Supporting Information

Photoremovable Chiral Auxiliary

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Experimental Section

Materials and methods

NMR spectra were recorded on a 300 MHz spectrometer in chloroform-*d*, and were calibrated to the residual peak of a solvent. Gas chromatography was performed on a chromatograph equipped with a 15-m (5% diphenyldimethylsiloxane) or 58-m (DB-XLB) column and an FID detector, or a chromatograph equipped with a 30-m (Betadex 120, 0.25 mm i.d., 0.25 μm film) column and an FID detector. Mass spectra were recorded on a GC-coupled (30-m DB-XLB column) mass spectrometer in a positive mode with EI. HRMS data were obtained on a UPLC/MS-TOF apparatus equipped with an ESI interface and a C-18 (1.7 μm, 2.1×50 mm) column, using an ammonium carbonate (0.005 M)/methanol mobile phase. High-performance liquid chromatography was performed on a chromatograph equipped with a C-18 column and a UV-Vis detector, or a chromatograph equipped with a Chiracel OD-H (150 mm, 2.1 mm i.d., cellulose tris(3,5-dimethylphenylcarbamate on 5 μm particle diameter silica) column and a UV-Vis/CD detector. UV spectra were obtained with matched 1.0-cm quartz cells. IR spectra were obtained on an FT spectrometer; KBr was used for preparation of the tablets. Optical rotation was measured on an automatic polarimeter. Elemental analyses were performed on an automatic analyzer. All preparative column chromatography procedures were performed on silica.

The reagents and solvents of the highest purity available were used as purchased or purified/dried by standard procedures when necessary. Cyclopentadiene was freshly distilled prior to use. THF, diethyl ether, and toluene were freshly distilled from sodium; all other solvents were distilled from CaH_2. All anhydrous reactions were performed under an N_2 or Ar atmosphere using oven-dried glassware.

Synthesis of the analytical standards

These compounds served as the authentic standards for determination of the absolute stereochemistry of the esters **7**.

Methyl bicyclo[2.2.1]hept-5-ene-2-carboxylates (**7**, four stereoisomers). First, a mixture of 4 stereoisomers **3m-p** (Scheme 4 of the main text; **m** and **o** are the endo isomers; **n** and **p** are the exo isomers) was prepared according to a known procedure.[1] They were then converted to the corresponding methyl esters **7m-p**.[2] The reported endo/exo isomers concentration ratio was 4:1;[1] therefore, this analytical standard served to distinguish the endo and exo pairs of enantiomers.

Cyclopentadiene (18 mL, 0.21 mol) and acrylic acid (14.7 g, 0.20 mol) were mixed at 0 ºC, and the solution was stirred for 2 days at 20 ºC. Dichloromethane (50 mL) was then added, and the mixture was washed with aq NaOH (20%, 100 mL). The aqueous layer was separated, carefully neutralized with concentrated aq HCl to pH ≈5, and extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to give **3m-p**. Yield (all isomers; a 4:1 endo/exo isomers mixture): 24.9 g (89%); colorless viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.28 (d, 0.8H, J = 8.3 Hz), 1.34–1.48 (m, 2H), 1.54 (d, 0.2H, J = 8.3 Hz), 1.86–1.98 (m, 1H), 2.21–2.28 (m, 0.2H), 2.91 (bs, 1H), 2.94–3.04 (m, 0.8H), 3.10 (bs, 0.2H), 3.23 (bs, 0.8H), 5.99 (dd, 1H, J_1 = 5.4 Hz, J_2 = 3.0 Hz), 6.08–6.16 (m, 0.4H), 6.19 (dd, 1H, J_1 = 5.3 Hz, J_2 = 3.0 Hz), 11.98 (bs, 1H, -COOH). ^{13}C NMR (75.5 MHz, $CDCl_3$): **3m**,**o**: δ (ppm) 29.2, 42.7, 43.4, 45.8, 49.8, 132.6, 137.9, 181.6; **3n**,**p**: δ (ppm) 30.4, 41.8, 43.3, 46.5, 46.8, 135.8, 138.2, 183.1. MS

(EI, *m/z*): 138 (8), 93 (2), 91 (10), 77 (6), 66 (100), 55 (4), 39 (10), 32 (15). These compounds were also characterized before.[1]

In the next step, a solution of **3m-p** (2.5 g, 18.1 mmol) and *p*-toluenesulfonic acid (50 mg, 0.2 mmol) in methanol (25 mL) was refluxed for 20 h. The reaction mixture was then cooled to 20 ºC, poured into cold water (75 mL), and extracted with hexane (3 × 20 mL). The organic extracts were washed with cold water (2 × 20 mL), saturated aq $NaHCO_3$ (20 mL), and brine (20 mL). The hexane extracts were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was distilled to give pure **7m-p** (as a 4:1 endo/exo mixture). Yield 2.6 g (95%); colorless viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.28 (d, 1H, J = 8.3 Hz), 1.38–1.46 (m, 2.4H), 1.53 (d, 0.2H, J = 8.3 Hz), 1.86–1.96 (m, 1.2H), 2.23 (dd, 0.2H, J_1 = 10.2 Hz, J_2 = 4.0 Hz), 2.88–2.99 (m, 2.2H), 3.04 (bs, 0.2H), 3.20 (bs, 1H), 3.62 (s, 3H), 3.69 (s, 0.6H), 5.93 (dd, 1H, J_1 = 5.6 Hz, J_2 = 2.6 Hz), 6.08–6.16 (m, 0.4H), 6.19 (dd, 1H, J_1 = 5.6 Hz, J_2 = 2.9 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 29.5, 30.5, 41.8, 42.7, 43.2, 43.4, 45.9, 46.6, 46.8, 49.8, 51.6, 51.8, 132.6, 135.9, 137.9, 138.2, 175.4 (carboxylate C_q of the minor stereoisomer was not observed). MS (EI, *m/z*): 152 (10), 121 (10), 93 (8), 91 (12), 87 (11), 77 (7), 66 (100), 55 (13), 51 (3), 39 (10). These compounds were also characterized before.[1]

Methyl (1*S*, 2*S*, 4*S*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (7m). This enantiopure compound was synthesized according to Poll, Chang and their coworkers.[3,4] Triethylamine (4.2 mL, 30 mmol) was added dropwise to a solution of (*R*)-pantolactone (2.6 g, 20 mmol) in dry dichloromethane (25 mL) at –24 ºC. Acryloyl chloride (2.0 mL, 25 mmol) was then added dropwise over 30 min and the reaction mixture was vigorously stirred overnight while a white precipitate appeared. Aq HCl (1 M, 14 mL) was added, and the resulting solution was washed with saturated aq $NaHCO_3$ (25 mL), water (2 × 25 ml) and brine (25 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to give a viscous oil ((*R*)-4,4-dimethyl-2-oxo-tetrahydrofuran-3-yl acrylate). Yield: 3.44 g (94%); slightly yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.11 (s, 3H), 1.20 (s, 3H), 4.04 (s, 2H), 5.41 (s, 1H), 5.95 (dd, 1H, J_1 = 10.4 Hz, J_2 = 1.3 Hz), 6.20 (ddd, 1H, J_1 = 17.3 Hz, J_2 = 10.4 Hz, J_3 = 1.4 Hz), 6.50 (dd, 1H, J_1 = 17.3 Hz, J_2 = 1.4 Hz) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 20.0, 23.1, 40.5, 75.3, 76.4, 127.2, 132.9, 164.9, 172.4.

