

Supplementary Information

Photochemical Generation, Intramolecular Reactions, and Spectroscopic Detection of Oxonium Ylide and Carbene Intermediates in a Crystalline *ortho*-(1,3-Dioxolan-2-yl)-diaryldiazomethane

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- Figure SI-1. ^1H NMR Spectrum of diazo compound **1a**
- Figure SI-2. ^{13}C NMR spectrum (125 MHz, CDCl_3) of diazo compound **1a**.
- Figure SI-3. ^1H NMR spectrum (500 MHz, CDCl_3) of 1,3-dioxane **8**.
- Figure SI-4. ^{13}C NMR spectrum (125 MHz, CDCl_3) of 1,3-dioxane **8**.
- Figure SI-5. ^1H (500 MHz)- ^{13}C (125 MHz) gradient HMQC NMR spectrum (CDCl_3) of 1,3-dioxane **8**.
- Figure SI-6. ^1H NMR spectrum (500 MHz, benzene- d_6) of *ortho*-quinodimethane (*o*-QDM) **6**.
- Figure SI-7. ^1H - ^1H gradient COSY NMR spectrum (500 MHz, benzene- d_6) of *ortho*-quinodimethane (*o*-QDM) **6**.
- Figure SI-8. 2-D NOESY spectrum (500 MHz, benzene- d_6) of *ortho*-quinodimethane (*o*-QDM) **6**.
- Figure SI-9. ^1H NMR spectrum (500 MHz, CDCl_3) of 1,4-dioxane **9**.
- Figure SI-10. ^{13}C NMR spectrum (125 MHz, CDCl_3) of 1,4-dioxane **9**.
- Figure SI-11. ^1H NMR spectrum (500 MHz, CDCl_3) of solid-state product benzocyclobutane acetal **10**.
- Figure SI-12. ^{13}C NMR spectrum (125 MHz, CDCl_3) of solid-state product benzocyclobutane acetal **10**.
- Figure SI-13. ^{13}C DEPT 135 NMR spectrum (125 MHz, CDCl_3) of solid-state product benzocyclobutane acetal **10**.

Figure SI-1. ^1H NMR Spectrum (500 MHz, CDCl_3) of diazo compound **1a**.

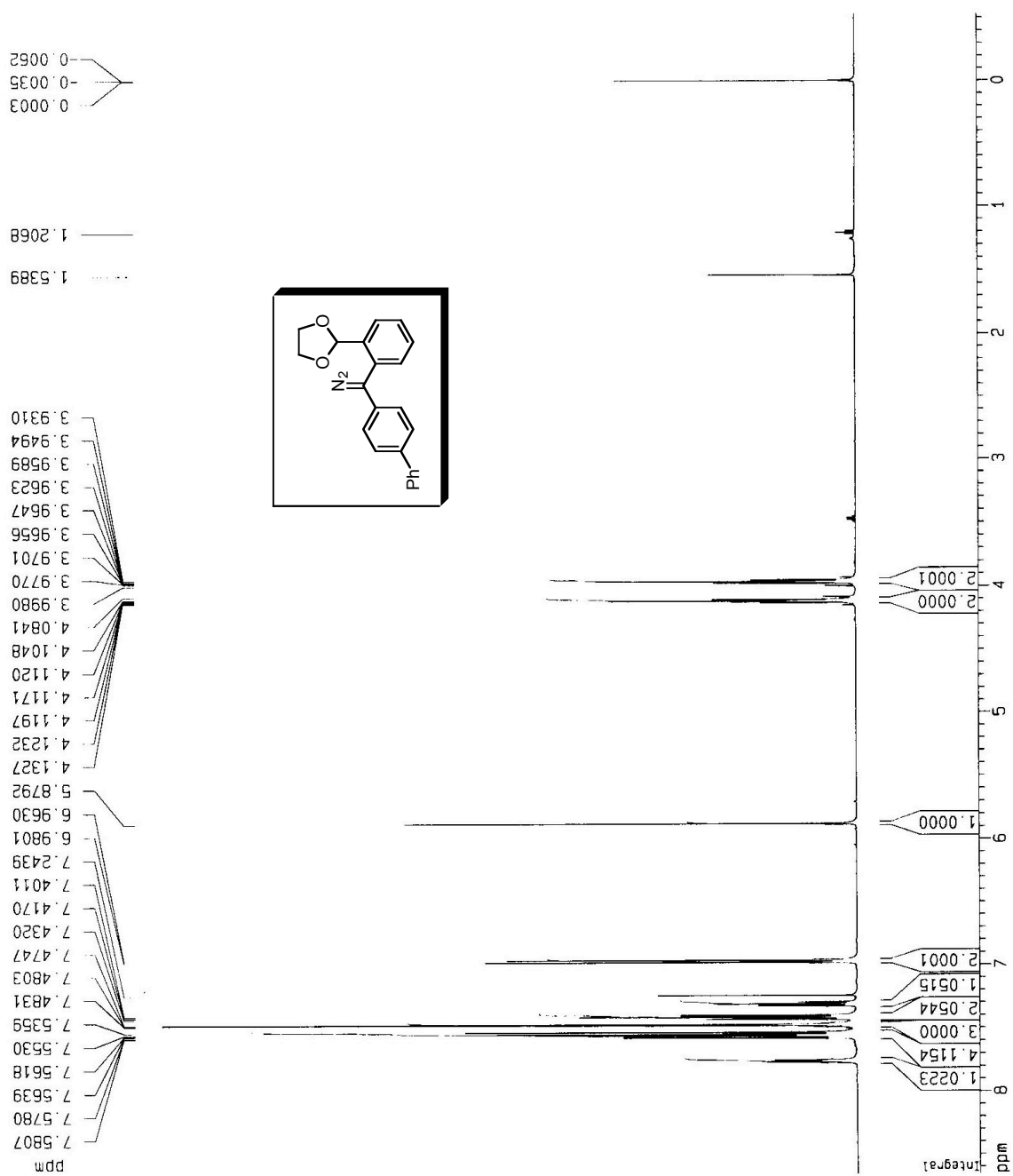


Figure SI-2 ^{13}C NMR spectrum (125 MHz, CDCl_3) of diazo compound **1a**.

