. Most of these compounds are monoazo compounds, which have the common structure unit of –N=N–, linking two aromatic systems. Despite the toxicity of some azo dyes, dozens of additional mono azo dyes are applied in drugs and cosmetics [5].

Aromatic azo compounds are known to be involved in various fields such as dyeing of textile fibers, coloring of different materials like wood, wool, leather, metal foil and plastic, biological and medical investigations and even the organic synthesis [6–8]. The use of heterocyclic intermediates in the synthesis of azo dyes is well established and the resultant dyes exhibit good tinctorial strength [9]. It is well known that coumarin compounds and its derivatives play an important role in organic chemistry [10–13]. They are the structural unit of several natural products [14]. Their applications range from pharmaceuticals [15], to optical brighteners [16] and laser dyes [17]. Also coumarins and functionalized coumarins have shown activity such as antimicrobials and chemotherapeutics [18]. While coumarin is a colorless compound, some of its derivatives exhibit color and intense fluorescence [19].

The coumarin compounds have absorption and a luminous maximum in visible region and have satisfactory thermo-stability. They have various usages as light absorbing agents or luminous agents in the fields of photochemical polymerization, solar cells, optical filters, dying, dye lasers, analysis, etc., [20].

In continuation of our programmatic interest on the heterocyclic synthesis [21–25], herein we wish to report a very simple procedure for synthesis of novel azo-coumarin dyes obtained by the diazotization of 7-amino coumarins **3** followed by coupling with phenol derivatives **5**.

Experimental

General

The chemicals were purchased from Merck and Aldrich chemical companies. The reactions were monitored by

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TLC (silica–gel 60 F 254, hexane: EtOAc). Fourier transform infrared (FT-IR) spectroscopy spectra were recorded on a Shimadzu-470 spectrometer, using KBr pellets and the melting points were determined on a KRUSS model instrument. ^{1}H NMR and ^{13}CNMR spectra were recorded on a FT-NMR Bruker Avance Ultra Shield Spectrometer at 400.13 and 100.62 MHz, in which DMSO-d_6 was used as solvent and TMS as the internal standard. UV–visible spectra were obtained by JASCO V-570 spectrometer. Elemental analyses (C, H, N) were performed with a Heraeus CHN–O-Rapid analyzer. The results agreed favorably with the calculated values.

General procedure for the synthesis of 7-amino-4-substituted coumarins 3

β-Ketoester **2** (1 mmol) was added to a mixture of *m*-amino phenol **1** (1 mmol) and $ZrOCl_2{\cdot}8H_2O/SiO_2$ (0.27 g, 10 mol %) in a screw-cap vial. The mixture was stirred in a preheated oil bath (90 °C). After completion of the reaction, the resulting solid product was suspended in H_2O (20 ml), filtered and recrystallized from hot EtOH to give the pure product **3**.

General procedure for the synthesis of azo-coumarin dyes 7a-h

The 7-amino coumarins **3** (1 mmol) were dissolved in concentrated HCl (1 ml) and water (2 ml). The solution was then cooled to 0–5 °C in ice-bath and maintained at this temperature. Within 10 min sodium nitrite solution (0.38 g, 20 ml water) was dropped into mixture with stirring. Coupling component solution prepared by dissolving **5** or **6** (1 mmol) and adding NaOH solution (2 ml, 10 %). This solution was added portion-wise to the diazonium solution and was stirred for 2 h. The obtained precipitate was isolated by filtration and washed with water and cold ethanol. The crude dye was purified using recrystallization method.

