Electronic Supporting Information

Methyl 5-Imino-2-methyl-1,10a-dihydro-5*H*-chromeno[2,3-*b*]pyridine-3-carboxylate

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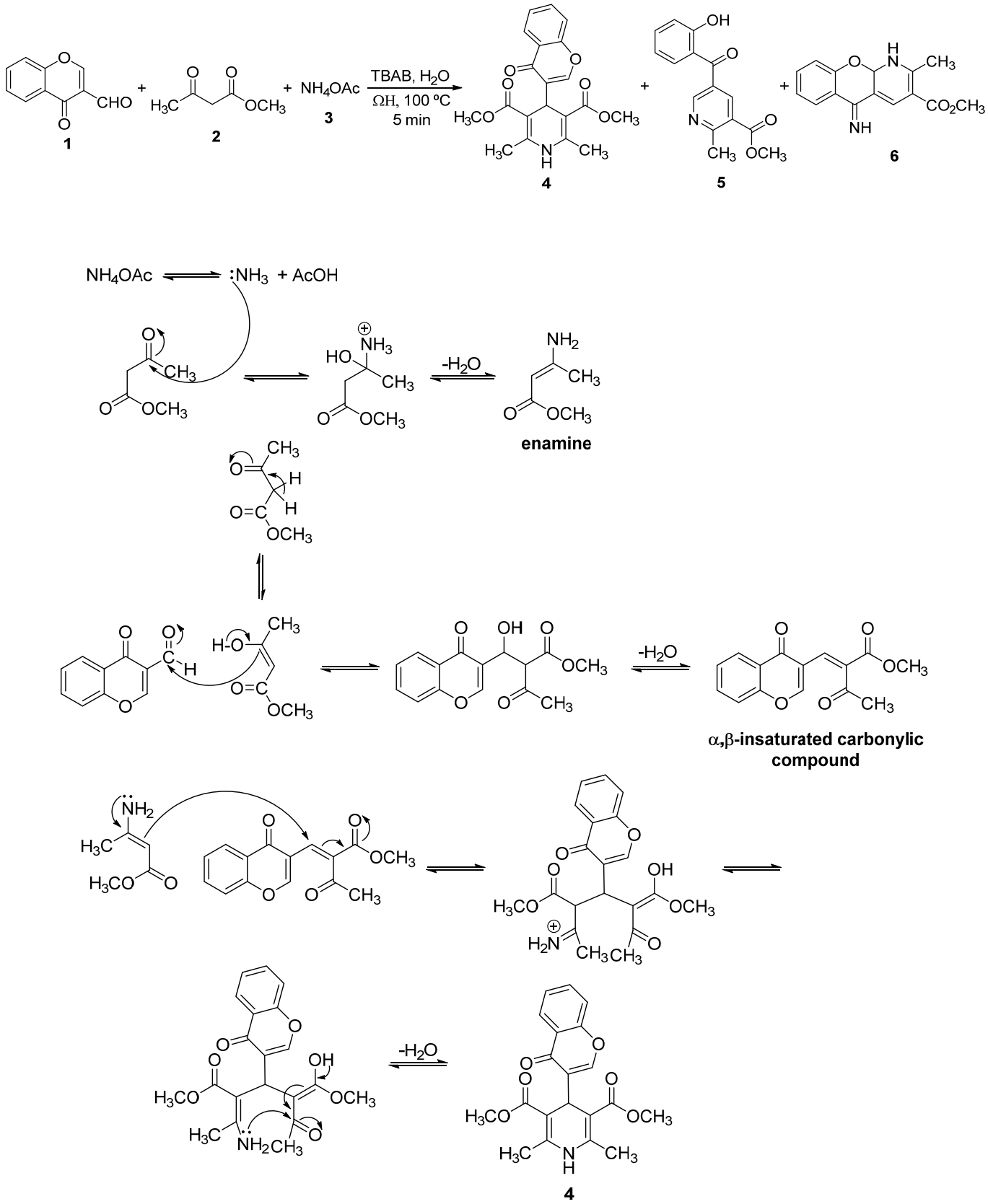
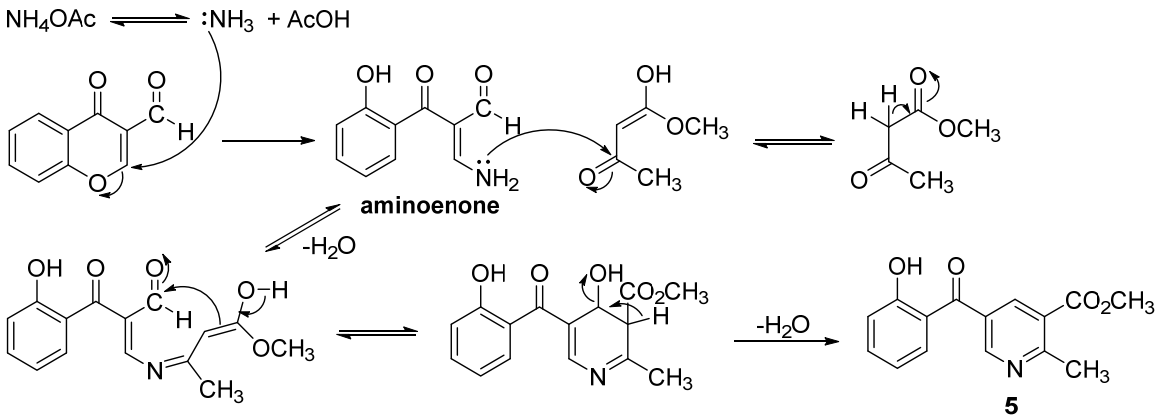
1. Mechanisms for the formation of products 4 and 5

