Supplementary Material

The synthesis of new functionalized 1,3,5-triazine-based stable bi- and trinitroxides of the 2,5-dihydroimidazole series

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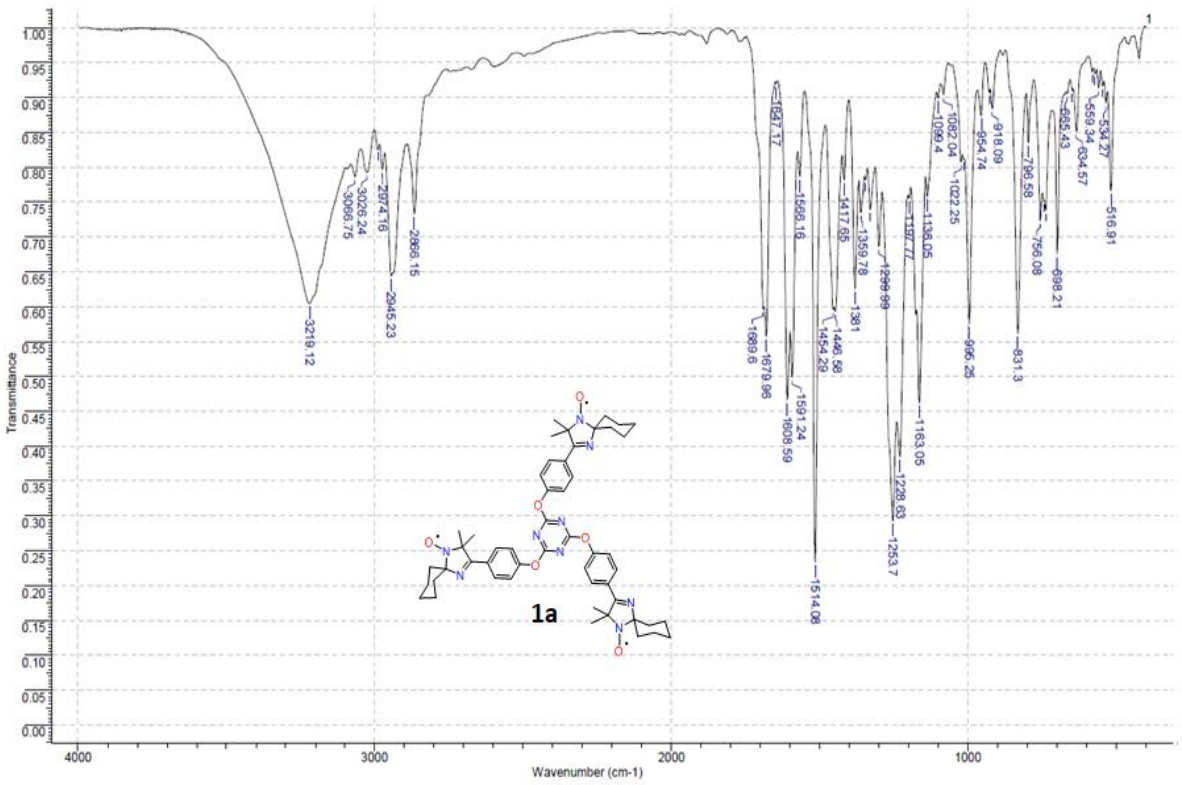
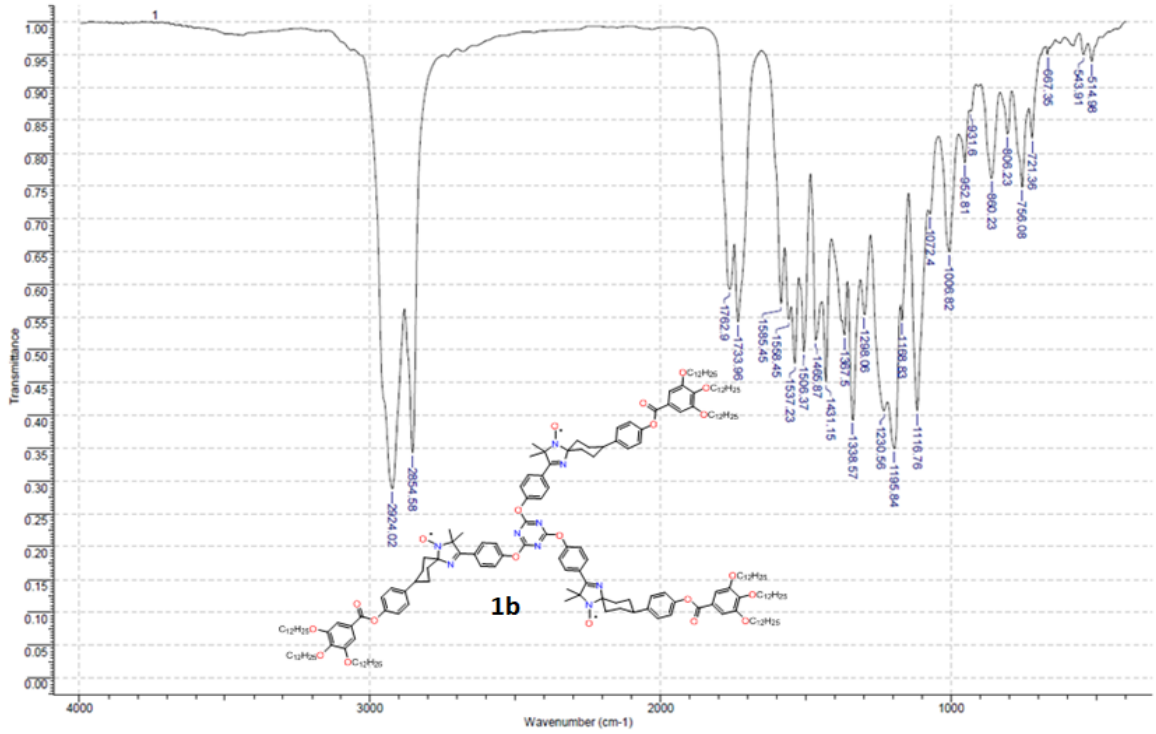
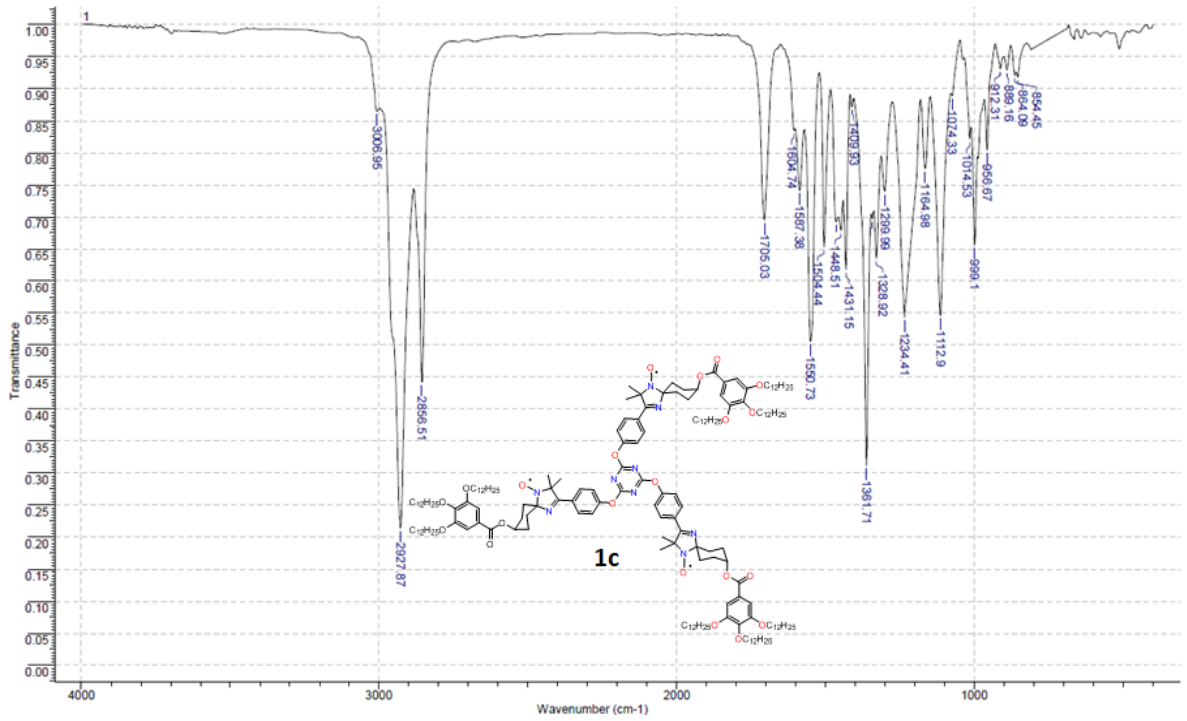
IR spectra



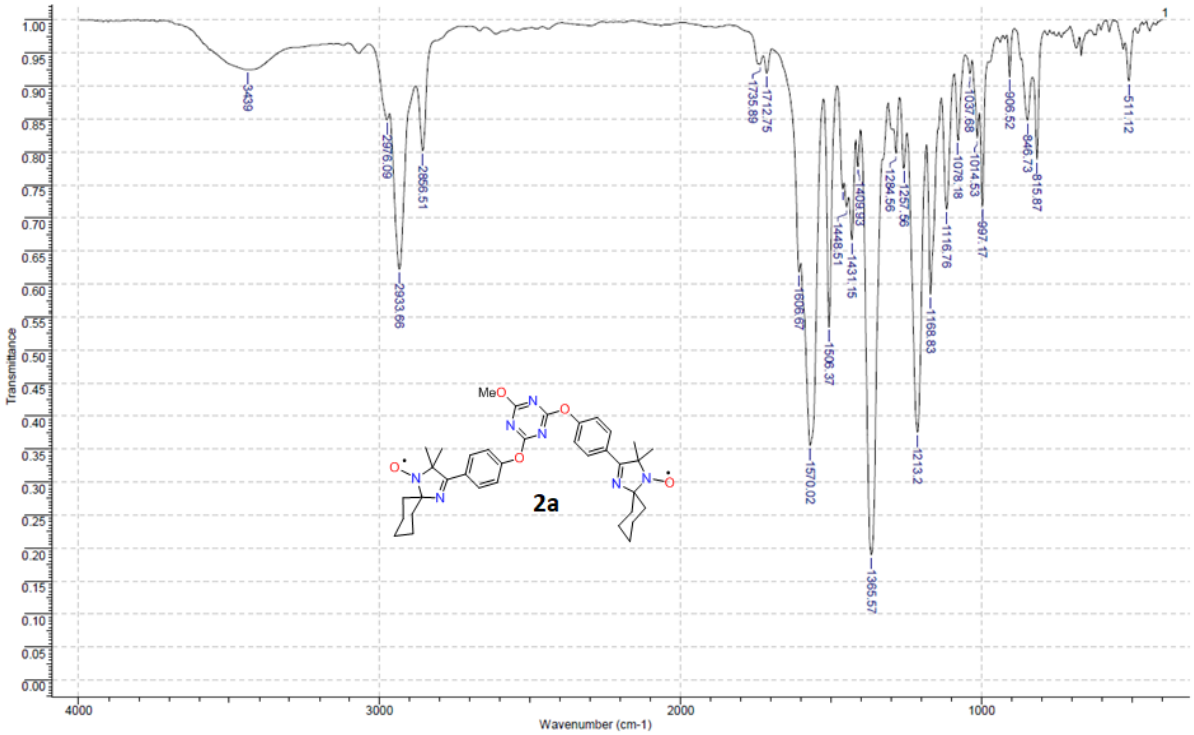
Spectrum 1. IR (KBr) spectrum of compound **1a**



