Synthesis of *exo*-Imidazolidin-2-one Dienes, their Isomerization and Selectivity in Diels-Alder Cycloadditions

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SUPPORTING INFORMATION

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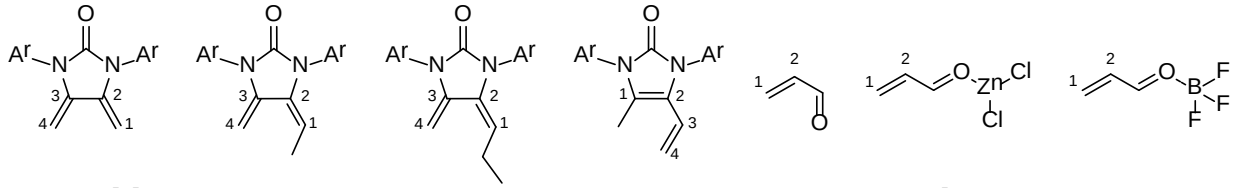
1. Frontier Molecular Orbitals of Dienes **5c**, **12a**, **14** and **16a** and Dienophiles **18a**, **18a**-$ZnCl_2$ and **18a**-BF_3.

TABLE S1. HF/6-31G(d,p) Energies (eV) and Coefficients (C_i) of the Frontier Molecular Orbitals for Dienes **5c**, **12a**, **14** and **16a** and Dienophiles **18a**, **18a**-$ZnCl_2$ and **18a**-BF_3[a].



5c, Ar = C_6H_4-4-OMe **12a** **14** **16a** **18a** **18a**-$ZnCl_2$ **18a**-BF_3

		HOMO					LUMO					
Compd[b]	*E* (eV)	C_1	C_2	C_3	C_4	ΔC_I[c]	*E* (eV)	C_1	C_2	C_3	C_4	ΔC_I[c]
5c	-7.729	0.221	0.112	-0.112	-0.221	0.000	2.987	0.251	-0.239	-0.239	0.251	0.000
12a	-7.610	0.223	0.104	-0.140	-0.238	0.015	3.084	0.256	-0.234	-0.227	0.270	0.014
14	-7.602	0.225	0.105	-0.141	-0.236	0.011	3.053	0.252	-0.228	-0.226	0.264	0.012
16a	-7.171	0.252	0.253	-0.068	-0.156	0.096	3.229	0.376	-0.225	-0.215	0.464	0.088
18a	-10.736	0.345	0.352			-0.007	2.472	0.323	-0.207			0.116
18a-$ZnCl_2$	-11.724	0.058	0.062			-0.004	0.646	0.324	-0.148			0.176
18a-BF_3	-11.822	0.335	0.373			-0.038	0.965	0.325	-0.151			0.173

[a] These are the values of the p_z coefficients, the relative p_z' contributions and their ΔC_i are analogous. [b] For the most stable planar *s-cis* conformation for alkene **18a**, and *s-trans* conformation for metal-complexed alkenes. [c] Carbon 4–carbon 1 for the dienes; carbon 1–carbon 2 for the dienophile.

TABLE S2. Calculated [M06-2X/6-31+G(d,p)] Relative Zero Point-Corrected Energies (kcal/mol) of the Supramolecular Complexes (SCs), TSs (TS1 and TS2), Zwitterionic Intermediates (ZI), and Adducts Located in the Potential Surfaces of the Diels-Alder Reactions of Diene 12a and Dienophiles 18a, 18a-$ZnCl_2$ and 18a-BF_3

Cycloaddends	SC	TS1	ZI	TS2	diff[a]	diff[b]	diff[c]
12a/**18a**-*ortho-endo*	0.00	17.05	-	-	0.00	-	-
12a/**18a**-*ortho-exo*	1.98	21.49	-	-	4.44	-	-
12a/**18a**-*meta-endo*	1.42	22.77	-	-	5.72	-	-
12a/**18a**-*meta-exo*	1.75	22.03	-	-	4.98	-	-

12a/**18a**-$ZnCl_2$-*ortho-endo*	6.76	13.66	1.36	6.60	0.00	0.00	0.00
12a/**18a**-$ZnCl_2$-*ortho-exo*	0.00	17.46	6.50	11.79	3.80	5.14	5.19
12a/**18a**-$ZnCl_2$-*meta-endo*	15.61	22.86	20.35	23.14	9.48	18.99	16.54
12a/**18a**-$ZnCl_2$-*meta-exo*	0.98	20.93	14.44	24.78	11.12	23.42	18.18
12a/**18a**-BF_3-*ortho-endo*	1.74	4.71	-15.12	-5.78	0.00	0.00	0.00
12a/**18a**-BF_3-*ortho-exo*	0.83	7.81	-4.96	2.20	3.10	10.16	7.98
12a/**18a**-BF_3-*meta-endo*	0.00	7.05	1.00	1.02	2.34	16.12	6.80
12a/**18a**-BF_3-*meta-exo*	2.60	8.67	1.71	4.18	3.96	16.83	9.96

[a] Energy differences for the rate-determining TS, relative to the most stable approach of the series for the same catalyst. [b] Energy differences for the ZIs, relative to the most stable approach of the series for the same catalyst. [c] Energy differences for the TS2s, relative to the most stable approach of the series for the same catalyst.

2. Calculation of synchronicities of the Diels-Alder cycloadditions of diene **16a** and maleimide (**6**).

The synchronicities of the Diels-Alder cycloadditions of diene **16a** and maleimide (**6**) to yield *endo* and *exo* cycloadducts **32a** and **33a**, respectively, were computed as follows. Bond indexes, B(*A*,*B*), for the bonds involved in the chemical reaction under study, were obtained through Wiberg analysis[1] of the corresponding transition states in the NBO basis.[2] The relative variation of the bond index at the transition states was determined for each bond involved in the chemical process according to the following expression:[3]

$$\delta B_i = \frac{\delta B_i^{TS} - \delta B_i^{SC}}{\delta B_i^{P} - \delta B_i^{SC}} \qquad \text{(Eq. S1)}$$

where superscripts *TS*, *SC* and *P* refer to the transition structures, supramolecular complexes and products (**32a** or **33a**), for the *endo* and *exo* reaction coordinates, respectively. The *i* subscripts refer to the each of the sets of atom pairs (*A*,*B*) involved in the [4+2] cycloaddition, indicated in Figure 6 as (*1*,*2*), (*2*,*3*), (*3*,*4*), (*4*,*5*), (*5*,*6*) and (*1*,*6*). The average value δB_{av} over all these bonds is:[3]

$$\delta B_{av} = \frac{1}{n}\sum_{i=1}^{n} \delta B_i \qquad \text{(Eq. S2)}$$

where *n* is the number of sets of atom pairs under consideration (n = 6). An average value of $\delta B_{av} < 0.5$ corresponds to an early transition state, while a value of $\delta B_{av} > 0.5$ describes a late transition structure. Since the δB_{av} values for the *endo* and *exo* manifolds are 0.39 and 0.42, we concluded that both [4+2] cycloadditions occur via early transition structures and that the *endo* route takes place through an earlier saddle point than that associated with the *exo* reaction coordinate.

The synchronicities (*Sy*) of the ***endo*-SC → *endo*-TS → 32a** and ***exo*-SC → *exo*-TS → 33a** [4+2] cycloadditions were computed according to the following equation:

$$Sy = 1 - \frac{1}{2n-2}\sum_{i=1}^{n} \frac{\left|\delta B_i - \delta B_{av}\right|}{\delta B_{av}} \qquad \text{(Eq. S3)}$$

A value of *Sy* = 1 would correspond to a fully synchronous cycloaddition reaction.

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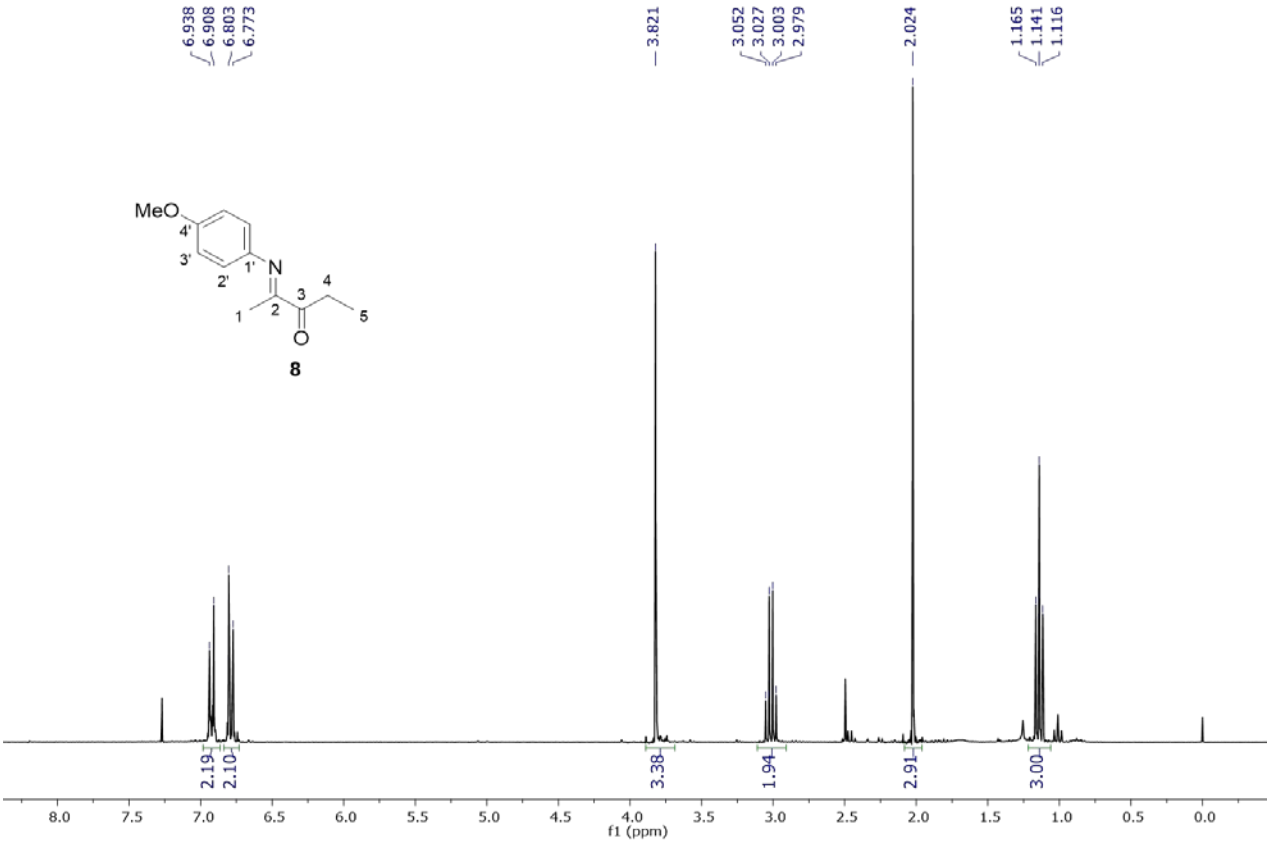
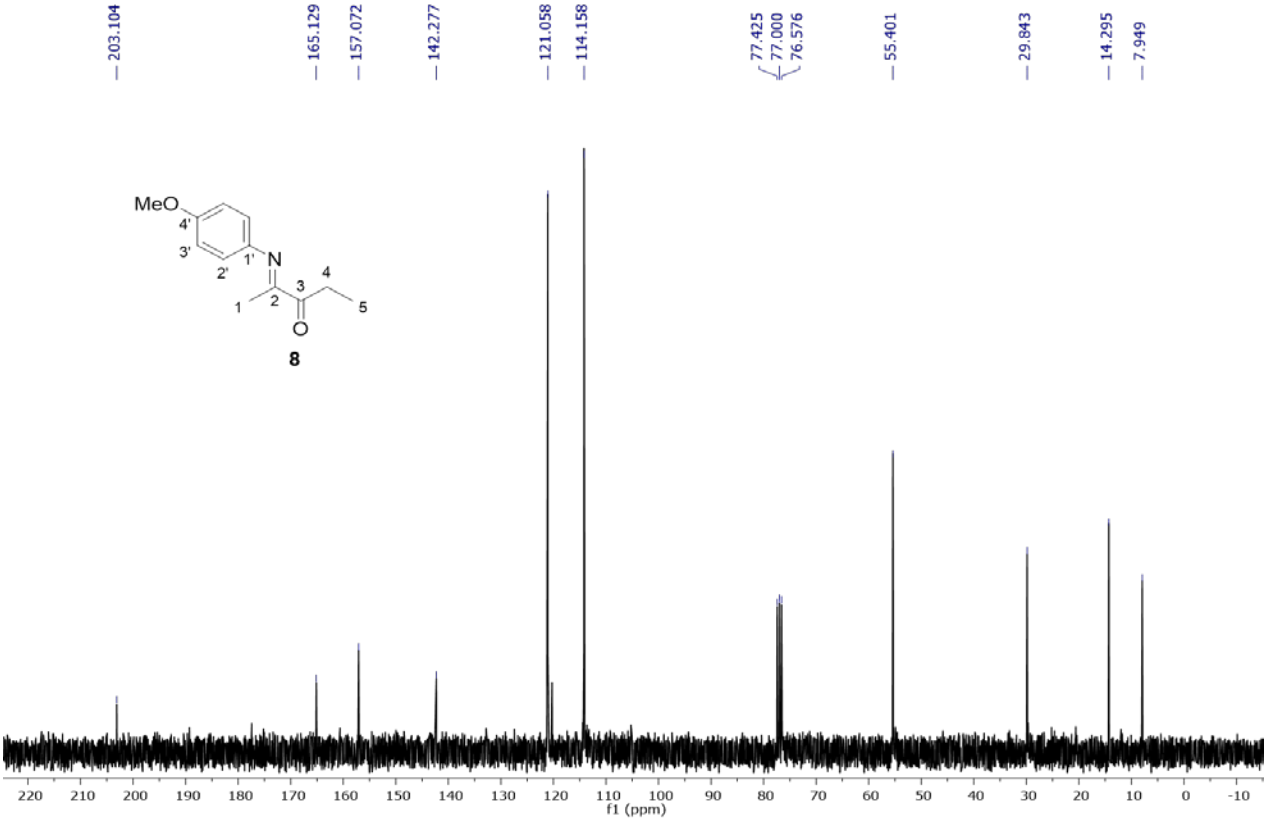
1. Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083–1096.
2. (a) NBO 5.0: Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F., Theoretical Chemistry Institute, University of Wisconsin: Madison, 2001. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev*. **1988**, *88*, 899–926. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735–746.
3. (a) Moyano, A.; Pericàs, M. A.; Valentí, E. *J. Org. Chem.* **1989**, *54*, 573–582. (b) Lecea, B.; Arrieta, A.; Lopez, X.; Ugalde, J. M.; Cossío, F. P. *J. Am. Chem. Soc.* **1995**, *117*, 12321–12314. (c) Schleyer, P. v. R.; Wu, J. I.; Cossío, F. P.; Fernández, I. *Chem. Soc. Rev.* **2014**, 43, 4909-4921.

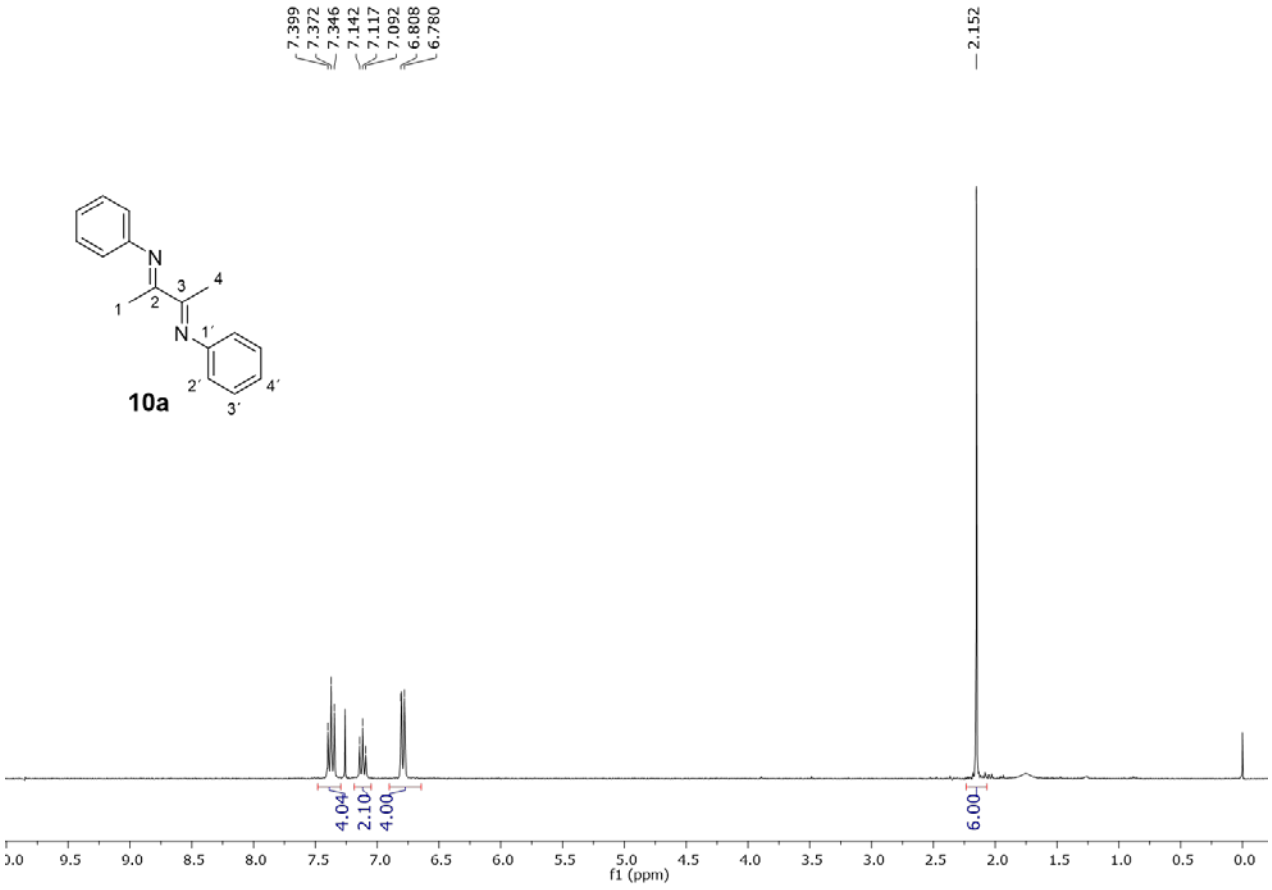
3. ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds.



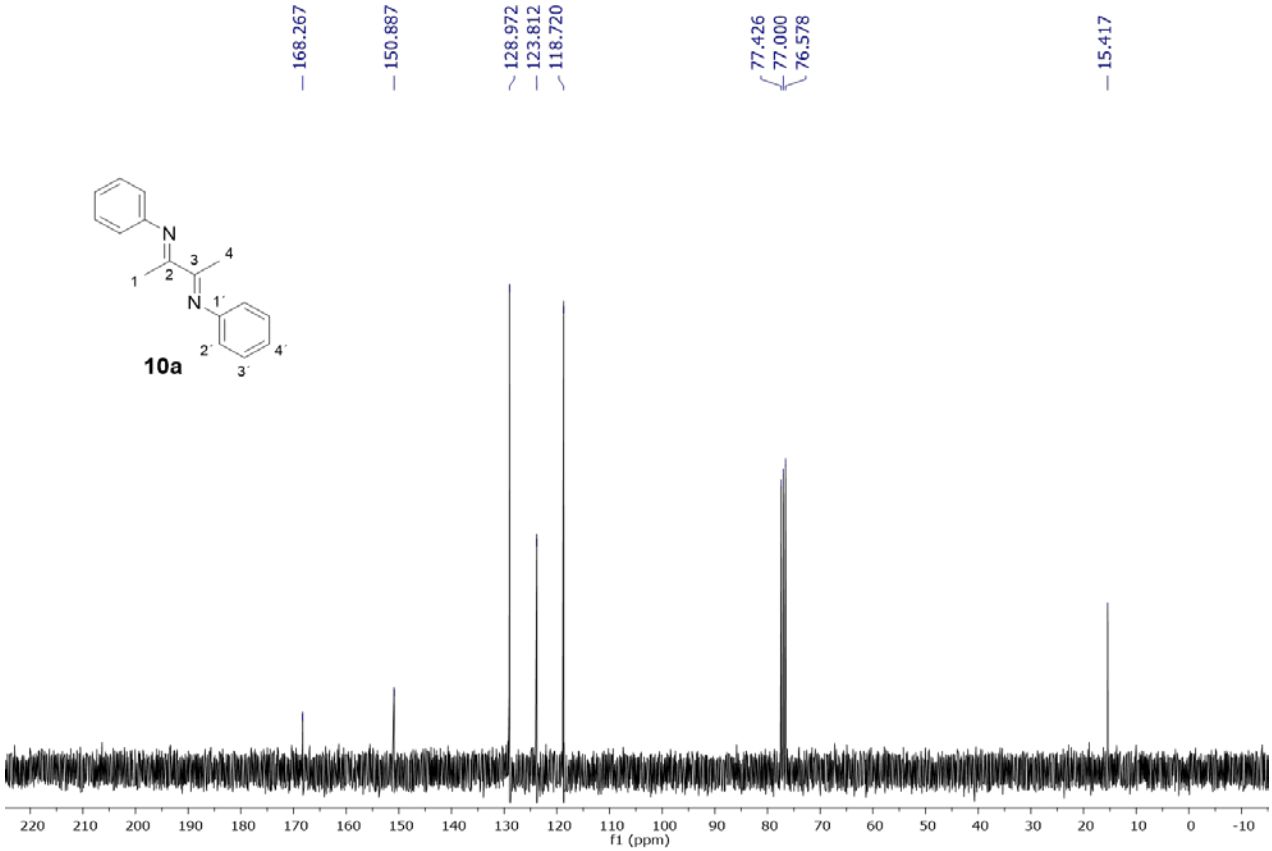
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **8**.



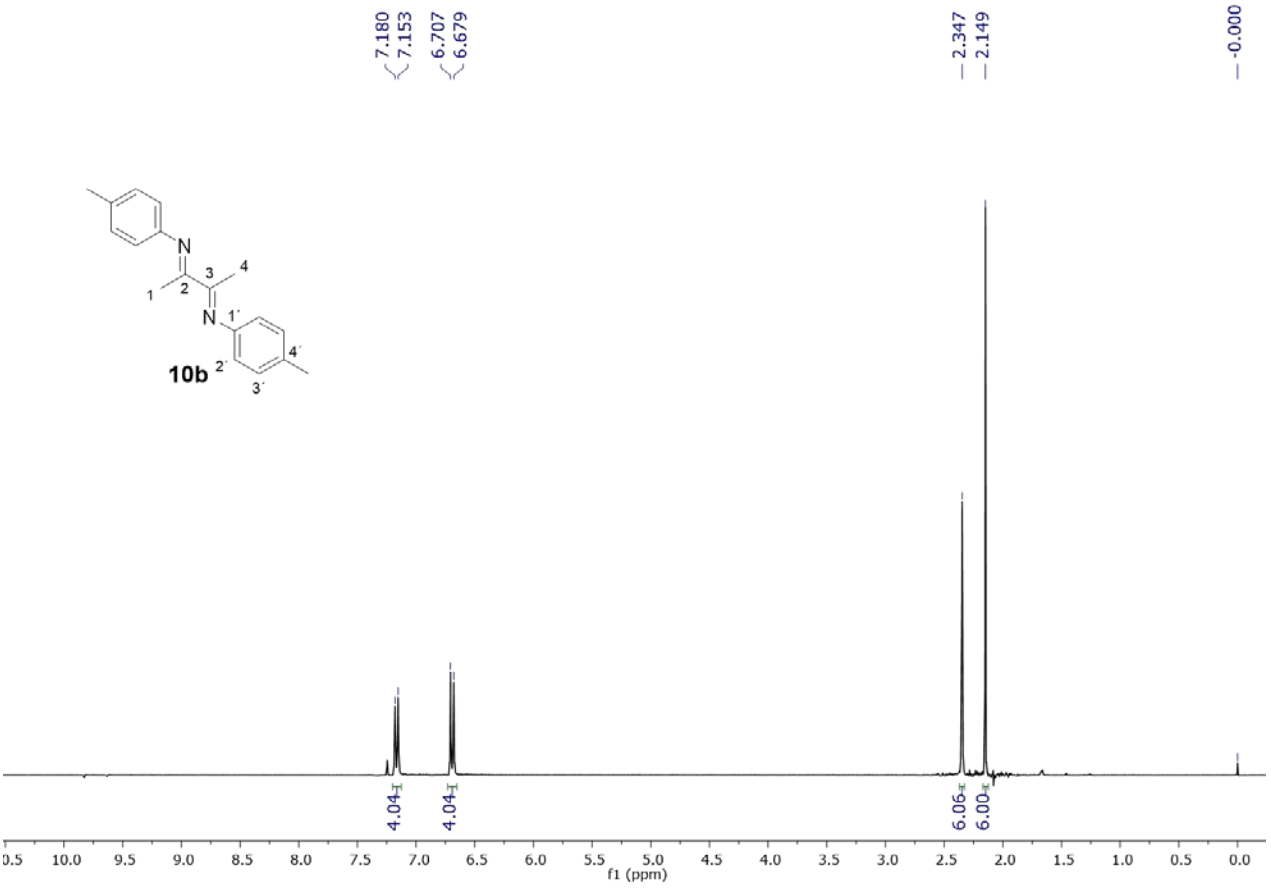
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of **8**.



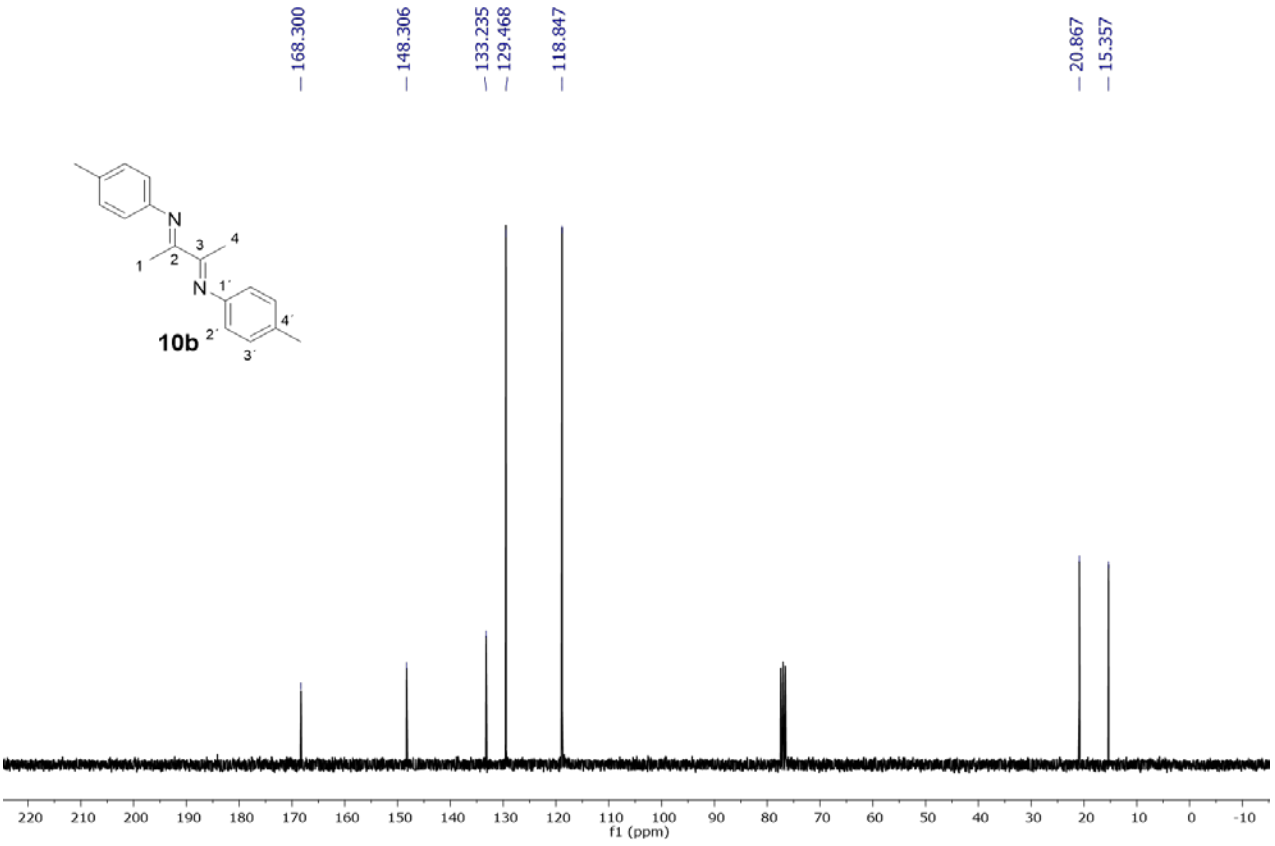
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **10a**.



^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **10a**.



^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **10b**.



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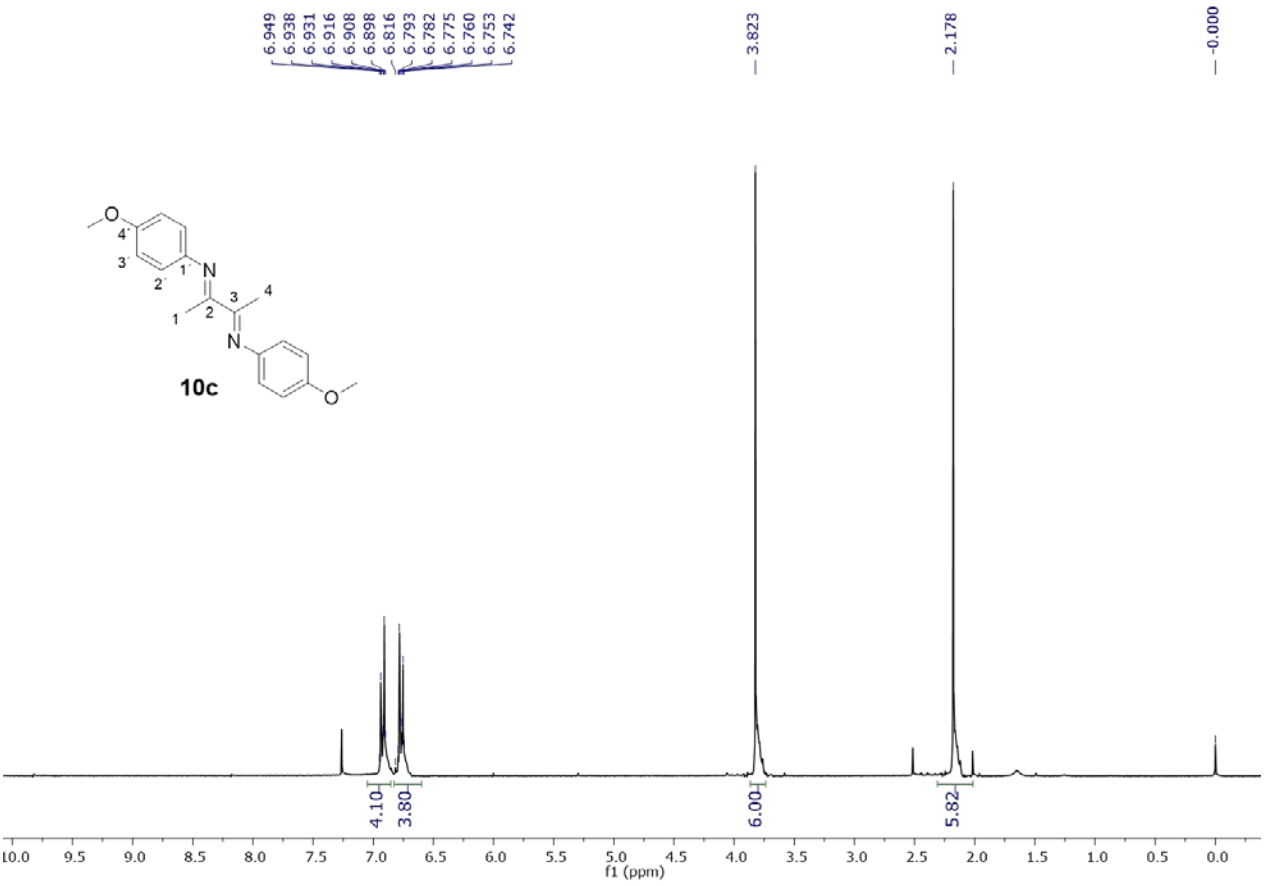

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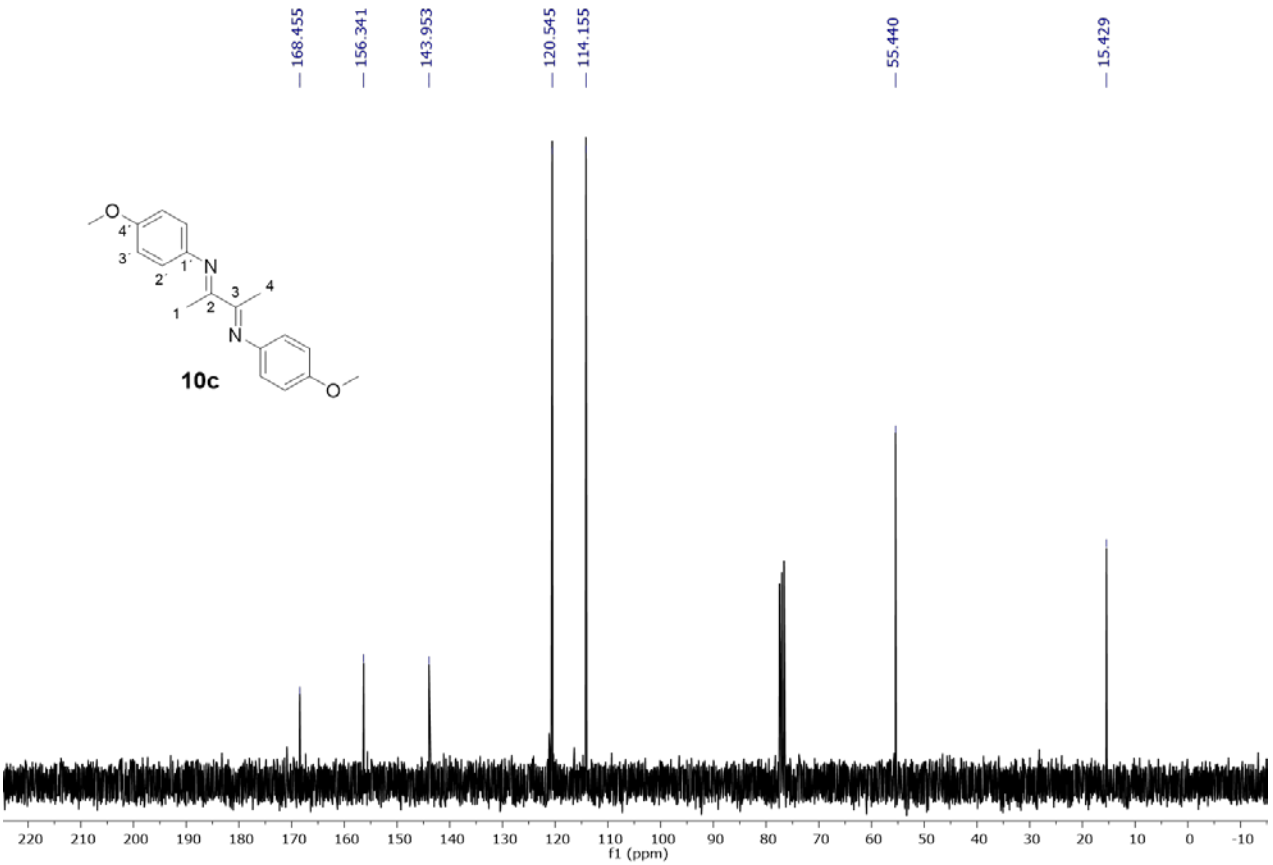

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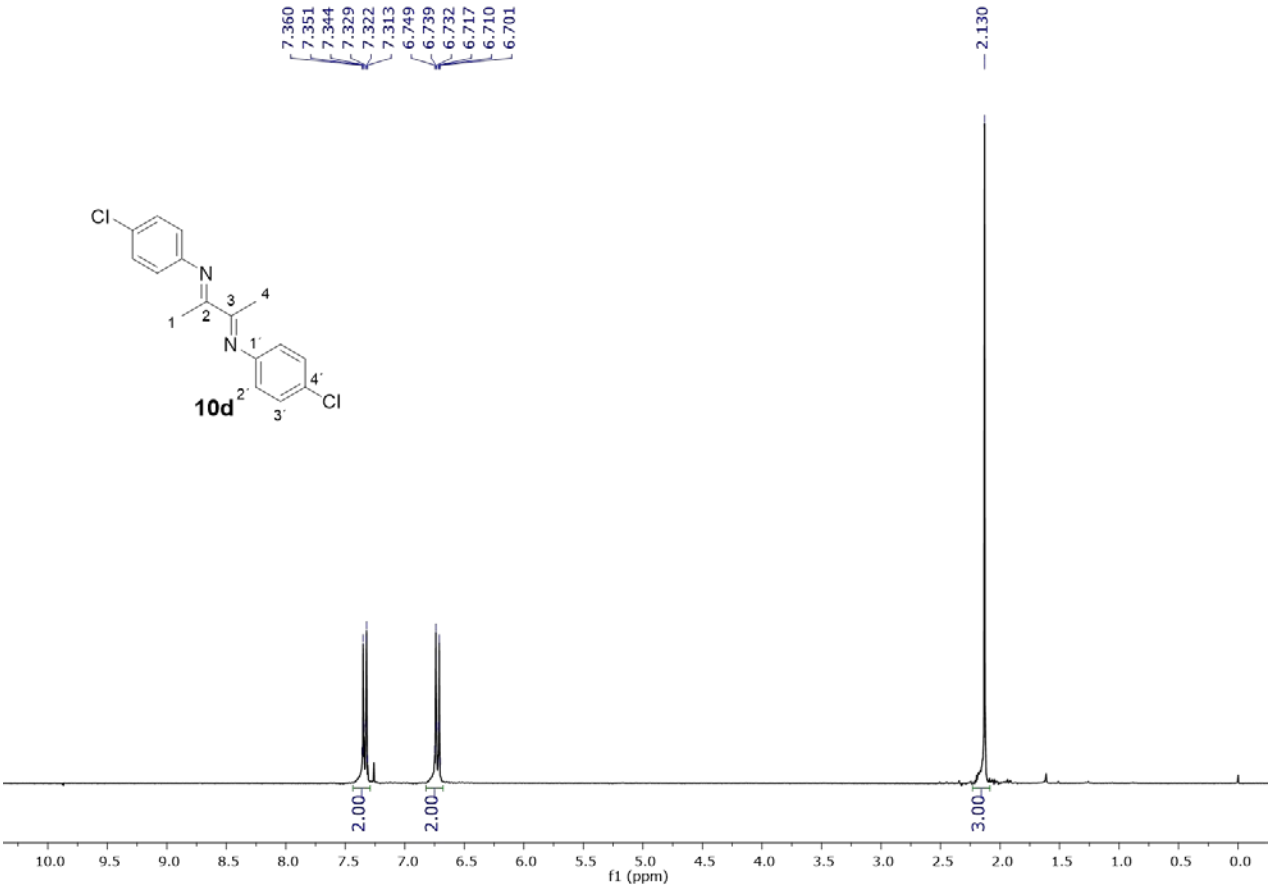

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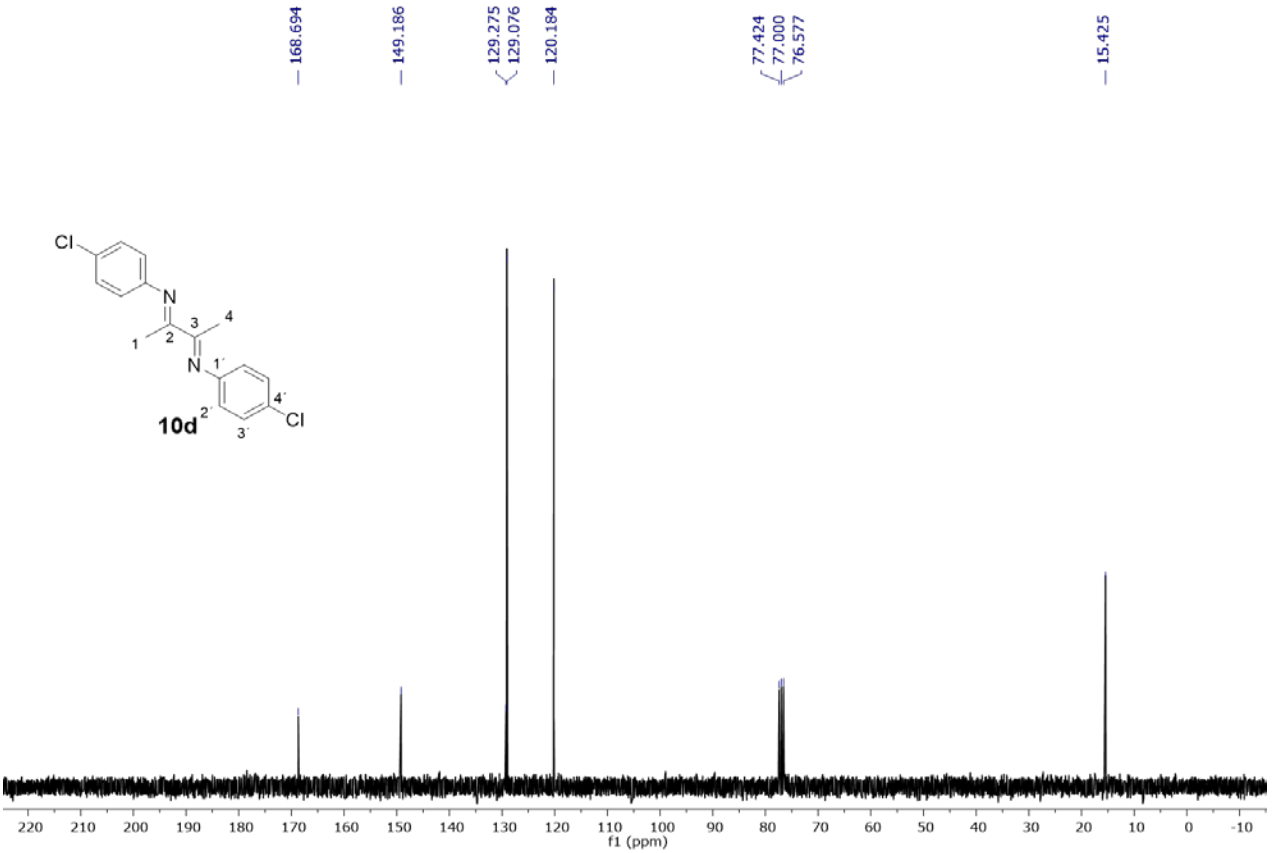

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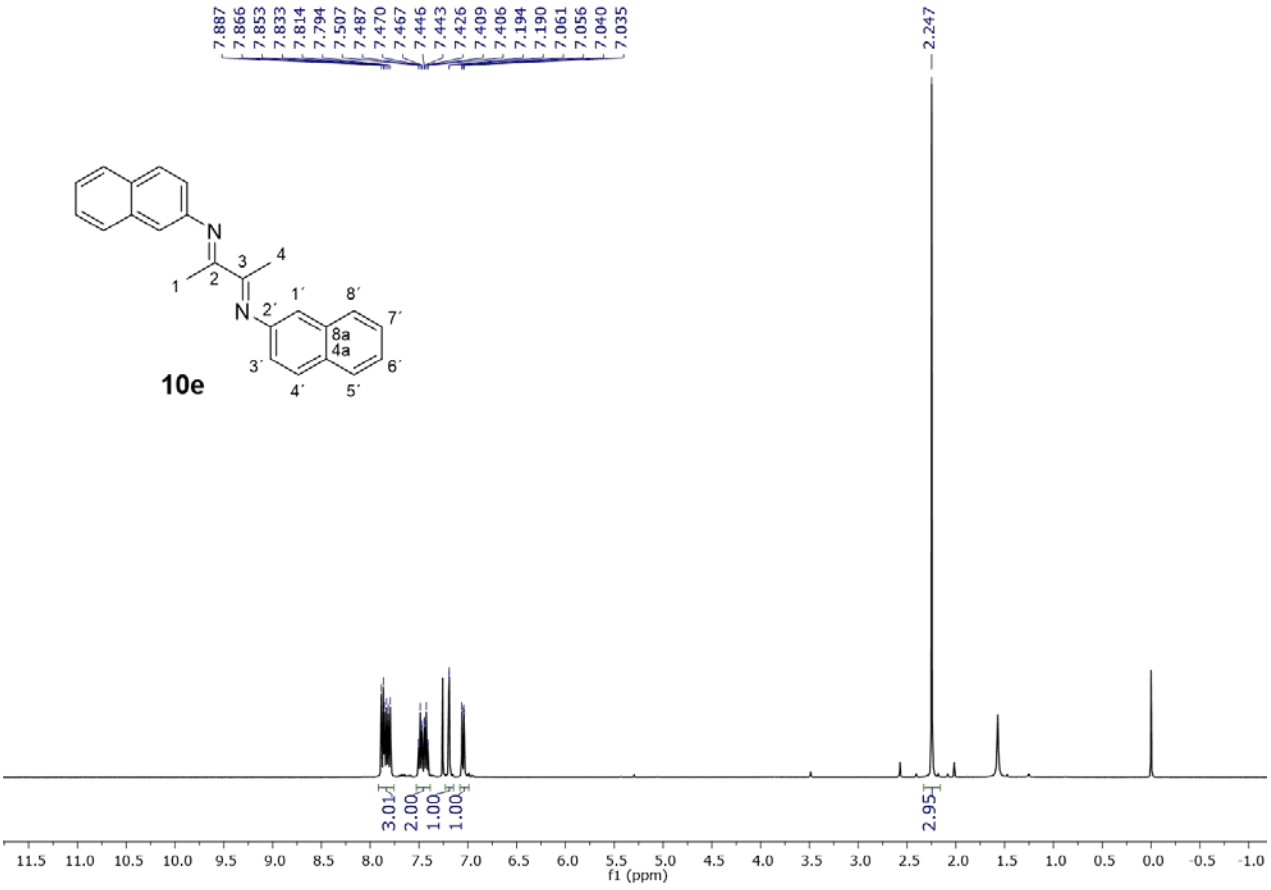

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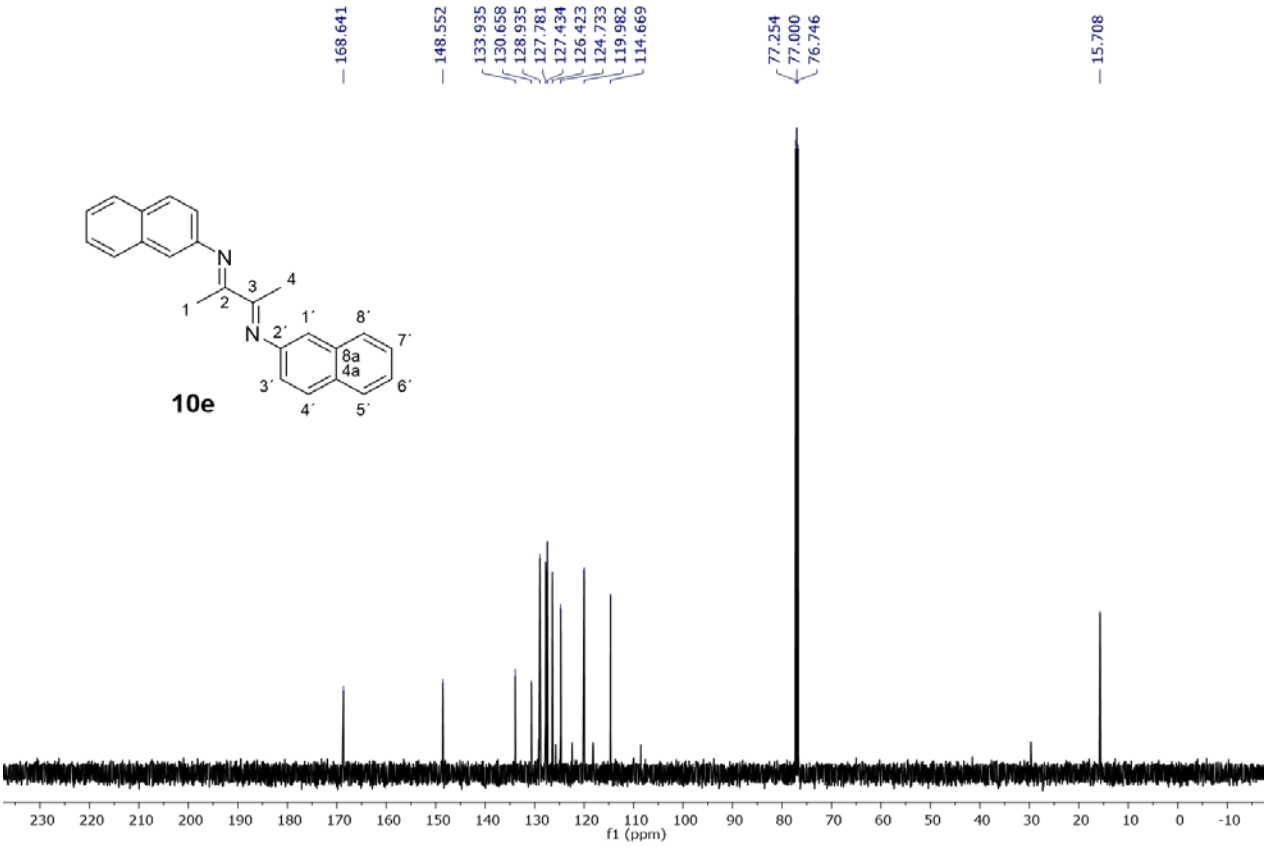

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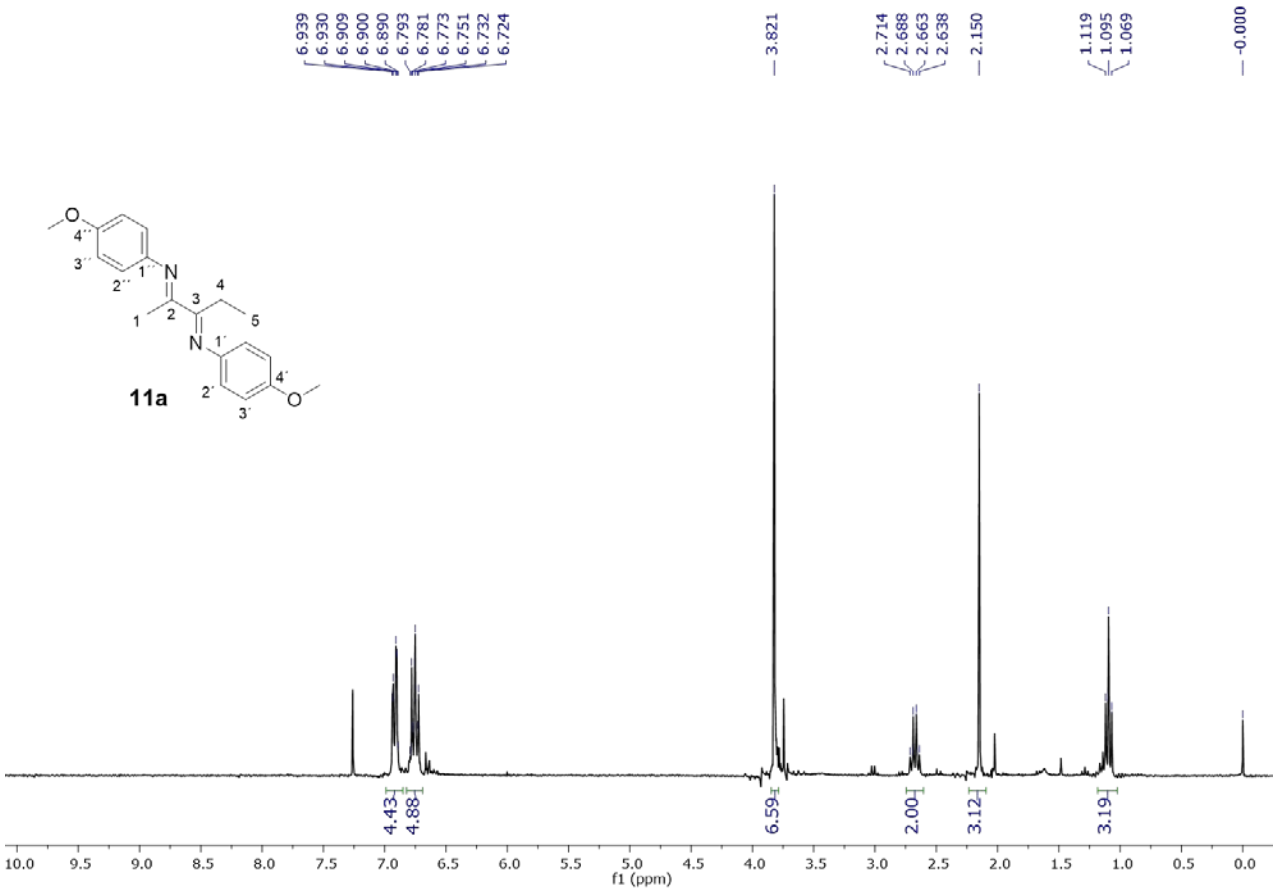
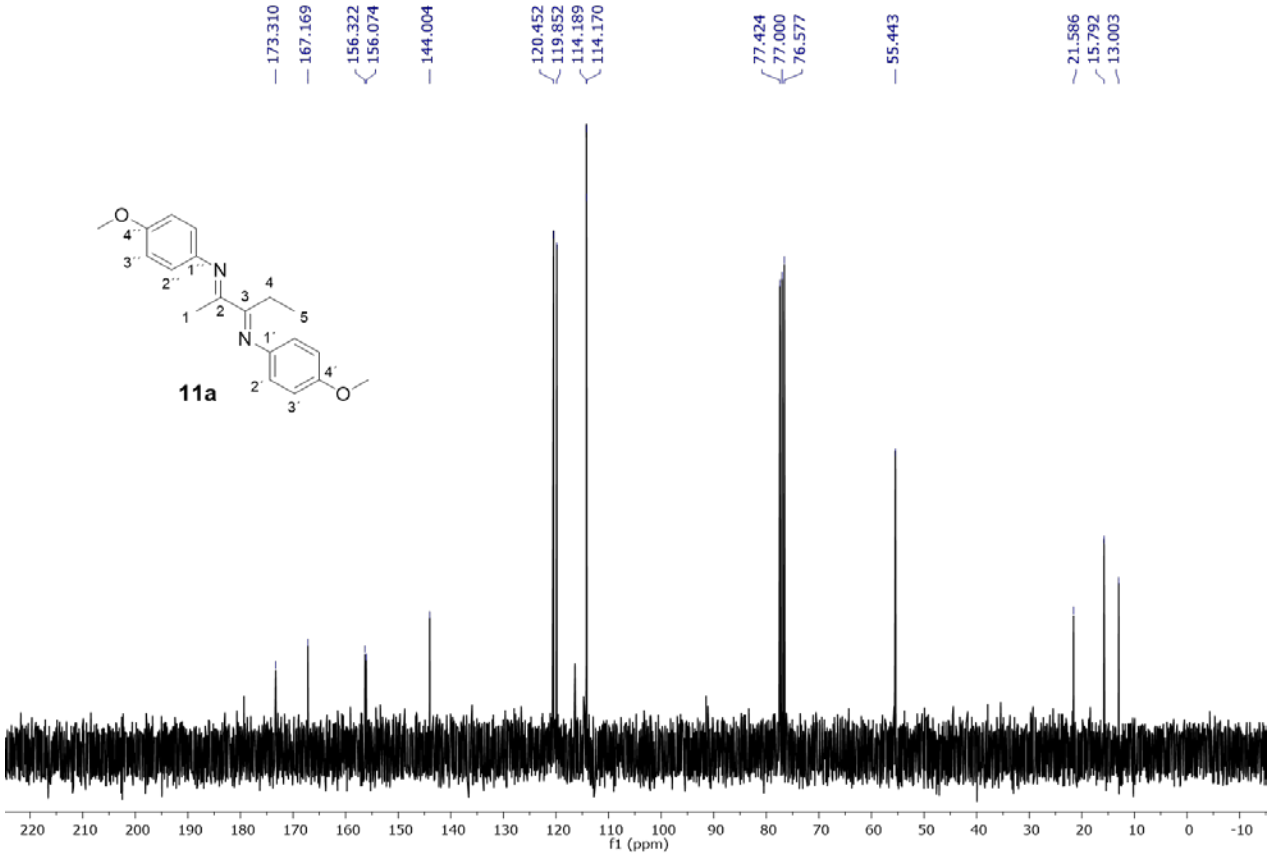
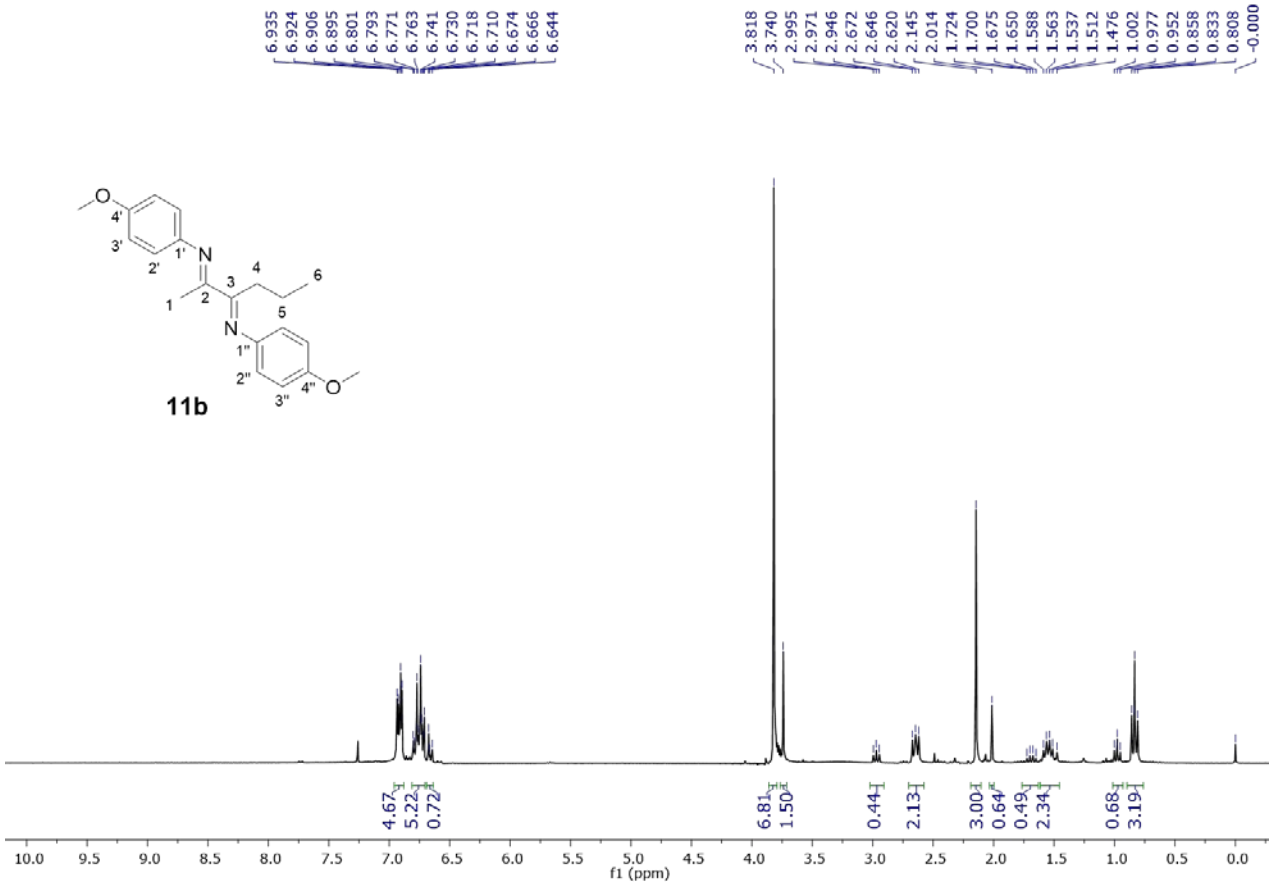


^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **11a**.



^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **11a**.



