Supporting Information

Radical Carbooxygenations of Alkenes Using Hydroxamic Acids

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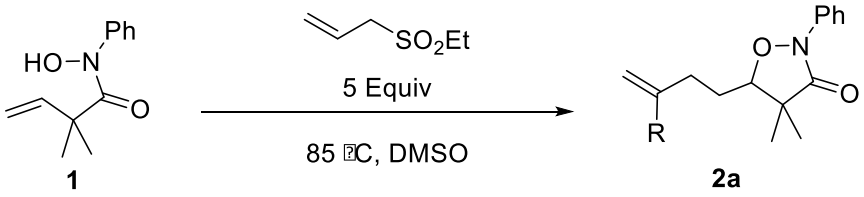
General Methods

Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400, DRX 500, or a Bruker AVANCE III 600 CryoProbe (^{1}H NMR at 400, 500 or 600 MHz and ^{13}C NMR at 100, 126 or 151 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.28 ppm, C_6D_6 at 7.16 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tdd = triplet of doublet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a Micromass Quattro II (triplequad) equipped with nanoelesctrospray ionization. Thin layer chromatography (TLC) was performed on SiliaPlate 250µm 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.

Table S1: Additive Optimization for Oxyallylation of **1**

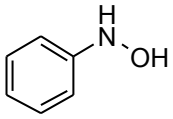


1 **2a**

Entry	Additive	mol %	Time [h]	Yield [%]
1	$PhSO_2NH_2$	10	48	43
2	$PhSO_2NH_2$	20	40	52
3	$PhSO_2NH_2$	50	36	53
4	$PhSO_2NH_2$	100	36	52
5	$TolSO_2NHSO_2Tol$	50	40	32
6	trifluoro-methanesulfonic acid amide	50	10	18
7	1,4-benzoquinone	20	22	38
8	1,4-benzoquinone	50	20	44

All reactions were carried out according to oxyallylation general **Method A** outlined below (S8).

Compound Preparation

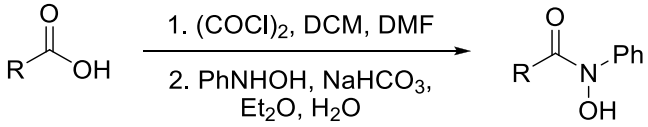


N-Phenylhydroxylamine was synthesized according to literature procedures.[1,2] Physical and spectral data were in accordance with literature data.[3]

[1] Evans, D.A.; Song, H.J.; Fandrick, K.R. *Org. Lett*., **2006**, *8*, 3351.
[2] Schmidt, V.A.; Alexanian, E.J. *Angew. Chem. Int. Ed.* **2010**, *49*, 4491.
[3] Corminboeuf, O.; Renaud, P. *Org. Lett.* **2002**, *4*, 1731.

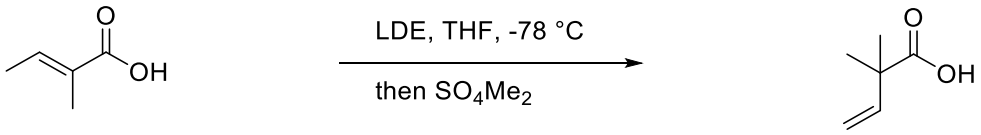
General Procedure for Preparation of *N*-Phenyl Hydroxamic Acids[3]

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



To a 0 ºC 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 ºC for 15 min. then warmed to room temperature for 40 min. The resultant yellow solution was evaporated almost to dryness under reduced pressure before sodium bicarbonate (2 mmol) was added and redissolved in H_2O/Et_2O (1 mL/2 mL). The solution was then again cooled to 0 ºC and phenylhydroxylamine (1 mmol) was added and the reaction was stirred at 0 ºC until phenylhydroxylamine has been consumed as visualized by TLC. The layers were separated, the aqueous layer was acidified with 1 M $NaHSO_4$ and extracted with Et_2O (x 3). The combined organic layers were then washed with brine, dried ($MgSO_4$), and concentrated to give an oil that was purified by flash chromatography to yield the corresponding *N*-phenyl hydroxamic acid.

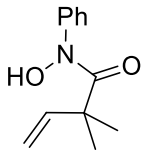
Synthesis of 1



The corresponding carboxylic acid of **1** was synthesized via an alkylation of tiglic acid with dimethylsulfate as previously described.[2]

The procedure is as follows: Under a gentle stream of Ar, Hexanes was removed from a commercially available solution of n-BuLi (88.0 mL of a 1.52M solution, 133 mmol). The nearly dry reagent was cooled to -78 ºC, and taken up in THF (40 mL). Diethylamine (13.2 mL, 128 mmol, 2.1 equiv) was added to the cold solution and the resultant mixture was warmed to 0 ºC and stirred 15 min. The reaction mixture was cooled again to -78 ºC, tiglic acid (6.00 g, 59.9 mmol, 1.0 equiv) was added as a solution in THF (65 mL) before warming to 0 ºC and stirring for 30 min. The reaction mixture was cooled again to -78 ºC and a solution of dimethylsulfate (5.67 mL, 59.9 mmol, 1.0 equiv) in THF (125 mL) was added. The reaction mixture was allowed to come to rt, stirred 1 h and then quenched by slow addition of water. The reaction mixture was extracted with EtOAc (3 x), the combined organic layers discarded; the aqueous layer was acidified using conc. HCl until cloudiness persisted, extracted with EtOAc (4 x), washed with

brine, dried ($MgSO_4$) and concentrated *in vacuo*. The crude acid product was purified via vacuum distillation to afford 2,2-dimethylbut-3-enoic acid (5.64 g, 82%) as a pale yellow liquid.

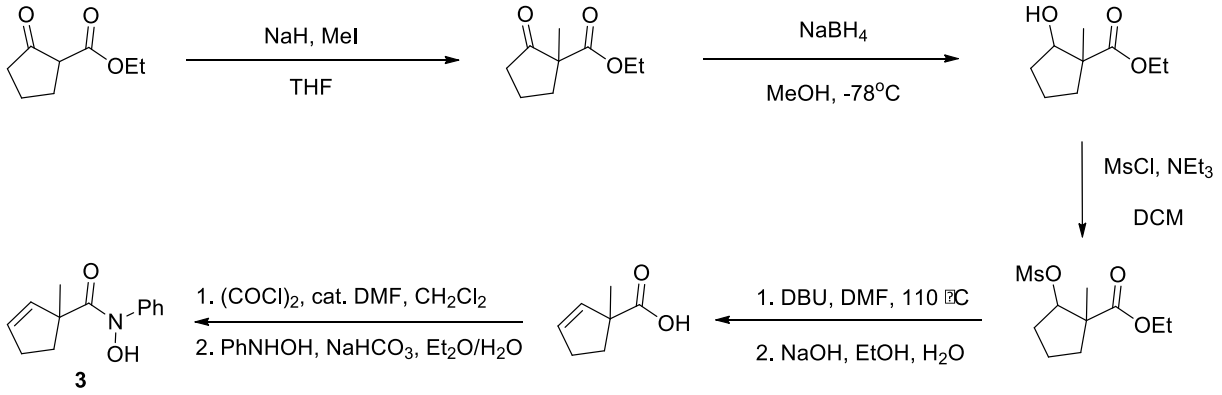


1

1 was synthesized via the general method in 58% yield (840.0 mg) as a pale yellow solid.

Analytical data for **1**: **^{1}H NMR** (500 MHz, CHLOROFORM-*d*) δ ppm 8.14 (br. s., 1 H) 7.47 (m, 2 H) 7.40 (m, 2 H) 7.34 (m, 1 H) 5.95 (m, 1 H) 4.97 (m, 2 H) 1.35 (s, 6 H) ppm; **^{13}C NMR** (126 MHz, METHYLENE CHLORIDE-d_2) 174.3, 143.2, 141.1, 128.6 (2 C), 127.3, 124.8, 112.3 (2 C), 45.2, 25.4 (2 C); **IR** (thin film, cm^{-1}) 3216, 2978, 2931, 1945, 1622, 1592, 1495, 1384, 1355, 1235, 1184, 1084, 1068, 913, 759, 701; **HRMS** (ESI) Calcd. for $[C_{12}H_{15}NO_2+Na]^+$ = 228.10, Found = 228.10. (For NMR spectra see ref. 2)

Synthesis of 3, and general route to 5 and 7

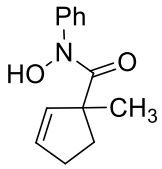


3

The corresponding carboxylic acid of **3** was synthesized according the procedure developed by S. Pichlmair *et. al.*[4] outlined above. Procedure for the saponification of ethyl 1-methylcyclopent-2-enecarboxylate follows: The crude ester (1.16 g, 7.52 mmol) was heated to reflux in a solution of EtOH (8 mL) and NaOH (400 mg, 10 mmol) for 2 h. The reaction mixture was diluted with Et_2O and acidified with 1N HCl. The aqueous layer was extracted with Et_2O (4 x) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated to give crude acid product that was purified via flash

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

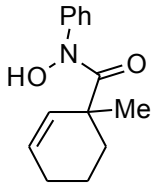
chromatography (20% EtOAc/Hexanes) to give 1-methylcyclopent-2-enecarboxylic acid (619 mg, 4.91 mmol, 65%) as a pale liquid. Physical and spectral data were in accordance with literature data.[5]



3

3 was synthesized via the general procedure in 75% yield (641.0 mg) as pale yellow solid.

Analytical data for **3**: **^{1}H NMR** (400 MHz, CHLOROFORM-*d*) δ ppm 8.53 (br. s., 1 H) 7.41 (m, 5 H) 5.56 (m, 1 H) 5.50 (m, 1 H) 2.39 (m, 1 H) 2.29 (m, 2 H) 1.70 (ddd, *J*=12.63, 7.58, 4.89 Hz, 1 H) 1.30 (s, 3 H) ppm; **^{13}C NMR** (126 MHz, METHYLENE CHLORIDE-d_2) 175.5, 141.1, 135.6 (2 C) 130.3, 128.6 (2 C), 127.3, 124.8, 56.2, 35.7, 31.3, 24.5; **IR** (thin film, cm^{-1}) 3200, 2930, 2850, 1622, 1592, 1494, 1454, 1381, 1065, 921, 758, 694; **LRMS** (ESI) Calcd. for $[C_{13}H_{15}NO_2+Na]^+$ = 240.10, Found = 240.10. (For NMR spectra see ref. 2)



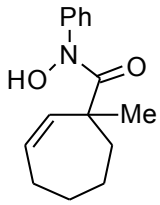
5

The corresponding carboxylic acid of **5** was synthesized via the same route as 1-methylcyclopent-2-enecarboxylic acid (see above), beginning with the cyclohexane analog. **5** was synthesized via the general procedure in 80% yield (790.0 mg) as an off-white solid.

Analytical data for **5**: **^{1}H NMR** (CHLOROFORM-*d*, 500MHz): d = 8.74 (br. s, 1 H), 7.32 - 7.45 (m, 5 H), 5.44 (m, 1 H), 5.10 - 5.39 (m, 1 H), 2.26 - 2.37 (m, 1 H), 1.80 - 1.97 (m, 2 H), 1.56 - 1.68 (m, 2 H), 1.38 (ddd, *J*=12.8, 8.4, 4.2 Hz, 1 H), 1.29 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 126 MHz) 174.0, 140.2, 130.9, 128.8, 128.6, 127.4, 127.2, 43.4, 33.9, 26.4, 24.5, 19.5 ; **IR** (thin film, cm^{-1}) 3205, 3036, 2933, 2871, 2834, 1615, 1591, 1491, 1452, 1355, 1306, 1066, 758, 695; **LRMS** (ESI) Calcd. for $[C_{14}H_{17}NO_2+Na]^+$ = 254.12, Found = 254.14.

Hydroxamic acid **15** was prepared via the same route as **5,** but alkylation was carried out using allyl bromide.

[5] Burger, U.; Zellweger, D. *Helv. Chim. Acta.* **1986**, *69*, 676.



7

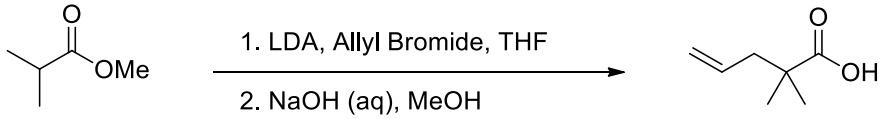
The corresponding carboxylic acid of **7** was synthesized via the same route as 1-methylcyclopent-2-enecarboxylic acid (see above), beginning with the cycloheptane analog.

Spectral data for 1-methylcyclohept-2-enecarboxylic acid : **^{1}H NMR** (CHLOROFORM-*d*, 400MHz): δ = 10.94 - 12.90 (m, 1 H), 5.84 (dt, *J*=11.7, 6.0 Hz, 1 H), 5.61 (dd, *J*=11.7, 0.6 Hz, 1 H), 2.14 - 2.21 (m, 2 H), 2.02 - 2.11 (m, 1 H), 1.77 - 1.84 (m, 2 H), 1.50 - 1.75 (m, 3 H), 1.38 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 101MHz): δ = 183.8, 134.4, 132.3, 48.4, 37.0, 28.1, 27.4, 27.1, 25.8 ppm.

7 was synthesized via the general procedure in 61% yield (544.0 mg) as an off-white solid.

Analytical data for **7**: **^{1}H NMR** (CHLOROFORM-*d*, 400MHz): δ = 7.30 - 7.60 (m, 5 H), 5.45 (br. s., 1 H), 4.91 - 5.28 (m, 1 H), 2.27 (ddd, *J*=13.5, 5.7, 3.6 Hz, 1 H), 1.72 - 2.09 (m, 4 H), 1.43 - 1.65 (m, 3 H), 1.32 - 1.39 (m, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 126 MHz) 174.4, 171.7, 171.2, 170.7, 140.6, 136.5, 136.0, 131.0, 128.7, 127.9, 126.0, 125.0, 124.7, 117.1, 117.0, 116.8, 87.5, 85.5, 85.4, 84.0, 51.0, 49.0, 48.3, 47.7, 38.3, 37.4, 34.8, 31.9, 30.7, 29.5, 28.3, 27.2, 26.5, 26.3, 23.8, 23.7 ppm (*Note*: Due to the high reactivity of this hydroxamic acid, it was only able to be isolated in 90% purity; therefore oxyallylation reactions were performed immediately following isolation); **IR** (thin film, cm^{-1}) 3237, 3019, 2927, 2860, 1698, 1668, 1623, 1593, 1495, 1453, 1373, 1352, 757, 690; **LRMS** (ESI) Calcd. for $[C_{15}H_{19}NO_2+Na]^+$ = 268.13, Found = 268.15.

Synthesis of 9

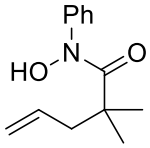


The corresponding carboxylic acid of **9** was synthesized according the procedure developed by Trost *et. al* [6] followed by base hydrolysis of the alkylated ester.

The procedure is as follows: A 2.5M solution of n-BuLi in Hexanes (12.9 mL, 32.3 mmol, 1.1 equiv) was added to a -78 ºC solution of diisopropylamine (4.6 mL, 32.3 mmol, 1.1 equiv) in THF (155 mL).

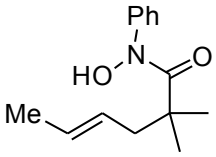
[6] Trost, B.M.; Toste, F.D. *J. Am. Chem. Soc.* **2002**, *124*, 5025.

The resultant solution was warmed to 0 ºC for 15 min, then cooled to -78 ºC and methyl isobutyrate (3.4 mL, 29.4 mmol, 1.0 equiv) added dropwise and stirred cold 1 h. Allyl bromide (2.5 mL, 29.4 mmol, 1.0 equiv) was added to the -78 ºC reaction mixture, stirred cold for 30 min and then allowed to slowly warm to rt overnight. The reaction mixture was then diluted with Et_2O, washed with 1M $NaHSO_4$ (3 x), brine, dried ($MgSO_4$) and concentrated *in vacuo* to provide methyl 2,2-dimethylpent-4-enoate (1.17 g, 30 % yield) as a yellow liquid. The crude ester (1.17 g, 8.23 mmol) was heated to reflux in a solution of MeOH (33 mL), water (8 mL) and NaOH (1.65 g, 41.1 mmol, 5.0 equiv) for 2 h. The reaction mixture was diluted with Et_2O and acidified with 1N HCl. The aqueous layer was extracted with Et_2O (4 x) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated to give crude acid product (879.0 mg, 83%) that was used without further purification.



9

9 was synthesized via the general procedure in 79% yield (809.0 mg) as an orange oil that crystallizes upon scratching. Analytical data for **9**: **^{1}H NMR** (500 MHz, CHLOROFORM-*d*) δ = 8.85 (br. s., 1 H) 7.44 (m, 5 H) 5.79 (m, 1 H) 5.09 (m, 2 H) 2.32 (d, *J*=7.33 Hz, 2 H) 1.10 (s, 6 H) ppm; **^{13}C NMR** (126 MHz, CHLOROFORM-*d*) 173.9, 140.1, 134.3, 129.4, 129.2 (2 C), 128.2, 118.1 (2 C), 45.5, 42.4, 26.3 (2 C); **IR** (thin film, cm^{-1}) 3194, 2976, 1614, 1591, 1496, 1391, 1361, 1271, 1067, 997, 916, 761, 690; **LRMS** (ESI) Calcd. for $[C_{13}H_{17}NO_2+Na]^+$ = 242.12, Found = 242.12. (For NMR spectra see ref. 2)



11

The corresponding carboxylic acid of **11** was synthesized via an alkylation of methyl isobutyrate with crotyl bromide followed by base hydrolysis using literature procedures as with **9** (see above for general alkylation and hydrolysis procedures).

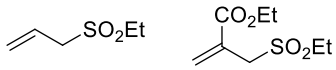
11 was synthesized via the general procedure in 78% yield (1.02 g) as an orange oil that crystallizes upon scratching.

Analytical data for **11**: **^{1}H NMR** (CHLOROFORM-*d*, 500MHz): δ = 8.68 - 9.08 (m, 1 H), 7.31 - 7.43 (m, 5 H), 5.43 - 5.63 (m, 1 H), 5.32 - 5.42 (m, 1 H), 2.21 - 2.35 (m, 2 H), 1.54 - 1.70 (m, 3 H), 1.04 - 1.15 (m,

6 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 126 MHz) 174.7, 140.6, 128.8, 128.4, 126.9, 126.7, 126.6, 125.8, 43.7, 42.9, 42.8, 37.5, 25.9, 25.8, 18.0, 13.0; **IR** (thin film, cm^{-1}) 3189, 2969, 2930, 1613, 1591, 1494, 1390, 1360, 1067, 968, 760, 701; **LRMS** (ESI) Calcd. for $[C_{14}H_{19}NO_2+Na]^+$ = 256.13, Found = 256.15.

General Oxyallylation Conditions

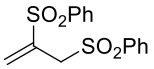
Method A (Sulfones i and ii)



i **ii**

A new 1-dram vial containing a magnetic stir bar was charged with unsaturated hydroxamic acid (1.0 equiv) and sulfone **i** or **ii** (5.0 equiv) and benzene sulfonamide (0.5 equiv). The vial was then brought into a dry glovebox and the mixture was dissolved in de-gassed DMSO to make a 0.45M solution. The vial was fitted with a PTFE-lined screw cap, taken out of the glovebox, and allowed to stir at 85˚C. Upon disappearance of the hydroxamic acid substrate (24-50 h), as indicated by TLC analysis, the reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with H_2O (10 mL), and extracted with CH_2Cl_2 (3 x 3mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated. The resulting cyclic hydroxamate was purified by flash chromatography using the specified solvent system.

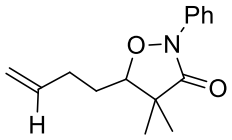
Method B (Sulfone iii)



iii

A new 1-dram vial containing a magnetic stir bar was charged with unsaturated hydroxamic acid (1.0 equiv) and sulfone **iii** (5.0 equiv) and benzene sulfonamide (0.5 equiv). The vial was then brought into a dry glovebox and the mixture was dissolved in de-gassed DMSO to make a 0.45M solution. The vial was fitted with a PTFE-lined screw cap, taken out of the glovebox, and allowed to stir at 85˚C. Upon disappearance of the hydroxamic acid substrate (24-50 h), as indicated by TLC analysis, the reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with H_2O (10 mL), and extracted with CH_2Cl_2 (3 x 3mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated. The resulting crude mixture was dissolved in EtOH (1-2 mL) and cooled to 0˚C to induce precipitation of unreacted sulfone. The sulfone was then filtered off, and the filtrate was concentrated under reduced

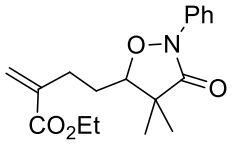
pressure. The resulting cyclic hydroxamate was purified by flash chromatography using the specified solvent system.



2a

2a was prepared via **Method A** using **1** (20.1 mg, 0.098 mmol), sulfone **i** (65.8 mg, 0.490 mmol), benzene sulfonamide (7.75 mg, 0.049 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The crude reaction mixture was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **2a** (12.7 mg, 0.052 mmol, 53% yield) as a clear oil.

Analytical data for **2a**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.75 (d, *J* = 8.5 Hz, 2 H), 7.40 (t, *J* = 8.0 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 5.90 (tdd, *J* = 6.7, 10.3, 17.0 Hz, 1 H), 5.19 - 5.04 (m, 2 H), 4.23 (dd, *J* = 3.3, 9.8 Hz, 1 H), 2.48 - 2.35 (m, 1 H), 2.28 (qd, *J* = 7.2, 14.5 Hz, 1 H), 1.96 - 1.82 (m, 1 H), 1.77 - 1.64 (m, 1 H), 1.29 (s, 3 H), 1.21 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 172.1, 137.2, 128.7, 124.4, 116.3, 115.8, 86.9, 46.2, 29.9, 27.1, 21.3, 17.7 ppm; **IR** (thin film, cm^{-1}) 3076, 2972, 1704, 1641, 1595, 1496, 1389, 1306, 1180, 914, 752; **LRMS** (ESI) Calcd. for $[C_{15}H_{19}NO_2+H]^+$ = 246.14, Found = 246.13.

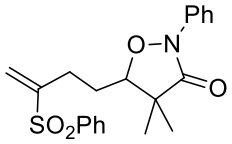


2b

2b was prepared via **Method A** using **1** (20.3 mg, 0.098 mmol), sulfone **ii** (98.1 mg, 0.490 mmol), benzene sulfonamide (7.8 mg, 0.049 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **2b** (17.3 mg, 0.054 mmol, 56% yield) as a clear oil.

Analytical data for **2b**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.74 (d, *J* = 8.5 Hz, 2 H), 7.39 (t, *J* = 8.0 Hz, 2 H), 7.16 (t, *J* = 1.0 Hz, 1 H), 6.27 (s, 1 H), 5.68 (s, 1 H), 4.30 - 4.19 (m, 3 H), 2.73 - 2.61 (m, 1 H), 2.53 (ddd, *J* = 6.5, 8.7, 14.7 Hz, 1 H), 2.01 - 1.79 (m, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 1.29 (s, 3 H), 1.21 (s, 3 H); **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 171.9, 166.8, 136.9, 139.6, 137.2, 128.7, 125.7, 124.4, 116.3, 87.0, 60.8, 46.2, 28.6 , 26.8, 21.3, 17.7, 14.2 ppm; **IR** (thin film, cm^{-1}) 2972, 2932, 1710,

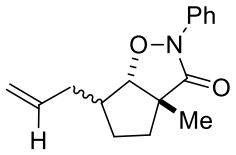
1631, 1594, 1495, 1388, 1362, 1306, 1177, 1025, 753, 690; **LRMS** (ESI) Calcd. for $[C_{18}H_{23}NO_4+H]^+$ = 318.16, Found = 318.23.



2c

2c was prepared via the **Method B** method on a 100mg scale using **1** (100.5 mg, 0.49 mmol), sulfone **iii** (560.1.6 mg, 1.70 mmol, 3.5 equiv), benzene sulfonamide (38.75 mg, 0.245 mmol) in DMSO (1.2 mL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 52 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **2c** (168.7 mg, 0.441 mmol, 90% yield) as a grey white residue.

Analytical data for **2c**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.93 (d, *J* = 7.3 Hz, 2 H), 7.66 (d, *J* = 8.8 Hz, 3 H), 7.57 (t, *J* = 1.0 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 6.47 (s, 1 H), 5.86 (s, 1 H), 4.11 (dd, *J* = 3.0, 10.0 Hz, 1 H), 2.70 - 2.58 (m, 1 H), 2.47 (td, *J* = 8.2, 16.0 Hz, 1 H), 1.96 - 1.76 (m, 3 H), 1.22 (s, 3 H), 1.13 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 171.6, 149.4, 138.6, 137.0, 133.8, 129.4, 128.8, 128.3, 124.6, 124.5, 116.3, 86.2, 46.1, 26.4, 26.2, 21.3, 17.6 ppm; **IR** (thin film, cm^{-1}) 2973, 2252, 2090, 1643, 1494, 1364, 1305, 1137, 1081, 909 ; **LRMS** (ESI) Calcd. for $[C_{21}H_{23}NO_4S+H]^+$ = 386.13, Found = 386.21.



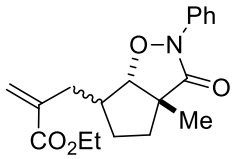
4a

4a was prepared via **Method A** using **3** (20.0 mg, 0.092 mmol), sulfone **i** (65.1 mg, 0.460 mmol), benzene sulfonamide (7.6 mg, 0.046 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 48 h. The crude reaction mixture was worked up and purified by flash chromatography (15% EtOAc/hexanes) to afford **4a** (7.8 mg, 0.052 mmol, 30% yield) as a clear oil.

