SUPPORTING INFORMATION

Thermodynamically Driven, *syn*-Selective Vinylogous Aldol Reaction of Tetronamides

Milandip Karak[a, b], Luiz C. A. Barbosa[a, b] *, Jaime A. M. Acosta[a], Ariel M. Sarotti[c] and John Boukouvalas[d]

[a]*Departament of Chemistry, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Pres. Antônio Carlos, 6627, Campus Pampulha, Belo Horizonte, 31270-901, MG, Brazil. E-mail: lcab@ufmg.br*

[b] *Departament of Chemistry, Universidade Federal de Viçosa, Viçosa, 36570-900, MG, Brazil.*

[c]*Instituto de Química Rosario (IQUIR), Universidad Nacional de Rosario–CONICET, Suipacha 531, S2002LRK Rosario, Argentina.*

[d]*Département de Chimie, Pavillon Alexandre-Vachon, Universitè Laval, 1045 Avenue de la Médecine, Quebec City, Quebec G1V 0A6, Canada.*

Contents

1. Computational methods

All molecular mechanics calculations were performed using Hyperchem with the MM+ force field,[1] and the quantum mechanical calculations were performed using Gaussian 09.[2] Conformational searches were run to locate the minimum energy conformers of all the structures. Initially, the conformational search was done in the gas phase using the MM+ force field, with the number of steps large enough to find all low-energy conformers at least 10 times. All conformers within 5 kcal/mol of the lowest energy conformer were subjected to further reoptimization at the HF/3-21G level of theory. With the most stable conformers in hand (up to 5 kcal/mol of the lowest energy conformer) were then further optimized at the B3LYP/6-31G* level of theory. Frequency calculations were used to confirm the nature of the stationary points and to evaluate the thermochemical properties, that were calculated at 1 atm and 298.15 K. Energies in solution were computed on the structures optimized in the gas phase at the B3LYP/6-31G* level of theory with the Polarizable Continuum Model (PCM) as implemented in Gaussian 09 using chloroform as the solvent.[3]

The next step was the shielding constants single point calculation using the GIAO (gauge including atomic orbitals) method,[4] with the mPW1PW91 functional[5] (one of the most reliable DFT functionals for NMR calculations)[6] and the 6-31+G** basis set, with the PCM model using chloroform as the solvent. The NMR shielding constants were subjected to Boltzmann averaging over all conformers according to:

$$\sigma^x = \frac{\sum_i \sigma^x{}_i \exp(-E_i / RT)}{\sum_i \exp(-E_i / RT)}$$

[1] Hyperchem Professional Release 7.52, Hypercube, Inc., 2005.

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. Kitao, O.; Nakai, H. Vreven, T.; Montgomery, J. A., Jr.,; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J. Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.

[3] For a review on continuum solvation models, see: Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999-3093.

[4] (a) R. Ditchfield, *J. Chem. Phys.* **1972**, *56*, 5688-5691. (b) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789-807. (c) C. M. Rohlfing, L. C. Allen and R. Ditchfield, *Chem. Phys.* **1984**, *87*, 9-15. (d) K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260.

[5] C. Adamo and V. Barone, *J. Chem. Phys.* **1998**, *108*, 664-675.

[6] Lodewyk, M.W.; Siebert, M.R.; Tantillo, D.J. *Chem. Rev.* **2012**, *112*, 1839-1862.

Where σ^x is the Boltzmann-averaged shielding constant for nucleus x, σ^x_i is the shielding constant for nucleus x in conformer i, R is the molar gas constant (8.3145 J K^{-1} mol^{-1}), T is the temperature (298 K), and E_i is the B3LYP/6-31G* energy in solution of conformer i (relative to the lowest energy conformer).

Once the shielding constants were computed, the chemical shifts were calculated according to:[7]

$$\delta^x_{calc} = \sigma_{ref} - \sigma^x + \delta_{ref}$$

where σ_{ref} is the NMR isotropic magnetic shielding values for the reference compound, and δ_{ref} is the experimental chemical shift of the reference compound in deuterated chloroform. In this study the multi-standard approach (MSTD) to calculate the NMR chemical shifts was used. Therefore, methanol (δ_{ref} = 50.41 ppm for ^{13}C) and benzene (δ_{ref} =128.37 ppm for ^{13}C) were used as reference standards for sp^3 and sp-sp^2 hybridized carbon atoms, or for the protons attached to them, respectively.[12] Sarotti and Pellegrinet have recently found that this simple modification allowed much better accuracy and lower dependence on the theory level employed, both for ^{13}C and ^{1}H NMR shift calculation procedure.[12] The CP3 parameters were computed as described by Goodman.[8] The *J* values were computed at the B3LYP/6-31G**//B3LYP/6-31G* level of theory using the nmr=spinspin keyword as implemented in Gaussian 09. The M062X/6-311+G** calculations were carried out from the most stable conformations found at the B3LYP/6-31G* level (up to 2 kcal/mol from the global minima) and reoptimized at the M062X/6-311+G** level. Frequency calculations were used to confirm the nature of the stationary points and to evaluate the thermochemical properties, that were calculated at 1 atm and 298.15 K.

[7] (a) A. M. Sarotti and S. C. Pellegrinet, *J. Org. Chem.* **2009**, *74*, 7254-7260. (b) A. M. Sarotti and S. C. Pellegrinet, *J. Org. Chem.* **2012**, *77*, 6059-6065.

[8] Smith, S.G.; Goodman, J.M. *J. Org. Chem.* **2009**, *74*, 4597-4607.

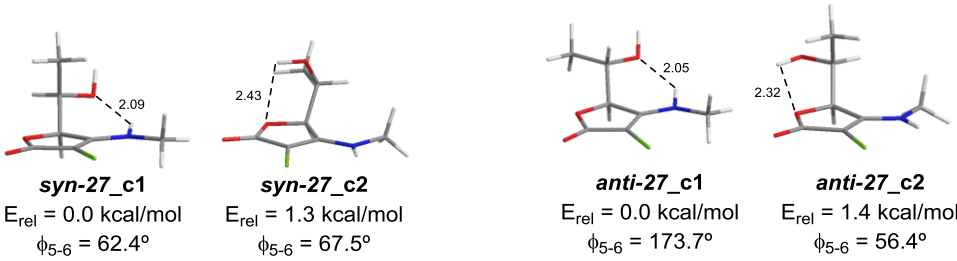


Figure S1. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***syn*-27** and ***anti*-27**.

Table S1. B3LYP/6-31G**//B3LYP/6-31G* total nuclear spin-spin coupling $J_{5\text{-}6}$

Conformer	$J_{5\text{-}6}$
***syn*-27_c1**	4.5 Hz
***syn*-27_c2**	0.9 Hz
Boltzmann averaged	*4.1 Hz*
***anti*-27_c1**	7.8 Hz
***anti*-27_c2**	3.3 Hz
Boltzmann averaged	*7.4 Hz*

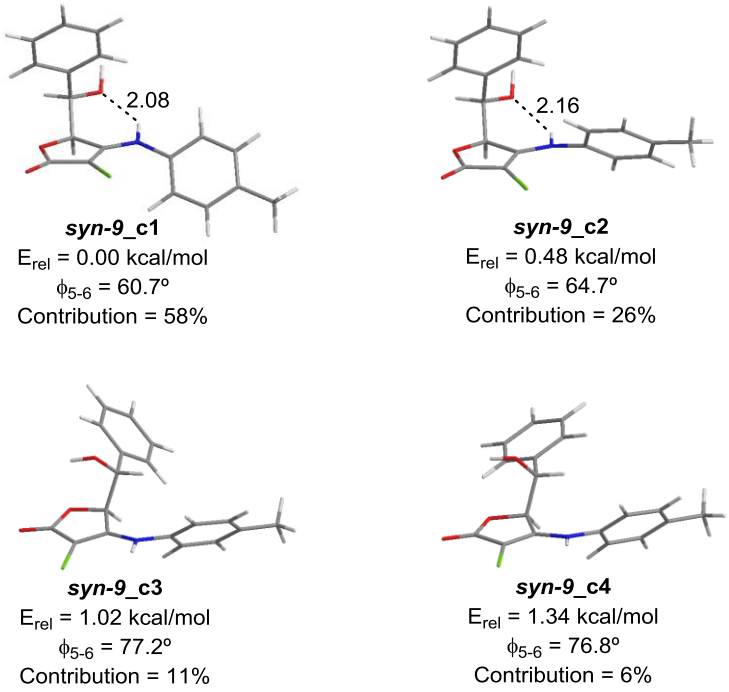


Figure S2. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***syn*-9**.

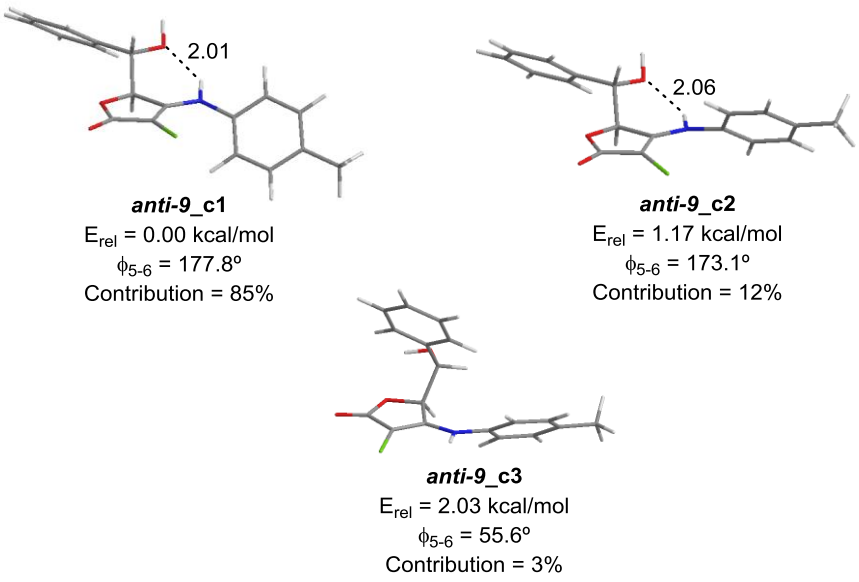


Figure S3. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***anti-9***.

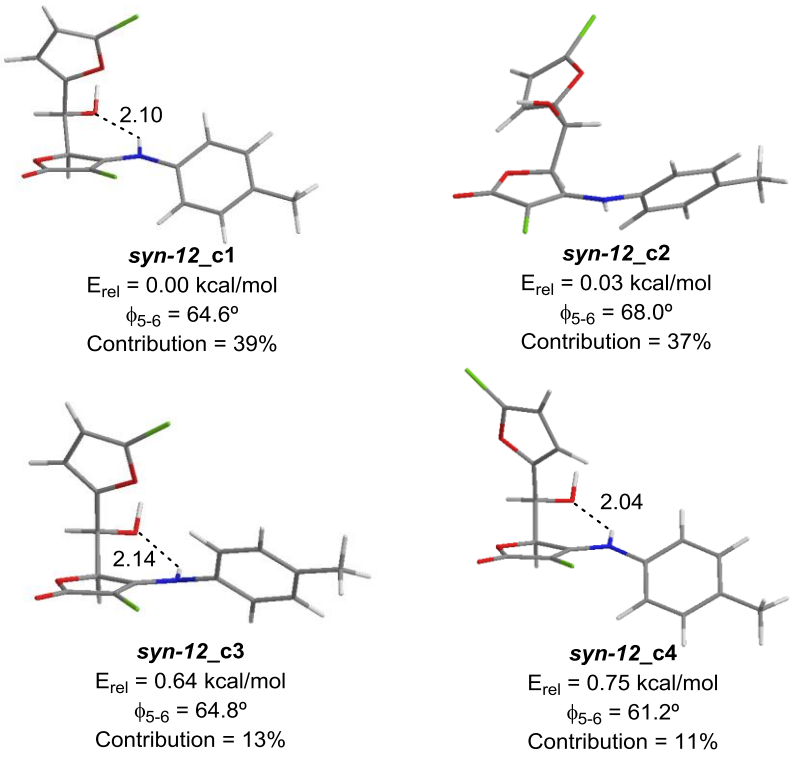


Figure S4. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***syn-12***.

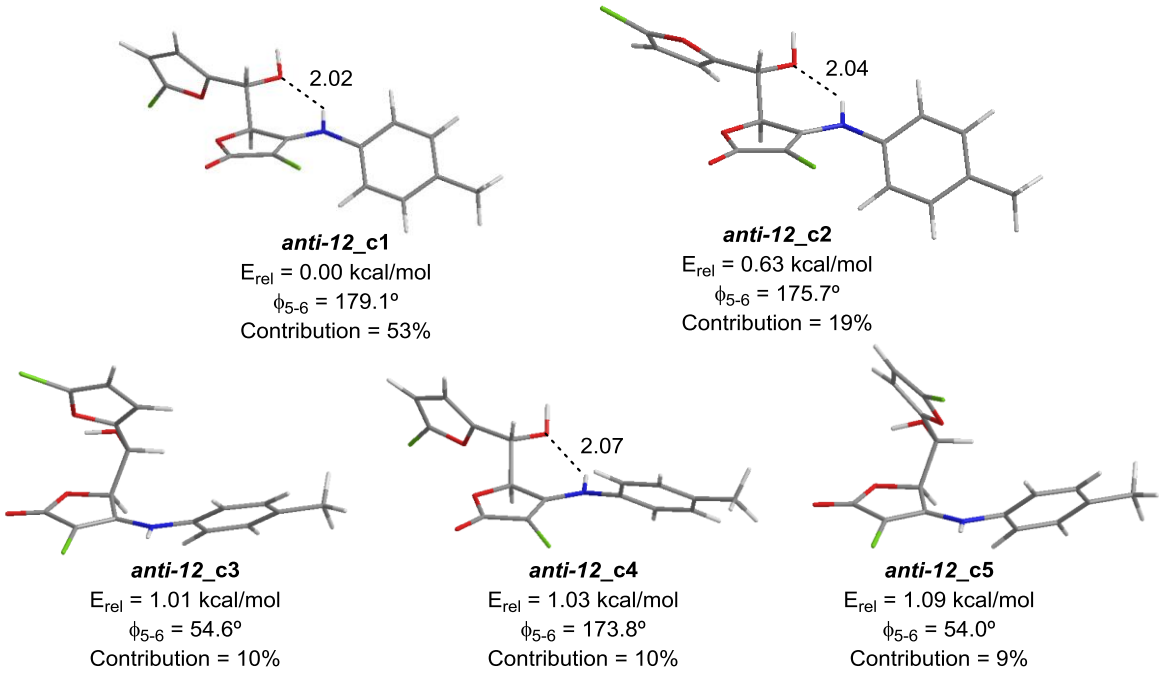


Figure S5. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***anti-12***.

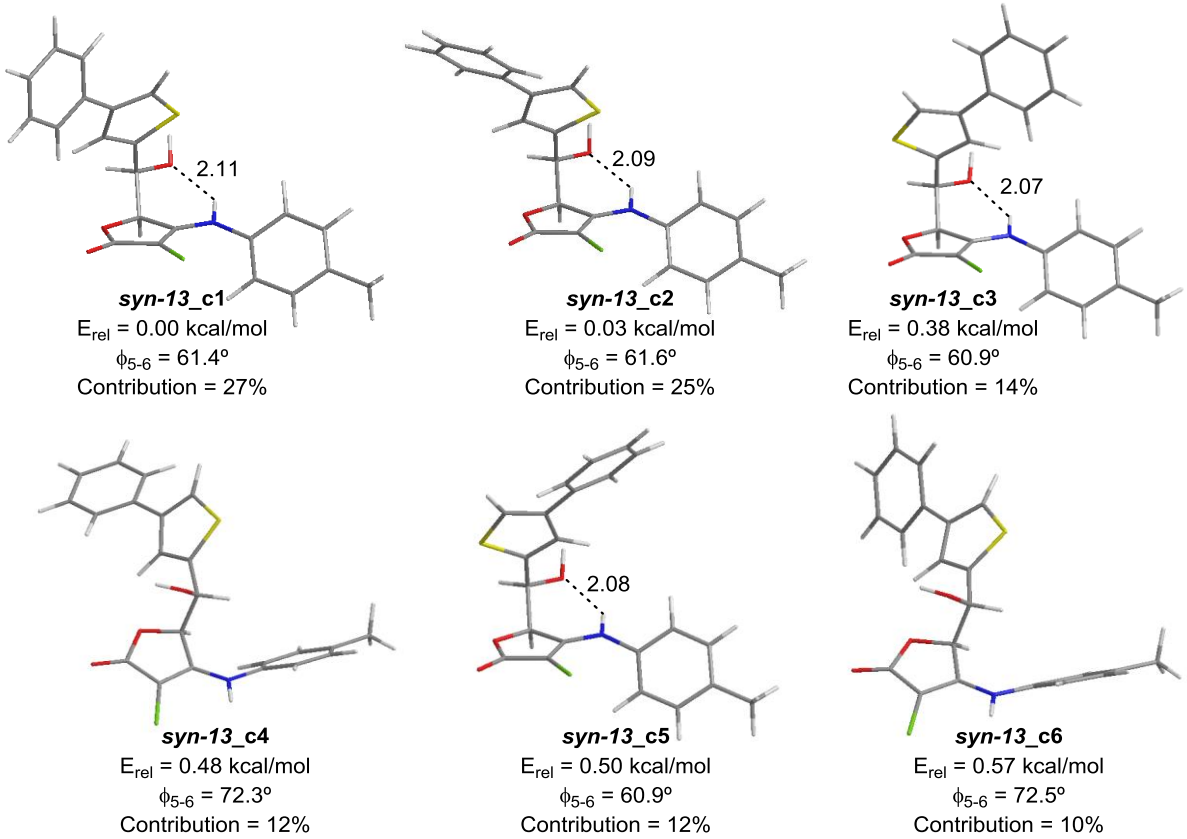


Figure S6. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***syn-13***.

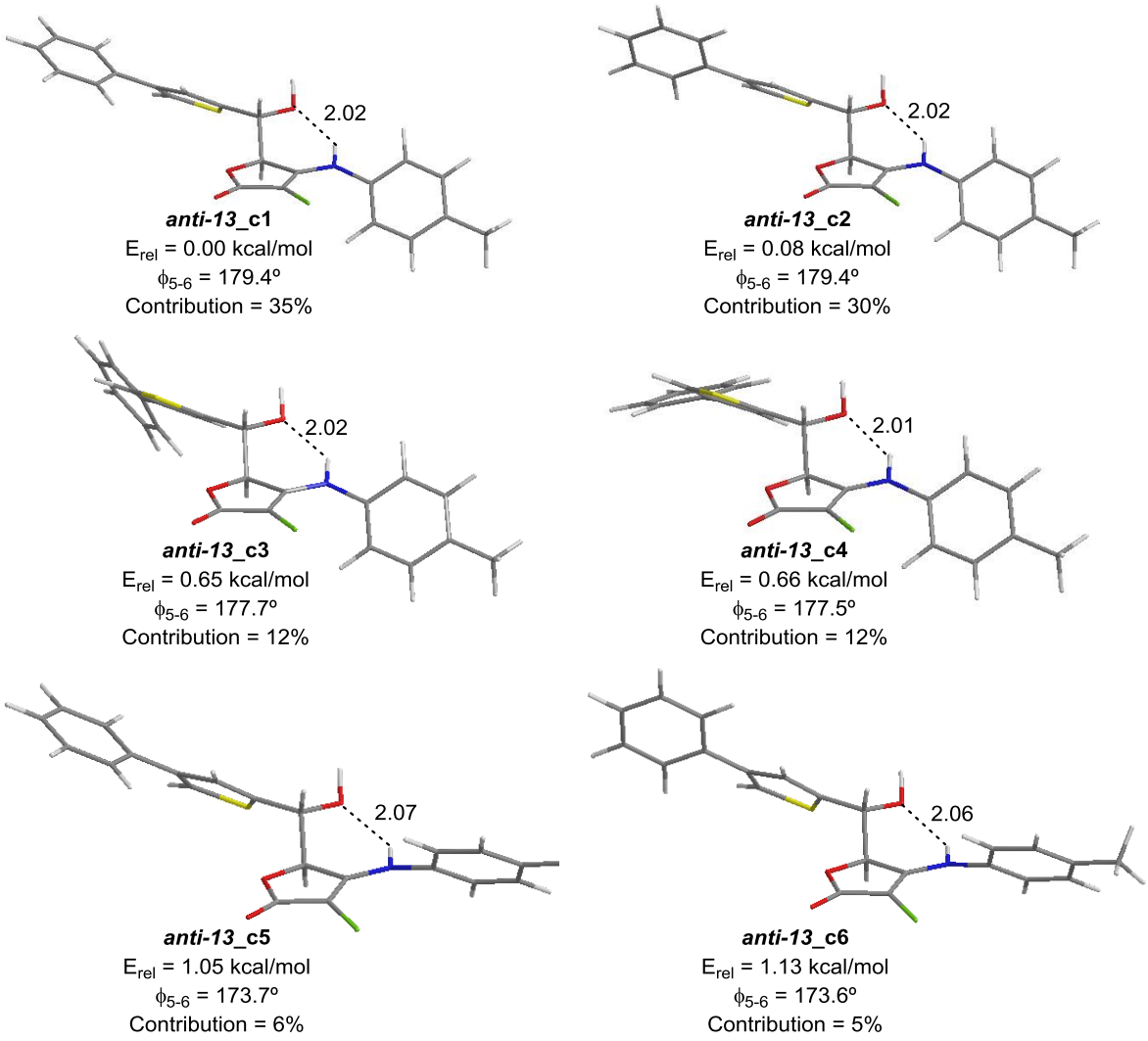


Figure S7. B3LYP/6-31G* optimized geometries of all significantly populated conformers of ***anti-13***.

Table S2. NMR isotropic magnetic shielding values (σ) calculated at the PCM/mPW1PW91/6-31+G**// B3LYP/6-31G* (solvent: chloroform) level of theory for all significantly populated conformers of ***syn-9***. The Boltzmann averaged σ values and the calculated chemical shifts (δ) are also shown.

	σ_{calc} (ppm)				Boltzmann	
Atom	***syn-9*_c1**	***syn-9*_c2**	***syn-9*_c3**	***syn-9*_c4**	**Averaged**	δ_{calc} **(ppm)**
C2	32.2445	32.1395	33.1571	32.9341	32.3558	166.6
C3	100.2693	101.4880	97.5681	97.1264	100.1063	98.9
C4	44.5904	43.7099	40.4748	40.7212	43.6926	155.3
C5	119.2578	119.3672	114.4740	115.9469	118.5796	76.1
C6	118.8525	118.3416	125.4437	122.4767	119.6363	75.0
C7	61.6275	61.7769	57.5463	55.5285	60.8616	138.1
C8-C12	72.0148	70.5726	73.6667	70.0562	71.6955	127.3
C9-C11	70.5550	71.5220	70.7957	70.3087	70.8145	128.2
C10	69.4609	69.1683	71.3548	69.7519	69.6023	129.4
C2′	64.0640	64.6396	63.6449	63.1517	64.1123	134.9
C3′-C7′	76.7358	74.2856	75.9390	77.1090	76.0430	122.9
C4′-C6′	70.0286	70.0735	68.4980	68.3082	69.7734	129.2
C5′	61.9732	61.4277	60.2698	60.8774	61.5860	137.4
C8′	172.0505	174.1211	173.9584	174.4729	172.9343	21.7

Table S3. NMR isotropic magnetic shielding values (σ) calculated at the PCM/mPW1PW91/6-31+G**// B3LYP/6-31G* (solvent: chloroform) level of theory for all significantly populated conformers of ***anti-9***. The Boltzmann averaged σ values and the calculated chemical shifts (δ) are also shown.

	σ_{calc} (ppm)				
Atom	***anti-9*_c1**	***anti-9*_c2**	***anti-9*_c3**	**Boltzmann Averaged**	δ_{calc} **(ppm)**
C2	32.0058	32.2929	34.2982	32.1061	166.9
C3	99.7825	102.1730	98.7877	100.0427	98.9
C4	41.6922	41.1546	43.1743	41.6697	157.3
C5	116.7954	117.7026	116.0438	116.8834	77.8
C6	117.2778	116.9278	121.5396	117.3575	77.3
C7	57.8197	58.5333	60.2356	57.9750	141.0
C8-C12	72.3946	70.5854	72.3180	72.1739	126.8
C9-C11	69.5467	71.1033	70.4295	69.7599	129.2
C10	70.3363	68.5202	70.1488	70.1117	128.9
C2′	64.4313	63.8808	61.9521	64.2939	134.7
C3′-C7′	76.7427	73.7066	79.2941	76.4491	122.5
C4′-C6′	70.3089	70.1073	67.1040	70.1929	128.8
C5′	62.4630	60.5988	61.2134	62.2022	136.8
C8′	175.1467	173.2063	173.2666	174.8586	19.8

Table S4. NMR isotropic magnetic shielding values (σ) calculated at the PCM/mPW1PW91/6-31+G**// B3LYP/6-31G* (solvent: chloroform) level of theory for all significantly populated conformers of ***syn-12***. The Boltzmann averaged σ values and the calculated chemical shifts (δ) are also shown.

	σ_{calc} (ppm)				Boltzmann	
Atom	***syn-12*_c1**	***syn-12*_c2**	***syn-12*_c3**	***syn-12*_c4**	**Averaged**	δ_{calc} **(ppm)**
C-2	29.1651	30.2117	30.2161	28.9032	29.5172	169.5
C-3	96.8194	93.6065	93.6031	98.2697	95.6110	103.4
C-4	40.9397	37.8907	37.8905	39.5255	39.7099	159.3
C-5	115.7230	112.9355	112.9301	116.1420	114.7591	79.9
C-6	118.6979	125.8871	125.8877	119.2053	121.5403	73.1
C-7	47.7961	40.6677	40.6603	47.6169	44.8125	154.2
C-8	79.4989	82.9251	82.9206	78.6674	80.9196	118.1
C-9	87.8954	88.4846	88.4837	87.8970	87.8334	111.1
C-10	49.6824	51.7156	51.7144	48.9494	50.3955	148.6
C-2’	61.7281	60.1429	60.1509	61.3163	60.8560	138.1
C-3’, 7’	73.4535	74.2275	74.2374	70.9471	73.5556	125.4
C-4’, 6’	67.8650	65.1273	65.1212	66.9734	66.5761	132.4
C-5’	58.9082	57.1284	57.1303	56.7139	57.9658	141.0
C-8’	169.9259	170.2918	170.0937	167.8506	169.6417	25.0

Table S5. NMR isotropic magnetic shielding values (σ) calculated at the PCM/mPW1PW91/6-31+G**// B3LYP/6-31G* (solvent: chloroform) level of theory for all significantly populated conformers of ***anti-12***. The Boltzmann averaged σ values and the calculated chemical shifts (δ) are also shown.

	σ_{calc} (ppm)					Boltzmann	
Atom	***anti-12*_c1**	***anti-12*_c2**	***anti-12*_c3**	***anti-12*_c4**	***anti-12*_c5**	**Averaged**	δ_{calc} **(ppm)**
C-2	28.8828	29.1386	31.2477	29.1532	31.3783	29.4059	169.6
C-3	96.0896	96.1711	94.2718	98.4081	93.9173	95.9584	103.0
C-4	39.6092	39.5744	40.8751	39.0317	40.2348	39.7269	159.3
C-5	115.3289	111.5871	112.0858	115.7917	113.7372	114.2186	80.5
C-6	118.5392	118.0781	124.4703	120.0426	122.5394	119.5293	75.1
C-7	45.1771	41.3397	44.8291	44.4559	44.1555	44.2716	154.7
C-8	80.7407	84.0563	83.8306	87.9029	83.3224	82.5699	116.4
C-9	87.2762	86.6546	87.8604	80.4175	88.4470	86.6650	112.3
C-10	49.2350	50.2729	49.7952	49.4920	51.7160	49.7226	149.3
C-2′	61.2012	61.2932	59.3668	61.5203	59.5520	60.9248	138.1
C-3′, 7′	74.2880	73.6773	76.0515	71.6365	73.0941	73.9923	125.0
C-4′, 6′	67.5905	67.4827	64.9381	67.7243	65.5758	67.1467	131.8
C-5′	59.0301	59.5998	57.8339	57.4264	56.5753	58.6524	140.3
C-8′	170.3838	171.1770	169.9321	171.1296	168.6014	170.4037	24.3

Table S6. NMR isotropic magnetic shielding values (σ) calculated at the PCM/mPW1PW91/6-31+G**// B3LYP/6-31G* (solvent: chloroform) level of theory for all significantly populated conformers of ***syn-13***. The Boltzmann averaged σ values and the calculated chemical shifts (δ) are also shown.

	σ_{calc} (ppm)						Boltzmann Averaged	δ_{calc} (ppm)
Atom	***syn-13*_c1**	***syn-13*_c2**	***syn-13*_c3**	***syn-13*_c4**	***syn-13*_c5**	***syn-13*_c6**		
C-2	31.6070	32.3244	32.3036	33.1346	32.2362	33.1676	32.3038	166.7
C-3	98.9225	99.6440	99.4796	97.4321	99.5380	96.7892	98.8557	100.1
C-4	44.1649	44.7146	44.4877	41.1852	44.6104	41.4851	43.7675	155.2
C-5	119.5933	119.6555	119.4672	116.5163	119.9439	116.1639	118.9089	75.8
C-6	120.8618	120.1649	122.1525	128.3658	121.6778	128.6772	122.6701	72.0
C-7	52.0275	52.0820	53.2279	47.9978	52.0624	48.4295	51.3617	147.6
C-8	72.6532	70.6256	73.9952	74.0055	75.4617	72.6183	72.8164	126.2
C-9	54.3540	57.2871	57.0947	54.9820	56.1839	55.7529	55.9145	143.1
C-10	72.3611	71.1118	70.2067	70.4238	69.0322	71.8537	71.0704	127.9
C-13	59.8010	60.3289	61.4748	61.8461	62.1601	61.7282	60.8893	138.1
C-14, 18	71.3044	72.8634	72.2887	72.3807	71.9866	71.8302	72.0991	126.9
C-15, 17	70.0039	69.2326	69.6823	69.1428	69.7750	70.0242	69.6367	129.3
C-16	71.5599	72.3152	71.8221	72.1600	72.0867	71.8323	71.9484	127.0
C-2’	63.9701	62.8938	64.7041	63.3277	65.1280	63.5087	63.8130	135.2
C-3’, 7’	75.8445	76.1760	76.4663	77.2211	76.5136	77.3458	76.4139	122.6
C-4’, 6’	70.5436	70.0542	70.2121	68.5051	70.4828	68.3912	69.8997	129.1
C-5’	61.8806	62.5345	62.1161	60.5865	62.4231	60.5424	61.8486	137.1
C-8’	173.7237	175.1282	174.5726	175.1354	174.8839	175.3896	174.6740	20.0

Table S7. NMR isotropic magnetic shielding values (σ) calculated at the PCM/mPW1PW91/6-31+G**// B3LYP/6-31G* (solvent: chloroform) level of theory for all significantly populated conformers of ***anti-13***. The Boltzmann averaged σ values and the calculated chemical shifts (δ) are also shown.

	σ_{calc} (ppm)						Boltzmann Averaged	δ_{calc} (ppm)
Atom	***anti-13*_c1**	***anti-13*_c2**	***anti-13*_c3**	***anti-13*_c4**	***anti-13*_c5**	***anti-13*_c6**		
C-2	31.8256	32.0803	32.3932	32.4611	32.0234	32.2736	32.0790	166.9
C-3	100.1485	100.3562	100.6915	100.3599	102.5867	102.7276	100.5845	98.4
C-4	42.5007	42.8120	43.0852	43.4508	41.7050	41.8080	42.6889	156.3
C-5	118.0359	118.0716	116.4930	116.2970	118.3189	118.0235	117.6805	77.0
C-6	119.3960	119.3572	120.7856	120.9178	120.2244	120.1230	119.8125	74.9
C-7	48.8433	48.4229	48.9306	48.8848	48.2705	48.0231	48.6525	150.3
C-8	71.0225	70.4891	75.0367	74.7102	71.1622	70.8922	71.7615	127.2
C-9	55.4914	56.7899	55.8614	54.3402	54.0426	53.4242	55.6001	143.4
C-10	70.6022	70.5912	69.7743	69.4542	70.5354	70.3642	70.3521	128.6
C-13	61.5548	60.3823	62.3820	62.8235	61.5212	62.1835	61.4737	137.5
C-14, 18	71.2994	72.4950	70.6507	72.2689	70.0342	70.0580	71.5550	127.4
C-15, 17	70.3431	69.4193	70.9789	69.5830	71.2789	71.4956	70.1680	128.8
C-16	71.0750	72.5207	71.1922	71.3200	70.3638	70.4003	71.4776	127.5
C-2′	64.5595	64.3986	63.9488	63.5954	64.0827	64.0406	64.2710	134.7
C-3′, 7′	76.7426	76.8457	77.0367	77.4963	74.2948	74.3617	76.6211	122.4
C-4′, 6′	70.6653	70.6257	69.4205	68.6874	69.2337	69.1652	70.1121	128.9
C-5′	62.1853	62.2149	62.5149	62.9750	60.7124	60.7670	62.1598	136.8
C-8′	175.9752	175.8580	174.2148	172.8042	173.8209	173.7453	175.1178	19.6

Table S8. CP3 values computed for the matched pairs.

Pair	CP3 (based on ^{13}C data)
major-***syn*-9**/ minor-***anti*-9**	0.54
major- ***syn*-12**/ minor- ***anti*-12**	0.35
major- ***syn*-13**/ minor- ***anti*-13**	0.37

Table S9. CP3 values computed for the mismatched pairs.

Pair	CP3 (based on ^{13}C data)
major- ***anti*-9**/ minor- ***syn*-9**	-0.58
major- ***anti*-12** / minor- ***syn*-12**	-0.55
major- ***anti*-13**/ minor- ***syn*-13**	-1.47

***syn*-27_c1**

B3LYP/6-31G* geometry

C 0	0.545674	-0.172266	-0.511932
C 0	1.709186	-0.819319	-0.230580
C 0	-0.466263	-1.239671	-0.901073
C 0	1.529818	-2.264542	-0.367259
C 0	-1.763131	-1.257676	-0.073169
Cl 0	3.249320	-0.176918	0.252094
N 0	0.169703	1.123613	-0.553222
O 0	2.298598	-3.174005	-0.196568
O 0	0.207086	-2.485848	-0.751775
C 0	0.990428	2.262204	-0.163530
C 0	-1.542773	-1.352914	1.431893
O 0	-2.451669	-0.052435	-0.449359
H 0	-0.745862	-1.111814	-1.955178
H 0	-2.336545	-2.131991	-0.413650
H 0	-0.833675	1.260222	-0.606853
H 0	1.947844	2.241844	-0.687680
H 0	1.186592	2.289539	0.915829
H 0	0.459314	3.174005	-0.447376
H 0	-0.997340	-0.481732	1.808645
H 0	-0.976283	-2.256382	1.676344
H 0	-2.505262	-1.411451	1.955178
H 0	-3.249320	0.020678	0.096930

B3LYP/6-31G* Energy = -1013.37436055
B3LYP/6-31G* Free Energy = -1013.240778
B3LYP/6-31G* Energy ($CHCl_3$) = -1013.38545961
Number of Imaginary Frequencies = 0

***syn*-27_c2**

B3LYP/6-31G* geometry

C 0	0.869409	0.019203	-0.252148
C 0	1.899646	-0.846629	-0.066123
C 0	-0.346659	-0.799346	-0.641898
C 0	1.480246	-2.212505	-0.329377
C 0	-1.528701	-0.761385	0.357858
Cl 0	3.513007	-0.419937	0.399229
N 0	0.901518	1.365547	-0.158931
O 0	2.072824	-3.258637	-0.279704
O 0	0.130581	-2.152000	-0.697151
C 0	-0.214511	2.280055	-0.324995
C 0	-2.708707	-1.595330	-0.148157
O 0	-1.099657	-1.168982	1.644308
H 0	-0.699533	-0.519950	-1.644308
H 0	-1.850220	0.277976	0.479737
H 0	1.771701	1.754105	0.181446
H 0	-0.805766	2.402061	0.592276
H 0	-0.875525	1.935978	-1.125911
H 0	0.175764	3.258637	-0.616805
H 0	-2.405352	-2.635320	-0.307938
H 0	-3.098112	-1.205961	-1.096487
H 0	-3.513007	-1.573608	0.592859
H 0	-0.782715	-2.084198	1.557582

B3LYP/6-31G* Energy = -1013.37147906
B3LYP/6-31G* Free Energy = -1013.238629
B3LYP/6-31G* Energy ($CHCl_3$) = -1013.38337349
Number of Imaginary Frequencies = 0

***anti*-27_c1**

B3LYP/6-31G* geometry

C 0	0.866686	0.026124	-0.219826
C 0	1.866889	-0.870955	-0.002597
C 0	-0.399071	-0.781669	-0.478182
C 0	1.346069	-2.235215	-0.061663
C 0	-1.564337	-0.472471	0.476066
Cl 0	3.549098	-0.599282	0.335899
N 0	0.806995	1.373264	-0.287421
O 0	1.891743	-3.296623	0.089523
O 0	-0.018801	-2.147297	-0.336306
O 0	-1.946689	0.878903	0.164806
C 0	1.901164	2.285643	0.017496
C 0	-2.732688	-1.434570	0.294712
H 0	-0.745540	-0.614340	-1.507513
H 0	-1.185295	-0.530149	1.507513
H 0	-0.136699	1.742094	-0.238498
H 0	-2.661462	1.136157	0.767095
H 0	1.579422	3.296623	-0.244219
H 0	2.782906	2.038577	-0.576539
H 0	2.181553	2.267460	1.078479
H 0	-2.421743	-2.461266	0.504415
H 0	-3.114897	-1.382733	-0.730591
H 0	-3.549098	-1.175855	0.980596

B3LYP/6-31G* Energy = -1013.37496157
B3LYP/6-31G* Free Energy = -1013.241725
B3LYP/6-31G* Energy ($CHCl_3$) = -1013.38595740
Number of Imaginary Frequencies = 0

***anti*-27_c2**

B3LYP/6-31G* geometry

C 0	0.373101	0.023421	-0.591170
C 0	1.409628	-0.831170	-0.385566
C 0	-0.823701	-0.808880	-0.998741
C 0	1.014088	-2.202807	-0.671749
C 0	-2.041244	-0.807878	-0.041640
Cl 0	3.008343	-0.385984	0.112373
N 0	0.370987	1.368945	-0.477283
O 0	1.624560	-3.238173	-0.624268
O 0	-0.325983	-2.154341	-1.067014
O 0	-3.008343	-1.706639	-0.562117
C 0	-0.740891	2.261224	-0.760946
C 0	-1.684758	-1.130268	1.409994
H 0	-1.180411	-0.537589	-2.000688
H 0	-2.514731	0.178864	-0.091017
H 0	1.238557	1.783781	-0.163292
H 0	-2.565856	-2.569798	-0.638913
H 0	-1.403980	2.399152	0.103216
H 0	-1.333284	1.883512	-1.599510
H 0	-0.343620	3.238173	-1.048015
H 0	-1.025240	-0.371498	1.845671
H 0	-1.183699	-2.101350	1.483693
H 0	-2.604271	-1.173564	2.000688

B3LYP/6-31G* Energy = -1013.37196067
B3LYP/6-31G* Free Energy = -1013.238974
B3LYP/6-31G* Energy ($CHCl_3$) = -1013.38349205
Number of Imaginary Frequencies = 0

***syn-9*_c1**

B3LYP/6-31G* geometry

C	0	-0.895666	0.471884	0.957116
C	0	-1.059986	1.507277	0.091502
C	0	-2.091088	0.487730	1.895771
C	0	-2.300764	2.226145	0.399891
C	0	-2.961329	-0.793284	1.902527
Cl	0	-0.111583	1.975906	-1.275047
N	0	0.048591	-0.488022	1.142853
O	0	-2.803441	3.185267	-0.122323
O	0	-2.892270	1.589484	1.488758
C	0	1.391595	-0.534692	0.697001
C	0	4.105216	-0.738064	-0.068920
C	0	1.960822	-1.783360	0.417937
C	0	2.190130	0.612227	0.613535
C	0	3.523001	0.501833	0.224450
C	0	3.299784	-1.878229	0.048196
C	0	5.545013	-0.839312	-0.514776
C	0	-3.518326	-1.186742	0.546987
C	0	-4.582991	-1.876136	-1.957040
C	0	-4.712452	-0.606919	0.097517
C	0	-2.865090	-2.117050	-0.271172
C	0	-3.396640	-2.461976	-1.514750
C	0	-5.238139	-0.944773	-1.148610
O	0	-2.120728	-1.798117	2.485210
H	0	-1.752257	0.656514	2.926306
H	0	-3.800776	-0.574500	2.578226
H	0	-0.267649	-1.264170	1.716450
H	0	1.349452	-2.680017	0.487913
H	0	1.776581	1.581399	0.867747
H	0	4.127600	1.403748	0.163032
H	0	3.722898	-2.857947	-0.161546
H	0	5.980442	-1.808280	-0.248332
H	0	6.161425	-0.055839	-0.060817
H	0	5.634367	-0.730936	-1.604127
H	0	-4.995171	-2.142918	-2.926306
H	0	-5.222549	0.120886	0.722284
H	0	-1.935887	-2.569748	0.061373
H	0	-2.879263	-3.185267	-2.139266
H	0	-6.161425	-0.482439	-1.486331
H	0	-2.593196	-2.644322	2.435643

B3LYP/6-31G* Energy = -1436.16554714
B3LYP/6-31G* Free Energy = -1435.911751
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17723048
Number of Imaginary Frequencies = 0

***syn-9*_c2**

B3LYP/6-31G* geometry

C	0	-1.440597	1.447333	0.720379
C	0	-1.621461	2.246559	-0.364850
C	0	-2.780291	1.359877	1.431213
C	0	-3.026219	2.653215	-0.458065
C	0	-3.332277	-0.065978	1.664012
Cl	0	-0.474384	2.848026	-1.510221
N	0	-0.377607	0.818781	1.285367
O	0	-3.595373	3.337378	-1.266516
O	0	-3.695072	2.097654	0.631792
C	0	0.879499	0.490712	0.703172
C	0	3.395161	-0.272613	-0.326208
C	0	2.018285	0.529507	1.514654
C	0	0.995269	0.052230	-0.620951
C	0	2.242738	-0.311996	-1.122484
C	0	3.255760	0.143847	1.003806
C	0	4.744714	-0.647803	-0.891991
C	0	-3.405899	-0.925018	0.415257
C	0	-3.579487	-2.482248	-1.914257
C	0	-4.502280	-0.793782	-0.448084
C	0	-2.399234	-1.846544	0.100115
C	0	-2.488252	-2.623569	-1.056564
C	0	-4.585061	-1.562587	-1.608172
O	0	-2.486242	-0.608952	2.684142
H	0	-2.709649	1.837067	2.418627
H	0	-4.349344	0.073631	2.058266
H	0	-0.608574	0.316367	2.136469
H	0	1.931001	0.869221	2.543450
H	0	0.112406	-0.020502	-1.246022
H	0	2.317082	-0.648141	-2.154183
H	0	4.130232	0.178557	1.649382
H	0	5.438184	-0.958957	-0.103798
H	0	5.205895	0.199504	-1.416806
H	0	4.663460	-1.468018	-1.613805
H	0	-3.647839	-3.085810	-2.815180
H	0	-5.285815	-0.078582	-0.214107
H	0	-1.541749	-1.955374	0.757147
H	0	-1.701680	-3.337378	-1.286441
H	0	-5.438184	-1.445994	-2.270684
H	0	-2.735466	-1.537511	2.815180

B3LYP/6-31G* Energy = -1436.16482485
B3LYP/6-31G* Free Energy = -1435.910997
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17646592
Number of Imaginary Frequencies = 0

***syn-9*_c3**

B3LYP/6-31G* geometry

C	0	-1.943010	-2.691555	-0.150432
C	0	-3.180732	-3.234370	-0.255652
C	0	-2.070383	-1.204960	-0.424284
C	0	-4.159776	-2.215024	-0.613685
C	0	-1.725003	-0.308831	0.804845
Cl	0	-3.597863	-4.891049	0.017415
N	0	-0.803202	-3.323843	0.232090
O	0	-5.346939	-2.279167	-0.795061
O	0	-3.458500	-1.013779	-0.738229
C	0	0.534511	-2.867704	0.106345
C	0	3.229294	-2.037292	-0.104147
C	0	0.992871	-2.237462	-1.057151
C	0	1.434446	-3.103366	1.153521
C	0	2.762363	-2.701200	1.039051
C	0	2.319913	-1.817273	-1.146081
C	0	4.660258	-1.563871	-0.200472
C	0	-1.607340	1.159553	0.402069
C	0	-1.361987	3.850399	-0.367389
C	0	-2.510332	2.116399	0.871303
C	0	-0.567339	1.568277	-0.444255
C	0	-0.445147	2.902729	-0.828449
C	0	-2.391032	3.453378	0.485978
O	0	-2.658677	-0.547371	1.835945
H	0	-1.488437	-0.886333	-1.292416
H	0	-0.758933	-0.642899	1.198311

H 0 -0.933312 -4.261325 0.595140
H 0 0.327101 -2.111732 -1.905250
H 0 1.086375 -3.594614 2.058383
H 0 3.446459 -2.896967 1.861276
H 0 2.659110 -1.332358 -2.058383
H 0 4.788324 -0.584902 0.280278
H 0 4.978056 -1.458944 -1.242889
H 0 5.346939 -2.259095 0.294229
H 0 -1.268950 4.891049 -0.665963
H 0 -3.295979 1.818996 1.557804
H 0 0.163043 0.840756 -0.794151
H 0 0.368554 3.204028 -1.483055
H 0 -3.103135 4.184971 0.858463
H 0 -3.541222 -0.424394 1.445053

B3LYP/6-31G* Energy = -1436.16380795
B3LYP/6-31G* Free Energy = -1435.911025
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17560943
Number of Imaginary Frequencies = 0

***syn-9*_c4**
B3LYP/6-31G* geometry
C 0 -1.971273 -2.771660 -0.011712
C 0 -3.270955 -3.156687 -0.028023
C 0 -1.929397 -1.285454 -0.318517
C 0 -4.136512 -2.031677 -0.356329
C 0 -1.406052 -0.434238 0.873651
Cl 0 -3.873475 -4.739184 0.326622
N 0 -0.901074 -3.536765 0.327727
O 0 -5.332086 -1.945781 -0.457205
O 0 -3.299067 -0.938701 -0.579500
C 0 0.477511 -3.255026 0.152117
C 0 3.248476 -2.778744 -0.152613
C 0 1.378057 -3.628109 1.158330
C 0 0.970795 -2.664286 -1.017801
C 0 2.336418 -2.419237 -1.152623
C 0 2.742103 -3.400105 0.997384
C 0 4.724223 -2.493016 -0.300837
C 0 -1.106123 1.011724 0.501062
C 0 -0.508756 3.700126 -0.068194
C 0 0.116838 1.572334 0.891016
C 0 -2.029720 1.818244 -0.182112
C 0 -1.730681 3.152110 -0.462671
C 0 0.416634 2.905626 0.609760
O 0 -2.296207 -0.550805 1.973798
H 0 -1.351717 -1.056059 -1.218175
H 0 -0.474430 -0.895045 1.214864
H 0 -1.131127 -4.436828 0.733470
H 0 1.003596 -4.089815 2.068362
H 0 0.297055 -2.430927 -1.835774
H 0 2.700288 -1.959468 -2.068362
H 0 3.425047 -3.701875 1.787904
H 0 4.986048 -1.516523 0.128154
H 0 5.025014 -2.475848 -1.353569
H 0 5.332086 -3.245716 0.212184
H 0 -0.279246 4.739184 -0.288888
H 0 0.839312 0.958687 1.424433
H 0 -2.978997 1.401909 -0.504223
H 0 -2.455432 3.763340 -0.993949
H 0 1.370887 3.322400 0.921088
H 0 -3.126010 -0.115636 1.716355

B3LYP/6-31G* Energy = -1436.16356203
B3LYP/6-31G* Free Energy = -1435.912010
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17510120
Number of Imaginary Frequencies = 0

***anti-9*_c1**
B3LYP/6-31G* geometry
C 0 0.245430 -0.101237 0.063537
C 0 0.416614 1.243305 -0.051420
C 0 -1.221484 -0.332205 0.412131
C 0 -0.852579 1.934253 0.193090
C 0 -2.000900 -1.194653 -0.607312
Cl 0 1.811128 2.148279 -0.524967
N 0 1.063164 -1.179360 -0.056596
O 0 -1.125020 3.105580 0.174083
O 0 -1.811059 0.962603 0.460480
O 0 -1.363509 -2.479861 -0.572325
C 0 2.476031 -1.247623 -0.011208
C 0 5.283157 -1.550293 0.125157
C 0 3.127261 -2.205512 -0.798300
C 0 3.230913 -0.453975 0.860780
C 0 4.614625 -0.604051 0.912627
C 0 4.509562 -2.354431 -0.721891
C 0 6.787075 -1.684345 0.172980
C 0 -3.480001 -1.285071 -0.284907
C 0 -6.211779 -1.430277 0.329412
C 0 -3.955723 -2.257957 0.603750
C 0 -4.384213 -0.384831 -0.860552
C 0 -5.742340 -0.455080 -0.553212
C 0 -5.315944 -2.331605 0.906667
H 0 -1.307071 -0.801128 1.400823
H 0 -1.867931 -0.729879 -1.595074
H 0 0.567788 -2.050186 -0.223789
H 0 -1.866501 -3.077729 -1.147653
H 0 2.547197 -2.829552 -1.473999
H 0 2.737124 0.263760 1.506240
H 0 5.184991 0.022182 1.594734
H 0 4.995783 -3.105580 -1.340172
H 0 7.106904 -2.706370 -0.056967
H 0 7.181635 -1.421536 1.160393
H 0 7.270872 -1.020634 -0.556329
H 0 -7.270872 -1.487141 0.565672
H 0 -3.257882 -2.959866 1.051643
H 0 -4.020950 0.379478 -1.542231
H 0 -6.434068 0.250658 -1.004717
H 0 -5.674684 -3.092162 1.595074

B3LYP/6-31G* Energy = -1436.16655161
B3LYP/6-31G* Free Energy = -1435.913055
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17832530
Number of Imaginary Frequencies = 0

***anti-9*_c2**
B3LYP/6-31G* geometry
C 0 -0.249108 0.021527 -0.545175
C 0 -0.421500 1.361024 -0.377209
C 0 1.251726 -0.214042 -0.685674
C 0 0.879695 2.029813 -0.313013
C 0 1.844209 -1.242394 0.302987
Cl 0 -1.872227 2.299930 -0.297168

N 0	-1.082710	-1.042652	-0.664444
O 0	1.160327	3.188007	-0.149775
O 0	1.858979	1.055426	-0.479457
O 0	1.263832	-2.491977	-0.097059
C 0	-2.461990	-1.142270	-0.323579
C 0	-5.181814	-1.509204	0.341004
C 0	-3.289933	-1.927740	-1.133144
C 0	-2.992384	-0.551122	0.827994
C 0	-4.338841	-0.726591	1.140443
C 0	-4.629584	-2.109510	-0.798134
C 0	-6.631120	-1.721734	0.711044
C 0	3.360132	-1.283599	0.271572
C 0	6.162558	-1.335122	0.200597
C 0	4.030523	-2.089139	-0.657572
C 0	4.105859	-0.503694	1.163109
C 0	5.499267	-0.526944	1.126583
C 0	5.425427	-2.116324	-0.690619
H 0	1.484619	-0.557687	-1.703164
H 0	1.505911	-0.968710	1.313177
H 0	-0.595617	-1.927716	-0.767217
H 0	1.630772	-3.188007	0.470645
H 0	-2.882625	-2.380462	-2.033345
H 0	-2.355094	0.038833	1.477214
H 0	-4.738191	-0.251282	2.033345
H 0	-5.259683	-2.718450	-1.442319
H 0	-7.248669	-1.902062	-0.175215
H 0	-7.041503	-0.853497	1.237377
H 0	-6.751570	-2.589790	1.373282
H 0	7.248669	-1.355811	0.174631
H 0	3.455395	-2.698563	-1.348809
H 0	3.592805	0.131390	1.880459
H 0	6.066947	0.084557	1.822465
H 0	5.935453	-2.746842	-1.414073

B3LYP/6-31G* Energy = -1436.16437633
B3LYP/6-31G* Free Energy = -1435.911896
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17646450
Number of Imaginary Frequencies = 0

