Supplementary Material for Publication of manuscript "Toxicity of a novel antifungal compound is modulated by ERAD components", by Raj et al.

Fig. S1: Synthetic pathways for sr7575 and related compounds.

Fig. S2: Growth of *A. fumigatus*, *A. flavus*, *S. cerevisiae*, *C. albicans* and *C. neoformans* cells in liquid medium in the presence of various concentrations of sr7575.

Fig. S3: sr7575 profile shows little correlation with a previously published large-scale chemogenomics dataset.

Fig. S4: Perturbation of PGA3 function shows similarities with the sensitivity profile for sr7575.

Fig. S5: Susceptibility testing of yeast strains against sr7575.

Fig. S6: Susceptibility of multidrug resistant *S. cerevisiae* strains and azole resistant *C. albicans* strains to sr7575.

Table S1: List of 76 compounds from the CERMN chemical library showing 90% or more growth inhibition of *A.fumigatus* at 25 µg/mL.

Table S2: Analogues of sr7575 and MIC_{100} values against *A. fumigatus*.

Table S3: Analogues of sr7576 and MIC_{100} values against *A. fumigatus*.

Table S4: List of strains and plasmids used in this study.

Table S5: List of oligonucleotides used in this study.

Table S6 (provided as a separate xls file): Sensitivity of *S. cerevisiae* deletion and DAmP strains to 0.125 µg/mL sr7575.

Text S1: Synthesis of sr7575 and related compounds.

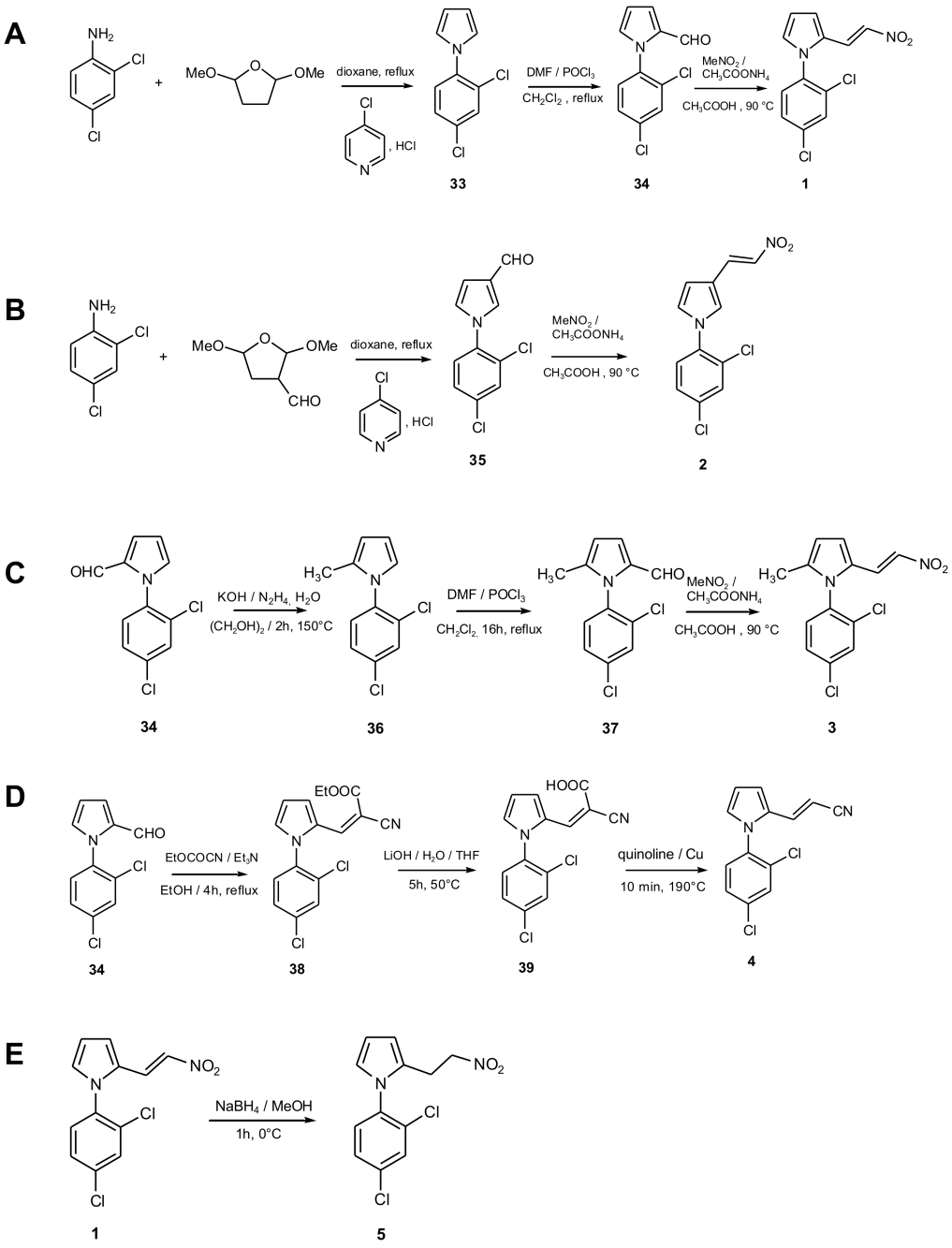


Figure S1. Synthetic pathways for sr7575 and related compounds. Pathways detailing the synthesis of sr7575 and analogues 2-5.

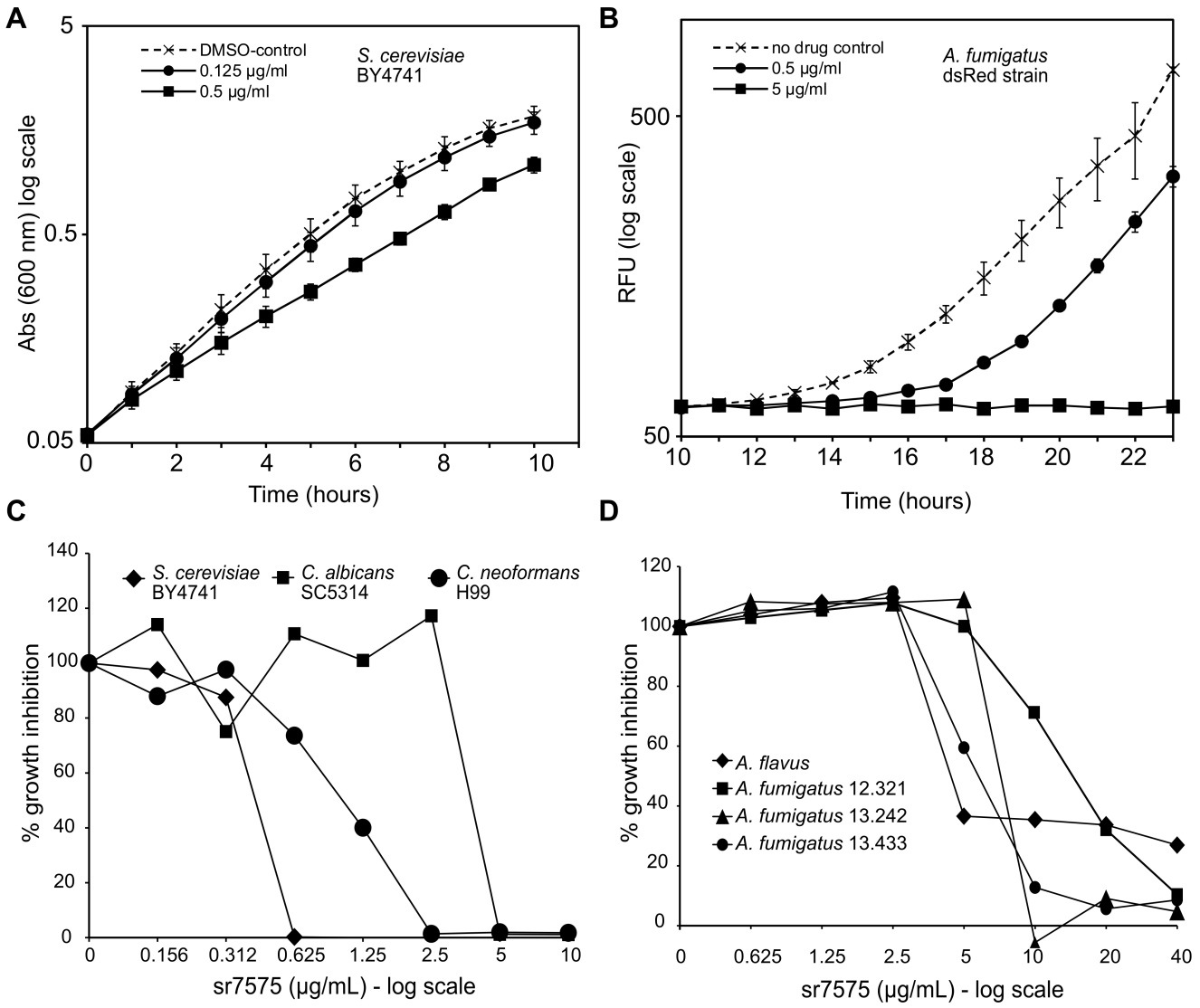


Figure S2. Growth of *A. fumigatus*, *A. flavus*, *S. cerevisiae*, *C. albicans* and *C. neoformans* cells in liquid medium in the presence of various concentrations of sr7575. (A) Log-phase cultures of *S. cerevisiae* WT strain BY4741 were grown in the presence of increasing concentrations of sr7575 with DMSO as vehicle control. The Abs600 was determined every hour for 10 h. (**B**) *A. fumigatus* strain Af293-dsRed was grown for 23 h in RPMI-1640 medium in the presence of increasing concentrations of sr7575. Fluorescence (ex 254 nm/ em 291 nm) was measured and relative fluorescence units (RFU) plotted against time. (**C**) Growth inhibition estimates were obtained at various concentrations of sr7575 by measuring absorbance at 600 nm for *S. cerevisiae* (BY4741, YPD, 30°C, 48 h), *C. albicans* (SC5314, RPMI, 37°C, 48 h) and *C. neoformans* (H99, RPMI, 37°C, 72 h). (**D**) Growth inhibition estimates for *A. flavus* and three *A. fumigatus* clinical isolates (12.321, 13.242, 13.433) were obtained by the resazurin reduction assay in RPMI medium, 37°C, 39 h at concentrations of sr7575 up to 40 µg/ml.

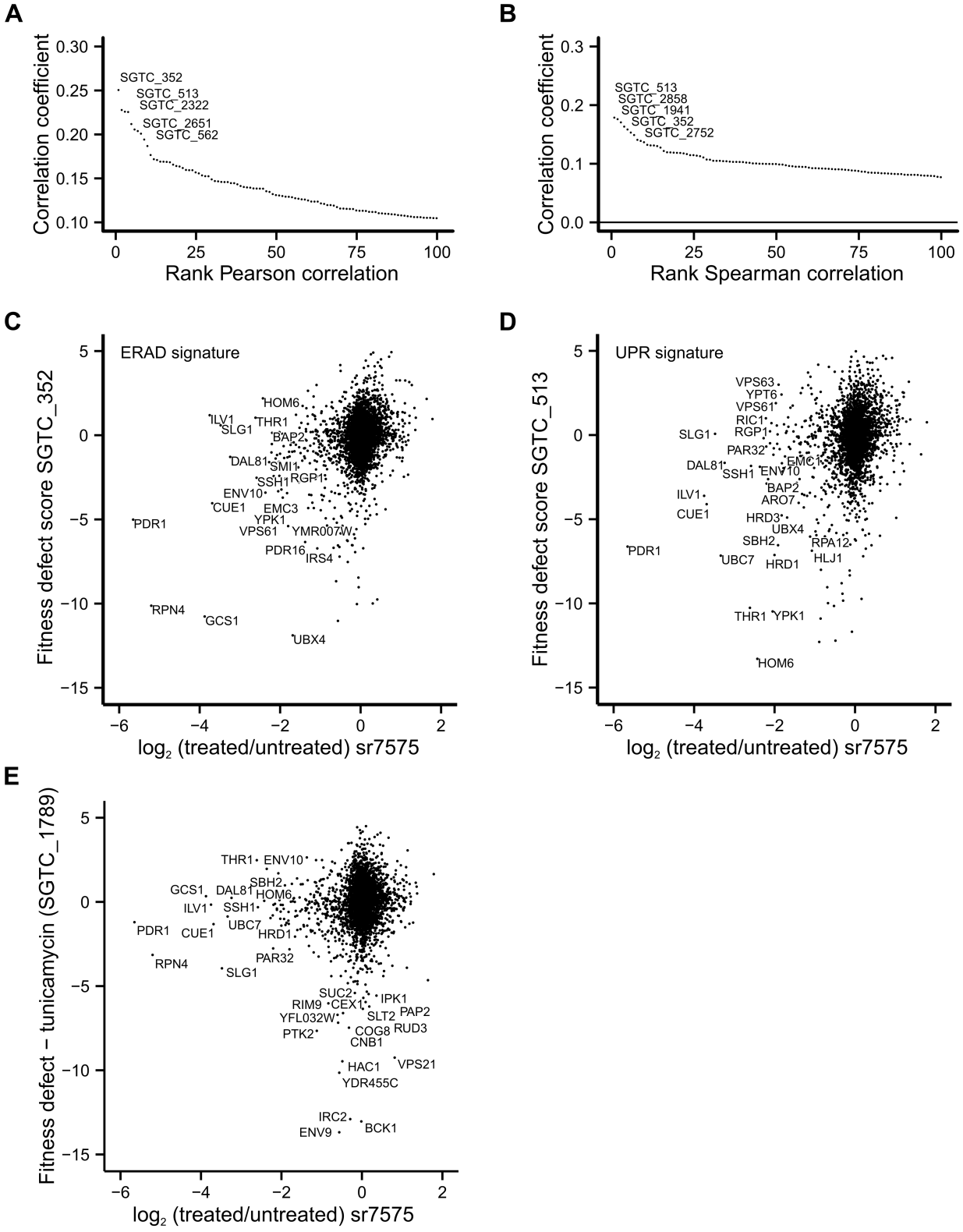


Figure S3. sr7575 profile shows little correlation with a previously published large-scale chemogenomics dataset. Computed Pearson **(A)** and Spearman **(B)** correlation coefficients between sr7575 values and previously published growth scores obtained with 3,356 compounds were ranked in descending order and the top 100 values are indicated. Among the highest correlations, we identified SGTC 352, a drug showing an ERAD signature **(C)** and SGTC 513, a compound with a UPR signature

(D) as being closest to the sr7575 profile. (E) The sr7575 profile showed no correlation with the one published for tunicamycin.

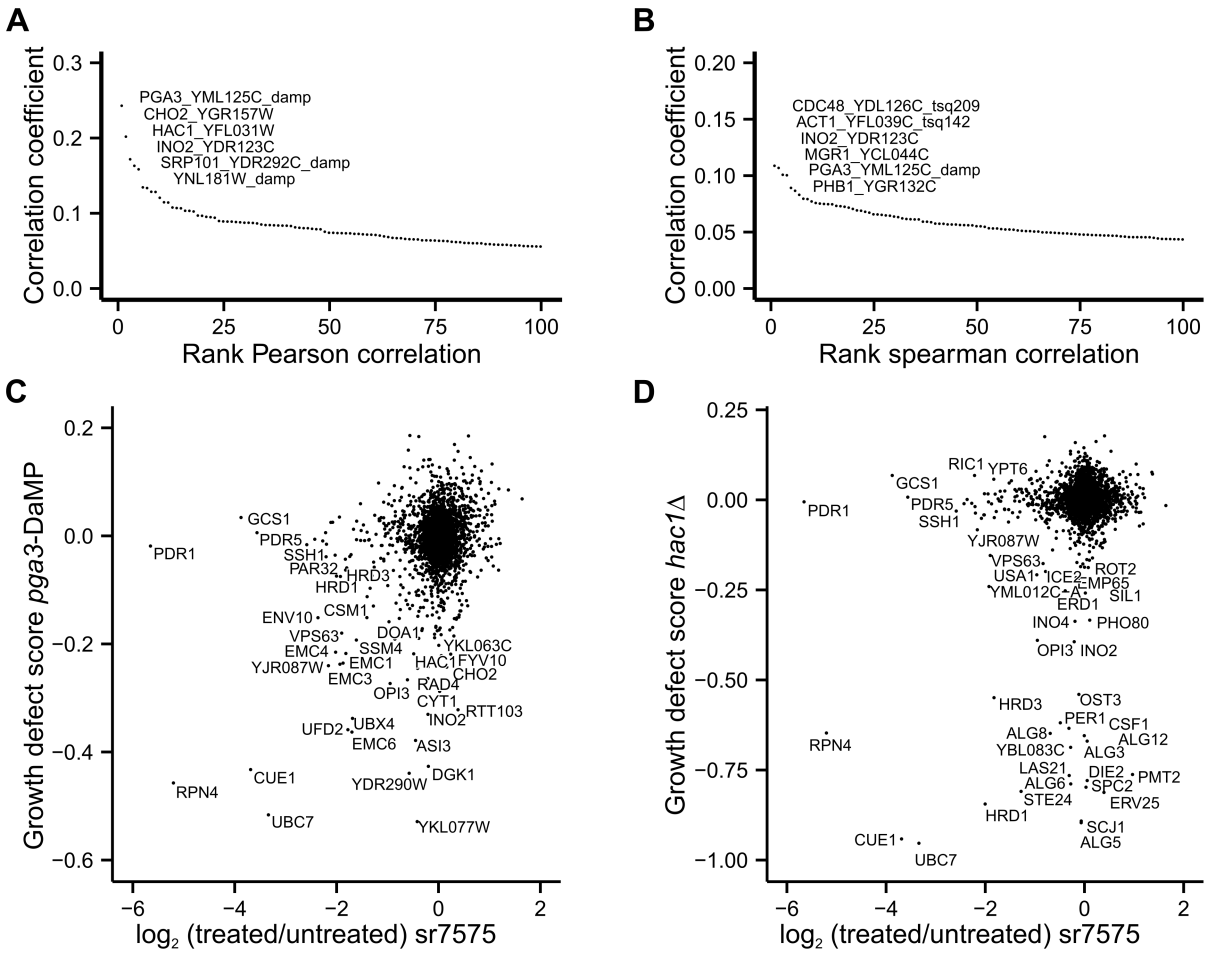


Figure S4. Perturbation of *PGA3* function shows similarities with the sensitivity profile for sr7575. Pearson **(A)** and Spearman **(B)** correlations between the sr7575 profile and 1711 previously published SGA profiles . Fitness defect scores for DAmP modification of *PGA3* are shown in **(C)**, while the interactions of *hac1*Δ and ERAD depleted strains are depicted in **(D)**.