Analytical data for **4a**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.76 (d, *J* = 7.5 Hz, 2 H), 7.42 - 7.36 (m, *J* = 7.5, 8.8 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 5.91 - 5.79 (m, 1 H), 5.16 - 5.08 (m, 2 H), 4.39 (d, *J* = 3.0 Hz, 1 H), 2.45 - 2.36 (m, 1 H), 2.36 - 2.21 (m, 2 H), 2.21 - 2.11 (m, 1 H), 2.01 (qd, *J* = 7.6, 13.1 Hz, 1 H), 1.79 (td, *J* = 7.7, 13.4 Hz, 1 H), 1.64 - 1.52 (m, 2 H), 1.48 (s, 2 H) ppm; **^{13}C NMR** (CHLOROFORM-

d, 100MHz): 171.1, 137.1, 136.0, 128.7, 124.6, 116.7, 93.3, 55.0, 45.8, 36.6, 35.9, 29.6, 21.7 ppm; **IR** (thin film, cm^{-1}) 3073, 2961, 2931, 2871, 1697, 1594, 1495, 1458, 1376, 1307, 994, 915, 753, 690 ; **LRMS** (ESI) Calcd. for $[C_{16}H_{19}NO_2+H]^+$ = 258.14, Found = 258.12.

See attached 2D spectra for stereochemical assignment.

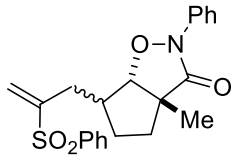


4b

4b was prepared via **Method A** using **3** (20.0 mg, 0.092 mmol), sulfone **ii** (94.8 mg, 0.460 mmol), benzene sulfonamide (7.6 mg, 0.046 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 48 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **4b** (16.6 mg, 0.050 mmol, 55% yield) as a clear yellow oil.

Analytical data for **4b**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.74 (d, *J* = 7.8 Hz, 2 H), 7.38 (t, *J* = 1.0 Hz, 2 H), 7.15 (t, *J* = 1.0 Hz, 1 H), 6.30 (s, 0 H), 5.65 (s, 1 H), 4.38 (d, *J* = 3.3 Hz, 1 H), 4.28 - 4.17 (m, 2 H), 2.60 - 2.47 (m, 2 H), 2.47 - 2.37 (m, 1 H), 2.32 (td, *J* = 7.0, 13.7 Hz, 1 H), 2.06 - 1.92 (m, 1 H), 1.81 (td, *J* = 7.4, 13.6 Hz, 1 H), 1.56 (td, *J* = 6.7, 13.4 Hz, 1 H), 1.49 (s, 3 H), 1.32 (t, *J* = 7.2 Hz, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 171.0, 166.9, 138.8, 137.0, 128.7, 126.3, 124.6, 116.7, 93.3, 60.9, 54.8, 45.3, 35.6, 34.6, 29.6, 21.9, 14.2 ppm; **IR** (thin film, cm^{-1}) 2961, 2872, 1710, 1630, 1594, 1494, 1459, 1375, 1306, 1189, 1155, 1024, 952, 734, 690; **LRMS** (ESI) Calcd. for $[C_{16}H_{23}NO_4+H]^+$ = 330.16, Found = 330.32.

Stereochemical assignment based on analogy to **4a**.

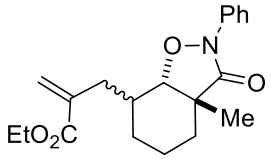


4c

4c was prepared via **Method B** using **3** (20.1 mg, 0.092 mmol), sulfone **iii** (148.1 mg, 0.460 mmol, 5 equiv), benzene sulfonamide (7.2 mg, 0.046 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 48 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **4c as a mixture with some residual sulfone. The yield was determined by NMR using 2,4,6 trimethoxybenzene as an internal standard.**

Analytical data **4c**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.91 (d, *J* = 8.3 Hz, 2 H), 7.70 (d, *J* = 7.8 Hz, 2 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.59 - 7.52 (m, 4 H), 7.40 (t, *J* = 8.0 Hz, 2 H), 7.18 (t, *J* = 1.0 Hz, 1 H), 6.52 (s, 1 H), 5.89 (s, 1 H), 4.22 (d, *J* = 2.8 Hz, 1 H), 2.56 - 2.40 (m, 2 H), 2.39 - 2.20 (m, 2 H), 2.04 - 1.90 (m, *J* = 7.5, 13.3 Hz, 1 H), 1.68 (td, *J* = 7.5, 13.6 Hz, 1 H), 1.50 - 1.39 (m, 2 H), 1.37 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 100MHz): 170.5, 148.6, 138.8, 136.9, 133.8, 129.4, 128.8, 128.3, 124.8, 124.6, 116.7, 92.9, 54.9, 44.3, 52.5, 31.9, 29.7, 21.6 ppm; **IR** (thin film, cm^{-1}) 3065, 2927, 2251, 1694, 1593, 1494, 1449, 1379, 1305, 1139, 1081, 912, 750, 690; **LRMS** (ESI) Calcd. for $[C_{22}H_{23}NO_4S+H]^+$ = 398.13, Found = 398.20

Stereochemical assignment based on analogy to **4a**.



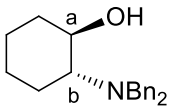
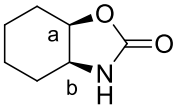
6b

6b was prepared via **Method A** using **5** (20.3 mg, 0.086 mmol), sulfone **ii** (88.6 mg, 0.430 mmol), benzene sulfonamide (6.5 mg, 0.043 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **6b** (20.9 mg, 0.059 mmol, 69% yield) as a clear oil. **6b** was isolated as a 58:42 mixture of inseparable diastereomers.

Analytical data for **6b**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.74 (t, *J* = 7.7 Hz, 2 H), 7.39 (dt, *J* = 4.8, 8.0 Hz, 2 H), 7.15 (dt, *J* = 4.4, 7.3 Hz, 1 H), 6.28 (dd, *J* = 1.4, 12.9 Hz, 1 H), 5.77 - 5.49 (m, 1 H), 4.25 (q, *J* = 7.0 Hz, 1 H), 4.18 - 3.95 (dd, *cis J*=2.8, *trans J*=8.4 Hz, 1 H), 4.15-4.01 (m, 1H), 2.80 - 2.44 (m, 2 H), 2.42 - 2.22 (m, 1 H), 2.05 - 1.83 (m, 1 H), 1.76 (dd, *J* = 3.4, 9.7 Hz, 1 H), 1.70 - 1.57 (m, 3 H), 1.40 - 1.30 (m, 4 H), 1.26 (s, 2 H), 1.19 (t, *J* = 7.0 Hz, 2 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 100MHz): 172.6, 170.5, 167.0, 166.9, 138.8, 137.7, 137.6, 137.5, 128.8, 128.7, 127.4, 126.7, 124.3, 116.3, 116.2, 88.7, 84.5, 60.8, 60.7, 47.6, 45.6, 37.7, 37.0, 34.9, 34.3, 31.4, 29.9, 29.7, 28.2, 26.8, 23.7, 21.8, 20.8, 16.7, 14.2, 14.1 ppm; **IR** (thin film, cm^{-1}) 2934, 2863, 1710, 1629, 1594, 1495, 1457, 1363, 1303, 1213, 1159, 1024, 967, 753, 690; **LRMS** (ESI) Calcd. for $[C_{20}H_{25}NO_4+H]^+$ = 343.18, Found = 343.20.

Based on the coupling constants reported for *trans* and *cis* aminoalcohols of cyclohexanes as well as with analogous compounds previously reported by our group,[7] the diastereomer exhibiting the greater coupling constant suggests a *trans* relationship for substituted 6-membered rings.

Table 2 – Literature examples of *J* values for *trans* vs. *cis* O- and N-functionality on cyclohexanes

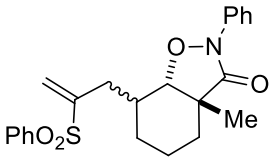
	 *trans* 2-(dibenzylamino)cyclohexanol	 *cis* hexahydrobenzo[*d*]oxazol-2(*3H*)-one
H_a	3.52 ppm, 1H (dt, *J* = 3.7, 9.3 Hz)	4.6 ppm, 1H (dt, *J* = 6 Hz)
H_b	2.36 ppm, 1H (dt, *J* = 3.0, 10.1 Hz)	3.70 ppm, 1H (q, *J* = 6 Hz)

The reported values of H_a and H_b for *trans*-2-(dibenzylamino)cyclohexanol[8] show that a large coupling constant (~10 Hz) suggests a *trans* substitution pattern.

Conversely, *cis*-hexahydrobenzo[*d*]oxazol-2(*3H*)-one[9] demonstrates that a smaller coupling constant (~6 Hz or fewer) would be evidence of a *cis* substitution pattern.

6b shows a doublet of doublets at 4.18 - 3.95 ppm with coupling constants of *J*=2.8 and *J*=8.4 Hz. Based on the evidence above, the isomer with the smaller coupling constant (2.8 Hz) suggests a *cis* configuration, while the isomer with the larger coupling constant (8.4 Hz) is suggestive of the *trans* diastereomer.

[7] a) V. A. Schmidt, E. J. Alexanian, *Angew. Chem.* **2010**, *122*, 4593−4596; *Angew. Chem. Int. Ed.* **2010**, *50*, 1882−1884; b) V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 11402−11405; c) B. C. Giglio, V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 13320−13322; d) V. A. Schmidt, E. J. Alexanian, *Chem. Sci.* **2012**, *3*, 1672−1674.
[8] Miyano, S.; Lu, L.D.L.; Viti, S. M.; Sharpless, K.B. *J. Org. Chem.*, **1985**, *50*, 4350.
[9] De Parrodi, C.A.; Juaristi, E.; Quintero, L.; Clara-Sosa, A. *Tetrahedron. Asym.*, **1997**, *8*, 1075.

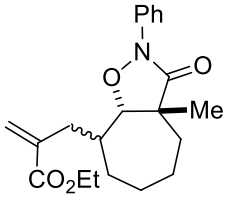


6c

6c was prepared via **Method B** using **5** (20.0 mg, 0.086 mmol), sulfone **iii** (96.9 mg, 0.300 mmol, 3.5 equiv), benzene sulfonamide (6.8 mg, 0.043 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **6c** (29.7 mg, 0.072 mmol, 84% yield) as a grey white residue. **6c** was isolated as a 52:48 mixture of inseparable diastereomers.

Analytical data for **6c**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.96 - 7.90 (m, 1 H), 7.77 - 7.54 (m, 5 H), 7.48 - 7.32 (m, 3 H), 7.23 - 7.09 (m, 1 H), 6.53 - 6.44 (m, 1 H), 5.96 - 5.69 (m, 1 H), 4.09 - 3.77 (dd, 1H, *cis* *J*=2.8, *trans* *J*=8.4), 2.93 - 2.31 (m, 2 H), 2.29 - 1.90 (m, 1 H), 1.77 - 1.46 (m, 4 H), 1.44 - 1.20 (m, 4 H), 1.18 (s, 2 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 100 MHz at 320 K): 172.3, 170.0, 147.7, 147.3, 138.9, 138.7, 137.5, 137.3, 133.8, 133.6, 129.4, 129.2, 128.9, 128.8, 128.3, 128.2, 128.1, 126.8, 126.7, 126.0, 125.9, 124.6, 124.5, 116.2, 116.1, 88.5, 88.4, 83.7, 83.6, 47.6, 45.4, 36.7, 34.4, 33.7, 32.9, 31.2, 29.7, 27.0, 26.8, 23.8, 23.7, 21.6, 20.6, 16.6, 16.5 ppm; **IR** (thin film, cm^{-1}) 3064, 2935, 2862, 1703, 1594, 1496, 1458, 1447, 1381, 1363, 1304, 1142, 1081, 968, 914, 750, 689; **LRMS** (ESI) Calcd. for $[C_{23}H_{25}NO_4S+H]^+$ = 412.15, Found = 412.24.

Stereochemistry was assigned by analogy to **6b**.



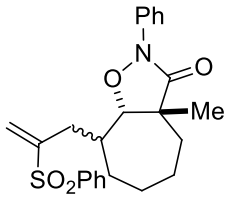
8b

8b was prepared via **Method A** using **7** (21.6 mg, 0.088 mmol), sulfone **ii** (90.6 mg, 0.440 mmol), benzene sulfonamide (6.9 mg, 0.044 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **8b** (20.8 mg, 0.055 mmol, 63% yield) as a clear oil. **8b** was isolated as a 69:31 mixture of inseparable diastereomers.

Analytical data for **8b**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.85 - 7.70 (m, 2 H), 7.45 - 7.34 (m, 2 H), 7.21 - 7.11 (m, 1 H), 6.29 (s, 1 H), 5.68 - 5.56 (m, 1 H), 4.27 - 4.16 (m, 2 H), 4.39 and 4.09-4.07 (s, indicates *cis* and d, *J*=8.4 Hz indicates *trans*, 1 H), 2.91 - 2.46 (m, 2 H), 2.36 - 2.04 (m, 2 H), 2.03 - 1.51

(m, 5 H), 1.50 - 1.20 (m, 10 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 100MHz): 171.6, 166.9, 138.8, 138.7, 136.9, 128.7, 128.6, 127.2, 126.6, 124.6, 124.4, 116, 7, 116.4, 91.3, 88.9, 91.3, 88.9, 60.8, 60.7, 50.6, 50.3, 40.1, 39.0, 37.6, 37.1, 36.9, 31.7, 30.1, 29.5, 28.4, 28.2, 24.6, 24.1, 23.3, 22.8, 14.2, 14.1 ppm; **IR** (thin film, cm^{-1}) 2927, 2857, 1710, 1594, 1495, 1367, 1304, 1187, 1157, 1025, 952, 753, 690; **LRMS** (ESI) Calcd. for $[C_{21}H_{27}NO_4+H]^+$ = 358.19, Found = 358.25.

Based on the previously demonstrated preference of cyclic hydroxamic acids to form the *trans* diastereomer,[7] a *trans* assignment was made by analogy as the major product of **8b**.

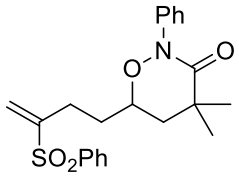


8c

8c was prepared via **Method B** using (20.2 mg, 0.081 mmol), sulfone **iii** (91.9 mg, 0.290 mmol, 3.5 equiv), benzene sulfonamide (6.4 mg, 0.041 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **8c** (29.7 mg, 0.069 mmol, 86% yield) as a grey white residue. **8c** was isolated as a 72:28 mixture of inseparable diasteremoers.

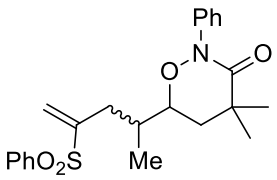
Analytical data for **8c**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.96 - 7.33 (m, 9 H), 7.23 - 7.13 (m, 1 H), 6.55 - 6.45 (m, 1 H), 5.87 - 5.74 (m, 1 H), 4.21 and 3.90-3.78 (s, and d, *J*=8.8 Hz, 1 H), 2.86 - 2.42 (m, 2 H), 2.19 - 2.02 (m, 2 H), 1.88 - 1.55 (m, 4 H), 1.54 - 1.43 (m, 1 H), 1.42 - 1.26 (m, 2 H), 1.23 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 171.2, 148.7, 138.8, 136.8, 133.8133.5, 129.4, 129.2, 128.8, 128.7, 128.3, 126.1, 124.7, 126.6, 115.7, 116.4, 91.1, 88.1, 50.5, 50.2, 38.6, 37.4, 36.8, 36.4, 34.2, 31.6, 29.7, 29.0, 28.2, 28.0, 24.7, 24.0, 23.4, 23.5 ppm; **IR** (thin film, cm^{-1}) 3065, 2929, 2857, 2251, 1696, 1593, 1494, 1449, 1385, 1306, 1145, 1081, 957, 913, 749, 690 ; **LRMS** (ESI) Calcd. for $[C_{24}H_{27}NO_4S+H]^+$ = 426.14, Found = 426.22.

Stereochemistry was assigned by analogy to **8b**.



10

10 was prepared via **Method B** using **9** (20.3 mg, 0.091 mmol), sulfone **iii** (296.1 mg, 0.910 mmol, 10 equiv), benzene sulfonamide (6.8 mg, 0.046 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 52 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **10 as a mixture with some residual sulfone. The yield (37%) was determined by NMR using 2,4,6 trimethoxybenzene as an internal standard.** Analytical data for **10**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.89 (d, *J* = 8.0 Hz, 1 H), 7.71 - 7.63 (m, 1 H), 7.62 - 7.52 (m, 4 H), 7.35 (t, *J* = 8.0 Hz, 2 H), 7.22 - 7.12 (m, 1 H), 6.38 (s, 1 H), 5.71 (s, 1 H), 4.28 - 4.16 (m, 1 H), 2.58 - 2.33 (m, 2 H), 2.04 (dd, *J* = 7.3, 13.6 Hz, 1 H), 1.99 - 1.80 (m, 2 H), 1.76 (dd, *J* = 8.5, 13.8 Hz, 1 H), 1.40 (s, 3 H), 1.35 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 100MHz): 174.7, 149.6, 139.6, 138.7, 133.7, 129.3, 128.6, 128.3, 125.1, 124.1, 119.6, 79.1, 42.7, 39.1, 33.3, 27.2, 26.1, 25.9 ppm; **IR** (thin film, cm^{-1}) 3065, 2967, 2930, 2870, 1677, 1593, 1490, 1448, 1390, 1354, 1305, 1144, 1081, 954, 913, 750, 690, 573; **LRMS** (ESI) Calcd. for $[C_{22}H_{25}NO_4S+H]^+$ = 400.15, Found = 400.19



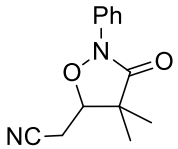
12

12 was prepared via **Method B** using **11** (20.5 mg, 0.085 mmol), sulfone **iii** (276.1 mg, 0.850 mmol, 10 equiv), benzene sulfonamide (6.8 mg, 0.043 mmol) in DMSO (200 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 52 h. The crude reaction mixture was worked up and purified by flash chromatography (20% EtOAc/hexanes) to afford **12 as a mixture with some residual sulfone. The yield (41%) was determined by NMR using 2,4,6 trimethoxybenzene as an internal standard.** Analytical data for **12**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.88 (t, *J* = 7.7 Hz, 2 H), 7.64 (t, *J* = 7.3 Hz, 2 H), 7.59 - 7.51 (m, 3 H), 7.41 - 7.30 (m, 2 H), 7.21 - 7.12 (m, 1 H), 6.44 (d, *J* = 18.1 Hz, 1 H), 5.72 (d, *J* = 10.8 Hz, 1 H), 4.11 - 3.89 (m, 1 H), 2.81 - 2.44 (m, 1 H), 2.38 - 2.01 (m, 3 H), 2.00 - 1.85 (m, 2 H), 1.41 (s, 4 H), 1.34 (s, 3 H), 1.02 - 0.89 (m, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 100MHz): δ = 174.6, 174.5, 148.4, 148.2, 139.5, 139.4, 138.7, 133.7, 133.6, 129.7, 129.6, 129.3, 129.2, 128.8, 128.6, 128.4, 128.3, 127.9, 125.8, 125.3, 125.1, 119.6, 83.9, 82.9, 40.6, 40.6, 40.3, 39.0, 38.9, 35.8, 35.44, 33.6,

33.1, 27.8, 27.7, 26.2, 26.1, 14.5, 14.0 ppm; **IR** (thin film, cm^{-1}) 3065, 2971, 2932, 1676, 1593, 1490, 1449, 1390, 1354, 1304, 1142, 1081, 961, 912, 751, 690, 571; **LRMS** (ESI) Calcd. for $[C_{23}H_{27}NO_4S+H]^+$ = 414.17, Found = 414.24.

General Oxycyanation Conditions

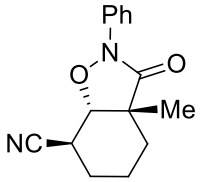
A new 1-dram vial containing a magnetic stir bar was charged with unsaturated hydroxamic acid (1.0 equiv) and *p*-toluenesulfonyl cyanide (TsCN, 3.0 equiv) and dissolved in specified nitrile solvent to make a 0.5M solution. While not necessary for reactivity, the addition of specified radical initiators in some reactions resulted in improved product yields and reaction times, and is indicated below when used. The vial was fitted with a PTFE-lined screw cap and argon was bubbled through the solution for 5-8 min. The reaction was allowed to stir under 1 atm argon at the specified temperature. Upon disappearance of the hydroxamic acid substrate, as indicated by TLC analysis, the solvent was removed under reduced pressure. The resulting cyclic hydroxamate was purified by flash chromatography using the specified solvent system.



13

13 was prepared using **1** (20.0 mg, 0.0974 mmol), TsCN (53.0 mg, 0.292 mmol), DLP (10 mol %, 3.9 mg, 0.0097 mmol) in EtCN (210 µL). The reaction was completed, as indicated by TLC, after heating at 60 ºC for 21 h. The solvent was removed from the crude reaction mixture under reduced pressure and the crude material was purified by flash chromatography (33% EtOAc/hexanes) to afford **13** (13.7 mg, 0.0595 mmol, 61 % yield) as a clear, colorless oil.

Analytical data for **13**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.76 - 7.68 (m, 2 H), 7.47 - 7.35 (m, 2 H), 7.24 - 7.15 (m, 1 H), 4.56 (dd, *J* = 5.8, 7.8 Hz, 1 H), 2.87 (dd, *J* = 8.0, 17.1 Hz, 1 H), 2.75 (dd, *J* = 5.8, 16.8 Hz, 1 H), 1.45 - 1.40 (m, 3 H), 1.29 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 169.92, 136.56, 128.92, 125.19, 116.58, 115.47, 82.15, 46.35, 21.98, 17.77, 17.51 ppm; **IR** (thin film, cm^{-1}) 3068, 2974, 2932, 2254, 1708, 1594, 1494, 1392, 1361, 1308, 1180, 1149, 1083, 1051, 910, 754, 690; **LRMS** (ESI) Calcd. for $[C_{13}H_{14}N_2O_2+H]^+$ = 231.11, Found = 230.97.



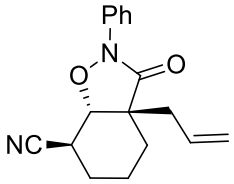
14

14 was prepared using **5** (100.0 mg, 0.433 mmol), TsCN (235.1 mg, 0.259 mmol, 3.0 equiv.) in MeCN (930 µL). The reaction was completed, as indicated by TLC, after heating at 60 ºC for 40 h with the addition of two portions of DLP (17.1mg, 0.043 mmol). The solvent was removed from the crude reaction mixture under reduced pressure and the crude material was purified by flash chromatography (20% EtOAc/hexanes) to afford **14 as a 60:40 mixture of diastereomers** (less polar isomer 30.9 mg, and more polar isomer 25.5 mg, 0.220 mmol total, 51% yield) as a colorless oil.

Analytical data for **14 major** *:* **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.76 - 7.68 (m, 2 H), 7.45 - 7.37 (m, 2 H), 7.24 - 7.16 (m, 1 H), 4.48 (d, *J* = 7.8 Hz, indicates *trans*, 1 H), 2.91 (ddd, *J* = 4.1, 7.7, 10.5 Hz, 1 H), 2.26 - 2.17 (m, 1 H), 2.16 - 2.06 (m, 1 H), 1.83 - 1.64 (m, 2 H), 1.55 - 1.37 (m, 2 H), 1.46 (s, 3 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 169.13, 136.99, 128.96, 125.15, 119.83, 116.47, 83.36, 46.93, 30.16, 30.01, 26.18, 22.26, 20.51 ppm; **IR** (thin film, cm^{-1}) 3067, 2935, 2869, 2246, 1833, 1710, 1594, 1494, 1455, 1363, 1306, 1180, 1142, 1014, 973, 912, 754, 688; **LRMS** (ESI) Calcd. for $[C_{15}H_{16}N_2O_2+H]^+$ = 257.13, Found = 257.12.

Analytical data for **14 minor***:* **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.81 - 7.74 (m, 2 H), 7.47 - 7.37 (m, 2 H), 7.24 - 7.15 (m, 1 H), 4.44 (d, *J* = 3.3 Hz, indicates *cis*, 1 H), 2.98 (ddd, *J* = 3.3, 5.0, 12.3 Hz, 1 H), 2.12 - 1.95 (m, 2 H), 1.91 - 1.81 (m, 1 H), 1.81 - 1.68 (m, 2 H), 1.50 - 1.37 (m, 1 H), 1.36 - 1.30 (m, 3 H)) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 170.42, 136.86, 128.87, 125.03, 118.32, 116.53, 80.51, 44.99, 28.88, 28.17, 24.64, 19.63, 16.96 ppm; **IR** (thin film, cm^{-1}) 2928, 2867, 2246, 1707, 1593, 1495, 1458, 1364, 1305, 1154, 980, 903, 754, 691; **LRMS** (ESI) Calcd. for $[C_{15}H_{16}N_2O_2]^+$ = 257.13, Found = 257.12.

See S13 for further stereochemical assignment support.



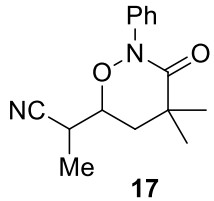
16

16 was prepared using **15** (60.0 mg, 0.233 mmol), TsCN (126.8 mg, 0.699 mmol), DLP (10 mol %, 9.4 mg, 0.023 mmol) in EtCN (500 μL). The reaction was completed, as indicated by TLC, after heating at 60 ºC for 36 h. The solvent was removed from the crude reaction mixture under reduced pressure and the crude material was purified by flash chromatography (gradient of 15-20-25% EtOAc/hexanes) to afford **16 as a 68:32 mixture of diastereomers** (less polar isomer 23.2 mg, 0.0822 mmol, and more polar isomer 10.8 mg, 0.0383, total 52% yield) as a colorless oil.