***anti-9*_c3**
B3LYP/6-31G* geometry

C 0	1.553632	-1.769099	-0.254070
C 0	2.743582	-2.333892	-0.581075
C 0	1.711082	-1.152771	1.120438
C 0	3.712026	-2.168989	0.496542
C 0	1.557548	0.391726	1.217433
Cl 0	3.119925	-3.123756	-2.073518
N 0	0.452020	-1.698327	-1.047461
O 0	4.859235	-2.514323	0.598750
O 0	3.049061	-1.493073	1.520017
O 0	1.858652	0.762057	2.554304
C 0	-0.857786	-1.259764	-0.737942
C 0	-3.504704	-0.391305	-0.235909
C 0	-1.582306	-0.572689	-1.722092
C 0	-1.473954	-1.534512	0.489159
C 0	-2.772356	-1.088423	0.732547
C 0	-2.886949	-0.156824	-1.472115
C 0	-4.903375	0.104221	0.045278
C 0	2.357268	1.159186	0.174866
C 0	3.790580	2.575760	-1.785065
C 0	1.702351	1.703106	-0.936795
C 0	3.741022	1.343901	0.298056
C 0	4.451877	2.044591	-0.675941
C 0	2.411834	2.405041	-1.912526
H 0	1.038296	-1.592285	1.862840
H 0	0.496225	0.621049	1.081346
H 0	0.609890	-1.982784	-2.007726
H 0	2.724226	0.373497	2.765681
H 0	-1.116593	-0.362181	-2.681793
H 0	-0.959827	-2.124360	1.240107
H 0	-3.231225	-1.310268	1.692963
H 0	-3.431552	0.370134	-2.252001
H 0	-4.892991	1.140173	0.409581
H 0	-5.397343	-0.503993	0.810016
H 0	-5.525017	0.084196	-0.856233
H 0	4.346246	3.123756	-2.541221
H 0	0.625498	1.583444	-1.035151
H 0	4.272872	0.941522	1.154767
H 0	5.525017	2.175376	-0.566910
H 0	1.885804	2.825670	-2.765681

B3LYP/6-31G* Energy = -1436.16357311
B3LYP/6-31G* Free Energy = -1435.911033
B3LYP/6-31G* Energy ($CHCl_3$) = -1436.17509217
Number of Imaginary Frequencies = 0

***syn-12*_c1**
B3LYP/6-31G* geometry

C 0	1.187180	-1.222688	0.053313
C 0	1.297571	-1.862897	-1.142046
C 0	2.404825	-1.616394	0.873932
C 0	2.530572	-2.655184	-1.175337
C 0	3.306731	-0.448808	1.342081
Cl 0	0.293141	-1.778179	-2.545878
N 0	0.284416	-0.384058	0.621135
O 0	2.997337	-3.347940	-2.039855
O 0	3.173346	-2.480300	0.049655
C 0	-1.037077	-0.073183	0.216358
C 0	-3.702761	0.598217	-0.432462
C 0	-1.491219	1.243133	0.356602
C 0	-1.924189	-1.059502	-0.230723
C 0	-3.233325	-0.716053	-0.558595
C 0	-2.808852	1.566570	0.041743
C 0	-5.118800	0.960213	-0.814597
C 0	3.785808	0.453751	0.253968
C 0	3.544349	2.066303	-1.207979
C 0	4.950911	0.524118	-0.450538
C 0	4.797568	1.575282	-1.411182
O 0	2.535963	0.239499	2.334662
O 0	2.904807	1.409001	-0.208900
Cl 0	2.680780	3.347940	-1.952649
H 0	2.091896	-2.161791	1.773790
H 0	4.195319	-0.915976	1.789858
H 0	0.655875	0.141896	1.406776
H 0	-0.806119	2.012879	0.703082
H 0	-1.595584	-2.090178	-0.305845
H 0	-3.909188	-1.493844	-0.906529
H 0	-3.144166	2.594533	0.158349
H 0	-5.461640	1.853978	-0.282792
H 0	-5.816015	0.145525	-0.590066
H 0	-5.201020	1.168861	-1.889779
H 0	5.816015	-0.109958	-0.314235

H 0 5.512991 1.917998 -2.143555
H 0 2.987642 1.072099 2.545878

B3LYP/6-31G* Energy = -1893.53096494
B3LYP/6-31G* Free Energy = -1893.319496
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54291010
Number of Imaginary Frequencies = 0

***syn-12*_c2**
B3LYP/6-31G* geometry
C 0 2.440488 -1.661588 0.025098
C 0 3.373450 -2.645035 0.057126
C 0 1.134366 -2.286995 -0.427923
C 0 2.798903 -3.915107 -0.367275
C 0 0.025627 -2.239923 0.652384
Cl 0 5.020147 -2.474305 0.557683
N 0 2.596520 -0.371795 0.416381
O 0 3.275740 -5.014188 -0.469053
O 0 1.463815 -3.659781 -0.690253
C 0 1.719525 0.722996 0.194998
C 0 0.026546 2.951218 -0.199386
C 0 1.489385 1.632038 1.235533
C 0 1.119889 0.944645 -1.050203
C 0 0.273280 2.037638 -1.231243
C 0 0.662949 2.733377 1.031006
C 0 -0.905421 4.123046 -0.397170
C 0 -1.266771 -2.789316 0.128381
C 0 -3.453737 -2.902880 0.127245
C 0 -1.610421 -3.777559 -0.749248
C 0 -3.041217 -3.853970 -0.754927
O 0 0.459904 -2.882080 1.843191
O 0 -2.407240 -2.242599 0.676755
Cl 0 -5.020147 -2.409553 0.631178
H 0 0.758424 -1.849614 -1.357165
H 0 -0.136559 -1.194632 0.930915
H 0 3.462861 -0.172628 0.903609
H 0 1.952224 1.465666 2.204702
H 0 1.341968 0.287592 -1.885223
H 0 -0.185334 2.193334 -2.204702
H 0 0.498979 3.430111 1.849555
H 0 -1.909533 3.900754 -0.012439
H 0 -1.010740 4.376076 -1.457001
H 0 -0.547399 5.014188 0.129655
H 0 -0.922157 -4.384384 -1.319775
H 0 -3.670646 -4.517100 -1.329446
H 0 0.532234 -3.830239 1.640602

B3LYP/6-31G* Energy = -1893.53161525
B3LYP/6-31G* Free Energy = -1893.320654
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54287003
Number of Imaginary Frequencies = 0

***syn-12*_c3**
B3LYP/6-31G* geometry
C 0 1.365130 -1.740303 -0.077237
C 0 1.502314 -2.259648 -1.327708
C 0 2.723062 -1.862958 0.595077
C 0 2.891441 -2.665306 -1.553942
C 0 3.331713 -0.556573 1.152738
Cl 0 0.317005 -2.534648 -2.556478
N 0 0.335726 -1.249677 0.655940
O 0 3.424383 -3.147075 -2.517914
O 0 3.600669 -2.402656 -0.381163
C 0 -0.950138 -0.822336 0.212403
C 0 -3.516962 0.091181 -0.519192
C 0 -2.058848 -1.112810 1.013517
C 0 -1.120420 -0.057454 -0.946301
C 0 -2.393350 0.379508 -1.305394
C 0 -3.323200 -0.652649 0.651671
C 0 -4.894847 0.552068 -0.933044
C 0 3.462865 0.559765 0.173086
C 0 2.699275 2.153256 -1.120728
C 0 4.538314 1.093787 -0.473317
C 0 4.045009 2.134278 -1.324163
O 0 2.512491 -0.228156 2.282734
O 0 2.313600 1.212815 -0.222961
Cl 0 1.458876 3.147075 -1.767629
H 0 2.654937 -2.561985 1.440196
H 0 4.351859 -0.811450 1.473503
H 0 0.614658 -0.917681 1.574216
H 0 -1.926586 -1.705576 1.914798
H 0 -0.259927 0.208883 -1.549139
H 0 -2.511402 0.971630 -2.209926
H 0 -4.175181 -0.885543 1.286125
H 0 -5.565799 0.634517 -0.071573
H 0 -5.354918 -0.152446 -1.638796
H 0 -4.859367 1.528322 -1.428832
H 0 5.565799 0.773947 -0.367672
H 0 4.605692 2.775845 -1.987248
H 0 2.720099 0.679188 2.556478

B3LYP/6-31G* Energy = -1893.52964905
B3LYP/6-31G* Free Energy = -1893.318242
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54188373
Number of Imaginary Frequencies = 0

***syn-12*_c4**
B3LYP/6-31G* geometry
C 0 -0.360873 0.424827 0.698861
C 0 -0.441137 1.488091 -0.143854
C 0 -1.523679 0.547411 1.671965
C 0 -1.604855 2.314406 0.199532
C 0 -2.501834 -0.648087 1.709411
Cl 0 0.519691 1.883274 -1.524439
N 0 0.476619 -0.638547 0.827367
O 0 -2.023483 3.323358 -0.300911
O 0 -2.235713 1.714246 1.286124
C 0 1.800196 -0.807406 0.349959
C 0 4.461553 -1.261272 -0.484960
C 0 2.227860 -2.095894 0.007819
C 0 2.712796 0.252608 0.293219
C 0 4.019209 0.019801 -0.129785
C 0 3.542549 -2.314620 -0.396000
C 0 5.874901 -1.493016 -0.965166
C 0 -3.135049 -0.984944 0.398899
C 0 -4.895083 -1.288305 -0.869392
C 0 -2.677078 -1.387008 -0.824411
C 0 -3.823341 -1.584590 -1.657007
O 0 -1.727579 -1.734843 2.253396
O 0 -4.512666 -0.929632 0.377435
Cl 0 -6.581956 -1.300970 -1.180396
H 0 -1.139341 0.683009 2.691294

H 0 -3.310117 -0.372682 2.399352
H 0 0.097364 -1.386481 1.401545
H 0 1.526378 -2.925437 0.056598
H 0 2.407918 1.248587 0.594068
H 0 4.714437 0.855151 -0.169277
H 0 3.856155 -3.323358 -0.654408
H 0 6.200367 -2.521064 -0.774242
H 0 6.581956 -0.817830 -0.471041
H 0 5.962863 -1.318736 -2.045984
H 0 -1.642640 -1.518510 -1.108438
H 0 -3.849265 -1.893515 -2.691294
H 0 -2.252269 -2.546161 2.164305

B3LYP/6-31G* Energy = -1893.52988476
B3LYP/6-31G* Free Energy = -1893.318353
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54171700
Number of Imaginary Frequencies = 0

***anti-12*_c1**
B3LYP/6-31G* geometry
C 0 -0.007243 -0.026072 -0.248342
C 0 -0.285700 1.304026 -0.313567
C 0 1.497423 -0.170139 -0.447386
C 0 0.945253 2.066114 -0.543307
C 0 2.242374 -0.830685 0.734286
Cl 0 -1.779625 2.136976 -0.067193
N 0 -0.751377 -1.147294 -0.065140
O 0 1.127140 3.249655 -0.651367
O 0 1.993596 1.153006 -0.610998
O 0 1.709980 -2.163082 0.818075
C 0 -2.144264 -1.339178 -0.229958
C 0 -4.893944 -1.888918 -0.581682
C 0 -2.797278 -2.258436 0.600361
C 0 -2.865241 -0.710166 -1.251936
C 0 -4.222473 -0.980191 -1.409778
C 0 -4.150608 -2.530220 0.417723
C 0 -6.371913 -2.152890 -0.748662
C 0 3.720706 -0.829433 0.558677
C 0 5.565696 -1.321748 -0.508456
C 0 4.747813 -0.308080 1.288524
O 0 4.219399 -1.462944 -0.558425
C 0 5.959228 -0.627031 0.594761
Cl 0 6.457359 -2.036408 -1.787985
H 0 1.708245 -0.748231 -1.355251
H 0 2.015727 -0.257302 1.644228
H 0 -0.211986 -1.952122 0.239413
H 0 2.222276 -2.654375 1.479350
H 0 -2.241952 -2.755806 1.391962
H 0 -2.364008 -0.027566 -1.928916
H 0 -4.767393 -0.481466 -2.207931
H 0 -4.638817 -3.249655 1.071123
H 0 -6.637277 -3.167025 -0.431296
H 0 -6.685052 -2.032591 -1.791368
H 0 -6.972395 -1.456623 -0.147768
H 0 4.655164 0.253847 2.207931
H 0 6.972395 -0.376140 0.870879

B3LYP/6-31G* Energy = -1893.53142423
B3LYP/6-31G* Free Energy = -1893.320922
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54365810
Number of Imaginary Frequencies = 0

***anti-12*_c2**
B3LYP/6-31G* geometry
C 0 0.022482 0.018122 0.027582
C 0 0.104344 1.363468 -0.153376
C 0 -1.399531 -0.277266 0.489037
C 0 -1.184117 1.992294 0.156954
C 0 -2.186917 -1.231226 -0.438670
Cl 0 1.406426 2.325287 -0.757791
N 0 0.885879 -1.021428 -0.110796
O 0 -1.523439 3.144445 0.120316
O 0 -2.064389 0.977732 0.525830
O 0 -1.520744 -2.495525 -0.320130
C 0 2.300635 -1.015890 -0.174652
C 0 5.121453 -1.165249 -0.252068
C 0 2.939920 -1.974312 -0.970258
C 0 3.075515 -0.144448 0.600016
C 0 4.465130 -0.219316 0.546278
C 0 4.330260 -2.047419 -0.999020
C 0 6.629672 -1.216904 -0.319720
C 0 -3.626759 -1.357025 -0.057344
C 0 -5.750305 -0.885863 -0.263420
C 0 -4.280043 -2.074016 0.903228
O 0 -4.528617 -0.624036 -0.787696
C 0 -5.672818 -1.768358 0.771489
Cl 0 -7.083949 -0.094728 -0.995553
H 0 -1.392466 -0.711208 1.497207
H 0 -2.126759 -0.835123 -1.462132
H 0 0.429747 -1.926065 -0.182289
H 0 -2.013619 -3.144445 -0.847406
H 0 2.344477 -2.658080 -1.570559
H 0 2.594166 0.575408 1.252475
H 0 5.051580 0.466856 1.152853
H 0 4.808006 -2.799947 -1.622082
H 0 6.986552 -2.221928 -0.568581
H 0 7.083949 -0.923564 0.632911
H 0 7.018373 -0.534176 -1.087278
H 0 -3.824098 -2.740472 1.622082
H 0 -6.496992 -2.147113 1.357285

B3LYP/6-31G* Energy = -1893.53022465
B3LYP/6-31G* Free Energy = -1893.318701
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54265465
Number of Imaginary Frequencies = 0

***anti-12*_c3**
B3LYP/6-31G* geometry
C 0 -1.079448 1.499689 -0.166129
C 0 -2.212501 2.195250 -0.435520
C 0 -1.261571 0.859466 1.195779
C 0 -3.159692 2.098289 0.671940
C 0 -1.252340 -0.693412 1.223937
Cl 0 -2.546590 3.072685 -1.888218
N 0 -0.013812 1.338093 -0.995090
O 0 -4.253676 2.570213 0.825305
O 0 -2.545174 1.313511 1.646175
O 0 -1.598506 -1.112113 2.533994
C 0 1.233172 0.715384 -0.747150
C 0 3.752235 -0.516849 -0.364011
C 0 1.823635 -0.034813 -1.773213
C 0 1.920898 0.868042 0.463542
C 0 3.153587 0.243575 0.648268

C 0 3.067803 -0.629769 -1.581786
C 0 5.079855 -1.202995 -0.145742
C 0 -2.090171 -1.337752 0.163945
C 0 -3.993592 -1.856926 -0.788069
C 0 -1.791789 -2.122170 -0.909910
O 0 -3.453543 -1.166969 0.247708
C 0 -3.034113 -2.462332 -1.539661
Cl 0 -5.703500 -1.827944 -0.919434
H 0 -0.526311 1.201398 1.930528
H 0 -0.222458 -1.022899 1.058340
H 0 -0.164880 1.671994 -1.940395
H 0 -2.474730 -0.731104 2.719756
H 0 1.301660 -0.152430 -2.719756
H 0 1.516575 1.500298 1.246806
H 0 3.670144 0.373142 1.596227
H 0 3.510097 -1.201754 -2.393935
H 0 4.943530 -2.215013 0.258331
H 0 5.703500 -0.651563 0.565610
H 0 5.639869 -1.300096 -1.081719
H 0 -0.801196 -2.428517 -1.217512
H 0 -3.193869 -3.072685 -2.415954

B3LYP/6-31G* Energy = -1893.53009670
B3LYP/6-31G* Free Energy = -1893.319620
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54205196
Number of Imaginary Frequencies = 0

***anti-12*_c4**
B3LYP/6-31G* geometry
C 0 0.083211 -0.087841 -0.835920
C 0 -0.168127 1.247001 -0.748759
C 0 1.599514 -0.247485 -0.833146
C 0 1.088074 1.986600 -0.603978
C 0 2.147191 -1.195644 0.255076
Cl 0 -1.663328 2.110519 -0.846546
N 0 -0.681418 -1.200082 -0.973528
O 0 1.296024 3.163839 -0.475592
O 0 2.125296 1.057960 -0.635269
O 0 1.680493 -2.497280 -0.136957
C 0 -2.078530 -1.362330 -0.752803
C 0 -4.824338 -1.853418 -0.314052
C 0 -2.783038 -2.239964 -1.583606
C 0 -2.745226 -0.740741 0.309053
C 0 -4.103014 -0.978322 0.509060
C 0 -4.136507 -2.482594 -1.359307
C 0 -6.288662 -2.127816 -0.062964
C 0 3.630211 -1.146656 0.376830
C 0 5.665515 -1.317515 -0.405391
C 0 5.808278 -0.969678 0.903405
O 0 4.361692 -1.434983 -0.753681
C 0 4.473191 -0.859808 1.409526
Cl 0 6.817673 -1.636894 -1.635665
H 0 1.942127 -0.626347 -1.805103
H 0 1.724857 -0.899336 1.225793
H 0 -0.143817 -2.060763 -1.007151
H 0 2.051798 -3.151396 0.475783
H 0 -2.269867 -2.717995 -2.413903
H 0 -2.204215 -0.079631 0.976721
H 0 -4.608899 -0.478868 1.332120
H 0 -4.669562 -3.163839 -2.018333
H 0 -6.783888 -2.510585 -0.961239
H 0 -6.817673 -1.222380 0.254009
H 0 -6.424922 -2.875958 0.729525
H 0 6.737200 -0.811516 1.430375
H 0 4.180692 -0.585467 2.413903

B3LYP/6-31G* Energy = -1893.52943138
B3LYP/6-31G* Free Energy = -1893.318887
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54201848
Number of Imaginary Frequencies = 0

***anti-12*_c5**
B3LYP/6-31G* geometry
C 0 1.899381 -1.862524 -0.833812
C 0 3.141271 -2.200208 -1.266025
C 0 1.881299 -2.049502 0.668097
C 0 3.973392 -2.649937 -0.156597
C 0 1.701597 -0.764485 1.528972
Cl 0 3.711001 -2.111533 -2.896574
N 0 0.872367 -1.380628 -1.576822
O 0 5.112869 -3.028793 -0.113018
O 0 3.168203 -2.597618 0.985596
O 0 1.917068 -1.118348 2.880755
C 0 -0.447706 -1.083337 -1.143467
C 0 -3.092067 -0.471437 -0.362161
C 0 -1.010734 0.157696 -1.463151
C 0 -1.215982 -2.026167 -0.450180
C 0 -2.514568 -1.709773 -0.053931
C 0 -2.319208 0.448109 -1.084724
C 0 -4.493815 -0.130631 0.085306
C 0 2.598786 0.371960 1.127817
C 0 3.203104 2.022098 -0.180589
C 0 3.707735 0.928938 1.686881
O 0 2.272019 1.044148 -0.029973
C 0 4.109507 2.009431 0.831965
Cl 0 3.030391 3.028793 -1.563333
H 0 1.126940 -2.769114 1.000141
H 0 0.656834 -0.446006 1.445281
H 0 1.123610 -1.083272 -2.512733
H 0 2.740786 -1.637876 2.896574
H 0 -0.415233 0.895839 -1.993256
H 0 -0.812695 -3.014373 -0.251260
H 0 -3.097335 -2.452561 0.485434
H 0 -2.742238 1.415440 -1.344693
H 0 -4.488020 0.368638 1.063403
H 0 -5.112869 -1.028519 0.182969
H 0 -4.986912 0.545555 -0.620911
H 0 4.179977 0.620403 2.608062
H 0 4.947739 2.678794 0.955129

B3LYP/6-31G* Energy = -1893.53111652
B3LYP/6-31G* Free Energy = -1893.319963
B3LYP/6-31G* Energy ($CHCl_3$) = -1893.54192490
Number of Imaginary Frequencies = 0

***syn-13*_c1**
B3LYP/6-31G* geometry
C 0 1.222203 0.434846 1.275266
C 0 0.766166 1.598780 0.738212
C 0 0.370138 0.150911 2.500454
C 0 -0.359522 2.104993 1.527457
C 0 -0.443502 -1.167787 2.460690

Cl 0	1.232174	2.411366	-0.713508
N 0	2.204728	-0.449076	0.963392
O 0	-1.066834	3.065262	1.366873
O 0	-0.544953	1.233930	2.598965
C 0	3.320129	-0.290899	0.104555
C 0	5.621789	-0.097133	-1.521767
C 0	3.760187	-1.393677	-0.636597
C 0	4.045622	0.905078	0.047919
C 0	5.172466	0.993470	-0.765426
C 0	4.899689	-1.293836	-1.431078
C 0	6.831610	0.022067	-2.418445
C 0	-1.344834	-1.284660	1.260786
C 0	-2.372139	-1.851745	-0.935556
C 0	-2.506865	-0.606322	1.017959
C 0	-3.106497	-0.913382	-0.250009
O 0	0.530393	-2.213972	2.531070
C 0	-4.344102	-0.275311	-0.746975
S 0	-0.947662	-2.337348	-0.078070
C 0	-4.604956	1.076192	-0.462757
C 0	-5.764373	1.689148	-0.935706
C 0	-6.681943	0.966728	-1.700917
C 0	-6.431942	-0.376252	-1.990552
C 0	-5.275392	-0.992287	-1.515621
H 0	0.995648	0.126017	3.401686
H 0	-1.060948	-1.160408	3.370339
H 0	2.086544	-1.363282	1.388787
H 0	3.202873	-2.326261	-0.594437
H 0	3.739378	1.754244	0.648564
H 0	5.723283	1.930613	-0.799505
H 0	5.226983	-2.162078	-1.998340
H 0	7.302386	-0.951864	-2.588836
H 0	7.585332	0.690908	-1.988537
H 0	6.560970	0.429852	-3.401686
H 0	-2.566596	-2.254345	-1.920412
H 0	-2.936682	0.093511	1.725281
H 0	0.063867	-3.065262	2.536463
H 0	-3.881991	1.655950	0.105286
H 0	-5.945590	2.736944	-0.711778
H 0	-7.585332	1.446122	-2.068229
H 0	-7.143692	-0.948856	-2.579588
H 0	-5.099872	-2.044998	-1.721364

B3LYP/6-31G* Energy = -1987.97842179
B3LYP/6-31G* Free Energy = -1987.684206
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.99037479
Number of Imaginary Frequencies = 0

***syn-13*_c2**
B3LYP/6-31G* geometry

C 0	1.445244	0.997925	0.278985
C 0	1.111145	1.553000	-0.916465
C 0	0.529837	1.617587	1.321747
C 0	0.018688	2.514919	-0.734932
C 0	-0.366157	0.633686	2.113957
Cl 0	1.705463	1.217293	-2.503791
N 0	2.364380	0.088601	0.696471
O 0	-0.559190	3.206764	-1.529861
O 0	-0.305326	2.527560	0.620806
C 0	3.533869	-0.376856	0.047057
C 0	5.929472	-1.346481	-1.095598
C 0	3.931920	-1.703613	0.250615
C 0	4.347760	0.471619	-0.712726
C 0	5.520855	-0.019364	-1.280868
C 0	5.117066	-2.173579	-0.309280
C 0	7.192009	-1.871816	-1.737680
C 0	-1.259329	-0.236335	1.275259
C 0	-2.240270	-2.053586	-0.114159
C 0	-2.503161	0.064878	0.791999
C 0	-3.082328	-0.970337	-0.017807
O 0	0.543455	-0.123655	2.922544
C 0	-4.416892	-0.886850	-0.648439
S 0	-0.756311	-1.826692	0.744992
C 0	-4.679084	-1.522996	-1.873488
C 0	-5.942243	-1.454983	-2.457673
C 0	-6.968696	-0.742666	-1.834126
C 0	-6.719959	-0.099474	-0.620526
C 0	-5.457828	-0.171655	-0.033301
H 0	1.125982	2.173254	2.057484
H 0	-1.005671	1.265177	2.747324
H 0	2.164216	-0.308164	1.609376
H 0	3.306977	-2.366914	0.843608
H 0	4.073201	1.512121	-0.844429
H 0	6.140097	0.653067	-1.870037
H 0	5.410106	-3.206764	-0.137654
H 0	7.623857	-2.695237	-1.158923
H 0	7.951925	-1.088095	-1.828249
H 0	6.997192	-2.252341	-2.749442
H 0	-2.429261	-2.994776	-0.612400
H 0	-2.983718	1.019721	0.974990
H 0	0.030763	-0.789210	3.409039
H 0	-3.877673	-2.050730	-2.383142
H 0	-6.121358	-1.948874	-3.409039
H 0	-7.951925	-0.684949	-2.292911
H 0	-7.511522	0.457221	-0.125951
H 0	-5.282519	0.316018	0.921664

B3LYP/6-31G* Energy = -1987.97756436
B3LYP/6-31G* Free Energy = -1987.683806
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.99031970
Number of Imaginary Frequencies = 0

***syn-13*_c3**
B3LYP/6-31G* geometry

C 0	0.762721	-2.469684	0.233116
C 0	0.716532	-2.730616	1.566099
C 0	0.030968	-3.604881	-0.463343
C 0	-0.004996	-3.985508	1.807079
C 0	-1.192024	-3.191591	-1.319144
Cl 0	1.271321	-1.787399	2.903430
N 0	1.291092	-1.482046	-0.537357
O 0	-0.259210	-4.560082	2.831255
O 0	-0.406103	-4.480259	0.566966
C 0	2.300029	-0.536941	-0.229792
C 0	4.340096	1.367497	0.219906
C 0	2.242923	0.723926	-0.836577
C 0	3.392993	-0.851772	0.586459
C 0	4.387063	0.097870	0.810229
C 0	3.254406	1.655440	-0.617083
C 0	5.413067	2.395520	0.491879
C 0	-2.239125	-2.398267	-0.584726
C 0	-4.247920	-1.657685	0.682396
C 0	-2.310091	-1.038203	-0.428809

C 0	-3.463064	-0.593710	0.300778
O 0	-0.639468	-2.453189	-2.417298
C 0	-3.758293	0.822659	0.604635
S 0	-3.602238	-3.177977	0.174357
C 0	-2.717160	1.737645	0.835631
C 0	-2.991697	3.072293	1.130185
C 0	-4.311897	3.520043	1.202914
C 0	-5.356027	2.621061	0.975823
C 0	-5.082179	1.288057	0.675746
H 0	0.721519	-4.146704	-1.122911
H 0	-1.633309	-4.131327	-1.680990
H 0	0.920251	-1.461109	-1.482693
H 0	1.402484	0.973347	-1.480234
H 0	3.474110	-1.837986	1.029019
H 0	5.227729	-0.163603	1.448668
H 0	3.192664	2.627604	-1.100674
H 0	5.516318	3.098063	-0.341895
H 0	6.387475	1.923666	0.658333
H 0	5.182230	2.986294	1.388600
H 0	-5.148098	-1.631288	1.281587
H 0	-1.571123	-0.359125	-0.838416
H 0	-1.380200	-2.056312	-2.903430
H 0	-1.686416	1.394626	0.812552
H 0	-2.171322	3.761240	1.313208
H 0	-4.525518	4.560082	1.433780
H 0	-6.387475	2.960440	1.022525
H 0	-5.900261	0.602326	0.472177

B3LYP/6-31G* Energy = -1987.97683192
B3LYP/6-31G* Free Energy = -1987.683084
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.98977280
Number of Imaginary Frequencies = 0

***syn-13*_c4**
B3LYP/6-31G* geometry

C 0	3.745071	-2.017069	-0.160044
C 0	3.749280	-3.372923	-0.159726
C 0	2.295819	-1.565731	-0.136388
C 0	2.388011	-3.892757	-0.161289
C 0	1.920697	-0.797071	1.157891
Cl 0	5.147479	-4.390427	-0.125449
N 0	4.827395	-1.200077	-0.089560
O 0	1.962045	-5.017336	-0.151609
O 0	1.539708	-2.784787	-0.192191
C 0	4.894346	0.202118	-0.292173
C 0	5.128163	2.994331	-0.673346
C 0	5.732375	0.964502	0.532011
C 0	4.192357	0.837709	-1.323451
C 0	4.301232	2.217166	-1.493500
C 0	5.850917	2.336985	0.332065
C 0	5.226396	4.490608	-0.853708
C 0	0.520218	-0.235195	1.099591
C 0	-1.531998	1.114983	1.530818
C 0	-0.573278	-0.669924	0.398223
C 0	-1.763226	0.101896	0.629470
O 0	2.133932	-1.616211	2.298757
C 0	-3.064757	-0.166162	-0.018874
S 0	0.102054	1.140839	2.095065
C 0	-3.435691	-1.475245	-0.370276
C 0	-4.665185	-1.731933	-0.975229
C 0	-5.551885	-0.686851	-1.239860
C 0	-5.195672	0.619200	-0.897146
C 0	-3.964424	0.876895	-0.297776
H 0	2.027214	-0.965976	-1.010184
H 0	2.634311	0.025624	1.265744
H 0	5.701557	-1.668405	0.120770
H 0	6.282647	0.478392	1.333545
H 0	3.592957	0.254731	-2.015112
H 0	3.746772	2.692945	-2.298757
H 0	6.509963	2.909990	0.979890
H 0	4.519172	5.017336	-0.199232
H 0	4.998352	4.785722	-1.883117
H 0	6.228718	4.859033	-0.610527
H 0	-2.246655	1.827154	1.920870
H 0	-0.534113	-1.511462	-0.283128
H 0	1.451471	-2.308305	2.276430
H 0	-2.765420	-2.301129	-0.149204
H 0	-4.932500	-2.752997	-1.234238
H 0	-6.509963	-0.887431	-1.711577
H 0	-5.873849	1.442244	-1.107089
H 0	-3.683895	1.900319	-0.063606

B3LYP/6-31G* Energy = -1987.97719404
B3LYP/6-31G* Free Energy = -1987.684560
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.98960715
Number of Imaginary Frequencies = 0

***syn-13*_c5**
B3LYP/6-31G* geometry

C 0	0.291944	-2.308658	0.150161
C 0	0.245398	-2.624003	1.471484
C 0	-0.402538	-3.435398	-0.596185
C 0	-0.443629	-3.905804	1.657482
C 0	-1.628807	-3.026232	-1.449085
Cl 0	0.770836	-1.722216	2.848292
N 0	0.800923	-1.278630	-0.575983
O 0	-0.689756	-4.527377	2.655972
O 0	-0.823387	-4.361860	0.395435
C 0	1.792059	-0.329138	-0.226105
C 0	3.800531	1.587858	0.303136
C 0	1.713958	0.954567	-0.779888
C 0	2.889362	-0.659333	0.577999
C 0	3.867922	0.296301	0.841357
C 0	2.709984	1.892479	-0.521631
C 0	4.856490	2.621285	0.617741
C 0	-2.709297	-2.290360	-0.702306
C 0	-4.705564	-1.663536	0.641976
C 0	-2.849335	-0.936253	-0.540829
C 0	-3.995537	-0.557191	0.235809
O 0	-1.089120	-2.232867	-2.513724
C 0	-4.361952	0.839317	0.554136
S 0	-4.000969	-3.145042	0.099540
C 0	-4.995933	1.162591	1.765772
C 0	-5.351525	2.477784	2.058091
C 0	-5.073343	3.501227	1.149709
C 0	-4.437860	3.195796	-0.054888
C 0	-4.087710	1.879113	-0.349993
H 0	0.309075	-3.931811	-1.269054
H 0	-2.037570	-3.965597	-1.848822
H 0	0.435573	-1.226783	-1.522029
H 0	0.867797	1.217169	-1.410471
H 0	2.986099	-1.661396	0.980097

H 0	4.712479	0.022740	1.469523
H 0	2.631668	2.883083	-0.963594
H 0	4.956776	3.352228	-0.191716
H 0	5.836061	2.157819	0.777281
H 0	4.609666	3.179265	1.531041
H 0	-5.622081	-1.685767	1.215937
H 0	-2.133382	-0.220812	-0.929064
H 0	-1.837493	-1.855816	-3.003884
H 0	-5.185787	0.378944	2.493927
H 0	-5.836061	2.705278	3.003884
H 0	-5.345998	4.527377	1.380362
H 0	-4.219680	3.983522	-0.771280
H 0	-3.615961	1.651229	-1.302088

B3LYP/6-31G* Energy = -1987.97643247
B3LYP/6-31G* Free Energy = -1987.683444
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.98958073
Number of Imaginary Frequencies = 0

***syn-13*_c6**
B3LYP/6-31G* geometry

C 0	-3.727162	2.031850	0.099546
C 0	-3.685438	3.386367	0.140702
C 0	-2.294241	1.533038	0.047836
C 0	-2.308723	3.861604	0.096574
C 0	-1.891580	0.712725	1.302723
Cl 0	-5.045767	4.447295	0.266488
N 0	-4.833139	1.249264	0.191772
O 0	-1.845148	4.970877	0.122159
O 0	-1.500622	2.728075	-0.005437
C 0	-4.956046	-0.143879	-0.043140
C 0	-5.296962	-2.916641	-0.481731
C 0	-5.788168	-0.899214	0.793777
C 0	-4.314860	-0.775710	-1.115417
C 0	-4.476033	-2.146414	-1.313998
C 0	-5.959710	-2.261492	0.565891
C 0	-5.452190	-4.404046	-0.692732
C 0	-0.517877	0.100179	1.165097
C 0	1.483887	-1.359250	1.453013
C 0	0.609001	0.600263	0.566548
C 0	1.771687	-0.229966	0.721200
O 0	-2.027549	1.504386	2.473942
C 0	3.102219	0.089983	0.161315
S 0	-0.169651	-1.421884	1.951285
C 0	4.278904	-0.347640	0.793189
C 0	5.530995	-0.057932	0.255138
C 0	5.636164	0.684871	-0.922681
C 0	4.476439	1.133762	-1.556537
C 0	3.223397	0.838385	-1.021729
H 0	-2.081809	0.951599	-0.853333
H 0	-2.629210	-0.087464	1.416532
H 0	-5.680886	1.739585	0.453751
H 0	-6.291389	-0.415805	1.627248
H 0	-3.721936	-0.195428	-1.814898
H 0	-3.967830	-2.619770	-2.150551
H 0	-6.612729	-2.828921	1.224688
H 0	-4.772011	-4.970877	-0.043176
H 0	-5.227388	-4.687485	-1.725997
H 0	-6.470251	-4.737773	-0.464575
H 0	2.148829	-2.178016	1.692648
H 0	0.621107	1.553954	0.052375
H 0	-1.318574	2.168857	2.446694
H 0	4.209990	-0.897891	1.727580
H 0	6.427283	-0.402983	0.763997
H 0	6.612729	0.915854	-1.339325
H 0	4.545435	1.712345	-2.473942
H 0	2.328666	1.176612	-1.536645

B3LYP/6-31G* Energy = -1987.97699019
B3LYP/6-31G* Free Energy = -1987.684565
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.98947368
Number of Imaginary Frequencies = 0

***anti-13*_c1**
B3LYP/6-31G* geometry

C 0	1.854542	-0.045660	0.206504
C 0	1.928409	1.312403	0.175149
C 0	0.425421	-0.401192	0.602479
C 0	0.629453	1.894471	0.524199
C 0	-0.347572	-1.234241	-0.448646
Cl 0	3.233856	2.340941	-0.298416
N 0	2.737765	-1.052766	-0.018531
O 0	0.276767	3.041948	0.596764
O 0	-0.246675	0.841765	0.769522
O 0	0.373656	-2.468626	-0.561445
C 0	4.152984	-1.026471	-0.020616
C 0	6.977047	-1.142632	0.009095
C 0	4.838234	-1.893540	-0.880717
C 0	4.883487	-0.231524	0.870615
C 0	6.275143	-0.288908	0.869742
C 0	6.229137	-1.951263	-0.856641
C 0	8.487266	-1.174722	0.000943
C 0	-1.781168	-1.465892	-0.070370
C 0	-3.888558	-2.327337	0.930432
C 0	-2.876189	-0.715075	-0.393987
S 0	-2.225414	-2.805572	0.965799
C 0	-4.103274	-1.197716	0.175657
C 0	-5.421553	-0.560153	-0.028974
C 0	-5.526748	0.833295	-0.175475
C 0	-6.768900	1.439374	-0.357864
C 0	-7.930762	0.666520	-0.395432
C 0	-7.839884	-0.719569	-0.251845
C 0	-6.598194	-1.326669	-0.074732
H 0	0.418170	-0.944597	1.555725
H 0	-0.315306	-0.673457	-1.394121
H 0	2.297701	-1.944613	-0.223683
H 0	-0.104929	-3.041948	-1.181496
H 0	4.277669	-2.518868	-1.571519
H 0	4.366456	0.414212	1.571519
H 0	6.826094	0.336850	1.568034
H 0	6.741852	-2.633399	-1.530975
H 0	8.866950	-2.160189	-0.289514
H 0	8.898519	-0.931704	0.986576
H 0	8.898320	-0.445646	-0.710344
H 0	-4.619566	-2.897528	1.487667
H 0	-2.817735	0.158665	-1.033653
H 0	-4.632617	1.447964	-0.120145
H 0	-6.828415	2.519372	-0.462841
H 0	-8.898519	1.139682	-0.537534
H 0	-8.737325	-1.331564	-0.288470
H 0	-6.534043	-2.408460	0.006208

B3LYP/6-31G* Energy = -1987.97877587
B3LYP/6-31G* Free Energy = -1987.685094
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.99143489
Number of Imaginary Frequencies = 0

***anti-13*_c2**
B3LYP/6-31G* geometry
C 0 -1.865008 -0.055276 -0.449577
C 0 -1.935434 1.303129 -0.460871
C 0 -0.435607 -0.426231 -0.831257
C 0 -0.634498 1.871045 -0.826678
C 0 0.332433 -1.228345 0.246945
Cl 0 -3.238697 2.349683 -0.021954
N 0 -2.751399 -1.052868 -0.195514
O 0 -0.280419 3.014887 -0.936602
O 0 0.239808 0.808902 -1.035914
O 0 -0.394245 -2.456291 0.396389
C 0 -4.166437 -1.023464 -0.196777
C 0 -6.990809 -1.134248 -0.226625
C 0 -4.854753 -1.865291 0.685928
C 0 -4.894142 -0.251977 -1.110494
C 0 -6.286050 -0.306155 -1.109499
C 0 -6.245619 -1.920723 0.661755
C 0 -8.501109 -1.162875 -0.218726
C 0 1.766211 -1.480754 -0.116046
C 0 3.862238 -2.346389 -1.136585
C 0 2.866536 -0.734318 0.200802
S 0 2.198742 -2.823024 -1.154090
C 0 4.086983 -1.218233 -0.382020
C 0 5.410686 -0.589981 -0.185799
C 0 6.392840 -0.645115 -1.189225
C 0 7.643873 -0.062396 -0.997823
C 0 7.937991 0.596070 0.197974
C 0 6.969440 0.664487 1.200715
C 0 5.719754 0.076487 1.011664
H 0 -0.428033 -0.999412 -1.766944
H 0 0.300414 -0.638433 1.174521
H 0 -2.313926 -1.938871 0.038373
H 0 0.084779 -3.014887 1.029366
H 0 -4.296321 -2.472645 1.394285
H 0 -4.374941 0.372978 -1.828348
H 0 -6.834895 0.301505 -1.825192
H 0 -6.760581 -2.583163 1.353816
H 0 -8.883309 -2.147387 0.071997
H 0 -8.911463 -0.919260 -1.204503
H 0 -8.910652 -0.432834 0.492453
H 0 4.597296 -2.957658 -1.642607
H 0 2.806468 0.168778 0.798277
H 0 6.161840 -1.125615 -2.135989
H 0 8.386405 -0.111682 -1.789882
H 0 8.911463 1.055797 0.344743
H 0 7.187721 1.173098 2.135989
H 0 4.982155 0.118472 1.808322

B3LYP/6-31G* Energy = -1987.97839153
B3LYP/6-31G* Free Energy = -1987.684762
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.99130253
Number of Imaginary Frequencies = 0

***anti-13*_c3**
B3LYP/6-31G* geometry
C 0 1.964081 0.446132 -0.046652
C 0 2.461547 1.672390 0.267750
C 0 0.451483 0.524066 0.133374
C 0 1.370820 2.577131 0.642931
C 0 -0.367234 0.221580 -1.144158
Cl 0 4.080770 2.269233 0.176541
N 0 2.511485 -0.730811 -0.446902
O 0 1.387887 3.732620 0.973661
O 0 0.181697 1.859334 0.541750
O 0 -0.072266 -1.144712 -1.462103
C 0 3.846109 -1.188716 -0.333453
C 0 6.450560 -2.264301 -0.114659
C 0 4.352606 -2.032588 -1.329177
C 0 4.638635 -0.899251 0.784178
C 0 5.924270 -1.425976 0.877161
C 0 5.634261 -2.564908 -1.212261
C 0 7.856134 -2.808113 -0.010665
C 0 -1.847873 0.411605 -0.951396
C 0 -4.184550 1.255252 -0.893031
C 0 -2.745065 -0.517273 -0.492136
S 0 -2.648799 1.908275 -1.343299
C 0 -4.100717 -0.046574 -0.453870
C 0 -5.251581 -0.858194 -0.004080
C 0 -6.528847 -0.674893 -0.560652
C 0 -7.613927 -1.433923 -0.126931
C 0 -7.444697 -2.400117 0.867003
C 0 -6.180327 -2.597415 1.424582
C 0 -5.095896 -1.833887 0.995043
H 0 0.124531 -0.166068 0.921360
H 0 0.001128 0.891679 -1.934713
H 0 1.850559 -1.357218 -0.896564
H 0 -0.642590 -1.406089 -2.202787
H 0 3.741174 -2.266149 -2.197519
H 0 4.245201 -0.280545 1.582917
H 0 6.526106 -1.189571 1.751672
H 0 6.008610 -3.220264 -1.995263
H 0 7.972155 -3.732620 -0.586027
H 0 8.127901 -3.021179 1.029074
H 0 8.592056 -2.089651 -0.396100
H 0 -5.064781 1.882674 -0.932684
H 0 -2.453608 -1.525492 -0.219361
H 0 -6.664690 0.052908 -1.355980
H 0 -8.592056 -1.277521 -0.574159
H 0 -8.289993 -2.994792 1.202231
H 0 -6.037834 -3.342598 2.202787
H 0 -4.122486 -1.978691 1.455598

B3LYP/6-31G* Energy = -1987.97735964
B3LYP/6-31G* Free Energy = -1987.684120
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.99040437
Number of Imaginary Frequencies = 0

***anti-13*_c4**
B3LYP/6-31G* geometry
C 0 -1.783248 0.601818 -0.098339
C 0 -2.262443 1.844160 -0.375656
C 0 -0.266310 0.671752 -0.241841
C 0 -1.155313 2.751817 -0.691194
C 0 0.520379 0.309729 1.040463
Cl 0 -3.877787 2.453528 -0.297894
N 0 -2.349028 -0.584555 0.244467

O 0	-1.154581	3.919270	-0.977525
O 0	0.024664	2.019163	-0.591077
O 0	0.209042	-1.066878	1.293194
C 0	-3.685879	-1.024464	0.092313
C 0	-6.296084	-2.066352	-0.207757
C 0	-4.216187	-1.899830	1.047679
C 0	-4.457447	-0.686218	-1.026189
C 0	-5.746151	-1.196801	-1.159007
C 0	-5.500437	-2.415232	0.890787
C 0	-7.704677	-2.592253	-0.354304
C 0	2.006183	0.495097	0.889866
C 0	4.339804	1.346866	0.857801
C 0	2.900314	-0.402823	0.367082
S 0	2.809321	1.964177	1.370318
C 0	4.253607	0.074803	0.338762
C 0	5.401331	-0.701829	-0.176508
C 0	6.494551	-0.061579	-0.784525
C 0	7.580788	-0.795273	-1.257214
C 0	7.594876	-2.186789	-1.141133
C 0	6.512389	-2.836889	-0.546239
C 0	5.428367	-2.102396	-0.067919
H 0	0.072124	0.010042	-1.049106
H 0	0.138642	0.948344	1.850540
H 0	-1.702416	-1.234474	0.681419
H 0	0.762153	-1.363713	2.033495
H 0	-3.621169	-2.171336	1.916418
H 0	-4.045528	-0.042203	-1.795038
H 0	-6.331492	-0.922098	-2.033495
H 0	-5.893072	-3.095388	1.643099
H 0	-7.837017	-3.539404	0.179159
H 0	-7.963397	-2.758209	-1.405856
H 0	-8.439768	-1.884157	0.051372
H 0	5.230235	1.946075	0.991864
H 0	2.598764	-1.372539	-0.013317
H 0	6.478838	1.017631	-0.909405
H 0	8.413181	-0.279154	-1.728244
H 0	8.439768	-2.758996	-1.514288
H 0	6.513524	-3.919270	-0.447669
H 0	4.602704	-2.618606	0.414300

B3LYP/6-31G* Energy = -1987.97724939
B3LYP/6-31G* Free Energy = -1987.683857
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.99037661
Number of Imaginary Frequencies = 0

***anti-13*_c5**
B3LYP/6-31G* geometry

C 0	-1.797859	0.018233	-1.032916
C 0	-1.880859	1.376257	-1.072046
C 0	-0.346710	-0.340947	-1.337128
C 0	-0.554739	1.953030	-1.303514
C 0	0.336824	-1.226785	-0.269687
Cl 0	-3.258308	2.415427	-0.951801
N 0	-2.686596	-0.990766	-0.851796
O 0	-0.198663	3.099335	-1.378994
O 0	0.342729	0.897492	-1.437321
O 0	-0.343971	-2.486010	-0.360095
C 0	-4.005043	-0.941386	-0.315709
C 0	-6.611769	-1.016642	0.766739
C 0	-4.971746	-1.795852	-0.855234
C 0	-4.338359	-0.133253	0.777369
C 0	-5.630278	-0.167330	1.295980
C 0	-6.255179	-1.832842	-0.313585
C 0	-8.000304	-1.062787	1.360381
C 0	1.813460	-1.380886	-0.484044
C 0	4.063604	-2.065867	-1.292388
C 0	4.138081	-1.052128	-0.365787
C 0	5.395051	-0.434966	0.108929
S 0	2.436568	-2.555654	-1.622404
C 0	2.830449	-0.670373	0.089058
C 0	6.575811	-1.188128	0.220724
C 0	7.760598	-0.598391	0.657137
C 0	7.788047	0.755361	0.998670
C 0	6.620702	1.514061	0.896966
C 0	5.436282	0.926013	0.455505
H 0	-0.280969	-0.864811	-2.300651
H 0	0.172037	-0.758290	0.711823
H 0	-2.263324	-1.913192	-0.877503
H 0	0.069886	-3.099335	0.268135
H 0	-4.718074	-2.418919	-1.708845
H 0	-3.589732	0.512980	1.221851
H 0	-5.875886	0.474158	2.139234
H 0	-6.995503	-2.499866	-0.748908
H 0	-8.710904	-1.540827	0.678609
H 0	-8.373742	-0.057420	1.585262
H 0	-8.014864	-1.629949	2.300651
H 0	4.881270	-2.541303	-1.817223
H 0	2.659311	0.101546	0.831519
H 0	6.556246	-2.248874	-0.014568
H 0	8.661836	-1.200145	0.740560
H 0	8.710904	1.214268	1.342751
H 0	6.632162	2.569876	1.154105
H 0	4.540897	1.532881	0.353509

B3LYP/6-31G* Energy = -1987.97669190
B3LYP/6-31G* Free Energy = -1987.684731
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.98976411
Number of Imaginary Frequencies = 0

***anti-13*_c6**
B3LYP/6-31G* geometry

C 0	-1.814954	0.023008	-1.380465
C 0	-1.900173	1.380862	-1.413940
C 0	-0.363340	-0.331993	-1.687936
C 0	-0.575117	1.961110	-1.644818
C 0	0.321925	-1.225823	-0.628803
Cl 0	-3.279466	2.417182	-1.290040
N 0	-2.701974	-0.988585	-1.204336
O 0	-0.222550	3.108364	-1.718857
O 0	0.324462	0.907516	-1.781227
O 0	-0.359843	-2.484750	-0.730063
C 0	-4.021110	-0.944807	-0.669990
C 0	-6.629520	-1.031760	0.407914
C 0	-4.984328	-1.800615	-1.213720
C 0	-4.358856	-0.141242	0.425137
C 0	-5.651548	-0.181068	0.941435
C 0	-6.268526	-1.843415	-0.674354
C 0	-8.018906	-1.084187	0.999065
C 0	1.797798	-1.382338	-0.842610
C 0	4.042170	-2.003196	-1.715547
C 0	4.122783	-1.055094	-0.721997
C 0	5.385389	-0.476305	-0.215822

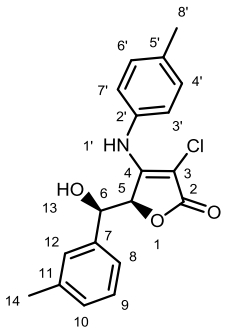
S 0	2.414513	-2.478955	-2.059922
C 0	2.818411	-0.711178	-0.228999
C 0	5.510213	-0.089104	1.128814
C 0	6.702975	0.447988	1.610541
C 0	7.797337	0.606965	0.758831
C 0	7.686548	0.227878	-0.580555
C 0	6.492602	-0.303800	-1.063546
H 0	-0.298946	-0.849190	-2.655246
H 0	0.159120	-0.767010	0.357537
H 0	-2.277207	-1.910164	-1.235419
H 0	0.065432	-3.108364	-0.119914
H 0	-4.727331	-2.420112	-2.068947
H 0	-3.613088	0.505979	0.872948
H 0	-5.900566	0.456995	1.786295
H 0	-7.005991	-2.511394	-1.113069
H 0	-8.726582	-1.563242	0.314964
H 0	-8.396368	-0.080663	1.225484
H 0	-8.033167	-1.653469	1.938069
H 0	4.860314	-2.490248	-2.228859
H 0	2.647512	0.045633	0.529105
H 0	4.672955	-0.228460	1.807171
H 0	6.778348	0.737895	2.655246
H 0	8.726582	1.026917	1.133917
H 0	8.528490	0.358093	-1.255316
H 0	6.405038	-0.564680	-2.114657

B3LYP/6-31G* Energy = -1987.97632037
B3LYP/6-31G* Free Energy = -1987.684429
B3LYP/6-31G* Energy ($CHCl_3$) = -1987.98963881
Number of Imaginary Frequencies = 0

2. Characterization of all synthesized compounds

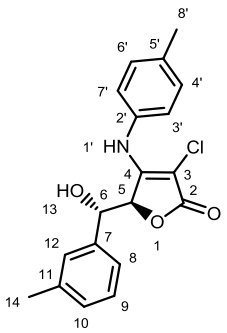
2.1. Characterization of aldol products (*incl. products **23a-b***)

3-chloro-5-[hydroxy(m-tolyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (***syn*-10**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (75:25 v/v) to afford pure *syn*-**10** as white solid in 74% yield (227 mg, 0.66 mmol). Mp: 170.3-172.8 °C. FTIR (KBr) ν_{max} 3409, 3284, 3257, 3062, 3031, 2967, 2939, 2919, 1751, 1633, 1608, 1511, 1390, 1195, 1008, 707 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$:DMSO-d_6; 3:1) δ: 8.43 (s, 1H, -NH), 7.16-6.97 (m, 6H, H-8 to H-10, H-12, H-4′, H-6′), 6.94 (d, J = 7.8 Hz, 2H, H-3′ and H-7′), 5.12 (br, 1H, H-5), 4.95 (br, 1H, H-6), 2.28 (s, 3H, H-14), 2.24 (s, 3H, H-8′). ^{13}C NMR (75 MHz, $CDCl_3$:DMSO-d_6; 3:1) δ: 169.85 (C-2), 156.43 (C-4), 139.21 (C-7), 137.44 (C-11), 135.34 (C-2′), 134.51 (C-5′), 129.23 (2C, C-4′ and C-6′), 128.60 (C-12), 127.93 (C-9), 127.21 (C-10), 124.13 (2C, C-3′ and C-7′), 123.70 (C-8), 88.70 (C-3), 79.71 (C-5), 71.41 (C-6), 21.46 (C-14), 20.97 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{19}H_{17}ClNO_3$, 342.0897; found, 342.0891