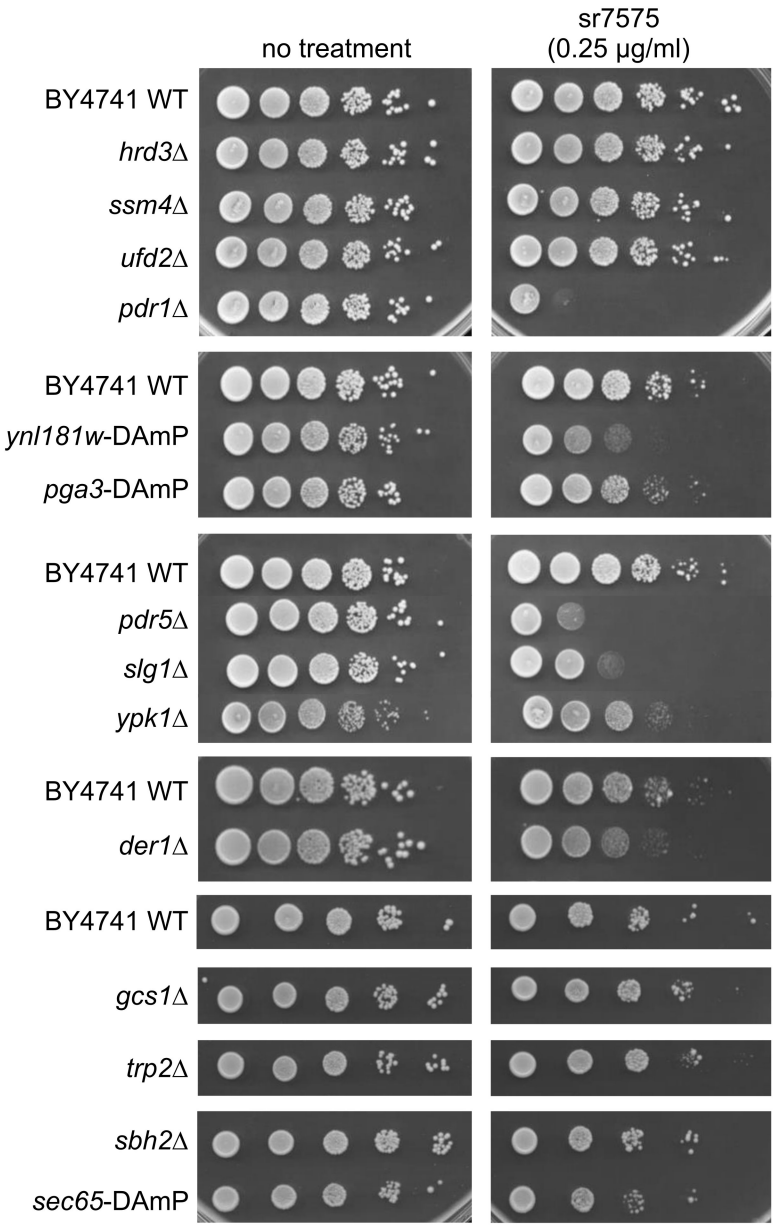


Figure S5. Susceptibility testing of yeast strains against sr7575. Mutants from the haploid deletion background were serially spotted onto SC plates supplemented with sr7575. Plates were incubated at 30°C for 48 h.

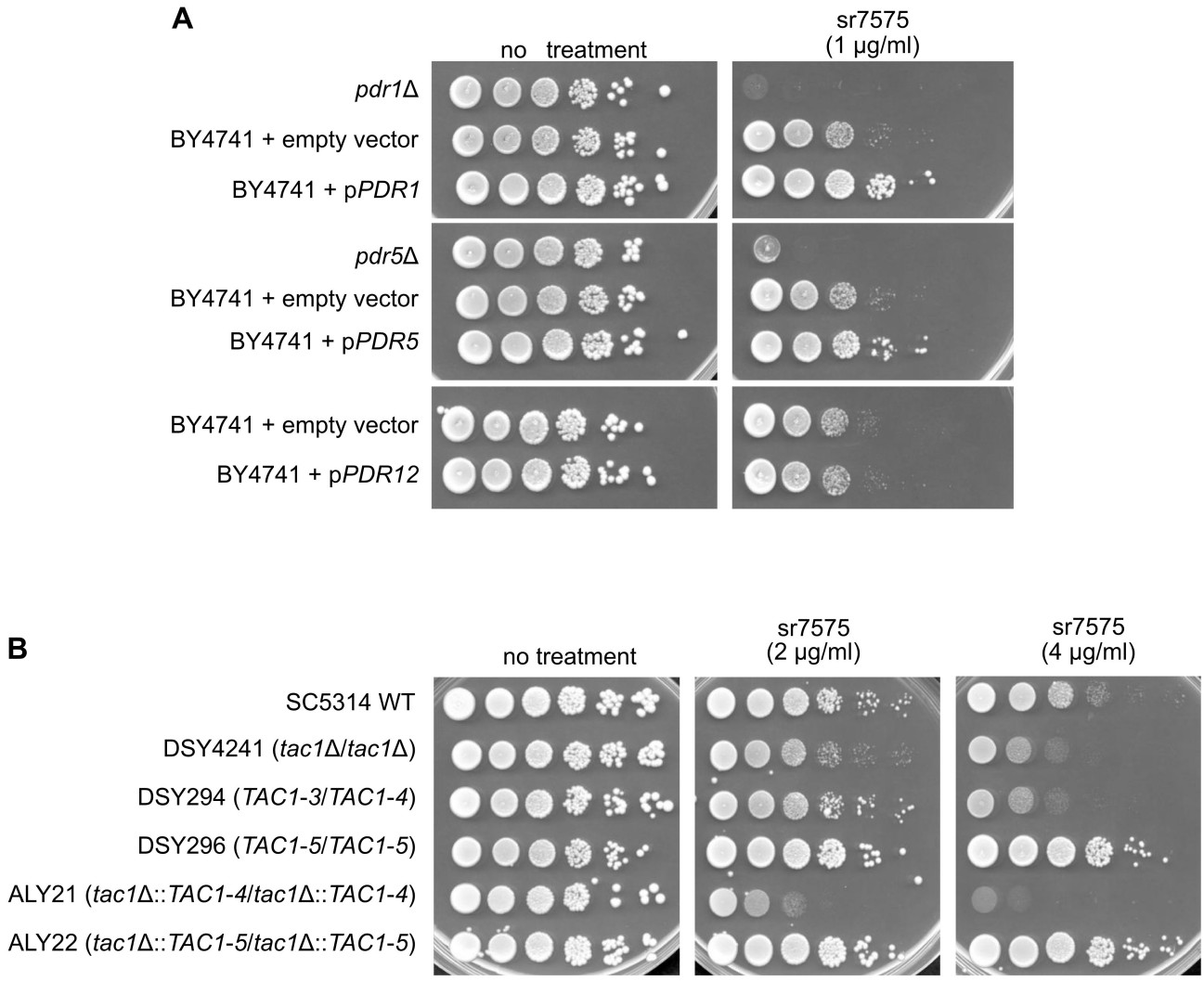
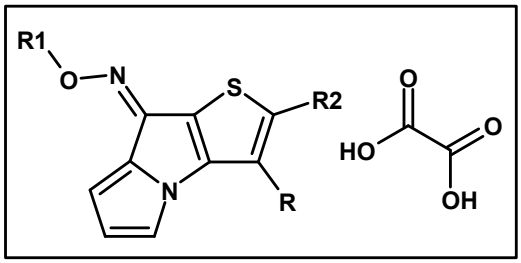
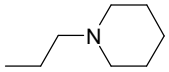
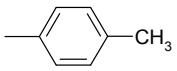
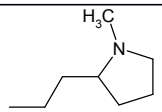
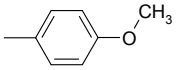
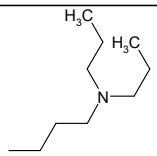
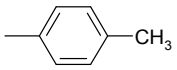
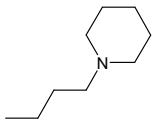
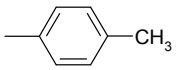
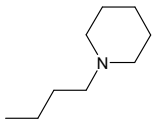
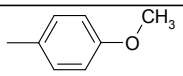
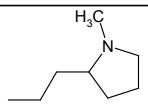
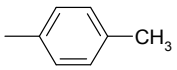


Figure S6. Susceptibility of multidrug resistant *S. cerevisiae* strains and azole resistant *C. albicans* strains to sr7575. (**A**) *S. cerevisiae* strains with deletions of or overexpressing *PDR1*, *PDR5* and *PDR12* were tested for susceptibility to sr7575 (1 µg/mL, SC medium, 30°C, 48 h). (**B**) Comparison of growth inhibition of *C. albicans* strains: WT (SC5314), *TAC1* transcription factor homozygous deletion strain (DSY4241), azole susceptible clinical isolate DSY294, azole resistant clinical isolate DSY296, azole susceptible laboratory generated strain ALY21 and azole resistant laboratory generated strain ALY22 (SC medium in the presence of 2 and 4 µg/mL sr7575, 37°C, 48 h).

Supplementary Table S1 - list of 76 compounds from the CERMN chemical library showing 90% or more growth inhibition of *Aspergillus fumigatus* at 25 µg/mL.

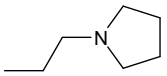
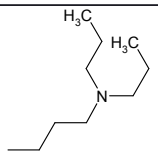
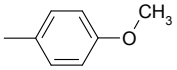
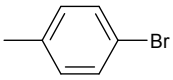
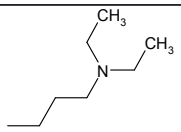
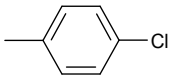
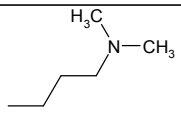
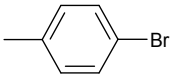
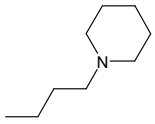
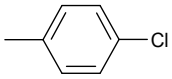
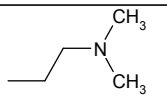
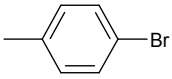
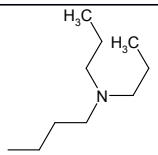
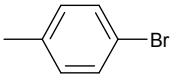
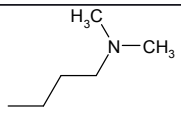
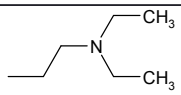
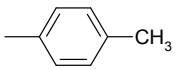
→ Family A:



Compound	R	R1	R2	% viability
sr1304[1]	-H			2
sr1308[2]	-H			0
sr3163[2]	-H			0
sr3164[2]	-H			0
sr3168[3]	-H			0
sr3169[2]	-H			0

1 S. Rault, S. Lemaître, F. Dauphin, A. Kervabon, M. Boulouard, J.-C. Lancelot, PCT Int. Appl., WO2001014381, (2001).

2 Dual Histamine H3R/Serotonin 5-HT4R Ligands with Antiamnesic Properties: Pharmacophore-Based Virtual Screening and Polypharmacology, Lepailleur, Alban; Freret, Thomas; Lemaitre, Stephane; Boulouard, Michel; Dauphin, Francois; Hinschberger, Antoine; Dulin, Fabienne; Lesnard, Aurelien; Bureau, Ronan; Rault, Sylvain; Journal of Chemical Information and Modeling (2014), 54(6), 1773-1784.

sr3172[1]	-H		$-OCH_3$	0
sr3174[3]	-H			0
sr3179[2]			-H	0
sr3180[2]			-H	0
sr3181[3]			-H	0
sr3182[2]			-H	0
sr3185[3]			-H	0
sr3186[1]			-H	0
sr3188[2]	-H			0

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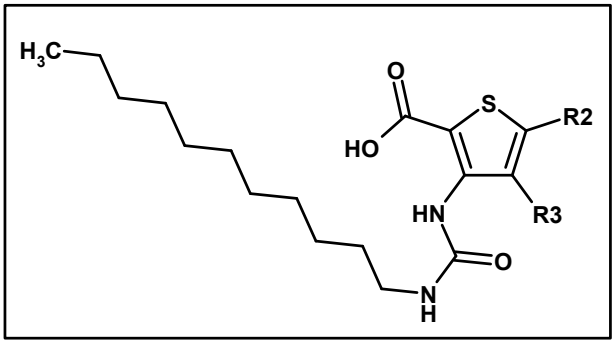
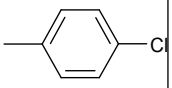
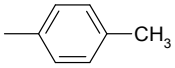
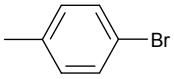
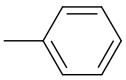
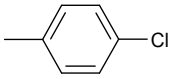


Compound	R2	R3	% viability
sr4045[1]	-H		2
sr4046[1]		-H	0
sr4049[1]		-H	0
sr4050[3]	-H		0
sr4051[1]		-H	0
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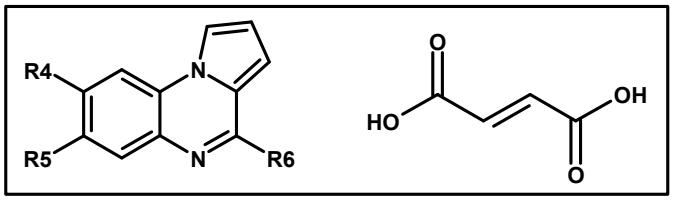
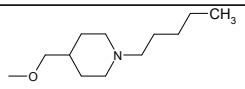
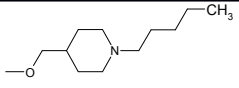
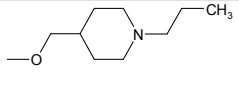
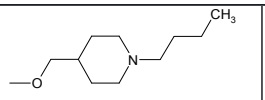
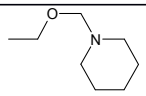
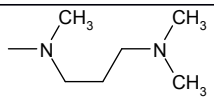
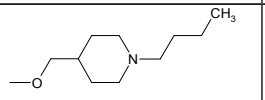
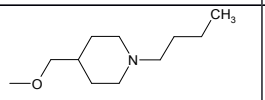
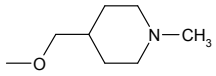
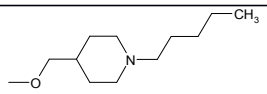
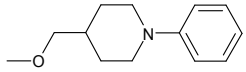
→ **Family C:**_____

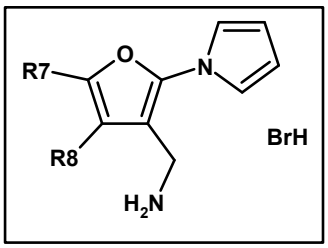


Compound	R4	R5	R6	% viability
mr22450[2]	-H	$-CH_3$		0
mr22442[2]	-H	-Cl		0
mr22455[2]	-H	-Cl		0

3 Solution-phase parallel synthesis of a 1140-member ureidothiophene carboxylic acid library, Le Foulon, Francois-Xavier; Braud, Emmanuelle; Fabis, Frederic; Lancelot, Jean-Charles; Rault, Sylvain, Journal of Combinatorial Chemistry (2005), 7(2), 253-257.

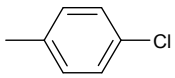
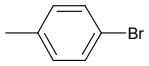
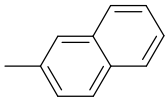
mr22461[2]	-H	-Cl		0
mr22478[2]	-H	-Cl		4
mr18993[4]	-Cl	-Cl		4
mr23269[3]	-H	-H		1
mr23270[1]	-H	-F		0
mr24316[1]	-H	-Cl		0
mr24344[3]	-H	-H		3
sr1832[5]	-H	-H		0
sr2823[1]	-H	-CH3		0

→ **Family D:**

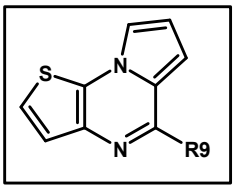


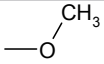
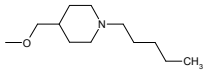
4 Synthesis of new pyrrolo[1,2-a]quinoxalines: potential non-peptide glucagon receptor antagonists, Guillon, Jean; Dallemagne, Patrick; Pfeiffer, Bruno; Renard, Pierre; Manechez, Dominique; Kervran, Alain; Rault, Sylvain, European Journal of Medicinal Chemistry (1998), 33(4), 293-308

5 Novel and Selective Partial Agonists of 5-HT3 Receptors. 2. Synthesis and Biological Evaluation of Piperazinopyridopyrrolopyrazines, Piperazinopyrroloquinoxalines, and PiperazinopyridopyrroloquinoxalinesPrunier, Herve; Rault, Sylvain; Lancelot, Jean-Charles; Robba, Max; Renard, Pierre; Delagrange, Philippe; Pfeiffer, Bruno; Caignard, Daniel-Henri; Misslin, Rene; Guardiola-Lemaitre, Beatrice; et al, Journal of Medicinal Chemistry (1997), 40(12), 1808-1819.

Compound	R7	R8	% viability
sr1457[1]		-H	0
sr1460[1]		-H	0
sr1462[1]		-H	2

→ **Family E:**

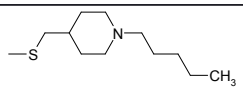
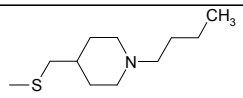


Compound	R9	% viability
sr2845[6]		0
sr3584[7]		0
mr22410[8]		6

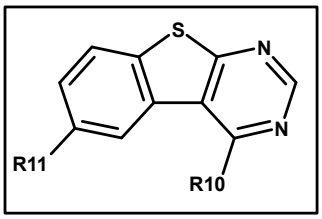
6 Novel Selective and Partial Agonists of 5-HT3 Receptors. Part 1. Synthesis and Biological Evaluation of Piperazinopyrrolothienopyrazines, Rault, Sylvain; Lancelot, Jean-Charles; Prunier, Herve; Robba, Max; Renard, Pierre; Delagrange, Philippe; Pfeiffer, Bruno; Caignard, Daniel-Henri; Guardiola-Lemaitre, Beatrice; Hamon, Michel, Journal of Medicinal Chemistry (1996), 39(10), 2068-80.

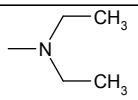
7 Pyrrolo[1,2-a]thieno[3,2-e]pyrazines, Rault, Sylvain; Cugnon de Sevricourt, Michel; Nguyen-Huy Dung; Robba, Max, Journal of Heterocyclic Chemistry (1981), 18(4), 739-42.

8 Novel antagonists of serotonin-4 receptors: Synthesis and biological evaluation of pyrrolothienopyrazines, Lemaitre, Stephane; Lepailleur, Alban; Bureau, Ronan; Butt-Gueulle, Sabrina; Lelong-Boulouard, Veronique; Duchatelle, Pascal; Boulouard, Michel; Dumuis, Aline; Daveu, Cyril; Lezoualc'h, Frank; et al, Bioorganic & Medicinal Chemistry (2009), 17(6), 2607-2622.

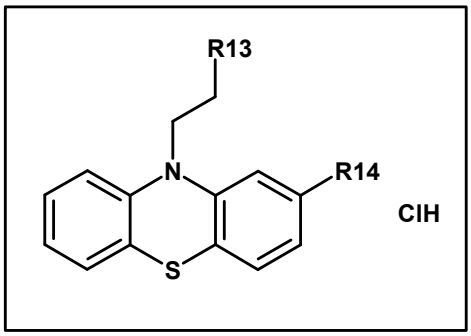
mr22422[1]		0
mr24356[1]		3

→ **Family F:**



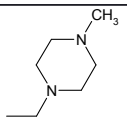
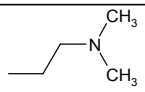
Compound	R10	R11	% viability
sr2205[9]		-H	3
sr2210[1]		-H	3
sr2634[1]	-Cl	$-NO_2$	0

→ **Family G:**

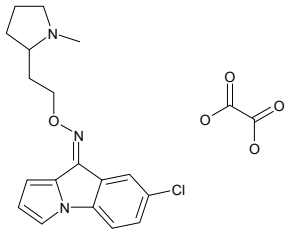
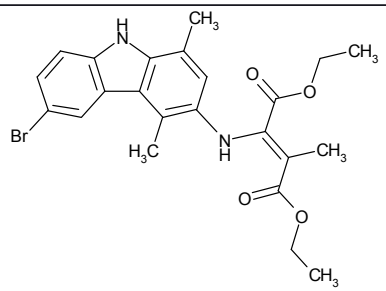
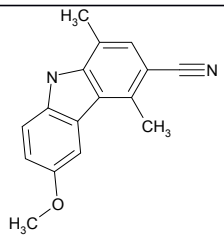


Compound	R13	R14	% viability

9 Scott, William J.; Bierer, Donald E.; Stolle, Andreas, PCT Int. pl. (2003), WO 2003057149

pa2[10]		$-CF_3$	0
pa18[11]		-Cl	0

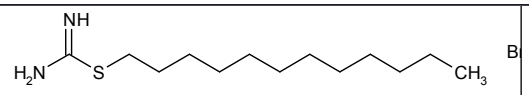
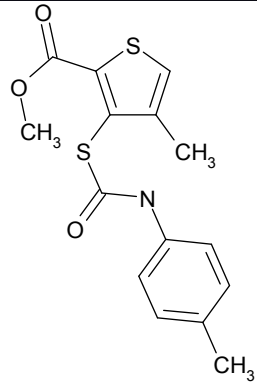
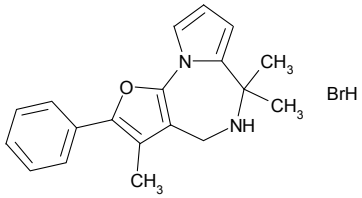
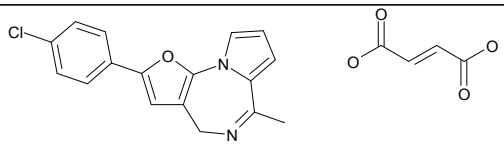
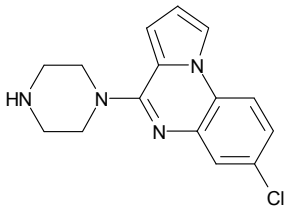
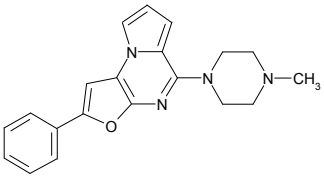
→ **Singletons:**

Compound	Structure	% viability
mr19807[1]		0
mr15010a[1]		4
mr15059[12]		4

10 Trifluoperazine (DCI) dihydrochloride; New (trifluoromethyl)phenothiazine derivatives, Craig, P. N.; Nodiff, E. A.; Lafferty, J. J.; Ullyot, G. E., Journal of Organic Chemistry (1957), 22, 709-11.