Analytical data for **16 major**: **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.77 - 7.70 (m, 2 H), 7.46 - 7.39 (m, 2 H), 7.25 - 7.17 (m, 1 H), 5.92 - 5.77 (m, 1 H), 5.30 - 5.21 (m, 2 H), 4.62 (d, *J* = 8.3 Hz, indicates *cis,* 1 H), 2.88 (ddd, *J* = 4.3, 8.2, 11.4 Hz, 1 H), 2.56 - 2.51 (m, 2 H), 2.24 - 2.16 (m, 1 H), 2.15 - 2.07 (m, 1 H), 1.85 - 1.74 (m, 1 H), 1.68 - 1.50 (m, 3 H), 1.45 - 1.30 (m, 1 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 167.89, 136.85, 131.37, 128.95, 125.21, 120.71, 119.99, 116.52, 80.93, 50.53, 39.54, 30.42, 27.84, 26.22, 20.67 ppm; **IR** (thin film, cm^{-1}) 3076, 2927, 2865, 2246, 1703, 1593, 1494, 1455, 1368, 1307, 1206, 1142, 1082, 987, 919, 754, 689; **LRMS** (ESI) Calcd. for $[C_{17}H_{18}N_2O_2+H]^+$ = 283.15, Found = 283.15.

Analytical data for **16 minor***:* **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.81 - 7.72 (m, 2 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.25 - 7.16 (m, 1 H), 5.95 - 5.79 (m, 1 H), 5.28 - 5.15 (m, 2 H), 4.63 (d, *J* = 3.3 Hz, indicates *cis,* 1 H), 2.94 (ddd, *J* = 3.3, 5.3, 11.8 Hz, 1 H), 2.64 (dd, *J* = 6.1, 14.2 Hz, 1 H), 2.39 (dd, *J* = 8.7, 14.4 Hz, 1 H), 2.11 - 1.96 (m, 2 H), 1.90 - 1.71 (m, 3 H), 1.59 (s, 3 H), 1.56 - 1.45 (m, 1 H) ppm; **^{13}C NMR** (CHLOROFORM-*d,* 100 MHz) 169.09, 136.69, 132.19, 128.83, 125.07, 119.84, 118.38, 116.57, 77.43, 48.09, 36.03, 28.31, 27.95, 24.13, 19.57 ppm; **IR** (thin film, cm^{-1}) 3075, 2925, 2857, 2247, 1832, 1705, 1594, 1494, 1456, 1365, 1305, 1177, 1143, 988, 914, 754, 690; **LRMS** (ESI) Calcd. for $[C_{17}H_{18}N_2O_2+H]^+$ = 283.15, Found = 283.15.

See S13 for further stereochemical assignment support.



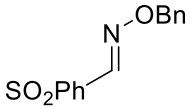
17

17 was prepared using **11** (25.0 mg, 0.107 mmol), TsCN (58.3 mg, 0.321 mmol), (tBuON)$_2$ (1.9 mg, 0.011 mmol, 10 mol % x3) in EtCN (250 µL). The reaction was completed, as indicated by TLC, after heating at 60 ºC for 28 h. The solvent was removed from the crude reaction mixture under reduced pressure and the crude material was purified by flash chromatography (20% EtOAc/hexanes) to afford **17** (less polar isomer 6.6 mg, 0.0255 mmol and more polar isomer 8.4 mg, 0.0325 mmol, 54% combined yield) as clear, colorless oils.

Analytical data for **17 TS:** **^{1}H NMR** (600MHz, CHLOROFORM-d) δ = 7.61 (d, J = 8.7 Hz, 2 H), 7.40 (t, J = 7.7 Hz, 2 H), 7.26 - 7.17 (m, 1 H), 4.36 (q, J = 7.9 Hz, 1 H), 3.04 (quin, J = 7.1 Hz, 1 H), 2.28 (dd, J = 7.3, 13.7 Hz, 1 H), 2.11 (dd, J = 8.7, 13.9 Hz, 1 H), 1.48 (s, 3 H), 1.46 (d, J = 7.2 Hz, 3 H), 1.43 (s, 3 H); **^{13}C NMR** (CHLOROFORM-*d,* 151 MHz) 174.70, 139.07, 128.70, 125.66, 119.94, 119.47, 79.50, 40.02, 39.03, 30.58, 27.01, 25.33, 14.66 ppm; **IR** (thin film, cm^{-1}) 3064, 2926, 2244, 1679, 1594, 1491, 1391, 1355, 1300, 1177, 1059, 965, 755, 692; **LRMS** (ESI) Calcd. for $[C_{15}H_{18}N_2O_2+H]^+$ = 259.14, Found = 259.12.

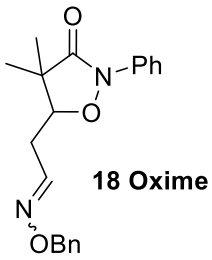
Analytical data for **17 LS:** **^{1}H NMR** (400MHz, CHLOROFORM-d) δ = 7.73 (d, J = 8.7 Hz, 2 H), 7.44 - 7.38 (m, 2 H), 7.23 - 7.17 (m, 1 H), 4.38 - 4.33 (m, 1 H), 2.93 (quin, J = 7.1 Hz, 1 H), 2.16 (dd, J = 7.5, 13.9 Hz, 1 H), 2.01 (dd, J = 9.0, 13.9 Hz, 1 H), 1.49 (s, 3 H), 1.47 (d, J = 6.8 Hz, 3 H), 1.42 (s, 3 H); **^{13}C NMR** (CHLOROFORM-*d,* 151 MHz) 174.33, 139.16, 128.73, 125.47, 119.50, 79.78, 40.56, 39.11, 30.63, 27.34, 25.54, 14.31 ppm; **IR** (thin film, cm^{-1}) 3064, 2926, 2244, 1679, 1594, 1491, 1391, 1355, 1300, 1177, 1059, 965, 755, 692; **LRMS** (ESI) Calcd. for $[C_{15}H_{18}N_2O_2+H]^+$ = 259.14, Found = 259.12.

General Oxyacylation Conditions



iv

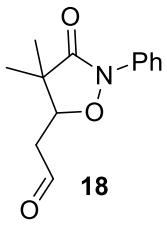
A new 1-dram vial containing a magnetic stir bar was charged with unsaturated hydroxamic acid (1.0 equiv), sulfone **iv** (5.0 equiv) and benzene sulfonamide (0.5 equiv). The vial was then brought into a dry glovebox and the mixture was dissolved in de-gassed DMSO to make a 0.45M solution. The vial was fitted with a PTFE-lined screw cap, taken out of the glovebox, and allowed to stir at 85˚C. Upon disappearance of the hydroxamic acid substrate (24-50 h), as indicated by TLC analysis, the reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with H_2O (10 mL), and extracted with CH_2Cl_2 (3 x 3mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated. The resulting crude mixture was dissolved in EtOH (1-2 mL) and cooled to 0˚C to induce precipitation of the unreacted sulfone which was removed by filtration. The filtrate was then concentrated under reduced pressure, dissolved in THF (1-3mL) and camphorsulfonic acid (4.0 equiv) and aqueous formaldehyde (37%, 10.0 equiv) were added. The reaction was stirred at room temperature, overnight. The mixture was then diluted with Et_2O (10 mL), washed with $NaHCO_3$ (5 mL), and extracted with Et_2O (2x10mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction mixture was purified using column chromatography in the specified solvent system



18 Oxime

18 Oxime was prepared according to the general procedure (but isolated prior to hydrolysis) on a 100mg scale using **1** (100.1 mg, 0.49 mmol), sulfone **iv** (673.5 mg, 2.45 mmol), benzene sulfonamide (50 mol %, 35.5 mg, 0.25 mmol) in DMSO (1.2 mL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 52 h. The crude material was purified by flash chromatography (16% hexanes/DCM) to afford **18 Oxime** as a 50:50 mixture of E/Z isomers (121.4 mg, 0.075 mmol, 72 % yield) as a clear, grey residue.

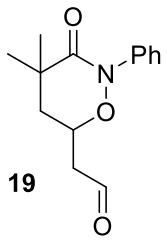
Analytical data for **18 Oxime**: ^{1}H NMR (600MHz, CHLOROFORM-d) δ = 7.76 - 7.66 (m, 2 H), 7.60 (dd, *J* = 5.3, 6.8 Hz, 0.5 H), 7.45 - 7.32 (m, 7 H), 7.20 - 7.12 (m, 2 H), 6.94 (t, *J* = 5.3 Hz, 0.5 H), 5.18 (s, 1H), 5.13 (2, 1 H), 4.43 (ddd, *J* = 4.6, 9.1, 11.6 Hz, 1 H), 2.88 - 2.73 (m, 1 H), 2.69 (ddd, *J* = 5.5, 9.3, 14.9 Hz, 0.5 H), 2.64 - 2.54 (m, 0.5 H), 1.29 (d, *J* = 11.4 Hz, 3 H), 1.22 (d, *J* = 3.7 Hz, 3 H); **^{13}C NMR** (CHLOROFORM-*d*, 150MHz): 171.3, 171.2, 146.3, 146.2, 137.5, 137.4, 136.9, 136.8, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 124.7, 124.6, 116.4, 116.3, 84.9, 84.6, 76.2, 75.9, 46.3, 28.8, 25.2, 21.4, 21.3, 17.7, 17.6 ppm; **IR** (thin film, cm^{-1}) 3064, 3032, 2970, 2930, 2875, 1702, 1594, 1494, 1459, 1388, 1361, 1307, 1180, 1021, 902, 752, 659; **LRMS** (ESI) Calcd. for $[C_{20}H_{22}N_2O_3+H]^+$ = 339.16, Found = 339.07



18

18 was prepared from the hydrolysis of **18 Oxime** (36.0 mg, 0.106 mmol), using CSA (100.2 mg, 0.371 mmol), formaldehyde (0.75 mL, 37% aq, 1.06 mmol) in THF (1.1mL). The reaction was completed, as indicated by TLC, after stirring at rt overnight. The crude material was purified by flash chromatography (15% Et_2O/Pentanes) to afford **18** (23.1 mg, 0.098 mmol, 93 % yield, 71% over 2 steps) as a clear oil.

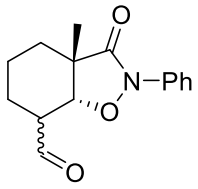
Analytical data for **18**: **^{1}H NMR** (600MHz, CHLOROFORM-d) δ = 9.93 (s, 1 H), 7.70 (d, *J* = 8.1 Hz, 2 H), 7.39 (t, *J* = 7.9 Hz, 2 H), 7.17 (t, *J* = 7.3 Hz, 1 H), 4.84 (dd, *J* = 3.9, 9.0 Hz, 1 H), 2.97 (ddd, *J* = 1.8, 9.2, 17.2 Hz, 1 H), 2.75 (ddd, *J* = 1.1, 3.7, 17.6 Hz, 1 H), 1.34 (s, 3 H), 1.22 (s, 3 H); **^{13}C NMR** (CHLOROFORM-*d*, 150MHz): 197.8, 179.9, 136.8, 128.8, 124.8, 116.4, 81.8, 46.0, 42.2, 21.3, 18.0ppm; **IR** (thin film, cm^{-1}) 2975, 2875, 2733, 1726, 1701, 1593, 1494, 1464, 1388, 1360, 1308, 1041, 918, 754; **LRMS** (ESI) Calcd. for $[C_{13}H_{15}NO_3+H+MeOH]^+$ = 266.13, Found = 266.04.



19

19 was prepared according to the general procedure using **9** (20.3. mg, 0.091 mmol), sulfone **iv** (246.2.4 mg, 0.912 mmol), benzene sulfonamide (50 mol %, 6.8 mg, 0.046 mmol) in DMSO (210 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 48 h. The reaction was worked up according to the general procedure and the crude product was subjected to the hydrolysis conditions: CSA (100.2 mg, 0.371 mmol), formaldehyde (0.75 mL, 37% aq, 1.06 mmol) in THF (1.2 mL µL). The reaction was completed, as indicated by TLC, after stirring at RT overnight. The crude material was purified by flash chromatography (15% Et_2O/Pentanes) to afford **19** (7.9 mg, 0.031 mmol, 34% over 2 steps) as a clear oil.

Analytical data for **19**: **^{1}H NMR** (600MHz, CHLOROFORM-d) δ = 9.85 (s, 1 H), 7.67 (d, *J* = 7.7 Hz, 2 H), 7.38 (t, *J* = 8.1 Hz, 2 H), 7.18 (t, *J* = 7.3 Hz, 1 H), 4.91 (dq, *J* = 5.1, 7.9 Hz, 1 H), 3.03 (ddd, *J* = 1.7, 8.1, 17.8 Hz, 1 H), 2.80 - 2.74 (m, 1 H), 2.25 (dd, *J* = 7.3, 13.9 Hz, 1 H), 1.87 (dd, *J* = 8.4, 13.9 Hz, 1 H), 1.45 (s, 3 H), 1.41 (s, 3 H); **^{13}C NMR** (CHLOROFORM-*d*, 150MHz): 200.7, 174.4, 139.2, 128.7, 125.5, 119.5, 115.9, 74.8, 41.4, 39.1, 26.8, 25.3, 23.2 ppm; **IR** (thin film, cm^{-1}) 2925, 2360, 1725, 1676, 1592, 1489, 1353, 1302, 1059, 754, 690; **LRMS** (ESI) Calcd. for $[C_{14}H_{17}NO_3 + H + MeOH]^+$ = 280.15, Found = 380.02.



20

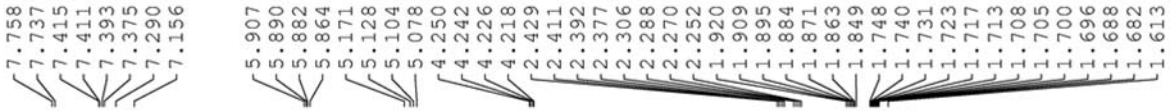
20 was prepared according to the general procedure using **5** (31.2. mg, 0.134 mmol), sulfone **iv** (177.4 mg, 0.671 mmol), benzene sulfonamide (50 mol %, 10.3 mg, 0.067 mmol) in DMSO (210 µL). The reaction was completed, as indicated by TLC, after heating at 85 ºC for 36 h. The reaction was worked up according to the general procedure and the crude product was subjected to the hydrolysis conditions: CSA (100.2 mg, 0.371 mmol), formaldehyde (0.75 mL, 37% aq, 1.06 mmol) in THF (1.2mL). The reaction was completed, as indicated by TLC, after stirring at rt overnight. The crude material was purified by flash chromatography (15% Et_2O/Pentanes) to afford **20** as a 60:40 mixture of diastereomers (19.1 mg, 0.074 mmol, 54% over two steps) as a clear oil. The diastereomers were later separated by additional flash chromatography (7% Et_2O/Pentanes).

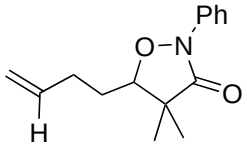
Analytical data for **20 Major**: **^{1}H NMR** (600MHz, CHLOROFORM-d) δ = 9.82 (s, 1 H), 7.72 (d, *J* = 8.1 Hz, 2 H), 7.40 (t, *J* = 7.9 Hz, 2 H), 7.18 (t, *J* = 7.5 Hz, 1 H), 4.70 (d, *J* = 6.6 Hz, 1 H; indicates *trans*), 2.77 - 2.71 (m, 1 H), 2.27 - 2.21 (m, 1 H), 2.10 - 2.04 (m, 1 H), 1.74 - 1.68 (m, 1 H), 1.47 - 1.38 (m, 6 H) ppm; **^{13}C NMR** (CHLOROFORM-*d*, 150 MHz): 200.7, 170.1, 137.3, 128.9, 124.8, 116.3, 81.5, 50.3,

46.9, 30.8, 22.9, 22.4, 20.9 ppm; **IR** (thin film, cm^{-1}) 2928, 2858, 1705, 1594, 1494, 1458, 1380, 1362, 1303, 975, 754; **LRMS** (ESI) Calcd. for $[C_{15}H_{17}NO_3 + H + MeOH]^+$ = 292.15, Found = 292.07.

Analytical data for **20 Minor**: **^{1}H NMR** (600MHz, CHLOROFORM-d) δ = 9.91 (s, 1 H), 7.67 (d, *J* = 8.8 Hz, 2 H), 7.39 (t, *J* = 7.7 Hz, 2 H), 7.16 (t, *J* = 7.3 Hz, 1 H), 4.75 (d, *J* = 2.9 Hz, 1 H indicates *cis*), 2.64 (td, *J* = 3.8, 12.7 Hz, 1 H), 2.03 - 1.97 (m, 1 H), 1.93 - 1.87 (m, 1 H), 1.81 (dq, *J* = 3.5, 13.1 Hz, 1 H), 1.76 - 1.72 (m, 2 H), 1.47 - 1.42 (m, 1 H), 1.35 (s, 3 H)ppm; **^{13}C NMR** (CHLOROFORM-*d*, 150 MHz): 200.6, 171.3, 137.1, 128.9, 128.8, 124.8, 116.4, 116.3, 81.6, 48.5, 45.4, 29.6, 20.4, 19.6, 16.6 ppm; **IR** (thin film, cm^{-1}) 3001, 2985, 1706, 1592, 1493, 1461, 1384, 1359, 1300, 975, 754; **LRMS** (ESI) Calcd. for $[C_{15}H_{17}NO_3 + H + MeOH]^+$ = 292.15, Found = 292.07.

1H, 13C, and 2-D NMR Spectra





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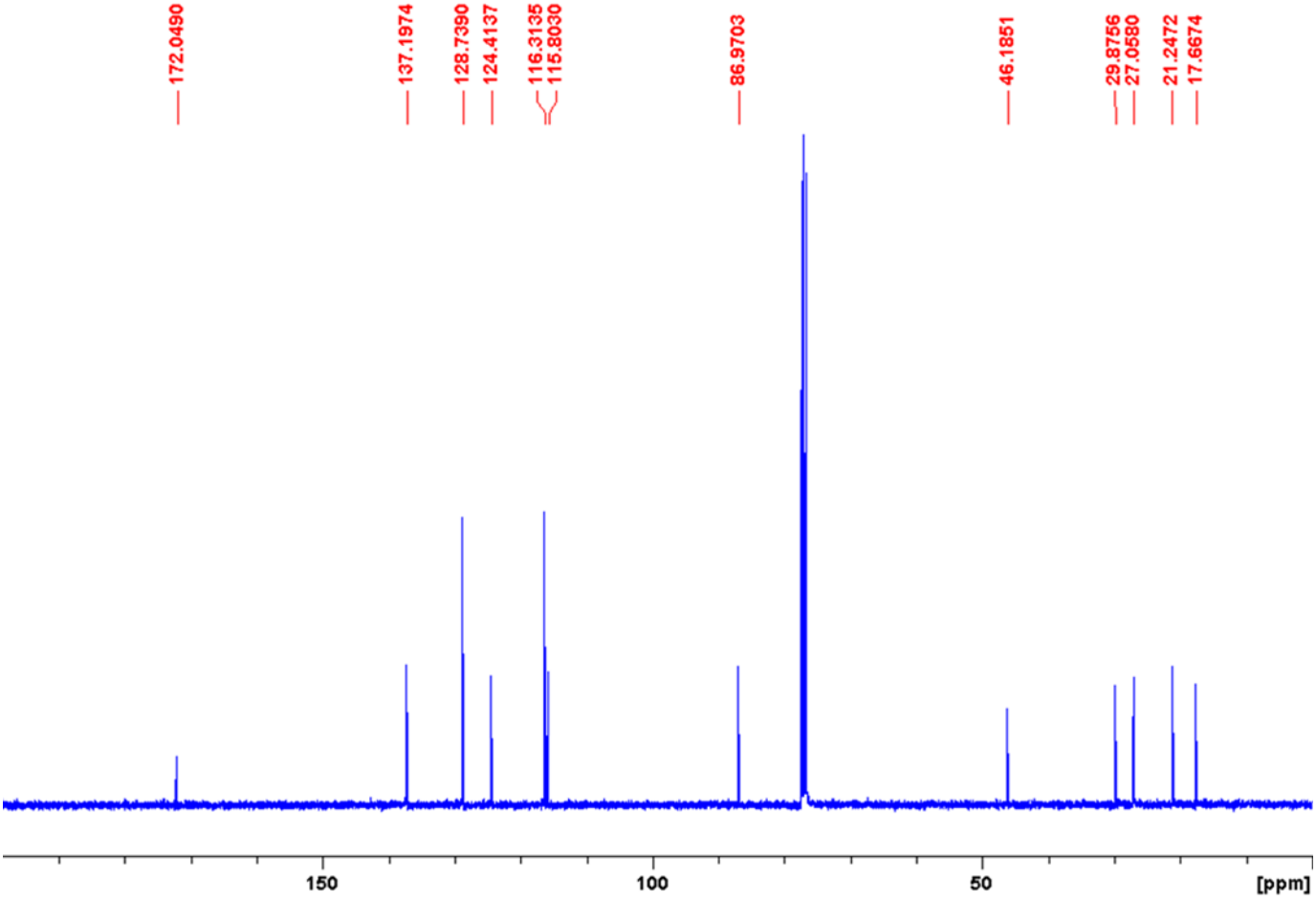

