Supporting information

SYNTHESIS OF TRICYCLIC DIOXETANES THAT EXHIBIT INTRAMOLECULAR CHARGE-TRANSFER-INDUCED DECOMPOSITION: RELATIONSHIP BETWEEN STRUCTURE AND CHEMILUMINESCENCE EFFICIENCY

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***CL and FL spectra ------Figure SI-electronic spectra**
***Stereochemistry for 1,2-addition of singlet oxygen to 5-aryl-4-tert-butyl- 2,3-dihydrofurans --------Scheme SI-1, and SI-2**
***^{1}H NMR and ^{13}C NMR spectra -----Figure S1–S30.**

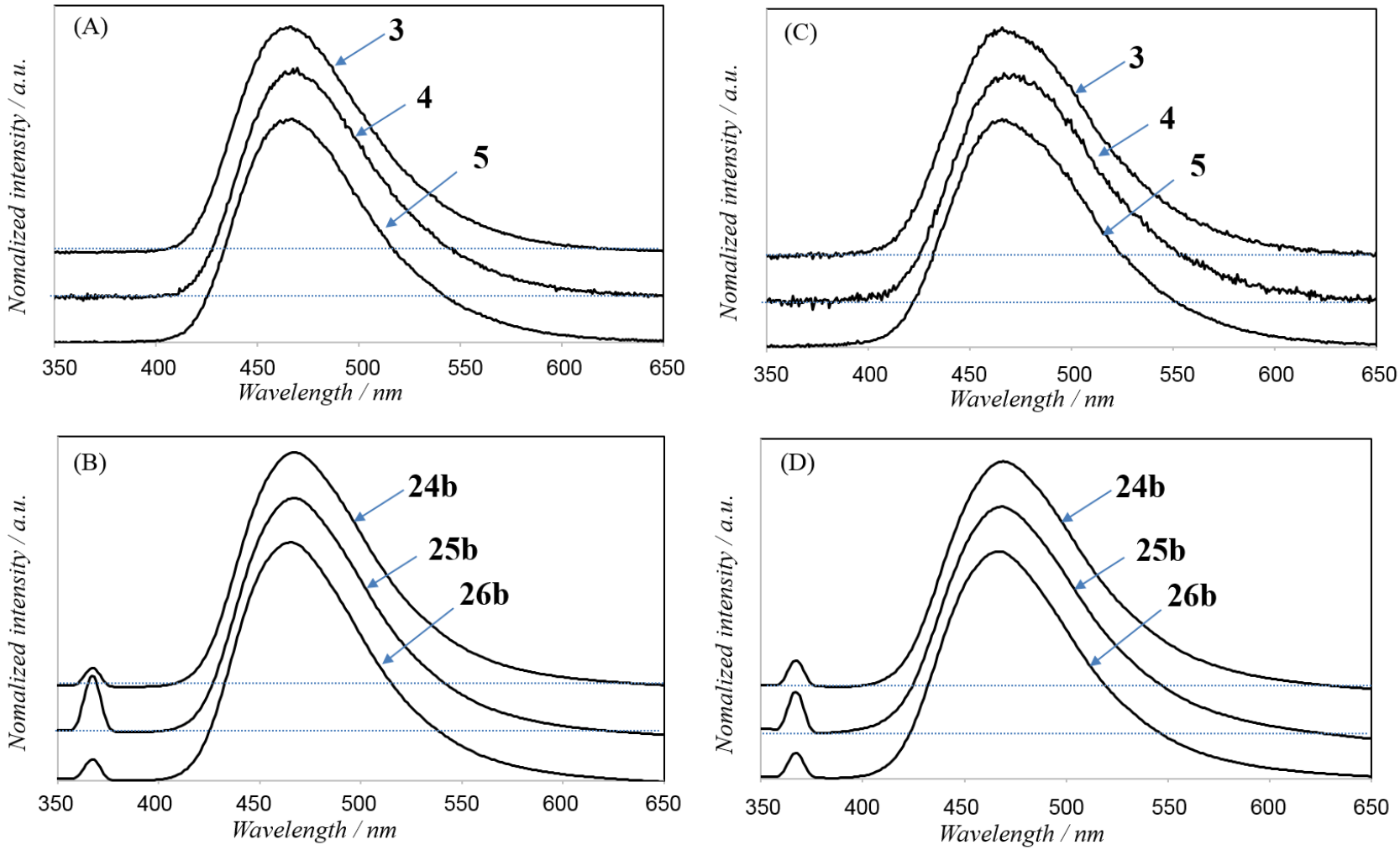
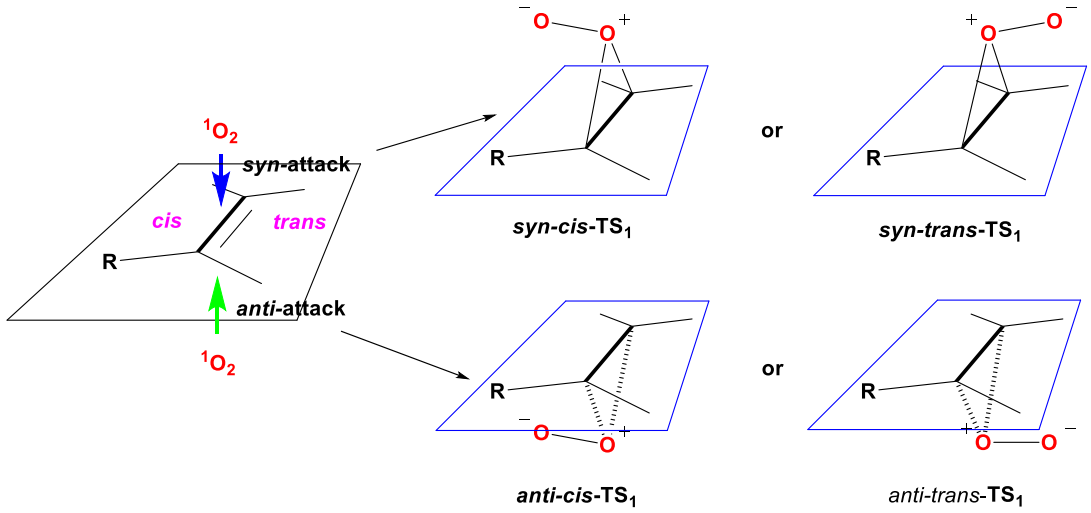


Figure SI-electronic spectra.
(A): Chemiluminescence spectra of dioxetane **3**,**4** and **5** in TBAF/DMSO;
(B): Fluorescence spectra of keto ester **24b**,**25b** and **26b** in TBAF/DMSO;
(C): Chemiluminescence spectra of dioxetane **3**,**4** and **5** in TBAF/acetonitrile;
(D): Fluorescence spectra of keto ester **24b**,**25b** and **26b** in TBAF/acetonitrile

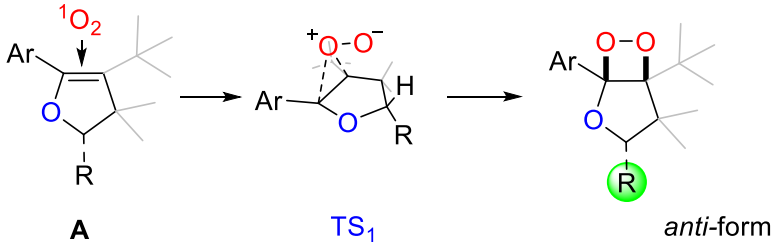
Stereochemistry for 1,2-addition of singlet oxygen to 5-aryl-4-tert-butyl- 2,3-dihydrofurans

Various mechanistic investigations for singlet oxygenation of olefins have suggested that 1,2-cycloaddition of $^1O_2$ proceeds through peroxirane **TS_1** as a transient species. Scheme SI-1 shows that **TS_1** can possess four types of stereochemistry, *syn-cis*-**TS_1**, *syn-trans*-**TS_1**, *anti-cis*-**TS_1** and *anti-trans*-**TS_1**. First of all, when $^1O_2$ attacks upper π-face of olefin, *syn*-**TS_1** forms, while *anti*-**TS_1** forms upon the attack of $^1O_2$ to the opposite π-face (**π-face selectivity**). On the other hand, **TS_1** can further exhibit two stereochemistries depending on the orientation of the terminal O^- in respect of a substituent R: for *cis*-**TS_1**, the O^- lays on the same side (*cis*) of R, while for *trans*-**TS_1**, the O^- lays on the opposite side (*trans*) of R (**side selectivity**)



Scheme SI-1

For parent dihydrofuran, 4-*tert*-butyl-3,3-dimethyl-5-(3-siloxyphenyl)-2,3-dihydro furan (**A**), 1,2-addition of $^1O_2$ is thought to proceed through *cis*-**TS_1**, in respect of dihydrofuran O atom, due to *steering (guiding) effect* of an O atom in dihydrofuran and steric effect of a bulky 4-*tert*-butyl group. Thus, a substituent R at the 2-position in **A** would prevent the attack of $^1O_2$ on the *syn*-face in respect of R (Scheme SI-2). In fact, 1,2-addition of $^1O_2$ has been reported for dihydrofurans bearing a 2-R (R = Me, Ph, *tert*-Bu) to proceed with high π-face selectivity to give the corresponding dixetanes with *anti*-stereochemistry. This π-face selectivity was also the case for the present 1,2-cycloaddition of $^1O_2$ to **6b**, **7b** and **8b**: for these dihydrofurans, dissymmetric substitution at the 3-position presumably also participated synergistically in π-face selectivity.



Scheme SI-2.

References: (1) "Control of mode selectivity in singlet oxygenation of olefins" by M. Matsumoto, *Photochemistry*, 1998, **28**, 31-38.
(2) M. Matsumoto, Y. Ito, J. Matsubara, T. Sakuma, Y. Mizoguchi, N. Watanabe, *Tetrahedron Lett.*, 2001, **42**, 2349.

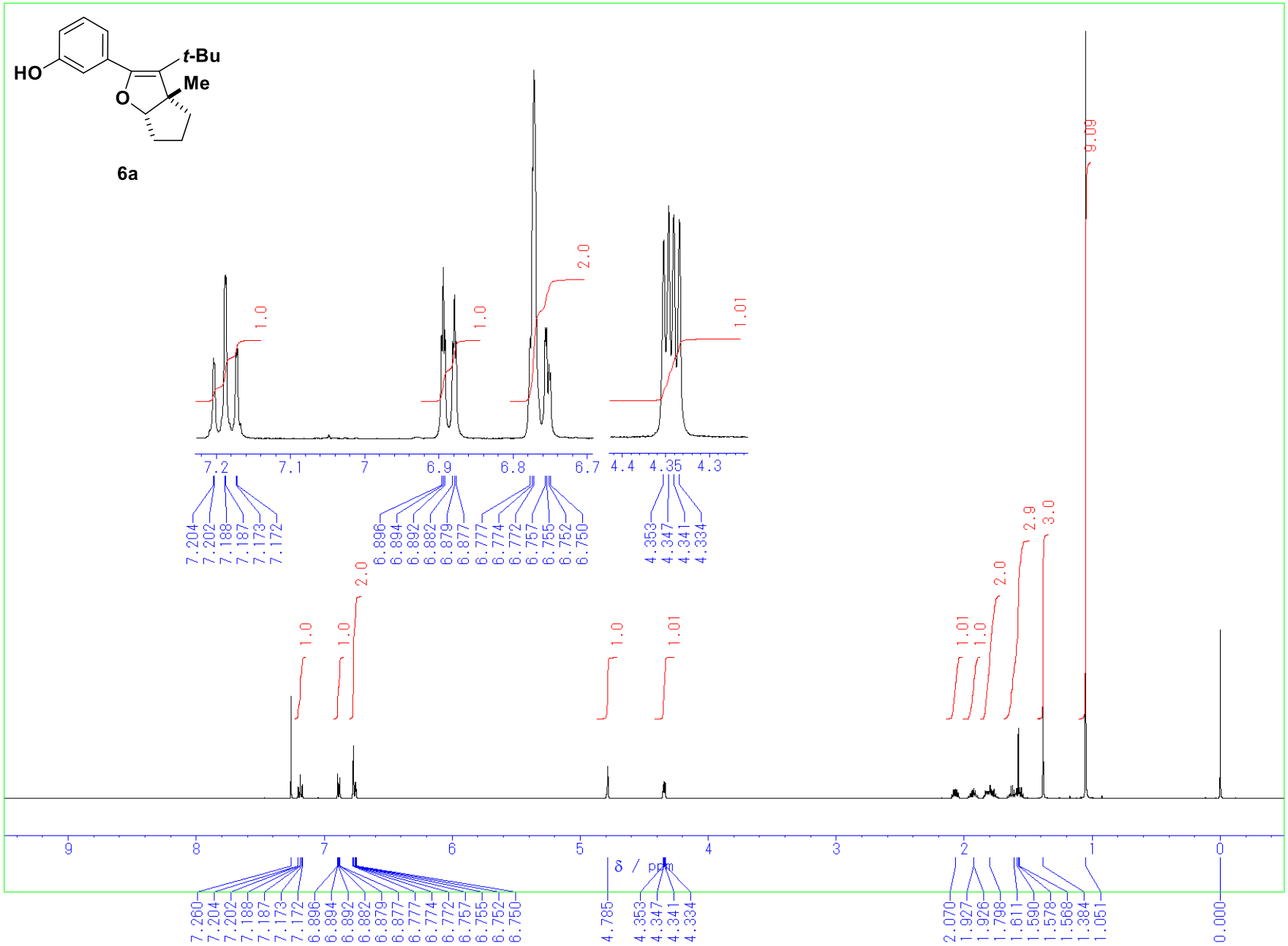


Figure S1. ^{1}H NMR spectrum of *cis*-4-*tert*-butyl-3-(3-hydroxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(6a)** in $CDCl_3$.

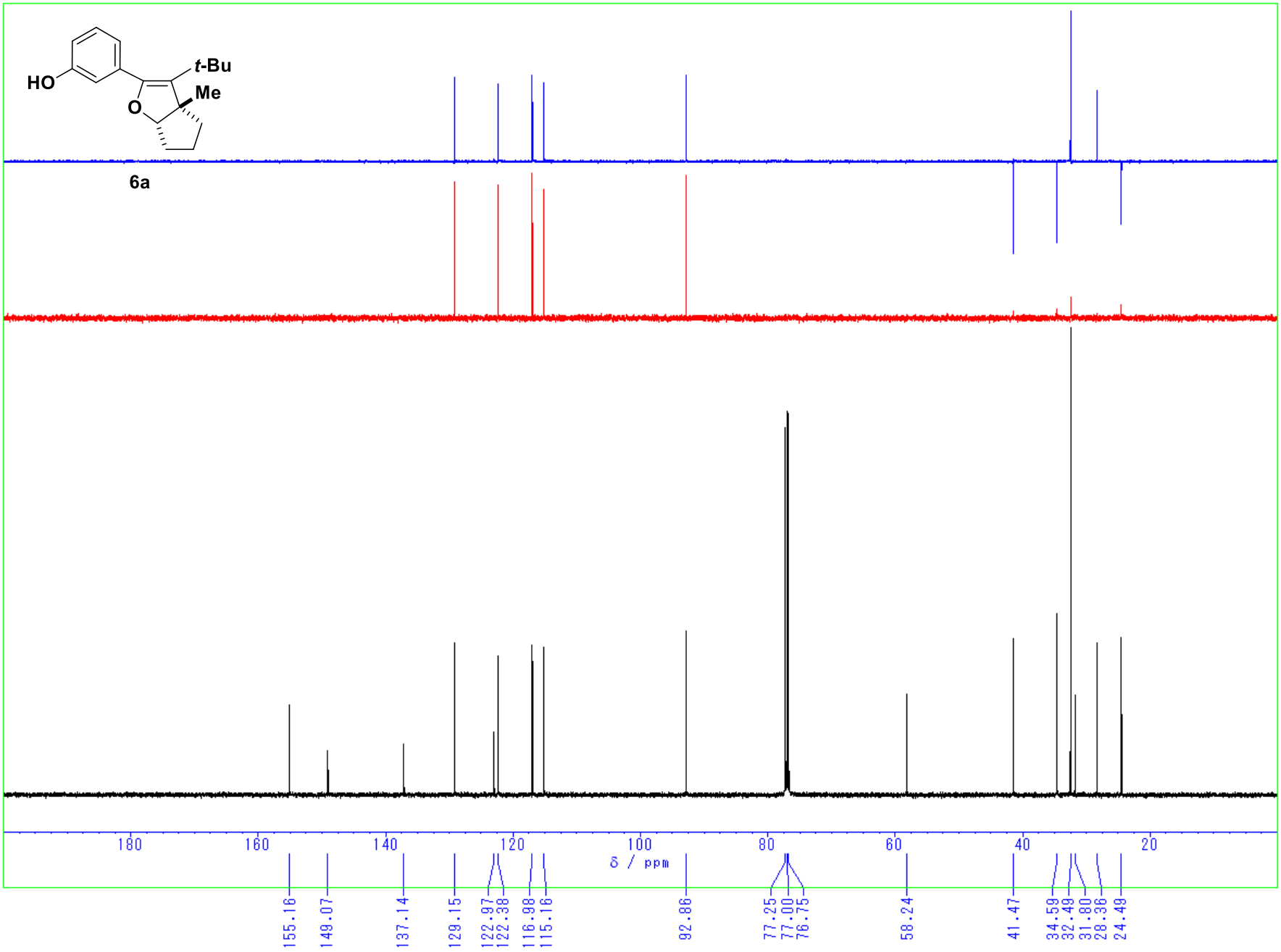


Figure S2. ^{13}C NMR spectrum of *cis*-4-*tert*-butyl-3-(3-hydroxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(6a)** in $CDCl_3$.

