SUPPORTING INFORMATION

New electron-donor and –acceptor architectures from benzofurazans and sym-triaminobenzenes: intermediates, products and unusual nitro group shift

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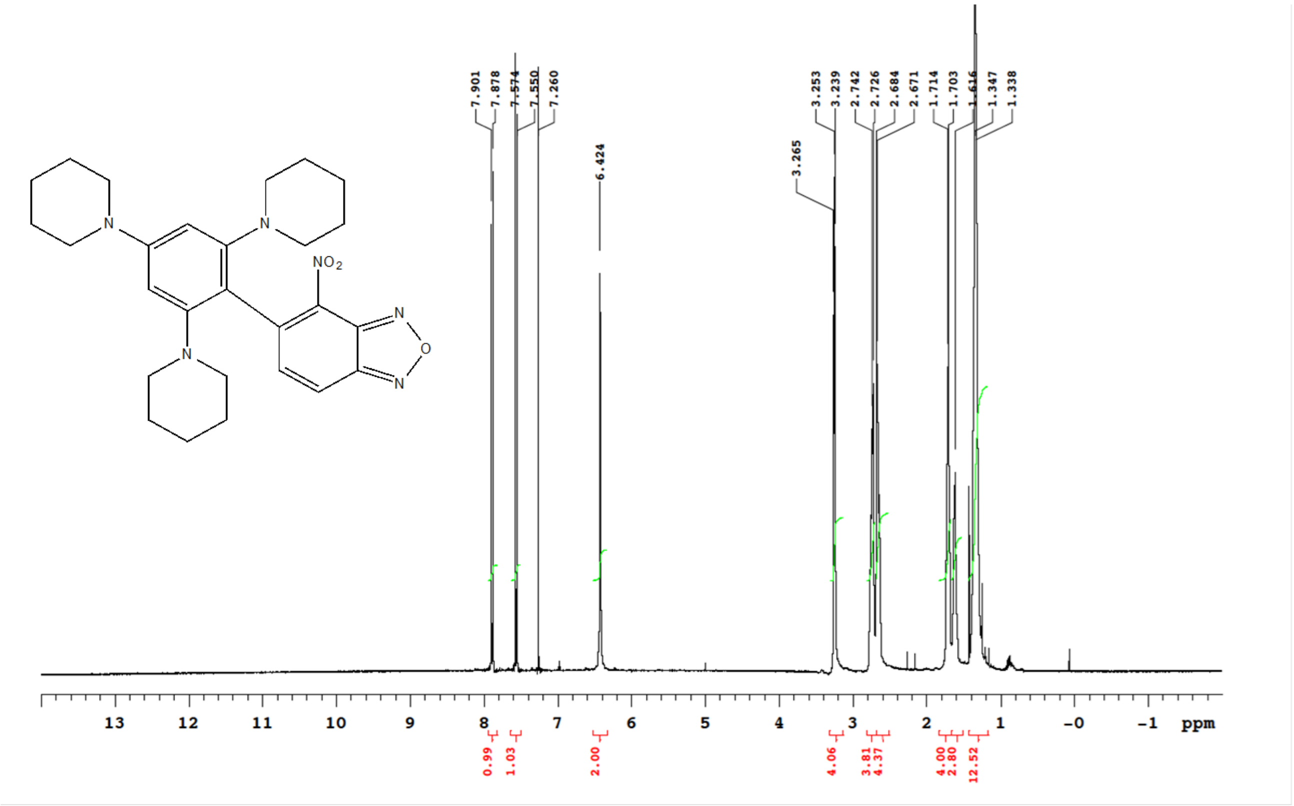


Fig. SI-1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8**.

