

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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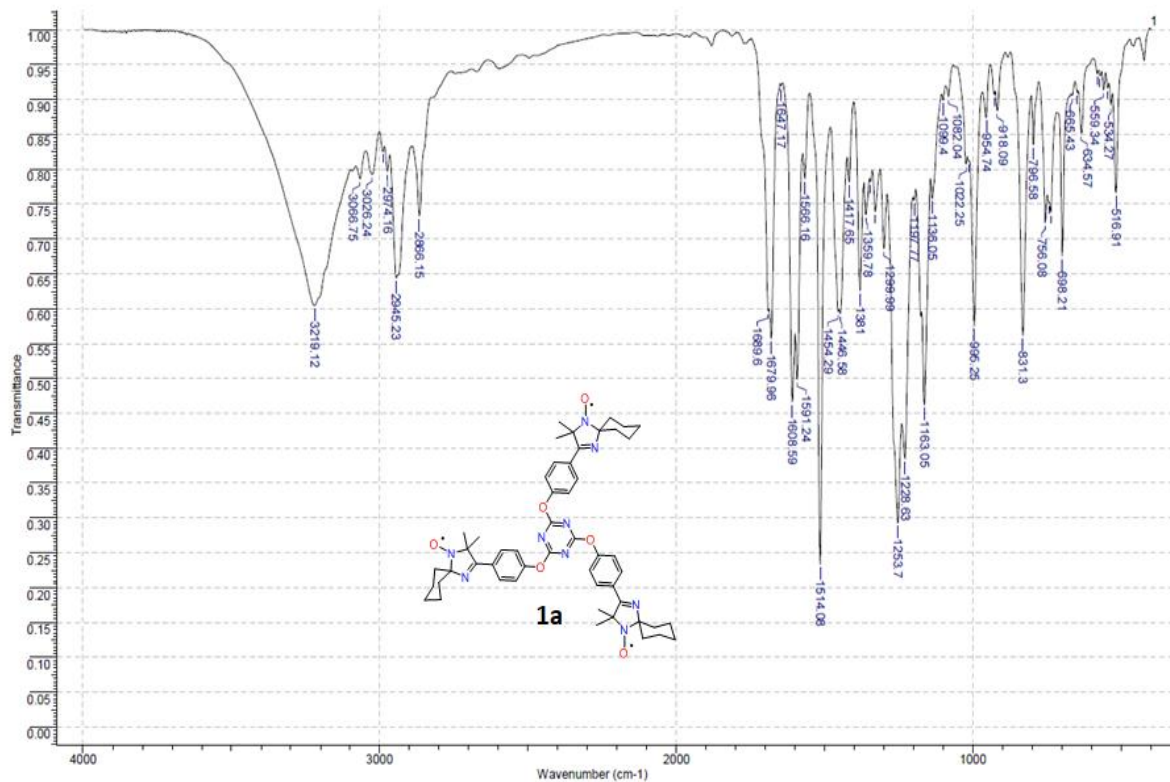
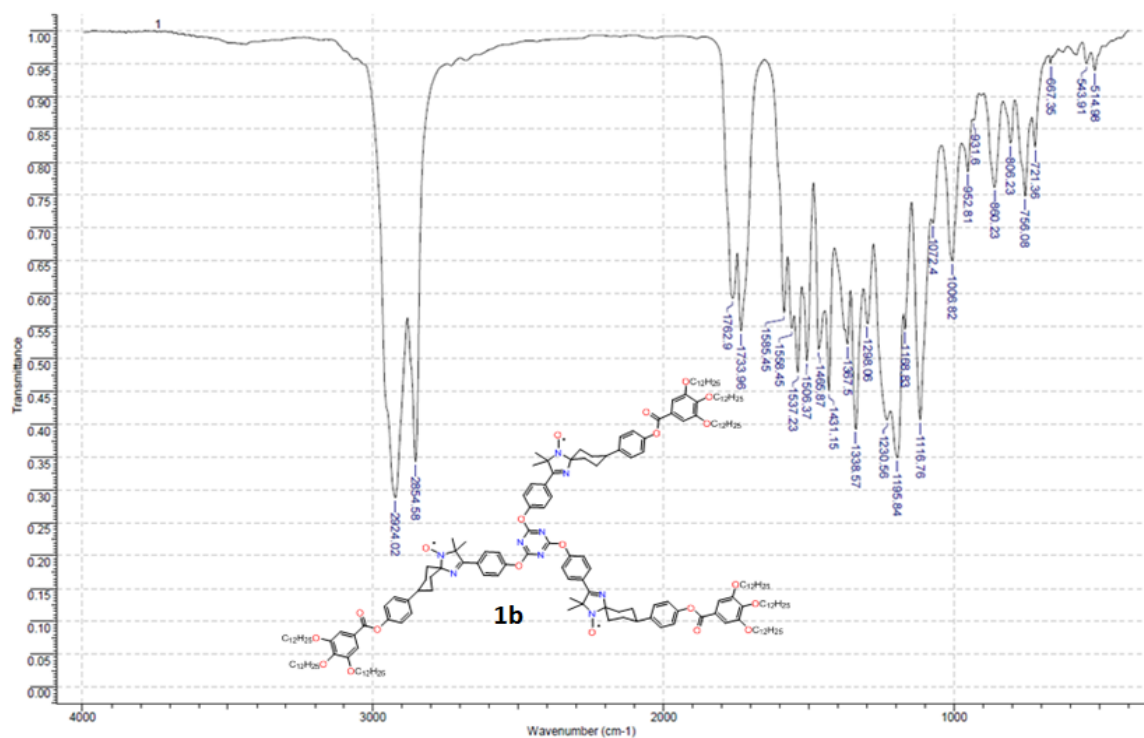
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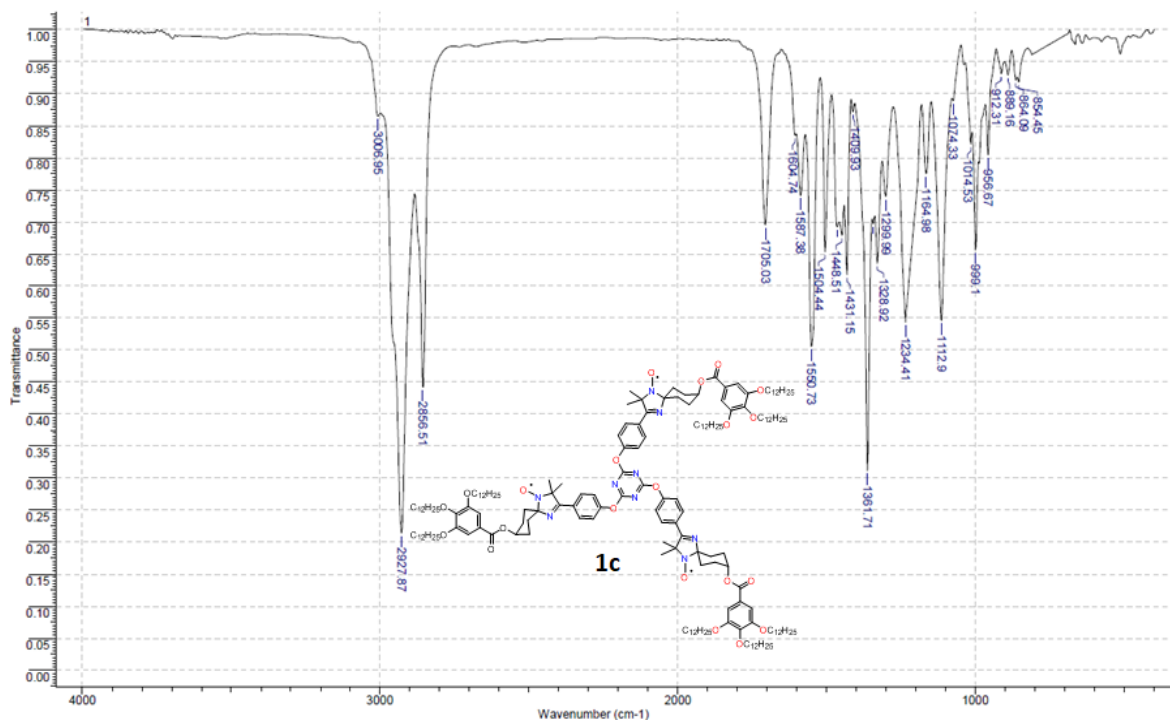
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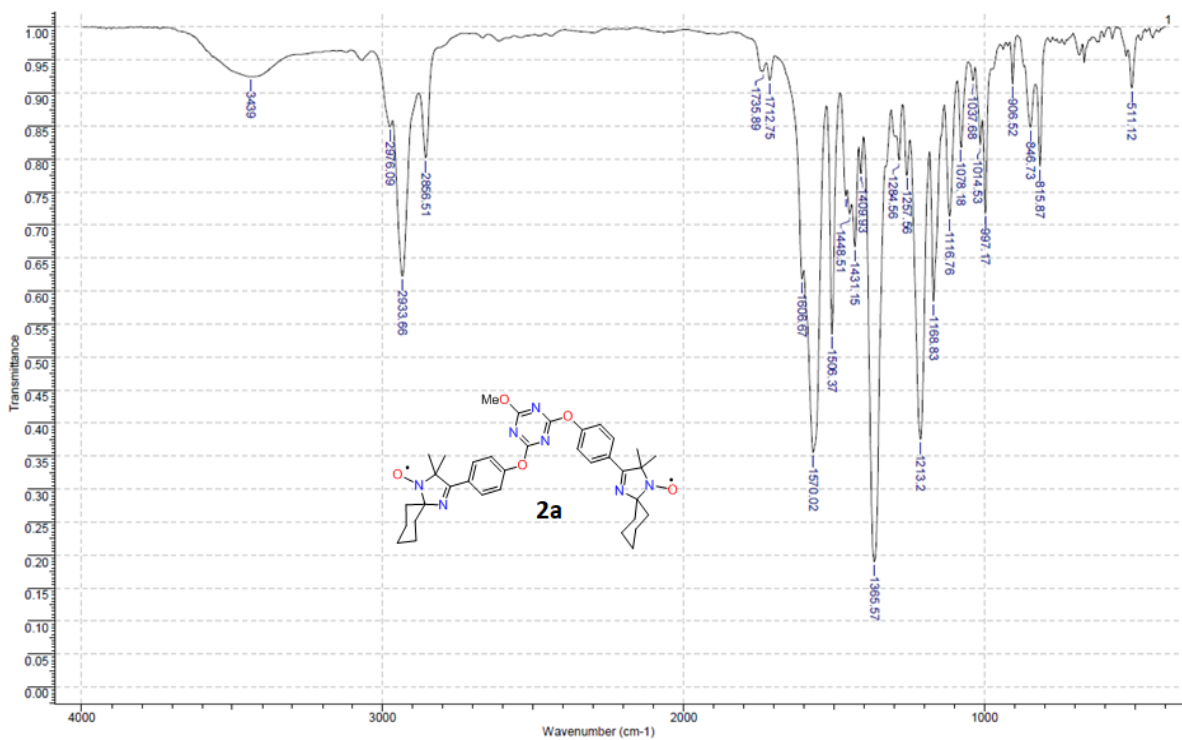
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IR spectra

