Supporting Information

Screening of Palladium/Charcoal Catalysts for Hydrogenation of Diene Carboxylates with Isolated-Rings (Hetero)aliphatic Scaffold

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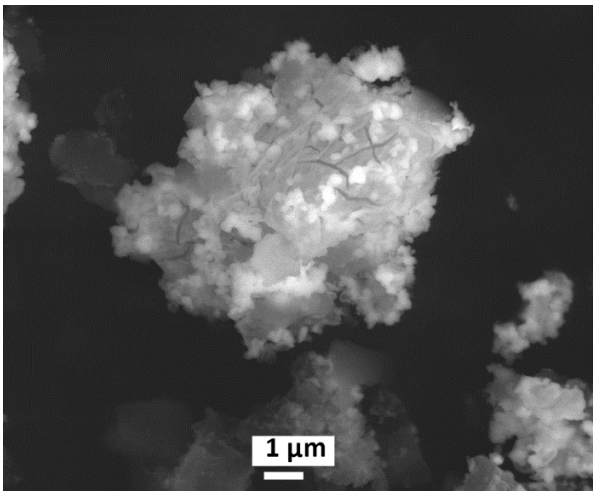


Figure S1. SEM image in backscattered electron mode for $Pd(OH)_2$/C-2 showing one particle covered by hydrated PdO.

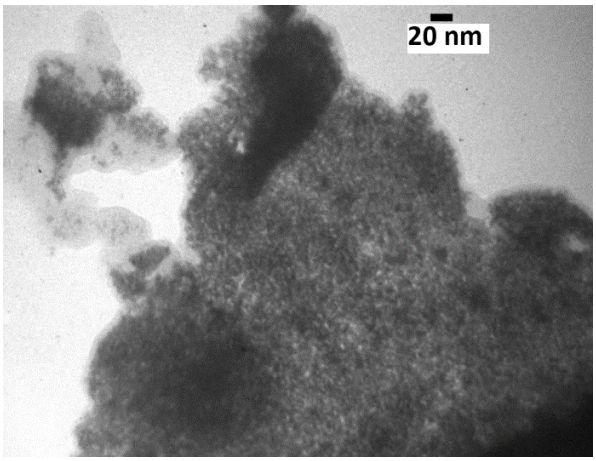


Figure S2. TEM image of $Pd(OH)_2$/C-2 after hydrogenation reaction.

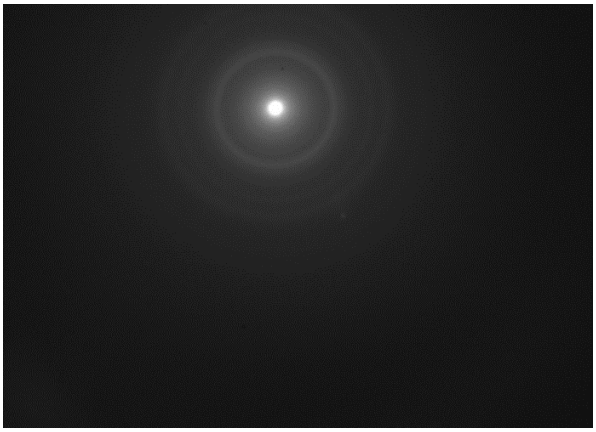


Figure S3. Electron diffraction pattern of $Pd(OH)_2/C$-2 after hydrogenation reaction.

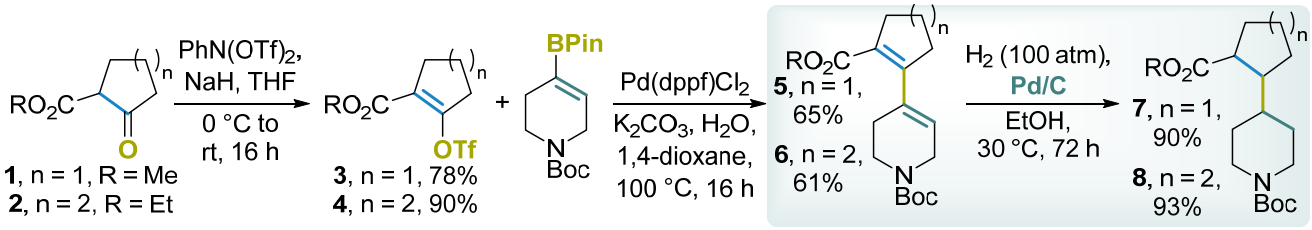


Figure S4. Reaction scheme for preparation of **1** and **2**

The general procedure for the preparation of alkenyl triflates. 0.2 M solution of the corresponding *α*-ketoester (57.0 mmol) in THF (285) was cooled to 0 °C, and NaH (60% in mineral oil, 2.30 g) was added in portions. The reaction mixture was stirred at 0 °C for 30 min, then $PhN(OTf)_2$ (20.5 g) was added. The resulting mixture stirred at rt overnight, then poured into H_2O (500 mL) and extracted with EtOAc (2 × 300 mL). Combined organic layers were washed with brine (2 × 100 mL), dried over Na_2SO_4, filtered, and evaporated in *vacuo* to dryness. The crude product was purified via column chromatography on silica gel using hexanes – EtOAc (20:1, v/v) as an eluent.

The general procedure for the Suzuki cross-coupling reaction. The corresponding triflate (3.65 mmol) was dissolved in 1,4-dioxane – H_2O (14 mL, 7:2, v/v), then K_2CO_3 (1.51 g, 10.9 mmol), $Pd(dppf)Cl_2$ (267 mg, 0.365 mmol), and *tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dihydropyridine-1(2*H*)-carboxylate (1.24 g, 4.01 mmol). The reactor was degassed, purged with Ar, and the reaction mixture was stirred at 100 °C for 18 h. The resulting mixture was cooled to rt, EtOAc (40 mL) was added, the resulting solution was washed with H_2O (3 × 15 mL) and brine (3 × 15 mL), dried over Na_2SO_4, filtered, and evaporated in *vacuo* to dryness. The crude product was purified via column chromatography on silica gel using hexanes – EtOAc (20:1, v/v) as an eluent.