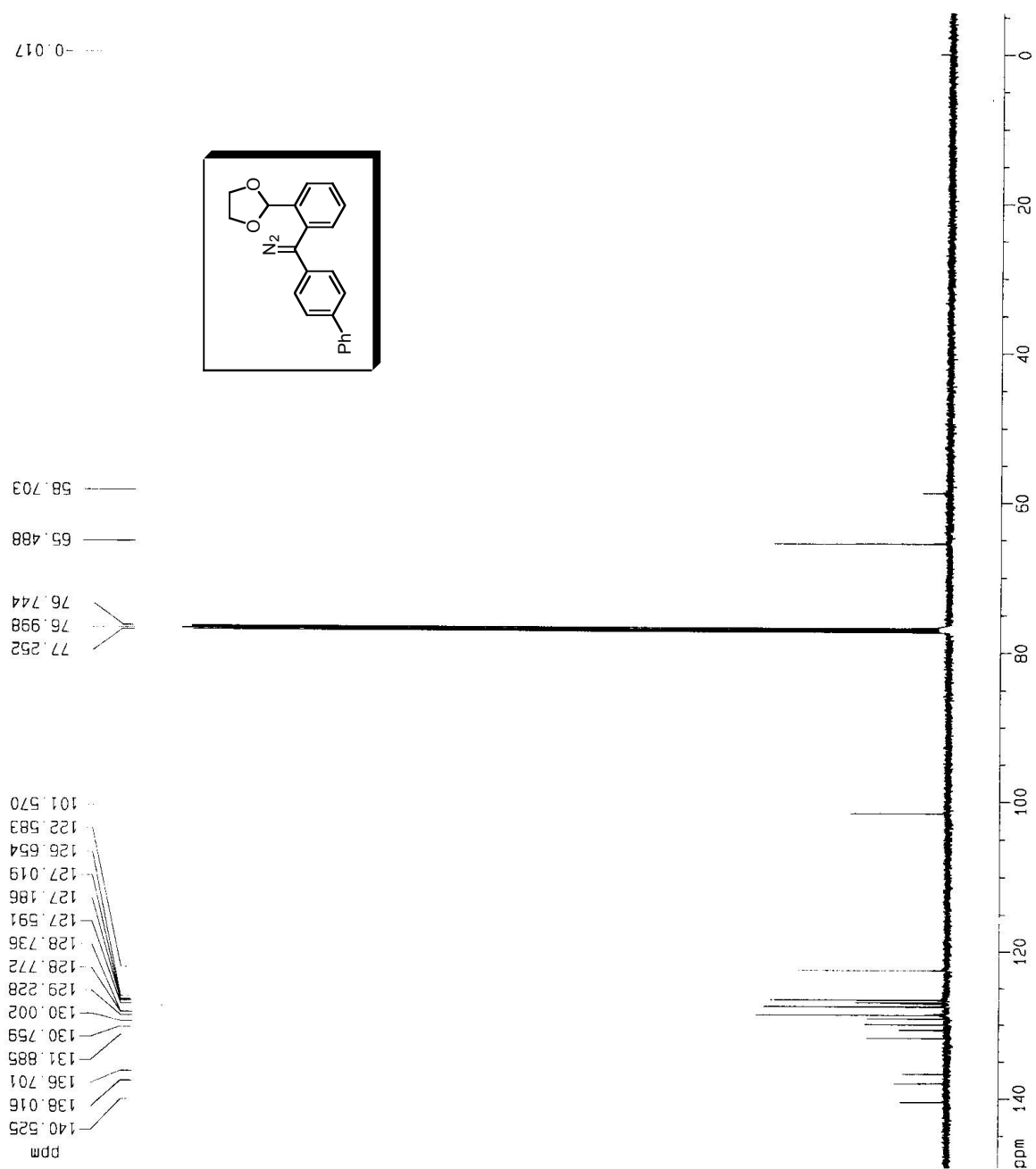


Figure SI-3. ^1H NMR spectrum (500 MHz, CDCl_3) of 1,3-dioxane **8**.