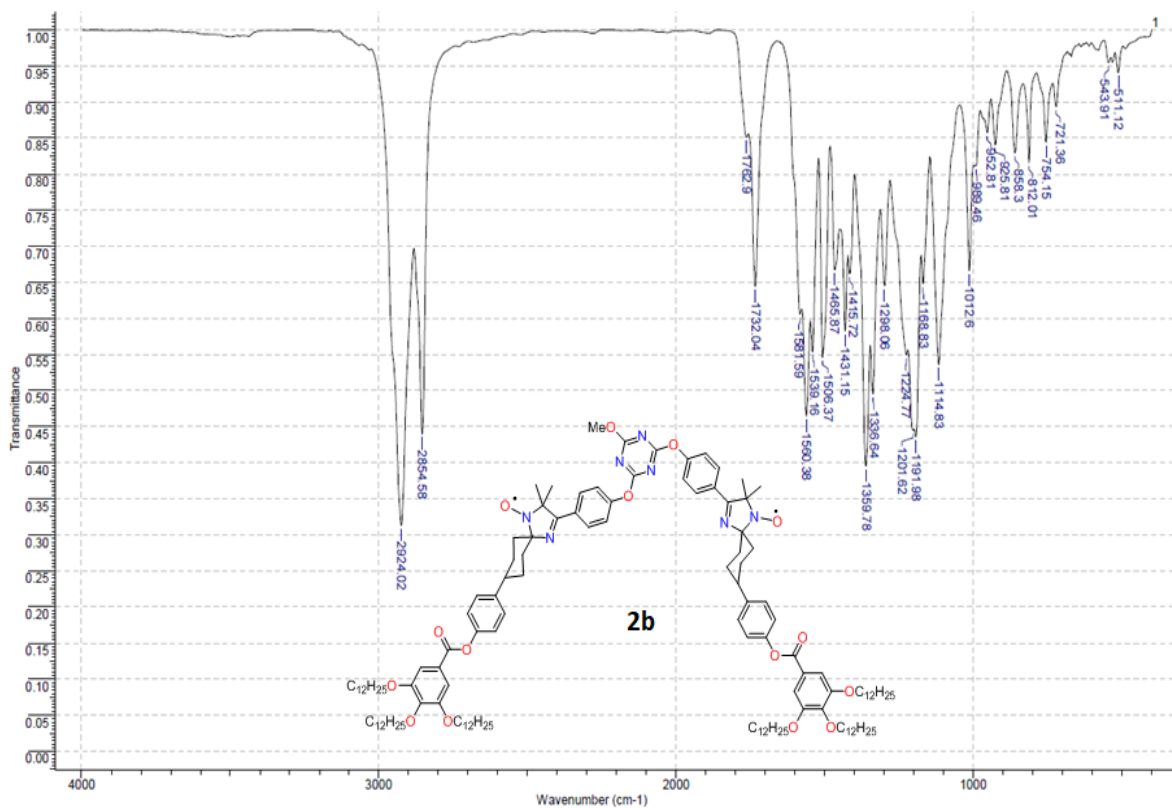
Spectrum 1. IR (KBr) spectrum of compound **1a**Spectrum 2. IR (KBr) spectrum of compound **1b**



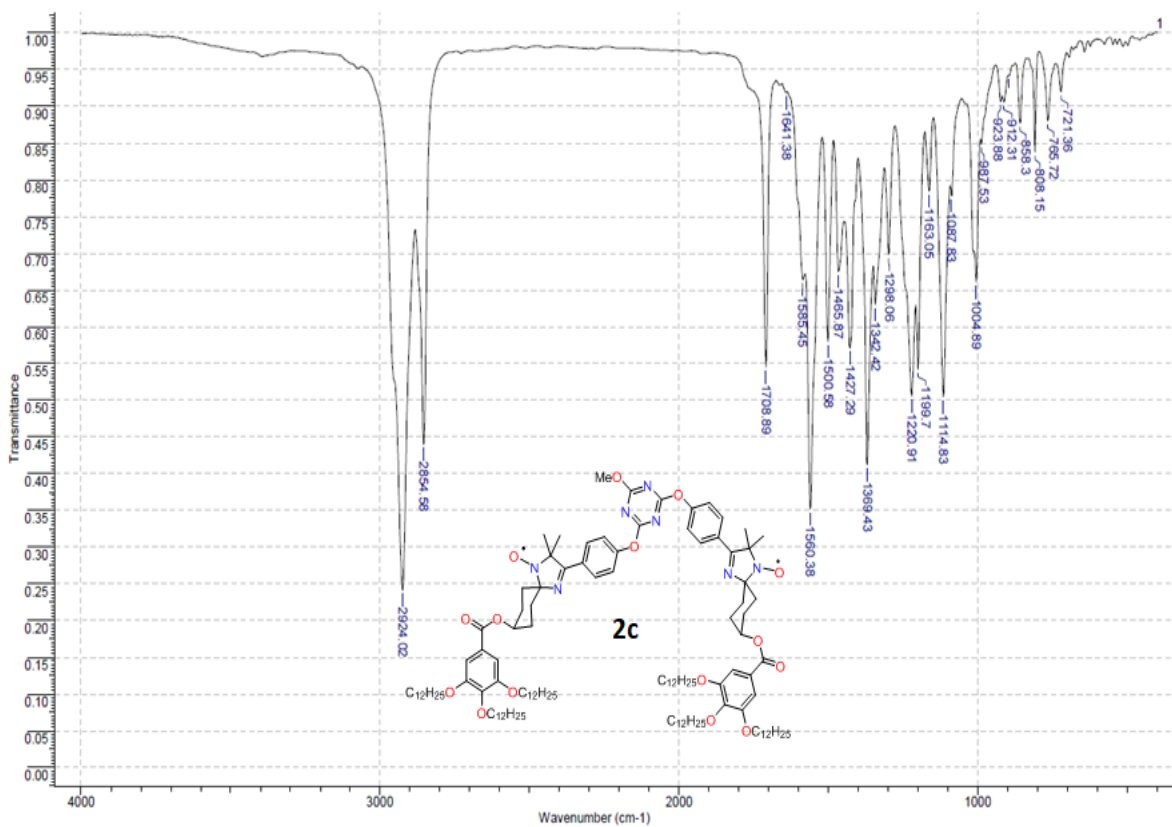
Spectrum 3. IR (KBr) spectrum of compound 1c



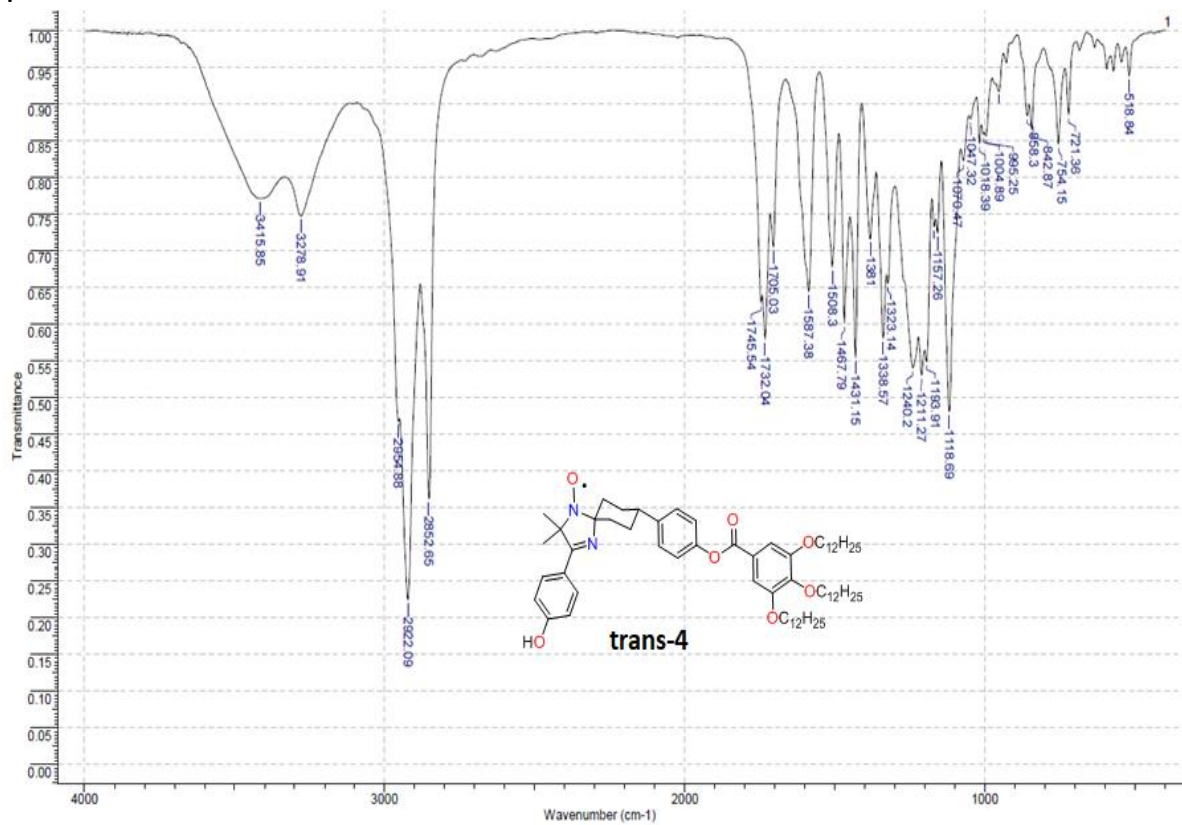
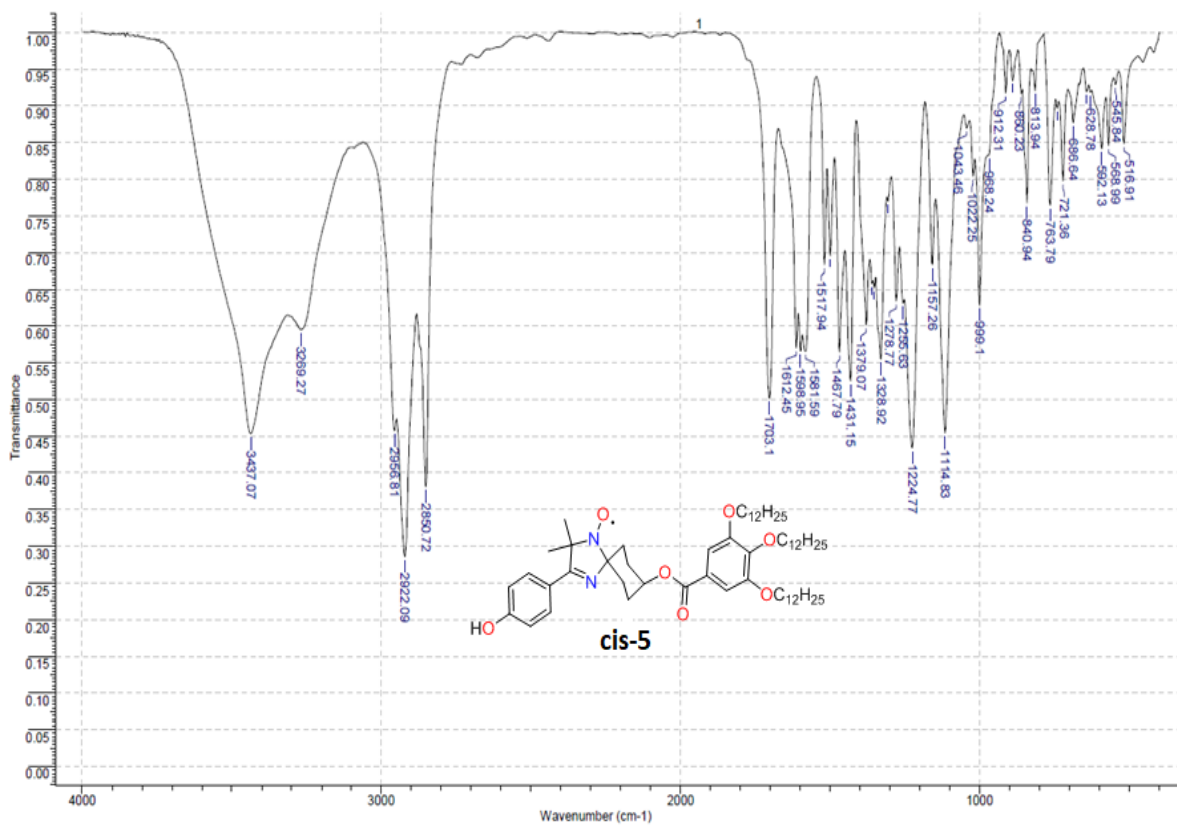
Spectrum 4. IR (KBr) spectrum of compound 2a

