Electronic Supplementary Material (ESI) for Chemical Science

Metal-Free Diamination of Alkenes Employing Halide Catalysis

Patricia Chavez, Jonathan Kirsch, Claas H. Hövelmann, Jan Streuff, Marta Martinez-Belmonte, Eduardo C. Escudero-Adan, Eddy Martin, and Kilian Muñiz

Supporting Information

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1 General

All solvents, reagents and all deuterated solvents were purchased from Aldrich. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2 mm). NMR spectra were recorded on a Bruker Avance 300 and Avance 400 MHz spectrometer, respectively. All chemical shifts in NMR experiments are reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ δ = 7.26 and 77.0 ppm, acetone-d_6 δ = 2.09 and 30.6 ppm, respectively. MS (ESI-LCMS) experiments were performed using an Agilent 1100 HPLC with a Bruker micro-TOF-instrument (ESI). Unless otherwise stated, a Supelco C8 (5cm x 4.6mm, 5 µm particles) column was used with a linear elution gradient from 100% H_2O (0.5% HCO_2H) to 100% MeCN in 13 min at a flow rate of 0.5 mL/min. Melting points were determined in open capillary tubes on a Büchi Melting point B-545 instrument. MS(EI) and HRMS experiments were performed on a Kratos MS 50 within the service centers at ICIQ.

2 General procedures for synthesis of starting materials

The general syntheses were described previously:

Ureas:

J. Streuff, C. H. Hövelmann, M. Nieger and K. Muñiz, *J. Am. Chem. Soc*. 2005, **127**, 14587; K. Muñiz, C. H. Hövelmann and J. Streuff, *J. Am. Chem. Soc.* 2008, **130**, 763; K. Muñiz, C. H. Hövelmann, E. Campos-Gómez, J. Barluenga, J. M. González, J. Streuff and M. Nieger, *Chem. Asian J.,* 2008, **2**, 776.

Acrylates:

P. Chávez, J. Kirsch, J. Streuff and K. Muñiz, *J. Org. Chem.,* 2012, **77**, 1922.

Sulfamides:

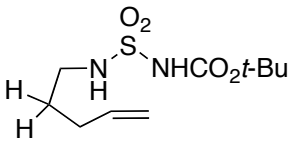
Adapted from: K. Muñiz, J. Streuff, C. H. Hövelmann and A. Nuñez, *Angew. Chem. Int. Ed*. 2007, **46**, 7125.

Synthesis of DMAP-Burgess reagents: J.-Y. Winum, J.-Y., L. Toupet, L., V. Barragan, G. Dewynter and J.-L. Montero, *Org. Lett.* 2001, **3**, 2241.

Synthesis of readily *N*-protected sulfamide starting materials: The crude amine (1.0 eq.) is dissolved in dichloromethane (3 mL/mmol), the desired DMAP-Burgess reagent (1.0 eq.; containing carbamate from Me, CH_2Ph, *t*Bu) is added and the solution is stirred 24-48h. The mixture is extracted with saturated aqueous ammonium chloride solution. The organic layer is dried over $MgSO_4$ and concentrated to yield the crude product. Short column chromatography provides the pure sulfamate.

3 Characterization of starting materials

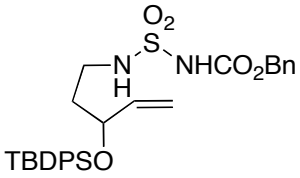
tert-Butyl *N*-(pent-4-en-1-yl)sulfamoylcarbamate 1i



Obtained from reaction between the DMAP-Burgess reagent and 5-amino pentene. Isolated as a white solid in 60% yield.

Mp. 75°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 5.79 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.60 (t, *J* = 6.3 Hz, 1H), 5.06 (ddd, *J* = 17.0, 3.1, 1.6 Hz, 1H), 5.01 (ddd, *J* = 10.2, 3.1, 1.1 Hz, 1H), 3.10 (dd, *J* = 13.3, 6.3 Hz, 2H), 2.14 (dd, *J* = 14.6, 6.9 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.5, 137.1, 115.6, 83.6, 43.1, 30.5, 28.1, 28.0. IR (cm^{-1}): 3283, 3209, 3083, 2982, 2936, 2879, 1696, 1642, 1438, 1370, 1343, 1254, 1137, 1082, 910, 817, 784, 719, 579. MS (ESI-TOF): *m/z* (%): 287.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{10}H_{20}N_2NaO_4S$ $[M+Na]^+$: 287.1041; found: 287.1053.

Benzyl *N*-(3-((*tert*-butyldiphenylsilyl)oxy)pent-4-en-1-yl)sulfamoylcarbamate 1j

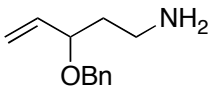


Obtained from reaction between the DMAP-Burgess reagent and the corresponding free primary amine, which was synthesized accordingly to a literature protocol (H. H. Wasserman, J. D. Cook and C. B. Vu, *Tetrahedron Lett.,* 1990, **31**, 4945). The pure product was obtained as a white solid in 87% yield. Mp. 64°C.

Mp. 64°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.66 (m, 6H), 7.50 – 7.34 (m, 10H), 5.76 (ddd, *J* = 17.1, 10.5, 5.8 Hz, 1H), 5.37 (t, *J* = 5.9 Hz, 1H), 5.19 (d, *J* = 1.6 Hz, 2H), 5.14 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.05 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.38 – 4.30 (m,

1H), 3.13 – 3.04 (m, 2H), 1.78 – 1.68 (m, 1H), 1.67 – 1.58 (m, 1H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.8, 138.8, 135.7, 135.6, 134.5, 129.7, 129.5, 129.4, 128.5, 128.4, 128.1, 127.5, 127.4, 127.3, 115.3, 72.1, 68.1, 39.5, 35.4, 26.7, 19.0. IR (cm^{-1}): 3279, 3071, 2956, 2931, 2890, 2858, 1721, 1452, 1427, 1353, 1227, 1155, 1110, 1080, 1027, 997, 908, 841, 821, 733, 699, 608, 578, 503, 487, 428. MS (ESI-TOF): *m/z* (%): 575.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{29}H_{36}N_2NaO_5SSi$ $[M+Na]^+$: 575.2012; found: 575.2007.

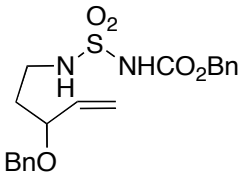
3-(Benzyloxy)pent-4-en-1-amine



The nitrile (10 mmol), previously synthesized accordingly to a literature protocol (D-Y. Ma, D-X. Wang, J. Pan, Z-T. Huang and M-X Wang, *J. Org. Chem.*, 2008, **11**, 4087), was dissolved in 100 mL of Et_2O at 0ºC and $LiAlH_4$ (1.2 equiv., 12 mmol) was added slowly within 4 successive portions. After 12 hours, the reaction was quenched with water at -10ºC until a bright white solid appeared. $MgSO_4$ was then added, the reaction mixture was stirred during 5 minutes, filtrated and washed with CH_2Cl_2. After evaporation under reduced pressure the product was obtained as yellow oil in 87% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 – 7.22 (m, 4H), 7.21 – 7.04 (m, 1H), 5.78 – 5.60 (m, 1H), 5.20 – 5.17 (m, 1H), 5.16 – 5.11 (m, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.27 (d, *J* = 11.9 Hz, 1H), 3.78 (td, *J* = 7.8, 5.2 Hz, 1H), 2.71 (t, *J* = 6.9 Hz, 2H), 1.73 – 1.60 (m, 1H), 1.59 – 1.53 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.7, 128.3, 127.7, 127.4, 126.7, 117.1, 78.6, 70.0, 39.3, 38.6. IR (cm^{-1}): 461, 596, 696, 732, 924, 993, 1051, 1084, 1025, 1453, 1495, 1587, 1641, 2861, 2932, 3063, 3179, 3361. MS (ESI-TOF): *m/z* (%): 192.1 $[M+H]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{12}H_{18}NO$ $[M+H]^+$: 192.1388; found: 192.1384.

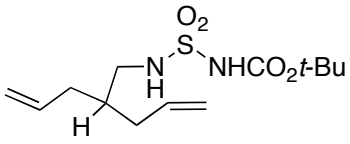
Benzyl *N*-(3-(benzyloxy)pent-4-en-1-yl)sulfamoylcarbamate 1k



Obtained from reaction between the DMAP-Burgess reagent and the corresponding free primary amine described above. The final product was obtained as a white solid in 42% yield.

Mp. 68°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.27 (m, 11H), 5.78 (pseudo-t, *J* = 5.4 Hz, 1H), 5.77 – 5.68 (m, 1H), 5.31 – 5.25 (m, 2H), 5.17 (s, 2H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.28 – 3.18 (m, 1H), 3.18 – 3.11 (m, 1H), 1.88 – 1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.4, 137.9, 137.5, 134.7, 128.6, 128.6, 128.4, 128.3, 128.3, 127.8, 127.6, 126.9, 117.9, 78.2, 70.2, 68.2, 40.7, 34.3. IR (cm^{-1}): 499, 574, 596, 698, 750, 840, 1022, 1072, 1152, 1246, 1349, 1454, 1472, 1733, 2866, 2941, 3216, 3271. MS (ESI-TOF): *m/z* (%): 427.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{20}H_{24}N_2NaO_5S$ $[M+Na]^+$: 427.1304; found: 427.1306.