11 Chlorpromazine (DCI) hydrochloride; Substituted 10-(dimethylaminopropyl)phenothiazines, Charpentier, Paul; Gailliot, Paul; Jacob, Robert; Gaudechon, Jacques; Buisson, Paul, Compt. rend. (1952), 235, 59-60.

12 Anti-tumor heterocycles. Part 13. The syntheses of two new pyridocarbazoles (ellipticines) and some pyrrolocarbazole analogs, Chunchatprasert, Laddawan; Dharmasena, Priyanthi; Oliveira-Campos, Ana M. F.; Queiroz, Maria J. R. P.; Raposo, Maria M. M.; Shannon, Patrick V. R. Journal of Chemical Research, Synopses (1996), (2), 84-5.

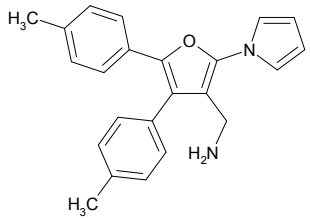
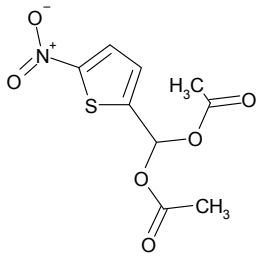
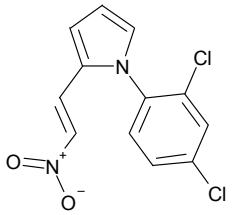
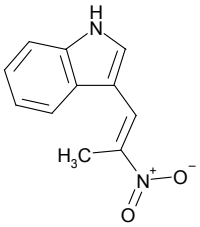
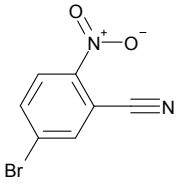
mr22633[13]		0
mr16310[14]		2
mr21034[15]		10
mr21018[1]		8
mr18499[16]		0
sr1429[1]		0

13 Comparative effect of a family of substituted thiopseudoureas on protein synthesis by rat liver and Walker carcinoma ribosomes, Carmona, Andres; Gonzalez-Cadavid, Nestor F., Chemico-Biological Interactions (1978), 22(2-3), 309-27.

14 Preparation of 3-mercapto-2-thiophenecarboxylic acid derivatives as intermediates for herbicides, Rault, Sylvain; Lancelot, Jean Charles; Letois, Bertrand; Robba, Max; Labat, Yves Fr. Demande (1993), FR 2689129 A1 19931001.

15 First synthesis of 5,6-dihydro-4H-furo[3,2-f]pyrrolo[1,2-a][1,4]diazepines, Feng, Xiao; Lancelot, Jean-Charles; Gillard, Alain-Claude; Landelle, Henriette; Rault, Sylvain, Journal of Heterocyclic Chemistry (1998), 35(6), 1313-1316.

16 Preparation of pyrrolopyrazines as 5-HT3 ligands, Lancelot, Jean-Charles; Prunier, Herve; Robba, Max; Delagrange, Philippe; Renard, Pierre; Adam, Gerard, Eur. Pat. Appl. (1994), EP 623620 A1 19941109.

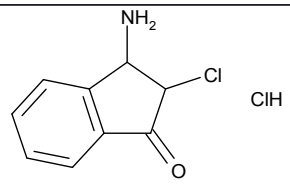
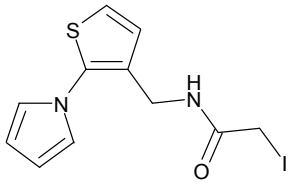
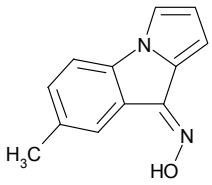
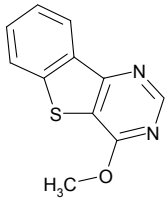
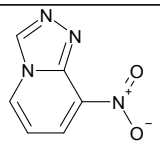
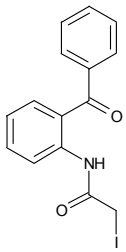
sr1461[17]		1
sr1475[18]		0
sr1810[1]		9
sr1821[19]		0
sr1922[20]		0

17 First synthesis of 4H-furo[3,2-f]pyrrolo[1,2-a][1,4]diazepines, Feng, Xiao; Lancelot, Jean-Charles; Prunier, Herve; Rault, Sylvain, Journal of Heterocyclic Chemistry (1996), 33(6), 2007-2011.

18 Synthesis and in vitro antibacterial evaluation of N-[5-(5-nitro-2-thienyl)-1,3,4-thiadiazol-2-yl] piperazinylquinolones, Foroumadi, Alireza; Mansouri, Shahla; Kiani, Zahra; Rahmani, Afsaneh, European Journal of Medicinal Chemistry (2003), 38(9), 851-854.

19 Alpha-ethyltryptamines as dual dopamine-serotonin releasers, Blough, Bruce E.; Landavazo, Antonio; Partilla, John S.; Decker, Ann M.; Page, Kevin M.; Baumann, Michael H.; Rothman, Richard B., Bioorganic & Medicinal Chemistry Letters (2014), 24(19), 4754-4758.

20 Synthesis of nitrile and benzoyl substituted poly(biphenylene oxide)s via nitro displacement reaction In, Insik; Kim, Sang Youl, Polymer (2006), 47(13), 4549-4556

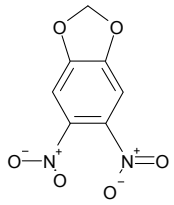
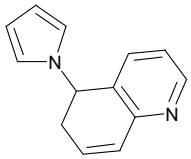
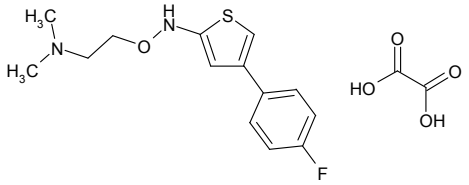
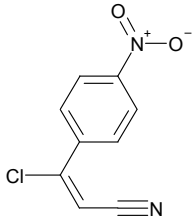
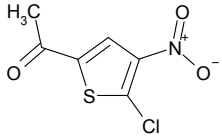
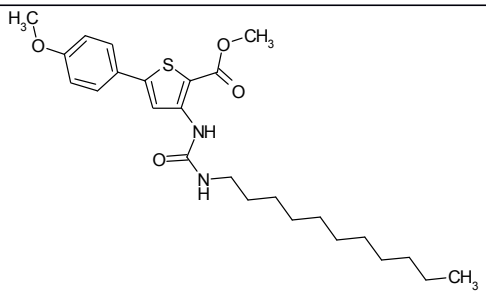
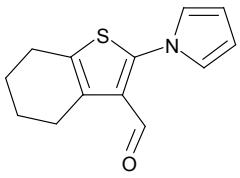
sr2223		8
sr2323[1]		0
sr2565[21]		5
sr2627[22]		1
sr2970[23]		6
sr2809[24]		0

21 First tricyclic oximino derivatives as 5-HT3 ligands, Baglin, I.; Daveu, C.; Lancelot, J. C.; Bureau, R.; Dauphin, F.; Pfeiffer, B.; Renard, P.; Delagrange, P.; Rault, S., Bioorganic & Medicinal Chemistry Letters (2001), 11(4), 453-457.

22 [1]Benzothienopyrimidines. I. Study of 3H-benzothieno[3,2-d]pyrimid-4-one, Robba, Max; Touzot, Paulette; El-Kashef, Hussein, Journal of Heterocyclic Chemistry (1980), 17(5), 923-8.

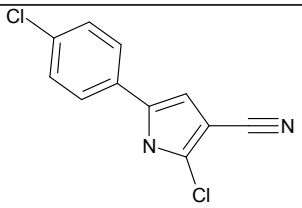
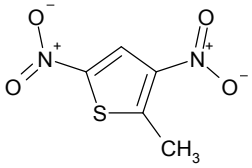
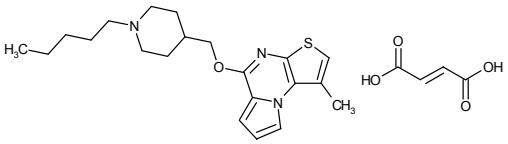
23 Synthesis and physicochemical study of 1,2,4-triazolo[4,3-a]pyridines and of 1,2,4-triazolo[2,3-a]pyridines, Bouteau, Brigitte; Lancelot, Jean Charles; Robba, Max,Journal of Heterocyclic Chemistry (1990), 27(6), 1649-51.

24 Method of producing 2-iodoacetylaminobenzophenones, Mazurov, A. A.; Andronati, S. A.; Yakubovskaya, L. N. U.S.S.R. (1991), SU 1622365 A1 19910123.

sr2967[25]		3
mr12044[1]		3
sr3184[1]		0
sr3456[2]		0
sr3355[26]		0
sr5443[1]		6
sr4274[1]		2

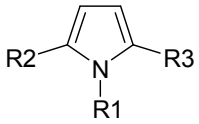
25 Synthesis, in vitro cytotoxic and in vivo antitumor activities of new pyrrolo[2,1-c][1,4]benzodiazepines. Part IFoloppe, M. P.; Caballero, E.; Rault, S.; Robba, M., European Journal of Medicinal Chemistry (1992), 27(3), 291-5.

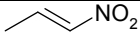
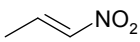
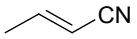
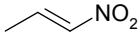
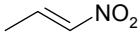
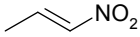
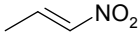
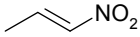
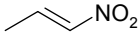
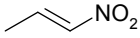
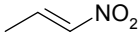
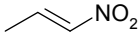
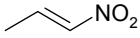
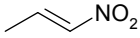
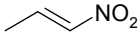
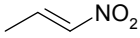
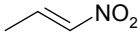
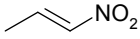
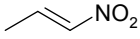
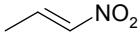
26 Selective Dual Inhibitors of the Cancer-Related Deubiquitylating Proteases USP7 and USP47, Weinstock, Joseph; Wu, Jian; Cao, Ping; Kingsbury, William D.; McDermott, Jeffrey L.; Kodrasov, Matthew P.; McKelvey, Devin M.; Suresh Kumar, K. G.; Goldenberg, Seth J.; Mattern, Michael R.; et al, ACS Medicinal Chemistry Letters (2012), 3(10), 789-792.

sr4080[27]		8
sr4211[28]		8
mr24355[10]		0

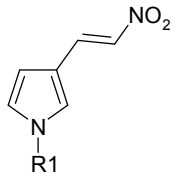
27 Insecticidal action and mitochondrial uncoupling activity of AC-303,630 and related halogenated pyrroles, Black, Bruce C.; Hollingworth, Robert M.; Ahammadsahib, Kabeer I.; Kukel, Christine D.; Donovan, Stephen Pesticide Biochemistry and Physiology (1994), 50(2), 115-28.

28 Synthesis of dinitro-substituted furans, thiophenes, and azoles, Katritzky, Alan R.; Vakulenko, Anatoliy V.; Sivapackiam, Jothilingam; Draghici, Bogdan; Damavarapu, Reddy Synthesis (2008), (5), 699-706.



Compound	R1	R2	R3	MIC_{100} (µg/ml)
sr7575 (1)	2,4-dichlorophenyl	H		2.4-4.8
3	2,4-dichlorophenyl	CH_3		> 26-32
4	2,4-dichlorophenyl	H		> 26-32
5	2,4-dichlorophenyl	H		> 26-32
6	4-chlorophenyl	H		2.4-4.8
7	3-chlorophenyl	H		9.6
8	2-chlorophenyl	H		13 - 26
9	3,4-dichlorophenyl	H		9.6
10	2,3-dichlorophenyl	H		19.2
11	2,5-dichlorophenyl	H		> 38.5
12	3,5-dichlorophenyl	H		9.6
13	2,6-dichlorophenyl	H		19.2
14	2,4,5-trichlorophenyl	H		9.6
15	2,4,6-trichlorophenyl	H		26 - 32
16	2-fluoro-4-chlorophenyl	H		13 - 26
17	2-chloro-4-fluorophenyl	H		13
18	2,4-dibromophenyl	H		13 - 26
19	2-bromo-4-chlorophenyl	H		13 - 26
20	2-chloro-4-bromophenyl	H		13
21	2-iodo-4-chlorophenyl	H		26
22	2-chloro-4-iodophenyl	H		26

Supplementary Table S2: Analogues of sr7575 and MIC values against *A. fumigatus*.



Compound	R1	MIC_{100} (µg/ml)
sr7576 (2)	2,4-dichlorophenyl	> 38.5
23	3-chlorophenyl	26 - 32
24	3,4-dichlorophenyl	26 - 32
25	3,5-dichlorophenyl	26 - 32
26	2,6-dichlorophenyl	38.5
27	2,4,6-trichlorophenyl	38.5
28	2-bromo-4-chlorophenyl	> 26 - 32
29	2-chloro-4-bromophenyl	> 26 - 32
30	2,4-dibromorophenyl	> 26 - 32
31	2-iodo-4-chlorophenyl	> 26 - 32
32	2-chloro-4-iodophenyl	>26 - 32

Supplementary Table S3: Analogues of sr7576 and MIC values against *A. fumigatus*.

Supplementary Table S4 - Strains and plasmids used in this study

Strain	Genotype	Reference
BY4741	MATa;*his3*Δ 1;*leu2*Δ 0;*met15*Δ 0;*ura3*Δ 0	Brachmann et al, 1998

(Deletion mutants were generated in the Sc BY4741 background)		Reference
*aro7*Δ	*aro7*::KanMX4	Giaever et al, 2002
*cue1*Δ	*cue1*::KanMX4	
*der1*Δ	*der1*::KanMX4	
*doa10*Δ	*doa10*::KanMX4	
*emc1*Δ	*emc1*::KanMX4	
*emc3*Δ	*emc3*::KanMX4	
*gcs1*Δ	*gcs1*::KanMX4	
*hac1*Δ	*hac1*::KanMX4	
*hrd1*Δ	*hrd1*::KanMX4	
*hrd3*Δ	*hrd3*::KanMX4	
*ire1*Δ	*ire1*::KanMX4	
*pdr1*Δ	*pdr1*::KanMX4	
*pdr5*Δ	*pdr5*::KanMX4	
pga3-DAmP	*pga3*-DAmP (KanMX4)	
*rpn4*Δ	*rpn4*::KanMX4	
*sbh2*Δ	*sbh2*::KanMX4	
sec65-DAMP	*sec65*-DAmP (KanMX4)	
*slg1*Δ	*slg1*::KanMX4	
*ssh1*Δ	*ssh1*::KanMX4	
*trp2*Δ	*trp2*::KanMX4	
*ubc7*Δ	*ubc7*::KanMX4	
*ufd2*Δ	*ufd2*::KanMX4	
ynl181w-DAmP	*ynl181w*-DAmP (KanMX4)	
*ypk1*Δ	*ypk1*::KanMX4	

***A. fumigatus* strains used in this study:**

Strain	Genotype	Reference
kuA	akuA::*ptrA*	Krappmann et al, 2006
*derA*Δ	akuA::ptr*A, derA*::*hph*	Richie DL et al 2011
*hacA*Δ	akuA::*ptrA, hacA*::*hph*	Richie DL et al 2009
*hrdA*Δ	akuA::*ptrA, hrdA*::*hph*	Krishnan K et al 2013
*ireA*Δ	akuA::*ptrA, ireA*::*ble*	Jeng X et al 2011
*derA*Δ/*hacA*Δ	akuA:*ptrA, hacA*::*hph,derA*::*ble*	Richie DL et al 2011
*derA*Δ/*hrdA*Δ	akuA::*ptrA, hrdA*::*hph, derA*::*ble*	Krishnan K et al 2013

Other yeast strains used in this study:

Strain	Genotype	Reference
C. albicans SC5314	wild type	Lohberger et al, 2014
DSY4241	*tac1*Δ::*FRT*/*tac1*Δ::*FRT*	
DSY294	azole susceptible clinical isolate (*TAC1-3/TAC1-4*)	
DSY296	azole resistant clinical isolate (*TAC1-5*/*TAC1-5* ; N977D mutation)	
ALY21	*tac1*Δ::*TAC1-4-FRT*/*tac1*Δ::*TAC1-4-FRT*	
ALY22	*tac1*Δ::*TAC1-5-FRT*/*tac1*Δ::*TAC1-5-FRT*	
C. neoformans H99	wild type	Perfect et al, 1980

MoBY plasmid (library v1.1) complemented *S. cerevisiae* strains:

Strain	Genotype+ MoBY clone identifier	Reference
*aro7*Δ+*ARO7*	*aro7*::KanMX4+ YPR060C::29NP_C9	Ho et al, 2009
*cue1*Δ+*CUE1*	*cue1*::KanMX4+ YMR264W::33NP_H12	
*emc1*Δ+*EMC1*	*emc1*::KanMX4+ YCL045C::41NP_D8	
*emc3*Δ+*EMC3*	*emc3*::KanMX4+ YKL207W::8NP_A12	
*hrd1*Δ+*HRD1*	*hrd1*::KanMX4+ YOL013C::12NP_G12	
*rpn4*Δ+*RPN4*	*rpn4*::KanMX4+ YDL020C::30NP_F2	
*ssh1*Δ+*SSH1*	*ssh1*::KanMX4+ YBR283C::37NP_A11	
*ubc7*Δ+*UBC7*	*ubc7*::KanMX4+ YMR022W::36NP_G3	

YGPM systematic overexpression library in *S. cerevisiae* strains:

Strain	Genotype+ YGPM clone identifier	Reference
Control	BY4741+ YGPM22k06 chrIII:151898...152647	Jones et al, 2008
PDR1	BY4741+ YGPM26h12 chrVII:466658...477209	
PDR5	BY4741+ YGPM33k24 chrXV:619141...631341	
PDR12	BY4741+ YGPM8p07 chrXVI:444386...454435	

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Brachmann CB, Davies A, Cost GJ, Caputo E, Li J, Hieter P, Boeke JD. Yeast. 1998 14(2):115-32.
Krappmann S, Sasse C, Braus GH. Eukaryot Cell. 2006 5(1):212-5.
Jones GM, Stalker J, Humphray S, West A, Cox T, Rogers J,
Dunham I, Prelich G. Nature Methods. 2008 5:239-241
Lohberger A, Coste AT, Sanglard D. Eukaryot Cell. 2014 13(1):127-42
Perfect, JR, Lang SDR, and Durack DT. Am. J. Pathol. 1980 101:177-194.

