

Supporting Information

Metal-Free Ketoxygenation of Alkenes Using Hydroxamic Acids

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Table of Contents

General Methods	S1
Compound Preparation	S2-S16
¹H, ¹³C, and 2-D NMR Spectra	S17-S45

General Methods

Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Bruker model DRX 400, DRX 500, or a Bruker AVANCE III 600 CryoProbe (¹H NMR at 400 MHz, 500 MHz or 600 MHz and ¹³C NMR at 101, 126, or 151 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR: CDCl₃ at 7.26 ppm, CD₃OD at 3.35 ppm; ¹³C NMR: CDCl₃ at 77.0 ppm, CD₃OD at 49.2 ppm). ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, sxt = sextet, m = multiplet, br. s. = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a positive ion mode flow injection ESI (electrospray ionization) on a Bruker Daltonics, Inc., Billerica, MA, USA, BioToF Mass Spectrometer. Thin layer chromatography (TLC) was performed on SiliaPlate 250 μm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), aqueous basic potassium permanganate solution, or ethanolic acidic *p*-anisaldehyde solution followed by heating. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle. Tetrahydrofuran, diethyl ether, and dichloromethane were dried by passage through a column of neutral alumina under nitrogen prior to use. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. Compressed oxygen was purchased from Airgas, National Welders Supply Company.

Compound Preparation

Styrene, β -methylstyrene, *p*-methoxystyrene, *o*-bromostyrene were purchased from commercial sources, purified by distillation, deoxygenated via multiple freeze-pump-thaw cycles, and stored at -35 °C under an inert atmosphere prior to use. Norbornene was purified by sublimation and stored under an inert atmosphere.

Para-trifluoromethylstyrene^{1,2} and 2-vinylnaphthalene^{1,3} were prepared according to standard procedures. All physical and spectral data were in accordance with literature data.

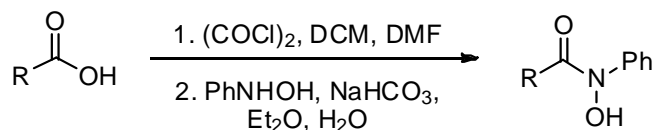
N-Phenylhydroxylamine was synthesized according to literature procedures.^{4,5} Physical and spectral data were in accordance with literature data.⁶

General Procedure for Preparation of *N*-Phenyl Hydroxamic Acids

Unsaturated hydroxamic acids **1**, **3**, **7**, **9**, **11**, and **15** were synthesized as previously described using either *Method A* or *B* as described below.^{5,7}

Note: All N-aryl hydroxamic acids should be purified promptly upon formation and stored neat at -40 °C.

*Method A*⁴



To a 0 °C solution of carboxylic acid (1 mmol) in DCM (1.4 mL) and DMF (10 drops) was added oxalyl chloride (2 mmol) dropwise under an argon atmosphere. The solution was stirred at 0 °C for 15 min., warmed to room temperature and stirred for 2 h. The resultant yellow solution was then evaporated almost to dryness under reduced pressure before sodium bicarbonate (2 mmol) was added and the mixture redissolved in H₂O/Et₂O (1 mL/2 mL). The solution was then cooled to 0 °C, *N*-phenylhydroxylamine (1 mmol) added, and the reaction stirred at 0 °C for 3.5 h. The layers were separated, the aqueous layer was acidified with 1 M NaHSO₄ and extracted with Et₂O (x 3). The combined organic layers were then washed with brine, dried (MgSO₄), and concentrated to give crude product that was purified by flash chromatography to yield the corresponding *N*-phenyl hydroxamic acid.

¹ Casalnuovo, A.L.; RajanBabu, T.V.; Ayers, T.A.; Warren, T.H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

² Lebel, H.; Davi, M.; Díez-González, S.; Nolan, S.P. *J. Org. Chem.* **2007**, *72*, 144.

³ Denmark, S.E.; Butler, C.R. *Org. Lett.* **2006**, *8*, 63.

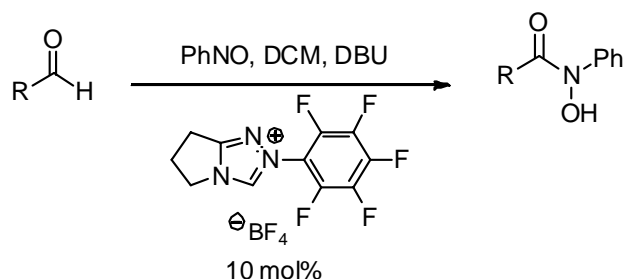
⁴ Evans, D.A.; Song, H.J.; Fandrick, K.R. *Org. Lett.*, **2006**, *8*, 3351.

⁵ Schmidt, V.A.; Alexanian, E.J. *Angew. Chem. Int. Ed.* **2010**, *49*, 4491.

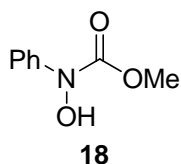
⁶ Corminboeuf, O.; Renaud, P. *Org. Lett.* **2002**, *4*, 1731.

⁷ Schmidt, V.A.; Alexanian, E.J. *J. Am. Chem. Soc.* **2011**, *133*, 11402-11405.

Method B⁸



To a solution of aldehyde (1 mmol), nitrosobenzene (1 mmol), and triazolium salt (0.10 mmol) in CH₂Cl₂ (4.5 mL) under Ar was added DBU (0.10 mmol). The solution color rapidly changed from green-blue to amber over 15 min. stirring at rt. Upon TLC visualization of consumption of aldehyde, solvent was removed under reduced pressure and the resultant oil was purified via flash chromatography to yield the corresponding *N*-phenyl hydroxamic acid. *Note: this procedure was not effective for the synthesis of α -disubstituted *N*-aryl hydroxamic acids.*



Synthesis of 18: To a 0 °C solution of methyl chloroformate (1.6 mL, 20.2 mmol, 1.1 equiv.) in Et₂O (40 mL) and a saturated aqueous solution of sodium bicarbonate (20 mL) was added *N*-phenylhydroxylamine (2.0 g, 18.3 mmol, 1.0 mmol). The solution was stirred at 0 °C for 3 h then warmed to room temperature. The layers were separated, the aqueous layer was acidified with 1 M NaHSO₄ and extracted with Et₂O (x 3). The combined organic layers were then washed with brine, dried (MgSO₄), and concentrated to give an oil that was purified by flash chromatography to give methyl *N*-hydroxy(phenyl)carbamate **18** (2.92 g, 17.5 mmol, 95% yield) as an off-white solid. All spectra were in accordance with literature data.⁹

⁸ Wong, F.T.; Patra, P.K.; Seayad, J.; Zhang, Y.; Ying, J.Y. *Org. Lett.* **2008**, *10*, 2333.

⁹ Santos, P.F.; Almeida, P.S.; Lobo, A.M.; Prabhakar, S. *Heterocycles* **2001**, *55*, 1029.

General Ketoxyamination Conditions

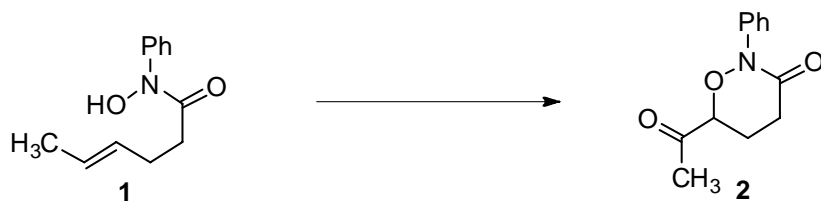
Caution! Aerobic reactions in organic solvents may produce potentially explosive peroxides. Alkylhydroperoxides are produced using the following conditions. While no problems were encountered in this work, alkylhydroperoxides are prone to rapid exothermic decomposition and appropriate care should be taken in their handling.

For Intramolecular Ketoxygenations

A new 1-dram vial containing a magnetic stir bar was charged with unsaturated hydroxamic acid (1.0 equiv.) and dissolved in *n*BuOAc to make a 0.1M solution. The vial was fitted with a PTFE-lined screw cap and O₂ was bubbled through the solution for 10 min. The reaction was allowed to stir under 1 atm O₂ at 60 °C. Upon disappearance of the hydroxamic acid substrate, as indicated by TLC analysis, the reaction mixture was cooled to rt and 4-(dimethylamino)pyridine (DMAP, 10 mol %) and acetic anhydride (Ac₂O, 1 equiv) were added under Ar. Upon completion of the elimination, as indicated by TLC analysis, the crude reaction mixture was diluted with EtOAc (10 mL), washed with H₂O (2 x 5 mL) then brine, dried (MgSO₄), and concentrated. The resulting cyclic hydroxamate was purified by flash chromatography using the specified solvent system.

For Intermolecular Ketoxygenations

A new 1-dram vial containing a magnetic stir bar was charged with **18** (50.0 mg, 0.299 mmol, 1.0 equiv), dilauroyl peroxide (DLP, 3.0 mg, 0.007 mmol, 2.5 mol %), alkene (0.359 mmol, 1.2 equiv.) and dissolved in *n*BuOAc (300 μL, 1.0M). The vial was fitted with a PTFE-lined screw cap and O₂ was bubbled through the solution for 5 minutes. The reaction was allowed to stir under 1 atm O₂ at 60 °C. Upon disappearance of **18**, as indicated by TLC analysis, the reaction mixture was cooled to rt, *n*BuOAc (300 μL; dilute by a factor of 2), 4-(dimethylamino)pyridine (DMAP, 3.7 mg, 0.030 mmol, 10 mol %) and acetic anhydride (Ac₂O, 28.2 μL, 0.299 mmol, 1 equiv) were added under Ar. Upon completion of the elimination, as indicated by TLC analysis, the crude reaction mixture was diluted with EtOAc (10 mL), washed with H₂O (2 x 5 mL) then brine, dried (MgSO₄), and concentrated. The resulting hydroxamate was purified by flash chromatography using the specified solvent system.



1 was synthesized via the procedure previously outlined using *Method B*.⁵

2 was prepared using **1** (60.0 mg, 0.292 mmol), DLP (11.7 mg, 0.029 mmol) in *n*BuOAc (2.70 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 24 h. The crude reaction mixture was cooled to rt, DMAP (3.6 mg, 0.029 mmol) and Ac₂O (27.6 μL, 0.292 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 3 h. The mixture was then worked up and purified by flash chromatography (25% EtOAc/hexanes) to afford **2** (50.9 mg, 0.233 mmol, 80% yield) as a clear residue.

Analytical data for **2**: ¹H NMR (CHLOROFORM-*d*, 400MHz): δ = 7.67 - 7.60 (m, 2 H), 7.44 - 7.36 (m, 2 H), 7.25 - 7.18 (m, 1 H), 4.63 (dd, *J* = 7.3, 9.3 Hz, 1 H), 2.77 - 2.62 (m, 2 H), 2.54 - 2.44 (m, 1 H), 2.44 - 2.32 (m, 1 H), 2.30 (s, 3 H); ¹³C NMR (CHLOROFORM-*d*, 101 MHz) 205.0, 171.1, 138.7, 128.8, 125.7, 119.7, 83.1, 29.9, 27.1, 23.5 ppm; IR (thin film, cm⁻¹) 3069, 3044, 2959, 2925, 2250, 1954, 1721, 1683, 1595, 1493, 1362, 1179, 1065, 756; LRMS (ESI) Calcd. for [C₁₂H₁₃NO₃+H]⁺ = 220.10, Found = 220.03.



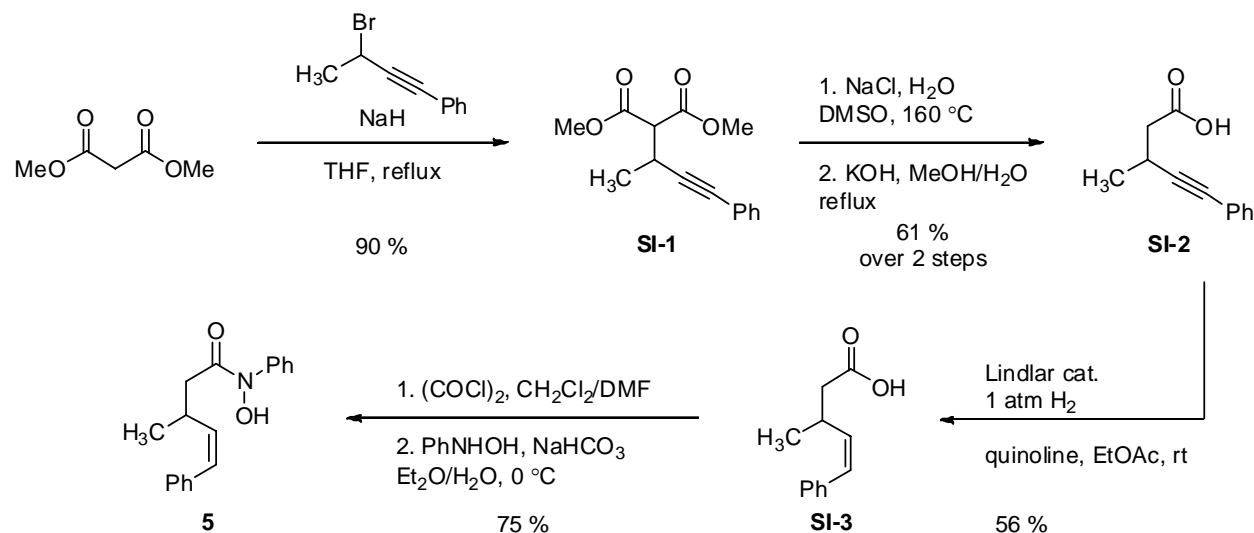
3 was synthesized via the procedure previously outlined using *Method B*.⁵

4 was prepared using **3** (60.0 mg, 0.224 mmol), DLP (8.0 mg, 0.022 mmol; a second portion was added after 24 h of heating) in *n*BuOAc (2.20 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 48 h. The crude reaction mixture was cooled to rt, DMAP (2.7 mg, 0.022 mmol) and Ac₂O (21.0 μL, 0.224 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 3 h. The mixture was then worked up and purified by flash chromatography (33% EtOAc/hexanes) to afford **4** (45.2 mg, 0.161 mmol, 72% yield) as a clear residue.

Analytical data for **4**: ¹H NMR (CHLOROFORM-*d*, 400MHz): δ = 8.02 - 7.89 (m, 2 H), 7.68 - 7.54 (m, 3 H), 7.53 - 7.44 (m, 2 H), 7.36 - 7.24 (m, 2 H), 7.20 - 7.06 (m, 1 H), 5.57 (dd, *J* = 6.6, 9.3 Hz, 1 H), 2.91 - 2.64 (m, 3 H), 2.55 - 2.41 (m, 1 H); ¹³C NMR (CHLOROFORM-*d*, 126 MHz) 194.2, 170.9, 138.7,

134.5, 134.0, 128.9, 128.8, 128.6, 125.5, 119.7, 79.4, 30.1, 23.9 ppm; **IR** (thin film, cm^{-1}) 3064, 2930, 2359, 2341, 1692, 1596, 1494, 1368, 755, 690; **LRMS** (ESI) Calcd. for $[\text{C}_{17}\text{H}_{15}\text{NO}_3+\text{Na}]^+$ = 304.10, Found = 304.10.

Synthesis of 5



SI-1 was prepared via dropwise addition of dimethylmalonate (1.64 mL, 14.3 mmol, 3.0 equiv) to a 0 °C suspension of NaH (210.0 mg of a 60 % dispersion in mineral oil, 5.26 mmol, 1.1 equiv). Stirring cold for 5 minutes was followed by dropwise addition of (3-bromobut-1-yn-yl)benzene (1.00 g, 4.78 mmol, 1.0 equiv). The reaction mixture was then heated to reflux for 10 h, cooled to rt and quenched with a saturated NH₄Cl (aq) solution. The mixture was extracted with Et₂O (4x), washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude alkylation product was then purified via flash chromatography (17.5% EtOAc/hexanes) to give **SI-1** (1.12 g, 4.30 mmol, 90% yield) as a colorless oil.

Analytical data for **SI-1**: **¹H NMR** (CHLOROFORM-*d*, 400MHz): δ = 7.44 - 7.35 (m, 2 H), 7.33 - 7.25 (m, 3 H), 3.80 (s, 6 H), 3.56 (d, J = 9.3 Hz, 1 H), 3.53 - 3.44 (m, 1 H), 1.38 (d, J = 6.8 Hz, 3 H); **¹³C NMR** (CHLOROFORM-*d*, 101 MHz) 168.0, 167.9, 131.6, 128.2, 128.0, 123.2, 89.9, 82.5, 57.6, 52.7, 52.6, 27.0, 19.0 ppm; **IR** (thin film, cm^{-1}) 3055, 3033, 2980, 2953, 2879, 2845, 1956, 1757, 1739, 1490, 1436, 1339, 1243, 1069, 1018, 759, 693; **LRMS** (ESI) Calcd. for $[\text{C}_{15}\text{H}_{16}\text{O}_4+\text{H}]^+$ = 261.12, Found = 261.07.

SI-2 was prepared using a 2 step, decarboxylation and hydrolysis route. A round-bottom flask was charged with **SI-1** (1.12 g, 4.30 mmol, 1.0 equiv), NaCl (251.0 mg, 4.30 mmol, 1.0 equiv), water (155.0

μL , 8.60 mmol, 2.0 equiv) and DMSO (30 mL). The reaction was observed to be complete after heating at 160 °C for 8 h. The crude mixture was cooled to rt, diluted with water (30 mL), extracted with CH_2Cl_2 (4x) then the combined organic layers were washed with brine, dried (MgSO_4) and concentrated under reduced pressure to give a yellow liquid. This crude ester (609.0 mg, 3.01 mmol, 1 equiv) was taken up into MeOH (9 mL) and water (5 mL) and KOH (372.0 mg, 6.62 mmol, 2.2 equiv) added. The mixture was heated to reflux for 2 h, cooled to rt then acidified to pH 1 using 6N HCl. The cloudy solution was then extracted with Et_2O (4x), the combined organic layers washed with brine, dried (MgSO_4) and concentrated under reduced pressure to give **SI-2** (492.0 mg, 2.61 mmol, 60 % yield over 2 steps) as a yellow oil that did not require further purification.

Analytical data for **SI-2**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 400MHz): δ = 10.66 (br. s., 1H), 7.44 - 7.39 (m, 2 H), 7.33 - 7.28 (m, 3 H), 3.21 (sxt, J = 7.0 Hz, 1 H), 2.75 (dd, J = 7.0, 16.1 Hz, 1 H), 2.58 (dd, J = 7.5, 15.6 Hz, 1 H), 1.38 (d, J = 7.0 Hz, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 101 MHz) 177.7, 131.6, 128.2, 127.8, 123.4, 92.1, 81.3, 41.4, 23.2, 20.8 ppm; **IR** (thin film, cm^{-1}) 3418, 2976, 2934, 1711, 1599, 1490, 1442, 1291, 1230, 915, 757, 691; **LRMS** (ESI) Calcd. for $[\text{C}_{12}\text{H}_{12}\text{O}_2+\text{H}]^+$ = 189.09, Found = 189.00.

Synthesis of **SI-3**

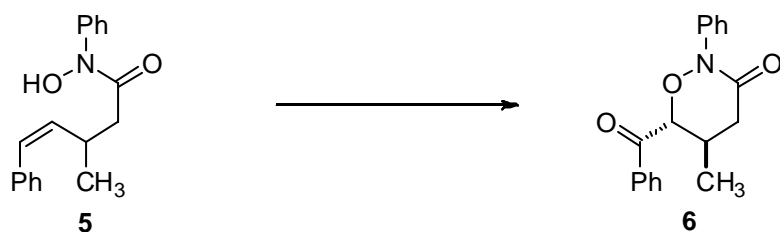
SI-2 (492.0 mg, 2.61 mmol, 1 equiv) was added to a flask containing Lindlar catalyst (5% Pd on CaCO_3 , 261 mg catalyst, 0.131 mmol Pd) and quinoline (772.0 μL , 6.53 mmol, 2.51 equiv) in EtOAc (60 mL). The flask was evacuated and refilled with H_2 four times, and then allowed to stir rt under 1 atm H_2 for 2 h. The reaction mixture was then filtered through Celite, washed with EtOAc, and concentrated. The crude residue was purified via flash chromatography (15% EtOAc/Hex) to give **SI-3** (277.0 mg, 1.46 mmol, 56 % yield) as a clear, colorless oil.

Analytical data for **SI-3**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 400MHz): δ = 11.66 - 9.30 (br. s., 1 H), 7.41 - 7.19 (m, 5 H), 6.45 (d, J = 11.5 Hz, 1 H), 5.52 (t, J = 10.9 Hz, 1 H), 3.41 - 3.27 (m, 1 H), 2.50 - 2.34 (m, 2 H), 1.20 - 1.14 (m, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 101 MHz) 178.4, 137.2, 136.1, 128.8, 128.6, 128.3, 126.8, 41.7, 29.4, 20.8 ppm; **IR** (thin film, cm^{-1}) 3056, 2966, 2929, 2874, 1947, 1882, 1708, 1494, 1446, 1412, 1291, 1072, 917, 798, 769, 699; **LRMS** (ESI) Calcd. for $[\text{C}_{12}\text{H}_{14}\text{O}_2+\text{Na}]^+$ = 213.09, Found = 213.17.

5 was synthesized via *Method A* using **SI-3** in 75% yield (146.7 mg) as an off-white solid.

Analytical data for **5**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 500MHz): δ = 9.05 (br. s., 1 H), 7.41 (br. s., 3 H), 7.38 - 7.22 (m, 7 H), 6.39 (d, J = 11.3 Hz, 1 H), 5.42 - 5.29 (m, 1 H), 3.33 (m, 1 H), 2.38 (br. s., 2 H), 1.07 (d, J = 5.0 Hz, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 126 MHz) 166.9, 138.3, 137.1, 136.3, 136.2, 129.2, 128.5, 128.4, 128.2, 127.0, 126.7, 126.0, 39.4, 29.8, 20.7 ppm; **IR** (thin film, cm^{-1}) 3398, 2964,

2928, 2959, 1953, 1637, 1494, 1393, 1069, 916; **LRMS** (ESI) Calcd. for $[C_{18}H_{19}NO_2+H]^+$ = 282.15, Found = 282.17.

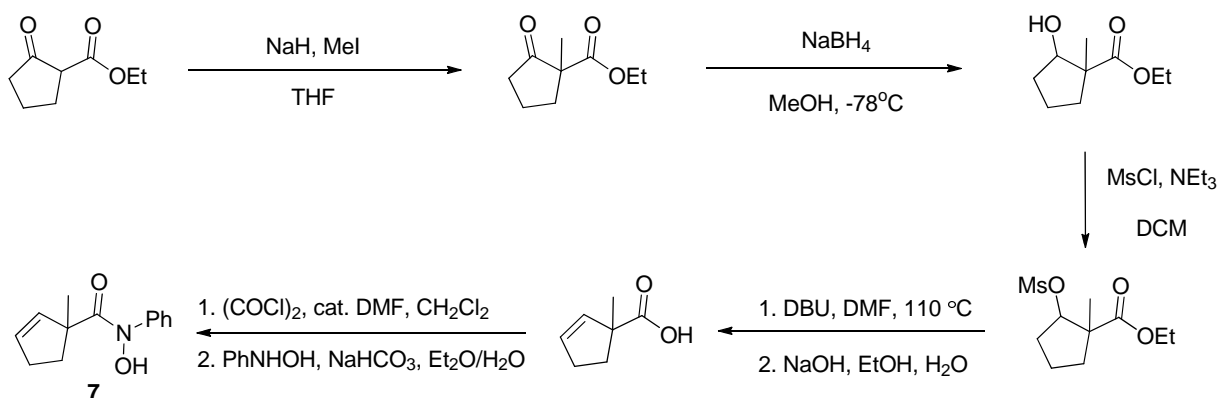


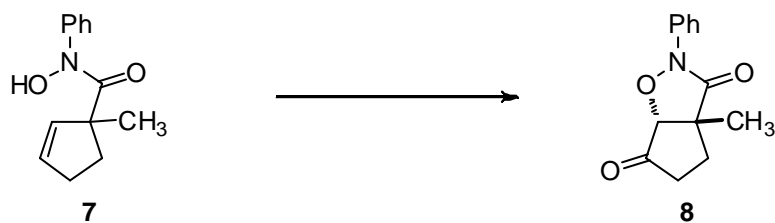
6 was prepared using **5** (75.1 mg, 0.267 mmol) in *n*BuOAc (2.50 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 9 h. The crude reaction mixture was cooled to rt, DMAP (3.3 mg, 0.027 mmol) and Ac₂O (25.2 μL, 0.267 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 3 h. The mixture was then worked up and purified by flash chromatography (33% EtOAc/hexanes) to afford **6** (56.8 mg, 0.192 mmol, 72% yield) as a clear residue.

Analytical data for **6**: **¹H NMR** (CHLOROFORM-*d*, 400MHz): δ = 8.01 - 7.94 (m, 2 H), 7.66 - 7.59 (m, 1 H), 7.52 - 7.45 (m, 4 H), 7.28 - 7.22 (m, 2 H), 7.15 - 7.08 (m, 1 H), 5.06 (d, *J* = 6.5 Hz, 1 H), 3.13 (td, *J* = 6.7, 13.4 Hz, 1 H), 2.93 (dd, *J* = 6.1, 14.7 Hz, 1 H), 2.56 (dd, *J* = 7.0, 14.6 Hz, 1 H), 1.28 (d, *J* = 7.0 Hz, 4 H); **¹³C NMR** (CHLOROFORM-*d*, 151 MHz) 194.5, 170.5, 138.5, 135.1, 134.0, 129.1, 128.8, 128.6, 125.4, 119.7, 85.8, 38.2, 30.1, 19.9 ppm; **IR** (thin film, cm⁻¹) 3064, 2966, 2931, 2874, 1682, 1596, 1494, 1449, 1361, 1304, 754, 689; **LRMS** (ESI) Calcd. for $[C_{18}H_{17}NO_3+H]^+$ = 296.13, Found = 296.12.

Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.

Synthesis of **7**, and general route to **9**, **11**, and **13**



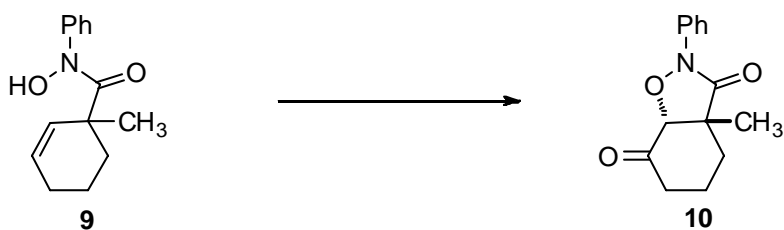


The corresponding carboxylic acid of **7** was synthesized according the procedure developed by S. Pichlmair *et. al.*¹⁰ outlined above and **7** using *Method A*.⁵

8 was prepared using **7** (60.0 mg, 0.276 mmol) in *n*BuOAc (2.50 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 8 h. The crude reaction mixture was cooled to rt, DMAP (3.4 mg, 0.028 mmol) and Ac₂O (26.0 μL, 0.276 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 10 h. The mixture was then worked up and purified by flash chromatography (33% EtOAc/hexanes) to afford **8** (51.9 mg, 0.224 mmol, 81% yield) as a clear residue.

Analytical data for **8**: ¹H NMR (CHLOROFORM-*d*, 600MHz): δ = 7.75 - 7.70 (m, 2 H), 7.42 - 7.36 (m, 2 H), 7.22 - 7.16 (m, 1 H), 4.37 (s, 1 H), 2.67 (ddd, *J* = 2.8, 10.2, 13.4 Hz, 1 H), 2.58 - 2.50 (m, 1 H), 2.41 - 2.31 (m, 1 H), 2.02 - 1.93 (m, 1 H), 1.60 (s, 3 H); ¹³C NMR (CHLOROFORM-*d*, 151 MHz) 213.5, 168.3, 136.3, 128.9, 125.6, 117.2, 84.6, 51.7, 36.1, 29.0, 20.3 ppm; IR (thin film, cm⁻¹) 3068, 2969, 2934, 2873, 1758, 1695, 1594, 1496, 1381, 994, 755, 689; LRMS (ESI) Calcd. for [C₁₃H₁₃NO₃+Na]⁺ = 254.08, Found = 254.07.

Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.



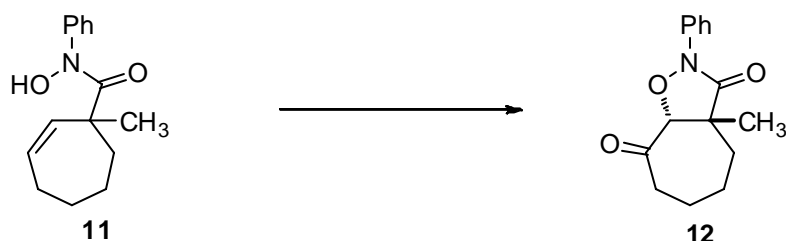
The corresponding carboxylic acid of **9** was synthesized via the same route as 1-methylcyclohex-2-enecarboxylic acid (see above), beginning with the cyclohexane analog.⁷

10 was prepared using **9** (60.0 mg, 0.259 mmol) in *n*BuOAc (2.50 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 6 h. The crude reaction mixture was cooled to rt, DMAP (3.2 mg, 0.026 mmol) and Ac₂O (24.5 μL, 0.259 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 2 h. The mixture was then worked up and purified by flash chromatography (33% EtOAc/hexanes) to afford **10** (55.7 mg, 0.227 mmol, 88% yield) as a white solid.

¹⁰ Pichlmair, S.; de Lera Ruiz, M.; Basu, K.; Paquette, L.A. *Tetrahedron* **2006**, *62*, 5178.

Analytical data for **10**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 400MHz): δ = 7.87 - 7.75 (m, 2 H), 7.46 - 7.35 (m, 2 H), 7.25 - 7.14 (m, 1 H), 4.51 - 4.45 (m, 1 H), 2.68 - 2.57 (m, 1 H), 2.45 - 2.31 (m, 2 H), 2.08 - 1.97 (m, 1 H), 1.81 - 1.70 (m, 2 H), 1.56 - 1.49 (m, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 101 MHz) 204.9, 168.1, 136.6, 128.8, 125.4, 117.4, 86.7, 52.1, 40.1, 31.1, 22.7, 22.2 ppm; **IR** (thin film, cm^{-1}) 2970, 2933, 2871, 1703, 1682, 1647, 1496, 1458, 1363, 999, 755; **LRMS** (ESI) Calcd. for $[\text{C}_{14}\text{H}_{15}\text{NO}_3+\text{Na}]^+$ = 268.10, Found = 268.04.

Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.



The corresponding carboxylic acid of **11** was synthesized via the same route as 1-methylcyclopent-2-enecarboxylic acid (see above), beginning with the cycloheptane analog.⁷

12 was prepared using **11** (60.0 mg, 0.245 mmol) in *n*BuOAc (2.00 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 2 h. The crude reaction mixture was cooled to rt, DMAP (3.0 mg, 0.025 mmol) and Ac_2O (23.0 μL , 0.245 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 3 h. The mixture was then worked up and purified by flash chromatography (25% EtOAc/hexanes) to afford **12** (47.6 mg, 0.184 mmol, 75% yield) as a clear residue.

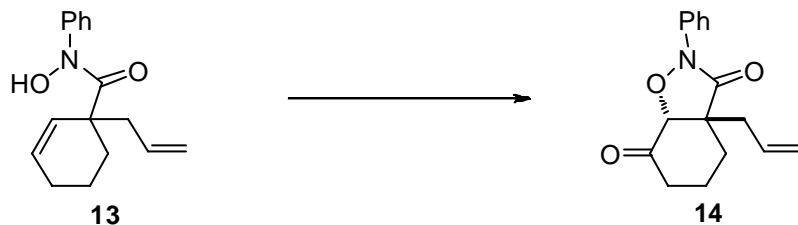
Analytical data for **12**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 400MHz): δ = 7.80 (d, J = 8.0 Hz, 2 H), 7.43 (t, J = 7.3 Hz, 2 H), 7.26 - 7.17 (m, 1 H), 4.83 (s, 1 H), 3.02 - 2.90 (m, 1 H), 2.55 - 2.45 (m, 1 H), 2.15 - 2.04 (m, 1 H), 2.02 - 1.92 (m, 1 H), 1.91 - 1.81 (m, 1 H), 1.71 - 1.52 (m, 3 H), 1.47 (s, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 101 MHz) 206.4, 168.8, 136.3, 128.9, 125.3, 117.1, 90.2, 48.4, 39.1, 35.8, 25.6, 23.0, 22.7 ppm; **IR** (thin film, cm^{-1}) 2935, 2867, 1702, 1595, 1496, 1385, 1012, 754, 690; **LRMS** (ESI) Calcd. for $[\text{C}_{15}\text{H}_{17}\text{NO}_3+\text{Na}]^+$ = 282.11, Found = 282.09.

Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.

The corresponding carboxylic acid of **13** was synthesized via the same route as 1-methylcyclopent-2-enecarboxylic acid (see above), beginning with the cyclohexane analog and alkylating with allyl bromide instead of iodomethane. **13** was synthesized via *Method A* in 76% yield (588.0 mg) as an off-white solid.

Analytical data for **13**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 500MHz): δ = 9.07 (br. s., 1 H), 7.50 - 7.29 (m, 5 H), 5.89 - 5.66 (m, 1 H), 5.45 - 5.28 (m, 1 H), 5.26 - 4.99 (m, 3 H), 2.51 (br. s., 1 H), 2.42 - 2.18 (m, 2 H), 1.85 (br. s., 2 H), 1.72 - 1.48 (m, 2 H), 1.36 (br. s., 1 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 126 MHz) 172.0,

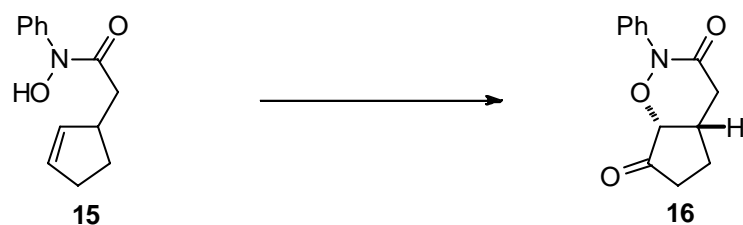
139.8, 133.7, 129.2, 128.7, 128.2, 118.2, 46.9, 44.4, 32.7, 24.7, 19.4 ppm; **IR** (thin film, cm^{-1}) 3412, 3036, 2936, 2870, 2834, 1621, 1591, 1490, 1452, 1362, 955, 914; **LRMS** (ESI) Calcd. for $[\text{C}_{16}\text{H}_{19}\text{NO}_2+\text{H}]^+ = 258.15$, Found = 258.16.



14 was prepared using **13** (43.2 mg, 0.168 mmol) in *n*BuOAc (1.70 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 4 h. The crude reaction mixture was cooled to rt, DMAP (2.1 mg, 0.017 mmol) and Ac_2O (15.9 μL , 0.168 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 3 h. The mixture was then worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **14** (38.2 mg, 0.141 mmol, 84% yield) as a clear residue.

Analytical data for **14**: **^1H NMR** (CHLOROFORM-*d*, 500MHz): $\delta = 7.84 - 7.75$ (m, 2 H), 7.44 - 7.37 (m, 2 H), 7.23 - 7.16 (m, 1 H), 5.91 (tdd, $J = 7.5, 9.9, 17.0$ Hz, 1 H), 5.31 - 5.22 (m, 2 H), 4.62 (s, 1 H), 2.65 - 2.53 (m, 3 H), 2.39 - 2.28 (m, 2 H), 2.10 - 2.00 (m, 1 H), 1.89 - 1.78 (m, 1 H), 1.78 - 1.65 (m, 1 H); **^{13}C NMR** (CHLOROFORM-*d*, 126 MHz) 205.3, 167.1, 136.5, 131.6, 128.8, 125.5, 120.8, 117.5, 84.1, 55.5, 40.1, 40.0, 28.6, 21.8 ppm; **IR** (thin film, cm^{-1}) 3077, 2928, 2871, 1731, 1698, 1594, 1496, 1371, 1309, 1003, 754, 689; **LRMS** (ESI) Calcd. for $[\text{C}_{16}\text{H}_{17}\text{NO}_3+\text{Na}]^+ = 294.11$, Found = 294.10.

Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.

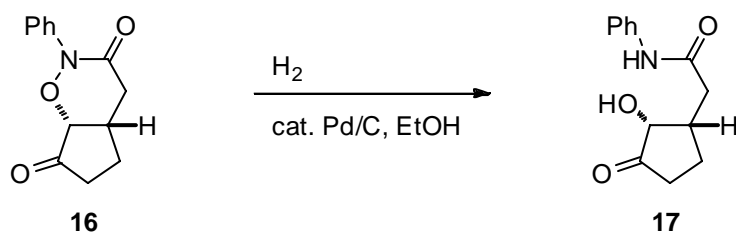


15 was prepared as previously reported using *Method A*.⁵

16 was prepared using **15** (300.0 mg, 1.38 mmol), DLP (55.0 mg, 0.138 mmol) in *n*BuOAc (13.0 mL). The dioxygenation reaction was completed, as indicated by TLC, after heating at 60 °C for 7 h. The crude reaction mixture was cooled to rt, DMAP (16.8 mg, 0.138 mmol) and Ac_2O (130.0 μL , 1.38 mmol) were added, and the mixture stirred at rt under an Ar atmosphere for 3 h. The mixture was then worked up and purified by flash chromatography (33% EtOAc/hexanes) to afford **16** (267.2 mg, 1.16 mmol, 84% yield) as a white solid.

Analytical data for **16**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 600MHz): δ = 7.80 - 7.67 (m, 2 H), 7.38 (t, J = 7.9 Hz, 2 H), 7.19 (t, J = 7.3 Hz, 1 H), 4.59 (d, J = 9.4 Hz, 1 H), 3.27 - 3.14 (m, 1 H), 2.92 (dd, J = 6.0, 14.7 Hz, 1 H), 2.67 (dd, J = 5.8, 14.5 Hz, 1 H), 2.48 - 2.40 (m, 2 H), 2.39 - 2.32 (m, 1 H), 1.91 - 1.80 (m, 1 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 101 MHz) 212.0, 170.2, 138.7, 128.7, 125.7, 119.4, 81.4, 36.7, 36.4, 34.4, 25.9 ppm; **IR** (thin film, cm^{-1}) 3066, 2970, 1754, 1688, 1594, 1493, 1365, 757, 690; **LRMS** (ESI) Calcd. for $[\text{C}_{13}\text{H}_{13}\text{NO}_3+\text{Na}]^+$ = 254.08, Found = 254.06.

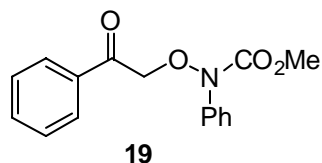
Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.



17 was prepared by charging a flask with **16** (75.0 mg, 0.324 mmol), 10 % Pd on carbon (20.0 mg) in EtOH (13 mL). The flask was evacuated and refilled with H_2 four times, and then allowed to stir rt under 1 atm H_2 for 1.5 h. The reaction mixture was then filtered through Celite and concentrated. The residue was taken up in CH_2Cl_2 , dried (MgSO_4) and concentrated to give **17** in quantitative yield (75.3 mg) as a white solid.

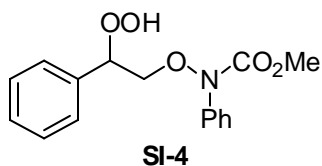
Analytical data for **17**: $^1\text{H NMR}$ (METHANOL-*d*₄, 600MHz): δ = 7.60 - 7.52 (m, 2 H), 7.36 - 7.27 (m, 2 H), 7.12 - 7.09 (m, 1 H), 5.52 (s, 1 H), 4.26 (d, J = 7.2 Hz, 1 H), 2.91 (tdd, J = 3.1, 6.6, 9.7 Hz, 1 H), 2.64 (dd, J = 5.5, 14.9 Hz, 1 H), 2.34 - 2.24 (m, 2 H), 2.18 (dd, J = 9.4, 14.7 Hz, 1 H), 2.14 - 2.06 (m, 1 H), 1.92 (m, 1 H); $^{13}\text{C NMR}$ (METHANOL-*d*₄, 101 MHz) 217.6, 172.0, 138.4, 128.4, 123.8, 119.9, 76.2, 37.5, 34.4, 31.7, 21.7 ppm; **IR** (thin film, cm^{-1}) 3434, 2524, 2089, 1645, 1498, 1443, 1119; **LRMS** (ESI) Calcd. for $[\text{C}_{13}\text{H}_{15}\text{NO}_3+\text{H}]^+$ = 234.12, Found = 234.10.

This reduction was also attempted using our previously reported N-O bond cleavage conditions of cyclic hydroxamates.^{5,7} Zn/Acetic acid and Raney Nickel reductions resulted in various undesired byproducts, presumably involving over reduction.



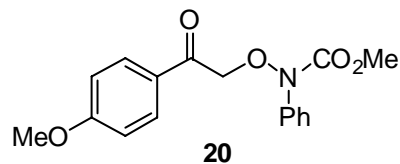
19 was prepared using styrene (49.4 μL , 0.431 mmol), under the standard conditions using **18** (60.0 mg, 0.359 mmol), DLP (14.3 mg, 0.036 mmol, 10 mol %) in EtOAc (360 μL ; optimization proved that for this substrate only, EtOAc was a more efficient solvent than *n*BuOAc). **18** was consumed, as indicated by TLC, after heating at 60 $^{\circ}\text{C}$ for 12 h, and the elimination was complete after 3 h at rt. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **19** (90.2 mg, 0.316 mmol, 88% yield) as a white solid.

Analytical data for **19**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 400MHz): δ = 8.02 - 7.89 (m, 2 H), 7.66 - 7.57 (m, 1 H), 7.55 - 7.43 (m, 4 H), 7.42 - 7.34 (m, 2 H), 7.28 - 7.20 (m, 1 H), 5.21 (s, 2 H), 3.85 (s, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 101 MHz) 193.2, 155.2, 139.6, 134.5, 133.7, 128.7, 18.6, 128.1, 126.4, 122.7, 76.9, 53.5 ppm; **IR** (thin film, cm^{-1}) 2955, 2852, 1730, 1701, 1647, 1598, 1494, 1440, 1348, 1231, 970; **LRMS** (ESI) Calcd. for $[\text{C}_{16}\text{H}_{15}\text{NO}_4+\text{Na}]^+$ = 308.09, Found = 308.09.



SI-4 was prepared as above but isolated prior to the dehydration step to support the intermediacy of alkyl hydroperoxides in an intermolecular context.

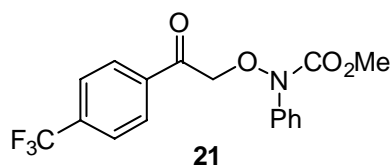
Analytical data for **SI-4**: $^1\text{H NMR}$ (CHLOROFORM-*d*, 500MHz): δ = 9.90 (br. s., 1 H), 7.47 - 7.33 (m, 9 H), 7.31 - 7.24 (m, 1 H), 5.28 (t, J = 5.7 Hz, 1 H), 4.32 (d, J = 5.4 Hz, 2 H), 3.88 (s, 3 H); $^{13}\text{C NMR}$ (CHLOROFORM-*d*, 126 MHz) 155.7, 139.5, 136.0, 128.9, 128.8, 128.7, 127.2, 126.8, 123.1, 84.5, 76.7, 53.9 ppm; **IR** (thin film, cm^{-1}) 3419, 2957, 2089, 1645, 1494, 1441, 1348, 751; **LRMS** (ESI) Calcd. for $[\text{C}_{16}\text{H}_{17}\text{NO}_5+\text{Na}]^+$ = 326.10, Found = 326.10.



20 was prepared using *p*-methoxystyrene (48.2 mg, 0.359 mmol), under the standard conditions. **18** was consumed, as indicated by TLC, after heating at 60 $^{\circ}\text{C}$ for 48 h, and the elimination was complete after 3

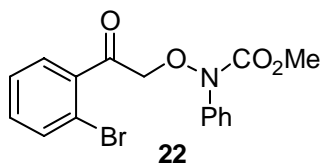
h at rt. The crude reaction mixture was worked up and purified by flash chromatography (2:1:1 Hexanes:CH₂Cl₂:Et₂O) to afford **20** (73.0 mg, 0.231 mmol, 77% yield) as a pale yellow solid.

Analytical data for **20**: ¹H NMR (CHLOROFORM-*d*, 400MHz): δ = 8.01 - 7.92 (m, 2 H), 7.53 - 7.45 (m, 2 H), 7.42 - 7.34 (m, 2 H), 7.27 - 7.19 (m, 1 H), 6.99 - 6.92 (m, 2 H), 5.14 (s, 2 H), 3.89 (s, 3 H), 3.85 (s, 3 H); ¹³C NMR (CHLOROFORM-*d*, 101 MHz) 191.8, 164.0, 155.3, 139.7, 130.7, 128.8, 127.8, 126.5, 122.8, 113.9, 76.9, 55.5, 53.6 ppm; IR (thin film, cm⁻¹) 3067, 3009, 2955, 2843, 2252, 2044, 1953, 1714, 1683, 1602, 1513, 1494, 1440, 1346, 1242, 1174, 1026, 973, 835, 694; LRMS (ESI) Calcd. for [C₁₇H₁₇NO₅+Na]⁺ = 338.10, Found = 338.08.



21 was prepared using *p*-trifluoromethylstyrene (61.8 mg, 0.359 mmol), under the standard conditions. **18** was consumed, as indicated by TLC, after heating at 60 °C for 48 h, and the elimination was complete after 3 h at rt. The crude reaction mixture was worked up and purified by flash chromatography (15% EtOAc/10% CH₂Cl₂ in hexanes) to afford **21** (76.0 mg, 0.215 mmol, 72% yield) as a white solid.

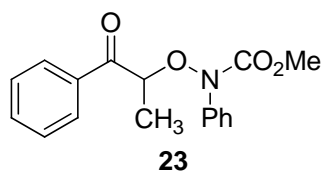
Analytical data for **21**: ¹H NMR (CHLOROFORM-*d*, 400MHz): δ = 8.08 (d, *J* = 8.3 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.46 - 7.40 (m, 2 H), 7.39 - 7.31 (m, 2 H), 7.28 - 7.21 (m, 1 H), 5.18 (s, 2 H), 3.83 (s, 3 H); ¹³C NMR (CHLOROFORM-*d*, 101 MHz) 193.0, 155.4, 139.6, 137.4, 135.1, 134.7, 128.8, 127.0, 125.8, 125.7, 125.6, 124.8, 123.3, 122.1, 77.3, 53.7 ppm; IR (thin film, cm⁻¹) 3071, 2958, 2927, 2854, 1946, 1731, 1712, 1442, 1327, 1171, 1066, 846, 753; LRMS (ESI) Calcd. for [C₁₇H₁₄F₃NO₄+Na]⁺ = 376.08, Found = 376.00.



22 was prepared using *o*-bromostyrene (65.7 mg, 0.359 mmol) under the standard conditions. **18** was consumed, as indicated by TLC, after heating at 60 °C for 18 h, and the elimination was complete after 3 h at rt. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **22** (82.3 mg, 0.226 mmol, 76% yield) as a waxy white solid.

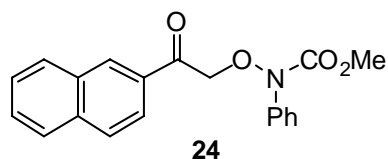
Analytical data for **22**: ¹H NMR (CHLOROFORM-*d*, 400MHz): δ = 7.63 - 7.28 (m, 8 H), 7.27 - 7.19 (m, 1 H), 5.10 (s, 2 H), 3.82 (s, 3 H); ¹³C NMR (CHLOROFORM-*d*, 101 MHz) 197.7, 155.5, 139.8, 138.3,

133.8, 132.5, 129.7, 128.7, 127.4, 126.7, 123.0, 119.5, 78.5, 53.7 ppm; **IR** (thin film, cm^{-1}) 3065, 2955, 2910, 2359, 1945, 1730, 1588, 1494, 1439, 1347, 1258, 1104, 1027, 757, 693; **LRMS** (ESI) Calcd. for $[\text{C}_{16}\text{H}_{14}\text{BrNO}_4+\text{Na}]^+$ = 386.00, Found = 385.99.



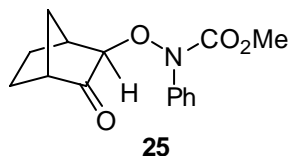
23 was prepared using *trans*- β -methylstyrene (46.6 μL , 0.359 mmol) under the standard conditions. **18** was consumed, as indicated by TLC, after heating at 60 $^{\circ}\text{C}$ for 20 h, and the elimination was complete after 3 h at rt. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **23** (84.3 mg, 0.287 mmol, 94% yield) as a pale yellow solid.

Analytical data for **23**: **^1H NMR** (CHLOROFORM-*d*, 400MHz): δ = 8.04 - 7.91 (m, 2 H), 7.62 - 7.54 (m, 1 H), 7.49 - 7.41 (m, 2 H), 7.40 - 7.30 (m, 4 H), 7.27 - 7.15 (m, 1 H), 5.44 (q, J = 6.8 Hz, 1 H), 3.77 (s, 3 H), 1.58 (d, J = 6.8 Hz, 3 H); **^{13}C NMR** (CHLOROFORM-*d*, 101 MHz) 197.3, 156.3, 141.0, 135.0, 133.5, 129.0, 128.6, 126.8, 123.9, 82.2, 53.6, 16.8 ppm; **IR** (thin film, cm^{-1}) 3064, 2990, 2954, 2853, 1966, 1731, 1693, 1597, 1493, 1440, 1337, 1103, 965, 759; **LRMS** (ESI) Calcd. for $[\text{C}_{17}\text{H}_{17}\text{NO}_4+\text{Na}]^+$ = 322.11, Found = 322.08.



24 was prepared using 2-vinylnaphthalene (55.4 mg, 0.359 mmol) under the standard conditions. **18** was consumed, as indicated by TLC, after heating at 60 $^{\circ}\text{C}$ for 36 h, and the elimination was complete after 3 h at rt. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **24** (82.1 mg, 0.245 mmol, 82% yield) as a pale yellow solid.

Analytical data for **24**: **^1H NMR** (CHLOROFORM-*d*, 600MHz): δ = 8.51 (s, 1 H), 8.00 (dd, J = 1.5, 8.7 Hz, 1 H), 7.96 (d, J = 8.3 Hz, 1 H), 7.93 - 7.88 (m, 2 H), 7.65 (dt, J = 1.3, 7.4 Hz, 1 H), 7.61 - 7.57 (m, 1 H), 7.54 - 7.49 (m, 2 H), 7.41 - 7.36 (m, 2 H), 7.27 - 7.22 (m, 1 H), 5.34 (s, 2 H), 3.87 (s, 3 H); **^{13}C NMR** (CHLOROFORM-*d*, 151 MHz) 193.3, 155.4, 139.7, 135.9, 132.4, 130.4, 129.7, 128.9, 128.8, 128.7, 127.9, 127.0, 126.6, 123.5, 122.9, 77.1, 53.7 ppm; **IR** (thin film, cm^{-1}) 3060, 2955, 2023, 2851, 1731, 1696, 1627, 1596, 1494, 1439, 1348, 1191, 822, 750, 693; **LRMS** (ESI) Calcd. for $[\text{C}_{20}\text{H}_{17}\text{NO}_4+\text{Na}]^+$ = 358.11, Found = 358.12.

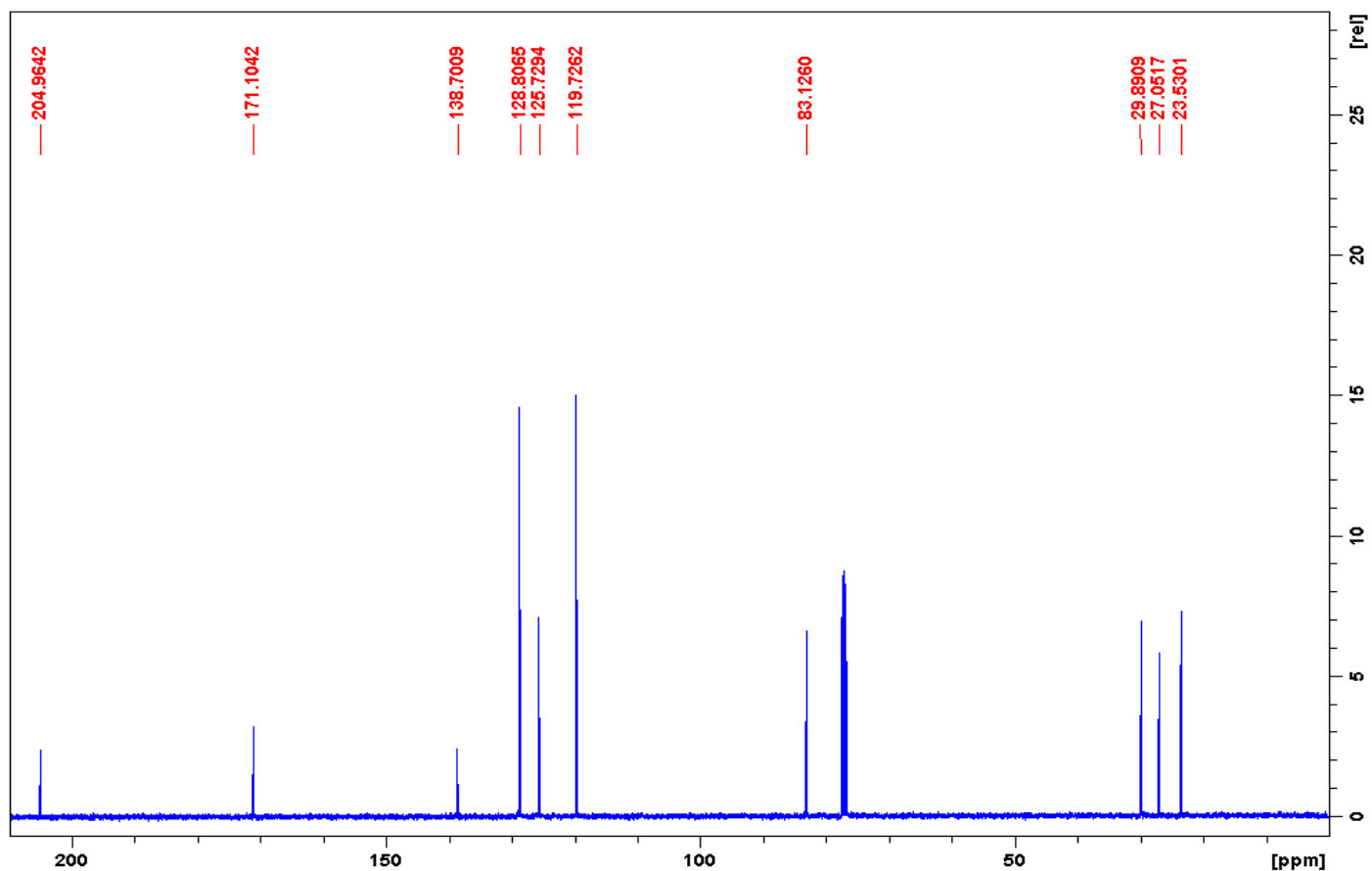
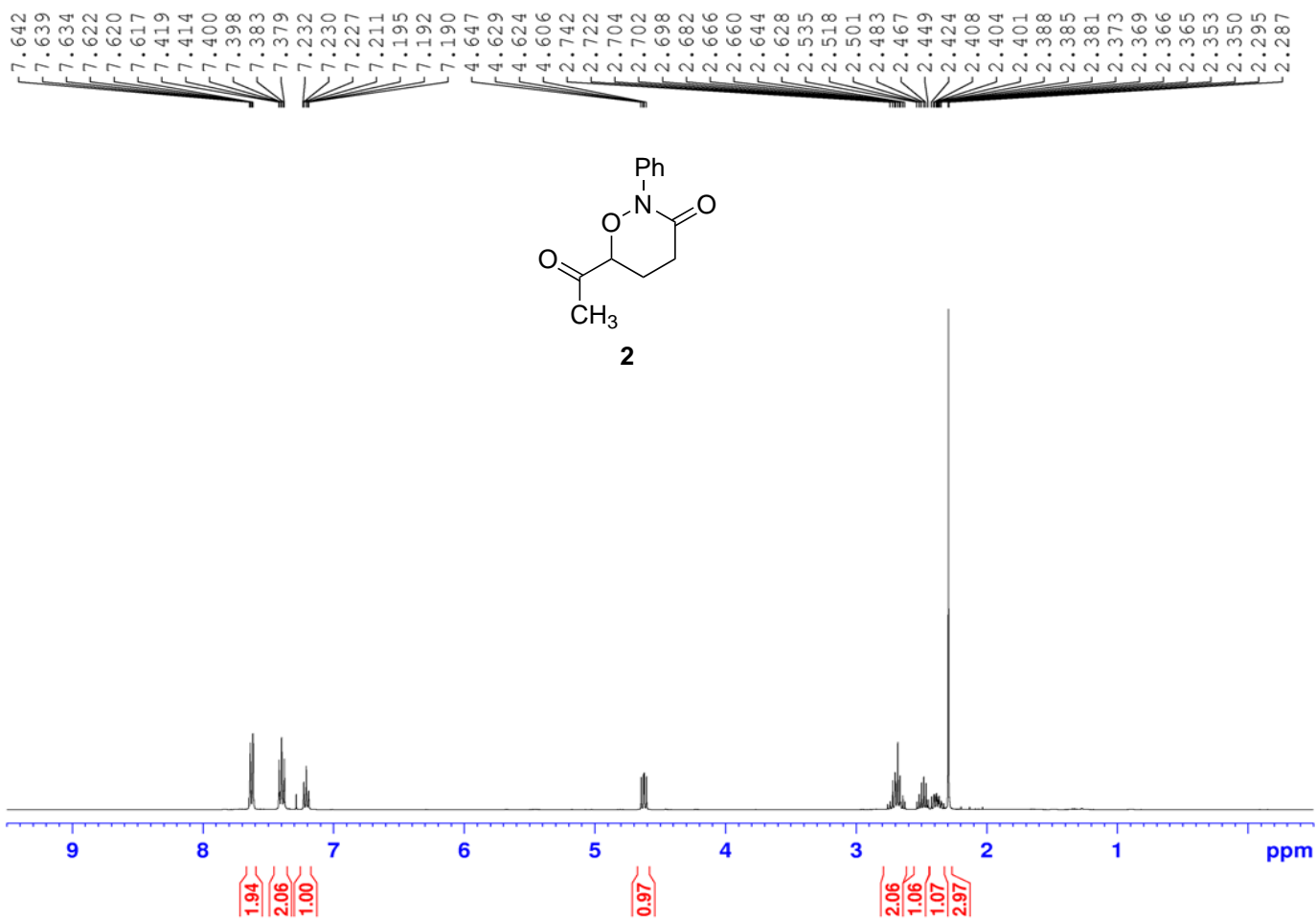


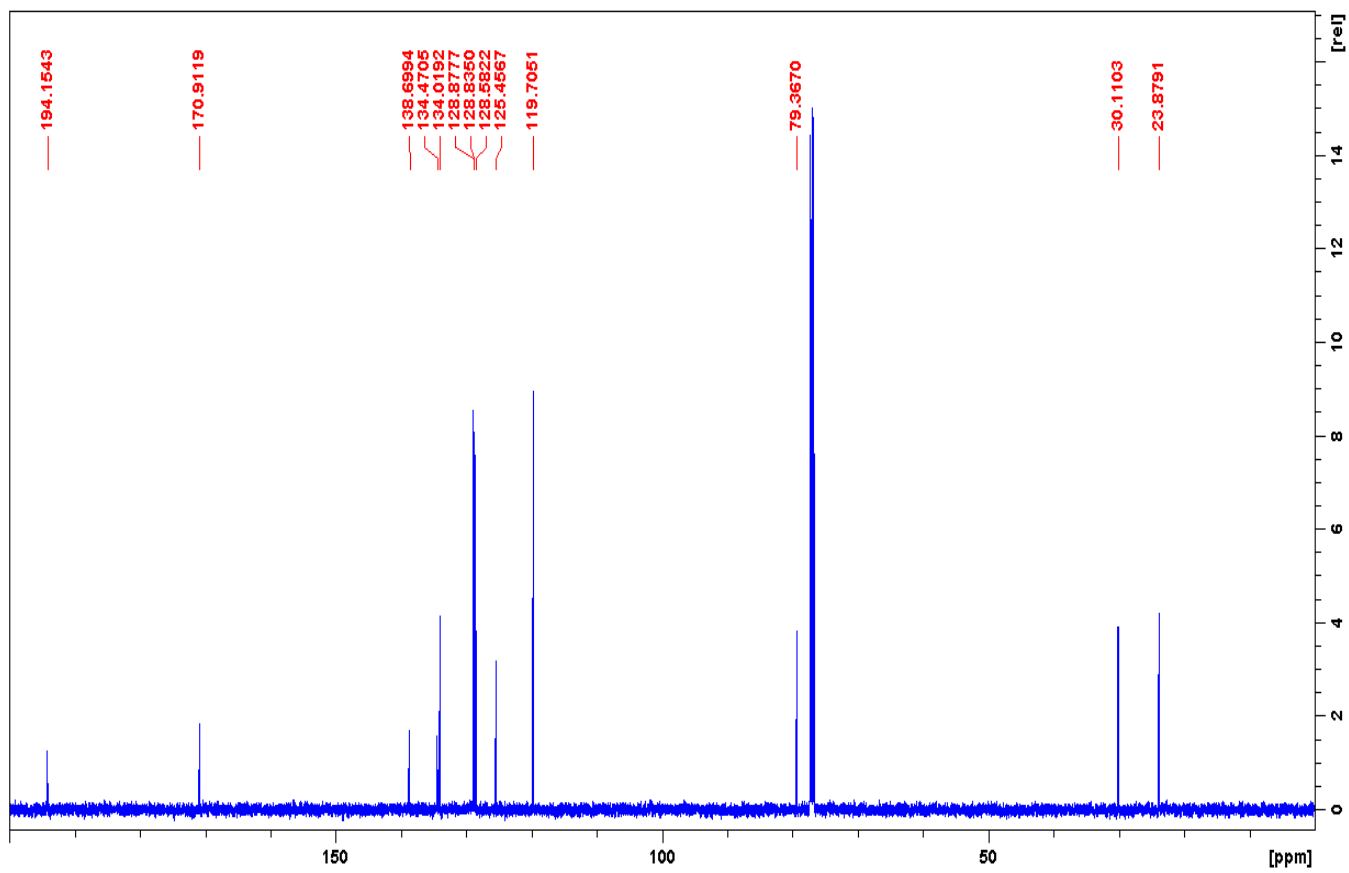
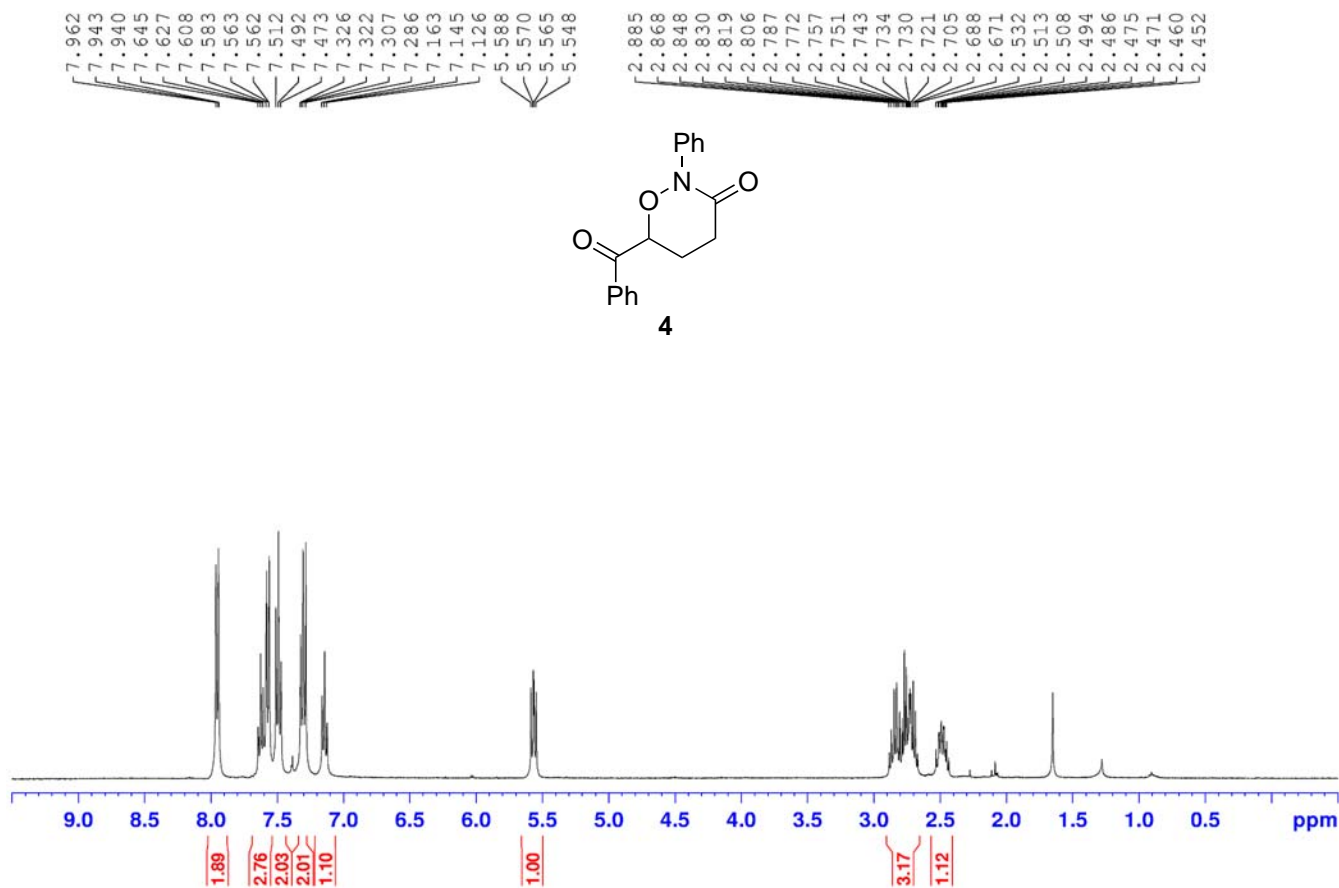
25 was prepared using norbornene (141.0 mg, 1.50 mmol, 5.0 equiv) under the standard conditions. **18** was consumed, as indicated by TLC, after heating at 60 °C for 40 h, and the elimination was complete after 3 h at rt. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **25** (63.1 mg, 0.229 mmol, 77% yield) as a waxy white solid.

