Electronic Supplementary Information

Regioselectivity in the adiabatic photocleavage of DNA-based oxetanes

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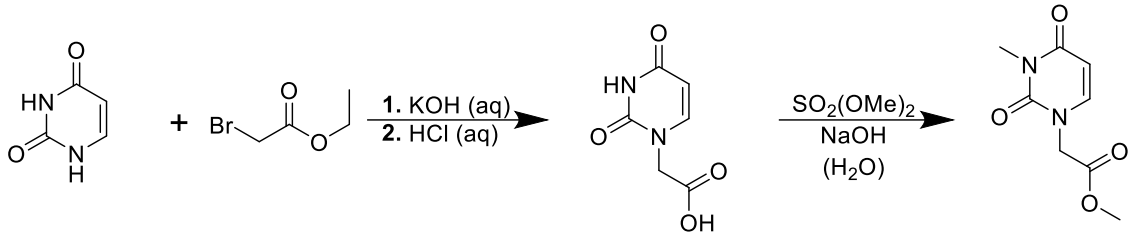
Fig. S13 LFP decay traces at 530 nm for dyad 2 (black) and HH-8 (blue) after excitation at 266 nm in deaerated acetonitrile.

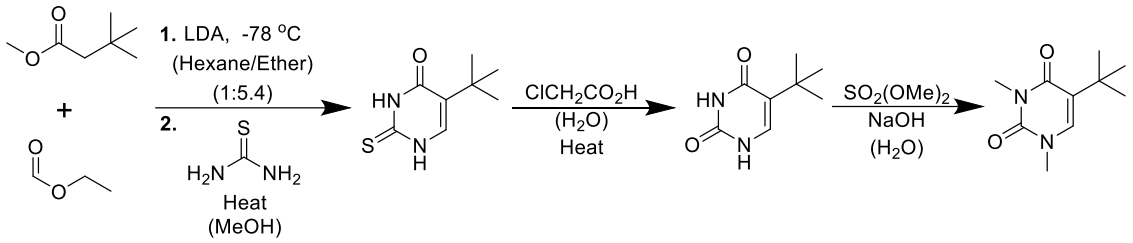
Synthesis of the uracil and thymine derivatives. Scheme and experimental protocol of the synthesis of the unknown uracil and thymine intermediates by ^{1}H and ^{13}C NMR, and HRMS.



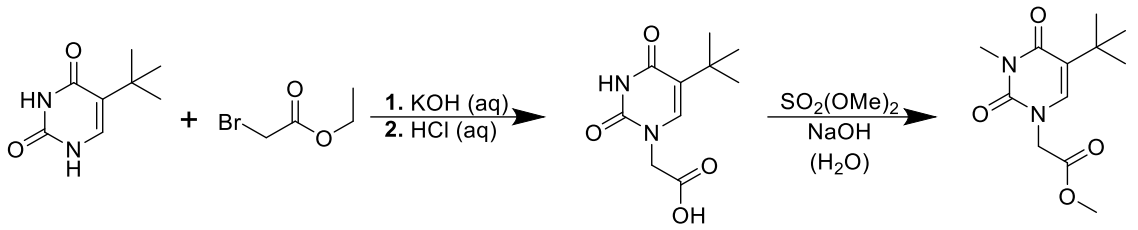
Synthesis of methyl 3-methyluracil-1-acetate. The intermediate uracil-1-acetic acid was synthesized earlier.[1] Briefly, to a suspension of 5.4 g (45 mmol) of uracil in 110 mL of water, 110 mL of potassium hydroxide (1M) were added. The solution was stirred until clear and then 11 mL of ethyl bromoacetate (90 mmol) were added dropwise. The mixture was stirred overnight under reflux, then cooled down to 0 ^{o}C and acidified to pH 1 with concentrated hydrochloric acid. The resulting white precipitate was filtered under vacuum and washed with cold HCl (1M). The intermediate uracil-1-acetic acid (6.4 g) was obtained as a pure white solid (84% yield).

To a solution of 4.5 g of NaOH in water (42 mL), 6 g of uracil-1-acetic acid (35 mmol) were added upon stirring. After a few minutes, 8.4 mL of dimethyl sulphate (88 mmol) were added dropwise, and the solution was stirred overnight. The crude product was extracted with ethyl acetate. The final product was purified via silica gel chromatography using ethyl acetate as eluent. The final product methyl 3-methyluracil-1-acetate (2.77 g) was obtained as a white solid.

^{1}H NMR (400 MHz, CD_3OD) δ 7.54 (d, *J* = 7.6 Hz, 1H), 5.77 (d, *J* = 7.6 Hz, 1H), 4.58 (s, 2H), 3.77 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 168.6, 164.1, 151.8, 143.9, 100.3, 51.7, 49.5, 26.6; Yield: 40%. HRMS (ESI): *m/z* calcd. for $C_8H_{11}N_2O_4$ $[M+H]^+$: 199.0719, found: 199.0717.

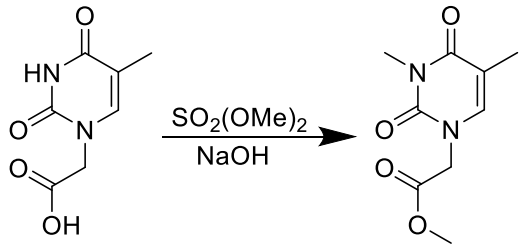


Synthesis of 1,3-dimethyl-5-*tert*-butyluracil. The synthesis of the different uracil intermediates and the final derivative has been described earlier.[2, 3] Briefly, 16 mL of lithium diisopropylamide (LDA) were dissolved in a mixture of 40 mL anhydrous diethyl ether and 25 mL dry hexane at -78°C in nitrogen atmosphere. A separate solution of 5.8 mL of methyl 3,3-dimethylbutanoate (0.04 mol) in 35 mL of anhydrous diethyl ether was prepared at -78°C and purged with N_2 for 15 minutes; then, it was added quickly via a purged glass syringe to the LDA solution. Another solution of 12.5 mL of ethyl formate (0.13 mol) in 60 mL of anhydrous diethyl ether was prepared at -78°C and purged with N_2 for 10 min, and then it was added via a purged glass syringe to the mother solution. The mixture was the stirred under N_2 atmosphere at -78°C for 6 hours. The solvent was removed under reduced pressure. The crude was kept in the freezer overnight under N_2. The crude product was subsequently transferred to a 25 mL round-bottom flask and 3.04 g of thiourea (0.04 mol) in 10 mL of anhydrous methanol was added. The solution was purged with N_2 for 15 mins and then refluxed for 6 hours; afterwards, it was cooled down to -10°C under vigorous stirring and acidified down to pH<3 with HCl. The solution was stirred for 1 hour and the final intermediate uracil derivative was filtered under vacuum and washed with cold methanol. About 650 mg of this product (3 mmol) was dissolved in 26 mL of water and 3.9 g of chloroacetic acid (18 mmol) were added. The solution was stirred under reflux for 4 hours. The precipitated *tert*-butyl uracil was filtered under vacuum (615 mg, 95% yield). About 200 mg of the *tert*-butyl uracil (1.2 mmol) was dissolved in 2 mL of NaOH (2.5 M). Then, 0.4 mL of dimethyl sulphate (4.2 mmol) were added dropwise under stirring. The solution was stirred for 16 hours. The crude product was extracted with ethyl acetate and dried with $MgSO_4$. The solvent was removed under reduced pressure to get the final 1,3-dimethyl-5-*tert*-butyluracil (185 mg, 79% yield).