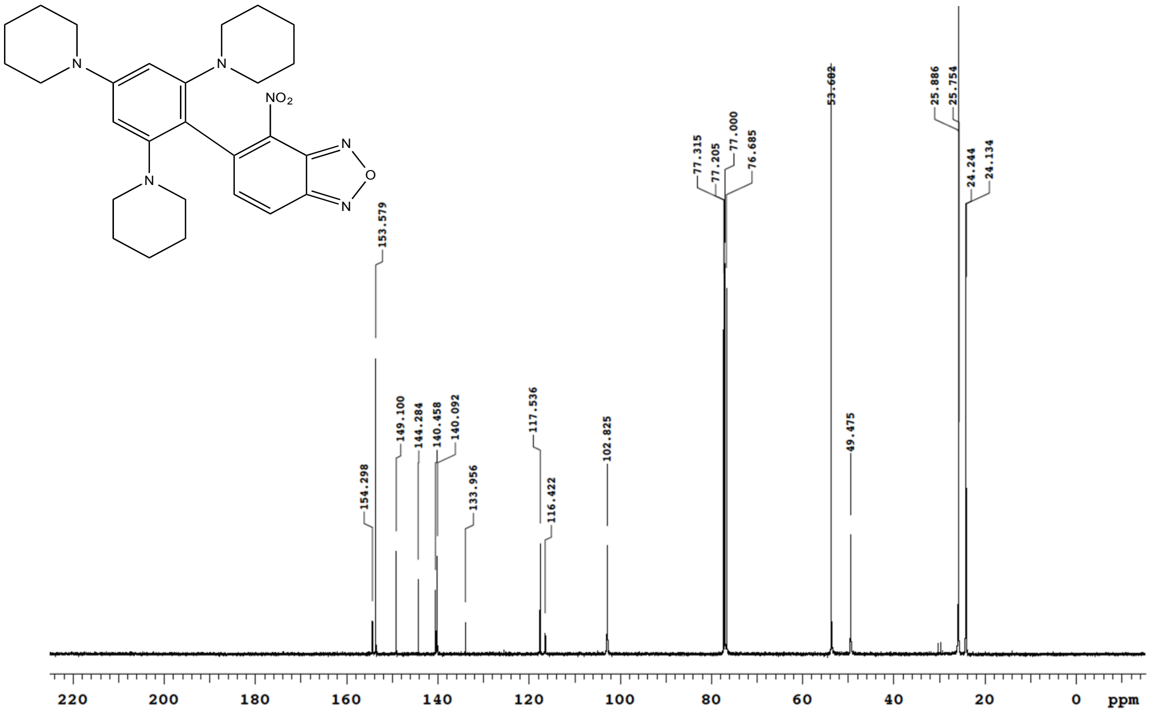


Fig. SI-2. ^{13}C NMR spectrum ($CDCl_3$, 100.46 MHz) of compound **8**

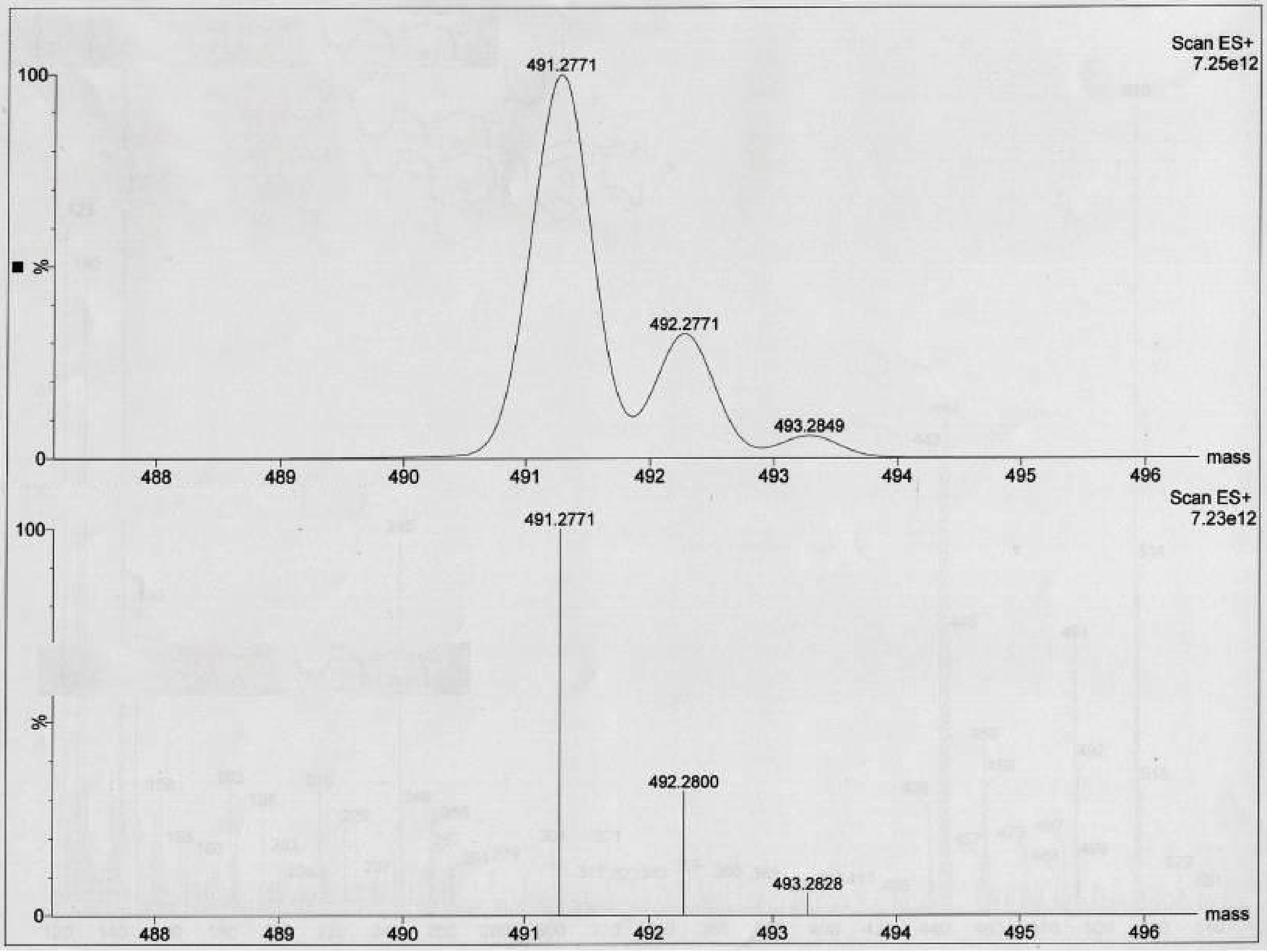


Fig. SI-3. Mass spectrum (ESI$^+$-HRMS mode) of compound **8**

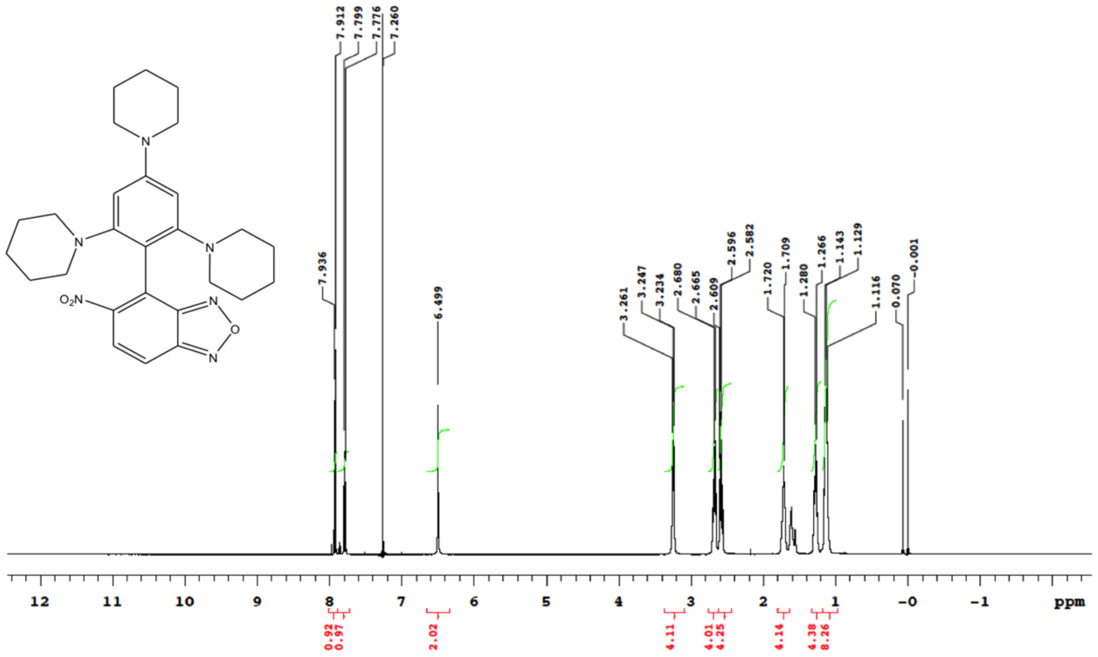


Fig. SI-4. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of compound **9**

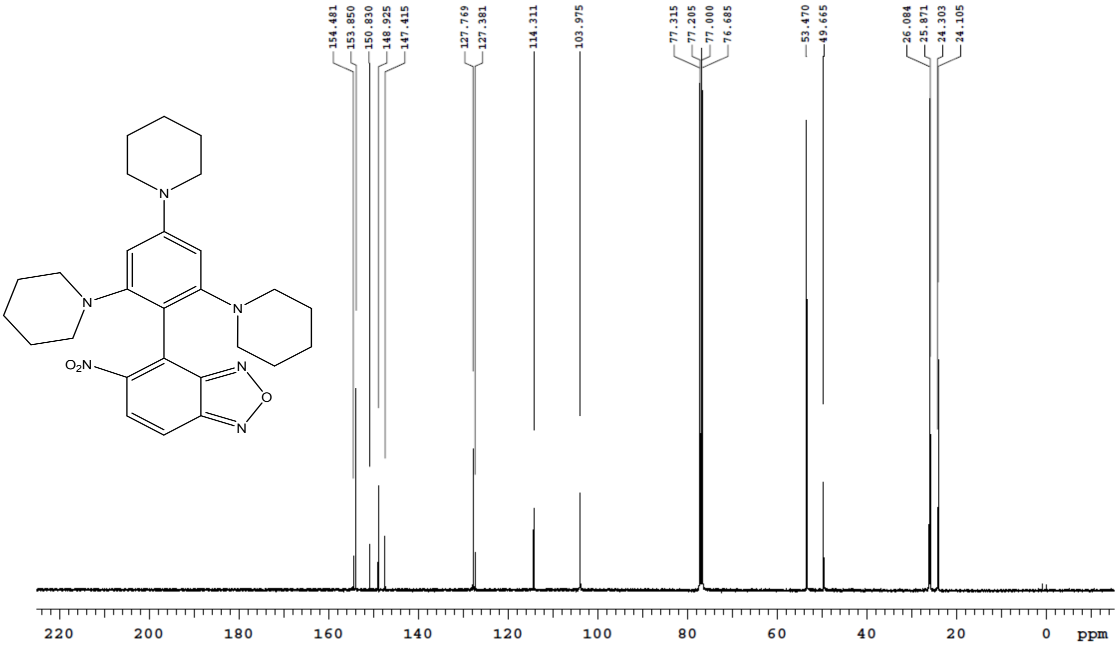


Fig. SI-5. ^{13}C NMR spectrum (CDCl$_3$, 100.46 MHz) of compound **9**

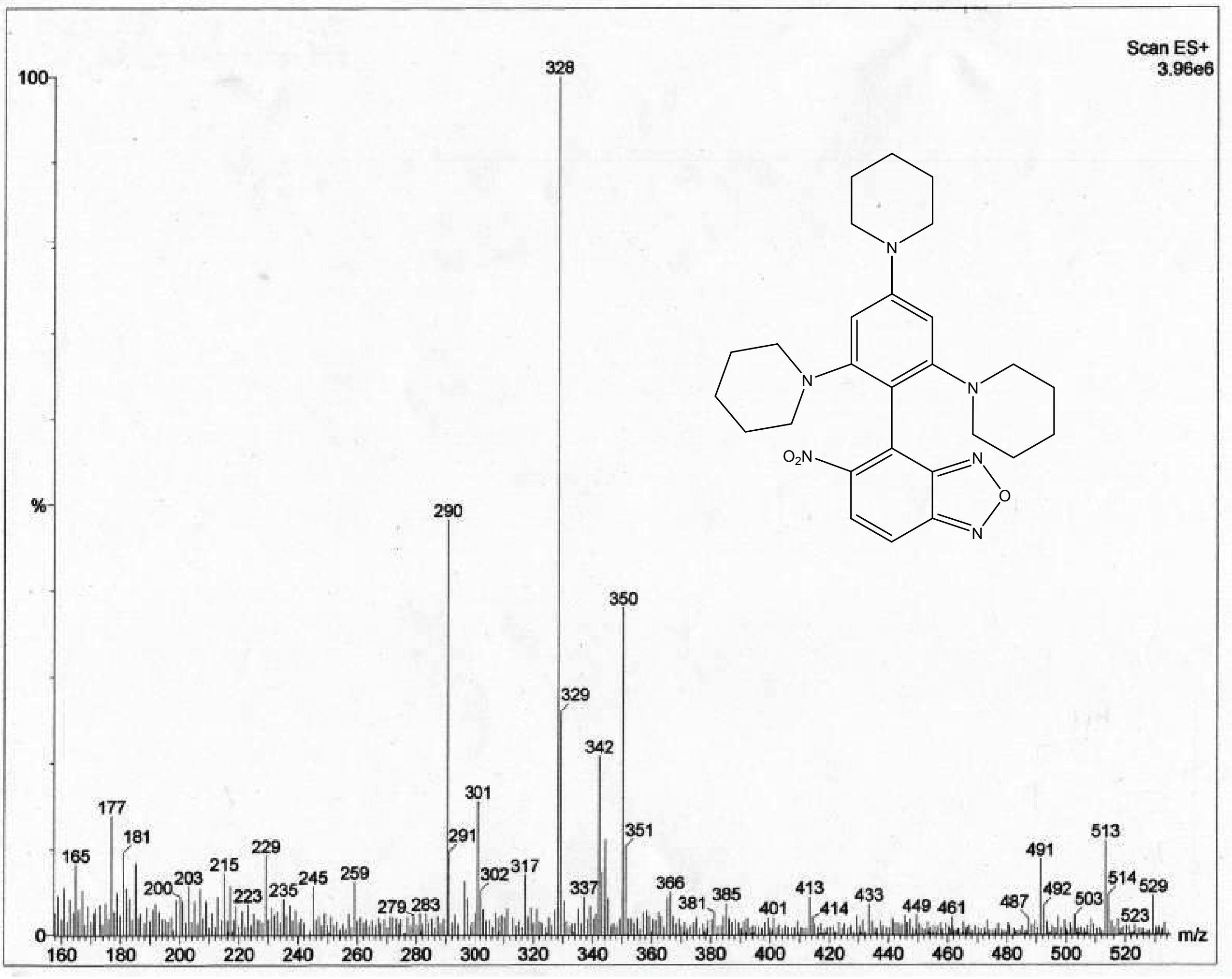


Fig. SI-6. Mass spectrum (ESI$^+$ mode) of compound **9**

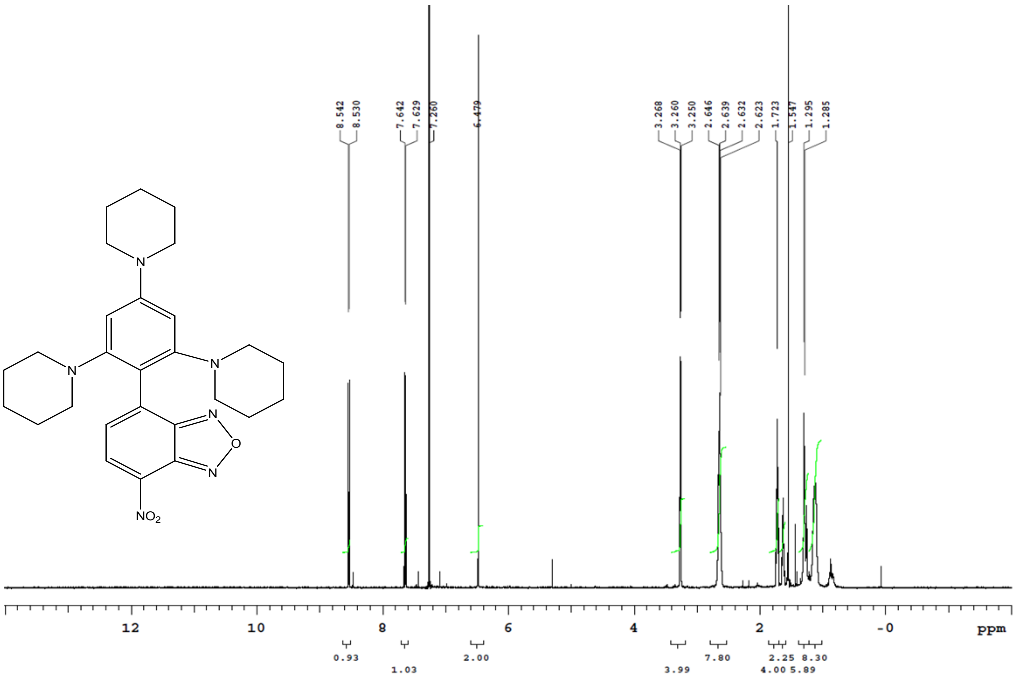


Fig. SI-7. ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of compound **10**