Supplementary Table S5 - list of oligonucleotides used in this study

List of oligonucleotides to screen deletion/DAmP mutants:

Gene	Primer name	Sequence
Kanamycin	KANMX-FW	5'-AGATGCGAAGTTAAGTGCGC-3'
ARO7	ARO7dR	5'-GAGAGAAGGTCATGGATGTG-3'
CUE1	CUE1dR	5'-GTAAGGGGAGAAGAACGTTC-3'
DER1	DER1dR	5'-TCTGCAAACGGACACCAAGT-3'
EMC1	EMC1dR	5'-GCACATCATTTCCAGACGAG-3'
EMC3	EMC3dR	5'-GCGAGGACTTTTTGCCATAC-3'
GCS1	GCS1dR	5'-GTGGTAGTTCTCTCTCCTTG-3'
HAC1	HAC1dR	5'-AGAGCCGTGAGAGTGAGAGT-3'
HRD1	HRD1dR	5'-TATGTCACCTTCCTATGCCG-3'
HRD3	HRD3dR	5'-ATGAACGGCAATTTGAGACC-3'
IRE1	IRE1dR	5'-TCTTGCACTTTTCGCCATGC-3'
PDR1	PDR1dR	5'-TGGCAACTATGTGGTGCAAT-3'
PDR5	PDR5dR	5'-GCATCTTGCTCTTTCCTCTC-3'
RPN4	RPN4dR	5'-CTGGGTACGAATTCAAGGAG-3'
SBH2	SBH2dR	5'-CATGCACCCTTAACATCGTC-3'
SEC65	SEC65-DAmP	5'-GGAAGTTGTGAGTACTGACG-3'
SLG1	SLG1dR	5'-TATATCGTCTTTCAACGCGG-3'
SSH1	SSH1dR	5'-CCACGAAGCAAGGTAACAAG-3'
SSM4	SSM4dR	5'-GACGAGGGCTAAGCAGTTTG-3'
TRP2	TRP2dR	5'-CCAAACCACATTGGTCTAGG-3'
UBC7	UBC7dR	5'-TACTGTACGGCTTGGAAGAG-3'
UFD2	UFD2dR	5'-ACCGTCATCAACGAACAACA-3'
YPK1	YPK1dR	5'-CCGTTCGTGGTTAAGGTAAG-3'

List of oligonucleotides to screen MoBY plasmids:

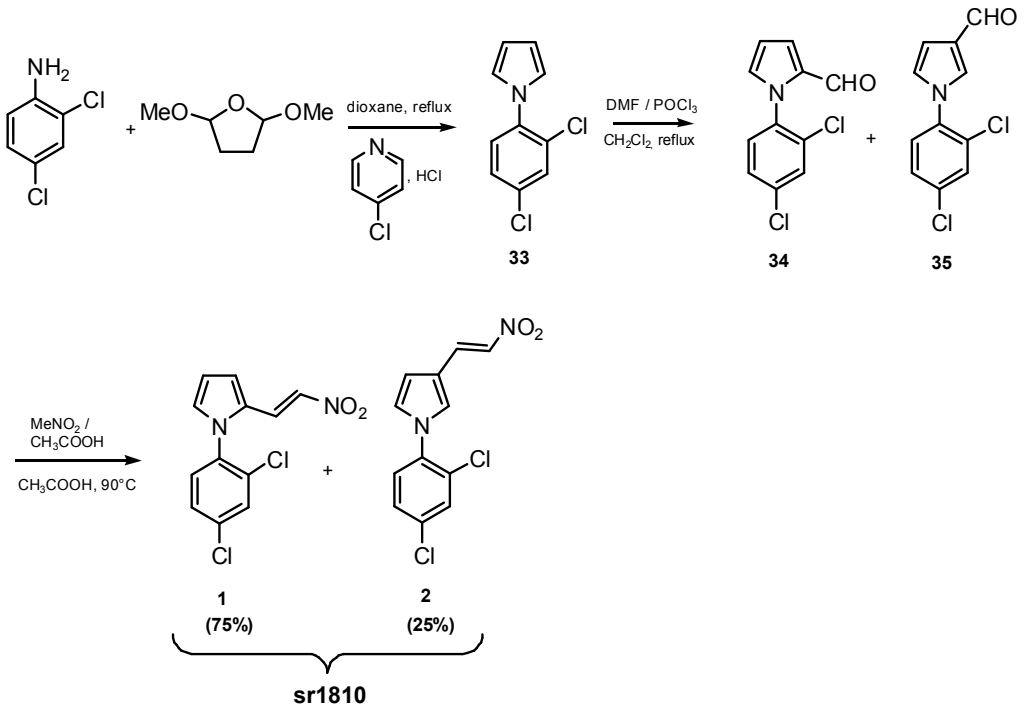
Gene	Primer name	Sequence
ARO7	ARO7iF	5'-TCGCCACATGTCCTTCAGTT-3'
	ARO7iR	5'-GCAAGTATTCCACCTCAACTTCC-3'
CUE1	CUE1iF	5'-ATGGAGGATTCGAGATTGCTT-3'
	CUE1iR	5'-CTGGCTTGCCAAACCAACAA-3'
EMC1	EMC1iF	5'-TGCCCCTTCTACGACCATTT-3'
	EMC1iR	5'-TGCCATTCGTGTCATGCTCT-3'
EMC3	EMC3iF	5'-ACCAGCTGAAGTATTGGGTCC-3'
	EMC3iR	5'-TATCCCGGCCTGAATACCCA-3'
HRD1	HRD1iF	5'-TGCGTGTATTCAGCCACCAA-3'
	HRD1iR	5'-GCCAAGATATCCCACACCACA-3'
RPN4	RPN4iF	5'-GCGAAACCCCATTGCAGAAG-3'
	RPN4iR	5'-TGGTGATGCAGTCGAAGGTT-3'
SSH1	SSH1iF	5'-TTGGTCGGTGCTGGCATATT-3'
	SSH1iR	5'-GGATGCACCCGTAACAGCT-3'
UBC7	UBC7iF	5'-CGAAAACCGCTCAGAAACGT-3'
	UBC7iR	5'-GCATCAATGTTGGCACCACT-3'

Supporting information (S1) - Synthesis of sr7575-related compounds.

General Methods

All chemical reagents and solvents were purchased from commercial sources and used without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates. Silica gel 0.06−0.2 mm, 60 Å was used for all column chromatography. Melting points were determined on a Kofler melting point apparatus. NMR spectra were recorded on a BRUKER AVANCE III 400 MHz (^{1}H NMR at 399.8 MHz and ^{13}C NMR at 100 MHz) with the solvents indicated. Chemical shifts are reported in parts per million (ppm) on the δ scale and referenced to the appropriate solvent peak. High-resolution mass spectral (HRMS) were performed on a BRUKER maxis mass spectrometer by the "fédération de Recherche" ICOA / CBM (FR2708) platform. LC-MS Analysis was performed on a Waters alliance 2695 using the following gradient: A (95%)/B (5%) to A (5%)/B (95%) in 4 min. This ratio was held for 1.5 min before returning to initial conditions in 0.5 min. Initial conditions were then maintained for 2 min (A, H $_2$O; B, MeCN; each containing 0.1% HCOOH; column, C18 Xbridge 4.6 x 50 mm / 2.5 µm). MS detection was performed with a SQDetector.

Compound sr1810: Mixture of (*E*) 1-(2,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole [75%] and (*E*) 1-(2,4-Dichlorophenyl)-3-(2-nitrovinyl)-1H-pyrrole [25%].



1-(2,4-Dichlorophenyl)-1*H*-pyrrole (**33**).[1] 4-chloropyridine, hydrochloride (9.25 g, 0.0617 mol) and 2,5-dimethoxytetrahydrofuran (8.15 g, 0.0617 mol) were stirred in 150 mL of dioxane at room temperature for 30 min. 2,4-dichloroaniline (10 g, 0.0617 mol) was then added and the mixture was stirred at reflux for 4 h. The reaction was cooled down to room temperature and concentrated under vacuum. 150 mL of water were added to the residue, followed by 200 mL of Et $_2$O. The aqueous layer was extracted with Et $_2$O (2x 100 mL). The

[1] Azizi, N. *et al.* Iron-catalyzed inexpensive and practical synthesis of N-substituted pyrroles in water. *Synlett*, **14**, 2245-2248 (2009).

combined organic layers were washed with HCl 1N (200 mL) and water (2x 200 mL), dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was purified by chromatography on silica gel using CH_2Cl_2 as eluant to give compound **33** as a brown oil (11.4 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.7 and 2.3 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 6.92 (t, *J* = 2.1 Hz, 2H), 6.39 (t, *J* = 1.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.3, 130.5, 130.4, 128.5, 127.9, 122.1, 109.7.

Mixture of 1-(2,4-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**34**) and 1-(2,4-Dichlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**35**). Dimethylformamide (2.20 mL, 0.0283 mol) was stirred at 0°C. Phosphorus oxychloride (2.7 mL, 0.0283 mol) was then added dropwise and the white solid obtained was stayed cold for 30 min. After this time, a solution of compound **33** (6 g, 0.0283 mol) in 120 mL of CH_2Cl_2 was slowly added dropwise to the reaction mixture. The reaction was refluxed for 20 h. After cooling, 120 mL of water were added and the mixture was stirred at room temperature for 30 min. Then, the layers were separated and the aqueous layer was alkalized with 20% sodium hydroxide solution. This aqueous layer was extracted with Et_2O (2x 120 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The mixture of compound **34** and **35** was engaged in the next tape without further purification and was obtained as brown solid (4.4 g, 65%). LC-MS (ESI): t_R = 4.66 and 4.79 min; $[M+H]^+$ 240.35. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9977 , measured: 239.9974.
Compound **34**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.26 (dd, *J* = 8.6 and 2.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 1.4 and 4.0 Hz, 1H), 6.86 (m, 1H), 6.37 (dd, *J* = 4.0 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 136.0, 135.2, 132.9, 132.9, 131.1, 130.0, 129.6, 127.7, 123.2, 111.2.
Compound **35**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.40 (t, *J* = 1.7 Hz, 1H), 7.31 (dd, *J* = 8.5 and 2.3 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.80 (t, *J*= 2.8 Hz, 1H), 6.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 136.1, 135.0, 130.8, 130.7, 130.0, 128.4, 128.2, 127.8, 124.8, 108.8.

sr1810: Mixture of (*E*) 1-(2,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**1**) and (*E*) 1-(2,4-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**2**). Nitromethane (54 mL, 1 mol) and ammonium acetate (15.4 g, 0.2 mol) were stirred in 100 mL of acetic acid at 30°C for 30 min. Then, the mixture of compounds **34** and **35** (12 g, 0.05 mol) was added and the solution was heated at 90°C for 24 h. Then, the reaction was concentrated under vacuum. A saturated solution of sodium hydrogenocarbonate (100 mL) was added to the residue. This aqueous layer was extracted with EtOAc (2x 100mL). The organic layers were washed with water (2x 100 mL), dried over $MgSO_4$ and concentrated under vacuum. The mixture of compound **1** and **2** was obtained as a yellow solid (8.7 g, 61%). Mp: 114 °C. LC-MS (ESI): t_R = 5.22 and 5.32 min; $[M+H]^+$ 283.31. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0035.
Compound **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.3 Hz, 1H), 7.56 (d, *J* = 13.3 Hz, 1H), 7.45 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 13.4 Hz, 1H), 7.00 (m, 1H), 6.95 (m, 1H), 6.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.3, 133.4, 132.6, 130.8, 130.3, 130.0, 128.4, 127.4, 125.8, 116.7, 112.3.
Compound **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 13.4 Hz, 1H), 7.58 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 13.2 Hz, 1H), 7.39 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.30-7.26 (m, 2H), 6.92 (m, 1H), 6.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 134.9, 134.2, 133.2, 130.9, 130.8, 128.3, 128.2, 127.9, 125.5, 116.8, 108.3.

(*E*) 1-(2,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (1 or sr7575**)**. See **Supplementary Fig.1a**.

1-(2,4-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**34**). Dimethylformamide (2.20 mL, 0.0283 mol) was stirred at 0°C. Phosphorus oxychloride (2.7 mL, 0.0283mol) was then added dropwise and the white solid obtained was cooled for 30 min. After this time, a solution of compound **33** (6 g, 0.0283 mol) in 120 mL of CH_2Cl_2 was added dropwise to the reaction mixture. The reaction was refluxed for 20 h. After cooling to room temperature, 120 mL of water were added and the mixture was stirred at room temperature for 30 min. Then, the layers were separated and the aqueous layer was alkalized with 20% sodium hydroxide solution. This aqueous layer was extracted with Et_2O (2x 120 mL) and the organic layers were dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel using cyclohexane and CH_2Cl_2 as eluants (50/50) to afford compound **34** as a beige solid (2.1 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.44 (d, J = 2.3 Hz, 1H), 7.26 (dd, J = 8.6 and 2.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.04 (dd, J = 4.0 and 1.4 Hz, 1H), 6.86 (m, 1H), 6.37 (dd, J = 4.0 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 136.0, 135.2, 132.9, 132.9, 131.1, 130.0, 129.6, 127.7, 123.2, 111.2. LC-MS (ESI): t_R = 4.79 min; $[M+H]^+$ 240.35. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9977 , measured: 239.9974.

(*E*) 1-(2,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole **(1)**. Nitromethane (54 mL, 1 mol) and ammonium acetate (15.4 g, 0.2 mol) were stirred in 100 mL of acetic acid at 30°C for 30 min. Then, 1-(2,4-dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (12 g, 0.05 mol) was added and the mixture was heated at 90°C for 24 h. Then, the reaction was concentrated under vacuum. A saturated solution of sodium hydrogenocarbonate (100 mL) was added to the residue. The aqueous layer was extracted with EtOAc (2x 100mL). The combined organic layers were washed with water (2x 100 mL), dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was purified by chromatography on silica gel using cyclohexane and CH_2Cl_2 as eluant (50/50) to obtain compound **1** as a yellow solid (6.6 g, 47%). Mp: 118°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.3 Hz, 1H), 7.56 (d, J = 13.3 Hz, 1H), 7.45 (dd, J = 2.3 and 8.3 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.17 (d, J = 13.4 Hz, 1H), 7.00 (m, 1H), 6.95 (m, 1H), 6.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.3, 133.4, 132.6, 130.8, 130.3, 130.0, 128.4, 127.4, 125.8, 116.7, 112.3. LC-MS (ESI): t_R= 5.20 min; $[M+H]^+$ 283.44. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0036.

(*E*) 1-(2,4-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (2 or sr7576**)**. See **Supplementary Fig.1b**.

1-(2,4-Dichlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**35**).[2] 4-chloropyridine, hydrochloride (9.88 g, 0.0617 mol) and 2,5-Dimethoxy-3-tetrahydrofurancarboxaldehyde (8.15 g, 0.0617 mol) were stirred in 150 mL of dioxane at room temperature for 30 min. 2,4-dichloroaniline (10 g, 0.0617 mol) was then added and the mixture was stirred at reflux for 4 h. The reaction was cooled to room temperature and concentrated under vacuum. 150 mL of water were added to the residue, followed by 200 mL of Et_2O. The aqueous layer was extracted with Et_2O (2x 100 mL). The combined organic layers were washed with 1N HCl (200 mL) and water (2x 200 mL), dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was purified by chromatography on silica gel using CH_2Cl_2 as eluant to afford compound **35** as a

[2] Dallemagne, P. *et al*. A convenient rearrangement of 1-phenylpyrrole-2-carboxaldehydes into their 3-isomers. *Synthetic Communications*. **13**, 1855-1857 (1994).

beige solid (5.2 g, 35%). Mp: 186°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.40 (t, *J* = 1.7 Hz, 1H), 7.31 (dd, *J* = 8.5 and 2.3 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.80 (t, *J* = 2.8 Hz, 1H), 6.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 136.1, 135.0, 130.8, 130.7, 130.0, 128.4, 128.2, 127.8, 124.8, 108.8. LC-MS (ESI): t_R= 4.66 min; $[M+H]^+$ 240.35.

(*E*) 1-(2,4-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**2**). Nitromethane (54 mL, 1 mol) and ammonium acetate (15.4 g, 0.2 mol) were stirred in 100 mL of acetic acid at 30°C for 30 minutes. Then, 1-(2,4-dichloro-phenyl)-1 *H*-pyrrole-2-carbaldehyde (12 g, 0.05 mol) was added and the mixture was heated at 90°C for 24 h. The reaction was concentrated under vacuum. A saturated solution of sodium hydrogenocarbonate (100 mL) was added to the residue. This aqueous layer was extracted with EtOAc (2x 100 mL). The organic layers were washed with water (2x 100 mL), dried over $MgSO_4$ and concentrated under vacuum. The solid resulting residue was purified by chromatography on silica gel using cyclohexane and CH_2Cl_2 as eluant (50/50) to give compound **2** as a yellow solid (6.1 g, 43%). Mp: 186 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, *J* = 13.3 Hz, 1H), 7.95 (d, *J* = 13.3 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.78 (m, 1H), 7.60 (dd, *J* = 6.4 and 8.5 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.19 (m, 1H), 6.86 (m, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 136.5, 134.8, 134.6, 134.0, 130.6, 130.2, 130.0, 129.7, 129.0, 126.3, 117.5, 109.3. LC-MS (ESI): t_R= 5.34 min; $[M+H]^+$ 283.40. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$calculated mass: 283.0035, measured: 283.0036.

(*E*) 1-(2,4-dichlorophenyl)-2-methyl-5-(2-nitrovinyl)-1*H*-pyrrole (**3**). See **Supplementary Fig.1c**.

1-(2,4-Dichlorophenyl)-2-methyl-1*H*-pyrrole (**36**). A mixture of 1-(2,4-Dichlorophenyl)-1 *H*-pyrrole-2-carbaldehyde (**34**) (1g, 0.02 mol), potassium hydroxide (0.7g, 0.06 mol) and hydrazine monohydrate (0.61 ml, 0.06 mol) in ethylene glycol (20 ml) was stirred at room temperature for 30 min, then slowly heated to 150°C and maintained for 2 h. The reaction mixture was allowed to cool to room temperature, poured into ice-water and extracted with Et_2O (2x 20 ml). The combined organic layers were washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude compound was purified by chromatography on silica gel using cyclohexane and CH_2Cl_2 as eluant (90/10) to afford compound **36** as an orange oil (0.78 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.2 Hz, 1H), 7.33 (dd, *J* = 8.5 and 2.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 6.60 (dd, *J* = 2.8 and 1.9 Hz, 1H), 6.22 (t, *J* = 3.0 Hz, 1H), 6.04 (m, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 134.6, 133.7, 130.5, 130.1, 130.0, 127.7, 121.3, 108.5, 107.4, 12.1. HRMS for $C_{11}H_{10}Cl_2N$ $[M+H]^+$calculated mass: 226.0184, measured: 226.0185.

Synthetic procedure for the compound (**3**) is the similar as that described for the compound (**1**) and spectra data are shown below.

1-(2,4-Dichlorophenyl)-5-methyl-1*H*-pyrrole-2-carbaldehyde (**37**). Yellow oil (61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.5 and 2.4 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 3.9 Hz, 1H), 6.22 (d, *J* = 3.9 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 140.1, 135.4, 134.8, 133.7, 132.7, 130.4, 130.1, 128.0, 123.8, 110.4, 12.1. LC-MS (ESI): t_R= 4.52 min; $[M+H]^+$ 254.37. HRMS for $C_{12}H_{10}Cl_2NO$ $[M+H]^+$calculated mass: 254.0133, measured: 254.0133.

(E) 1-(2,4-Dichlorophenyl)-2-methyl-5-(2-nitrovinyl)-1 *H*-pyrrole (**3**). Orange solid (50%). Mp: 90°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.4 Hz, 1H), 7.47 (m, 2H), 7.28 (m,

1H), 6.99 (d, *J* = 13.4 Hz, 1H), 6.90 (d, *J* = 4.0 Hz, 1H), 6.27 (d, *J* = 4.0 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 136.8, 134.5, 133.1, 131.1, 130.9, 130.6, 128.7, 127.7, 125.3, 118.0, 111.7, 12.8. LC-MS (ESI): t_R = 5.35 min; $[M+H]^+$ 297.42. HRMS for $C_{13}H_{11}Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 297.0192, measured: 297.0193.

(*E*) 3-[1-(2,4-Dichlorophenyl)-1*H*-pyrrol-2-yl]-acrylonitrile (4). See **Supplementary Fig.1d**.