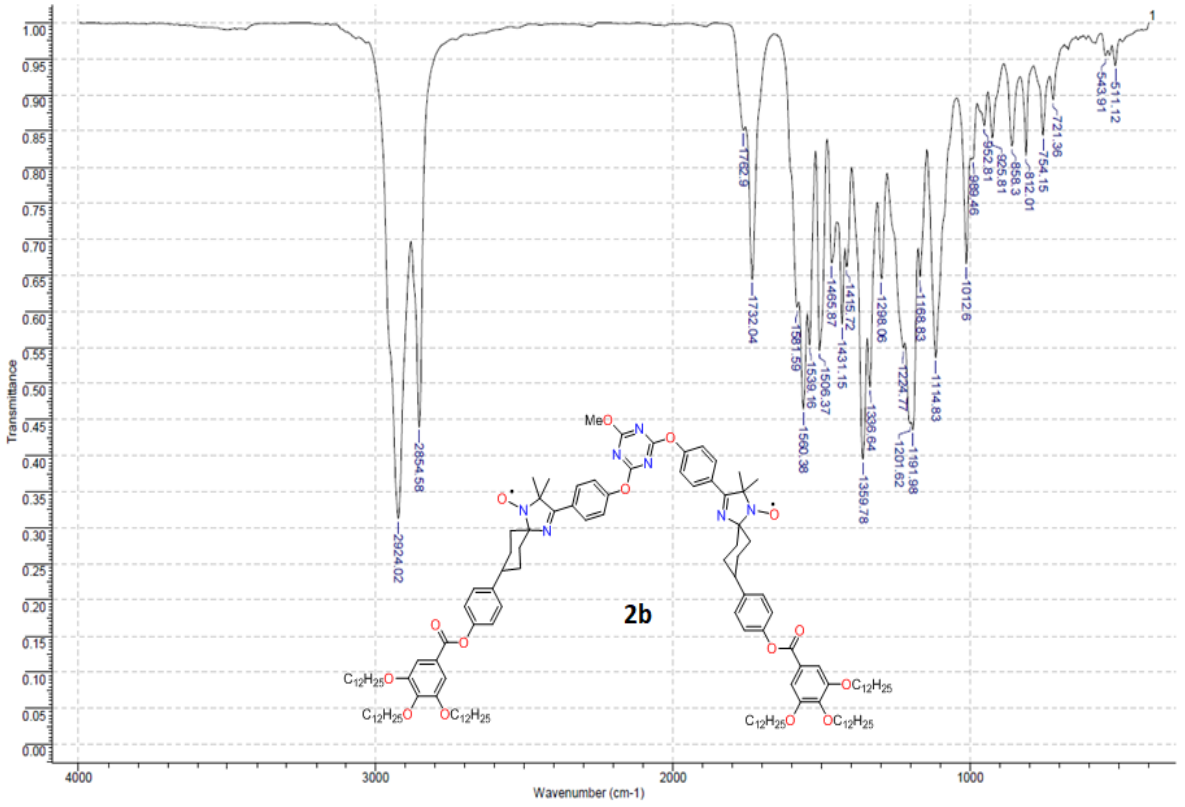
Spectrum 2. IR (KBr) spectrum of compound **1b**



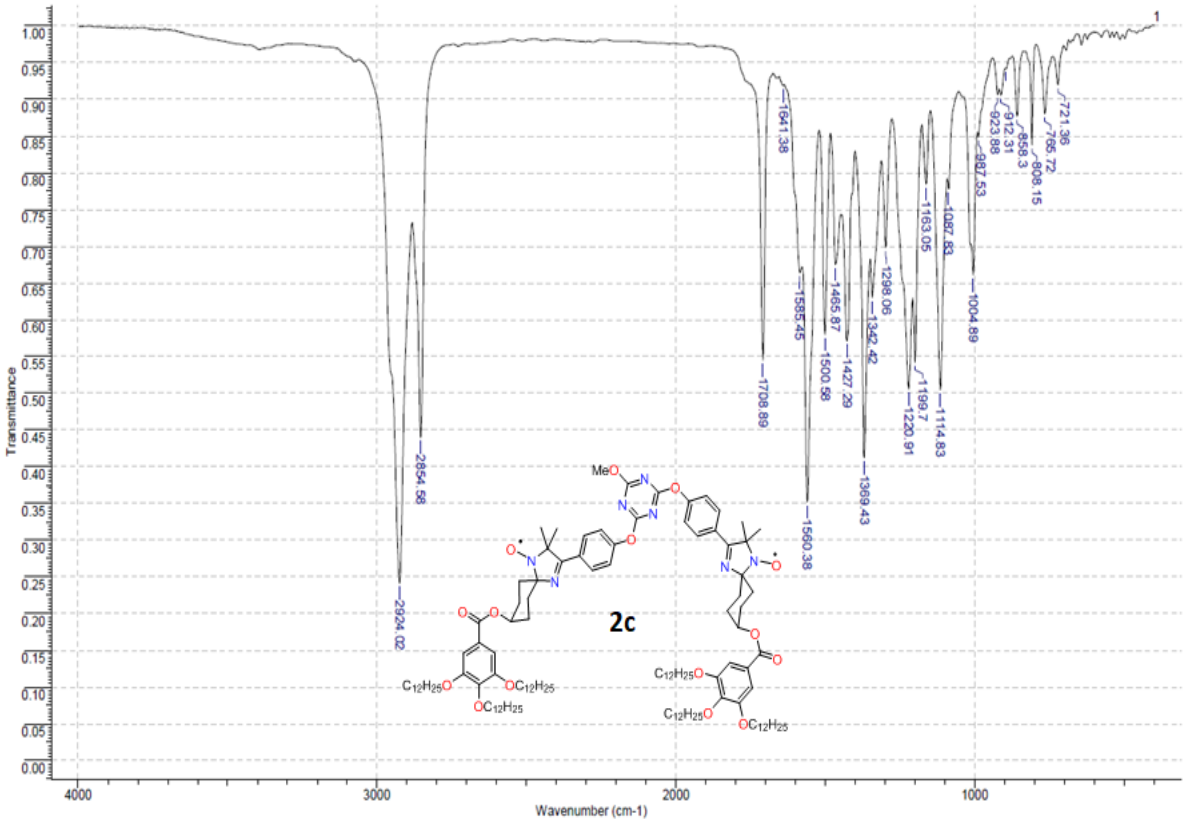
Spectrum 3. IR (KBr) spectrum of compound **1c**



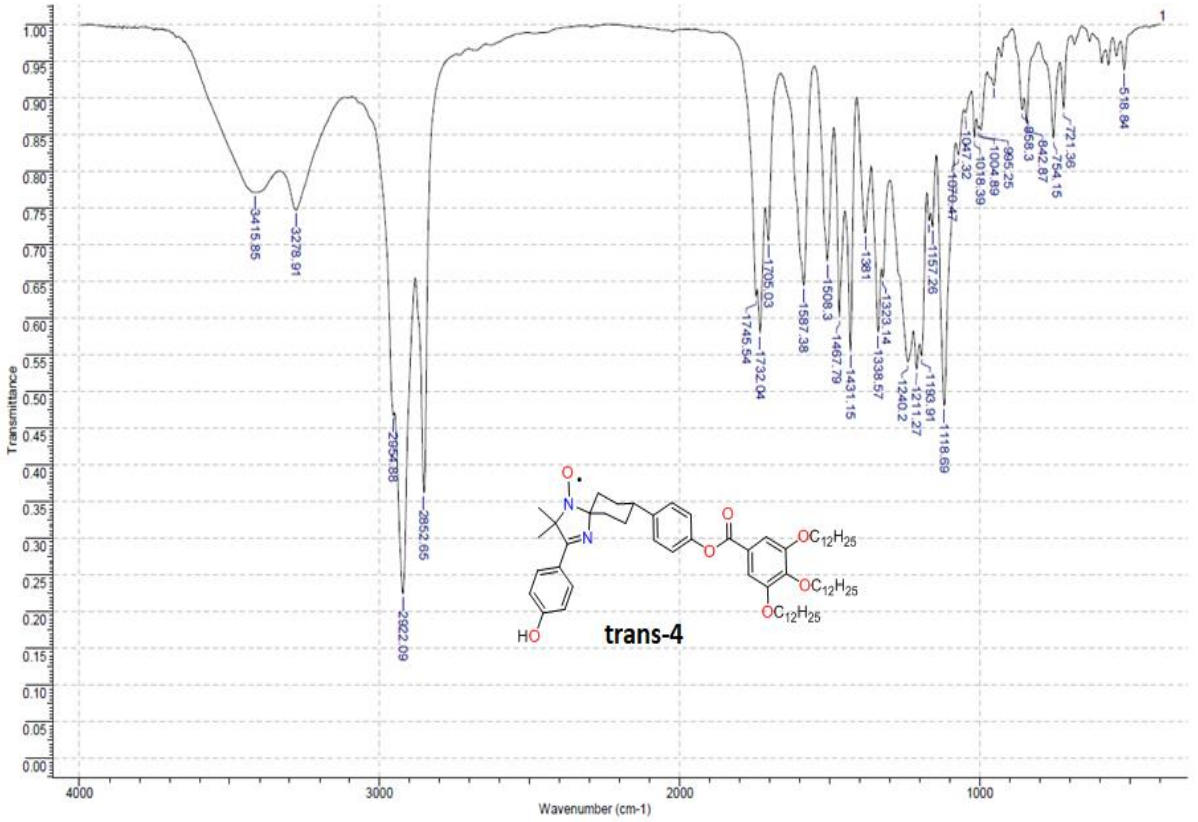
Spectrum 4. IR (KBr) spectrum of compound **2a**



