Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

for

[3,3]-Sigmatropic rearrangements of propargyl alkynyl ethers. Synthesis of complex dienoates and unsaturated lactones.

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General Information

Distilled water was used in all of the experiments. Organic extracts were dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator at aspirator pressure (20-30 mmHg). Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, 230-400 mesh). All glassware used in the reactions described below were flame-dried under vacuum and then flushed with argon gas at room temperature prior to the addition of reagents and solvents. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured in $CDCl_3$ at 400 MHz and 100 MHz, respectively, using Me_4Si as internal standard. Chemical shifts are reported in ppm downfield (δ) from Me_4Si.

General Procedure A: Preparation of α-alkoxy ketones **1** from propargylic alcohols and diazoketones:

A solution of α-diazoacetophenone (365 mg, 2.5 mmol) in benzene (3 mL) was added dropwise over 2 hours via syringe pump to a solution of propargylic alcohol (3.75 mmol) and indium triflate (210 mg, 0.375 mmol) in benzene (3 mL) at room temperature. The mixture was allowed to stir for an additional 2 hours and was quenched with a saturated solution of $NaHCO_3$ (5 mL) and ether (5 mL). The layers were separated, and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic extracts were washed once with saturated aqueous NaCl (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude oil. Purification of the residue by flash chromatography (20:1 → 10:1 hexanes: Et_2O) afforded α-alkoxy ketones **1**.

General Procedure B: Synthesis of α-alkoxyketones **1** from alcohols and bromoacetic acid:

A solution of alcohol (5 mmol) in THF (5 mL) was added slowly to a solution of NaH (11 mmol) in THF (20 mL) at 0 °C. After 30 minutes, bromoacetic acid (5 mmol) was directly added to the solution at 0 °C, and the mixture was warmed to room temperature. After 10 minutes, the mixture was refluxed for 18 h and then cooled to rt. Water (20 mL) and ether (20 mL) were added, and the layers were separated. The aqueous layer was acidified with concentrated HCl to pH=2. The aqueous layer was extracted with three 30 mL portions of ether and the combined organics were dried over sodium sulfate, filtered and evaporated. The crude acid was dissolved in CH_2Cl_2 (15 mL) and then EDC (7.48 mmol), N,O-dimethylhydroxylamine (7.48 mmol) and pyridine (2.5 mL) was added. The mixture was stirred overnight and was diluted with saturated $NaHCO_3$ solution. The layers were separated and the aqueous layer was extracted with three 30 mL portions of ethyl acetate. The combined organics were dried over sodium sulfate, filtered, and evaporated. The crude material was purified by column chromatography (20:1 → 3:1 Hexanes: ethyl acetate) to afford the Weinreb amide as a pale oil. The Weinreb amide was dissolve in THF (10 mL) and cooled to -78 °C. Separately, the Grignard or organolithium reagent (7.5 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. The Grignard or organolithium reagent solution was then cannulated into the THF solution of Weinreb amide at – 78 °C and the solution was allowed to warm to rt. The mixture was quenched with a saturated solution of ammonium chloride (10 mL) and the layers were separated. The aqueous layer was extracted with three 30 mL portions of ether and the combined organics were dried over sodium sulfate, filtered and evaporated. Purification of the residue by column chromatography (20:1 → 10:1 Hexanes:ethyl acetate) afforded the α-alkoxy ketone.

General Procedure C: Synthesis of propargyl-1,1-dichlorovinyl ethers **3** from propargylic alcohols:

The alcohol (10 mmol) was dissolved in pyridine (10 mL) and cooled to 0 °C. Formic acetic anhydride (10 mL) was added. And the mixture was stirred at 0°C for 30 minutes. When TLC had indicated completion of the reaction, the mixture was concentrated *in vacuo* with toluene (10 mL x 5) to remove excess pyridine. The crude material was then taken up in THF (100 mL) and treated with PPh_3 (30 mmol) and heated to 60 °C. CCl_4 (10 mL) was slowly added via syringe pump over 8 hours to the THF solution at 60°C. After 10 hours, the heating bath was removed and the mixture was allowed to cool to rt. The mixture was diluted with a saturated solution of $NaHCO_3$ (10 mL) and ether (10 mL) and the layers were separated. The aqueous layer was extracted with three 30 mL portions of ether and the combined organics were dried over sodium sulfate, filtered and evaporated. Purification of the residue by column chromatography (Hexanes→ 30:1 hexanes: ether) afforded the 1,1–dichlorovinyl ether.

General Procedure D: Conversion of α-alkoxy ketones **1** to rearranged dienes **2**:

A solution of hexamethyldisilazane (314 μL, 1.5 mmol) in THF (1 mL) was cooled to 0 °C and treated dropwise with *n*-butyllithium (0.75 mL, 2M in cyclohexane, 1.5 mmol). After 10 minutes, the solution was cooled to -78 °C and a solution of α-alkoxy ketone **1** (1 mmol) in THF (2 mL) was added dropwise. The solution was allowed to stir at -78 °C for one hour. Then a solution of Comins' reagent (589 mg, 1.5 mmol) in 2:1 THF:HMPA (2 mL) was added rapidly (1s) and the solution was allowed to warm to room temperature and stir for 30 minutes. Then a saturated solution of $NaHCO_3$ (5 mL) and ether (5 mL) was added. The layers were separated, and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic extracts were washed with a saturated aqueous solution of copper sulfate (2 x 10 mL) and saturated aqueous NaCl (1 x 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude oil. The crude material was rapidly filtered through a pad of silica gel

with 10:1 hexanes/ether and the fractions collected were concentrated *in vacuo*. The intermediate enol triflate was dissolved in THF (3 mL) and cooled to -78 °C. A 1M solution of potassium tert-butoxide in THF (2.5 equiv, 2.5 ml) was then added and the solution was stirred at -78 °C for 30 minutes, at which time TLC indicated conversion to a higher rf spot. The cooling bath was removed, and the mixture was allowed to warm to room temperature. Then a saturated solution of $NaHCO_3$ (5 mL) and ether (5 mL) was added. The layers were separated, and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic extracts were washed once with saturated aqueous NaCl (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude oil. Purification of the residue by flash chromatography (100:1 → 10:1 hexanes: Et_2O) afforded dienes **2**.

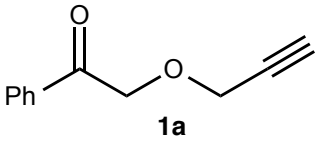
General Procedure E: Conversion of propargyl-1,1-dichlorovinyl ethers **3** to unsaturated dienoates **4**

The propargyl-1,1-dichlorovinyl ether (1 mmol) was dissolved in THF (1 mL) and cooled to -78°C. Then n-butyllithium (1.1 mL, 2.2 mmol, 2M in cyclohexane) was added dropwise and the brown mixture was stirred at -78 °C for 15 minutes. Then methanol (1 mL) was added rapidly and the mixture was allowed to warm to room temperature. A solution of saturated sodium bicarbonate (10 mL) and ether (10 mL) were added and the layers were separated. The aqueous layer was extracted with three 30 mL portions of ether and the combined organics were dried over sodium sulfate, filtered and evaporated. Purification of the residue by column chromatography (100:1→ 10:1 hexanes: ether) afforded the unsaturated dienoate **4** .

General Procedure F: Conversion of propargyl-1,1-dichlorovinyl ethers **3** to unsaturated lactones **6**

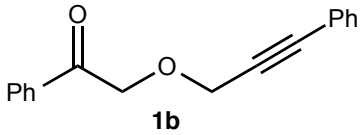
The propargyl-1,1-dichlorovinyl ether (1 mmol) was dissolved in THF (1 mL) and cooled to -78°C. Then n-butyllithium (1.1 mL, 2.2 mmol, 2M in cyclohexane) was added dropwise and the brown mixture was stirred at -78 °C for 15 minutes. The mixture was then allowed to warm to 0 °C and

stirred for 30 minutes. The mixture was then allowed to warm to rt and stirred for 10 minutes. At this point the appropriate ketone or aldehyde (1.8 mmol) was added dropwise and the mixture was stirred for one hour at rt. A solution of saturated sodium bicarbonate (10 mL) and ether (10 mL) were added and the layers were separated. The aqueous layer was extracted with three 30 mL portions of ether and the combined organics were dried over sodium sulfate, filtered and evaporated. Purification of the residue by column chromatography (20:1→ 3:1 hexanes: ethyl acetate) afforded the unsaturated lactones **6** .



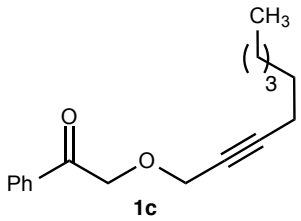
1a

1a (spectra pages S28 and S29): Prepared from propargyl alcohol and diazoacetophenone according to General procedure A. Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 Hexanes:EtOAc) afforded **1a** (221 mg, 1.27 mmol, 51%) as a colorless oil. **1a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=6.32 Hz, 2H); 7.58 (t, *J*=6.8 Hz, 1H); 7.50 (t, *J*=7.8 Hz, 2H), 4.89 (s, 2H); 4.39 (d, *J*=2.4 Hz, 2H); 2.52 (t, *J*=2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.5, 134.8, 134.7, 133.6, 129.2, 128.7, 127.8, 78.8, 75.6, 71.5, 58.4. IR: 2902 cm^{-1}, 2119, 1695, 1597. Spectral data matches that of known compound, reference: Yadav, J. S.; Reddy, B. V. S.; Vishnumurthy, P. *Tetrahedron Lett*. **2003**, *44*, 5691-5694.



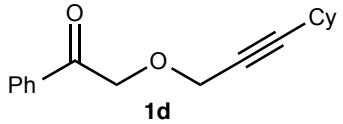
1b

1b (spectra pages S30 and S31): Prepared from 3-phenyl-2-propyn-1-ol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1b** (432 mg, 1.73 mmol, 69%) as a pale yellow oil. **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=7.86 Hz, 2H); 7.57-7.44 (m, 5H); 7.33-7.31 (m, 3H); 4.95 (s, 2H); 4.61 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.7, 134.9, 134.8, 133.6, 131.8, 129.2, 128.7, 128.6, 128.3, 127.9, 127.8, 122.3, 87.3, 84.2, 75.0, 71.7, 59.2. IR: 2977 cm^{-1}, 2226, 1692, 1597. Spectral data matches that of known compound, reference: Fu, W.; Nie, M; Wang, A.; Cao, Z.; Tang, W. *Angew. Chem. Int. Ed*. **2015**, *54*, 2520-2524.



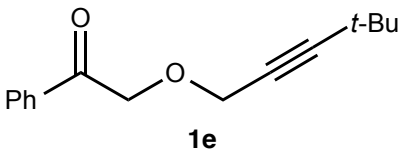
1c

1c (spectra pages S32 and S33): Prepared from 2-nonyne-1-ol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1c** (310 mg, 1.2 mmol, 48%) as a colorless oil. **1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J*=8.1 Hz, 2H); 7.58 (t, *J*=6.7 Hz, 1H); 7.46 (t, *J*=7.8 Hz, 2H); 4.83 (s, 2H); 4.33 (t, *J*=2.2 Hz, 2H); 2.21 (m, 2H); 1.47 (m, 2H); 1.37 (m, 2H); 1.28 (m, 4H); 0.97 (t, *J*=6.8 Hz, 3H) . ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.8, 134.9, 133.5, 128.6, 127.8, 88.4, 75.0, 71.4, 59.0, 31.2, 28.5, 28.4, 22.5, 18.7, 13.9. HRMS (QTOF) calculated for $C_{17}H_{22}NaO_2$ 281.1517, found 281.1513 $(M+Na)^+$. IR: 2981 cm^{-1}, 2936, 2923, 2864, 2844, 2220, 1699, 1598.



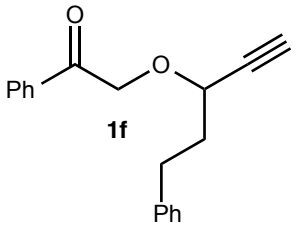
1d

1d (spectra pages S34 and S35): Prepared according from 3-cyclohexyl-2-propyn-1-ol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1d** (545 mg, 2.13 mmol, 85%) as a light yellow oil. **1d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J*=8.1 Hz, 2H); 7.61 (t, *J*=7.4 Hz, 1H); 7.47 (t, *J*=9.2, Hz, 2H); 4.85 (s, 2H); 4.37 (d, *J*=2.0 Hz, 2H); 2.41 (m, 1H); 1.80 (m, 2H); 1.72 (m, 2H); 1.52-1.40 (m, 3H); 1.29 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.9; 134.9, 133.5, 128.7, 128.6, 127.9, 92.4, 74.8, 71.4, 59.0, 32.5, 29.0, 25.8, 24.8. HRMS (QTOF) calculated for $C_{17}H_{20}NaO_2$ 279.1361, found 279.1354 $(M+Na)^+$. IR: 2928 cm^{-1}, 2853, 2225, 1699, 1598.



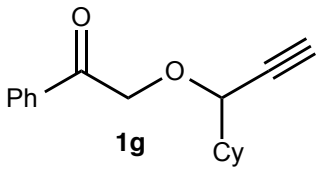
1e

1e (spectra pages S36 and S37): Prepared according from 4,4-dimethyl-2-pentyn-1-ol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1e** (402 mg, 1.75 mmol, 70%) as a light yellow oil. **1e**:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J*=8.1 Hz, 2H); 7.58 (t, *J*=7.4 Hz, 1H); 7.46 (t, *J*=6.6 Hz, 2H); 4.82 (s, 2H); 4.34 (s, 2H); 1.22 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.9, 134.9, 133.5, 128.7, 127.9, 96.5, 73.4, 71.5, 59.0, 30.8, 27.5. IR: 2982 cm^{-1}, 2865, 2227, 1699, 1598. Spectral data matches that of known compound, reference: Zhang, X.-W; Zhu, M.-H.; Zeng, H.-X.; Li, Q.-Y.; Liu, W.-B. *Angew. Chem., Int. Ed.* **2021**, *60*, 27225-27229.



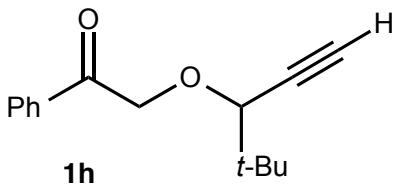
1f

1f (spectra pages S38 and S39): Prepared from 5-phenyl-1-pentyne-3-ol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1f** (570 mg, 2.05 mmol, 82%) as a viscous colorless oil. **1f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J*=8.2 Hz, 2H); 7.61 (t, *J*=5.5 Hz, 1H); 7.50 (t, *J*=7.5 Hz, 2H); 7.30 (q, *J*=5.4 Hz, 2H); 7.26 (m, 3H); 5.04 (d, *J*=16.5, Hz, 1H); 4.86 (d, *J*=16.5 Hz, 1H); 4.32 (td, *J*=2.1, 6.5 Hz, 1H); 2.91 (t, *J*=7.9 Hz, 2H); 2.56 (d, *J*=2.1 Hz, 1H); 2.28-2.11 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.8, 141.2, 135.0, 133.5, 128.9, 128.7, 128.5, 128.4, 128.3,128.0, 125.9, 81.8, 75.2, 71.0, 69.2, 37.0, 31.2. HRMS (QTOF) calculated for $C_{19}H_{19}O_2$ 279.1385, found 279.1389 $(M+H)^+$. IR: 2981 cm^{-1}, 2873, 2938, 2922, 2865, 2844, 2221, 1698, 1598.



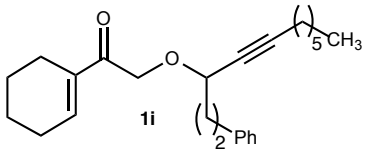
1g

1g (spectra pages S40 and S41): Prepared from α-ethynyl cyclohexanemethanol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1g** (576 mg, 2.25 mmol, 90%) as a pale oil. **1g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J*=7.9 Hz, 2H); 7.59 (t, *J*=6.1 Hz, 1H); 7.48 (t, *J*=8.4 Hz, 2H); 4.98 (d, *J*=16.4 Hz, 1H); 4.83 (d, *J*=16.4 Hz, 1H); 4.10 (dd, *J*=2.1, 6.2 Hz, 1H); 2.5 (d, *J*=2.1 Hz, 1H); 1.94 (m, 2H); 1.77 (m, 3H); 1.68 (m, 1H); 1.28-1.15 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.1; 135.0, 133.4, 128.6, 128.0, 81.1, 75.5, 74.7, 71.1, 42.3, 28.9, 28.2, 26.3, 25.9, 25.8. HRMS (QTOF) calculated for $C_{17}H_{20}NaO_2$ 279.1361, found 279.1358 $(M+Na)^+$. IR: 2924 cm^{-1}, 2852, 2222, 1701, 1598.

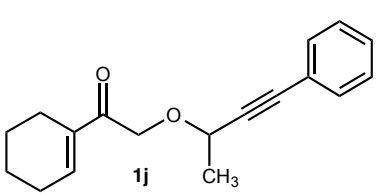


1h

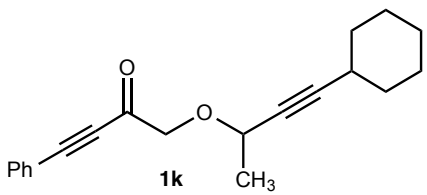
1h (spectra pages S42 and S43): Prepared from α-trimethylsilylethynyl 4,4-dimethyl-pentyn-3-ol and diazoacetophenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1h** (528 mg, 1.75 mmol, 70%) as a pale oil. **1h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J*=6.3 Hz, 2H); 7.61 (t, *J*=6.7 Hz, 1H); 7.50 (t, *J*=7.6, Hz, 2H); 5.00 (d, *J*=16.2 Hz, 1H); 4.81 (d, *J*=16.2 Hz, 1H); 3.95 (d, *J*=2.1 Hz, 1H); 2.48 (d, *J*= 2.1 Hz, 1H); 1.06 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.5, 135.2, 133.4, 128.6, 128.2, 80.8, 78.6, 75.5, 71.6, 35.5, 30.9, 25.6. HRMS (QTOF) calculated for $C_{15}H_{19}O_2$ 231.1385, found 231.1384 $(M+H)^+$. IR: 2981 cm^{-1}, 2972, 2922, 2866, 2844, 2237, 1701, 1598.



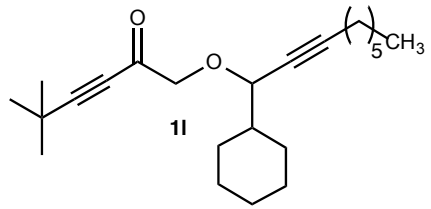
1i (spectra pages S45 and S46): Prepared from 1-phenyl-3-hydroxy undec-4-yne and diazo-1-acetylcyclohexenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **1i** (457 mg, 1.25 mmol, 50%) as a yellow oil. **1i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H); 6.91 (s, 1H); 4.68 (d, *J*= 15.8 Hz, 1H); 4.53 (d, *J*=15.8 Hz, 1H); 4.22 (t, *J*=6.5 Hz, 1H); 2.84 (t, *J*=7.9 Hz, 2H); 2.26 (m, 6H); 2.06 (m, 2H); 1.54 (m, 4H); 1.51 (m, 2H); 1.45 (m, 2H); 1.32 (m, 4H); 0.92 (t, *J*= 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.9, 141.7, 140.3, 137.6, 128.5, 128.4, 128.3, 125.8; 87.6, 78.2, 69.9, 69.5, 37.5, 31.5, 31.3, 28.6, 28.5, 26.0, 22.9, 22.6, 21.8, 21.5, 18.7, 14.0. HRMS (QTOF) calculated for $C_{25}H_{34}NaO_2$ 389.2457, found 389.2454 $(M+Na)^+$. IR: 2929 cm^{-1}, 2860, 2229, 1679, 1636, 1603.



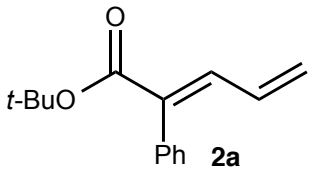
1j (spectra pages S47 and S48): Prepared from 4-phenyl-3-butyn-2-ol and diazo-1-acetylcyclohexenone according to General Procedure A: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes : EtOAc) afforded **1j** (270 mg, 1.0 mmol, 40%) as a yellow oil. **1j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.40 (m, 2H); 7.30-7.28 (m, 3H); 6.91 (m, 1H); 4.72 (d, *J*= 16.0 Hz, 1H); 4.60-4.52 (m, 2H); 2.26 (m, 4H); 1.64-1.57 (m, 4H); 1.60 (d, *J*=6.5Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 142.7, 140.4, 137.5, 131.7, 128.4, 128.2, 122.5, 88.4, 85.6, 74.5, 69.9, 66.1, 25.9, 22.8, 22.0, 21.7, 21.4. HRMS (QTOF) calculated for $C_{18}H_{20}NaO_2$ 291.1361, found 291.1347 $(M+Na)^+$. IR: 2923 cm^{-1}, 2867, 1696, 1629, 1598.



1k (spectra pages S49 and S50): Prepared from 4-cyclohexyl-3-butyn-2-ol according to General Procedure B: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes : EtOAc) afforded **1k** (880 mg, 3.0 mmol, 60%) as a yellow oil. **1k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 2H); 7.46 (m, 1H); 7.42-7.38 (m, 2H); 4.48-4.39 (m, 3H); 2.43-2.38 (m, 1H); 1.80 (m, 2H); 1.79-1.79 (m, 2H); 1.52 (d, *J*= 6.5 Hz, 3H); 1.48-1.40 (m, 3H); 1.33-1.27 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.5, 133.1, 130.9, 128.6, 119.7, 93.5, 91.2, 85.9, 78.7, 73.9, 66.3, 32.6, 28.9, 25.8, 24.7, 22.4. HRMS (TOF) calculated for $C_{20}H_{22}O_2$ 294.1620, found 294.1616 $(M)^+$. IR: 2985 cm^{-1}, 2929, 2854, 2199, 1686, 1669.

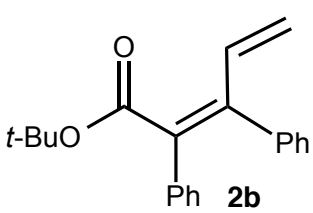


1l (spectra pages S51 and S52): Prepared from α-1-octyn-ylcyclohexanemethanol according to General Procedure B: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes : EtOAc) afforded **1l** (860 mg, 2.5 mmol, 50%) as a yellow oil. **1l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (dd, *J*= 17.2 Hz, 1H); 4.26 (d, *J*=17.2 Hz, 1H); 4.02 (m, 1H); 2.24 (td, *J*=6.9, 2.0 Hz, 2H); 1.90-1.88 (m, 2H); 1.77 (m, 2H); 1.68 (m, 2H); 1.53-1.40 (m, 2H); 1.39 (m, 2H); 1.38 (s, 9H); 1.29-1.13 (m, 9 H); 0.86 (t, *J*=6.8 Hz, 3H) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.9, 104.1, 88.3, 76.7, 75.2, 74.1, 42.7, 31.2, 29.9, 29.0, 28.6, 28.4, 28.2, 27.8, 26.4, 25.9, 25.8, 22.5, 18.6, 13.9. HRMS (TOF) calculated for $C_{23}H_{36}O_2$ 344.2715, found 344.2714 $(M)^+$. IR: 2926 cm^{-1}, 2854, 2213, 1693, 1675.



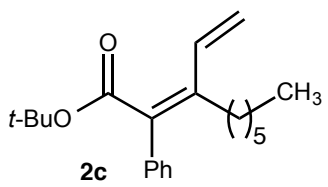
2a

2a (spectra pages S53 and S54): Prepared from **1a** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2a** (207 mg, 0.9 mmol, 90%) as a yellow oil. **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4H); 7.22 (d, *J*=6.6 Hz, 2H); 6.45 (m, 1H); 5.66 (dd, *J*=1.7, 16.9 Hz, 1H); 5.41 (dd, *J*=1.8, 10.1 Hz, 1H); 1.51 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 139.2, 135.3, 135.1, 133.5, 130.2, 127.7, 127.5, 124.7, 80.9, 28.1. HRMS (QTOF) calculated for $C_{11}H_{11}O_2$ 175.0759, found 175.0754 (M(-*t*Bu)+2H)$^+$. IR: 2981 cm^{-1}, 2973, 2937, 2923, 2866, 2844, 1704, 1626, 1598. Reference: Chen, S.; Wang, J. *Chem*. *Commun*. **2008**, 4198-4200.

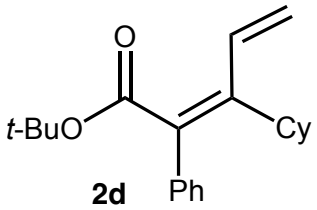


2b

2b (spectra pages S55, and S56): Prepared from **1b** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded an inseparable 3:1 ratio of *E*-**2b** and *Z*-**2b** (211 mg, 0.69 mmol, 69%) as a pale yellow oil. *E*-**2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.37 (m, 2 H); 7.21 (m, 2H); 7.15 (m, 5H); 7.04 (m, 2H); 5.42 (dd, *J*=1.4, 10.6 Hz, 1H); 5.08 (dd, *J*=1.4, 17.0 Hz, 1H); 1.56 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.6, 142.1, 138.6, 137.2, 136.7, 136.3, 136.2, 135.2, 130.5, 129.8, 129.4, 128.2, 127.8, 127.5, 127.4, 127.1, 81.8, 28.1. HRMS (QTOF) calculated for $C_{21}H_{22}NaO_2$ 329.1517, found 329.1509 (M+Na)$^+$. IR: 2981 cm^{-1}, 2973, 2937, 2922, 1713 (br), 1600. Reference: Wang, S.; Shao, P.; Chen, C.; Xi, C. *Org*. *Lett*. **2015**, *17*, 5112-5115

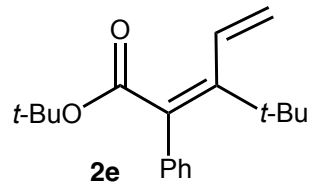


2c (spectra pages S57, S58, and S59): Prepared from **1c** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded an inseparable 5:1 ratio of *Z*-**2c** and *E*-**2c** (267 mg, 0.85 mmol, 85%) as a yellow oil. *E*-**2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H); 6.91 (dd, *J*=11.0, 17.5 Hz, 1H); 5.51 (d, *J*=17.4 Hz, 1H); 5.36 (d, *J*=11.0 Hz, 1H); 2.20 (t, *J*=7.9 Hz, 2H); 1.46 (s, 9H); 1.29-1.16 (m, 8H); 0.86 (t, *J*=6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.3, 141.8, 137.5, 134.9, 134.6, 129.6, 128.7, 128.0, 127.9, 127.2, 117.0, 81.2, 31.3, 29.4, 29.2, 28.6, 28.0, 22.4, 13.9. HRMS (QTOF) calculated for $C_{17}H_{23}O_2$ 259.1698, found 259.1688 $(M(-t\text{-Bu})+2H)^+$. IR: 2966 cm^{-1}, 2923, 2864, 2844, 1712 (br), 1601. References: Matsumoto, K.; Shindo, M. *Adv. Synth. Catal.* **2012**, *354*, 642-650; Wang, S.; Shao, P.; Chen, C.; Xi, C. *Org. Lett.* **2015**, *17* 5112-5115. Li, T.-L; Wu, Y.L.; Walsgrove, T. C. *Tetrahedron* **1984**, *40*, 4701-410.



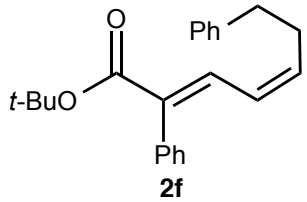
2d (spectra pages S60, S61, and S463): Prepared from **1d** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2d** (>10:1 *E*:*Z*, 224 mg, 0.72 mmol, 72%) as a yellow oil. **2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H); 7.25 (m, 3H); 6.49 (dd, *J*=11.3, 17.5 Hz, 1H); 5.37 (dd, *J*=2.0, 17.5 Hz, 1H); 5.27 (dd, *J*=2.5, 11.3 Hz, 1H); 2.29 (m, 1H); 1.66 (m, 2H); 1.60 (m, 3H); 1.41-1.32 (m, 11 H); 1.09 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.1, 146.6, 137.2, 134.7, 133.0, 128.9, 128.7, 128.2, 128.1,

127.2, 118.4, 80.7, 40.7, 32.4, 27.9, 26.1, 25.9. HRMS (TOF) calculated for $C_{21}H_{28}O_2$ 312.2089, found 312.2088 $(M)^+$. IR: 2979 cm^{-1}, 2927, 2854, 1714, 1622, 1598.



2e

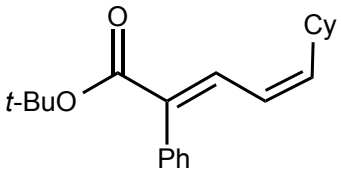
2e (spectra pages S63, S64, and S65): Prepared from **1e** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2e** (9:1 *E:Z*, 194 mg, 0.68 mmol, 68%) as a yellow oil. **2e**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 5H); 6.50 (dd, *J*=10.9, 17.3 Hz, 1H); 5.32 (d, *J*=17.3 Hz, 1H); 5.18 (d, *J*=11.0 Hz, 1H); 1.35 (s, 9H); 0.94 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 148.4, 138.2, 137.6, 133.8, 129.6, 129.4, 127.8, 127.7, 127.1, 117.9, 80.5, 36.3, 30.7, 27.8. HRMS (QTOF) calculated for $C_{19}H_{26}NaO_2$ 309.1830, found 309.1819 $(M+Na)^+$. IR: 2972 cm^{-1}, 2869, 1715, 1622, 1598.



2f

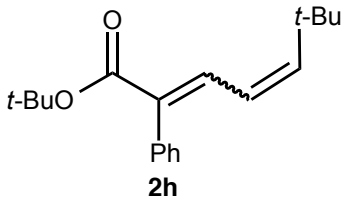
2f (spectra pages S66, S67, and S68): Prepared from **1f** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2f** (237 mg, 0.71 mmol, 71%), as an inseparable 4:1 mixture of *E* and *Z* stereoisomers at the α,β-alkene, as a yellow oil. ***E*-2f:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J*=8.1 Hz, 1H); 7.32-7.22 (m, 5H); 7.20-7.19 (m, 5H); 6.06 (t, *J*=12.0 Hz, 1H); 5.78 (dt, *J*=11.9, 7.5 Hz, 1 H); 2.80 (m, 2H); 2.70 (m, 2H); 1.51 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 142.5, 141.2, 139.4,

139.0, 135.4, 134.3, 133.5, 130.2, 128.5, 128.4, 128.3, 127.7, 127.6, 127.3, 127.2, 126.0, 125.9, 125.6, 80.7, 35.6, 30.0, 28.1. HRMS (QTOF) calculated for $C_{23}H_{26}NaO_2$ 357.1830, found 357.1822 $(M+Na)^+$. IR: 2973 cm^{-1}, 2937, 2922, 2865, 2844, 1701, 1627, 1603.



2g

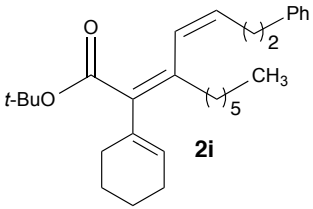
2g (spectra pages S69, S70, and S71): Prepared from **1g** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2g** (184 mg, 0.59 mmol, 59%), an inseparable 3:1 mixture of *E* and *Z* stereoisomers at the α,β-alkene, as a yellow oil. ***E*-2g**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J*=7.8 Hz, 1H); 7.34 (m, 3H); 7.21 (d, *J*=8.3 Hz, 2H); 5.93 (t, *J*=11.9 Hz, 1H); 5.59 (t, *J*=10.8 Hz, 1H); 2.67 (m, 1H); 1.79 (m, 5H); 1.59 (s, 9H); 1.36-1.11 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.0, 146.5, 135.6, 134.2, 133.9, 130.2, 127.6, 127.1, 122.8, 80.7, 37.2, 33.0, 28.2, 28.1, 25.8, 25.6. HRMS (QTOF) calculated for $C_{21}H_{28}NaO_2$ 335.1987, found 335.1975 $(M+Na)^+$. IR: 2924 cm^{-1}, 2851, 1703, 1625, 1598.



2h

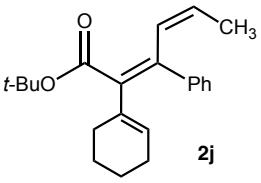
2h (spectra pages S72, S73, and S74): Prepared from **1h** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2h** (125 mg, 0.44 mmol, 44%), an inseparable 1.4:1 mixture of *E* and *Z* stereoisomers at the α,β-alkene, as a yellow oil. **2h**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J*=12.0 Hz, 1H); 7.37-7.31 (m, 8H); 7.23 (d, *J*=8.3 Hz, 2H); 7.15 (d, *J*= 12.3 Hz, 1H); 6.38 (t, *J*=12.1 Hz, 1H); 5.87 (t, *J*=12.2 Hz, 1H); 5.71 (d, *J*=12.1 Hz, 1H); 5.70 (d, *J*=12.3 Hz, 1H); 1.58 (s, 9H); 1.51 (s, 9H); 1.27 (s, 9H); 1.25

(s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 166.7, 149.8, 147.0, 137.6, 135.7, 135.0, 134.6, 133.9, 130.3, 130.2, 128.3, 128.0, 127.6, 127.6, 127.2, 126.6, 122.9, 122.8, 81.8, 80.6, 34.6, 31.6, 31.4, 29.1, 28.2, 28.1. HRMS (QTOF) calculated for $C_{15}H_{19}O_2$ 231.1385, found 231.1380 $(M(-t\text{-Bu})+2H)^+$. IR: 2981 cm^{-1}, 2966, 2922, 2866, 2844, 2826, 1704, 1628, 1598.



2i

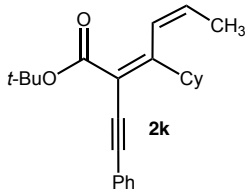
2i (spectra pages S75, S76, and S77): Prepared from **1i** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:EtOAc) afforded **2i** (300 mg, 0.71 mmol, 71%), as an inseparable 1:3 mixture of *E* and *Z* stereoisomers at the γ,δ-alkene, as a yellow oil. **2i** (major isomer): ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H); 6.07 (d, *J*=11.5 Hz, 1H); 5.58 (m, 1H); 5.56 (dt, *J*=1.9, 11.5 Hz, 1H); 2.68 (t, *J*=7.4 Hz, 2H); 2.37 (m, 2H); 2.12-2.05 (m, 7H); 1.69-1.58 (m, 4H); 1.44 (s, 9H); 1.28-1.24 (m, 7H); 0.91 (t, *J*=6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.3, 142.6, 142.0, 135.8, 134.8, 132.8, 130.3, 129.8, 128.4, 128.3, 128.2, 126.7, 125.7, 79.9, 35.8, 34.1, 31.5, 30.6, 29.7, 29.4, 28.9, 28.3, 28.1, 28.0, 25.3, 22.9, 22.5, 22.0, 14.0. HRMS (TOF) calculated for $C_{29}H_{42}O_2$ 422.3185, found 422.3186 $(M)^+$. IR: 2981 cm^{-1}, 2973, 2966, 2937, 2923, 2864, 2844, 2829, 1712 (br), 1603.



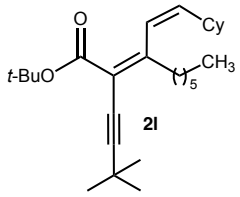
2j

2j (spectra pages S78, S79, and S80): Prepared from **1j** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:Et_2O) afforded **2j** (155 mg, 0.48 mmol, 48%), as an inseparable 3:1 mixture of *E* and *Z* stereoisomers at the α,β-alkene, as a yellow oil. **2j**: ^1H NMR (400 MHz,

$CDCl_3$) δ 7.29 – 7.21 (m, 5H); 6.28-6.25 (d, *J*=11.6 Hz, 1H); 5.72-5.68 (dd, *J*=11.4, 7.1 Hz, 1H); 5.52-5.50 (m, 1H); 1.93 (m, 4H); 1.51 (s, 9H); 1.43 (d, *J*=7.1 Hz, 3H); 1.41-1.28 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.0, 140.5, 137.5, 134.6, 130.0, 129.2, 128.9, 128.3, 128.1, 127.9, 127.6, 80.5, 54.7, 29.6, 28.5, 28.0, 27.7, 27.3, 25.6, 22.8, 21.7, 14.8. HRMS (TOF) calculated for $C_{22}H_{28}O_2$ 324.2089, found 324.2100 $(M)^+$. IR: 2981 cm^{-1}, 2973, 2937, 2923, 2865, 2844, 2828, 1711 (br), 1598.

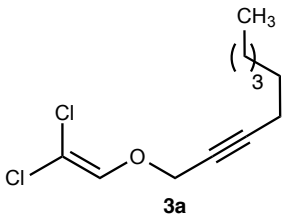


2k (spectra pages S81 and S82): Prepared from **1k** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:Et_2O) afforded **2k** (192 mg, 0.55 mmol, 55%, as a >10:1 mixture of *Z* and *E* stereoisomers at the α,β-alkene), as a yellow oil. **2k** (major isomer): ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H); 7.36-7.32 (m, 3H); 6.01 (dd, *J*=11.7, 1.7 Hz, 1H); 5.69 (dq, *J*=4.8, 11.7 Hz, 1H); 3.08 (m, 1H); 1.87-1.70 (m, 4H); 1.69 (dd, *J*=1.9, 6.7 Hz, 3H); 1.51 (s, 9H); 1.35-1.28 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.1, 159.4, 131.3, 128.2, 128.0, 127.6, 126.5, 123.6, 115.0, 94.8, 85.5, 80.9, 45.4, 30.3, 27.9, 26.3, 25.9, 14.7. HRMS (TOF) calculated for $C_{24}H_{30}O_2$ 350.2246, found 350.2251 $(M)^+$. IR: 2981 cm^{-1}, 2973, 2937, 2844, 2865, 2827, 2205, 1721 (br).



2l (spectra pages S83, S84, and S85): Prepared from **1l** according to General Procedure D: Purification of the residue by flash chromatography (SiO_2, 100:1→10:1 hexanes:Et_2O) afforded **2l** (298 mg, 0.75 mmol, 75%, as a >10:1 mixture of *Z* and *E* stereoisomers at the α,β-alkene) as a light yellow oil. **2l** (major isomer): ^1H NMR (400 MHz,

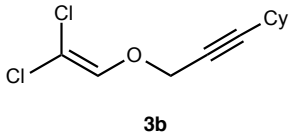
$CDCl_3$) δ 6.19 (d, *J*=11.8 Hz, 1H); 5.32 (t, *J*=11.8, 1H); 2.53 (t, *J*=7.7 Hz, 2H); 2.25-2.10 (m, 2H); 1.72-1.60 (m, 7H); 1.49 (s, 9H); 1.30 (s, 9H); 1.30-1.24 (m, 4H); 1.23 (m, 4H); 1.11 (m, 2H); 0.95 (t, *J*=6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.8, 156.9, 137.8, 126.2, 115.4, 104.0, 80.7, 75.6, 38.1, 37.5, 32.5, 31.6, 30.9, 29.5, 28.2, 28.0, 27.9, 25.9, 25.6, 22.5, 14.0. HRMS (QTOF) calculated for $C_{23}H_{37}O_2$ 345.2794, found 345.2799 $(M(-tBu)+2H)^+$. IR: 2967 cm^{-1}, 2923, 2863, 2844, 2219, 1716, 1675.



3a

3a (spectra pages S86 and S87): Prepared according to General Procedure C from 2-nonyne-1-ol: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:EtOAc) afforded **3a** (1.5 g, 6.4 mmol, 64%). **3a**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 1H); 4.50 (s, 1H); 2.27 (m, 2H); 1.58 (m, 2H); 1.45-1.27 (m, 7H); 0.93 (t, *J*= 6.7 Hz, 3H) . $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 105.4, 90.1, 73.6, 60.7, 31.2, 28.4, 28.2, 22.5, 18.7, 14.0. IR: 2930 cm^{-1}, 2861, 2229, 1650.

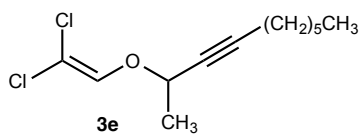
Note: Dichlorovinyl ethers such as **3a-3i** give unsatisfactory results on exact mass analysis due to degradation processes occurring in the mass spectrometer. A possible mechanism may involve thermal rearrangement of the propargyl dichlorovinyl ether and subsequent decomposition of the resultant aldehyde. Even using the soft ionization technique of QTOF (or ESI)-MS did not provide the expected molecular ion. See Supporting Information in reference 3 (main text) and: Morimoto, T.; Sekiya, M. *Synthesis* **1981**, 308−310.



3b

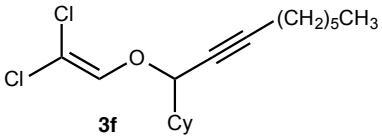
3b (spectra pages S88 and S89): Prepared according to General Procedure C from 3-cyclohexyl-2-proyn-1-ol: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:EtOAc) afforded **3b** (1.18 g,

5.1 mmol, 51%). **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (s, 1H); 4.51 (d, *J* =2.0 Hz, 2H); 2.44 (m, 1H); 1.82-1.79 (m, 2H); 1.74-1.67 (m, 2H); 1.54-1.42 (m, 3H); 1.35-1.29 (m, 3H) . ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 105.5, 94.1, 73.6, 60.8, 32.3, 29.0, 25.8, 24.7. IR: 2929 cm^{-1}, 2855, 2231, 1650.



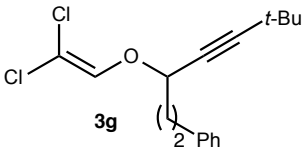
3e

3e (spectra pages S90 and S91): Prepared according to General Procedure C from 3-decyne-2-ol: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:EtOAc) afforded **3e** (2.25 g, 9.1 mmol, 91%). **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H); 4.64 (m, 1H); 2.26 (td, *J*=1.9, 6.9 Hz, 2H); 1.53 (m, 1H); 1.51 (d, *J*=6.6 Hz, 3H); 1.45-1.27 (m, 7H); 0.93 (t, *J*=6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.6, 104.9, 88.5, 68.6, 31.2, 28.4, 28.3, 22.5, 22.2, 18.6, 13.9. IR: 2980 cm^{-1}, 2972, 2938, 2922, 2866, 2844, 2825, 2240, 1651.

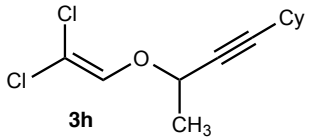


3f

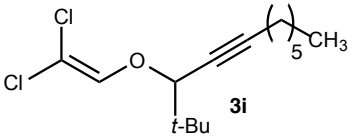
3f (spectra pages S92 and S93): Prepared according to General Procedure C from α-1-octyn-ylcyclohexanemethanol: Purification of the residue by flash chromatography (SiO_2, 100:1→40:1 hexanes:EtOAc) afforded **3f** (2.55 g, 8.1 mmol, 81%). **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H); 4.27 (dt, *J*=2.0, 6.6 Hz, 1H); 2.26 (t, *J*=7.0 Hz, 2H); 1.89 (m, 2H); 1.77 (m, 2H); 1.67 (m, 2H); 1.54-1.50 (m, 3H); 1.45 (m, 2H); 1.40-1.10 (m, 8H); 0.93 (t, *J*=6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.1, 104.5, 89.9, 77.6, 75.9, 42.7, 37.1, 31.9, 31.2, 29.7, 28.6, 28.4, 26.2, 25.7, 22.6, 18.7, 14.0. IR: 2926 cm^{-1}, 2855, 2230, 1640.



3g (spectra pages S94 and S95): Prepared according to General Procedure C from α-1-(3,3-dimethyl)butynyl-hydrocinnamylmethanol: Purification of the residue by flash chromatography (SiO_2, 100:1→40:1 hexanes:EtOAc) afforded **3g** (1.83 g, 5.9 mmol, 59%). **3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H); 7.24 (m, 3H); 6.82 (s, 1H); 4.48 (t, *J*=6.3 Hz, 1H); 2.87 (t, *J*=9.4 Hz, 2H); 2.22-2.04 (m, 2H); 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.7, 140.5, 128.6, 128.5, 126.1, 105.4, 97.9, 75.1, 71.7, 37.4, 31.2, 30.8, 27.5,14.0. IR: 2969 cm^{-1}, 2866, 2844, 2239, 1640.

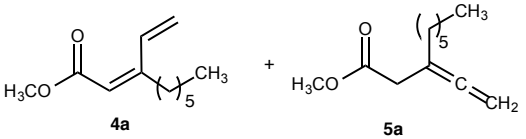


3h (spectra pages S96 and S97): Prepared according to General Procedure C from 4-cyclohexyl-3-butyn-2-ol: Purification of the residue by flash chromatography (SiO_2, 100:1→40:1 hexanes:EtOAc) afforded **3h** (1.94 g, 7.9 mmol, 79%). **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H); 4.67 (qd, *J*=1.8, 6.6 Hz, 1H); 2.45 (m, 1H); 1.82-1.68 (m, 4H); 1.51 (d, *J*=5.9 Hz, 3H); 1.50-1.42 (m, 3H); 1.37-1.31 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.6, 105.0, 92.5, 77.7, 68.7, 32.3, 28.8, 25.8, 24.6, 22.4. IR: 2981 cm^{-1}, 2966, 2930, 2856, 2237, 1640.

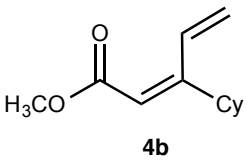


3i (spectra pages S98 and S99): Prepared according to General Procedure C from 2,2-dimethyl-4-undecyn-3-ol: Purification of the residue by flash chromatography (SiO_2, 100:1→40:1 hexanes:EtOAc) afforded **3i** (2.49 g, 8.6 mmol, 86%). **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H); 4.10 (t, *J*=2.0 Hz, 1H); 2.27 (dt, *J*=6.9, 2.0 Hz, 2H); 1.58-1.51 (m, 2H); 1.46-1.39 (m, 2H); 1.35-1.29 (m, 4H); 1.04 (s, 9H); 0.92 (t, *J*=6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

δ 141.6, 104.6, 89.8, 81.5, 75.6, 35.8, 31.3, 28.5, 25.5, 22.5, 18.6, 13.9. IR: 2980 cm^{-1}, 2966, 2957, 2936, 2923, 2865, 2844, 2827, 2230, 1640.

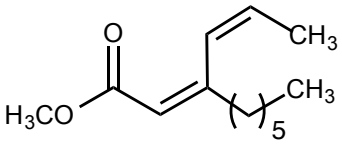


4a (spectra pages S100, S101, and S102): Prepared according to General Procedure E from **3a**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:EtOAc) afforded **4a** (117 mg, 0.60 mmol, 60%, as an inseparable 5:1 **4a**:**5a** mixture). **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J*=6.7, 16.9 Hz, 1H); 5.72 (s, 1H); 5.65 (d, *J*=17.7 Hz, 1H); 5.47 (dt, *J*=1.4, 11.1 Hz, 1H); 3.72 (s, 3H); 2.37 (t, *J*=7.5 Hz, 2H); 1.54 (m, 2H); 1.31 (m, 6H); 0.92 (t, *J*=6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 155.3, 133.1, 120.0, 116.6, 51.0, 33.5, 31.6, 29.2, 29.0, 14.0. HRMS (QTOF) calculated for $C_{12}H_{21}O_2$ 197.1542, found 197.1541 $(M+H)^+$. IR: 2936 cm^{-1}, 2863, 2844, 1708, 1633. Reference: Kazuhiro, Y.; Hidetoshi, T.; Imamoto, T. *Chem. Eur. J.* **2008**, *14*, 8246-8261.; Xu, Y.-H.; Lu, J.; Loh, T.-P. *J. Am. Chem. Soc.* **2009**, *131*, 1372-1373.



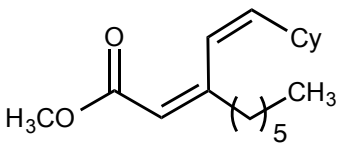
4b (spectra pages S103 and S104): Prepared according to General Procedure E from **3b**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:EtOAc) afforded **4b** (as an inseparable 5:1 mixture of *E*:*Z* stereoisomers, 132 mg, 0.68 mmol, 68%). ***E*-4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J*= 17.8, 6.6 Hz, 1H); 5.70 (s, 1H); 5.65-5.60 (d, *J*=17.8 Hz, 1H); 5.43 (d, *J*=11.2 Hz, 1H); 3.72 (s, 3H); 2.51 (t, *J*=11.7 Hz, 1H); 1.84-1.60 (m, 5H); 1.38-1.20

(m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 167.2, 160.3, 133.2, 118.6, 114.5, 51.1, 40.2, 33.2, 26.7, 26.2. HRMS (TOF) calculated for $C_{12}H_{18}O_2$ 194.1307, found 194.1308 $(M)^+$. IR: 2981 cm^{-1}, 2973, 2936, 2923, 1715, 1629.



4e

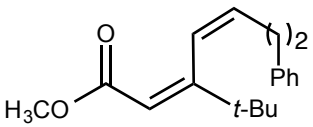
4e (spectra pages S105, S106, and S107): Prepared according to General Procedure E from **3e**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:EtOAc) afforded **4e** (100 mg, 0.48 mmol, 48%, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene). **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, *J*= 11.9 Hz, 1H); 5.75-5.70 (m, 2H); 3.68 (s, 3H); 2.30 (t, *J*=7.5 Hz, 2H); 1.68 (d, *J*=7.0 Hz, 3H); 1.49 (m, 2H); 1.39-1.27 (m, 6H); 0.91 (t, *J*=6.7 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 157.2, 128.3, 127.8, 116.8, 50.9, 38.6, 31.6, 28.9, 28.0, 22.5, 15.0, 14.0. HRMS (QTOF) calculated for $C_{13}H_{23}O_2$ 211.1698, found 211.1699 $(M+H)^+$. IR: 2925 cm^{-1}, 2859, 1718, 1634, 1613.



4f

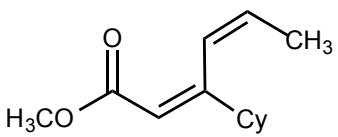
4f (spectra pages S108 and S109): Prepared according to General Procedure E from **3f**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:Et_2O) afforded **4f** (144 mg, 0.52 mmol, 52% as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene). **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (d, *J*=12.0 Hz, 1H); 5.712 (s, 1H); 5.41 (t, *J*= 10.8 Hz, 1H); 3.68 (s, 3H); 2.27 (t, *J*=7.2 Hz, 2H); 2.12 (m, 1H); 1.73-1.60 (m, 8H); 1.50-1.47 (m, 2H); 1.26-1.07 (m, 8H); 0.90 (t, *J*=6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 166.6, 157.8, 138.8. 125.0, 116.6, 50.8, 39.2, 38.3,

32.9, 31.6, 29.0, 28.1, 25.9, 25.7, 22.5, 14.0. HRMS (QTOF) calculated for $C_{18}H_{31}O_2$ 279.2324, found 279.2325 $(M+H)^+$. IR: 2923 cm^{-1}, 2858, 1721, 1631.



4g

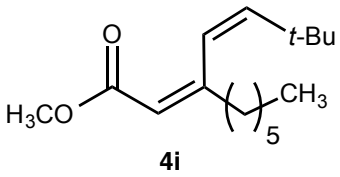
4g (spectra pages S110, S111 and S112): Prepared according to General Procedure E from **3g**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:Et_2O) afforded **4g** (193 mg, 0.71 mmol, 71%) as an inseparable 1:2.3 mixture of *E* and *Z* stereoisomers at the γ,δ-alkene. ***Z*-4g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H); 7.22-7.17 (m, 3H); 6.08 (dt, *J*=1.4, 11.8 Hz, 1H); 5.86 (s, 1H); 5.75-5.69 (m, 1H); 3.69 (s, 3H); 2.67 (t, *J*=8.3 Hz, 2H); 2.27 (q, *J*=8.2 Hz, 2H); 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 167.2, 163.0, 141.9, 134.9, 132.5, 128.4, 128.3, 126.2, 125.8, 125.2, 114.8, 51.0, 37.5, 35.3, 31.0, 29.7, 29.1. HRMS (QTOF) calculated for $C_{18}H_{25}O_2$ 273.1855, found 273.1858 $(M+H)^+$. IR: 2966 cm^{-1}, 2951, 2923, 2867, 2844, 1730, 1625, 1605.



4h

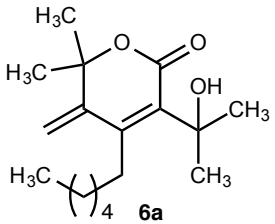
4h (spectra pages S113, S114, and S115): Prepared according to General Procedure E from **3h**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:Et_2O) afforded **4h** (137 mg, 0.66 mmol, 66% as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene). **4h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (d, *J*=11.8 Hz, 1H); 5.76 (s, 1H); 5.75-5.70 (m, 1H); 3.67 (s, 3H); 2.12 (t, *J*=8.9 Hz, 1H); 1.81-1.60 (m, 5H); 1.58 (d, *J*=6.9 Hz, 3H); 1.30-

1.15 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 166.9, 161.3, 127.8, 127.5, 115.1, 51.0, 46.7, 31.7, 26.5, 26.0, 14.7. HRMS (TOF) calculated for $C_{13}H_{20}O_2$ 208.1463, found 208.1462 $(M)^+$. IR: 2923 cm^{-1}, 2863, 1731, 1630.



4i

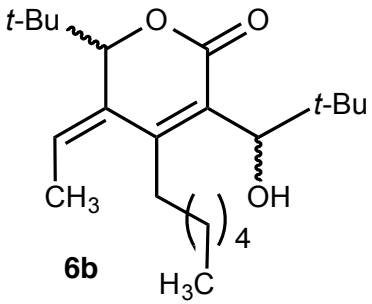
4i (spectra pages S116, S117, and S118): Prepared according to General Procedure E from **3i**: Purification of the residue by flash chromatography (SiO_2, 100:1→20:1 hexanes:Et_2O) afforded **4i** (224 mg, 0.89 mmol, 89% as a separable 5:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene). ***Z*-4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dd, *J*=13.2, 1.9 Hz, 1H); 5.68 (s, 1H); 5.39 (d, *J*=13.2 Hz, 1H); 3.68 (s, 3H); 2.29 (t, *J*=7.5 Hz, 2H); 1.52-1.48 (m, 2H); 1.31 (m, 6H); 1.04 (s, 9H); 0.91 (t, *J*= 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 166.5, 159.4, 139.6, 124.5, 116.2, 50.8, 40.8, 34.5, 31.6, 30.2, 29.0, 27.6, 22.5, 14.0. HRMS (QTOF) calculated for $C_{16}H_{29}O_2$ 253.2168, found 253.2152 $(M+H)^+$. IR: 2950 cm^{-1}, 2864, 2844, 1729, 1622.