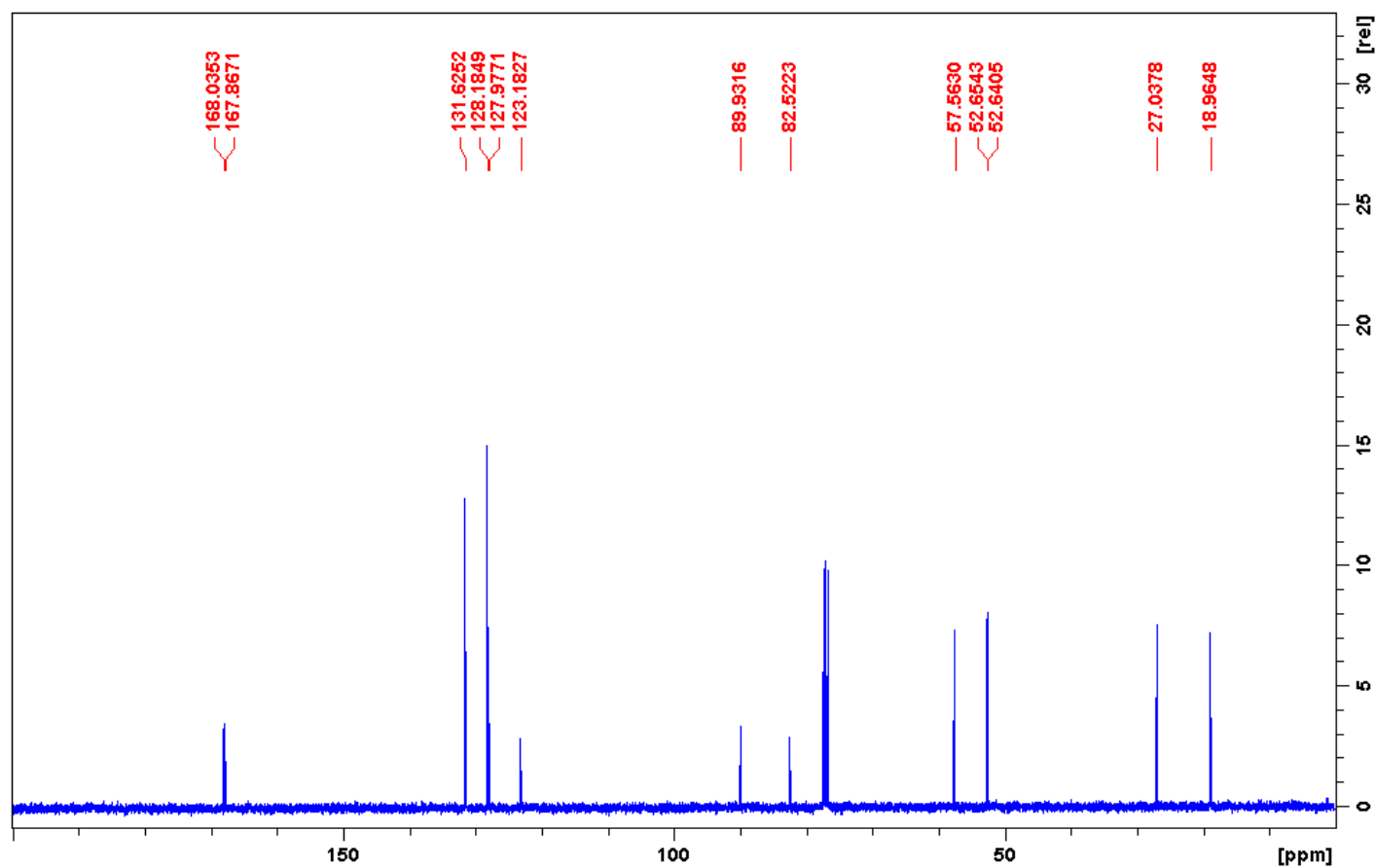
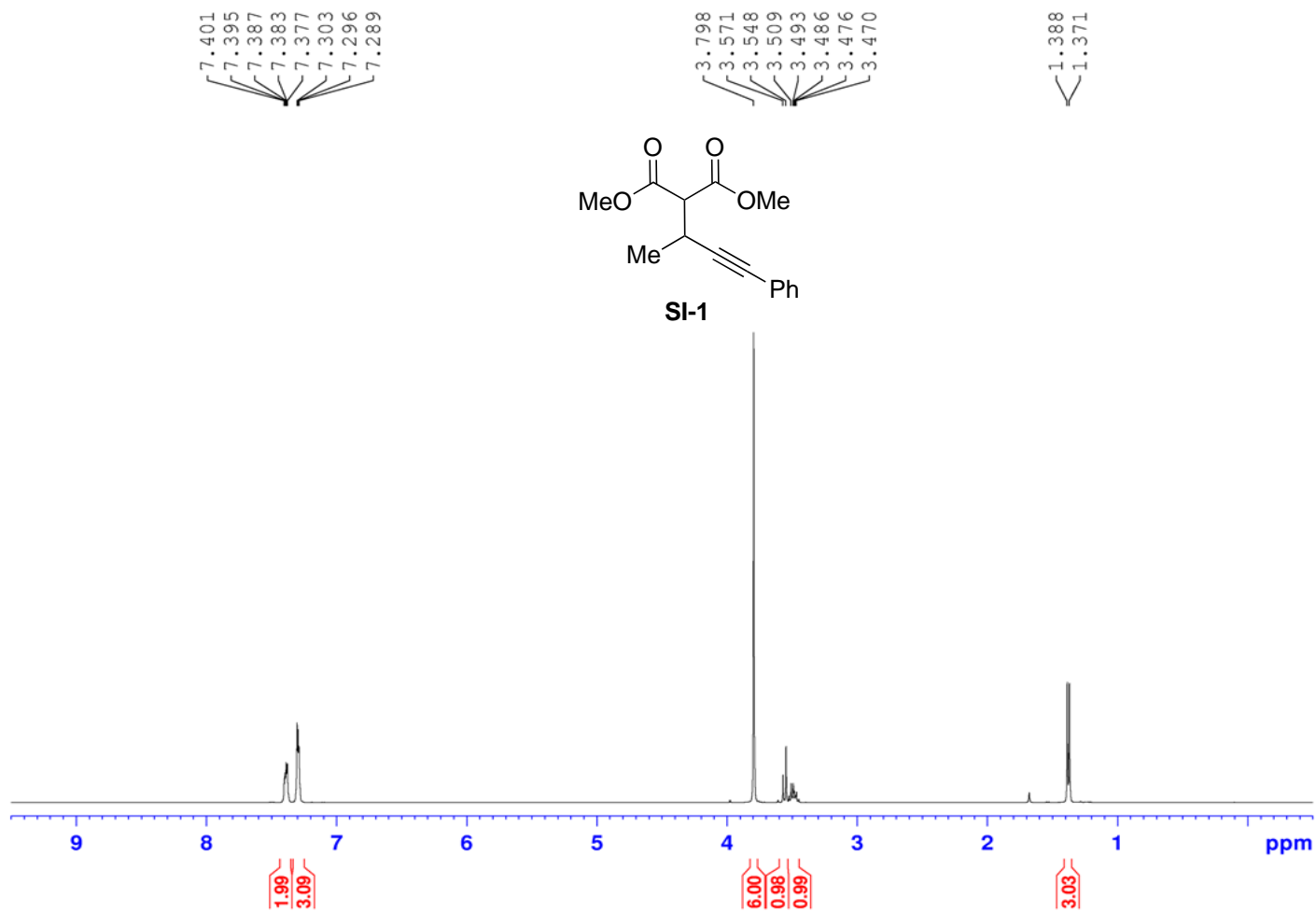
Analytical data for **25**: **¹H NMR** (CHLOROFORM-*d*, 400MHz): δ = 7.49 – 7.47 (m, 2 H), 7.41 – 7.37 (m, 2 H), 7.26 – 7.22 (m, 1 H), 3.81 (s, 3 H), 3.74 (d, J = 2.4 Hz, 1 H), 2.72 (s, 1 H), 2.65 (s, 1 H), 2.38 (d, J = 10.8 Hz, 1 H), 1.86 – 1.79 (m, 2 H), 1.59 (d, J = 10.4 Hz, 1 H), 1.50 – 1.47 (m, 1 H), 1.34 – 1.30 (m, 1 H); **¹³C NMR** (CHLOROFORM-*d*, 101 MHz) 211.1, 155.4, 139.8, 128.7, 126.5, 123.2, 84.2, 53.5, 48.4, 39.4, 34.4, 24.6, 23.2 ppm; **IR** (thin film, cm⁻¹) 3064, 2956, 2879, 1756, 1731, 1595, 1494, 1440, 1349, 1192, 909, 755; **LRMS** (ESI) Calcd. for [C₁₅H₁₇NO₄+H]⁺ = 276.13, Found = 276.06.

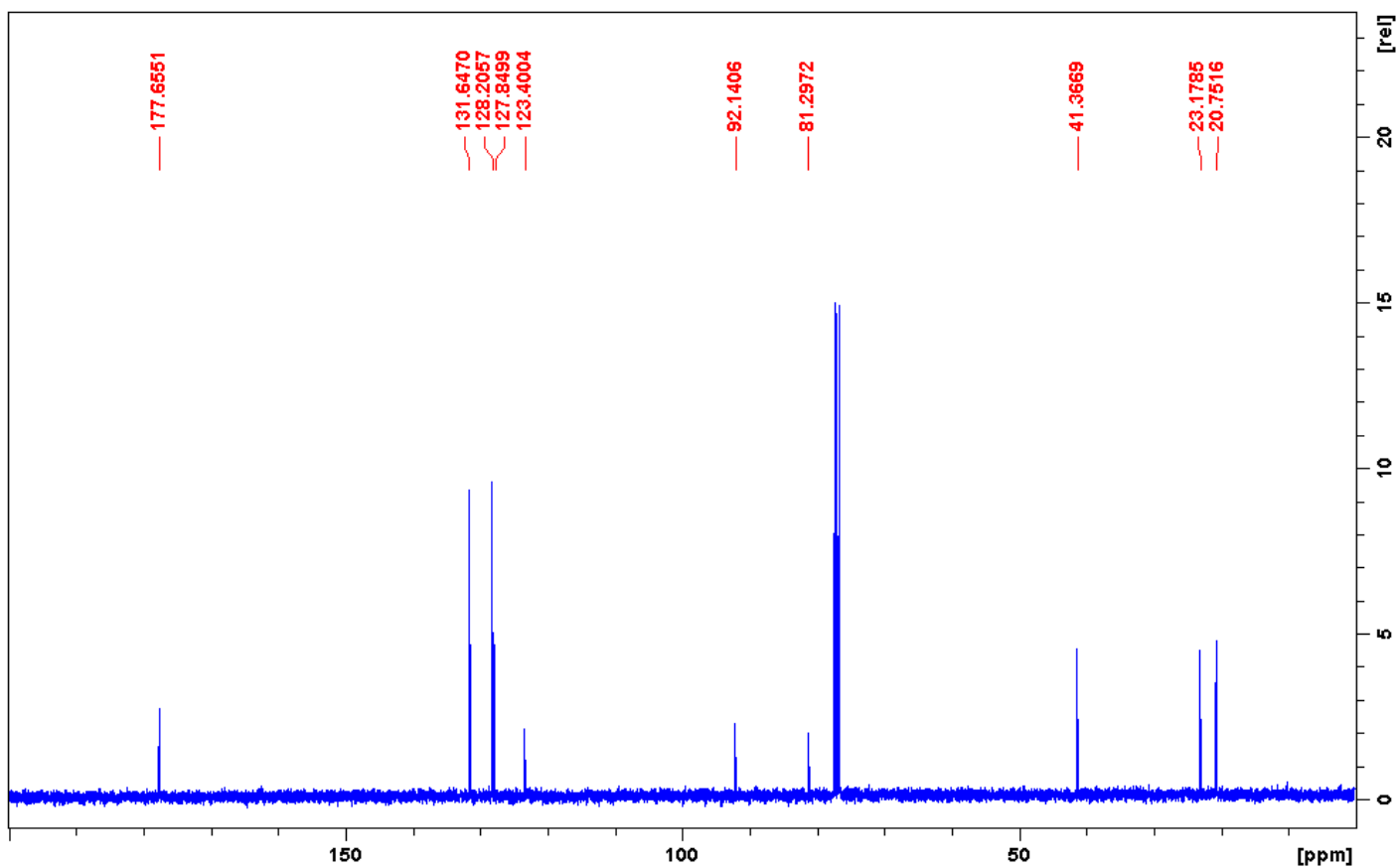
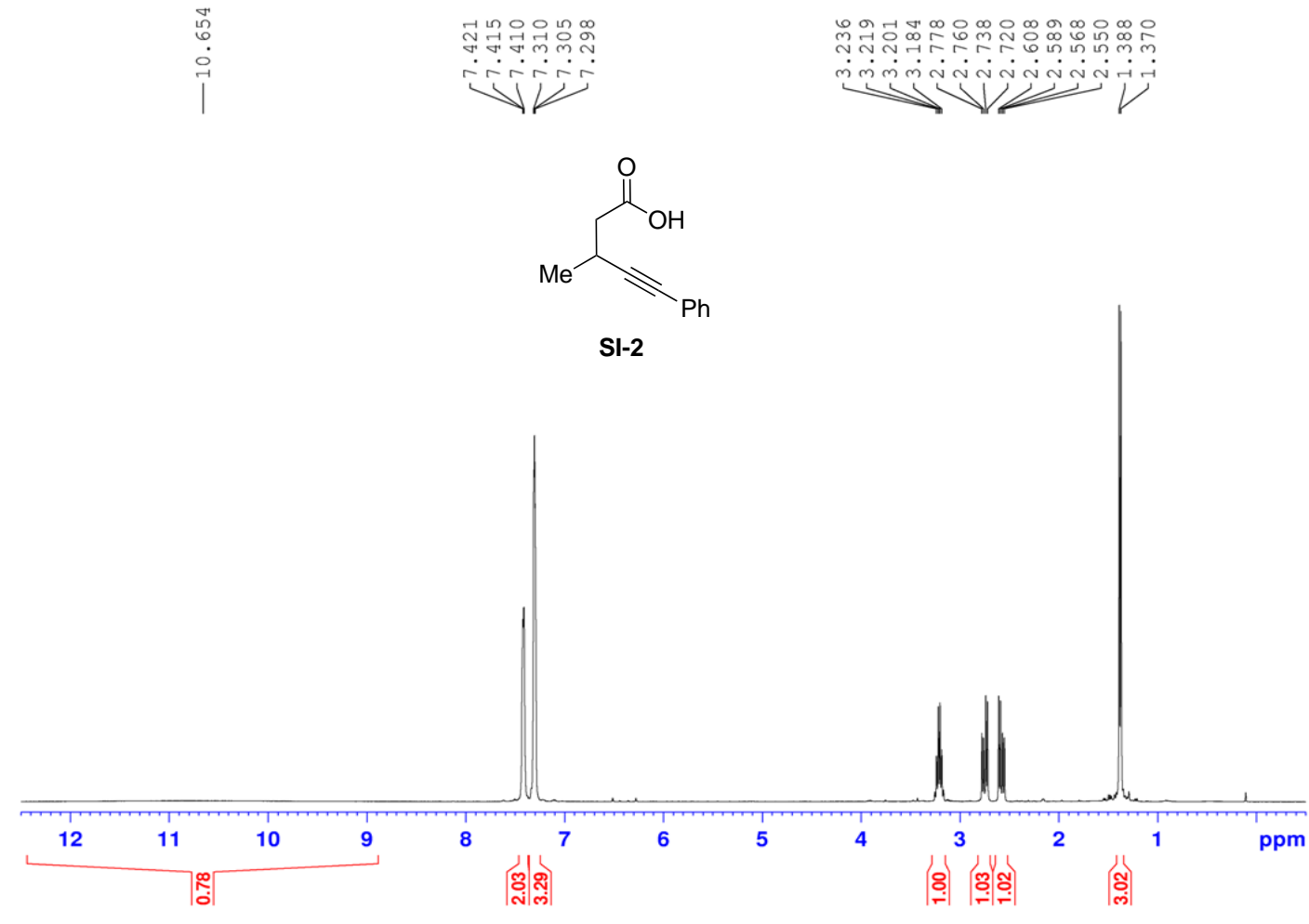
Stereochemistry was determined by 2-D NMR analysis; For details, see attached spectra.

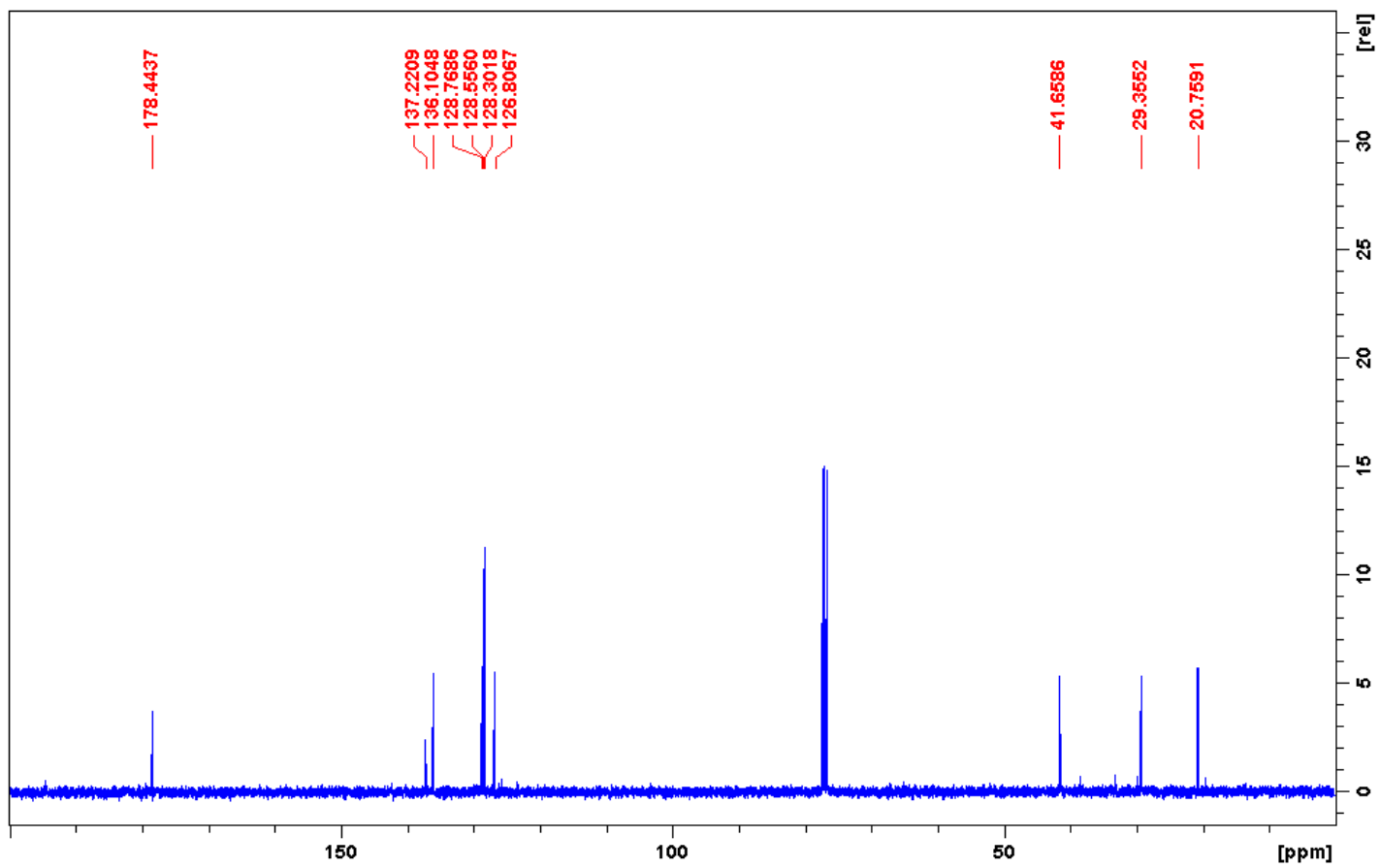
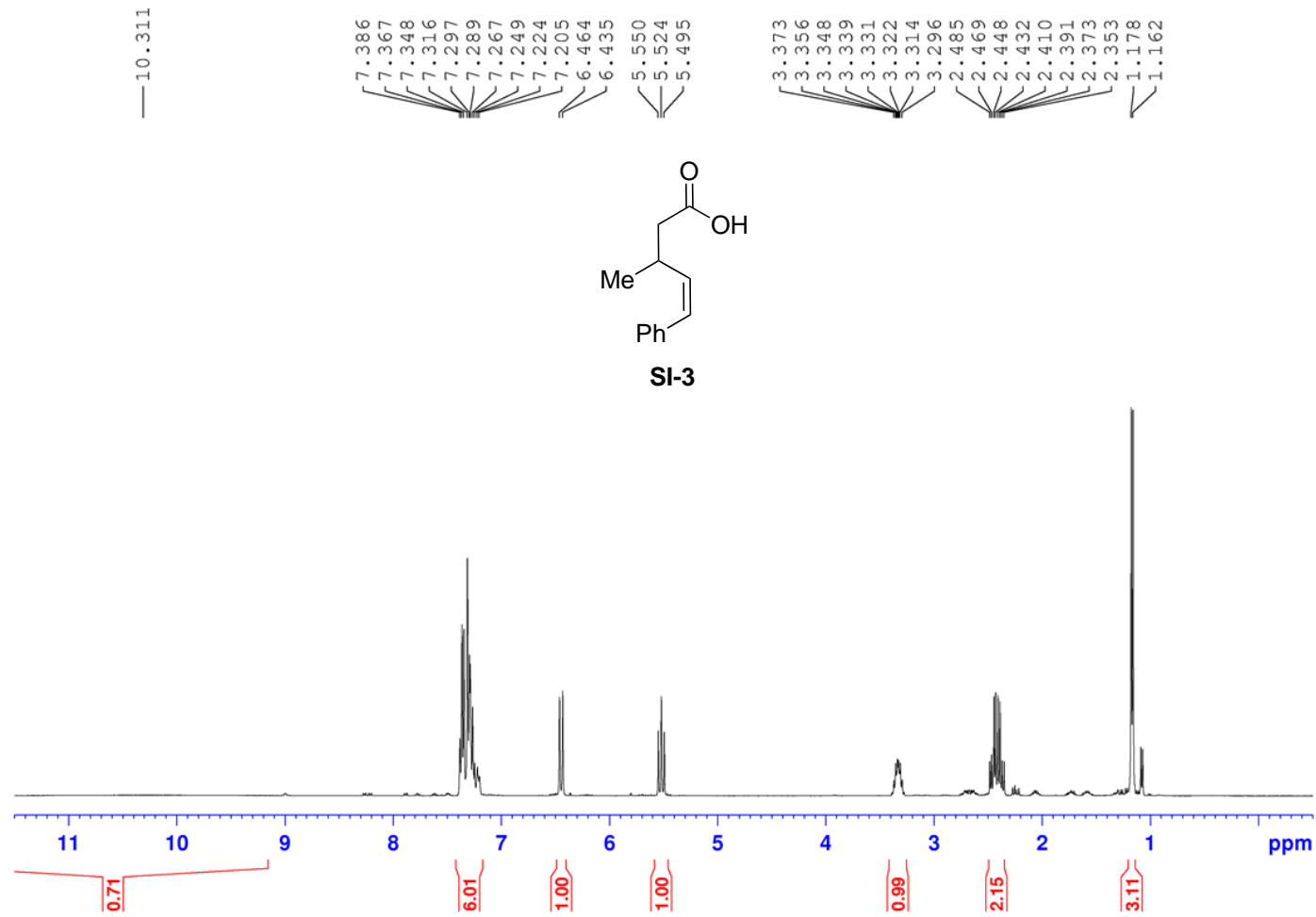
¹H, ¹³C and 2-D NMR Spectra

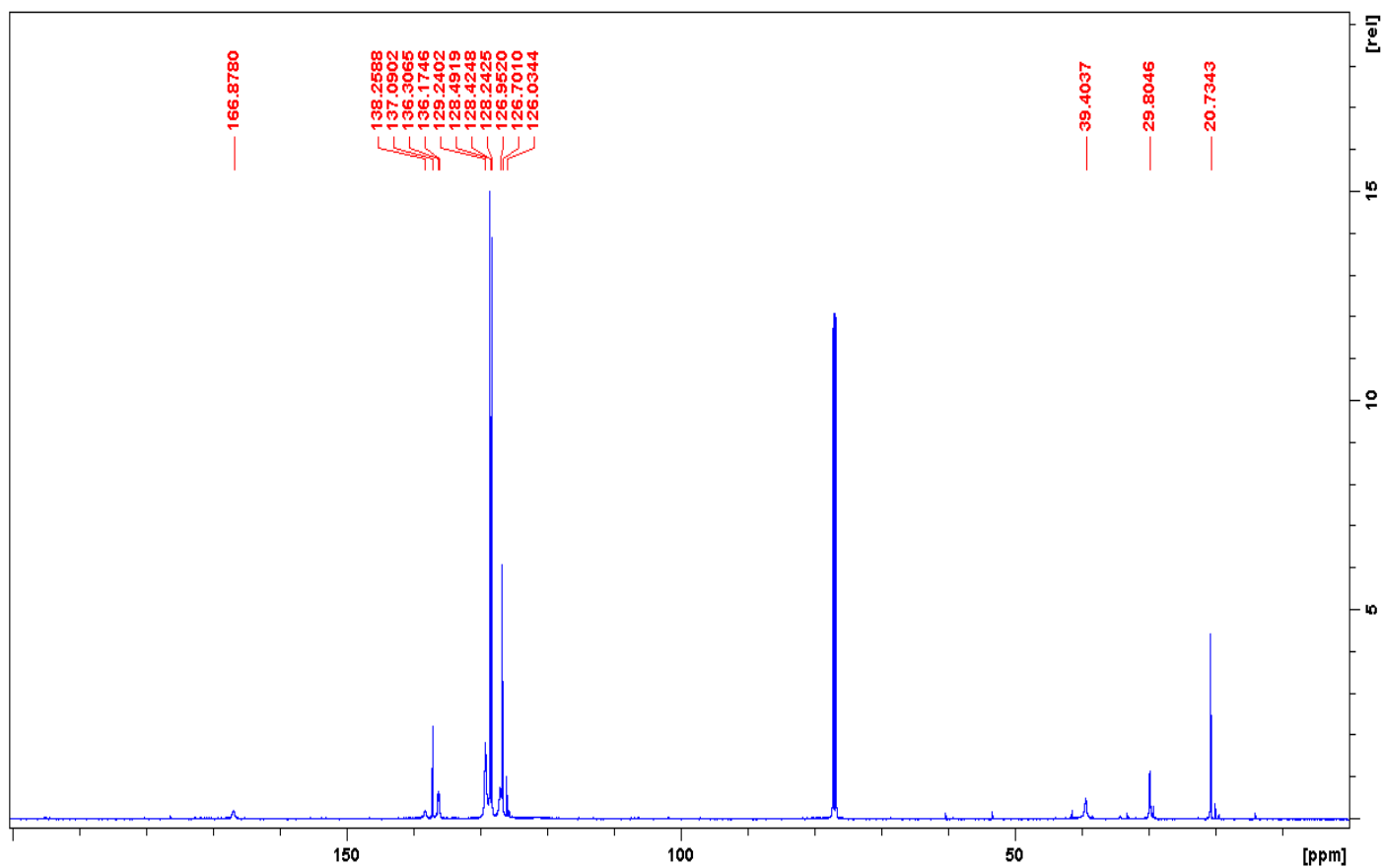
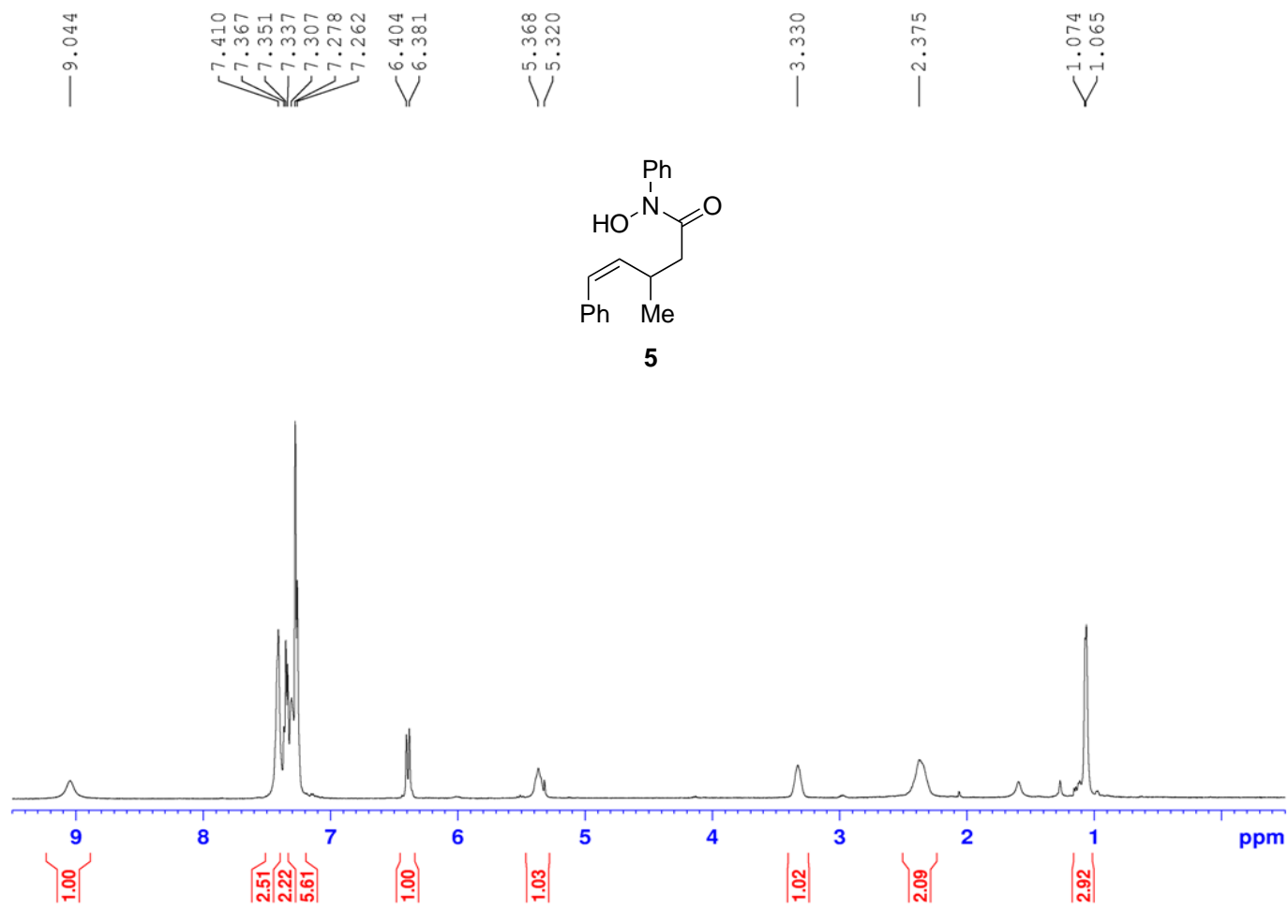


