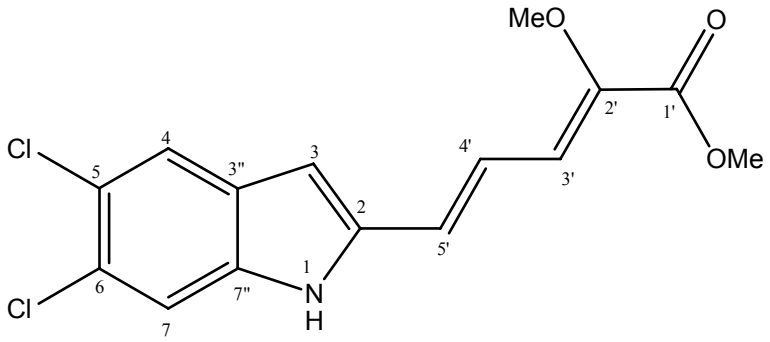
Methyl (2*Z*, 4*E*)-5-(5,6-dichloro-2-indolyl)-2-methoxy-2,4-pentadienoate



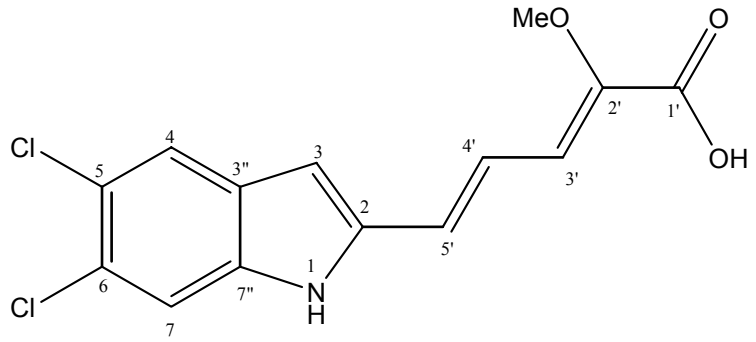
Methyl (2*Z*, 4*E*)-5-(5,6-dichloro-2-indolyl)-2-methoxy-2,4-pentadienoate, yellow crystalline solid, m.p. 200-202°C; *Rf* 0.25 (EtOAc: Petrol; 1:4); ν_{max}/cm^{-1} (nujol mull) 3334 (NH), 2925 (CH), 2855 9CH), 1697 (C=O), 1605 (C=C); δ_H (300 MHz, DMSO) 11.81 (1 H, s, NH), 7.73 (1 H, s, H_4), 7.51 (1 H, s, H_7), 7.19 (1 H, dd, *J* **11.0** and **16.0**, H_4'), 6.97 (1 H, d, *J* **16.0**, H_5'), 6.88 (1 H, d, *J* **11**.0, H_3'), 6.59 (1 H, s, H_3), 3.75 (3 H, s, $CO.OCH_3$), 3.72 (3 H, s, αOCH_3); δ_C (75 MHz, DMSO) 163.8 (C=O), 145.3 (C_2'), 138.9 (C_2), 136.9 (C_7"), 128.5 (δC), 127.6 (C_3'), 125.5 (C_5), 125.1 (C_6), 122.3 (C_3"), 121.9 (C_7), 121.6 (C_4'), 112.7 (C_4), 104.8 (C_3), 60.6 (OCH_3), 52.3 (OCH_3); *m/z* (EI) 325.0271 (895, M^+ $C_{15}H_{13}NO_3Cl_2$ requires 325.0272), 327 (36, M^+ $C_{15}H_{13}NO_3Cl^{35}Cl^{37}$), 325 (57, M^+ $C_{15}H_{13}NO_3Cl_2^{35}$), 295 (45, M^+-MeOH), 293 (72, M^+-MeOH), 268 (54, M^+-CO_2Me), 266 (81, M^+-CO_2Me), 250 (41, M^+-75), 233 (34, M^+-94), 231 (100, M^+-94), 224 (49, M^+-103), 223 (35, M^+-102), 222 (70, M^+-103), 216 (32, M^+-109), 188 (71, M^+-137).