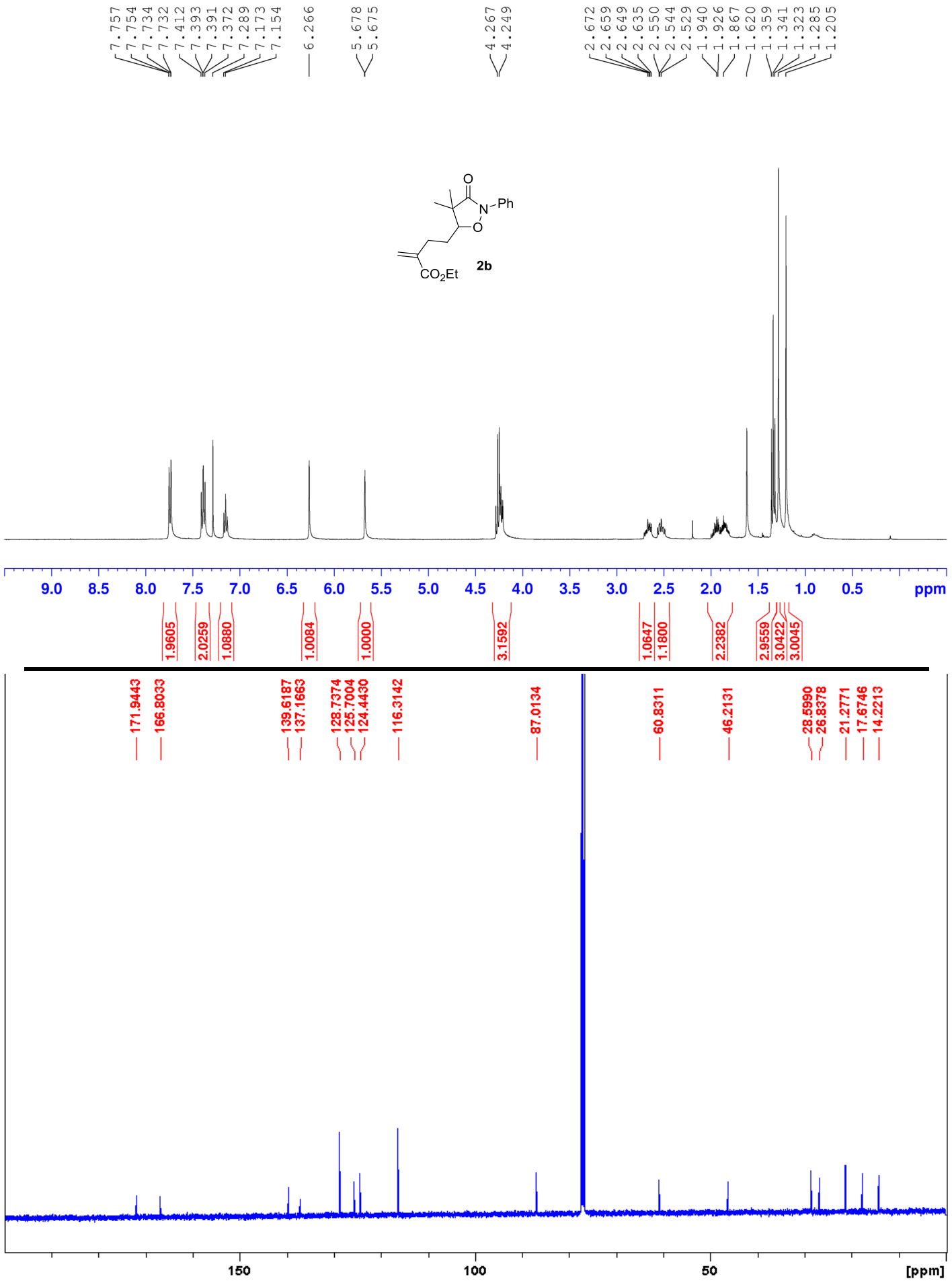

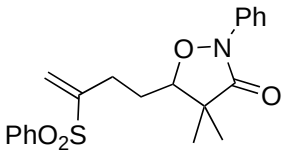

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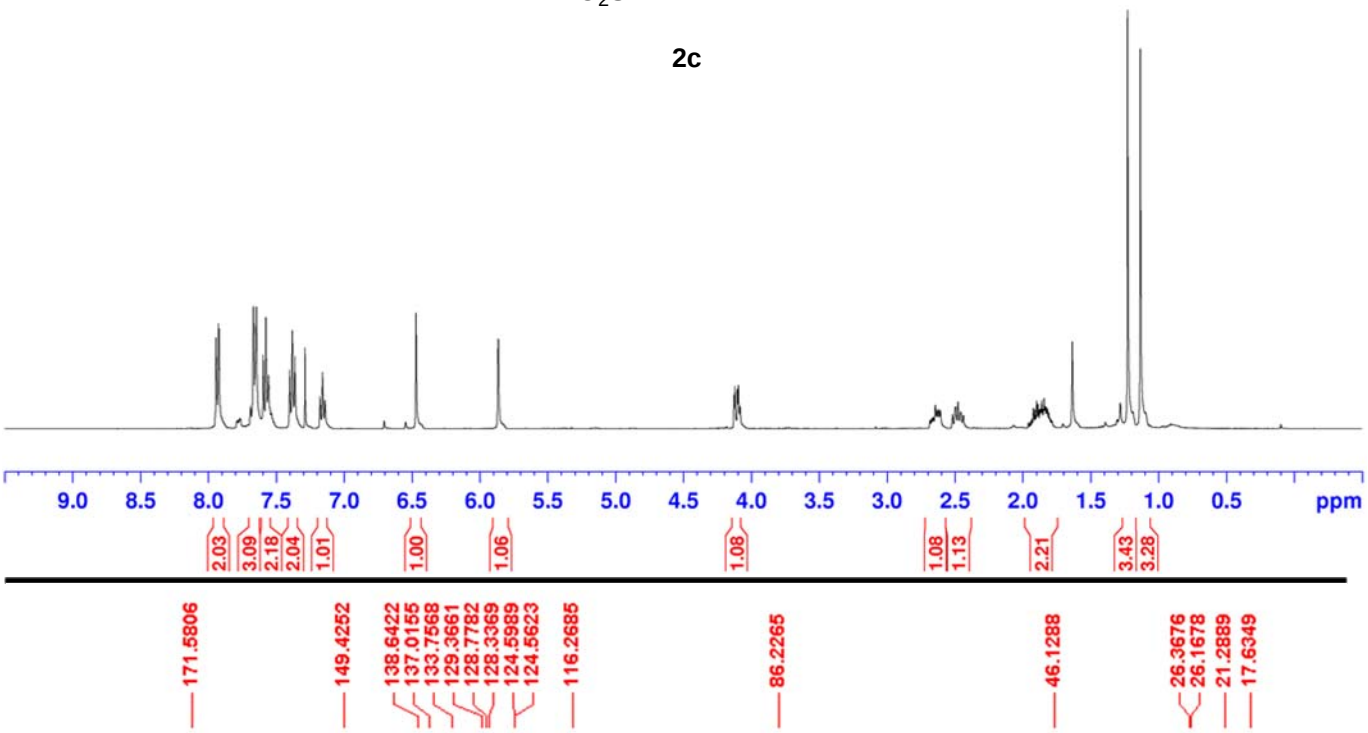
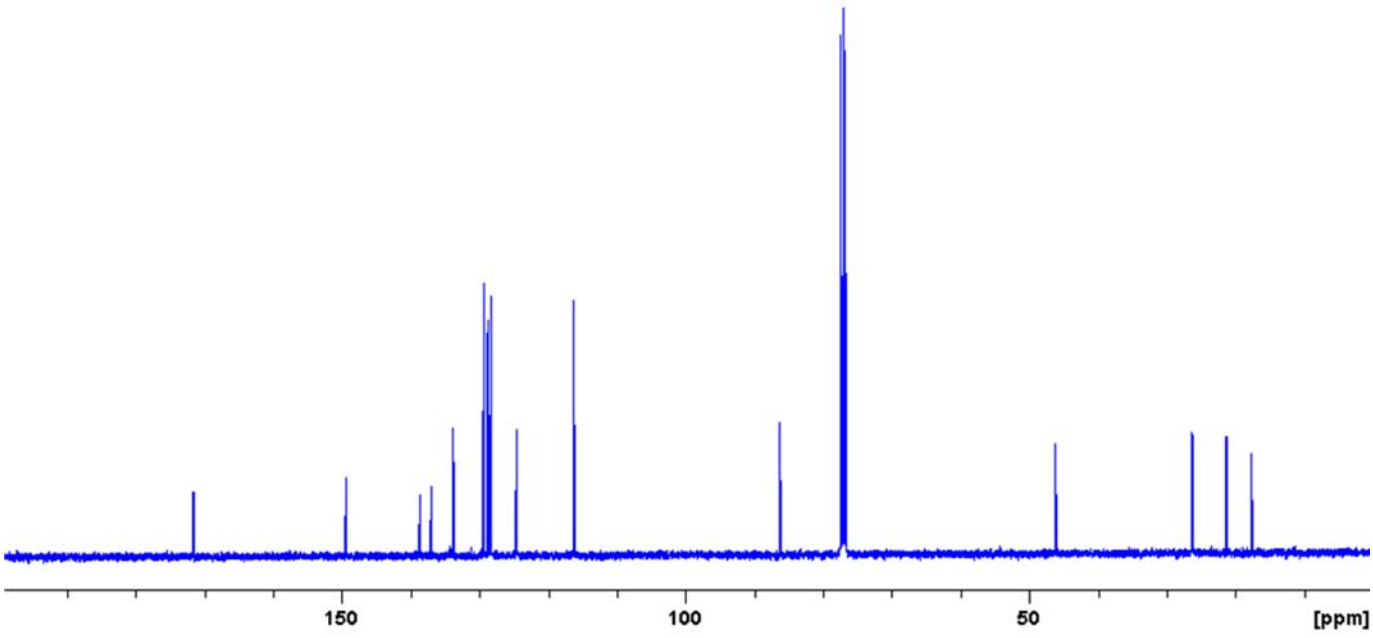
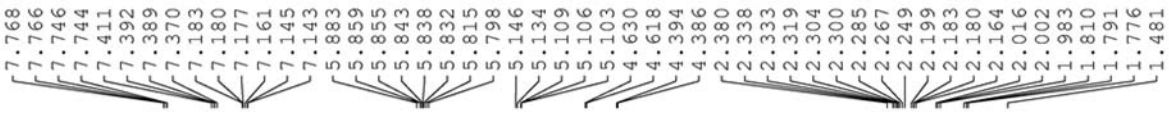
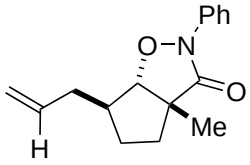
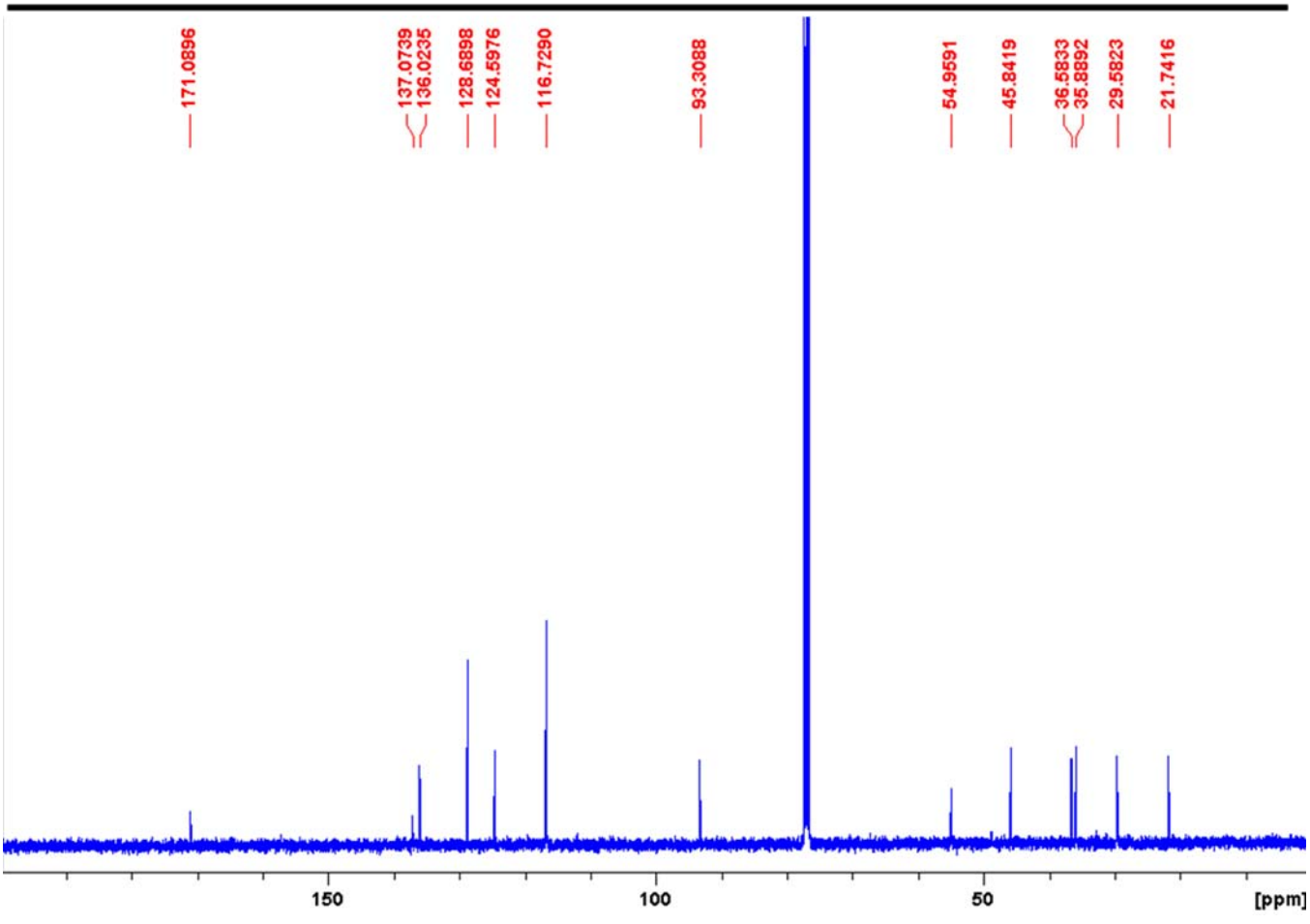




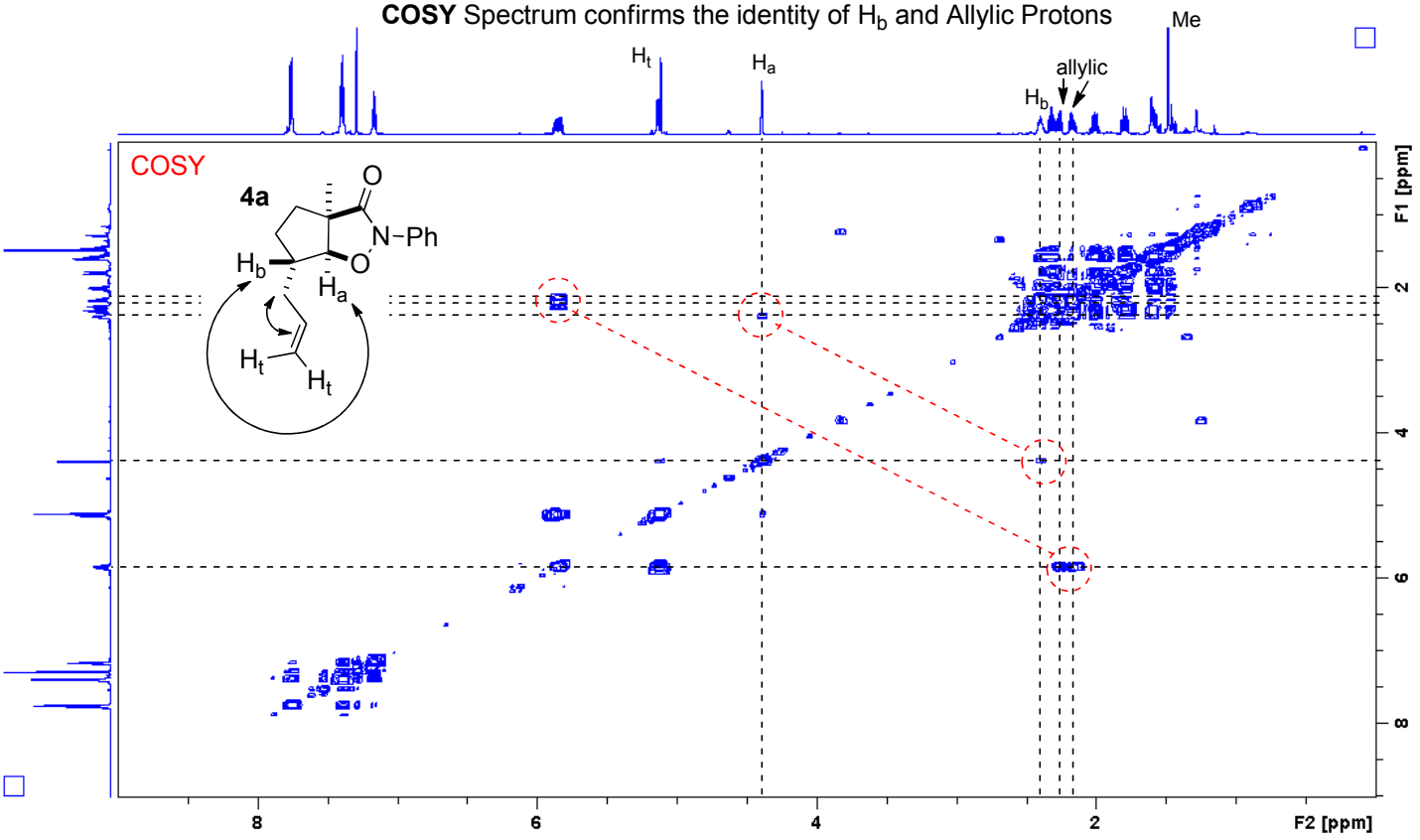




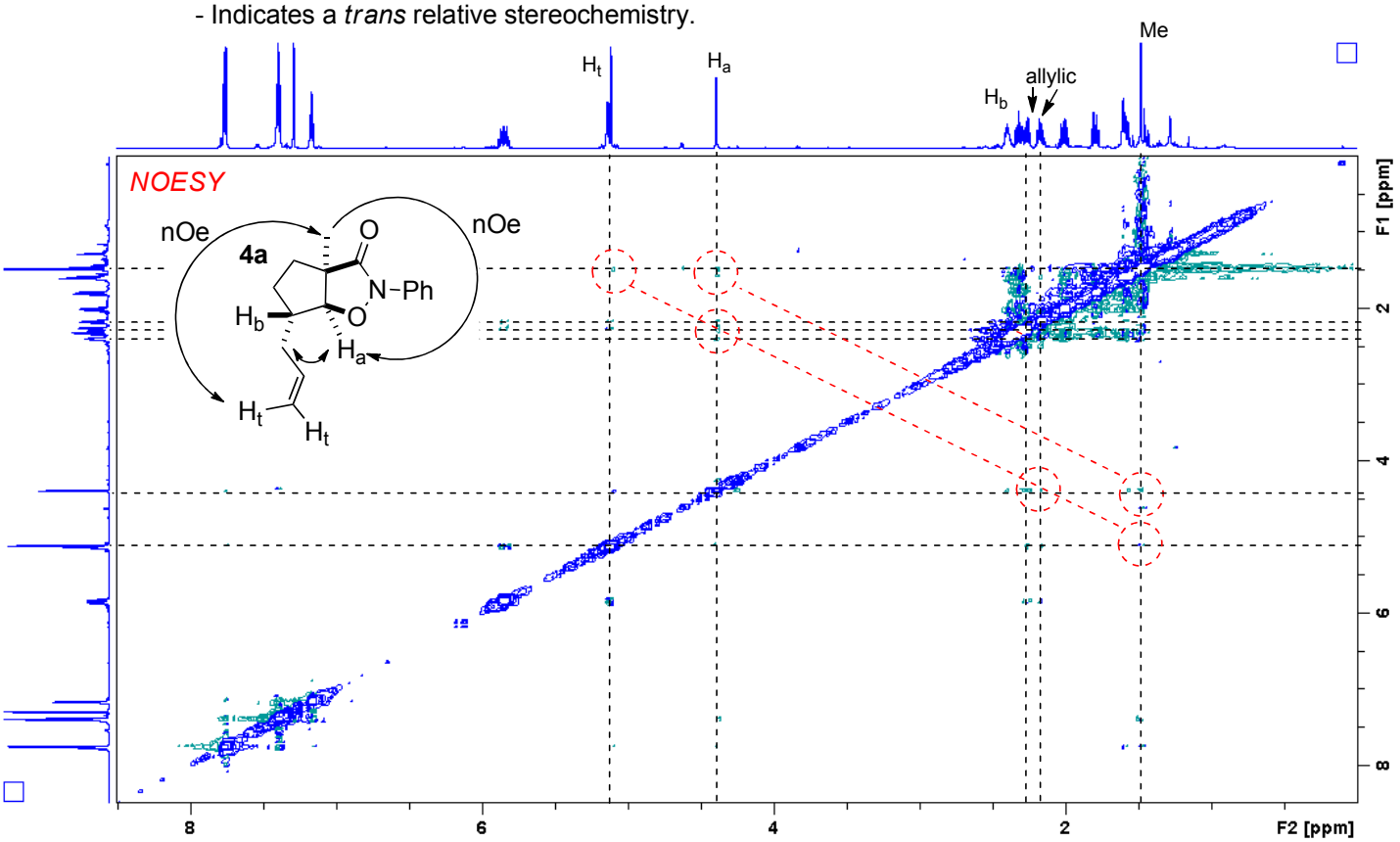
4a

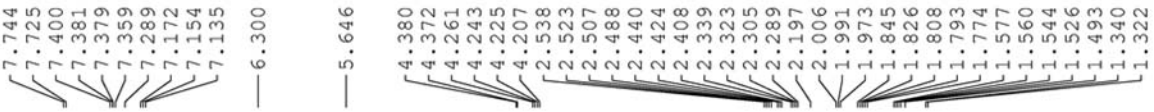


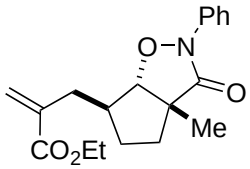
COSY Spectrum confirms the identity of H_b and Allylic Protons



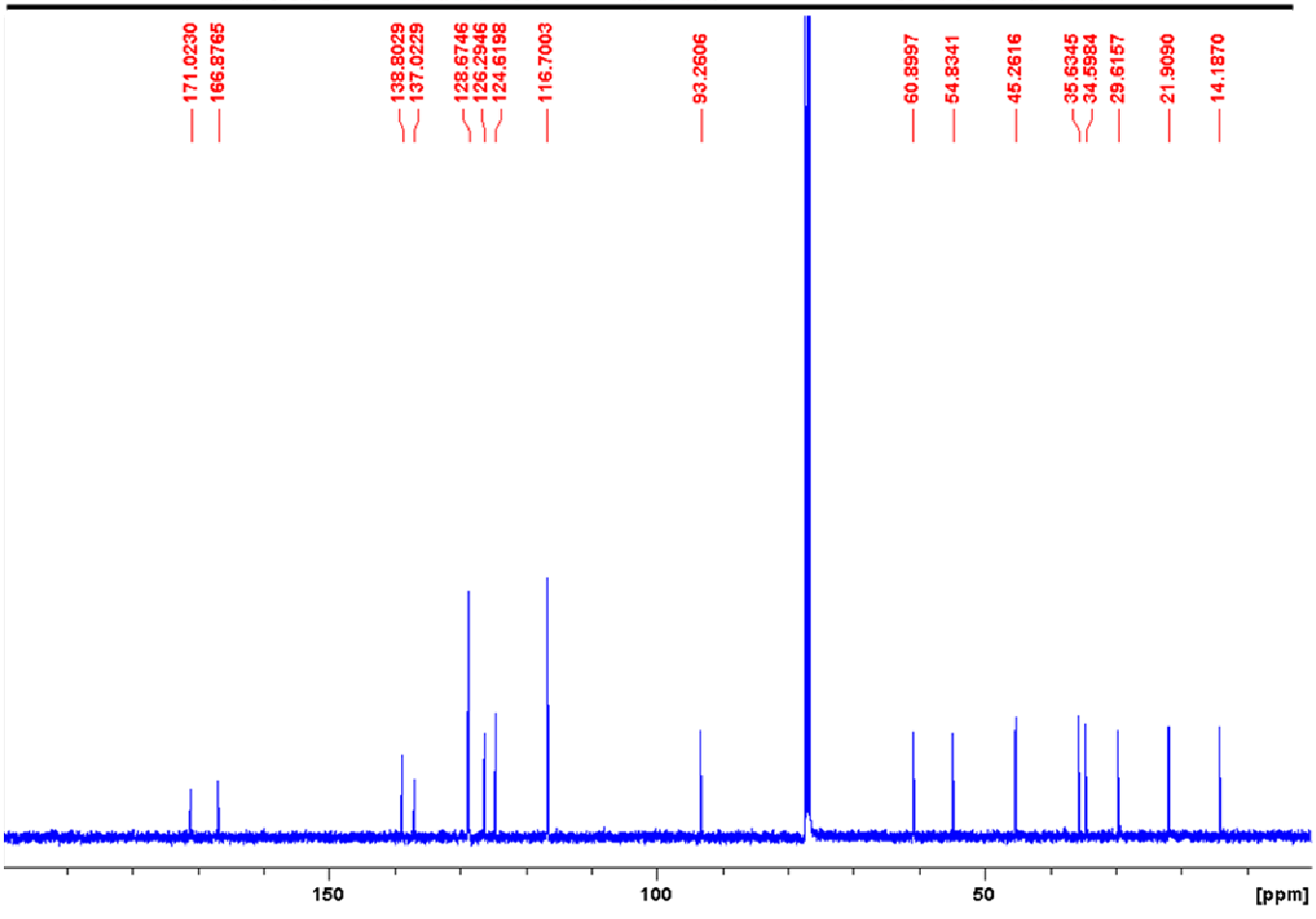
NOESY Spectrum shows a number of interactions:
(1) There is an nOe between H_a and Me, confirming *cis* ring junction
(2) There is an nOe between H_a and the allylic H's, as well as H_t and Me.
This suggests that the allyl group, Me, and H_a are all on same side of ring.
- Indicates a *trans* relative stereochemistry.

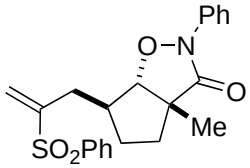






4b





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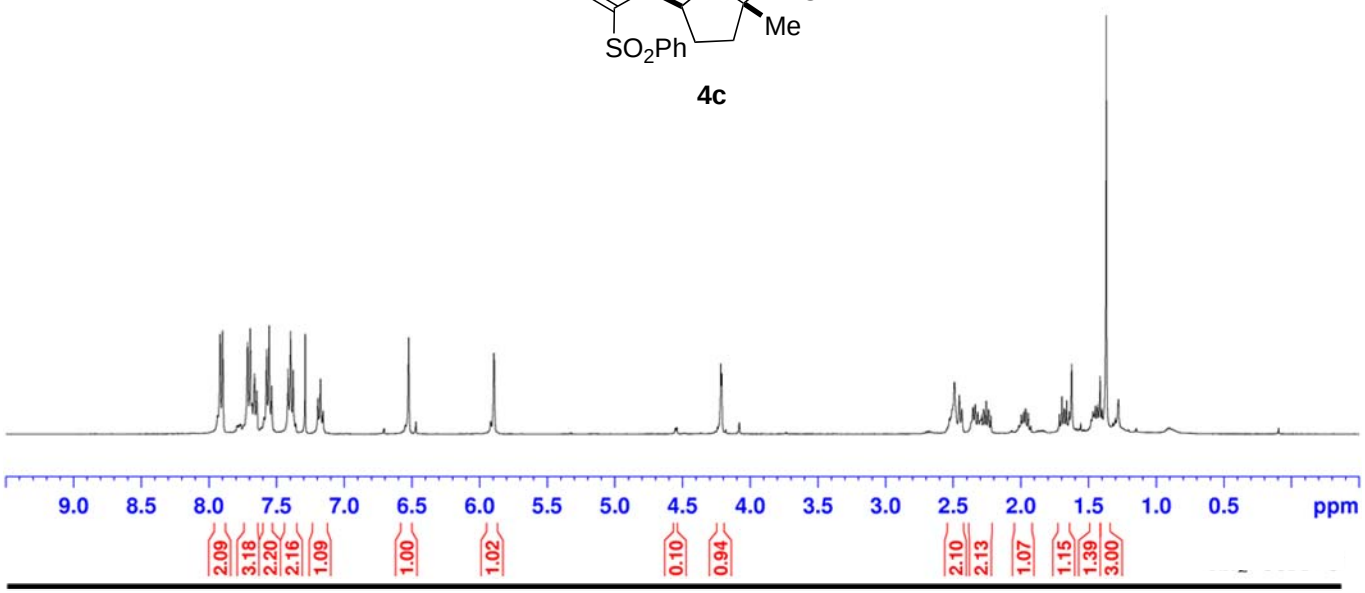

