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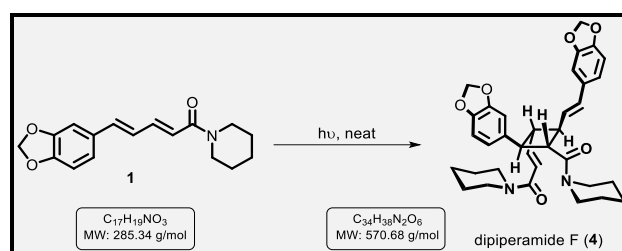
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1. General procedures

Reactions were carried out under an argon atmosphere when required. All reagent-grade chemicals and other solvents were obtained from commercial suppliers and were used as received. **Batch reactions** were performed using an Hepatochem® PhotoRedOx Box™ photoreactor: <https://hepatochem.com/photoreactors-leds-accessories/photoredox-box/> **Batch and flow reactions** were performed using a Kessil® PR160L blue LEDs lamp [456 nm] : https://kessil.com/products/science_PR160L.php **Analytical and preparative TLC** were performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by direct observation or UV light and by staining upon heating with vanillin solution (2 g vanillin, 1 mL conc. H₂SO₄, 100 mL EtOH). **Flash column chromatography** employed VWR (230–400 mesh) silica gel. **Automated chromatography** were performed on a Serlabo Combiflash Ez Prep chromatography system equipped with a Buchi FlashPure silica cartridge. The **NMR spectra** were recorded on a Bruker Avance-300 (300 MHz) spectrometer and on a Bruker Avance-400 (400 MHz) spectrometer and on a Bruker Avance-NEO (ASCEND 500 MHz) equipped with a Cryo-Prob-3mm (500 MHz) spectrometer. ¹H NMR spectra were recorded at 300 MHz or at 400 MHz and residual solvent peaks were used as an internal reference (chloroform-*d* 7.26 ppm, DMSO-*d*₆ 2.50 ppm, methanol-*d*₄ 3.31 ppm). Data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, p = pentuplet, m = multiplet or overlap of non-equivalent resonances), coupling constants, and integration. ¹³C{¹H} NMR spectra were recorded at 75 MHz or at 101 MHz and residual solvent peaks were used as an internal reference (chloroform-*d* d 76.1 ppm, DMSO-*d*₆ 39.5 ppm, methanol-*d*₄ 49.0 ppm) using a UDEFT sequence (Uniform Driven Equilibrium Fourier Transform) or a JMOD sequence (*J*-Modulated Spin-Echo). **IR spectra** were recorded with a Shimadzu IR Affinity-1S spectrometer and are reported in frequency of absorption at the peak maximum (cm⁻¹). **HRESIMS** and LC/MS (Agilent HPLC HP1290) were run using Electrospray Ionization (ESI) on an Agilent QToF 6546 spectrometer with a Sunfire® analytical C18 column (150 × 2.1 mm; 3.5 μm, Waters).

2. Dimerization of piperine

2.1. Procedure for the dimerization of piperine (solid state)



A solution of piperine (**1**) (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was evaporated in a crystallizing dish ($\varnothing = 8$ cm) and then irradiated with a blue LEDs light [LEDs strip Lights – RGB 5050 RGB – 150 LEDs – ~ 465 nm] for 10 d. Purification by preparative TLC on silica gel (eluent: $CH_2Cl_2/MeOH$, 99:1) afforded dipiperamide F (**4**) as a white solid (11 mg, 22 %).

2.2. Screening of photocatalytic conditions for the dimerization of piperine

A solution of piperine (**1**) (30 mg, 0.105 mmol, 1.0 equiv), catalyst (0.005 mmol, 0.05 equiv) and additive (see Table S1) in solvent (1.0 mL) was prepared in a glass tube. Solution was irradiated in an Hepatochem® PhotoRedOx Box™ photoreactor equipped with a Kessil® PR160L blue LEDs lamp [456 nm]. After 16 h reaction mixtures were analyzed by HPLC-MS analysis.

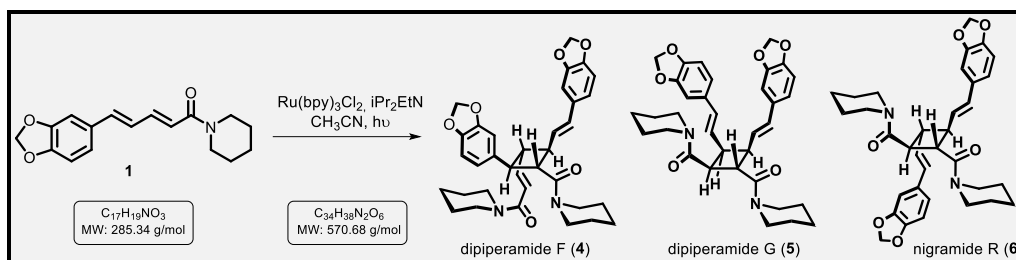
Table S1 : Screening of conditions for the dimerization of piperine (**1**)

Entry	catalyst	conditions	Result / isolated yield
1	-	Neat 10d white lamp ^[a]	> 10 dimers
2	-	Neat 10d blue LEDs	4 : 22%
3	-	CH_3CN , 10d blue LEDs	No reaction
4	$Ru(bpy)_3Cl_2$ 5%-mol	CH_3CN , Ar atm. blue LEDs, 16h	Low conversion (<10%)
5	$Ru(bpy)_3Cl_2$ 5%-mol	CH_3CN , Air atm. blue LEDs, 16h	Low conversion (<10%)
6	$Ru(bpy)_3Cl_2$ 5%-mol	CH_3CN , $MVCl_2$ ^[a] (2 equiv). blue LEDs, 16h	Low conversion
7	$Ru(bpy)_3Cl_2$ 5%-mol	CH_3CN , 4,4-di-tbu-biphenyl (2 equiv). blue LEDs, 16h	Low conversion
8	$Ru(bpy)_3Cl_2$ 5%-mol	CH_3CN , iPr_2EtN (2.0 equiv.) blue LEDs, 16h	4 : 7%; 5 : 26% 6 : 45%
9	$Ru(bpy)_3Cl_2$ 5%-mol	CH_3CN , iPr_2EtN (2.0 equiv.) no light	No conversion
10	$Ru(bpy)_3Cl_2$ 5%-mol	DMSO, iPr_2EtN (2.0 equiv.) blue LEDs, 16h	1 : 6%; 4 : 9%; 5 : 15% 6 : 31%

12	Ru(bpy) ₃ Cl ₂ 5%-mol	DMF, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	1: 11%; 4: 10%; 5: 33% 6: 38%
13	Ru(bpy) ₃ Cl ₂ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.), LiBF ₄ (4 equiv.), blue LEDs, 16h	4: 17%; 6: 15%, 10: 15%
14	Ru(bpy) ₃ Cl ₂ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.), LiBF ₄ (4.0 equiv.), blue LEDs, 40h	4: 17%; 10: 33%
15	Ru(phen) ₃ Cl ₂ 5%-mol	CH ₃ CN, Ar atm. blue LEDs, 7d	4: 8%; 5: 12% 6: 34%
16	Ru(phen) ₃ Cl ₂ 5%-mol	CH ₃ CN, Ar atm. blue LEDs, 40h	< 5% conversion
17	Ru(phen) ₃ Cl ₂ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.) blue LEDs, 40h	< 5% conversion
18	Ru(phen) ₃ Cl ₂ 5%-mol	CH ₃ CN, air atm. blue LEDs, 40h	< 5% conversion
19	Ru(bpz) ₃ (PF ₆) ₂ 5%-mol	CH ₃ CN, Ar atm. blue LEDs, 16h	No conversion
20	Ru(bpz) ₃ (PF ₆) ₂ 5%-mol	CH ₃ CN, Air atm. blue LEDs, 16h	No conversion
21	Ru(bpz) ₃ (PF ₆) ₂ 5%-mol	CH ₃ CN, MVCl ₂ ^[a] (2 equiv.) blue LEDs, 16h	No conversion
22	Ru(bpz) ₃ (PF ₆) ₂ 5%-mol	CH ₃ CN, 4,4-di-tbu-biphenyl (2 equiv.) blue LEDs, 16h	No conversion
23	Ru(bpz) ₃ (PF ₆) ₂ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	No conversion
24	Ru(bpm) ₃ Cl ₂ 5%-mol	CH ₃ CN, air atm. blue LEDs, 40h	< 5% conversion
25	Ru(bpm) ₃ Cl ₂ 5%-mol	CH ₃ CN, Ar atm. blue LEDs, 16h	No conversion
26	Ru(bpm) ₃ Cl ₂ 5%-mol	CH ₃ CN, Air atm. blue LEDs, 16h	No conversion
27	Ru(bpm) ₃ Cl ₂ 5%-mol	CH ₃ CN, MVCl ₂ ^[a] (2 equiv.) blue LEDs, 16h	No conversion
28	Ru(bpm) ₃ Cl ₂ 5%-mol	CH ₃ CN, 4,4-di-tbu-biphenyl (2 equiv.) blue LEDs, 16h	No conversion
29	Ru(bpm) ₃ Cl ₂ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	No conversion
30	Ir(ppy) ₃ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	11: 53%; 12: 12%
31	Ir(ppy) ₃ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.) no light	No conversion
32	Ir(ppy) ₃ 5%-mol	CH ₃ CN, Ar atm. blue LEDs, 16h	No conversion
33	Ir(ppy) ₃ 5%-mol	CH ₃ CN, Air atm. blue LEDs, 16h	No conversion
34	Ir(ppy) ₃ 5%-mol	CH ₃ CN, morpholine (2.0 equiv.) blue LED, 16h	11: 41%; 12: 19%
35	Ir(ppy) ₃ 5%-mol	DMSO, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	11: 36%; 12: 8%
36	Ir(ppy) ₃ 5%-mol	DMF, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	11: 46%; 12: 16%
37	[Ir(dtbbpy)(ppy) ₂] PF ₆ 5%-mol	CH ₃ CN, Ar atm. blue LEDs, 16h	No conversion
38	[Ir(dtbbpy)(ppy) ₂] PF ₆ 5%-mol	CH ₃ CN, Air atm. blue LEDs, 16h	No conversion
39	[Ir(dtbbpy)(ppy) ₂] PF ₆ 5%-mol	CH ₃ CN, MVCl ₂ ^[a] (2 equiv.) blue LEDs, 16h	< 15% conversion
40	[Ir(dtbbpy)(ppy) ₂] PF ₆ 5%-mol	CH ₃ CN, 4,4-di-tbu-biphenyl (2 equiv.) blue LEDs, 16h	< 15% conversion
41	[Ir(dtbbpy)(ppy) ₂] PF ₆ 5%-mol	CH ₃ CN, iPr ₂ EtN (2.0 equiv.) blue LEDs, 16h	degradation

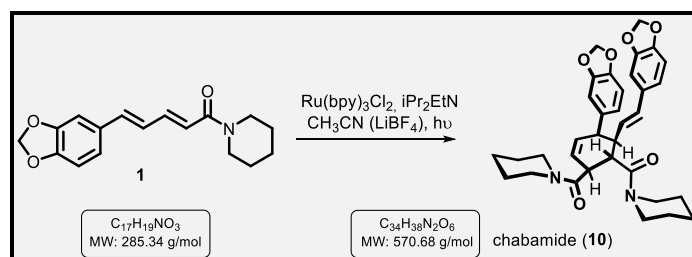
42	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2-(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , Ar atm. blue LEDs, 16h	< 10% conversion
43	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2-(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , Air atm. blue LEDs, 16h	< 10% conversion
44	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2-(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , $\text{MVC1}_2^{\text{[a]}}$ (2 equiv). blue LEDs, 16h	degradation
45	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2-(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , 4,4-di-tbu-biphenyl (2 equiv). blue LEDs, 16h	degradation
46	$[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , Ar atm. blue LEDs, 16h	No conversion
47	$[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , Air atm. blue LEDs, 16h	No conversion
47	$[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , $\text{MVC1}_2^{\text{[a]}}$ (2 equiv). blue LEDs, 16h	No conversion
47	$[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$ 5%-mol	CH_3CN , 4,4-di-tbu-biphenyl (2 equiv). blue LEDs, 16h	No conversion

2.3. [2+2] cycloadditions dimerization of piperine mediated by Ru(bpy)₃Cl₂



A solution of piperine (**1**) (30 mg, 0.105 mmol, 1.0 equiv), Ru(bpy)₃Cl₂ (3.8 mg, 0.005 mmol, 0.05 equiv) and *i*Pr₂EtN (37 μ L, 0.212 mmol, 2.0 equiv) in CH₃CN (1.0 mL) was prepared in a glass tube. Solution was irradiated in an Hepatochem® PhotoRedOx Box™ photoreactor with a blue LEDs light [Kessil®, PR160L, 456 nm, 50W, 100% intensity]. After 16 h of reaction 4 batches were combined and concentrated under reduced pressure. Purification by preparative TLC on silica gel (eluent: CH₂Cl₂/MeOH, 99:1) afforded nigramide R (**6**) as white solid (R_f = 0.39, 54 mg, 45 %), dipiperamide G (**5**) as white solid (R_f = 0.26, 31 mg, 26 %) and dipiperamide F (**4**) as white solid (R_f = 0.19, 8 mg, 7 %).

2.4. [4+2] cycloadditions dimerization of piperine mediated by Ru(bpy)₃Cl₂

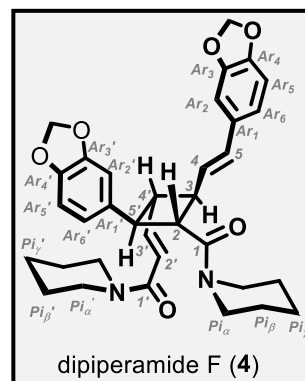


A solution of piperine (**1**) (30 mg, 0.105 mmol, 1.0 equiv), Ru(bpy)₃Cl₂ (3.8 mg, 0.005 mmol, 0.05 equiv) and *i*Pr₂EtN (37 μ L, 0.212 mmol, 2.0 equiv) in CH₃CN (1.0 mL) was prepared in a glass hemolysis tube. A solution of LiBF₄ in CH₃CN (1.0 M, 420 μ L, 0.420 mmol, 4.0 equiv) was added. Solution was irradiated in an Hepatochem® PhotoRedOx Box™ photoreactor with a blue LEDs light [Kessil®, PR160L, 456 nm, 50W, 100% intensity]. Then, the reaction mixture was concentrated under reduced pressure. Purification by preparative TLC on silica gel (eluent: CH₂Cl₂/MeOH, 199:1) afforded chabamide (**10**) as a white solid (R_f = 0.37, 10 mg, 33 %) and dipiperamide F (**4**) as white solid (R_f = 0.19, 5 mg, 17 %).