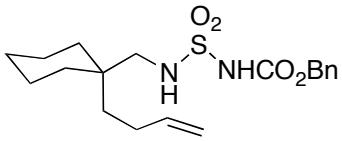
***tert*-Butyl *N*-(2-allylpent-4-en-1-yl)sulfamoylcarbamate 1m**



Obtained from reaction between the DMAP-Burgess reagent and the corresponding free primary amine obtained from a literature protocol (S. H. Hong, R. H. Grubbs, *J. Am. Chem. Soc.*, 2006, **128**, 3508). The final product was obtained as a white solid in 68% yield. Mp. 74°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (s, 1H), 5.75 (ddt, *J* = 17.3, 10.3, 7.2 Hz, 2H), 5.12 – 5.05 (m, 5H), 2.99 (t, *J* = 6.3 Hz, 2H), 2.14 – 2.05 (m, 4H), 1.82 – 1.68 (m, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.1, 135.4(2x), 117.4, 83.8, 46.3, 37.3, 35.7(2x), 27.9. IR (cm^{-1}): 3283, 3228, 2980, 2931,

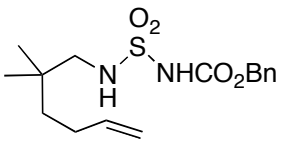
1702, 1641, 1440, 1371, 1351, 1251, 1177, 1137, 912, 817, 781, 721, 578. MS (ESI-TOF): *m/z* (%): 327.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{13}H_{24}N_2NaO_4S$ $[M+Na]^+$: 327.1354; found: 327.1368.

Benzyl *N*-((1-(but-3-en-1-yl)cyclohexyl)methyl)sulfamoylcarbamate 3a



Obtained from reaction between the DMAP-Burgess reagent and the corresponding free primary amine. Isolated as a white solid in 85% yield.
Mp. 75°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.38 (m, 5H), 5.83 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.23 (s, 2H), 5.06 (ddd, *J* = 16.8, 3.4, 1.5 Hz, 1H), 4.99 (ddt, *J* = 10.1, 2.5, 1.5 Hz, 1H), 2.90 (s, 2H), 2.00 – 1.87 (m, 2H), 1.49 – 1.24 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.3, 138.8, 134.6, 128.8, 128.7, 128.5, 114.5, 68.6, 49.7, 35.6, 34.6, 33.3, 27.1, 26.0, 21.2. IR (cm^{-1}): 3283, 3241, 2926, 2862, 1708, 1639, 1464, 1346, 1246, 1217, 1151, 1063, 1009, 903, 832, 773, 752, 698, 591, 548. MS (ESI-TOF): *m/z* (%): 403.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{19}H_{28}N_2NaO_4S$ $[M+Na]^+$: 403.1667; found: 403.1657.

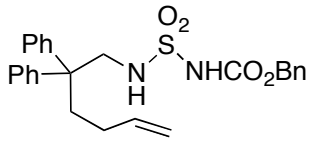
Benzyl *N*-(2,2-dimethylhex-5-en-1-yl)sulfamoylcarbamate 3b



Obtained from reaction between the DMAP-Burgess reagent and the corresponding free primary amine. Isolated as a white solid in 70% yield. Mp. 84°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (sbr, 1H), 7.40 – 7.31 (m, 5H), 5.80 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.49 (t, *J* = 6.7 Hz, 1H), 5.17 (s, 2H), 5.03 (ddd, *J* = 16.7, 3.3, 1.5 Hz, 1H), 4.97 – 4.92 (m, 1H), 2.80 (d, *J* = 6.7 Hz, 2H), 2.07 – 1.92 (m, 2H), 1.38 – 1.25 (m,

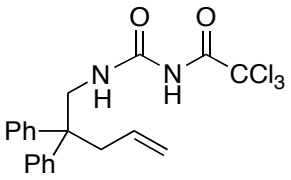
2H), 0.90 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.5, 138.7, 134.5, 128.7, 128.6, 128.4, 114.3, 68.41, 53.4, 38.5, 33.6, 28.1, 24.6(2x). IR (cm^{-1}): 3277, 3221, 3079, 2960, 2938, 1714, 1641, 1460, 1370, 1349, 1276, 1249, 1158, 1064, 985, 915, 874, 777, 738, 689, 629, 571. MS (ESI-TOF): *m/z* (%): 363.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{16}H_{24}N_2NaO_4S$ $[M+Na]^+$: 363.1354; found: 363.1367.

Benzyl *N*-(2,2-diphenylhex-5-en-1-yl)sulfamoylcarbamate 3c



Obtained from reaction between the DMAP-Burgess reagent and the corresponding free primary amine. Isolated as a white solid in 89% yield. Mp. 108°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 (s, 1H), 7.47 – 7.07 (m, 15H), 5.79 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.11 (s, 2H), 5.00 (dd, *J* = 16.8, 1.7 Hz, 1H), 4.96 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.73 (t, *J* = 6.4 Hz, 1H), 3.77 (d, *J* = 6.4 Hz, 2H), 2.33 – 2.26 (m, 2H), 1.90 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.0, 144.6, 138.1, 134.5, 128.7, 128.6, 128.4, 128.2, 127.6, 126.7, 114.7, 68.4, 50.3, 49.4, 35.8, 28.3. IR (cm^{-1}): 3274, 3206, 3060, 3031, 2942, 2349, 1709, 1637, 1471, 1447, 1354, 1245, 1158, 1078, 1002, 912, 874, 842, 776, 739, 695, 591. MS (ESI-TOF): *m/z* (%): 487.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{26}H_{28}N_2NaO_4S$ $[M+Na]^+$: 487.1667; found: 487.1683.

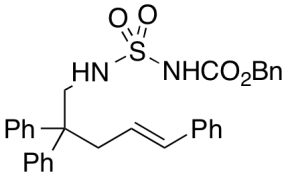
2,2,2-Trichloro-*N*-(2,2-diphenylpent-4-enylcarbamoyl)ethanamide 5e



Obtained as a white solid. Mp. 151°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.91 (s, 1H), 7.70 (t, *J* = 5.5 Hz, 1H), 7.22-7.39 (m, 10H), 5.46 (ddt, *J* = 7.0, 10.1, 17.0 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 5.05 (d, *J* = 10.1 Hz, 1H), 4.11 (d, *J* = 5.5 Hz, 2H), 3.0 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 161.6, 151.4, 144.8, 133.4, 128.3, 127.8, 126.6, 118.7, 49.8, 47.1, 41.9. IR (cm^{-1}): = 3448, 3319, 3234, 3087, 3060, 2933, 1717, 1704, 1539, 1496, 1237, 853. HRMS-ESI-TOF *m/z* calculated for $C_{20}H_{19}Cl_3N_2O_2$: 424.0512, found: 424.0504.

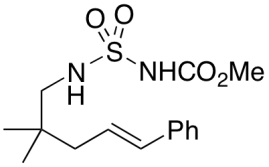
Reported previously : Y. Tamaru, M. Hojo, H. Higashimura and Z.-i. Yoshida *J. Am. Chem. Soc.,* 1988, **110**, 3994.

(*E*)-Benzyl *N*-(2,2,5-triphenylpent-4-en-1-yl)sulfamoylcarbamate 7a



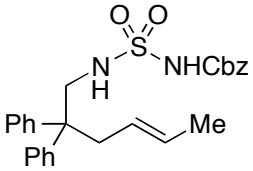
Obtained as a white solid. Mp. 165°C. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 7.39 – 7.06 (m, 20H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.70 (dt, *J* = 15.8, 7.4 Hz, 1H), 5.11 (s, 2H), 4.59 (t, *J* = 6.8 Hz, 0H), 3.72 (d, *J* = 6.8 Hz, 2H), 3.10 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 150.7, 144.4, 137.4, 134.5, 134.4, 128.8, 128.7, 128.5, 128.4, 128.4, 127.7, 127.2, 127.0, 126.2, 124.6, 68.6, 50.1, 49.8, 40.1. IR (cm^{-1}): 3302, 3165, 3063, 3030, 2954, 1706, 1495, 1468, 1428, 1361, 1238, 1170, 1073, 972, 880, 743, 698. MS (ESI-TOF): *m/z* (%): 549.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{31}H_{30}N_2NaO_4S$ $[M+Na]^+$: 549.1818; found: 549.1796.

(*E*)-Methyl *N*-(2,2-dimethyl-5-phenylpent-4-en-1-yl)sulfamoylcarbamate 7b



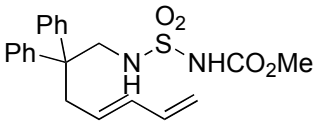
Obtained as a white solid. Mp. 147°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.05 (brs, 1H), 7.64 – 7.10 (m, 5H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.21 (ddd, *J* = 15.8, 7.4, 6.7 Hz, 1H), 5.57 (dd, *J* = 6.7, 6.6 Hz, 1H), 3.76 (s, 3H), 2.91 (d, *J* = 6.7 Hz, 2H), 2.19 (d, *J* = 7.4 Hz, 2H), 1.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.06, 137.36, 133.17, 128.43, 127.08, 126.06, 125.67, 53.49, 53.30, 42.84, 34.67, 24.84. IR (cm^{-1}): 3302, 3027, 2948, 1753, 1455, 1360, 1242, 1172, 1073, 985, 946, 880, 751, 701. MS (ESI-TOF): *m/z* (%): 349.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{15}H_{22}N_2NaO_4S$ $[M+Na]^+$: 349.1198; found: 349.1197.

(*E*)-Benzyl *N*-(2,2-diphenyl,5-methylpent-4-en-1-yl)sulfamoylcarbamate 7c



Obtained as a white solid. Mp. 130°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.44-7.08 (m, 15H), 5.53 (ddd, *J* = 12.3, 6.6, 2.2 Hz, 1H), 5.11 (s, 2H), 5.04-4.95 (m, 1H), 4.71 (s, 1H), 3.71 (s, 2H), 2.90 (d, *J* = 7.1 Hz, 1H), 1.59 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.9, 144.5, 129.9, 128.7, 128.6, 128.3, 128.3, 128.2, 127.7, 127.6, 126.6, 125.1, 68.3, 50.1, 49.3, 39.9, 18.0. IR (cm^{-1}): 3300, 3147, 1747, 1703, 1467, 1445, 1430, 1356, 1240, 1168, 945, 744, 695, 574, 543. MS (ESI-TOF): *m/z* (%): 487.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{26}H_{28}N_2NaO_4S$ $[M+Na]^+$: 487.1667; found: 487.1672.

(*E*)-Methyl *N*-(2,2-diphenylhepta-4,6-dienyl)sulfamoylcarbamate 7d



Synthesized from the corresponding free primary amine by treatment with the MeO-DMAP-Burgess reagent as described previously. Isolation by column chromatography provided the pure product as a viscous oil in 60% yield.