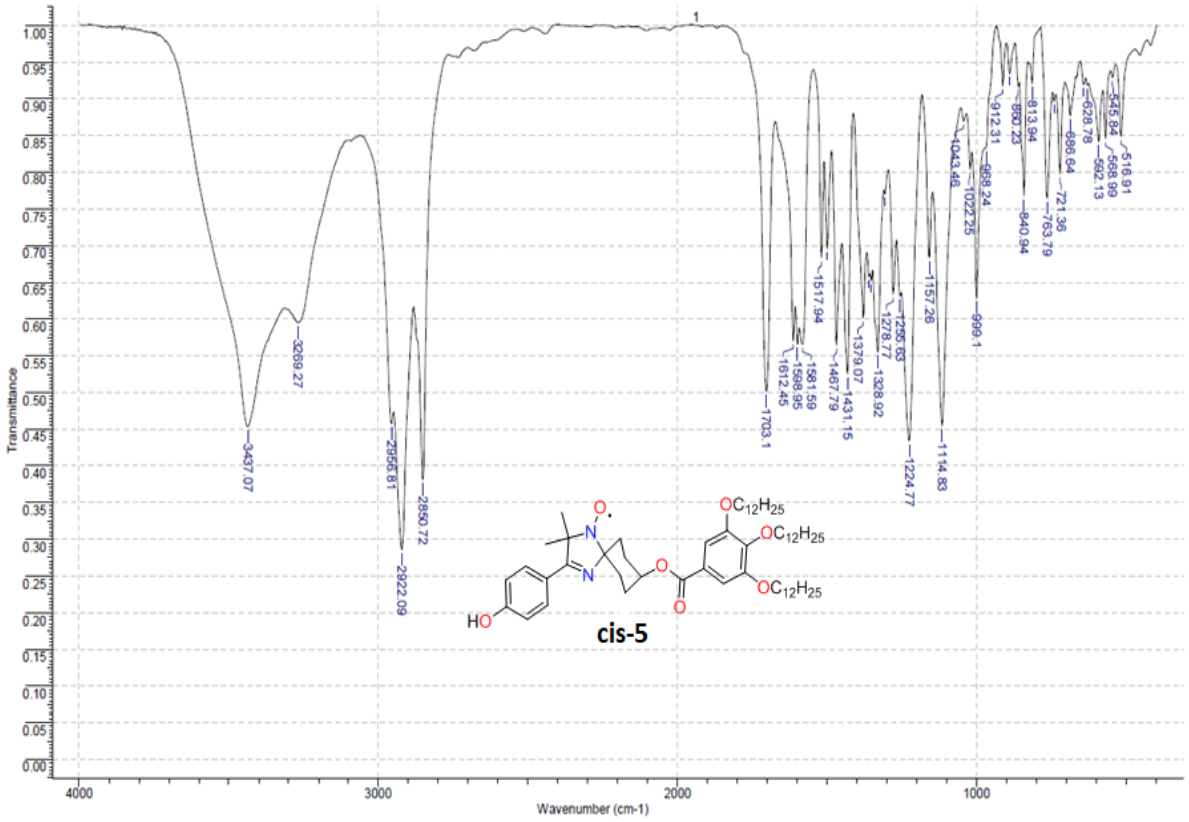
Spectrum 5. IR (KBr) spectrum of compound **2b**



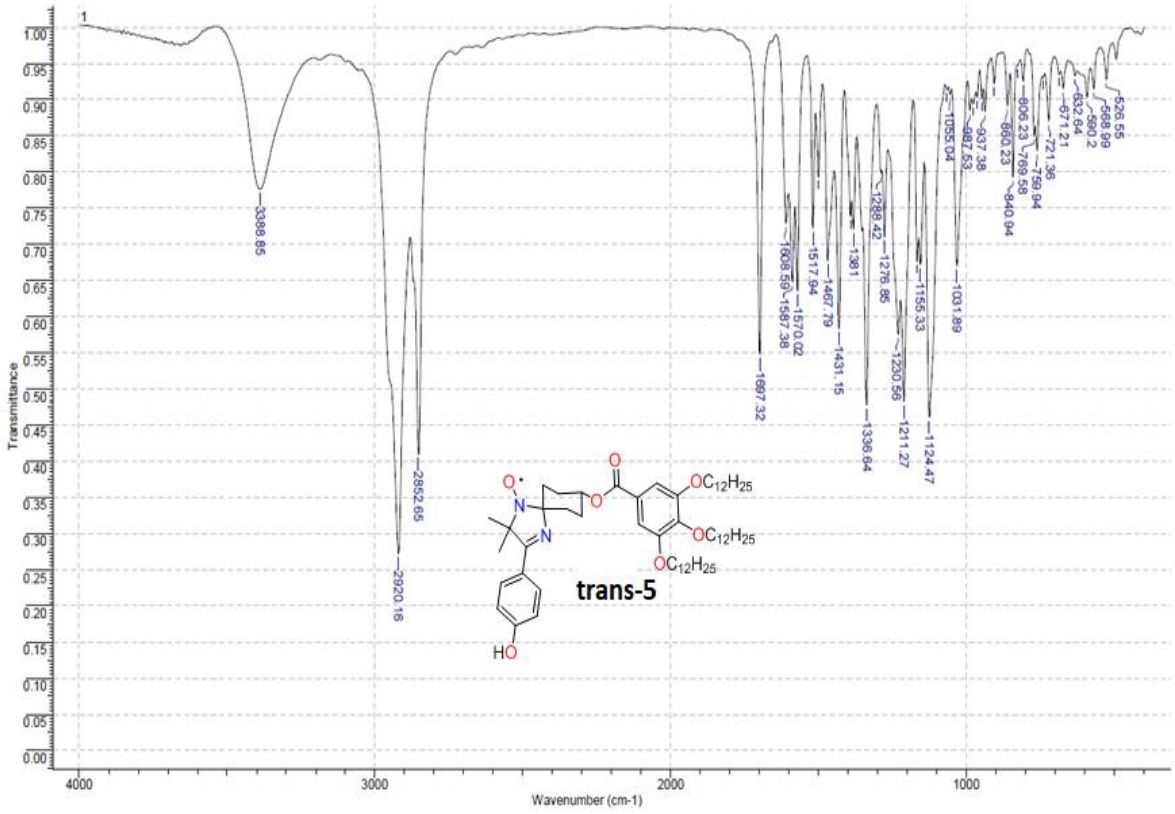
Spectrum 6. IR (KBr) spectrum of compound **2c**



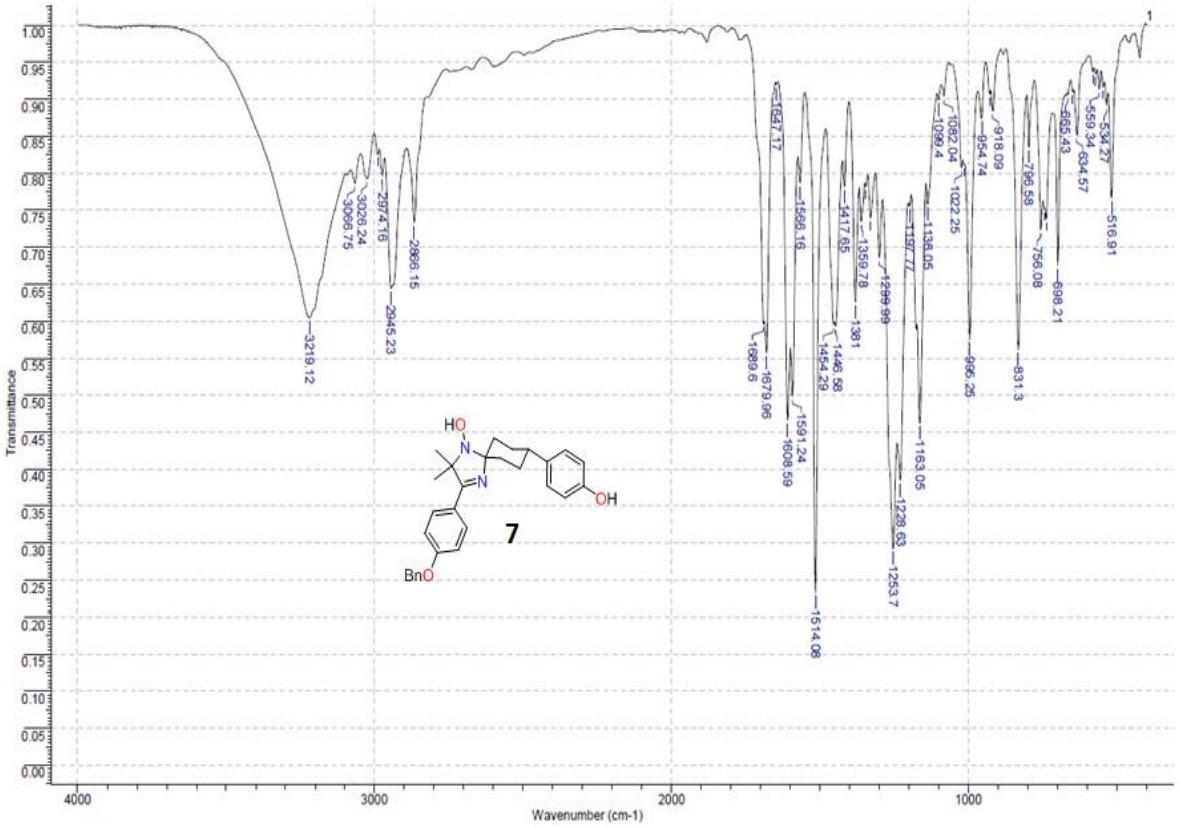
Spectrum 7. IR (KBr) spectrum of compound **trans-4**



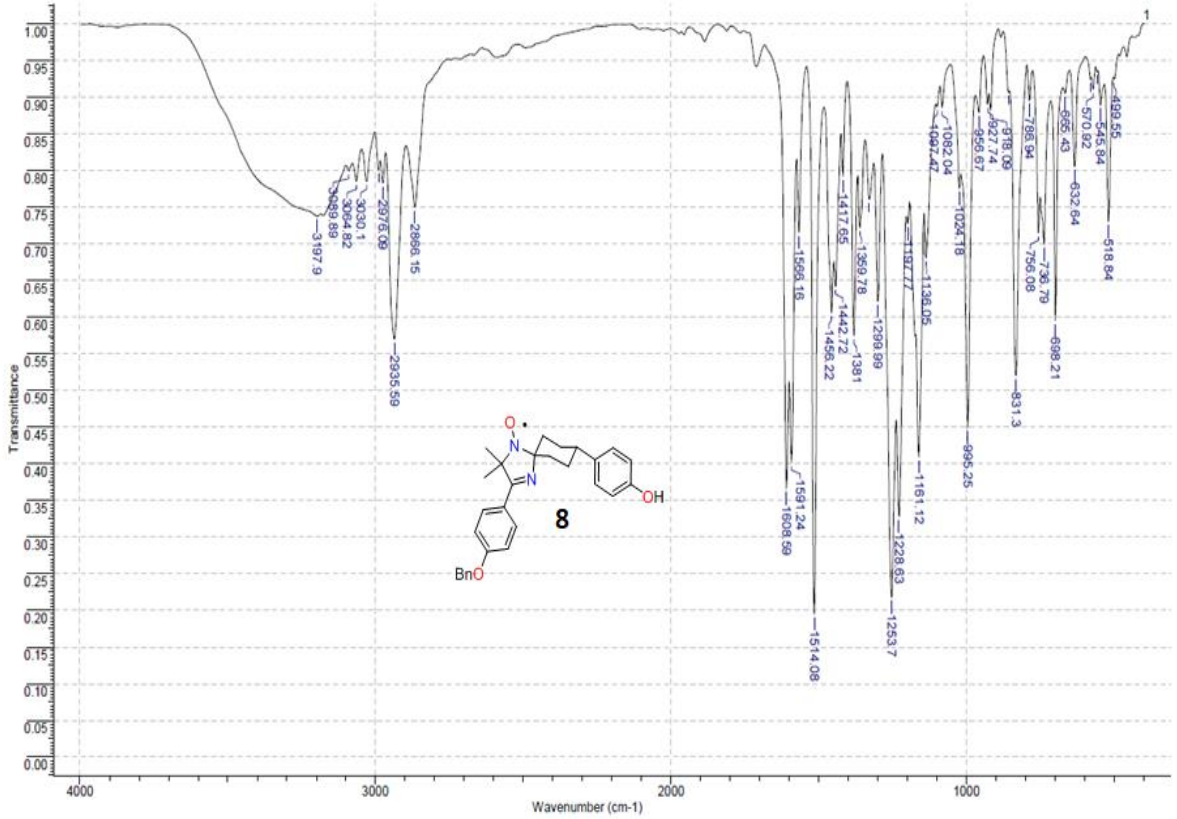
Spectrum 8. IR (KBr) spectrum of compound **cis-5**



