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Supporting Information

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Exploring the Nickel-Catalyzed Oxidation of Alkenes: A Diamination via Sulfamide-Transfer

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Table of Contents

Experimental procedures

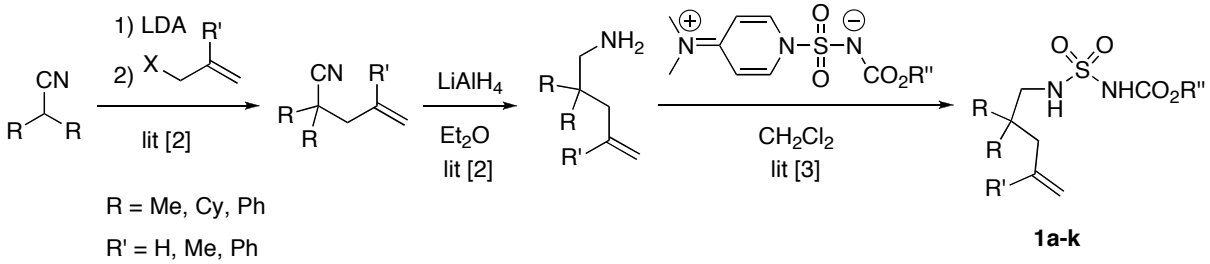
1 General.

All organic reagents, nickel chloride hexahydrate and zirconocene dichloride were purchased from Acros. $Ni(acac)_2$ was purchased from Merck and iodosobenzene diacetate was purchased from Aldrich. Schwartz reagent was synthesized on a 15 mmol scale from zirconocene dichloride in 75% isolated yield following a protocol by Buchwald.[1] Anhydrous nickel chloride was prepared from nickel chloride hexahydrate by stirring with thionyl chloride under absolute conditions followed by sublimation under reduced pressure. Guanidine **6b** was obtained from E. Campos and Prof. J. González (Universidad de Oviedo, Spain). Dichloromethane, ethyl acetate and hexanes were dried over calcium chloride, distilled and used without further manipulation. Absolute dmf was obtained through an Innovative Technology Inc. solvent purification system. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2mm). Nmr spectra were recorded on a Bruker Avance 400 MHz spectrometer. All chemical shifts in nmr experiments are reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ δ = 7.26 and 77.00ppm. MS (ESI-LCMS) experiments were performed using an Agilent 1100 HPLC with a Bruker micro-TOF instrument (ESI). Unless other wise stated, a Supelco C8 (5cm x 4.6mm, 5µm particles) column was used with an linear elution gradient from 100% H_2O (0.5% HCO_2H) to 100% MeCN in 13min at a flow rate of 0.5mL/min. MS (EI) and HRMS experiments were performed on a Kratos MS 50 within the service centers at the Kekulé-Department, Bonn.

2 Synthesis of starting materials

Synthesis of 1a-k

The starting materials were prepared from the corresponding nitriles. These were synthesized and reduced according to a literature procedure.[2] The free amines were then directly used without prior purification and reacted with a Burgess-type DMAP reagent.[3] Short flash chromatography yielded **1a-k** as analytically pure white solids:



R = Me, Cy, Ph
R' = H, Me, Ph
R'' = Me, Bz, *t*Bu
X = Br or Cl

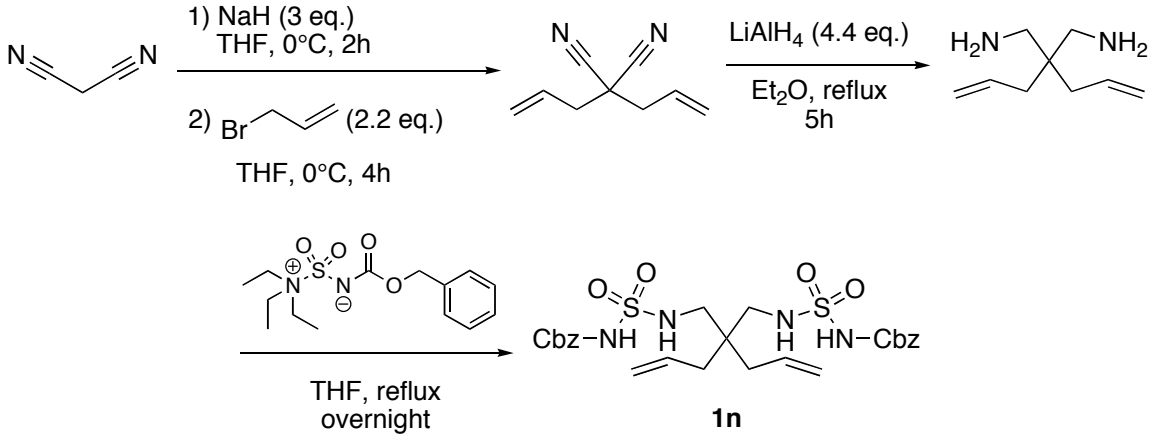
1a-k

1-Bromo-2-phenylpropene was used in the syntheses of **1j** and **1k** (R' = Ph) and prepared from 2-phenylpropene by treatment with NBS in CCl_4.[4] Remaining NBS was filtered off and the concentration of the substrate in CCl_4 was determined by NMR spectrometry. The resulting solution was used without further purification. Subsequent reaction with the lithiated nitrile went smoothly to give the product in 96% isolated yield after flash chromatography (hexanes /CH_2Cl_2 2:1, R_f = 0.4).

Preparation of 1l,m

Starting materials **1l** and **1m** were prepared from literature known (*rac*)-*syn*-2-allyl-cyclopentylamine[5] by treatment with the DMAP-reagents.

Preparation of *N,N'*-Di(benzyloxycarbonylsulfonamido)-2,2-diallylpropane-1,3-diamine 1n



To a stirred suspension of NaH (60 mmol, 3 eq.) in dry THF (100 mL), malononitrile (20 mmol, 1 eq.) is added at 0°C. The mixture is stirred for 2h at r.t. Allylbromide (44 mmol, 2.2 eq.) is slowly added at 0°C and stirring is continued for 4h at r.t. The reaction is quenched with H_2O, the organic phase is separated and the aqueous phase extracted with CH_2Cl_2 (3x) to provide the crude bisnitrile, which is used in the next step without additional purification.

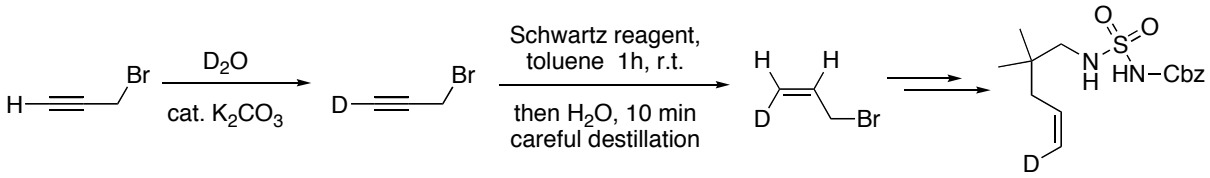
To a stirred suspension of $LiAlH_4$ (88 mmol, 4.4eq.) in dry Et_2O (50 mL), 2,2-di-(2-propenyl)-malononitrile (20mmol, 1eq.) is added slowly. The mixture is refluxed for 4h and THF/H_2O (9:1, v:v) (10 mL) is added slowly to quench the reaction. 5 mL of 15% aqueous NaOH are added and the mixture is stirred vigorously for 10 minutes. The white solid is filtered off. The mother liquor is concentrated to provide the crude diamine as a yellow oil, which was used without further purification.

2,2-Di-(2-propenyl)-1,3-diaminopropane (7 mmol) is dissolved in dry THF (20 mL) under absolute conditions. Benzyl Burgess reagent (benzyl *N*-(triethylammoniumsulphonyl)-carbamate) (3eq.) is added and the mixture is refluxed overnight. The reaction is quenched by addition of sat. aqueous NH_4Cl solution and extracted with CH_2Cl_2 several times. Flash-chromatography (Hex/EtOAC 2:1, v:v, then EtOAc) yields the analytically pure product as the last fraction in 20% yield.

Preparation of urea 6a

Urea **6a** was prepared by treatment of the corresponding free amine with 1.1eq. of TosNCO in absolute DCM (c = 0.5M) at 0°C and warming to room temperature. After 1h the solvent was evaporated and the pure urea was obtained from crystallization of the crude product from methanol or by flash-chromatography (hexanes/EtOAc 3:1, v:v) in 96% yield.

Terminally (*Z*)-deuterated material was synthesized starting from propargylic bromide by terminal deuteration with D_2O[6] and subsequent treatment with Schwartz reagent according to a literature procedure.[7]



The reaction was carried out as described for the stannylated compound (**13b** in reference 7) and the solvent was changed to toluene to allow purification by careful destillation (bp: 83-85 °C, 760 mm Hg) using a 25 cm Vigreux column. The purified allylic bromide was used immediately.

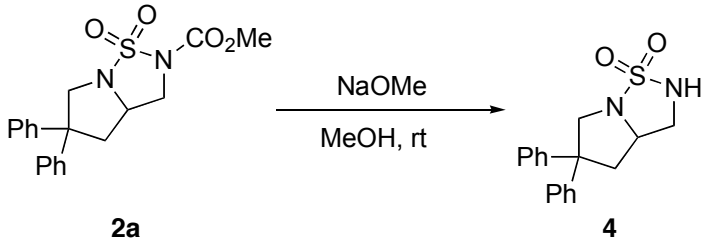
Terminally (*E*)-deuterated material was obtained via the same route but using deuterated Schwartz reagent and H_2O for quenching.

3 Representative diamination procedure

The sulfamide starting material (0.15 mmol, 1.0 eq.), iodosobenzene diacetate (0.3 mmol, 2.0 eq.) and sodium acetate (0.3 mmol, 2.0 eq.) were weighed into a flame-dried Schlenk tube equipped with a magnetic stirrer bar and set under nitrogen atmosphere. Then 1 mL of a solution of the described nickel(II) salt (c = 0.015M) was added (alternatively the nickel salt and dmf can be added separately). The resulting mixture was stirred for 18 hours. The reaction was quenched by addition of sat. aqueous $Na_2S_2O_3$ solution and a small additional amount of water is added. The organic phase was separated and the aqueous phase extracted with dichloromethane several times. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. All products were purified by flash-chromatography.

4 Deprotection procedures

Deprotection of a methyl carbamate protected sulfoximidazolidine

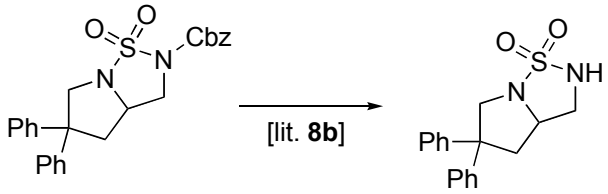


2a **4**

A solution of the sulfamide **2a** (0.312 g, 0.84 mmol) and NaOMe (0.136 g, 2.52 mmol) in MeOH (4.2 mL) was stirred at r.t. for 3h, then quenched with NH_4Cl and extracted with dichloromethane several times. The combined

organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by flash chromatography on silica gel using 10% EtOAc in CH_2Cl_2 to provide 0.245 g, 95% of the deprotected sulfamide **4** as a white solid.

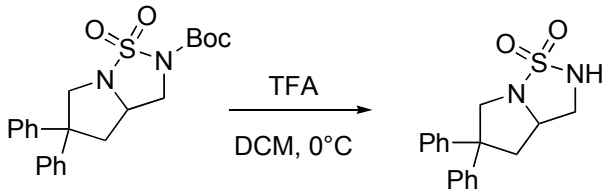
Deprotection of a Cbz protected sulfoximidazolidine



2b **4**

The deprotection of the Cbz-group in **2b** proceeds conveniently according to a literature procedure.[8b] The pure free sulfamide is obtained in 97% isolated yield.

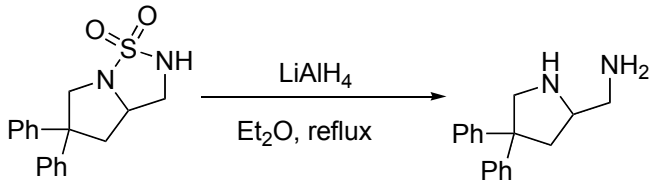
Deprotection of a Boc protected sulfoximidazolidine



2c **4**

Sulfamide **2c** (0.14 mmol) is dissolved in anhydrous CH_2Cl_2 (0.5 mL) and TFA (0.5 mL) is slowly added at 0°C. The reaction is monitored by TLC [CH_2Cl_2, R_f (**4**) = 0.25]. After completion of the reaction, toluene (approx. 2 mL) is added and the solvents are evaporated. After column chromatography (DCM) the product is obtained as a white solid (72% yield).

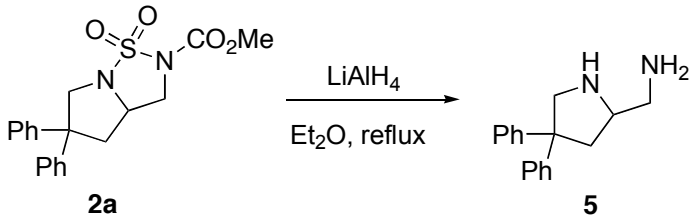
Synthesis of the free diamine from partially deprotected sulfoximidazolidine[8a,b]



4 **5**

The deprotected sulfamide **4** (0.157 g, 0.5 mmol, 1 eq.) was treated with lithium aluminium hydride (0.056 g, 1.5 mmol, 3 eq.) in Et_2O (10 mL). The mixture was refluxed for 3h, then quenched with water (0.16 mL), 15% NaOH solution (0.17 mL) and finally ice/water (0.32 mL). Then the mixture was filtered and treated with HCl (1M). The aqueous phase was separated and NaOH was added until a pH of 14. Finally the aqueous phase was extracted with dichloromethane several times. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and 0.100 g (80%) of the free diamine **5** was obtained as analytically pure pale-yellow oil.

Direct complete deprotection of sulfamide 2a

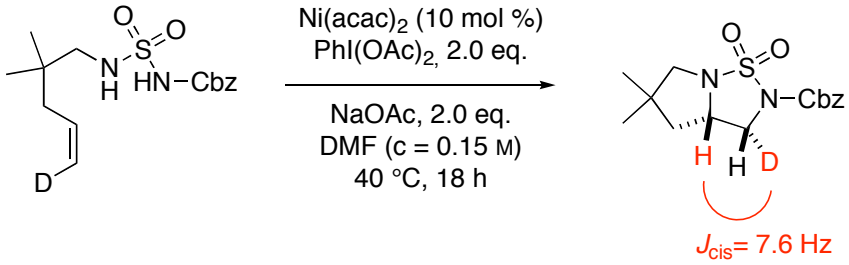


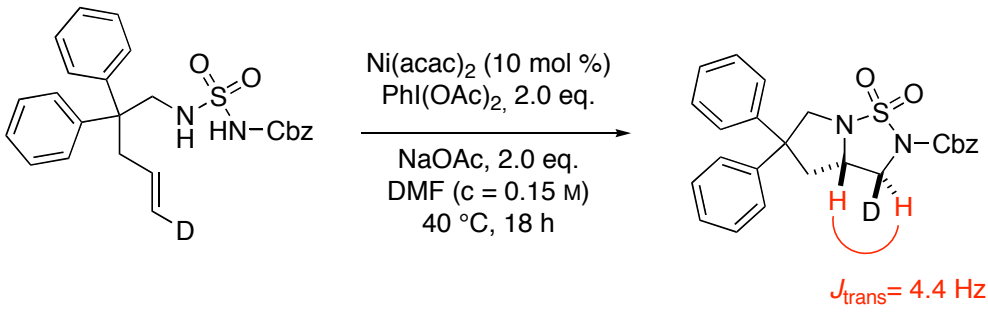
2a **5**

Lithium aluminium hydride (0.3 mmol, 3eq.) is suspended in 4mL dry Et_2O, sulfamide **2a** (0.1 mmol, 1 eq.) is slowly added and the mixture refluxed. After 5h first 0.07 mL H_2O and then 0.07 mL NaOH (15% aqueous solution) are added carefully. After stirring for 10 min additional 0.2 mL of H_2O are added, the mixture is filtered over $MgSO_4$ and washed with Et_2O (40mL). The collected mother liquor is concentrated and a colourless oil is obtained, which is treated with 1mL of 6M HCl and extracted with DCM (3 mL). Solid NaOH is added to the aqueous phase until a pH of 14. The aqueous phase is extracted with CH_2Cl_2 (3x), the organic phase is collected and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure yields the product as a white solid (79% yield).

5. Deuterium experiments

Following the general procedure, diamination of the (*Z*)-deuterated sulfamide precursor with $Ni(acac)_2$ yielded a single diastereomer in 73% isolated yield. According to the coupling constant of J_{HHcis}= 7.6 Hz (vs. $J_{HHtrans}$ = 7.0 Hz) a *syn*-stereochemistry was established. The same experiment starting from a (*E*)-deuterated sulfamide gave the corresponding *trans*-configured diamine with an even more significant difference ($J_{HHtrans}$= 4.4 Hz vs. J_{HHcis} = 7.3 Hz):

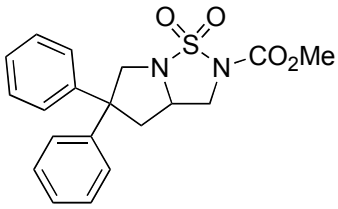




Analytical data of new compounds

6 Characterization of diamination products

N-Methoxycarbonyl-6,6-diphenylpyrrolidino[1,2-*c*]sulfoximidazolidine



2a

Isolated after flash chromatography (hexanes / EtOAc 1:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.42 (dd, *J* = 12.3 Hz, 8.5 Hz, 1H), 2.80 (dd, *J* = 12.4 Hz, 6.1 Hz, 1H), 3.66 (dd, *J* = 10.2 Hz, 4.4 Hz, 1H), 3.80 (s, 3H), 3.95 (d, *J* = 10.2 Hz, 1H), 3.98 (d, *J* = 10.2 Hz, 1H), 4.05 (m, 1H), 4.17 (dd, *J* = 10.2 Hz, 1.2 Hz, 1H), 7.11-7.25 (m, 10H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 44.02, 48.62, 54.35, 55.47, 56.01, 59.63, 126.45, 126.60, 126.90, 127.14, 128.63, 128.72, 144.14, 144.18, 151.72.

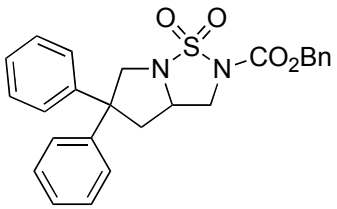
m/z = 373.1 $[M+H^+]^+$ (40), 341.10 (6), 307.2 (24), 275.2 (14), 252.1 (6), 231.2 (8), 220.2 (84), 192.1 (100), 179.1 (42), 165.1 (36), 144.1 (10), 127.1 (18), 115.1 (22), 101.1 (68), 91.1 (14), 59.1 (6).