This crude compound (3.44 g, 18.7 mmol) was dissolved in dry dichloromethane (30 mL) and petroleum ether (4.5 mL), and the solution was purged with argon for 10 min and cooled to –10 °C. $TiCl_4$ (1 M solution in toluene, 1.9 mL, 1.9 mmol) was then added dropwise under stirring and the mixture turned dark red. After 45 min, cyclopentadiene (1.9 mL, 22.6 mmol) was added dropwise in 20 min, and the reaction mixture was stirred for 1 h. Na_2CO_3 (0.8 g) and water (1.35 mL) were then added, and the mixture was stirred for 30 min, filtered, and concentrated under reduced pressure to obtain crude (*R*)-4,4-dimethyl-2-oxo-tetrahydrofuran-3-yl bicyclo[2.2.1]hept-5-ene-2-carboxylate. Yield: 4.62 g (98%); yellow crystals. The crude product was purified by recrystallization from *n*-hexane/ethyl acetate (5:3).

A solution of this compound (0.57 g, 2.3 mmol) and $LiOH·H_2O$ (0.40 g, 9.6 mmol) in a THF/water (18 mL, 5:4, v/v) mixture was vigorously stirred at 20 ºC for 48 h. THF was then removed under reduced pressure and the aqueous phase was acidified using aq HCl (1 M) and extracted with an *n*-pentane/dichloromethane (3 × 25 mL, 98:2, v/v) mixture. The collected organic layers were dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure to obtain a viscous oil, the crude product **3m**. Yield 0.29 g (97%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.24 (d, 1H, J = 8.2 Hz), 1.31–1.44 (m, 2H), 1.81–1.92 (m, 1H), 2.86 (bs, 1H), 2.89–2.98 (m, 1H), 3.18 (bs, 1H), 5.94 (dd, 1H, J_1 = 5.3 Hz, J_2 = 2.4 Hz), 6.14 (dd, 1H, J_1 = 5.2 Hz, J_2 = 2.9 Hz), 11.97 (bs, 1H, –COOH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 29.2, 42.6, 43.3, 45.7, 49.7, 132.5, 137.8, 180.0. $[\alpha]^{25}_D$ = –133 (c = 0.21 M,

EtOH) ($[\alpha]^{25}_D$ = –144.53 (*c* = 1.5 M, 90.5% EtOH),[4] $[\alpha]^{25}_D$ = –146.9 (*c* = 3.0 M, 95% EtOH),[3] ($[\alpha]^{25}_D$ = –139 (*c* = 1.38 M, EtOH).[5]

3m was then converted to **7m** according to the same procedure as described previously. **7m**; yield: 80%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.24 (d, 1H, J = 7.9 Hz), 1.35–1.43 (m, 2H), 1.83–1.93 (m, 1H), 2.89 (bs, 1H), 2.88–2.95 (m, 1H), 3.16 (bs, 1H), 3.59 (s, 3H), 5.89 (dd, 1H, J_1 = 5.5 Hz, J_2 = 2.9 Hz), 6.15 (dd, 1H, J_1 = 5.5 Hz, J_2 = 2.9 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 29.4, 42.6, 43.3, 45.8, 49.7, 51.5, 132.5, 137.8, 175.3. MS (EI, *m/z*): 152 (10), 121 (10), 93 (8), 91 (12), 87 (11), 77 (7), 66 (100), 55 (13), 51 (3), 39 (10).

Methyl (1*S*, 2*R*, 4*S*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (7n). This compound was prepared according to Byun and coworkers.[6] A mixture of methyl (1*S*, 2*S*, 4*S*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (**7n**, 163 mg, 1.1 mmol) and DBU (230 µL, 1.5 mmol) in DMF (3 mL) was stirred at 80 °C for 8 days and cooled to 20 ºC. Water (20 mL) was then added, and the resulting solution was neutralized with aq HCl (1 M) and extracted with diethyl ether (3 × 20 mL). The organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Only 3 and 9% conversion of **7m** into **7n** was observed after 16 and 192 h, respectively, contrary to the original work (reporting a 25% conversion after 8 h[6]). The prepared mixture of **7m** / **7n** (91:9) was used to determine the absolute configuration of the remaining isomers of **7**.

Solvolysis of (*S*)-benzoin norbornenates 2a, b

A mixture of a Diels-Alder adduct (**2a** or **b**, 50 mg, 0.15 mmol) and K_2CO_3 (21 mg, 0.15 mmol) in a mixture of MeOH (15 mL) and H_2O (15 mL) was stirred at 0 °C for 3 h. Water (50 mL) was then added, and the reaction mixture was extracted with ethyl acetate (2 × 20 mL). The organic layers were washed with brine (2 × 20 mL), dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure to give a residue that was purified by column chromatography (1:4 diethyl ether/petroleum ether) to give an enantiopure (HPLC) benzoin derivative **5**.

Calculation methods

Conformations of (*S*)-**1b** were generated with a CICADA program[7] using molecular mechanics and the MM3 force field.[8,9] Obtained local minima were re-optimized using a semi-empirical method AM1 implemented in the MOPAC2009 software.[10] 29 of the resulting conformations were then fully optimized using the B3LYP level of theory with the LANL2DZ basis set implemented in the Gaussian 03 program.[10] The frequencies of all points were calculated to confirm the real minima and the zero-point vibration energies (ZPVE) of all stationary points.

The modeled complexes of (*S*)-**1b** with $SnCl_4$ were optimized using a semi-empirical AM1 method implemented in the MOPAC2009 software, followed by a full optimization using the B3LYP/LANL2DZ method.[11] This method and the basis set were selected as the best compromise between time demand and calculation accuracy. The same method has been tested before, for example, to study the interactions between tin tetrachloride and phosphoryl ligands.[12] Localization of the frontier molecular orbitals and the interaction energies between $SnCl_4$ and (*S*)-**1b** were analyzed.

The transition states for 4 different attack orientations of cyclopentadiene toward the double bond of (*S*)-**1b** were localized using a TRITON[13] and DRIVER[14] software using the semi-empirical AM1 level. A differently oriented cyclopentadiene molecule was placed at a distance of 3.5 Å from the carbons atoms of the double bond. This distance was decreased

using a 0.05 Å step until a new bond was formed at a distance of 1.4 Å. The DFT B3LYP/LANL2DZ transition state was then optimized. Frequency analysis for the transition states was also performed. Only one imaginary frequency that corresponds to the new C–C bond formation between cyclopentadiene and (*S*)-**1b** was identified. The energy barriers calculated for all 4 possible transition states, including the ZPVE energy, were used to determine the rate constants and, subsequently, the diastereomeric and enantiomeric excesses. Localization of the frontier molecular orbitals and the interaction energies between tin tetrachloride and (*S*)-**1b** were analyzed.