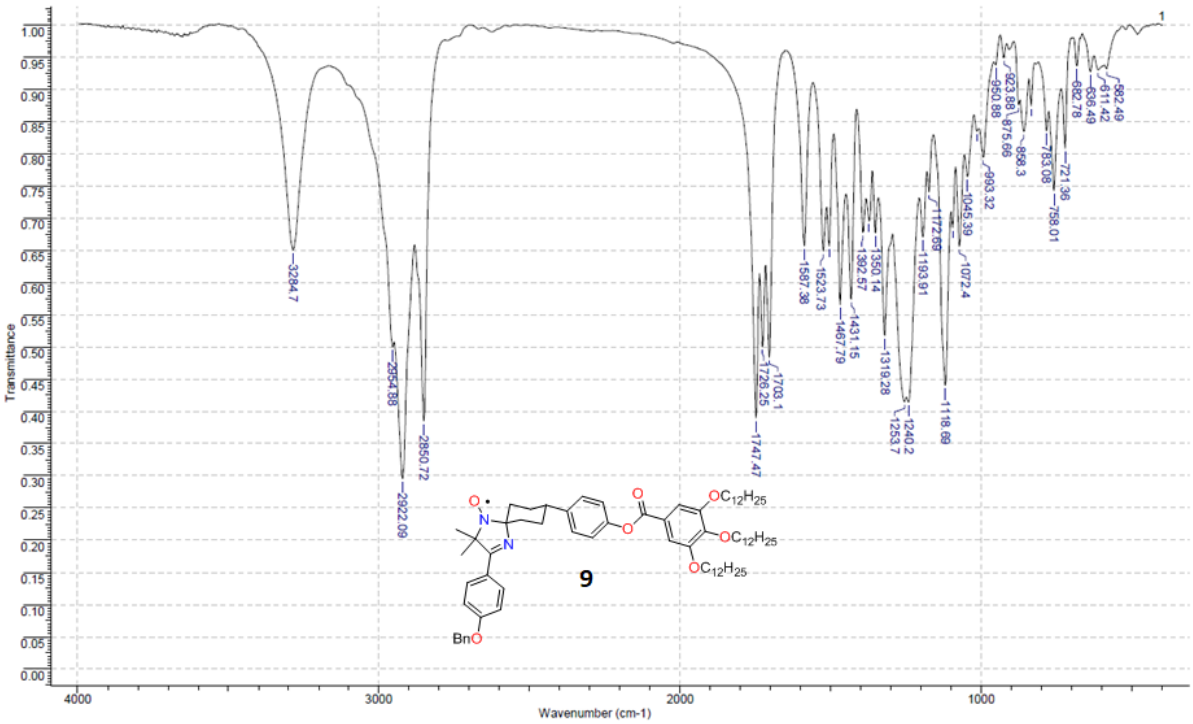
Spectrum 9. IR (KBr) spectrum of compound **trans-5**



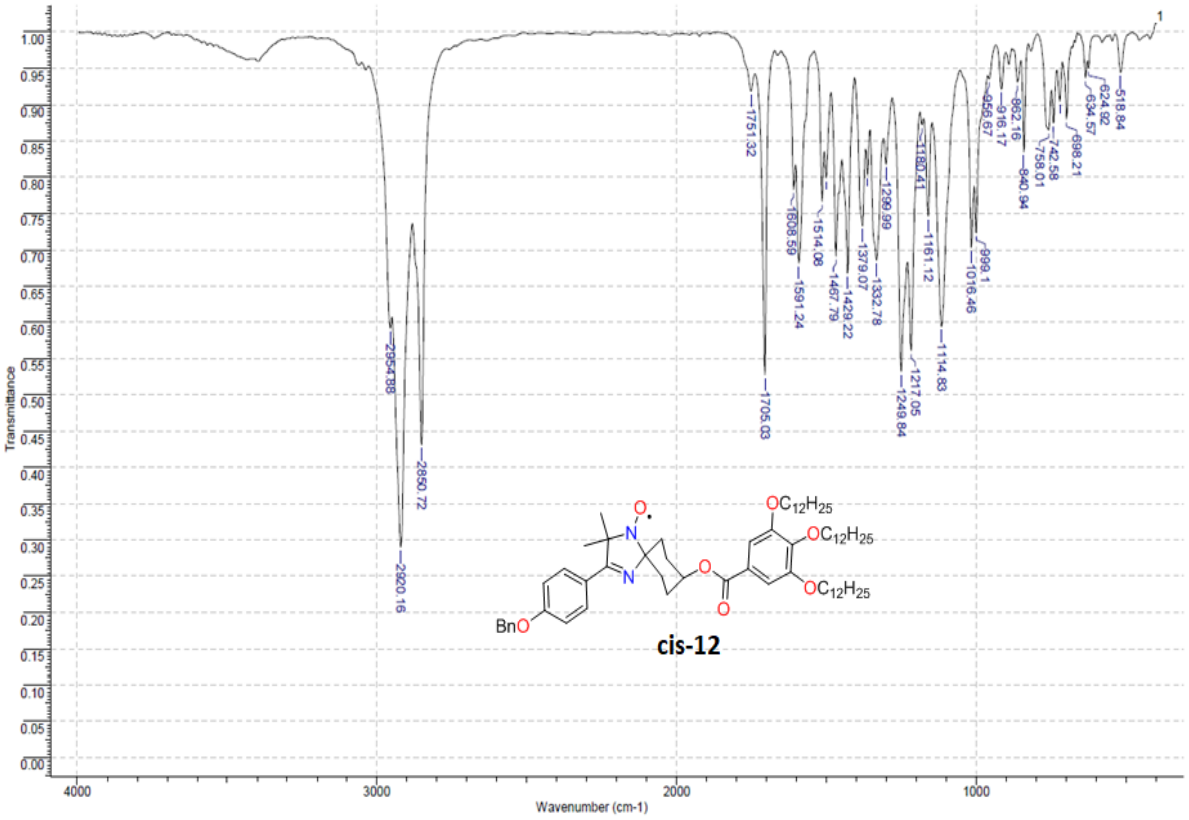
Spectrum 10. IR (KBr) spectrum of compound **7**



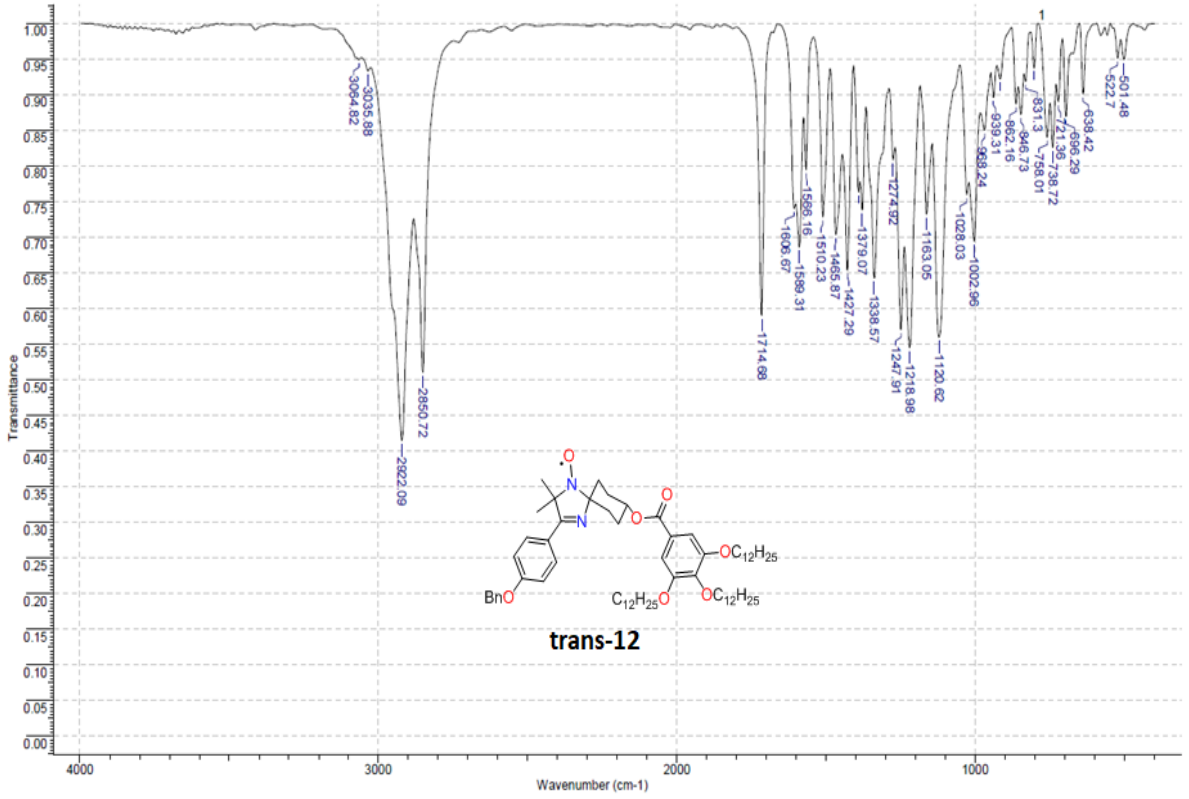
Spectrum 11. IR (KBr) spectrum of compound **8**



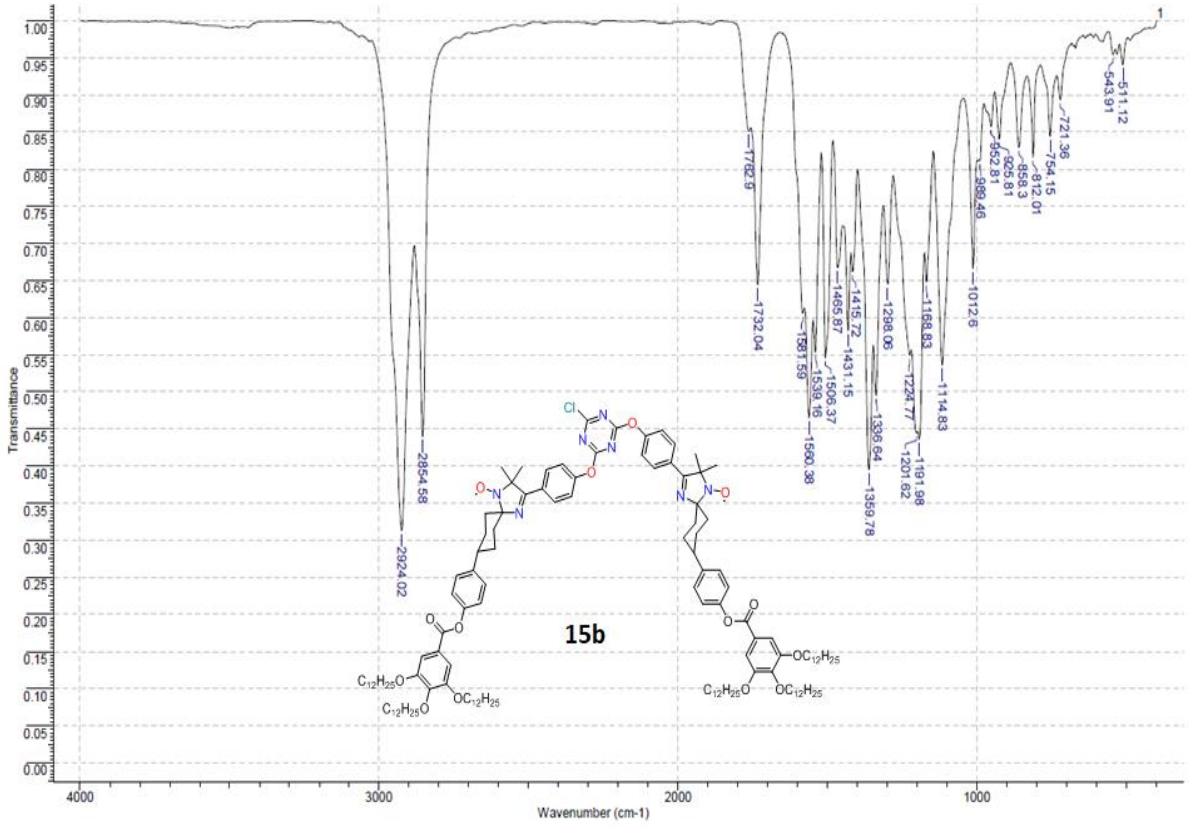
Spectrum 12. IR (KBr) spectrum of compound **9**



