SUPPORTING INFORMATION

Influence of Base and Structure in the Reversible Covalent Conjugate Addition of Thiol to Polycyclic Enone Scaffolds

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General. All glassware was flame dried and cooled under dry N_2 or Ar prior to use. All moisture-sensitive reactions were performed under an atmosphere of dry N_2 or Ar. TEA was distilled from CaH_2 and stored over KOH; and CH_2Cl_2 was purified by distillation from CaH_2. Concentrating under reduced pressure refers to the use of a rotary evaporator connected to a PIAB Lab Vac H40 to remove solvent.

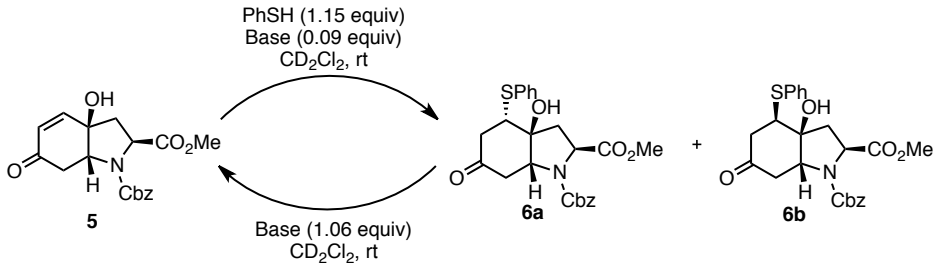
Melting points were determined using a Laboratory Devices Mel-Temp II in open capillary tubes and are uncorrected. Infrared spectra were obtained from neat solids or oils on a Smiths Detection IdentifyIR FT-IR spectrometer. High-resolution mass spectra were obtained on a Micromass UK Limited or a Q-TOF Ultima API a Thermo Scientific Exactive Orbitrap LC-MS. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 300MHz, 400 MHz, and 500 MHz instruments. $CDCl_3$ was filtered though basic Al_2O_3 immediately prior to sample preparation. Chemical shifts (δ) were reported in parts per million with the residual solvent peak used as an internal standard δ ^{1}H / ^{13}C (Solvent); 7.26 / 77.16 ($CDCl_3$); 5.32 / 53.84 (CD_2Cl_2) and are tabulated as follows:

chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). ^{13}C NMR spectra were obtained at 100 MHz and 125 MHz using a proton-decoupled pulse sequence and are tabulated by observed peak. Thin-layer chromatography was performed using pre-coated silica gel 60 F_{254} plates (EMD, 250 μm thickness) and visualization was accomplished with a 254 nm UV light and by staining with a $KMnO_4$ solution (3 g of $KMnO_4$ and 4 g of K_2CO_3 in 200 mL of a 5% NaOH solution) or Vaughn's reagent (5 g of $(NH_4)_6Mo_7O_{24}$•4 H_2O and 2 g of $Ce(SO_4)_2$ in 180 mL of H_2O and 20 mL of conc. aq. H_2SO_4). Flash chromatography on SiO_2 (Silicycle, Silia-P Flash Silica Gel or SiliaFlash® P60, 40-63 μm) was used to purify crude reaction mixtures. All desired products were placed under high vacuum (0.5-4 mmHg) to remove trace solvent.

General Notes for Equilibrium Experiments by ^1H NMR:

All experiments were run with a delay time (d1) of 5 s and the spin off on a Bruker Avance 500 mHz NMR. Samples were auto tuned and matched (atma), auto shimmed (topshim), and calibrated to CD_2Cl_2 (δ 5.32). Each sample was analyzed three consecutive times at each time point to account for variations due to manual integration.

Experimental set up for equilibrium study for enone 5 and thiophenol adduct 6.



Reaction	Base	ΔG
5 to **6**	Et_3N	≤ −4.6 kcal/mol
5 to **6**	DBU	≤ −4.6 kcal/mol
6 to **5**	Et_3N	+1.8 ± 0.03 kcal/mol
6 to **5**	DBU	≤ −3.8 kcal/mol

For **5** to **6** using Et_3N as a base:

To a solution of enone (0.0290 g, 0.0840 mmol) in CD_2Cl_2 (0.75 mL) was added thiophenol (10.0 μL, 96.6 μmol) and Et_3N (1.0 μL, 8.5 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 12, 23, and 38 h while monitoring the ratio of **5** (δ 5.95 (dd)) and **6** (minor diastereomer: δ 4.29 (app t), 4.22 (app t); major diastereomer: δ 4.17 (dd)). The ratio of **6**:**5** was >50:1. $K_{eq} = \geq 2.6 \times 10^3$ and $\Delta G = \leq -4.6$ kcal/mol. The *dr* of **6** was observed to be 2.7 to 1 (**6a** to **6b**) from the peaks for the minor diastereomer: δ 4.29 (app t, 0.5 H), 4.22 (app t, 0.5 H); and the major diastereomer: δ 4.17 (dd, 1 H).

For **5** to **6** using DBU as a base:

To a solution of enone (0.0290 g, 0.0840 mmol) in CD_2Cl_2 (0.75 mL) was added thiophenol (10.0 μL, 96.6 μmol) and DBU (1.0 μL, 6.7 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm, and analyzed by ^1H NMR at 10 and 23 h while monitoring the ratio of **5** (δ 5.95 (dd)) and **6** (minor diastereomer: δ 4.30 (app t), 4.23 (app. t); major diastereomer: δ 4.18 (m)). The ratio of **6**:**5** was >50:1. $K_{eq} = \geq 2.6 \times 10^3$ and $\Delta G = \leq -4.6$ kcal/mol. The *dr* of **6** was observed to be 1.6 to 1 (**6a** to **6b**) from the peaks for the minor diastereomer: δ 4.30 (app. t, 0.5 H), 4.23 (app. t, 0.5 H); and the major diastereomer: δ 4.18 (m, 1 H).

For **6** to **5** using Et_3N as a base:

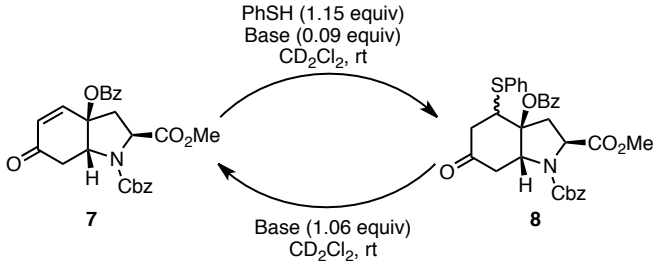
To a solution of thiophenol adduct **6** (0.0128 g, 0.0281 mmol) in CD_2Cl_2 (0.75 mL) was added Et_3N (4.2 μL, 3.0 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 10, 24, and 30 h while monitoring the ratio of **6** (minor diastereomer: δ 4.29 (app t), 4.22 (app t); major diastereomer: δ 4.17 (dd)) to **5** (δ 5.95 (dd)). The ratio of **5**:**6** was 1:4.3. $K_{eq} = 5.0 \pm 0.2 \times 10^{-2}$ and $\Delta G = 1.8 \pm 0.03$ kcal/mol. The *dr* of **6** was

observed to be 1.8 to 1 (**6a** to **6b**) from the peaks for the minor diastereomer: δ 4.29 (app t, 0.5 H), 4.22 (app t, 0.5 H); and the major diastereomer: δ 4.17 (dd, 1 H).

For **6** to **5** using DBU as a base:

To a solution of thiophenol adduct **6** (0.0128 g, 0.0281 mmol) in CD_2Cl_2 (0.75 mL) was added DBU (4.5 μL, 3.0 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^{1}H NMR at 10, 24, and 30 h while monitoring the ratio of **6** (minor diastereomer: δ 4.30 (app t), 4.23 (app t); and the major diastereomer: δ 4.18 (m)) to **5** (δ 5.95 (dd)). The ratio of **5**:**6** was >50:1. $K_{eq} = \geq 6.3 \times 10^2$ and $\Delta G = \leq -3.8$ kcal/mol.

Experimental set up for equilibrium study for enone 7 and thiophenyl adduct 8.



Reaction	Base	ΔG
7 to **8**	Et_3N	−4.1 ± 0.06 kcal/mol
7 to **8**	DBU	−4.0 ± 0.02 kcal/mol
8 to **7**	Et_3N	+1.0 ± 0.001 kcal/mol
8 to **7**	DBU	≤ −3.8 kcal/mol

For **7** to **8** using Et_3N as a base:

To a solution of enone **7** (0.0247 g, 0.0550 mmol) in CD_2Cl_2 (0.3 mL) was added thiophenol (0.100 mL, 0.0633 mmol, 0.633 M in CD_2Cl_2) and Et_3N (0.10 mL, 5.0 μmol, 0.050 M in CD_2Cl_2). The solution was transferred to a J-Young NMR tube, flushed with argon, sealed and analyzed by ^{1}H NMR for 13 d while monitoring the ratio of **7** (δ 6.10 (app t, 1 H)) and **8** (minor diastereomer: δ 7.99-7.95 (m, 2 H); major diastereomer: 7.71-7.67 (m, 2 H)). After 150 h, the ratio of **8**:**7** was 22:1. $K_{eq} = 1.0 \pm$

0.09 x 10^3 and $\Delta G = -4.1 \pm 0.06$ kcal/mol. The *dr* of **8** was observed to be 2.6 to 1 from the peaks for the minor diastereomer: δ 7.99-7.95 (m, 2 H), and the major diastereomer: δ 7.71-7.67 (m, 2 H). The relative configuration of the diastereomers could not be determined.

For **7** to **8** using DBU as a base:

To a solution of enone **7** (0.0247 g, 0.0550 mmol) in CD_2Cl_2 (0.3 mL) was added thiophenol (0.100 mL, 0.0633 mmol, 0.633 M in CD_2Cl_2) and DBU (0.10 mL, 5.0 μmol, 0.050 M in CD_2Cl_2). The solution was transferred to a J-Young NMR tube, flushed with argon, sealed and analyzed by ^{1}H NMR for 14 d while monitoring the ratio of **7** (δ 6.10 (app t, 1 H)) and **8** (minor diastereomer: δ 7.99-7.95 (m, 2 H); major diastereomer: 7.71-7.67 (m, 2 H)). After 150 h, the ratio of **8**:**7** was 21:1. $K_{eq} = 9.7 \pm 0.3$ x 10^2 and $\Delta G = -4.0 \pm 0.02$ kcal/mol. The *dr* of **8** was observed to be 2.1 to 1 from the peaks for the minor diastereomer: δ 7.99-7.95 (m, 2 H), and the major diastereomer: δ 7.71-7.67 (m, 2 H). The relative configuration of the diastereomers could not be determined.

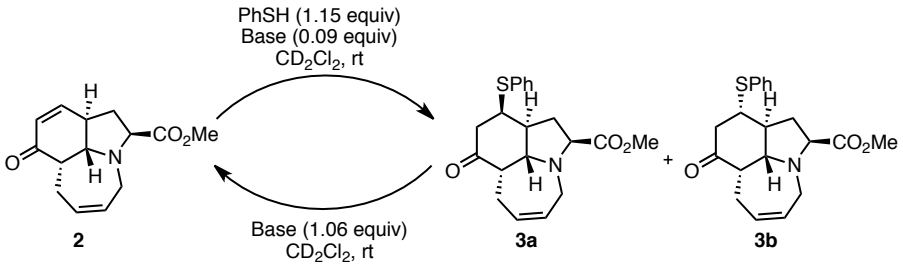
For **8** to **7** using Et_3N as a base:

To a solution of the major diastereomer of the thiophenol adduct **8** (0.0157 g, 0.0280 mmol) in CD_2Cl_2 (0.75 mL) was added Et_3N (4.2 μL, 3.0 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm, and analyzed by ^{1}H NMR for 24 h while monitoring the ratio of **8** (minor diastereomer: δ 7.98-7.94 (m, 2 H); major diastereomer: 7.71-7.67 (m, 2 H)) to **7** (δ 6.10 (app t)). The ratio of **7**:**8** was 1:2.3. $K_{eq} = 1.8 \pm 0.004$ x 10^{-1} and $\Delta G = 1.0 \pm 0.001$ kcal/mol. The *dr* of **8** was observed to be 6.7:1 from the peaks for the minor diastereomer: δ 7.98-7.94 (m, 2 H), and the major diastereomer: 7.71-7.67 (m, 2 H).

For **8** to **7** using DBU as a base:

To a solution of the major diastereomer of the thiophenol adduct **8** (0.0126 g, 0.0225 mmol) in CD_2Cl_2 (0.6 mL) was added DBU (3.5 μL, 2.4 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm, and analyzed by ^1H NMR at 8 and 22 h while monitoring the ratio of **8** (minor diastereomer: δ 7.98-7.94 (m, 2 H); major diastereomer: 7.71-7.67 (m, 2 H)) to **7** (δ 6.10 (app t)). The ratio of **7**:**8** was ≥ 50:1. $K_{eq} = \geq 6.1 \times 10^2$ and $\Delta G = \leq -3.8$ kcal/mol.

Experimental set up for equilibrium study for enone 2 and thiophenol adduct 3.



Reaction	Base	ΔG
2 to **3**	Et_3N	≤ −4.6 kcal/mol
2 to **3**	DBU	≤ −4.6 kcal/mol
3 to **2**	Et_3N	+3.4 ± 0.1 kcal/mol
3 to **2**	DBU	≤ −2.6 kcal/mol

For **2** to **3** using Et_3N as a base:

To a solution of enone **2** (0.012 g, 0.0485 mmol) in CD_2Cl_2 (0.45 mL) was added thiophenol (5.7 μL, 55.8 μmol) and Et_3N (0.61 μL, 4.4 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 6, 10, and 22 h while monitoring the ratio of **2** (δ 6.96 (d)) and **3** (δ 5.70-5.62 (m)). The ratio of **3**:**2** was >50:1. $K_{eq} = \geq 2.8 \times 10^3$ and $\Delta G = \leq -4.6$ kcal/mol. The *dr* of **3** was observed to be 3.8 to 1 (**3a** to **3b**) from the methyl ester peaks at δ 3.70 (s) and 3.68 (s).

For **2** to **3** using DBU as a base:

To a solution of enone **2** (0.0120 g, 0.0485 mmol) in CD_2Cl_2 (0.45 mL) was added thiophenol (5.7 μL, 55.8 μmol) and DBU (0.65 μL, 4.4 μmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm, and analyzed by ^{1}H NMR at 6, 10, and 22 h while monitoring the ratio of **2** (δ 6.96 (d)) and **3** (δ 5.70-5.62 (m)). The ratio of **3**:**2** was >50:1. $K_{eq} = \geq 2.8 \times 10^3$ and $\Delta G = \leq -4.6$ kcal/mol. The *dr* of **3** was observed to be 2.7 to 1 (**3a** to **3b**) from the methyl ester peaks at δ 3.70 (s) and 3.68 (s).

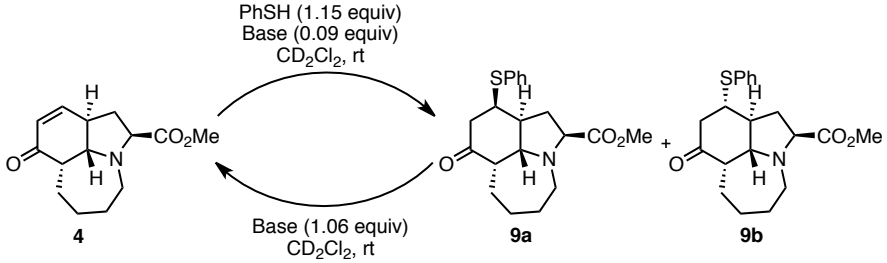
For **3b** to **2** using Et_3N as a base:

To a solution of ketone **3b** (0.0060 g, 0.017 mmol, minor diastereomer **3b**) in CD_2Cl_2 (0.45 mL) was added Et_3N (2.5 μL, 0.018 mmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^{1}H NMR at 19 and 24 h while monitoring the ratio of **3b** (δ 5.70-5.62 (m)) and **2** (δ 6.98 (dd)). The ratio of **2**:**3b** was 1:17.1. $K_{eq} = 3.3 \pm 0.7 \times 10^{-3}$ and $\Delta G = +3.4 \pm 0.1$ kcal/mol. Product **3** was observed as a single diastereomer (**3b**).

For **3b** to **2** using DBU as a base:

To a solution of ketone **3b** (0.0083 g, 0.023 mmol, minor diastereomer **3b**) in CD_2Cl_2 (0.620 mL) was added DBU (3.7 μL, 0.025 mmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^{1}H NMR at 19 and 24 h while monitoring the ratio of **3b** (δ 5.70-5.62 (m)) and **2** (δ 5.76-5.71 (m)). The ratio of **2**:**3b** was >12.4:1. $K_{eq} = \geq 84$ and $\Delta G = \leq -2.6$ kcal/mol.

Experimental set up for equilibrium study for enone 4 and thiophenol adduct 9.



Reaction	Base	ΔG
4 to **9**	Et_3N	≤ −4.6 kcal/mol
4 to **9**	DBU	≤ −4.6 kcal/mol
9 to **4**	Et_3N	+2.3 ± 0.03 kcal/mol
9 to **4**	DBU	−2.9 ± 0.2 kcal/mol[a]

[a]During the reaction of **9** to **4** with DB, enone **4** was formed as a 2.5:1 mixture of diastereomers (epimerization α to ketone).

For **4** to **9** using Et_3N as a base:

To a solution of enone **4** (0.0133 g, 0.0533 mmol) in CD_2Cl_2 (0.3 mL) was added thiophenol (0.100 mL, 61.3 μmol, 0.613 M in CD_2Cl_2) and Et_3N (0.100 mL, 4.80 μmol, 0.0480 M in CD_2Cl_2). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 9 and 22 h while monitoring the ratio of **4** (δ 5.91 (dd)) and **9** (δ 4.02 (dd, major diastereomer) and 3.98 (dd, minor diastereomer). The ratio of **9**:**4** was >50:1. $K_{eq} = \geq 2.8 \times 10^3$ and $\Delta G = \leq -4.6$ kcal/mol. The *dr* of **9** was observed to be 3.6 to 1 (**9a**:**9b**) from the peaks at δ 4.02 (dd) and 3.98 (dd).