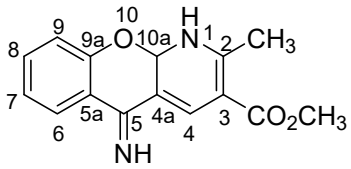


Scheme S1. Hantzsch reaction scheme and mechanism for the formation of compound **4**.



Scheme S2. Plausible mechanism for the formation of compound **5**.

2. NMR spectra of the title compound 6



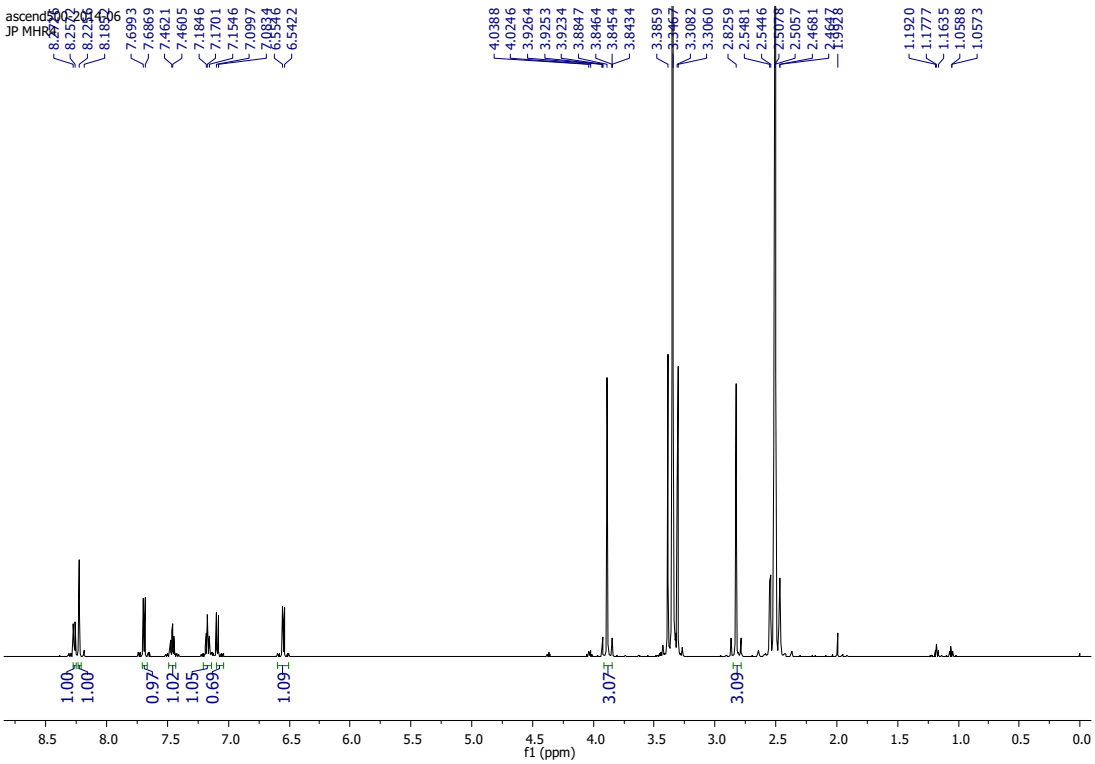


Figure S1. ^{1}H-NMR spectrum of compound **6** (500.13 MHz, DMSO-d$_6$).

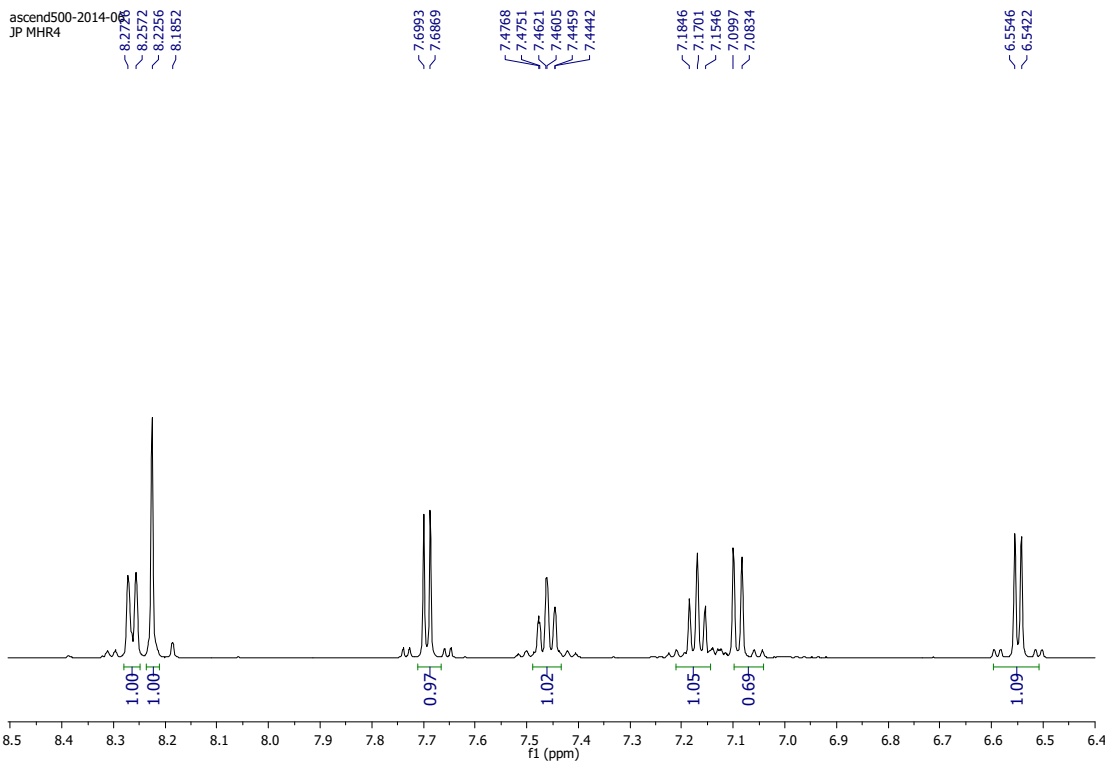


Figure S2. Expansion of ^{1}H-NMR spectrum of compound **6** (500.13 MHz, DMSO-d_6).