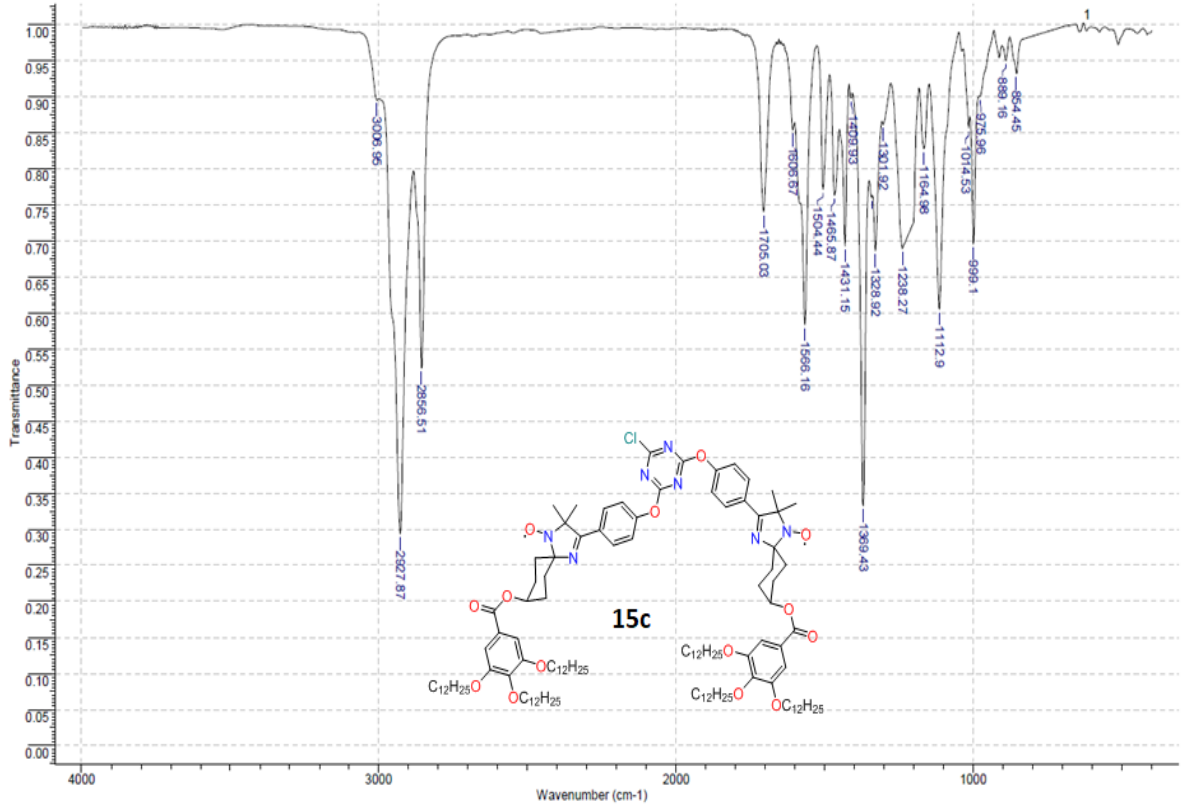
Spectrum 13. IR (KBr) spectrum of compound **cis-12**