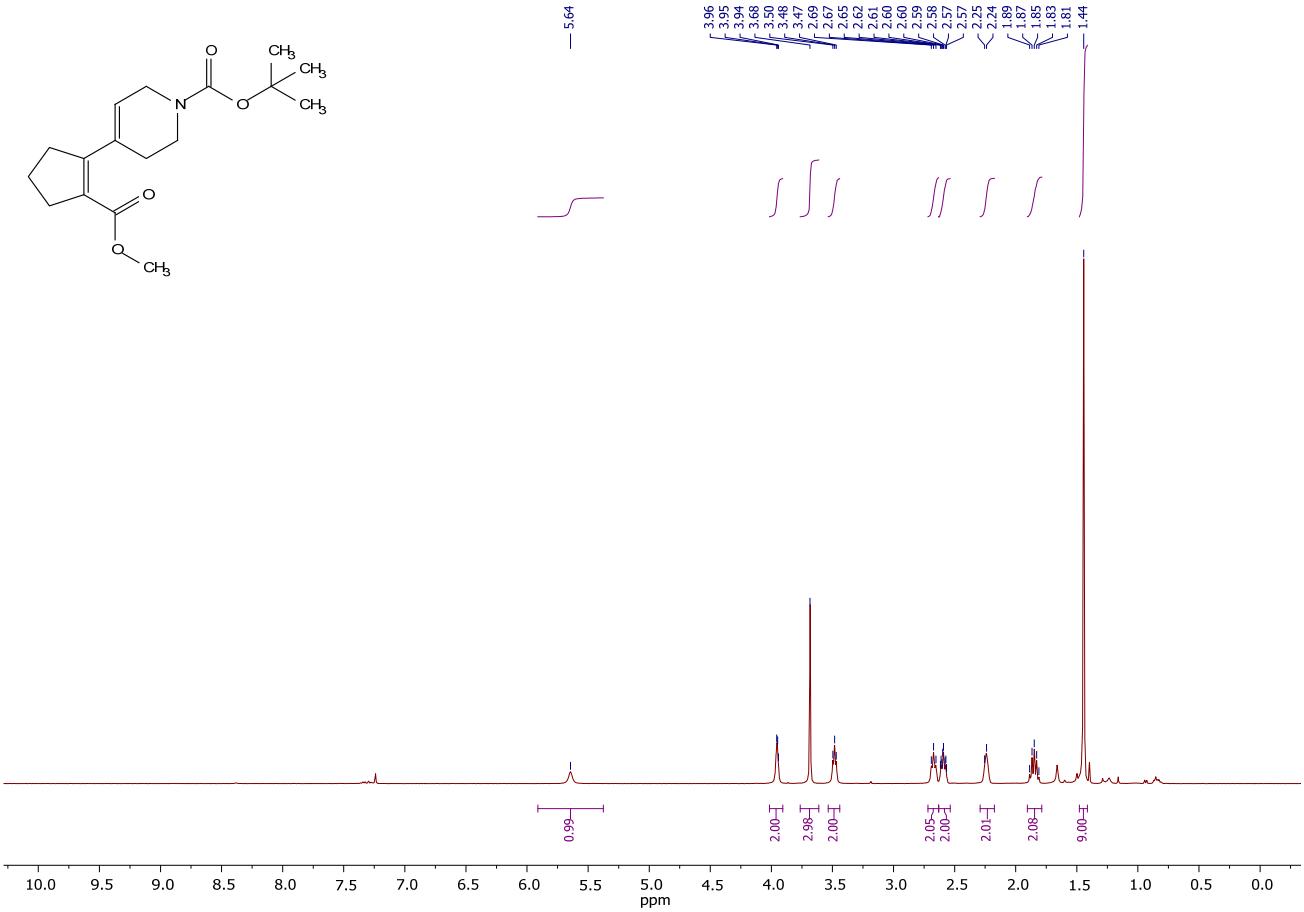


Figure S5. ^{1}H NMR of *tert*-Butyl 4-(2-(methoxycarbonyl)cyclopent-1-en-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate (**1**) (400 MHz, $CDCl_3$)

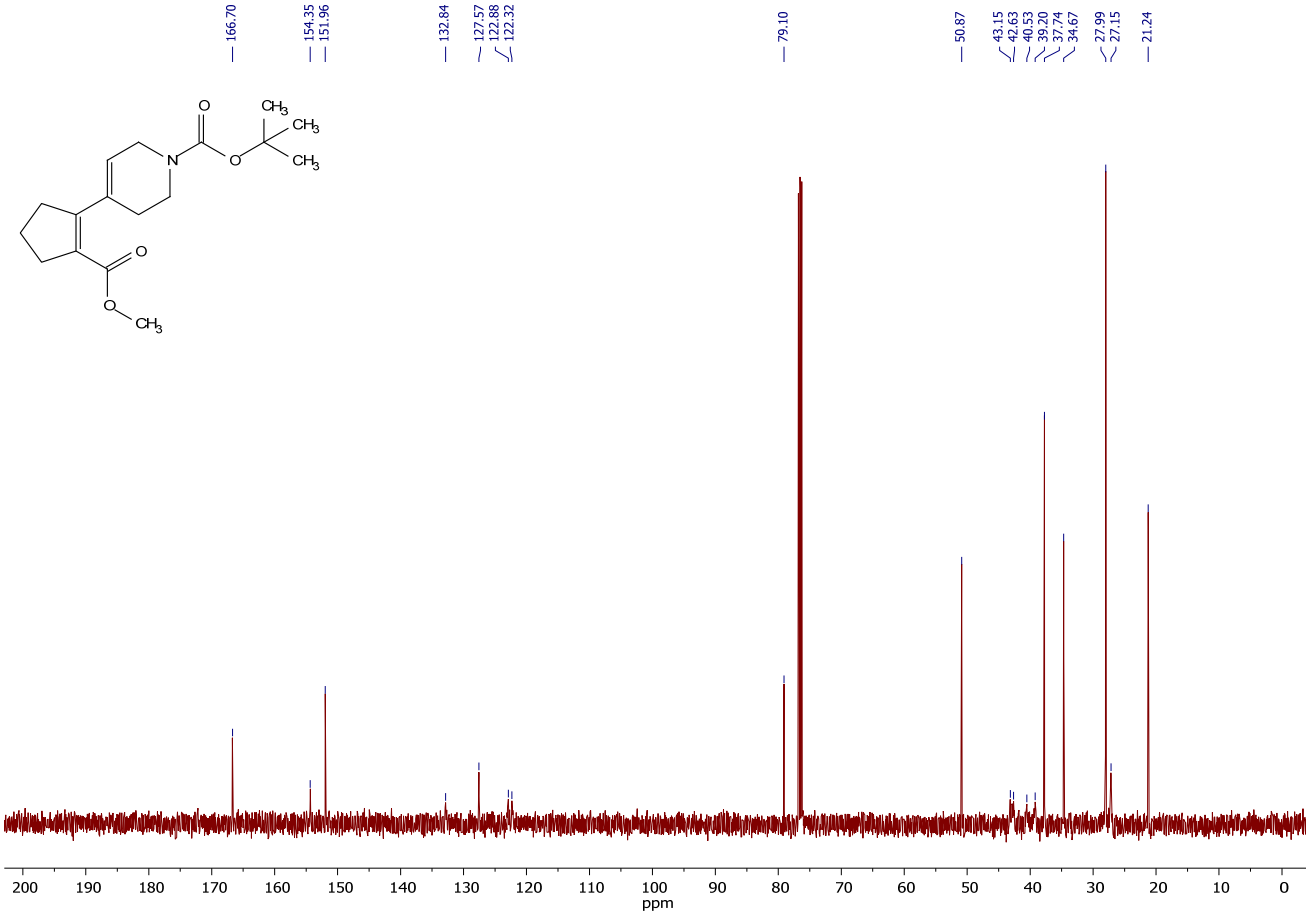


Figure S6. ^{13}C NMR of *tert*-Butyl 4-(2-(methoxycarbonyl)cyclopent-1-en-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate (**1**) (126 MHz, $CDCl_3$)