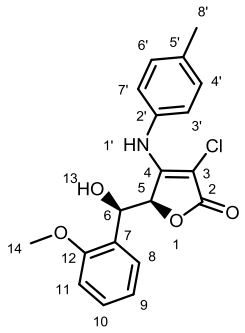
3-chloro-5-[hydroxy(m-tolyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (***anti*-10**)



Compound *anti*-**10** was synthesized using a method similar to that described for compound *anti*-**9.** The crude residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (81:19 v/v) to afford the *syn*-**10** as white solid and eluting with hexane/ethyl acetate (80:20 v/v) to afford *anti*-**10** as pale yellow solid in 33% yield (101 mg, 0.30 mmol)**.** Data for *anti*-**10**: Mp: 158.4-159.2 °C. FTIR

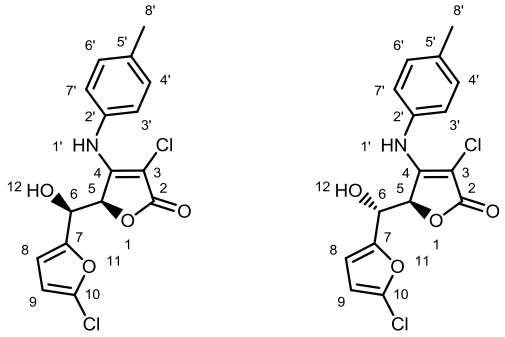
(KBr) ν_{max} 3413, 3287, 3261, 3059, 3027, 2966, 2942, 2923, 1749, 1632, 1610, 1513, 1392, 1197, 1013, 704 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 9.49 (s, 1H, -NH), 7.39-6.80 (m, 8H, H-8 to H-10, H-12, H-3′, H-4′, H-6′ and H-7′), 5.93 (d, *J*= 3.3 Hz, 1H, -OH), 5.49 (d, *J*= 4.1 Hz, 1H, H-5), 4.80 (br, 1H, H-6), 2.28 (s, 3H, H-14), 2.23 (s, 3H, H-8′). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 169.07 (C-2), 156.63 (C-4), 138.31 (C-7), 136.85 (C-11), 135.50 (C-2′), 134.72 (C-5′), 129.72 (2C, C-4′ and C-6′), 128.90 (C-12), 128.38 (C-9), 127.90 (C-10), 124.81 (C-8), 123.57 (2C, C-3′ and C-7′), 88.49 (C-3), 80.57 (C-5), 72.89 (C-6), 21.47 (C-14), 20.93 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{19}H_{17}ClNO_3$, 342.0897; found, 342.0899

3-chloro-5-[hydroxy(2-methoxyphenyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (***syn*-11**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (74:26 v/v) to afford pure *syn*-**11** as white solid in 64% yield (206 mg, 0.57 mmol). Mp: 202.4-204.0 °C. FTIR (KBr) ν_{max} 3424, 3286, 3178, 3070, 3004, 2989, 2960, 2933, 2834, 1741, 1627, 1608, 1492, 1390, 1240, 1078, 1022, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$:DMSO-d_6; 3:1) δ: 8.46 (s, 1H, -NH), 7.43 (d, *J*= 6.6 Hz, 1H, H-8), 7.21-7.01 (m, 5H, H-9, H-3′, H-4′, H-6′ and H-7′), 6.85 (t, *J* = 7.4 Hz, 1H, H-10), 6.72 (d, *J* = 8.1 Hz, 1H, H-11), 5.33 (d, *J* = 1.3 Hz, 1H, H-5), 5.04 (br, 1H, H-6), 3.60 (s, 3H, H-14), 2.30 (s, 3H, H-8′). ^{13}C NMR (75 MHz, $CDCl_3$:DMSO-d_6; 3:1) δ: 169.76 (C-2), 157.95 (C-12), 155.43 (C-4), 135.52 (C-2′), 135.18 (C-5′), 129.54 (2C, C-4′ and C-6′), 128.54 (C-10), 128.25 (C-7), 128.02 (C-8), 123.99 (2C, C-3′ and C-7′), 120.42 (C-9), 109.86 (C-11), 89.91 (C-3), 79.07 (C-5), 65.05 (C-6), 55.03 (C-14), 20.99 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{19}H_{17}ClNO_4$, 358.0846; found, 358.0853

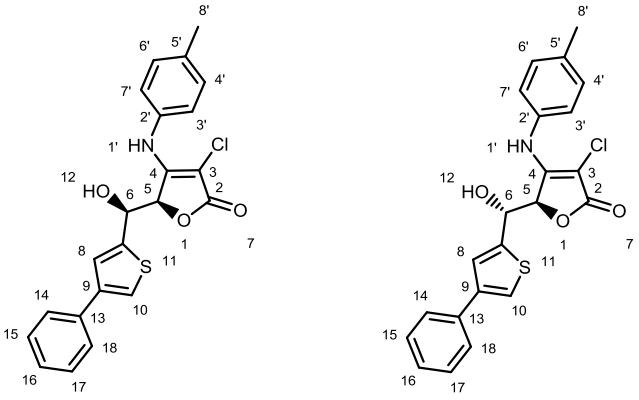
3-chloro-5-[(5-chlorofuran-2-yl)(hydroxyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (***syn*-12/ *anti*-12**)



The crude residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (79:21 v/v) to afford the *syn*-**12** as white solid in 53% yield (168 mg, 0.47 mmol) and eluting with hexane/ethyl acetate (79.5:20.5 v/v) to afford *anti*-**12** as light yellow solid in 15% yield (48 mg, 0.13 mmol). Data for *syn*-**12**: Mp: 184.7-186.4 °C. FTIR (KBr) ν_{max} 3239, 3208, 3124, 3033, 3006, 1722, 1621, 1598, 1517, 1351, 1280, 1197, 1031, 1006, 792 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6) δ: 8.56 (s, 1H, -NH), 7.21 (apparent singlet, 4H, H-3′, H-4′, H-6′and H-7′), 6.47 (d, J = 3.3 Hz, 1H, H-9), 6.30 (d, J = 3.3 Hz, 1H, H-8), 5.57 (d, J = 1.8 Hz, 1H, H-5), 5.29 (br, 1H, -OH), 4.94 (br, 1H, H-6), 2.33 (s, 3H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6) δ: 168.27 (C-2), 156.11 (C-4), 153.38 (C-7), 135.28 (C-2′), 134.90 (C-10), 129.45 (2C, C-4′ and C-6′), 123.77 (2C, C-3′ and C-7′), 123.73 (C-5′), 110.15 (C-8), 107.27 (C-9), 89.62 (C-3), 77.84 (C-5), 65.61 (C-6), 20.01 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{16}H_{12}Cl_2NO_4$, 352.0143; found, 352.0135

Data for *anti*-**12:** Mp: 131.5-133.4 °C. FTIR (KBr) ν_{max} 3305, 3257, 3145, 3060, 3031, 2966, 1718, 1621, 1602, 1535, 1511, 1348, 1186, 1029, 1008, 786 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6) δ: 8.52 (s, 1H, -NH), 7.21 (d, J = 8.4 Hz, 2H, H-4′ and H-6′), 7.15 (d, J = 8.4 Hz, 2H, H-3′ and H-7′), 6.44 (d, J = 3.3 Hz, 1H, H-9), 6.27 (d, J = 3.3 Hz, 1H, H-8), 5.48 (d, J = 4.7 Hz, 2H, -OH and H-5), 4.90 (d, J = 4.7 Hz, 1H, H-6), 2.33 (s, 3H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6) δ: 168.12 (C-2), 156.24 (C-4), 152.15 (C-7), 135.28 (C-2′), 135.20 (C-10), 129.37 (2C, C-4′ and C-6′), 123.86 (2C, C-3′ and C-7′), 123.82 (C-5′), 110.93 (C-8), 107.25 (C-9), 89.22 (C-3), 78.18 (C-5), 67.87 (C-6), 20.04 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{16}H_{12}Cl_2NO_4$, 352.0143; found, 352.0157

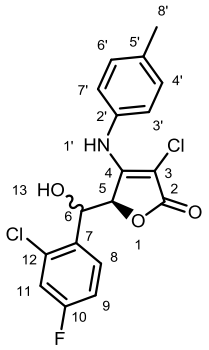
3-chloro-5-[hydroxy(5-phenylthiophen-2-yl)methyl]-4-(p-tolylamino) furan-2(5H)-one (***syn*-13/ *anti*-13**)



The crude residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (78:22 v/v) to afford the *syn*-**13** as white solid in 60% yield (221 mg, 0.54 mmol) and eluting with hexane/ethyl acetate (79:21 v/v) to afford *anti*-**13** as light grey solid in 12% yield (44 mg, 0.11 mmol). Data for *syn*-**13**: Mp: 196.7-198.2 °C. FTIR (KBr) ν_{max} 3253, 3214, 3029, 1729, 1621, 1600, 1511, 1496, 1187, 1112, 1014, 736 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$: DMSO-d_6; 9:1) δ: 7.88 (s,1H, -NH), 7.44 (d, J = 7.4 Hz, 2H, H-8 and H-10), 7.33-7.14 (m, 5H, H-14 to H-18), 7.04 (d, J = 8.1 Hz, 2H, H-4′ and H-6′), 6.92 (d, J = 8.1 Hz, 2H, H-3′ and H-7′), 6.20 (d, J = 5.1 Hz, 1H, -OH), 5.32 (d, J = 3.7 Hz, 1H, H-5), 5.18 (d, J= 3.7 Hz, 1H, H-6), 2.25 (s, 3H, H-8′). ^{13}C NMR (75 MHz, $CDCl_3$: DMSO-d_6; 9:1) δ: 169.60 (C-2), 155.56 (C-4), 142.22 (C-7), 141.77 (C-9), 135.72 (C-13), 135.49 (C-2′), 133.89 (C-5′), 129.14 (2C, C-4′ and C-6′), 128.72 (2C, C-15 and C-17), 127.11 (C-16), 126.16 (2C, C-14 and C-18), 124.44 (C-10), 124.36 (2C, C-3′ and C-7′), 119.93 (C-8), 88.99 (C-3), 78.01 (C-5), 69.18 (C-6), 20.91 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{22}H_{17}ClNO_3S$, 410.0618; found, 410.0605

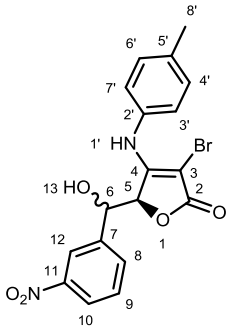
Data for *anti*-**13:** Mp: 158.4-160.2 °C. FTIR (KBr) ν_{max} 3261, 3058, 3033, 1731, 1627, 1606, 1513, 1411, 1265, 1193, 1020, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$:DMSO -d_6; 9:1) δ: 7.77 (s, 1H,-NH), 7.51 (d, J =7.7 Hz, 2H, H-8 and H-10), 7.41-7.23 (m, 5H, H-14 to H-18), 7.12 (d, J = 7.7 Hz, 2H, H-4′ and H-6′), 6.98 (d, J = 7.7 Hz, 2H, H-3′ and H-7′), 5.66 (br, 1H, -OH), 5.15 (d, J= 6.2 Hz, 1H, H-5), 5.08 (br, 1H, H-6), 2.32 (s, 3H, H-8′). ^{13}C NMR (75 MHz, $CDCl_3$: DMSO-d_6; 9:1) δ: 169.48 (C-2), 156.36 (C-4), 143.16 (C-7), 141.95 (C-9), 135.80 (C-13), 135.45 (C-2′), 134.04 (C-5′), 129.43 (2C, C-4′ and C-6′), 128.81 (2C, C-15 and C-17), 127.26 (C-16), 126.23 (2C, C-14 and C-18), 125.08 (C-10), 123.90 (2C, C-3′ and C-7′), 120.50 (C-8), 89.73 (C-3), 79.22 (C-5), 70.69 (C-6), 20.95 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{22}H_{17}ClNO_3S$, 410.0618; found, 410.0585

3-chloro-5-[(2-chloro-4fluorophenyl)(hydroxy)-methyl)]-4-(p-tolylamino) furan-2(5H)-one (***syn/anti*-14**)



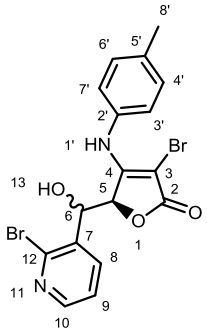
The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (76:24 v/v) to afford mixture of *syn/anti*-**14**, in a *91:09* ratio as a white solid in 78% yield (267 mg, 0.70 mmol). Mp: 223.5-226.1 °C. The spectroscopic data are for the mixture compound, and in case of NMR, the assinments were made as much as possible. FTIR (KBr) ν_{max} 3396, 3241, 3108, 3083, 3041, 2962, 2923, 1751, 1629, 1581, 1488, 1392, 1220, 1197, 1025, 1008, 792, 659 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6:DMSO-d_6; 9:1) δ: 8.93 (s, 0.91H, -NH), 8.64 (s, 0.09H, -NH), 7.72 (dd, J = 6.4, 9.6 Hz, 1H, H-9), 7.29 (d, J = 8.5 Hz, 2H, H-4′ and H-6′), 7.24 (d, J = 8.5 Hz, 2H, H-3′ and H-7′), 7.20-6.98 (m, 2H, H-8 and H-11), 6.08 (d, J = 4.7Hz, 0.09H, -OH), 5.65 (d, J = 5.8 Hz, 0.91H, -OH), 5.49 (d, J = 4.2 Hz, 0.09H, H-5), 5.43 (br, 0.91H, H-5), 5.16 (d, J = 2.1 Hz, 0.91H, H-6), 5.00 (br, 0.09H, , H-6), 2.34 (s, 0.91H, H-8′) and 2.30 (s, 0.09H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6: DMSO-d_6; 9:1) δ: 168.45 (0.91C, C-10), 168.28 (0.09C, C-10), 163.41 (0.91C, C-2), 163.55 (0.09C, C-2), 157.64 (0.91C, C-4), 157.51 (0.09C, C-4), 135.91 (0.91C, C-2′), 135.78 (0.09C, C-2′), 135.39 (0.91C, C-12), 135.39 (0.09C, C-12), 134.79 (0.91C, C-7), 134.30 (0.09C, C-7), 131.59 (0.91C, C-5′), 131.42 (0.09C, C-5′), 131.47 (0.91C, C-8), 131.28 (0.09C, C-8), 129.73 (0.91C, C-4′ and C-6′) and 129.02 (0.09C, C-4′ and C-6′), 124.58 (0.91C, C-7′ and C-3′), 123.15 (0.09C, C-7′ and C-3′), 115.75 (0.91C, C-11), 115.41 (0.09C, C-11), 113.75 (0.91C, C-9), 114.03 (0.09C, C-9), 89.97 (0.91C, C-3), 89.93 (0.09C, C-3), 78.11 (0.91C, C-5), 79.14 (0.09C, C-5), 66.33 (0.91C, C-6), 66.24 (0.09C, C-6), 20.11 (0.91C, C-8′) and 20.05 (0.09H, C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{18}H_{13}Cl_2FNO_3$, 380.0257; found, 380.0239

3-bromo-5-[hydroxy(3-nitrophenyl)methyl)-4-(p-tolylamino]furan-2(5H)-one (***syn/anti*-15**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (76:24 v/v) to afford mixture of *syn/anti*-**15**, in a *56:44* ratio as a yellow solid in 54% yield (169 mg, 0.40 mmol). Mp: 103.2-105.9 °C. The spectroscopic data are for the mixture compound, and in case of NMR, the assinments were made as much as possible. FTIR (KBr) ν_{max} 3212, 3058, 3029, 3004, 1727, 1621, 1600, 1523, 1346, 1191, 1046, 997, 727 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6) δ: 8.62 and 8.53 (s, -NH), 8.27-8.11 (m, 2H, H-10 and H-12), 7.82 (d, J = 7.8 Hz, 0.56H, H-8) 7.76 (d, J = 7.8 Hz, 0.44H, H-8), 7.65 (t, J = 5.9 Hz, 0.56H, H-9), 7.60 (t, J = 5.9 Hz, 0.44H, H-9), 7.32-7.16 (m, 4H, H-3′, H-4′, H-6′ and H-7′), 5.70 (d, J = 3.5 Hz, 0.44H, H-5), 5.59 (d, J = 1.9 Hz, 0.56H, H-5), 5.49 (br, -OH), 5.12 (br, 0.56H, H-6) and 5.08 (d, J = 3.5 Hz, 0.44H, H-6), 2.36 and 2.34 (s, 3H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6) δ: 168.60, 168.04 (C-2), 159.26, 159.11 (C-4), 148.17, 147.81 (C-11), 143.05, 140.62 (C-7), 135.71, 135.47 (C-2′), 135.07, 134.46 (C-8), 133.54, 132.67 (C-9), 129.76, 129.57 (C-4′ and C-6′), 129.40, 129.11 (C-5′), 124.43, 124.40, 123.77, 123.74 (C-3′ and C-7′), 122.80, 122.43 (C-12), 121.98, 121.12 (C-10), 80.75, 80.70 (C-5), 76.75, 76.68 (C-3), 71.93, 69.61 (C-6), 20.06, 20.02 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{18}H_{14}BrN_2O_5$, 417.0086; found, 417.0075

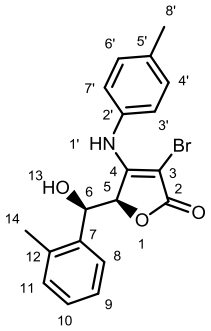
5-[(2-bromopyridin-3-yl)(hydroxy)methyl]-3-bromo-4-(p-tolylamino) furan-2(5H)-one (***syn/anti*-16**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (60:40 v/v) to afford mixture of *syn/anti*-**16**, in a *80:20* ratio as a white solid in 62% yield (210 mg, 0.46 mmol). Mp: 204.8-207.1 °C. The spectroscopic data are for the mixture compound, and in case of NMR,

the assinments were made as much as possible. FTIR (KBr) ν_{max} 3442, 3330, 3131, 3060, 3023, 2942, 1733, 1621, 1604, 1575, 1560, 1400, 1191, 1022, 993, 734, 576 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6:DMSO-d_6; 9:1) δ: 8.94 (s, 0.8H, -NH) and 8.69 (s, 0.2H, -NH), 8.26 (dd, J = 2.0, 4.7 Hz, 0.8H, H-10), 8.23 (d, J = 2.0, 0.2H, H-10), 7.99 (dd, J = 1.9, 7.7 Hz, 1H, H-8), 7.44 (dd, J = 4.7, 7.7 Hz, 1H, H-9), 7.35 (d, J = 8.3 Hz, 0.8H, H-4′ and H-6′), 7.12 (d, J = 8.4 Hz, 0.2H, H-4′ and H-6′), 7.27 (d, J = 8.3 Hz, 0.8H, H-3′ and H-7′), 7.05 (d, J = 8.4 Hz, 0.2H, H-3′ and H-7′), 6.29 (d, J = 4.8 Hz, 0.2H, -OH), 5.87 (d, J = 5.7 Hz, 0.8H, -OH), 5.57 (d, J = 3.6 Hz, 0.2H, H-5), 5.51 (br, 0.8H, H-5), 5.35 (br, 0.2H, H-6), 5.02 (d, J = 1.3 Hz, 0.8H, H-6), 2.34 (s, 0.8H, H-8′) and 2.30 (s, 0.2H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6: DMSO-d_6; 9:1) δ: 168.76 (C-2), 160.75 (0.8C, C-4), 158.68 (0.2C, C-4), 149.34 (0.8C, C-10), 149.53 (0.2C, C-10), 142.03 (0.2C, C-7), 140.12 (0.8C, C-7), 139.14 (0.8C, C-12), 138.86 (0.2C, C-12), 137.71 (0.8C, C-8), 137.67 (0.2C, C-8), 136.02 (0.2C, C-2′), 135.92 (0.8C, C-2′), 135.75 (0.8C, C-5′), 134.43 (0.2C, C-5′), 130.00 (0.8C, C-4′ and C-6′), 129.09 (0.2C, C-4′ and C-6′), 125.26 (0.8C, C-3′ and C-7′), 123.56 (0.2C, C-3′ and C-7′), 123.14 (0.8C, C-9), 123.08 (0.2C, C-9), 80.17 (0.2C, C-5), 78.73 (0.8C, C-5), 77.39 (0.8C, C-3), 76.87 (0.2C,C-3), 71.63 (0.2C, C-6), 68.02 (0.8C, C-6), 20.18 (0.8C, C-2) and 20.14 (0.2C, C-2). HRMS (ESI) $[M-H]^-$ calculated for $C_{17}H_{13}Br_2N_2O_3$, 450.9293; found, 450.9252

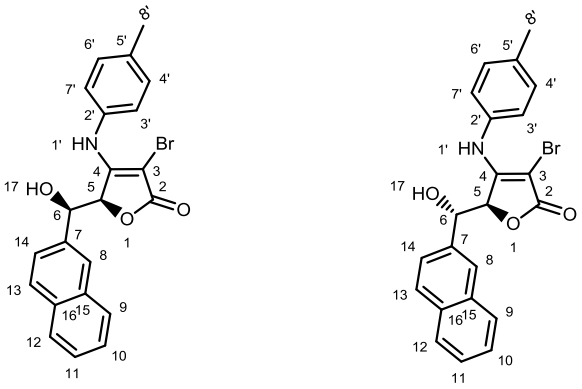
3-bromo-5-[hydroxy(o-tolyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (***syn*-17**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (79:21 v/v) to afford pure *syn*-**17** as a white solid in 77% yield (223 mg, 0.57 mmol). Mp: 174.6-175.8 °C. FTIR (KBr) ν_{max} 3406, 3280, 3251, 3063, 3032 2968, 2938, 2923, 1749, 1632, 1609, 1510, 1392, 1197, 1009, 708 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.40 (s, 1H, -NH), 7.46 (d, J = 6.9 Hz, 1H, H-11), 7.21 (apparent singlet, 4H, H-3′, H-4′, H-6′ and H-7′), 7.18-7.07 (m, 2H, H-9 and H-10), 5.57 (d, J = 6.7 Hz, 1H, H-8), 5.60 (d, J = 3.8 Hz, 1H, -OH), 5.35 (br, 1H, H-5), 4.85 (br, 1H, H-6), 2.30 (s, 1H, H-8′), 1.89 (s, 1H, H-14). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 169.98 (C-2), 161.44 (C-4), 139.57 (C-2′), 135.95 (C-7), 135.40 (C-12), 134.29 (C-5′), 130.12 (C-11), 129.98 (2C, C-4′ and C-6′), 128.24 (C-10),

127.52 (C-8), 125.79 (C-9), 124.07 (2C, C-3′ and C-7′), 80.14 (C-5), 76.26 (C-3), 66.30 (C-6), 20.98 (C-14), 18.84 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{19}H_{17}BrNO_3$, 386.0392; found, 386.0390

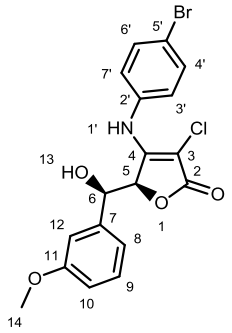
3-bromo-5-[hydroxy(naphthalen-2-yl)methyl)-4-(p-tolyl amino]furan-2(5H)-one (***syn*-18/ *anti*-18**)



The crude residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (76:24 v/v) to afford the *syn*-**18** as white solid in 43% yield (136 mg, 0.32 mmol) and eluting with hexane/ethyl acetate (75.5:24.5 v/v) to afford *anti*-**18** as white solid in 24% yield (76 mg, 0.18 mmol). Data for *syn*-**18**: Mp: 170.7-173.0 °C. FTIR (KBr) ν_{max} 3235, 3216, 3120, 3037, 2913, 2852, 1720, 1619, 1594, 1525, 1510, 1319, 1191, 1106, 1006, 806, 738 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6 :DMSO-d_6; 9:1) δ: 8.94 (s, 1H, -NH), 7.92-7.78 (m, 4H, H-8, H-9, H-12 and H-13), 7.55-7.44 (m, 3H, H-10, H-11 and H-14), 7.26 (apparent singlet, 4H, H-3′, H-4′, H-6′ and H-7′), 5.57 (d, J = 5.7 Hz, 1H, -OH), 5.53 (d, J = 1.6 Hz, 1H, H-5), 5.14 (br, 1H, H-6), 2.36 (s, 1H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6:DMSO-d_6; 9:1) δ: 169.13 (C-2), 159.83 (C-4), [138.73, 135.49, 135.21, 133.14, 133.01, 129.40 (2C), 127.89, 127.60, 127.49, 126.04, 125.78, 125.19, 124.68, 124.44 (2C)] (C-7 to C-16 and C-2′ to C-7′), 81.51 (C-5), 76.33 (C-3), 70.50 (C-6), 20.14 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{22}H_{17}BrNO_3$, 422.0392; found, 422.0331

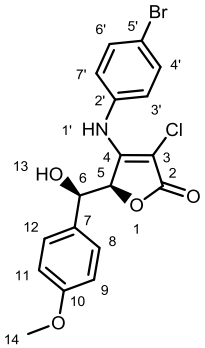
Data for *anti*-**18:** Mp: 155.5-157.9 °C. FTIR (KBr) ν_{max} 3378, 3224, 3052, 3025, 1710, 1693, 1618, 1591, 1531, 1292, 1187, 1016, 995, 748 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6) δ: 8.46 (s, 1H, -NH), 7.92-7.78 (m, 4H, H-8, H-9, H-12 and H-13), 7.62-7.44 (m, 3H, H-10, H-11 and H-14), 7.24 (apparent singlet, 4H, H-3′, H-4′, H-6′ and H-7′), 5.67 (d, J = 3.8 Hz, 1H, H-5), 5.31 (br, 1H, -OH), 5.08 (d, J = 3.8 Hz, 1H, H-6), 2.34 (s, 1H, H-8′).^{13}C NMR (75 MHz, Acetone-d_6) δ: 168.19 (C-2), 159.56 (C-4), [136.06, 135.46, 135.27, 133.33, 132.95, 129.59 (2C), 127.95, 127.57, 127.34, 126.47, 125.95 (2C), 125.19, 123.87 (2C)] (C-7 to C-16 and C-2′ to C-7′), 81.17 (C-5), 77.23 (C-3), 73.28 (C-6), 20.04 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{22}H_{17}BrNO_3$, 422.0392; found, 422.0389

4-[(4-bromophenyl)amino)-3-chloro-5-(hydroxyl (3-methoxy phenyl)methyl]furan-2(5H)-one (***syn*-19**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (76:24 v/v) to afford pure *syn*-**19** as a white solid in 68% yield (200 mg, 0.47 mmol). Mp: 170.3-172.8 °C. FTIR (KBr) ν_{max} 3347, 3193, 3083, 3018, 2996, 2950, 2929, 1752, 1656, 1635, 1587, 1486, 1029, 703 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$: DMSO-d_6; 3:2) δ: 9.09 (s, 1H, -NH), 7.38 (d, J = 8.6 Hz, 2H, H-4′ and H-6′), 7.15 (t, J = 8.0 Hz, 1H, H-9), 6.97 (d, J = 8.6 Hz, 2H, H-3′and H-7′), 6.89 (d, J = 7.6 Hz, 2H, H-8 and H-12), 6.73 (dd, J = 1.7, 8.6 Hz, 1H, H-10), 5.14 (d, J = 1.6 Hz, 1H, H-5), 4.95 (br, 1H, H-6), 3.69 (s, 3H, H-14). ^{13}C NMR (75 MHz, $CDCl_3$: DMSO-d_6; 3:2) δ: 169.62 (C-2), 159.39 (C-11), 155.77 (C-4), 141.97 (C-7), 136.88 (C-2′), 131.50 (2C, C-4′ and C-6′), 129.11 (C-9), 125.26 (2C, C-3′ and C-7′), 118.70 (C-8), 117.68 (C-5′), 113.01 (C-10), 112.37 (C-12), 90.08 (C-3), 80.62 (C-5), 70.94 (C-6), 55.16 (C-14). HRMS (ESI) $[M-H]^-$ calculated for $C_{18}H_{14}BrClNO_4$, 421.9795; found, 421.9789

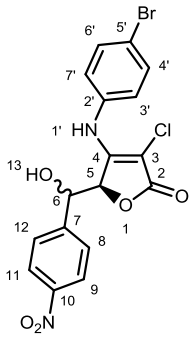
4-[(4-bromophenyl)amino)-3-chloro-5-(hydroxy(4-methoxyphenyl) methyl]furan-2(5H)-one (***syn*-20**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (77:23 v/v) to afford pure *syn*-**20** as a white solid in 75% yield (221 mg, 0.52 mmol). Mp: 170.3-172.8 °C. FTIR (KBr) ν_{max} 3212, 3174, 3031, 3010, 2989, 2929, 2886, 1714, 1614, 1581, 1511, 1251, 1191, 1170, 1022, 744 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6) δ: 8.88 (s, 1H, -NH), 7.56 (d, J = 8.7, 2H, H-4′ and H-6′), 7.34 (d, J = 8.7 Hz, 2H, H-8 and H-12), 7.20 (d, J = 8.7 Hz, 2H, H-9 and H-11), 6.89 (d, J =

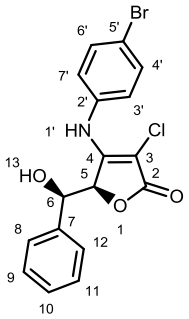
8.7 Hz, 2H, H-3′ and H-7′), 5.35 (d, *J* = 2.3 Hz, 2H, H-5), 5.29 (d, *J* = 4.9 Hz, 1H, -OH), 5.06 (br, 1H, H-6), 3.78 (s, 3H, H-14). ^{13}C NMR (75 MHz, Acetone-d_6) *δ*: 168.50 (C-2), 159.33 (C-10), 155.78 (C-4), 137.44 (C-2′), 132.22 (C-7), 131.62 (2C, C-4′ and C-6′), 127.74 (2C, C-8 and C-12), 125.26 (2C, C-3′ and C-7′), 117.26 (C-5′), 113.28 (2C, C-9 and C-11), 90.69 (C-3), 80.39 (C-5), 70.81 (C-6), 54.63 (C-14). HRMS (ESI) [M-H]$^-$ calculated for $C_{18}H_{14}BrClNO_4$, 421.9795; found, 421.9804

4-[(4-bromophenyl)amino)-3-chloro-5-(hydroxyl (4-nitrophenyl) methyl]furan-2(5H)-one (***syn/anti*-21**)



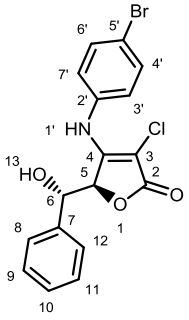
The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (79:21 v/v) to afford mixture of *syn/anti*-**21**, in a *93:07* ratio as a yellow solid in 81% yield (247 mg, 0.56 mmol). Mp: 127.2-129.3 °C. The spectroscopic data are for the mixture compound, and in case of NMR, the assinments were made as much as possible. FTIR (KBr) ν_{max} 3241, 3187, 3145, 3052, 2969, 2805, 1718, 1619, 1585, 1515, 1486, 1344, 1191, 1031, 1010, 821, 703 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6) *δ*: 8.85 (s, 0.93H, -NH) and 8.70 (s, 0.07H, -NH), 8.22 (d, *J* = 8.8 Hz, 0.93H, H-9 and H-11), 8.17 (d, *J* = 8.6 Hz, 0.07H, H-9 and H-11), 7.71 (d, *J* = 8.8 Hz, 0.93H, H-8 and H-12),7.7 (d, *J* = 8.6 Hz, 0.07H, H-8 and H-12), 7.58 (d, *J* = 8.56 Hz, 0.93H, H-4′ and H-6′),7.53 (d, *J* = 8.8 Hz, 0.07H, H-4′ and H-6′), 7.25 (d, *J* = 8.6 Hz, 0.93H, H-3′ and H-7′),7.19 (d, *J* = 8.8 Hz, 0.07H, H-3′ and H-7′), 5.62 (d, *J* = 5.3 Hz, 0.93H, -OH), 5.57 (d, *J* = 1.8 Hz, 0.93H, H-5) and 5.32 (d, *J* = 1.8 Hz, 0.93H, H-6). ^{13}C NMR (75 MHz, Acetone-d_6) *δ*: 168.32 (C-2), 155.42 (C-4), 147.82 (C-10), 147.56 (C-7), 137.16 (C-2′), 131.82 (2C, C-4′ and C-6′), 127.59 (2C, C-8 and C-12), 125.34 (2C, C-3′ and C-7′), 123.09 (2C, C-9 and C-11), 117.74 (C-5′), 91.02 (C-3), 79.92 (C-5), 70.32 (C-6). HRMS (ESI) [M-H]$^-$ calculated for $C_{17}H_{11}BrClN_2O_5$, 436.9540; found, 436.9519

4-[(4-bromophenyl)amino)-3-chloro-5-(hydroxyl (phenyl)methyl] furan-2(5H)-one (***syn*-22**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (77:23 v/v) to afford pure *syn*-**22** as a white solid in 86% yield (235 mg, 0.60 mmol). Mp: 225.3-227.7 °C. FTIR (KBr) ν_{max} 3390, 3222, 3101, 3064, 2967, 2923, 2902, 1754, 1635, 1581, 1477, 1378, 1195, 1016, 829, 696 cm^{-1}. ^1H NMR (300 MHz,$CDCl_3$:DMSO-d_6; 3:2) δ: 9.21 (s, 1H, -NH), 7.39 (d, J = 8.5 Hz, 2H, H-4′ and H-6′), 7.35-7.14 (m, 5H, H-8 to H-12), 7.00 (d, J = 8.5 Hz, 2H, H-3′ and H-7′), 5.16 (br, 1H, H-5), 4.97 (br, 1H, H-6). ^{13}C NMR (75 MHz, $CDCl_3$: DMSO-d_6; 3:2) δ: 169.52 (C-2), 155.86 (C-4), 140.60 (C-7), 137.01 (C-2′), 131.52 (2C, C-4′ and C-6′), 128.08 (2C, C-9 and C-11), 127.70 (C-10), 126.60 (2C, C-8 and C-12), 125.25 (C-3′ and C-7′), 117.59 (C-5′), 90.04 (C-3), 80.76 (C-5), 70.89 (C-6). HRMS (ESI) $[M-H]^-$ calculated for $C_{17}H_{12}BrClNO_3$, 391.9689; found, 391.9676

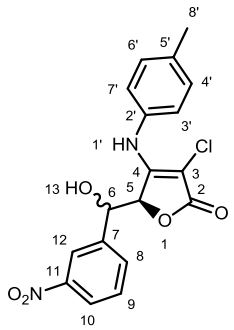
4-[(4-bromophenyl)amino)-3-chloro-5-(hydroxyl (phenyl)methyl] furan-2(5H)-one (***anti*-22**)



Compound *anti*-**22** was synthesized using a method similar to that described for compound *anti*-**9.** The crude residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (81:19 v/v) to afford the *syn*-**22** as white solid and eluting with hexane/ethyl acetate (80:20 v/v) to afford *anti*-**22** as white solid in 41% yield (156 mg, 0.39 mmol)**.** Data for *anti*-**22**: Mp: 208.7-210.1 °C. FTIR (KBr) ν_{max} 3394, 3226, 3105, 3062, 2973, 2921, 2898, 1751, 1634, 1583, 1471, 1381, 1198, 1011, 824, 689 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 9.63 (s, 1H, -NH), 7.54 (d, J = 8.4 Hz, 2H, H-4′ and H-6′), 7.32-7.16 (m, 5H, H-8 to H-12), 7.05 (d, J = 8.4 Hz, 2H, H-3′ and H-7′), 6.03 (br, 1H, -OH), 5.53 (d, J=

3.2, 1H, H-5), 4.85 (br, 1H, H-6). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 168.83 (C-2), 156.08 (C-4), 138.33 (C-7), 137.53 (C-2′), 132.10 (2C, C-4′ and C-6′), 128.37 (C-10), 128.06 (2C, C-9 and C-11), 127.64 (2C, C-8 and C-12), 125.25 (2C, C-3′ and C-7′), 117.40 (C-5′), 89.97 (C-3), 80.71 (C-5), 72.93 (C-6). HRMS (ESI) $[M-H]^-$ calculated for $C_{17}H_{12}BrClNO_3$, 391.9689; found, 391.9684

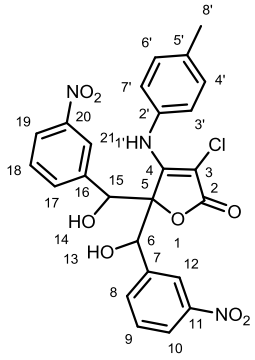
3-chloro-5-[(hydroxy(3-nitrophenyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (***syn/anti*-23**)



The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (77:23 v/v) to afford mixture of *syn/anti*-**23**, in a *53:47* ratio as a yellow solid in 51% yield (171 mg, 0.46 mmol). Mp: 224.5-226.8 °C. The spectroscopic data are for the mixture compound, and in case of NMR, the assinments were made as much as possible. FTIR (KBr) ν_{max} 3261, 3060, 3029, 3006, 1724, 1627, 1604, 1523, 1348, 1020, 811, 680 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6) δ: 8.68 and 8.59 (s, -NH), 8.31-8.11 (m, H-12 and H-8), 7.82 (t, *J*= 8.8, H-9) 7.71-7.56 (m, H-10), 7.30-7.10 (m, 4H, H-3′ to H-7′), 5.65 (d, *J* = 3.8 Hz, 0.47H, H-5 and -OH), 5.55 (d, *J* = 3.1 Hz, 0.53H, H-5 and -OH), 5.22 (br, 0.53H, H-6), 5.15 (d, *J* = 3.8 Hz, 0.47H, H-6), 2.33 and 2.35 (s, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6) δ: 168.35, 167.78 (C-2), 156.24, 156.24(C-4), 148.17, 147.86 (C-11), 142.95, 140.77 (C-7), 135.42, 135.38 (C-2′), 135.24, 135.20 (C-8), 133.59, 132.75 (C-9), 129.63, 129.45 (2C, C-4′ and C-6′), 129.41, 129.18 (C-5′), 124.00, 123.44 (2C, C-3′ and C-7′), 122.86, 122.48 (C-12), 121.99, 121.16 (C-10), 90.16, 89.52 (C-3), 79.72, 79.60 (C-5), 72.32, 69.95 (C-6), 20.06 and 20.01 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{18}H_{14}ClN_2O_5$, 373.0591; found, 373.0598

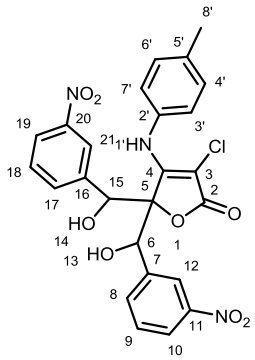
During the purification of crude compound **23** by column chromatography on silica gel, two new compounds were also isolated, namely, **23a** and **23b**. Products structure were proposed by ^{1}H and ^{13}C NMR data and HRMS analysis. The stereochemistry of proposed compounds were not assigned.

3-chloro-5-[hydroxy(3-nitrophenyl)methyl]-5-[hydroxyl(3-nitrophenyl)methyl]-4-(p-tolylamino)furan-2(5H)-one (**23a**)



Compound **23a** was eluted with hexane/ethyl acetate (64:36 v/v) as a yellow solid in 9% yield (42 mg, 0.08 mmol). ^{1}H NMR (300 MHz, Acetone-d_6) δ: 8.52 (br, 2H, H-12 and H-21), 8.25-8.16 (m, 2H, H-10 and H-19), 8.10 (br, 1H, H-8), 8.08 (br, 1H, H-17), 7.64 (br dd, J =8.00Hz, 2H, H-9 and H-18), 7.10 (d, J = 8.00 Hz, 2C, H-3′ and H-7′), 6.82 (d, J = 8.30 Hz, 2C, H-4′ and H-6′), 6.09 (br, 2H, -OH), 5.84 (s, 2H, H-6 and H-15), 2.28 (s, 3H, H-8′).^{13}C NMR (75 MHz, Acetone-d_6) δ: 167.66 (C-2), 154.62 (C-4), 147.86(C-11), 147.86 (C-20), 140.94 (2C, C-7 and C-16), 135.69 (C-2′), 134.32 (2C, C-8 and C-17), 133.75 (C-5′), 129.28 (2C, C-9 and C-18), 128.73 (2C, C- C-4′ and C-6′), 124.83 (2C, C-3′ and C-7′), 123.13 (2C, C-12 and C-21), 122.74 (2C, C-10 and C-19), 89.88 (C-5), 87.51 (C-3), 73.93 (2C, C-6 and C-15) and 20.01 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{25}H_{19}ClN_3O_8$, 524.0861; found, 524.0820

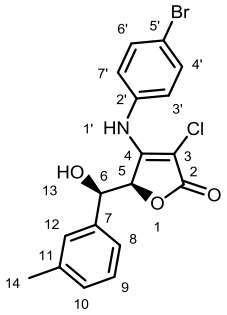
3-chloro-5-hydroxy(3-nitrophenyl)methyl)-5-(hydroxyl(3-nitrophenyl)methyl)-4-(p-tolylamino)furan-2(5H)-one (**23b)**



Compound **23b** was eluted with hexane/ethyl acetate (60:40 v/v) as a yellow solid in 7% yield (33 mg, 0.06 mmol). ^{1}H NMR (300 MHz, Acetone-d_6) δ: 8.72 (s, 1H, -NH), 8.52 (br, 2H, H-12 and H-21), 8.25-8.12(m, 2H, H-10 and H-19), 8.06 (d, J = 7.80 Hz, 1H, H-8), 7.91 (d, J = 7.70Hz, 1H, H-17), 7.64 (dd, J

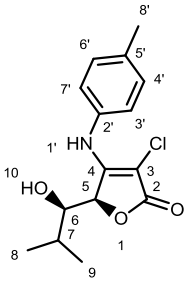
=8.10, 8.10 Hz, 2H, H-9 and H-18), 7.13 (d, *J* = 8.1 Hz, 2C, H-3′ and H-7′), 6.93 (d, *J* = 8.30 Hz, 2H, H-4′ and H-6′), 6.56 (br, 1H, -OH), 6.02 (s, 1H, H-6), 5.94 (s, 1H, H-15), 5.82 (br, 1H, -OH) and 2.30 (s, 3H, H-8′). ^{13}C NMR (75 MHz, Acetone-d_6) δ: 166.88 (C-2), 155.10 (C-4), 147.83 (C-11), 147.74 (C-20), 141.46 (C-7), 141.34 (C-16), 135.77 (C-2′), 134.20 (C-8), 133.96 (C-17), 133.79 (C-5′), 129.20 (C-9), 128.99 (C-18), 128.70 (2C, C- C-4′ and C-6′), 125.03 (2C, C-3′ and C-7′), 123.05 (C-12), 122.88 (C-21),122.60 (C-19), 121.79 (C-10), 88.51 (C-5) 86.21 (C-3),72.44 (C-6), 71.61 (C-15) and 20.03 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{25}H_{19}ClN_3O_8$, 524.0861; found, 524.0815

4-[(4-bromophenyl)amino]-3-chloro-5-[hydroxy(m-tolyl)methyl]furan-2(5H)-one (***syn*-24**)



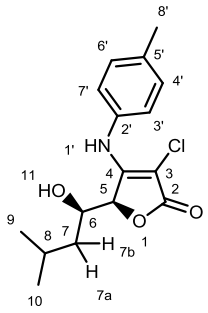
The crude residue was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (70:30 v/v) to afford pure *syn*-**24** as white solid in 71% yield (201 mg, 0.49 mmol). Mp: 197.5-198.8 °C. FTIR (KBr) ν_{max} 3416, 3292, 3266, 3054, 3030, 2961, 2943, 2920, 1756, 1626, 1613, 1516, 1394, 1195, 1013, 706 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.63 (s, 1H, -NH), 7.57 (d, *J* = 8.6 Hz, 2H, H-4′ and H-6′), 7.29-7.01 (m, 6H, H-8 to H-10, H-12, H-3′, H-7′), 5.76 (br, 1H, -OH), 5.36 (apparent singlet, 1H, H-5), 4.87 (br, 1H, H-6), 2.29 (s, 3H, H-14). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 169.42 (C-2), 156.68 (C-4), 141.62 (C-7), 137.59 (C-11), 137.39 (C-2′), 131.96 (2C, C-4′ and C-6′), 128.34 (C-10), 128.31 (C-9), 127.15 (C-12), 125.57 (2C, C-3′ and C-7′), 123.73 (C-8), 117.28 (C-5′), 89.64 (C-3), 81.31 (C-5), 70.35 (C-6) and 21.59 (C-14). HRMS (ESI) $[M-H]^-$ calculated for $C_{18}H_{14}BrClNO_3$, 405.9846; found, 405.9841

3-chloro-5-(1-hydroxy-2-methylpropyl)-4-(p-tolylamino)furan-2(5H)-one (***syn*-25**)



The crude residue of compound **25** was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (70:30 v/v) to afford pure *syn*-**25** as a white solid in 79% yield (209 mg, 0.71 mmol). Mp: 203.2-204.5 ºC. FTIR (KBr) ν_{max} 3381, 3284, 3225, 3071, 3031, 2976, 1748, 1632, 1191, 1024, 644 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.30 (s, 1H, -NH), 7.14 (d, J = 8.2 Hz, 2H, H-4′ and H-6′), 7.06 (d, J= 8.2 Hz, 2H, H-3′ and H-7′), 5.35 (apparent singlet, 1H, H-5), 4.87 (d, J = 7.7 Hz, 1H, -OH), 3.19 (t, J = 8.1 Hz, 1H, H-6), 2.27 (s, 3H, H-8′), 1.79-1.67 (m, 1H, H-7) and 0.88-0.78 (m, 6H, H-8 and H-9). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 169.78 (C-2), 158.80 (C-4), 135.71 (C-2′), 134.57 (C-5′), 129.52 (2C, C-4′ and C-6′), 123.94 (2C, C-3′ and C-7′), 87.74 (C-3), 78.21 (C-5), 73.58 (C-6), 31.60 (C-7), 20.92 (C-8′), 20.18 (C-8) and 19.34 (C-9). HRMS (ESI) $[M-H]^-$ calculated for $C_{15}H_{17}ClNO_3$, 294.0897; found, 294.0893

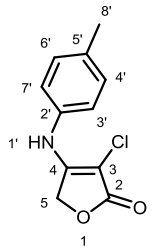
3-chloro-5-[1-hydroxy-3-methylbutyl]-4-(p-tolylamino)furan-2(5H)-one (***syn*-26**)



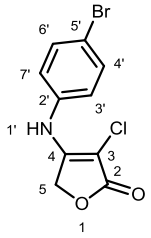
The crude residue of compound **26** was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (70:30 v/v) to afford pure *syn*-**26** as a white solid in 76% yield (210 mg, 0.68 mmol). Mp: 206.7-208.1 ºC. FTIR (KBr) ν_{max} 3383, 3289, 3232, 3079, 3023, 2972, 1746, 1627, 1196, 1021, 635 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.32 (s, 1H, -NH), 7.15 (d, J = 7.8 Hz, 2H, H-4′ and H-6′), 7.07 (d, J= 7.8 Hz, 2H, H-3′ and H-7′), 5.11 (apparent singlet, 1H, H-5), 4.80 (d, J = 7.1 Hz, 1H, -OH), 3.69 (apparent singlet, 1H, H-6), 2.27 (s, 3H, H-8′), 1.74-1.55 (m, 1H, H-8), 1.54-1.43 (m, 1H, H-7a) 1.32-1.14 (m, 1H, H-7b) and 0.86-0.65 (m, 6H, H-9 and H-10). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 169.66 (C-2), 158.29 (C-4), 135.64 (C-2′), 134.66 (C-5′), 129.49 (2C, C-4′ and C-6′), 124.06 (2C, C-3′ and C-7′), 87.56 (C-3), 80.29 (C-5), 66.10 (C-6), 43.04 (C-7), 24.22 (C-8), 23.37 (C-9), 22.20 (C-10) and 20.85 (C-8′). HRMS (ESI) $[M-H]^-$ calculated for $C_{16}H_{19}ClNO_3$, 308.1053; found, 308.1049

2.2. Characterization of retro-aldol products

Mixture of *3-chloro-4-(p-tolylamino)furan-2(5H)-one* (**8a**) and *4-[(4-bromophenyl)amino]-3-chlorofuran-2(5H)-one* (**8b**)



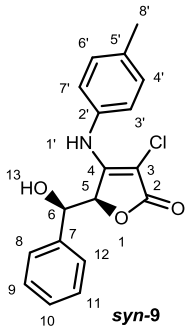
8a



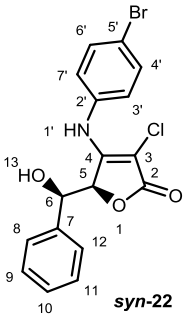
8b

The crude mixture was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (82:18 v/v) to afford mixture of **8a/8b**, in a *47:53* ratio as a brown solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.69 (s, -NH, 8b), 9.55 (s, - NH, 8a), 7.52 (d, J = 8.6 Hz, H-4′/6′, 8b), 7.18 (d, J= 8.6 Hz, H-3′/7′, 8b), 7.15-7.08 (m, H-3′ to 7′, 8a), 5.10 (s, H-5, 8b), 5.02 (s, H-5, 8a) and 2.26 (s, H-8′, 8a). HRMS (ESI) $[M-H]^-$ calculated for $C_{11}H_9ClNO_2$ and $C_{10}H_6BrClNO_2$ 222.0322 and 285.9270 respectively; found, 222.0323 and 285.9269

Mixture of *3-chloro-5-[hydroxy(phenyl)methyl]-4-(p-tolylamino)furan-2(5H)-one* (***syn*-9**) and *4-[(4-bromophenyl)amino)-3-chloro-5-(hydroxyl (phenyl)methyl] furan-2(5H)-one* (***syn*-22**)



***syn*-9**

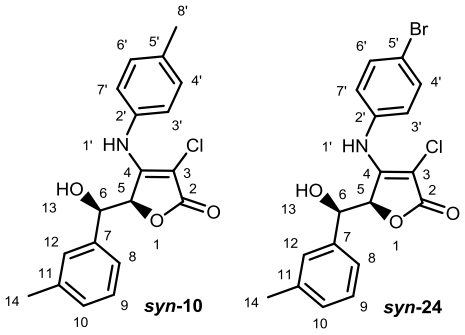


***syn*-22**

The crude mixture was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (80:20 v/v) to afford mixture of *syn*-**9**/*syn*-**22**, in a *33:67* ratio as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.65 (s, -NH, *syn*-**22**), 9.49 (s, -NH, *syn*-**9**), 7.57 (d, J = 8.5 Hz, H-4′/6′, *syn*-**22**), 7.41-7.10 (m, H-3′/7′, H-8 to 12, *syn*-**22** and H-3′ to 7′, H-8 to 12, *syn*-**9**), 5.81 (br, -OH, *syn*-**22**), 5.76 (d, J = 5.7 Hz, -OH, *syn*-**9**), 5.39 (apparent singlet, H-5, *syn*-**22**/*syn*-**9**), 4.91 (apparent singlet, H-6, *syn*-**22**),

4.85 (d, *J* = 2.1 Hz, H-5, *syn*-**9**), 2.35 (s, H-8′, *syn*-**9**). HRMS (ESI) $[M-H]^-$ calculated for $C_{18}H_{15}ClNO_3$ and $C_{17}H_{12}BrClNO_3$ 328.0740 and 391.9689 respectively; found, 328.0732, and 391.9681

Mixture of *3-chloro-5-[hydroxy(m-tolyl)methyl]-4-(p-tolylamino)furan-2(5H)-one* (***syn*-10**) and *4-[(4-bromophenyl)amino]-3-chloro-5-[hydroxy(m-tolyl)methyl]furan-2(5H)-one* (***syn*-24**)



The crude mixture was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (79:21 v/v) to afford mixture of *syn*-**10**/*syn*-**24**, in a *76:24* ratio as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.64 (s, -NH, *syn*-**24**), 9.48 (s, -NH, *syn*-**10**), 7.57 (d, *J* = 8.6 Hz, H-4′/6′, *syn*-**24**), 7.23-7.02 (m, H-3′/7′, H-8 to 12, *syn*-**24** and H-3′ to 7′, H-8 to 12, *syn*-**10**), 5.76 (d, *J* = 5.1 Hz, -OH, *syn*-**24**), 5.71 (d, *J* = 5.8 Hz, -OH, *syn*-**10**), 5.35 (apparent singlet, H-5, *syn*-**10**/*syn*-**24**), 4.87 (d, *J* =2.0 Hz, H-6, *syn*-**24**), 4.82 (d, *J* = 1.9 Hz, H-5, *syn*-**10**), 2.30 (s, H-14, *syn*-**10**/*syn*-**24**) and 2.29 (s, H-8′, *syn*-**10**). HRMS (ESI) $[M-H]^-$ calculated for $C_{19}H_{17}ClNO_3$ and $C_{18}H_{14}BrClNO_3$ 342.0897 and 405.9846 respectively; found, 342.0894, and 405.9842

