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ORIGINAL PAPER

Simple and one-pot *C*-arilation from reaction between azines (isoquinoline or phenanthridine) and acetylenic esters in the presence of phenol derivatives

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Abstract Three-component condensation reactions between azines (isoquinoline or phenanthridine) and acetylenic esters were undertaken in the presence of phenol derivatives (2,6-di-tert-butyl-phenol, 2,4-di-tert-butyl-phenol, 2,6-dimethyl phenol and 2,4-dimethyl phenol) for generation of *C*-arilation in good yields. The reactions proceeded smoothly at room temperature without using any catalyst. This method is very useful to functionalize aza-aromatic compounds in a one-pot operation.

Keywords Three-component reactions · Phenanthridine or isoquinoline · Acetylenic esters · Phenol derivatives · *C*-arilation

Introduction

The development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic synthesis [1]. Nitrogen-containing heterocycles are abundant in nature and exhibit divers and important biological properties [2].

Phenanthridines are important core structures found in a variety of natural products and other biologically important molecules with a wide range of biological activities and applications [3–6], including antibacterial, antiprotozoal, anticancer, antimicrobial, anti-inflammatory, antivirial, anti-oxidant [7–12] and also with applications as drugs [13], DNA targeting agents [14], dyes [15], and probes [16]. Isoquinoline is also present in various natural products such as cryptaustoline and cryptowoline [17]. They are known to exhibit various biological activities [18–20] such as antileukaemic [21], tubulin polymerization inhibitory [22], and anti-tumour activities [23]. In the current work, we now describe a new three-component reaction as an efficient synthetic route of compounds **4** and **8** using isoquinoline **1** or phenanthridine **5** as the two typical categories (see Scheme 1).

Results and discussions

The reaction between azines (isoquinoline **1** or phenanthridine **5**) and acetylenic esters **2** or **6** as a Michael acceptor [24–30] was undertaken in the presence of phenol derivatives (2,6-di-tert-butyl-phenol, 2,4-di-tert-butyl-phenol, 2,6-dimethyl phenol and 2,4-dimethyl phenol) at ambient temperature (see Scheme 2 and Table 1). Reactions were carried out by first mixing the phenanthridine or isoquinoline and phenol derivatives and then the acetylenic ester was added slowly. The reactions proceeded smoothly in CH_2Cl_2 and then the whole reaction mixture solidified into yellow or brown solid within a few hours. The ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of compounds **4a–g** and **8 h–i**. No product

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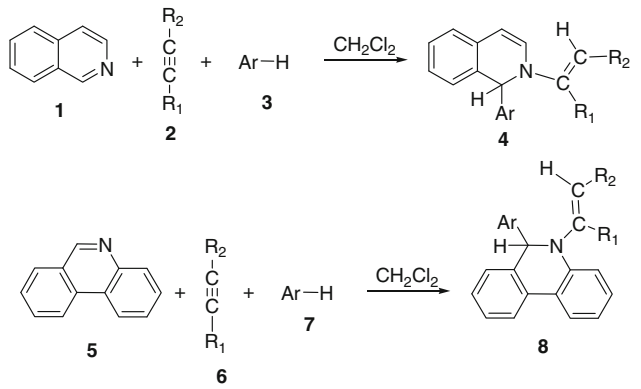


Scheme 1 Reaction of isoquinoline or phenanthridine with acetylenic esters in the precense of phenolderivatives