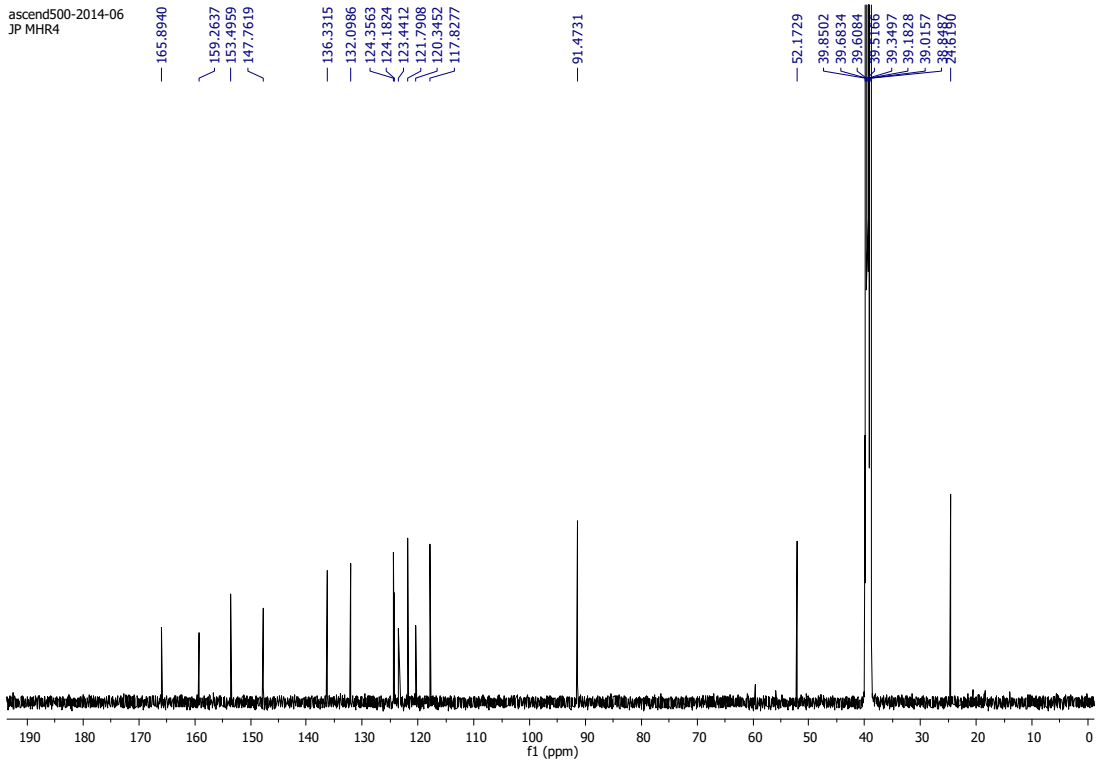


Figure S3. ^{13}C-NMR spectrum of compound **6** (125.77 MHz, DMSO-d_6).