2-Cyano-3-(1-(2,4-dichlorophenyl)-1*H*-pyrrol-2-yl)-acrylic acid ethyl ester (**38**). To a solution of 1-(2,4-dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**34**) (1g, 4.16 mmol) in ethanol (10 ml), were added ethylcyanoacetate (0.49 ml, 4.58 mmol) and triethylamine (0.58 ml, 4.16 mmol). The mixture was refluxed for 4 h. After removal of the solvent under vacuum, CH_2Cl_2 was added to the residue and the organic layer was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude compound was purified by chromatography on silica gel using CH_2Cl_2 as eluant to obtain compound **34** as a yellow solid (1.2 g, 86%). Mp: 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 4.2 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.52 (s, 1H), 7.41 (dd, *J* = 8.3 and 1.5 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.07 (m, 1H), 6.59 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 140.1, 136.5, 133.6, 133.5, 130.7, 130.7, 130.6, 128.3, 128.3, 119.4, 116.6, 113.3, 95.2, 62.2, 14.2. HRMS for $C_{16}H_{13}Cl_2N_2O_2$ $[M+H]^+$calculated mass: 335.0348, measured: 335.0346.

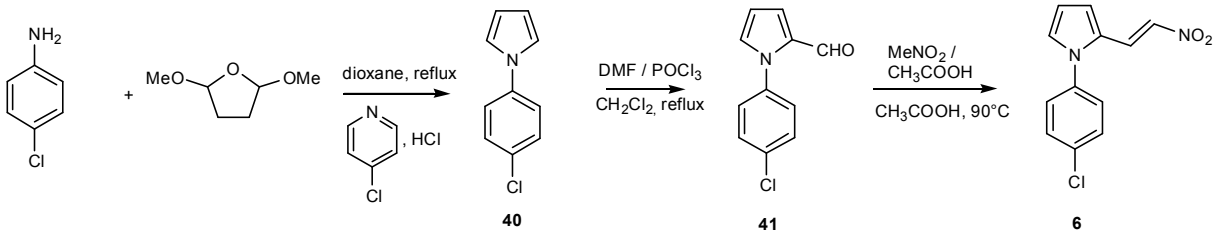
2-Cyano-3-(1-(2,4-dichlorophenyl)-1*H*-pyrrol-2-yl)-acrylic acid (**39**). To a solution of lithium hydroxyde (340 mg, 0.014 mol) in water (50 ml) was added a solution of 2-cyano-3-(1-(2,4-dichlorophenyl)-1*H*-pyrrol-2-yl)-acrylic acid ethyl ester (**38**) (3.2 g, 9.54 mmol) in THF (50 ml) and the mixture was heated at 50°C for 5h. After removing THF under vacuum, the aqueous layer was acidified with 6N HCl and then extracted with EtOAc (2x 50 mL). The organic layers were washed with water (2x 50 mL), dried over $MgSO_4$ and concentrated in vacuo. The product was purified by recrystallization in CH_2Cl_2 to obtain compound **39** as a yellow solid (1.1 g, 37%). Mp: 110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 4.1 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.56 (s, 1H), 7.46 (dd, *J* = 8.3 and 2.2 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.15 (m, 1H), 6.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 141.2, 136.7, 133.5, 133.2, 131.8, 130.8, 130.6, 128.4, 128.3 120.7, 116.0, 113.8, 93.8. LC-MS (ESI): t_R = 4.55 min; $[M+H]^+$ 307.32. HRMS for $C_{14}H_9Cl_2N_2O_2$ $[M+H]^+$calculated 307.0035, measured: 307.0034.

3-(1-(2,4-Dichlorophenyl)-1*H*-pyrrol-2-yl)-acrylonitrile (**4**). To a solution of copper (155 mg, 2.44 mmol) in quinoleine (10 ml), heated at 190°C, was added 2-cyano-3-(1-(2,4-dichlorophenyl)-1*H*-pyrrol-2-yl)-acrylic acid (**39**) (500 mg, 1.62 mmol). The mixture was stirred vigorously. After the carbon dioxide evolution stopped and TLC indicated complete consumption of the starting material, the reaction was cooled to room temperature and 1N HCl (10 ml) was added. The aqueous layer was extracted with CH_2Cl_2 (2x 15 mL). The combined organic layers were washed with water (2x 20 mL), dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was purified by chromatography on silica gel using cyclohexane and CH_2Cl_2 as eluant (50/50 to 30/70) to obtain compound **4** as a white solid (150 mg, 36%). Mp: 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.3 Hz, 1H), 7.53 (m, 1H), 7.39 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 6.86 (m, 1H), 6.49 (t, *J* = 3.2 Hz, 1H), 6.44 (d, *J* = 12.1 Hz, 1H), 5.01 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 135.1, 134.5, 133.7, 130.8, 130.4, 129.3, 128.1, 126.4, 118.2, 114.3, 111.6,

88.7. LC-MS (ESI): t_R = 5.18 min; $[M+H]^+$ 263.51. HRMS for $C_{13}H_9Cl_2N_2$ $[M+H]^+$calculated mass: 263.0137, measured: 263.0136.

1-(2,4-Dichlorophenyl)-2-(2-nitroethyl)-1*H*-pyrrole (5). See **Supplementary Fig.1e**. 1-(2,4-Dichlorophenyl)-2-(2-nitroethyl)-1*H*-pyrrole (**5**). To a solution of (*E*) 1-(2,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole **(1)** (200 mg, 0.70 mmol) in methanol (7 ml) was added portionwise sodium borohydride (53 mg, 1.41 mmol) at 0°C. After the addition, the reaction mixture was stirred at 0°C for 1 h. Then a mixture of ice / water (10 ml) was added and the aqueous layer was extracted with EtOAc (2x 20 ml). The combined organic layers were washed with water (2x 30 ml), dried over $MgSO_4$, filtered and concentrated under vacuum to give compound **5** as a brown oil (0.1 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 6.64 (dd, *J* = 2.9 and 1.7 Hz, 1H), 6.27 (t, *J* = 3.2 Hz, 1H), 6.13 (m, 1H), 4.48 (dd, *J* = 15.2 and 7.7 Hz, 2H), 3.09 (dd, *J* = 15.4 and 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.4, 133.7, 130.6, 130.3, 128.1, 127.6, 122.8, 109.2, 108.0, 74.1, 24.3. HRMS for $C_{12}H_{11}Cl_2N_2O_2$ $[M+H]^+$calculated mass: 285.0192, measured: 285.0189.

(*E*) 1-(4-Chlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (6).



Synthetic procedure for compound (**6**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(4-chlorophenyl)-1*H*-pyrrole (**40**).[3] Beige solid (85%). Mp: 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.2 Hz, 2H), 7.21 (d, *J* = 9.1 Hz, 2H), 6.94 (t, *J* = 2.2 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 131.1, 129.8, 121.6, 119.3, 110.8.

1-(4-chlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**41**).[4] Orange solid (30%). Mp: 98°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.07 (dd, *J* = 4.0 and 1.7 Hz, 1H), 6.97 (m, 1H), 6.34 (dd, *J* = 4.1 and 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 137.5, 134.1, 132.4, 131.3, 129.2, 127.2, 123.7, 111.1. LC-MS (ESI): t_R= 4.52 min; $[M+H]^+$ 206.39.

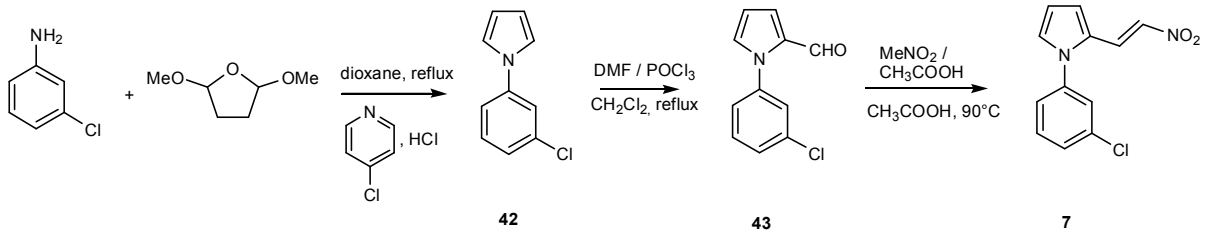
(*E*) 1-(4-chlorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**6**).Yellow solid (54%). Mp: 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 13.3 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* =

[3] Das, B. *et al*. Novel approach for the synthesis of N-substituted pyrroles starting directly from nitro compounds in water. *Synthetic Communications*. **4**, 548-553 (2012)

[4] Pina, M. *et al* . Synthesis and spectral data of 1-aryl-2-formylpyrroles. *Khimiya Geterotsiklicheskikh Soedinenii*. **2**, 180-184, (1989).

13.4 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.07 (m, 1H), 6.91 (d, *J* = 3.8 Hz, 1H), 6.42 (t, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 134.9, 132.8, 130.0, 129.9, 127.8, 127.6, 125.2, 116.5, 112.1. LC-MS (ESI): t_R= 5.07 min; $[M+H]^+$ 249.44. HRMS for $C_{12}H_{10}ClN_2O_2$ $[M+H]^+$ calculated mass: 249.0425, measured: 249.0425.

(*E*) 1-(3-Chlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (7).



42 43 7

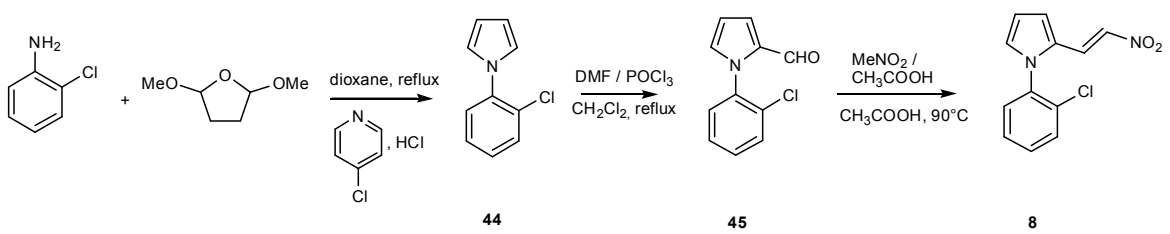
Synthetic procedure for compound (**7**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(3-chlorophenyl)-1*H*-pyrrole (**42**).[5] Brown solid (90%). Mp: 54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.18 (ddd, *J* = 8.1, 2.1 and 1.2 Hz, 1H), 7.11 (ddd, *J* = 7.9, 2.0 and 1.2 Hz, 1H), 6.97 (t, *J* = 2.2 Hz, 2H), 6.26 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 135.2, 130.6, 125.6, 120.6, 119.2, 118.4, 111.1.

1-(3-chlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**43**).[4] Brown solid (50%). Mp: 68°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.31-7.27 (m, 3H), 7.18-7.15 (m, 1H), 7.06 (dd, *J* = 4.0 and 1.7 Hz, 1H), 6.97 (m, 1H), 6.33 (dd, *J* = 3.9 and 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 140.0, 134.6, 132.4, 131.2, 130.0, 128.4, 126.3, 124.4, 123.5, 111,2. LC-MS (ESI): t_R = 4.42 min; $[M+H]^+$ 206.34.

(*E*) 1-(3-Chlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**7**)**.** Red oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 13.3 Hz, 1H), 7.50-7.48 (m, 2H), 7.35 (m, 1H), 7.32 (d, *J* = 13.3 Hz, 1H), 7.20-7.23 (m, 1H), 7.12 (dd, *J* = 2.6 and 1.1 Hz, 1H), 6.95 (dd, *J* = 4.0 and 2.6 Hz, 1H), 6.45 (dd, *J*= 3.8 and 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 135.5, 132.9, 130.7, 129.8, 129.1, 127.7, 126.6, 125.2, 124.7, 116.5, 112.2. LC-MS (ESI): t_R = 5.06 min; $[M+H]^+$ 249.40. HRMS for $C_{12}H_{10}ClN_2O_2$ $[M+H]^+$ calculated mass: 249.0425, measured: 249.0425.

(*E*) 1-(2-Chlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (8).



44 45 8

[5] Corsi, C. *et al*. Preparation of pyrrole derivatives as plant growth regulators. PCT Int. Appl., 2010069879, 24 Jun 2010.

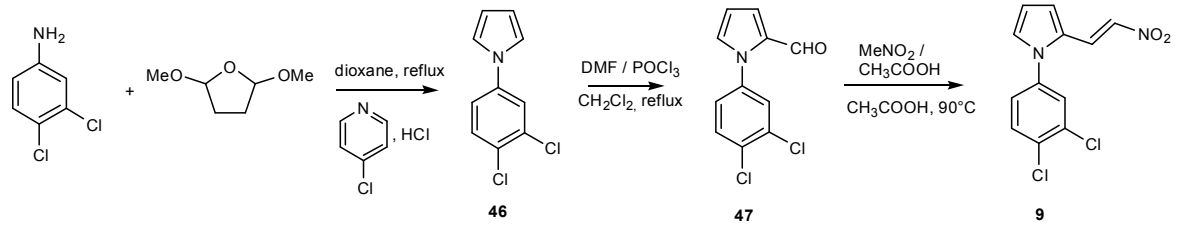
Synthetic procedure for compound (**8**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2-Chlorophenyl)-1*H*-pyrrole (**44**)[1]**.** Brown oil (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m , 1H), 7.32-7.22 (m, 3H), 6.88 (t, *J* = 2.2 Hz, 2H), 6.31 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 130.7, 129.7, 128.3, 127.9, 127.6, 122.2, 109.3.

1-(2-Chlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**45**).[4] Beige solid (29%). Mp: 94°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 0.5 Hz, 1H), 7.44 (m, 1H), 7.35-7.27 (m, 2H), 7.05 (dd, *J* = 4.0 and 1.7 Hz, 1H), 7.07 (dd, *J* = 4.0 and 1.8 Hz, 1H), 6.89 (m, 1H), 6.37 (dd, *J* = 4.0 and 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 137.1, 133.0, 132.0, 131.0, 130.2, 130.0, 129.0, 127.4, 122.2, 110.9. LC-MS (ESI): t_R = 4.38 min; $[M+H]^+$ 206.39.

(*E*) 1-(2-Chlorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**8**)**.** Brown oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 2H), 7.51 (dt, *J* = 7.5 and 1.7 Hz, 1H), 7.46 (dt, *J* = 7.6 and 1.5 Hz, 1H), 7.38 (dd, *J* = 7.6 and 1.7 Hz, 1H), 7.09 (d, *J* =13.3 Hz, 1H), 7.04 (dd, *J* = 2.5 and 0.9 Hz, 1H), 6.95 (dd, *J* = 2.6 and 1.1 Hz, 1H), 6.49 (dd, *J* = 2.7 and 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 132.5, 132.3, 131.0, 130.9, 130.3, 129.6, 128.0, 127.8, 125.8, 116.9, 112.0. LC-MS (ESI): t_R = 4.95 min; $[M+H]^+$ 249.44. HRMS for $C_{12}H_{10}ClN_2O_2$ $[M+H]^+$ calculated mass: 249.0425, measured: 249.0425.

(*E*) 1-(3,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (9).



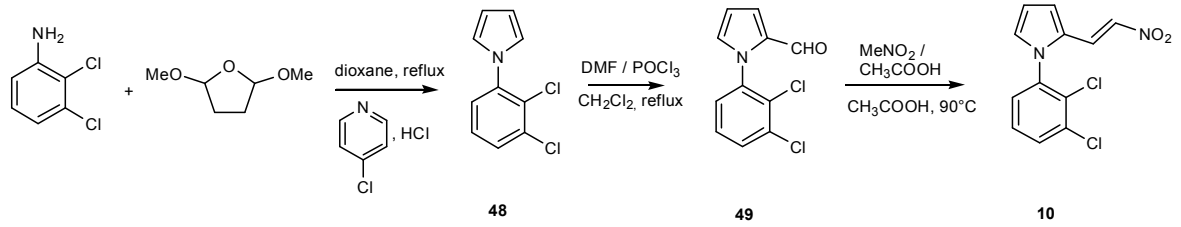
Synthetic procedure for compound (**9**) is similar as that described for compound **(1**) and spectra data are shown below.

1-(3,4-Dichlorophenyl)-1*H*-pyrrole (**46**)**.** Brown solid (77%). Mp: 56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.24 (dd, *J* = 8.7 and 2.6 Hz, 1H), 7.05 (t, *J* = 2.1 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 133.5, 131.2, 129.2, 122.1, 119.4, 119.2, 111.4.

1-(3,4-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**47**)**.** Brown solid (40%). Mp: 104°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 0.7 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.14 (dd, *J* = 8.5 and 2.5 Hz, 1H), 7.07 (dd, *J* = 4.0 and 1.8 Hz, 1H), 6.97 (m, 1H), 6.35 (dd, *J* = 4.0 and 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 138.3, 132.9, 132.5, 132.2, 131.6, 130.6, 127.8, 125.5, 124.6, 111,4. LC-MS (ESI): t_R = 4.81 min; $[M+H]^+$ 240.30. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9977, measured: 239.9975.

(*E*) 1-(3,4-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**9**) : yellow solid (65%). Mp: 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 13.3 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 13.3 Hz, 1H), 7.17 (dd, *J* = 8.5 and 2.4 Hz, 1H), 7.10 (dd, *J* = 2.6 and 1.1 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.3 Hz, 1H), 6.49 (dd, *J* = 3.9 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 132.5, 132.3, 131.0, 130.9, 130.3, 129.6, 128.0, 127.8, 125.8, 116.9, 112.0. LC-MS (ESI): t_R = 5.29 min; $[M+H]^+$ 283.44. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0035.

(*E*) 1-(2,3-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (10).

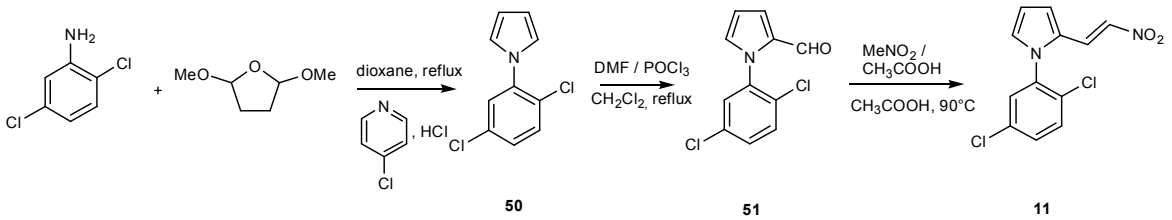


Synthetic procedure for compound (**10)** is similar as that described for compound (**1**) and spectra data are shown below.

1-(2,3-Dichlorophenyl)-1*H*-pyrrole (**48**).[3] Pink oil (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H), 7.27 (m, 2H), 6.90 (t, *J* = 2.1 Hz, 2H), 6.36 (t, *J* = 2.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 134.4, 129.2, 129.0, 127.5, 126.2, 122.2, 109.6.
1-(2,3-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**49**). Yellow solid (32%). Mp: 92°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.59 (dd, *J* = 7.6 and 2.1 Hz, 1H), 7.35-7.28 (m, 2H), 7.15 (dd, *J* = 4.0 and 1.6 Hz, 1H), 6.98 (m, 1H), 6.48 (dd, *J* = 4.1 and 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 139.0, 134.0, 132.9, 131.3, 131.0, 130.8, 127.3, 127.2, 122.9, 111,1. LC-MS (ESI): t_R = 4.69 min; $[M+H]^+$ 240.30. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9977, measured: 239.9975.

(*E*) 1-(2,3-Dichlorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**10**). Yellow solid (53%). Mp: 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.56 (d, *J* = 13.3 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 7.9 and 1.5 Hz, 1H), 7.17 (d, *J* = 13.3 Hz, 1H), 7.03 (dd, *J* = 2.5 and 1.5 Hz, 1H), 6.96 (m, 1H), 6.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 134.8, 132.6, 131.9, 131.8, 130.0, 128.0, 127.9, 127.4, 125.7, 116.7, 112.3. LC-MS (ESI): t_R = 5.11 min; $[M+H]^+$ 283.44. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0035.

(*E*) 1-(2,5-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (11).