other than **4a–g** and **8 h–i** could be detected by NMR spectroscopy. The structures of compounds **4a–g** and **8 h–i** were confirmed by elemental analyses, mass, IR, ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR 500 MHz spectrum of **4a** exhibited two singlets identified as tert-butyl ($\delta = 1.40$, 18H, s, 2CMe_3) and methoxy ($\delta = 3.72$, 3H, s, OMe), olefinic protons ($\delta = 5.18$ and 8.30, 2d, $^{3}J_{HH} = 13.8$ Hz, N–C*H* = C*H*-CO_2CH_3), and also two sharp line ($\delta = 5.16$ and 5.80 ppm) for the OH and NC*H*C group, respectively. Aromatic protons, along with multiplets at $\delta = 7.02$–8.20 ppm for the isoquinoline and phenol moiety. The ^{13}C NMR spectrum of **4a** showed **27** distinct resonances in agreement with the proposed structure. In addition, product **4a** displayed ^{13}C NMR resonances at $\delta = 90.77$, 122.68 and 124.85 ppm, respectively for the N*C*HC, N–CH = *C*H–CO_2CH_3, and N–*C*H = CH–CO_2CH_3 units. The carbonyl group resonance in the ^{13}C NMR spectrum of **4a** appear at $\delta = 169.06$ ppm. The ^{1}H and ^{13}C NMR spectra of compounds **4b–g** and **8 h–i** are similar to those of **4a**. The ^{1}H NMR of each of the isolated product **4f–g** and **8 h–i** exhibited a N–C = C*H* proton signal at about 5.06-5.46 ppm, which is in agreement with the (*Z*) configuration for the vinyl moiety in **4f–g** and **8 h–i** [31, 32] (see Scheme 2 and Table 1).

Briefly, we have developed a new method to access a novel class of heterocyclic derivatives. The present procedure has the advantage that, not only is the reaction performed under neutral conditions, but also the reactants can be mixed without any prior activation or modification. It seems that, this procedure is very useful to functionalize azines in a one-pot operation.

Experimental

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. The ^{1}H and ^{13}C NMR spectra were obtained with a BRUKER DRX-500 AVANCE instrument using $CDCl_3$ as applied solvent and TMS as internal standard at 500.1 and 125.8 MHz, respectively. In addition, the mass spectra were recorded on a GCMS-QP5050A mass spectrometer operating at an ionization potential of 70 eV. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. All the chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General procedure for the synthesis of compounds 4 and 8

*(2E)-methyl 3-(1-(3,5-di-tert-butyl-4-hydroxyphenyl) isoquinoline-2(1H)-yl) acrylate (**4a**).*