6a

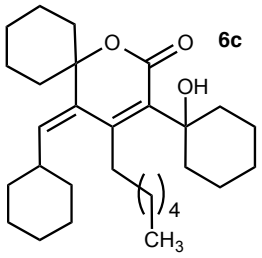
6a (spectra pages S119, S120, and S121): Prepared according to General Procedure F from **3a**: Purification of the residue by flash chromatography (SiO_2, 20:1→4:1 hexanes:EtOAc) afforded **6a** (229 mg, 0.82 mmol, 82%). **6a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (d, *J*=5.0 Hz, 2H); 4.71 (s, 1H); 4.23, 2.20 (m, 1H); 2.46-2.52 (m, 2H); 1.60 (s, 6H); 1.57 (s, 6H); 1.50-1.43 (m, 4H); 1.39-1.27 (m, 3H); 0.90 (t, *J*=4.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100

MHz, $CDCl_3$) 165.6, 146.5, 145.5, 134.4, 114.1, 80.4, 72.2, 31.4, 31.3, 30.3, 30.0, 29.8, 28.5, 27.0, 22.5, 18.7, 14.0. HRMS (TOF) calculated for $C_{17}H_{28}O_3$ 280.2038, found 280.2042 $(M)^+$. IR: 3455 cm^{-1}, 2936, 2864, 2844, 1682 (br).



6b

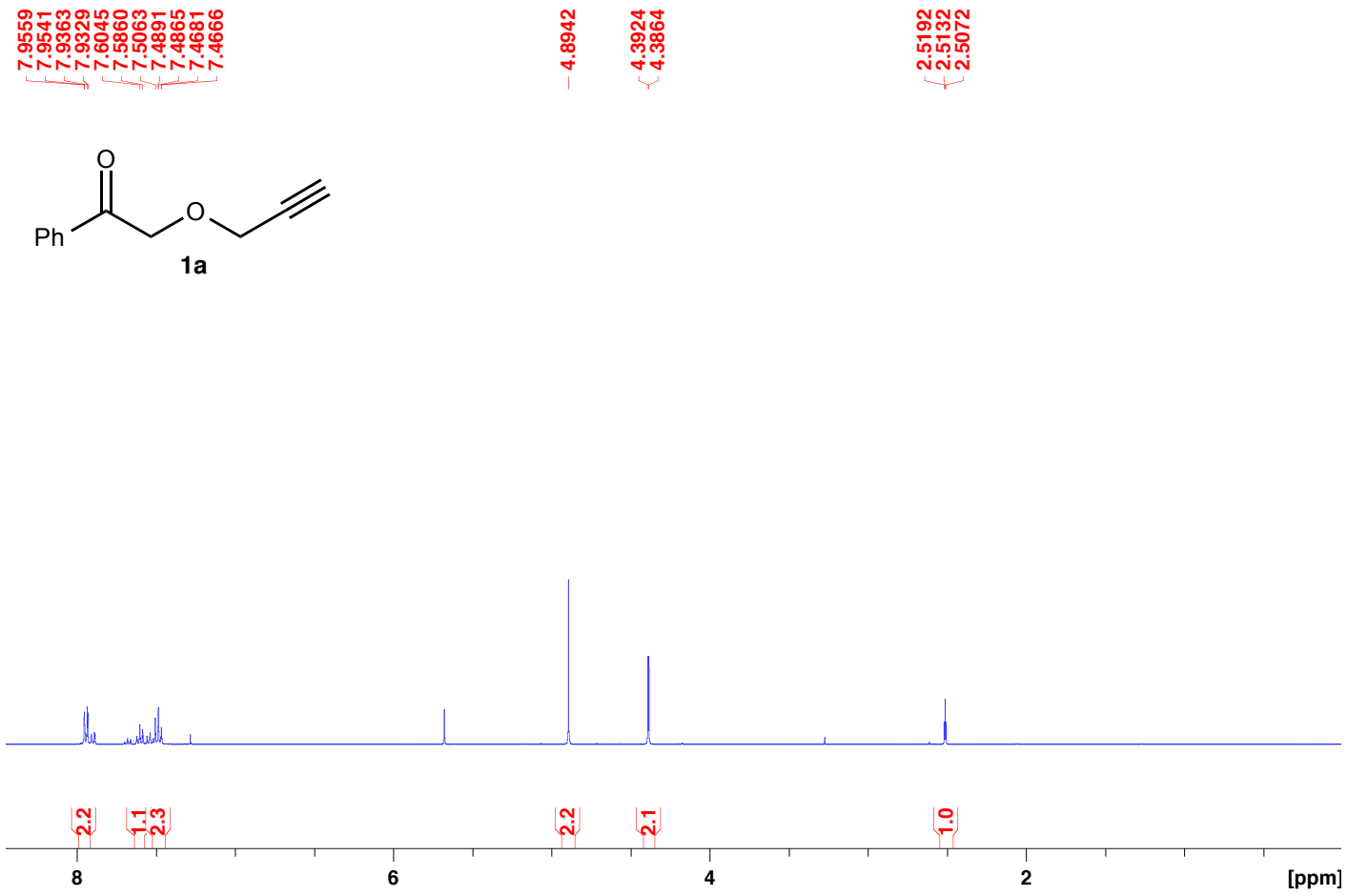
6b (1:1 syn:anti) (spectra pages S122-S127): Prepared according to General Procedure F from **3e**: Purification of the residue by flash chromatography (SiO_2, 20:1→4:1 hexanes:EtOAc) afforded **6b** (213 mg, 0.61 mmol, 61%, as a separable 1:1 mixture of *syn*:*anti* diastereomers). **6b (*syn*)**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.66 (m, 2H); 4.44 (m, 2H); 2.67 (m, 2H); 1.89 (d, *J*=7.3Hz, 3H); 1.42 (m, 3H); 1.33-1.29 (m, 5H); 0.99 (s, 9H); 0.98 (s, 9H); 0.93 (t, *J*=7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 166.2, 152.8, 133.2, 128.6, 125.9, 92.2, 37.8, 36.3, 31.4, 31.2, 30.0, 27.2, 26.9, 26.8, 22.6, 15.5, 13.9. HRMS (QTOF) calculated for $C_{22}H_{38}NaO_3$ 373.2719, found 373.2714 $(M+Na)^+$. IR: 3440 cm^{-1}, 2955, 2934, 2869, 1674 (br), 1629. **6b (anti)**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.72 (q, *J*=7.4 Hz, 1H); 4.44 - 4.39 (m, 3H); 2.69 (m, 1H); 2.50 (m, 1H); 1.89 (d, *J*=7.4 Hz, 3H); 1.42-1.40 (m, 3H); 1.38-1.29 (m, 5H); 0.97 (s, 9H); 0.95 (s, 9H); 0.90 (t, *J*= 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 164.7, 151.8, 132.0, 129.1, 127.2, 92.7, 76.5, 38.2, 36.6, 32.4, 31.5, 30.0, 28.3, 27.4, 27.3, 26.5, 26.4, 26.3, 22.5, 15.5, 13.9. HRMS (QTOF) calculated for $C_{22}H_{39}O_3$ 351.2899, found 351.2897 $(M+H)^+$. IR: 3446 cm^{-1}, 2981, 2966, 2952, 2937, 2922, 2866, 2844, 2826, 1738, 1681, 1635.



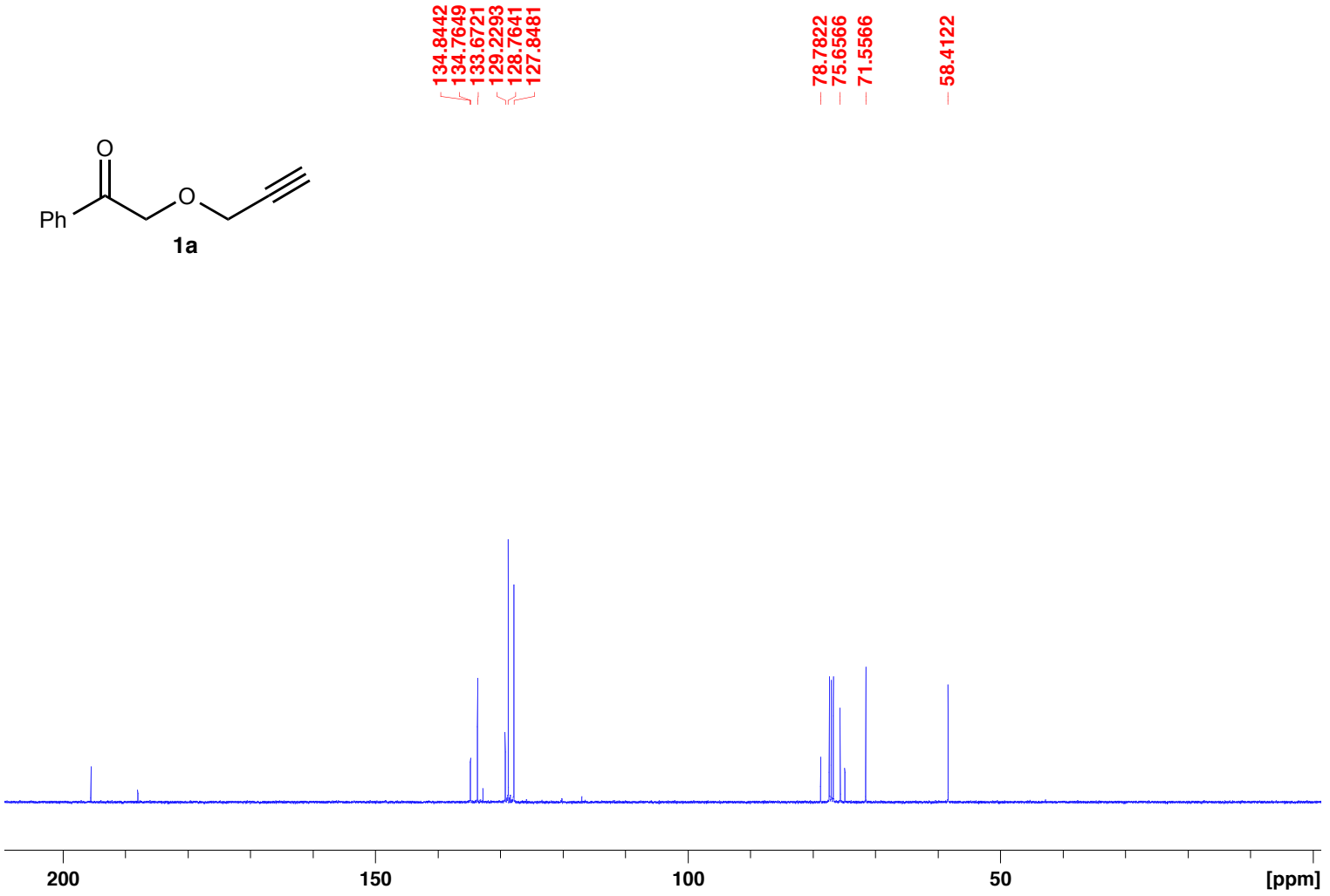
6c (spectra pages S128, S129, and S130): Prepared according to General Procedure G from **3c**: Purification of the residue by flash chromatography (SiO_2, 20:1→4:1 hexanes:EtOAc) afforded **6c** (260 mg, 0.59 mmol, 59%). **6c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (d, *J*=10.2 Hz, 1H); 4.53 (s, 1H); 3.76 (m, 1H); 2.66 (m, 2H); 2.09 (m, 2H); 1.92 (m, 4H); 1.88-1.56 (m, 18H); 1.46-1.31 (m, 12H); 1.20 (m, 2H); 0.93 (t, *J*=6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz,$CDCl_3$) 166.8, 147.1, 136.0, 135.8, 134.4, 82.3, 73.8, 38.4, 36.9, 34.1, 33.1, 32.9, 31.4, 29.8, 28.8, 25.8, 25.6, 25.5, 25.4, 22.5, 22.0, 21.6, 14.0. HRMS (QTOF) calculated for $C_{29}H_{46}NaO_3$ 465.3345, found 465.3348 $(M+Na)^+$. IR: 3480 cm^{-1}, 2981, 2966, 2923, 2845, 2860, 1683, 1636.

^{1}H NMR and ^{13}C NMR spectra for compounds **1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 2a, 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2i, 2j, 2k, 2l, 3a, 3b, 3e, 3f, 3g, 3h, 3i, 4a, 4b, 4e, 4f, 4g, 4h, 4i, 6a, 6b(syn), 6b(anti), 6c**: pp. S22-S83

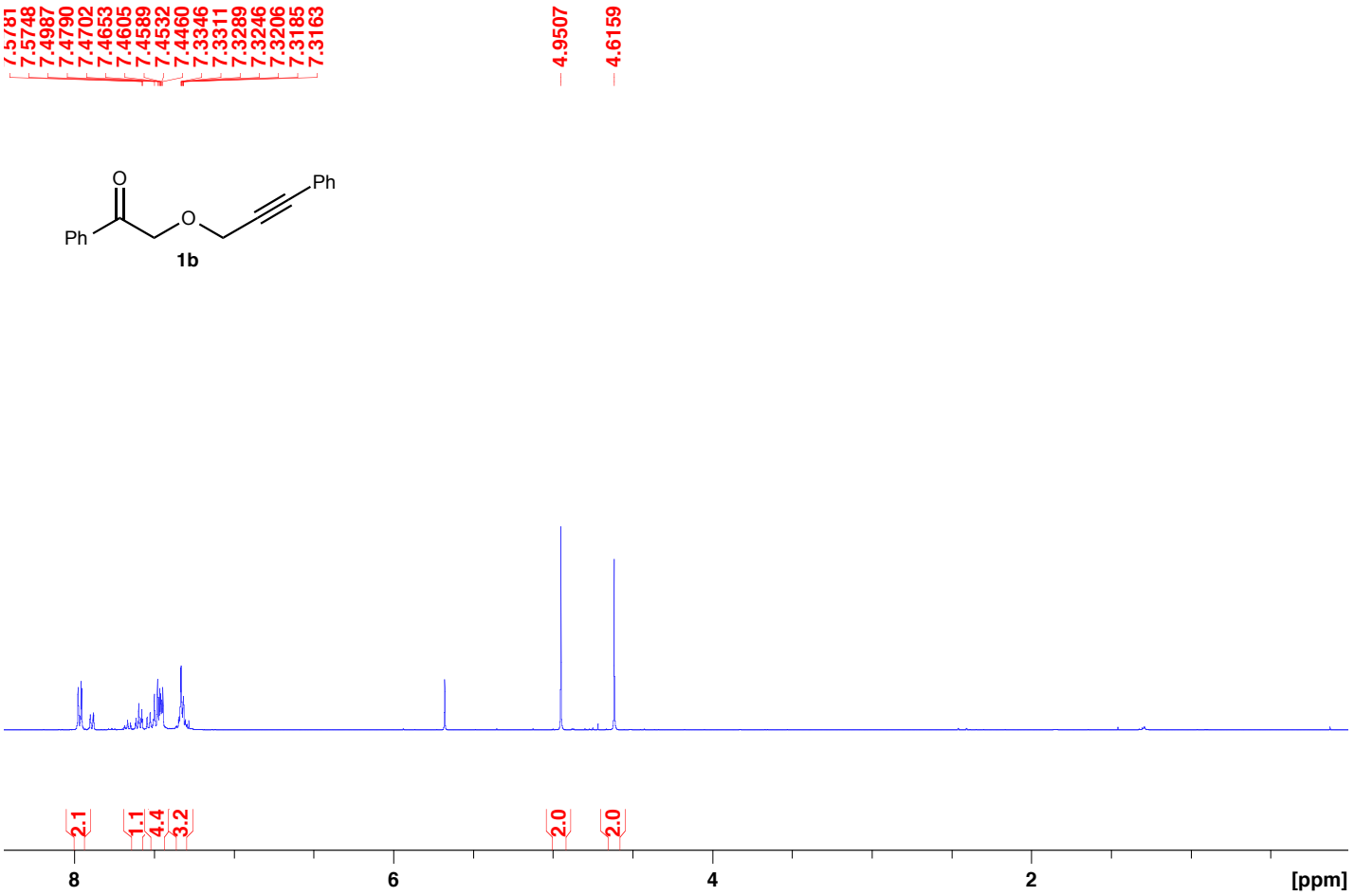
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 4:1 mixture with diazoacetophenone



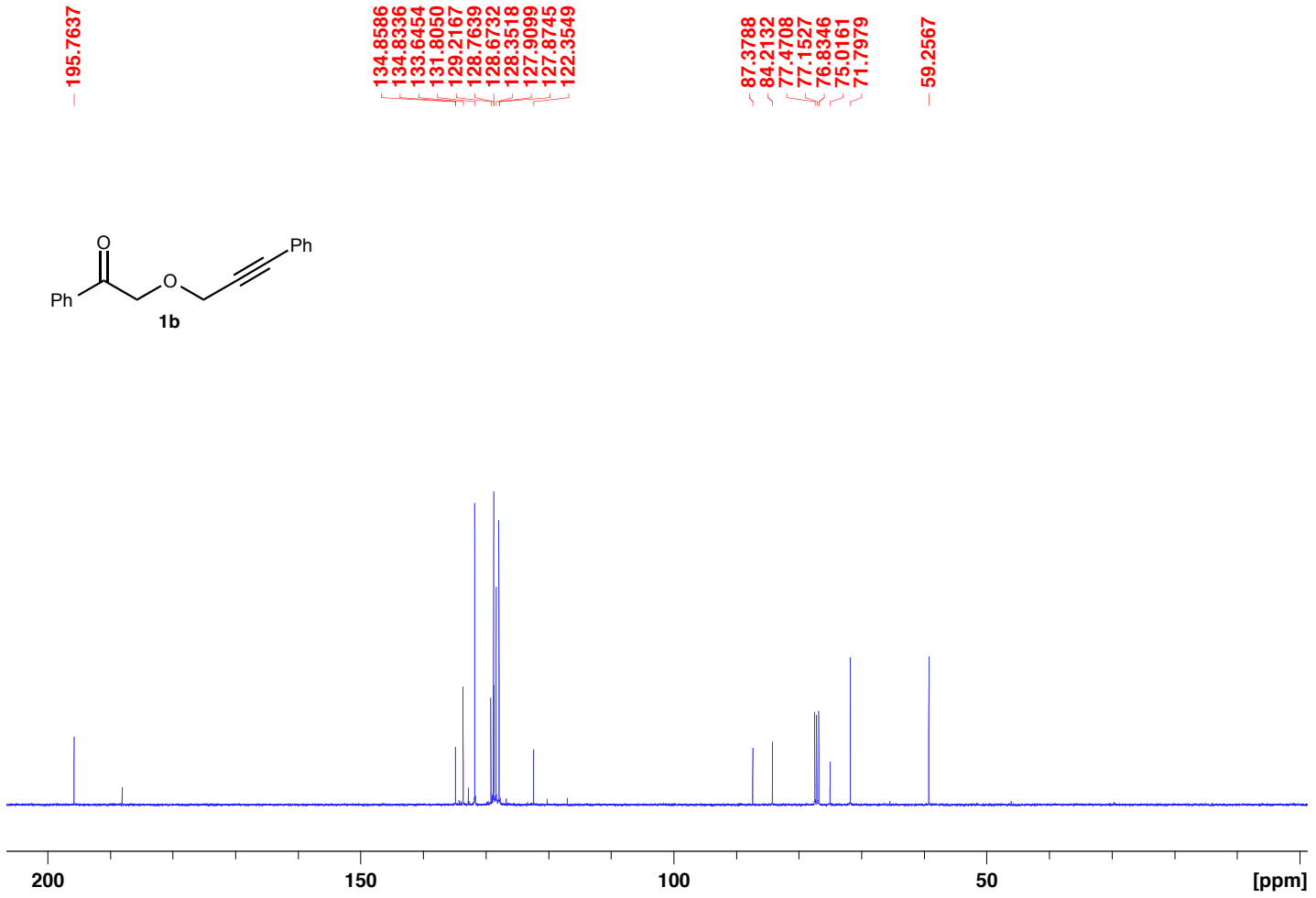
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 4:1 mixture with diazoacetophenone



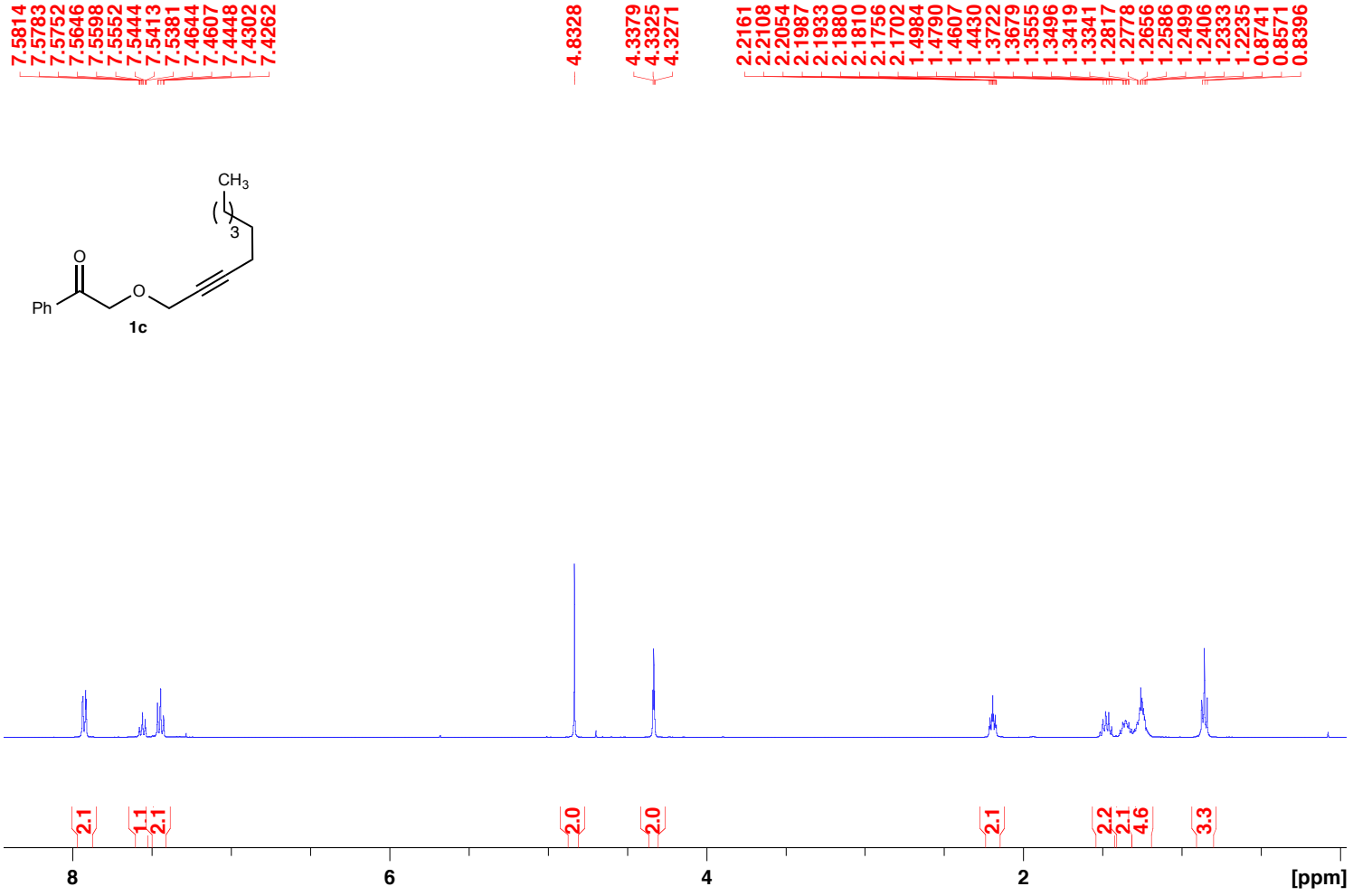
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 3:1 mixture with diazoacetophenone



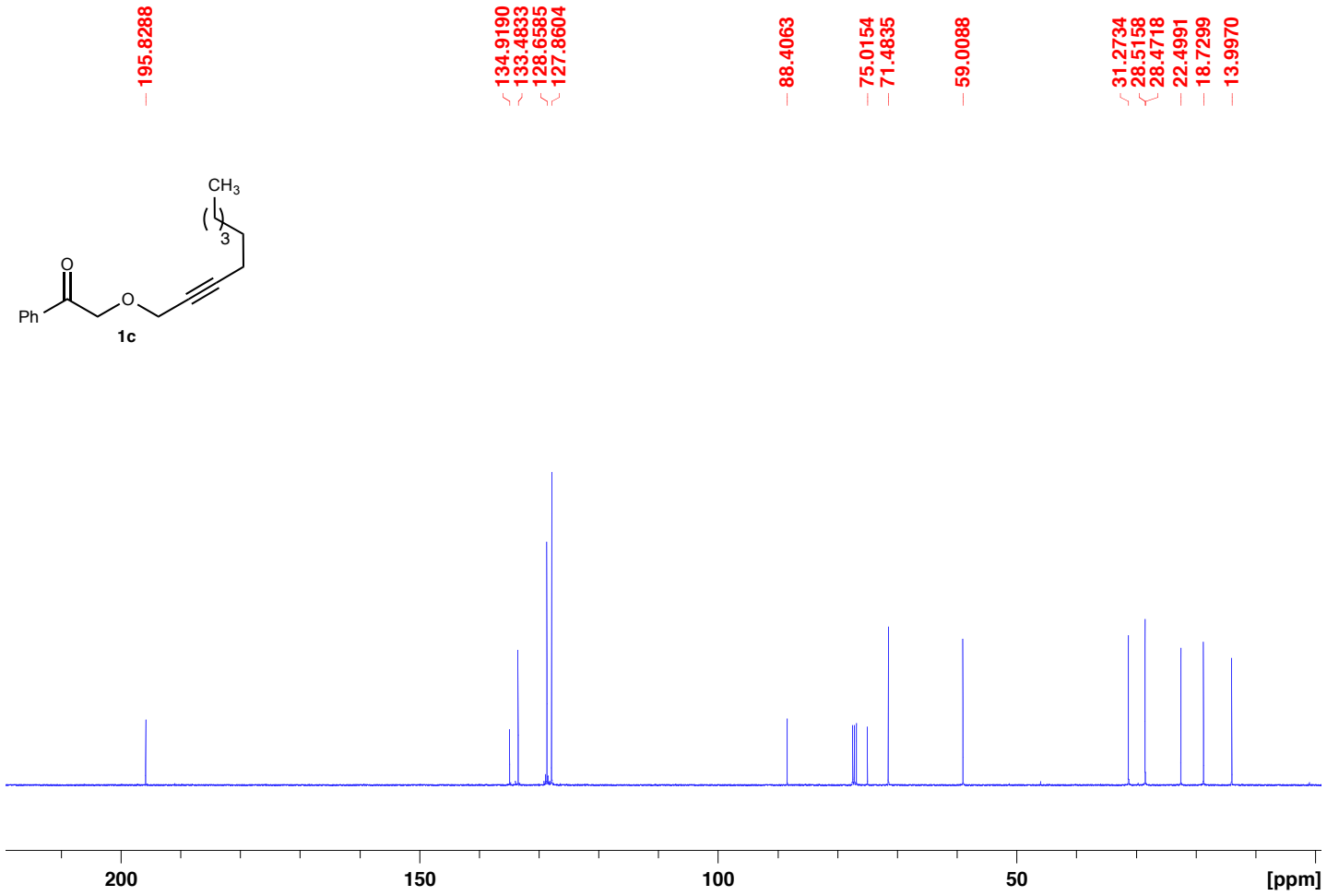
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



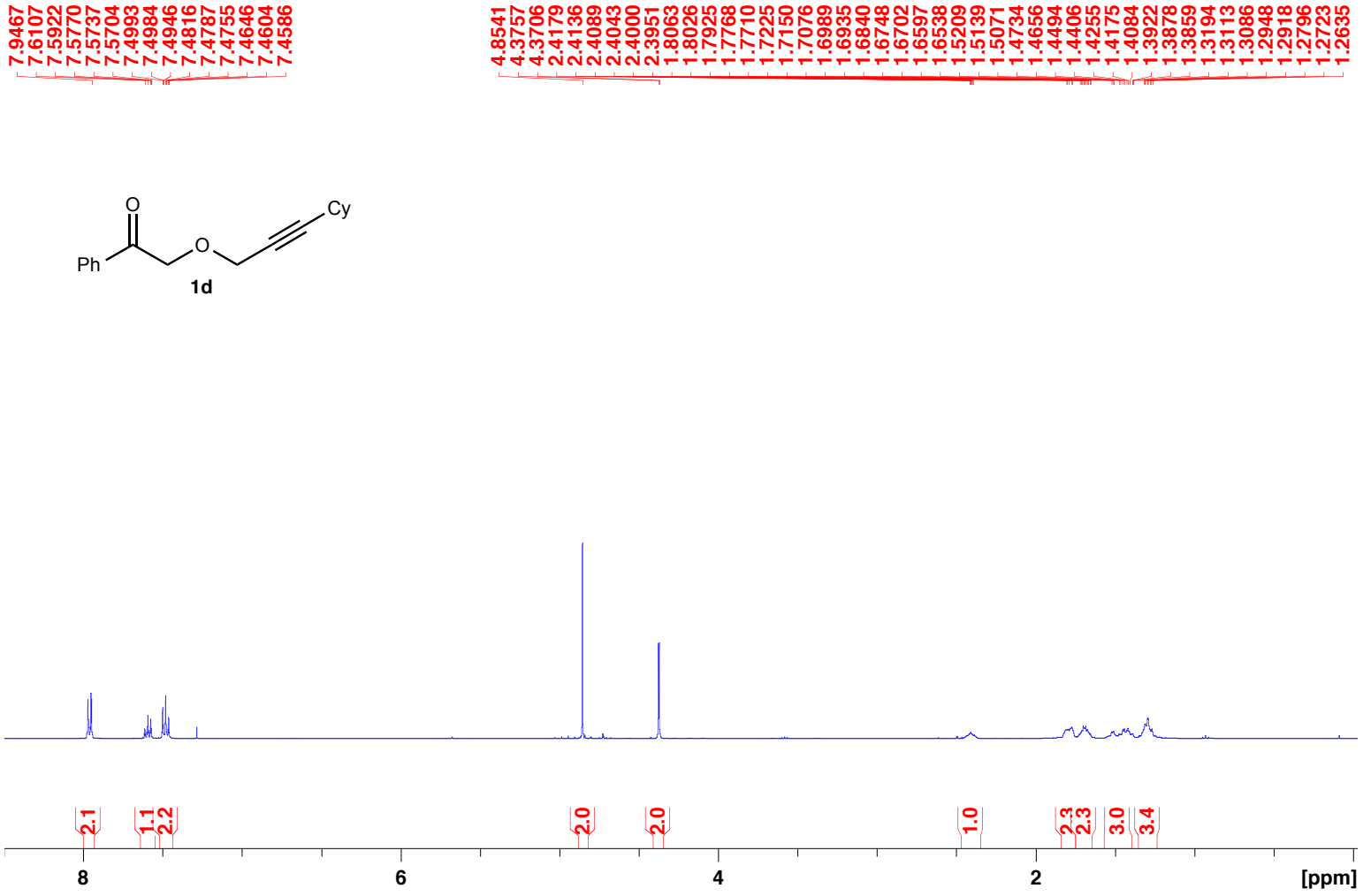
^{1}H NMR (400 MHz), $CDCl_3$



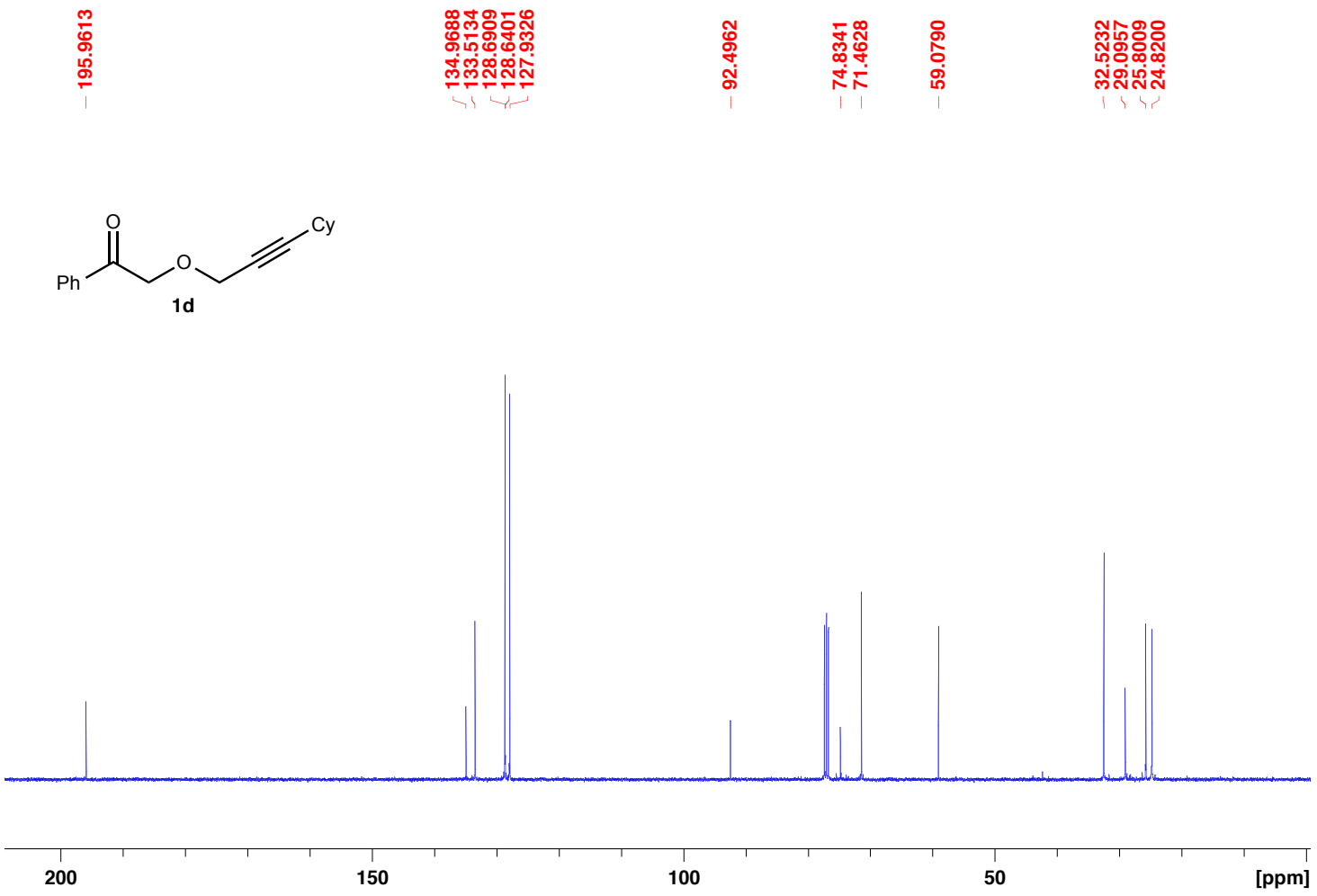
$^{3}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$

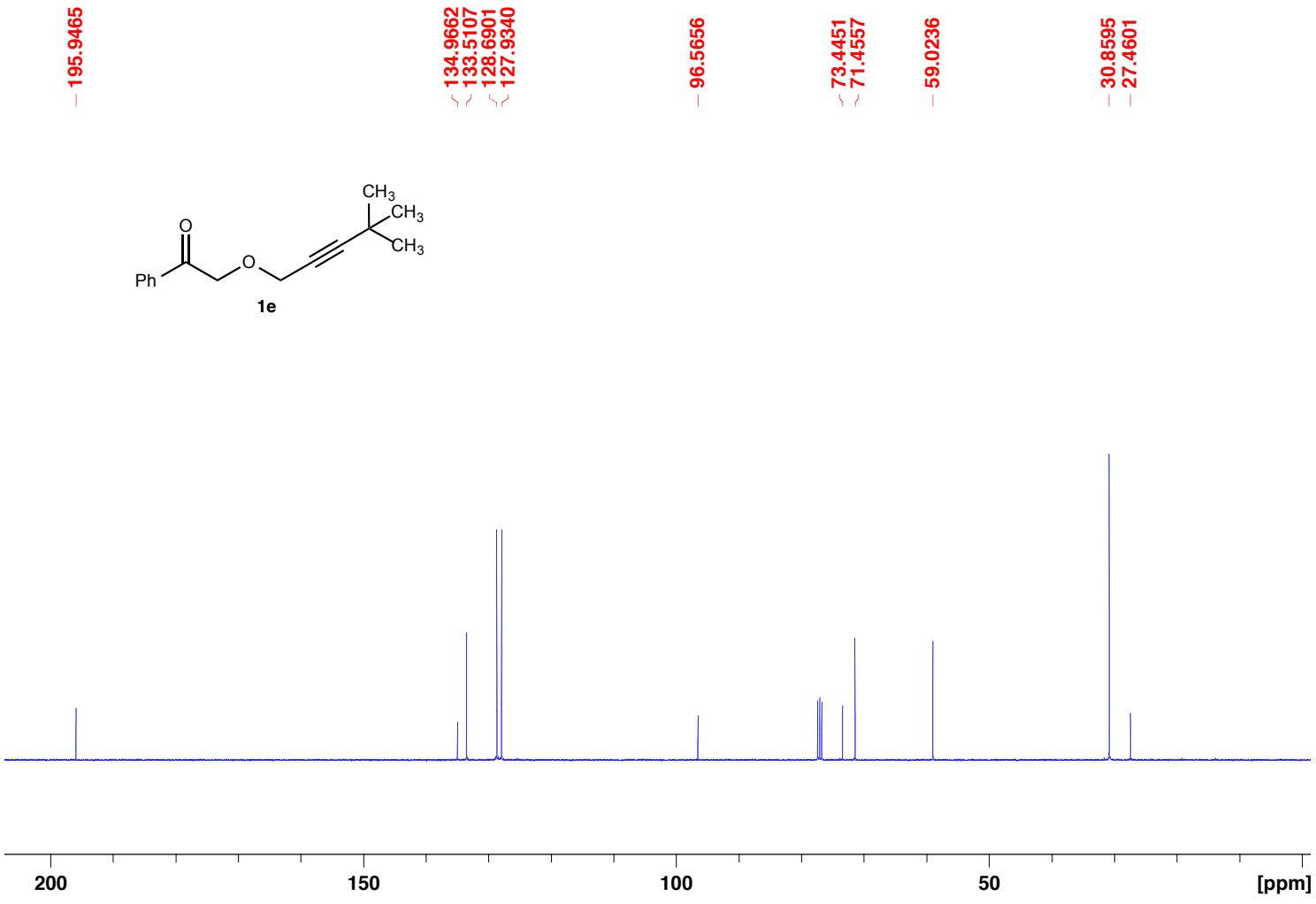


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



H^1 NMR (400 MHz), $CDCl_3$

$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$

7.6140
7.6033
7.6001
7.5969
7.5255
7.5217
7.5060
7.4873
7.3357
7.3174
7.3039
7.2993
7.2840
7.2618
7.2583
7.2409
7.2228

5.0454
5.0042
4.8671
4.8259
4.3559
4.3507
4.3397
4.3346
4.3233
4.3182
2.9155
2.8958
2.8760
2.5658
2.5606
2.2881
2.2710
2.2689
2.2540
2.2523
2.2371
2.2346
2.2177
2.2152
2.2015
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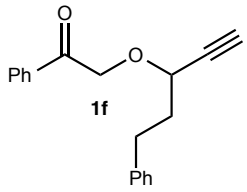

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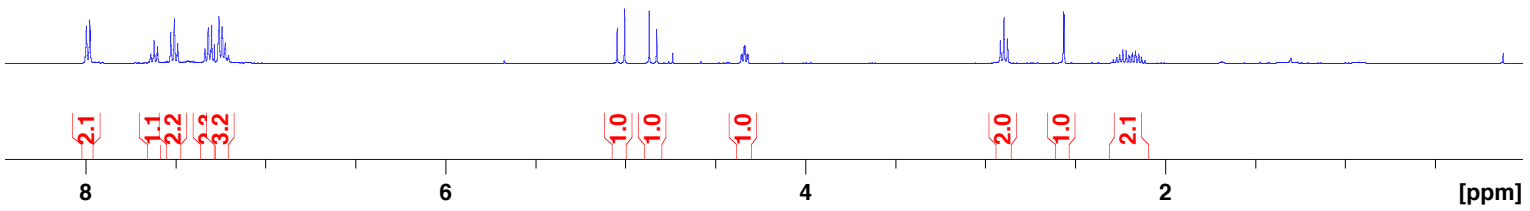
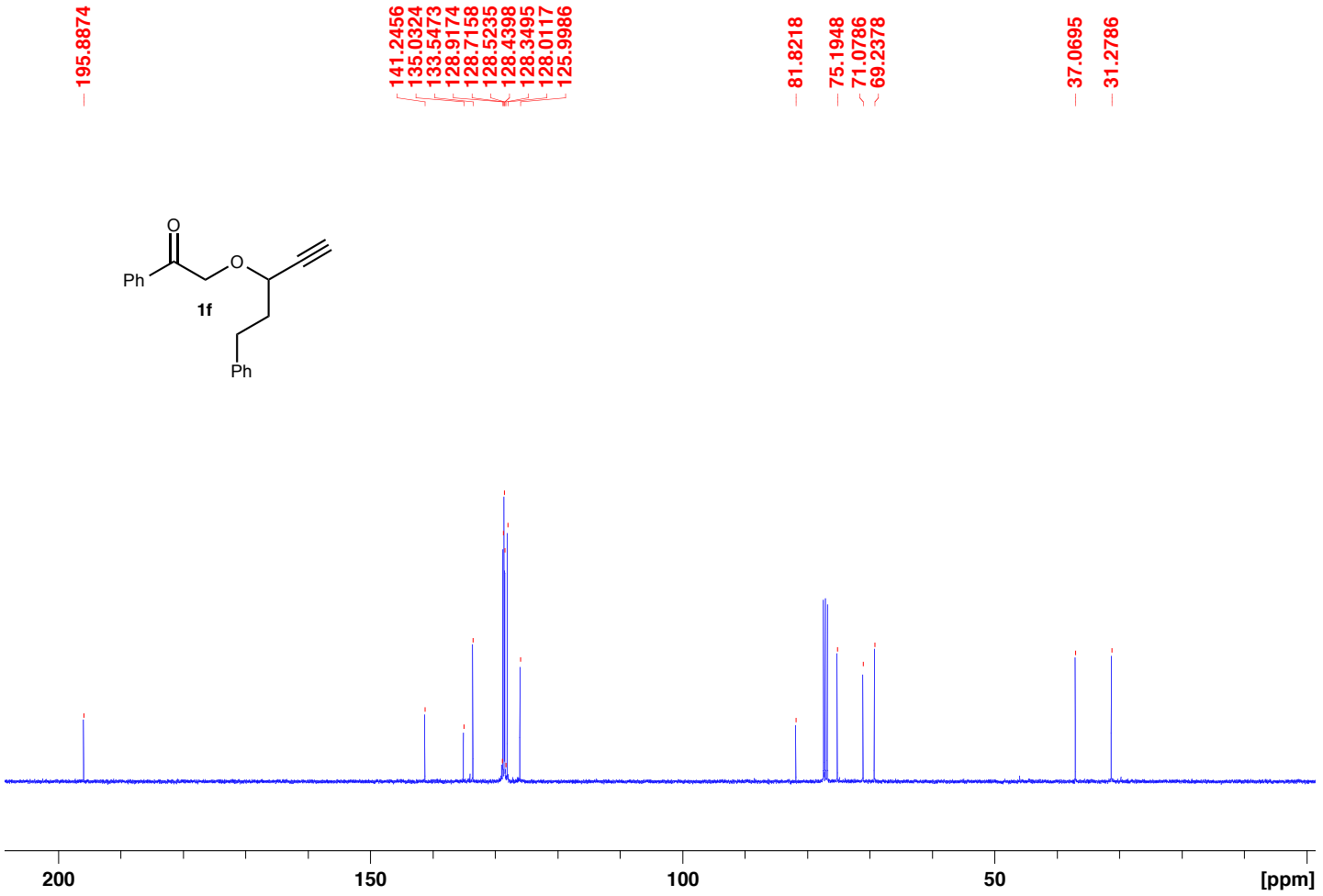
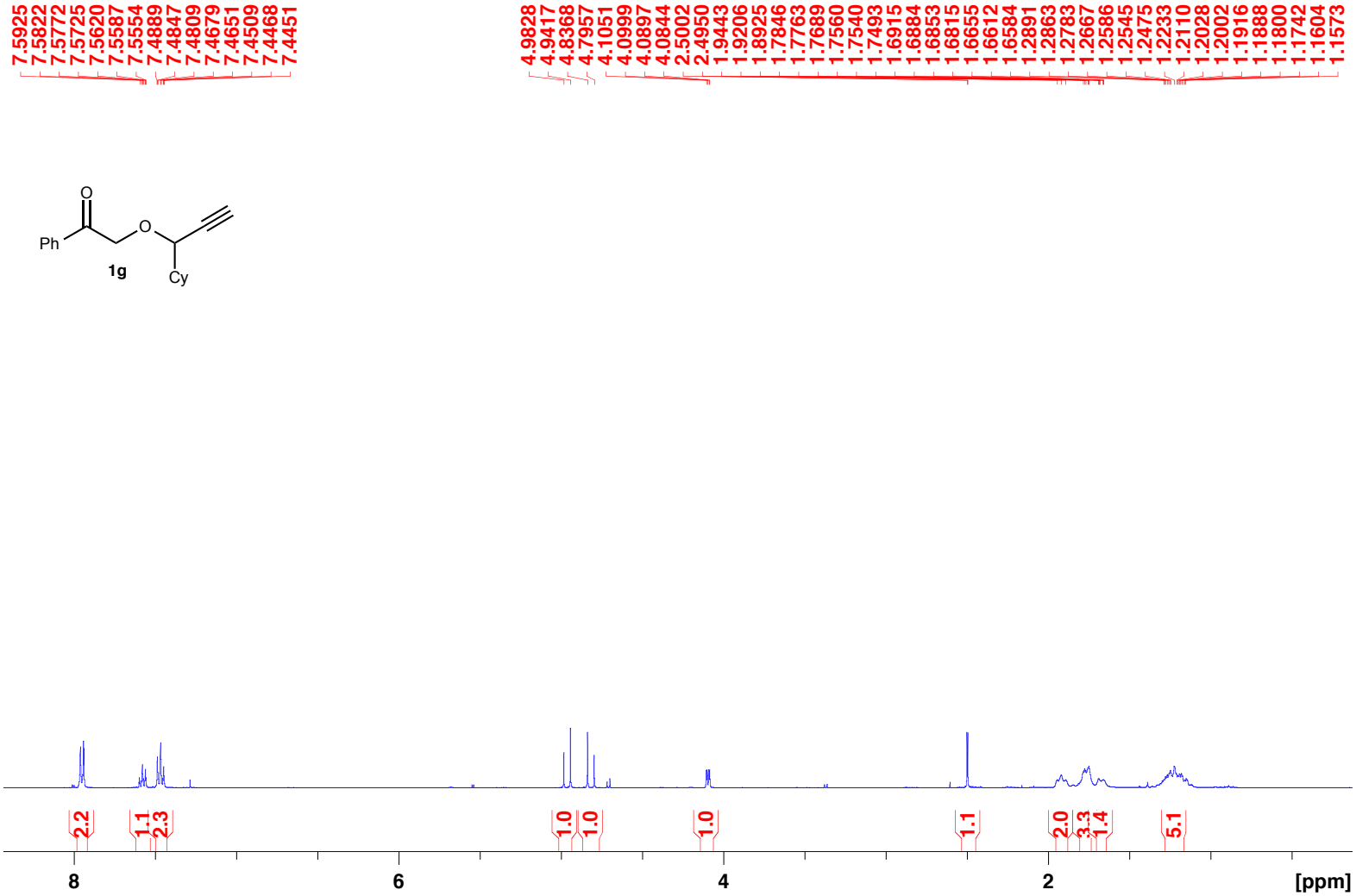


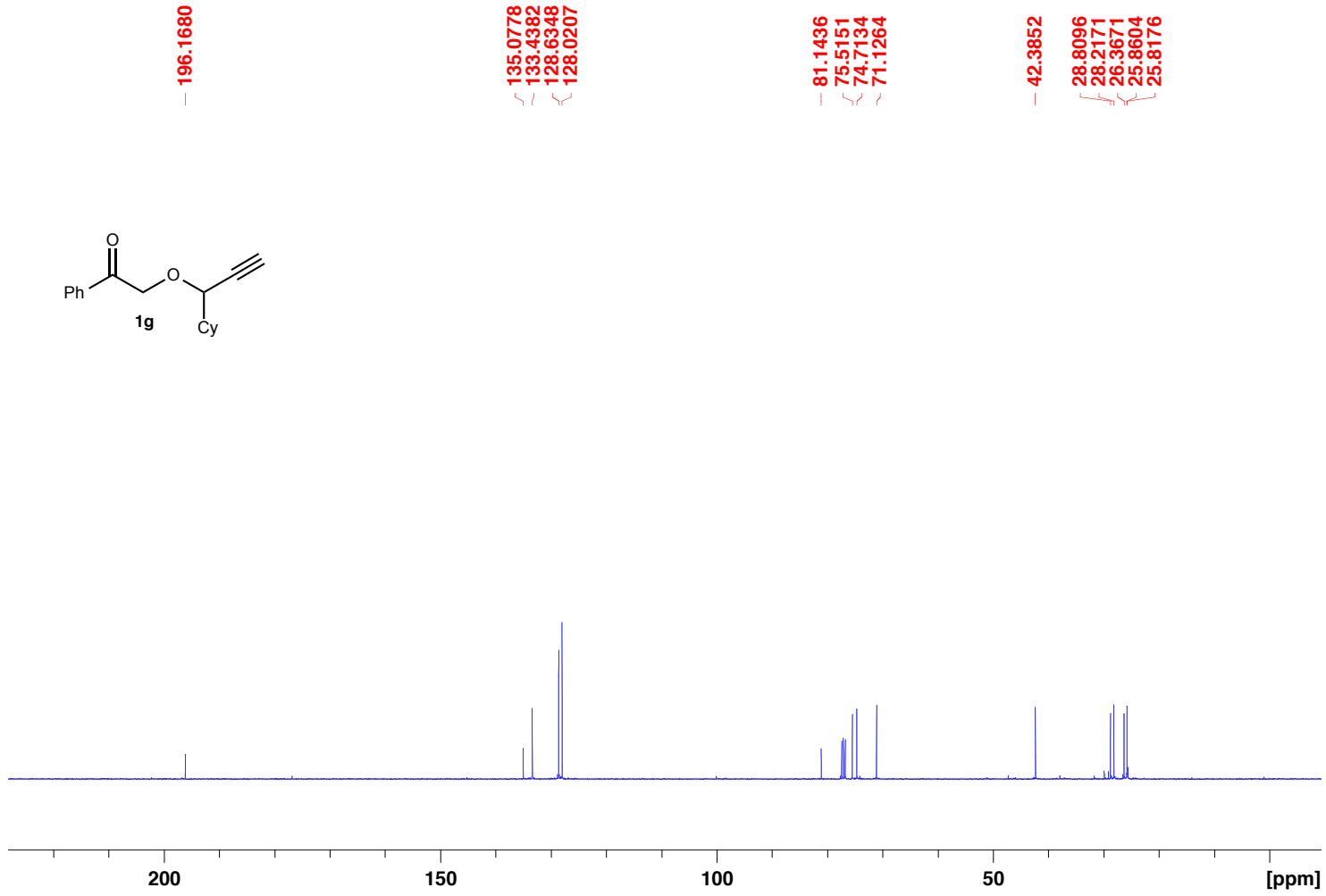
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