3. NMR spectra of all synthesized compounds

3.1. NMR spectra of tetronamides

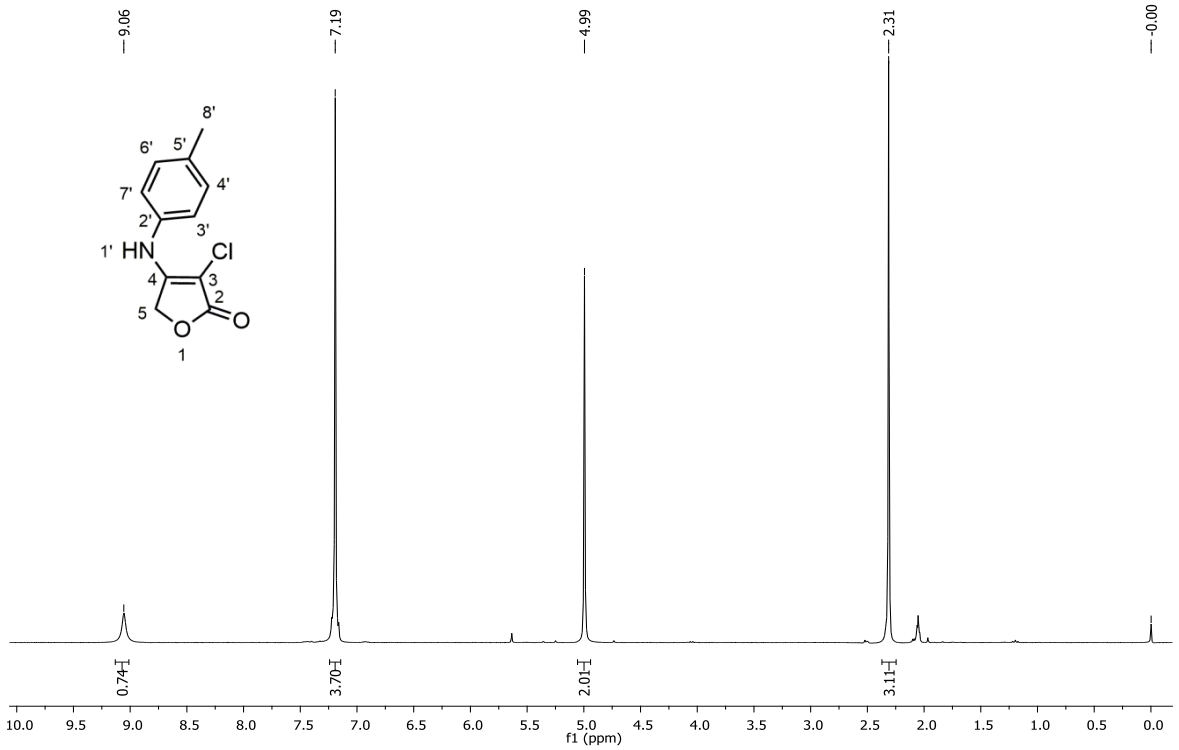


Figure S8 ^{1}H NMR spectrum (300 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound **8a**

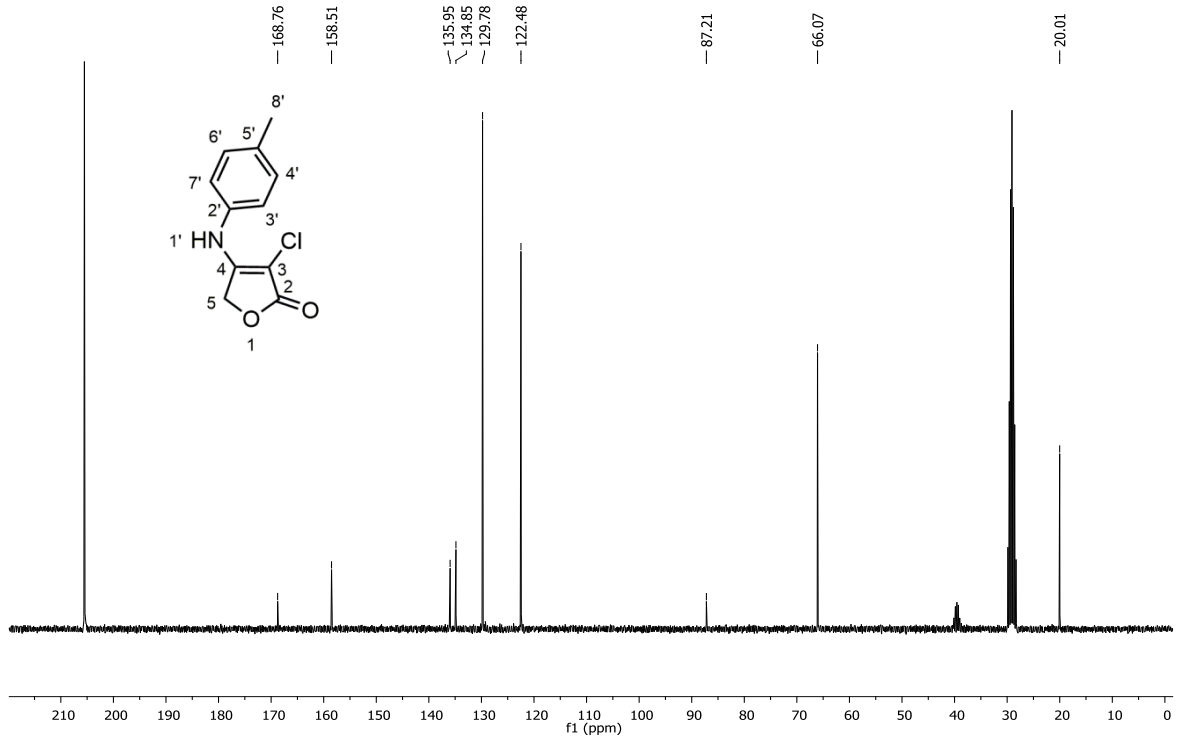


Figure S9 ^{13}C NMR spectrum (75 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound **8a**

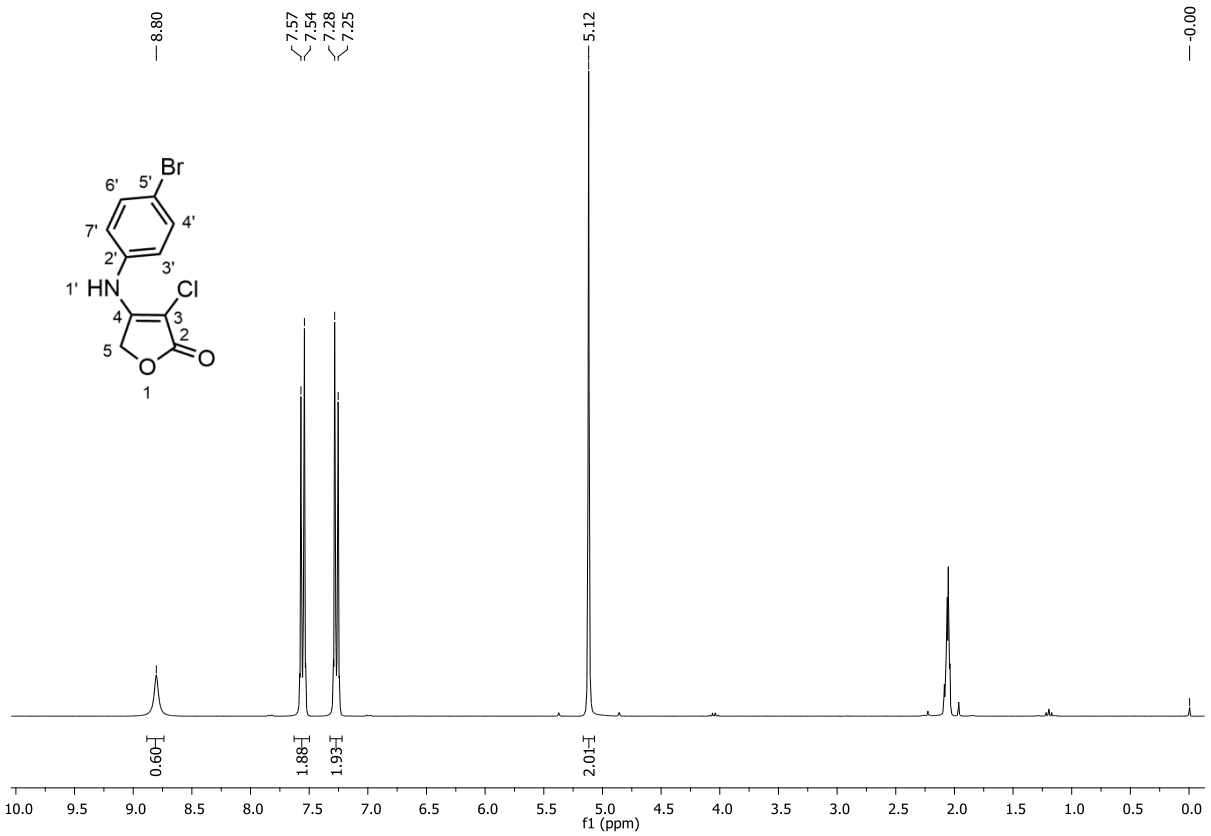


Figure S10 ^{1}H NMR spectrum (300 MHz, Acetone-d_6) of compound **8b**

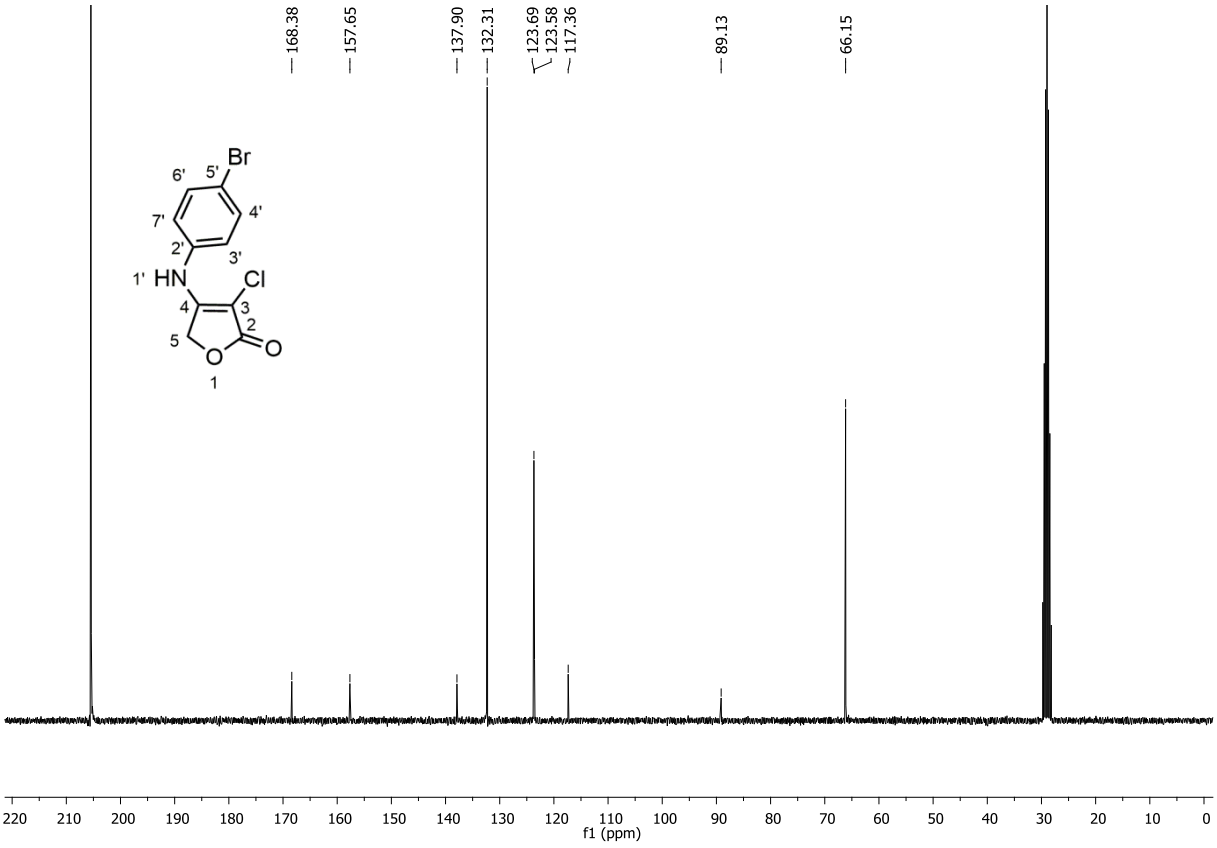


Figure S11 ^{13}C NMR spectrum (300 MHz, Acetone-d_6) of compound **8b**

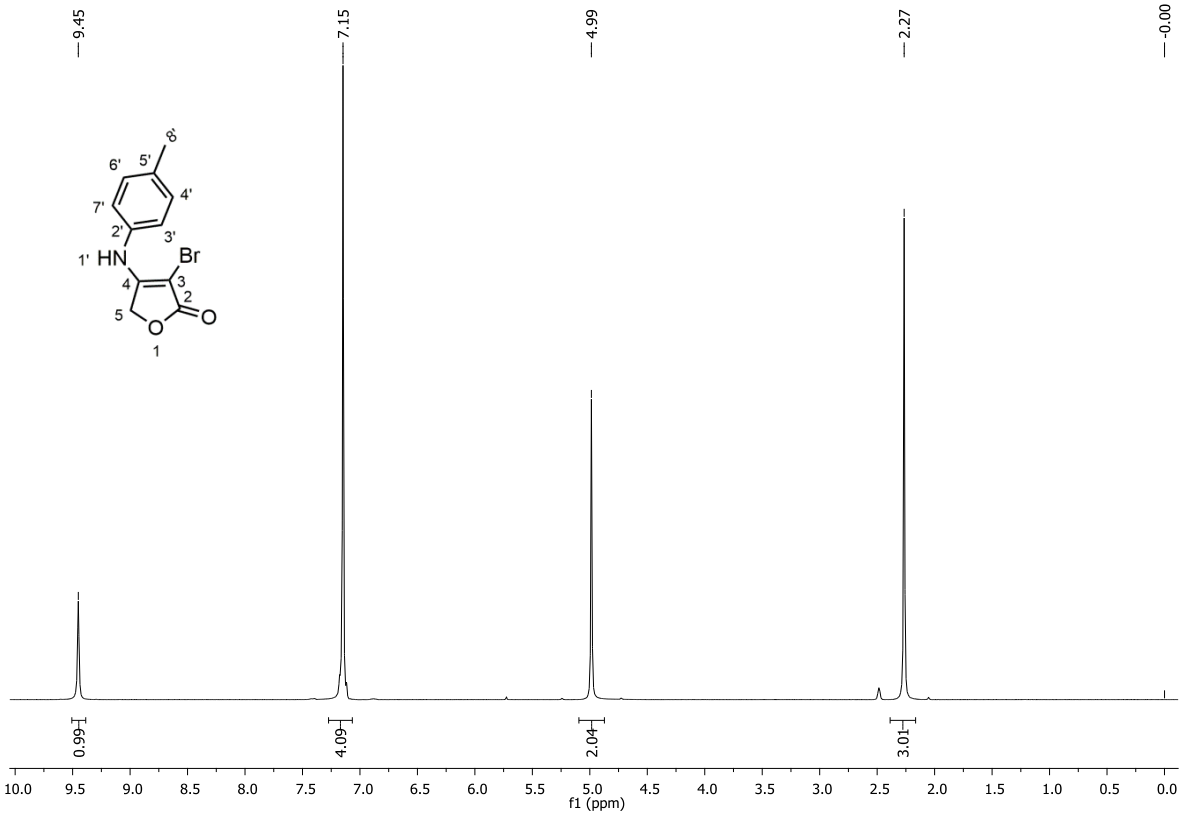


Figure S12 ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **8c**

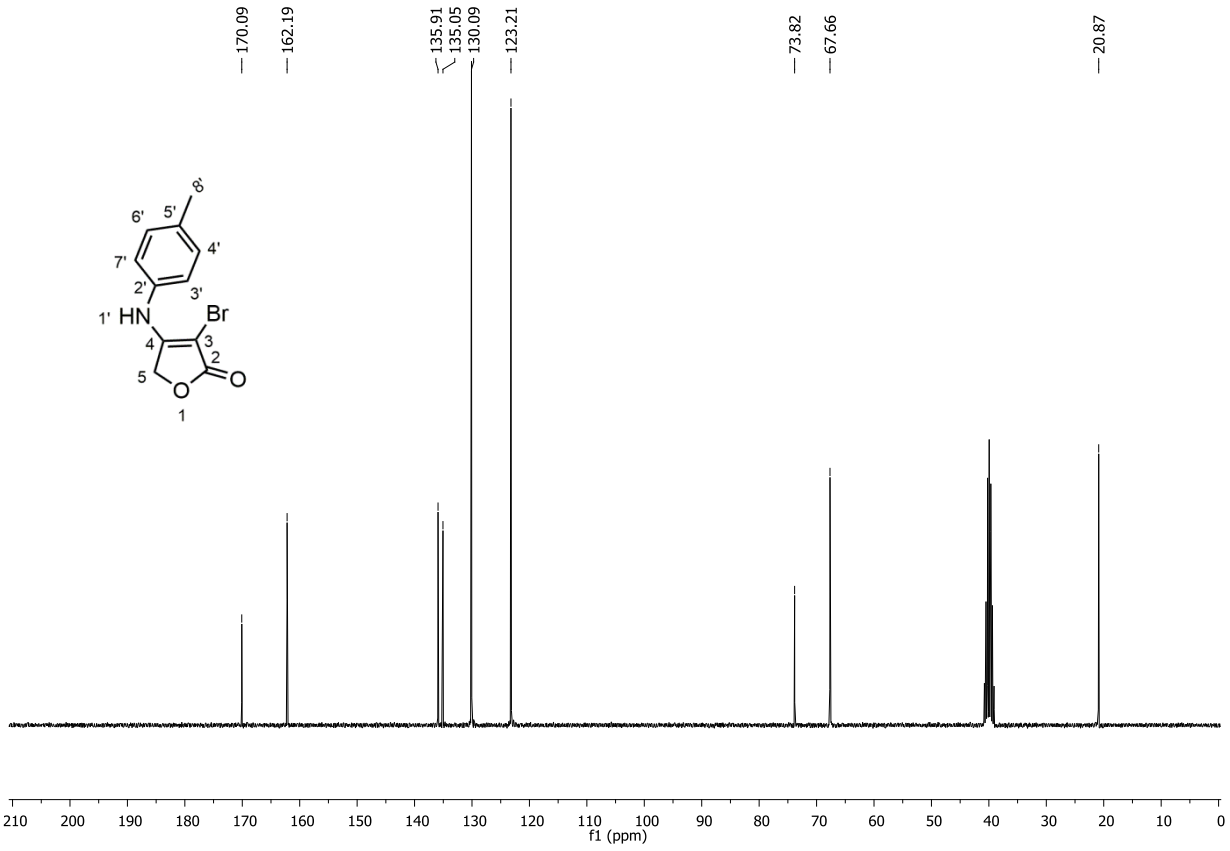


Figure S13 ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of compound **8c**

3.2. NMR spectra of aldol products

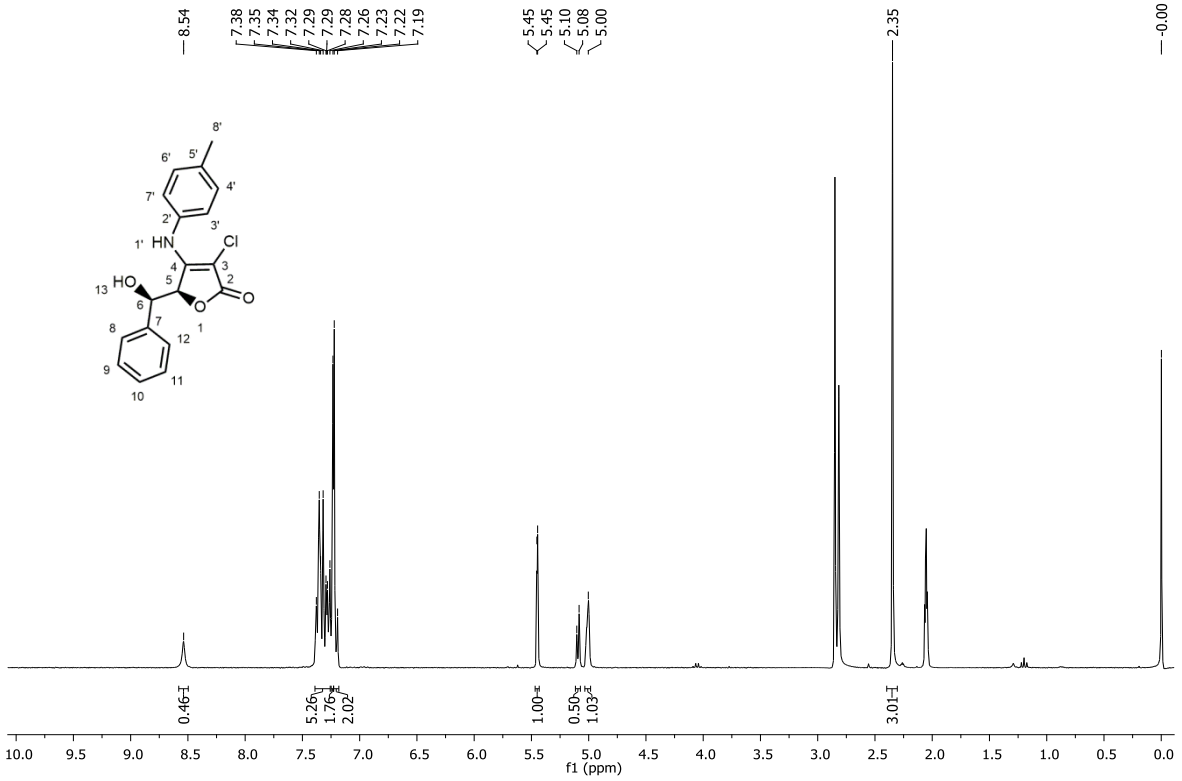


Figure S14 ^{1}H NMR spectrum (300 MHz, Acetone-d_6) of compound ***syn*-9**

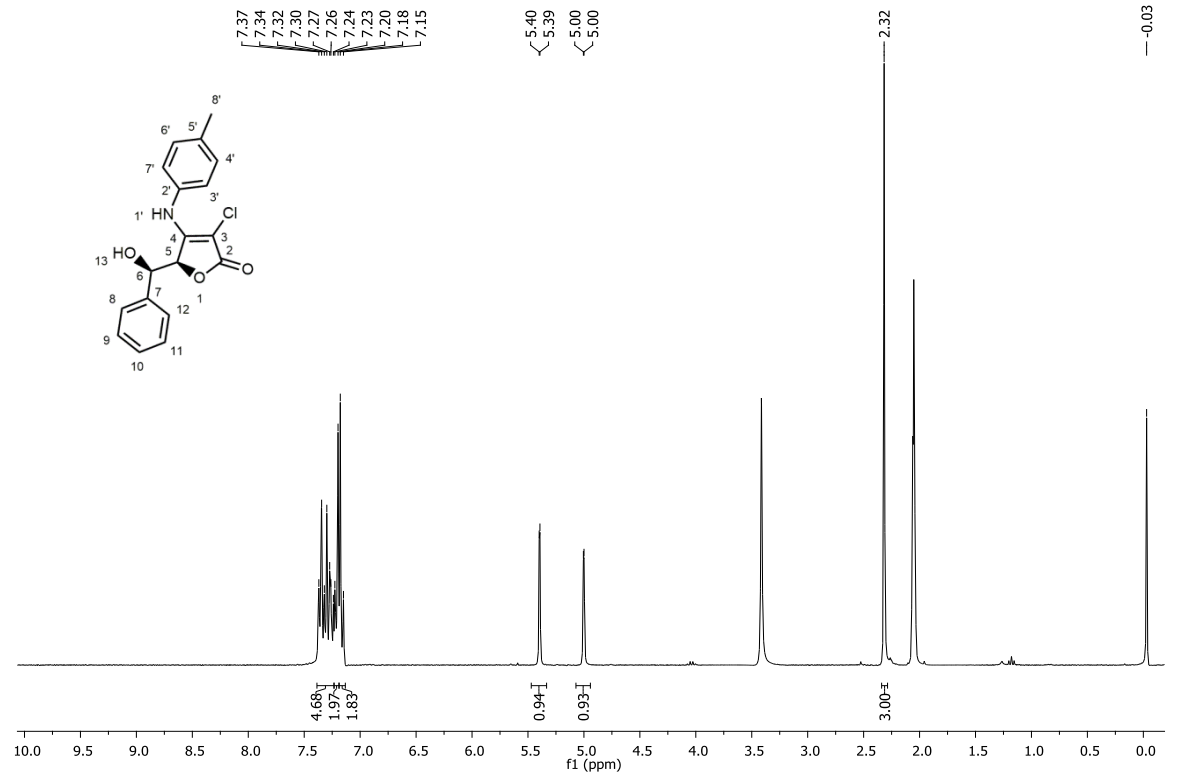


Figure S15 ^{1}H NMR spectrum (300 MHz, Acetone-d_6 + D_2O) of compound ***syn*-9**

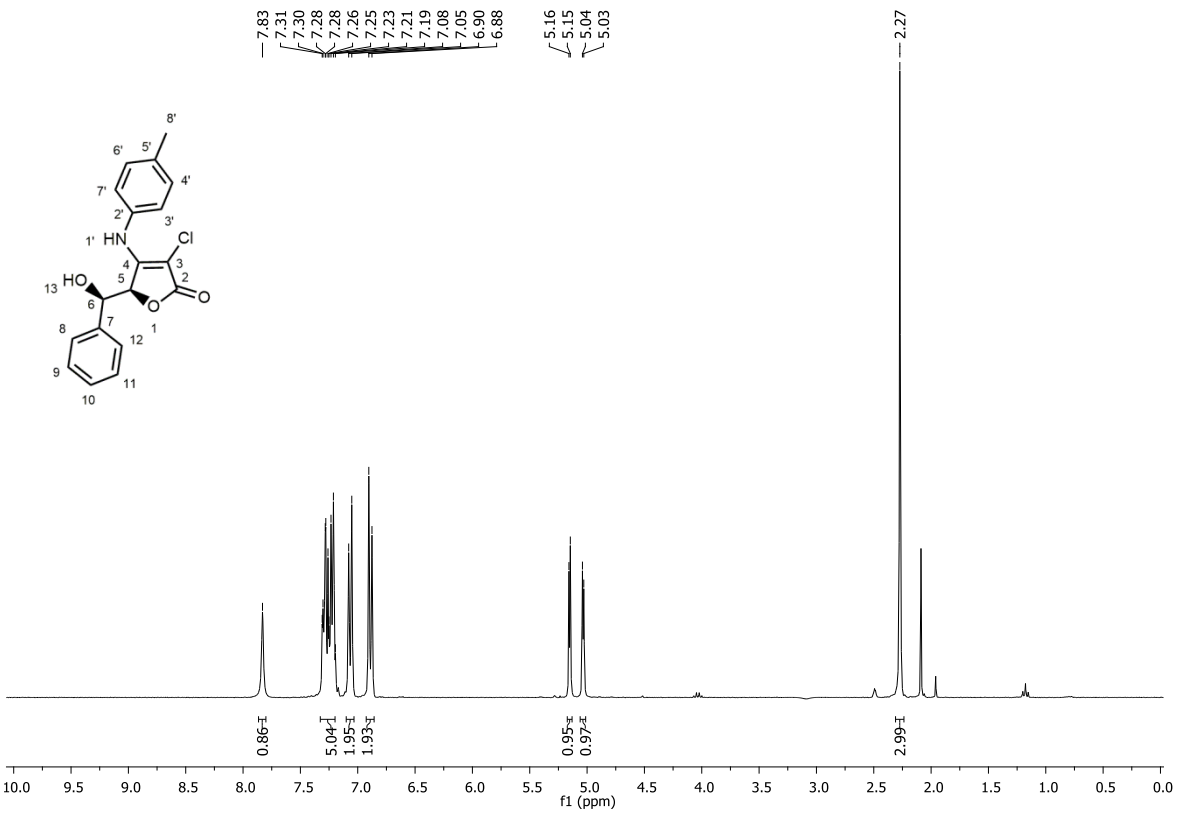


Figure S16 ^{1}H NMR spectrum (300 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***syn*-9**

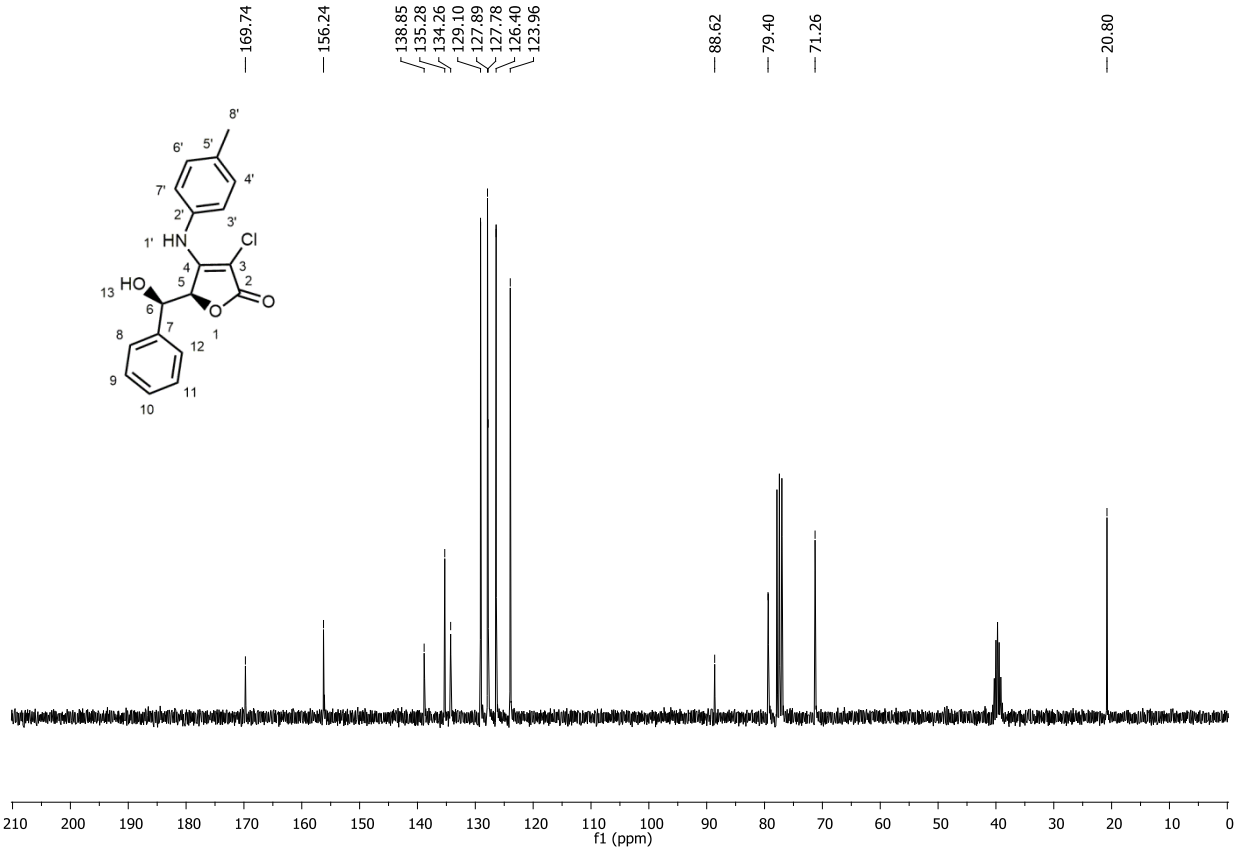


Figure S17 ^{13}C NMR spectrum (75 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***syn*-9**

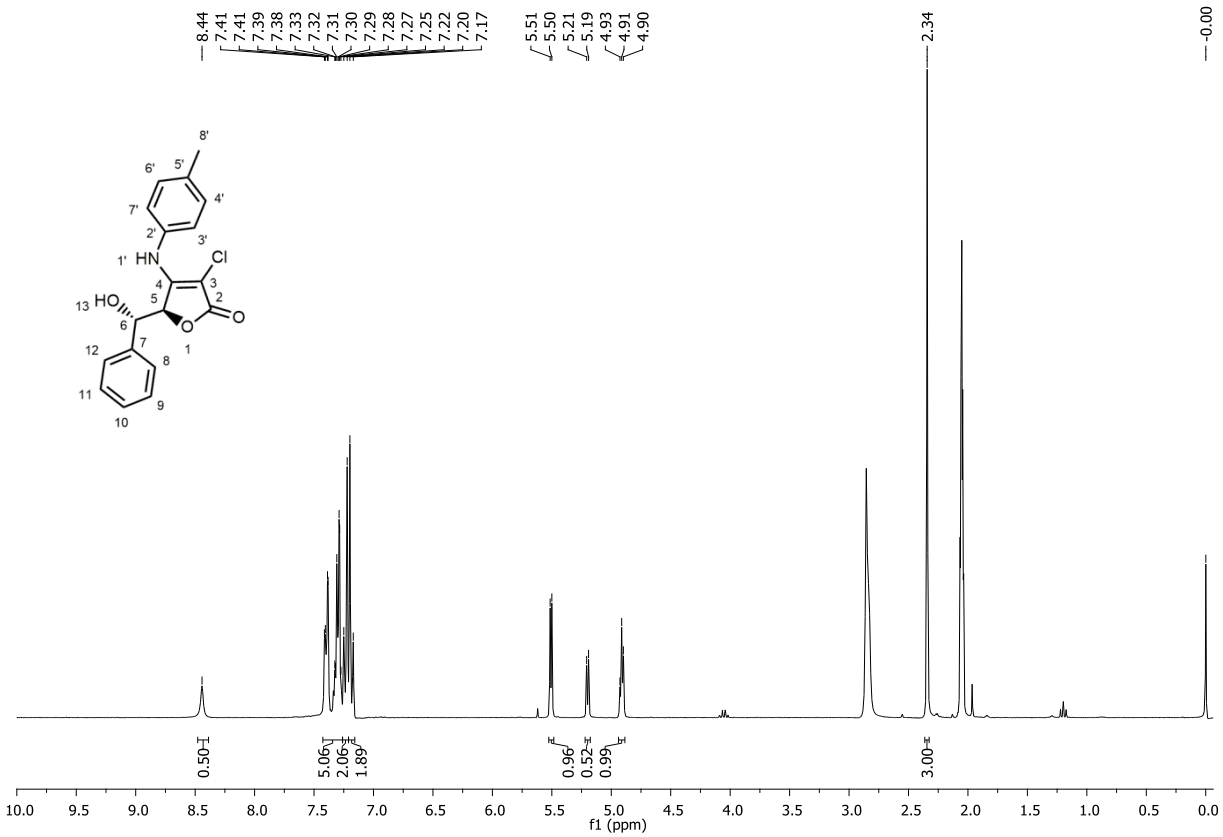


Figure S18 ^{1}H NMR spectrum (300 MHz, Acetone-d_6) of compound ***anti*-9**

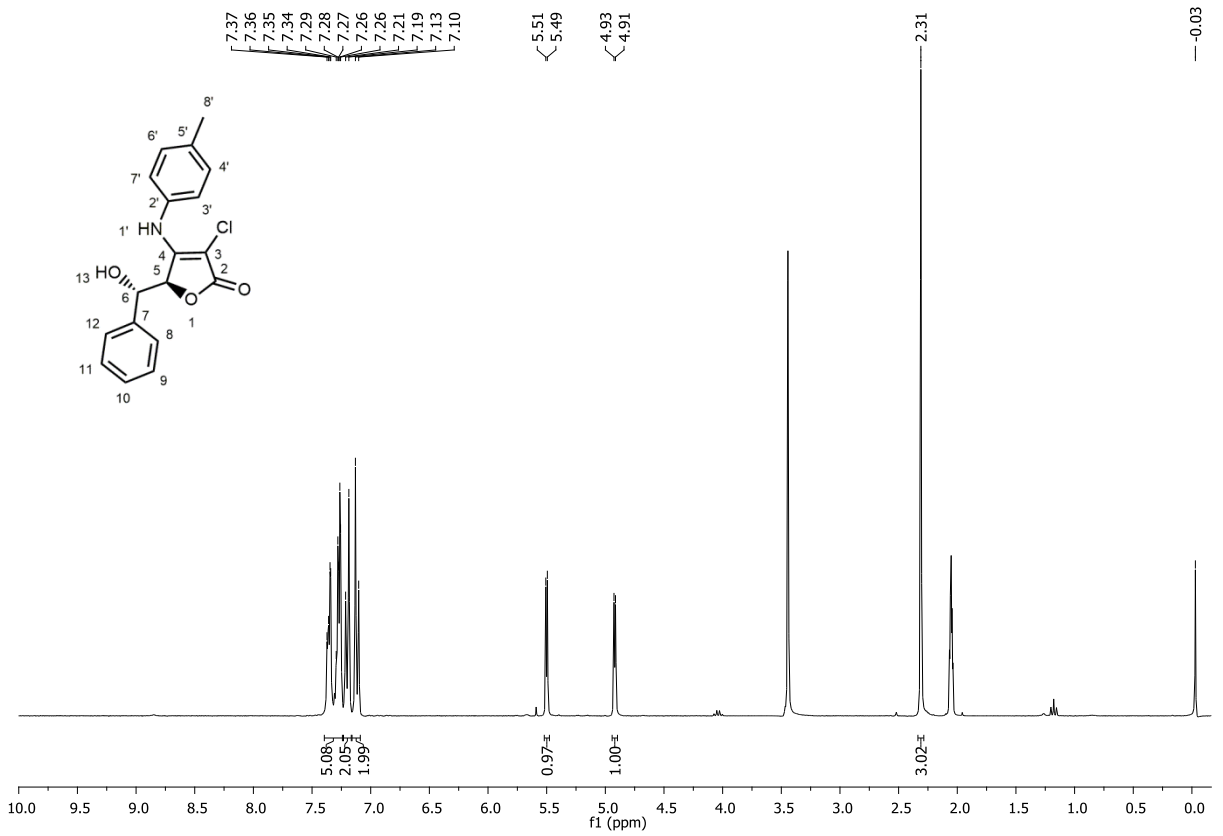


Figure S19 ^{1}H NMR spectrum (300 MHz, Acetone-d_6 + D_2O) of compound ***anti*-9**

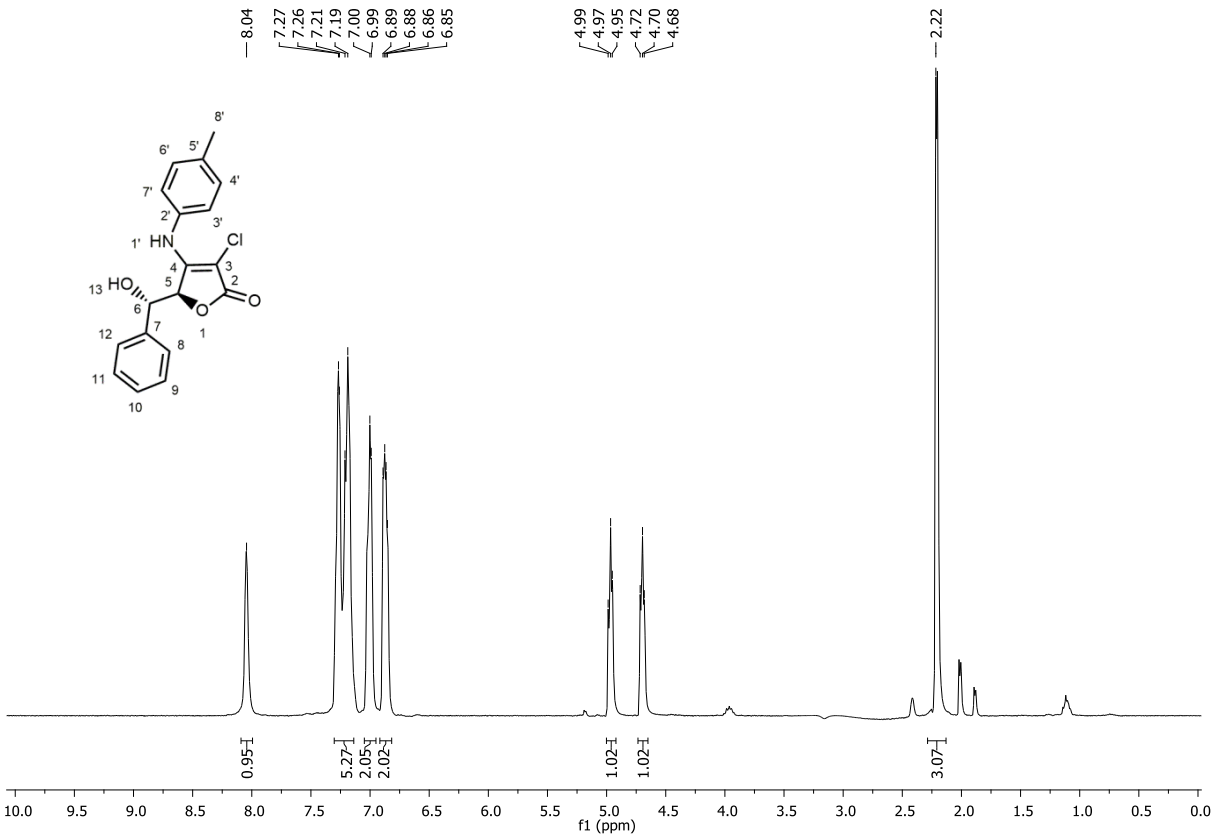


Figure S20 ^{1}H NMR spectrum (300 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***anti*-9**

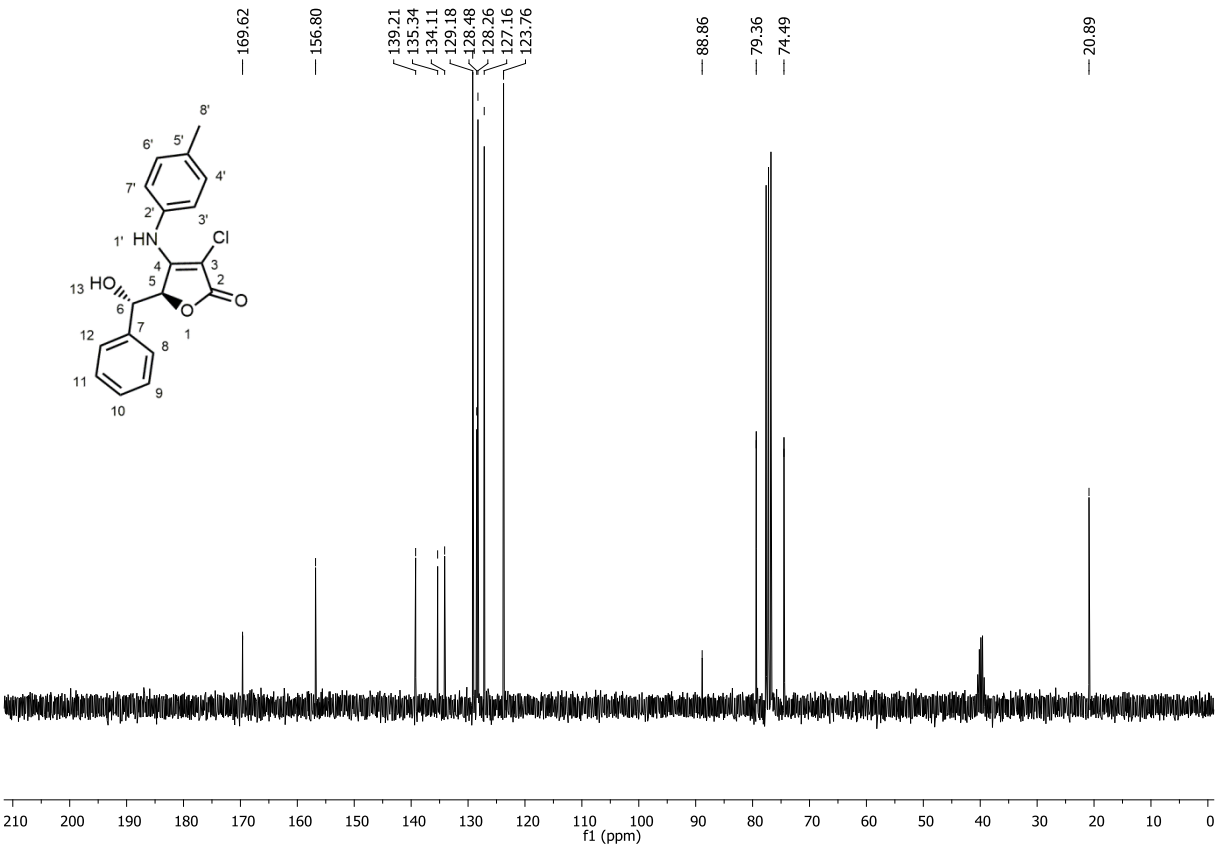


Figure S21 ^{13}C NMR spectrum (75 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***anti*-9**

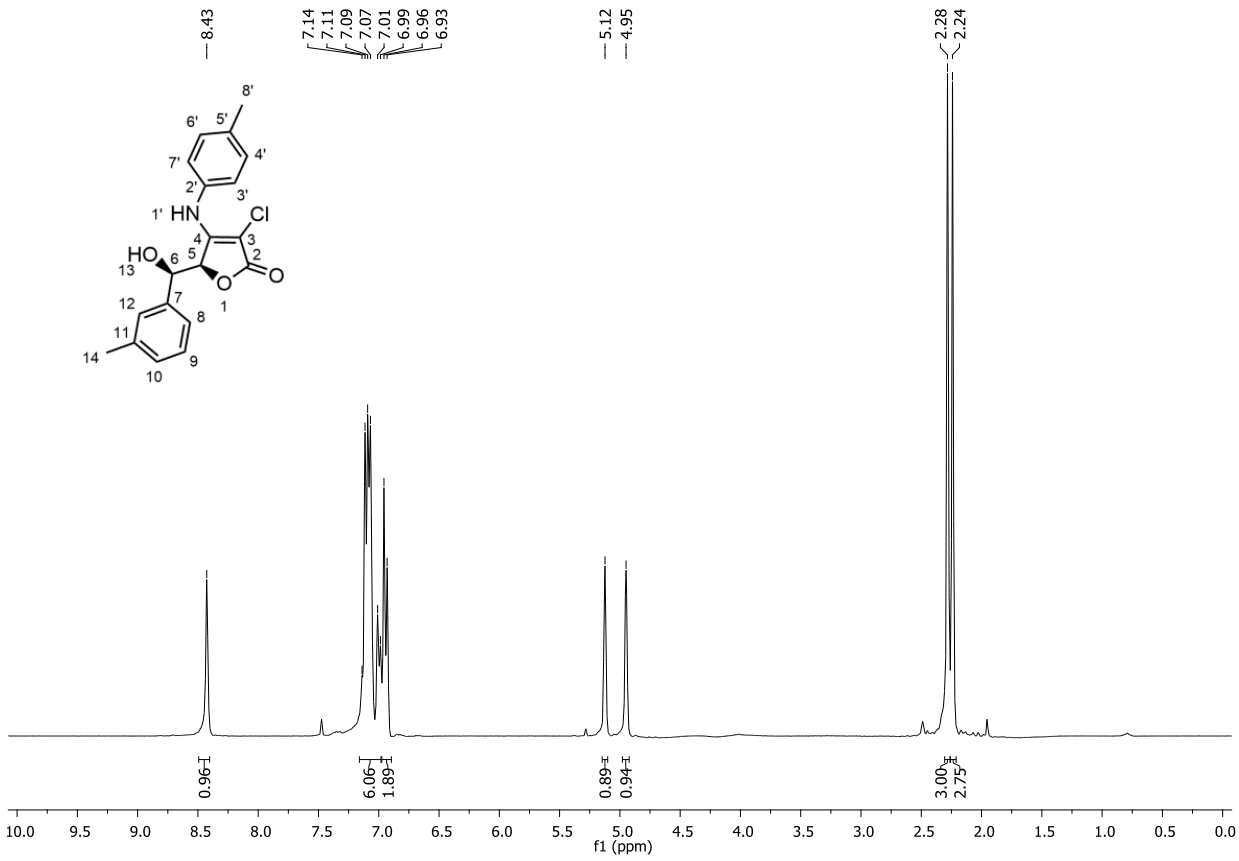


Figure S22 ^{1}H NMR spectrum (300 MHz, $CDCl_3$:DMSO-d_6; 3:1) of compound ***syn*-10**

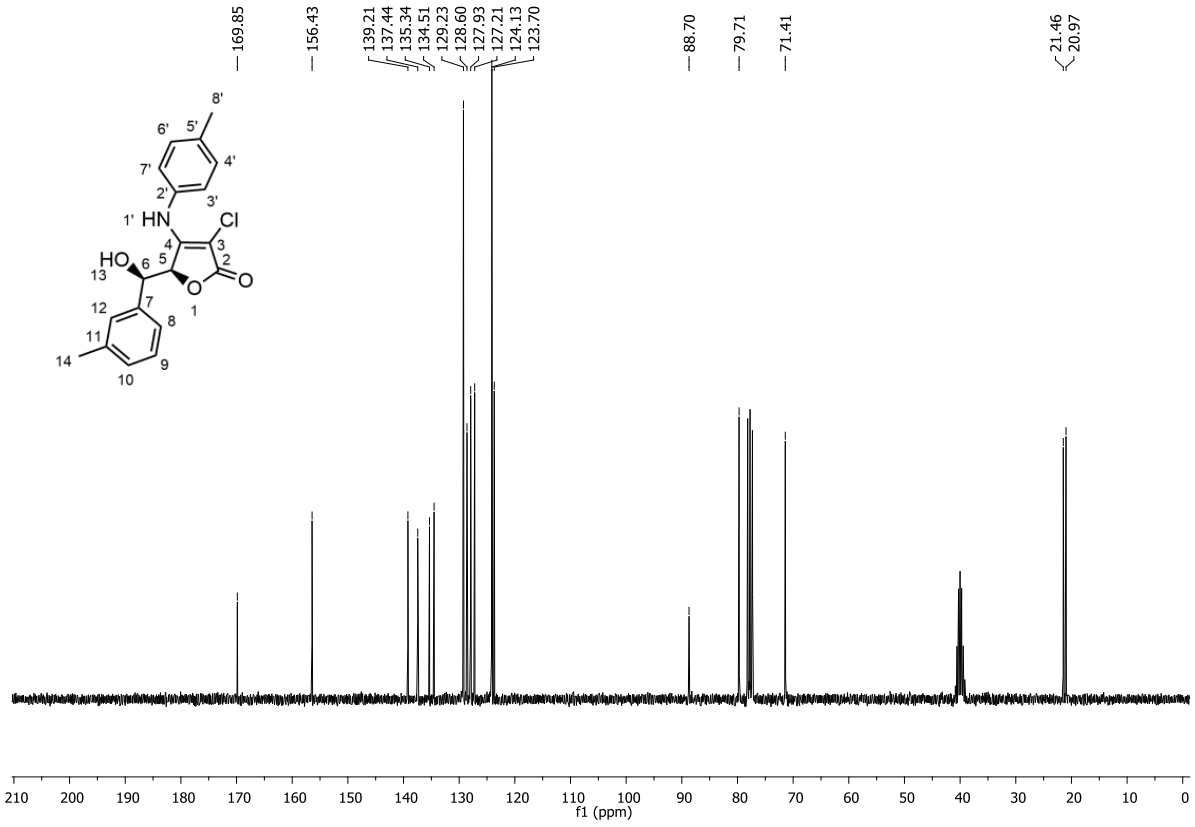


Figure S23 ^{13}C NMR spectrum (75 MHz, $CDCl_3$:DMSO-d_6; 3:1) of compound ***syn*-10**