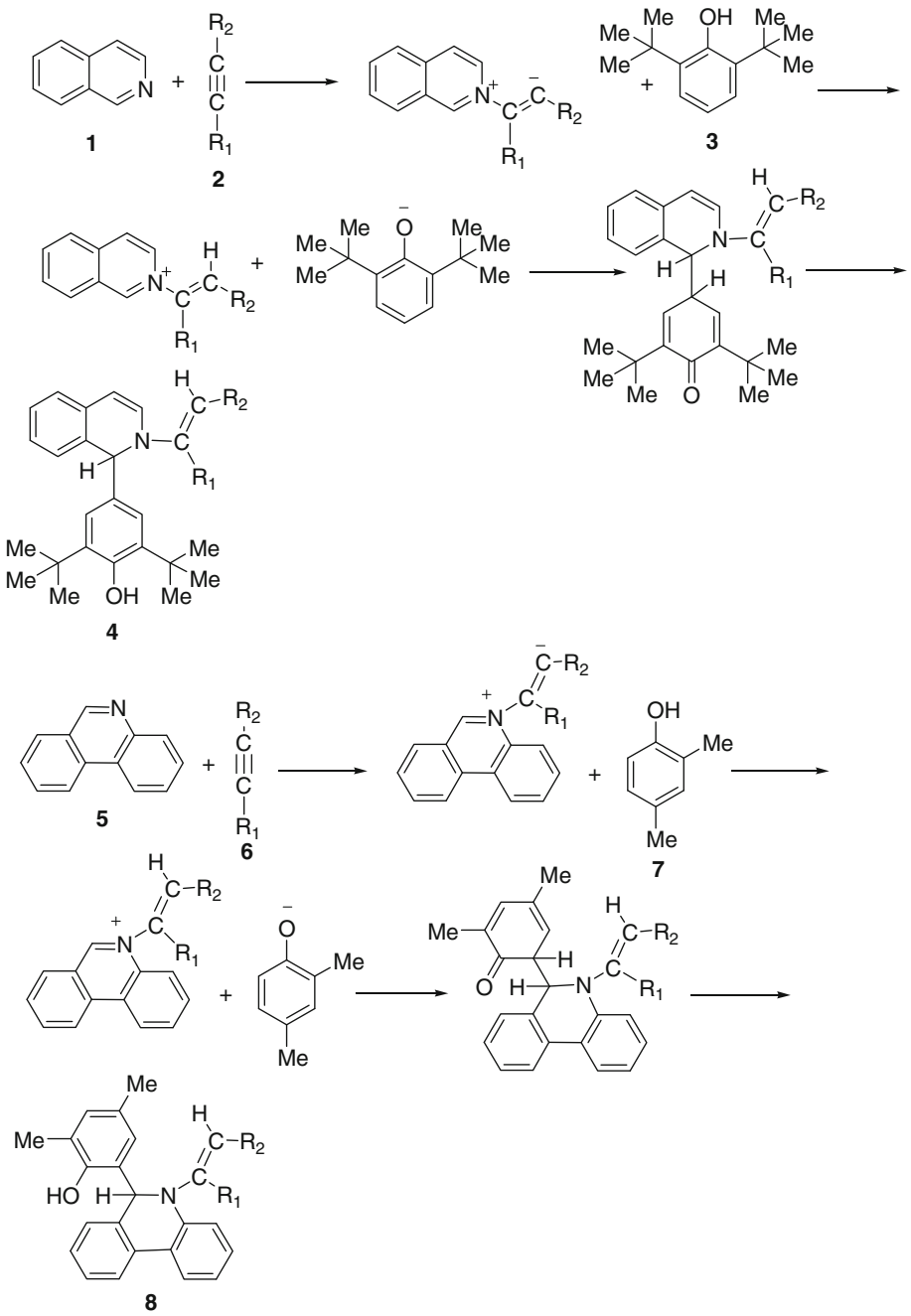
To a magnetically stirred solution of isoquinoline (1 mmol) and 2,6-di-tert-butyl-phenol (0.21 g, 1 mmol) in CH_2Cl_2 (10 mL) was added, dropwise, a mixture of methyl propiolate (1 mmol) in CH_2Cl_2 (5 mL) at −10 °C over 10 min. After approximately a few hours stirring at ambient temperature, the whole reaction mixture solidified into a yellow solid, the solvent was then removed under reduced pressure and product washed with cold n-hexane (2 × 5 mL). Then the product was recrystallized from a mixture of n-hexane and ethyl acetate.

Yellow powder, yield 95 %, 0.40 g, mp: 191–193 °C; IR (ν_{max}, cm^{-1}): 1,672 cm^{-1} (C = O), 3,232 cm^{-1} (OH): ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.40$ (18H, s, 2CMe_3), 3.72 (3H, s, OCH_3), 5.16 (1H, s, OH), 5.18 (1H, d, $^{3}J_{HH} = 13.8$ Hz, N–CH = C*H*–CO_2CH_3), 5.80 (1H, s, NC*H*C), 5.87 (1H, d, $^{3}J_{HH} = 7.4$ Hz, C_4-H, isoquinoline), 6.53 (1H, d, $^{3}J_{HH} = 7.4$ Hz, C_3-H isoquinoline), 7.02–8.20 ($7H_{aro}$, m, isoquinoline and phenol), 8.30 (1H, d, $^{3}J_{HH} = 13.8$ Hz, N–C*H* = CH-CO_2Me) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 30.13$ (s, 2CMe_3), 50.86 (OCH_3), 90.77 (N*C*HC), 122.68 (N–CH = *C*H–CO_2CH_3), 124.85 (N–*C*H = CH–CO_2CH_3), 126.79, 127.02, 127.63, 129.47, 131.70, 132.00, 135.85, 147.64 and 153.39 ($14C_{aro}$, isoquinoline and phenol), 169.06 (C = O, ester). MS, *m/z* (%) = 419 (M, 5), 360 (M–CO_2Me, 15), 334 (M–C4H5O2 , 10), 277 (M–$C_4H_5O_2$ and CMe_3, 13), 205 ($C_{14}H_{21}O$, 38), 85 ($C_4H_5O_2$, 24); *Anal*. Calcd for $C_{27}H_{33}NO_3$ (419.56): C, 77.30; H, 7.93; N, 3.34 %, Found: C, 77.15; H, 8.01; N, 3.44 %.