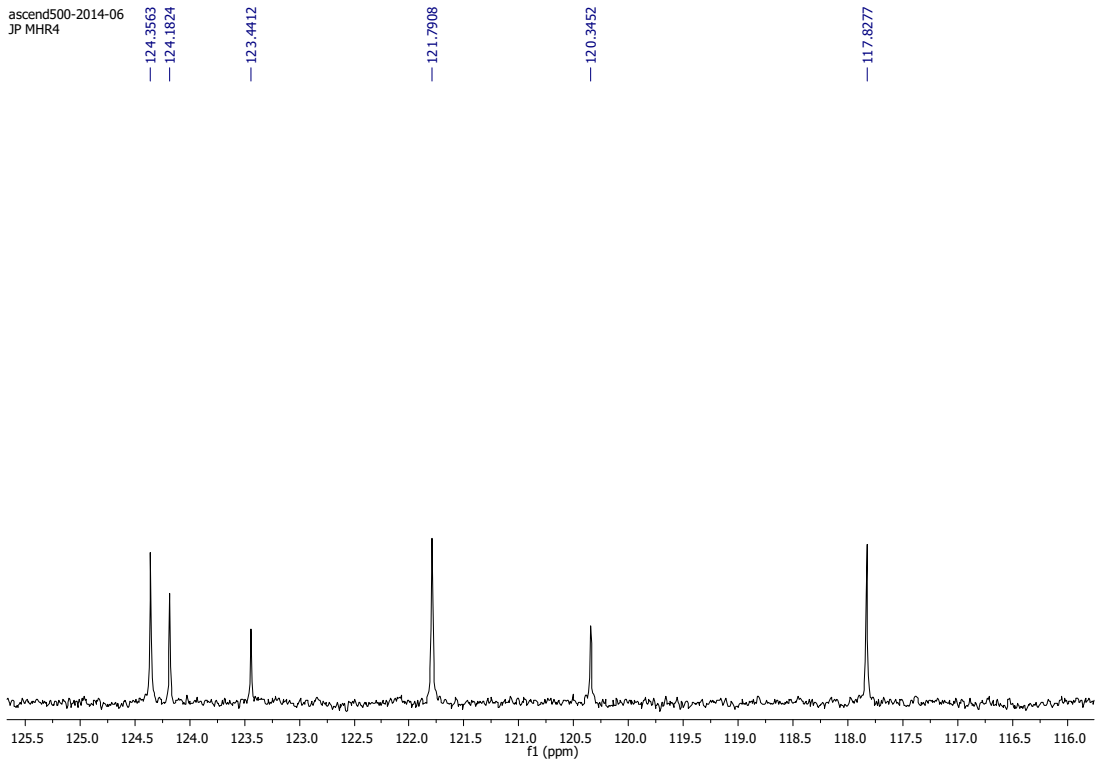


Figure S4. Expansion of ^{13}C-NMR spectrum of compound **6** (125.77 MHz, DMSO-d$_6$).

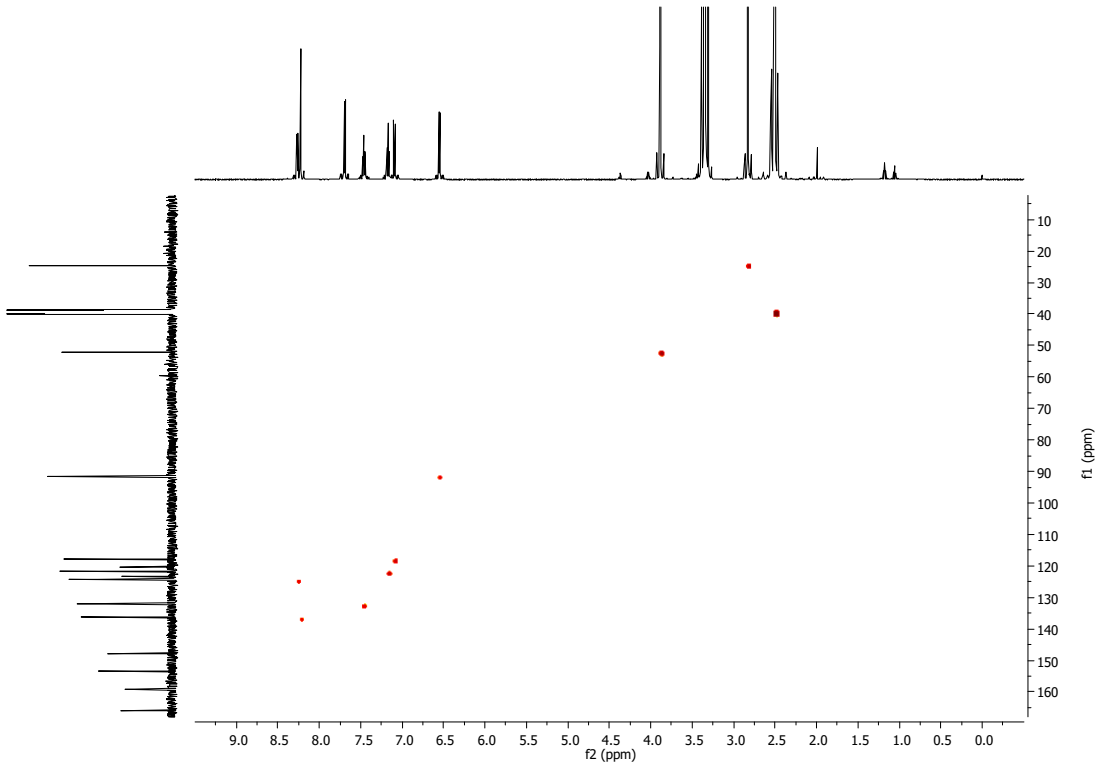


Figure S5. HSQC spectrum of compound **6**.