Synthesis of methyl 5-*tert*-butyl-3-methyluracil-1-acetate. The synthesis of the intermediate has been described earlier.[4] Briefly, 2.5 g of *tert*-butyl uracil (15 mmol) was dissolved in 33 mL of water. Then, 33 mL of potassium hydroxide 2 M was added. Under vigorous stirring, 3.33 mL of ethyl bromoacetate (30 mmol) were added dropwise, and the solution was left under reflux for 13 hours. The solution was then acidified to pH 1 with 37% hydrochloric acid and cooled down in an ice-salt bath. The white precipitate was filtered off and washed with cold hydrochloric acid 1M to give pure 5-*tert*-butyluracil-1-acetic acid. Then, 1.5 g of this compound (6.6 mmol) was dissolved in 8 mL of sodium hydroxide 2.5 M, and subsequently 1.57 mL of dimethyl sulphate (16.5 mmol) were added dropwise. The solution was stirred for 5 hours. The crude was extracted with ethyl acetate, dried with $MgSO_4$ and the organic solvent was removed under reduced pressure to get the final product methyl 5-*tert*-butyl-3-methyluracil-1-acetate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 4.46 (s, 2H), 3.80 (s, 3H), 3.33 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 162.3, 151.4, 136.8, 122.0, 52.8, 50.0, 33.2, 28.7, 27.9; Yield: 35%. HRMS (ESI): *m/z* calcd. for $C_{12}H_{19}N_2O_4$ $[M+H]^+$: 255.1345, found: 255.1346.



Synthesis of methyl 3-methyl-thymine-1-acetate. The synthesis has been previously reported.[5] Briefly, 2g of thymine-1-methylacetate (12 mmol) was dissolved in 13 mL of NaOH (2.5 M). Then, 2.6 mL of dimethyl sulphate (27 mmol) were added dropwise under stirring. The mixture was stirred 24 hours. The crude product was extracted with ethyl acetate and dried with $MgSO_4$ to get the final product as a white solid.

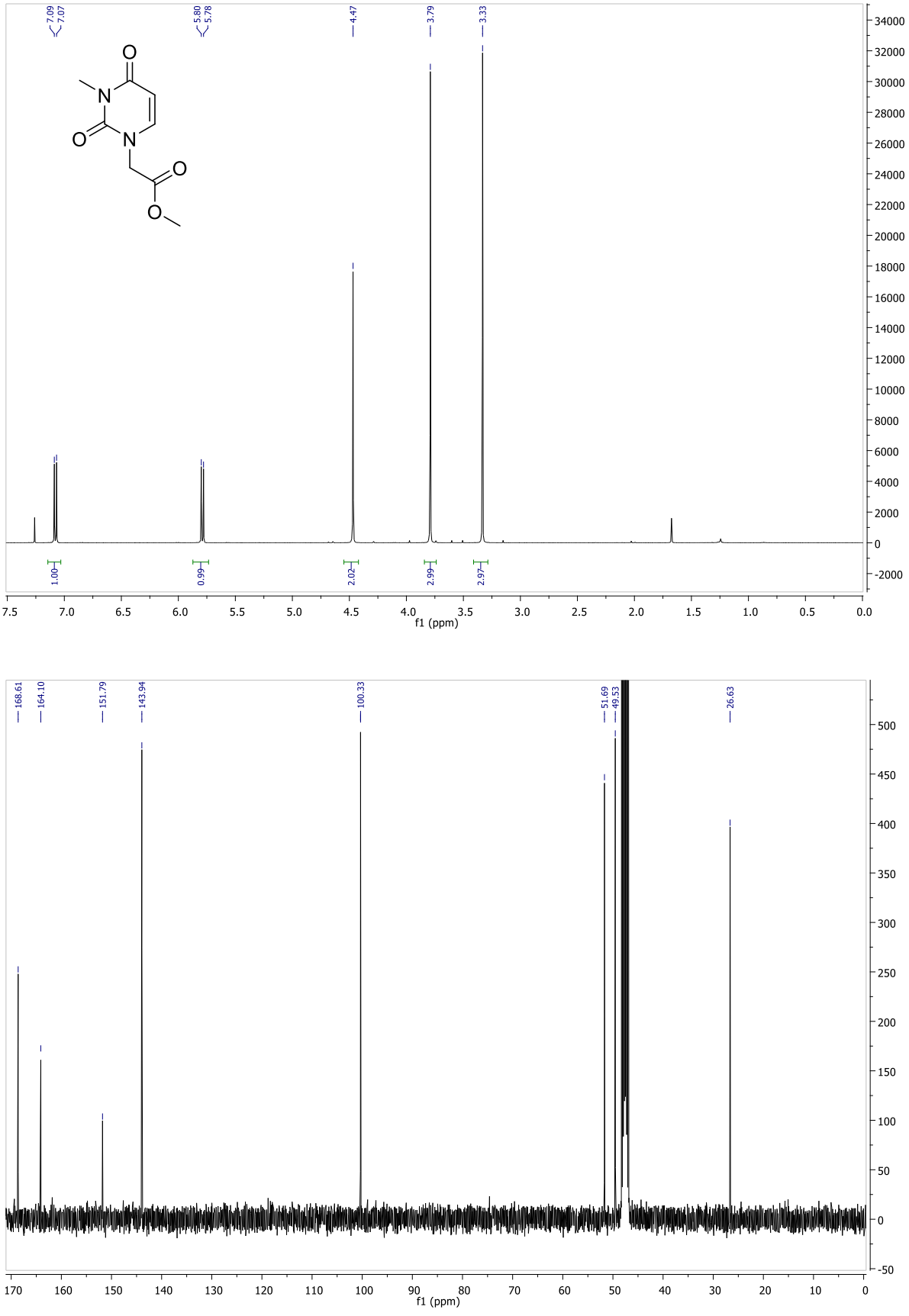


Fig. S1 ^{1}H- and ^{13}C-NMR for methyl 3-methyluracil-1-acetate in CD_3OD.