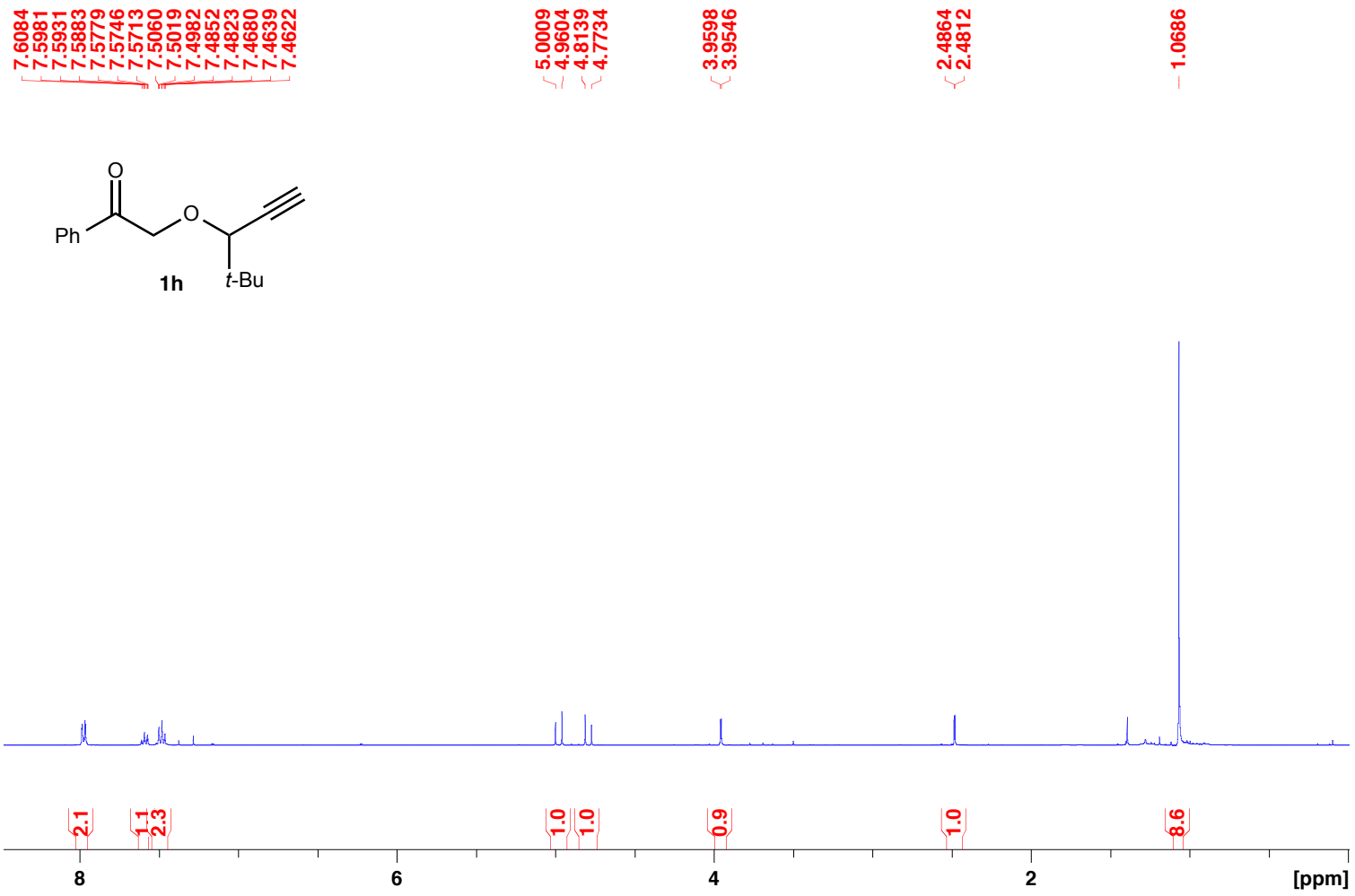
^{1}H NMR (400 MHz), $CDCl_3$



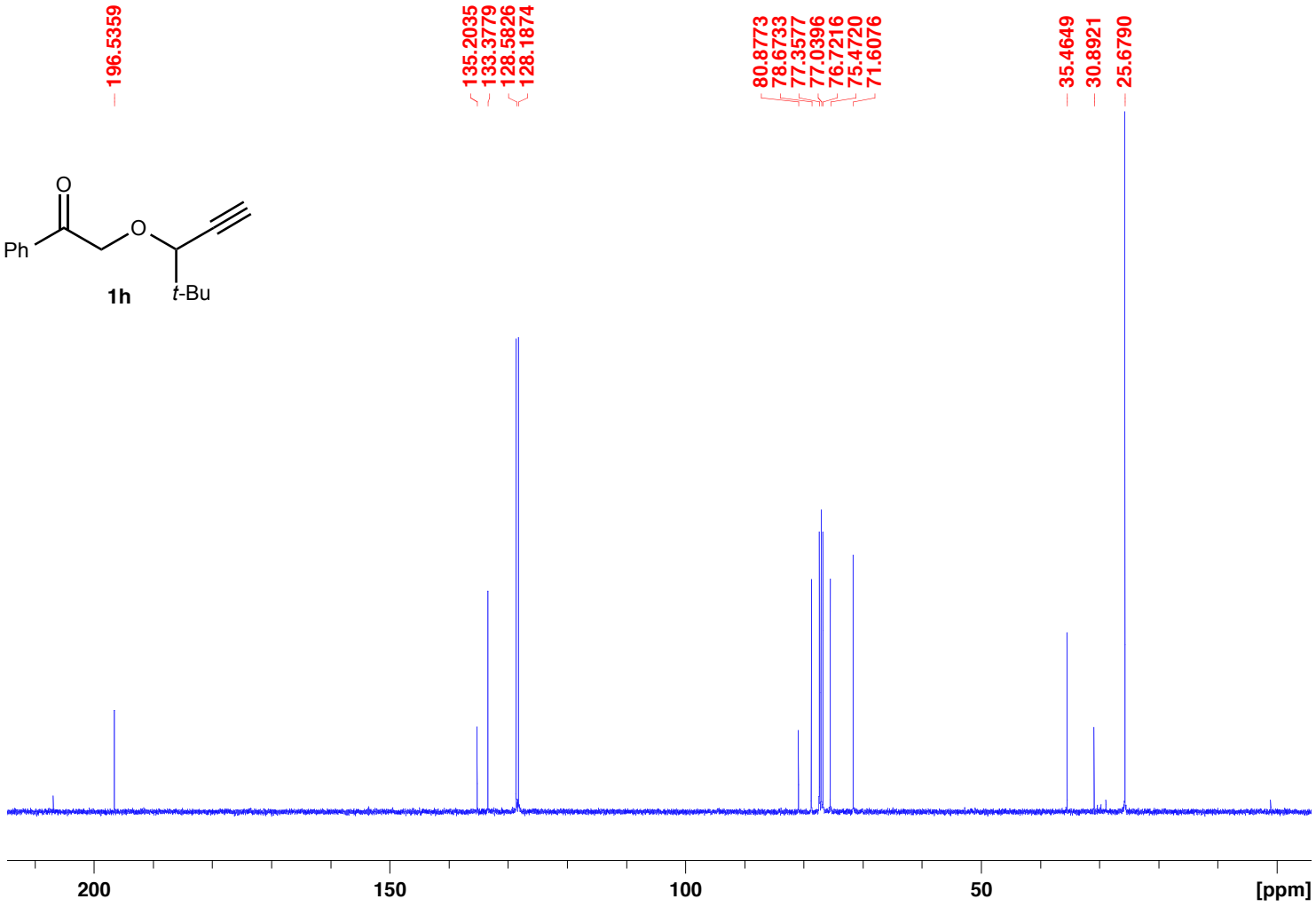
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



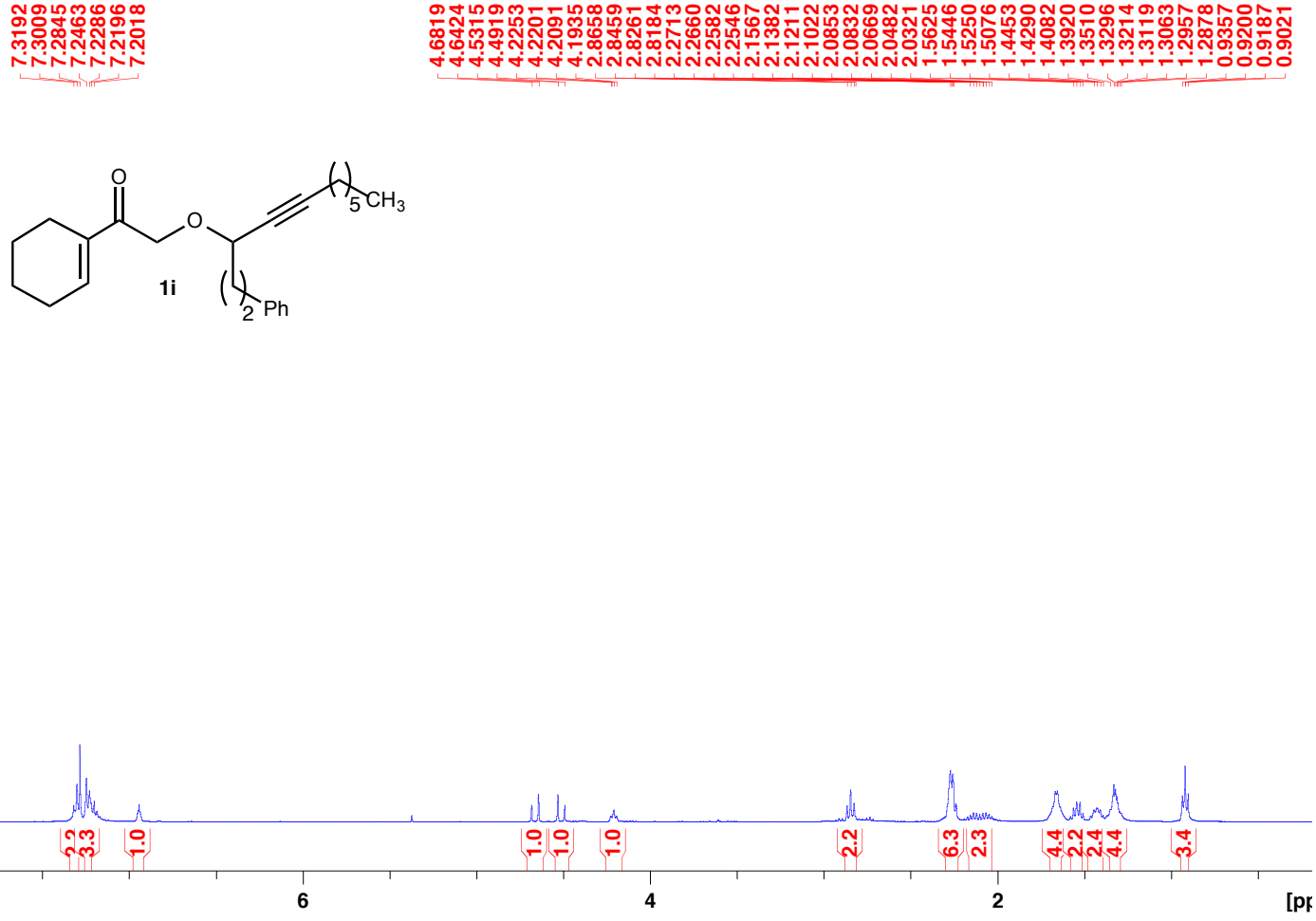
^{1}H NMR (400 MHz), $CDCl_3$



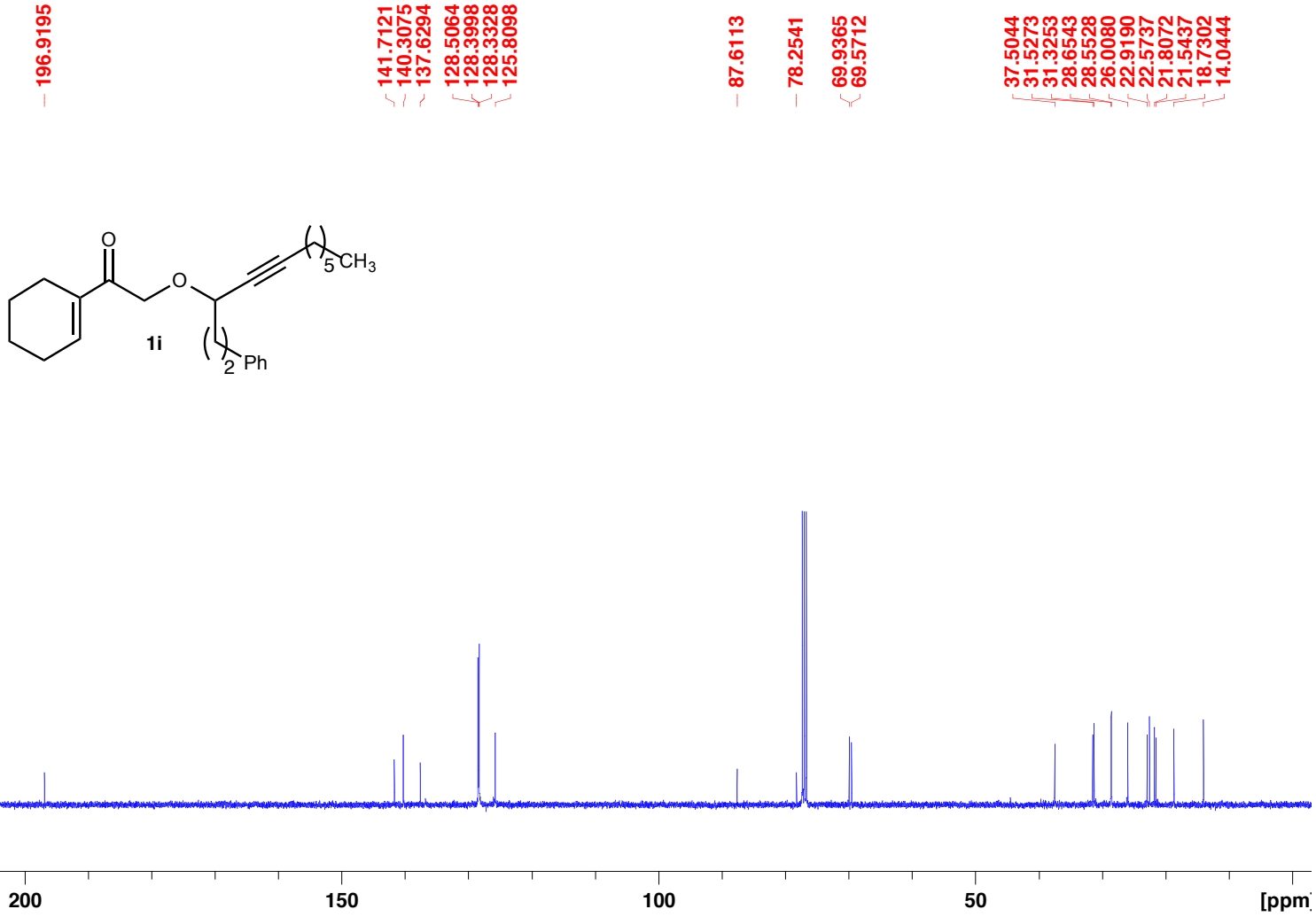
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



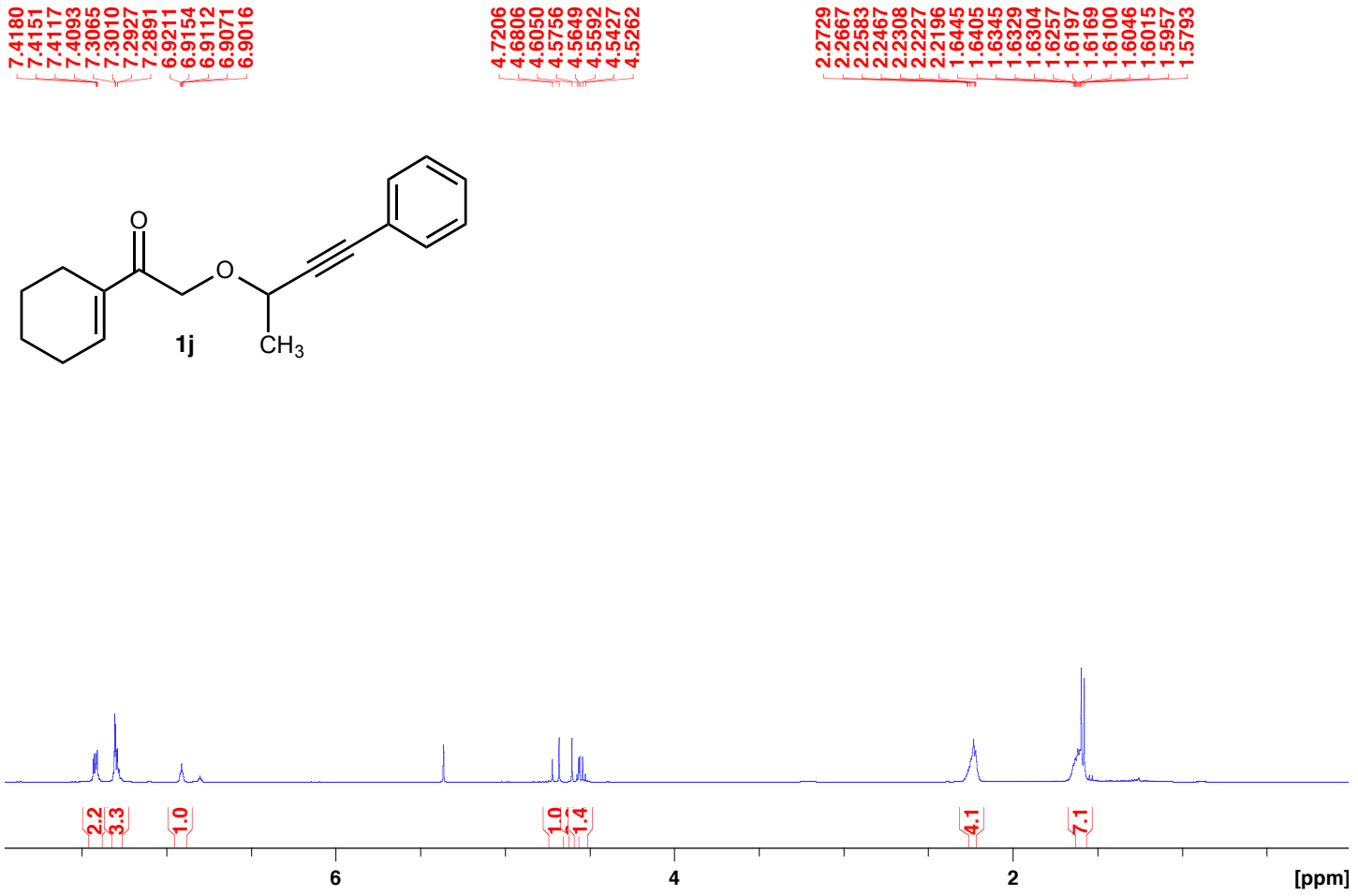
^{1}H NMR (400 MHz), $CDCl_3$



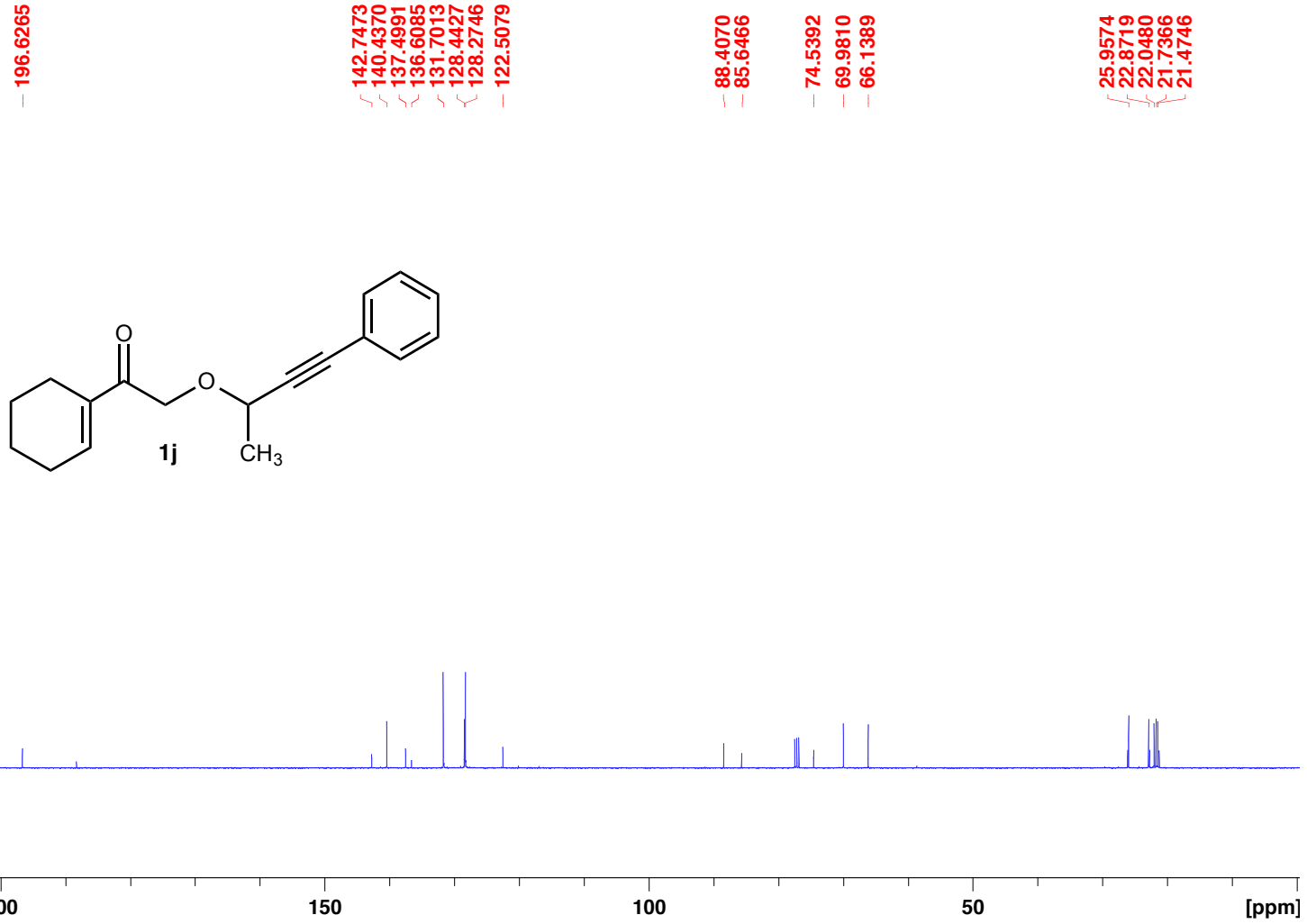
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



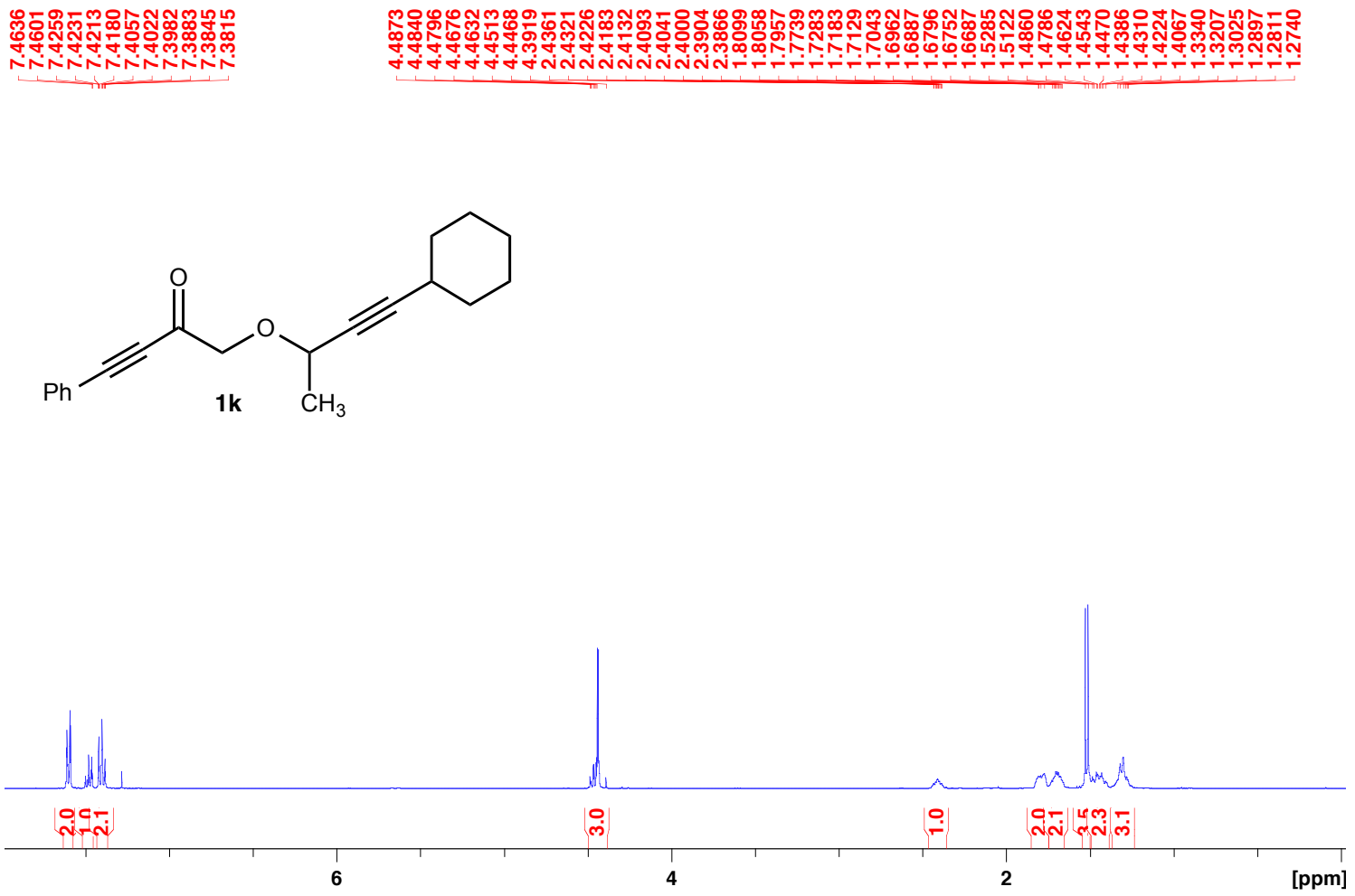
^{1}H NMR (400 MHz), $CDCl_3$



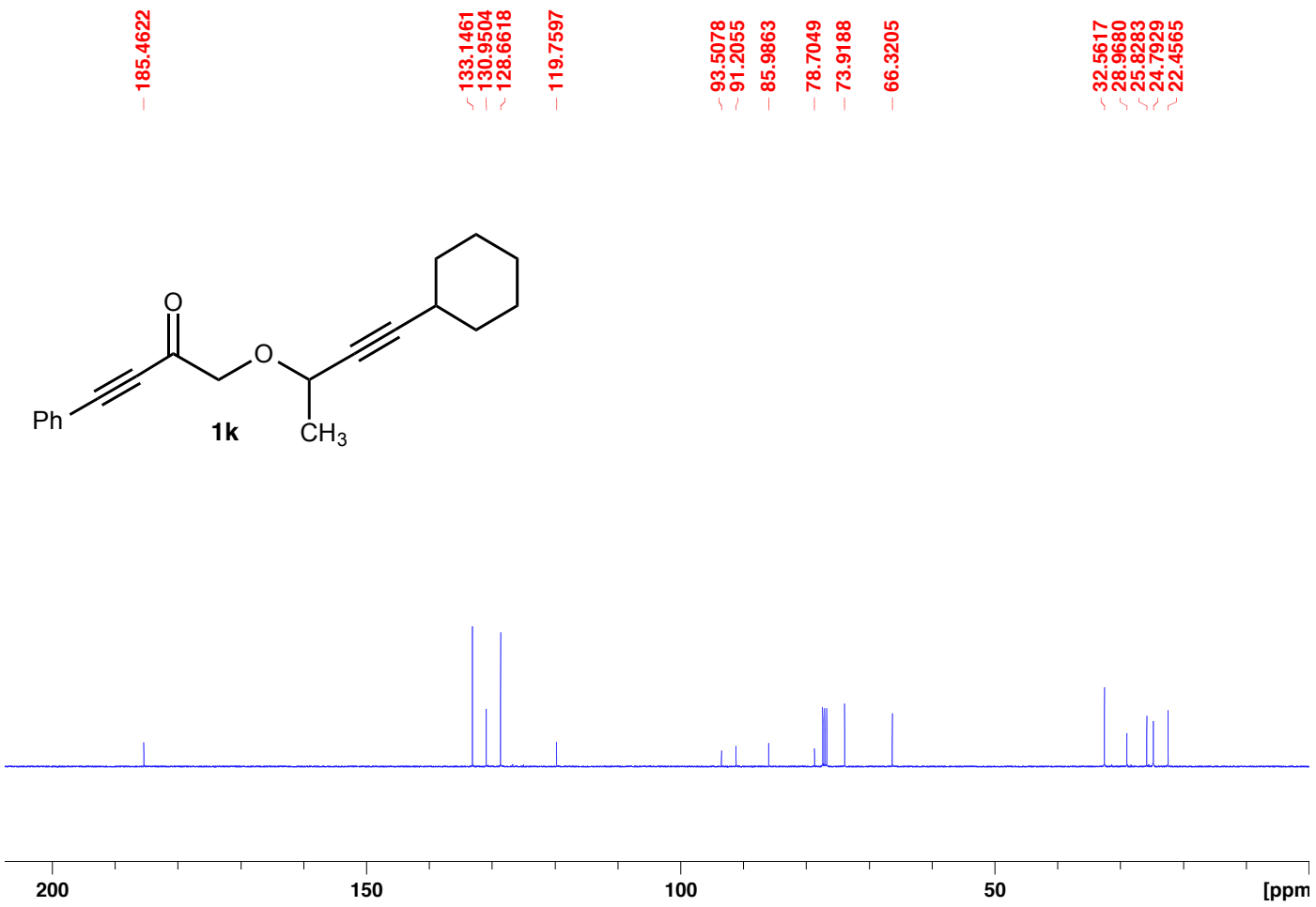
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



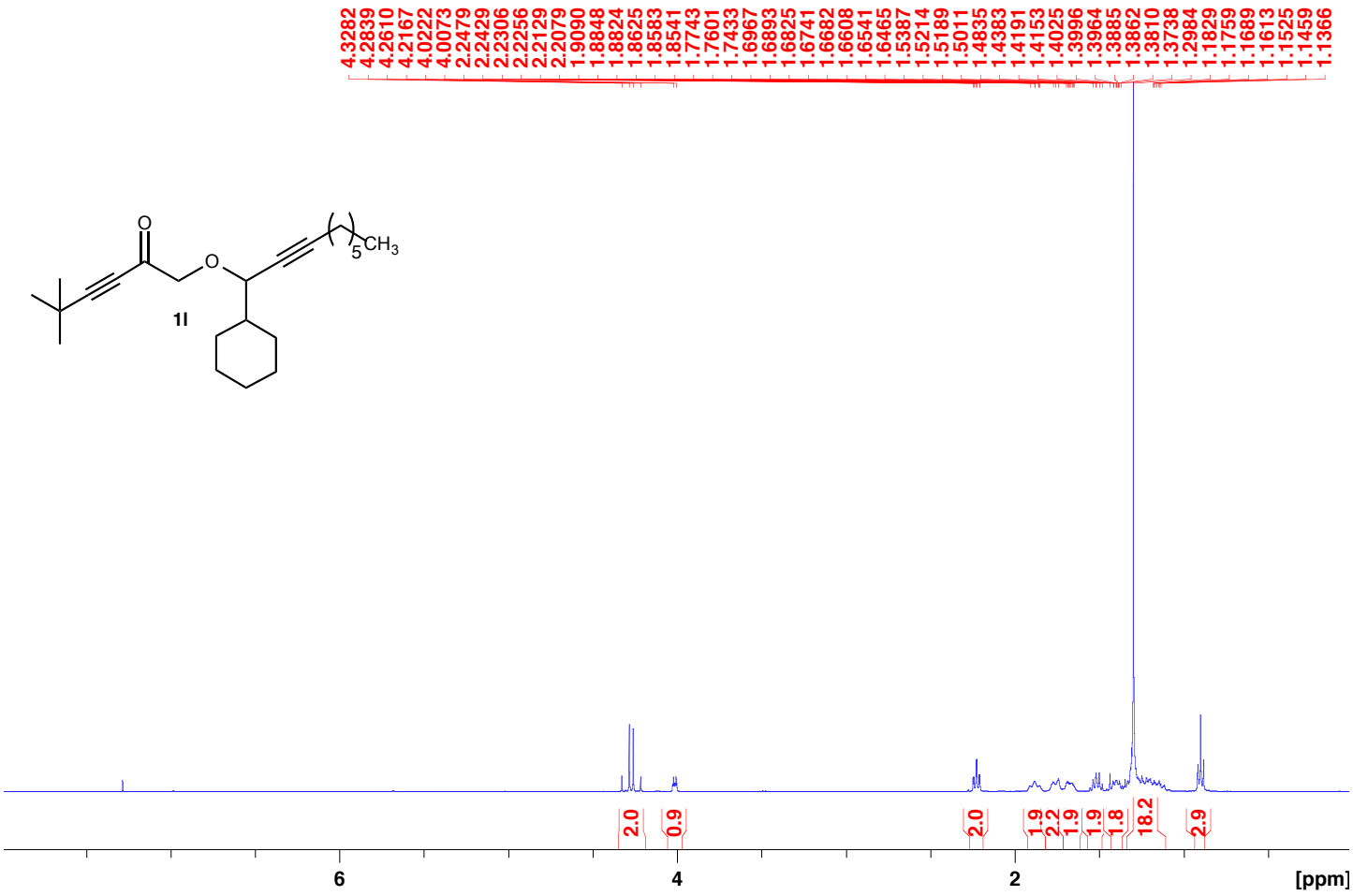
^{1}H NMR (400 MHz), $CDCl_3$



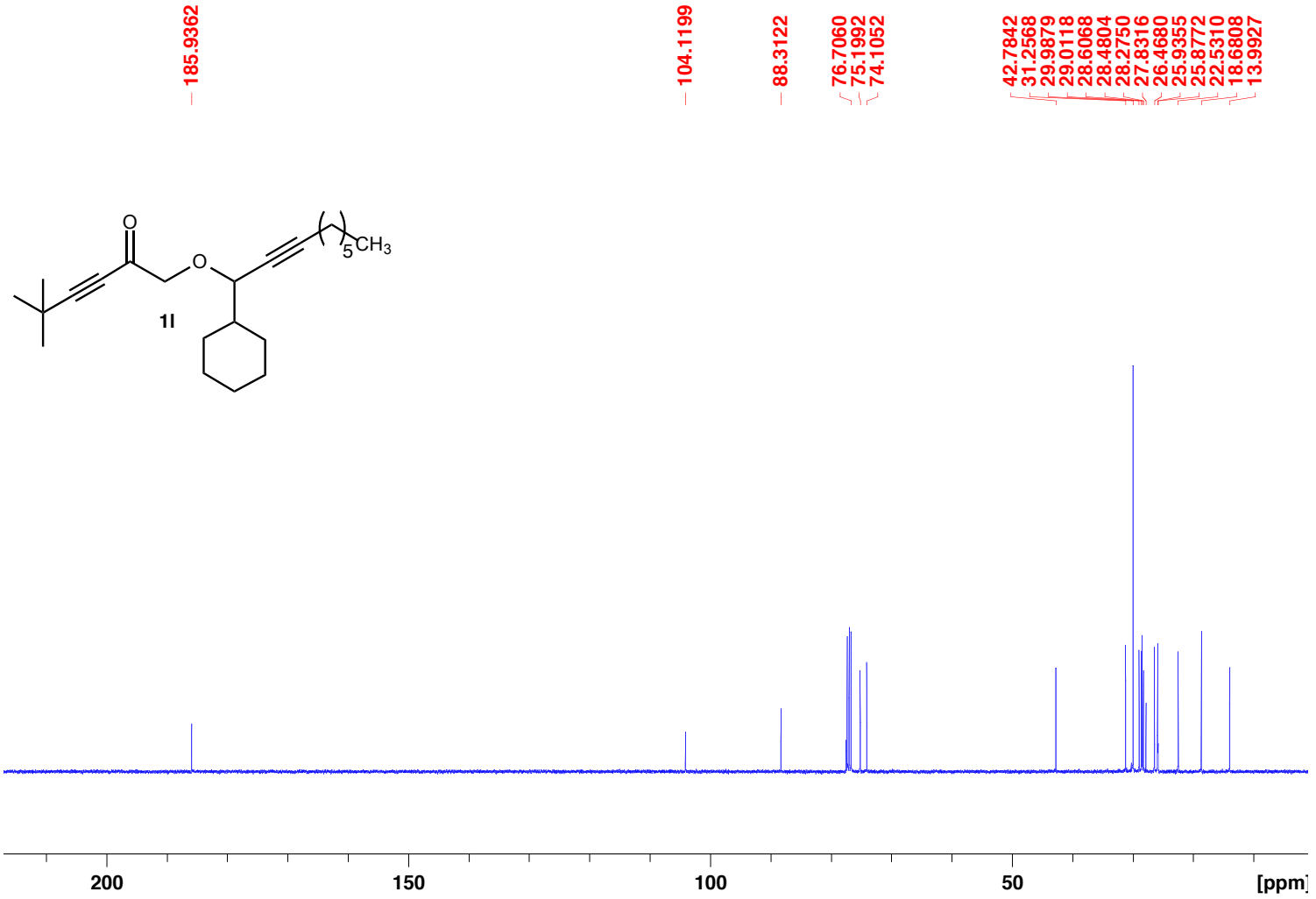
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



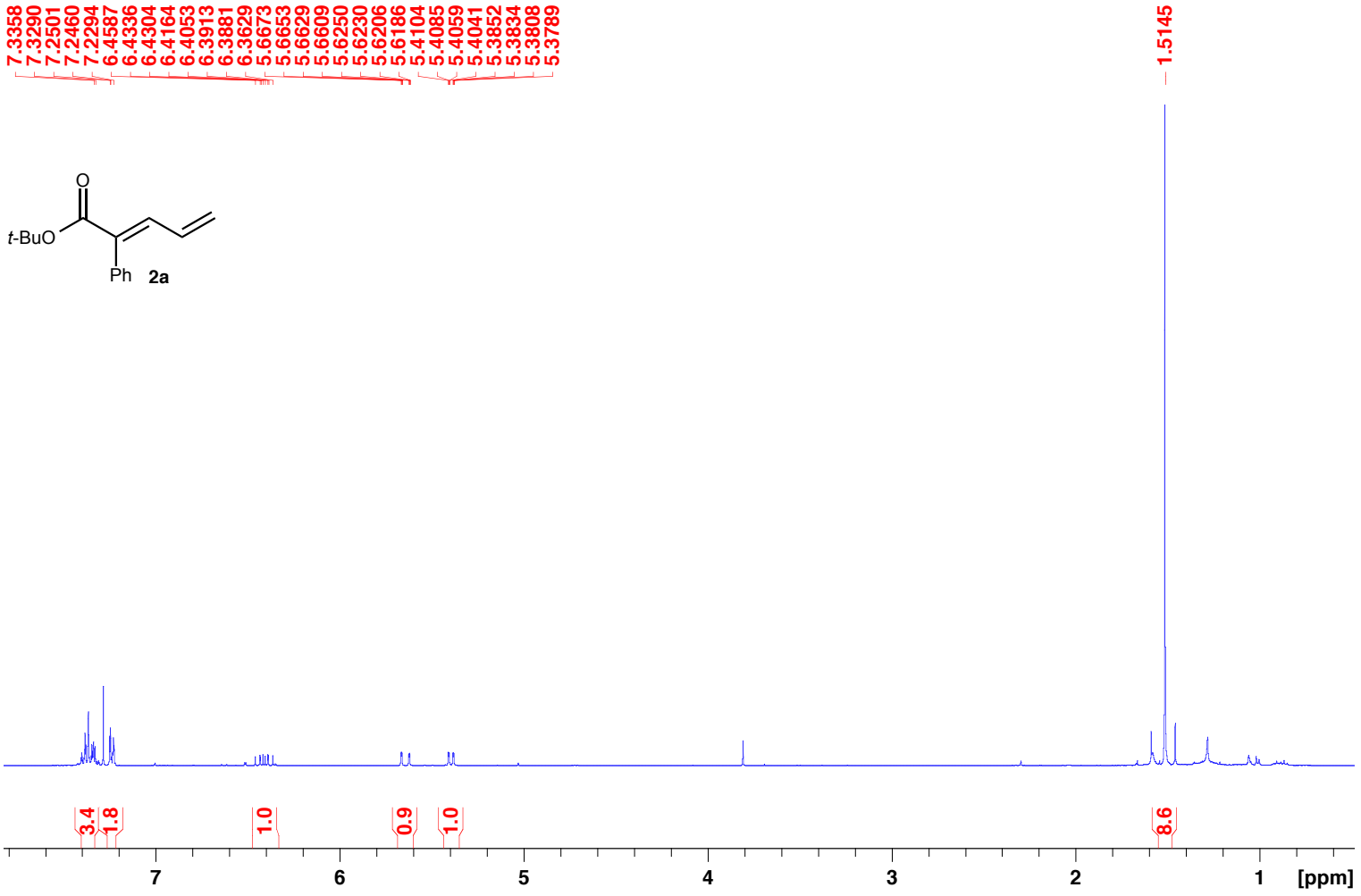
^{1}H NMR (400 MHz), $CDCl_3$



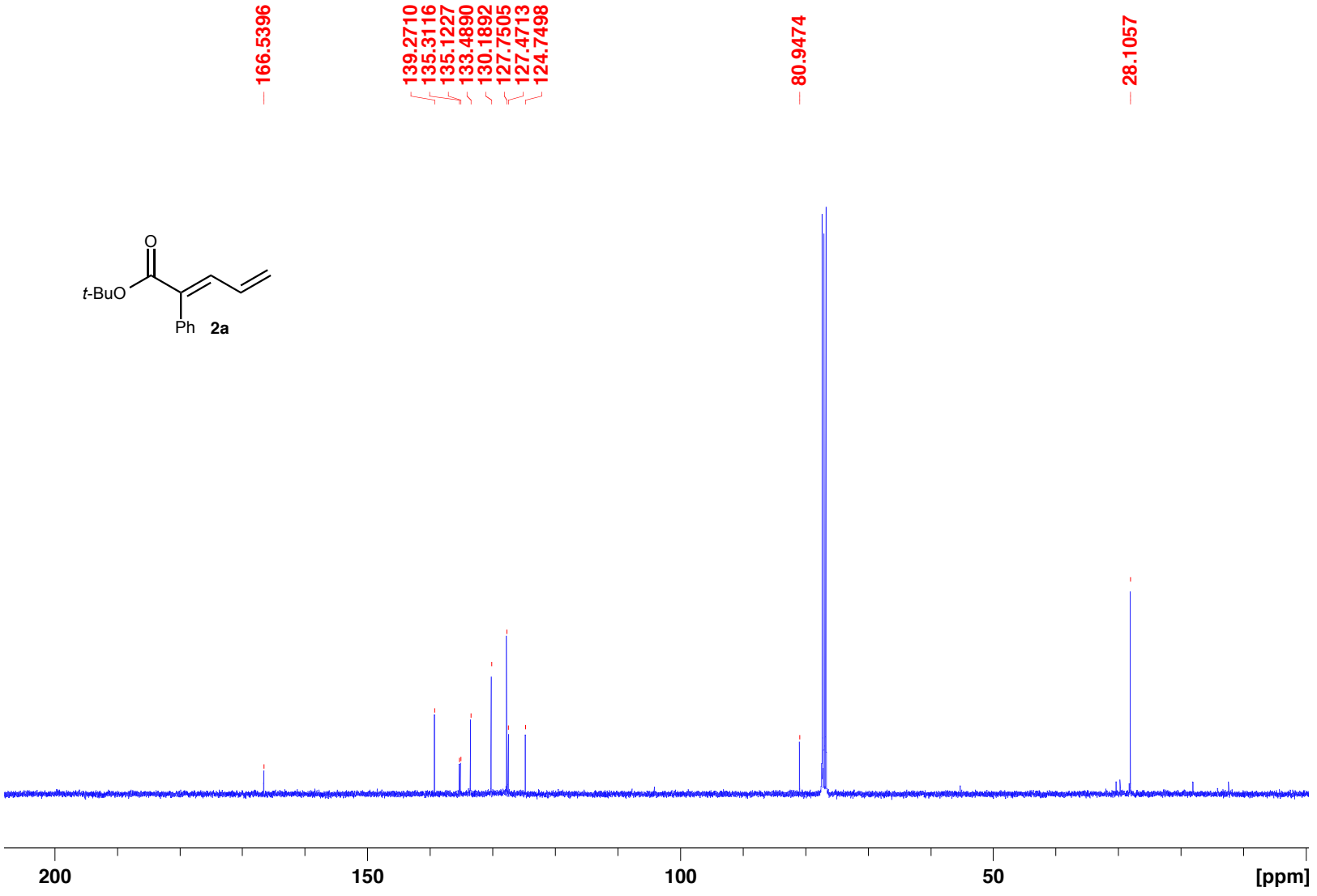
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



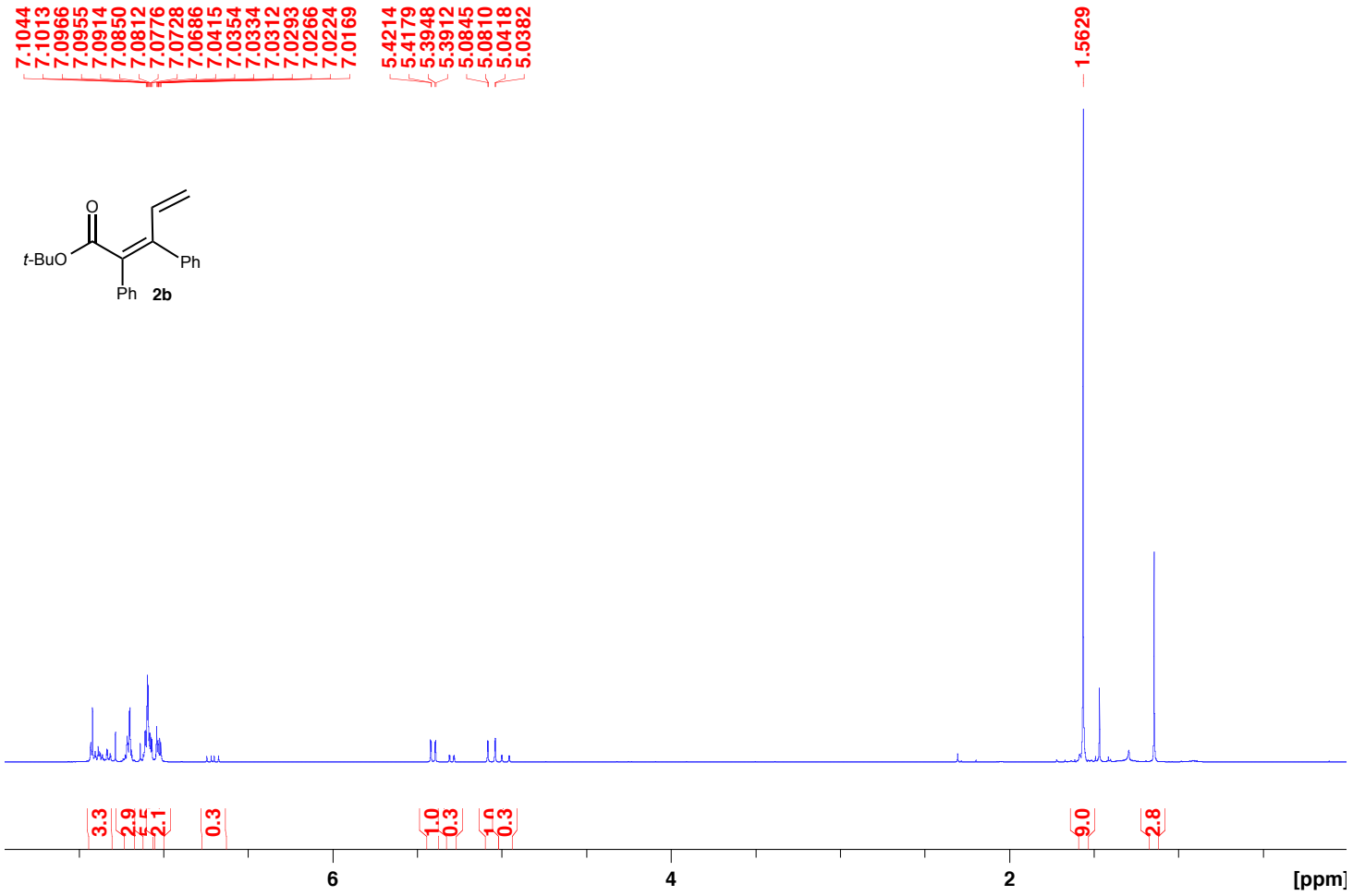
^{1}H NMR (400 MHz), $CDCl_3$



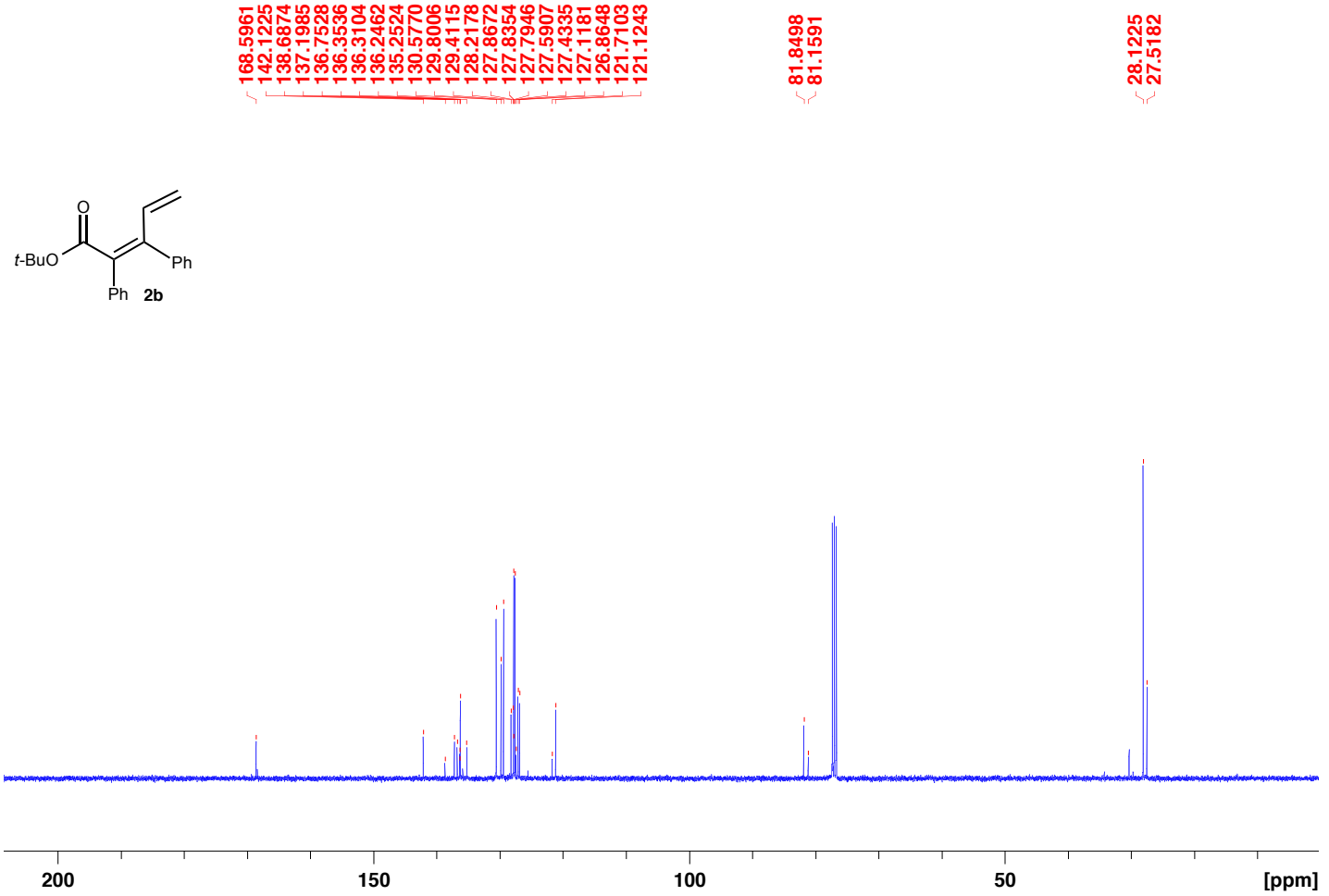
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



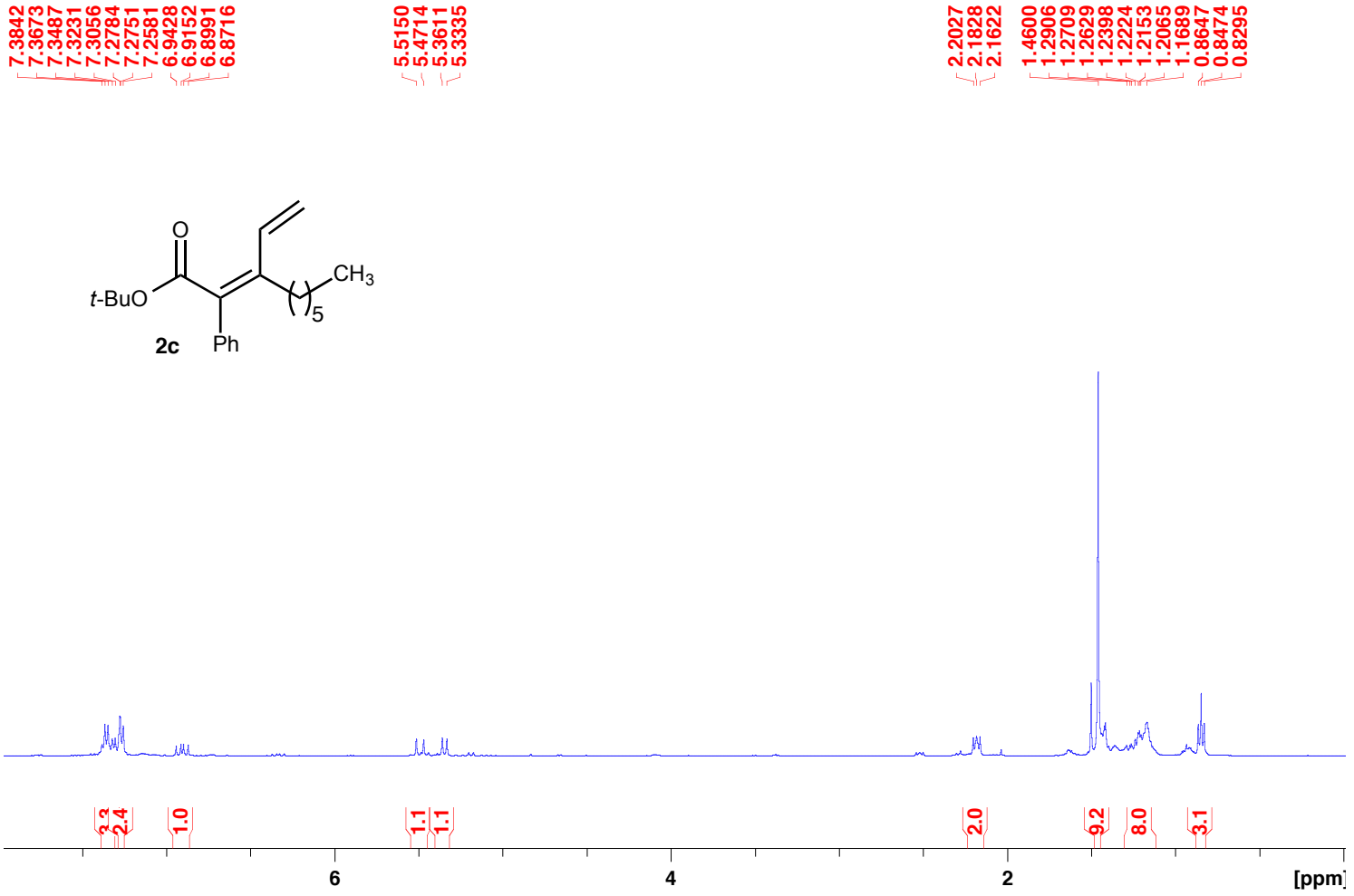
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 3:1 *E*:*Z* mixture of stereoisomers



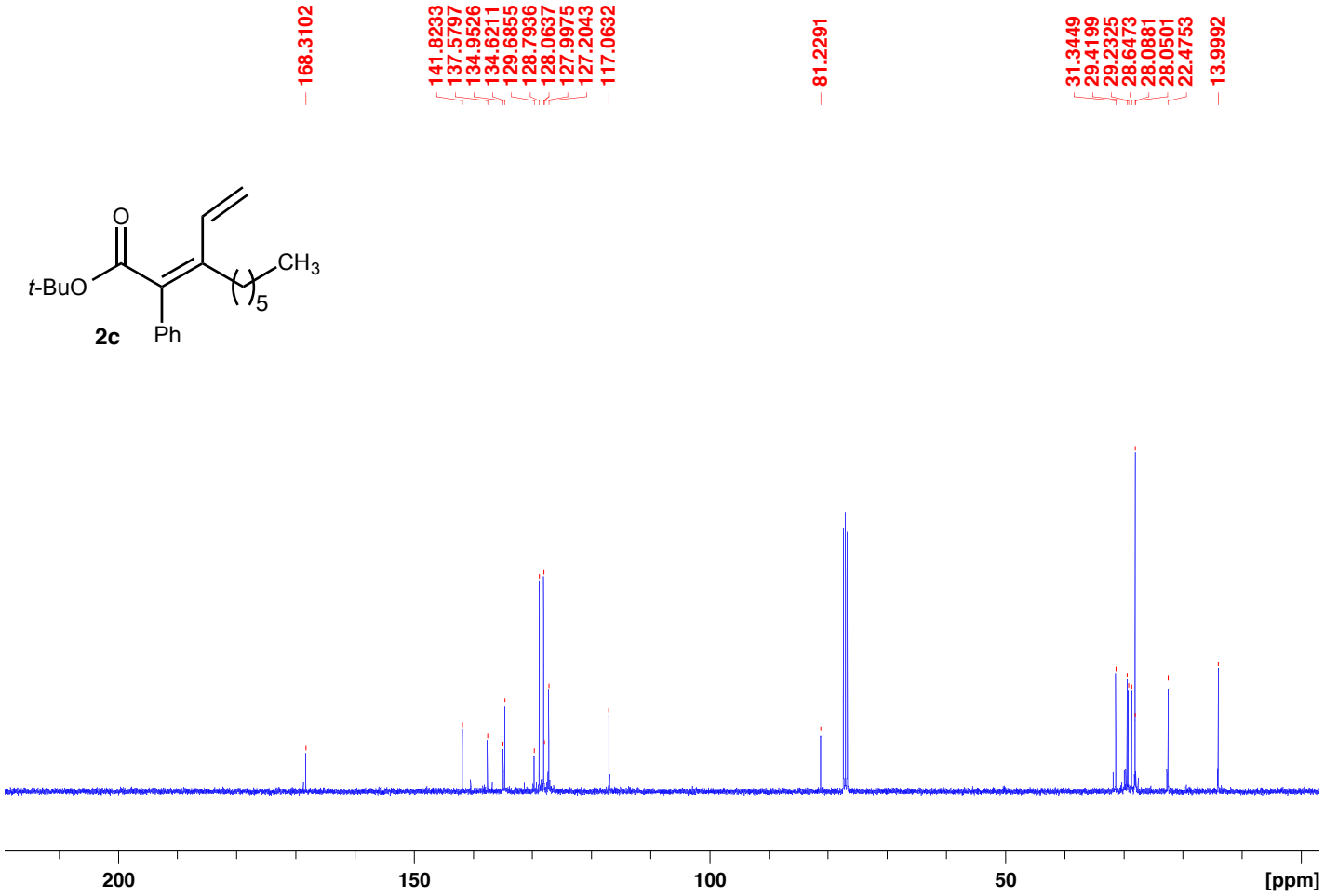
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 3:1 *E*:*Z* mixture of stereoisomers



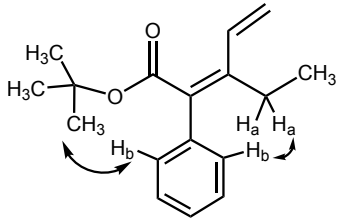
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 1:5 *E*:*Z* mixture of stereoisomers



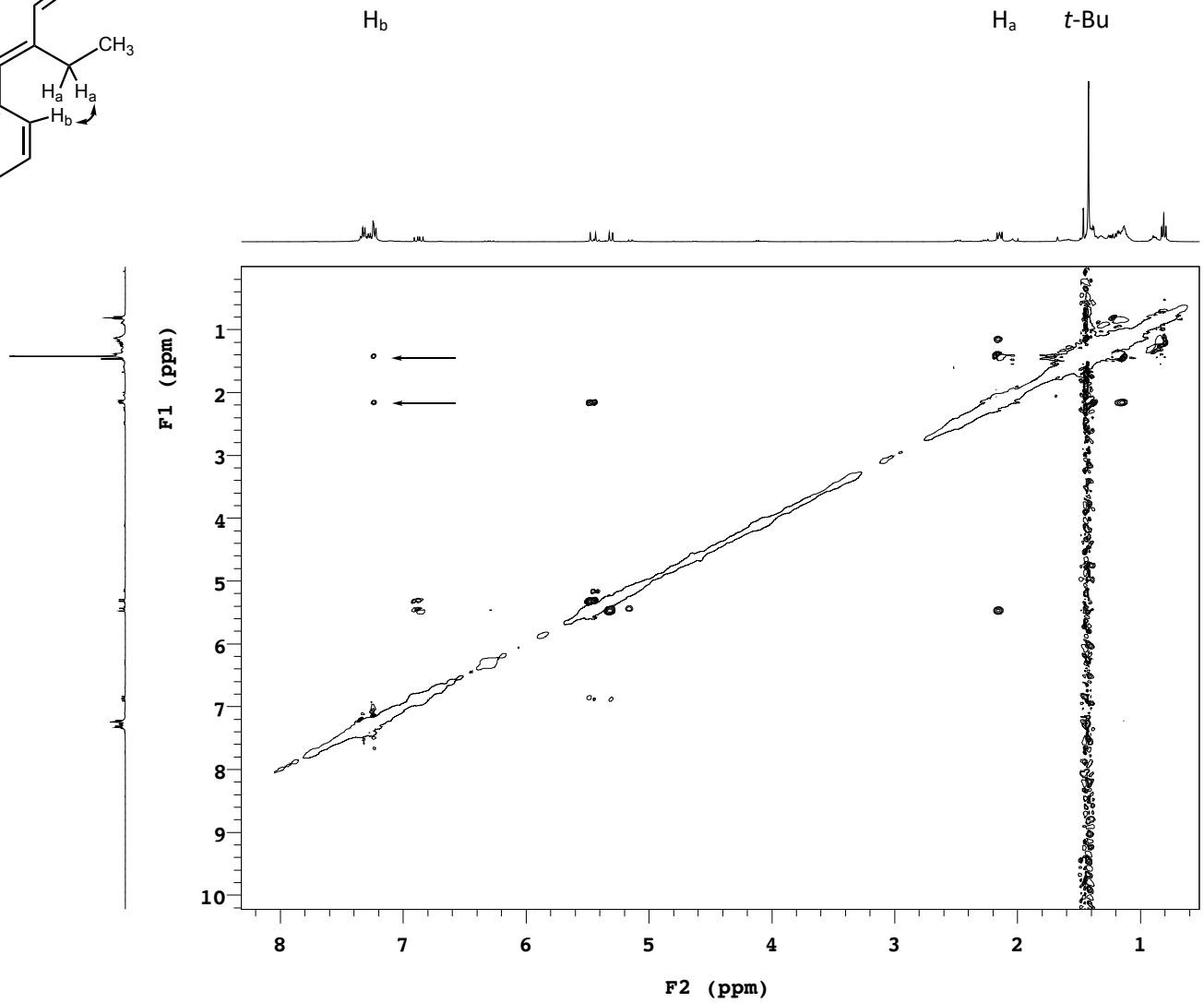
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 1:5 *E*:*Z* mixture of stereoisomers



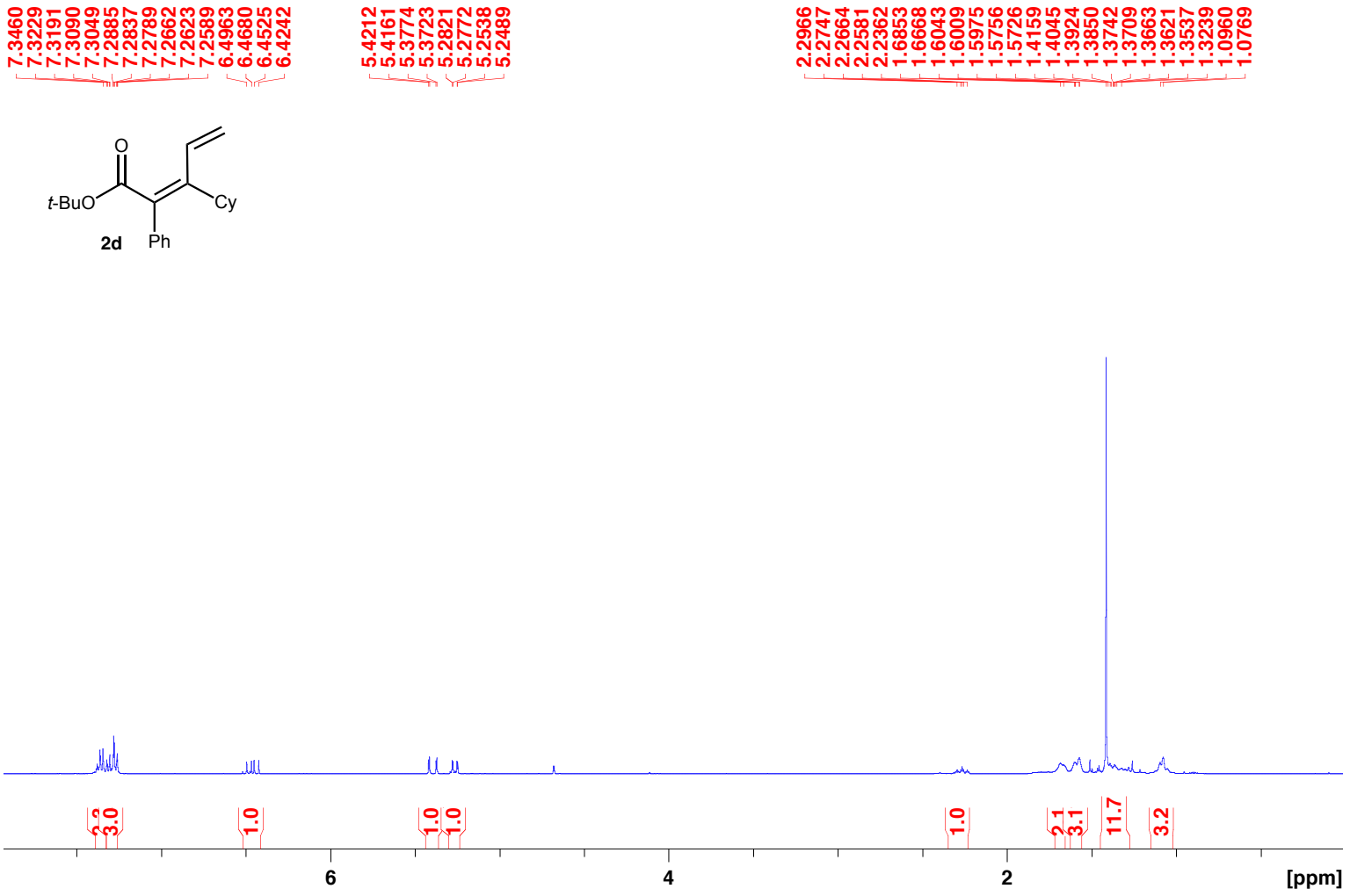
2c


O
H3C
H3C
O
CH3
CH3
Ha Ha
Hb
Hb

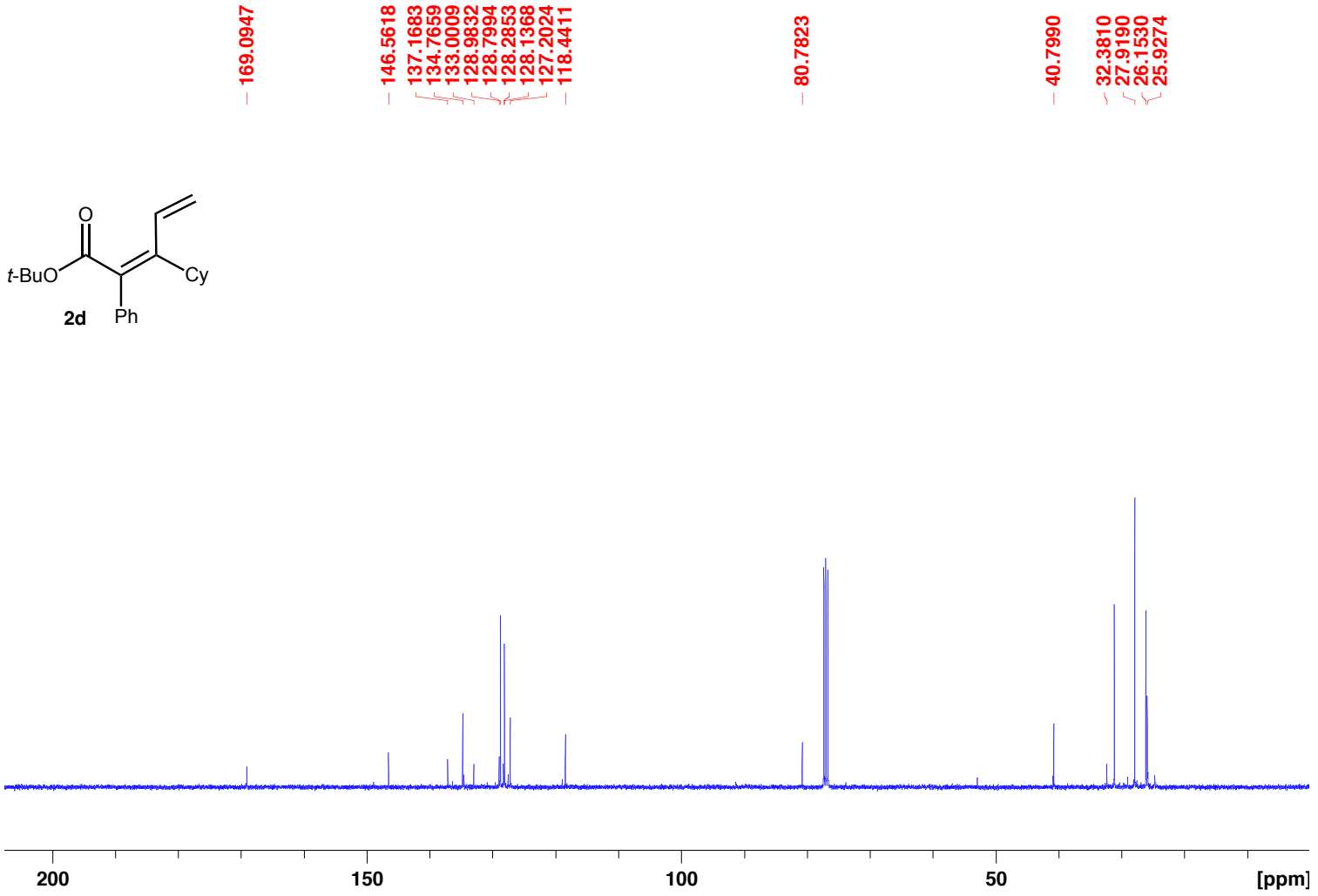
NOESY

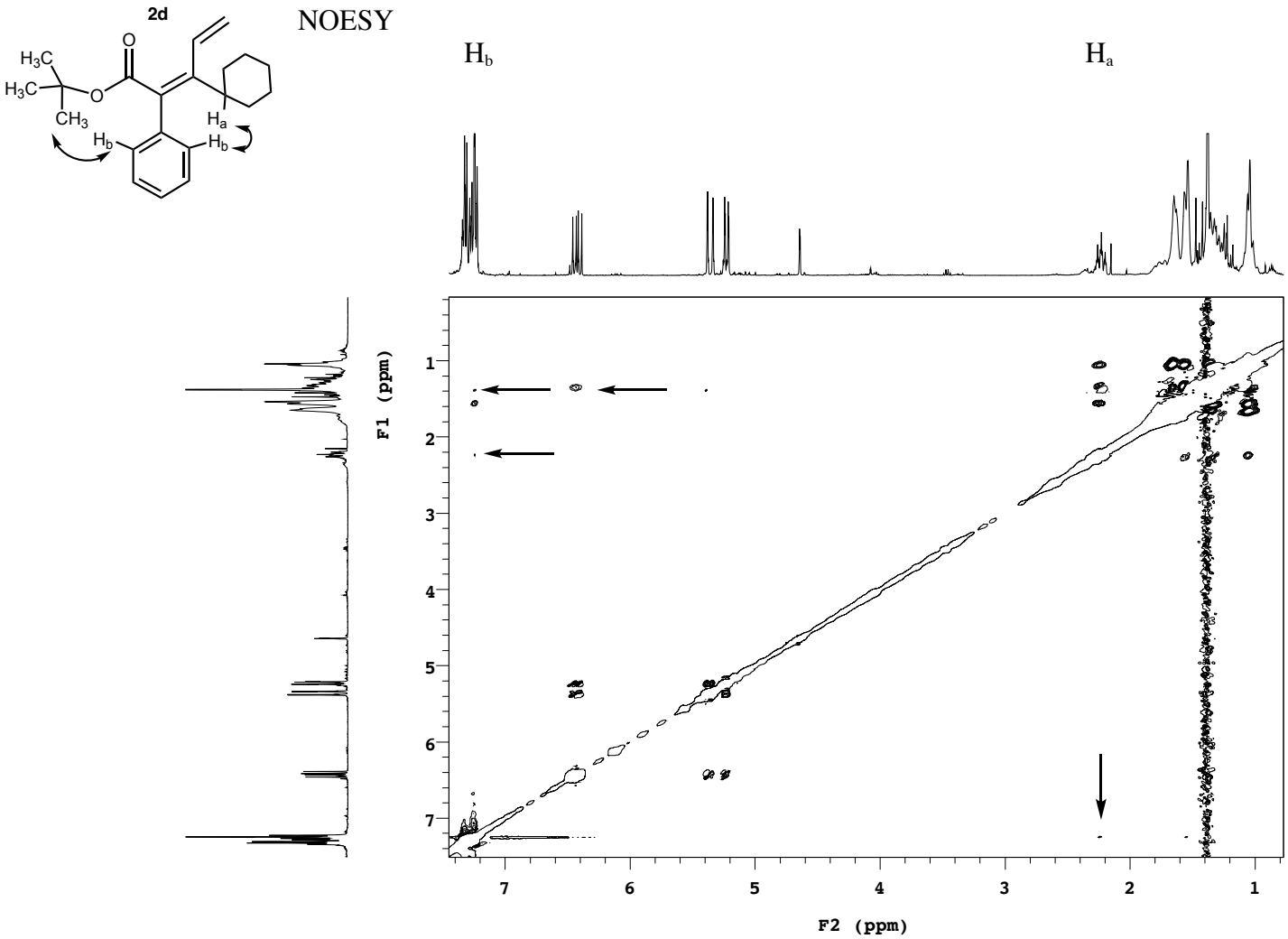

Hb
Ha
t-Bu
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
9
10
8
7
6
5
4
3
2
1

^{1}H NMR (400 MHz), $CDCl_3$, as a >10:1 mixture of *E* and *Z* stereoisomers

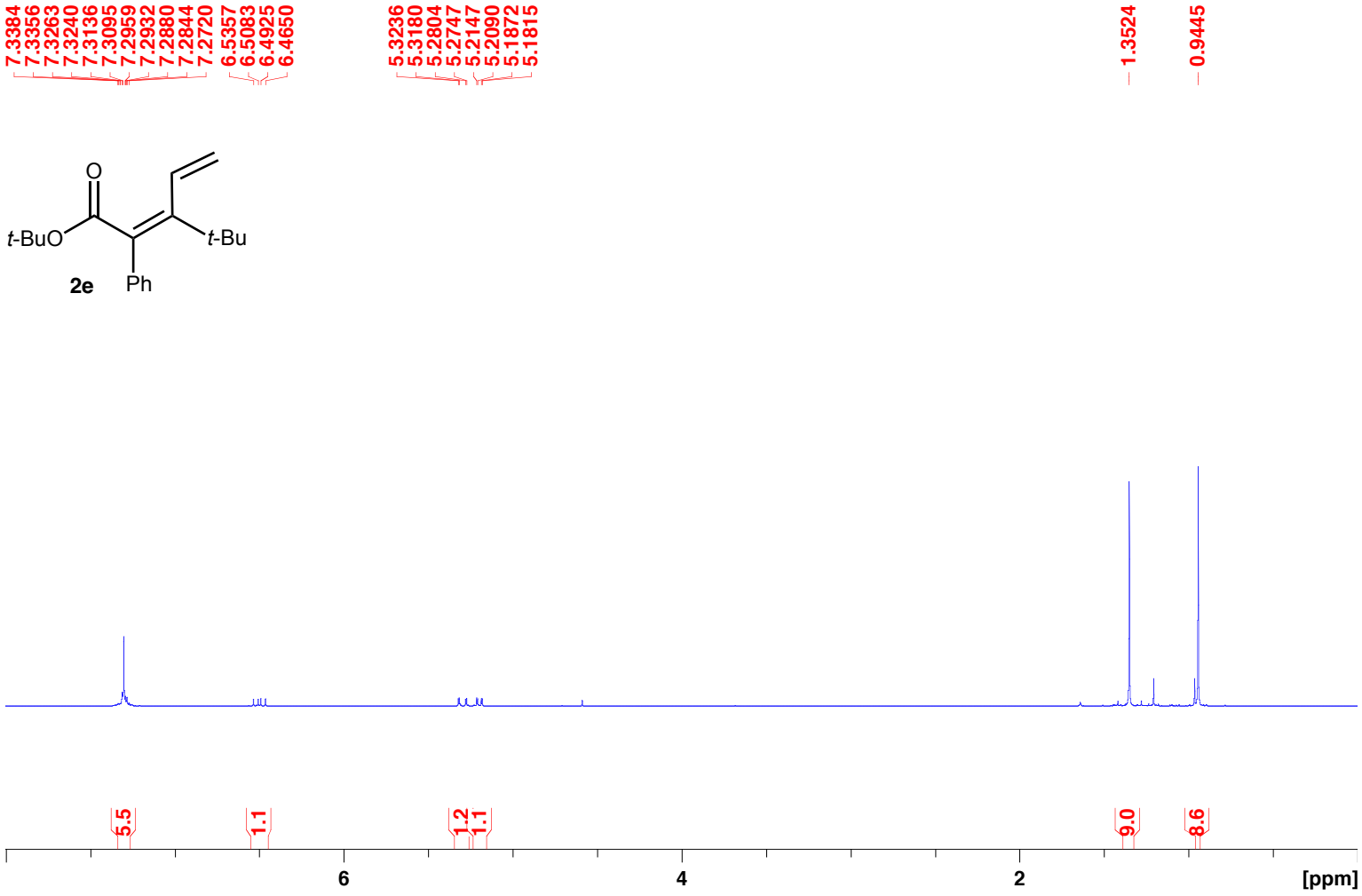


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a >10:1 mixture of *E* and *Z* stereoisomers

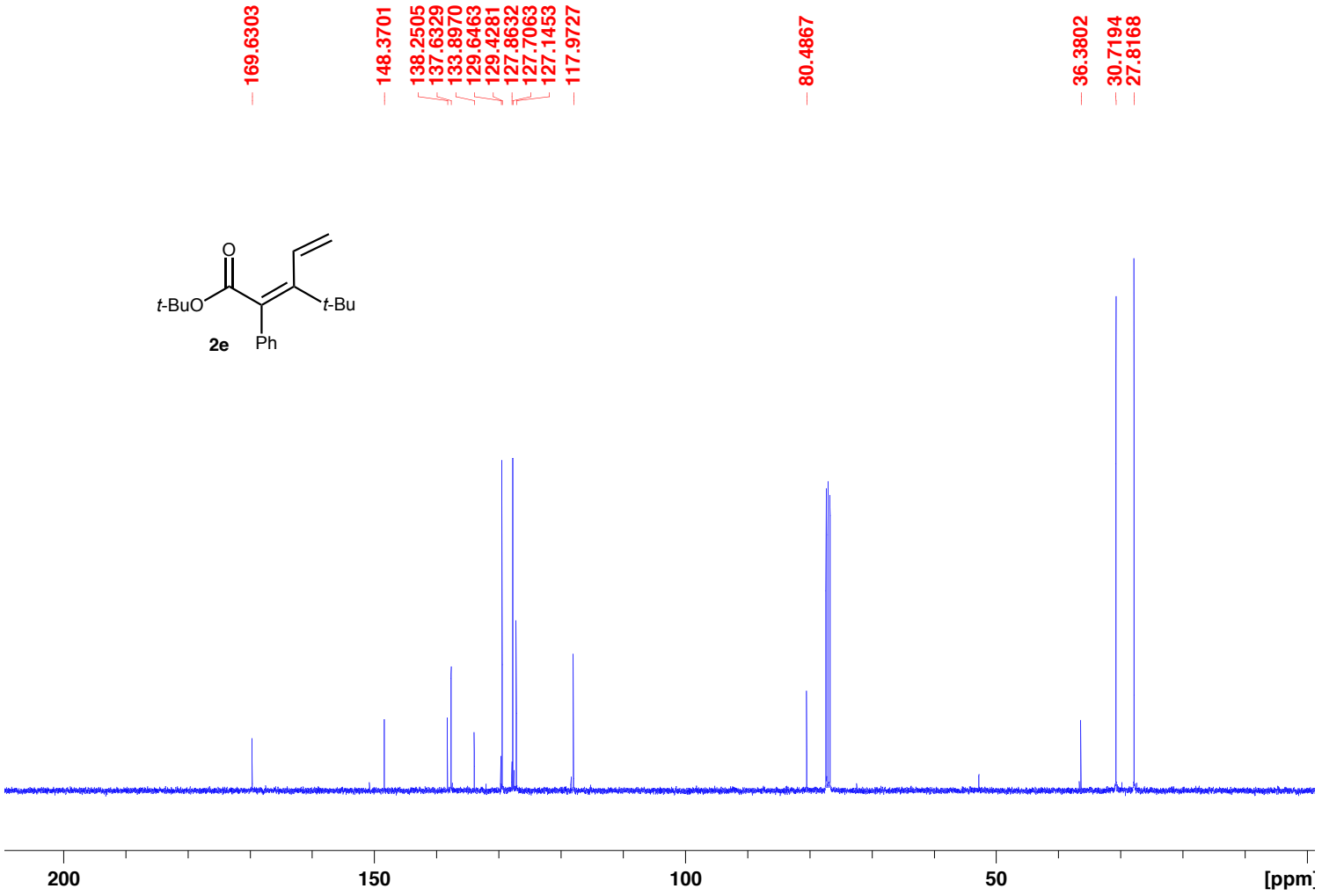


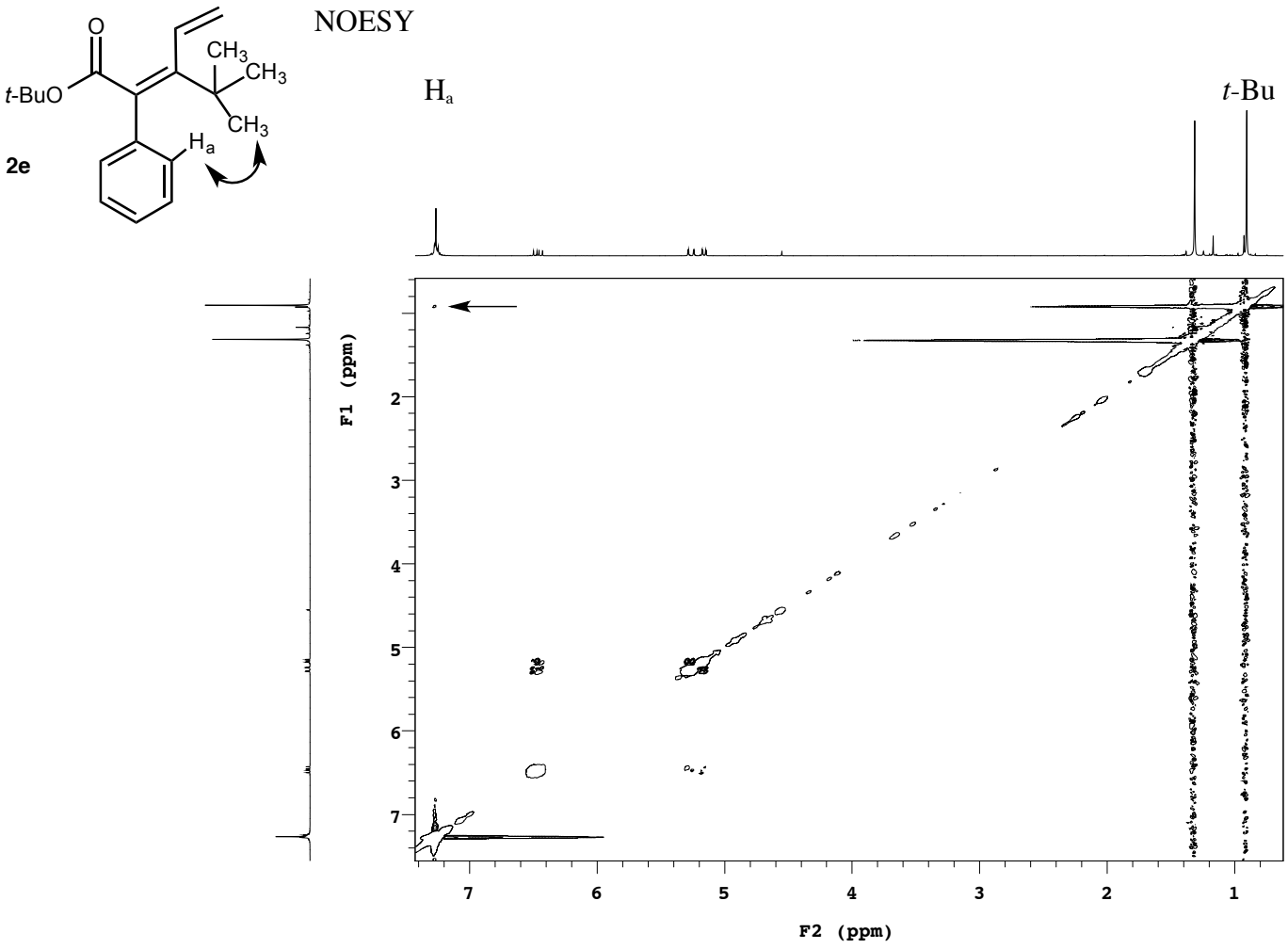

2d
NOESY
H_b
H_a
F1 (ppm)
F2 (ppm)

^{1}H NMR (400 MHz) , $CDCl_3$, as a 9:1 mixture of *E* and *Z* stereoisomers



$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$ as a 9:1 mixture of *E* and *Z* stereoisomers




NOESY
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t-BuO
CH3
CH3
CH3
Ha
2e
Ha
t-Bu
F1 (ppm)
F2 (ppm)
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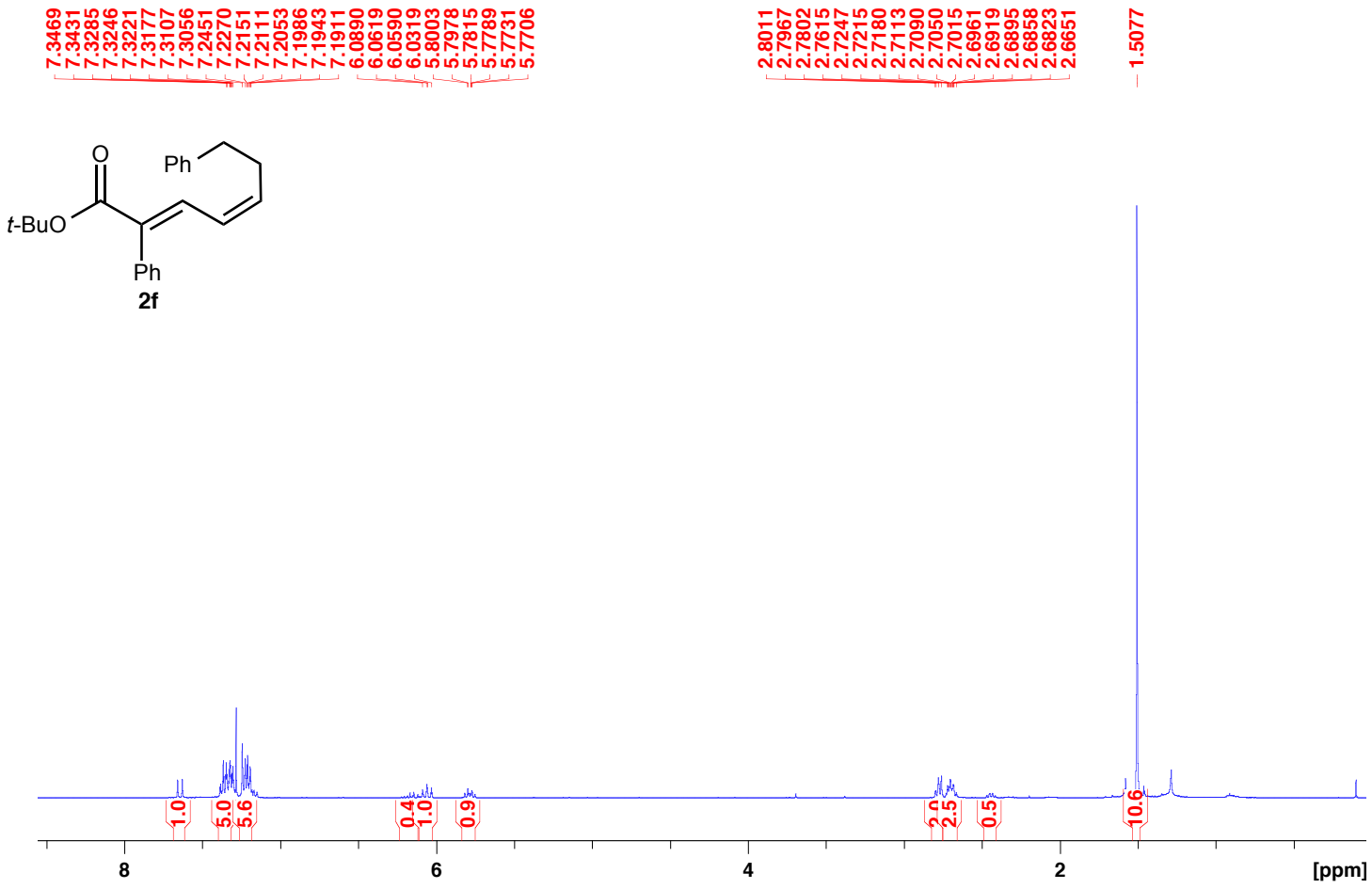
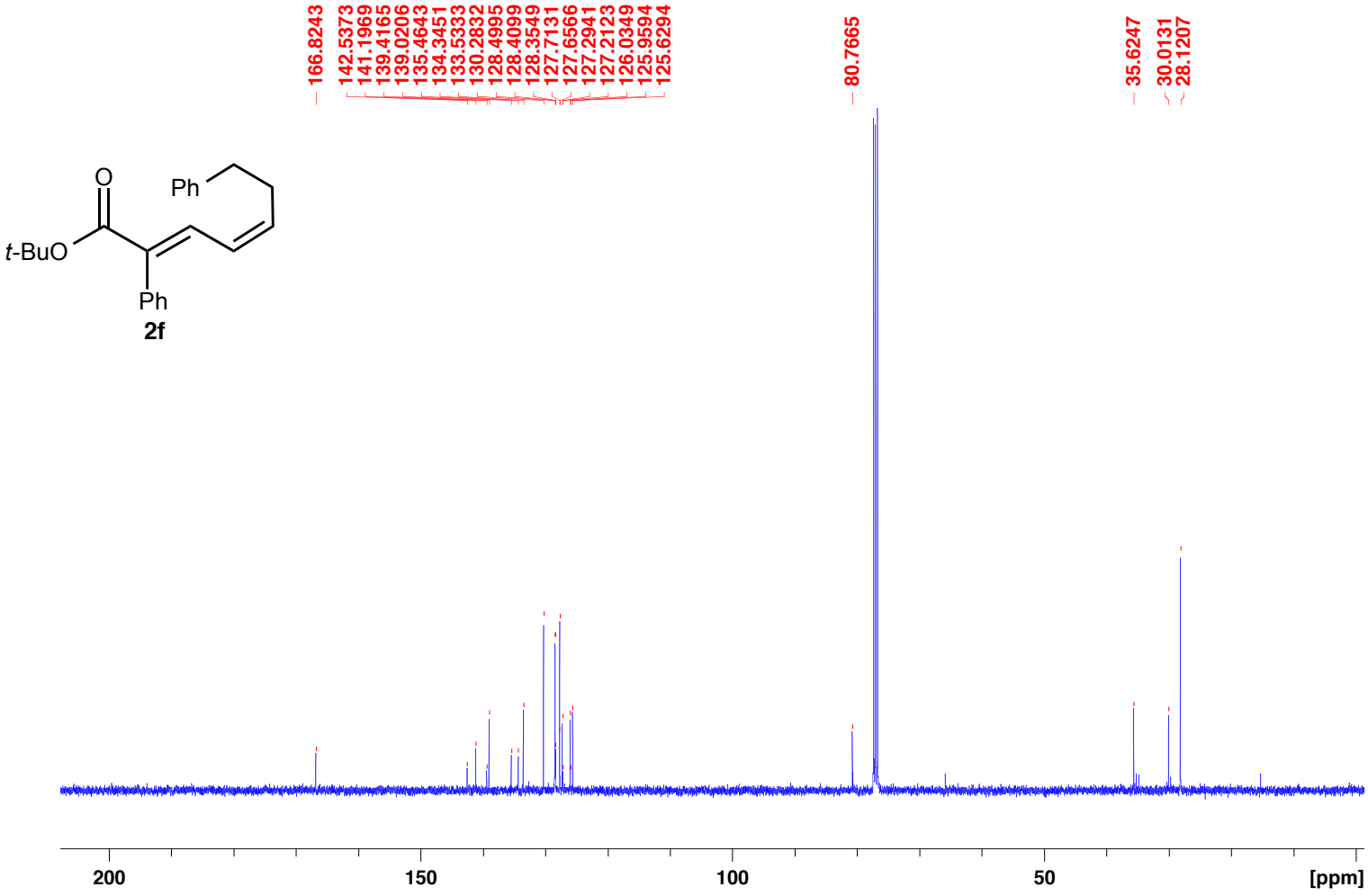
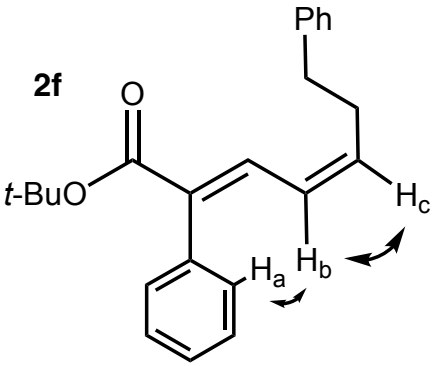
2
3
4
5
6
7

^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 4:1 *E*:*Z* mixture of stereoisomers at the α,β–alkene

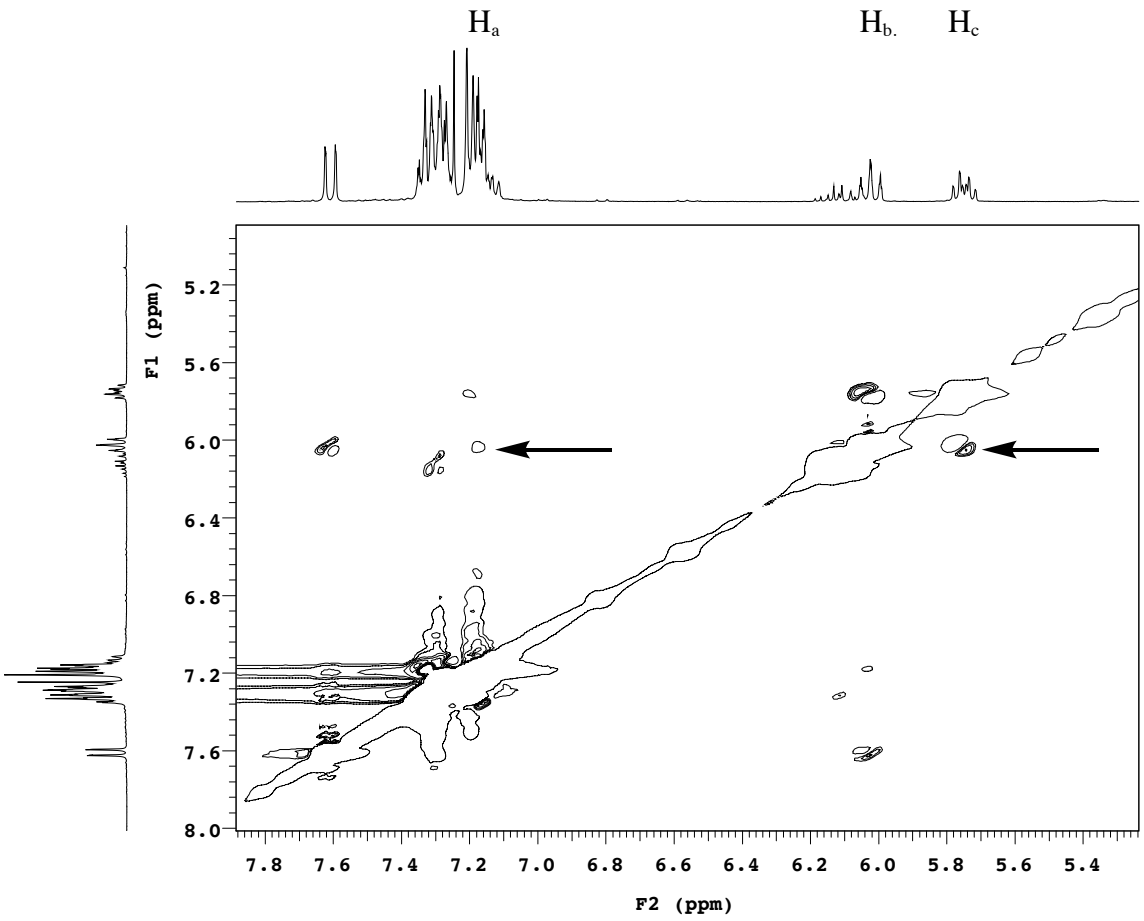


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 4:1 *E*:*Z* mixture of stereoisomers at the α,β–alkene

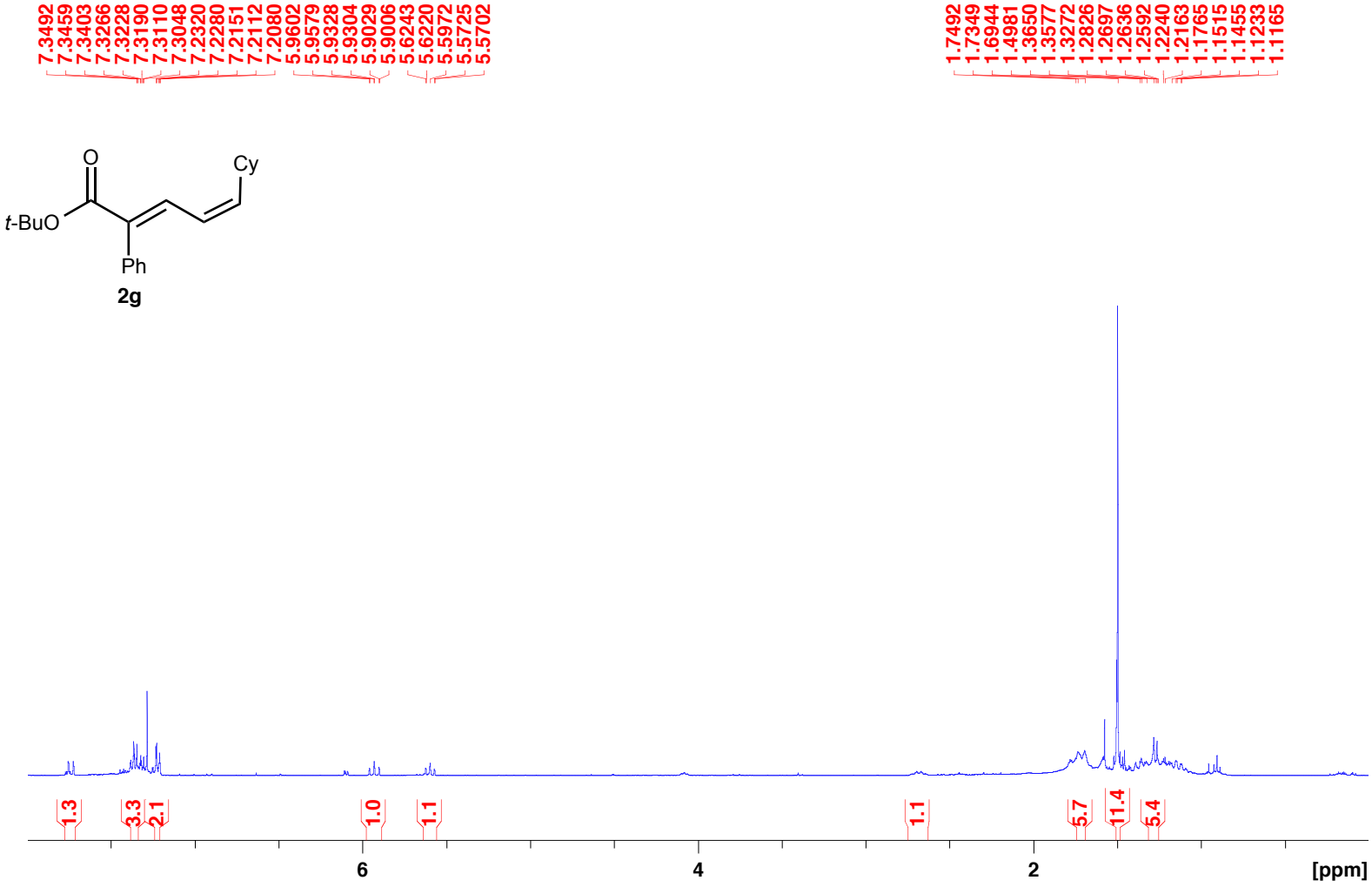



Ph
2f
O
t-BuO
Hc
Ha
Hb

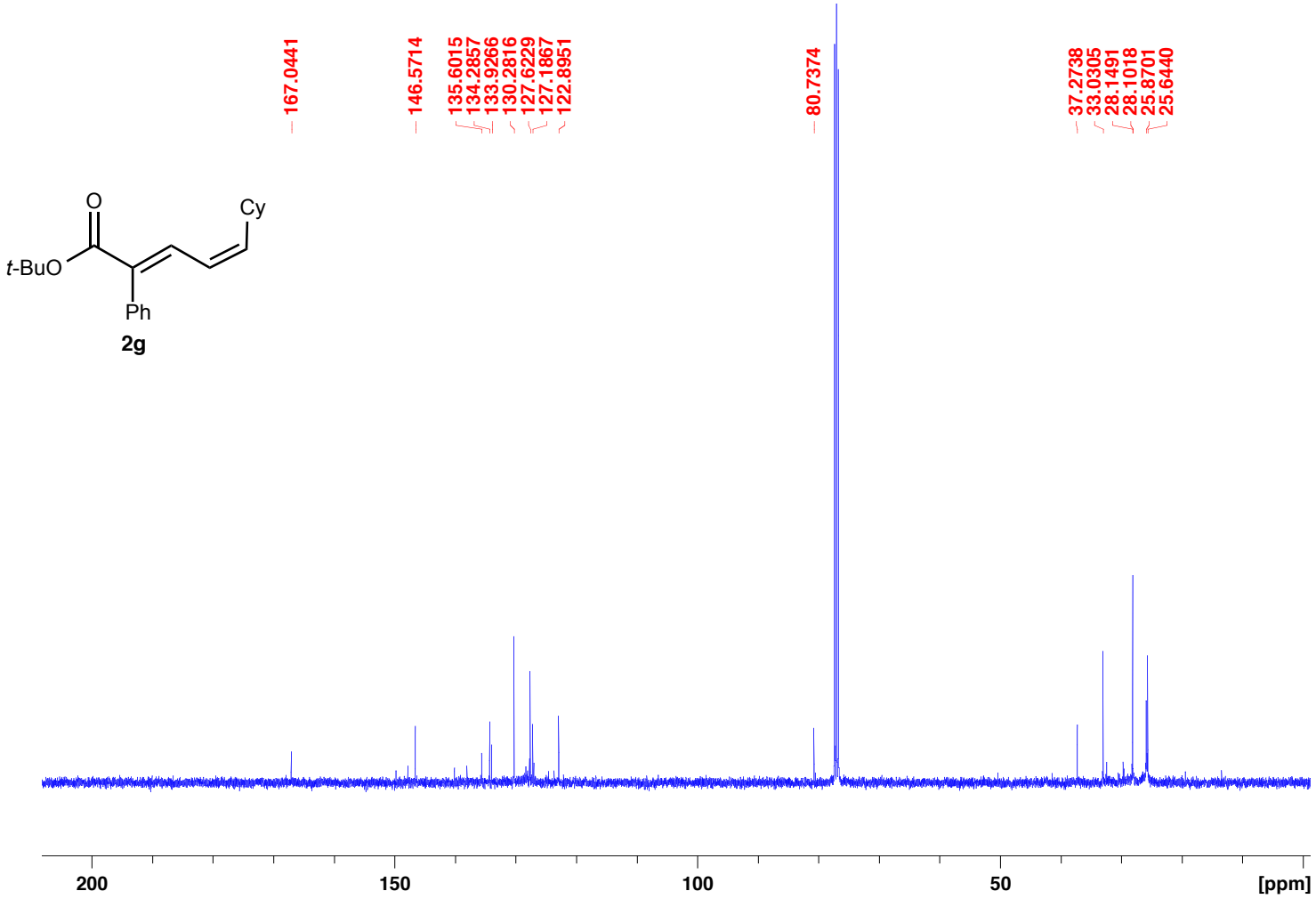
NOESY

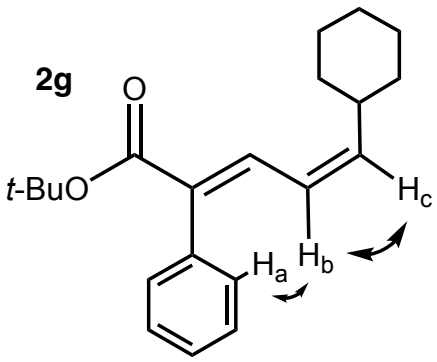

Ha
Hb.
Hc
F1 (ppm)
5.2
5.6
6.0
6.4
6.8
7.2
7.6
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
F2 (ppm)

^{1}H NMR (400 MHz) $CDCl_3$, as an inseparable 3:1 *E*:*Z* mixture of stereoisomers at the α,β-alkene

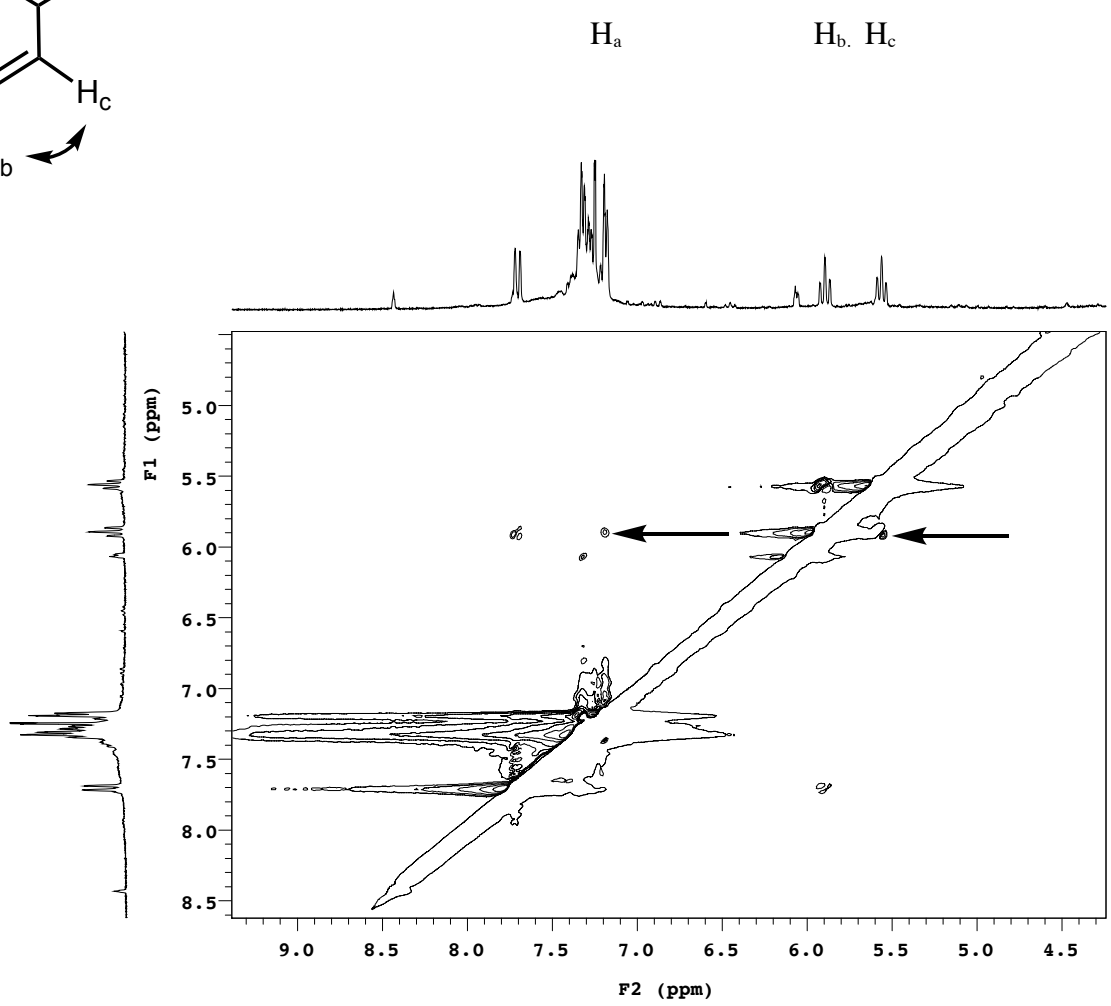


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 3:1 *E*:*Z* mixture of stereoisomers at the α,β-alkene

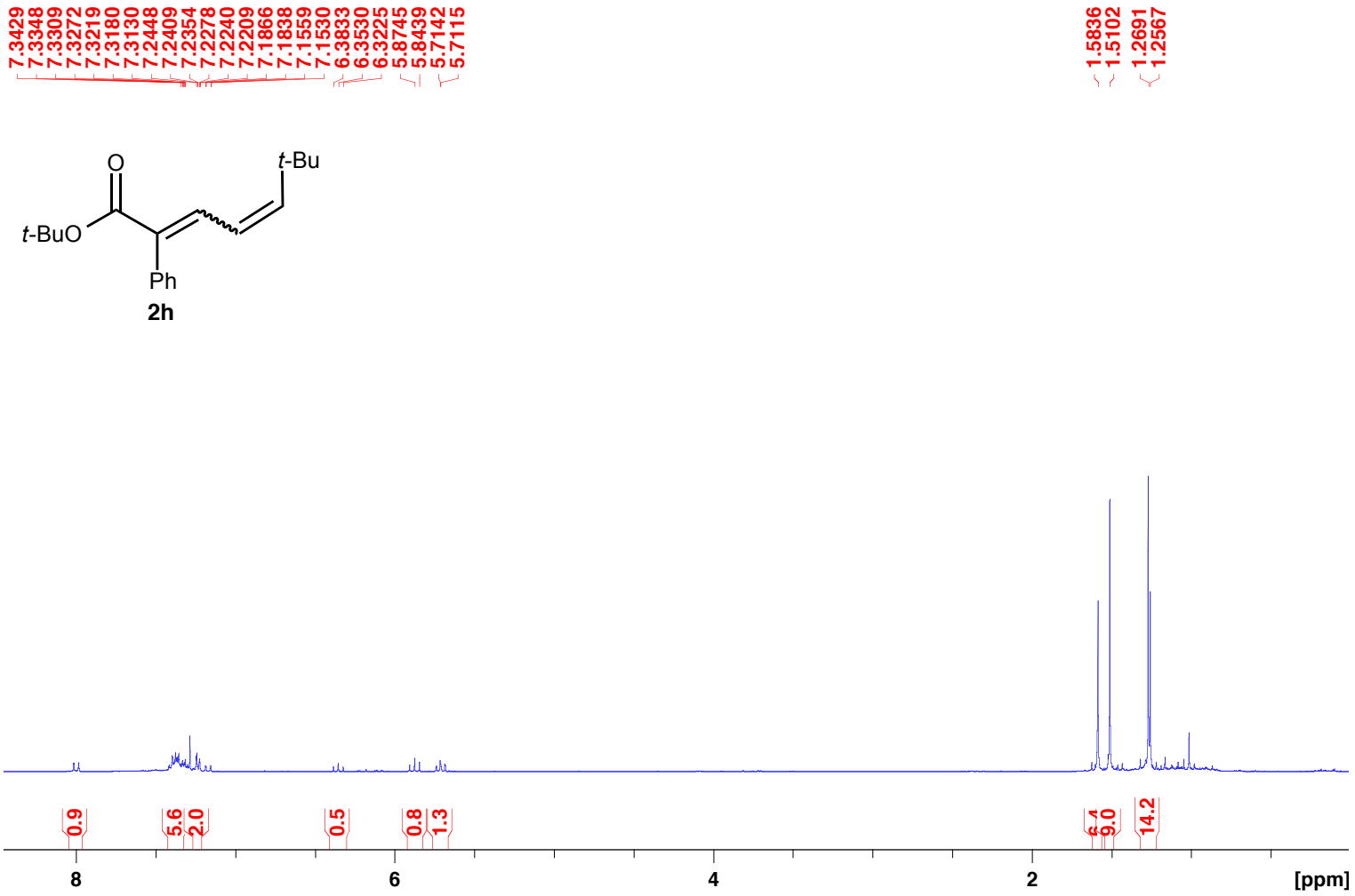



2g
O
t-BuO
Hc
Ha
Hb

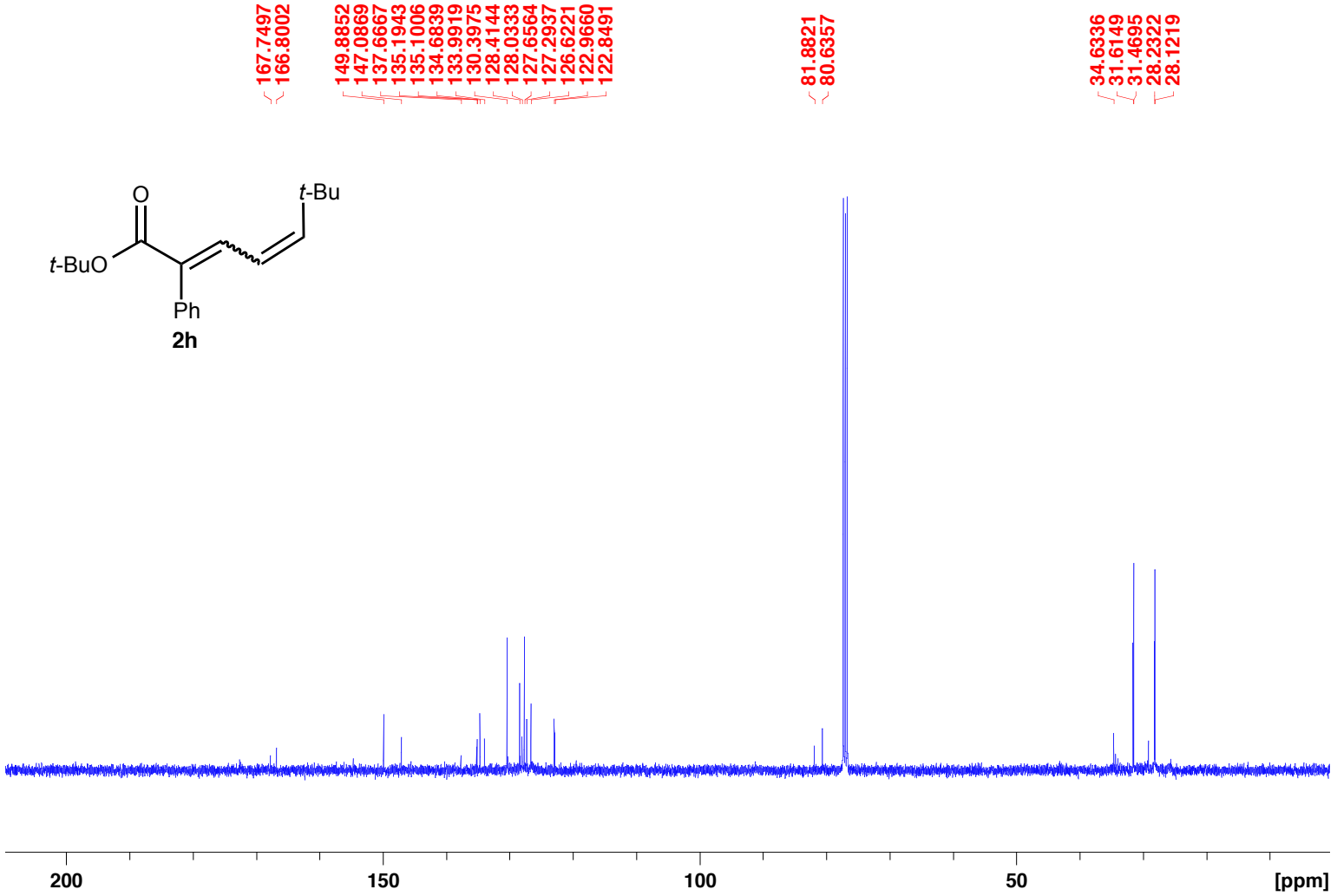
NOESY


Ha
Hb. Hc
F1 (ppm)
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
F2 (ppm)

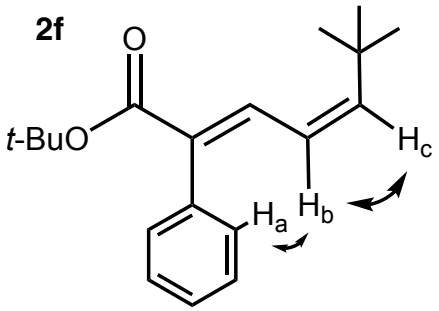
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 1.4:1 *E*:*Z* mixture of stereoisomers at the α,β-alkene



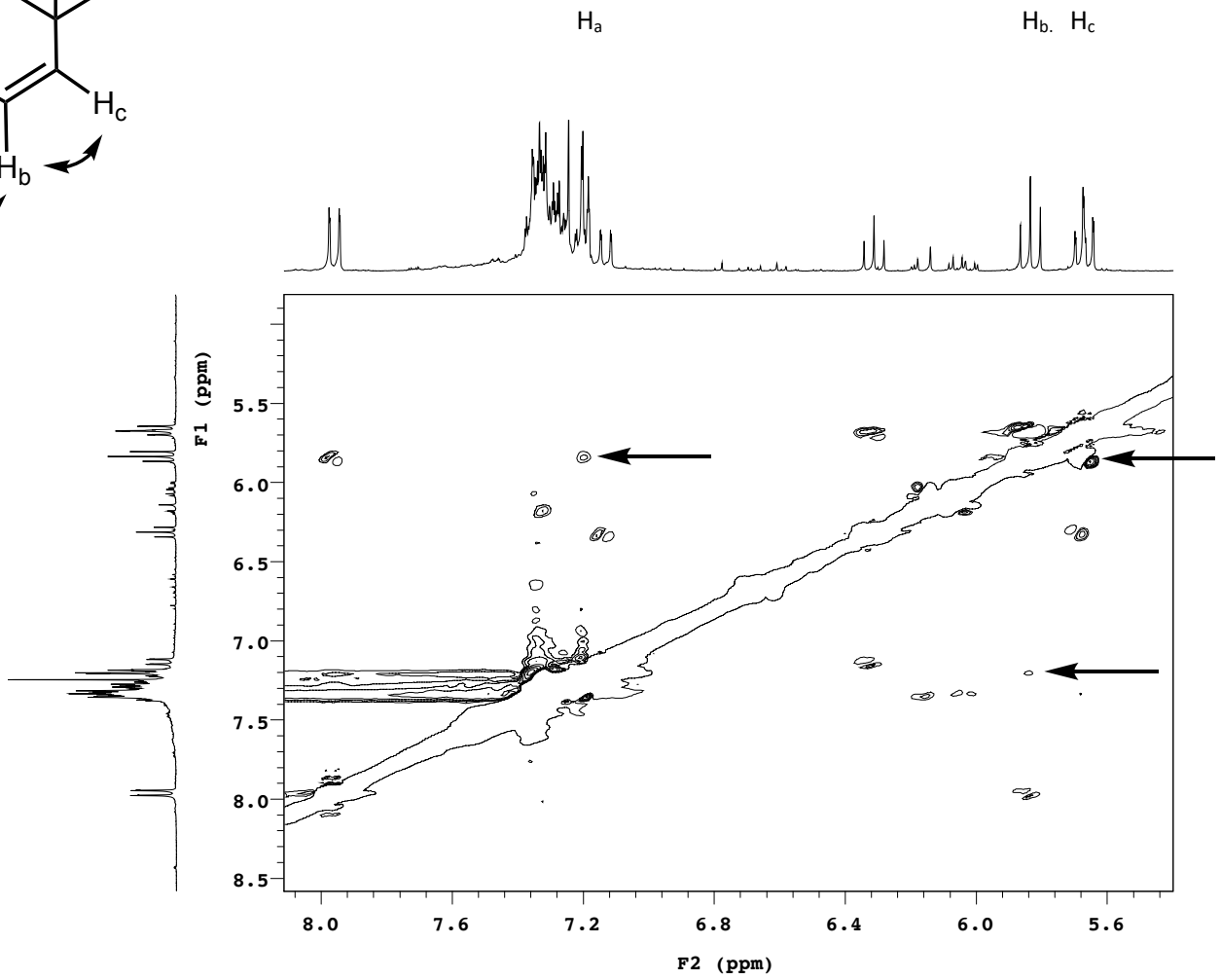
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 1.4:1 *E*:*Z* mixture of stereoisomers at the α,β-alkene



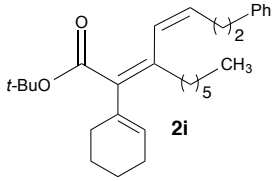
2f


O
t-BuO
Hc
Ha
Hb

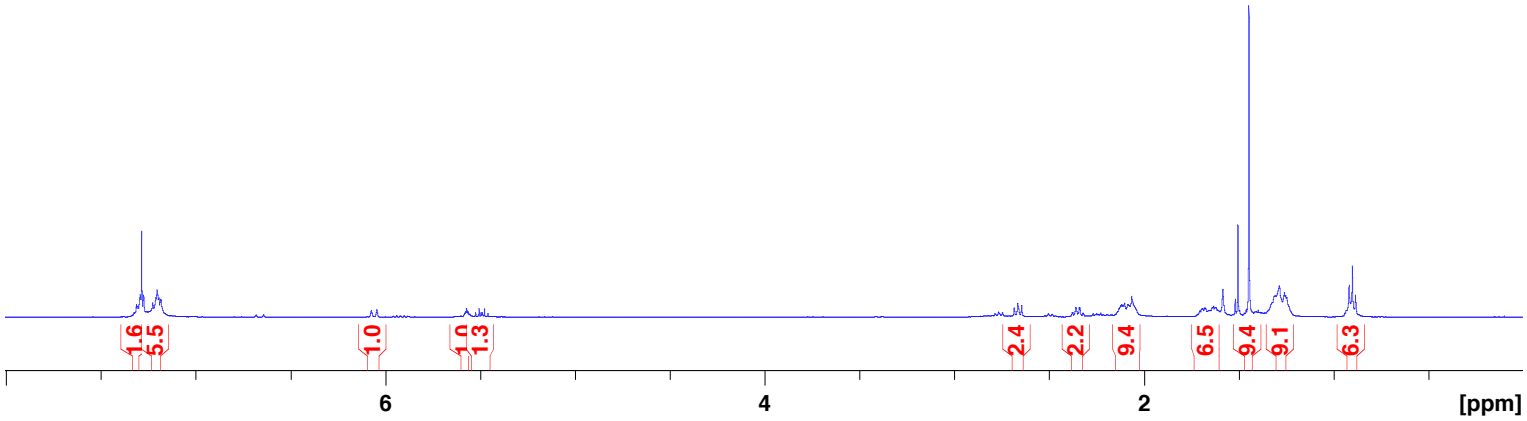
NOESY


Ha
Hb. Hc
F1 (ppm)
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.0
7.6
7.2
6.8
6.4
6.0
5.6
F2 (ppm)

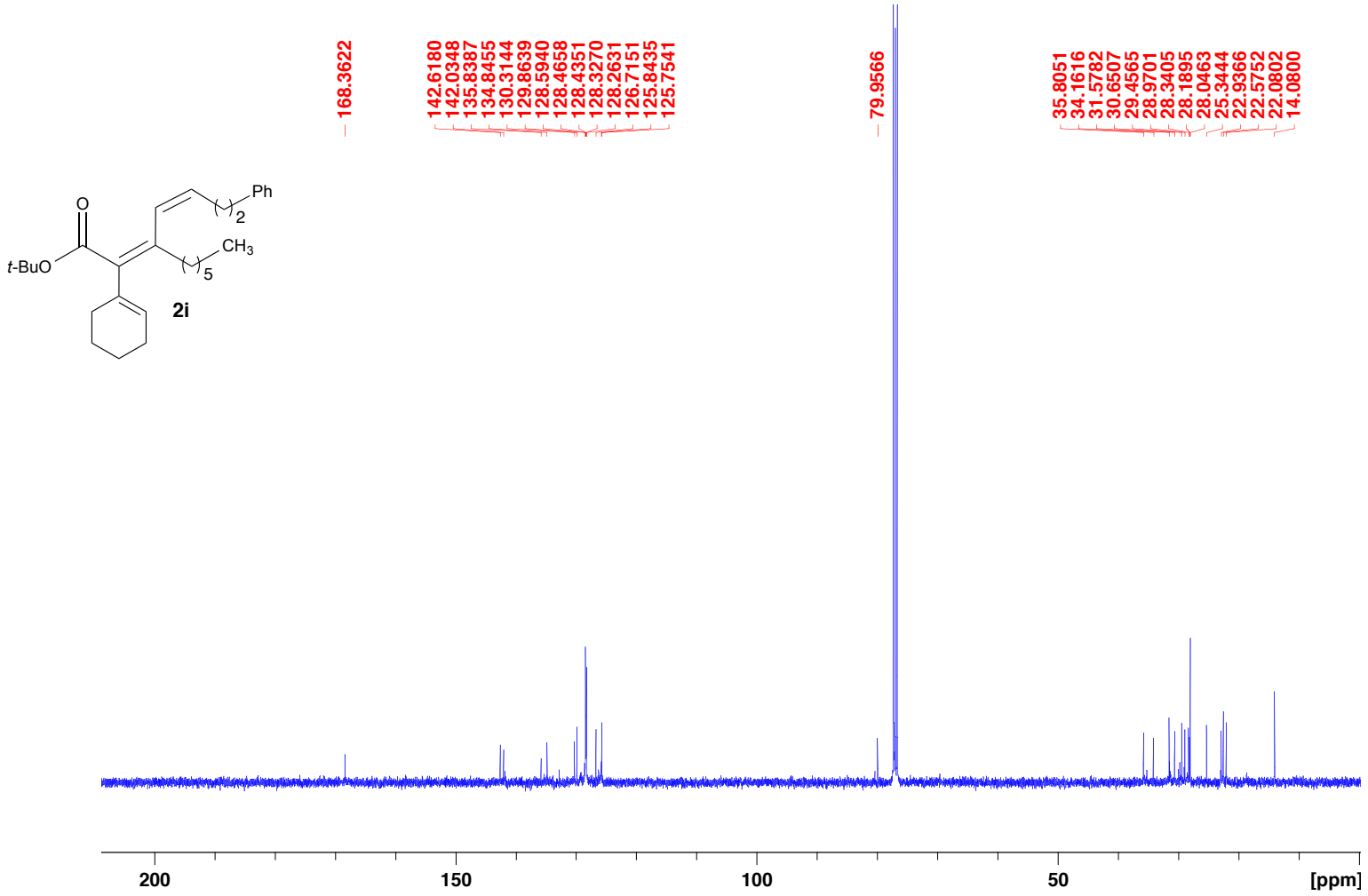
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 1:3 *E*:*Z* mixture of stereoisomers at the γ,δ-alkene

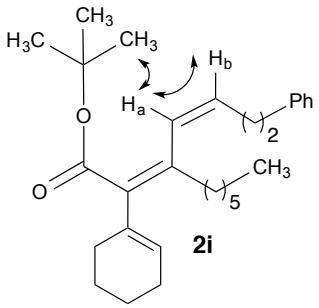


2i



$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 1:3 *E*:*Z* mixture of stereoisomers at the γ,δ-alkene

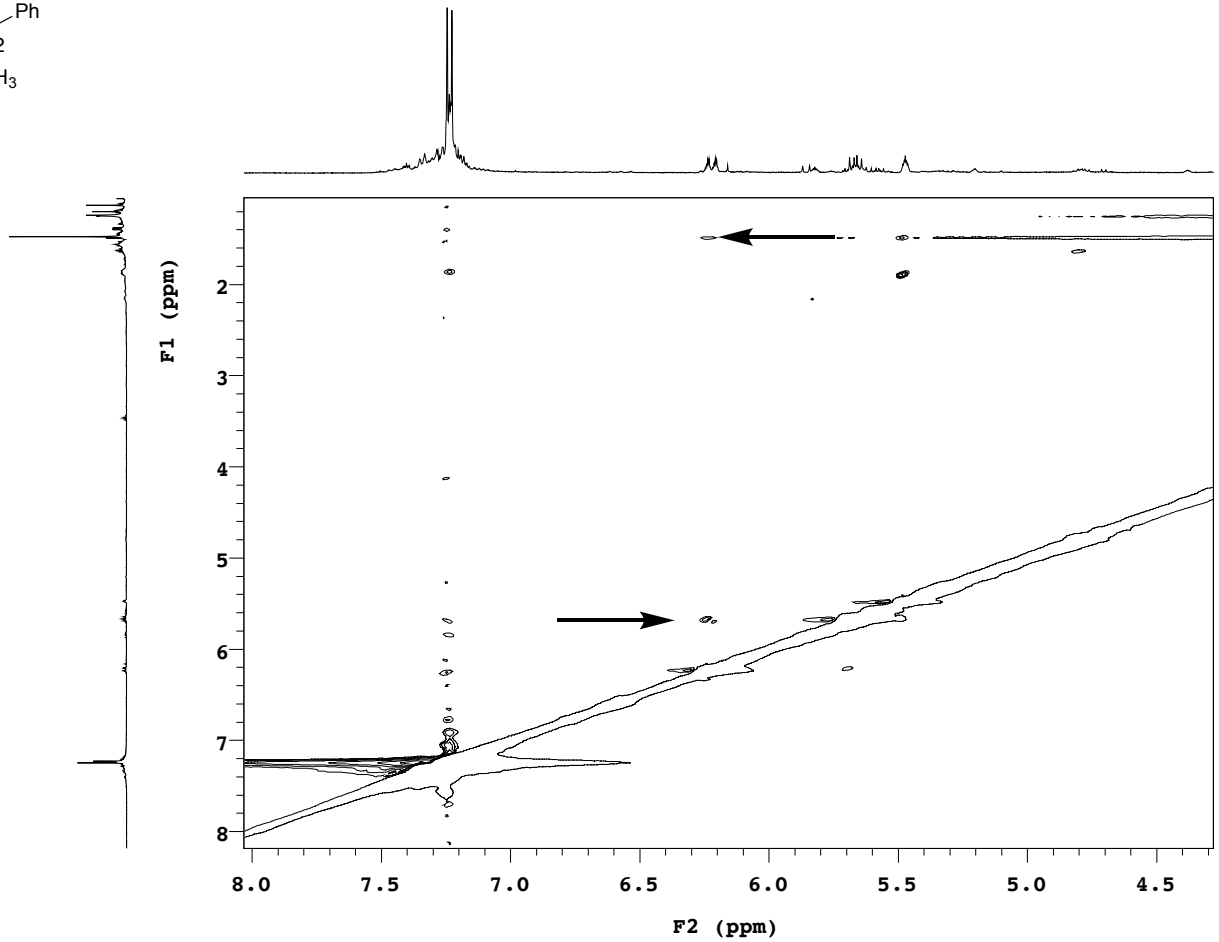




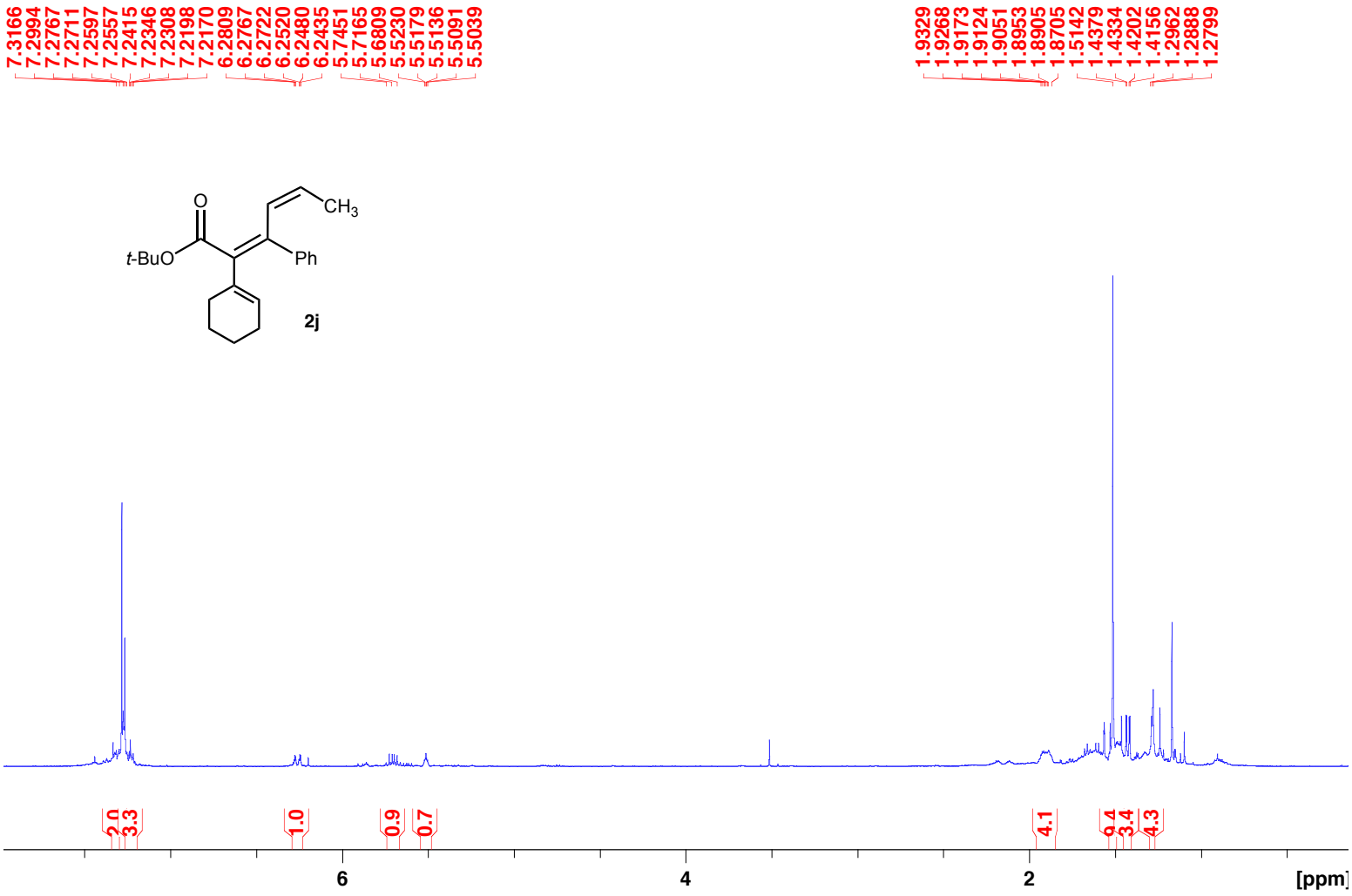
2i

NOESY

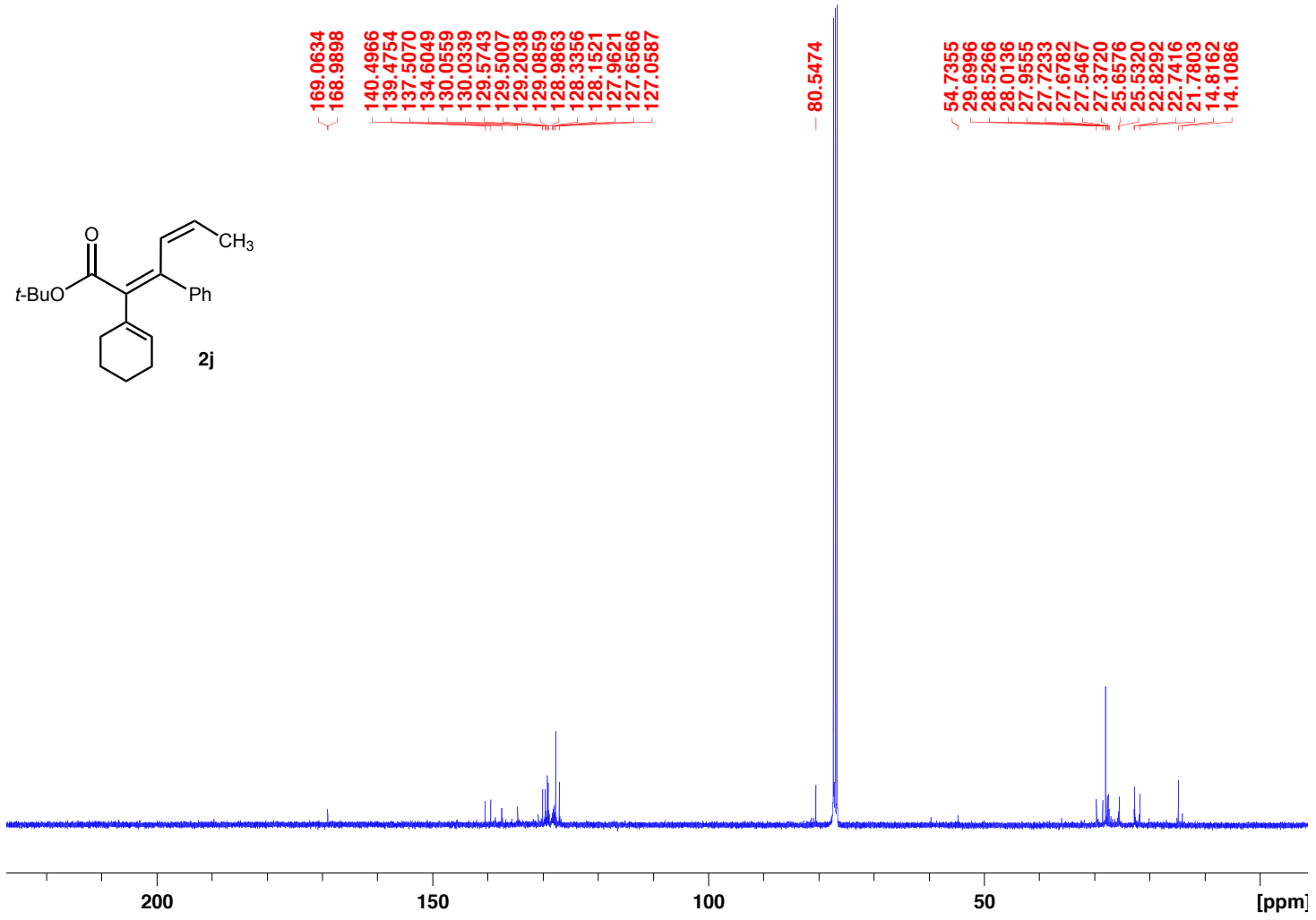
H_a H_b

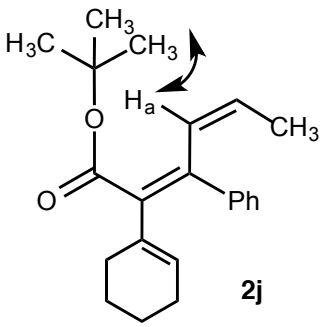


^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 3:1 *E:Z* mixture of stereoisomers at the α,β-alkene



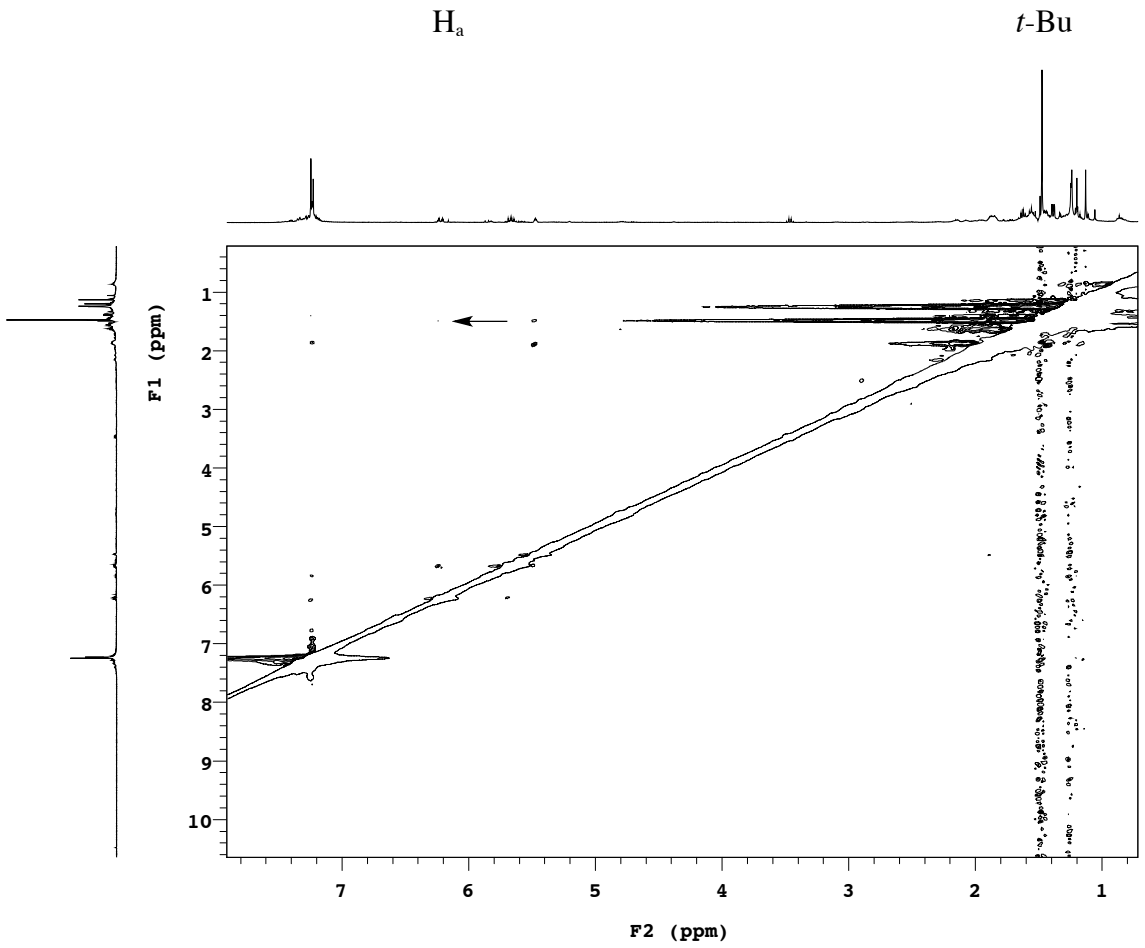
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 3:1 *E:Z* mixture of stereoisomers at the α,β-alkene



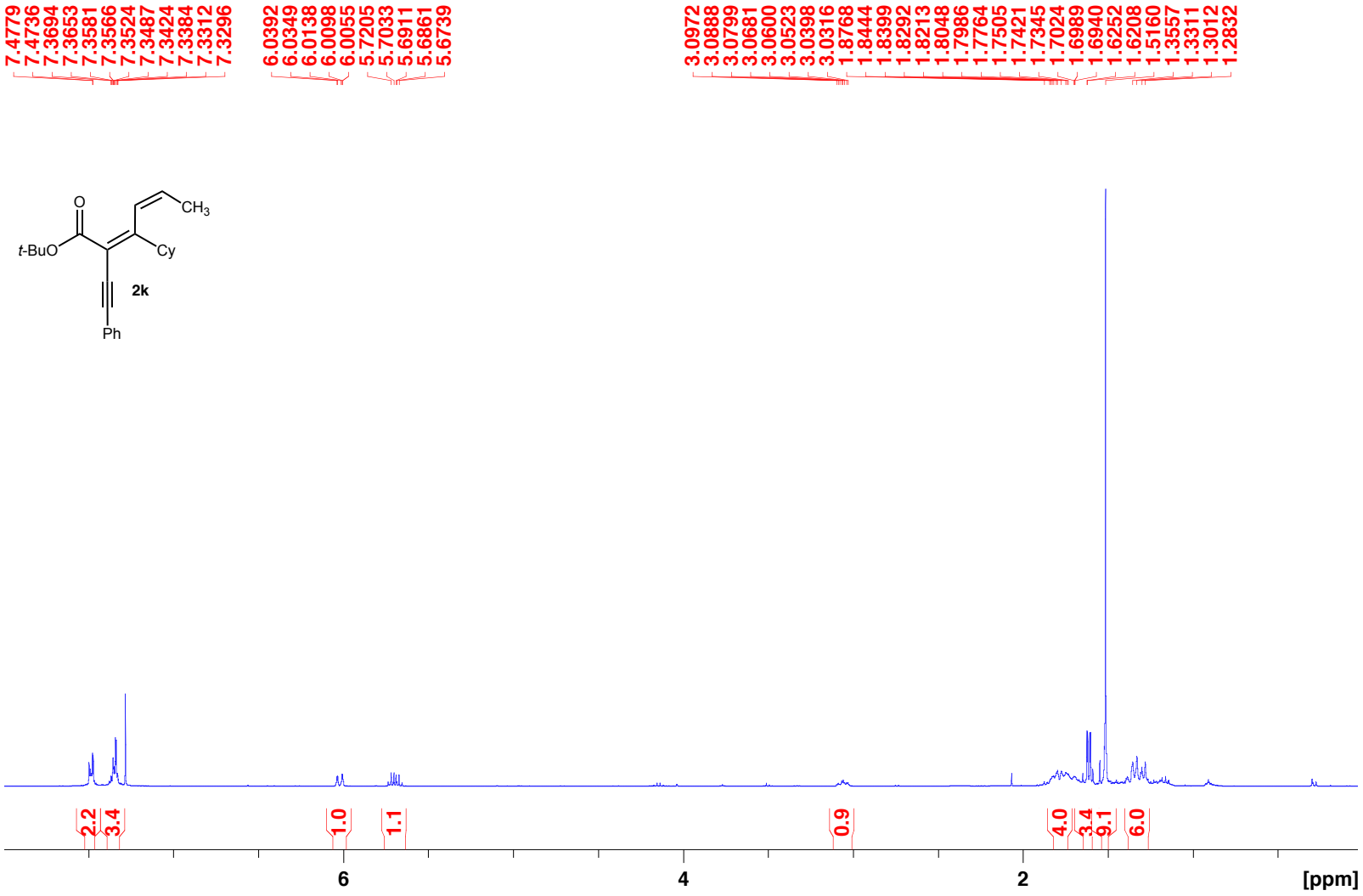

CH3
H3C
CH3
Ha
O
CH3
O
Ph

2j

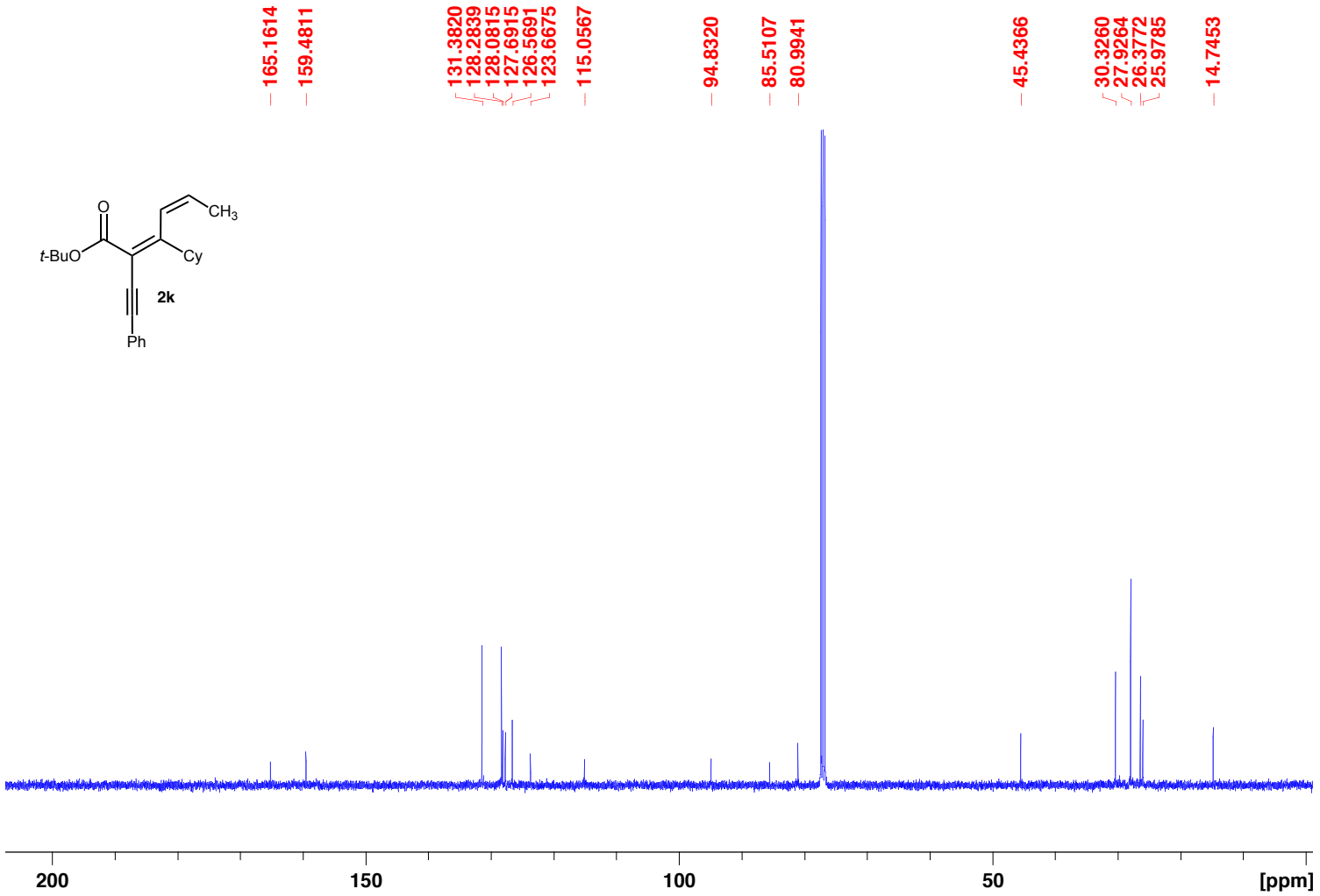
NOESY


Ha
t-Bu
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
9
10
7
6
5
4
3
2
1

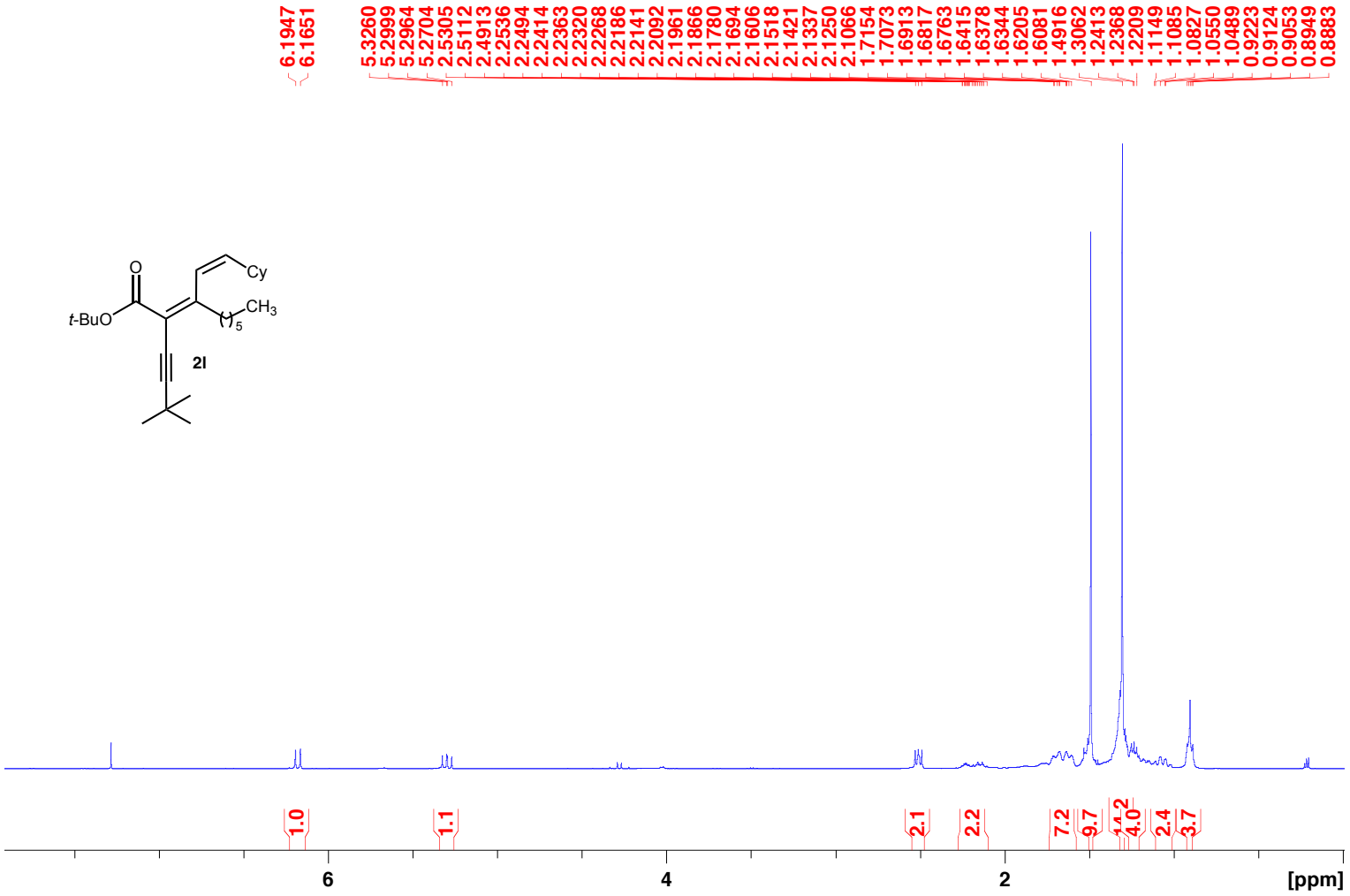
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 1:10 *E:Z* mixture of stereoisomers at the α,β-alkene



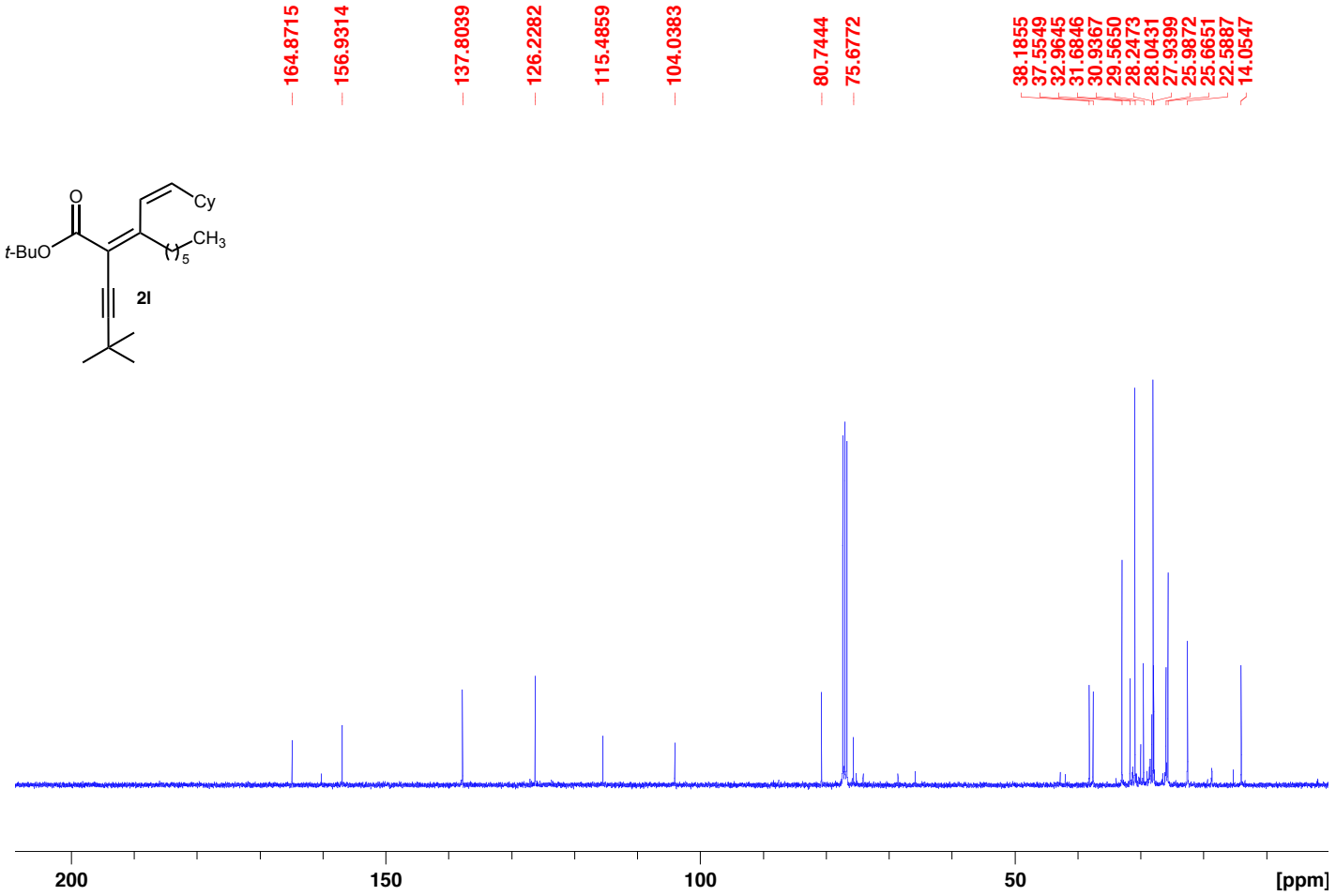
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 1:10 *E:Z* mixture of stereoisomers at the α,β-alkene

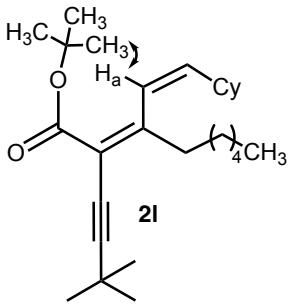


^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 1:10 *E:Z* mixture of stereoisomers at the α,β-alkene



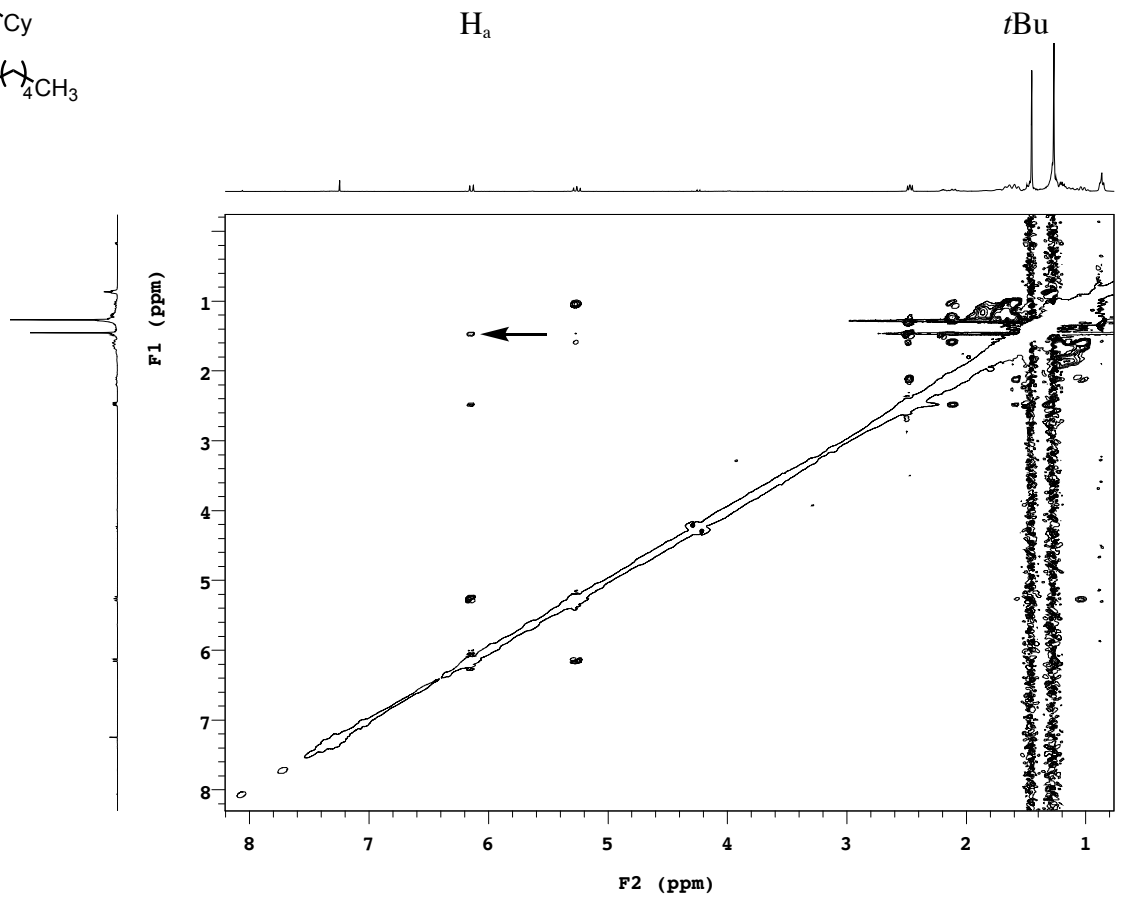
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 1:10 *E:Z* mixture of stereoisomers at the α,β-alkene