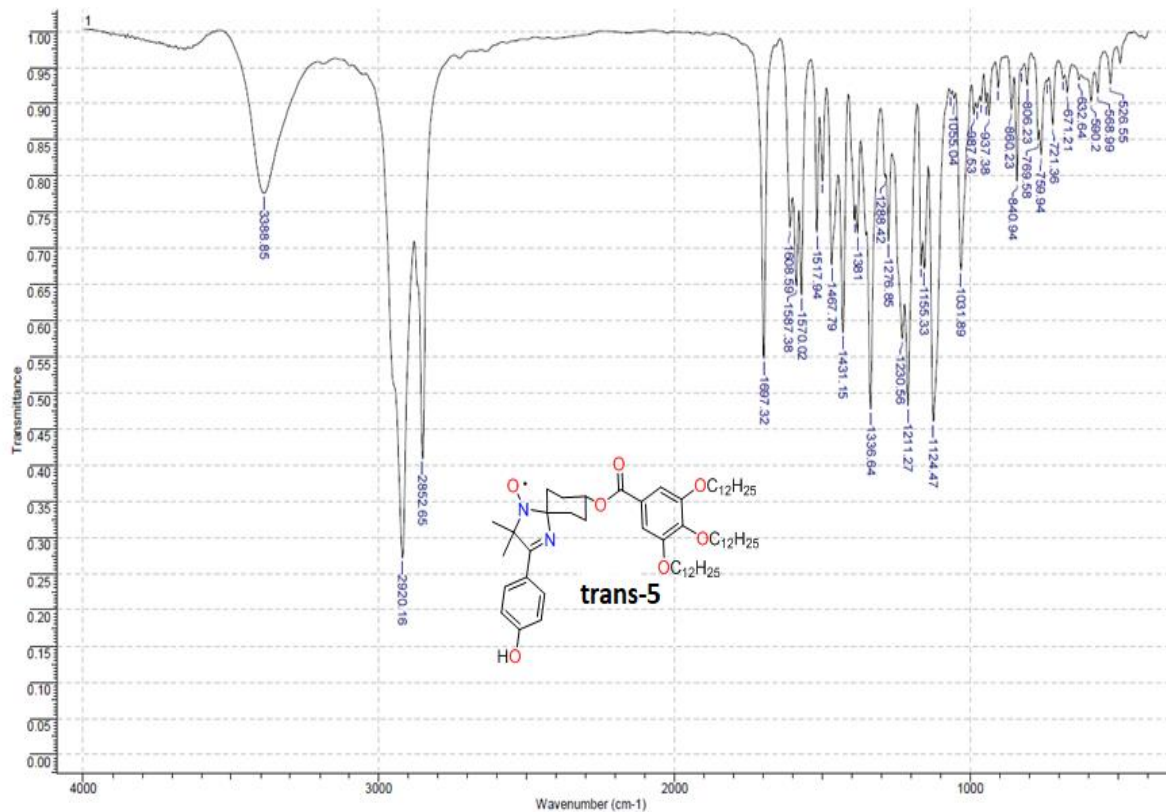
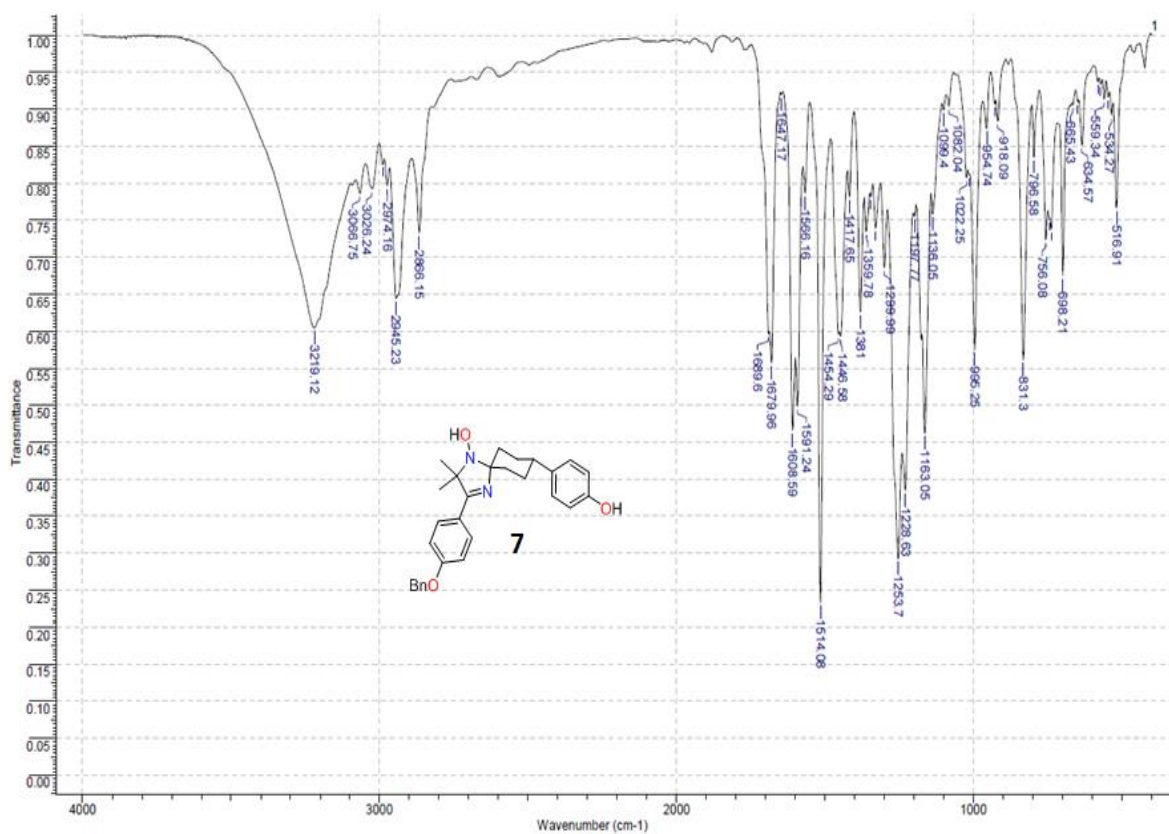