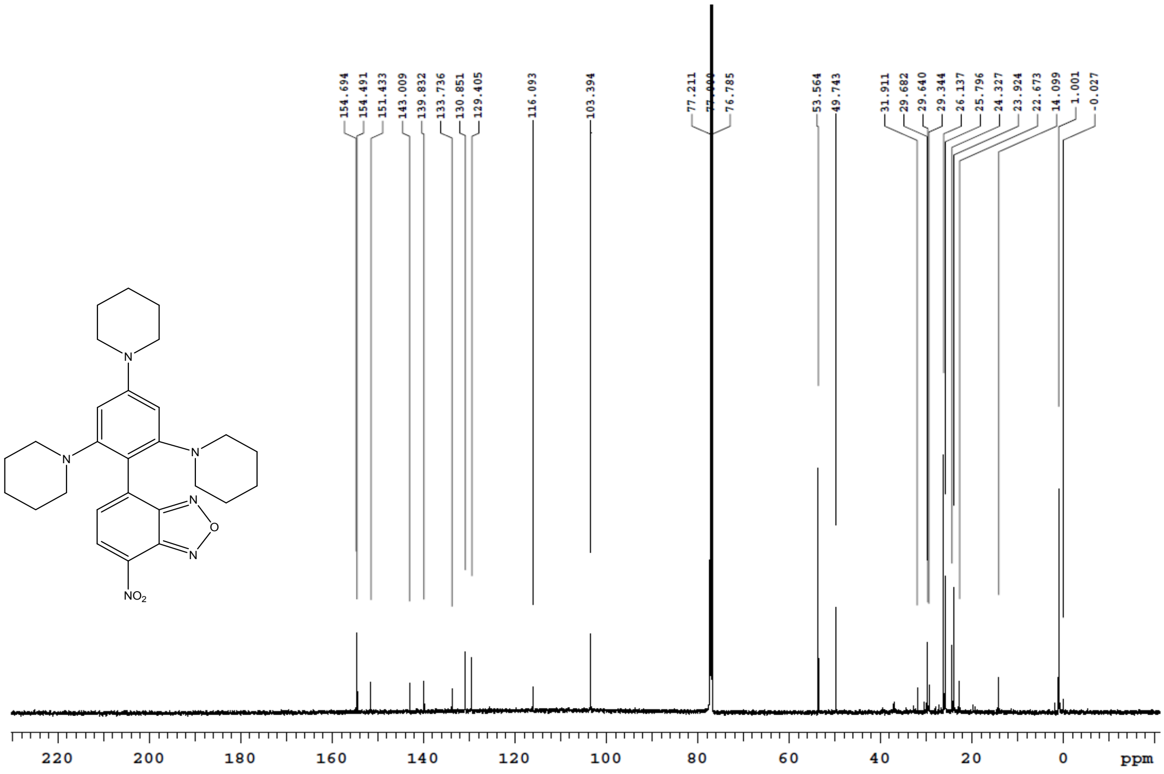


Fig. SI-8. ^{13}C NMR spectrum (CDCl$_3$, 150.80 MHz) of compound **10**

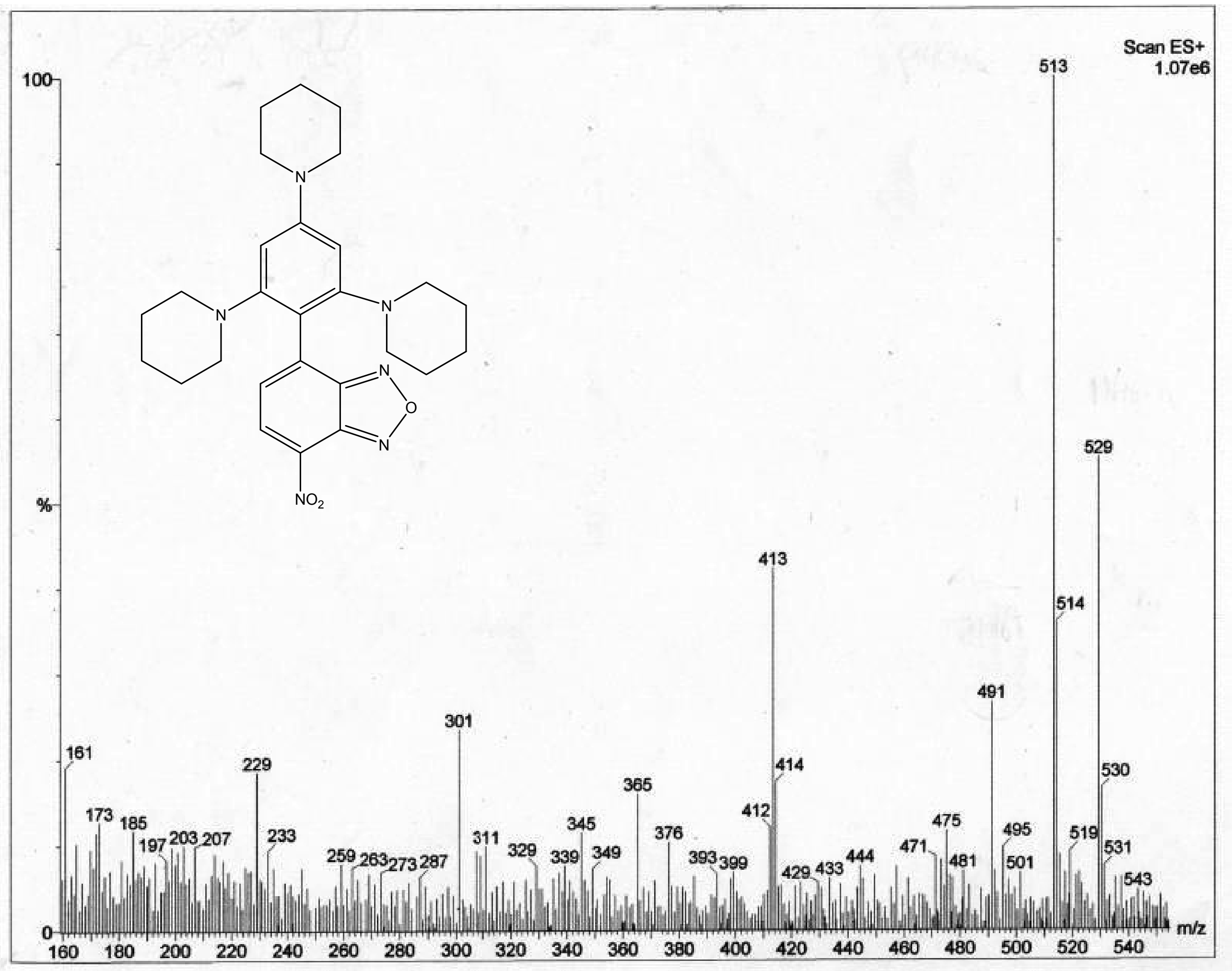


Fig. SI-9. Mass spectrum (ESI$^+$ mode) of compound **10**

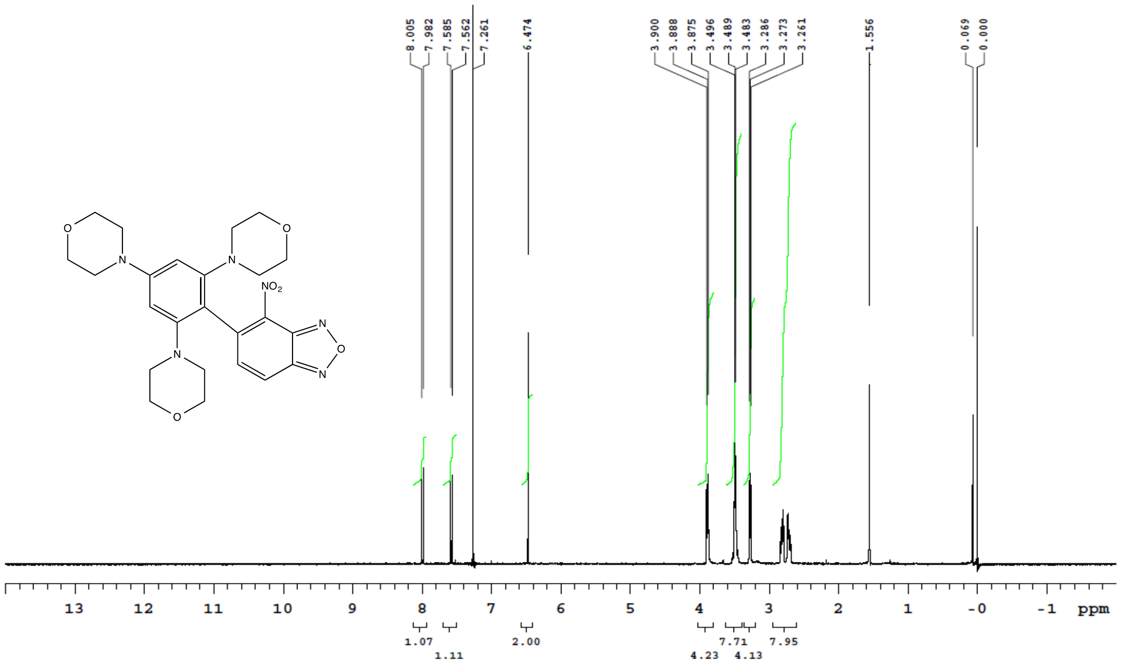


Fig. SI-7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **12**

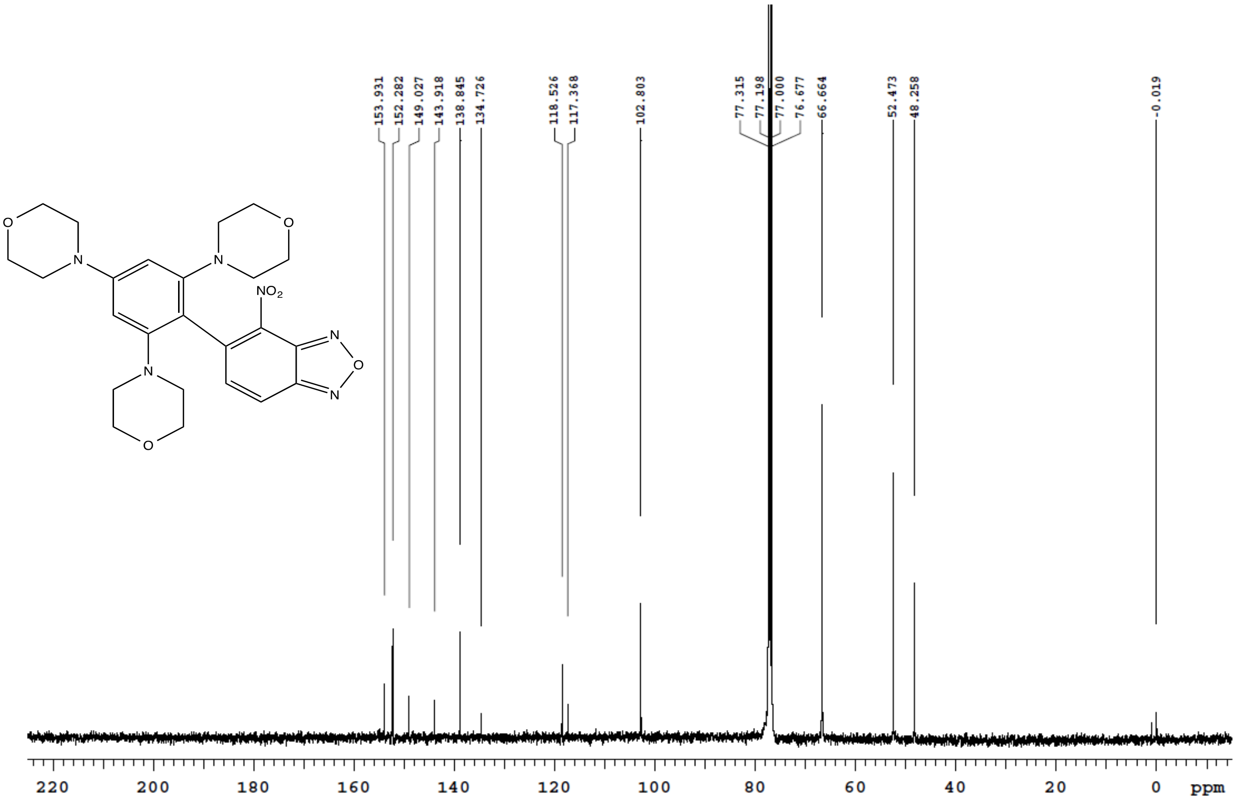


Fig. SI-8. ^{13}C NMR spectrum ($CDCl_3$, 100.46 MHz) of compound **12**

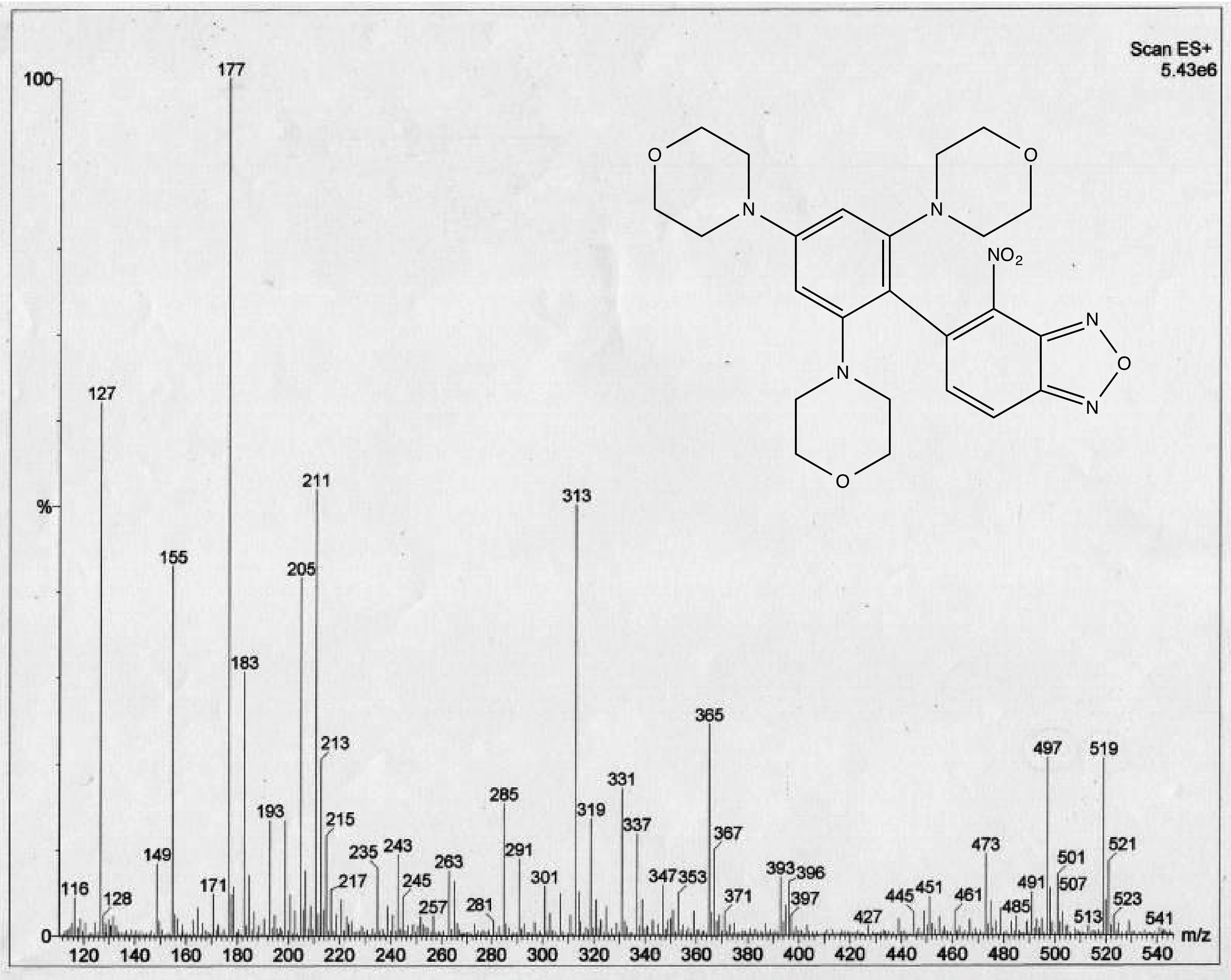


Fig. SI-9. Mass spectrum (ESI$^+$ mode) of compound **12**

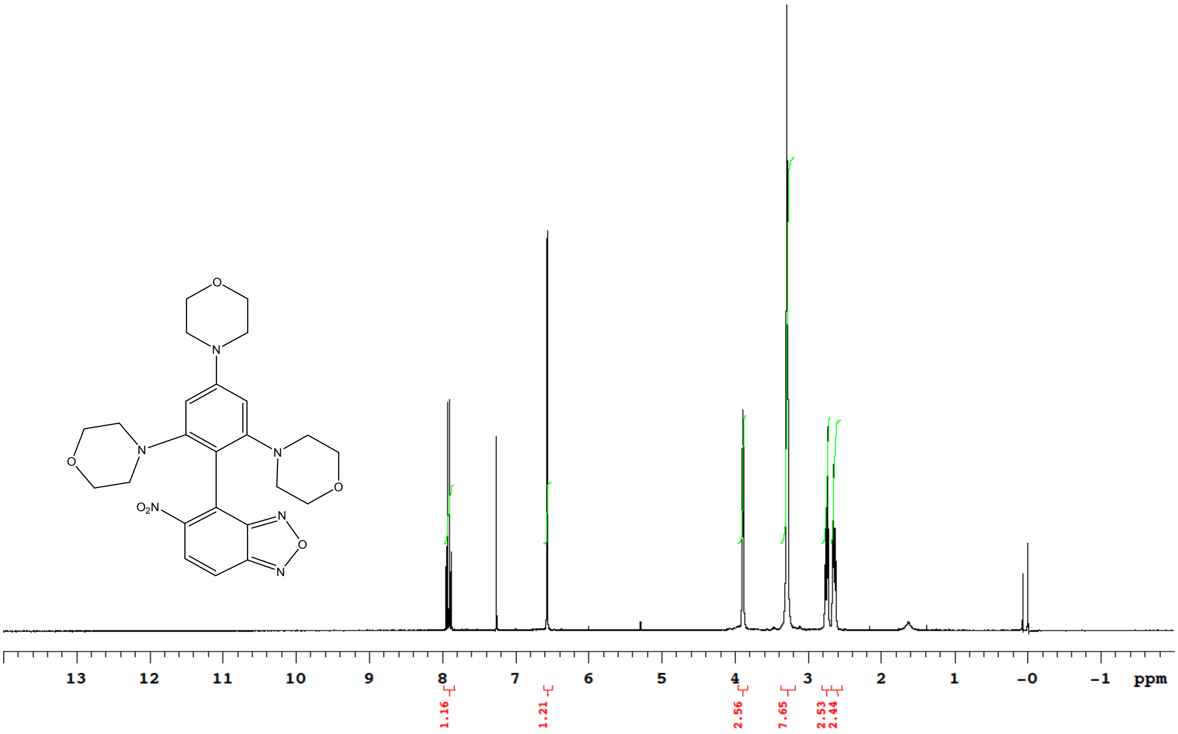


Fig. SI-10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **13**