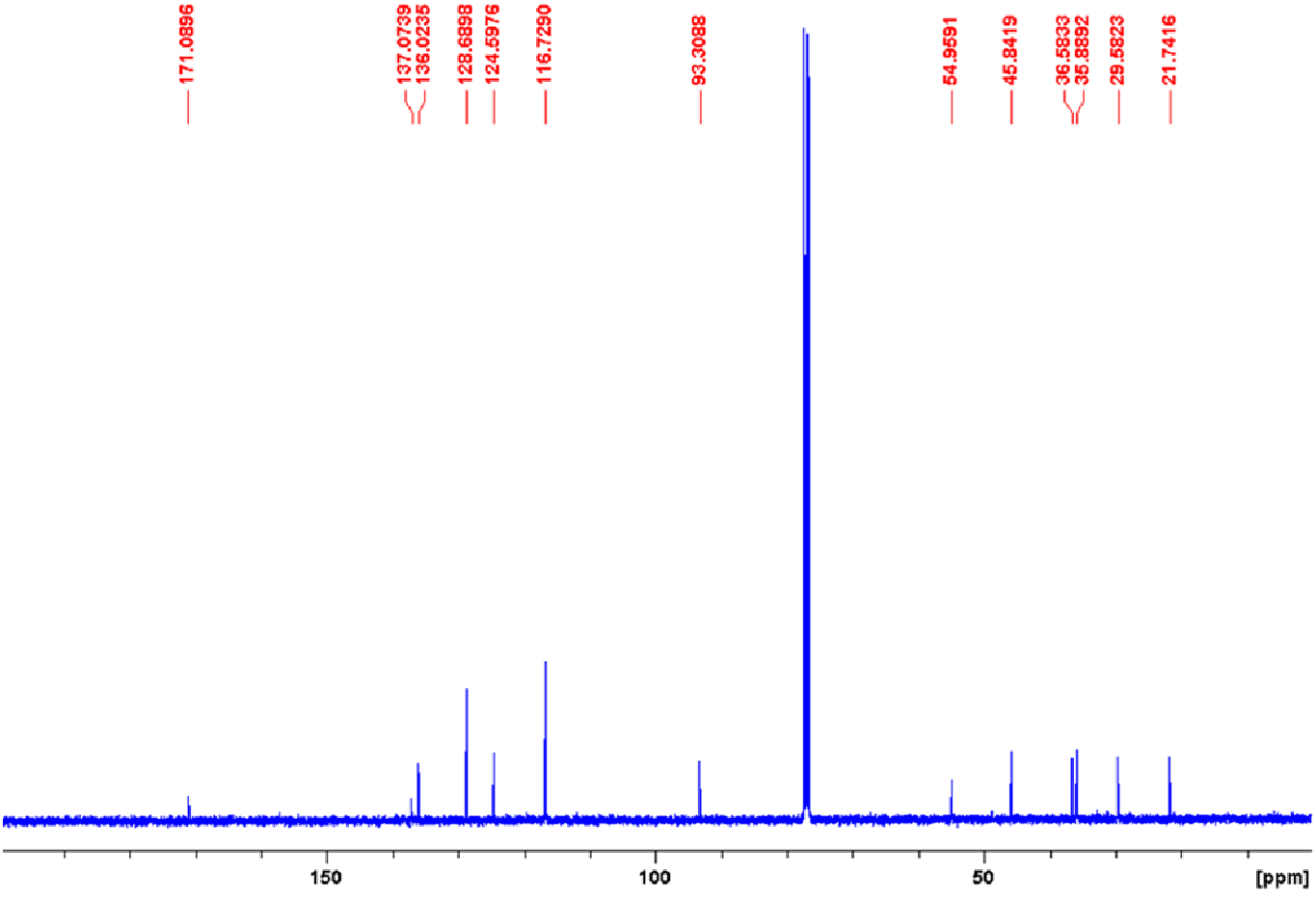

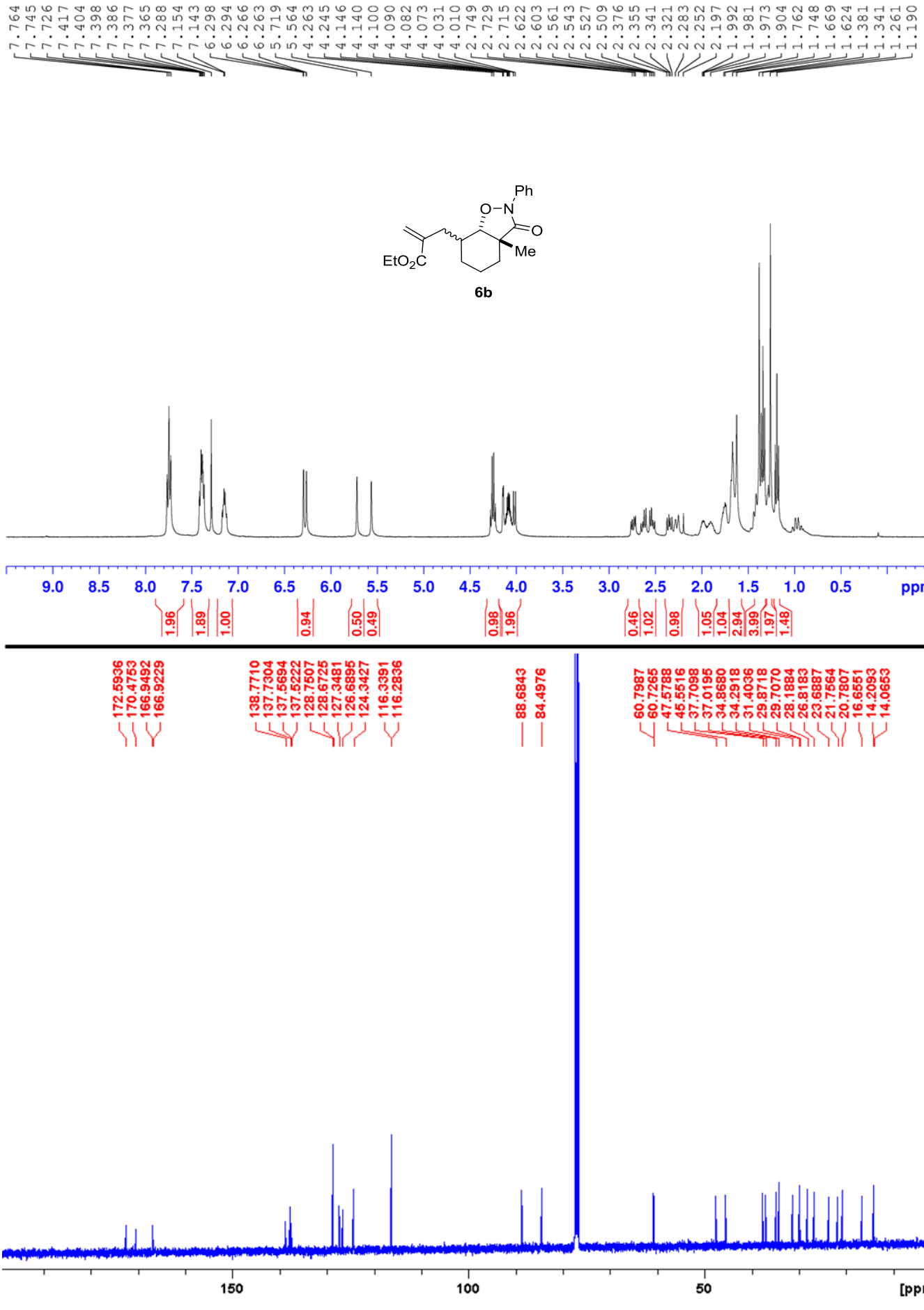
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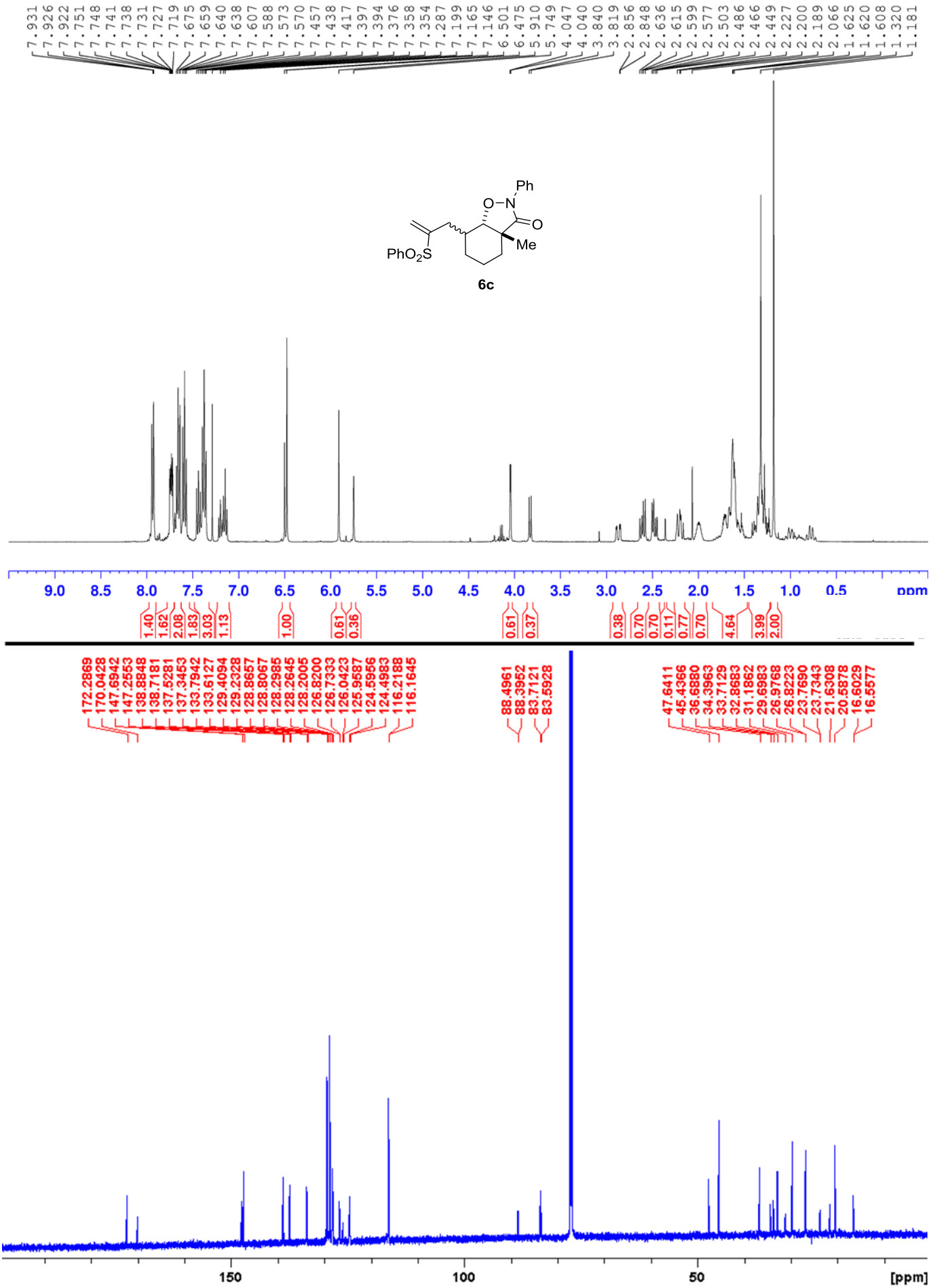

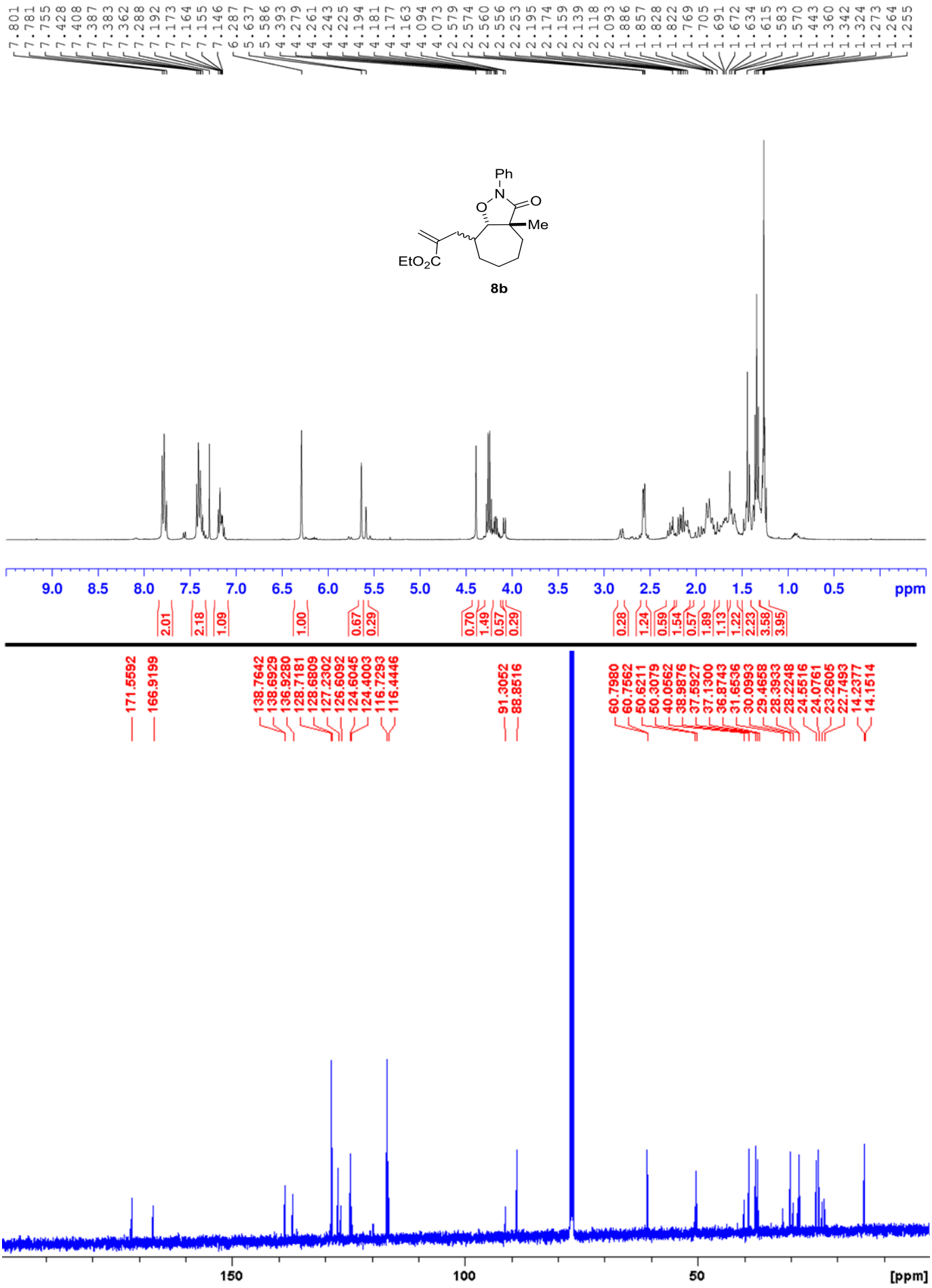

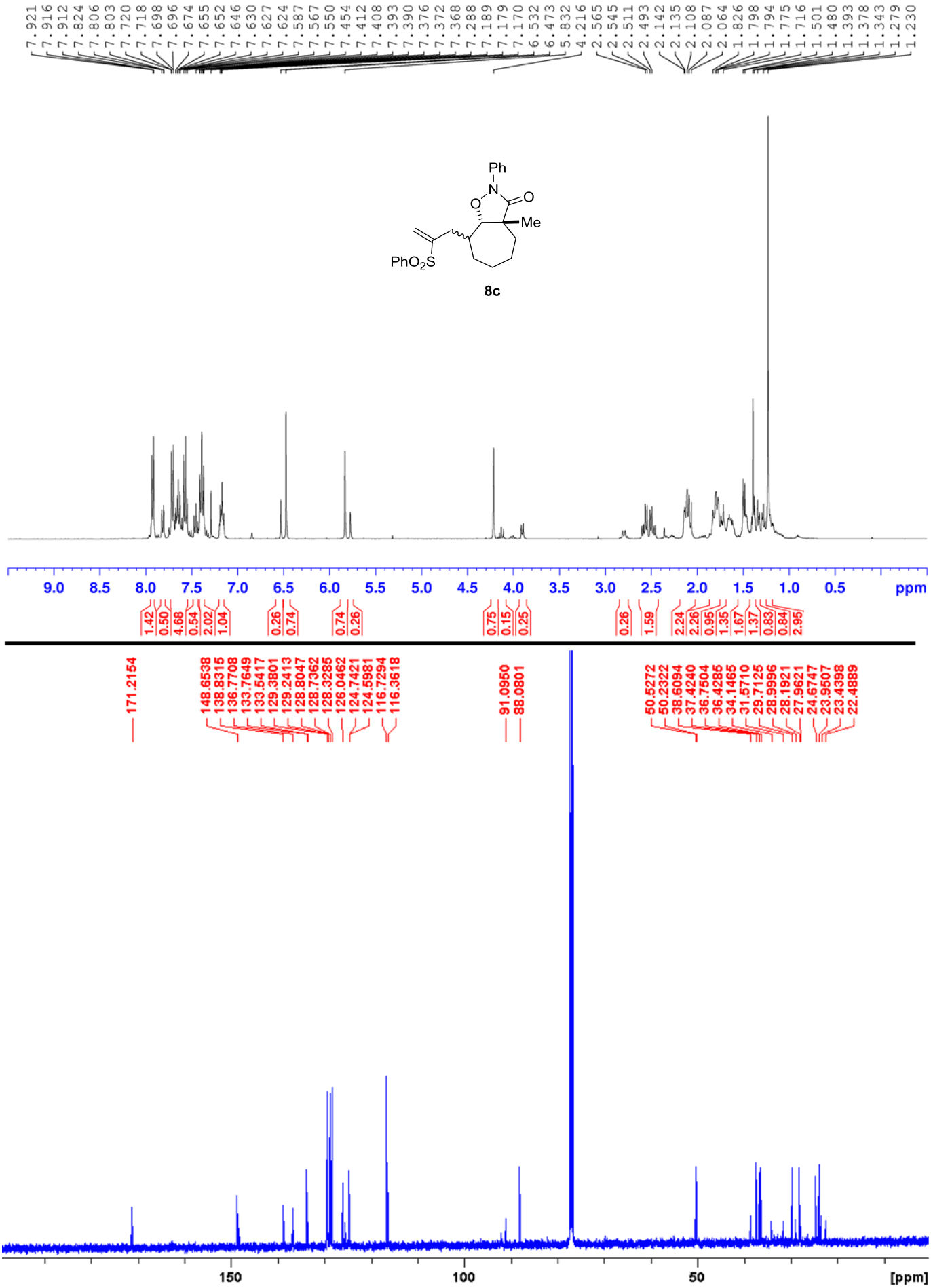

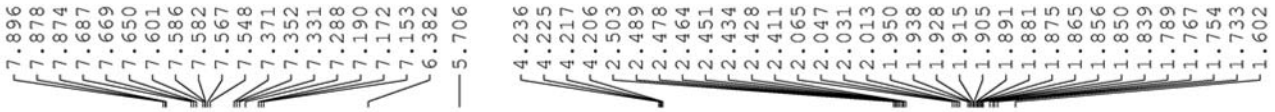

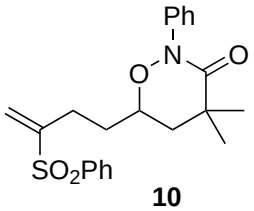

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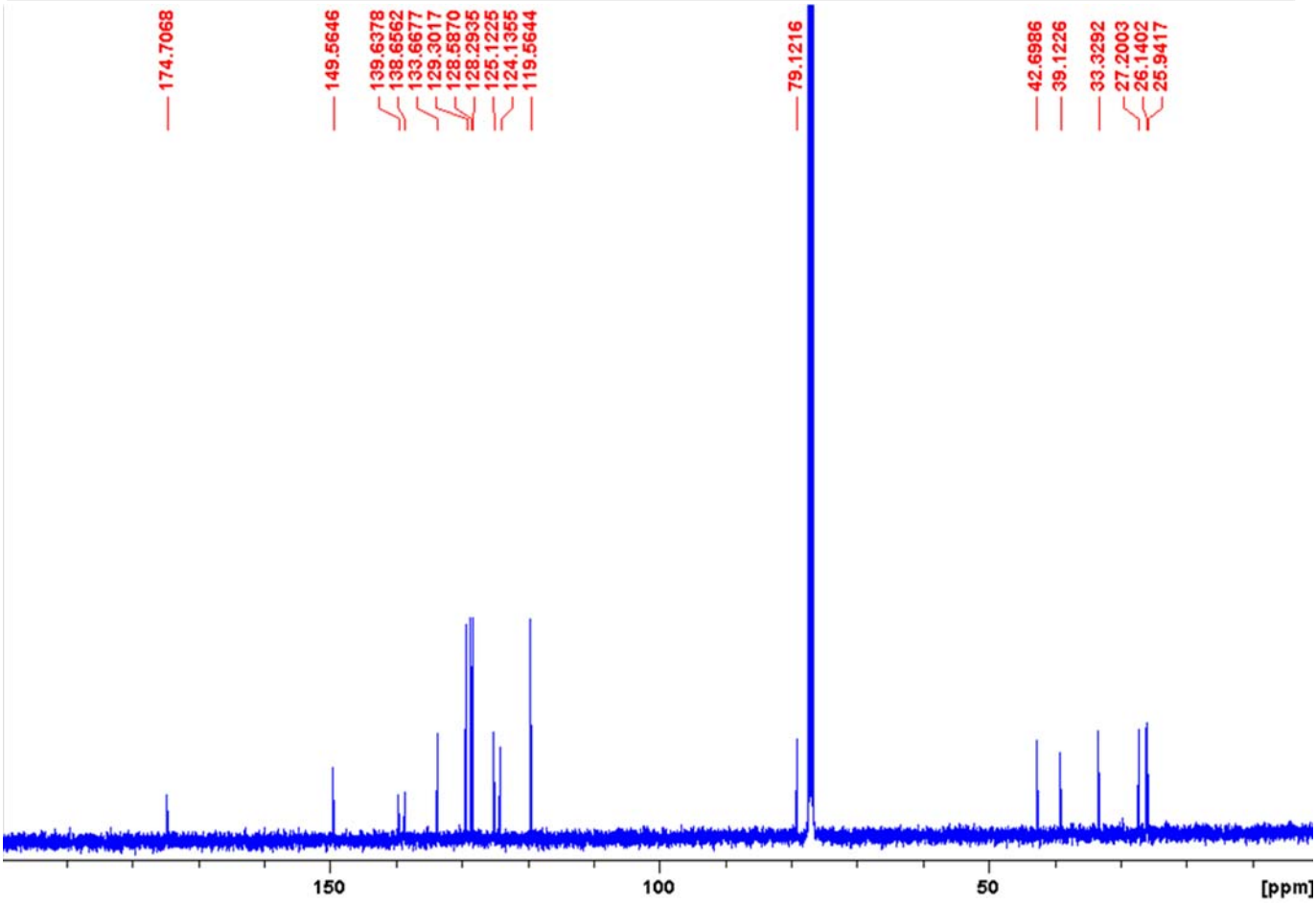

