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# Acylation of *o*-Imidoylphenol Lithium Dianions: Synthesis of 4*H*-Chromen-4-ylidenamines

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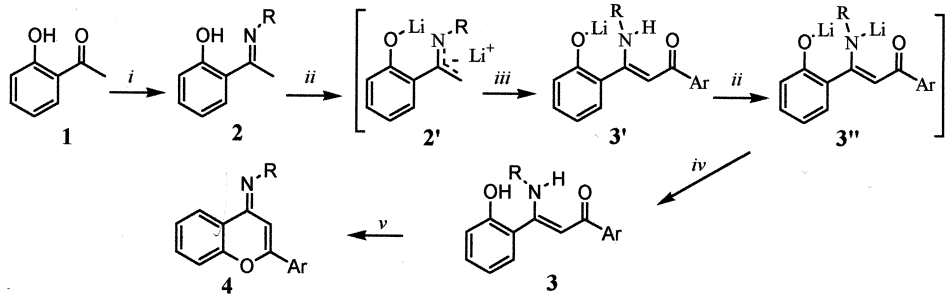
**Abstract**—A method is described to obtain 4*H*-chromen-4-ylidenamines **4**, through the reaction of *o*-imidoyl phenol dianions **2′** with aromatic esters and subsequent acid cyclisation of the 3-(2-hydroxyphenyl)-3-(amino)-1-phenylprop-2-en-1-ones **3** obtained. 

Chromones and flavones belong to a widely explored family of organic compounds largely present in the plant kingdom. Flavones and flavonoids show a general tendency to have biological activity and many compounds have found uses in medicine and industry.[1] 4*H*-Chromen-4-ylidenamines **4** are derivatives of flavones, almost absent from the literature, that have awakened new interest because the simplest of them (2-phenyl-*4H*-chromen-4-imine), has been the object of patents[2] for treatment of cell proliferative diseases and for its antihypoxic, hypotensive, and antiallergic properties.

We now report the use of *o*-imidoylphenols **2** as precursors of *4H*-chromen-4-ylideneamines **4**, through the reaction of their dianions with esters, as described in Scheme 1.

Several papers show that it is not possible to prepare *4H*-chromen-4-ylidenamines **4** by condensation of the corresponding chromones with the relevant amine.[3] The reaction of chromone **6** with ammonia and primary and secondary amines results in the opening of the pyran ring, yielding the corresponding enamino ketone **7**, which reverts the starting material in acidic medium as shown in Scheme 2(a). On the other hand Zagorevskii et al. prepared imino-chromenes **9** in a very low yield by treatment of 4,4-dichloro-chromene **8** with primary amines as in Scheme 2(b).[4]

*o*-Imidoylphenols **2** can be readily prepared by condensation[5] of the appropriate *o*-acyl phenol **1** and the amine according to a described procedure.[6] Upon treatment with LDA (lithium diisopropylamide) they give O,C-dianions **2′** that can react with electrophiles. We have found that alkylated *o*-imidoylphenols can be obtained by alkylation of these dianions with alkyl halides.[7] In the present case the dianion is allowed to react with aromatic esters and in all the reactions we have isolated the acylation products 3-(2-hydroxyphenyl)-3-(amino)-1-phenylprop-2-en-1-ones **3**. We have found the best results in the acylation reaction with an excess of 3.5 mol of LDA per mole of starting




**Scheme 1.** (i) $RNH_2$, benzene, $H^+$, reflux; (ii) LDA, 0°C, 1 h; (iii) ArCOOR′, −80°C, 2 h; (iv) $H_3O^+$, $CH_2Cl_2$, rt; (v) $H_2O$/THF/AcOH=2/2/1, 40°C, 0.5 h.

*Keywords*: imidoylphenol; chromenes; acylation; cyclisation.