2.5. Dipiperamide F (4)

Consistent with the literature description.¹

- **R_f** = 0.19 (CH₂Cl₂/MeOH, 99:1);
- **¹H NMR** (400 MHz, chloroform-d) δ: 6.95 (dd, *J* = 15.2, 6.6 Hz, 1H), 6.89 (d, *J* = 1.5 Hz, 1H), 6.79 – 6.69 (m, 5H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.28 (dd, *J* = 15.2, 1.3 Hz, 1H), 6.09 (dd, *J* = 15.7, 7.4 Hz, 1H), 5.95 (s, 2H), 5.93 (s, 2H), 3.66 – 3.38 (m, 7H), 3.26 (m, 1H), 3.16 (m, 1H), 3.12 (m, 1H), 3.09 (m, 1H), 2.94 (q, *J* = 8.6 Hz, 1H), 1.69 – 1.59 (m, 4H), 1.58 – 1.16 (m, 8H);
- **¹³C{¹H} NMR ppm** (101 MHz, chloroform-d): δ 169.9, 165.1, 148.1, 147.9, 147.2, 146.4, 145.1, 135.7, 131.3, 131.1, 128.4, 120.9, 120.3, 120.2, 108.33, 108.27, 107.3, 105.5, 101.1, 101.0, 48.9, 48.1, 46.9, 46.6, 45.6, 45.0, 43.4 (2C), 26.9 (2C), 26.8 (2C), 24.6, 24.4;
- **IR** (neat) ν = 2919, 2852, 1651, 1606, 1504, 1489, 1443, 1250, 1038 cm⁻¹;
- **HRMS(ESI)**: *m/z* calcd. for C₃₄H₃₉N₂O₆⁺ [M + H]⁺ 571.2803; found 571.28075.



¹ R. Muharini, Z. Liu, W. Lin, P. Proksch, *Tetrahedron Lett.* **2015**, 56, 2521–2525.

Table S2: Comparison of the ¹H NMR and ¹³C NMR data of synthetic and natural dipiperamide F in chloroform-*d*.

Attribution	synthetic			natural			Δ ¹ H	synthetic		natural	
	¹ H δ (ppm)	m, J (Hz)	int.	¹ H δ (ppm)	m, J (Hz)	¹³ C δ (ppm)		¹³ C δ (ppm)	Δ ¹³ C		
1	-	-	-	-	-	-	169.9	169.9	0.0		
2	3.09	m	1	3.09	m	0.00	48.9	44.3	-4.6		
3	3.12	m	1	3.12	m	0.00	45.0	44.8	-0.2		
4	6.09	dd (J = 15.7, 7.4 Hz)	1	6.09	dd (J = 15.7, 7.6 Hz)	0.00	128.4	127.8	-0.6		
5	6.40	d (J = 15.7 Hz)	1	6.40	d (J = 15.7 Hz)	0.00	131.0	130.8	-0.2		
Ar₁	-	-	-	-	-	-	131.3	131.4	0.1		
Ar₂	6.89	d (J = 1.5 Hz)	1	6.89	d (J = 1.3 Hz)	0.00	105.5	105.0	-0.5		
Ar₃	-	-	-	-	-	-	147.9	147.6	-0.3		
Ar₄	-	-	-	-	-	-	146.4	146.6	0.2		
Ar₅	6.79 – 6.69	m	1	6.72	d (J = 8.9 Hz)	-	108.3	107.9	-0.4		
Ar₆	6.79 – 6.69	m	1	6.75	dd (J = 8.9, 1.3 Hz)	-	120.9	119.9	-1.0		
[O-CH₂-O]	5.93*	s	2	5.91	s	-0.02	101.0*	100.9	-0.1		
1'	-	-	-	-	-	-	165.1				
2'	6.28	dd (J = 15.2, 1.3 Hz)	1	6.29	dd (J = 15.1, 1.3 Hz)	0.01	120.3	120.0	0.3		
3'	6.95	dd (J = 15.2, 6.6 Hz)	1	6.94	dd (J = 15.1, 6.6 Hz)	-0.01	145.1	144.3	-0.8		
4'	2.94	q (J = 8.6 Hz)	1	2.94	q (J = 8.3 Hz)	0.00	48.0	47.3	-0.7		
5'	3.59	m	1	3.59	m	0.00	45.6	45.2	-0.4		
Ar₁'	-	-	-	-	-	-	135.7	135.0	-0.3		
Ar₂'	6.79 – 6.69	m	1	6.78	d (J = 1.3 Hz)	-	107.3	106.9	-0.4		
Ar₃'	-	-	-	-	-	-	148.0	147.6	-0.4		
Ar₄'	-	-	-	-	-	-	147.2	147.0	-0.2		
Ar₅'	6.79 – 6.69	m	1	6.72	d (J = 8.2 Hz)	-	108.3	108.0	-0.3		
Ar₆'	6.79 – 6.69	m	1	6.75	dd (J = 8.2, 1.3 Hz)	-	120.1	120.6	-0.5		
[O-CH₂-O]'	5.95*	s	2	5.93	s	-0.02	101.1*	100.9	-0.2		
PI_a	3.54 – 3.16	m	4	3.60	m	-	43.3	43.1	-0.2		
				3.43	m	-					
				3.22	m	-	46.9	46.8	0.2		
				3.12	m	-					
PI_b	1.58 – 1.16	m	4	1.50	m	-	26.8*	25.2	-0.6		
				1.23	m	-		25.2			
PI_v	1.58 – 1.16	m	2	1.50	m	-	24.6	24.5	0.1		
PI_a'	3.54 – 3.46	m	4	3.54	m	-	43.3	42.7	-0.6		
				3.40	m	-	46.6	46.3	-0.3		
PI_b'	1.58 – 1.16	m	4	1.50	m	-	26.9*	25.9	-0.2		
PI_v'	1.67 – 1.58	m	2	1.60	m	-	24.4	24.7	-0.3		

*signals interchangeable

2.6. Dipiperamide G (5)

Consistent with the literature description.¹

- **R_f** = 0.26 (CH₂Cl₂/MeOH, 99:1);
- **¹H NMR** (400 MHz, chloroform-d) δ: 6.88 (d, *J* = 1.5 Hz, 1H), 6.80 (s, 1H), 6.76 – 6.67 (m, 4H), 6.39 – 6.28 (m, 2H), 6.20 (dd, *J* = 15.0, 8.2 Hz, 1H), 6.04 (dt, *J* = 14.9, 7.5 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 2H), 5.91 (q, *J* = 1.4 Hz, 2H), 4.21 (m, 1H), 3.91 (m, 1H), 3.81 – 3.33 (m, 9H), 3.23 (m, 1H), 1.70 – 1.40 (m, 12H);
- **¹³C{¹H} NMR ppm** (101 MHz, chloroform-d): δ 171.0, 169.0, 148.0, 147.9, 147.1, 147.0, 133.2, 131.6, 131.5, 131.4, 127.1, 124.9, 120.8, 120.7, 108.2 (2C), 105.8, 105.6, 101.0, 100.9, 46.9, 45.9, 44.7, 43.3, 42.7 (2C), 41.5, 40.9, 26.9, 26.2, 25.7, 25.6, 24.6, 24.4;
- **IR** (neat) *ν* = 2923, 2855, 1630, 1504, 1489, 1443, 1251, 1039 cm⁻¹;
- **HRMS(ESI)**: *m/z* calcd. for C₃₄H₃₉N₂O₆⁺ [M + H]⁺ 571.2803; found 571.2806.

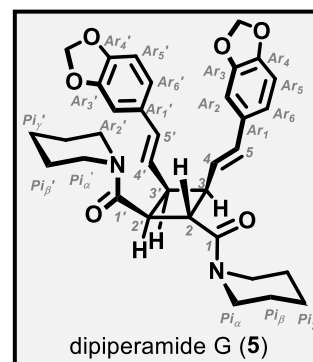


Table S3: Comparison of the ^1H NMR and ^{13}C NMR data of synthetic and natural dipiperamide G in chloroform- d .

Attribution	synthetic			natural			Δ ^1H	synthetic		natural	
	^1H δ (ppm)	m, J (Hz)	int.	^1H δ (ppm)	m, J (Hz)			^{13}C δ (ppm)	^{13}C δ (ppm)	Δ ^{13}C	
1	-	-	-	-	-	-	171.0	171.1	0.1		
2	4.21	m	1	4.18	t (J = 8.7 Hz)	-0.03	40.9	40.7	-0.2		
3	3.44	m	1	3.44	m	0.00	43.3	43.4	0.01		
4	6.04	dt (J = 14.9, 7.5 Hz)	1	6.04	q (J = 15.5, 8.5 Hz)	0.00	127.1	126.9	-0.2		
5	6.35 – 6.28	m	1	6.31	d (J = 15.5 Hz)		131.6	131.0	-0.6		
Ar ₁	-	-	-	-	-	-	131.4	131.7	0.3		
Ar ₂	6.80	s	1	6.81	s	0.01	105.6	105.4	-0.2		
Ar ₃	-	-	-	-	-	-	147.0*	146.9	-0.1		
Ar ₄	-	-	-	-	-	-	147.9 [#]	147.3	-0.6		
Ar ₅	6.74 – 6.67		1	6.68	overlapped	-		108.0			
Ar ₆	6.76 – 6.67		1	6.72	overlapped	-		120.6			
[O-CH ₂ -O]	5.93	d (J = 1.1 Hz)	2	5.93	m	0.00	101.1	101.0	-0.1		
1'	-	-	-	-	-	-	169.0	168.8	-0.2		
2'	3.91	m	1	3.88	t (J = 8.7 Hz)	-0.03	41.5	41.2	-0.3		
3'	3.50 – 3.43	m	1	3.46	m	-	44.7	44.4	-0.3		
4'	6.20	dd (J = 15.0, 8.2 Hz)		6.20	dd (J = 15.5, 10.1 Hz)	0.00	124.9	124.7	-0.2		
5'	6.35 – 6.27	-	1	6.29	d (J = 15.5 Hz)	-	133.2	133.0	-0.2		
Ar ₁ '	-	-	-	-	-	-		131.4			
Ar ₂ '	6.88	d (J = 1.5 Hz)		6.88	d (J = 1.3 Hz)	0.00	105.8	105.6	-0.2		
Ar ₃ '	-	-	-	-	-	-	147.1*	146.9	-0.2		
Ar ₄ '	-	-	-	-	-	-	148.0 [#]	147.3	-0.7		
Ar ₅ '	6.74 – 6.67		1	6.68	overlapped	-		108.0			
Ar ₆ '	6.76 – 6.67		1	6.72	overlapped	-		120.6			
[O-CH ₂ -O]'	5.91	q (J = 1.4 Hz)	2	5.89	m	-0.02	101.0	101.0	0.0		
PI _a	3.36 – 3.21	m	2	3.30	m	-	45.9	45.7	-0.2		
				3.24	m	-					
	3.52 – 3.39	m	2	3.68	m	-	42.6	43.1	0.5		
				3.37	m	-					
PI _b	1.58 – 1.30	m	2	1.46	m	-	26.9 [§]	26.4	-0.5		
	1.58 – 1.30	m	2	1.46	m	-	25.7 [§]	25.6	-0.1		
PI _v	1.65 – 1.45	m	2	1.54	m	-	24.4	24.4	0.0		
PI _a '	3.52 – 3.39	m	2	3.42	m	-	42.6	43.0	-0.4		
	3.66 – 3.46	m	2	3.62	m	-	46.9	46.6	-0.3		
				3.48	m	-					
PI _b '	1.58 – 1.30	m	2	1.46	m	-	26.2 [§]	26.4	0.2		
	1.58 – 1.30	m	2	1.54	m	-	25.6 [§]	25.6	0.0		
PI _v '	1.65 – 1.45	m	2	1.62	m	-	24.6	24.7	0.1		

*#§ signals interchangeable

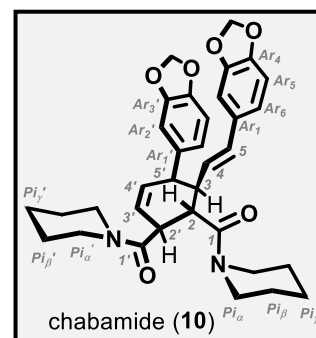
Table S4: Comparison of the ¹H NMR and ¹³C NMR data of synthetic and natural nigramide R in chloroform-*d*.