IR (KBr): ν [cm^{-1}] = 3059, 3026, 2958, 2899, 1740, 1599, 1495, 1443, 1367, 1313, 1173, 1028, 908, 798, 756, 700, 633, 590.

Elemental Analysis calcd (%) for $C_{19}H_{20}N_2O_4S$: C 61.27, H 5.41, N 7.52;
found: C 61.08, H 5.31, N 7.32.

HRMS calc. for $C_{19}H_{20}N_2O_4S$: 372.1144, found: 372.1142.

***N*-Benzyloxycarbonyl-6,6-diphenylpyrrolidino[1,2-*c*]sulfoximidazolidine**



2b

Isolated after flash chromatography (hexanes/CH_2Cl_2/Et_2O 6:6:1, v:v:v) as white crystals.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.39 (dd, *J* = 12.3 Hz, 8.8 Hz, 1H), 2.77 (ddd, *J* = 12.3 Hz, 6.1 Hz, 1.5 Hz, 1H), 3.62 (dd, *J* = 10.2 Hz, 4.4 Hz, 1H), 3.84 (dd, *J* = 10.2 Hz, 7.3 Hz, 1H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.93 (dddd, *J* = 8.8 Hz, 7.3 Hz, 6.1 Hz, 4.4 Hz, 1H), 4.14 (dd, *J* = 10.2 Hz, 1.5 Hz, 1H), 5.24 (d, *J* = 12.6 Hz, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 7.09-7.32 (m, 15H).

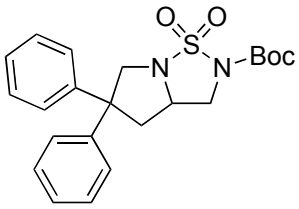
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 44.12, 48.72, 55.54, 56.08, 59.70, 69.01, 126.57, 126.69 , 126.98, 127.22, 128.01, 128.55, 128.69, 128.73, 128.81, 134.92, 144.29, 151.19.

m/z = 449.22 $[M+H]^+$ (100), 405.30 (37), 369.30 (15), 313.22 (6), 285.27 (8), 195.16 (26), 181.01 (6), 91.27 (68).

IR (KBr): ν [cm^{-1}] = 3063, 3032, 2971, 2904, 1737, 1506, 1455, 1317, 1178, 1035, 753, 712, 641, 589.

HRMS calc. for $C_{25}H_{24}N_2O_4S$: 448.1457, found: 448.1472.

***N-tert*-Butoxycarbonyl-6,6-diphenylpyrrolidino[1,2-*c*]sulfoximidazolidine**



2c

Isolated after flash chromatography (hexanes/EtOAc 5:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.54 (s, 9H), 2.49 (dd, *J* = 12.3 Hz, 9.1 Hz, 1H), 2.84 (ddd, *J* = 12.3 Hz, 5.8 Hz, 1.2 Hz, 1H), 3.66 (dd, *J* = 10.2 Hz, 4.1 Hz, 1H), 3.89 (d, *J* = 10.5 Hz, 1H), 3.94 (d, *J* = 10.3 Hz, 1H), 4.00 (m, 1H), 4.25 (dd, *J* = 10.2 Hz, 1.4 Hz, 1H), 7.19-7.35 (m, 10H).

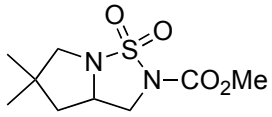
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.91, 44.02, 48.09, 55.36, 55.59, 59.66, 84.51, 126.47, 126.63, 126.81, 127.04, 128.56, 128.64, 144.27, 144.35, 150.08.

m/z = 415.31 $[M+H]^+$ (11), 400.24 (8), 359.21 (25), 341.17 (10), 315.20 (100), 298.16 (8), 279.22 (4), 248.19 (2), 222.20 (15), 195.19 (65).

IR (KBr): ν [cm^{-1}] = 3093, 3068, 3042, 3012, 2981, 2945, 2894, 1742, 1475, 1455, 1373, 1322, 1189, 1143, 1076, 1030, 856, 764, 707, 646, 600.

HRMS calc. for $C_{18}H_{18}N_2O_4S$ $[M\text{-}C_4H_9+H]^+$: 358.0987, found: 358.0995.

***N*-Methoxycarbonyl-6,6-dimethylpyrrolidino[1,2-*c*]sulfoximidazolinine**



2d

Isolated after flash chromatography (CH_2Cl_2/EtOAc 25:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.10 (s, 3H), 1.13 (s, 3H), 1.55 (dd, *J* = 12.8 Hz, 6.4 Hz, 1H), 2.03 (dd, *J* = 12.8 Hz, 7.6 Hz, 1H), 3.06 (d, *J* = 9.6 Hz, 1H), 3.18 (d, *J* = 9.6 Hz, 1H), 3.57 (dd, *J* = 10.0 Hz, 6.8 Hz, 1H), 3.80 (s, 3H), 3.97 (dd, *J* = 10.0 Hz, 7.2 Hz, 1H), 4.16 (quint, *J* = 6.8 Hz, 1H).

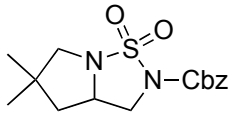
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.44, 27.18, 40.56, 45.60, 50.72, 54.16, 56.51, 61.95, 151.53.

m/z = 249.20 $[M+H]^+$ (26), 235.15 (17), 217.10 (67), 191.17 (4), 169.24 (19), 155.24 (100), 97.28 (6), 95.28 (12).

IR (KBr): ν [cm^{-1}] = 3007, 2966, 2935, 2873, 1731, 1455, 1352, 1322, 1184, 1102, 917, 810, 769, 641, 564.

HRMS calc. for $C_9H_{16}N_2O_4S$: 248.0831, found: 248.0835.

***N*-Benzyloxycarbonyl-6,6-dimethylpyrrolidino[1,2-*c*]sulfoximidazolinine**



2e

Isolated after flash chromatography (hexanes/EtOAc 2:1, v:v) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$,):δ = 1.18 (s, 3H), 1.20 (s, 3H), 1.60 (dd, *J* = 12.9 Hz, 6.4 Hz, 1H), 2.09 (dd, *J* = 12.9 Hz, 7.3 Hz, 1H), 3.16 (d, *J* = 9.4 Hz, 1H), 3.27 (d, *J* = 9.6 Hz, 1H), 3.64 (dd, *J* = 10.2 Hz, 7.0, Hz, 1H), 4.05 (dd, *J* = 10.2 Hz, 7.3 Hz, 1H), 4.23 (quint, *J* = 7.3 Hz, 1H), 5.27 (d, *J* = 12.6 Hz, 1H), 5.31 (d, *J* = 12.6 Hz, 1H), 7.40-7.34 (m, 5H).

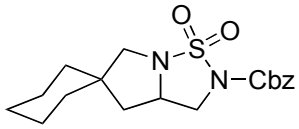
^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.38, 27.16, 40.47, 45.49, 50.63, 56.45, 61.86, 68.74, 127.76, 128.28, 128.47, 134.83, 150.87.

m/z = 325.22 $[M+H]^+$ (13), 281.19 (50), 245.19 (11), 181.14 (21), 155.25 (3), 98.32 (9), 91.31 (100).

IR (KBr): ν [cm^{-1}] = 3060, 3037, 2963, 2877, 1735, 1463, 1396, 1349, 1333, 1308, 1172, 1090, 1028, 908, 860, 750, 696, 632.

HRMS calc. for $C_{15}H_{20}N_2O_4S$: 324.1144, found: 324.1140.

_N_-Benzyloxycarbonyl-6-spirocyclohexylpyrrolidino[1,2-_c_]sulfoximidazolidine



2f

Isolated after flash chromatography (hexanes/EtOAc 3:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.37-1.57 (m, 11H), 2.16 ppm (dd, *J* = 7.9 Hz, 12.9 Hz, 1H), 3.20 ppm (d, *J* = 9.9 Hz, 1H), 3.32 (d, *J* = 9.8 Hz, 1H), 3.60 (dd, *J* = 7.5 Hz, 9.9 Hz, 1H), 4.01 (dd, *J* = 10.2 Hz, 7.4 Hz, 1H), 4.28 (m, 1H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.30 (d, *J* = 12.2 Hz, 1H), 7.29-7.45 (m, 5H).

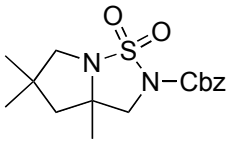
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.86, 23.83, 25.57, 35.74, 36.94, 42.92, 44.37, 50.83, 56.07, 59.68, 68.69, 127.83, 128.33, 128.53, 134.92, 150.92.

m/z (ESI-LCMS) = 365.24 $[M+H]^+$ (20), 321.24 (100), 285.29 (37), 181.16 (18), 138.25 (13), 91.35 (76).

HRMS calcd. for $C_{18}H_{24}N_2O_4S$: 364,1457 found: 364.1451

IR (KBr): ν [cm^{-1}] = 3263, 3099, 3063, 3027, 2966, 2894, 1752, 1465, 1368, 1250, 1168, 1086, 1040, 866, 794, 758, 718, 589.

_N_-Benzyloxycarbonyl-6,6,7a-trimethylpyrrolidino[1,2-_c_]sulfoximidazolidine



2g

Isolated after flash chromatography (hexanes/EtOAc 3:2, v:v) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 3H), 1.21 (s, 3H), 1.60 (s, 3H), 1.85 (d, *J* = 13.2 Hz, 1H), 1.90 (d, *J* = 13.2 Hz, 1H), 3.21 (d, *J* = 10.0 Hz, 1H), 3.32 (d, *J* = 10.0 Hz, 1H), 3.76 (d, *J* = 10.5 Hz, 1H), 3.79 (d, *J* = 10.3 Hz, 1H), 5.27 (d, *J* = 12.3 Hz, 1H), 5.31 (d, *J* = 12.5 Hz, 1H), 7.43-7.31 (m, 5H).

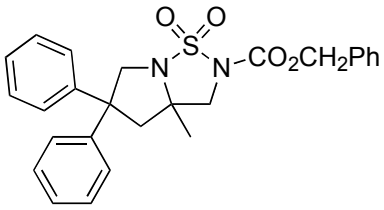
^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.01, 27.97, 28.16, 39.53, 53.38, 58.29, 63.21, 65.41, 68.72, 127.81, 128.33, 128.55, 134.96, 150.87.

m/z = 339.25 $[M+H]^+$ (13), 295.25 (75), 259.24 (4), 181.20 (13), 112.34 (10), 91.34 (100).

IR (KBr): ν [cm^{-1}] = 3035, 2964, 2875, 1735, 1458, 1390, 1344, 1314, 1167, 1069, 956, 778, 762, 739, 699, 587.

HRMS calcd. for $C_{16}H_{22}N_2O_4S$: 388.1300 found: 388.1293.

***N*-Benzyloxycarbonyl-6,6-diphenyl-7a-methylpyrrolidino[1,2-*c*]sulfoximidazol-idine**



2h

Isolated after flash chromatography (hexanes/EtOAc 3:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (s, 3H), 2.84 (d, *J* = 13.1 Hz, 1H), 2.91 (d, *J* = 13.1 Hz, 1H), 3.55 (d, *J* = 10.1 Hz, 1H), 3.60 (d, *J* = 10.1 Hz, 1H), 4.19 (d, *J* = 11.2 Hz, 1H), 4.25 (d, *J* = 11.1 Hz, 1H), 5.22 (d, *J* = 12.6 Hz, 1H), 5.26 (d, *J* = 12.6 Hz, 1H), 7.16-7.41 (m, 15H).

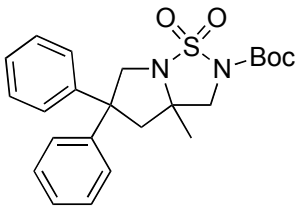
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.81, 51.43, 54.40, 57.67, 59.42, 64.53, 68.67, 126.31, 126.51, 126.68, 126.98, 127.84, 128.36, 128.54, 128.63, 128.72, 134.94, 144.25, 144.83, 150.66.

m/z = 463.26 $[M+H]^+$ (100), 445.24 (8), 419.26 (63), 383.35 (5), 326.35 (6), 285.21 (5), 248.14 (4), 190.15 (6), 91.32 (56).

IR (KBr): ν [cm^{-1}] = 3058, 3032, 2966, 2935, 2889, 1742, 1455, 1399, 1358, 1306, 1178, 1137, 1086, 968, 917, 794, 764, 733, 702, 620, 589.

HRMS calcd. for $C_{26}H_{26}N_2NaO_4S$: 485.1505 found: 485.1505.

***N*-*tert*-Butoxycarbonyl-6,6-diphenyl-7a-methylpyrrolidino[1,2-*c*]sulfoximidazol-idine**



2i

Isolated after flash chromatography (hexanes/EtOAc 5:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (s, 3H), 1.54 (s, 9H), 2.86 (dd, *J* = 12.9 Hz, 0.9 Hz, 1H), 2.95 (d, *J* = 12.9 Hz, 1H), 3.56 (s, 2H), 4.16 (d, *J* = 11.1 Hz, 1H), 4.30 (dd, *J* = 11.1 Hz, 0.9 Hz, 1H), 7.18-7.30 (m, 10H).

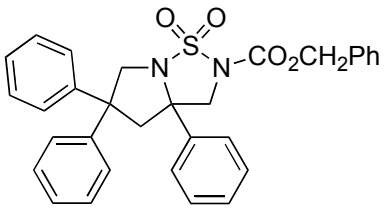
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.83, 27.95, 51.51, 54.31, 57.59, 59.54, 64.01, 84.16, 126.38, 126.60, 126.63, 126.92, 128.60, 128.68, 144.54, 144.91, 149.73.

m/z = 429.33 $[M+H]^+$ (13), 414.27 (10), 373.17 (36), 355.19 (33), 329.17 (100), 312.13 (18), 293.26 (6), 258.18 (7), 236.26 (20), 219.13 (4) 195.19 (13), 176.16 (4), 135.15 (6), 91.32 (4).

IR (KBr): ν [cm^{-1}] = 3058, 3027, 2986, 2940, 2868, 1721, 1496, 1450, 1388, 1327, 1178, 1148, 1081, 917, 856, 825, 712, 620.

HRMS calcd. for $C_{23}H_{28}N_2NaO_4S$: 451.1662 found: 451.1657.

***N*-Benzyloxycarbonyl-6,6,7a-triphenylpyrrolidino[1,2-*c*]sulfoximidazolidine**



2j

Isolated after flash chromatography (hexanes/EtOAc 4:1, v:v) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.19 (d, *J* = 13.2 Hz, 1H), 3.26 (d, *J* = 13.2 Hz, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 4.01 (d, *J* = 10.4 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 5.17 (d, *J* = 12.7 Hz, 1H), 5.23 (d, *J* = 12.6 Hz, 1H), 7.00-7.40 (m, 20H).

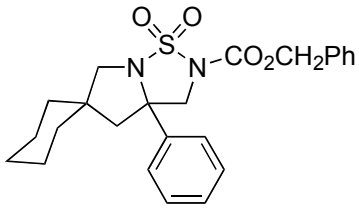
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.69, 54.95, 57.77, 59.52, 68.68, 70.12, 125.00, 126.23, 126.32, 126.49, 126.99, 127.39, 127.80, 128.27, 128.33, 128.50, 128.76, 134.80, 143.02, 143.53, 143.82, 150.30.

m/z = 525.37 $[M+H]^+$ (73), 507.36 (8), 481.35 (100), 476.21 (5), 429.31 (10), 389.29 (11), 357.33 (16), 327.26 (10), 313.15 (44), 298.05 (33), 285.26 (14), 248.16 (5), 220.32 (4), 195.18 (9), 174.09 (4), 91.44 (40).

IR (KBr): ν [cm^{-1}] = 3059, 3031, 2962, 2926, 2898, 1735, 1449, 1353, 1303, 1214, 1177, 1028, 910, 850, 752, 699, 632, 606, 532.

HRMS calcd. for $C_{31}H_{28}N_2O_4S$: 524.1770 found: 524.1770.

***N*-Benzyloxycarbonyl-6-spirocyclohexyl-7a-phenylpyrrolidino[1,2-*c*]sulfox-imidazolidine**



2k

Isolated after flash chromatography (hexanes/EtOAc 3:1, v:v) as a white solid.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.17-1.76 (m, 10H), 2.21 (d, *J* = 13.2 Hz, 1H), 2.32 (d, *J* = 13.2 Hz, 1H), 3.35 (d, *J* = 10.8 Hz, 1H), 3.73 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.2 Hz, 1H), 4.12 (d, *J* = 10.2 Hz, 1H), 5.25 (s, 2H), 7.26-7.40 (m, 8H), 7.49 (dt, *J* = 7.2 Hz, 1.2 Hz, 2H).

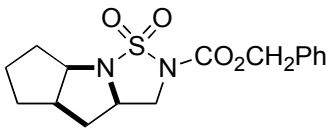
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.07, 23.61, 25.51, 35.88, 36.52, 44.57, 52.60, 57.98, 60.21, 68.85, 70.79, 124.89, 127.65, 127.81, 128.35, 128.53, 128.79, 134.73, 144.03, 150.70.

m/z = 441.25 $[M+H]^+$ (100), 423.34 (6), 397.29 (55), 361.31 (3), 333.19 (8), 305.23 (7), 214.24 (19), 181.15 (10), 91.32 (80).

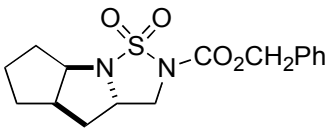
IR (KBr): ν [cm^{-1}] = 3070, 3033, 2929, 2854, 1735, 1449, 1388, 1346, 1307, 1174, 766, 700, 636, 595, 533.

HRMS calcd. for $C_{24}H_{28}N_2NaO_4S$: 463.1662 found: 463.1666.

(*syn,syn*)- and (*syn,anti*)-Benzyloxycarbonylpenta[*b*]pyrrolidino[1,2-*c*]sulfox-imidazolidine



and



2l and 2m

Isolated after flash chromatography (CH_2Cl_2) as white solids.

1st Diastereomer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50-1.76 (m, 5H), 1.85-1.97 (m, 2H), 2.11 (ddd, *J* = 8.8 Hz, 4.4 Hz, 1.2 Hz, 1H), 2-87 (m, 1H), 3.51 (t, *J* = 9.6 Hz, 1H), 3.92 (dd, *J* = 10.0 Hz, 6.7 hz, 1H), 4.26 (ss, *J* = 14.3 Hz, 6.7 Hz, 1H), 4.35 (dd, *J* = 6.7 Hz, 1.8 Hz, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 5.35 (d, *J* = 12.6 Hz, 1H), 7.35-7.47 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.52, 32.94, 34.67, 35.95, 41.12, 50.02, 59.21, 68.07, 68.69, 127.85, 128.36, 128.59, 135.04, 151.03.

m/z (ESI-LCMS)= 337.16 $[M+H]^+$ (4), 293.21 (47), 257.27 (24), 201.08 (3), 181.19 (15), 167.23 (8), 110.32 (5), (91.31 (100).