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Figure S1. ^{1}H NMR ($CDCl_3$, 300 MHz): (*S*)-2-Hydroxy-1-(2-methoxyphenyl)-2-phenylethanone (**5b**)

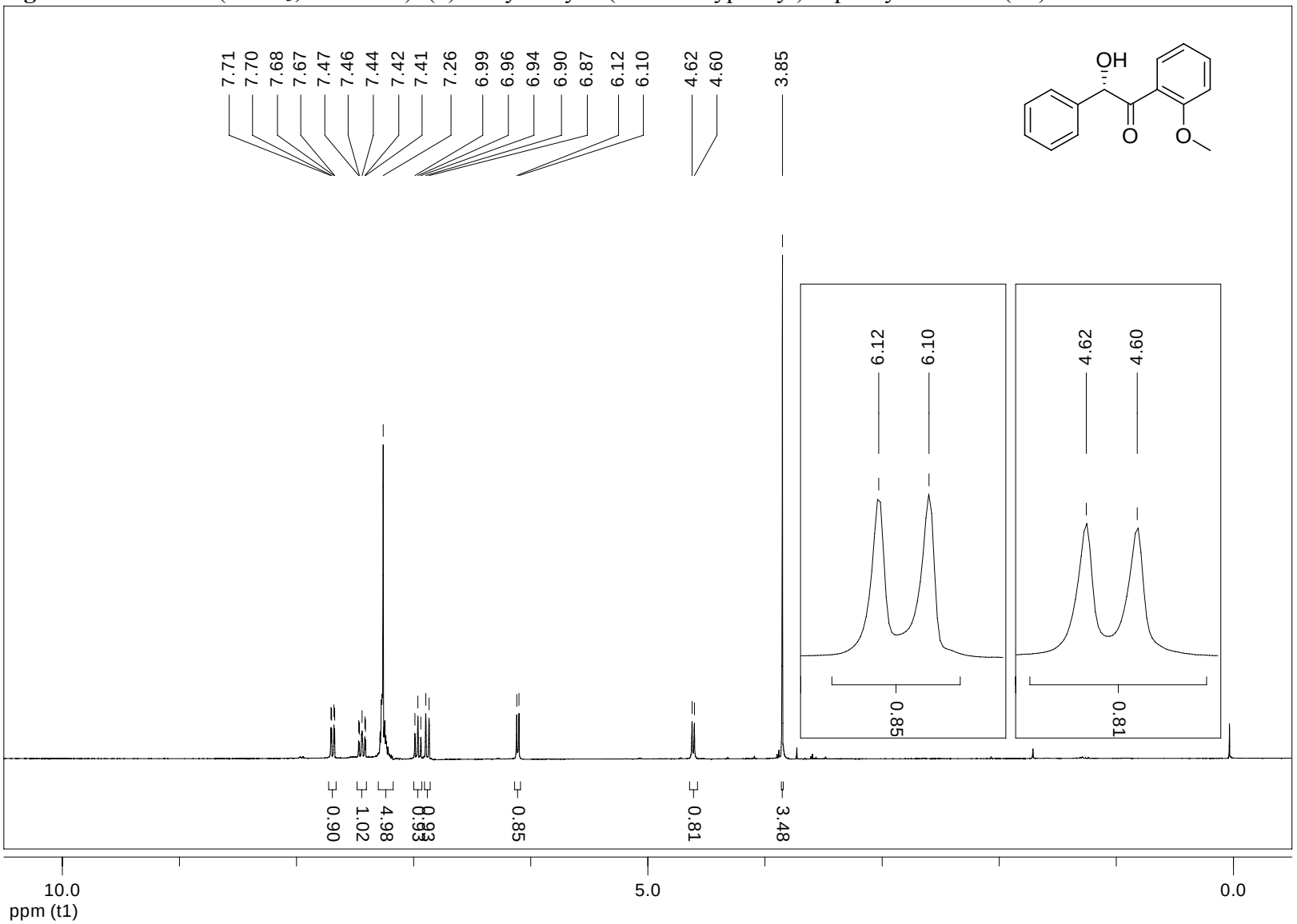

Figure S2. ^{13}C NMR ($CDCl_3$, 75.5 MHz): (*S*)-2-Hydroxy-1-(2-methoxyphenyl)-2-phenylethanone (**5b**)

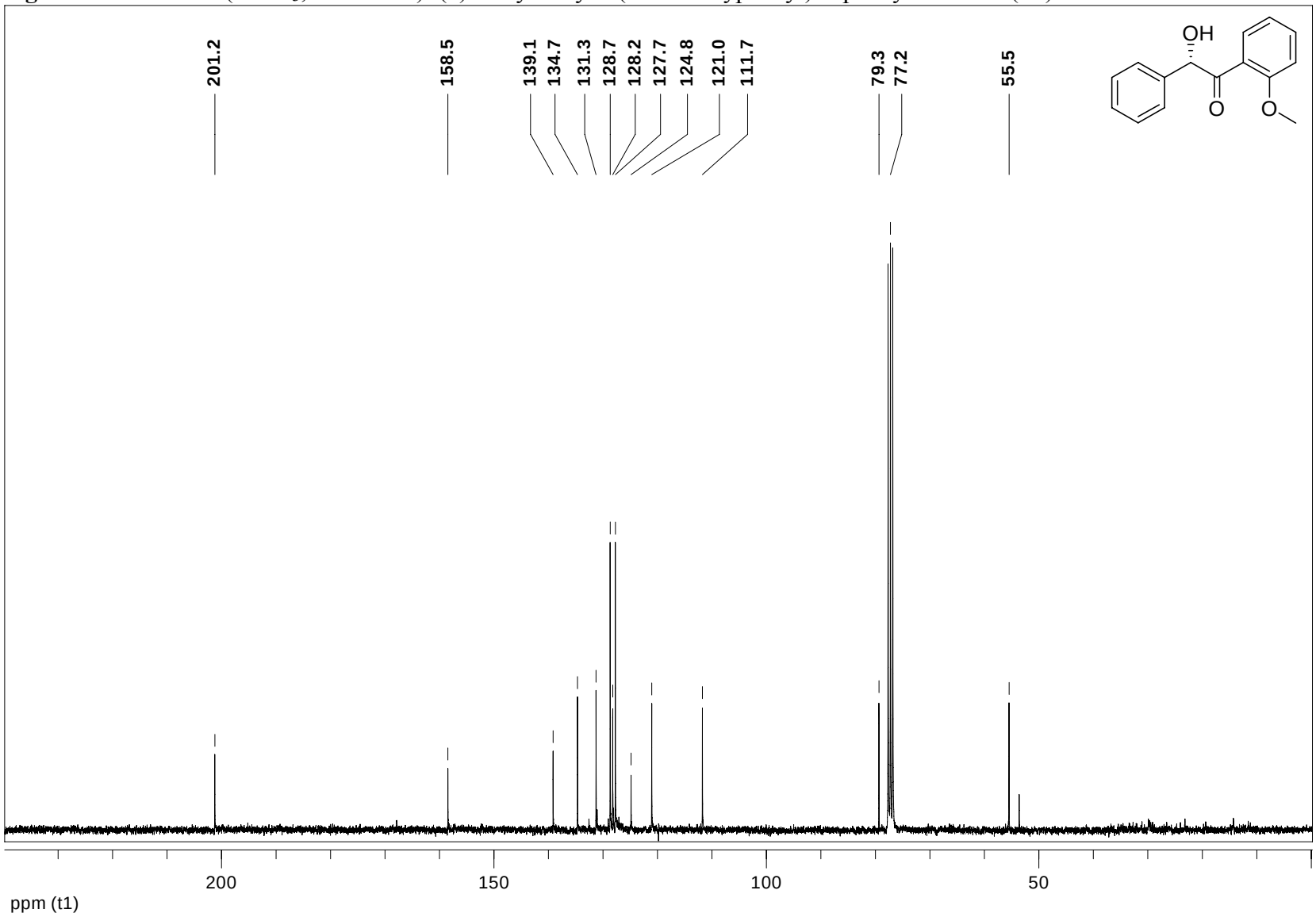

Figure S3. ^{1}H NMR ($CDCl_3$, 300 MHz): (*S*)-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl acrylate (**1b**)