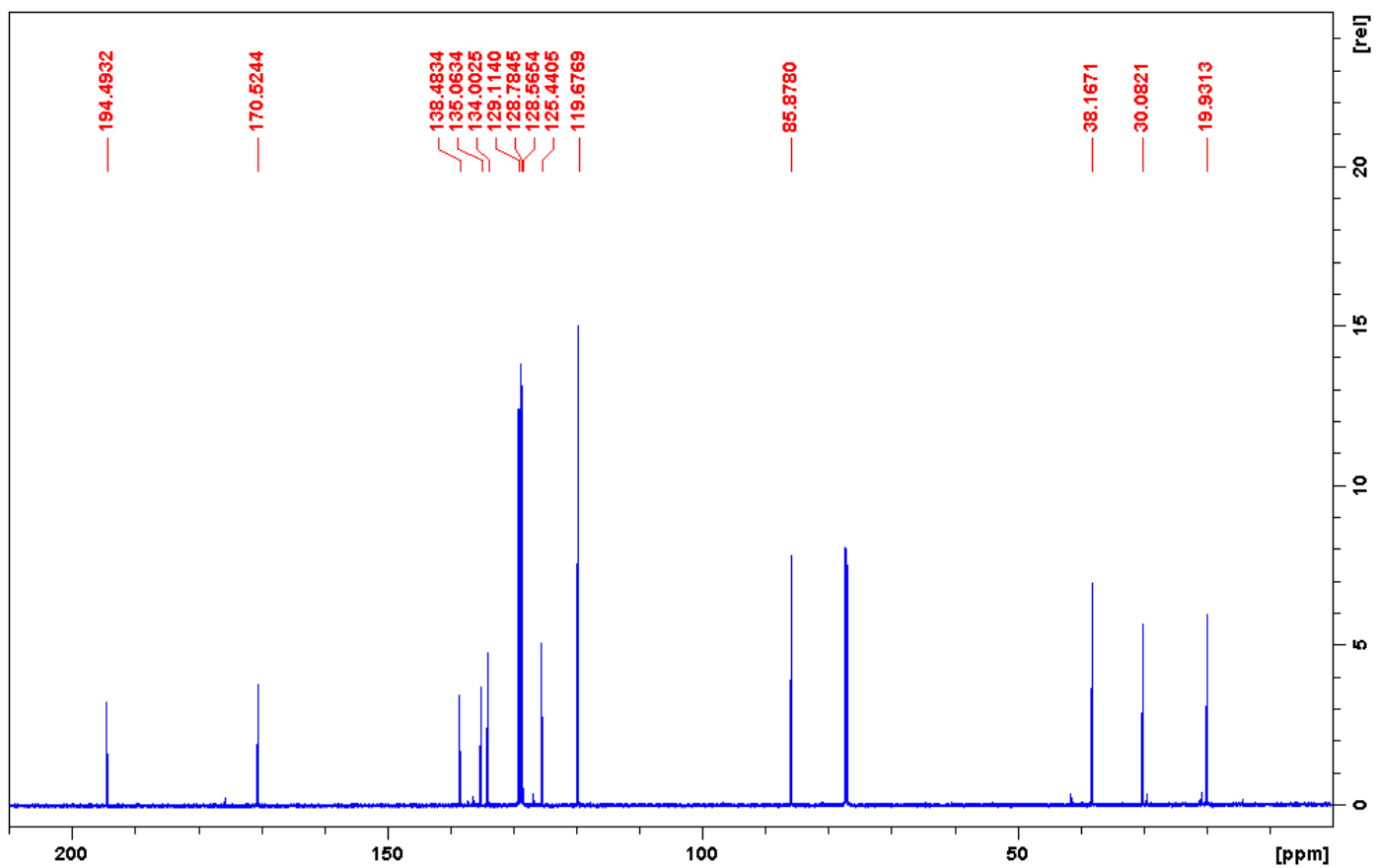
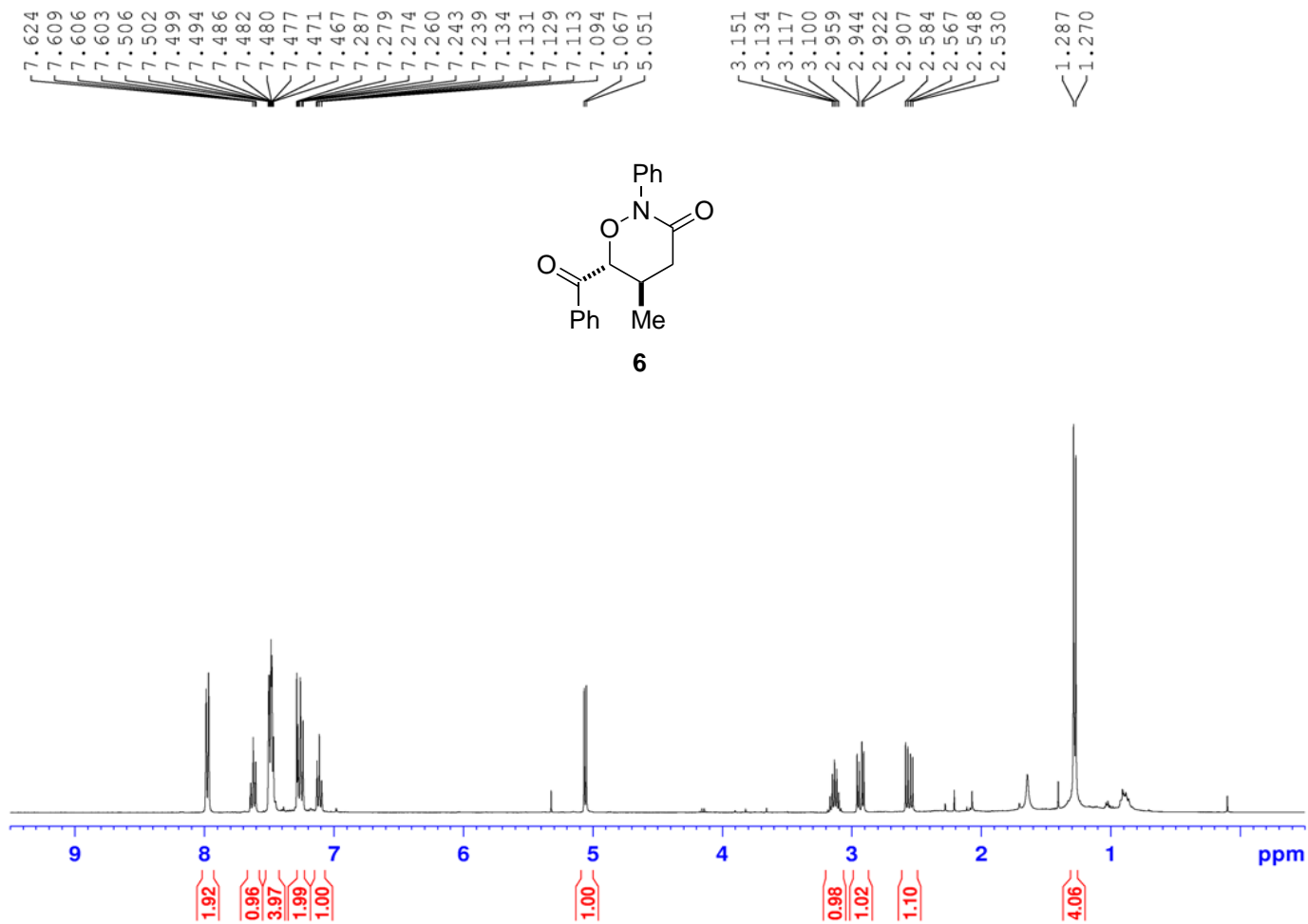




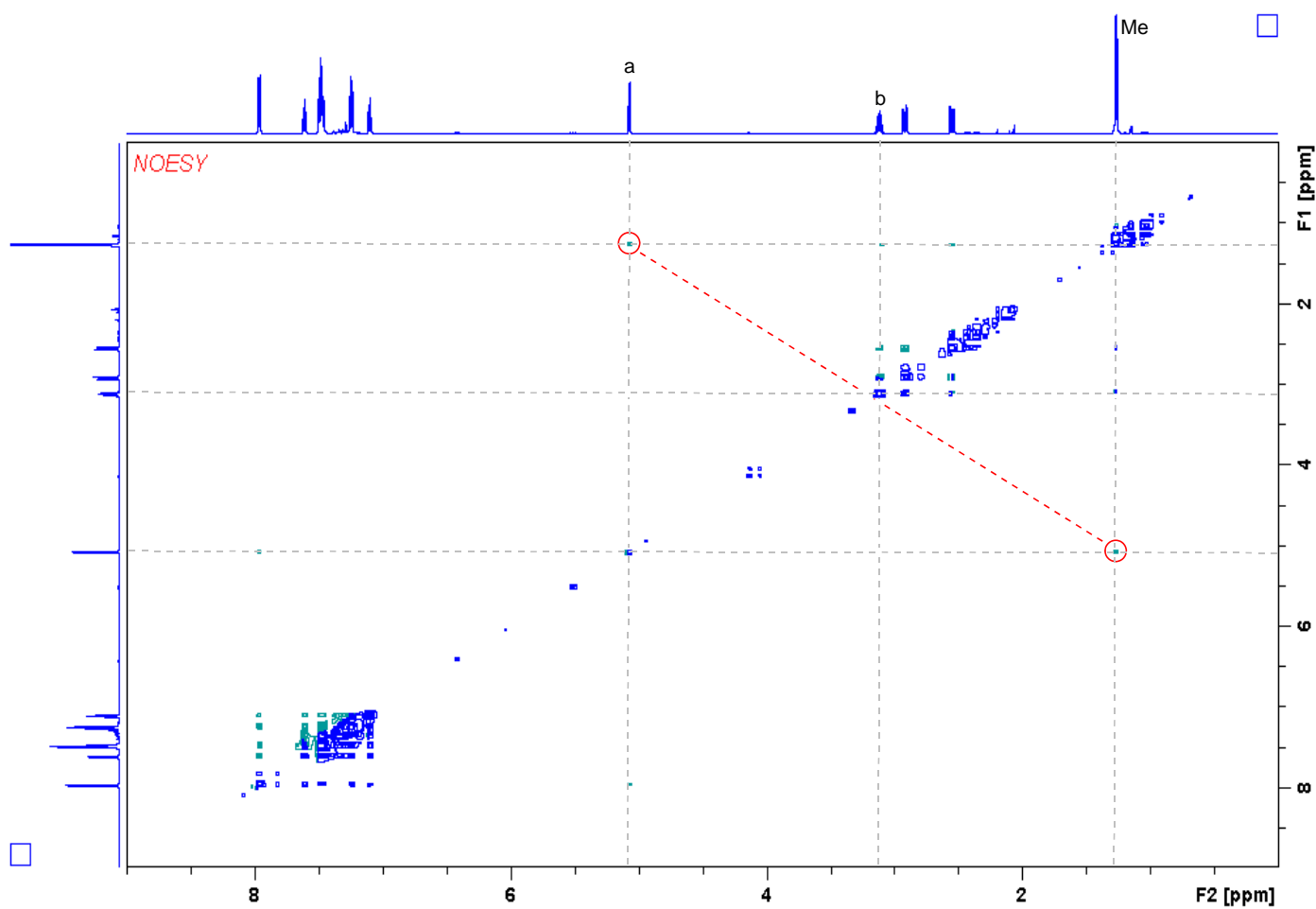
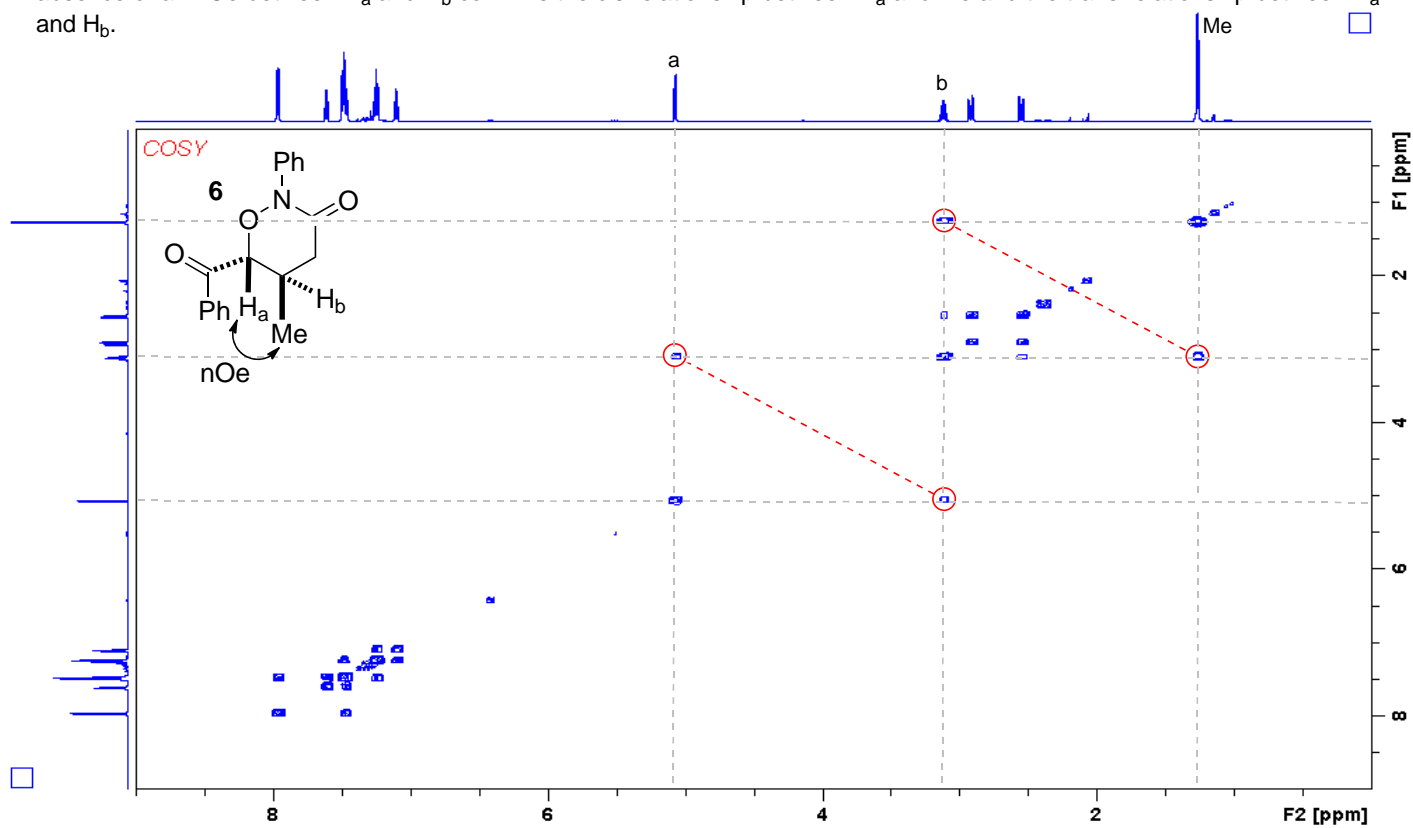


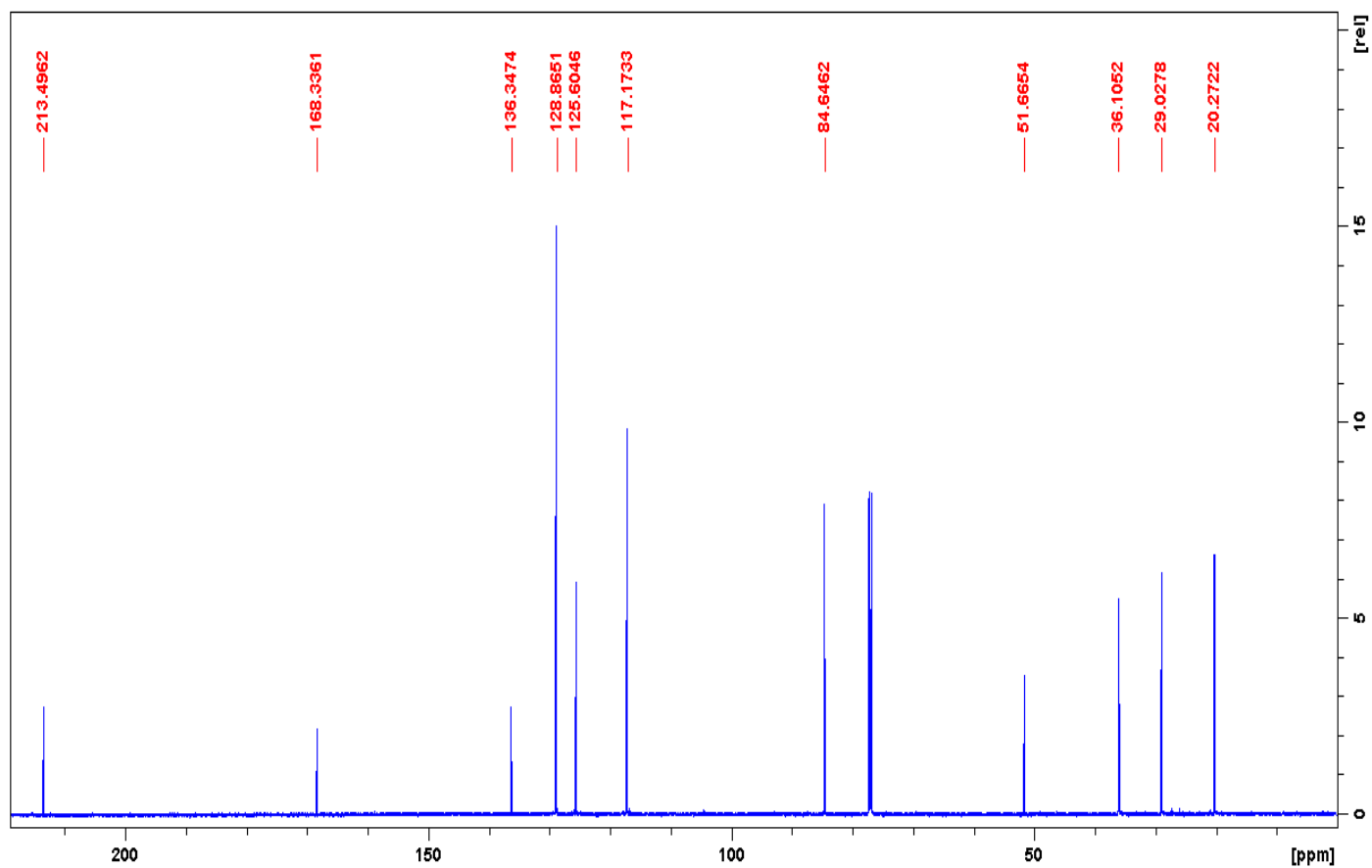
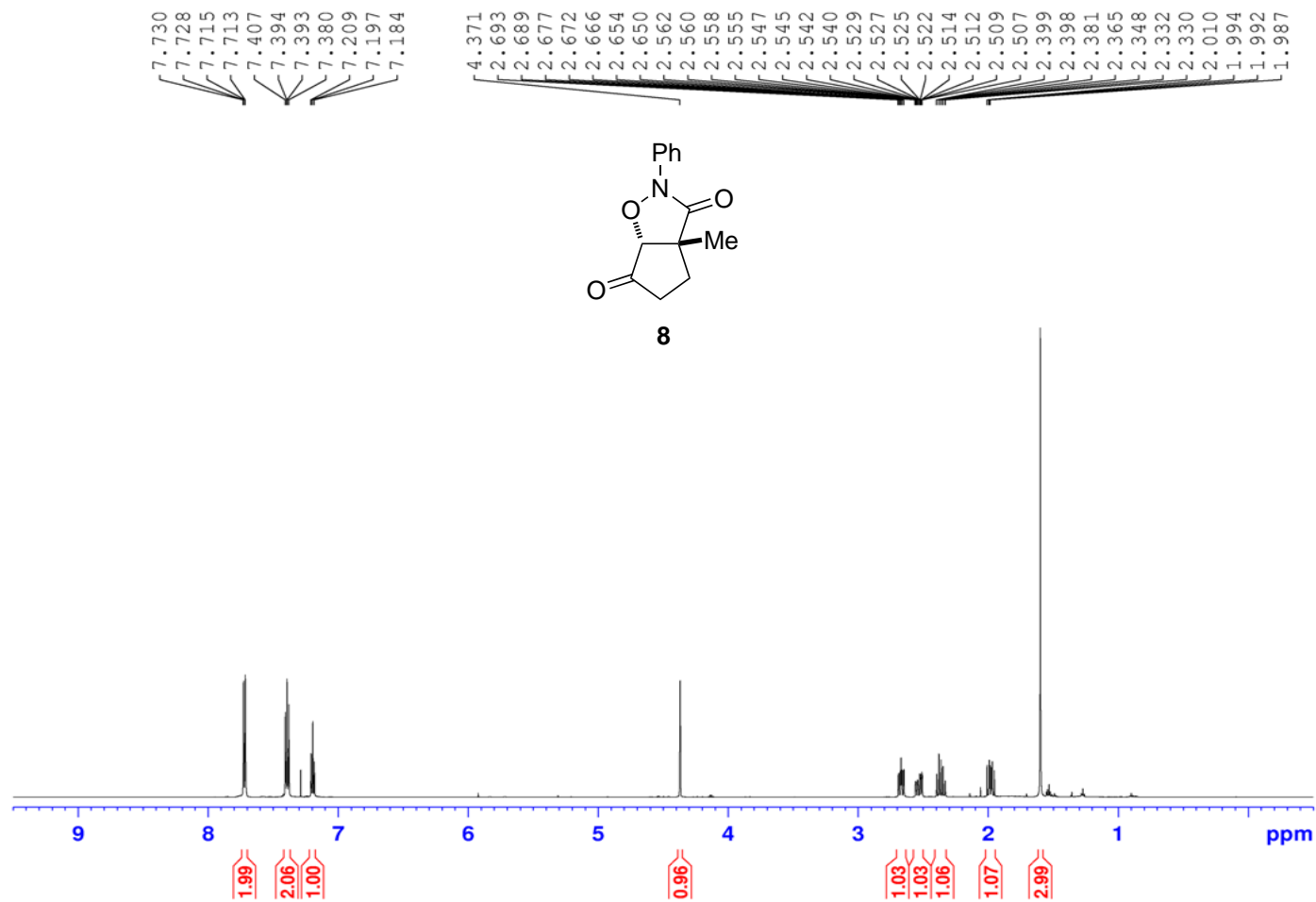


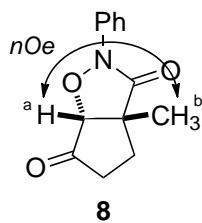




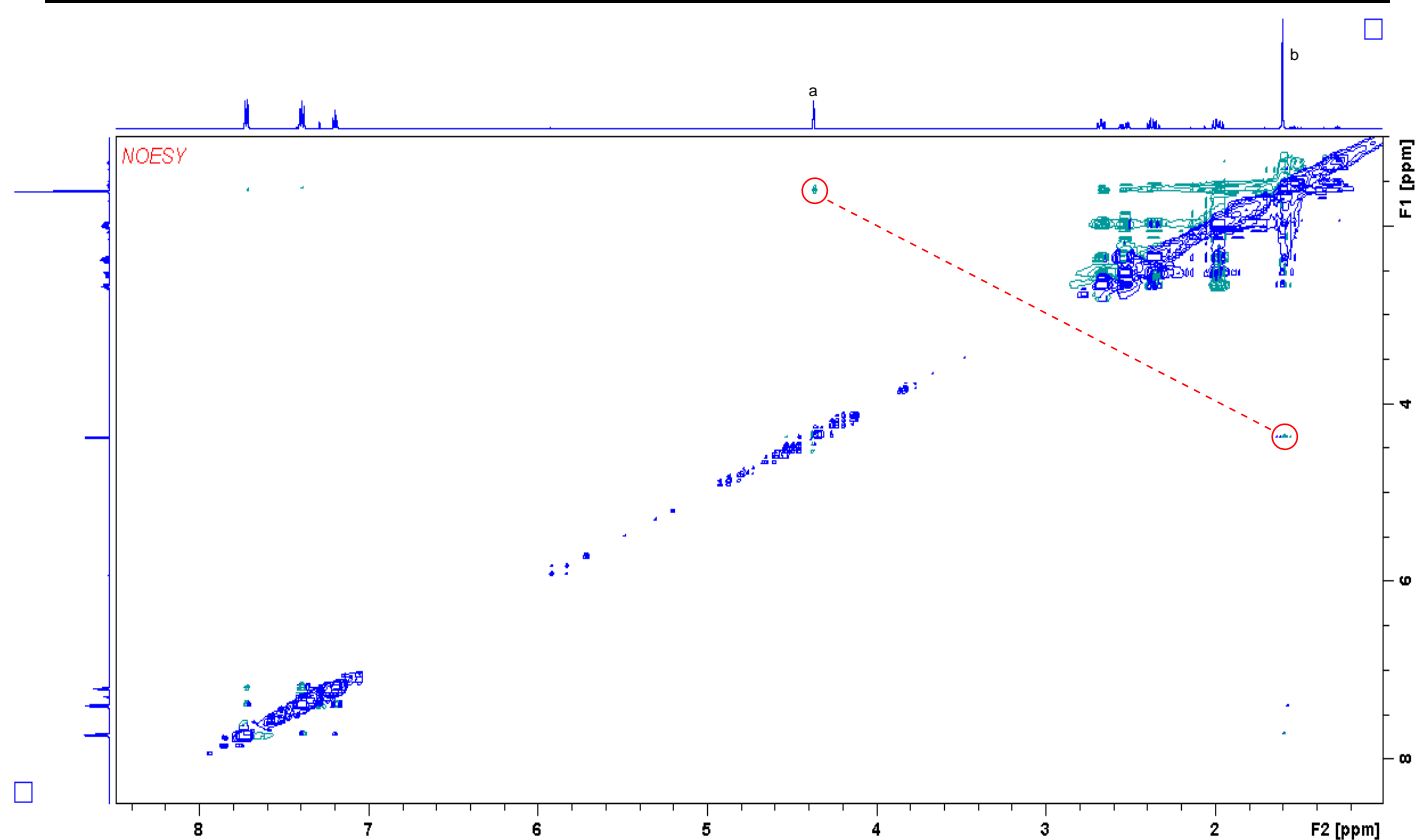
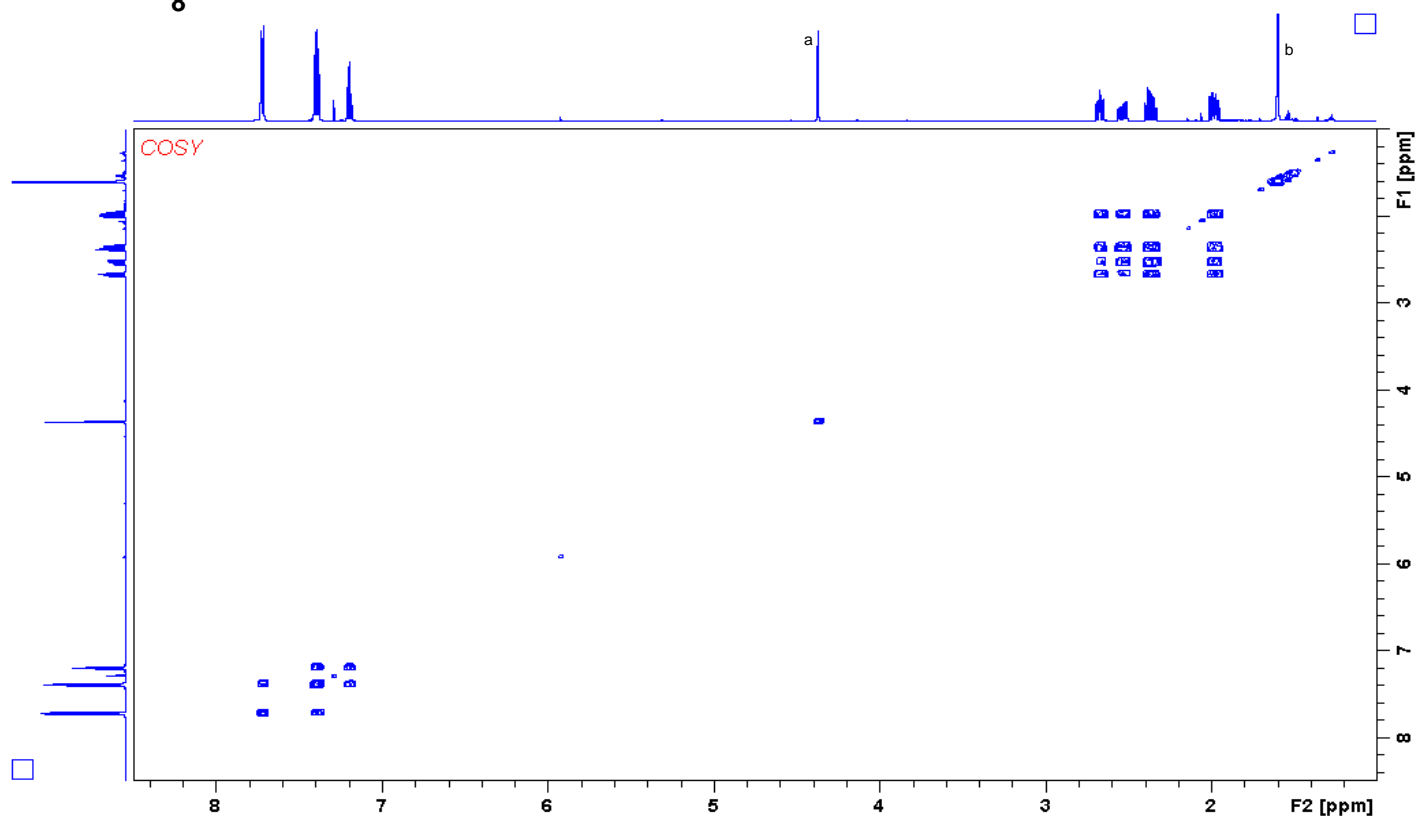
The COSY between H_a and the m at 3.1 ppm identifies H_b . The nOe between H_a and the Me group in conjunction with the absence of an nOe between H_a and H_b confirms the cis relationship between H_a and Me and the trans relationship between H_a and H_b .