IR (KBr): ν [cm^{-1}] = 3066, 3033, 2957, 2899, 2870, 1734, 1389, 1369, 1326, 1177, 761, 699, 614, 547.

HRMS calcd. for $C_{16}H_{20}N_2NaO_4S$: 359.1036 found: 359.1031.

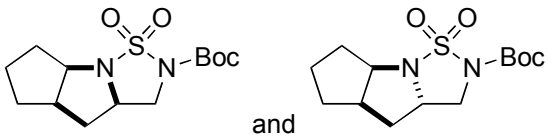
2nd Diastereomer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.52-1.83 (m, 6H), 2.00-2.48 (m, 1H), 2.31 (ddd, *J* = 12.0 Hz, 8.8 Hz, 5.6 Hz, 1H), 3.08 (dquint, *J* = 7.9 Hz, 2.3 Hz, 1H), 3.54 (dd, *J* = 9.7 Hz, 8.7 Hz, 1H), 3.85-4.03 (m, 3H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.31 (d, *J* = 12.4 Hz, 1H), 7.29-7.44 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.19, 31.32, 31.81, 34.83, 47.05, 50.71, 59.26, 62.00, 68.63, 127.80, 128.33, 128.56, 135.03.

HRMS calcd. for $C_{16}H_{20}N_2NaO_4S$: 359.1036 found: 359.1033.

(*syn,syn*)- and (*syn,anti*)-*tert*-Butoxycarbonylpenta[*b*]pyrrolidino[1,2-*c*]sulfox-imidazolidine



2n and 2o

1st Diastereomer

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.53 (s, 9H), 1.59-1.74 (m, 5H), 1.83-1.95 (m, 2H), 2.10 (ddd, *J* = 13.4 Hz, 9.1Hz, 1.8 Hz, 1H), 2.88 (quint, *J* = 7.0 Hz, 1H), 3.45 (t, *J* = 9.6 Hz, 1H), 3.82 (dd, *J* = 10.0 Hz, 6.7 Hz, 1H), 4.19 (m, 1H), 4.29 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.57, 28.01, 32.96, 34.66, 36.01, 41.13, 49.64, 58.85, 67.96, 84.03.

m/z (ESI-LCMS)= 325.3 $[M+Na]^+$ (4), 269.1 (8), 229.1 (20), 203.2 (100), 167.2 (90), 110.4 (52), 85.4 (23).

IR (KBr): ν [cm^{-1}] = 2955, 2870, 1718, 1342, 1260, 1157, 814, 682, 544.

HRMS calcd. for $C_{13}H_{22}N_2NaO_4S$: 325.1192 found: 325.1189.

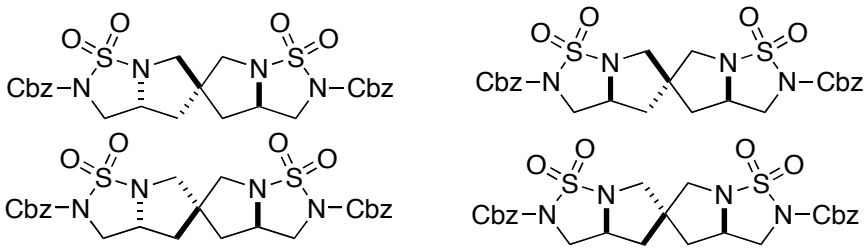
2nd Diastereomer

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.52 (s, 9H), 1.54-1.70 (m, 5H), 1.77 (m, 1H), 2.03 (m, 1H), 2.28 (ddd, *J* = 12.3 Hz, 9.1 Hz, 5.8 Hz, 1H), 3.02 (dquint, *J* = 8.8 Hz, 2.3 Hz, 1H), 3.46 (dd, *J* = 9.4 Hz, 8.2 Hz, 1H), 3.78-3.89 (m, 2H), 3.96 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.16, 28.01, 31.32, 34.80, 47.05, 50.17, 58.98, 61.66, 84.06, 149.58.

HRMS calcd. for $C_{13}H_{22}N_2NaO_4S$: 325.1192 found: 325.1186.

Tetramines from diamination of 1n



After flash chromatography, a mixture of all four possible stereoisomers (ratio 1:1:1:1) was collected in a single fraction.

^{1}H NMR ($CHCl_3$, 400 MHz): δ = 1.80 (dd, *J* = 13.2 Hz, 7.0 Hz, 1H), 1.89 (m, 2H), 2.03 (dd, *J* = 13.5 Hz, 7.6 Hz, 1H), 2.30-2.57 (m, 4H), 3.37 (d, *J* = 10.5 Hz, 1H), 3.42 (d, *J* = 10.5 Hz, 1H), 3.45 (d, *J* = 10.5 Hz, 2H), 3.53-3.75 (m, 8H), 4.10 (dd, *J* = 10.5 Hz, 7.6 Hz, 2x2H), 4.18-4.29 (m, 4H), 5.31 (d, *J* = 12.6 Hz, 4H), 5.35 (d, *J* = 12.6 Hz, 4H), 7.36-7.46 (m, 20H).

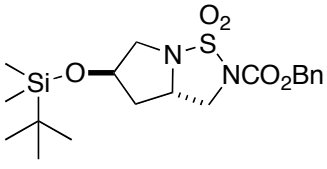
^{13}C NMR ($CHCl_3$, 100 MHz): δ =40.22, 40.50, 42.48, 42.89, 49.60, 49.69, 49.89, 50.22, 50.78, 50.97 (2C), 55.75, 56.03 (2C), 56.08, 56.18, 57.22, 57.27, 58.85, 59.30, 68.95 (4C), 127.90 (8C), 128.49 (8C), 128.58 (4C), 134.65 (4C), 150.59, 150.66 (2C), 150.71

m/z (ESI-LCMS)= 599.5 $[M+Na]^+$ (4), 533.4 (3), 497.5 (2), 438.1 (8), 350.3 (4), 271.2 (10), 222.2 (12), 181.2 (100), 166.2 (18), 91.3 (67), 56.5 (12).

IR (KBr): ν [cm^{-1}] = 3066, 3033, 2957, 2887, 1725, 1393, 1362, 1330, 1305, 1231, 1174, 1079, 907, 852, 793, 763, 736, 696, 622, 584, 541.

HRMS calcd. for $C_{25}H_{28}N_4NaO_8S_2$: 599.1241 found: 599.1246.

***N*-Benzyloxycarbonyl-6-(tert-butyldimethylsilyloxy)-pyrrolidino[1,2-*c*]sulfoximidazolidine**



2p

Isolated after flash chromatography (hexanes/EtOAc 3:1, v:v) as a white solid.

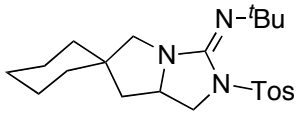
^{1}H NMR ($CDCl_3$, 400 MHz): δ = -0.05 (s, 6H), 0.98 (s, 9H), 1.22 (m, 1H), 1.93 (m, 1H), 2.87-3.20 (m, 6H), 5.34 (d, *J* = 10.4 Hz, 1H), 5.44 (d, *J* = 10.4 Hz, 1H), 7.12-7.26 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = -5.5, 19.7, 25.6, 37.1, 45.7, 47.3, 53.1, 68.9, 72.2, 127.8, 128.5,129.0, 143.6, 163.2.

m/z (ESI-LCMS) = 427.4 $[M+H]^+$ (32), 292.4 (100).

HRMS calcd. for $C_{19}H_{30}N_2O_5SSi$: 426.1645; found: 426.1678.

_N_-Tosyl-6-spirocyclohexylpyrrolidino[1,2-*c*]-*tert*-butyliminoimidazolidine



7b

Isolated after flash chromatography (hexanes/EtOAc 2:1, v:v) as a white solid.

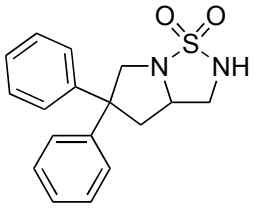
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17-1.46 (m, 9H), 1.30 (s, 9H), 1.91 (dd, *J* = 12.6 Hz, 6.4 Hz, 1H), 2.44 (s, 3H), 2.80 (d, *J* = 11.7 Hz, 1H), 3.41 (d, *J* = 11.7 Hz, 1H), 3.66 (dd, *J* = 9.7 Hz, 3.8 Hz, 1H), 3.86 (dddd, *J* = 12.6 Hz, 8.5 Hz, 6.4 Hz, 3.8 Hz, 1H), 4.02 (dd, *J* = 9.7 Hz, 8.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.56, 23.07, 23.60, 25.43, 28.66, 36.18, 37.62, 43.77, 44.66, 48.06, 51.36, 54.09, 56.29, 127.88, 129.55, 134.81, 144.70, 150.20, 156.29.

m/z (ESI-LCMS): 349.21 $[M(urea)+H]^+$ (100), 248.13 (2), 198.29 (1), 193.20 (2), 118.20 (1), 79.29 (1). [9]

HRMS calcd for $C_{22}H_{33}N_3O_2S$: 403.2293 found: 403.2297.

6,6-diphenylpyrrolidino[1,2-*c*]sulfoximidazolidine



4

^{1}H NMR ($CDCl_3$, 400 MHz):δ = 2.44 (t, *J* = 10.3 Hz, 1H), 2.66 (dd, *J* = 12.0 Hz, 5.9 Hz, 1H), 3.31 (dd, *J* = 11.4 Hz, 3.8 Hz, 1H), 3.61 (dd, *J* = 11.4 Hz, 7.0 Hz, 1H), 3.75 (d, *J* = 10.0 Hz, 1H), 4.11 (m, 1H), 4.21 (d, *J* = 10.0 Hz, 1H), 4.64 (s, 1H), 7.19 -7.39 (m, 10H).

^{13}C NMR ($CDCl_3$, 100 MHz):δ = 42.92, 46.37, 57.38, 58.08, 63.95, 126.44, 126.70, 126.74, 127.97, 128.50, 128.61, 144.38, 144.63.

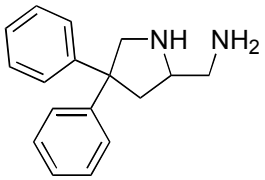
m/z (EI) = 314.1 $[M]^+$ (30), 298.1 (5), 249.1 (10), 233.1 (24), 220.1 (100), 205.1 (32), 192.1 (76), 192.1 (34), 165.1 (36), 144.1 (18), 134.0 (25), 115.0 (24), 91.0 (16), 57.1 (6).

HRMS calcd for $C_{17}H_{18}N_2O_2S$: 314,1089 found: 314.1084

Elemental Analysis calcd (%) for $C_{17}H_{18}N_2O_2S$: C 64.94, H 5.77, N 8.91;
found: C 64.75, H 5.75, N 8.55.

IR (KBr): ν [cm^{-1}] = 3222, 3068, 3022, 2976, 2925, 2884, 1491, 1455, 1399, 1347, 1327, 1178, 789, 712, 615, 600.

(4,4-Diphenylpyrrolidin-2-yl)methylamine



5

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.92 (dd, *J* = 12.9 Hz, 9.1 Hz, 1H), 2.49 (s, 3H), 2.59 (dd, *J* = 12.3 Hz, 7.9 Hz, 1H), 2.67 (dd, *J* = 12.3 Hz, 4.4 Hz, 1H), 2.76 (ddd, *J* = 12.9 Hz, 7.0 Hz, 1.6 Hz, 1H), 3.23-3.30 (m, 2H), 3.61(dd, *J* = 11.7 Hz, 1.7 Hz, 1H), 7.07-7.26 (m, 10H).

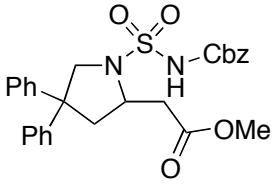
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 42.13, 47.09, 56.81, 57.11, 59.67, 126.12, 126.18, 126.79, 127.02, 128.32, 128.46, 146.09, 147.04.

m/z = 253.21 $[M+H]^+$ (60), 236.20 (100), 198.31 (10), 158.13 (10), 141.11 (6), 95.25 (25), 79.28 (15).

IR (KBr): ν [cm^{-1}] = 3390, 3150, 3056, 3025, 2963, 2923, 2878, 1650, 1600, 1494, 1446, 1361, 1262, 1157, 1096, 1031, 757, 699, 586.

HRMS calcd for $C_{17}H_{21}N_2$ $[(M+H)^+]$: 253.1699 found: 253.1704.

Methyl 2-(1-(*N*-(benzyloxycarbonyl)sulfamoyl)-4,4-diphenylpyrrolidin-2-yl)-acetate



8

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.26 (dd, *J* = 16.4 Hz, 9.1 Hz, 1H), 2.50 (dd, *J* = 13.2 Hz, 6.4 Hz, 1H), 2.93 (dd, *J* = 16.7 Hz, 3.8 Hz, 1H), 3.10 (dd, *J* = 12.9 Hz, 7.6 Hz, 1H), 3.63 (s, 3H), 4.16 (d, *J* = 10.5 Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 4.44-4.52 (m, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 7.15-7.35 (m, 15H), 7.47 (s, 1H).

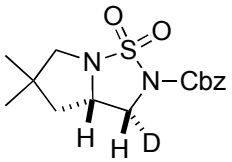
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.88, 38.94, 43.34, 51.65, 52.70, 56.84, 58.50, 68.42, 126.52, 126.76, 128.43, 128.65, 128.72, 134.58, 144.11, 144.70, 150.82, 171.60.

m/z = 509.39 $[M+H]^+$ (7), 435.24 (8), 406.29 (10), 316.22 (100), 296.25 (12), 205.19 (20), 91.33 (30).

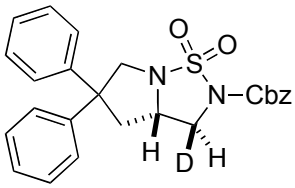
IR (KBr): ν [cm^{-1}] = 3246, 3063, 3033, 2954, 1736, 1449, 1362, 1295, 1219, 1166, 1080, 1055, 857, 752, 700, 613.

HRMS calcd for $C_{27}H_{28}N_2O_6S$: 508.1668 found: 508.1670.

(*syn*)-*N*-Benzyloxycarbonyl-1-deutero-6,6-dimethylpyrrolidino[1,2-*c*]-sulfoximidazolidine



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17 (s, 3H), 1.18 (s, 3H), 1.59 (dd, *J* = 13.2 Hz, 6.4 Hz, 1H), 2.07 (dd, *J* = 13.2 Hz, 7.6 Hz, 1H), 3.14 (d, *J* = 9.2 Hz, 1H), 3.25 (d, *J* = 9.2 Hz, 1H), 4.02 (d, *J* = 7.6 Hz, 1H), 4.21 (ddd, *J* = 7.6 Hz, 7.6 Hz, 6.4 Hz, 1H), 5.27 (d, *J* = 12.4 Hz, 1H), 5.31 (d, *J* = 12.4 Hz, 1H), 7.30-7.43 (m, 5H).



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.39 (dd, *J* = 12.3 Hz, 8.8 Hz, 1H), 2.77 (ddd, *J* = 12.3 Hz, 6.1 Hz, 1.5 Hz, 1H), 3.62 (d, *J* = 4.4 Hz, 1H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.93 (ddd, *J* = 8.8 Hz, 6.1 Hz, 4.4 Hz, 1H), 4.14 (dd, *J* = 10.2 Hz, 1.5 Hz, 1H), 5.24 (d, *J* = 12.6 Hz, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 7.09-7.32 (m, 15H).

7 References

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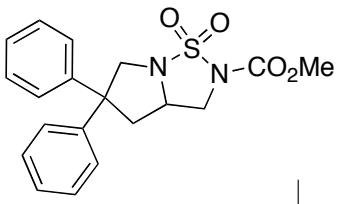
(9) The guanidine product is found to be unstable under standard ESI-LCMS conditions giving rise to the corresponding urea.