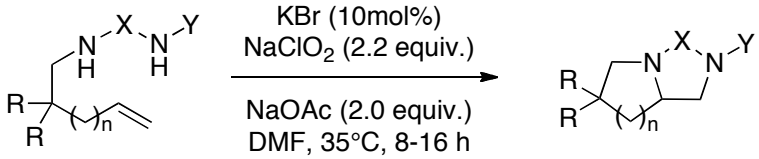
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (br, 1NH), 7.15-7.37 (m, 10H), 6.16 (m, 2H), 5.23 (dt, *J* = 14.6 Hz, 7.6 Hz, 1H), 5.10 (d, *J* = 16.7 Hz, 1H), 4.98 (d, *J* = 9.9 Hz, 1H), 4.65 (t, *J* = 6.5 Hz, 1NH), 3.72 (d, *J* = 6.4 Hz, 2H), 3.68 (s, 3H), 3.02 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 151.4, 144.3, 136.7, 135.3, 128.7, 128.5, 127.7, 126.9, 116.1, 53.6, 50.2, 49.7, 39.9. MS (ESI-LCMS): m/z (%): 423.3 $[M+Na]^+$ (10), 294.2 (8), 203.7 (34), 195.2 (100), 167.2 (40), 129.4 (27), 91.5 (69). HRMS calcd for $C_{21}H_{24}N_2O_4S$: 400,1457, found: 400.1458. IR (KBr): ν [cm^{-1}] = 3266, 3062, 2963, 1717, 1470, 1426, 1371, 1348, 1259, 1166, 1062, 859, 699.

4 General procedures for diamination

General procedure for the KBr-catalysed intramolecular diamination of alkenes with $PhI(OAc)_2$ (Table 2):

A pyrex tube equipped with a stirrer bar is charged with sulfamide or urea substrate (0.5 mmol), $PhI(OAc)_2$ (177mg, 0.55 mmol, 1.1 eq.), NaOAc (41mg, 0.5 mmol, 1 eq.) and NaBr (10 mol%). DMF (2.5 mL, 0.2M) is added and the mixture is stirred at r.t. for 16 h. The reaction is stopped by addition of saturated aqueous $Na_2S_2O_3$ solution (2 mL) and brine (5 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phase is dried over $MgSO_4$ and the solvent removed under reduced pressure. Filtration over a small pad of silica and evaporation of residues of iodobenzene and DMF gives analytically pure products as white solids.

General procedure for the KBr-catalysed intramolecular diamination of alkenes with $NaClO_2$:

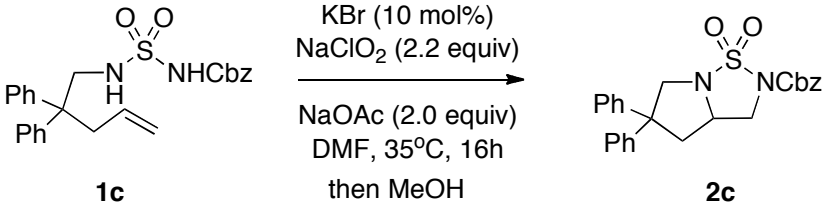


A pyrex tube equipped with a stirrer bar was charged with KBr (6.0 mg, 0.05 mmol, 0.10 equiv), $NaClO_2$ (49.7 mg, 0.55 mmol, 1.1 equiv), NaOAc (82.0 mg, 1.0 mmol, 2.0 equiv) and alkene (0.5 mmol, 1.0 equiv). Then dry DMF (5.0 mL, 0.1 M) was added and the mixture was stirred for 4-8 h at 35°C (40°C for internal alkenes). Then $NaClO_2$ (49.7 mg, 0.55 mmol, 1.1 equiv) were added and the reaction mixture was stirred 4-8 h more at 35°C (40°C for internal alkenes) then allowed to cool to room temperature. Then quenched with NH_4Cl and extracted with EtOAc several times. The combined organic layers were dried over Mg_2SO_4. The solvent was removed under reduced pressure. The crude reaction mixture was then analysed by NMR and the conversion of alkene was 65-99%. For scales of up to 1 mmol, products were purified

by short flash-chromatography (5 cm height, 2.5 cm diameter) on silica gel using hexanes/EtOAc.

Diamination reactions of compounds **1c, 1f, 3a, 5a, 7c** and **9a** were also performed using DMF with reagent grade and/or technical grade purity without observable loss in yield.

Large scale syntheses for compound 2c:

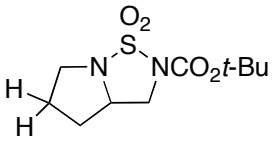


1c **2c** 91%

A 500mL-Schlenk tube equipped with a stirrer bar was charged with KBr (133.3 mg, 1.11 mol, 0.10 equiv), $NaClO_2$ (740 mg, 3.7 mol), NaOAc (1.82g, 22.2 mol, 2.0 equiv) and alkene **1a** (5g, 11.11 mol, 1.0 equiv). Then dry DMF (100 mL) was added and the mixture was stirred for 4h at 35°C. Upon disappearance of the yellow solution color, a second charge of $NaClO_2$ (740 mg, 3.7 mol) was added, followed by a third charge of $NaClO_2$ (740 mg, 3.7 mol) after 10h. After a total of 16h, the reaction mixture was allowed to cool to room temperature. It was quenched with NH_4Cl and extracted with EtOAc (4 x 75 mL). The combined organic layers were dried over Mg_2SO_4 and the solvent was removed under reduced pressure. The remaining colorless oil was dissolved in 25 mL warm methanol and left standing for crystallization to give the title compound **2c** as a white solid (4.53g, 91%).

Characterization of diamination products

tert-Butyl tetrahydropyrrolo[1,2-*b*][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 2i



Obtained as a white solid in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.20 (ddd, *J* = 14.9, 7.2, 2.9 Hz, 1H), 3.97 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.76 (ddd, *J* = 11.0, 7.8, 5.7 Hz, 1H), 3.47 – 3.35 (m, 2H), 2.31 – 2.19 (m, 1H), 2.08 – 1.99 (m, 2H), 1.89 (dddd, *J* = 12.2, 7.4, 4.7, 3.0 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.8, 84.2, 56.6, 50.3, 49.9, 30.8, 28.0, 23.9. IR (cm^{-1}): 2989, 2976, 2937, 1715, 1493, 1456, 1332, 1259, 1176, 1136, 1051, 972, 914, 855, 765, 622, 530. MS (ESI-TOF): *m/z* (%): 285.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{10}H_{18}N_2NaO_4S$ $[M+Na]^+$: 285.0885; found: 285.0897.

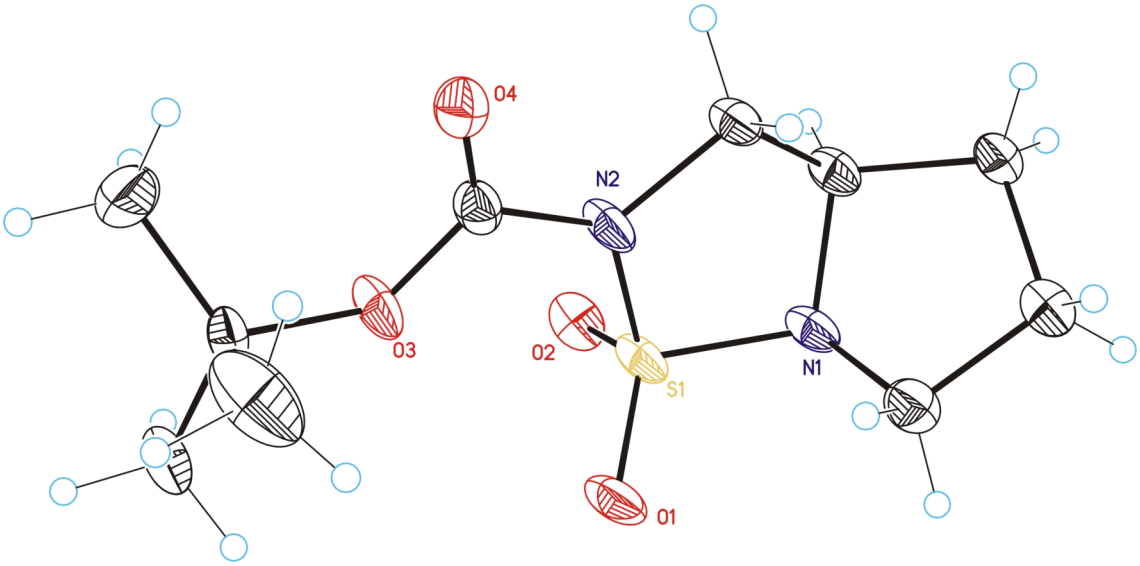
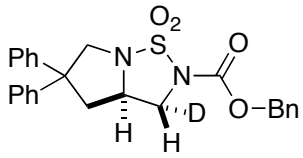


Table S-1. Crystal data and structure refinement for compound **2i**.