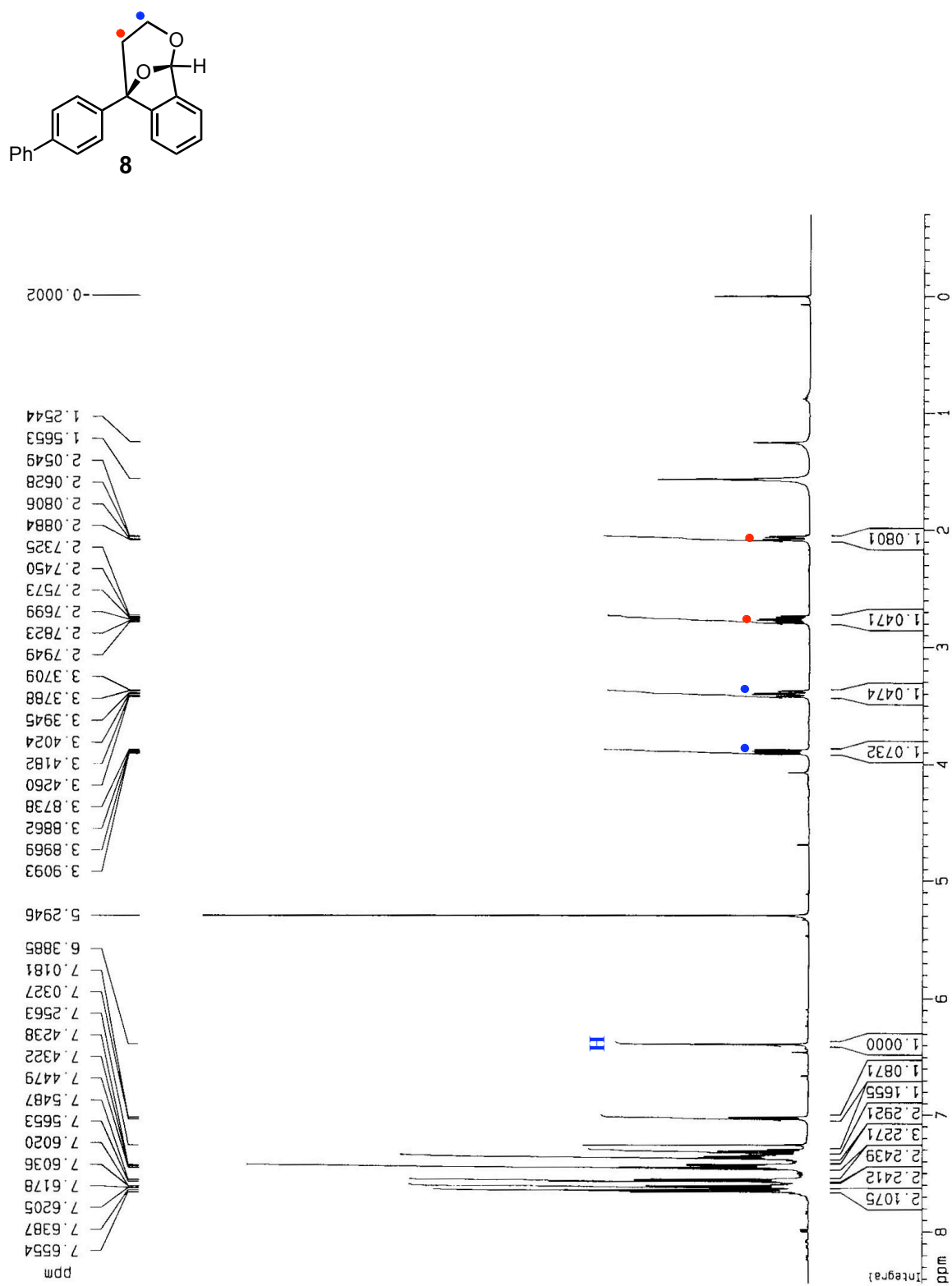


Figure SI-4. ^{13}C NMR spectrum (125 MHz, CDCl_3) of 1,3-dioxane **8**.

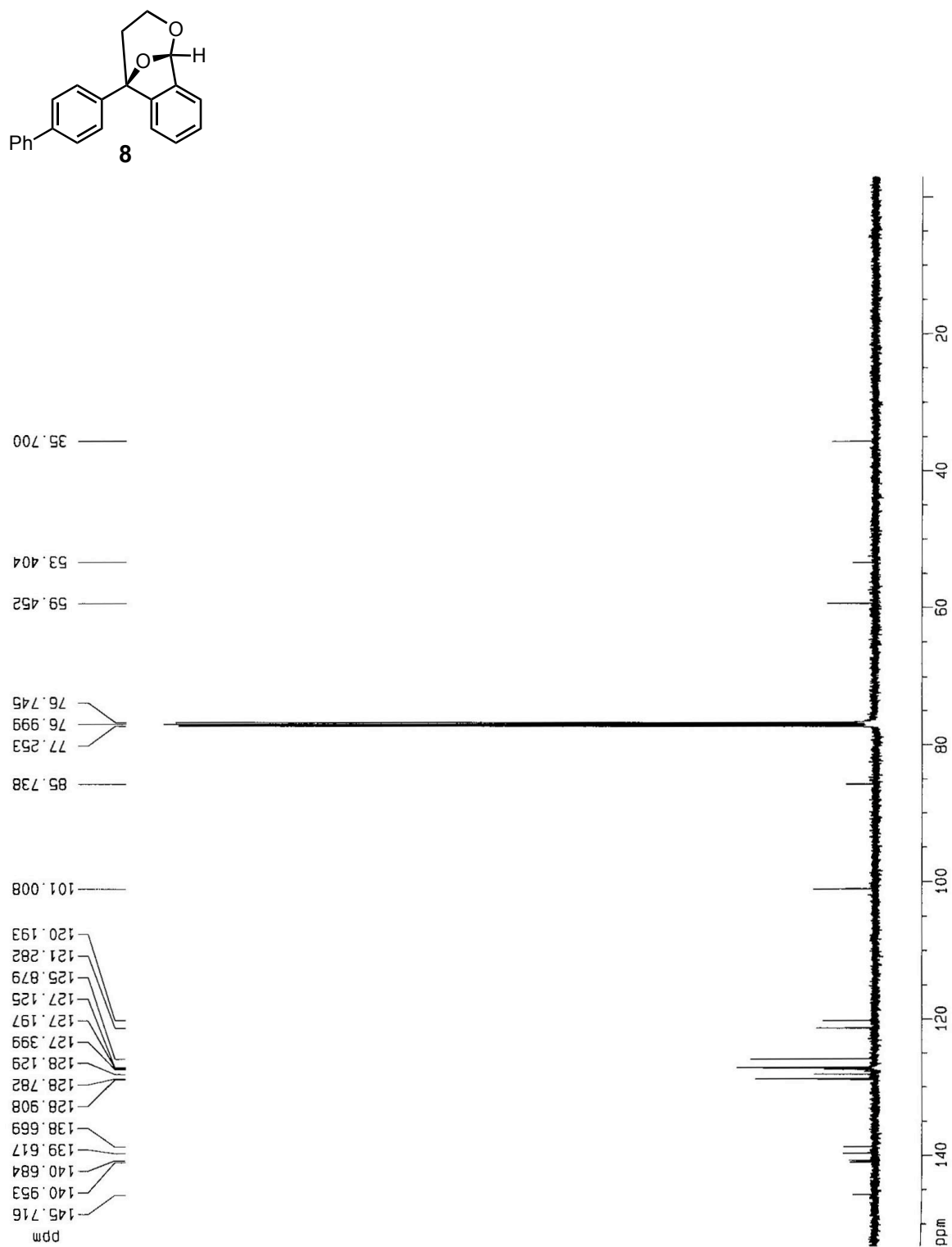


Figure SI-5. ^1H (500 MHz)- ^{13}C (125 MHz) gradient HMQC NMR spectrum (CDCl_3) of 1,3-dioxane **8**.