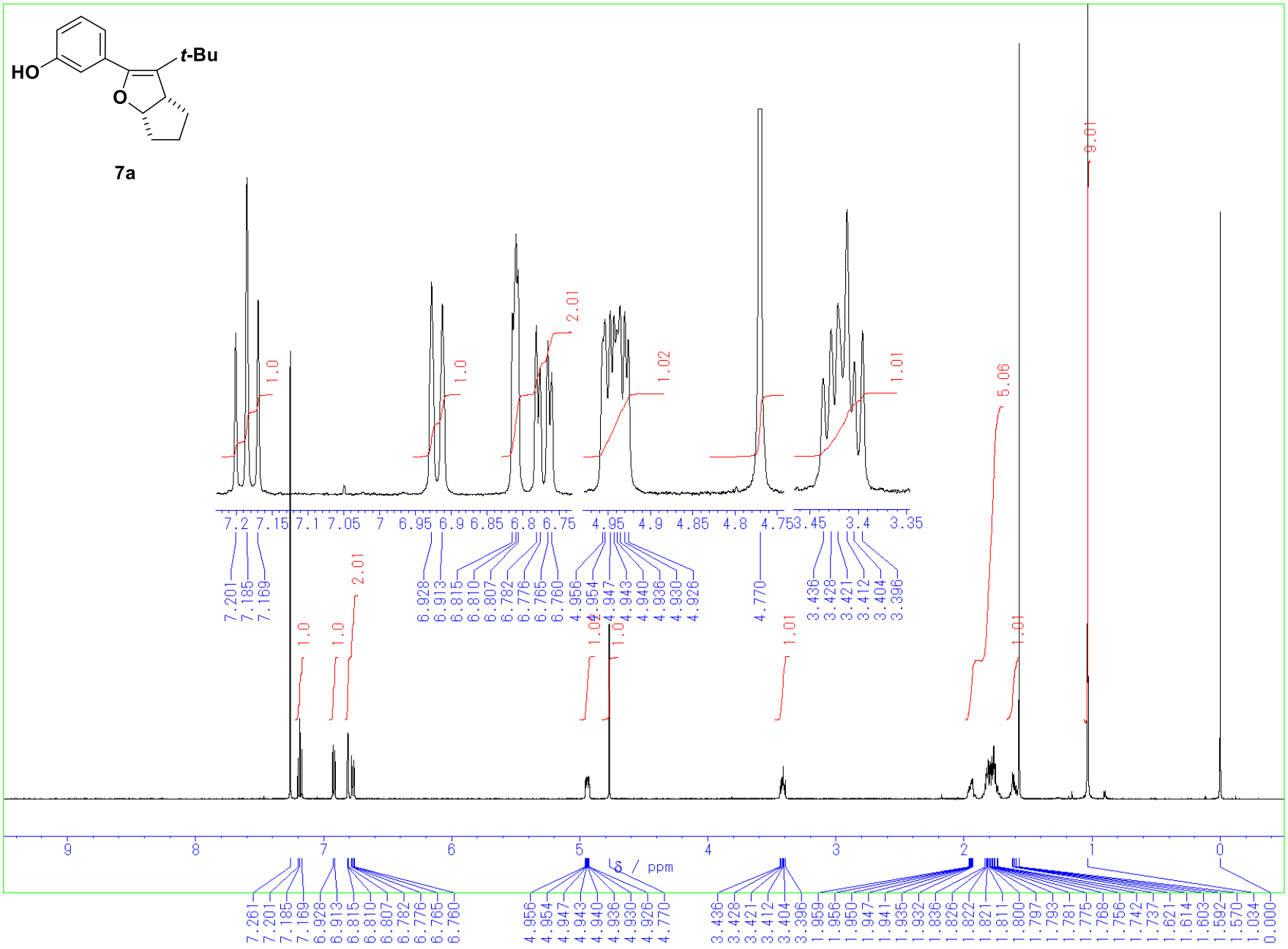


Figure S3. ^{1}H NMR spectrum of *cis*-4-*tert*-butyl-3-(3-hydroxyphenyl)-2-oxabicyclo[3.3.0]oct-3-ene **(7a)** in $CDCl_3$.

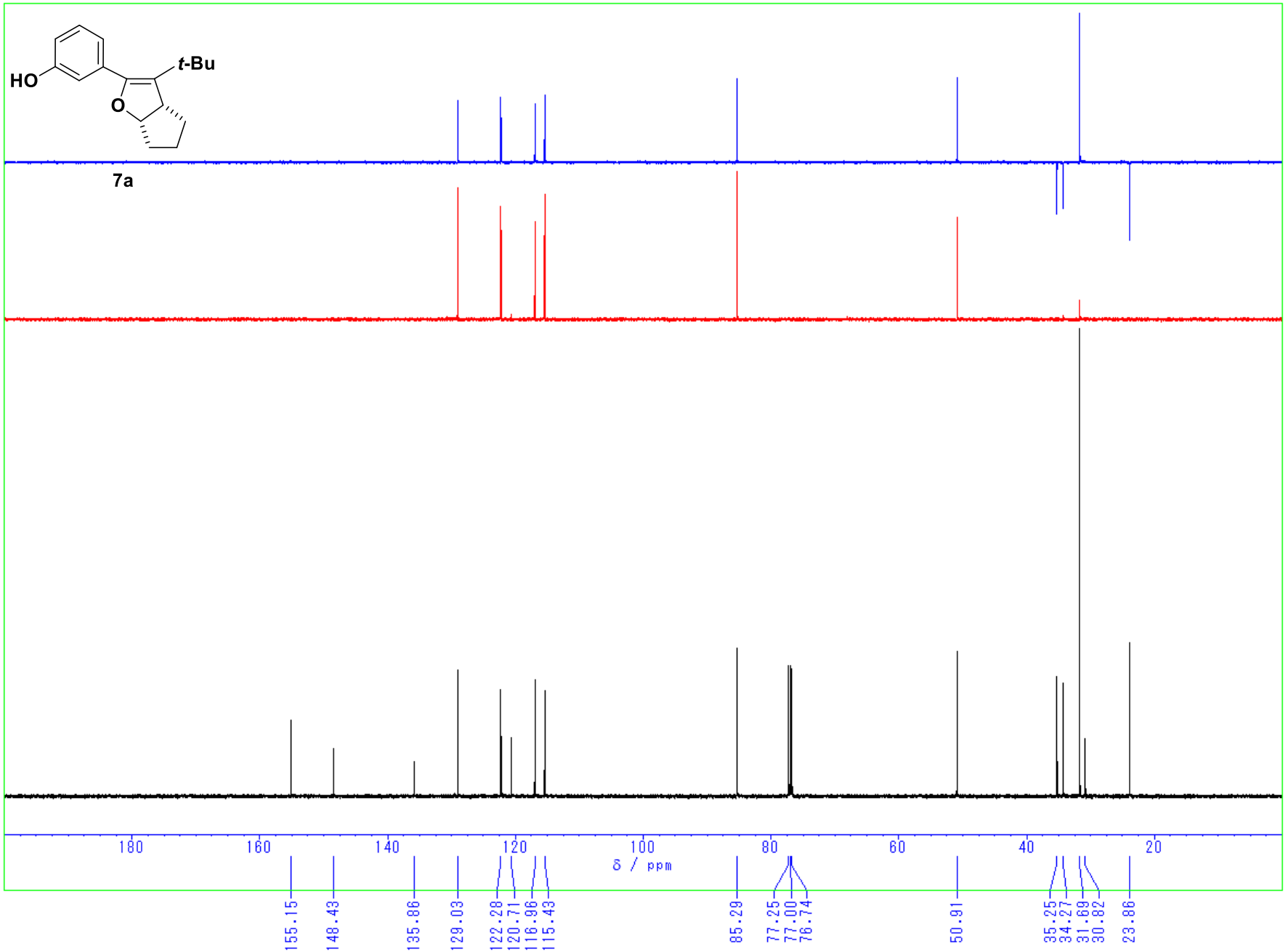


Figure S4. ^{13}C NMR spectrum of *cis*-4-*tert*-butyl-3-(3-hydroxyphenyl)-2-oxabicyclo[3.3.0]oct-3-ene **(7a)** in $CDCl_3$.

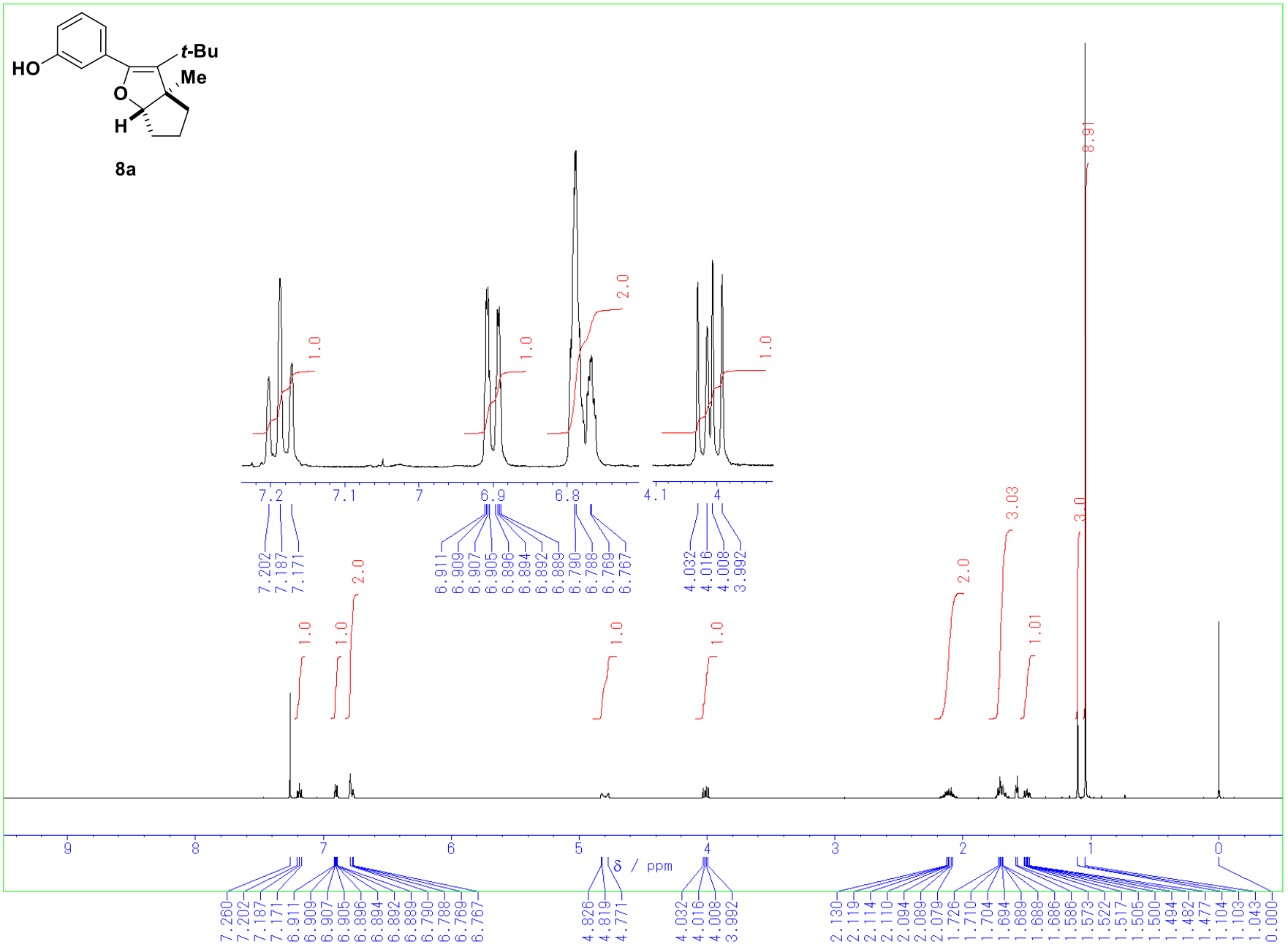


Figure S5. ^{1}H NMR spectrum of *trans*-4-*tert*-butyl-3-(3-hydroxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(8a)** in $CDCl_3$.

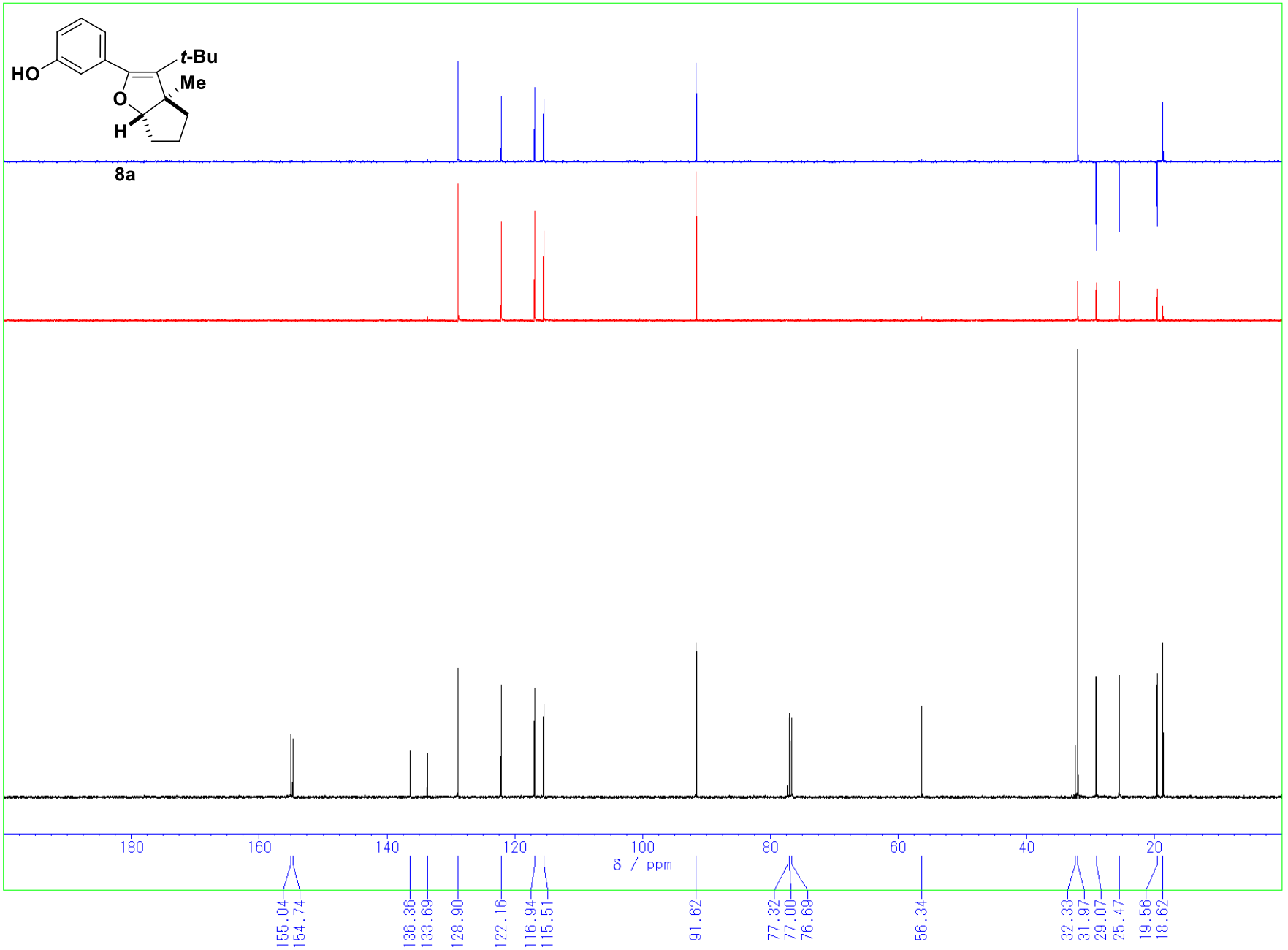


Figure S6. ^{13}C NMR spectrum of *trans*-4-*tert*-butyl-3-(3-hydroxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(8a)** in $CDCl_3$.