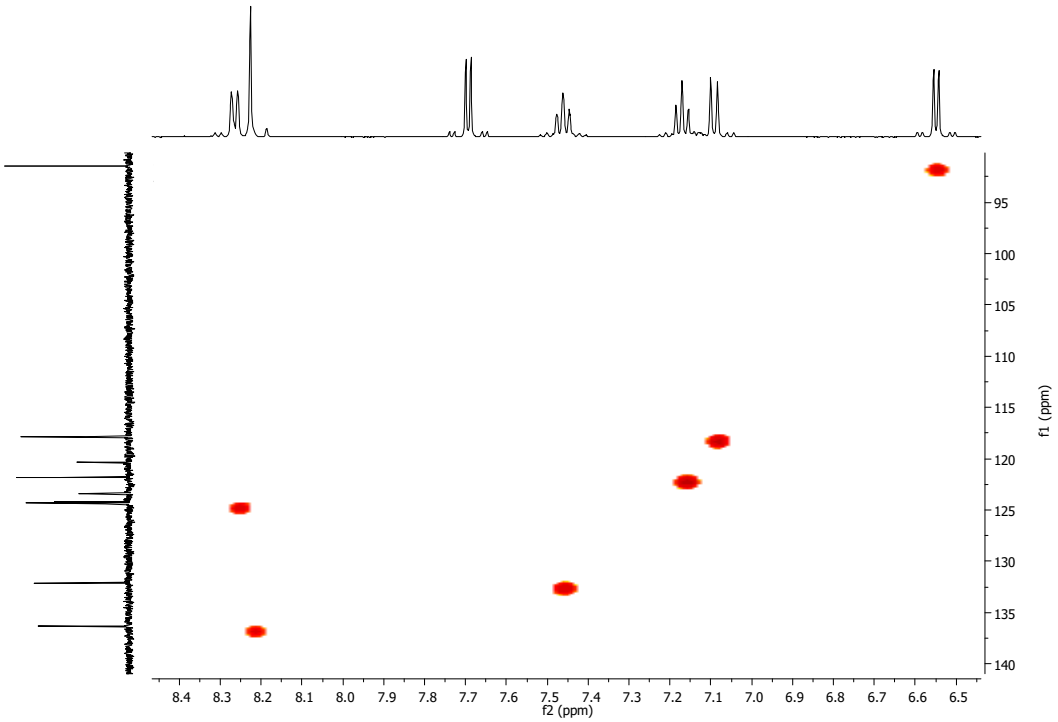


Figure S6. Expansion of HSQC spectrum of compound **6**.