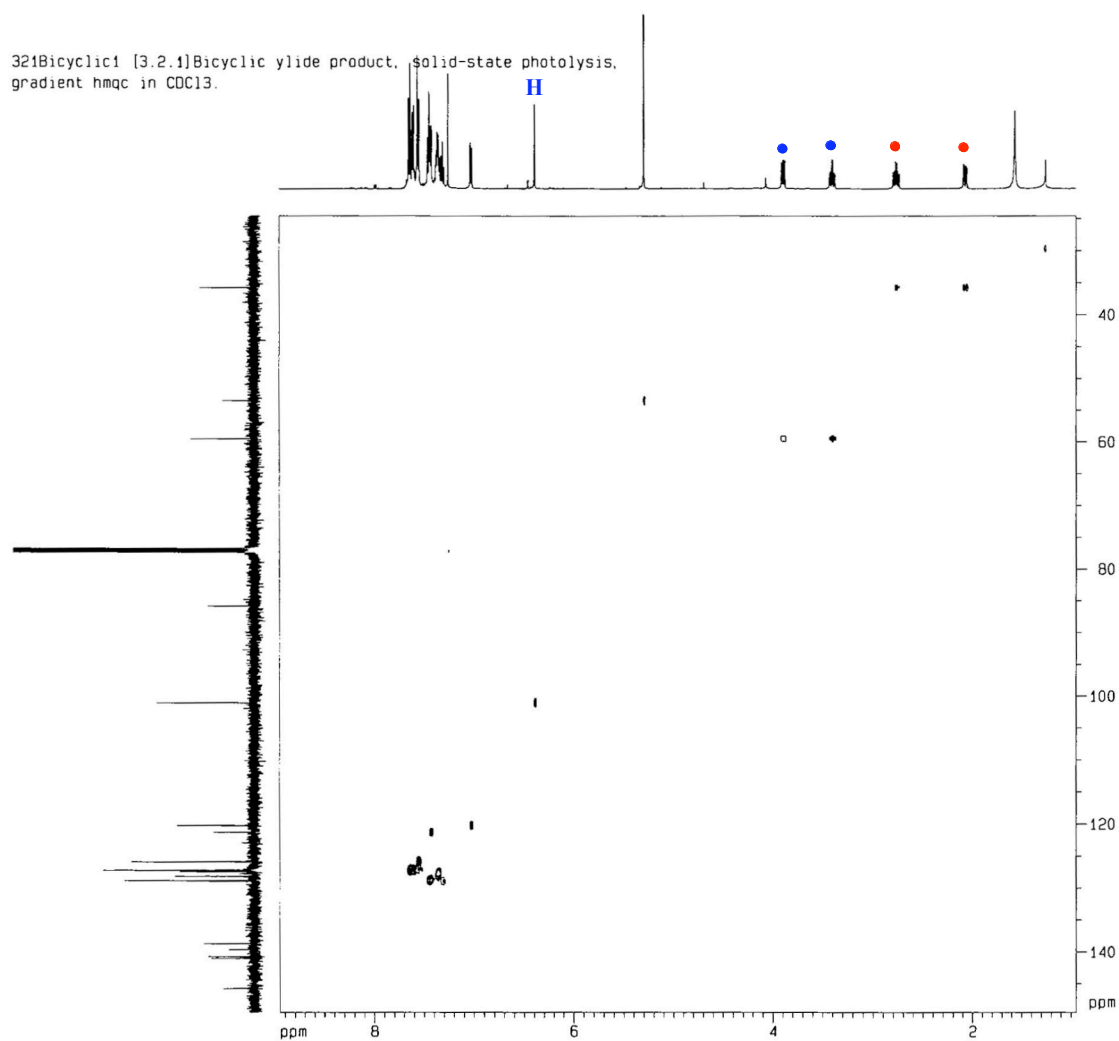
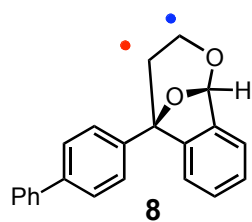


Figure SI-6. ^1H NMR spectrum (500 MHz, benzene- d_6) of *ortho*-quinodimethane (*o*-QDM) **6**.