Attribution	synthetic			natural			Δ ¹ H	synthetic		natural	
	¹ H δ (ppm)	m, J (Hz)	int.	¹ H δ (ppm)	m, J (Hz)	¹³ C δ (ppm)		¹³ C δ (ppm)	Δ ¹³ C		
1	-	-	-	-	-	-	-	170.4	170.4	0.0	
2	3.66	m	2	3.66	m	0.00	42.1	42.1	0.0		
3	2.99	tt (<i>J</i> = 5.6 – 2.6 Hz)	2	2.99	m	0.00	46.2	46.3	0.1		
4	6.11	ddd (<i>J</i> = 15.6, 6.0, 2.3 Hz)	2	6.11	ddd (<i>J</i> = 15.6, 8.3, 2.3 Hz)	0.00	128.6	128.7	0.1		
5	6.36	d (<i>J</i> = 15.7 Hz)	2	6.36	d (<i>J</i> = 15.8 Hz)	0.00	131.1	131.1	0.0		
Ar₁	-	-	-	-	-	-	131.4	131.4	0.0		
Ar₂	6.87	d (<i>J</i> = 1.6 Hz)	2	6.87	d (<i>J</i> = 1.6 Hz)	0.00	105.6	105.6	0.0		
Ar₃	-	-	-	-	-	-	148.0	148.0	0.0		
Ar₄	-	-	-	-	-	-	147.1	147.2	0.1		
Ar₅	6.72	d (<i>J</i> = 8.0 Hz)	2	6.72	d (<i>J</i> = 8.0 Hz)	0.00	108.3	108.3	0.0		
Ar₆	6.75	dd (<i>J</i> = 8.0, 1.6 Hz)	2	6.75	dd (<i>J</i> = 8.0, 1.6 Hz)	0.00	120.9	120.9	0.0		
[O-CH₂-O]	5.93	s	4	5.93	s	0.00	101.0	101.1	0.0		
PI_a	3.54 – 3.35	m	4	3.51	ddd (<i>J</i> = 13.5, 6.7, 3.9 Hz)		47.6	46.7	-0.9		
				3.40	m						
	3.72 – 3.64	m	2	3.68	ddd (<i>J</i> = 13.1, 6.2, 4.2 Hz)		43.3	43.3	0.0		
	3.44 – 3.34	m	2	3.40	m						
PI_B	1.53 – 1.47	m	4	1.53	m		26.8	26.9	0.1		
	1.47 – 1.36	m	4	1.44	m		25.7	25.7	0.0		
PI_y	1.65 – 1.52	m	4	1.59			24.5	24.9	0.4		

2.8. Chabamide (10)

Consistent with the literature description.³

- **R_f** = 0.37 (CH₂Cl₂/MeOH, 99:1);
- **¹H NMR** (400 MHz, chloroform-d) δ: 6.83 (s, 1H), 6.81 (s, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.66 – 6.61 (m, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.92 (s, 2H), 5.86 (ddd, *J* = 9.9, 4.9, 2.6 Hz, 1H), 5.75 (d, *J* = 9.9 Hz, 1H), 5.21 (dd, *J* = 15.6, 10.1 Hz, 1H), 4.18 (dd, *J* = 9.6, 2.5 Hz, 1H), 3.67 (dd, *J* = 11.8, 9.5 Hz, 1H), 3.57 (t, *J* = 5.5 Hz, 4H), 3.48 (t, *J* = 4.5 Hz, 1H), 3.43 – 3.23 (m, 4H), 2.97 (td, *J* = 10.9, 5.7 Hz, 1H), 1.73 – 1.38 (m, 12H);
- **¹³C{¹H} NMR ppm** (101 MHz, chloroform-d): δ 172.4, 171.1, 147.8, 147.5, 146.8, 146.5, 133.6, 132.0, 131.2, 130.3, 128.0, 125.5, 123.5, 120.8, 110.8, 108.2, 107.9, 105.4, 101.0, 100.9, 47.1, 47.1, 46.0, 45.3, 43.4, 43.0, 42.9, 37.8, 26.7, 26.4, 25.8, 25.6, 24.6, 24.5;
- **IR** (neat) *ν* = 2919, 2852, 1633, 1504, 1488, 1443, 1251, 1039 cm⁻¹;
- **HRMS(ESI)**: *m/z* calcd. for C₃₄H₃₉N₂O₆⁺ [M + H]⁺ 571.2803; found 571.2805.

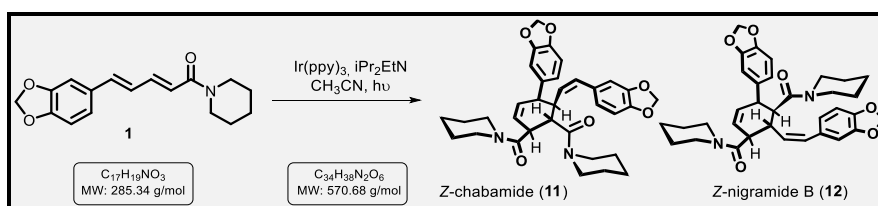


³ T. Rukachaisirikul, S. Prabpai, P. Champung, A. Suksamrarn, *Planta Med.* **2002**, *68*, 853–855.

Table S5: Comparison of the ^1H NMR and ^{13}C NMR data of synthetic and natural chabamide in chloroform-*d*.

Attribution	synthetic			natural			Δ ^1H	synthetic		natural	
	^1H δ (ppm)	<i>m</i> , <i>J</i> (Hz)	int.	^1H δ (ppm)	<i>m</i> , <i>J</i> (Hz)			^{13}C δ (ppm)	^{13}C δ (ppm)	Δ ^{13}C	
1	-	-	-	-	-	-	-	172.4	172.2	-0.2	
2	3.67	dd (<i>J</i> = 11.8, 9.5 Hz)	1	3.64	dd (<i>J</i> = 11.8, 9.6 Hz)	-0.03	37.8	37.7	-0.1		
3	2.97	td (<i>J</i> = 10.9, 5.7 Hz)	1	2.91	ddd (<i>J</i> = 11.8, 10.2, 5.7 Hz)	-0.06	45.3	45.4	0.1		
4	5.21	dd (<i>J</i> = 15.6, 10.1 Hz)	1	5.19	dd (<i>J</i> = 15.6, 10.2 Hz)	-0.02	128.0	128.1	0.01		
5	6.33	d (<i>J</i> = 15.7 Hz)	1	6.29	d (<i>J</i> = 15.9 Hz)	-0.04	131.2	131.0	-0.2		
Ar ₁	-	-	-	-	-	-	132.0	131.9	-0.1		
Ar ₂	6.66 – 6.61	<i>m</i>	1	6.60	d (<i>J</i> = 1.6 Hz)	-	105.4	105.3	-0.1		
Ar ₃	-	-	-	-	-	-	147.8	147.8	0.0		
Ar ₄	-	-	-	-	-	-	146.8	146.7	-0.1		
Ar ₅	6.69	d (<i>J</i> = 7.8 Hz)	1	6.67	d (<i>J</i> = 6.9 Hz)	-0.02	108.2	108.2	0.0		
Ar ₆	6.66 – 6.64	<i>m</i>	1	6.63	dd (<i>J</i> = 6.9, 1.6 Hz)	-	120.8	120.7	-0.1		
[O-CH ₂ -O]	5.92	<i>s</i>	2	5.92	<i>s</i>	0.00	100.9	100.89	0.1		
1'	-	-	-	-	-	-	171.1	171.1	0.0		
2'	4.18	dd (<i>J</i> = 9.6, 2.5 Hz)	1	4.12	ddt (<i>J</i> = 9.6, 2.3, 2.3 Hz)	-0.06	42.9	42.9	0.0		
3'	5.75	d (<i>J</i> = 9.9 Hz)	1	5.73	ddd (<i>J</i> = 10.0, 2.3, 2.3 Hz)	-0.02	125.5	125.5	0.02		
4'	5.86	ddd (<i>J</i> = 9.9, 4.9, 2.6 Hz)	1	5.84	ddd (<i>J</i> = 10.0, 5.0, 2.3 Hz)	-0.02	130.3	130.3	0.0		
5'	3.48	t (<i>J</i> = 4.5 Hz)	1	3.45	<i>m</i>	-0.03	46.0	45.9	-0.1		
Ar ₁ '	-	-	-	-	-	-	133.6	133.6	0.0		
Ar ₂ '	6.83	<i>s</i>	1	6.79	<i>s</i>	-0.04	100.8	100.8	0.0		
Ar ₃ '	-	-	-	-	-	-	147.5	147.5			
Ar ₄ '	-	-	-	-	-	-	146.5	146.4	-0.1		
Ar ₅ '	6.81	<i>s</i>	1	6.80	d (<i>J</i> = 11.4 Hz)	-0.01	108.0	107.9	-0.1		
Ar ₆ '	6.81	<i>s</i>	1	6.80	d (<i>J</i> = 11.4 Hz)		123.5	123.5	0.0		
[O-CH ₂ -O]'	5.99	d (<i>J</i> = 1.5 Hz)	1	5.96	d (<i>J</i> = 1.5 Hz)	-0.03	101.0	100.92	0.1		
	5.96	d (<i>J</i> = 1.5 Hz)	1	5.94	d (<i>J</i> = 1.5 Hz)	-0.02					
PI _a	3.59 – 3.52	<i>m</i>	2	3.33	<i>m</i>	-	47.0	46.9	-0.1		
	3.42 – 3.24	<i>m</i>	2	3.26	<i>m</i>	-	43.0	42.8	-0.2		
					<i>m</i>	-					
PI _b	1.70 – 1.10	<i>m</i>	4	1.12	<i>m</i>	-	26.4	26.4	0.0		
				1.43	<i>m</i>	-					
				1.25	<i>m</i>	-	25.6	25.6	0.0		
PI _y	1.50 – 1.35	<i>m</i>	2	1.43	<i>m</i>	-	24.5	24.5	0.0		
				1.34	<i>m</i>	-					
PI _a '	3.59 – 3.52	<i>m</i>	2	3.54	<i>m</i>	-	47.1	47.1	0.0		
	3.42 – 3.24	<i>m</i>	2				43.4	43.3	-0.1		
PI _b '	1.70 – 1.10	<i>m</i>	4	1.58	<i>m</i>	-	26.7	26.7	0.0		
				1.51	<i>m</i>	-	25.8	25.8	0.0		
PI _y '	1.70 – 1.60	<i>m</i>	2	1.63	<i>m</i>	-	24.6	24.6	0.0		

2.9. [4+2] cycloadditions dimerization of piperine mediated by Ir(ppy)₃



A solution of piperine (**1**) (33 mg, 0.11 mmol, 1.0 equiv), Ir(ppy)₃ (3.3 mg, 0.005 mmol, 0.05 equiv) and *i*Pr₂EtN (37 μ L, 0.212 mmol, 2.0 equiv) in CH₃CN (1.0 mL) was prepared in a glass tube. Solution was irradiated in an Hepatochem® PhotoRedOx Box™ photoreactor with a blue LEDs light [465 nM]. After 16 h of reaction 4 batches were combined and concentrated under reduced pressure. Purification by flash chromatography on silica gel (gradient of elution: CH₂Cl₂/EtOH = 99:1 then 98:2) and further preparative (TLC CH₂Cl₂/EtOH = 99:1) afforded Z-chabamide (**11**) as a white solid (R_f = 0.43, 70 mg, 53%) and then Z-nigramide B (**12**) as a white solid (R_f = 0.43, 16 mg, 12%).

2.10. Z-chabamide (11)

- R_f = 0.43 (CH₂Cl₂/MeOH, 99:1);
- ¹H NMR (400 MHz, chloroform-d) δ : 6.94 (d, *J* = 1.6 Hz, 1H), 6.88 – 6.84 (m, 2H), 6.81 (s, 1H), 6.80 (d, *J* = 6.0 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.29 (d, *J* = 11.7 Hz, 1H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.95 (d, *J* = 1.5 Hz, 1H), 5.94 – 5.92 (m, 2H), 5.81 (ddd, *J* = 9.9, 5.0, 2.7 Hz, 1H), 5.69 (dt, *J* = 10.0, 1.8 Hz, 1H), 4.67 (dd, *J* = 11.7, 10.8 Hz, 1H), 4.09 (dq, *J* = 9.4, 2.4 Hz, 1H), 3.62 (dd, *J* = 11.5, 9.4 Hz, 1H), 3.58 – 3.46 (m, 6H), 3.45 – 3.26 (m, 4H), 1.71 – 1.60 (m, 2H), 1.60 – 1.44 (m, 12H), 1.44 – 1.37 (m, 2H).
- ¹³C{¹H} NMR ppm (101 MHz, chloroform-d): δ 172.4, 171.5, 147.6, 147.4, 146.5, 146.4, 133.5, 131.8, 131.5, 130.1, 125.8, 123.6, 122.5, 111.3, 109.2, 108.4, 108.0, 101.0, 100.9, 47.3, 47.3, 45.4, 43.5, 43.2, 42.9, 39.2, 37.4, 27.0, 26.6, 26.0, 26.0, 24.8 (2C).
- IR (neat) ν = 2933, 2856, 1629, 1487, 1438, 1234, 1037 cm⁻¹;
- HRMS(ESI): *m/z* calcd. for C₃₄H₃₉N₂O₆⁺ [M + H]⁺ 571.2803; found 571.2808.

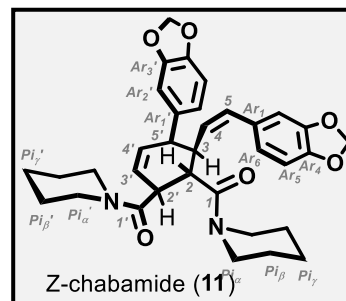


Table S6: ¹H NMR and ¹³C NMR data of Z-chabamide in chloroform-*d*.