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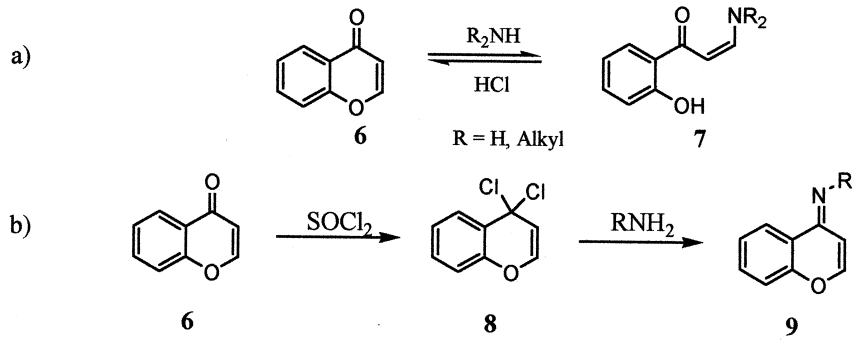


**Scheme 2.**

material: 2 equiv. are necessary for proton abstraction in forming the dianion **2′**, while another metallates the product **3′** preventing proton abstraction by **2′** more basic that **3″**.

The yields obtained in the acylation step (Table 1) are not very high and moreover are not constant for the same reaction in different preparations: this probably happens because during the chromatographic purification a partial cyclisation take place, that we have not quantified. However, cyclisation by aqueous AcOH, before chromatographic purification of the crude reaction mixture containing the acylation product **3ca**, resulted in a 78% of yield of the final 4*H*-chromen-4-ylidene amine **4ca**.

Cyclisation also takes place on heating the acylated product. Enaminoketone **3aa** in refluxing toluene after 0.5 h produces the chromenimine **4aa** (64% yield) with a partial decomposition. For this reason we were unable to register the mass spectra of all acylated products **3** because GC-MS analysis showed for every product **3** the mass spectrum of the corresponding chromen imine **4**.

Attempts to perform the reaction with aliphatic esters were unsuccessful. In the reactions with ethyl propionate and ethyl phenylacetate, although we could observe in the mass spectra of both crude reaction mixtures the peaks corresponding to the chromen imines, all attempts to isolate the products failed, as the mixtures decomposed after a few minutes to a blue oil not containing any relevant product.

The purified 3-(2-hydroxyphenyl)-3-(amino)-1-phenylprop-2-en-1-ones **3** were heated in acid solution and in all cases a single product was isolated in almost quantitative yield (Table 1) that was shown by spectroscopy to have a *4H*-chromen-4-ylidenamine structure **4**.

**Table 1.** Acylation of *o*-imidoyl phenol **2** and cyclisation of the intermediate hydroxyphenyl enaminone **3** to 4*H*-chromen-4-ylidene amines **4**

| **2** | R | Ar | **3** | Yield[a] (%) | **4** | Yield[a] (%) |
|---|---|---|---|---|---|---|
| **2a** | Me | Ph | **3aa** | 72 | **4aa** | 92 |
| **2a** | Me | 4-MeO-Ph | **3ab** | 63 | **4ab** | 85 |
| **2a** | Me | 4-Py | **3ac** | 67 | **4ac** | 66 |
| **2b** | $Pr^i$ | Ph | **3ba** | 42 | **4ba** | 72 |
| **2b** | $Pr^i$ | 4-MeO-Ph | **3bb** | 47 | **4bb** | 81 |
| **2c** | Bn | Ph | **3ca** | 64 | **4ca** | 94 (78)[b] |
| **2c** | Bn | 4-MeO-Ph | **3cb** | 37 | **4cb** | 87 |
| **2c** | Bn | 4-Py | **3cc** | 36 | **4cc** | 76 |

[a] Of the pure isolated product.
[b] Yield of the one pot preparation starting from the crude reaction mixture of **3ca**.

In summary, starting from cheap and commercially available starting materials, with known easily performed procedures, we have found a useful strategy for the preparation of *4H*-chromen-4-ylidenamines **4** in satisfactory yields, a class of compounds of renewed interest.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded with a Varian VXR 300 instrument. Chemical shifts are given in ppm downfield from $Me_4Si$ in $CDCl_3$ solution. Coupling constants are given in Hertz. IR spectra were recorded with a Perkin–Elmer 257 spectrometer. GC-MS analyses were performed with an HP 59970 workstation formed by an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector. All melting points are uncorrected. THF was dried by refluxing over sodium wires until the blue colour of benzophenone ketyl persisted and then distilled into a dry receiver under nitrogen atmosphere. All reagents and solvents were distilled prior to use or were of commercial quality from freshly opened containers. Commercial butyllithium solutions (Aldrich) were employed under dry atmosphere.