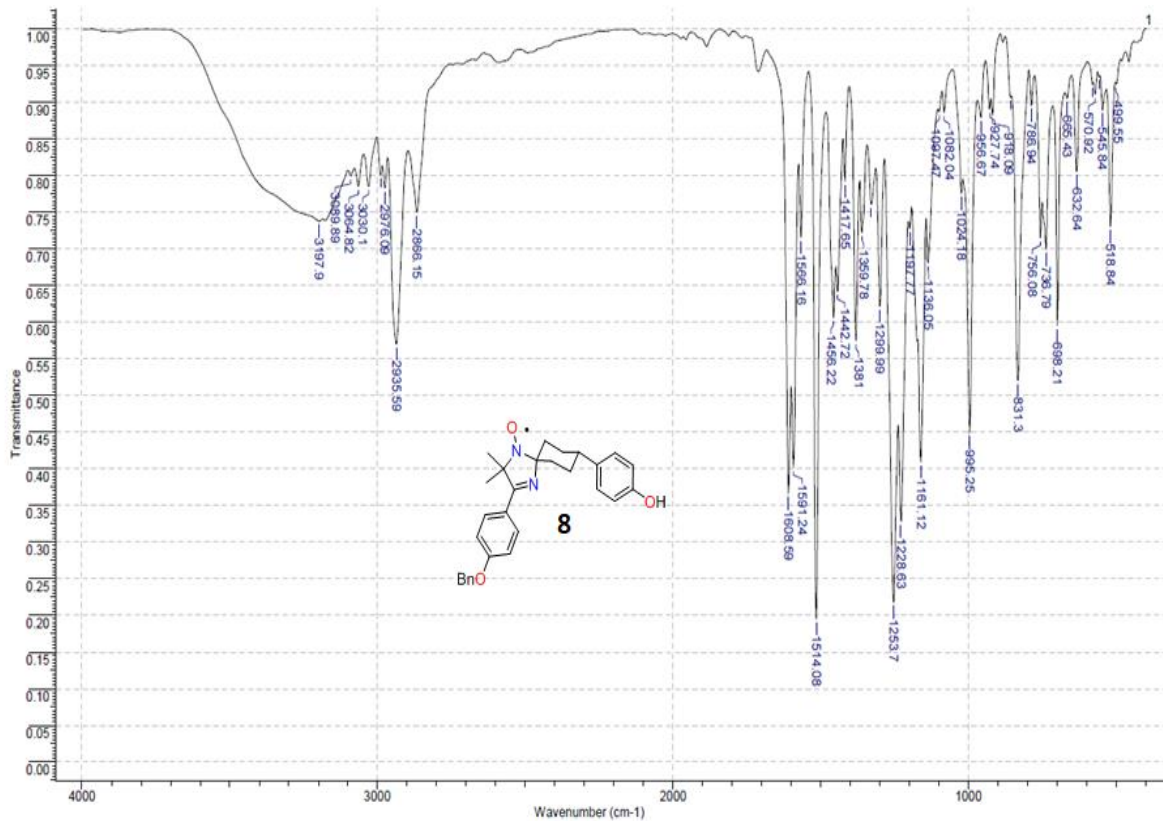
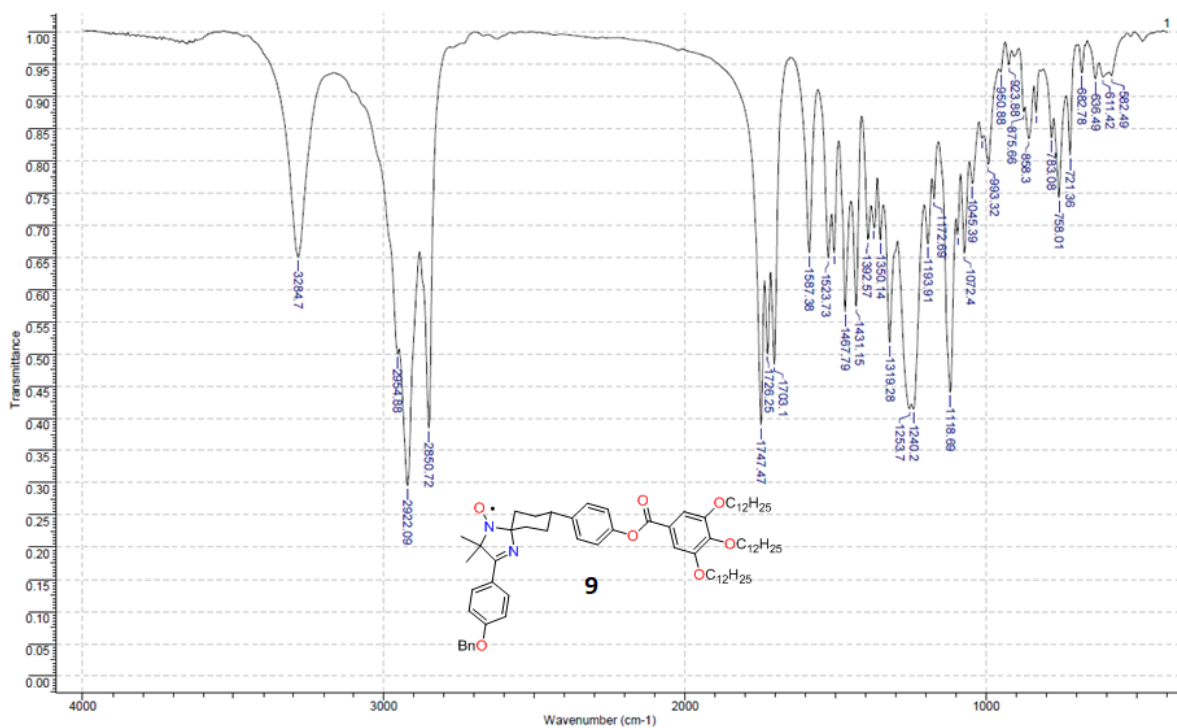
Spectrum 5. IR (KBr) spectrum of compound **2b**

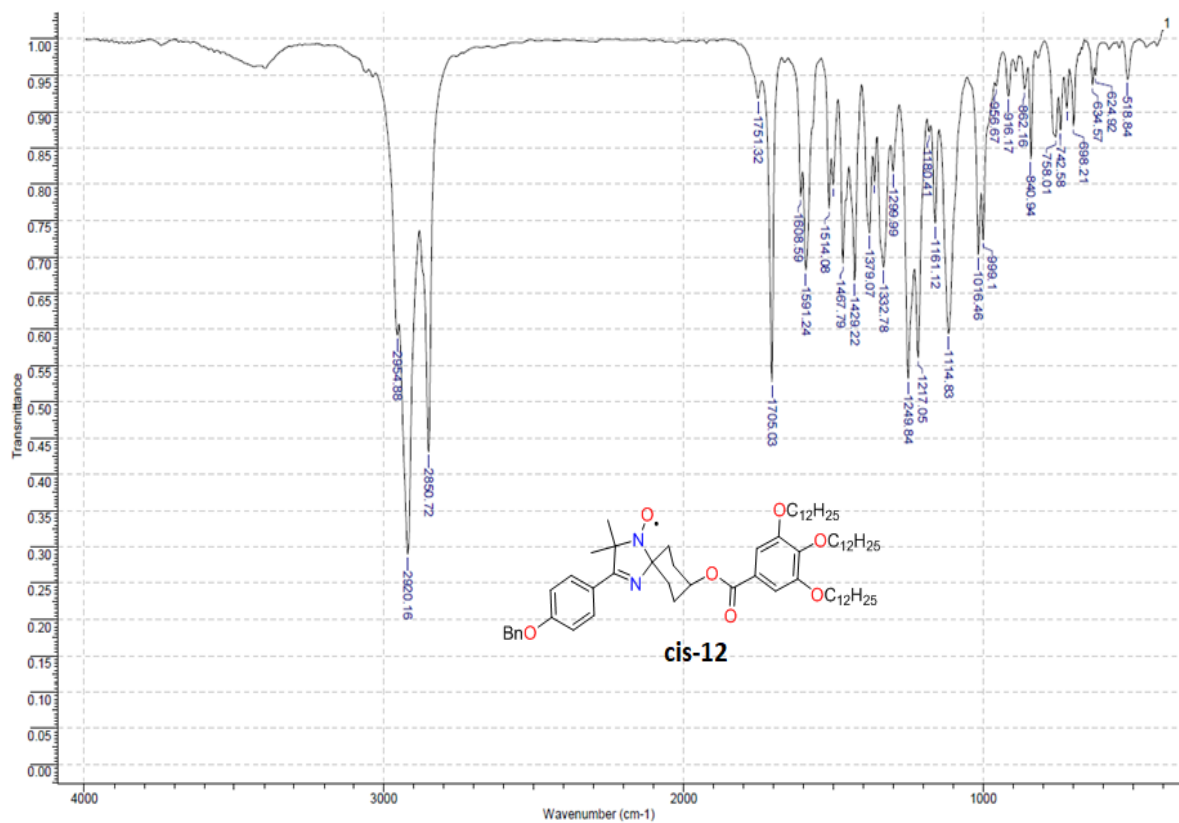
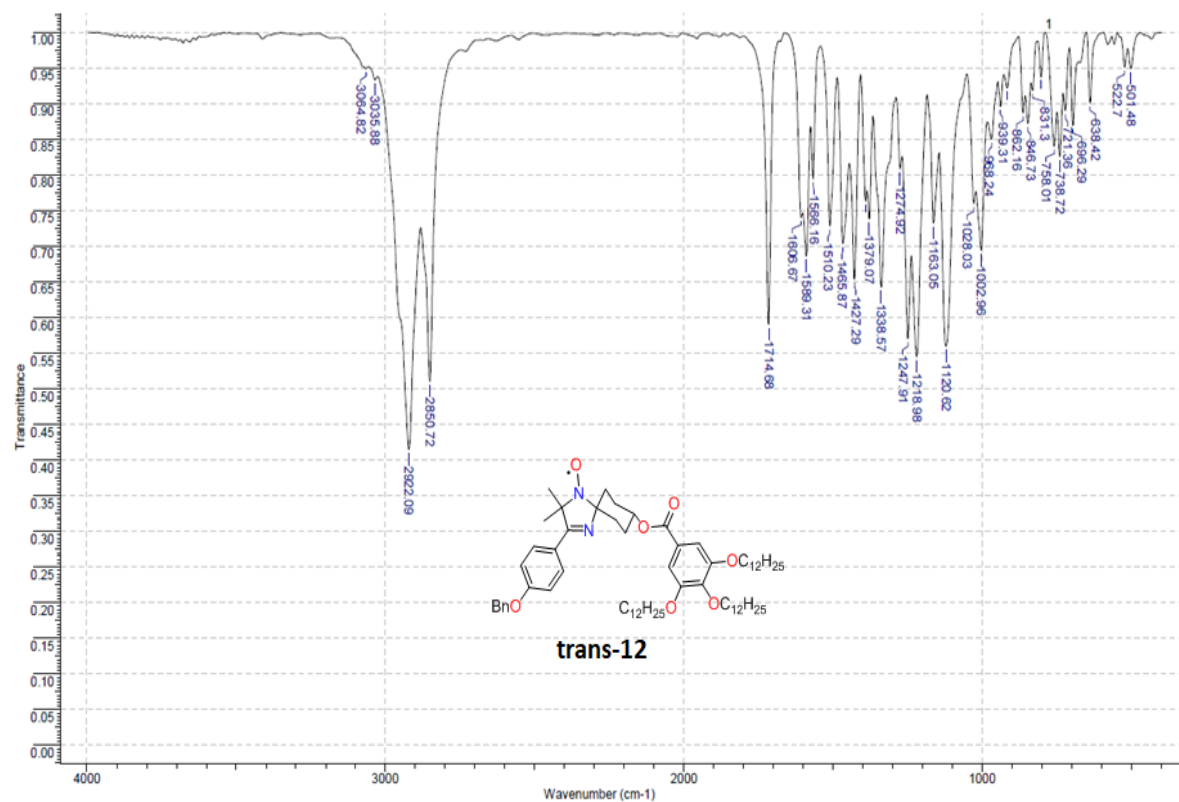