For **4** to **9** using DBU as a base:

To a solution of enone **4** (0.0133 g, 0.0533 mmol) in CD_2Cl_2 (0.3 mL) was added thiophenol (0.100 mL, 61.3 μmol, 0.613 M in CD_2Cl_2) and DBU (0.100 mL, 4.80 μmol, 0.0480 M in CD_2Cl_2). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 12 and 22 h while monitoring the ratio of **4** (δ 5.91 (dd)) and **9** (δ 4.02 (dd,

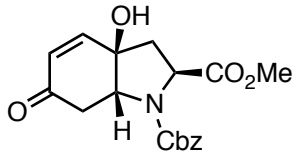
major diastereomer) and 3.98 (dd, minor diastereomer). The ratio of **9**:**4** was > 50:1. $K_{eq} = \geq 2.8 \times 10^3$ and $\Delta G = \leq -4.6$ kcal/mol. The *dr* of **9** was observed to be 3.5 to 1 (**9a**:**9b**) from the peaks at δ 4.02 (dd) and 3.98 (dd).

For **9** to **4** using Et_3N as a base:

To a solution of ketone **9a** (0.0083 g, 0.023 mmol, major diastereomer) in CD_2Cl_2 (0.6 mL) was added Et_3N (3.4 μL, 0.025 mmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 23 h while monitoring the ratio of **9** (δ 4.02 (dd, major diastereomer) and 3.98 (dd, minor diastereomer) and **4** (δ 3.89 (app. t)). The ratio of **4:9** was 1:6.7. $K_{eq} = 2.1 \pm 0.1 \times 10^{-2}$ and $\Delta G = +2.3 \pm 0.03$ kcal/mol. The *dr* of **9** shifted from a single isomer to a ratio of 3.1:1 (**9a**:**9b**).

For **9** to **4** using DBU as a base:

To a solution of ketone **9b** (0.0069 g, 0.019 mmol, minor diastereomer) in CD_2Cl_2 (0.45 mL) was added DBU (3.0 μL, 0.020 mmol). The solution was transferred to an NMR tube, flushed with argon, capped, sealed with parafilm and analyzed by ^1H NMR at 23 h while monitoring the ratio of **9** (δ 3.98 (app. t)) and **4** (δ 5.95 (dd) and 5.91 (dd) epimers). The ratio of **4:9** was 15.8:1. $K_{eq} = 140 \pm 40$ and $\Delta G = -2.9 \pm 0.2$ kcal/mol. During the reaction enone **4** was epimerized to a 2.5:1 mixture of diastereomers at the α-position to the ketone.



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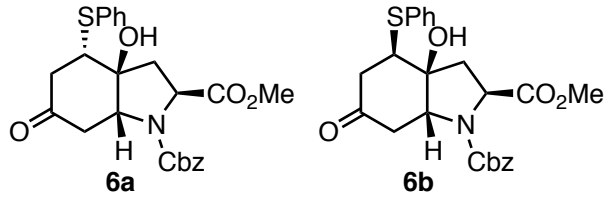
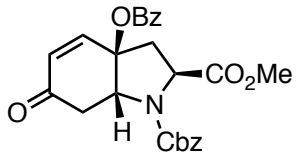
(2*S*,3a*R*,7a*R*)-1-Benzyl 2-methyl 3a-hydroxy-6-oxo-3,3a,7,7a-tetrahydro-1*H*-indole-1,2(2*H*,6*H*)-dicarboxylate (5).[1] The enone **5** was prepared according to the literature to give **5** (11.04 g, 71%) as a pale orange foam: ^{1}H NMR ($CDCl_3$, 400 MHz, 1:2 mixture of rotamers) δ 7.39-7.26 (m, 5 H), 6.82 (d, 0.66 H, *J* = 10.3 Hz), 6.80 (d, 0.33 H, *J* = 10.3 Hz), 6.02 (d, 0.33 H, *J* = 10.3 Hz), 6.01 (d, 0.66 H, *J* = 10.3 Hz), 5.21 (d, 1 H, *J* = 12.2 Hz), 5.10 (d, 0.66 H, *J* = 12.2 Hz), 5.01 (d, 0.33 H, *J* = 12.1 Hz), 4.58-4.51 (m, 1.33 H), 4.48-4.42 (m, 0.66 H), 3.85 (s, 2 H), 3.56 (s, 1 H), 3.27 (dd, 0.33 H, *J* = 16.6, 6.4 Hz), 3.05 (dd, 0.66 H, *J* = 16.6, 6.4 Hz), 2.60-2.50 (m, 1 H), 2.31 (d, 0.33 H, *J* = 14.2 Hz), 2.29 (d, 0.66 H, *J* = 14.3 Hz), 2.19 (d, 0.66 H, *J* = 16.6 Hz), 2.16 (d, 0.33 H, *J* = 16.6 Hz).



(2*S*,3a*S*,4*S*,7a*R*)-1-Benzyl 2-methyl 3a-hydroxy-6-oxo-4-(phenylthio)octahydro-1*H*-indole-1,2-dicarboxylate (6a) and (2*S*,3a*S*,4*R*,7a*R*)-1-benzyl 2-methyl 3a-hydroxy-6-oxo-4-(phenylthio)octahydro-1*H*-indole-1,2-dicarboxylate (6b). To a solution of enone **5** (0.150 g, 0.434 mmol) in CH_2Cl_2 (3.9 mL) was added thiophenol (0.051 mL, 0.50 mmol) and Et_3N (0.005 mL, 0.04 mmol). The reaction mixture was stirred at rt for 16.5 h, concentrated under reduced pressure and purified by chromatography on SiO_2 (1:4 to 1:2; EtOAc:hexanes) to give the thiol addition products **6a** and **6b** (0.1544 g, 79%) as a colorless foam and an inseparable 2.3:1 (**6a**:**6b**) mixture of diastereomers: IR (ATR) 3433, 3057, 2951, 1702, 1404, 1346, 1113, 736, 693 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz, 1:1 mixture of rotamers, peaks for major diastereomer **6a**) δ 7.52-7.45 (m, 2 H), 7.38-7.27 (m, 8 H), 5.19 (m, 2 H), 5.01 (app d, 1 H, *J* = 12.3 Hz), 4.54-4.47 (m, 1 H), 4.16 (dd, 1 H, *J* = 11.8, 5.3 Hz), 3.78 (s,

[1] (a) Wipf, P.; Rector, S. R.; Takahashi, H. *J. Am. Chem. Soc.* **2002**, *124*, 14848. (b) Wipf, P.; Spencer, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 225. (c) Pierce, J. G.; Kasi, D.; Fushimi, M.; Cuzzupe, A.; Wipf, P. *J. Org. Chem.* **2008**, *73*, 7807.

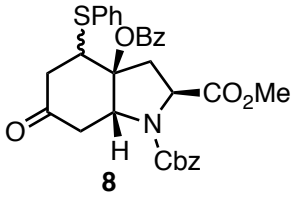
1.5 H), 3.61 (s, 1.5 H), 3.50 (dt, 1 H, J = 11.4, 4.2 Hz), 3.17 (dd, 0.5 H, J = 16.4, 5.3 Hz), 3.00 (dd, 0.5 H, J = 16.4, 5.2 Hz), 2.71-2.45 (m, 3 H), 2.45-2.20 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.9, 206.7, 205.6, 204.8, 175.1, 174.7, 174.5, 174.2, 155.25, 154.86, 136.8, 136.7, 134.1, 134.0, 133.62, 133.51, 133.3, 129.9, 129.7, 129.0, 128.9, 128.7, 128.50, 128.48, 81.2, 80.5, 80.1, 68.0, 67.9, 67.8, 65.9, 65.6, 65.2, 64.6, 60.8, 59.7, 59.6, 58.4, 58.3, 53.3, 53.1, 51.65, 51.4, 45.0, 44.9, 44.6, 44.0, 43.8, 43.0, 42.9, 42.8, 42.2, 40.9, 37.2, 36.7; HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{26}NO_6S$ (M^++H) 456.1475, found 456.1568.



7

(2*S*,3a*R*,7a*R*)-1-Benzyl 2-methyl 3a-(benzoyloxy)-6-oxo-3,3a,7,7a-tetrahydro-1*H*-indole-1,2(2*H*,6*H*)-dicarboxylate (7).[1a,b] To solution of alcohol **5** (1.000 g, 2.896 mmol), benzoic anhydride (1.021 g, 4.513 mmol), and DMAP (0.0367 g, 0.300 mmol) in CH_2Cl_2 (14 mL) was added pyridine (1.15 mL, 14.22 mmol). The light yellow solution was heated to reflux for 17 h, treated with DMAP (44.3 mg, 0.363 mmol), and heated for 26 h. The reaction was not complete yet and more DMAP (101.2 mg, 0.828 mmol) was added. The mixture was stirred at reflux for an additional 21 h, quenched with 10% aq. HCl (50 mL), and extracted with $CHCl_3$ (3 x 20 mL). The combined organic layers were washed with 1 M HCl (2 x 50 mL), sat. aq. $NaHCO_3$ (1 x 50 mL) and brine (1 x 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude oil was purified by chromatography on SiO_2 (1:4 to 2:3; EtOAc:hexanes) to give benzyolated compound **7** (0.9027 g, 69 %) as a colorless foam: ^{1}H NMR (CD_2Cl_2, 500 MHz, 1:1 mixture of rotamers) δ 7.94-7.91 (m, 2 H), 7.63-7.58 (m, 1 H), 7.48-7.44 (m, 2 H), 7.38-7.36 (m, 2 H), 7.36-7.39 (m, 3 H), 7.05 (d, 0.5 H, J = 10.5 Hz), 7.01 (d, 0.5 H, J = 10.4 Hz), 6.10 (app t, 1 H, J = 10.6 Hz), 5.20 (AB d, 0.5 H, J_{AB} = 12.3 Hz),

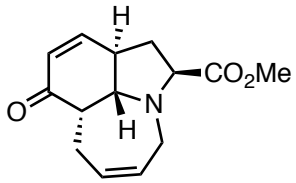
5.16 (AB d, 0.5 H, J_{AB} = 12.4 Hz), 5.11 (AB d, 0.5 H, J_{AB} = 12.4 Hz), 5.03 (AB d, 0.5 H, J_{AB} = 12.7 Hz), 5.01 (dt, 1 H, *J* = 10.1, 1.1 Hz), 4.72 (dd, 0.5 H, *J* = 9.8, 1.4 Hz), 4.66 (dd, 0.5 H, *J* = 9.5, 1.9 Hz), 3.59 (s, 1.5 H), 3.40 (s, 1.5 H), 3.83 (ddd, 0.5 H, *J* = 16.8, 6.7, 0.6 Hz), 3.22 (ddd, 0.5 H, *J* = 16.7, 6.7, 0.7 Hz), 3.08 (dt, 0.5 H, *J* = 6.2, 1.5 Hz), 3.05 (dt, 0.5 H, *J* = 6.3, 1.6 Hz), 2.75 (dd, 0.5 H, *J* = 14.3, 9.5 Hz), 2.69 (dd, 0.5 H, *J* = 14.5, 9.9 Hz), 2.50 (dd, 0.5 H, *J* = 16.7, 9.9 Hz), 2.42 (dd, 0.5 H, *J* = 16.7, 10.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, 1:1 mixture of rotamers) δ 195.0, 194.9, 171.4, 170.8, 165.5, 165.3, 154.2, 153.9, 145.0, 144.1, 136.1, 135.9, 133.9, 133.8, 130.3, 130.0, 129.9, 129.8, 129.39, 129.36, 128.8, 128.6, 128.53, 128.45, 128.4, 128.3, 84.0, 82.8, 68.0, 67.6, 62.0, 61.4, 58.6, 58.4, 52.7, 52.5, 42.9, 41.6, 39.6, 38.8.



8

(2*S*,3a*S*,7a*R*)-1-Benzyl 2-methyl 3a-(benzoyloxy)-6-oxo-4-(phenylthio)octahydro-1*H*-indole-1,2-dicarboxylate (8). To a solution of enone **7** (0.0762 g, 0.170 mmol) and thiophenol (0.020 mL, 0.20 mmol) was added Et_3N (0.0035 mL, 0.025 mmol). The mixture was stirred at rt for 10 h., concentrated under reduced pressure and purified by chromatography on SiO_2 (1:4; 1:2; 2:3; EtOAc:hexanes) to give thiol addition product **8** as a mixture of diastereomers (major diastereomer (0.0597 g, 63%); minor diastereomer (0.0273 g, 29%, containing a trace of **7**). Major diastereomer: IR (ATR) 2951, 1746, 1705, 1282, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, 3:1 mixture of rotamers) δ 7.72-7.67 (m, 2 H), 7.55-7.48 (m, 1 H), 7.38-7.27 (m, 9 H), 7.04-6.94 (m, 3 H), 5.18 (d, 0.75 H, *J* = 12.3 Hz), 5.15 (d, 0.25 H, *J* = 14.4 Hz), 5.07 (dd, 0.75 H, *J* = 12.2, 6.2 Hz), 5.00-4.85 (m, 2.25 H), 4.68 (d, 0.25 H, *J* = 8.9 Hz), 4.59 (d, 0.75 H, *J* = 9.0 Hz), 3.58, (s, 0.75 H), 3.30 (s, 2.25 H), 3.24 (app d, 1.5 H, *J* = 4.5 Hz), 3.18 (dd, 0.25 H, *J* = 15.6, 6.5 Hz), 2.97 (app d, 0.25 H, *J* = 15.5 Hz), 2.92-2.82 (m, 2

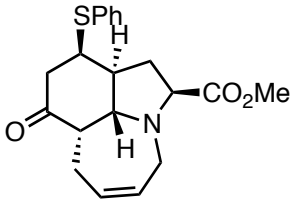
H), 2.67-2.57 (m, 1 H), 2.48-2.37 (m, 1 H); ^{13}C NMR (CD_2Cl_2, 100 MHz, major rotamer) δ 206.0, 172.4, 166.2, 155.5, 136.8, 134.0, 133.9, 130.1, 129.6, 129.1, 129.0, 128.7, 128.5, 90.4, 67.8, 63.9, 59.0, 52.8, 46.2, 43.4, 43.1, 37.1; HRMS (ESI$^+$) *m/z* calcd for $C_{31}H_{29}NO_7SNa$ (M^++Na) 582.1557, found 582.1551. Minor diastereomer: IR (ATR) 2951, 1752, 1705, 1702, 1405, 1277, 1245, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, 3:2 mixture of rotamers) δ 7.99-7.94 (m, 2 H), 7.60-7.55 (m, 1 H), 7.47-7.34 (m, 7 H), 7.34-7.23 (m, 5 H), 5.27-5.17 (m, 1.6 H), 5.06 (d, 0.4 H, *J* = 12.1 Hz), 4.96 (t, 0.6 H, *J* = 6.4 Hz), 4.86 (t, 0.4 H, *J* = 7.8 Hz), 4.66-4.62 (m, 1.4 H), 4.57 (d, 0.6 H, *J* = 9.0 Hz), 4.49 (dd, 0.6 H, *J* = 16.8, 7.6 Hz), 3.33 (s, 1.2 H), 3.30-3.25 (m, 1.4 H), 3.14 (s, 1.8 H), 2.87-2.78 (m, 1 H), 2.70-2.57 (m, 2.6 H), 2.40 (dd, 0.4 H, *J* = 16.6, 7.4 Hz); ^{13}C NMR (CD_2Cl_2, 100 MHz, 3:2 mixture of rotamers) δ 205.6, 204.9, 171.9, 171.3, 166.1, 166.0, 154.8, 154.7, 136.9, 134.5, 134.4, 134.1, 133.0, 132.7, 130.5, 130.4, 130.3, 129.9, 129.1, 129.0, 128.8, 128.63, 128.57, 89.0, 88.2, 68.1, 67.8, 62.4, 61.6, 58.6, 58.4, 52.7, 49.5, 49.3, 45.1, 43.8, 42.5, 38.3, 37.0; HRMS (ESI$^+$) *m/z* calcd for $C_{31}H_{29}NO_7SNa$ (M^++Na) 582.1557, found 582.1553.



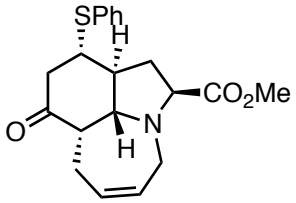
2

(2*S*,3^1*S*,7a*S*,10a*R*)-Methyl 8-oxo-1,2,3^1,4,7,7a,8,10a-octahydroazepino[3,2,1-*hi*]indole-2-carboxylate (2).[1a,b] The enone **2** was prepared according to the literature to give enone **2** as a light yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98 (dd, 1 H, *J* = 9.8, 1.9 Hz), 5.99 (dd, 1 H, *J* = 9.8, 2.9 Hz), 5.80-5.74 (m, 1 H), 5.59 (ddd, 1 H, *J* = 8.4, 5.2, 2.3 Hz), 4.01 (dd, 1 H, *J* = 8.4, 6.0 Hz), 3.71 (s, 3 H), 3.62-3.55 (m, 2 H), 3.30 (dd, 1 H, *J* = 17.6, 6.0 Hz), 2.94 (ddd, 1 H, *J* = 12.4, 7.2, 2.0 Hz), 2.78-2.69 (m, 1 H), 2.60 (dt, 1 H, *J* = 12.3, 8.3 Hz), 2.59-2.51 (m, 1 H), 2.18 (dd, 1 H, *J* = 16.2, 8.1 Hz),

1.81 (td, 1 H, *J* = 11.8, 5.9 Hz); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 200.7, 174.4, 148.5, 130.5, 129.5, 128.6, 65.2, 63.2, 51.4, 50.4, 47.4, 37.2, 32.2, 24.2.