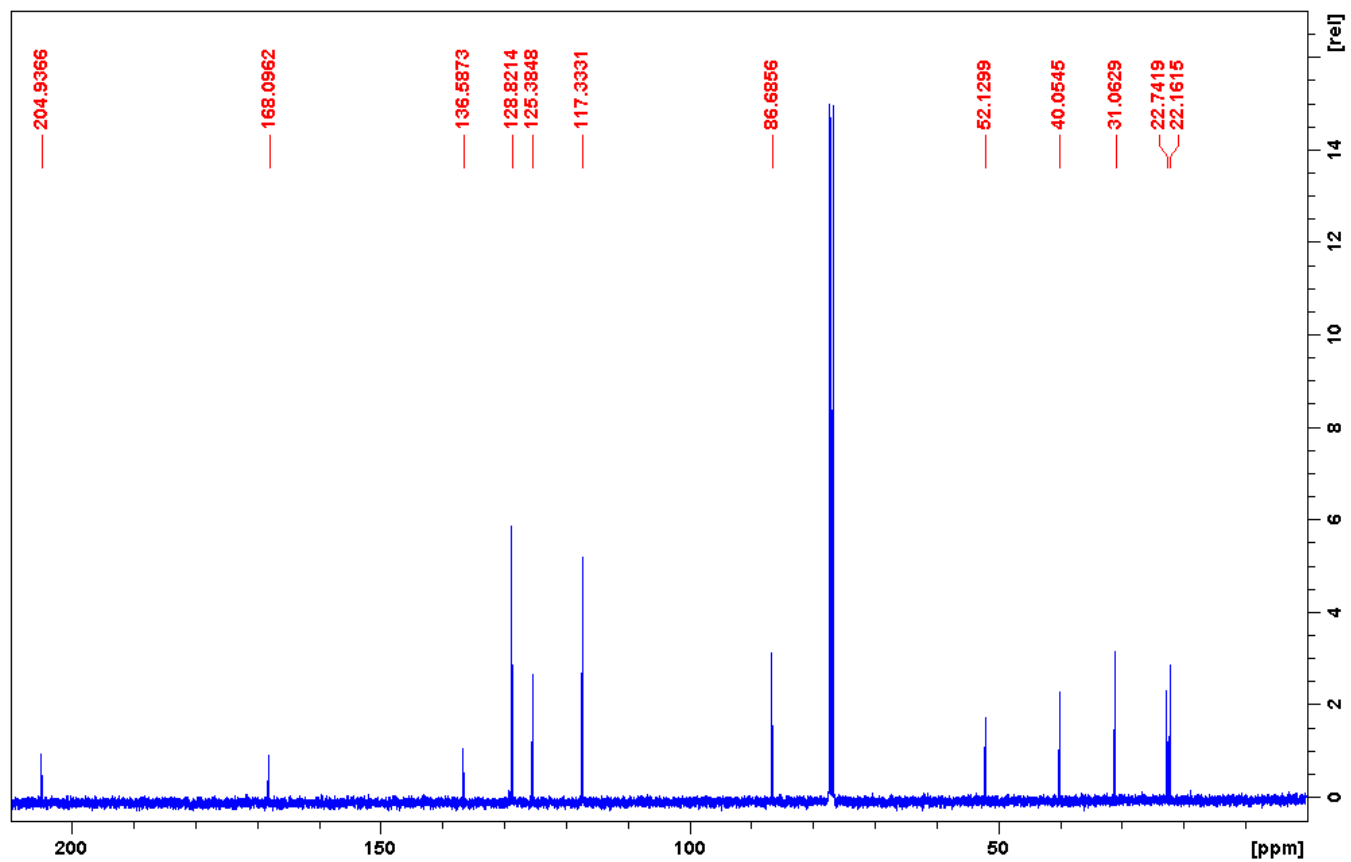
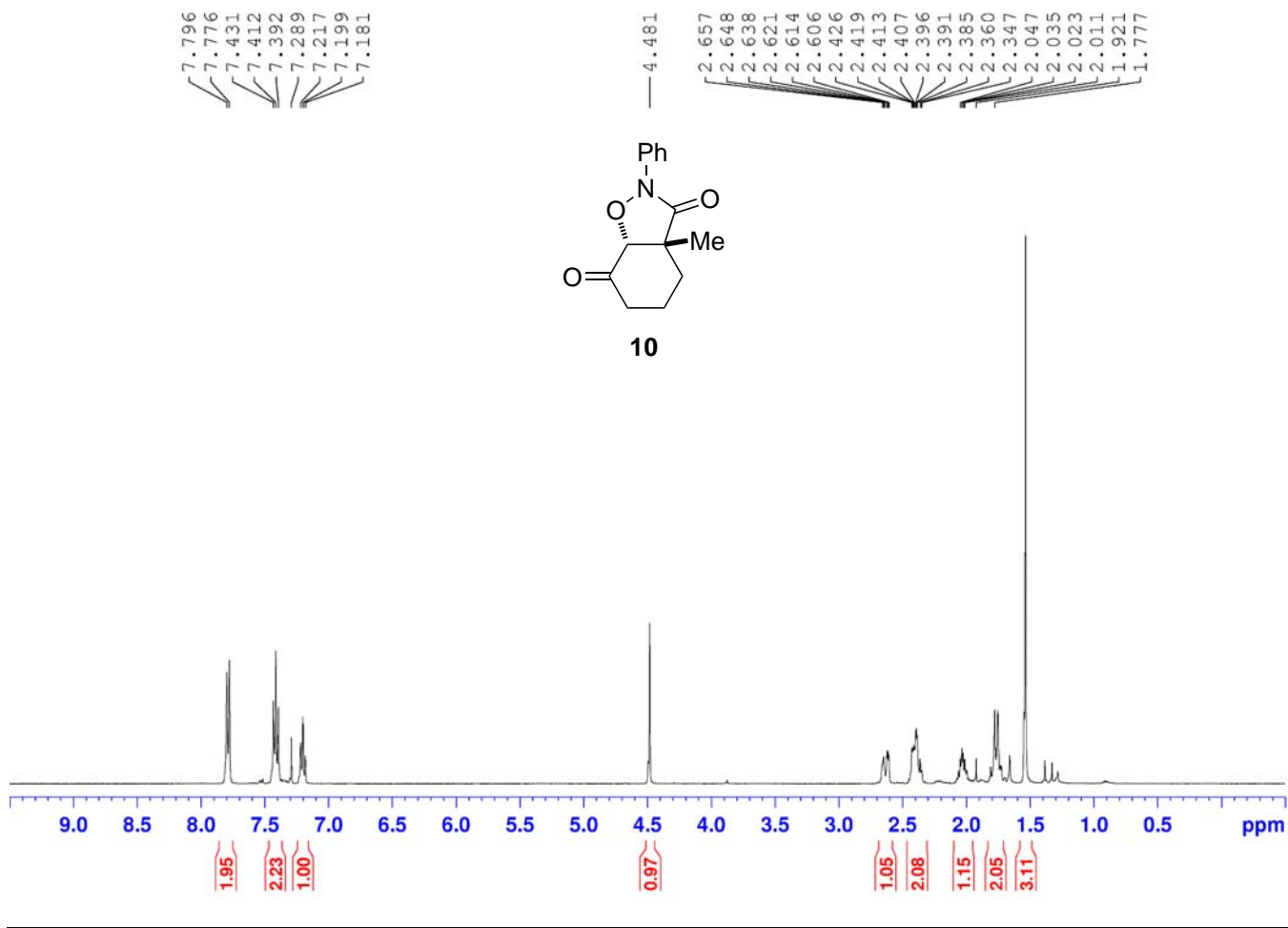


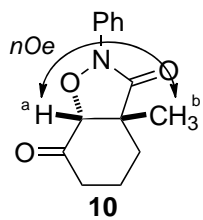




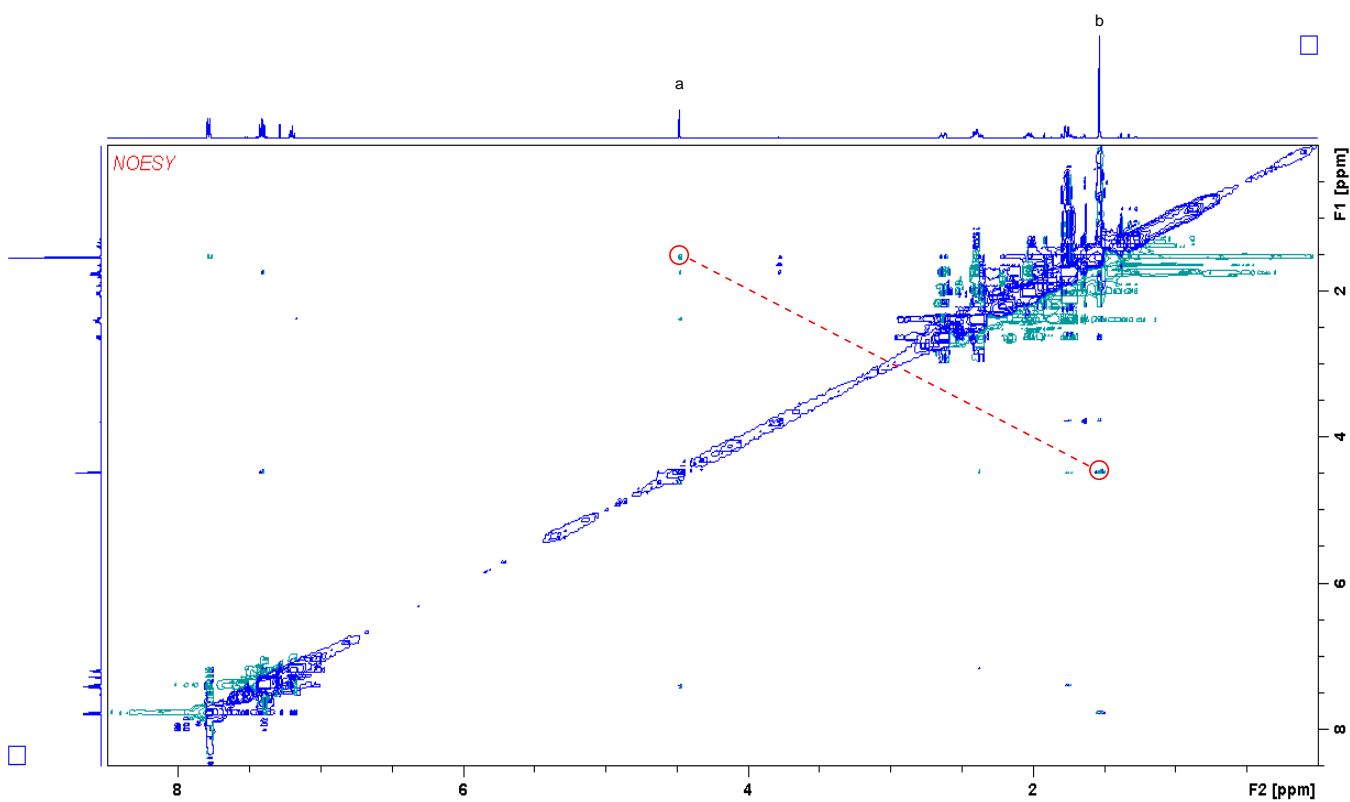
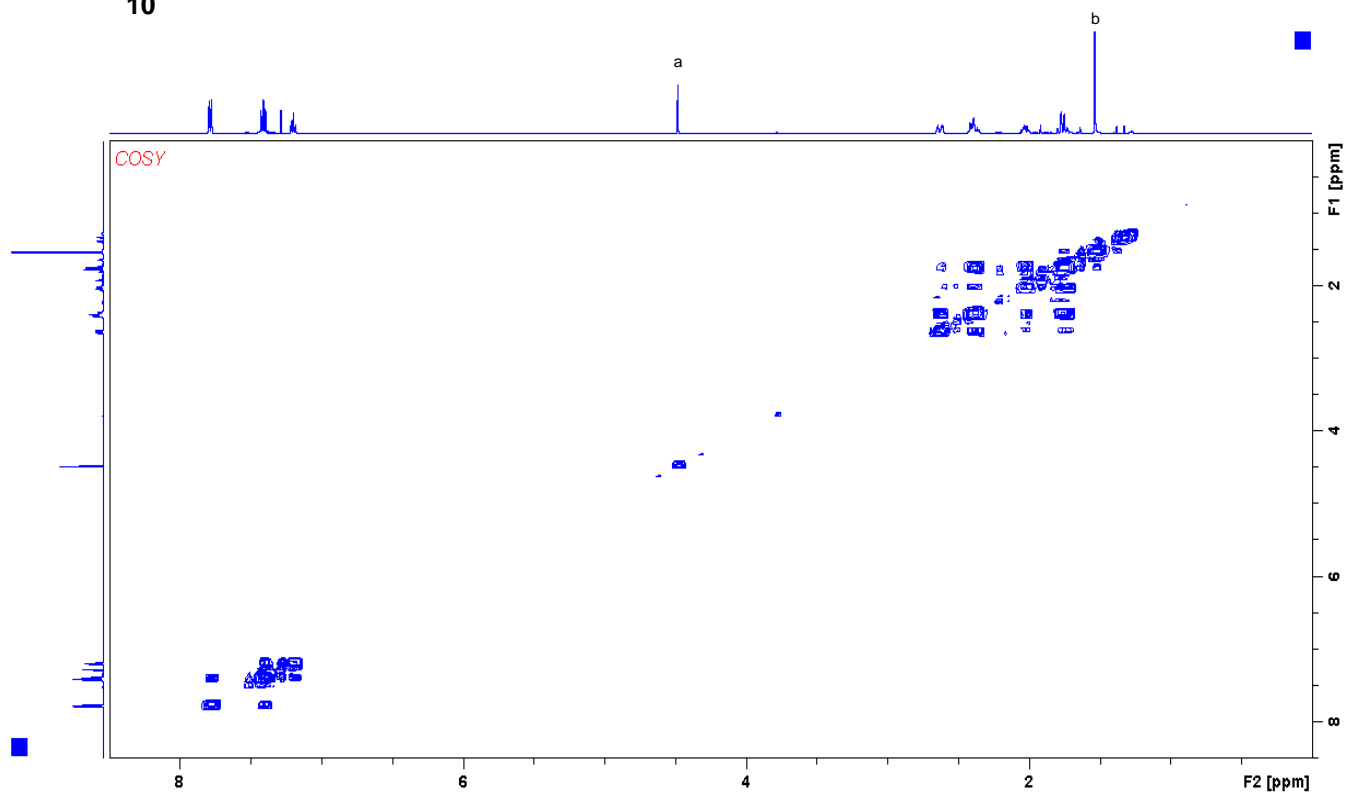
An nOe observed between H_a and H_b confirms a *cis* ring junction.

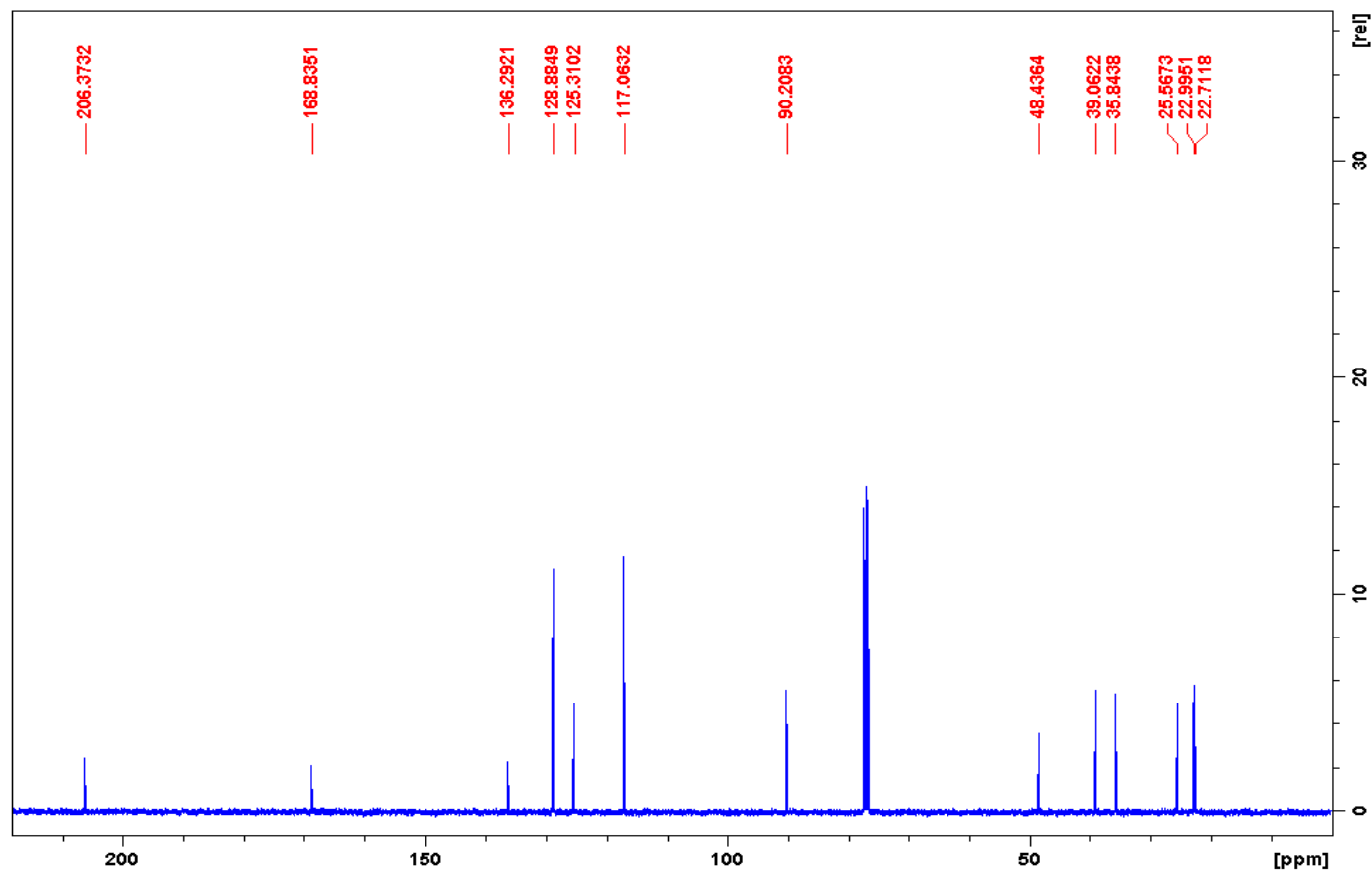
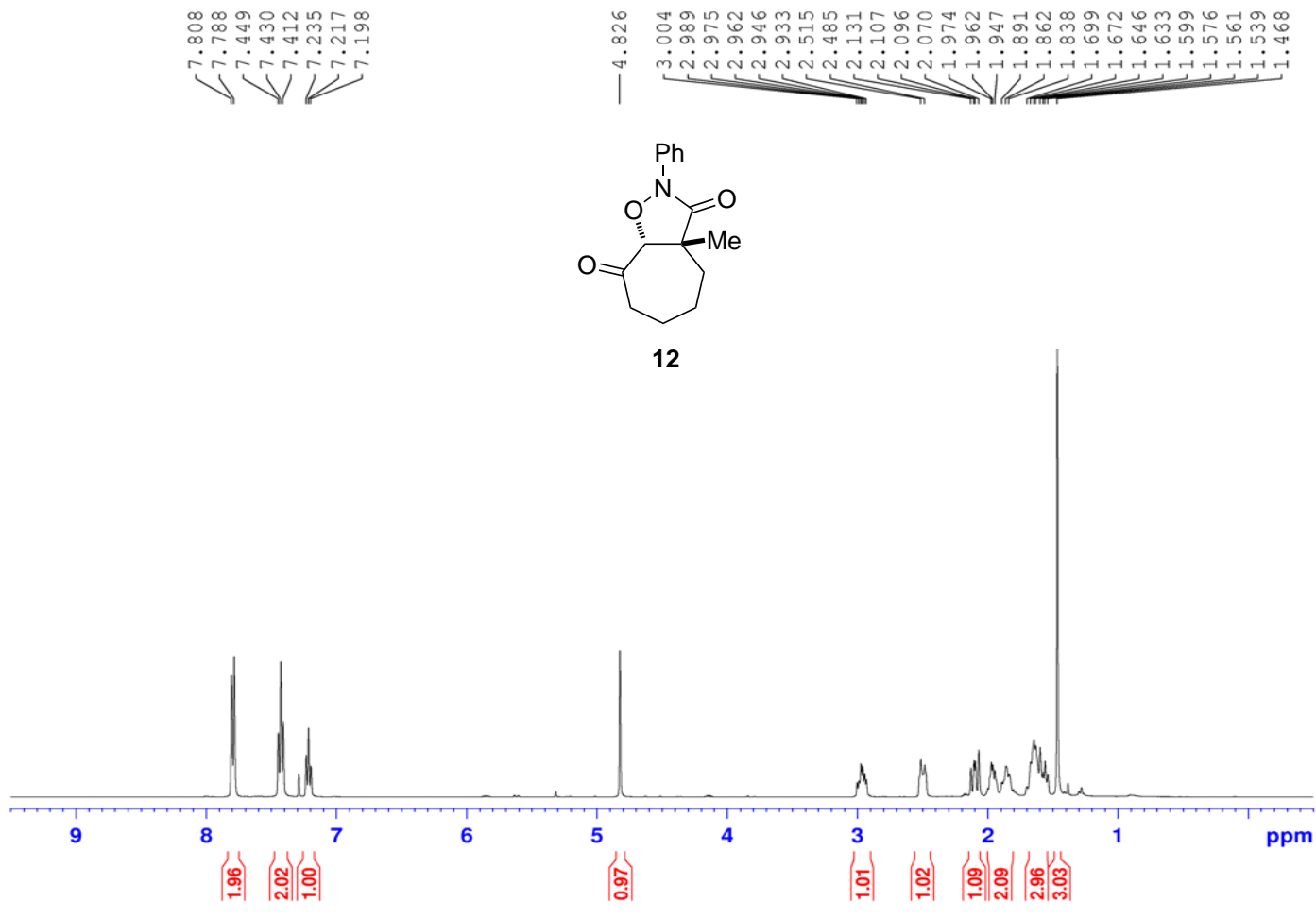


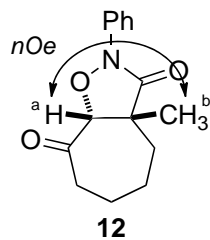




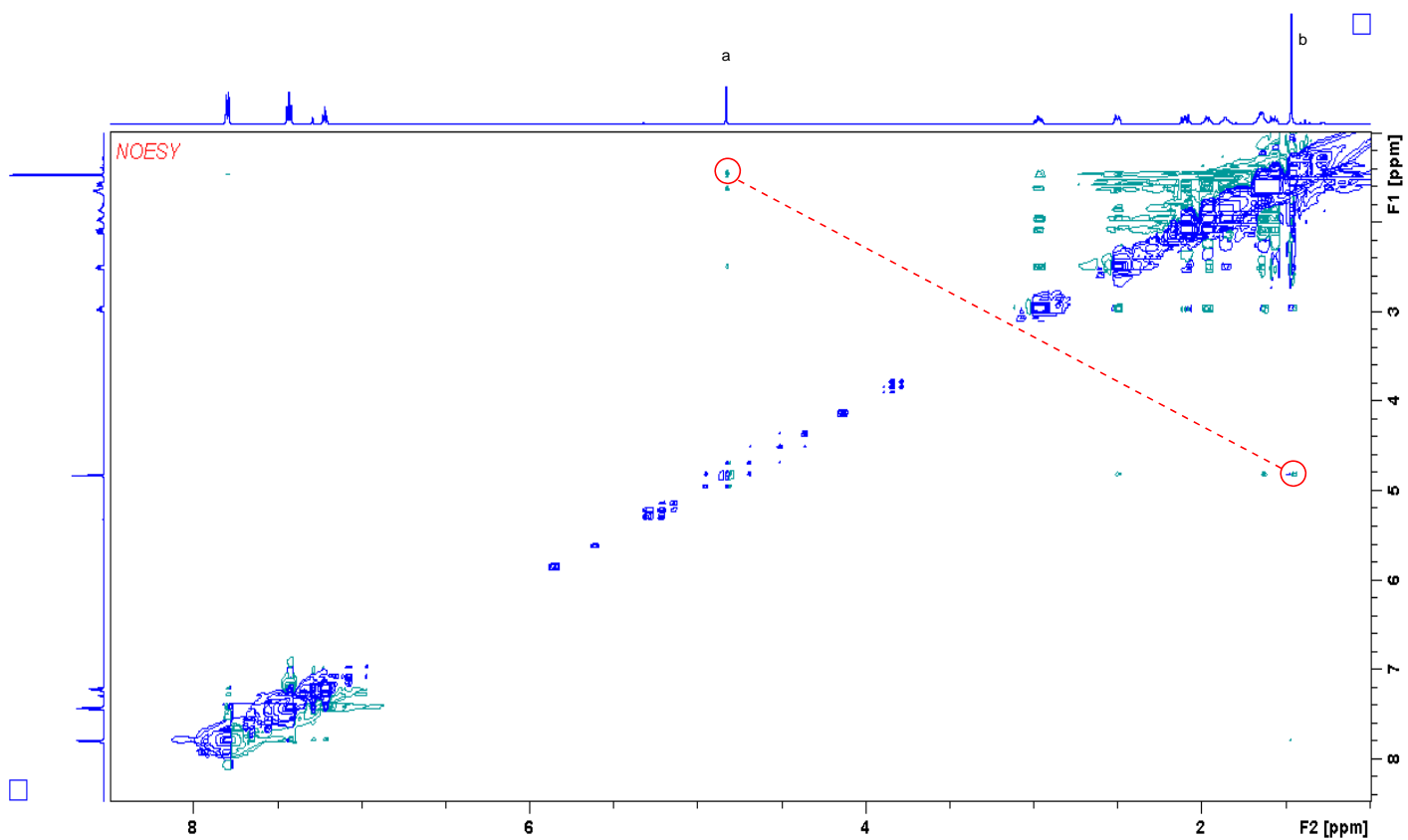
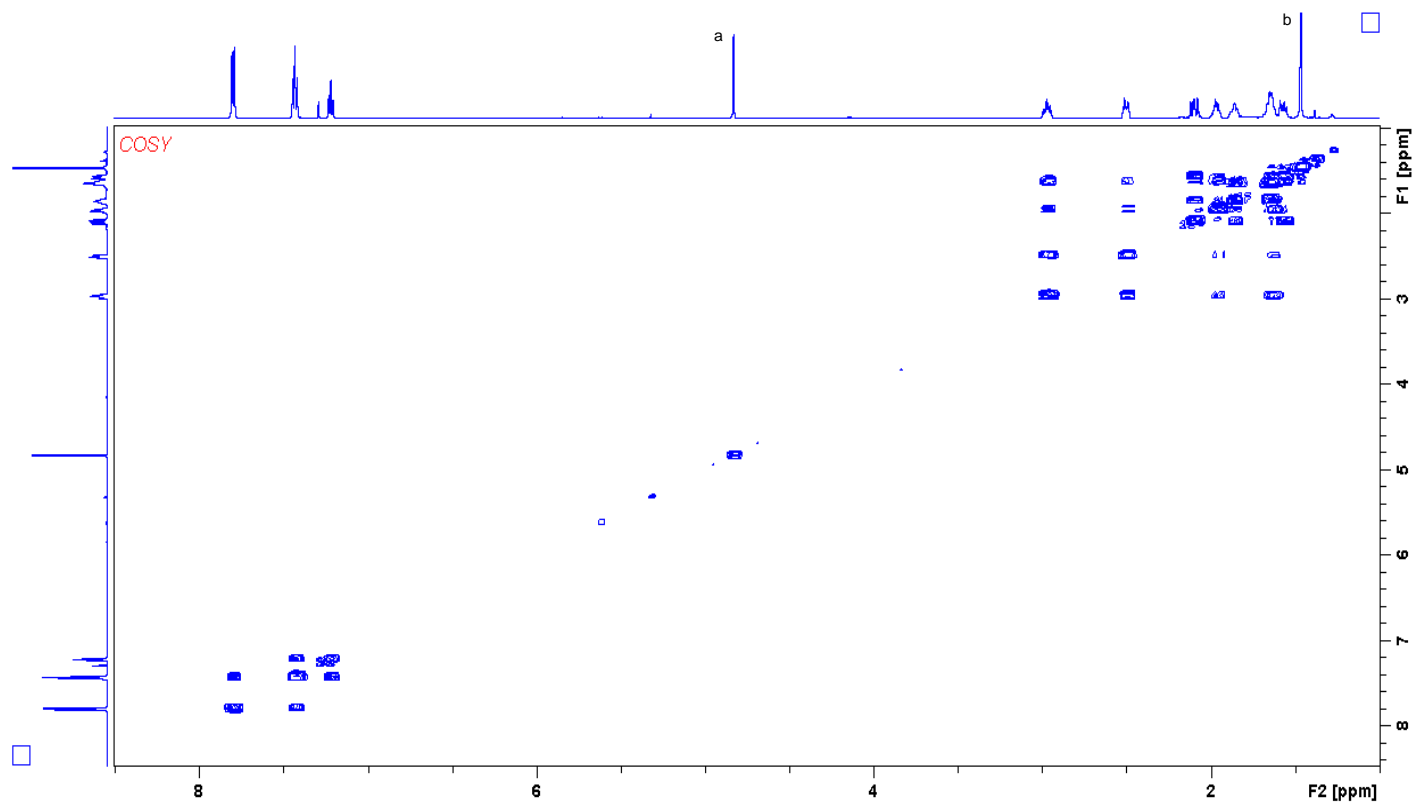
An nOe observed between H_a and H_b confirms a *cis* ring junction.

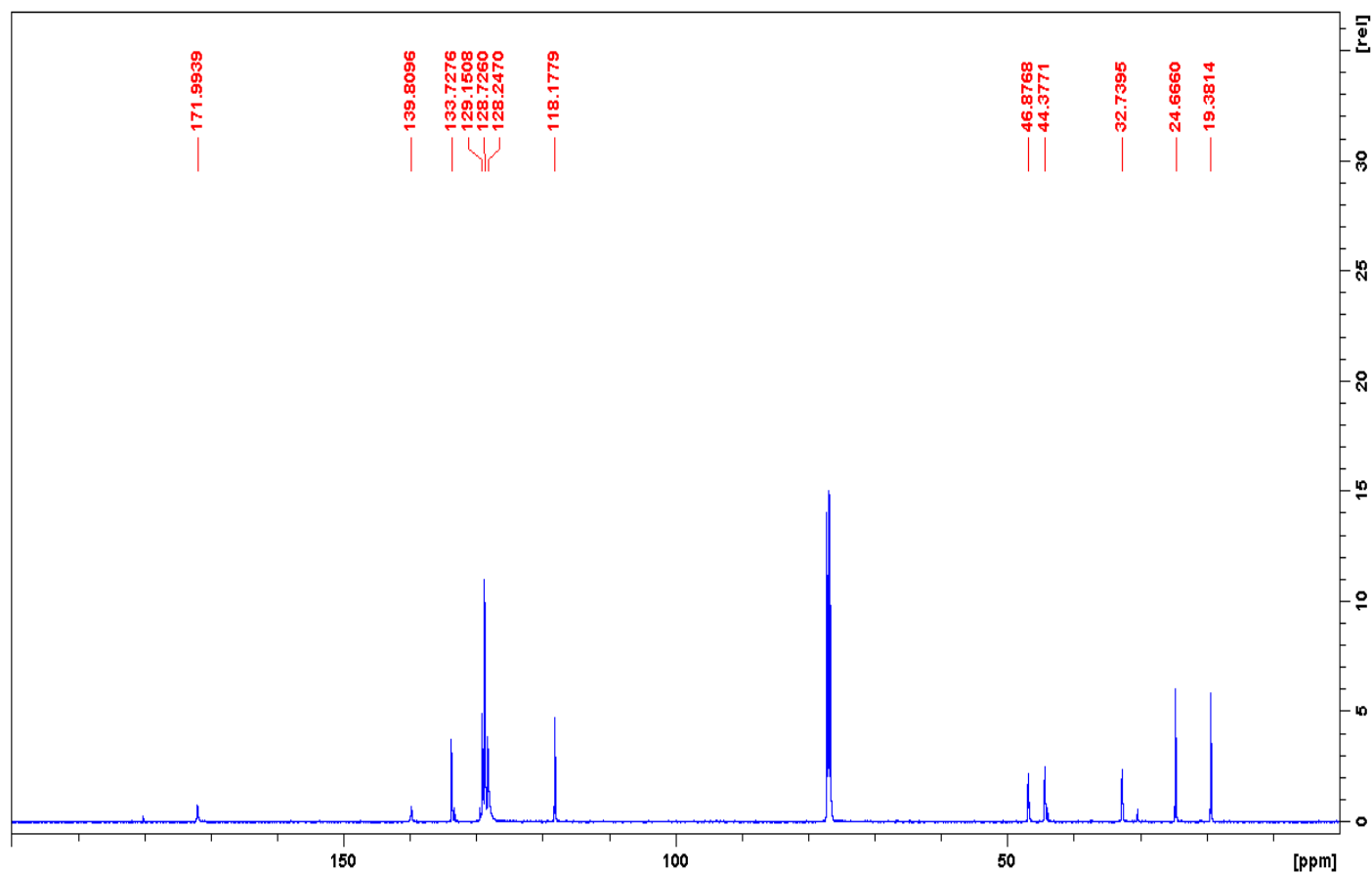
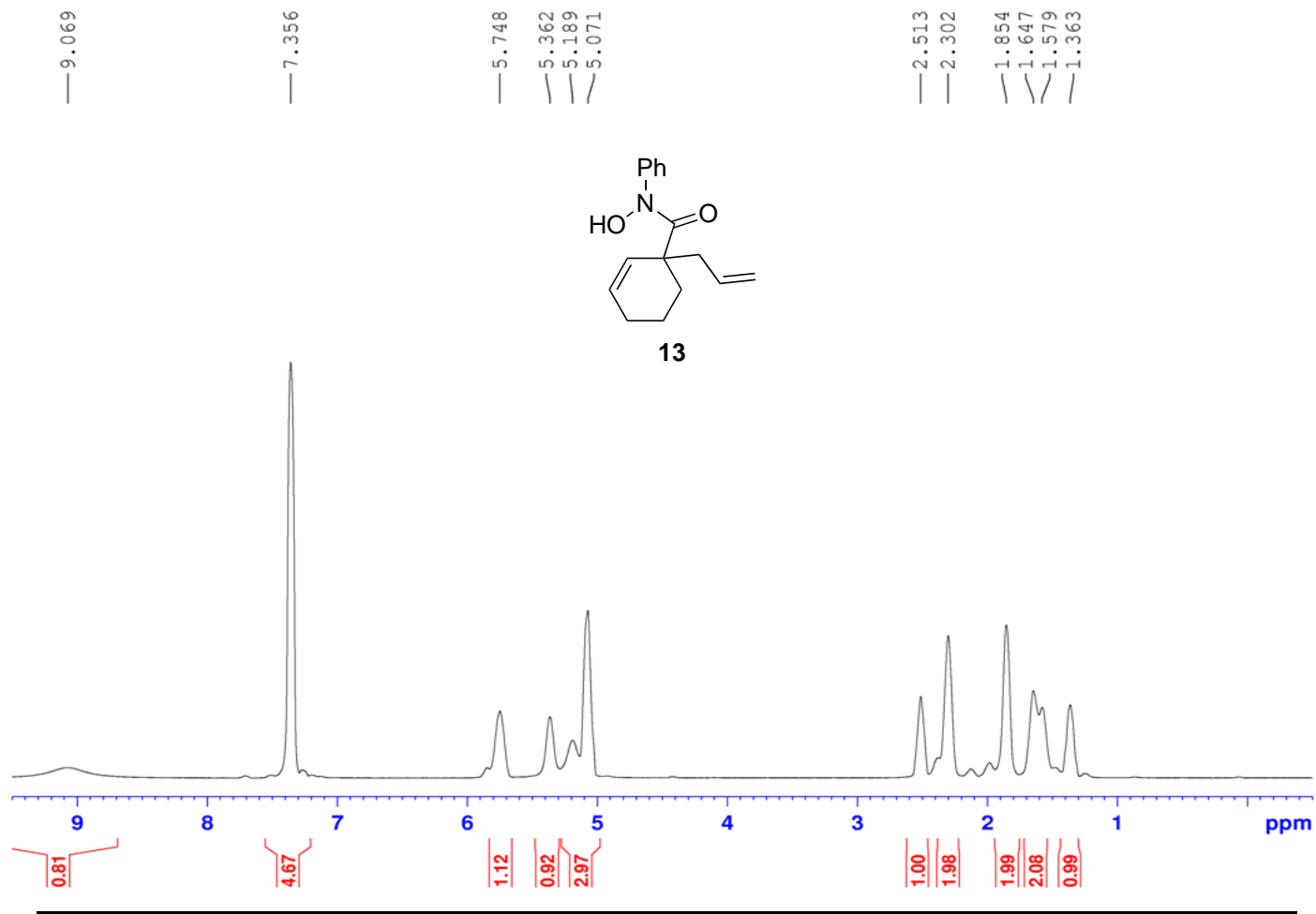