Identification code	CCDC 8663464	
Empirical formula	C10 H18 N2 O4 S	
Formula weight	262.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.5431(11) Å	a= 90.00 °.
	b = 9.8350(12) Å	b = 92.891(3) °.
	c = 12.1245(10) Å	g = 90.00 °.
Volume	1255.6(2) $Å^3$	
Z	4	
Density (calculated)	1.388 Mg/m^3	
Absorption coefficient	0.264 mm^{-1}	
F(000)	560	
Crystal size	0.25 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.93 to 29.67 °.	
Index ranges	-14 <=h<=11 ,-12 <=k<=12 ,-14 <=l<=16	
Reflections collected	5723	
Independent reflections	2977 [R(int) = 0.0607]	
Completeness to theta =29.67 °	0.838 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9869 and 0.9370	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2977 / 0 / 157	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0724 , wR2 = 0.1810	
R indices (all data)	R1 = 0.1069 , wR2 = 0.2067	
Largest diff. peak and hole	0.997 and -0.668 $e.Å^{-3}$	

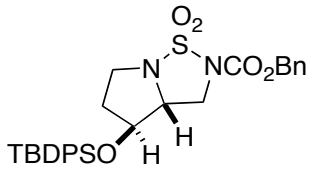
anti-Benzyl-5,5-diphenyl-3-deuteriumtetrahydropyrrolo[1,2-_b_][1,2,5]thiadiazole-2(3_H_)-carboxylate 1,1-dioxide _trans_-2c-d_1



Obtained as a white solid in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 7.16 (m, 15H), 5.31 (d, *J* = 12.4 Hz, 1H), 5.27 (d, *J* = 12.4 Hz, 1H), 4.25 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.04 (ddd, *J* = 8.8, 6.2, 4.5 Hz, 1H), 3.96 (d, *J* = 10.2 Hz, 1H), 3.71 (d, *J* = 4.5 Hz, 1H), 2.87 (ddd, *J* = 12.3, 6.2, 1.3 Hz, 1H), 2.49 (dd, *J* = 12.3, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.1, 144.2 (2x), 134.8, 128.7, 128.6, 128.6, 128.4, 127.9, 127.1, 126.9, 126.6, 126.4, 68.9, 59.6, 55.9, 55.4, 48.3 (t, $J_{C\text{-}D}$ = 22.3), 44.0. IR (cm^{-1}): 3059, 3030, 2954, 2896, 1728, 1597, 1495, 1447, 1363, 1292, 1169, 1025, 904, 747, 695, 630, 583, 540. MS (ESI-TOF): *m/z* (%): 472.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{25}H_{23}DN_2NaO_4S$ $[M+Na]^+$: 472.1417; found: 472.1431.

anti-Benzyl 4-((_tert_-butyldiphenylsilyl)oxy)tetrahydropyrrolo[1,2-_b_][1,2,5]thiadiazole-2(3_H_)-carboxylate 1,1-dioxide 2j

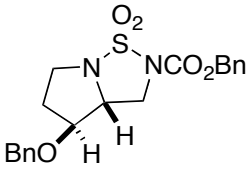


Obtained as a white solid in 75% yield.

Mp. 98°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 – 7.63 (m, 4H), 7.54 – 7.37 (m, 11H), 5.37 (d, *J* = 12.5 Hz, 1H), 5.33 (d, *J* = 12.5 Hz, 1H), 4.61 (ddd, *J* = 7.3, 6.6, 5.9 Hz, 1H), 4.10 (dd, *J* = 10.2, 7.7 Hz, 1H), 3.94 (dt, *J* = 7.7, 5.9 Hz, 1H), 3.82 (ddd, *J* = 11.3, 8.6, 5.2 Hz, 1H), 3.77 (ddd, *J* = 10.2, 7.7, 5.2 Hz, 1H), 3.27 (ddd, *J* = 11.2, 7.9, 7.7 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 150.9, 135.6, 135.5, 135.0, 132.7, 132.4, 130.4, 130.2, 128.6, 128.4, 128.1, 127.9,

127.9, 73.0, 68.7, 58.4, 47.9, 45.4, 31.7, 26.7, 19.1. IR (cm^{-1}): 3070, 3049, 2953, 2927, 2855, 1730, 1589, 1459, 1427, 1362, 1302, 1220, 1173, 1105, 1059, 1009, 973, 931, 851, 821, 740, 698, 626, 574, 561, 503. MS (ESI-TOF): *m/z* (%): 573.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{29}H_{34}N_2NaO_5SSi$ $[M+Na]^+$: 573.1855; found: 573.1841.

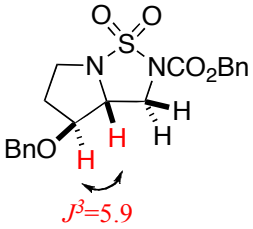
anti- Benzyl 4-(benzyloxy)tetrahydropyrrolo[1,2-*b*][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 2k

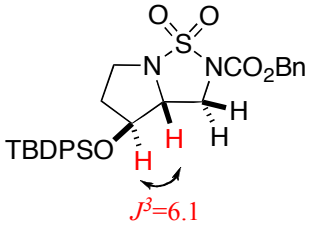


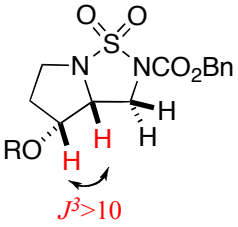
Obtained as a colorless wax in 71% yield.

Mp. 113°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.28 (m, 10H), 5.33 – 5.25 (m, 2H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.34 (ddd, *J* = 6.6, 6.4, 6.1 Hz, 1H), 4.15 (ddd, *J* = 7.7, 7.6, 6.1 Hz, 1H), 3.99 (dd, *J* = 10.4, 7.7 Hz, 1H), 3.83 – 3.76 (m, 1H), 3.72 (dd, *J* = 10.4, 7.7 Hz, 1H), 3.41 – 3.31 (m, 1H), 2.20 – 2.09 (m, 1H), 2.09 – 1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.81, 136.97, 134.91, 128.56, 128.50, 128.30, 128.15, 127.82, 127.63, 78.01, 72.38, 68.64, 57.60, 47.89, 45.05, 29.22. IR (cm^{-1}): 3064, 3032, 2953, 2904, 1727, 1497, 1454, 1386, 1358, 1301, 1214, 1173, 1110, 1061, 1027, 972, 916, 851, 782, 737, 697, 630, 575, 539. HRMS-ESI-TOF *m/z* calculated for $C_{20}H_{22}N_2NaO_5S$ $[M+Na]^+$: 425.1147; found: 425.1151.

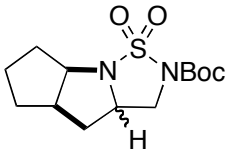
Tentative assignments of the relative configuration were made on the coupling constants for hydrogens at the stereogenic centers :







tert-Butyl octahydro-2*H*-cyclopenta[4,5]pyrrolo[1,2-*b*][1,2,5]thiadiazole-2-carboxylate 1,1-dioxide 2l

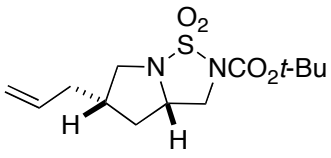


Obtained as a viscous oil. Mixture of two diastereomers in a ratio of 7:3 (91% combined yield). A 1 :1-mixture had been described earlier (K. Muñiz, J. Streuff, C. H. Hövelmann and A. Nuñez, *Angew. Chem. Int. Ed*. 2007, **46**, 7125). NMR data for major and minor diastereomer could now be deduced from spectra containing a product mixture.

Major : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.34-4.27 (m, 1H), 4.22-4.19 (m, 1H), 3.82 (dd, *J* = 10.0 Hz, 6.7 Hz, 1H), 3.45 (t, *J* = 9.6 Hz, 1H), 2.95-2.80 (m, 1H), 2.34-2.25 (m, 1H), 2.10 (ddd, *J* = 13.4 Hz, 9.1Hz, 1.8 Hz, 1H), 1.74-1.59 (m, 5H), 1.54 (s, 9H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.3, 83.7, 67.7, 61.4, 58.7, 49.4, 46.8, 35.7, 34.6, 32.7, 31.1, 27.8, 23.9.

Minor : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.08-3.92 (m, 1H), 3.89-3.78 (m, 2H), 3.55-3.02 (dquint, *J* = 8.8 Hz, 2.3 Hz, 1H), 2.28 (ddd, *J* = 12.3 Hz, 9.1 Hz, 5.8 Hz, 1H), 2.08-2.00 (m, 1H), 1.83-1.67 (m, 1H), 1.54 (s, 9H), 1.70-1.54 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.7, 83.8, 67.7, 61.4, 58.6, 49.9, 40.9, 34.4, 31.6, 27.7, 23.3.

tert-Butyl 5-allyltetrahydropyrrolo[1,2-*b*][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 2m



Obtained as a white solid in 82% yield.

Mp. 77°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.77 – 5.66 (m, 1H), 5.07 – 5.00 (m, 2H), 4.06 (dt, *J* = 7.3, 6.8 Hz, 1H), 3.93 (dd, *J* = 10.2, 7.3 Hz, 1H), 3.56 (dd, *J* = 10.2, 6.5 Hz, 1H), 3.47 (dd, *J* = 9.7, 6.8 Hz, 1H), 3.09 (pseudo t, *J* = 10.0 Hz, 1H), 2.46 – 2.39

(m, 1H), 2.38 – 2.31 (m, 1H), 2.2 (pseudo dt, J = 7.0, 6.8 Hz, 2H), 1.51 (s, 9H), 1.39 (ddd, J = 12.6, 9.7, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.2, 135.5, 117.2, 84.6, 57.0, 55.0, 50.2, 39.5, 37.3, 37.3, 28.2. IR (cm^{-1}): 3078, 2979, 2931, 1721, 1477, 1455, 1357, 1389, 1259, 1177, 1144, 1066, 995, 912, 849, 816, 766, 733, 676, 629, 574, 462. MS (ESI-TOF): *m/z* (%): 325.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{13}H_{22}N_2NaO_4S$ $[M+Na]^+$: 325.1198; found: 325.1209.

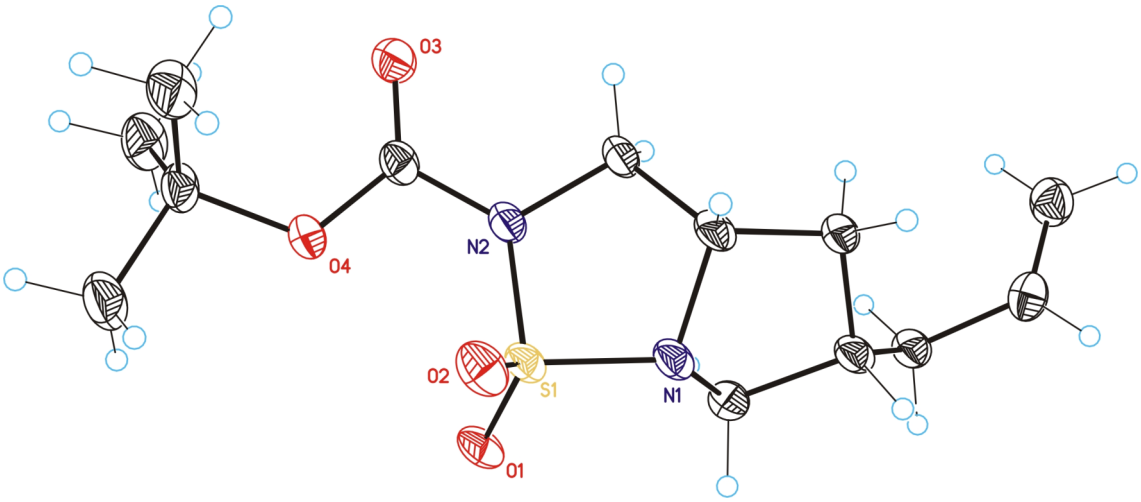
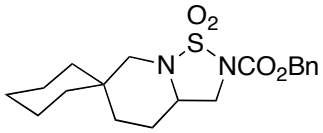


Table S-2. Crystal data and structure refinement for compound **2l/2l**.