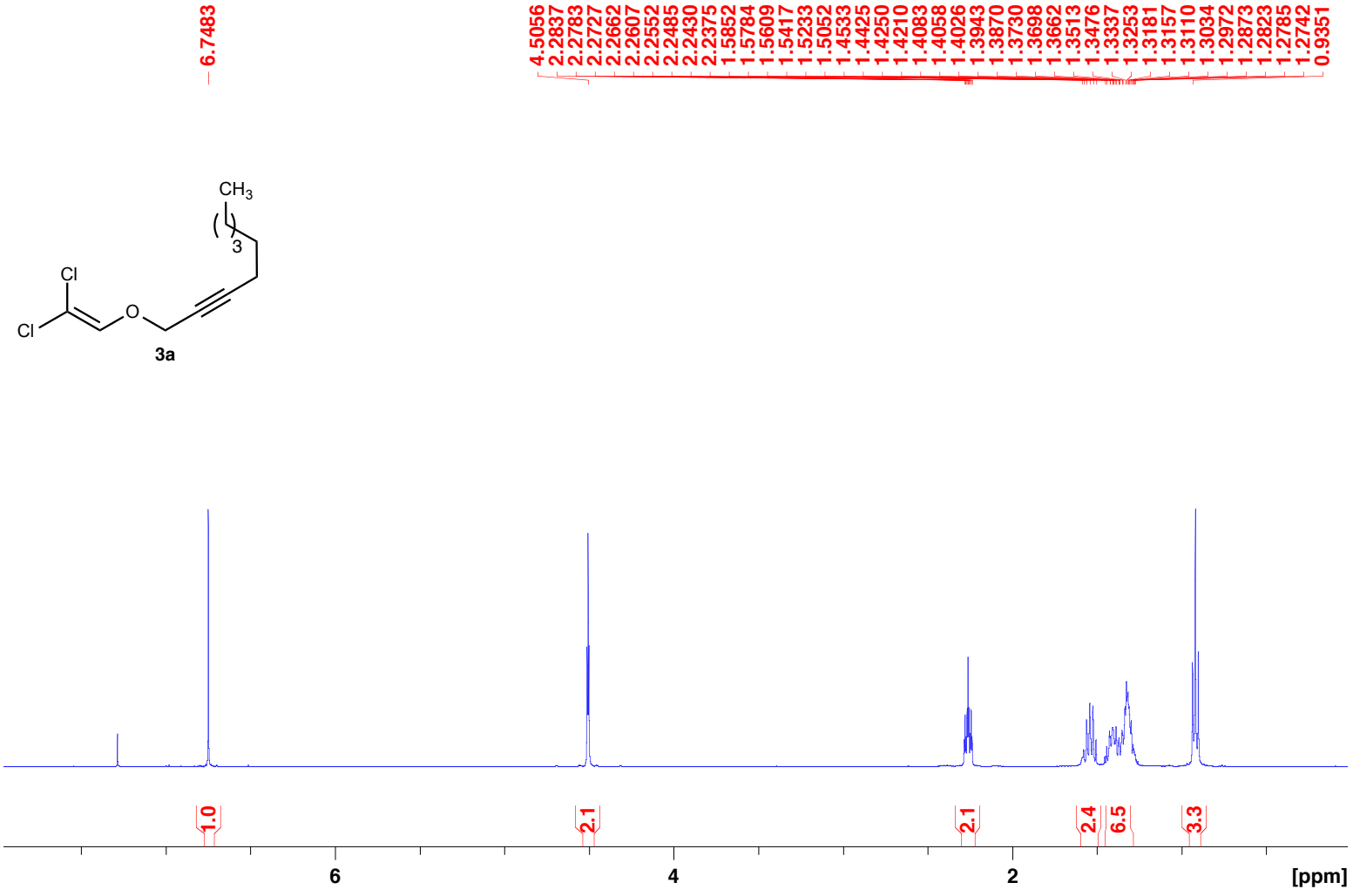


2l

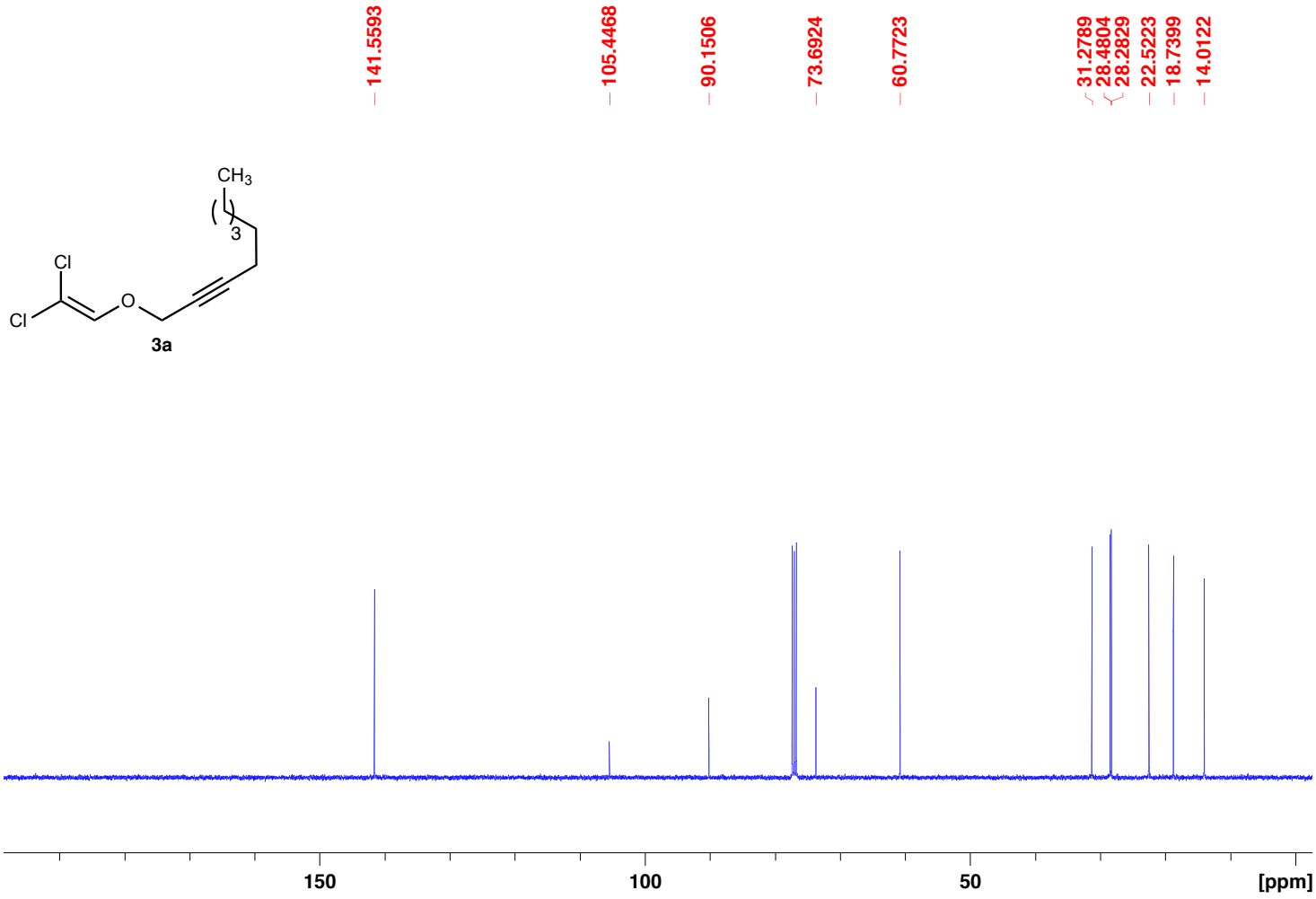
NOESY



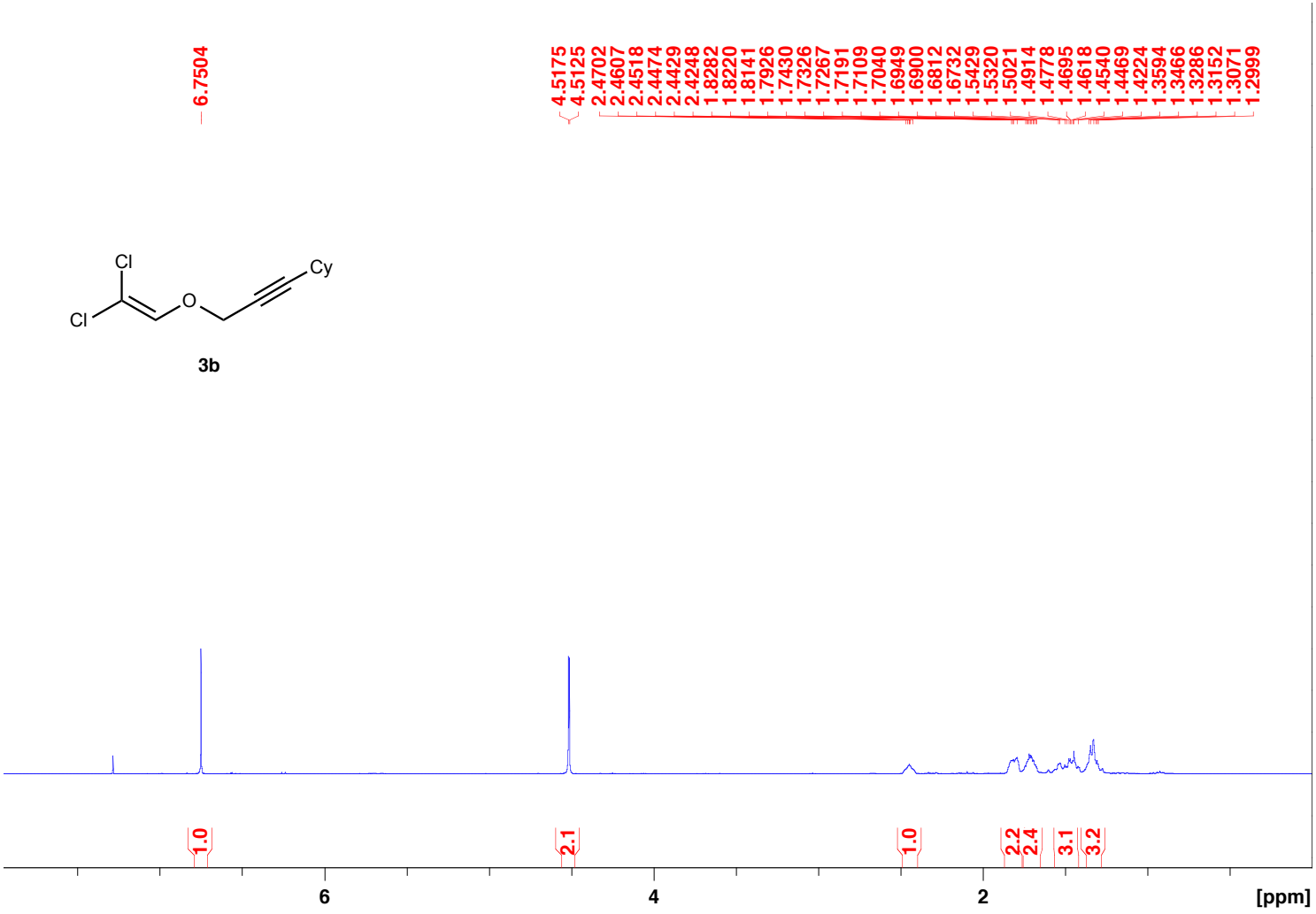
^{1}H NMR (400 MHz) , $CDCl_3$



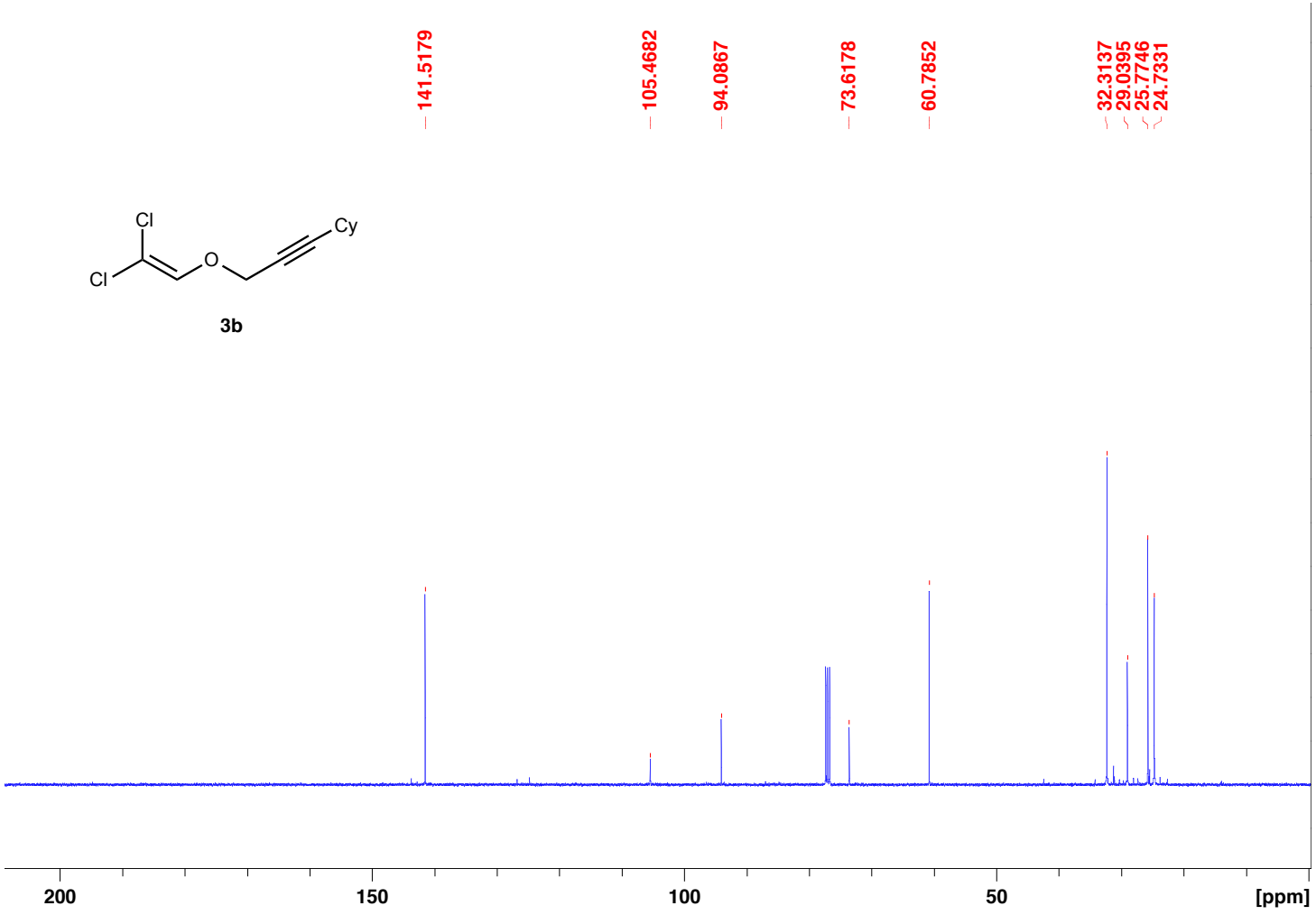
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



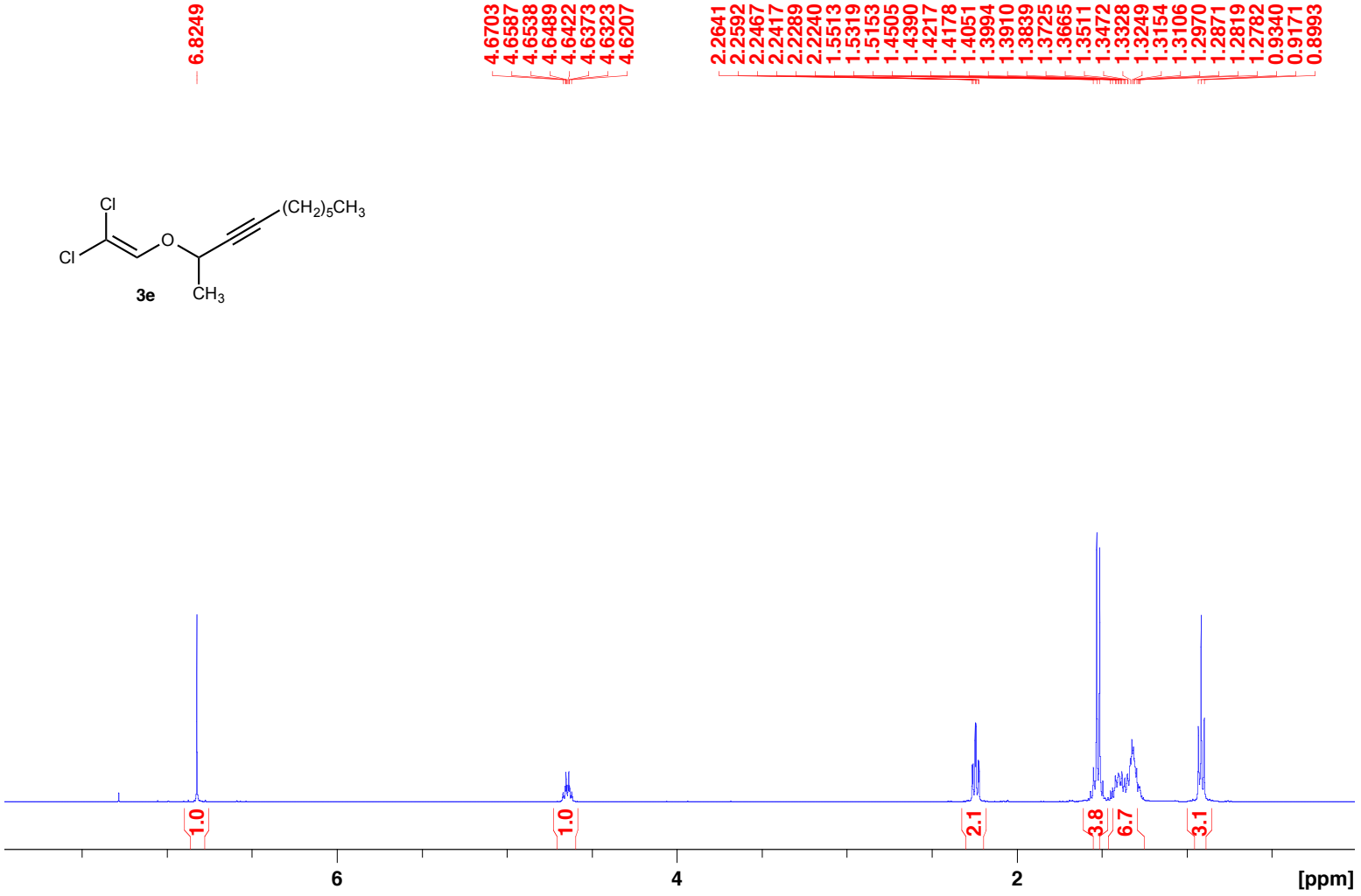
^{1}H NMR (400 MHz) , $CDCl_3$



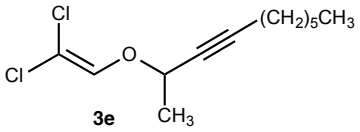
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



^{1}H NMR (400 MHz) , $CDCl_3$

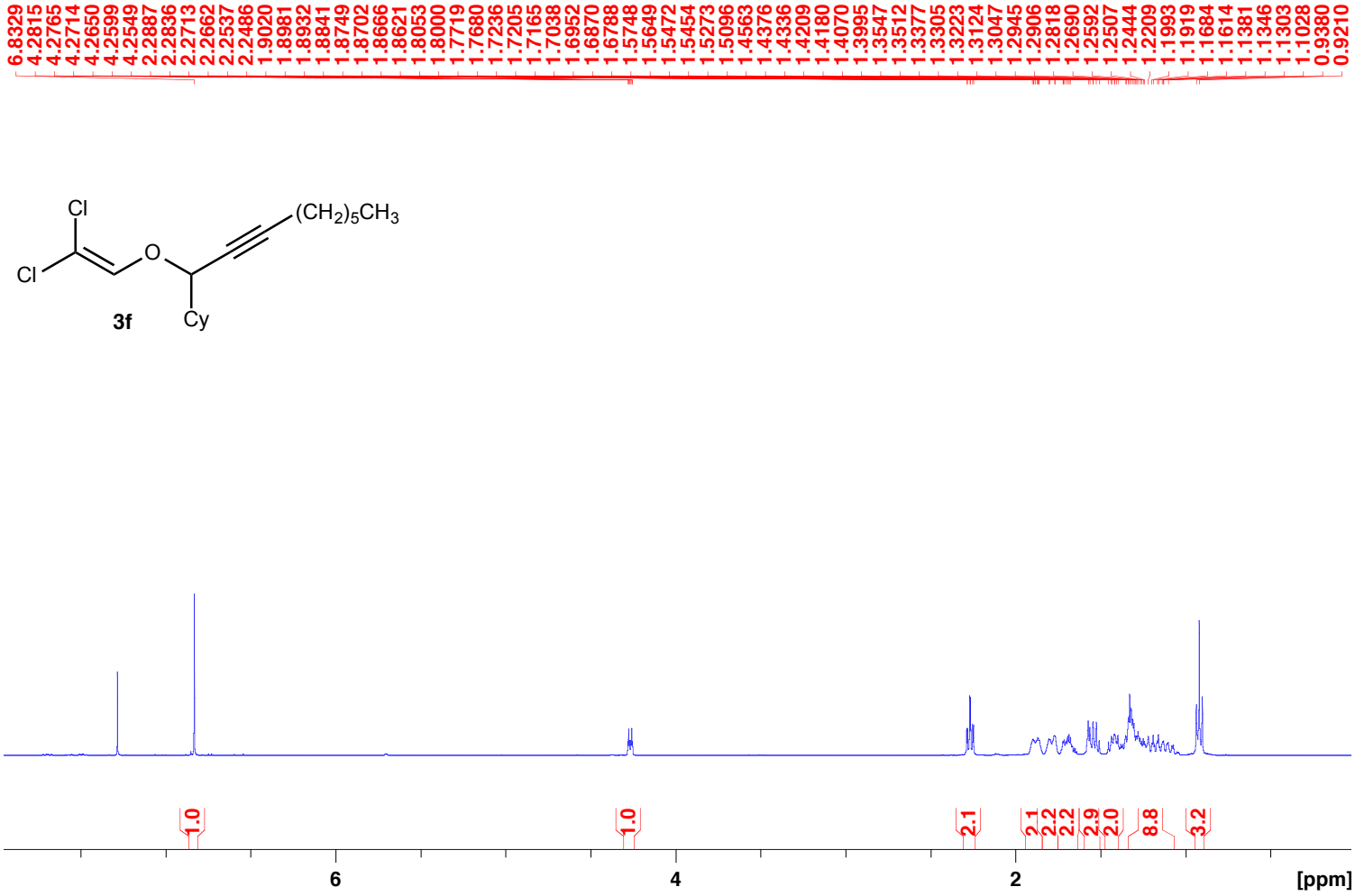


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$

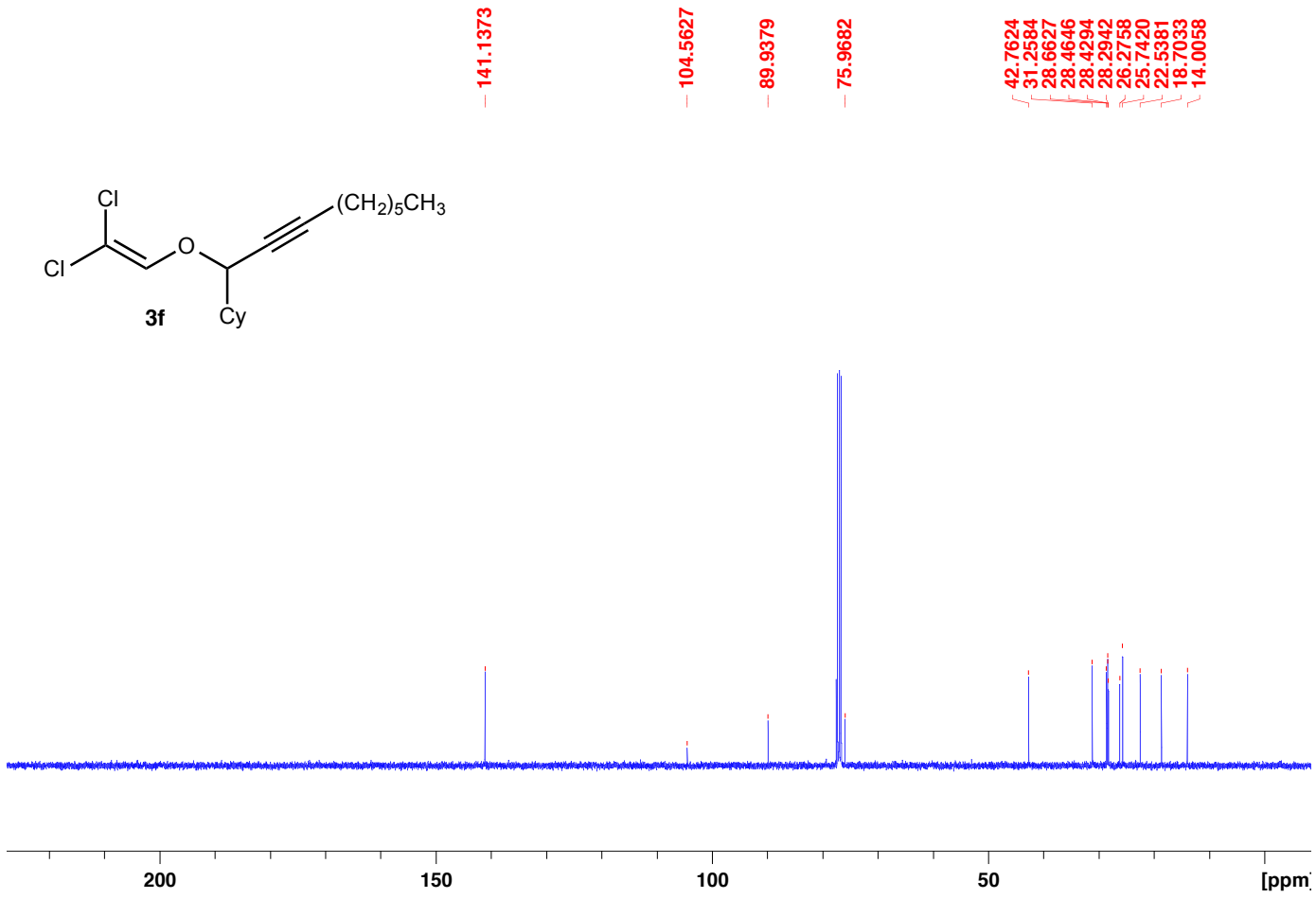


3e

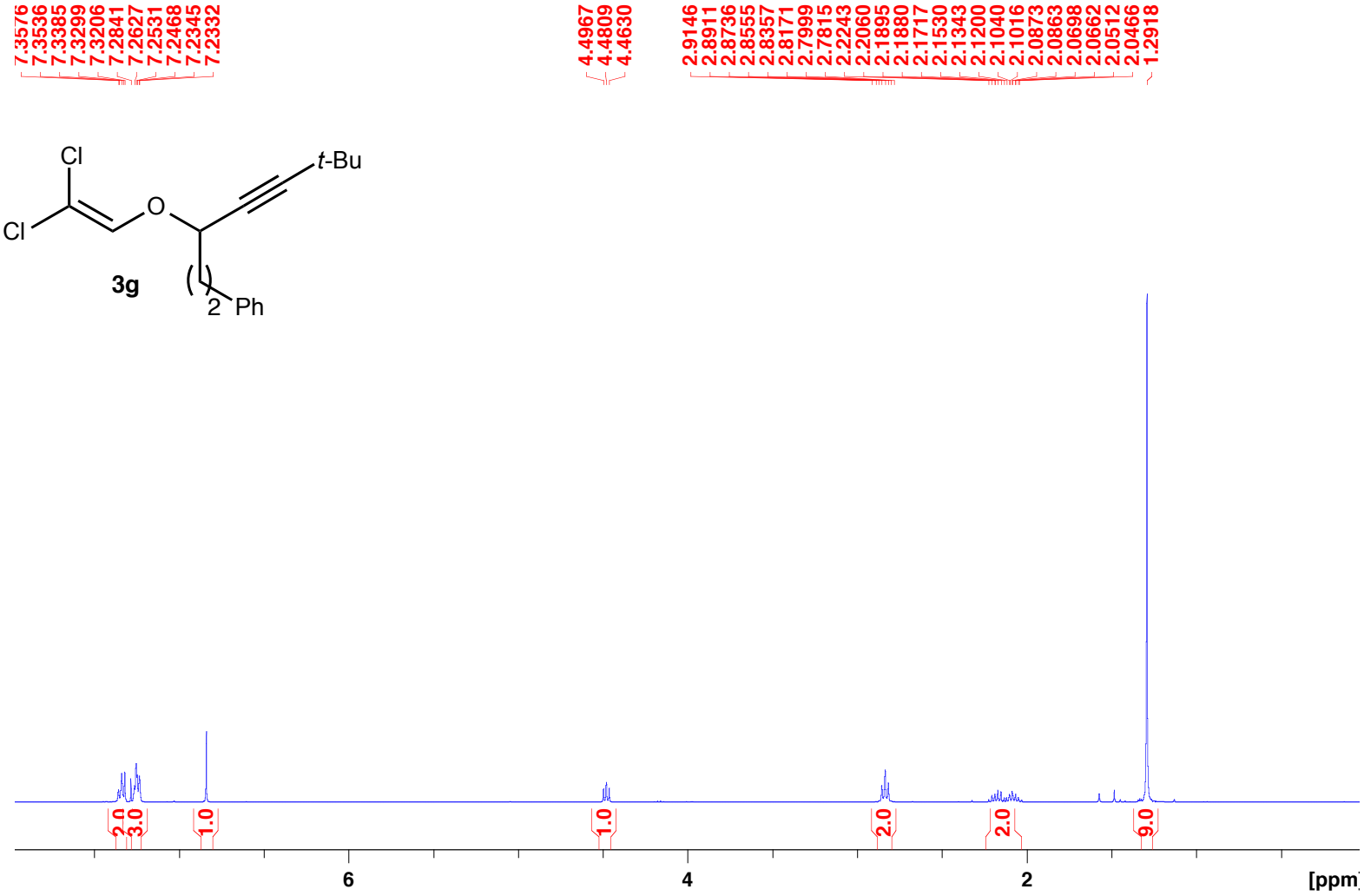
^{1}H NMR (400 MHz), $CDCl_3$



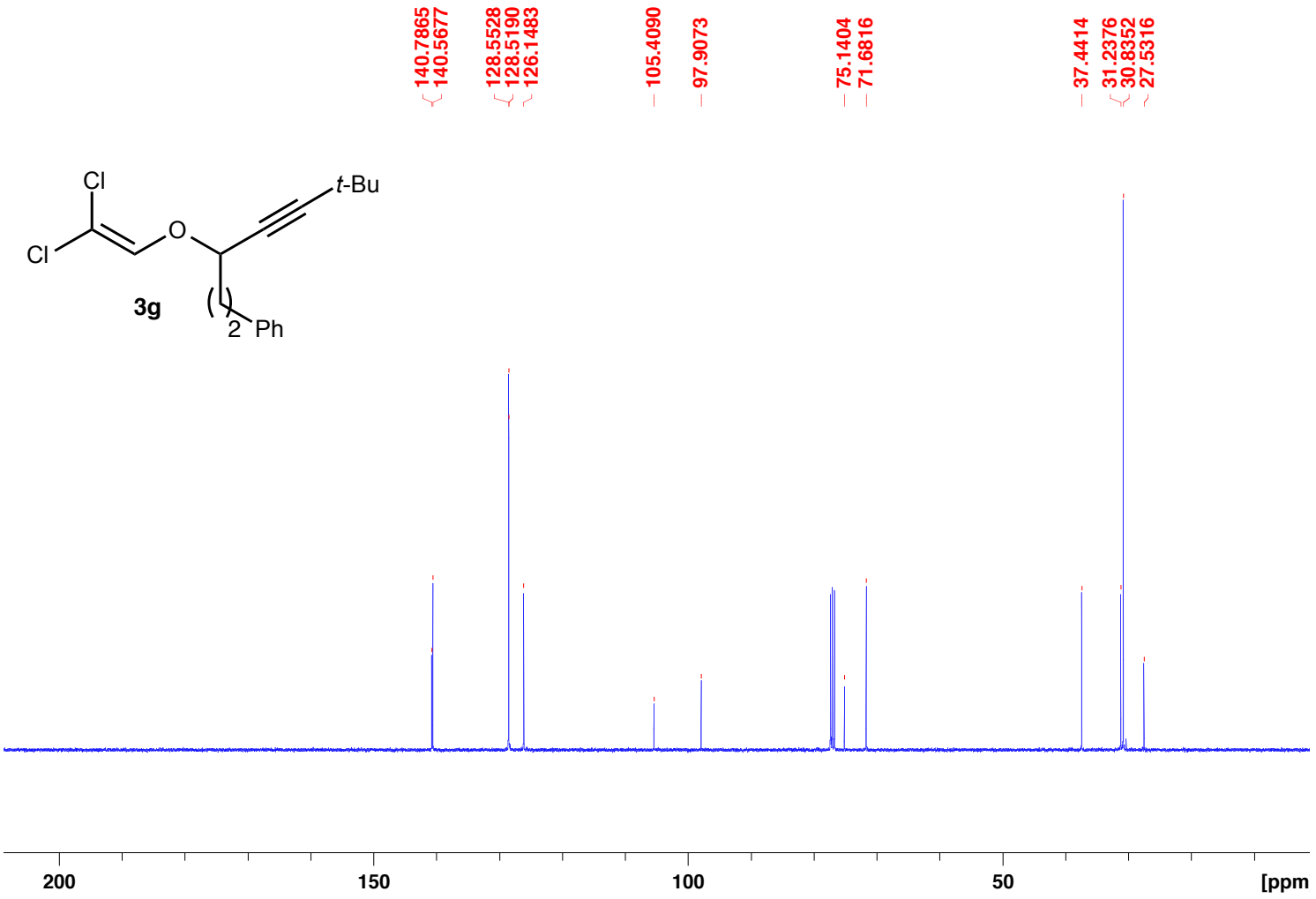
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



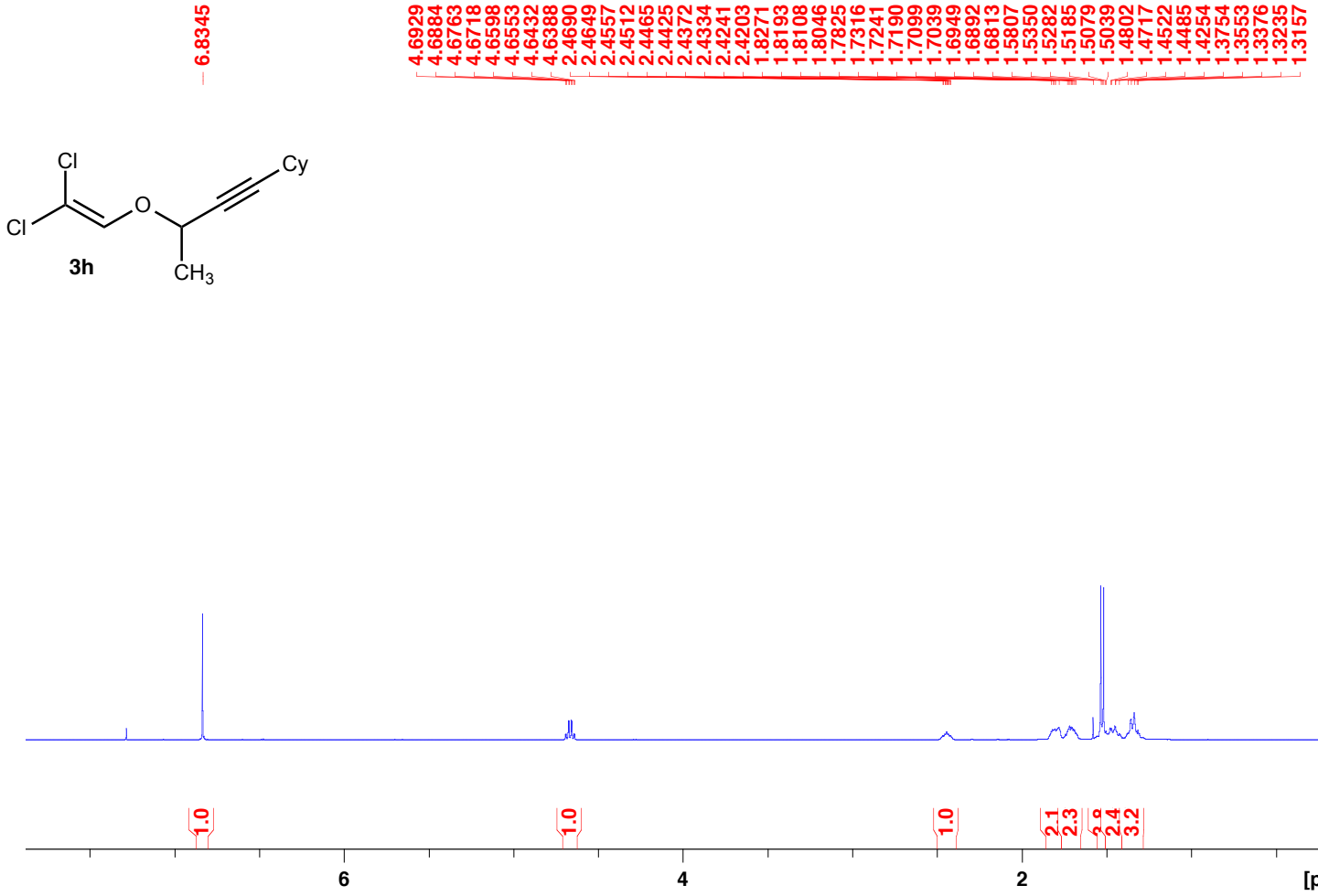
^{1}H NMR (400 MHz), $CDCl_3$



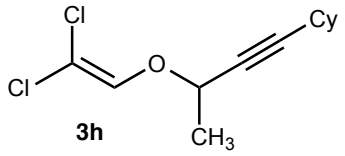
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$

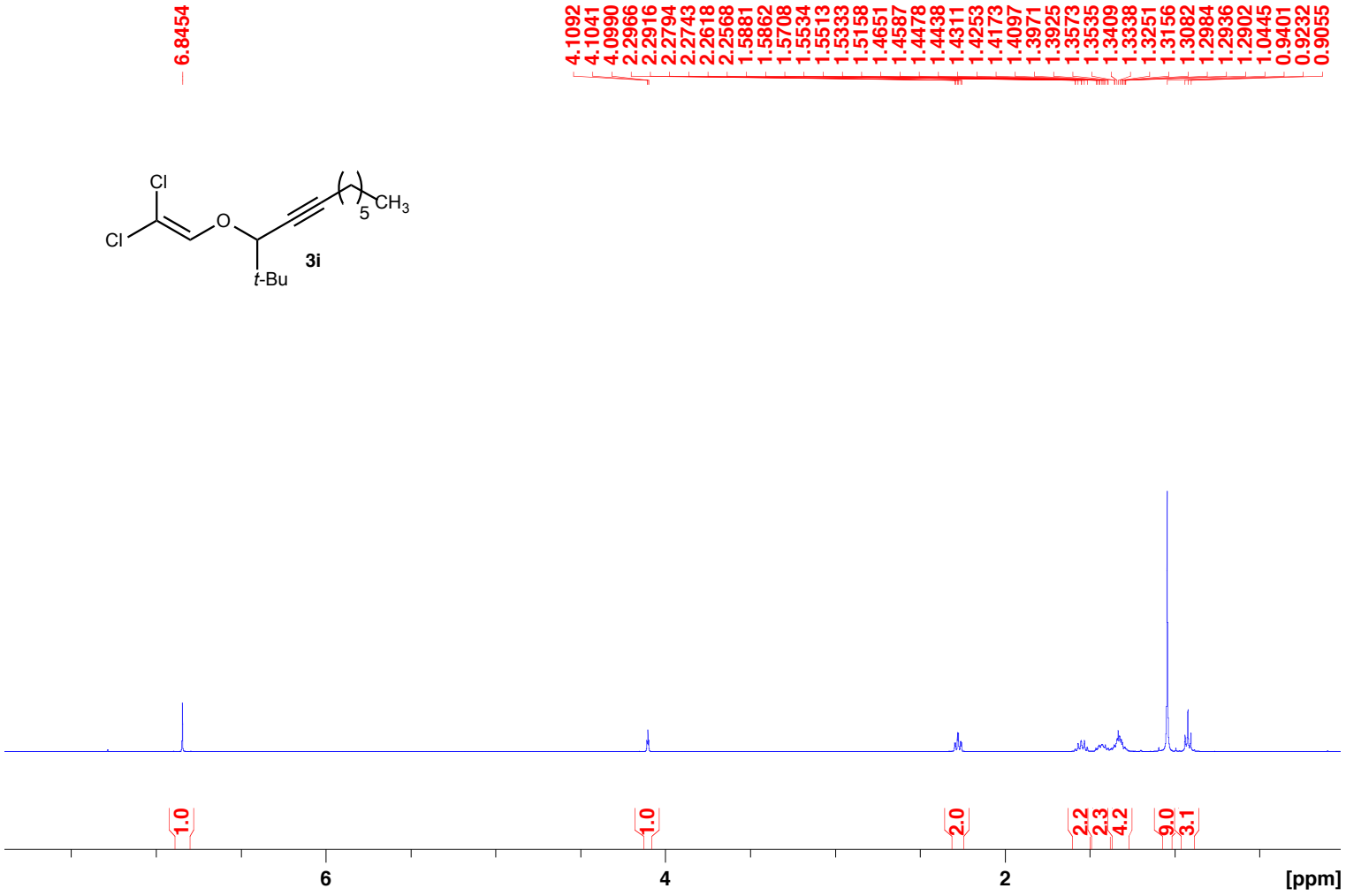


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$

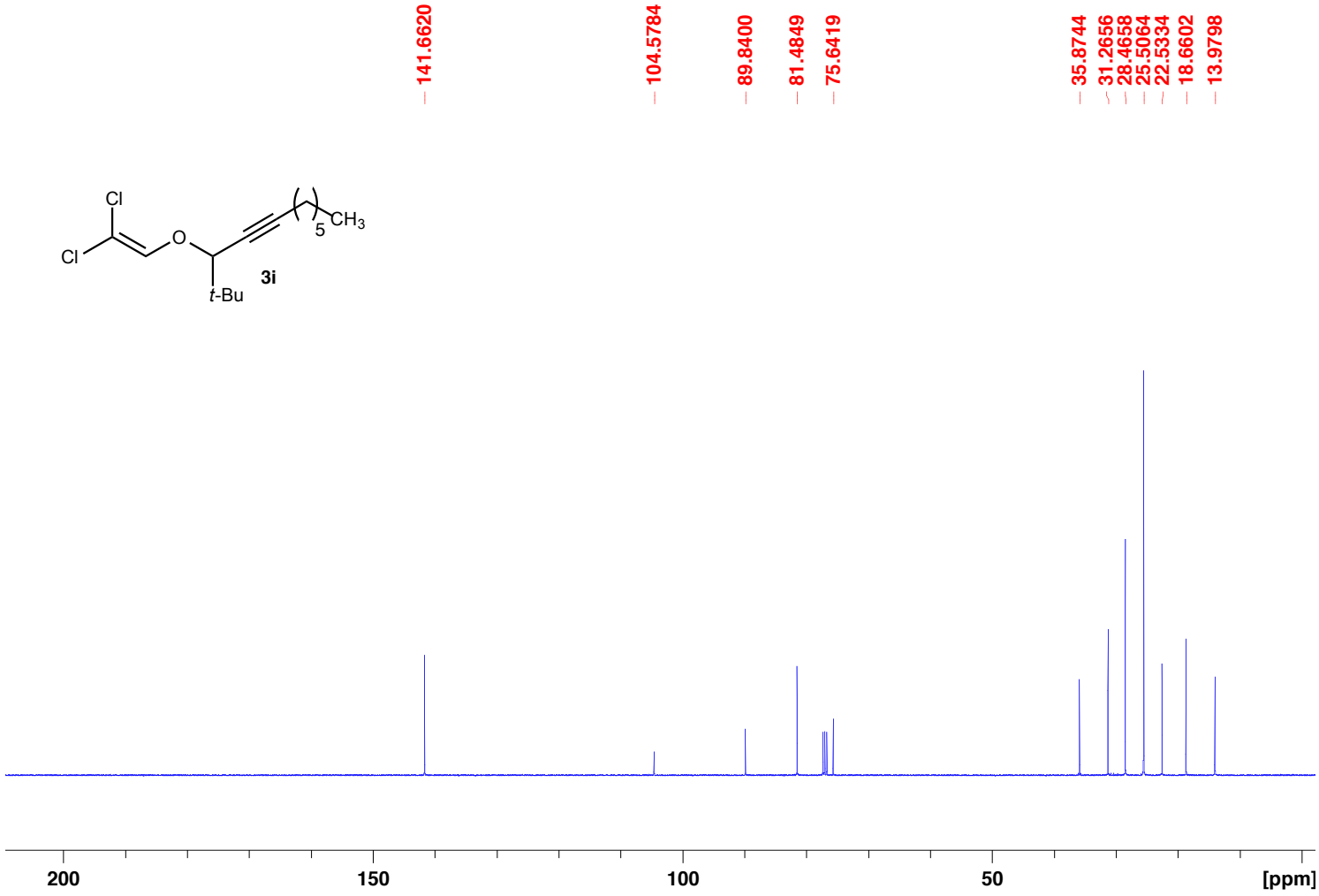


3h

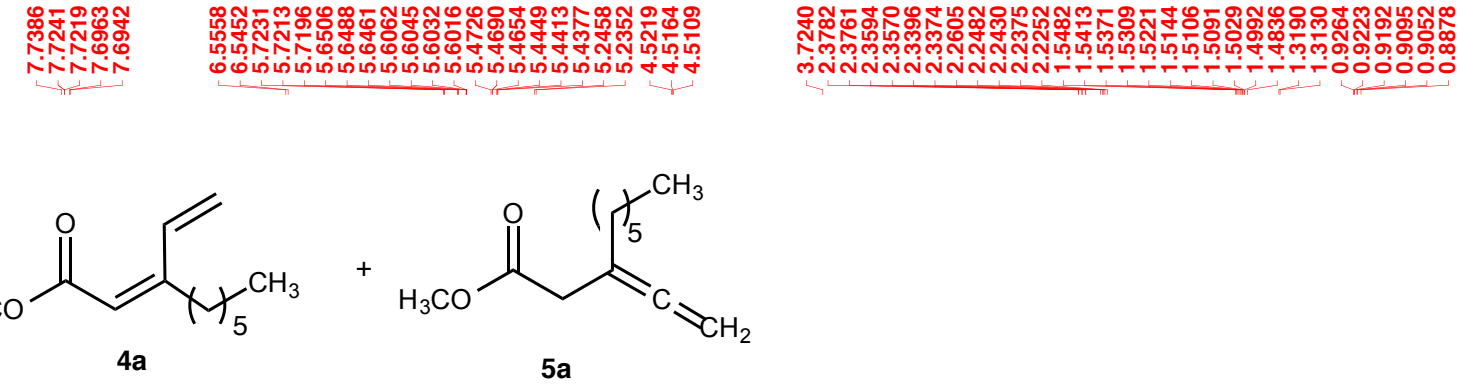
^{1}H NMR (400 MHz), $CDCl_3$

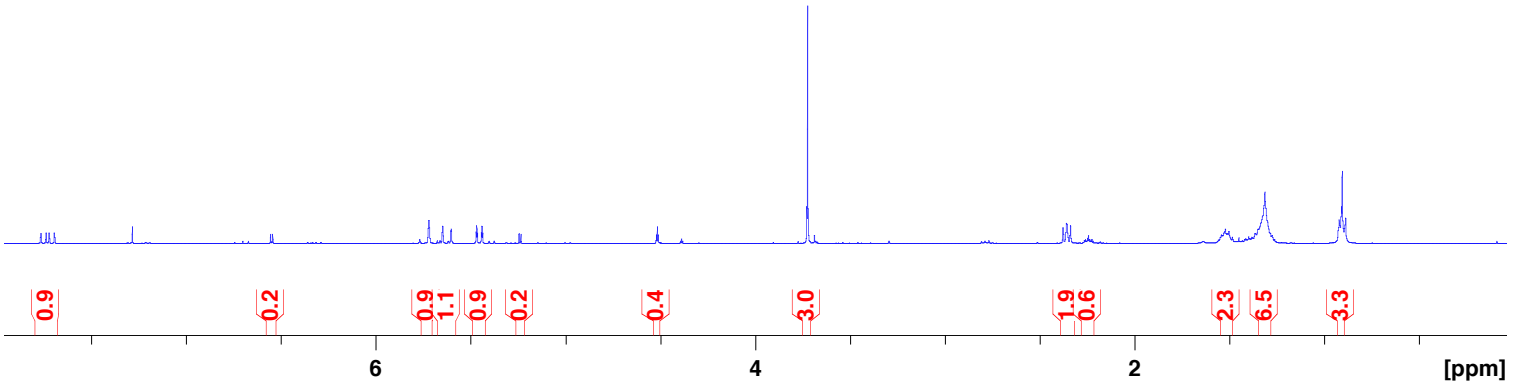


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$

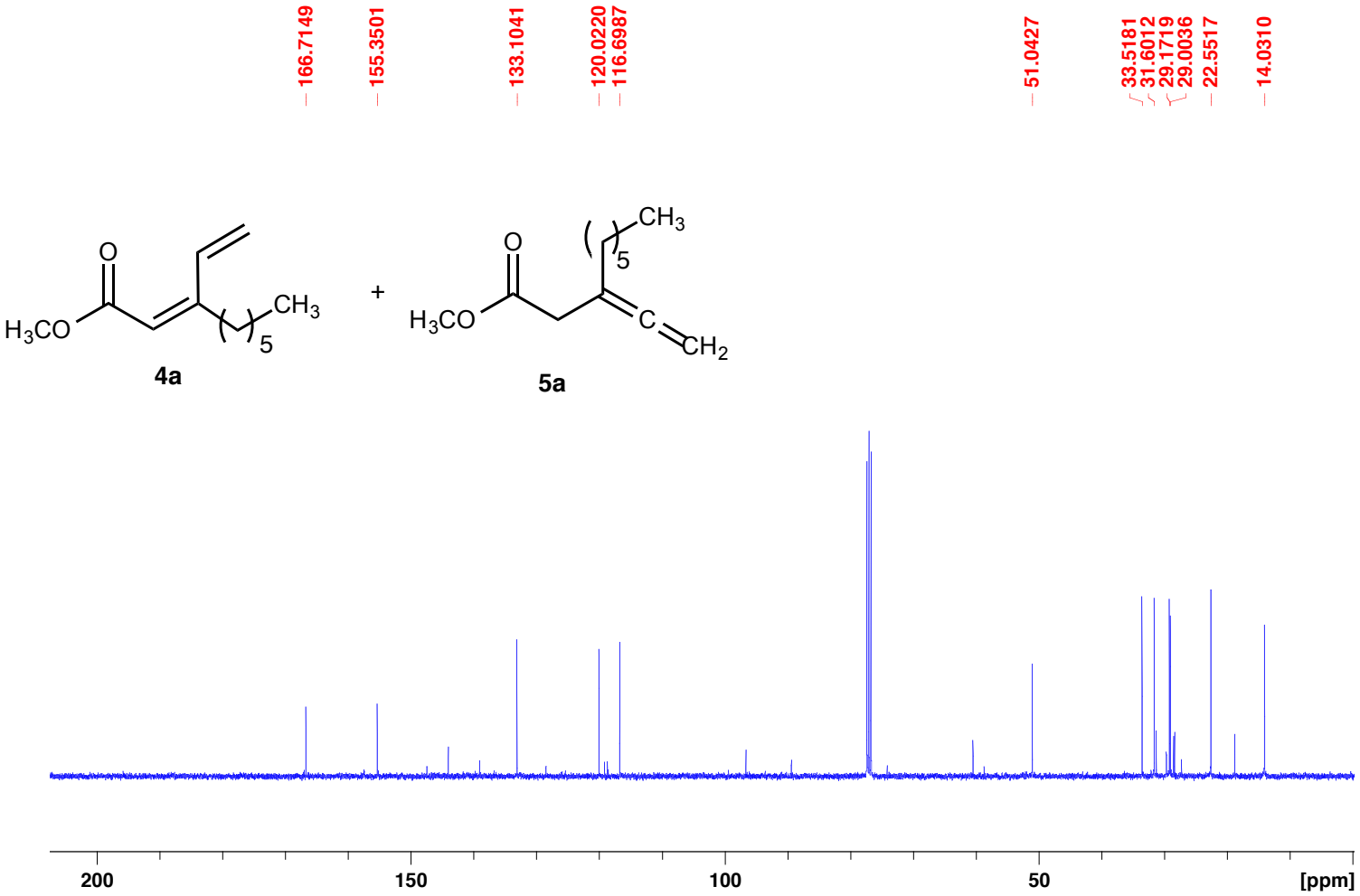


^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 5:1 mixture of **4a** and **5a**.