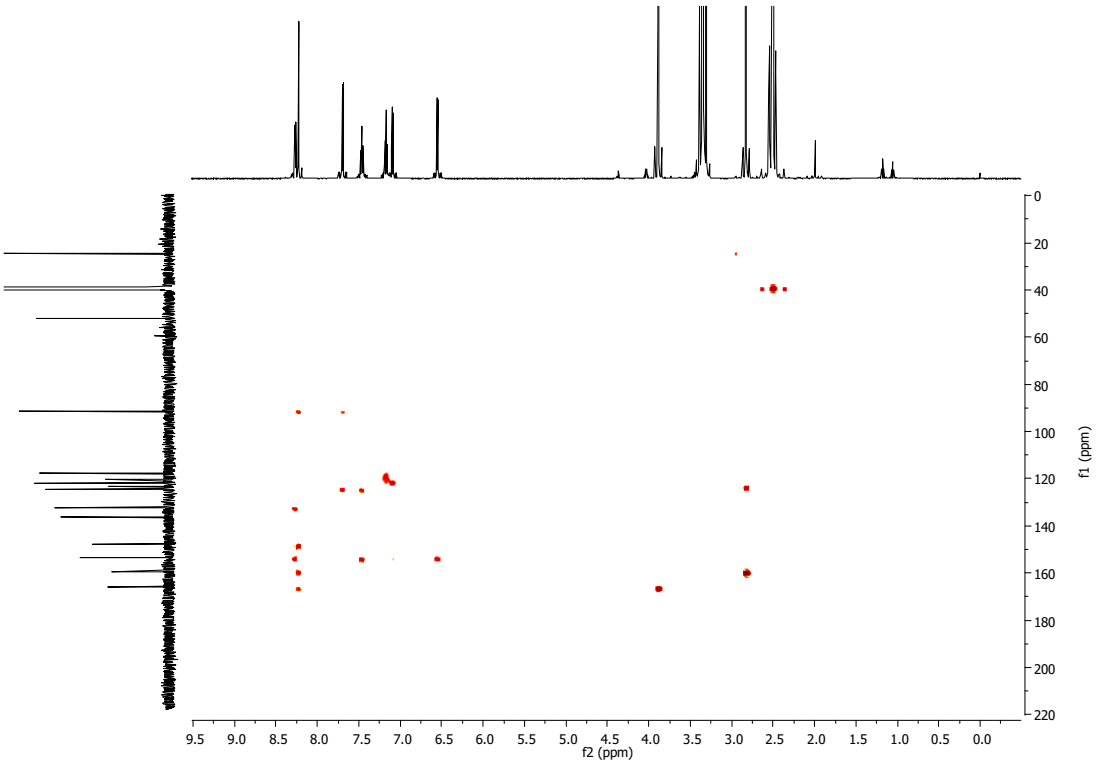


Figure S7. HMBC spectrum of compound **6**.