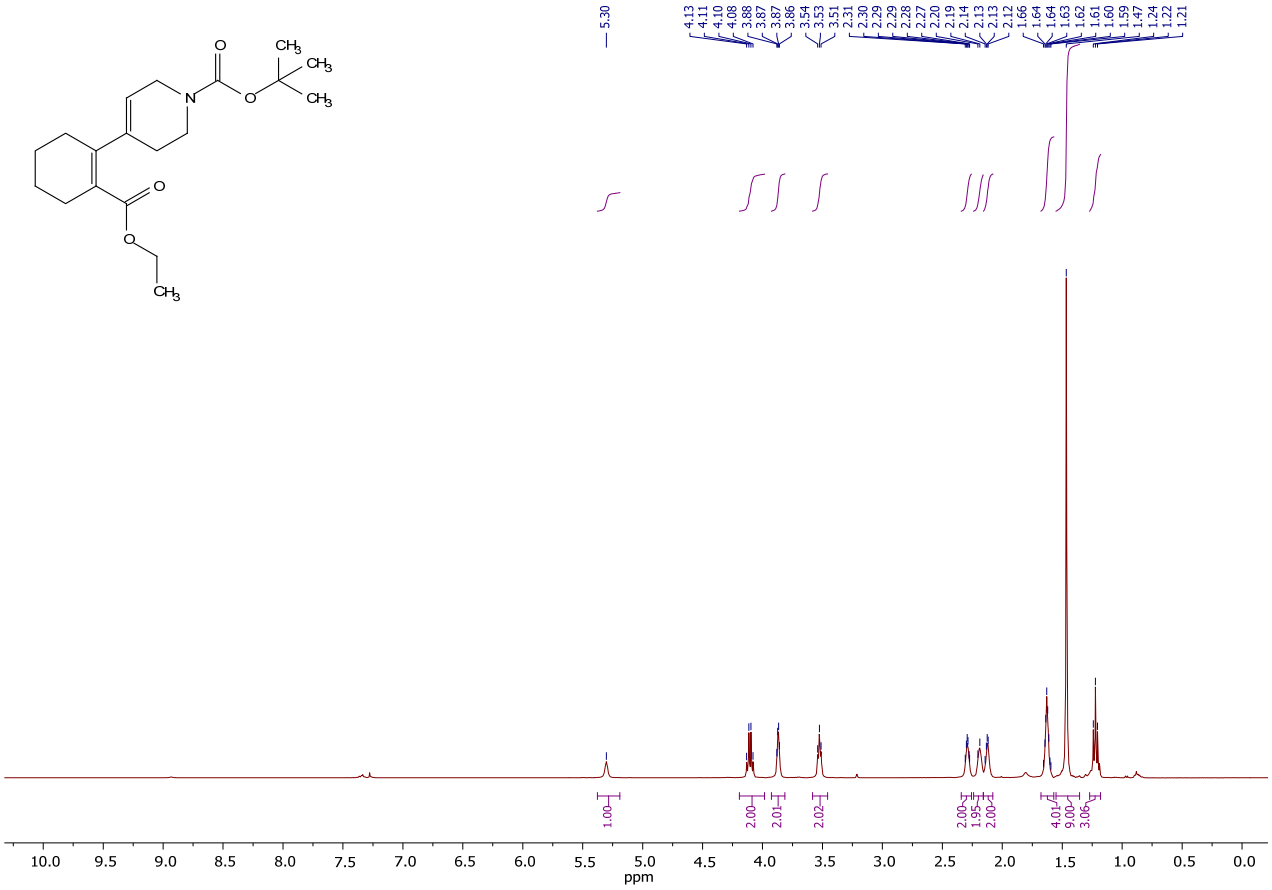


Figure S7. ^{1}H NMR of *tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohex-1-en-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate (**2**) (400 MHz, $CDCl_3$)

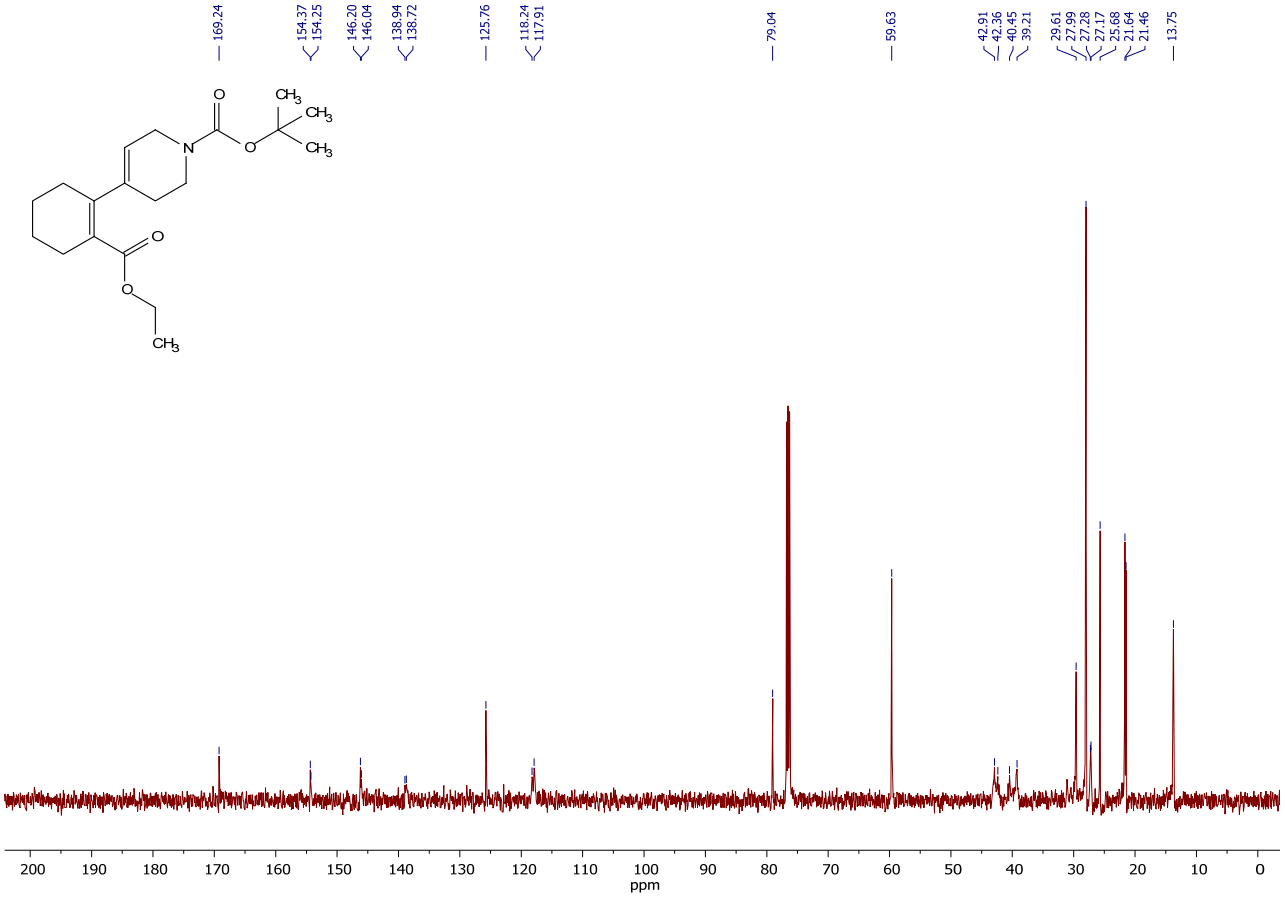


Figure S8. ^{13}C NMR of *tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohex-1-en-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate (2) (126 MHz, $CDCl_3$)