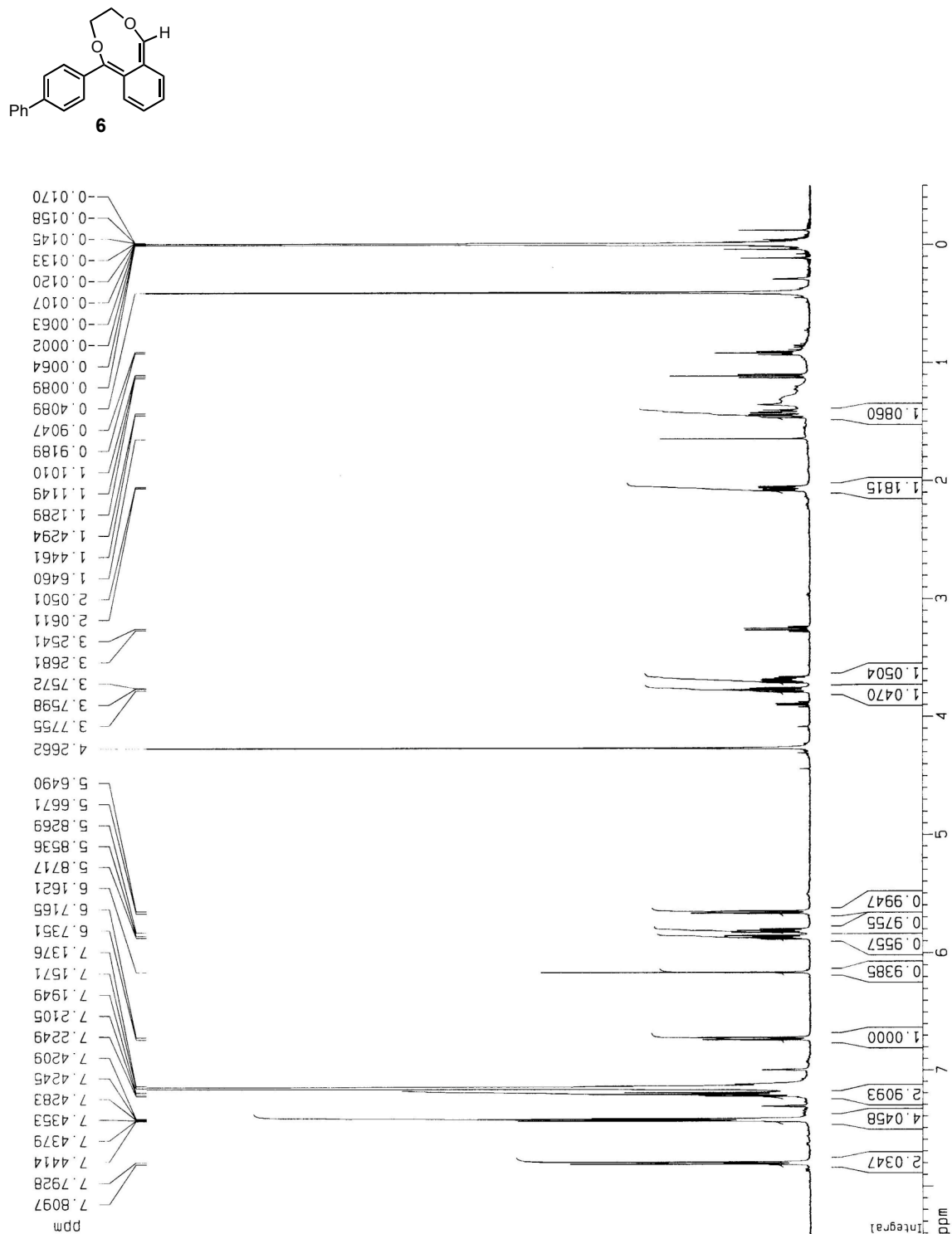


Figure SI-7. ^1H - ^1H gradient COSY NMR spectrum (500 MHz, benzene- d_6) of *ortho*-quinodimethane (o-QDM) **6**.

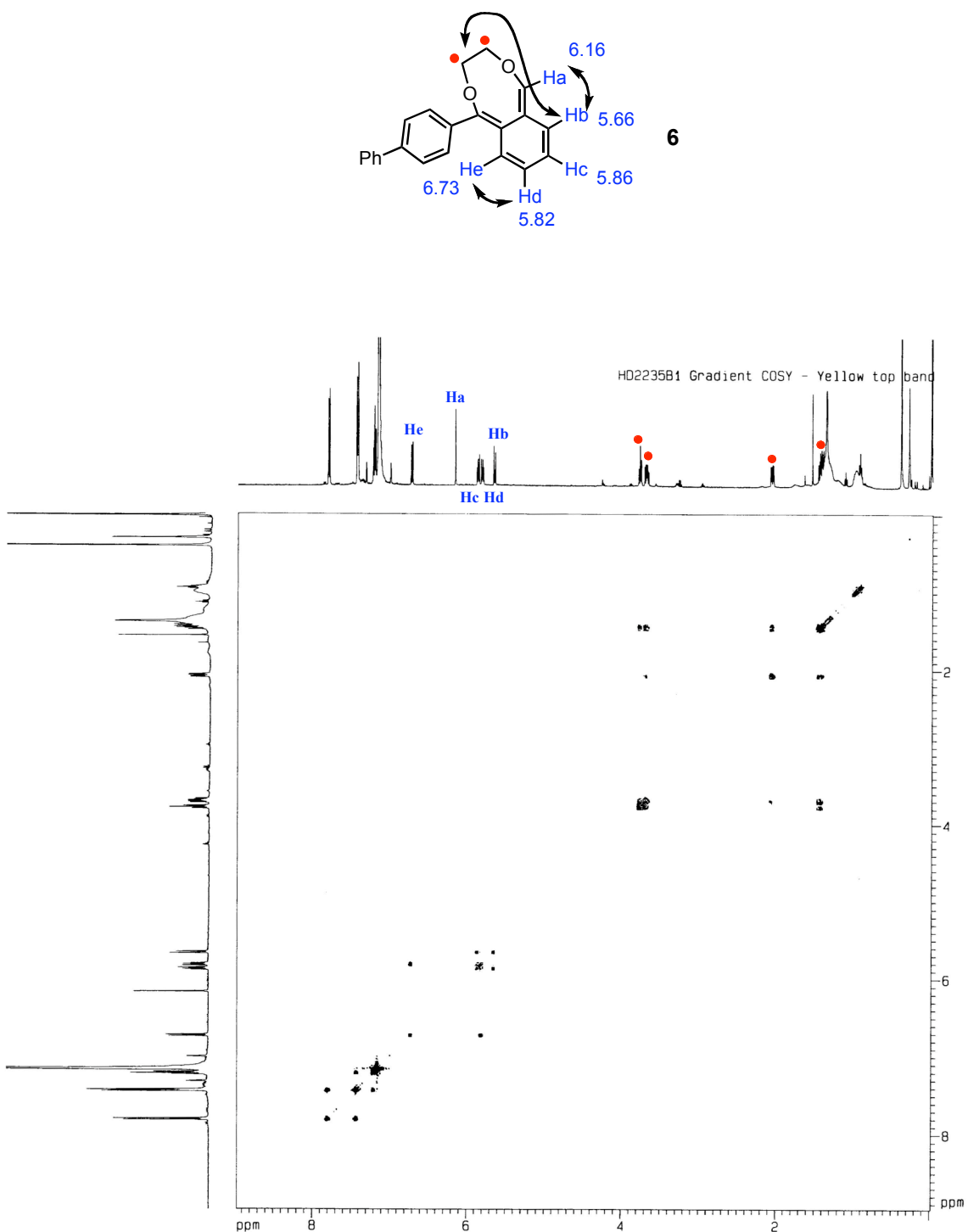


Figure SI-8. 2-D NOESY spectrum (500 MHz, benzene-*d*₆) of *ortho*-quinodimethane (*o*-QDM) **6**.