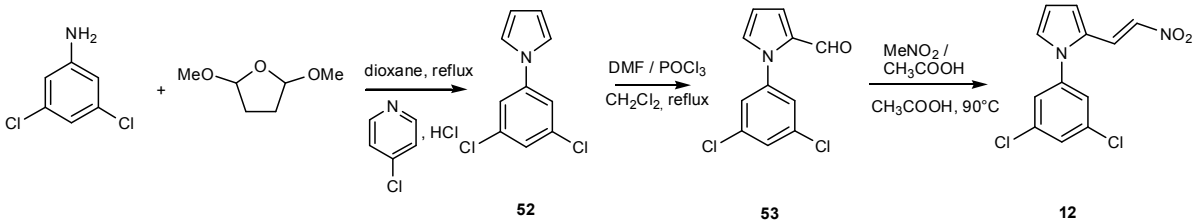
Synthetic procedure for compound (**11)** is similar as that described for compound (**1**) and spectra data are shown below.

1-(2,5-Dichlorophenyl)-1*H*-pyrrole (**50).** Brown oil (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.6 and 2.4 Hz, 1H), 6.82 (t, *J* = 2.2 Hz, 2H), 6.26 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 133.1, 131.6, 128.1, 127.8, 127.7, 122.0, 109.9. HRMS for $C_{10}H_9Cl_2N$ $[M+H]^+$ calculated mass: 212.0028, measured: 212.0030.

1-(2,5-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**51**)**.** Orange solid (45%). Mp: 126°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.40 (m, 1H), 7.37 (m, 1H), 7.13 (dd, *J* = 4.0 and 1.8 Hz, 1H), 6.95 (m, 1H), 6.46 (dd, *J* = 3.9 and 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 138.2, 132.9, 132.8, 130.9, 130.8, 130.6, 130.0, 129.0, 123.1, 111.2. LC-MS (ESI): t_R = 4.72 min; $[M+H]^+$ 240.35. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9977, measured: 239.9972.

(*E*) 1-(2,5-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**11**) Yellow solid (59%). Mp: 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 13.2 Hz, 1H), 7.53 (s, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 2.3 Hz, 1H), 7.16 (d, *J* = 13.4 Hz, 1H), 7.01 (dd, *J* = 2.7 and 1.5 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.3 Hz, 1H), 6.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 133.7, 132.8, 131.6, 131.2, 131.1, 129.9, 129.8, 127.4, 125.8, 116.8, 112.5. LC-MS (ESI): t_R= 5.13 min; $[M+H]^+$ 283.49. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0035.

(*E*) 1-(3,5-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (12).



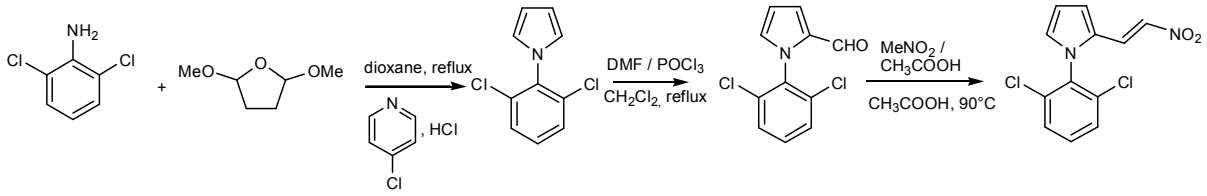
Synthetic procedure for compound (**12**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(3,5-Dichlorophenyl)-1*H*-pyrrole (**52**)**.** Brown solid (79%). Mp: 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.8 Hz, 2H), 7.23 (t, *J* = 1.8 Hz, 1H), 7.05 (t, *J* = 2.2 Hz, 2H), 6.38 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 135.9, 125.4, 119.1, 118.7, 111.6. HRMS for $C_{10}H_8Cl_2N$ $[M+H]^+$ calculated mass: 212.0028, measured: 212.0032.

1-(3,5-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**53**). Yellow solid (50%). Mp: 144°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.34 (t, *J* = 1.8 Hz, 1H), 7.20 (d, *J* = 1.8 Hz, 2H), 7.07 (dd, *J* = 3.9 and 1.6 Hz, 1H), 6.98 (m, 1H), 6.35 (dd, *J* = 3.9 and 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 140.7, 135.1, 132.2, 131.3, 128.4, 124.8, 124.6, 111.5. LC-MS (ESI): t_R = 4.69 min; $[M+H]^+$ 240.26. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9975, measured: 239.9977.

(*E*) 1-(3,5-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**12**). Orange solid (65%). Mp: 120°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 13.3 Hz, 1H), 7.52 (t, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 13.3 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.10 (dd, *J* = 2.6 and 1.5 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.3 Hz, 1H), 6.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 136.2, 133.4, 129.6, 129.2, 127.2, 125.2, 125.1, 116.7, 112.5. LC-MS (ESI): t_R = 5.33 min; $[M+H]^+$ 283.44. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0036.

(*E*) 1-(2,6-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (13)



Synthetic procedure for compound (**13**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2,6-Dichlorophenyl)-1*H*-pyrrole (**54**).[6] Orange solid (83%). Mp: 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.33-7.29 (m, 1H), 6.76 (t, *J* = 2.3 Hz, 2H), 6.43 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.5, 129.6, 128.7, 121.9, 109.4.

1-(2,6-Dichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**55**).[6] Orange solid (45%). Mp: 94°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.45 (m, 2H), 7.34 (dd, *J* = 9.0 and 7.3 Hz, 1H), 7.16 (dd, *J* = 3.8 and 1.6 Hz, 1H), 6.92 (m, 1H), 6.52 (dd, *J* = 3.9 and 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 135.6, 134.2, 132.3, 130.4, 130.2, 128.4, 123.1, 111,4. LC-MS (ESI): t_R = 4.61 min; $[M+H]^+$ 240.35.

(*E*) 1-(2,6-Dichlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**13**). Orange solid (60%). Mp: 120°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.53 (d, *J* = 12.9 Hz, 1H), 7.46 (m, 1H), 7.03-7.01 (d, *J* = 13.1 Hz, 1H), 6.99 (dd, *J* = 4.0 and 1.4 Hz, 1H), 6.96 (dd, *J* = 2.7 and 1.4 Hz, 1H), 6.55 (dd, *J* = 3.9 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 133.8, 132.3, 131.4, 129.5, 129.1, 127.2, 125.1, 117.5, 112.7. LC-MS (ESI): t_R = 5.05 min; $[M+H]^+$ 283.40. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035 , measured: 283.0035.

(*E*) 1-(2,4,5-Trichlorophenyl)- 2-(2-nitrovinyl)-1*H*-pyrrole (14).

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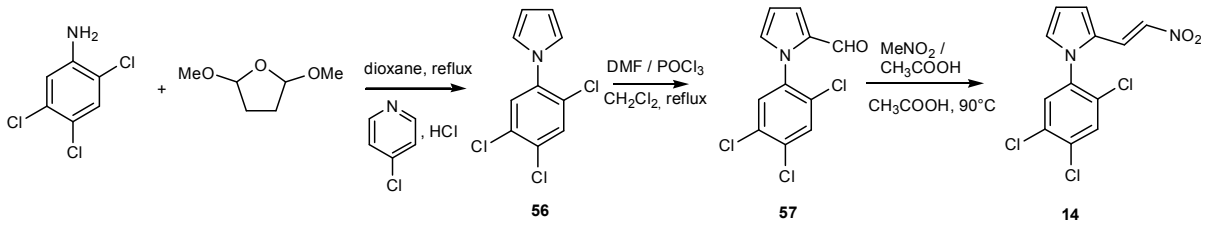
[6] Ikegami, H. *et al*. Hydrazide compound and their preparation, formulation and pesticidal use. PCT Int. Appl., 2007043677, 19 Apr 2007



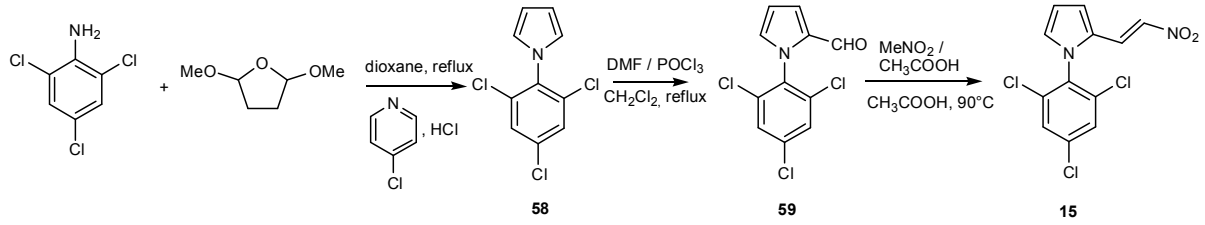
Synthetic procedure for compound (**14**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2,4,5-Trichlorophenyl)-1*H*-pyrrole (**56**).[7] Brown solid (79%). Mp: 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.38 (s, 1H), 6.80 (t, *J* = 2.2 Hz, 2H), 6.27 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 131.7, 131.7, 131.6, 128.8, 128.2, 122.0, 110.2.

1-(2,4,5-Trichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**57**)**.** Beige solid (32%). Mp: 96°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.62 (s, 1H), 7.46 (s, 1H), 7.13 (dd, *J* = 4.0 and 1.5 Hz, 1H), 6.94 (m, 1H), 6.47 (dd, *J* = 3.9 and 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 136.7, 133.7, 132.9, 131.4, 131.1, 131.0, 130.9, 130.0, 123.7, 111.4. LC-MS (ESI): t_R = 5.07 min; $[M+H]^+$ 274.26. HRMS for $C_{11}H_7Cl_3NO$ $[M+H]^+$ calculated mass: 273.9587, measured: 273.9587.

(*E*) 1-(2,4,5-Trichlorophenyl)- 2-(2-nitrovinyl)-1*H*-pyrrole (**14**)**.** Yellow solid (62%). Mp: 166 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.46-7.43 (m, 2H), 7.14 (d, *J* = 13.3 Hz, 1H), 6.91 (dd, *J* = 2.7 and 1.5 Hz, 1H), 6.88 (dd, *J* = 4.0 and 1.3 Hz 1H), 6.42 (dd, *J* = 3.8 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.9, 133.0, 132.3, 131.8, 131.5, 130.8 129.7, 127.1, 125.8, 116.6, 112.7. LC-MS (ESI): t_R = 5.42 min; $[M+H]^+$ 317.27. HRMS for $C_{12}H_8Cl_3N_2O_2$ $[M+H]^+$ calculated mass: 316.9645, measured: 316.9645.

(*E*) 1-(2,4,6-Trichlorophenyl)- 2-(2-nitrovinyl)-1*H*-pyrrole (15).



Synthetic procedure for compound (**15**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2,4,6-Trichlorophenyl)-1*H*-pyrrole (**58**). Beige solid (88%). Mp: 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 6.60 (t, *J* = 2.2 Hz, 2H), 6.30 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 135.1, 134.6, 128.6, 121.8, 109.7. HRMS for $C_{10}H_7Cl_3N$ $[M+H]^+$ calculated mass: 245.9638, measured: 245.9642.

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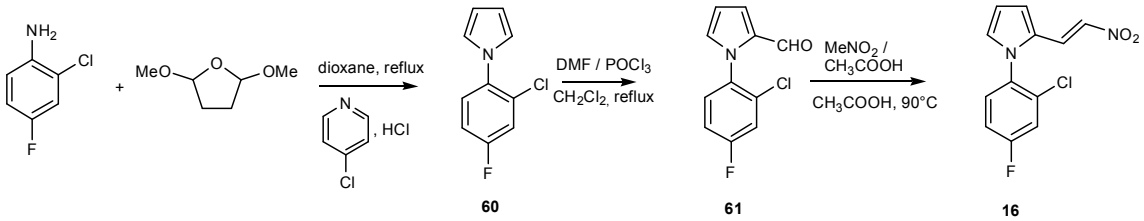
[7] Ma, F *et al* . A recyclable magnetic nanoparticles supported antimony catalyst for the synthesis of N-substituted pyrroles in water. *Applied Catalysis* , *A: General* , **457**, 34-41 (2013)

1-(2,4,6-Trichlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**59**). Yellow solid (30%). Mp: 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.46 (s, 2H), 7.15 (dd, *J* = 4.0 and 1.5 Hz, 1H), 6.89 (m, 1H), 6.52 (dd, *J* = 4.0 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 135.3, 134.8, 134.6, 132.2, 130.4, 128.5, 123.6, 111,7. LC-MS (ESI): t_R = 4.97 min; $[M+H]^+$ 274.31. HRMS for $C_{11}H_7Cl_3NO$ $[M+H]^+$ calculated mass: 273.9587, measured: 273.9587.

(*E*) 1-(2,4,6-Trichlorophenyl)- 2-(2-nitrovinyl)-1 *H*-pyrrole (**15**). Light brown solid (50%). Mp: 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.47 (d, *J* = 13.3 Hz, 1H), 7.10 (d, *J* = 13.3 Hz, 1H), 6.98 (dd, *J* = 4.0 and 1.3 Hz, 1H), 6.92 (dd, *J* = 2.7 and 1.4 Hz 1H), 6.55 (dd, *J* = 3.8 and 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.7, 132.7, 132.6, 129.3, 129.2, 126.8, 125.1, 117.3, 113.0. LC-MS (ESI): t_R = 5.32 min; $[M+H]^+$ 317.32. HRMS for $C_{12}H_8Cl_3N_2O_2$ $[M+H]^+$ calculated mass: 316.9645, measured: 316.9645.

(*E*) 1-(2-Chloro-4-fluorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (16).



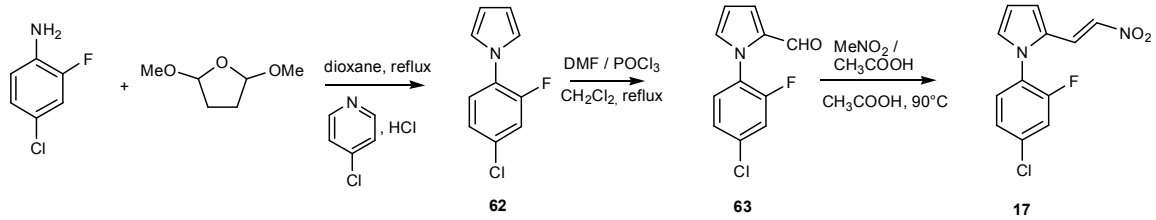
Synthetic procedure for compound (**16**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2-Chloro-4-fluorophenyl)-1*H*-pyrrole (**60**). Orange oil (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 8.6 and 7.6 Hz, 1H), 6.76 (t, *J* = 2.3 Hz, 2H), 6.43 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 250.7 Hz), 135.3 (d, *J* = 3.9 Hz), 131.0 (d, *J* = 10.7 Hz), 129.0 (d, *J* = 10.7 Hz), 122.3 (s), 117.7 (d, *J* = 25.8 Hz), 114.6 (d, *J* = 21.9 Hz), 109.5 (s). HRMS for $C_{10}H_8ClFN$ $[M+H]^+$ calculated mass: 196.0323, measured: 196.0326.

1-(2-Chloro-4-fluorophenyl)-1*H*-pyrrole-2-carbaldehyde (**61**)**.** White solid (61%). Mp: 104°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.25 (dd, *J* = 8.7 and 5.4 Hz, 1H), 7.18 (dd, *J* = 8.0 and 2.8 Hz, 1H), 7.04 (dd, *J* = 4.0 and 1.6 Hz, 1H), 7.02-6.97 (m, 1H), 6.86 (m, 1H), 6.37 (dd, *J* = 4.0 and 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6 (s), 162.1 (d, *J* = 250.9 Hz), 133.6 (d, *J* = 3.7 Hz), 133.1 (d, *J* = 10.5 Hz), 133.0 (s), 131.2 (s), 129.9 (d, *J* = 9.2 Hz), 123.0 (bs), 117.5 (d, *J* = 25.9 Hz), 114,6 (d, *J* = 21.6 Hz), 111.0 (s). LC-MS (ESI): t_R = 4.49 min; $[M+H]^+$ 224.40. HRMS for $C_{11}H_8ClFNO$ $[M+H]^+$ calculated mass: 224.0272, measured: 224.0272.

(*E*) 1-(2-Chloro-4-fluorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**16**). Orange solid (55%). Mp: 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 13.4 Hz, 1H), 7.40-7.34 (m, 2H), 7.20-7.15 (m, 1H), 7.12 (d, *J* = 13.3 Hz, 1H), 7.01 (dd, *J* = 2.6 and 1.5 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.3 Hz, 1H), 6.49 (dd, *J* = 3.8 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 257.9 Hz), 133.9 (d, *J* = 10.9 Hz), 132.5 (s), 132.0 (d, *J*= 3.7 Hz), 130.8 (d, *J* = 9.5 Hz), 130.3 (s), 127.5 (s), 125.9 (s), 118.3 (d, *J* = 25.7 Hz), 116.8 (s), 115.4 (d, *J* = 22.3 Hz), 112.3 (s). LC-MS (ESI): t_R = 4.95 min; $[M+H]^+$ 267.41. HRMS for $C_{12}H_9ClFN_2O_2$ $[M+H]^+$ calculated mass: 267.0331, measured: 267.0329.

(*E*) 1-(4-Chloro-2-fluorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (17).



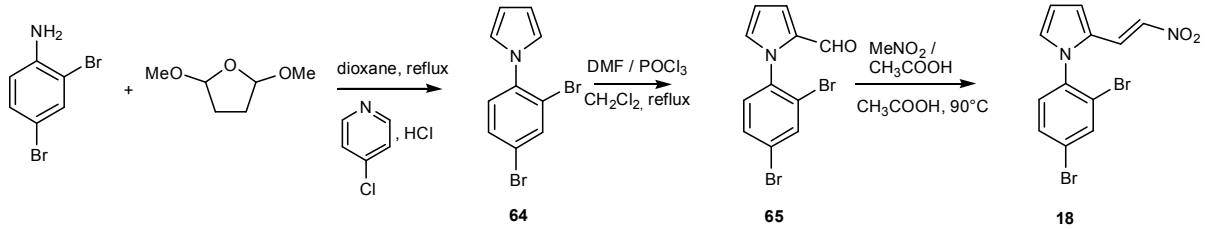
Synthetic procedure for compound (**17**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(4-Chloro-2-fluorophenyl)-1*H*-pyrrole (**62**). Orange oil (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 8.5 Hz, 1H), 7.27 (m, 1H), 7.21 (ddd, *J* = 8.4, 2.2 and 1.2 Hz, 1H), 7.03 (q, *J* = 2.1 Hz, 2H), 6.38 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7 (d, *J* = 255.7 Hz), 131.9 (d, *J* = 9.8 Hz), 127.8 (d, *J* = 10.5 Hz), 125.5 (d, *J* = 2.0 Hz), 125.1 (d, *J* = 4.1 Hz), 121.2 (d, *J* = 4.8 Hz), 117.8 (d, *J* = 23.7 Hz), 110.3 (s). HRMS for $C_{10}H_8ClFN$ $[M+H]^+$ calculated mass: 196.0323, measured: 196.0329.

1-(4-Chloro-2-fluorophenyl)-1*H*-pyrrole-2-carbaldehyde (**63**)**.** White solid (60%). Mp: 82°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.32-7.23 (m, 3H), 7.15 (m, 1H), 7.01 (m, 1H), 6.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6 (s), 156.9 (d, *J* = 253.8 Hz), 135.0 (d, *J* = 9.2 Hz), 132.8 (s), 131.5 (s), 128.9 (s), 126.3 (d, *J* = 12.9 Hz), 124.7 (d, *J* = 3.7 Hz), 124,0 (bs), 117,2 (d, *J* = 22.8 Hz), 111.3 (s). LC-MS (ESI): t_R = 4.55 min; $[M+H]^+$ 224.35. HRMS for $C_{11}H_8ClFNO$ $[M+H]^+$ calculated mass: 224.0272, measured: 224.0272.