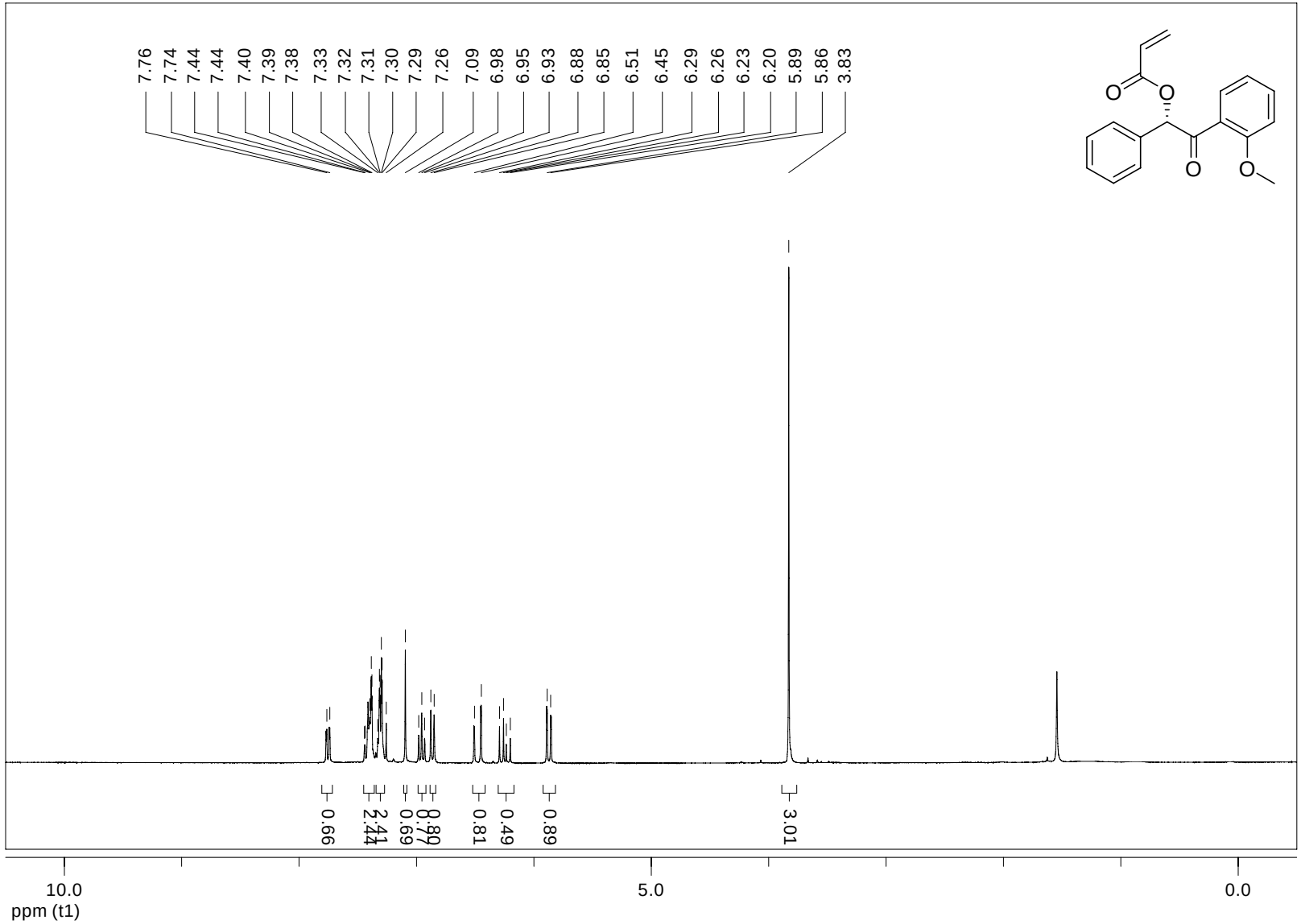

Figure S4. ^{13}C APT NMR ($CDCl_3$, 75.5 MHz): (*S*)-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl acrylate (**1b**)