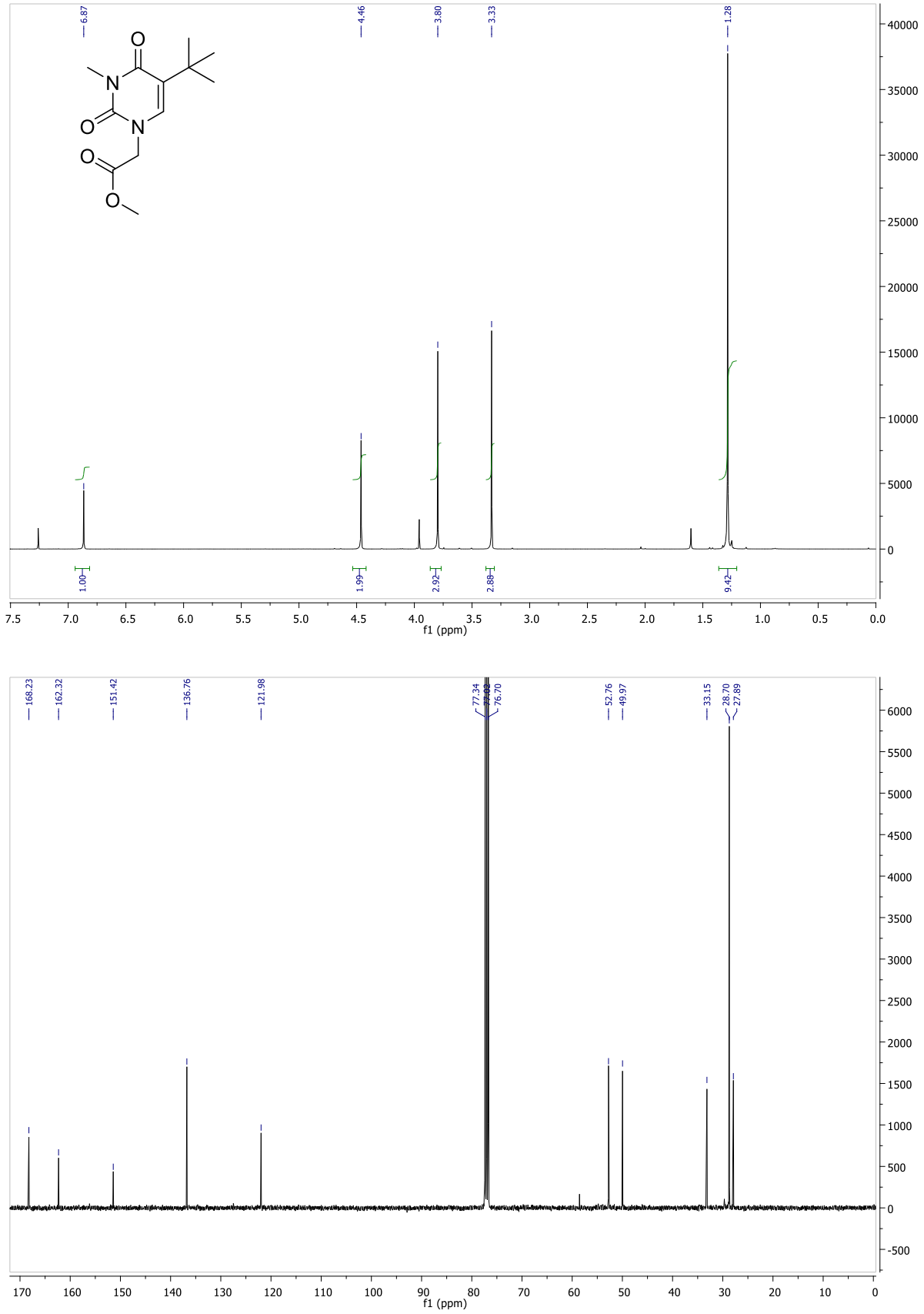


Fig. S2 ^{1}H- and ^{13}C-NMR for methyl 5-*tert*-butyl-3-methyluracil-1-acetate in $CDCl_3$.