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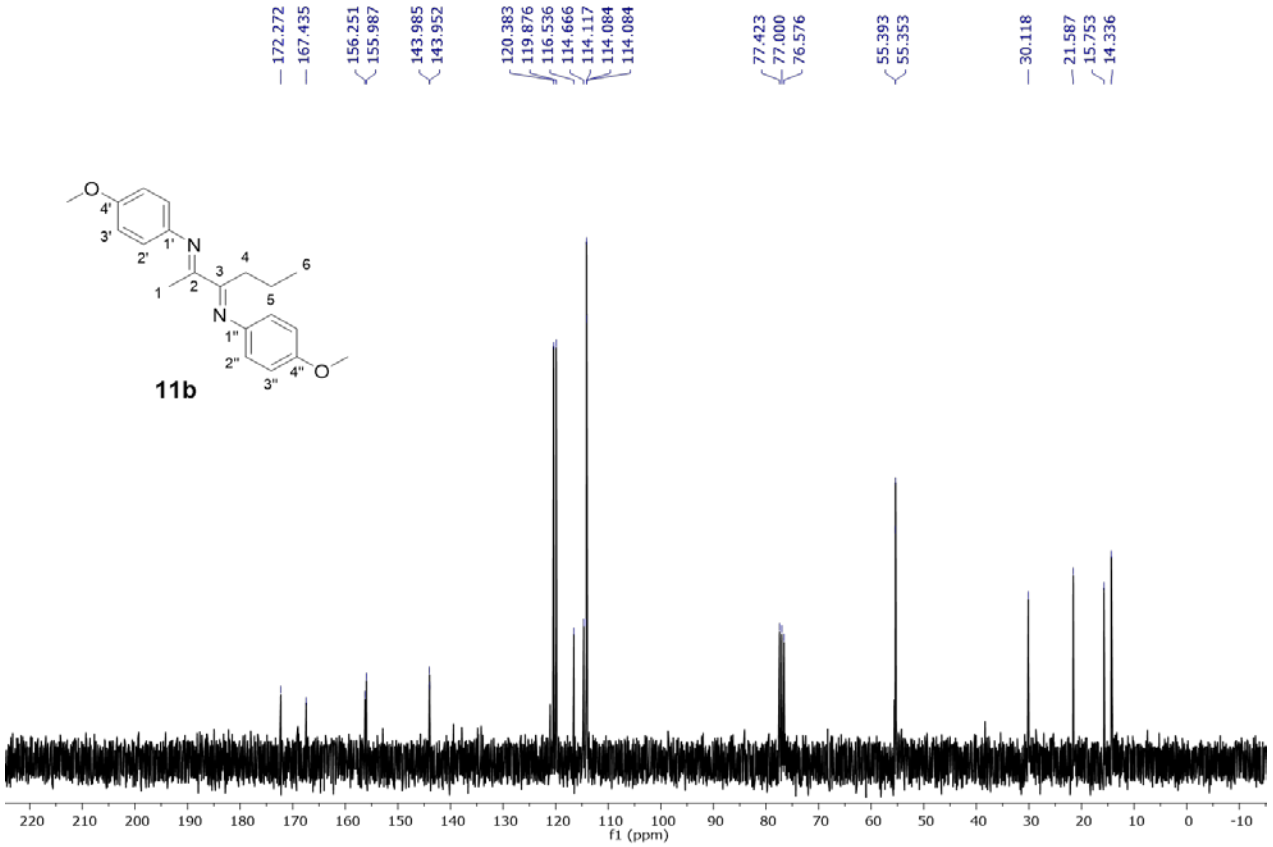

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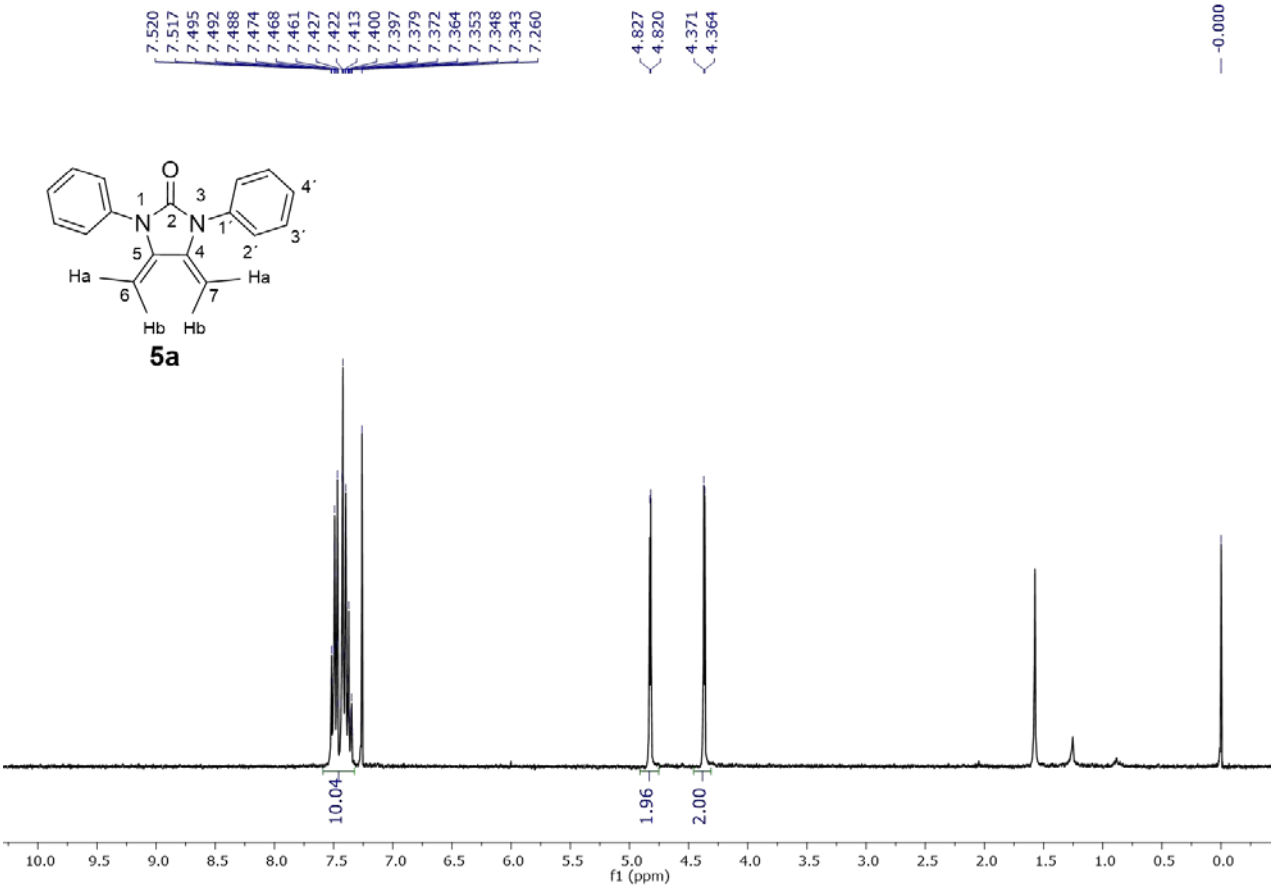

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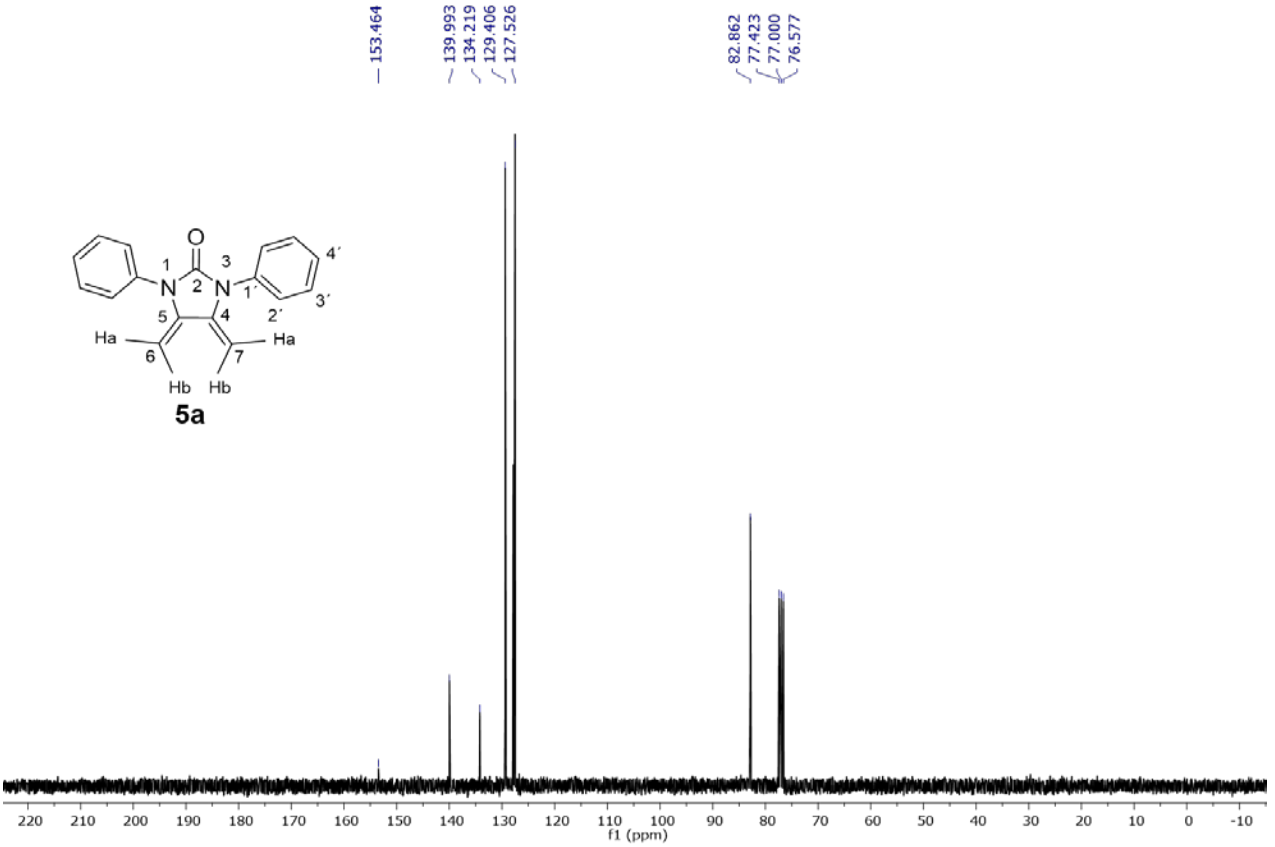

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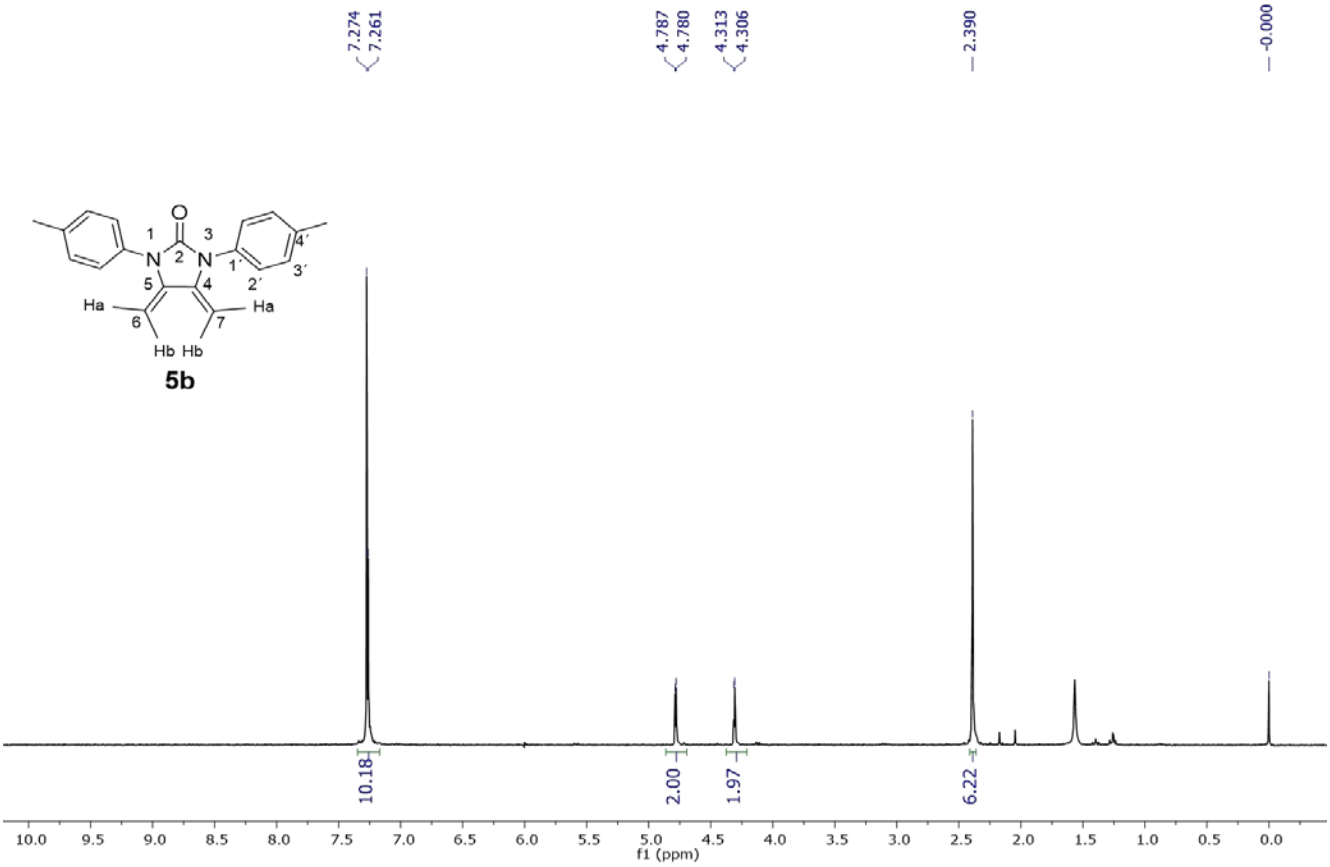

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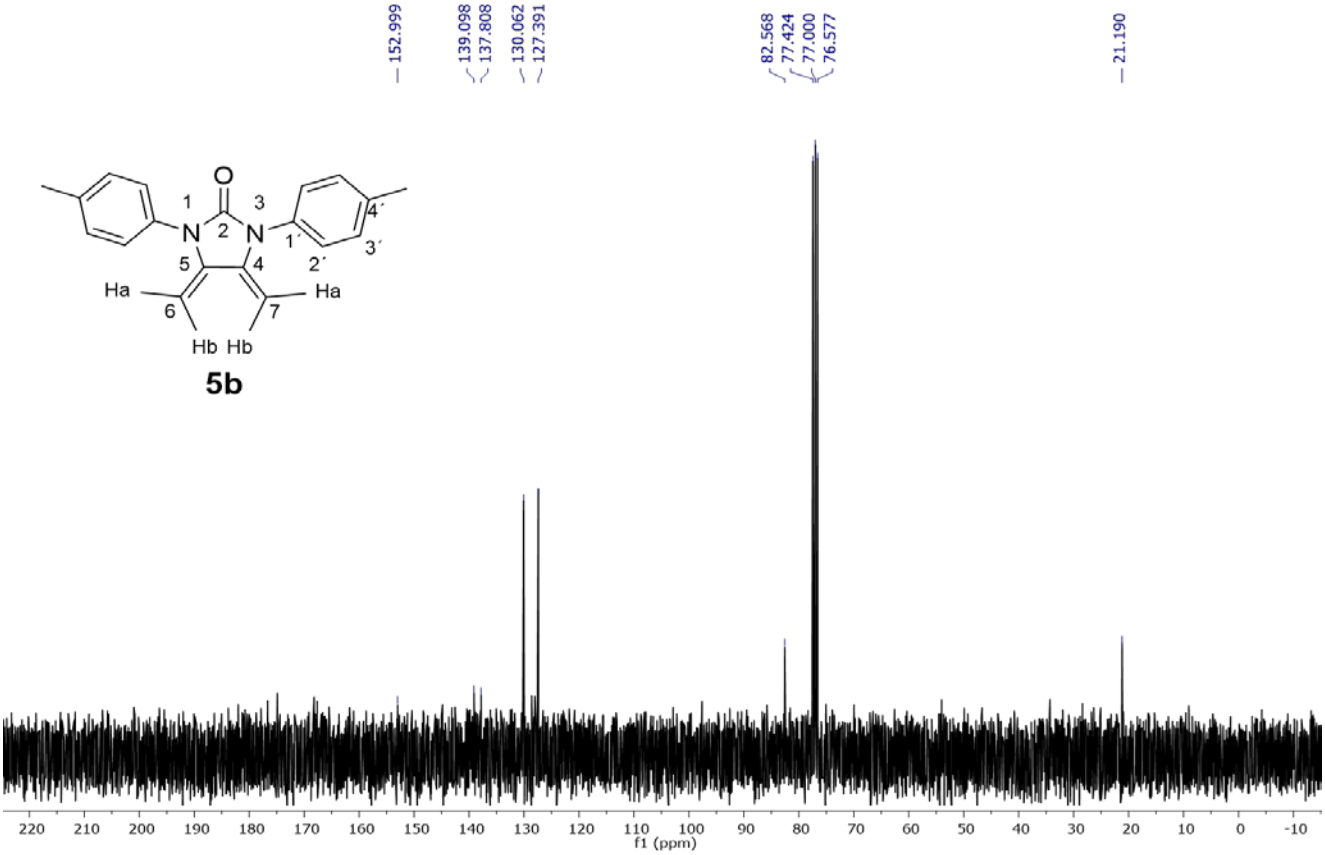
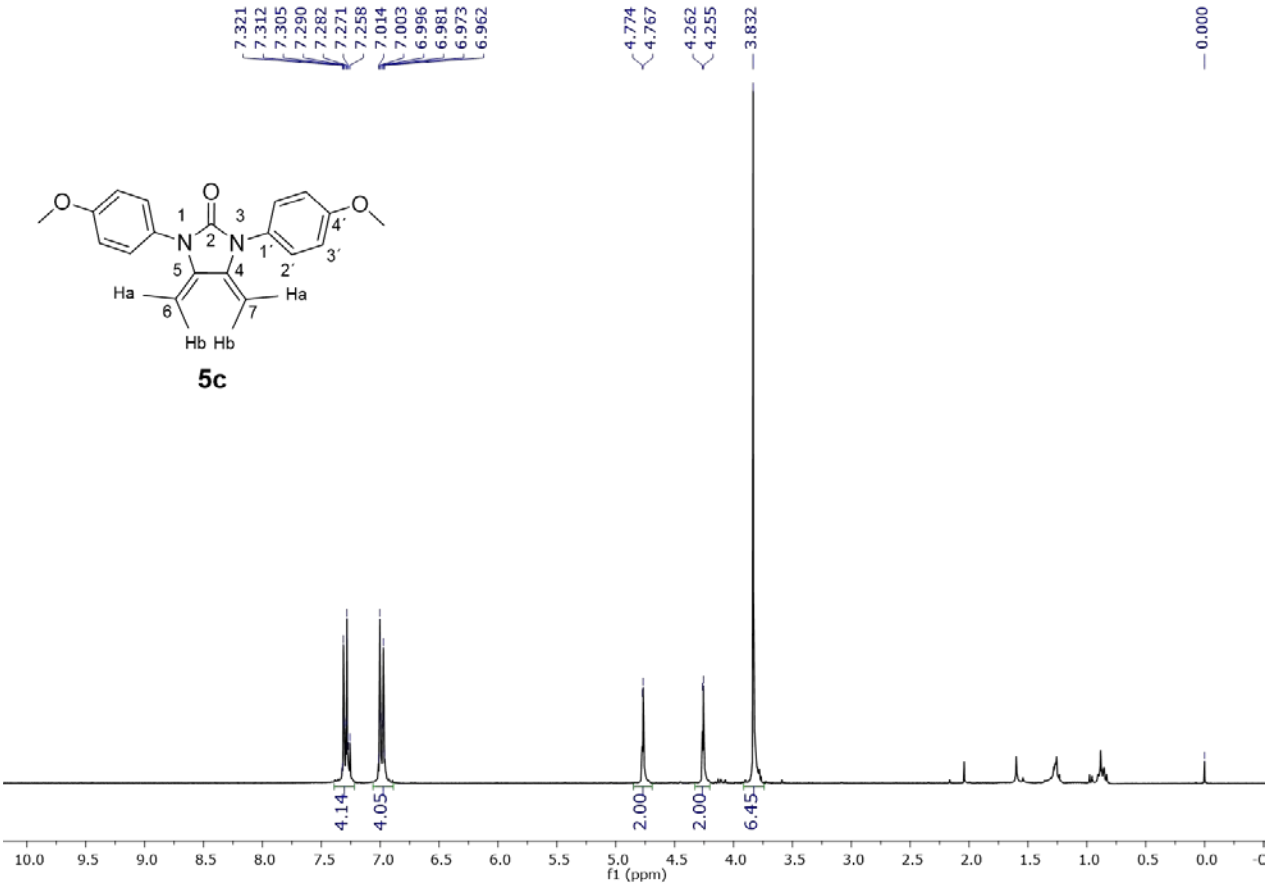
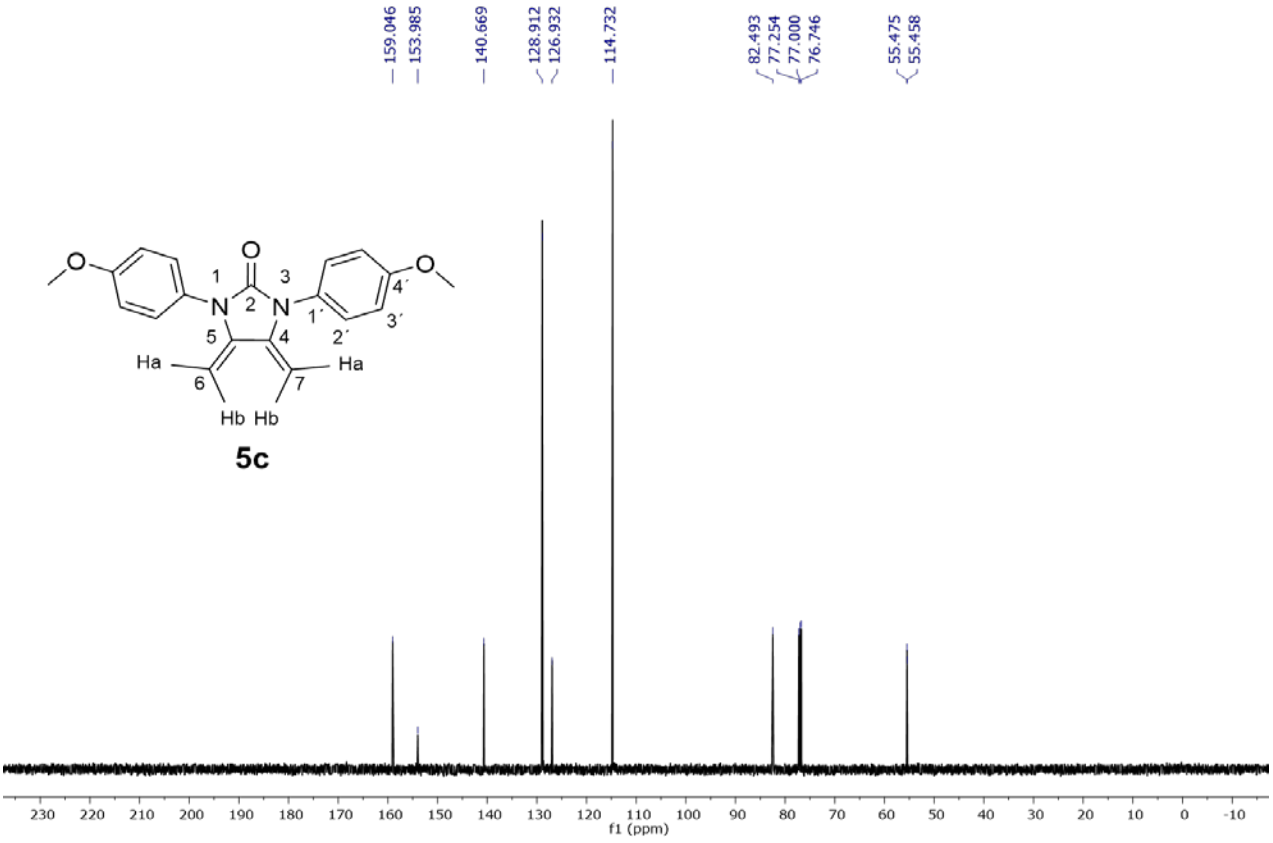


^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **5b**.



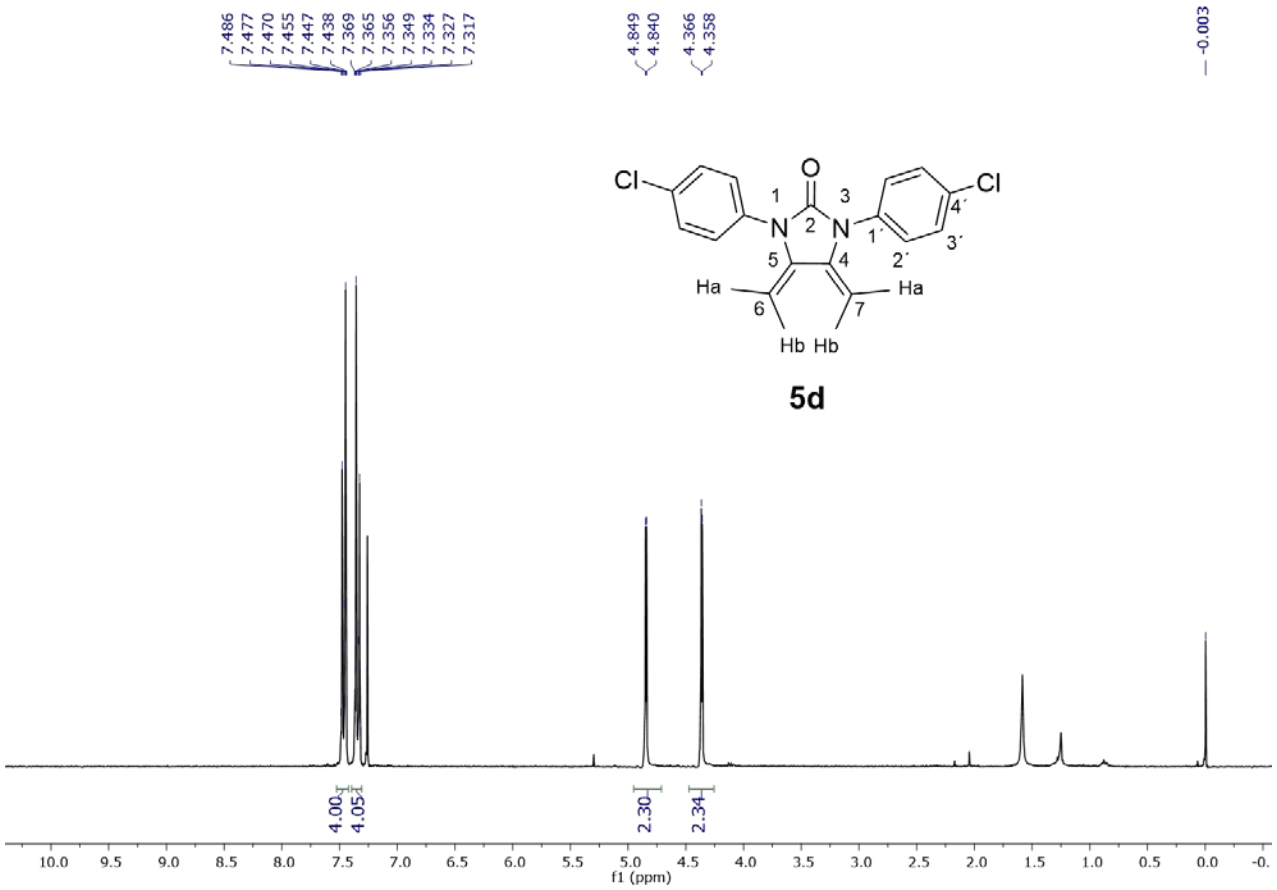
5c

^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **5c**.

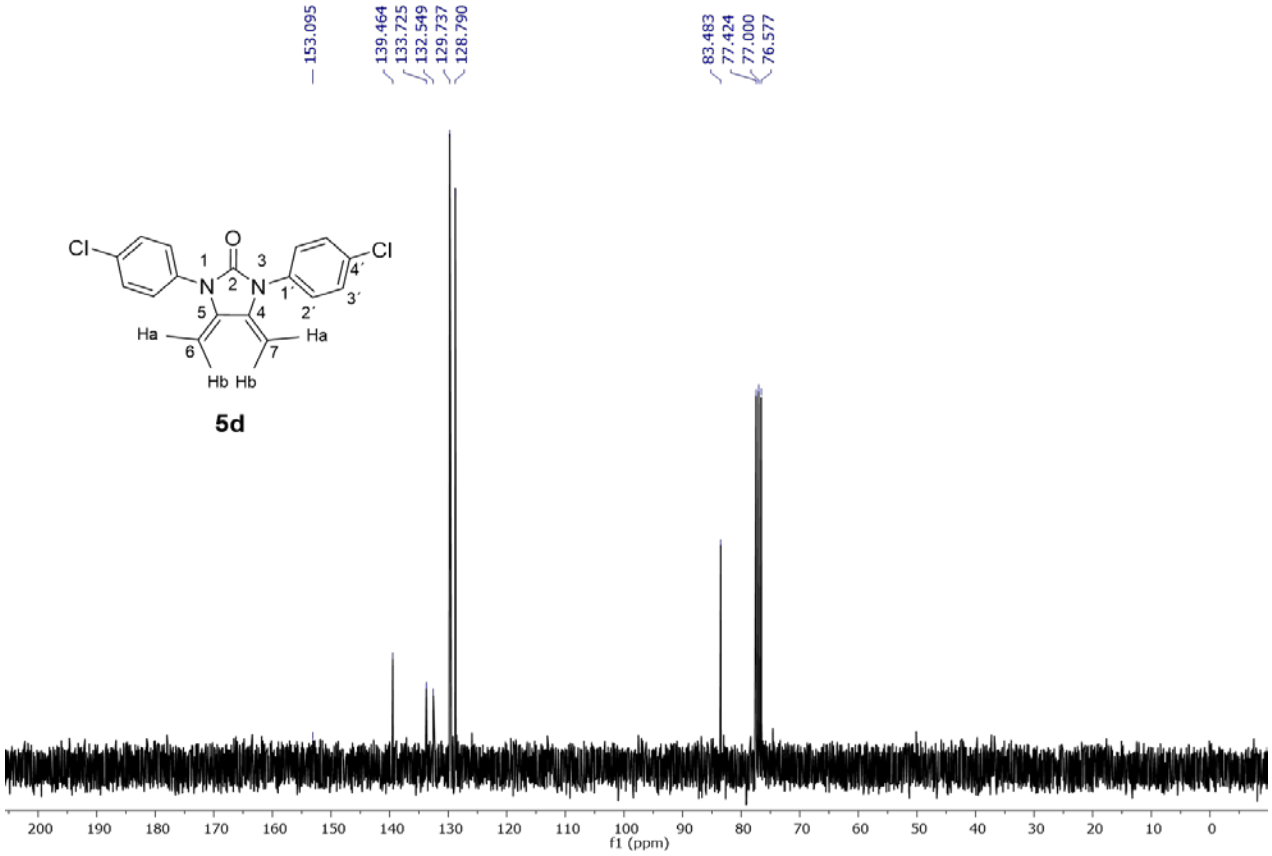


5c

^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of **5c**.



^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5d**.



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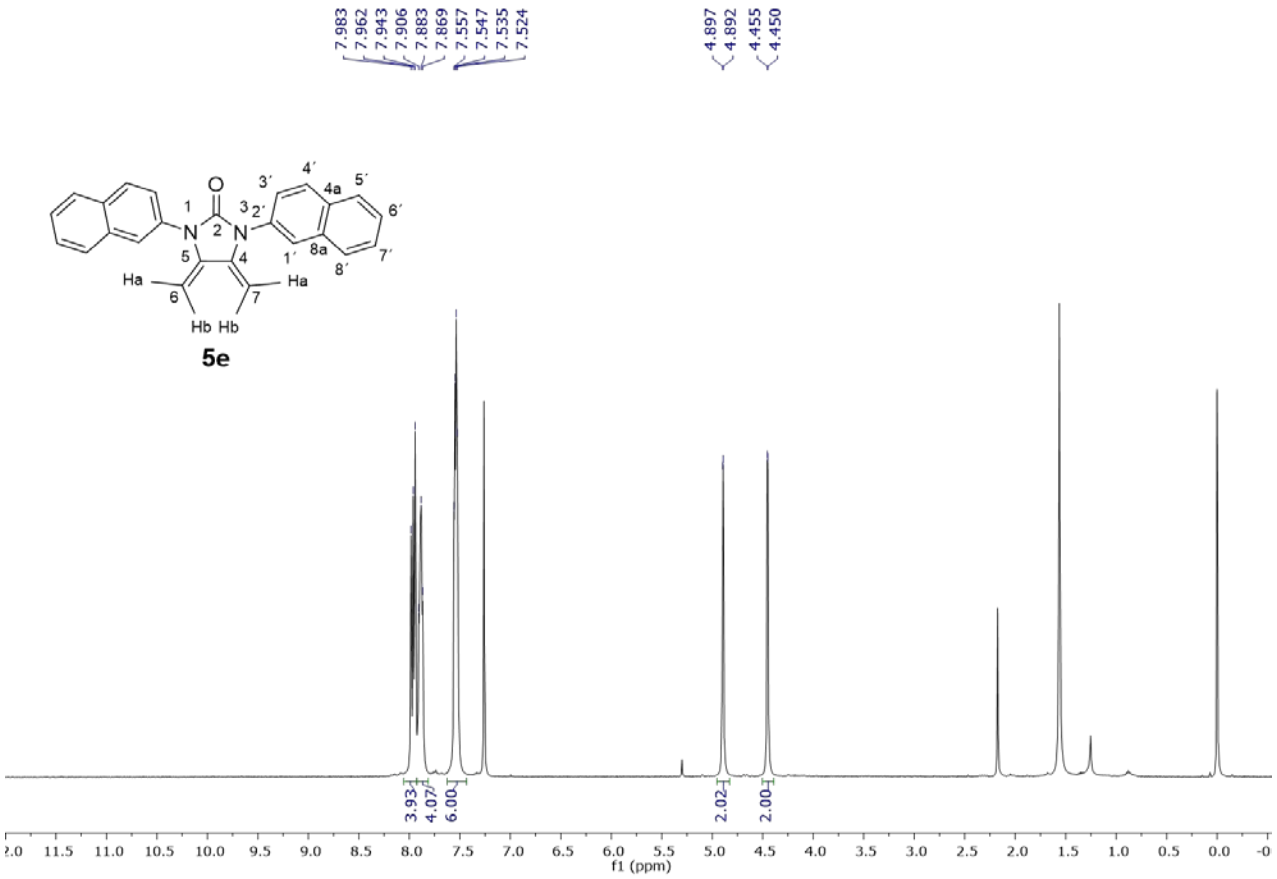

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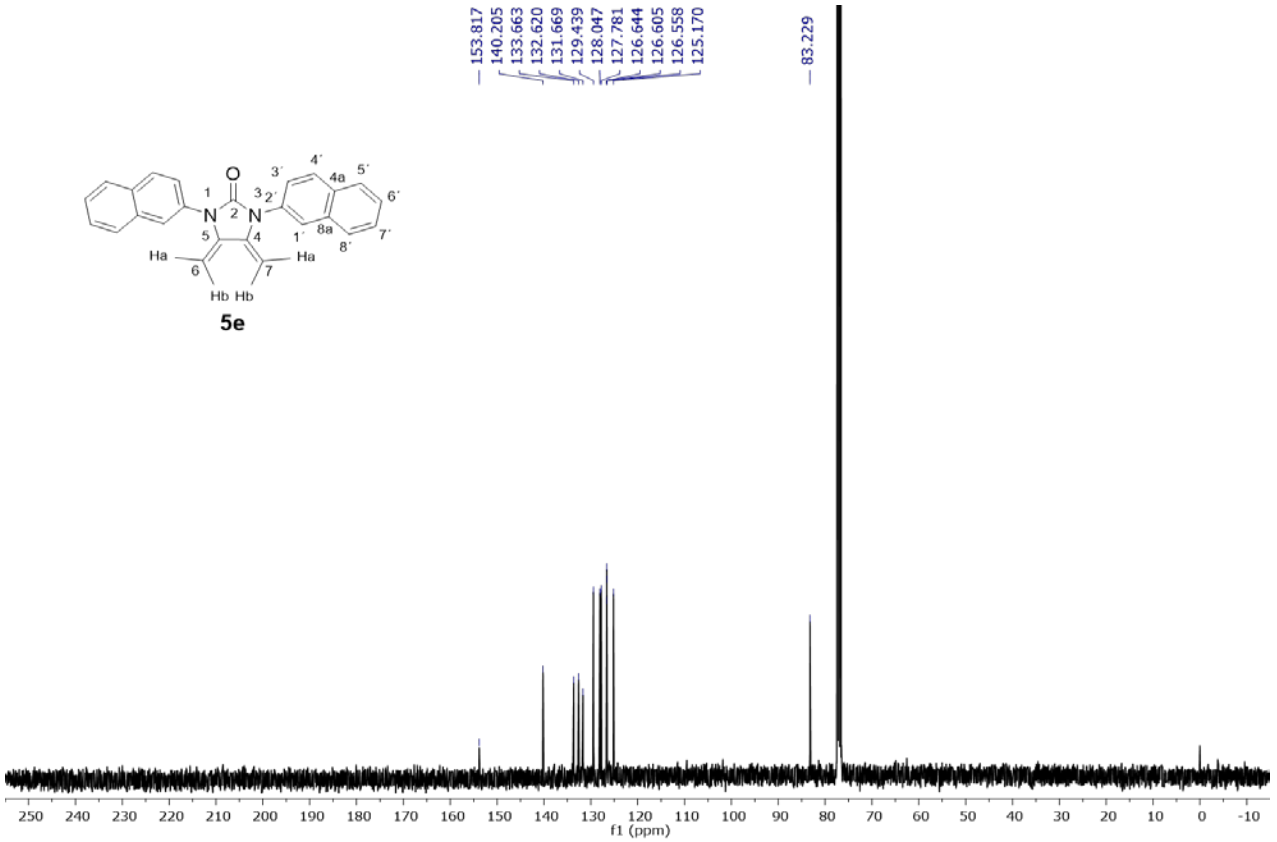
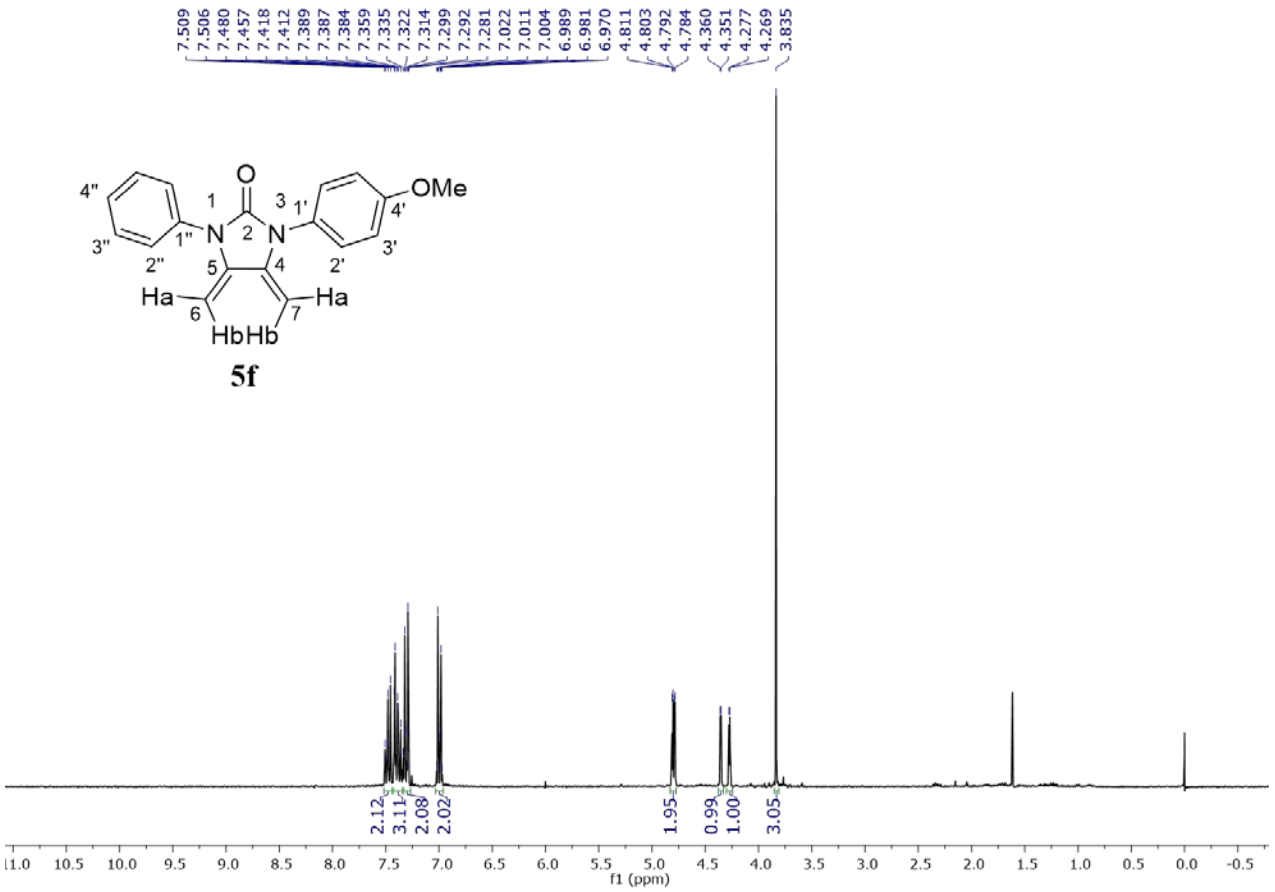
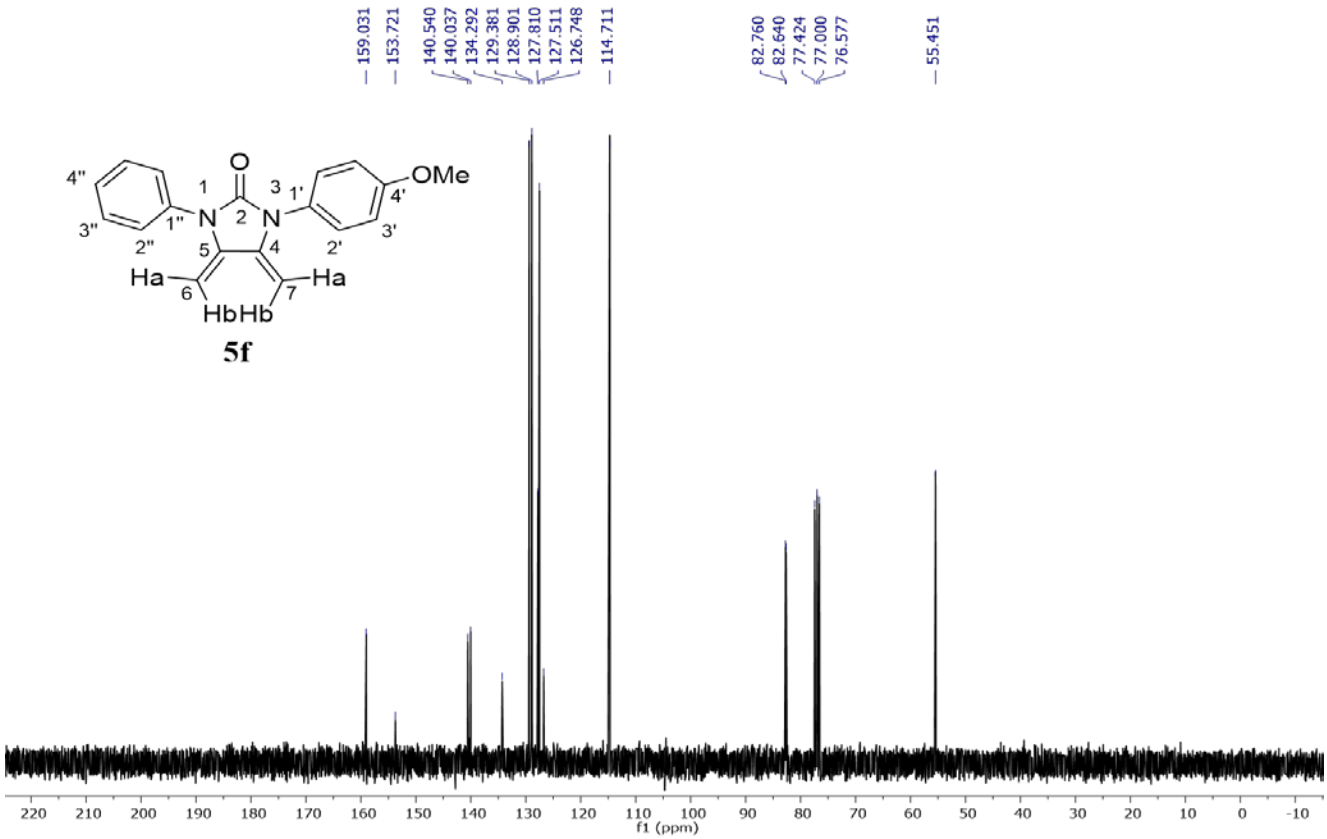


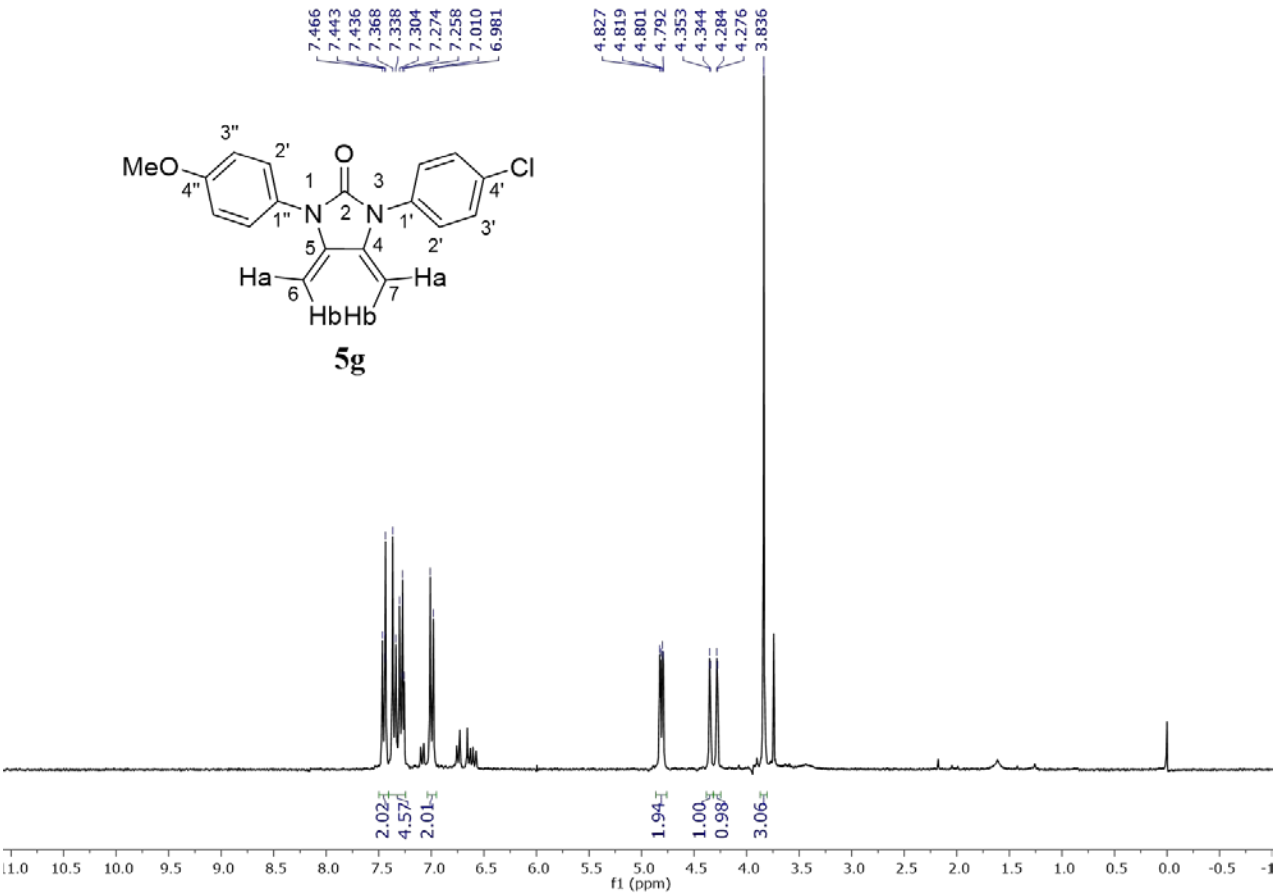
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5e**.



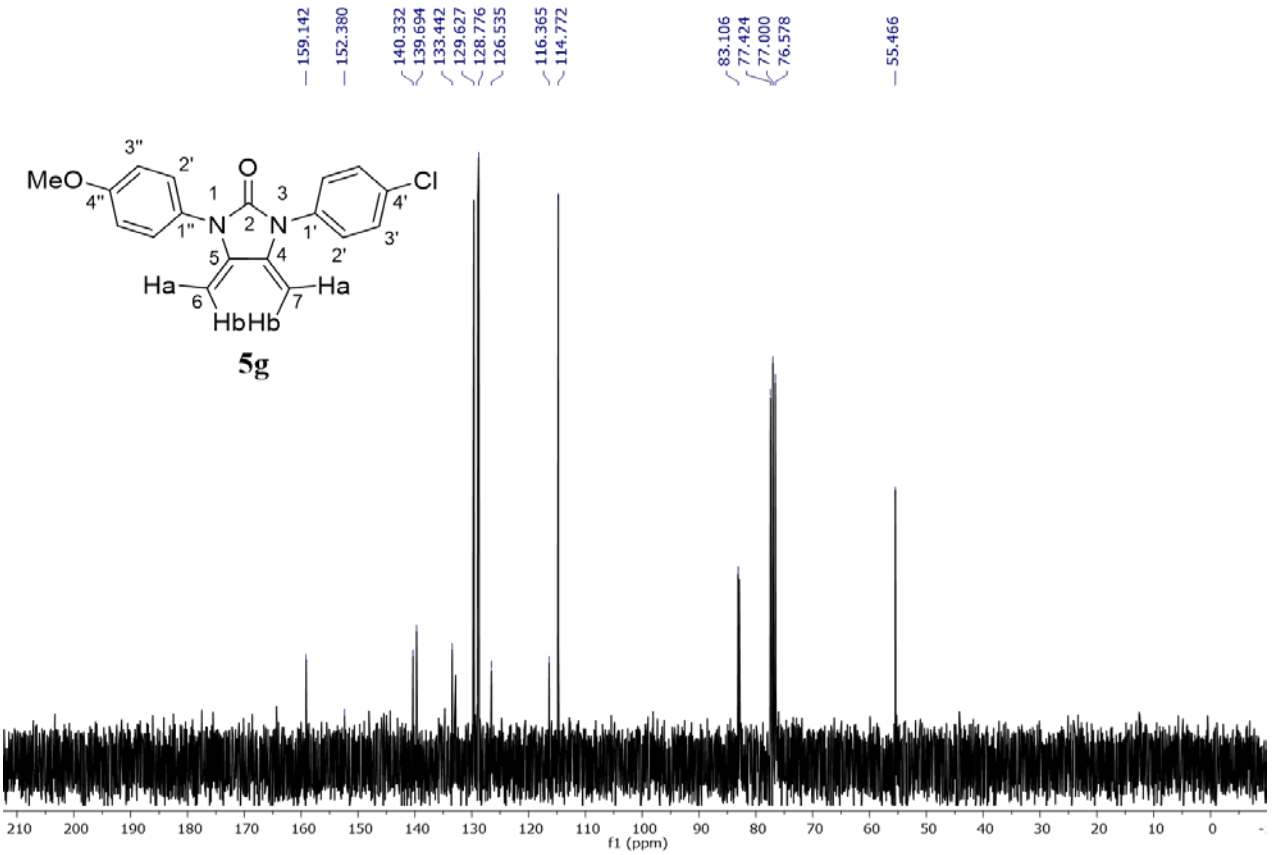
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5f**.



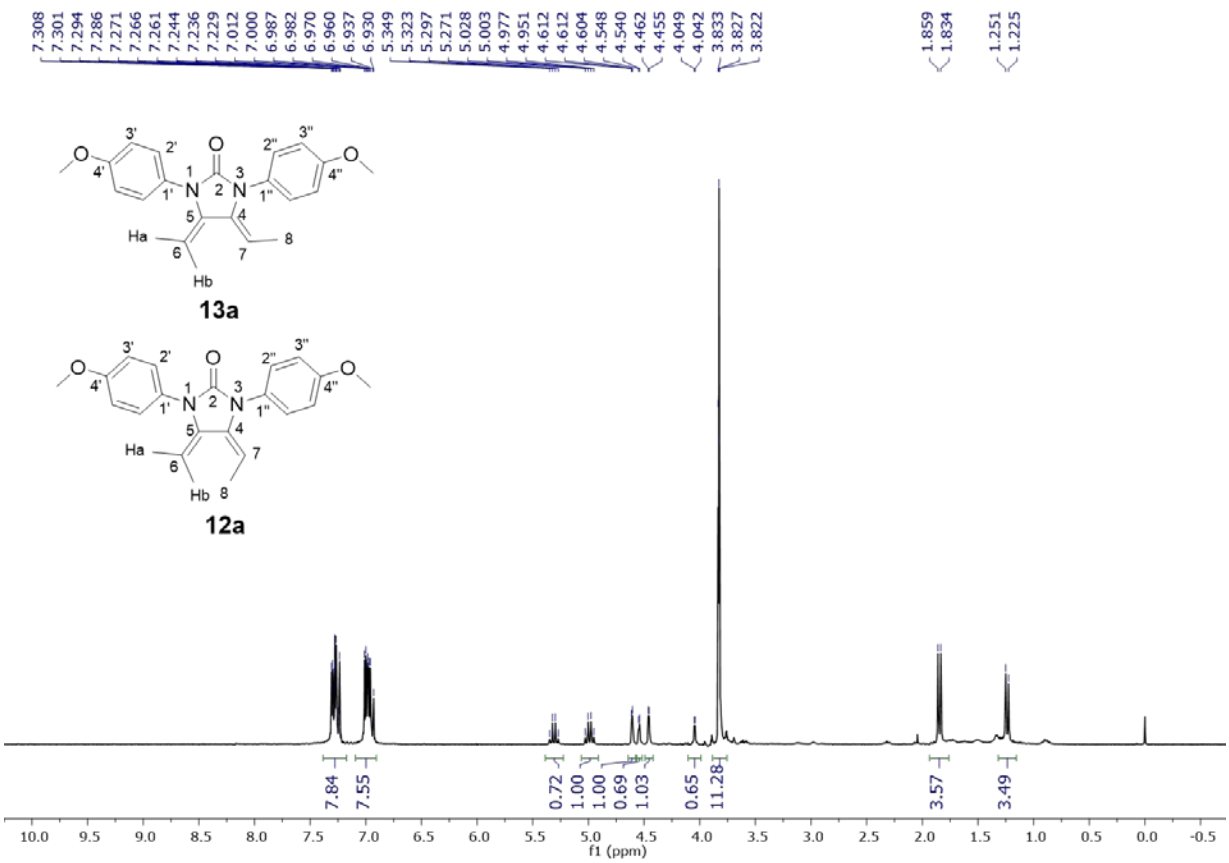
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **5f**.



^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5g**.



^{13}C NMR ($CDCl_3$, 74.5 MHz) spectrum of **5g**.



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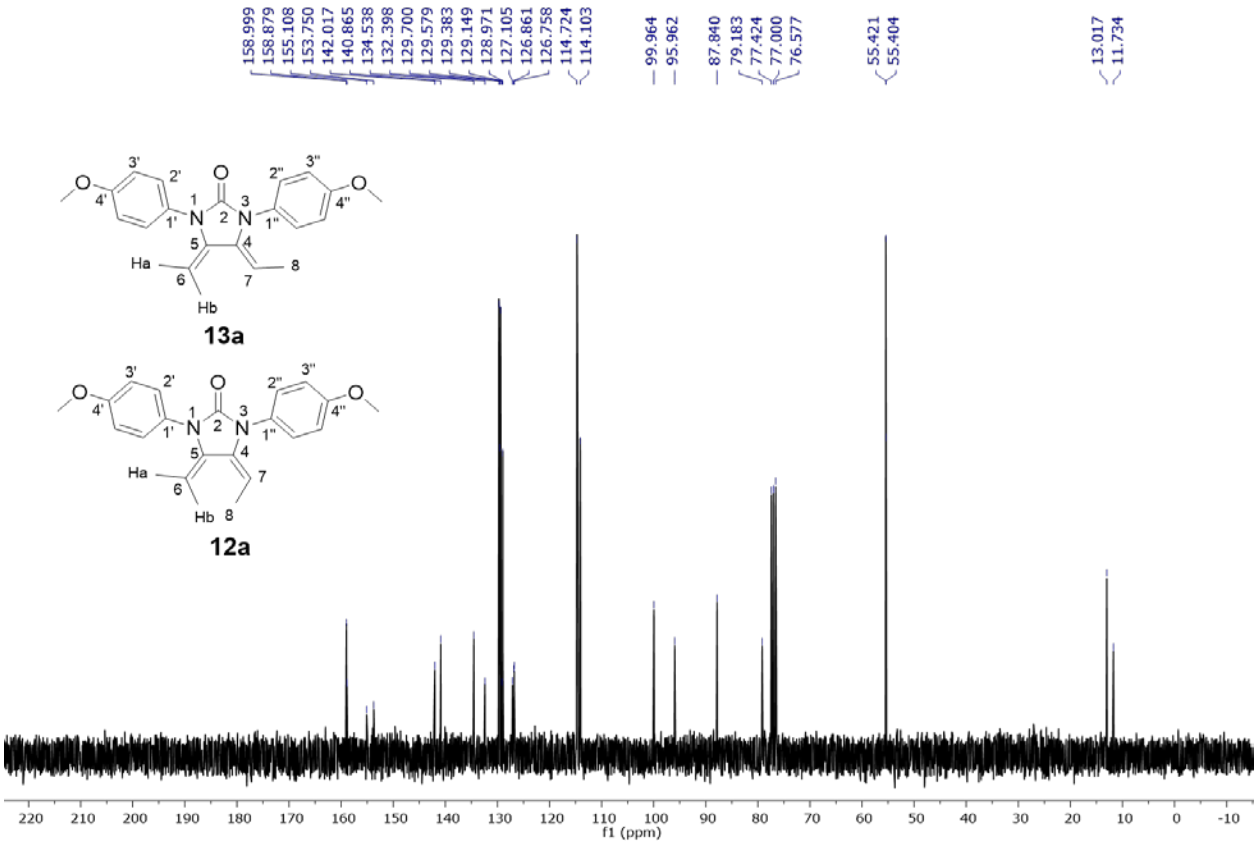
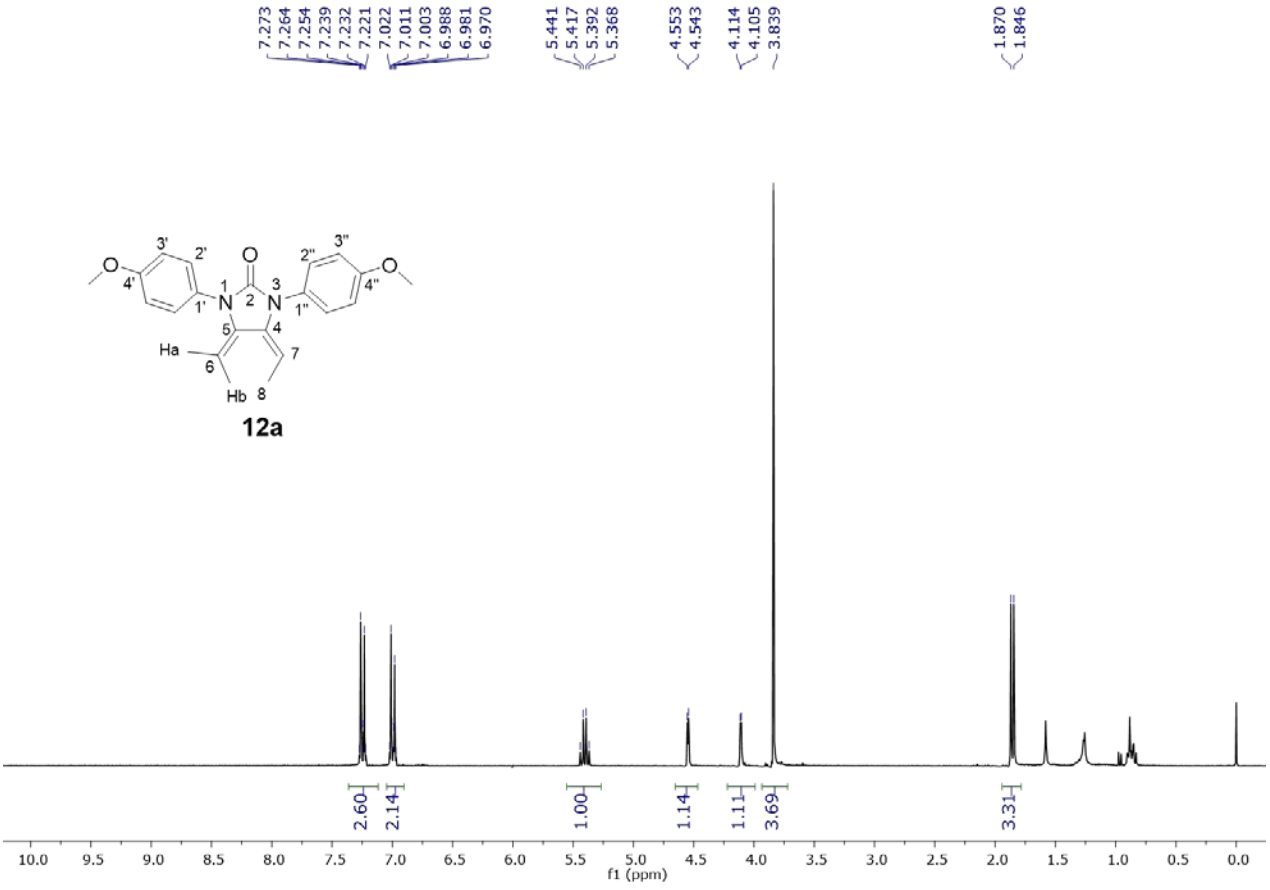
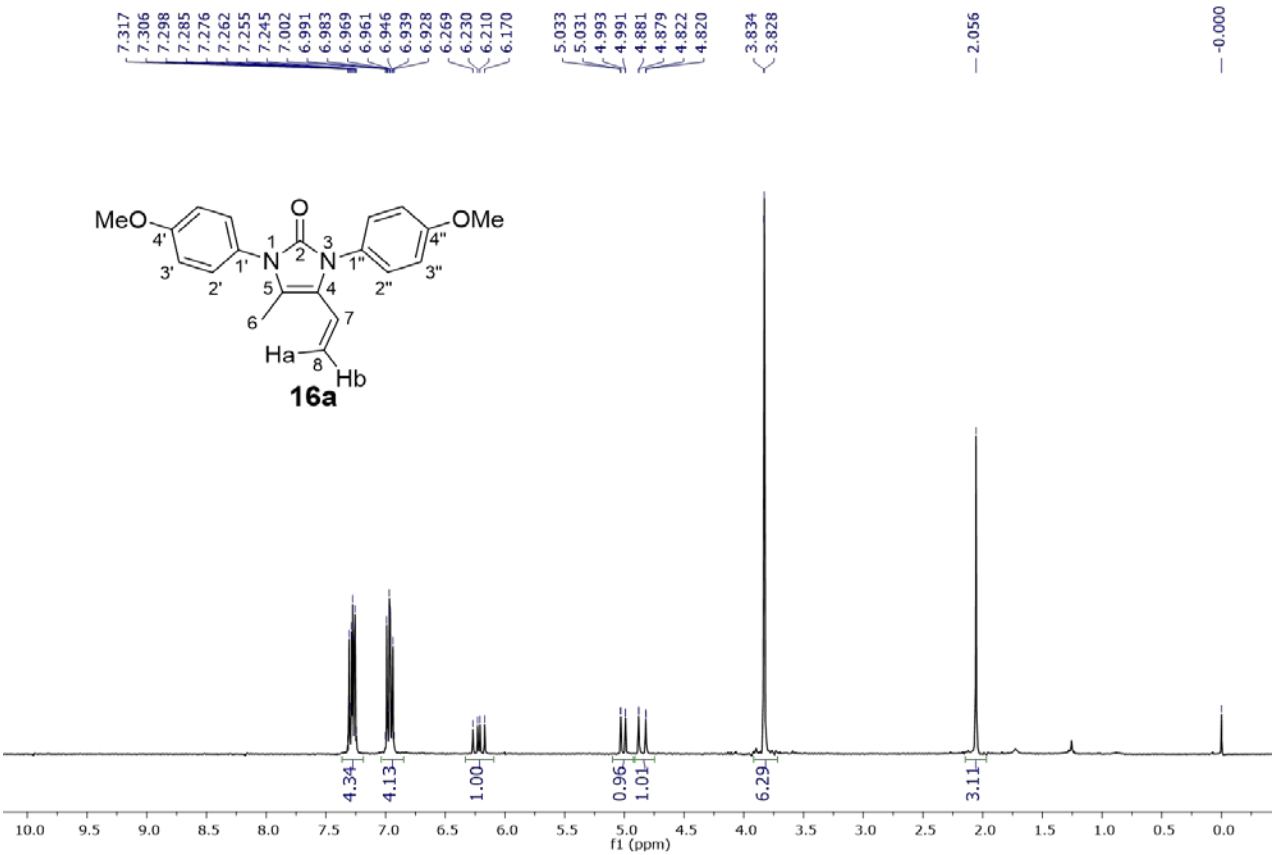


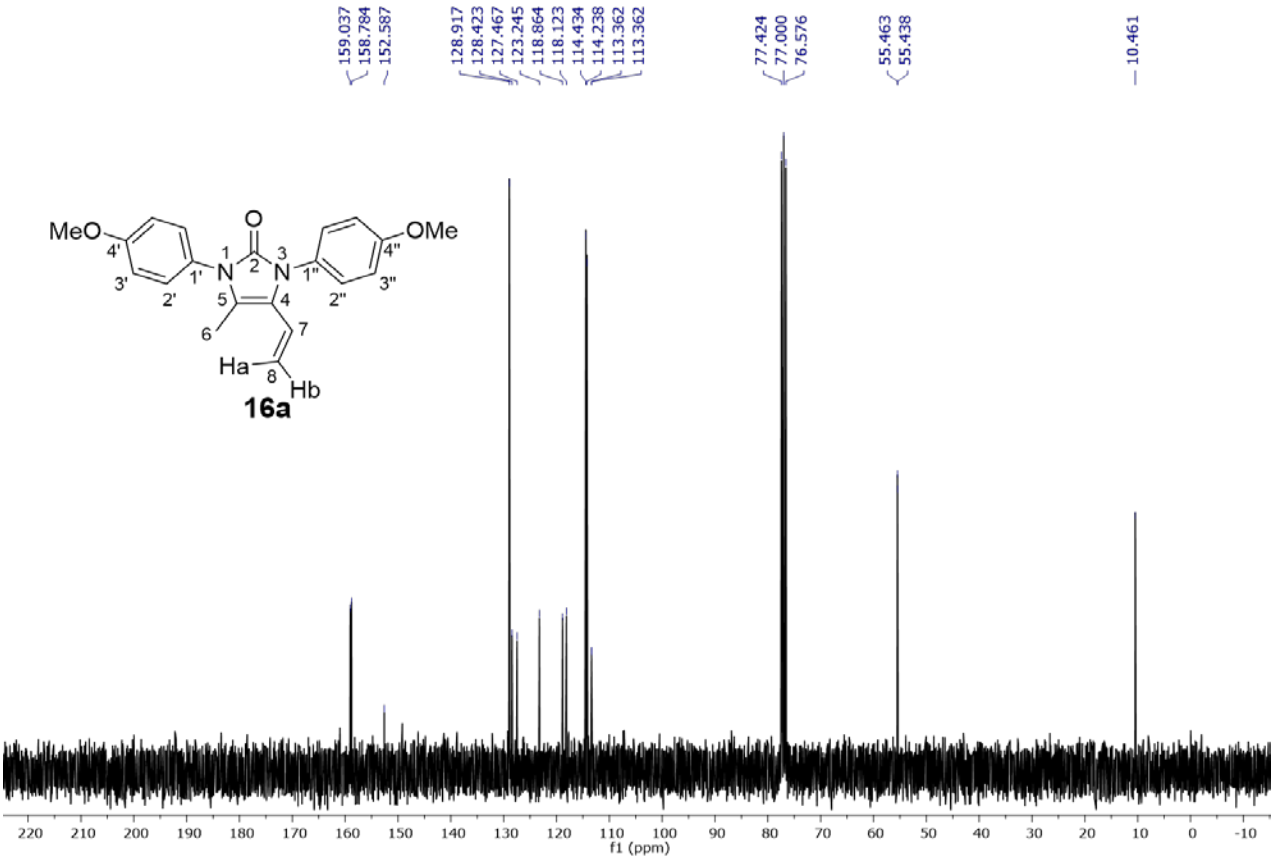
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **12a** and **13a**.



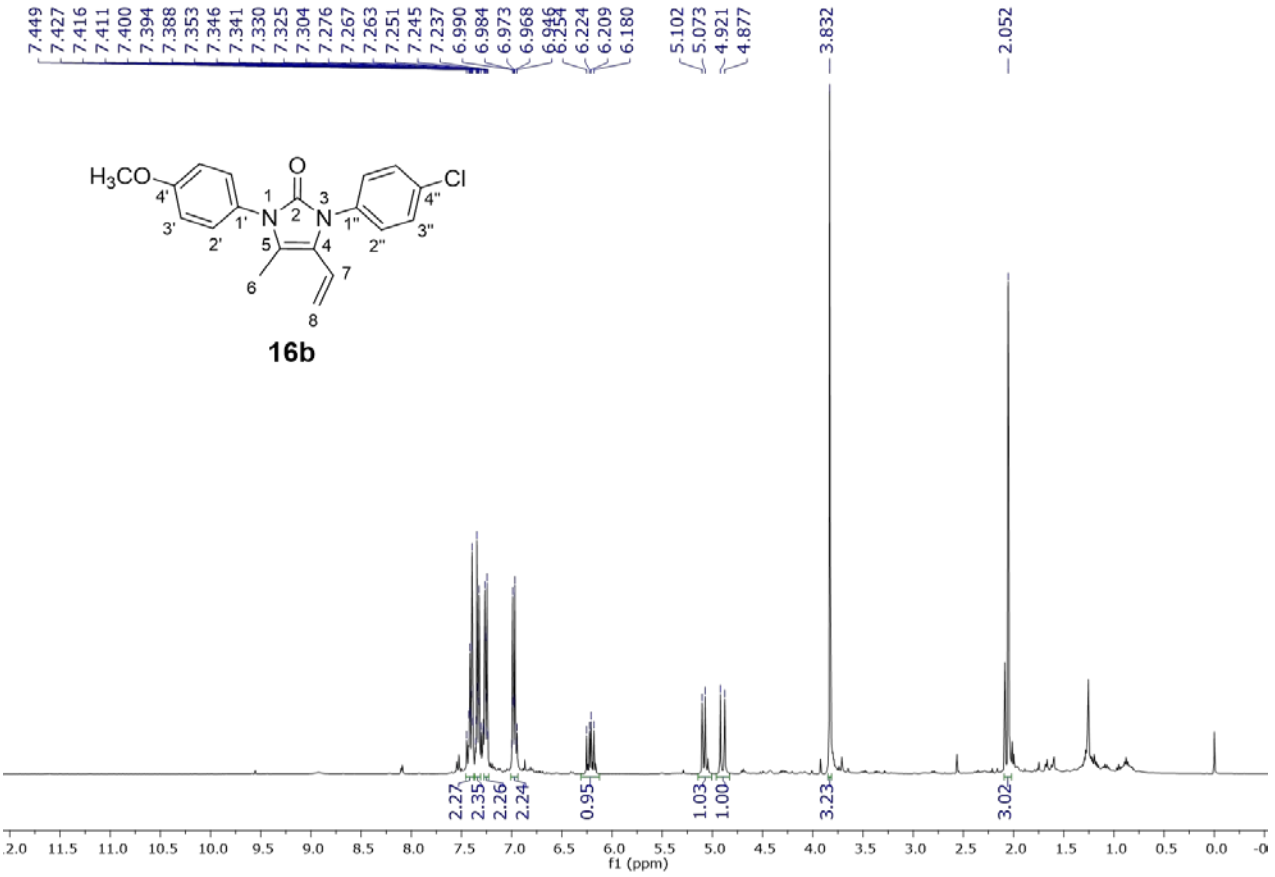
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **12a**.



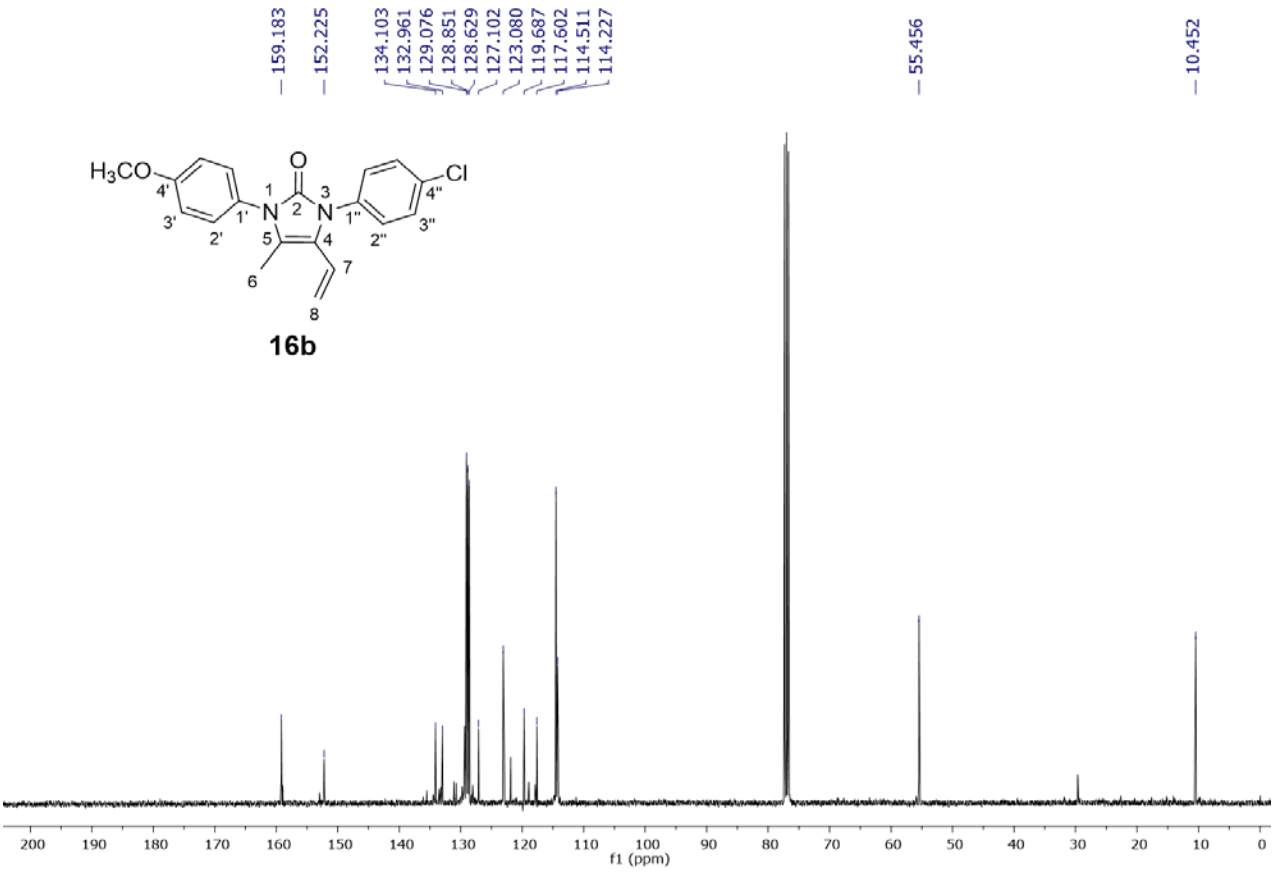
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **16a**.