Representative spectral data

*7-((1-Hydroxynaphthalen-2-yl)diazenyl)-4-methyl-2H-chromen-2-one (**7a**)*

IR (KBr) (ν_{max}, cm^{-1}): 3447, 1725, 1613, 1528, 1389, 1271, 1212, 1067, 750. UV (CH_3OH) (λ_{max} nm) 474. ^{1}HNMR (400 MHZ, DMSO): δ_H 11.37 (b, 1H, OH), 7.51 (d, 3H, aromatic CH), 6.64–6.7 (m, 6H, aromatic CH), 6.13 (s, 1H, CH), 2.34 (s, 3H, CH_3). ^{13}CNMR (100 MHZ, DMSO): δ_C 162.06, 159.40, 159.23, 147.95, 140.46, 140.33, 126.16, 116.94, 112.78, 111.27, 111.16, 99.99, 99.92, 18.473. MS (m/z): 330 $[C_{20}H_{14}N_2O_3]^+$, 171 $[C_{10}H_7N_2O]^+$, 159 $[C_{10}H_7O_2]^+$, 143 $[C_{10}H_7O]^+$, 115 $[C_9H_7]^+$, 103, 91, 77, 51. Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.24; N, 8.48. Found: C, 72.58; H, 4.13; N, 8.31.

*7-((2-Hydroxynaphthalen-1-yl) diazenyl)-4-methyl-2H-chromen-2-one (**7b**)*

IR (KBr) (ν_{max}, cm^{-1}): 3432, 1731, 1614, 1498, 1384, 1246, 1127, 1064, 835, 750. UV (CH_3OH) (λ_{max} nm) 491. ^{1}HNMR(400 MHZ, DMSO): δ_H 15.7 (b, 1H, OH), 8.50 (b, 1H, aromatic CH), 7.4–8.00 (m, 7H, aromatic CH), 6.75 (d, 1H, aromatic CH), 6.35 (s, 1H, CH), 2.45 (s, 3H, CH_3). ^{13}CNMR(100 MHZ, DMSO): δ_C 160.67, 154.95, 152.01, 146.29, 142.60, 133.21, 133.62, 131.28, 129.62, 128.99, 128.40, 127.02, 125.90, 122.26, 117.85, 117.59, 113.98, 113.87, 104.57, 18.71. MS (*m*/*z*): 330 $[C_{20}H_{14}N_2O_3]^+$, 171 $[C_{10}H_7N_2O]^+$, 159 $[C_{10}H_7O_2]^+$, 143 $[C_{10}H_7O]^+$, 115 $[C_9H_7]^+$, 103, 89, 77, 51. Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.24; N, 8.48. Found: C, 72.45; H, 4.33; N, 8.22.

*3-((1-Hydroxynaphthalen-2-yl)diazenyl)-7,8,9,10-tetrahydrobenzo[c]chromen-6-one (**7c**)*

IR (KBr) (ν_{max}, cm^{-1}): 3413, 2933, 1709, 1521, 1383, 1268, 1097, 1033, 760. UV (CH_3OH) (λ_{max} nm) 488. ^{1}HNMR (400 MH_Z, DMSO): δ_H 10.09 (s, 1H, OH), 7.34 (d, J = 8.4 Hz, 2H, aromatic CH), 6.39–7.35 (m, 6H, aromatic CH), 5.92 (s, 1H, aromatic CH), 2.68 (t, J = 4.4 Hz, 4H, $2CH_2$), 1.7 (m, J = 2.8 Hz, 4H, $2CH_2$). ^{13}CNMR (100 MHZ, DMSO): δ_C 168.25, 159.91, 159.77, 157.96, 154.28, 153.36, 147.41, 142.90, 133.43, 132.74, 130.87, 128.33, 127.06, 111.35, 109.33, 103.15, 101.56, 98.17, 98.06, 30.46, 29.75, 24.02, 21.86. MS (*m*/*z*): 370 $[C_{23}H_{18}N_2O_3]^+$, 199 $[C_{13}H_{11}O_2]^+$, 171 $[C_{10}H_7\ N_2O]^+$, 143 $[C_{10}H_7O]^+$, 115 $[C_9H_7]^+$, 97, 71, 57. Anal. Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.59; H, 4.86; N, 7.56. Found: C, 74.34; H, 4.53; N, 7.75.