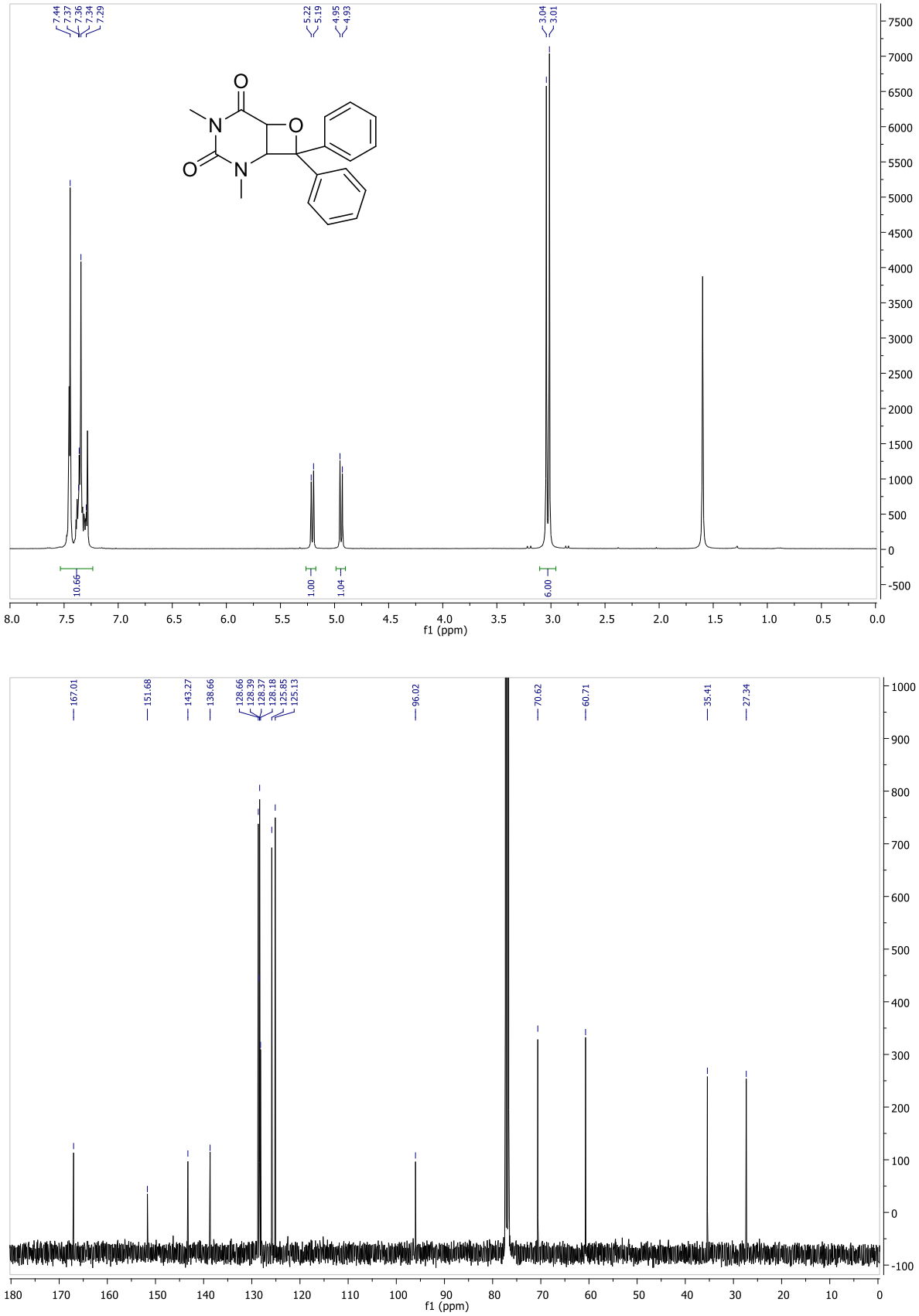


Fig. S3 ^{1}H- and ^{13}C-NMR for HH-1 in $CDCl_3$.

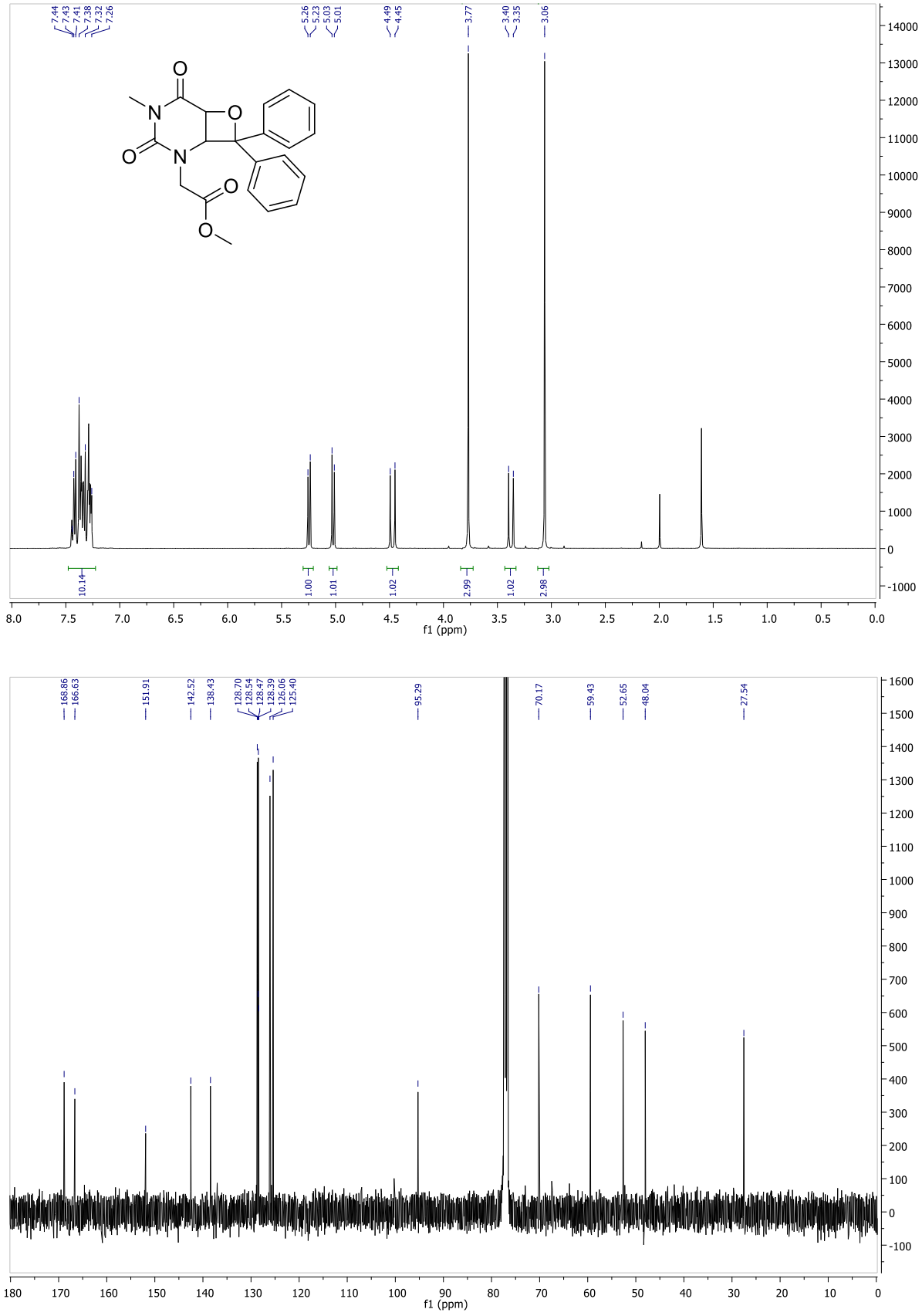


Fig. S4 ^{1}H- and ^{13}C-NMR for HH-2 in $CDCl_3$.