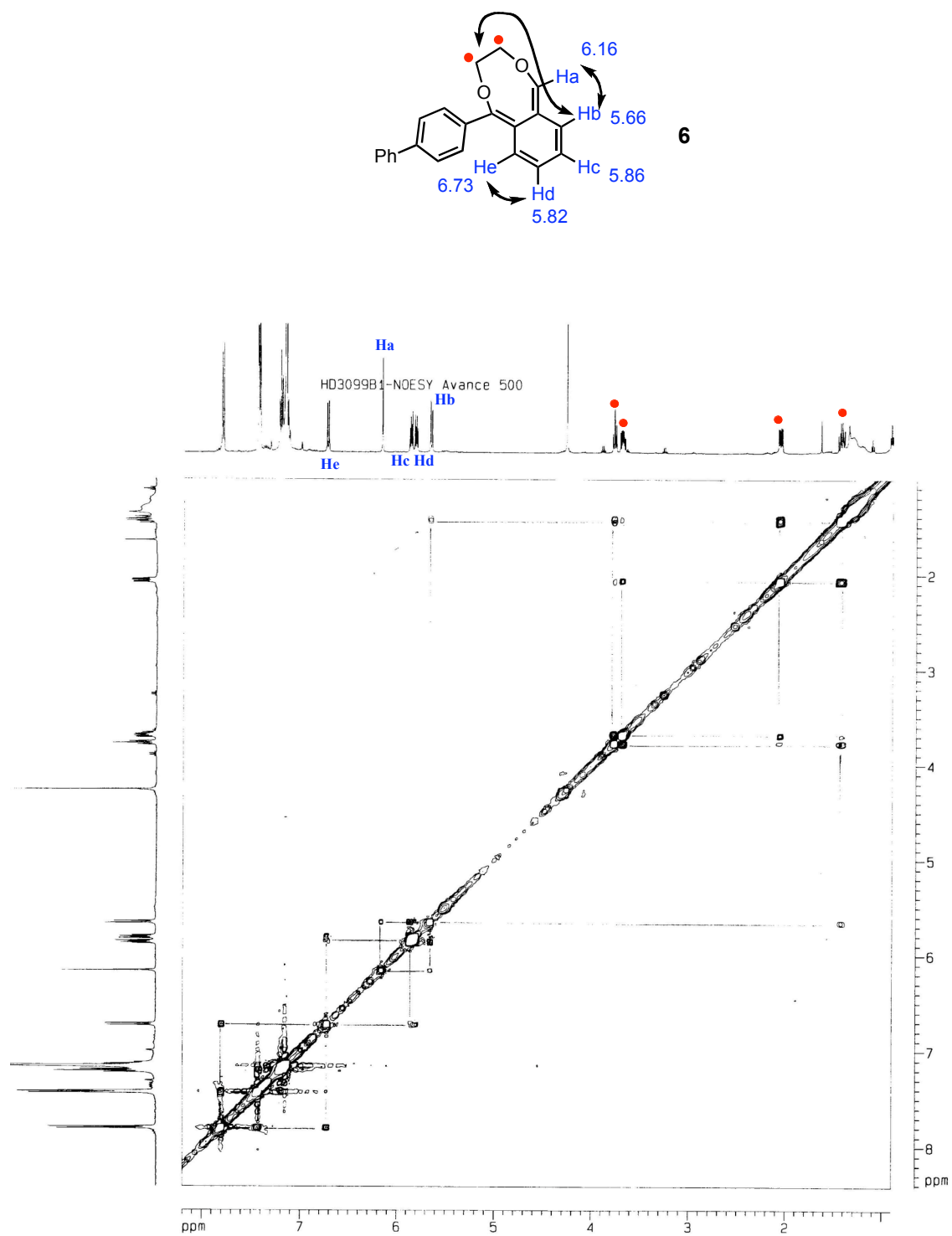


Figure SI-9. ^1H NMR spectrum (500 MHz, CDCl_3) of 1,4-dioxane **9**.

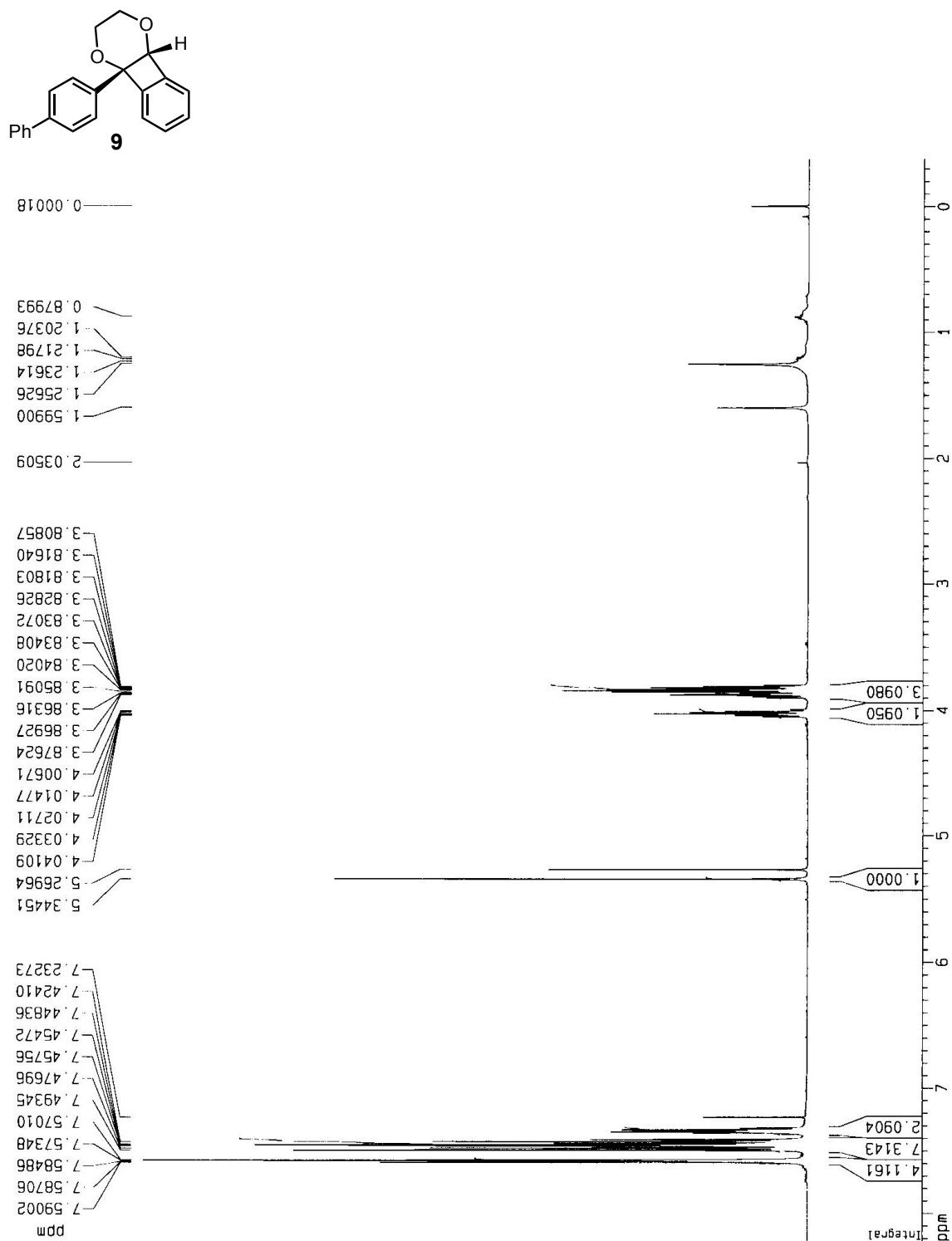


Figure SI-10. ^{13}C NMR spectrum (125 MHz, CDCl_3) of 1,4-dioxane **12**.