(*E*) 1-(4-Chloro-2-fluorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**17**). Yellow solid (60%). Mp: 134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 13.4 and 0.6 Hz, 1H), 7.34 (dd, *J* = 1.9 and 0.5 Hz, 1H), 7.32 (m, 1H), 7.29 (m, 1H), 7.26-7.23 (m, 1H), 7.03 (m, 1H), 6.94 (dd, *J* = 4.0 and 1.4 Hz, 1H), 6.49 (dd, *J* = 3.8 and 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, *J* = 257.9 Hz), 136.2 (d, *J* = 9.6 Hz), 133.0 (s), 130.2 (s), 129.7 (s), 127.3 (s), 125.8 (s), 125.7 (d, *J* = 3.7 Hz), 124.6 (d, *J* = 12.3 Hz), 118.1 (d, *J* = 22.7 Hz), 116.5 (s), 112.5 (s). LC-MS (ESI): t_R = 5.02 min; $[M+H]^+$ 267.45. HRMS for $C_{12}H_9ClFN_2O_2$ $[M+H]^+$ calculated mass: 267.0331, measured: 267.0330.

(*E*) 1-(2,4-Dibromophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (18).



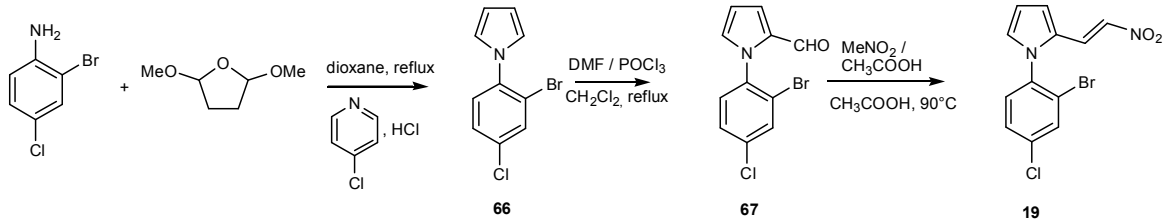
Synthetic procedure for compound (**18**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2,4-Dibromophenyl)-1*H*-pyrrole (**64**). Orange oil (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.2 Hz, 1H), 7.52 (dd, *J* = 8.1 and 1.9 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 2.4 Hz, 2H), 6.35 (t, *J* = 2.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 136.1, 131.3, 129.2, 122.1, 121.4, 120.6, 109.6. HRMS for $C_{10}H_8Br_2N$ $[M+H]^+$ calculated mass: 299.9018, measured: 299.9017.

1-(2,4-Dibromophenyl)-1*H*-pyrrole-2-carbaldehyde (**65**)**.** White solid (30%). Mp: 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.54 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.12 (dd, *J* = 3.9 and 1.7 Hz, 1H), 6.93 (m, 1H), 6.45 (dd, *J* = 3.8 and 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 138.1, 135.7, 132.7, 131.3, 130.9, 130.0, 123.2, 123.0, 122.9, 111.1. LC-MS (ESI): t_R = 4.92 min; $[M+H]^+$ 328.25. HRMS for $C_{11}H_8Br_2NO$ $[M+H]^+$ calculated mass: 327.8967, measured: 327.8963.

(*E*) 1-(2,4-Dibromophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**18**). Orange solid (60%). Mp: 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.4 and 2.2 Hz, 1H), 7.53 (d, *J* = 13.4 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 13.5 Hz, 1H), 7.00 (dd, *J* = 2.7 and 1.5 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.4 Hz, 1H), 6.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.3, 133.4, 132.6, 130.8, 130.3, 130.0, 128.4, 127.4, 125.8, 116.7, 112.3. LC-MS (ESI): t_R = 5.30 min; $[M+H]^+$ 371.30. HRMS for $C_{12}H_9Br_2N_2O_2$ $[M+H]^+$ calculated mass: 370.9025, measured: 370.9023.

(*E*) 1-(2-Bromo-4-chlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (19).



66 67 19

Synthetic procedure for compound (**19**) is is similar as that described for compound (**1**) and spectra data are shown below.

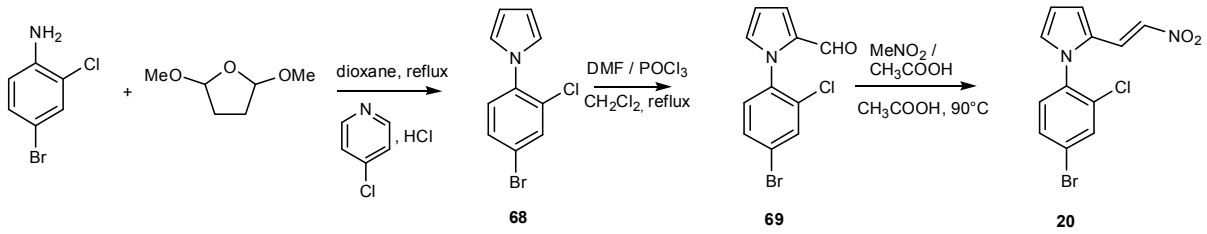
1-(2-Bromo-4-chlorophenyl)-1*H*-pyrrole (**66**).[8] Orange oil (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.25 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 2.2 Hz, 2H), 6.24 (t, *J* = 2.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 134.6, 133.6, 128.9, 128.5, 122.2, 120.4, 109.6.

1-(2-Bromo-4-chlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**67**). White solid (30%). Mp: 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.31 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.04 (dd, *J* = 4.1 and 1.7 Hz, 1H), 6.85 (m, 1H), 6.38 (dd, *J* = 3.9 and 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 137.6, 135.4, 133.0, 132.8, 131.0, 129.6, 128.3, 123.0, 122.6, 111.1. LC-MS (ESI): t_R = 4.80 min; $[M+H]^+$ 284.30. HRMS for $C_{11}H_8BrClNO$ $[M+H]^+$ calculated mass: 283.9472, measured: 283.9470.

[8] Sugita, K *et al* . Preparation of tricyclic compounds such as pyrrolobenzoxazepine derivatives and analogs thereof for treatment of hypercholesteremia, hyperlipemia, and arteriosclerosis. Jpn. Kokai Tokkyo Koho, 2008291018, 04 Dec 2008

(*E*) 1-(2-Bromo-4-chlorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**19**). Yellow solid (53%). Mp: 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 13.3 Hz, 1H), 7.48 (dd, *J* = 8.3 and 2.3 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 13.3 Hz, 1H), 6.99 (dd, *J* = 2.5 and 1.5 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.3 Hz, 1H), 6.49 (dd, *J* = 3.8 and 2.7 Hz 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.0, 133.7, 132.6, 130.4, 130.0, 129.0, 127.4, 125.7, 123.3, 116.9, 112.3. LC-MS (ESI): t_R = 5.23 min; $[M+H]^+$ 327.35. HRMS for $C_{12}H_9BrClN_2O_2$ calculated mass: 326.9530, measured: 326.9529

(*E*) 1-(4-Bromo-2-chlorophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (20).



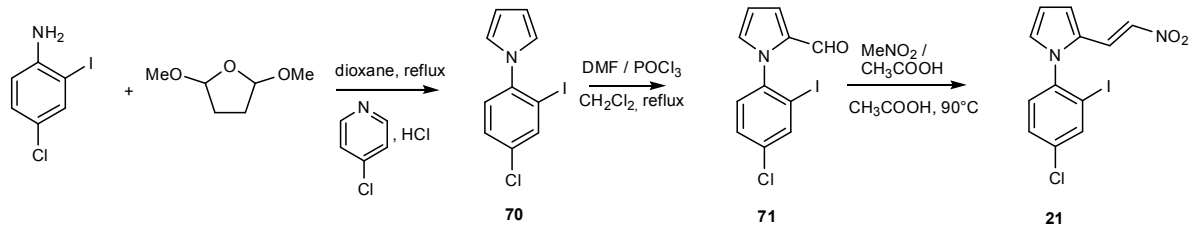
Synthetic procedure for compound (**20**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(4-Bromo-2-chlorophenyl)-1*H*-pyrrole (**68**). Orange oil (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.3 Hz, 1H), 7.47 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 2.1 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 133.3, 130.8, 130.6, 128.8, 122.0, 120.8, 109.7. HRMS for $C_{10}H_8BrClN$ $[M+H]^+$ calculated mass: 255.9523, measured: 255.9523.

1-(4-Bromo-2-chlorophenyl)-1*H*-pyrrole-2-carbaldehyde (**69**). Beige solid (31%). Mp: 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.50 (dd, *J* = 8.4 and 2.2 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.13 (dd, *J* = 4.0 and 1.7 Hz, 1H), 6.94 (m, 1H), 6.46 (dd, *J* = 3.9 and 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 136.5, 133.1, 132.9, 132.8 131.1, 130.7, 129.9, 123.2, 122.9, 111.2. LC-MS (ESI): t_R = 4.83 min; $[M+H]^+$ 284.25. HRMS for $C_{11}H_8BrClNO$ $[M+H]^+$ calculated mass: 283.9472, measured: 283.9468.

(*E*) 1-(4-Bromo-2-chlorophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**20**). Orange solid (57%). Mp: 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.1 Hz, 1H), 7.59 (dd, *J* = 8.3 and 2.1 Hz, 1H), 7.54 (d, *J* = 13.3 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 13.3 Hz, 1H), 7.00 (dd, *J* = 2.7 and 1.4 Hz, 1H), 6.95 (dd, *J* = 4.0 and 1.4 Hz, 1H), 6.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 133.6, 133.7, 132.6, 131.4, 130.6, 130.0, 127.4, 125.7, 124.1, 116.7, 112.4. LC-MS (ESI): t_R = 5.26 min; $[M+H]^+$ 327.35. HRMS for $C_{12}H_9BrClN_2O_2$ calculated mass: 326.9530, measured: 326.9529.

(*E*) 1-(4-Chloro-2-iodophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (21).



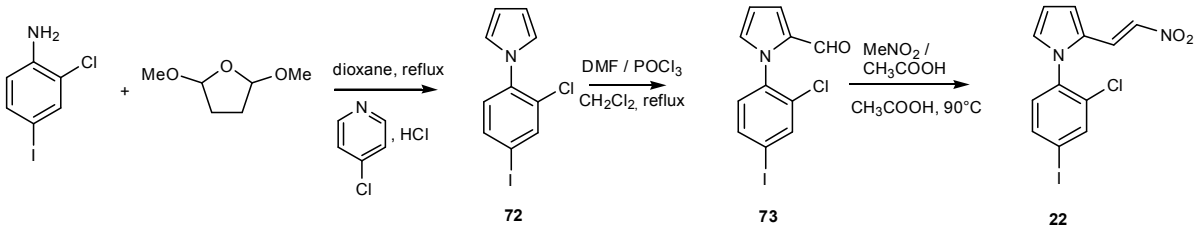
Synthetic procedure for compound (**21**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(4-Chloro-2-iodophenyl)-1*H*-pyrrole (**70**).[9] Yellow solid (88%). Mp: 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 2.3 Hz, 1H), 7.31 (dd, J = 8.4 and 2.2 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 6.74 (t, J = 2.2 Hz, 2H), 6.26 (t, J = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 139.2, 134.2, 129.1, 128.4, 122.1, 109.5, 96.0.

1-(4-Chloro-2-iodophenyl)-1*H*-pyrrole-2-carbaldehyde (**71**). Pink solid (30%). Mp: 62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.42 (dd, J = 8.3 and 2.2 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.12 (dd, J = 4.0 and 1.7 Hz, 1H), 6.90 (m, 1H), 6.46 (dd, J = 4.0 and 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 141.2, 138.8, 135.3, 132.5, 130.8, 129.1, 128.8, 122.9, 111.2, 97.8. LC-MS (ESI): t_R = 4.86 min; $[M+H]^+$ 332.23. HRMS for $C_{11}H_8ClINO$ $[M+H]^+$ calculated mass: 331.9333, measured: 331.9329.

(*E*) 1-(4-Chloro-2-iodophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**21**). Orange solid (57%). Mp: 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 2.0 Hz, 1H), 7.52 (m, 2H), 7.28 (d, J = 8.2 Hz, 1H), 7.07 (d, J = 13.3 Hz, 1H), 6.94 (m, 2H), 6.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 136.5, 132.6, 132.5, 129.9, 129.8, 129.5, 127.5, 125.4, 117.2, 112.4, 98.6. LC-MS (ESI): t_R = 5.35 min; $[M+H]^+$ 375.29. HRMS for $C_{12}H_9ClIN_2O_2$ calculated mass: 374.9391, measured: 374.9391

(*E*) 1-(2-Chloro-4-iodophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (22).



Synthetic procedure for compound (**22**) is similar as that described for compound (**1**) and spectra data are shown below.

1-(2-Chloro-4-iodophenyl)-1*H*-pyrrole (**72**). Orange oil (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 2.0 Hz, 1H), 7.57 (dd, J = 8.3 and 1.9 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.80 (t, J = 2.3 Hz, 2H), 6.27 (t, J = 2.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.6, 137.8,

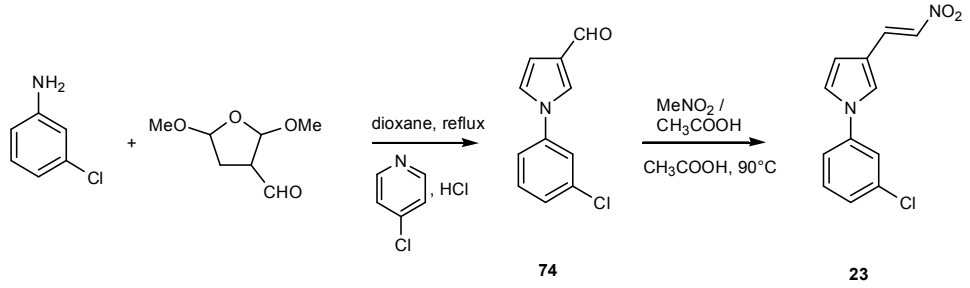
[9] Chai, D. *et al* . Mechanistic Studies of Pd-Catalyzed Regioselective Aryl C-H Bond Functionalization with Strained Alkenes: Origin of Regioselectivity. *Chemistry - A European Journal*, **29**, 8175-8188, S8175/1-S8175/54 (2011).

130.5, 129.0, 122.0, 109.8, 91.6. HRMS for $C_{10}H_8ClIN$ $[M+H]^+$ calculated mass: 303.9384, measured: 303.9384.

1-(2-Chloro-4-iodophenyl)-1*H*-pyrrole-2-carbaldehyde (**73**). Yellow solid (32%). Mp: 92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.69 (dd, *J* = 8.3 and 2.0 Hz, 1H), 7.13 (dd, *J* = 3.8 and 1.6 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.94 (m, 1H), 6.46 (dd, *J* = 3.9 and 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 138.5, 137.2, 136.6, 133.0, 132.8, 131.0, 130.1, 123.2, 111.2, 94.1. LC-MS (ESI): t_R = 4.98 min; $[M+H]^+$ 332.28. HRMS for $C_{11}H_8ClINO$ $[M+H]^+$ calculated mass: 331.9333, measured: 331.9329.

(*E*) 1-(2-Chloro-4-iodophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (**22**). Orange solid (57%). Mp: 96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.78 (dd, *J* = 8.2 and 1.9 Hz, 1H), 7.56 (d, *J* = 13.4 Hz, 1H), 7.17 (d, *J* = 13.3 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 7.00 (dd, *J* = 2.1 and 1.3 Hz, 1H), 6.95 (m, 1H), 6.49 (t, *J* = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.3, 135.5, 133.4, 132.6, 130.8, 130.0, 127.4, 125.7, 116.8, 112.4, 95.4. LC-MS (ESI): t_R = 5.35 min; $[M+H]^+$ 375.29. HRMS for $C_{12}H_9ClIN_2O_2$ calculated mass: 374.9391, measured: 374.9391.

(*E*) 1-(3-Chlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (23).



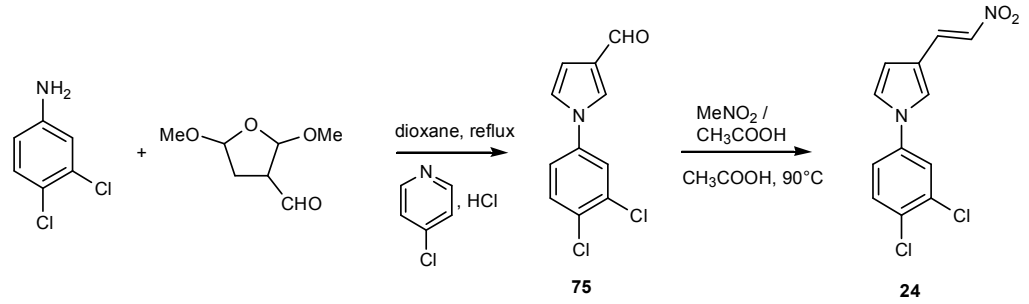
Synthetic procedure for compound (**23**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(3-Chlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**74**).[10] Brown solid (50%). Mp: 68°C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.66 (t, *J* = 2.0 Hz, 1H), 7.44 (t, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.37-7.31 (m, 2H), 7.07 (m, 1H), 6.81 (dd, *J* = 3.1 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 140.5, 135.6, 131.0, 128.5, 127.4, 127.0, 122.2, 121.4, 119.2, 110,0. LC-MS (ESI): t_R = 4.42 min; $[M+H]^+$ 206.34.

(*E*) 1-(3-chlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**23**). Brown solid (50%). Mp: 104 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 13.3 Hz, 1H), 7.46 (d, *J* = 13.3 Hz, 1H), 7.43-7.40 (m, 3H), 7.33 (dt, *J* = 8.1 and 1.0 Hz, 1H), 7.39 (dt, *J* = 8.0 and 1.0 Hz, 1H), 7.11 (t, *J* = 2.7 Hz, 1H), 6.57 (dd, *J* = 3.0 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 135.7, 134.3, 133.1, 131.0, 127.2, 124.9, 122.7, 121.1, 118.8, 118.2, 109.5. LC-MS (ESI): t_R = 5.15 min; $[M+H]^+$ 249.40. HRMS for $C_{12}H_{10}ClN_2O_2$ $[M+H]^+$ calculated mass: 249.0425, measured: 249.0424.

[10] McInnes, Campbell and Liu, Shu. Cyclin based inhibitors of CDK2 and CDK4. U.S. Pat. Appl. Publ., 20130289240, 31 Oct 2013.

(*E*) 1-(3,4-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (24) .

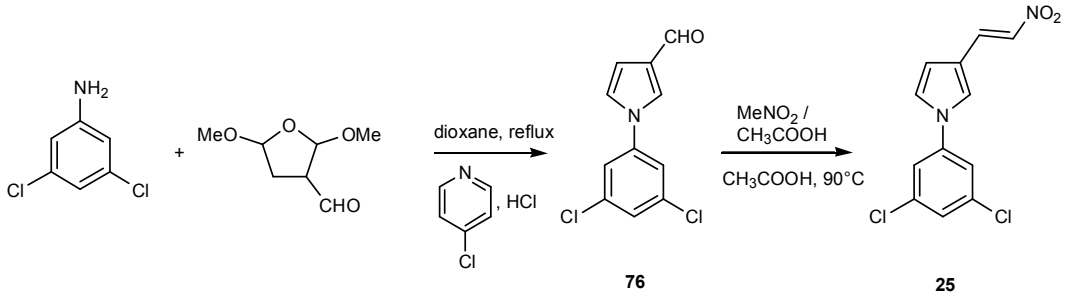


Synthetic procedure for compound (**24**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(3,4-Dichlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**75**).[11] Orange solid (30%). Mp: 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.56 (t, *J* = 1.9 Hz, 1H), 7.48 (m, 2H), 7.21 (dd, *J* = 8.6 and 2.6 Hz, 1H), 6.98 (t, *J* = 2.6 Hz, 1H), 6.74 (dd, *J* = 3.0 and 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 138.8, 134.0, 131.6, 131.4, 128.7, 126.8, 123.0, 122.1, 120.2, 110.0. LC-MS (ESI): t_R = 4.92 min; $[M+H]^+$ 240.26.