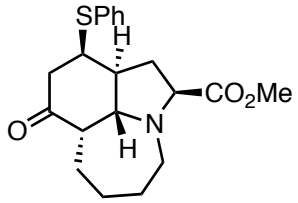
3a



3b

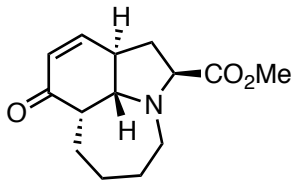
(2*S*,3^1*R*,7a*S*,10*R*,10a*S*)-Methyl 8-oxo-10-(phenylthio)-1,2,3^1,4,7,7a,8,9,10,10a-decahydroazepino[3,2,1-*hi*]indole-2-carboxylate (3a) and (2*S*,3^1*R*,7a*S*,10*S*,10a*S*)-methyl 8-oxo-10-(phenylthio)-1,2,3^1,4,7,7a,8,9,10,10a-decahydroazepino[3,2,1-*hi*]indole-2-carboxylate (3b). To a solution of enone **2** (0.0604 g, 0.244 mmol) in CH_2Cl_2 (2.2 mL) was added thiophenol (29.0 μL, 0.283 mmol) and Et_3N (5.5 μL, 39 μmol). The solution was stirred at rt for 3 h, concentrated under reduced pressure and purified by chromatography on SiO_2 (0:1; 5:95; 1:9; 1:4; to 1:1; EtOAc:hexanes) to give the major diastereomer **3a** (0.0553 g, 63%) as a colorless solid and the minor diastereomer **3b** (0.0198 g, 23%) as a light yellow oil. Major diastereomer **3a**: Mp 142.5-143.6 °C (dec., $CHCl_3$); IR (ATR) 3014, 2962, 2898, 2811, 1728, 1694, 1193, 1152, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.36 (m, 2 H), 7.31-7.28 (m, 2 H), 7.26-7.23 (m, 1 H), 5.72-5.66 (m, 1 H), 5.57-5.52 (m, 1 H), 4.04 (dd, 1 H, *J* = 8.9, 5.1 Hz), 3.83 (dd, 1 H, *J* = 10.8, 7.4 Hz), 3.78-3.70 (m, 1 H), 3.74 (s, 3 H), 3.62-3.55 (m, 1 H), 3.32 (ddt, 1 H, *J* = 17.8, 5.8, 1.8 Hz), 2.95 (dd, 1 H, *J* = 11.6, 7.4 Hz), 2.69 (ddd, 1 H, *J* = 16.2, 3.3, 0.9 Hz), 2.65-2.58 (m, 1 H), 2.61 (dd, 1 H, *J* = 16.1 , 5.7 Hz), 2.52 (tdd, 1 H, *J* = 10.4, 8.4, 3.9 Hz), 2.41 (dt, 1 H *J* = 12.9, 8.7 Hz), 2.24 (ddd, 1 H, *J* = 12.9, 10.2, 5.0 Hz), 2.03 (dd, 1 H, *J* = 15.6, 8.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 210.8, 174.5, 134.6, 132.3, 129.7, 129.3, 127.9, 127.5, 63.9, 61.2, 54.4, 51.7, 48.5, 46.0, 44.7, 42.3, 30.5, 25.9; HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{24}NO_3S$ (M^++H) 358.1471, found 358.1461. Minor diastereomer **3b**: IR (ATR) 3018, 2947, 2915, 1728, 1702, 1437, 1199 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.44 (dd, 2 H, *J* = 8.1, 1.6 Hz), 7.36-7.29 (m, 3 H), 5.65 (ddd, 1 H, *J* =

10.1, 10.1, 1.1 Hz), 5.52 (m, 1 H), 3.98 (dd, 1 H, *J* = 8.9, 5.4 Hz), 3.68 (s, 3 H), 3.51 (m, 1 H), 3.47 (dd, 1 H, *J* = 10.1, 7.6 Hz), 3.34-3.24 (m, 2 H), 2.80 (dd, 1 H, *J* = 11.7, 7.6 Hz), 2.75 (dd, 1 H, *J* = 16.5, 5.9 Hz), 2.64 (dt, 1 H, *J* = 13.2, 8.3 Hz), 2.53-2.44 (m, 1 H), 2.33 (dd, 1 H, *J* = 16.4, 9.5 Hz), 2.05-1.94 (m, 2 H), 1.74 (ddd, 1 H, *J* = 13.1, 10.3, 5.3 Hz); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 200.1, 164.5, 123.4, 122.6, 119.5, 119.1, 117.9, 117.8, 54.8, 53.4, 43.6, 41.4, 38.2, 36.9, 35.4, 33.6, 23.0, 15.7; HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{24}NO_3S$ (M^++H) 358.1471, found 358.1459.



9a

(2*S*,3[1]*R*,7a*S*,10*R*,10a*S*)-Methyl 8-oxo-10-(phenylthio)dodecahydroazepino[3,2,1-*hi*]indole-2-carboxylate (9). To a solution of thioether **3a** (0.0553 g, 0.155 mmol) in CH_2Cl_2:EtOH (1:4; 4.3 mL) was added Wilkinson's catalyst (0.0317 g, 0.0343 mmol). The suspension was stirred under an atmosphere of H_2 (balloon) at rt for 14 h and concentrated under reduced pressure to give a red oil. The crude oil was purified by chromatography on SiO_2 (0:1; 5:95; 1:9: 15:85; 1:4; EtOAc:hexanes) to give **9** (34.2 mg, 62%) as a light red-orange solid: Mp 135.3-136.4 °C (dec., $CHCl_3$); IR (ATR) 2917, 2902, 2820, 2848, 1726, 1689, 1431, 1202, 1167, 749, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (d, 2 H, *J* = 7.4 Hz), 7.28 (d, 2 H, *J* = 7.2 Hz), 7.22 (app. t, 1 H, *J* = 7.3 Hz), 4.03 (dd, 1 H, *J* = 8.1, 6.5 Hz), 3.79 (dd, 1 H, *J* = 10.9, 7.4 Hz), 3.72 (s, 3 H), 3.74-3.68 (m, 1 H), 2.85 (dt, 1 H, *J* = 14.7, 3.2 Hz), 2.81-2.76 (m, 1 H), 2.66 (dd, 1 H, *J* = 11.3, 7.8 Hz), 2.63-2.57 (m, 2 H), 2.42 (ddt, 1 H, *J* = 11.0, 7.8, 3.8 Hz), 2.33 (dt, 1 H, *J* = 12.5, 8.0 Hz), 2.15 (ddd, 1 H, *J* = 12.3, 10.8, 6.3 Hz), 1.96-1.89 (m, 1 H), 1.79-1.70 (m, 1 H), 1.67-1.57 (m, 2 H), 1.46-1.37 (m, 1 H), 1.32-1.22 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 211.7, 175.4, 134.7, 132.2, 129.2, 127.4, 63.7, 61.2, 56.4, 51.7, 47.5, 45.8, 45.0, 42.6, 30.9, 30.41, 3.38, 27.0, ; HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{26}NO_3S$ (M^++H) 360.1628, found 360.1612.



4

(2*S*,3^1*S*,7a*S*,10a*R*)-Methyl 8-oxo-1,2,3^1,4,5,6,7,7a,8,10a-decahydroazepino[3,2,1-*hi*]indole-2-carboxylate (4).[1a,b] To a solution of ketone **9a** (0.0219 g, 0.0610 mmol) in CH_2Cl_2 (1.85 mL) was added DBU (10.0 μL, 0.0669 mmol). The reaction mixture was placed under an Ar atmosphere, stirred at rt for 2 h, concentrated under reduced pressure, and purified by chromatography on SiO_2 (1:9 to 2:3; EtOAc:hexanes) to give enone **4** (9.5 mg, 63%) as a light yellow oil: ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 6.96 (d, 1 H, *J* = 9.7 Hz), 5.91 (dd, 1 H, *J* = 9.7, 2.2 Hz), 3.89 (app. t, 1 H, *J* = 7.9 Hz), 3.68 (s, 3 H), 3.50 (dd, 1 H, *J* = 10.0, 6.1 Hz), 2.94-2.78 (m, 2 H), 2.72-2.63 (m, 2 H), 2.52 (dt, 1 H, *J* = 11.8, 7.2 Hz), 1.97-1.91 (m, 1 H), 1.79-1.66 (m, 3 H), 1.64-1.56 (m, 1 H), 1.52-1.40 (m, 1 H), 1.39-1.27 (m, 1 H).

Computational Methodology and Data

The geometries listed below were optimized at the B3LYP/6-31G(d) level of theory in the gas phase. Thermochemical corrections were obtained from frequency calculations at this level and are unscaled. Single-point energies were computed at the M06-2X/6-311G(2d,p) level on the B3LYP geometries, and were used in conjunction with the B3LYP thermochemical corrections to obtain gas-phase free energies. Free energies of solvation in dichloromethane were obtained from single-point calculations with the SMD method at the B3LYP/6-31G(d) level.

Underneath the coordinates for the species below are listed the following energies:

B3LYP/6-31G(d) electronic energy (`E`)

B3LYP/6-31G(d) zero-point energy (`ZPE`)

B3LYP/6-31G(d) enthalpy at 298.15 K (`H`)

B3LYP/6-31G(d) Gibbs free energy at 298.15 K and 1 mol/L (`G`)

M06-2X/6-311G(2d,p) single-point electronic energy (E_{M06-2X})

Sum of B3LYP/6-31G(d) potential energy and free energy of solvation in dichloromethane at 298.15 K and 1 mol/L (E_{solv})

All energies are given in Hartree.

PhSH

```
S   -0.083506    2.294071    0.000000
C    0.000000    0.506944    0.000000
C   -1.209256   -0.201597    0.000000
C   -1.201851   -1.595436    0.000000
C    0.004582   -2.298324    0.000000
C    1.207601   -1.591499    0.000000
C    1.210960   -0.196307    0.000000
H   -2.153796    0.335958    0.000000
H   -2.146537   -2.132748    0.000000
H    0.006897   -3.384451    0.000000
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H    2.154617   -2.124888    0.000000
H    2.156180    0.340148    0.000000
H    1.246518    2.518157    0.000000
0 imaginary frequencies
E = -630.434123
ZPE = 0.099602
H = -630.327286
G = -630.368174
E_M06-2X = -630.389699
E_solv = -630.446549
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Enone 2

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C   -1.907002    0.485521   -0.460764
C   -3.056358   -0.534135   -0.637882
C   -2.815540   -1.967064   -0.329455
C   -1.742880   -2.383661    0.366415
C   -0.751522   -1.372420    0.859413
C   -0.591385   -0.236811   -0.157120
O   -4.147658   -0.156789   -1.040190
H   -3.595369   -2.649386   -0.656873
H   -1.617321   -3.436721    0.615246
H   -1.150285   -0.928158    1.783498
C    0.714867   -1.760301    1.122814
N    0.446467    0.546028    0.504304
H   -0.226029   -0.681058   -1.101471
C   -2.268776    1.591204    0.555675
H   -1.832825    0.980457   -1.437468
C    1.487741   -0.416921    0.925362
H    0.876306   -2.174433    2.122136
H    1.055985   -2.492809    0.385553
H    1.959009   -0.058950    1.846500
C    2.580303   -0.569669   -0.140210
O    3.710518    0.079804    0.217176
O    2.447984   -1.145378   -1.201089
C    4.773978    0.048784   -0.751645
H    5.593417    0.612455   -0.305201
H    5.078428   -0.981920   -0.951325
H    4.452122    0.511017   -1.688403
C   -1.427819    2.839316    0.387956
H   -3.320869    1.850480    0.397358
H   -2.192221    1.209271    1.583776
C   -0.129263    2.922549    0.079250
H   -1.968422    3.778439    0.502821
H    0.296185    3.916203   -0.062992
C    0.873143    1.803359   -0.090281
H    1.142871    1.697849   -1.161926
H    1.800087    2.105468    0.414303
0 imaginary frequencies
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ZPE = 0.294122
H = -823.787619
G = -823.851042
E_M06-2X = -824.005844
E_solv = -824.119360
```

Thioether 3

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C    2.470776   -1.051289    0.930974
C    0.950993   -1.226481    1.219891
C    0.304179    0.065897    0.684863
C    1.340035    0.607392   -0.311899
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N	2.586253	0.317191	0.390517
C	1.089621	2.103792	-0.608682
C	-0.429436	2.376141	-0.598653
C	-1.323059	1.177370	-0.908885
C	-1.078130	-0.039286	0.030312
C	1.854890	3.070414	0.312251
C	3.331105	3.148799	-0.008763
C	4.152193	2.131438	-0.286354
C	3.841465	0.654478	-0.269556
O	-0.883910	3.486333	-0.403693
C	2.950200	-2.101958	-0.079006
O	2.383810	-2.379694	-1.117474
O	4.124644	-2.654141	0.296574
C	4.676313	-3.616780	-0.619461
H	-2.364689	1.503212	-0.901942
S	-2.329950	-0.183528	1.395142
H	0.247210	0.799519	1.502073
H	1.270061	0.034981	-1.254914
H	1.408585	2.316235	-1.640679
H	0.763116	-1.374126	2.285902
H	0.561786	-2.098675	0.686977
H	3.089558	-1.136742	1.829745
H	5.602633	-3.961561	-0.159522
H	3.982637	-4.449440	-0.761979
H	4.875853	-3.151771	-1.588431
H	1.401220	4.059059	0.198894
H	1.703433	2.780785	1.360995
H	3.754381	4.152309	-0.039764
H	5.185577	2.359218	-0.548858
H	3.892477	0.249996	-1.302316
H	4.645851	0.148251	0.281078
H	-1.083534	0.863581	-1.935973
H	-1.137613	-0.962481	-0.554331
C	-3.834214	-0.523334	0.476056
C	-4.829902	0.458875	0.388506
C	-6.021924	0.191018	-0.288635
C	-6.222617	-1.051570	-0.890578
C	-5.232124	-2.033565	-0.805636
C	-4.047008	-1.776353	-0.117133
H	-4.666667	1.426828	0.852560
H	-6.789660	0.957735	-0.349547
H	-7.148613	-1.257273	-1.420703
H	-5.387755	-3.005880	-1.265699
H	-3.286909	-2.547624	-0.030386

0 imaginary frequencies
E = -1454.558907
ZPE = 0.399566
H = -1454.135713
G = -1454.217924
E_{M06-2X} = -1454.433155
E_{solv} = -1454.588783

Enone 4

C	1.562089	0.045269	0.813923
C	1.086672	-1.420266	1.141794
C	-0.434203	-1.355693	0.906730
C	-0.533281	-0.270348	-0.172889
N	0.347007	0.736401	0.403574
C	-1.975679	0.142083	-0.488479
C	-2.876602	-1.111461	-0.594385

C	-2.338783	-2.439231	-0.199941
C	-1.199515	-2.579019	0.500224
C	-2.583795	1.208666	0.449742
C	-2.120321	2.639070	0.114670
C	-0.660403	2.992163	0.445384
C	0.411607	2.076626	-0.167855
O	-4.021274	-1.005860	-1.011393
C	2.655452	-0.002462	-0.259452
O	2.498662	0.203535	-1.443771
O	3.845349	-0.333105	0.292619
C	4.942672	-0.458039	-0.628459
H	-2.962046	-3.288108	-0.468220
H	-0.859171	-3.565403	0.813808
H	-0.894855	-0.950293	1.819342
H	-0.107558	-0.690912	-1.103676
H	-2.009681	0.568119	-1.500772
H	1.355541	-1.712276	2.160261
H	1.553199	-2.139247	0.459331
H	1.998304	0.522313	1.700221
H	5.805553	-0.733555	-0.021500
H	4.733473	-1.230612	-1.373289
H	5.121095	0.490142	-1.142428
H	-3.671856	1.160942	0.329824
H	-2.362976	0.972526	1.499283
H	-2.301902	2.816832	-0.955742
H	-0.471736	4.022930	0.112874
H	0.339684	2.058941	-1.266840
H	1.398054	2.496260	0.061210
H	-0.521914	2.979854	1.534849
H	-2.767609	3.346033	0.650764

0 imaginary frequencies
E = -825.331489
ZPE = 0.318047
H = -824.996364
G = -825.060566
E_{M06-2X} = -825.233202
E_{solv} = -825.351844

Thioether 9 (*trans* isomer)

Note: The calculations predict that the addition of PhSH to **9** should favor the epimer where SPh is *trans* to CO_2Me, whereas experimentally the *cis* isomer is favored. The *cis* isomer of **9** is predicted to be 1.5 kcal/mol higher in energy than the *trans* isomer by B3LYP ($\Delta\Delta E$). M06-2X calculations in the gas phase are closer to experiment ($\Delta\Delta E$ = 0.4 kcal/mol), but when thermochemical and solvation corrections are applied, the total difference in energy ($\Delta\Delta G$) amounts to 1.2 kcal/mol.

C	2.493572	1.138768	-0.748582
C	0.957544	1.347800	-1.004088
C	0.347377	-0.038614	-0.721514
C	1.338406	-0.607914	0.308027
N	2.598612	-0.250576	-0.328229
C	1.137729	-2.095610	0.629130
C	-0.358778	-2.404119	0.830851
C	-1.406018	-1.626208	0.023228
C	-1.081572	-0.139523	-0.198145
C	1.776134	-3.079267	-0.386728
C	3.283154	-3.293722	-0.142765
C	4.211337	-2.115797	-0.478619
C	3.859354	-0.774410	0.184777

O	-0.702388	-3.300210	1.577773
C	2.978329	2.149247	0.296515
O	3.099817	1.936911	1.484440
O	3.235867	3.344193	-0.281079
C	3.643831	4.391508	0.615867
H	-1.463999	-2.113347	-0.962314
S	-2.248558	0.667413	-1.400016
H	0.425809	-0.648793	-1.631233
H	1.196440	-0.051865	1.255834
H	1.587905	-2.319640	1.603668
H	0.760878	1.704963	-2.017169
H	0.544727	2.091670	-0.313773
H	3.072611	1.311155	-1.663939
H	3.799797	5.270166	-0.010579
H	2.867425	4.583558	1.361327
H	4.568392	4.116616	1.130356
H	1.275937	-4.048935	-0.276058
H	1.600788	-2.740523	-1.415661
H	3.421601	-3.577655	0.910678
H	5.236555	-2.392403	-0.193974
H	3.849910	-0.862708	1.282462
H	4.650249	-0.053039	-0.050784
H	4.215908	-1.955264	-1.564988
H	3.607297	-4.160984	-0.733411
H	-2.374826	-1.771051	0.507909
H	-1.169259	0.411892	0.746008
C	-3.794864	0.625605	-0.485698
C	-4.809756	-0.260975	-0.869132
C	-6.030255	-0.265665	-0.190560
C	-6.241737	0.605391	0.878956
C	-5.232482	1.491072	1.264301
C	-4.017349	1.509702	0.579794
H	-4.638798	-0.941726	-1.697448
H	-6.812625	-0.955553	-0.495408
H	-7.190358	0.597390	1.408810
H	-5.395293	2.176521	2.091808
H	-3.240531	2.214220	0.862963

0 imaginary frequencies
E = -1455.793122
ZPE = 0.423633
H = -1455.345432
G = -1455.428219
E_{M06-2X} = -1455.660748
E_{solv} = -1455.822328

Enone 5

C	4.332320	-0.298713	-0.838177
C	3.324817	-1.174265	-0.414246
C	3.290305	-1.574399	0.929214
C	4.247235	-1.104822	1.829239
C	5.249745	-0.232701	1.397615
C	5.291692	0.170467	0.061318
C	2.278895	-1.662099	-1.386027
O	1.092686	-0.823205	-1.353154
C	0.092108	-1.225578	-0.523493
O	0.081165	-2.266768	0.112659
N	-0.908872	-0.298421	-0.506534
C	-2.113916	-0.492492	0.311432
C	-2.622369	0.955718	0.496919
C	-2.234601	1.623526	-0.851327