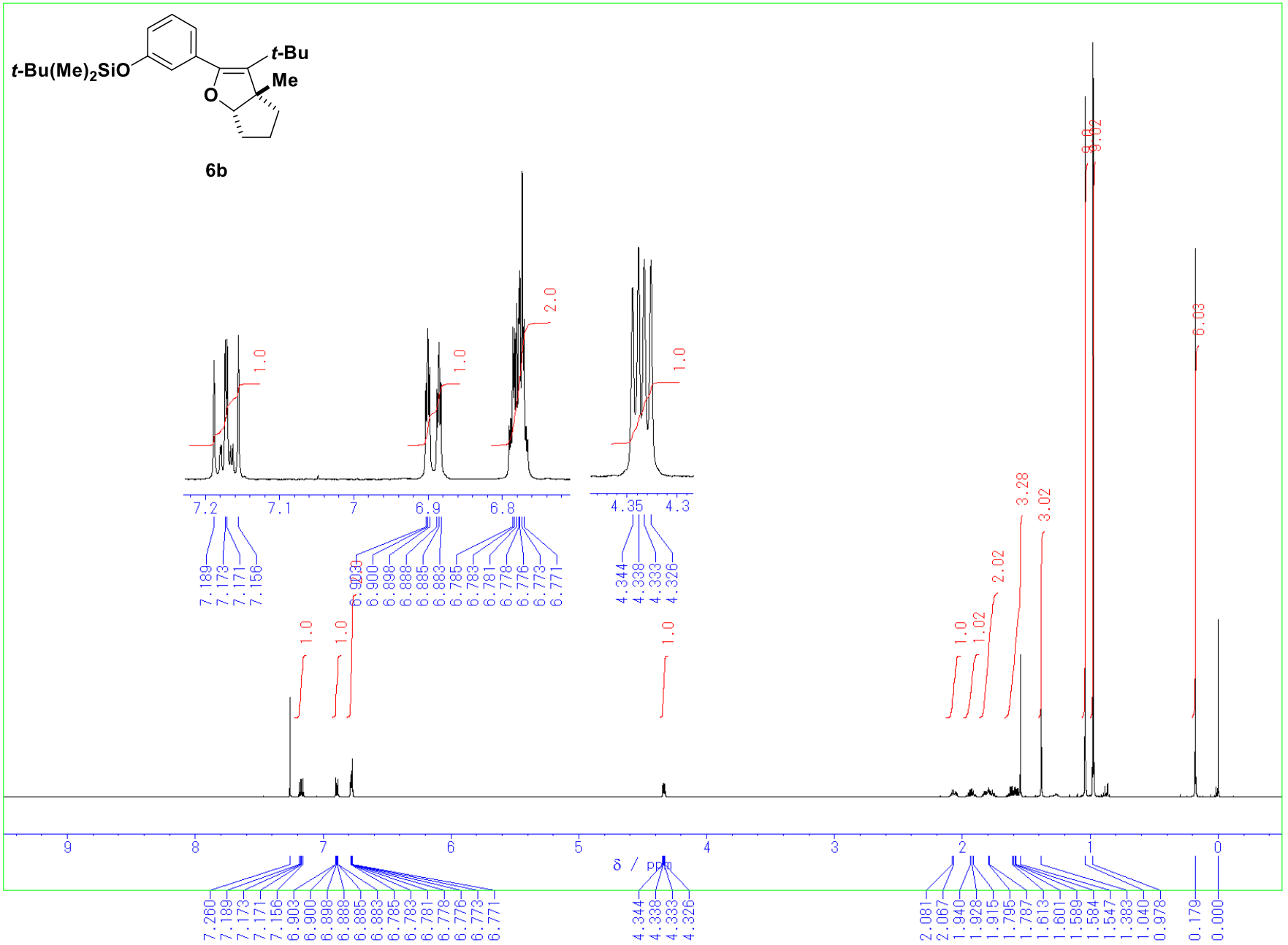


Figure S7. ^{1}H NMR spectrum of *cis*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(6b)** in $CDCl_3$.

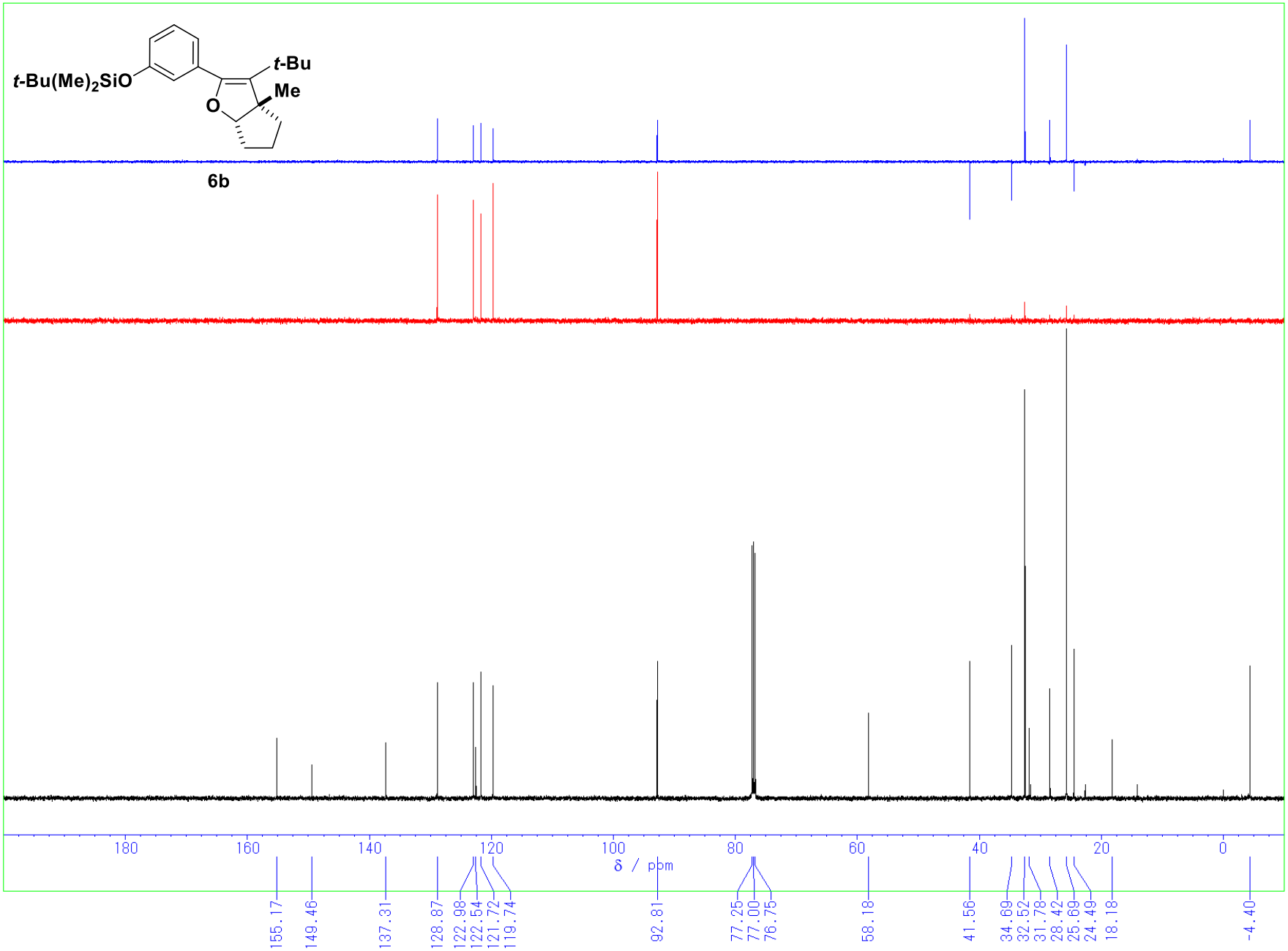


Figure S8. ^{13}C NMR spectrum of *cis*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(6b)** in $CDCl_3$.

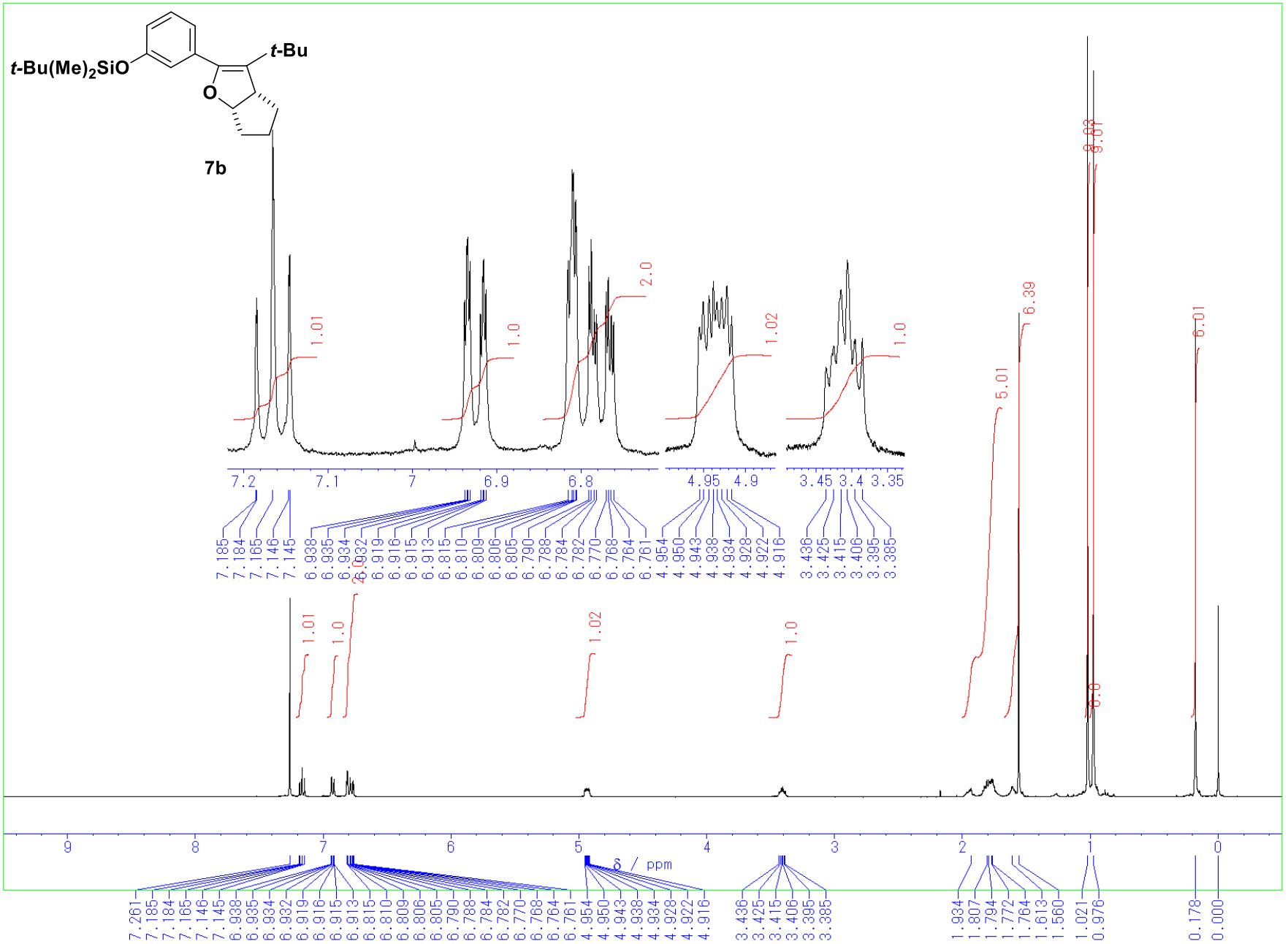


Figure S9. ^{1}H NMR spectrum of *cis*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-2-oxabicyclo[3.3.0]oct-3-ene **(7b)** in $CDCl_3$.

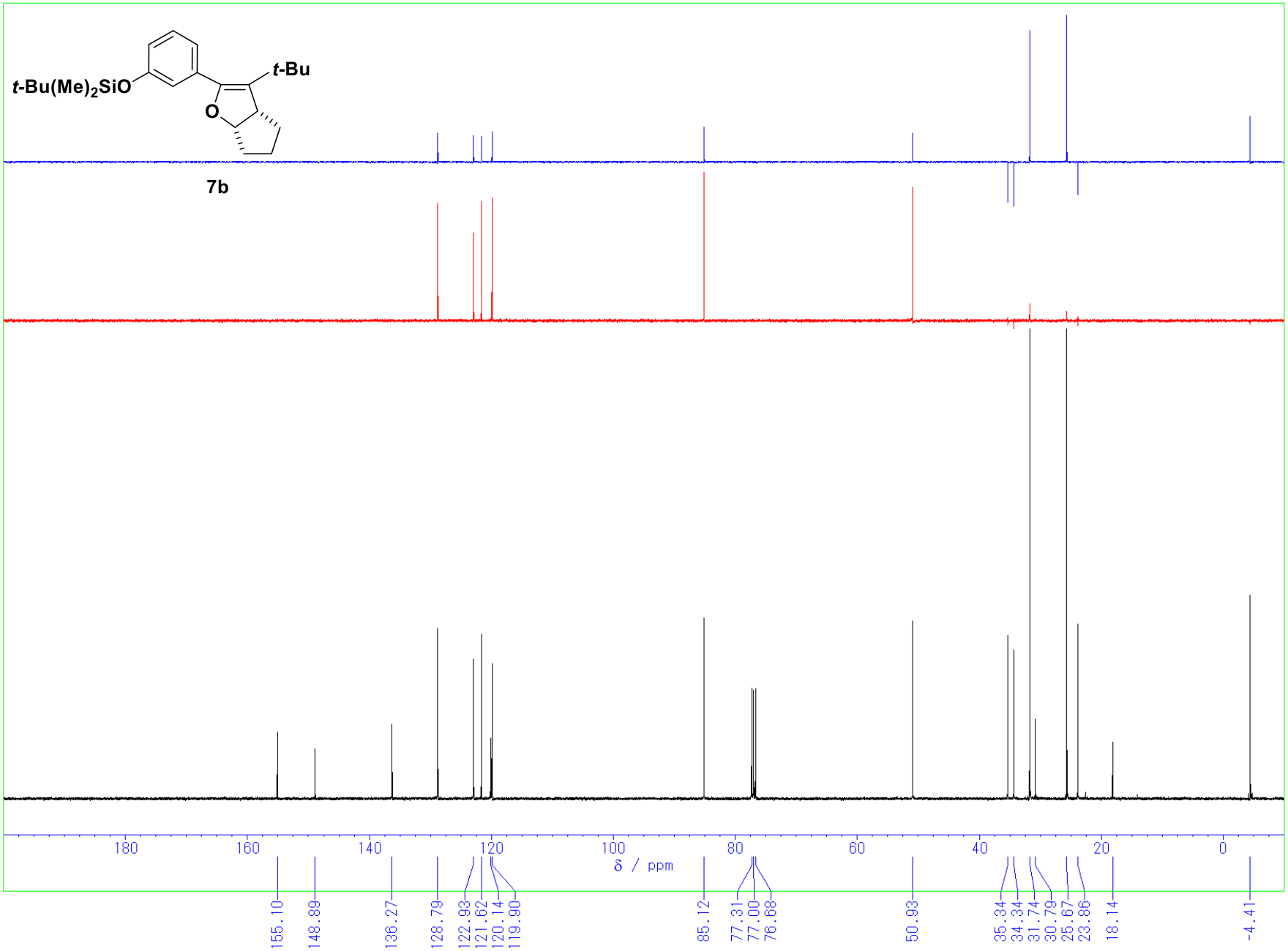


Figure S10. ^{13}C NMR spectrum of *cis*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-2-oxabicyclo[3.3.0]oct-3-ene **(7b)** in $CDCl_3$.