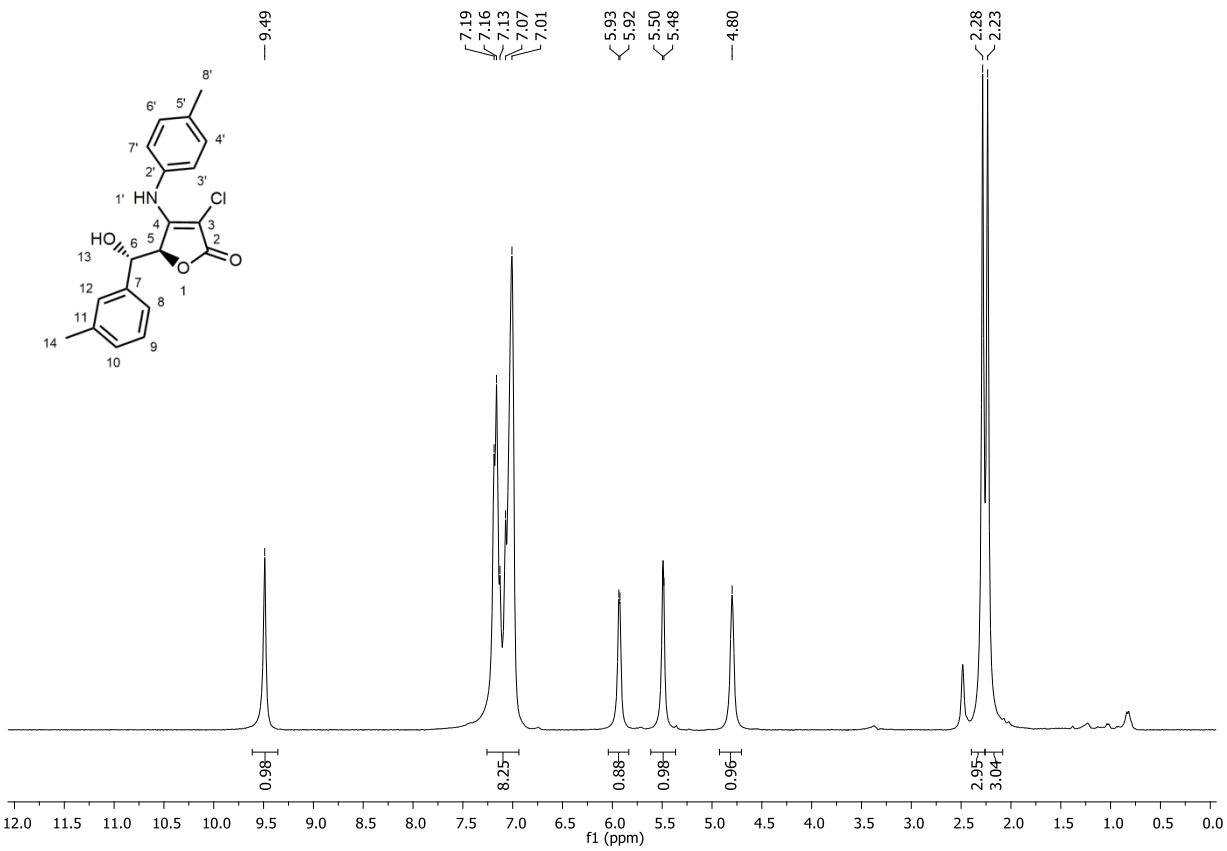


Figure S24 ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound ***anti*-10**

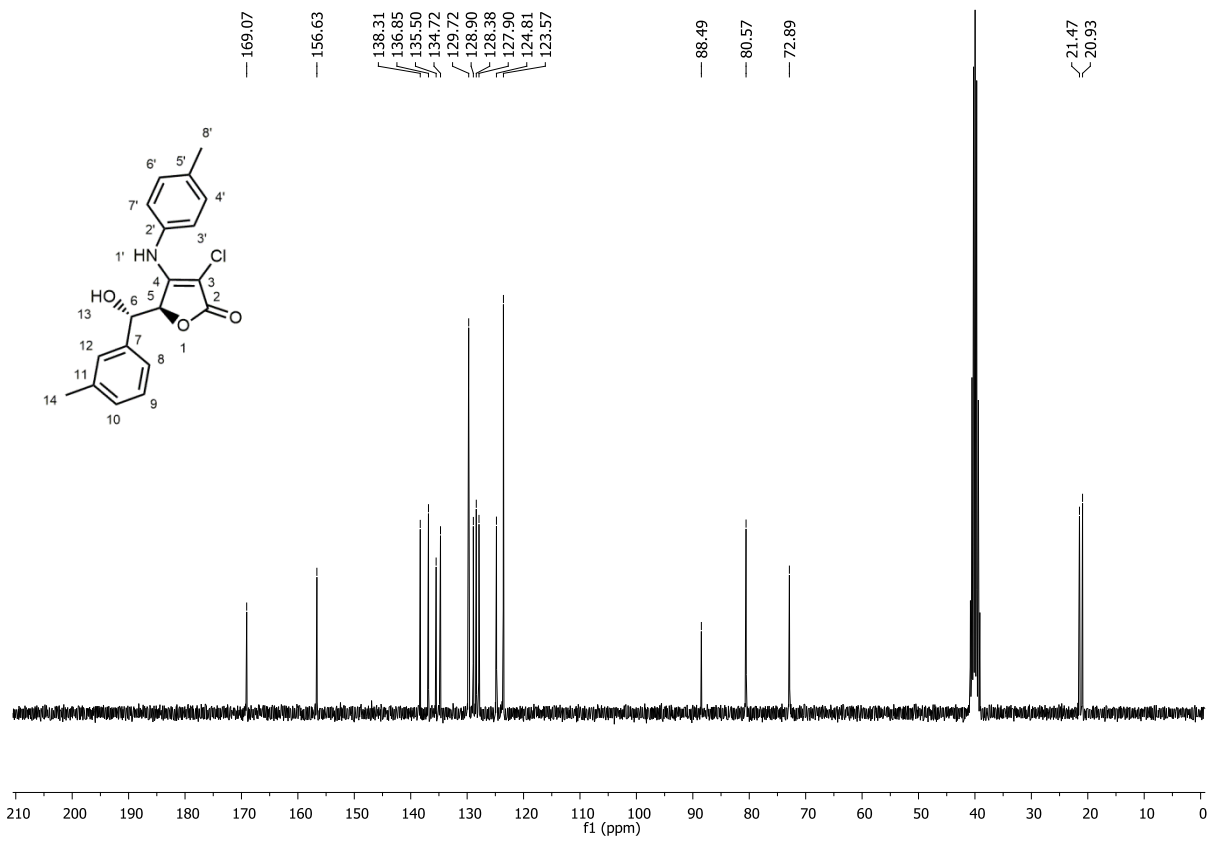


Figure S25 ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of compound ***anti*-10**

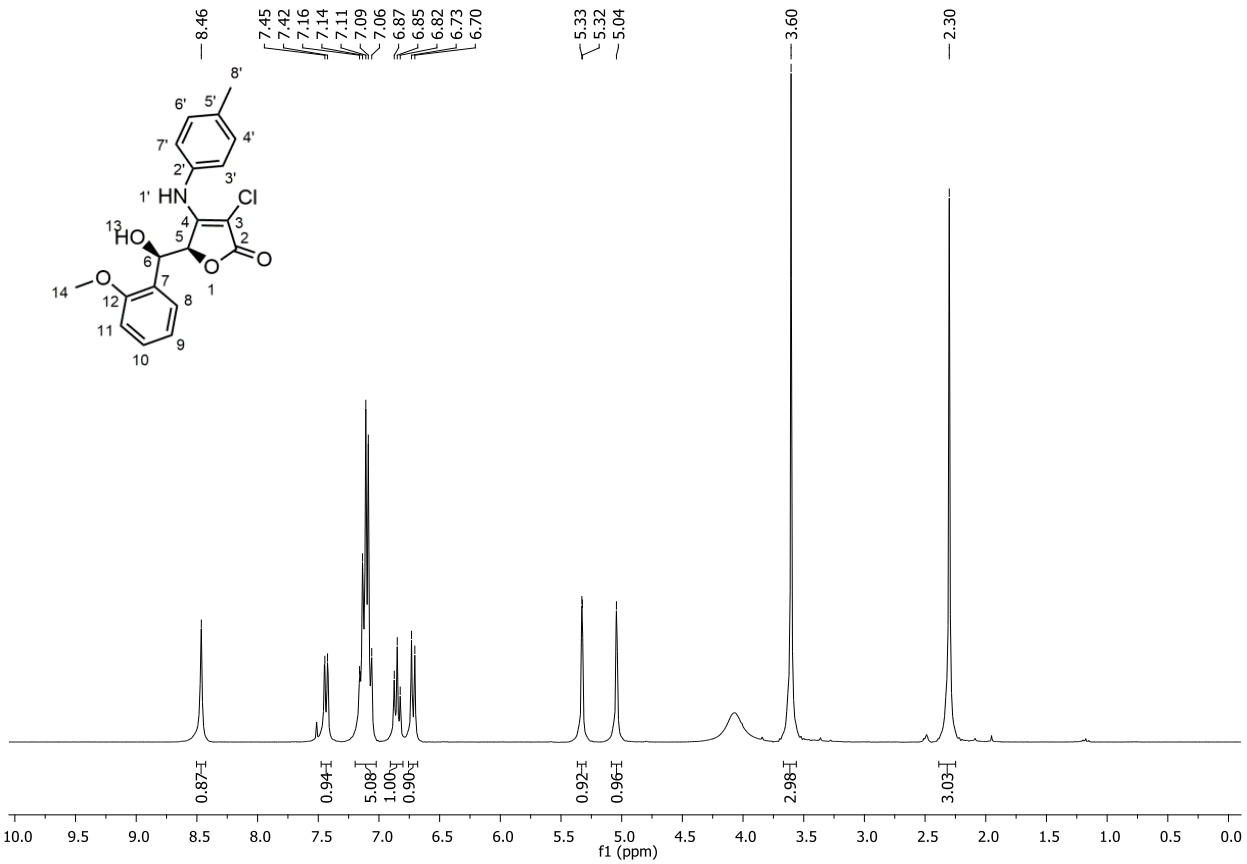


Figure S26 ^{1}H NMR spectrum (300 MHz, $CDCl_3$:DMSO-d_6; 3:1) of compound ***syn*-11**

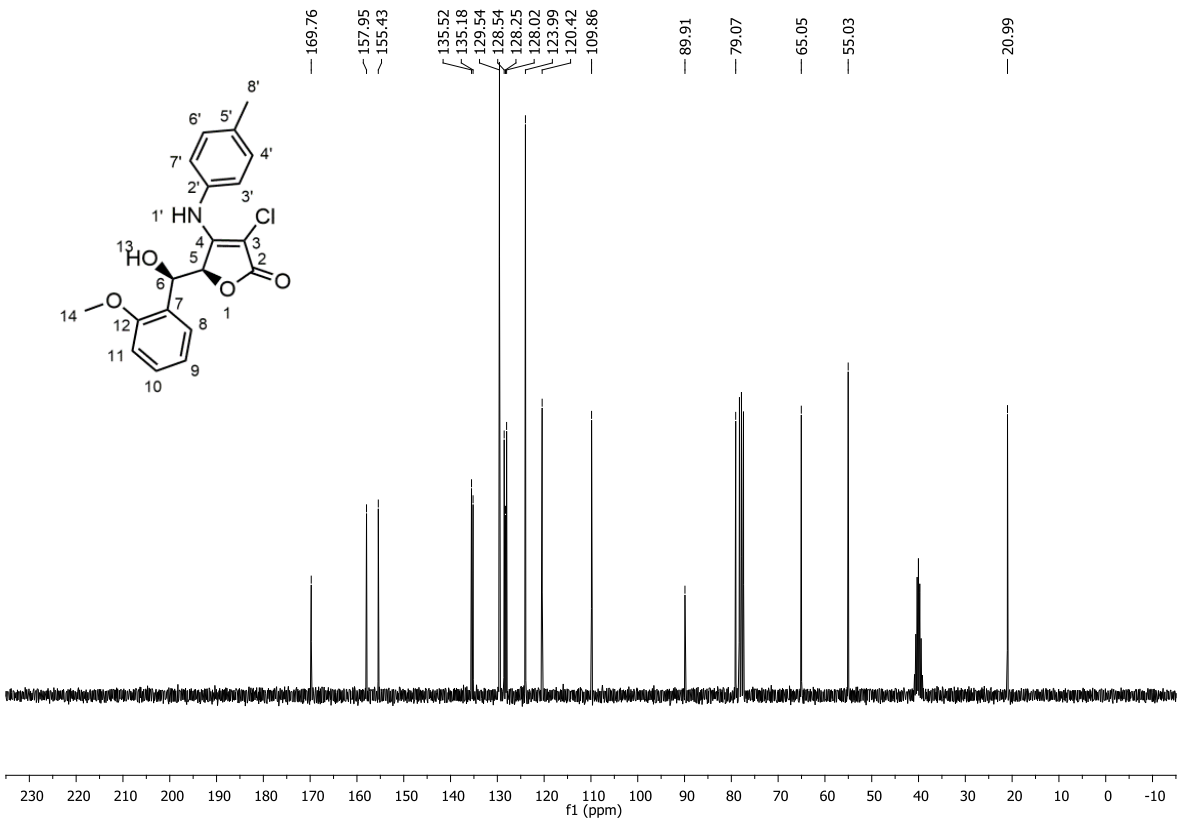


Figure S27 ^{13}C NMR spectrum (75 MHz, $CDCl_3$:DMSO-d_6; 3:1) of compound ***syn*-11**

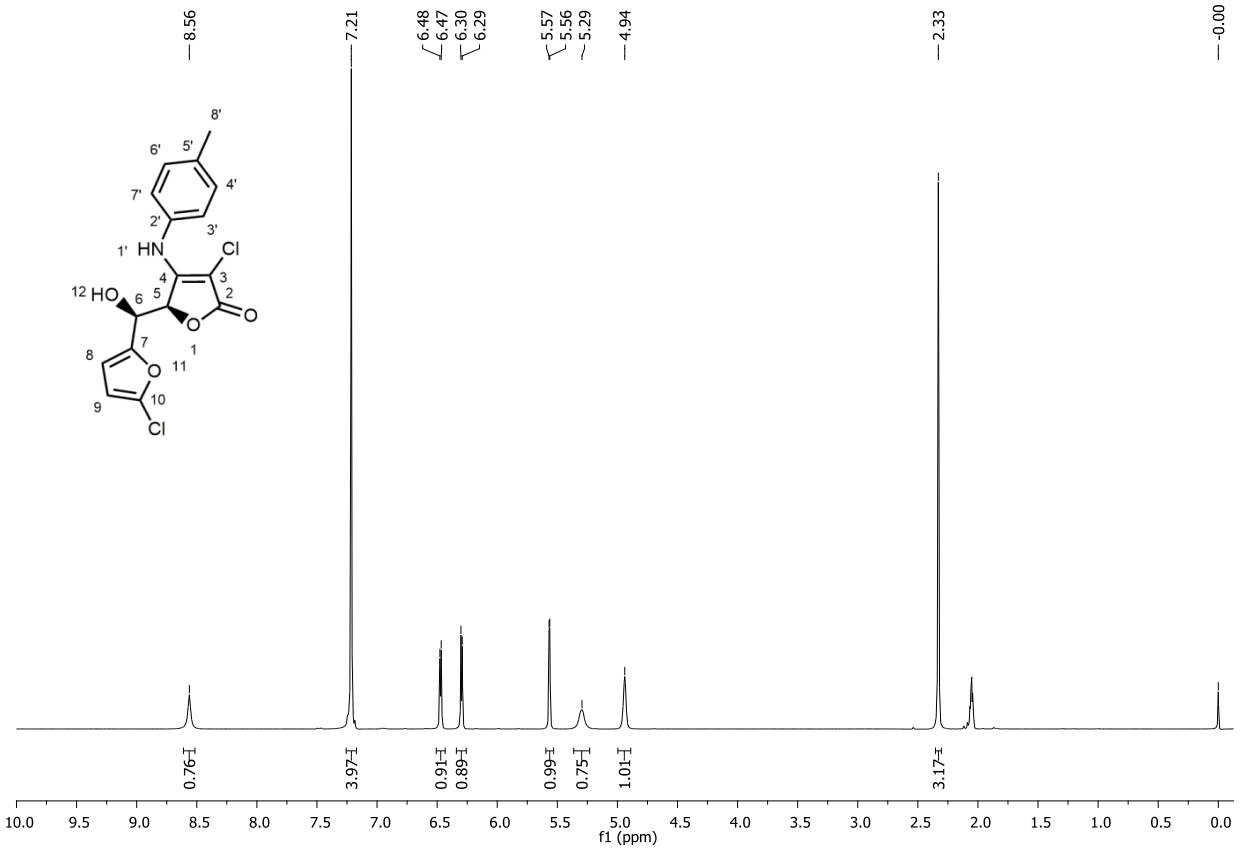


Figure S28 ^{1}H NMR spectrum (300 MHz, Acetone-d_6) of compound ***syn*-12**

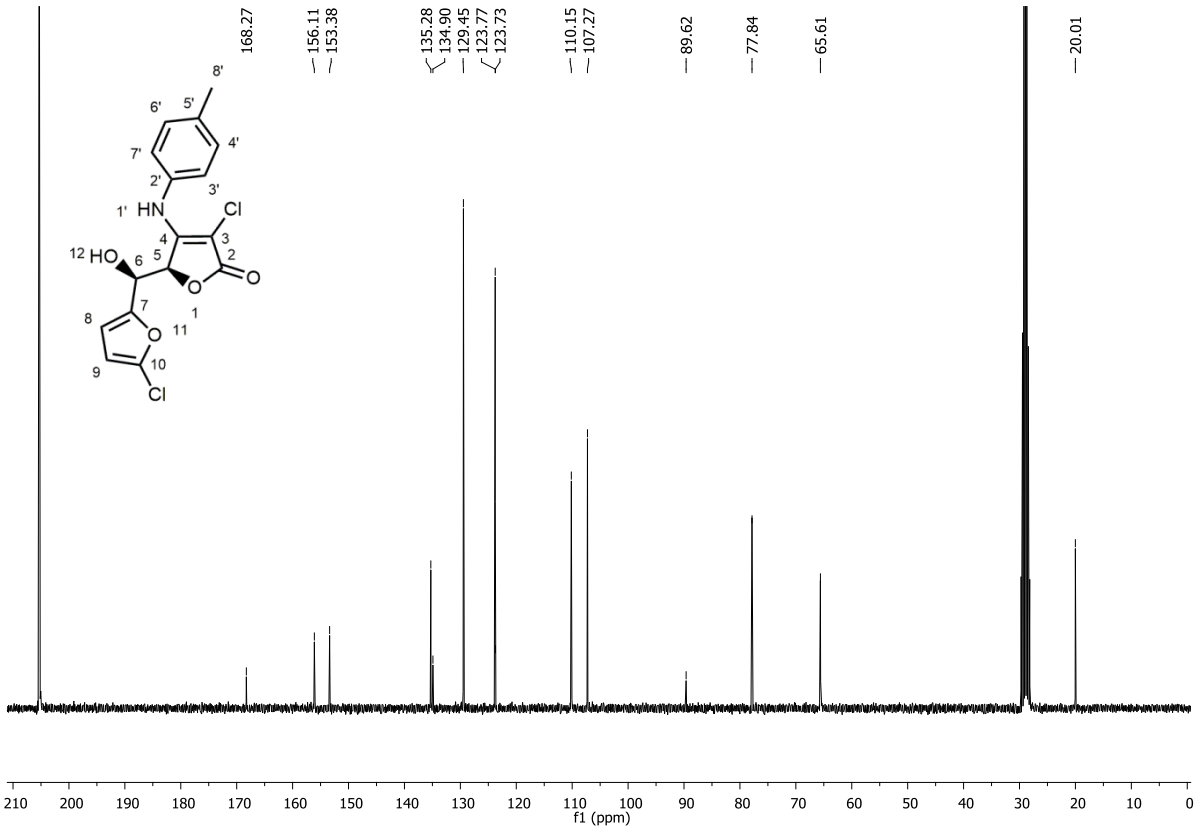


Figure S29 ^{13}C NMR spectrum (75 MHz, Acetone-d_6) of compound ***syn*-12**

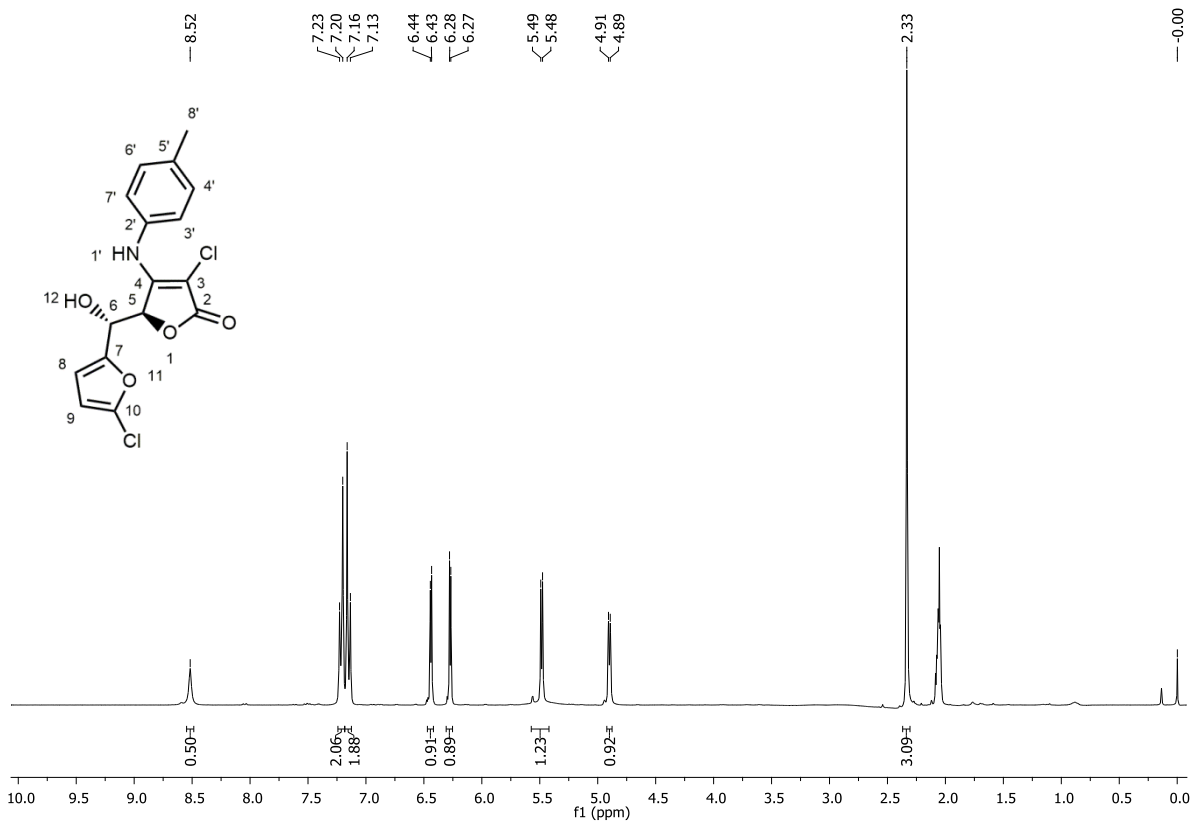


Figure S30 ^{1}H NMR spectrum (300 MHz, Acetone-d_6) of compound ***anti*-12**

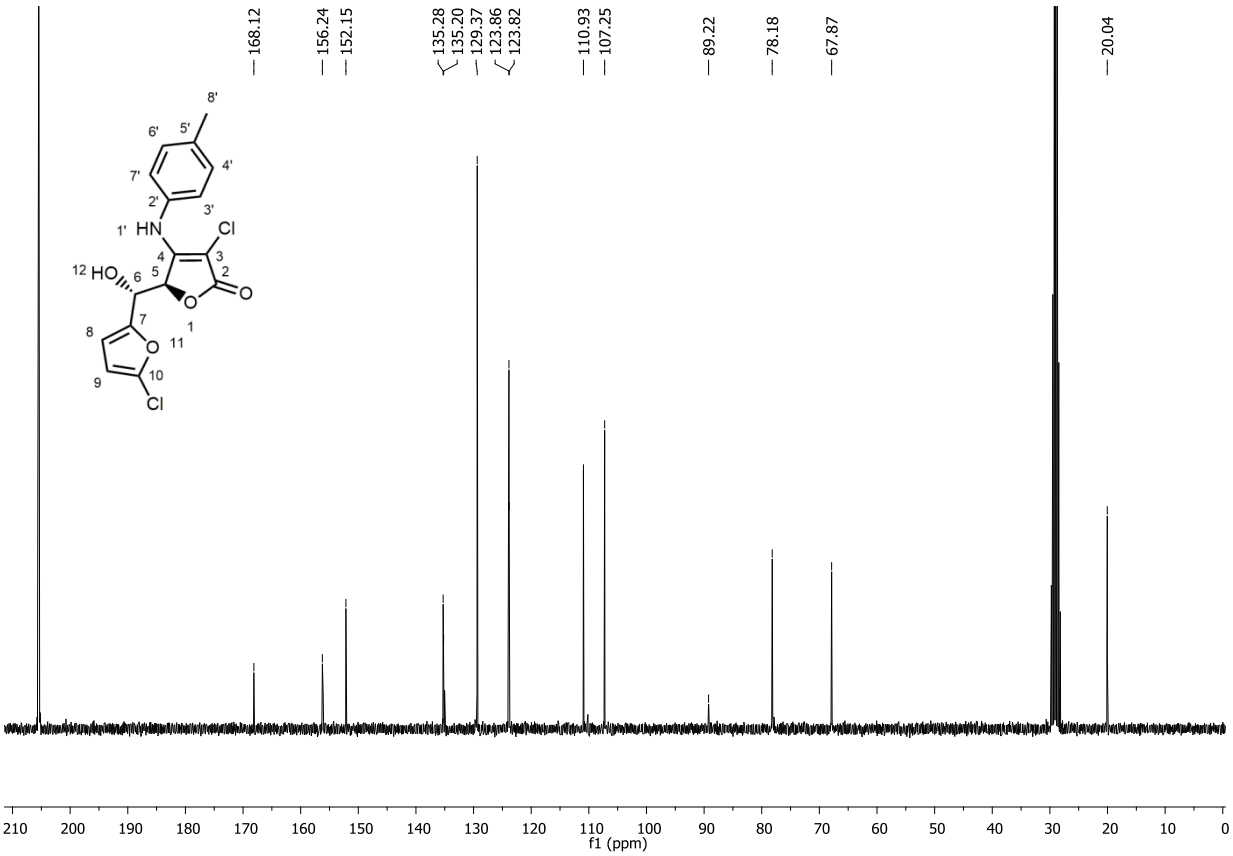


Figure S31 ^{13}C NMR spectrum (75 MHz, Acetone-d_6) of compound ***anti*-12**

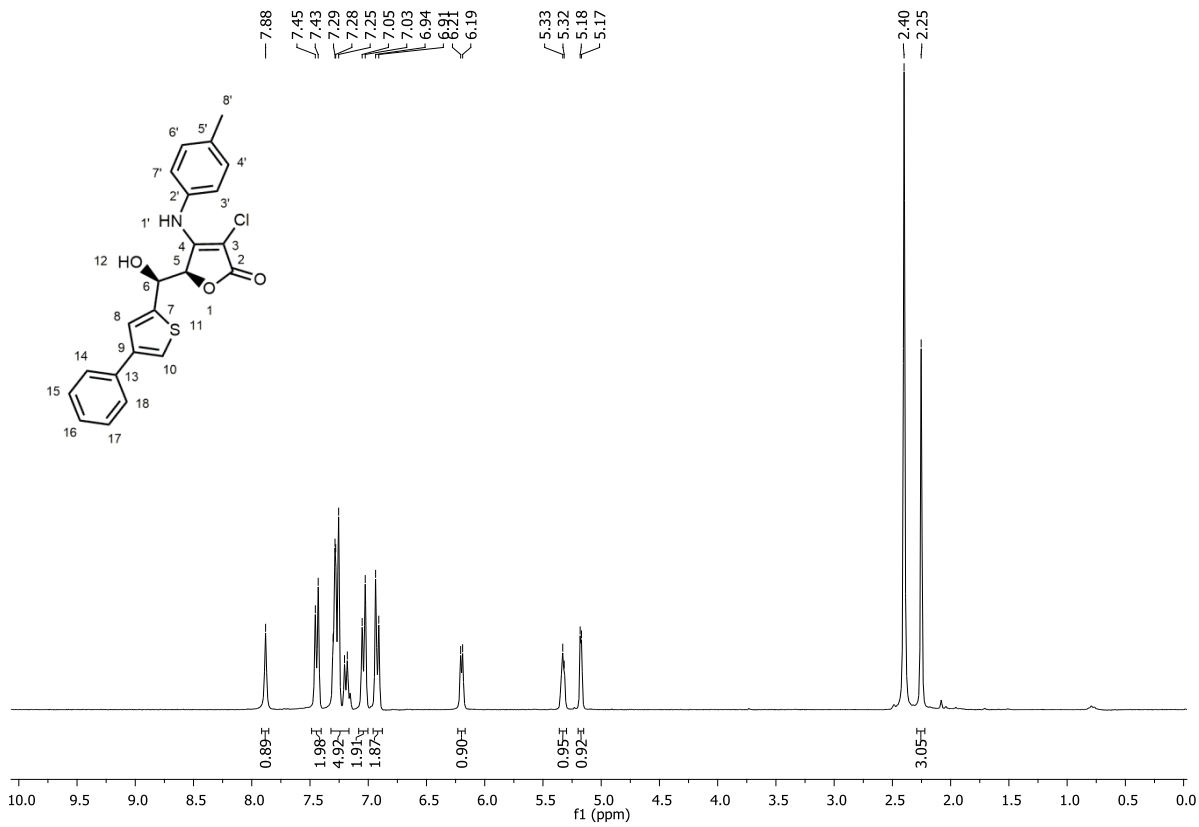


Figure S32 ^{1}H NMR (300 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***syn*-13**

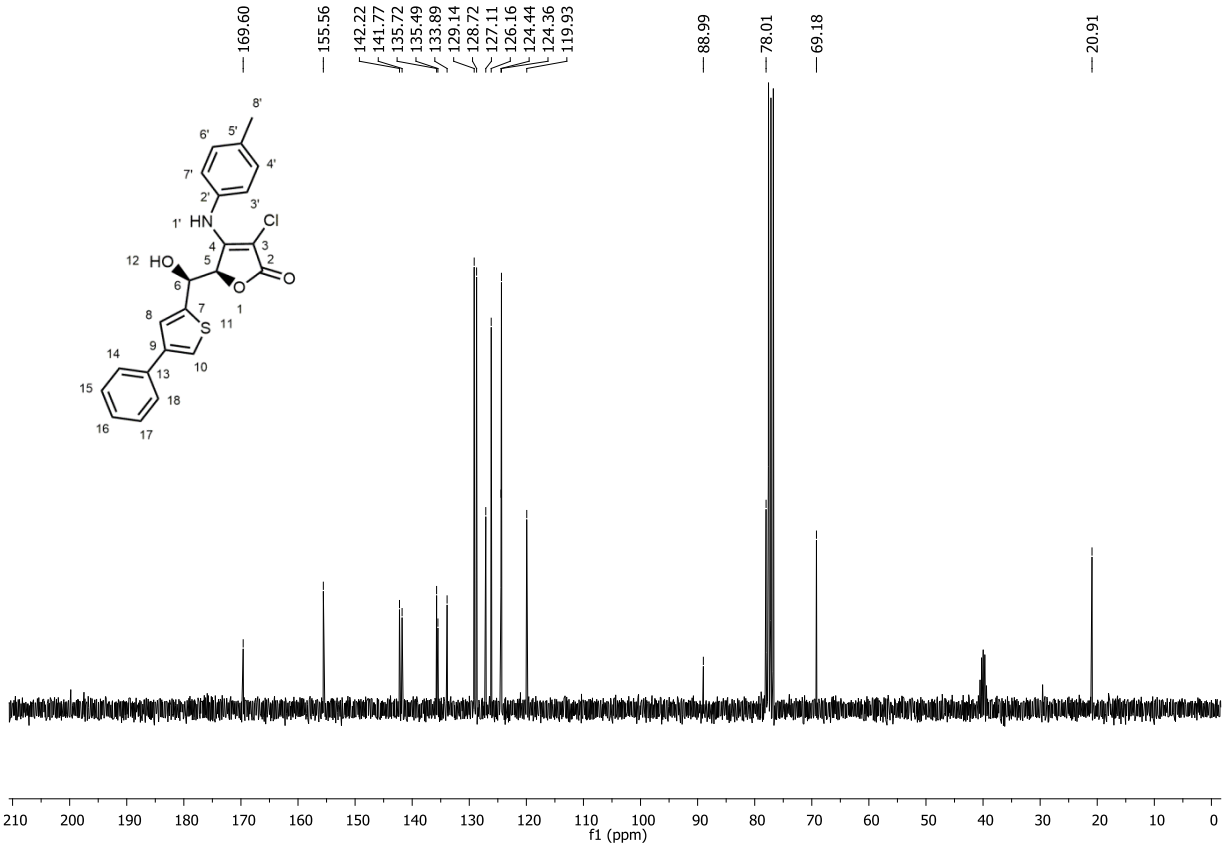


Figure S33 ^{13}C NMR (75 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***syn*-13**

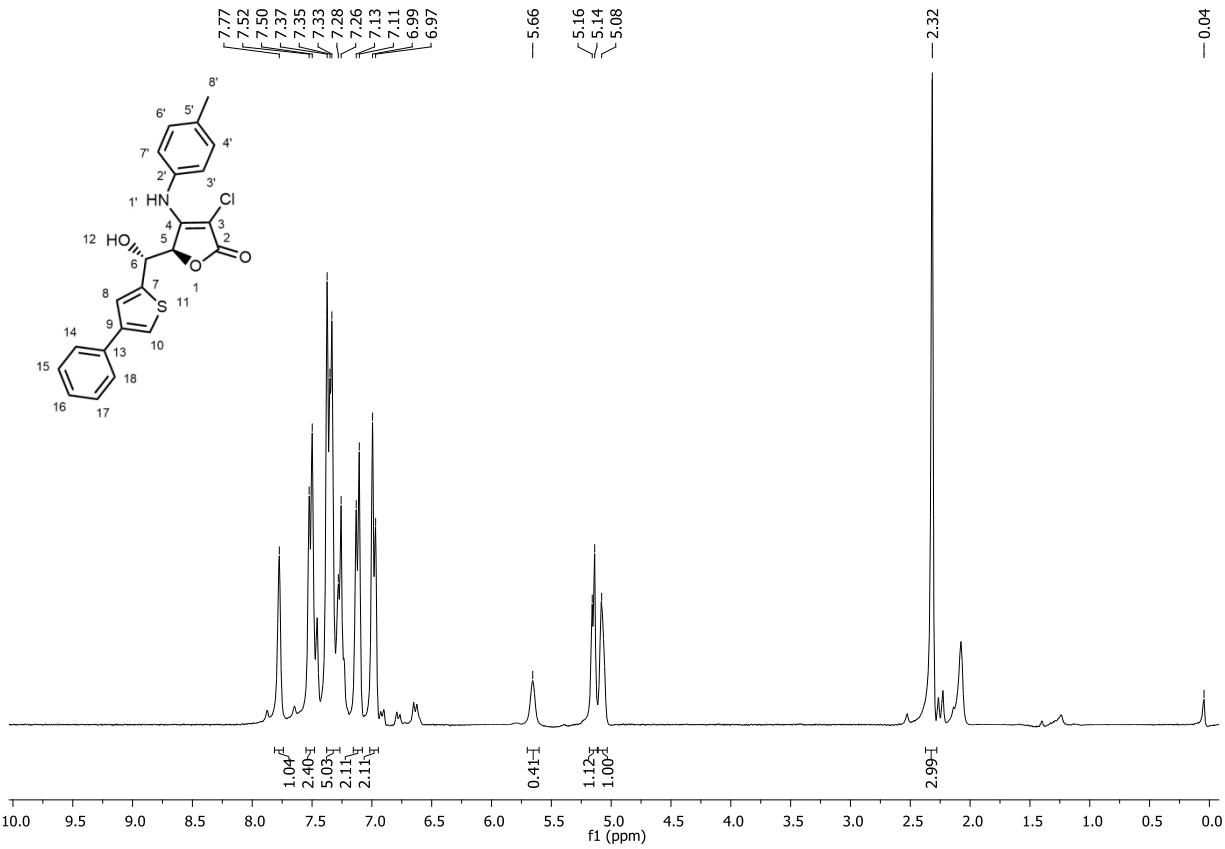


Figure S34 ^{1}H NMR (300 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***anti*-13**

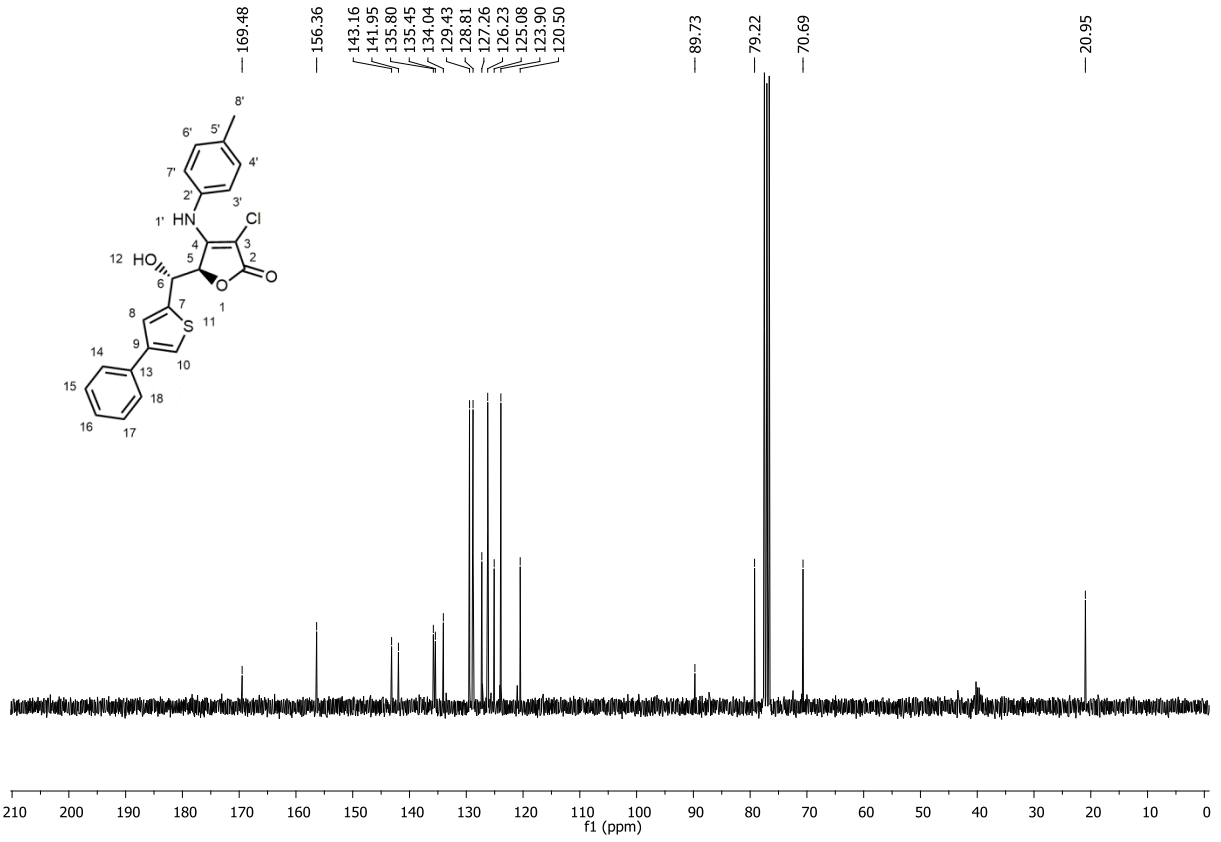


Figure S35 ^{13}C NMR (75 MHz, $CDCl_3$:DMSO-d_6; 9:1) of compound ***anti*-13**

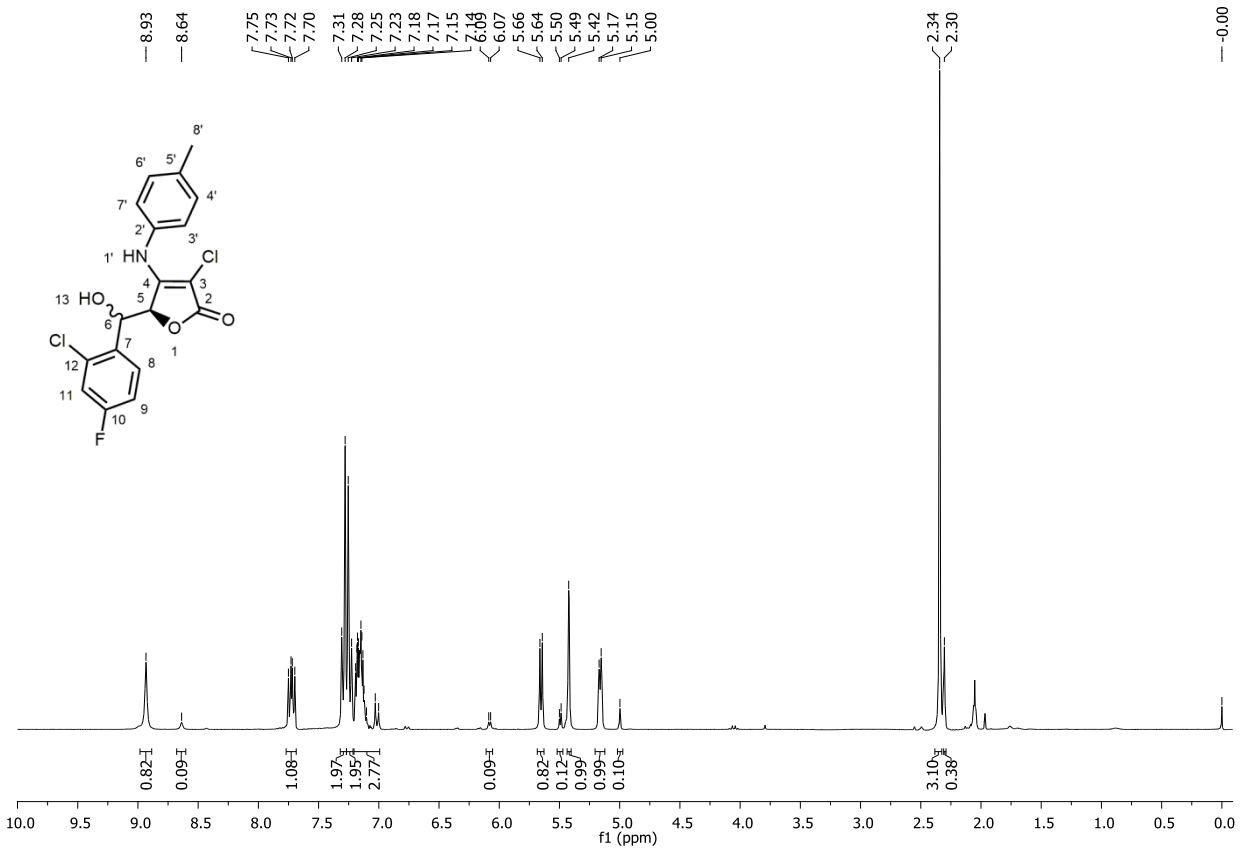


Figure S36 ^{1}H NMR (300 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound ***syn/anti*-14**

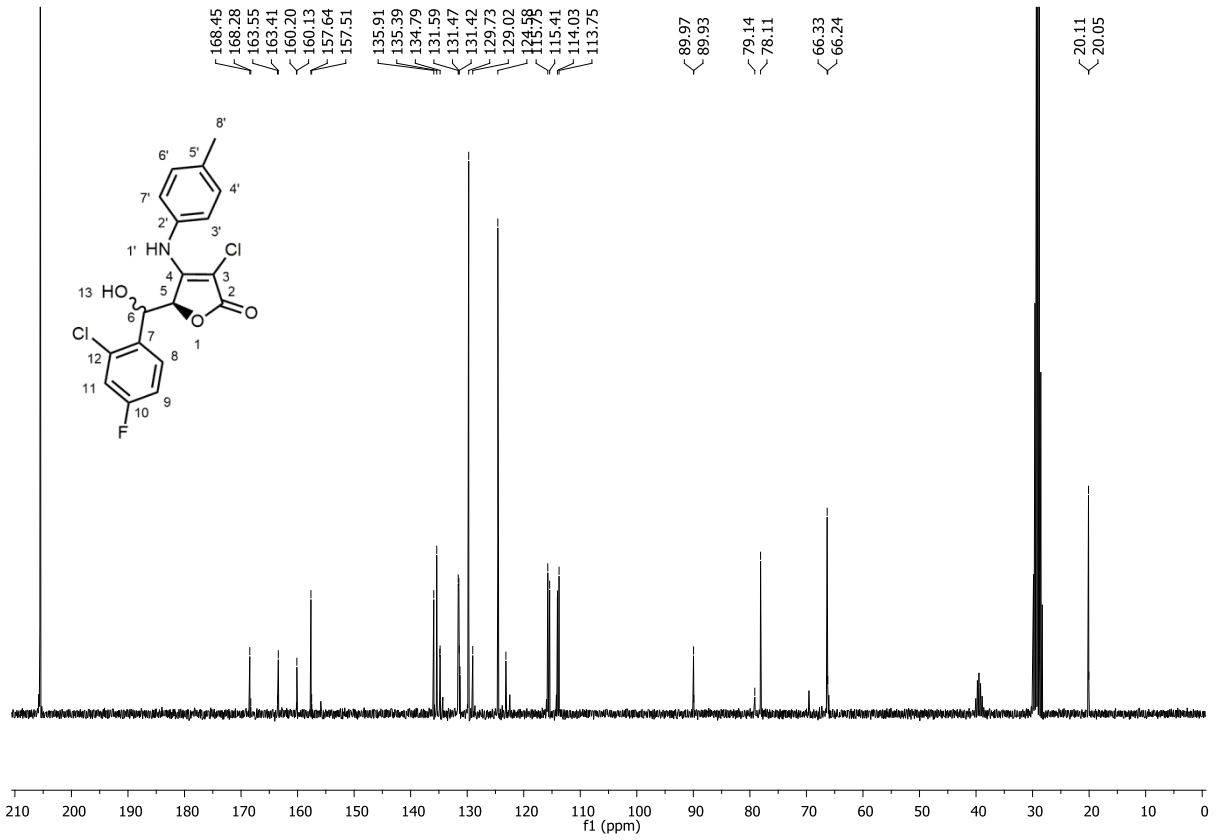


Figure S37 ^{13}C NMR (75 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound ***syn/anti*-14**

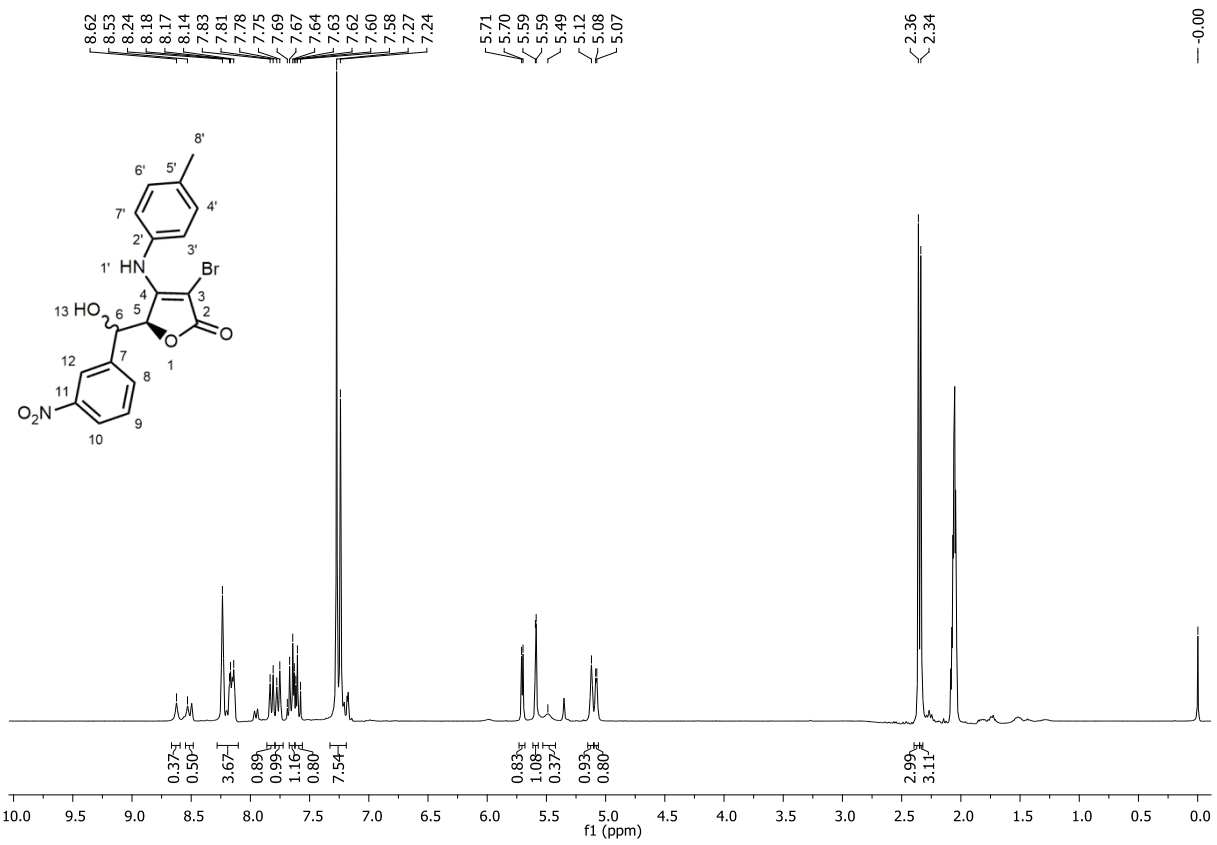


Figure S38 ^{1}H NMR (300 MHz, Acetone-d_6) of compound ***syn/anti*-15**

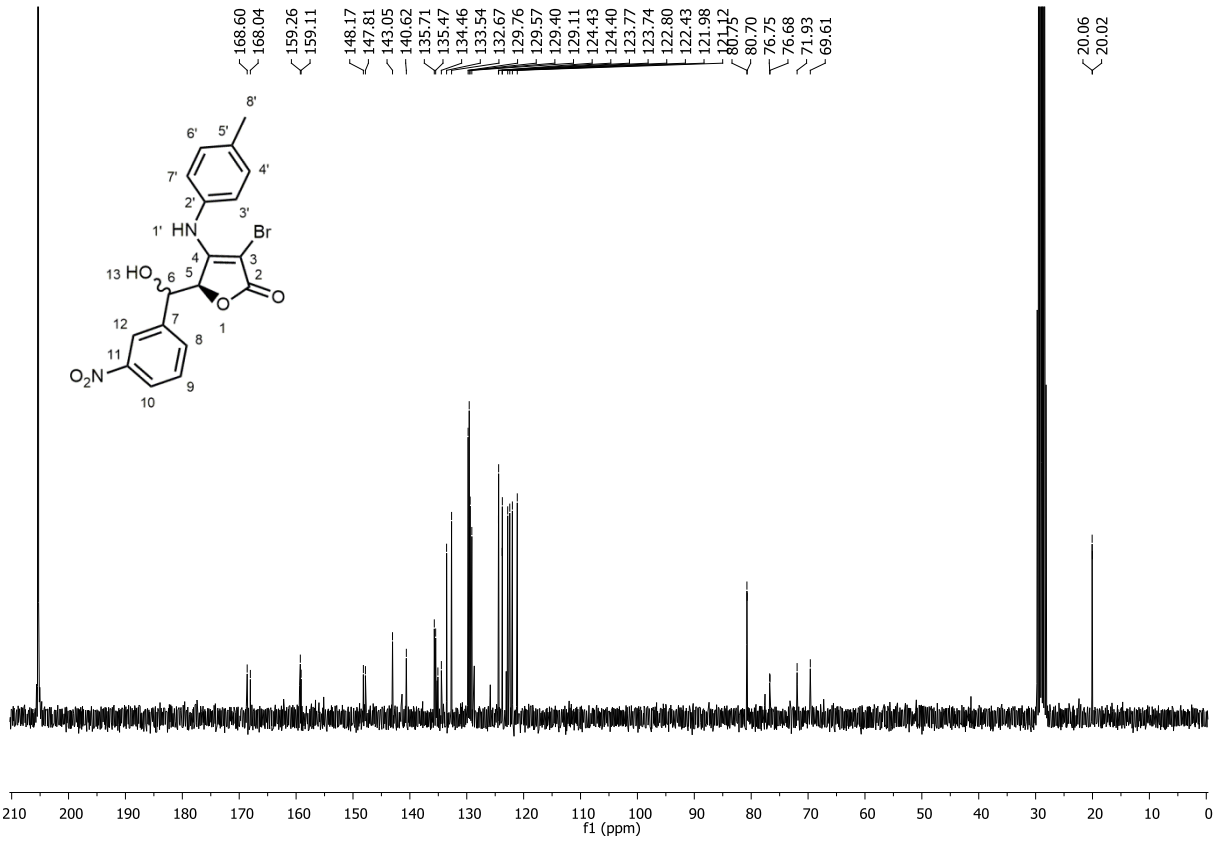


Figure S39 ^{13}C NMR (75 MHz, Acetone-d_6) of compound ***syn/anti*-15**

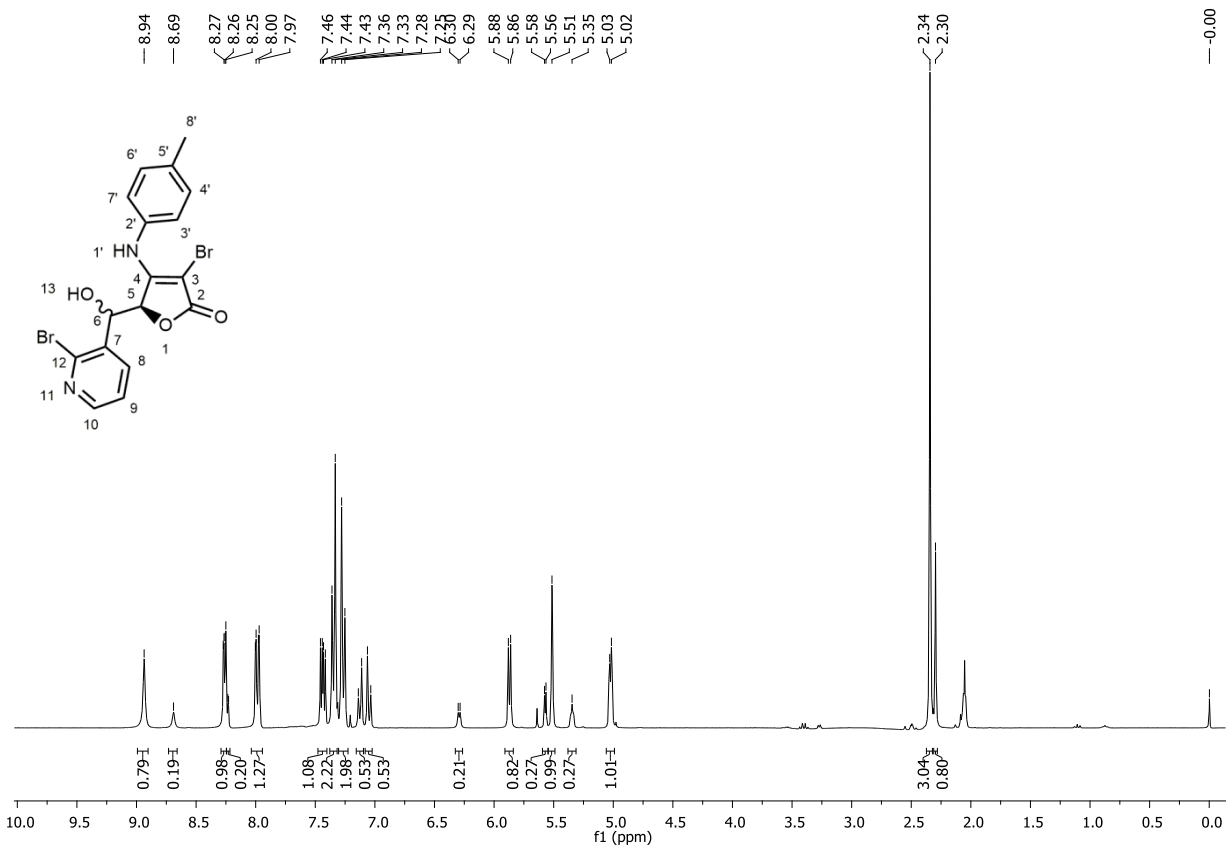


Figure S40 ^{1}H NMR (300 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound ***syn/anti*-16**