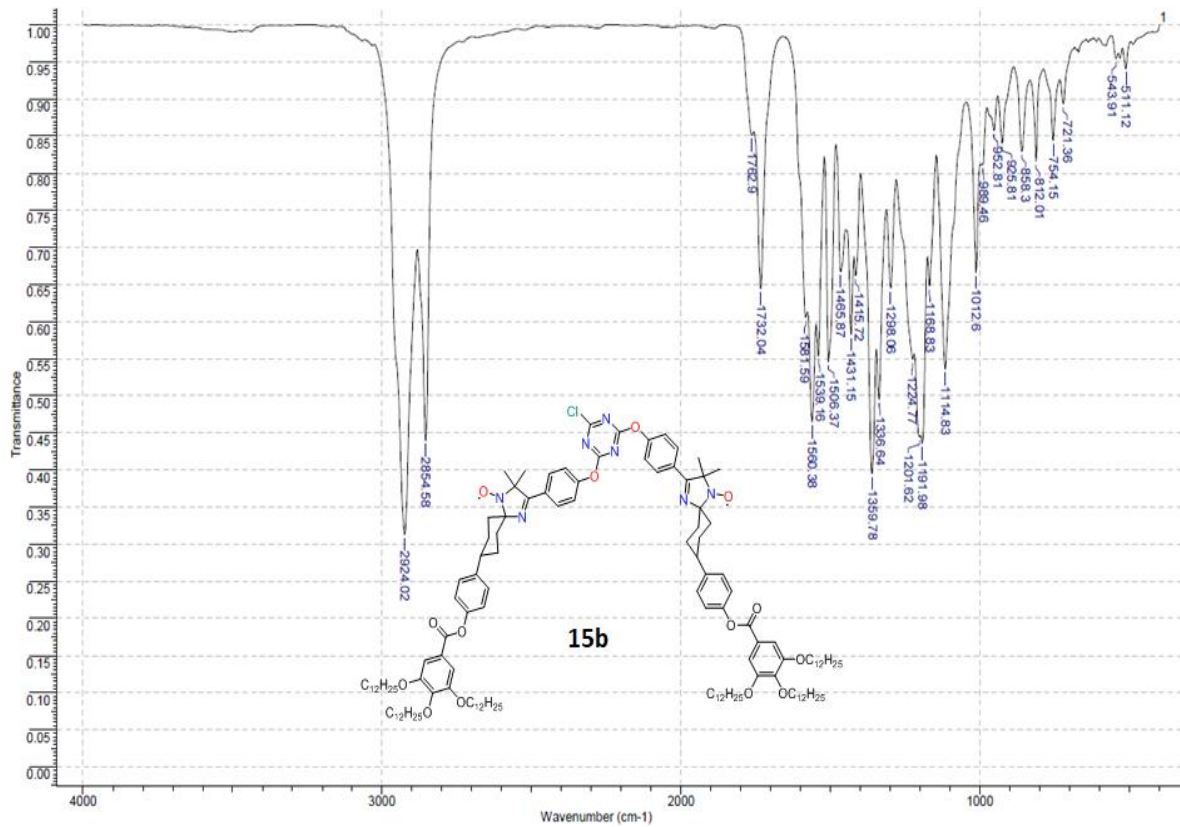
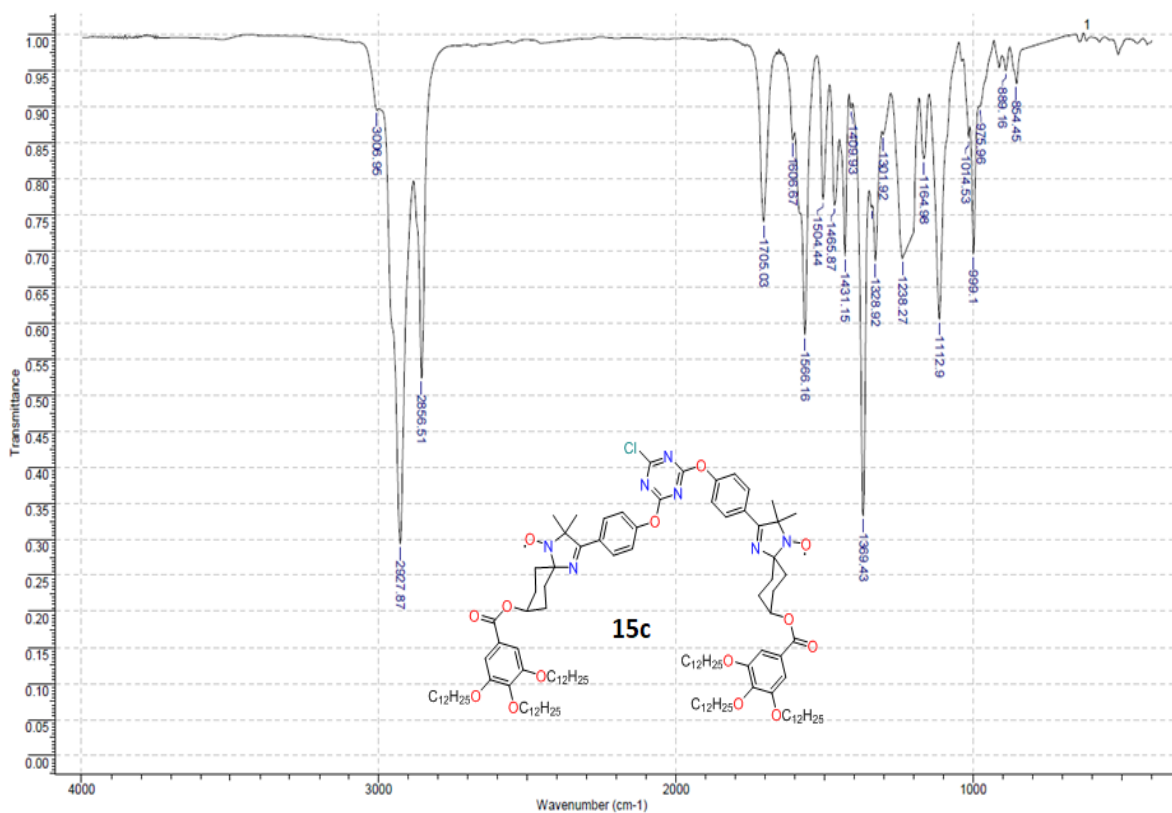
Spectrum 6. IR (KBr) spectrum of compound **2c**

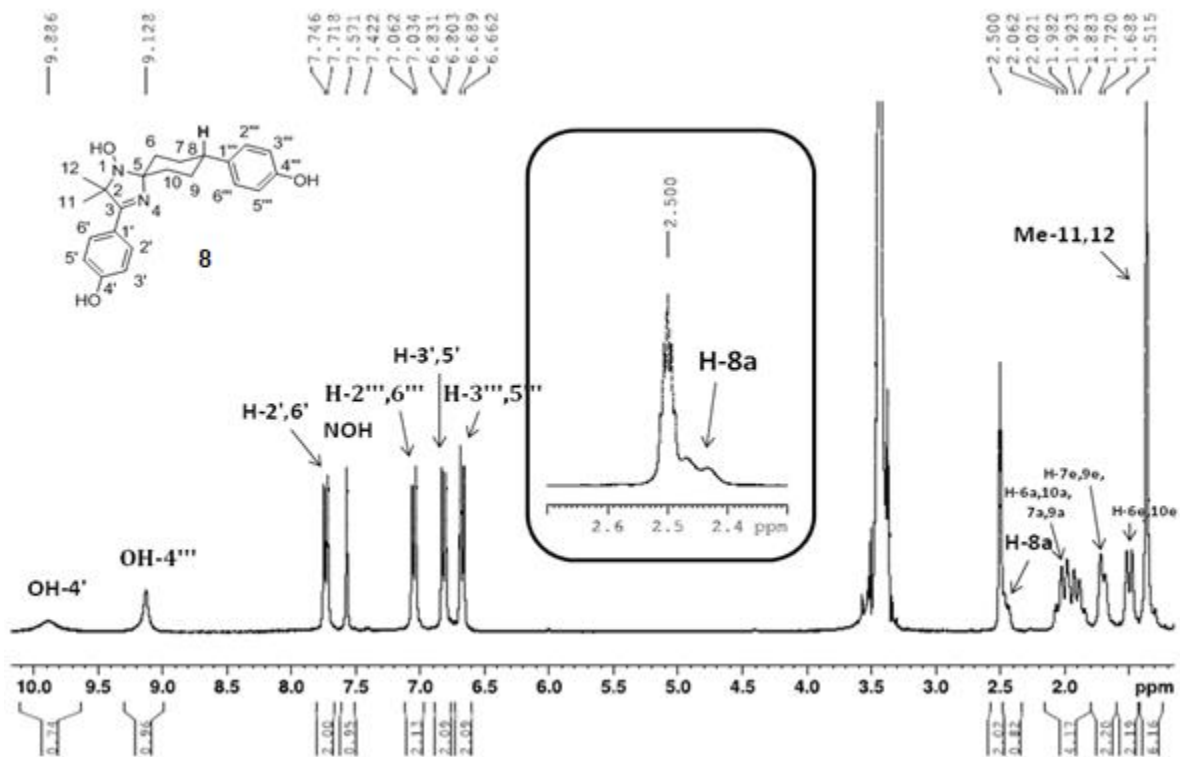
Spectrum 7. IR (KBr) spectrum of compound **trans-4**Spectrum 8. IR (KBr) spectrum of compound **cis-5**

Spectrum 9. IR (KBr) spectrum of compound **trans-5**Spectrum 10. IR (KBr) spectrum of compound **7**

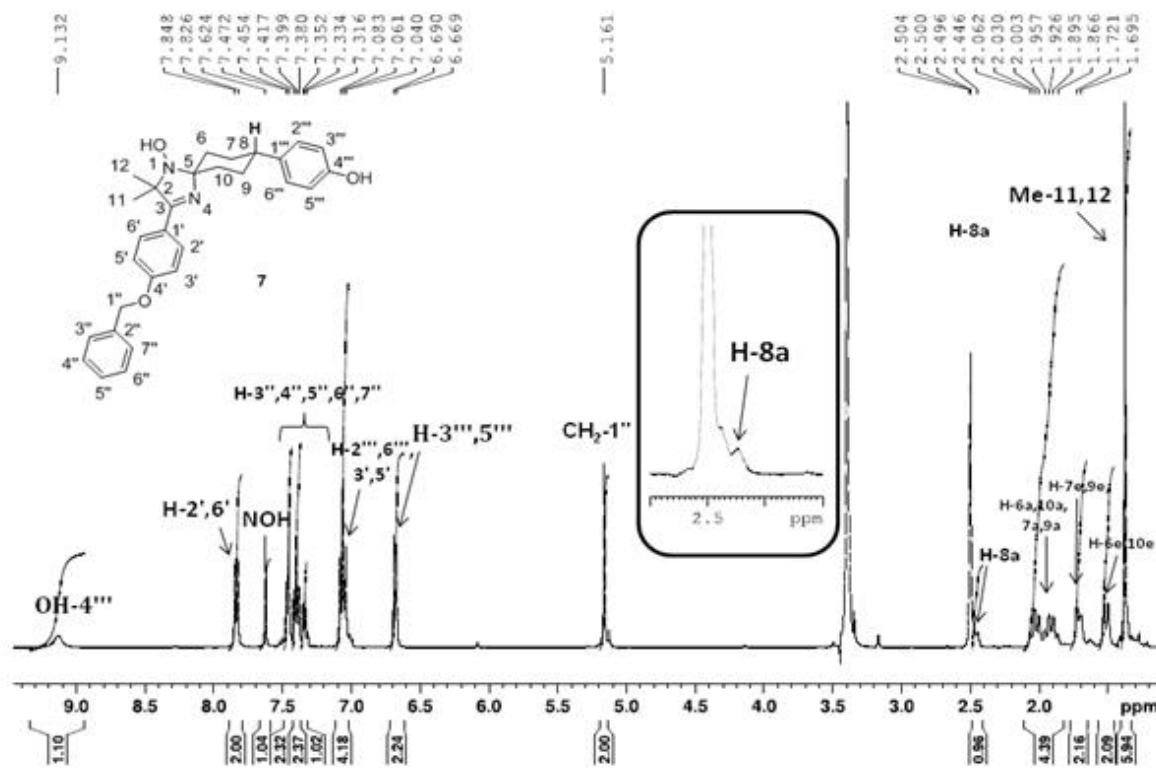
Spectrum 11. IR (KBr) spectrum of compound **8**Spectrum 12. IR (KBr) spectrum of compound **9**