NMR Spectra of new diamine compounds



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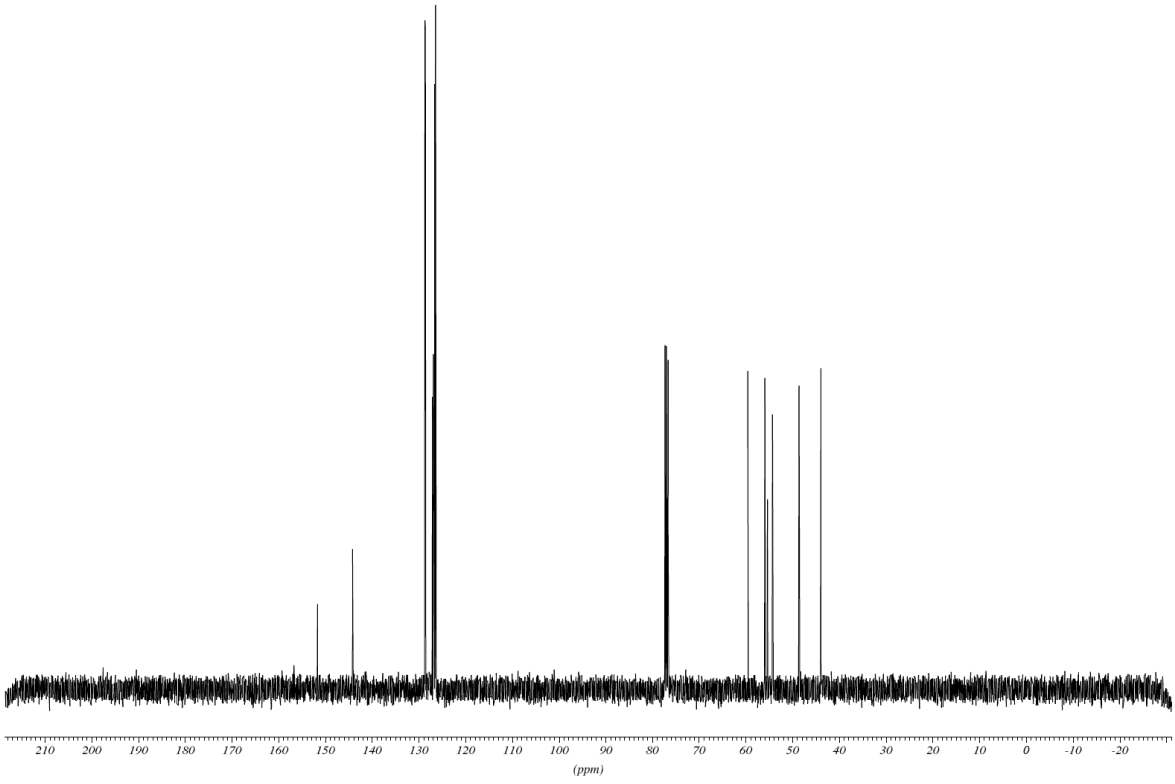

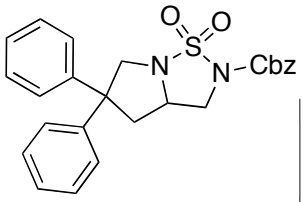
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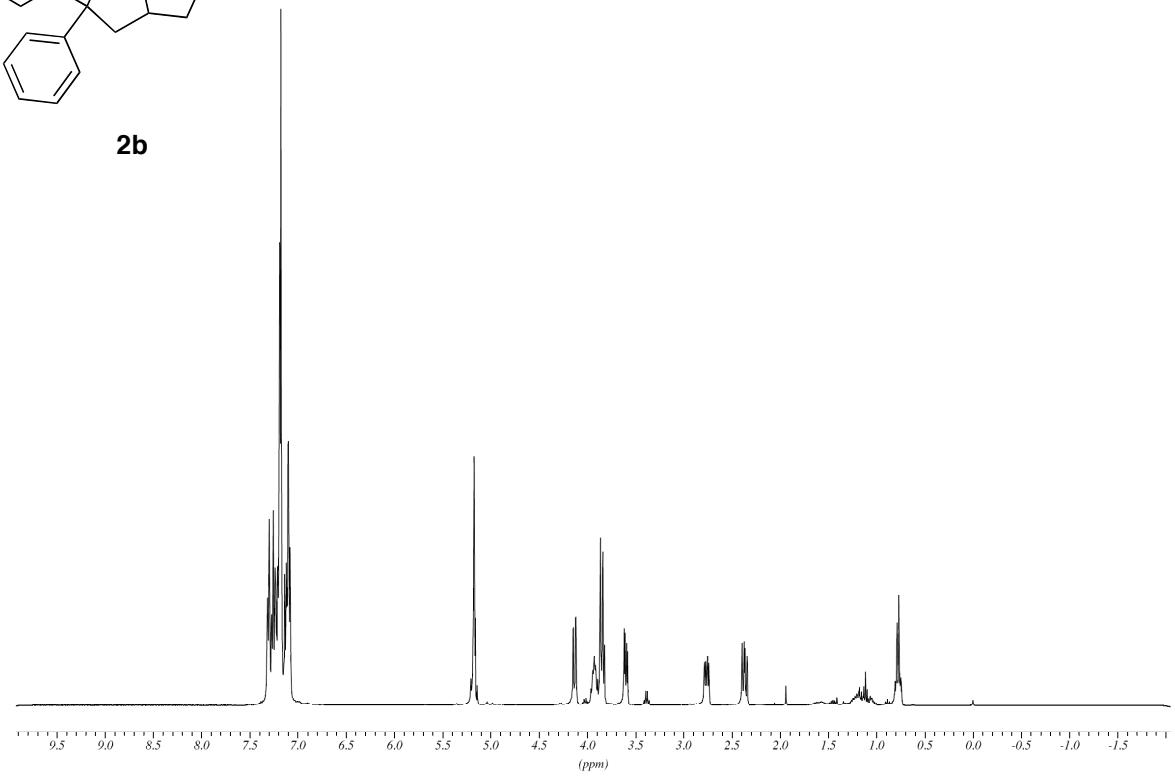
O
S
N
N
Cbz

2b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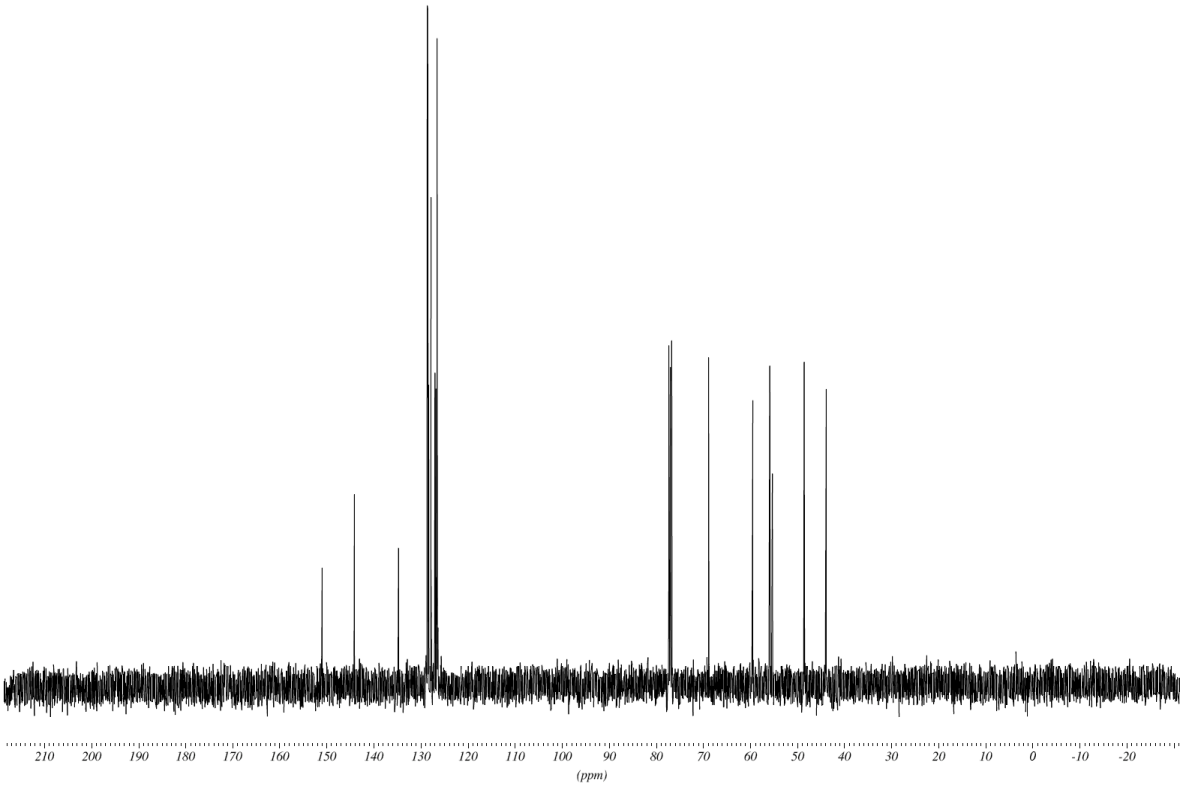
(ppm)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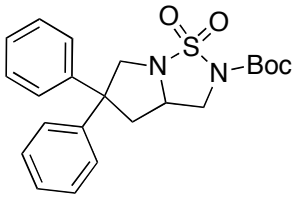
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O
S
N
N
Boc

2c

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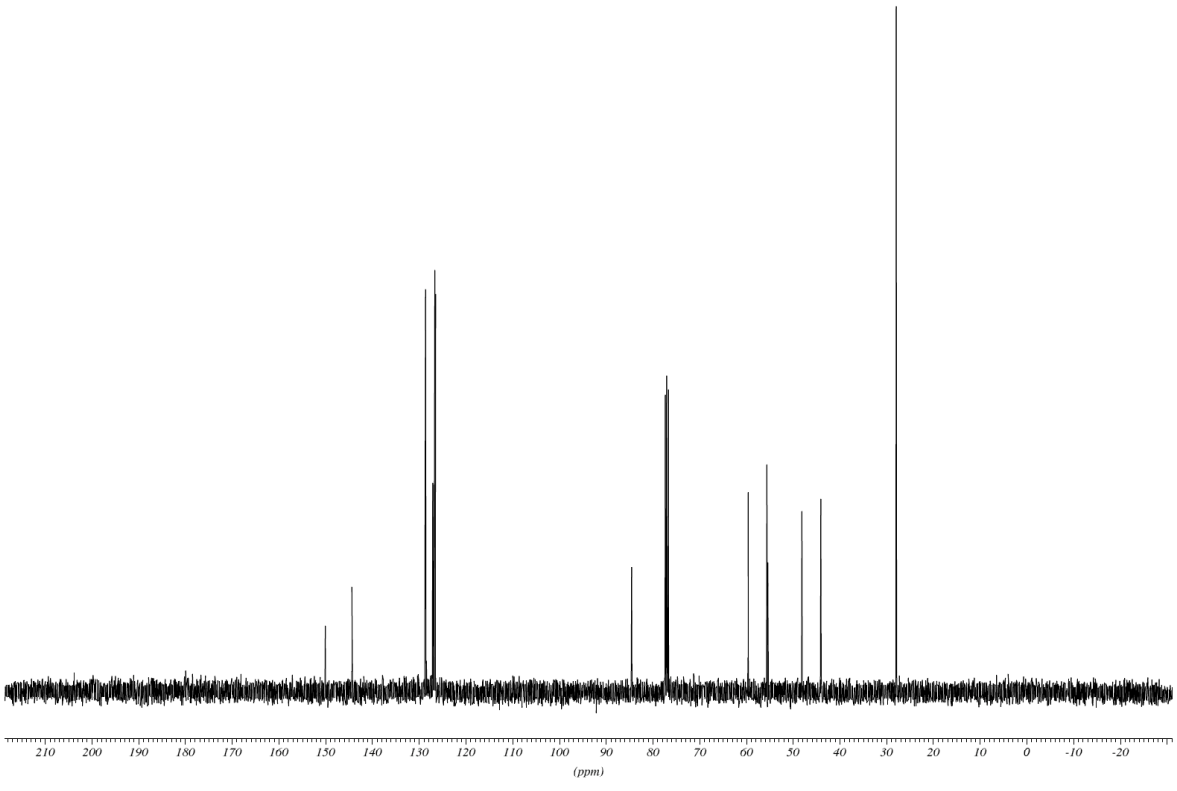
-1.5
(ppm)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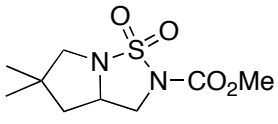
-10
-20
(ppm)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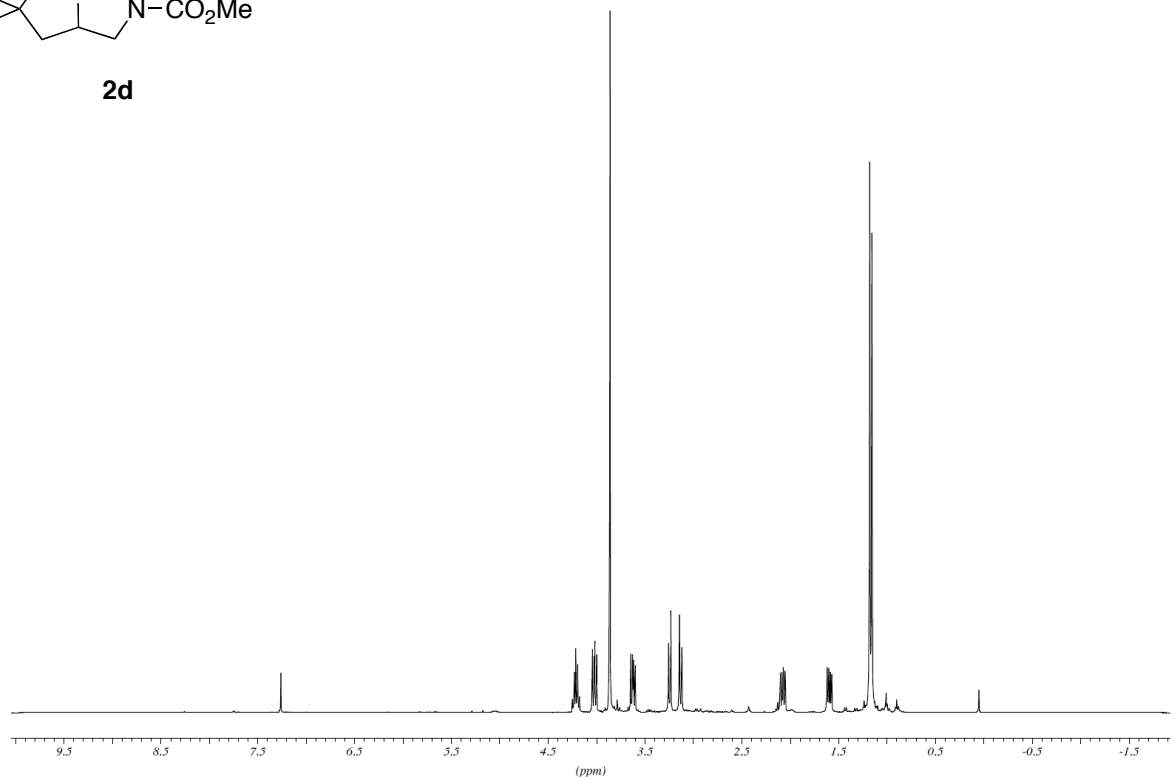
O
N
S
N−CO2Me

2d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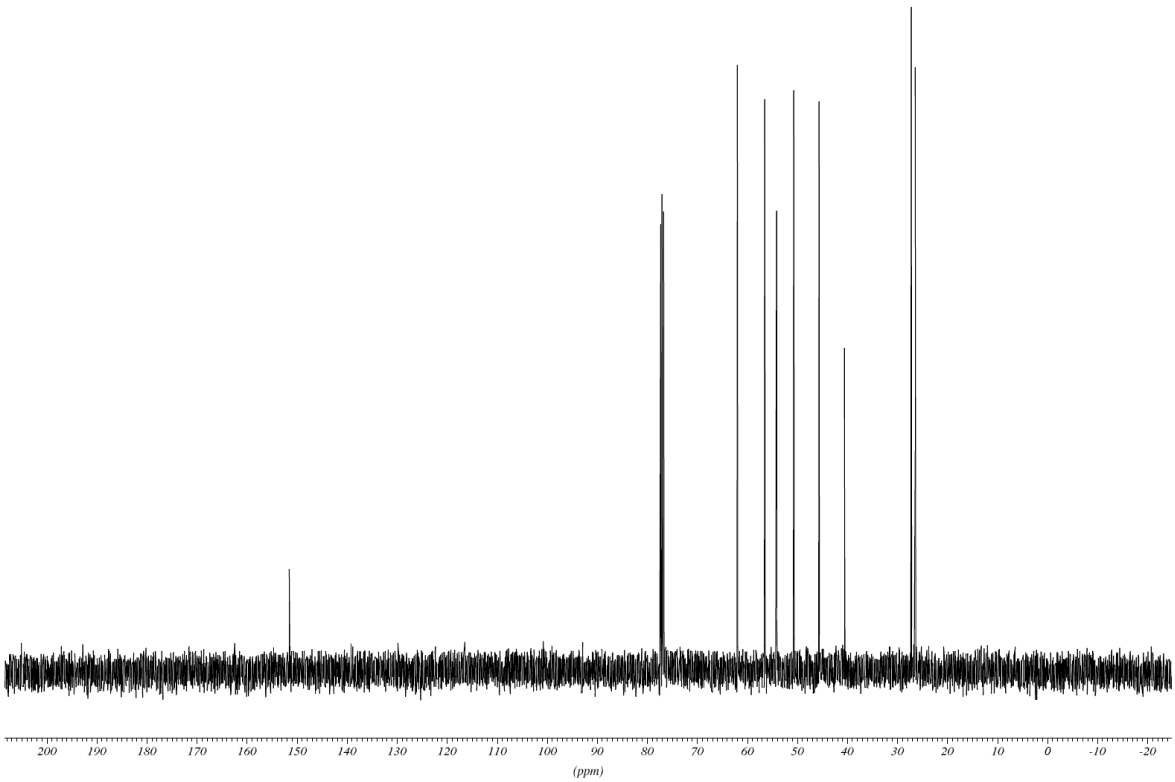
(ppm)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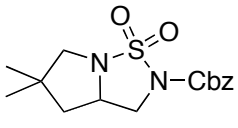
-20
(ppm)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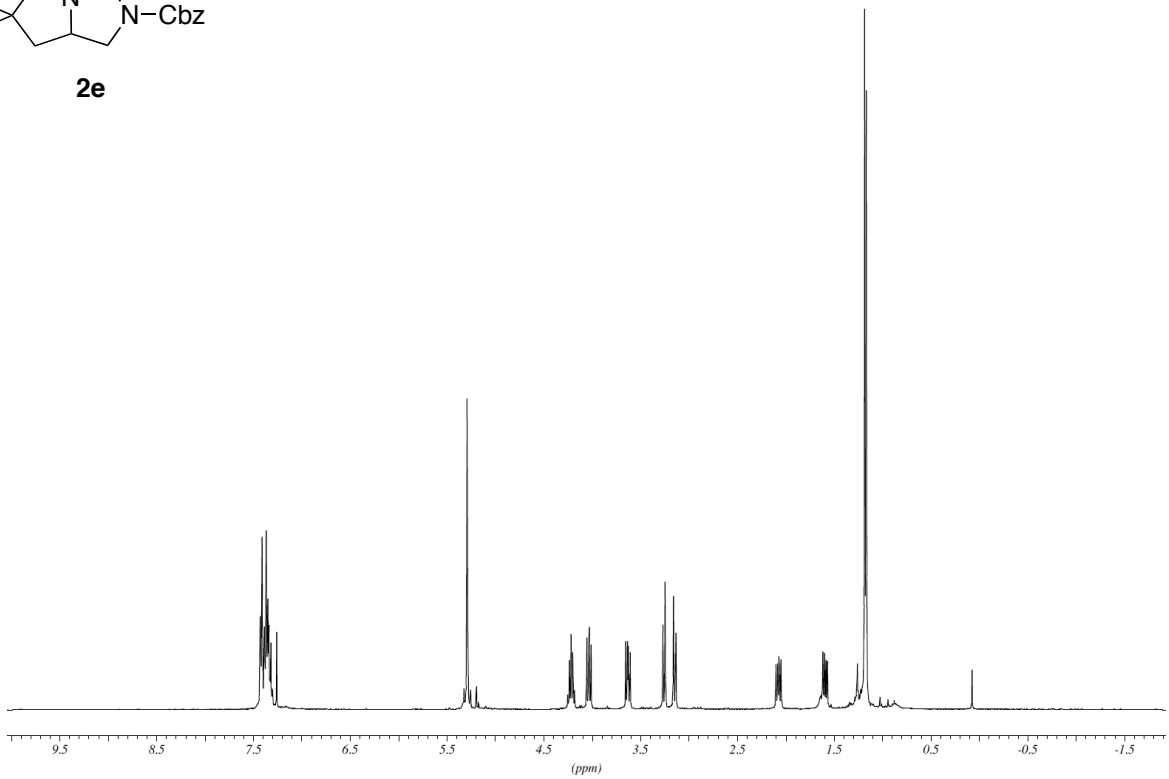
O
N
S
N−Cbz