Spectrum 14. IR (KBr) spectrum of compound **trans-12**

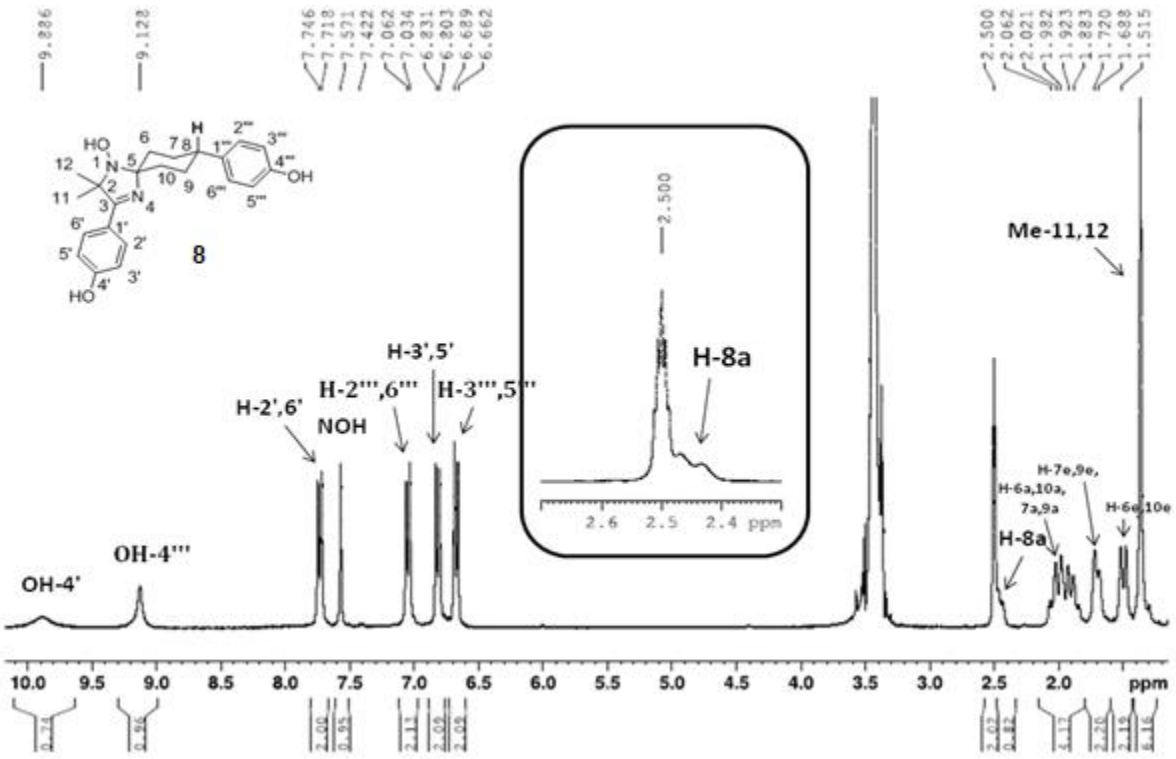


Spectrum 15. IR (KBr) spectrum of compound **15b**

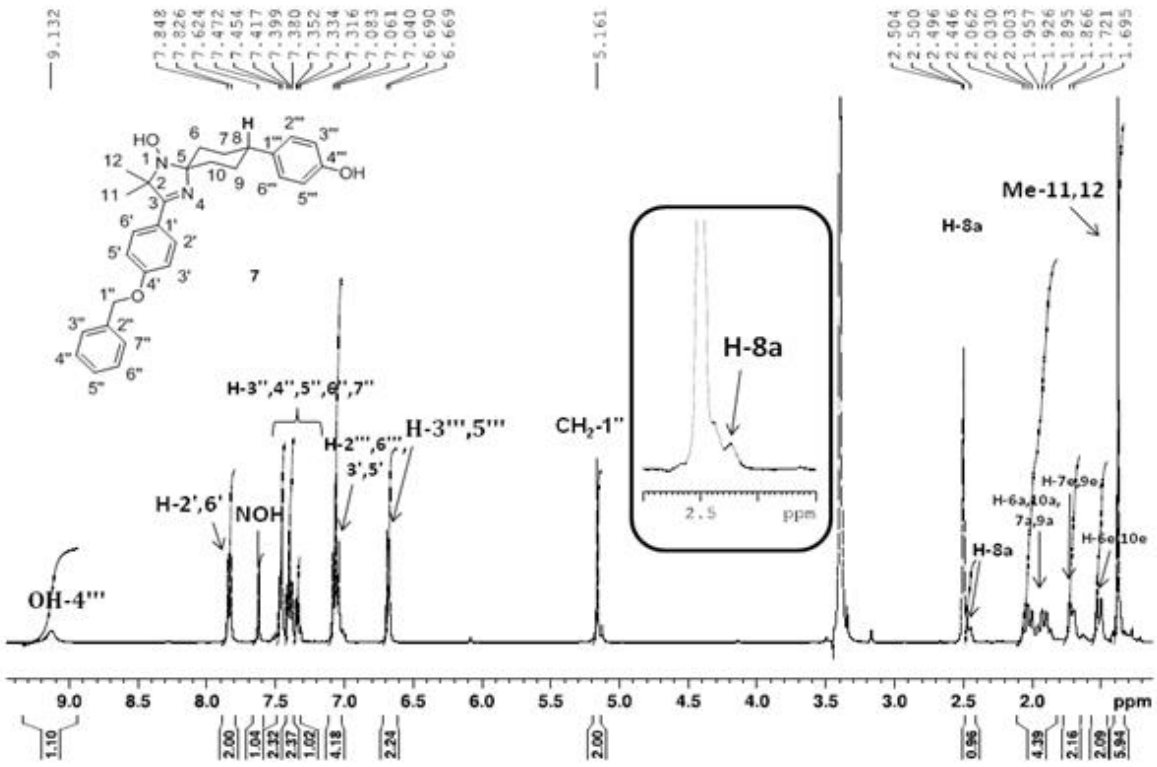


Spectrum 16. IR (KBr) spectrum of compound **15c**

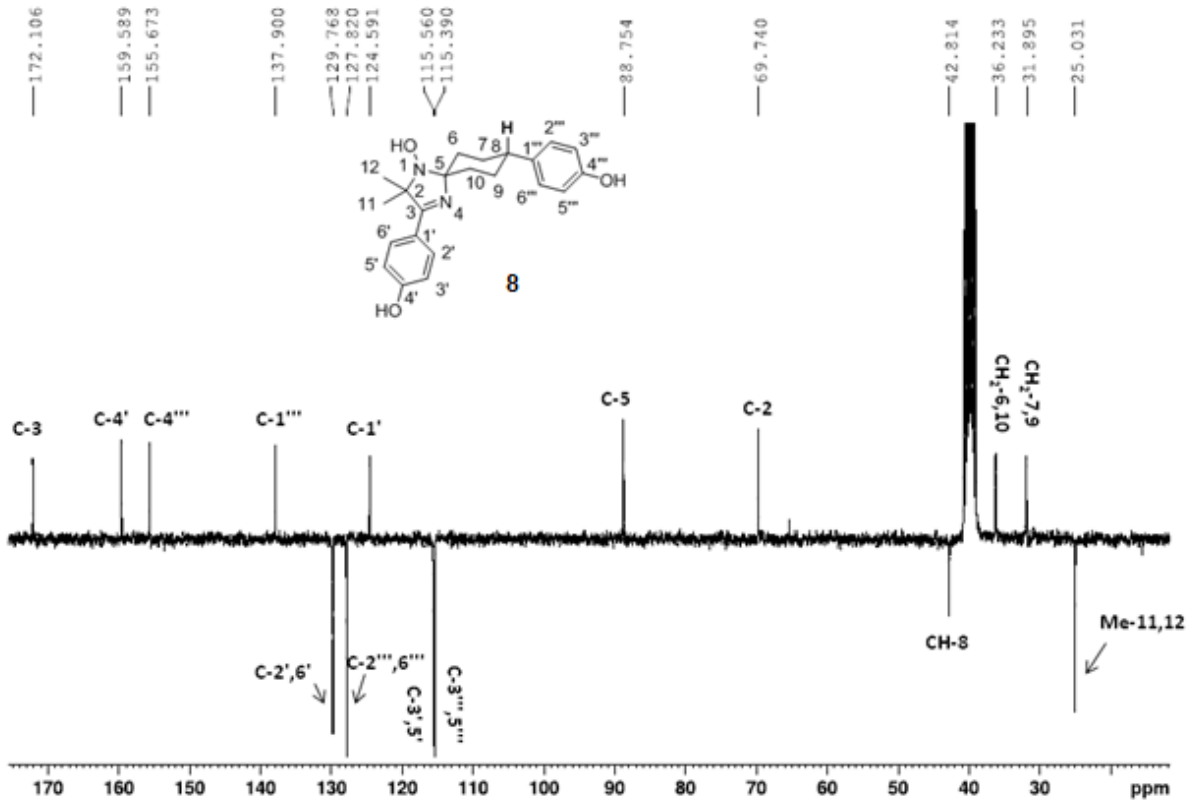
NMR spectra



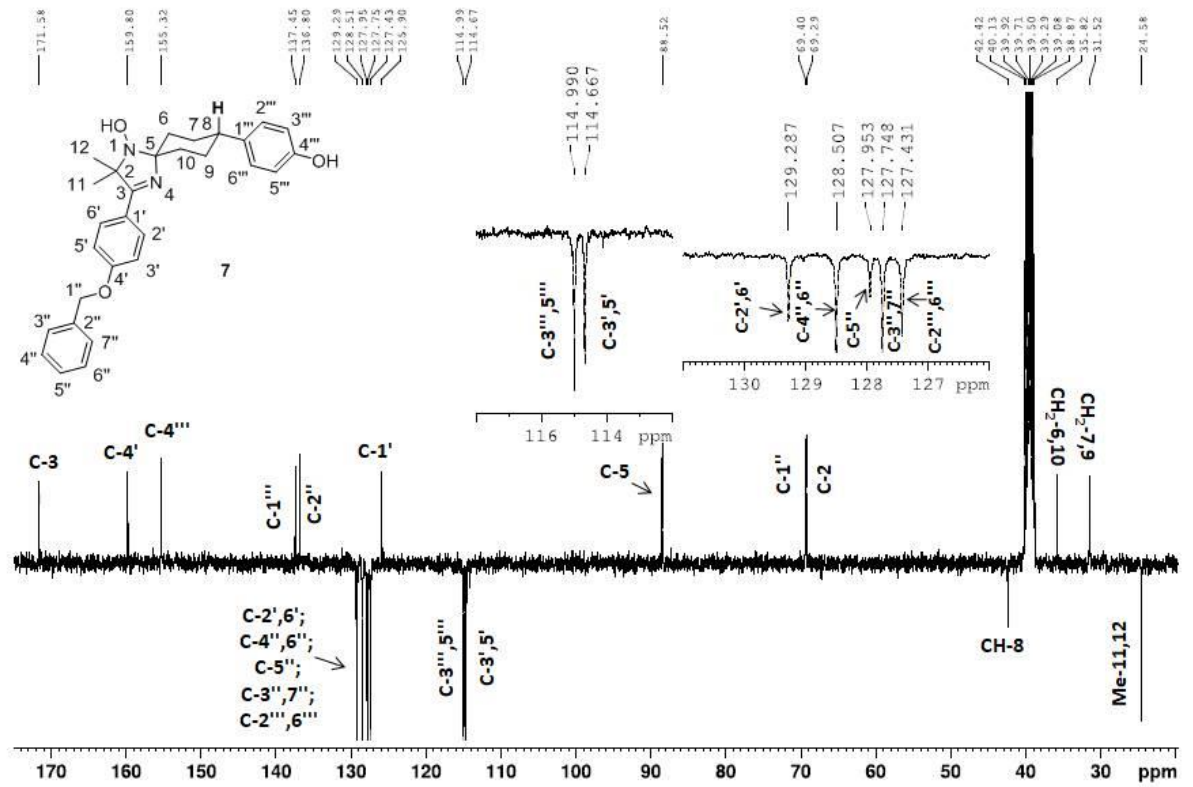
Spectrum 17. ^{1}H NMR (DMSO-d_6) spectrum of compound **8**