Spectrum 13. IR (KBr) spectrum of compound **cis-12**Spectrum 14. IR (KBr) spectrum of compound **trans-12**

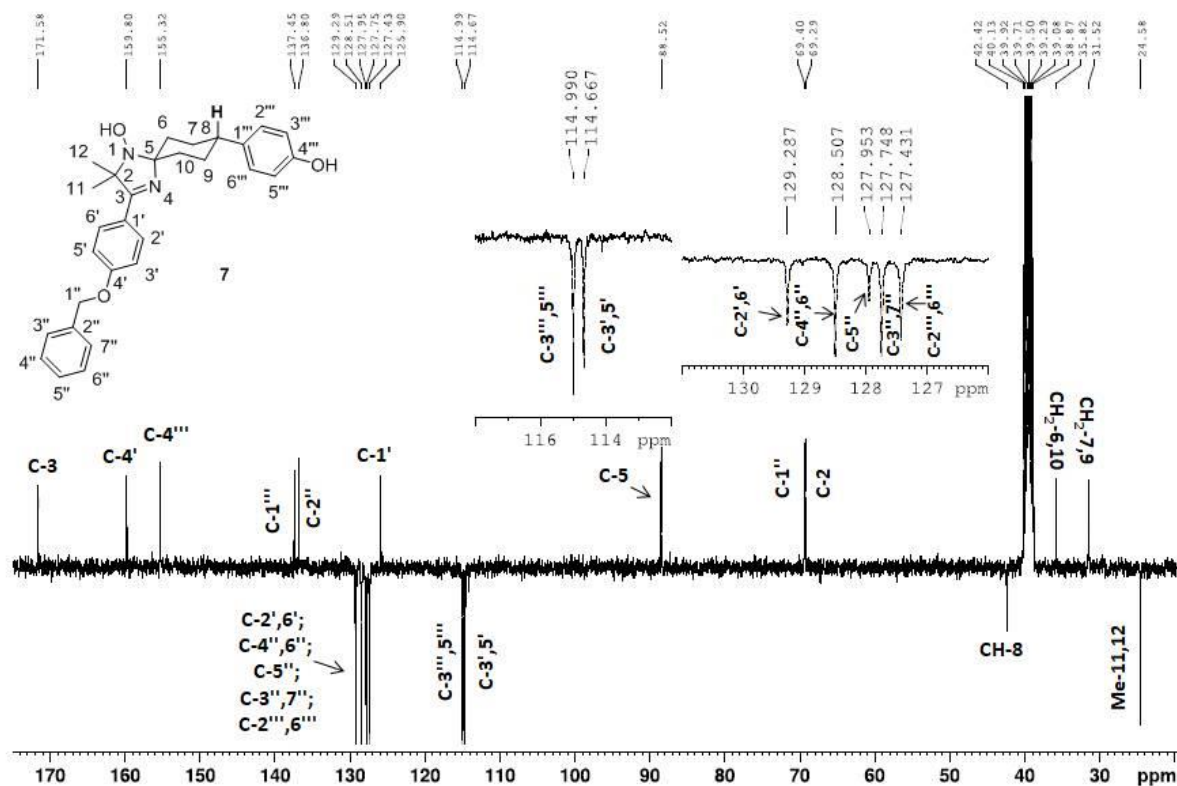
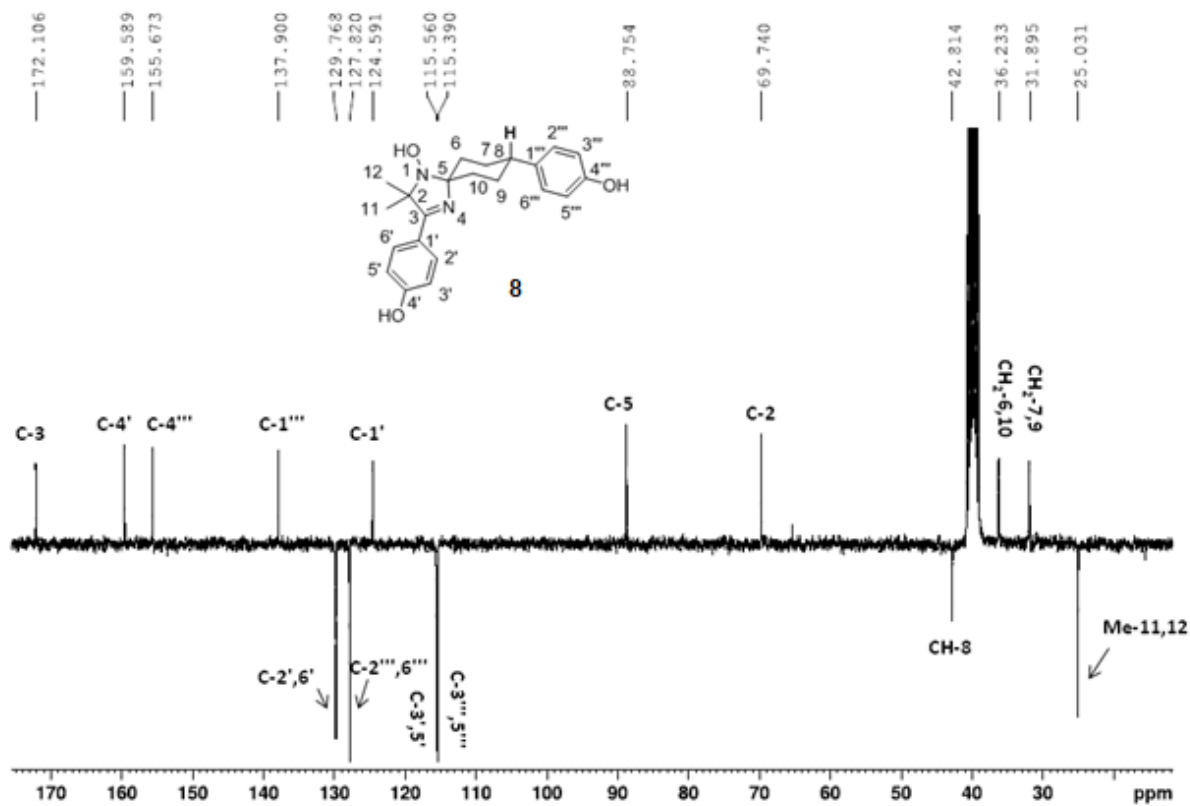
Spectrum 15. IR (KBr) spectrum of compound **15b**Spectrum 16. IR (KBr) spectrum of compound **15c**



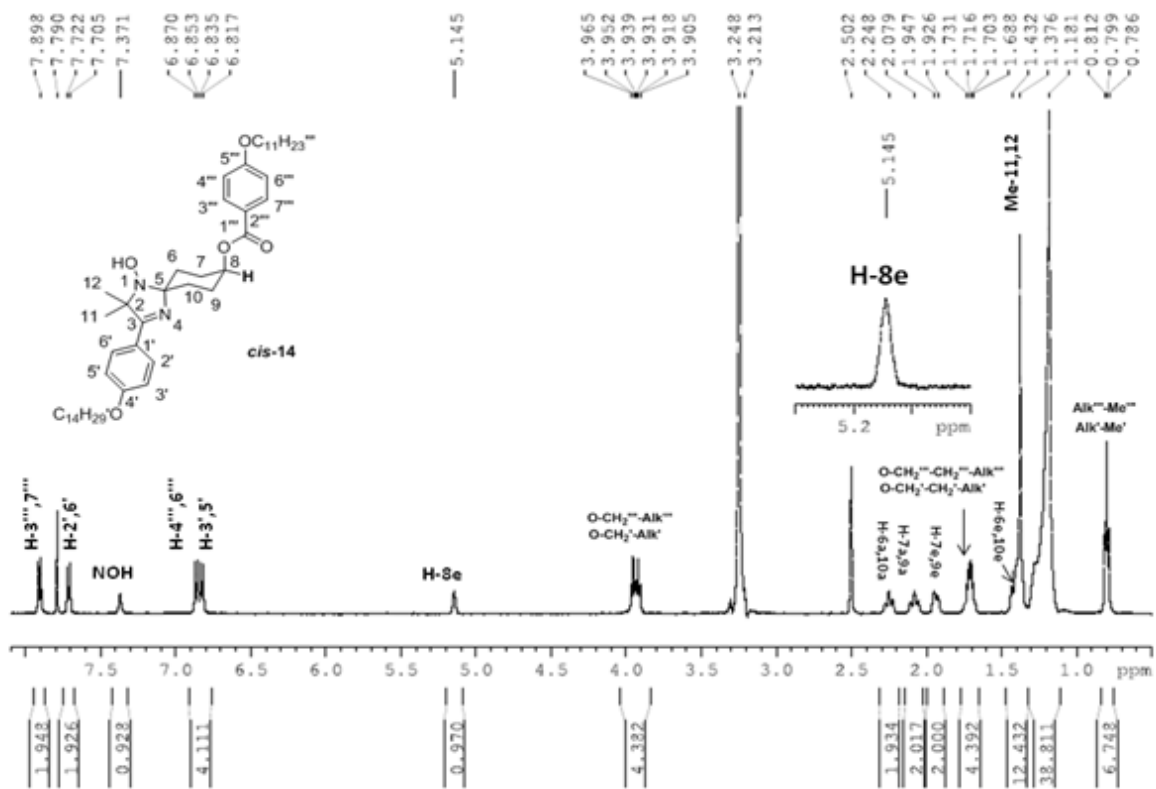
Spectrum 17. ^1H NMR ($\text{DMSO-}d_6$) spectrum of compound 8