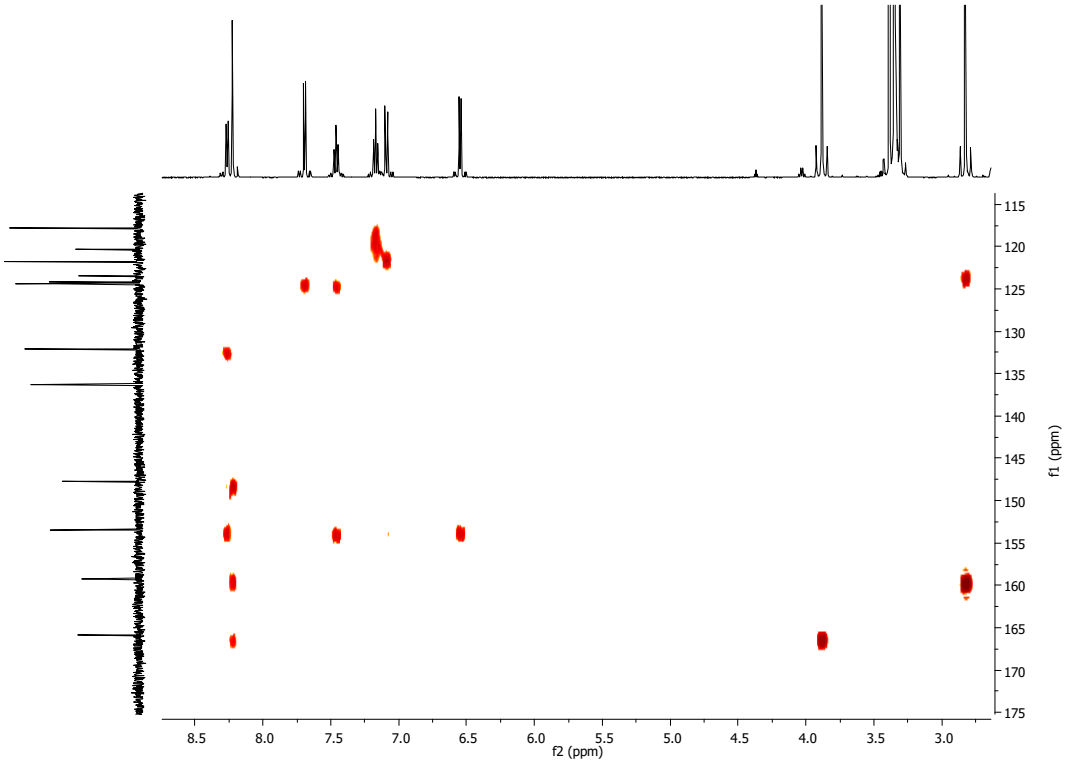
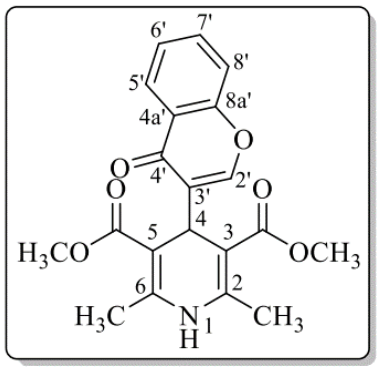
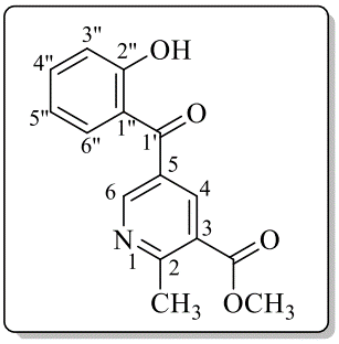