Attribution	¹ H δ (ppm)	m	J (Hz)	int.	¹³ C δ (ppm)
1	-				172.4
2	3.62	dd	11.5 – 9.4 Hz	1	39.2
3	3.53 – 3.46	m		1	37.4
4	4.67	dd	11.7 – 10.8 Hz	1	131.8
5	6.29	d	11.7 Hz	1	130.1
Ar ₁	-				131.5
Ar ₂	6.94	d	1.6 Hz	1	109.2
Ar ₃	-				147.6
Ar ₄	-				146.5
Ar ₅	6.79	d	7.9 Hz	1	108.4
Ar ₆	6.88 – 6.84	m		1	122.5
1'	-				171.5
2'	4.09	dq	9.4 – 2.4 Hz	1	42.9
3'	5.69	dt	10.0 – 1.8 Hz	1	125.8
4'	5.81	ddd	9.9 – 5.0 – 2.7 Hz	1	131.8
5'	3.37 – 3.32	m		1	45.4
Ar ₁ '	-				133.5
Ar ₂ '	6.81	s		1	112.3
Ar ₃ '	-				147.4
Ar ₄ '	-				146.5
Ar ₅ '	6.80	d	6.0 Hz	4	108.0
Ar ₆ '	6.88 – 6.84	m		1	123.6
[O-CH ₂ -O]'	5.96	d	1.5 Hz	1	101.0 or 100.9
	5.95	d	1.5 Hz	1	
[O-CH ₂ -O]	5.94 – 5.92	m		2	101.0 or 100.9
PI _α & PI _α '	3.58 – 3.26	m		8	47.4
					47.3
					43.5
					43.2
PI _β & PI _β '	1.60 – 1.44	m		8	27.0
					26.6
					26.0
					25.9
PI _γ & PI _γ '	1.60 – 1.44	m		2	24.8
	1.44 – 1.37	m		2	

2.11. Z-nigramide B (12)

- $R_f = 0.40$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 99:1);
- $^1\text{H NMR}$ (400 MHz, chloroform-d) δ : 6.82 – 6.75 (m, 4H), 6.75 – 6.69 (m, 2H), 6.55 (d, $J = 11.4$ Hz, 1H), 5.94 (d, $J = 1.4$ Hz, 1H), 5.93 (d, $J = 1.4$ Hz, 1H), 5.92 (d, $J = 1.4$ Hz, 1H), 5.90 (d, $J = 1.4$ Hz, 1H), 5.87 – 5.76 (m, 3H), 4.20 (dq, $J = 10.0, 2.1$ Hz, 1H), 3.80 – 3.57 (m, 3H), 3.54 (dd, $J = 10.0, 3.0$ Hz, 1H), 3.55 – 3.44 (m, 1H), 3.38 (m, 1H), 3.36 – 3.32 (m, 1H), 3.21 – 3.12 (m, 1H), 3.05 (d, $J = 11.2$ Hz, 1H), 2.65 (ddd, $J = 12.0, 8.3, 3.5$ Hz, 1H), 2.53 (ddd, $J = 13.4, 6.7, 3.5$ Hz, 1H), 1.84 – 1.72 (m, 1H), 1.70 – 1.23 (m, 8H), 1.21 – 1.11 (m, 2H), 0.85 – 0.70 (m, 1H).
- $^{13}\text{C}\{^1\text{H}\}$ NMR ppm (101 MHz, chloroform-d): δ 171.2, 171.1, 147.9, 147.7, 146.5, 146.4, 136.6, 131.8, 131.5, 130.9, 128.0, 127.0, 122.1, 121.8, 109.2, 109.1, 108.3, 108.2, 101.2, 101.1, 47.1, 47.0, 45.8, 43.8, 42.8, 40.8, 38.0, 37.2, 26.9, 25.8, 25.8, 25.3, 24.9, 24.6.
- IR (neat) $\nu = 2933, 2856, 1637, 1487, 1438, 1247, 1037$ cm^{-1} ;
- HRMS(ESI): m/z calcd. for $\text{C}_{34}\text{H}_{39}\text{N}_2\text{O}_6^+$ $[\text{M} + \text{H}]^+$ 571.2803; found 571.2807.

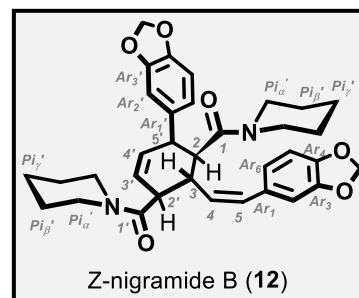
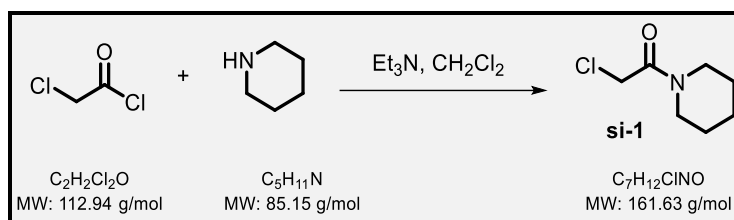


Table S7: ¹H NMR and ¹³C NMR data of Z-nigamide B in chloroform-*d*.

Attribution	¹ H δ (ppm)	m	J (Hz)	int.	¹³ C δ (ppm)
1	-				171.1 or 171.2
2	4.20	dq	10.0 – 2.1 Hz	1	38.0
3	3.54	dd	10.0 – 3.0 Hz	1	37.2
4	5.84 – 5.77	m		1	131.5
5	6.55	d	11.4 Hz	1	130.9
Ar ₁	-				131.8
Ar ₂	6.72 – 6.70	m		1	109.2
Ar ₃	-				147.7 or 147.9
Ar ₄	-				146.5 or 146.6
Ar ₅	6.80 – 6.77	m		1	108.3
Ar ₆	6.72 – 6.69	m		1	122.1
1'	-				171.1 or 171.2
2'	3.05	d	11.2 Hz	1	40.8
3'	5.85 – 5.78	m		1	128.0
4'	5.87 – 5.83	m		1	127.0
5'	3.38	m		1	47.0
Ar ₁ '	-				136.6
Ar ₂ '	6.80 – 6.78	m		1	109.1
Ar ₃ '	-				147.7 or 147.9
Ar ₄ '	-				146.5 or 146.6
Ar ₅ '	6.75 – 6.80	m		1	108.2
Ar ₆ '	6.76 – 8.82	m		1	121.8
[O-CH ₂ -O] ¹	5.94	d	1.4 Hz	1	101.1 and 101.2
	5.93	d	1.4 Hz	1	
	5.92	d	1.4 Hz	1	
	5.90	d	1.4 Hz	1	
PI _α & PI _α '	3.77 – 3.61	m		2	47.1
	2.65	ddd	12.0 – 8.3 – 3.5 Hz	1	45.8
	2.53	ddd	13.4 – 6.7 – 3.5 Hz	1	
	3.73 – 3.60	m		1	43.8
	3.55 – 3.44	m		1	
	3.36 – 3.32	m		1	42.8
	3.21 – 3.12	m		1	
PI _β & PI _β '	1.84 – 1.72	m		1	26.9
	1.67 – 1.58	m		1	
	1.65 – 1.40	m		3	25.8 and 25.7
	1.21 – 1.11	m		1	
	1.21 – 1.11	m		1	25.3
	0.85 – 0.70	m		1	
PI _γ & PI _γ '	1.70 – 1.29	m		4	24.9 and 24.6

3. Synthesis of ilepcimide and piperettine

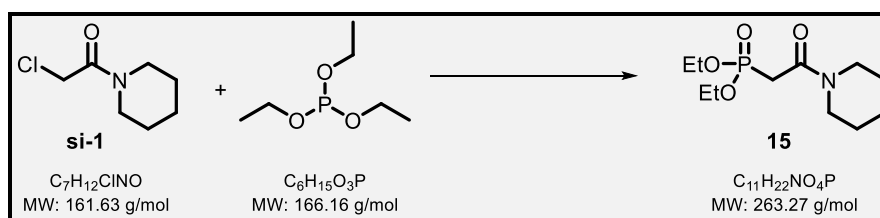
3.1. 1-(Chloracetyl)-piperidine (si-1)



Prepared by adapting the literature procedure.⁴ To a solution of piperidine (2.35 mL, 23.8 mmol, 1.0 equiv) and Et_3N (9.25 mL, 66.4 mmol, 2.8 equiv) in CH_2Cl_2 (60 mL), chloroacetyl chloride (2.10 mL, 26.5 mmol, 1.1 equiv) was added dropwise. After 90 min of stirring, the reaction mixture was quenched with HCl (2M, 50 mL). The organic layer was separated, washed with an aqueous solution of K_2CO_3 (5%, 2 x 40 mL) and then H_2O (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford **si-1** as a brown oil (1.85 g, 48%).

- $R_f = 0.18$ (CH_2Cl_2);
- $^1\text{H NMR}$ (300 MHz, chloroform-d) δ : 4.05 (s, 2H), 3.55 (t, $J = 5.5$ Hz, 2H), 3.43 (t, $J = 5.0$ Hz, 2H), 1.73 – 1.51 (m, 8H);
- $^{13}\text{C}\{^1\text{H}\}$ NMR ppm (75 MHz, chloroform-d): δ 161.2, 47.6, 43.5, 41.3, 26.5, 25.5, 24.4;
- IR (neat) $\nu = 2940, 1641, 1444, 1280, 1250, 1224, 1135, 1120, 1024$ cm^{-1} ;
- HRMS(ESI): m/z calcd. for $\text{C}_7\text{H}_{12}\text{NO}_2^{35}\text{ClNa}^+$ [$\text{M} + \text{Na}$] $^+$ 184.0500; found 184.0473.

3.2. Diethyl (2-oxo-2-(piperidin-1-yl)-ethyl)-phosphonate (15)



Prepared by adapting the literature procedure.⁵ A mixture of chloroacetyl piperidine **si-1** (1.85 g, 11.5 mmol, 1.0 equiv) and $\text{P}(\text{OEt})_3$ (2.5 mL, 14.6 mmol, 1.3 equiv) was

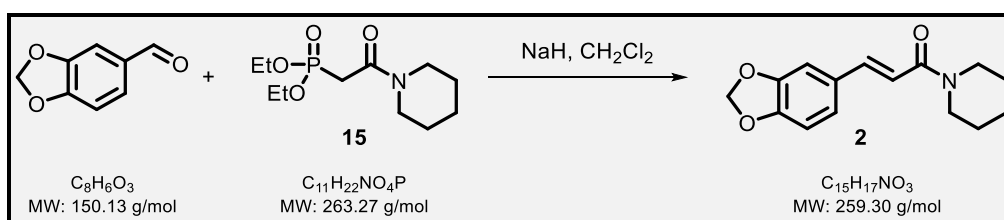
⁴ A. Ohta, Y. Tomomura, J. Sawaki, H. Akkike, M. Ikuta, M. Shimazaki, *Heterocycles*. **1991**, 32, 965–973.

⁵ J. K. Mannisto, A. Sahari, K. Lagerblom, T. Niemi, M. Nieger, G. Sztanó, T. Repo, *Chem. – Eur. J.* **2019**, 25, 10284–10289.

heated to 150°C for 2.5 h. After cooling, purification by flash chromatography on silica gel (gradient of elution: CH₂Cl₂/Et₂O = 199:1 then 98:2) afforded **15** as a pale-yellow oil (2.35 g, 79%).

- **R_f** = 0.15 (CH₂Cl₂);
- **¹H NMR** (300 MHz, chloroform-*d*) δ: 4.16 (tt_{app}, *J* = 8.2, 6.5 Hz, 4H), 3.52 (s br, 4H), 3.06 (d, *J* = 22.0, 2H), 1.74 – 1.50 (m, 6H), 1.47 – 1.17 (m, 5H);
- **¹³C{¹H} NMR ppm** (75 MHz, chloroform-*d*): δ 163.2, 62.7, 62.7, 48.2, 43.3, 33.5 (d, *J* = 133.3 Hz), 26.5, 25.7, 24.5, 16.5, 16.4;
- **IR** (neat) *ν* = 3400 large, 298, 2939, 2858, 1622, 1444, 1274, 1054, 974 cm⁻¹;
- **HRMS(ESI)**: *m/z* calcd. for C₁₁H₂₂NO₄PNa⁺ [M + Na]⁺ 286.1179; found 286.1165.

3.3. Ilepcimide (**2**)



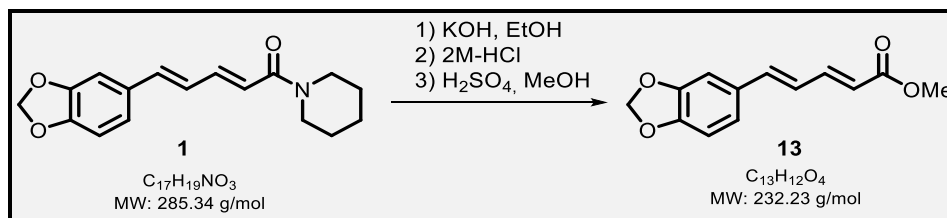
To a solution of piperonal (300 mg, 2.0 mmol, 1.0 equiv) and **15** (600 mg, 2.3 mmol, 1.14 equiv) in CH₂Cl₂ (20 mL), NaH (60%, 160 mg, 4.0 mmol, 2.0 equiv) was added. After 12 h of stirrings, the reaction mixture was quenched with H₂O (5 mL). The organic layer was separated, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash chromatography on silica gel (eluent: CH₂Cl₂/Et₂O = 99:1) afforded **2** as an off-white solid (500 mg, 96%). Consistent with the literature description.⁶

- **R_f** = 0.15 (CH₂Cl₂);
- Aniseed scent
- **¹H NMR** (300 MHz, chloroform-*d*) δ: 7.55 (d, *J* = 15.4 Hz, 1H), 7.02 (s, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 15.4 Hz, 1H), 5.97 (s, 1H), 5.97 (s, 1H), 3.60 (t, *J* = 5.3 Hz, 4H), 1.77 – 1.51 (m, 6H);
- **¹³C{¹H} NMR ppm** (75 MHz, chloroform-*d*): δ 165.6, 149.0, 148.3, 142.1, 130.1, 123.7, 115.8, 108.6, 106.5, 101.5, 45.3 (2C), 26.3 (2C), 24.8;

⁶ X. Xia, P. H. Toy, *Synlett* **2015**, 26, 1737–1743.

- **IR** (neat) $\nu = 2937, 2854, 1642, 1606, 1504, 1489, 1444, 1354, 1248, 1215, 1140, 1122, 1101, 1037 \text{ cm}^{-1}$;
- **HRMS(ESI)**: m/z calcd. for $\text{C}_{15}\text{H}_{18}\text{NO}_3^+ [\text{M} + \text{H}]^+$ 260.1282; found 260.1293.

3.4. Methyl piperate (**13**)

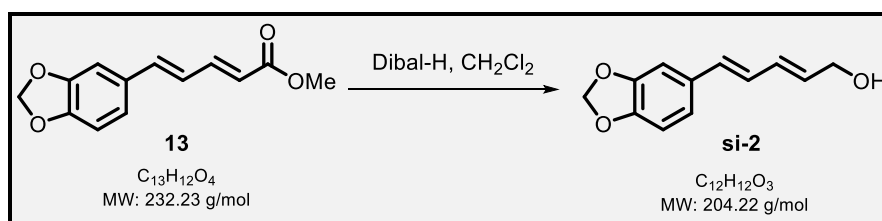


Prepared by adapting literature procedure.⁷ A solution of piperine (**1**) (3.0 g, 10.5 mmol, 1.0 equiv) and KOH (6.8 g, 119.3 mmol, 11.4 equiv) in EtOH (25 mL) was heated to reflux for 16h. After cooling, the precipitate was collected by filtration and then dissolved in H_2O (20 mL). The solution was acidified with HCl (2M, pH = 2-3). Precipitate was collected by filtration and washed with H_2O (2 x 5 mL) to afford crude piperic acid. To crude piperic acid suspended in MeOH (40.0 mL) conc- H_2SO_4 (5 drops) was added. The reaction mixture was heated to reflux for 16 h. After cooling, the reaction mixture was concentrated under reduced pressure. Crude product was dissolved in CH_2Cl_2 (40 mL), washed with a saturated aqueous solution of NaHCO_3 (2 x 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography on silica gel (eluent: CH_2Cl_2) afforded **13** as a yellow solid (1.29 g, 53%).