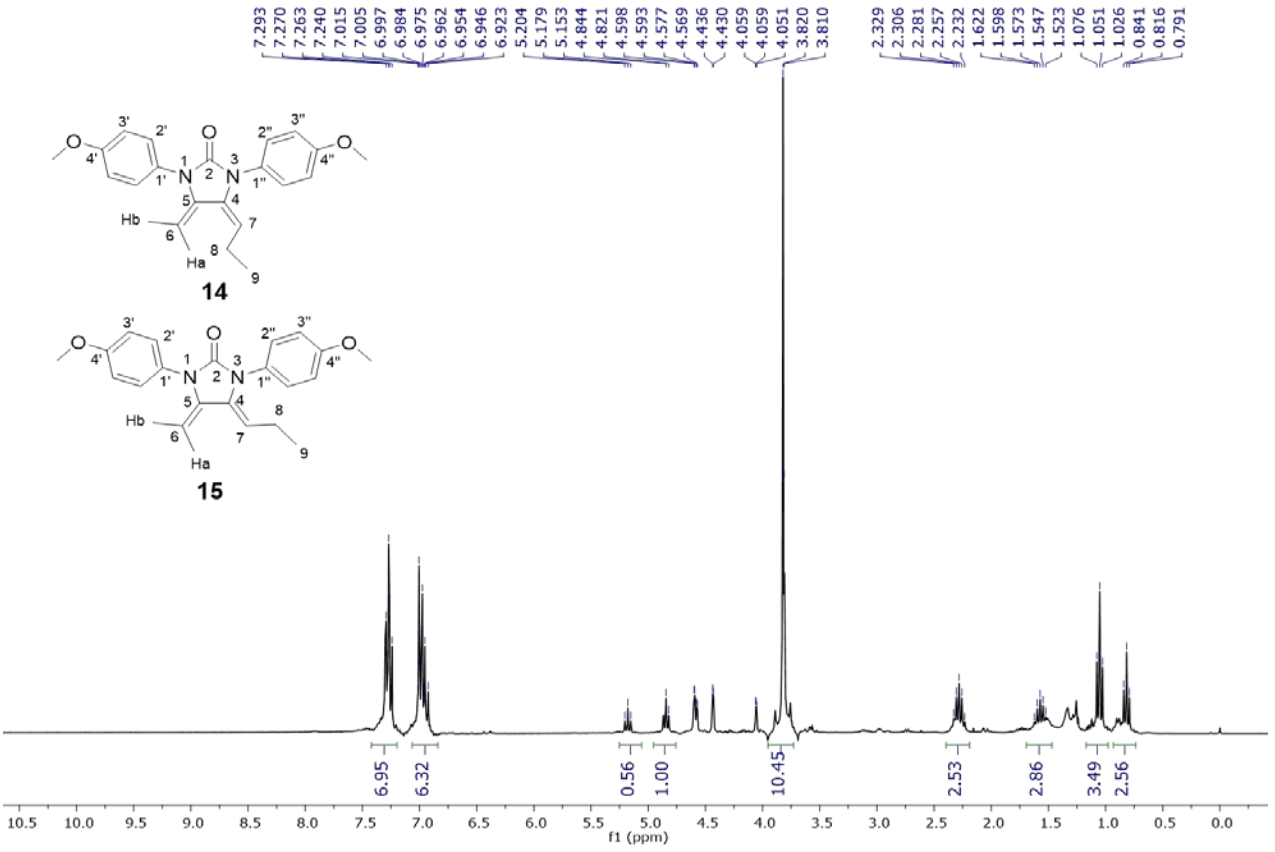
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **16a**.



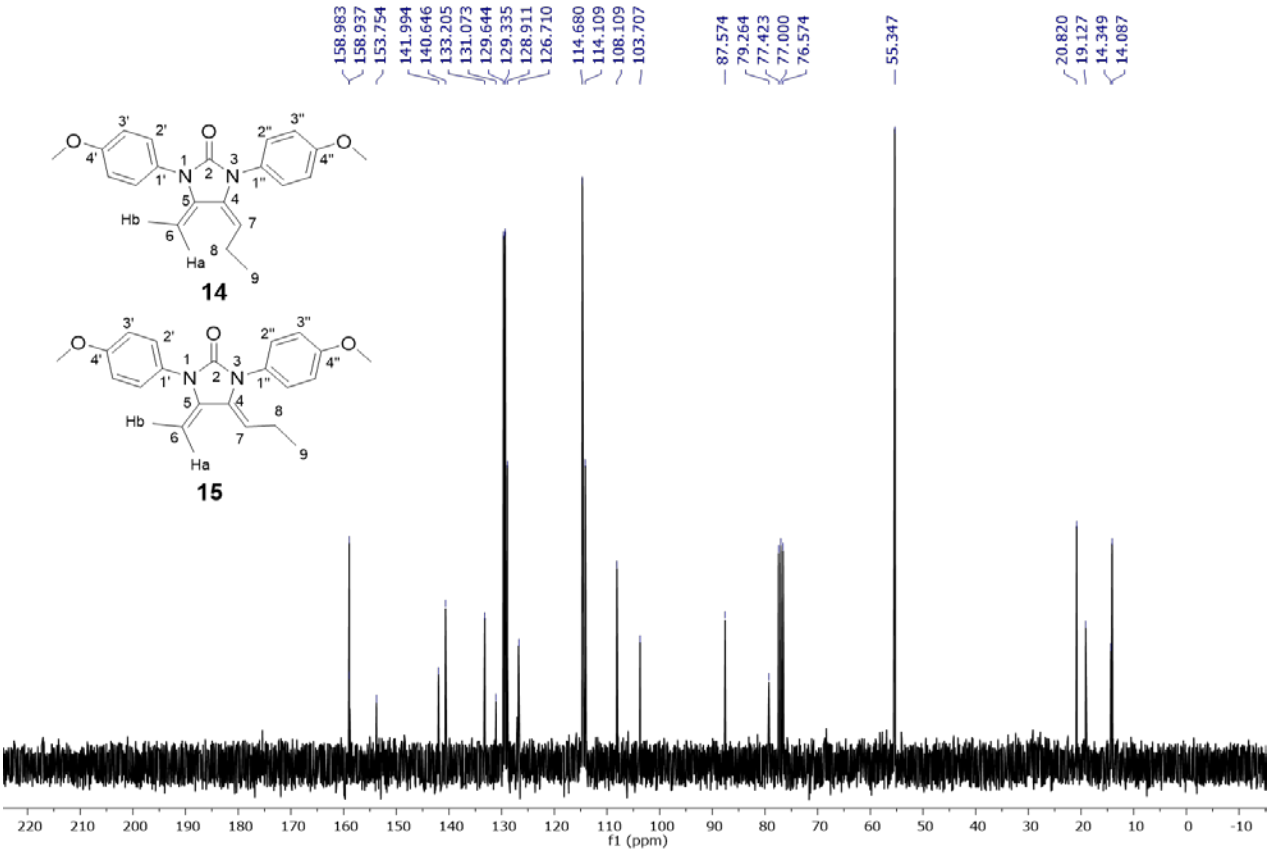
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16b**.



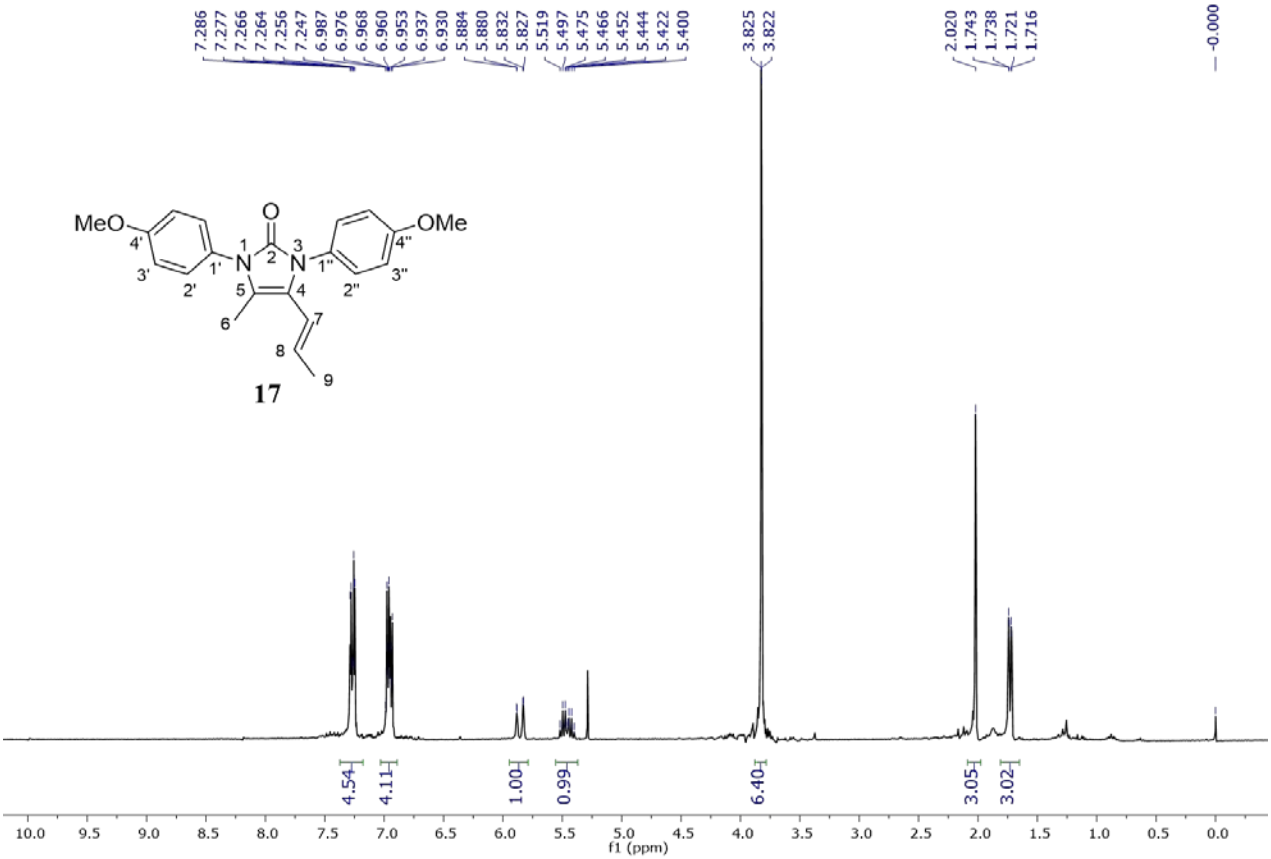
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **16b**.



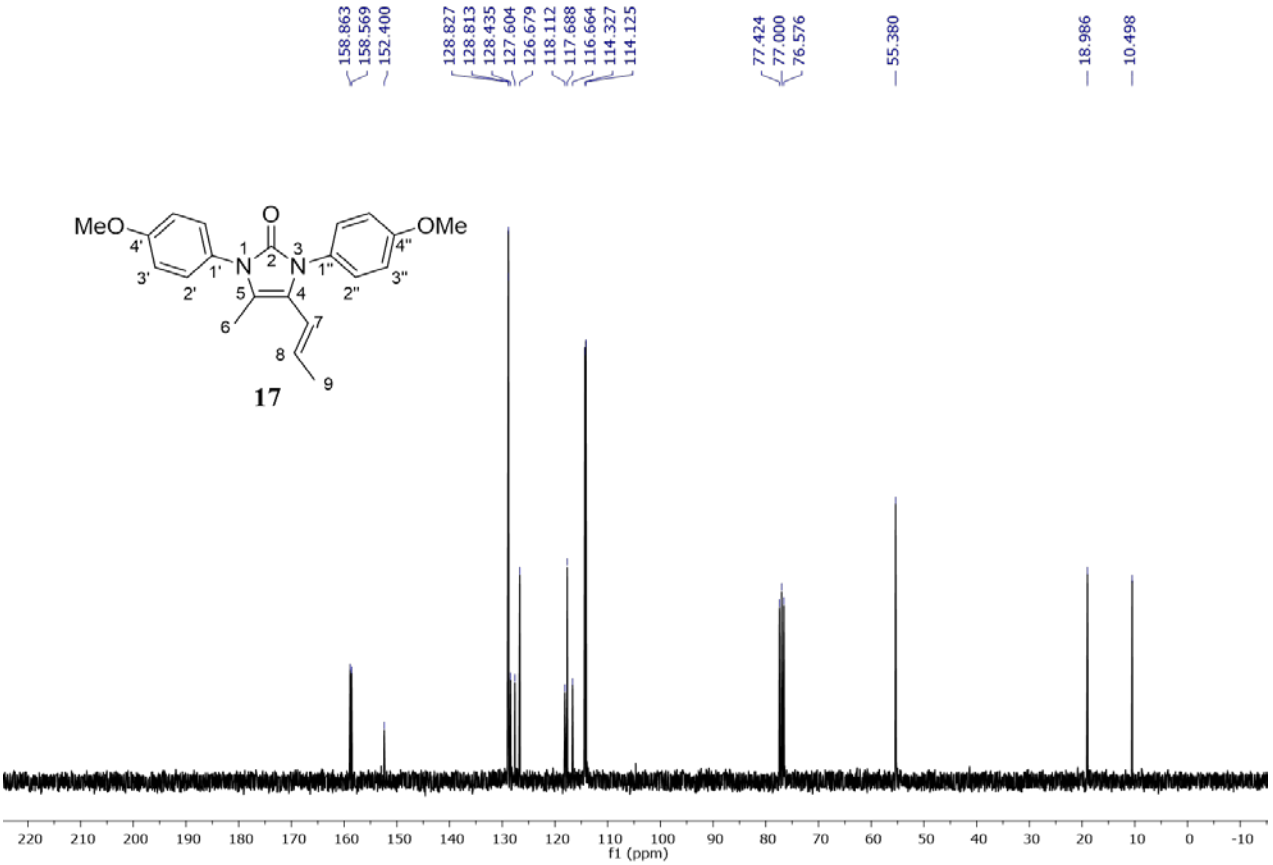
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **14** and **15**.



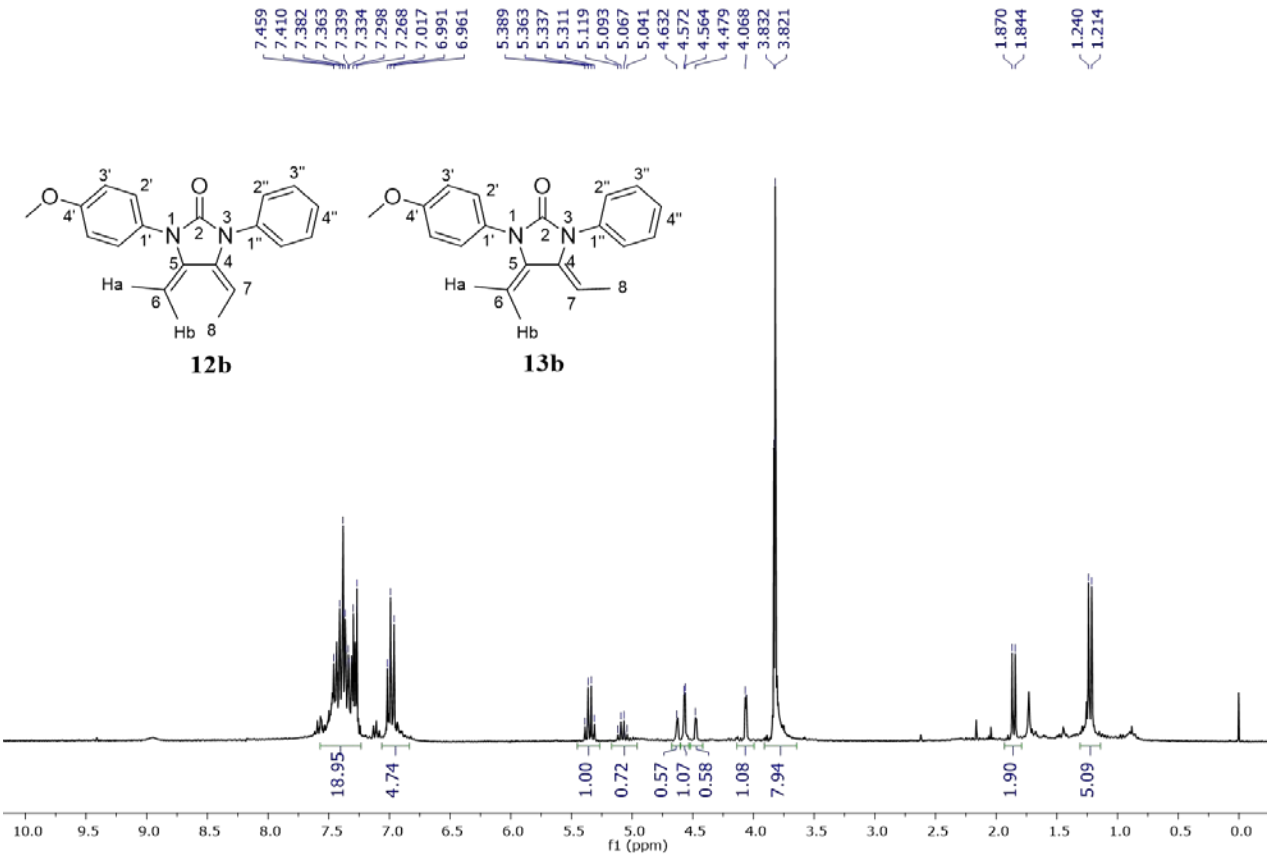
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **14** and **15**.



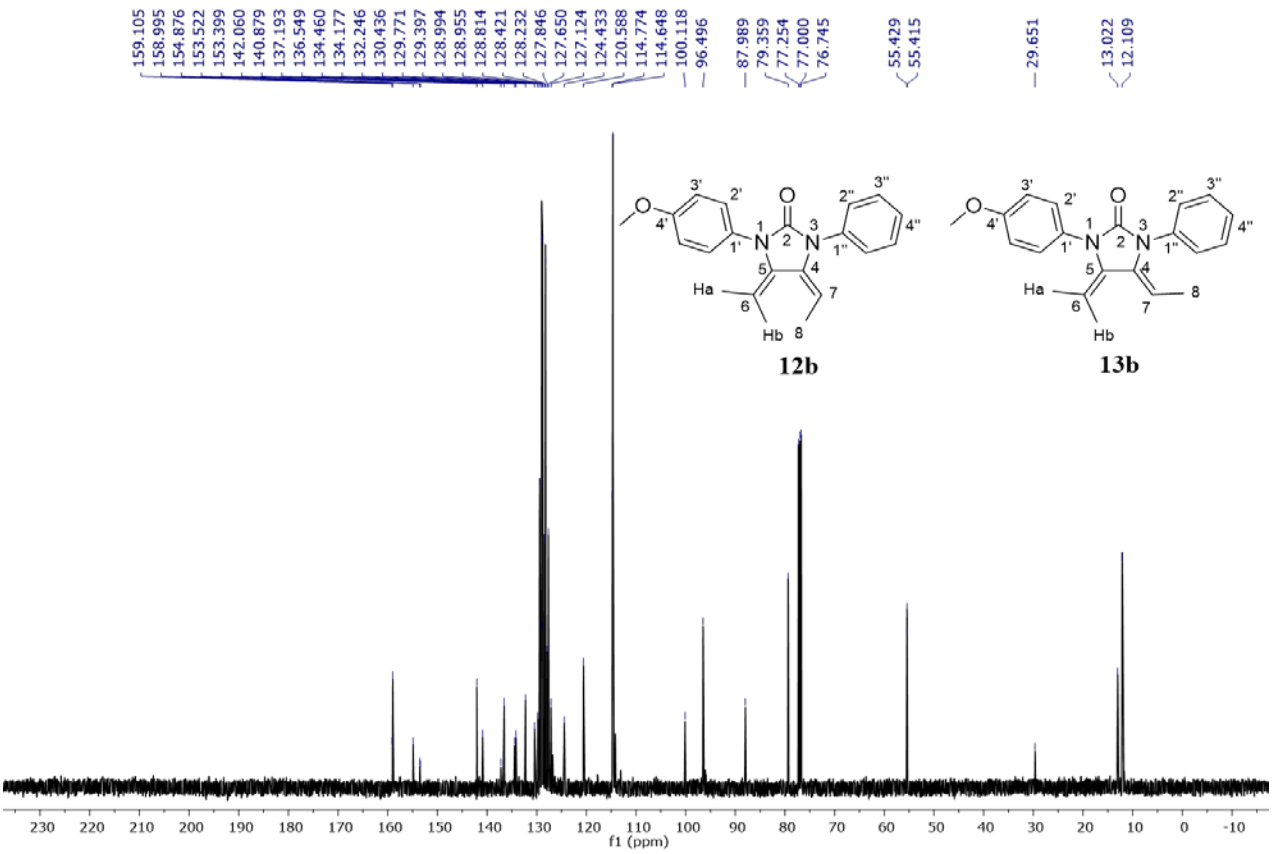
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **17**.



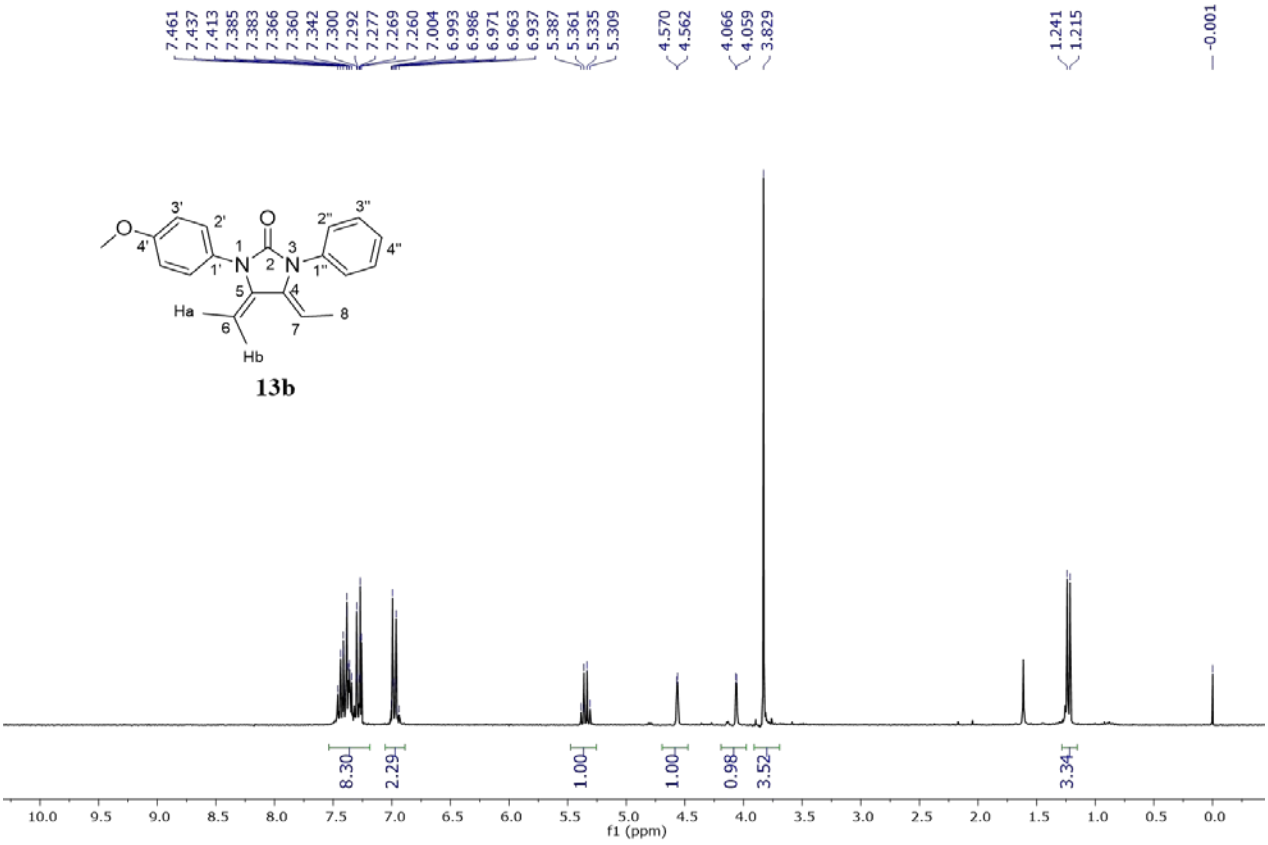
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **17**.



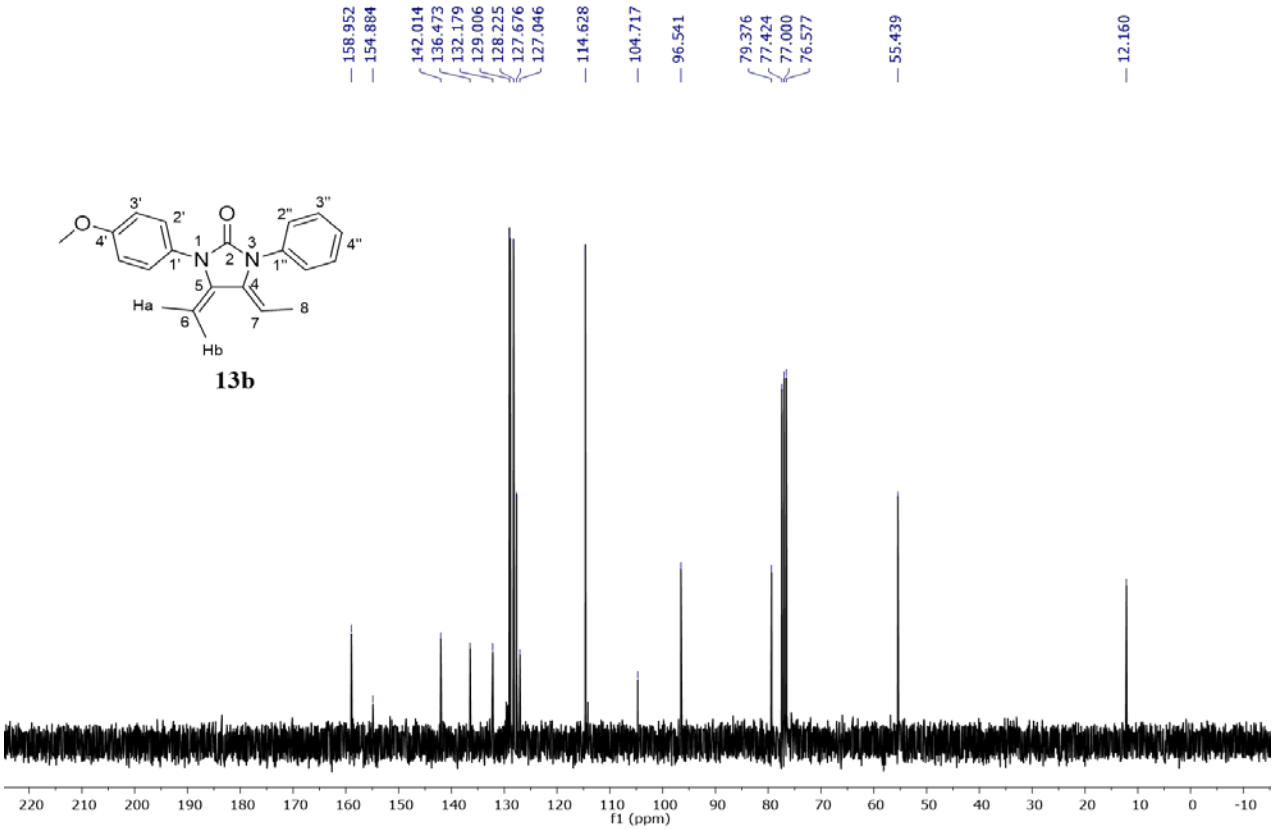
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **12b** and **13b**.



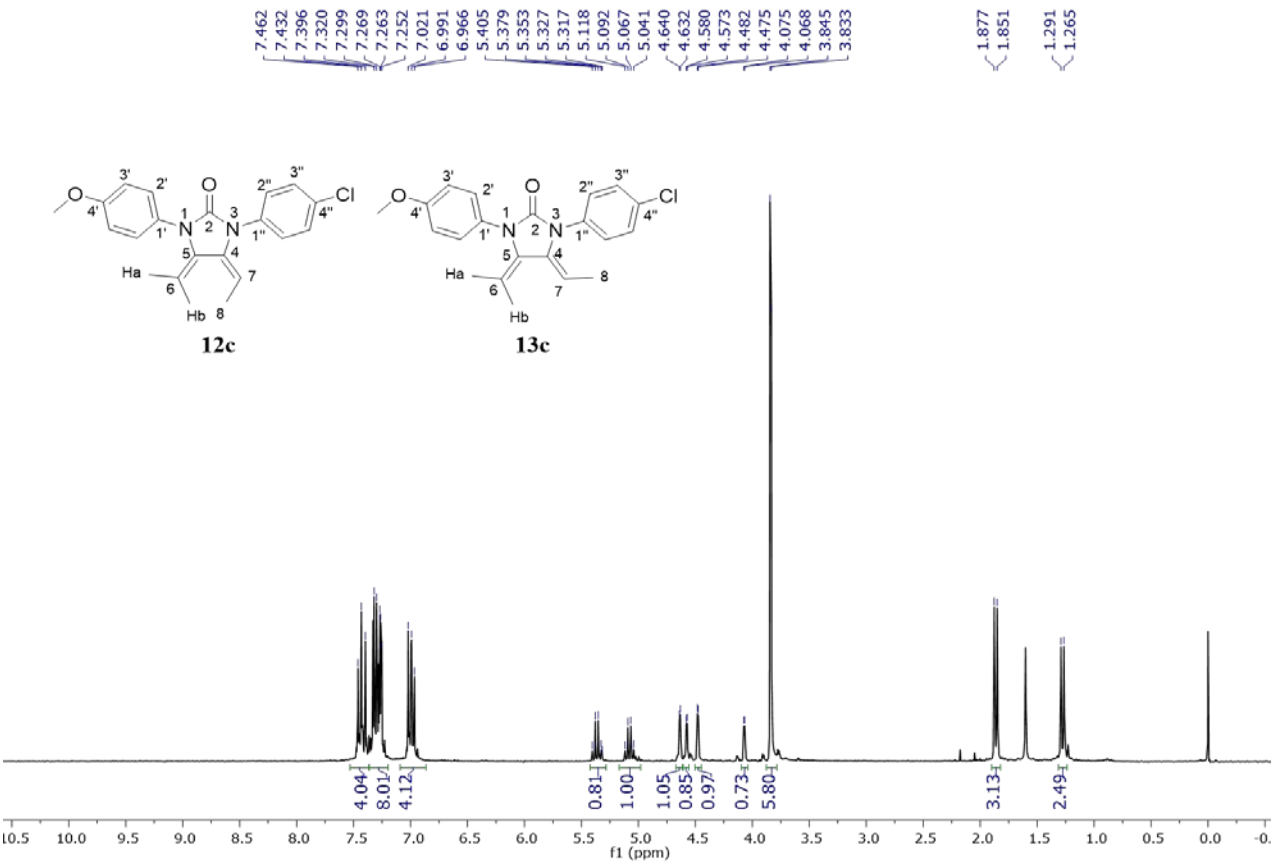
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **12b** and **13b**.



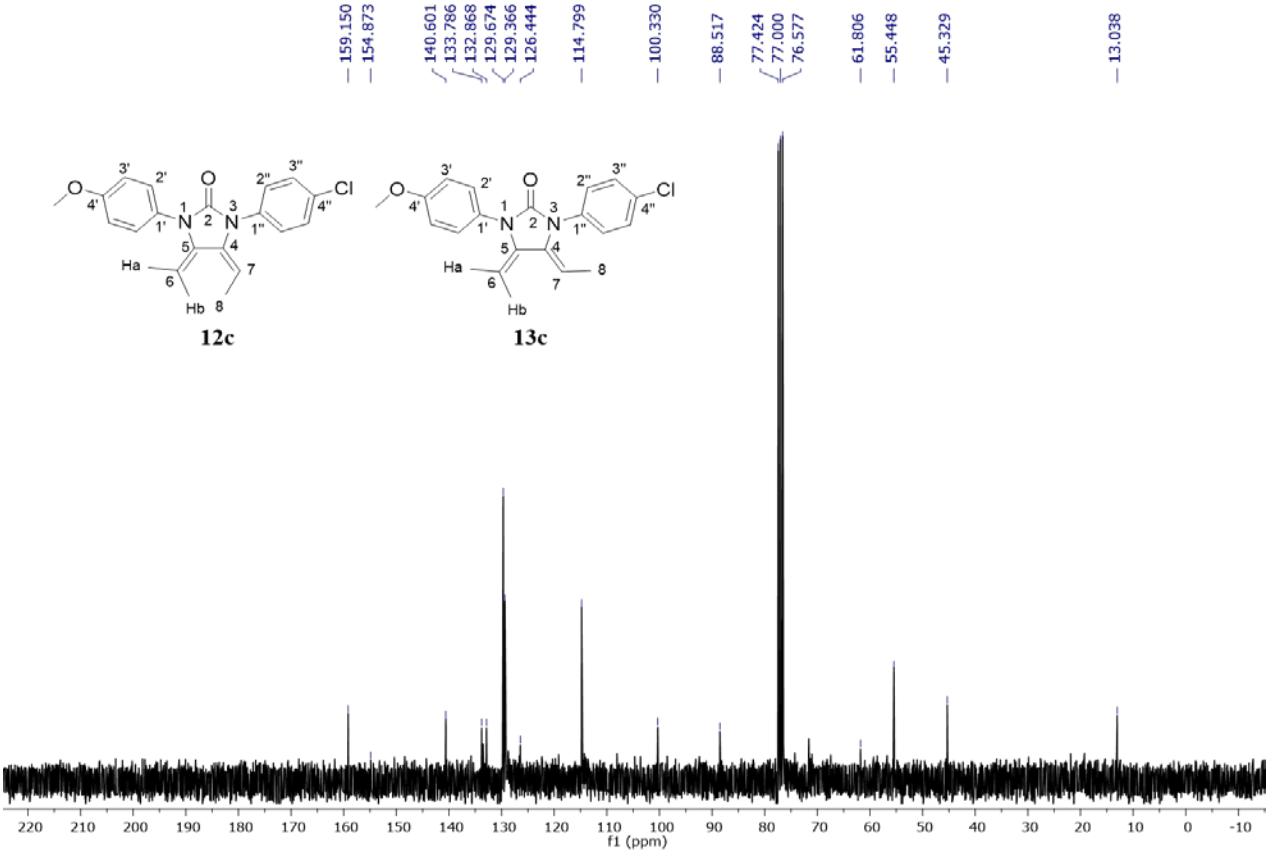
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **13b**.



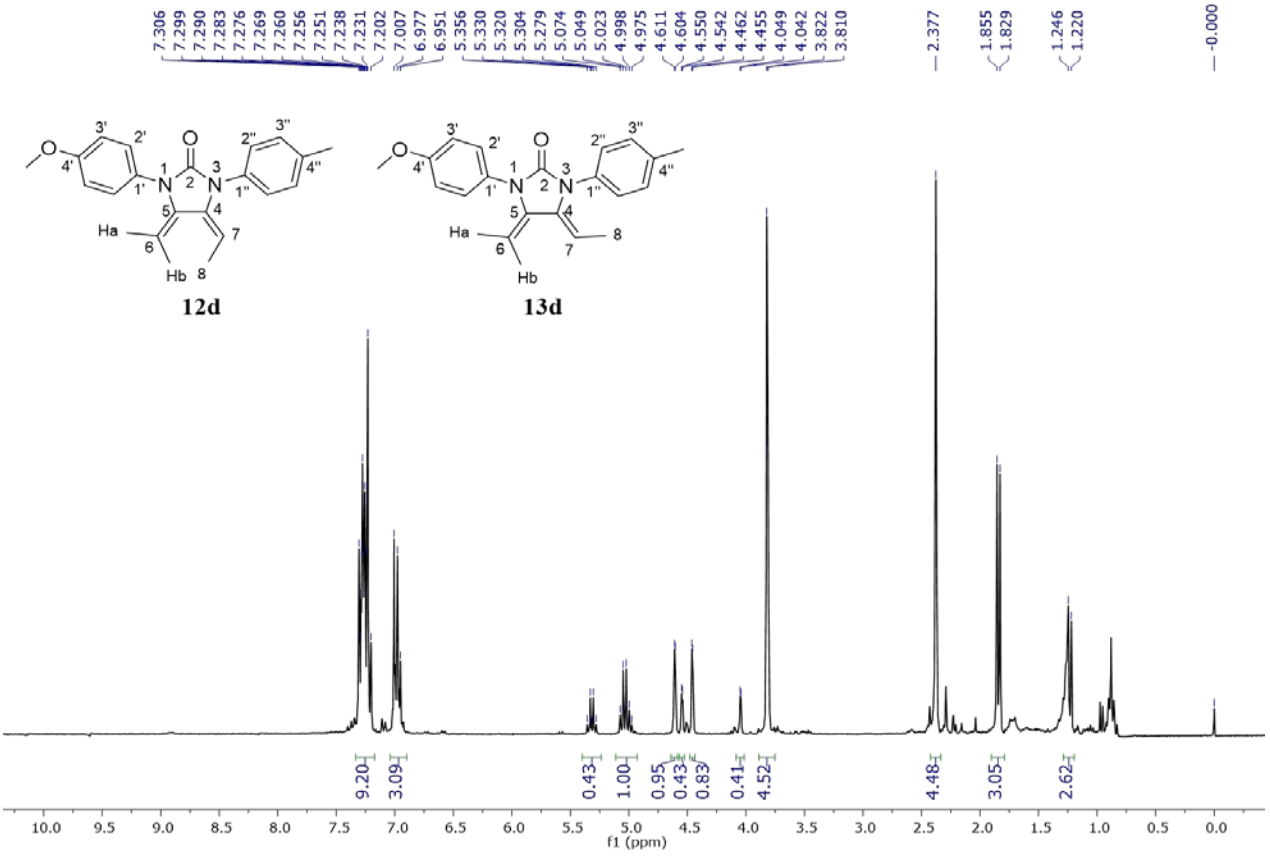
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **13b**.



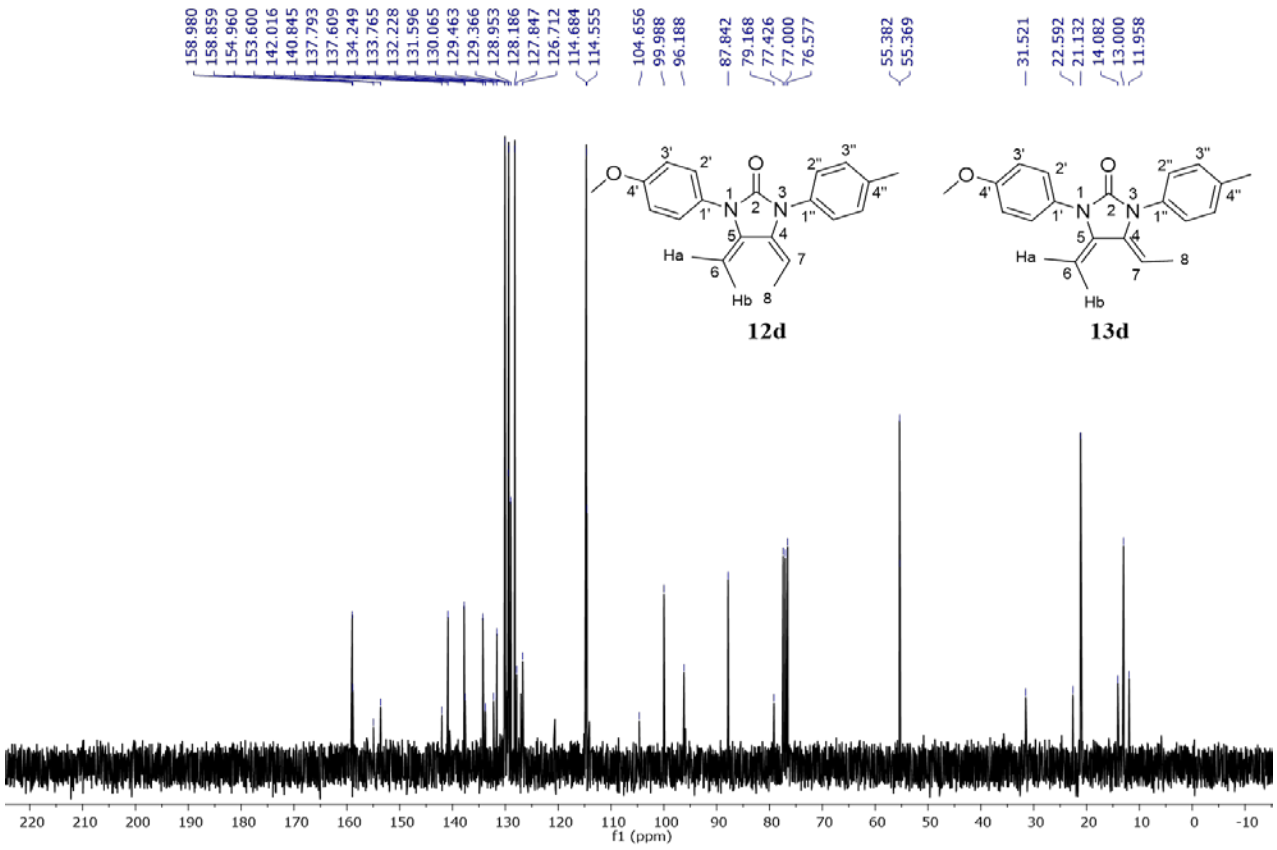
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **12c** and **13c**.



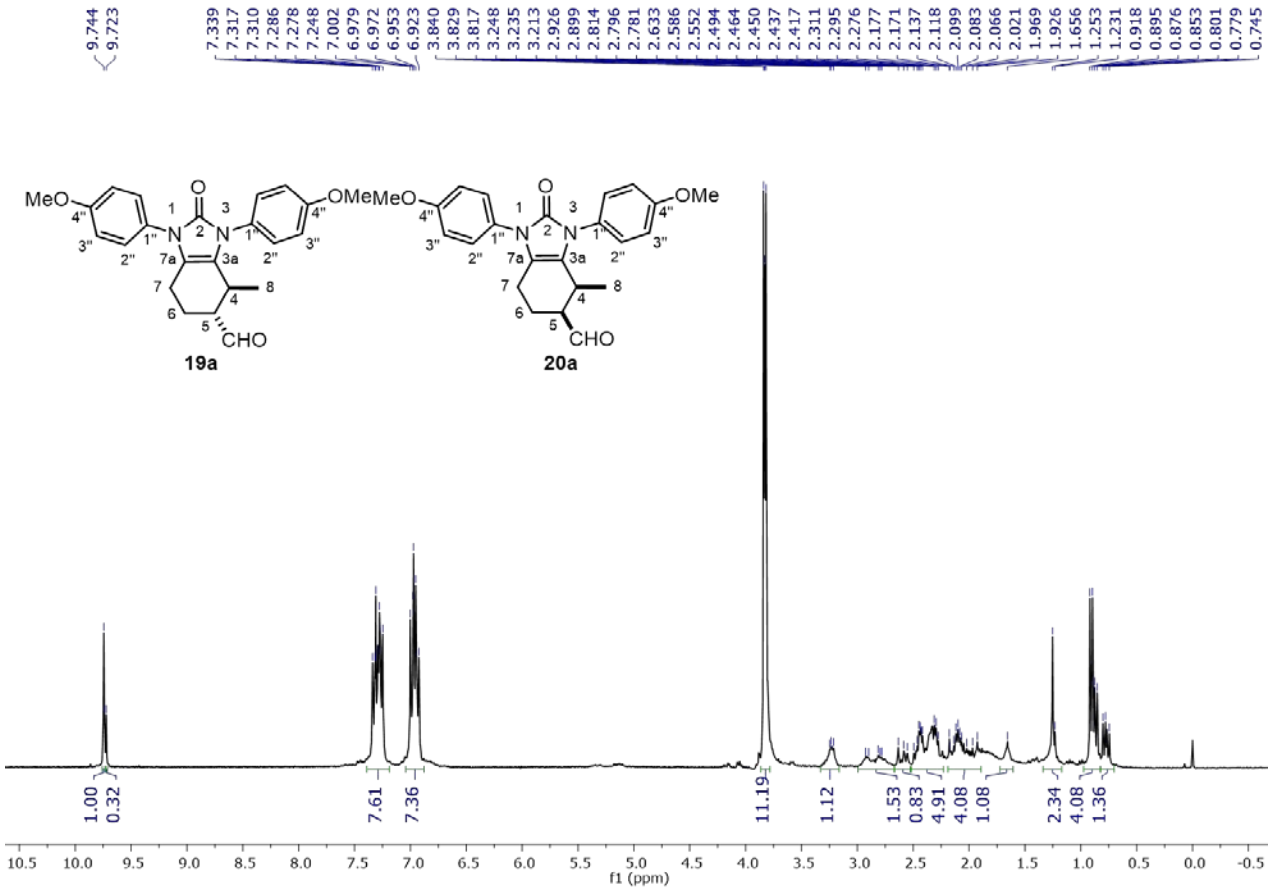
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **12c** and **13c**.



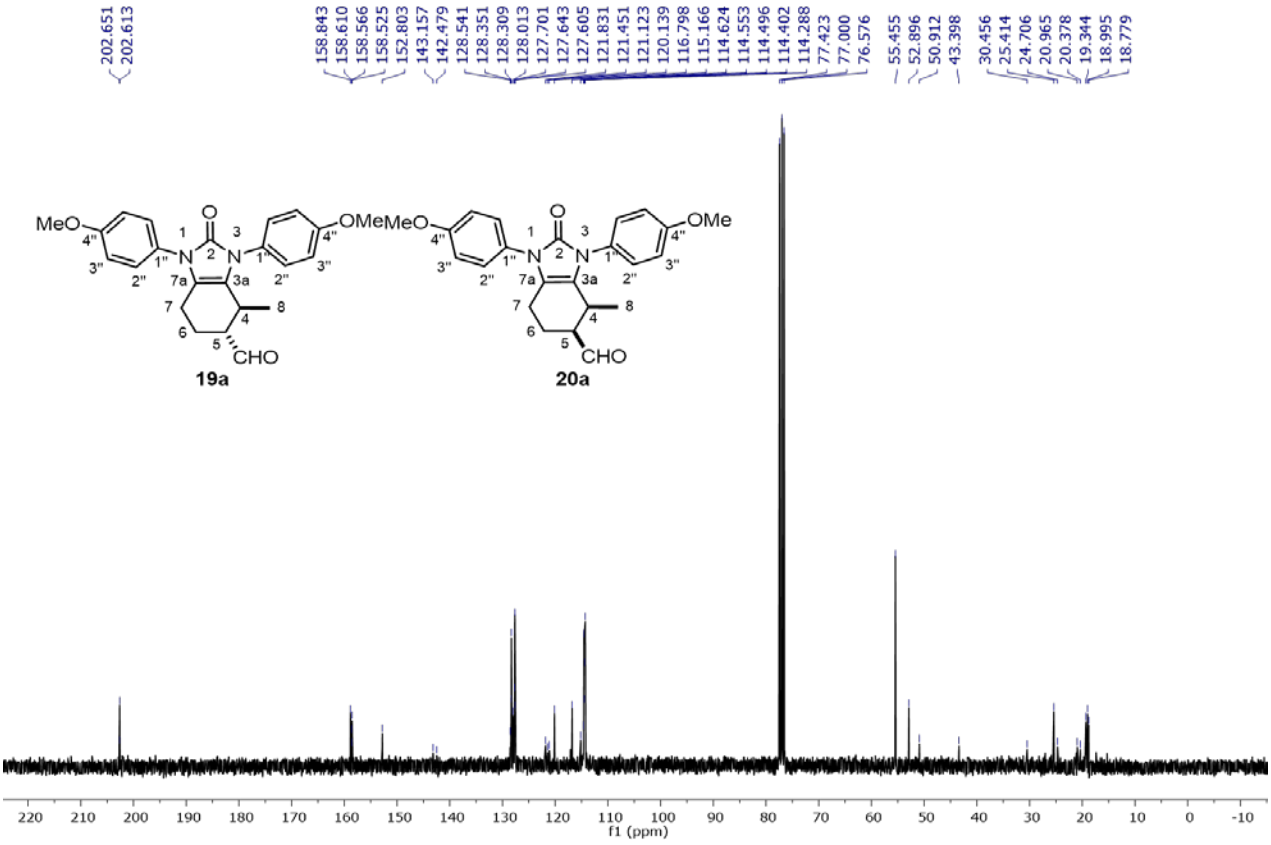
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **12d** and **13d**.



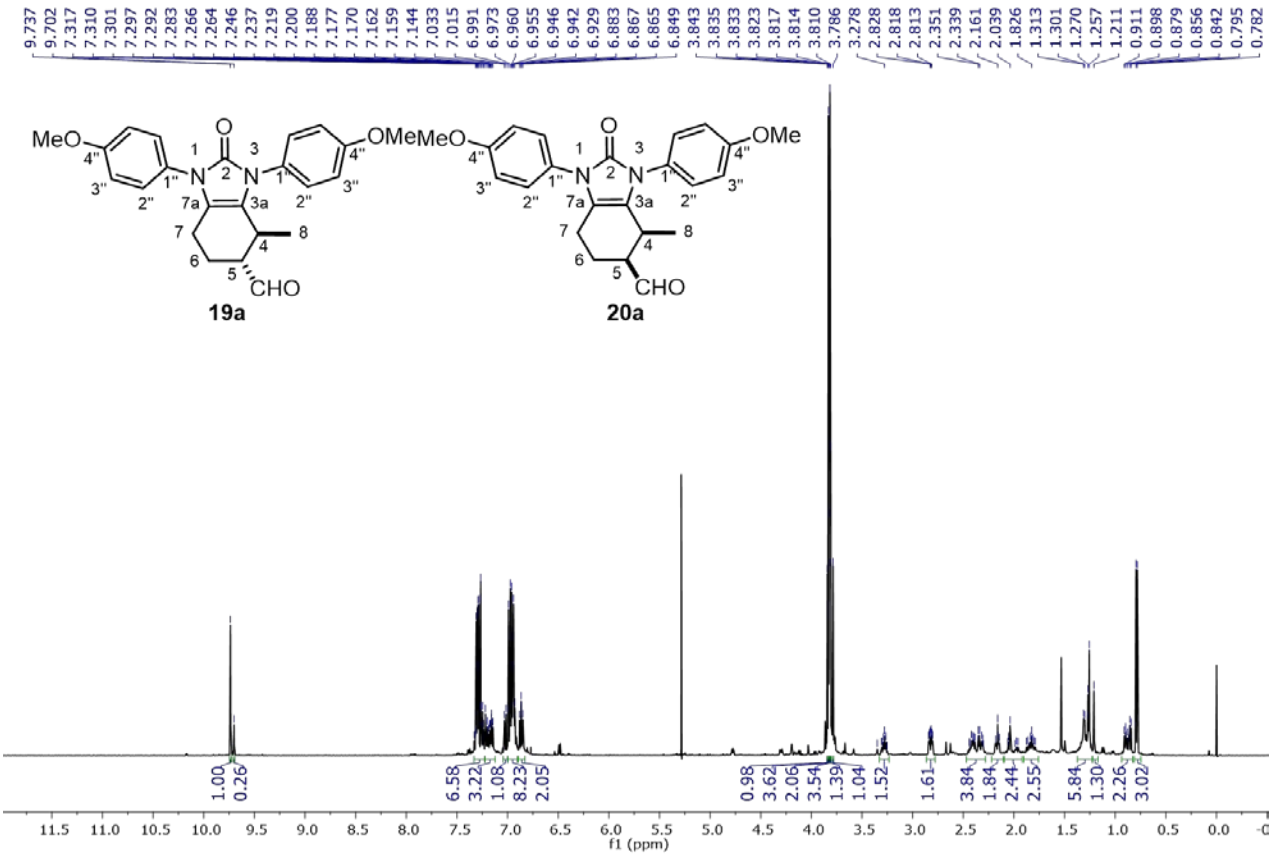
^{13}C NMR ($CDCl_3$, 75.4 MHz) spectrum of **12d** and **13d**.



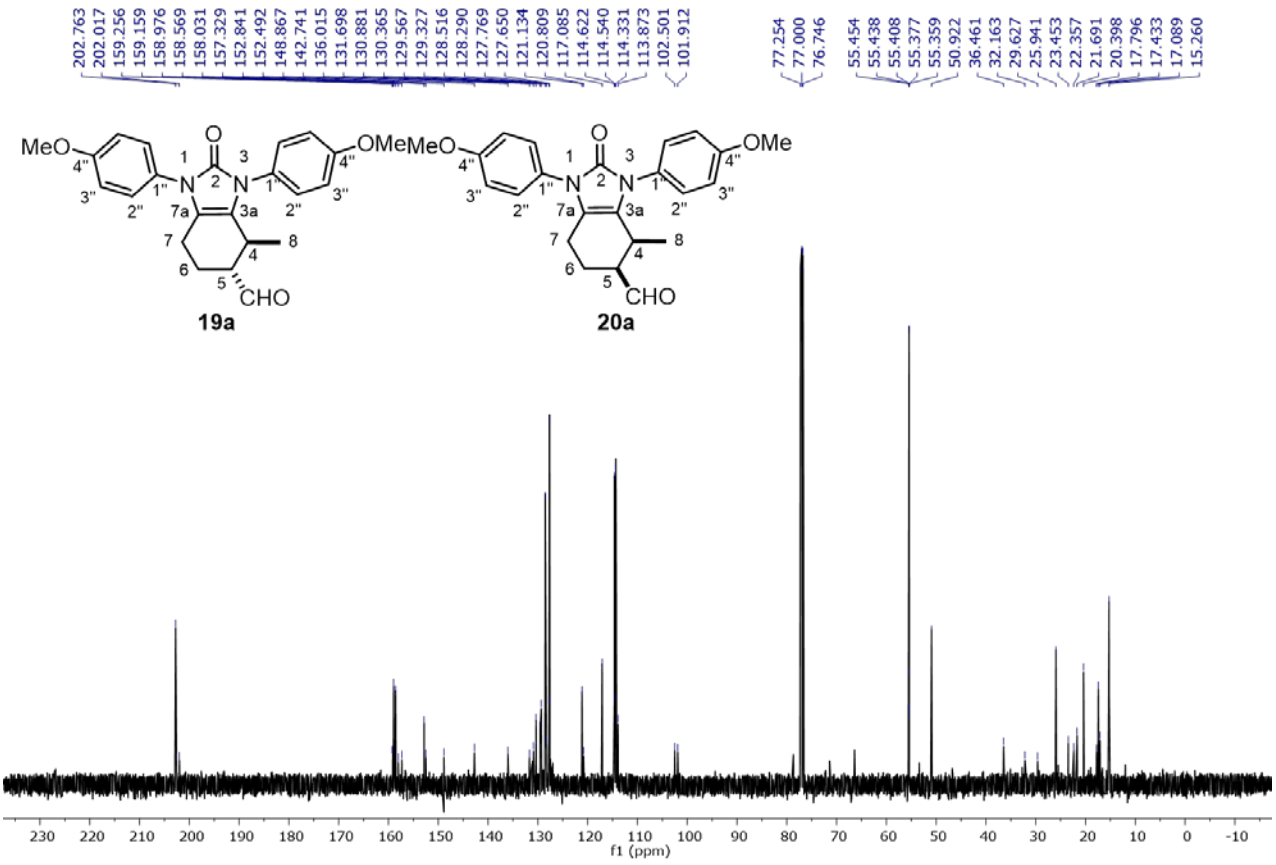
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the mixture of **19a** and **20a**. (BF_3OEt_2)



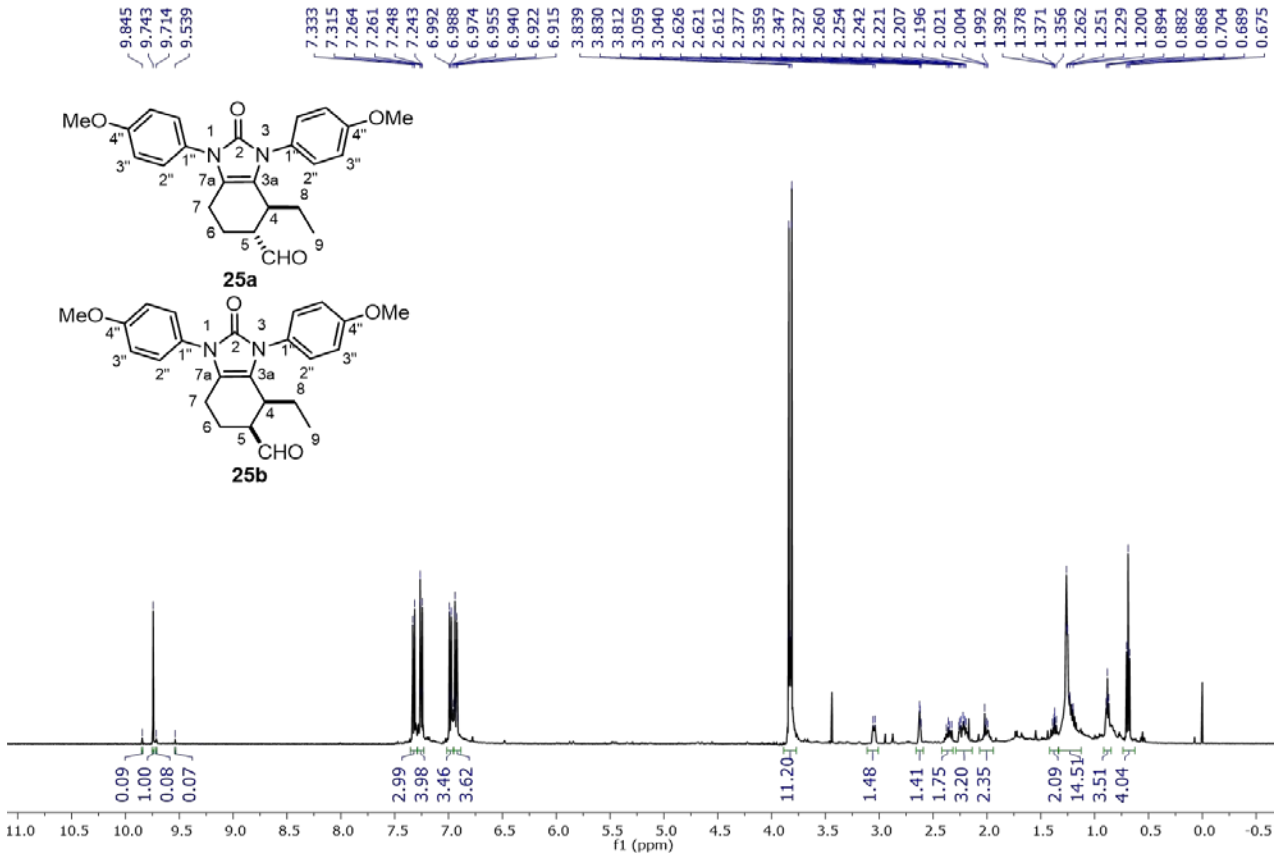
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the mixture of **19a** and **20a**. (BF_3OEt_2)



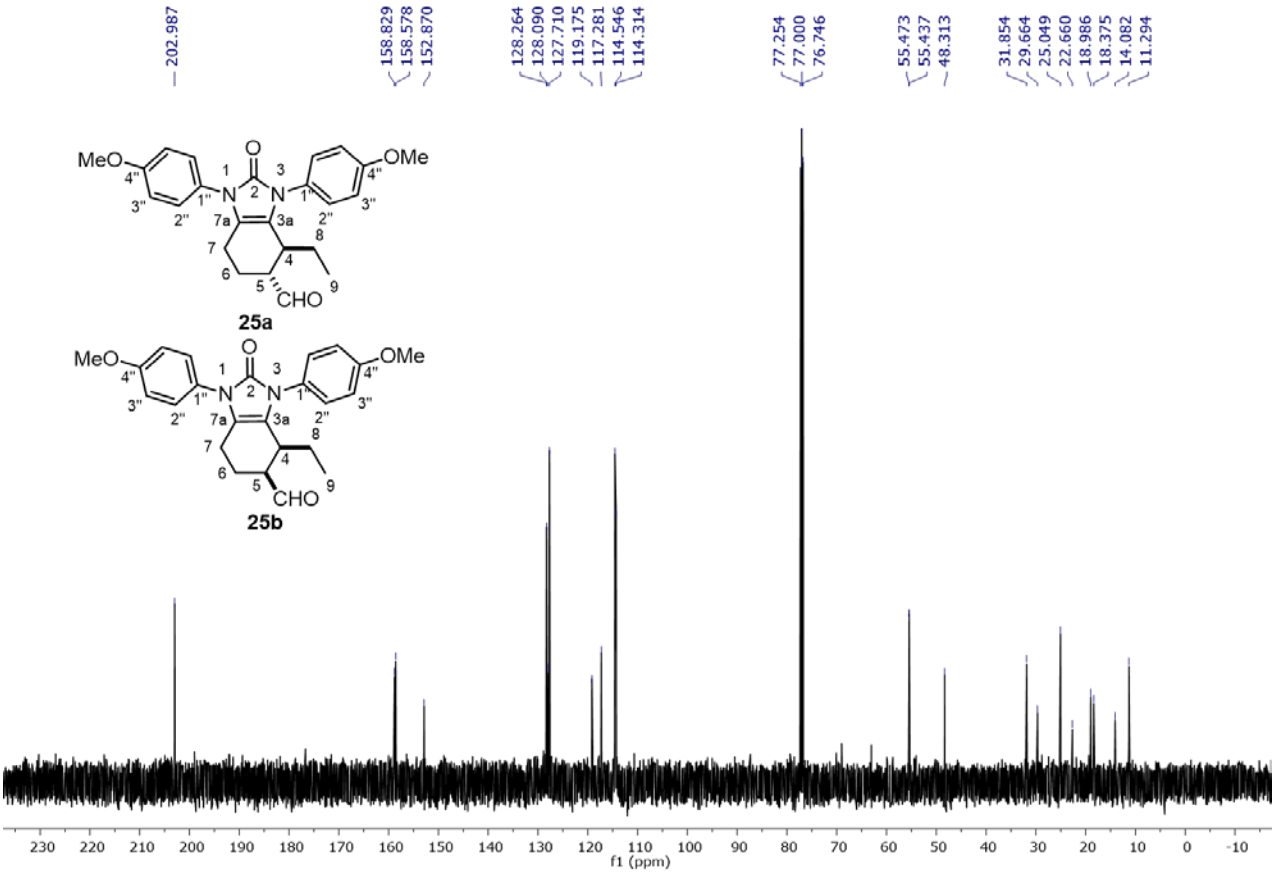
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the mixture of **19a** and **20a**. ($ZnCl_2$)



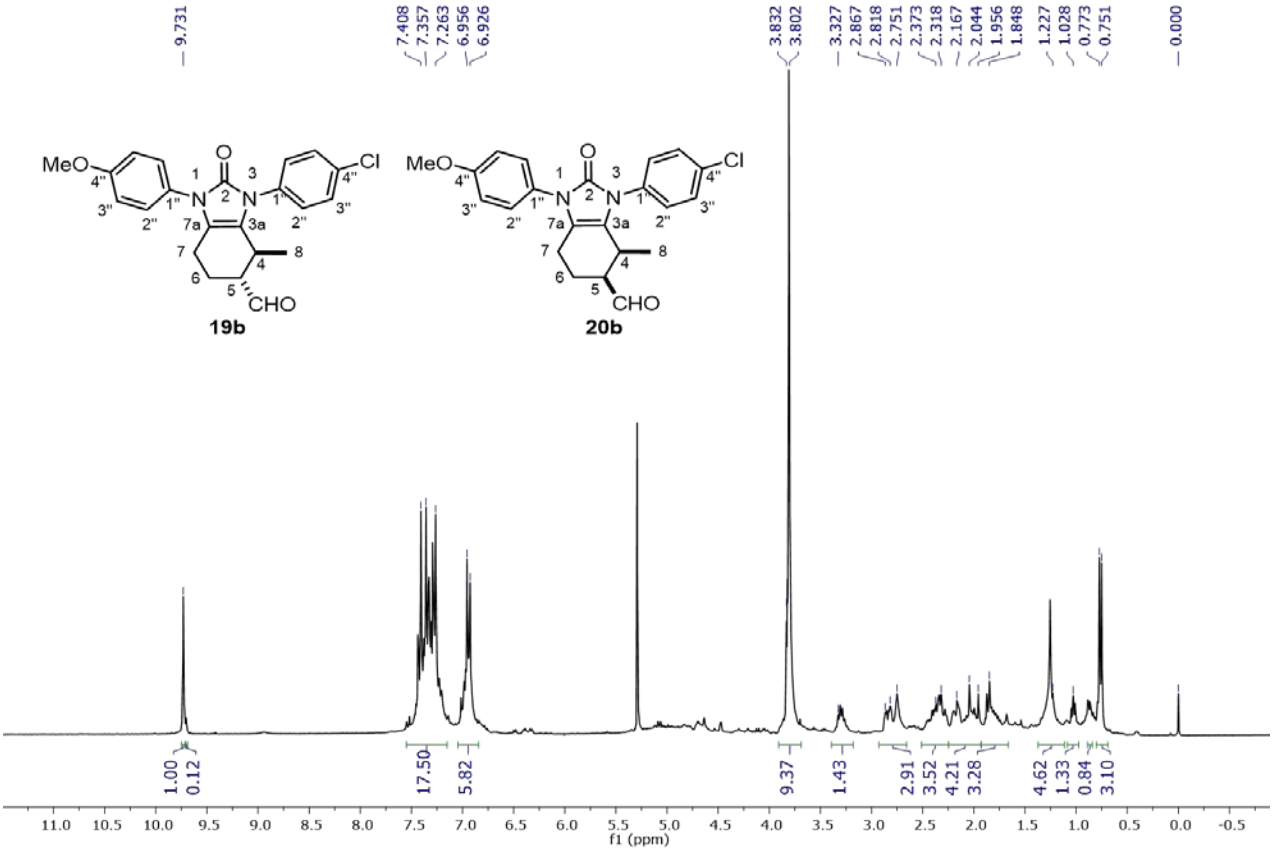
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the mixture of **19a** and **20a**. ($ZnCl_2$)



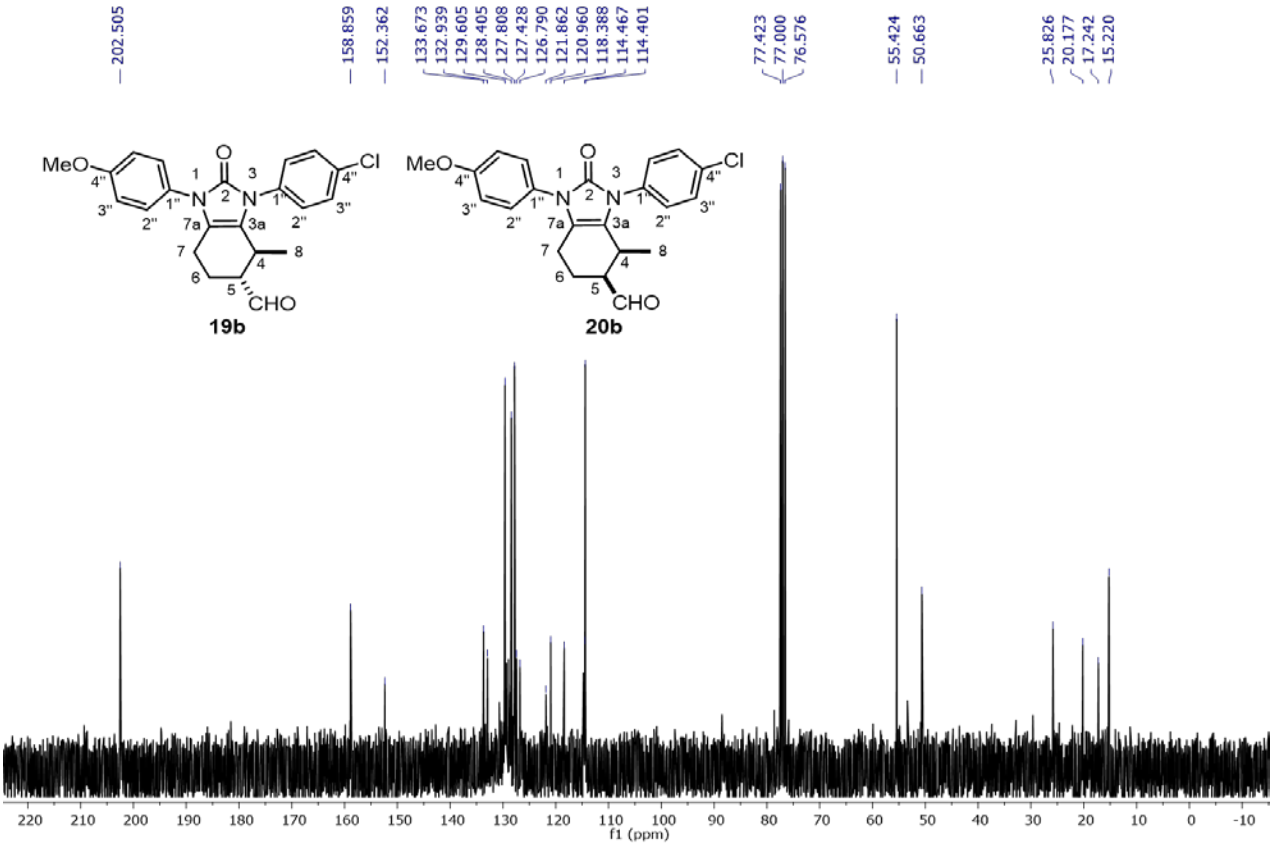
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the mixture of **25a** and **25b**.