Spectrum 18. ^{1}H NMR (DMSO-d_6) spectrum of compound **7**

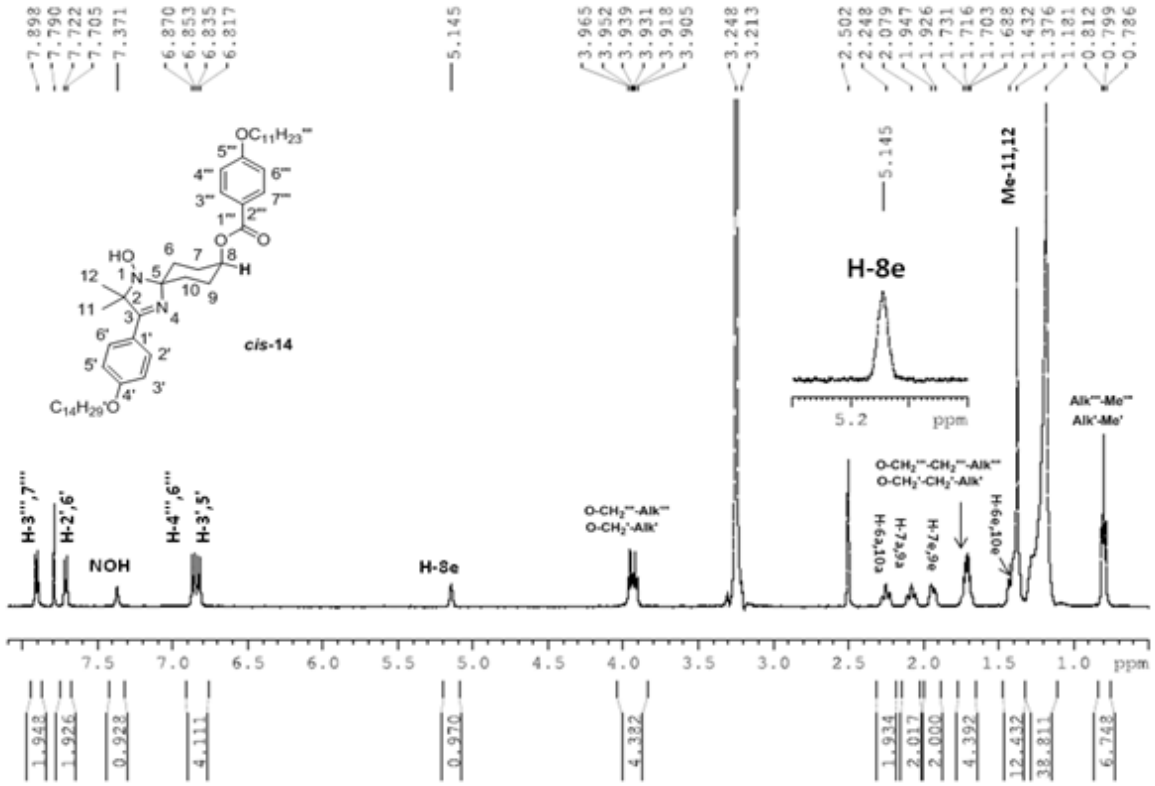


Spectrum 19. ^{13}C NMR (DMSO-d_6) spectrum of compound **8**

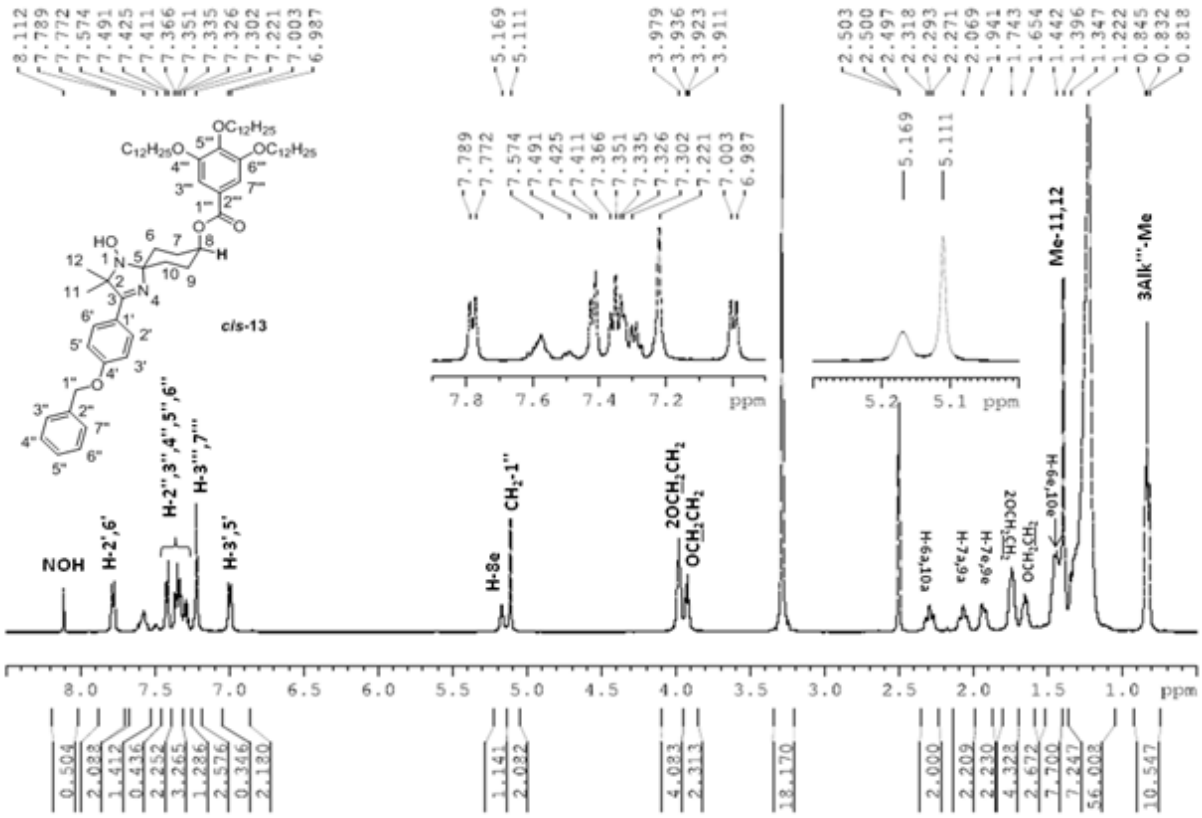


Spectrum 20. ^{13}C NMR (DMSO-d_6) spectrum of compound **7**

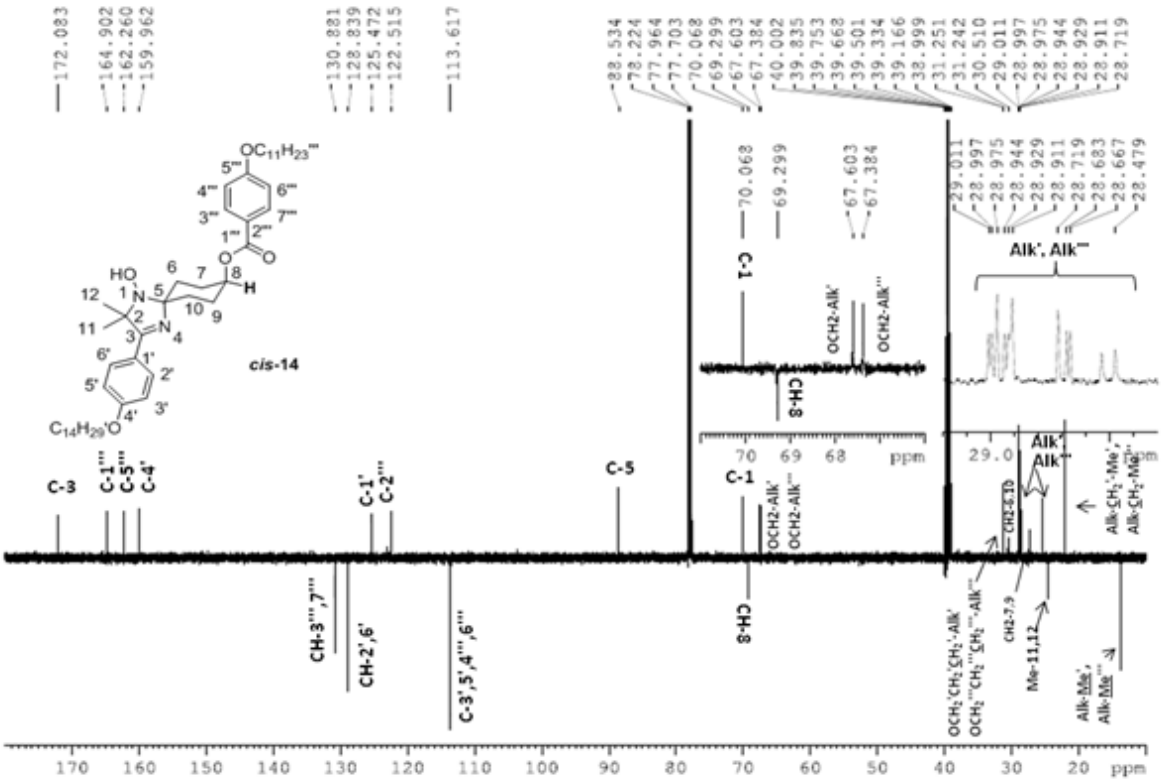
Spectra 17-20 represent ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra recorded for the DMSO-d_6 solutions of **7** and **8**. The only difference in the chemical structures of these two compounds is that the H-4''' atom in **8** is replaced to benzyl substituent in **7**. Both compounds have been obtained through the condensation of the corresponding hydroxylaminoketone and 4-(4-hydroxyphenyl)cyclohexanone (**6**) in presence of ammonium acetate in methanol saturated with ammonia. As compound **8** has been already determined to be *trans*-*ee*-isomer on the base of analisys of its ^{1}H,^{13}C, NOESY and ROESY NMR spectra supporting with the quantum chemical conformational analysis data[1], and the ^{1}H and ^{13}C NMR spectra of the similar fragments of these two compounds have the similar chemical shifts and coupling constants, it is reasonable to suggest that the geometry of **7** was similar to **8**. Finally, compound **8** has been also determined to be *trans*-*ee*-isomer.



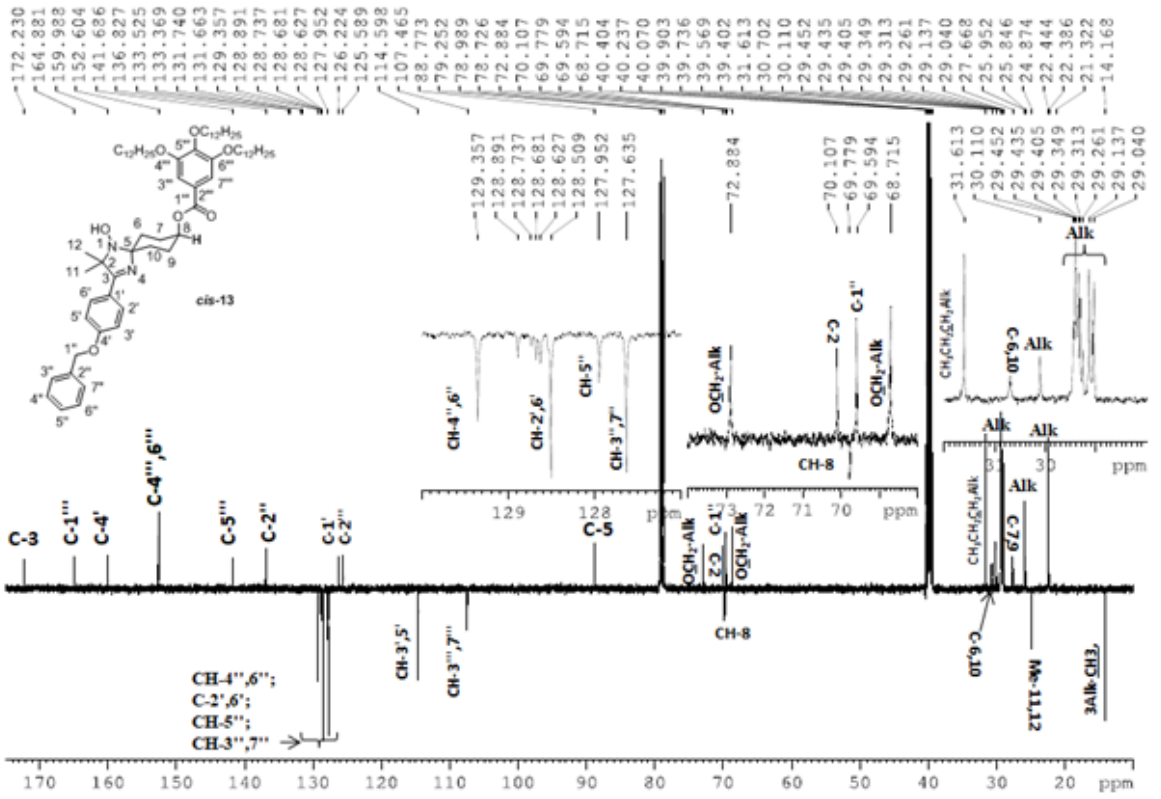
Spectrum 21. ^{1}H NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***cis*-14**



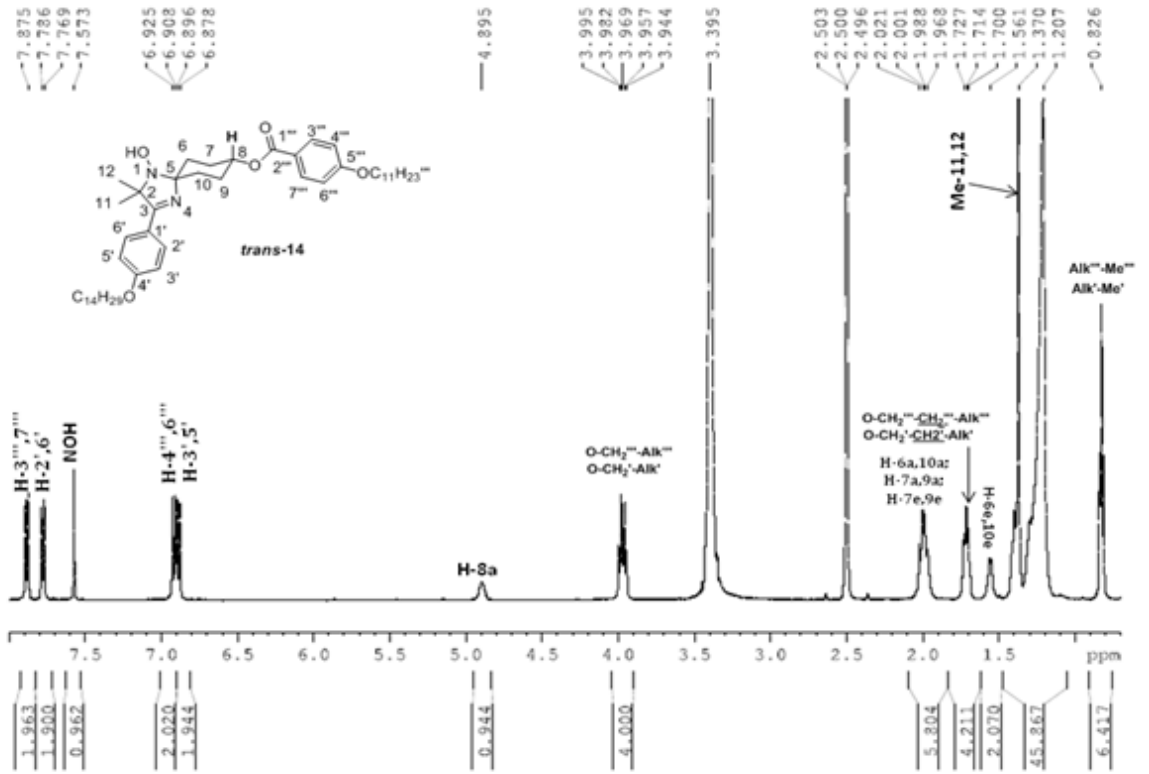
Spectrum 23. ^{1}H NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***cis*-13**