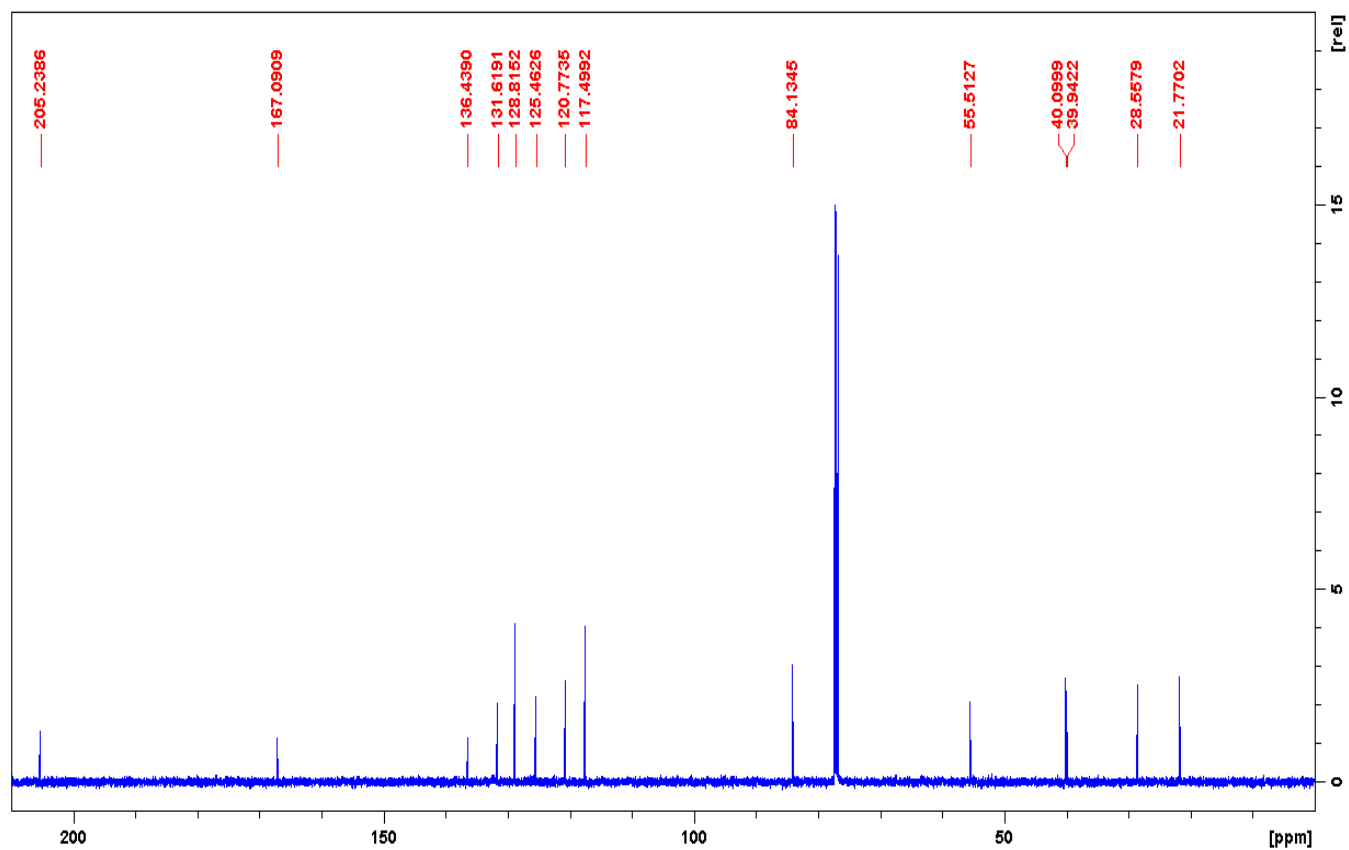
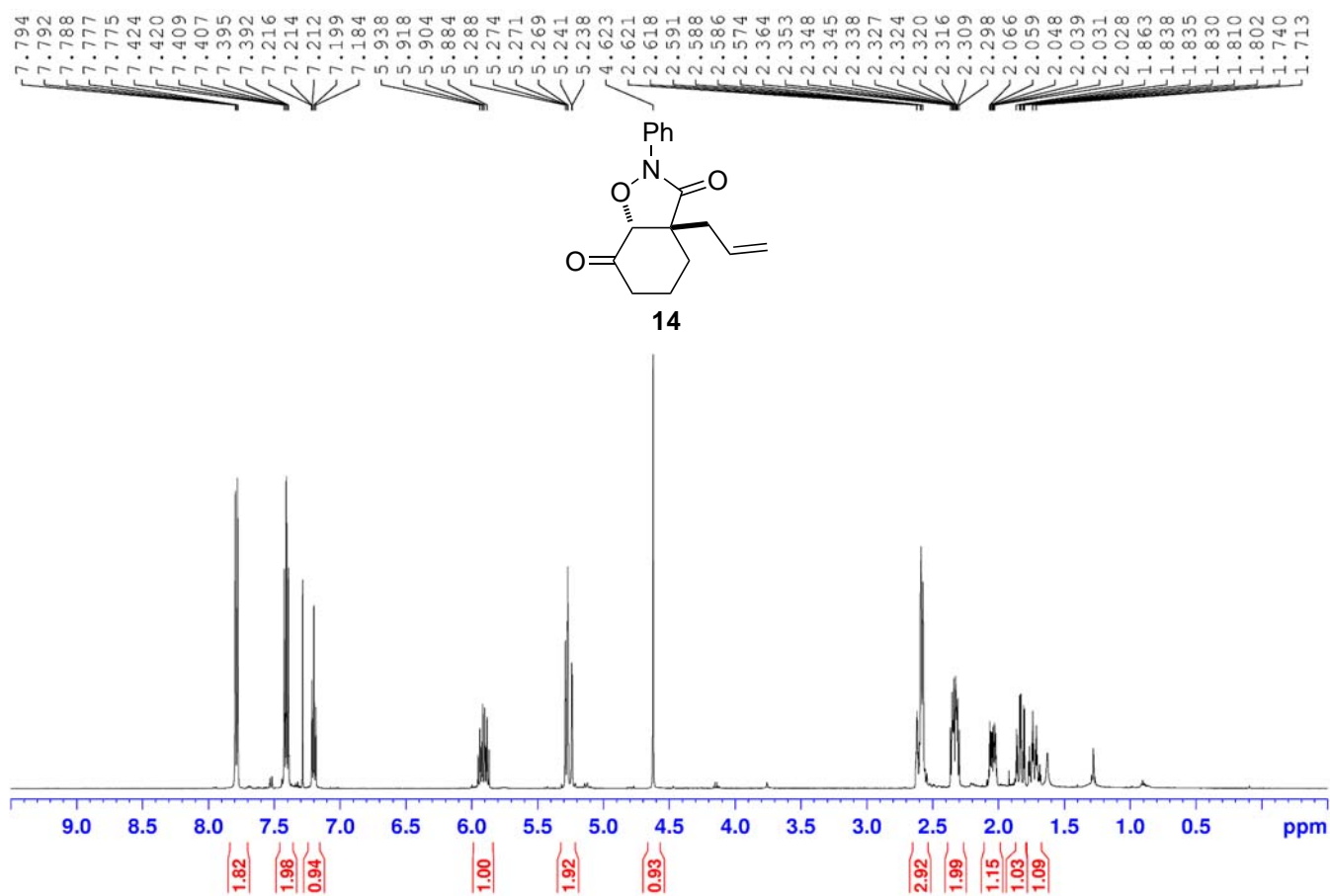


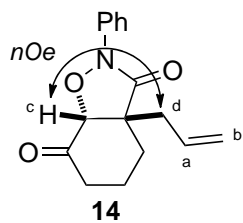


An nOe observed between H_a and H_b confirms a *cis* ring junction.

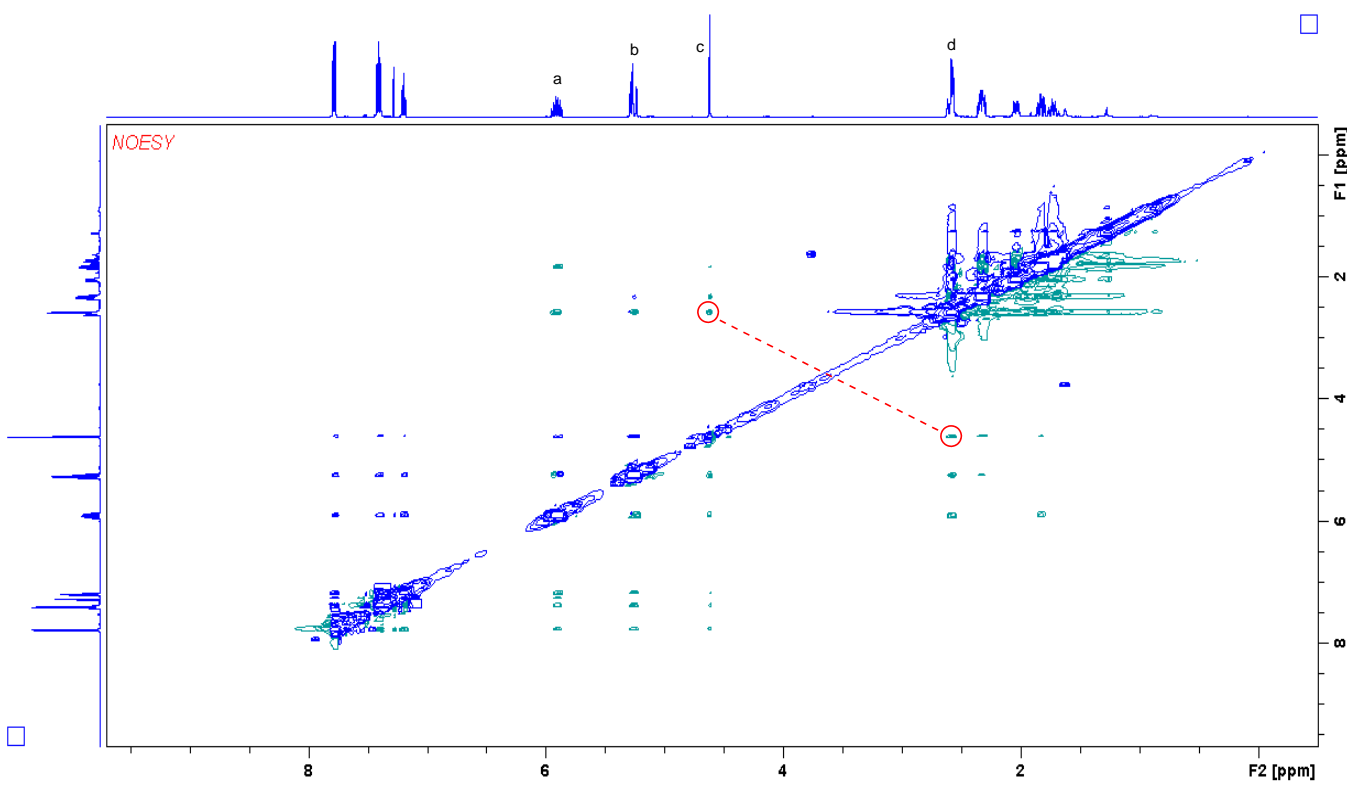
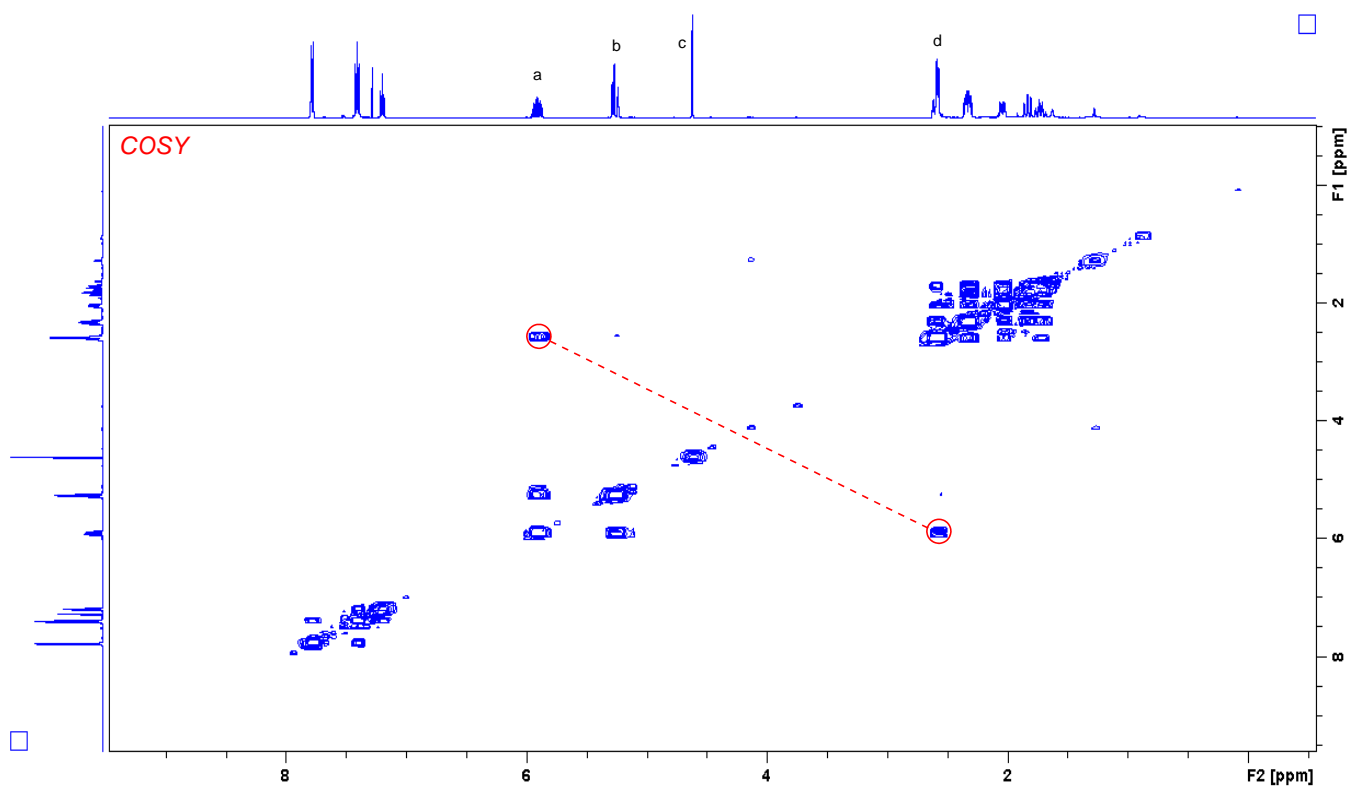


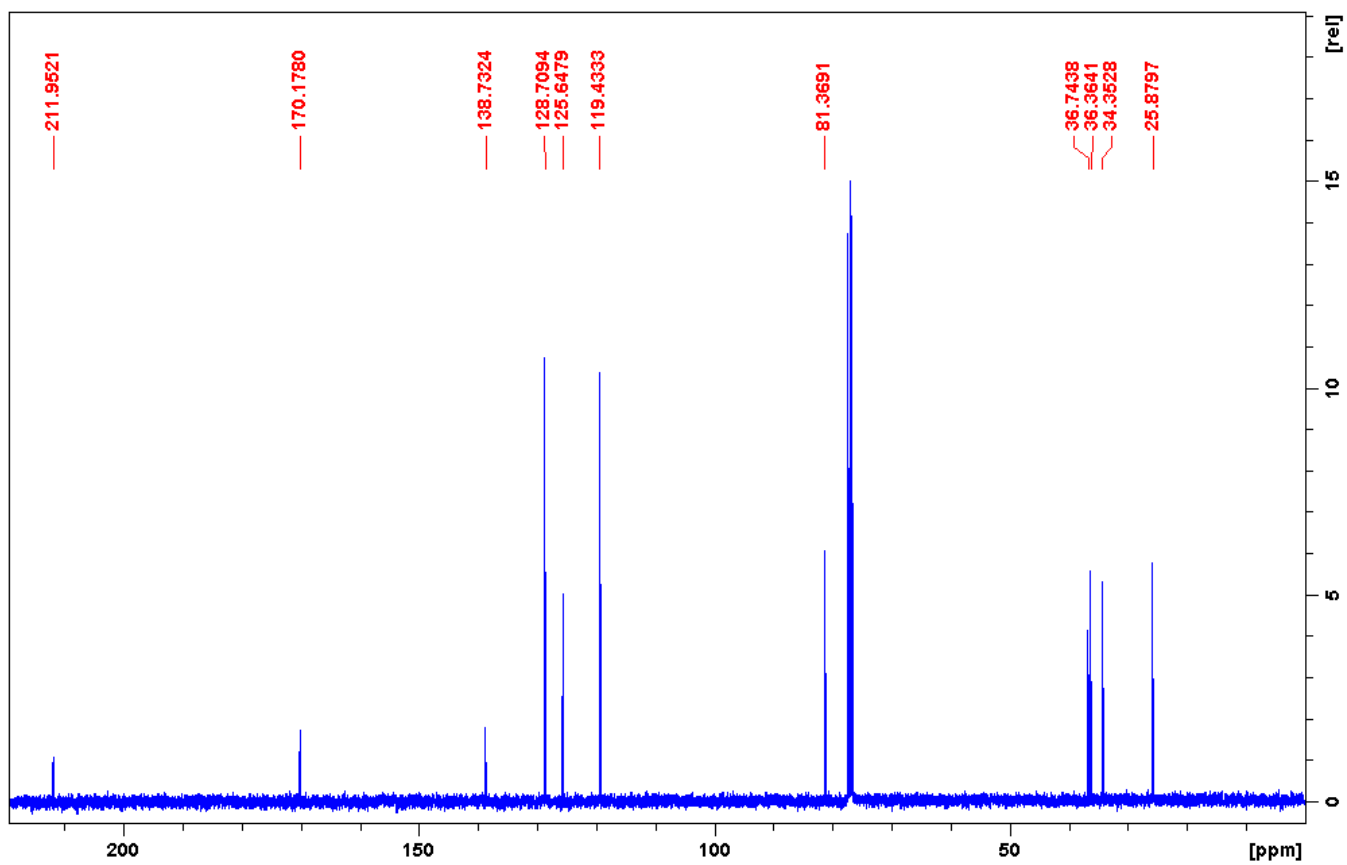
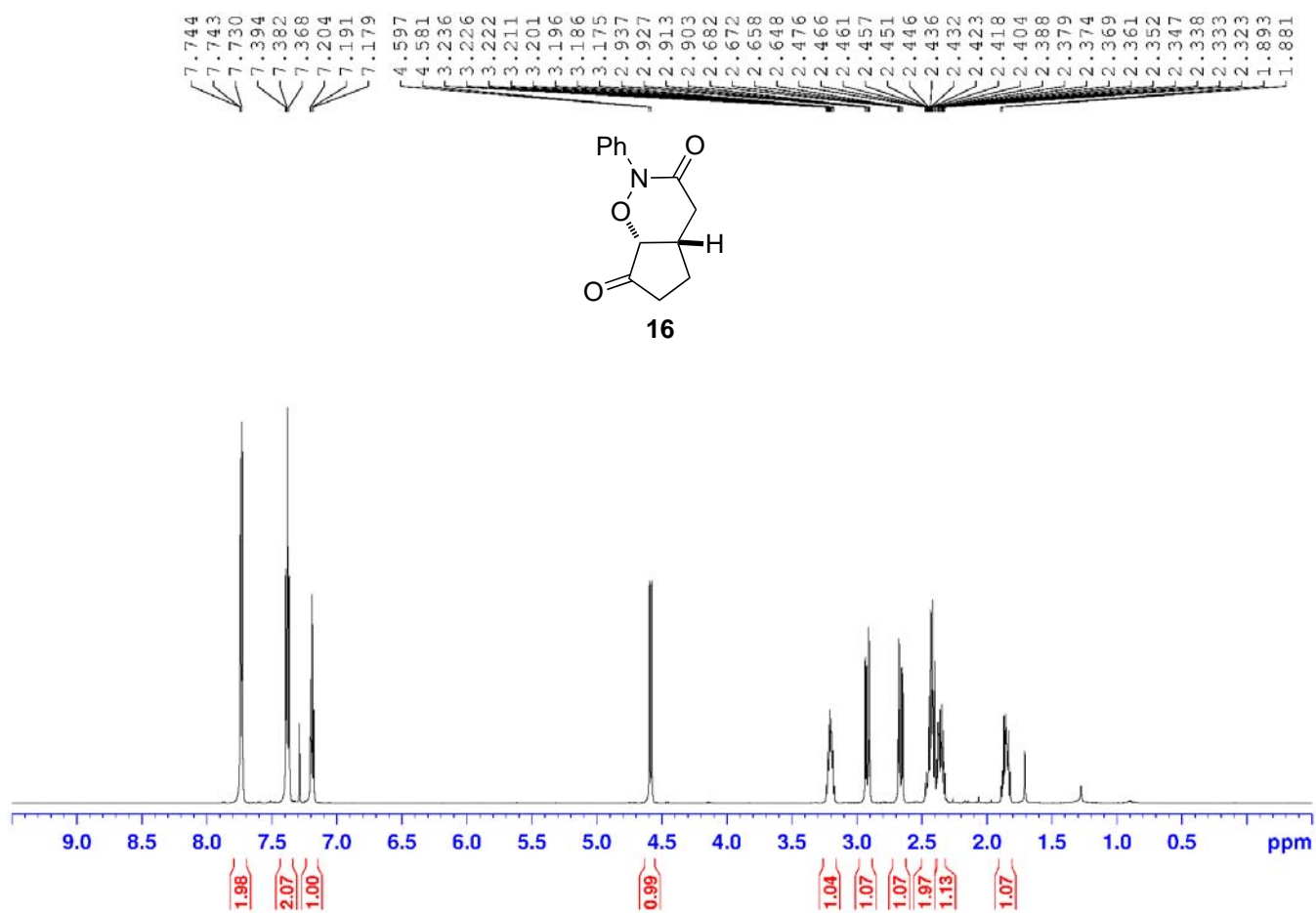


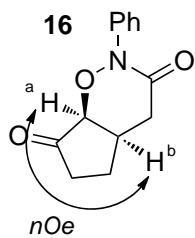




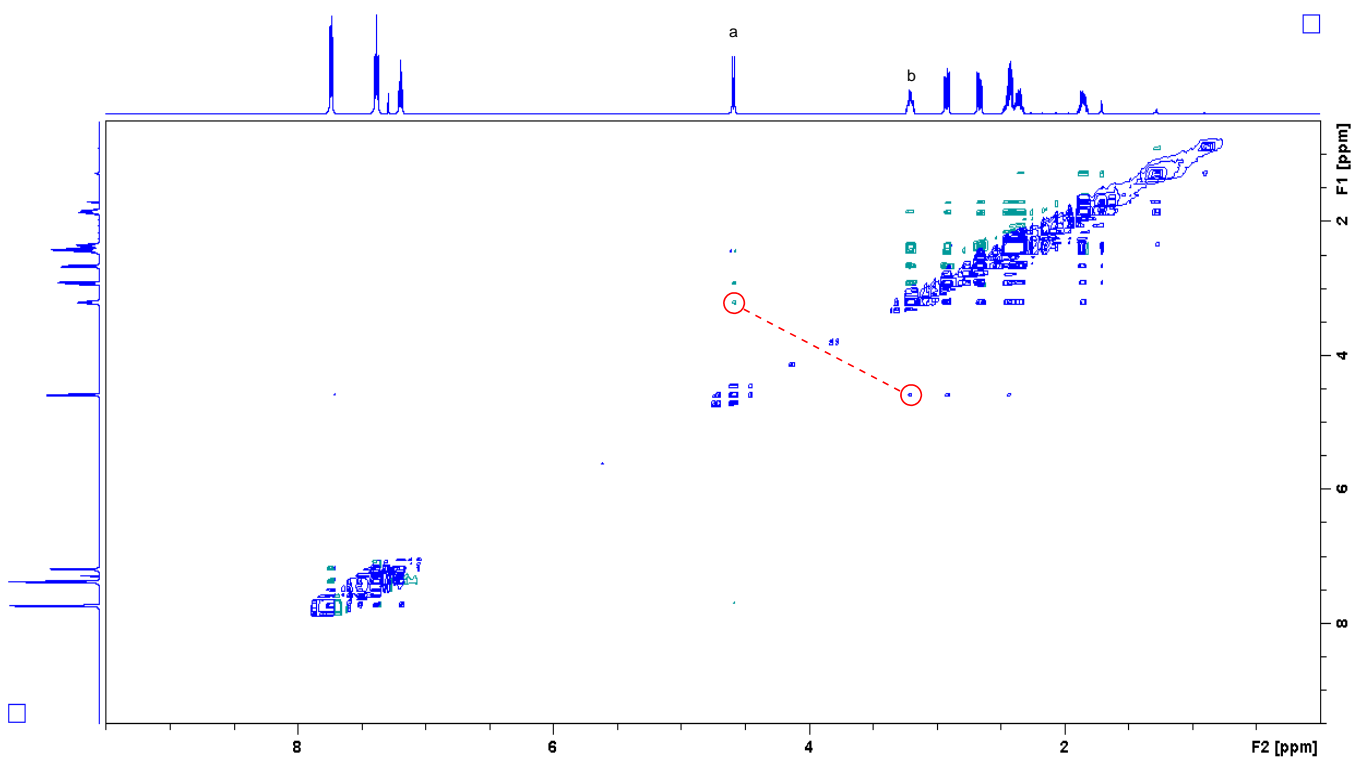
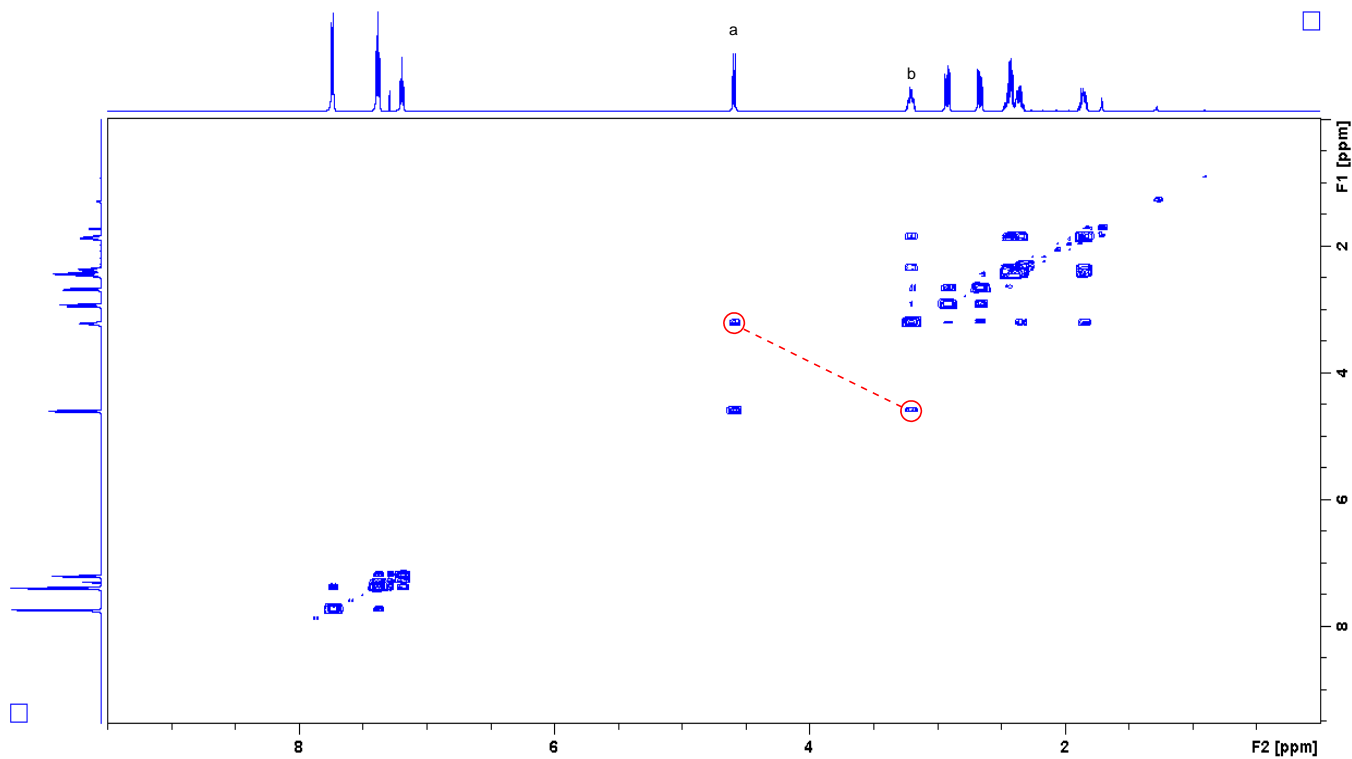
The strong COSY between H_a and the multiplet at 2.6 ppm identifies H_d.
The nOe between H_c and H_d indicates that the ring junction is *cis*.