2e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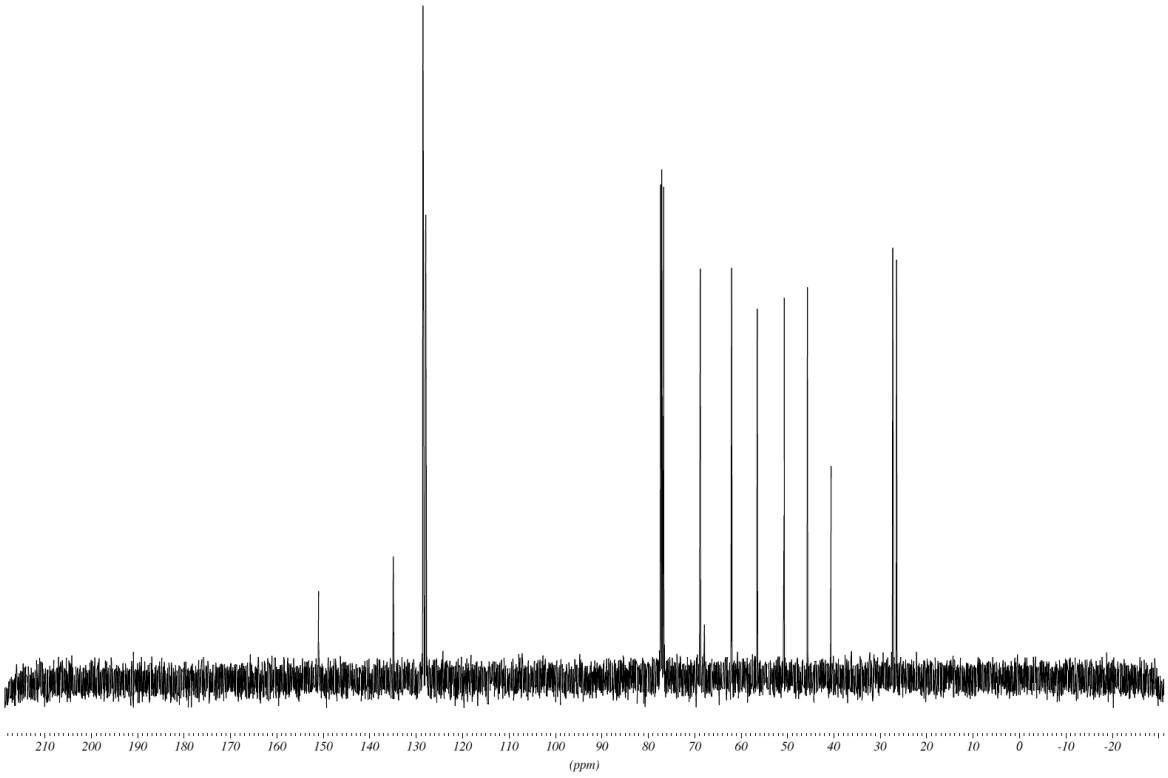
(ppm)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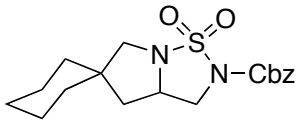
-10
-20
(ppm)


O
O
N
S
N−Cbz

2f

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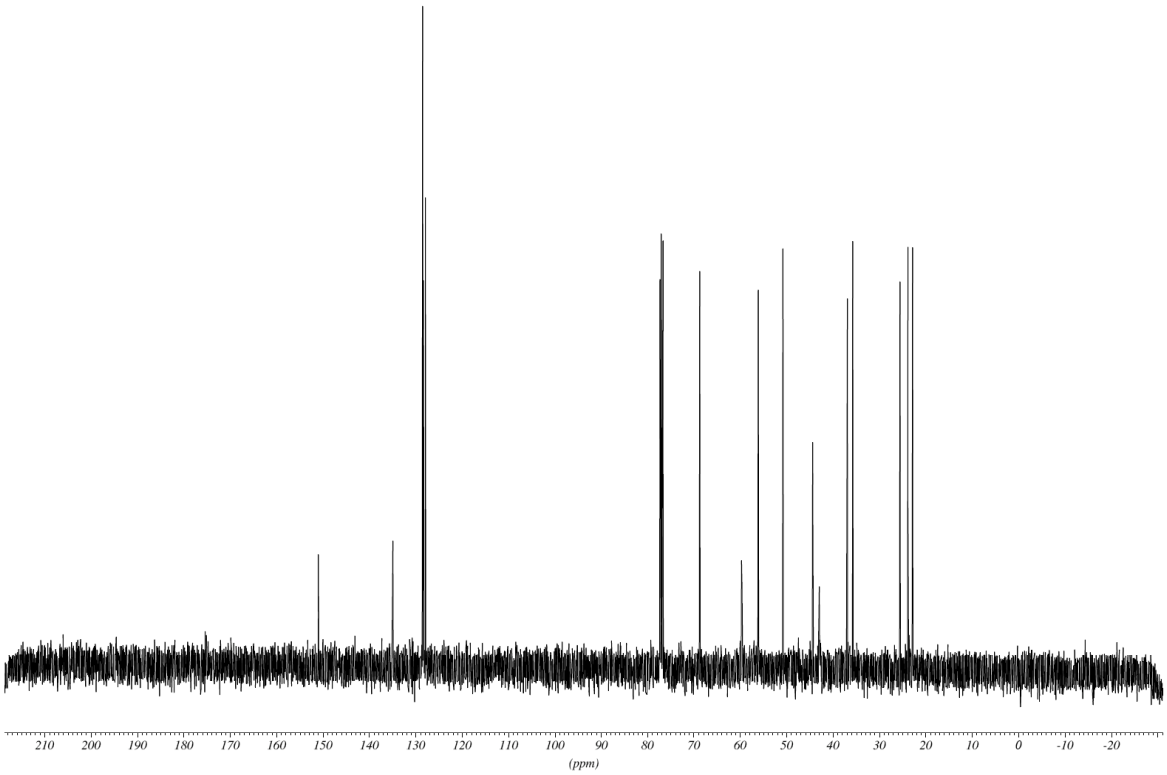
-1.5
(ppm)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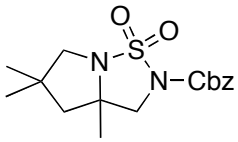
O
O
N
S
N−Cbz

2g

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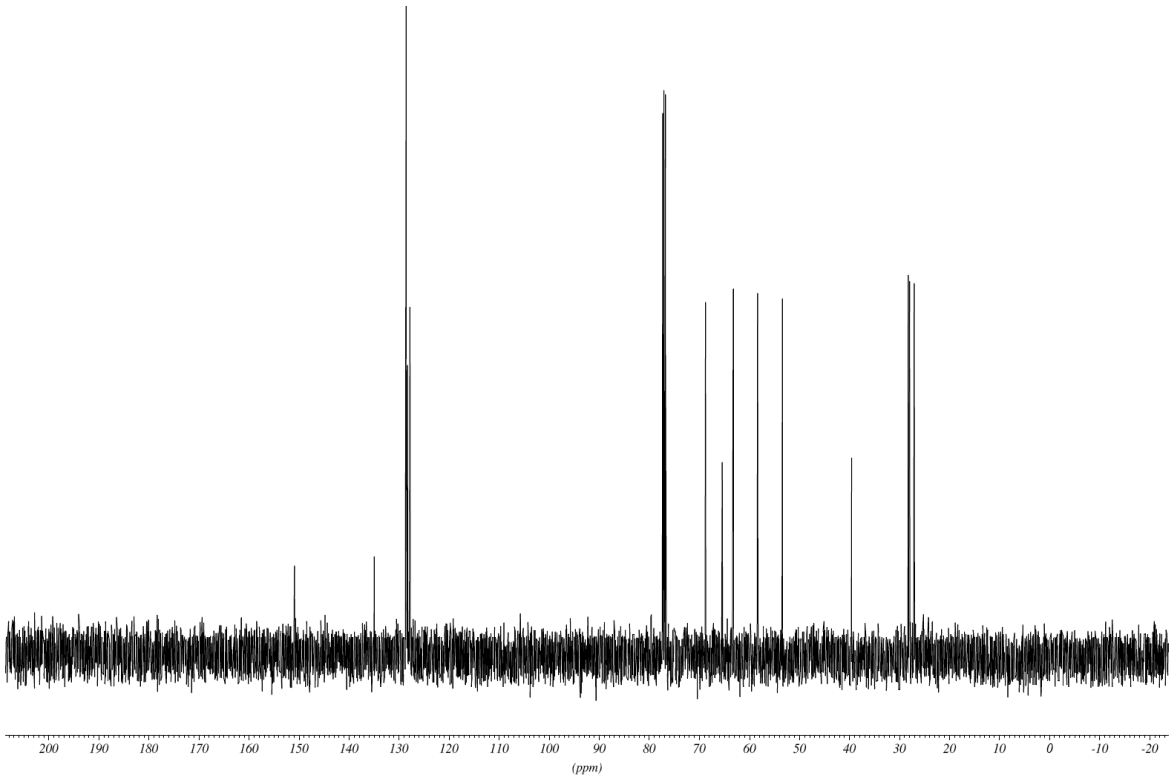
(ppm)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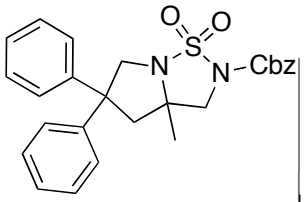
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S
N
N
Cbz

2h

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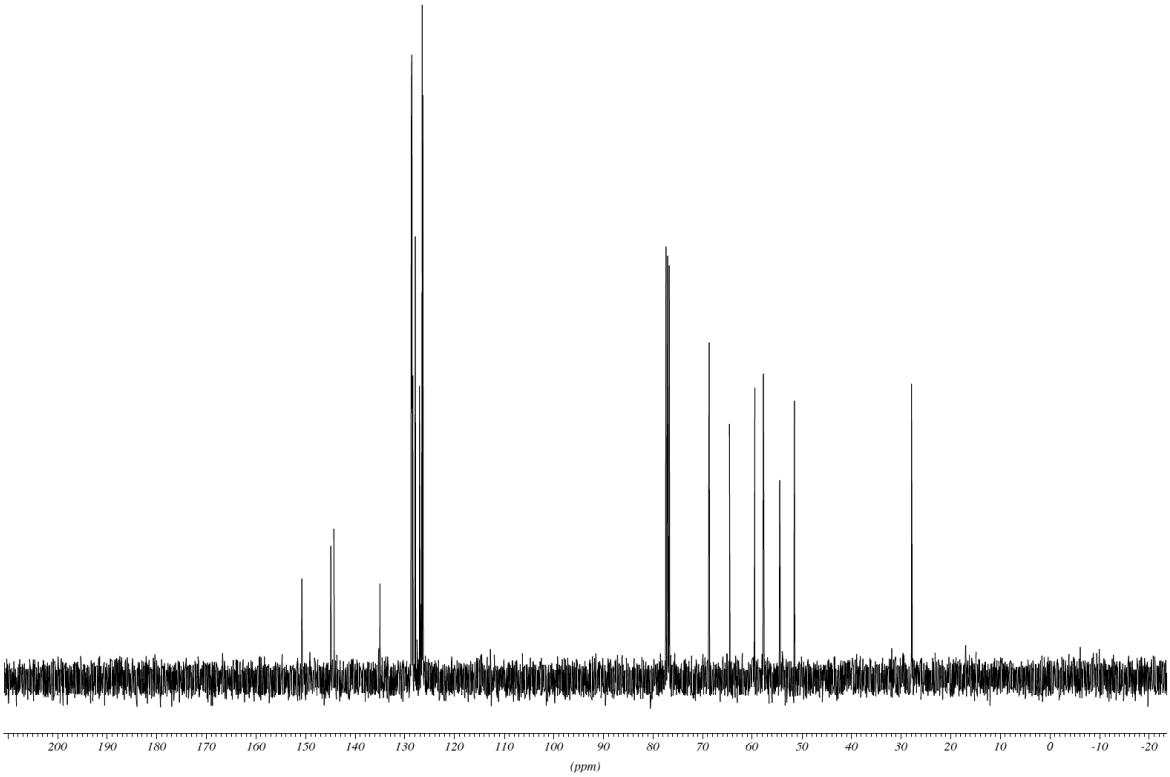
(ppm)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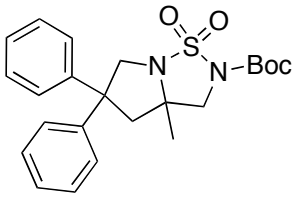
O
O
S
N
N
Boc

2i

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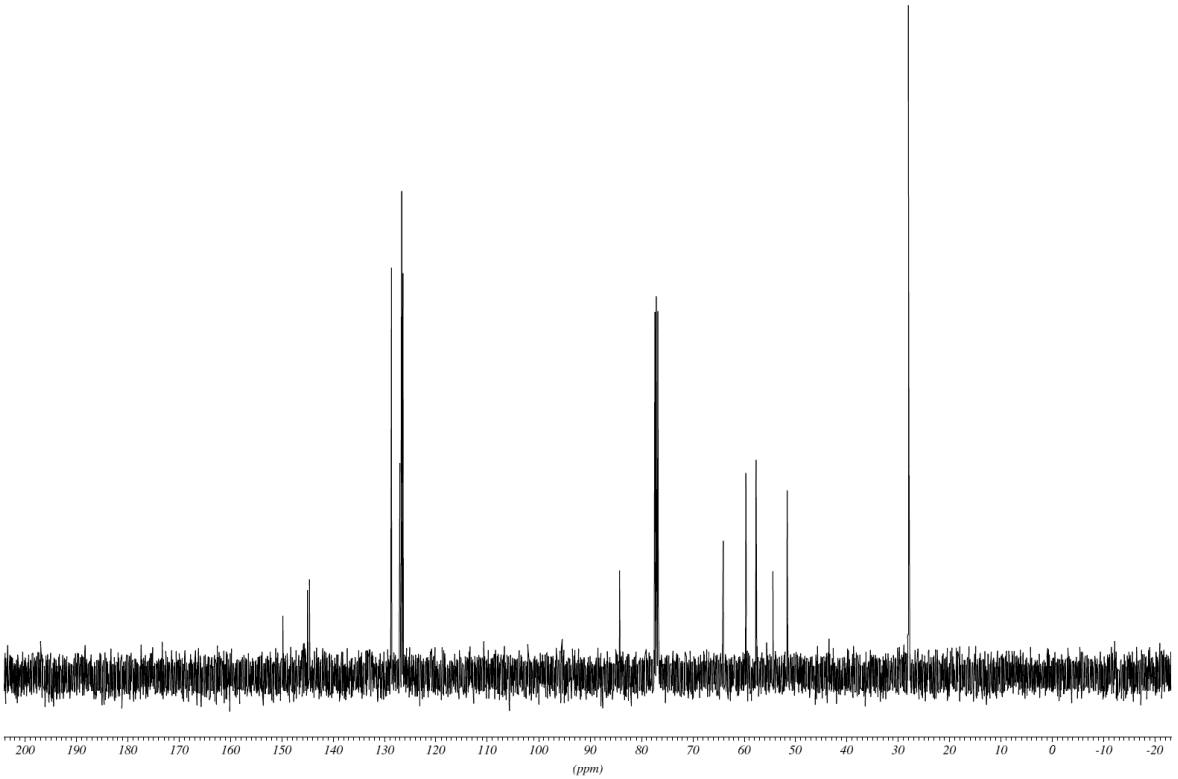
(ppm)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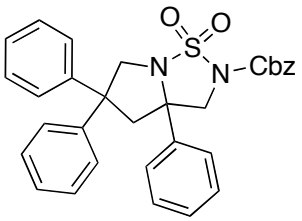
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Cbz

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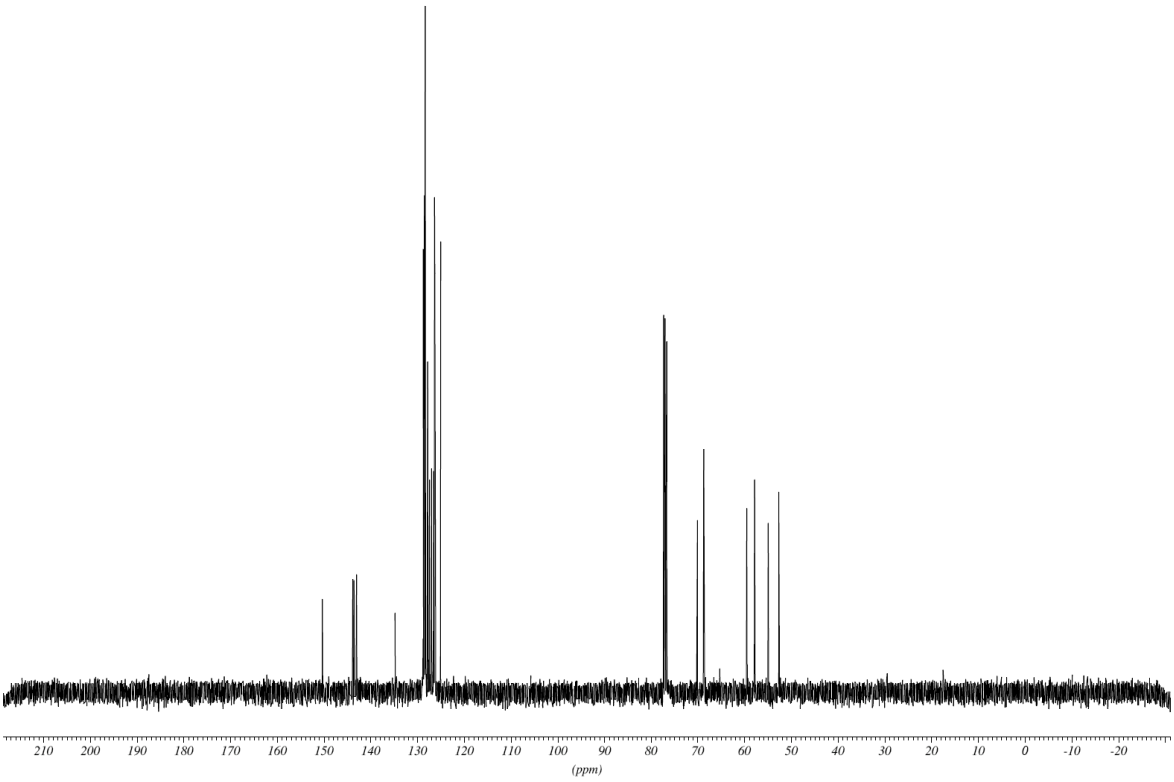
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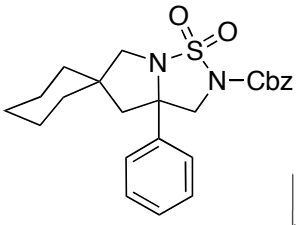
O
O
N
S
N−Cbz