- **R_f** = 0.78 (CH_2Cl_2);
- **¹H NMR** (300 MHz, chloroform-d) δ : 7.42 (dd, $J = 15.2, 10.4 \text{ Hz}$, 1H), 6.99 (d, $J = 1.7 \text{ Hz}$, 1H), 6.91 (dd, $J = 8.0, 1.7 \text{ Hz}$, 1H), 6.86 – 6.64 (m, 3H), 5.98 (s, 3H), 5.94 (d, $J = 15.0 \text{ Hz}$, 1H), 3.76 (s, 3H);
- **¹³C{¹H} NMR ppm** (101 MHz, chloroform-d): δ 167.7, 148.7, 148.5, 145.1, 140.4, 130.7, 124.7, 123.1, 120.1, 108.7, 106.1, 101.5, 51.6;
- **IR** (neat) $\nu = 2949, 2918, 2849, 1707, 1620, 1606, 1505, 1493, 1452, 1436, 1331, 1311, 1265, 1241, 1141, 1039, 1001 \text{ cm}^{-1}$;
- **HRMS(ESI)**: m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_4^+ [\text{M} + \text{H}]^+$ 233.0808; found 233.0819.

⁷ H. Qu, X. Yu, X. Zhi, M. Lv, H. Xu, *Bioorg. Med. Chem. Lett.* **2013**, 23, 5552–5557.

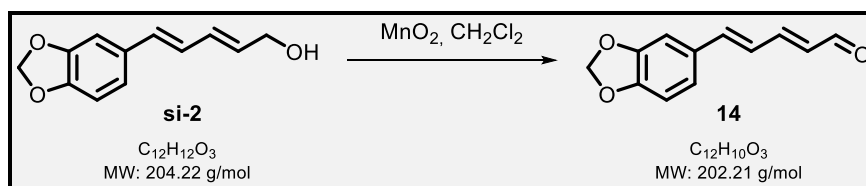
3.5. (E,E)-5-(1,2-methylenedioxy-benzen-4-yl)-penta-2,4-dien-1-ol (si-2)



Prepared by adapting literature procedure.⁷ To a solution of **13** (410 mg, 1.76 mmol, 1.0 equiv) in CH₂Cl₂ (25 mL) a solution of Dibal-H (1.1 M, 6.0 mL, 6.60 mmol, 3.75 equiv) in cyclohexane was added. After 4h of stirring at 0°C, the reaction mixture was quenched with H₂O (15 mL). The organic layer was separated, washed with H₂O (5 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash chromatography on silica gel (gradient of elution: CH₂Cl₂/EtOH = 99:2 then 95:5) afforded **si-2** as a pale yellow solid (320 mg, 88%).

- **R_f** = 0.20 (CH₂Cl₂);
- **¹H NMR** (300 MHz, chloroform-d) δ: 6.94 (s, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.62 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.39 (m, 1H), 5.95 (s, 2H), 5.90 (dt, *J* = 9.6, 6.2 Hz, 1H), 4.23 (d, *J* = 5.9 Hz, 2H);
- **¹³C{¹H} NMR ppm** (75 MHz, chloroform-d): δ 148.1, 147.3, 146.5, 132.5, 131.8, 131.7, 126.5, 121.3, 108.4, 105.5, 101.1, 63.5;
- **IR** (neat) ν = 3340 large, 2921, 2851, 1503, 1488, 1446, 1355, 1250, 1192, 1094, 1038, 985 cm⁻¹;
- **HRMS(ESI)**: *m/z* calcd. for C₁₂H₁₃O₃⁺ [M - H₂O + H]⁺ 187.0754; found 187.0754.

3.6. (E,E)-5-(1,2-methylenedioxy-benzen-4-yl)-penta-2,4-dienal (14)

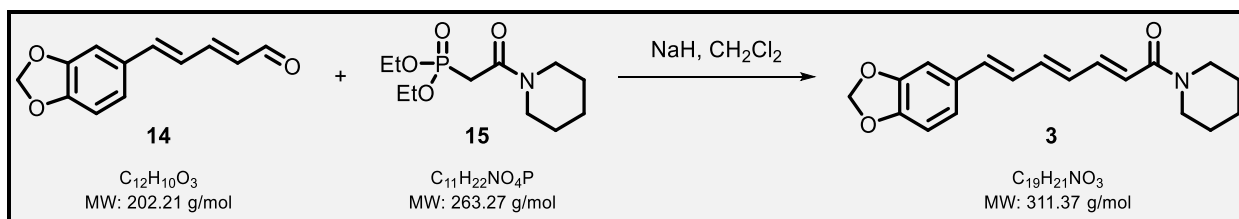


Prepared by adapting literature procedure.⁷ To a solution of **si-2** (320 mg, 1.56 mmol, 1.0 equiv) in CH₂Cl₂ (20 mL), 8 batches of MnO₂ (500 mg, 5.75 mmol, 8 x 3.7 equiv) were added every 30 min. 30 after the addition of the last batch, the reaction mixture

was filtered through a silica plug (CH₂Cl₂ washes). The filtrate was concentrated under reduced pressure to afford **14** as yellow solid (300 mg, 94%).

- **R_f** = 0.39 (CH₂Cl₂);
- **¹H NMR** (300 MHz, chloroform-d) δ: 9.59 (d, *J* = 7.9 Hz, 1H), 7.23 (dd, *J* = 15.2, 10.2 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.92 – 6.86 (m, 1H), 6.86 – 6.77 (m, 2H), 6.23 (dd, *J* = 15.0, 7.9 Hz, 1H), 6.00 (s, 2H);
- **¹³C{¹H} NMR ppm** (75 MHz, chloroform-d): δ 193.5, 152.3, 149.2, 148.5, 142.3, 131.0, 130.3, 124.6, 123.7, 108.7, 106.2, 101.6;
- **IR** (neat) *v* = 2850, 1672, 1617, 1597, 1503, 1487, 1447, 1360, 1250, 1194, 1156, 1132, 1111, 1036, 1010, 984, 929 cm⁻¹;
- **HRMS(ESI)**: *m/z* calcd. for C₁₂H₁₁O₃⁺ [M + H]⁺ 203.0703; found 203.0723.

3.7. Piperettine (**3**)



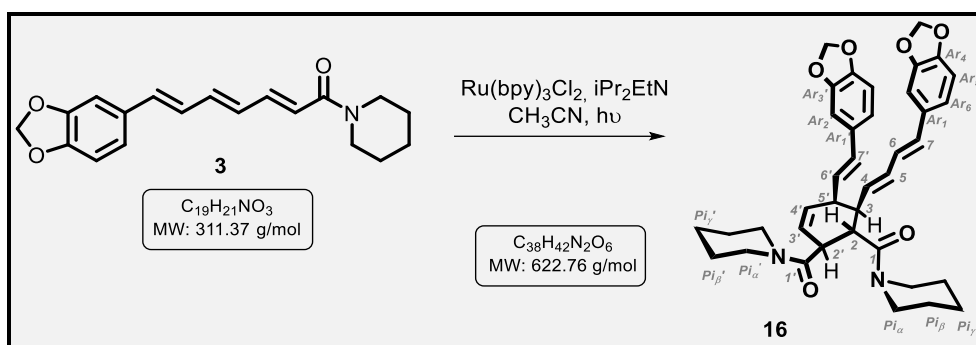
To a solution of **14** (300 mg, 1.49 mmol, 1.0 equiv) and **15** (560 mg, 2.13 mmol, 1.4 equiv) in CH₂Cl₂ (20.0 mL), NaH (60%, 160 mg, 4.0 mmol, 2.7 equiv) was added. After 18 h of stirring, the reaction mixture is quenched with H₂O (15 mL). The organic layer was separated, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash chromatography on silica gel (eluent: CH₂Cl₂/MeOH, 99:1) afforded **3** as a yellow solid (220 mg, 48%). Consistent with the literature description.⁸

- **R_f** = 0.49 (CH₂Cl₂/MeOH, 99:1);
- Aniseed scent
- **¹H NMR** (300 MHz, chloroform-d) δ: 7.35 (dd, *J* = 14.7, 11.2 Hz, 1H), 6.96 (d, *J* = 1.7 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.71 – 6.55 (m, 3H), 6.47 – 6.33 (m, 2H), 5.96 (s, 2H), 3.56 (m, 4H), 1.83 – 1.51 (m, 6H);

⁸ N. Nandakumar, S. Muthuraman, P. Gopinath, P. Nithya, J. Gopas, R. S. Kumar, *Eur. J. Med. Chem.* **2017**, *125*, 1076–1087.

- $^{13}\text{C}\{^1\text{H}\}$ NMR ppm (75 MHz, chloroform-d): δ 165.6, 148.4, 147.9, 142.4, 139.2, 135.4, 131.7, 130.6, 126.9, 122.1, 120.3, 108.6, 105.7, 101.4, 47.1, 43.4, 26.88, 25.9, 24.8;
- IR (neat) ν = 2935, 2854, 1634, 1575, 1504, 1488, 1434, 1251, 1136, 1118, 1038, 1033, 929 cm^{-1} ;
- HRMS(ESI): m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 312.1595; found 312.1602.

3.8. Compound 16



A solution of piperettine (**3**) (35 mg, 0.11 mmol, 1.0 equiv), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (3.8 mg, 0.005 mmol, 0.05 equiv) or $\text{Ir}(\text{ppy})_3$ (3.3 mg, 0.005 mmol, 0.05 equiv) and $i\text{Pr}_2\text{EtN}$ (37 μL , 0.212 mmol, 2.0 equiv) in CH_3CN (1.0 mL) was prepared in a glass tube. Solution was irradiated in an Hepatochem® PhotoRedOx Box™ photoreactor with a blue LEDs light [465 nm]. After 16 h of reaction mixture was concentrated under reduced pressure. Alternative, reaction can also be performed with $\text{Ru}(\text{phen})_3\text{Cl}_2$ (3.6 mg, 0.005 mmol, 0.05 equiv) (without $i\text{Pr}_2\text{EtN}$) under an argon atmosphere for 4 days. Purification by preparative (TLC $\text{CH}_2\text{Cl}_2/\text{EtOH} = 99:1$) afforded B (**16**) as a white solid. Conditions with $\text{Ru}(\text{bpy})_3\text{Cl}_2$: 5 mg, 15%; conditions with $\text{Ir}(\text{ppy})_3$: 3.5 mg, 15%; conditions with $\text{Ru}(\text{phen})_3\text{Cl}_2$: 5 mg, 15%.

- $R_f = 0.35$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 99:1);
- ^1H NMR (400 MHz, chloroform-d) δ : 6.97 (d, $J = 1.7$ Hz, 1H), 6.89 (d, $J = 1.7$ Hz, 1H), 6.84 (dd, $J = 8.0, 1.7$ Hz, 1H), 6.81 – 6.70 (m, 3H), 6.50 (dd, $J = 15.7, 10.1$ Hz, 1H), 6.42 – 6.34 (m, 2H), 6.23 (dd, $J = 15.0, 10.2$ Hz, 1H), 6.06 (m, 1H), 5.96 (s, 2H), 5.93 (d, 5.3 Hz, 2H), 5.78 (ddd, $J = 10.0, 5.1, 2.8$ Hz, 1H), 5.63 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.56 (dd, $J = 15.0, 10.0$ Hz, 1H), 4.08 (dq, $J = 7.4, 2.4$ Hz, 1H), 3.63 (dd, $J = 10.8, 9.6$ Hz, 1H), 3.58 – 3.44 (m, 7H), 3.37 (m, 1H), 3.05 (d, $J = 10.0$ Hz, 1H), 2.84 (td, $J = 10.8, 5.2$ Hz, 1H), 1.74 – 1.44 (m, 12H).

- **$^{13}\text{C}\{^1\text{H}\}$ NMR ppm** (101 MHz, chloroform-d): δ 172.4, 171.1, 148.2, 148.2, 147.3, 147.2, 133.3, 132.9, 132.8, 132.2, 132.1, 131.5, 130.6, 127.4, 127.4, 125.3, 121.3, 121.1, 108.5, 108.4, 106.0, 105.5, 101.2 (2C), 47.2, 47.2, 45.3, 43.6, 43.6, 43.5, 43.1, 38.6, 26.9, 26.6, 25.9, 25.9, 24.8 (2C);
- **IR** (neat) ν = 2953, 2934, 2557, 1708, 1618, 1489, 1445, 1355, 1252 cm^{-1} ;
- **HRMS(ESI)**: m/z calcd. for $\text{C}_{38}\text{H}_{43}\text{N}_2\text{O}_6^+$ $[\text{M} + \text{H}]^+$ 623.3116; found 623.3123.

Table S8: ¹H NMR and ¹³C NMR data of compound **16** in chloroform-*d*.