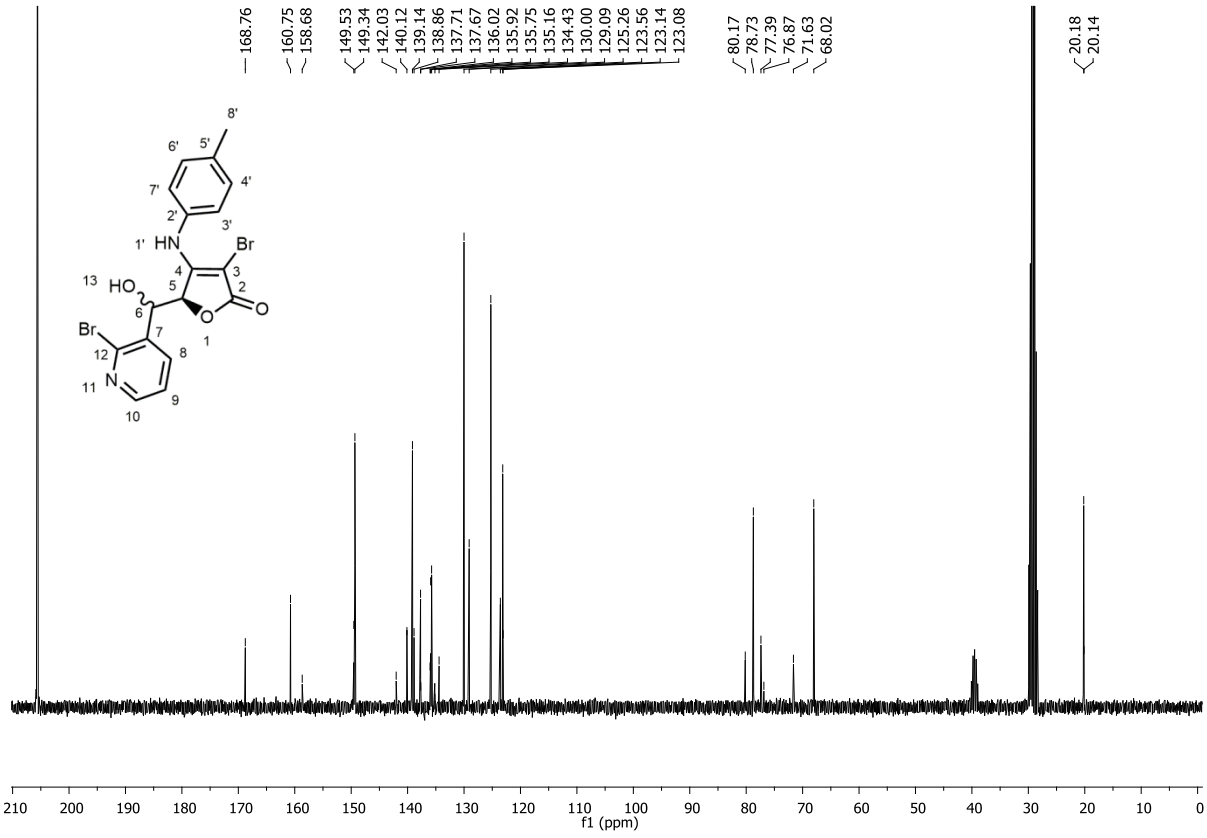


Figure S41 ^{13}C NMR (75 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound ***syn/anti*-16**

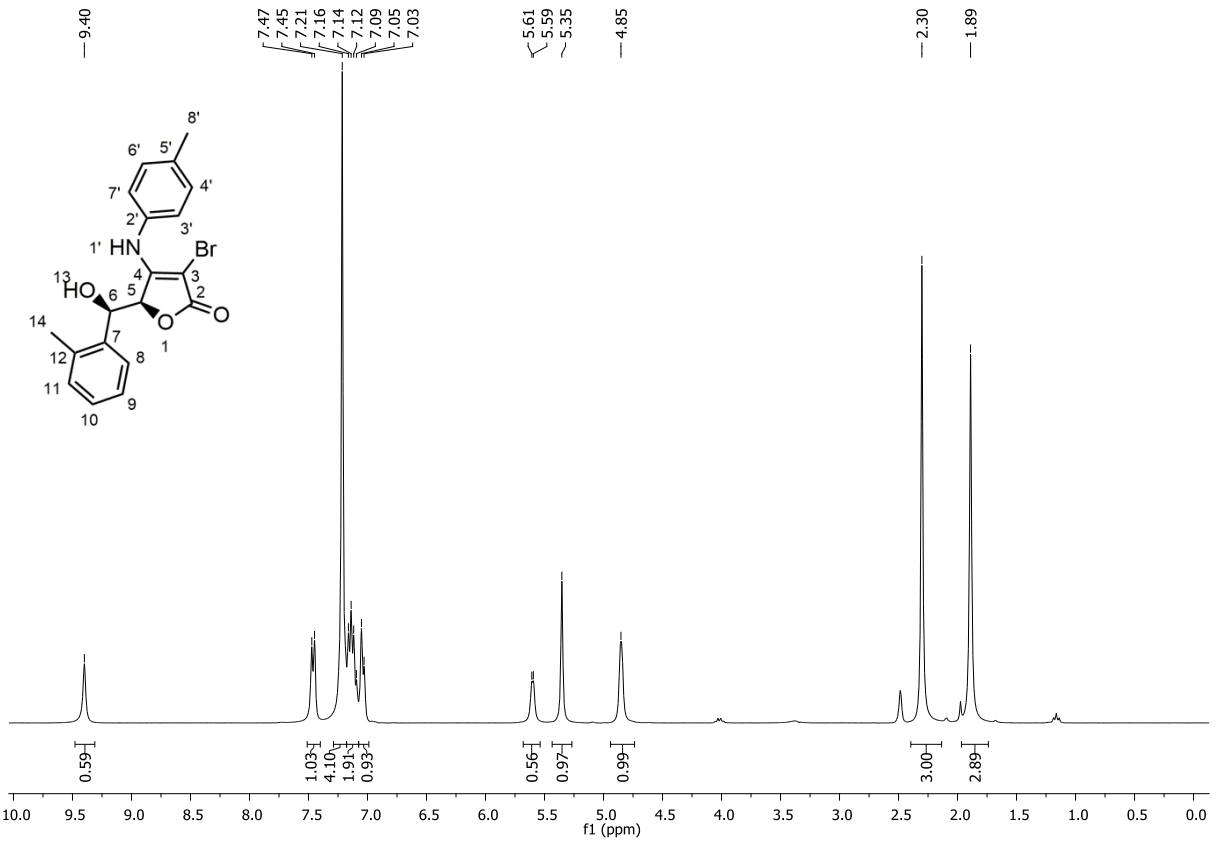


Figure S42 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***syn* -17**

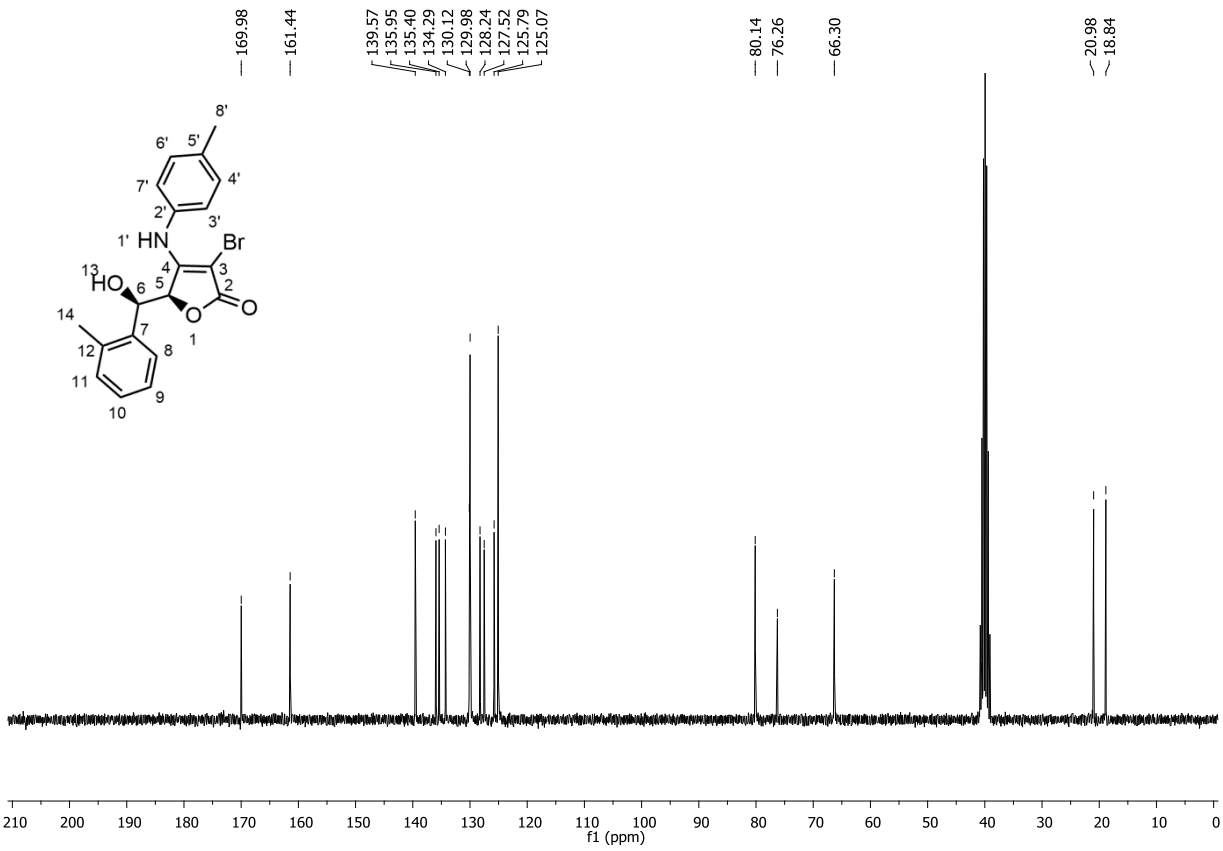


Figure S43 ^{13}C NMR (75 MHz, DMSO-d_6) of compound ***syn* -17**

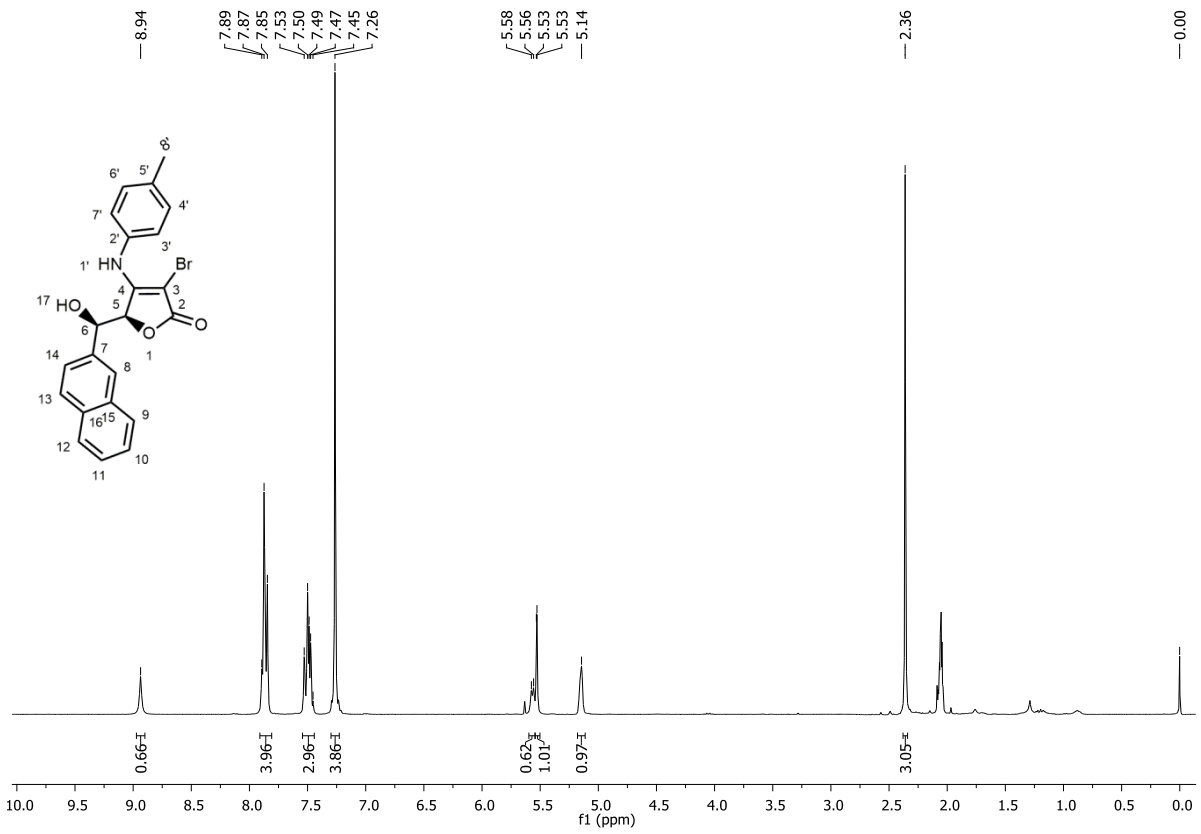


Figure S44 ^{1}H NMR (300 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound ***syn* -18**

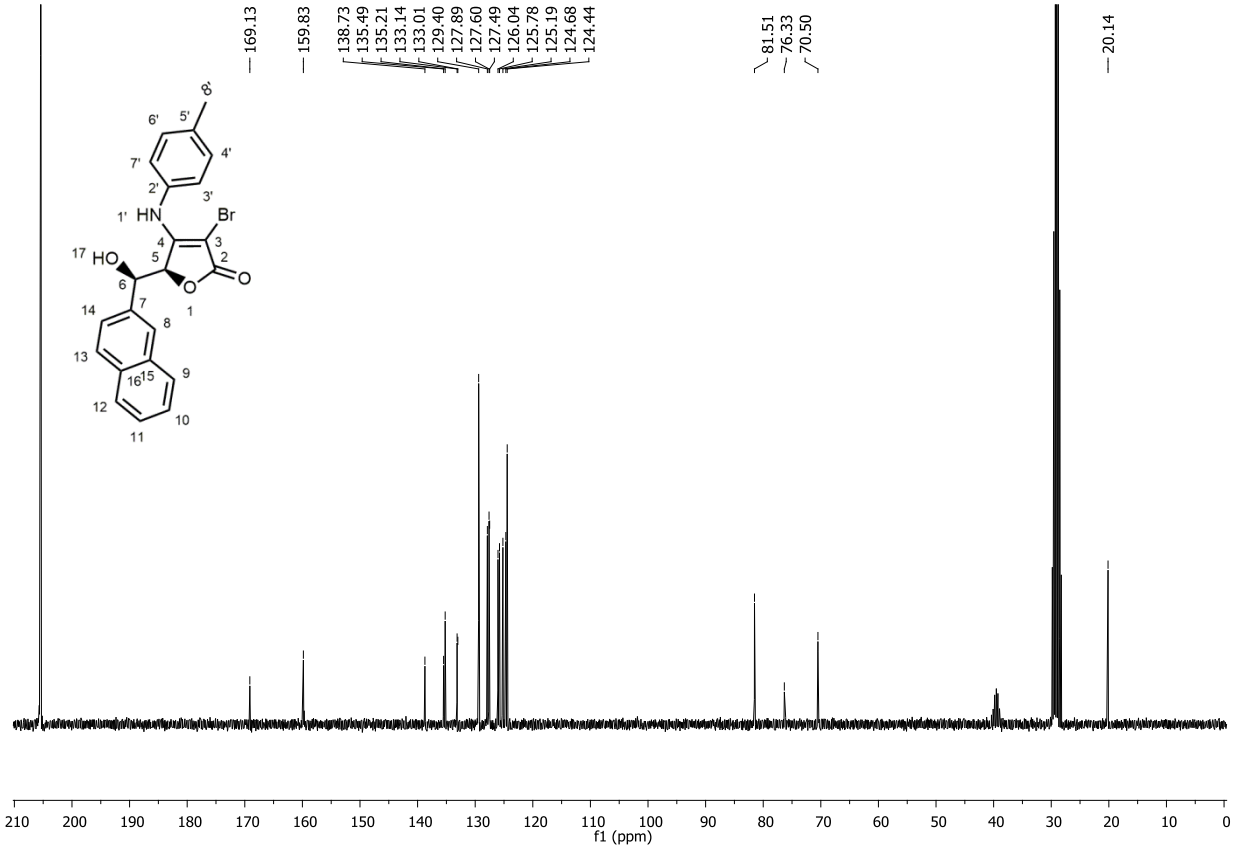


Figure S45 ^{13}C NMR (75 MHz, Acetone-d_6:DMSO-d_6; 9:1) of compound ***syn* -18**