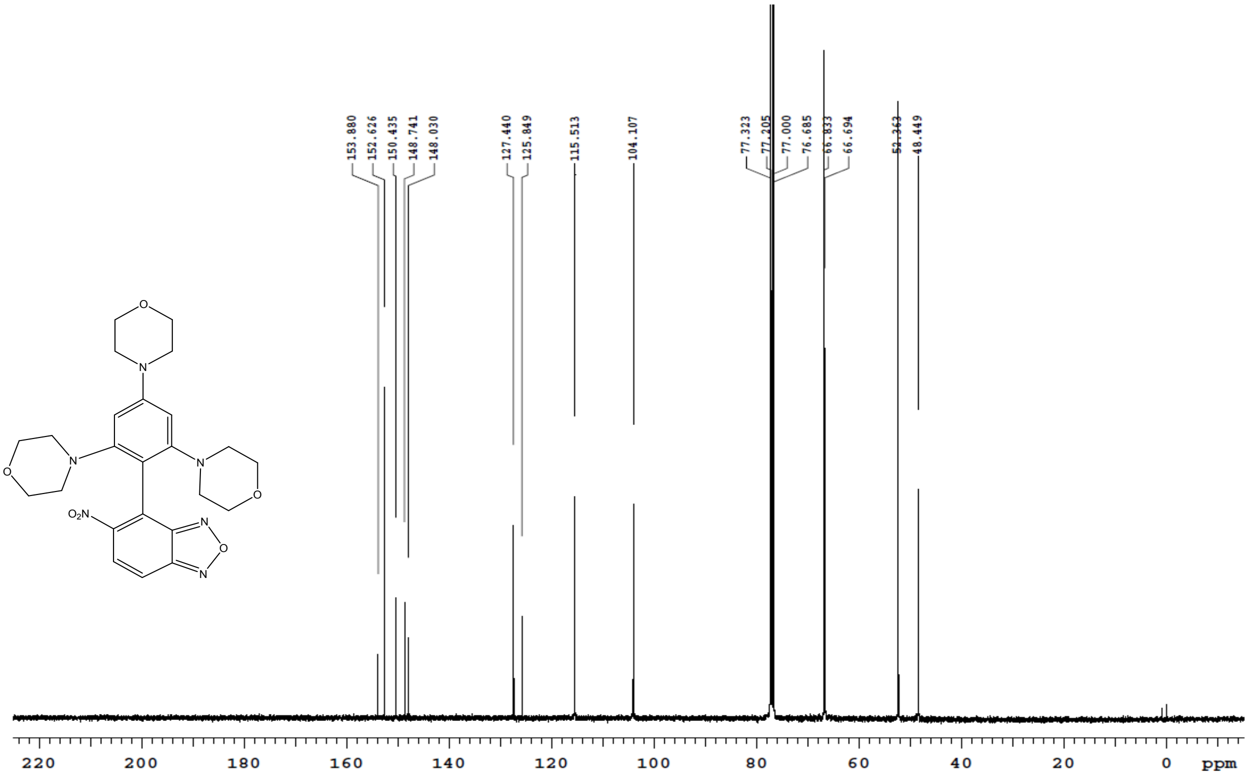


Fig. SI-11. ^{13}C NMR spectrum ($CDCl_3$, 100.46 MHz) of compound **13**

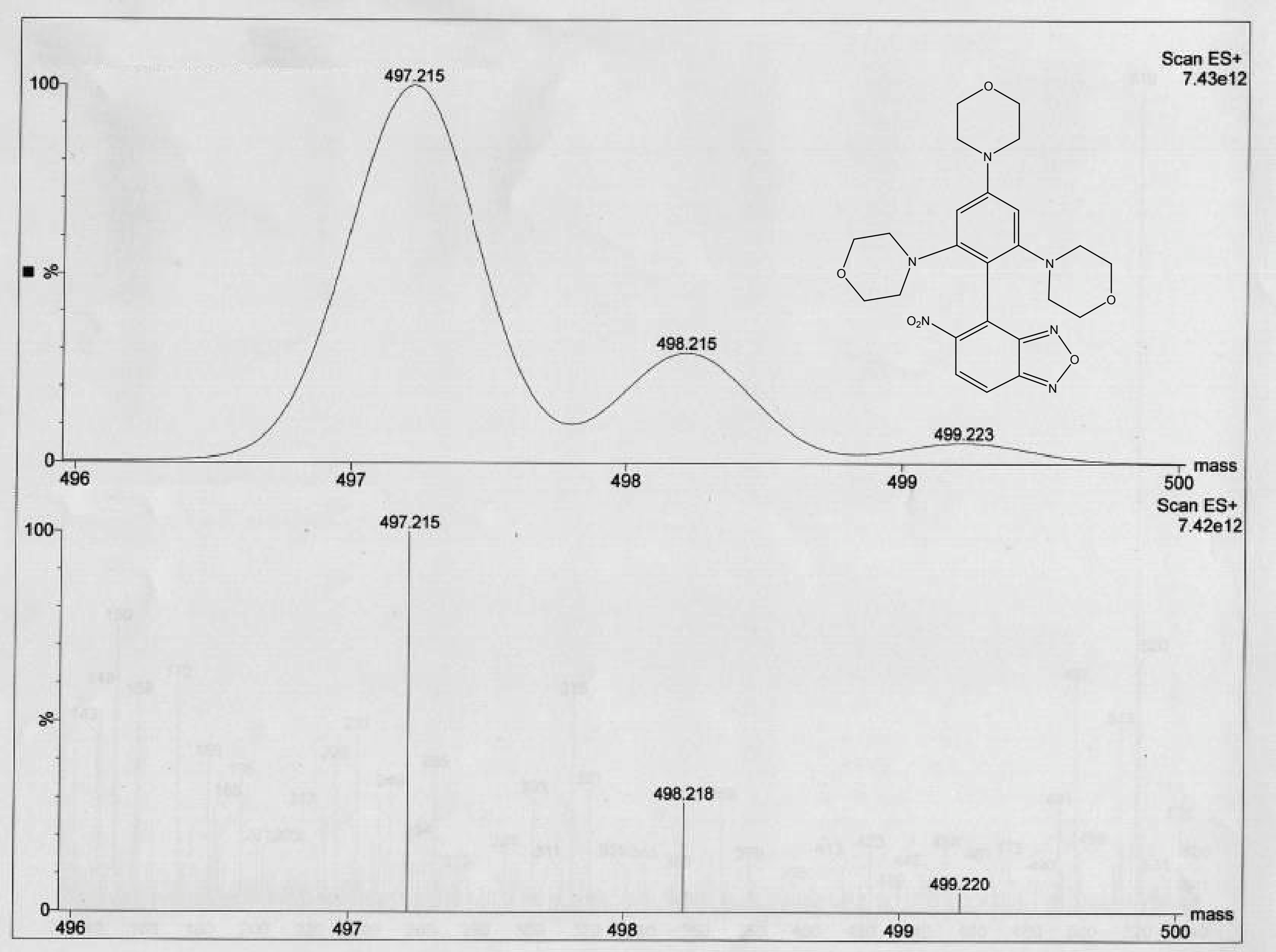


Fig. SI-12. Mass spectrum (ESI^+-HRMS mode) of compound **13.**

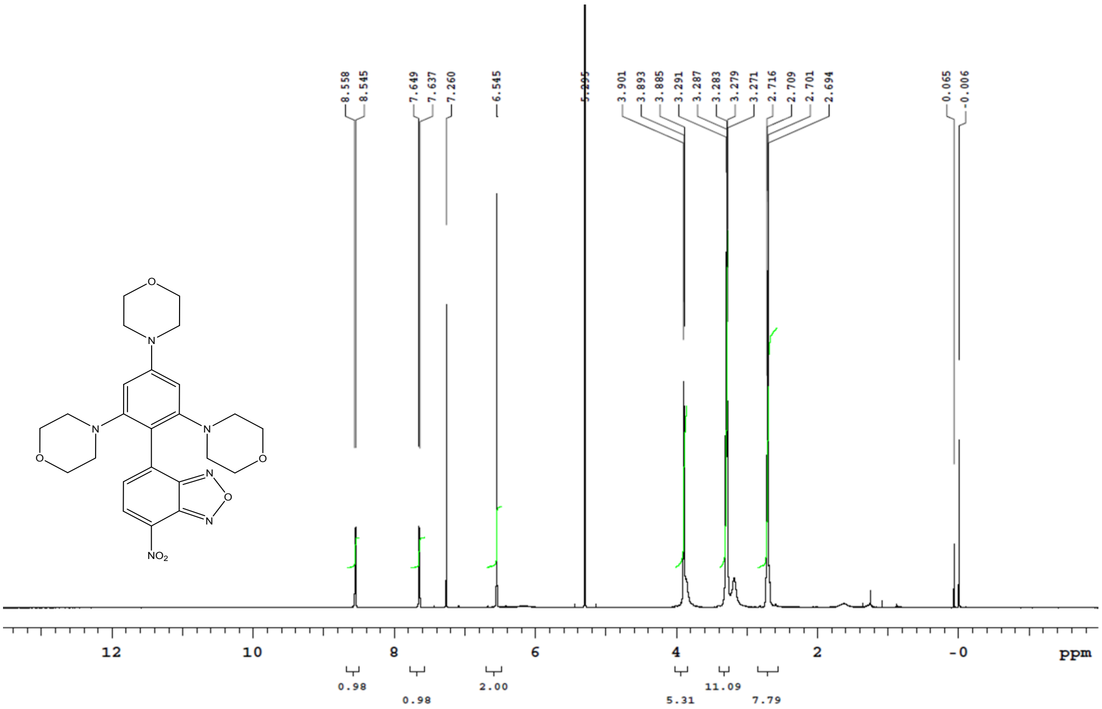


Fig. SI-13. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **14**

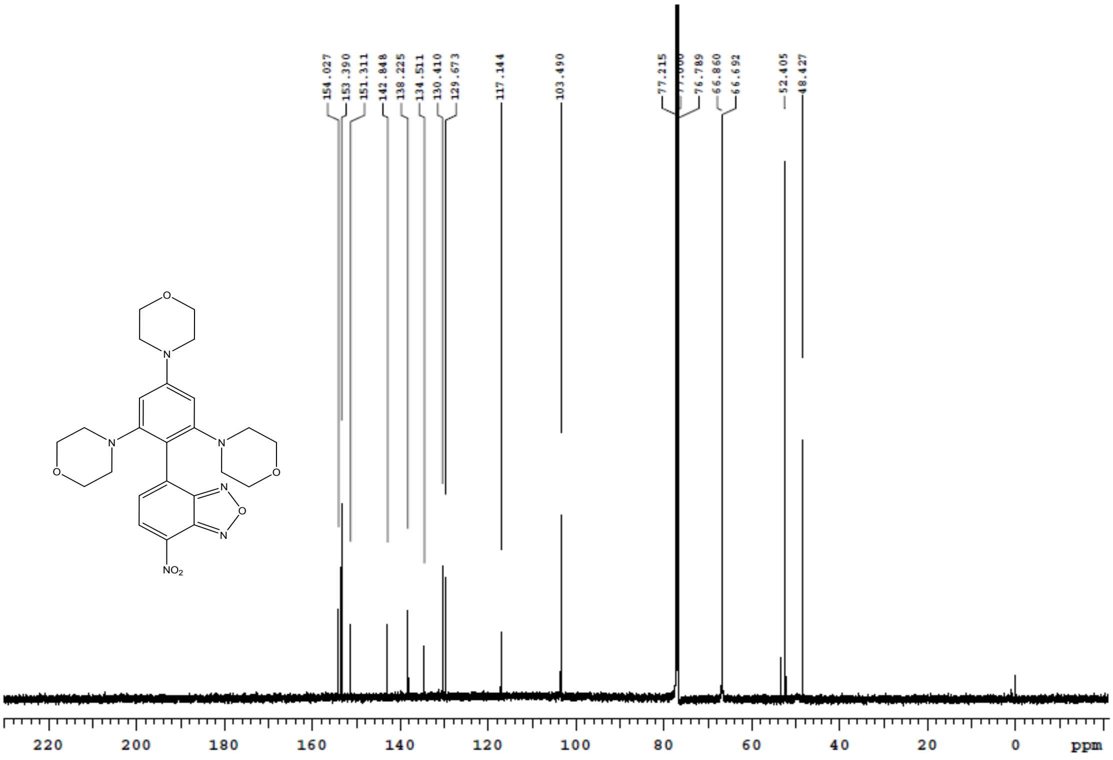


Fig. SI-14. ^{13}C NMR spectrum ($CDCl_3$, 150.80 MHz) of compound **14**

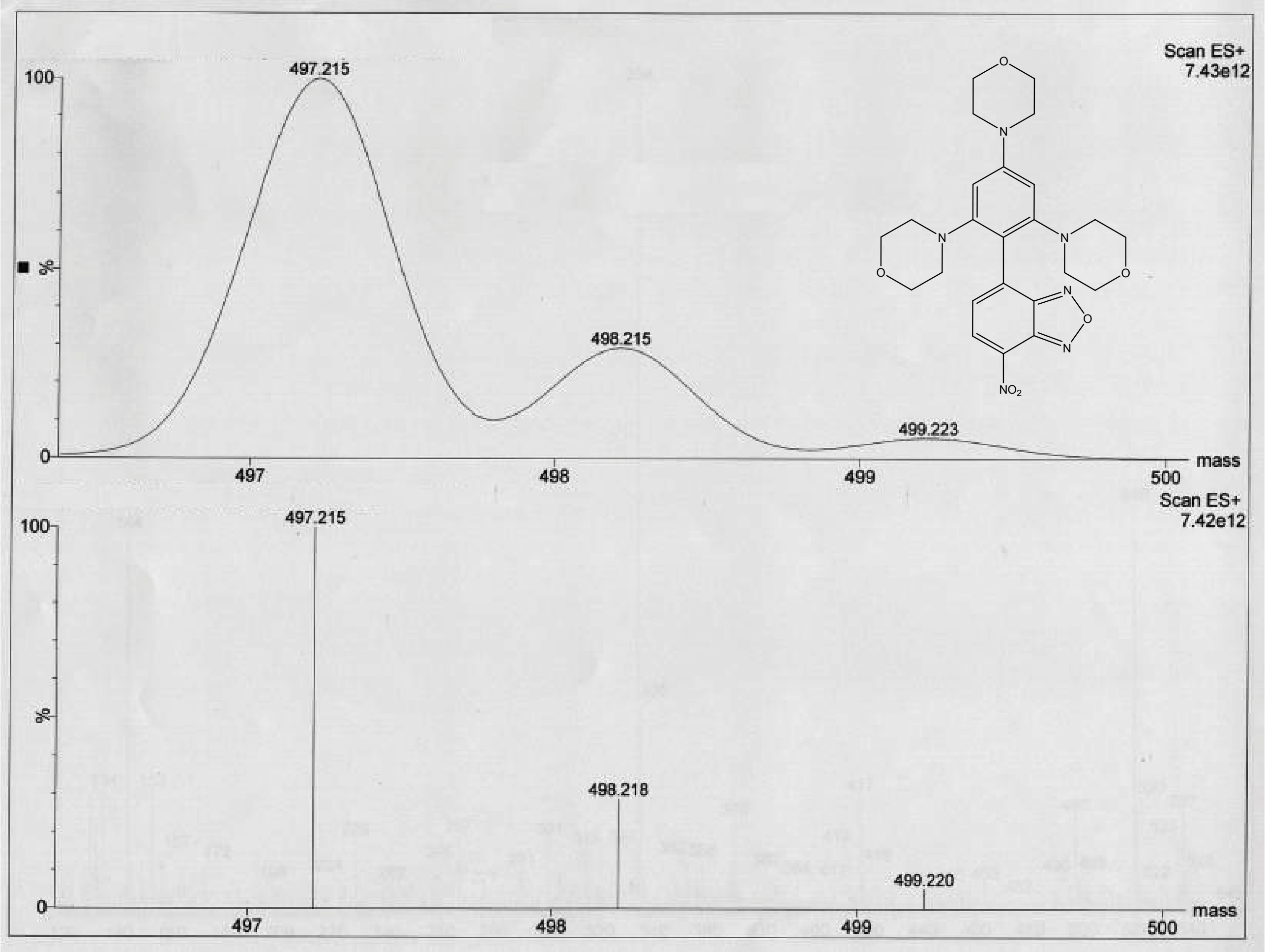


Fig. SI-15. Mass spectrum (ESI$^+$-HRMS mode) of compound **14**

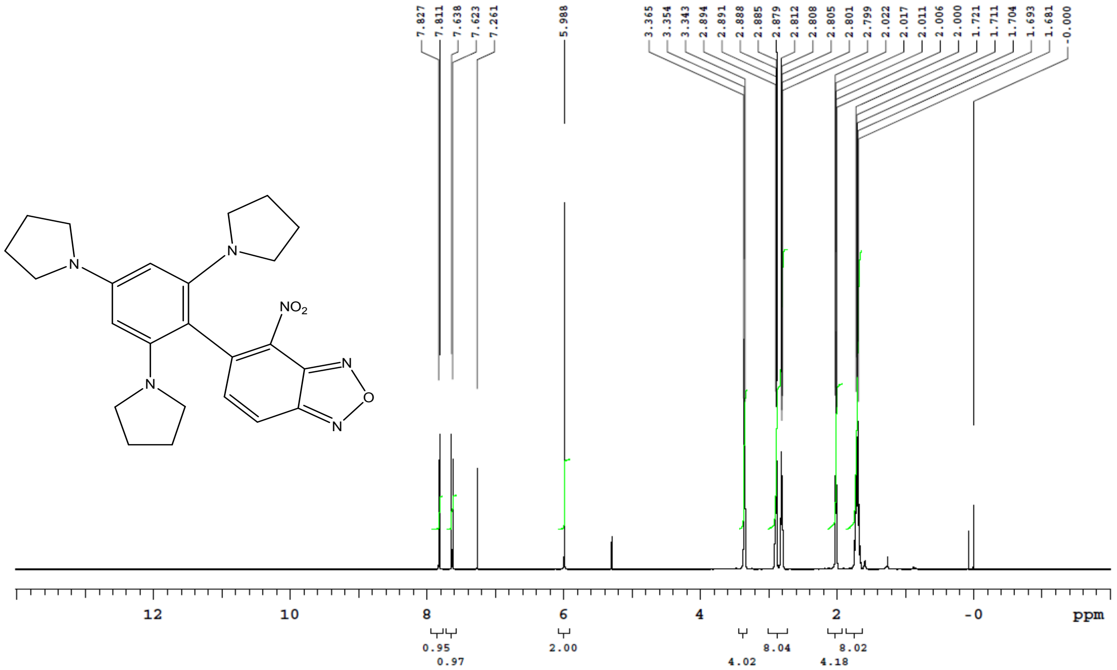


Fig. SI-16. ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of compound **16**