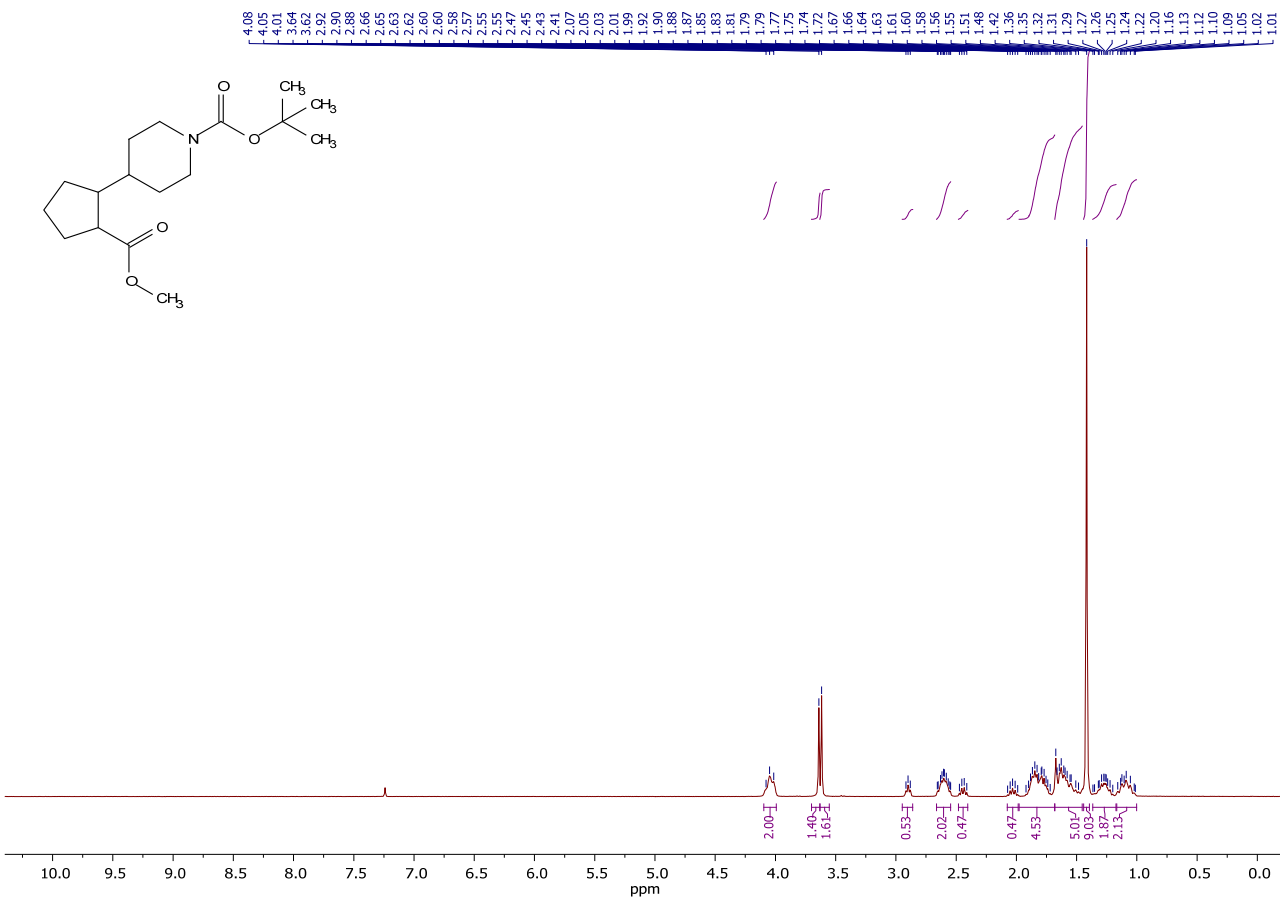


Figure S9. ^{1}H NMR of *tert*-Butyl 4-(2-(ethoxycarbonyl)cyclopentyl)piperidine-1-carboxylate (3, ca. 8:7 mixture of diastereomers) (400 MHz, $CDCl_3$)