*3-((2-Hydroxynaphthalen-1-yl)diazenyl)-7,8,9,10-tetrahydrobenzo[c]chromen-6-one (**7d**)*

IR (KBr) (ν_{max}, cm^{-1}): 3374, 1706, 1612, 1566, 1509, 1446, 1393, 1255, 1098, 1031, 837, 753. UV (CH_3OH) (λ_{max} nm) 491. ^{1}HNMR(400 MH_Z, DMSO): δ_H 11.58 (s, 1H, OH), 8.57 (d, J = 8 Hz, 1H, aromatic CH), 8.09 (s, 1H, aromatic CH), 7.7 (m, 3H, aromatic CH), 7.4 (m, 2H, aromatic CH), 7.1 (d, J = 8 Hz, 1H, aromatic CH), 6.82 (d, J = 9.6 Hz, 1H, aromatic CH), 2.68 (t, J = 8 Hz, 2H, CH_2), 2.3 (t, J = 8 Hz, 2H, CH_2), 1.7 (m, 4H, $2CH_2$). Anal. Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.59; H, 4.86; N, 7.56. Found: C, 74.47; H, 4.79; N, 7.32.

*7-((2,4-Dihydroxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one (**7e**)*

IR (KBr) (ν_{max}, cm^{-1}): 3433, 1718, 1611, 1498, 1387, 1243, 1127, 1064, 668, 450. UV (CH_3OH) (λ_{max} nm) 430. ^{1}HNMR(400 MHZ, DMSO): δ_H 11.94 (b, 1H, OH), 10.75 (b, 1H, OH), 7.86 (d, 3H, aromatic CH), 7.68 (d, 2H, aromatic CH), 6.48 (m, 2H, aromatic CH), 1.29 (s, 3H, CH_3). ^{13}CNMR(100 MHZ, DMSO): δ_C 161.31, 159.29, 154.28, 134.36, 133.14, 130.24, 130.03, 127.84, 126.49, 121.98, 119.91, 116.26, 111.27, 109.97, 104.59, 24.83. MS (*m*/*z*):296 $[C_{16}H_{12}N_2O_4]^+$, 159 $[C_{10}H_7O_2]^+$, 137 $[C_6H_5N_2O_2]^+$, 109 $[C_6H_5O_2]^+$, 113, 71, 57. Anal. Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.05; N, 9.46. Found: C, 64.63; H, 4.13; N, 9.33.

*7-((4-Hydroxybiphenyl-3-yl)diazenyl)-4-methyl-2H-chromen-2-one (**7f**)*

IR (KBr) (ν_{max}, cm^{-1}): 3446, 1743, 1621, 1480, 1425, 1383, 1255, 1193, 1148, 885, 756. UV (CH_3OH) (λ_{max} nm) 495. ^{1}HNMR(400 MH_Z, DMSO): δ_H 10.99 (s, 1H, OH), 8.00 (m, 4H, aromatic CH), 7.81 (dd, $j = 2.4$ Hz, $J = 7.81$ Hz, 1H, aromatic CH), 7.68 (d, $J = 7.6$ Hz, 2H, aromatic CH), 7.48 (t, $J = 7.6$ Hz, 2H, aromatic CH), 7.38 (m, 1H, aromatic CH), 7.2 (d, $J = 8.4$ Hz, 1H, aromatic CH), 6.49 (s, 1H, CH), 2.48 (s, 3H, CH_3). ^{13}CNMR(400 MH_Z, DMSO): δ_C 160.17, 155.90, 154.09, 153.20, 139.48, 139.20, 133.36, 132.35, 129.46, 129.26, 128.20, 127.66, 126.89, 126.82, 126.71, 126.42, 122.05, 120.21, 119.61, 109.84, 18.65. Anal. Calcd. for $C_{22}H_{16}N_2O_3$: C, 74.15; H, 4.49; N, 7.86. Found: C, 74.02; H, 4.53; N, 7.69.