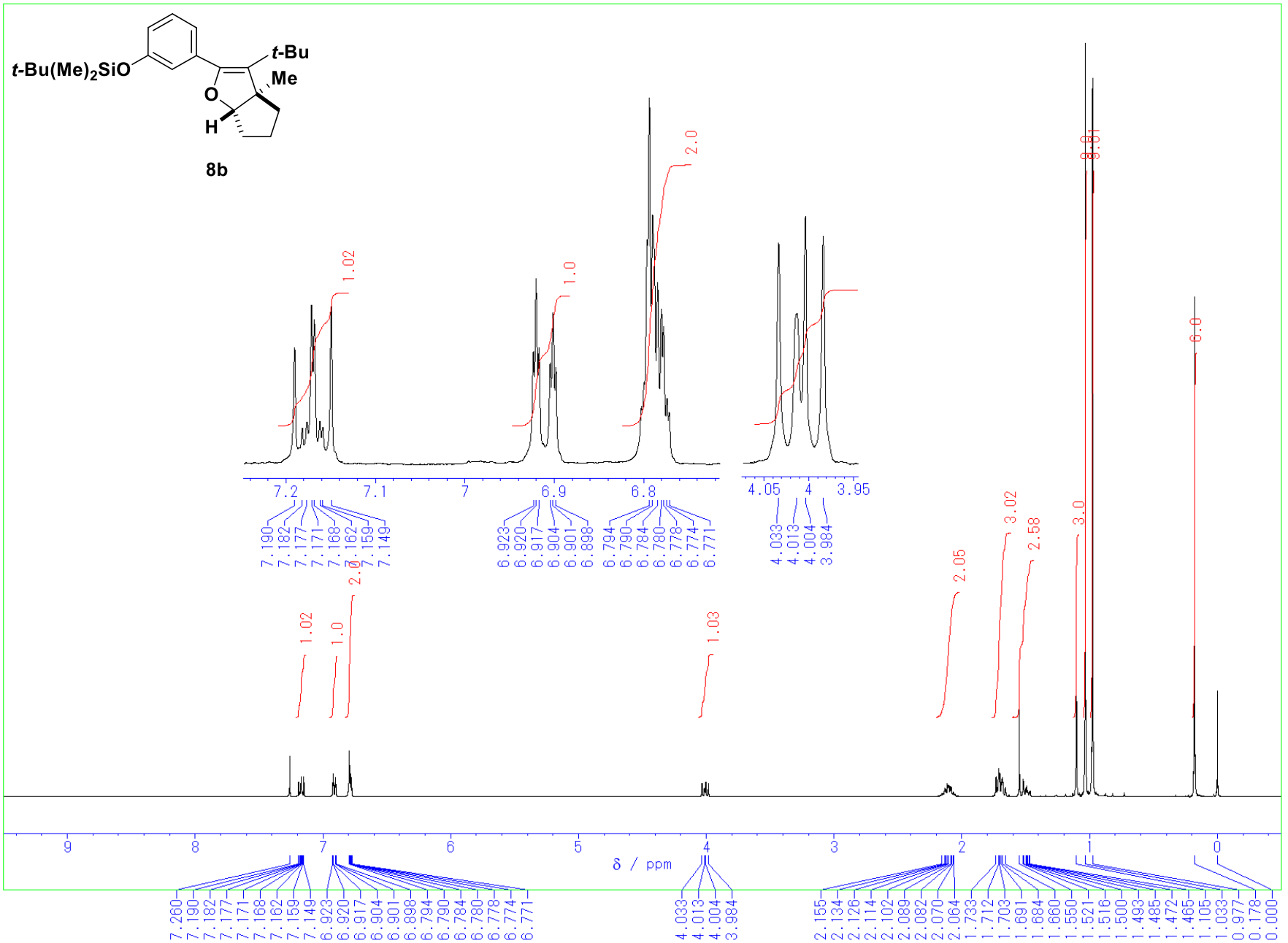


Figure S11. ^{1}H NMR spectrum of *trans*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(8b)** in $CDCl_3$.

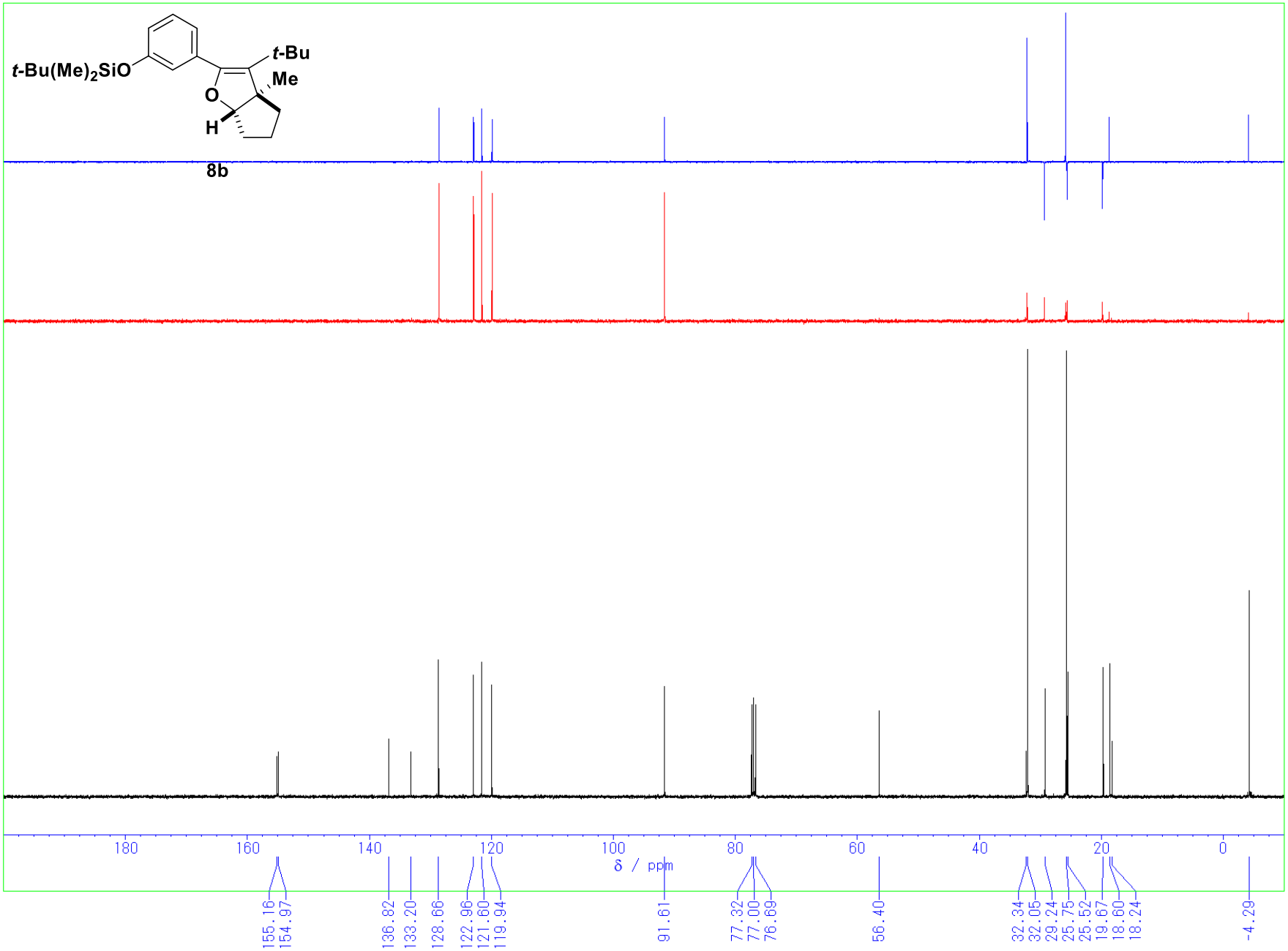


Figure S12. ^{13}C NMR spectrum of *trans*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene **(8b)** in $CDCl_3$.

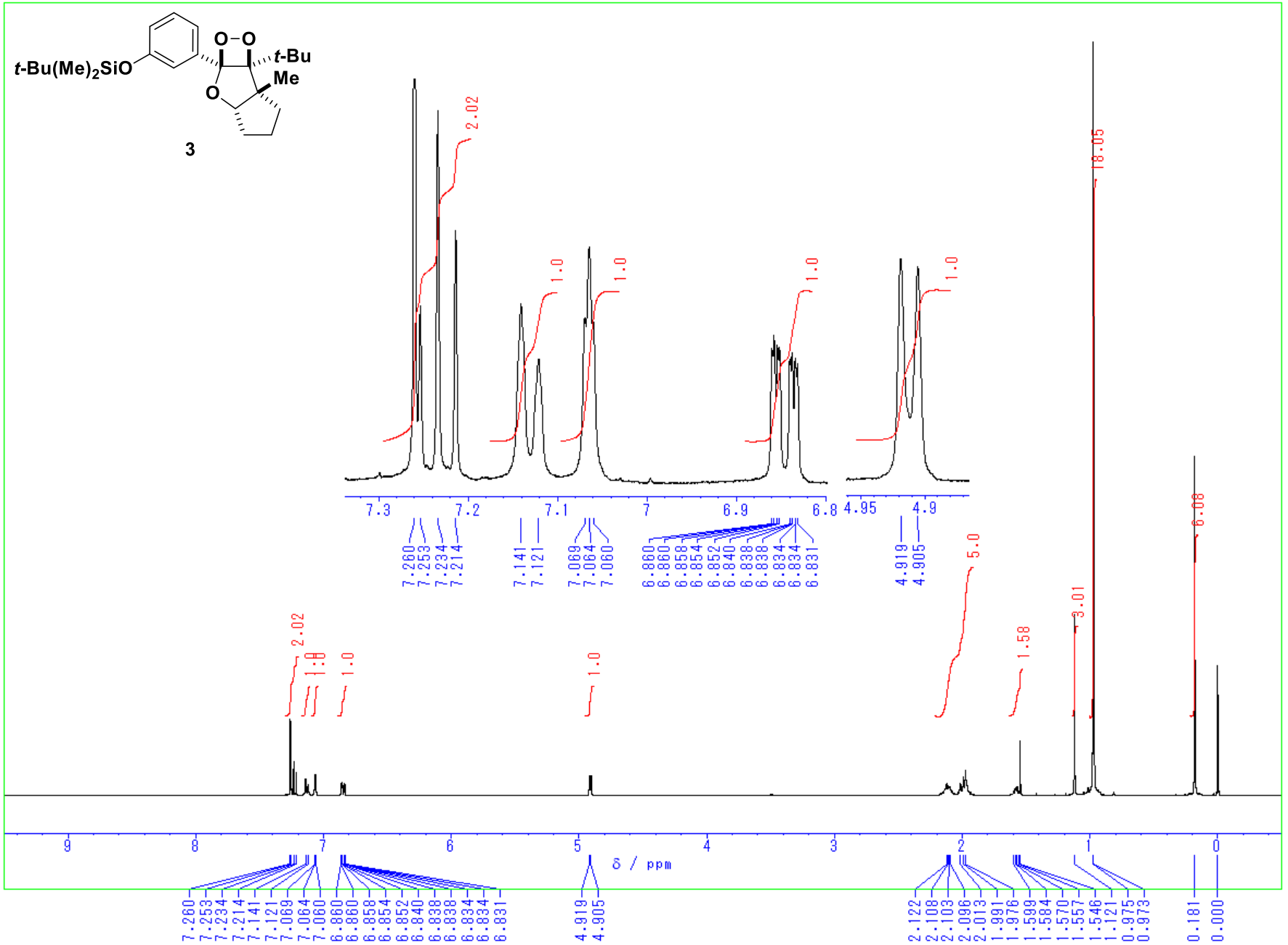


Figure S13. ^{1}H NMR spectrum of *cis*-1-*transoid*-1,3-*cis*-3-(6-*tert*-butyl)-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-7-methyl-2,4,5-trioxatricyclo-[5.3.0.0^{3,6}]decane **(3)** in $CDCl_3$.

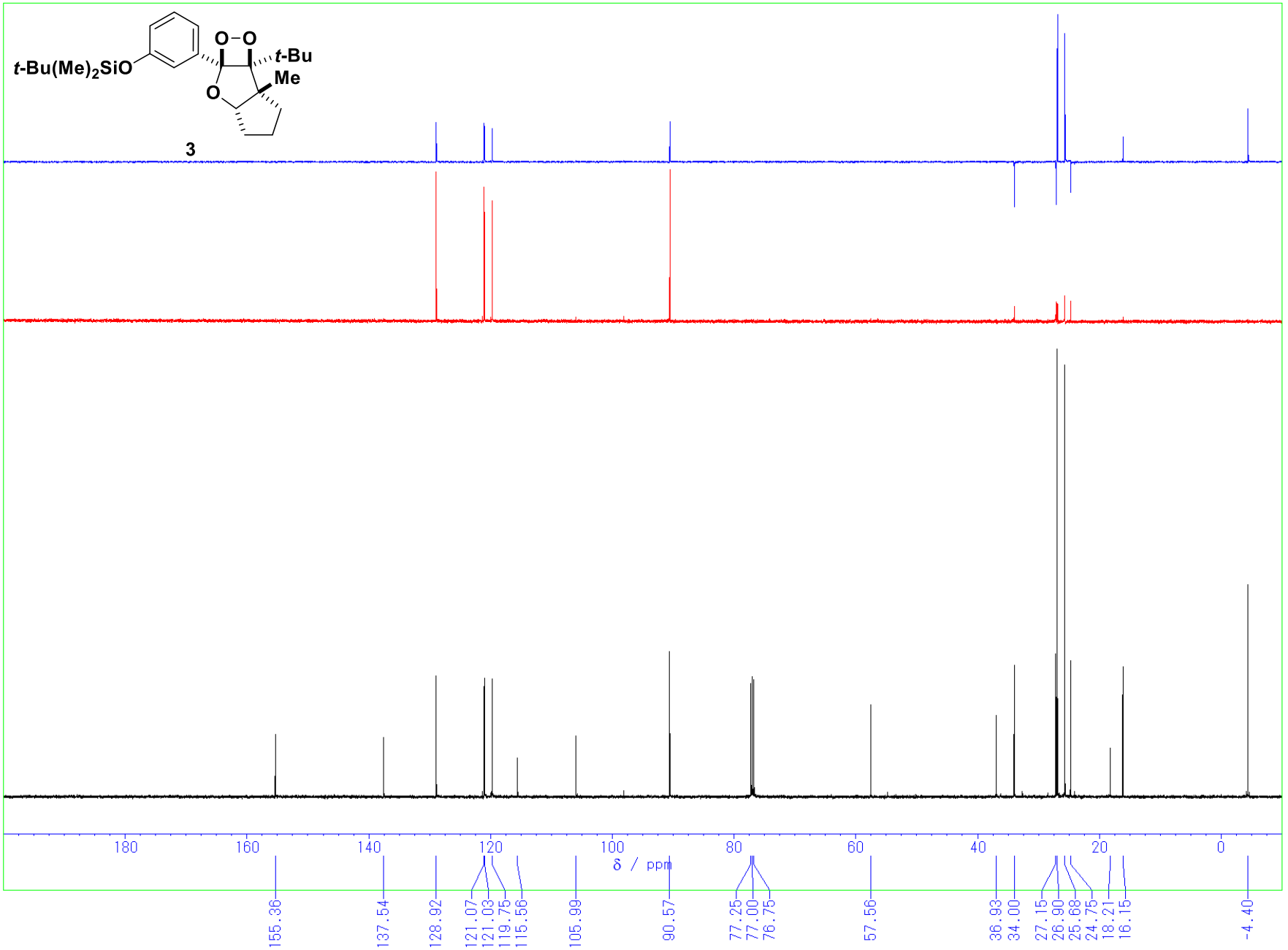


Figure S14. ^{13}C NMR spectrum of *cis*-1-*transoid*-1,3-*cis*-3-(6-*tert*-butyl)-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-7-methyl-2,4,5-trioxatricyclo-[5.3.0.$0^{3,6}$]decane **(3)** in $CDCl_3$.