Attribution	¹ H δ (ppm)	m	int.	J (Hz)	¹³ C δ (ppm)
1	-				172.4
2	3.66	dd	1	11.8 – 9.6 Hz	38.6
3	2.84	td	1	10.8 – 5.2 Hz	45.3
4	5.56	dd	1	15.0 – 10.0 Hz	133.3
5	6.23	dd	1	15.0 – 10.2 Hz	132.9
6	6.50	dd	1	15.7 – 10.1 Hz	127.4
7	6.38	m	1		131.5
Ar ₁	-				132.2
Ar ₂	6.89	d	1	1.7 Hz	105.5
Ar ₃	-				148.2
Ar ₄	-				147.3
Ar ₅	6.73	m	1		108.5
Ar ₆	6.77	m	1		121.3
[O-CH ₂ -O]	5.93	d	2	5.3 Hz	101.2
1'	-				171.1
2'	4.08	dq	1	7.4 – 2.4 Hz	43.6
3'	5.78	ddd	1	10.0 – 5.1 – 2.8 Hz	125.3
4'	5.63	dt	1	10.0 – 1.6 Hz	130.6
5'	3.05	d	1	10.0 Hz	43.6
6'	6.06	m	1		127.4
7'	6.39	m	1		132.8
Ar ₁ '	-				132.1
Ar ₂ '	6.97	d	1	1.7 Hz	106.0
Ar ₃ '	-				148.2
Ar ₄ '	-				147.2
Ar ₅ '	6.75	m	1		108.4
Ar ₆ '	6.84	dd	1	8.0 – 1.7 Hz	121.1
[O-CH ₂ -O]'	5.96	s	2		101.2
Pi _α & Pi _α '	3.58 – 3.34	m	6		47.2
					47.2
					43.5
	3.58 – 3.34	m	1		43.1
	3.37	m	1		
Pi _β & Pi _β '	1.74 – 1.44	m	8		26.6
					26.6
					25.9
					25.9
Pi _γ & Pi _γ '	1.74 – 1.44	m	4		24.8

4. Assemblies performed in 3D printed continuous-flow system

4.1. Continuous flow reactor

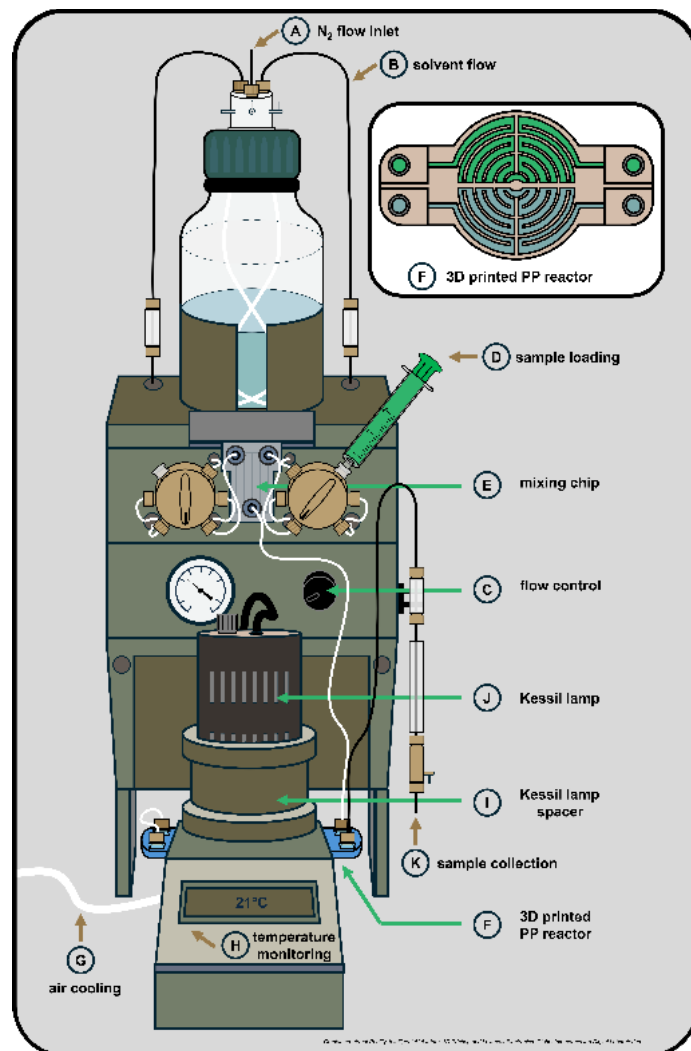
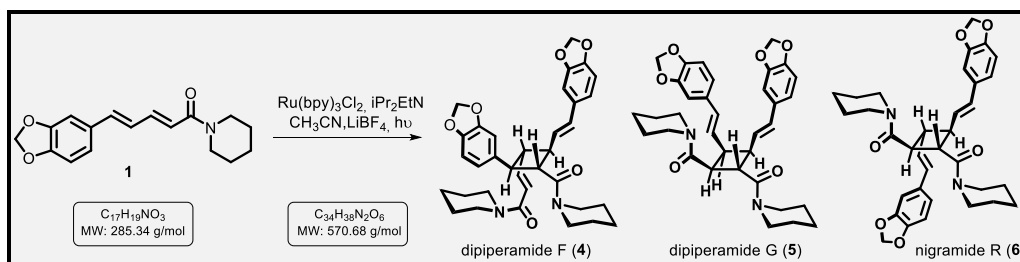


Figure S1 : 3D printed nitrogen (or air) driven continuous-flow system.

A: Nitrogen (or compress air) flow inlet; **B:** Solvent flow from the solvent bottle; **C:** Flow control; **D:** Sample loading (6 port injection loop); **E:** 3D printed polypropylene mixing chip; **F:** 3D printed polypropylene reactor (1 chamber way = 1.0 mL, 2 chamber way = 2.0 mL); **G:** Reactor compress cooling air; **H:** Digital temperature monitoring; **I:** Kessil® lamp spacer; **J:** Kessil® lamp; **K:** Sample collection.

4.2. Continuous flow assembly of piperine (1)

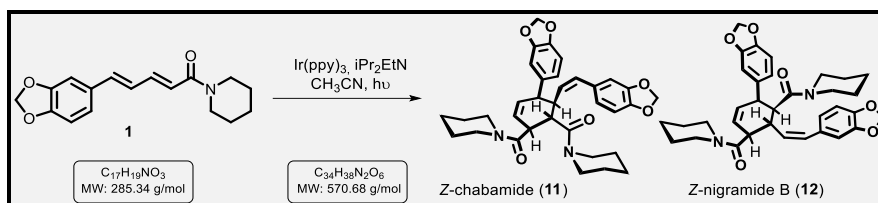


A solution of piperine (**1**) (34 mg, 0.12 mmol, 1.0 equiv.), Ru(bpy)₃Cl₂·6H₂O (4.5 mg, 0.006 mmol, 0.05 equiv.) and *i*Pr₂EtN (42 μL, 0.24 mmol, 2.0 equiv) and in CH₃CN (1.0 mL) was prepared. A solution of LiBF₄ in CH₃CN (1.0 M, 420 μL, 0.42 mmol, 4.0 equiv) was added. The reaction mixture was injected into the 3D printed continuous-flow system (25 min total duration). The solvent flow is maintained at 0.1 mL/min using N₂ flow. The flow reactor (2 mL, 20 min residence time) was irradiated with a blue LEDs light [Kessil®, PR160L, 456 nm, 50W, 100% intensity]. The reaction mixture was collected in a round bottom flask and concentrated under vacuum. Three batches were combined and purified by preparative TLC on silica gel (eluent: CH₂Cl₂/MeOH, 99:1) to afford nigramide R (**6**) as white solid (R_f = 0.39, 51 mg, 50 %), dipiperamide G (**5**) as white solid (R_f = 0.26, 13 mg, 13 %) and dipiperamide F (**4**) as white solid (R_f = 0.19, 17 mg, 17 %).

Table S9 : Screening of conditions for the dimerization of piperine (**1**) with the 3D printed continuous-flow system

Entry	Catalyst	Conditions	Result
Batch (20 min)	Ru(bpy) ₃ Cl ₂ 5%-mol	CH ₃ CN, <i>i</i> Pr ₂ EtN (2.0 equiv.)	<5 % conversion*
1	Ru(bpy) ₃ Cl ₂ 5%-mol	CH ₃ CN, <i>i</i> Pr ₂ EtN (2.0 equiv.)	60 % conversion*
2	Ru(bpy) ₃ Cl ₂ 2%-mol	CH ₃ CN, <i>i</i> Pr ₂ EtN (2.0 equiv.)	50 % conversion*
3	Ru(bpy) ₃ Cl ₂ 5%-mol	CH ₃ CN, <i>i</i> Pr ₂ EtN (2.0 equiv.), LiBF ₄	Full conversion, dipiperamides F (4): 17 %; dipiperamides G (5): 13 %; nigramide R (6): 50% (isolated yields).
Batch (20 min)	Ir(bpy) ₃ 2.5%-mol	CH ₃ CN, <i>i</i> Pr ₂ EtN (2.0 equiv.)	<5 % conversion*
3	Ir(bpy) ₃ 2.5%-mol	CH ₃ CN, <i>i</i> Pr ₂ EtN (2.0 equiv.)	Full conversion, Z-chabamide (11): 44 %; Z-nigramide B (11): 15 %; (isolated yields).

* Determined by NMR of the crude reaction mixture



A solution of piperine (**1**) (34 mg, 0.12 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.0 mg, 0.003 mmol, 0.025 equiv.) and iPr_2EtN (42 μ L, 0.24 mmol, 2.0 equiv) and in CH_3CN (1.0 mL) was prepared. The reaction mixture was injected into the 3D printed continuous-flow system (40 min total duration). The solvent flow is maintained at 0.1 mL/min using air flow. The flow reactor (2 mL, 20 min residence time) was irradiated with a blue LEDs light [Kessil[®], PR160L, 456 nm, 50W, 100% intensity]. The reaction mixture was collected in a round bottom flask and concentrated under vacuum. The crude product was purified by preparative TLC on silica gel (eluent: $CH_2Cl_2/MeOH$, 99:1) to afford Z-chabamide (**11**) as white solid (R_f = 0.43, 15 mg, 44 %) and Z-nigramide B (**12**) as white solid (R_f = 0.40, 5 mg, 15 %).

5. Electrochemical analysis

5.1. General procedures for electrochemical analysis

Electrochemical potentials of starting materials were determined by measuring half-wave potentials ($E_{1/2}$). The electrochemical measurements were recorded at room temperature with an AUTOLAB potentiostat/galvanostat (model: PGSTAT302N) using an undivided three-electrodes cell fitted with glassy carbon working electrode (\varnothing = 2mm), a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference. Scan rate: 100 $mV \cdot s^{-1}$. A 0.1 M solution of nBu_4NPF_6 in CH_3CN was used as supporting electrolyte.

5.2. Cyclic voltammetry of piperine (1) [oxidation potential]

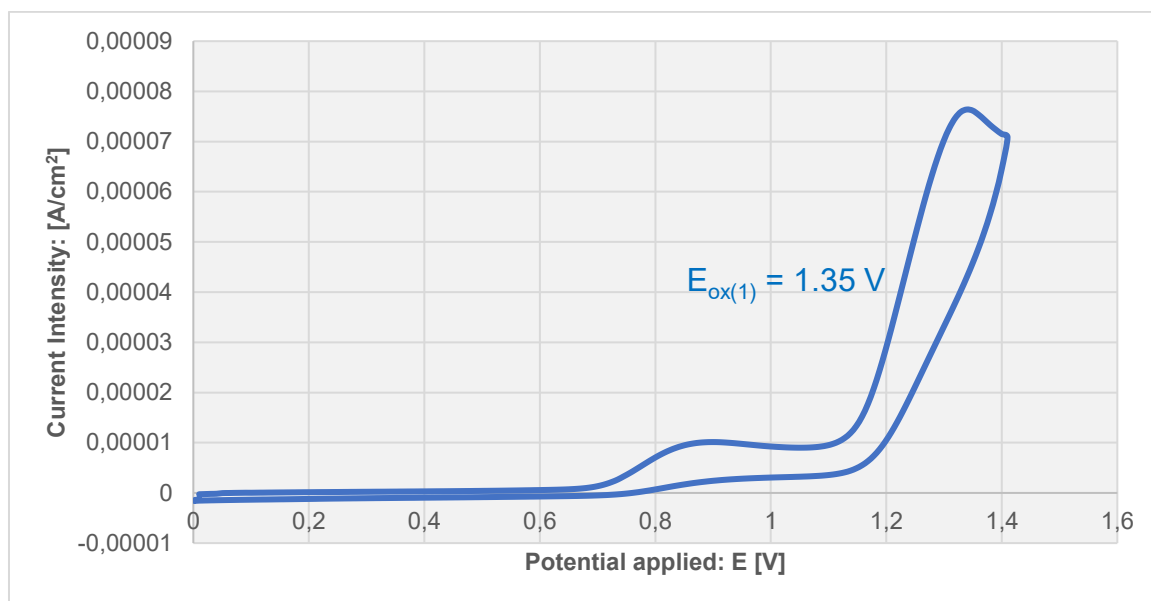


Figure 2: Cyclic voltammogram of piperine (1); 0.1 mM in a 0.1 M solution of $n\text{Bu}_4\text{NPF}_6$ in CH_3CN ; scan rate = 100 $\text{mV}\cdot\text{s}^{-1}$; 0.0 mV \rightarrow 1.4 mV \rightarrow 0.0 mV; glassy carbon working electrode ($\varnothing = 2\text{mm}$)– Pt counter electrode – reference: saturated calomel electrode (SCE).