Identification code	CCDC 8663468	
Empirical formula	C13 H22 N2 O4 S	
Formula weight	302.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.355(3) Å	a= 90.00 °.
	b = 10.423(2) Å	b = 107.797(7) °.
	c = 11.320(2) Å	g = 90.00 °.
Volume	1500.3(6) Å^3	

Z	4
Density (calculated)	1.339 Mg/m^3
Absorption coefficient	0.230 mm^{-1}
F(000)	648
Crystal size	0.30 x 0.15 x 0.03 mm^3
Theta range for data collection	2.53 to 27.43 °.
Index ranges	-17 <=h<=17 ,-13 <=k<=13 ,-14 <=l<=14
Reflections collected	19152
Independent reflections	3354 [R(int) = 0.0648]
Completeness to theta =27.43 °	0.982 %
Absorption correction	Empirical
Max. and min. transmission	0.9931 and 0.9341
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3354 / 86 / 239
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0498 , wR2 = 0.1171
R indices (all data)	R1 = 0.0811 , wR2 = 0.1298
Largest diff. peak and hole	0.413 and -0.458 e.Å^{-3}

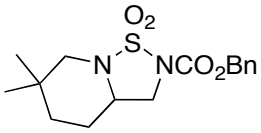
Benzyl tetrahydrospiro[[1,2,5]thiadiazolo[2,3-*a*]pyridine-6,1'-cyclohexane]-2(7*H*)-carboxylate 1,1-dioxide 4a



Obtained as a white solid in 89% yield.

Mp. 82°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48 – 7.32 (m, 5H), 5.36 (d, *J* = 12.5 Hz, 1H), 5.31 (d, *J* = 12.5 Hz, 1H), 3.96 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.51 – 3.45 (m, 1H), 3.41 (d, *J* = 11.2 Hz, 1H), 3.27 – 3.19 (m, 1H), 2.42 (d, *J* = 11.2 Hz, 1H), 1.83 – 1.75 (m, 2H), 1.66 – 1.55 (m, 2H), 1.54 – 1.34 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.40, 134.92, 128.55, 128.36, 127.84, 68.76, 53.96, 50.50, 49.36, 37.66, 33.55, 32.38, 31.37, 26.33, 24.56, 21.37, 21.23. IR (cm^{-1}): 3065, 3032, 2926, 2851, 1730, 1499, 1453, 1391, 1320, 1217, 1164, 1073, 1054, 1037, 1003, 969, 907, 866, 848, 784, 754, 696, 665, 616, 599, 558, 511. MS (ESI-TOF): *m/z* (%): 401.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{19}H_{26}N_2NaO_4S$ $[M+Na]^+$: 401.1511; found: 401.1513.

Benzyl 6,6-dimethylhexahydro-2*H*-[1,2,5]thiadiazolo[2,3-*a*]pyridine-2-carboxylate 1,1-dioxide 4b

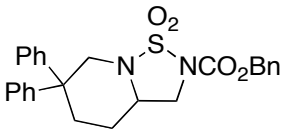


Obtained as a white solid in 80% yield.

Mp. 77°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 7.31 (m, 5H), 5.33 (d, *J* = 12.4 Hz, 1H), 5.29 (d, *J* = 12.4 Hz, 1H), 3.94 (dd, *J* = 9.4, 5.8 Hz, 1H), 3.48 (dd, *J* = 10.5, 9.4 Hz, 1H), 3.22 – 3.12 (m, 1H), 3.04 (dd, *J* = 11.0, 1.5 Hz, 1H), 2.51 (d, *J* = 11.0 Hz, 1H), 1.81 (ddd, *J* = 13.8, 7.2, 3.9 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.56 – 1.51 (m, 1H), 1.34 – 1.30 (m, 1H), 1.07 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.4, 134.9, 128.8, 128.6, 128.5, 128.4, 127.9, 68.8, 53.6, 53.1, 49.3, 35.6, 30.0, 28.7,

25.4, 23.9. IR (cm^{-1}): 3090, 3065, 3033, 2954, 2856, 1730, 1536, 1499, 1454, 1390, 1320, 1241, 1212, 1163, 1139, 1079, 1045, 996, 902, 843, 787, 753, 697, 599, 556, 508. MS (ESI-TOF): *m/z* (%): 361.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{16}H_{22}N_2NaO_4S$ $[M+Na]^+$: 361.1198; found: 361.1212.

Benzyl 6,6-diphenylhexahydro-2*H*-[1,2,5]thiadiazolo[2,3-*a*]pyridine-2-carboxylate 1,1-dioxide 4c



Obtained as a white solid in 97% yield.

Mp. 131°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 7.10 (m, 15H), 5.36 (d, *J* = 12.4 Hz, 1H), 5.31 (d, *J* = 12.4 Hz, 1H), 4.29 (dd, *J* = 12.1, 2.0 Hz, 1H), 3.96 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.50 – 3.36 (m, 2H), 3.00 (d, *J* = 12.1 Hz, 1H), 2.66 (ddd, *J* = 8.9, 5.3, 2.8 Hz, 1H), 2.36 (dt, *J* = 13.1, 3.1 Hz, 1H), 1.93 (ddd, *J* = 13.1, 6.3, 3.1 Hz, 1H), 1.38 (qd, *J* = 13.1, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.3, 145.9, 143.5, 134.8, 128.6 (2x), 128.4(2x), 128.0(2x), 126.9, 126.5, 126.3, 68.9, 53.2, 49.9, 49.3, 45.0, 33.5, 25.1. IR (cm^{-1}): 2962, 2931, 2877, 1727, 1494, 1448, 1395, 1351, 1295, 1214, 1173, 1045, 1024, 911, 760, 727, 695, 630, 605, 531. MS (MALDITOF): *m/z* (%): 485.2 $[M+Na]^+$ (100). HRMS-MALDITOF *m/z* calculated for $C_{26}H_{26}N_2NaO_4S$ $[M+Na]^+$: 485.1511; found: 485.1507.

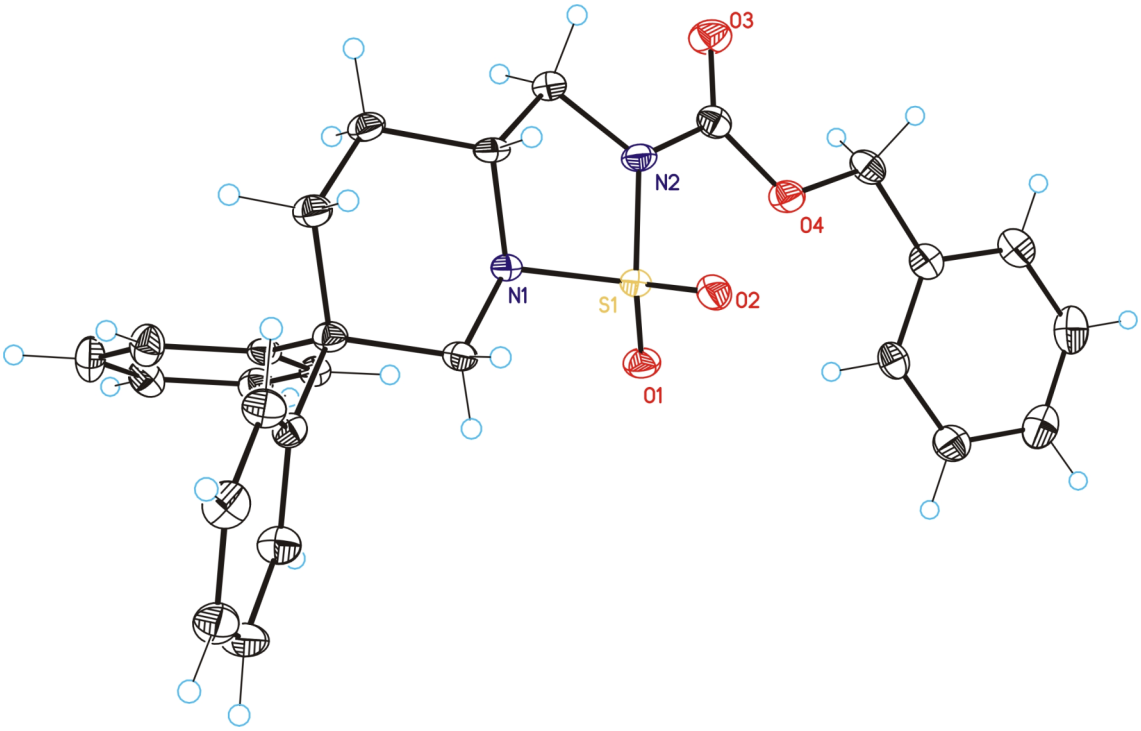
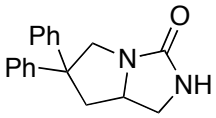


Table S-3. Crystal data and structure refinement for compound **4c**.