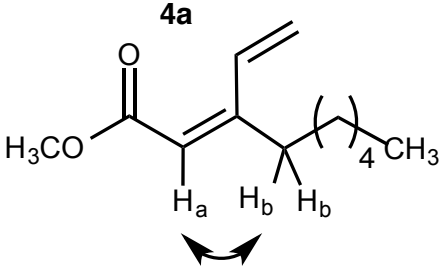




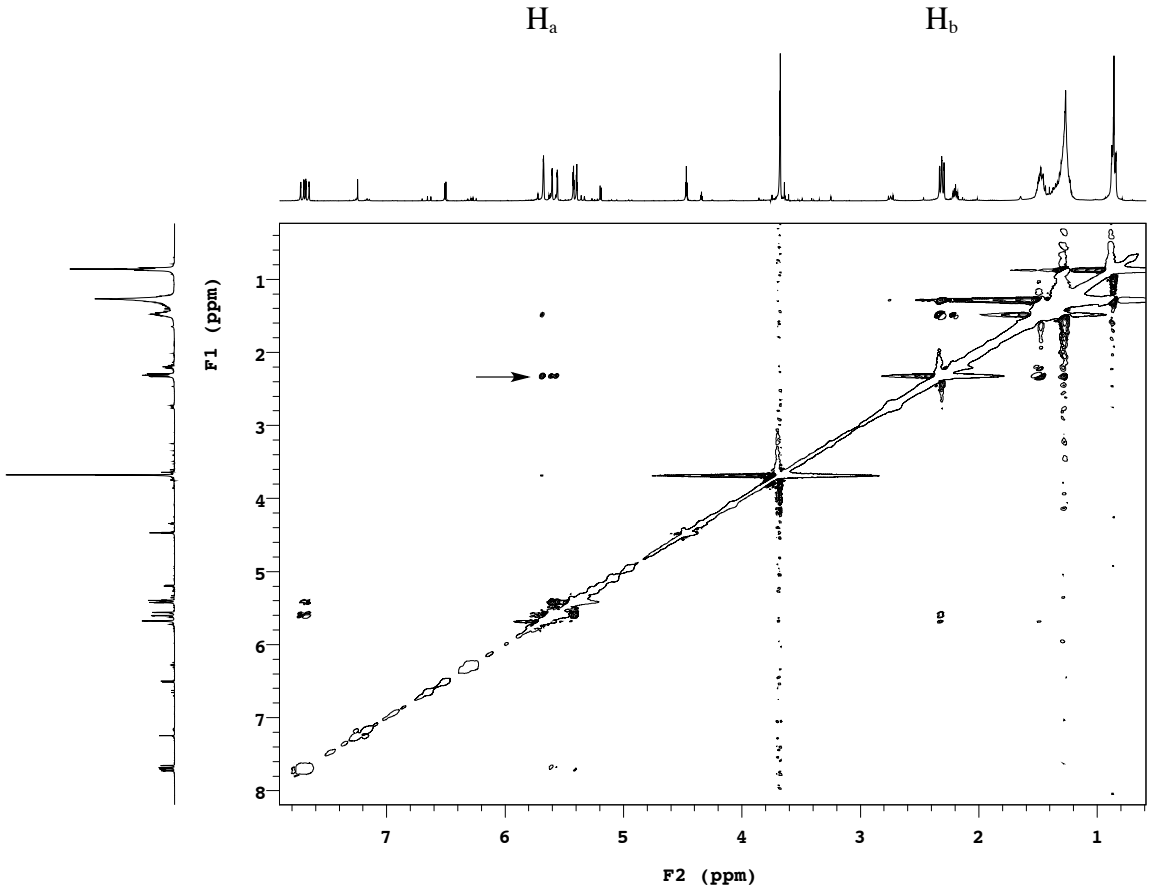
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$ as an inseparable 5:1 mixture of **4a** and **5a**.



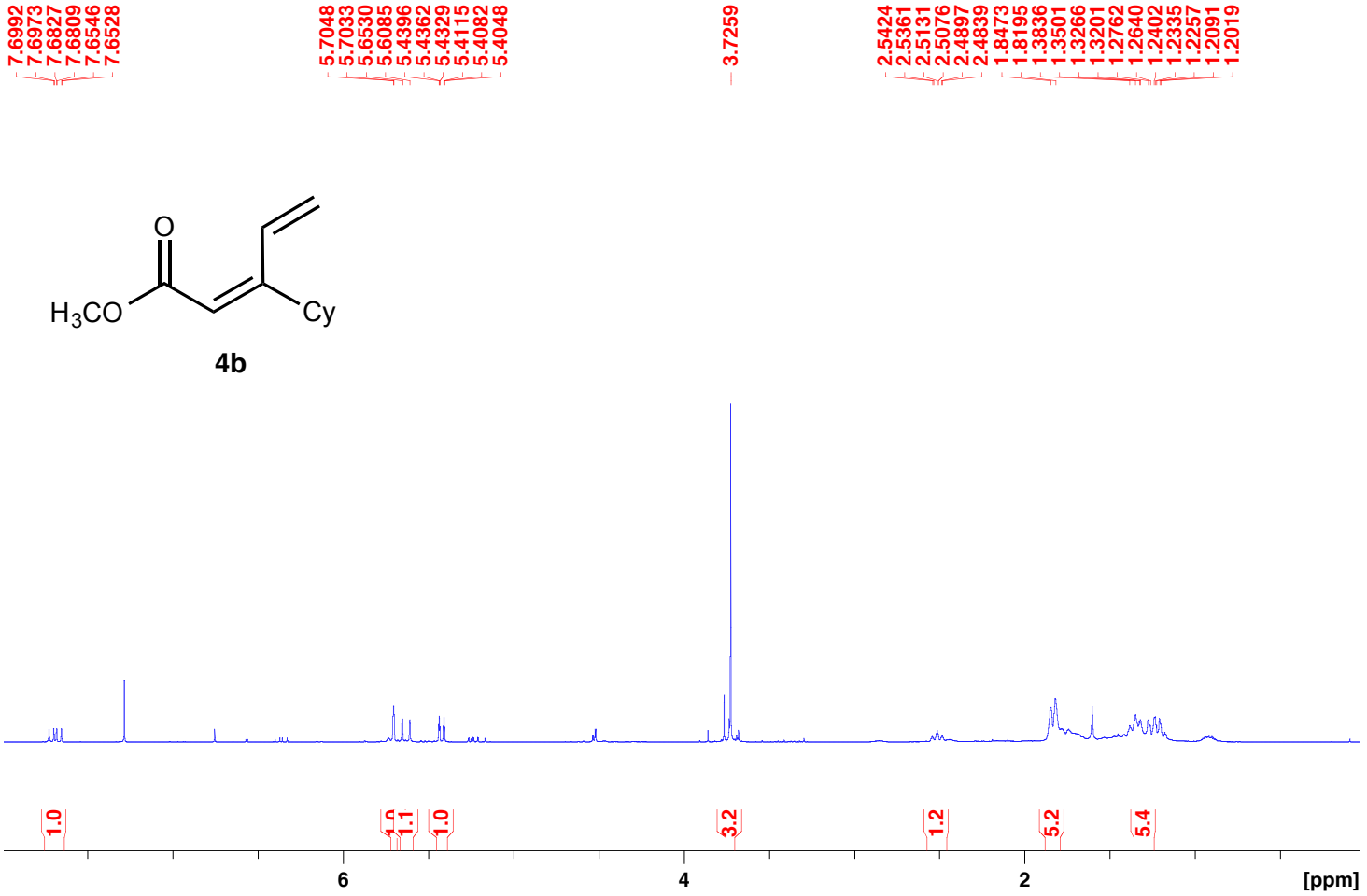
4a



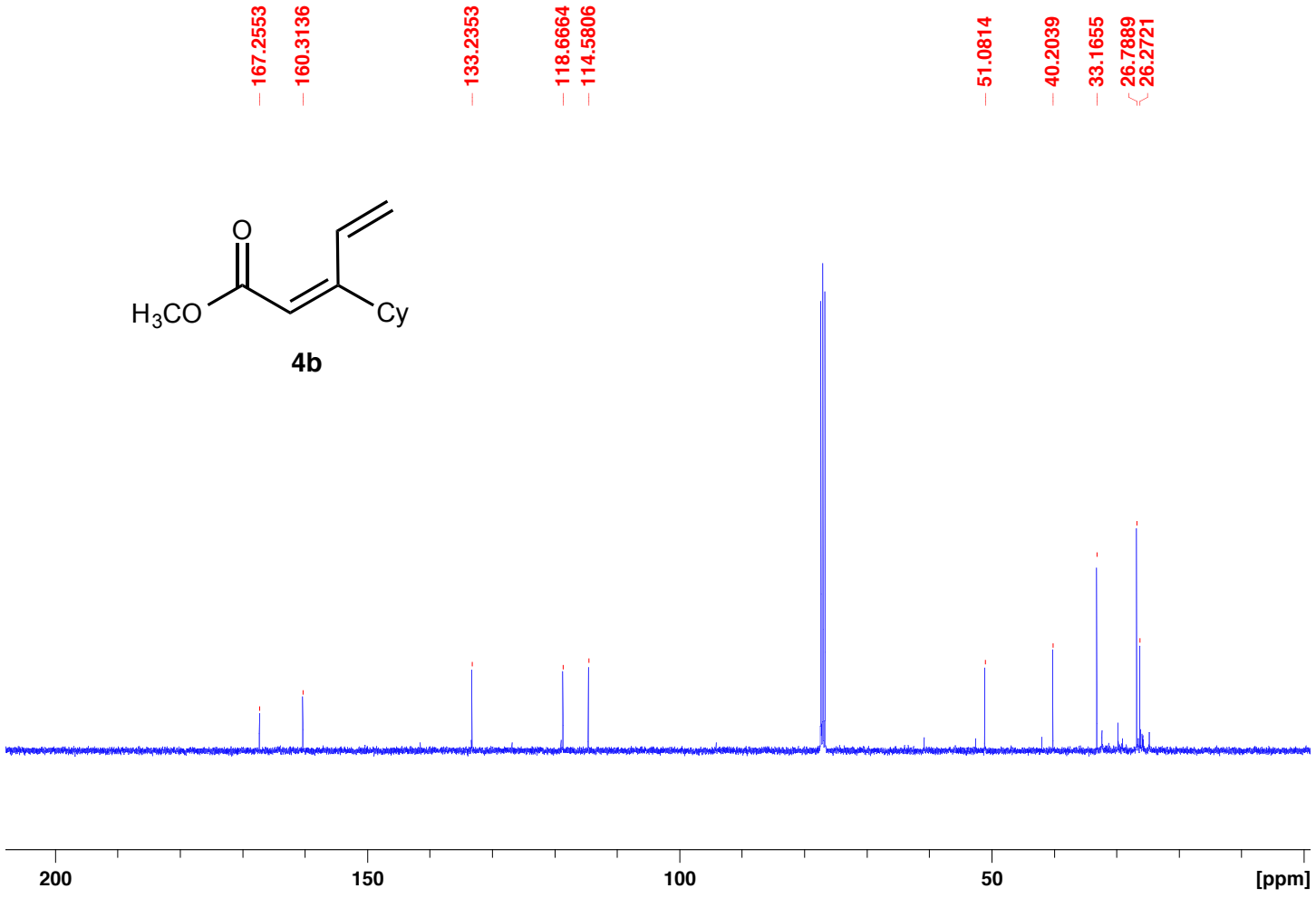
NOESY



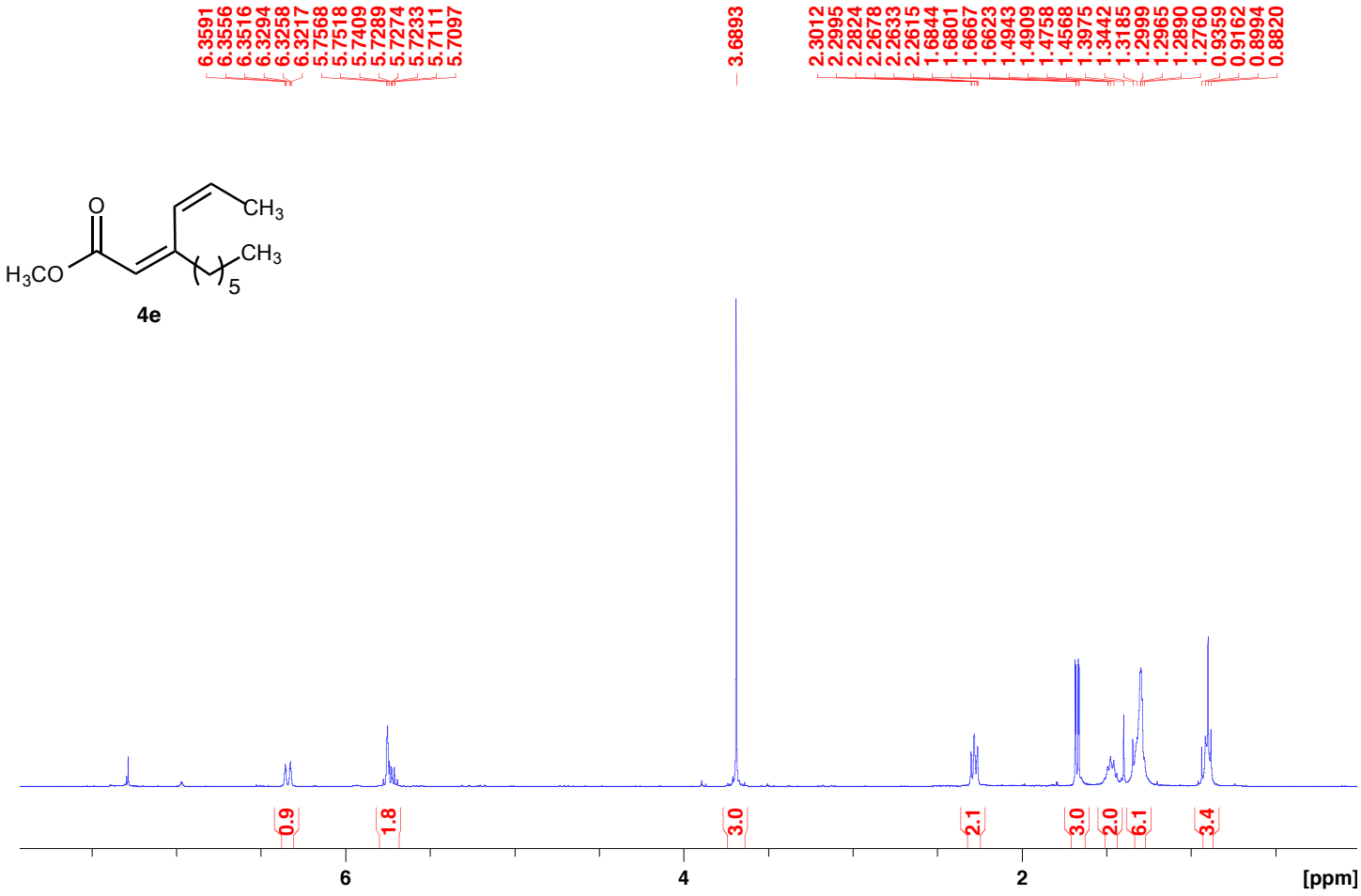
^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 5:1 mixture of *E* and *Z* stereoisomers.



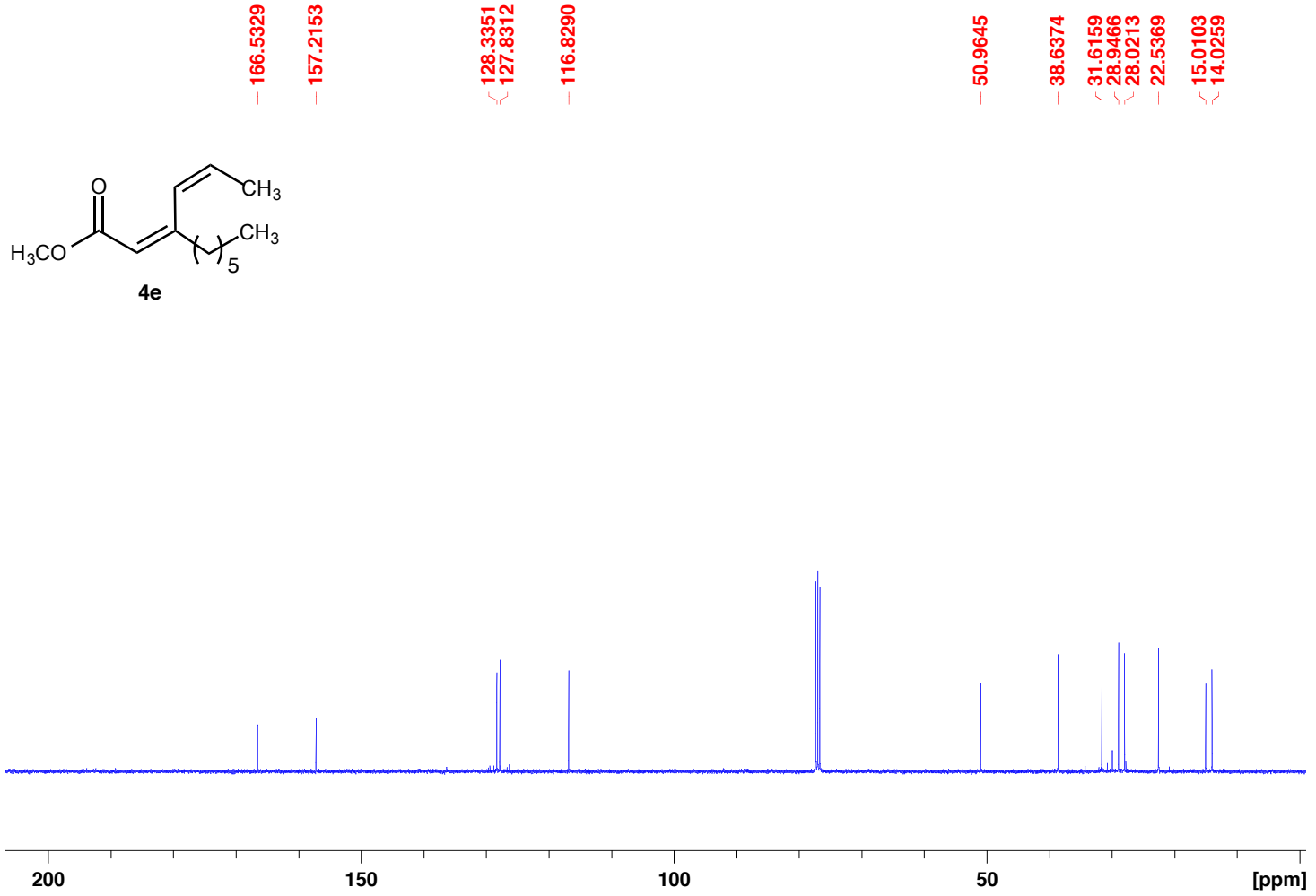
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$ as an inseparable 5:1 mixture of *E* and *Z* stereoisomers.

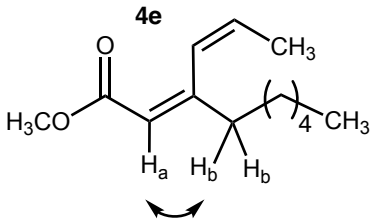


^{1}H NMR (400 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

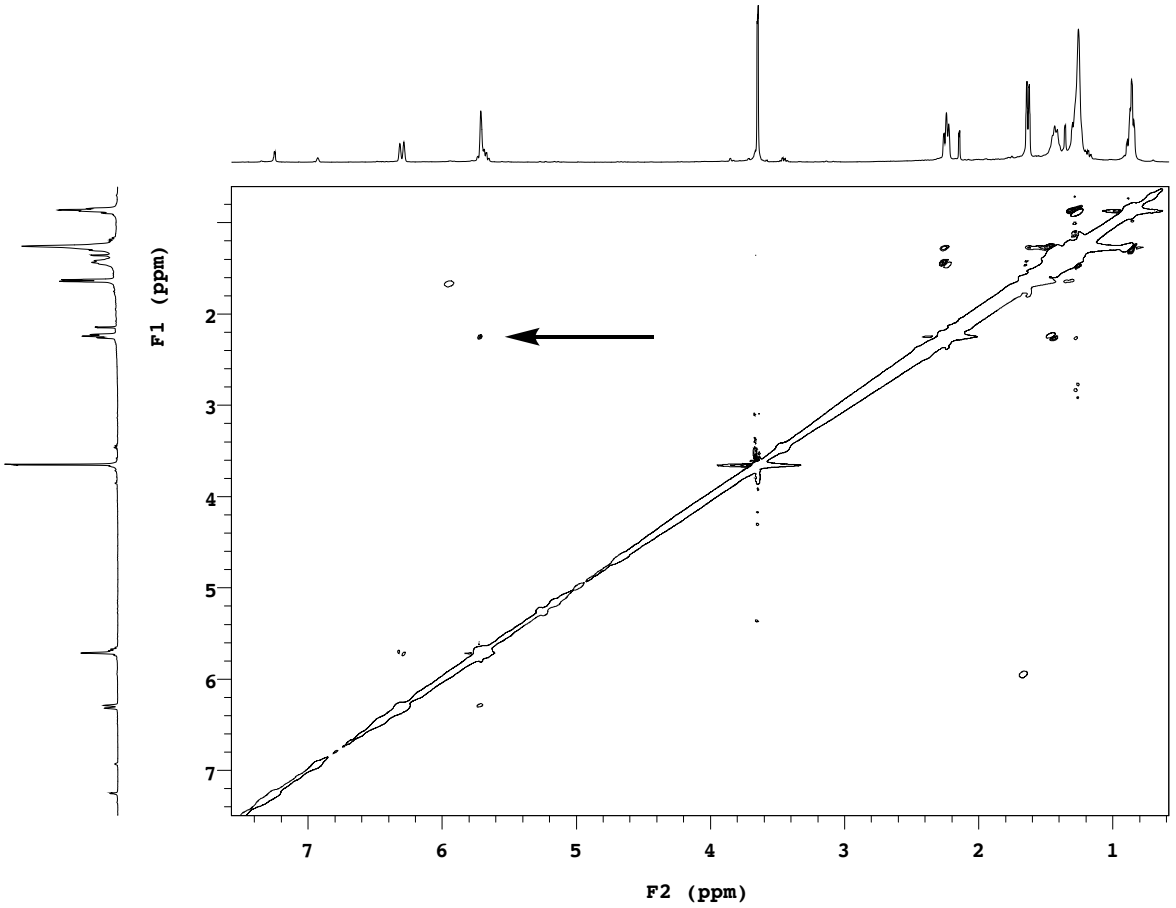


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

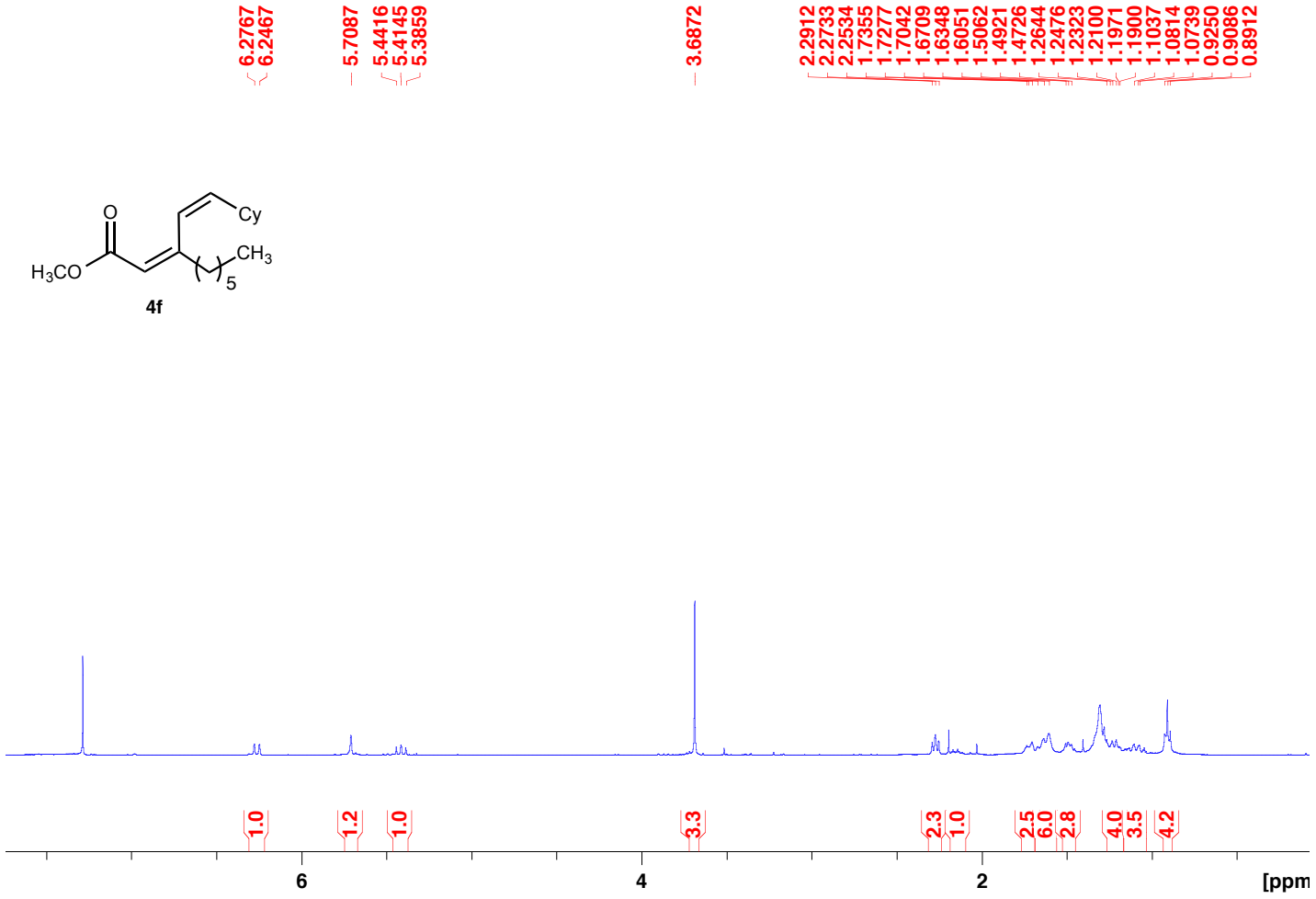




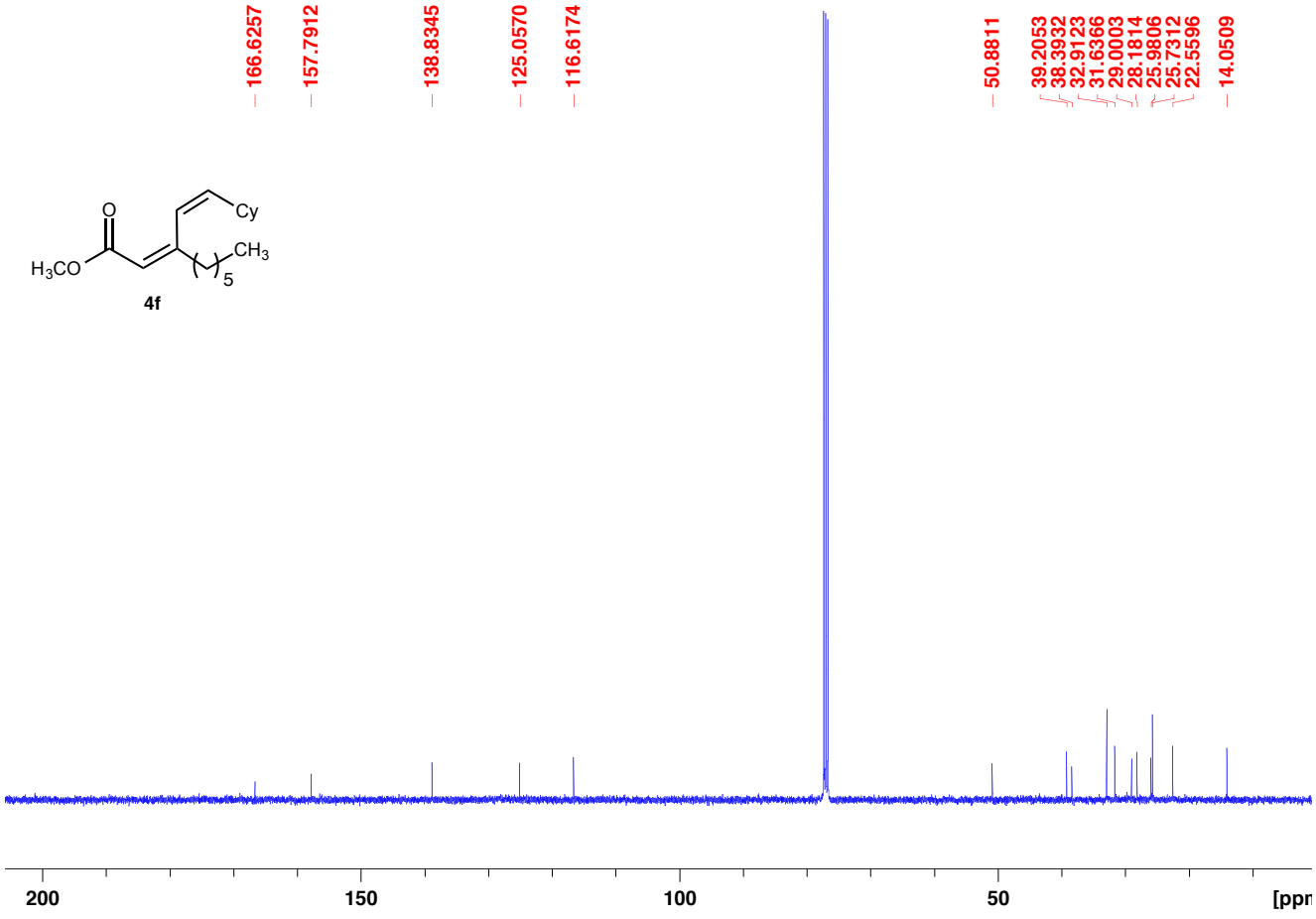
NOESY



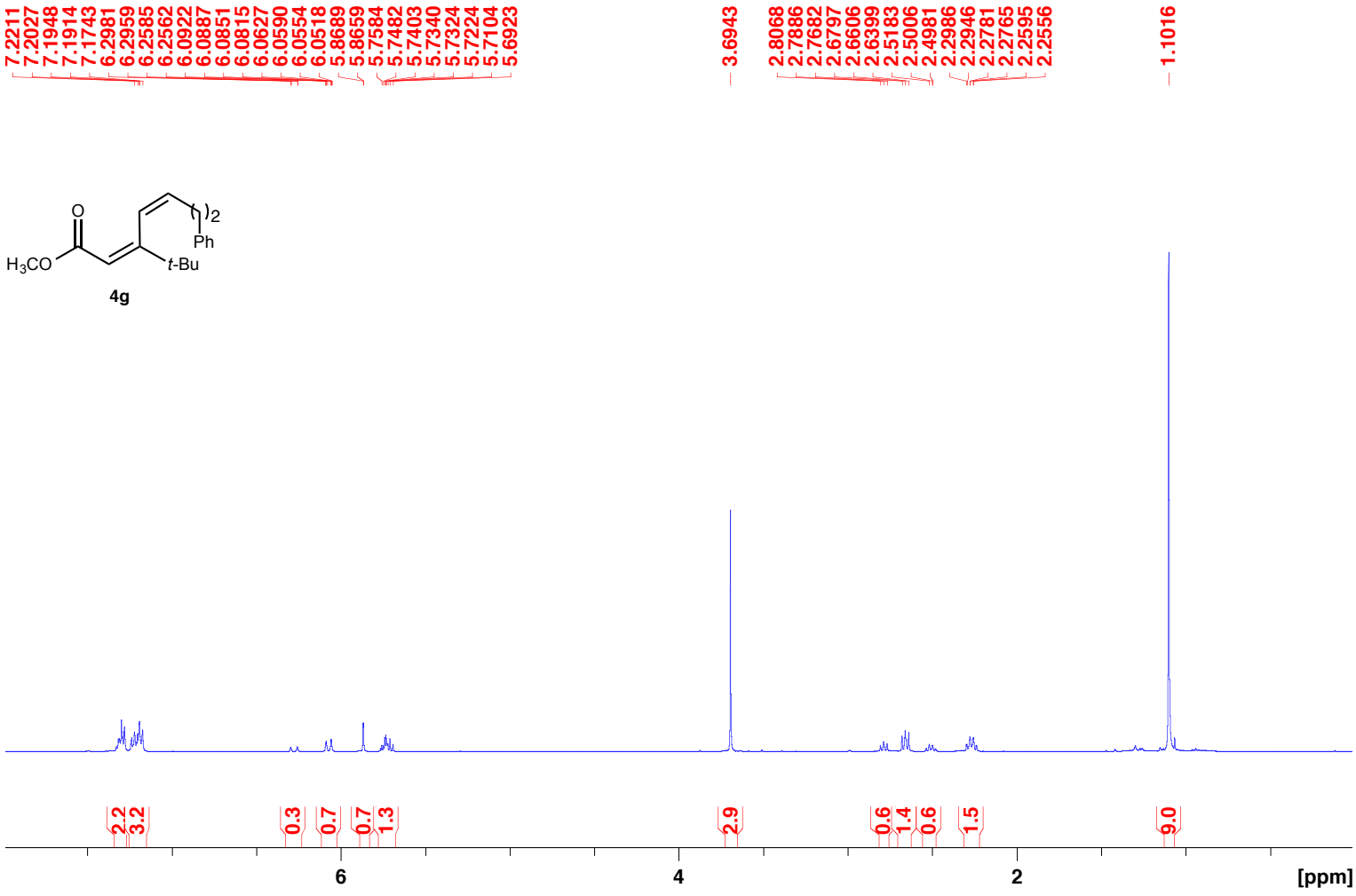
^{1}H NMR (400 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene



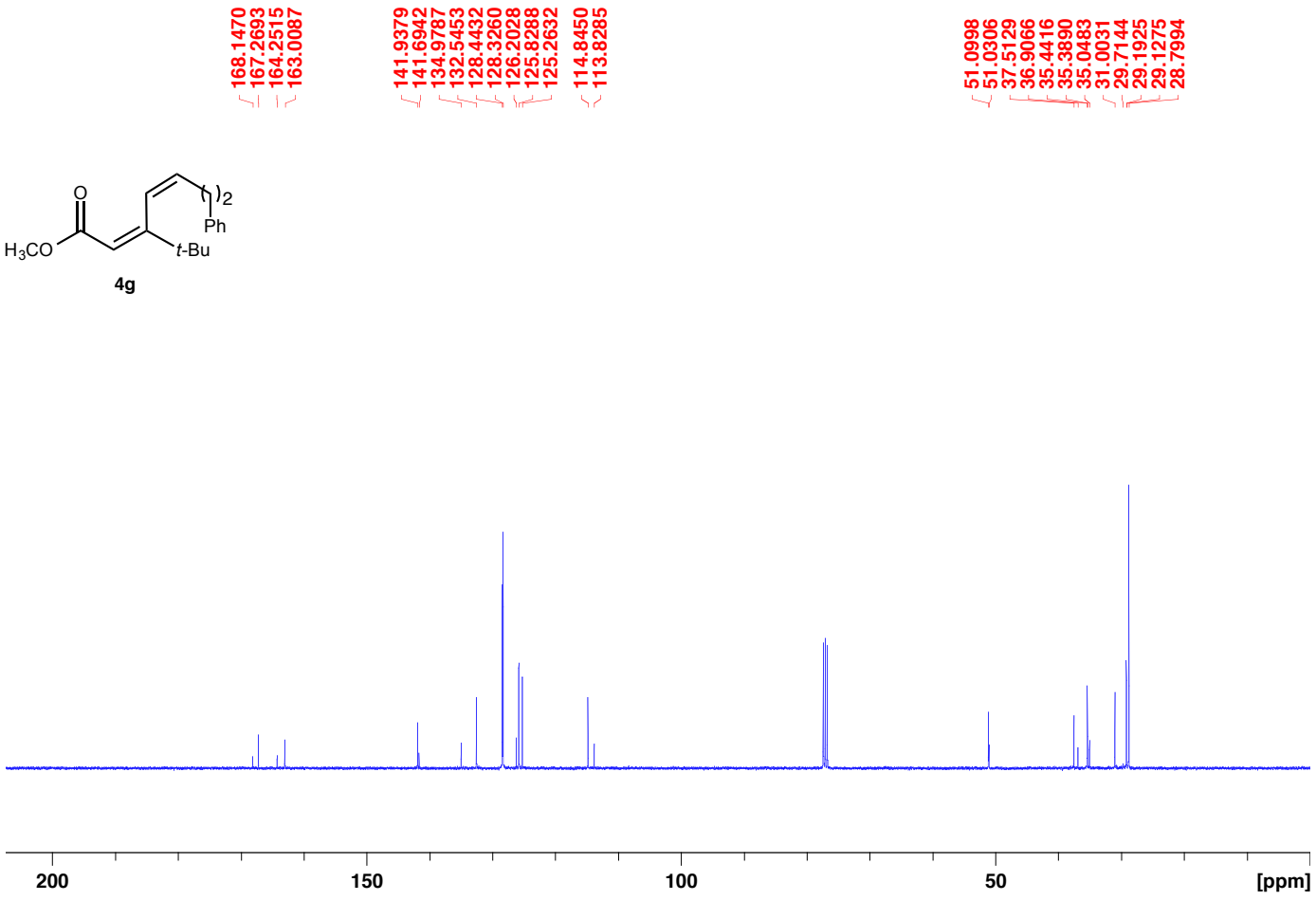
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

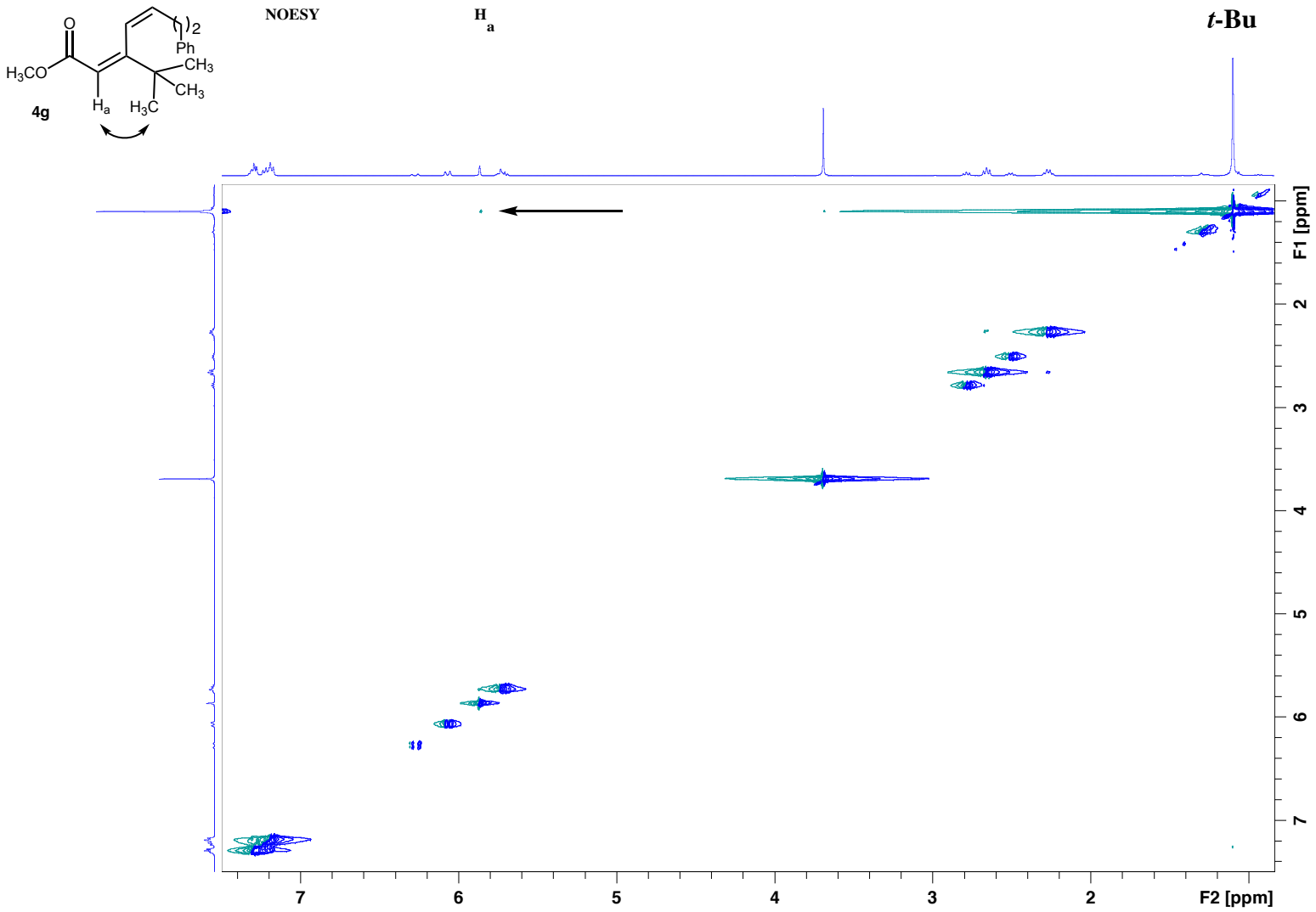


^{1}H NMR (400 MHz), $CDCl_3$, as a 2.3:1 mixture of *Z* and *E* stereoisomers (γ,δ-olefin)

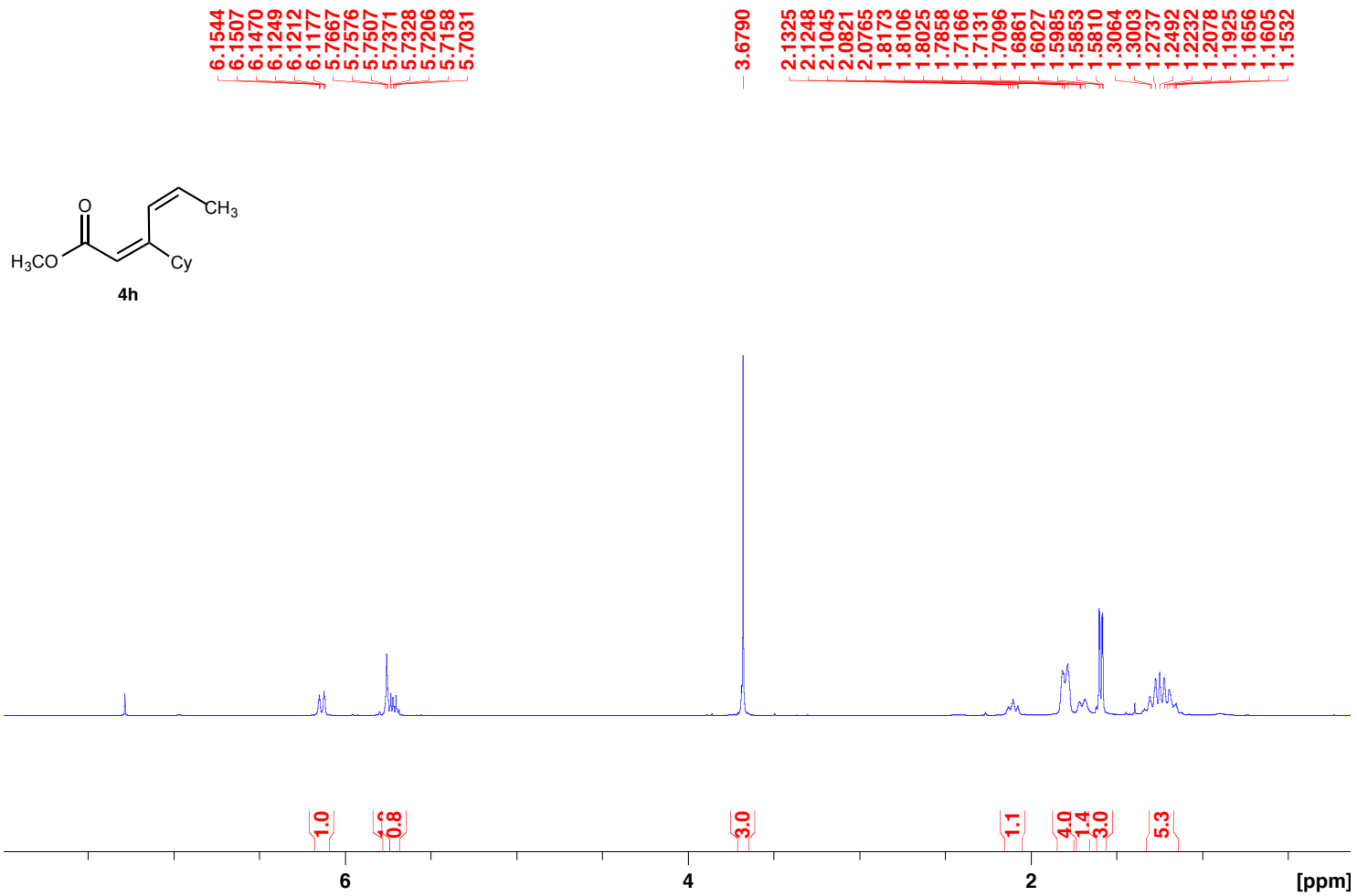


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a 2.3:1 mixture of *Z* and *E* stereoisomers

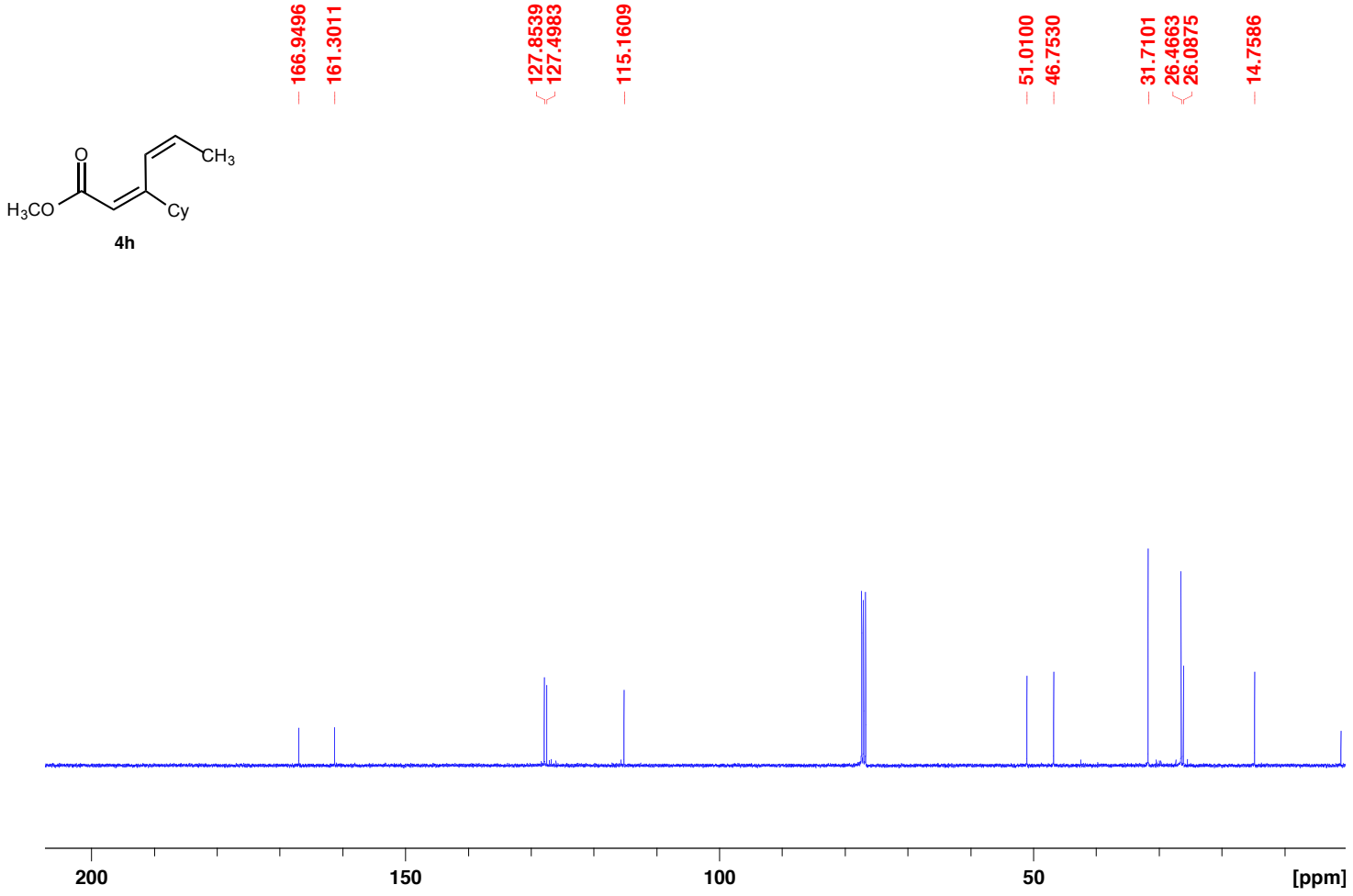


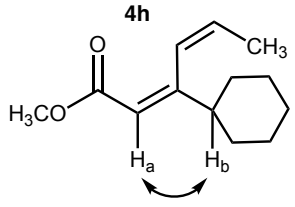

NOESY
H a
t-Bu
O
H3CO
2
Ph
CH3
CH3
Ha
H3C
4g
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2