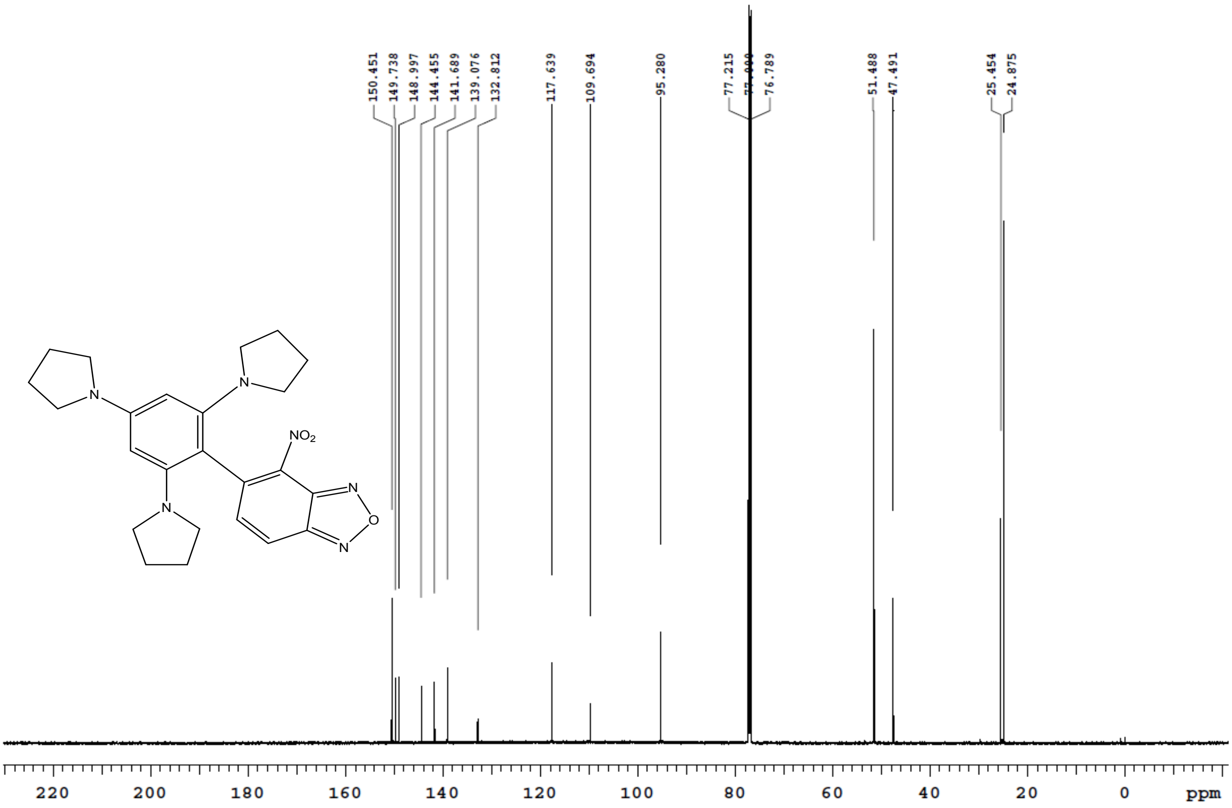


Fig. SI-17. ^{13}C NMR spectrum (CDCl$_3$, 150.80 MHz) of compound **16**

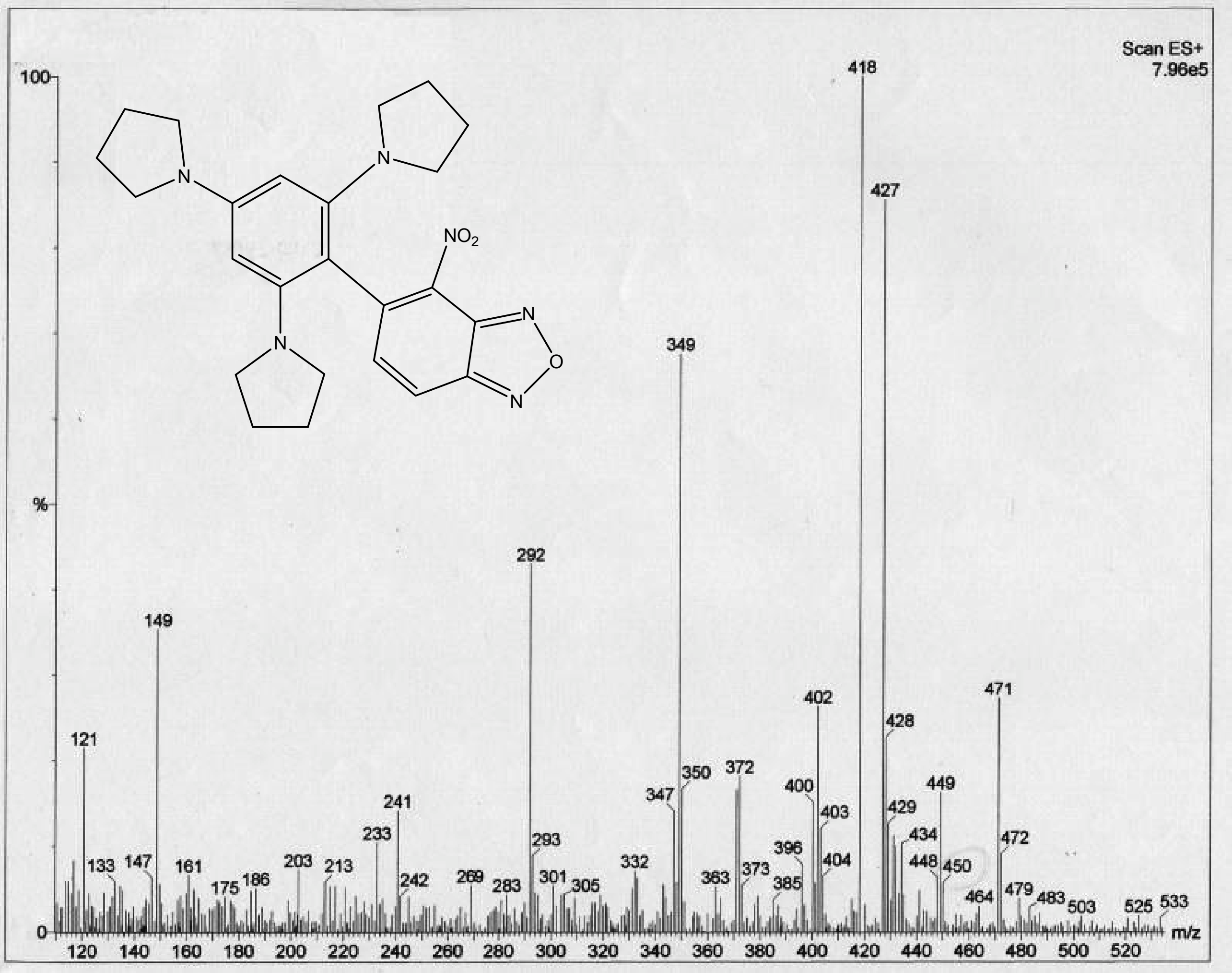


Fig. SI-18. Mass spectrum (ESI$^+$ mode) of compound **16**

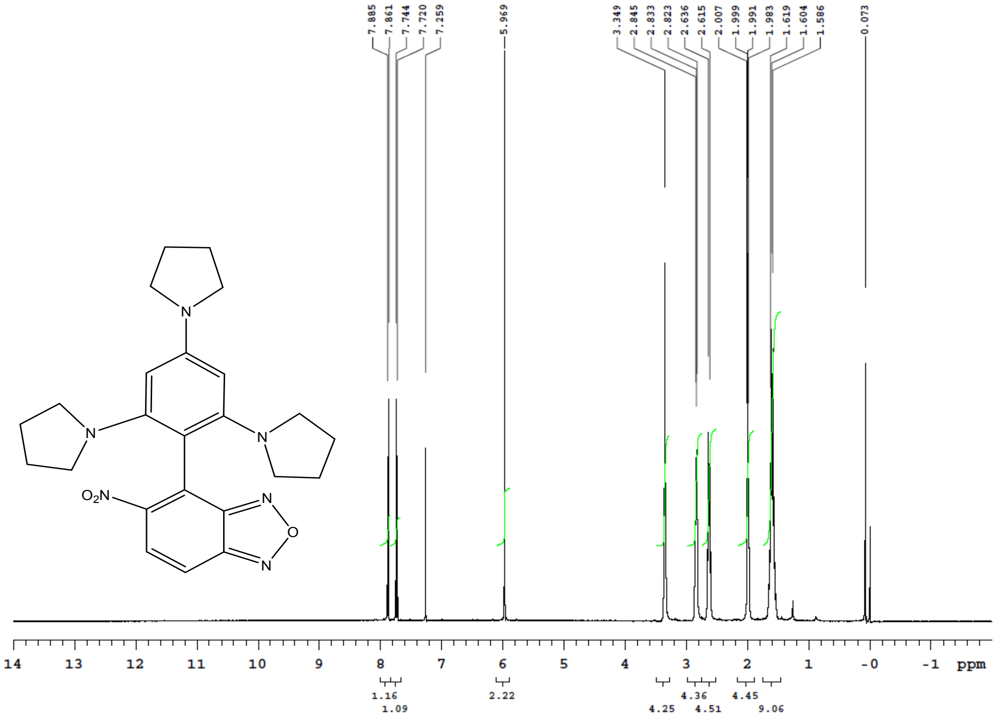


Fig. SI-19. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **17**

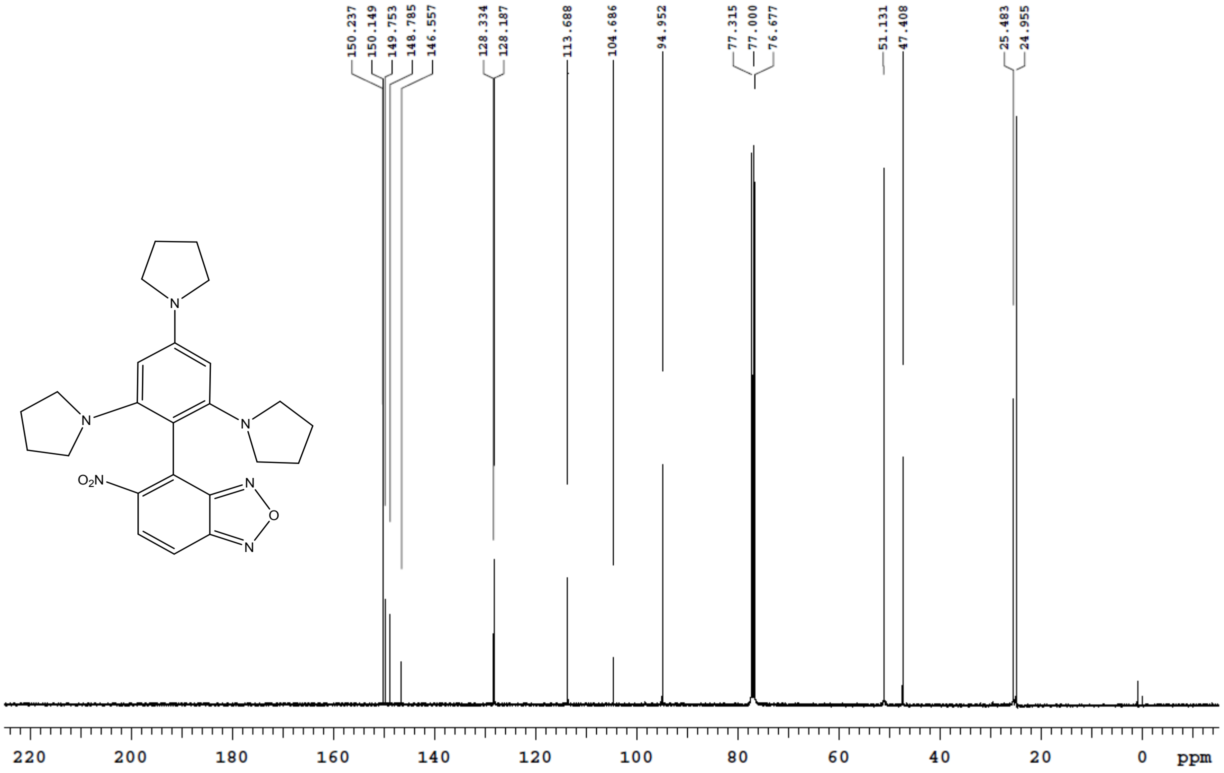


Fig. SI-20. ^{13}C NMR spectrum ($CDCl_3$, 100.46 MHz) of compound **17**

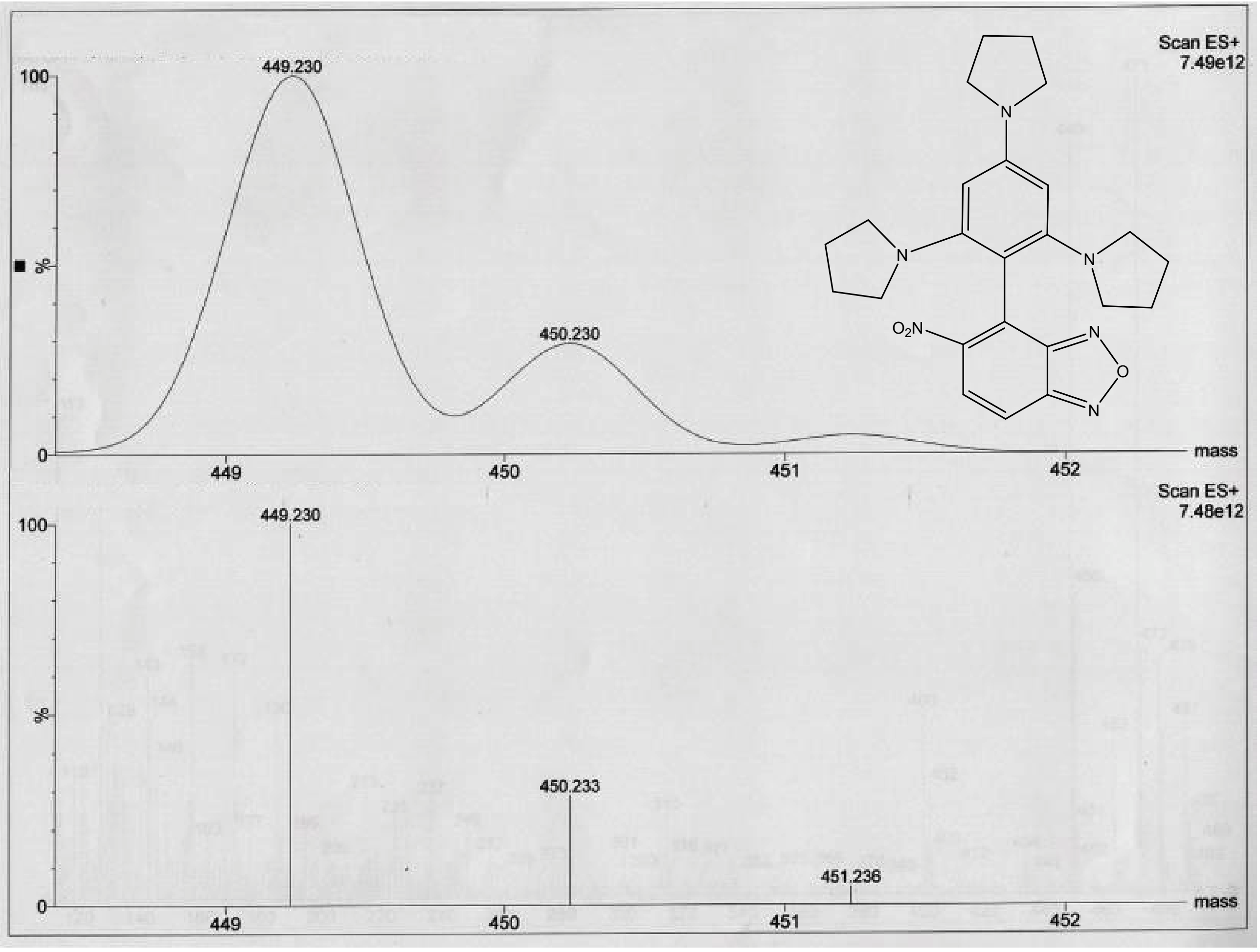


Fig. SI-21. Mass spectrum (ESI^{+}-HRMS mode) of compound **17**

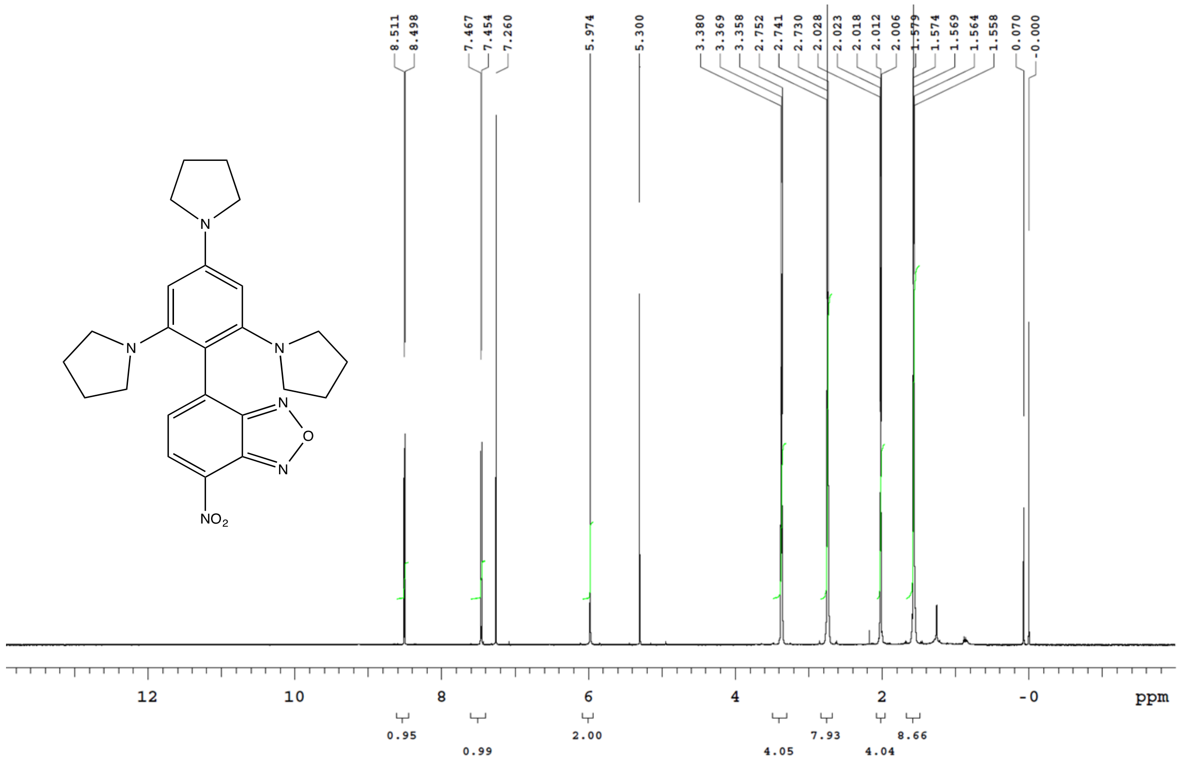


Fig. SI-22. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **18**

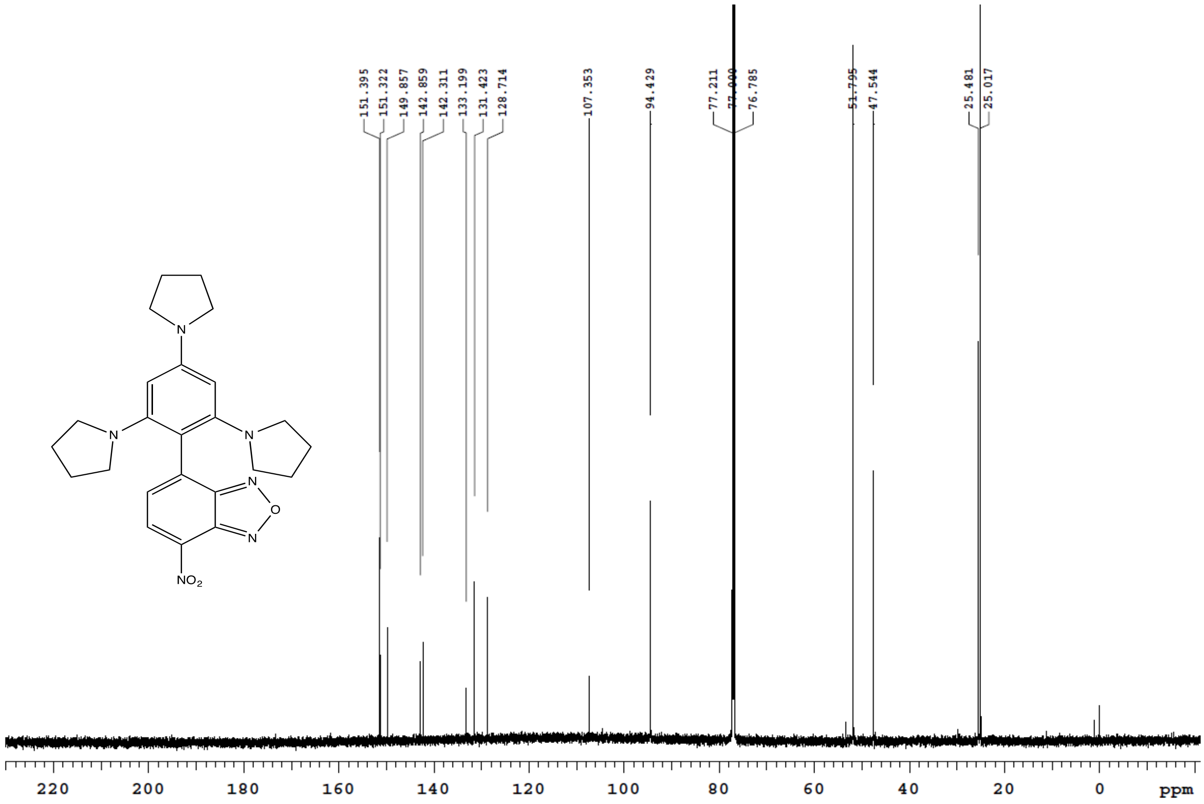


Fig. SI-23. ^{13}C NMR spectrum ($CDCl_3$, 150.80 MHz) of compound **18**

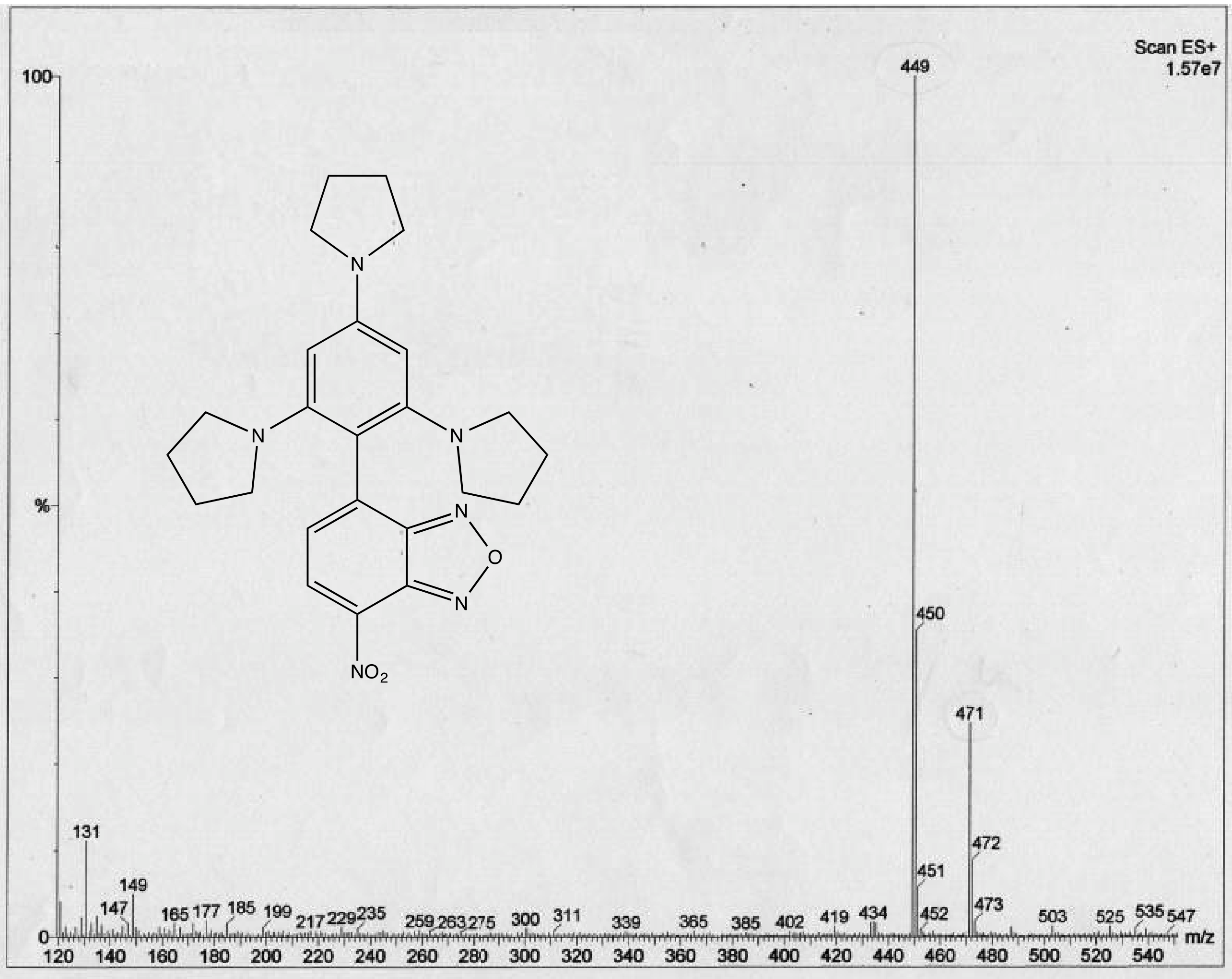


Fig. SI-24. Mass spectrum (ESI$^+$ mode) of compound **18**