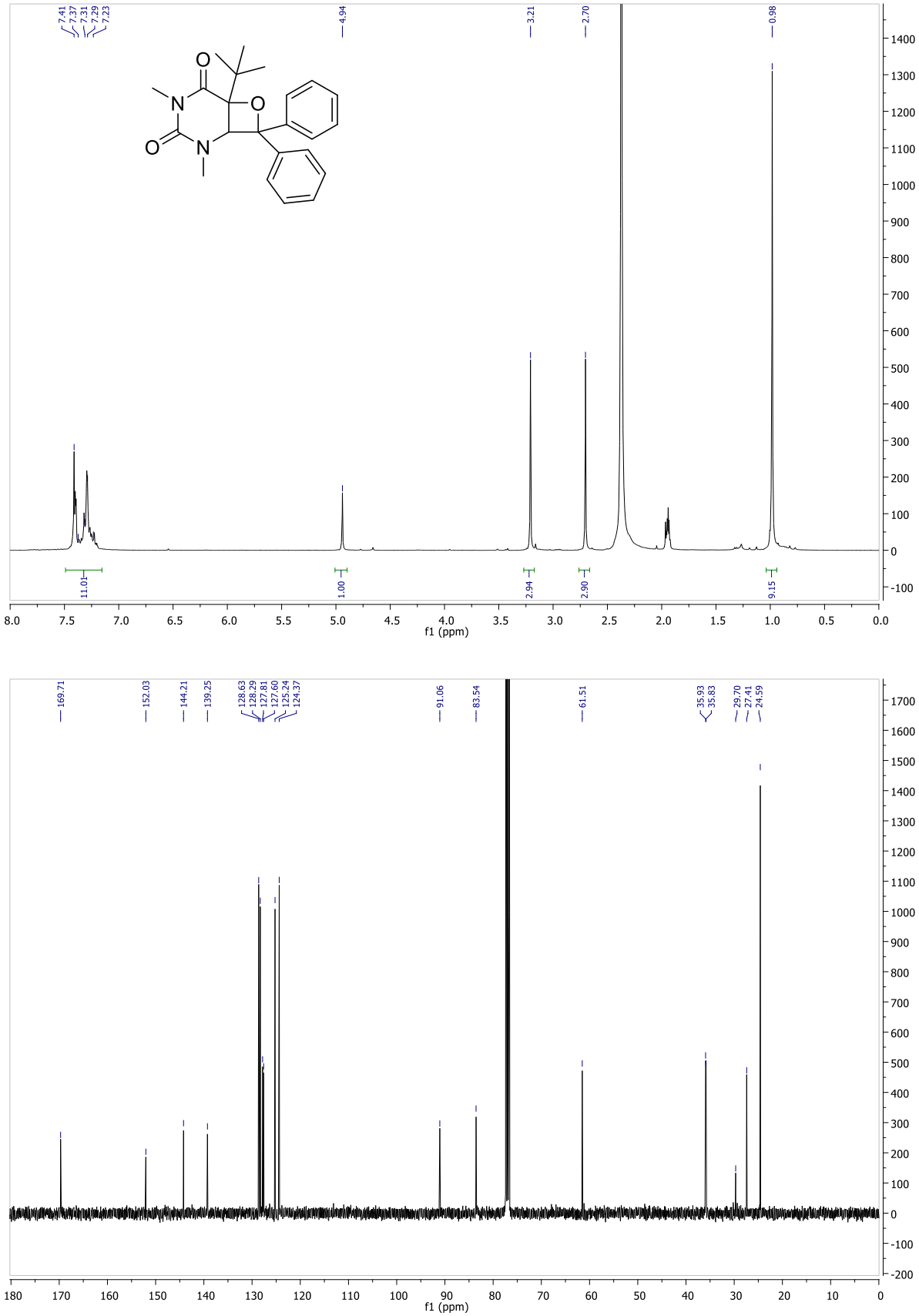


Fig. S5 ^{1}H- and ^{13}C-NMR for HH-3 in $CDCl_3$.

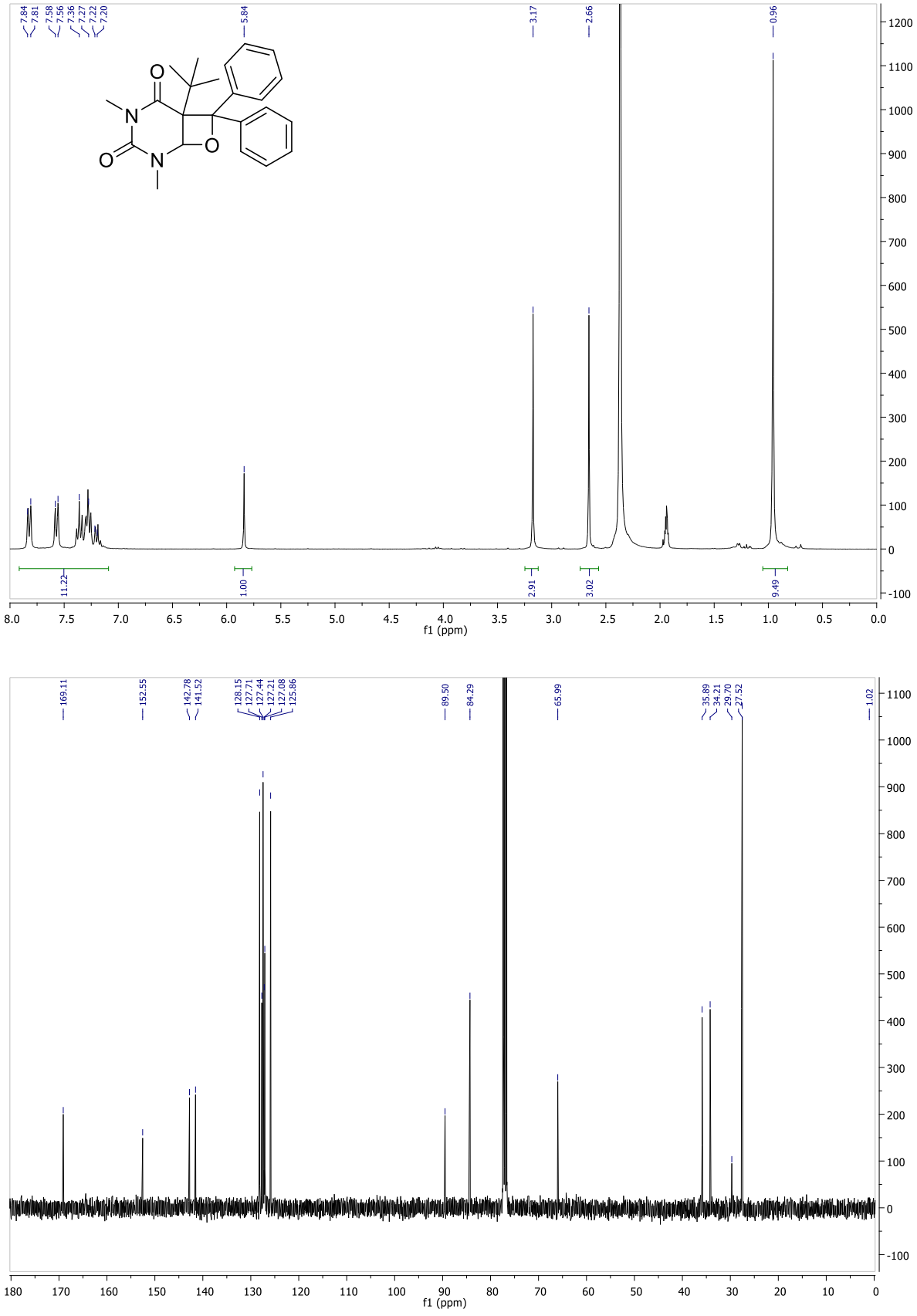


Fig. S6 ^{1}H- and ^{13}C-NMR for HT-3 in $CDCl_3$.