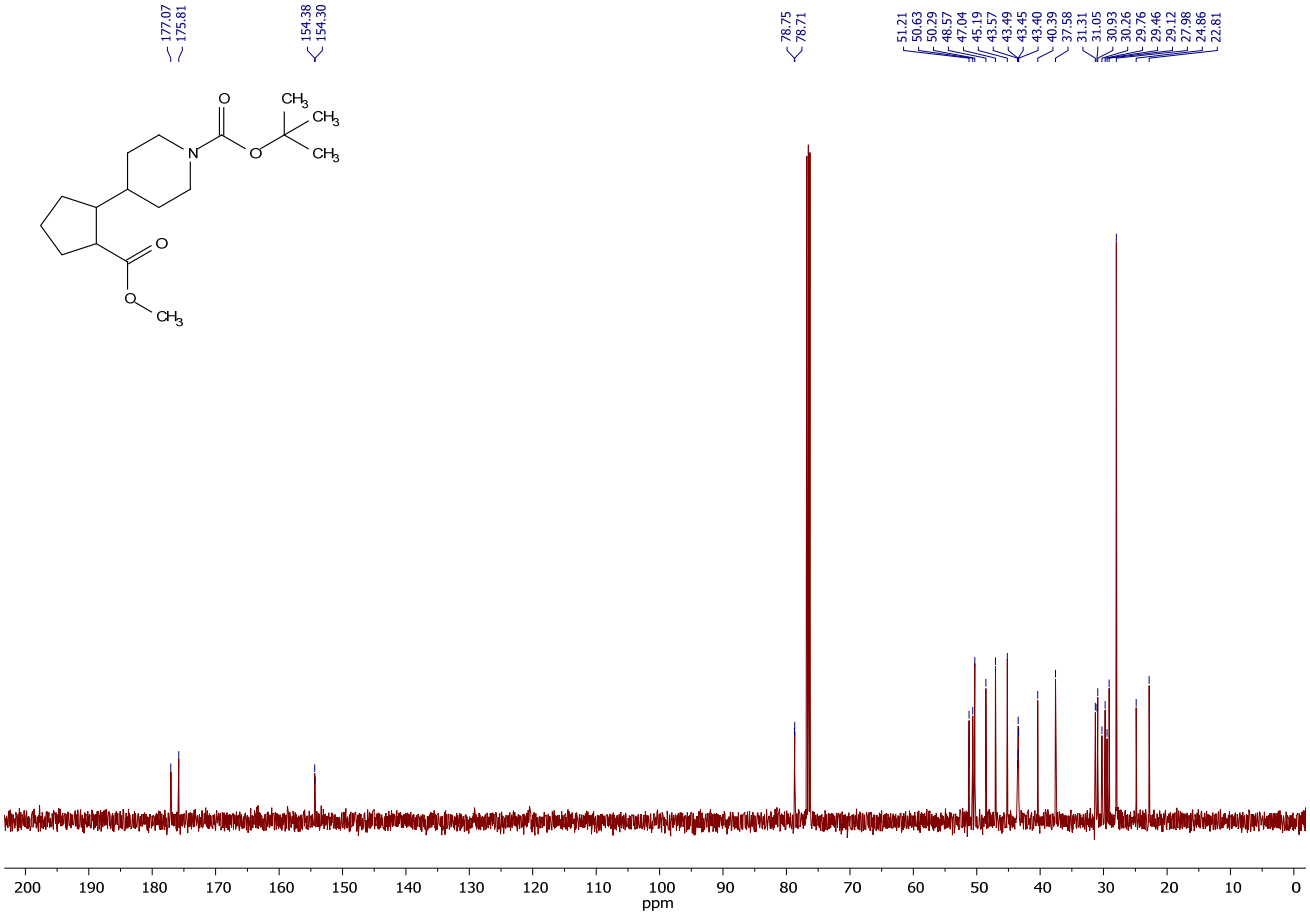


Figure S10. ^{13}C NMR of *tert*-Butyl 4-(2-(ethoxycarbonyl)cyclopentyl)piperidine-1-carboxylate (3, ca. 8:7 mixture of diastereomers) (126 MHz, $CDCl_3$)

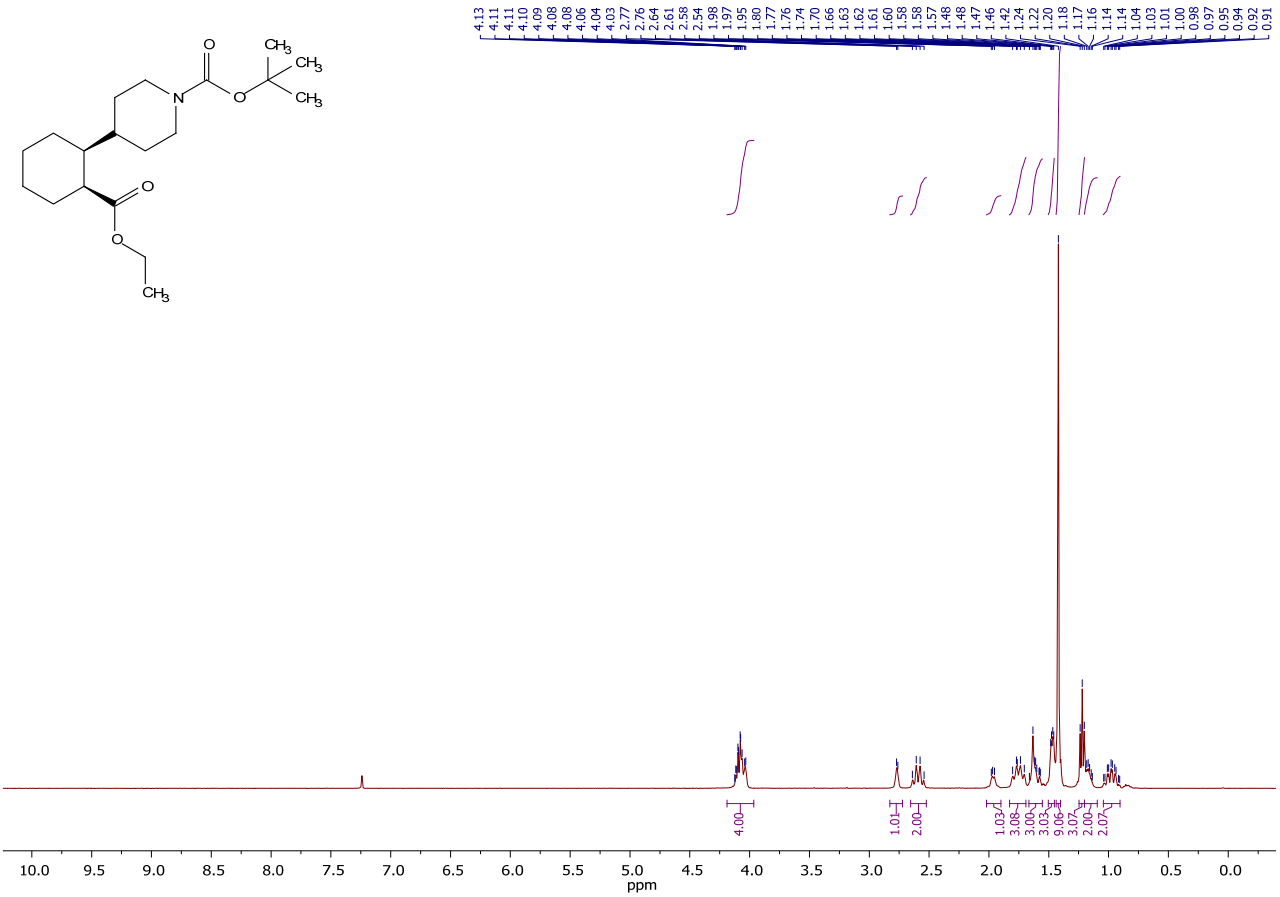


Figure S11. ^{1}H NMR of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**) (400 MHz, $CDCl_3$)

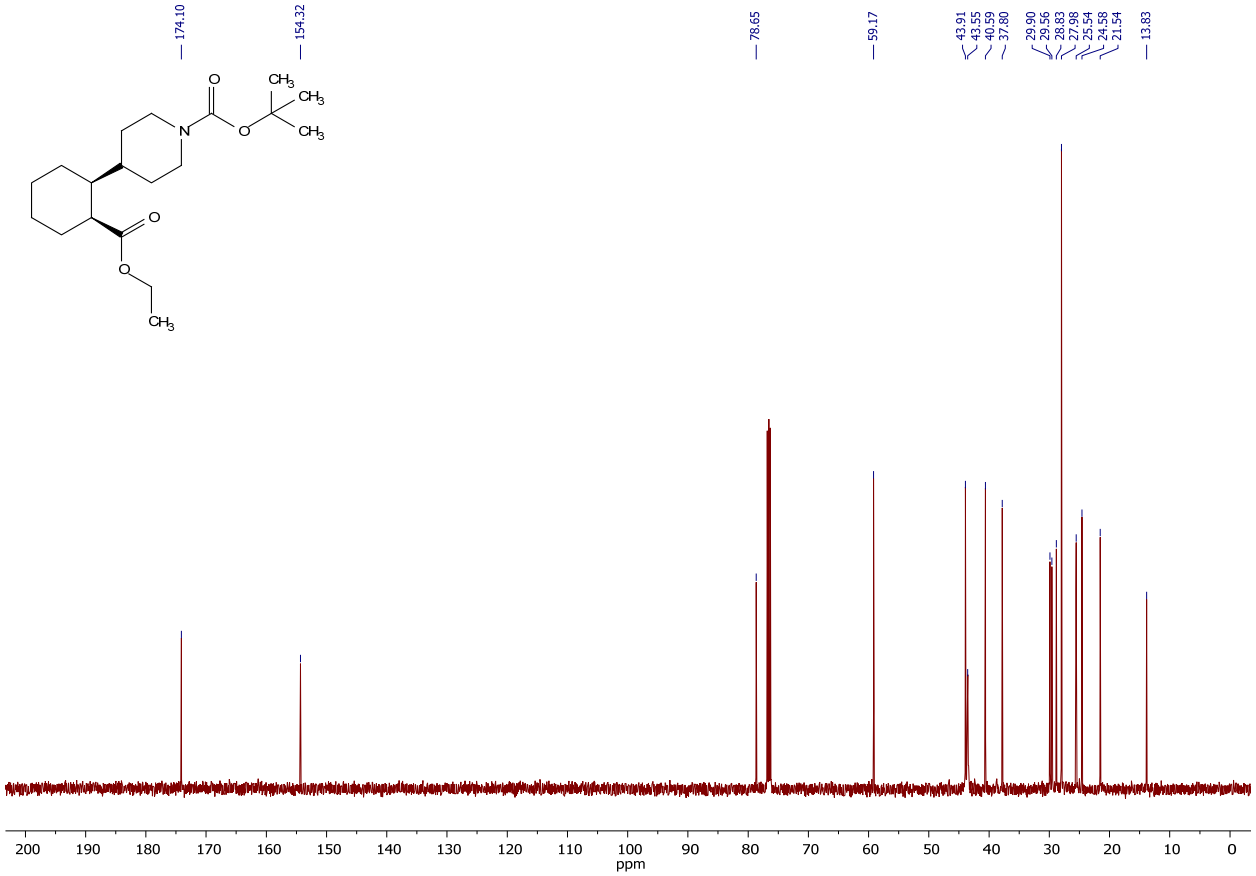


Figure S12. ^{13}C NMR of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**) (126 MHz, $CDCl_3$)

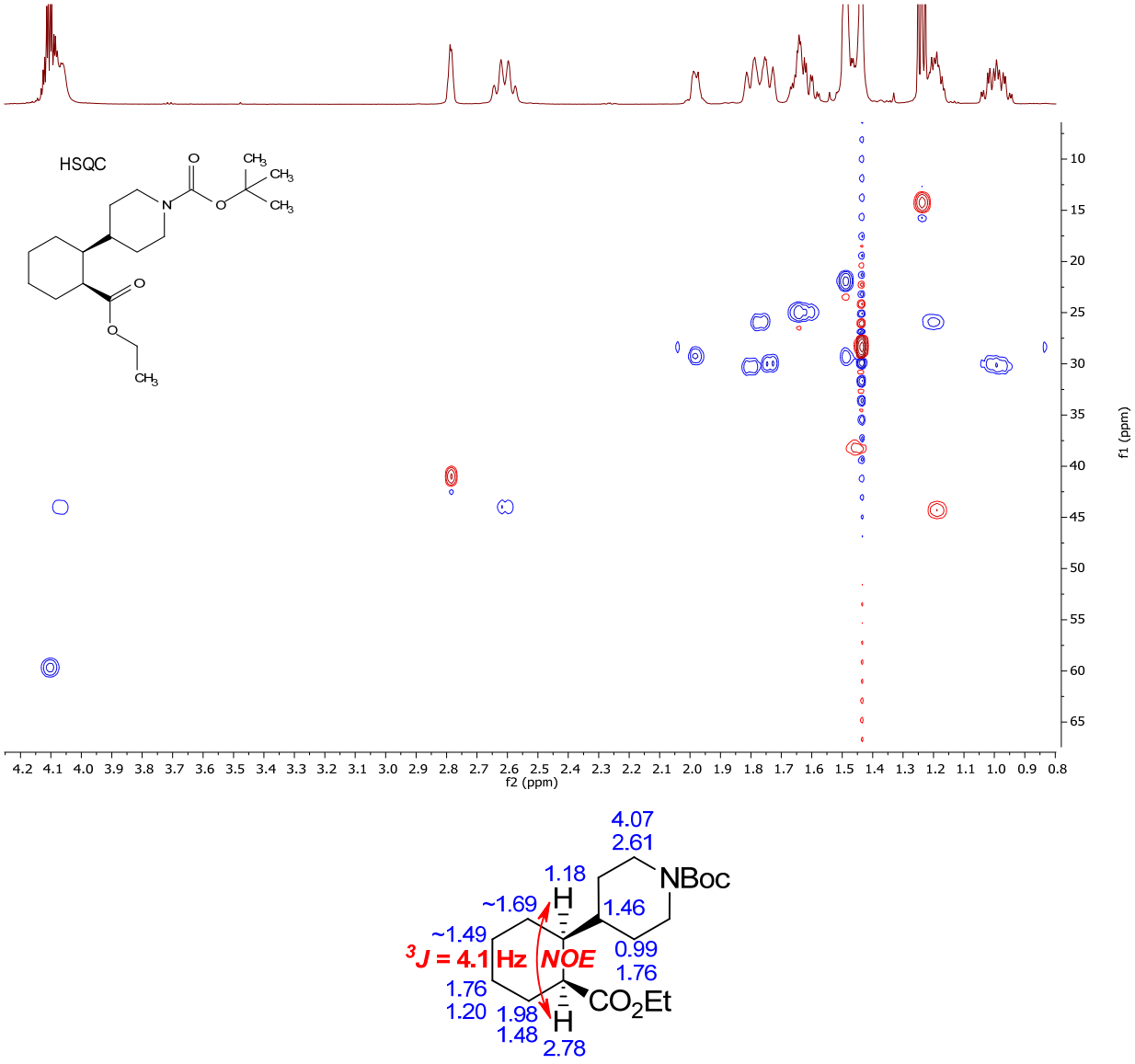


Figure S13. HSQC of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**)

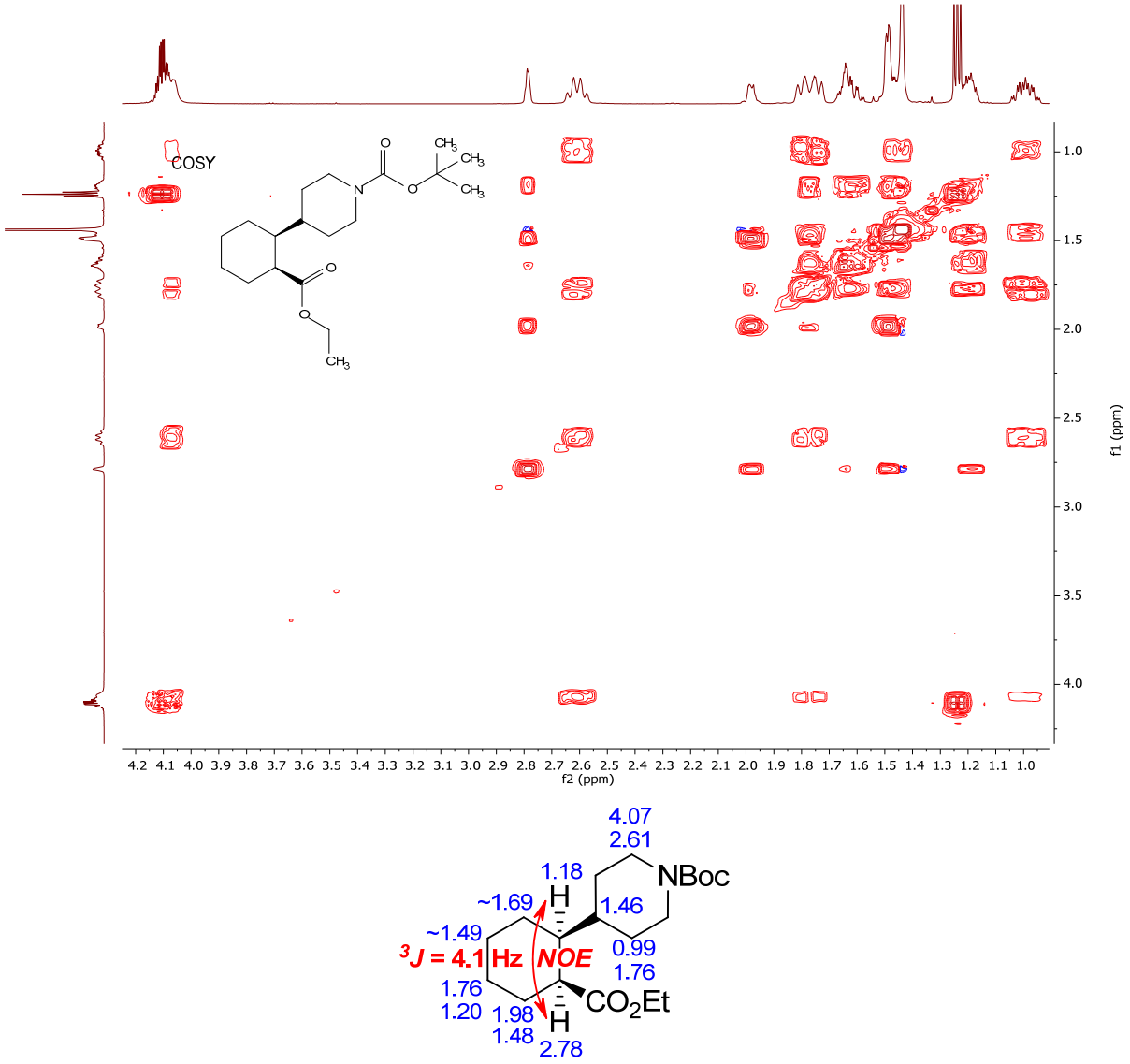


Figure S14. COSY of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**)

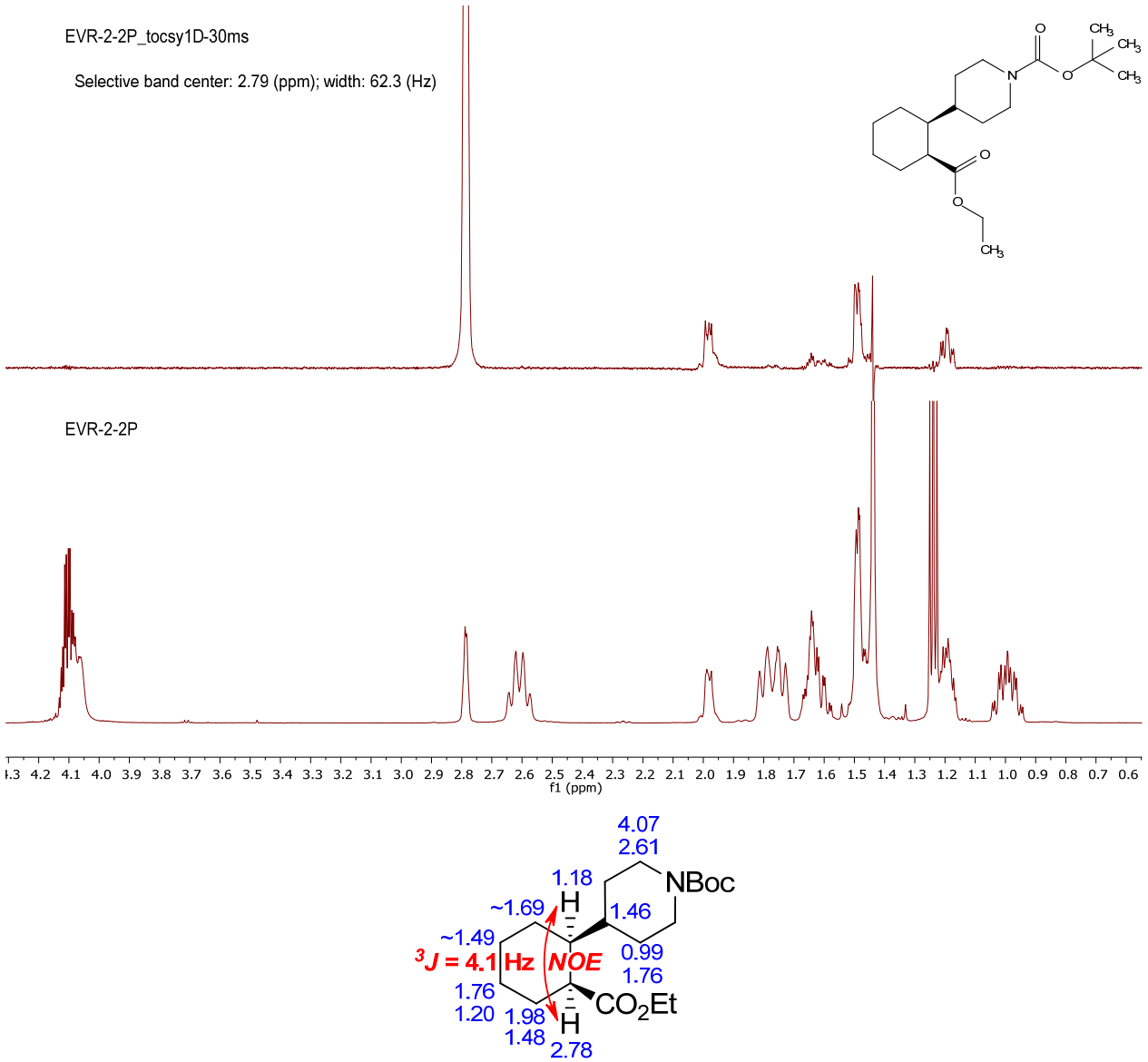


Figure S15. TOCSY of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**)