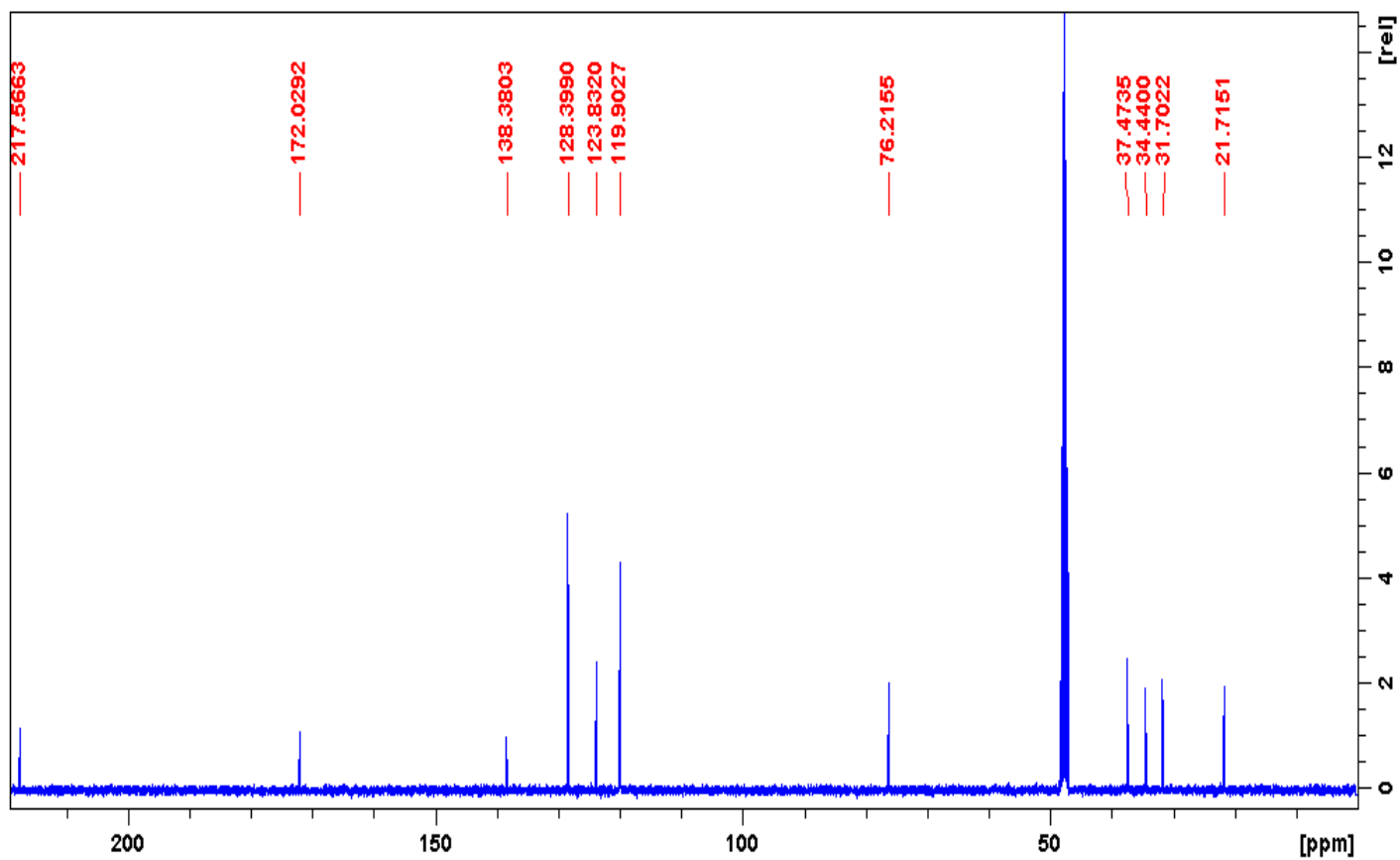
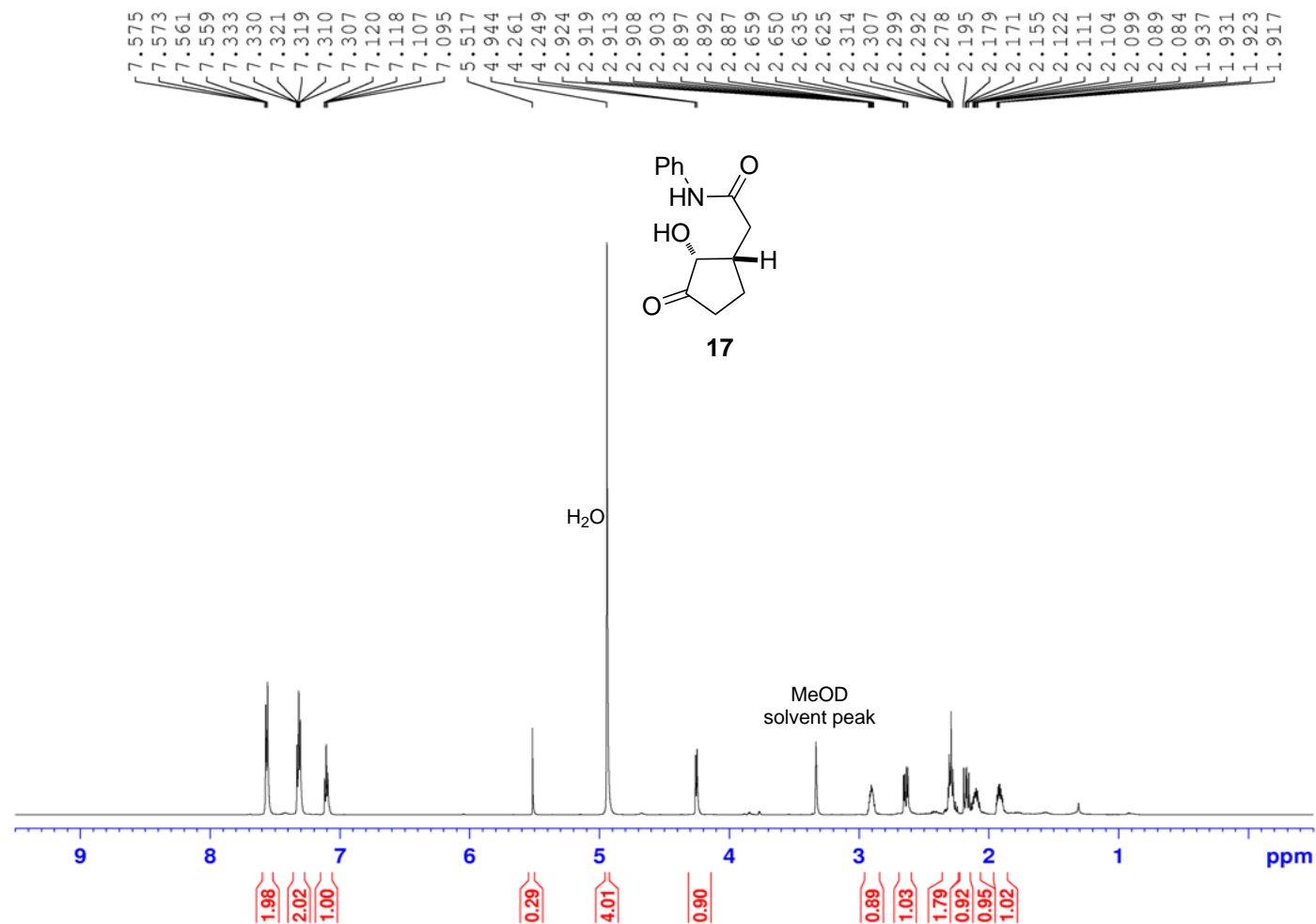


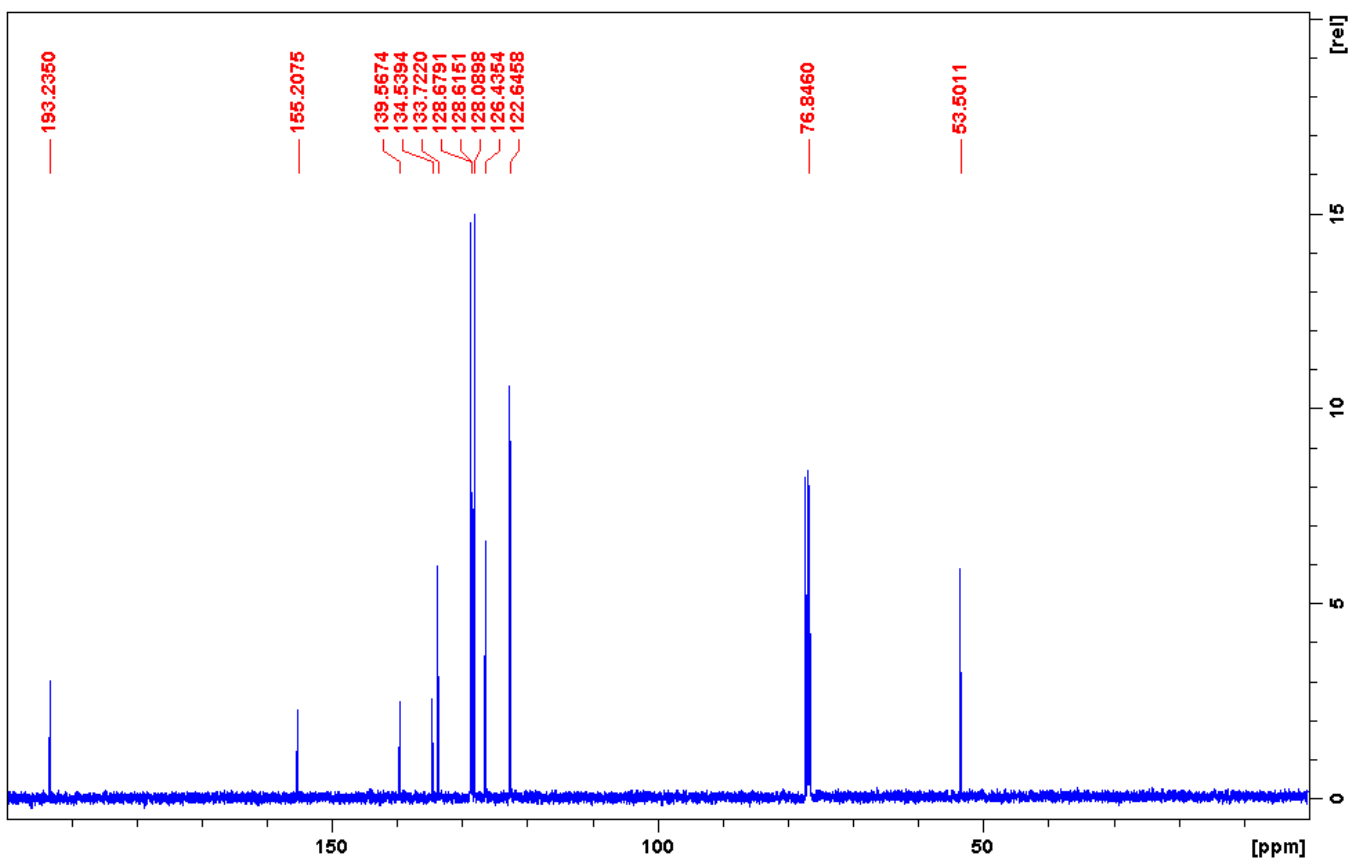
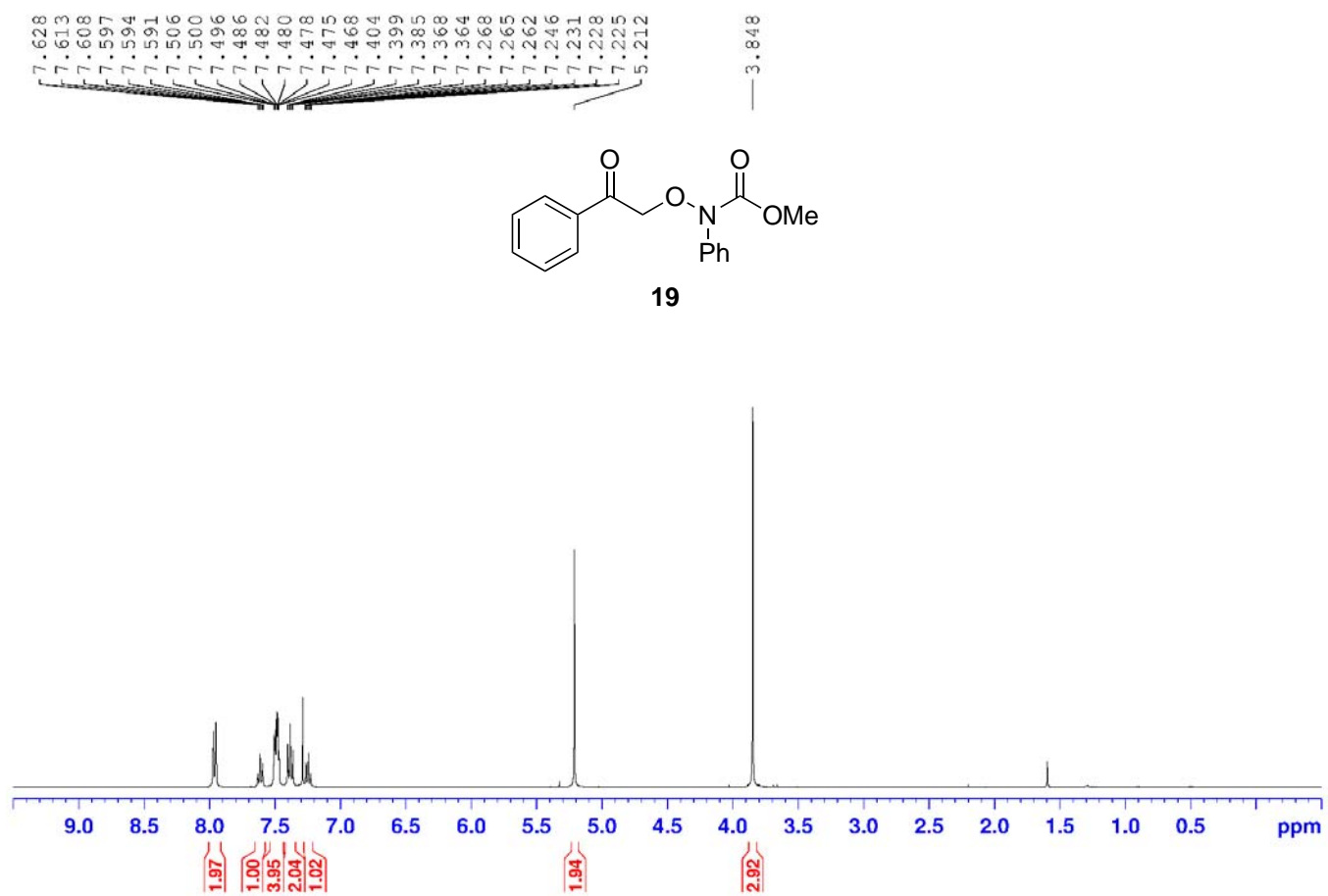


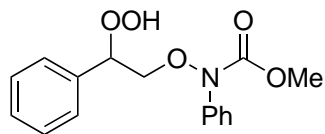
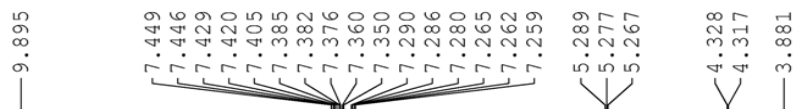


The strong COSY between H_a and the multiplet at 3.2 ppm identifies H_b .
The nOe between H_a and H_b indicates that the ring junction is *cis*.
Additionally, H_a appears as a doublet at 4.3 ppm, $J = 9.4$ Hz.

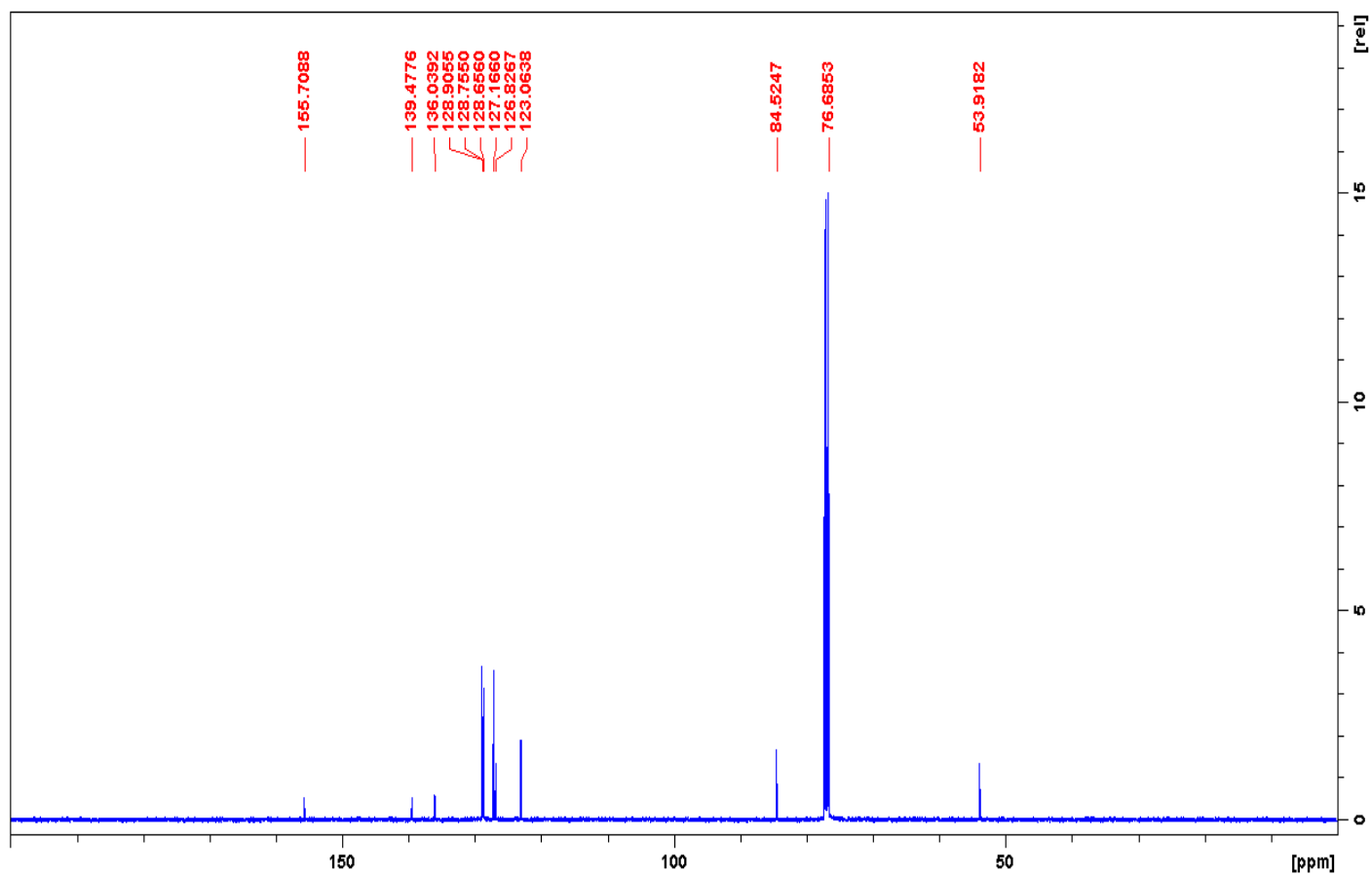
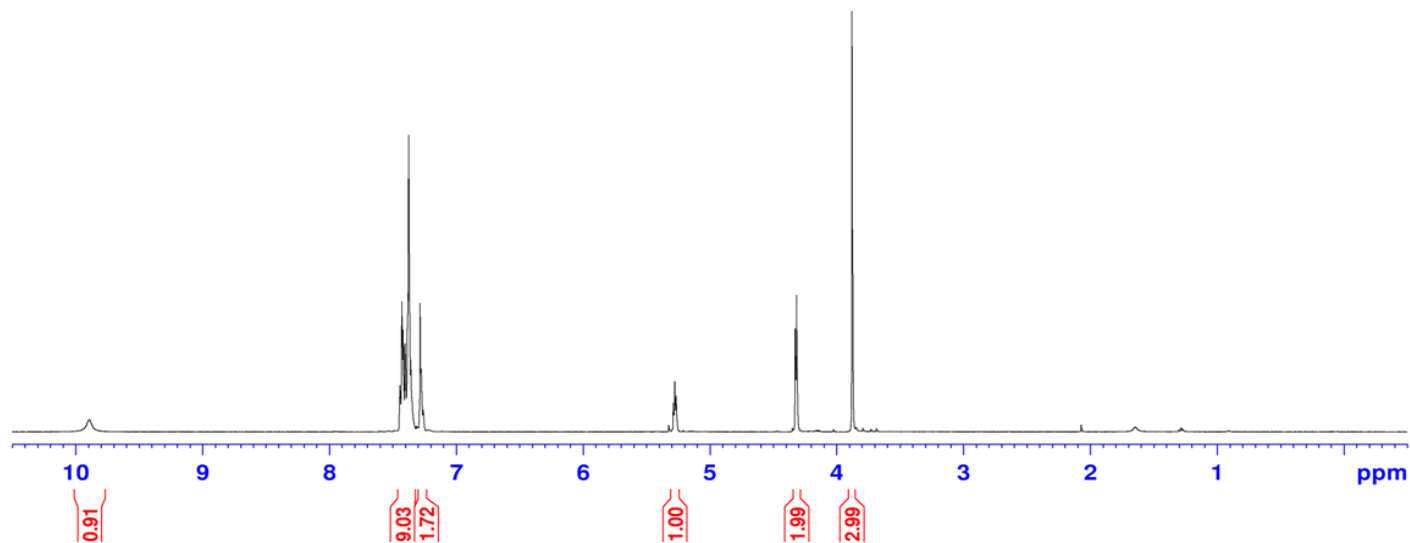


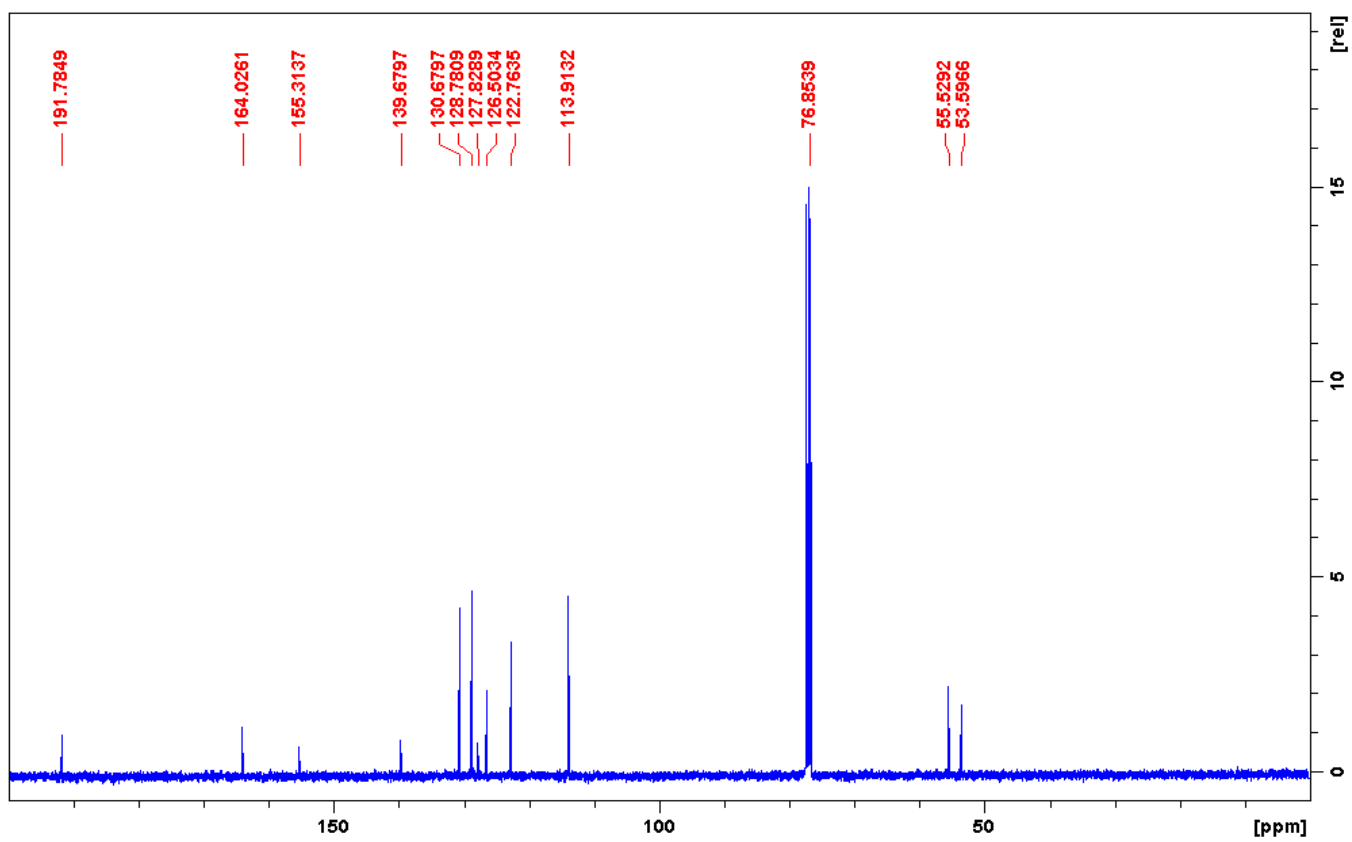
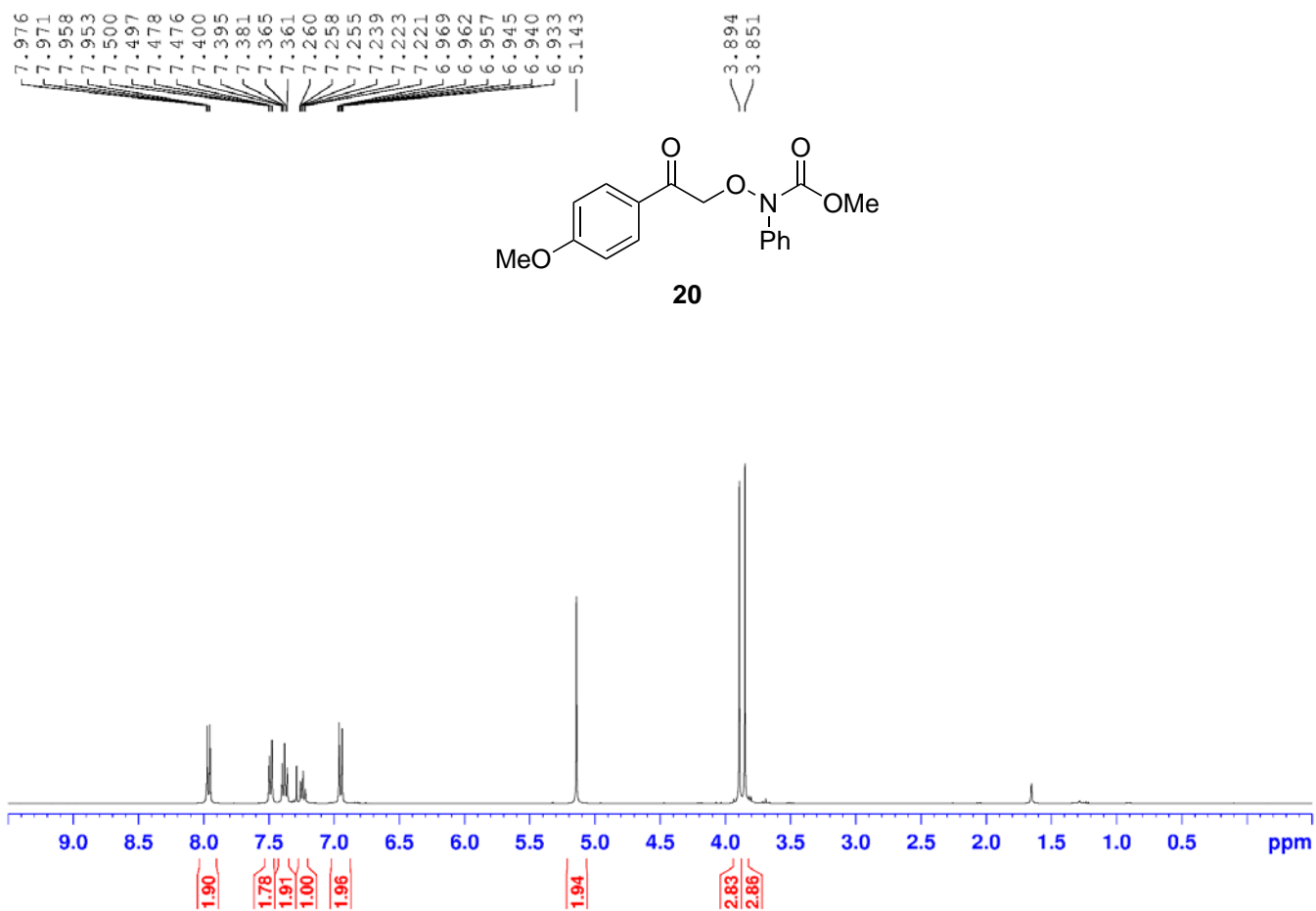


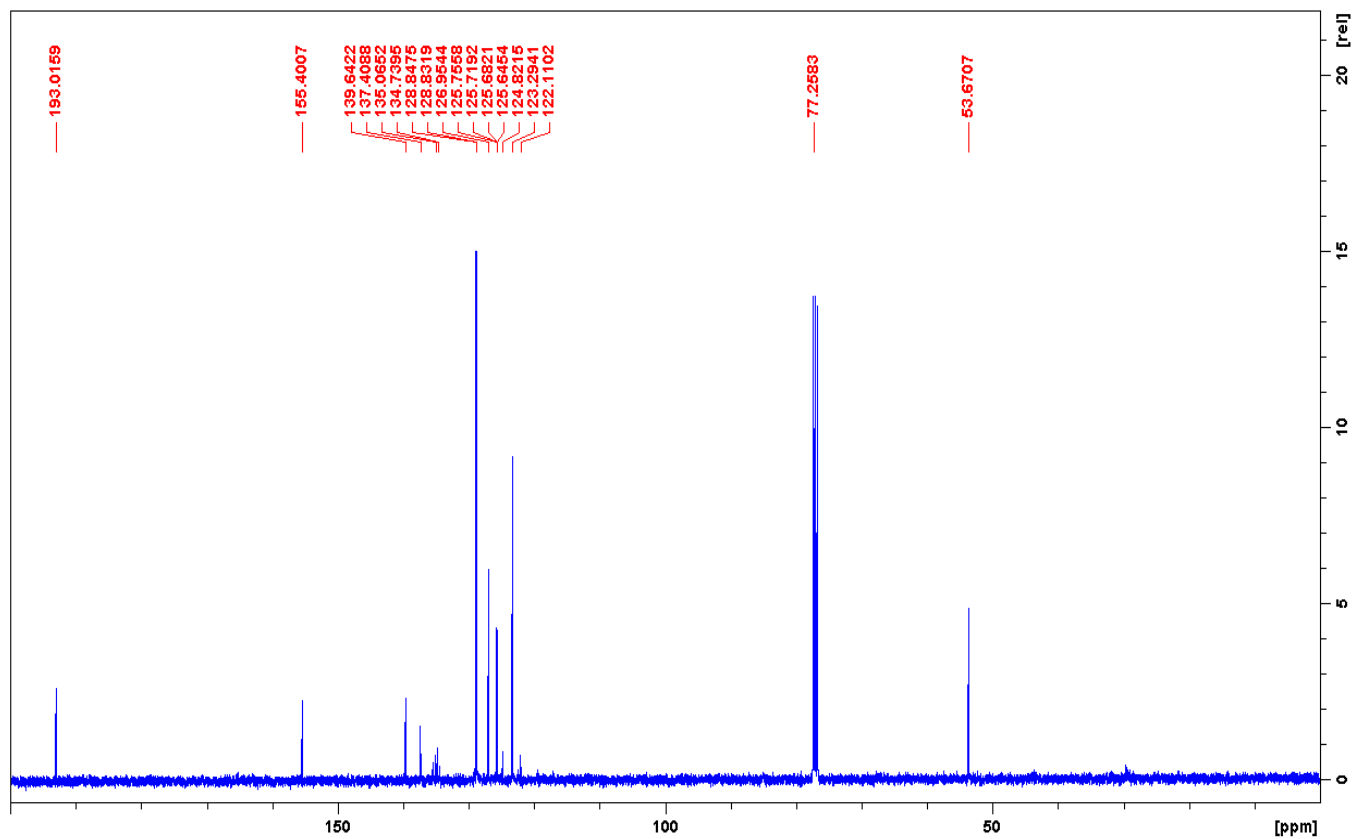
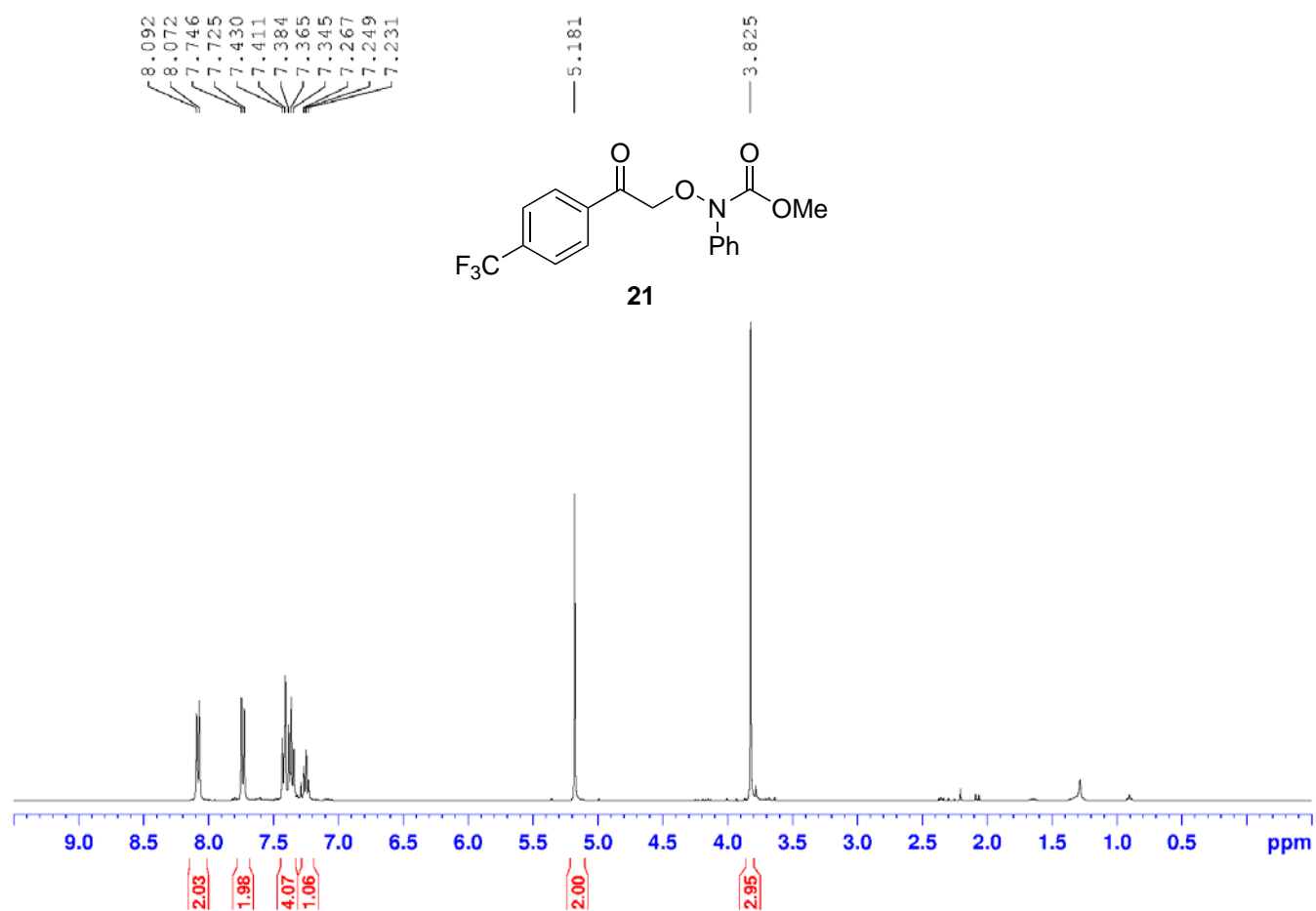