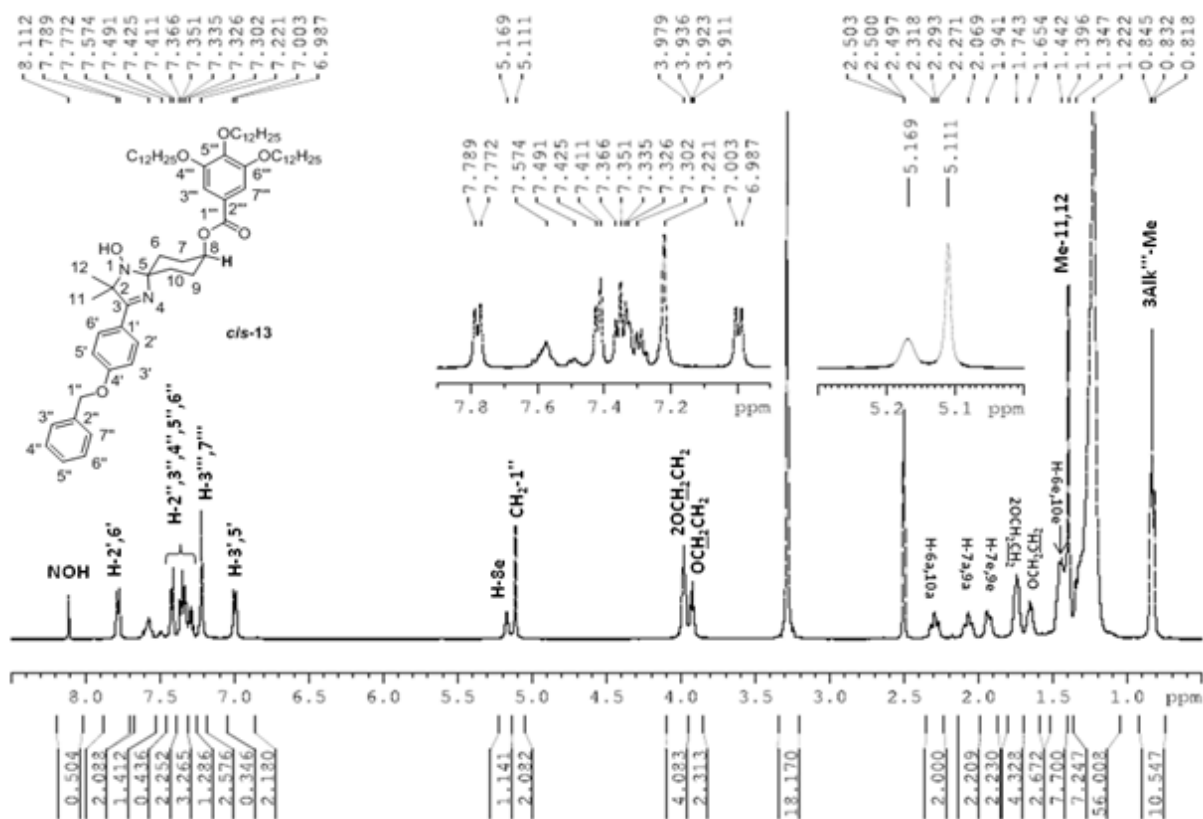
Spectrum 18. ^1H NMR ($\text{DMSO-}d_6$) spectrum of compound 7



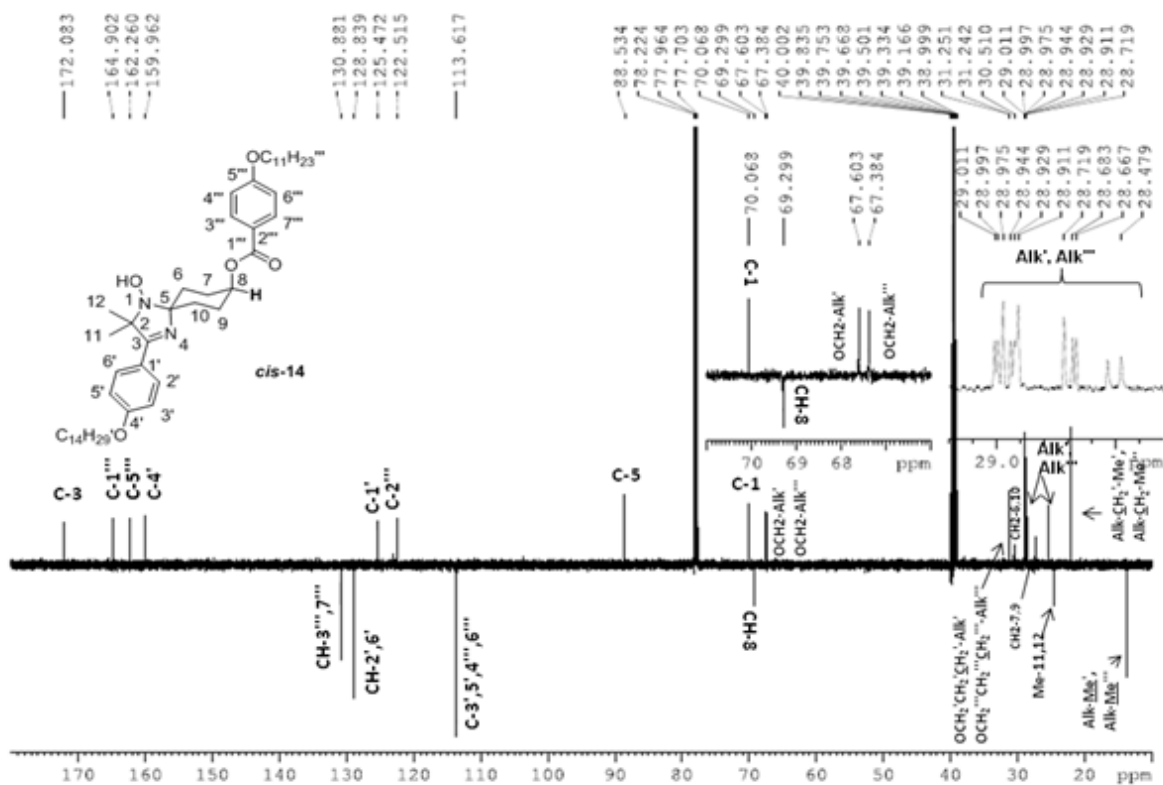
Spectra 17-20 represent ^1H (400 MHz) and ^{13}C (100 MHz) spectra recorded for the DMSO- d_6 solutions of **7** and **8**. The only difference in the chemical structures of these two compounds is that the H-4''' atom in **8** is replaced to benzyl substituent in **7**. Both compounds have been obtained 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 analysis of its ^1H , ^{13}C , NOESY and ROESY NMR spectra supporting with the quantum chemical conformational analysis data¹, and the ^1H 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.



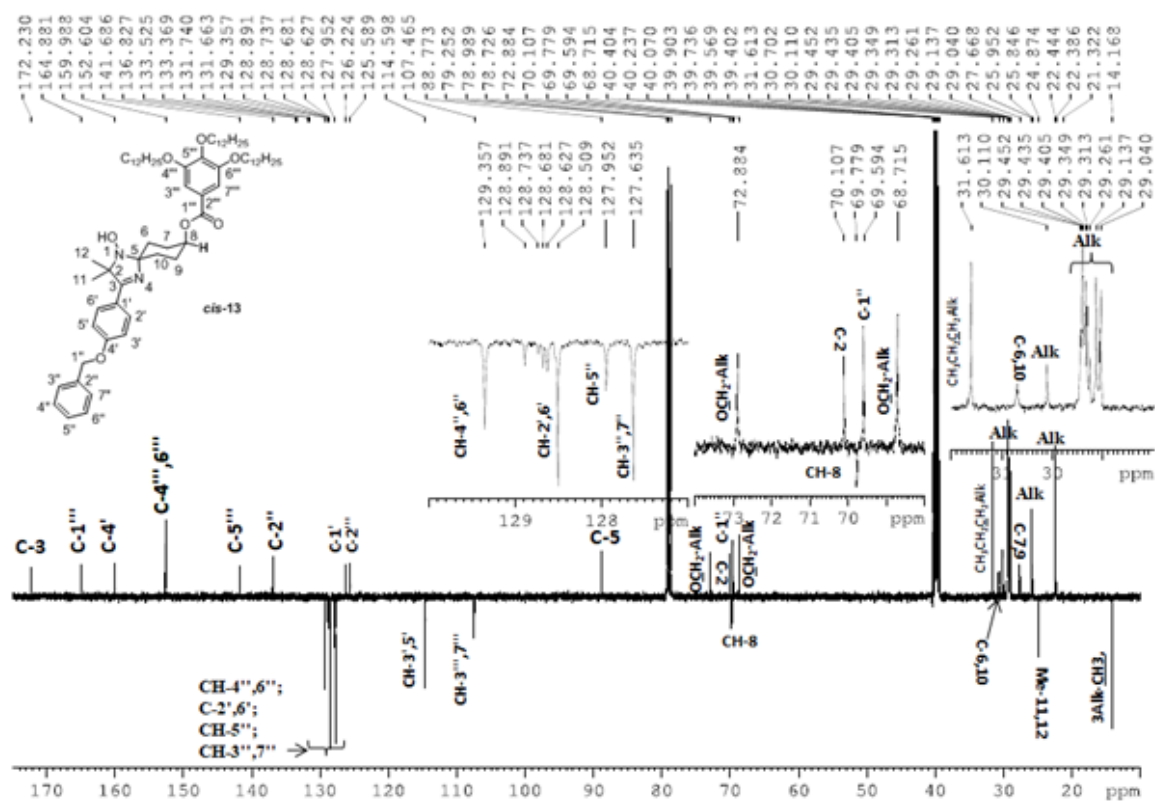
Spectrum 21. ¹H NMR (CDCl₃+DMSO-*d*₆) spectrum of compound *cis*-14