*(2E)-ethyl 3-(1-(3,5-di-tert-butyl-4-hydroxyphenyl) isoquinoline-2(1H)-yl)acrylate(**4b**).*

Yellow powder, yield 93 %, 0.40 g, mp: 180-182 °C; IR (ν_{max}, cm^{-1}): 1,659 cm^{-1} (C = O), 3,197 (OH) cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.29$ (3H, t, $^{3}J_{HH} = 7.2$

Scheme 2 Proposed mecanisem fo formation of compounds 4 and 8

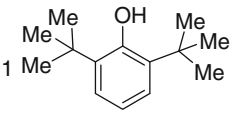
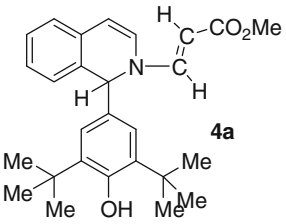
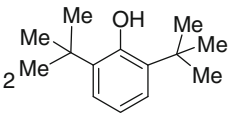
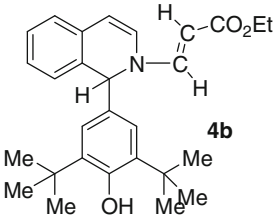
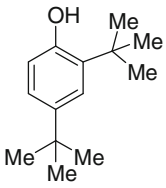
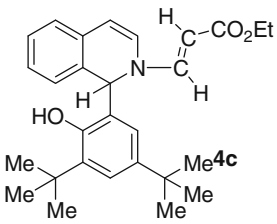
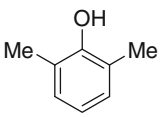
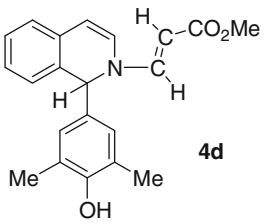
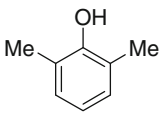
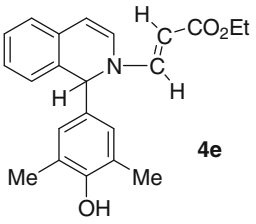
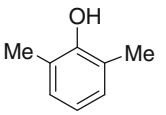
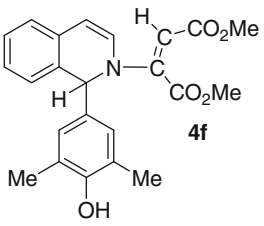


HZ, $CO_2CH_2CH_3$), 1.39 (18H, s, 2CMe_3), 4.17 (2H, q, $^3J_{HH}$ = 7.2 HZ, $CO_2CH_2CH_3$), 5.16 (1H, s, OH), 5.18 (1H, d, $^3J_{HH}$ = 13.5 Hz, N–CH = C*H*-CO_2Et), 5.81 (1H, s, NC*H*C), 5.87 (1H, d, $^3J_{HH}$ = 7.8 Hz, C_4-H isoquinoline), 6.52 (1H, d, $^3J_{HH}$ = 7.8 Hz, C_3-H isoquinoline), 7.08–7.29 ($7H_{aro}$, m, isoquinoline and phenol), 7.57 (1H, d, $^3J_{HH}$ = 13.5 Hz, N–C*H* = CH-CO_2Et) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.42 ($CO_2CH_2CH_3$), 30.12 (2CMe_3), 59.39 ($CO_2CH_2CH_3$), 91.25 (NCHC), 122.77 (N–CH = *C*H-CO_2Et), 124.81 (N–*C*H = CH–CO_2Et), 126.79, 126.98, 127.61, 129.56, 131.63, 131.98, 135.81, 147.45 and 153.37 ($14C_{aro}$, isoquinoline and phenol), 168.63 (C = O, ester). MS, *m/z* (%) = 433 (M, 22), 277 (M–$C_5H_7O_2$ and CMe_3, 24), 220 (M–$C_5H_7O_2$ and 2CMe_3, 26), 205 ($C_{14}H_{21}O$, 67); *Anal*. Calcd for $C_{28}H_{35}NO_3$ (433.58): C, 77.57; H, 8.13; N, 3.23 %, Found: C, 77.70; H, 8.04; N, 3.35 %.