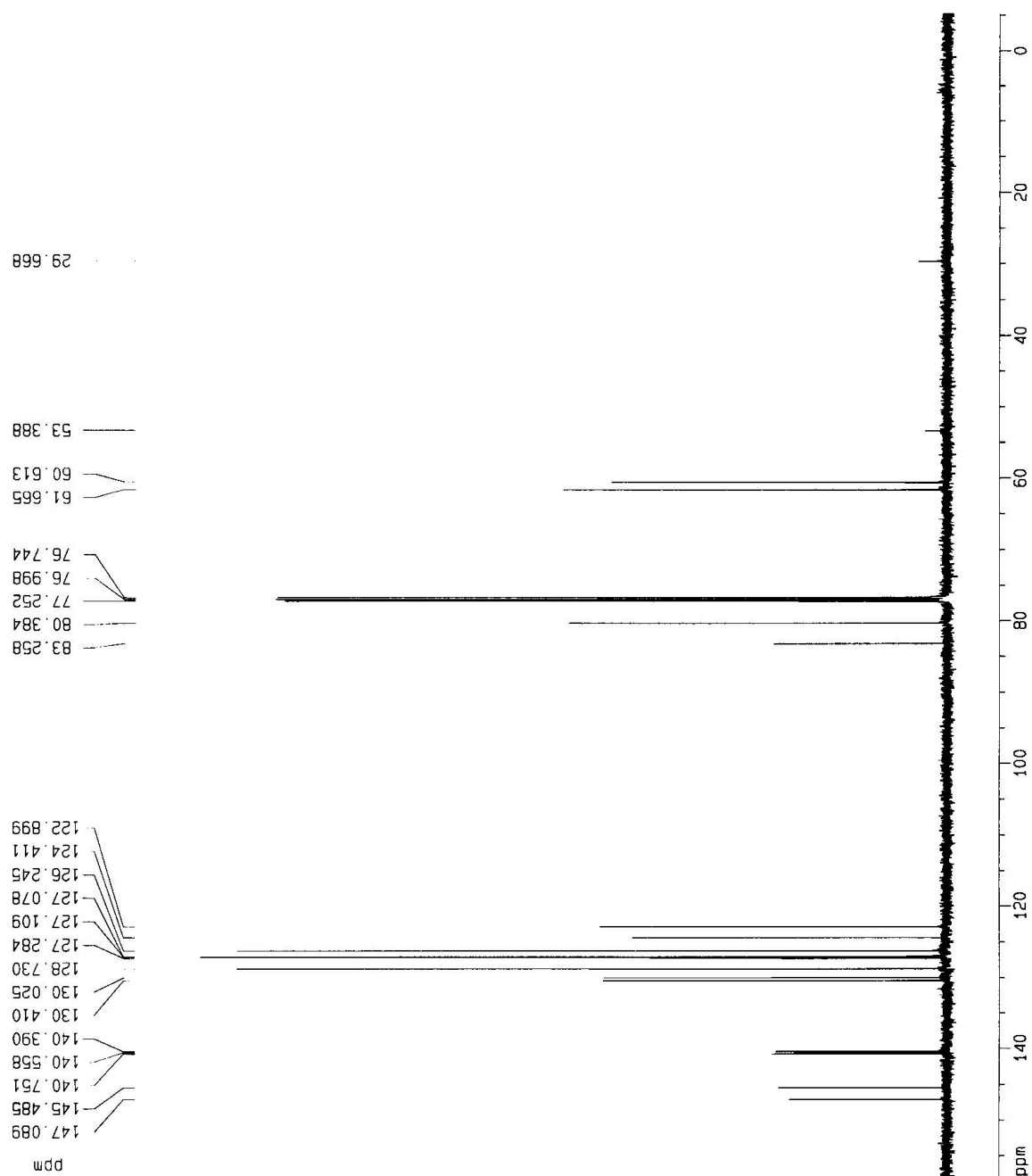
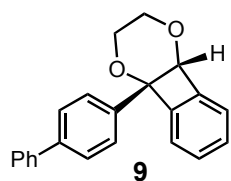


Figure SI-11. ^1H NMR spectrum (500 MHz, CDCl_3) of solid-state product benzocyclobutane acetal **10**.