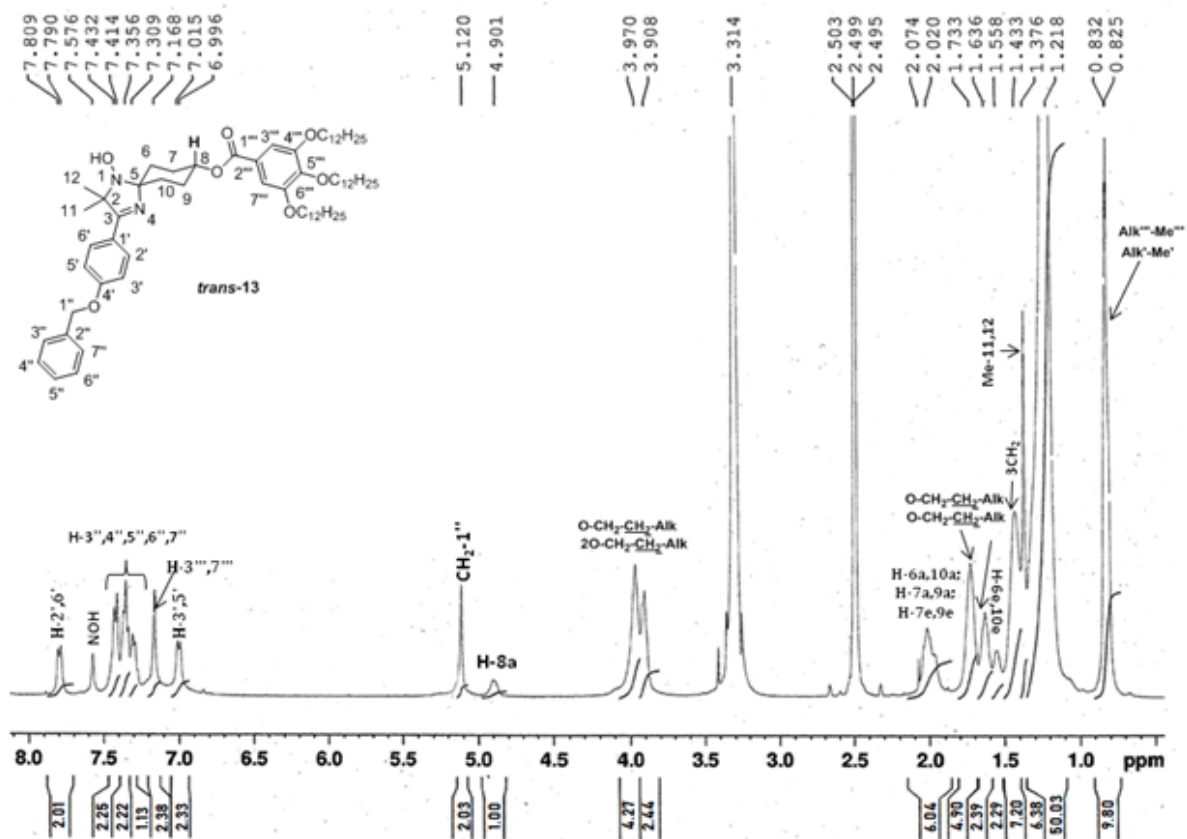
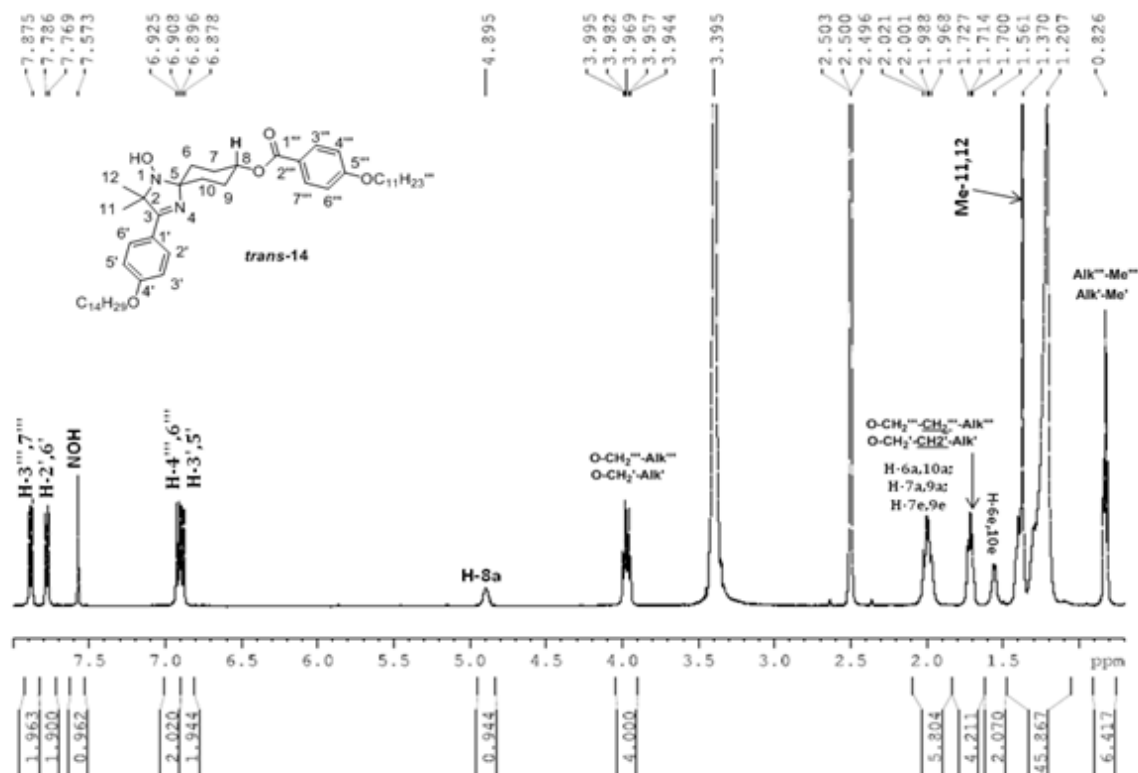
Spectrum 23. ¹H NMR (CDCl₃+DMSO-*d*₆) spectrum of compound *cis*-13

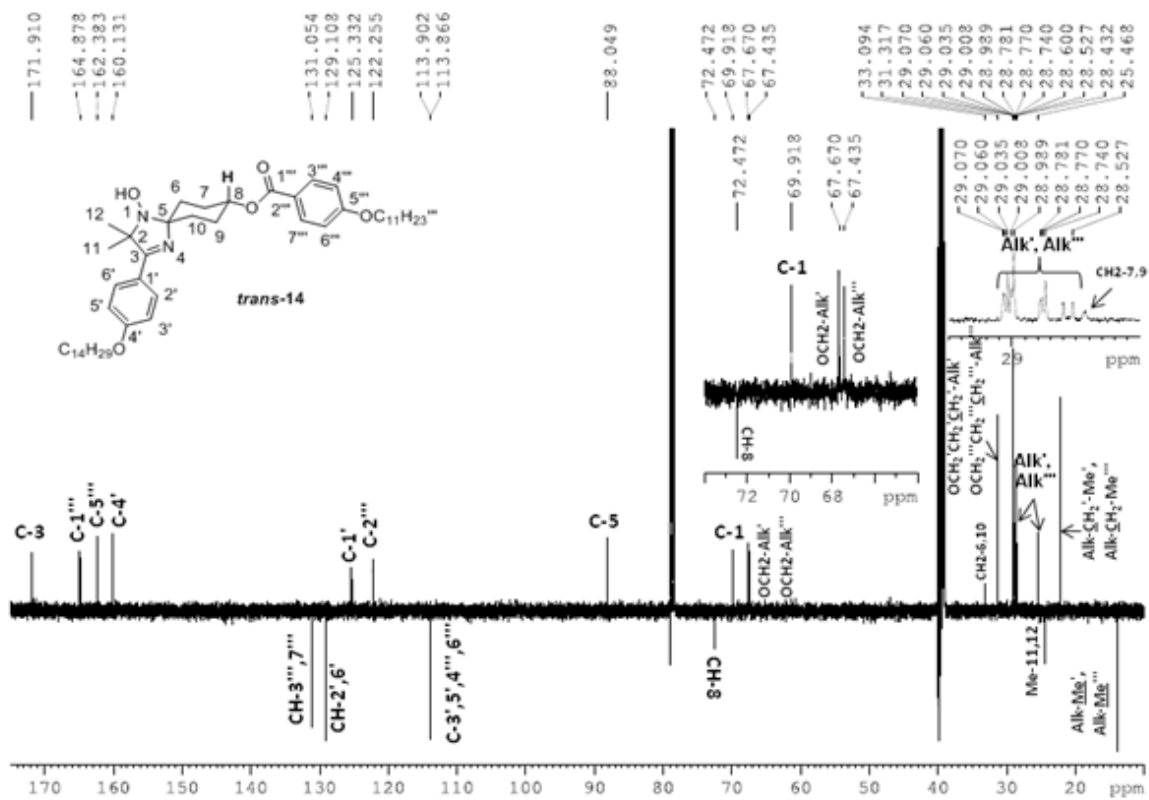


Spectrum 22. ^{13}C NMR ($\text{CDCl}_3+\text{DMSO}-d_6$) spectrum of compound *cis*-14

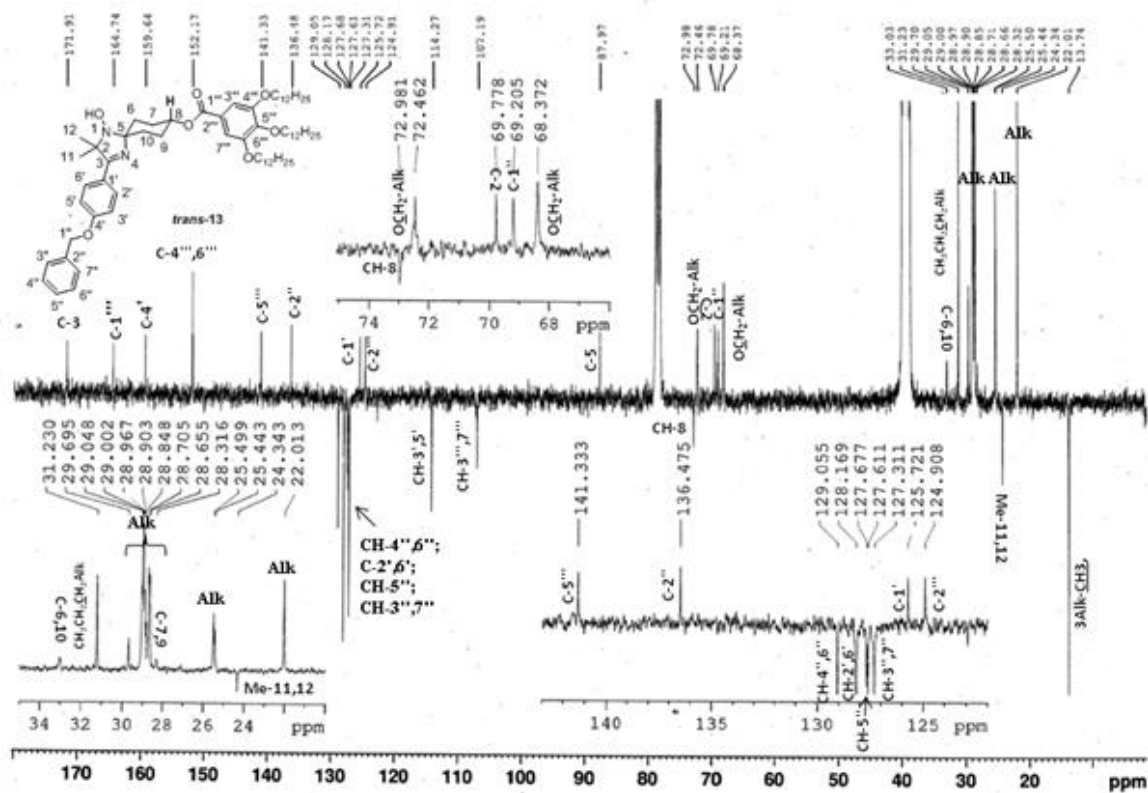


Spectrum 24. ^{13}C NMR ($\text{CDCl}_3+\text{DMSO}-d_6$) spectrum of compound *cis*-13





Spectrum 27. ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$) spectrum of compound *trans-14*



Spectrum 28. ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$) spectrum of compound *trans-13*

Spectra 21-28 represent ^1H (400 MHz) and ^{13}C (100 MHz) spectra recorded for the $\text{CDCl}_3+\text{DMSO}-d_6$ solutions of ***cis-13***, ***trans-13*** and ***cis-14*** and ***trans-14***. Only the side parts of the molecules are different, but the main skeletons 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-alkoxysubstituted benzoic acid or 3,4,5-alkoxysubstituted 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 analysis of their ^1H , ^{13}C , NOESY and ROESY NMR, and the ^1H 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
<i>trans-4</i>	Cr ₁ 78 (2) Cr ₂ 96 (15) I
<i>trans-5</i>	Cr 82 (20) I
<i>cis-5</i>	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>