*(2E)-ethyl 3-(1-(3,5-di-tert-butyl-2-hydroxyphenyl) isoquinoline-2(1H)-yl)acrylate**(**4c**)*.

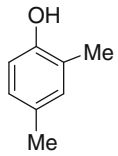
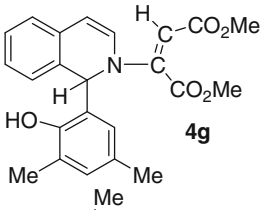
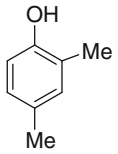
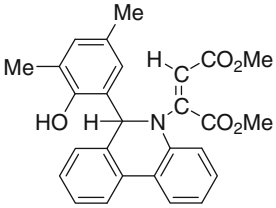
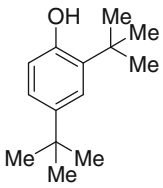
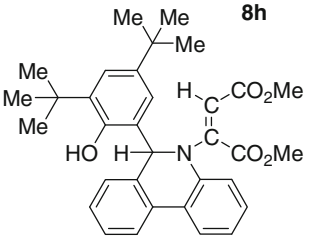
Yellow powder, yield 92 %, 0.40 g, mp: 176–178 °C; IR (ν_{max}, cm^{-1}): 1,664 cm^{-1} (C = O), 3,162 cm^{-1} (OH): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.32 (3H, t, $^3J_{HH}$ = 7.2

Table 1 Reaction of isoquinoline or phenanthridine with acetylenic esters in the presence of phenol derivatives

Entry	Ar-H	R_1	R_2	Z or E	Product	Yield%
1		H	CO_2Me	E	 **4a**	95%
2		H	CO_2Et	E	 **4b**	93%
3		H	CO_2Et	E	 **4c**	92%
4		H	CO_2Me	E	 **4d**	94%
5		H	CO_2Et	E	 **4e**	96%
6		CO_2Me	CO_2Me	Z	 **4f**	92%

HZ, $CO_2CH_2CH_3$), 1.43 (18H, s, 2CMe_3), 4.23 (2H, q, $^3J_{HH}$ = 7.2 HZ, $CO_2CH_2CH_3$), 5.20 (1H, s, OH), 5.25 (1H, d, $^3J_{HH}$ = 13.3 Hz, N–CH = C*H*-CO_2Et), 5.89 (1H, s, NC*H*C), 5.97 (1H, d, $^3J_{HH}$ = 7.6 Hz, C_4–H isoquinoline), 6.52 (1H, d, $^3J_{HH}$ = 7.6 Hz, C_3-H isoquinoline), 7.12–7.37 ($7H_{aro}$, m, isoquinoline and phenol), 7.64 (1H, d, $^3J_{HH}$ = 13.3 Hz, N–C*H* = CH-CO_2Et) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.86 ($CO_2CH_2CH_3$), 30.26 (2CMe_3), 58.79 ($CO_2CH_2CH_3$), 90.54 (NCHC), 121.97 (N–CH = *C*H–CO_2Et), 123.76 (N–*C*H = CH–CO_2Et),

Table 1 continued

Entry	Ar-H	R_1	R_2	Z or E	Product	Yield%
7		CO_2Me	CO_2Me	Z	 **4g**	91%
8		CO_2Me	CO_2Me	Z	 **8h**	90%
9		CO_2Me	CO_2Me	Z	 **8i**	94%

125.70, 126.91, 127.54, 128.72, 131.90, 131.98, 134.80, 146.65 and 153.70 ($14C_{aro}$, isoquinoline and phenol), 169.13 (C = O, ester). MS, *m/z* (%) = 433 (M, 9), 404 (M–Et, 48), 388 (M–OEt, 80), 360 (M–CO_2Et, 56), 205 ($C_{14}H_{21}O$, 52), 129 (C_9H_7N, 100). *Anal*. Calcd for $C_{28}H_{35}NO_3$ (433.58): C, 77.57; H, 8.13; N, 3.23 %, Found: C, 77.43; H, 8.19; N, 3.19 %.