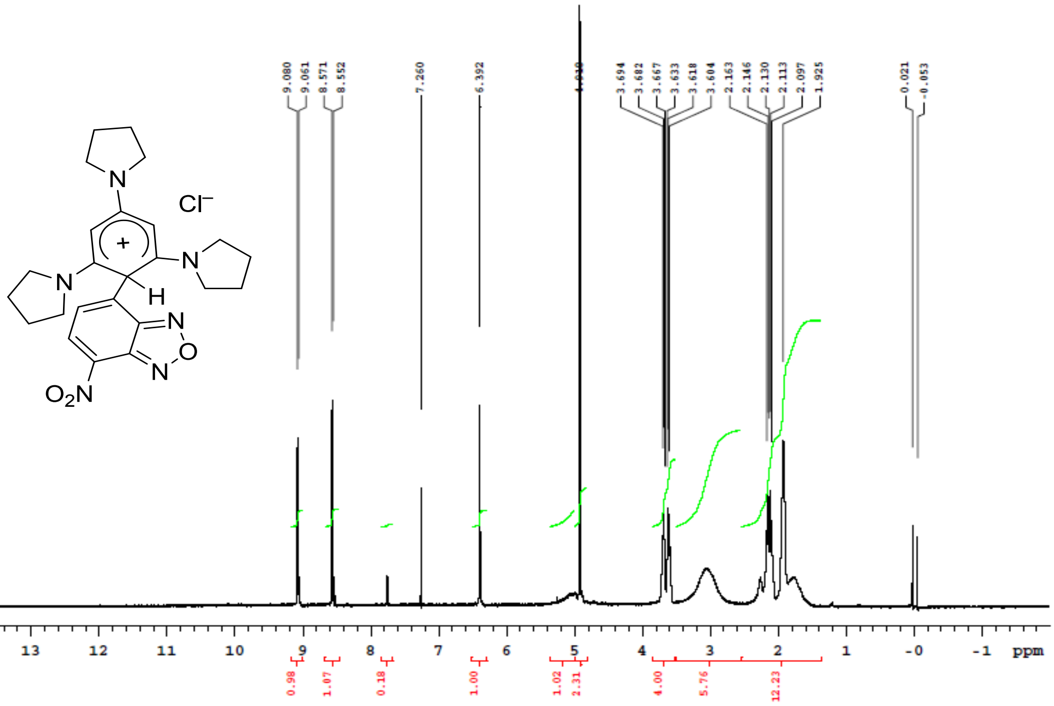


Fig. SI-25. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **20**

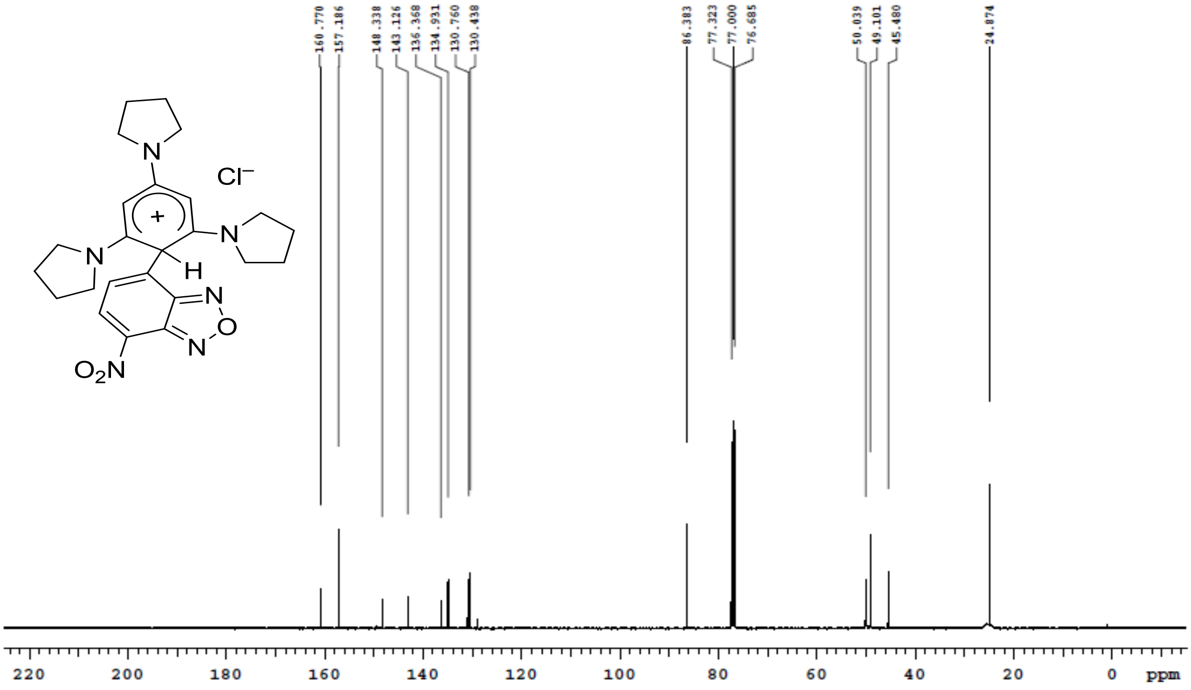


Fig. SI-26. ^{13}C NMR spectrum ($CDCl_3$, 100.46 MHz) of compound **20**

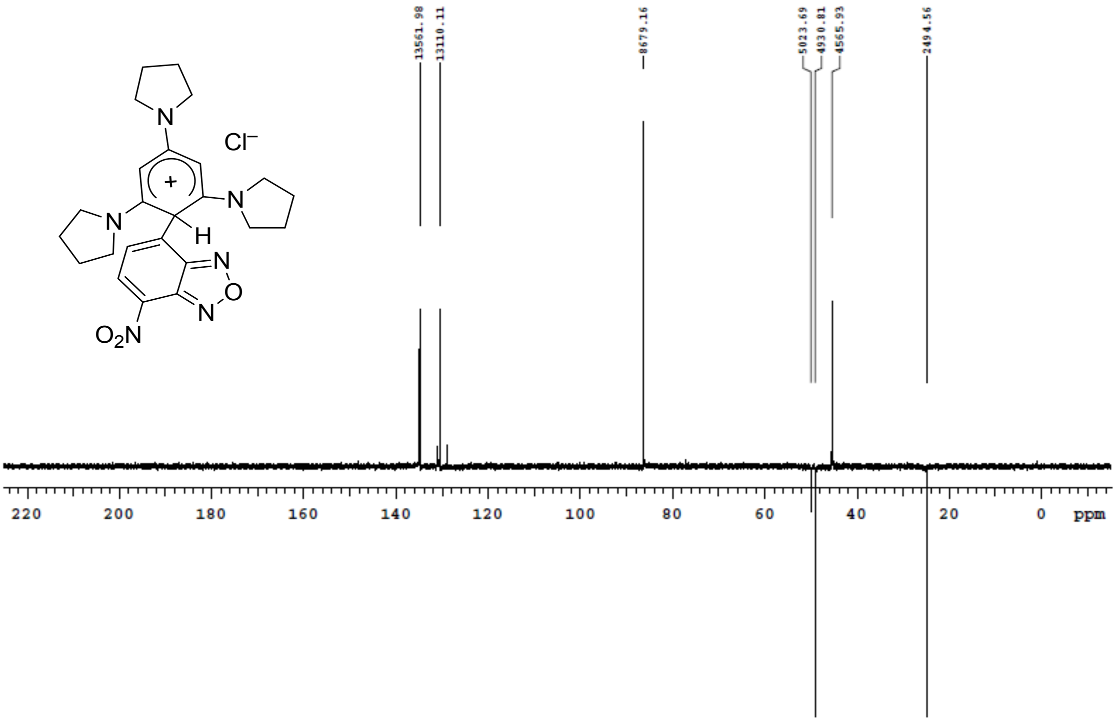


Fig. SI-27. DEPT spectrum ($CDCl_3$, 100.46 MHz) of compound **20**

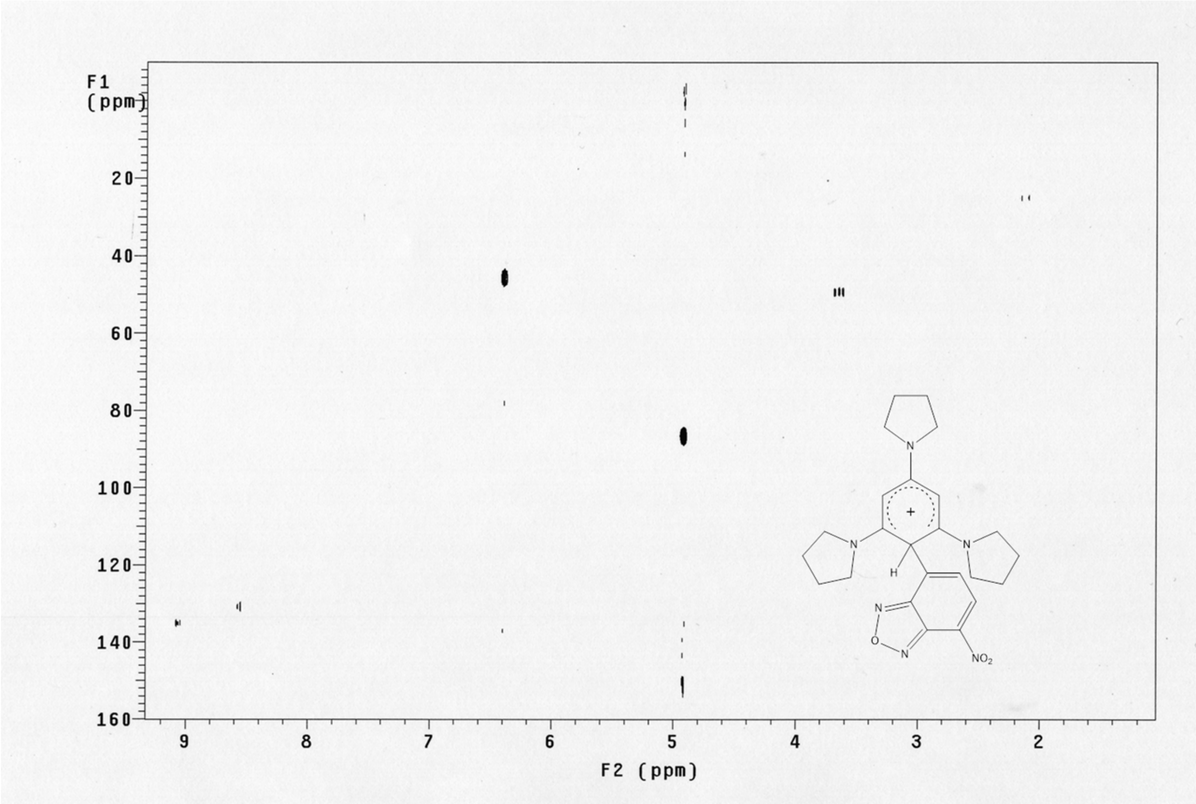


Fig. SI-28. *g*-HSQC spectrum ($CDCl_3$, 100.46 MHz) of compound **20**

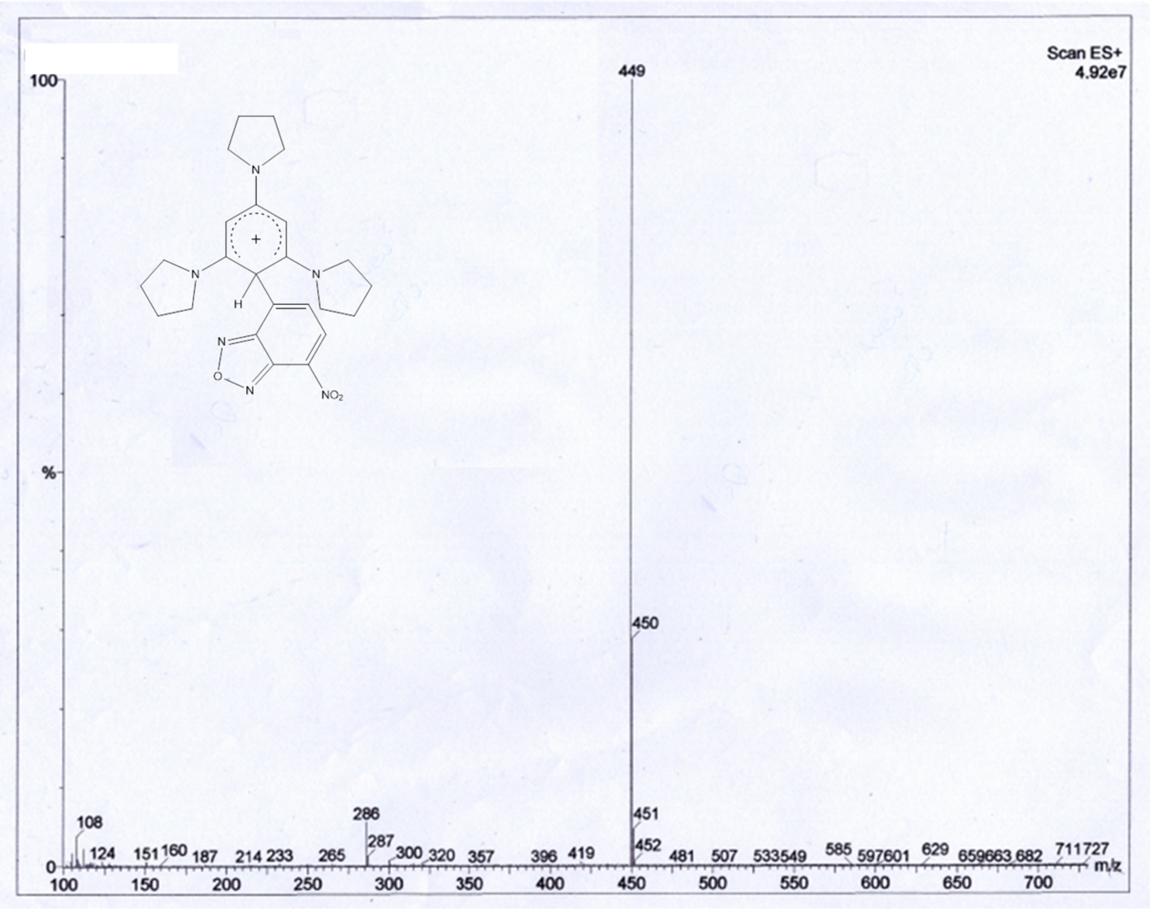


Fig. SI-29. Mass spectrum (ESI$^+$ mode) of compound **20.**

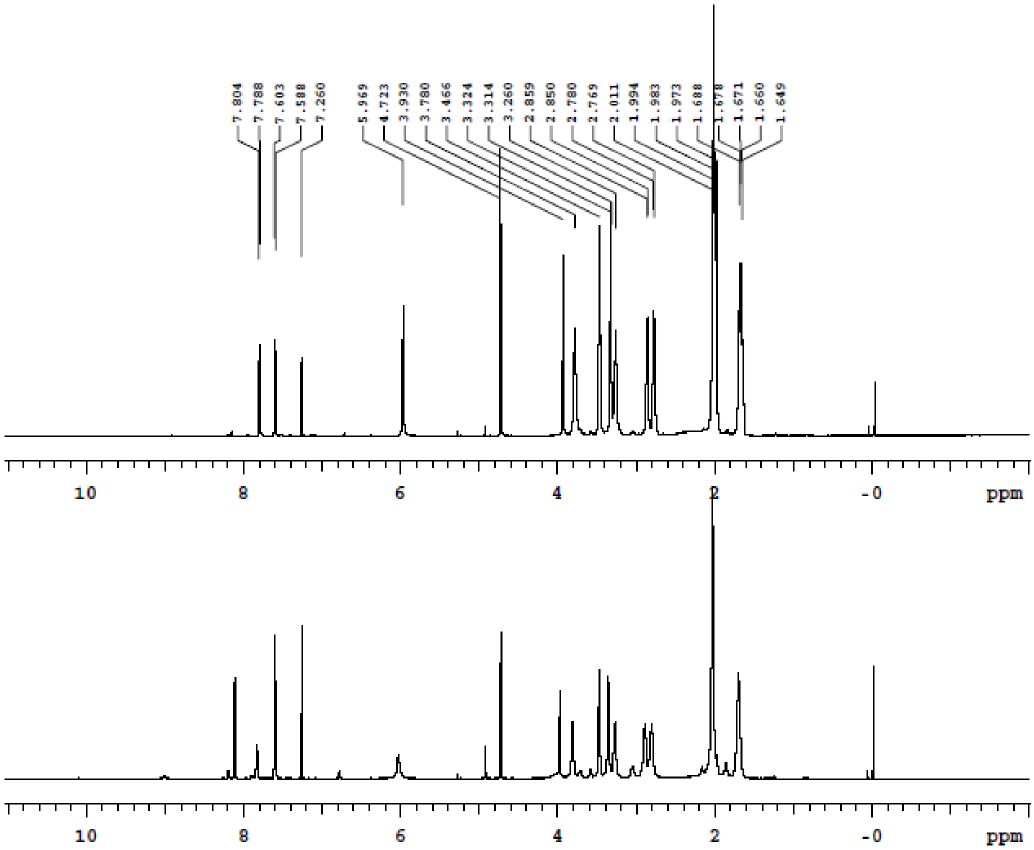


Fig. SI-30. Bottom: ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 °C) of the crude reaction mixture between equimolar amount of **4** and **3** with signals of **16** and **E3** (with typical signals at 4.72 and 3.93 ppm) together with unreacted **4** and traces of **3**. Up: the same reaction mixture after addition of a second equivalent of **3** showing mainly signals of **16** and **E3**.