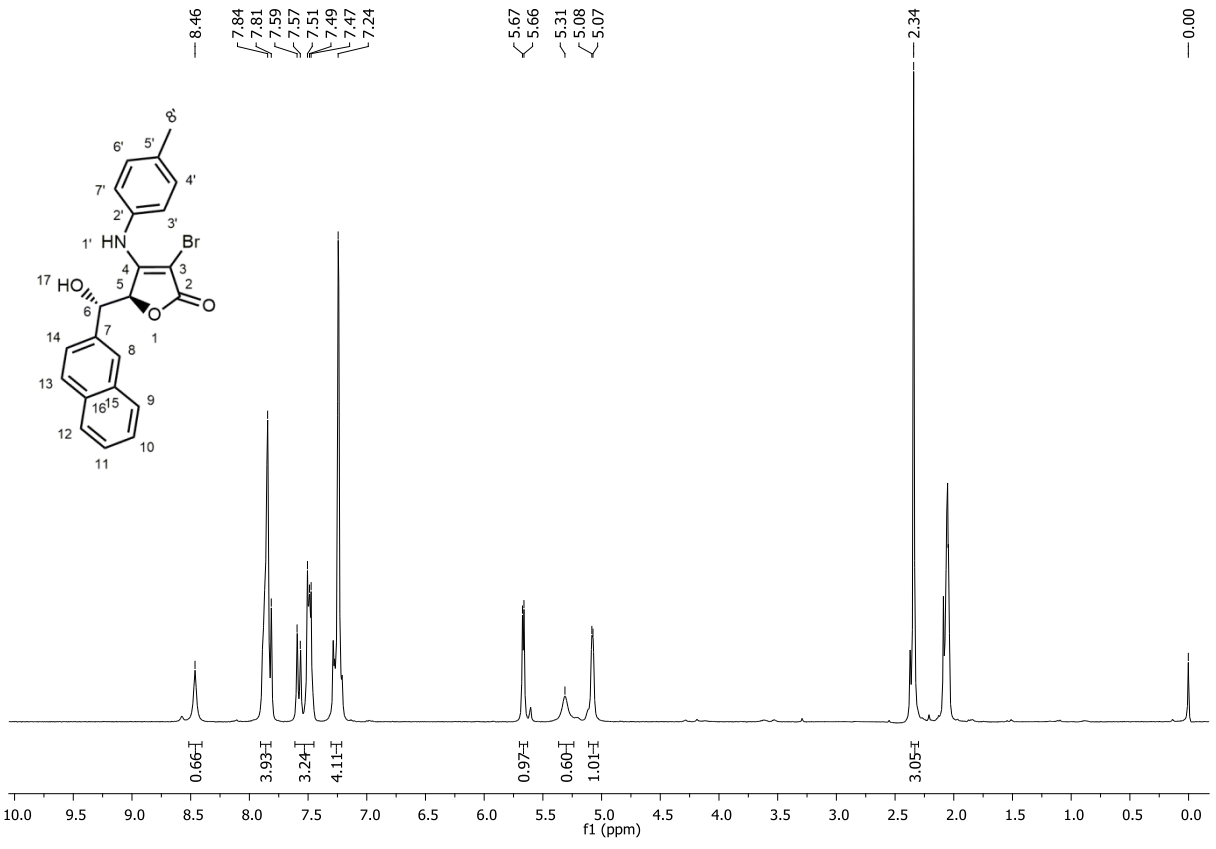


Figure S46 ^{1}H NMR (300 MHz, Acetone-d_6) of compound ***anti*** **-18**

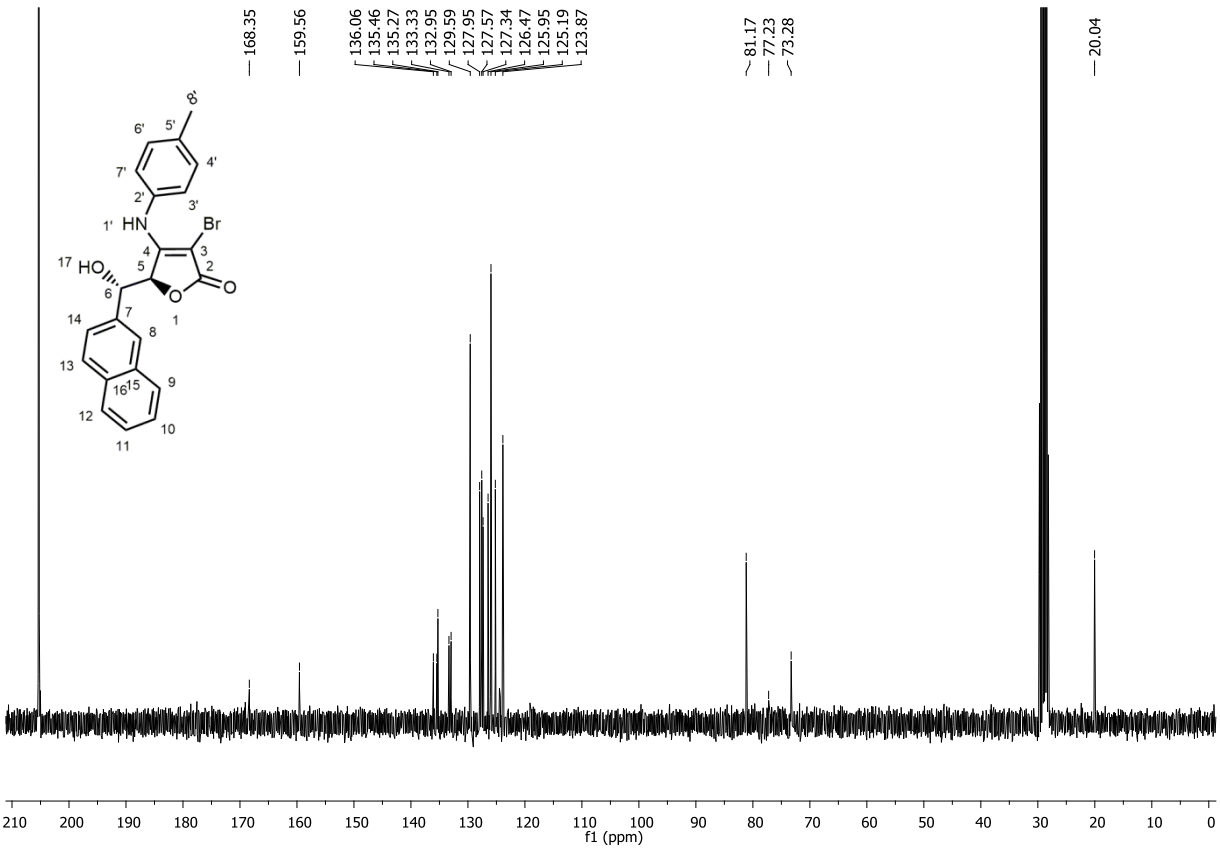


Figure S47 ^{13}C NMR (75 MHz, Acetone-d_6) of compound ***anti*** **-18**

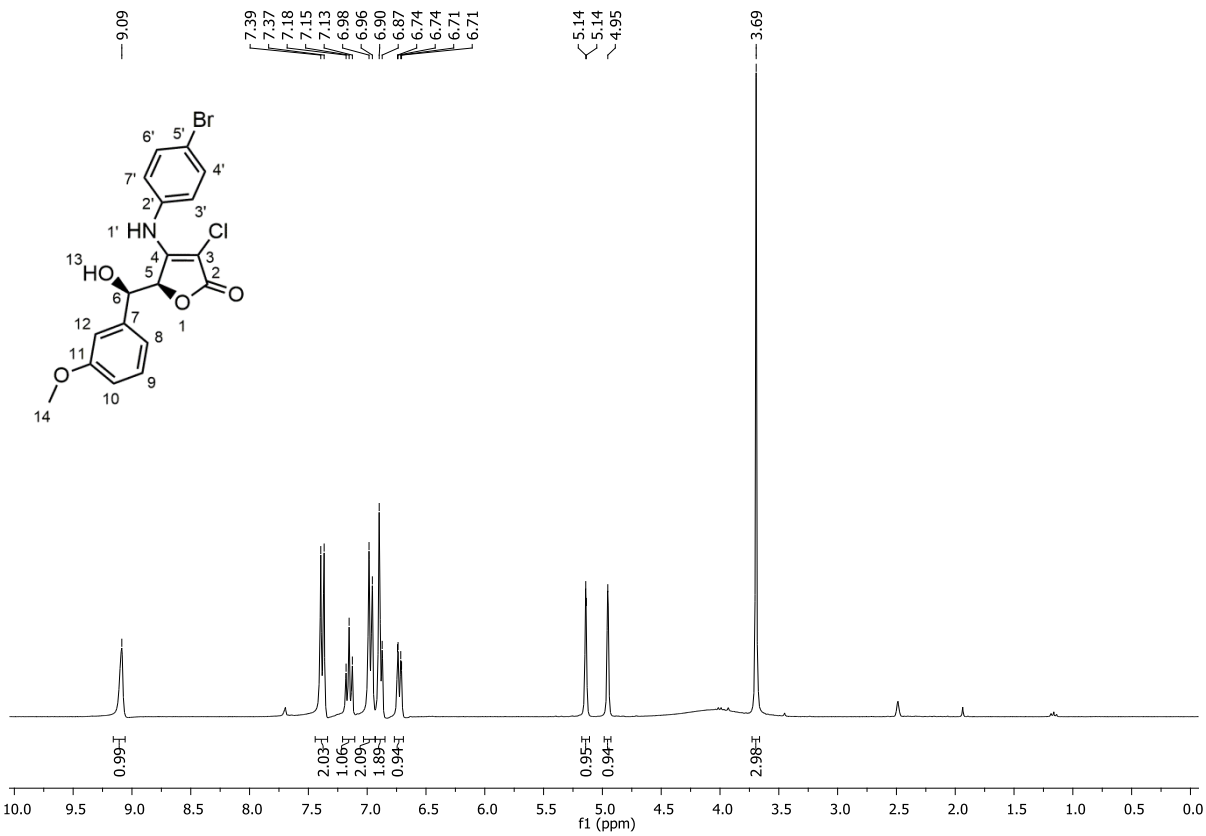


Figure S48 ^{1}H NMR (300 MHz, $CDCl_3$:DMSO-d_6; 3:2) of compound ***syn* -19**

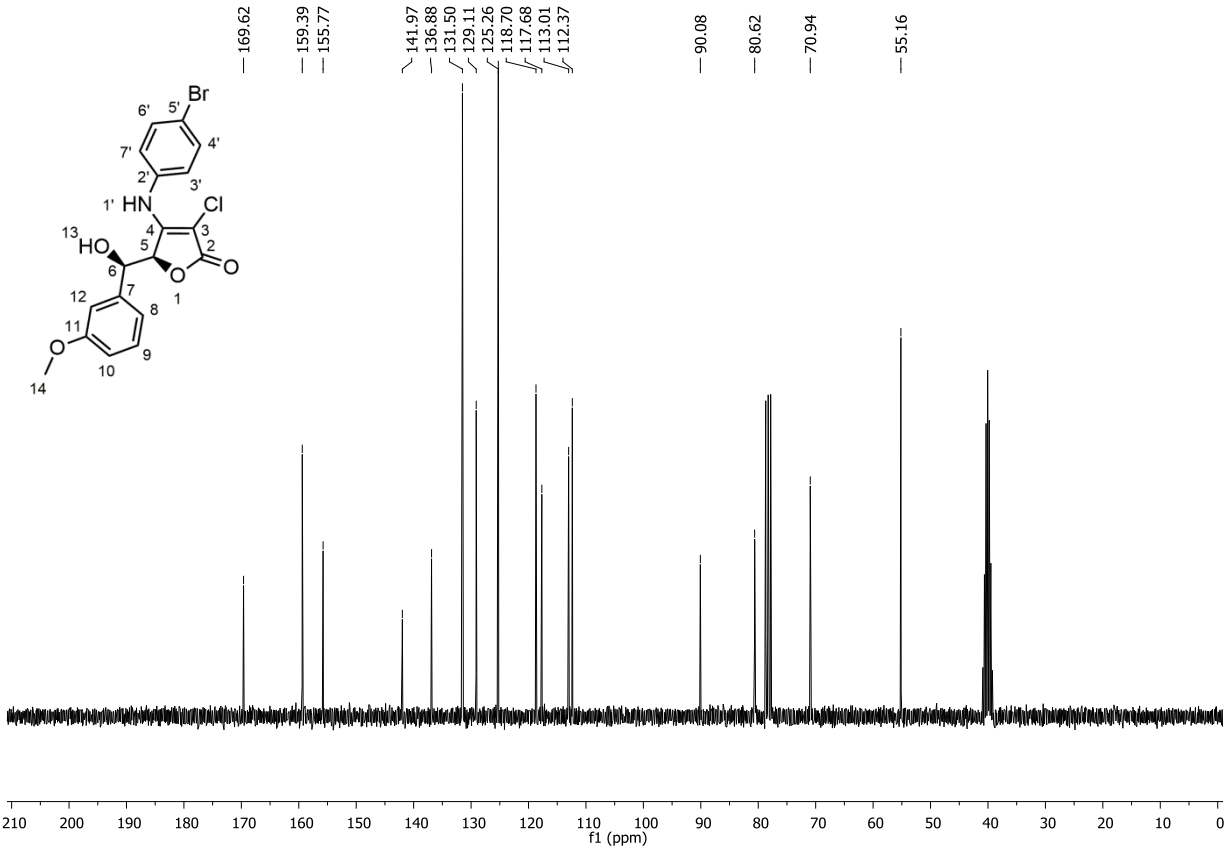


Figure S49 ^{13}C NMR (75 MHz, $CDCl_3$:DMSO-d_6; 3:2) of compound ***syn* -19**

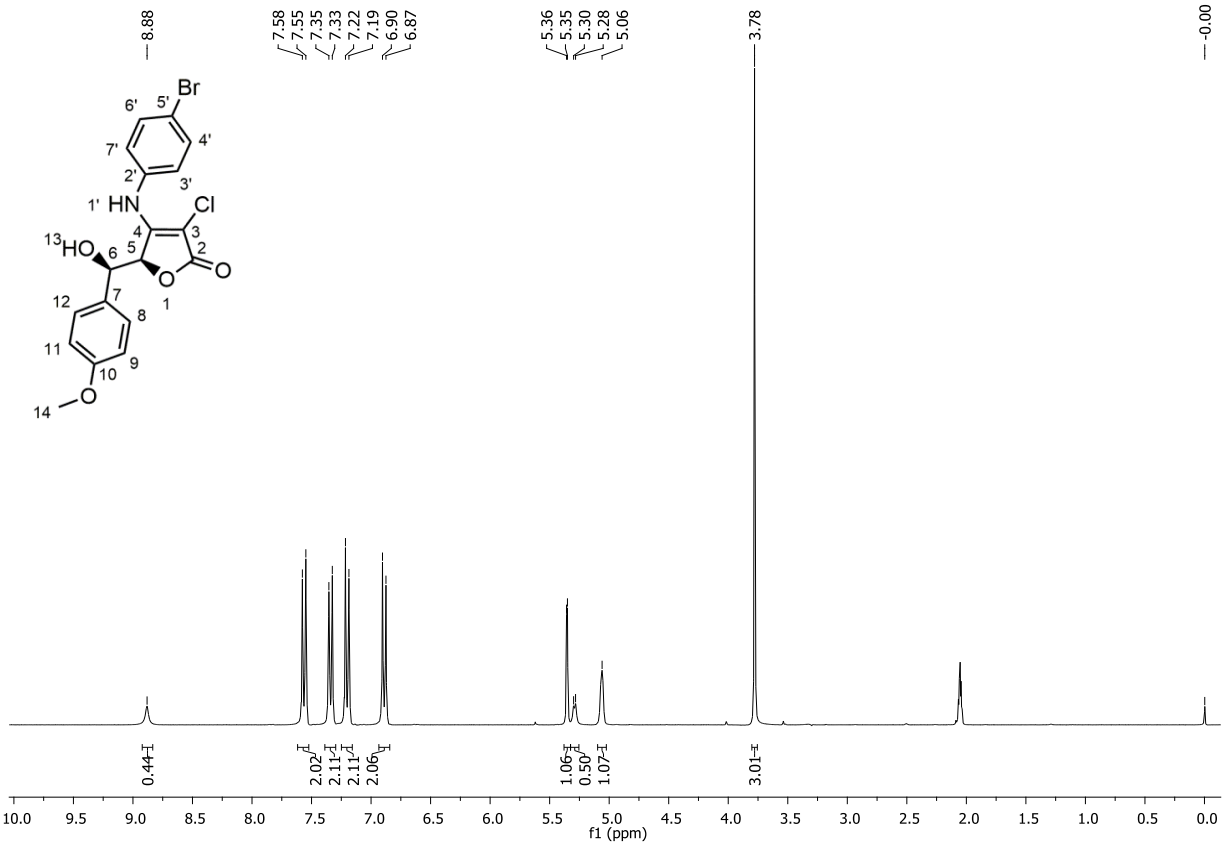


Figure S50 ^{1}H NMR (300 MHz, Acetone-d_6) of compound ***syn* -20**

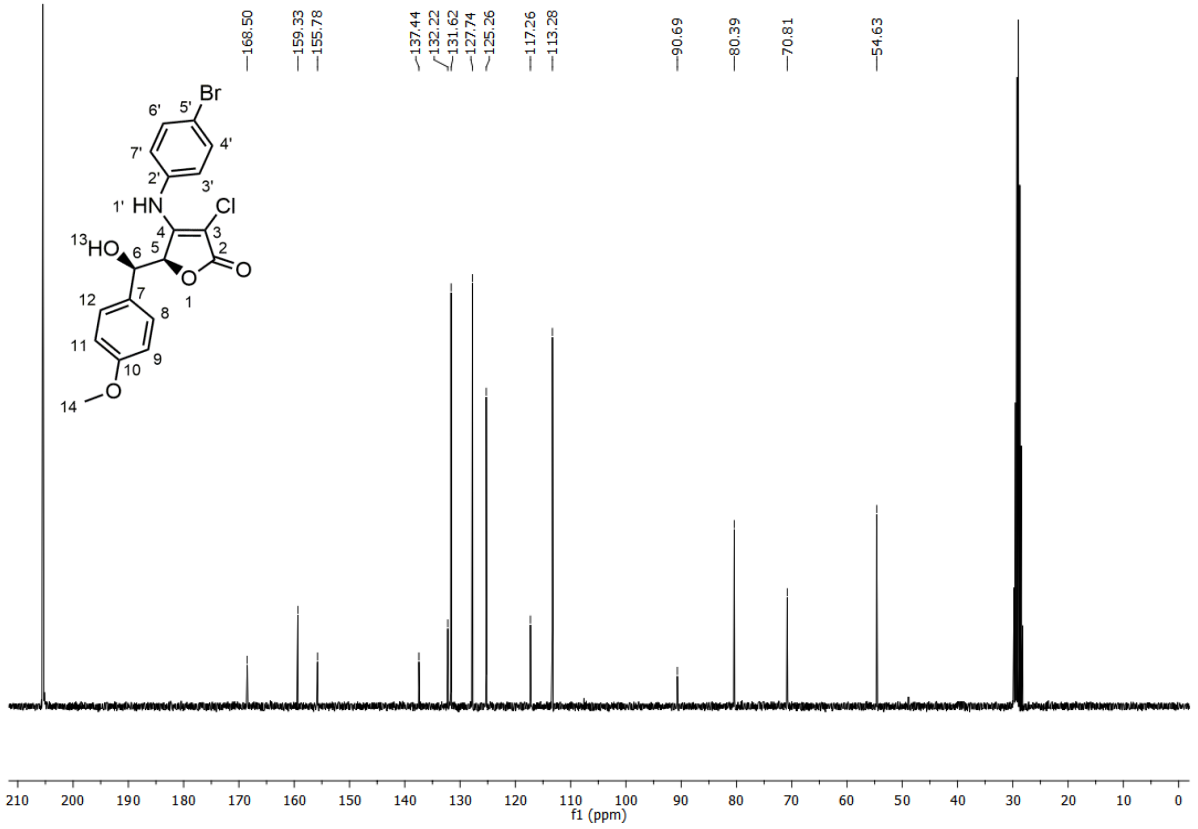


Figure S51 ^{13}C NMR (75 MHz, Acetone-d_6) of compound ***syn* -20**

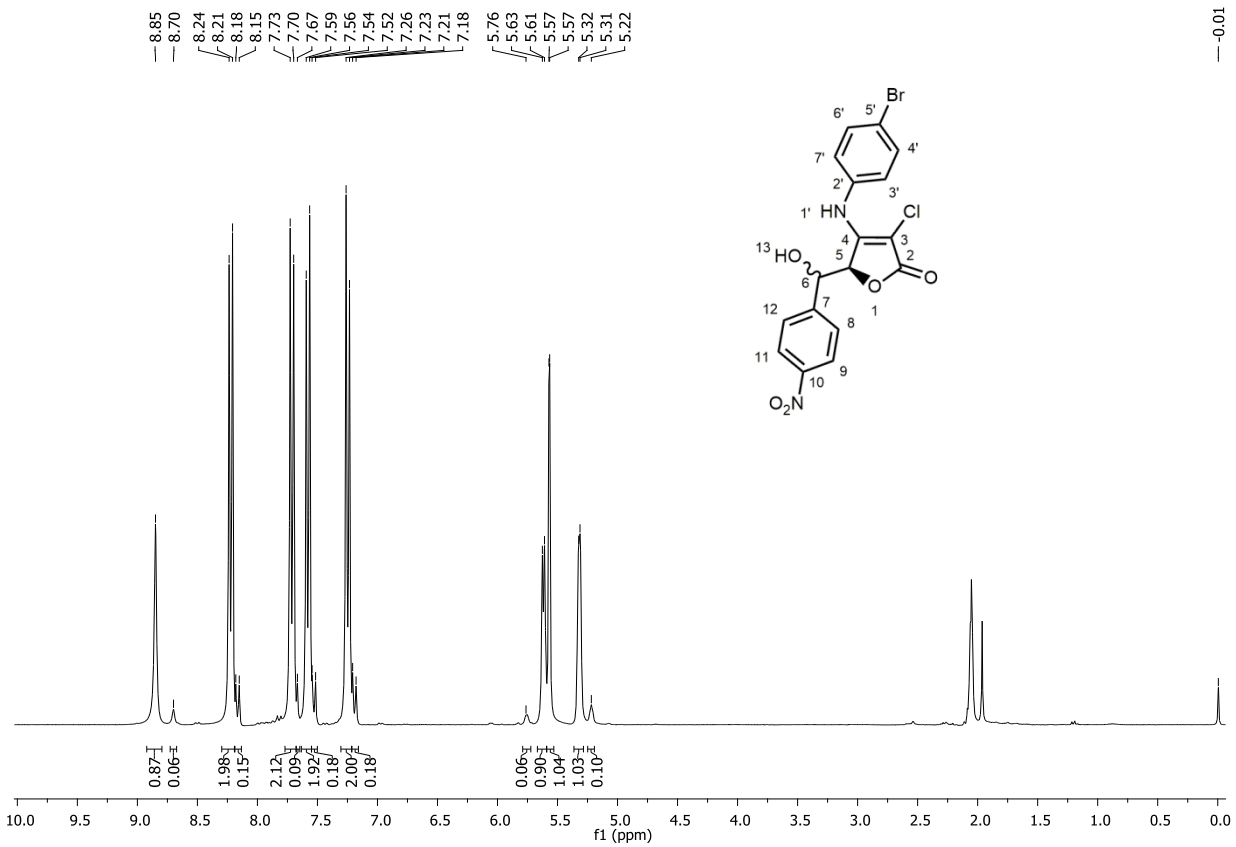


Figure S52 ^{1}H NMR (300 MHz, Acetone-d_6) of compound ***syn/anti* -21**

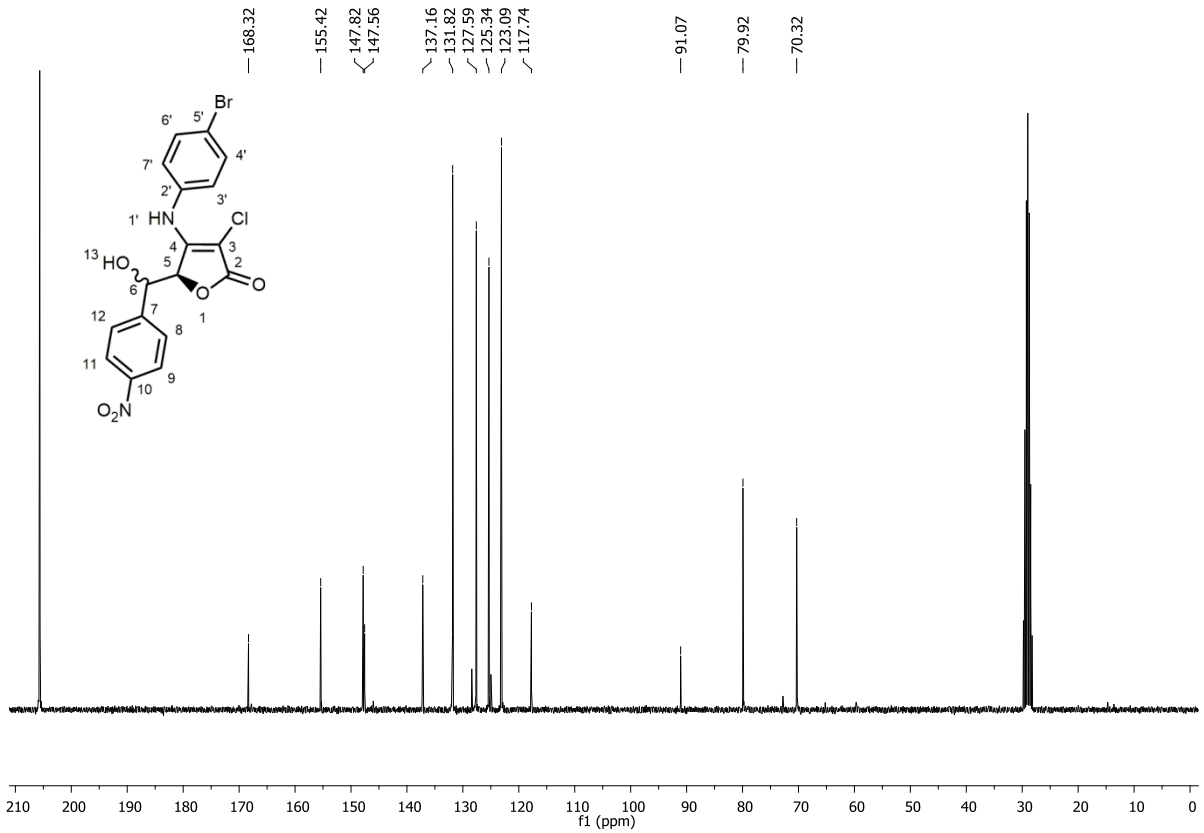


Figure S53 ^{13}C NMR (75 MHz, Acetone-d_6) of compound ***syn/anti* -21**

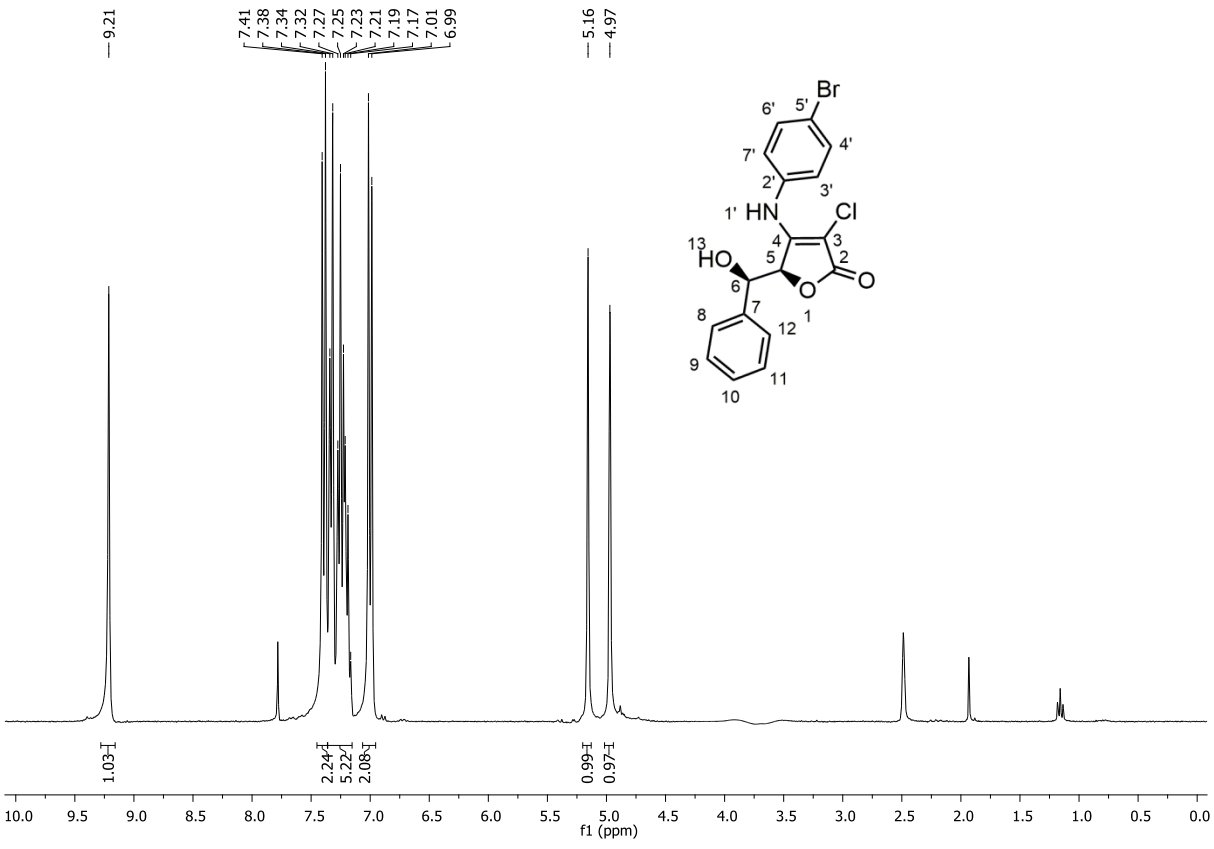


Figure S54 ^{1}H NMR (300 MHz, $CDCl_3$:DMSO-d_6; 3:2) of compound ***syn*-22**

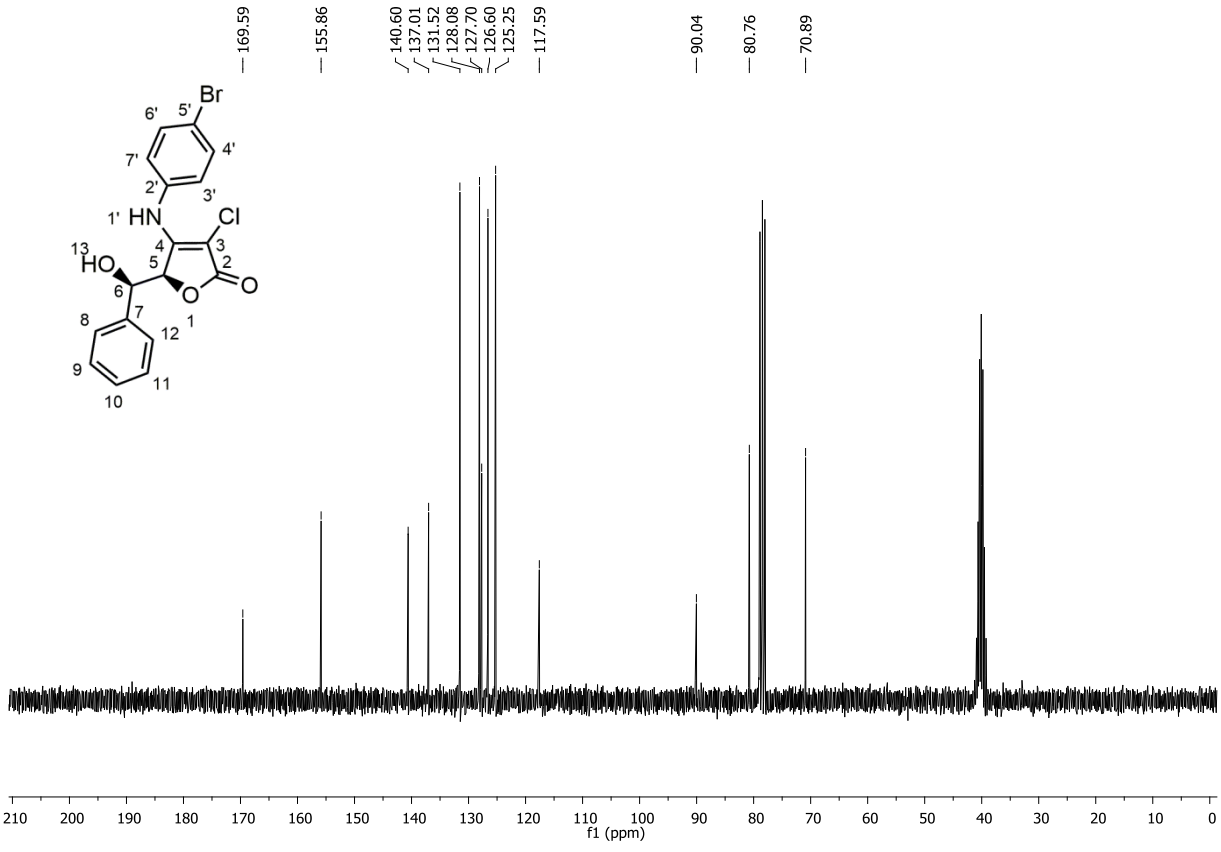


Figure S55 ^{13}C NMR (75 MHz, $CDCl_3$:DMSO-d_6; 3:2) of compound ***syn*-22**

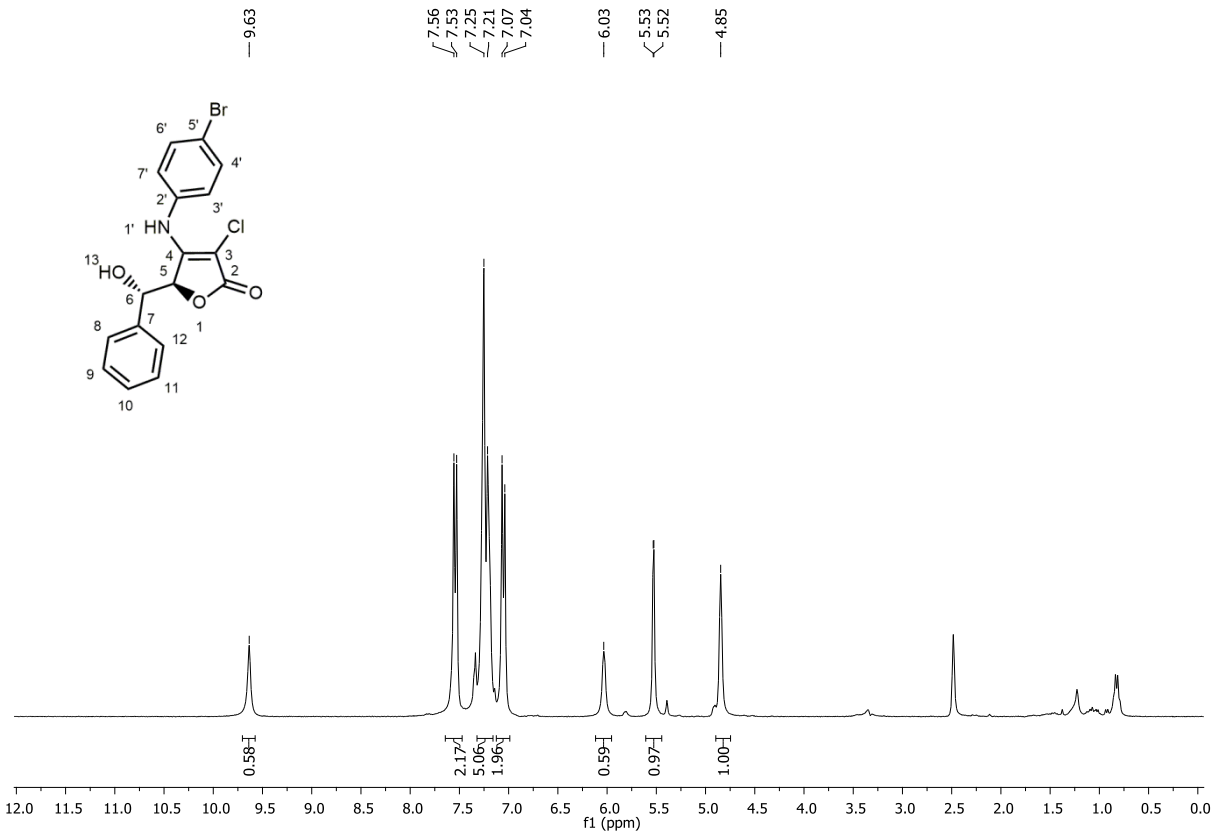


Figure S56 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***anti*-22**

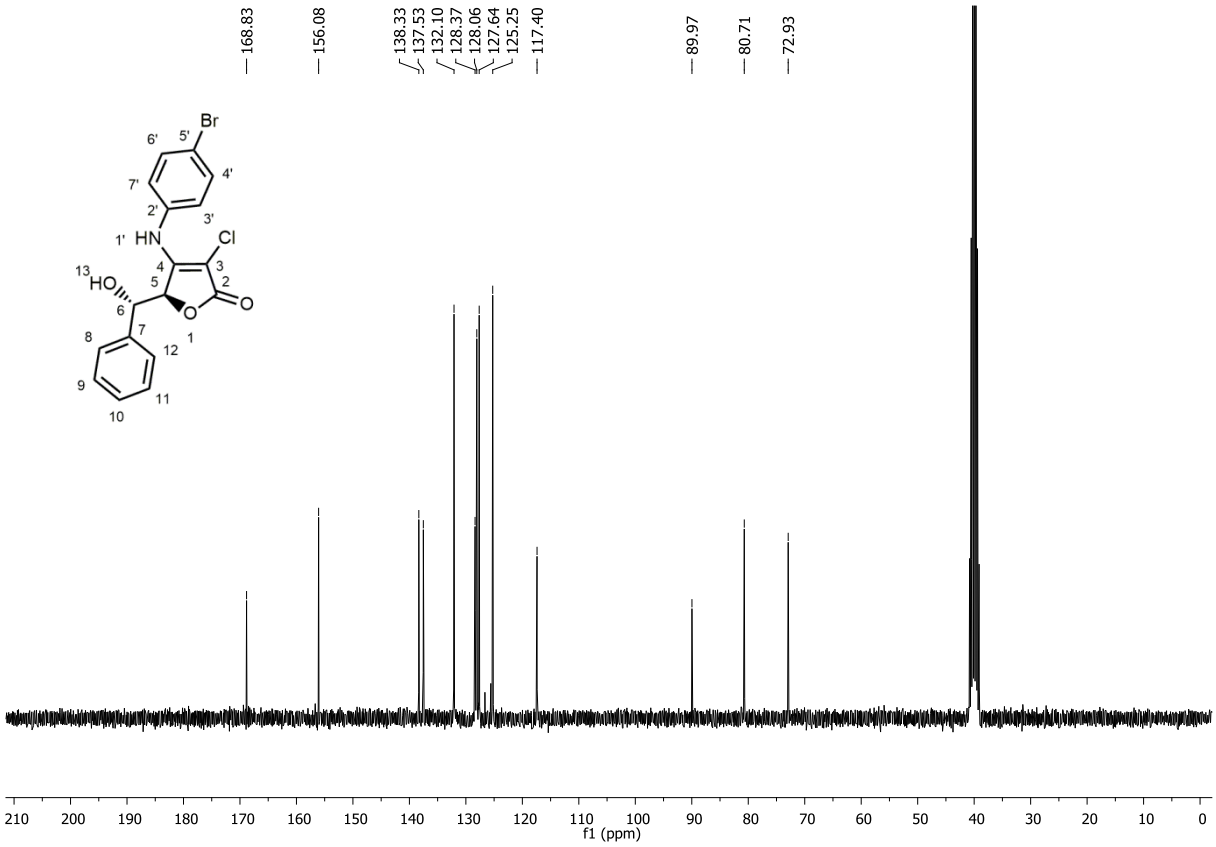


Figure S57 ^{13}C NMR (75 MHz, DMSO-d_6) of compound ***anti*-22**

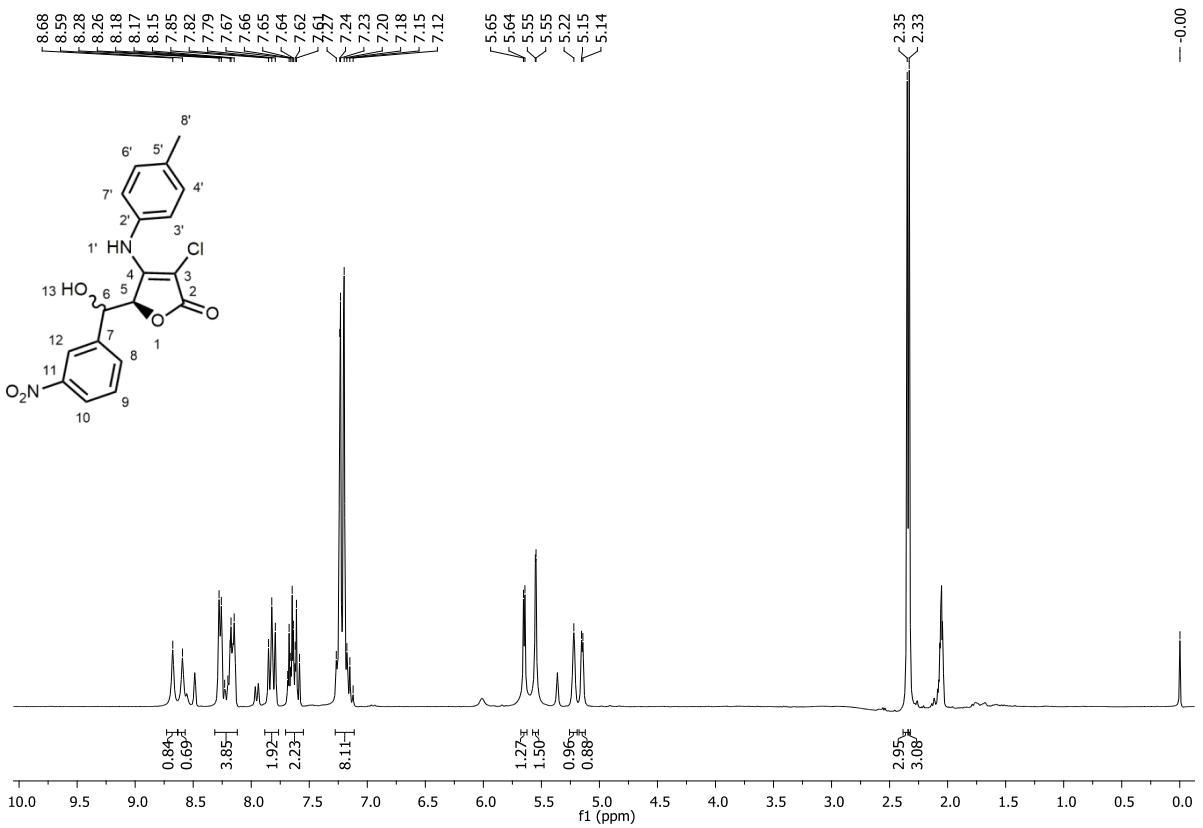


Figure S58 ^{1}H NMR (300 MHz, Acetone-d_6) of compound ***syn/anti*-23**

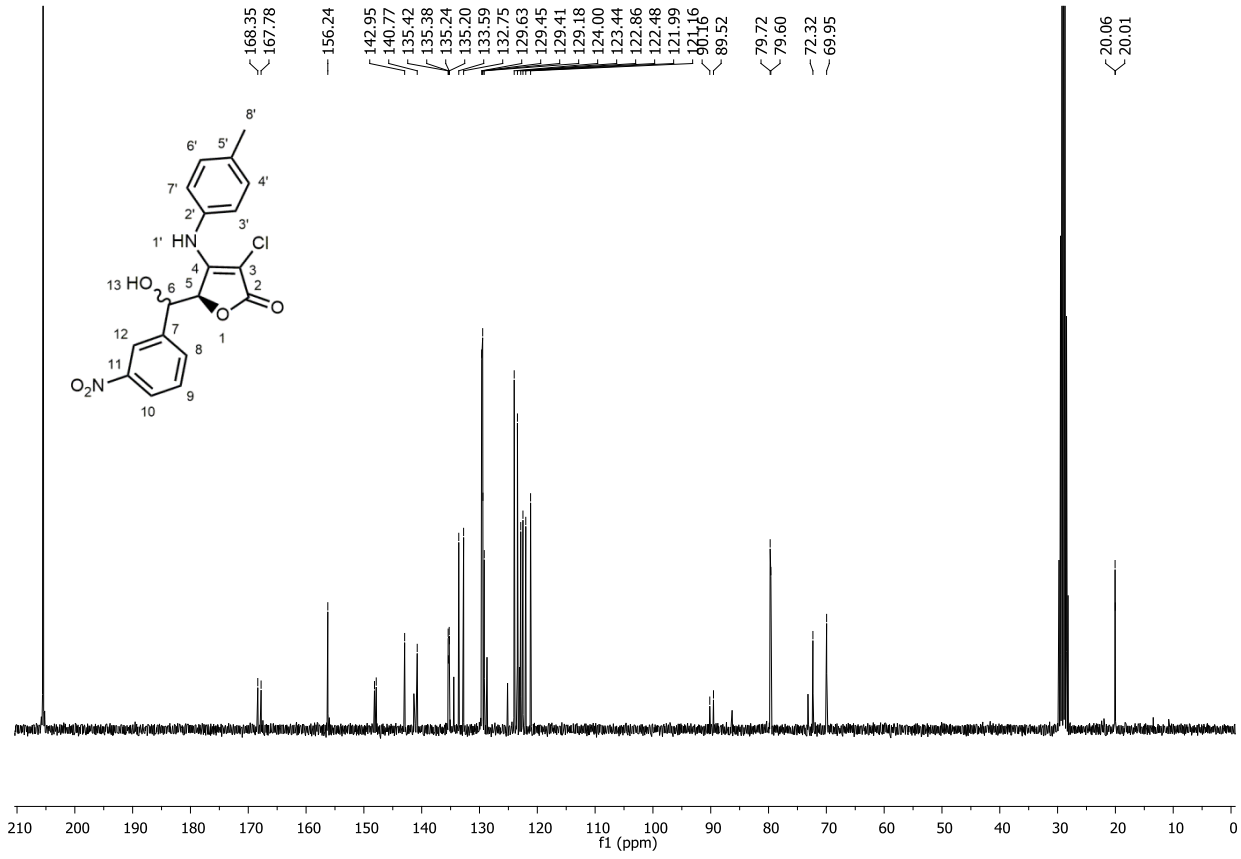


Figure S59 ^{13}C NMR (75 MHz, Acetone-d_6) of compound ***syn/anti*-23**

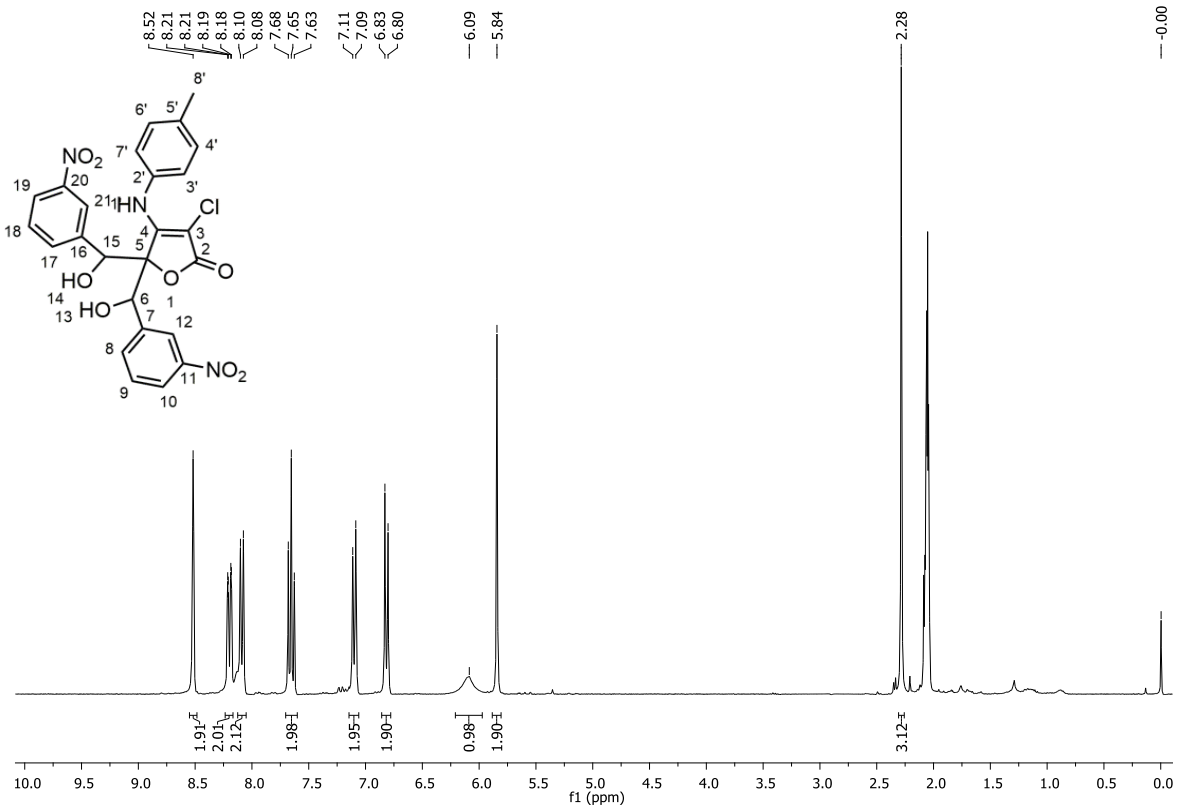


Figure S60 ^{1}H NMR (300 MHz, Acetone-d_6) of compound **23a**

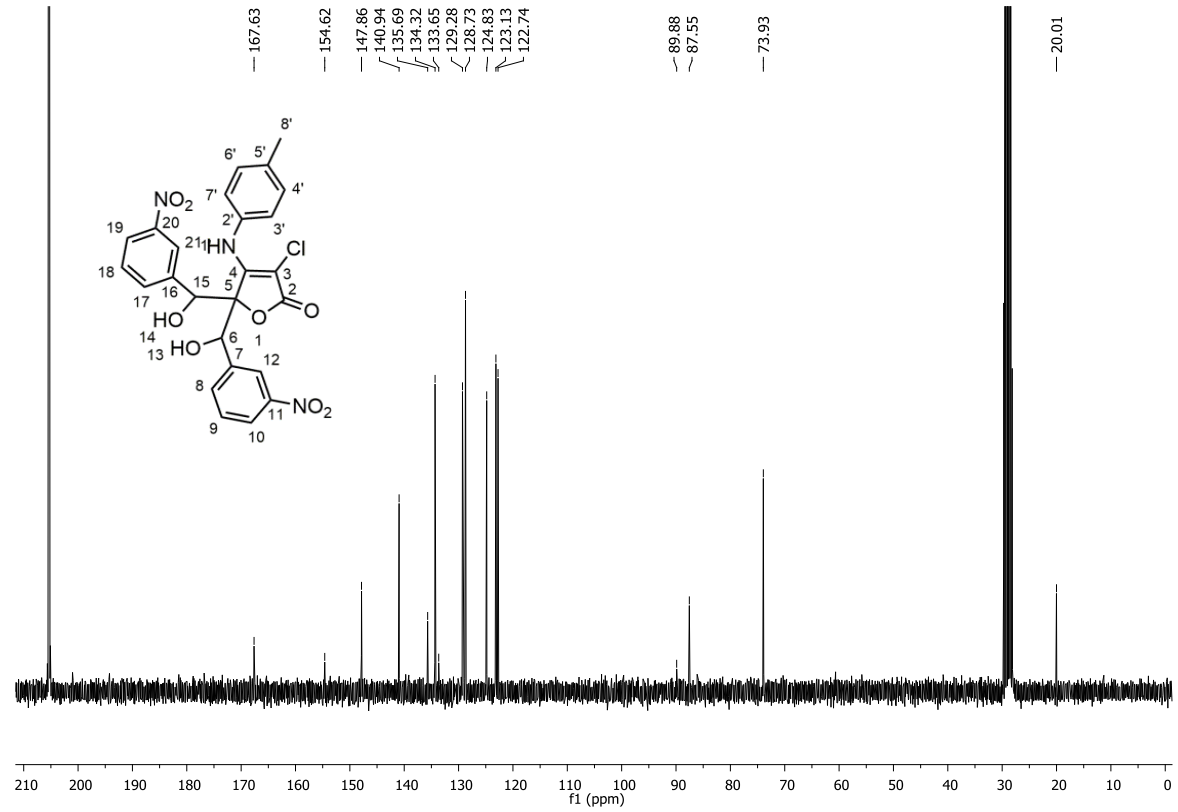


Figure S61 ^{13}C NMR (75 MHz, Acetone-d_6) of compound **23a**

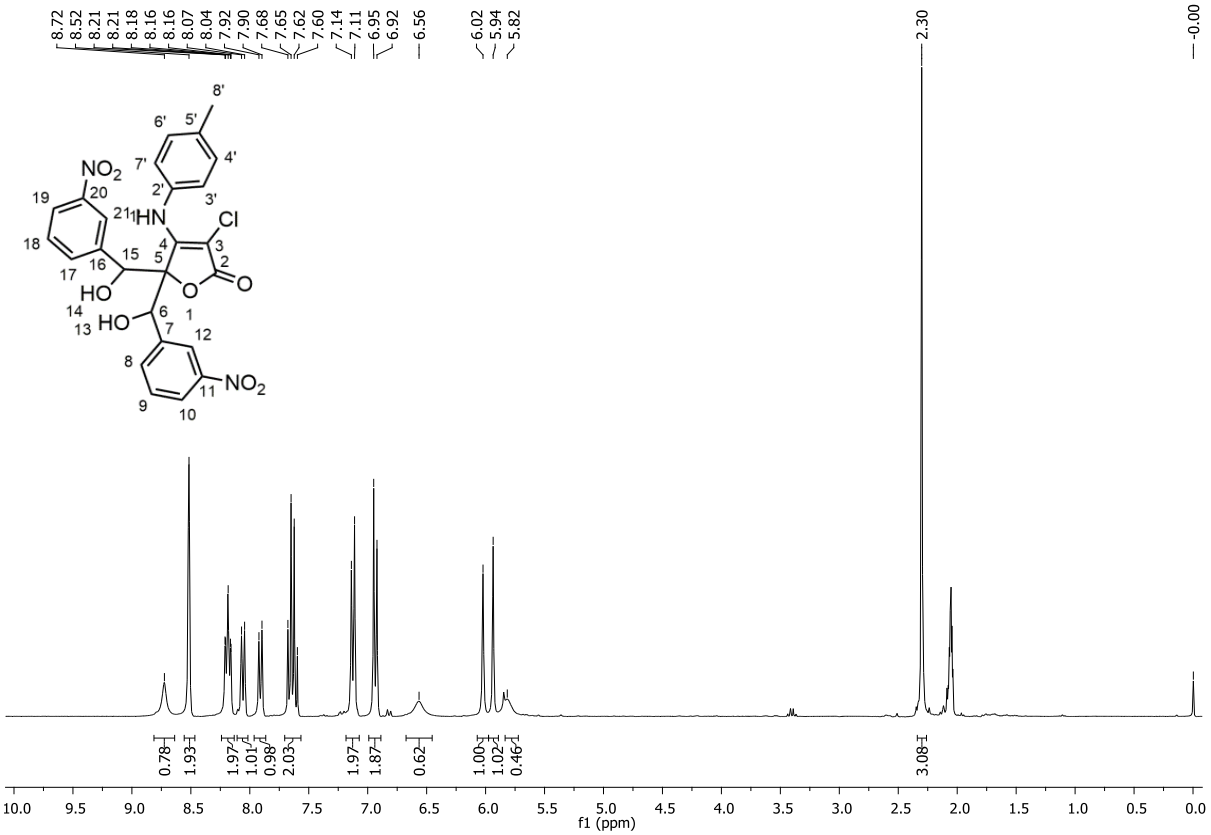


Figure S62 ^{1}H NMR (300 MHz, Acetone-d_6) of compound **23b**

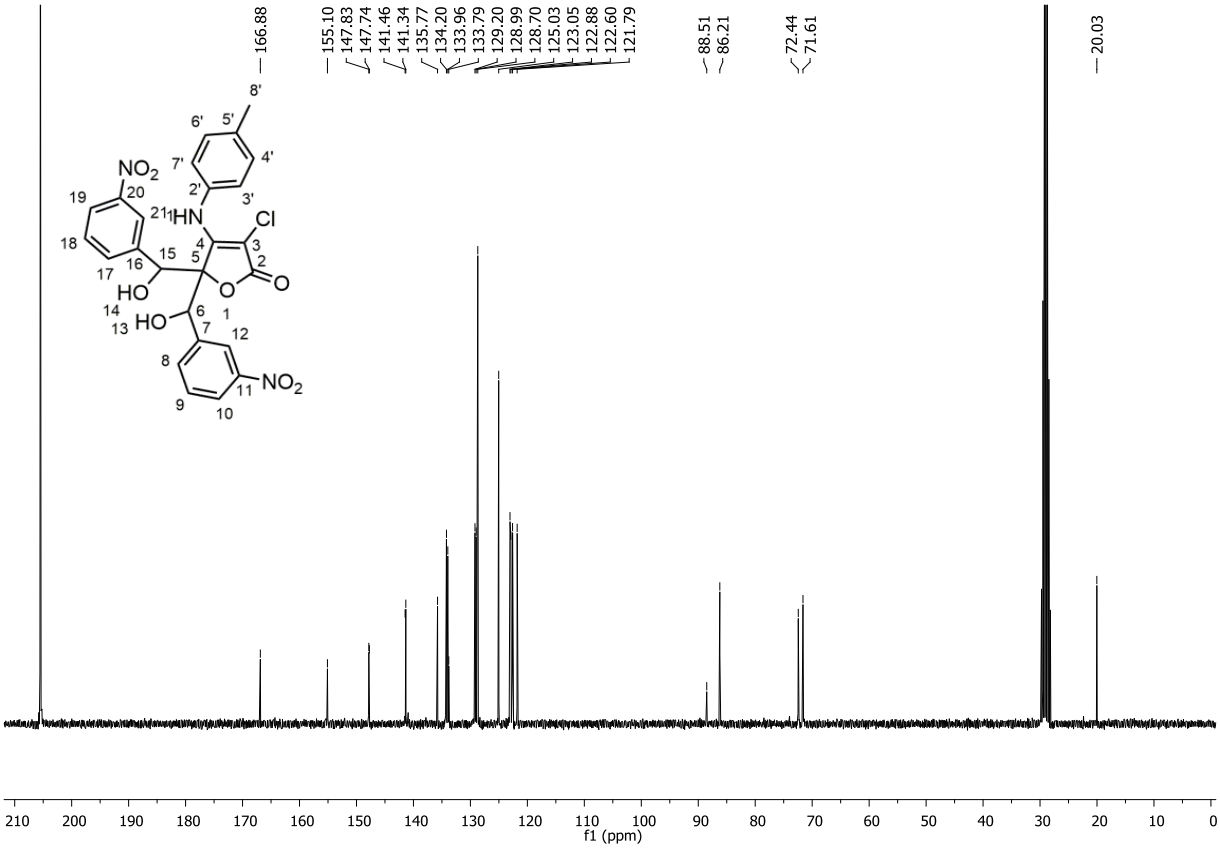


Figure S63 ^{13}C NMR (75 MHz, Acetone-d_6) of compound **23b**

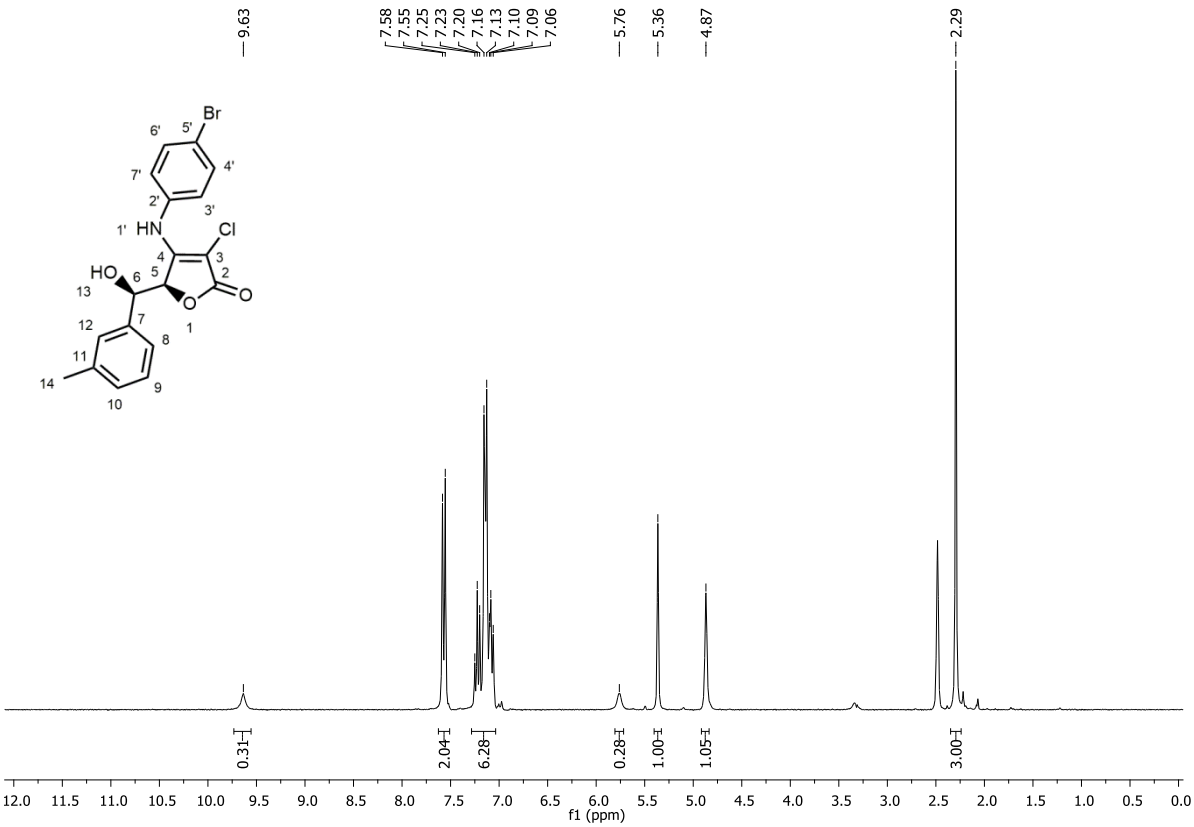


Figure S64 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***syn*-24**

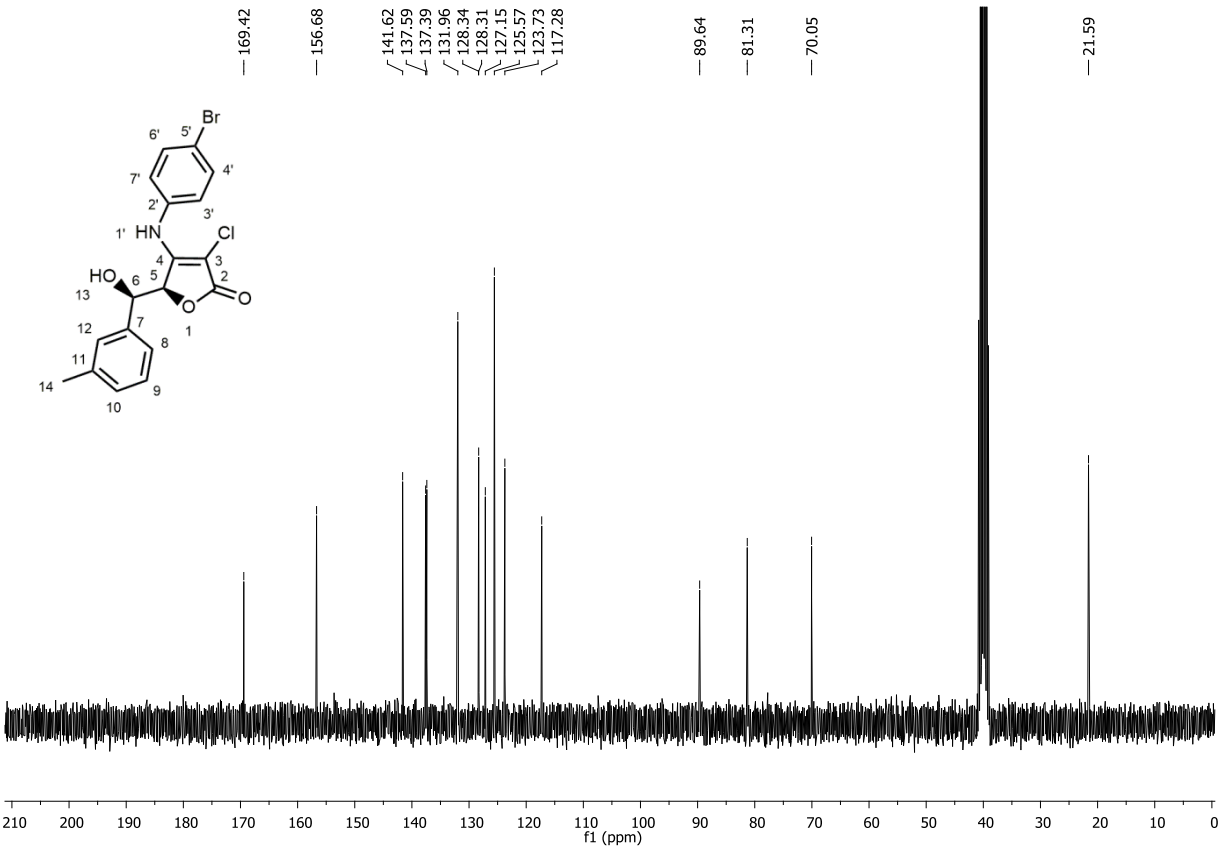


Figure S65 ^{13}C NMR (75 MHz, DMSO-d_6) of compound ***syn*-24**

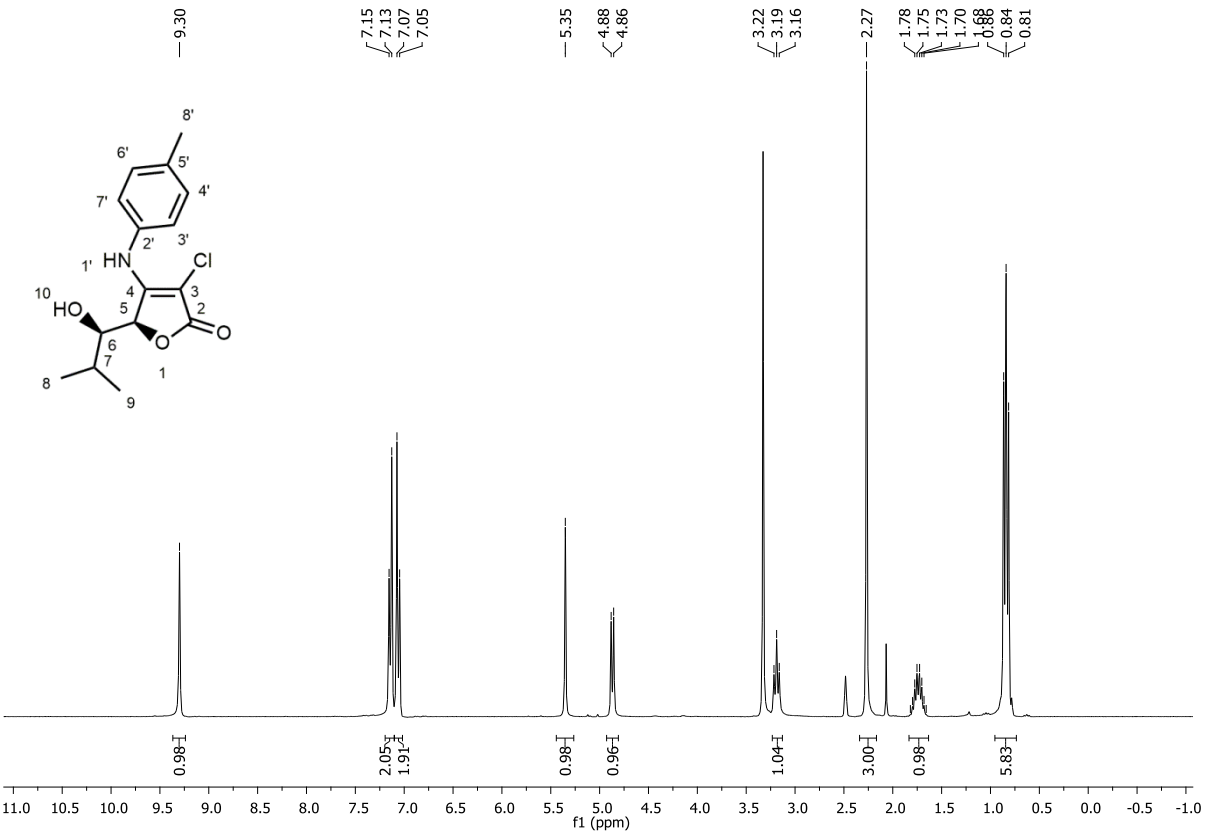


Figure S66 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***syn*-25**

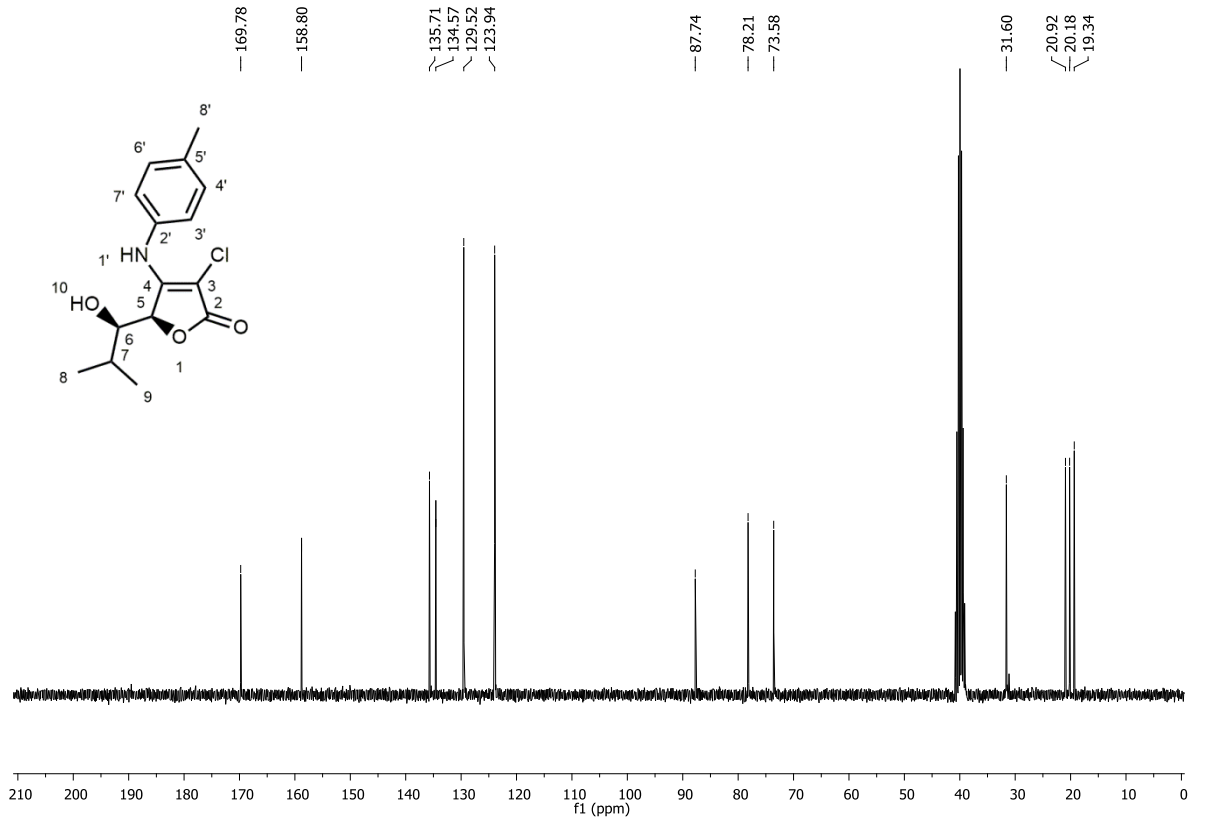


Figure S67 ^{13}C NMR (75 MHz, DMSO-d_6) of compound ***syn*-25**

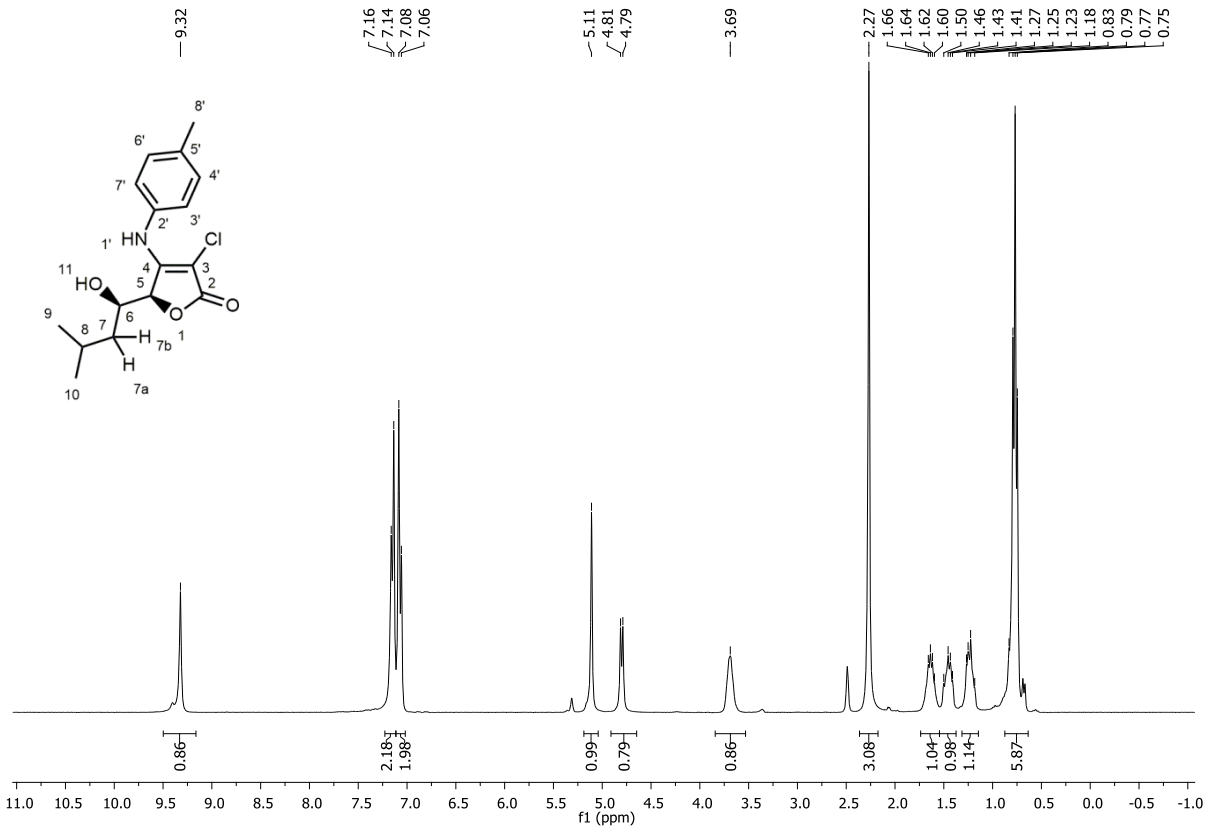


Figure S68 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***syn*-26**

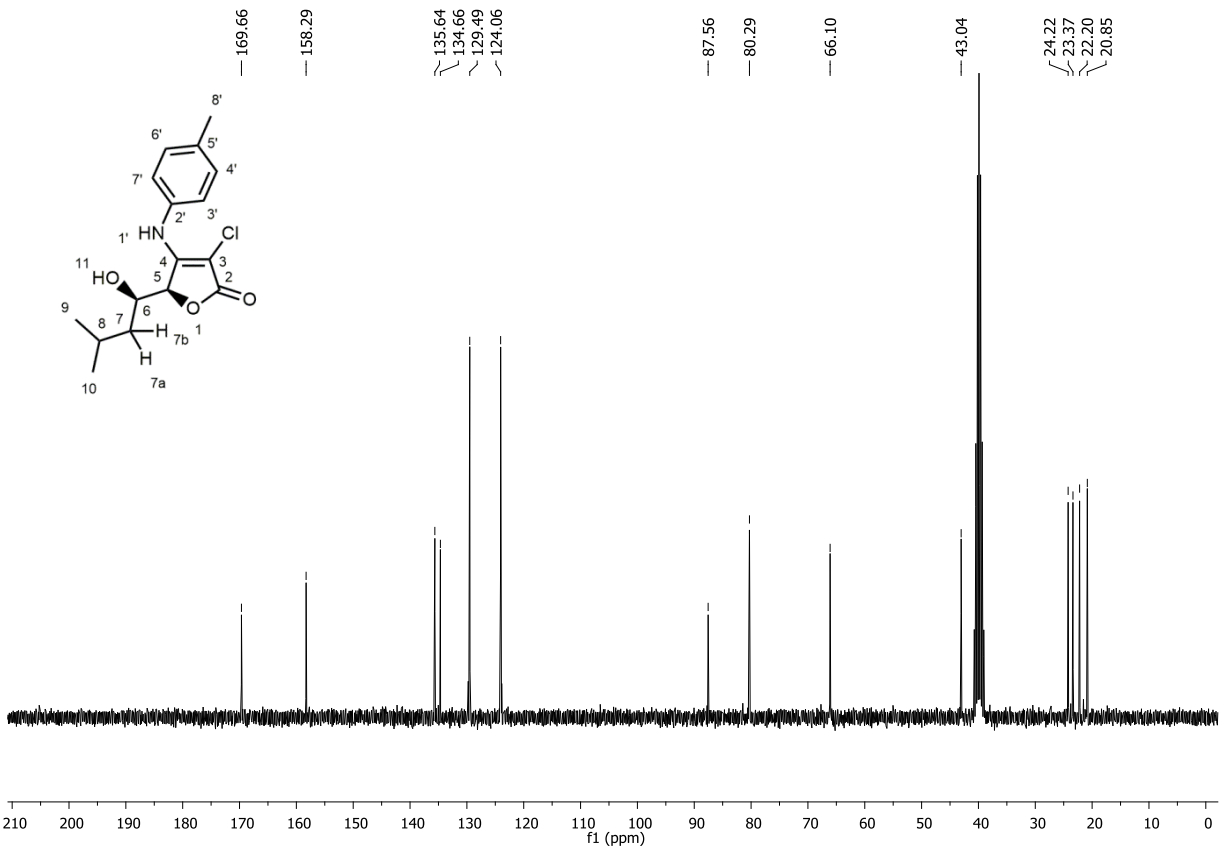


Figure S69 ^{13}C NMR (75 MHz, DMSO-d_6) of compound ***syn*-26**

3.3. NMR spectra of retro-aldol products

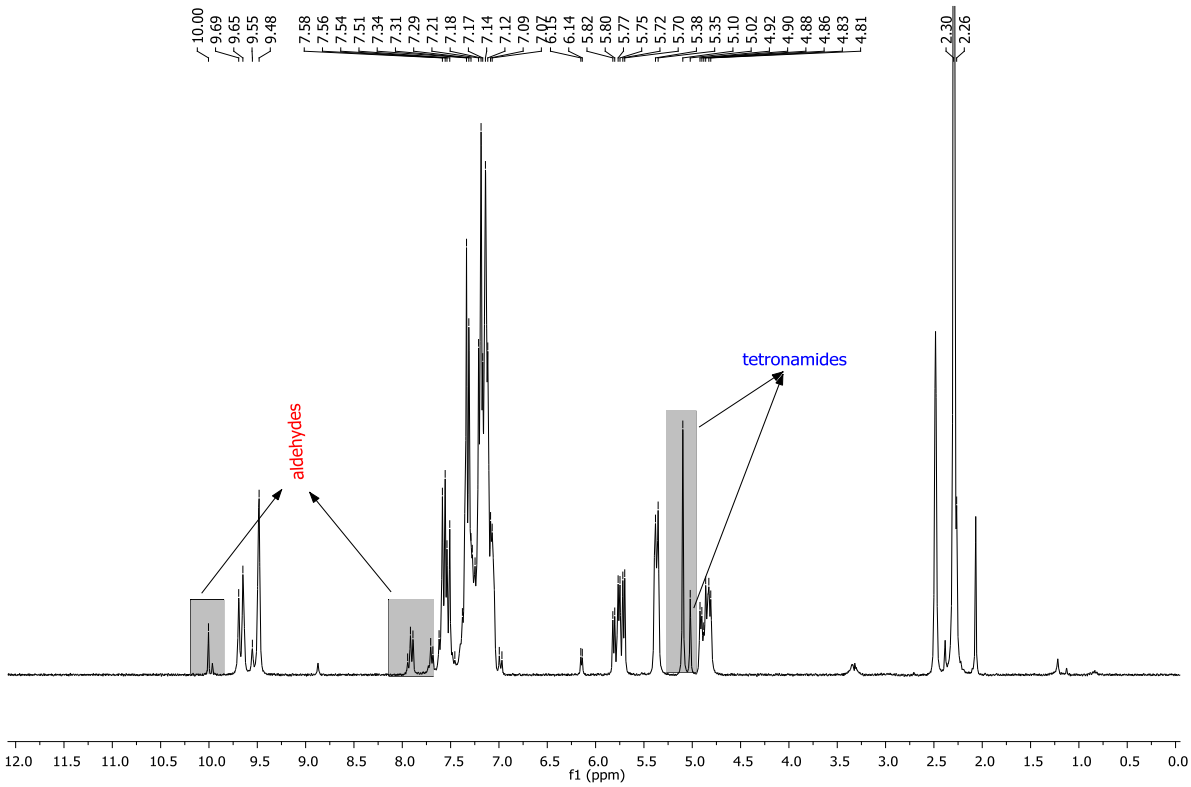


Figure S70 ^{1}H NMR (300 MHz, DMSO-d_6) of the crude (retro-aldol products)