2k

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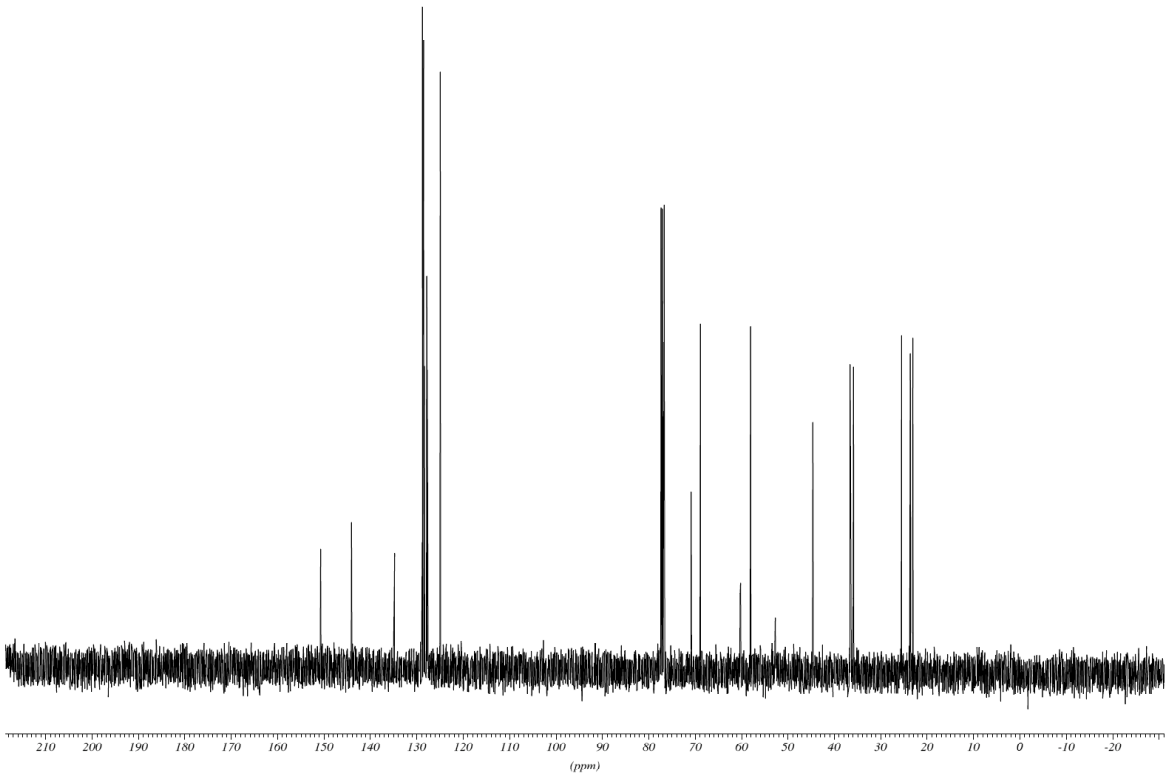
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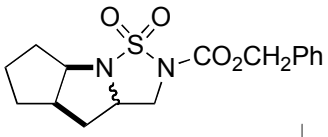
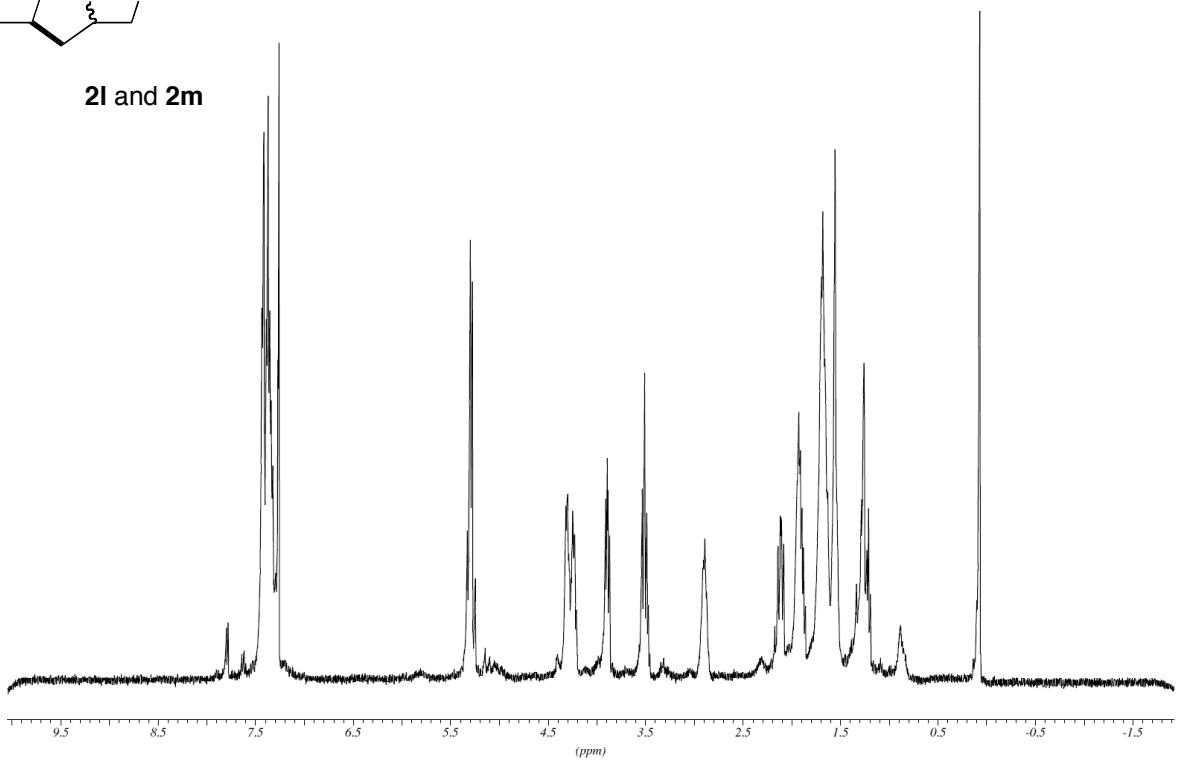
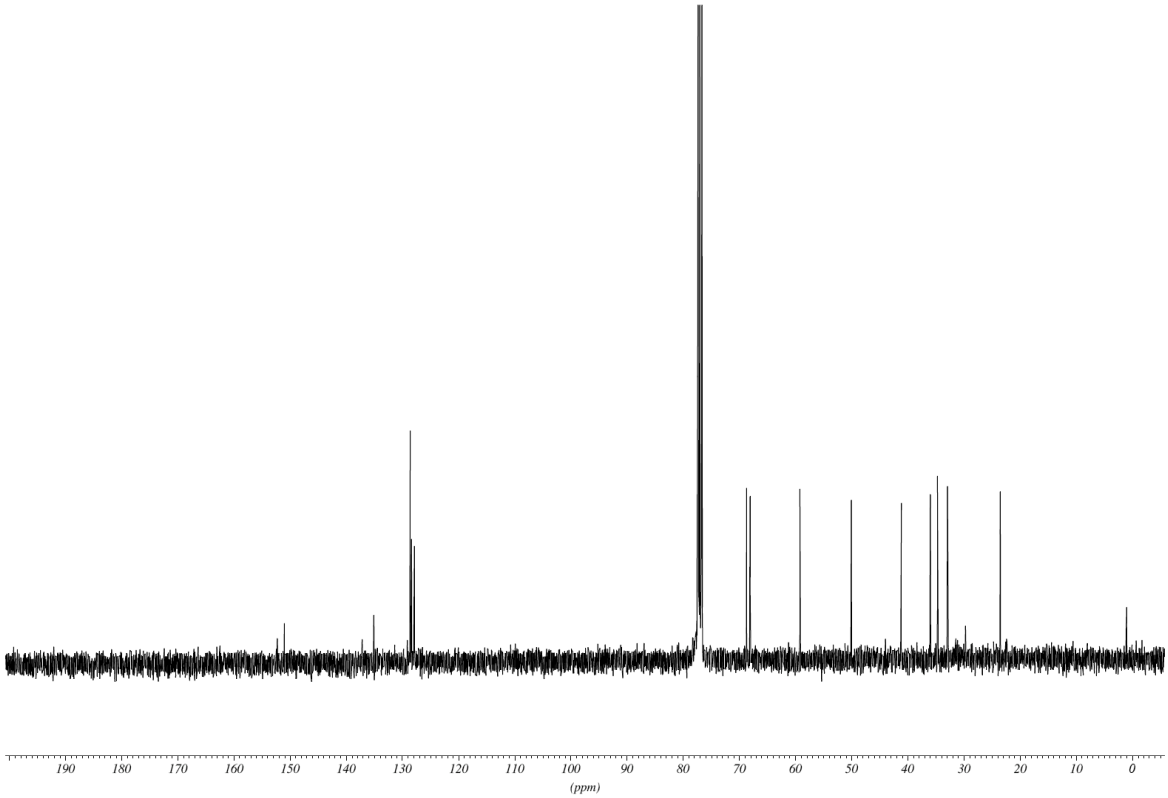
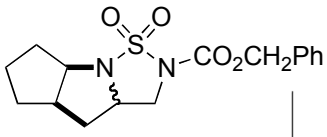