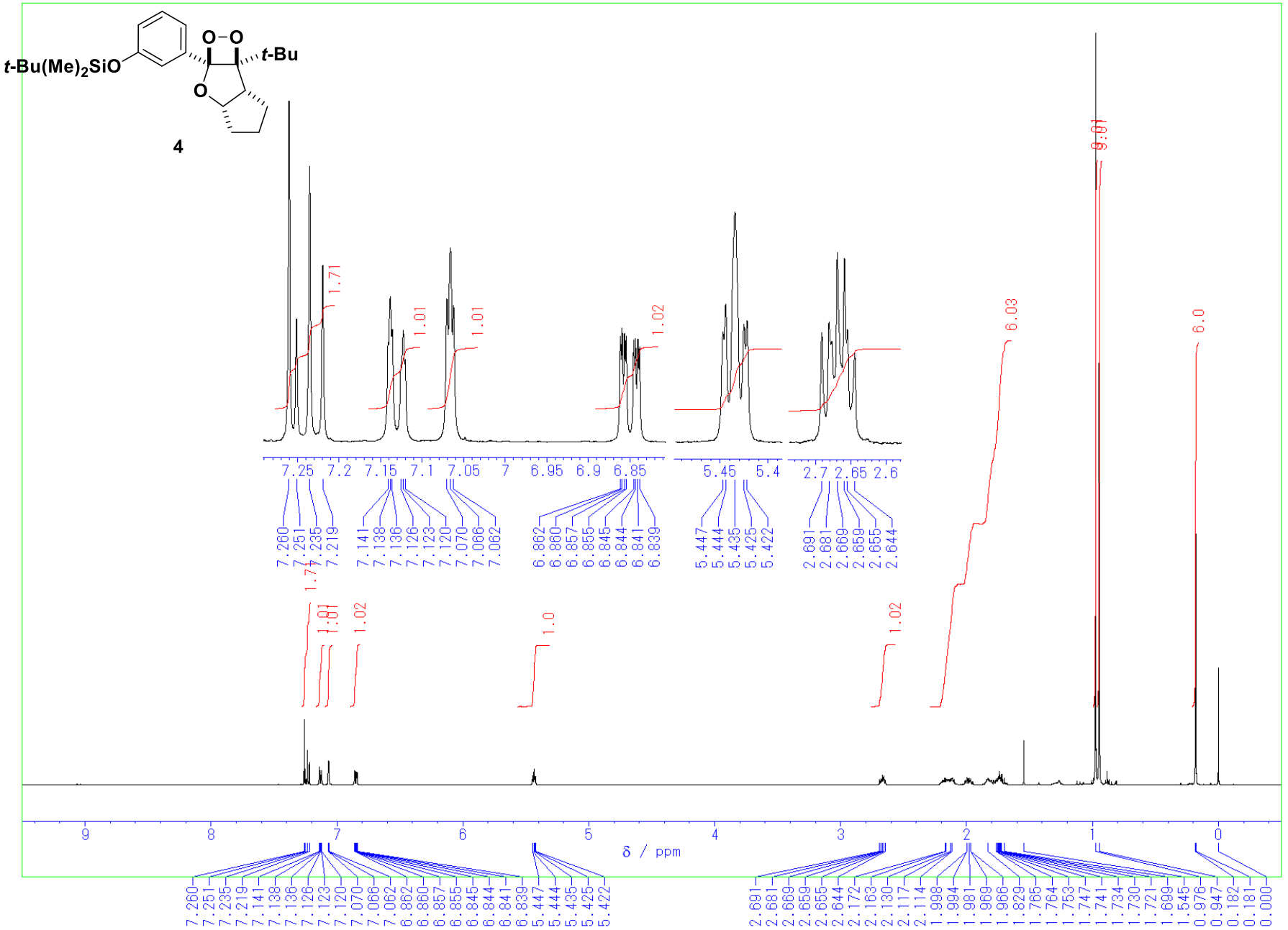


Figure S15. ^{1}H NMR spectrum of *cis*-1-*transoid*-1,3-*cis*-3-(6-*tert*-butyl)-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-2,4,5-trioxatricyclo-[5.3.0.0^{3,6}]decane **(4)** in $CDCl_3$.

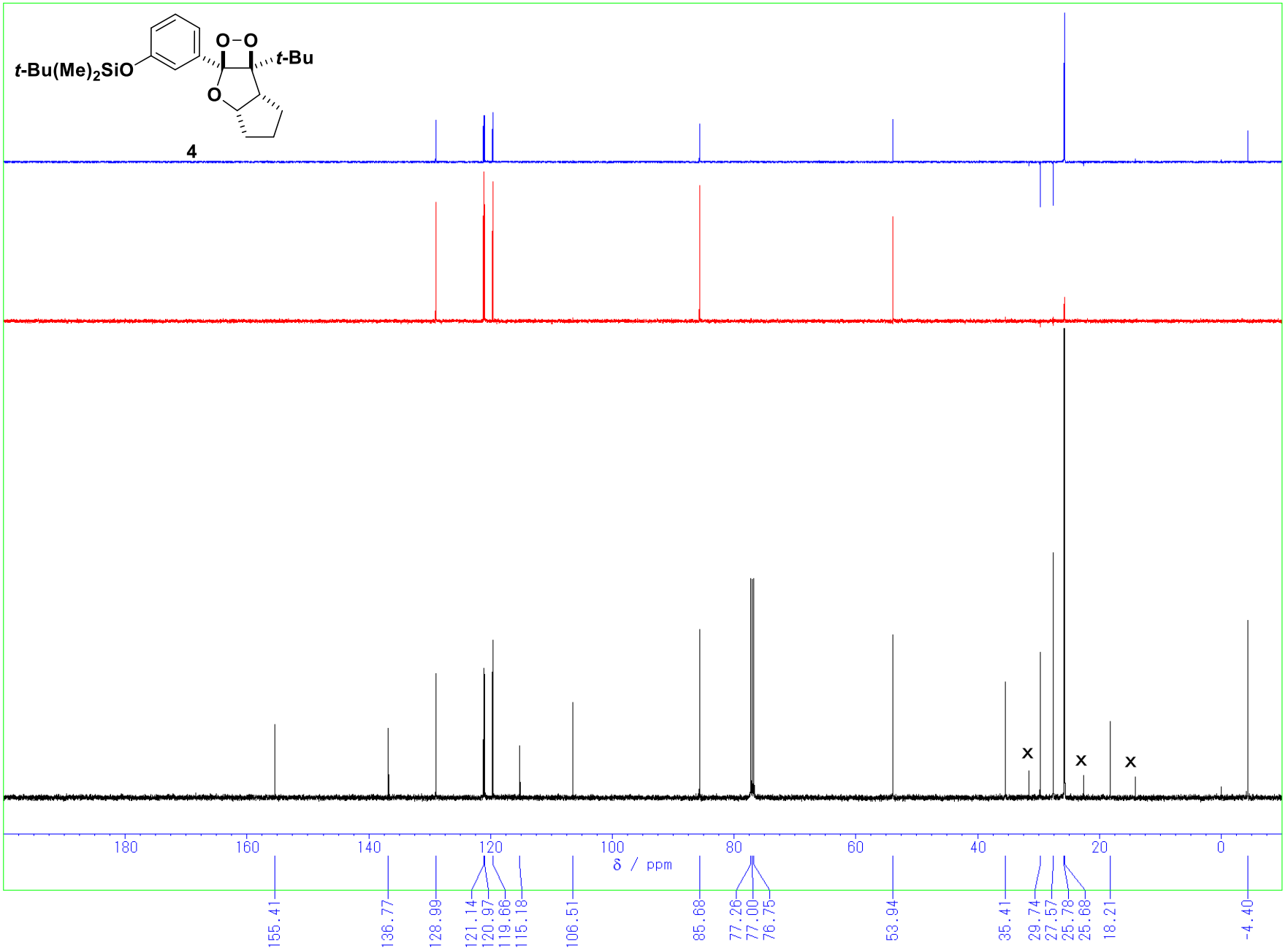


Figure S16. ^{13}C NMR spectrum of *cis*-1-*transoid*-1,3-*cis*-3-(6-*tert*-butyl)-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-2,4,5-trioxatricyclo-[5.3.0.0^{3,6}]decane **(4)** in $CDCl_3$.

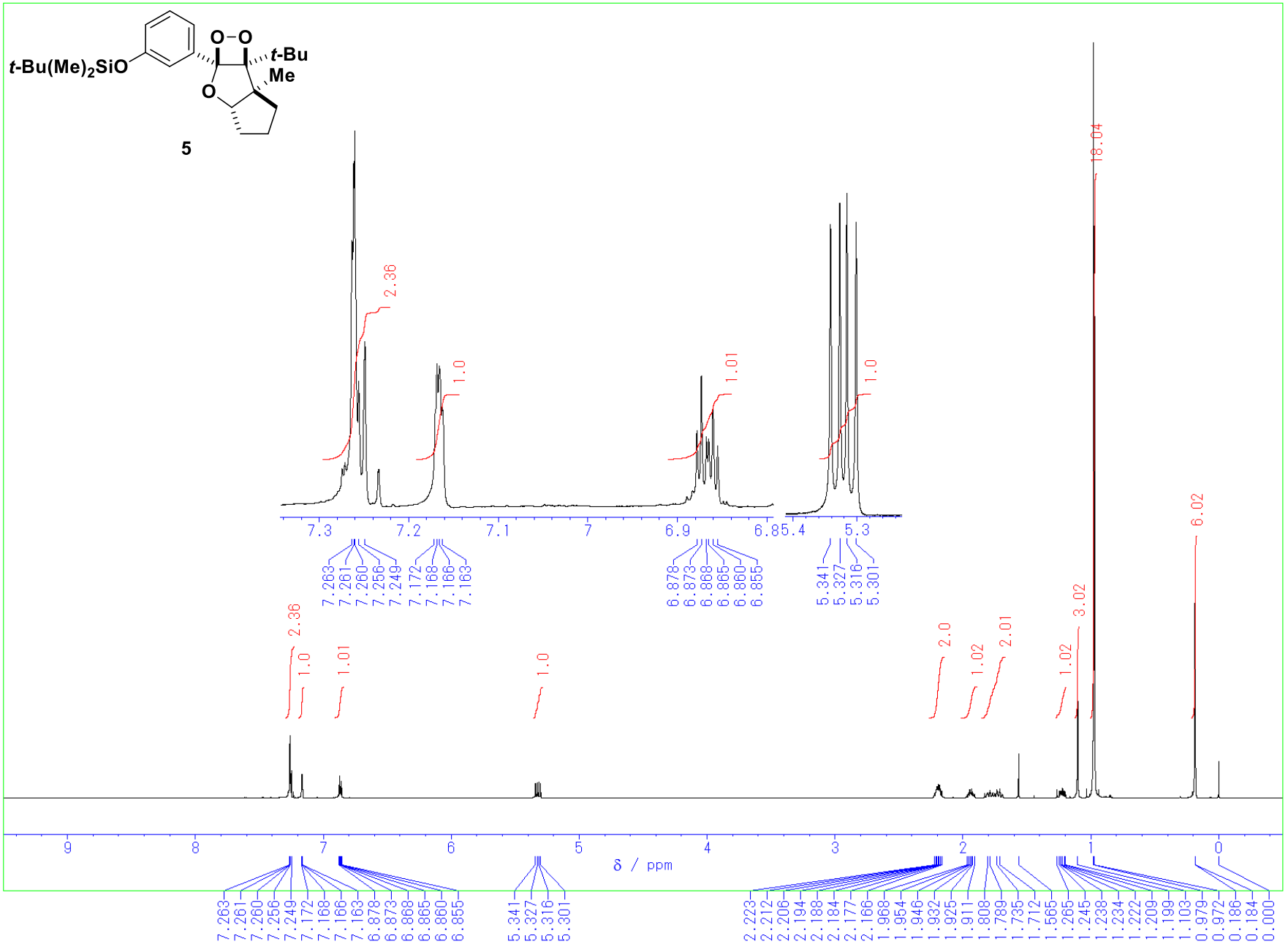


Figure S17. ^{1}H NMR spectrum of *cis*-1-*transoid*-1,3-*trans*-3-(6-*tert*-butyl)-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-7-methyl-2,4,5-trioxatricyclo-[5.3.0.0^{3,6}]decane **(5)** in $CDCl_3$.

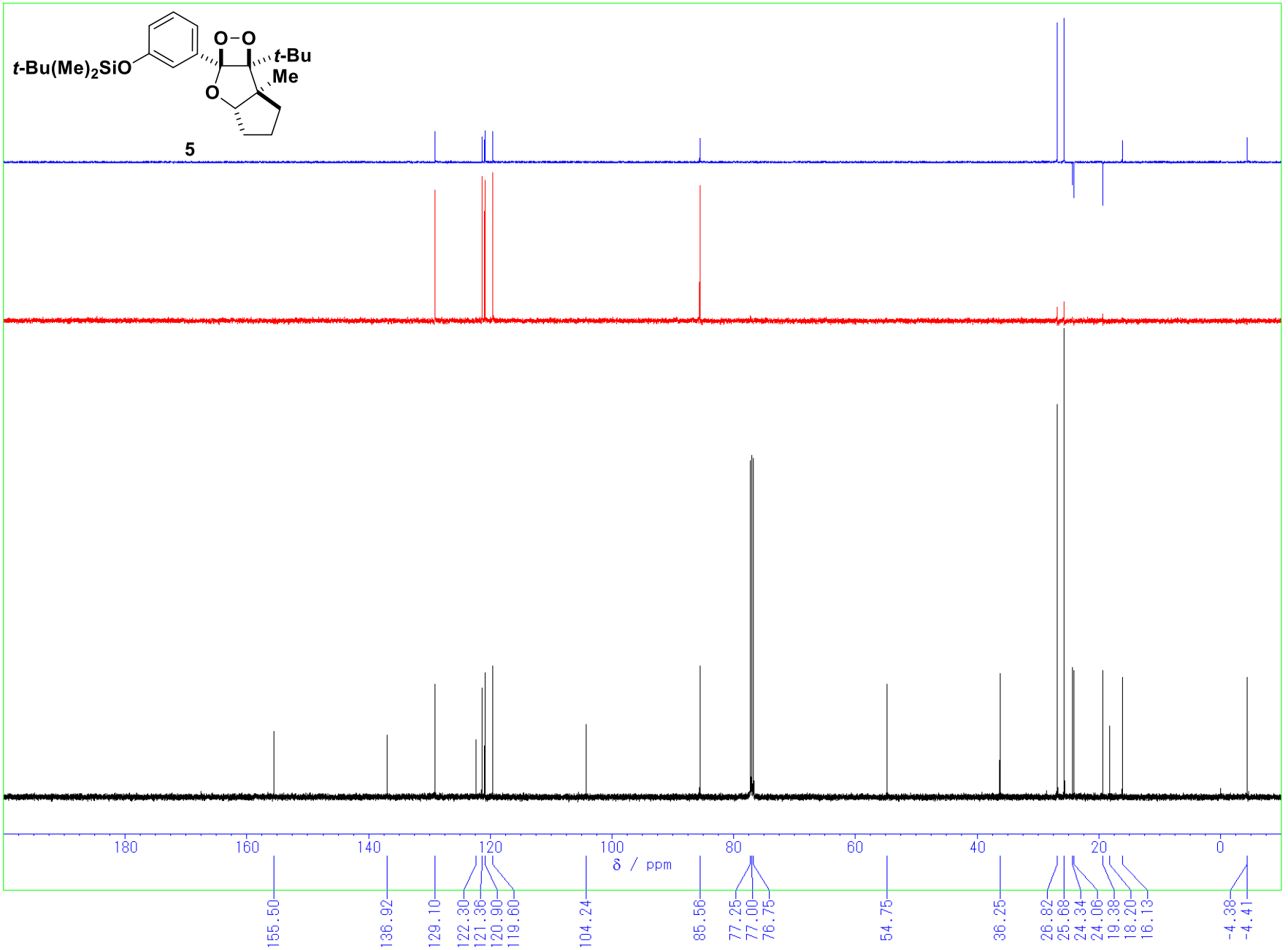


Figure S18. ^{13}C NMR spectrum of *cis*-1-*transoid*-1,3-*trans*-3-(6-*tert*-butyl)-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-7-methyl-2,4,5-trioxatricyclo-[5.3.0.0^{3,6}]decane **(5)** in $CDCl_3$.