Identification code	CCDC 8663467	
Empirical formula	C26 H26 N2 O4 S	
Formula weight	462.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.5173(6) Å	a= 90.00 °.
	b = 21.874(2) Å	b = 90.991(3) °.
	c = 15.6036(13) Å	g = 90.00 °.
Volume	2224.2(3) $Å^3$	
Z	4	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	0.183 mm^{-1}	
F(000)	976	
Crystal size	0.30 x 0.01 x 0.01 mm^3	
Theta range for data collection	1.60 to 27.50 °.	
Index ranges	-8 <=h<=8 ,-28 <=k<=27 ,-20 <=l<=18	

Reflections collected	17043
Independent reflections	5087 [R(int) = 0.0416]
Completeness to theta =27.50 °	0.995 %
Absorption correction	Empirical
Max. and min. transmission	0.9982 and 0.9472
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5087 / 0 / 298
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0414 , wR2 = 0.0965
R indices (all data)	R1 = 0.0691 , wR2 = 0.1074
Largest diff. peak and hole	0.451 and -0.486 e.$Å^{-3}$

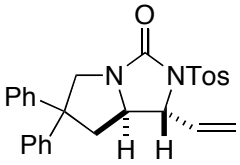
6,6-Diphenyltetrahydro-1*H*-pyrrolo[1,2-*c*]imidazol-3(2*H*)-one 6e



Obtained in 80% isolated yield.

Mp. 83°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15-7.30 (m, 10H), 5.63 (s, 1H), 4.13 (d, *J* = 11.3 Hz, 1H), 3.93 (dddd, *J* = 3.6, 5.0, 9.1, 10.5 Hz, 1H), 3.78 (d, *J* = 11.3 Hz, 1H), 3.60 (pst, *J* = 9.0 Hz, 1H), 3.32 (dd, *J* = 3.6, 9.0 Hz, 1H), 2.44 (dd, *J* = 5.0, 11.5 Hz, 1H), 2.33 (dd, *J* = 10.6, 11.5 Hz, 1H). ^{13}C -NMR (100 MHz, $CDCl_3$): δ = 165.9, 146.4, 146.3, 128.3, 128.3, 127.0, 126.7, 126.5, 126.3, 59.1, 57.9, 57.1, 56.9, 43.6, 43.0. MS (ESI-TOF): *m/z* (%): 278.1 [M^+] (100). HRMS-ESI-TOF *m/z* calculated for $C_{18}H_{18}N_2O$: 278,1419, found: 278.1422.

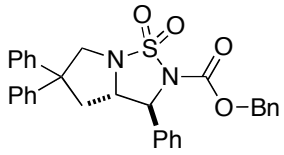
***trans*-6,6-Diphenyl-2-tosyl-1-vinyltetrahydro-1*H*-pyrrolo[1,2-*c*]imidazol-3(2*H*)-one 6i**



A pyrex tube equipped with a stirrer bar is charged with the desired diene (1.0 eq.), NBS (10 mol%), iodosobenzene diacetate (2.0 eq.) and dichloromethane (10 mL/mmol). The reaction is stirred at room temperature for the given time and quenched by addition of aqueous sat. Na_2SO_3 solution. Dichloromethane is added (10 mL/mmol) and the organic layer is washed with water. The organic layer is separated and the aqueous phase extracted with dichloromethane (3x). The combined organic layers are dried over $MgSO_4$, filtrated and concentrated under reduced pressure to give the crude reaction mixture, which is analysed by NMR. Column chromatography yields the pure product in 30% yield.

Characterised previously: K. Muñiz, J. Streuff, P. Chávez and C. H. Hövelmann, *Chem. Asian J.* 2008, **3**, 1248.

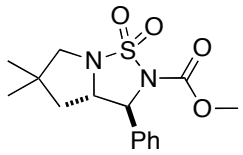
trans-Benzyl 3,5,5-triphenyltetrahydropyrrolo[1,2-*b*][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 8a



Obtained as a white solid in 87% yield.

Mp. 167°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.17 (m, 20H), 5.22 (d, *J* = 12.4 Hz, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 4.73 (d, *J* = 7.0 Hz, 1H), 4.34 (d, *J* = 10.4 Hz, 1H), 4.20 (dd, *J* = 10.4, 0.8 Hz, 1H), 4.12 (ddd, *J* = 7.0, 6.9, 5.5 Hz, 1H), 3.14 (ddd, *J* = 12.9, 7.0, 0.8 Hz, 1H), 2.78 (dd, *J* = 12.9, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.9, 144.9, 144.4, 138.5, 134.8, 129.1, 128.8, 128.6, 128.4, 128.2, 127.9, 127.2, 126.8, 126.5 (2x), 126.4(2x), 68.6, 67.3, 64.7, 59.8, 55.4, 43.9. IR (cm^{-1}): 3061, 3033, 2952, 2869, 2324, 2115, 1980, 1729, 1495, 1448, 1364, 1291, 1173, 1026, 751, 695, 639, 610, 526. MS (ESI-TOF): *m/z* (%): 401.2 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{31}H_{28}N_2NaO_4S$ $[M+Na]^+$: 547.1667; found: 547.1680.

anti-Methyl 5,5-dimethyl-3-phenyltetrahydropyrrolo[1,2-*b*][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 8b



Obtained as a white solid in 65% yield.

Mp. 147°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.31 (m, 5H), 4.85 (d, *J* = 7.4 Hz, 1H), 4.02 (ddd, *J* = 7.4, 7.2, 4.8 Hz, 1H), 3.76 (s, 3H), 3.31 (d, *J* = 9.6 Hz, 1H), 3.24 (dd, *J* = 9.6, 0.7 Hz, 1H), 2.10 (ddd, *J* = 13.2, 7.4, 0.7 Hz, 1H), 1.82 (dd, *J* = 13.2, 4.8

Hz, 1H), 1.26 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.9, 138.2, 129.2, 128.7, 126.4, 68.4, 65.5, 62.6, 54.0, 45.1, 40.3, 28.2, 27.1. IR (cm^{-1}): 3032, 2961, 2924, 2872, 1727, 1460, 1432, 1365, 1296, 1227, 1173, 1136, 1085, 1041, 997, 960, 911, 857, 798, 757, 719, 701, 658, 611, 568, 534. MS (ESI-TOF): *m/z* (%): 347.1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{15}H_{20}N_2NaO_4S$ $[M+Na]^+$: 347.1041; found: 347.1055.

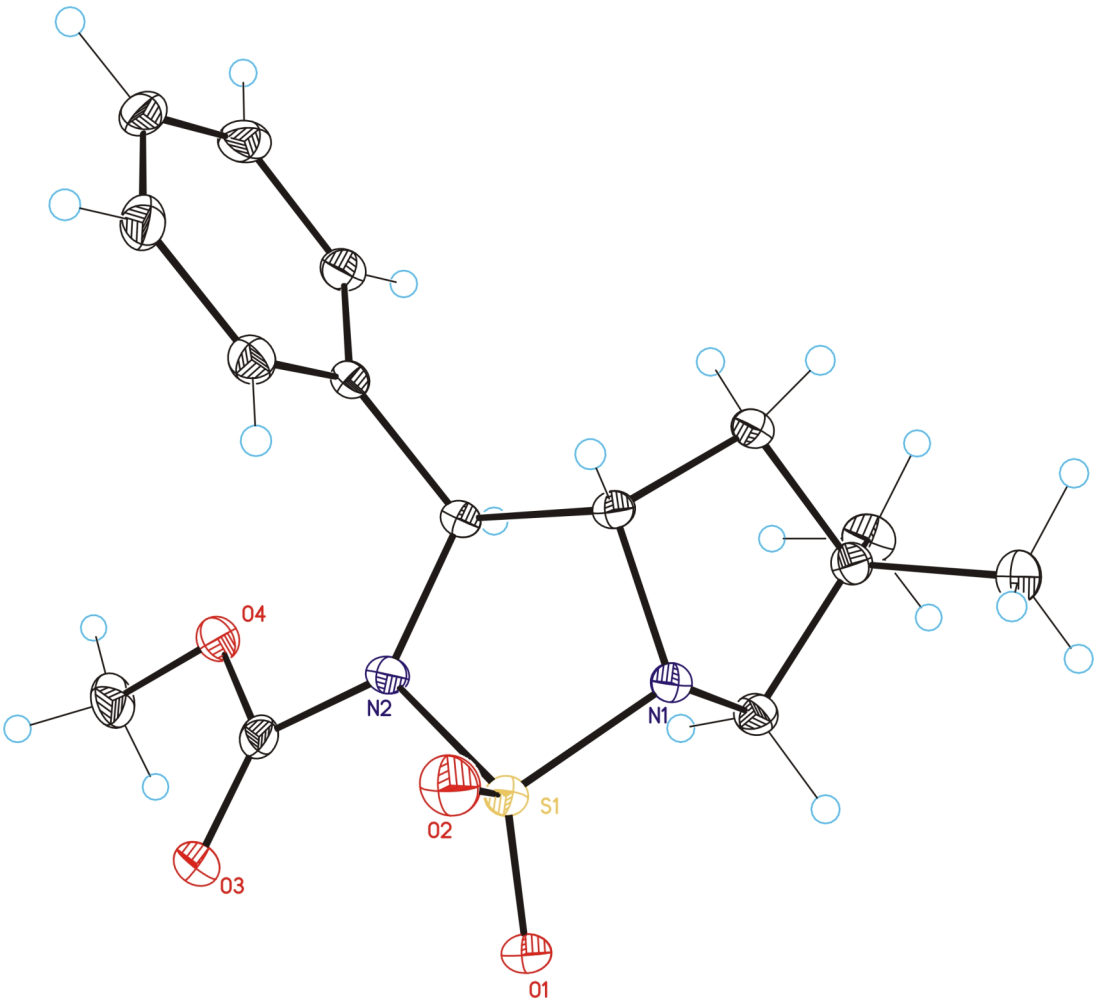
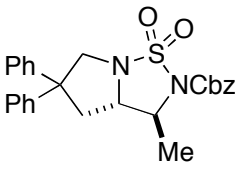


Table S-4. Crystal data and structure refinement for compound **8b**.