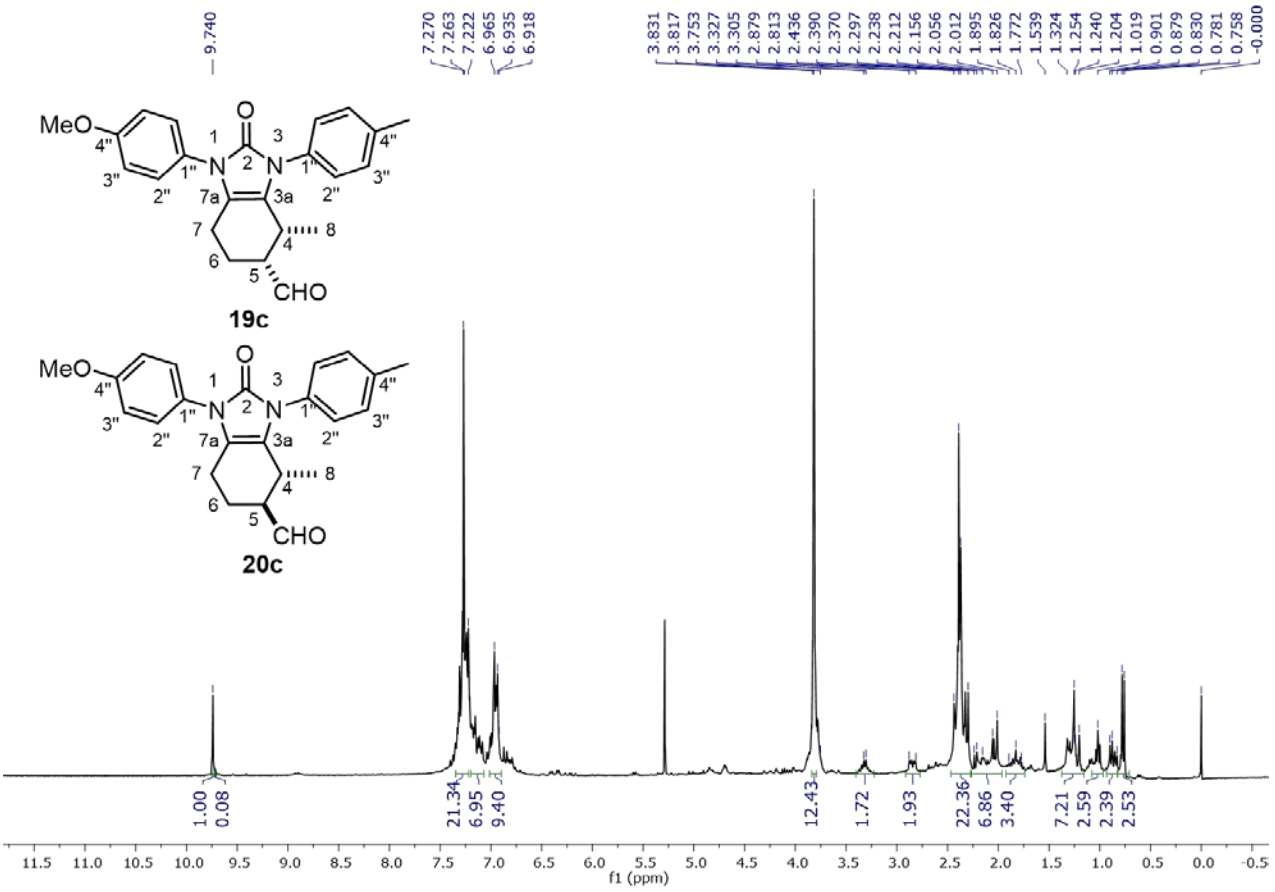
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the mixture of **25a** and **25b**.



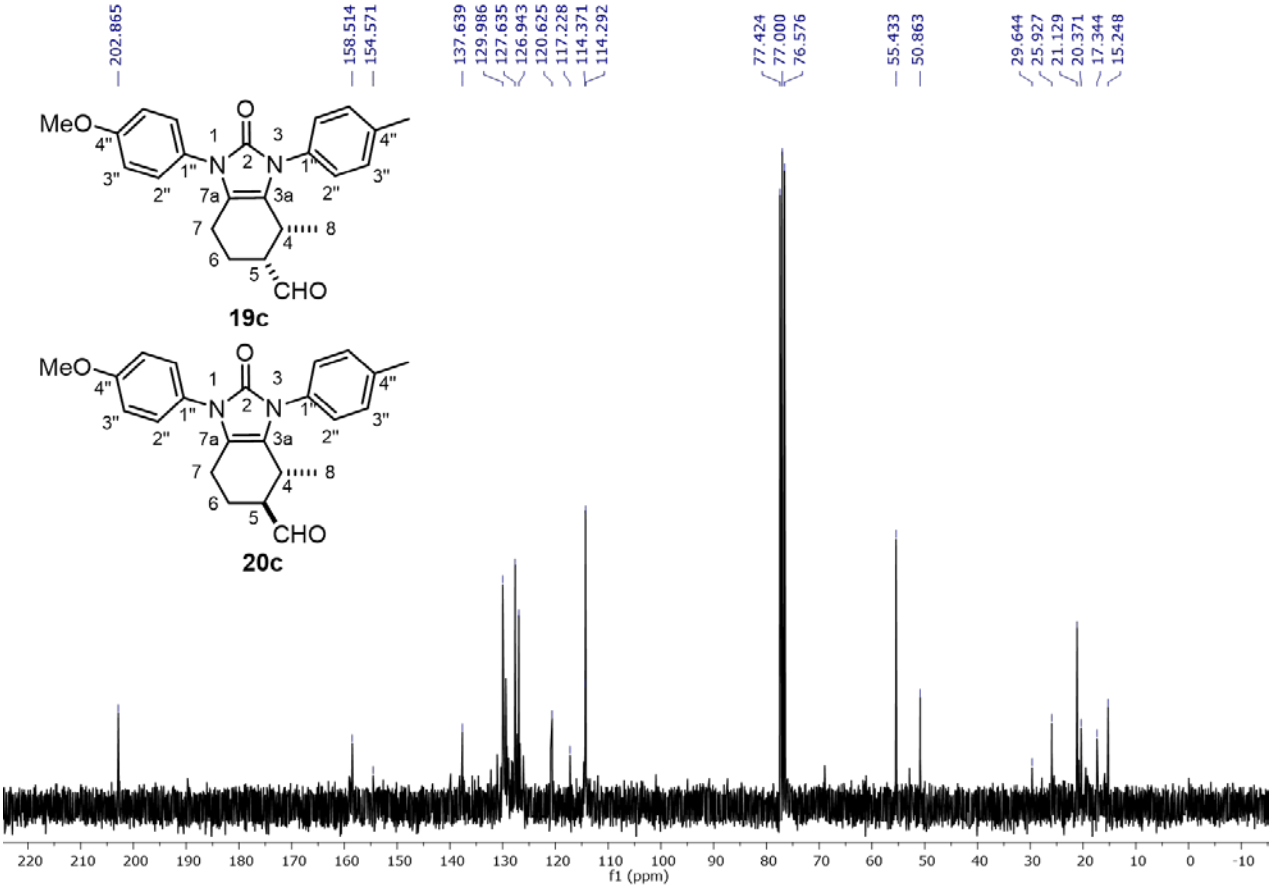
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the mixture of **19b** and **20b**.



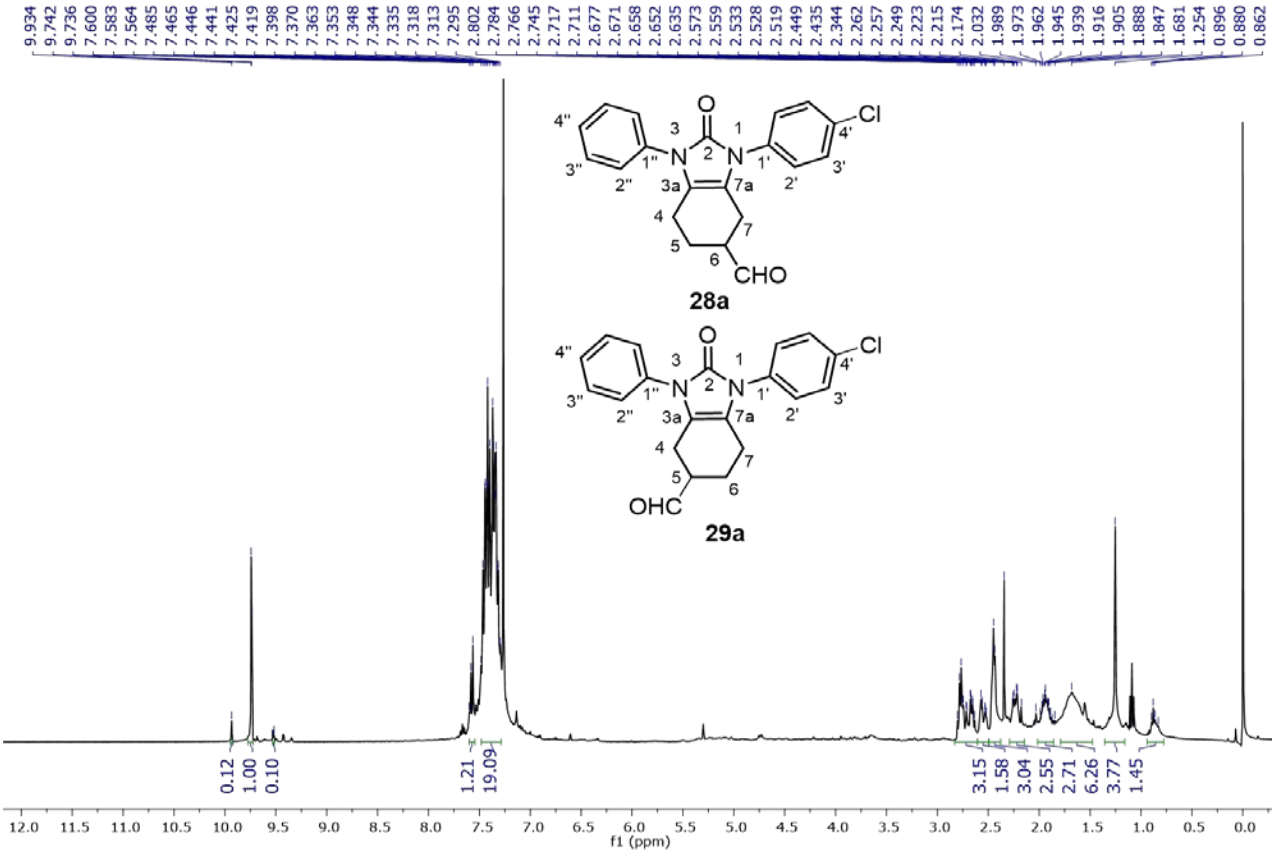
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of the mixture of **19b** and **20b**.



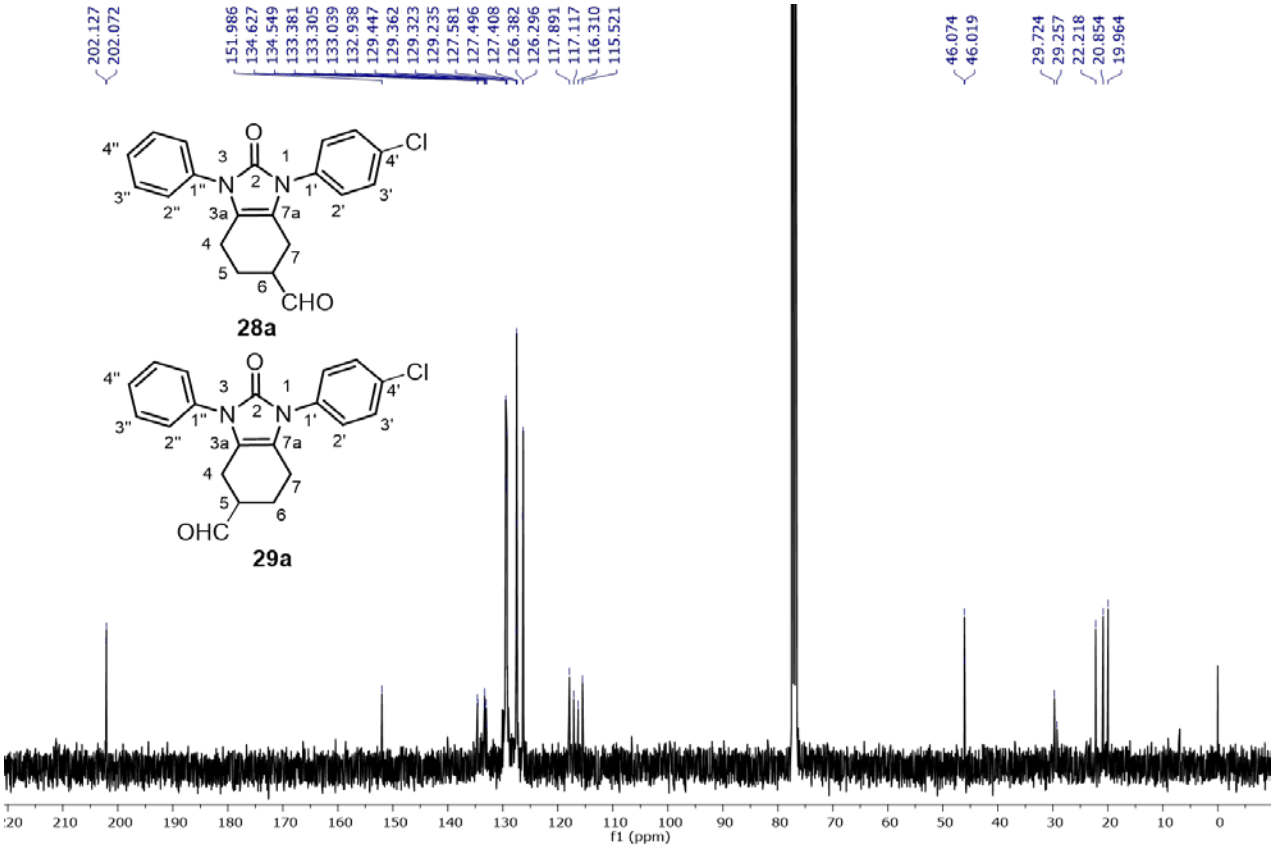
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the mixture of **19c** and **20c**.



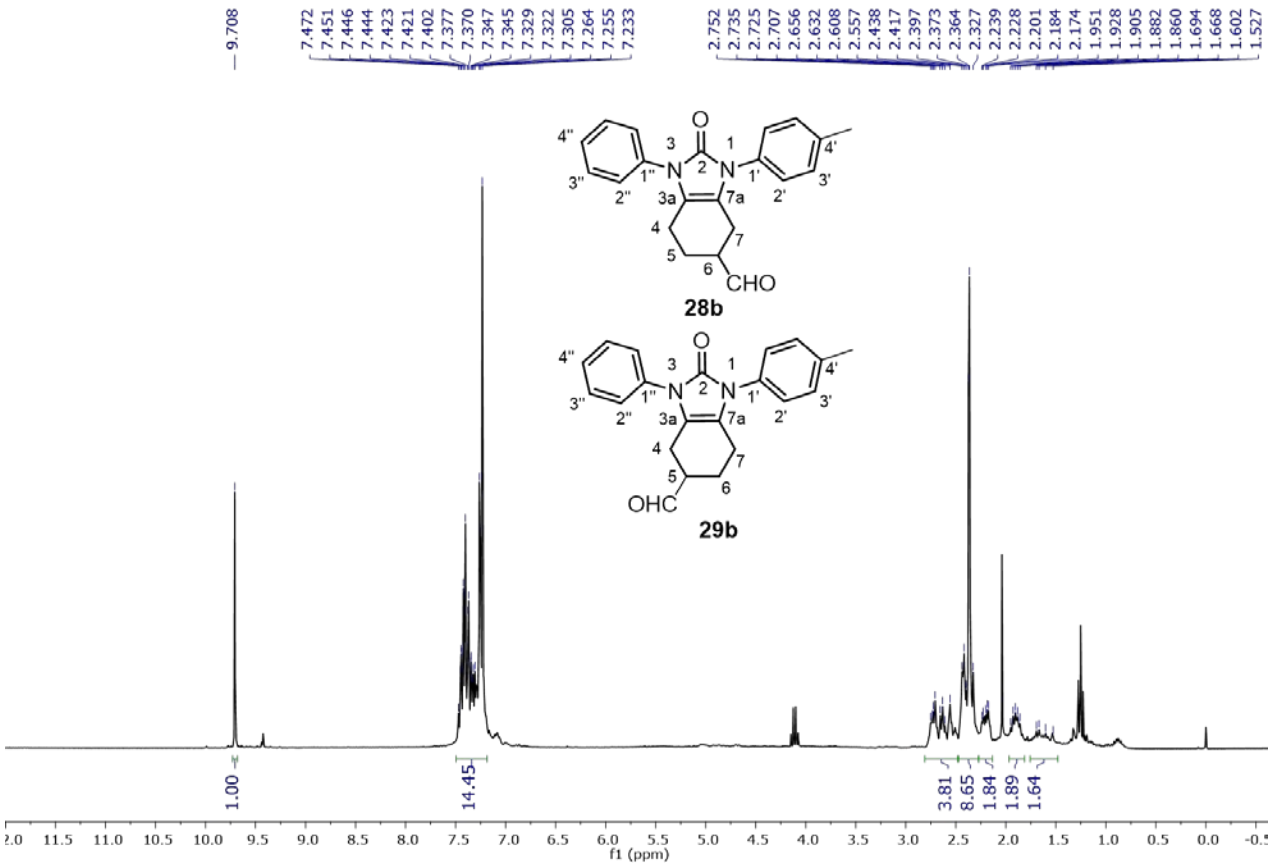
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of the mixture of **19c** and **20c**.



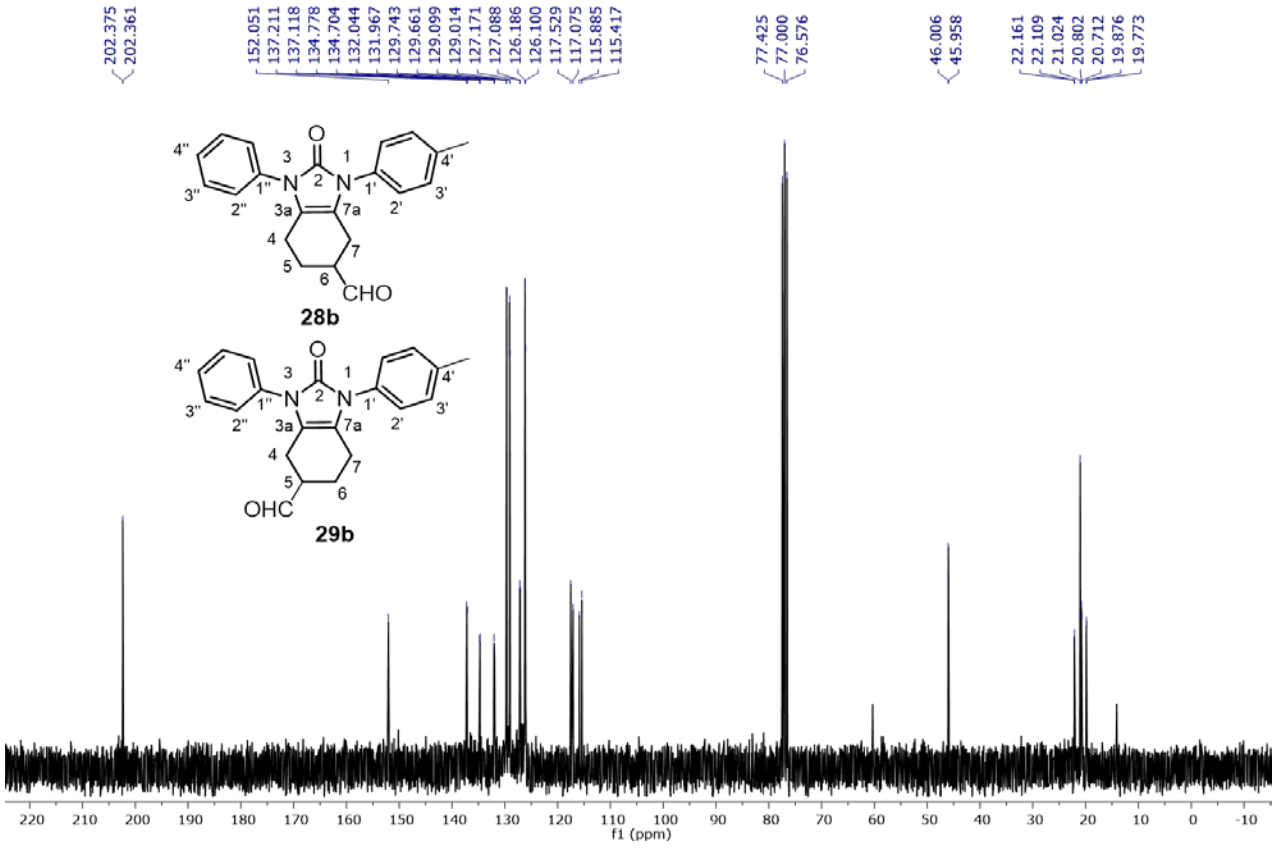
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the mixture of **28a** and **29a**.



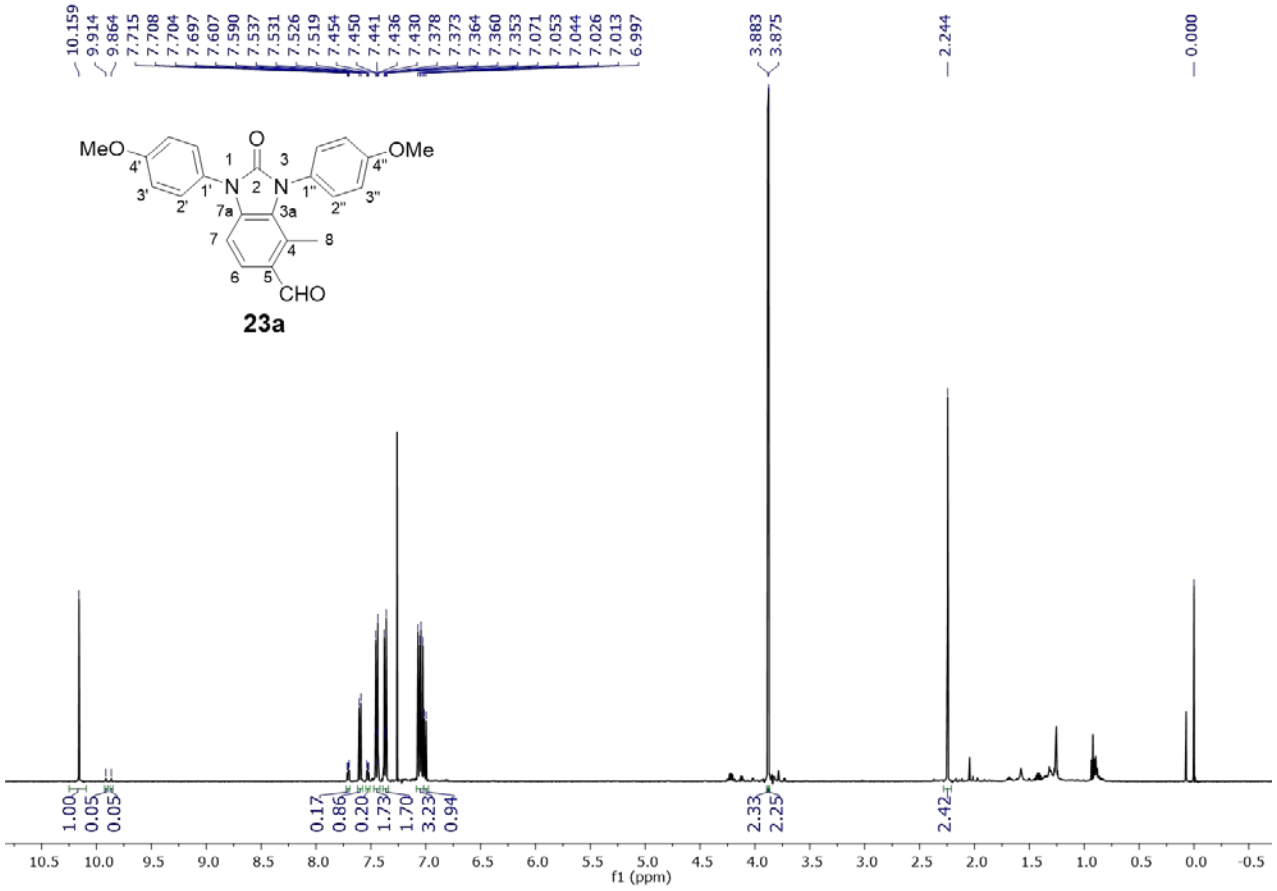
^{1}H NMR (101 MHz, $CDCl_3$) spectrum of the mixture of **28a** and **29a**.



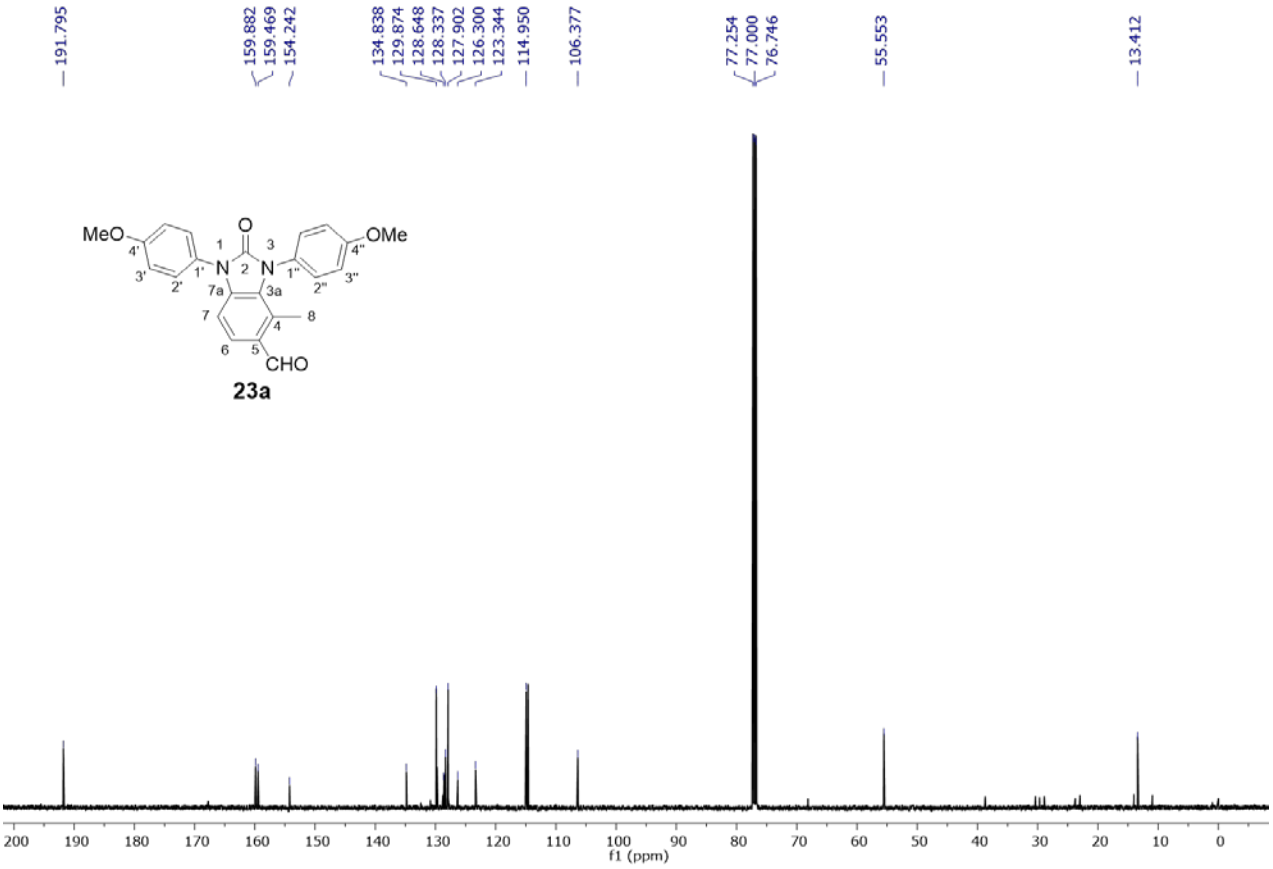
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the mixture of **28b** and **29b**.



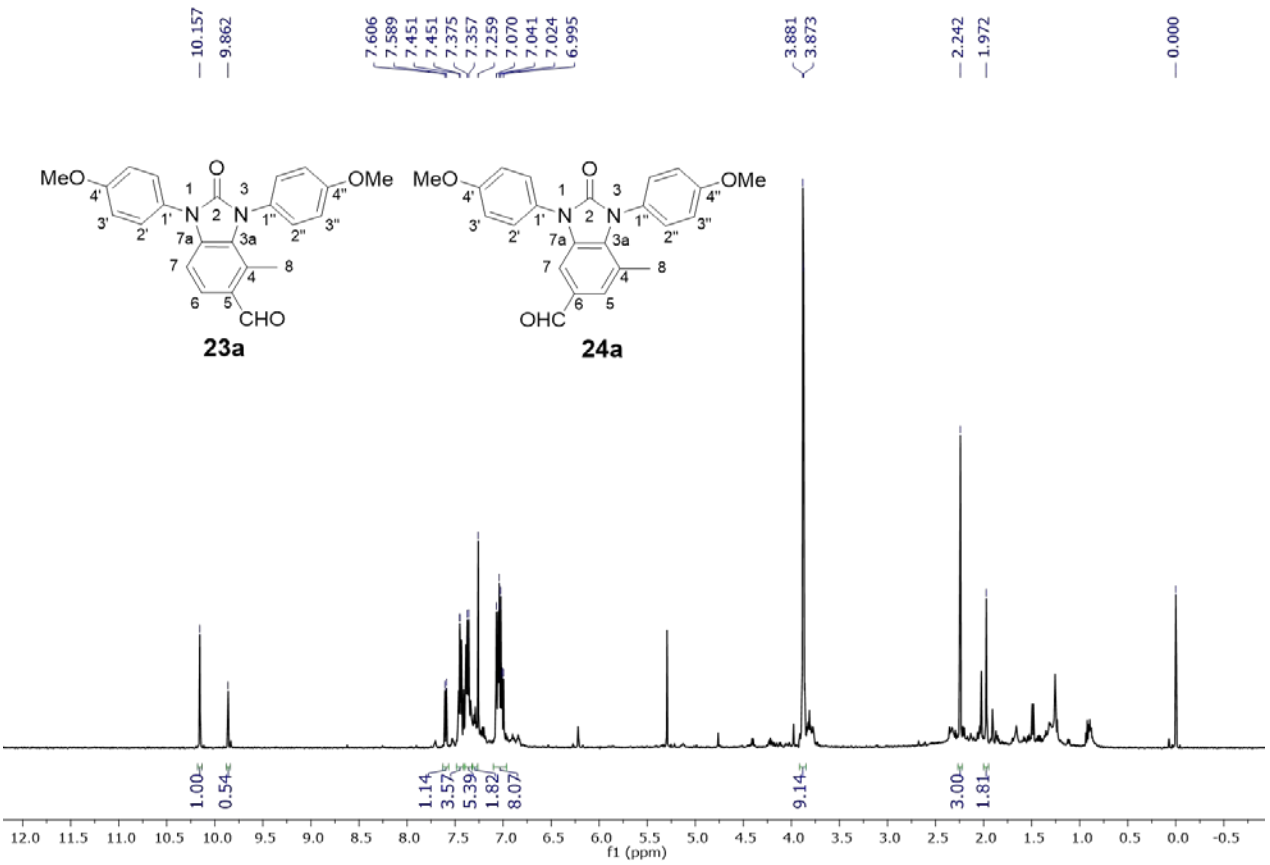
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of the mixture of **28b** and **29b**.



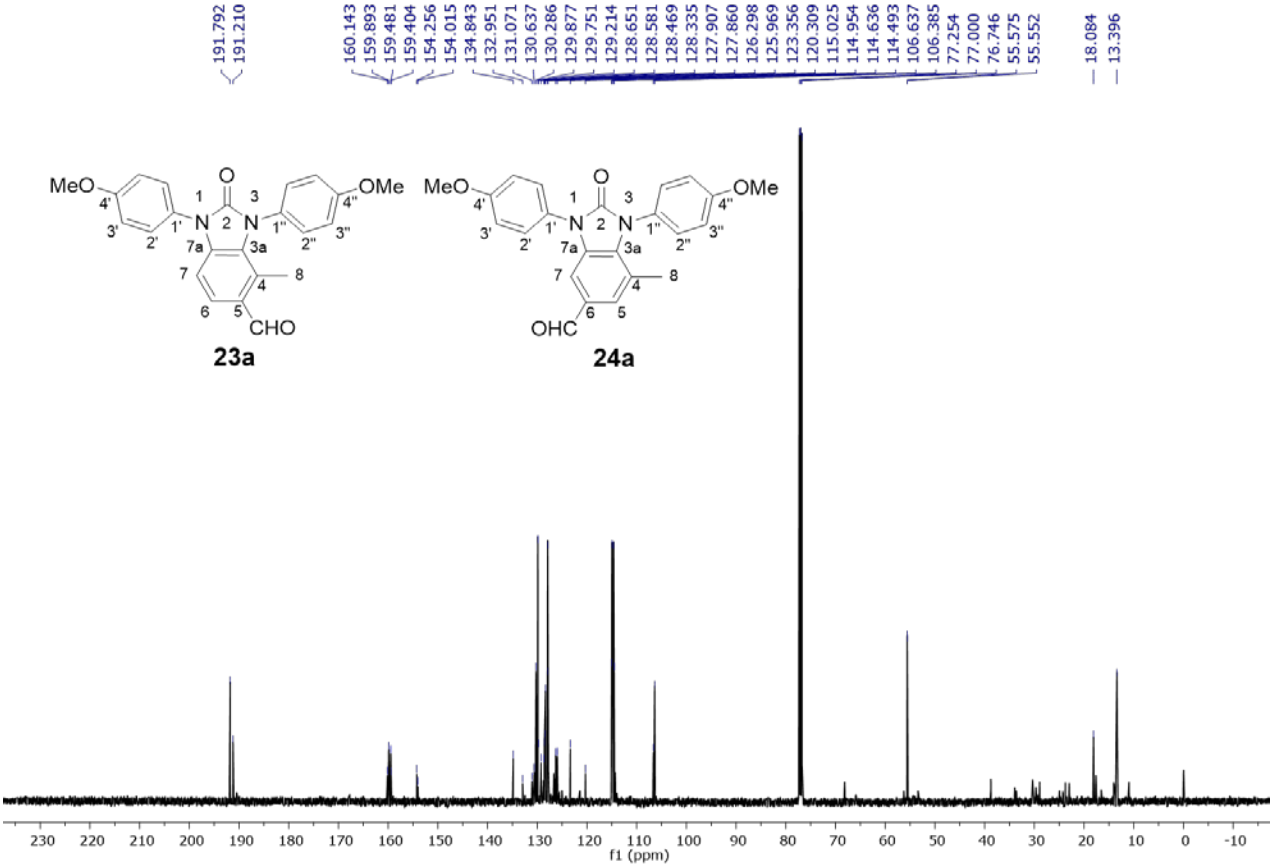
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **23a**.



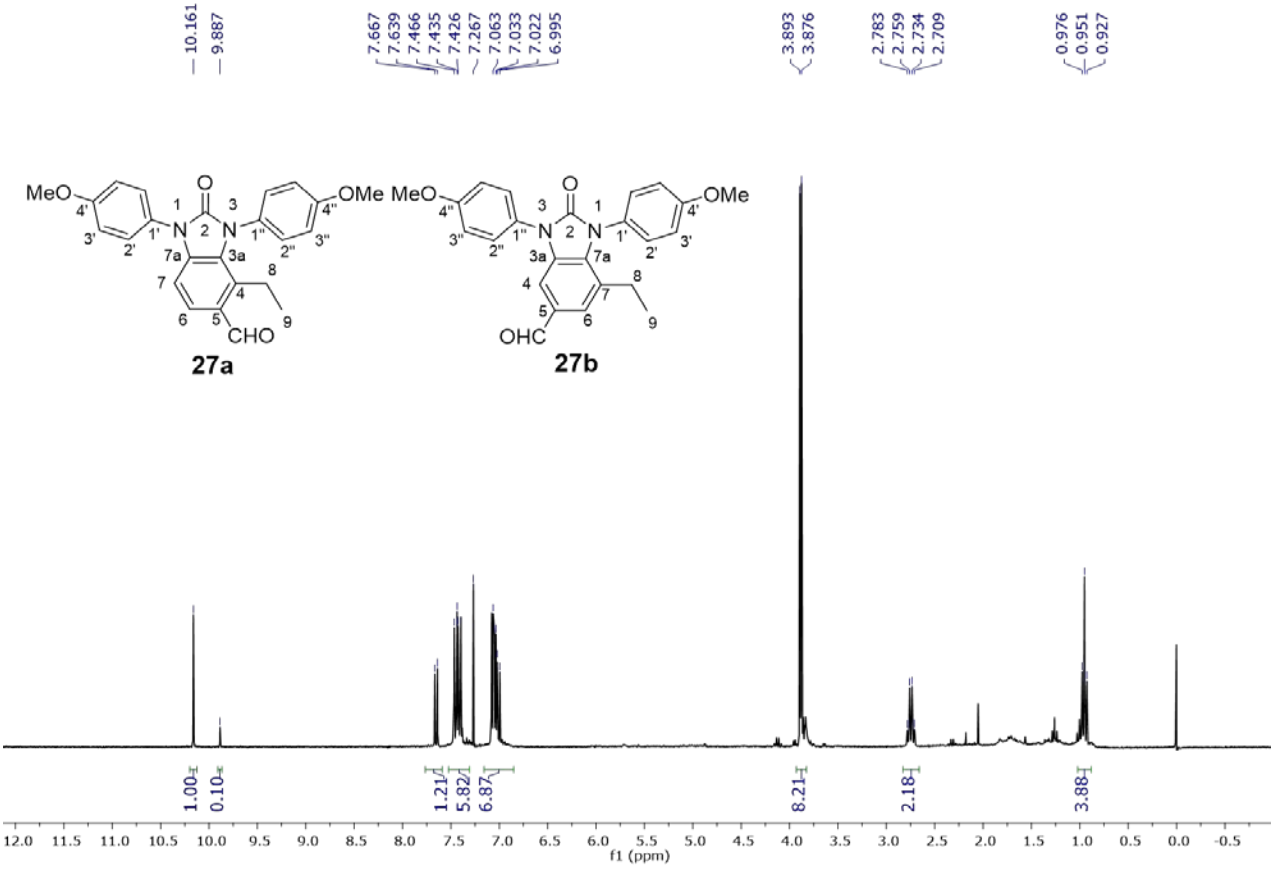
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **23a**.



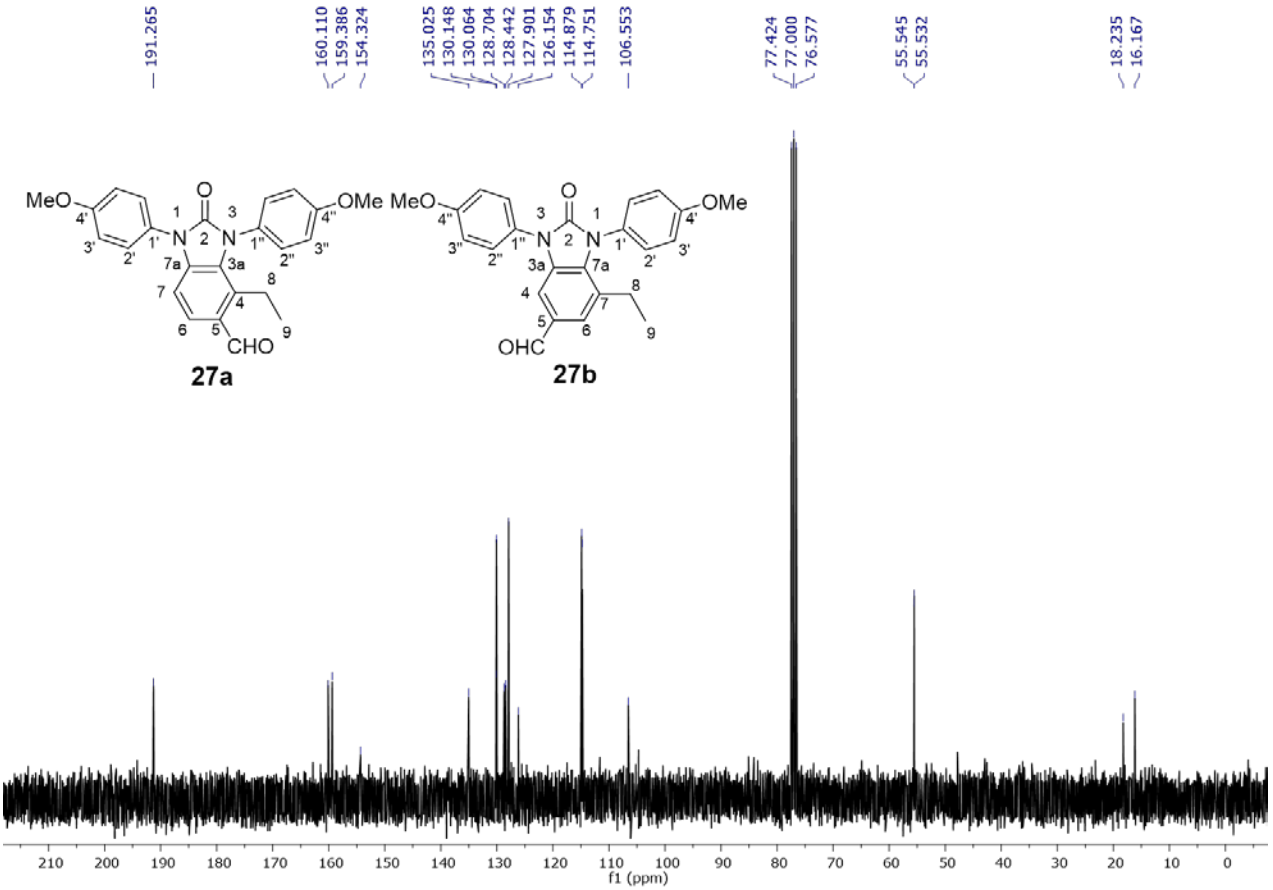
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the mixture of **23a** and **24a**. (BF_3OEt_2)



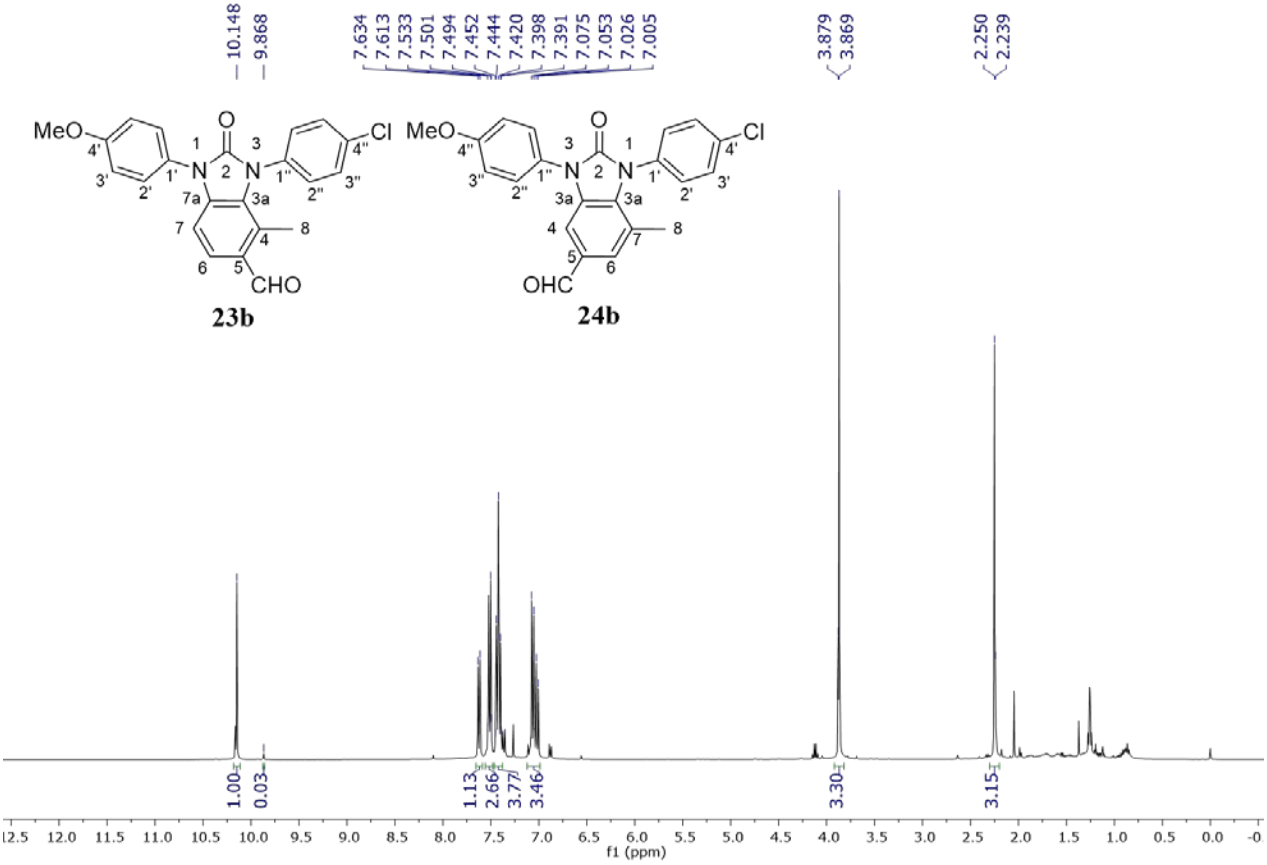
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the mixture of **23a** and **24a**. (BF_3OEt_2)



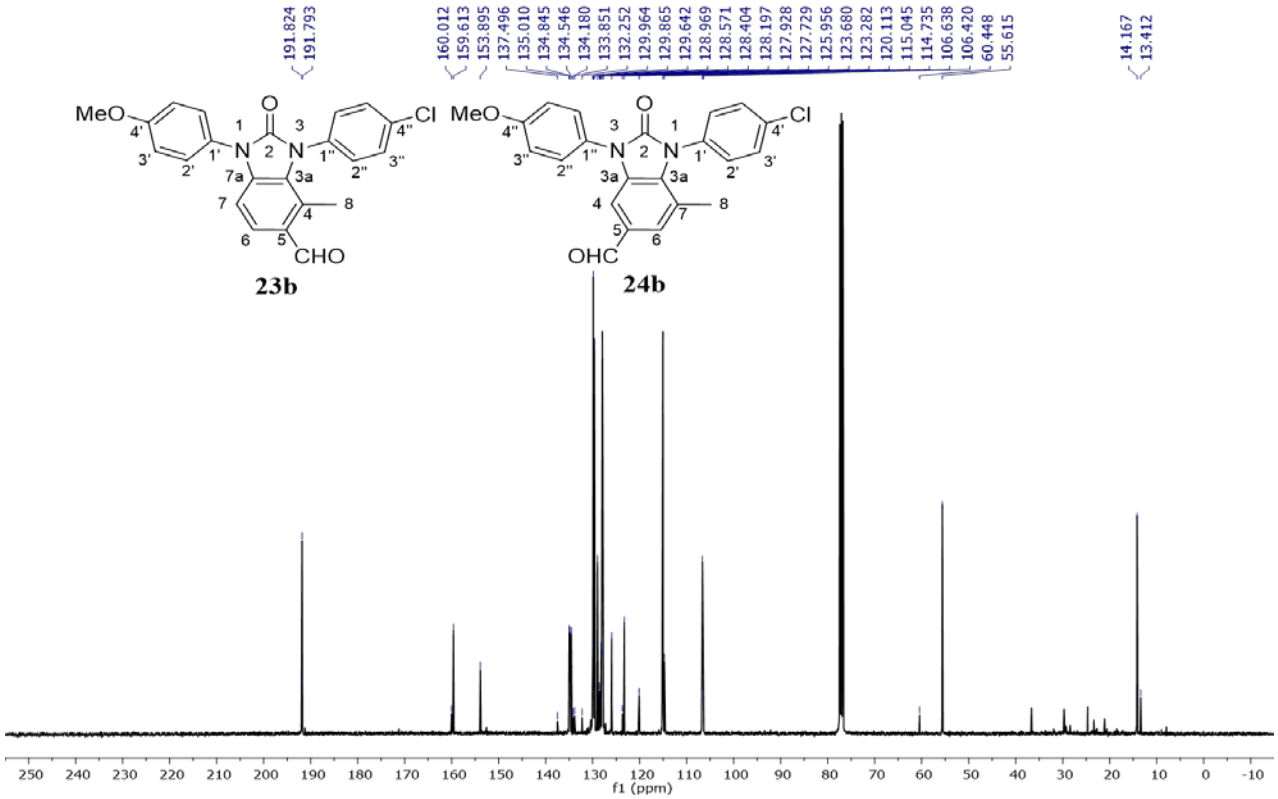
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the mixture of **27a** and **27b**.



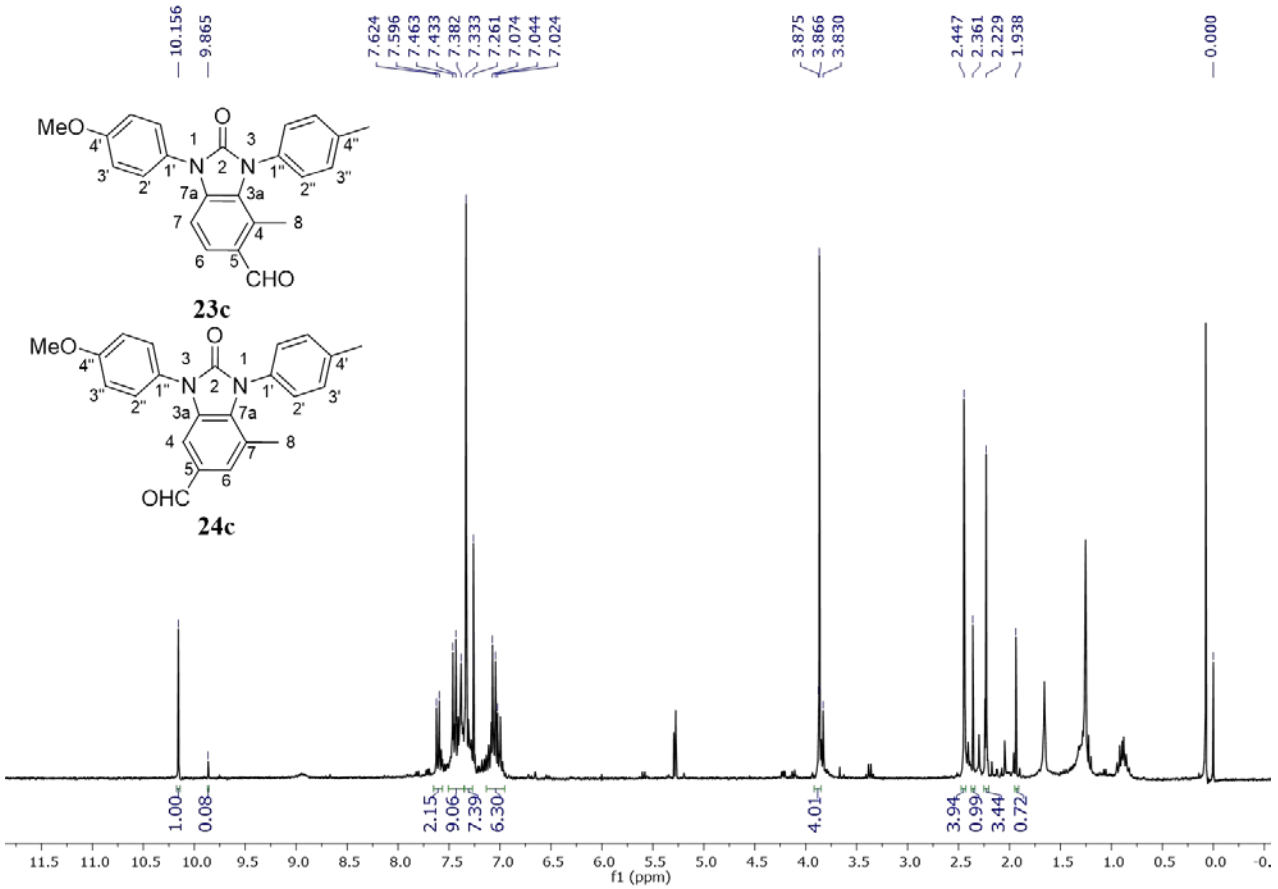
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the mixture of **27a** and **27b**.



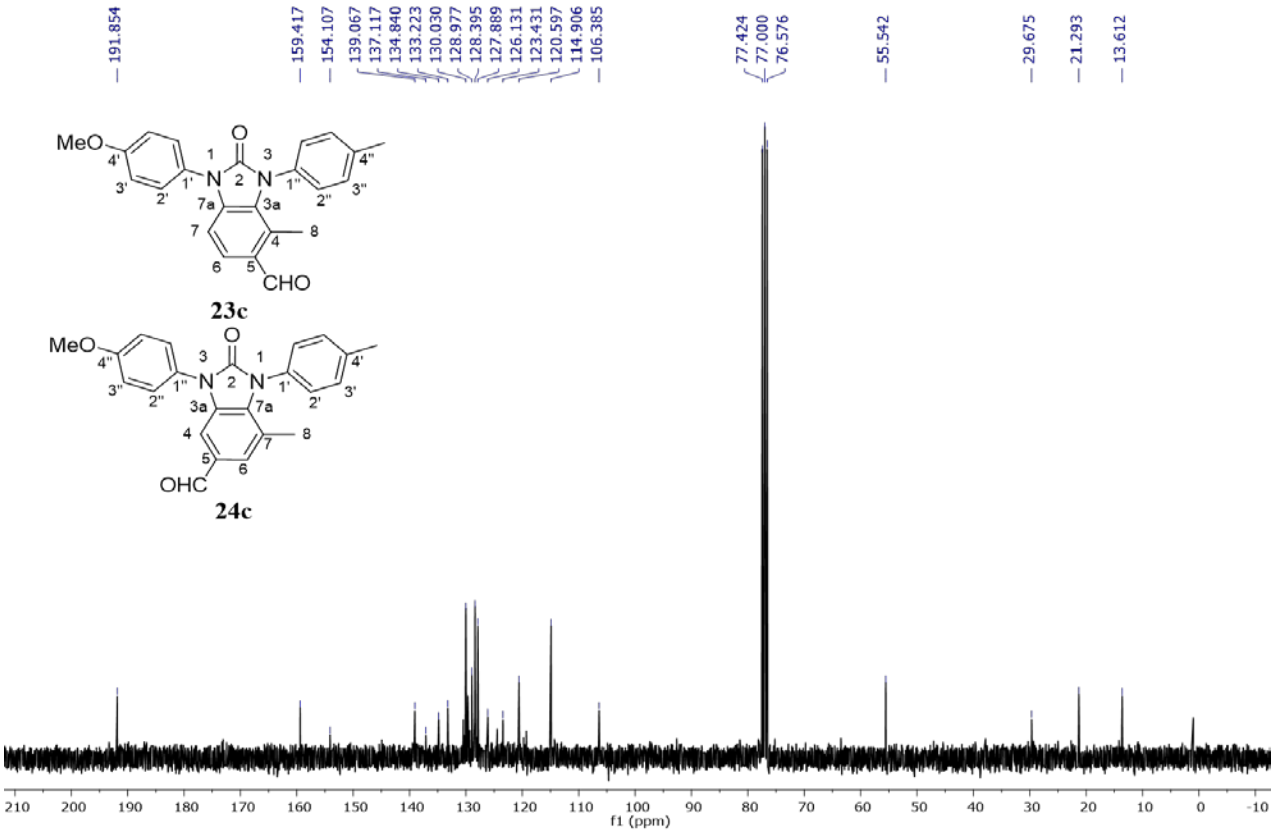
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the mixture of **23b** and **24b**.



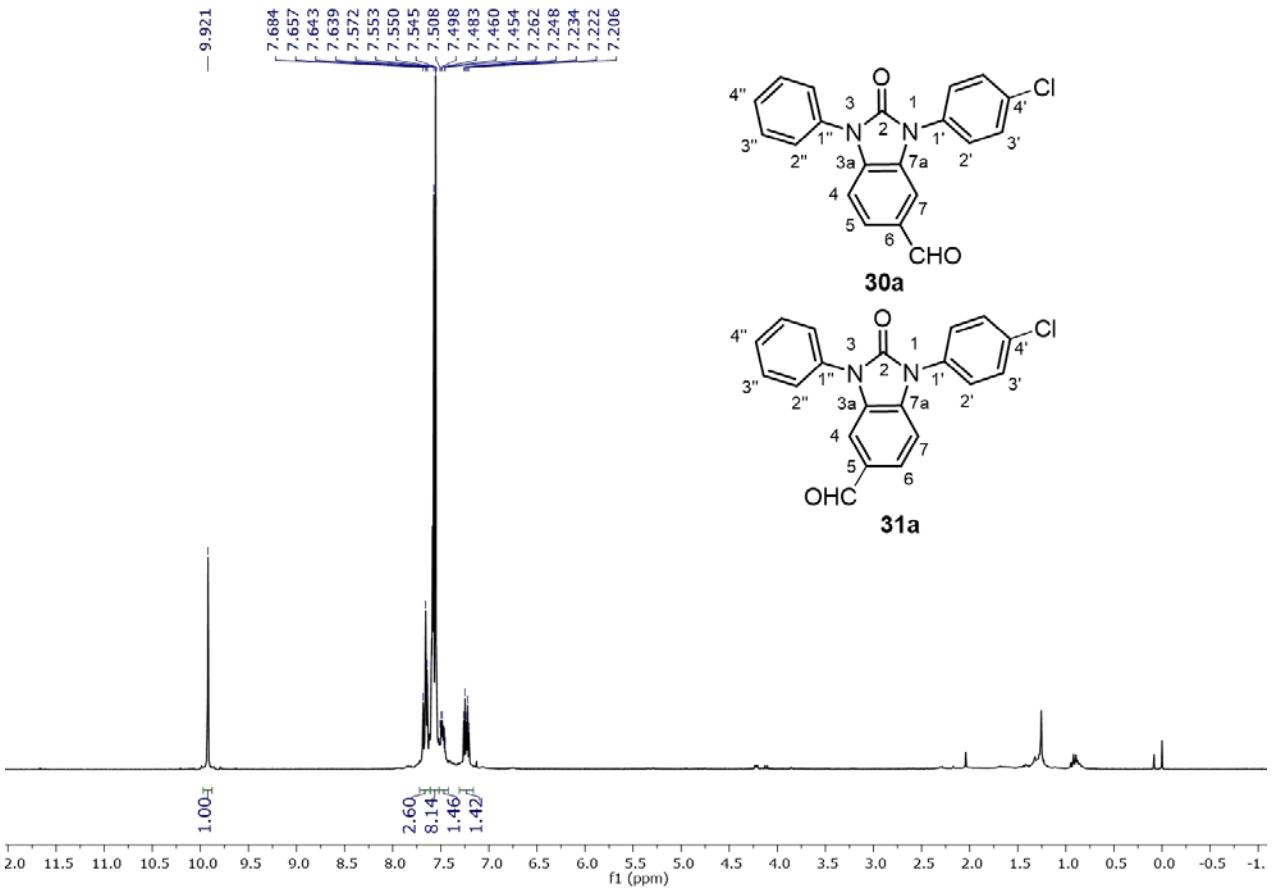
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of the mixture of **23b** and **24b**.



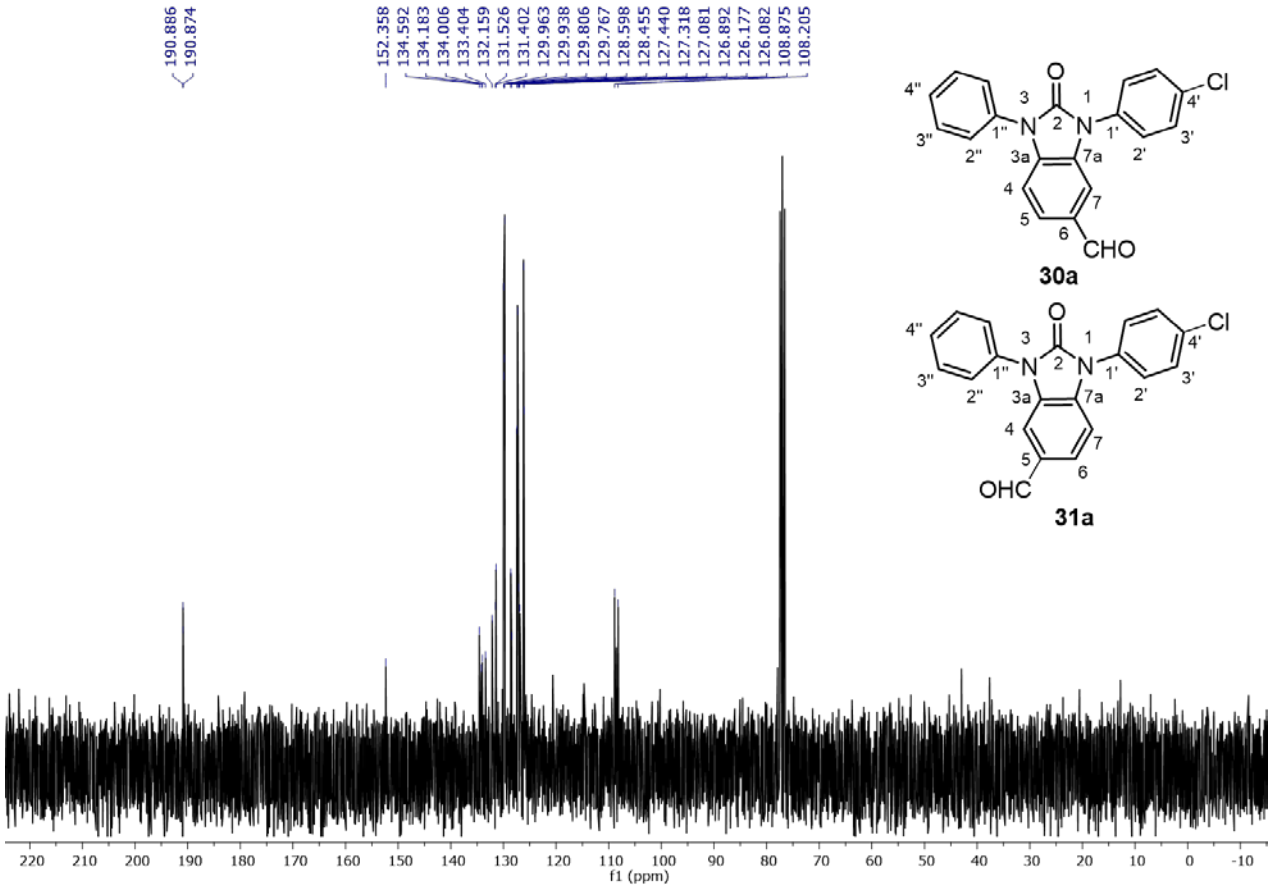
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the mixture of **23c** and **24c**.



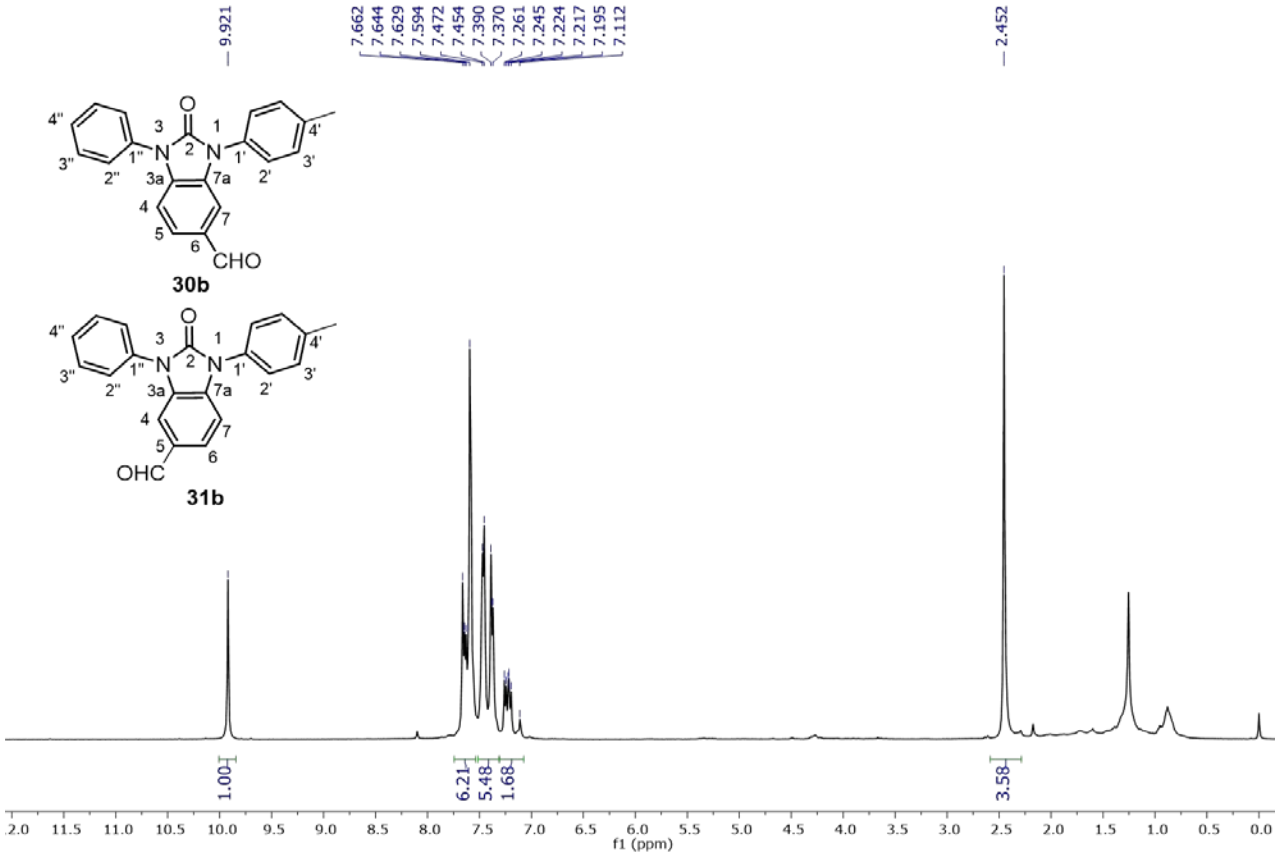
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of the mixture of **23c** and **24c**.



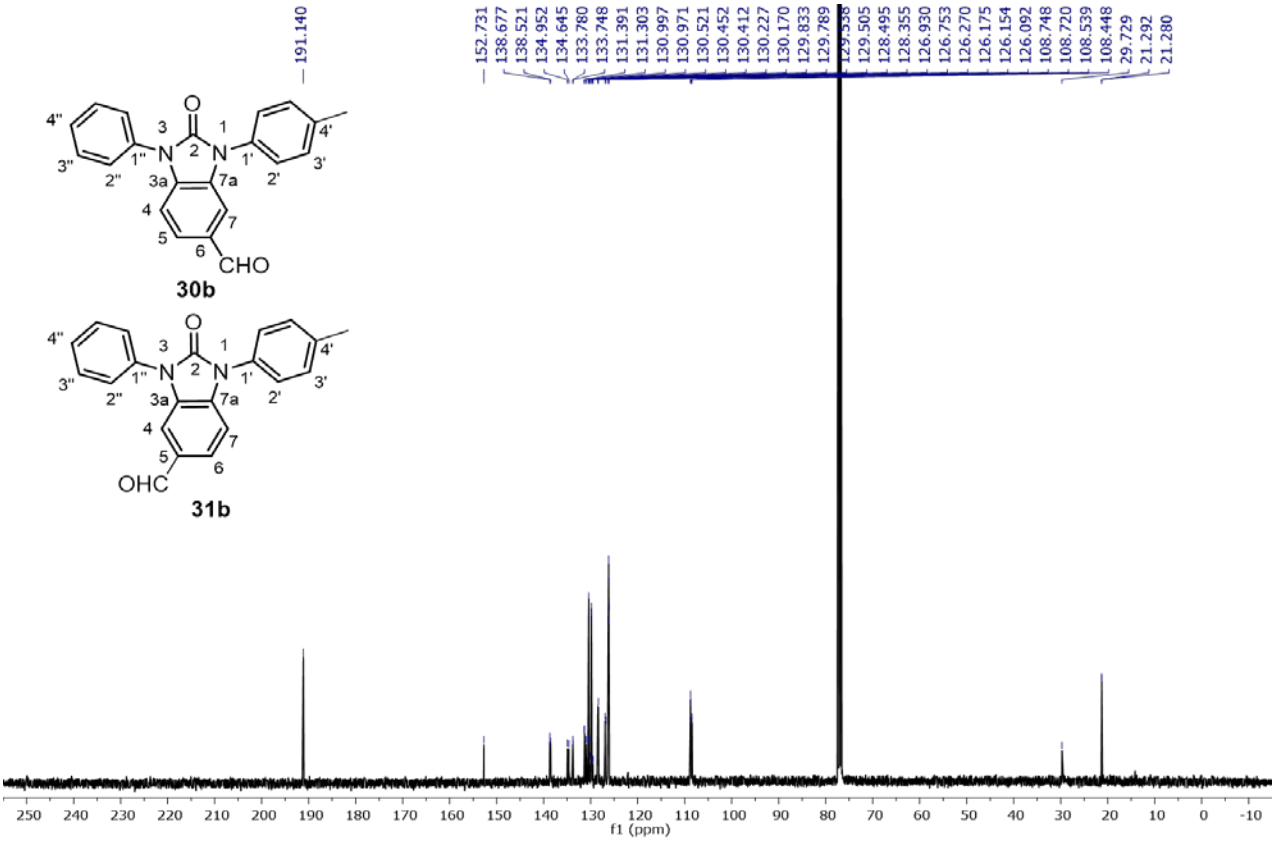
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the mixture of **30a** and **31a**.