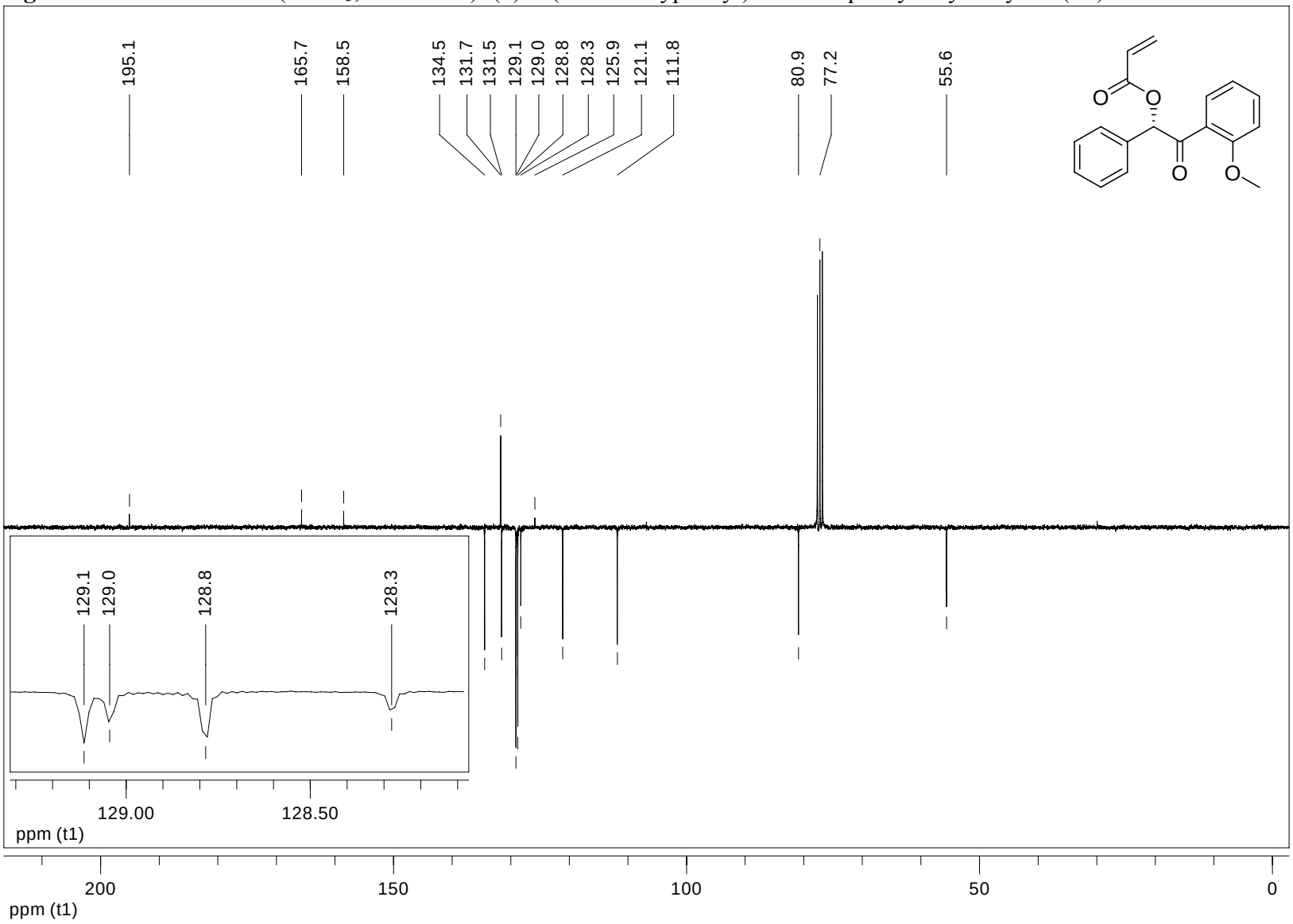

Figure S5. ^{1}H NMR ($CDCl_3$, 300 MHz): *(S)*-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl acetate (**6b**)

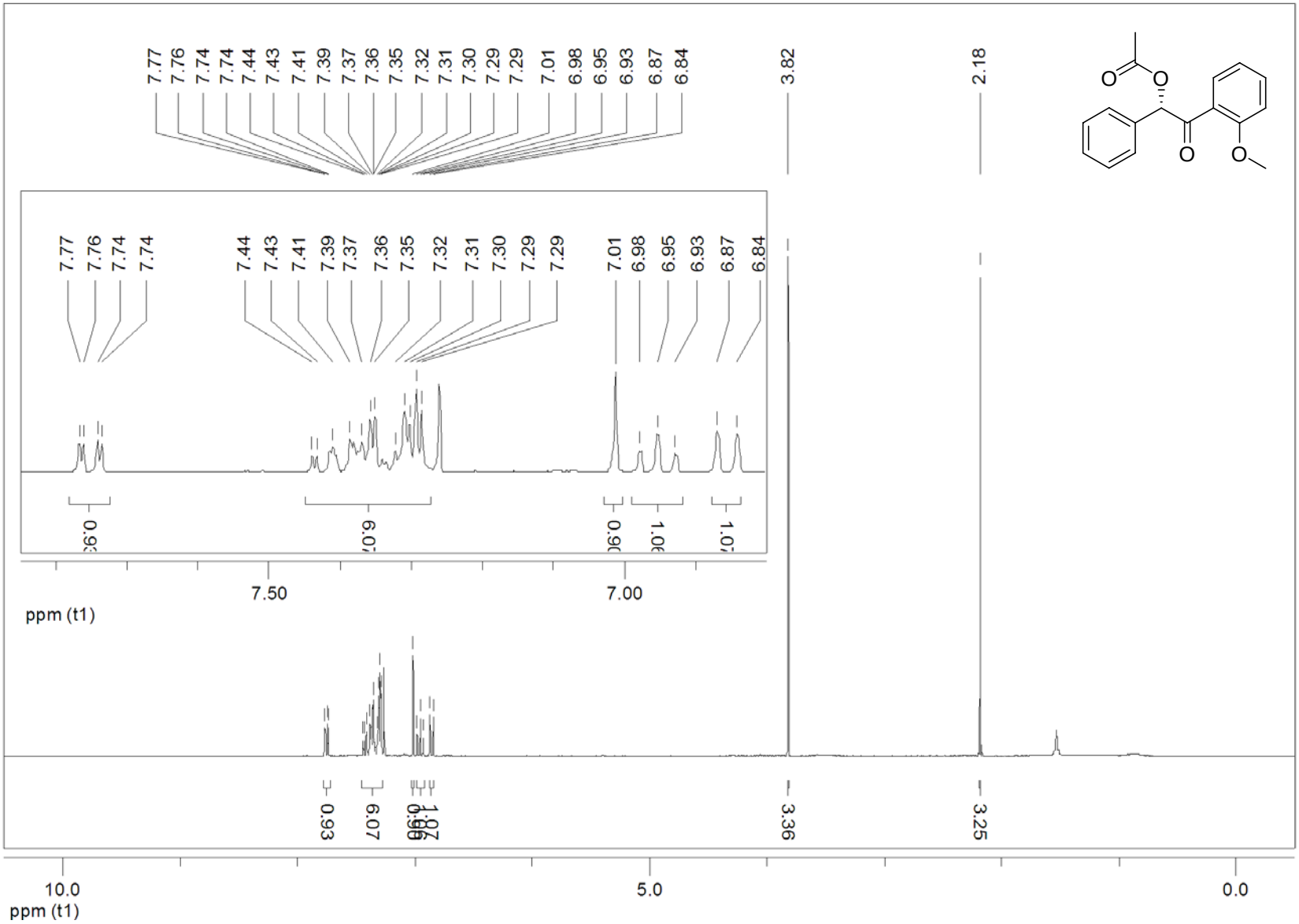

Figure S6. ^{13}C APT NMR ($CDCl_3$, 75.5 MHz): *(S)*-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl acetate (**6b**)