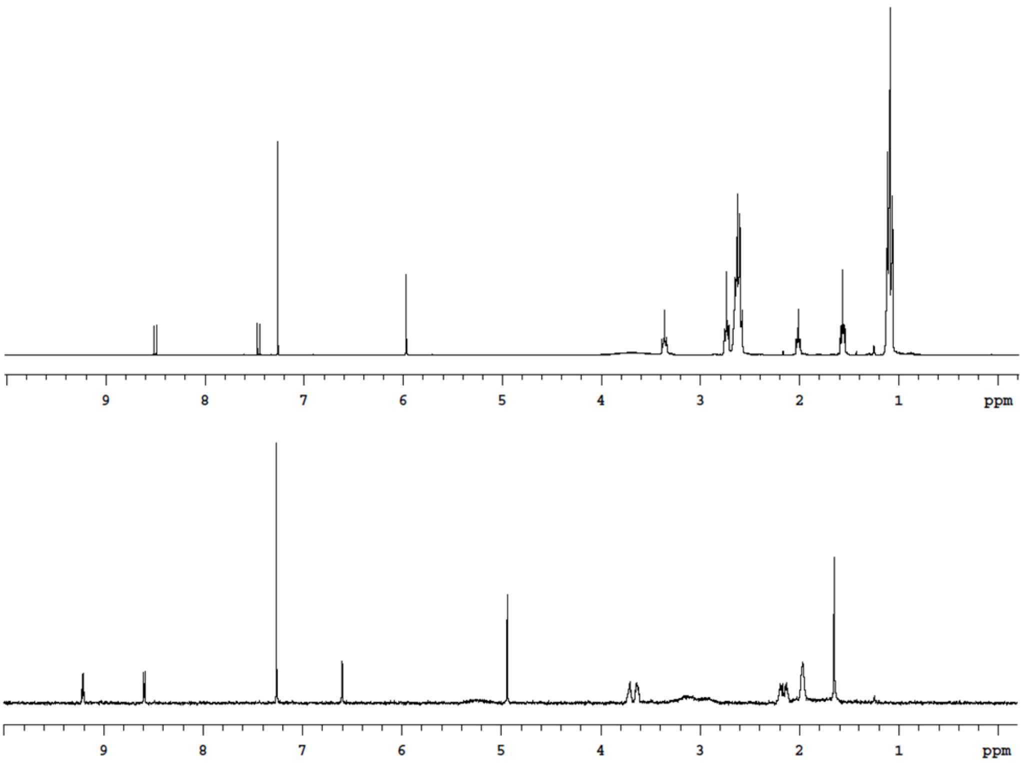


Figure SI-31. ^{1}H NMR spectra of Wheland intermediate **20** (bottom) that, after addition of triethylamine (up) evolved to product **18**.

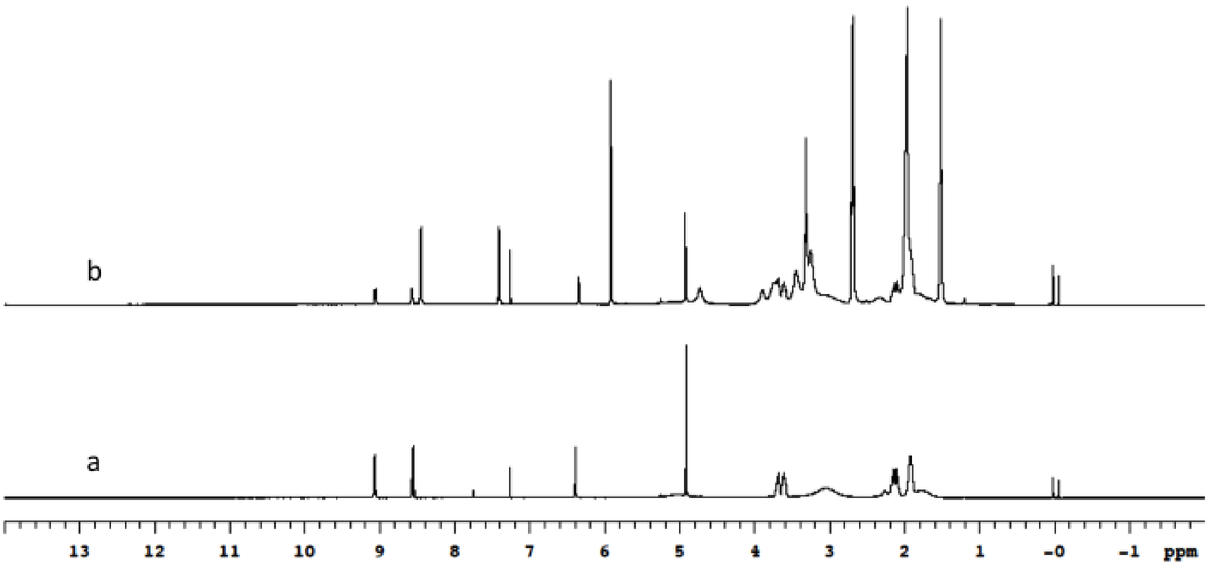
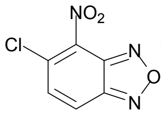


Fig. SI-32 a) ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **20**; b) ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) after addition of 1 equivalent of 1,3,5-tris(*N*-piperidinyl)benzene (**3**) to the crude reaction mixture.

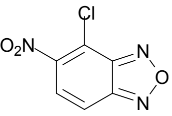
SI-33. Supplementary discussion on the relative reactivity of the electrophiles 4-7

Even if the dissection of inductive and mesomeric effects of the substituents is always difficult and arduous, we attempted to interpret the data reported in main text by considering the two effects separately.