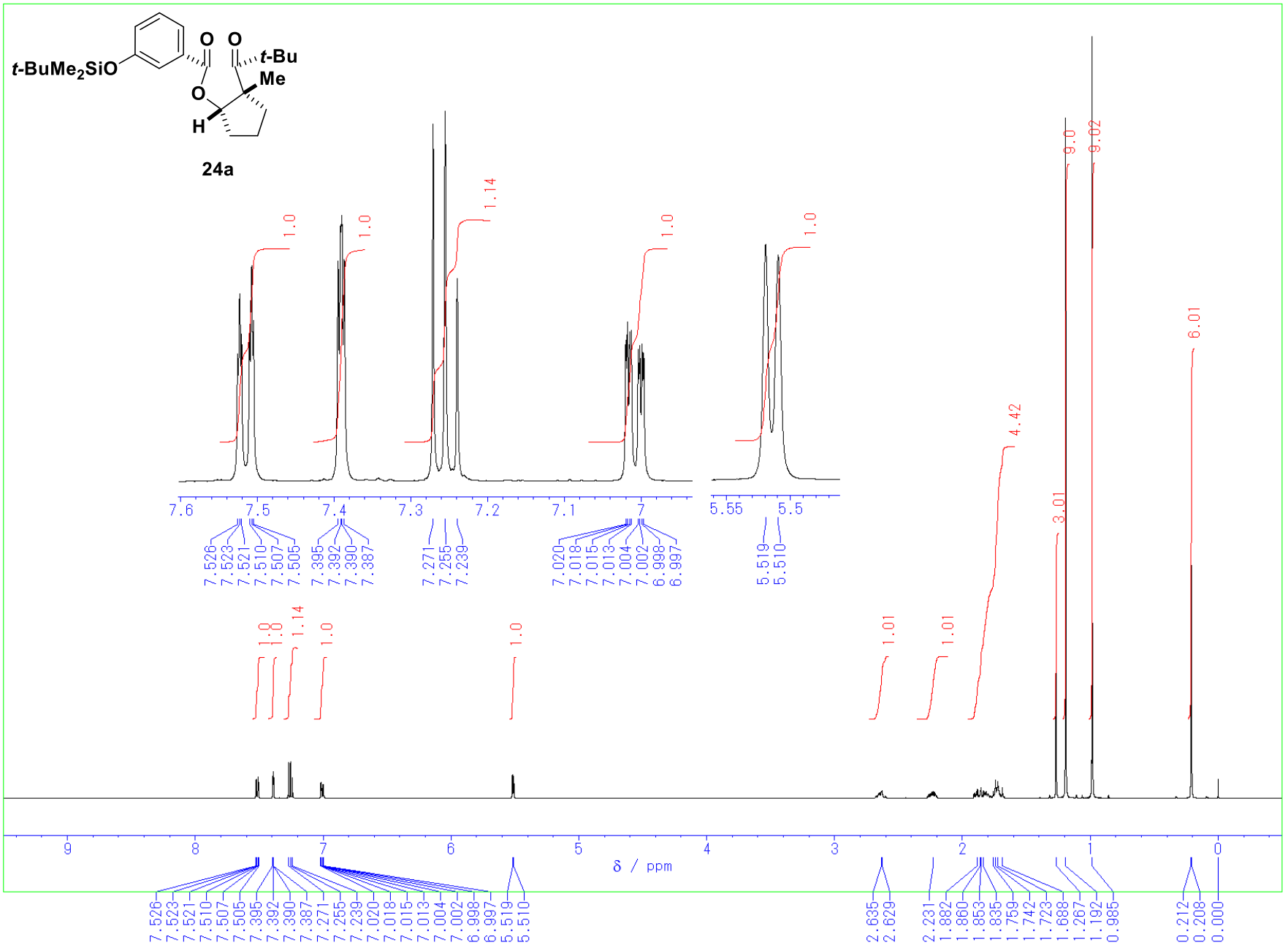


Figure S19. ^{1}H NMR spectrum of *t*-methyl-*c*-2-pivaloylcyclopentyl *r*-3-(*tert*-butyldimethylsiloxy)benzoate (**24a**) in $CDCl_3$.

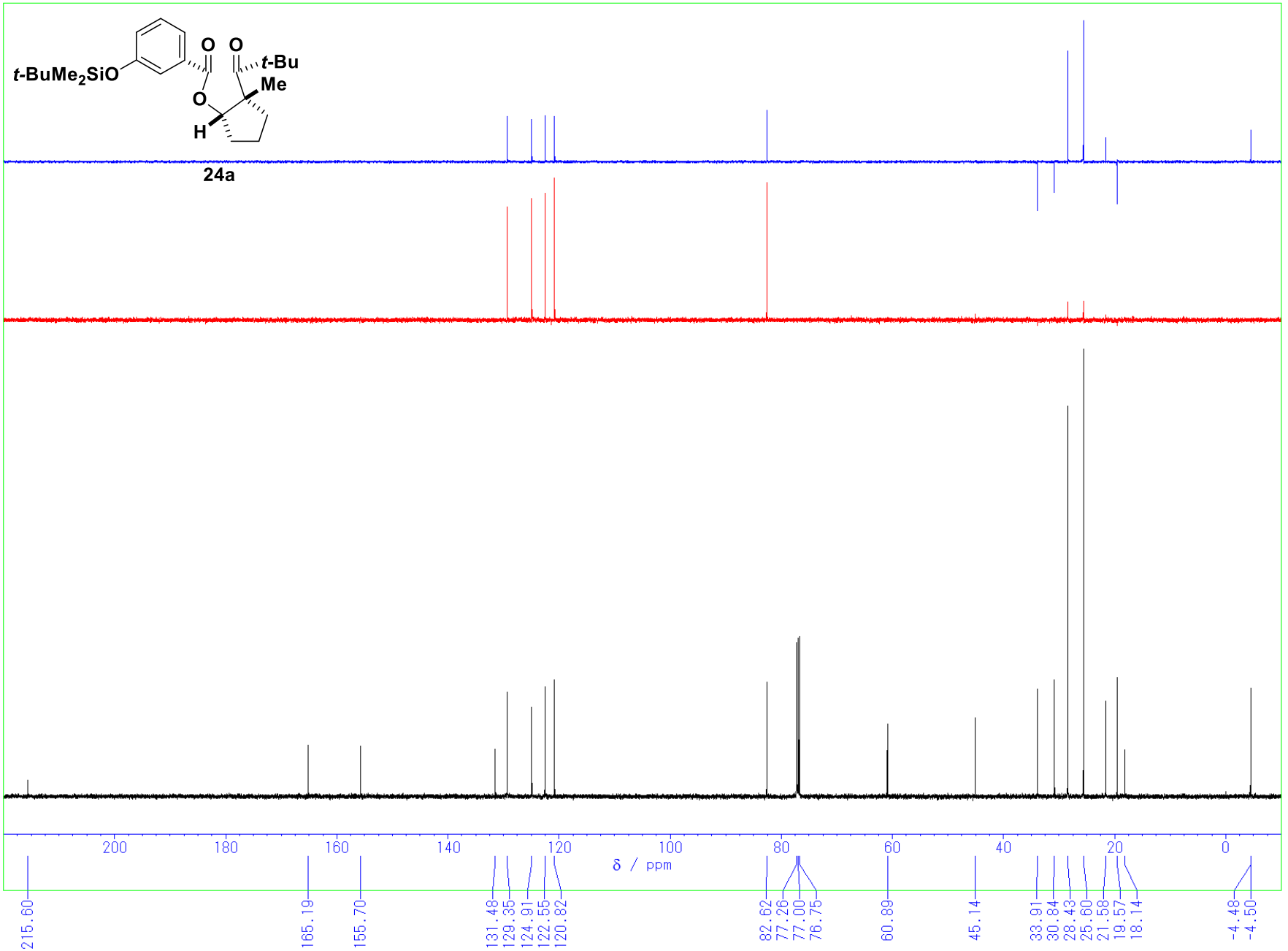


Figure S20. ^{13}C NMR spectrum of *t*-methyl-*c*-2-pivaloylcyclopentyl *r*-3-(*tert*-butyldimethylsiloxy)benzoate (**24a**) in $CDCl_3$.

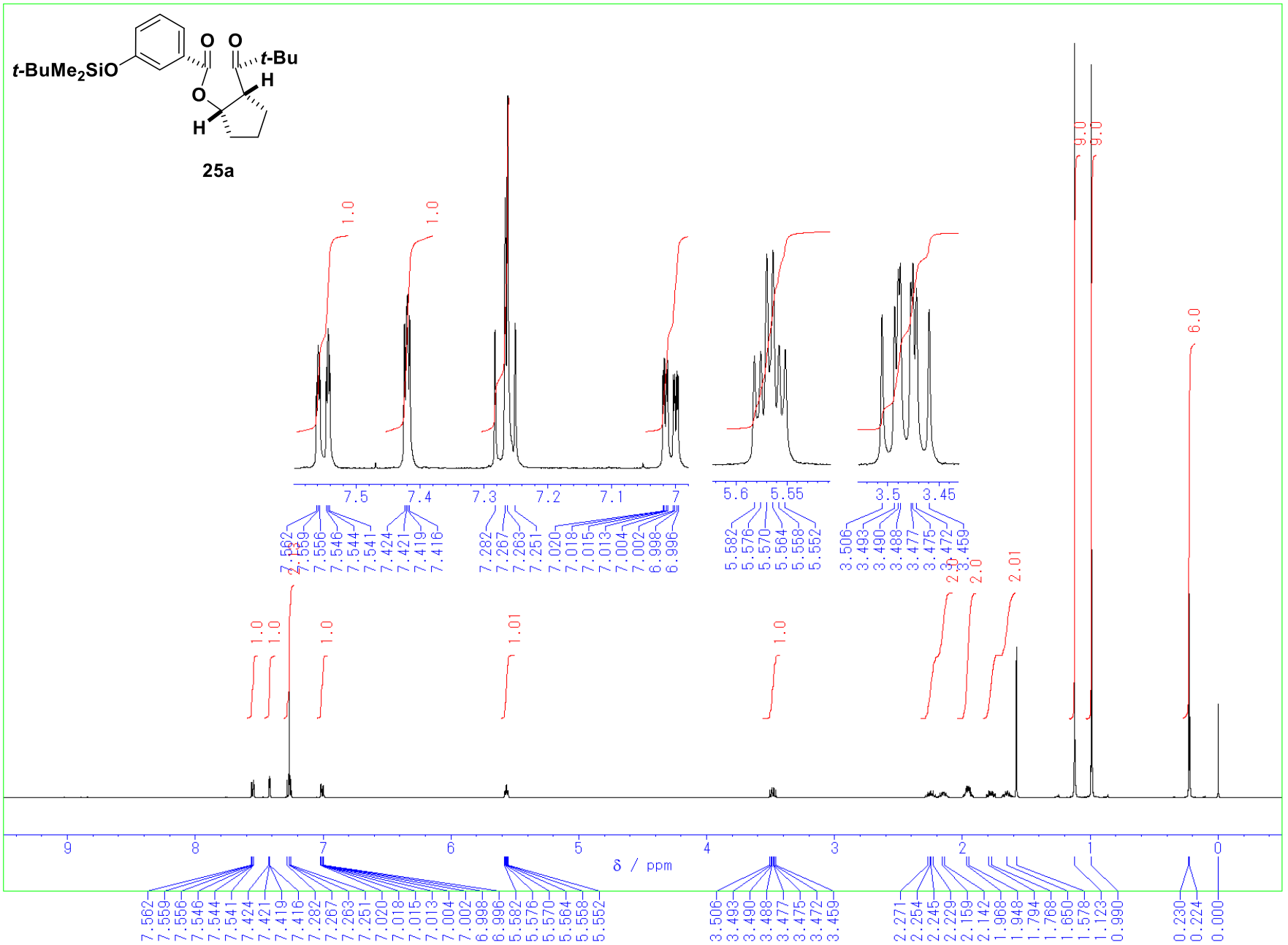


Figure S21. ^{1}H NMR spectrum of *cis*-2-pivaloylcyclopentyl 3-(*tert*-butyldimethylsiloxy)benzoate (**25a**) in $CDCl_3$.

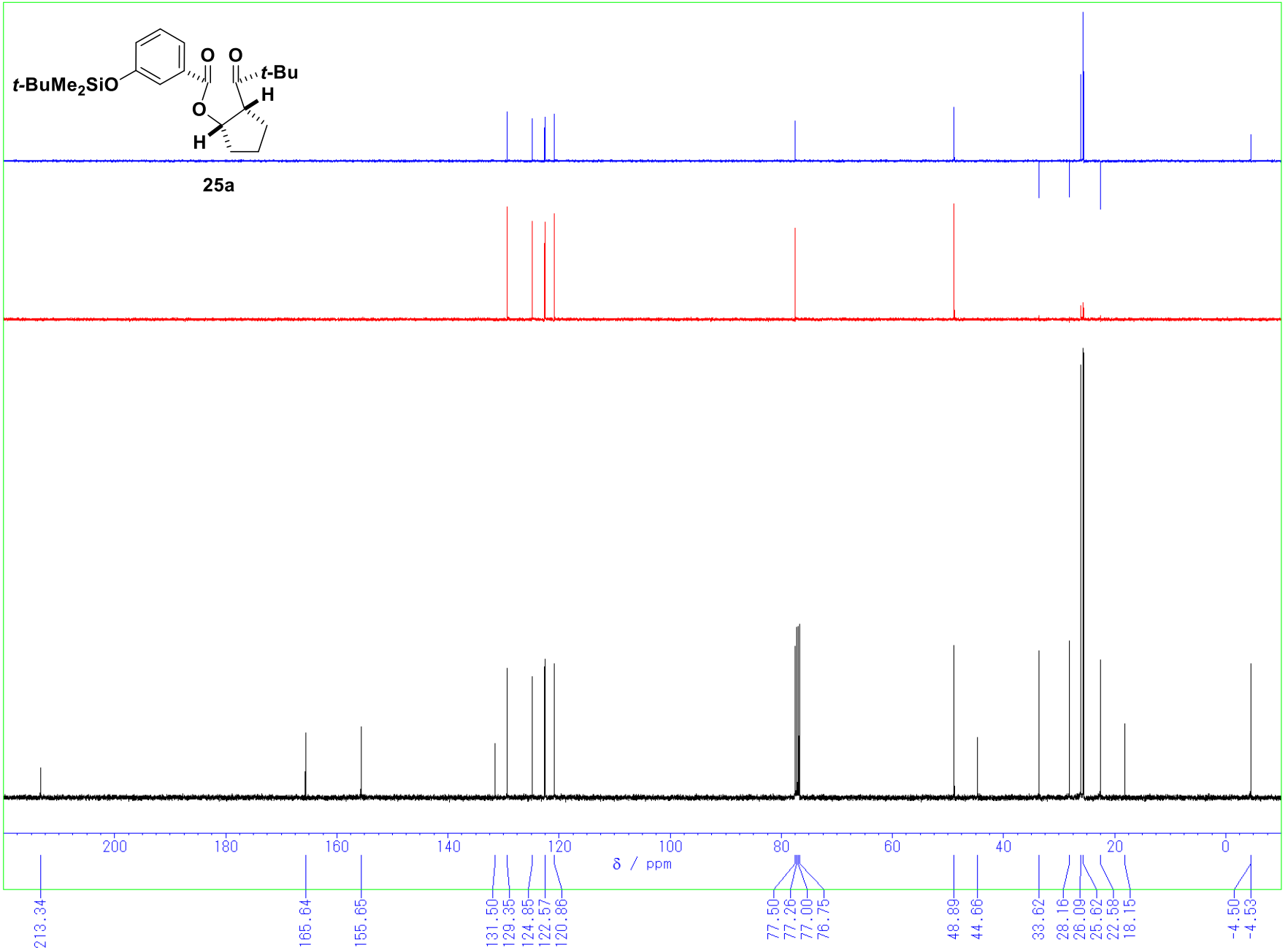


Figure S22. ^{13}C NMR spectrum of *cis*-2-pivaloylcyclopentyl 3-(*tert*-butyldimethylsiloxy)benzoate (**25a**) in $CDCl_3$.