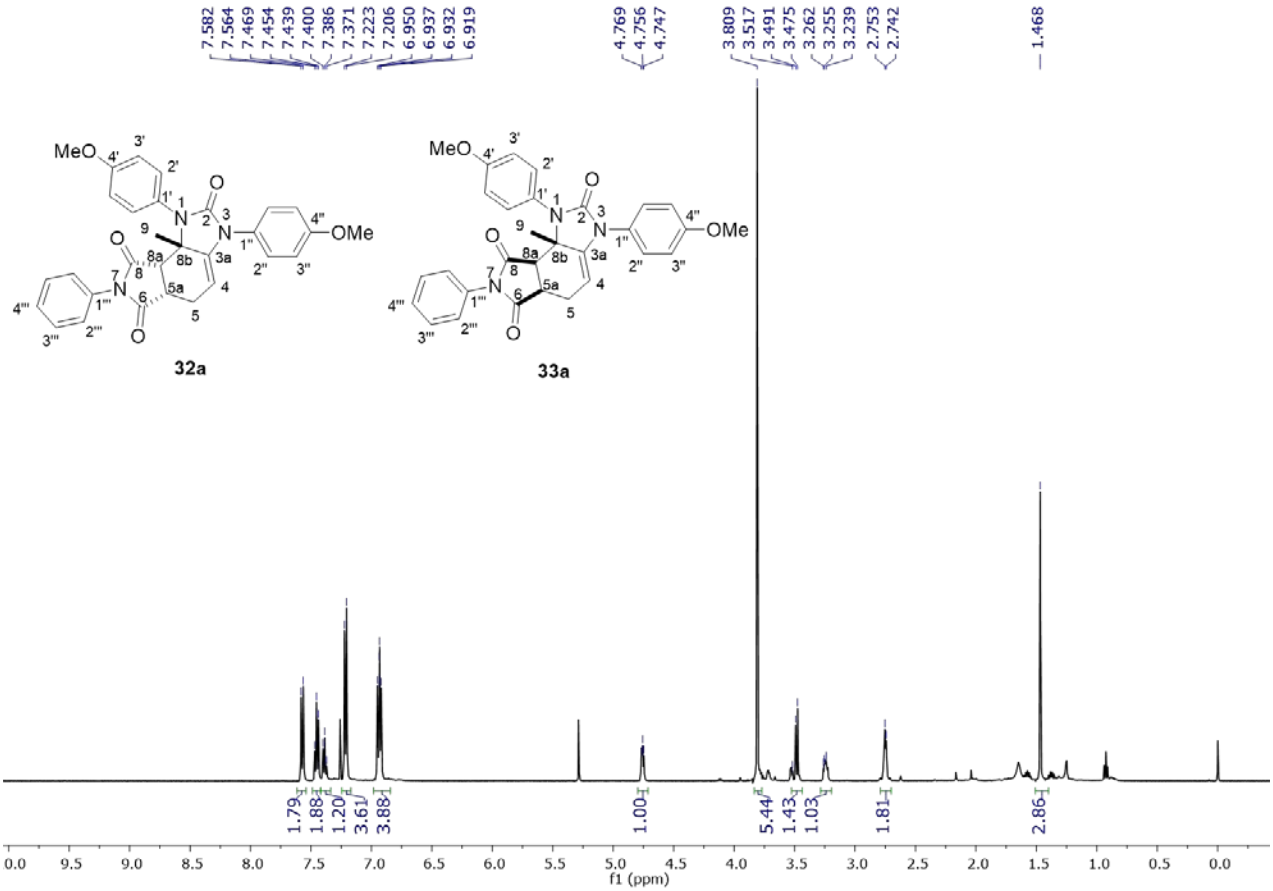
^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of the mixture of **30a** and **31a**.



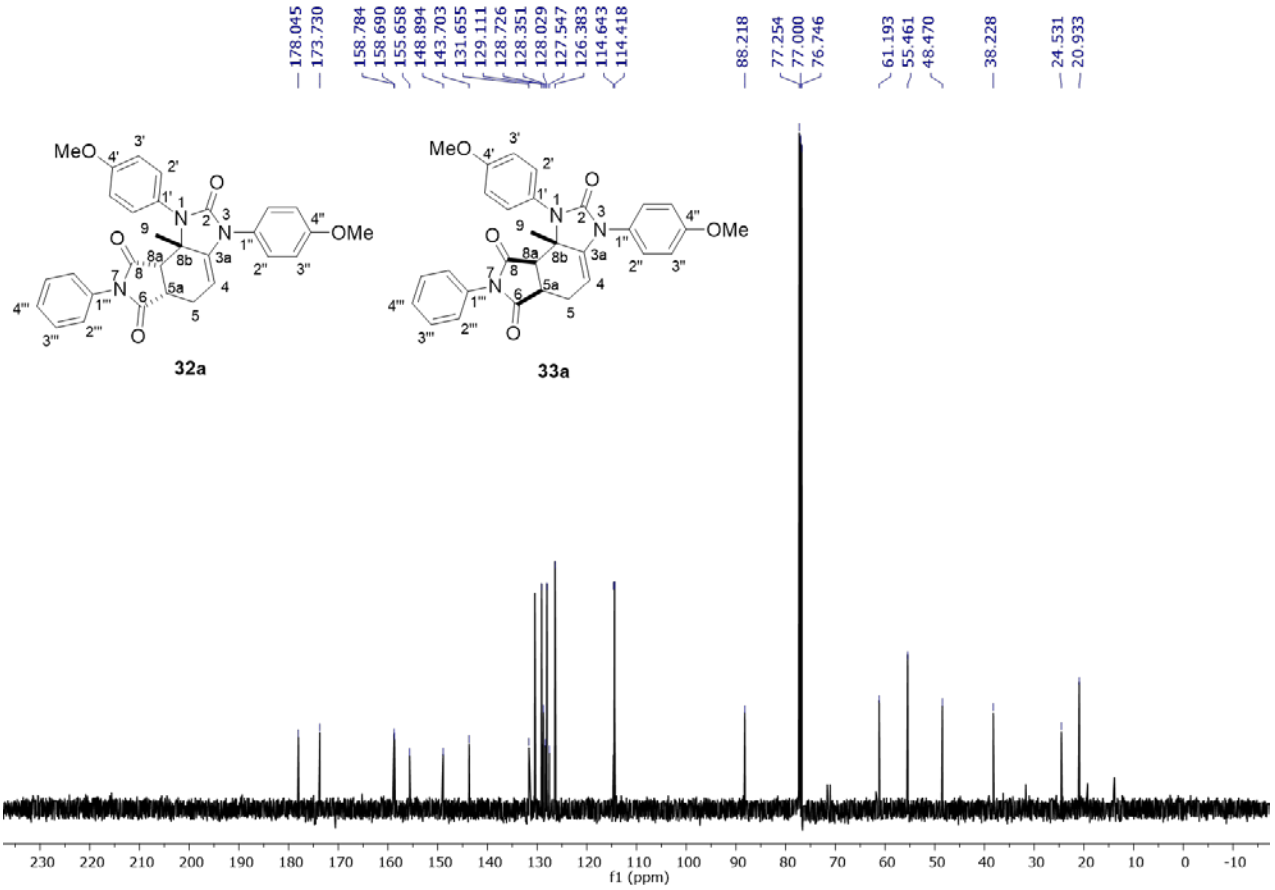
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the mixture of **30b** and **31b**.



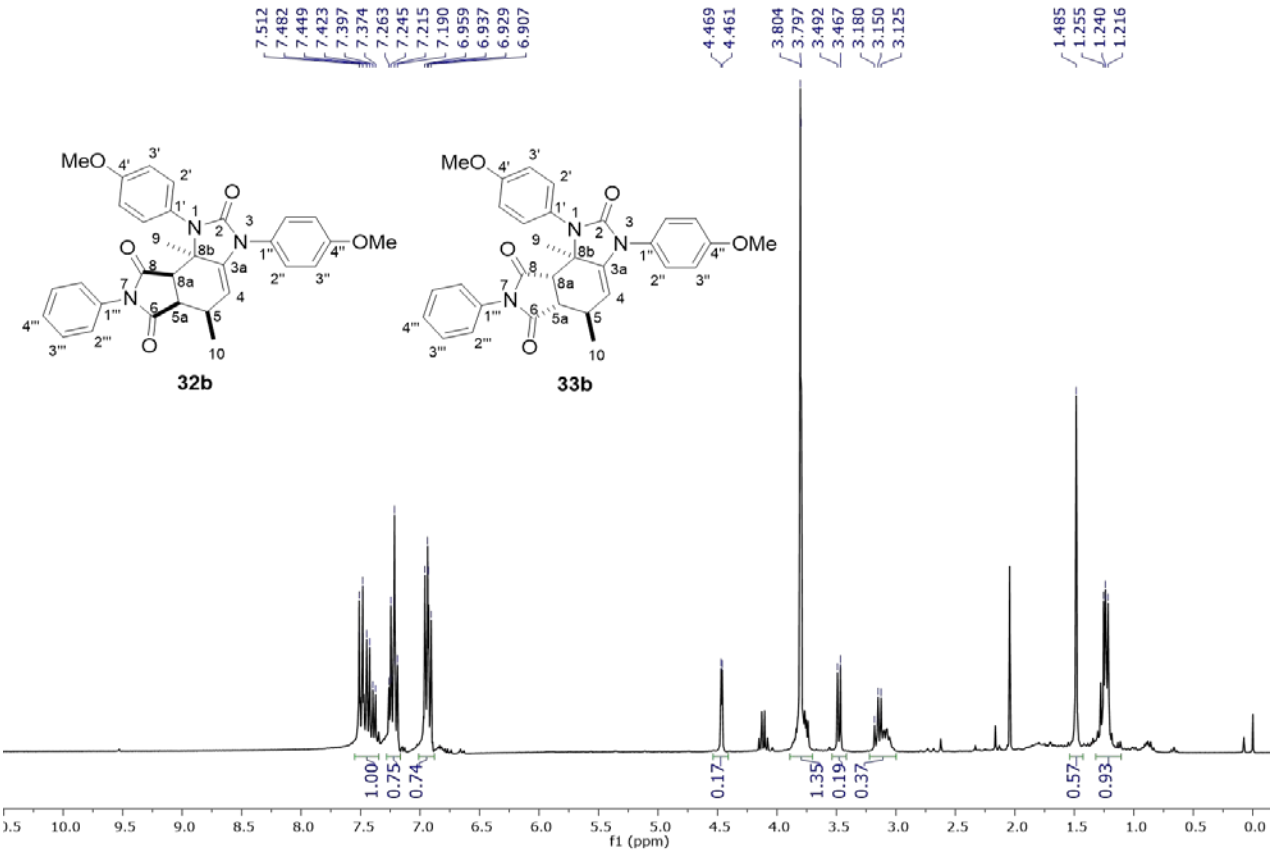
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of the mixture of **30b** and **31b**.



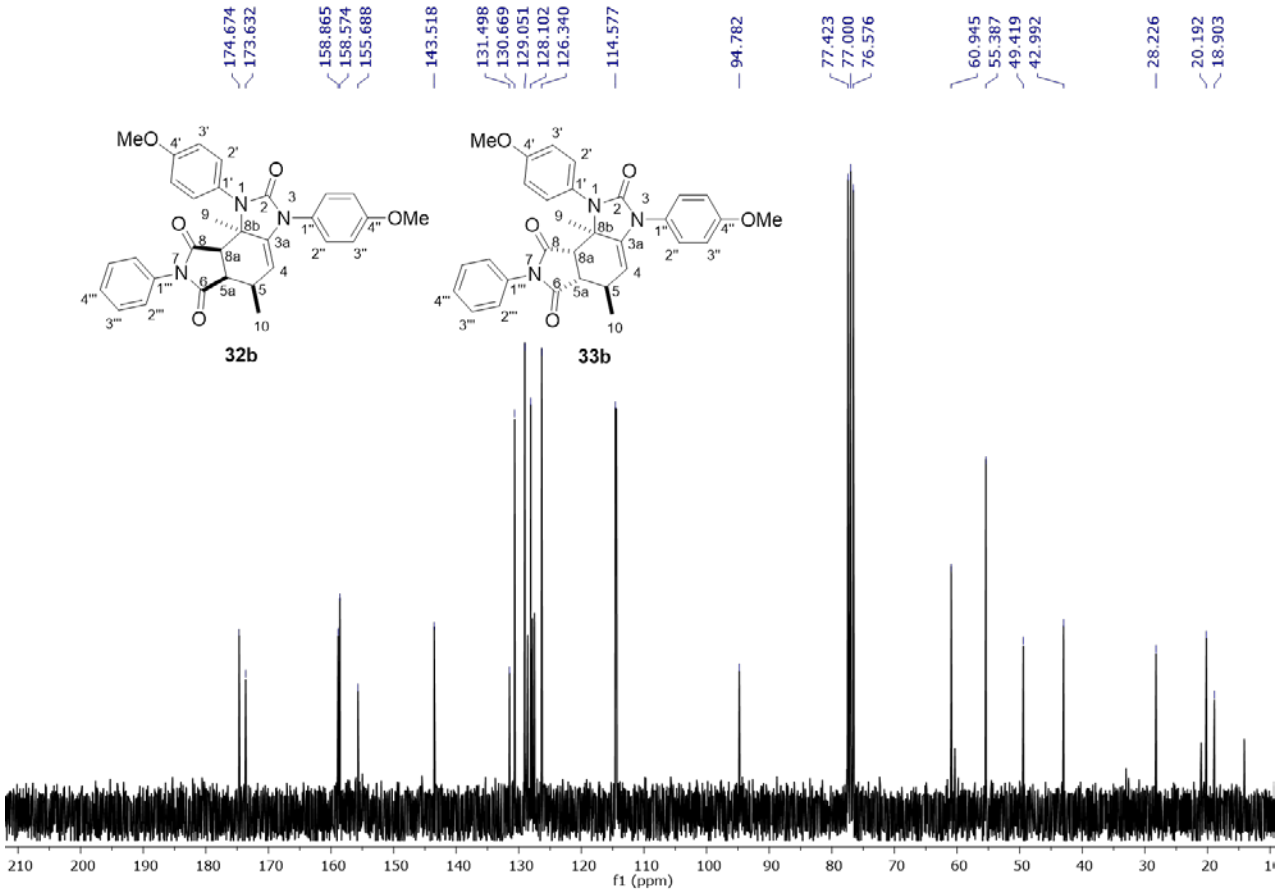
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the mixture of **32a** and **33a**.



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the mixture of **32a** and **33a**.

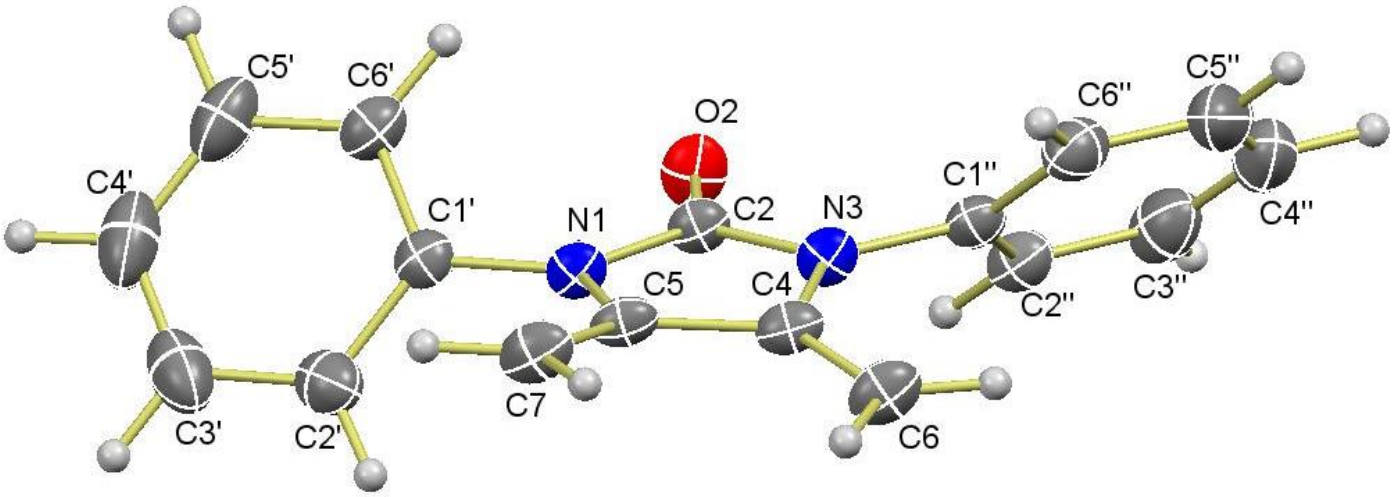


^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the mixture of **32b** and **33b**.



^{13}C NMR (75.4 MHz, $CDCl_3$) spectrum of the mixture of **32b** and **33b**.

4. X-Ray crystallographic structure of 5a (CCDC-1503136)



X-ray structure of **5a** (ellipsoids at the 30% probability level)

5. M06-2X/6-31+G(d,p) Relative ZPE-corrected energies (kcal/mol) of the stationary points of the non-assisted Diels-Alder cycloadditions of 12a/18a

Table S3. M06-2X/6-31+G(d,p) zero-point corrected electronic energies (Hartree) for supramolecular complexes (**SC**), transition states (**TS**) and Adducts (**AD**) of the Diels-Alder reactions of **12a** and **18a.**

	SC	TS	AD
(a) 12a-18a-*ortho-endo*	-1300.3319	-1300.30473	-1300.3909
(c) 12a-18a-*ortho-exo*	-1300.32874	-1300.29766	-1300.38905
(b) 12a-18a-*meta-endo*	-1300.32963	-1300.29562	-1300.3883
(d) 12a-18a-*meta-exo*	-1300.32912	-1300.29679	-1300.3865

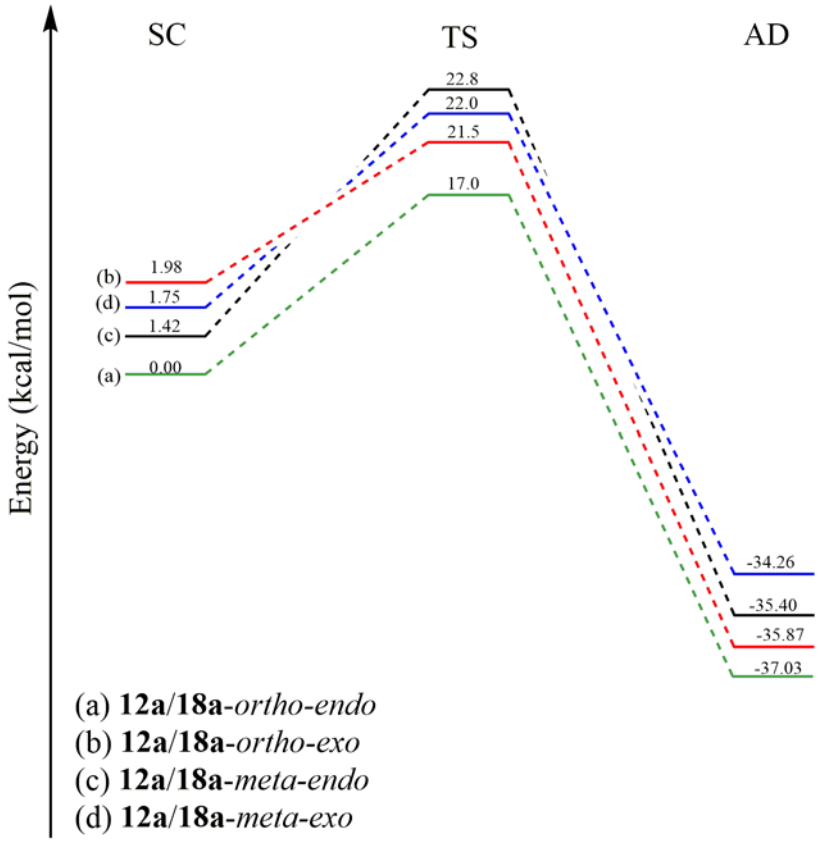
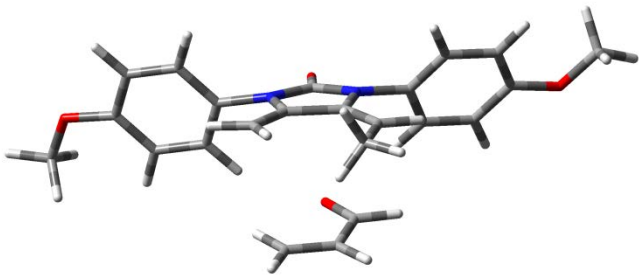


Figure S1. M06-2X/6-31+G(d,p) Relative ZPE-corrected energies (kcal/mol) of the stationary points of the **12a/18a** cycloadditions for the four possible approaches *ortho-endo* (green), *ortho-exo* (red), *meta-endo* (black), and *meta-exo* (blue). SC = Supramolecular complex; TS = Transition state; AD = Adduct.

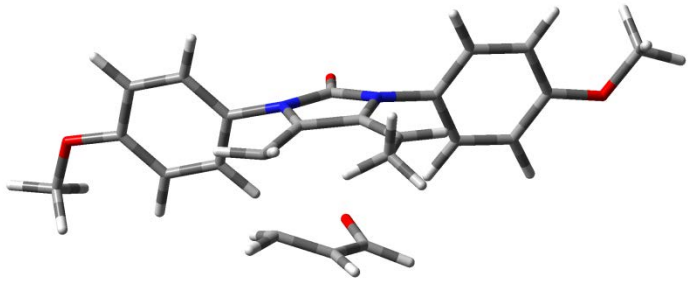
6. M06-2X/6-31+G(d,p) Optimized geometries and Z-matrices of the supramolecular complexes, transition states and adducts of the non-assisted and catalyzed Diels-Alder cycloadditions of 12a/18a.

Figure S2. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*ortho*-*endo* (Supramolecular Complex).



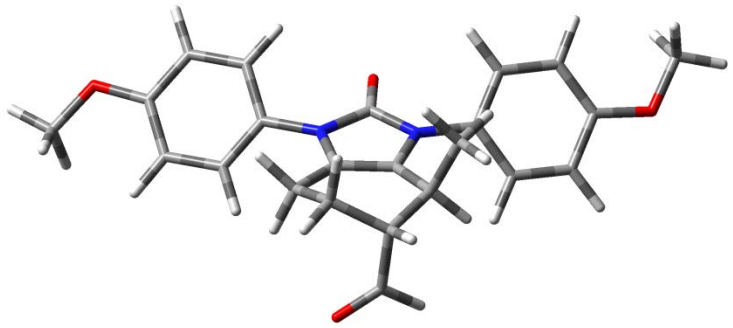
0 1				C	-4.68392100	-0.81406800	-1.53123100
O	-0.09084100	-1.96480000	-0.30777300	H	-5.39188200	-0.86737200	-2.35111600
C	-0.05632200	-0.78766100	-0.58019300	C	-4.23499200	-1.11507900	0.83251700
N	-1.13854200	0.04087600	-0.85400900	H	-4.55212400	-1.38762700	1.83162400
C	-0.73923800	1.37078900	-1.04360600	C	-5.12096800	-1.16213700	-0.24666200
C	0.73645300	1.35886900	-0.91562800	O	-6.42475400	-1.53477700	-0.15015600
N	1.07825500	0.00967200	-0.71108800	C	-6.90698000	-1.92037000	1.12060700
C	2.37327300	-0.46735400	-0.37629800	H	-6.35733200	-2.78716000	1.50571200
C	3.41709100	-0.34874600	-1.28546700	H	-7.95316100	-2.18761400	0.97697700
C	4.69797100	-0.79692500	-0.95865400	H	-6.83626700	-1.09462300	1.83848700
C	4.91875000	-1.39034700	0.28621500	C	1.60316100	2.38825800	-0.90604500
C	3.86127800	-1.52668400	1.19465600	H	2.65050000	2.14623300	-0.74935600
C	2.59689800	-1.06285100	0.87029800	C	1.24630700	3.83107000	-1.11666800
H	1.76421600	-1.16833300	1.55987000	H	2.13585400	4.45618300	-1.02060000
H	4.05881400	-2.00284100	2.14902000	H	0.82401500	4.00629900	-2.11361500
H	5.49729800	-0.69104400	-1.68178400	H	0.50880100	4.17912900	-0.38274900
H	3.22786400	0.09480400	-2.25860800	C	-1.57554600	2.39958200	-1.25694400
O	6.12133600	-1.86758200	0.70356900	H	-1.21072700	3.40293300	-1.40493500
H	7.43635900	-0.73551600	-0.43936600	H	-2.64570400	2.23037200	-1.28993300
C	7.21095300	-1.77951000	-0.19063900	H	-1.83375000	2.33011600	1.82976100
H	7.01299400	-2.33993200	-1.11195300	H	-1.50217200	4.15854000	1.96520900
H	8.06185900	-2.22065300	0.32690200	C	-1.12447100	3.14108400	1.97460500
H	-2.20879400	-0.66205300	1.44557400	C	0.17241100	2.87127200	2.14531200
C	-2.91605100	-0.71036700	0.62269000	H	0.91512600	3.65514800	2.27083600
C	-2.48378200	-0.37339600	-0.65404000	C	0.66341500	1.47306900	2.13036300
C	-3.36786200	-0.43037800	-1.73368300	H	1.76065300	1.33764100	2.19858600
H	-3.01226800	-0.17440600	-2.72728700	O	-0.06263100	0.50206200	2.04178500

Figure S3. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*ortho*-*endo* (Transition State)



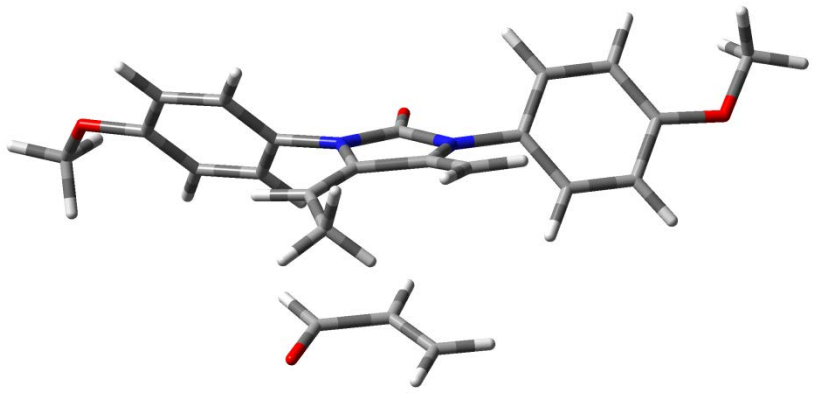
0 1				C	-4.60823700	-1.03436500	-1.48733500
O	-0.03197700	-2.03682400	-0.45303400	H	-5.31140000	-1.19092200	-2.29791500
C	0.01314000	-0.84798200	-0.65418400	C	-4.15855800	-1.08548400	0.89695800
N	-1.09375000	-0.00062300	-0.88587200	H	-4.47188300	-1.26650900	1.91768000
C	-0.70299400	1.30902300	-0.94797500	C	-5.03796900	-1.26808000	-0.17445800
C	0.74288800	1.32229600	-0.86914900	O	-6.32767200	-1.67086300	-0.04272200
N	1.12085000	-0.02952500	-0.73955600	C	-6.80323000	-1.94940200	1.25930000
C	2.42027000	-0.46996700	-0.35420100	H	-6.22609800	-2.75584200	1.72599900
C	3.41221500	-0.63313500	-1.31013700	H	-7.83871000	-2.26504700	1.13926200
C	4.69337900	-1.04213000	-0.93447900	H	-6.76454500	-1.05639100	1.89392500
C	4.96066700	-1.29585000	0.41299900	C	1.60832700	2.35777000	-0.76111700
C	3.95354300	-1.13460000	1.37462600	H	2.64005100	2.06589800	-0.56944400
C	2.68801400	-0.71818400	0.99606500	C	1.40528500	3.81751100	-1.04235800
H	1.88718400	-0.57917100	1.71830300	H	2.08045400	4.40549000	-0.41585000
H	4.19242300	-1.34524000	2.41149200	H	1.66215300	4.03642400	-2.08717800
H	5.45605100	-1.16650400	-1.69321800	H	0.39579100	4.17261400	-0.85337600
H	3.18174500	-0.44369400	-2.35421300	C	-1.56864000	2.40373300	-0.85581900
O	6.16688300	-1.70305600	0.88735900	H	-1.23964900	3.32266600	-1.31973300
H	7.45607600	-0.97378000	-0.56975200	H	-2.62166500	2.18160900	-1.01049200
C	7.20915000	-1.90418700	-0.04459000	H	-2.15680200	2.06161200	1.32844700
H	6.94263700	-2.67687500	-0.77525800	H	-2.18901300	3.82563400	0.85942800
H	8.07110700	-2.23342200	0.53425400	C	-1.58779600	2.92983300	1.00137500
H	-2.14283500	-0.50894700	1.46052100	C	-0.32816500	3.08246700	1.61324000
C	-2.85160400	-0.66505000	0.65075400	H	0.15370800	4.04995500	1.70606400
C	-2.43244200	-0.43794600	-0.65460100	C	0.34598700	1.91581200	2.06468700
C	-3.30540400	-0.62653200	-1.72609000	H	1.30326700	2.06071400	2.60245200
H	-2.95384500	-0.45571500	-2.73899100	O	-0.07009000	0.75989100	1.86396000

Figure S4. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*ortho*-*endo* (Adduct)



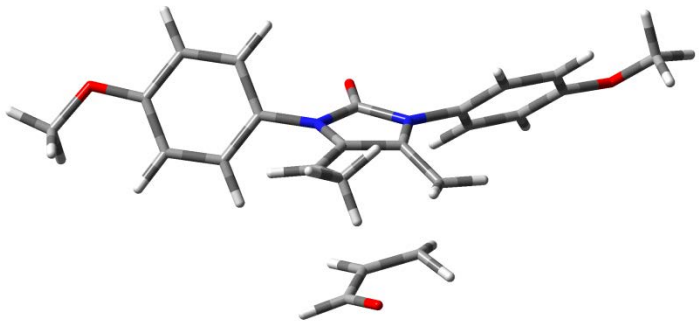
0 1				C	-4.14307800	-2.32337300	-0.80553100
O	0.00971800	-2.25941700	0.03488100	H	-4.44381400	-3.19487300	-1.37684400
C	-0.02764100	-1.04400500	-0.06247700	C	-4.74399800	-0.56751000	0.74594100
N	-1.15405100	-0.22967100	-0.15833400	H	-5.46185500	-0.06139700	1.37958400
C	-0.76710800	1.11246800	-0.26364700	C	-5.10302300	-1.68234800	-0.01205100
C	0.58196100	1.15648100	-0.21116400	O	-6.35154300	-2.22068000	-0.04223700
N	1.04818500	-0.16150800	-0.09206800	C	-7.34552900	-1.61783100	0.75954400
C	2.39100500	-0.57279200	0.10727200	H	-7.07491500	-1.65665900	1.82140600
C	2.93212900	-1.58607700	-0.67613900	H	-8.25546000	-2.19376000	0.59569000
C	4.25224400	-1.99526400	-0.48944900	H	-7.51498000	-0.57551700	0.46379900
C	5.03934700	-1.37189600	0.48164000	C	1.42517100	2.36333200	-0.48477200
C	4.49220000	-0.35777400	1.27626900	H	2.19904600	2.46746000	0.28836200
C	3.17235400	0.02708500	1.09999100	C	2.14520000	2.26029900	-1.83567100
H	2.73281400	0.78064500	1.74656400	H	2.77327500	3.14071800	-2.00390300
H	5.11538200	0.09578300	2.03933500	H	2.78667000	1.37451300	-1.86064000
H	4.64812500	-2.79366200	-1.10497900	H	1.42634300	2.17953300	-2.65637000
H	2.31013400	-2.06858100	-1.42205800	C	-1.66856400	2.26650600	-0.56492300
O	6.33736800	-1.68595500	0.73507700	H	-2.43776400	1.96047800	-1.28257000
H	6.93441500	-2.48156000	-1.08930200	H	-2.19107500	2.60941200	0.33494900
C	6.92156500	-2.72711500	-0.02078100	H	-1.39835100	4.34790400	-1.08721800
H	6.38817800	-3.67279500	0.13080500	H	-0.60777300	3.22153100	-2.19451800
H	7.94419100	-2.82449000	0.34134500	C	-0.82772200	3.41752700	-1.14003200
H	-3.13728900	0.73986500	1.32352600	C	0.49708400	3.59144800	-0.38308100
C	-3.42699500	-0.10478200	0.70670400	H	1.04162700	4.45543600	-0.79477200
C	-2.48180300	-0.72583600	-0.10138400	C	0.24368000	3.92993400	1.07588900
C	-2.84430700	-1.84745200	-0.85646800	H	1.09007100	3.73059600	1.76924700
H	-2.09568300	-2.34733200	-1.46023800	O	-0.78495400	4.40340800	1.49446900

Figure S5. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*ortho*-*exo* (Supramolecular Complex)



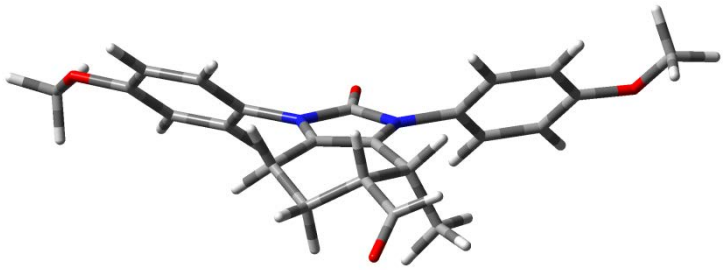
0 1				O	6.05598500	-2.23579100	0.00190100
C	-0.22308000	-0.82930600	0.19789000	O	-6.59044700	-1.21177000	-0.64880800
N	0.92401800	-0.17684800	0.62893700	C	-7.16915700	-2.42397000	-0.20925500
C	0.62859300	1.12023000	1.10717100	H	-6.64553700	-3.28849400	-0.63368200
C	-0.84958700	1.19175300	1.13551200	H	-8.19853100	-2.41197100	-0.56492600
N	-1.28426700	0.02627600	0.47914300	H	-7.16114500	-2.49192500	0.88493300
O	-0.29045800	-1.92114100	-0.32432400	C	6.50832600	-2.70645000	-1.25171600
C	2.22683600	-0.70810900	0.43742100	H	7.53134000	-3.04532200	-1.09423000
C	4.79012400	-1.75010500	0.07644600	H	6.49955600	-1.90594200	-2.00070700
C	3.10883600	-0.79338400	1.51982100	H	5.89549400	-3.54450100	-1.60370000
C	2.62856500	-1.15533600	-0.81558500	C	-1.64541900	2.12133600	1.68255800
C	3.90608700	-1.68531600	-1.00230000	H	-1.22908900	2.96276000	2.21404200
C	4.38490000	-1.29955300	1.33972400	H	-2.72329800	2.02517700	1.63126800
H	2.78358600	-0.45930100	2.50050200	C	1.53772600	2.07221600	1.37280500
H	1.93077400	-1.11457800	-1.64589900	C	-0.55767100	3.52801400	-1.73207300
H	4.19217900	-2.03805000	-1.98541600	H	-0.16040900	4.53370500	-1.62052300
H	5.08631000	-1.36987000	2.16392100	H	-1.62913400	3.41090100	-1.85498900
C	-2.63668900	-0.31638900	0.21517000	C	0.27078400	2.48226400	-1.71858600
C	-5.28976100	-0.98032600	-0.33300300	H	-0.08979100	1.45970000	-1.82418700
C	-3.16510200	-1.51400900	0.67968800	C	1.73559000	2.67299000	-1.53712100
C	-3.43686000	0.55108400	-0.53514700	H	2.34872100	1.75044600	-1.54537400
C	-4.75730100	0.22894600	-0.79901100	O	2.25819400	3.75736600	-1.38988400
C	-4.48896300	-1.85682400	0.40153100	H	2.58461000	1.80060200	1.26575100
H	-2.53344800	-2.19316800	1.24186700	C	1.22754500	3.49659800	1.71990300
H	-3.01203100	1.47975600	-0.90490500	H	2.11092500	4.11626900	1.55808900
H	-5.39675500	0.88858900	-1.37540500	H	0.42237000	3.88828200	1.08537000
H	-4.87586900	-2.80122700	0.76375600	H	0.91877400	3.61472900	2.76573600

Figure S6. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*ortho*-*exo* (Transition State)



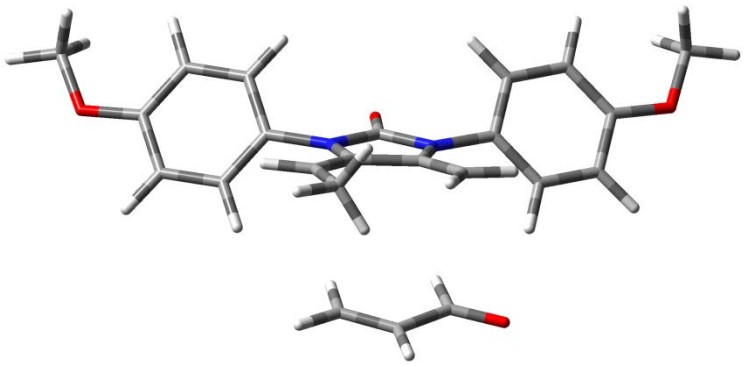
0 1				O	6.18419800	-2.39452600	0.05234800
C	-0.08172800	-1.06399700	0.00654000	O	-6.43353600	-1.83052400	-0.62917600
N	1.03466400	-0.30493600	0.30850500	C	-7.43741600	-1.61581400	0.34228900
C	0.66248800	0.95912500	0.81080300	H	-7.20371100	-2.14255700	1.27489100
C	-0.76223500	1.01503600	0.71077700	H	-8.35654200	-2.01796100	-0.08139400
N	-1.18068200	-0.22316100	0.25252700	H	-7.56694600	-0.54657600	0.54724800
O	-0.12100400	-2.21238600	-0.37780200	C	7.16708600	-1.82047200	-0.78579300
C	2.35746700	-0.82231000	0.22686600	H	8.06708300	-2.41752600	-0.64591200
C	4.94968500	-1.83130600	0.06001600	H	7.37032700	-0.78115500	-0.50220000
C	2.71996500	-1.94233100	0.98058700	H	6.86128000	-1.86076000	-1.83769600
C	3.28626200	-0.22280400	-0.61427500	C	-1.48364900	2.20366000	0.54740700
C	4.59059900	-0.71285900	-0.69544000	H	-1.14376300	3.07505900	1.09227400
C	4.00573000	-2.44728100	0.89274300	H	-2.56307800	2.12194600	0.45453900
H	1.98160800	-2.41876200	1.61691100	C	1.51185700	1.98074000	1.11602300
H	2.98920700	0.63240800	-1.21492800	C	-1.00197400	2.78312700	-1.21574700
H	5.29982900	-0.22617700	-1.35337600	H	-1.57753000	3.70442300	-1.13573200
H	4.30922300	-3.32001900	1.46039300	H	-1.49067000	1.98941800	-1.77798100
C	-2.52726600	-0.63251300	0.05139300	C	0.37529500	2.96877800	-1.43087600
C	-5.17359500	-1.41635200	-0.34116700	H	0.97330100	2.20203900	-1.91483800
C	-3.47639000	-0.40481500	1.04091300	C	1.00904400	4.20628400	-1.08582000
C	-2.89685300	-1.26825500	-1.13815100	H	2.06579500	4.31708200	-1.40336100
C	-4.21046500	-1.66223700	-1.32806000	O	0.46672900	5.11734700	-0.45427800
C	-4.80517900	-0.78294400	0.84809000	H	2.56708700	1.80438500	0.92118600
H	-3.17810400	0.07003800	1.97103500	C	1.17644200	3.17061200	1.96476200
H	-2.14662900	-1.46550100	-1.89581800	H	2.04885600	3.43042400	2.56957900
H	-4.52007400	-2.16279700	-2.23887300	H	0.91379300	4.06160200	1.37954700
H	-5.52815200	-0.59053900	1.63109600	H	0.34781000	2.95247000	2.64415500

Figure S7. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*ortho*-*exo* (Adduct)



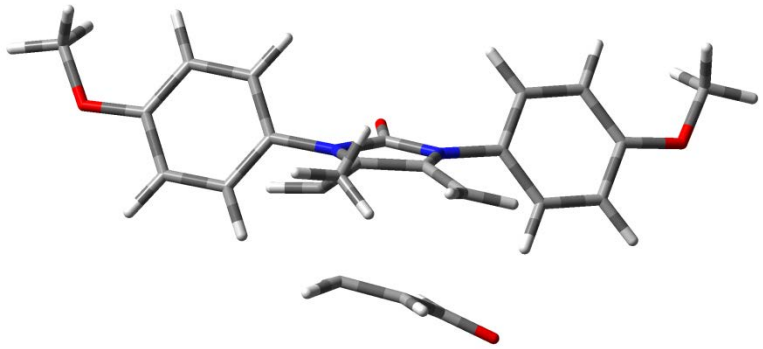
0 1				O	5.87331700	-2.81276400	0.15332600
C	-0.31565400	-1.08112900	0.07122800	O	-6.75357800	-1.24728500	-0.41114300
N	0.87660100	-0.36555400	0.02174100	C	-7.36055200	-2.17527900	0.46419400
C	0.60701400	1.00296200	-0.13495400	H	-6.91926100	-3.17254600	0.35147900
C	-0.73284200	1.15434400	-0.18217600	H	-8.41260500	-2.20974400	0.18402000
N	-1.31186200	-0.11740700	-0.07010900	H	-7.27112200	-1.85195300	1.50809900
O	-0.45325100	-2.28668300	0.19999000	C	6.84024400	-2.55722600	-0.84404800
C	2.15067800	-0.98958400	0.01902300	H	7.71331200	-3.15093500	-0.57648400
C	4.67237800	-2.18573000	0.04603200	H	7.11395900	-1.49559100	-0.86747700
C	2.48803200	-1.89006500	1.03570900	H	6.47909300	-2.86384000	-1.83283300
C	3.06713300	-0.71367400	-0.98840300	C	-1.45814600	2.46242000	-0.17166700
C	4.33694800	-1.29567500	-0.97496400	H	-2.33052500	2.40426000	0.48834500
C	3.73659700	-2.48714600	1.04462700	H	-1.83927700	2.71168000	-1.17082600
H	1.75641100	-2.12367700	1.80133200	C	1.60968700	2.10912400	-0.02317600
H	2.78575700	-0.05375000	-1.80330800	C	-0.49151500	3.55664200	0.30135500
H	5.03494200	-1.06109100	-1.76921300	H	-0.35634900	3.48988600	1.38636800
H	4.01723500	-3.19275500	1.81900100	H	-0.90526900	4.54818100	0.10035400
C	-2.69376700	-0.42789100	-0.13902000	C	0.86805000	3.42305100	-0.38671700
C	-5.41922400	-1.02552400	-0.27073100	H	0.71261800	3.40774800	-1.47872300
C	-3.25387000	-1.33671800	0.75301100	C	1.77196700	4.60453100	-0.12535300
C	-3.49951000	0.16927300	-1.11417800	H	2.78866800	4.52739400	-0.57019900
C	-4.85448600	-0.11559000	-1.17133500	O	1.45875100	5.58327000	0.50754600
C	-4.61268100	-1.64400500	0.68676800	H	2.41545100	1.96797700	-0.75557900
H	-2.62017400	-1.82195100	1.48632100	C	2.24771500	2.13937500	1.37536000
H	-3.05722000	0.84640000	-1.83780900	H	3.02119900	2.91098600	1.44328200
H	-5.49492000	0.34056300	-1.91837400	H	1.49447200	2.33709500	2.14339000
H	-5.02279000	-2.36168300	1.38664200	H	2.71615300	1.17685400	1.59951800

Figure S8. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*meta-endo* (Supramolecular Complex)



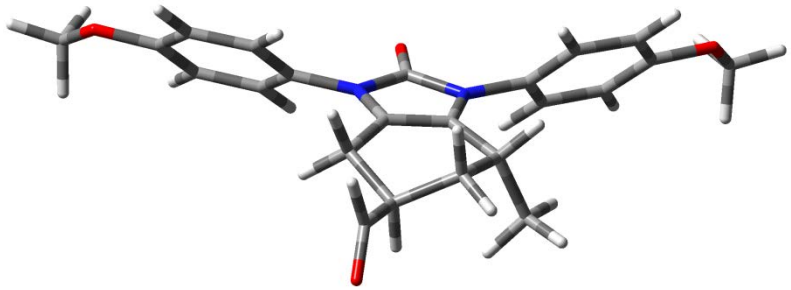
0 1				H	-1.87849200	-2.39676200	1.03382700
C	-0.68573400	1.13752000	1.03523300	C	-4.93972200	-1.54570000	-0.16261100
C	-1.55008000	1.98647200	1.61113600	H	-5.43152400	0.33412300	-1.06640900
C	1.64412500	2.02024300	1.62178500	H	-4.14338500	-3.32999000	0.77430200
C	0.79645300	1.15873500	1.03638900	O	-6.22061500	-1.95773700	-0.35249100
H	-2.61806100	1.82817900	1.52407400	C	-6.56141800	-3.26239800	0.06833700
H	-1.20762300	2.84191300	2.17003500	H	-7.61499300	-3.39185300	-0.17599300
H	2.70531300	1.81486500	1.51687500	H	-5.96789600	-4.01669000	-0.46160400
C	0.07864200	-0.71086600	-0.12803000	H	-6.42019100	-3.37931400	1.14939500
O	0.09435600	-1.76092700	-0.73173700	C	1.24663700	3.23216300	2.41134000
N	1.18168200	0.02831700	0.28426800	H	2.13446000	3.76913800	2.74916800
N	-1.04360300	-0.00249700	0.29093300	H	0.64358300	3.92467700	1.80981300
C	2.51513800	-0.40951500	0.06234400	H	0.65878400	2.97003500	3.29925500
C	3.43033100	0.41853800	-0.59591500	H	5.45465600	0.62017800	-1.31808200
C	2.91275600	-1.67349600	0.48075700	O	6.41690300	-1.61741800	-0.65966800
C	4.72969600	-0.00857500	-0.81276600	C	6.85833500	-2.90324600	-0.27271900
H	3.11789900	1.40145500	-0.93496500	H	6.28000900	-3.68702000	-0.77559100
C	4.21329800	-2.12184400	0.24858600	H	7.90148900	-2.96774900	-0.57914800
H	2.19450400	-2.32149800	0.97121800	H	6.78757100	-3.03530600	0.81331900
C	5.12730800	-1.28467700	-0.39407800	C	0.94570100	3.47959700	-1.27696900
H	4.49426700	-3.11618700	0.57293100	H	1.08844200	2.43753700	-1.55916200
C	-2.36504000	-0.51278600	0.13685100	H	1.83663700	4.06796700	-1.08079500
C	-3.36250800	0.25946400	-0.46846800	C	-0.28606100	3.98568400	-1.18142700
C	-2.66062800	-1.79564800	0.58283400	H	-0.48835700	5.01760500	-0.90780400
C	-4.64354600	-0.25131800	-0.60546100	C	-1.44654000	3.11578500	-1.45041400
H	-3.15010600	1.26302100	-0.82558900	H	-1.18860700	2.06129600	-1.69445200
C	-3.94232700	-2.32332700	0.42921600	O	-2.60112200	3.48168200	-1.41694500

Figure S9. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*meta-endo* (Transition State)



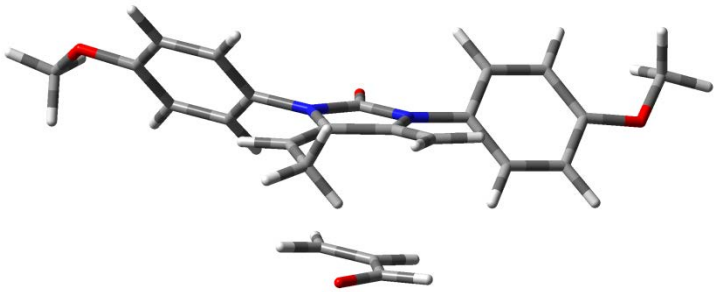
0 1				H	-2.02253600	-2.32996800	1.27219400
C	-0.65178200	1.10697700	0.92337900	C	-4.99075500	-1.49669700	-0.15361200
C	-1.43701000	2.18652800	1.21335000	H	-5.35331300	0.27489500	-1.30426700
C	1.55474600	2.28134200	1.06333600	H	-4.32180200	-3.18987400	1.02259700
C	0.76897800	1.14175600	0.86917800	O	-6.28135500	-1.87182700	-0.34942400
H	-2.50470700	2.16815800	1.02420800	C	-6.70210000	-3.10149900	0.20442800
H	-1.06082000	2.97216100	1.84691400	H	-7.75020200	-3.21218900	-0.07058200
H	2.60297500	2.12843100	0.80965600	H	-6.12573200	-3.93840400	-0.20709100
C	0.05615200	-0.80350000	-0.13117700	H	-6.60990400	-3.09578500	1.29699900
O	0.08202200	-1.90468300	-0.63544200	C	1.34163900	3.21245700	2.25039100
N	1.16374000	0.00152000	0.17691900	H	2.30388300	3.61806500	2.57087800
N	-1.05015600	-0.07979900	0.28876200	H	0.69516300	4.06198500	2.01124500
C	2.50210900	-0.44038600	-0.03195800	H	0.90245900	2.68298800	3.10064600
C	3.32371100	0.20697800	-0.95808300	H	5.28395400	0.26746500	-1.86250600
C	2.98681600	-1.53242000	0.67677200	O	6.40127900	-1.66842300	-0.69511400
C	4.62762100	-0.22041200	-1.15035900	C	6.93264900	-2.79107500	-0.01908800
H	2.93021300	1.03855500	-1.53485600	H	6.36259300	-3.69771400	-0.25216900
C	4.29171500	-1.98177300	0.47958200	H	7.95469700	-2.90146100	-0.37852000
H	2.33411800	-2.04390500	1.37676100	H	6.94185500	-2.63131600	1.06538700
C	5.11711100	-1.31908500	-0.43284700	C	0.98678300	3.40905400	-0.49745500
H	4.64576000	-2.84049700	1.03627100	H	1.31485000	2.73298800	-1.28648600
C	-2.38728500	-0.54969700	0.13876600	H	1.71103700	4.18094400	-0.24716200
C	-3.31640500	0.18579100	-0.60498500	C	-0.36870500	3.76104400	-0.49382400
C	-2.75833700	-1.75660900	0.71811700	H	-0.71905800	4.66963400	-0.01217200
C	-4.61471400	-0.28105600	-0.73736800	C	-1.29436400	3.09063200	-1.39084700
H	-3.03085300	1.11930900	-1.08308500	H	-0.87087100	2.17608400	-1.87198200
C	-4.05721100	-2.24175200	0.57114900	O	-2.43657400	3.43716100	-1.64798400

Figure S10. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*meta-endo* (Adduct)



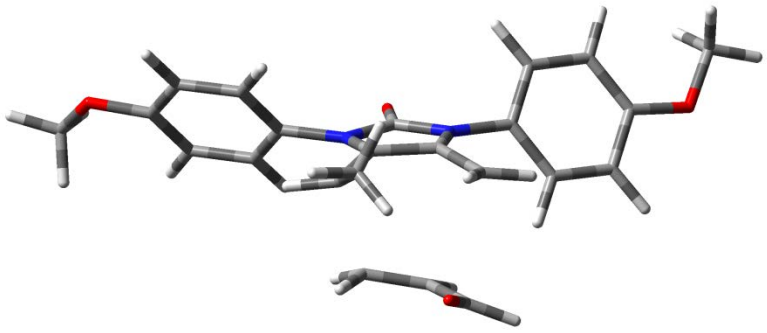
0 1				H	2.05184000	-2.16211500	-1.45304700
C	0.70494600	1.08794800	0.23096600	C	4.99581400	-1.79342600	0.20668000
C	1.62804100	2.26061500	0.16018800	H	5.33544000	-0.44013600	1.83145600
C	-1.45462500	2.40476200	0.14740500	H	4.34394500	-3.06821600	-1.41786300
C	-0.64193500	1.15033300	0.23238100	O	6.28323400	-2.21834600	0.30998100
H	2.07590600	2.47741800	1.14108400	C	6.71123800	-3.23711700	-0.57036000
H	2.45791800	2.04996900	-0.52388500	H	7.75371900	-3.43148600	-0.32158100
H	-2.22492600	2.40929900	0.92812100	H	6.12500800	-4.15291100	-0.43034200
C	-0.06451100	-1.05538500	0.02827300	H	6.63949200	-2.91323400	-1.61542800
O	-0.12109000	-2.26872100	-0.08767900	C	-2.16621900	2.52206300	-1.20815400
N	-1.12724800	-0.16019800	0.11142000	H	-2.77106900	3.43316700	-1.24262200
N	1.07529800	-0.25933000	0.11671300	H	-1.44247000	2.55364300	-2.02836400
C	-2.48294500	-0.57514300	0.17127000	H	-2.82789300	1.66714100	-1.37487200
C	-3.30937700	-0.13361700	1.20928300	H	-5.29954200	-0.18135900	2.04512300
C	-2.99266100	-1.43128800	-0.79828900	O	-6.47041200	-1.69433700	0.39892400
C	-4.64124500	-0.51500600	1.25036400	C	-7.02660700	-2.57788400	-0.55327600
H	-2.89780300	0.49400700	1.99357100	H	-6.51586900	-3.54780000	-0.53818600
C	-4.32580200	-1.83821200	-0.75107400	H	-8.06894400	-2.71150900	-0.26683500
H	-2.33775100	-1.79403800	-1.58284200	H	-6.97697500	-2.15389000	-1.56318500
C	-5.15687300	-1.36990600	0.26939300	C	-0.51454300	3.59389500	0.42761500
H	-4.69751000	-2.51292600	-1.51237800	H	-0.31075200	3.64980700	1.50536200
C	2.39316000	-0.78109500	0.14886200	H	-1.02073800	4.52244200	0.14168800
C	3.31262900	-0.30704100	1.09060100	C	0.82977300	3.48506000	-0.32275700
C	2.77647700	-1.77456700	-0.74632300	H	0.64932000	3.41419800	-1.40056900
C	4.60838000	-0.79798500	1.11062500	C	1.61456400	4.75083900	-0.07894100
H	3.00352600	0.43604100	1.81891700	H	1.99081700	4.88152800	0.96123400
C	4.07261900	-2.28868600	-0.71659700	O	1.82166600	5.59924100	-0.91126100

Figure S11. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*meta-exo* (Supramolecular Complex)



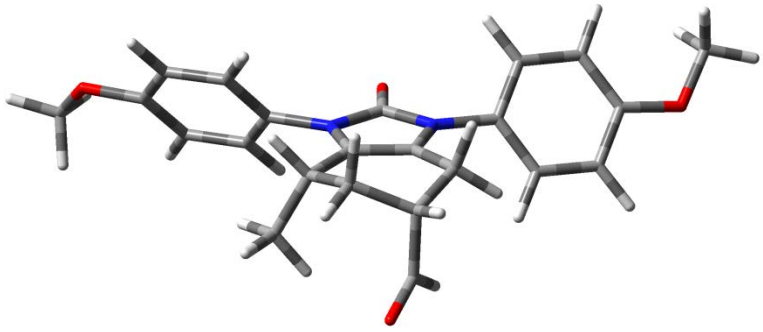
0 1				C	-4.15492000	-2.04155700	0.57099300
C	-0.74192100	1.36956500	1.03994700	H	-2.12149600	-2.21960700	1.25494600
C	-1.56344100	2.30519800	1.54334300	C	-5.08920300	-1.22031700	-0.06250100
C	-0.61294700	1.82155700	-2.25715500	H	-5.45002100	0.67383000	-0.99571000
C	0.57972600	1.24931500	-2.43527000	H	-4.42087600	-3.03348200	0.91493400
C	1.59822100	2.39402400	1.13198800	O	-6.38206900	-1.56612700	-0.29746200
C	0.73425300	1.38863000	0.92647100	C	-6.80755400	-2.84566800	0.12547500
H	-2.63351200	2.14325800	1.57889100	H	-7.85731900	-2.92146300	-0.15489100
H	-1.17124600	3.21913700	1.95968400	H	-6.23727100	-3.63718900	-0.37464100
C	-0.03723600	-0.65314000	0.16453600	H	-6.71047500	-2.95546800	1.21198500
O	-0.06593300	-1.76819000	-0.31397000	H	4.40562700	-2.07556800	-1.82386800
N	1.08600200	0.09586200	0.46922500	O	6.27053100	-1.91748200	0.16784500
N	-1.13759000	0.12596400	0.51786400	C	6.73420100	-2.57247000	-0.99501400
C	2.40538800	-0.41597900	0.35557500	H	6.71049000	-1.90229000	-1.86246500
C	2.82232700	-1.04895900	-0.80901700	H	7.76367000	-2.86148100	-0.78752900
C	3.28685500	-0.31753900	1.43952600	H	6.13881400	-3.46800600	-1.20833500
C	4.11135900	-1.57616700	-0.90903100	H	1.48811100	1.77349100	-2.14582700
H	2.12673700	-1.16415400	-1.63182100	H	0.66599300	0.25273900	-2.85674200
C	4.57266400	-0.82025000	1.34179500	H	2.64646800	2.18275800	0.94077000
H	2.95334800	0.15427300	2.35853600	C	1.24711700	3.78014600	1.58574700
C	4.99345600	-1.45280000	0.16462200	H	2.12968400	4.41990300	1.54166200
H	5.26991300	-0.74958500	2.16959400	H	0.48140700	4.22913700	0.94433600
C	-2.47273100	-0.31905200	0.33170700	H	0.88143200	3.78974800	2.62000100
C	-3.40979400	0.49441600	-0.31566900	C	-0.73075700	3.18285200	-1.67255200
C	-2.85333500	-1.58183200	0.77227600	O	0.21480700	3.90787700	-1.45081100
C	-4.70957500	0.05349600	-0.50240200	H	-1.75922100	3.52459800	-1.44023400
H	-3.11715900	1.47974800	-0.66490400	H	-1.53359500	1.30346000	-2.51514800

Figure S12. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*meta-exo* (Transition State)



0 1				C	-4.23589900	-2.16253100	0.72893600
C	-0.73078400	1.10016900	0.70557900	H	-2.26848400	-2.16240200	1.60928900
C	-1.51689600	2.21282000	0.76987900	C	-5.07565200	-1.55379600	-0.20696300
C	-0.36514300	3.22674900	-1.32129200	H	-5.27004800	-0.04401000	-1.71442700
C	1.00527800	3.03667200	-1.12187900	H	-4.57781200	-2.99327200	1.33363200
C	1.49553400	2.24656200	0.68454000	O	-6.36073000	-1.92470000	-0.43689500
C	0.69388800	1.10479500	0.68968000	C	-6.88070800	-3.00492500	0.31241100
H	-2.58544400	2.14427800	0.59587900	H	-7.90713100	-3.13853000	-0.02626300
H	-1.14416300	3.11781700	1.22388700	H	-6.31182500	-3.92347200	0.12761500
C	-0.02295400	-0.97153300	0.00320500	H	-6.87608800	-2.77995300	1.38531000
O	-0.01179400	-2.13170500	-0.34820900	H	4.48383800	-2.35196200	-1.90153800
N	1.08956600	-0.14989200	0.23306500	O	6.31516200	-2.06161500	0.10519800
N	-1.12648800	-0.17936700	0.27975600	C	6.80710000	-2.76868900	-1.01563200
C	2.42342400	-0.63988700	0.17384000	H	6.78518700	-2.14505600	-1.91701100
C	2.86450900	-1.31622800	-0.95609800	H	7.83792300	-3.02814400	-0.77846400
C	3.28544500	-0.46433700	1.26215600	H	6.22980800	-3.68423300	-1.18926000
C	4.16530800	-1.81847600	-1.01459600	H	1.59265200	3.93080300	-0.92144300
H	2.18276800	-1.47103800	-1.78517000	H	1.50263400	2.27495400	-1.71702500
C	4.58312800	-0.94242500	1.20317800	H	2.54448500	2.03905300	0.47933300
H	2.92982800	0.04632000	2.15223100	C	1.26303400	3.40839900	1.64119500
C	5.03030000	-1.62456800	0.06369000	H	2.22825200	3.82896000	1.93348300
H	5.26945300	-0.81492800	2.03319900	H	0.68139100	4.21934600	1.19501600
C	-2.46351800	-0.63786600	0.11973800	H	0.75610900	3.07303500	2.55112500
C	-3.29953400	-0.04487200	-0.83100800	C	-1.02077800	4.48460300	-1.01037000
C	-2.93253900	-1.69339900	0.89076300	O	-0.53636700	5.39054900	-0.34392800
C	-4.60182900	-0.49058900	-0.98631900	H	-2.04560100	4.59563800	-1.42014300
H	-2.91792800	0.76100800	-1.45134400	H	-0.93580400	2.51048700	-1.90478800

Figure S13. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-*meta-exo* (Adduct)

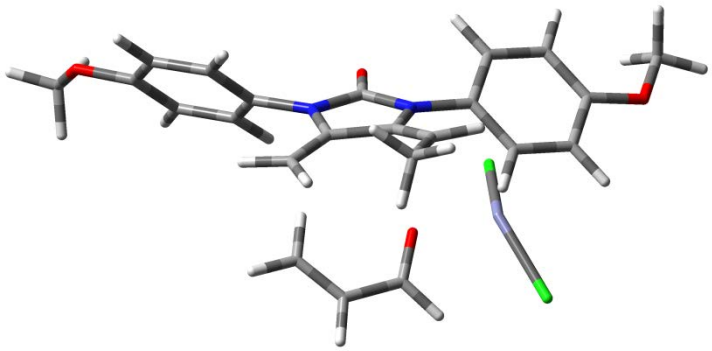


0 1				H	2.91741000	0.81163300	1.55592900
C	0.71998700	1.17291900	-0.45894700	C	4.34387600	-2.01921200	-0.67330900
C	1.56339900	2.37194100	-0.73790300	H	2.38403600	-2.06447500	-1.57026100
C	0.71220900	3.62774800	-0.51104300	C	5.15855100	-1.40132400	0.27820300
C	-0.69327600	3.51288700	-1.14036700	H	5.29104500	0.08184400	1.81786900
C	-1.53722100	2.32423700	-0.63069800	H	4.71384800	-2.83175800	-1.28635600
C	-0.62937400	1.14513900	-0.46800400	O	6.45373000	-1.73843700	0.51369200
H	2.44879500	2.39995800	-0.09212400	C	7.00660600	-2.79607500	-0.24304600
H	1.94004300	2.34515200	-1.76829100	H	8.03342700	-2.90828900	0.10249900
H	-2.27873800	2.10928200	-1.41008100	H	6.45949600	-3.73089100	-0.07415000
C	0.09208200	-0.99334700	-0.07870000	H	7.00522800	-2.55953700	-1.31362800
O	0.11746000	-2.19265200	0.14199300	C	-2.31765600	2.61434300	0.66132600
N	-1.02688300	-0.17924200	-0.23154800	H	-2.97180800	1.77246500	0.90763300
N	1.17581200	-0.13321600	-0.23091000	H	-1.64684700	2.77741800	1.50900800
C	-2.35440200	-0.68295200	-0.19511600	H	-2.93688000	3.50807700	0.54037000
C	-2.79626900	-1.39068300	0.91656300	H	-4.41771300	-2.44122500	1.84157100
C	-3.21695200	-0.48332100	-1.27708400	O	-6.25793400	-2.08125100	-0.14574000
C	-4.09899200	-1.88550400	0.96834000	C	-6.74779400	-2.81467700	0.95845700
H	-2.11076600	-1.56797500	1.73835300	H	-6.71559600	-2.21629600	1.87656400
C	-4.52048800	-0.95161600	-1.22495400	H	-7.78214000	-3.06016900	0.72132300
H	-2.85582900	0.02597300	-2.16507400	H	-6.17653400	-3.73897200	1.10380500
C	-4.96838700	-1.65509100	-0.10070600	C	0.61637400	3.95772600	0.96875700
H	-5.20742800	-0.80348200	-2.05106400	O	0.08936700	4.95946300	1.38734500
C	2.52146300	-0.55379900	-0.06099800	H	1.07329100	3.22534800	1.67191600
C	3.33107100	0.04073300	0.91217700	H	-0.55961300	3.41387100	-2.22357400
C	3.02915900	-1.58529800	-0.84168000	H	-1.23280500	4.44768700	-0.95912700
C	4.64550300	-0.36792900	1.07138300	H	1.20578600	4.49350600	-0.97012700

Table S4. M06-2X/6-31+G(d,p) zero-point corrected electronic energies (Hartree) for supramolecular complexes (**SC**), transition states (**TS1**, **TS2**), zwitterionic intermediates (**ZI**), and Adducts (**AD**) of the Diels-Alder reactions of **12a** and **18a** with $ZnCl_2$

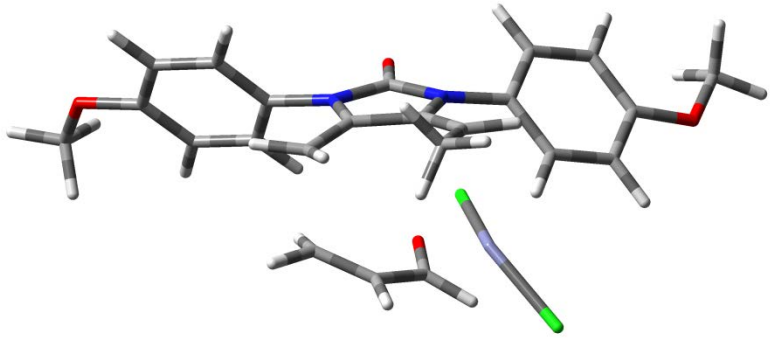
	SC	**TS1**	**ZI**	**TS2**	**AD**
12a-18a-$ZnCl_2$-*ortho-endo*	-4000.351672	-4000.340679	-4000.360285	-4000.351921	-4000.405414
12a-18a-$ZnCl_2$-*meta-endo*	-4000.337573	-4000.32601	-4000.330021	-4000.325572	-4000.403438
12a-18a-$ZnCl_2$-*ortho-exo*	-4000.362445	-4000.334622	-4000.352083	-4000.34366	-4000.407079
12a-18a-$ZnCl_2$-*meta-exo*	-4000.360882	-4000.329092	-4000.339429	-4000.32296	-4000.405198

Figure S14. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho*-*endo* (Supramolecular Complex)



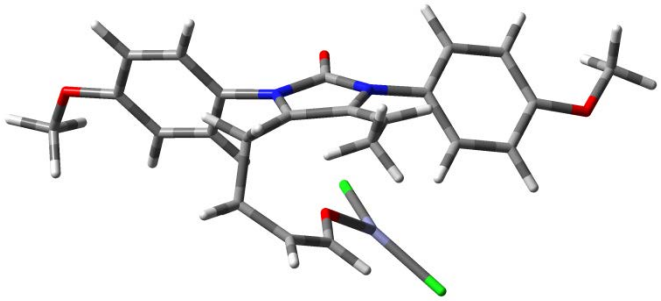
0 1				C	-4.80085900	-1.60817000	0.64428400
O	-0.93813600	-1.49932300	-0.96620600	H	-4.88330100	-2.38193500	1.39746800
C	-0.99354600	-0.29439400	-1.04586100	C	-5.91620500	-1.17326000	-0.07365500
N	-2.12786800	0.49491600	-0.86183200	O	-7.17573600	-1.64670300	0.10432500
C	-1.82479600	1.86222300	-0.95790800	C	-7.36799200	-2.66199400	1.06958200
C	-0.40778200	1.91789900	-1.39105200	H	-6.78683300	-3.55753800	0.82139800
N	0.04837000	0.58082100	-1.34073400	H	-8.43050100	-2.89996700	1.04754100
C	1.38532100	0.13262600	-1.46074400	H	-7.09233900	-2.31209500	2.07127000
C	1.67116300	-1.04903100	-2.14142300	C	0.29955200	2.96823500	-1.83648000
C	2.97182800	-1.54327300	-2.19684600	H	1.31957200	2.77972200	-2.15623500
C	4.01636300	-0.84781200	-1.58580200	C	-0.21123400	4.37214900	-1.97999100
C	3.74520200	0.35861200	-0.92513800	H	-1.19389200	4.39703700	-2.46372500
C	2.43622300	0.83857600	-0.85093900	H	-0.30573800	4.87932500	-1.01205100
H	2.24304000	1.77304100	-0.33117400	H	0.47965100	4.95899300	-2.58721600
H	4.56091200	0.89909500	-0.45561600	C	-2.66044700	2.86879000	-0.65675700
H	3.14938100	-2.48654700	-2.69803700	H	-2.33057400	3.89483400	-0.69008100
H	0.86384600	-1.61163200	-2.59304900	H	-3.67798700	2.66754700	-0.34386000
O	5.30390000	-1.25538200	-1.56824500	H	-1.87911300	0.76068700	1.66406200
H	5.39229900	-2.66799700	-3.09325000	H	-2.85593600	2.08079600	2.53449800
C	5.58182100	-2.57061600	-2.01812200	C	-1.89274200	1.63756200	2.30491000
H	4.98326300	-3.30151400	-1.46354800	C	-0.75108700	2.13459000	2.79328400
H	6.64003900	-2.73467400	-1.82127400	H	-0.72930500	3.00103100	3.44645700
H	-2.67711600	-1.40194400	0.92458200	C	0.53877900	1.51684300	2.47324300
C	-3.55006400	-1.04448200	0.38806400	H	1.44225000	1.92410500	2.95077400
C	-3.40647100	-0.06230800	-0.58637600	O	0.65552900	0.56581900	1.69755200
C	-4.52266300	0.35301000	-1.32166300	Zn	2.56620000	-0.34755300	1.38558900
H	-4.40366500	1.09751800	-2.10276200	Cl	2.40813100	-2.51894700	1.20515800
C	-5.76958000	-0.18830500	-1.05944600	Cl	3.83894700	1.11877500	2.48722300
H	-6.64695700	0.12136000	-1.61676600				

Figure S15. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-endo* (Transition State 1)