Figure S8. Expansion of HMBC spectrum of compound **6**.

3. NMR structural characterization data for compounds 4 and 5



Dimethyl 2,6-dimethyl-4-(4-oxo-4*H*-chromen-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**4**) (33.0 mg, 9%). ^{1}H-NMR (300.13 MHz, DMSO-d$_6$): δ 8.97 (s, 1H, N-*H*), 8.19 (d, J = 8.3 Hz, 1H, H-8'), 8.01 (dd, J = 7.4, 1.5 Hz, 1H, H-5'), 7.95 (s, 1H, H-2'), 7.75 (ddd, J = 8.3, 7.4, 1.5 Hz, 1H, H-7'); 7.44 (dt, J = 7.4, 1.0 Hz, 1H, H-6'), 4.85 (s, 1H, H-4), 3.57 (s, 6H, 3-CO_2CH_3 and 5-CO_2CH_3), 2.09 (s, 6H, 2-CH_3 and 6-CH_3) ppm; ^{13}C-NMR (75.47 MHz, DMSO-d$_6$): δ 175.3 (C-4'), 167.3 (3-CO_2CH_3 and 5-CO_2CH_3), 155.3 (C-8a'), 154.2 (C-2'), 146.7 (C-2,6), 133.6 (C-7'), 127.0 (C-6'), 126.0 (C-3'), 125.1 (C-5'), 124.0 (C-4a'), 118.1 (C-8'), 97.8 (C-3,5), 50.5 (3-CO_2CH_3 and 5-CO_2CH_3), 33.1 (C-4), 18.1 (2-CH_3 and 6-CH_3) ppm.



Methyl 5-(2-hydroxybenzoyl)-2-methylnicotinate (**5**) (75.7 mg, 28%). ^{1}H-NMR (300.13 MHz, DMSO-d$_6$): δ 10.4 (br s, 1H, 2”-O*H*), 8.85 (d, *J* = 8.8 Hz, 1H, H-6), 8.38 (d, *J* = 2.2 Hz, 1H, H-4), 7.48 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H, H-4’’), 7.44 (dd, *J* = 7.8, 1.5 Hz, 1H, H-6’’), 7.00-7.02 (m, 1H, H-3’’), 6.95-7.00 (m, 1H, H-5’’), 3.87 (s, 3H, 3-CO$_2$C*H*$_3$), 2.80 (s, 3H, 2-C*H*$_3$) ppm. ^{13}C-NMR (75.47 MHz, DMSO-d$_6$): δ 194.6 (C-1’), 165.8 (3-*C*O$_2$CH$_3$), 162.4 (C-2), 156.9 (C-2’’), 151.9 (C-6), 138.2 (C-4), 134.2 (C-4’’), 130.9 (C-5), 130.7 (C-6’’), 124.7 (C-3), 124.0 (C-1’’), 119.5 (C-5’’), 116.9 (C-3’’), 52.6 (3-CO$_2$*C*H$_3$), 24.6 (2-*C*H$_3$) ppm.