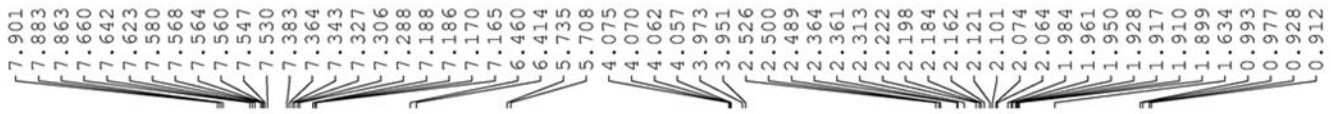

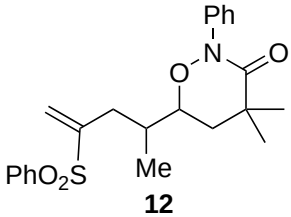

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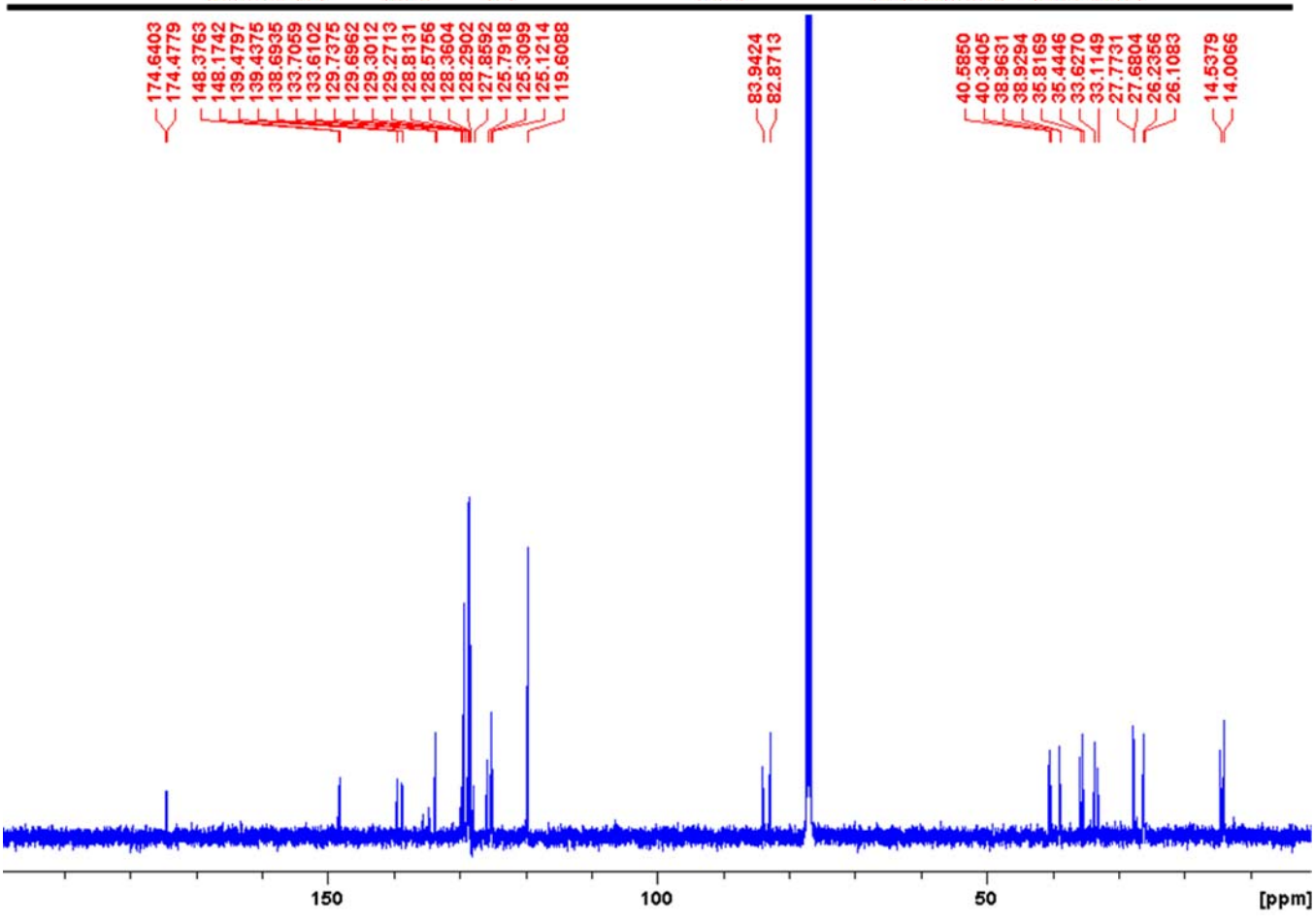
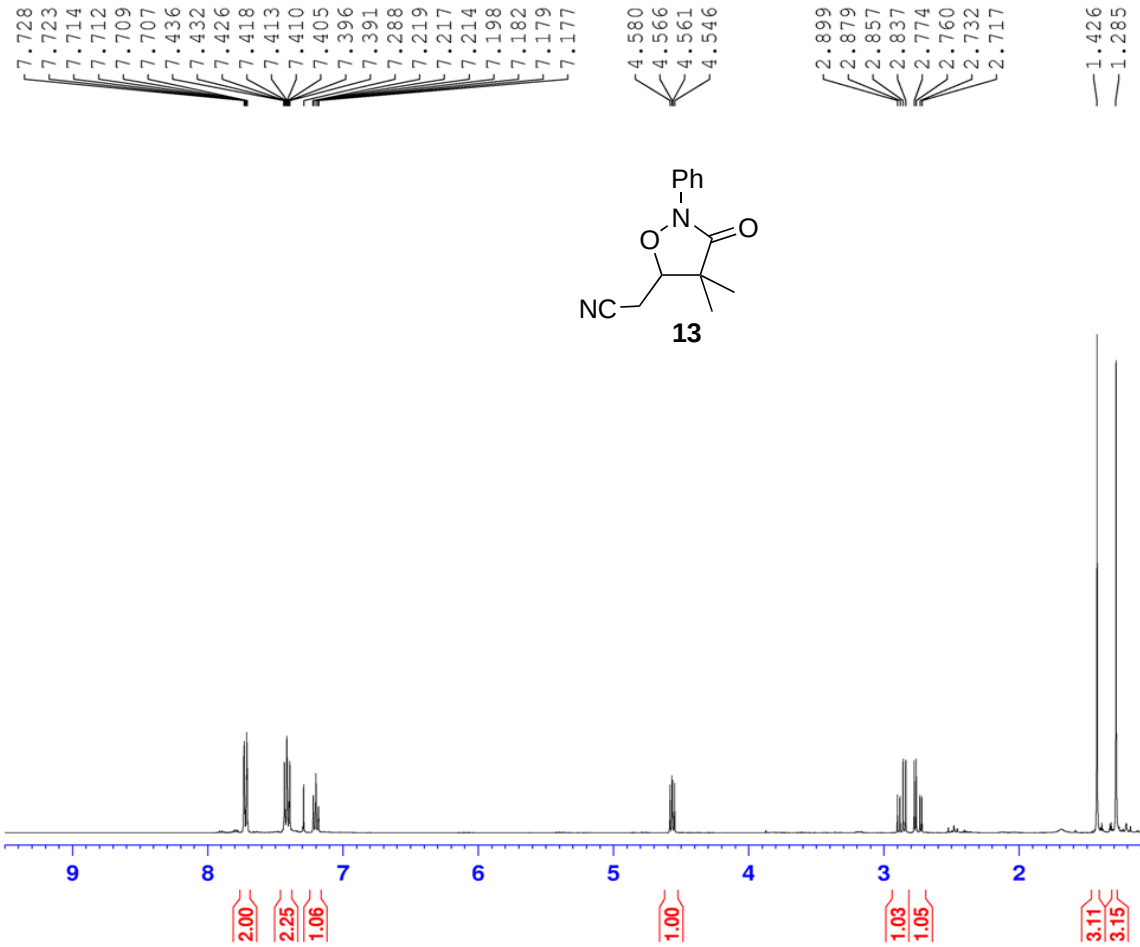
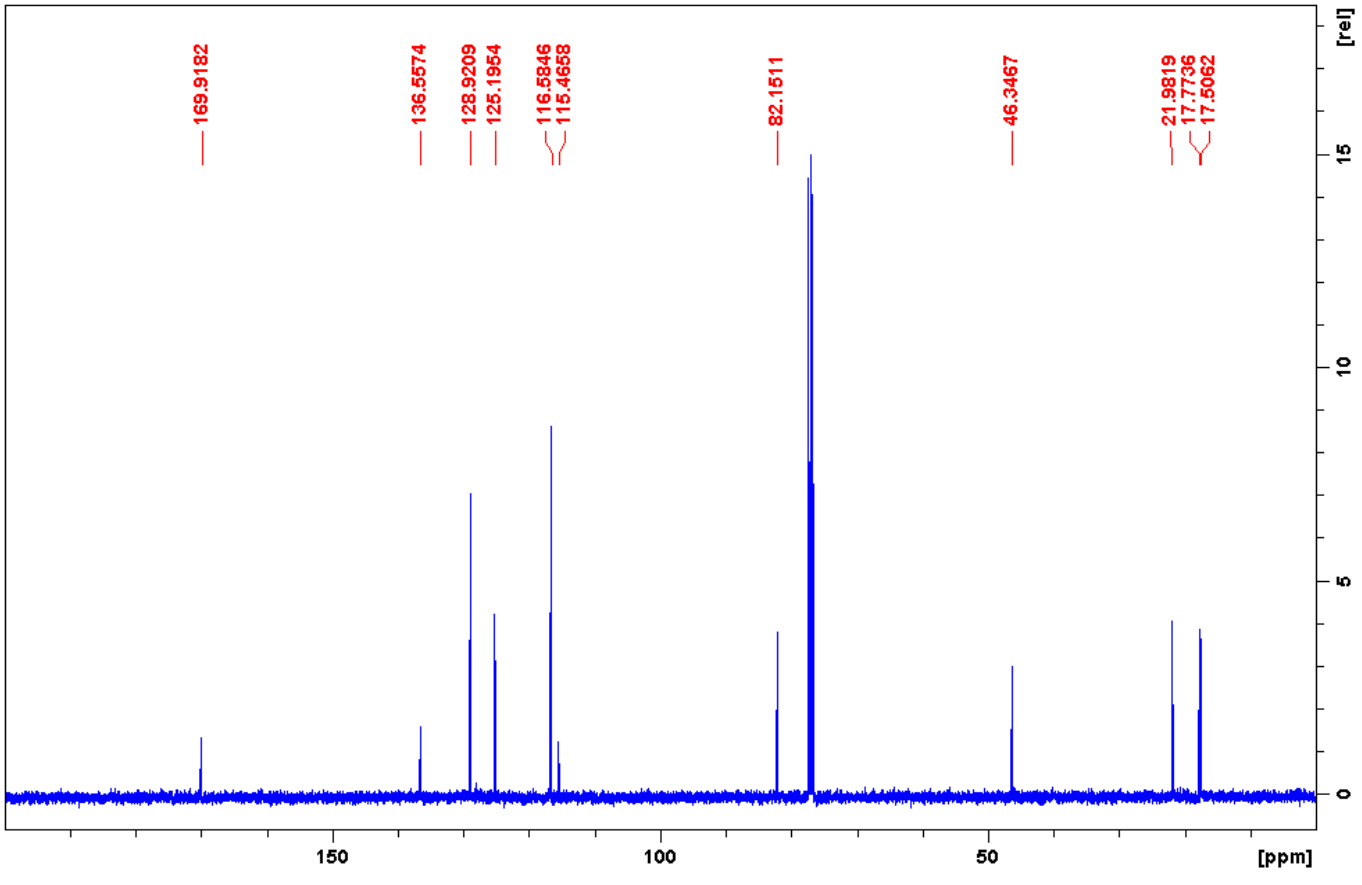
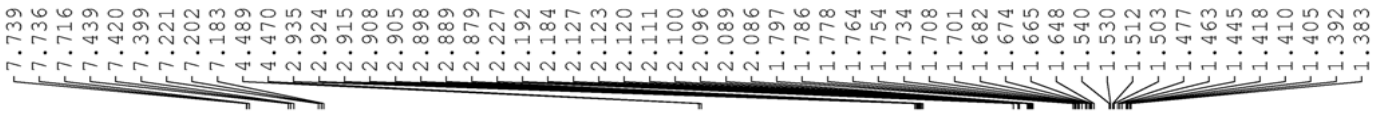
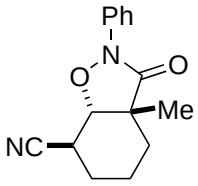


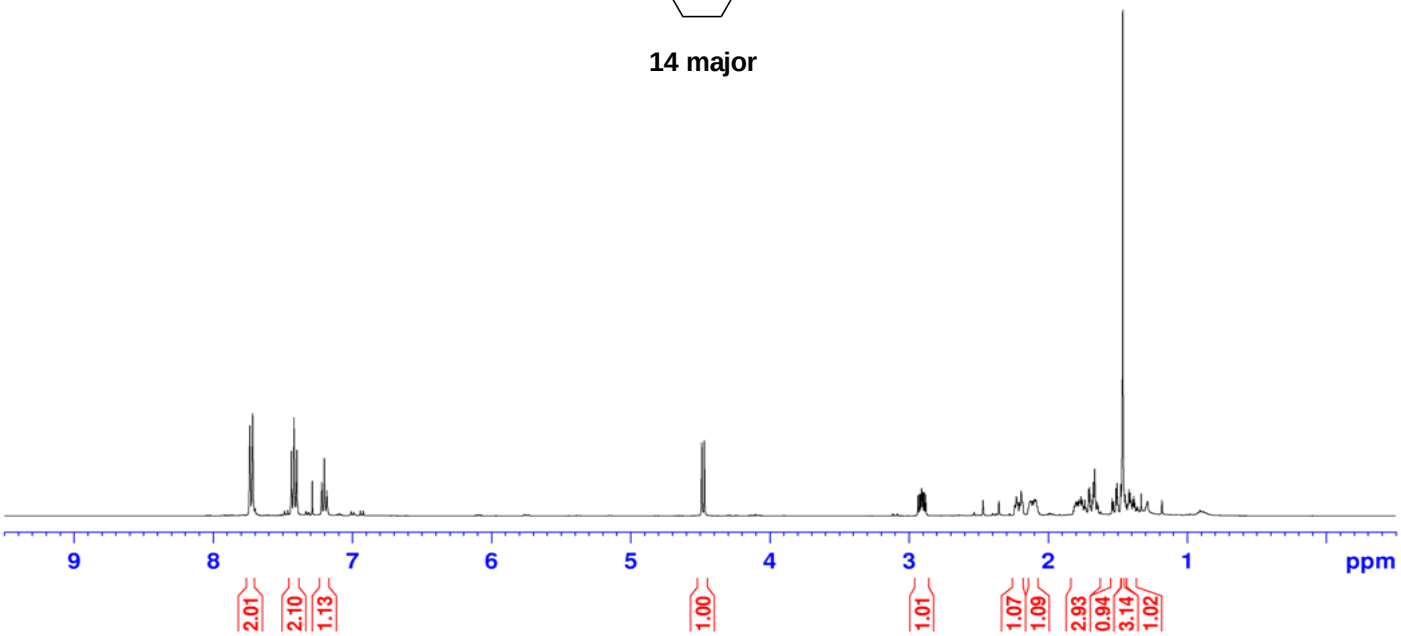


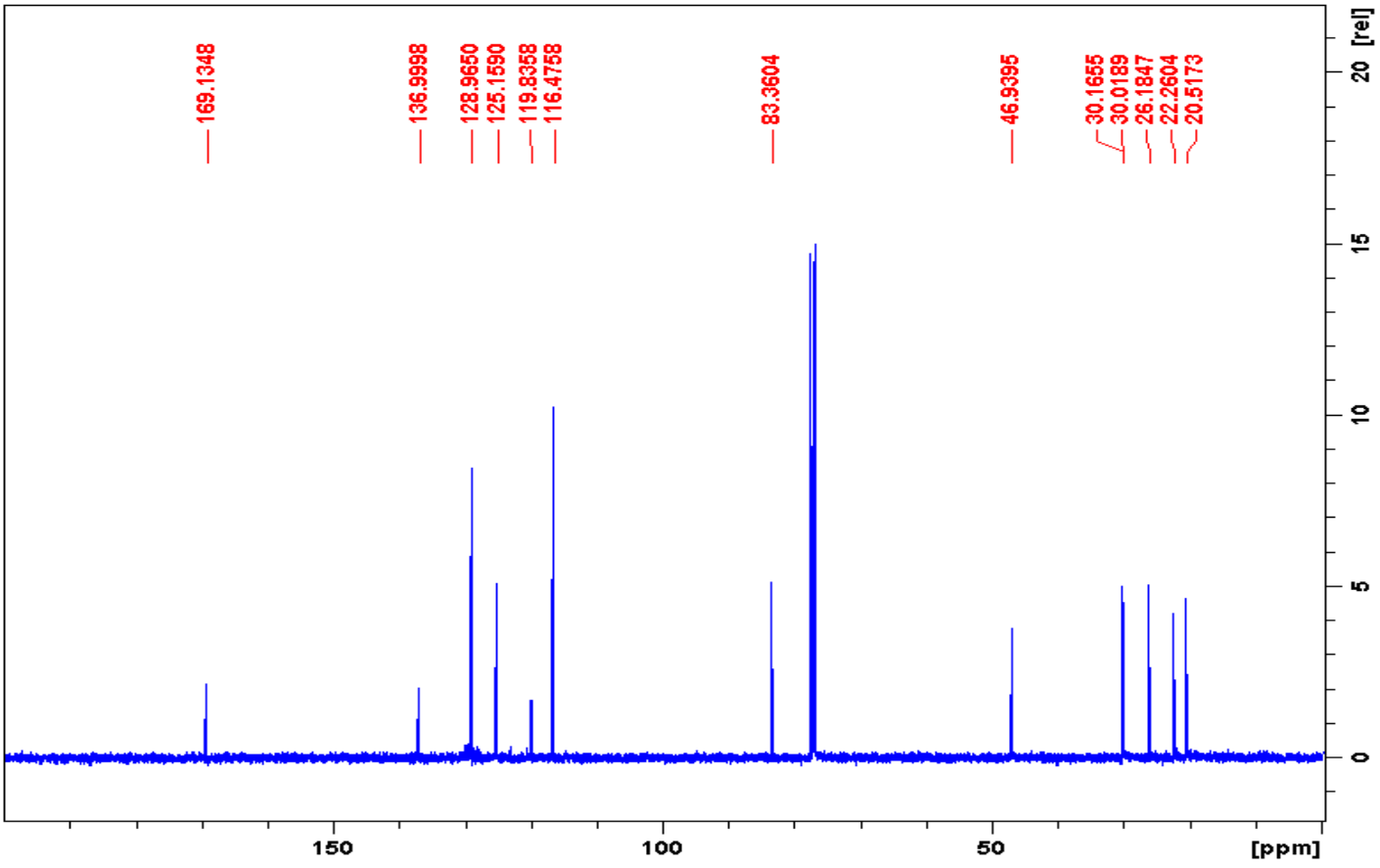


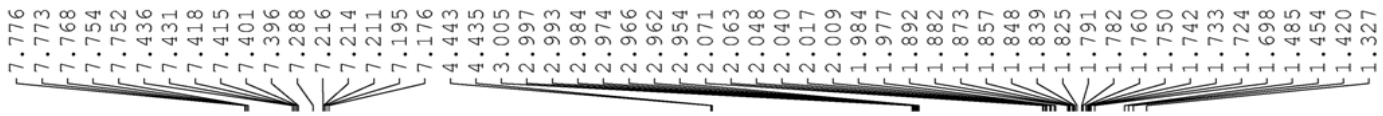


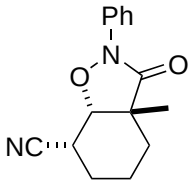


14 major

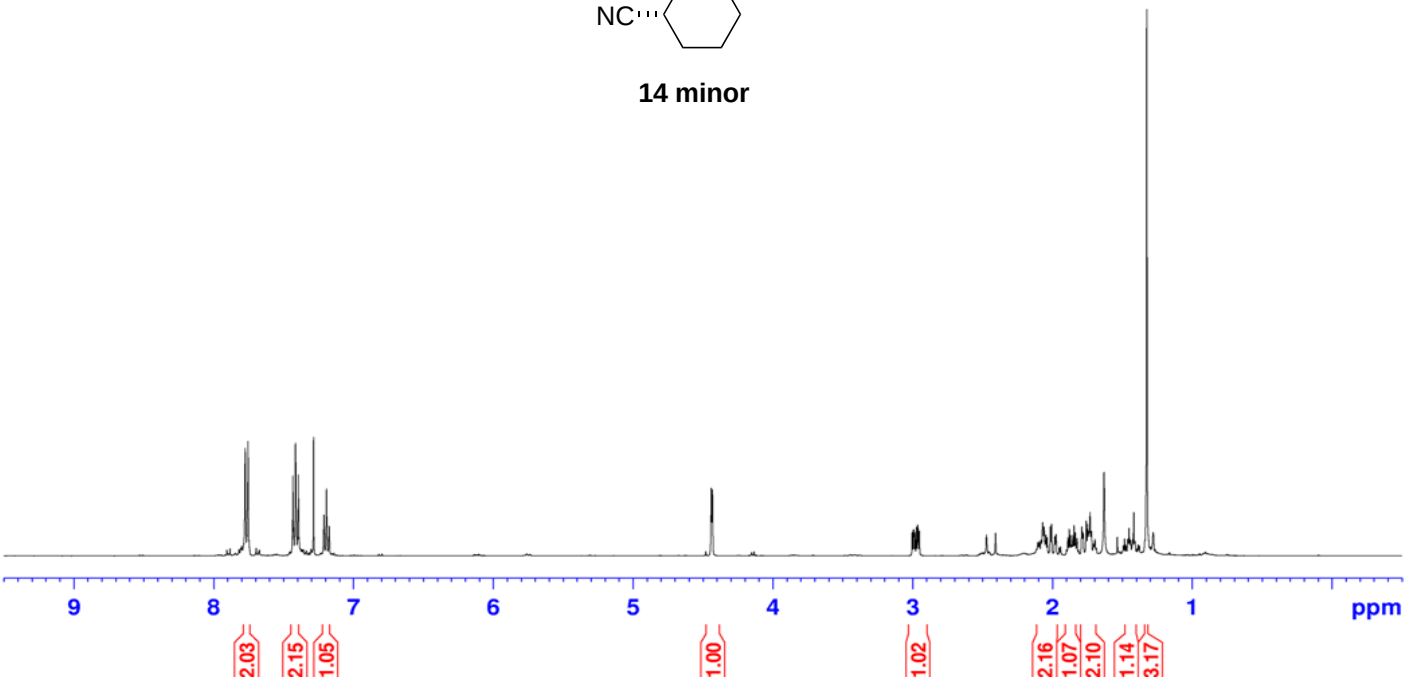


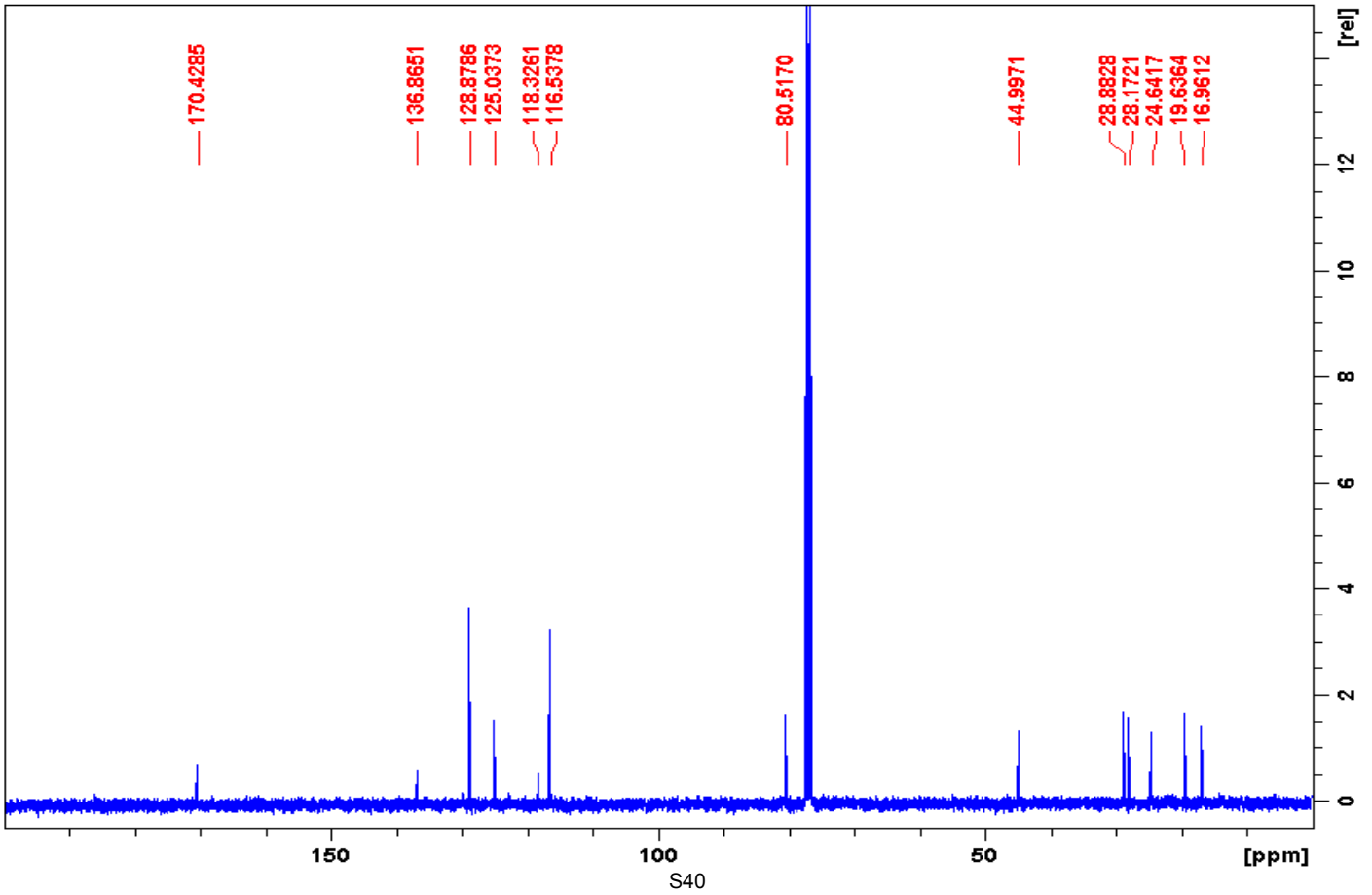


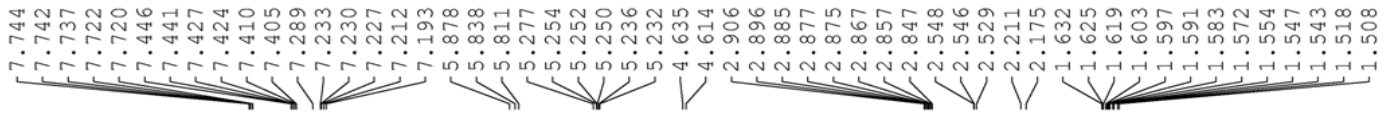


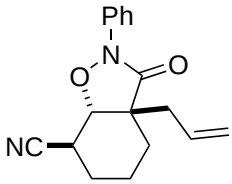


14 minor









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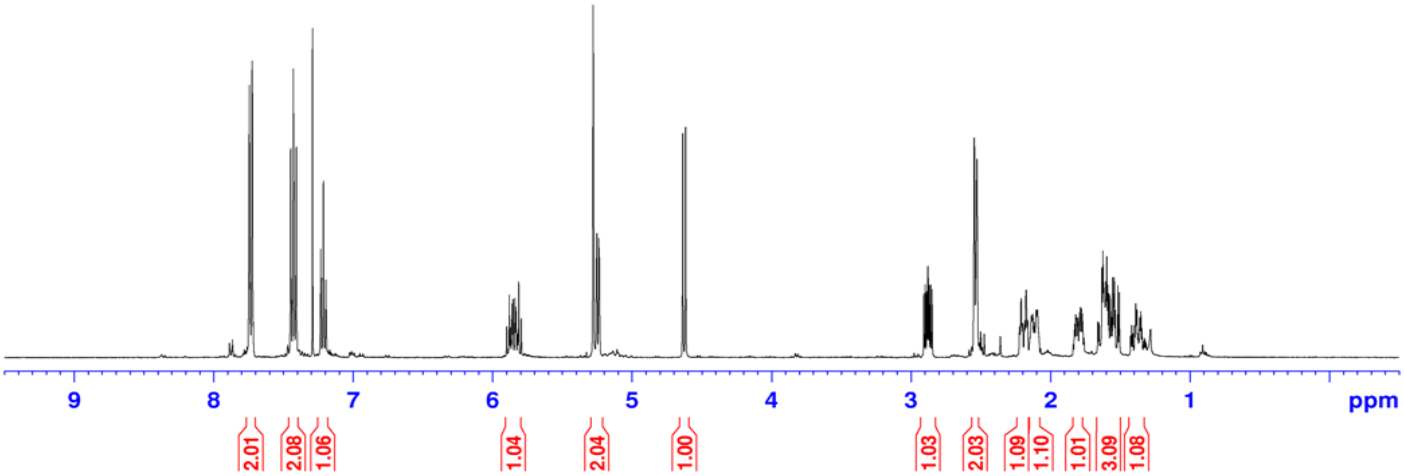