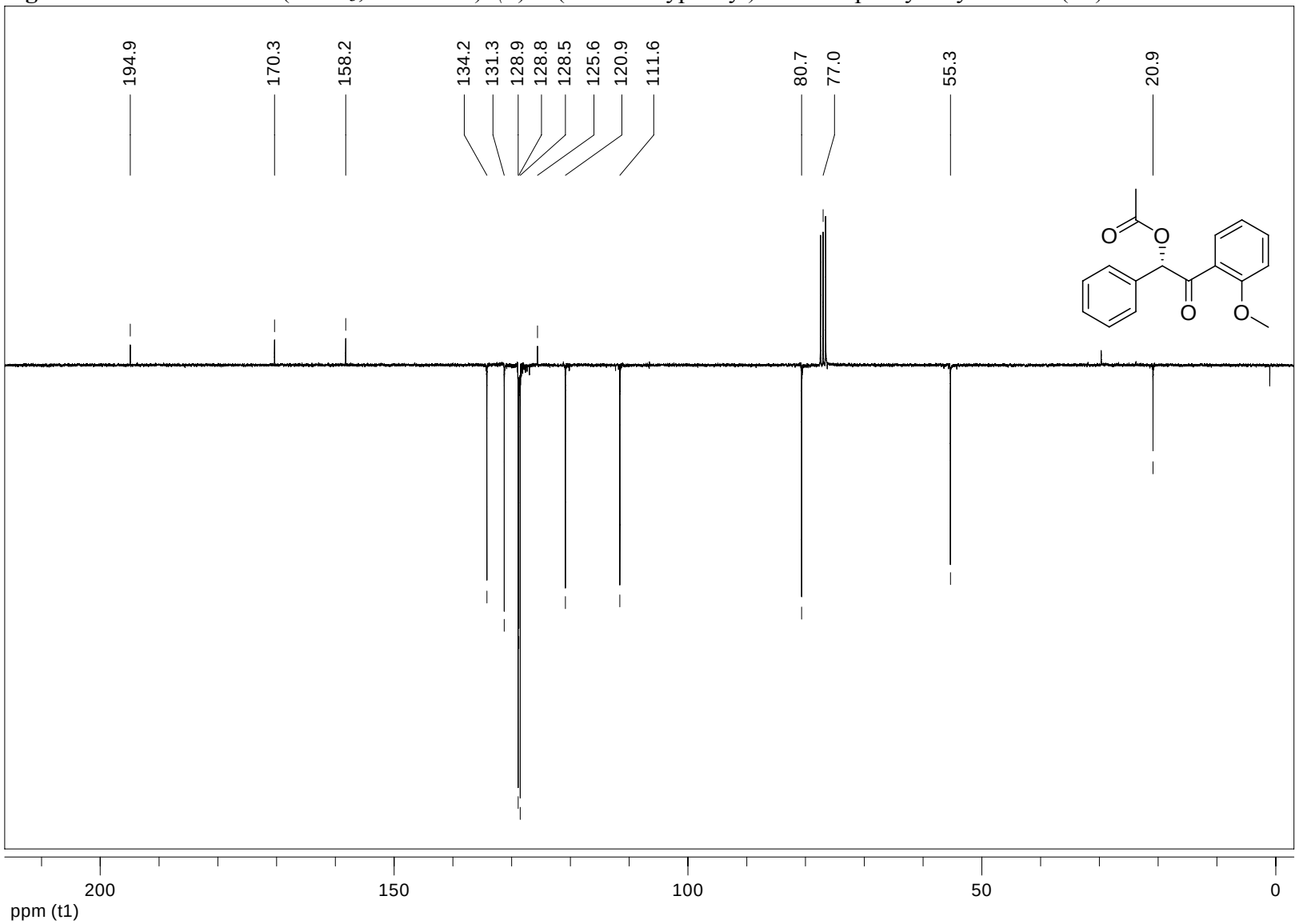

Figure S7. UV-Vis (CH_3OH): 2-Oxo-1,2-diphenylethyl acetate (**6a**) and *(S)*-2-(2-methoxyphenyl)-2-oxo-1-phenylethyl acetate (**6b**)

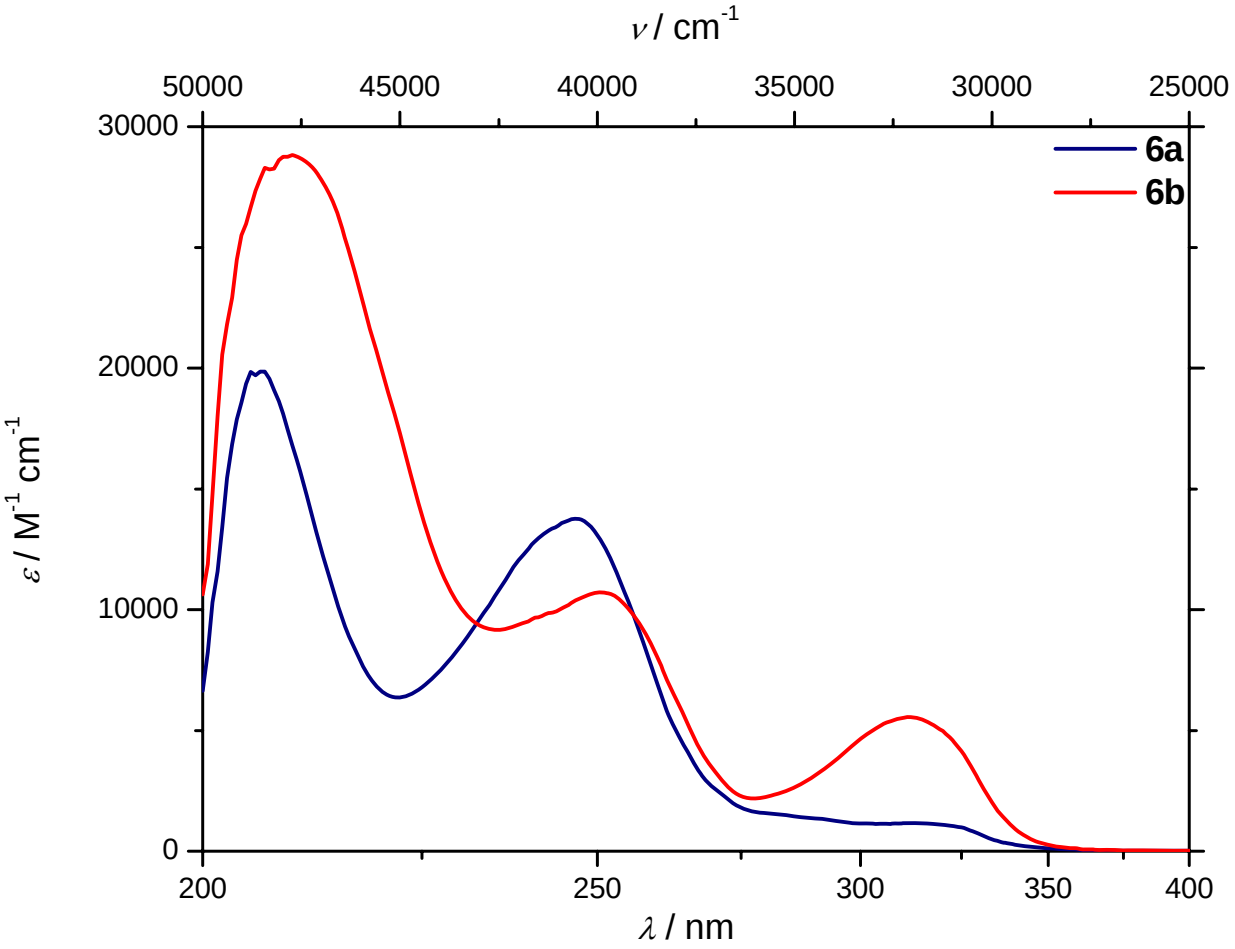

Figure S8. ^{1}H NMR ($CDCl_3$, 300 MHz): (*S*)-2-Oxo-1,2-diphenylethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**2a**)