### Preparation of starting 2-imidoyl phenols 2a–c

The 2-imidoyl phenols **2a**–**c** were prepared by condensation of the appropriate *o*-acylphenol[4] and the amine according to described procedure.[5]

### Acylation of dianions of 2-imidoyl phenols 2a–c

2-Imidoyl phenols **2a**–**c** (3 mmol) were dissolved in anhydrous THF (5 $cm^3$) under nitrogen atmosphere at 0°C and treated with a solution in THF of LDA, obtained by mixing butyllithium (10.5 mmol) with an equimolecular amount of diisopropylamine in THF (3 $cm^3$). The reaction mixture was allowed to stand for 1 h, then was cooled to −80°C and treated with a solution of an aromatic ester (10.5 mmol) in THF (2 $cm^3$). The reaction was monitored by TLC with *n*-hexane/ethyl acetate=70/30 as eluent and after a variable time (2–3 h), when the starting material was consumed, was quenched with $NH_4Cl$ saturated solution (5 $cm^3$) and brine (2 $cm^3$) and extracted with $CH_2Cl_2$

(2×20 $cm^3$). The solution was dried with anhydrous $Na_2SO_4$ then filtered and the solvent evaporated under reduced pressure. Chromatographic separation of the crude oil obtained, with cyclohexane/ethyl acetate=70/30 as eluent afforded the acylated product **3** in 36–72% yield.

**(*Z*)-3-(2-Hydroxyphenyl)-3-(methylamino)-1-phenylprop-2-en-1-one (3aa).** Yellow crystals; mp 128–132°C ($CH_2Cl_2$/*n*-hexane); $\nu_{max}$ (Nujol) 1608, 1579, 1342, 1259, 769, 686 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.85 (d, 3 H, *J*=5.3 Hz), 5.78 (s, 1 H), 6.50 (br s, 1 H), 6.92–7.86 (m, 9 H), 11.27 (br s, 1 H). $\delta_C$ 31.27, 93.44, 116.84, 122.28, 126.00, 127.50, 128.00, 129.00, 130.50, 131.29, 140.31, 153.36, 154.17, 188.64. Anal. Calcd for $C_{16}H_{15}NO_2$, MW 253.296: C, 75.87; H, 5.97; N, 5.53%. Found: C, 75.76; H, 5.80; N, 5.68%.

**(*Z*)-3-(2-Hydroxyphenyl)-1-(4-methoxyphenyl)-3-(methylamino)prop-2-en-1-one (3ab).** Oil; $\nu_{max}$ (liquid film) 1909, 1709, 1367, 878 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.86 (d, 3 H, *J*=5.3 Hz), 3.85 (s, 3 H), 5.80 (s, 1 H), 6.40 (br s, 1 H), 6.83–7.83 (m, 8 H), 11.10 (br s, 1 H). $\delta_C$ 31.11, 55.36, 92.87, 113.47, 117.09, 120.71, 122.42, 129.31, 129.48, 131.58, 133.07, 153.72, 162.41, 163.87, 188.56. Anal. Calcd for $C_{17}H_{17}NO_3$, MW 283.322: C, 72.07; H, 6.05; N, 4.94%. Found: C, 72.20; H, 6.12; N, 4.68%.

**(*Z*)-3-(2-Hydroxyphenyl)-3-(methylamino)-1-pyridin-4-ylprop-2-en-1-one (3ac).** Orange oil; $\nu_{max}$ (liquid film) 1600, 1580, 1240, 754, 681 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.97 (d, 3 H, *J*=5.3 Hz), 3.41 (br s, 1 H), 5.72 (s, 1 H), 6.82–8.85 (m, 8 H), 11.60 (br d, 1 H, *J*=5.2 Hz). $\delta_C$ 31.74, 93.58, 117.09, 118.38, 120.73, 129.42, 131.90, 147.62, 150.33, 151.23, 153.88, 166.90, 185.70. Anal. Calcd for $C_{15}H_{14}N_2O_2$, MW 254.284: C, 70.85; H, 5.55; N, 11.02%. Found: C, 70.92; H, 5.87; N, 10.89%.

**(*Z*)-3-(2-Hydroxyphenyl)-3-(isopropylamino)-1-phenylprop-2-en-1-one (3ba).** Yellow crystals, mp 136–138°C ($CH_2Cl_2$/*n*-hexane); $\nu_{max}$ (Nujol) 2715, 1719, 1382, 1121, 1074, 813, 712 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 1.33 (d, 6 H, *J*=6.3 Hz), 3.60 (d hept, 1 H, *J*=6.3, 9.6 Hz), 5.77 (s, 1 H), 6.60–7.89 (m, 9 H), 11.20 (d, 1 H, *J*=9.6 Hz). $\delta_C$ 24.04, 47.41, 94.10, 117.22, 121.22, 123.75, 128.17, 129.37, 130.06, 132.00, 133.89, 141.38, 154.50, 162.10, 188.30. Anal. Calcd for $C_{18}H_{19}NO_2$, MW 281.349: C, 76.84; H, 6.81; N, 4.98%. Found: C, 76.57; H, 6.53; N, 5.14%.

**(*Z*)-3-(2-Hydroxyphenyl)-3-(isopropylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (3bb).** Oil; $\nu_{max}$ (liquid film) 1734, 1567, 1458, 1022, 973, 850, 797 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 1.19 (d, 6 H, *J*=6.2 Hz), 3.53 (d hept, 1 H, *J*=6.3, 9.8 Hz), 3.84 (s, 3 H), 5.75 (s, 1 H), 6.60 (br s, 1 H), 6.86–7.05 (m, 4 H), 7.20–7.40 (m, 2 H), 7.80–7.90 (m, 2 H), 11.02 (br d, 1 H, *J*=9.8 Hz). $\delta_C$ 23.87, 46.73, 55.35, 93.32, 113.47, 116.30, 120.33, 122.40, 128.56, 129.04, 130.95, 132.48, 152.91, 161.02, 162.01, 188.25. Anal. Calcd for $C_{19}H_{21}NO_3$, MW 311.375: C, 73.29; H, 6.80; N, 4.50%. Found: C, 73.54; H, 6.65; N, 4.74%.

**(*Z*)-3-(Benzylamino)-3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (3ca).** Yellow crystals, mp 174–176°C (ethyl acetate/*n*-hexane). $\nu_{max}$ (Nujol) 1605, 1560, 1352, 1309, 765, 691 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 4.35 (d, 2 H, *J*=6.2 Hz), 5.87 (s, 1 H), 6.40 (br s, 1 H), 6.90–7.90 (m, 14 H), 11.55 (br s, 1 H). $\delta_C$ 49.03, 94.45, 117.02, 121.01, 122.16, 125.16, 126.05, 127.68, 128.03, 128.77, 129.24, 129.35, 131.63, 131.78, 136.22, 137.13, 153.35, 163.00. Anal. Calcd for $C_{22}H_{19}NO_2$, MW 329.392: C, 80.22; H, 5.81; N, 4.25%. Found: C, 79.97; H, 6.03; N, 4.40%.

**(*Z*)-3-(Benzylamino)-3-(2-hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (3cb).** Yellow crystals, mp 154°C ($CH_2Cl_2$/*n*-hexane); $\nu_{max}$ (Nujol) 1733.8, 1611.7, 1565.9, 1247.7, 1168.0, 699.2 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 3.83 (s, 3 H), 4.31 (d, 2 H, *J*=6.3 Hz), 5.83 (s, 1 H), 6.60 (br s, 1 H), 6.80–7.90 (m, 13 H), 11.50 (br s, 1 H). $\delta_C$ 48.66, 55.54, 93.96, 113.65, 116.78, 120.46, 122.00, 127.40, 127.64, 128.89, 129.156, 129.37, 131.35, 132.58, 138.26., 153.40, 162.25, 162.61, 188.62. Anal. Calcd for $C_{23}H_{21}NO_3$, MW 359.418: C, 76.86; H, 5.89; N, 3.90%. Found: C, 77.03; H, 5.74; N, 3.84%.

**(*Z*)-3-(Benzylamino)-3-(2-hydroxyphenyl)-1-pyridin-4-ylprop-2-en-1-one (3cc).** Oil; $\nu_{max}$ (liquid film) 1596, 1566, 1537, 1413, 1341, 1313, 1148, 1007, 909 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 4.46 (s, 2 H), 5.78 (s, 1 H), 6.50 (br s, 1 H), 6.80–8.70 (m, 13 H), 11.97 (br s, 1 H). $\delta_C$ 48.88, 93.71, 116.31, 119.83, 119.95, 121.40, 122.07, 127.46, 127.63, 128.74, 129.29, 131.40, 137.44, 147.83, 149.18, 154.25, 166.58, 184.76. Anal. Calcd for $C_{21}H_{18}N_2O_2$, MW 330.380: C, 76.34; H, 5.49; N, 8.48%. Found: C, 76.61; H, 5.77; N, 8.36%.

### Cyclisation of 3-(2-hydroxyphenyl)-3-(amino)-1-phenylprop-2-en-1-ones 3

The enaminoketones **3** obtained from the previous step (3 mmol) were dissolved in a water/THF/acetic acid solution in the ratio 2/2/1 (10 $cm^3$) and heated at 40°C for 0.5 h. After this time the mixture was neutralised with saturated solution of $Na_2CO_3$ and extracted with $CH_2Cl_2$ (2×30 $cm^3$). The solution was dried with anhydrous $Na_2SO_4$, then filtered and the solvent evaporated under reduced pressure. The products obtained were submitted to chromatographic purification or recrystallised. In all cases a single product was isolated, in 66–94% yield, which spectral data identified as a 4*H*-chromen-4-ylidenamine **4**. Prolonged heating of the mixture (5 h) results only in a little decomposition of the product to unidentified products.

***N*-Methyl-*N*-(2-phenyl-4*H*-chromen-4-ylidene)amine (4aa).** Yellow oil; $\nu_{max}$ (liquid film) 2854, 1636, 1221, 984, 762, 689 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 3.38 (s, 3 H), 6.75 (s, 1 H), 7.20–7.40 (m, 2 H), 7.42–7.63 (m, 4 H), 7.80–8.00 (m, 2 H), 8.18–8.22 (m, 1 H). $\delta_C$ 38.15, 95.54, 118.02, 124.57, 125.27, 126.33, 129.25, 130.98, 131.43, 133.57, 134.50, 153.50, 154.00, 157.50; *m/z* 235 ($M^+$, 68), 234 (100); 206 (13); 105 (12); 77 (13). Anal. Calcd for $C_{16}H_{13}NO$, MW 235.281: C, 81.68; H, 5.57; N, 5.95%. Found: C, 81.97; H, 5.76; N, 5.87%.

***N*-[2-(4-Methoxyphenyl)-4*H*-chromen-4-ylidene]-*N*-methylamine (4ab).** Yellow oil; $\nu_{max}$ (liquid film) 2896, 1640, 1220, 769, 702 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 3.36 (s, 3 H), 3.87 (s, 3 H), 6.65 (s, 1 H), 6.96–7.01 (m, 2 H),

7.20–7.50 (m, 3 H), 7.80–7.90 (m, 2 H), 8.20 (d, 1 H, $J$=9.4 Hz). $\delta_C$ 37.88, 55.92, 95.17, 114.66, 117.92, 123.44, 124.63, 125.20, 125.89, 127.92, 131.39, 153.54, 154.14, 157.46, 162.03. *m*/*z* 265 ($M^+$, 55), 264 (72), 221 (25), 112 (36), 105 (32), 84 (100). Anal. Calcd for $C_{17}H_{15}NO_2$, MW 265.307: C, 76.96; H, 5.70; N, 5.28%. Found: C, 76.78; H, 5.87; N, 5.44%.

***N*-Methyl-*N*-(2-pyridin-4-yl-4*H*-chromen-4-ylidene)amine (4ac).** Red oil; $\nu_{max}$ (liquid film) 2898, 1621, 1120, 972, 753, 685 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 3.35 (s, 3 H), 6.81 (s, 1 H), 7.20–8.75 (m, 8 H). $\delta_C$ 30.00, 98.12, 115.55, 119.17, 121.12, 128.33, 128.94, 137.05, 138.22, 152.44, 154.09, 158.64, 164.18. Anal. Calcd for $C_{15}H_{12}N_2O$, MW 236.269: C, 76.25; H, 5.12; N, 11.86%. Found: C, 76.32; H, 5.27; N, 11.69%.

***N*-(2-Phenyl-4*H*-chromen-4-ylidene)propan-2-amine (4ba).** Yellow oil; $\nu_{max}$ (liquid film) 2901 1611, 1498, 1231, 863, 691 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 1.31 (d, 6 H, $J$=6.3 Hz), 4.00 (hept, 1 H, $J$=6.3 Hz), 6.75 (s, 1 H), 7.26–7.85 (m, 9 H). $\delta_C$ 23.71, 49.29, 96.38, 117.38, 121.58, 124.31, 124.84, 125.88, 128.79, 130.54, 131.13, 132.28, 146.12, 151.24, 157.06. Anal. Calcd for $C_{18}H_{17}NO$, MW 263.334: C, 82.10; H, 6.51; N, 5.32%. Found: C, 82.36; H, 6.74; N, 5.23%.

***N*-[2-(4-Methoxyphenyl)-4*H*-chromen-4-ylidene]propan-2-amine (4bb).** Yellow crystals, mp 86–88°C ($CH_2Cl_2$/*n*-hexane); $\nu_{max}$ (Nujol) 1968, 1608, 1510, 1218, 1116, 830, 790, 664 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 1.30 (d, 6 H, $J$=3.1 Hz), 3.88 (s, 3 H), 3.70–4.10 (m, 1 H), 6.65 (s, 1 H), 6.95–8.40 (m, 8 H). $\delta_C$ 24.30, 50.00, 56.30, 96.00, 115.37, 117.42, 118.49, 124.19, 127.20, 127.58, 128.73, 146.03, 151.04, 154.00, 156.80, 162.15. Anal. Calcd for $C_{19}H_{19}NO_2$, MW 293.360: C, 77.79; H, 6.53; N, 4.77%. Found: C, 77.91; H, 6.70; N, 4.54%.

***N*-Benzyl-*N*-(2-phenyl-4*H*-chromen-4-ylidene)amine (4ca).** Yellow crystals, mp 94–96°C ($CH_2Cl_2$/*n*-hexane). $\nu_{max}$ (Nujol) 1633, 1575, 1412, 1349, 1072, 821, 760 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 4.83 (s, 2 H), 6.82 (s, 1 H), 7.20–8.50 (m, 14 H). $\delta_C$ 53.98, 96.50, 117.50, 124.71, 124.82, 125.59, 125.92, 126.50, 127.13, 127.65, 128.40, 128.80, 130.59, 131.14, 133.06, 141.00, 152.63, 153.26. Anal. Calcd for $C_{19}H_{19}NO_2$, MW 311.377: C, 84.86; H, 5.50; N, 4.50%. Found: C, 84.92; H, 5.32; N, 4.46%.

***N*-Benzyl-*N*-[2-(4-methoxyphenyl)-4*H*-chromen-4-ylidene]-amine (4cb).** Yellow crystals, mp 132–133°C ($CH_2Cl_2$/*n*-hexane); $\nu_{max}$ (Nujol) 1630, 1608, 1572, 1288, 1179, 1077, 983, 958, 917, 902, 874, 855, 818 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 3.88 (s, 3 H), 4.82 (s, 2 H), 6.72 (s, 1 H), 7.00 (d, 2 H, $J$=8.8 Hz), 7.30–7.41 (m, 5 H), 7.47–7.53 (m, 3 H), 7.82 (d, 2 H, $J$=8.9 Hz), 8.42 (d, 1 H, $J$=8.1 Hz). $\delta_C$ 53.67, 55.46, 95.33, 114.18, 117.38, 117.78, 124.70, 125.37, 126.47, 127.49, 127.54, 127.67, 128.40, 131.03, 133.18, 141.13, 152.68, 153.24, 161.57. Anal. Calcd for $C_{23}H_{19}NO_2$, MW 341.402: C, 80.92; H, 5.61; N, 4.10%. Found: C, 80.82; H, 5.87; N, 4.34%.

***4H*-Benzyl-*N*-(2-pyridin-4-yl-4*H*-chromen-4-ylidene)-methanamine (4cc).** Orange crystals, mp 102–104°C ($CH_2Cl_2$/*n*-hexane); $\nu_{max}$ (Nujol) 1611, 1573, 1546, 1495, 1325, 1229, 863, 839, 679, 661 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 4.82 (s, 2 H), 6.91 (s, 1 H), 7.26–8.75 (m, 13 H). $\delta_C$ 53.89, 98.37, 117.46, 119.56, 123.61, 124.76, 125.24, 126.66, 127.60, 128.49, 131.46, 140.31, 141.23, 150.54, 152.03, 153.12, 154.52. Anal. Calcd for $C_{21}H_{16}N_2O$, MW 312.365: C, 80.75; H, 5.16; N, 8.97%. Found: C, 80.52; H, 5.39; N, 8.84%.

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