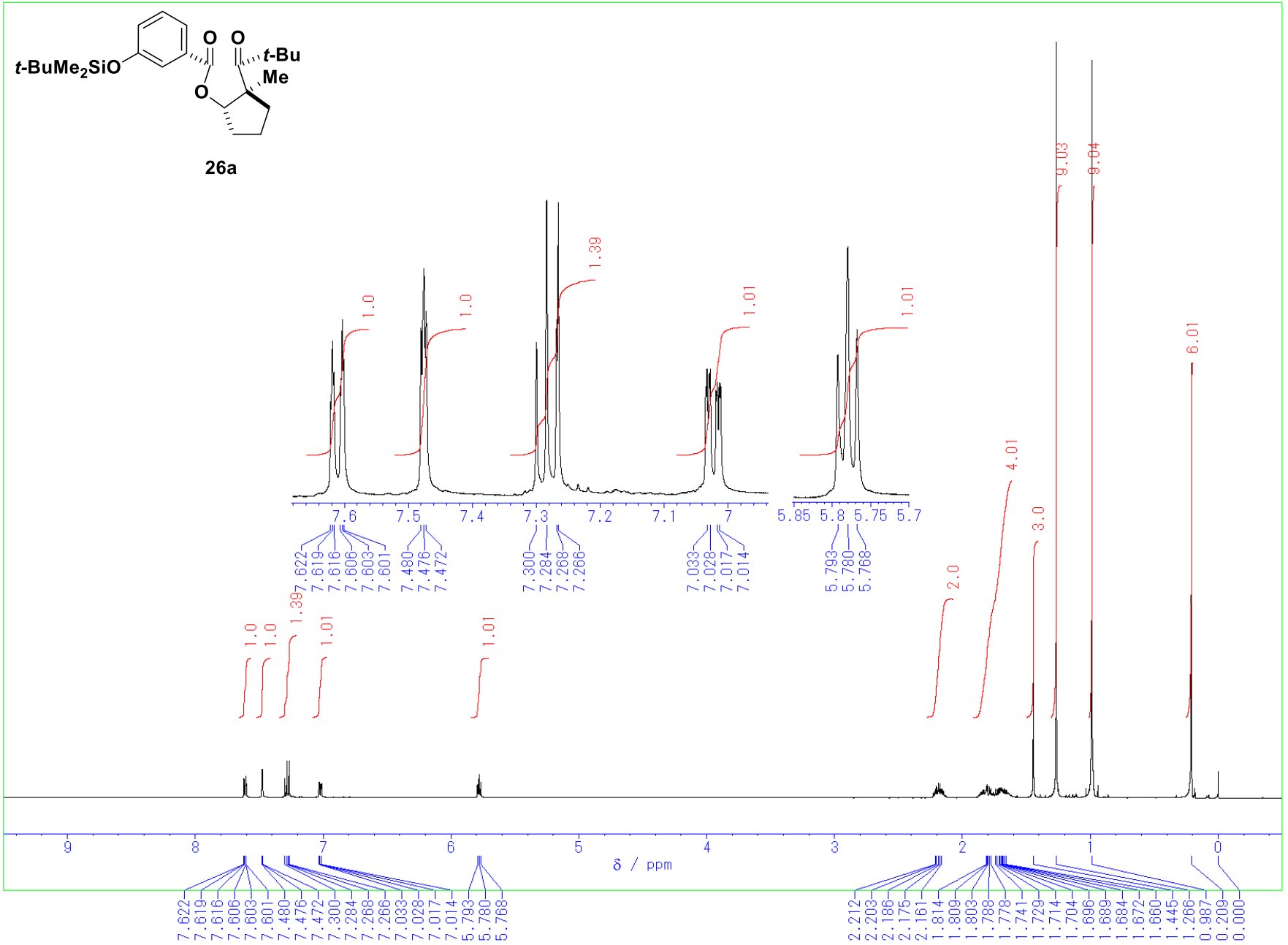


Figure S23. ^{1}H NMR spectrum of *c*-methyl-*t*-2-pivaloylcyclopentyl *r*-3-(*tert*-butyldimethylsiloxy)benzoate (**26a**) in $CDCl_3$.

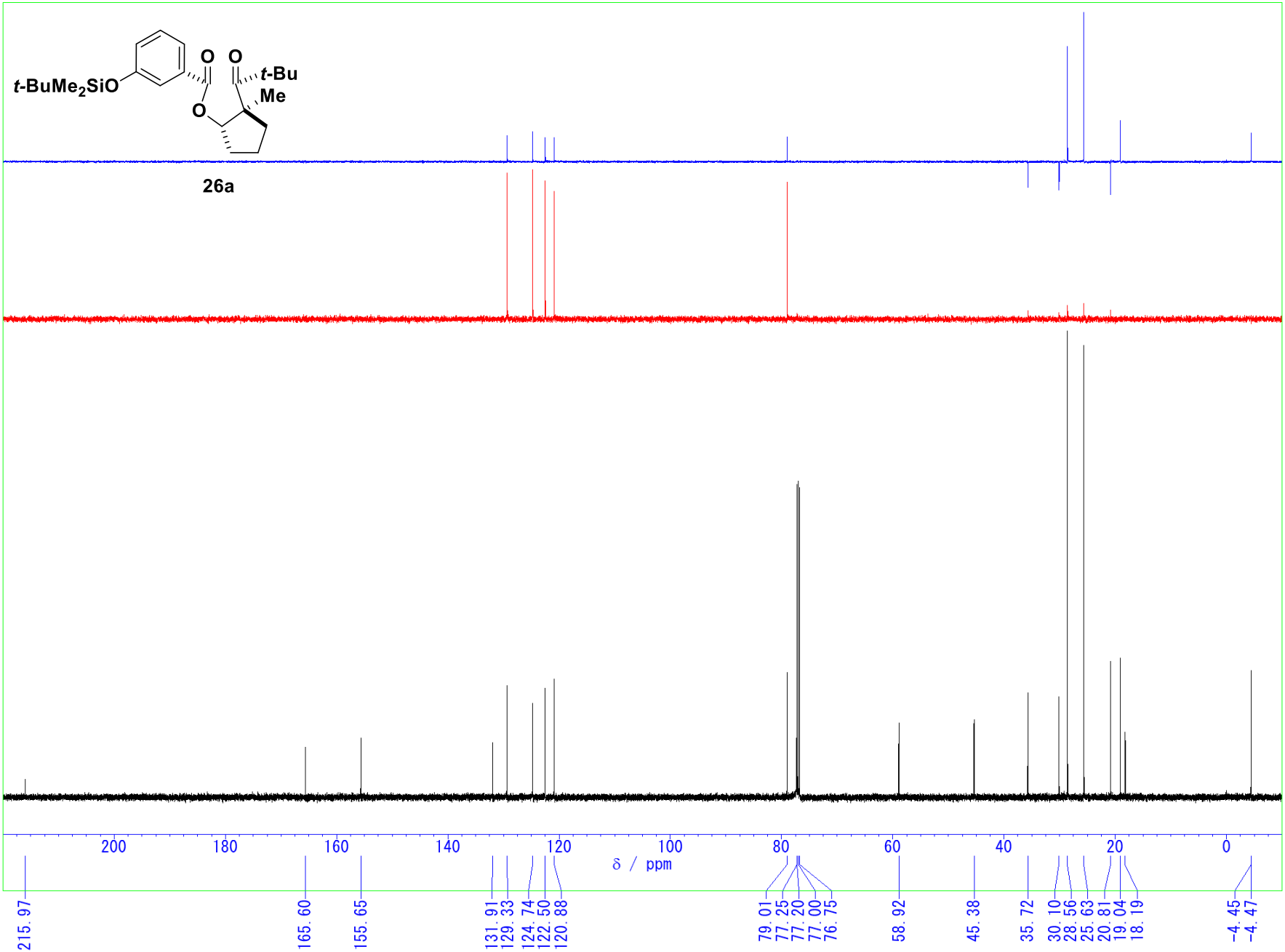


Figure S24. ^{13}C NMR spectrum of *c*-methyl-*t*-2-pivaloylcyclopentyl *r*-3-(*tert*-butyldimethylsiloxy)benzoate (**26a**) in $CDCl_3$.

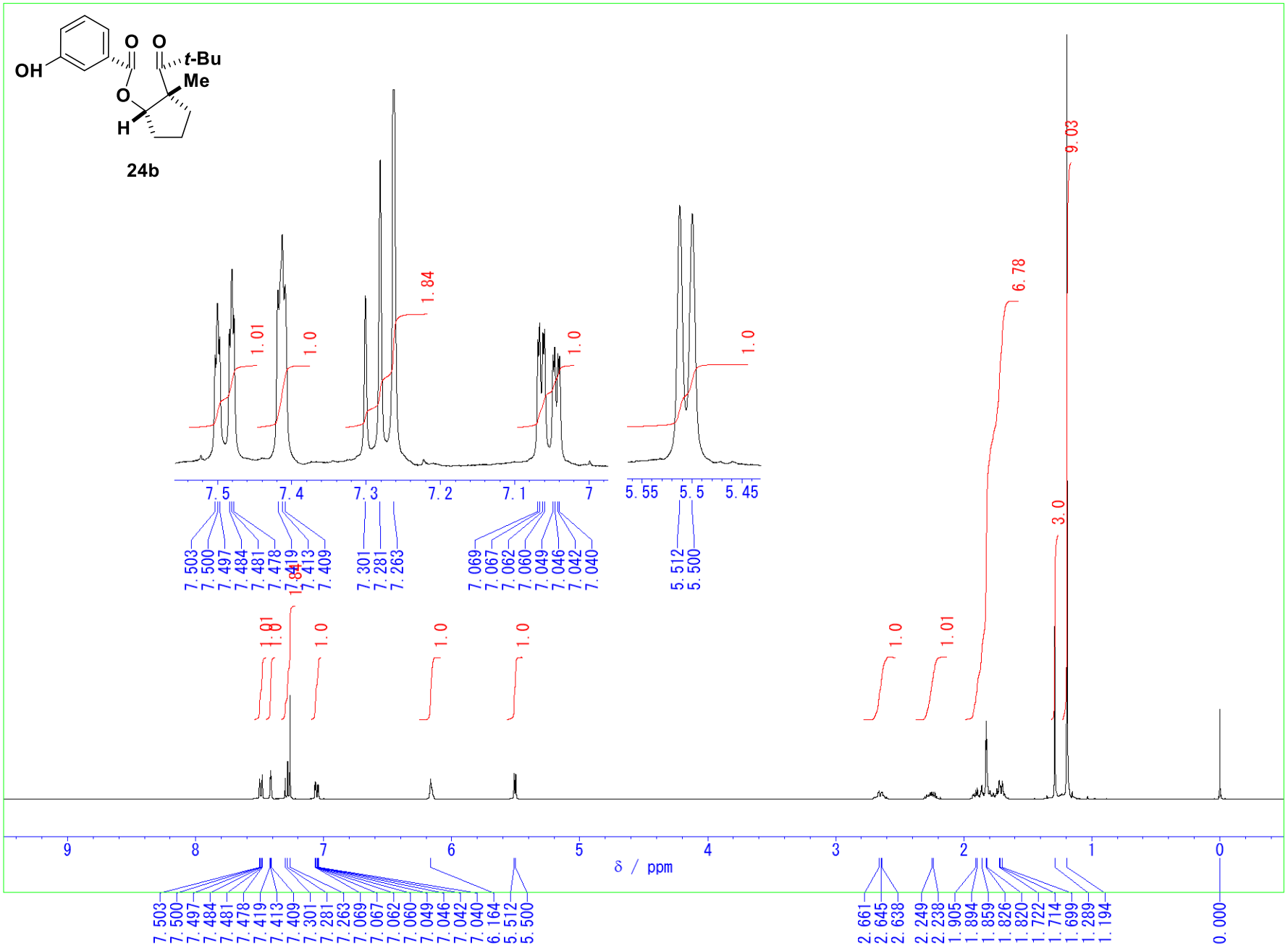


Figure S25. ^{1}H NMR spectrum of *t*-2-methyl-*c*-2-pivaloylcyclopentyl *r*-3-hydroxybenzoate (**24b**) in $CDCl_3$.

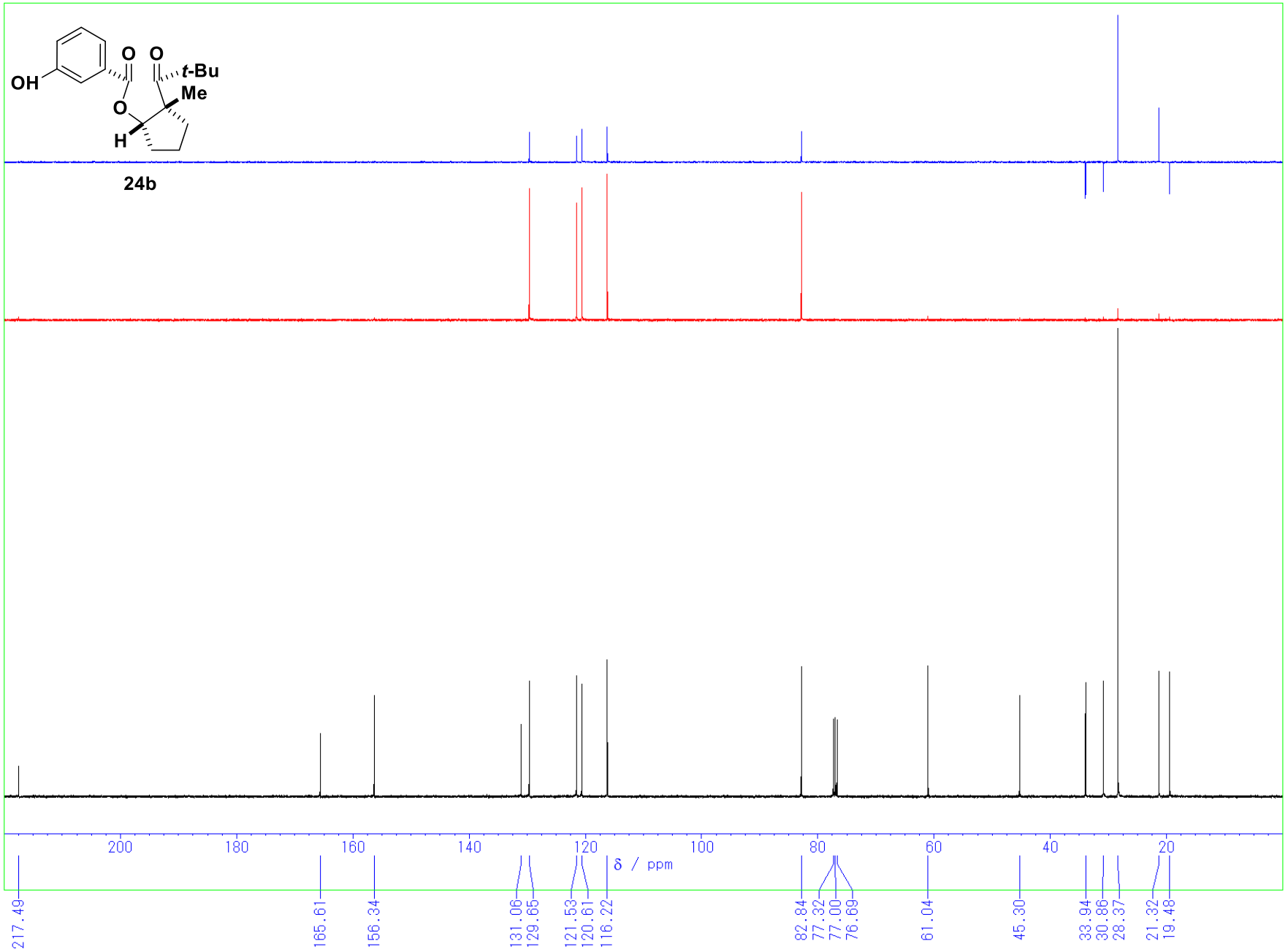


Figure S26. ^{13}C NMR spectrum of *t*-2-methyl-*c*-2-pivaloylcyclopentyl *r*-3-hydroxybenzoate (**24b**) in $CDCl_3$.