Diastereomer 1

2l and **2m**

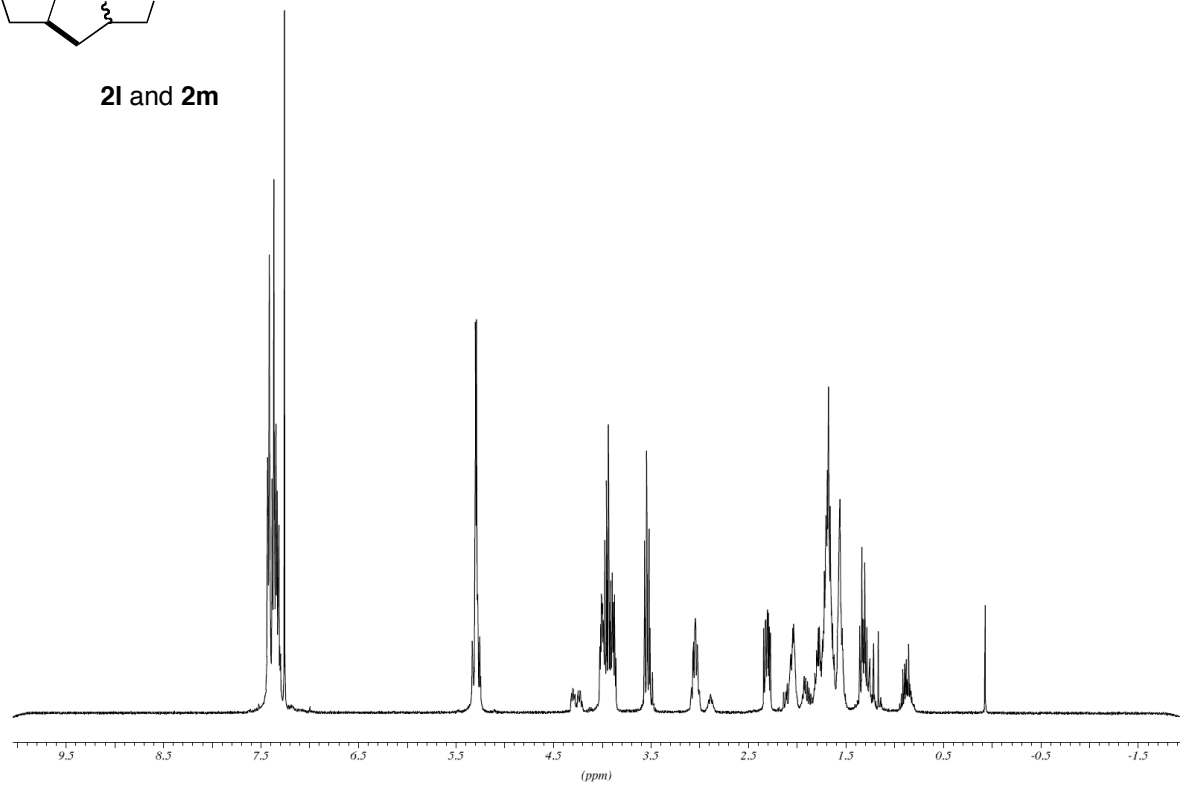


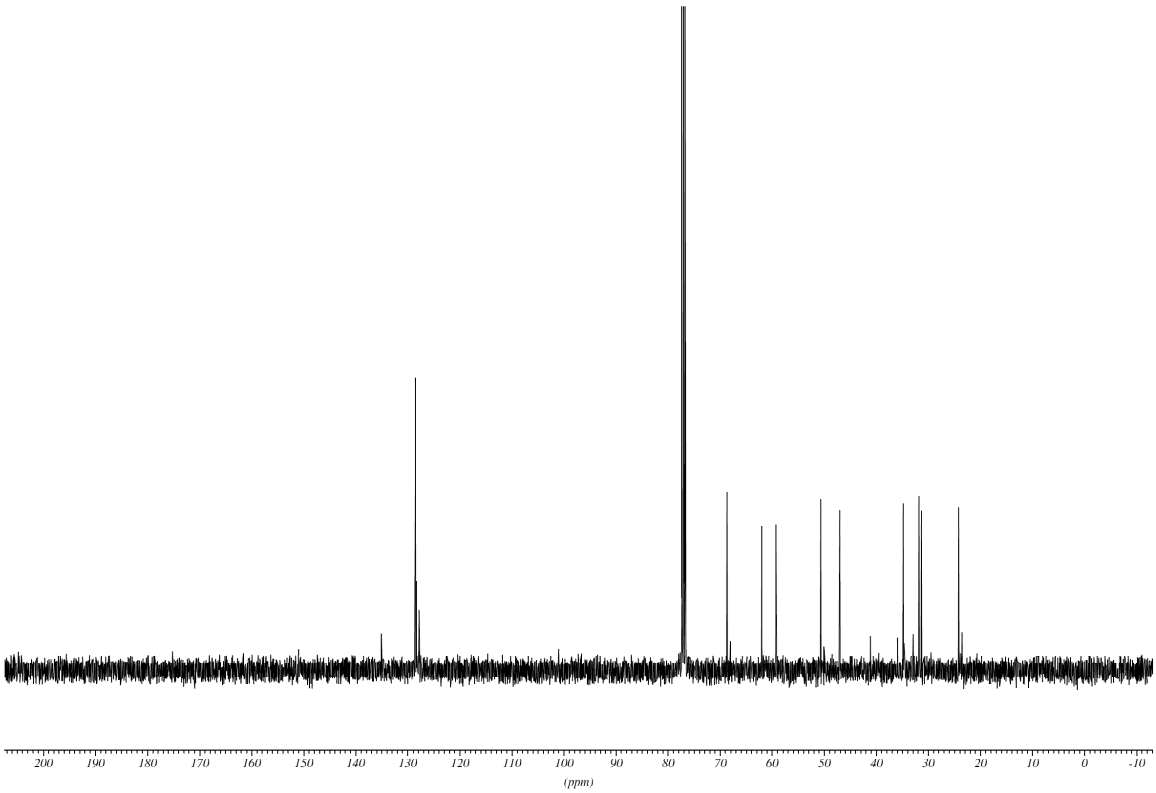




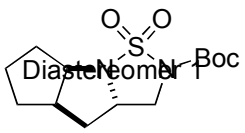
Diastereomer 2

2l and **2m**

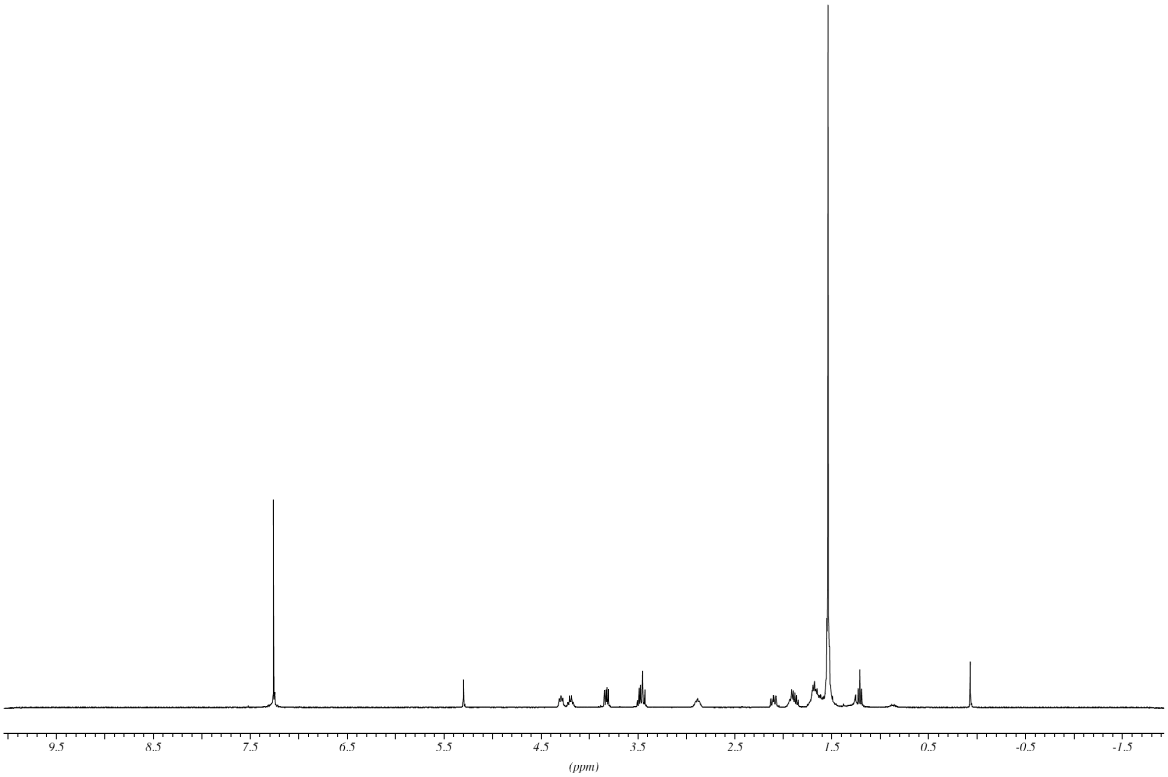


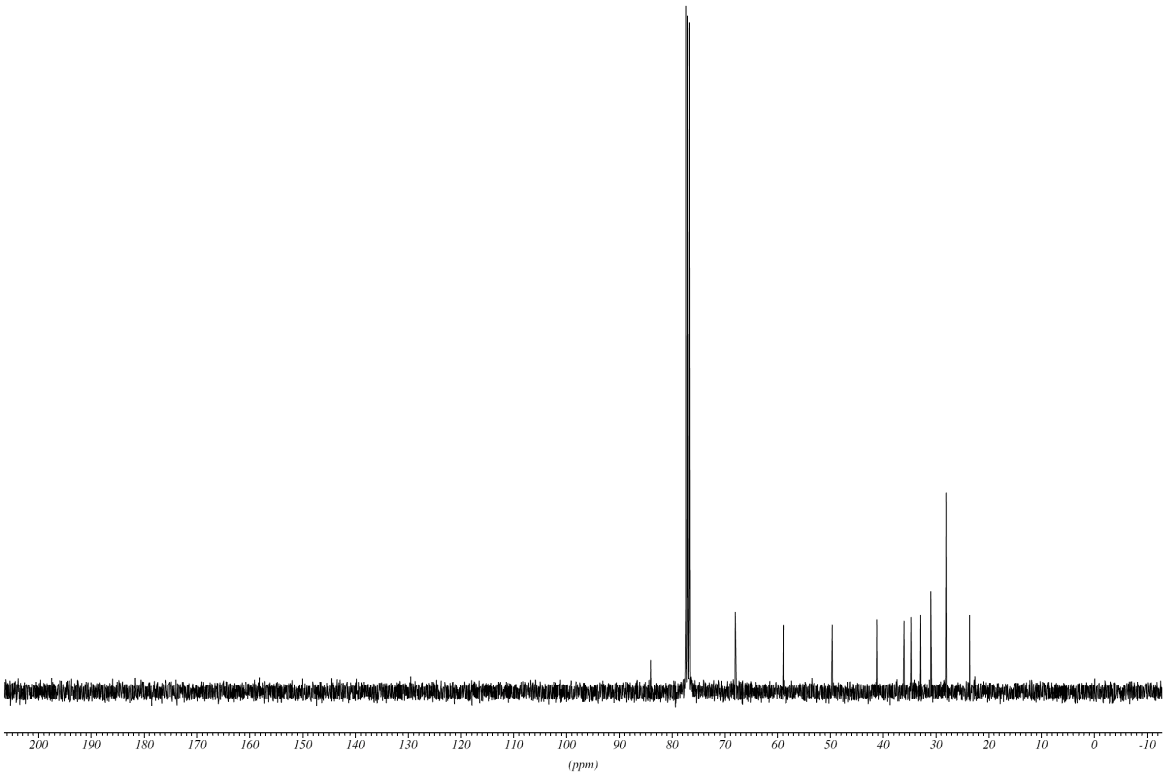


and

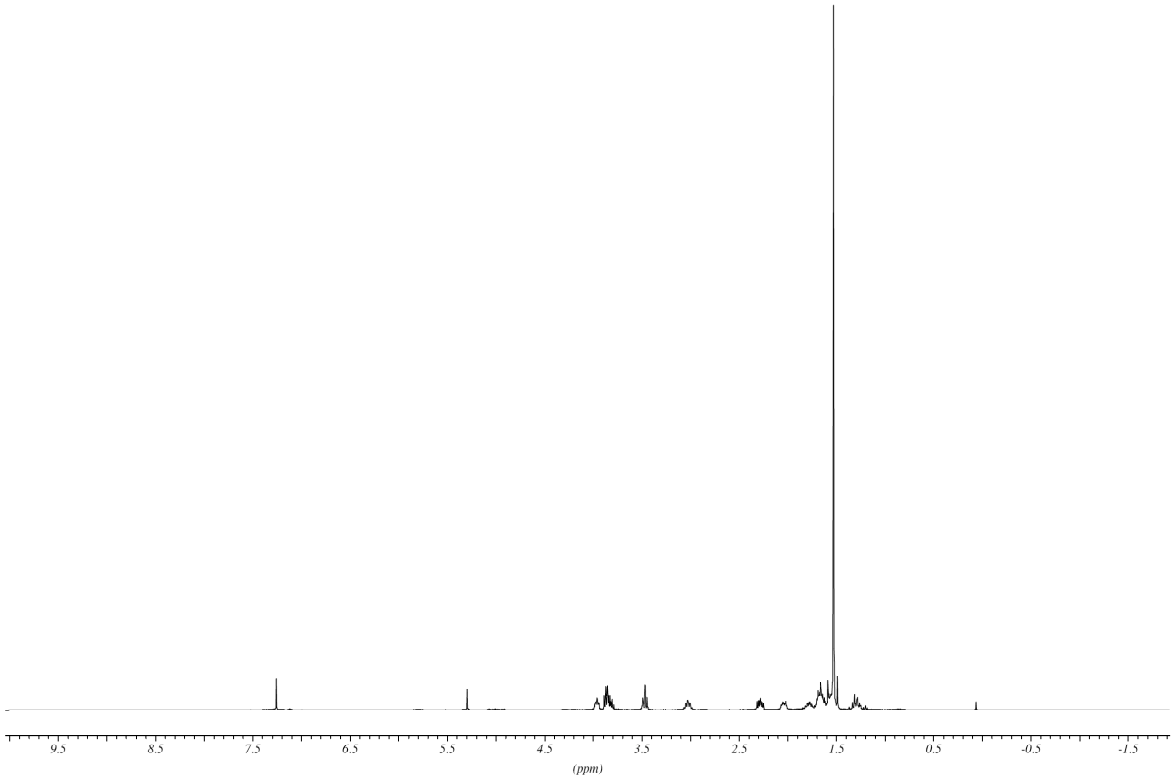


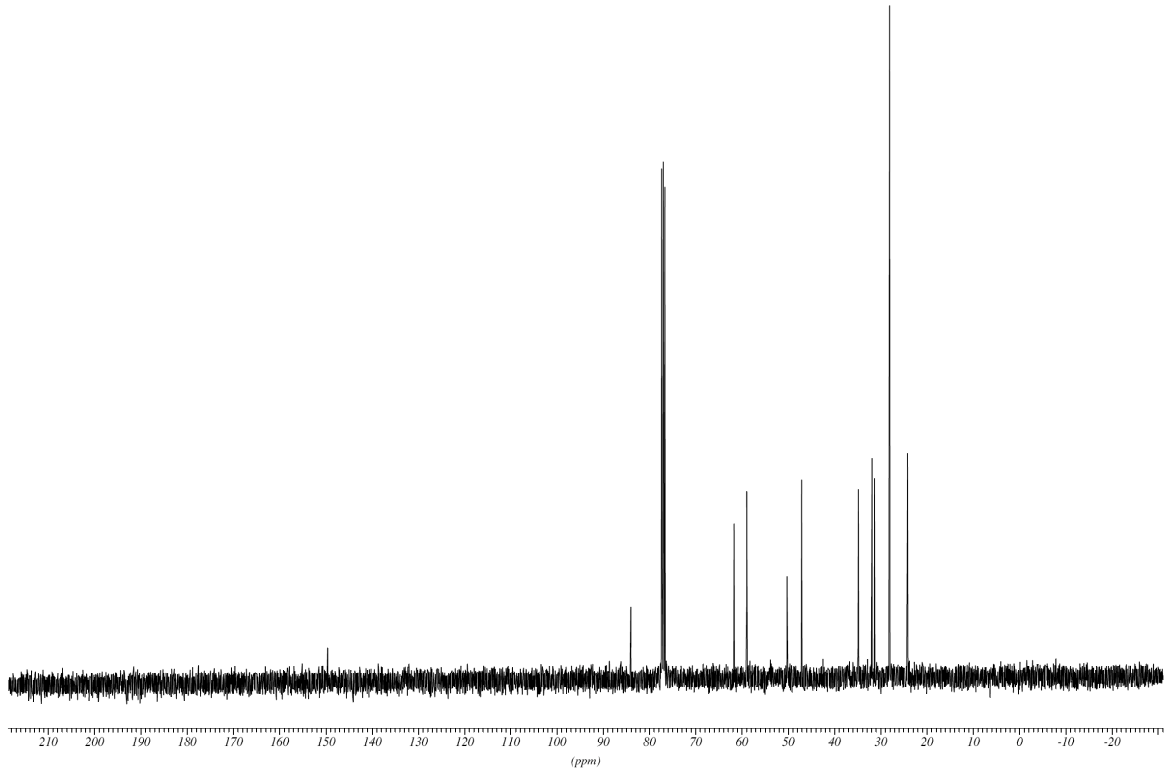
Diastereomer 1



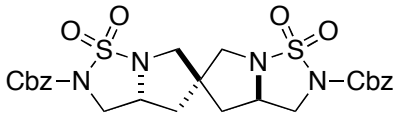


Diastereomer 2

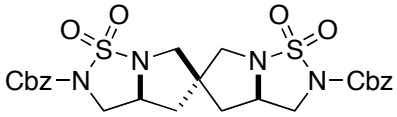




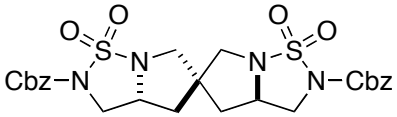
unseparated 1:1:1:1 mixture of all four possible stereoisomers