*(2E)-methyl 3-(1-(4-hydroxy-3,5-dimethylphenyl) isoquinoline-2(1H)-yl)acrylate(**4d**).*

Yellow powder, yield 94 %, 0.32 g, mp: 87–89 °C; IR (ν_{max}, cm^{-1}): 1,670 cm^{-1} (C = O), 3,395 cm^{-1} (OH) : ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.20 (6H, s, 2*Me*), 3.71 (3H, s, OCH_3), 5.11 (1H, d, $^3J_{HH}$ = 13.5 Hz, N–CH = C*H*-CO_2CH_3), 5.76 (1H, s, OH), 5.87 (1H, d, $^3J_{HH}$ = 7.6 Hz, C_4-H, isoquinoline), 6.53 (1H, d, $^3J_{HH}$ = 7.6 Hz, C_3-H isoquinoline), 6.92 (1H, s, NC*H*C), 7.06–7.29 ($6H_{aro}$, m, isoquinoline and phenol), 7.57 (1H, d, $^3J_{HH}$ = 13.5 Hz, N–C*H* = CH-CO_2Me) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 16.16 (s, 2*Me*), 50.88 (OCH_3), 91.01 (N*C*HC), 105.61 (N–CH = *C*H-CO_2CH_3), 123.45 (N–*C*H = CH-CO_2CH_3), 124.95, 125.94, 126.34, 126.74, 127.09, 127.47, 127.63, 128.49, 131.70, 133.52, 147.55 and 152.09 ($14C_{aro}$, isoquinoline and phenol), 169.01 (C = O, ester). MS, *m/z* (%) = 335 (M, 38), 305 (M–2Me, 18), 276 (M–CO_2Me, 20), 250 (M–C4H5O2 , 48), 130 (C_9H_8N, 100); *Anal*. Calcd for $C_{21}H_{21}NO_3$ (335.39): C, 75.20; H, 6.31; N, 4.17 %, Found: C, 75.27; H, 6.23; N, 4.24 %.

*(2E)-ethyl 3-(1-(4-hydroxy-3,5-dimethylphenyl) isoquinoline-2(1H)-yl)acrylate(**4e**).*

Yellow powder, yield 96 %, 0.34 g, mp: 92–94 °C; IR (ν_{max}, cm^{-1}): 1,754 cm^{-1} (C = O), 3,450 cm^{-1} (OH): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.28 (3H, t, $^3J_{HH}$ = 7.1 HZ, $CO_2CH_2CH_3$), 2.18 (6H, s, 2*Me*), 4.19 (2H, q, $^3J_{HH}$ = 7.1 HZ, $CO_2CH_2CH_3$), 5.11 (1H, d, $^3J_{HH}$ = 13.5 Hz, N–CH = C*H*–CO_2Et), 5.76 (1H, s, OH), 5.82 (1H, d, $^3J_{HH}$ = 7.4 Hz, C_4–H isoquinoline), 6.54 (1H, d, $^3J_{HH}$ = 7.4 Hz, C_3-H isoquinoline), 6.99 (1H, s, NC*H*C), 7.05–7.20 ($6H_{aro}$, m, isoquinoline and phenol), 7.58 (1H, d, $^3J_{HH}$ = 13.5 Hz, N–C*H* = CH–CO_2Et) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.40 ($CO_2CH_2CH_3$), 15.81 (2*Me*), 59.66 ($CO_2CH_2CH_3$), 91.40 (N*C*HC), 106.14 (N–CH = *C*H–CO_2Et), 123.48 (N–*C*H = CH–CO_2Et), 124.92, 125.93, 126.73, 126.99, 127.61, 128.49, 130.28, 131.52, 133.53, 147.42 and 152.11 ($14C_{aro}$, isoquinoline and phenol), 168.66 (C = O, ester). MS, *m/z* (%) = 349 (M, 3), 334 (M–Me, 10), 228 (M–C_8H_9O, 26), 129 (C_9H_7N, 89); *Anal*. Calcd for $C_{22}H_{23}NO_3$ (349.42): C, 75.62; H, 6.63; N, 4.01 %, Found: C, 75.49; H, 6.70; N, 4.10 %.

*Dimethyl 2-(1-(4-hydroxy-3,5-dimethylphenyl) isoquinoline-2(1H)-yl)maleate(**4f**).*

Brown powder, yield 92 %, 0.36 g, mp: 153-155 °C; IR (ν_{max}, cm^{-1}): 1,720 and 1,655 cm^{-1} (C = O), 3285 cm^{-1} (OH): ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.18$ (6H, s, 2*Me*), 3.55 and 3.98 (6H, 2 s, $2OCH_3$), 5.20 (1H, s, N–C = C*H*-CO_2Me), 5.75 (1H, s, OH), 5.93 (1H, d, $^3J_{HH} = 7.6$ Hz, C_4-H, isoquinoline), 6.49 (1H, d, $^3J_{HH} = 7.6$ Hz, C_3-H isoquinoline), 6.95 (1H, s, NC*H*C), 6.99–7.28 ($7H_{aro}$, m, isoquinoline and phenol) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 16.14$ (s, 2*Me*), 51.86 and 53.10 ($2OCH_3$), 91.07 (N*C*HC), 109.23 (N–C = *C*H–CO_2CH_3), 123.63 (N–*C* = CH-CO_2CH_3), 125.02, 125.55, 126.20, 126.43, 127.09, 127.74, 128.45, 130.65, 131.99, 132.01, 150.04 and 152.21 ($14C_{aro}$, isoquinoline and phenol), 165.28 and 167.24 (2C = O, ester). MS, *m/z* (%) = 393 (M, 3), 334 (M–CO_2Me, 36), 250 (M–$C_6H_7O_4$, 46), 143 ($C_6H_7O_4$, 6), 130 (C_9H_8N, 100); *Anal*. Calcd for $C_{23}H_{23}NO_5$ (393.43): C, 70.22; H, 5.89; N, 3.56 %, Found: C, 70.28; H, 5.96; N, 3.68 %.

*Dimethyl 2-(1-(2-hydroxy-3,5-dimethylphenyl) isoquinoline-2(1H)-yl)maleate(**4 g**).*

Brown powder, yield 91 %, 0.36 g, mp: 118-120 °C; IR (ν_{max}, cm^{-1}): 1,742 and 1,704 cm^{-1} (C = O), 3320 cm^{-1} (OH): ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.10$ and 2,27 (6H, s, 2*Me*), 3.65 and 3.83 (6H, 2 s, $2OCH_3$), 5.43 (1H, s, N–C = C*H*-CO_2Me), 5.71 (1H, s, OH), 5.86 (1H, d, $^3J_{HH} = 7.5$ Hz, C_4-H, isoquinoline), 6.37 (1H, d, $^3J_{HH} = 7.5$ Hz, C_3-H isoquinoline), 6.63 (1H, s, NC*H*C), 7.03-7.32 ($6H_{aro}$, m, isoquinoline and phenol) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 13.46$ and 14.09 (2 s, 2*Me*), 51.44 and 52.63 ($2OCH_3$), 90.17 (N*C*HC), 110.13 (N–C = *C*H-CO_2CH_3), 124.36 (N–*C* = CH-CO_2CH_3), 124.65, 125.22, 126.09, 126.29, 126.73, 127.19, 127.74, 128.81, 129.25, 132.80, 133.11, 149.14 and 151.82 ($14C_{aro}$, isoquinoline and phenol), 166.28 and 168.17 (2C = O, ester). MS, *m/z* (%) = 393 (M, 7), 362 (M–OMe, 62), 334 (M–CO_2Me, 11), 272 (M–C_8H_9O, 18), 143 ($C_6H_7O_4$, 26), 129 (C_9H_7N, 83), 121 (C_8H_9O, 44); *Anal*. Calcd for $C_{23}H_{23}NO_5$ (393.43): C, 70.22; H, 5.89; N, 3.56 %, Found: C, 70.13; H, 5.81; N, 3.69 %.