Identification code	CCDC 8663466
Empirical formula	C15 H20 N2 O4 S
Formula weight	324.39
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 5.8032(8) Å	a= 90.00 °.
	b = 20.518(3) Å	b = 97.101(4) °.
	c = 12.8411(17) Å	g = 90.00 °.
Volume	1517.3(4) $Å^3$	
Z	4	
Density (calculated)	1.420 Mg/m^3	
Absorption coefficient	0.234 mm^{-1}	
F(000)	688	
Crystal size	0.40 x 0.20 x 0.08 mm^3	
Theta range for data collection	1.88 to 29.89 °.	
Index ranges	-8 <=h<=7 ,-28 <=k<=28 ,-17 <=l<=17	
Reflections collected	41843	
Independent reflections	4176 [R(int) = 0.0330]	
Completeness to theta =29.89 °	0.953 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9816 and 0.9123	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4176 / 0 / 202	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0349 , wR2 = 0.0869	
R indices (all data)	R1 = 0.0435 , wR2 = 0.0908	
Largest diff. peak and hole	0.450 and -0.465 $e.Å^{-3}$	

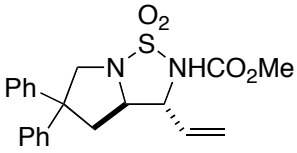
trans-Benzyl 3-methyl-5,5-diphenyltetrahydropyrrolo[1,2-_b_][1,2,5]thiadiazole-2(3_H_)-carboxylate 1,1-dioxide 8c



Obtained as a colorless solid in 85% yield.

Mp. 80°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.21 (m, 15H), 5.36 (d, *J* = 12.5 Hz, 1H), 5.29 (d, *J* = 12.5 Hz, 1H), 4.25 (d, *J* = 10.4 Hz, 1H), 4.12-4.03 (m, 1H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.73-3.68 (m, 1H), 2.96 (ddd, *J* = 10.9, 6.4, 1.4 Hz, 1H), 2.53 (dd, *J* = 12.3, 8.4 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.3, 144.3, 144.2, 134.9, 128.7, 128.6, 128.5, 128.3, 127.8, 127.0, 126.8, 126.6, 126.5, 68.6, 63.5, 59.9, 57.5, 55.0, 44.1, 19.5. IR (cm^{-1}): 2933, 1725, 1447, 1293, 1215, 1167, 1084, 750, 695, 633, 581. MS (ESI-TOF): *m/z* (%): 485.6 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{26}H_{26}N_2NaO_4S$ $[M+Na]^+$: 485.1511; found: 485.1522.

trans-Methyl 6,6-diphenyl-1-vinyltetrahydro-1_H_-pyrrolo[1,2-_c_]sulfoximidazole-2(3_H_)-carboxylate 8d

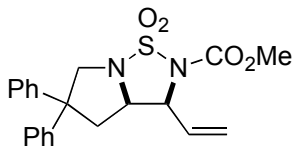


A pyrex tube equipped with a stirrer bar is charged with substrate (1.0 eq.), Bu_4NI (20 mol%), $PhI(OAc)_2$ (2.0 eq.) and dichloromethane (10 mL/mmol). The reaction is stirred overnight at room temperature and quenched by addition of aqueous sat. Na_2SO_3 solution. Dichloromethane is added (10 mL/mmol) and the organic layer is washed with water. The organic layer is separated and the aqueous phase extracted with dichloromethane (3x). The combined organic layers are dried over $MgSO_4$, filtrated and concentrated under reduced pressure to give the crude reaction mixture. Both diastereoisomers were isolated by column chromatography in a combined yield

of 99%. Compound **8d** was eluted first and could be obtained in a highly enriched form.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.10-7.34 (m, 10H), 5.83 (ddd, *J* = 8.8, 10.4, 17.2 Hz, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.31 (dd, *J* = 4.4, 8.8 Hz, 1H), 4.15 (d, *J* = 10.4 Hz, 1H), 3.93 (d, *J* = 10.4 Hz, 1H), 3.27 (m, 1H), 3.78 (s, 3H), 2.92 (ddd, *J* = 0.8, 6.4, 12.4 Hz, 1H), 2.50 (dd, *J* = 7.6, 12.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 150.84, 144.33, 144.21, 138.09, 128.76, 128.64, 127.16, 126.84, 126.58, 126.49, 115.00, 64.35, 60.10, 55.09, 54.05, 43.88, 33.99. m/z = 399.18 [M+H$^+$] (70), 322.2 (8), 303.2 (4), 247.2 (12), 221.2 (20), 192.2 (100), 165.1 (18), 144.1 (4), 115.1 (6), 91.1 (5), 55.2 (3). IR (Ge): ν [cm^{-1}] = 3410, 3061, 3026, 2956, 1740, 1495, 1441, 1369, 1308, 1176, 1093, 1041, 953, 802, 756, 700, 633, 586, 534. HRMS calc.: 398.1300 found: 398.1301.

syn-Methyl 6,6-diphenyl-1-vinyltetrahydro-1_H_-pyrrolo[1,2-_c_]sulfoximidazole-2(3_H_)-carboxylate 8d´



Mp. 71°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.08-7.32 (m, 10H), 5.76 (ddd, *J* = 16.1 Hz, 11.1 Hz, 8.2 Hz, 1H), 5.33 (d, *J* = 16.1 Hz, 1H), 5.32 (d, *J* = 11.1 Hz, 1H), 4.70 (dd, *J* = 7.6, 7.4 Hz, 1H), 4.23 (ddd, *J* = 7.6, 7.4 Hz, 2.6 Hz, 1H), 4.18 (d, *J* = 9.4 Hz, 1H), 3.81 (s, 3H), 3.73 (d, *J* = 9.4 Hz, 1H), 2.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 150.82, 144.48, 132.34, 128.73, 128.65, 128.29, 127.11, 126.90, 126.49, 120.48, 61.46, 60.49, 58.40, 56.41, 54.33, 38.90. m/z = 399.18 [M+H$^+$] (70), 334.2 (4), 322.2 (12), 303.2 (3), 246.2 (4), 221.2 (24), 192.2 (100), 180.2 (16), 165.1 (12), 144.2 (6), 115.1 (8), 91.1 (8), 68.2 (2). IR (Ge): ν [cm^{-1}] = 3447, 3058, 3027, 2965, 2919, 2858, 1741, 1500, 1444, 1316, 1260, 1173, 1034, 809, 763, 707, 630, 589. HRMS calc.: 398.1300 found: 398.1294.

Crystal Structure of compound 10g

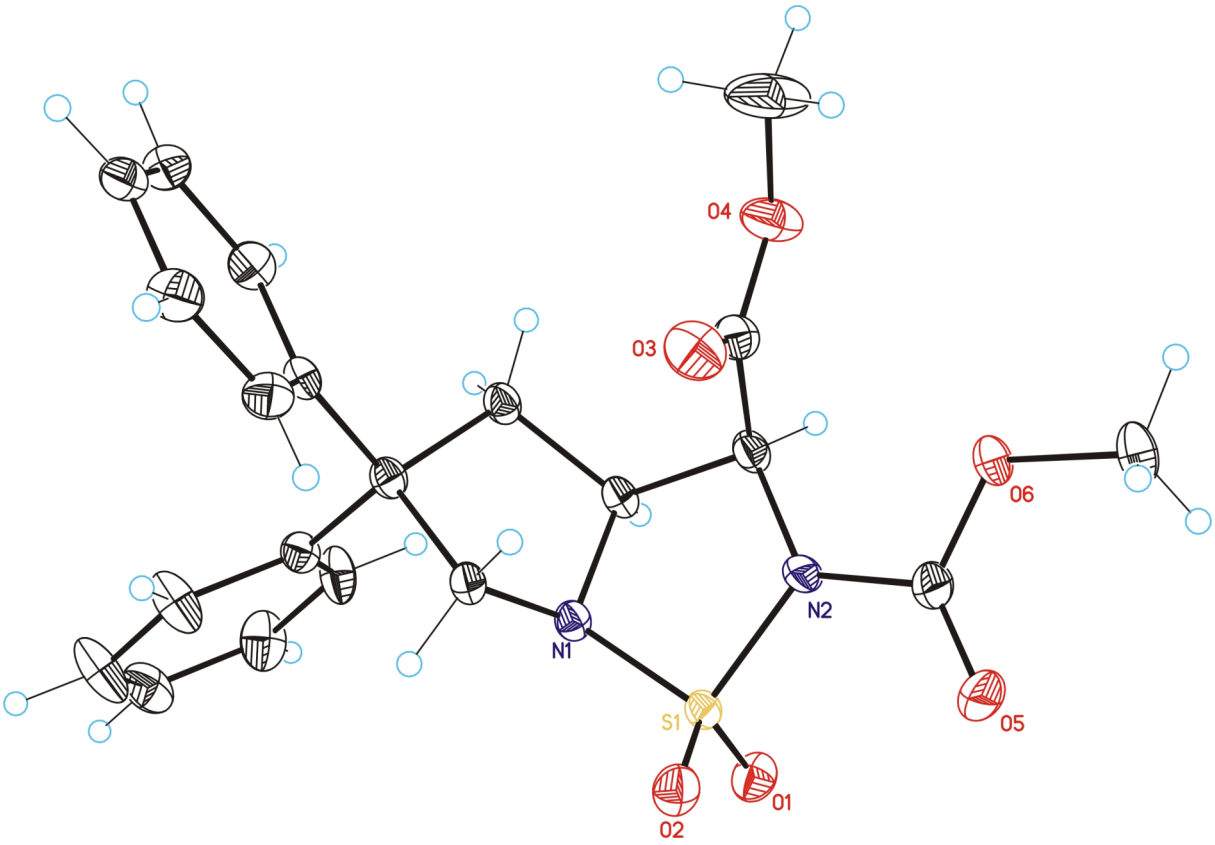
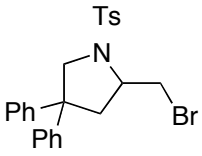


Table S-5. Crystal data and structure refinement for compound **10g**.