C	-0.870410	0.978347	-1.222228
C	-4.090768	1.034469	0.817557
C	-4.952256	0.014332	0.696309
C	-4.544782	-1.318352	0.195863
C	-3.132495	-1.425997	-0.368764
O	-5.318354	-2.262431	0.187931
O	-1.970298	1.599250	1.587916
C	0.320154	1.870343	-0.851716
O	0.692352	1.729004	0.443209
C	1.829730	2.516504	0.856975
O	0.835375	2.646847	-1.619535
H	-3.201777	-1.168661	-1.436018
H	-2.798943	-2.465236	-0.313204
H	-1.831764	-0.903824	1.284010
H	-4.416975	1.995983	1.208939
H	-5.996026	0.115120	0.981527
H	-2.969271	1.383025	-1.626093
H	-2.183311	2.711118	-0.758400
H	-0.783737	0.833693	-2.302314
H	2.632972	-1.588444	-2.416516
H	1.975720	-2.688359	-1.172007
H	1.955008	2.307937	1.918956
H	2.714427	2.203063	0.299218
H	1.639233	3.578174	0.685062
H	2.504655	-2.247031	1.261224
H	4.214242	-1.424806	2.867364
H	5.998651	0.126511	2.098605
H	6.073121	0.843183	-0.282178
H	4.367851	0.013540	-1.879570
H	-1.007786	1.556663	1.436150

0 imaginary frequencies
E = -1203.456660
ZPE = 0.353246
H = -1203.080062
G = -1203.160282
E_{M06-2X} = -1203.348270
E_{solv} = -1203.485877

Thioether 6

C	4.733039	0.678196	1.801362
C	5.074442	-0.042102	0.647661
C	5.967348	0.525275	-0.269404
C	6.512974	1.790373	-0.041805
C	6.165463	2.501599	1.107991
C	5.274572	1.943009	2.027904
C	4.474452	-1.401580	0.389459
O	3.140830	-1.291565	-0.179046
C	2.101678	-1.382686	0.693118
O	2.205598	-1.592788	1.890688
N	0.912584	-1.214977	0.038101
C	-0.334368	-1.094803	0.811894
C	-1.320795	-0.400377	-0.190454
C	-0.705734	-0.701633	-1.582568
C	0.819528	-0.761153	-1.350671
C	-0.813148	-2.453268	1.376724
C	-1.634529	-3.230593	0.370538
C	-2.830108	-2.467656	-0.205942
C	-2.757593	-0.939297	-0.016713

O	-1.386684	-4.371575	0.034844
S	-3.989597	-0.155971	-1.166654
C	-4.947699	0.935524	-0.112745
C	-6.344135	0.874968	-0.224225
C	-7.144210	1.741300	0.521644
C	-6.560702	2.655338	1.400445
C	-5.170190	2.708727	1.516964
C	-4.359016	1.866657	0.754505
O	-1.358731	0.990875	0.067734
C	1.471773	0.614724	-1.526562
O	2.243922	0.667647	-2.611936
C	2.899336	1.929841	-2.859023
O	1.280350	1.561012	-0.780804
H	0.033295	-3.045390	1.727514
H	-1.459542	-2.245055	2.242242
H	-3.738549	-2.847474	0.278668
H	-2.925159	-2.745071	-1.261149
H	-3.082209	-0.667790	0.992360
H	-3.278107	1.927263	0.819757
H	-4.708354	3.422761	2.194298
H	-7.185054	3.321183	1.990123
H	-8.225700	1.687835	0.426771
H	-6.798950	0.145143	-0.887723
H	-1.030214	-1.676426	-1.958060
H	-1.009998	0.056501	-2.307496
H	1.314023	-1.462412	-2.025210
H	3.388388	1.815777	-3.826174
H	2.168044	2.740599	-2.884461
H	3.634398	2.123472	-2.074035
H	5.047153	-1.949221	-0.362292
H	4.404927	-1.993857	1.303469
H	6.242815	-0.030556	-1.163254
H	7.211551	2.216254	-0.757343
H	6.590080	3.485466	1.289148
H	5.004132	2.492505	2.925570
H	4.036989	0.241565	2.511922
H	-0.456115	1.351356	-0.059113
H	-0.168946	-0.415192	1.651814

0 imaginary frequencies
E = -1833.915803
ZPE = 0.459146
H = -1833.426683
G = -1833.523704
E_{M06-2X} = -1833.772436
E_{solv} = -1833.952832

Enone 7

C	1.198506	3.606631	0.324188
C	1.078747	2.073271	0.401730
C	2.036105	1.331600	-0.557910
C	3.358607	2.026107	-0.764292
C	3.631251	3.264494	-0.327410
C	2.631518	4.115236	0.357509
C	1.176419	1.116336	-1.822162
C	-0.235518	0.838468	-1.257561
N	-0.247818	1.610825	-0.025485
C	-1.336449	1.785977	0.782881
O	-1.299141	2.323182	1.876619
O	2.259414	0.041906	0.104750
C	-0.508363	-0.653746	-1.007506

O	-0.682446	-1.175745	0.070111
O	2.935812	5.186167	0.856755
O	-2.459390	1.312236	0.183381
C	-3.671970	1.382131	0.969464
C	-4.609576	0.293154	0.514875
C	-5.909137	0.602330	0.103159
C	-6.794469	-0.408474	-0.279406
C	-6.381166	-1.740065	-0.261231
C	-5.080508	-2.056455	0.142567
C	-4.200034	-1.048316	0.531030
O	-0.544018	-1.308894	-2.183095
C	-0.814941	-2.721059	-2.101726
H	0.763139	3.952102	-0.624975
H	0.623622	4.067814	1.129805
H	1.273163	1.747472	1.427193
H	4.112625	1.440590	-1.279141
H	4.617067	3.702205	-0.461981
H	1.160517	2.045701	-2.400805
H	1.556490	0.321761	-2.462320
H	-1.007358	1.183820	-1.952411
H	-4.119578	2.372706	0.834522
H	-3.399761	1.279199	2.023584
H	-0.771870	-3.085187	-3.128142
H	-0.064149	-3.217791	-1.482590
H	-1.806703	-2.889586	-1.674297
H	-3.186054	-1.294500	0.833625
H	-4.754662	-3.093497	0.160716
H	-7.066807	-2.528605	-0.560128
H	-7.802334	-0.153078	-0.595719
H	-6.232583	1.640671	0.081469
C	2.981559	-0.939188	-0.496728
O	3.537952	-0.812796	-1.572643
C	3.014843	-2.183191	0.320350
C	2.194909	-2.367620	1.443574
C	2.268504	-3.559351	2.162957
C	3.157365	-4.563293	1.771532
C	3.971767	-4.382192	0.649872
C	3.898374	-3.197652	-0.077395
H	1.493942	-1.593018	1.730282
H	1.629273	-3.704722	3.029113
H	3.214045	-5.488690	2.338730
H	4.661682	-5.163894	0.344463
H	4.517508	-3.036493	-0.953791

0 imaginary frequencies
E = -1547.859369
ZPE = 0.443990
H = -1547.385386
G = -1547.482576
E_{M06-2X} = -1547.706365
E_{solv} = -1547.895113

Thioether 8

C	4.660672	3.550683	-1.349466
C	4.265374	2.389086	-0.674494
C	4.869053	2.056025	0.547377
C	5.842484	2.891991	1.093512
C	6.239458	4.047981	0.416138
C	5.652015	4.371616	-0.807255
S	3.041071	1.306682	-1.420865
C	1.678473	1.447384	-0.162885

C	0.696401	0.265486	-0.299722
C	-0.435791	0.304395	0.787515
C	-0.557589	1.662556	1.511268
C	-0.332201	2.851597	0.597866
C	0.945195	2.794716	-0.246747
C	-0.057762	0.213515	-1.643057
C	-1.351666	-0.542010	-1.311877
N	-1.649891	-0.055684	0.028565
C	-2.817075	-0.335450	0.690254
O	-2.985283	-0.174908	1.888834
O	1.379649	-1.019303	-0.256556
C	-1.150979	-2.062875	-1.434574
O	-0.825845	-2.592694	-2.475512
O	-1.087092	3.800481	0.535646
O	-3.760434	-0.788745	-0.173420
C	-5.066603	-1.079609	0.393988
C	-6.015047	0.083980	0.245045
C	-6.945719	0.109383	-0.800005
C	-7.821312	1.186234	-0.947049
C	-7.770249	2.252412	-0.048045
C	-6.843445	2.236377	0.997384
C	-5.972151	1.157957	1.145845
O	-1.383066	-2.720403	-0.287622
C	-1.240740	-4.151532	-0.349839
H	-1.524767	1.739909	2.007613
H	0.223334	1.686307	2.285207
H	1.613996	3.591583	0.101224
H	0.687074	3.056145	-1.278373
H	2.160920	1.356068	0.809936
H	4.189896	3.807206	-2.293607
H	5.955682	5.269890	-1.338162
H	7.005234	4.691585	0.840381
H	6.301852	2.631814	2.043426
H	4.577164	1.145591	1.063496
H	-0.312223	1.221984	-1.976258
H	0.529254	-0.275257	-2.421805
H	-2.156805	-0.284300	-2.003880
H	-1.558880	-4.517043	0.626506
H	-1.869639	-4.562046	-1.143385
H	-0.198337	-4.420098	-0.537757
H	-4.928496	-1.354526	1.441201
H	-5.418587	-1.946188	-0.170502
H	-5.246817	1.141986	1.954035
H	-6.801134	3.064417	1.699893
H	-8.450688	3.092475	-0.160052
H	-8.541104	1.192190	-1.761334
H	-6.986223	-0.720810	-1.502031
C	2.123846	-1.389039	0.812466
H	-0.239829	-0.458531	1.543437
O	2.252018	-0.714119	1.819146
C	2.759019	-2.720909	0.610950
C	2.625413	-3.445958	-0.583172
C	3.243915	-4.688932	-0.710791
C	3.995024	-5.211813	0.345027
C	4.129991	-4.490168	1.534026
C	3.514985	-3.248049	1.667356
H	2.043292	-3.037452	-1.401606
H	3.142906	-5.247479	-1.637085
H	4.476477	-6.180528	0.240575
H	4.714550	-4.895883	2.354946
H	3.606497	-2.670793	2.581484

0 imaginary frequencies
E = -2178.315473
ZPE = 0.550221
H = -2177.728665
G = -2177.842449
E_{M06-2X} = -2178.130937
E_{solv} = -2178.359102

Et_3N

N	0.000000	0.000000	0.019586
C	-1.017336	-0.968655	0.447458
C	-0.330212	1.365366	0.447458
C	1.347548	-0.396711	0.447458
H	-0.572298	-1.967739	0.400851
H	-1.302637	-0.810013	1.506575
C	-2.264025	-0.959409	-0.439634
C	0.301140	2.440408	-0.439634
H	-1.417963	1.479494	0.400851
H	-0.050173	1.533123	1.506575
H	1.990261	0.488245	0.400851
H	1.352810	-0.723110	1.506575
C	1.962885	-1.480999	-0.439634
H	0.000000	3.438960	-0.101342
H	1.395966	2.403825	-0.420559
H	-0.020490	2.311046	-1.478165
H	2.978227	-1.719480	-0.101342
H	1.383791	-2.410855	-0.420559
H	2.011670	-1.137778	-1.478165
H	-2.978227	-1.719480	-0.101342
H	-2.779757	0.007030	-0.420559
H	-1.991180	-1.173268	-1.478165

0 imaginary frequencies
E = -292.416140
ZPE = 0.206988
H = -292.198801
G = -292.245038
E_{M06-2X} = -292.344457
E_{solv} = -292.424093

DBU

N	-1.466334	-1.455444	-0.143900
C	-2.722297	-0.742755	0.054042
C	-2.534126	0.622008	0.722671
C	-1.508279	1.429236	-0.068361
N	-0.313369	0.625392	-0.331274
C	-0.397184	-0.758977	-0.327959
C	0.896129	-1.530228	-0.518314
C	1.972232	-1.272260	0.558915
C	2.815728	-0.008950	0.335928
C	2.029556	1.308571	0.319704
C	0.896299	1.348919	-0.720142
H	-3.384081	-1.374981	0.659078
H	-3.227189	-0.614601	-0.917310
H	-3.477716	1.176958	0.784341
H	-2.169234	0.474809	1.747020
H	-1.209883	2.323061	0.494820
H	-1.950434	1.779892	-1.015534
H	0.595608	2.388974	-0.882866
H	1.598583	1.509216	1.310056
H	1.267952	0.988034	-1.689938

H	2.725845	2.131149	0.105159
H	3.347447	-0.109640	-0.622571
H	3.592491	0.048253	1.109952
H	2.649715	-2.135506	0.578179
H	1.490420	-1.237993	1.545497
H	0.599160	-2.580841	-0.505256
H	1.320883	-1.329813	-1.513313

0 imaginary frequencies
E = -462.094502
ZPE = 0.247048
H = -461.836674
G = -461.885812
E_{M06-2X} = -462.012101
E_{solv} = -462.111860

$Et_3NH^+PhS^-$ (optimized in solution)

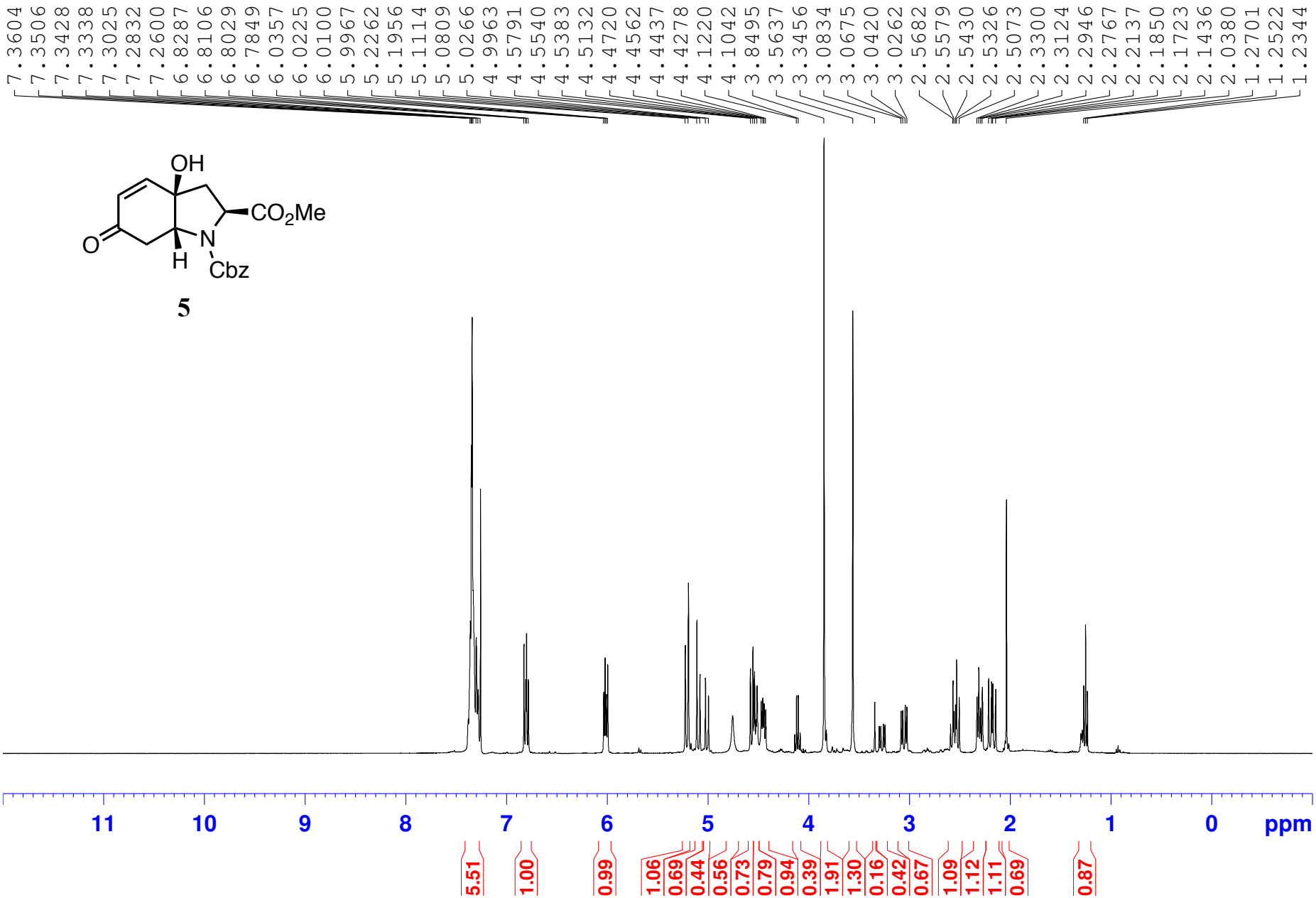
N	1.892917	0.076724	-0.190275
C	3.012793	0.194143	0.815202
H	3.273802	-0.828611	1.090504
H	3.869497	0.635440	0.298994
C	2.635792	0.982646	2.063047
H	3.453114	0.888037	2.786100
H	1.726952	0.584002	2.525286
H	2.492500	2.048539	1.862995
C	1.271568	1.398014	-0.585666
H	0.440495	1.141571	-1.246390
H	0.844689	1.819550	0.325365
C	2.217870	2.385060	-1.254700
H	3.048064	2.676906	-0.603494
H	1.648315	3.290821	-1.489155
H	2.627135	2.001431	-2.194209
C	2.291117	-0.733426	-1.402169
H	1.425601	-0.707663	-2.068963
H	3.117455	-0.210538	-1.889290
C	2.663305	-2.176477	-1.083898
H	3.605146	-2.260497	-0.534103
H	1.871194	-2.674799	-0.515977
H	2.787347	-2.710986	-2.031963
H	-4.304800	1.768382	1.194738
H	1.098287	-0.459555	0.287413
S	-0.550977	-1.445089	1.219154
C	-1.921536	-0.588618	0.471809
C	-2.322618	-0.845220	-0.858781
C	-3.403084	-0.177924	-1.438973
C	-4.128823	0.770073	-0.711021
C	-3.752258	1.036019	0.609095
C	-2.670400	0.371222	1.188895
H	-2.392730	0.592115	2.216652
H	-4.971616	1.287803	-1.161906
H	-3.681515	-0.404789	-2.466464
H	-1.776066	-1.585884	-1.437732

0 imaginary frequencies
E = -922.842932
ZPE = 0.312984
H = -922.512230
G = -922.581483
E_{M06-2X} = -922.735960
E_{solv} = -922.884221

$DBUH^+PhS^-$ (optimized in solution)