*Dimethyl 2-(6-(2-hydroxy-3,5-dimethylphenyl) phenanthridine-5(6H)-yl)maleate(**8 h**).*

Brown powder, yield 90 %, 0.40 g, mp: 107-109 °C; IR (ν_{max}, cm^{-1}): 1,743 and 1,654 cm^{-1} (C = O), 3,400 cm^{-1} (OH): ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.13$ and 2,25 (6H, s, 2*Me*), 3.70 and 3.81 (6H, 2 s, $2OCH_3$), 5.46 (1H, s, N–C = C*H*-CO_2Me), 5.83 (1H, s, OH), 6.71 (1H, s, NC*H*C), 6.90–7.91 ($6H_{aro}$, m, phenanthridine and phenol) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 14.07$ and 14.13 (2 s, 2*Me*), 51.64 and 52.79 ($2OCH_3$), 91.11 (N*C*HC), 109.18 (N–C = *C*H–CO_2CH_3), 123.97 (N–*C* = CH–CO_2CH_3), 124.25, 125.39, 125.58, 126.09, 126.80, 127.49, 127.63, 128.80, 128.95, 130.28, 132.18, 148.74, 152.36 and 153.05 ($18C_{aro}$, phenanthridine and phenol), 165.71 and 167.13 (2C = O, ester). MS, *m/z* (%) = 443 (M, 6), 428 (M–Me, 17), 384 (M–CO_2Me, 21), 322 (M–C_8H_9O, 63), 300 (M–$C_6H_7O_4$, 41), 143 ($C_6H_7O_4$, 100), 121 (C_8H_9O, 8); *Anal*. Calcd for $C_{27}H_{25}NO_5$ (443.50): C, 73.12; H, 5.68; N, 3.16 %, Found: C, 73.02; H, 5.77; N, 3.04 %.

*Dimethyl 2-(6-(3,5-di-tert-butyl-2-hydroxyphenyl) phenanthridine-5(6H)-yl)maleate(**8i**).*

Brown powder, yield 94 %, 0.50 g, mp: 142-144 °C; IR (ν_{max}, cm^{-1}): 1,740 and 1,665 cm^{-1} (C = O), 3,395 cm^{-1} (OH), ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 0.89$ and 1,41 (18H, 2 s, $2CMe_3$), 3.56 and 3.99 (6H, 2 s, $2OCH_3$), 5.06 (1H, s, N–C = C*H*–CO_2Me), 5.89 (1H, s, OH), 6.04 (1H, s, NC*H*C), 6.95–7.89 ($11H_{aro}$, m, phenanthridine and phenol) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 30.11$ and 30.23 (2 s, $2CMe_3$), 51.70 and 53.19 ($2OCH_3$), 92.21 (N*C*HC), 109.78 (N–C = *C*H–CO_2CH_3), 124.17 (N–*C* = CH–CO_2CH_3), 124.65, 124.79, 125.30, 126.39, 126.47, 127.40, 127.71, 128.12, 128.54, 131.18,, 131.91, 132.20, 148.76, 151.83 and 153.15 ($18C_{aro}$,phenanthridine and phenol), 167.12 and 168.93 (2C = O, ester). MS, *m/z* (%) = 527 (M, 52), 496 (M–OMe, 38), 468 (M–CO_2Me, 100), 322 (M–$C_{14}H_{21}O$, 30), 205 ($C_{14}H_{21}O$, 32), 180 ($C_{13}H_{10}N$, 56); *Anal*. Calcd for $C_{33}H_{37}NO_5$ (527.65): C, 75.12; H, 7.07; N, 2.65 %, Found: C, 75.23; H, 7.16; N, 2.57 %.

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