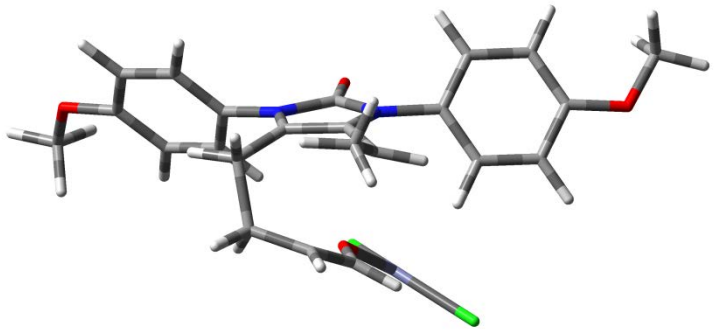
0 1				C	-4.36740200	-1.58738200	0.65535300
O	-0.68838900	-1.60320500	-1.44073700	H	-4.39969200	-2.25340300	1.50840600
C	-0.68926700	-0.40206500	-1.38072900	C	-5.51667600	-1.30030700	-0.08673000
N	-1.82823700	0.40530800	-1.16647600	O	-6.74622100	-1.79989200	0.18686900
C	-1.50679100	1.73252800	-1.16266100	C	-6.87181800	-2.68695000	1.28272500
C	-0.07229900	1.81347200	-1.45489500	H	-6.25471300	-3.58077100	1.13824900
N	0.37364100	0.47990500	-1.52917300	H	-7.92241000	-2.97101800	1.31858700
C	1.71884100	0.01696100	-1.48718700	H	-6.59320500	-2.19527400	2.22173700
C	2.07803700	-1.11781100	-2.20589600	C	0.68662400	2.91200200	-1.63992600
C	3.35297400	-1.66458400	-2.07227800	H	1.73941400	2.73924800	-1.84409500
C	4.28584200	-1.06892900	-1.22116300	C	0.21490500	4.33871000	-1.71077900
C	3.93510100	0.08599100	-0.51162700	H	-0.62322100	4.45204100	-2.40719000
C	2.66008600	0.62166400	-0.63989400	H	-0.10027300	4.72044200	-0.73556000
H	2.40804400	1.51797000	-0.07968000	H	1.02800400	4.97422900	-2.06385000
H	4.65682400	0.53321600	0.16353500	C	-2.35808100	2.74631800	-0.77485800
H	3.59410900	-2.56474300	-2.62388700	H	-2.08620900	3.77205300	-0.96518000
H	1.34677200	-1.60552100	-2.83832800	H	-3.41712900	2.52585800	-0.70240000
O	5.54370100	-1.52756000	-1.02034700	H	-2.20952200	1.70152800	1.41339200
H	5.88590100	-2.66476900	-2.72670100	H	-2.78779100	3.44877600	1.46045500
C	5.90603700	-2.74970200	-1.63376900	C	-1.96600400	2.75579800	1.30656900
H	5.24190000	-3.56031000	-1.31353300	C	-0.67233900	3.15897700	1.61733700
H	6.92294900	-2.95893900	-1.30527800	H	-0.43338100	4.20027900	1.80325700
H	-2.24564000	-1.23813000	0.84968900	C	0.36564300	2.21218600	1.69252700
C	-3.15071200	-1.01231900	0.29185500	H	1.35322200	2.54359000	2.04362200
C	-3.08442200	-0.16624500	-0.80886300	O	0.21643500	0.98918700	1.39350800
C	-4.22630900	0.10442300	-1.56588600	Zn	1.74383600	-0.32425700	1.72950900
H	-4.15411600	0.74197500	-2.44229300	Cl	1.16440100	-2.39300000	1.34877100
C	-5.44118400	-0.45050700	-1.19915400	Cl	3.24581000	0.82179200	2.89727500
H	-6.34525200	-0.25818000	-1.76622800				

Figure S16. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-endo* (Zwitterionic Intermediate)



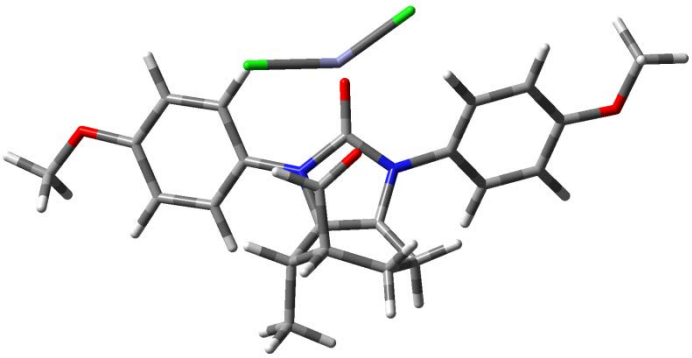
0 1				C	-4.22228600	-1.34441900	0.74496000
O	-0.46156200	-1.97599200	-1.32901200	H	-4.34660300	-1.70998900	1.75638000
C	-0.37934100	-0.78399200	-1.39229900	C	-5.27262000	-1.38103600	-0.17767000
N	-1.51715100	0.11994700	-1.30876300	O	-6.51150300	-1.84862500	0.09835900
C	-1.14788200	1.37688500	-1.44246500	C	-6.75745700	-2.35235600	1.39953300
C	0.28632700	1.38795200	-1.70721100	H	-6.10443700	-3.20360900	1.62078000
N	0.69599000	0.04034400	-1.59361400	H	-7.79620200	-2.67854800	1.40120600
C	2.03585500	-0.40771600	-1.38156300	H	-6.61655200	-1.57238700	2.15601200
C	2.49714800	-1.54884900	-2.02054000	C	1.11388900	2.38795800	-2.06857200
C	3.77238500	-2.03911700	-1.73602200	H	2.13792000	2.07163100	-2.26465900
C	4.58184500	-1.37521100	-0.81123500	C	0.87423700	3.84970500	-2.24477800
C	4.11198900	-0.21991900	-0.17074500	H	1.58788300	4.39535700	-1.61851400
C	2.84552800	0.25930100	-0.45410900	H	1.08308200	4.13001600	-3.28373400
H	2.48573000	1.15275700	0.05157700	H	-0.11872200	4.18302200	-1.96110700
H	4.73480100	0.26869800	0.57072100	C	-2.10181900	2.50135800	-1.35153200
H	4.11011600	-2.94093800	-2.23110800	H	-1.81386000	3.28873800	-2.04611100
H	1.85238300	-2.07658200	-2.71439200	H	-3.09346000	2.13935200	-1.63237900
O	5.83001700	-1.77271400	-0.46623400	H	-2.55559600	2.25756500	0.74082100
H	6.40606400	-2.89217600	-2.11988900	H	-2.95814300	3.84866800	0.07481200
C	6.32263300	-2.97224800	-1.02954300	C	-2.18627300	3.07534600	0.11115200
H	5.67969300	-3.82126000	-0.77071500	C	-0.90529700	3.60868000	0.66584800
H	7.31226700	-3.12046200	-0.59996100	H	-0.73778000	4.67801600	0.73178600
H	-2.14506400	-0.82358500	1.05436400	C	0.02782600	2.75085300	1.13509200
C	-2.98214600	-0.83955100	0.35980800	H	0.94977900	3.12411800	1.59487900
C	-2.81049100	-0.37800100	-0.93765100	O	-0.12490500	1.43864600	1.05135600
C	-3.84322600	-0.42911900	-1.87323900	Zn	1.01303000	0.22882500	2.07059600
H	-3.67447200	-0.09269500	-2.89208400	Cl	0.22269100	-1.82276400	2.00844000
C	-5.07858400	-0.92219600	-1.48912900	Cl	2.73824900	1.25975800	3.00106700
H	-5.90740500	-0.97774200	-2.18582400				

Figure S17. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-endo* (Transition State 2)



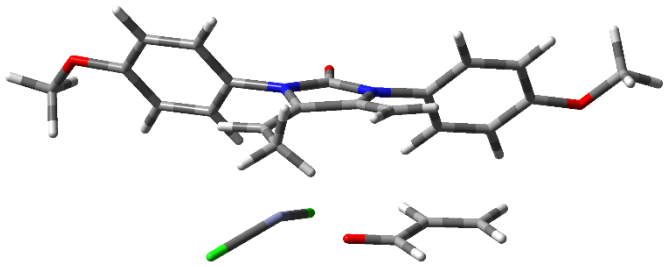
0 1				C	-4.38903800	-1.42667600	0.42361200
O	-0.46219800	-1.89209500	-1.16916200	H	-4.56650900	-1.96999500	1.34325400
C	-0.40943300	-0.69179600	-1.26294000	C	-5.41820100	-1.18631000	-0.49130800
N	-1.53029100	0.19567900	-1.28387100	O	-6.70021500	-1.59027700	-0.32110000
C	-1.12622300	1.47024500	-1.45093500	C	-7.01408200	-2.31953300	0.85117100
C	0.27943000	1.46902300	-1.56609200	H	-6.43929500	-3.25098500	0.90072500
N	0.68603500	0.13117800	-1.40366100	H	-8.07642700	-2.54922700	0.78456000
C	2.02014200	-0.36811500	-1.35066500	H	-6.82372800	-1.72184100	1.74967100
C	2.42832000	-1.34796000	-2.24648400	C	1.10113800	2.57596700	-1.51833100
C	3.71164900	-1.88575800	-2.16158300	H	2.14089500	2.36164000	-1.27191000
C	4.58914700	-1.43216700	-1.17179000	C	0.92009900	3.88970400	-2.22032800
C	4.17490400	-0.44676600	-0.26687900	H	1.46804100	4.67697000	-1.69984900
C	2.89543100	0.07595800	-0.35457400	H	1.36064400	3.79256700	-3.22128600
H	2.57915700	0.82375800	0.36661300	H	-0.11361900	4.20384400	-2.33807400
H	4.85254400	-0.12522100	0.51659300	C	-1.95400300	2.65666000	-1.19818700
H	4.00644400	-2.65820800	-2.86091000	H	-1.82965600	3.39542400	-1.98809000
H	1.73287700	-1.71179400	-2.99547800	H	-3.00966100	2.38454600	-1.15474500
O	5.85369600	-1.89068000	-1.00655900	H	-1.97735300	2.63323600	0.95678200
H	6.30630000	-2.60518700	-2.90501100	H	-2.14876500	4.24946000	0.23997300
C	6.29938300	-2.92816600	-1.85730900	C	-1.57577300	3.31940000	0.20523600
H	5.67234200	-3.82087100	-1.75174700	C	-0.14414700	3.57795400	0.51886400
H	7.31600200	-3.15815100	-1.54184100	H	0.26654600	4.57902600	0.45105900
H	-2.29366500	-1.14844100	0.85915500	C	0.58308400	2.59593000	1.16091500
C	-3.10246200	-0.96233600	0.15649600	H	1.58390300	2.81458500	1.55714600
C	-2.85429500	-0.26930700	-1.02126600	O	0.11747300	1.40021100	1.28488700
C	-3.87266900	-0.04357300	-1.94964500	Zn	0.94181800	0.00184300	2.40677600
H	-3.65312200	0.47183300	-2.88051000	Cl	-0.34861600	-1.75202500	2.60424100
C	-5.15517300	-0.49095500	-1.68016000	Cl	2.87077900	0.75882500	3.17698800
H	-5.96882200	-0.33162000	-2.37896700				

Figure S18. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-endo* (Adduct)



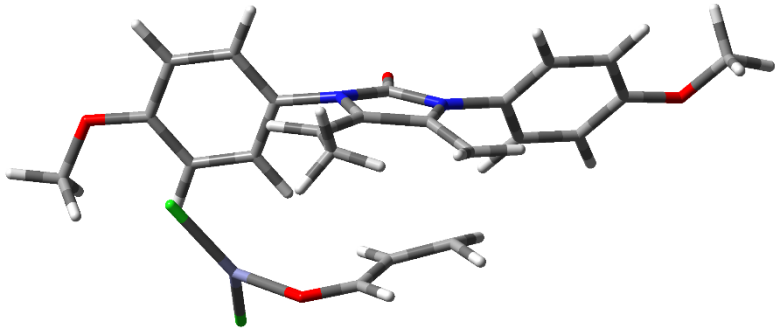
0 1				C	4.48779900	0.24298400	-1.10879500
O	0.21320800	1.03869800	-1.10323800	H	5.03657700	1.17518700	-1.05496800
C	0.06323000	-0.11958500	-0.65612900	C	5.08449100	-0.93229200	-1.56767500
N	1.06006800	-1.00366200	-0.33068100	O	6.37151600	-1.02712700	-1.98517900
C	0.52597000	-1.98876600	0.50389200	C	7.15769300	0.14951900	-1.96557400
C	-0.81323400	-1.81475100	0.55087100	H	6.72786500	0.92106600	-2.61422800
N	-1.11997800	-0.69578400	-0.24676900	H	8.13805300	-0.13907900	-2.34187300
C	-2.42279600	-0.40579900	-0.76037000	H	7.25639700	0.54084800	-0.94672100
C	-3.34600300	-1.44652900	-0.81782500	C	-1.56500800	-2.09488100	1.82829800
C	-4.63526200	-1.23355000	-1.30585400	H	-2.51014200	-1.53950200	1.80720000
C	-4.99295300	0.03411800	-1.76655400	C	-1.86654600	-3.56655600	2.10669000
C	-4.05298400	1.07009000	-1.73508000	H	-2.34119600	-3.68272400	3.08529000
C	-2.77919600	0.86191500	-1.23417600	H	-2.54511600	-3.96401700	1.34733800
H	-2.07356100	1.67850100	-1.20553500	H	-0.95860400	-4.17481800	2.09161400
H	-4.34719300	2.04833200	-2.09880700	C	1.29223400	-2.64148100	1.60666600
H	-5.33019500	-2.06363600	-1.33620100	H	1.21373700	-3.73020200	1.53785500
H	-3.05445000	-2.44437700	-0.50405300	H	2.35227100	-2.39462200	1.51684800
O	-6.21481700	0.35300000	-2.26536700	H	1.45760100	-1.45320400	3.42546600
H	-7.41366200	-1.04663600	-1.30732500	H	0.67835000	-3.01085200	3.66991600
C	-7.19301700	-0.66469900	-2.31131200	C	0.74116200	-2.15544300	2.99191800
H	-6.87362100	-1.49221500	-2.95605300	C	-0.63231700	-1.46897000	2.93341900
H	-8.08736300	-0.20431700	-2.72891200	H	-1.14484100	-1.54630600	3.90153600
H	2.71490800	1.15208100	-0.32645300	C	-0.55463500	-0.00290000	2.56837000
C	3.15585200	0.23352500	-0.69308400	H	-1.47268900	0.60015000	2.68368900
C	2.42205200	-0.94243300	-0.75211200	O	0.43312100	0.50900000	2.06114900
C	3.01376300	-2.12062400	-1.22168100	Zn	0.26989800	2.29829600	0.67004300
H	2.42450400	-3.03180700	-1.27964500	Cl	2.18683400	3.37252100	0.74024600
C	4.33975000	-2.11897900	-1.61799700	Cl	-1.79565200	2.83550900	1.28597600
H	4.82021100	-3.01916900	-1.98519800				

Figure S19. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho*-*exo* (Supramolecular Complex)



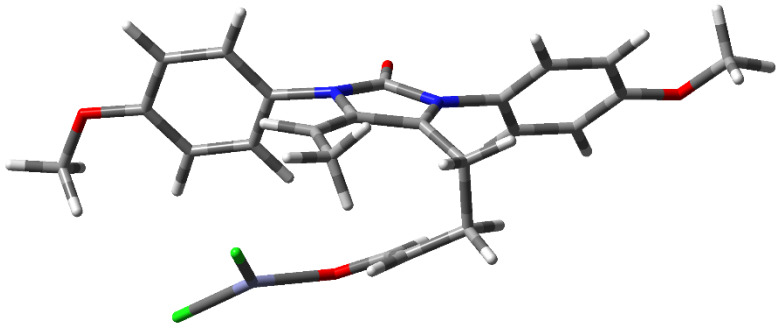
0 1				C	-4.91821800	-1.57060800	0.94756300
C	-0.85600400	0.25807400	1.53416500	H	-3.35785000	-1.25217800	2.39721800
C	-1.63748600	1.11085400	2.21224000	C	-5.21690300	-1.69446600	-0.41058100
C	-3.87068100	2.19305100	-0.75344200	H	-4.45186700	-1.68493600	-2.41346600
C	-2.53408100	2.13330900	-0.76102800	H	-5.68351400	-1.68782800	1.70494000
C	1.51889900	1.24262400	1.73007700	O	-6.45795000	-1.94310500	-0.90236900
C	0.62653200	0.26434500	1.42060300	C	-7.50774600	-2.14057200	0.02339500
H	-4.47263100	1.36258200	-1.11111400	H	-8.39781000	-2.34388700	-0.57028400
H	-2.71528800	1.00675600	2.19868300	H	-7.30087500	-2.99533900	0.67767100
H	-1.20486300	1.91443700	2.78829300	H	-7.67246800	-1.24408800	0.63301500
H	-4.39438900	3.06922400	-0.37579000	H	-1.97889600	1.27785800	-1.13432500
C	-0.17777500	-1.60083100	0.33970400	C	-1.77311500	3.25303000	-0.21795000
O	-0.21343500	-2.61841400	-0.30445500	O	-0.55292200	3.29755300	-0.09591900
N	0.95688100	-0.95019000	0.82670100	H	-2.35673600	4.12602100	0.12334400
N	-1.26929400	-0.84879400	0.78110600	Zn	1.12008100	2.08537300	-0.59347400
C	2.28335800	-1.40590200	0.57136400	Cl	0.30561400	0.60150200	-2.05130400
C	2.72548000	-1.60811200	-0.72940100	Cl	2.85372300	3.43867100	-0.57928200
C	3.13527200	-1.65711100	1.65220900	H	4.35225800	-2.21361300	-1.98257100
C	4.02608200	-2.05829100	-0.96185000	O	6.16467600	-2.71699900	-0.00333600
H	2.05260500	-1.41862800	-1.55814100	C	6.67399600	-2.91895800	-1.30722700
C	4.43051700	-2.08802400	1.42763100	H	6.65105900	-1.98942500	-1.88735800
H	2.77191900	-1.51168900	2.66549700	H	7.70576800	-3.24329700	-1.17910000
C	4.88235600	-2.29063700	0.11571200	H	6.10904700	-3.69561500	-1.83551300
H	5.11236500	-2.28544200	2.24744200	C	1.24852400	2.51198100	2.49836900
C	-2.60130500	-1.15373600	0.39231100	H	2.12606900	3.15655600	2.43638900
C	-2.90031900	-1.29042100	-0.96900700	H	0.40251100	3.08244800	2.10515300
C	-3.60205800	-1.31549300	1.34133700	H	1.05074700	2.29389900	3.55519600
C	-4.19800200	-1.56456400	-1.36565200	H	2.56496300	1.00255300	1.54986800
H	-2.10329600	-1.18715200	-1.70013300				

Figure S20. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-exo* (Transition State 1)



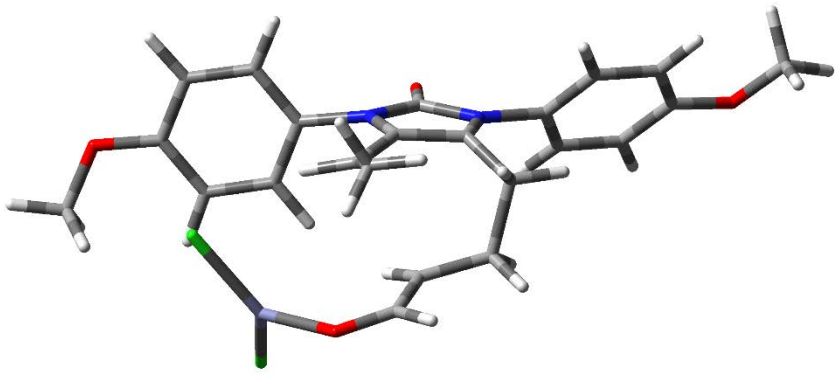
0 1				C	-6.06357800	0.37970400	-0.62082900
C	-1.73557300	-0.55460200	-1.25493000	H	-4.50441900	0.30523600	-2.10542700
C	-2.25759300	-1.83153500	-1.38257700	C	-6.34696900	0.49912200	0.74295100
C	-1.50218600	-2.65005600	0.37072300	H	-5.54941600	0.71637300	2.71946400
C	-0.13638200	-2.43231500	0.58143200	H	-6.85561700	0.30323600	-1.35526800
C	0.70110300	-0.73487200	-2.04800300	O	-7.59690000	0.51799600	1.26334000
C	-0.36375300	-0.11749900	-1.49315400	C	-8.69061700	0.43325500	0.36999200
H	-2.21896100	-2.11226300	0.98522000	H	-9.58595600	0.47528200	0.98815200
H	-3.31721300	-1.96903400	-1.19492100	H	-8.69101400	1.27431200	-0.33264400
H	-1.81630300	-2.50261800	-2.10304800	H	-8.67382400	-0.51157200	-0.18552200
H	-1.81660300	-3.65033000	0.07794700	H	0.21577200	-1.53135800	1.08070800
C	-1.44289600	1.51677300	-0.27800500	C	0.80657600	-3.35444600	0.11226700
O	-1.70414600	2.49637700	0.37417400	O	2.06177300	-3.23230800	0.12783200
N	-0.26700300	1.16234300	-0.89080400	H	0.41802600	-4.29001500	-0.32261800
N	-2.34750400	0.45500200	-0.56567200	Zn	3.07298500	-1.58281300	0.61996900
C	0.98736400	1.78611200	-0.60859600	Cl	2.87021100	-1.03580000	2.74071100
C	1.60775500	1.53599400	0.60928000	Cl	4.15786700	-0.81411700	-1.13116200
C	1.63014600	2.54963600	-1.58329000	H	3.35646300	1.79101000	1.80989100
C	2.88631900	2.02624600	0.86292300	O	4.80219300	3.24195600	-0.00021500
H	1.10239200	0.94529800	1.36936000	C	5.55118000	2.82389900	1.12811100
C	2.90328400	3.03972600	-1.34195800	H	5.60122300	1.73028600	1.17613300
H	1.13388100	2.73688200	-2.53064400	H	6.55072400	3.23387900	0.99100300
C	3.54379400	2.76289800	-0.12620400	H	5.11956800	3.21609000	2.05584100
H	3.43781900	3.61735300	-2.08782600	C	0.82614800	-2.03576000	-2.77026400
C	-3.70242300	0.47146600	-0.12304400	H	1.73547200	-2.53969300	-2.42457800
C	-3.98508300	0.59630000	1.23989600	H	-0.01513900	-2.71478600	-2.65092900
C	-4.73578200	0.37749800	-1.04667800	H	0.96631100	-1.83941800	-3.84001300
C	-5.30104100	0.61290700	1.66907200	H	1.63047300	-0.16646100	-2.01221300
H	-3.17109000	0.69899400	1.95013600				

Figure S21. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho*-*exo* (Zwitterionic Intermediate)



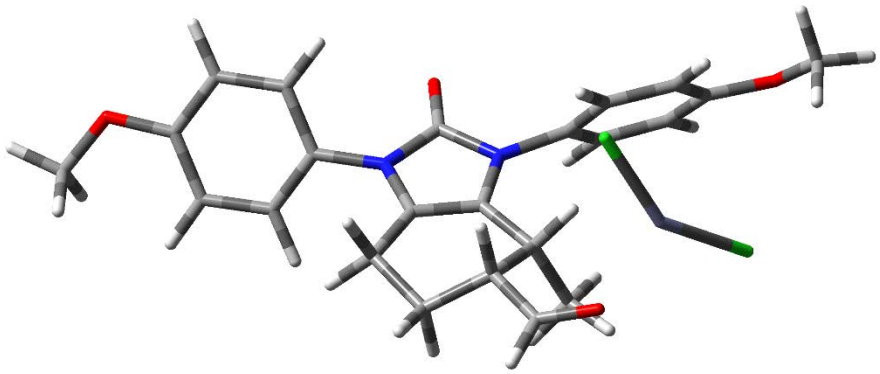
0 1			
C	0.98370000	-0.05909000	1.45165300
C	1.89880400	-0.91770600	2.26942500
C	2.65451000	-1.96537500	1.40359700
C	1.75722300	-2.48594400	0.32142500
C	-1.38728200	-0.78090300	2.04546300
C	-0.46514700	0.03057400	1.47999100
H	3.55556600	-1.50253700	0.98623200
H	2.59670400	-0.25319700	2.79333000
H	1.29664200	-1.42135100	3.02422700
H	2.98138800	-2.76720400	2.07470300
C	0.30478900	1.64157000	0.05012500
O	0.45465500	2.54191500	-0.72393500
N	-0.79613500	1.14039400	0.67114100
N	1.41177400	0.84700600	0.60198100
C	-2.12758000	1.61512600	0.44055500
C	-2.86914200	1.12616900	-0.62581900
C	-2.67443800	2.54950000	1.32371900
C	-4.17686600	1.56898400	-0.81862500
H	-2.42714600	0.39813600	-1.29787900
C	-3.97166900	2.99428600	1.13604200
H	-2.07607000	2.92282600	2.14959400
C	-4.72903800	2.50186100	0.06282700
H	-4.42520900	3.72077200	1.80105000
C	2.76207900	1.06818700	0.17494600
C	3.11706300	0.67028500	-1.11597800
C	3.67704800	1.66583500	1.02686400
C	4.42191500	0.85429300	-1.53577500
H	2.36918000	0.22212800	-1.76558700
C	4.99376000	1.85011400	0.60586200
H	3.36886700	1.99994800	2.01307400
C	5.36620600	1.43901100	-0.67803500
H	4.73927200	0.55513100	-2.52832200
H	5.70393600	2.31835200	1.27550700
O	6.61252400	1.57059000	-1.18437600
C	7.60423500	2.17091300	-0.37240100
H	8.51446800	2.17883600	-0.96960700
H	7.32879400	3.19883900	-0.11079800
H	7.77075400	1.58822300	0.54080400
H	1.61415600	-1.85145100	-0.55145300
C	1.03933000	-3.62868200	0.41065000
O	0.08461100	-4.01925400	-0.40923200
H	1.24368000	-4.31874800	1.24431000
Zn	-1.02480200	-2.58042300	-1.01360000
Cl	-0.22218900	-0.80967400	-2.15659200
Cl	-3.10322600	-2.44226000	-0.21102300
H	-4.74657900	1.16972500	-1.64811400
O	-5.98880800	2.98996000	-0.03507400
C	-6.80041700	2.51912300	-1.09537700
H	-6.94992900	1.43600400	-1.02520600
H	-7.75720300	3.02788300	-0.98760400
H	-6.36025200	2.76758700	-2.06758300
C	-1.18211300	-2.04151100	2.82056800
H	-2.08878300	-2.64373200	2.74802300
H	-0.35000000	-2.63456500	2.43496300
H	-1.00073900	-1.82277400	3.88055600
H	-2.42052600	-0.49047500	1.86210500

Figure S22. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-exo* (Transition State 2)



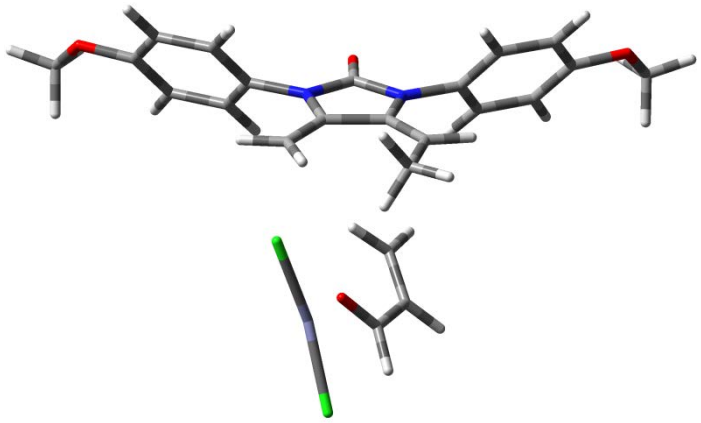
0 1				C	-6.11890500	0.16822200	-0.60981000
C	-1.76722100	-0.48535200	-1.18519900	H	-4.52916500	0.03018200	-2.05578700
C	-2.15203200	-1.89811100	-1.13112500	C	-6.43764900	0.42962500	0.72599100
C	-1.43833900	-2.52349800	0.17176600	H	-5.69683900	0.93415200	2.67203500
C	0.02962100	-2.34087700	0.30589300	H	-6.88837200	-0.04717500	-1.34049700
C	0.65446100	-0.78986700	-1.76193800	O	-7.69544600	0.42584800	1.22418600
C	-0.44226400	-0.04630200	-1.39269200	C	-8.76290200	0.15282000	0.33616900
H	-1.96931000	-2.09675900	1.02870000	H	-9.67071000	0.20469100	0.93493700
H	-3.22892000	-2.02789900	-1.01860800	H	-8.80927200	0.89960800	-0.46453800
H	-1.81625200	-2.44728200	-2.00684800	H	-8.66763100	-0.84912500	-0.09787000
H	-1.68388600	-3.58981300	0.12707100	H	0.41011900	-1.48736200	0.86635300
C	-1.53546300	1.58706700	-0.21623100	C	0.91493000	-3.34110900	-0.03340000
O	-1.84061800	2.58397700	0.38934300	O	2.19386200	-3.30639700	0.04464000
N	-0.33678200	1.21184500	-0.76388500	H	0.49658000	-4.26639400	-0.46050300
N	-2.42019800	0.49405400	-0.51802500	Zn	3.19682800	-1.71706800	0.60458800
C	0.91613800	1.85912500	-0.52083900	Cl	3.03126200	-1.06535900	2.70439200
C	1.60769500	1.55956000	0.64701700	Cl	4.19247400	-0.73567800	-1.11432300
C	1.49237700	2.67189200	-1.49707600	H	3.42569600	1.76543500	1.74685500
C	2.89505500	2.04898500	0.84623100	O	4.74866000	3.31545900	-0.07402300
H	1.15863400	0.91928100	1.40227100	C	5.57277900	2.83244900	0.97477700
C	2.77245600	3.16585100	-1.30582000	H	5.61882700	1.73798300	0.95620800
H	0.94136500	2.89449100	-2.40560600	H	6.56223900	3.24848300	0.79095400
C	3.48701500	2.83698500	-0.14495000	H	5.20875400	3.17323700	1.95044900
H	3.25794600	3.78270100	-2.05377100	C	0.78468300	-1.87747900	-2.77256000
C	-3.78092000	0.47823600	-0.09450700	H	1.54852100	-2.59020300	-2.44886900
C	-4.09765100	0.74867900	1.24016300	H	-0.13857900	-2.39701200	-3.01975700
C	-4.78534900	0.20557000	-1.01477400	H	1.17230500	-1.40688800	-3.68629300
C	-5.42032500	0.72518600	1.64468400	H	1.61608000	-0.34103700	-1.50046200
H	-3.30842200	0.98806600	1.94434500				

Figure S23. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*ortho-exo* (Adduct)



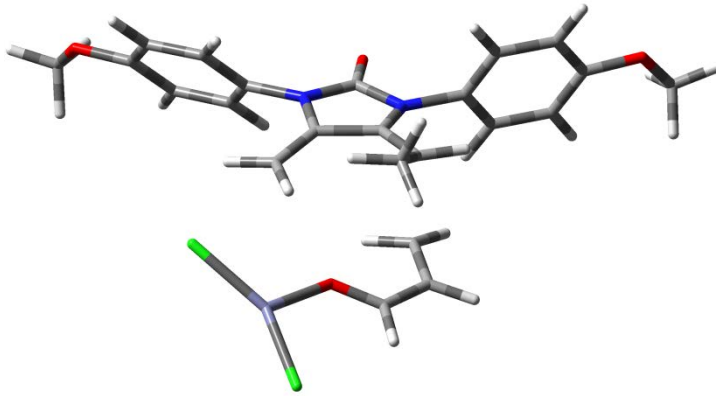
0 1			
C	-1.73136900	-0.77085300	-0.28763100
C	-2.13348400	-2.21007500	-0.31345600
C	-0.96450300	-3.04163600	-0.87006800
C	0.38519400	-2.58620400	-0.29199800
C	0.74487800	-1.13854000	-0.69331100
C	-0.46757300	-0.31961100	-0.40325000
H	-1.12951000	-4.10045600	-0.64273000
H	-2.39144600	-2.54246100	0.70128000
H	-3.02381800	-2.37508000	-0.92697900
H	-0.94018500	-2.94573000	-1.96194300
C	-1.77656300	1.50412000	-0.00365500
O	-2.15988500	2.64244300	0.19458200
N	-0.47811600	1.06825500	-0.24274300
N	-2.54930700	0.33853600	-0.04172000
C	0.68972500	1.87989100	-0.18291400
C	1.66118800	1.61057400	0.77615300
C	0.89878800	2.89148800	-1.12303200
C	2.87754600	2.29239500	0.76431700
H	1.47555000	0.85774800	1.53871600
C	2.09244700	3.59477500	-1.12291700
H	0.12270600	3.11267600	-1.84864200
C	3.09927200	3.27859000	-0.20019400
H	2.28410600	4.37999300	-1.84599400
C	-3.96096100	0.34361700	0.11423100
C	-4.53217200	0.92955300	1.24898400
C	-4.77997500	-0.21037900	-0.86205100
C	-5.90732000	0.93882100	1.40428600
H	-3.88748700	1.39086600	1.98922800
C	-6.16746000	-0.22415200	-0.70359500
H	-4.33703100	-0.61776200	-1.76600700
C	-6.73232100	0.35356800	0.43458500
H	-6.37276500	1.39422200	2.27156500
H	-6.78468300	-0.66497800	-1.47670600
O	-8.06630900	0.40350000	0.68655400
C	-8.94026700	-0.14391400	-0.27877000
H	-9.94747100	0.00446300	0.10826100
H	-8.83899900	0.37146100	-1.24117000
H	-8.75655200	-1.21621500	-0.41649000
H	0.31466100	-2.60497300	0.81221100
C	1.49564800	-3.55041300	-0.58021400
O	2.68384100	-3.28517400	-0.46300300
H	1.22889700	-4.57673600	-0.88619100
Zn	3.58894100	-1.61091400	0.45008700
Cl	2.79028600	-1.70519400	2.48048300
Cl	4.87076500	-0.57920300	-0.95060100
H	3.62974300	2.04297100	1.50319400
O	4.25063100	3.98393200	-0.31677700
C	5.33773500	3.60520700	0.50763800
H	5.59506800	2.55102400	0.35353600
H	6.17377500	4.23570500	0.20810900
H	5.11066900	3.78135500	1.56551100
C	1.22913600	-0.96494400	-2.14004600
H	2.15401200	-1.51702400	-2.33220300
H	0.45973800	-1.28759300	-2.84764600
H	1.43905900	0.09234200	-2.32583300
H	1.53606700	-0.78004500	-0.02184300

Figure S24. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-endo* (Supramolecular Complex)



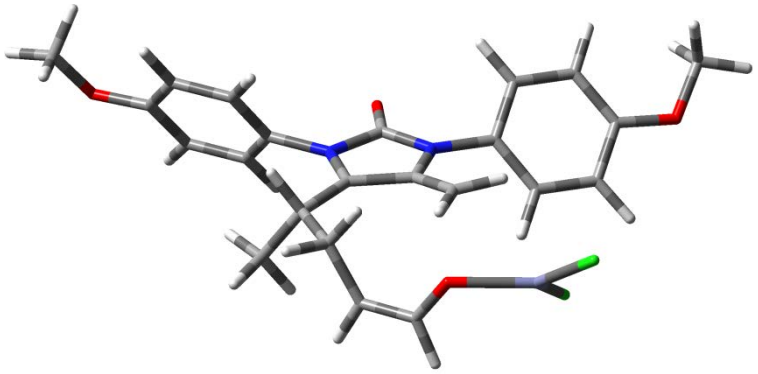
0 1				H	0.35006100	5.85941700	1.94498200
C	0.24241600	0.76179400	0.91917400	H	1.43228500	5.38189900	-2.18582500
C	-1.02448000	1.12157300	1.17757600	O	0.71919000	7.12370800	-0.20650500
C	0.35647700	-1.75217000	1.37729600	C	0.96211200	7.74614800	-1.45161900
C	0.87842200	-0.57566400	0.99254200	H	0.79510300	8.81070700	-1.29324600
H	-1.34054900	2.14670700	1.02292500	H	1.99519700	7.58286800	-1.78013800
H	-1.76125600	0.42024300	1.53833800	H	0.27107200	7.37812100	-2.21914100
H	0.99801000	-2.62518300	1.29784900	C	-1.03693700	-1.95582000	1.89769100
C	2.40898100	0.92985600	0.11560700	H	-1.18060800	-2.99598700	2.19460900
O	3.42069400	1.38534700	-0.37111000	H	-1.24870700	-1.32651100	2.76962800
N	2.17873500	-0.39414600	0.47379900	H	-1.79476000	-1.71219000	1.14254500
N	1.23989100	1.61845000	0.41452300	H	4.88882700	-3.65653500	2.25447300
C	3.18050700	-1.39466400	0.36719900	O	6.13111900	-4.30015400	0.15574600
C	3.58248500	-2.11485300	1.49781700	C	6.80072200	-4.56442100	-1.06049900
C	3.78886200	-1.64182000	-0.85707300	H	7.32704800	-3.67375700	-1.42293500
C	4.56342800	-3.08594600	1.39143000	H	7.52281000	-5.34981400	-0.84171100
H	3.12309100	-1.90234700	2.45834300	H	6.10148000	-4.91497400	-1.82882400
C	4.79312400	-2.60465200	-0.97035300	C	-0.44023100	-1.39337900	-1.79624800
H	3.50058500	-1.05456500	-1.72297300	H	0.60266600	-1.45735800	-2.09191400
C	5.17543500	-3.33559800	0.15578200	H	-0.73620500	-0.58216400	-1.13459700
H	5.26344100	-2.76723800	-1.93225600	C	-1.35414800	-2.27215500	-2.23227300
C	1.10552900	3.02038100	0.22502200	H	-1.11350700	-3.08172200	-2.91307300
C	0.75522500	3.83943600	1.30368000	C	-2.73816500	-2.15868600	-1.77903600
C	1.34136100	3.58416100	-1.02189100	H	-3.50307700	-2.81842600	-2.21666300
C	0.62459800	5.20580900	1.12426500	O	-3.07374600	-1.35253000	-0.90690000
H	0.58641600	3.39530100	2.27997900	Zn	-4.92612900	-1.28070400	0.02592600
C	1.23149500	4.96307100	-1.20752400	Cl	-6.18234000	-2.45745400	-1.30366000
H	1.63586000	2.94636500	-1.84839100	Cl	-4.63010300	-0.22431300	1.88896400
C	0.86473000	5.77546500	-0.13324100				

Figure S25. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-endo* (Transition State 1)



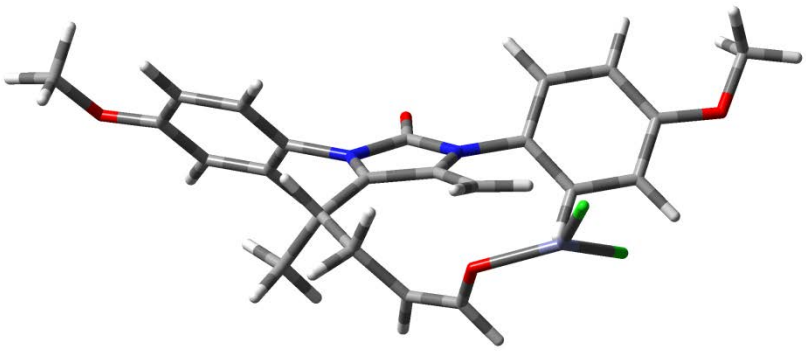
0 1				H	-1.12539400	5.54945100	1.89635900
C	0.07784000	0.68167400	0.55600200	H	0.75023800	5.72408200	-1.96649900
C	-1.26061400	0.73250200	0.50211100	O	-0.67324800	7.06947800	-0.06482300
C	0.61316000	-1.83707000	0.86079700	C	-0.37765700	7.84649200	-1.20875500
C	0.94299800	-0.50879200	0.64316000	H	-0.81186100	8.82806100	-1.02477800
H	-1.77585500	1.67367200	0.34459400	H	0.70493400	7.94565400	-1.34924000
H	-1.86524400	-0.16161000	0.57422400	H	-0.82709700	7.41042700	-2.10839600
H	1.47040300	-2.50729400	0.84599500	C	-0.50350400	-2.29377700	1.75961100
C	2.23352800	1.32473700	0.08566600	H	-0.08315500	-2.56352800	2.73396600
O	3.21329300	1.95902100	-0.21783400	H	-1.27360300	-1.54108100	1.91919900
N	2.18975000	-0.08365000	0.26498700	H	-0.97621500	-3.19189900	1.34843900
N	0.95380400	1.76645200	0.33273900	H	5.47386200	-2.58105600	2.30379000
C	3.37767200	-0.87497500	0.23949000	O	6.83091800	-3.14485000	0.25787600
C	3.89566700	-1.39900900	1.42789500	C	7.54843200	-3.39161500	-0.93709400
C	4.02721100	-1.09931900	-0.96549300	H	7.89603400	-2.45498800	-1.38728000
C	5.04965200	-2.16144400	1.39835600	H	8.40582100	-3.99862200	-0.65110700
H	3.38945900	-1.20097700	2.36820100	H	6.93417400	-3.94255200	-1.65838800
C	5.19871300	-1.85609700	-1.00347000	C	0.02633400	-2.18129200	-1.13508100
H	3.62571200	-0.66834100	-1.87731700	H	1.04199400	-2.24514500	-1.51762200
C	5.70832000	-2.39294300	0.18144200	H	-0.47435500	-1.22504500	-1.26617500
H	5.69708800	-2.01313200	-1.95177000	C	-0.79008300	-3.31405500	-1.16069700
C	0.55281600	3.12621300	0.19828900	H	-0.39175900	-4.30608300	-1.33932800
C	-0.16013700	3.73776100	1.23415900	C	-2.16531600	-3.16329700	-0.92632400
C	0.87038000	3.84362100	-0.94722400	H	-2.83633400	-4.02229100	-1.06277000
C	-0.56474100	5.05537000	1.11065600	O	-2.67442000	-2.05911700	-0.55644600
H	-0.39697600	3.17330400	2.13104200	Zn	-4.60253500	-1.79363000	-0.11053900
C	0.48384800	5.17852000	-1.06988200	Cl	-5.70043200	-3.60500100	-0.65501700
H	1.43833800	3.36806100	-1.73948100	Cl	-4.81424500	0.15541000	0.85536400
C	-0.24149500	5.78463300	-0.04189100				

Figure S26. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-endo* (Zwitterionic Intermediate)



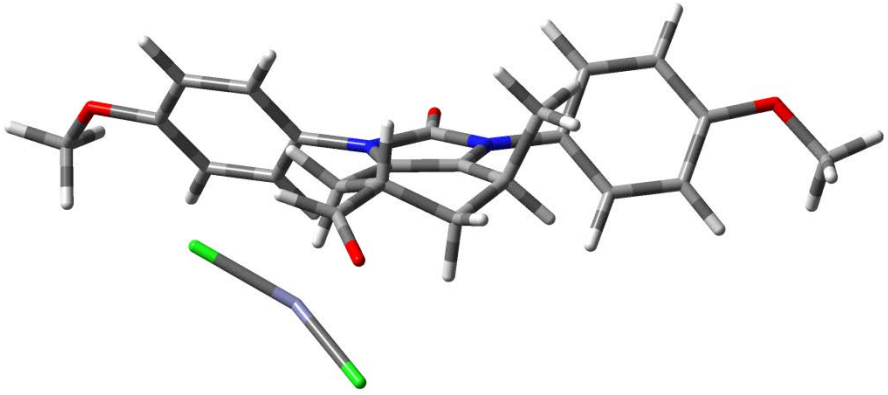
0 1				H	3.47661400	3.20630200	-1.55766600
C	-0.12459000	-0.01105900	0.18662900	H	1.21210900	5.44147400	1.34086900
C	1.08310700	-0.49380300	0.52702300	O	3.43013900	5.36877300	-0.24497000
C	-1.73355200	-2.18211800	0.03175300	C	3.34112700	6.53342500	0.55241700
C	-1.39335900	-0.71320500	0.06999700	H	4.21956700	7.12947300	0.31028700
H	1.90335500	0.19912700	0.69081200	H	2.43528200	7.10419100	0.31727600
H	1.29002500	-1.55246200	0.63879600	H	3.35230900	6.28205900	1.61922300
H	-2.40673000	-2.34544800	0.88382200	C	-2.53912800	-2.47575300	-1.25818400
C	-1.75010900	1.56934000	-0.07443100	H	-3.54231800	-2.05078800	-1.23696400
O	-2.40545800	2.56977100	-0.19106600	H	-2.01275200	-2.09994200	-2.13879200
N	-2.32724900	0.22406000	-0.01770600	H	-2.62818300	-3.56020400	-1.35820200
N	-0.41533600	1.36541400	0.03650800	H	-6.48937300	0.74180100	-1.88817900
C	-3.75337600	0.08293500	0.00597900	O	-7.85624800	-0.27700900	-0.03518700
C	-4.50226100	0.54099400	-1.08026700	C	-8.55621200	-0.84912200	1.05639400
C	-4.37217600	-0.46659100	1.11890500	H	-8.40688300	-0.26142000	1.96878600
C	-5.87717700	0.40216200	-1.06044400	H	-9.60836400	-0.82940200	0.77840800
H	-4.00374300	0.99699800	-1.92899200	H	-8.24052900	-1.88467400	1.22474800
C	-5.75845100	-0.61208200	1.14271500	C	-0.57015600	-3.18919400	0.15921200
H	-3.78180900	-0.77411500	1.97672100	H	-1.07039400	-4.15283300	0.33509100
C	-6.51328200	-0.18208800	0.04661800	H	0.02340400	-3.00874800	1.06017900
H	-6.22997400	-1.04419400	2.01615300	C	0.31835600	-3.27921700	-1.04867100
C	0.55774500	2.41357700	-0.01948800	H	-0.13681700	-3.42890000	-2.02233600
C	1.65254200	2.29034300	-0.88066700	C	1.66700200	-3.30027600	-0.98860800
C	0.40546200	3.53915500	0.77843400	H	2.21791400	-3.39234300	-1.93093700
C	2.60383500	3.29388000	-0.92032300	O	2.37580400	-3.20607400	0.12323600
H	1.77993400	1.40386300	-1.49555200	Zn	4.06779300	-2.27911500	0.12588000
C	1.34828000	4.56471500	0.72037700	Cl	5.68576600	-2.75257300	1.51439200
H	-0.45459400	3.62782300	1.43369300	Cl	3.84285500	-0.52006400	-1.26720300
C	2.45400400	4.43909100	-0.12596400				

Figure S27. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-endo* (Transition State 2)



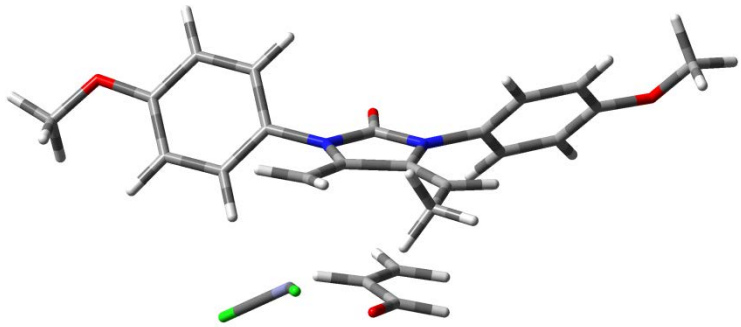
0 1				H	3.25999600	3.43593700	-1.63655900
C	-0.22323400	0.01455700	0.07808800	H	1.03620300	5.39077200	1.48392400
C	1.02977800	-0.50368000	0.19938300	O	3.20955200	5.48713900	-0.16229800
C	-1.65851000	-2.17581800	-0.25117400	C	3.12266200	6.58371700	0.72665500
C	-1.45053600	-0.70285900	0.01114400	H	3.98192100	7.21545100	0.50708500
H	1.90817100	0.13384500	0.11988300	H	2.19950100	7.15186200	0.56354800
H	1.20594700	-1.50882600	0.54751800	H	3.17110500	6.24971000	1.76941500
H	-2.18216400	-2.60232300	0.61328500	C	-2.56394300	-2.34403600	-1.49518800
C	-1.89054100	1.55644600	-0.09448100	H	-3.59037600	-2.01983500	-1.32506100
O	-2.55820800	2.55942900	-0.14062200	H	-2.16183200	-1.78657600	-2.34589400
N	-2.42975400	0.21293900	-0.04549900	H	-2.58265800	-3.40181100	-1.76584000
N	-0.53880500	1.38224500	-0.06788100	H	-6.72793500	0.77987000	-1.56512300
C	-3.83978600	0.00765200	0.04156700	O	-7.91924300	-0.58171500	0.18681600
C	-4.68331100	0.57475600	-0.91751500	C	-8.51445400	-1.34805700	1.21894200
C	-4.35914200	-0.74038400	1.08931400	H	-8.32961900	-0.89583600	2.19964900
C	-6.04602500	0.35607800	-0.83653200	H	-9.58330200	-1.34659100	1.01285900
H	-4.26600300	1.18076800	-1.71405100	H	-8.14047900	-2.37797000	1.20859700
C	-5.73148900	-0.97067400	1.17135600	C	-0.36362700	-3.01437600	-0.43782000
H	-3.69754200	-1.13894100	1.85269100	H	-0.72438900	-4.02392800	-0.67454000
C	-6.57836100	-0.42344100	0.20224600	H	0.17862500	-3.12949600	0.50633600
H	-6.12171300	-1.55694200	1.99365800	C	0.57817100	-2.54299300	-1.50868700
C	0.40351300	2.45653500	-0.07994600	H	0.17765700	-2.18445700	-2.45295400
C	1.47482700	2.42759700	-0.97846100	C	1.93633200	-2.62866800	-1.39124200
C	0.25309600	3.51849300	0.80187600	H	2.54733800	-2.28447900	-2.23323000
C	2.40523900	3.45177400	-0.96989600	O	2.54695100	-3.05446900	-0.31937400
H	1.58969700	1.60039700	-1.67328500	Zn	4.25284000	-2.27849500	0.21309800
C	1.17255800	4.56597400	0.79586100	Cl	5.50085800	-3.28544300	1.69148700
H	-0.59026400	3.53894400	1.48383100	Cl	4.38310700	-0.26759600	-0.76939800
C	2.25628400	4.52934700	-0.08660700				

Figure S28. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-endo* (Adduct)



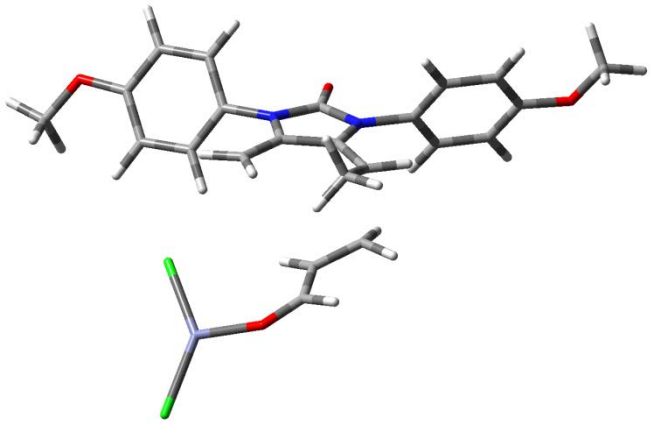
0 1				H	-0.26612800	5.38107500	1.87926300
C	0.57373100	0.52544500	0.10653700	H	1.69335800	5.72743900	-1.92880100
C	-0.91200500	0.65372500	0.14977600	O	0.34387800	7.02042000	0.06262100
C	0.67976300	-2.00323400	0.27712200	C	0.75538100	7.86978500	-0.99014000
C	1.26361700	-0.63319000	0.12434300	H	0.41180800	8.86787000	-0.72215800
H	-1.23074400	1.47403900	0.80100400	H	1.84685700	7.87299400	-1.09085800
H	-1.30730400	0.87573700	-0.85205100	H	0.29984400	7.56950100	-1.94095800
H	1.10891200	-2.67091100	-0.47886900	C	0.99441200	-2.60373300	1.65467100
C	2.78681600	1.06571100	-0.06496900	H	2.07518700	-2.64720500	1.81907900
O	3.82978900	1.68871000	-0.15732500	H	0.55945300	-1.99822800	2.45669000
N	2.62414500	-0.31504600	0.02382300	H	0.59599200	-3.61999200	1.72924400
N	1.49107400	1.57535300	-0.02126900	H	6.58454300	-1.91187100	1.71173000
C	3.71754300	-1.22299700	0.01307200	O	6.92068300	-3.84983400	0.13304200
C	4.72700200	-1.10121500	0.97398600	C	7.03955300	-4.89164800	-0.81440600
C	3.79430100	-2.22591500	-0.94496000	H	7.11940200	-4.49262600	-1.83236000
C	5.78711400	-1.99068100	0.98092500	H	7.95420200	-5.42574400	-0.56091000
H	4.67541900	-0.29524700	1.69832100	H	6.18713400	-5.57876300	-0.75578200
C	4.84982500	-3.14057200	-0.93352600	C	-0.83166300	-1.90432700	-0.00418200
H	3.03538200	-2.28848100	-1.71886000	H	-1.33137700	-2.81916700	0.32836400
C	5.84930200	-3.02198600	0.03377200	H	-1.00135200	-1.82568800	-1.08465800
H	4.88549200	-3.91720600	-1.68749000	C	-1.47438000	-0.68965800	0.67037900
C	1.20529800	2.96754800	-0.02131400	H	-1.28120600	-0.71492500	1.75620300
C	0.53824700	3.55191900	1.06003600	C	-2.96180700	-0.66770500	0.54392800
C	1.61644800	3.75903700	-1.08668700	H	-3.50215500	0.21337200	0.93280600
C	0.25261200	4.90764000	1.05287200	O	-3.60020400	-1.57741000	0.02677700
H	0.26410400	2.94106400	1.91536000	Zn	-5.70216100	-1.57545600	-0.15773900
C	1.35400400	5.12860800	-1.09273600	Cl	-6.31183200	-3.38390600	-1.15091500
H	2.16249400	3.30331100	-1.90586100	Cl	-6.20734400	0.32213800	0.78292700
C	0.66018400	5.70346600	-0.02504700				

Figure S29. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-exo* (Supramolecular Complex)



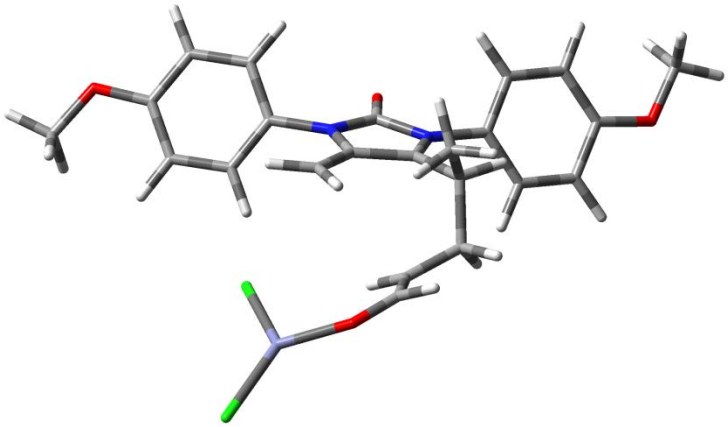
0 1				H	-2.68142800	0.69156300	-0.76980500
C	-0.27038800	-0.19165000	0.94832700	C	-3.59340900	3.71584800	0.45753000
C	-1.33360200	-0.86135600	1.46983000	H	-2.34679800	5.01805100	1.61687300
C	-0.07634500	-0.89726800	-2.19925900	H	-4.60019000	2.19800500	-0.72519200
C	0.86773500	-0.17713000	-2.81593100	O	-4.59335600	4.62724700	0.53992700
C	1.69425100	-1.82239800	1.13706600	C	-5.81770300	4.32242200	-0.10061900
C	1.14069000	-0.63408400	0.83235400	H	-6.47294500	5.17204100	0.08577700
H	-1.17850500	-1.76132200	2.04967300	H	-5.67702400	4.19769000	-1.18031900
H	-2.28679200	-0.34849300	1.56532600	H	-6.26621800	3.41440200	0.31807300
H	2.75694500	-1.91984200	0.93100000	C	1.00595100	-3.00192600	1.75230900
C	0.96522100	1.50469600	-0.00913000	H	0.58508900	-2.76077900	2.73530400
O	1.23527700	2.56888500	-0.51629800	H	0.18357400	-3.38338300	1.13644900
N	1.83198200	0.46508700	0.27893000	H	1.71625900	-3.81794000	1.88951600
N	-0.30501100	1.08373000	0.40809300	H	1.86269200	-0.58773000	-2.97882500
C	3.23873800	0.57373900	0.09674300	H	0.67990700	0.83485000	-3.16199300
C	4.10608500	0.28688700	1.14602800	H	6.13919300	0.15871800	1.80935600
C	3.75723800	1.01242100	-1.12588400	O	7.32144100	0.96017000	-0.51982100
C	5.48646900	0.39358200	0.97766900	C	8.24222500	0.68052200	0.51658200
H	3.70422300	-0.01749700	2.10753700	H	8.16791000	-0.36446100	0.83947500
C	5.12589800	1.13902700	-1.29579500	H	9.23053400	0.86128500	0.09667000
H	3.07978000	1.29330900	-1.92426600	H	8.08258700	1.34304600	1.37506800
C	6.00022100	0.81905300	-0.24996400	H	-1.08694900	-0.53332400	-2.02925700
H	5.54605700	1.49041300	-2.23179500	C	0.25651000	-2.24092600	-1.73247200
C	-1.42160500	1.97505900	0.41602400	O	-0.49465200	-2.96956400	-1.09087500
C	-1.32162500	3.19540200	1.09182900	H	1.25980700	-2.62042800	-1.98962600
C	-2.59461800	1.63575300	-0.24173400	Zn	-2.30300200	-2.53440100	-0.10777400
C	-2.39929200	4.06294800	1.10605000	Cl	-2.60566700	-4.14577400	1.36552200
H	-0.39442800	3.46260700	1.58793500	Cl	-3.60311800	-1.51588200	-1.58931700
C	-3.69237400	2.49667300	-0.21552700				

Figure S30. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta*-*exo* (Transition State 1)



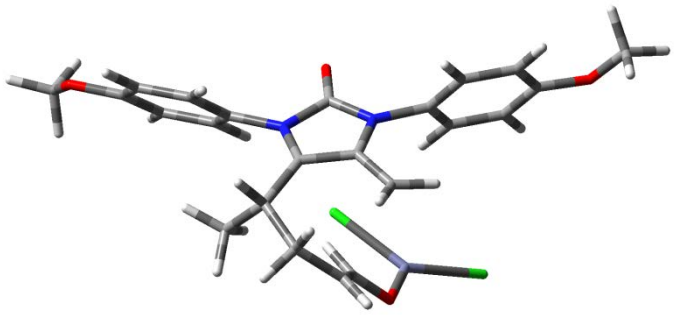
0 1				H	-1.78365900	1.52022700	-0.65957900
C	0.35385000	0.51695200	1.22233000	C	-2.13361500	4.83832600	-0.04062600
C	-0.79163100	0.20705700	1.85179200	H	-0.66331900	6.09280700	0.88455100
C	-0.52865100	-2.41686700	-0.20404500	H	-3.41190000	3.33145600	-0.94293700
C	0.86992300	-2.49946400	-0.19426900	O	-2.95341400	5.91183900	-0.15237200
C	1.74593500	-1.63601000	1.45012200	C	-4.22069500	5.71524500	-0.75136100
C	1.54888000	-0.31124600	1.07195300	H	-4.71164400	6.68719500	-0.73853600
H	-0.89849100	-0.72153200	2.39008500	H	-4.11757300	5.37019100	-1.78636700
H	-1.64155200	0.87867300	1.82364100	H	-4.81828700	4.99440500	-0.18213700
H	2.75188000	-1.99637400	1.25029400	C	1.05008200	-2.27439000	2.62661300
C	1.84541300	1.64739100	-0.10880800	H	1.02785500	-1.60929400	3.49565000
O	2.38713200	2.46966100	-0.80357800	H	0.01649100	-2.55055700	2.39042800
N	2.40215600	0.39382500	0.27024800	H	1.57699600	-3.18725000	2.91272800
N	0.60649600	1.68983300	0.48696300	H	1.30649900	-3.46412900	0.06373100
C	3.72153400	0.01157000	-0.11690000	H	1.44119200	-1.94031700	-0.93102400
C	4.70676900	-0.16444600	0.84654900	H	6.75138000	-0.67456600	1.23841200
C	4.02146400	-0.15937600	-1.47031000	O	7.51291500	-1.07514200	-1.35164700
C	5.99669300	-0.53982300	0.47368500	C	8.55963900	-1.26274300	-0.41788800
H	4.46842000	-0.00490500	1.89419800	H	8.32270600	-2.07205900	0.28226600
C	5.30286800	-0.51982300	-1.85024000	H	9.43710400	-1.53366100	-1.00270800
H	3.25144000	0.00970700	-2.21635000	H	8.76074800	-0.34015700	0.13825800
C	6.29571400	-0.71755400	-0.88072200	H	-1.04807400	-1.57045100	-0.64529700
H	5.56550700	-0.65192300	-2.89387900	C	-1.27756800	-3.46200300	0.35686100
C	-0.31524000	2.76377200	0.30014900	O	-2.53197500	-3.58747000	0.38196200
C	0.01129800	4.04834800	0.74003000	H	-0.70829300	-4.29340700	0.80490500
C	-1.53464100	2.52048400	-0.31774000	Zn	-4.02773500	-2.46727100	-0.27525200
C	-0.89092500	5.08323500	0.56083600	Cl	-5.69897500	-3.60684400	-1.07438000
H	0.97407800	4.22892200	1.20696200	Cl	-3.63433000	-0.30285000	-0.00980300
C	-2.45861000	3.55190100	-0.47868100				

Figure S31. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-exo* (Zwitterionic Intermediate)



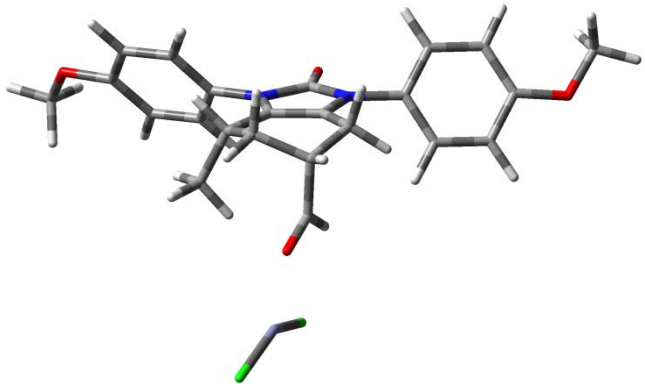
0 1				H	-1.99608100	-3.19779600	1.92244800
C	-0.40549100	-0.10824300	1.58556100	C	-4.61670100	-2.44958300	-0.10989700
C	-1.33179900	0.53878400	2.30638300	H	-4.63310800	-0.88144800	-1.58130900
C	0.43303600	3.17004500	2.38288600	H	-4.30694000	-3.93634000	1.43862300
C	1.32419300	2.16403800	3.06814800	O	-5.88789900	-2.76654800	-0.44948300
C	1.97809000	1.09738900	2.16525500	C	-6.51376900	-3.83528100	0.23255200
C	1.04828400	0.12392100	1.47045000	H	-7.51216600	-3.91865800	-0.19397500
H	-2.36291900	0.20179000	2.25933700	H	-5.96998900	-4.77437600	0.07778700
H	-1.08914600	1.41943400	2.88107100	H	-6.59121500	-3.62696700	1.30602500
H	2.54517300	0.44556700	2.84700200	C	3.00197800	1.73549100	1.17984000
C	0.41602800	-1.63353600	0.10056500	H	3.96464900	1.22241600	1.20982000
O	0.59255800	-2.50006300	-0.70345700	H	2.64844700	1.73118300	0.14655900
N	1.49794200	-0.79289900	0.64466900	H	3.14563600	2.77769300	1.47213500
N	-0.69248800	-1.20747100	0.75647400	H	4.76689300	-0.87621600	-2.53771300
C	2.84508800	-1.05352500	0.23113300	O	6.73196800	-1.80074900	-0.88694300
C	3.19116000	-0.82631900	-1.09282700	C	7.16611200	-1.57877700	-2.21793300
C	3.76572800	-1.55474500	1.15025800	H	7.05075700	-0.52586000	-2.49754700
C	4.49938000	-1.06437700	-1.50574900	H	8.22086000	-1.84751600	-2.23532900
H	2.44541600	-0.44568900	-1.78503900	H	6.61406900	-2.21194700	-2.92094900
C	5.06684800	-1.79199800	0.74225100	C	0.16125500	3.09755800	1.06683800
H	3.46370800	-1.76188600	2.17272900	O	-0.75423200	3.75895700	0.38363800
C	5.44082700	-1.54198600	-0.58685600	H	0.72591500	2.37023100	0.47596700
H	5.81279800	-2.18020700	1.42648100	H	0.77272800	1.65014100	3.87063800
C	-2.02011500	-1.64753900	0.44179000	H	2.16636500	2.65190100	3.57870900
C	-2.74687800	-0.98846400	-0.55396500	H	-0.09304000	3.88557400	3.00992100
C	-2.57901300	-2.69776300	1.15488900	Zn	-1.45130000	2.71484400	-1.05728500
C	-4.04437000	-1.38600400	-0.82308900	Cl	0.07807300	1.12089100	-1.69406600
H	-2.29183100	-0.17769800	-1.11506000	Cl	-3.50373300	2.58981000	-1.81669900
C	-3.88305000	-3.11087900	0.88071600				

Figure S32. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta-exo* (Transition State 2)



0 1				H	-2.13471200	-2.85768700	2.11071900
C	-0.19753900	-0.45931100	1.82810200	C	-4.47912200	-2.31871400	-0.29119100
C	-1.09609100	0.13068400	2.67266800	H	-4.19908500	-1.11373200	-2.04577600
C	-0.10280100	2.51775500	2.73178800	H	-4.46534000	-3.45738500	1.55420600
C	1.11694300	1.85536300	3.33108600	O	-5.74484900	-2.58714200	-0.69170700
C	1.97343200	0.90378100	2.44013000	C	-6.54334300	-3.41098700	0.13336300
C	1.19354600	-0.18028900	1.72564100	H	-7.50739800	-3.49120700	-0.36663200
H	-2.15836900	0.02996300	2.46538400	H	-6.10272400	-4.40918800	0.24023100
H	-0.81349500	0.48511200	3.64672500	H	-6.68204000	-2.96193700	1.12388900
H	2.65515200	0.40025100	3.13932700	C	2.83796000	1.72023200	1.43888500
C	0.57083500	-1.54439800	-0.02481900	H	3.83463600	1.29462800	1.31298400
O	0.70267000	-2.22976700	-1.00367300	H	2.37444200	1.78604500	0.45098000
N	1.64567400	-0.85402300	0.65909800	H	2.94596700	2.73674900	1.82388200
N	-0.53730600	-1.25364300	0.71943100	H	4.80027900	-0.47846000	-2.62099400
C	2.98535000	-0.96657200	0.18679600	O	6.90164800	-1.26197400	-1.06618800
C	3.27305400	-0.64688800	-1.13390400	C	7.26589400	-0.95141500	-2.39947200
C	3.98646000	-1.40511500	1.05541000	H	7.03725700	0.09366600	-2.63609800
C	4.58536500	-0.73553500	-1.59151200	H	8.34102100	-1.11210600	-2.45982800
H	2.47561600	-0.31541900	-1.79168500	H	6.75553200	-1.61129600	-3.10963400
C	5.29301200	-1.48680800	0.60636800	C	-0.36024100	2.54373000	1.38853300
H	3.73682200	-1.68524800	2.07492900	O	-1.34314600	3.12671700	0.77944500
C	5.59901900	-1.14901400	-0.72028900	H	0.31340400	1.96340600	0.74914900
H	6.09486700	-1.82274600	1.25425200	H	0.83118400	1.32615400	4.25188500
C	-1.86458600	-1.64262400	0.36240200	H	1.82723800	2.61837500	3.67182400
C	-2.43039500	-1.15495700	-0.81906400	H	-0.76299600	3.05251000	3.41015900
C	-2.59302400	-2.47241900	1.20422300	Zn	-1.69085000	2.45353800	-1.01271400
C	-3.73298700	-1.49354800	-1.14342400	Cl	0.15948500	1.33268100	-1.69573500
H	-1.83829200	-0.52783600	-1.47932400	Cl	-3.61571600	2.53632400	-2.03329200
C	-3.90851900	-2.81142400	0.88688000				

Figure S33. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-$ZnCl_2$-*meta*-*exo* (Adduct)