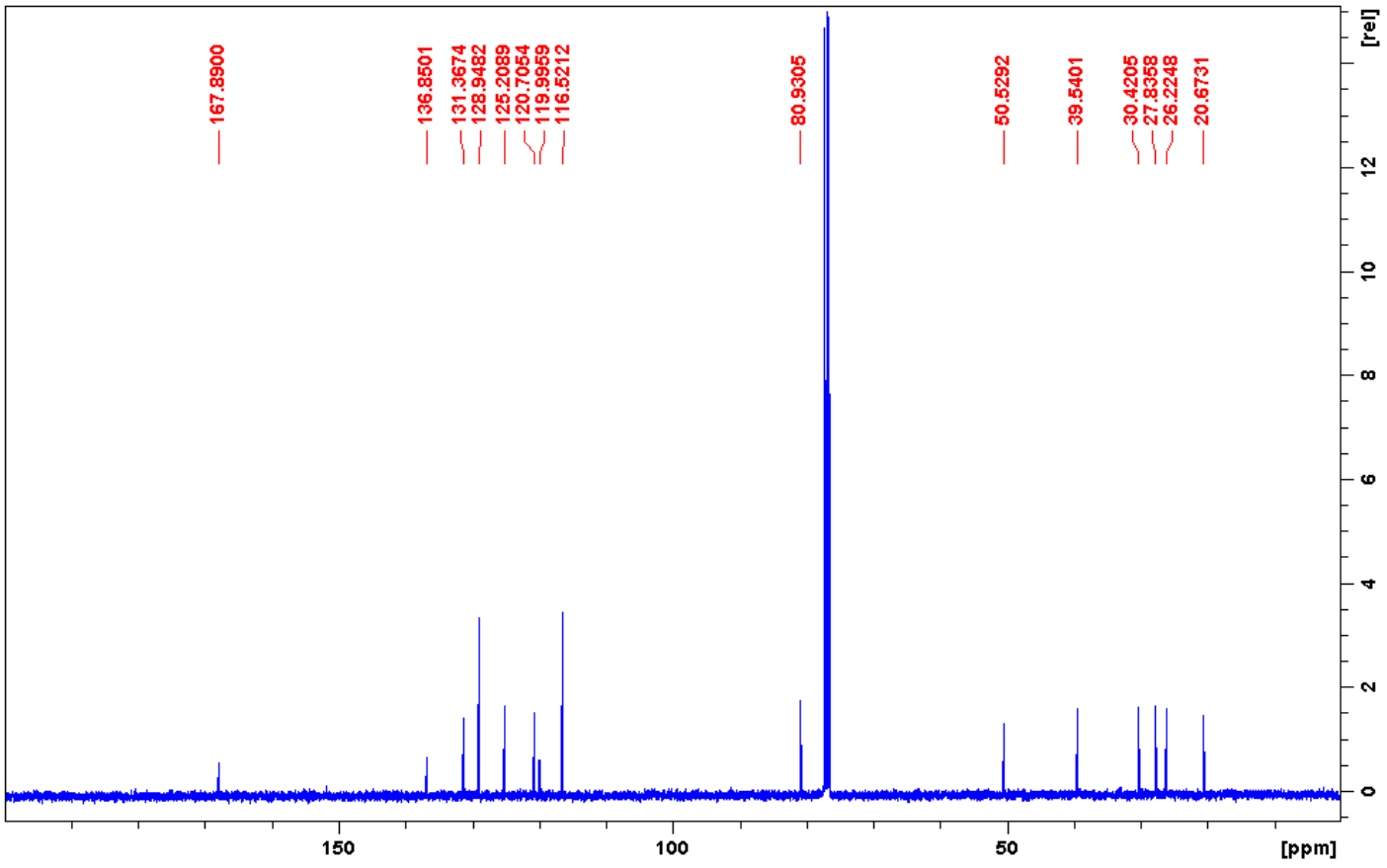

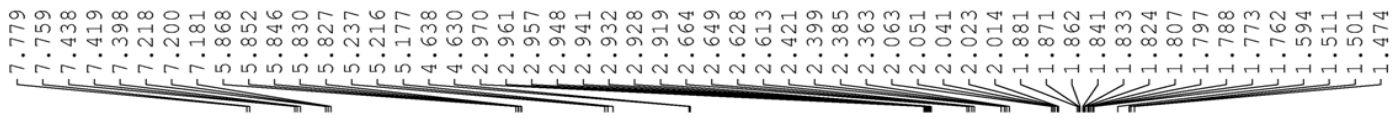

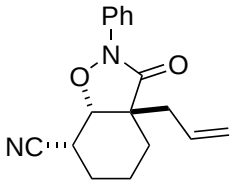

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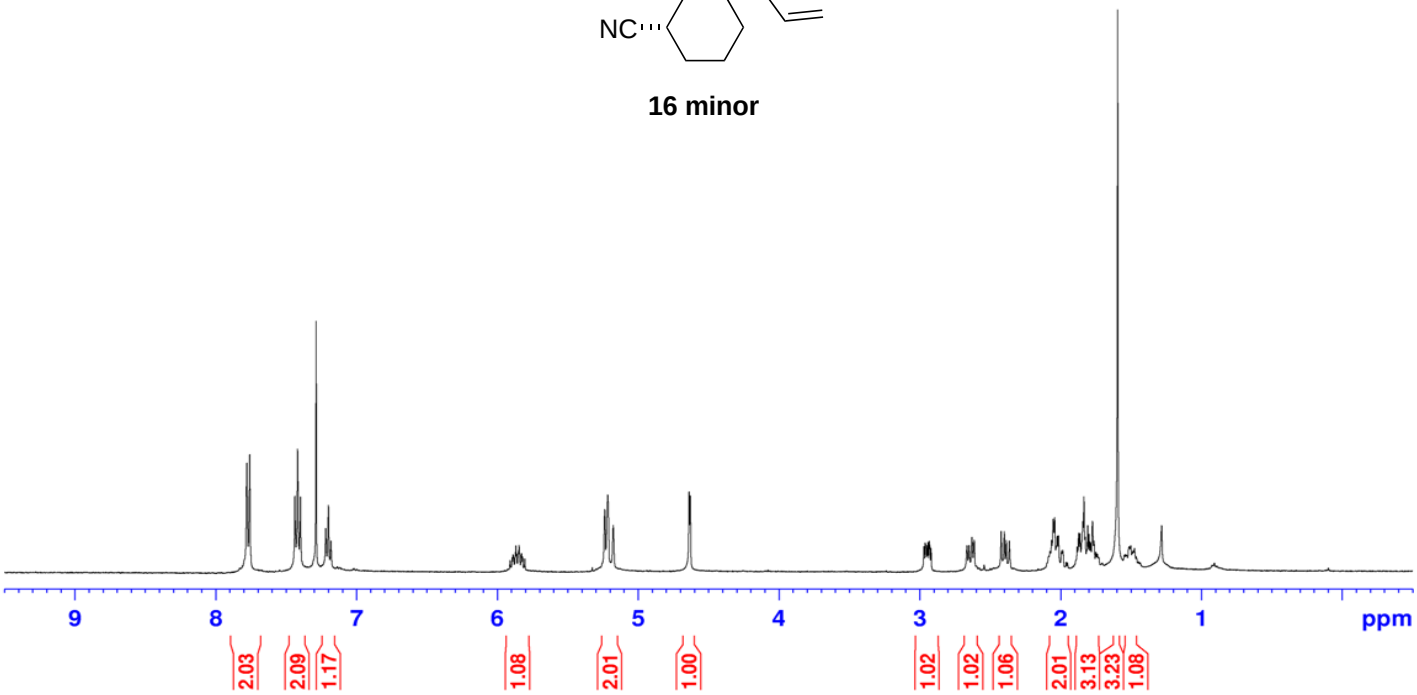

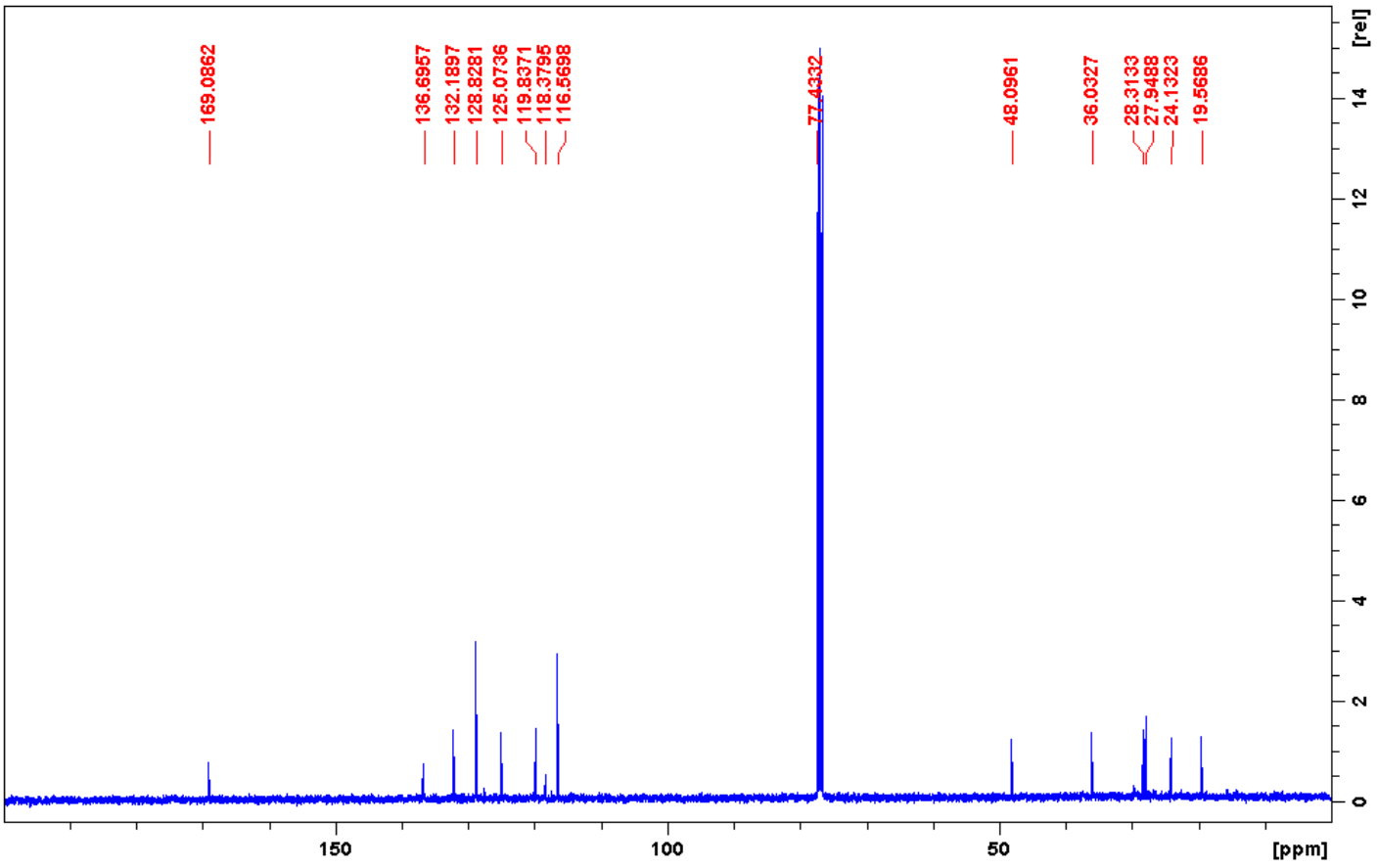

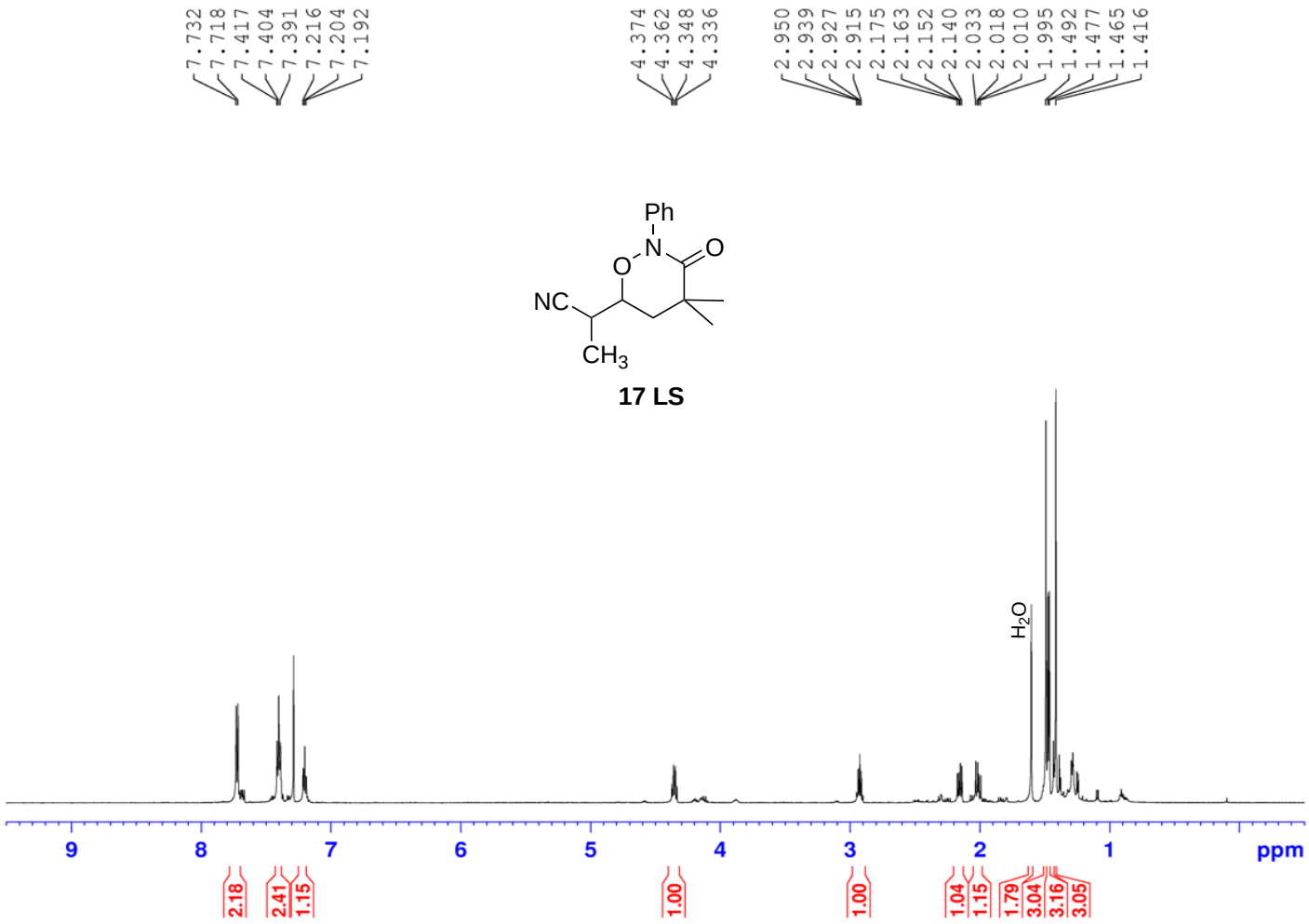

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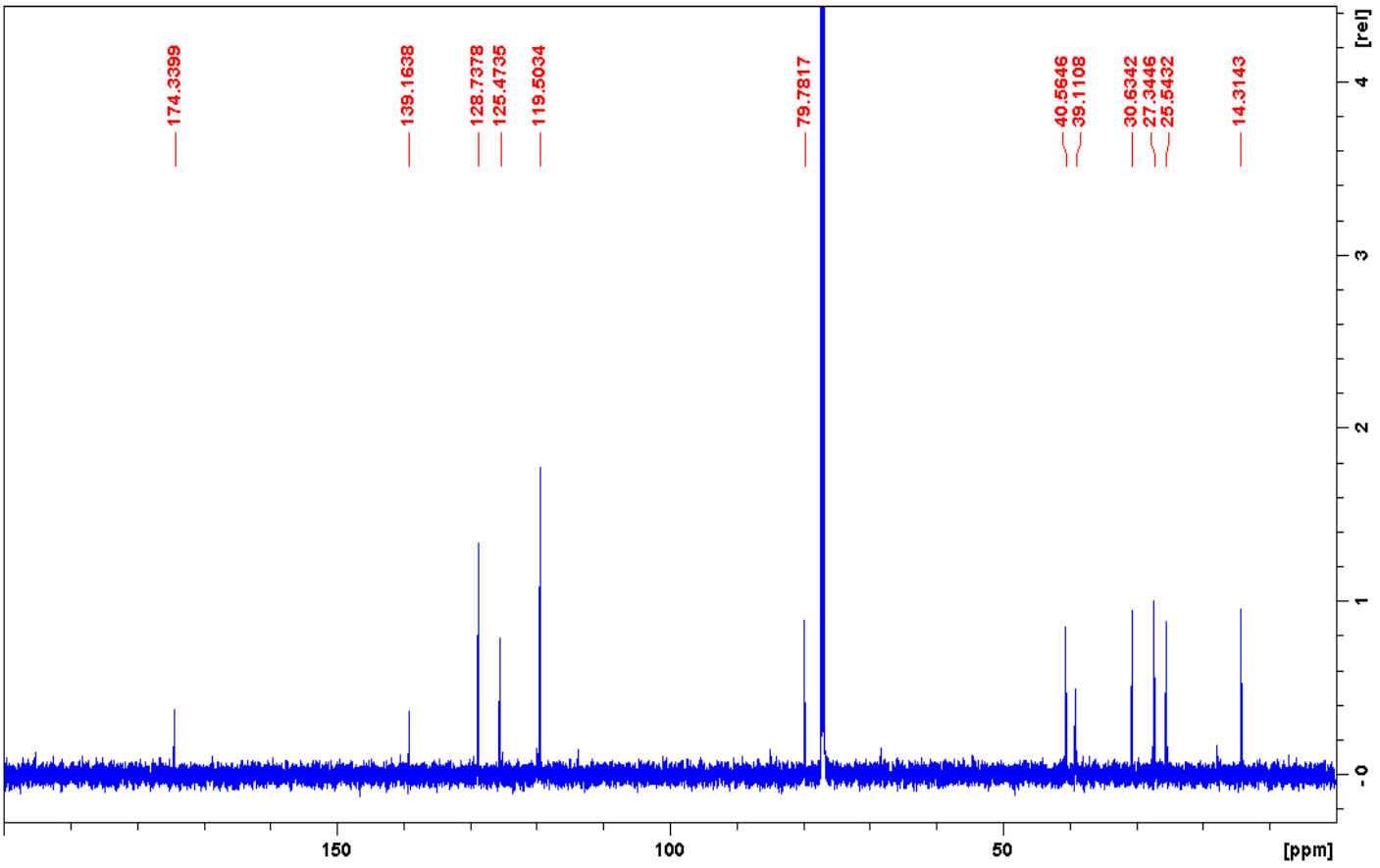

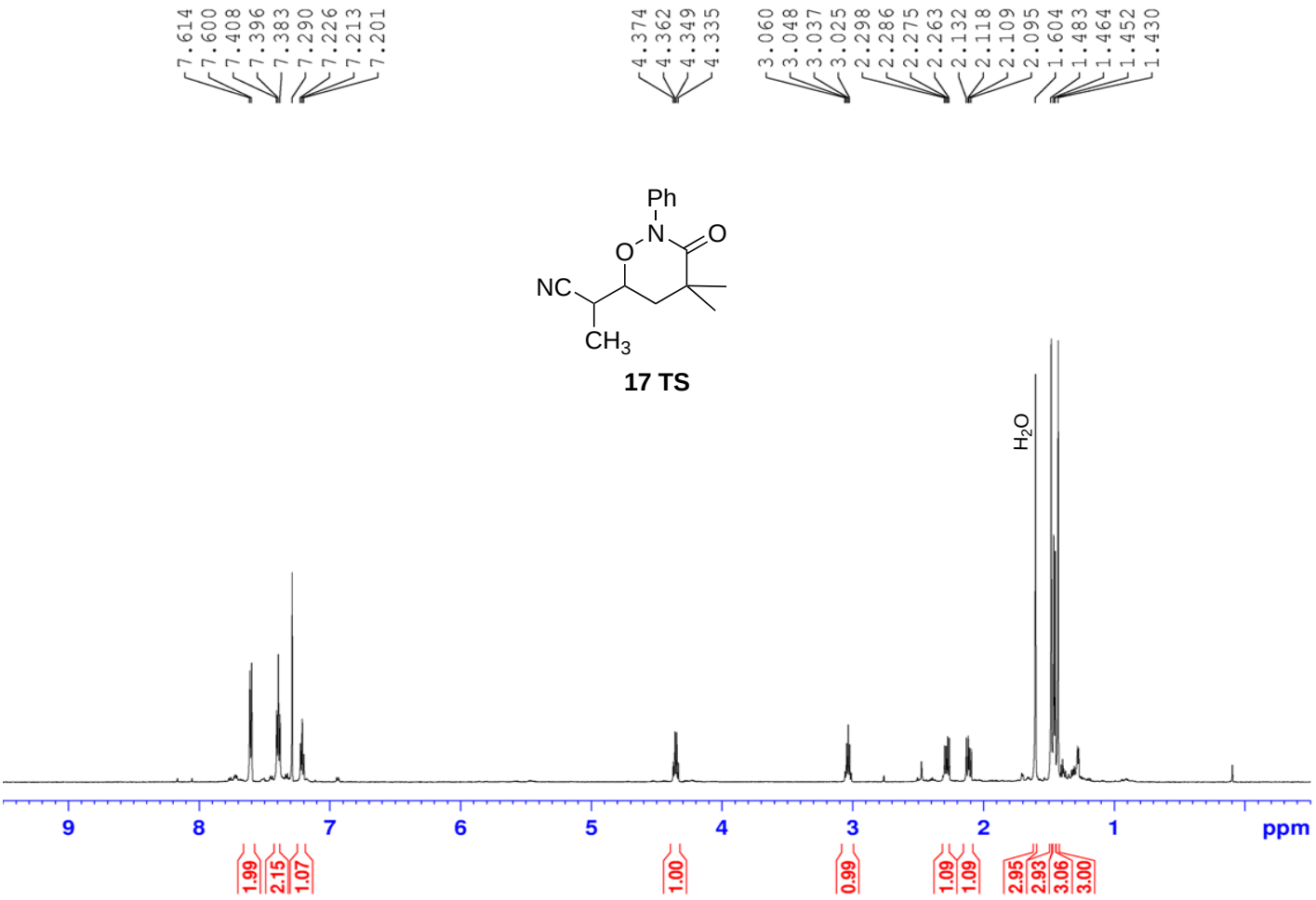

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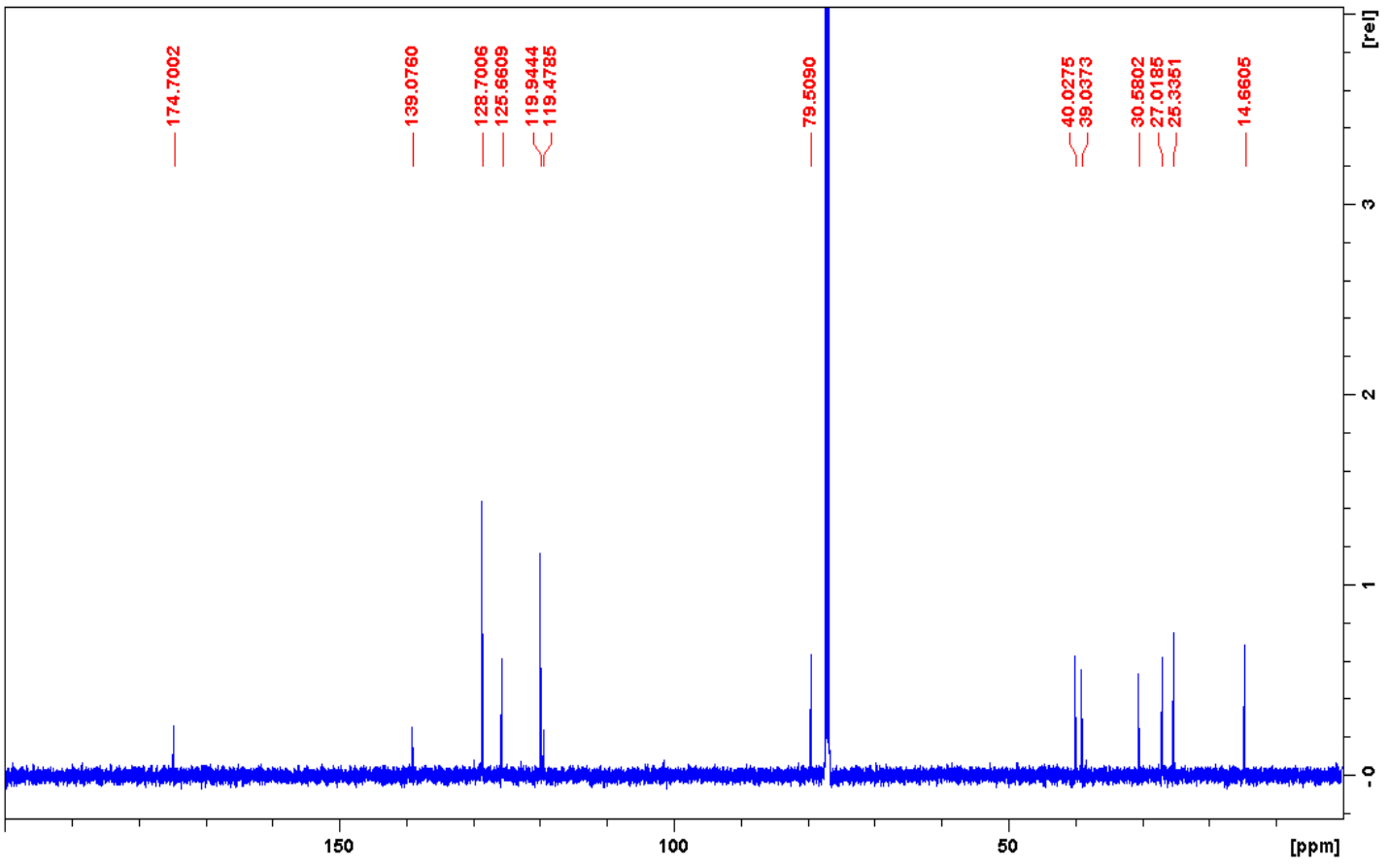