C	-3.040100	0.258346	0.844550
C	-3.283673	-0.450380	-0.354612
C	-4.637126	-0.711257	-0.671688
C	-5.678235	-0.289979	0.155943
C	-5.413438	0.411987	1.336609
C	-4.082511	0.680614	1.671129
S	-1.974197	-0.994549	-1.421642
N	0.625385	0.692424	-0.467623
C	1.656552	0.125226	0.136544
N	2.761819	0.812618	0.432466
C	2.909271	2.230621	0.039601
C	2.013352	2.573768	-1.145972
C	0.591403	2.098186	-0.872772
C	3.880487	0.209699	1.188340
C	4.675009	-0.837757	0.398038
C	3.996290	-2.211627	0.325678
C	2.594557	-2.215921	-0.297791
C	1.556086	-1.347606	0.448013
H	-0.039163	2.167157	-1.762701
H	0.122461	2.695277	-0.081101
H	2.028095	3.655081	-1.309875
H	2.395516	2.090524	-2.052287
H	2.674890	2.860844	0.906504
H	3.960079	2.390425	-0.216245
H	3.493908	-0.219360	2.119362
H	4.529455	1.041355	1.469319
H	4.872654	-0.448388	-0.609728
H	5.649733	-0.951619	0.888926
H	3.928313	-2.622202	1.343467
H	4.638209	-2.896853	-0.242108
H	2.214598	-3.244022	-0.297408
H	2.640991	-1.902763	-1.348914
H	0.545394	-1.665091	0.177013
H	1.657733	-1.492531	1.531116
H	-0.203049	0.100551	-0.716063
H	-4.864966	-1.254695	-1.585584
H	-6.706053	-0.511857	-0.125589
H	-6.224879	0.740799	1.980914
H	-3.851544	1.224471	2.585531
H	-2.013197	0.476860	1.128166

0 imaginary frequencies
E = -1092.530026
ZPE = 0.351962
H = -1092.159664
G = -1092.230807
$E_{M06\text{-}2X}$ = -1092.405941
E_{solv} = -1092.584568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6.0357
6.0225
6.0100
5.9967
5.2262
5.1956
5.1114
5.0809
5.0266
4.9963
4.5791
4.5540
4.5383
4.5132
4.4720
4.4562
4.4437
4.4278
4.1220
4.1042
3.8495
3.5637
3.3456
3.0834
3.0675
3.0420
3.0262
2.5682
2.5579
2.5430
2.5326
2.5073
2.3300
2.3124
2.2946
2.2767
2.2137
2.1850
2.1723
2.1436
2.0380
1.2701
1.2522
1.2344
OH
CO2Me
O
N
H
Cbz
11
10
9
8
7
6
5
4
3
2
1
0
ppm
5.51
1.00
0.99
1.06
0.69
0.44
0.56
0.73
0.79
0.94
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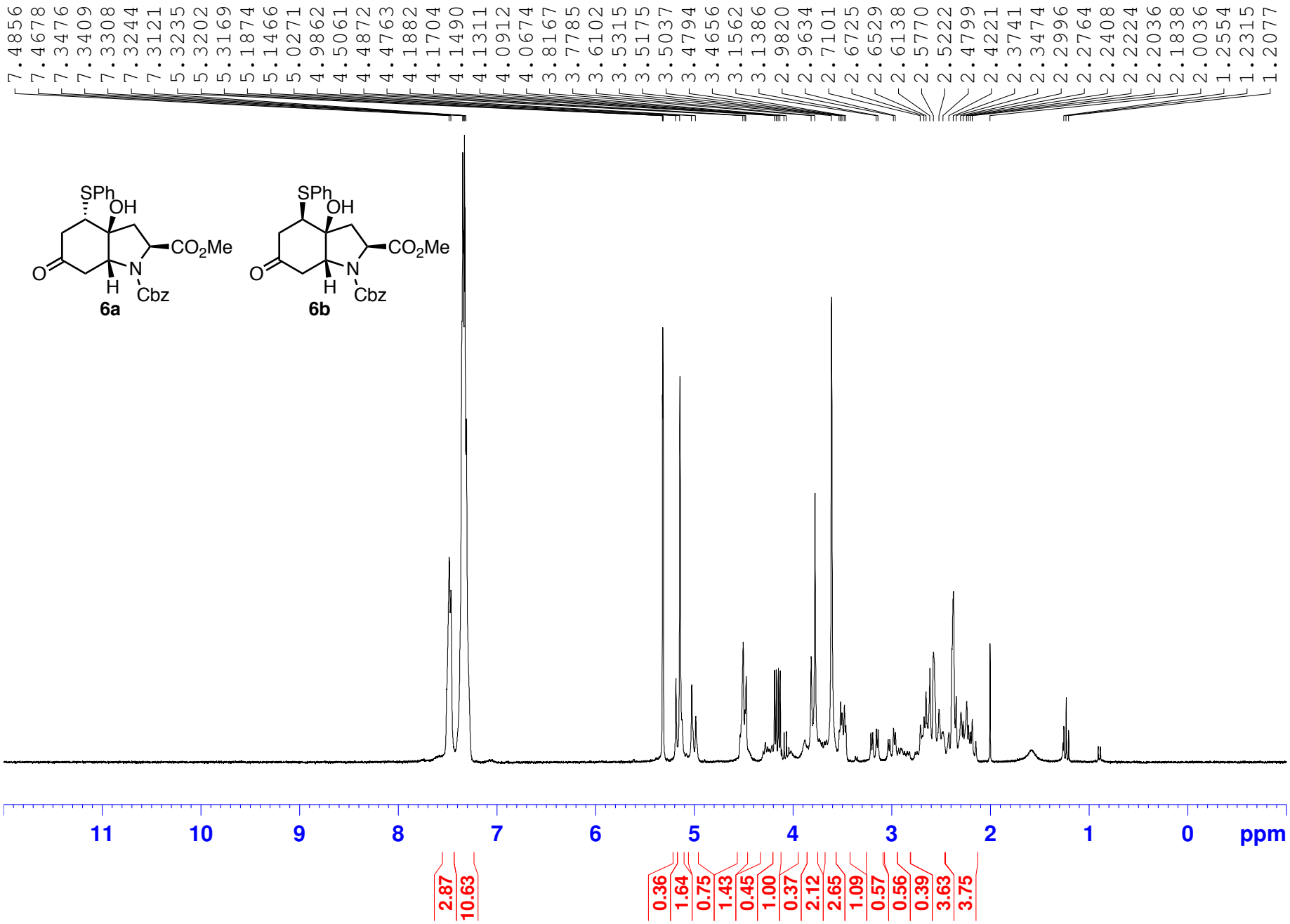
1.30
0.16
0.42
0.67
1.09
1.12
1.11
0.69
0.87

5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5.3202
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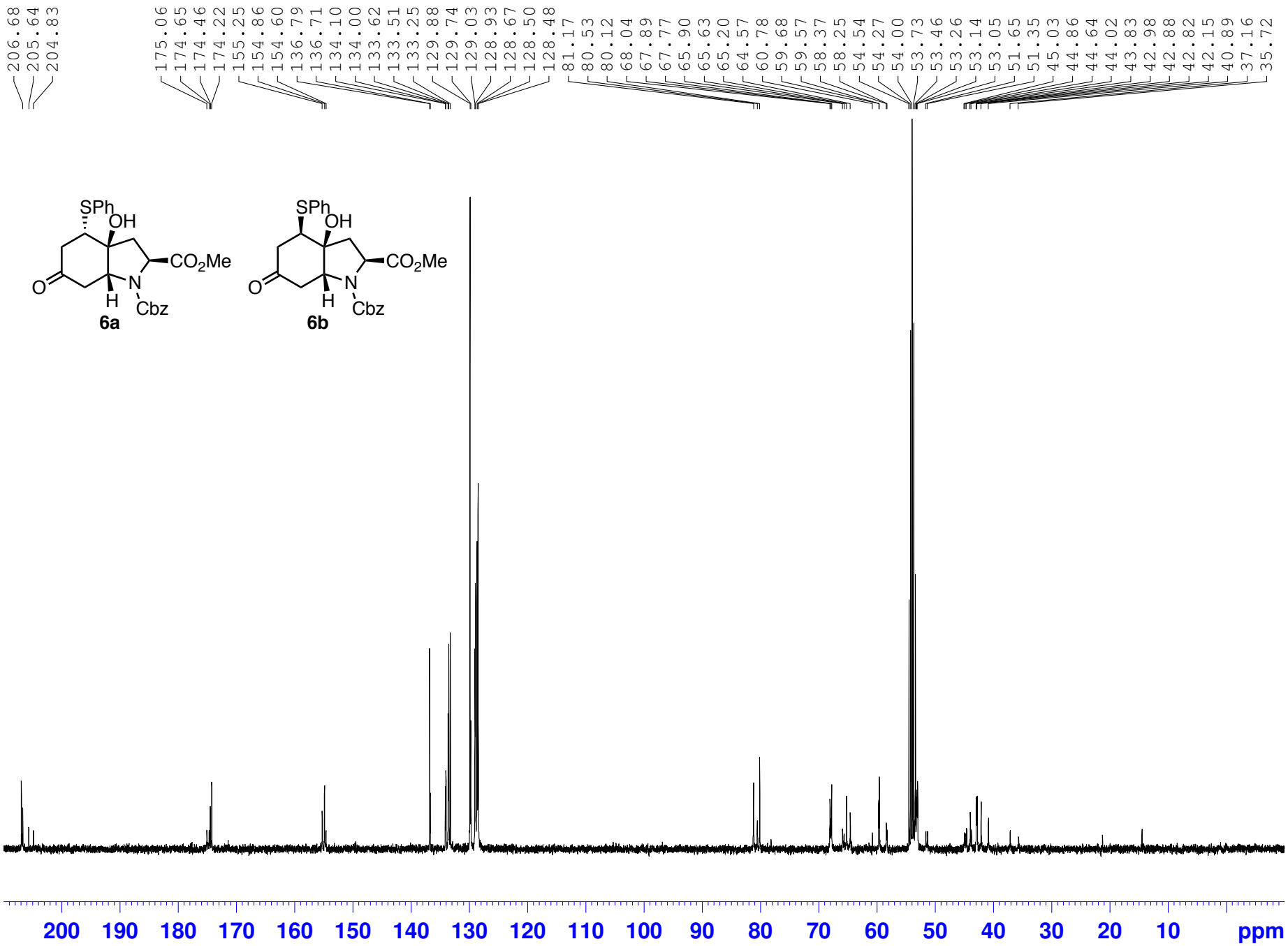
5.1466
5.0271
4.9862
4.5061
4.4872
4.4763
4.1882
4.1704
4.1490
4.1311
4.0912
4.0674
3.8167
3.7785
3.6102
3.5315
3.5175
3.5037
3.4794
3.4656
3.1562
3.1386
2.9820
2.9634
2.7101
2.6725
2.6529
2.6138
2.5770
2.5222
2.4799
2.4221
2.3741
2.3474
2.2996
2.2764
2.2408
2.2224
2.2036
2.1838
2.0036
1.2554
1.2315
1.2077
SPh
OH
CO2Me
O
N
H
Cbz
6a
SPh
OH
CO2Me
O
N
H
Cbz
6b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.87
10.63
0.36
1.64
0.75
1.43
0.45
1.00
0.37
2.12
2.65
1.09
0.57
0.56
0.39
3.63
3.75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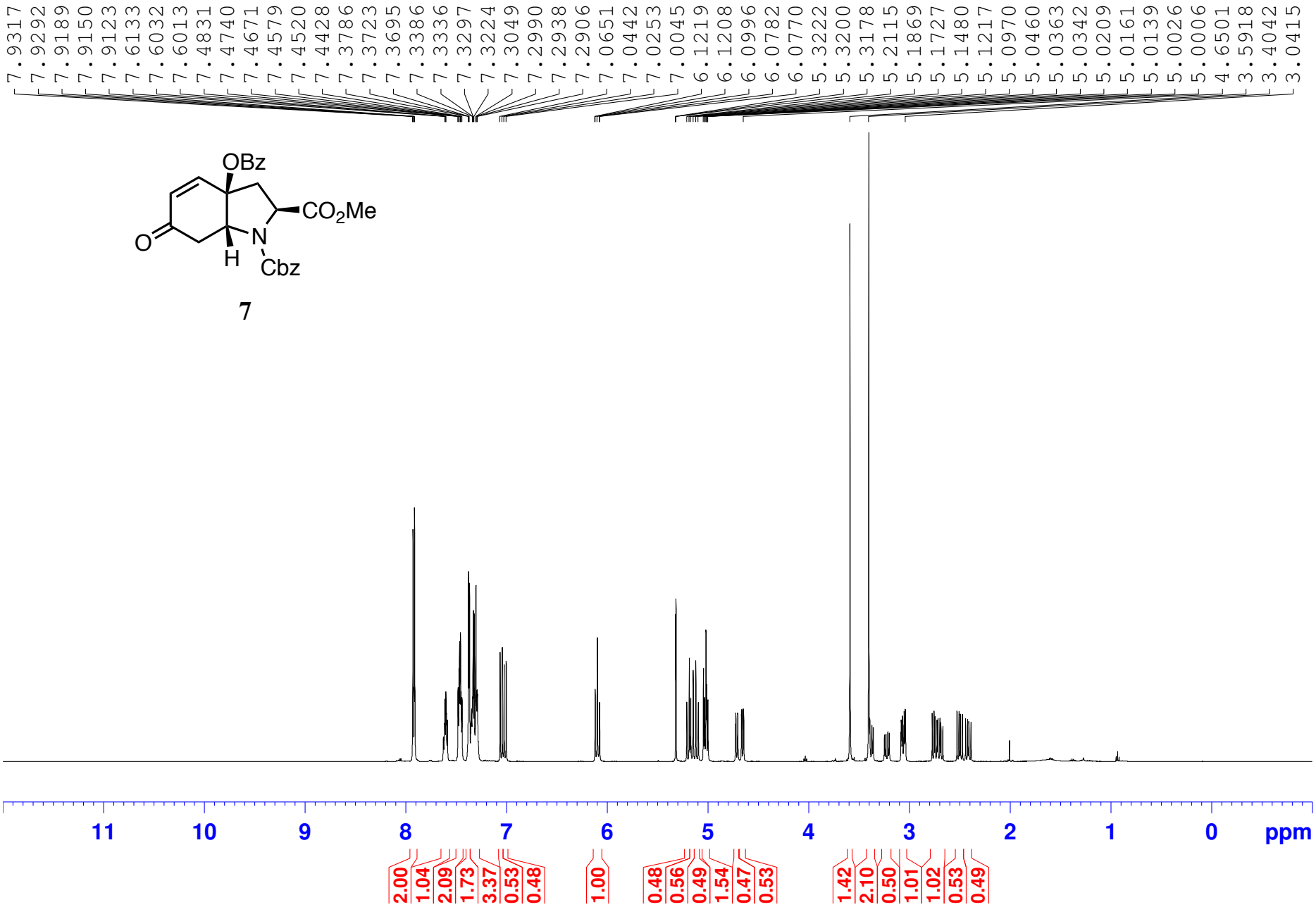
205.64
204.83
175.06
174.65
174.46
174.22
155.25
154.86
154.60
136.79
136.71
134.10
134.00
133.62
133.51
133.25
129.88
129.74
129.03
128.93
128.67
128.50
128.48
81.17
80.53
80.12
68.04
67.89
67.77
65.90
65.63
65.20
64.57
60.78
59.68
59.57
58.37
58.25
54.54
54.27
54.00
53.73
53.46
53.26
53.14
53.05
51.65
51.35
45.03
44.86
44.64
44.02
43.83
42.98
42.88
42.82
42.15
40.89
37.16
35.72
SPh
OH
CO2Me
O
N
H
Cbz
6a
SPh
OH
CO2Me
O
N
H
Cbz
6b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.4831
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7.4671
7.4579
7.4520
7.4428
7.3786
7.3723
7.3695
7.3386
7.3336
7.3297
7.3224
7.3049
7.2990
7.2938
7.2906
7.0651
7.0442
7.0253
7.0045
6.1219
6.1208
6.0996
6.0782
6.0770
5.3222
5.3200
5.3178
5.2115
5.1869
5.1727
5.1480
5.1217
5.0970
5.0460
5.0363
5.0342
5.0209
5.0161
5.0139
5.0026
5.0006
4.6501
3.5918
3.4042
3.0415
OBz
CO2Me
O
N
H
Cbz
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.04
2.09
1.73
3.37
0.53
0.48
1.00
0.48
0.56
0.49
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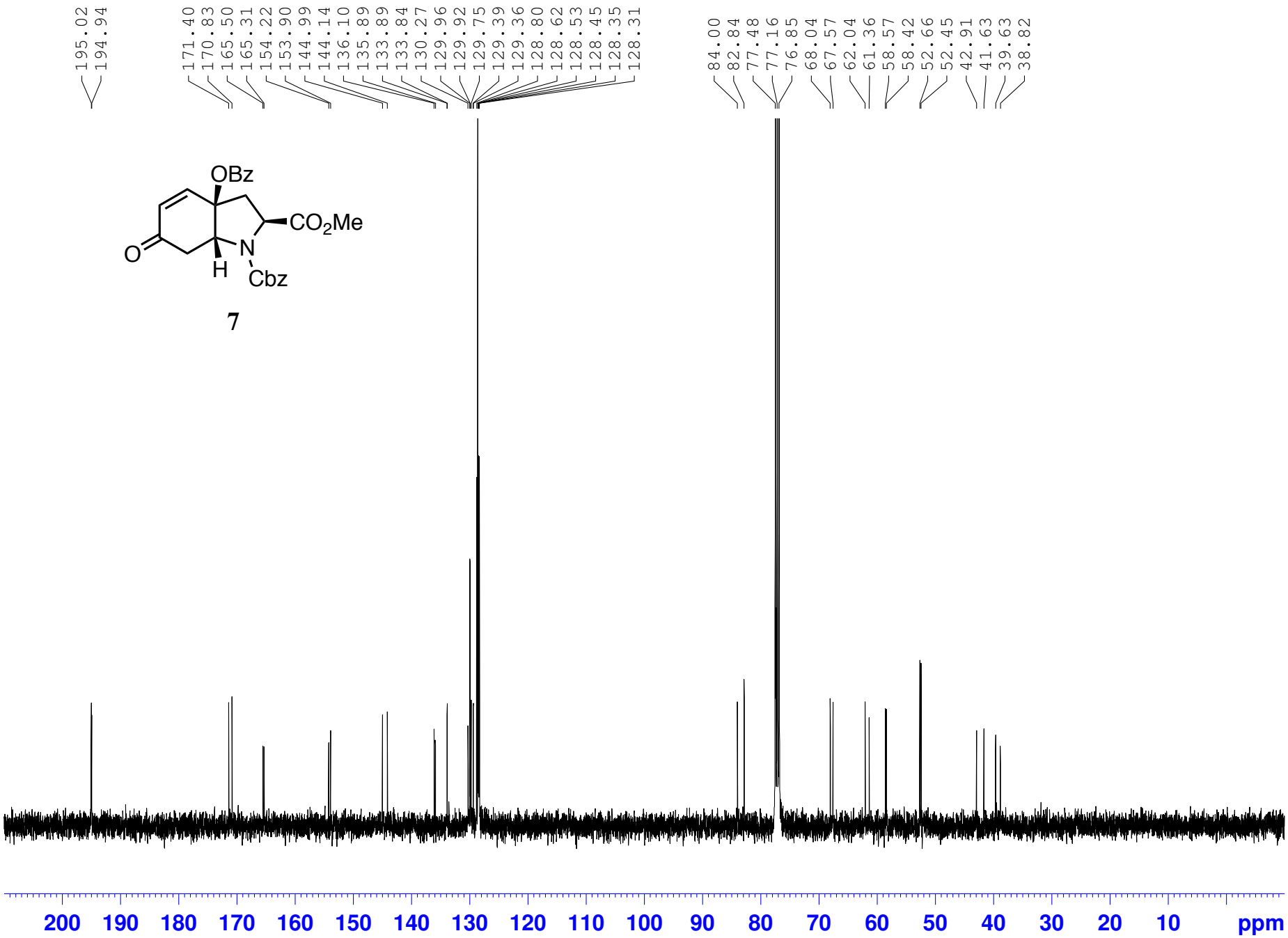
0.47
0.53
1.42
2.10
0.50
1.01
1.02
0.53
0.49