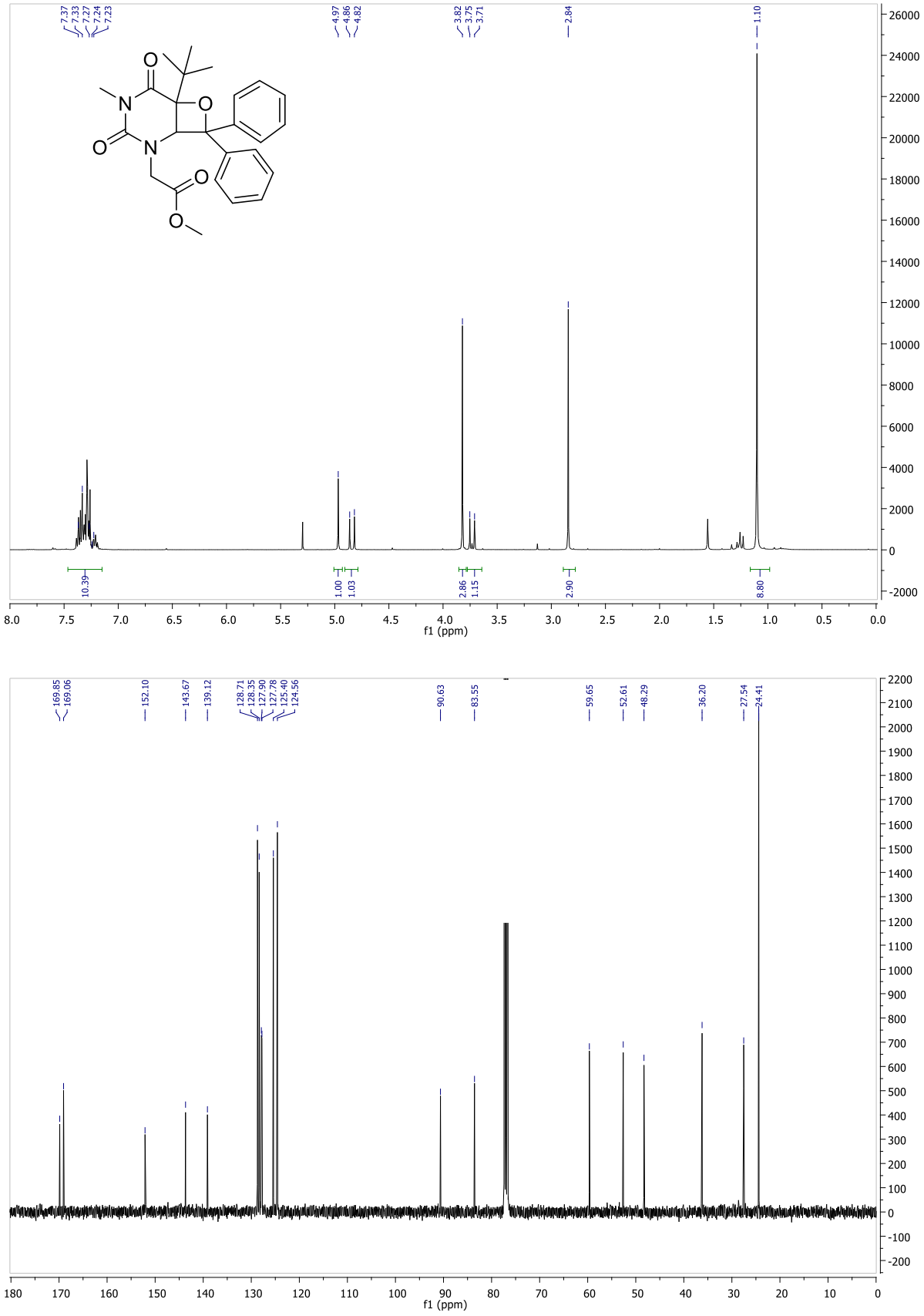


Fig. S7 ^{1}H- and ^{13}C-NMR for HH-4 in $CDCl_3$.

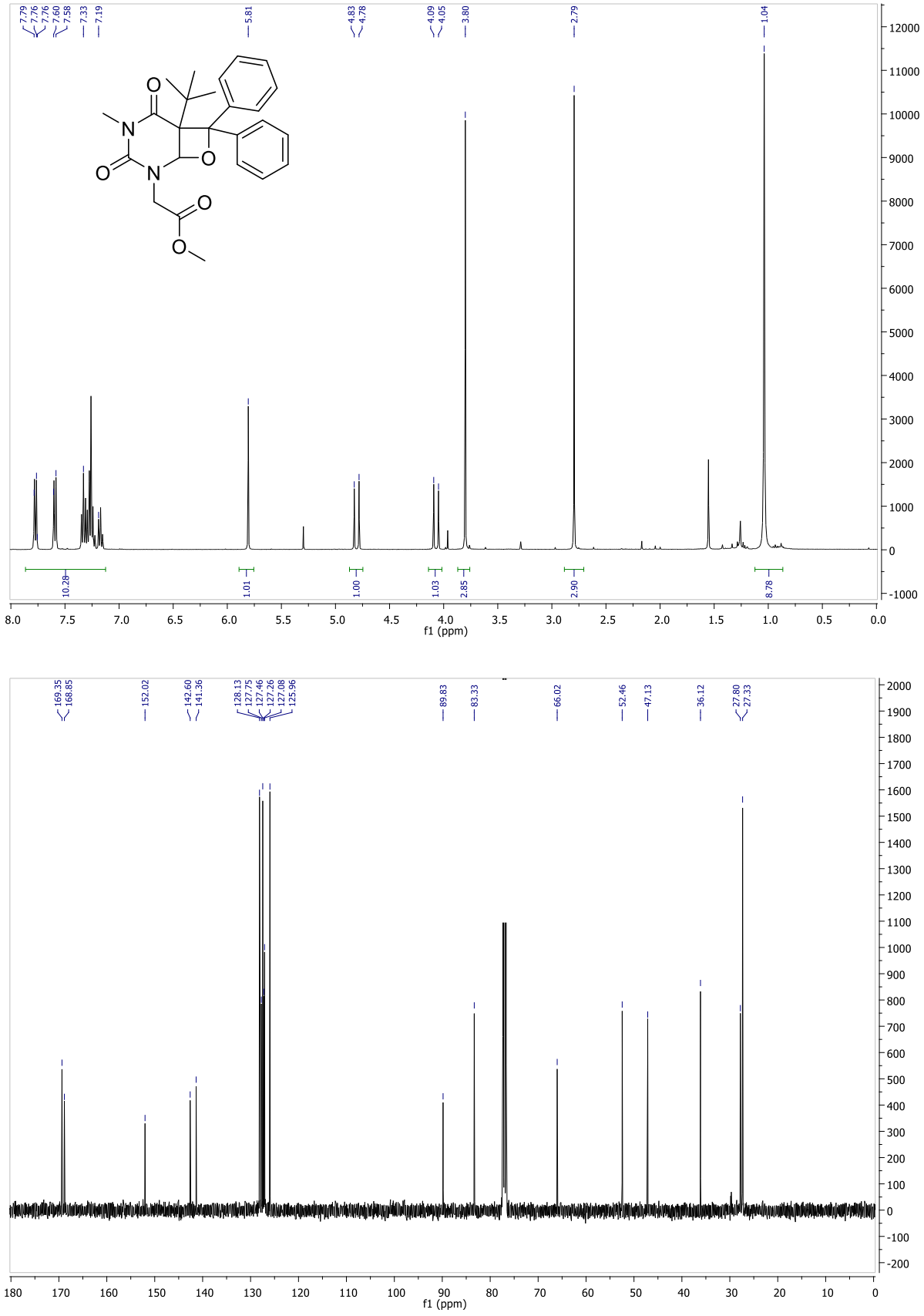


Fig. S8 ^{1}H- and ^{13}C-NMR for HT-4 in $CDCl_3$.

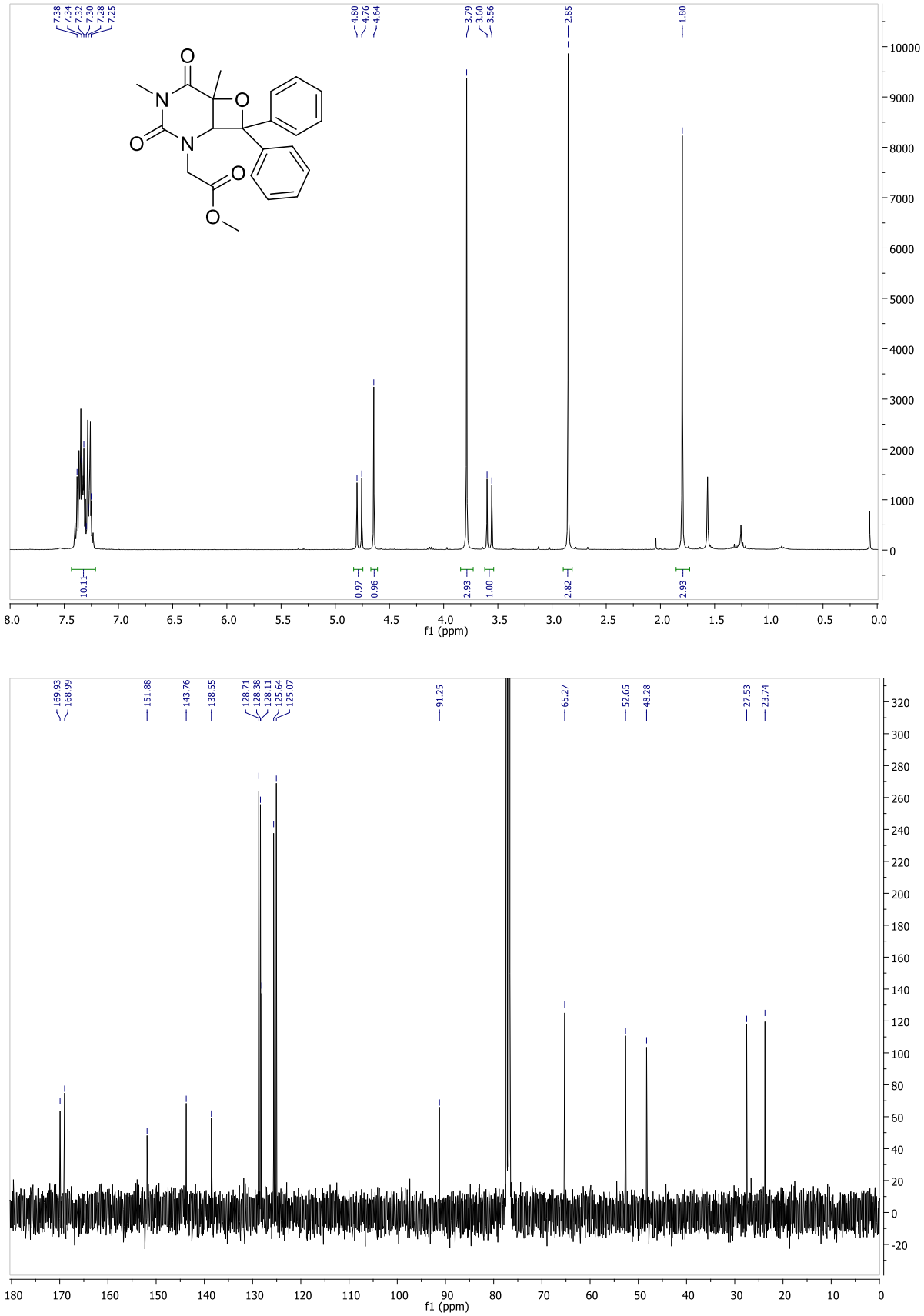


Fig. S9 ^{1}H- and ^{13}C-NMR for HH-5 in $CDCl_3$.

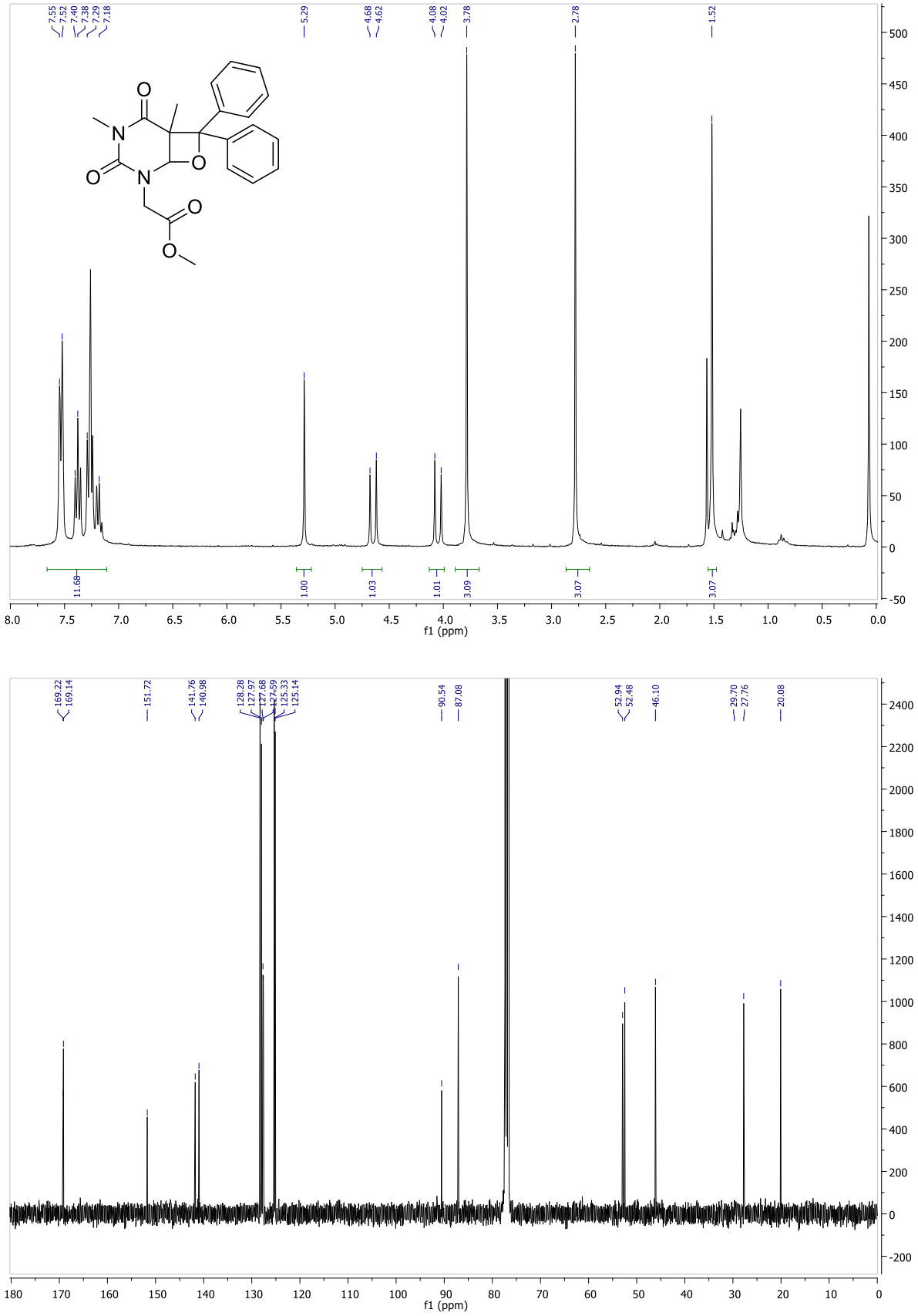


Fig. S10 ^{1}H- and ^{13}C-NMR for HT-5 in $CDCl_3$.

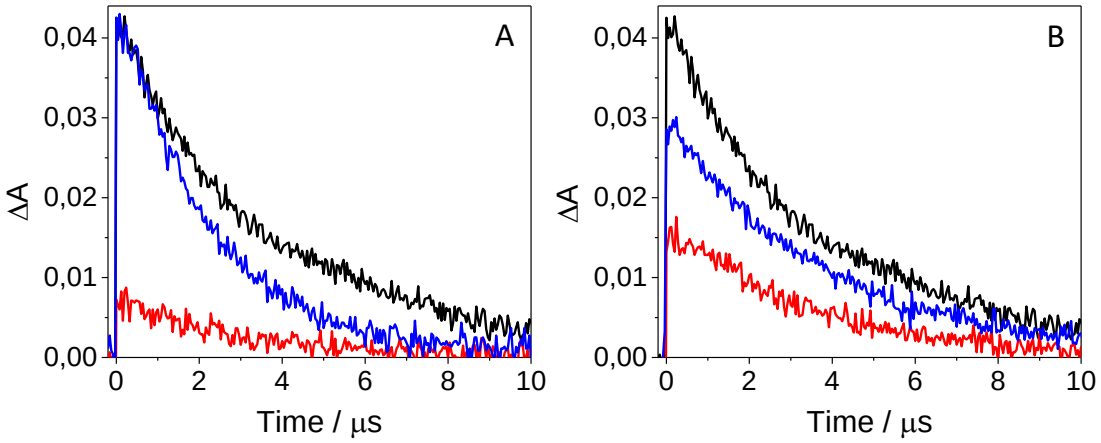


Fig. S11 LFP decay trances at 530 nm for A) BP (black), HH-4 (blue) and HT-4 (red) and B) BP (black), HH-5 (blue) and HT-5 (red) after excitation at 266 nm in deaerated acetonitrile.

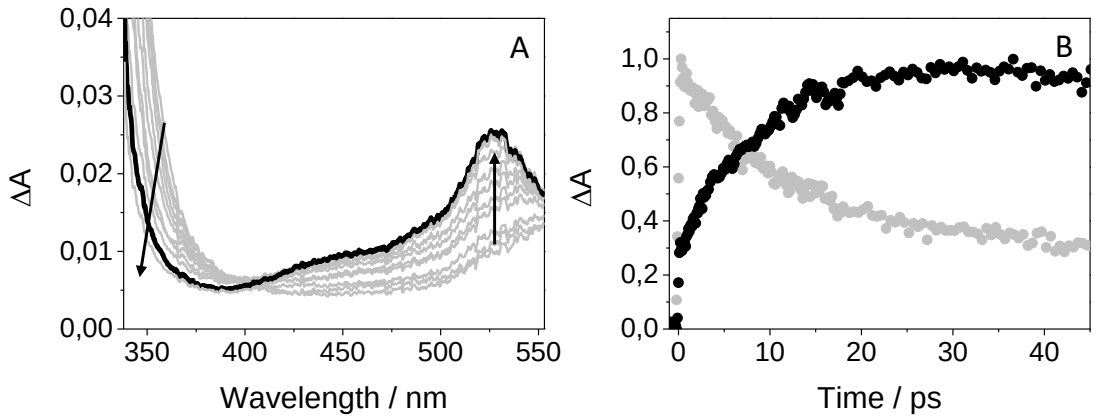


Fig. S12 A) Femtosecond transient absorption spectra from 0.5 to 40 ps and B) kinetic traces at 340 nm (gray) and 530 nm (black) for BP after excitation at 280 nm in acetonitrile.

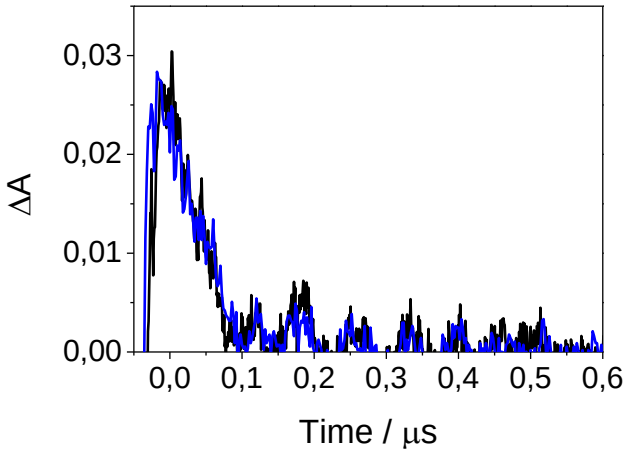


Fig. S13 LFP decay traces at 530 nm for dyad 2 (black) and HH-8 (blue) after excitation at 266 nm in deaerated acetonitrile.

References

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5. S. S. Chaudhari, A. Thomas, N. P. Patil, N. K. Joshi and I. Mukhopadhyay, *Indian Pat. Appl.*, 2010, **IN 2008MU02512**.