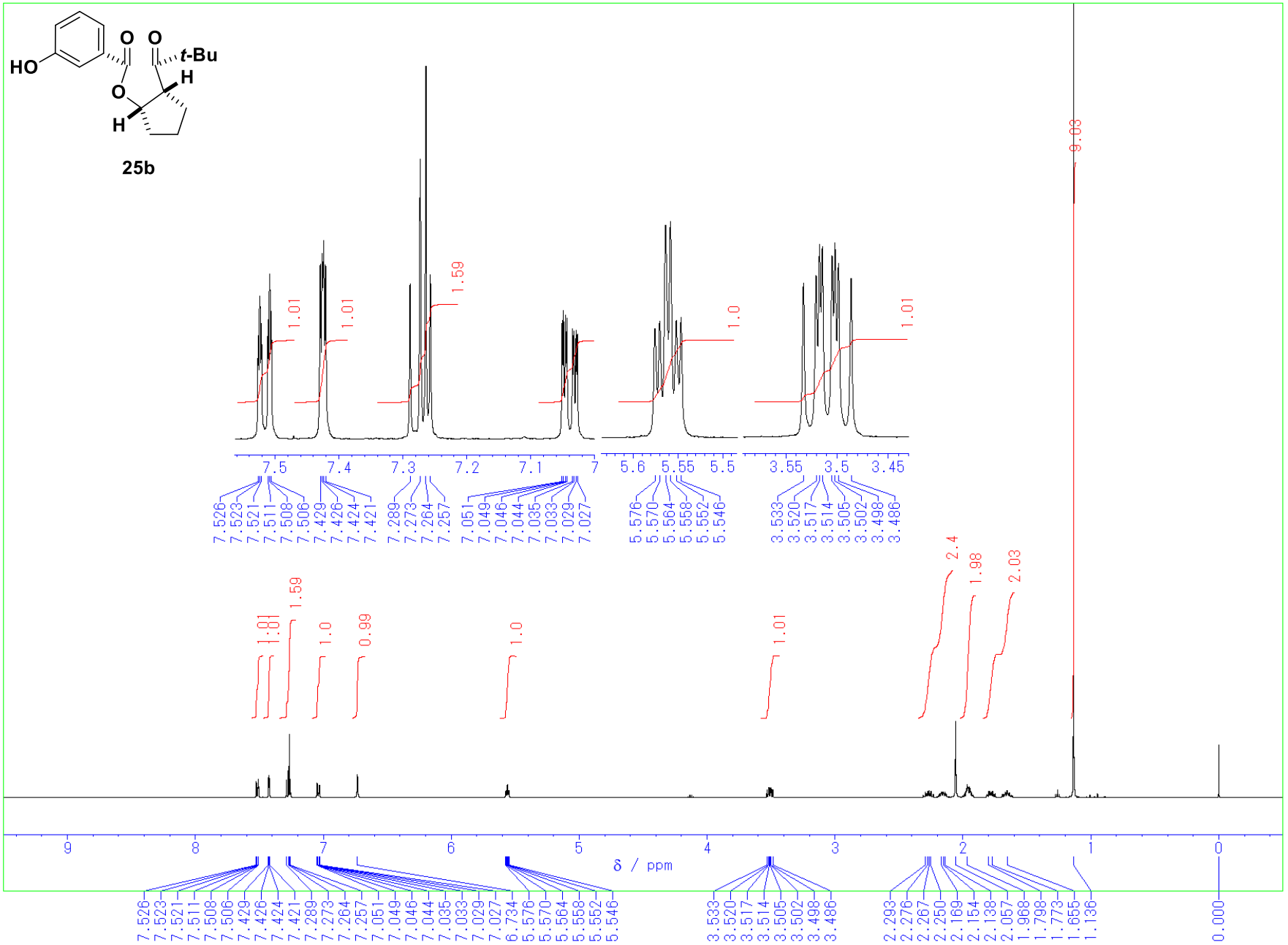


Figure S27. ^{1}H NMR spectrum of *cis*-2-pivaloylcyclopentyl 3-hydroxybenzoate (**25b**) in $CDCl_3$.

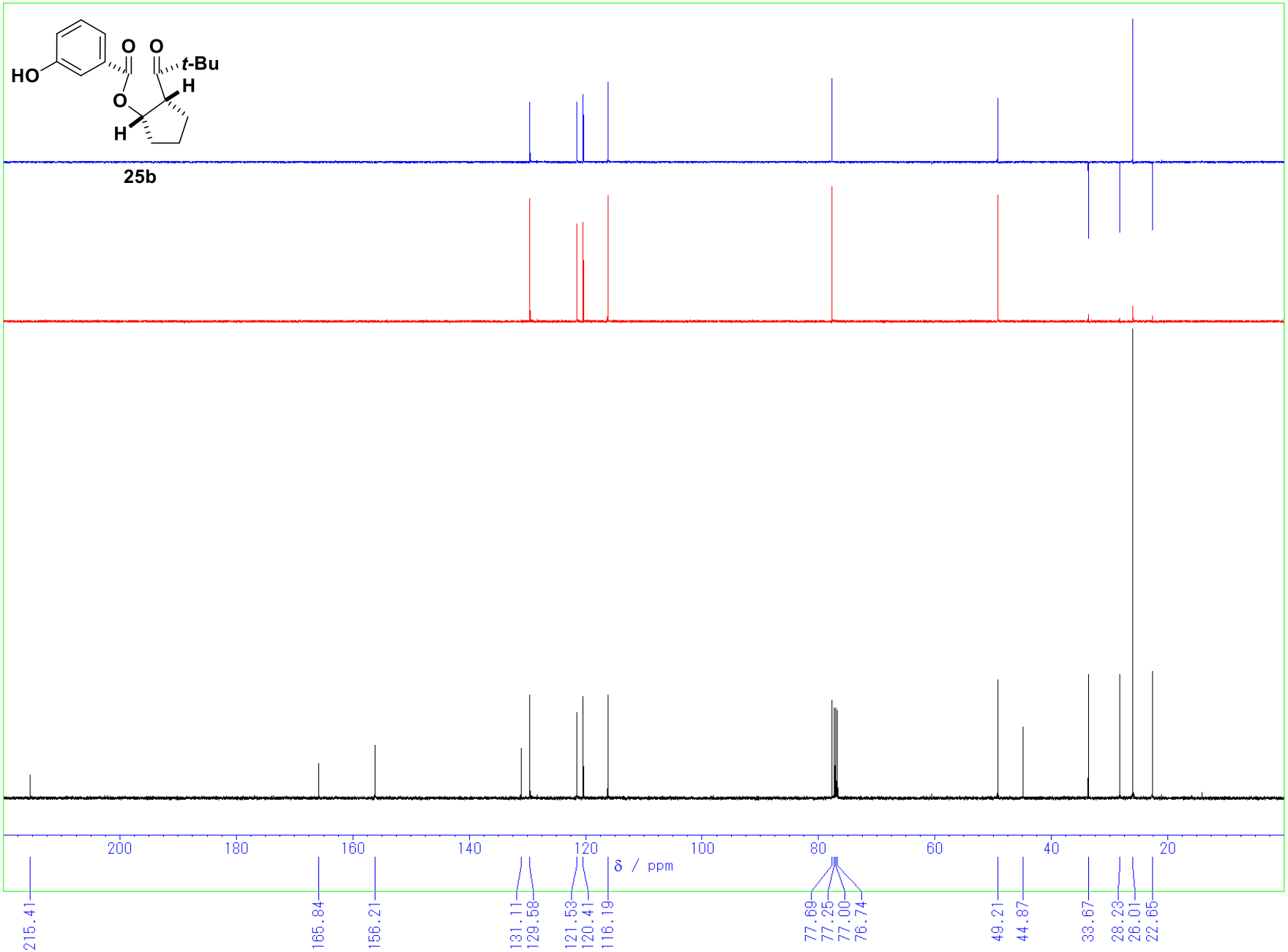


Figure S27. ^{13}C NMR spectrum of *cis*-2-pivaloylcyclopentyl 3-hydroxybenzoate (**25b**) in $CDCl_3$.

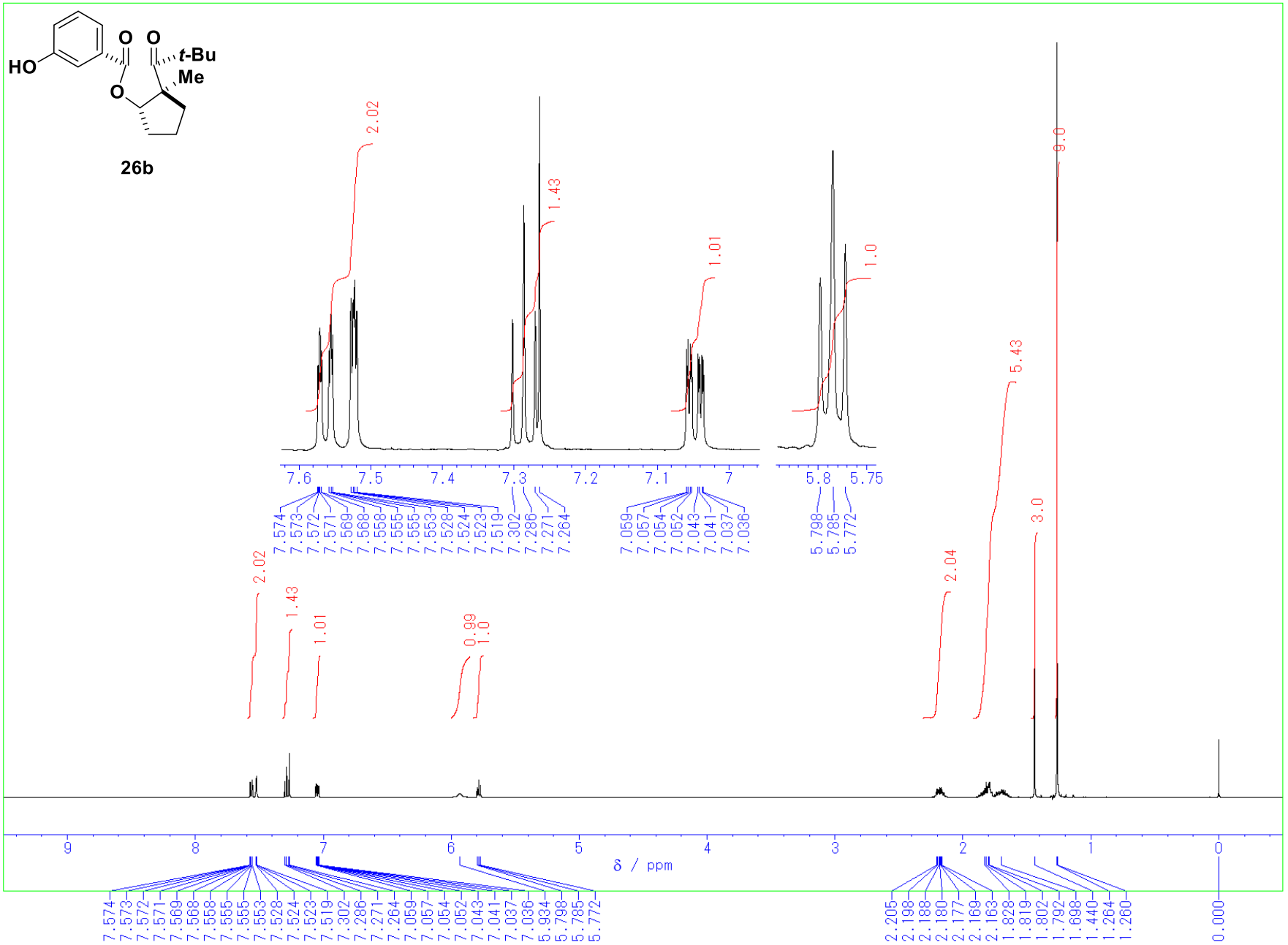


Figure S29. ^{1}H NMR spectrum of *c*-2-methyl-*t*-2-pivaloylcyclopentyl *r*-3-hydroxybenzoate (**26b**) in $CDCl_3$.

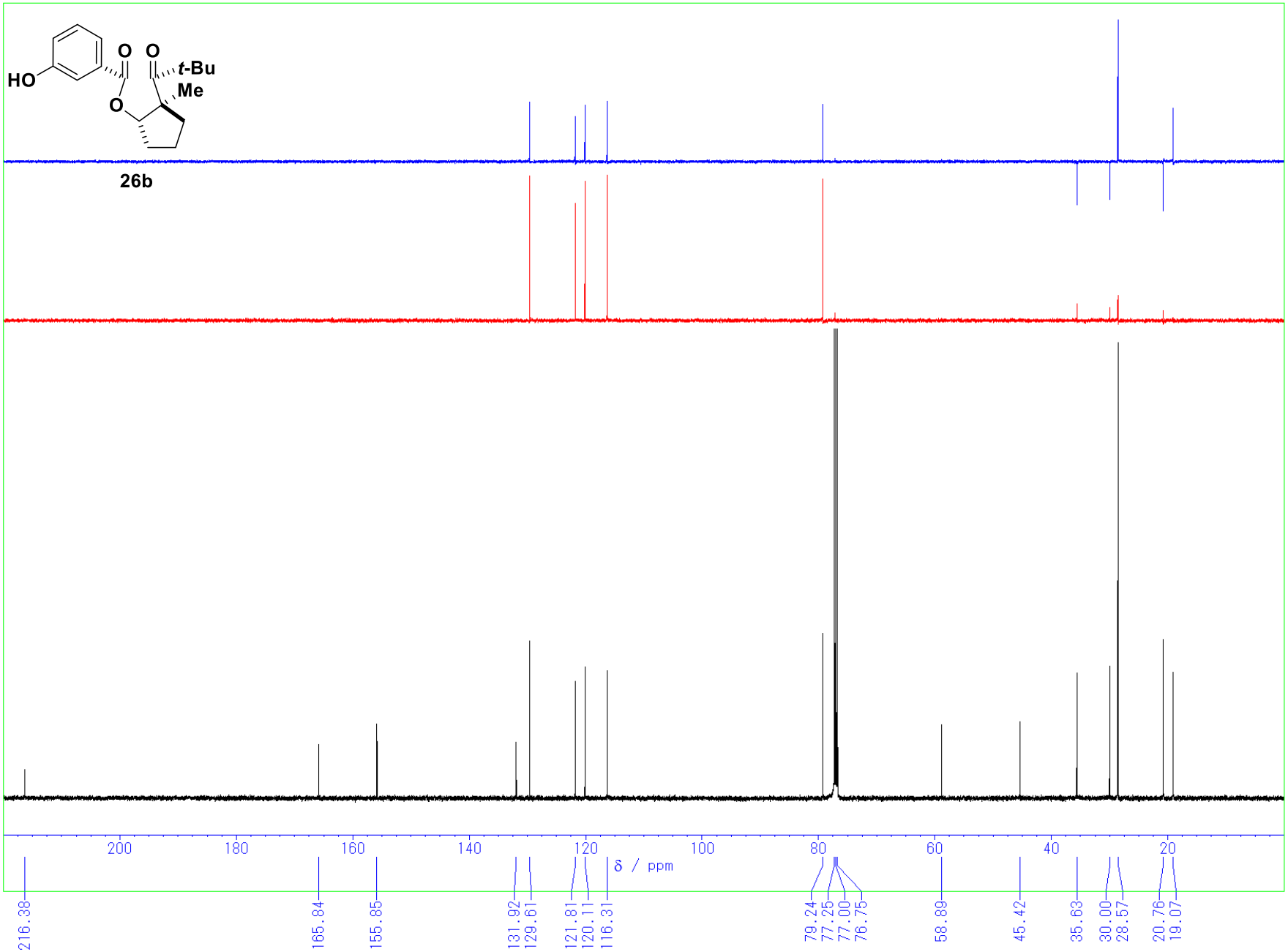


Figure S30. ^{13}C NMR spectrum of *c*-2-methyl-*t*-2-pivaloylcyclopentyl *r*-3-hydroxybenzoate (**26b**) in $CDCl_3$.