(*E*) 1-(3,4-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**24**) . Brown solid (40%). Mp: 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 13.2 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 2.9 Hz, 1H), 7.47 (d, *J* = 13.4 Hz, 1H), 7.41 (t, *J* = 2.0 Hz, 1H), 7.27 (dd, *J* = 8.6 and 2.6 Hz, 1H), 7.10 (t, *J* = 2.5 Hz, 1H), 6.59 (dd, *J* = 3.1 and 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6 134.6, 134.0, 132.8, 131.6, 131.2, 124.7, 122.7, 122.6, 119.9, 118.4, 109.8. LC-MS (ESI): t_R = 5.37 min; $[M+H]^+$ 283.44. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0036.

(*E*) 1-(3,5-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (25).



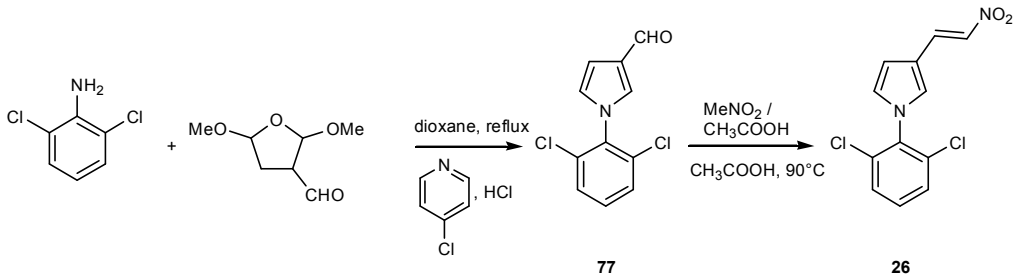
Synthetic procedure for compound (**25**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(3,5-Dichlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**76).** Brown solid (35%). Mp: 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.65 (t, *J* = 2.1 Hz, 1H), 7.36-7.34 (m, 3H), 7.07 (t, *J* = 2.8 Hz, 1H), 6.83 (dd, *J* = 3.0 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 141.1, 136.3, 128.8, 127.3, 126.7, 122.0, 119.7, 110.4. LC-MS (ESI): t_R = 4.85 min; $[M+H]^+$ 240.35. HRMS for $C_{11}H_8Cl_2NO$ $[M+H]^+$ calculated mass: 239.9975, measured: 239.9977.

[11] Haldar, P. *et al*. Sodium borohydride-iodine mediated reduction of γ-lactam carboxylic acids followed by DDQ mediated oxidative aromatization: a simple approach towards N-aryl-formylpyrroles and 1,3-diaryl-formylpyrroles. *Tetrahedron*, **14**, 3049-3056 (2007)

(*E*) 1-(3,5-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**25**) .Brown solid (40%). Mp: 190°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 13.3 Hz, 1H), 7.45 (d, *J* = 13.4 Hz, 1H), 7.41 (t, *J* = 1.9 Hz, 1H), 7.34 (t, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 2H), 7.10 (t, *J* = 2.7 Hz, 1H), 6.58 (dd, *J* = 3.0 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 136.3, 134.7, 132.6, 127.1, 124.5, 122.6, 119.3, 118.6, 109.9. LC-MS (ESI): t_R = 5.49 min; $[M+H]^+$ 283.40. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0035.

(*E*) 1-(2,6-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (26).

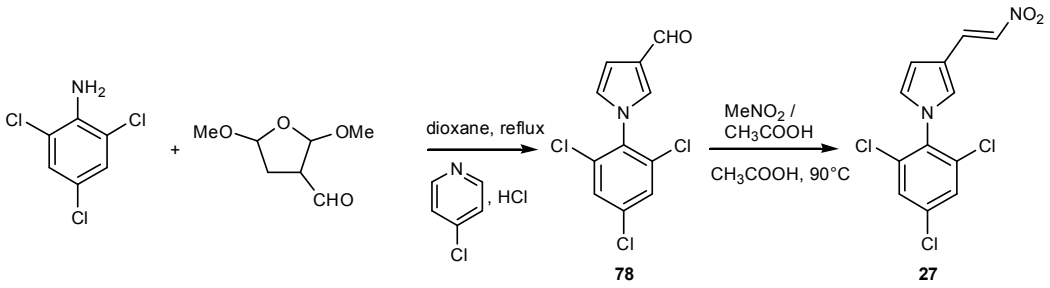


Synthetic procedure for compound (**26**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(2,6-Dichlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**77**).[6] White solid (30%). Mp: 92°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.42-7.39 (m, 2H), 7.30 (m, 1H), 7.27 (dd, *J* = 3.7 and 1.1 Hz, 1H), 6.75 (dd, *J* = 3.1 and 1.5 Hz, 1H), 6.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 135.5, 133.9, 130.6, 130.4, 128.9, 127.7, 124.7, 108.5. LC-MS (ESI): t_R = 4.85 min; $[M+H]^+$ 240.39.

(*E*) 1-(2,6-Dichlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**26**) .Yellow solid (50%). Mp: 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 13.2 Hz, 1H), 7.49-7.46 (m, 3H), 7.37 (dd, *J* = 8.8 and 7.3 Hz, 1H), 7.12 (m, 1H), 6.77 (m, 1H), 6.61-6.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 133.9, 133.4, 130.5, 129.9, 128.9, 128.1, 125.3, 117.1, 108.0. LC-MS (ESI): t_R = 5.08 min; $[M+H]^+$ 283.40. HRMS for $C_{12}H_9Cl_2N_2O_2$ $[M+H]^+$ calculated mass: 283.0035, measured: 283.0035.

(*E*) 3-(2-Nitrovinyl)-1-(2,4,6-trichlorophenyl)-1*H*-pyrrole (27).

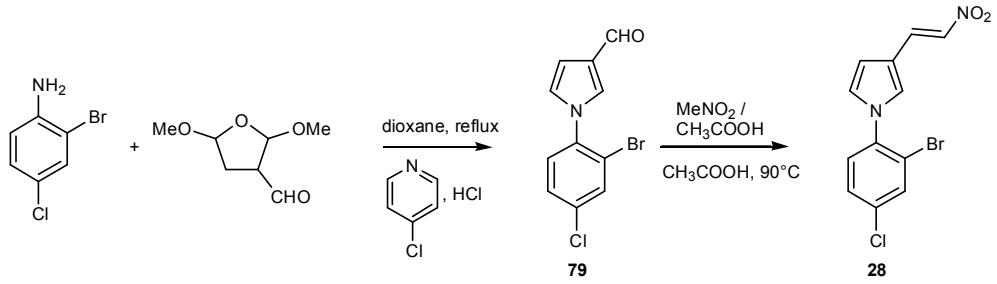


Synthetic procedure for compound (**27**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(2,4,6-Trichlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**78**)**.** Beige solid (30%). Mp: 74°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.50 (s, 2H), 7.31 (t, *J* = 2.0 Hz, 1H), 6.83 (dd, *J* = 3.1 and 1.5 Hz, 1H), 6.71-6.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 135.8, 134.6, 134.3, 130.1, 128.9, 127.9, 124.6, 108.8. LC-MS (ESI): t_R = 4.86 min; $[M+H]^+$ 274.31. HRMS for $C_{11}H_7Cl_3NO$ $[M+H]^+$ calculated mass: 273.9587, measured: 273.9582.

(*E*) 3-(2-Nitrovinyl)-1-(2,4,6-trichlorophenyl)-1*H*-pyrrole (**27**). Yellow solid (50%). Mp: 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 13.2 Hz, 1H), 7.50 (s, 2H), 7.47 (d, *J* = 13.3 Hz, 1H), 7.08 (t, *J* = 1.7 Hz, 1H), 6.73 (t, *J* = 6.7 Hz, 1H), 6.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 134.5, 134.3, 134.2, 133.1, 128.9, 127.9, 125.2, 117.3, 108.3. LC-MS (ESI): t_R = 5.39 min; $[M-H]^-$ 315.31. HRMS for $C_{12}H_8Cl_3N_2O_2$ $[M+H]^+$ calculated mass: 316.9645, measured: 316.9645.

(*E*) 1-(2-Bromo-4-chlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (28).



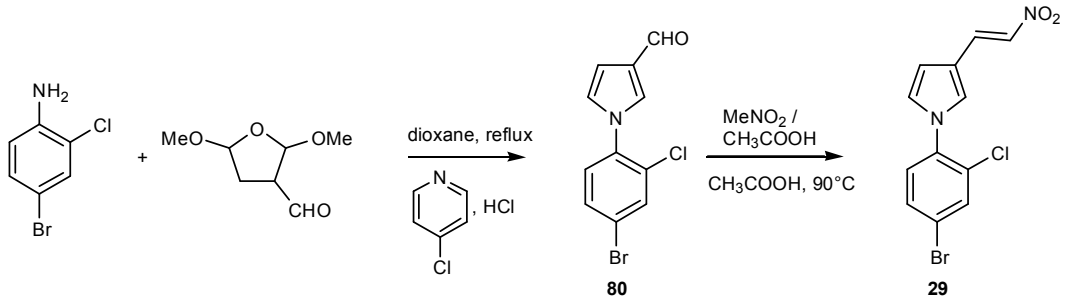
Synthetic procedure for compound (**28**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(2-Bromo-4-chlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**79**). Rose solid (32%). Mp: 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.74 (d, *J* = 2.3 Hz, 1H), 7.44 (t, *J* = 1.8 Hz, 1H), 7.42 (dd, *J* = 8.4 and 2.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.83 (m, 1H), 6.78 (dd, *J* = 3.0 and 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 137.8, 135.3, 133.7, 130.1, 128.7, 128.7, 127.7, 124.9, 120.4, 108.7. LC-MS (ESI): t_R = 4.72 min; $[M+H]^+$ 284.25. HRMS for $C_{11}H_8BrClNO$ $[M+H]^+$ calculated mass: 283.9472, measured: 283.9470.

(*E*) 1-(2-Bromo-4-chlorophenyl)-3-(2-nitrovinyl)-1 *H*-pyrrole (**28**). Yellow solid (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 13.2 Hz, 1H), 8.00 (d, *J* = 2.4 Hz, 1H), 7.93 (d, *J* = 13.1 Hz, 1H), 7.72 (t, *J* = 1.8 Hz, 1H), 7.61 (dd, *J* = 8.5 and 2.4 Hz, 1H), 7.53 (d, *J* = 8.6 Hz 1H), 7.13 (t, *J* = 1.8 Hz, 1H), 6.82 (dd, *J* = 2.8 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 138.2, 134.9, 134.5, 134.3, 133.3, 130.3, 130.0, 129.4, 126.4, 120.4, 117.4, 109.2. LC-MS (ESI): t_R = 5.36 min; $[M+H]^+$ 327.35. HRMS for $C_{12}H_9BrClN_2O_2$ $[M+H]^+$ calculated mass: 326.9530, measured: 326.9529.

(*E*) 1-(4-Bromo-2-chlorophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (29).

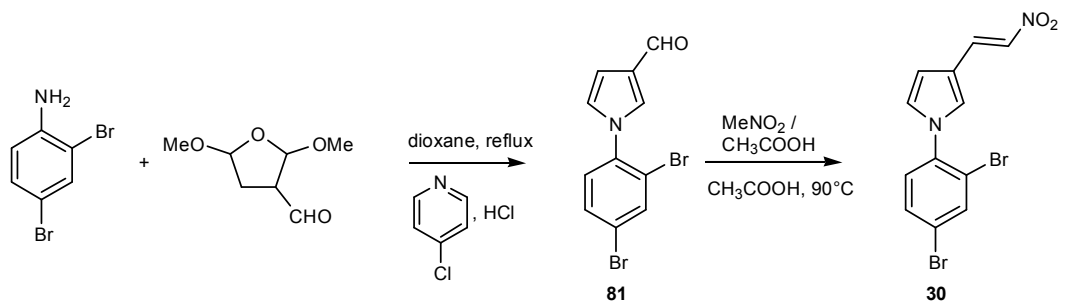


Synthetic procedure for compound (**29**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(4-Bromo-2-chlorophenyl)-1*H*-pyrrole-3-carbaldehyde (**80**). Orange solid (34%). Mp: 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.75 (d, *J* = 2.1 Hz, 1H), 7.55 (dd, *J* = 8.4 and 2.1 Hz, 1H), 7.50 (t, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 6.89 (t, *J* = 2.7 Hz, 1H), 6.82 (dd, *J* = 2.9 and 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 136.6, 133.6, 131.2, 130.8, 130.0, 128.7, 127.8, 124.8, 122.5, 108.9. LC-MS (ESI): t_R = 4.76 min; $[M+H]^+$ 284.21. HRMS for $C_{11}H_8BrClNO$ $[M+H]^+$ calculated mass: 283.9472, measured: 283.9470.

(*E*) 1-(4-Bromo-2-chlorophenyl)-3-(2-nitrovinyl)-1 *H*-pyrrole (**29**).Yellow solid (55%). Mp: 182°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, *J* = 13.3 Hz, 1H), 8.00 (dd, *J* = 2.1 and 0.9 Hz, 1H), 7.93 (d, *J* =13.3 Hz, 1H), 7.76 (bs, 1H), 7.71 (ddd, *J* = 8.5, 2.1, and 0.9 Hz, 1H), 7.49 (dd, *J* = 8.4 and 0.8 Hz, 1H), 7.17 (m, 1H), 6.83 (m, 2.8 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.9, 134.8, 134.6, 133.3, 132.0, 130.2, 130.1, 130.0, 126.3, 122.1, 117.6, 109.3. LC-MS (ESI): t_R = 5.38 min; $[M+H]^+$ 327.35. HRMS for $C_{12}H_9BrClN_2O_2$ $[M+H]^+$ calculated mass: 326.9530, measured: 326.9528.

(*E*) 1-(2,4-Dibromophenyl)-2-(2-nitrovinyl)-1*H*-pyrrole (30).

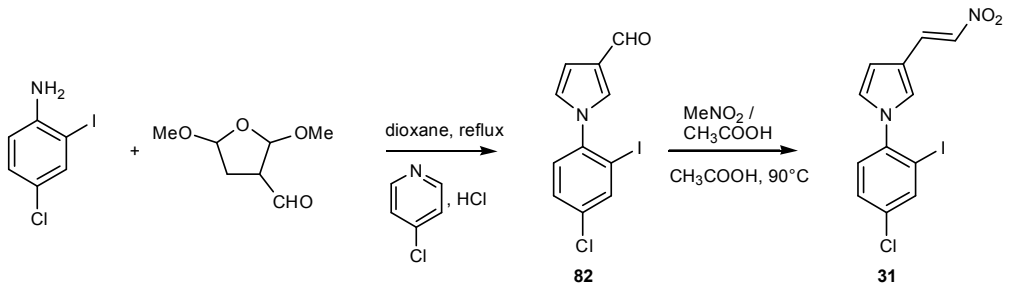


Synthetic procedure for compound (**30**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(2,4-Dibromophenyl)-1*H*-pyrrole-3-carbaldehyde (**81**). Pink solid (32%). Mp: 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.89 (d, *J* = 2.1 Hz, 1H), 7.57 (dd, *J* = 8.5 and 2.1 Hz, 1H), 7.45 (t, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.84 (m, 1H), 6.78 (m, 1H), . ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 138.2, 136.4, 131.7, 130.0, 129.1, 127.7, 124.8, 123.0, 120.6, 108.7. LC-MS (ESI): t_R = 4.81 min; $[M+H]^+$ 328.25.

(*E*) 1-(2,4-Dibromophenyl)-2-(2-nitrovinyl)-1 *H*-pyrrole (**30**). Yellow solid (52%). Mp: 190 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (s, 1H), 8.08 (d, *J* = 13.2 Hz, 1H), 7.92 (d, *J* = 13.1 Hz, 1H), 7.73 (dd, *J* = 8.4 and 2.1 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.12 (m, 1H), 7.17 (m, 1H), 6.80 (dd, 3.0 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.6, 136.0, 134.9, 134.5, 132.4, 130.3, 130.2, 126.4, 122.6, 120.6, 117.4, 109.2. LC-MS (ESI): t_R = 5.44 min; $[M+H]^+$ 369.37. HRMS for $C_{12}H_9Br_2N_2O_2$ $[M+H]^+$ calculated mass: 370.9025, measured: 370.9023.

(*E*) 1-(4-Chloro-2-iodophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (31).

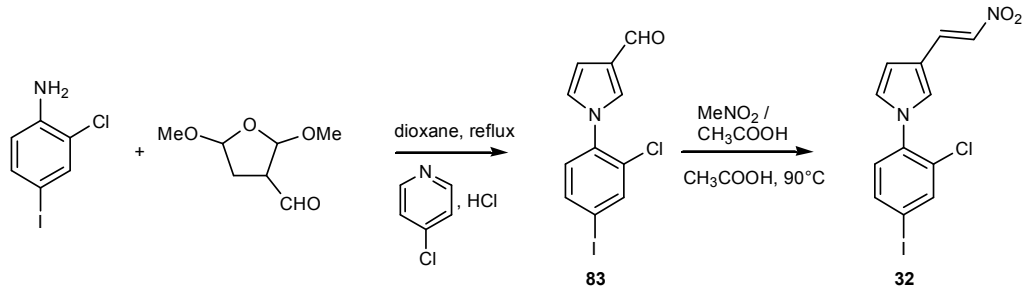


Synthetic procedure for compound (**31**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(4-Chloro-2-iodophenyl)-1*H*-pyrrole-3-carbaldehyde (**82**). Yellow solid (31%). Mp: 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.4 and 2.3 Hz, 1H), 7.31 (t, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 141.3, 139.5, 135.5, 130.0, 129.5, 128.2, 127.7, 124.8, 108.8, 95.6. LC-MS (ESI): t_R = 4.81 min; $[M+H]^+$ 332.23. HRMS for $C_{11}H_8ClINO$ $[M+H]^+$ calculated mass: 331.9333, measured: 331.9328.

(*E*) 1-(4-Chloro-2-iodophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**31**).Yellow solid (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 13.3 Hz, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 13.3 Hz, 1H), 7.45 (dd, *J* = 2.3 and 8.3 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 1.8 Hz, 1H), 6.82 (t, *J* = 2.8 Hz, 1H), 6.55 (dd, *J* =2.9 and 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.9, 137.2, 137.1, 134.2, 133.2, 130.5, 128.7, 127.8, 125.3, 117.3, 108.3. LC-MS (ESI): t_R = 5.40 min; $[M-H]^-$ 373.32. HRMS for $C_{12}H_9ClIN_2O_2$ $[M+H]^+$ calculated mass: 374.9391, measured: 374.9390.

(*E*) 1-(2-Chloro-4-iodophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (32).



Synthetic procedure for compound (**32**) is similar as that described for compound (**2**) and spectra data are shown below.

1-(4-Chloro-2-iodophenyl)-1*H*-pyrrole-3-carbaldehyde (**83**). Beige solid (35%). Mp: 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.91 (d, J = 1.8 Hz, 1H), 7.72 (dd, J = 8.3 and 1.8 Hz, 1H), 7.48 (t, J = 1.8 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.87 (m, 1H), 6.79 (dd, J = 3.2 and 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 139.3, 137.2, 137.1 130.6, 130.0, 128.9, 127.8, 124.7, 108.8, 93.5. LC-MS (ESI): t_R = 4.87 min; $[M+H]^+$ 332.28. HRMS for $C_{11}H_8ClINO$ $[M+H]^+$ calculated mass: 331.9333, measured: 331.9328.

(*E*) 1-(2-Chloro-4-iodophenyl)-3-(2-nitrovinyl)-1*H*-pyrrole (**32**). Yellow solid (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 13.4 Hz, 1H), 7.91 (d, J = 1.9 Hz, 1H), 7.72 (dd, J = 8.2 and 2.0 Hz, 1H), 7.46 (d, J = 13.5 Hz, 1H), 7.25 (t, 1.9 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.91(m, 1H), 6.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.9, 137.2, 137.1, 134.2, 133.2, 130.5, 128.7, 127.8, 125.3, 117.3, 108.3. LC-MS (ESI): t_R = 5.47 min; $[M-H]^-$ 373.27. HRMS for $C_{12}H_9ClIN_2O_2$ $[M+H]^+$ calculated mass: 374.9391, measured: 374.9390.