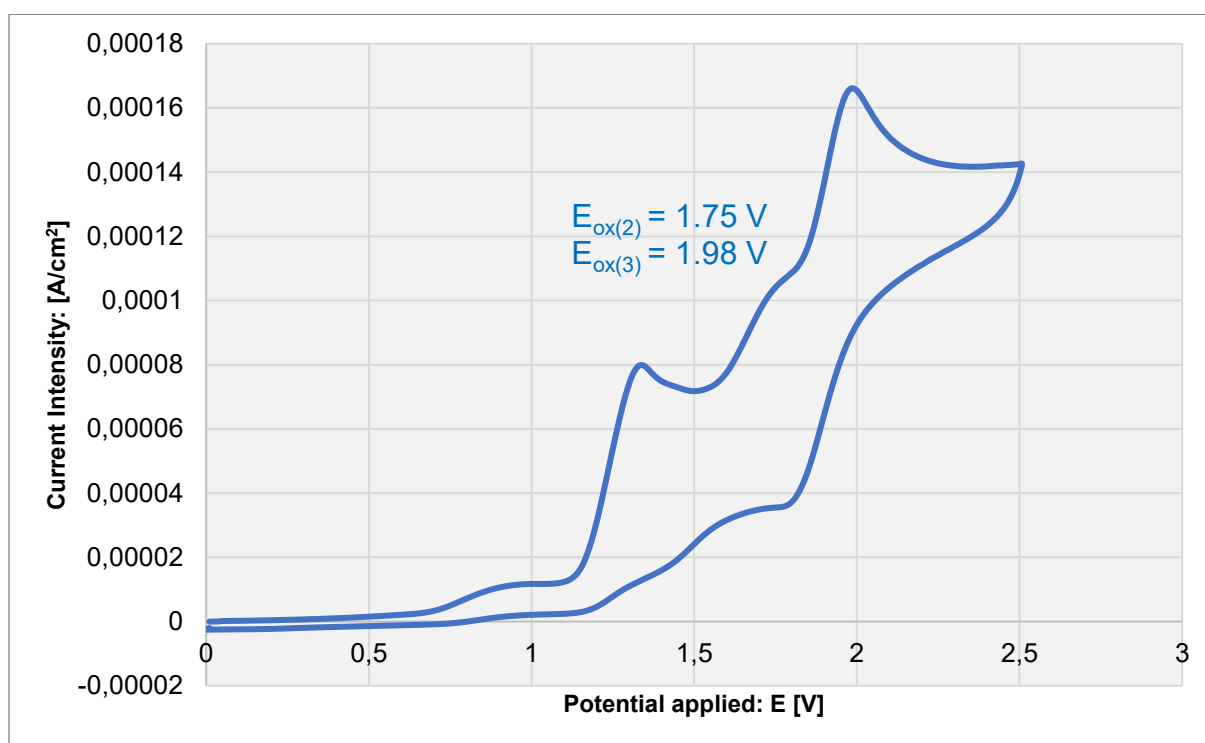


Figure 3: Cyclic voltammogram of piperine (1); 0.1 mM in a 0.1 M solution of $n\text{Bu}_4\text{NPF}_6$ in CH_3CN ; scan rate = 100 $\text{mV}\cdot\text{s}^{-1}$; 0.0 mV \rightarrow 2.5 mV \rightarrow 0.0 mV; glassy carbon working electrode ($\varnothing = 2\text{mm}$)– Pt counter electrode – reference: saturated calomel electrode (SCE).

5.3. Cyclic voltammetry of piperine (1) [reduction potential]

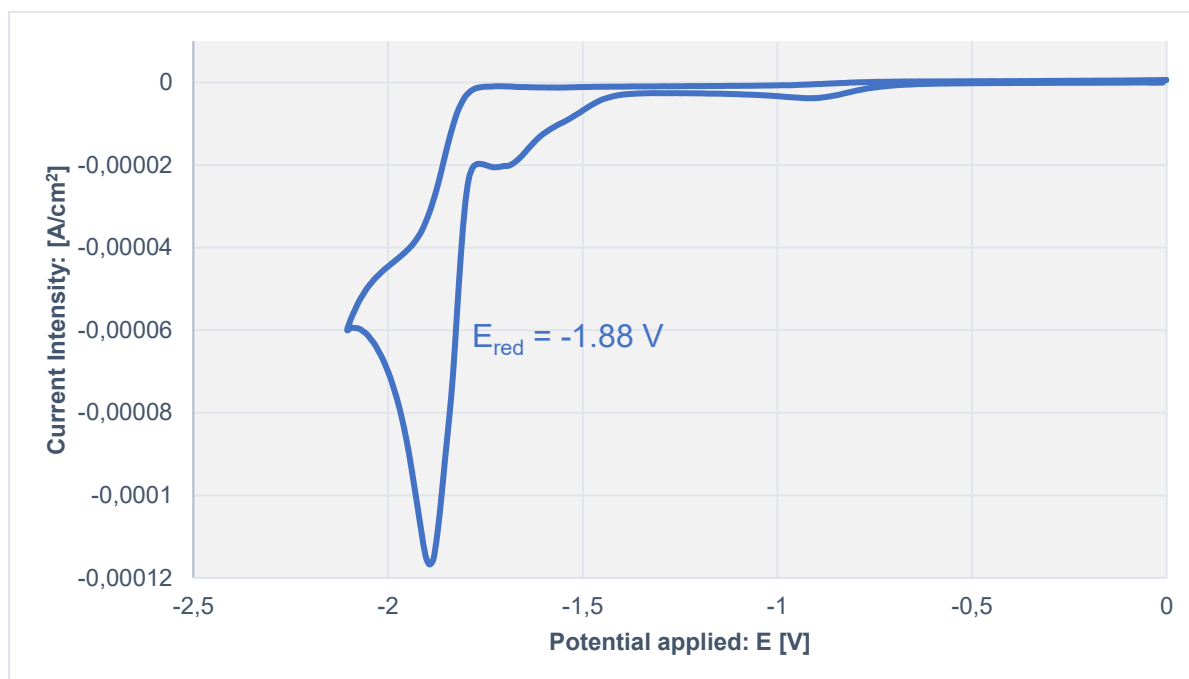
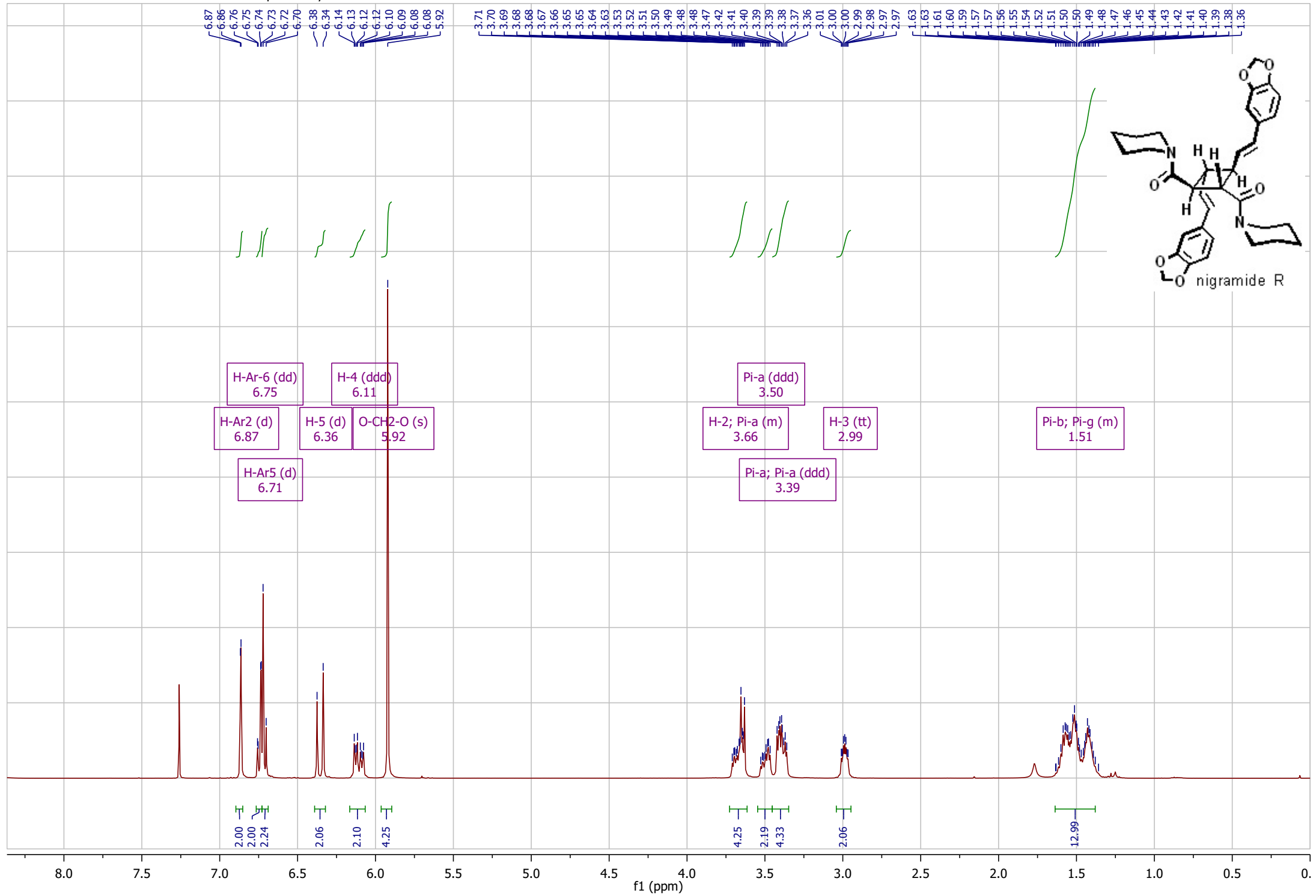
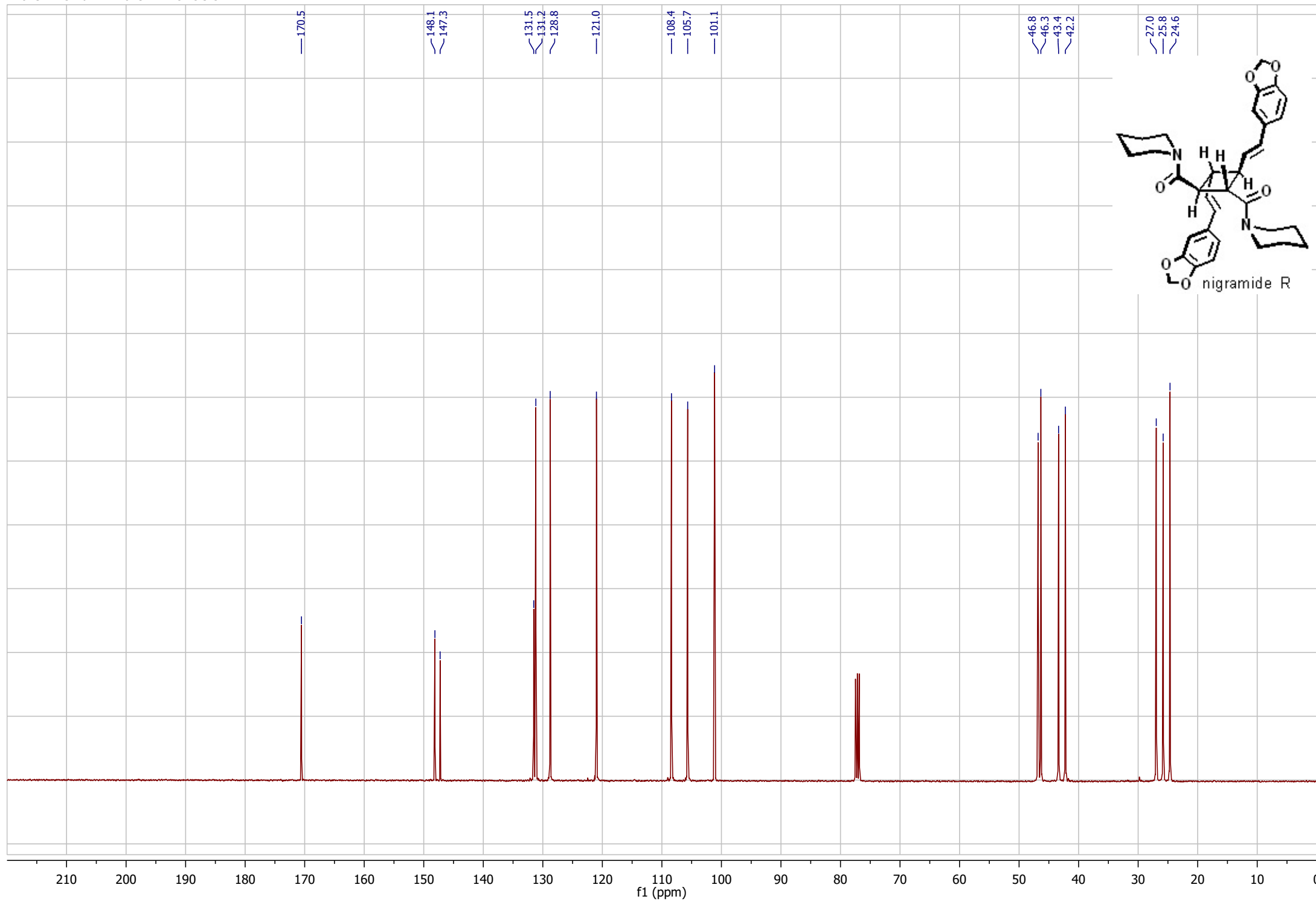
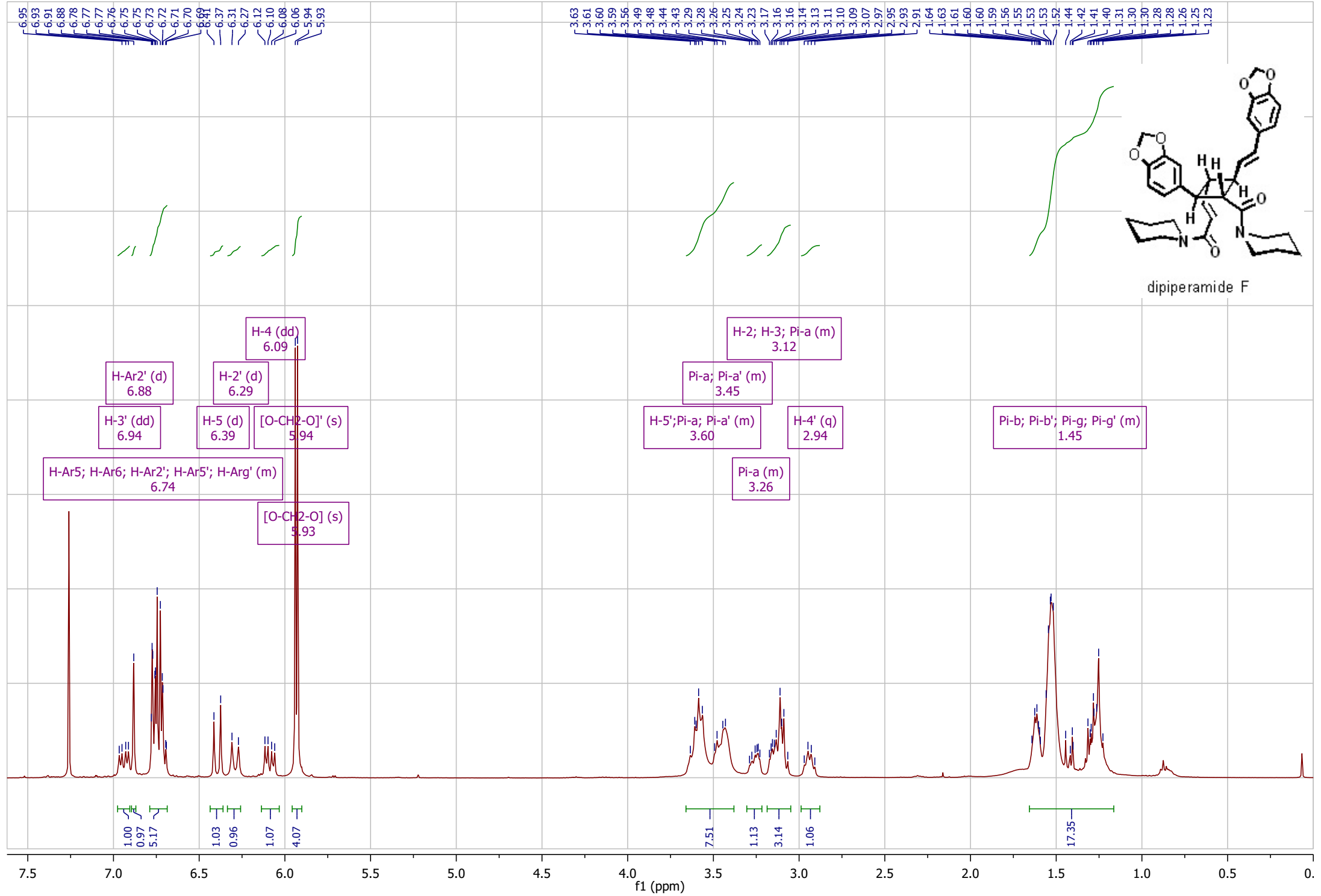
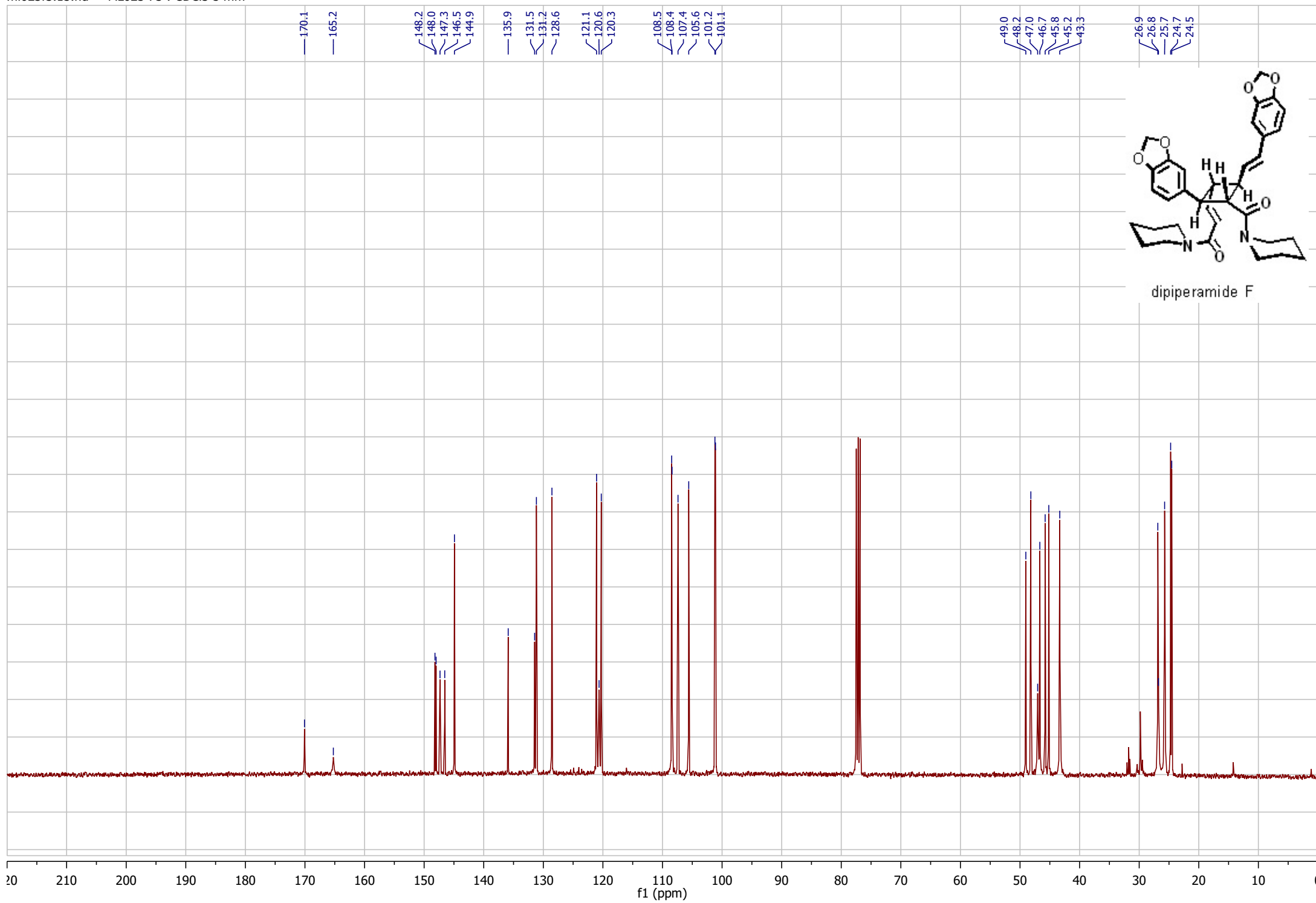