Literarture characterisation from reference 3b

the crude compound was purified by flash chromatography (hexane/EtOAc, 7/3). After trituration with $^iPr_2O$, methyl (2*Z*,4*E*)-5-(5,6-dichloro-2-indolyl)-2-methoxy-2,4-pentadienoate (**2**) (14 g, 89.6%) was obtained as a yellow powder, mp 202−204 °C. IR (Nujol): 3400, 1700, 1610 cm^{-1}. ^1H NMR (DMSO-d_6): δ 11.82 (s, 1H); 7.77 (s, 1H); 7.52 (s, 1H); 7.21 (dd, 1H); 7.00 (d, 1H); 6.89 (d, 1H); 6.62 (s, 1H); 3.76 (s, 1H); 3.73 (s, 1H). MS (ESI NEG): 324 (M − H). Anal. ($C_{15}H_{13}NO_3Cl_2$) C, H, N, Cl.

nOe irradiation	NH	H4	H7	H4'	H5'	H3'	H3	CO.OMe	αOMe
NH	**-100**	0	5.2	6.4	0	0	0	0	0
H4	0	**-100**	0	0	0	0	2.4	0	0
H7	1.6	0	**-100**	0	0	0	0	0	0
H4'	3.5	0	0	**-100**	0	2.1	1.3	0	1.9
H5'	0	0	0	0	**-100**	5.3	4.7	0	0
H3'	0	0	0	2.1	1.1	**-100**	0	0	0
H3	0	2.7	0	0	2.6	0	**-100**	0	0
CO.OMe	0	0	0	0	0	0.6	0	**-100**	0
αOMe	0	0	0	2.1	0	0	0	0	**-100**

(2*Z*, 4*E*)-5-(5,6-Dichloro-2-indolyl)-2-methoxy-2,4-pentadienoic acid



(13)

A suspension of methyl (2*Z*, 4*E*)-5-(5,6-dichloro-2-indolyl)-2-methoxy-2,4-pentadienoate (1 g, 3.1 mmol) and 20% NaOH (1.4 ml, 6.7 mmol) in MeOH (3 ml) and THF (5.5 ml) was heated at 55°C for 2h. After cooling to room temperature the organic solvent was evaporated and the residue wa acidified with 20% HCl, and ethe precipitate was collected by filtration, washed with water and dried at 60°C under vacuum to obtain **(**2*Z*, 4*E*)-5-(5,6-dichloro-2-indolyl)-2-methoxy-2,4-pentadienoic acid (0.7 g, 73%) as a green powder, m.p. 234-236°C; *Rf* 0.45 (MeOH: EtOAc, 1:4); ν_{max}/cm^{-1} 3382 (CH), 3055 (CH), 2987 (OH), 1676 (C=O), 1609 (C=O), δ_H (300 MHz, MeOH) 11.78 (1 h, bs, NH), 7.74 (1 H, s, ArH), 7.51 (1 H, s, ArH), 7.19 (1 H, dd, ***J* 11.2 and 15.7 H**z H_4'), 6.94 (1 H, d, *J* **15.7** Hz, H_5'), 6.84 (1 H, d, *J* **11.2 Hz**, H_3'), 3.73 (3 H, s, OCH_3); δ_C (75 MHz, MeOH) 164.8 (C=O), 146.3, 139.1, 136.9,

128.6, 126.8, 124.9, 124.7, 122.3, 121.6, 112.7, 104.4 (11 C), 60.4 (OCH_3); *m/z* (EI) 312.1 (40%, M^+), 311.1 (59, M^+), 281.1 (44, M^+-MeOH), 279.1 (64, M^+-MeOH), 266.1 (40, M^+-CO_2H), 231.1 (50, M^+-80), 224.1 (34, M^+-88), 223.1 (35, M^+-88), 222.1 (40, M^+-190), 200.1 (54, M^+-112), 198.1 (79, M^+-113), 183.0 (60, M^+-128).