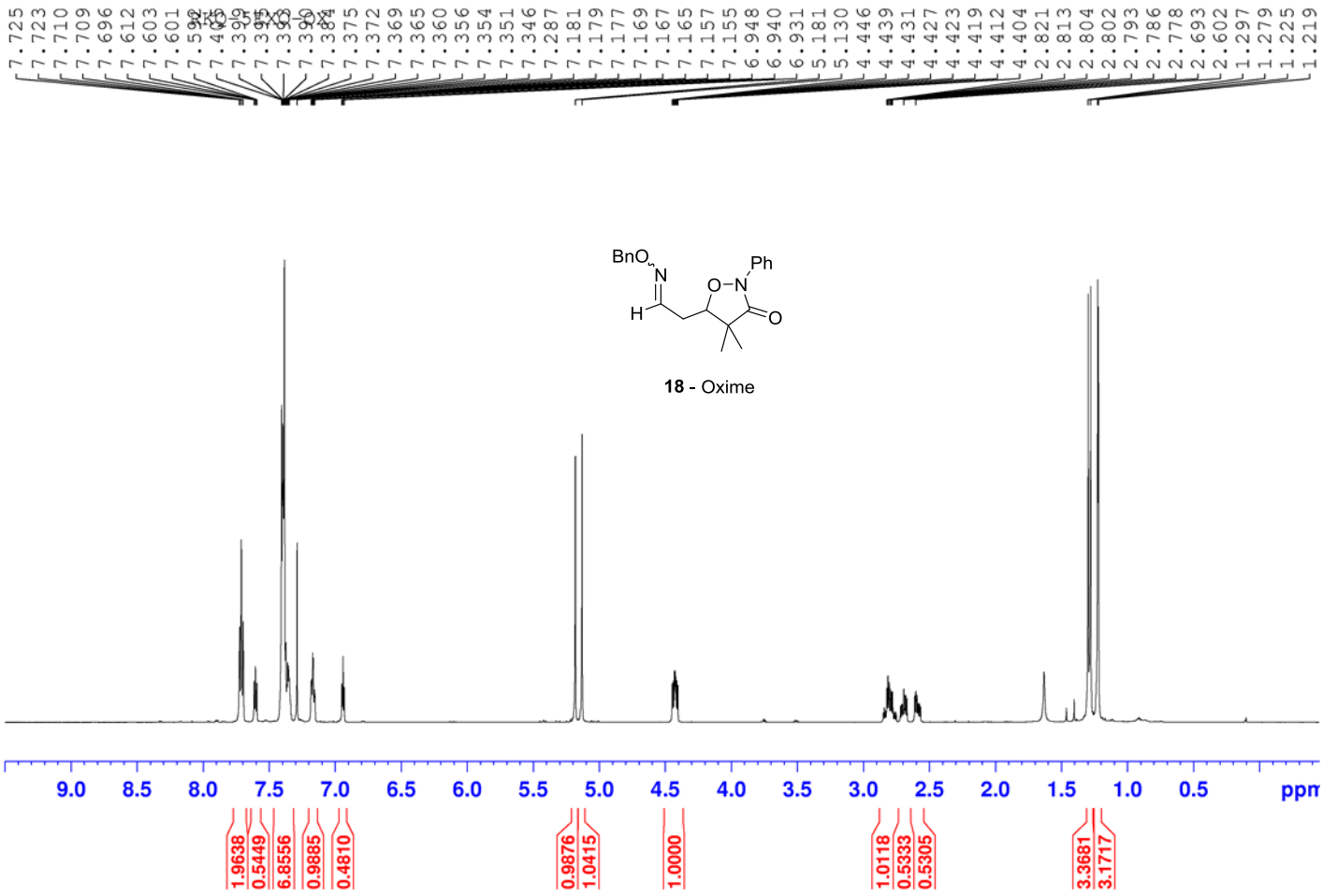

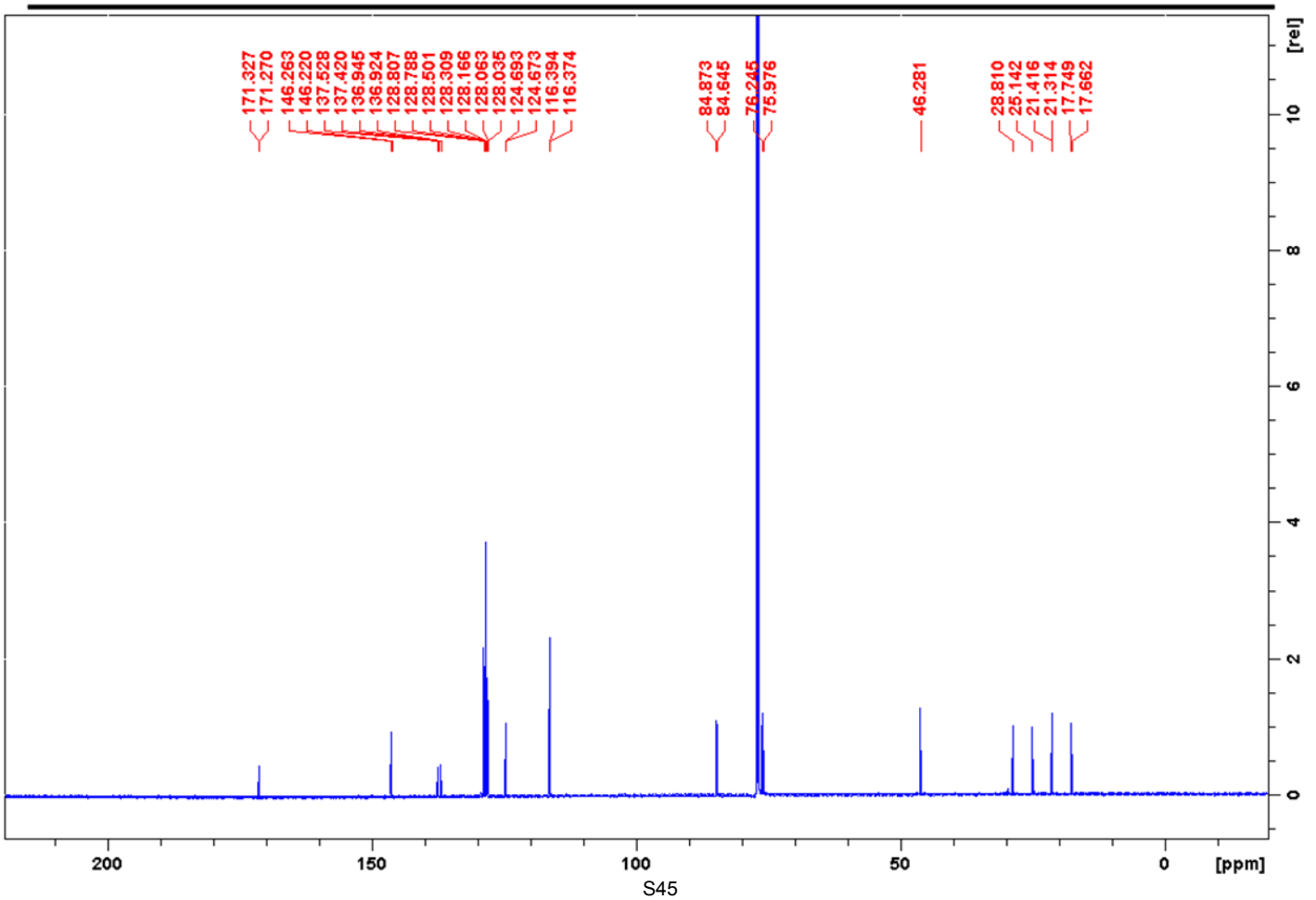

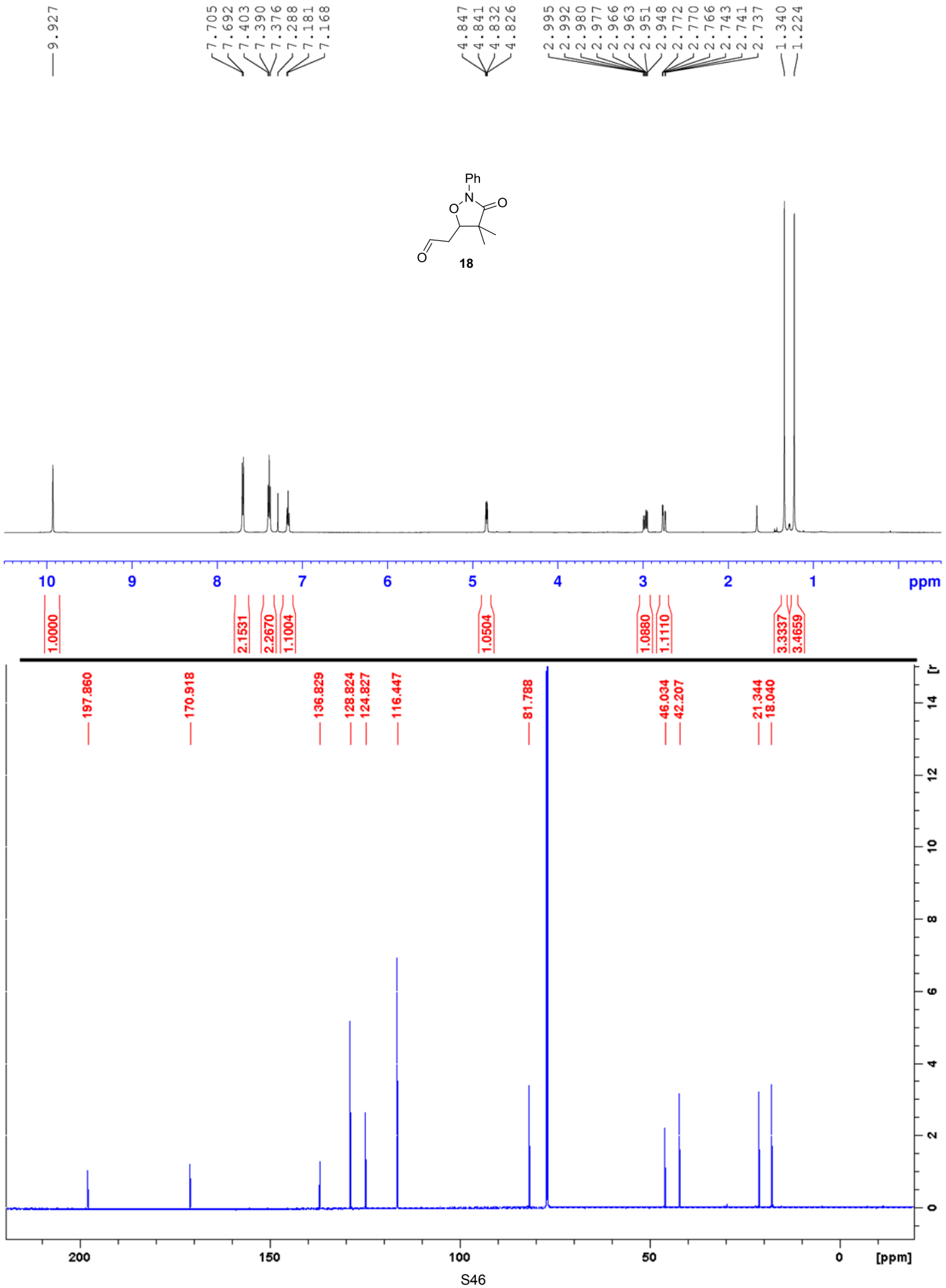

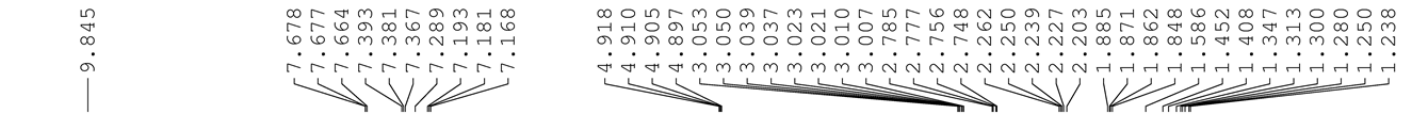
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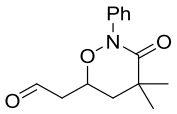
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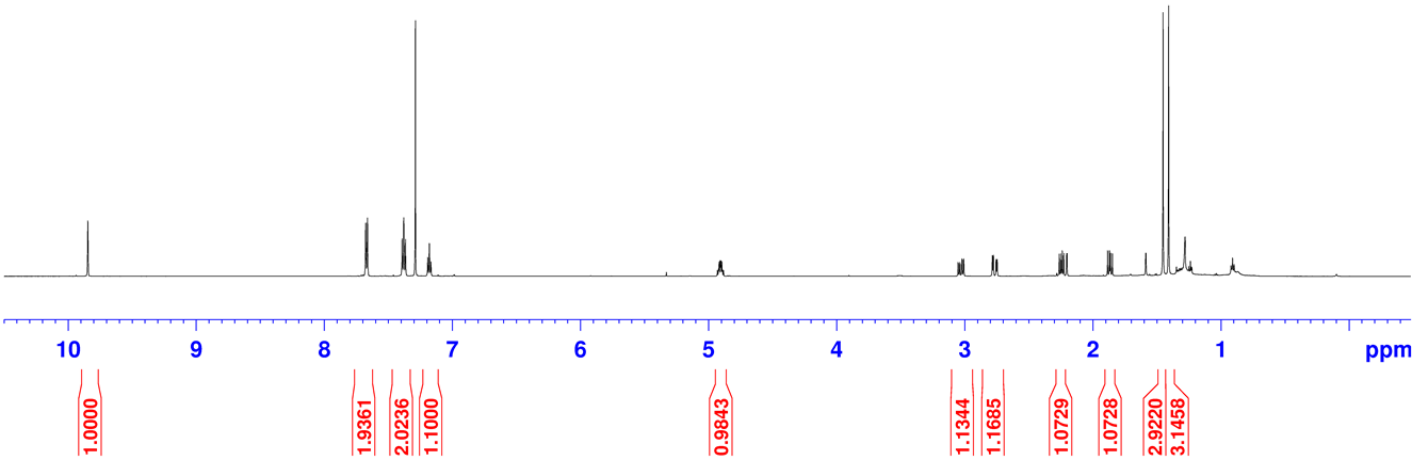
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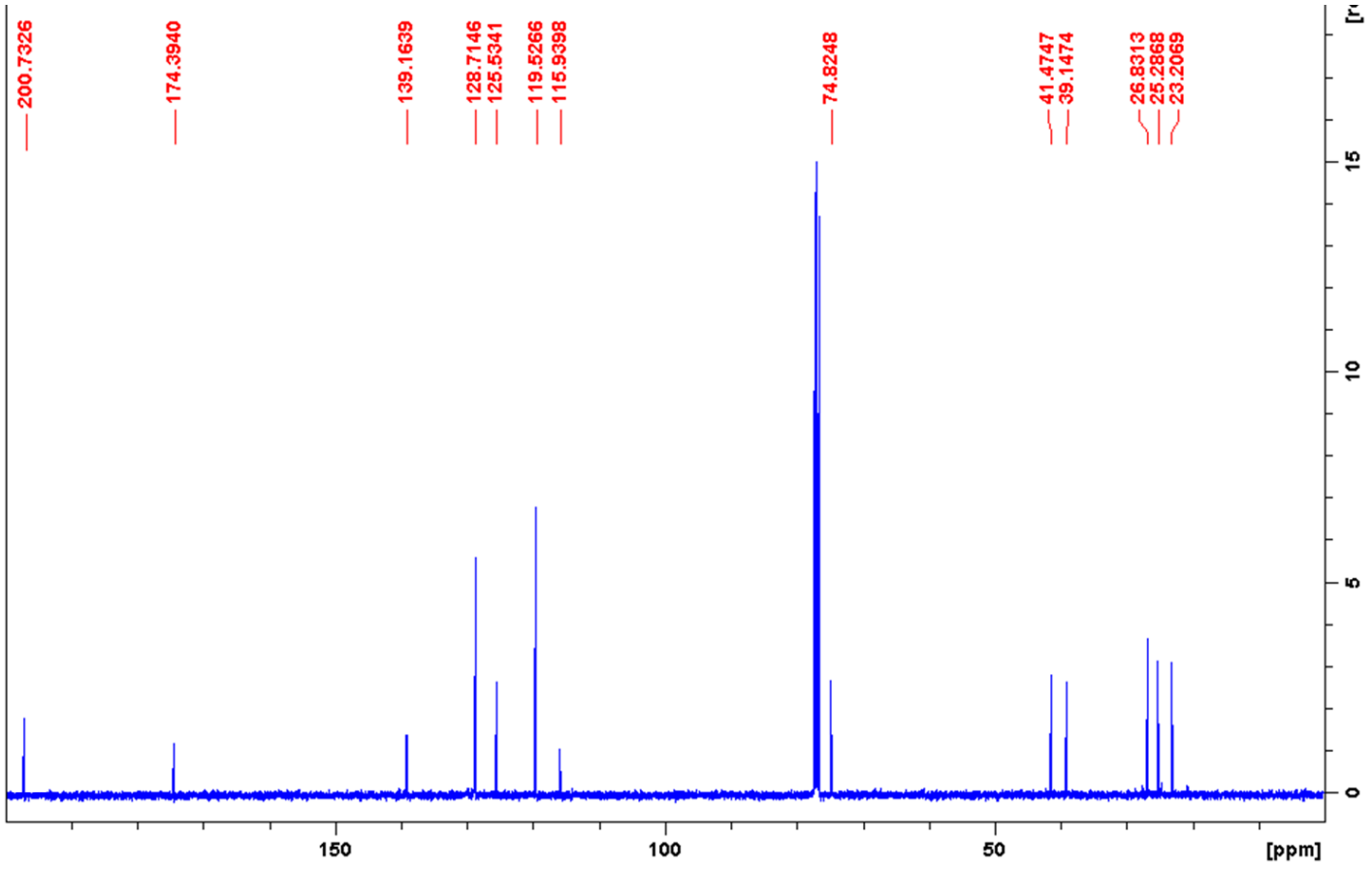
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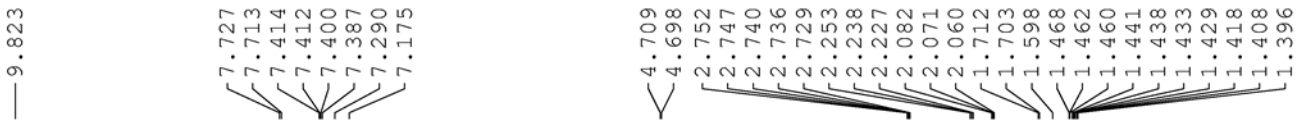
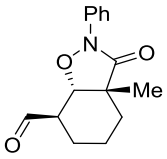
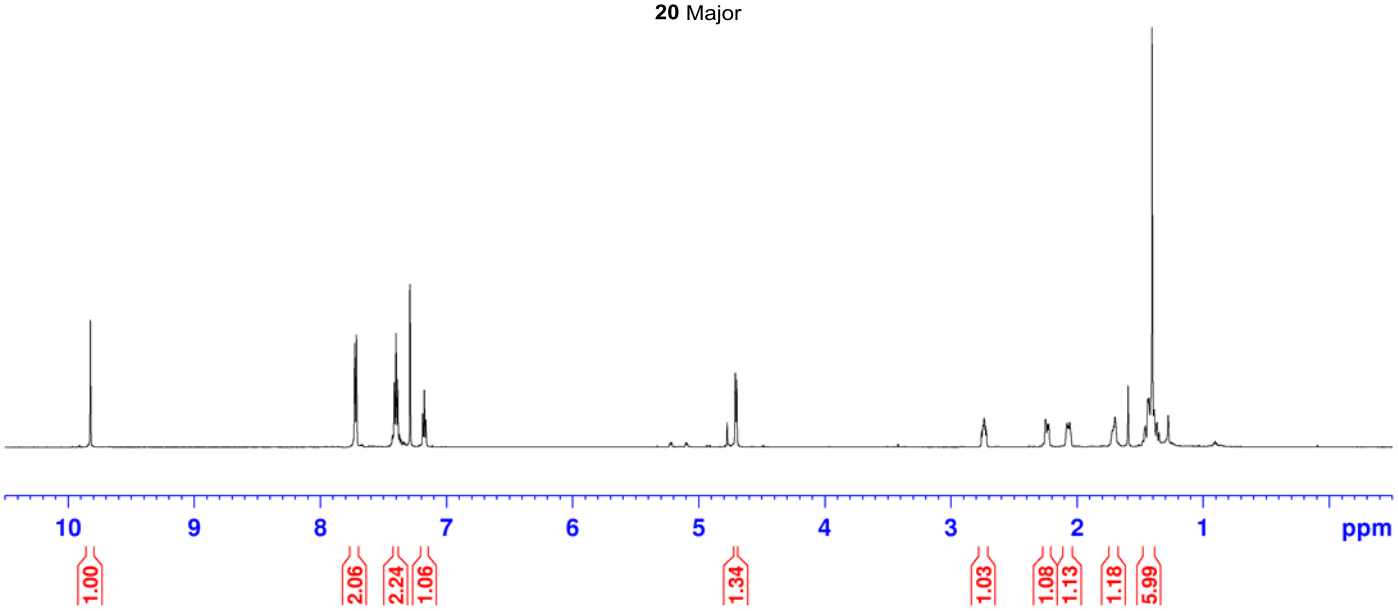
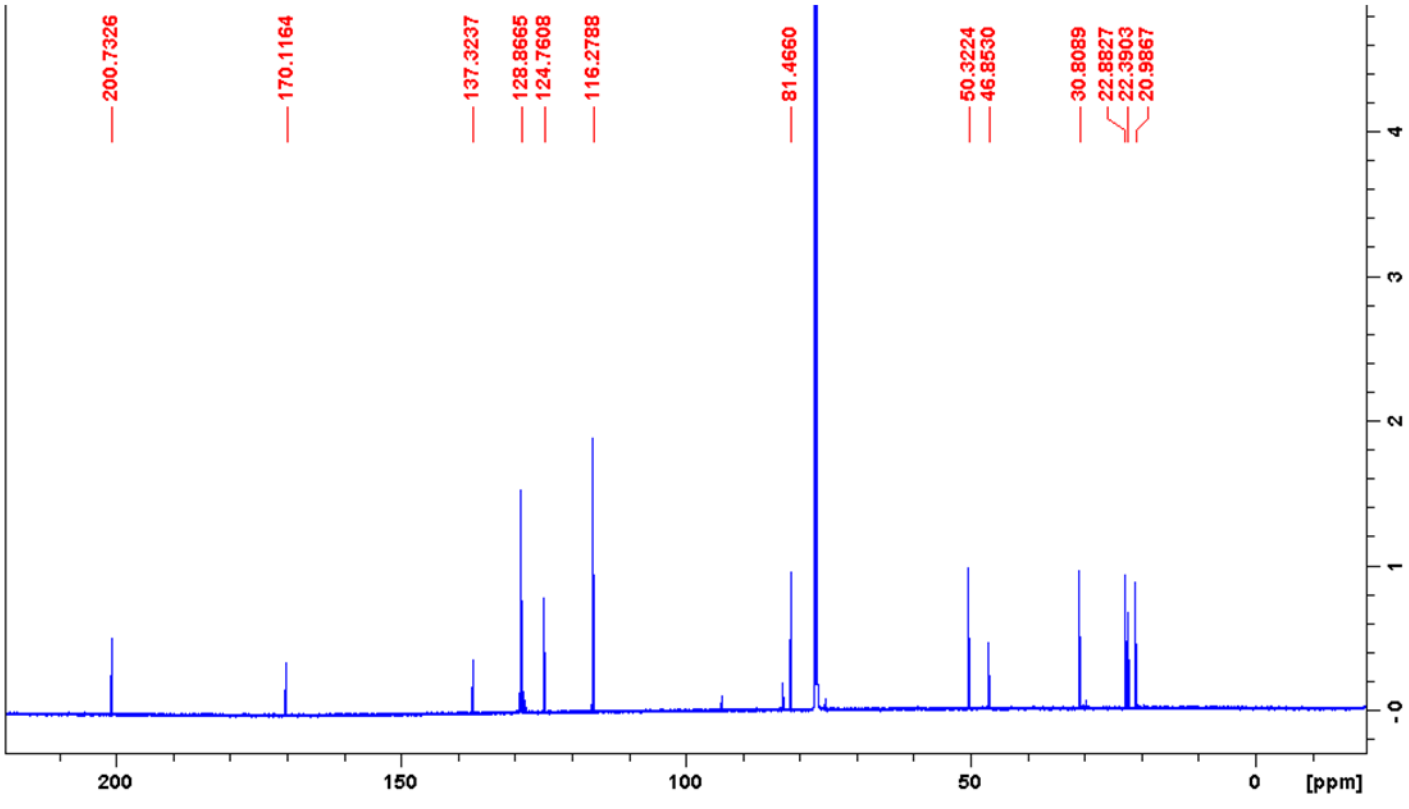
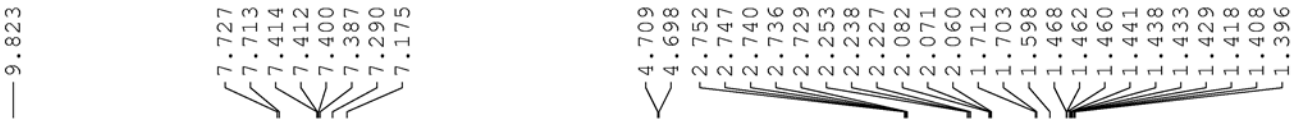


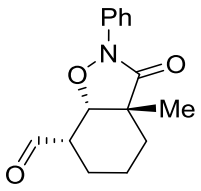


20 Major









20 Minor