Figure 4: Cyclic voltammogram of piperine (1); 0.1 mM in a 0.1 M solution of $n\text{Bu}_4\text{NPF}_6$ in CH_3CN]; scan rate = 100 $\text{mV}\cdot\text{s}^{-1}$; 0.0 mV \rightarrow -2.1 mV \rightarrow 0.0 mV; glassy carbon working electrode ($\varnothing = 2\text{mm}$) – Pt counter electrode – reference: saturated calomel electrode (SCE).

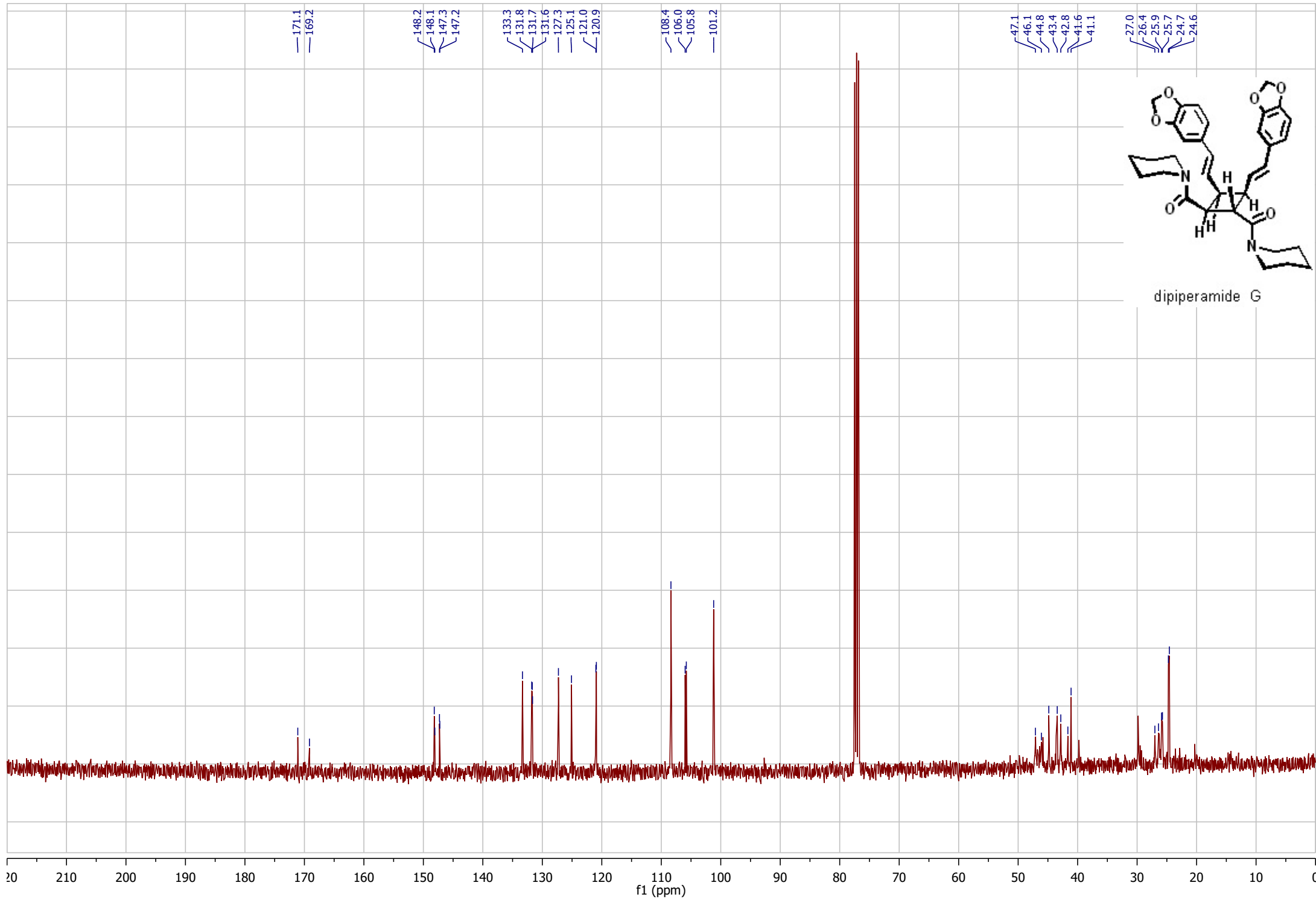






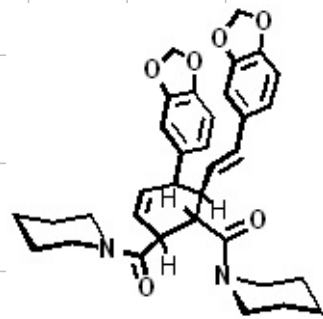
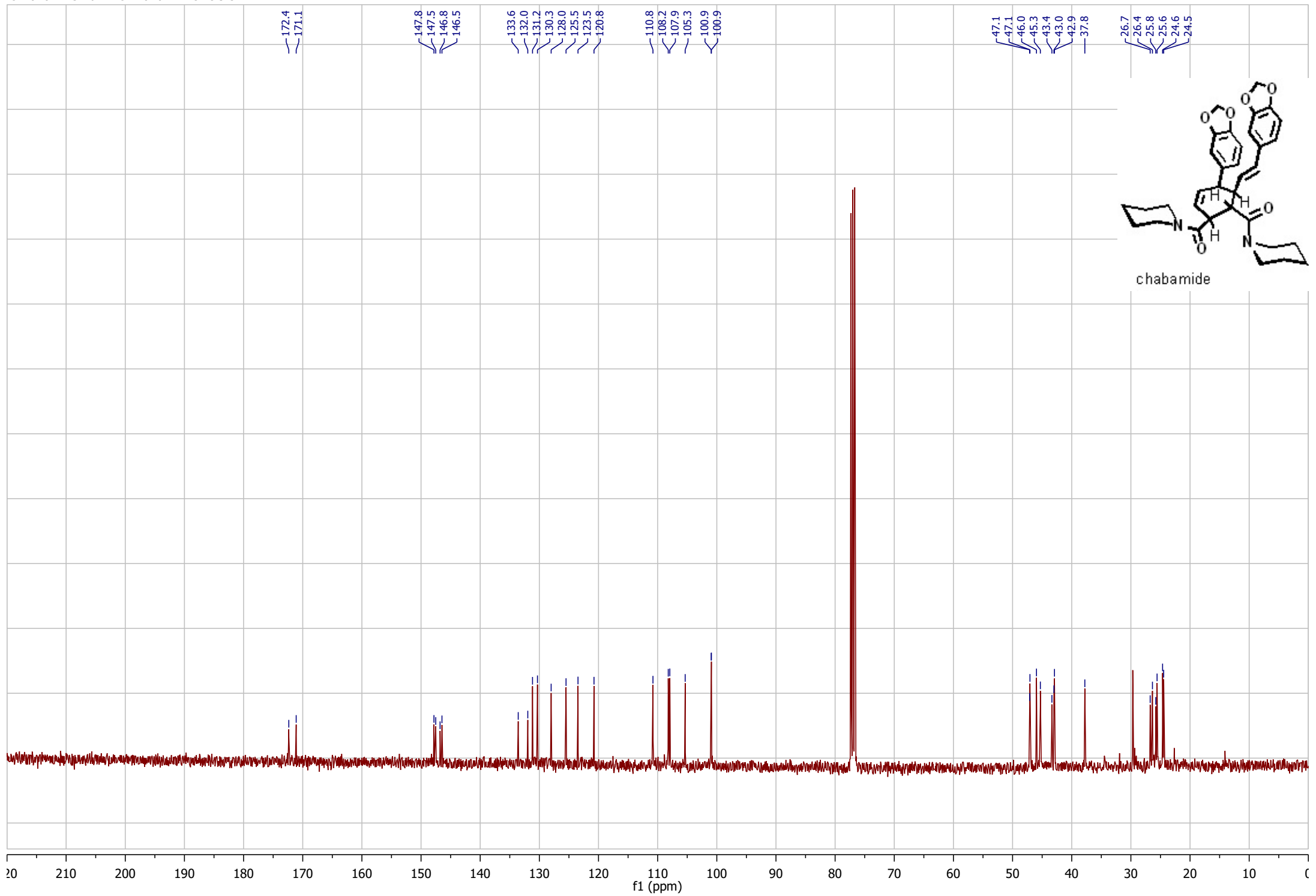






dipiperamide G





chabamide