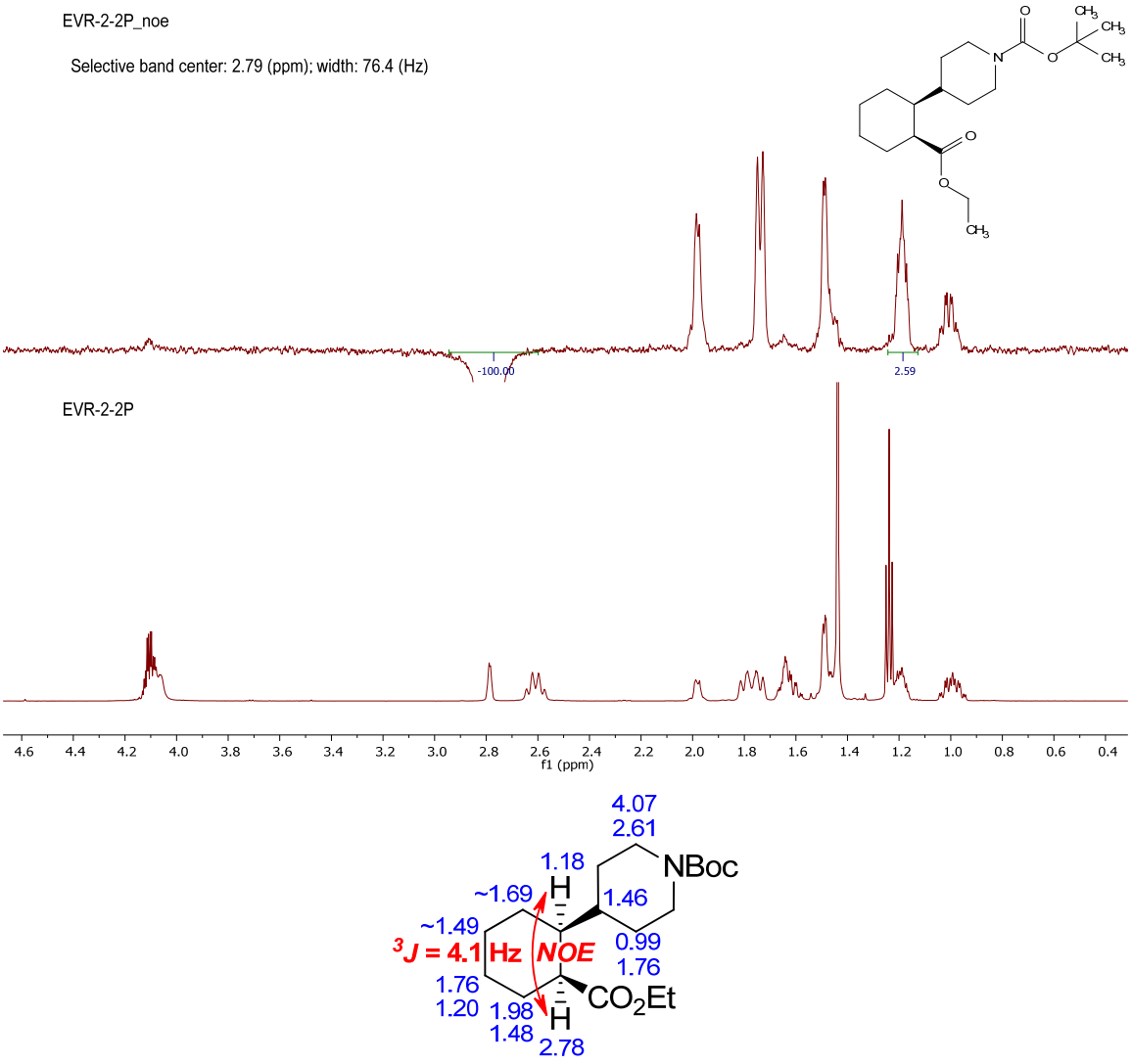


Figure S16. H–H NOE of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**)

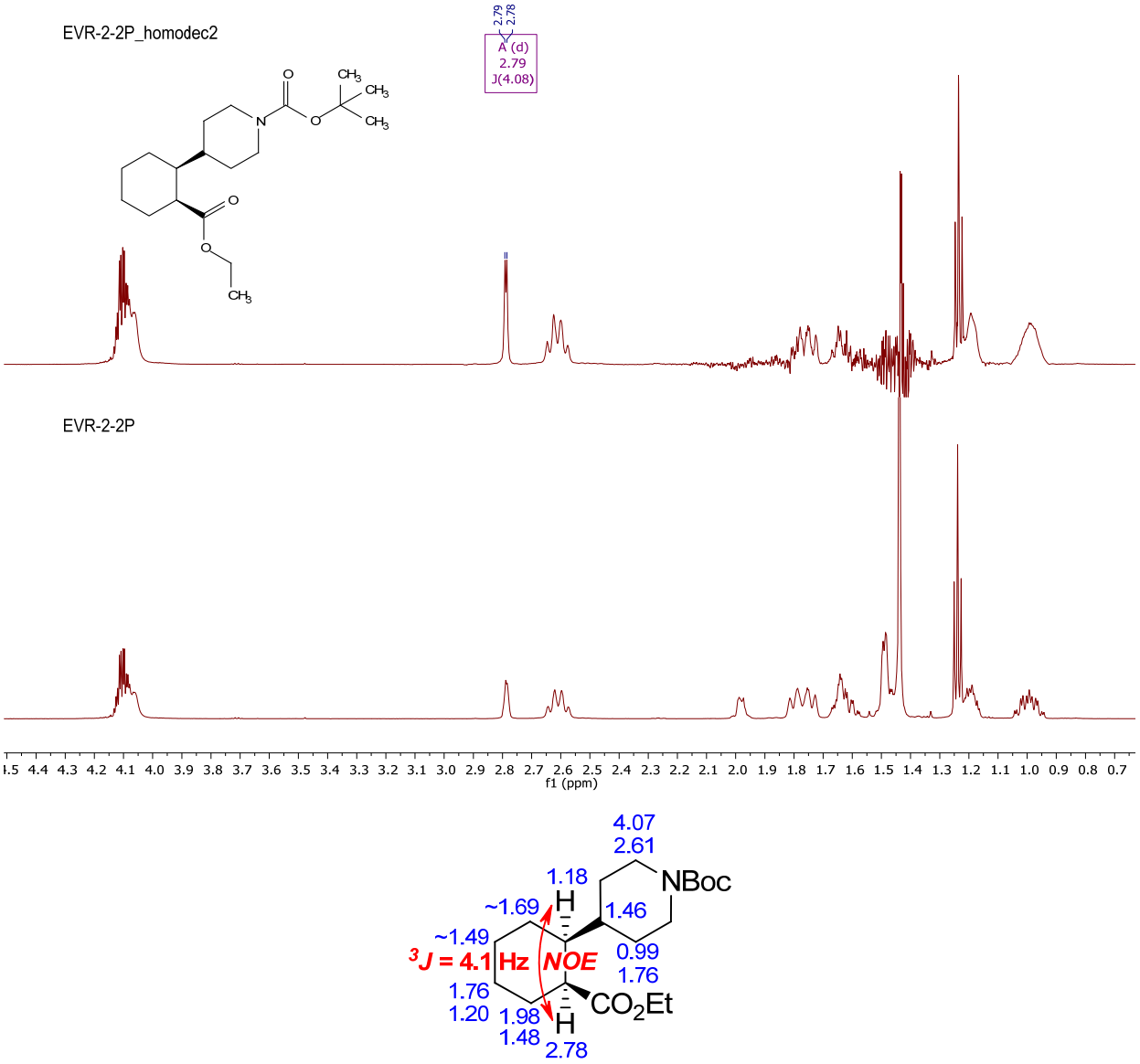


Figure S17. Homodecoupling spectra of *cis-tert*-Butyl 4-(2-(ethoxycarbonyl)cyclohexyl)piperidine-1-carboxylate (**4**)