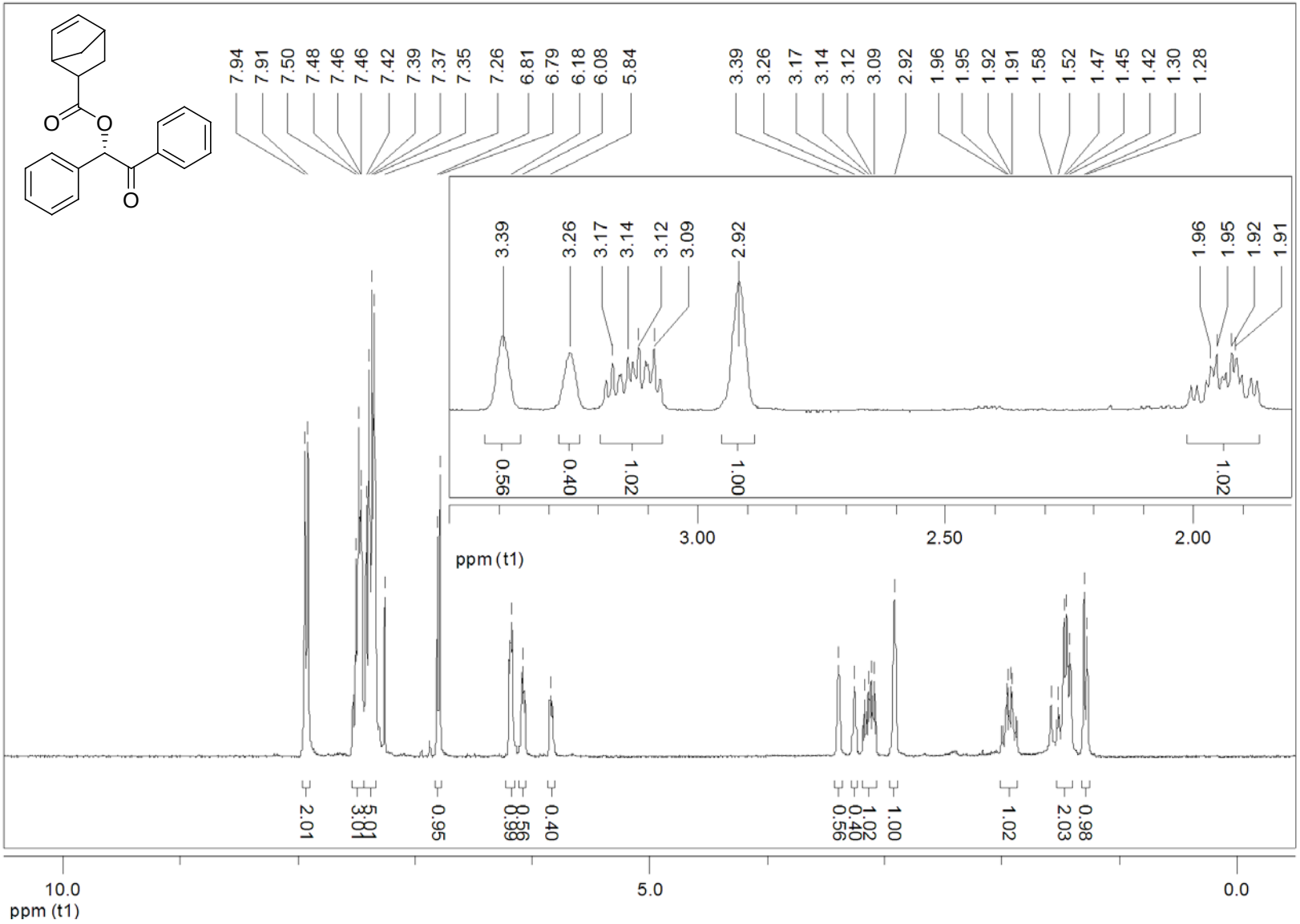

Figure S9. ^{13}C APT NMR ($CDCl_3$, 75.5 MHz): (*S*)-2-Oxo-1,2-diphenylethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**2a**)

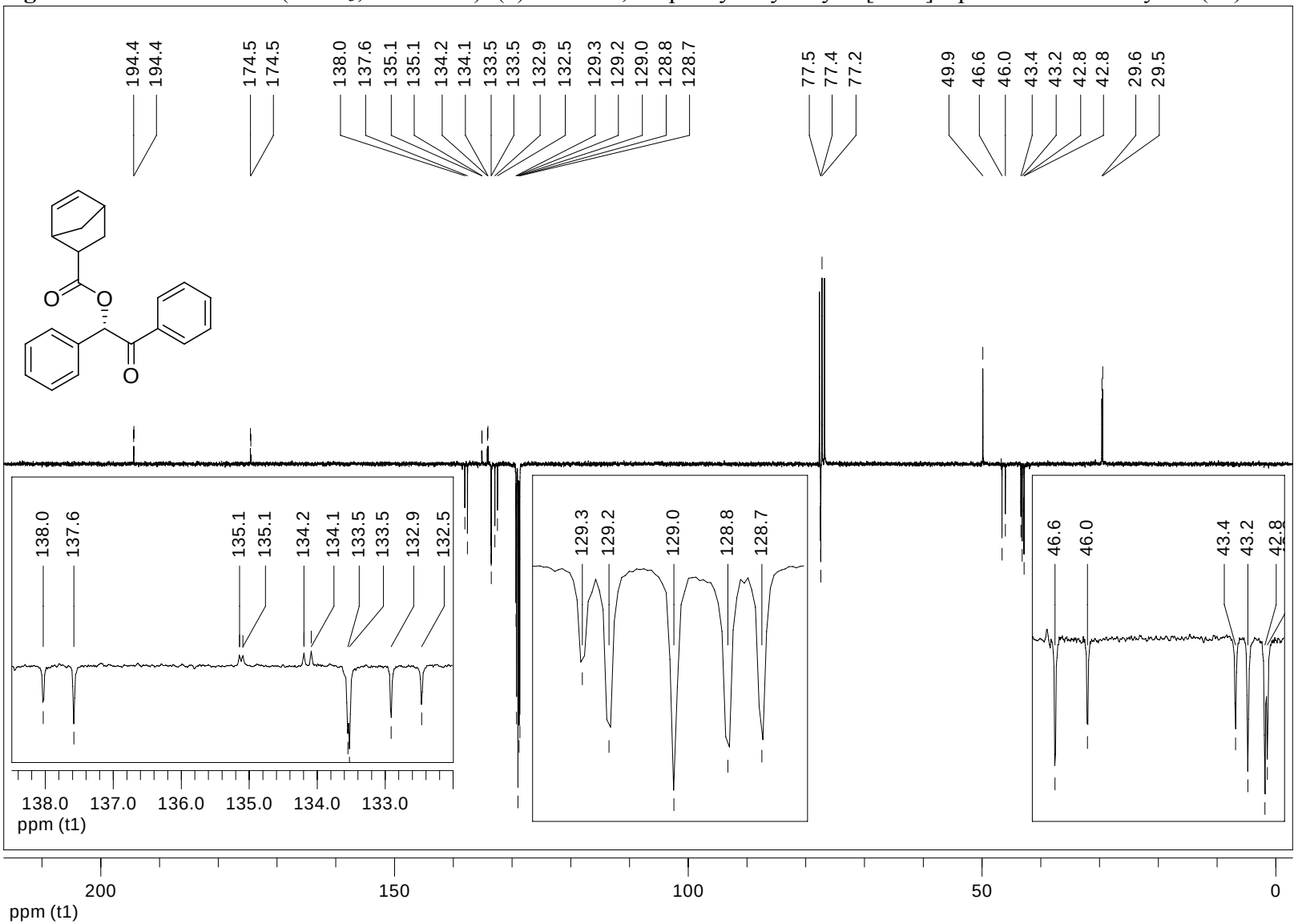

Figure S10. ^{1}H NMR ($CDCl_3$, 300 MHz): 2-(2-Methoxyphenyl)-2-oxo-1-phenylethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**2b**)