7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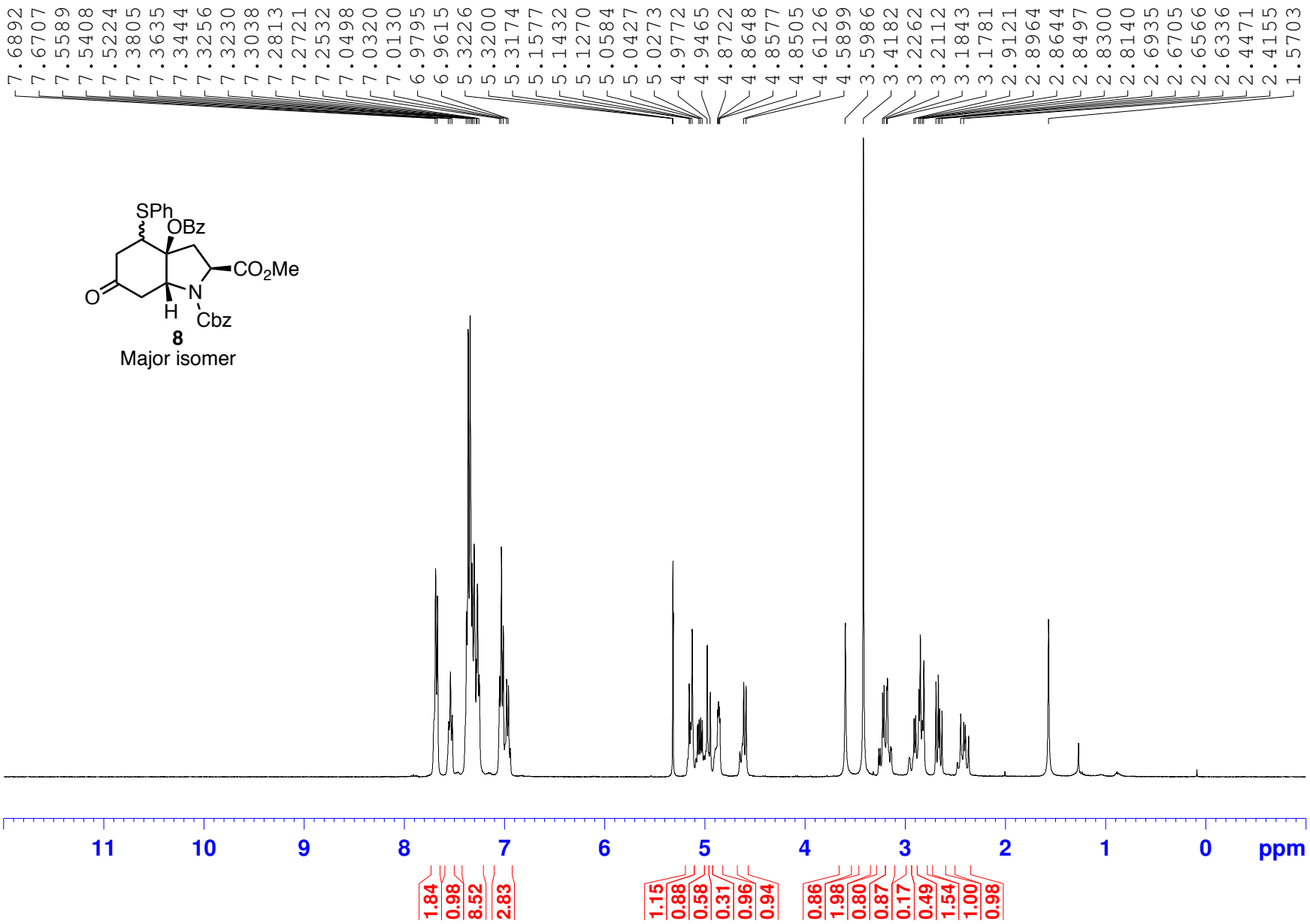
144.14
136.10
135.89
133.89
133.84
130.27
129.96
129.92
129.75
129.39
129.36
128.80
128.62
128.53
128.45
128.35
128.31
84.00
82.84
77.48
77.16
76.85
68.04
67.57
62.04
61.36
58.57
58.42
52.66
52.45
42.91
41.63
39.63
38.82
OBz
CO2Me
O
N
H
Cbz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

7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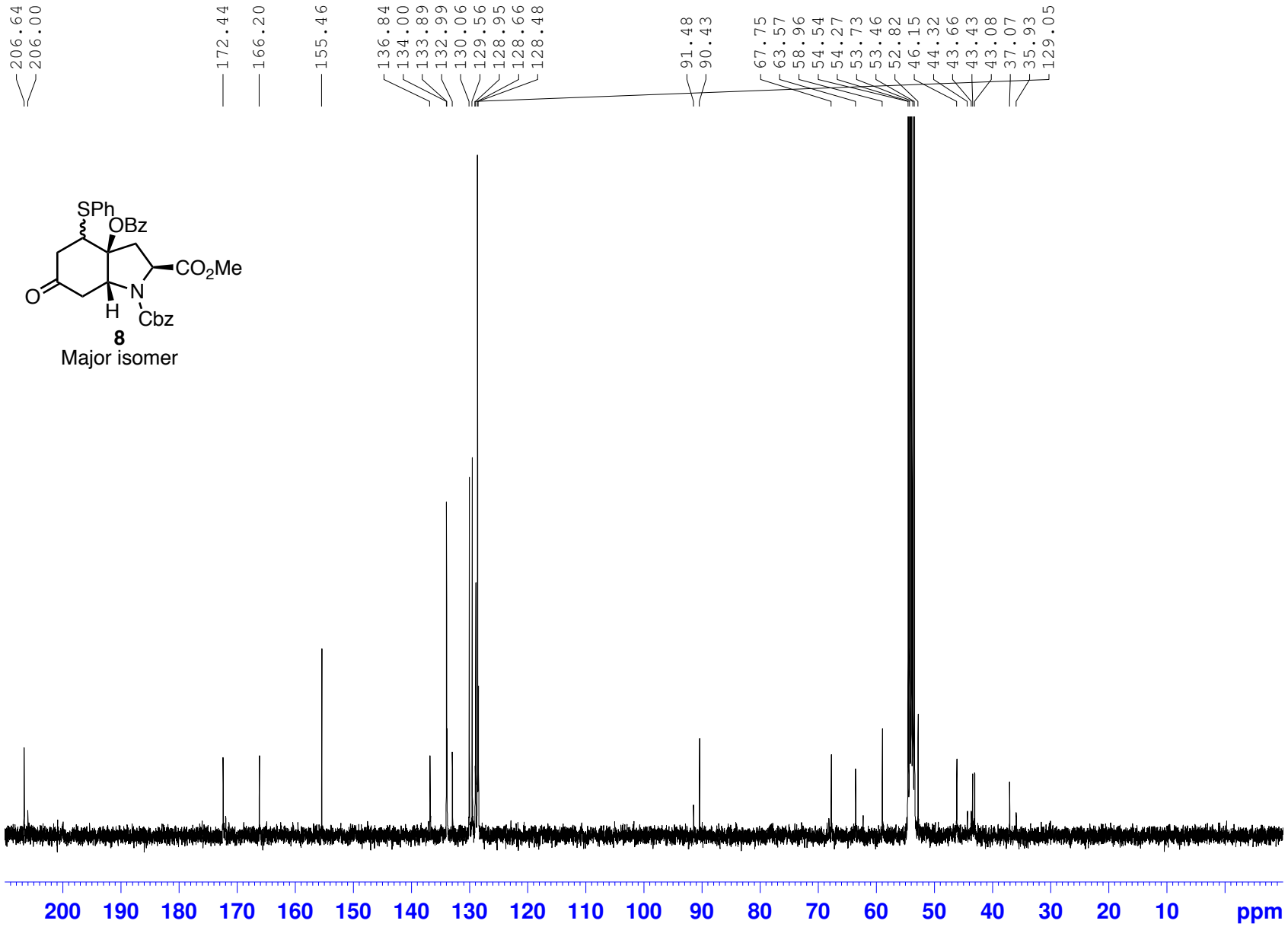
7.2813
7.2721
7.2532
7.0498
7.0320
7.0130
6.9795
6.9615
5.3226
5.3200
5.3174
5.1577
5.1432
5.1270
5.0584
5.0427
5.0273
4.9772
4.9465
4.8722
4.8648
4.8577
4.8505
4.6126
4.5899
3.5986
3.4182
3.2262
3.2112
3.1843
3.1781
2.9121
2.8964
2.8644
2.8497
2.8300
2.8140
2.6935
2.6705
2.6566
2.6336
2.4471
2.4155
1.5703
SPh
OBz
CO2Me
O
N
H
Cbz
8
Major isomer
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.84
0.98
8.52
2.83
1.15
0.88
0.58
0.31
0.96
0.94
0.86
1.98
0.80
0.87
0.17
0.49
1.54
1.00
0.98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132.99
130.06
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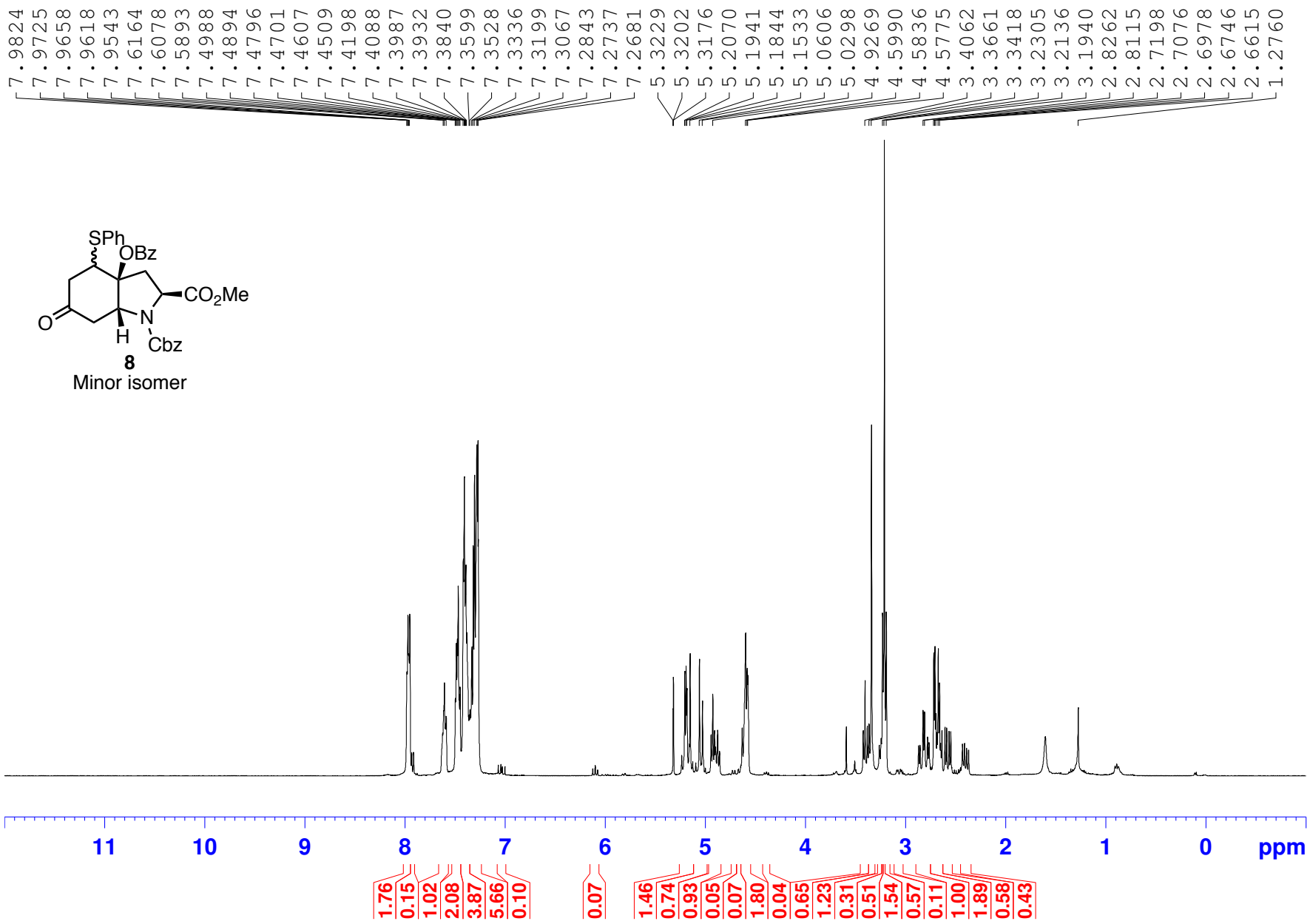
128.66
128.48
91.48
90.43
67.75
63.57
58.96
54.54
54.27
53.73
53.46
52.82
46.15
44.32
43.66
43.43
43.08
37.07
35.93
129.05
SPh
OBz
CO2Me
O
N
H
Cbz
8
Major isomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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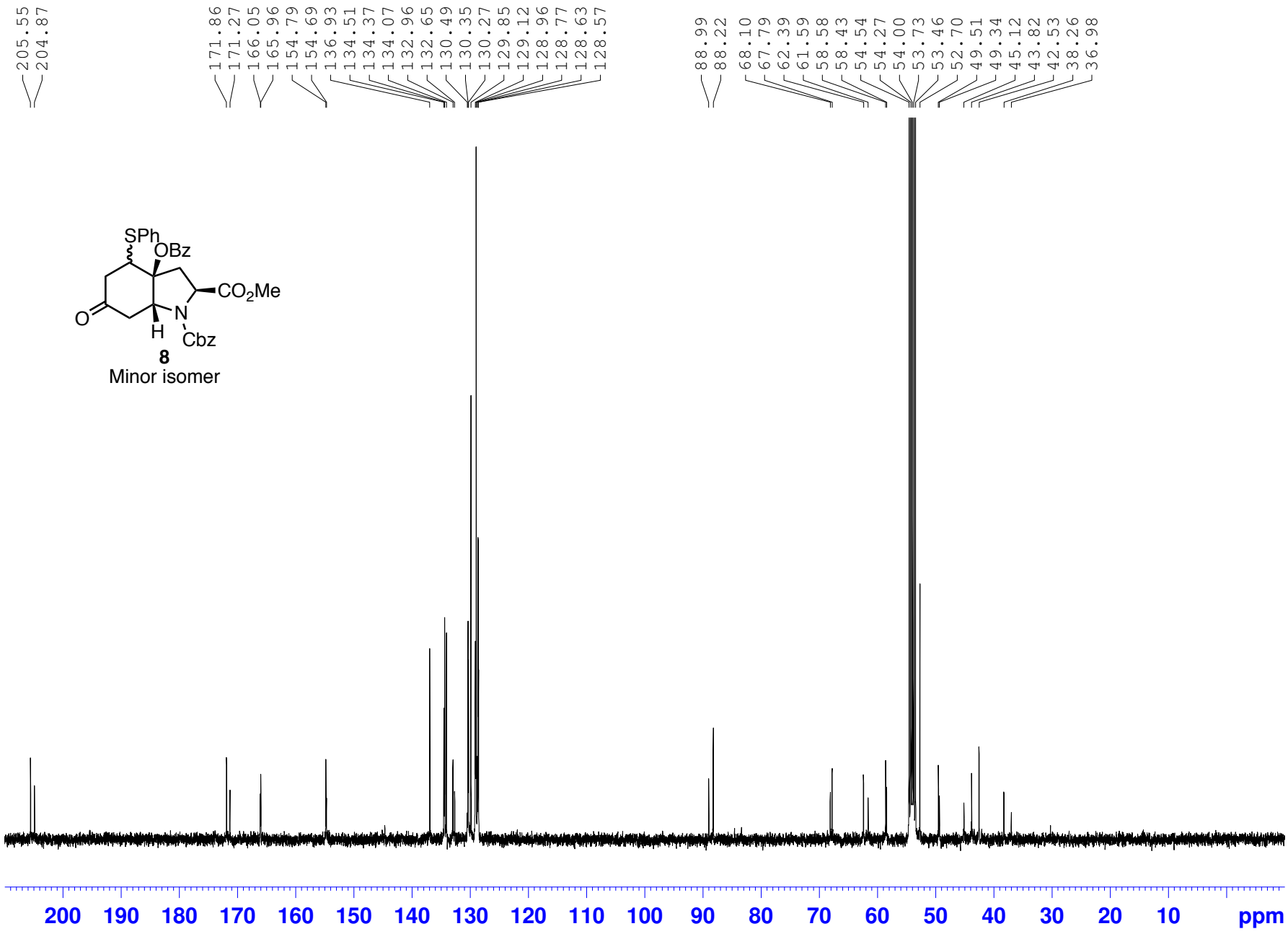
7.4894
7.4796
7.4701
7.4607
7.4509
7.4198
7.4088
7.3987
7.3932
7.3840
7.3599
7.3528
7.3336
7.3199
7.3067
7.2843
7.2737
7.2681
5.3229
5.3202
5.3176
5.2070
5.1941
5.1844
5.1533
5.0606
5.0298
4.9269
4.5990
4.5836
4.5775
3.4062
3.3661
3.3418
3.2305
3.2136
3.1940
2.8262
2.8115
2.7198
2.7076
2.6978
2.6746
2.6615
1.2760
SPh
OBz
CO2Me
O
N
H
Cbz
8
Minor isomer
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.76
0.15
1.02
2.08
3.87
5.66
0.10
0.07
1.46
0.74
0.93
0.05
0.07
1.80
0.04
0.65
1.23
0.31
0.51
1.54
0.57
0.11
1.00
1.89
0.58
0.43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204.87
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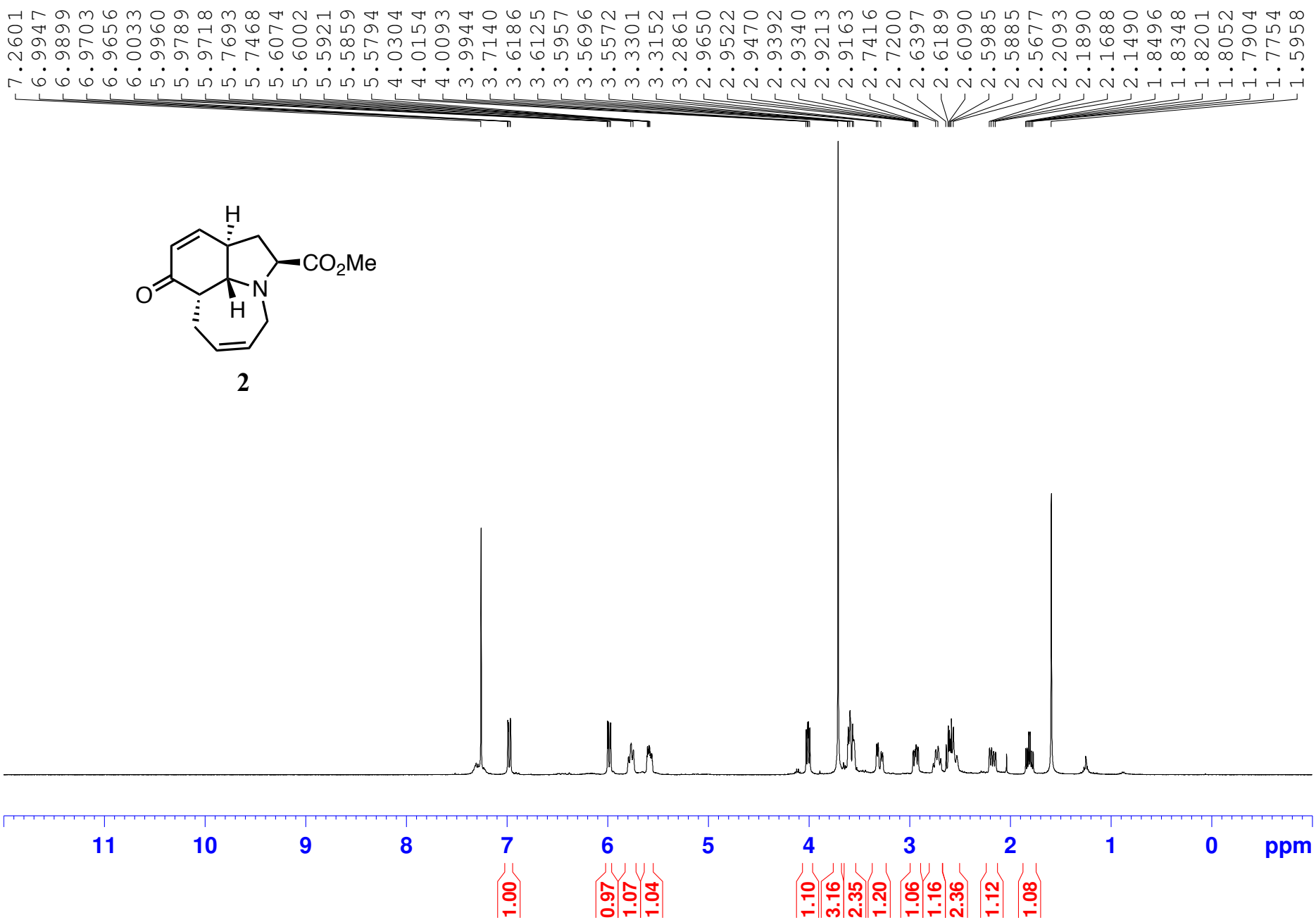
171.27
166.05
165.96
154.79
154.69
136.93
134.51
134.37
134.07
132.96
132.65
130.49
130.35
130.27
129.85
129.12
128.96
128.77
128.63
128.57
88.99
88.22
68.10
67.79
62.39
61.59
58.58
58.43
54.54
54.27
54.00
53.73
53.46
52.70
49.51
49.34
45.12
43.82
42.53
38.26
36.98
SPh
OBz
CO2Me
O
N
H
Cbz
8
Minor isomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.9899
6.9703
6.9656
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CO2Me
O
N
H
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10
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8
7
6
5
4
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1.08