^{1}H NMR (400 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

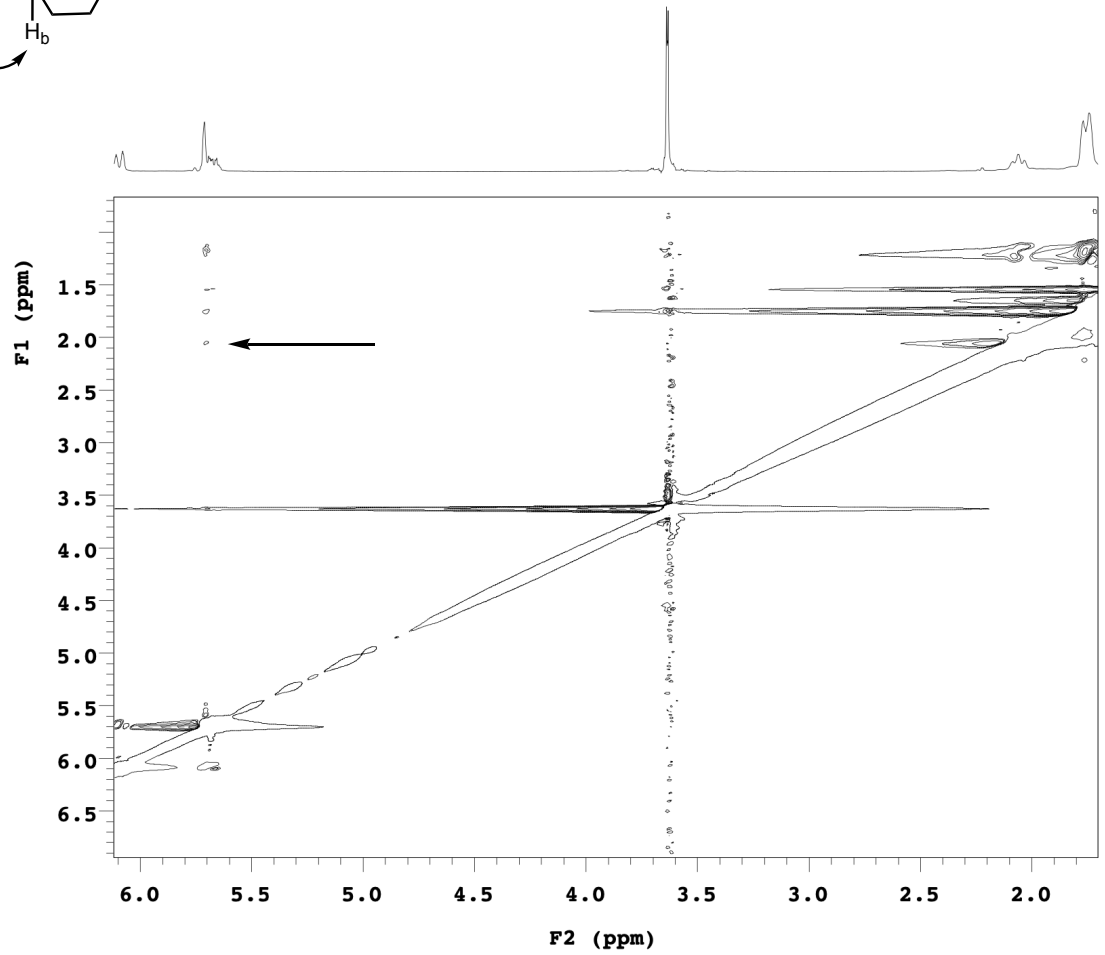


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

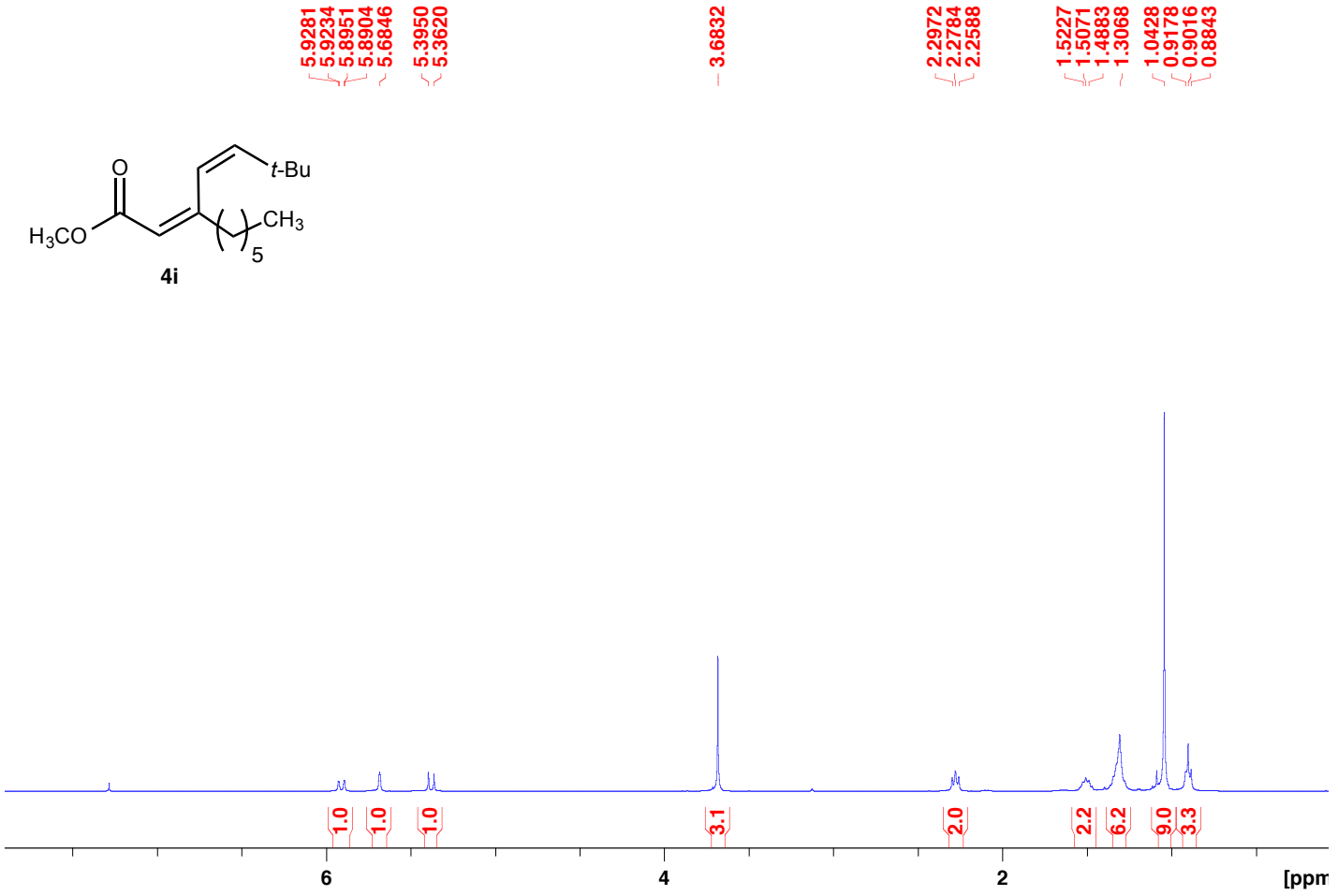



4h
O
CH3
H3CO
Ha
Hb

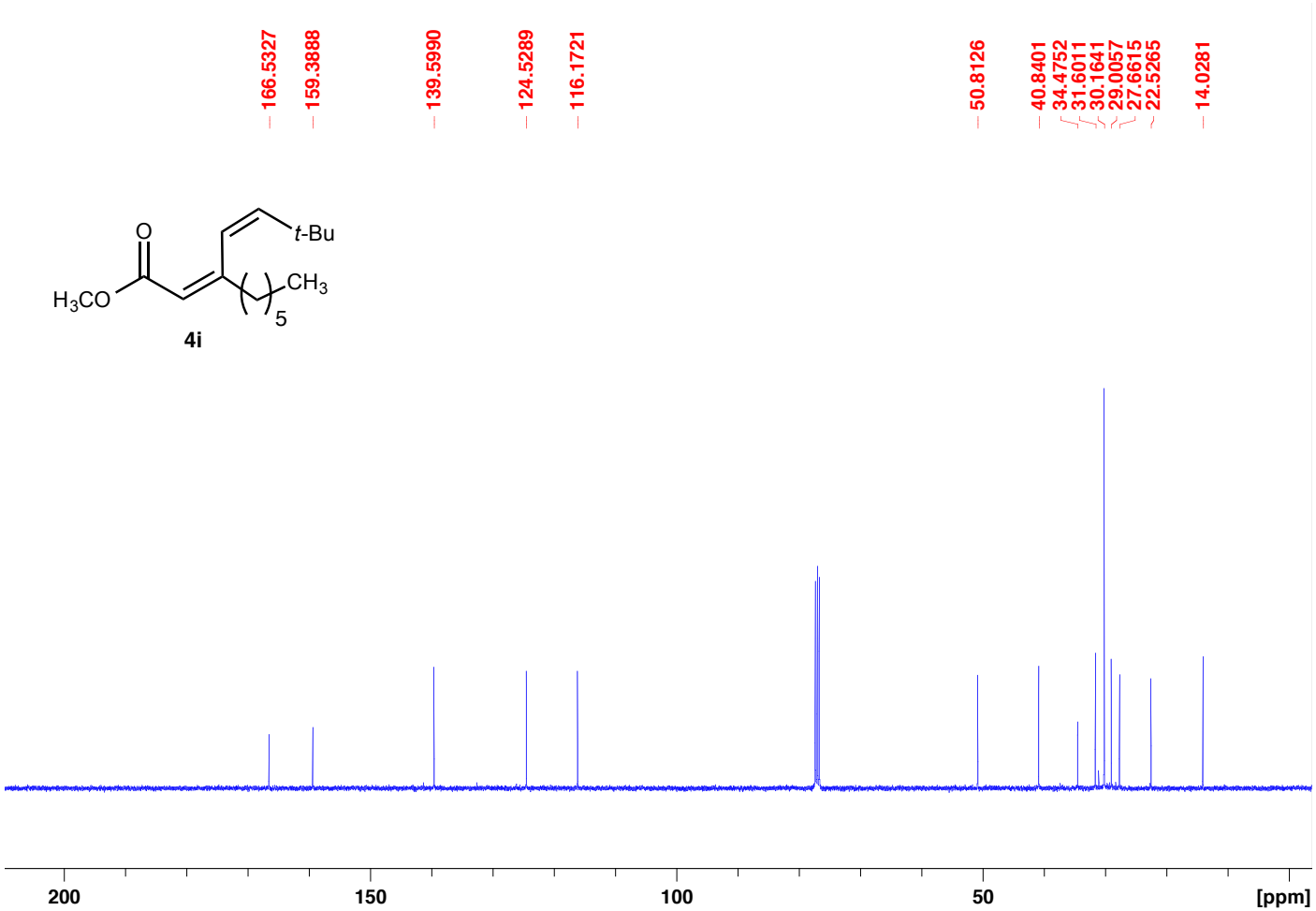
NOESY

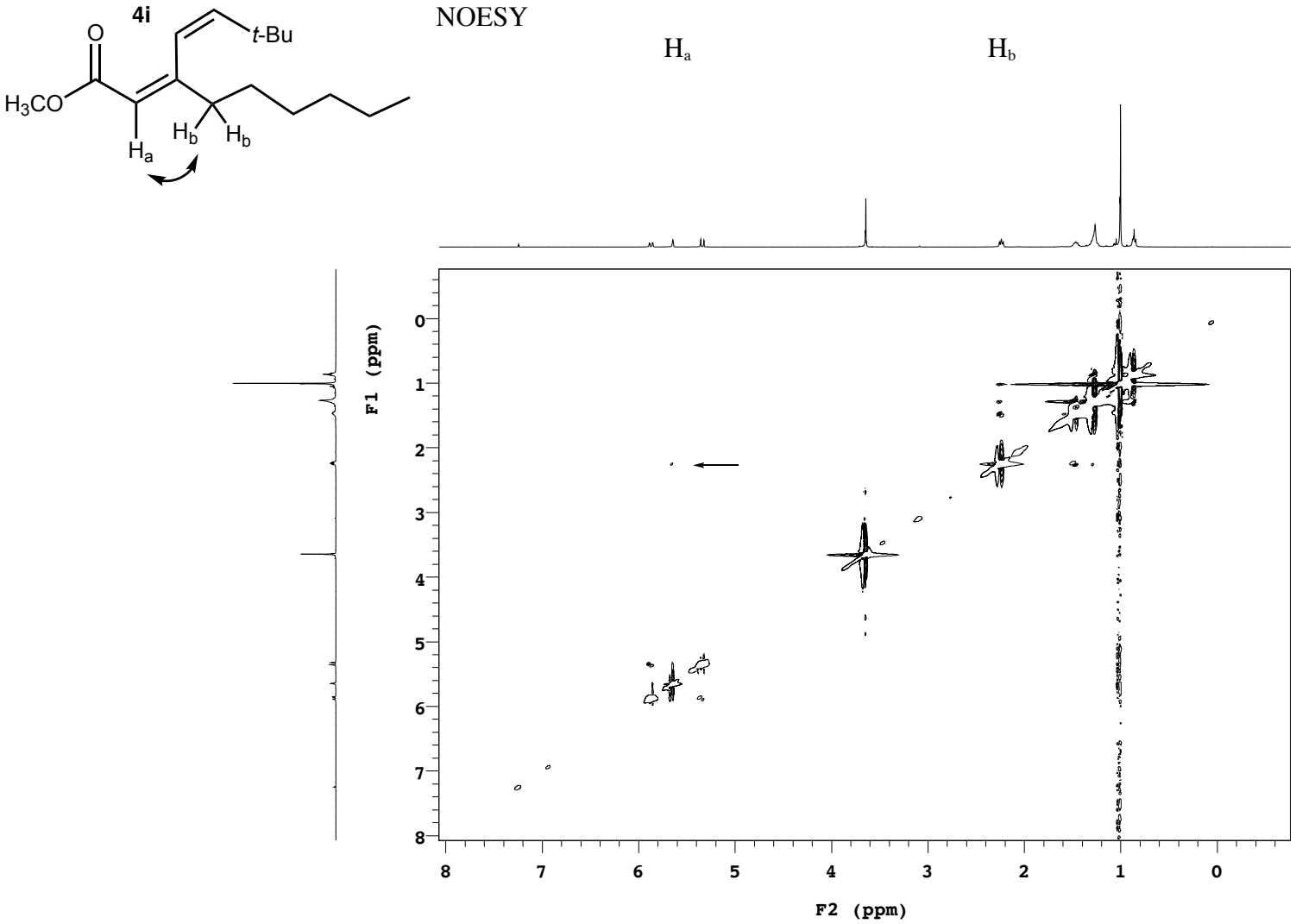

Ha
Hb
F1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
F2 (ppm)

^{1}H NMR (400 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

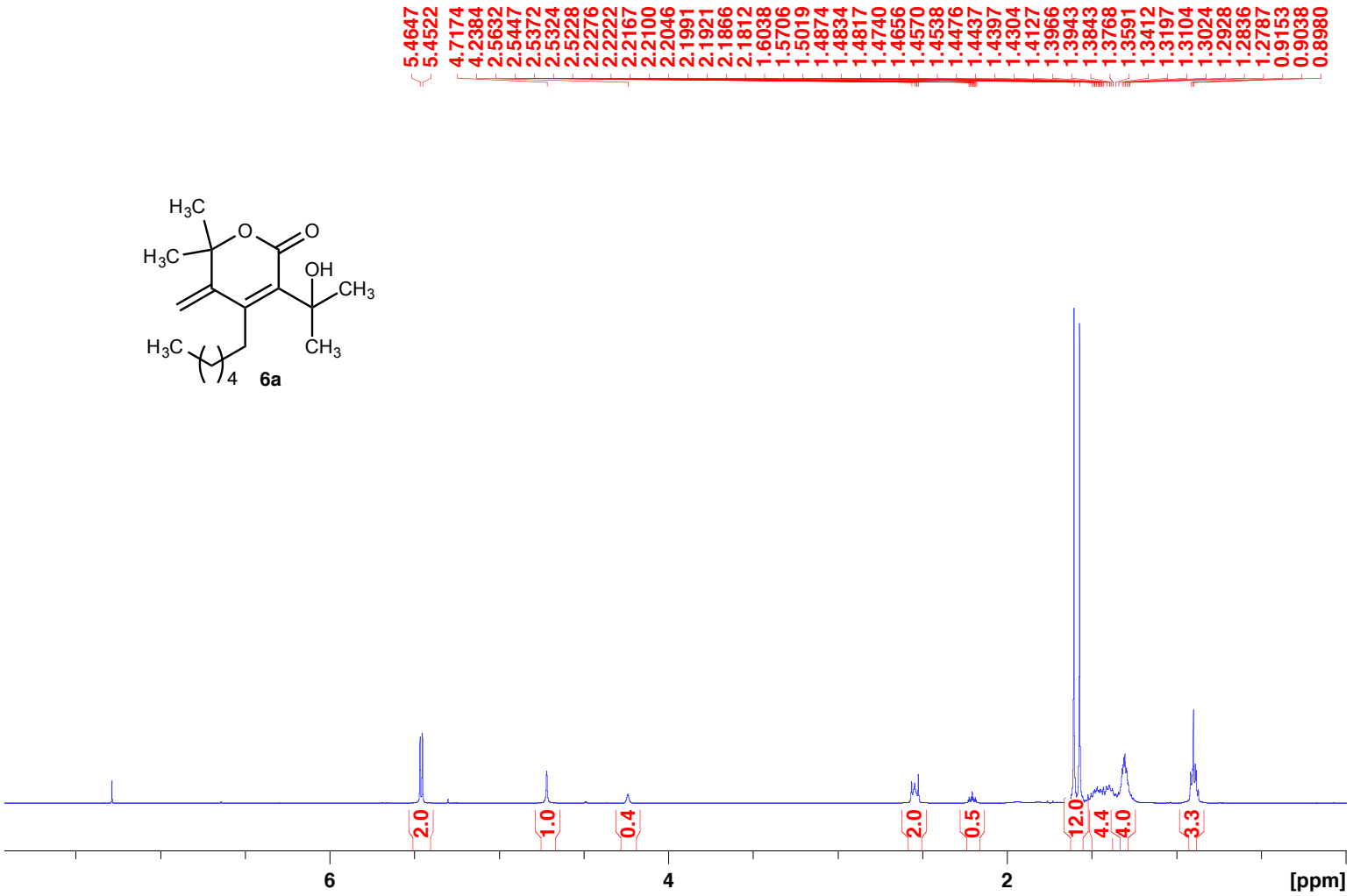


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a >10:1 *Z*:*E* mixture of stereoisomers at the α,β-alkene

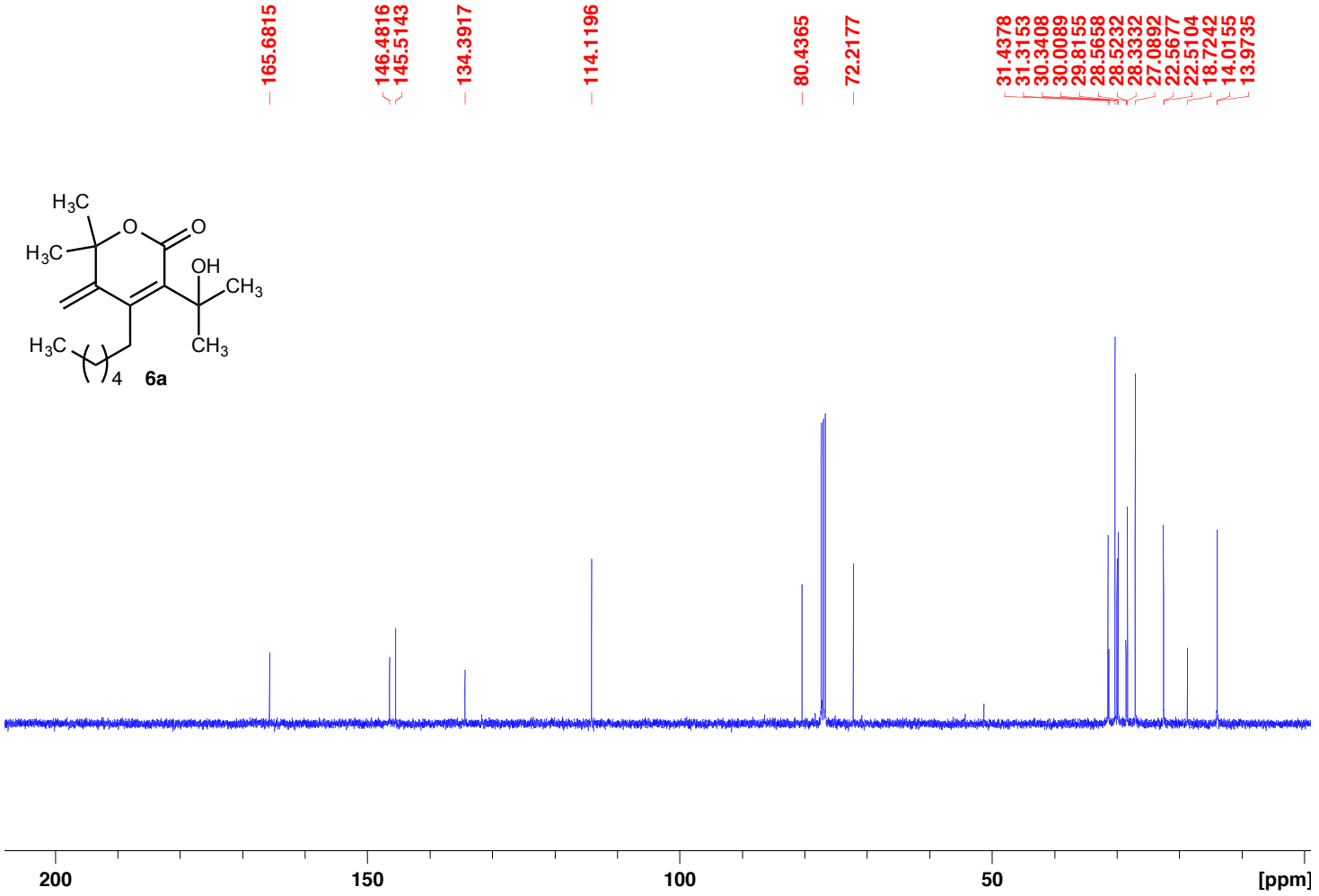


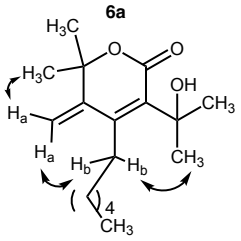

4i
O
t-Bu
H3CO
Ha
Hb
Hb
NOESY
Ha
Hb
F1 (ppm)
F2 (ppm)
0
1
2
3
4
5
6
7
8

^{1}H NMR (400 MHz), $CDCl_3$

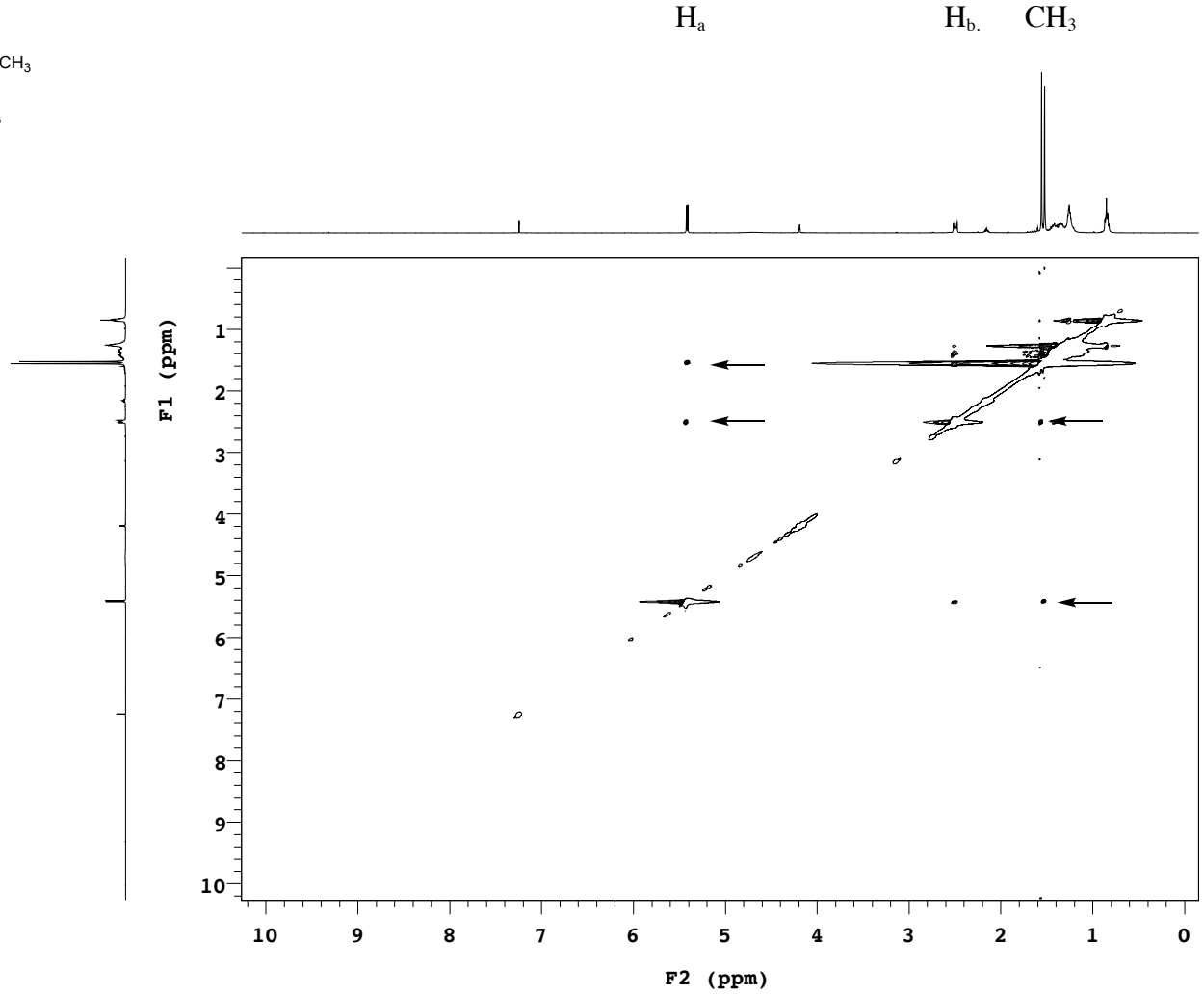


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$

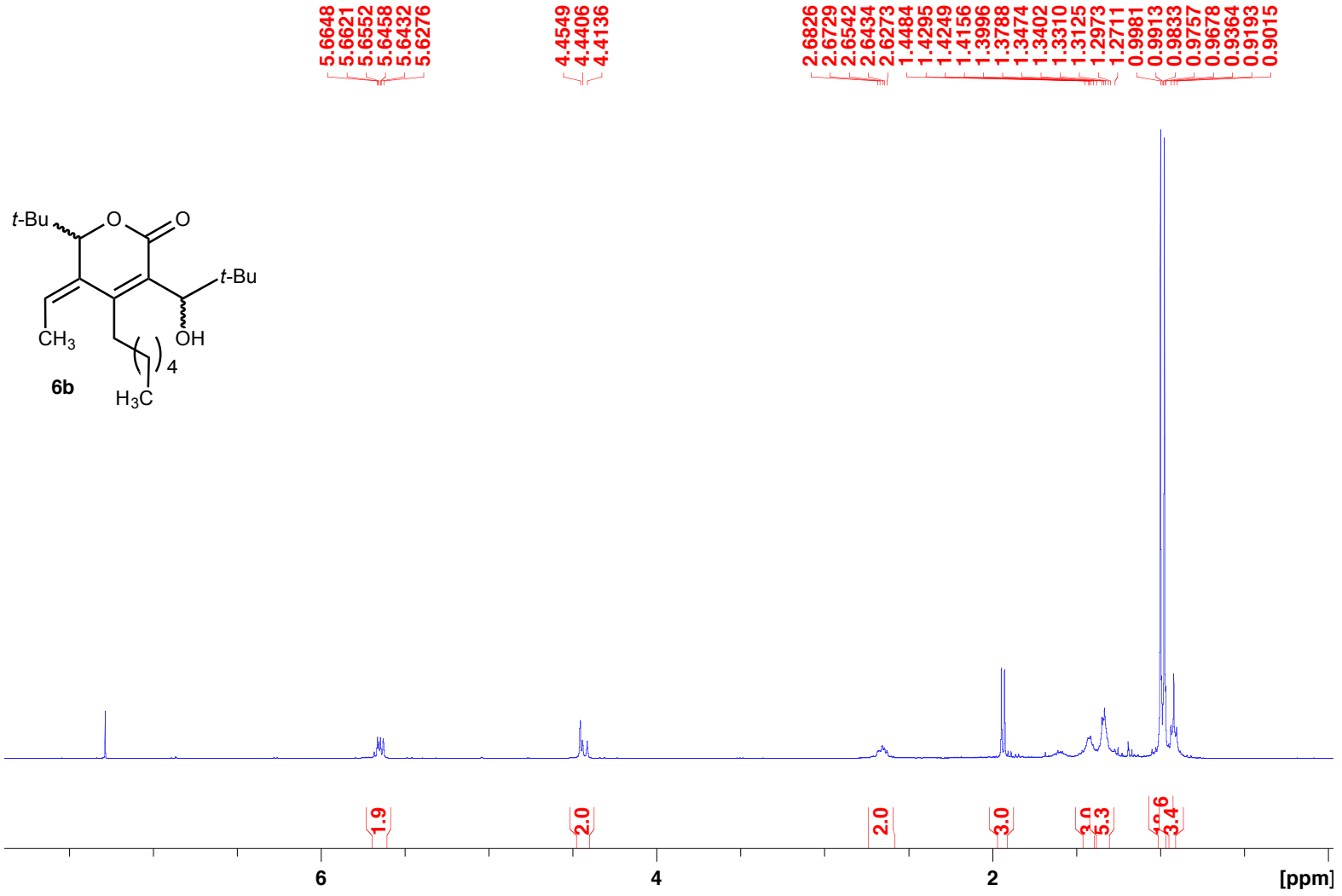



6a
H3C
O
O
H3C
OH
CH3
Ha
Ha
Hb
Hb
CH3
4
CH3

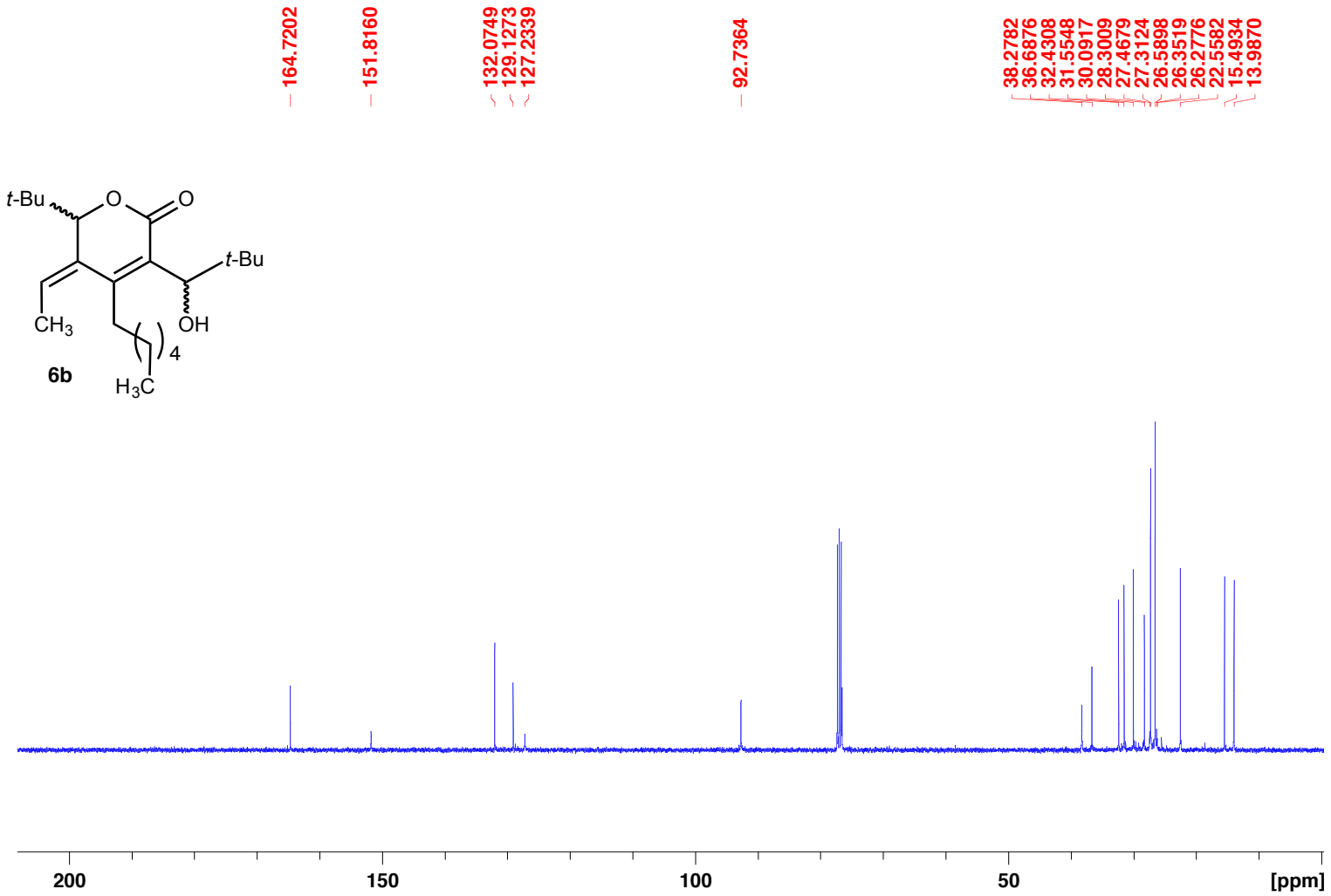
NOESY


Ha
Hb.
CH3
F1 (ppm)
1
2
3
4
5
6
7
8
9
10
10
9
8
7
6
5
4
3
2
1
0
F2 (ppm)

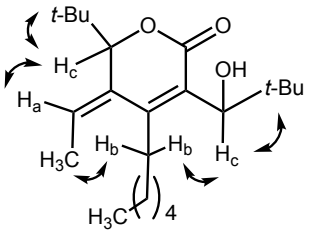
^{1}H NMR (400 MHz), $CDCl_3$, as a separable 1:1 mixture of *syn* and *anti* diastereomers.



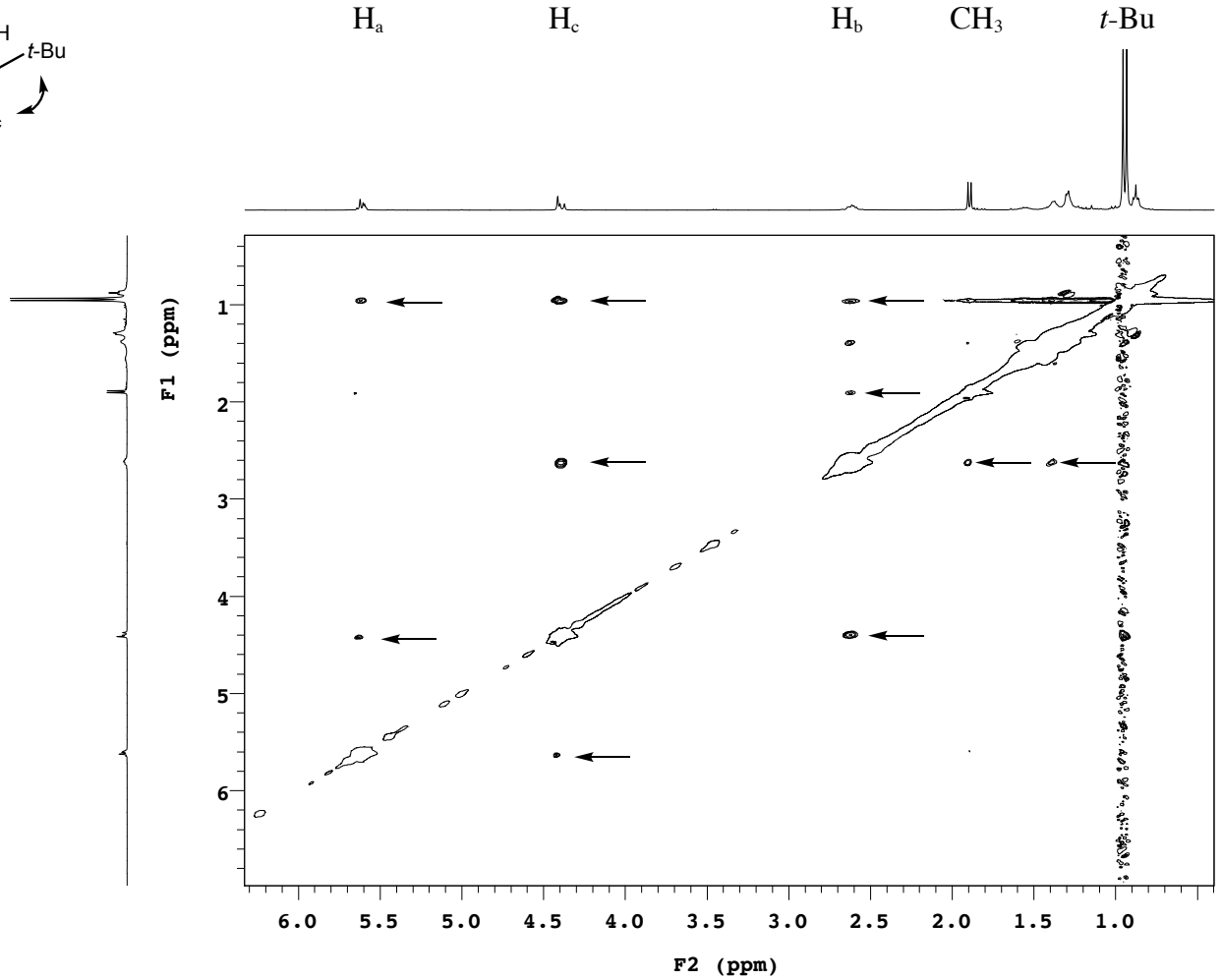
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a separable 1:1 mixture of *syn* and *anti* diastereomers.



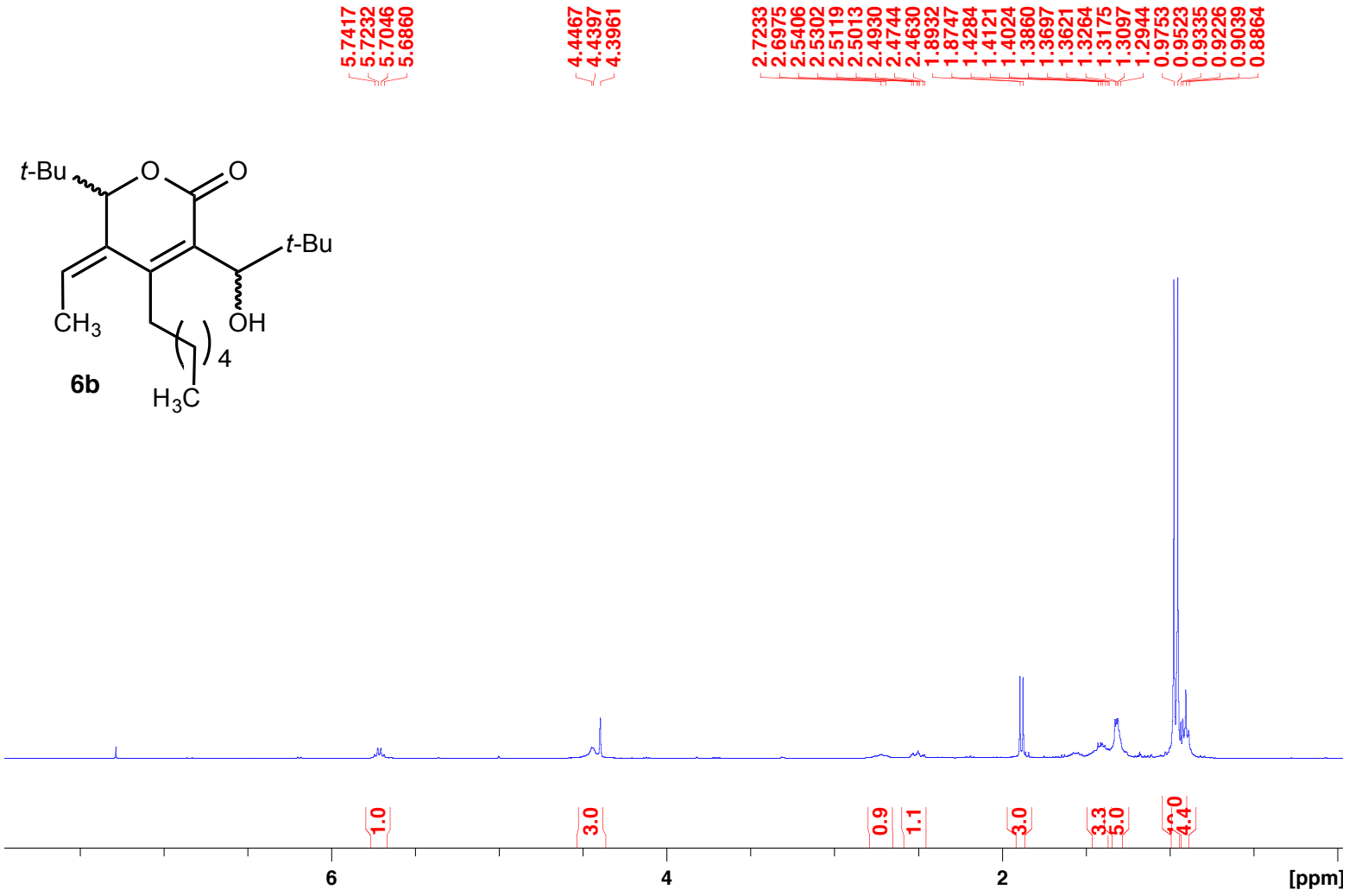
6b


t-Bu
O
O
Hc
OH
t-Bu
Ha
Hb
Hb
H3C
Hc
H3C
4

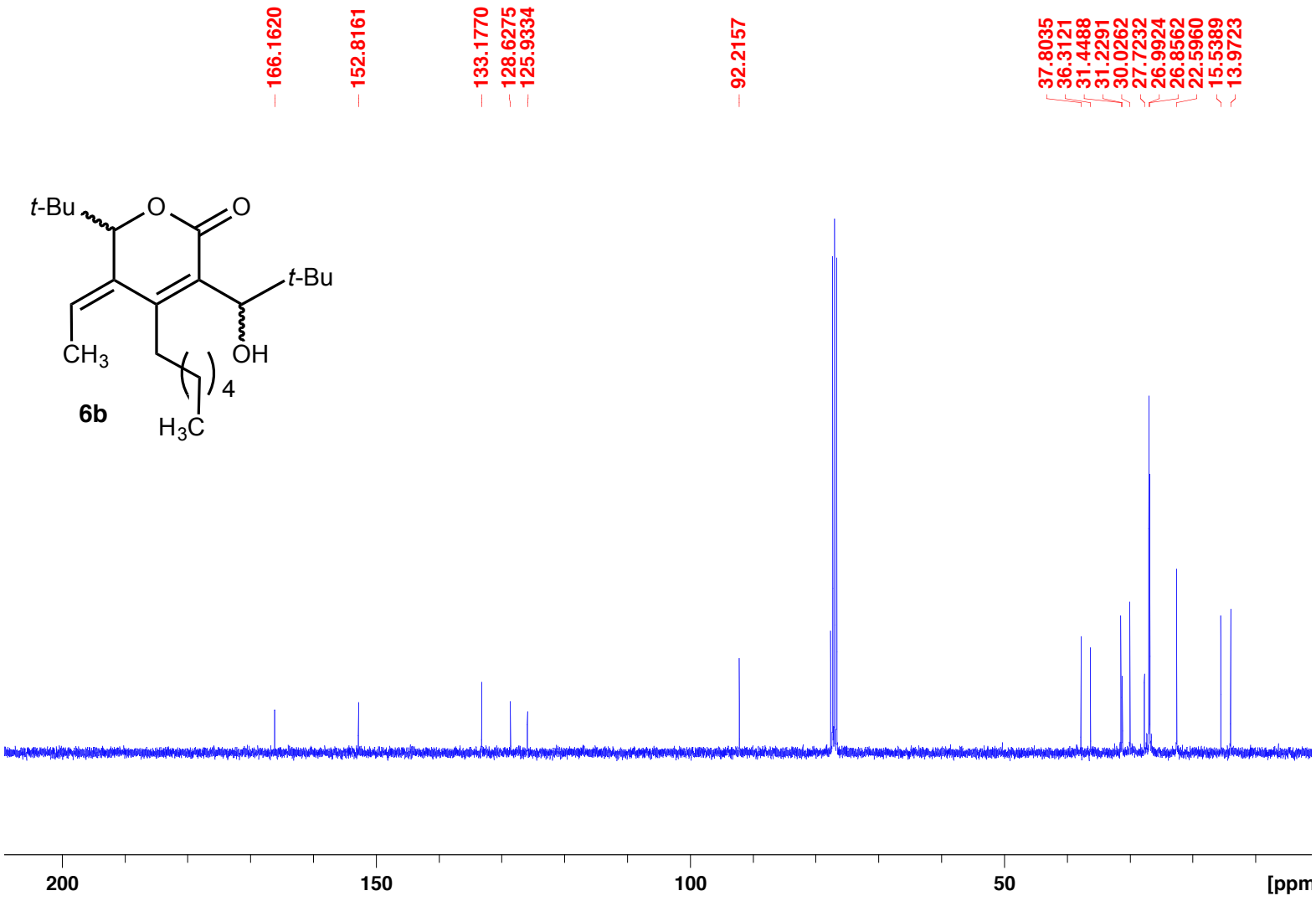
NOESY


Ha
Hc
Hb
CH3
t-Bu
F1 (ppm)
1
2
3
4
5
6
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 (ppm)

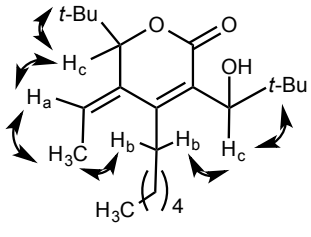
^{1}H NMR (400 MHz), $CDCl_3$, as a separable 1:1 mixture of *syn* and *anti* diastereomers



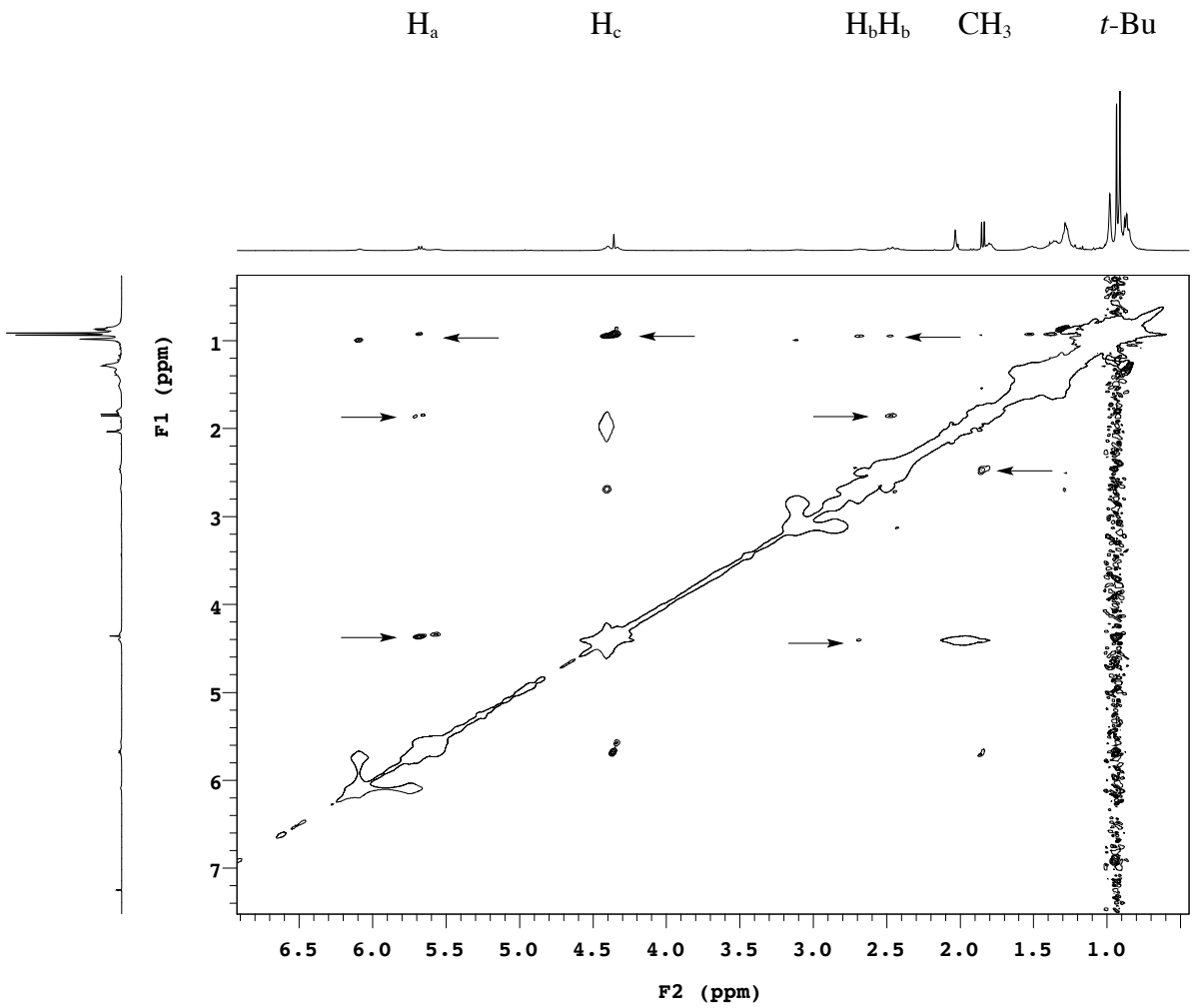
$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as a separable 1:1 mixture of *syn* and *anti* diastereomers



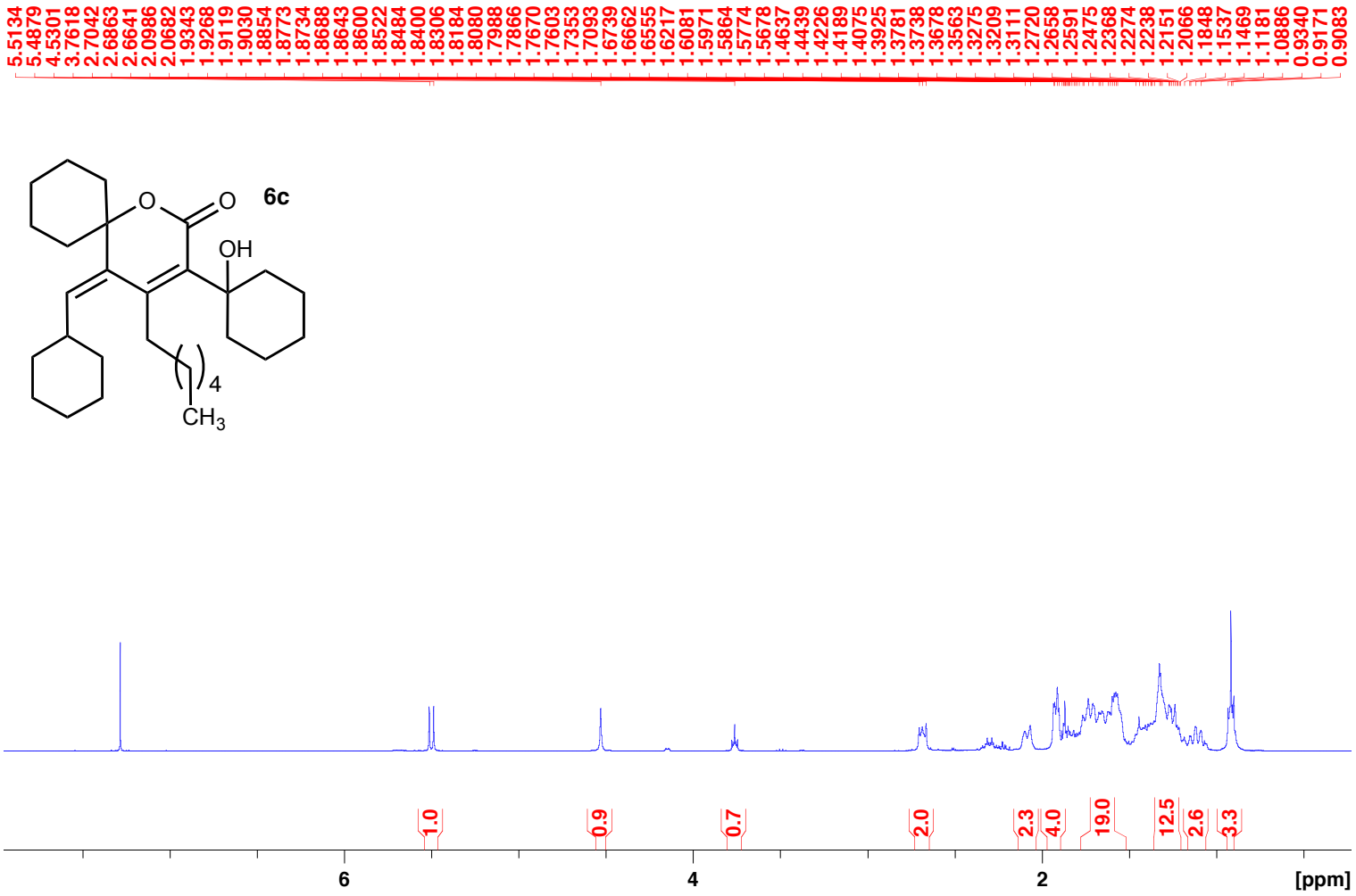
6b


t-Bu
O
O
H_c
OH
t-Bu
H_a
H_3C
H_b
H_b
H_c
H_3C
4

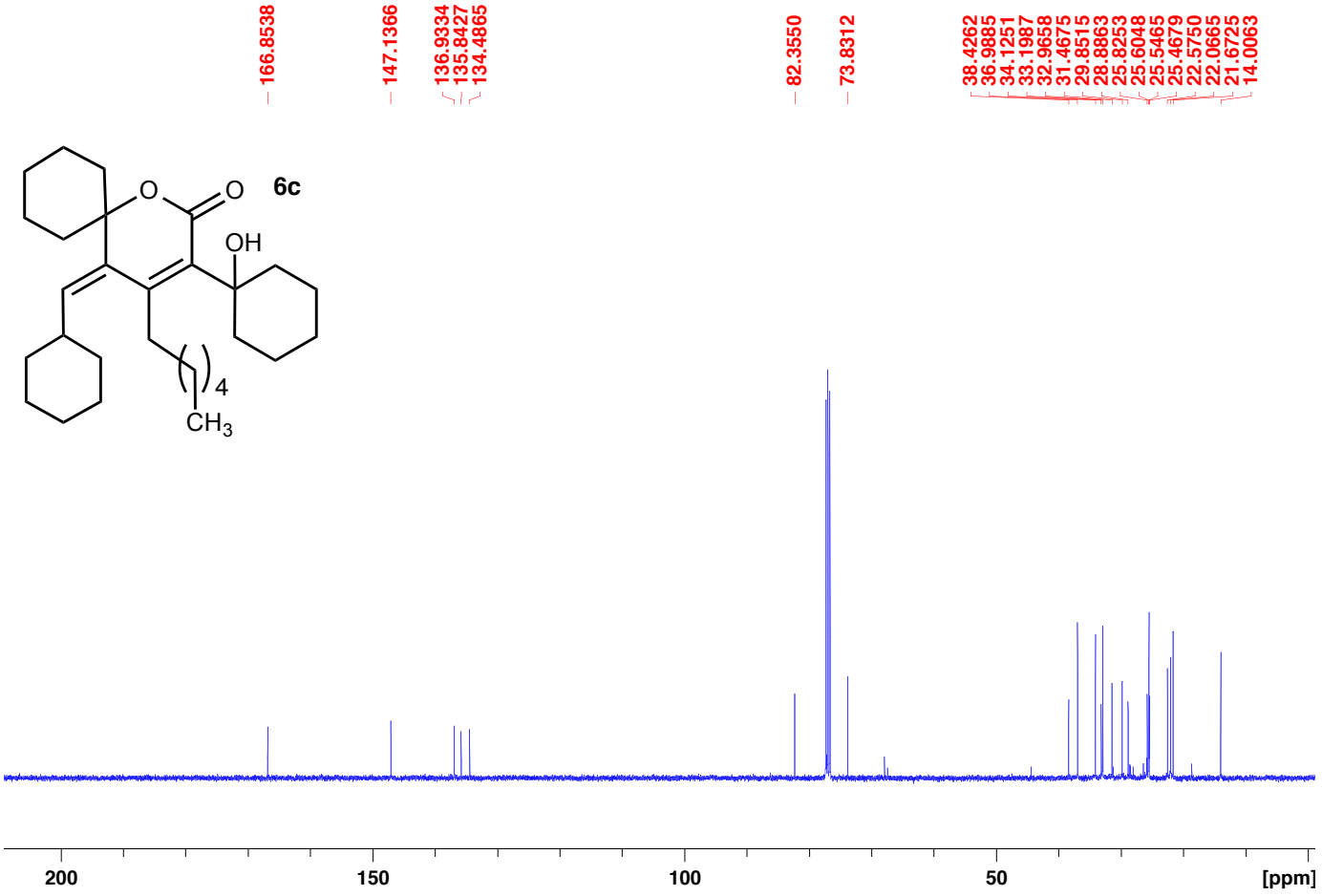
NOESY

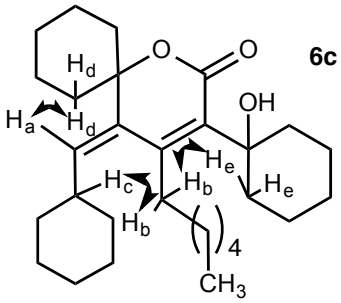

H_a
H_c
H_bH_b
CH_3
t-Bu
F1 (ppm)
1
2
3
4
5
6
7
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 (ppm)

^{1}H NMR (400 MHz), $CDCl_3$, as an inseparable 3:1 mixture of *Z* and *E* stereoisomers

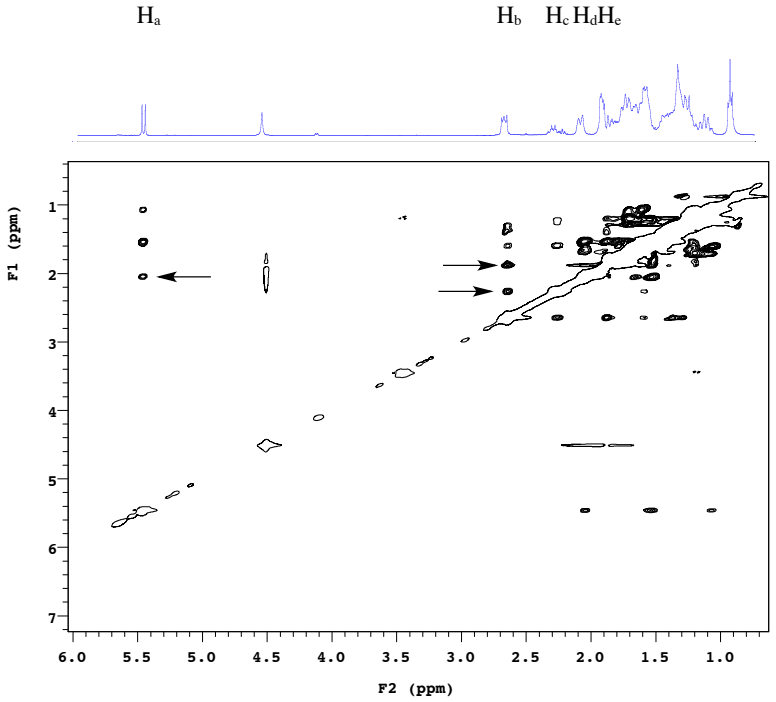


$^{13}C\{^{1}H\}$ NMR (100 MHz), $CDCl_3$, as an inseparable 3:1 mixture of *Z* and *E* stereoisomers




Hd
O
O
6c
OH
Ha
Hd
He
Hc
Hb
He
Hb
4
CH3

NOESY


Ha
Hb
Hc Hd He
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0