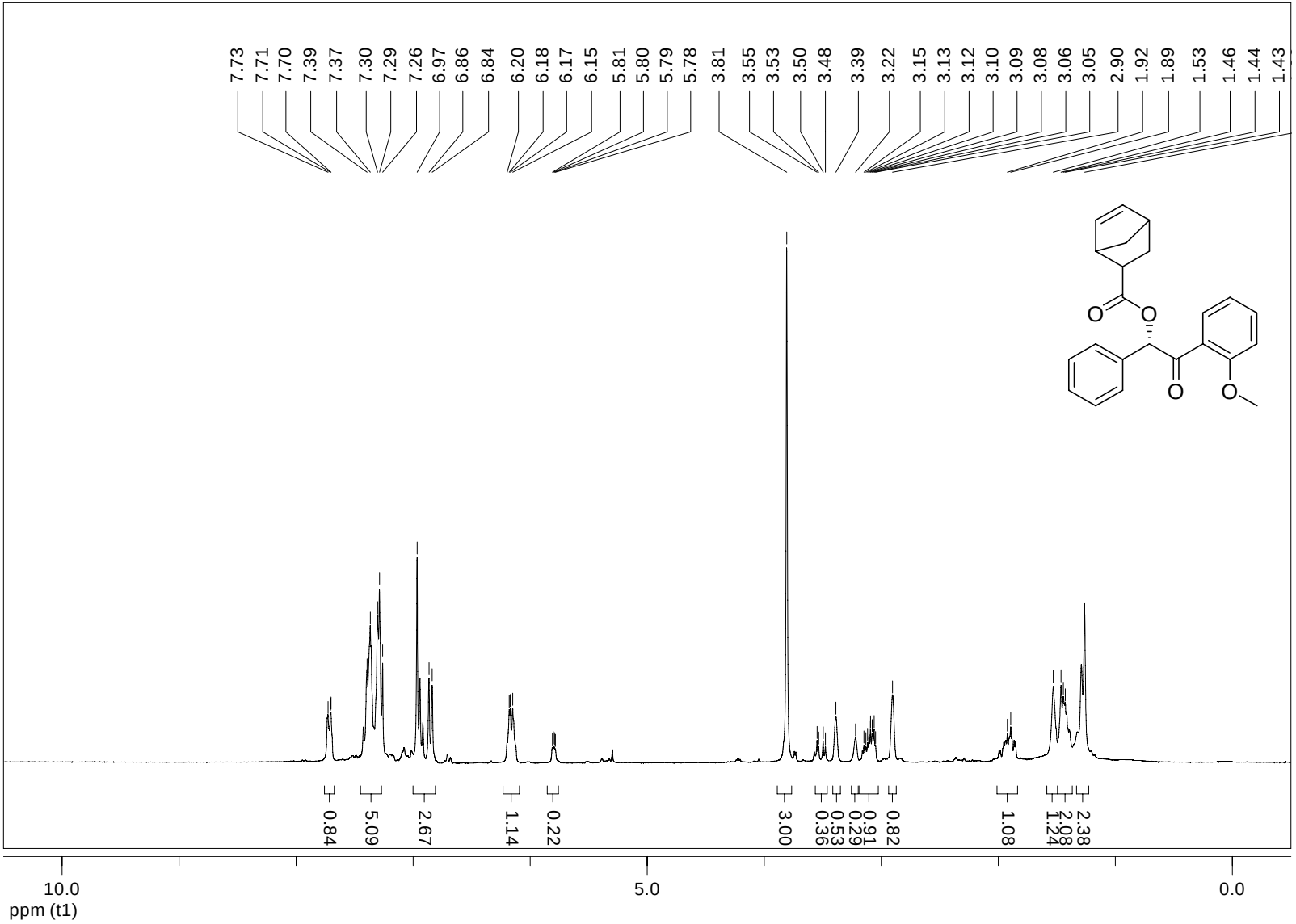

Figure S11. ^{13}C APT NMR ($CDCl_3$, 75.5 MHz): 2-(2-Methoxyphenyl)-2-oxo-1-phenylethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**2b**)

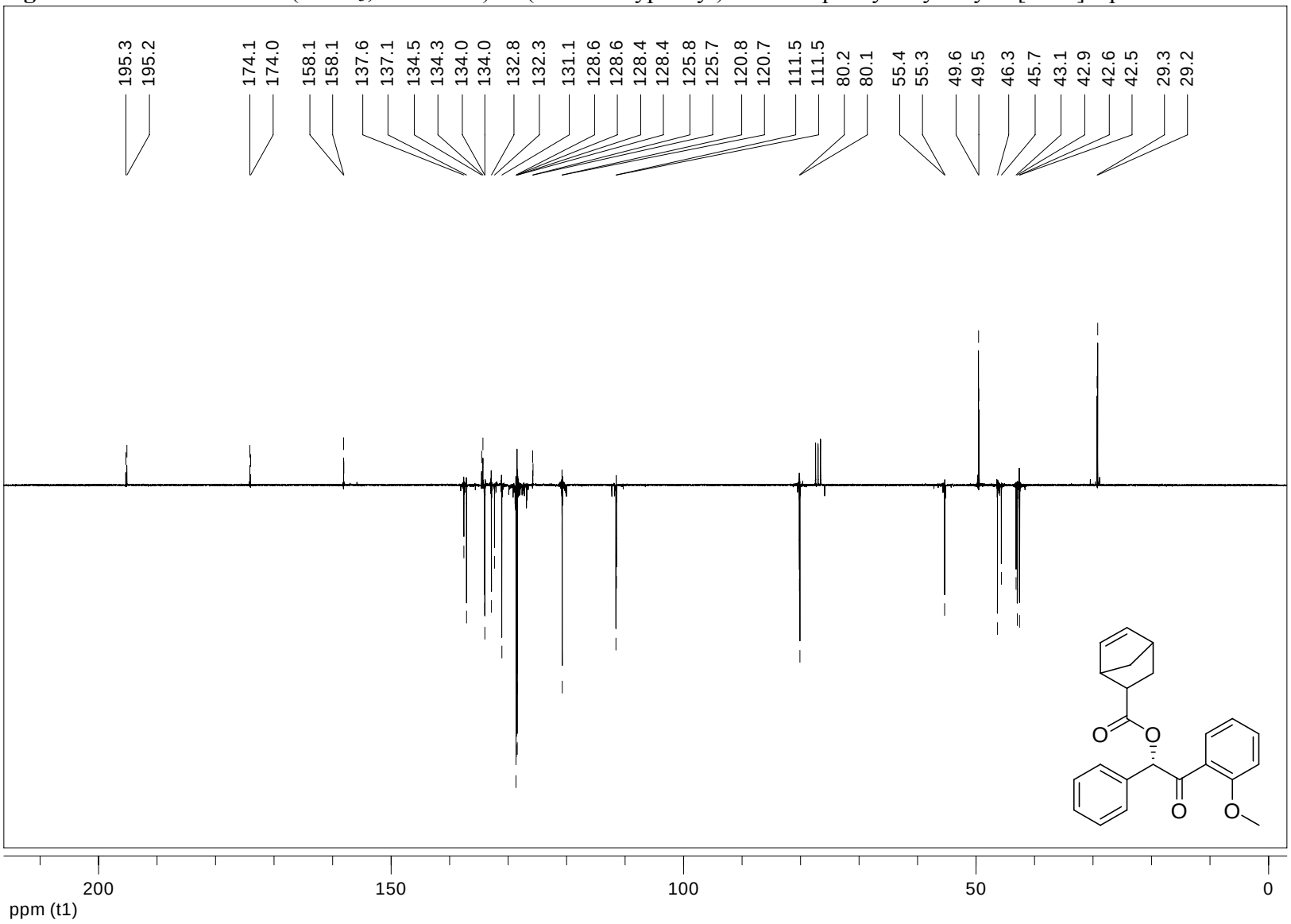

Figure S12. UV-Vis (CH_3OH): 2-(2-Methoxyphenyl)-2-oxo-1-phenylethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**2b**)