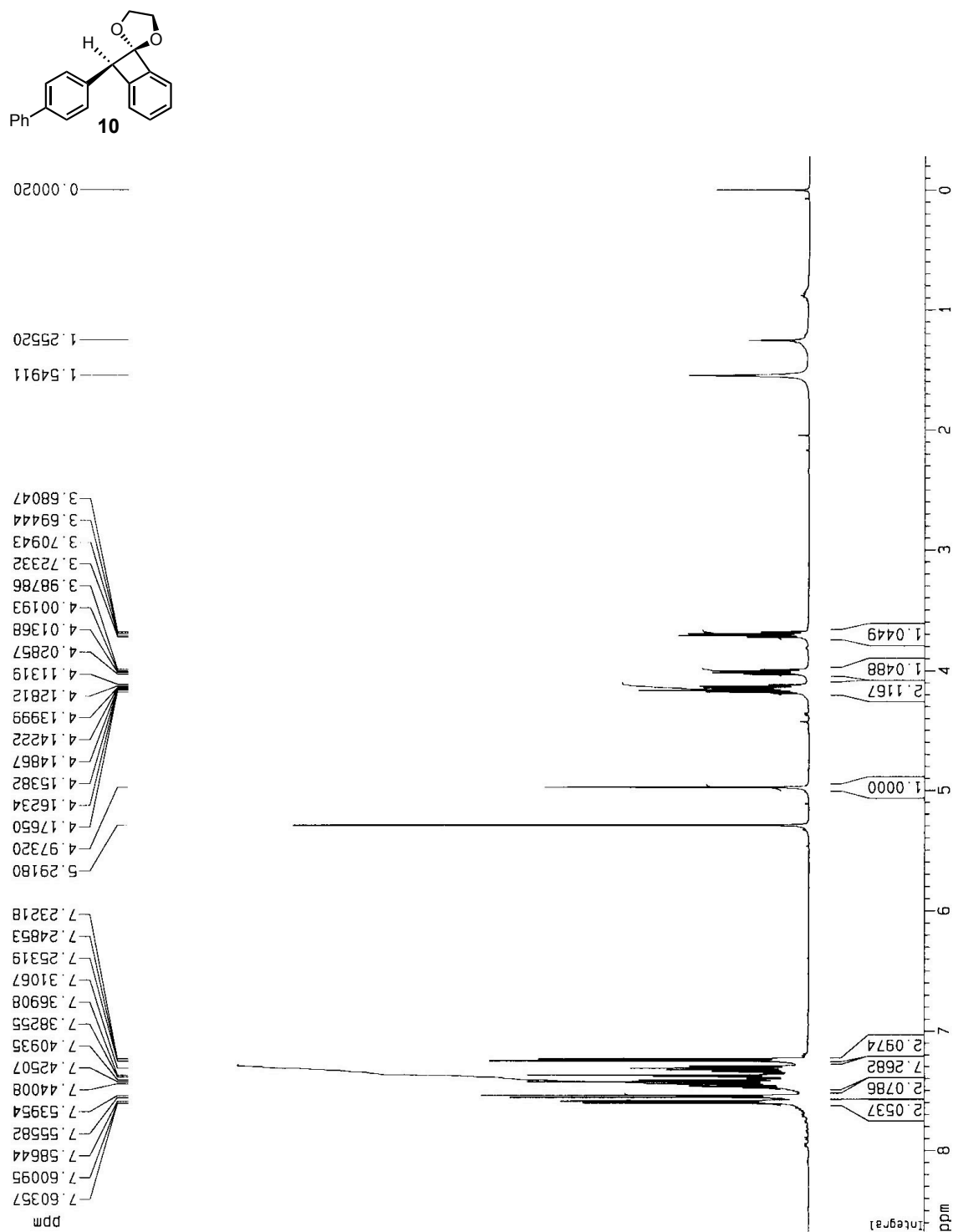


Figure SI-12. ^{13}C NMR spectrum (125 MHz, CDCl_3) of solid-state product benzocyclobutane acetal **10**.

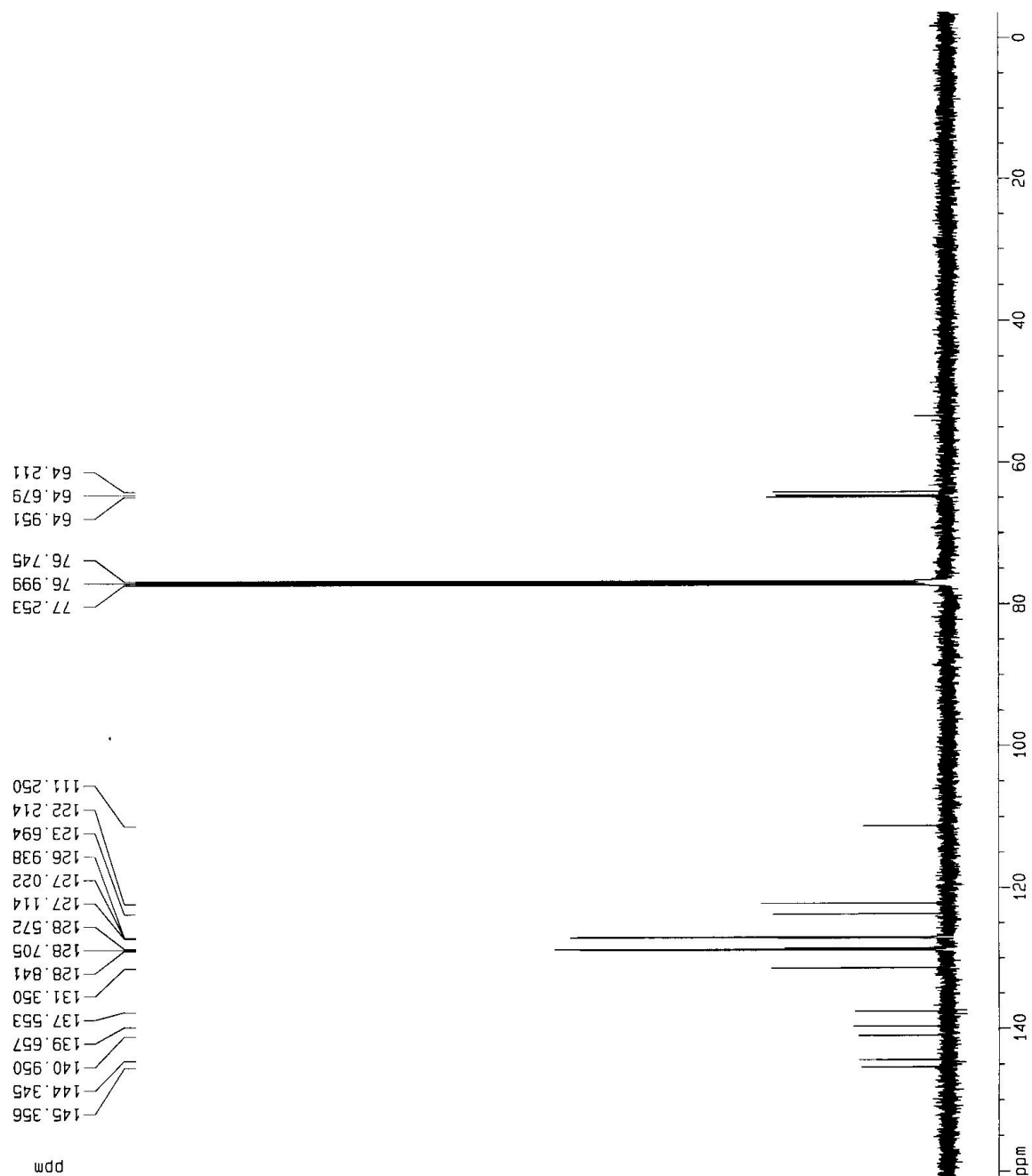
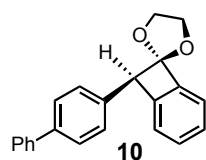


Figure SI-13. ^{13}C DEPT 135 NMR spectrum (125 MHz, CDCl_3) of solid-state product benzocyclobutane acetal **10**.