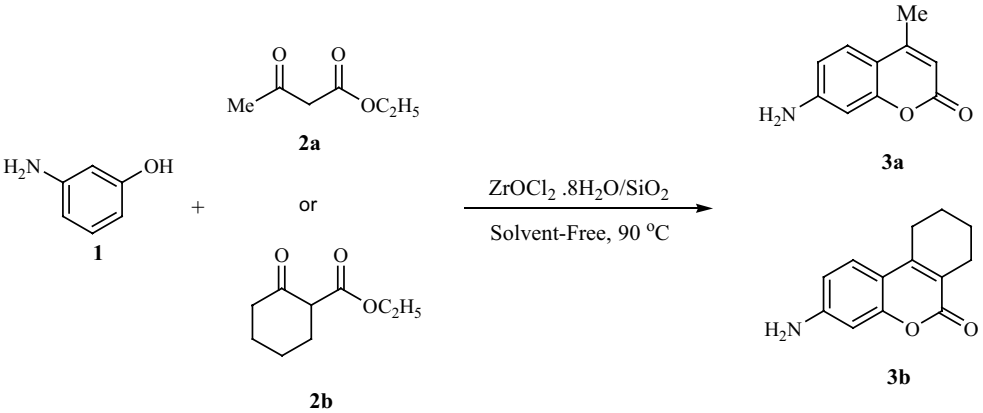
*3-((2,4-Dihydroxyphenyl)diazenyl)-7,8,9,10-tetrahydro-6H-benzo[c]chromen-6-one (**7g**)*

IR (KBr) (ν_{max}, cm^{-1}): 3227, 2934, 1674, 1602, 1425, 1319, 1235, 1160, 1035, 811, 749. UV (CH_3OH) (λ_{max} nm) 418. ^{1}HNMR (400 MH_Z, DMSO): δ_H 11.99 (s, 1H, OH), 10.71 (s, 1H, OH), 7.65–7.80 (m, 3H, aromatic CH), 6.37–6.51 (m, 3H, aromatic CH), 2.8 (t, 4H, $2CH_2$), 1.76 (m, $J = 7.2$ Hz, 4H, $2CH_2$). ^{13}CNMR (400 MH_Z, DMSO): δ_C 160.48, 156.92, 151.99, 151.88, 146.87, 132.59, 128.15, 127.99, 124.73, 123.42, 120.56, 118.37, 109.45, 108.24, 102.82, 24.63, 23.83, 20.93, 20.69. MS (*m*/*z*): 336 $[C_{19}H_{16}N_2O_4]^+$, 199 $[C_{13}H_{11}O_2]^+$, 137 $[C_6H_5N_2O_2]^+$, 109 $[C_6H_5O_2]^+$, 81, 53. Anal. Calcd. for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.76; N, 8.33. Found: C, 67.49; H, 4.43; N, 8.14.

*3-((4-Hydroxy-[1,1′-biphenyl]-3-yl)diazenyl)-7,8,9,10-tetrahydro-6H-benzo[c]chromen-6-one (**7h**)*

IR (KBr) (ν_{max}, cm^{-1}): 3421, 2926, 1714, 1611, 1428, 1262, 1162, 1096, 809, 757. UV (CH_3OH) (λ_{max} nm) 487. ^{1}HNMR (400 MH_Z, DMSO): δ_H 11.03 (s, 1H, OH), 7.95–8.09 (m, 4H, aromatic CH), 7.73–7.87 (m, 4H, aromatic CH), 7.24–7,55 (m, 3H, aromatic CH), 2.9 (t, $J = 6$ Hz, 4H, $2CH_2$), 1.86 (m, $J = 3.2$ Hz, 4H, $2CH_2$). ^{13}CNMR (400 MH_Z, DMSO): δ_C 160.45, 154.98, 152.38, 151.92, 146.86, 138.98, 138.63, 132.63, 131.89, 128.96, 127.16, 126.20, 124.87, 124.20, 121.70, 119.68, 118.95, 118.08, 109.14, 24.69, 23.92, 20.92, 20.71. MS (*m*/*z*): 396 $[C_{25}H_{20}N_2O_3]^+$, 199 $[C_{13}H_{11}O_2]^+$, 197 $[C_{12}H_9N_2O]^+$, 169 $[C_{12}H_9O]^+$, 141, 115, 77, 53. Anal. Calcd. for $C_{25}H_{20}N_2O_3$: C, 75.75; H, 5.05; N, 7.07. Found: C, 75.61; H, 4.93; N, 7.15.