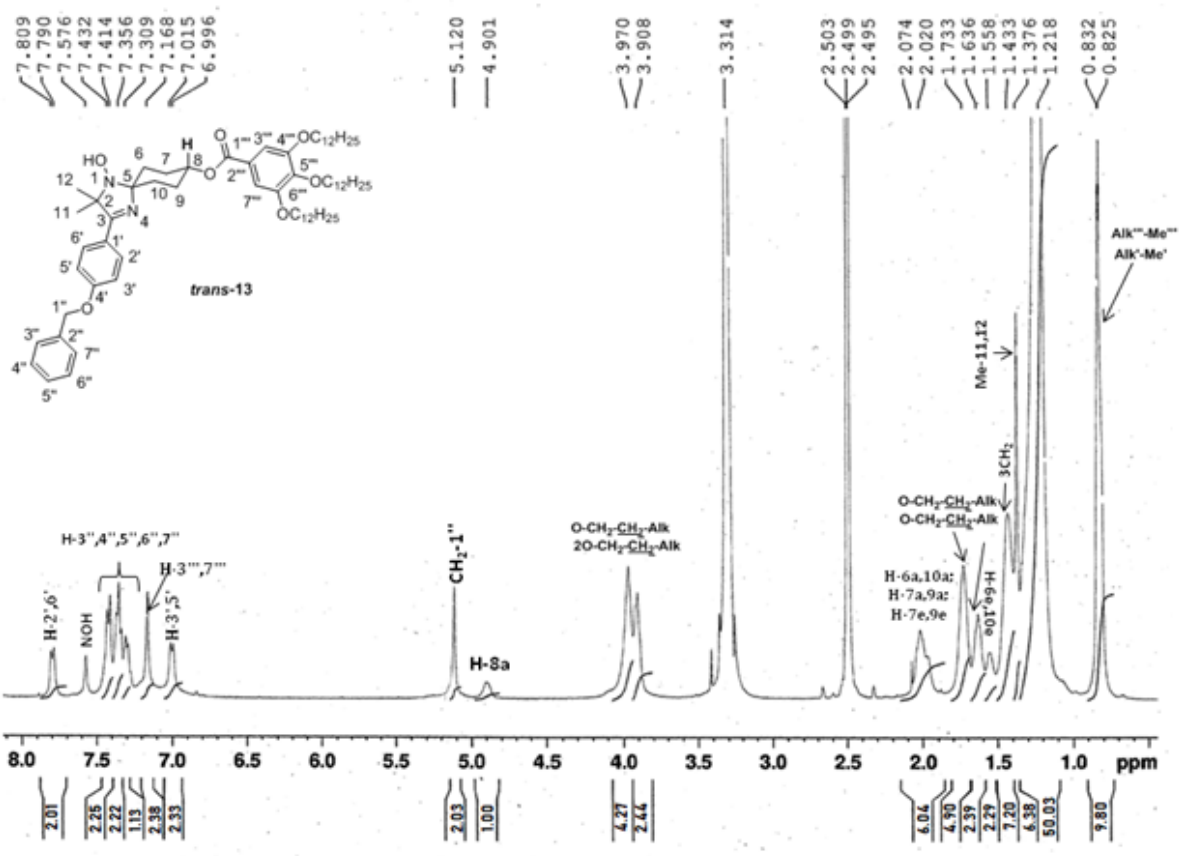
Spectrum 22. ^{13}C NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***cis*-14**



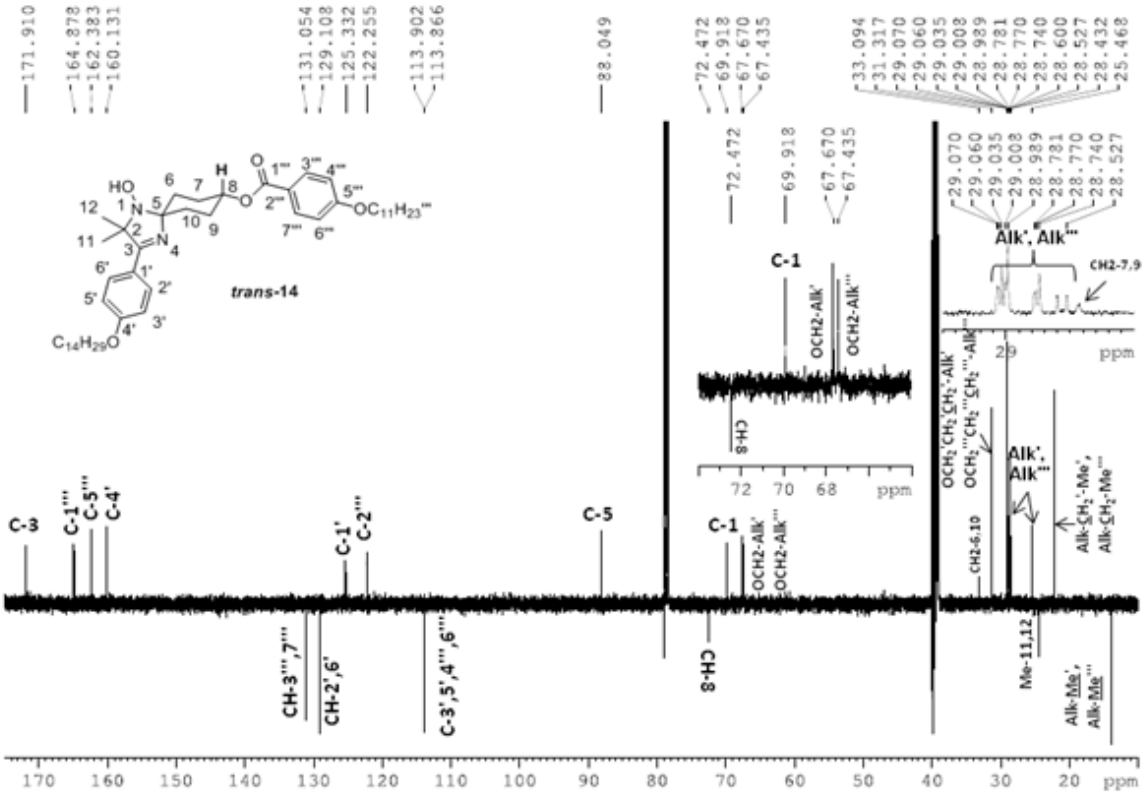
Spectrum 24. ^{13}C NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***cis*-13**



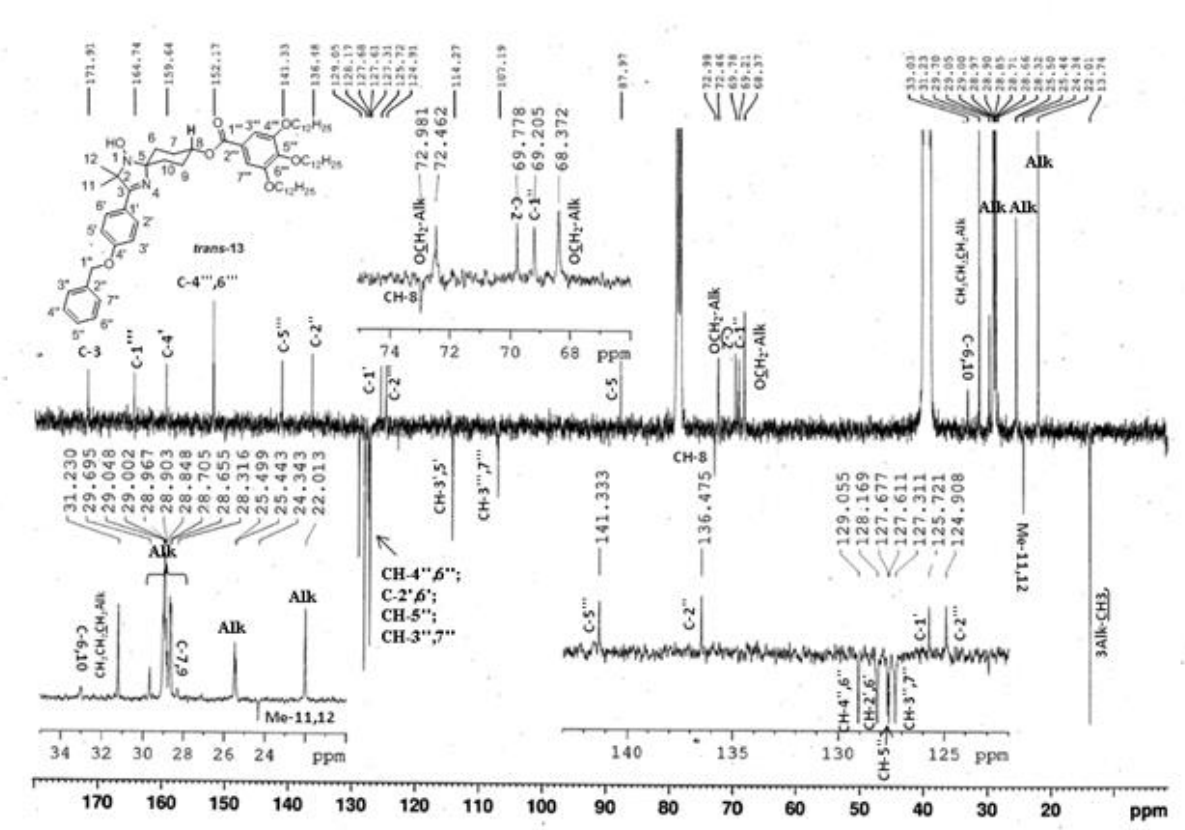
Spectrum 25. ^{1}H NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***trans*-14**



Spectrum 26. ^{1}H NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***trans*-13**



Spectrum 27. ^{13}C NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***trans*-14**



Spectrum 28. ^{13}C NMR ($CDCl_3$+DMSO-d_6) spectrum of compound ***trans*-13**

Spectra 21-28 represent ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra recorded for the $CDCl_3$+DMSO-d_6 solutions of ***cis*-13, *trans*-13** and ***cis*-14** and ***trans*-14**. Only the side parts of the molecules are different, but the main sceletons are the same. All the compounds have been synthesized through the similar synthetic way: condensation of the corresponding hydroxylaminoketone and 4-hydroxycyclohexanone in presence of ammonium acetate in methanol saturated with ammonia, following oxidation by means manganese dioxide and Mitsunobu acylation of the obtained derivatives using 4-alkoxysubtituted benzoic acid or 3,4,5-alkoxysubtituted benzoic acid, correspondingly. As ***cis*-14** and ***trans*-14** have been already determined to be *cis-ea*- and *trans-ee*-isomers on the base of analisys of their ^{1}H, ^{13}C, NOESY and ROESY NMR, and the ^{1}H and ^{13}C NMR spectra of the similar fragments of these two compounds have the similar chemical shifts and coupling constants, it is reasonable to suggest that the geometry of ***cis*-13** was similar to ***cis*-14** and the geometry of ***trans*-13** was similar to ***trans*-14**, correspondingly. Finally, compounds ***cis*-13** and ***trans*-14** have been determined to be cis-*ea*- and *trans-ee*-isomers, correspondingly.

Phase transition data

Compound	Phase transition data
***trans*-4**	Cr_1 78 (*2*) Cr_2 96 (*15*) I
***trans*-5**	Cr 82 (*20*) I
***cis*-5**	Cr 62 (*23*) I
1b	-
1c	Cr 3 (*10*) I
2b	Cr 50 (*9*) I
2c	Cr 72 (*14*) I
15b	-
15c	Cr 17 (*13*) I

Table S1. Transition temperatures (°C) and enthalpies (kJ/mol, in italics) determined by DSC (5 °C /min) in the heating mode: Cr = crystal; I = isotropic in the temperature intervals from 25 °C to 140 °C for ***trans*-4**, ***trans*-5**, ***cis*-5**, **1b**, **15b**, and **2c** and from -10 °C to 80 °C for **1c**, **15c** and **2b**.

References

1. Zaytseva, E. V.; Shernyukov, A. V.; Genaev, A. M.; Tamura, R.; Grigor'ev, I. A.; Mazhukin D. G. *Arkivoc* **2014**, (*vi*), 10. http://dx.doi.org//10.3998/ark.5550190.p008.808
2. Zaitseva, E. V.; Shernyukov, A. V.; Amitina, S. A.; Tamura, R.; Grigor`ev, I. A.; Mazhukin, D. G. *Chem. Heterocycl. Compd. (Engl. Transl.)* **2014**, *50*, 1113. http://dx.doi.org//10.1007/s10593-014-1571-7