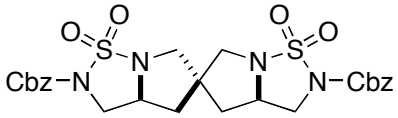
rac



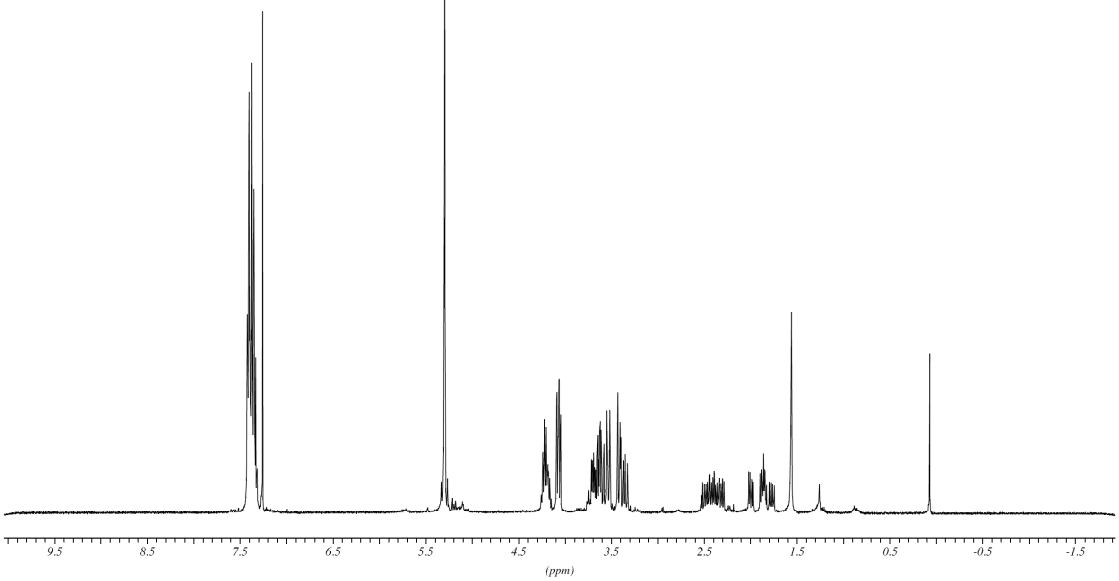
meso

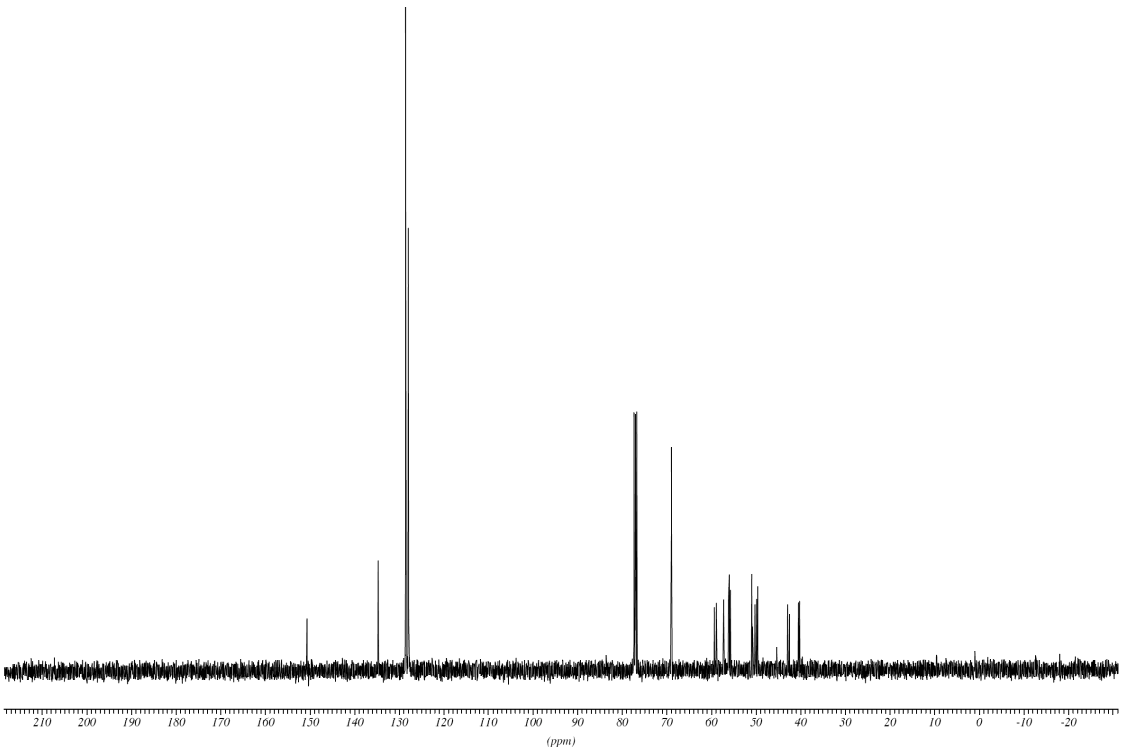


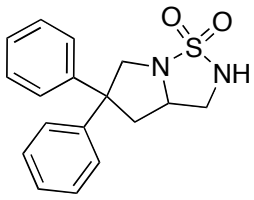
rac



meso

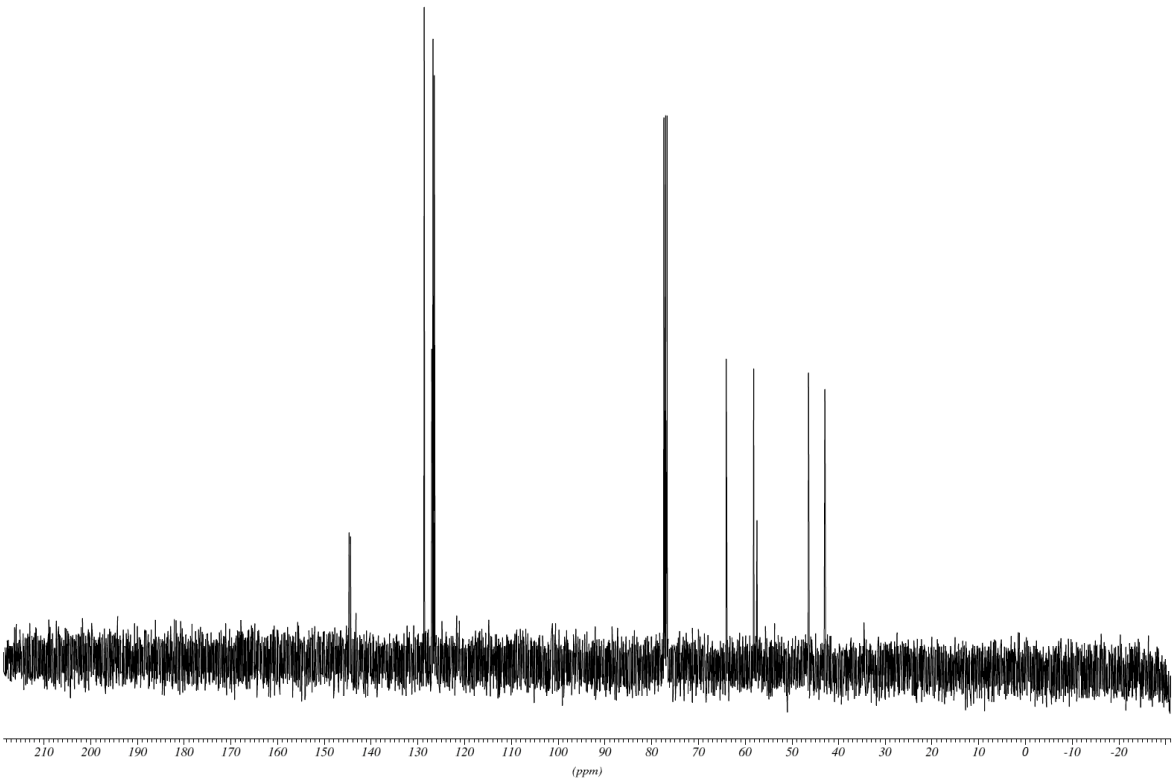


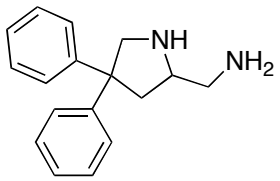



O
O
S
N
NH

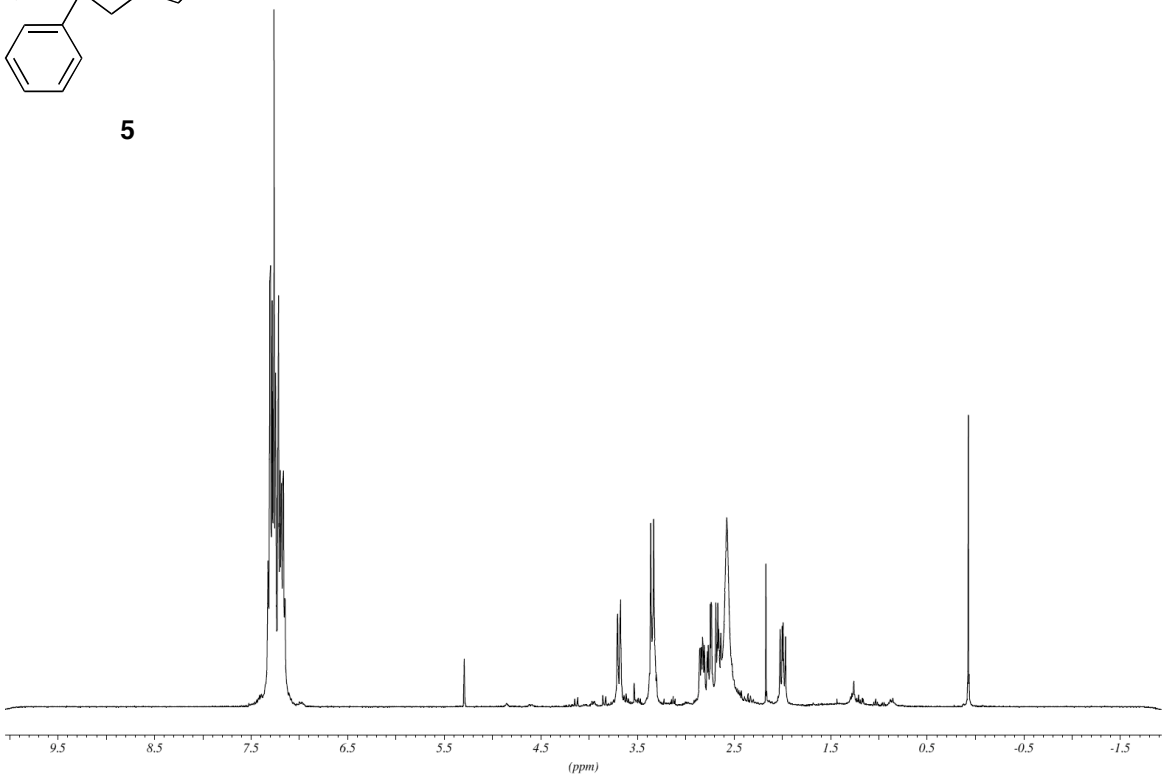
4

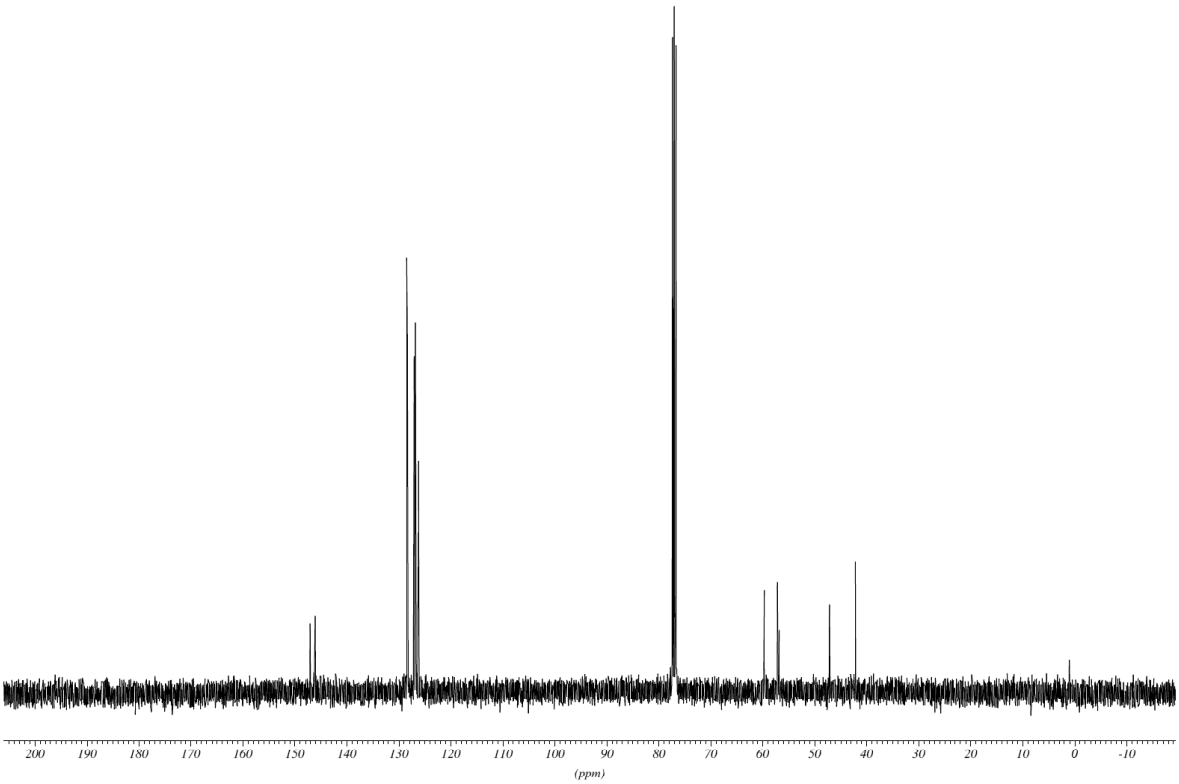
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
(ppm)

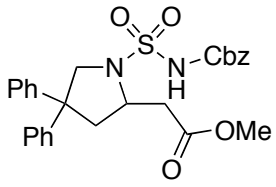

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
(ppm)


NH
NH2

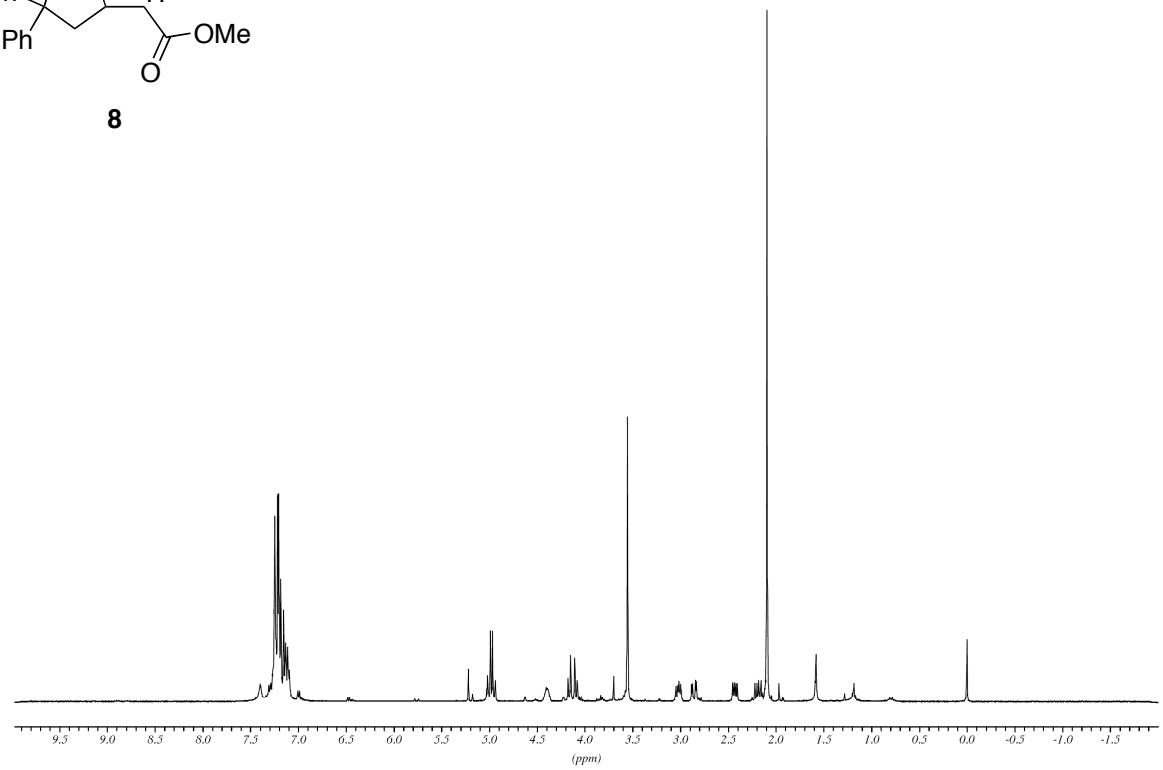
5

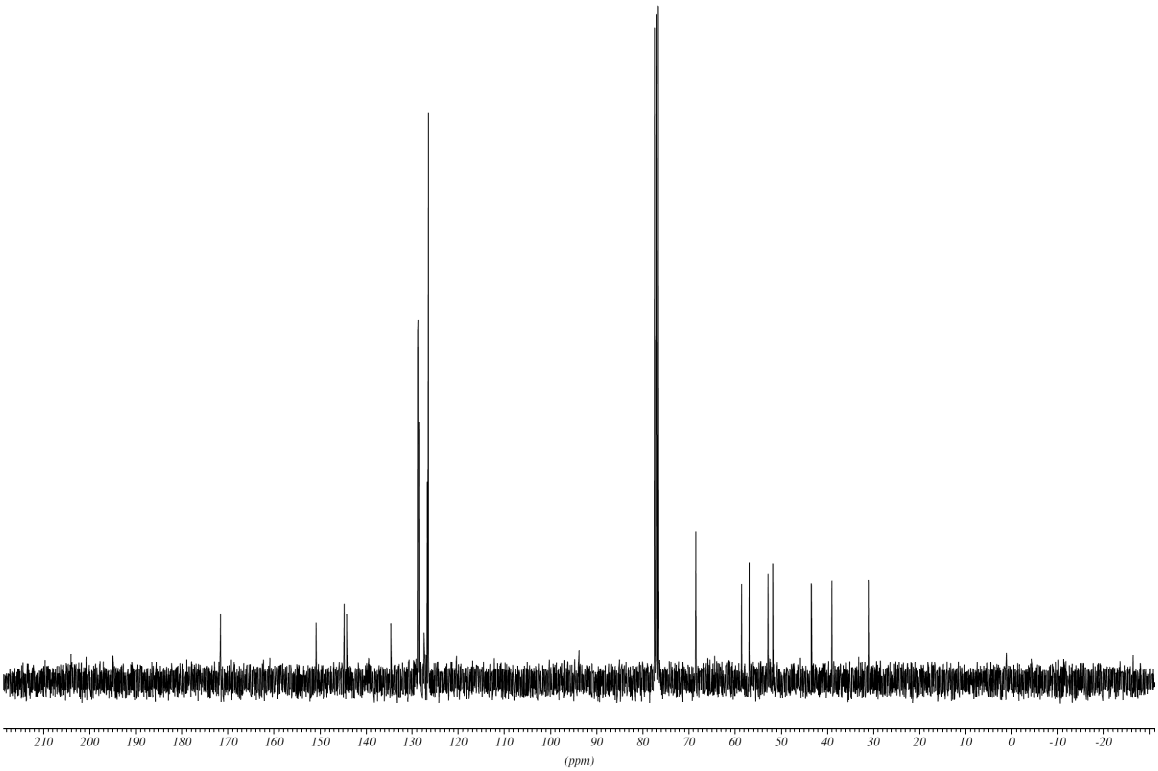

9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
(ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

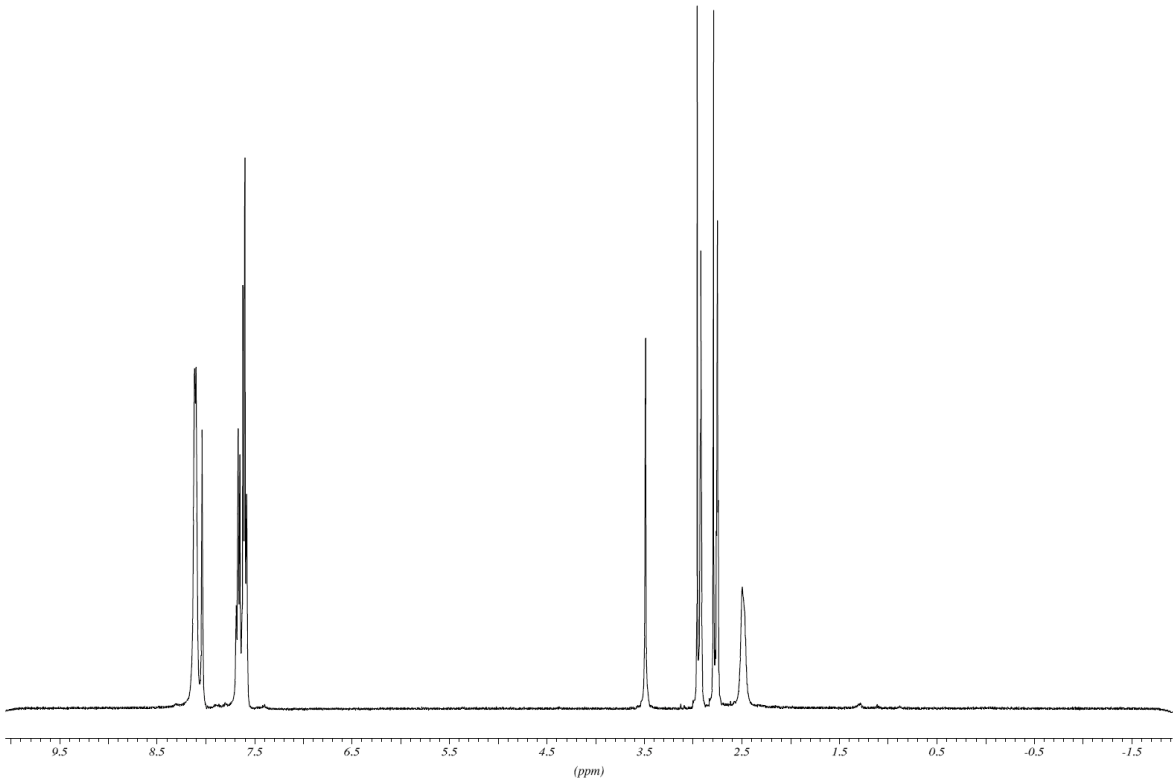

O
O
S
N
N
Cbz
H
Ph
Ph
OMe
O

8

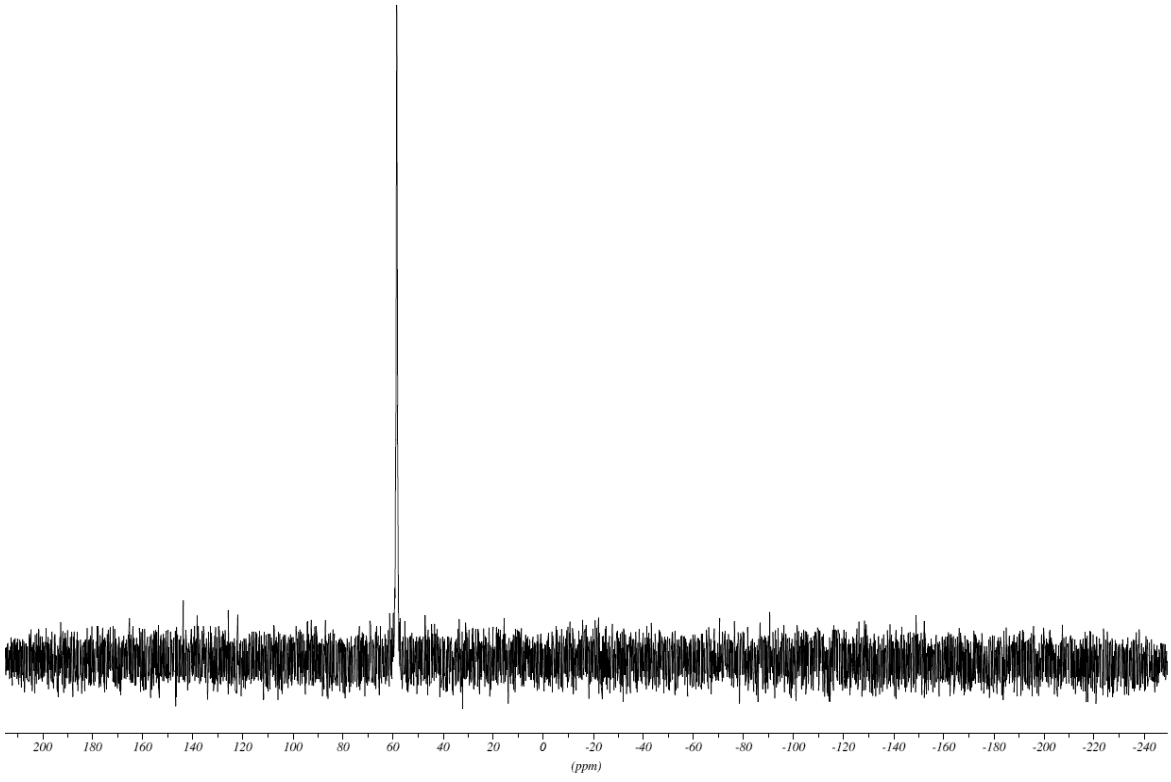

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
(ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
(ppm)

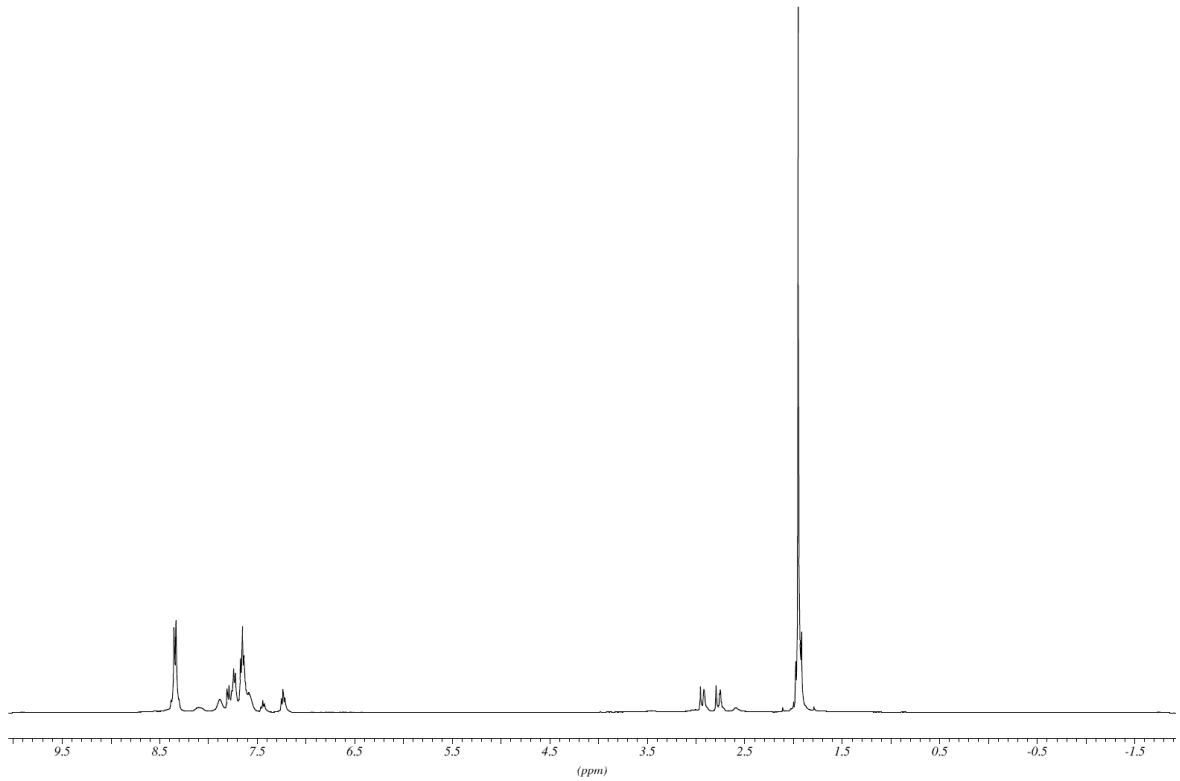
Ni(dppf)Cl_2 in DMF-*d7*



^{31}P Spectrum:



Ni(dppf)Cl_2 and 20 eq. PhI$(OAc)_2$ in DMF-*d7*



^{31}P-Spectrum of oxidative decomposition of Ni(dppf)Cl_2 catalyst precursor: