

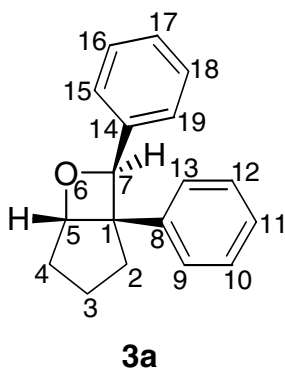
Characterization of Oxetanes **3a-c** and **4a-c**

The determination of the structures of oxetanes **3a-c** and **4a-c** was based on spectroscopic information (^1H NMR, ^{13}C NMR (BB and APT), COSY, HMQC, LRMS, HRMS and NOE difference) and elemental analyses. IUPAC numbering rules were used to number the structures. Each carbon atom and the hydrogen atoms attached to it share the same number. Different geminal hydrogens in the ^1H NMR spectra are differentiated by a prime. The characterization of oxetane **3a** is presented in detail below; the other oxetanes were characterized similarly. The COSY, HMQC and NOE difference spectra of compound **3a** are shown in Figures 1-3, respectively.

LR and HRMS spectra and elemental analysis of oxetane **3a** indicate that it is a constitutional isomer of the starting material **1a**. The FTIR spectrum shows no evidence of an obvious functional group, suggesting that the carbonyl group in starting ketone **1a** has been converted to an ether. The ^1H , ^{13}C and HMQC NMR spectra show that there are two methine groups present at fairly low field (5.43 and 5.40 ppm in ^1H NMR, and 90.05 and 88.12 ppm in the ^{13}C NMR). Therefore it is likely that these two groups are connected to the oxygen atom. Compared to the presence of four methylene groups in starting ketone **1a**, product **3a** has only three methylenes along with two more methines, indicating that at least one of the original methylene groups has been converted to a methine group. Hence, an oxetane structure was assigned. This assignment is strongly supported by the spectroscopic data for similar compounds in the literature.¹ The regiochemistry of compound **3a** was deduced on the basis of its COSY spectrum, which shows that the two methine hydrogens are not coupled, thus precluding the possibility of

the other regioisomer. The *exo*-stereochemistry for this oxetane was not determined until the NOE difference spectra were recorded (Figure 3). The most important interactions are summarized in Figure 4.

(1S*,5S*,7S*)-6-Oxa-1,7-diphenylbicyclo[3.2.0]heptane (3a)



colorless oil;

¹H NMR (C₆D₆, 400 MHz) δ 7.14 (m, 2H, H15&19), 6.99 (m, 2H, H16&18), 6.92-6.64 (m, 3H, H10, 12&17), 6.64-6.58 (m, 3H, H9, 13&11), 5.43 (d, *J* = 3.0 Hz, 1H, H5), 5.40 (s, 1H, H7), 2.37 (m, 1H, H3'), 2.20-2.08 (m, 2H, H2'&4'), 1.83 (dt, *J* = 6.6 and 12.5 Hz, 1H, H3), 1.51 (dt, *J* = 6.6 and 12.5 Hz, 1H, H2), 1.29 (m, 1H, H4) ppm;

¹³C NMR (C₆D₆, 100 MHz, APT: C, CH₂: +; CH, CH₃: -) δ 141.90 (+, C8 or C14), 141.51 (+, C8 or C14), 127.95 (-, C10&12), 127.87 (-, C16&18), 127.26 (-, C9&13), 127.19 (-, C17), 126.65 (-, C15&19), 125.98 (-, C11), 90.05 (-, C7), 88.12 (-, C5), 59.12 (+, C1), 39.42 (+, C2), 35.09 (+, C4), 25.03 (+, C3) ppm;

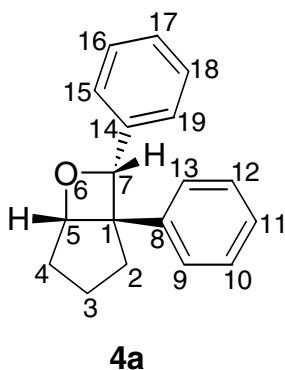
IR (neat) 3030, 2944, 1602, 1496, 1449, 1302, 1213, 1155, 1086, 1034, 995, 956, 928, 880, 851, 753, 698, 583, 548 cm⁻¹;

LRMS (EI) *m/z* 250 (M⁺), 145, 144(100), 143, 129, 115, 105, 91, 77, 66;

HRMS (EI) m/z 250.1361 (Calcd for $C_{18}H_{18}O$, 250.1358);

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.10; H, 7.20.

(1S*,5S*,7R*)-6-Oxa-1,7-diphenylbicyclo[3.2.0]heptane (4a)



colorless oil;

1H NMR (C_6D_6 , 400 MHz) δ 7.40-7.05 (m, 10H, ArH), 5.99 (s, 1H, H7), 5.38 (d, J = 3.5 Hz, 1H, H5), 2.10-1.94 (m, 2H, H4'&3'), 1.88 (dd, J = 7.7 and 13.2 Hz, 1H, H2'), 1.52-1.34 (m, 2H, H3&2), 1.22 (m, 1H, H4) ppm;

^{13}C NMR (C_6D_6 , 100 MHz, APT: C, CH_2 : +; CH, CH_3 : -) δ 145.94 (+), 139.97 (+), 128.91 (-), 128.35 (-), 127.19 (-), 126.50 (-), 126.37 (-), 125.16 (-), 89.64 (-, C5), 87.78 (-, C7), 58.48 (+, C1), 34.45 (+, C4), 34.38 (+, C2), 25.84 (+, C3) ppm;

IR (neat) 3027, 2948, 1602, 1495, 1447, 1305, 1212, 1158, 1070, 1031, 1001, 929, 893, 847, 760, 700, 644, 617, 558, 525 cm^{-1} ;

LRMS (CI+, NH_3) m/z 250 (M^+), 145, 144(100), 143, 129, 128, 115, 105, 91, 72;

HRMS (CI+, NH_3) m/z 250.1356 (Calcd for $C_{18}H_{18}O$, 250.1358);

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.81; H, 7.10.

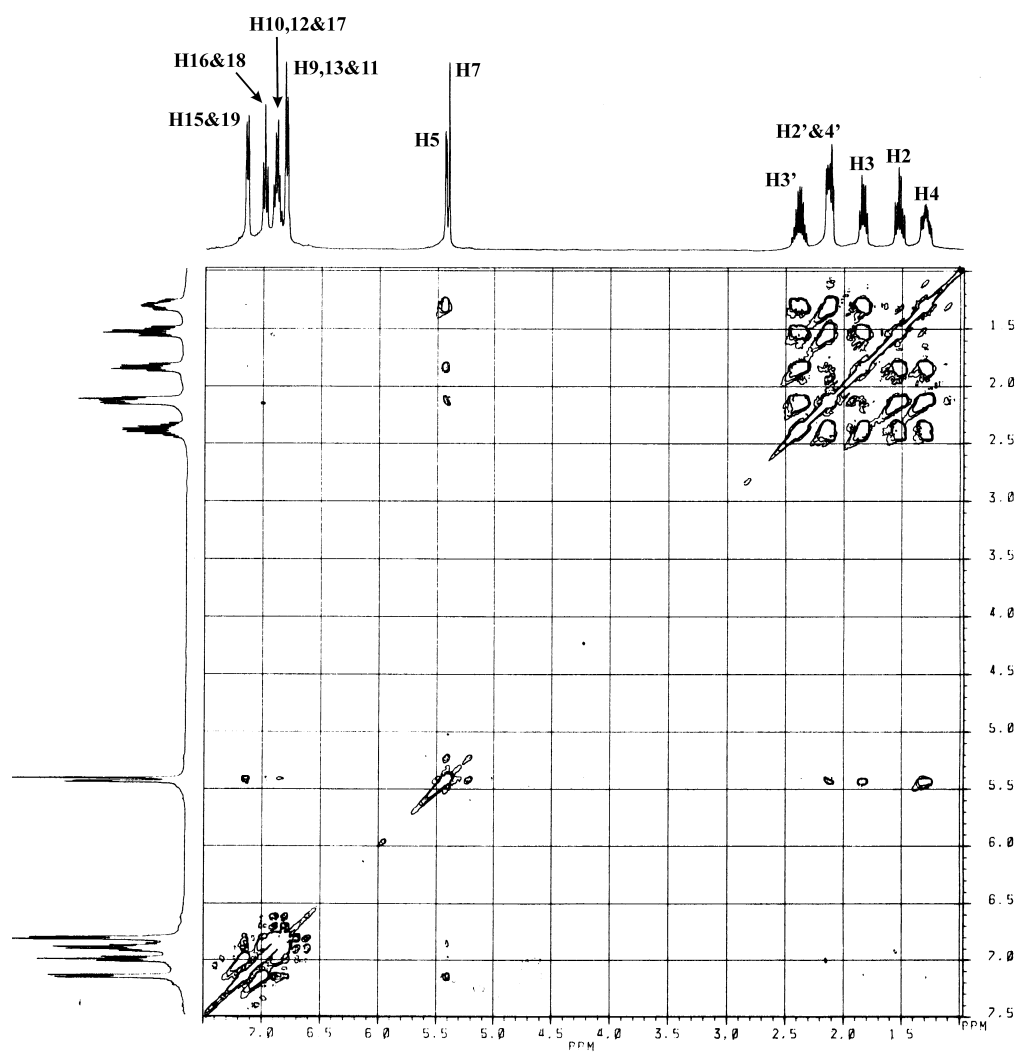


Figure 1. COSY spectrum (400 MHz, C₆D₆) of product **3a**

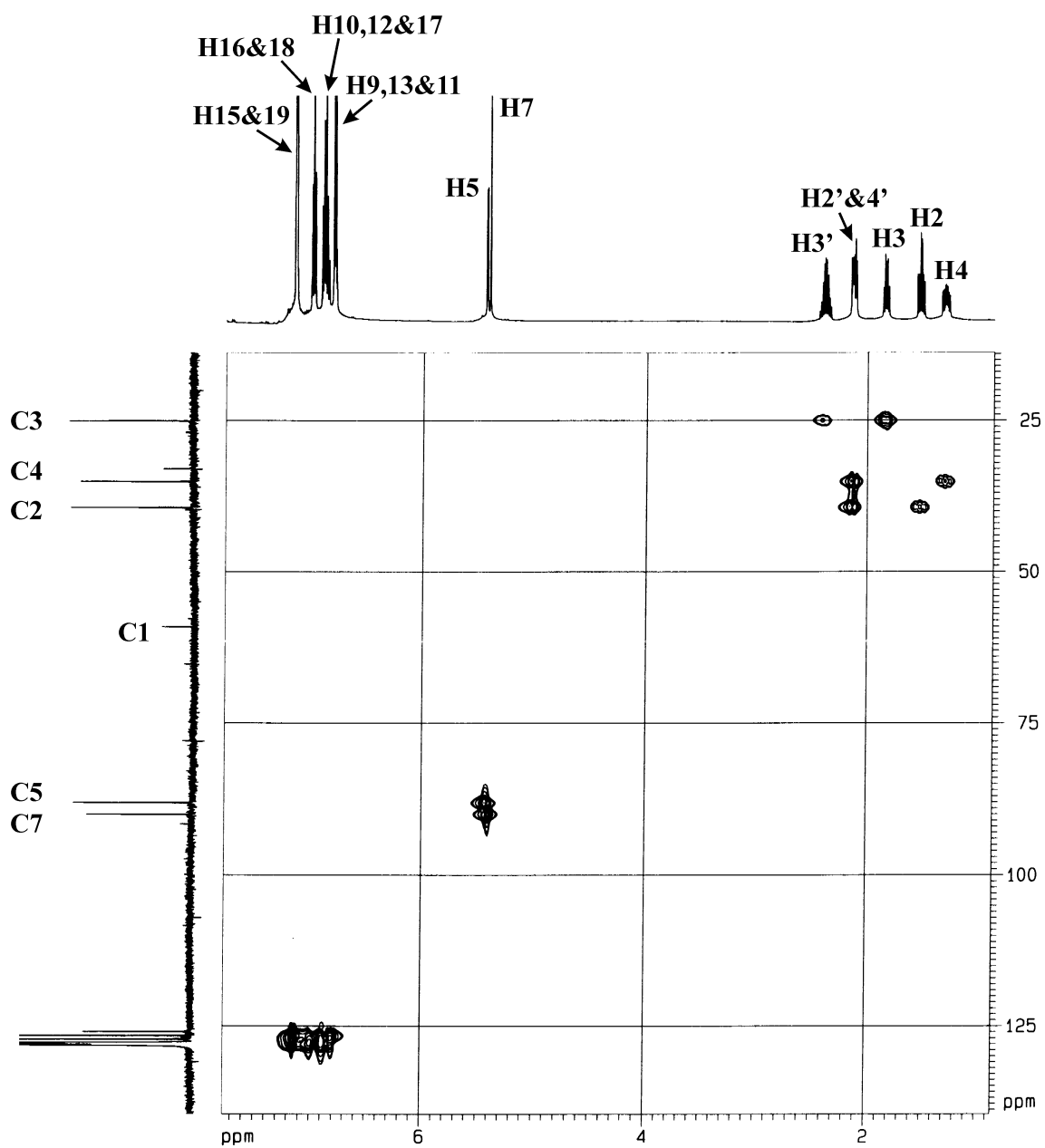


Figure 2. HMQC spectrum (500 MHz, C_6D_6) of product **3a**

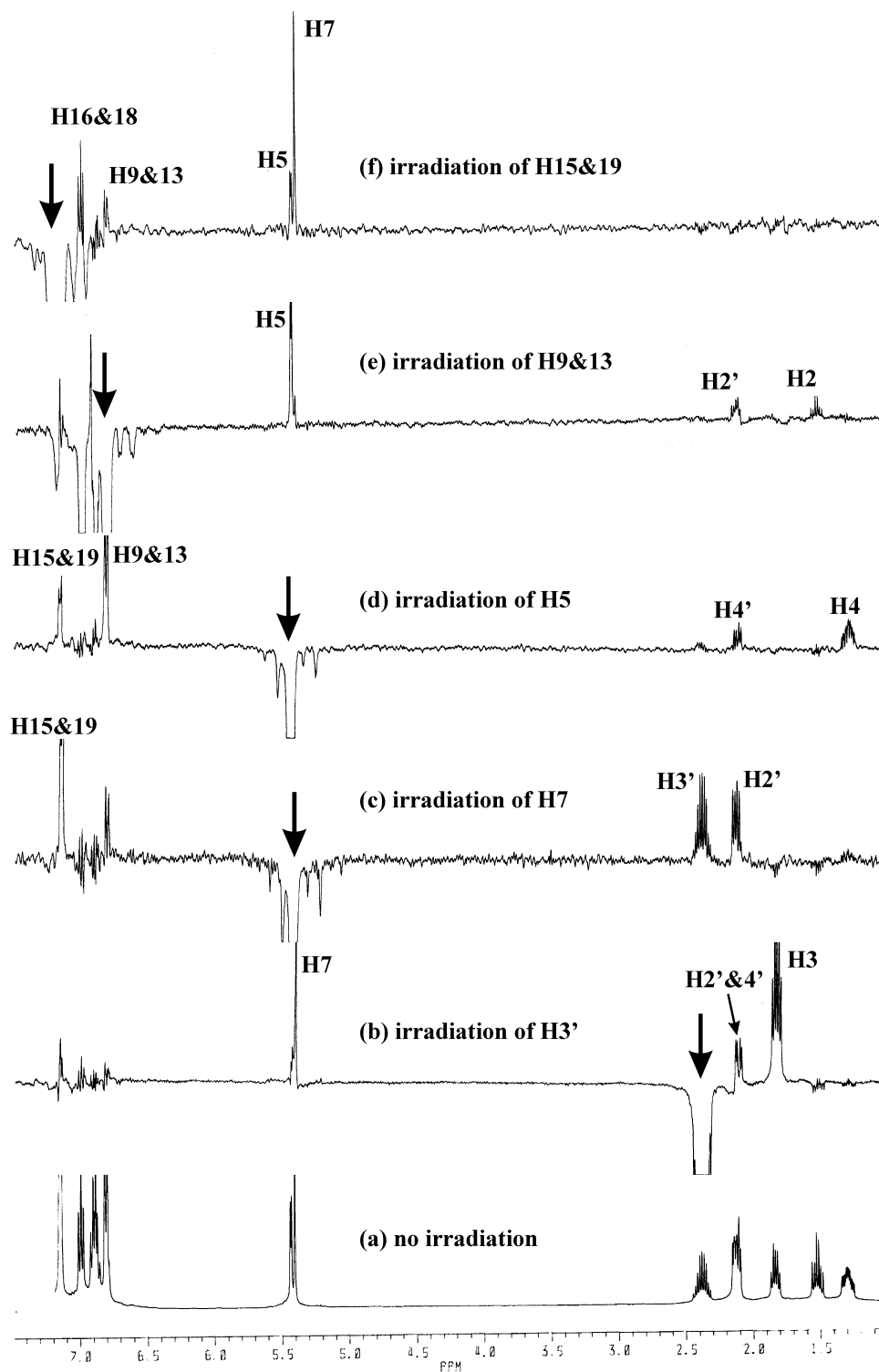


Figure 3. The NOE difference spectra (400 MHz, C_6D_6) of oxetane **3a** with irradiations at: (a) nil; (b) 2.38; (c) 5.40; (d) 5.43; (e) 6.81; (f) 7.14 ppm.

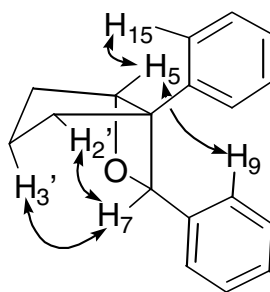


Figure 4. NOE interactions in oxetane **3a**

Similarly, compound **4a** was assigned as the corresponding *endo*-aryl oxetane.

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1. Griesbeck, A.G.; Stadtmüller, *J. Am. Chem. Soc.* **1991**, *113*, 6923.