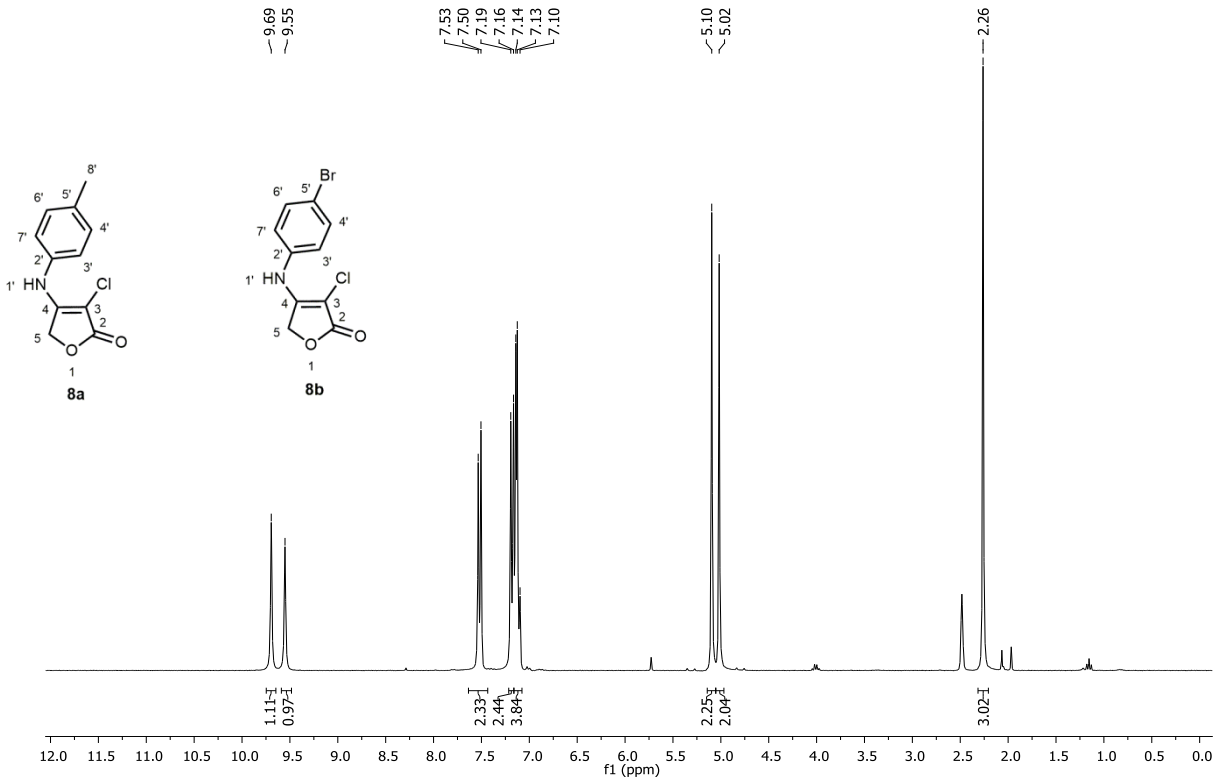


Figure S71 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***8a/8b***

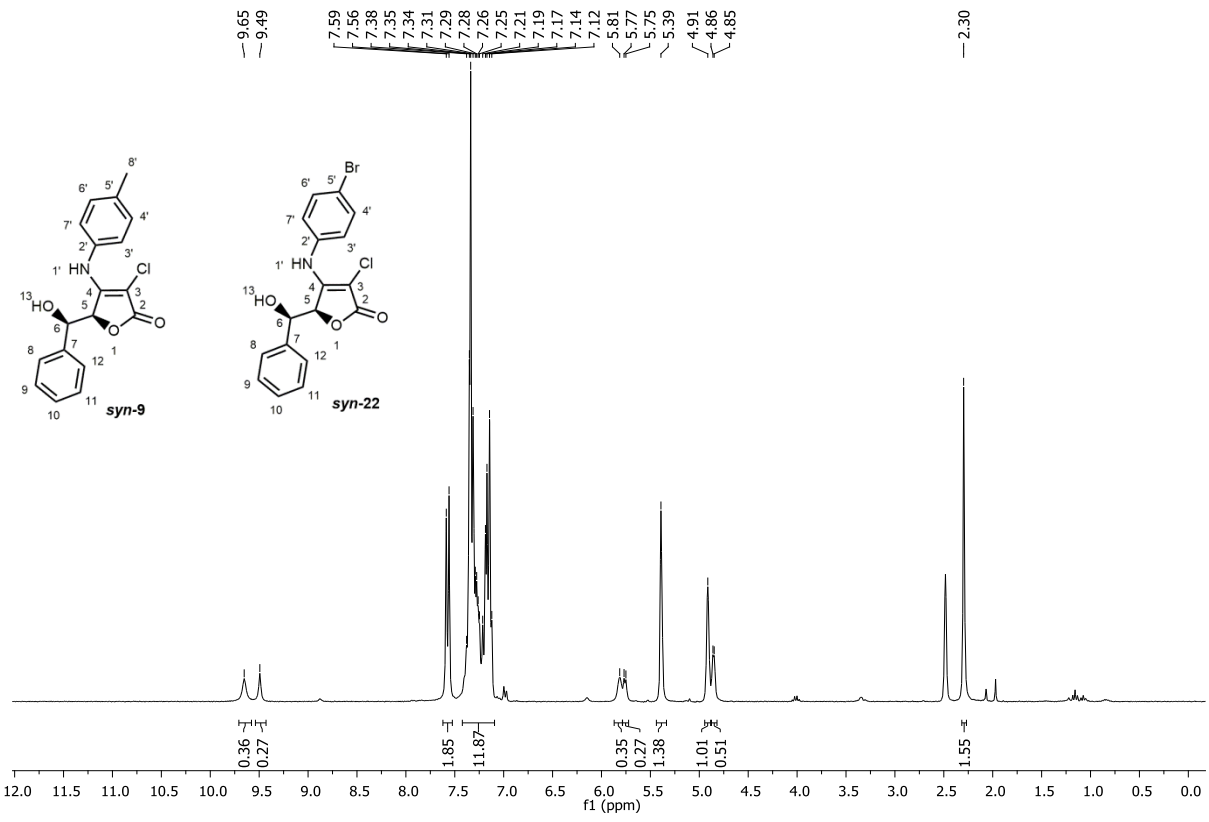


Figure S72 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***syn-9/syn-22***

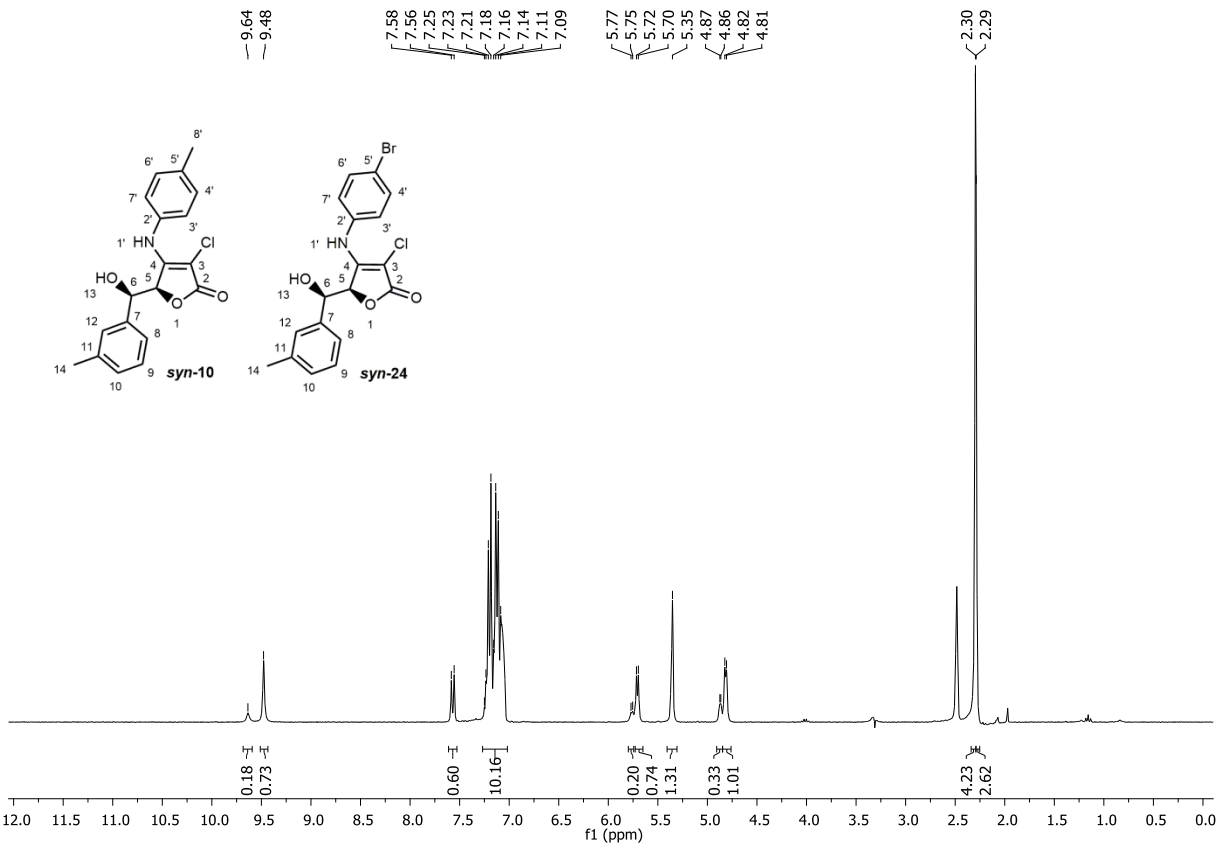


Figure S73 ^{1}H NMR (300 MHz, DMSO-d_6) of compound ***syn-10/syn-24***

4. ^{1}H-NMR spectra of *anti*-**9** for the 'D' incorporation vs. isomerization

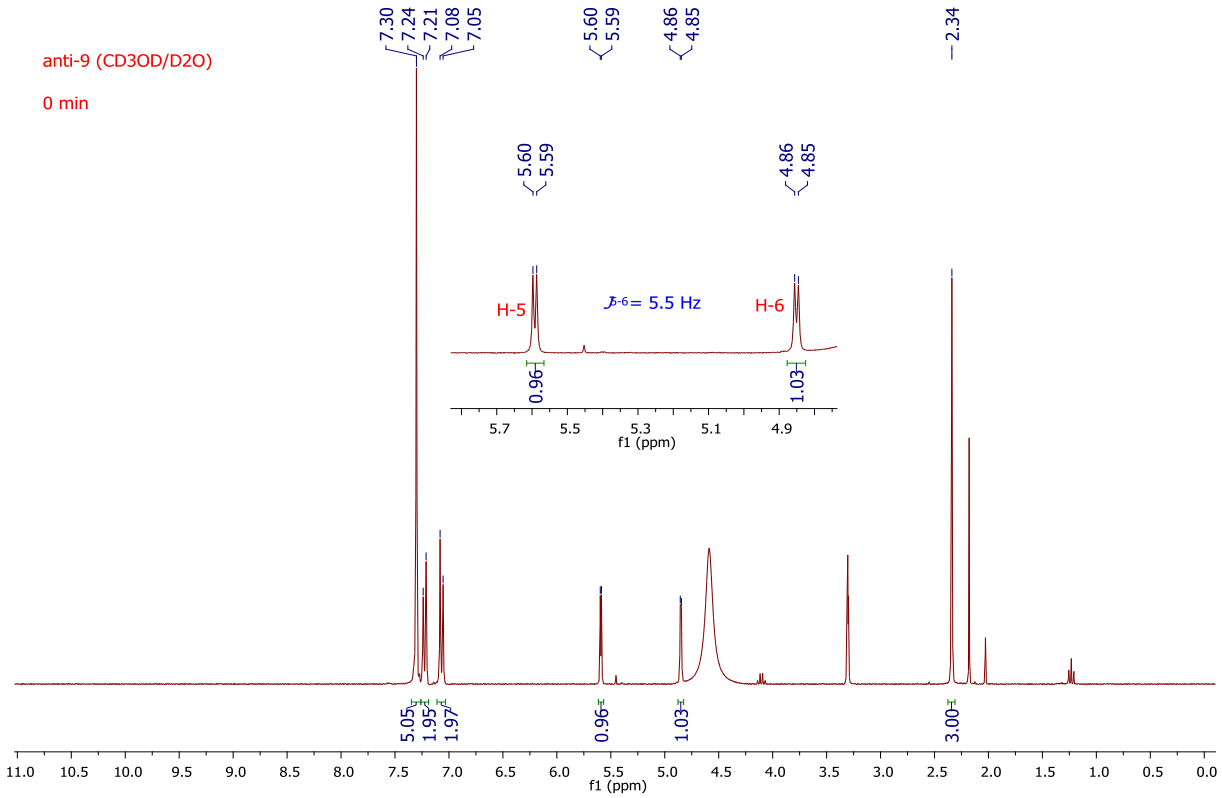


Figure S74 ^{1}H NMR (300 MHz, CD_3OD/D_2O; 2:1) recorded before addition of NaOH

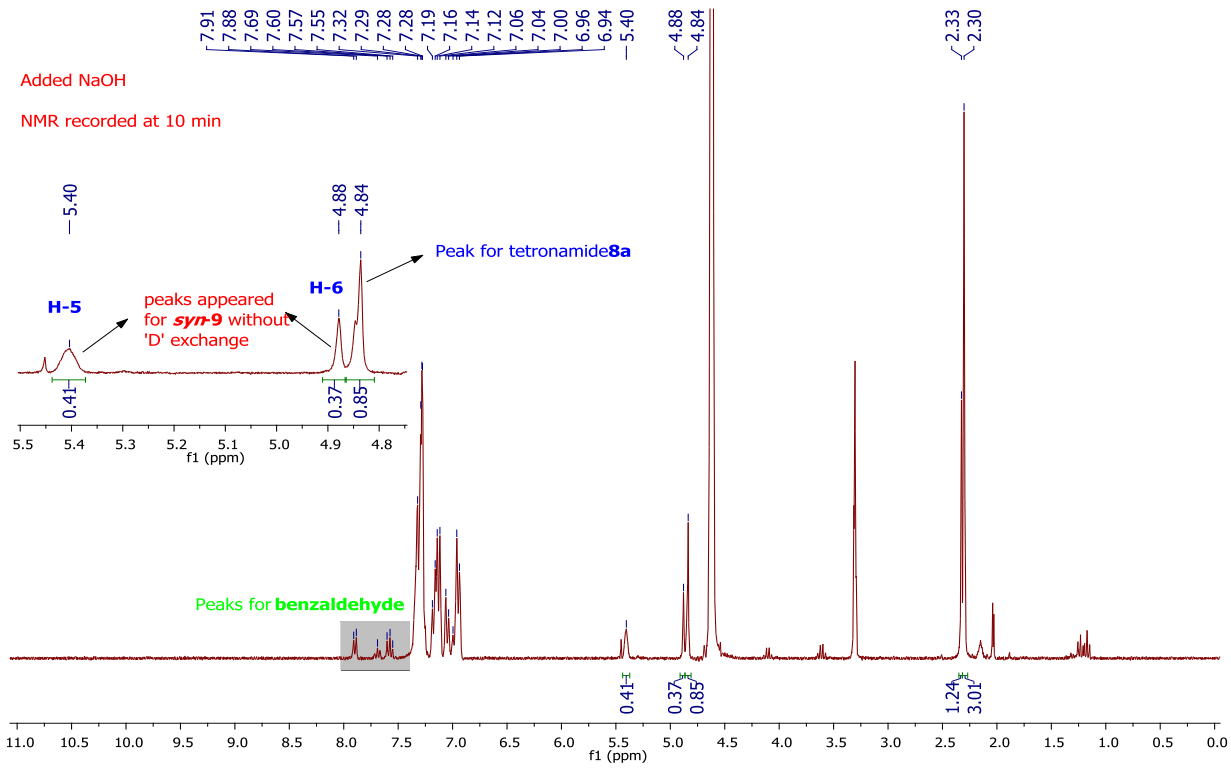


Figure S75 ^{1}H NMR (300 MHz, CD_3OD/D_2O; 2:1) recorded at 10 min after addition of NaOH

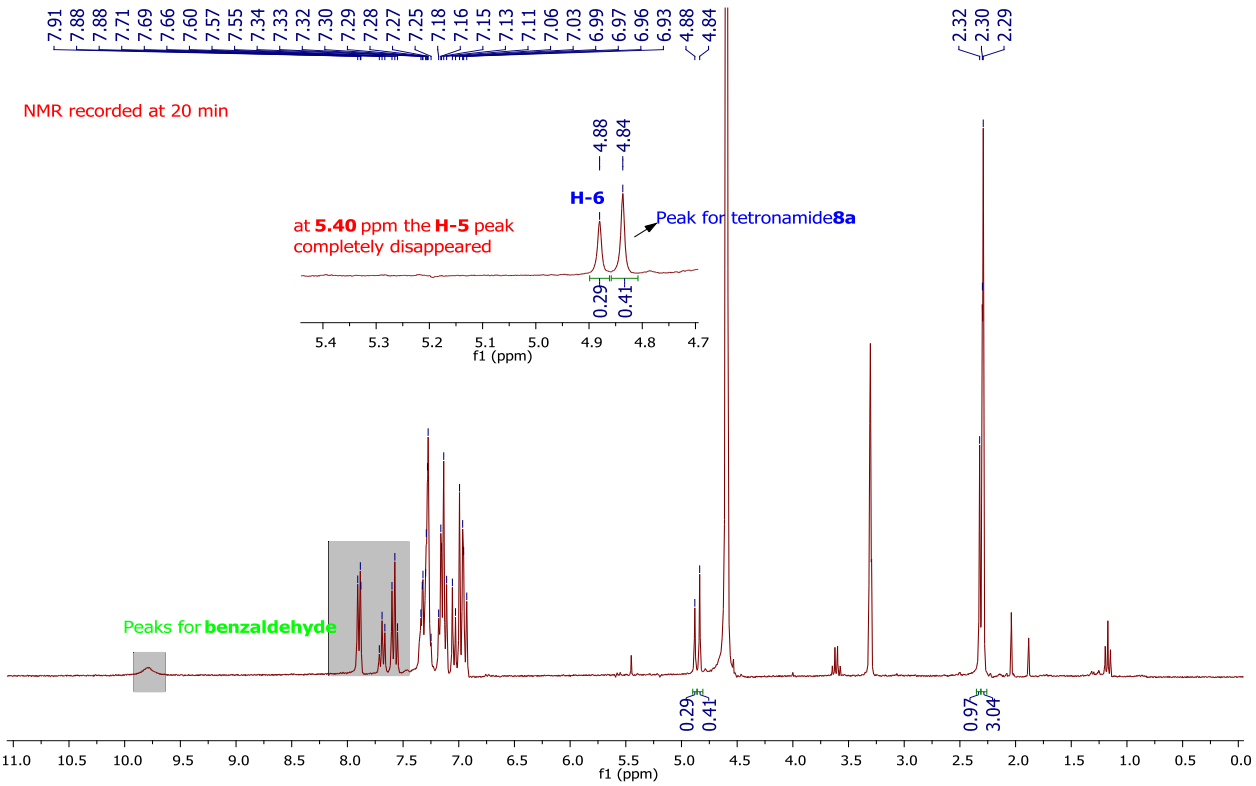


Figure S76 ^{1}H NMR (300 MHz, CD_3OD/D_2O; 2:1) recorded at 20 min after addition of NaOH.

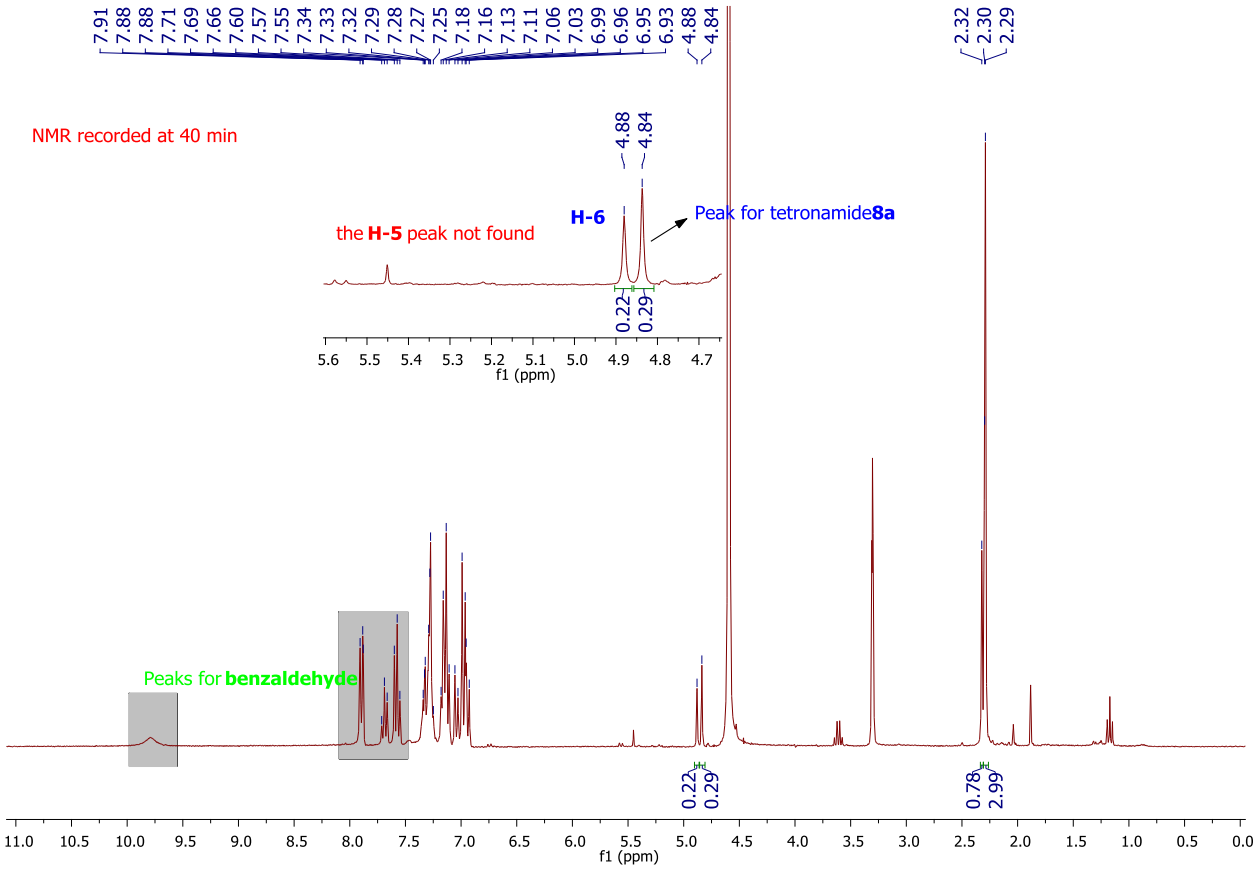


Figure S77 ^{1}H NMR (300 MHz, CD_3OD/D_2O; 2:1) recorded at 40 min after addition of NaOH.

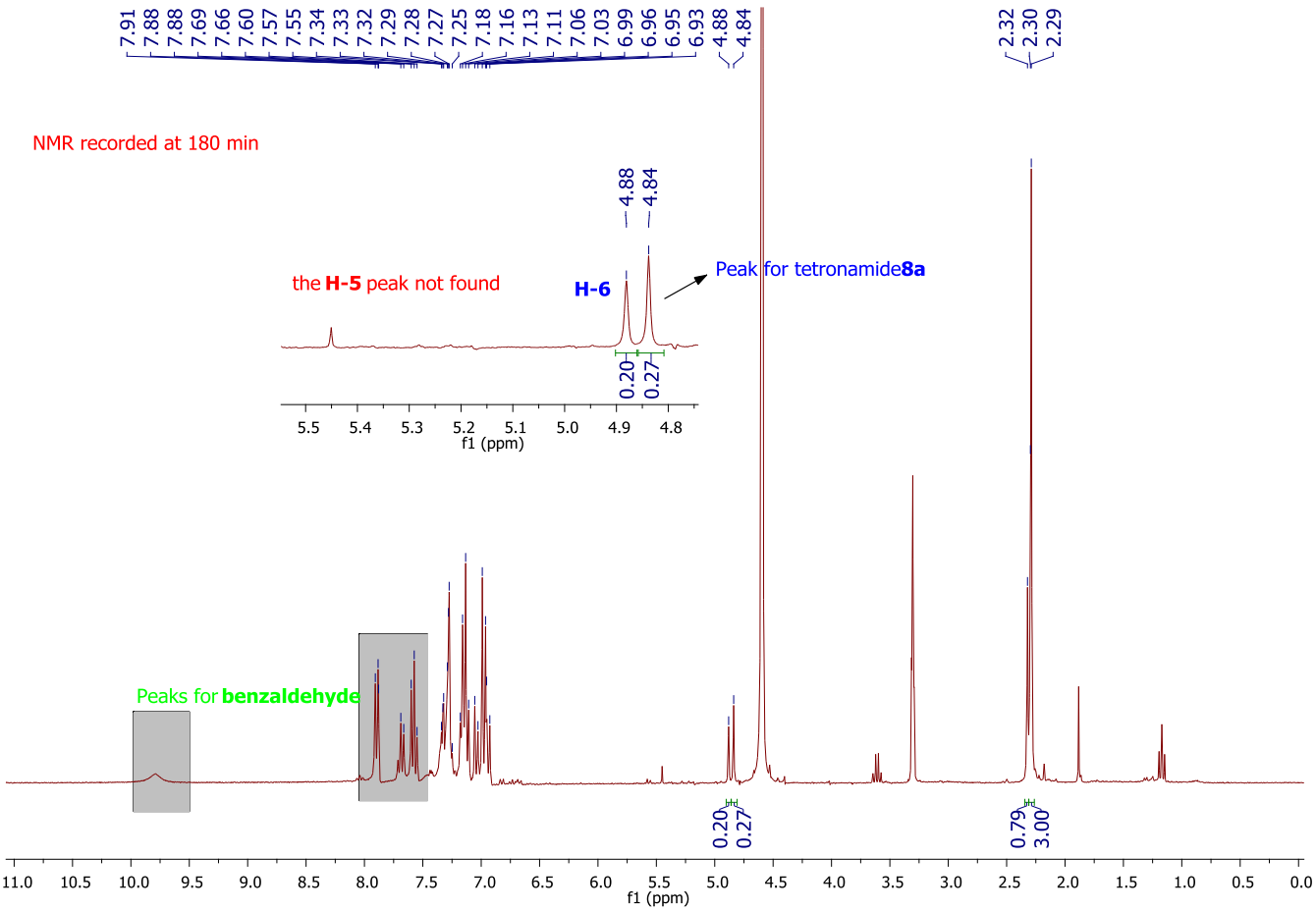


Figure S78 ^{1}H NMR (300 MHz, CD_3OD/D_2O; 2:1) recorded at 180 min after addition of NaOH.

5. Single crystal X-ray crystallography

5.1. X-ray data of aldol product ***syn*-12** (compound code: **MK49A**)

Table S10 Crystal data and structure refinement for MK49A.

Identification code	MK49A
Empirical formula	$C_{16}H_{13}Cl_2NO_4$
Formula weight	354.17
Temperature/K	100
Crystal system	orthorhombic
Space group	Pccn
a/Å	12.8328(2)
b/Å	26.5383(4)
c/Å	9.25770(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3152.81(8)
Z	8
ρ_{calc}g/cm^3	1.492
μ/mm^{-1}	3.886
F(000)	1456.0
Crystal size/mm^3	0.28 × 0.25 × 0.06
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.652 to 144.356
Index ranges	$-15 \leq h \leq 14$, $-32 \leq k \leq 32$, $-11 \leq l \leq 11$
Reflections collected	122420
Independent reflections	3102 [R_{int} = 0.0361, R_{sigma} = 0.0085]
Data/restraints/parameters	3102/0/217
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0805
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0806
Largest diff. peak/hole / e Å^{-3}	0.41/-0.38

Table S11 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for MK49A. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Cl1	5638.9(3)	3775.2(2)	5725.5(4)	18.24(11)
Cl2	6304.9(3)	7110.9(2)	6517.9(6)	43.89(15)
O1	5838.1(8)	4564.2(4)	8202.7(11)	21.8(2)
O2	6325.3(7)	5169.9(4)	6649.1(10)	16.8(2)
O3	8388.0(8)	5087.8(4)	5445.8(11)	15.6(2)
O4	6924.8(8)	6239.0(4)	5600.6(12)	20.4(2)
N1	6430.5(9)	4591.0(4)	3122.8(13)	16.3(2)
C1	5961.5(16)	2630.6(6)	606(2)	39.1(5)
C2	6111.4(12)	3147.7(6)	1255.6(18)	24.2(3)
C3	5467.2(13)	3543.9(6)	841.4(18)	27.4(4)
C4	5565.8(12)	4019.4(6)	1455.9(16)	21.9(3)
C5	6327.9(11)	4100.6(5)	2486.8(15)	15.7(3)
C6	7002.7(11)	3716.2(5)	2884.6(16)	18.8(3)
C7	6879.8(12)	3242.1(5)	2276.1(17)	21.8(3)
C8	6331.5(10)	4685.6(5)	4532.4(15)	14.1(3)
C9	6049.3(10)	4390.4(5)	5671.5(14)	14.7(3)
C10	6051.3(10)	4684.8(5)	6969.7(15)	16.2(3)
C11	6520.4(10)	5210.7(5)	5117.2(14)	14.6(3)
C12	7625.5(10)	5420.4(5)	4902.3(14)	13.8(3)
C13	7735.7(10)	5903.3(5)	5726.8(14)	14.8(3)
C14	8463.6(11)	6077.0(5)	6648.0(15)	17.5(3)
C15	8099.9(12)	6559.1(5)	7144.5(17)	21.7(3)
C16	7183.7(12)	6631.1(5)	6483.7(18)	23.3(3)

Table S12 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for MK49A. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	20.11(18)	15.38(17)	19.24(18)	-0.02(11)	1.70(12)	-4.83(12)
Cl2	30.2(2)	19.3(2)	82.2(4)	-15.7(2)	-8.4(2)	9.10(15)
O1	22.1(5)	26.8(5)	16.5(5)	-2.4(4)	3.7(4)	-9.6(4)
O2	17.6(5)	17.0(5)	15.9(5)	-3.5(4)	3.0(4)	-3.5(4)
O3	15.9(5)	15.3(5)	15.5(5)	-0.3(4)	-0.8(4)	4.4(4)
O4	16.7(5)	13.6(5)	31.0(6)	-1.7(4)	-4.4(4)	1.8(4)
N1	21.6(6)	13.6(6)	13.7(6)	0.6(5)	-1.3(5)	-1.6(5)
C1	44.1(11)	21.9(9)	51.4(11)	-12.6(8)	-15.7(9)	1.8(7)
C2	27.0(8)	18.1(7)	27.6(8)	-4.4(6)	-2.7(6)	-0.9(6)
C3	31.3(8)	21.4(8)	29.4(8)	-3.8(6)	-13.3(7)	-1.9(6)
C4	24.9(7)	17.5(7)	23.2(7)	0.4(6)	-6.4(6)	1.5(6)
C5	17.6(6)	14.9(6)	14.7(6)	-0.7(5)	1.9(5)	-2.3(5)
C6	16.6(7)	20.8(7)	19.0(7)	-1.2(5)	-1.5(5)	-0.2(5)
C7	20.1(7)	18.5(7)	26.8(8)	-1.3(6)	-0.2(6)	4.0(6)
C8	9.9(6)	15.4(6)	17.2(6)	-0.9(5)	-2.3(5)	0.9(5)
C9	12.7(6)	14.8(6)	16.7(6)	-1.2(5)	-0.4(5)	-1.6(5)
C10	10.9(6)	19.1(7)	18.7(7)	-1.1(5)	0.5(5)	-2.6(5)
C11	14.9(6)	15.0(6)	14.0(6)	-0.9(5)	-0.2(5)	0.9(5)
C12	13.8(6)	13.7(6)	13.8(6)	1.1(5)	-0.7(5)	0.8(5)
C13	14.2(6)	12.7(6)	17.7(7)	3.0(5)	1.6(5)	0.6(5)
C14	18.2(7)	14.7(6)	19.5(7)	2.8(5)	-1.4(5)	-1.7(5)
C15	25.5(8)	14.5(6)	25.2(7)	-2.1(6)	-1.4(6)	-4.8(6)
C16	23.5(7)	12.3(6)	34.0(8)	-3.8(6)	1.0(6)	0.4(5)

Table S13 Bond Lengths for MK49A.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C9	1.7161(14)	C3	C4	1.390(2)
Cl2	C16	1.7011(15)	C4	C5	1.383(2)
O1	C10	1.2166(18)	C5	C6	1.388(2)
O2	C10	1.3672(17)	C6	C7	1.388(2)
O2	C11	1.4441(16)	C8	C9	1.3627(19)
O3	C12	1.4106(15)	C8	C11	1.5145(18)
O4	C13	1.3750(16)	C9	C10	1.4335(19)
O4	C16	1.3643(18)	C11	C12	1.5364(18)
N1	C5	1.4344(17)	C12	C13	1.4982(18)
N1	C8	1.3349(18)	C13	C14	1.346(2)
C1	C2	1.511(2)	C14	C15	1.437(2)
C2	C3	1.391(2)	C15	C16	1.339(2)
C2	C7	1.389(2)			

Table S14 Bond Angles for MK49A.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O2	C11	109.17(10)	C10	C9	Cl1	119.64(10)
C16	O4	C13	105.02(11)	O1	C10	O2	120.60(12)
C8	N1	C5	124.27(12)	O1	C10	C9	130.01(13)
C3	C2	C1	120.08(15)	O2	C10	C9	109.37(11)
C7	C2	C1	121.69(14)	O2	C11	C8	104.74(10)
C7	C2	C3	118.23(14)	O2	C11	C12	108.32(11)
C4	C3	C2	121.27(14)	C8	C11	C12	115.77(11)
C5	C4	C3	119.23(14)	O3	C12	C11	111.56(10)
C4	C5	N1	119.31(13)	O3	C12	C13	106.74(10)
C4	C5	C6	120.63(13)	C13	C12	C11	109.33(11)
C6	C5	N1	120.05(12)	O4	C13	C12	116.08(11)
C7	C6	C5	119.20(13)	C14	C13	O4	110.91(12)
C6	C7	C2	121.37(14)	C14	C13	C12	132.94(12)
N1	C8	C9	132.35(13)	C13	C14	C15	106.39(13)
N1	C8	C11	120.48(12)	C16	C15	C14	105.42(13)
C9	C8	C11	107.15(12)	O4	C16	Cl2	114.87(11)
C8	C9	Cl1	130.62(11)	C15	C16	Cl2	132.87(12)
C8	C9	C10	109.58(12)	C15	C16	O4	112.25(13)

Table S15 Hydrogen Bonds for MK49A.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O3[1]	0.85(2)	2.06(2)	2.8168(16)	147.3(17)
O3	H3	O1[1]	0.83(2)	1.86(2)	2.6887(14)	176(2)

[1]3/2-X,+Y,-1/2+Z

Table S16 Torsion Angles for MK49A.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C9	C10	O1	3.5(2)	C8	N1	C5	C6	-61.28(19)
Cl1	C9	C10	O2	-175.17(9)	C8	C9	C10	O1	179.26(15)
O2	C11	C12	O3	63.62(13)	C8	C9	C10	O2	0.63(16)
O2	C11	C12	C13	-54.21(13)	C8	C11	C12	O3	-53.61(15)
O3	C12	C13	O4	-165.90(11)	C8	C11	C12	C13	-171.43(11)
O3	C12	C13	C14	10.6(2)	C9	C8	C11	O2	0.44(14)
O4	C13	C14	C15	-0.31(16)	C9	C8	C11	C12	119.64(13)
N1	C5	C6	C7	178.90(13)	C10	O2	C11	C8	-0.06(13)
N1	C8	C9	Cl1	-3.8(2)	C10	O2	C11	C12	-124.16(11)
N1	C8	C9	C10	-178.97(14)	C11	O2	C10	O1	-179.11(12)
N1	C8	C11	O2	179.01(12)	C11	O2	C10	C9	-0.33(14)
N1	C8	C11	C12	-61.79(16)	C11	C8	C9	Cl1	174.54(11)
C1	C2	C3	C4	177.89(17)	C11	C8	C9	C10	-0.65(15)
C1	C2	C7	C6	-179.00(16)	C11	C12	C13	O4	-45.10(15)
C2	C3	C4	C5	0.8(3)	C11	C12	C13	C14	131.41(16)
C3	C2	C7	C6	0.6(2)	C12	C13	C14	C15	-176.95(14)
C3	C4	C5	N1	-179.97(14)	C13	O4	C16	Cl2	179.35(10)
C3	C4	C5	C6	1.4(2)	C13	O4	C16	C15	0.02(17)
C4	C5	C6	C7	-2.4(2)	C13	C14	C15	C16	0.31(17)
C5	N1	C8	C9	-5.7(2)	C14	C15	C16	Cl2	-179.38(13)
C5	N1	C8	C11	176.13(12)	C14	C15	C16	O4	-0.20(18)
C5	C6	C7	C2	1.4(2)	C16	O4	C13	C12	177.45(12)
C7	C2	C3	C4	-1.7(3)	C16	O4	C13	C14	0.19(15)
C8	N1	C5	C4	120.05(16)					

Table S17 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for MK49A.

Atom	x	y	z	U(eq)
H1A	5401	2455	1119	59
H1B	6610	2438	694	59
H1C	5777	2664	-417	59
H3A	4950	3488	125	33
H4	5115	4285	1171	26
H6	7542	3777	3565	23
H7	7331	2977	2564	26
H11	6005	5448	4680	18
H12	7753	5483	3852	17
H14	9093	5913	6917	21
H15	8438	6780	7802	26
H1	6497(14)	4840(7)	2550(20)	23(5)
H3	8656(15)	4927(8)	4770(20)	29(5)

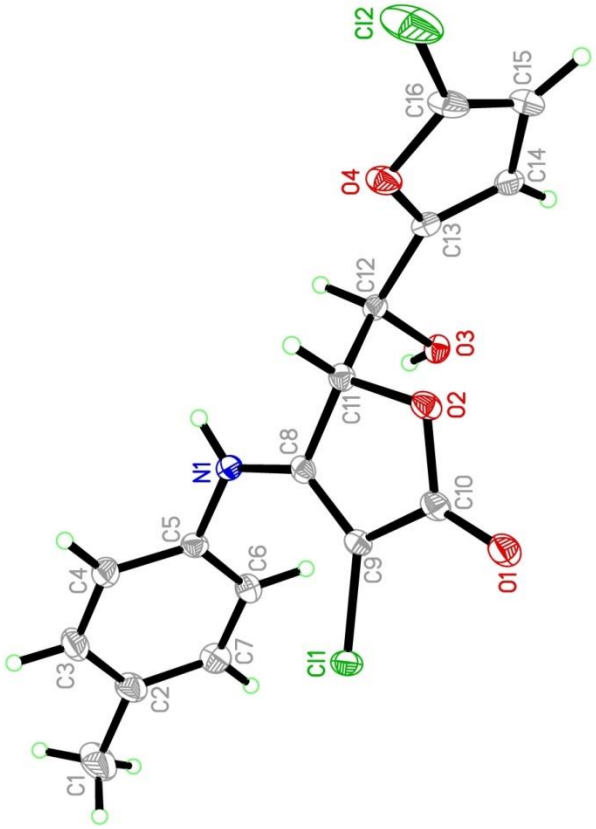


Figure S79 X-ray structure determined for major diastereomer of compound **12** and found to be ***syn*** (The ORTEP of one of the molecules in the asymmetric unit cell with thermal ellipsoids set at the 50% probability level).

5.2. X-ray data of aldol product ***anti*-12** (compound code: **MK49B**)

Table S18 Crystal data and structure refinement for MK49B.

Identification code	MK49B	
Empirical formula	$C_{16}H_{13}Cl_2NO_4$	
Formula weight	354.17	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.7051(13) Å	α= 90°.
	b = 7.9191(7) Å	β= 93.6625(13)°.
	c = 26.746(2) Å	γ = 90°.
Volume	3108.3(5) $Å^3$	
Z	8	
Density (calculated)	1.514 Mg/m^3	
Absorption coefficient	0.437 mm^{-1}	
F(000)	1456	
Crystal size	0.480 x 0.260 x 0.060 mm^3	
Theta range for data collection	2.776 to 28.280°.	
Index ranges	-19<=h<=19, -10<=k<=10, -35<=l<=35	
Reflections collected	15967	
Independent reflections	3856 [R(int) = 0.0335]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.974 and 0.873	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3856 / 0 / 214	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0759	
R indices (all data)	R1 = 0.0441, wR2 = 0.0816	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.315 and -0.359 $e.Å^{-3}$	

Table S19 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for MK49B. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9355(1)	-2972(2)	4661(1)	34(1)
C(2)	8875(1)	-2384(2)	5113(1)	24(1)
C(3)	8368(1)	-3486(2)	5389(1)	27(1)
C(4)	7920(1)	-2926(2)	5800(1)	24(1)
C(5)	7992(1)	-1249(2)	5948(1)	19(1)
C(6)	8509(1)	-131(2)	5681(1)	22(1)
C(7)	8931(1)	-707(2)	5264(1)	23(1)
N(1)	7582(1)	-726(2)	6391(1)	20(1)
C(8)	7251(1)	812(2)	6494(1)	17(1)
C(9)	6946(1)	2149(2)	6212(1)	18(1)
Cl(1)	6813(1)	2408(1)	5576(1)	27(1)
C(10)	6667(1)	3478(2)	6537(1)	18(1)
O(1)	6352(1)	4870(1)	6440(1)	23(1)
O(2)	6799(1)	2971(1)	7023(1)	18(1)
C(11)	7193(1)	1304(2)	7036(1)	18(1)
C(12)	8126(1)	1355(2)	7324(1)	19(1)
O(3)	7997(1)	2000(1)	7813(1)	22(1)
C(13)	8824(1)	2352(2)	7068(1)	19(1)
C(14)	9545(1)	1910(2)	6811(1)	27(1)
C(15)	9959(1)	3431(2)	6654(1)	29(1)
C(16)	9458(1)	4685(2)	6830(1)	23(1)
Cl(2)	9565(1)	6824(1)	6812(1)	37(1)
O(4)	8750(1)	4090(1)	7082(1)	21(1)

Table S20 Bond lengths [Å] and angles [°] for MK49B.

C(1)-C(2)	1.512(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(7)	1.389(2)
C(2)-C(3)	1.390(2)
C(3)-C(4)	1.390(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.388(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.392(2)
C(5)-N(1)	1.4264(18)
C(6)-C(7)	1.387(2)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
N(1)-C(8)	1.3468(18)
N(1)-H(1N)	0.835(19)
C(8)-C(9)	1.359(2)
C(8)-C(11)	1.5105(19)
C(9)-C(10)	1.441(2)
C(9)-Cl(1)	1.7128(14)
C(10)-O(1)	1.2168(17)
C(10)-O(2)	1.3631(16)
O(2)-C(11)	1.4411(17)
C(11)-C(12)	1.531(2)
C(11)-H(11)	1.0000
C(12)-O(3)	1.4280(16)
C(12)-C(13)	1.495(2)
C(12)-H(12)	1.0000
O(3)-H(3A)	0.8400
C(13)-C(14)	1.347(2)
C(13)-O(4)	1.3814(17)
C(14)-C(15)	1.425(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.340(2)
C(15)-H(15)	0.9500
C(16)-O(4)	1.3609(17)

C(16)-Cl(2)	1.7023(17)

C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(7)-C(2)-C(3)	117.95(14)
C(7)-C(2)-C(1)	120.39(15)
C(3)-C(2)-C(1)	121.66(15)
C(4)-C(3)-C(2)	121.17(15)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	119.86(14)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	119.88(13)
C(4)-C(5)-N(1)	119.01(13)
C(6)-C(5)-N(1)	120.98(13)
C(7)-C(6)-C(5)	119.25(14)
C(7)-C(6)-H(6)	120.4
C(5)-C(6)-H(6)	120.4
C(6)-C(7)-C(2)	121.84(14)
C(6)-C(7)-H(7)	119.1
C(2)-C(7)-H(7)	119.1
C(8)-N(1)-C(5)	127.56(12)
C(8)-N(1)-H(1N)	115.5(12)
C(5)-N(1)-H(1N)	116.8(12)
N(1)-C(8)-C(9)	134.64(13)
N(1)-C(8)-C(11)	118.17(12)
C(9)-C(8)-C(11)	107.17(12)
C(8)-C(9)-C(10)	109.34(12)
C(8)-C(9)-Cl(1)	131.06(11)
C(10)-C(9)-Cl(1)	119.53(11)
O(1)-C(10)-O(2)	119.96(13)
O(1)-C(10)-C(9)	130.69(13)
O(2)-C(10)-C(9)	109.35(12)
C(10)-O(2)-C(11)	109.02(10)

O(2)-C(11)-C(8)	105.06(11)
O(2)-C(11)-C(12)	109.50(11)
C(8)-C(11)-C(12)	112.69(11)
O(2)-C(11)-H(11)	109.8
C(8)-C(11)-H(11)	109.8
C(12)-C(11)-H(11)	109.8
O(3)-C(12)-C(13)	111.45(12)
O(3)-C(12)-C(11)	107.63(11)
C(13)-C(12)-C(11)	113.81(11)
O(3)-C(12)-H(12)	107.9
C(13)-C(12)-H(12)	107.9
C(11)-C(12)-H(12)	107.9
C(12)-O(3)-H(3A)	109.5
C(14)-C(13)-O(4)	109.79(13)
C(14)-C(13)-C(12)	133.07(14)
O(4)-C(13)-C(12)	117.14(12)
C(13)-C(14)-C(15)	107.26(14)
C(13)-C(14)-H(14)	126.4
C(15)-C(14)-H(14)	126.4
C(16)-C(15)-C(14)	105.52(14)
C(16)-C(15)-H(15)	127.2
C(14)-C(15)-H(15)	127.2
C(15)-C(16)-O(4)	111.90(14)
C(15)-C(16)-Cl(2)	132.35(13)
O(4)-C(16)-Cl(2)	115.72(11)
C(16)-O(4)-C(13)	105.53(11)

Symmetry transformations used to generate equivalent atoms:

Table S21 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for MK49B. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	34(1)	39(1)	29(1)	-11(1)	11(1)	-2(1)
C(2)	22(1)	30(1)	21(1)	-5(1)	2(1)	1(1)
C(3)	34(1)	21(1)	26(1)	-7(1)	6(1)	-2(1)
C(4)	31(1)	19(1)	21(1)	-2(1)	6(1)	-4(1)
C(5)	22(1)	20(1)	15(1)	-1(1)	2(1)	1(1)
C(6)	23(1)	19(1)	23(1)	-1(1)	2(1)	-2(1)
C(7)	20(1)	26(1)	25(1)	1(1)	5(1)	-1(1)
N(1)	30(1)	16(1)	15(1)	1(1)	6(1)	0(1)
C(8)	18(1)	18(1)	16(1)	-2(1)	4(1)	-5(1)
C(9)	21(1)	20(1)	14(1)	-1(1)	2(1)	-2(1)
Cl(1)	40(1)	27(1)	15(1)	0(1)	0(1)	5(1)
C(10)	16(1)	20(1)	18(1)	-1(1)	2(1)	-3(1)
O(1)	25(1)	20(1)	23(1)	-1(1)	1(1)	4(1)
O(2)	21(1)	18(1)	16(1)	-1(1)	4(1)	1(1)
C(11)	23(1)	15(1)	16(1)	-1(1)	6(1)	-2(1)
C(12)	26(1)	18(1)	14(1)	-1(1)	2(1)	2(1)
O(3)	32(1)	22(1)	12(1)	-1(1)	2(1)	4(1)
C(13)	21(1)	20(1)	16(1)	-2(1)	-1(1)	3(1)
C(14)	23(1)	30(1)	29(1)	-5(1)	4(1)	5(1)
C(15)	21(1)	40(1)	26(1)	-3(1)	7(1)	-3(1)
C(16)	18(1)	29(1)	21(1)	3(1)	1(1)	-4(1)
Cl(2)	31(1)	29(1)	53(1)	7(1)	4(1)	-9(1)
O(4)	20(1)	19(1)	23(1)	0(1)	5(1)	0(1)

Table S22 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for MK49B.

	x	y	z	U(eq)
H(1A)	9994	-3222	4760	50
H(1B)	9325	-2083	4406	50
H(1C)	9057	-3994	4524	50
H(3)	8328	-4642	5295	32
H(4)	7564	-3690	5980	28
H(6)	8573	1014	5784	26
H(7)	9266	67	5077	28
H(1N)	7586(12)	-1420(20)	6626(7)	27(5)
H(11)	6782	503	7203	21
H(12)	8353	169	7361	23
H(3A)	8264	1371	8029	33
H(14)	9741	792	6746	33
H(15)	10481	3533	6464	35

Table S23 Torsion angles [°] for MK49B.

C(7)-C(2)-C(3)-C(4)	0.8(2)
C(1)-C(2)-C(3)-C(4)	-179.08(16)
C(2)-C(3)-C(4)-C(5)	-1.6(2)
C(3)-C(4)-C(5)-C(6)	0.5(2)
C(3)-C(4)-C(5)-N(1)	-175.51(14)
C(4)-C(5)-C(6)-C(7)	1.3(2)
N(1)-C(5)-C(6)-C(7)	177.20(14)
C(5)-C(6)-C(7)-C(2)	-2.1(2)
C(3)-C(2)-C(7)-C(6)	1.0(2)
C(1)-C(2)-C(7)-C(6)	-179.09(15)
C(4)-C(5)-N(1)-C(8)	-150.92(15)
C(6)-C(5)-N(1)-C(8)	33.2(2)
C(5)-N(1)-C(8)-C(9)	22.5(3)
C(5)-N(1)-C(8)-C(11)	-156.15(14)
N(1)-C(8)-C(9)-C(10)	179.75(15)
C(11)-C(8)-C(9)-C(10)	-1.51(16)
N(1)-C(8)-C(9)-Cl(1)	2.8(3)
C(11)-C(8)-C(9)-Cl(1)	-178.43(11)
C(8)-C(9)-C(10)-O(1)	-179.59(15)
Cl(1)-C(9)-C(10)-O(1)	-2.3(2)
C(8)-C(9)-C(10)-O(2)	0.07(16)
Cl(1)-C(9)-C(10)-O(2)	177.40(9)
O(1)-C(10)-O(2)-C(11)	-178.81(13)
C(9)-C(10)-O(2)-C(11)	1.49(15)
C(10)-O(2)-C(11)-C(8)	-2.32(14)
C(10)-O(2)-C(11)-C(12)	118.96(12)
N(1)-C(8)-C(11)-O(2)	-178.68(12)
C(9)-C(8)-C(11)-O(2)	2.34(15)
N(1)-C(8)-C(11)-C(12)	62.17(16)
C(9)-C(8)-C(11)-C(12)	-116.82(13)
O(2)-C(11)-C(12)-O(3)	57.48(14)
C(8)-C(11)-C(12)-O(3)	174.02(11)
O(2)-C(11)-C(12)-C(13)	-66.55(14)
C(8)-C(11)-C(12)-C(13)	49.99(16)
O(3)-C(12)-C(13)-C(14)	133.26(17)
C(11)-C(12)-C(13)-C(14)	-104.79(19)
O(3)-C(12)-C(13)-O(4)	-47.11(16)

C(11)-C(12)-C(13)-O(4)	74.83(15)
O(4)-C(13)-C(14)-C(15)	0.28(17)
C(12)-C(13)-C(14)-C(15)	179.93(15)
C(13)-C(14)-C(15)-C(16)	0.22(18)
C(14)-C(15)-C(16)-O(4)	-0.65(18)
C(14)-C(15)-C(16)-Cl(2)	176.96(13)
C(15)-C(16)-O(4)-C(13)	0.82(16)
Cl(2)-C(16)-O(4)-C(13)	-177.23(10)
C(14)-C(13)-O(4)-C(16)	-0.66(16)
C(12)-C(13)-O(4)-C(16)	179.63(12)

Symmetry transformations used to generate equivalent atoms:

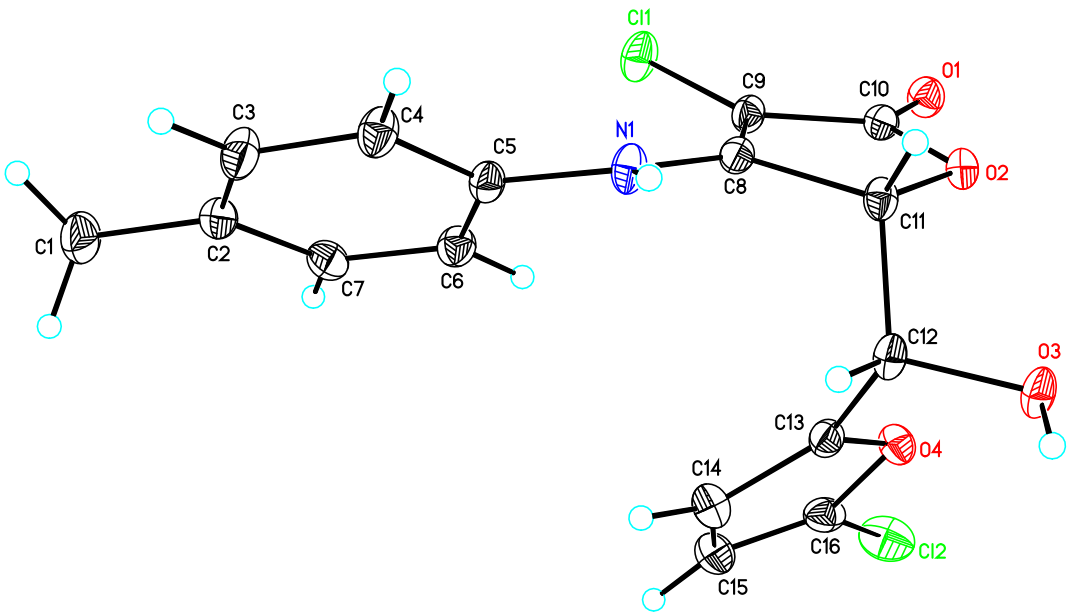


Figure S80 X-ray structure determined for minor diastereomer of compound **12** and found to be ***anti*** (The ORTEP of one of the molecules in the asymmetric unit cell with thermal ellipsoids set at the 50% probability level).