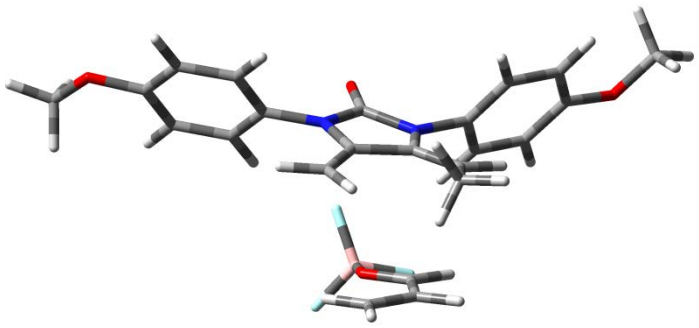


0 1				H	4.71356200	0.46353400	1.03706700
C	1.00510200	-0.23783100	1.21308000	C	5.31920900	-2.47026200	-0.57003600
C	0.75759500	-1.52288000	1.92904700	H	3.83317500	-3.69240000	-1.51270500
C	-0.74635000	-1.62991700	2.21745100	H	6.58915100	-1.02241600	0.42168900
C	-1.33483400	-0.30302300	2.76862100	O	6.26995300	-3.36015500	-0.95303900
C	-1.17780600	0.90679400	1.82511100	C	7.61570100	-3.06669400	-0.63462800
C	0.18525300	0.83547400	1.21135700	H	8.20553400	-3.88919700	-1.03674300
H	1.09307100	-2.38274500	1.33691300	H	7.93476500	-2.12625500	-1.09854700
H	1.32159700	-1.56304800	2.86919200	H	7.76170800	-3.00868800	0.45037100
H	-1.25318600	1.80336900	2.45274300	C	-2.27276200	1.01565700	0.75081600
C	2.04626500	1.39811200	0.00275500	H	-2.18872500	1.96808400	0.21958400
O	2.85018900	2.00810800	-0.67837500	H	-2.18796000	0.22434300	-0.00247100
N	0.81189900	1.84499100	0.47183500	H	-3.26661100	0.96462600	1.20643000
N	2.15312700	0.09568700	0.48597800	H	-0.44943500	5.19344500	-2.37640700
C	0.31446500	3.15246000	0.21996800	O	-1.20480400	6.95264900	-0.42788200
C	0.15713400	3.59298500	-1.08875100	C	-1.37192800	7.45085100	-1.74065500
C	-0.01265600	3.99931200	1.28278700	H	-2.07410600	6.83233200	-2.31161600
C	-0.34207500	4.86859400	-1.34891800	H	-1.77874700	8.45510200	-1.63091800
H	0.43820800	2.93810400	-1.90673100	H	-0.41287300	7.50015100	-2.26906100
C	-0.53066000	5.26049900	1.03366300	C	-1.48922400	-2.02643400	0.97930100
H	0.15622600	3.67016800	2.30363000	O	-2.65307200	-2.41415300	1.02801500
C	-0.69829600	5.70137900	-0.28479400	H	-0.98330200	-1.95177500	0.00000500
H	-0.79521400	5.93308800	1.84226100	H	-0.81455500	-0.09696500	3.71000400
C	3.22057200	-0.77478400	0.13405100	H	-2.39260700	-0.45770900	3.00231800
C	2.96686500	-1.93564700	-0.60382200	H	-0.94558800	-2.41016400	2.96143200
C	4.52365900	-0.45632000	0.49408300	Zn	-3.81323800	-2.75454300	-0.68710300
C	4.00620300	-2.78710000	-0.94118500	Cl	-2.43766400	-2.13188900	-2.26139400
H	1.95364400	-2.15338900	-0.93101400	Cl	-5.75300100	-3.49661900	-0.12184200
C	5.57979800	-1.29572600	0.14007200				

Table S5. M06-2X/6-31+G(d,p) zero-point corrected electronic energies (Hartree) for supramolecular complexes (**SC**), transition states (**TS1**, **TS2**), zwitterionic intermediates (**ZI**) and Adducts (**AD**) of the Diels-Alder reactions of **12a** and **18a** with BF_3

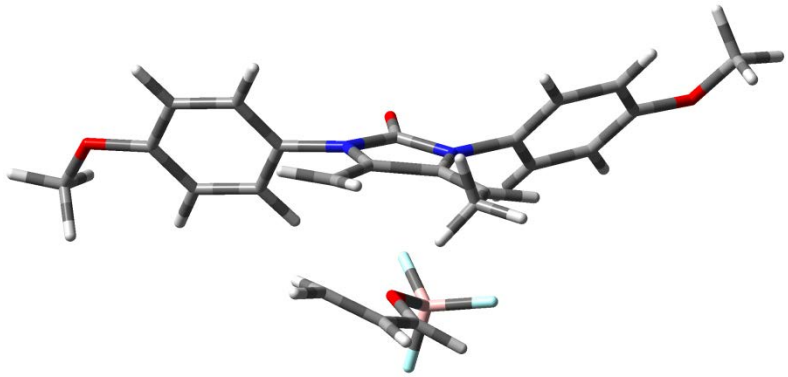
	SC	**TS1**	**ZI**	**TS2**	**AD**
12a-18a-BF_3-*ortho-endo*	-1625.258867	-1625.254771	-1625.289632	-1625.274676	-1625.323974
12a-18a-BF_3-*ortho-exo*	-1625.260166	-1625.250088	-1625.273194	-1625.261358	-1625.320321
12a-18a-BF_3-*meta-endo*	-1625.261144	-1625.251086	-1625.262623	-1625.262611	-1625.318147
12a-18a-BF_3-*meta-exo*	-1625.257267	-1625.248676	-1625.262411	-1625.258166	-1625.317545

Figure S34. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*endo* (Supramolecular Complex)



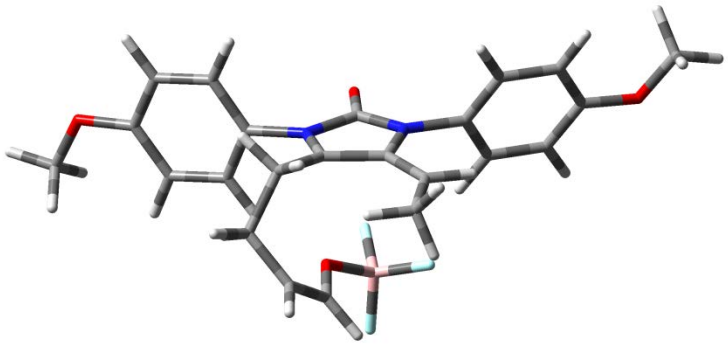
0 1				C	-4.37706300	-1.28209000	0.77347600
O	-0.16753900	-2.07999700	0.26492000	H	-4.74904000	-1.40488900	1.78310800
C	-0.12653500	-1.03715100	-0.33579700	C	-5.19499100	-1.51514200	-0.33384000
N	-1.19649900	-0.33428300	-0.88840900	O	-6.49667800	-1.89883700	-0.25796200
C	-0.76800100	0.80504700	-1.57255000	C	-7.05180600	-2.08904400	1.02780300
C	0.71091800	0.78245200	-1.49127800	H	-6.51718300	-2.87274800	1.57696300
N	1.01617500	-0.29577600	-0.65352300	H	-8.08419300	-2.39698600	0.86700100
C	2.32449300	-0.77023700	-0.35147700	H	-7.03359600	-1.15915700	1.60819600
C	3.16704800	-1.20836200	-1.36687000	C	1.61516700	1.59442500	-2.08065700
C	4.44735600	-1.67553900	-1.07070800	H	2.65984700	1.40219300	-1.85115300
C	4.86981700	-1.71781800	0.26127100	C	1.31487600	2.61587800	-3.14068700
C	4.01213600	-1.29311800	1.28296200	H	2.24187300	2.93729800	-3.61948800
C	2.74598900	-0.81815300	0.97955100	H	0.66132300	2.20134300	-3.91657500
H	2.07011100	-0.49713700	1.76529600	H	0.81837900	3.51346300	-2.75206700
H	4.35980200	-1.34865800	2.30869700	C	-1.56320800	1.73562400	-2.13069100
H	5.08887700	-2.01236100	-1.87570800	H	-1.14731400	2.58578400	-2.64808600
H	2.82100500	-1.18892400	-2.39628000	H	-2.64114400	1.63872900	-2.07784900
O	6.09165900	-2.15767500	0.65963600	H	-1.42313500	3.92759200	-0.00802300
H	7.23065000	-1.84692500	-1.05040800	H	-0.68060600	5.16214900	-1.18965900
C	6.97759900	-2.63535900	-0.33147500	C	-0.54123500	4.36280200	-0.46875600
H	6.54983900	-3.49274500	-0.86421300	C	0.68279300	3.91996400	-0.14618100
H	7.87825500	-2.94773500	0.19542800	H	1.58795300	4.32089700	-0.58953100
H	-2.40447200	-0.69583100	1.43335500	C	0.84602700	2.85428200	0.82488800
C	-3.05433500	-0.87977700	0.58426100	H	1.84683800	2.51061800	1.10909100
C	-2.55006300	-0.72797400	-0.70118300	O	-0.13797700	2.34248000	1.38434800
C	-3.36362400	-0.97937300	-1.80998400	B	0.01302000	1.32861500	2.63335800
H	-2.95340200	-0.87813100	-2.81052200	F	-0.80031500	1.87201900	3.57715400
C	-4.68300500	-1.35990000	-1.62874900	F	-0.39880600	0.12099200	2.14029600
H	-5.33572400	-1.55929000	-2.47168800	F	1.35405300	1.35503500	2.95514200

Figure S35. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho-endo* (Transition State 1)



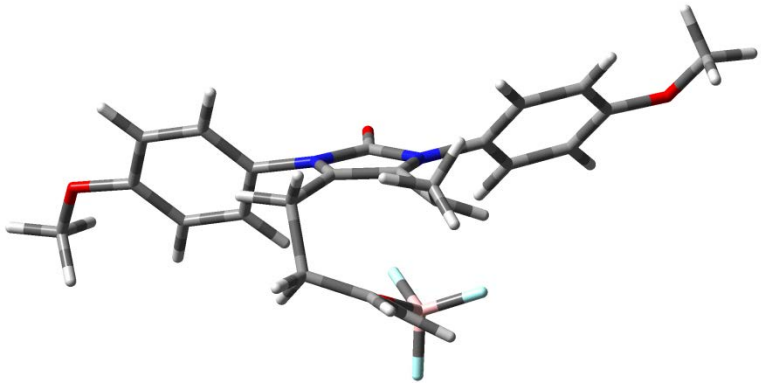
0 1							
O	-0.01000400	-2.08126100	-0.09444400	C	-4.19801600	-1.34982700	0.64280500
C	0.01104000	-0.95464900	-0.51471400	H	-4.54251700	-1.51856800	1.65546000
N	-1.08924300	-0.24250600	-1.03651300	C	-5.03324800	-1.57333600	-0.45536500
C	-0.70954300	0.98235300	-1.53311100	O	-6.31885500	-1.99753900	-0.36333500
C	0.73077600	1.10027800	-1.26307300	C	-6.83779900	-2.25761500	0.92664600
N	1.09897500	-0.10066600	-0.63937200	H	-6.26396700	-3.04303500	1.43139200
C	2.43108300	-0.56182100	-0.41448500	H	-7.86215800	-2.59493800	0.77510400
C	3.37387700	-0.50543700	-1.43432100	H	-6.83853800	-1.35085100	1.54248200
C	4.67005500	-0.97854000	-1.22641200	C	1.54916000	2.15512000	-1.46563600
C	5.00365800	-1.53678000	0.00975900	H	2.56158300	2.04387500	-1.08584100
C	4.04256600	-1.61462800	1.02453400	C	1.25850300	3.38567500	-2.28149000
C	2.76345500	-1.12577600	0.81982700	H	2.14015700	4.02781000	-2.30498900
H	2.01172400	-1.17828900	1.59845600	H	1.01203200	3.12400500	-3.31775700
H	4.32542100	-2.05967900	1.97205800	H	0.42970400	3.97798800	-1.88652800
H	5.39093800	-0.91973700	-2.03252100	C	-1.54938000	1.91925100	-2.06916700
H	3.10079000	-0.09489700	-2.40200300	H	-1.14660700	2.77119900	-2.59253200
O	6.23171200	-2.03206000	0.31727800	H	-2.58828800	1.66333800	-2.24155000
H	7.44505600	-0.96698600	-0.98995400	H	-2.47129000	2.31245000	0.24599000
C	7.22579200	-1.99721500	-0.68436200	H	-2.63580200	3.84784400	-0.77704400
H	6.92501800	-2.58217000	-1.56177700	C	-2.01279400	3.20830800	-0.16065100
H	8.11644400	-2.44064100	-0.24079600	C	-0.85526300	3.68710600	0.40161800
H	-2.22196800	-0.73797300	1.27635100	H	-0.45906600	4.66770700	0.16649100
C	-2.89254100	-0.90488100	0.43705600	C	-0.12076800	2.85960200	1.27663700
C	-2.42667500	-0.69617000	-0.85601300	H	0.77498800	3.22787400	1.78460600
C	-3.25191400	-0.94019900	-1.95575900	O	-0.48251800	1.66743800	1.50647100
H	-2.86386100	-0.80467600	-2.96108200	B	0.27656400	0.86387800	2.61329100
C	-4.55531100	-1.36594800	-1.75635500	F	-0.20551500	1.32604000	3.81477500
H	-5.22016300	-1.56385000	-2.58996800	F	-0.04119600	-0.44959600	2.35337800
				F	1.62076400	1.14724100	2.43908100

Figure S36. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho-endo* (Zwitterionic Intermediate)



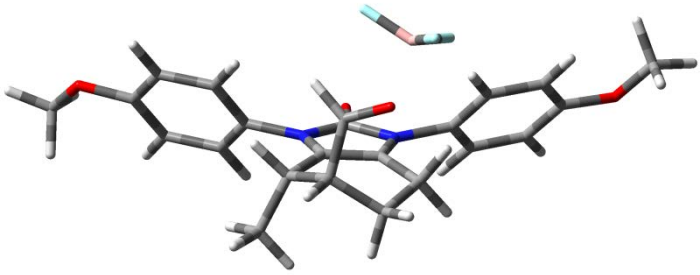
0 1							
O	0.10774700	-2.26719400	0.03420500	C	-4.21428600	-1.12001200	0.83460600
C	0.16165800	-1.15389100	-0.40255500	H	-4.67619200	-0.92674100	1.79452400
N	-1.00063300	-0.39290500	-0.84890200	C	-4.87780200	-1.84832600	-0.15810100
C	-0.66122000	0.78663900	-1.32270900	O	-6.12535900	-2.35597600	-0.02332500
C	0.78792200	0.89919900	-1.21056800	C	-6.79432100	-2.15712400	1.20882600
N	1.21654500	-0.33596000	-0.67527200	H	-6.23808600	-2.61193000	2.03588500
C	2.56146800	-0.67922700	-0.33688300	H	-7.76097700	-2.64761000	1.10590400
C	3.47584200	-0.93735900	-1.34899500	H	-6.94392600	-1.08998000	1.40772000
C	4.79415400	-1.27159800	-1.03682400	C	1.62164300	1.92919100	-1.44937100
C	5.17286400	-1.36230300	0.30555300	H	2.66140700	1.72683300	-1.19494200
C	4.23977900	-1.11213900	1.32089500	C	1.35408700	3.30921800	-1.94225400
C	2.93741000	-0.76414200	1.00594200	H	1.65327500	4.01103500	-1.15551400
H	2.20212500	-0.55104000	1.77432900	H	1.98556400	3.51632700	-2.81337400
H	4.56519500	-1.19122000	2.35224000	H	0.31378700	3.51585100	-2.17583100
H	5.49739900	-1.46808600	-1.83645500	C	-1.64133000	1.68349000	-1.99762000
H	3.15910500	-0.88171500	-2.38677000	H	-1.11271100	2.27263200	-2.74687800
O	6.42263900	-1.68717700	0.72228100	H	-2.34226600	1.02571000	-2.52321400
H	7.57169900	-1.08950200	-0.90209800	H	-3.04725200	1.98161700	-0.39037300
C	7.39850800	-1.96236900	-0.26147000	H	-3.19894300	3.11738100	-1.73233500
H	7.10579600	-2.81886900	-0.88008800	C	-2.48002700	2.62211600	-1.07446000
H	8.31248900	-2.20146700	0.28044500	C	-1.68093500	3.62729500	-0.29949200
H	-2.38092900	-0.07704700	1.34659900	H	-1.72068300	4.68022400	-0.55282300
C	-2.92892200	-0.63762000	0.59440500	C	-0.93057500	3.20851500	0.73111900
C	-2.33002200	-0.88533700	-0.63303600	H	-0.33237300	3.87855000	1.34848700
C	-2.97342100	-1.62642800	-1.62320200	O	-0.88904500	1.90862200	1.03152700
H	-2.46982400	-1.83292500	-2.56288100	B	0.11705600	1.44658400	2.02392500
C	-4.25291600	-2.10103600	-1.38785900	F	-0.13497500	2.00331600	3.26529400
H	-4.78805300	-2.68006400	-2.13203400	F	-0.00796200	0.04726800	2.03487700
				F	1.40099400	1.80991200	1.57492700

Figure S37. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*endo* (Transition State 2)



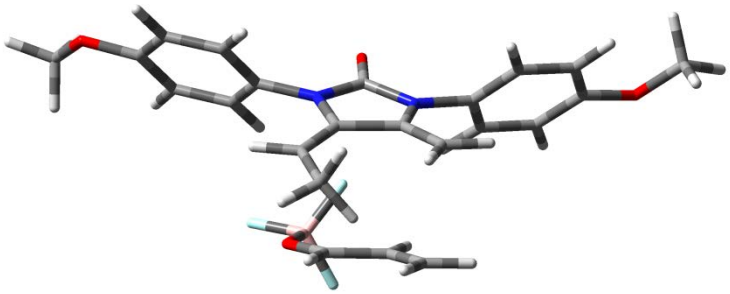
0 1				C	-4.30033500	-1.34924200	0.58827300
O	-0.17951700	-2.15650800	-0.33694600	H	-4.63410800	-1.64644400	1.57451200
C	-0.09909900	-0.98044600	-0.58622500	C	-5.16621700	-1.37408400	-0.50940700
N	-1.18129400	-0.13767500	-0.98752700	O	-6.46628900	-1.75397600	-0.44678500
C	-0.73388100	1.09638400	-1.30783300	C	-6.97386400	-2.17226900	0.80621400
C	0.65043300	1.11690100	-1.09257300	H	-6.42834200	-3.04593100	1.18018200
N	1.00614700	-0.15568100	-0.61765900	H	-8.01527800	-2.43936700	0.63296200
C	2.33236100	-0.65057600	-0.45922800	H	-6.92107700	-1.36297300	1.54334500
C	3.31058500	-0.34604300	-1.39723700	C	1.41259200	2.27010700	-0.93006400
C	4.61121400	-0.83167000	-1.24468700	H	2.29540100	2.12459300	-0.30339400
C	4.91019600	-1.65000200	-0.15424700	C	1.53663200	3.39491000	-1.91744300
C	3.91331000	-1.96806100	0.77733700	H	1.91300900	4.29910700	-1.43670400
C	2.63197400	-1.46666800	0.63549400	H	2.27792100	3.09029600	-2.66850800
H	1.85674400	-1.68409800	1.36137500	H	0.61162300	3.62923800	-2.44141700
H	4.17463200	-2.60235000	1.61711300	C	-1.57927900	2.28593300	-1.51369700
H	5.36098000	-0.57967700	-1.98442600	H	-1.23943700	2.83467100	-2.39237900
H	3.06276700	0.26312900	-2.26237900	H	-2.61587500	1.99098900	-1.68525400
O	6.13691000	-2.18443000	0.08668900	H	-2.17869900	2.76541200	0.49909700
H	7.37260900	-0.82522400	-0.88272700	H	-2.06445900	4.16748700	-0.57931900
C	7.16989500	-1.90195400	-0.83258400	C	-1.55914500	3.25322000	-0.25880700
H	6.92203000	-2.27395500	-1.83403900	C	-0.23754600	3.58222700	0.35404300
H	8.05368600	-2.41980100	-0.46200400	H	0.21086500	4.55832200	0.21165300
H	-2.28669100	-0.90908800	1.25453800	C	0.25110200	2.76712200	1.34849400
C	-2.98070500	-0.93497600	0.41791000	H	1.13397000	3.02950400	1.93463600
C	-2.53721300	-0.55672400	-0.84344100	O	-0.31200300	1.62391500	1.57034100
C	-3.39018000	-0.59883300	-1.94688800	B	0.36106200	0.66494700	2.54712000
H	-3.01586200	-0.33177400	-2.93107200	F	0.04968100	1.05922300	3.83091000
C	-4.70679100	-0.99600300	-1.77831900	F	-0.14667300	-0.58661300	2.22489000
H	-5.39665000	-1.03974300	-2.61377200	F	1.73498300	0.74615700	2.30550900

Figure S38. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*endo* (Adduct)



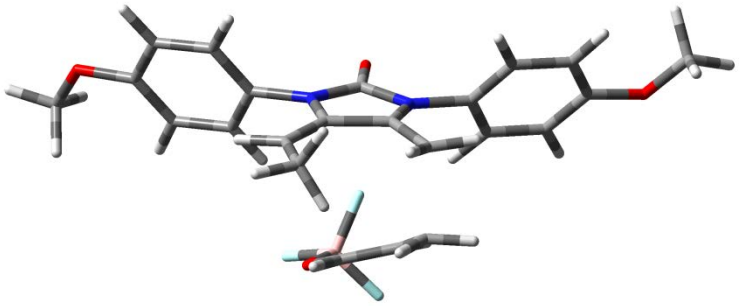
0 1							
O	-0.60475200	-2.69849200	-0.42937800	C	4.29975100	-1.46674800	-0.56481500
C	-0.43297400	-1.60043800	0.06476200	H	5.06399700	-0.88342100	-1.06322900
N	0.76590000	-1.03090400	0.49288500	C	4.54143000	-2.77487200	-0.14143100
C	0.53598000	0.24490300	1.00517000	O	5.72659700	-3.42182600	-0.29247000
C	-0.79006200	0.50343400	0.88450100	C	6.77525700	-2.73036200	-0.94023900
N	-1.39595700	-0.62315000	0.32242900	H	6.49598900	-2.45920200	-1.96500900
C	-2.75320000	-0.74265600	-0.07838500	H	7.61963200	-3.41802500	-0.96333100
C	-3.51854400	-1.81115400	0.37310800	H	7.05493200	-1.82646600	-0.38634700
C	-4.85219900	-1.93789100	-0.01450500	C	-1.49131400	1.70441800	1.43679900
C	-5.42349400	-0.97510600	-0.85048200	H	-2.18161800	2.11206600	0.68478400
C	-4.64949400	0.09669300	-1.31233100	C	-2.31636500	1.39633200	2.68987400
C	-3.31867000	0.20181400	-0.94087800	H	-2.80650600	2.30058200	3.06358500
H	-2.70245000	1.00318800	-1.33868800	H	-3.09150100	0.66239000	2.45132000
H	-5.10826300	0.81719400	-1.98060600	H	-1.69152500	0.97886100	3.48386400
H	-5.42650300	-2.78469400	0.34038000	C	1.53728000	1.06840600	1.74945100
H	-3.06213400	-2.55628200	1.01598500	H	2.07177600	0.43407200	2.46507200
O	-6.71237700	-0.99777900	-1.27611300	H	2.29396400	1.47876400	1.07152700
H	-7.63015100	-2.11104800	0.21962700	H	1.50278900	3.01359600	2.70848600
C	-7.52214800	-2.08358000	-0.87102900	H	0.40721900	1.84185400	3.43981800
H	-7.10959300	-3.03613300	-1.22296800	C	0.80446700	2.20340400	2.48735200
H	-8.49671300	-1.91814300	-1.32812300	C	-0.37221700	2.74531400	1.65041200
H	2.83839700	0.10259700	-0.73316600	H	-0.79154600	3.64565200	2.12317400
C	3.03918200	-0.90072300	-0.36686400	C	0.12377200	3.13626700	0.29193800
C	2.03976800	-1.62427000	0.27422300	H	-0.53699600	3.06662900	-0.58346200
C	2.27983600	-2.93654100	0.69202900	O	1.28090700	3.52426700	0.12400600
H	1.48243300	-3.50137900	1.16233300	B	1.91942500	3.69548100	-1.39032900
C	3.52230500	-3.50906500	0.47949900	F	2.61713100	4.85307200	-1.31609500
H	3.73262500	-4.52773400	0.78648500	F	2.66916800	2.55500900	-1.48968900
				F	0.82613800	3.72205400	-2.21692300

Figure S39. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*exo* (Supramolecular Complex)



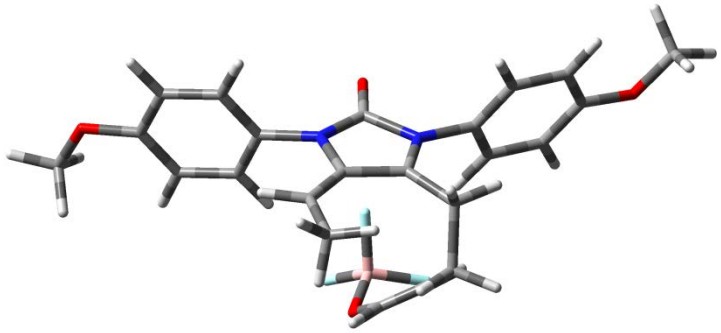
0 1				C	-7.40386500	-0.12067800	-1.95967300
C	-0.17500900	-0.64369300	-0.89168600	H	-7.14408000	-0.80159100	-2.77863500
N	0.90789000	-1.12303000	-0.16464900	H	-8.25985400	0.48694300	-2.25002900
C	0.49380600	-1.74783100	1.02330700	H	-7.65626200	-0.70292800	-1.06538700
C	-0.98935800	-1.74582600	0.97572200	C	6.71863500	0.64545900	-2.20377000
N	-1.31324400	-0.98121000	-0.14493800	H	7.75049300	0.46331600	-2.50135100
O	-0.15688000	-0.07216500	-1.95214000	H	6.69953300	1.32432400	-1.34342600
C	2.25383500	-0.96946200	-0.60178700	H	6.17081900	1.09819200	-3.03818000
C	4.88450400	-0.66462100	-1.46445500	C	-1.86351800	-2.30207700	1.83381900
C	3.07684100	-2.09161300	-0.74271200	H	-1.52575600	-2.90218300	2.66376900
C	2.74094000	0.29378400	-0.91000800	H	-2.93014300	-2.18898900	1.68421900
C	4.05612500	0.45252200	-1.34672500	C	1.32087200	-2.16557900	1.99987100
C	4.38824300	-1.93998300	-1.16095900	H	2.38401100	-2.02286100	1.82707400
H	2.68183100	-3.07956900	-0.52440000	C	-1.55574300	0.41708200	3.22815000
H	2.08908000	1.15595300	-0.83131200	H	-1.09070200	-0.28125600	3.91905700
H	4.40943300	1.44909300	-1.58070900	H	-2.64003500	0.43279800	3.19712800
H	5.04746100	-2.79361200	-1.27539300	C	-0.81782600	1.22929100	2.45443200
C	-2.61442400	-0.57321000	-0.54442200	H	-1.25420100	1.93938400	1.76284200
C	-5.15037400	0.27380900	-1.32791500	C	0.91608000	-2.82520900	3.28655000
C	-2.86771100	0.79077600	-0.73012700	H	1.78553100	-2.94688600	3.93450600
C	-3.61851200	-1.50497900	-0.77456700	H	0.48702100	-3.82098200	3.12220200
C	-4.89583900	-1.08835500	-1.15469800	H	0.16697700	-2.24374900	3.83895500
C	-4.12737400	1.20936700	-1.12323600	C	0.62021400	1.11805500	2.54647400
H	-2.05907300	1.50354100	-0.59415600	H	1.03147100	0.39356300	3.25858600
H	-3.40452800	-2.56400800	-0.66700000	O	1.44848100	1.77252000	1.89105000
H	-5.66564200	-1.83080700	-1.32534900	B	0.99184500	2.90772500	0.83275100
H	-4.34596200	2.25917900	-1.28562400	F	2.16170300	3.34247700	0.29720100
O	6.18090700	-0.61856200	-1.86815300	F	0.17914900	2.23404200	-0.05880900
O	-6.35231200	0.78596800	-1.69846200	F	0.30870300	3.82791800	1.58473200

Figure S40. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*exo* (Transition State 1)



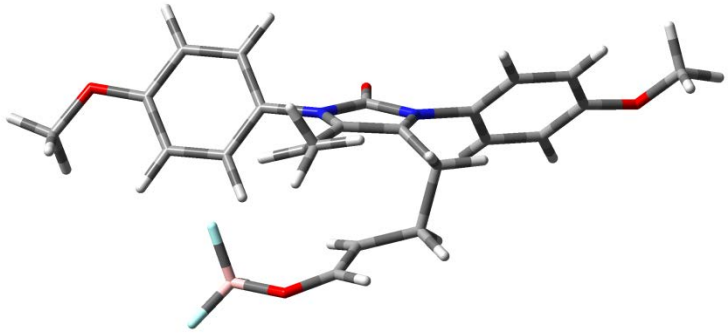
0 1				C	-7.33837600	-0.08813800	-1.97123400
C	-0.08875200	-0.58120500	-1.00701600	H	-7.08021200	-0.74655900	-2.80871100
N	0.98751900	-1.09608100	-0.32102700	H	-8.20002900	0.52106500	-2.24003700
C	0.57850700	-1.76203900	0.84480300	H	-7.57954600	-0.69265700	-1.08892900
C	-0.89045400	-1.69800400	0.84739300	C	6.85350300	0.95910700	-1.86827300
N	-1.23183700	-0.93846900	-0.21945400	H	7.88216800	0.82404600	-2.19963200
O	-0.12307700	0.00220200	-2.05370500	H	6.84575700	1.41727600	-0.87278100
C	2.34096800	-0.87290600	-0.71452200	H	6.32259700	1.60803600	-2.57380300
C	4.98255400	-0.44227000	-1.46113500	C	-1.75664300	-2.05471100	1.86755700
C	3.13666900	-1.95385700	-1.10364600	H	-1.43696100	-2.79613100	2.58471000
C	2.85690500	0.41632400	-0.70533300	H	-2.81890700	-2.01082500	1.66265400
C	4.18046300	0.63763400	-1.08563000	C	1.41813700	-2.25546200	1.77533700
C	4.45607800	-1.74208100	-1.46710900	H	2.47692500	-2.10161500	1.58100500
H	2.71367200	-2.95434400	-1.12143300	C	-1.60744800	-0.31240300	3.08981000
H	2.22664400	1.25031800	-0.41550600	H	-1.09378200	-0.84135500	3.88794900
H	4.56088900	1.65143000	-1.07692600	H	-2.68820500	-0.29174000	3.17643300
H	5.09831900	-2.56040000	-1.77369000	C	-0.95649400	0.77003700	2.49220700
C	-2.54393100	-0.52524000	-0.59760800	H	-1.48562200	1.45461700	1.84040200
C	-5.08411200	0.31182200	-1.34383000	C	1.05317100	-3.01389300	3.01839500
C	-2.80274000	0.84139400	-0.74403000	H	1.95753200	-3.35833800	3.52083700
C	-3.53461400	-1.46587600	-0.84503700	H	0.44072100	-3.89403300	2.79556700
C	-4.81653600	-1.05357500	-1.20954900	H	0.49799600	-2.39705300	3.73388700
C	-4.07072500	1.25326000	-1.11584100	C	0.41431400	0.91738400	2.69103400
H	-2.00143400	1.55668400	-0.57890700	H	0.91148500	0.23855600	3.39272300
H	-3.30773800	-2.52501100	-0.76345300	O	1.19114700	1.78068400	2.16056600
H	-5.57936400	-1.79858000	-1.39825100	B	0.68239500	2.75988800	1.08821800
H	-4.30307700	2.30494700	-1.24149800	F	1.79890100	3.41815500	0.63642800
O	6.28153000	-0.33483900	-1.83812300	F	0.10804400	1.97164000	0.07676700
O	-6.29027400	0.81965800	-1.69610400	F	-0.26459600	3.58027500	1.66659800

Figure S41. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*exo* (Zwitterionic Intermediate)



0 1							
C	0.04062100	-1.16144600	0.58570300	C	-7.15541300	-2.20668800	0.03108500
N	1.11510400	-0.49263200	1.09069100	H	-6.82110300	-3.13702900	0.50429500
C	0.72716500	0.71835700	1.69719600	H	-8.03343300	-2.40528100	-0.58142100
C	-0.72854900	0.78442100	1.55098800	H	-7.40703100	-1.46962900	0.80249300
N	-1.10692300	-0.30256300	0.92991800	C	6.94164300	-1.52882000	-1.35700200
O	-0.06103400	-2.21646600	0.03854200	H	7.96645100	-1.89529000	-1.32077500
C	2.46544300	-0.83804300	0.76172700	H	6.94404800	-0.45106600	-1.55482100
C	5.09105300	-1.46502000	0.12823700	H	6.39397800	-2.04675600	-2.15201300
C	3.26565500	-1.48424400	1.70520700	C	-1.68458200	1.85812800	1.96393600
C	2.96354000	-0.50559200	-0.49275500	H	-1.56379600	2.06461200	3.03295900
C	4.28236400	-0.82313000	-0.81456300	H	-2.69276100	1.46599300	1.81716700
C	4.57912600	-1.79377900	1.39182000	C	1.59217700	1.57018700	2.27700000
H	2.85097000	-1.74599400	2.67426300	H	2.63926000	1.28042500	2.19873900
H	2.31522800	-0.01651200	-1.21467600	C	-1.49994700	3.13514700	1.08941400
H	4.65481600	-0.56764200	-1.79865300	H	-0.71888600	3.77143400	1.51640700
H	5.22788000	-2.29922700	2.09857300	H	-2.43893200	3.69661400	1.14950400
C	-2.42859500	-0.66426400	0.49900900	C	-1.12774800	2.76093200	-0.31436400
C	-4.96057400	-1.38194800	-0.34267100	H	-1.83442200	2.19179900	-0.91249000
C	-2.74496100	-0.55468100	-0.85766200	C	1.32480600	2.85256100	2.98964200
C	-3.34373300	-1.13826300	1.42650000	H	1.61038800	3.69735900	2.35070100
C	-4.62493900	-1.49770400	1.01044000	H	1.95350700	2.90605700	3.88273000
C	-4.01792100	-0.91029100	-1.26799900	H	0.28691200	2.98486200	3.28850300
H	-2.00343400	-0.18841400	-1.56325400	C	0.11131300	3.00014300	-0.78198000
H	-3.06077800	-1.23590900	2.47071300	H	0.79145900	3.62154800	-0.18848500
H	-5.33489400	-1.86838400	1.73883900	O	0.66411200	2.56446100	-1.90294800
H	-4.30591900	-0.83292400	-2.31042900	B	0.17421200	1.32225800	-2.52618300
O	6.38289300	-1.81225200	-0.08710900	F	1.06731500	0.95973300	-3.51289000
O	-6.17159700	-1.70365000	-0.85191600	F	0.14765000	0.30275400	-1.51103900
				F	-1.13390700	1.45106100	-3.00809700

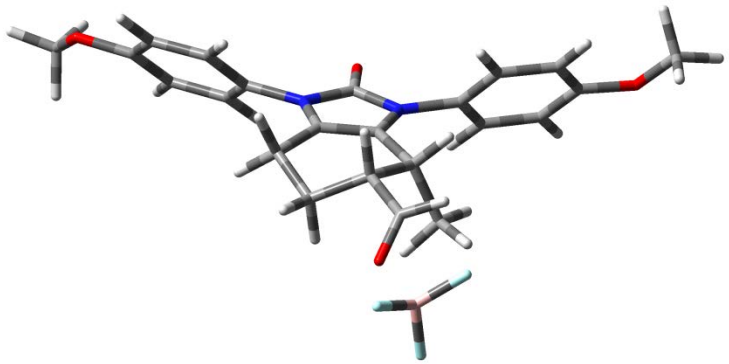
Figure S42. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho*-*exo* (Transition State 2)



0 1

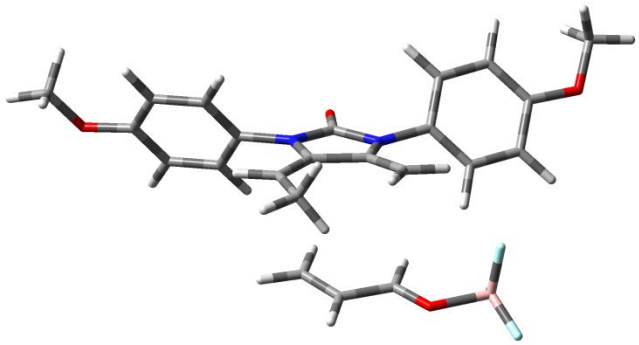
C	-0.93748200	-1.43231100	0.05150000
N	0.27576400	-0.96322200	0.48733000
C	0.12351200	0.28146800	1.13387900
C	-1.23174400	0.63680900	0.99658200
N	-1.86220900	-0.38551100	0.37254500
O	-1.22176200	-2.47877800	-0.47944500
C	1.49800900	-1.69092000	0.33591800
C	3.88553100	-3.08479300	0.06343600
C	1.64537900	-2.93586200	0.95196500
C	2.52807000	-1.15215000	-0.42597500
C	3.73386100	-1.84096700	-0.55344200
C	2.83201300	-3.63379900	0.80909000
H	0.82435000	-3.35302900	1.52613300
H	2.41798600	-0.18813400	-0.91797300
H	4.53012700	-1.39009100	-1.13222900
H	2.97495700	-4.60511800	1.26947600
C	-3.24383800	-0.46266600	0.03214900
C	-5.94186900	-0.60727900	-0.62623100
C	-3.62051000	-0.78697200	-1.27453000
C	-4.20776400	-0.23224200	1.00557000
C	-5.56261600	-0.29155600	0.68165300
C	-4.96343200	-0.85960800	-1.59850600
H	-2.85988300	-0.99336000	-2.01953400
H	-3.90267800	-0.01499400	2.02529700
H	-6.29995200	-0.10810500	1.45306700
H	-5.28605500	-1.11276700	-2.60219500
O	5.01190300	-3.83527500	-0.00116100
O	-7.22464700	-0.69849400	-1.04673700
C	-8.25295400	-0.47614600	-0.10033300
H	-8.19995700	-1.20492200	0.71642400
H	-9.18950100	-0.60293300	-0.64086700
H	-8.20044600	0.54003800	0.30704600
C	6.10724800	-3.31879100	-0.73488700
H	6.89876200	-4.06225900	-0.65310200
H	6.45067400	-2.36779600	-0.31291500
H	5.84337300	-3.17836100	-1.78911000
C	-1.70854500	2.02657000	0.96071300
H	-1.39687100	2.58683400	1.83840400
H	-2.79470600	2.08027600	0.87691300
C	1.17131200	1.11799600	1.45922100
H	2.15642500	0.79753300	1.12576700
C	-1.06969400	2.70857600	-0.33850200
H	-1.36850700	3.76050800	-0.27689100
H	-1.59319800	2.26958500	-1.19417600
C	0.40737000	2.59866000	-0.51800900
H	0.81936700	1.77423700	-1.08711600
C	1.23821600	2.16493800	2.51949100
H	1.93247300	2.95114900	2.21418100
H	1.68296900	1.67969600	3.39924900
H	0.28251900	2.58941000	2.81881900
C	1.21092800	3.67163500	-0.22580800
H	0.73737000	4.55589700	0.21790600
O	2.49040800	3.81059900	-0.36254000
B	3.47004100	2.71801000	-0.73372500
F	4.60489700	3.33731500	-1.18461800
F	3.71061600	1.97475000	0.43815900
F	2.90694400	1.87236000	-1.70061600

Figure S43. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*ortho-exo* (Adduct)



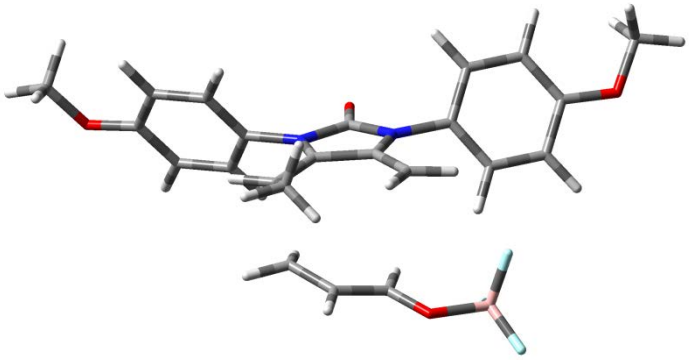
0 1				C	8.24903100	-0.94524800	0.64022700
C	1.53978600	1.45350600	0.11227500	H	8.33267400	0.14759700	0.62033400
N	0.15340500	1.38698500	-0.00091900	H	9.20492100	-1.38813600	0.36395200
C	-0.24002600	0.06679800	-0.25857700	H	7.97245900	-1.27318200	1.64914900
C	0.87324300	-0.69440600	-0.30532000	C	-4.04931500	6.16696600	-0.78655600
N	1.97324900	0.14422200	-0.09298800	H	-4.56308200	7.07718400	-0.48064700
O	2.21949000	2.44051900	0.33297400	H	-4.78044300	5.35964900	-0.91246800
C	-0.68191700	2.53489900	0.02626400	H	-3.52900300	6.34228800	-1.73543300
C	-2.35751000	4.76447400	0.10909900	C	0.90247600	-2.18692300	-0.38986800
C	-0.62659700	3.41138300	1.11552700	H	1.66734600	-2.58827300	0.28317800
C	-1.55503100	2.79297900	-1.02341900	H	1.16874800	-2.52387700	-1.40009100
C	-2.40850000	3.89783000	-0.98398700	C	-1.64996800	-0.43383000	-0.24772100
C	-1.45389600	4.52014600	1.15249700	C	-0.48206300	-2.72765700	-0.00972200
H	0.07911100	3.21919800	1.91637300	H	-0.62030100	-2.67006300	1.07497200
H	-1.55865400	2.14059300	-1.89160800	H	-0.56777100	-3.78277300	-0.28265900
H	-3.08329800	4.07560400	-1.81221600	C	-1.58544800	-1.92358100	-0.70275000
H	-1.42455800	5.21668900	1.98324400	H	-1.40183600	-1.91222900	-1.79044500
C	3.34175300	-0.22981900	-0.12994900	C	-2.94036400	-2.51413400	-0.54400700
C	6.03018500	-0.97953400	-0.20085800	H	-3.80134200	-2.01898800	-1.01566600
C	4.22023400	0.23057900	0.84495200	O	-3.13925600	-3.53605800	0.10749700
C	3.81558400	-1.05308600	-1.15665300	B	-4.68228100	-4.17087900	0.29680200
C	5.14638200	-1.43774500	-1.18467100	F	-4.55548400	-5.40354700	-0.25073400
C	5.56559600	-0.13499400	0.80996000	F	-4.84689300	-4.11930900	1.64093700
H	3.85524300	0.89443800	1.62028600	F	-5.47064100	-3.30112200	-0.41376900
H	3.14133400	-1.37709500	-1.94313800	H	-2.25389100	0.11222700	-0.98391600
H	5.53172400	-2.07778800	-1.97084100	C	-2.30481400	-0.25212700	1.13139800
H	6.23222000	0.24378700	1.57484300	H	-3.35654700	-0.55866000	1.12341600
O	-3.13422900	5.86875800	0.24836600	H	-1.78022900	-0.83376700	1.89461300
O	7.31595000	-1.40220000	-0.31807800	H	-2.27141100	0.80031700	1.42529700

Figure S44. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-endo* (Supramolecular Complex)



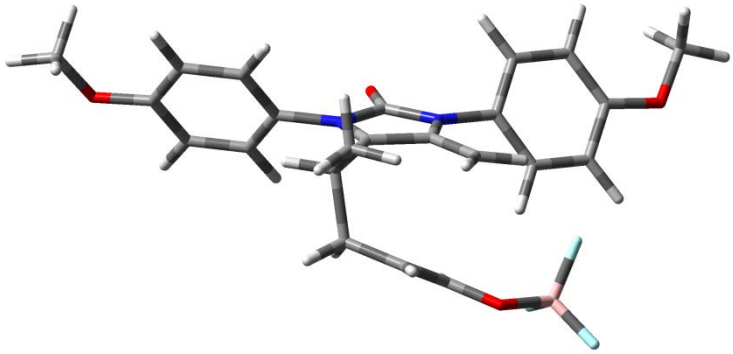
0 1				H	4.85903800	1.16634300	-0.82941000
C	0.25418500	-0.38940300	1.15324700	H	2.80824300	4.61678700	0.72138300
C	1.24145900	-1.04518000	1.78620000	O	5.16294800	3.60976600	-0.22606900
C	-1.88048900	-1.70987500	1.66578300	C	5.23125800	4.97357100	0.13595900
C	-1.19778900	-0.67792500	1.13424200	H	6.25427500	5.28749000	-0.06706200
H	2.27506000	-0.73625600	1.68504500	H	4.53823800	5.57693300	-0.46216600
H	1.03034300	-1.88188700	2.43334800	H	5.01134600	5.11163900	1.20120400
H	-2.95383200	-1.72323300	1.49838500	C	-1.28953200	-2.82483400	2.47427700
C	-0.79700600	1.20591400	-0.15093700	H	-2.05450900	-3.56640000	2.70997500
O	-0.98689600	2.16776900	-0.85985800	H	-0.47954800	-3.33431800	1.93574300
N	-1.76706800	0.34497200	0.35416700	H	-0.87079800	-2.46742000	3.42238200
N	0.42533100	0.73022400	0.31695300	H	-5.20767000	0.50139500	-2.68989100
C	-3.14212500	0.46164000	0.01515300	O	-7.12677200	0.77224800	-1.07660600
C	-3.53872100	0.40998900	-1.32455300	C	-8.13346600	0.96342400	-0.10242500
C	-4.09578000	0.63580500	1.01103000	H	-7.97471300	1.89602200	0.45121800
C	-4.87828000	0.52490500	-1.65694000	H	-9.07341200	1.02091100	-0.64932200
H	-2.78726700	0.30950200	-2.10154000	H	-8.16975800	0.12152500	0.59888000
C	-5.44944600	0.73462700	0.68813700	C	-0.97315700	-2.70401000	-1.08410300
H	-3.77887500	0.69632500	2.04801600	H	-0.83296400	-1.67181400	-1.40036300
C	-5.84171200	0.68014600	-0.65191400	H	-1.99044200	-3.08077500	-1.07826800
H	-6.17500000	0.86650200	1.48128700	C	0.07522900	-3.46745700	-0.73798100
C	1.63004300	1.48451200	0.18328900	H	-0.01776600	-4.50203400	-0.42311400
C	2.78480500	0.88850700	-0.32894100	C	1.39777100	-2.89109300	-0.77742400
C	1.65173600	2.82150800	0.56228700	H	1.51533100	-1.86038400	-1.13509100
C	3.95396000	1.62188200	-0.44306600	O	2.40485600	-3.54597200	-0.46399600
H	2.79019400	-0.15124100	-0.63598300	B	3.86457800	-2.84179200	-0.51531100
C	2.81843300	3.57355900	0.43097700	F	3.96368400	-2.19960400	0.69314100
H	0.74780200	3.28645200	0.94138400	F	4.72341700	-3.87212600	-0.70210600
C	3.97592800	2.97024600	-0.06779800	F	3.77834900	-1.95856900	-1.57459900

Figure S45. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-endo* (Transition State 1)



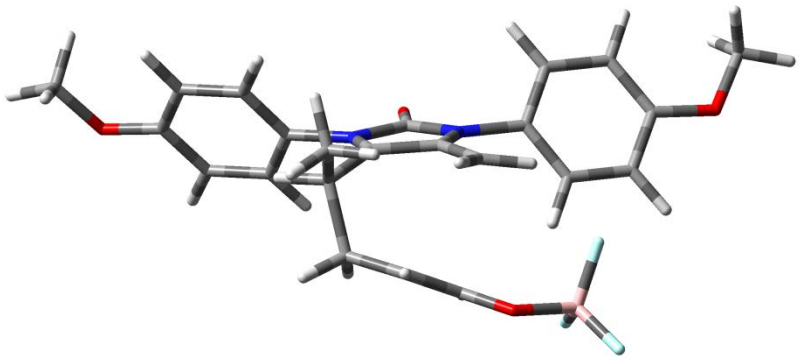
0 1							
C	-0.28294900	0.35450000	1.17147700	H	-4.85775900	-0.96645600	-1.03640500
C	-1.23178600	1.12738400	1.73373700	H	-3.26164600	-4.42516000	0.96959900
C	1.84863100	1.76112900	1.46289600	O	-5.42993500	-3.30609600	-0.25130000
C	1.14894700	0.62190900	1.08141200	C	-5.65494800	-4.62009700	0.21653900
H	-2.28590400	0.89407700	1.62404200	H	-6.68520100	-4.85899000	-0.04367500
H	-0.96409700	1.99894100	2.31061800	H	-4.97994300	-5.33406900	-0.26993000
H	2.91762100	1.69022300	1.27832800	H	-5.52973300	-4.67963800	1.30415100
C	0.67028800	-1.29216600	-0.11298500	C	1.45166200	2.64203700	2.62460900
O	0.85744200	-2.27581900	-0.78378200	H	2.28772600	3.29181300	2.89146000
N	1.67193800	-0.37255400	0.29750900	H	0.59933600	3.28428500	2.38776900
N	-0.50485200	-0.81346500	0.42399600	H	1.19162400	2.04760200	3.50631400
C	3.04349200	-0.54935600	-0.05228000	H	5.07093800	-0.67953800	-2.77745400
C	3.42208200	-0.51471100	-1.39638000	O	6.98661700	-1.05684000	-1.18381000
C	3.99270700	-0.77521300	0.93652800	C	7.99676700	-1.29772700	-0.22263500
C	4.75071400	-0.69329800	-1.74165500	H	7.80049800	-2.22282000	0.33112800
H	2.66791100	-0.36718000	-2.16294600	H	8.92476600	-1.39909000	-0.78297700
C	5.33523600	-0.94211300	0.59887600	H	8.08238800	-0.45908200	0.47792000
H	3.68362500	-0.82406800	1.97669500	C	1.36966700	2.88338600	-0.23024100
C	5.71517100	-0.90167400	-0.74621100	H	1.41477400	2.07377700	-0.95620400
H	6.06149900	-1.11462100	1.38331100	H	2.29872700	3.43705100	-0.12494300
C	-1.76316400	-1.47210000	0.26040200	C	0.16614400	3.57338900	-0.06505800
C	-2.80887100	-0.82147600	-0.39850400	H	0.13127000	4.53099800	0.44460200
C	-1.93107100	-2.75968300	0.75207200	C	-1.03518000	3.04176100	-0.54062300
C	-4.02880500	-1.46031600	-0.54177200	H	-1.02541000	2.09255100	-1.08985600
H	-2.68485300	0.18141000	-0.79546900	O	-2.15077800	3.64064000	-0.41589500
C	-3.14999300	-3.41687700	0.59089200	B	-3.44995200	2.89980800	-0.80207700
H	-1.10405900	-3.25876900	1.24702400	F	-3.78142400	2.12372300	0.30802800
C	-4.20393700	-2.76110300	-0.05275100	F	-4.37604700	3.85729700	-1.09245500
				F	-3.14314300	2.07334300	-1.88502000

Figure S46. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-endo* (Zwitterionic Intermediate)



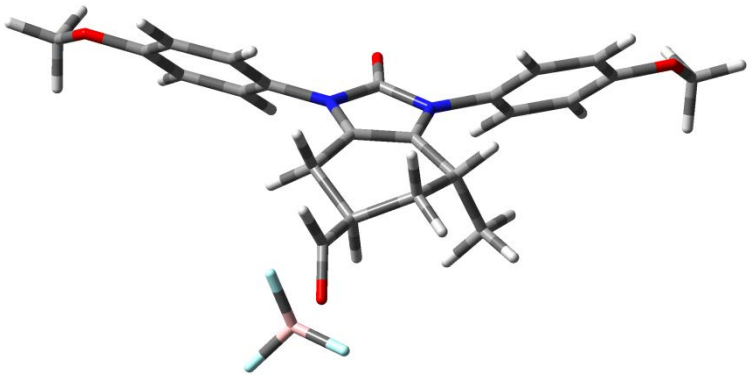
0 1				H	-4.80727200	-0.97869600	-1.08738500
C	-0.25808100	0.39208600	1.05160600	H	-3.30762000	-4.37766800	1.09258300
C	-1.20889600	1.20685800	1.56216800	O	-5.43468400	-3.27223300	-0.20769400
C	1.83303000	1.97214000	1.09591800	C	-5.69636000	-4.55536200	0.32312400
C	1.14270100	0.68278100	0.91129400	H	-6.72890100	-4.78283800	0.06209800
H	-2.26807700	0.98023900	1.46977400	H	-5.03316400	-5.30859300	-0.11822400
H	-0.93350700	2.10729900	2.08626300	H	-5.58534700	-4.56204100	1.41383700
H	2.88926000	1.79837800	0.87539800	C	1.73379200	2.62300600	2.47715500
C	0.69763300	-1.35824100	-0.05789700	H	2.38494000	3.50145700	2.49392900
O	0.93748200	-2.39254200	-0.62338800	H	0.72563300	2.96283600	2.71283900
N	1.69317700	-0.35606400	0.27261700	H	2.06308100	1.93900100	3.26386000
N	-0.47431300	-0.84513000	0.41768200	H	5.06395700	-1.08102800	-2.76064400
C	3.06777600	-0.54909500	-0.06770300	O	7.00275200	-1.13717400	-1.15420100
C	3.42439800	-0.73632600	-1.40497200	C	8.03420200	-1.17548800	-0.18458400
C	4.02919700	-0.57992400	0.93387800	H	7.87783000	-1.99776500	0.52251800
C	4.75402100	-0.93135000	-1.73260400	H	8.95721800	-1.34118800	-0.73738100
H	2.65925500	-0.73788400	-2.17406800	H	8.09823000	-0.22597200	0.35875500
C	5.37129600	-0.76801500	0.60917500	C	1.31411700	2.95692700	-0.06601300
H	3.73179100	-0.46336700	1.97240000	H	1.36296700	2.40341500	-1.01043200
C	5.73497400	-0.94377000	-0.73004500	H	2.09807300	3.72255600	-0.10212000
H	6.11004400	-0.78831700	1.40036500	C	-0.01510700	3.57332800	0.13384000
C	-1.74308900	-1.49277500	0.26743800	H	-0.12208200	4.40362600	0.82757100
C	-2.76386800	-0.84878500	-0.43652300	C	-1.11786200	3.14527900	-0.54130800
C	-1.93950700	-2.75213200	0.81714100	H	-1.02569900	2.32321600	-1.26154800
C	-3.99420700	-1.46991300	-0.56465000	O	-2.30453300	3.66878300	-0.40764900
H	-2.61867800	0.13532800	-0.87468400	B	-3.49684000	2.84076300	-0.78951400
C	-3.16942900	-3.39094900	0.66873000	F	-3.77361100	1.98458800	0.30214800
H	-1.12996000	-3.24320300	1.34774200	F	-4.54363600	3.68446900	-1.05140400
C	-4.20138500	-2.74352200	-0.01894400	F	-3.15986800	2.03544700	-1.89428200

Figure S47. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-endo* (Transition State 2)



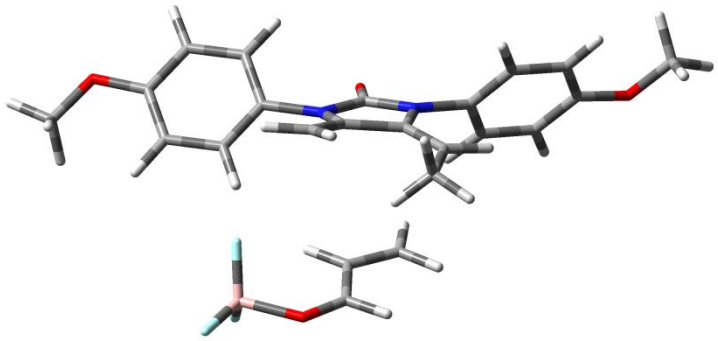
0 1				H	-4.79396600	-1.00825000	-1.07616100
C	-0.23519800	0.40246700	1.02988800	H	-3.25103600	-4.38262400	1.11207800
C	-1.18792900	1.23269200	1.52081500	O	-5.39728800	-3.30144200	-0.17731400
C	1.82725100	2.00073400	1.04338500	C	-5.64503100	-4.58285000	0.36407800
C	1.16014600	0.69477000	0.89239300	H	-6.67801400	-4.81961600	0.11319200
H	-2.24945100	1.02349100	1.40626300	H	-4.98001500	-5.33417000	-0.07782400
H	-0.91055700	2.10903300	2.08243900	H	-5.52491600	-4.58153100	1.45384900
H	2.87895200	1.85202300	0.78547900	C	1.76476500	2.66209000	2.42167800
C	0.72625500	-1.34880700	-0.07251300	H	2.36836100	3.57377200	2.39855900
O	0.96575500	-2.38902200	-0.62913600	H	0.75391200	2.94887300	2.71065600
N	1.71714800	-0.34630600	0.25542400	H	2.17064500	2.00368100	3.19427800
N	-0.45024800	-0.83284600	0.39302900	H	5.10499100	-1.16624900	-2.73476200
C	3.09371300	-0.53599400	-0.07392900	O	7.04158900	-1.11298900	-1.12504400
C	3.45725900	-0.78161200	-1.40018100	C	8.07065600	-1.08878300	-0.15270400
C	4.05417600	-0.50373300	0.92896800	H	7.92498000	-1.87827400	0.59305400
C	4.79057900	-0.97158900	-1.71563600	H	8.99774100	-1.26672700	-0.69482600
H	2.69417000	-0.83358600	-2.16936500	H	8.11874300	-0.11338200	0.34452000
C	5.40000600	-0.68498800	0.61582700	C	1.24161300	2.96124700	-0.10774800
H	3.75290300	-0.34391000	1.96063900	H	1.27662600	2.40293400	-1.04977000
C	5.76959100	-0.91946200	-0.71258800	H	2.00044700	3.75007600	-0.17280700
H	6.13701000	-0.65539300	1.40837100	C	-0.09598200	3.54298500	0.12765400
C	-1.71438700	-1.49165800	0.25583900	H	-0.20698300	4.36121700	0.83533700
C	-2.74587200	-0.86097000	-0.44406300	C	-1.20564000	3.11256100	-0.54097500
C	-1.89737500	-2.74905800	0.81495200	H	-1.11433000	2.30569700	-1.27810000
C	-3.97308100	-1.49108300	-0.55788100	O	-2.39192500	3.62390500	-0.38100300
H	-2.61171000	0.12032200	-0.89138900	B	-3.58732600	2.79676800	-0.76918800
C	-3.12371600	-3.39767500	0.68075300	F	-3.84920600	1.92398800	0.31091700
H	-1.07986200	-3.23093600	1.34170000	F	-4.63656700	3.64318700	-1.00810900
C	-4.16630900	-2.76238800	-0.00231800	F	-3.25292900	2.01468600	-1.88979100

Figure S48. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-endo* (Adduct)



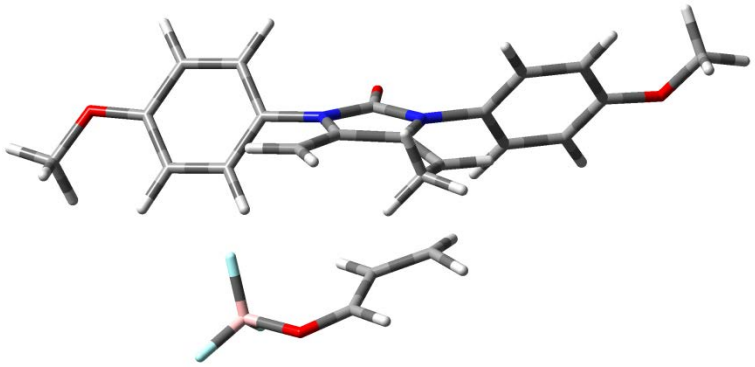
0 1				H	-4.60707800	-1.76672200	-1.22231700
C	-0.34572500	0.10318900	0.91737200	H	-2.67757500	-5.15192200	0.59196900
C	-1.39638800	0.78585100	1.72463000	O	-4.93510000	-4.19630400	-0.61371700
C	1.37694900	1.80788600	1.52499000	C	-5.01308100	-5.56396800	-0.26539900
C	0.91353200	0.57265000	0.82173800	H	-5.99930200	-5.89915200	-0.58373800
H	-2.40785800	0.48844200	1.42498600	H	-4.24331000	-6.14777200	-0.78368100
H	-1.30340200	0.50924800	2.78242400	H	-4.91137500	-5.70273000	0.81755600
H	2.24077100	2.23737800	1.00647200	C	1.81434900	1.47135700	2.95918800
C	0.92673500	-1.57328700	0.03663500	H	2.20707900	2.36009600	3.46244000
O	1.28357900	-2.63004300	-0.45016000	H	0.97290800	1.08618600	3.54509000
N	1.71053700	-0.44551000	0.29416100	H	2.59770100	0.70770900	2.94825600
N	-0.35936900	-1.21079700	0.44228000	H	5.17320900	1.70528000	-1.83198800
C	3.07071600	-0.33658700	-0.09860100	O	7.02147500	0.07684800	-1.28258800
C	3.49396100	0.75222100	-0.86770200	C	7.98242500	-0.90450300	-0.94893700
C	3.98096200	-1.32232800	0.26332400	H	7.72018500	-1.87732800	-1.38122200
C	4.82430000	0.86835300	-1.23680000	H	8.92403300	-0.55948700	-1.37419900
H	2.77053500	1.49490000	-1.19239900	H	8.08700600	-1.00255100	0.13816200
C	5.31697700	-1.22377100	-0.12399600	C	0.24284700	2.85653600	1.48598700
H	3.63904500	-2.18022600	0.83203200	H	0.34294700	3.41771900	0.54845100
C	5.74361800	-0.12042000	-0.86701900	H	0.39703400	3.58677800	2.28490000
H	6.00559900	-2.00965700	0.16084700	C	-1.23081500	2.32253900	1.59132800
C	-1.51183200	-1.99803600	0.17865400	H	-1.74978300	2.81856700	2.41456300
C	-2.60980700	-1.43231500	-0.47833200	C	-1.91370800	2.71908000	0.33078700
C	-1.54664800	-3.33480600	0.55626700	H	-1.63317500	2.21184500	-0.60505800
C	-3.74513400	-2.18905200	-0.71735700	O	-2.77254000	3.59704000	0.29685700
H	-2.56305400	-0.40262700	-0.82327100	B	-3.51790100	4.03304000	-1.13881300
C	-2.67697200	-4.10961800	0.29747600	F	-3.05008200	3.10369000	-2.03484700
H	-0.67932700	-3.77530100	1.03555400	F	-4.83112000	3.91412500	-0.82914200
C	-3.78451000	-3.53394400	-0.32984800	F	-3.05516600	5.29305000	-1.33448700

Figure S49. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-exo* (Supramolecular Complex)



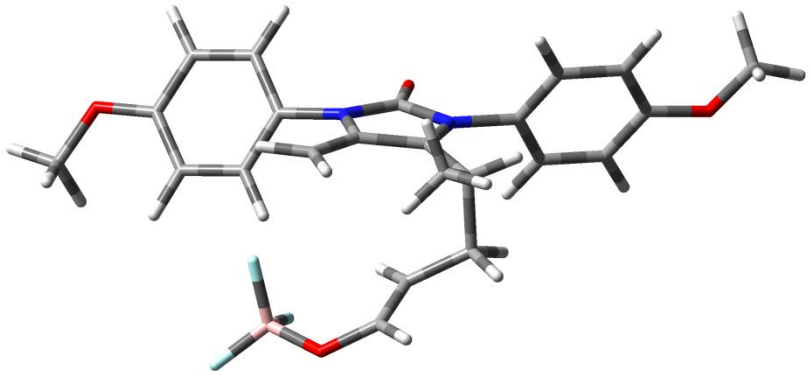
0 1				H	2.74799400	-0.02988800	-0.16575500
C	0.19839500	0.13019500	1.36774700	C	3.87972700	-3.22068900	0.00407100
C	1.15235000	0.65801800	2.14649200	H	2.69594600	-4.93564300	0.50011000
C	0.76171800	2.37226900	-1.02604100	H	4.80464000	-1.31366400	-0.46084100
C	-0.56258600	2.22968600	-1.20569600	O	4.96386100	-4.02702100	-0.13390900
C	-1.80669300	1.70356700	1.57375200	C	6.18728000	-3.42446600	-0.50644500
C	-1.21166600	0.55171000	1.21123000	H	6.91449200	-4.23310800	-0.56647500
H	0.93387600	1.47860300	2.81179800	H	6.10447000	-2.93306600	-1.48276100
H	2.15896700	0.25988200	2.14569300	H	6.51290000	-2.69423200	0.24351700
H	-2.85939900	1.81445000	1.32975900	C	-1.12879800	2.85093500	2.25975300
C	-0.87648500	-1.38638500	-0.00295500	H	-0.96675200	2.66532000	3.32840600
O	-1.09029800	-2.33214000	-0.72875600	H	-0.14263100	3.05621000	1.82186200
N	-1.82253000	-0.47788700	0.47094300	H	-1.73895000	3.75309500	2.17718700
N	0.34722700	-0.98124000	0.51444600	H	-1.24915500	3.05922100	-1.05171800
C	-3.18365500	-0.50948300	0.06686200	H	-0.99849000	1.28720600	-1.52261300
C	-4.19096700	-0.45455400	1.02364200	H	-6.29910600	-0.41689100	1.40964100
C	-3.51992300	-0.60324800	-1.28788500	O	-7.13520100	-0.57721200	-1.18658200
C	-5.53343900	-0.46437000	0.64512500	C	-8.19348300	-0.53490200	-0.25052400
H	-3.92466700	-0.40561600	2.07532400	H	-8.16999400	0.39411200	0.33129100
C	-4.85060500	-0.63127400	-1.67166800	H	-9.11228800	-0.57454200	-0.83381900
H	-2.73441400	-0.69074000	-2.03145400	H	-8.15428900	-1.39425800	0.42888300
C	-5.86487800	-0.55386500	-0.70921500	H	1.46965800	1.56576600	-1.17659500
H	-5.13337300	-0.71702800	-2.71515000	C	1.23602800	3.67352000	-0.61926700
C	1.54047800	-1.74073000	0.34240100	O	2.41203800	4.01004700	-0.41422000
C	1.52553800	-3.12555900	0.53896700	H	0.48305300	4.45983900	-0.47889600
C	2.72105200	-1.10570800	-0.02461000	B	3.66793000	2.98579200	-0.55377900
C	2.68588900	-3.85994700	0.36236400	F	3.42937400	2.03756700	0.41723400
H	0.59875300	-3.62032100	0.80728400	F	4.74773800	3.77114600	-0.33254100
C	3.89790400	-1.83775000	-0.18507300	F	3.56332700	2.47562100	-1.82513000

Figure S50. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-exo* (Transition State 1)



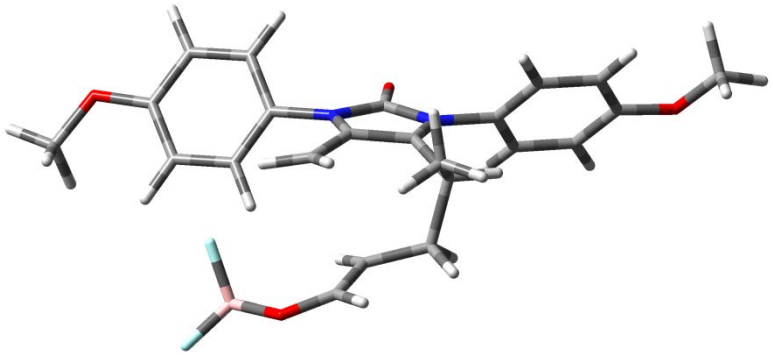
0 1				H	2.60649000	0.00046700	-0.45816100
C	0.26348700	0.16497200	1.33530500	C	4.10903500	-3.00289700	0.02664500
C	1.22901700	0.85476600	1.96213700	H	3.19708500	-4.72890200	0.91041800
C	0.30055000	2.58882300	-0.69923600	H	4.75025200	-1.11101200	-0.82568400
C	-1.08869400	2.53599400	-0.57352100	O	5.25459900	-3.71106000	-0.13467700
C	-1.72729900	1.78556800	1.30853300	C	6.35324300	-3.05733700	-0.74138600
C	-1.13172800	0.54726500	1.12040900	H	7.15687400	-3.79159100	-0.77537300
H	1.02191000	1.78924400	2.45778200	H	6.10715000	-2.73552200	-1.75960700
H	2.24885300	0.49095200	1.97931200	H	6.67240300	-2.19116100	-0.15081900
H	-2.78982600	1.81412600	1.08227600	C	-1.22456400	2.82955100	2.26905200
C	-0.75138100	-1.49145100	0.11056500	H	-1.05129200	2.41840700	3.26890500
O	-0.97856700	-2.49507700	-0.51801400	H	-0.28373700	3.27700800	1.92619300
N	-1.70513300	-0.48537900	0.42660600	H	-1.96098100	3.63092400	2.35836100
N	0.43086800	-1.06308500	0.66852300	H	-1.62440000	3.46577500	-0.38481600
C	-3.06926900	-0.58503300	0.02426000	H	-1.64783000	1.79202500	-1.13463000
C	-4.07854900	-0.56171400	0.97881300	H	-6.18828200	-0.62614900	1.35183600
C	-3.38530600	-0.72478600	-1.32987100	O	-6.99372100	-0.87960600	-1.24409600
C	-5.41571800	-0.64887700	0.59340400	C	-8.06284400	-0.86751100	-0.31748600
H	-3.82079400	-0.47848000	2.03069300	H	-8.08883800	0.07454400	0.24231000
C	-4.70989300	-0.82557900	-1.71947900	H	-8.97219300	-0.96395100	-0.90846900
H	-2.58853100	-0.77420000	-2.06516000	H	-7.98867900	-1.70936500	0.38023900
C	-5.73239600	-0.78185100	-0.76188000	H	0.86899600	1.73973700	-1.06056100
H	-4.98265400	-0.94257200	-2.76236600	C	0.96836100	3.77219900	-0.37944100
C	1.67964500	-1.72285200	0.45582200	O	2.21699800	4.01012500	-0.42638000
C	1.83878600	-3.05360500	0.84761000	H	0.36201100	4.63447700	-0.07677900
C	2.72329400	-1.03669800	-0.15483100	B	3.28869400	2.92799000	-0.69504400
C	3.04665700	-3.69351200	0.62545500	F	3.26330000	2.07503300	0.41077900
H	1.00986800	-3.58165200	1.30722200	F	4.46996300	3.60225300	-0.81772000
C	3.94782400	-1.67024200	-0.36101600	F	2.93057100	2.23159900	-1.84390800