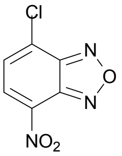
4NO$_2$5ClBFZ

4



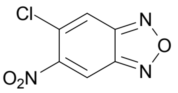
5NO$_2$4ClBFZ

5



7NO$_2$4ClBFZ

6



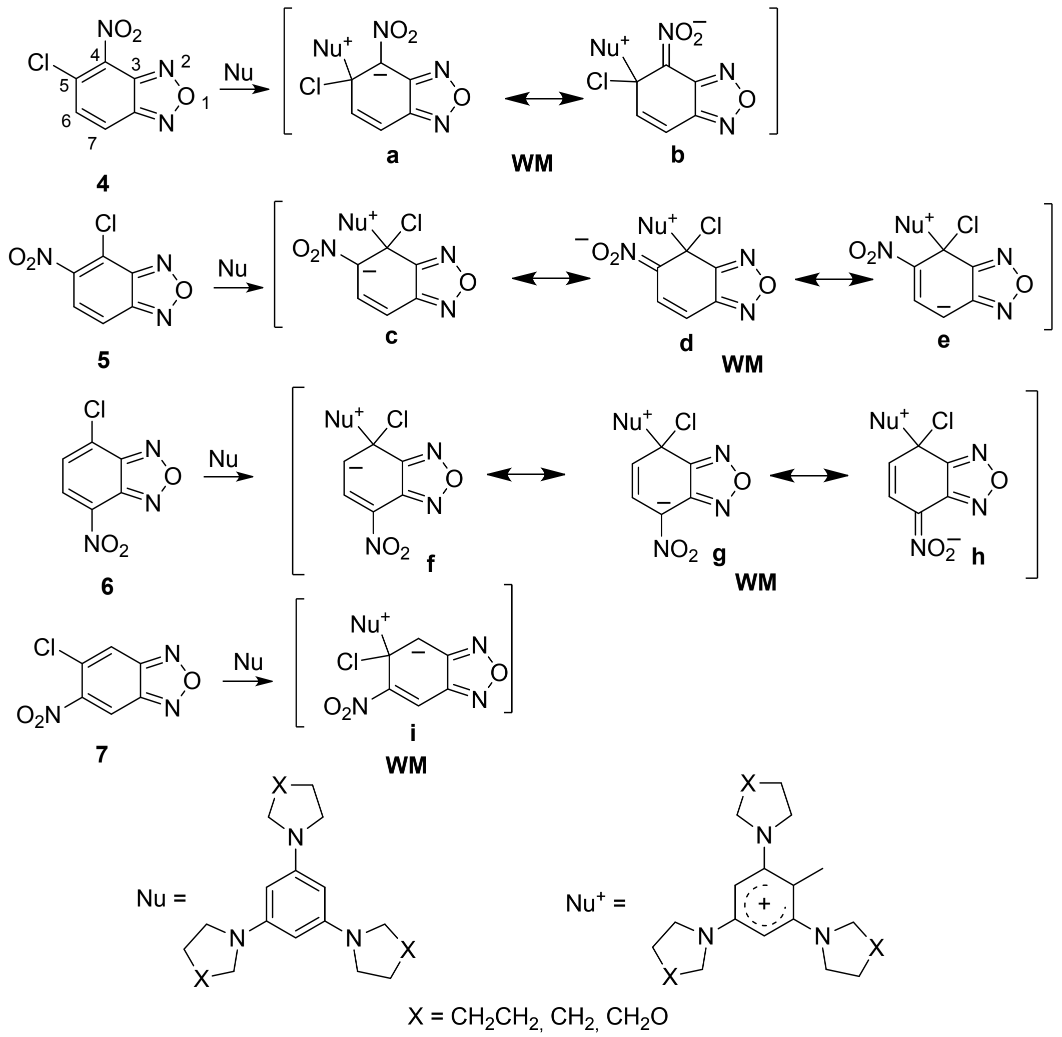
5Cl6NO$_2$BFZ

7

By considering the inductive effect, all reagents **4**–**7** possess chlorine as nucleofuge, thus his electron-withdrawing effect on the reactive center can be disregarded and the discussion can be focused on the effect of the other substituents and of the condensed heterocyclic ring.

Compounds **5** and **6** have the chlorine atom bound to the C-4 carbon atom, adjacent to the carbon atom fused with the furazane ring that, as it has been reported earlier (ref. 48 of the main text) exerts an electron-withdrawing effect greater than that of a nitro group. Thus, the effect of the condensed ring can be considered the same on the two compounds, that differ for the position of the nitro substituent in the homocyclic ring: in **5**, the nitro group is in *ortho* position with respect to the reactive centre (C-4) whereas in **6** the nitro group in *para*-position exerts a minor inductive effect. This might influence the results obtained for **6** with respect to **5** (compare entry 2 with entry 3, and entry 5 with entry 6, in Table 1 of the main text). Moreover, this finding is in line with previously reports on the *ortho/para* effect of the nitro group in S$_N$Ar reaction of halonitrobenzenes and dinitrobenzenes with alkoxides, mercaptides and amines (ref. 49 of the main text). In compounds **4** and **7**, the C-5 carbon atom that will undergo the attack by the nucleophile is adjacent to a carbon atom, C-4 and C-6, respectively, bound to the nitro group but in these cases the heterocyclic ring is far and his electron-withdrawing effect is minor. This might explain the minor reactivity observed for **4** and **7** with respect to **5** and **6**, but the lower difference of reactivity of **7** with respect to **4** and to all other compounds of the series, already observed also for reactions with other nucleophiles (ref. 35, 36 of the main text) cannot be understood on the basis of the only inductive effect. Shifting attention towards mesomeric effects, a comparison of the resonance forms of the σ-intermediate derived from the attack of the nucleophile to the carbon atom bound to the chlorine can be useful.

The resonance structures related to the Meisenheimer moiety of the zwitterionic Wheland-Meisenheimer intermediate (**WM)** formed by S_EAr/S_NAr C-C coupling are shown in Scheme SI-1. In all cases the electronic situation of the heterocyclic ring is ignored, being it common to all structures.



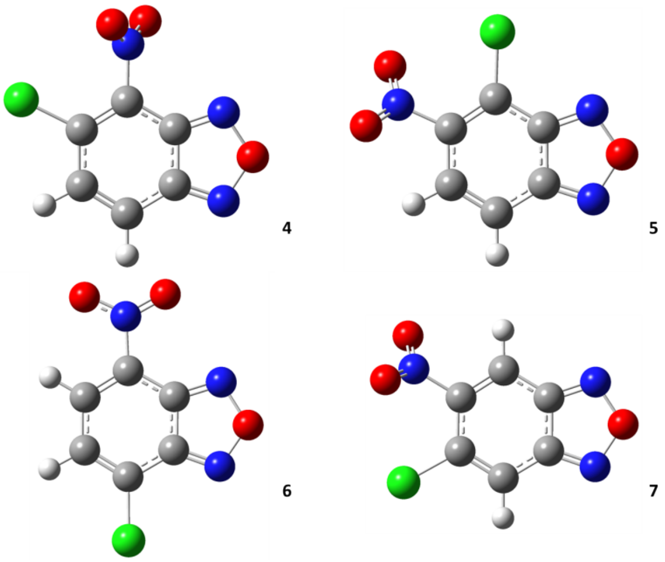
Scheme SI-1. Schematic representation of the canonical forms involving **4-7** in a S_NAr reaction

From an overview of canonical forms the possibility to have more resonance structures in case of electrophiles **5** and **6** with respect to **4** is evident. The lowest reactivity of **7** is related to the C5-C6 single bond that cannot permit charge delocalization by the nitro group. Intermediates deriving from **5** and **6** admit the same number of resonance structures, and the major reactivity of **5** with respect to **6** might be due to the different inductive effect of the nitro group in **5**. The major reactivity observed for **4** with respect to **6** can also be due to an important contribute of the inductive effect. These considerations agree with the reactivity order observed along the benzofurazan series.

SI-34. Supplementary theoretical data

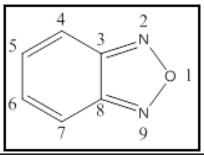
The importance of the inductive effect discussed above for compounds **4-7** was confirmed by some theoretical calculations that was optimized in gas phase with DFT at the B3LYP/6-311+G(d,p) level of theory,[1-4] known to produce reliable geometries and frequencies of the stationary points, with the Gaussian 09 program package (Rev. A.02).[5] Figure SI-33 shows the optimized structure of compounds **4-7** that reveals a non-planar structure for **4**, **5,** and **7** in which, because of the *ortho* position between the two substituents, the nitro group rotates and puts the oxygen atoms out of plane to reduce steric hindrance.

Figure SI-33. Structure of compounds 4-7 optimized in gas phase at the B3LYP/6-311+G(d,p) level of theory



In Table SI-1 are reported the calculated bond lengths for compounds **4-7**.

Table SI-1. Bond lengths of compounds **4-7** calculated at B3LYP/6-311+G(d.p) level of theory.

Compound	Substituent	Bond Lenght (Å)										
		C3-C4	C4-C5	C5-C6	C6-C7	C7-C8	C8-C3	O1-N2	N2-C3	C3-C8	C8-N9	N9-O1
4	5-Cl, 4-NO_2	1,424	1,367	1,441	1,362	1,424	1,434	1,360	1,317	1,434	1,316	1,366
5	4-Cl, 5-NO_2	1,430	1,372	1,437	1,361	1,424	1,434	1,365	1,318	1,434	1,317	1,359
6	4-Cl, 7-NO_2	1,429	1,366	1,427	1,367	1,427	1,440	1,355	1,316	1,440	1,319	1,366
7	5-Cl, 6-NO_2	1,420	1,361	1,447	1,365	1,422	1,432	1,367	1,319	1,432	1,318	1,360

From data of Table SI-1 it has to be noted the marked difference between the bond lengths of the six-membered ring, which go from 1,36 Å for C4-C5 and C6-C7 bonds to 1,44 Å for the others. These values are similar to those obtained from crystallographic data of some compounds containing the benzofurazan moiety [ref. 25 in main text] and confirm the partial dienic character of the carbocyclic ring of benzofurazan derivatives [ref. 2,33,35 of main text].

Moreover, as reported in the main text, the peculiar reactivity of nitrobenzofurazan derivatives is attributed to the poorly aromatic character of the six-membered ring which, sometimes, acts as a nitroalkene fragment. The best way to computationally investigate this behavior is to simply compare the bond lengths in the aromatic ring and use the most assessed methods for the evaluation of aromaticity.

Aromaticity of compounds **4–7** was evaluated using two quantitative criteria: the geometry-based Harmonic Oscillator Model of Aromaticity index (HOMA)[6] and Nucleus-Independent Chemical Shift (NICS).[7]

Bond lengths values, reported in Table 2 of the main text, were used to calculate the HOMA index, an aromaticity index based on the optimal bond length which attributes a value close to 1 for aromatic compounds and values close to 0 for non-aromatic compounds. The HOMA indexes calculated for compounds **4-7** and reported in Table SI-2 show values of about 0,6 and 0,4 for the six- and the 5-membered ring, respectively. This indicates a low aromaticity in both rings, which confirms the reactivity of the benzene ring but is unconsistent with the known aromaticity of the furazan ring. However, it is important to remember that HOMA is an index based on the mean length of bonds derived from benzenoid homocyclic aromatic compounds which is 1,388 Å. For the currently considered furazan rings, which contain three heteroatoms with higher electronegativity with respect to the carbon, it is expected to have, as also shown in Table SI-1, shorter bond lengths with respect to the one in carbon-carbon bonds in benzenoid compounds. Hence the HOMA index for this kind of heteroatomic rings could bring to erroneous evaluation of aromaticity.

In Table SI-1 we also reported the NICS values calculated at GIAO-B3LYP/6-311+G(d,p) level of theory using computed geometries. The NICS index is the negative absolute magnetic shielding in the center or above the center of the ring and represents the theoretical measure of the diamagnetic ring current. According to Schleyer [7a] the more negative the NICS value, the more aromatic the ring. The NICS(0) and NICS(1) calculation were performed by placing the probe dummy atoms (Bq) at the center of both rings and 1 Å above the plane of the rings respectively. The $\mathrm{NICS}(0)_{zz}$ and $\mathrm{NICS}(1)_{zz}$ indexes were calculated using the component of the magnetic shift tensor in the z direction, perpendicular to the plane of the ring, for the probe atoms at the center and 1 Å above the plane of the rings. These values, if compared with the ones calculated at same level of theory for benzene (NICS(0) = -8,044 ppm; NICS(1) = -9,825 ppm; $\mathrm{NICS}(0)_{zz}$ = -14,495 ppm and $\mathrm{NICS}(1)_{zz}$ = -28,935 ppm), indicate that the five member ring, on the contrary to the HOMA values obtained, is more aromatic than benzene. However, the six member ring, with very low NICSs values, is not to be considered aromatic, hence its reactivity is not to be associated to that of aromatic compounds. All these theoretical data well agree with the experimental data obtained in this work and with those previously reported (see references in the main text) for the same class of compounds.

Table SI-2. HOMA and NICS indexes of compounds **4-7** obtained at GIAO-B3LYP/6-311+G(d,p).

Compound	HOMA		Six member ring (values in ppm)				Five member ring (values in ppm)			
	6-member ring	5-member ring	NICS(0)	NICS(1)	NICS(0)$_{zz}$	NICS(1)$_{zz}$	NICS(0)	NICS(1)	NICS(0)$_{zz}$	NICS(1)$_{zz}$
4	0,63	0,42	-7,286	-7,404	-1,687	-17,352	-15,602	-12,930	-23,592	-33,777
5	0,63	0,42	-7,104	-7,605	-0,827	-15,877	-15,124	-14,038	-20,781	-35,047
6	0,64	0,39	-7,286	-7,900	-1,001	-16,701	-15,432	-14,184	-23,816	-35,273
7	0,62	0,45	-7,312	-7,815	-1,690	-16,960	-15,087	-14,160	-22,826	-35,607

Cartesian coordinates of all structures optimized at B3LYP/6-311+G(d,p)

Compound 4 (5Cl4NO$_2$BFZ)

C	0.97194400	0.90280600	-0.01959700
C	0.20847900	2.12513100	-0.04207300
C	-1.15309700	2.13024200	-0.02396800
C	-1.80848400	0.86661000	0.01299600
C	-1.06191500	-0.35713500	0.01734900
C	0.36126000	-0.31944000	0.00987000
N	-3.09193200	0.57101100	0.04724400
O	-3.13561300	-0.78821200	0.07463200
N	-1.90050000	-1.37098600	0.05777200

Cl	2.70039500	1.05312300	-0.07092200
N	1.11397300	-1.59106900	0.01178400
O	1.82798000	-1.81389800	0.97375600
O	0.94416700	-2.31777400	-0.95177000
H	0.76309800	3.05369600	-0.07486400
H	-1.72199500	3.05030600	-0.03746800

Compound 5 (4Cl5NO_2BFZ)

C	0.96152000	-0.54205600	0.04220000
C	0.42239500	-1.87348600	0.08032900
C	-0.91743400	-2.10945100	0.09976400
C	-1.76709200	-0.96804600	0.05243600
C	-1.22601300	0.35881100	-0.01100400
C	0.18519300	0.58749800	-0.01079500
N	-3.08198700	-0.88132800	0.04476700
O	-3.34087600	0.45718300	-0.02284500
N	-2.21863400	1.22291600	-0.05900400
Cl	0.76916600	2.20309400	-0.12919600
N	2.43950300	-0.46200900	0.03321500
O	2.97322600	0.36342100	0.75300500
O	3.01692800	-1.26186300	-0.69097300
H	1.13253100	-2.68953700	0.09128800
H	-1.32615200	-3.10967600	0.14112000

Compound 6 (4Cl7NO_2BFZ)

C	0.60779800	-1.67692500	0.00000100
C	-0.81507200	-1.78332200	0.00000000
C	-1.60857400	-0.67014400	0.00000000
C	-0.96767000	0.60504600	0.00000000
C	0.46720100	0.72229100	0.00000000
C	1.25201800	-0.47216700	0.00000000
N	-1.49292100	1.81171600	-0.00000100
O	-0.42702100	2.64845300	-0.00000100

N	0.77781300	2.00435300	0.00000000
Cl	-3.33407200	-0.77053100	-0.00000100
N	2.72161300	-0.43592800	0.00000100
O	3.24819600	0.66514200	-0.00000100
O	3.31362700	-1.50946700	0.00000300
H	1.20828000	-2.57729600	0.00000100
H	-1.26720900	-2.76635100	0.00000100

Compound 7 (5Cl6NO$_2$BFZ)

C	0.71811400	-0.53531300	-0.00677000
C	0.61389800	0.90816200	-0.03056300
C	-0.60613100	1.51975200	-0.02553500
C	-1.75555500	0.68332200	0.01397100
C	-1.63593600	-0.74357400	0.01177600
C	-0.35985400	-1.36621500	-0.01030900
N	-3.03575700	0.99857400	0.03585300
O	-3.68446900	-0.20476100	0.05019000
N	-2.84295900	-1.27323600	0.03652400
Cl	2.04796600	1.88400000	-0.15561900
N	2.04871600	-1.18739800	0.06454600
O	2.78968000	-0.82619800	0.96228100
O	2.28089600	-2.06216100	-0.75508200
H	-0.69703400	2.59613600	-0.06826300
H	-0.24446100	-2.44156300	-0.01919500

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