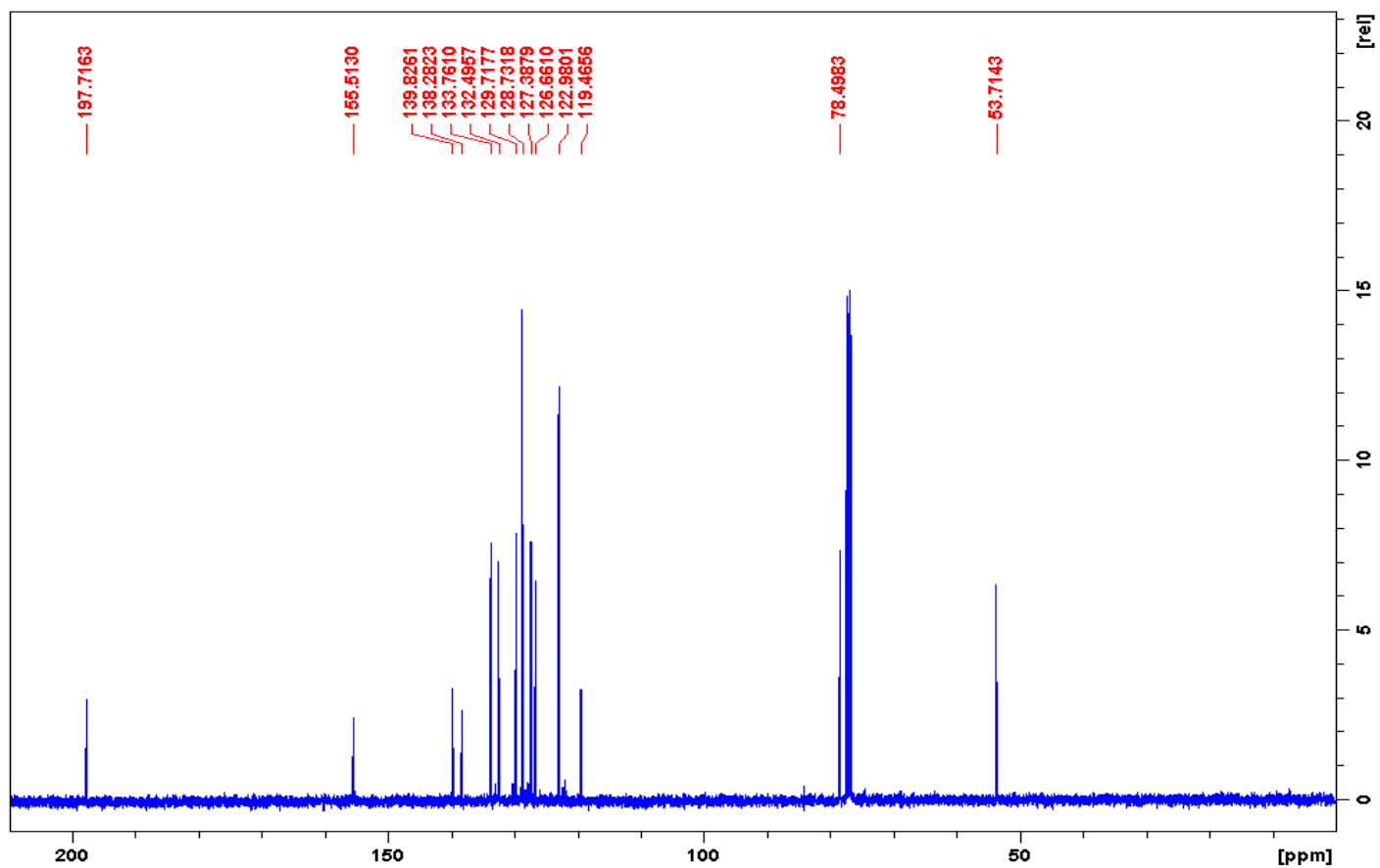
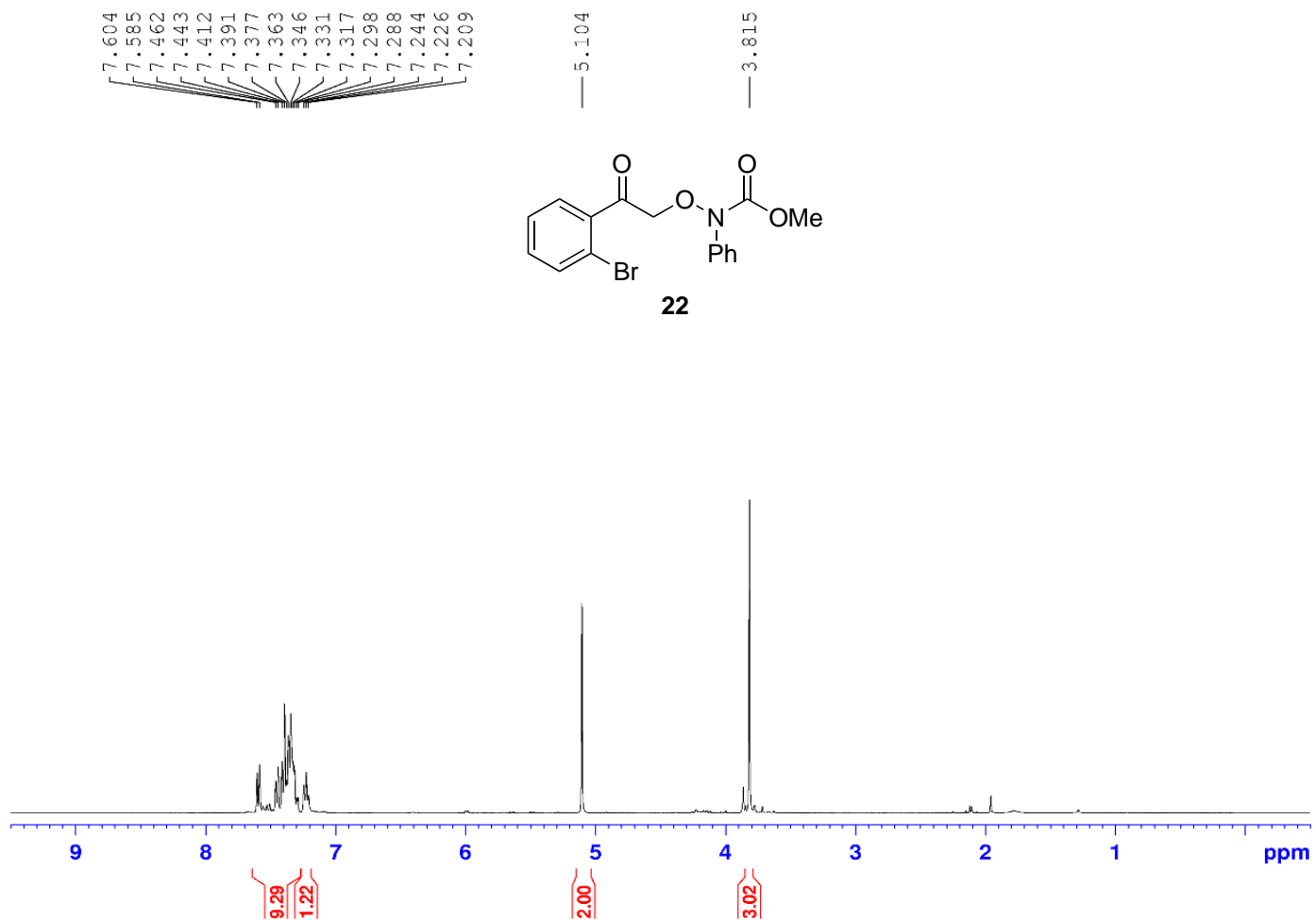


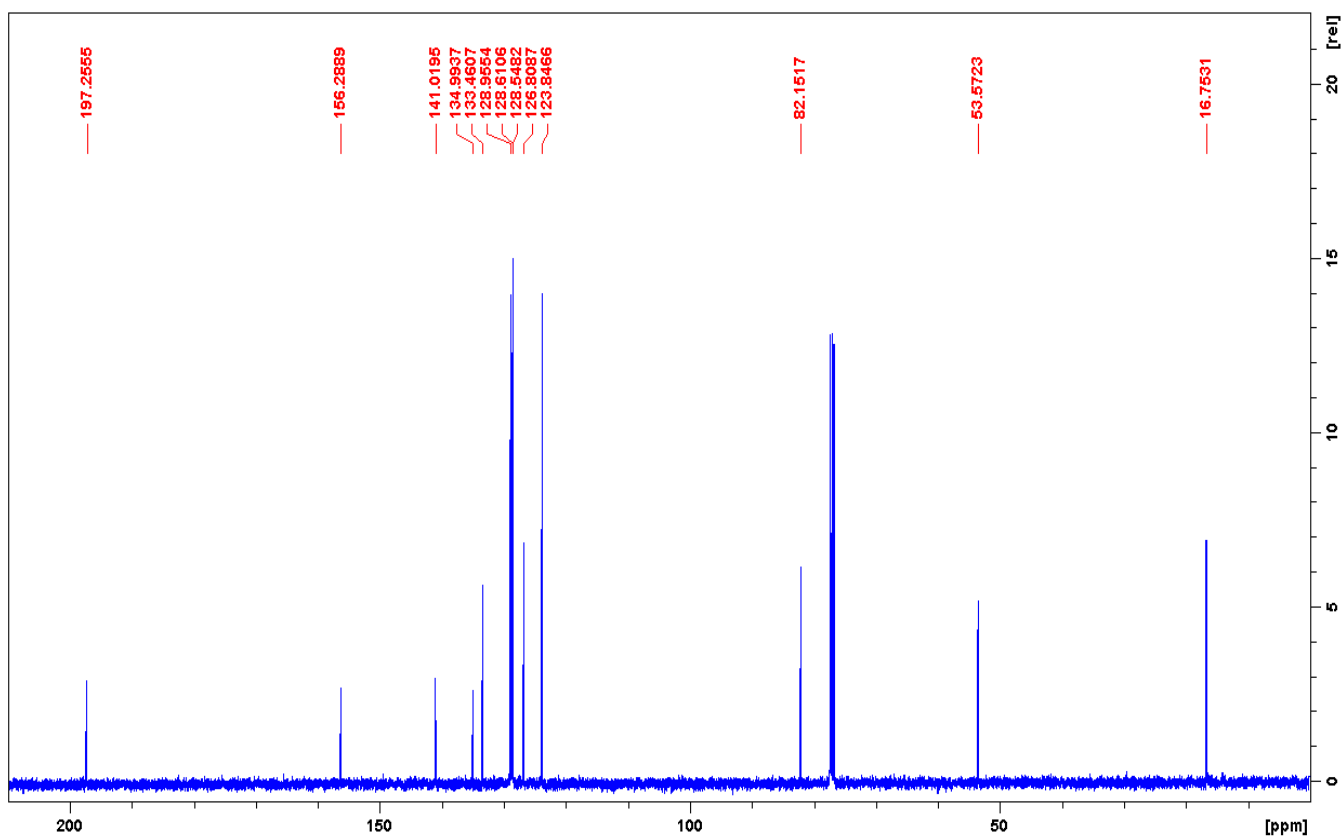
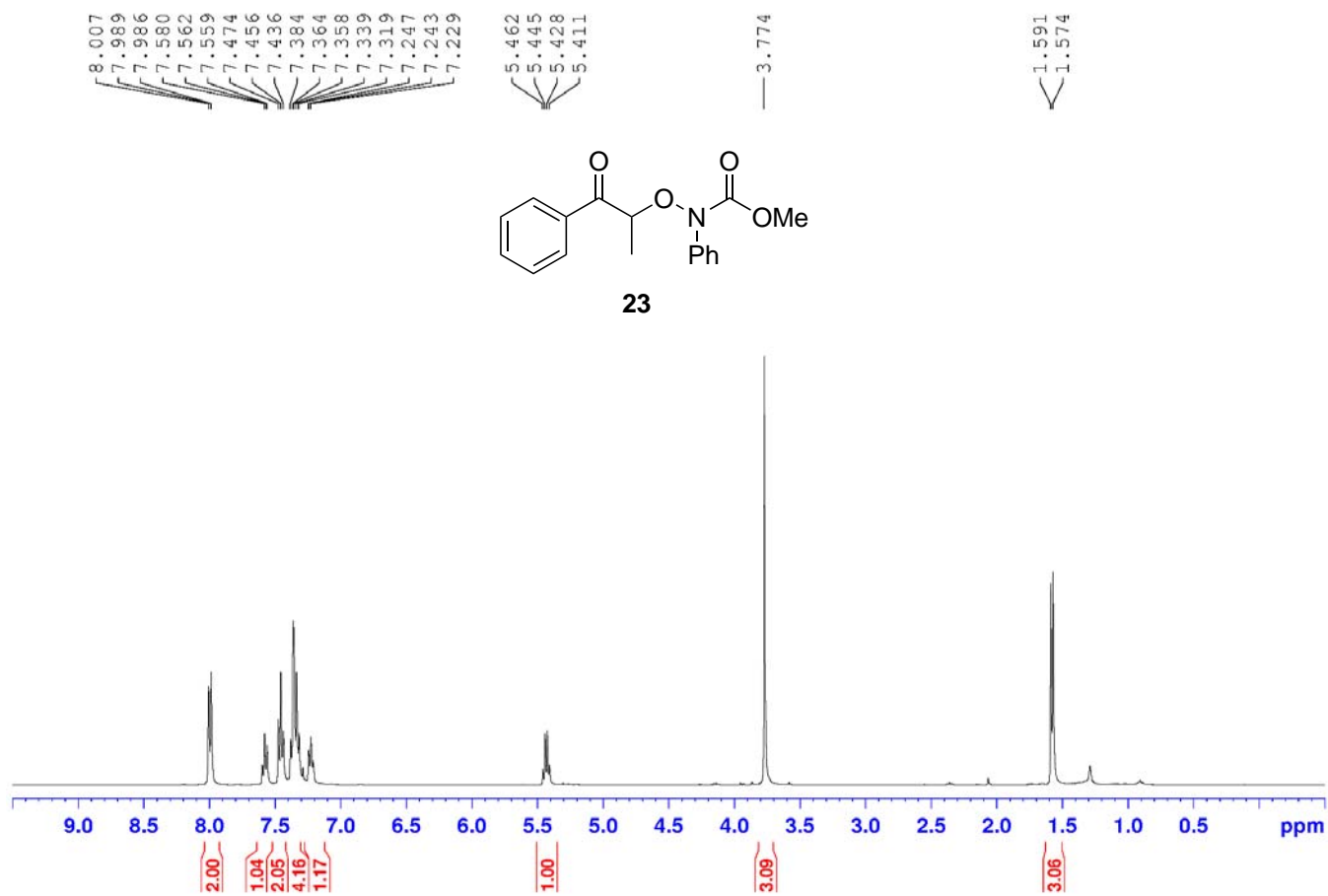
SI-4

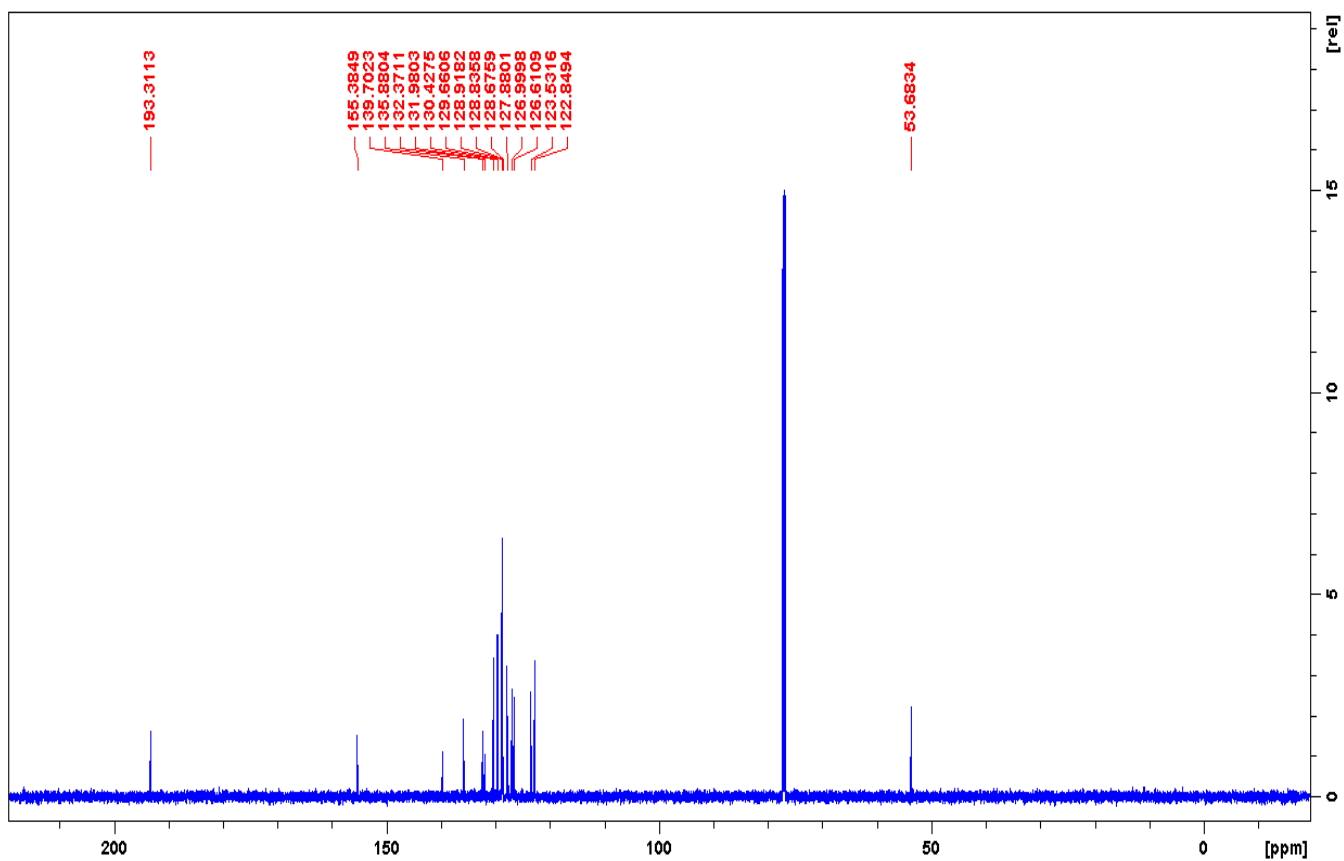
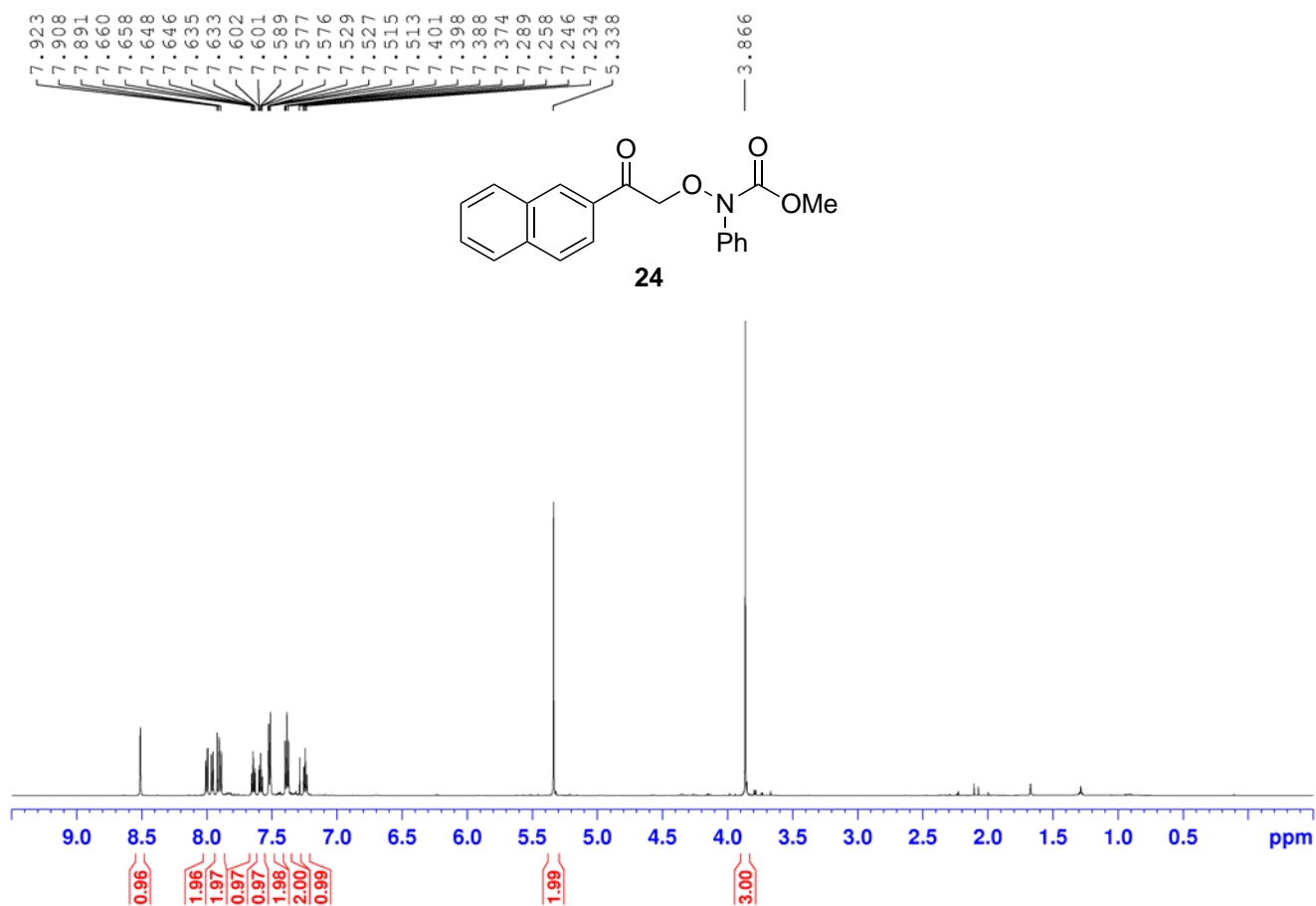


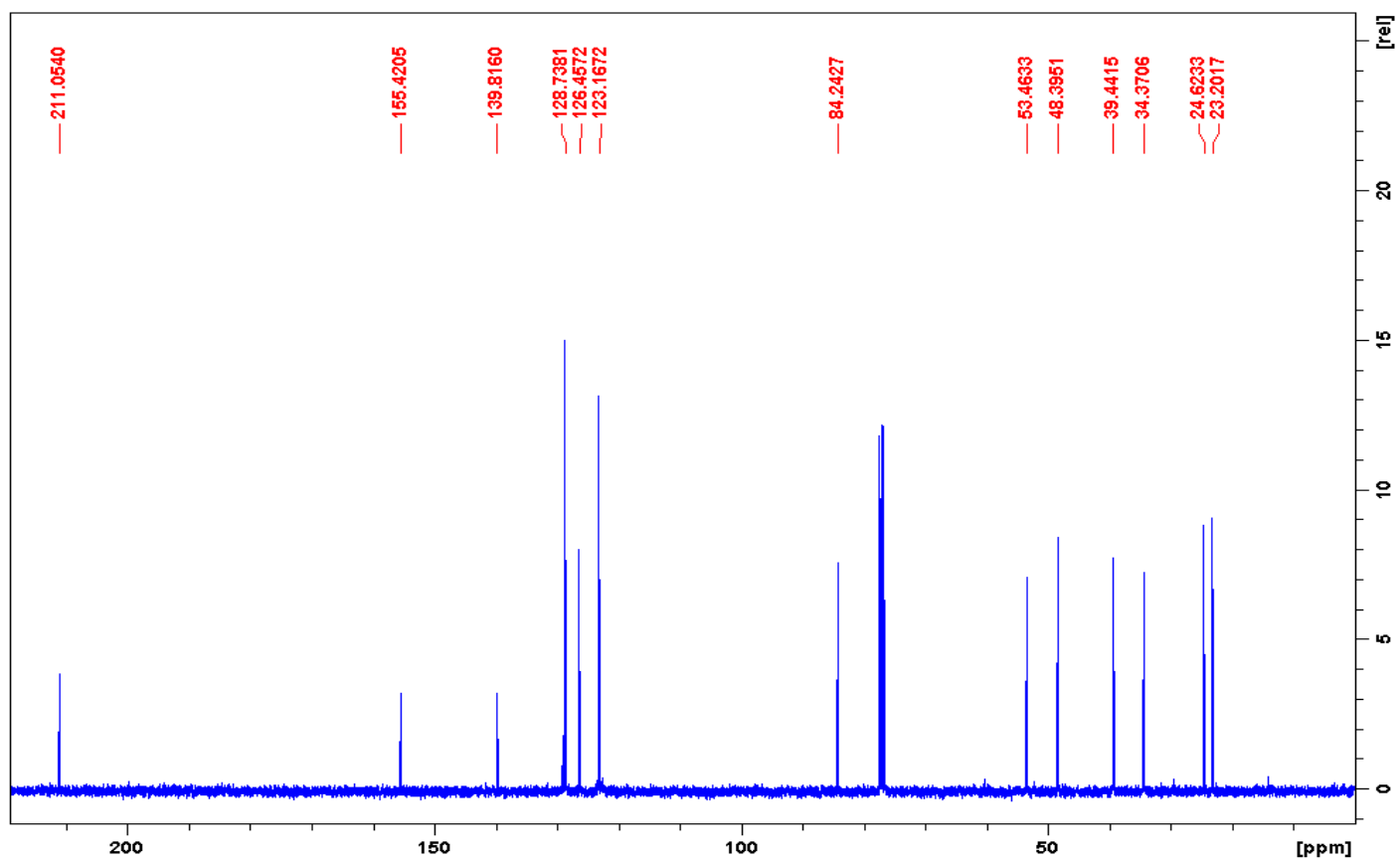
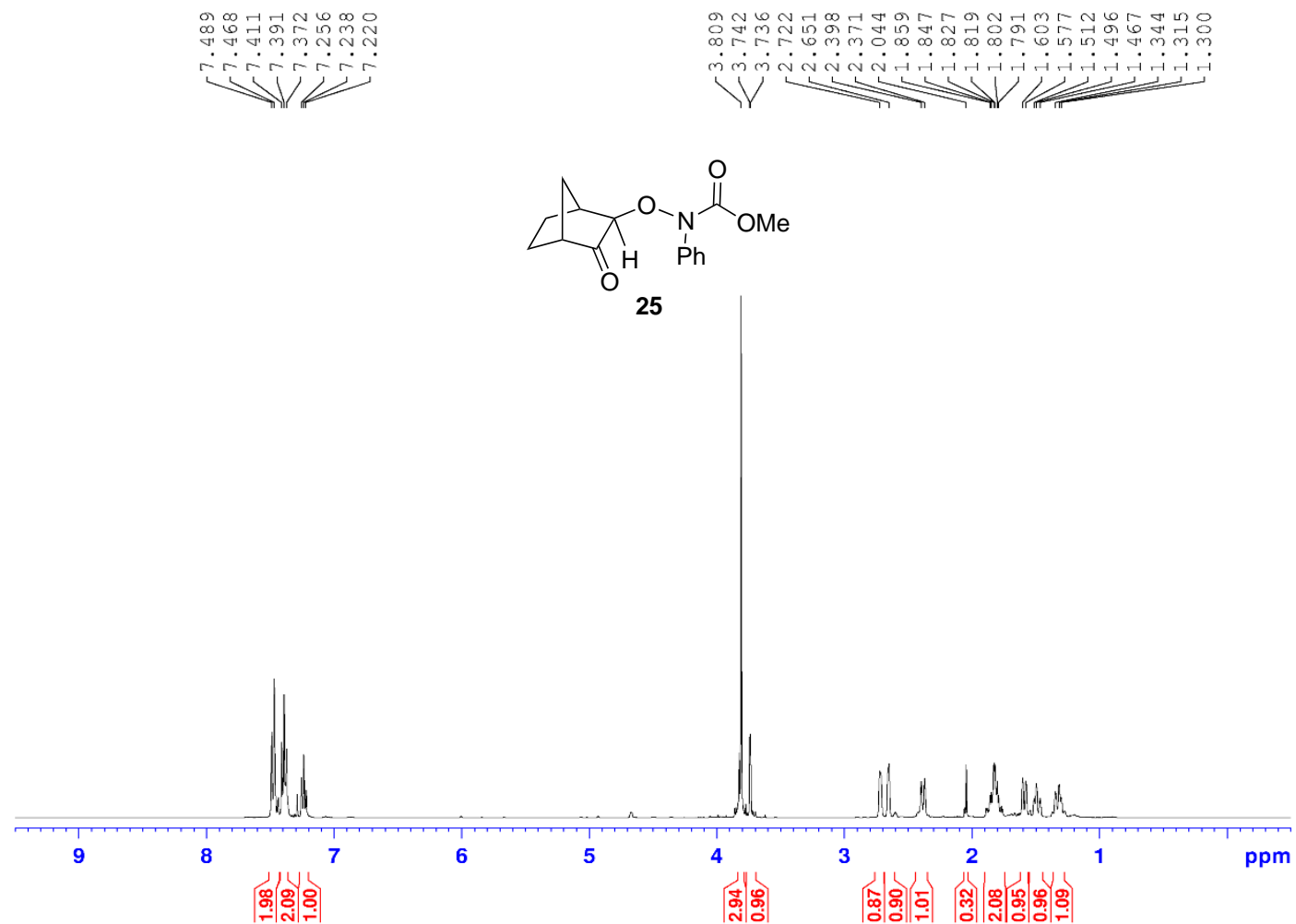


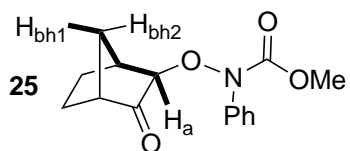












By analogy to our previously reported dioxygenation of norbornene and in conjunction with the strong COSY observed between H_a and H_{bh1} and the absence of an nOe between H_a and H_{bh2} , we assign the stereochemistry shown to the left.