Figure S51. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-exo* (Zwitterionic Intermediate)



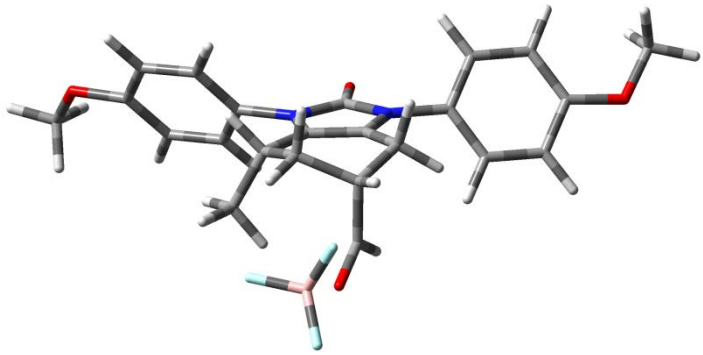
0 1				H	1.87649300	-3.02255600	-1.51473600
C	0.55860600	0.47651200	-1.16432800	C	4.74303600	-2.22855200	0.12752900
C	1.47534300	1.28085800	-1.72835500	H	5.04750800	-0.46095600	1.30542300
C	-0.32481400	3.85260500	-1.16448600	H	4.14685500	-3.90870700	-1.10778600
C	-1.20523800	3.02365400	-2.06239500	O	6.01014200	-2.61716700	0.40959100
C	-1.82874900	1.75652300	-1.44808500	C	6.46296100	-3.84560100	-0.12290100
C	-0.88549200	0.64581800	-1.03772100	H	7.48768400	-3.96406400	0.22618000
H	2.51812000	0.98348800	-1.73454100	H	5.85382300	-4.68163800	0.24005800
H	1.21468900	2.24764600	-2.12930000	H	6.44991000	-3.82998300	-1.21904900
H	-2.42485600	1.30135400	-2.25215800	C	-2.81168600	2.12274400	-0.29756900
C	-0.25094500	-1.37793400	-0.10731700	H	-3.75183900	1.57492900	-0.37633600
O	-0.42774700	-2.42509700	0.45165800	H	-2.38846300	1.93377100	0.69072300
N	-1.33719800	-0.45678700	-0.46418100	H	-3.01932900	3.19275300	-0.35870500
N	0.86538300	-0.76360600	-0.56368900	H	-4.76721700	-1.48868300	2.37354900
C	-2.69292000	-0.84693200	-0.21550000	O	-6.61083900	-1.94454200	0.41512400
C	-3.12155800	-1.00647800	1.09372500	C	-7.12443900	-2.11151200	1.72604600
C	-3.54926700	-1.09081100	-1.28948800	H	-7.06079600	-1.17672900	2.29369300
C	-4.44037800	-1.37342300	1.34800200	H	-8.16863500	-2.39294300	1.60249300
H	-2.43105400	-0.83635600	1.91359800	H	-6.59022800	-2.90647000	2.25757800
C	-4.86165900	-1.45344400	-1.04268300	C	0.08606300	3.44006300	0.04174800
H	-3.18651300	-1.00486700	-2.30944000	O	0.99791300	4.02884400	0.80428900
C	-5.31587800	-1.59052900	0.27796900	H	-0.30120700	2.51005400	0.46645400
H	-5.55578900	-1.64945300	-1.85209400	H	-0.65779600	2.74527600	-2.97628300
C	2.18975800	-1.25986400	-0.33168800	H	-2.06099100	3.61117100	-2.42023100
C	3.06301200	-0.52453400	0.47578200	H	0.09191100	4.76624700	-1.58007500
C	2.57649200	-2.46383100	-0.90141100	B	2.01628000	3.07939000	1.30221800
C	4.34158500	-1.00938400	0.69177800	F	2.79863200	3.68939400	2.24932500
H	2.73766600	0.41558900	0.91538500	F	2.79644700	2.63290600	0.19478900
C	3.85788700	-2.96254400	-0.66786900	F	1.37773100	1.91438800	1.82028700

Figure S52. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta-exo* (Transition State 2)



0 1				H	2.50756700	-0.08394400	-0.70084300
C	0.18274600	0.23506500	1.16822400	C	4.06421600	-2.97467500	0.14479500
C	1.15297000	1.11476300	1.54954000	H	3.18348400	-4.60607800	1.22094500
C	0.47260800	2.62258900	-0.44854900	H	4.67081900	-1.17853400	-0.91790000
C	-1.00504800	2.69745500	-0.30447200	O	5.22291900	-3.67310300	0.06897200
C	-1.68666500	1.97074000	0.96632900	C	6.31598600	-3.06571500	-0.59560400
C	-1.17354200	0.59094900	0.97348000	H	7.13548600	-3.78051200	-0.53732400
H	0.88585400	1.98881300	2.11903900	H	6.07634600	-2.86675500	-1.64612800
H	2.21036600	0.89795400	1.43765000	H	6.60662900	-2.13141500	-0.10271500
H	-2.75493200	1.93299700	0.74216500	C	-1.47361000	2.80524800	2.23824700
C	-0.83094200	-1.50469500	0.10049200	H	-1.51535800	2.19803700	3.14623500
O	-1.09483800	-2.55633000	-0.42634000	H	-0.51962000	3.33798100	2.21851100
N	-1.77528200	-0.44754500	0.35822600	H	-2.25880400	3.56267200	2.29901000
N	0.36092400	-1.02845800	0.58435300	H	-1.33129000	3.74048900	-0.21316800
C	-3.14683900	-0.55615000	-0.01738400	H	-1.49398300	2.27284000	-1.18712800
C	-4.13979700	-0.35084000	0.93227400	H	-6.24503400	-0.27982300	1.32665800
C	-3.48121600	-0.88792100	-1.33323900	O	-7.09019800	-0.88871400	-1.19631800
C	-5.48389100	-0.44382800	0.57427000	C	-8.14837800	-0.69328900	-0.27680700
H	-3.86566300	-0.12558500	1.95924600	H	-8.13149000	0.32326900	0.13253500
C	-4.81325600	-0.99253800	-1.69143500	H	-9.06682000	-0.84220000	-0.84207600
H	-2.69688100	-1.07313800	-2.05907100	H	-8.09877900	-1.42199000	0.54014200
C	-5.82180000	-0.76659400	-0.74354900	H	0.90579100	1.80198500	-1.00809600
H	-5.10412200	-1.25152100	-2.70328600	C	1.27505700	3.69954400	-0.15607400
C	1.61395900	-1.70065400	0.42787800	O	2.55014100	3.83058200	-0.32325400
C	1.79399000	-2.97535400	0.96900200	H	0.80754500	4.58990000	0.28108900
C	2.64168300	-1.07102000	-0.26429300	B	3.50066100	2.72775700	-0.74147400
C	3.01302200	-3.61360500	0.81876800	F	3.69340500	1.89713800	0.37898200
H	0.97546700	-3.46083500	1.49034000	F	4.66483500	3.33746800	-1.12772900
C	3.87860600	-1.70009400	-0.39559400	F	2.93190100	1.96682300	-1.77222800

Figure S53. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **12a**/**18a**-BF_3-*meta*-*exo* (Adduct)

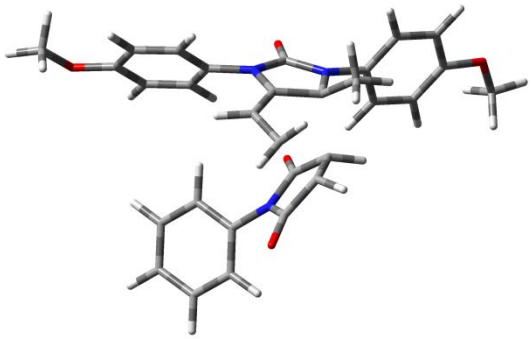


0 1				H	-2.86641700	-2.63532600	1.49806700
C	-0.75338600	0.36690500	0.58351800	C	-5.48618100	-1.51716500	-0.35765500
C	-1.43584000	1.64610900	0.93454900	H	-5.38100400	0.02682400	-1.83891000
C	-0.41842500	2.78757000	0.78621700	H	-5.27556700	-3.05370100	1.15454000
C	0.93790800	2.43734000	1.46071800	O	-6.81005500	-1.65763800	-0.62168800
C	1.63276900	1.18728600	0.88586900	C	-7.52239100	-2.65350100	0.08544700
C	0.58192900	0.15864800	0.60357000	H	-8.54783200	-2.60407500	-0.27794400
H	-2.31059200	1.82619100	0.29848900	H	-7.11085000	-3.64964400	-0.11399200
H	-1.81214100	1.62290200	1.96462800	H	-7.50713500	-2.45932000	1.16425500
H	2.30304000	0.81664100	1.67120000	C	2.50032700	1.47533100	-0.34844000
C	-0.41045900	-1.82859600	0.04691600	H	3.04351400	0.57601600	-0.65335700
O	-0.59016100	-2.99209700	-0.26564200	H	1.89414200	1.79602000	-1.20249600
N	0.80396800	-1.18368200	0.27376400	H	3.22149300	2.26768700	-0.13316600
N	-1.37399200	-0.84358500	0.25142800	H	3.92716600	-3.64635300	-1.98442100
C	2.05699500	-1.85167300	0.20065300	O	5.74703900	-3.73098300	0.05072400
C	2.43072500	-2.49406700	-0.97356200	C	6.16987400	-4.40263700	-1.11929100
C	2.91066200	-1.87450500	1.30726000	H	6.23722700	-3.71256300	-1.96841200
C	3.66035300	-3.14552000	-1.06203100	H	7.15848300	-4.80122100	-0.89599100
H	1.74887300	-2.49645500	-1.81738500	H	5.49100400	-5.22630700	-1.36881300
C	4.14406900	-2.50052600	1.22161400	C	-0.24913800	3.09995000	-0.66643400
H	2.59675500	-1.41317600	2.23850600	O	0.30163600	4.08968300	-1.14922000
C	4.52546400	-3.13932700	0.03533700	H	-0.66598900	2.38949300	-1.39683900
H	4.82456800	-2.52621300	2.06565900	H	0.70758600	2.27158900	2.51845800
C	-2.76254000	-1.06579000	0.04701100	H	1.60678400	3.29839900	1.39882600
C	-3.46284600	-0.32619200	-0.91128500	H	-0.78338900	3.70354600	1.26129300
C	-3.42399100	-2.04335800	0.78005400	B	1.09289700	5.33174100	-0.37441400
C	-4.81853500	-0.53744100	-1.10310900	F	0.99610200	6.33578300	-1.27301100
H	-2.93347000	0.40157600	-1.51997200	F	2.34477200	4.81483500	-0.19233400
C	-4.78354100	-2.27965900	0.57873000	F	0.39567400	5.52636200	0.79047500

Table S6. M06-2X/6-31+G(d,p) zero-point corrected electronic energies (Hartree) for supramolecular complexes (**SC**), transition states (**TS**) and adducts (**AD**) of the Diels-Alder reactions of **16a** and **6**.

	SC	**TS1**	**AD**
16a/6-*endo*	-1698.68922	-1698.66086	-1698.73466
16a/6-*exo*	-1698.68863	-1698.65478	-1698.73192

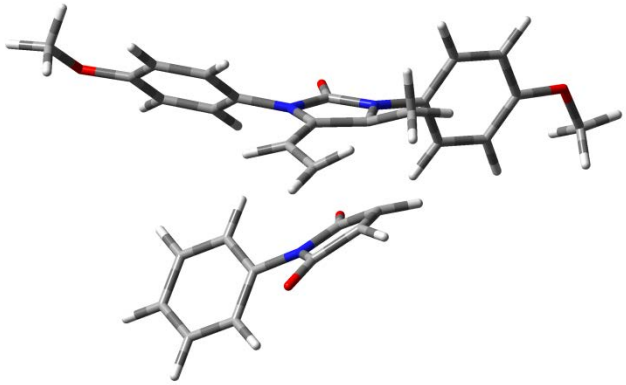
Figure S54. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **16a/6-*endo*** (Supramolecular Complex)



0 1

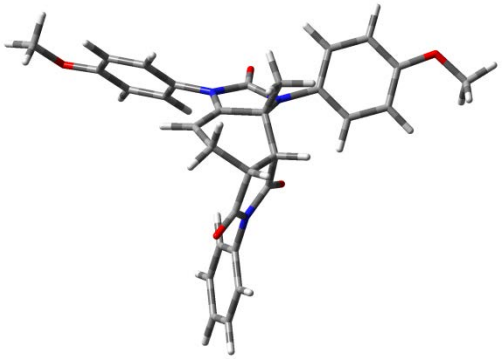
C	-0.39371100	2.40609400	2.18522400
C	0.66345200	1.25088700	3.26128400
C	1.04815400	0.08376800	2.45578800
C	0.11566700	-0.58528300	1.74394800
C	-1.32092800	-0.19407400	1.68332400
C	-1.14206500	1.62389600	1.16083700
H	2.10066300	-0.12360000	2.28914800
H	1.50290300	1.86784900	3.57762700
H	-0.00335000	1.06461600	4.09966700
H	-0.94663000	3.03301200	2.87969000
H	-2.17132900	1.91945700	0.95250500
C	-0.86605700	-1.76427900	0.02219400
O	-0.99386000	-2.48320800	-0.94012300
N	0.31289400	-1.54653400	0.75170000
N	-1.84952500	-1.01977600	0.65004500
C	1.57891300	-1.99323600	0.28771200
C	2.49222300	-2.54355400	1.17823200
C	1.91307100	-1.86833600	-1.06641500
C	3.75471400	-2.94904800	0.74124700
H	2.21823500	-2.65883500	2.22273900
C	3.15717600	-2.28517700	-1.50905300
H	1.18934200	-1.44979400	-1.75847300
C	4.08770600	-2.81999000	-0.60848900
H	4.45221400	-3.36824100	1.45588500
H	3.43568700	-2.20437500	-2.55447100
C	-3.17072800	-0.91711100	0.12093700
C	-4.22657200	-1.59966400	0.73232100
C	-3.40614400	-0.15192700	-1.01586100
C	-5.51129200	-1.49517300	0.22467300
H	-4.02744400	-2.22032300	1.60089900
C	-4.69508200	-0.04800900	-1.54051900
H	-2.56706600	0.34505500	-1.49327500
C	-5.75052300	-0.71643300	-0.91513000
H	-6.34600100	-2.01624300	0.68065700
H	-4.85608700	0.54520200	-2.43230500
C	-2.18683500	-0.15878700	2.92657700
H	-1.85513300	0.59051100	3.64208200
H	-3.21508400	0.07846700	2.64099100
H	-2.17821200	-1.14057200	3.41113100
N	0.79518000	2.51680900	0.18315300
C	-0.25733600	1.63139300	-0.06060100
O	-0.39018800	0.98175700	-1.07597800
C	0.69186900	3.12492700	1.44653100
O	1.40712500	4.01416100	1.84384500
C	1.87314100	2.74746500	-0.72032200
C	2.59524500	1.65705900	-1.20100400
C	2.20355100	4.04852800	-1.09178100
C	3.65313100	1.87271800	-2.07870800
H	2.32731800	0.65449900	-0.88430500
C	3.27118900	4.25426200	-1.96262000
H	1.63902300	4.88237100	-0.68979800
C	3.99272500	3.17035600	-2.46065600
H	4.21536000	1.02390900	-2.45537500
H	3.53784600	5.26550200	-2.25221300
H	4.82119800	3.33705000	-3.14167700
C	-7.32738100	0.06619400	-2.50733500
H	-8.39785300	-0.04262900	-2.67622500
H	-7.08488400	1.12645100	-2.37000700
H	-6.77849800	-0.32603100	-3.37116100
C	6.24816700	-3.74275700	-0.27298400
H	7.11691200	-3.96492600	-0.89126600
H	6.53120900	-3.03257100	0.51304500
H	5.87941300	-4.66810600	0.18504700
O	5.28345400	-3.18453200	-1.14112200
O	-7.03930800	-0.67811000	-1.34049100

Figure S55. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **16a/6-*endo*** (Transition State)



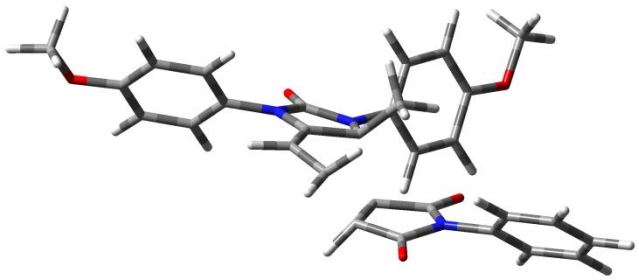
0 1				C	-5.82552400	-0.93715200	-0.70418800
C	-0.39183800	2.91083700	1.85382700	H	-6.17544400	-2.32362800	0.89218900
C	0.69770900	1.53871900	3.17815500	H	-5.17370400	0.44905600	-2.23641700
C	1.04385300	0.50270800	2.32155500	C	-2.23582400	0.31846600	2.78197300
C	0.08233900	-0.24242500	1.63803400	H	-1.98104300	1.25875100	3.26374800
C	-1.31969900	-0.02366300	1.63850300	H	-3.25985700	0.39995900	2.41063100
C	-1.16545900	2.18022400	0.95518100	H	-2.20712700	-0.48033900	3.53170300
H	2.07132900	0.42574100	1.97351300	N	0.88093800	2.57769300	-0.04954600
H	1.48517900	2.18459700	3.55401500	C	-0.35704800	1.94264400	-0.26090500
H	-0.17555300	1.46888900	3.81023300	O	-0.65783800	1.31045800	-1.25448000
H	-0.76576800	3.54390600	2.64838200	C	0.87292300	3.28626900	1.16659000
H	-2.24590700	2.13847000	0.90646600	O	1.74799200	4.03016600	1.54889100
C	-0.82132000	-1.48912000	-0.06844500	C	1.98051600	2.53859100	-0.95001200
O	-0.96067900	-2.24039400	-1.00793800	C	2.33136500	1.32164400	-1.53165300
N	0.35523900	-1.13637800	0.58779100	C	2.70396000	3.69726400	-1.23390200
N	-1.83206100	-0.81556600	0.62070800	C	3.41444300	1.25967000	-2.40193300
C	1.60095000	-1.76223500	0.30347400	H	1.74932700	0.43915700	-1.30035600
C	2.45527000	-2.13341000	1.33626100	C	3.79116000	3.62252000	-2.10185500
C	1.95755900	-2.04188200	-1.02271500	H	2.42724200	4.63451100	-0.76664000
C	3.68220000	-2.74028700	1.06254400	C	4.14890700	2.40963500	-2.68857900
H	2.16781900	-1.95649800	2.36762800	H	3.68542500	0.30706600	-2.84697800
C	3.16544000	-2.65919600	-1.29702200	H	4.35976900	4.52087400	-2.31996800
H	1.27465900	-1.78892800	-1.82590600	H	4.99677100	2.36097800	-3.36432200
C	4.04170200	-3.00197400	-0.25986000	C	-7.57267700	-0.31656900	-2.18655400
H	4.33105700	-3.00916000	1.88692900	H	-8.63102300	-0.54830600	-2.29733100
H	3.45593700	-2.88799400	-2.31684400	H	-7.44807000	0.76229300	-2.03783000
C	-3.19014700	-0.85654200	0.17791200	H	-7.03299700	-0.62731300	-3.08836400
C	-4.11801500	-1.66816500	0.83467400	C	6.11648100	-3.95816300	0.37875600
C	-3.57149400	-0.10142700	-0.92383500	H	6.97243700	-4.40055700	-0.12910700
C	-5.43323400	-1.70306700	0.40228200	H	6.44437000	-3.08418700	0.95395700
H	-3.79821800	-2.27320300	1.67801600	H	5.67205200	-4.69686100	1.05628200
C	-4.89283800	-0.13874000	-1.37125700	O	5.20791100	-3.58740900	-0.63754400
H	-2.82151400	0.49962100	-1.43045300	O	-7.13187600	-1.04134500	-1.05491600

Figure S56. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **16a/6-*endo*** (Adduct)



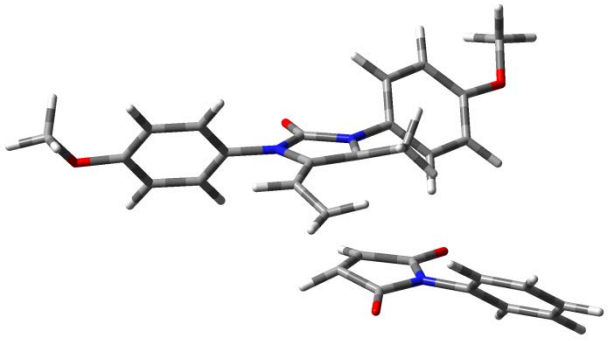
0 1				C	-5.32084000	-1.97165600	-0.62515500
C	-0.28175500	1.85248400	2.51404000	H	-4.79921800	-4.00132500	-0.17703500
C	0.86682100	1.02213600	3.15114600	H	-5.53485200	0.13820700	-1.06047700
C	1.47322300	0.06052000	2.16148300	C	-1.52342100	-1.06129900	2.58225400
C	0.64846600	-0.60102300	1.34087600	H	-1.22018900	-0.59706200	3.52191400
C	-0.85447800	-0.39066700	1.37492300	H	-2.61102800	-0.98502000	2.49013600
C	-1.10542800	1.14050300	1.41534200	H	-1.25214000	-2.12054200	2.61074300
H	2.54819300	-0.07168700	2.11429000	N	0.11232100	2.93821100	0.43869700
H	1.61850000	1.72535900	3.51858000	C	-0.71287000	1.85537100	0.12054800
H	0.48548900	0.49719400	4.03369000	O	-1.07364200	1.58632600	-0.99910600
H	-0.91844300	2.25291600	3.30754700	C	0.35998900	3.03828400	1.80652000
H	-2.17997500	1.31210500	1.55459900	O	1.00840700	3.90929900	2.33442100
C	-0.24443100	-1.77957000	-0.42711200	C	0.63380800	3.84466400	-0.53418600
O	-0.30754900	-2.52834300	-1.37655000	C	1.19854500	3.34101700	-1.70527000
N	0.91675100	-1.49251200	0.30969000	C	0.57578800	5.21734700	-0.29862700
N	-1.27410100	-1.05973800	0.14195400	C	1.70311800	4.22727600	-2.65243200
C	2.20550800	-1.95291900	-0.06678200	H	1.22968200	2.27054100	-1.87241000
C	3.05550100	-2.49493100	0.88986700	C	1.09228000	6.09280800	-1.25008700
C	2.62489200	-1.86526600	-1.39890000	H	0.14660300	5.58947000	0.62421800
C	4.33302700	-2.93452300	0.53906000	C	1.65329700	5.60201500	-2.42760900
H	2.71892800	-2.57988100	1.91871600	H	2.13900800	3.83900900	-3.56704600
C	3.88392800	-2.31624100	-1.75702300	H	1.05380500	7.16182000	-1.06805200
H	1.94917900	-1.46514100	-2.14661400	H	2.05165200	6.28865500	-3.16755200
C	4.74793700	-2.84656600	-0.79089900	C	-7.53738800	-1.38179900	-1.23225300
H	4.97840000	-3.34826600	1.30416100	H	-8.48893300	-1.89881800	-1.34957600
H	4.22666000	-2.26614900	-2.78478000	H	-7.63896000	-0.59788100	-0.47221600
C	-2.63457000	-1.36878800	-0.14798000	H	-7.24685500	-0.92883700	-2.18737000
C	-3.09672800	-2.68517400	-0.01985700	C	6.86342500	-3.80539900	-0.30574600
C	-3.51859500	-0.36825400	-0.53281300	H	7.76195200	-4.06217900	-0.86534300
C	-4.42525400	-2.98674900	-0.26198300	H	7.11619700	-3.08177800	0.47846800
H	-2.39828700	-3.47016100	0.25370700	H	6.44732200	-4.71056600	0.15232600
C	-4.86667700	-0.65956100	-0.75987200	O	5.96507300	-3.24921100	-1.24282600
H	-3.14241200	0.63618800	-0.69199900	O	-6.60576100	-2.36458700	-0.83016800

Figure S57. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **16a/6-*exo*** (Supramolecular Complex)



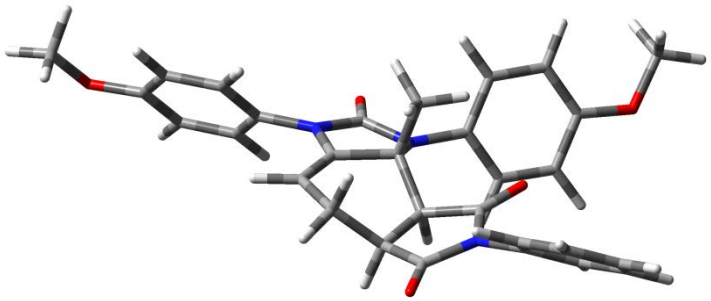
0 1				H	2.63851700	3.99813000	-1.98384400
C	0.65765700	-2.53722300	-0.97938300	C	0.71471400	-0.11364300	1.54690800
C	-0.42388200	-3.05821200	0.49331700	H	1.04746600	-1.11714700	1.81578500
C	-1.59742000	-2.17830000	0.45936900	H	1.59497100	0.51646200	1.39621700
C	-1.44609800	-0.84595800	0.34110100	H	0.12943800	0.29467500	2.37741500
C	-0.13852400	-0.12110900	0.29088600	N	2.89629700	-2.05014500	-0.48213700
C	0.83377300	-1.05647500	-1.04692300	C	2.30049000	-0.81741700	-0.78982000
H	-2.58693100	-2.61267800	0.35559500	O	2.88568600	0.24062300	-0.81032600
H	-0.63429400	-4.11106200	0.31877600	C	2.00246100	-3.12028400	-0.67098800
H	0.25630900	-2.94627600	1.33672400	O	2.28845600	-4.28871200	-0.55827900
C	-1.89614400	1.33744600	-0.23418600	C	4.25732200	-2.21157000	-0.08992600
O	-2.51032000	2.33845600	-0.52664500	C	5.26222100	-1.48650300	-0.73087400
N	-2.44580600	0.09386500	0.08333000	C	4.56797300	-3.10282100	0.93810600
N	-0.51924900	1.19434400	-0.14422200	C	6.58507400	-1.65412000	-0.32929900
C	-3.83662900	-0.18071600	-0.00124500	H	5.00620000	-0.79132200	-1.52080600
C	-4.48292400	-0.81516600	1.05305100	C	5.89499200	-3.26813800	1.32311400
C	-4.56192800	0.19172100	-1.13783500	H	3.77765800	-3.67063900	1.41560400
C	-5.84588900	-1.10592900	0.97960400	C	6.90607200	-2.54354100	0.69409500
H	-3.91949400	-1.08545200	1.94115300	H	7.36679000	-1.08650400	-0.82357400
C	-5.91833000	-0.07666100	-1.21017200	H	6.13683700	-3.96551400	2.11855200
H	-4.05964600	0.71105800	-1.94641500	H	7.93938800	-2.67264300	0.99949300
C	-6.56694300	-0.73272400	-0.15647500	C	2.70794900	6.63502200	0.93342900
H	-6.32560600	-1.60609400	1.81188900	H	3.42253100	7.41685600	0.67933900
H	-6.50257000	0.21122000	-2.07732600	H	1.71180500	7.07613600	1.05614600
C	0.31939100	2.35179000	-0.11781200	H	3.01241800	6.15229100	1.86960800
C	0.26512000	3.22219700	0.96451200	C	-8.59582100	-1.60135000	0.71573500
C	1.16682800	2.63445600	-1.18972900	H	-9.62944300	-1.67988900	0.38145700
C	1.05797200	4.36865900	0.99823100	H	-8.19572500	-2.60485200	0.90359600
H	-0.41669900	3.01148500	1.78355000	H	-8.55413300	-1.01185800	1.63920800
C	1.96550700	3.76506200	-1.16628700	O	-7.89491300	-0.96034600	-0.33005800
H	1.20655900	1.95602100	-2.03430700	O	2.73140700	5.72024200	-0.14286500
C	1.91482200	4.63707700	-0.07247100	H	0.48171400	-0.55653800	-1.94811800
H	0.99306000	5.03498800	1.84939400	H	0.16281100	-3.02282600	-1.81673000

Figure S58. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **16a/6-*exo*** (Transition State)



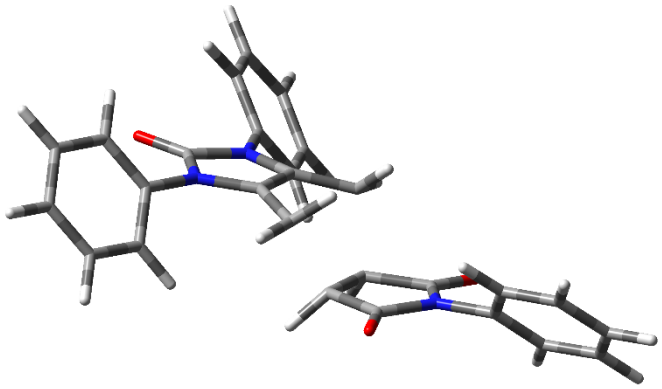
0 1				H	3.17074400	3.90075400	-1.04166400
C	0.46889100	-2.66074400	-0.78531300	C	1.14726200	0.30203800	1.60872600
C	-0.15272800	-2.72089900	1.08862600	H	2.05509700	0.30159400	0.99894700
C	-1.28317800	-1.89639700	1.05866800	H	1.17742500	1.20525700	2.22799500
C	-1.21721300	-0.53044000	0.80405000	H	1.15256900	-0.56543300	2.26717200
C	-0.10828300	0.33995000	0.79666200	N	2.75808900	-2.31188200	-0.55838800
C	0.74661900	-1.34642800	-1.18583900	C	2.17281500	-1.10705500	-1.03808300
H	-2.25620400	-2.36666800	0.94472500	O	2.81514300	-0.08996400	-1.24074000
H	-0.30427800	-3.78288000	1.26282200	C	1.79697400	-3.32481000	-0.51619300
H	0.78152100	-2.34771900	1.49543200	O	1.99712400	-4.48979100	-0.26407800
C	-1.90911100	1.48095400	-0.06297000	C	4.12673700	-2.48042400	-0.21622600
O	-2.57477000	2.36551300	-0.55897200	C	5.12363600	-1.88634300	-0.99236800
N	-2.30318500	0.20682300	0.28480600	C	4.46367400	-3.24701100	0.90156600
N	-0.54580000	1.54094200	0.28502000	C	6.45910500	-2.05563200	-0.63545900
C	-3.62149900	-0.27643700	0.05596400	H	4.84972900	-1.28887700	-1.85302300
C	-4.37538300	-0.77007600	1.11322900	C	5.80267100	-3.42011100	1.23870200
C	-4.16417500	-0.23962300	-1.23177100	H	3.68081300	-3.71650700	1.48688800
C	-5.66517600	-1.25755800	0.89688100	C	6.80441300	-2.82247200	0.47552400
H	-3.95488900	-0.77317600	2.11476900	H	7.23267700	-1.58810900	-1.23622100
C	-5.44958900	-0.70348100	-1.45218200	H	6.06124600	-4.02269600	2.10352100
H	-3.57810500	0.17167400	-2.04689100	H	7.84742100	-2.95557500	0.74403400
C	-6.20443700	-1.22140600	-0.39113100	C	1.98402800	7.42835200	0.24386900
H	-6.23287400	-1.64396500	1.73424200	H	2.75735300	8.16069100	0.01596400
H	-5.89628400	-0.67819700	-2.44001100	H	1.05525300	7.70572200	-0.26824300
C	0.21384000	2.74250200	0.15994900	H	1.81210400	7.40373700	1.32643100
C	-0.30563900	3.93352600	0.65481300	C	-8.25536700	-2.17636200	0.32665900
C	1.46319200	2.72068900	-0.46585000	H	-9.19706100	-2.46256300	-0.13945900
C	0.42280600	5.11627500	0.53959700	H	-7.79278600	-3.05745200	0.78673500
H	-1.28858100	3.94365900	1.11290000	H	-8.44326700	-1.41706200	1.09464400
C	2.19664600	3.89229400	-0.56509200	O	-7.44722500	-1.66052000	-0.71213100
H	1.85773600	1.79442600	-0.87516300	O	2.47244000	6.18739800	-0.22337500
C	1.68164400	5.09489000	-0.06705000	H	0.11882800	-0.67666600	-1.75568400
H	-0.00173300	6.03553100	0.92349700	H	-0.30892700	-3.27833400	-1.21782200

Figure S59. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **16a/6-*exo*** (Adduct)



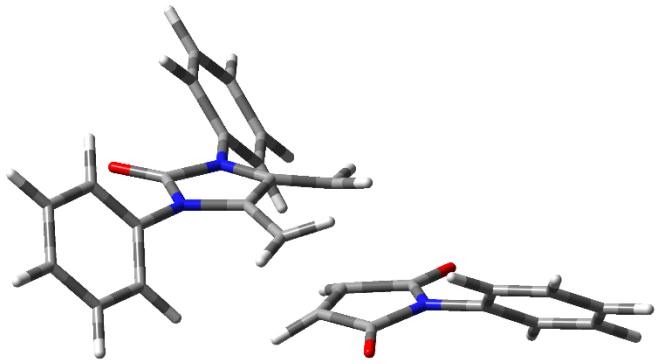
0 1				H	2.59626400	3.92638600	-2.17487300
C	0.65078400	-2.35666300	-0.98266300	C	0.23608800	-0.17171600	1.64239700
C	-0.38819500	-3.02674100	-0.06020200	H	0.50740300	-1.18202600	1.96397400
C	-1.65202000	-2.20817000	-0.03221700	H	1.09593800	0.48520100	1.78915300
C	-1.53485700	-0.87891100	0.03257500	H	-0.59570400	0.17475700	2.26290700
C	-0.19692700	-0.16973700	0.16659700	N	2.90063600	-1.96264000	-0.34448400
C	0.84559100	-0.84252700	-0.76610900	C	2.28956400	-0.70254900	-0.28931700
H	-2.62175500	-2.68959200	-0.09085700	O	2.83945100	0.31090600	0.06495000
H	-0.57892600	-4.03551600	-0.43193500	C	2.02076400	-2.96874000	-0.76245600
H	0.03544500	-3.14989900	0.94642700	O	2.30886200	-4.13390700	-0.89099300
C	-1.93572600	1.37351300	-0.21334800	C	4.27097500	-2.19189400	-0.01318300
O	-2.53859400	2.41586500	-0.33931500	C	5.24817100	-1.30943600	-0.47307000
N	-2.51171800	0.11299800	0.00378100	C	4.61530000	-3.29664900	0.76510100
N	-0.56695500	1.18546300	-0.27081600	C	6.58140000	-1.53815200	-0.14486000
C	-3.91222700	-0.11846900	-0.01904000	H	4.96332600	-0.44802700	-1.06549100
C	-4.49084400	-0.92921300	0.95067600	C	5.95326000	-3.51861500	1.07923100
C	-4.71529800	0.46233900	-1.00662100	H	3.84540700	-3.97980000	1.10375300
C	-5.86234000	-1.18679700	0.93837000	C	6.93786900	-2.64150500	0.62838300
H	-3.86640200	-1.36368200	1.72573700	H	7.34256100	-0.84998000	-0.49757400
C	-6.07984500	0.22587700	-1.01394700	H	6.22382400	-4.38097600	1.67966800
H	-4.26612600	1.11467600	-1.74671800	H	7.97912800	-2.81730500	0.87839600
C	-6.66089900	-0.60399800	-0.04749200	C	3.16351200	6.27173400	0.93031400
H	-6.28724000	-1.82589400	1.70263700	H	3.92267800	7.01008700	0.67530600
H	-6.72249600	0.67308800	-1.76446500	H	2.22669300	6.78287700	1.18145600
C	0.32419300	2.29908800	-0.22680500	H	3.50127300	5.68226100	1.79077400
C	0.43661800	3.07981400	0.91740500	C	-8.63627400	-1.59465100	0.81686300
C	1.09464700	2.61222500	-1.34894700	H	-9.69498700	-1.60012700	0.56089700
C	1.32501100	4.15368500	0.96424800	H	-8.24826400	-2.61987500	0.78658500
H	-0.18645500	2.85610600	1.77843600	H	-8.50639200	-1.18437800	1.82536300
C	1.98631200	3.67063000	-1.31546000	O	-8.00479500	-0.78121900	-0.14968500
H	0.98279800	2.02129800	-2.25291300	O	3.00956100	5.45886200	-0.21496400
C	2.10953500	4.44307700	-0.15467100	H	0.79018500	-0.32207600	-1.72747100
H	1.39097700	4.74876600	1.86664700	H	0.35637900	-2.56224000	-2.01564200

Figure S60. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **5a**/**6**-*exo* (Supramolecular complex)



0 1			
C	-1.20226600	0.76766200	0.95289100
C	-0.16465100	1.44507400	-0.48741100
C	1.07098500	0.67752900	-0.46092300
C	1.07090300	-0.68232800	-0.43557600
C	-0.16511500	-1.44930200	-0.43290800
C	-1.20043300	-0.72046200	0.98374600
H	-0.80551000	1.21037800	-1.33824200
H	-0.08845800	2.51911000	-0.34081400
H	-0.80033800	1.29239500	1.81682300
H	-0.80629200	-1.24243700	-1.29096000
H	-0.09009200	-2.51767900	-0.24891100
H	-0.79478400	-1.20964200	1.86645500
N	2.37678600	1.10862700	-0.20083900
N	2.37651300	-1.10404500	-0.15933900
C	3.21841300	0.00438400	-0.06333400
O	4.42555600	0.00715600	0.09366100
C	2.84345800	2.44905500	-0.13245600
C	3.92875600	2.84515700	-0.91379800
C	2.22379400	3.35396700	0.72984800
C	4.37911000	4.15992400	-0.84053800
H	4.41684800	2.11883300	-1.55381900
C	2.66840500	4.67296800	0.78171200
H	1.41184600	3.01905300	1.36857100
C	3.74627900	5.07797000	-0.00277500
H	5.22669700	4.46852200	-1.44372400
H	2.18108100	5.37757500	1.44766500
H	4.09788900	6.10339500	0.04477200
C	2.84255100	-2.44107600	-0.04043700
C	3.93062200	-2.86548700	-0.80293500
C	2.21977900	-3.31393600	0.85221100
C	4.38044200	-4.17674700	-0.68018700
H	4.42141100	-2.16274100	-1.46680300
C	2.66393500	-4.63023400	0.95363800
H	1.40595200	-2.95598800	1.47586800
C	3.74444700	-5.06368500	0.18819700
H	5.23019300	-4.50712500	-1.26861900
H	2.17421200	-5.30999400	1.64325000
H	4.09573000	-6.08669500	0.27447700
C	-2.60615700	-1.14775100	0.66727000
O	-3.03075300	-2.27737900	0.62358800
C	-2.60867400	1.17795800	0.61564300
O	-3.03249700	2.30531100	0.52167800
N	-3.35161800	0.00918300	0.37686800
C	-4.71400900	-0.00820500	-0.04536800
C	-5.62484100	0.89375500	0.50510000
C	-5.12051500	-0.93400400	-1.00710500
C	-6.95039800	0.86834400	0.07937100
H	-5.29332000	1.61343000	1.24362600
C	-6.45043900	-0.95512800	-1.41632200
H	-4.40461300	-1.63824400	-1.41481000
C	-7.36759200	-0.05409100	-0.87802600
H	-7.65858800	1.57312200	0.50275600
H	-6.76796800	-1.67855500	-2.16016600
H	-8.40286200	-0.07162700	-1.20278600

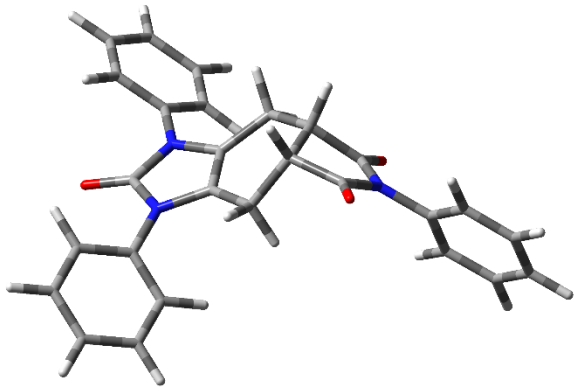
Figure S61. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **5a**/**6**-*exo* (Transition State)



0 1

C	1.16981200	0.72726700	-1.26016900
C	0.16808800	1.45689000	0.63812900
C	-0.98389900	0.70926500	0.59832500
C	-0.98156900	-0.71479800	0.57175100
C	0.17333700	-1.45898000	0.58234700
C	1.16804000	-0.65895700	-1.28948900
H	1.01081300	1.05615600	1.18859600
H	0.15071800	2.53482500	0.52372500
H	0.55915200	1.38128300	-1.86700400
H	1.01404100	-1.07290100	1.14682800
H	0.16015500	-2.53216200	0.42914200
H	0.55602000	-1.28526500	-1.92360300
N	-2.27327900	1.11322800	0.24652300
N	-2.26938600	-1.11004600	0.20543200
C	-3.09974300	0.00340000	0.05723300
O	-4.28704400	0.00553400	-0.17917700
C	-2.75145200	2.45137900	0.16711500
C	-3.86035300	2.83307900	0.92140700
C	-2.11572400	3.36487600	-0.67294100
C	-4.32378800	4.14271200	0.83929900
H	-4.35604100	2.10157400	1.54981700
C	-2.57468500	4.67855500	-0.73454500
H	-1.27722200	3.04434900	-1.28337800
C	-3.67885800	5.06889200	0.02013500
H	-5.18980800	4.44069900	1.42111700
H	-2.07539800	5.39092500	-1.38296400
H	-4.04018300	6.09055800	-0.03454400
C	-2.74289800	-2.44587900	0.07585100
C	-3.85157600	-2.85869600	0.81396000
C	-2.10330600	-3.32559100	-0.79677200
C	-4.31098100	-4.16571800	0.68250800
H	-4.35042900	-2.15235300	1.46816000
C	-2.55834400	-4.63740700	-0.90791800
H	-1.26527600	-2.98004900	-1.39409900
C	-3.66225500	-5.05885600	-0.16975300
H	-5.17690800	-4.48768400	1.25154700
H	-2.05628600	-5.32357300	-1.58196800
H	-4.02059000	-6.07876300	-0.26319000
C	2.51569000	-1.13230800	-0.86624100
O	2.92872200	-2.26705000	-0.82049200
C	2.51793600	1.17958100	-0.81465400
O	2.92670500	2.31330600	-0.71491100
N	3.24459000	0.01636500	-0.48990900
C	4.56506800	-0.00655800	0.03915800
C	5.51496000	0.91490000	-0.40454200
C	4.89888300	-0.96001300	1.00311300
C	6.80010800	0.88190400	0.13116600
H	5.24285200	1.65446200	-1.14738600
C	6.19071800	-0.99086000	1.51942000
H	4.15622000	-1.67970400	1.32846300
C	7.14394600	-0.06907800	1.08960500
H	7.53609500	1.60300000	-0.20956900
H	6.44979700	-1.73753100	2.26311000
H	8.14883500	-0.09299600	1.49851700

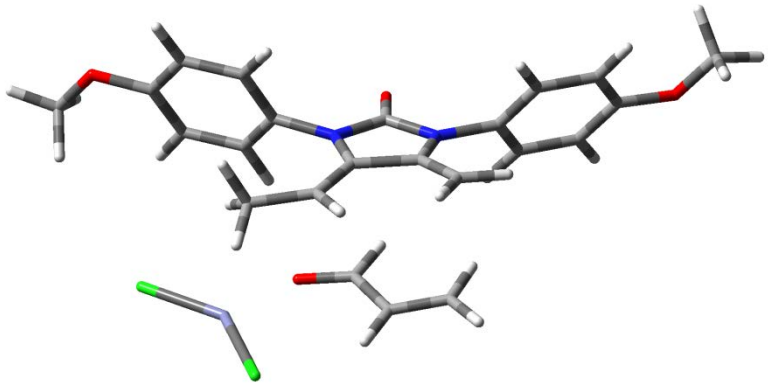
Figure S62. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **5a**/**6**-*exo* (Adduct)



0 1

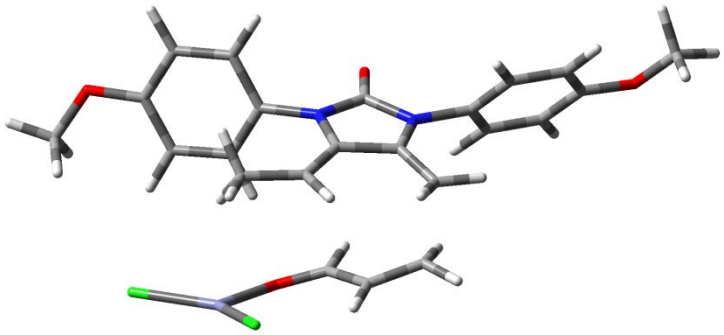
C	-1.20846600	0.19375500	1.61169200
C	-0.47525700	1.17409400	0.66134300
C	0.84651400	0.60308700	0.27607600
C	1.16637600	-0.70428900	0.29180200
C	0.28846500	-1.82055800	0.74420700
C	-1.06777100	-1.28935400	1.22864400
H	-1.09535400	1.36024500	-0.22636100
H	-0.35932600	2.13975200	1.16217400
H	-0.91604800	0.39350200	2.64392100
H	0.09192900	-2.54896300	-0.04980500
H	0.79337400	-2.36755900	1.54857700
H	-1.37373000	-1.88318400	2.09976200
N	2.00784700	1.32931600	-0.02569300
N	2.53442200	-0.81368200	0.00882200
C	3.08245900	0.45339700	-0.17908900
O	4.24084300	0.73188300	-0.43441000
C	2.10423100	2.72804500	-0.23475700
C	1.11417000	3.38982600	-0.96394800
C	3.19037000	3.43620400	0.28345400
C	1.19458500	4.76798200	-1.14648200
H	0.29721700	2.82492600	-1.40137500
C	3.27030900	4.81023700	0.07753000
H	3.96528600	2.90381300	0.82205200
C	2.27227300	5.48230600	-0.62741000
H	0.41993800	5.27876800	-1.70924200
H	4.11772200	5.35881500	0.47588400
H	2.33816900	6.55483000	-0.77770600
C	3.28267100	-2.01253900	-0.12044800
C	2.78017500	-3.06646500	-0.88515700
C	4.52240500	-2.12499100	0.51078700
C	3.50586300	-4.25094800	-0.98727600
H	1.83947500	-2.94936500	-1.41341200
C	5.24832700	-3.30572700	0.38567400
H	4.91076100	-1.28410200	1.07389100
C	4.74028800	-4.37416100	-0.35279100
H	3.11096100	-5.07056100	-1.57887300
H	6.21490800	-3.39111900	0.87160500
H	5.30833700	-5.29444800	-0.44120900
C	-2.20891600	-1.48785900	0.23687000
O	-2.30379800	-2.34856200	-0.60236300
C	-2.69742900	0.44447900	1.42968700
O	-3.34644800	1.34260600	1.90437400
N	-3.17551800	-0.51182900	0.51835000
C	-4.47784600	-0.47796300	-0.06754900
C	-4.62433800	-0.69930300	-1.43696400
C	-5.58663600	-0.22212600	0.73917500
C	-5.89836800	-0.66954000	-1.99798900
H	-3.75344900	-0.90616000	-2.04734400
C	-6.85323100	-0.18426700	0.16266200
H	-5.45320800	-0.04156600	1.79910800
C	-7.01333300	-0.41003500	-1.20327400
H	-6.01608900	-0.84749700	-3.06188300
H	-7.71686800	0.01997200	0.78700300
H	-8.00339100	-0.38386300	-1.64674000

Figure S63. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **13a**/**18a**-$ZnCl_2$-*ortho-endo* (Supramolecular Complex)



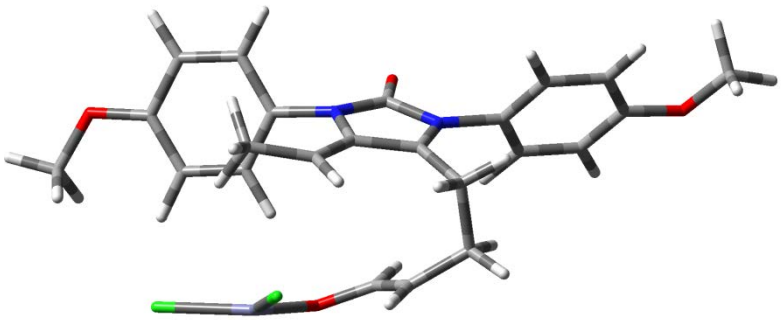
0 1				H	3.27217600	0.01775200	-2.00948700
C	1.77913300	-0.45320500	1.45927900	C	6.05651600	0.56684600	0.63343300
C	2.40928500	-1.38332600	2.18925300	H	4.44272300	0.74927400	2.04732600
C	1.60218600	-3.06709500	-0.38960100	C	6.39445300	0.36333600	-0.70689400
C	0.27677000	-2.88351800	-0.48373600	H	5.67350600	0.02399700	-2.69519600
C	-0.64031300	-0.77263800	2.09239800	H	6.81754000	0.73641900	1.38507200
C	0.33500300	-0.10207100	1.45647800	O	7.66492200	0.34618900	-1.18152700
H	2.30365100	-2.33409100	-0.78570100	C	8.71675700	0.57608800	-0.26494200
H	3.46723900	-1.57792100	2.06513300	H	9.63651400	0.53073900	-0.84618800
H	1.86410900	-1.95496600	2.92882200	H	8.62582900	1.56459600	0.19978300
H	-0.30663100	-1.59109700	2.72396400	H	8.73821300	-0.19549600	0.51356000
H	2.02529000	-3.94475500	0.08725900	C	-2.12223800	-0.53396300	2.03832400
C	1.41711400	1.24499900	-0.07552100	H	-2.45025100	0.17809600	2.80583900
O	1.62826100	2.07426500	-0.92905500	H	-2.44595300	-0.09892000	1.08486300
N	0.21070600	0.97175800	0.55461500	H	-2.65202900	-1.47318300	2.22204000
N	2.34672800	0.34334100	0.45519300	H	-0.45807000	-3.57794300	-0.08631300
C	-0.93722200	1.80788000	0.41258800	C	-0.19432600	-1.66642000	-1.11717800
C	-1.65384900	1.82296100	-0.77533600	O	-1.37082800	-1.32125800	-1.24634600
C	-1.36494400	2.57199200	1.50155000	H	0.57961500	-0.99351900	-1.52791600
C	-2.82471000	2.57126000	-0.87940600	Zn	-3.19073500	-1.94528400	-0.49978700
H	-1.31948900	1.22152500	-1.61361700	Cl	-3.00301600	-3.87122900	0.52522300
C	-2.53286000	3.31061000	1.41070100	Cl	-4.68138300	-0.50922500	-1.16450200
H	-0.78886800	2.55916200	2.42262800	H	-3.38829600	2.53834200	-1.80282500
C	-3.27740100	3.29984600	0.22262700	O	-4.42425800	4.02182900	0.23817700
H	-2.89966000	3.89637500	2.24654100	C	-5.27213400	3.92910100	-0.89290400
C	3.71504200	0.34997900	0.06993200	H	-5.55548700	2.88795900	-1.08418500
C	4.05713800	0.15111400	-1.27116300	H	-6.15811900	4.51428800	-0.65054800
C	4.71358300	0.57005800	1.01131700	H	-4.78949600	4.35051600	-1.78223500
C	5.38634800	0.16370000	-1.65885200				

Figure S64. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **13a**/**18a**-$ZnCl_2$-*ortho-endo* (Transition State 1)



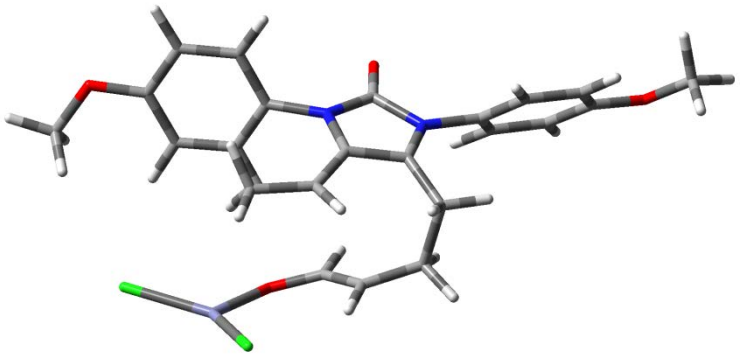
0 1				H	3.48413800	0.63753400	-2.03687100
C	1.74534700	-0.59295100	1.04832000	C	6.15842800	0.04832300	0.71493200
C	2.15134300	-1.89228400	1.26748200	H	4.49620700	0.03570500	2.08504500
C	1.42031000	-2.81984300	-0.49561100	C	6.54598100	0.18916300	-0.62078700
C	0.03124900	-2.78951000	-0.57639000	H	5.90808200	0.51917700	-2.63903600
C	-0.65031000	-0.77113100	1.68478800	H	6.88921900	-0.10381300	1.49941000
C	0.39690700	-0.06620700	1.19801100	O	7.82868700	0.13903000	-1.05207100
H	1.99931100	-2.17877300	-1.15807200	C	8.84743600	-0.04493300	-0.08772100
H	3.20344300	-2.13427500	1.16613500	H	9.78585200	-0.04538500	-0.63987700
H	1.58008700	-2.50188000	1.95541500	H	8.85184500	0.77353100	0.64109600
H	-0.41791300	-1.77443200	2.02823100	H	8.72927600	-1.00209900	0.43321900
H	1.91465900	-3.74201100	-0.20638100	C	-2.06795500	-0.32088000	1.84668100
C	1.67030800	1.51847600	0.13233700	H	-2.13309700	0.65393500	2.34038700
O	2.03583700	2.51731300	-0.43510300	H	-2.55975900	-0.17089600	0.87376300
N	0.42157700	1.22595100	0.64737300	H	-2.63502100	-1.05744600	2.41631200
N	2.46795200	0.37820700	0.40173000	H	-0.59146300	-3.54183500	-0.10165500
C	-0.72366000	2.05501400	0.42343400	C	-0.57377800	-1.71607100	-1.25342100
C	-1.63027500	1.71809200	-0.57357600	O	-1.80201600	-1.49408800	-1.43473800
C	-0.96200500	3.15454700	1.24906500	H	0.11600800	-0.98110200	-1.70875700
C	-2.81473100	2.43598900	-0.72182100	Zn	-3.43341300	-2.06254800	-0.44087900
H	-1.45148300	0.85697900	-1.21082600	Cl	-3.08639100	-3.71399900	0.97350300
C	-2.12771700	3.88819700	1.09704200	Cl	-5.04753200	-0.66910800	-0.94607300
H	-0.23827700	3.41659100	2.01448800	H	-3.52917900	2.11794800	-1.47075100
C	-3.07039900	3.51758000	0.12612600	O	-4.20069800	4.25939600	0.08574700
H	-2.34594100	4.74068000	1.73083300	C	-5.22204000	3.85214400	-0.81094700
C	3.84980400	0.31479400	0.05856500	H	-5.53329500	2.82129300	-0.60901300
C	4.23733300	0.45980300	-1.27605000	H	-6.05583900	4.53121300	-0.63969800
C	4.80612800	0.12339000	1.04775900	H	-4.88758000	3.93854900	-1.85078800
C	5.57873100	0.40125700	-1.61270600				

Figure S65. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **13a**/**18a**-$ZnCl_2$-*ortho-endo* (Zwitterionic Intermediate)



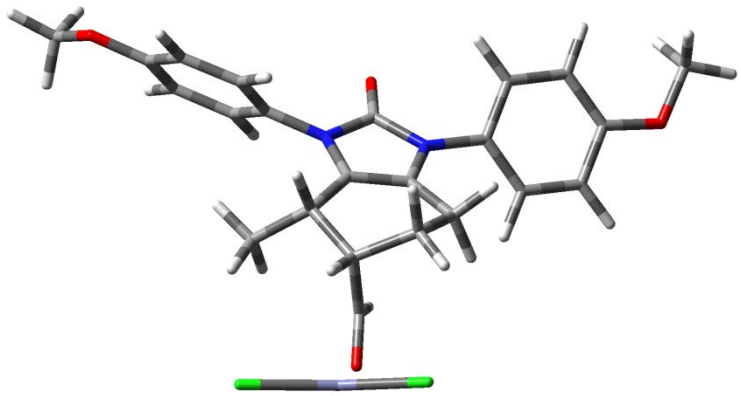
0 1				H	3.24590100	1.73825300	-1.43409000
C	2.03249300	-1.15505100	0.99506900	C	6.20552500	0.03181200	0.40923200
C	2.50365300	-2.51867100	0.60563700	H	4.69156500	-0.88958000	1.63043500
C	1.39713700	-3.19385300	-0.26229400	C	6.45360600	0.91576300	-0.64176600
C	-0.04877900	-2.95806800	0.24013400	H	5.60002000	2.21874800	-2.11056400
C	-0.07029100	-2.21400200	1.63919800	H	7.01514700	-0.44657100	0.94652100
C	0.77201000	-0.98511600	1.44776500	O	7.69286800	1.24513700	-1.09131400
H	1.49419600	-2.80454200	-1.28231600	C	8.80463600	0.67169300	-0.43549200
H	3.43664200	-2.46946500	0.03942200	H	9.68704500	1.06682300	-0.93695400
H	2.70025000	-3.12964200	1.49387000	H	8.82855800	0.95507000	0.62344600
H	0.51066900	-2.87596000	2.29289000	H	8.79490700	-0.42151700	-0.52171100
H	1.58972000	-4.26845400	-0.32359700	C	-1.45930000	-2.09214000	2.25967200
C	1.49064500	1.03170900	0.64017500	H	-1.37995000	-1.66935300	3.26435700
O	1.53706700	2.20806300	0.33190500	H	-2.14857000	-1.46929200	1.68759300
N	0.41434600	0.35353300	1.22215400	H	-1.90527700	-3.08701600	2.34315000
N	2.49295900	0.07004600	0.50600600	H	-0.60569100	-3.89396100	0.35385000
C	-0.88898600	0.92725000	1.24422800	C	-0.84377600	-2.06110700	-0.65549100
C	-1.46531400	1.32530800	0.04097800	O	-2.06725300	-2.08758600	-0.66160800
C	-1.58905700	1.10611300	2.43786800	H	-0.31130100	-1.29764700	-1.25606400
C	-2.75693100	1.86282000	0.01186700	Zn	-3.31918100	-0.51792600	-1.30101100
H	-0.89809900	1.25300600	-0.88346500	Cl	-2.33743000	0.15729300	-3.14834700
C	-2.87771800	1.61578600	2.42092800	Cl	-5.19756700	-0.80921800	-0.23403600
H	-1.11946100	0.83124200	3.37744200	H	-3.15766900	2.22035100	-0.93162400
C	-3.47517300	1.99492600	1.21047300	O	-4.72187900	2.49193200	1.29693900
H	-3.44574200	1.74423400	3.33553600	C	-5.37898100	2.86694900	0.09551700
C	3.82526100	0.36849300	0.12170100	H	-5.47923800	2.00638400	-0.57375500
C	4.07607800	1.25596100	-0.93176900	H	-6.36730300	3.21093100	0.39545500
C	4.88816200	-0.22726000	0.79208400	H	-4.84202300	3.68175400	-0.40312700
C	5.38151900	1.52923000	-1.30244000				

Figure S66. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **13a**/**18a**-$ZnCl_2$-*ortho-endo* (Transition State 2)



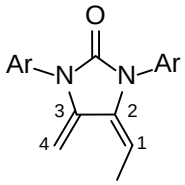
0 1				H	3.54522300	0.82180500	-1.99225600
C	1.78665300	-0.50773000	1.05930700	C	6.20694100	-0.11422600	0.67872100
C	2.08774700	-1.93910600	1.11313600	H	4.55857200	-0.13773100	2.06460600
C	1.43221500	-2.63848600	-0.18647900	C	6.58982600	0.10602400	-0.64770500
C	-0.04359700	-2.58796100	-0.30869500	H	5.95378400	0.61973000	-2.62816400
C	-0.57047600	-0.72798200	1.63065300	H	6.93488200	-0.36154900	1.44112000
C	0.49587900	0.03931900	1.23592900	O	7.86256500	0.02208800	-1.09688700
H	1.91740600	-2.16999500	-1.05036000	C	8.87925800	-0.29510400	-0.16443000
H	3.16120700	-2.12812000	1.08510200	H	9.81000500	-0.30521500	-0.72906100
H	1.66783900	-2.40545500	2.00532800	H	8.93823400	0.46212500	0.62550100
H	-0.30928700	-1.68661800	2.06243800	H	8.71065800	-1.28220200	0.28098800
H	1.78578900	-3.67177900	-0.12761500	C	-2.00596200	-0.34343400	1.68396800
C	1.76319600	1.60601200	0.16815800	H	-2.14442400	0.60682000	2.21229100
O	2.16894800	2.59379100	-0.38926100	H	-2.39207300	-0.15619000	0.67123700
N	0.51748000	1.32751800	0.67952800	H	-2.59604900	-1.12488200	2.16293400
N	2.53851000	0.42477000	0.43691200	H	-0.66274900	-3.32309000	0.19976000
C	-0.64713000	2.12868200	0.44088500	C	-0.62376900	-1.67299600	-1.15726000
C	-1.48465700	1.79814900	-0.61760000	O	-1.86521900	-1.46254000	-1.41852100
C	-0.99486300	3.14728100	1.32800000	H	0.07237300	-1.00036500	-1.69233700
C	-2.71154700	2.43767100	-0.76918500	Zn	-3.49512000	-2.04210600	-0.51186300
H	-1.22111900	0.98993200	-1.29398600	Cl	-3.30506000	-3.73165700	0.90265300
C	-2.20582700	3.80387400	1.17402500	Cl	-5.09503000	-0.57086800	-0.89584500
H	-0.32564100	3.40195000	2.14393400	H	-3.37533500	2.11805600	-1.56273700
C	-3.08205900	3.43261400	0.14202900	O	-4.26505700	4.08217500	0.10900800
H	-2.51346500	4.58957100	1.85517800	C	-5.23369300	3.63842500	-0.83161700
C	3.91293400	0.31954600	0.06915900	H	-5.44947100	2.57285600	-0.69796700
C	4.29355300	0.54945500	-1.25567200	H	-6.12800500	4.22734700	-0.63469600
C	4.86346900	0.00558700	1.03187300	H	-4.89362800	3.82191100	-1.85681500
C	5.62667100	0.44389500	-1.60954400				

Figure S67. M06-2X/6-31+G(d,p) optimized geometry of the cycloaddition of **13a**/**18a**-$ZnCl_2$-*ortho*-*endo* (Adduct)

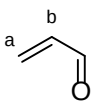


0 1			
C	1.78665300	-0.50773000	1.05930700
C	2.08774700	-1.93910600	1.11313600
C	1.43221500	-2.63848600	-0.18647900
C	-0.04359700	-2.58796100	-0.30869500
C	-0.57047600	-0.72798200	1.63065300
C	0.49587900	0.03931900	1.23592900
H	1.91740600	-2.16999500	-1.05036000
H	3.16120700	-2.12812000	1.08510200
H	1.66783900	-2.40545500	2.00532800
H	-0.30928700	-1.68661800	2.06243800
H	1.78578900	-3.67177900	-0.12761500
C	1.76319600	1.60601200	0.16815800
O	2.16894800	2.59379100	-0.38926100
N	0.51748000	1.32751800	0.67952800
N	2.53851000	0.42477000	0.43691200
C	-0.64713000	2.12868200	0.44088500
C	-1.48465700	1.79814900	-0.61760000
C	-0.99486300	3.14728100	1.32800000
C	-2.71154700	2.43767100	-0.76918500
H	-1.22111900	0.98993200	-1.29398600
C	-2.20582700	3.80387400	1.17402500
H	-0.32564100	3.40195000	2.14393400
C	-3.08205900	3.43261400	0.14202900
H	-2.51346500	4.58957100	1.85517800
C	3.91293400	0.31954600	0.06915900
C	4.29355300	0.54945500	-1.25567200
C	4.86346900	0.00558700	1.03187300
C	5.62667100	0.44389500	-1.60954400
H	3.54522300	0.82180500	-1.99225600
C	6.20694100	-0.11422600	0.67872100
H	4.55857200	-0.13773100	2.06460600
C	6.58982600	0.10602400	-0.64770500
H	5.95378400	0.61973000	-2.62816400
H	6.93488200	-0.36154900	1.44112000
O	7.86256500	0.02208800	-1.09688700
C	8.87925800	-0.29510400	-0.16443000
H	9.81000500	-0.30521500	-0.72906100
H	8.93823400	0.46212500	0.62550100
H	8.71065800	-1.28220200	0.28098800
C	-2.00596200	-0.34343400	1.68396800
H	-2.14442400	0.60682000	2.21229100
H	-2.39207300	-0.15619000	0.67123700
H	-2.59604900	-1.12488200	2.16293400
H	-0.66274900	-3.32309000	0.19976000
C	-0.62376900	-1.67299600	-1.15726000
O	-1.86521900	-1.46254000	-1.41852100
H	0.07237300	-1.00036500	-1.69233700
Zn	-3.49512000	-2.04210600	-0.51186300
Cl	-3.30506000	-3.73165700	0.90265300
Cl	-5.09503000	-0.57086800	-0.89584500
H	-3.37533500	2.11805600	-1.56273700
O	-4.26505700	4.08217500	0.10900800
C	-5.23369300	3.63842500	-0.83161700
H	-5.44947100	2.57285600	-0.69796700
H	-6.12800500	4.22734700	-0.63469600
H	-4.89362800	3.82191100	-1.85681500

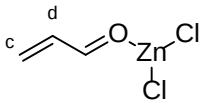
TABLE S7. Geometrical parameters (M06-2X/6-31+G(d,p)), Bond distances (Å) of the Transition States (TS1 and TS2) and Zwitterionic Intermediates (ZI), Located at the Potential Surfaces of the Diels-Alder Reactions of Diene **12a** and Dienophiles **18a,** **18a**-$ZnCl_2$ and **18a**-BF_3.



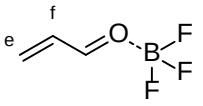
12a, Ar = C_6H_4-4-OMe



18a



18a-$ZnCl_2$



18a-BF_3

Cycloaddends	TS1	ZI	TS2
12a/**18a**-*ortho-endo*	(C_4-C_a) 1.93 (C_1-C_b) 3.15	n.d.	n.d.
12a/**18a**-*ortho-exo*	(C_4-C_a) 1.92 (C_1-C_b) 2.96	n.d.	n.d.
12a/**18a**-*meta-endo*	(C_4-C_b) 2.56 (C_1-C_a) 2.01	n.d.	n.d.
12a/**18a**-*meta-exo*	(C_4-C_b) 2.59 (C_1-C_a) 2.03	n.d.	n.d.
12a/**18a**-$ZnCl_2$-*ortho-endo*	(C_4-C_c) 2.12 (C_1-C_d) 3.54	(C_4-C_c) 1.57 (C_1-C_d) 3.61	(C_4-C_c) 1.60 (C_1-C_d) 2.59
12a/**18a**-$ZnCl_2$-*ortho-exo*	(C_4-C_c) 2.08 (C_1-C_d) 3.24	(C_4-C_c) 1.56 (C_1-C_d) 3.97	(C_4-C_c) 1.61 (C_1-C_d) 2.66
12a/**18a**-$ZnCl_2$-*meta-endo*	(C_4-C_d) 2.11 (C_1-C_c) 4.40	(C_4-C_d) 1.54 (C_1-C_c) 3.18	(C_4-C_c)1.55 (C_1-C_d) 2.70
12a/**18a**-$ZnCl_2$-*meta-exo*	(C_4-C_d) 2.05 (C_1-C_c) 3.34	(C_4-C_d) 1.54 (C_1-C_c) 3.17	(C_4-C_c) 1.56 (C_1-C_d) 2.59
12a/**18a**-BF_3-*ortho-endo*	(C_4-C_e) 2.35 (C_1-C_f) 3.41	(C_4-C_e) 1.56 (C_1-C_f) 3.89	(C_4-C_e) 1.58 (C_1-C_f) 2.47

12a/**18a**-BF_3-*ortho-exo*	(C_4-C_e) 2.13	(C_4-C_e) 1.56	(C_4-C_e) 1.60
	(C_1-C_f) 3.91	(C_1-C_f) 3.94	(C_1-C_f) 2.59
12a/**18a**-BF_3-*meta-endo*	(C_4-C_f) 2.09	(C_4-C_f) 1.61	(C_4-C_f) 1.61
	(C_1-C_e) 3.34	(C_1-C_e) 3.01	(C_1-C_e) 2.91
12a/**18a**-BF_3-*meta-exo*	(C_4-C_f) 2.12	(C_4-C_f) 1.54	(C_4-C_f) 1.61
	(C_1-C_e) 3.31	(C_1-C_e) 3.19	(C_1-C_e) 2.59

n.d. = not determined