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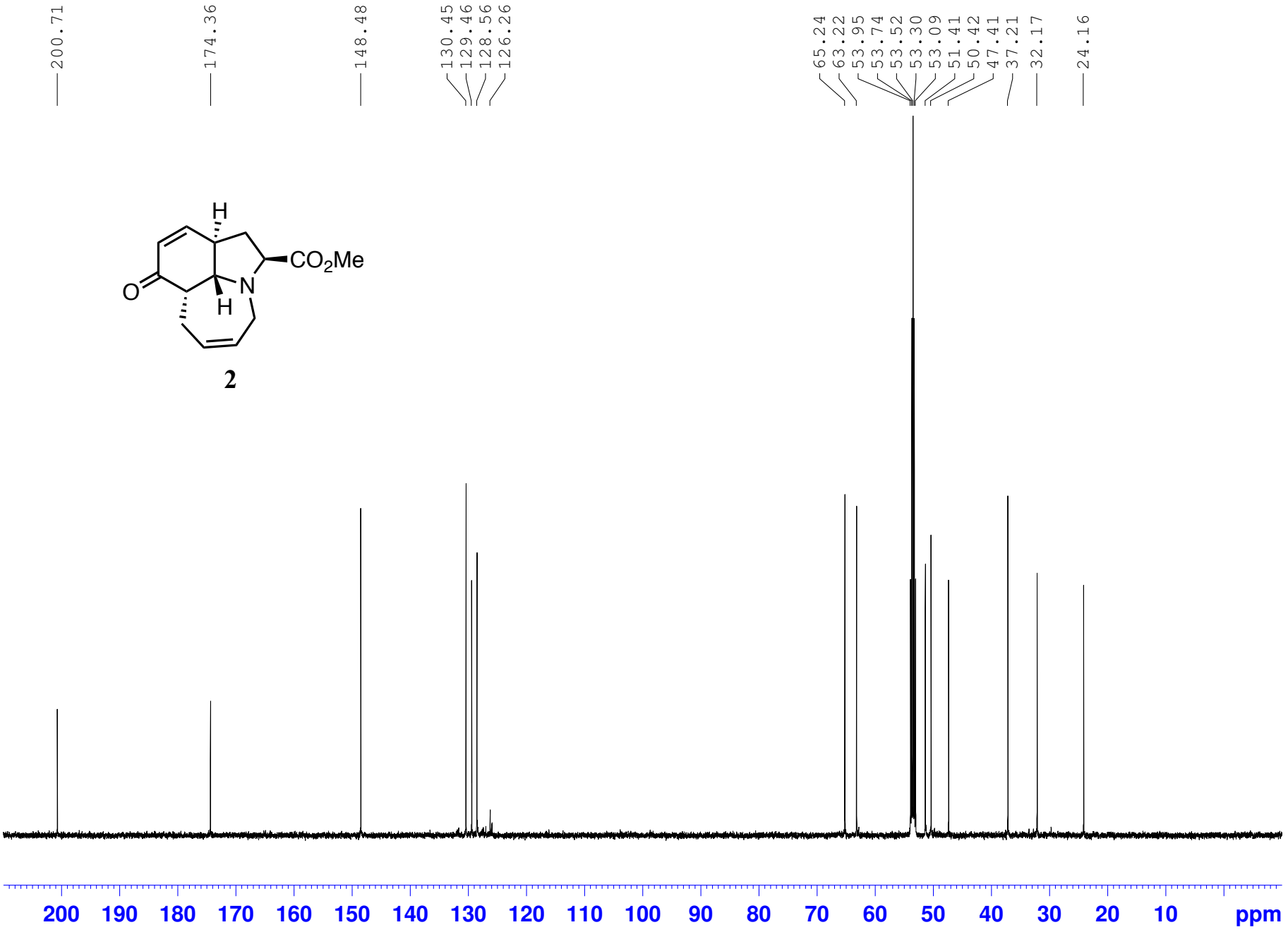
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51.41
50.42
47.41
37.21
32.17
24.16
H
CO2Me
O
N
H
200
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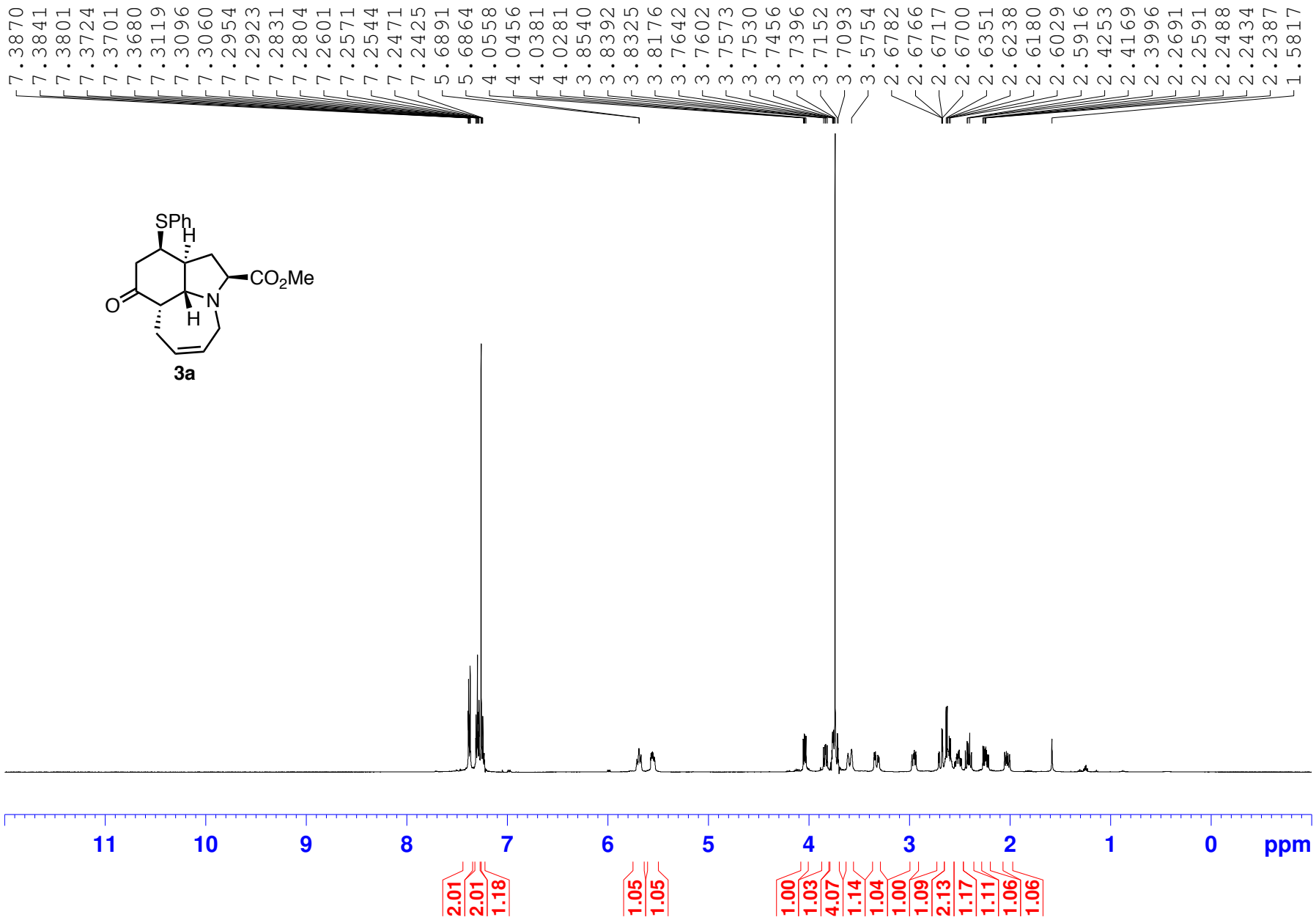
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7.2471
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5.6864
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4.0456
4.0381
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3.7602
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3.7530
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2.6717
2.6700
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2.3996
2.2691
2.2591
2.2488
2.2434
2.2387
1.5817
SPh
H
CO2Me
O
N
H
3a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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2.01
1.18
1.05
1.05
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1.00
1.09
2.13
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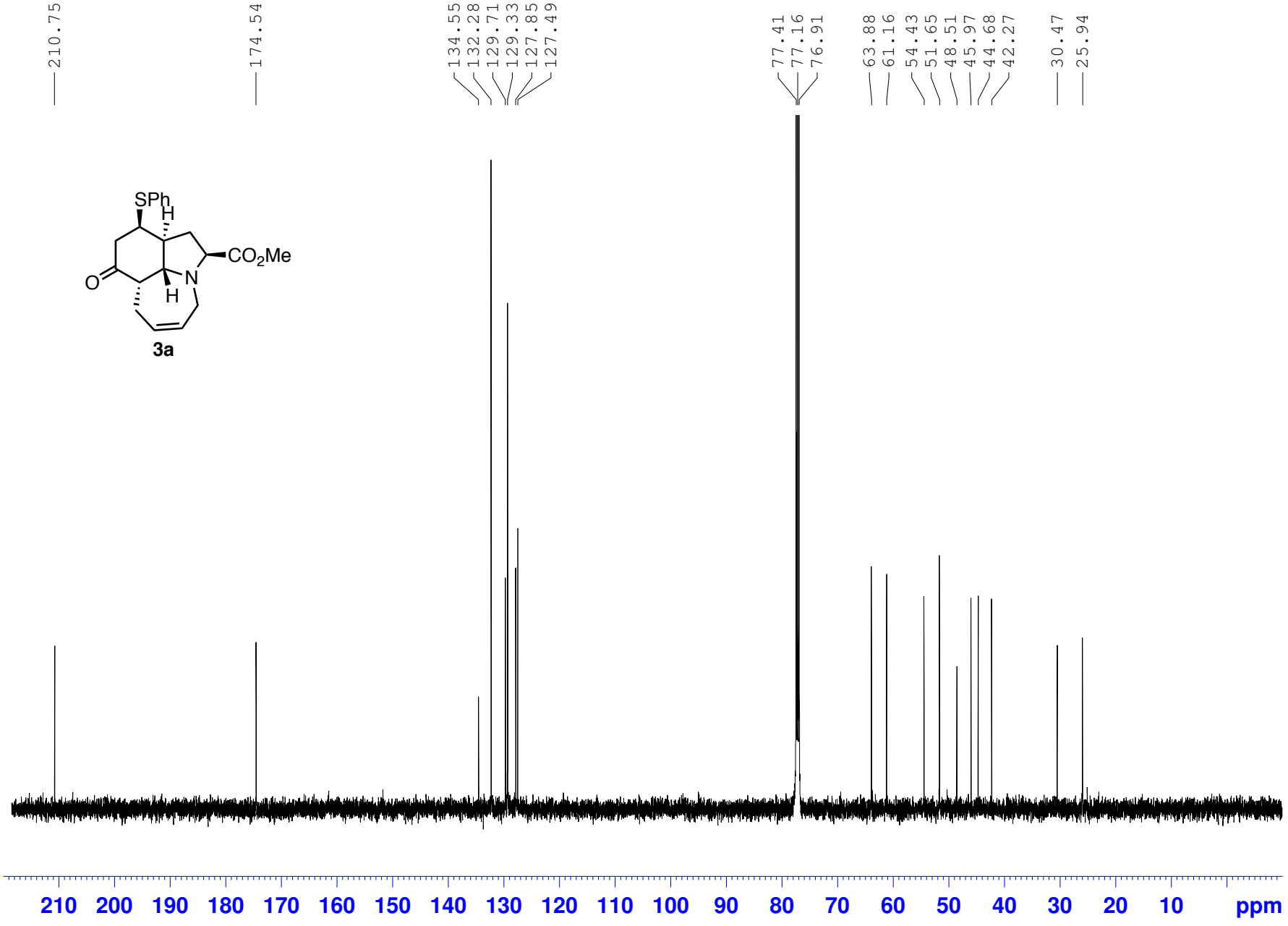
1.11
1.06
1.06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54.43
51.65
48.51
45.97
44.68
42.27
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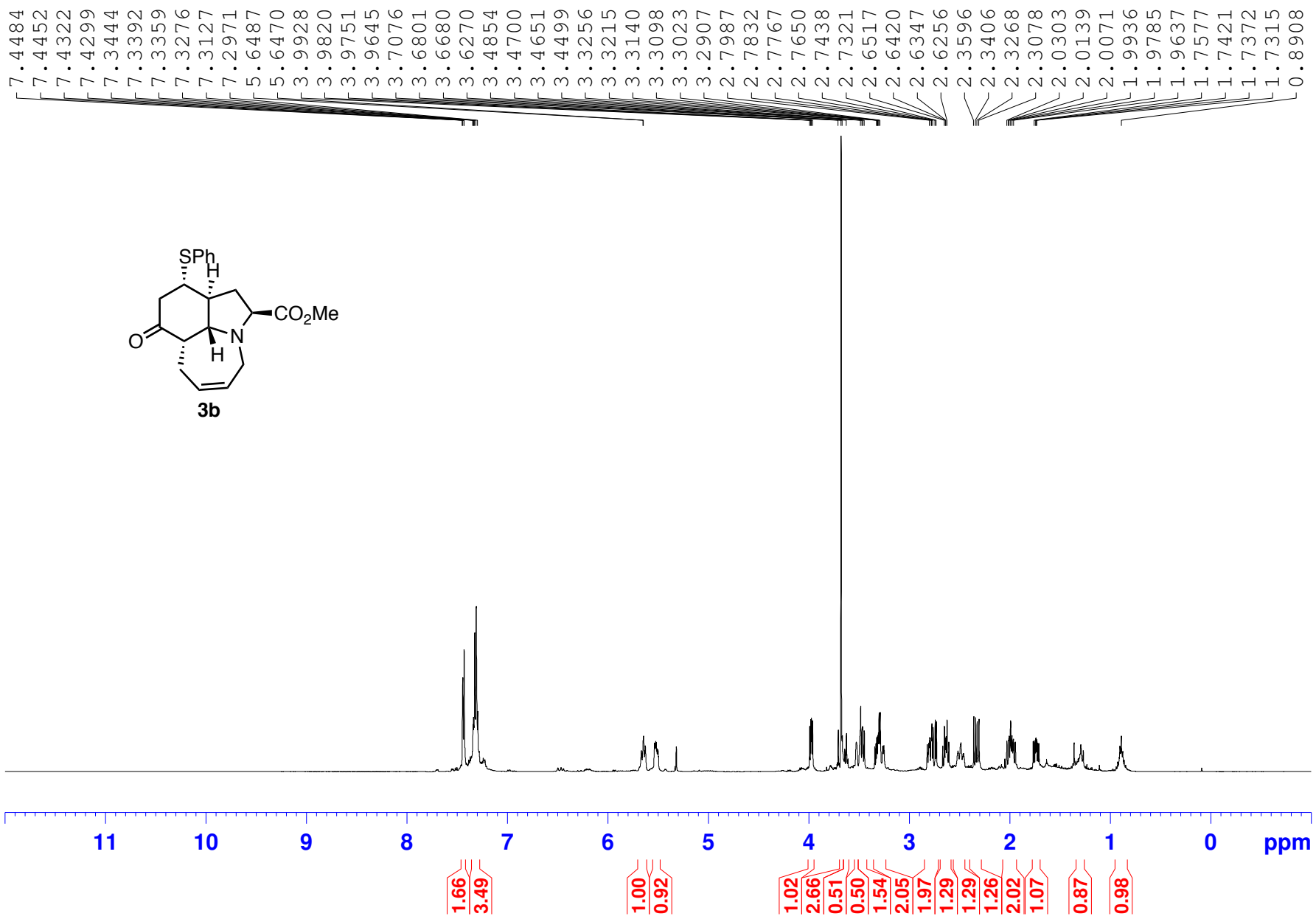
H
CO2Me
O
N
H
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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3.4499
3.3256
3.3215
3.3140
3.3098
3.3023
3.2907
2.7987
2.7832
2.7767
2.7650
2.7438
2.7321
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1.9936
1.9785
1.9637
1.7577
1.7421
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1.7315
0.8908