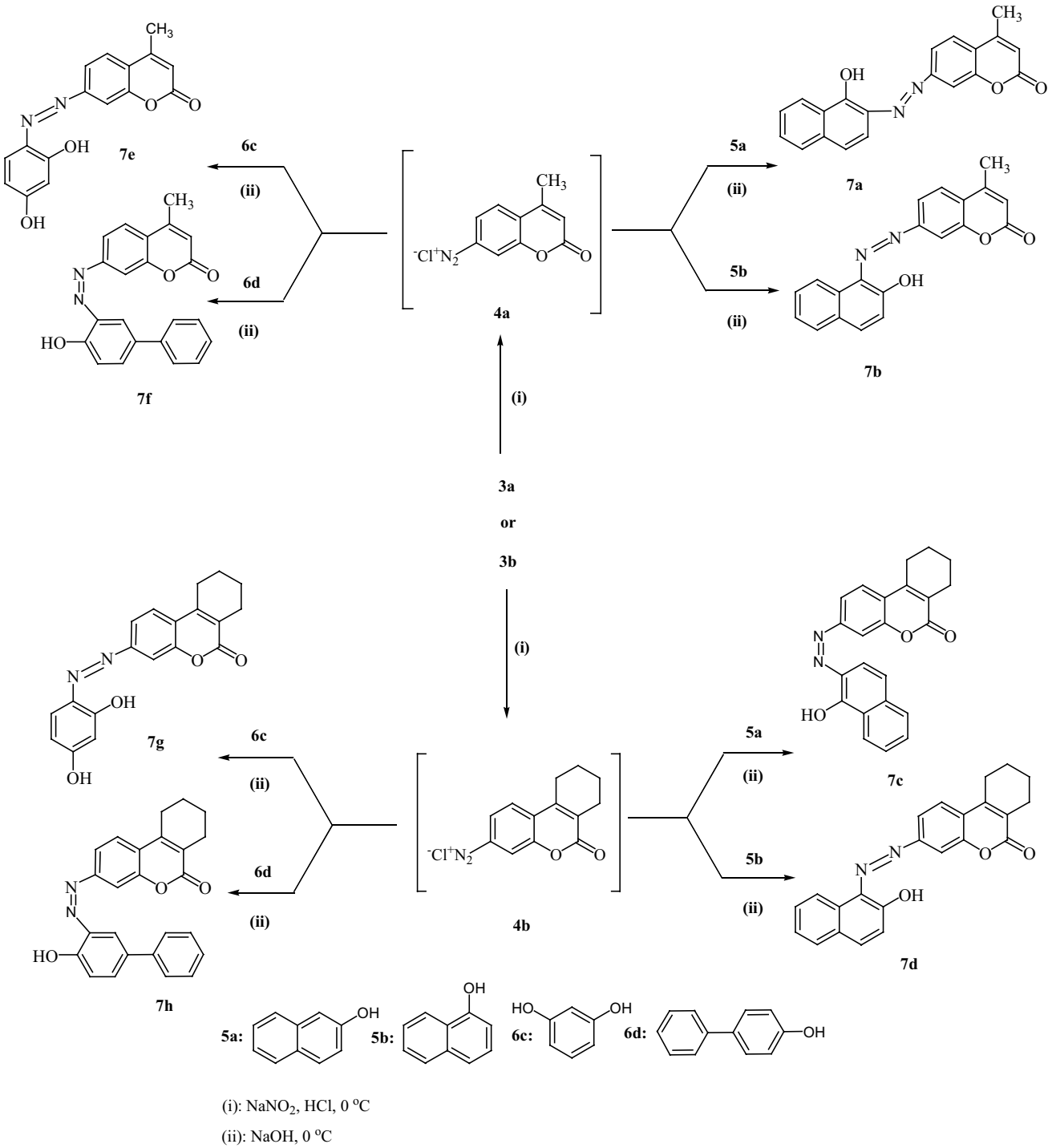
Scheme 1 Synthesis of 7-amino coumarins



Results and discussion

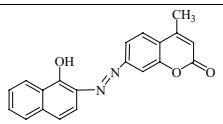
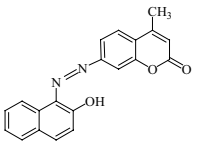
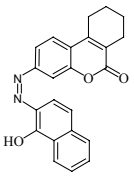
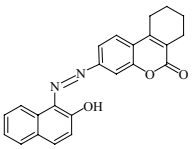
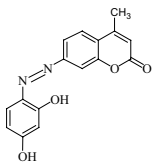
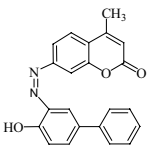
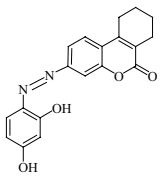
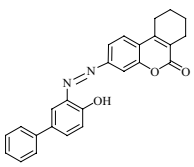
Firstly, 7-amino coumarins **3** were synthesized via the $ZrOCl_2.8H_2O/SiO_2$-catalyzed Pechmann condensation of *m*-amino phenol **1** with *β*-ketoester **2** under thermal and solvent- free conditions (Scheme 1) [21].

Subsequently, the novel azo-coumarin dyes **7** were prepared by the diazotization of 7-amino coumarins **3** followed by coupling with naphthols **5** or phenols **6**. (Scheme 2; Table 1).



Scheme 2 Synthesis of azo-coumarin dyes

Table 1 Synthesis of azo-coumarin dyes **7a–h** by the coupling of 7-amino coumarins and phenol derivatives

Entry	Product	Mp (°C)	Yield (%)[a]
7a		248–250	78
7b		206–208	80
7c		170–172	53
7d		210–212	74
7e		132–134	54
7f		112–114	58
7g		230–232	68
7h		188–190	71

[a] Isolated yield

As a representative sample, the ^{1}H NMR spectrum of **7b** exhibited a sharp singlet identified as methyl ($\delta = 2.41$), an olefinic C–H of the coumarin ring ($\delta = 6.40$), a singlet corresponded to the OH group ($\delta = 15.70$). The peaks appearing in the 6.7–8.5 ppm are attributed to aromatic rings protons. The proton decoupled ^{13}C NMR spectrum of **7b** showed 20 distinct resonances in agreement with the proposed structure.

The infrared spectra (IR) of these dyes show intense carbonyl bands appearing at 1700–1750 cm^{-1}. The broad bands in region of 3000–3450 cm^{-1} are attributed to ν (O–H) vibrations. The peaks appearing at 1000–1350 cm^{-1} are attributed to ν (C–N) and ν (C–O) stretching vibration. The spectra also show the existence of (–N=N–) group at 1450–1500 cm^{-1}.

Conclusions

In summary, a new series of azo-coumarin dyes **7a–h** were obtained by coupling of 7-amino coumarins and phenol derivatives. The use of coumarin as a diazotized aromatic amine is new. By this development, the scope of heterocyclic compounds was increased. Short reaction times, high yields, a clean process, simple methodology, easy workup and green conditions are advantages of these protocols.

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