SPh
H
CO2Me
O
N
H
3b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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3.49
1.00
0.92
1.02
2.66
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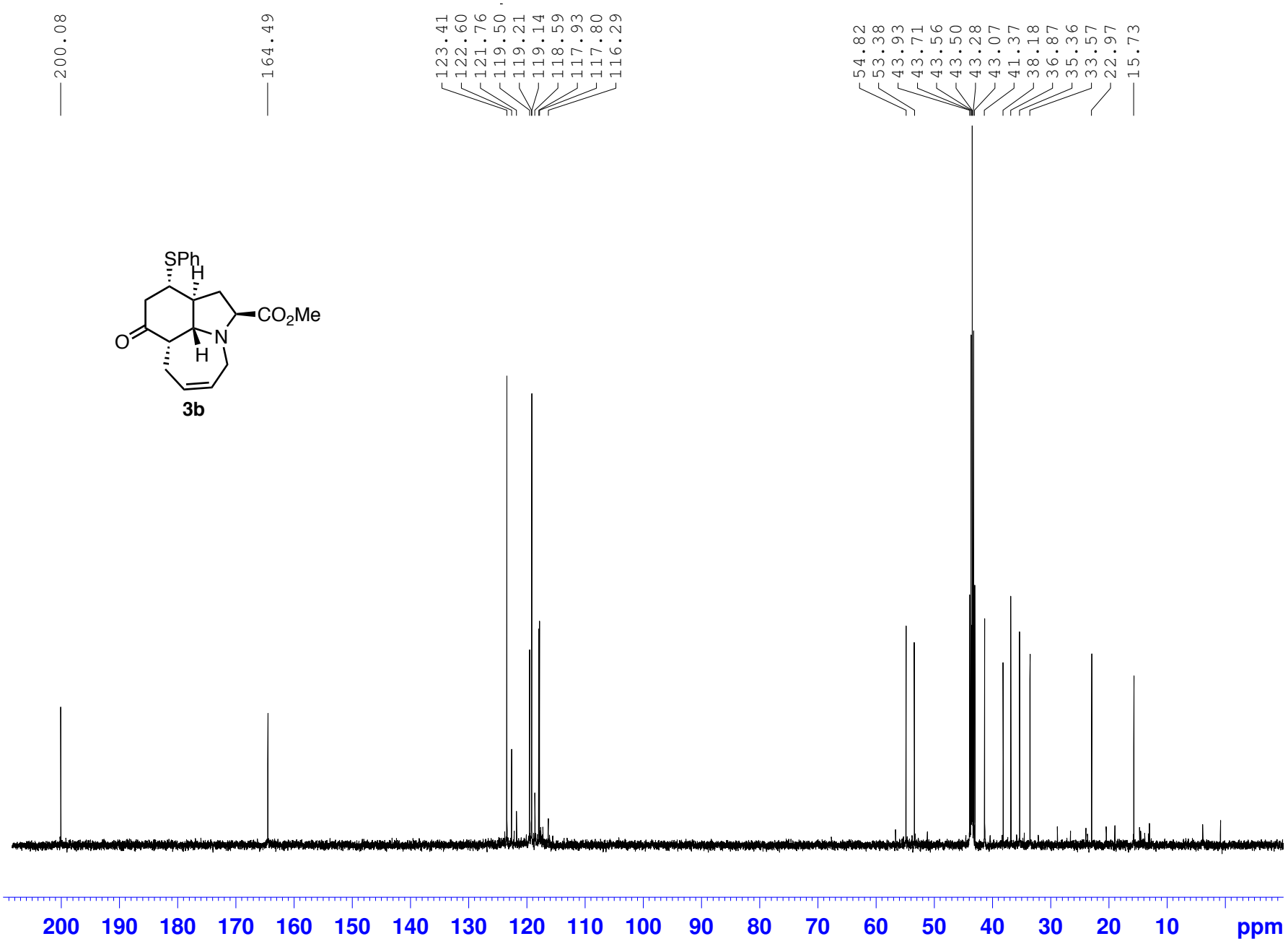
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43.93
43.71
43.56
43.50
43.28
43.07
41.37
38.18
36.87
35.36
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H
CO2Me
O
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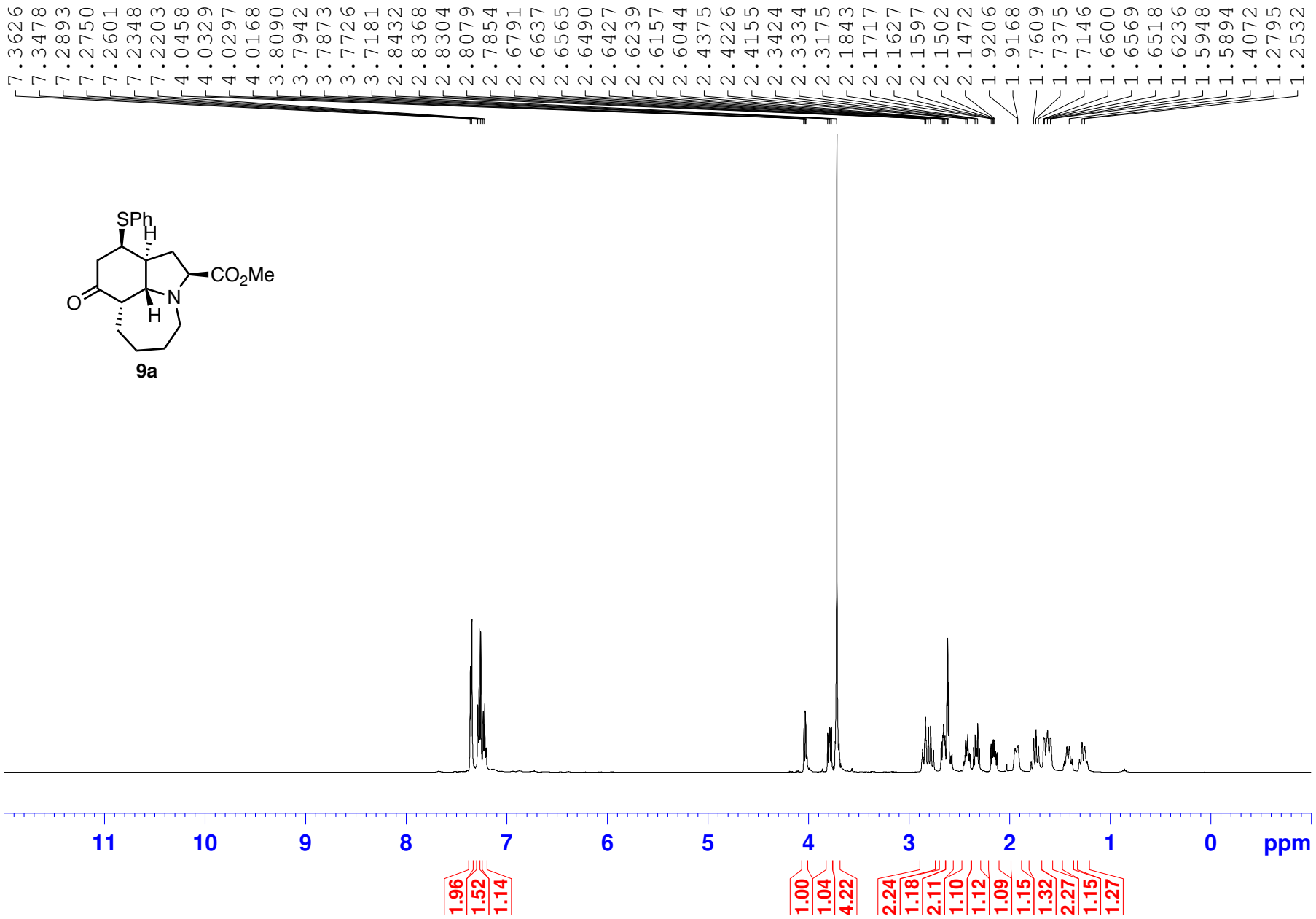
H
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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2.3175
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2.1472
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1.9168
1.7609
1.7375
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1.6600
1.6569
1.6518
1.6236
1.5948
1.5894
1.4072
1.2795
1.2532
SPh
H
CO2Me
O
N
H
9a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.52
1.14
1.00
1.04
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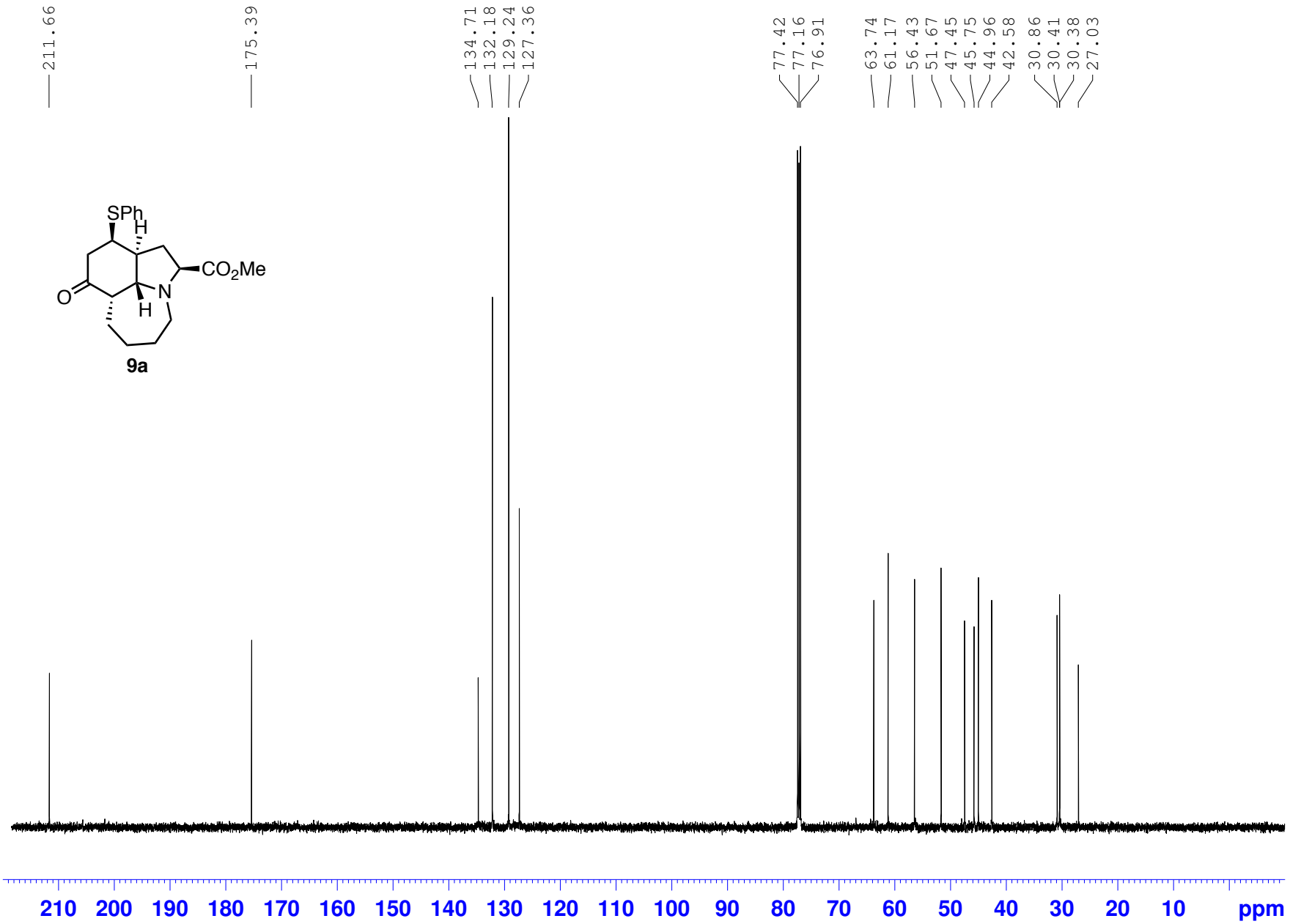
2.11
1.10
1.12
1.09
1.15
1.32
2.27
1.15
1.27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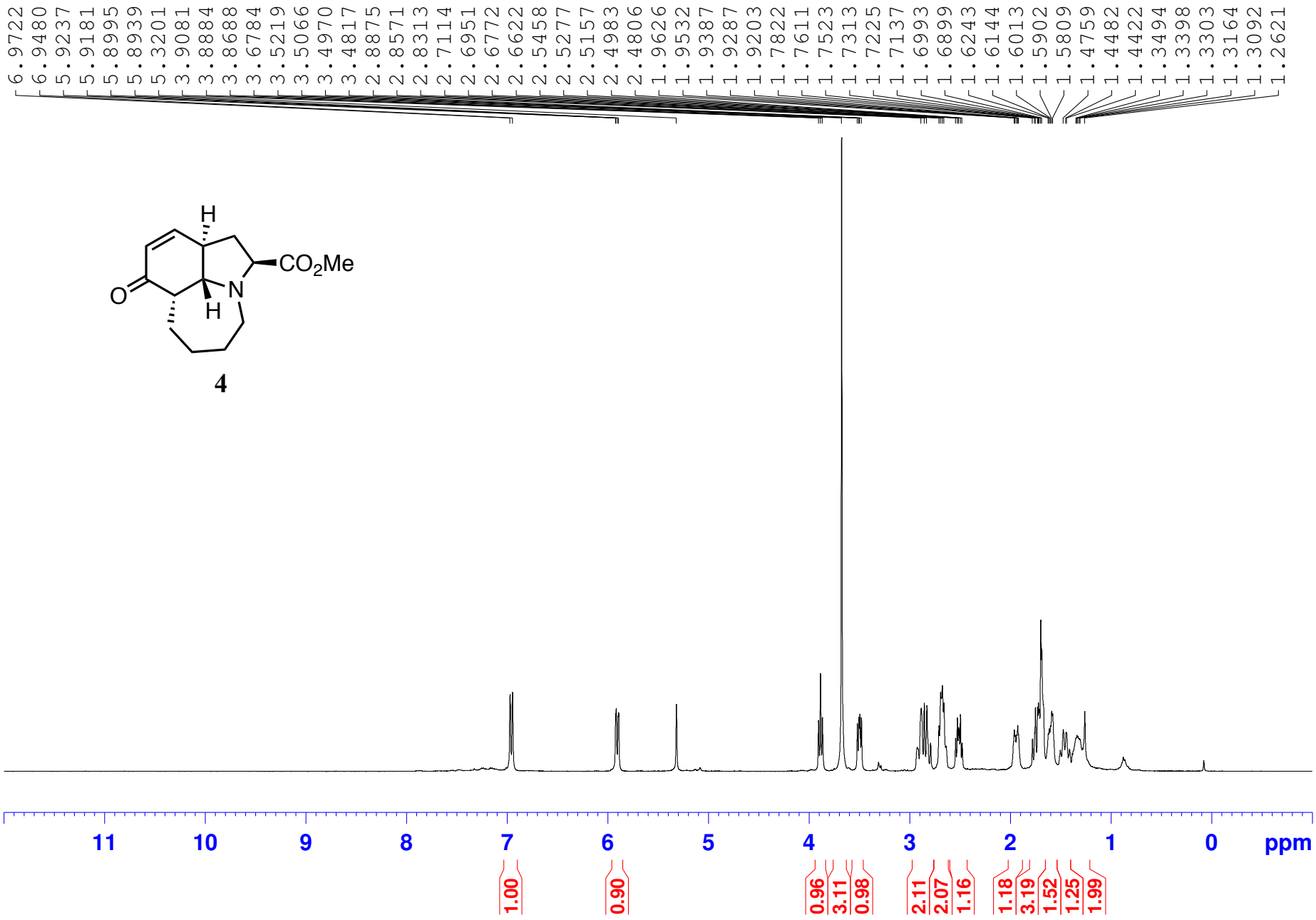
132.18
129.24
127.36
77.42
77.16
76.91
63.74
61.17
56.43
51.67
47.45
45.75
44.96
42.58
30.86
30.41
30.38
27.03
SPh
H
CO2Me
O
N
H
9a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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1.5809
1.4759
1.4482
1.4422
1.3494
1.3398
1.3303
1.3164
1.3092
1.2621
H
CO2Me
O
N
H
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.90
0.96
3.11
0.98
2.11
2.07
1.16
1.18
3.19
1.52
1.25
1.99

4