Identification code	CCDC 8663465	
Empirical formula	C19 H32 N2 O6 S	
Formula weight	416.53	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.1825(6) ≈	α= 90.00 ∞.
	b = 21.4793(14) ≈	β = 103.900(2) ∞.
	c = 20.4614(12) ≈	γ = 90.00 ∞.
Volume	4344.1(5) $≈^3$	

Z	8
Density (calculated)	1.274 Mg/m^3
Absorption coefficient	0.185 mm^{-1}
F(000)	1792
Crystal size	0.25 x 0.05 x 0.05 mm^3
Theta range for data collection	1.40 to 28.00 ∞.
Index ranges	-13 <=h<=12 ,-28 <=k<=28 ,-26 <=l<=26
Reflections collected	10358
Independent reflections	8294 [R(int) = 0.0498]
Completeness to theta =28.00 ∞	0.987 %
Absorption correction	Empirical
Max. and min. transmission	0.9908 and 0.9552
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10358 / 117 / 558
Goodness-of-fit on F^2	1.113
Final R indices [I>2sigma(I)]	R1 = 0.0613 , wR2 = 0.1464
R indices (all data)	R1 = 0.0793 , wR2 = 0.1554
Largest diff. peak and hole	1.209 and -0.500 $e.\approx^{-3}$

2-(Bromomethyl)-4,4-diphenyl-1-tosylpyrrolidine 12



To a pyrex tube containing a solution of the free *N*-tosylamide **12** (130 mg, 0.33 mmol) in DMF (3 mL) are added solid potassium carbonate (55 mg, 0.4 mmol, 1.2 equiv) and NBS (71 mg, 0.4 mmol, 1.2 equiv) in one portion. The resulting mixture is sealed and stirred for 12 h at room temperature. The reaction is quenched by addition of aqueous sat. Na_2SO_3 solution. Dichloromethane is added (10 mL) and the organic layer is washed with water. The organic layer is separated and the aqueous phase extracted with dichloromethane (3x). The combined organic layers are dried over $MgSO_4$, filtrated and concentrated under reduced pressure to give the crude reaction mixture. Column chromatography (hexanes/ethyl actetate, 2/1, v/v) gives the product as a colorless solid (137 mg, 87%).

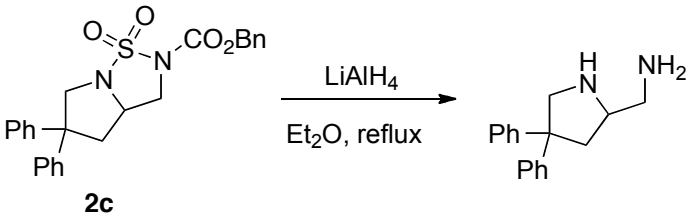
Mp. 61°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.10-7.40 (m, 10H), 4.45 (d, *J* = 9.7 Hz, 1H), 3.89-4.04 (m, 1H), 3.85 (dd, *J* = 3.3, 9.7 Hz, 1H), 3.77 (d, *J* = 9.9 Hz, 1H), 3.00 (t, *J* = 9.9 Hz, 1H), 2.79 (ddd, *J* = 5.3, 8.5, 13.2 Hz, 2H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 144.3, 144.0, 143.3, 133.5, 129.5, 128.4, 128.3, 127.0, 126.4, 126.2, 126.2, 126.0, 59.7, 58.5, 51.9, 41.7, 35.5, 21.2. IR (cm^{-1}): 2962, 2885, 1656, 1596, 1481, 1447, 1300, 1225, 1021, 1101, 775, 722, 646, 619, 523, 502, 461. MS (ESI-TOF): *m/z* (%): 492,1 $[M+Na]^+$ (100). HRMS-ESI-TOF *m/z* calculated for $C_{24}H_{24}BrNO_2$ $[M+Na]^+$: 492,0619; found: 492.0604.

Deprotection of sulfamides into the corresponding free diamines

The deprotection conditions for all kind of carbamate-protected cyclic sulfamides were reported in an earlier communication: K. Muñiz, J. Streuff, C. H. Hövelmann and A. Nuñez, *Angew. Chem. Int. Ed.*, 2007, **46**, 7125.

A representative example is as follows:

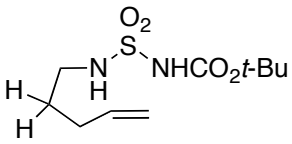
Direct complete deprotection of sulfamide 2c

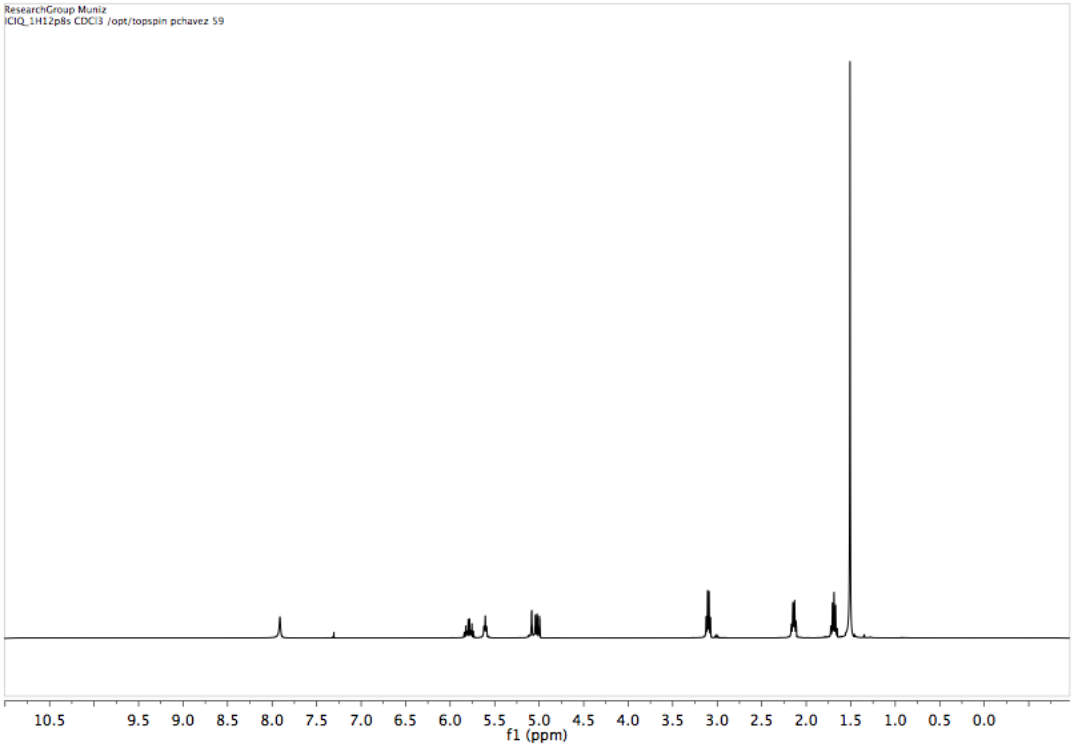


2c

Lithium aluminium hydride (0.3 mmol, 3eq.) is suspended in 4mL dry Et_2O, sulfamide **2c** (0.1 mmol, 1 eq.) is slowly added and the mixture refluxed. After 5h the reaction is cooled to room temperature and cooled by an external ice bath. Next, 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 (40 mL). The collected mother liquor is concentrated to give a colorless oil, 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 (83% yield).

Spectral characterization of starting materials.


O2
S
N
H
NHCO2t-Bu
H
H


ResearchGroup Muniz
ICIQ_1H12p8s CDCl3 /opt/topspin pchavez 59
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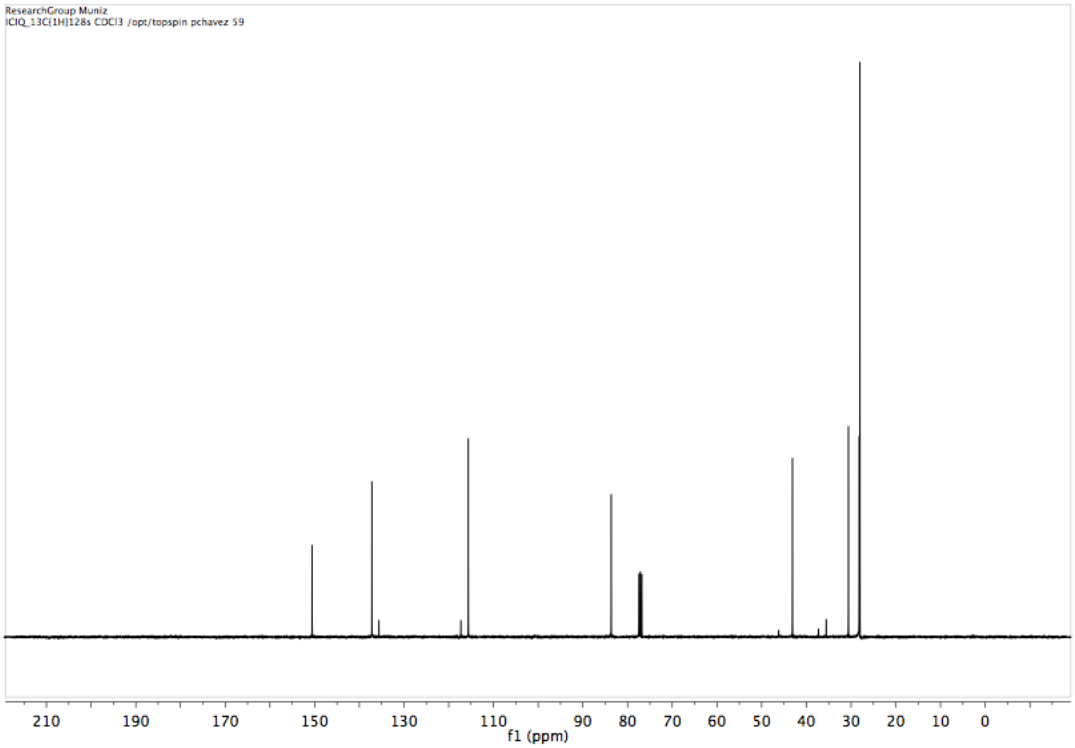
f1 (ppm)


ResearchGroup Muniz
ICIQ_13C{1H}128s CDCl3 /opt/topspin pchavez 59
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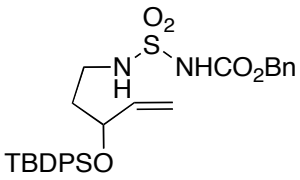
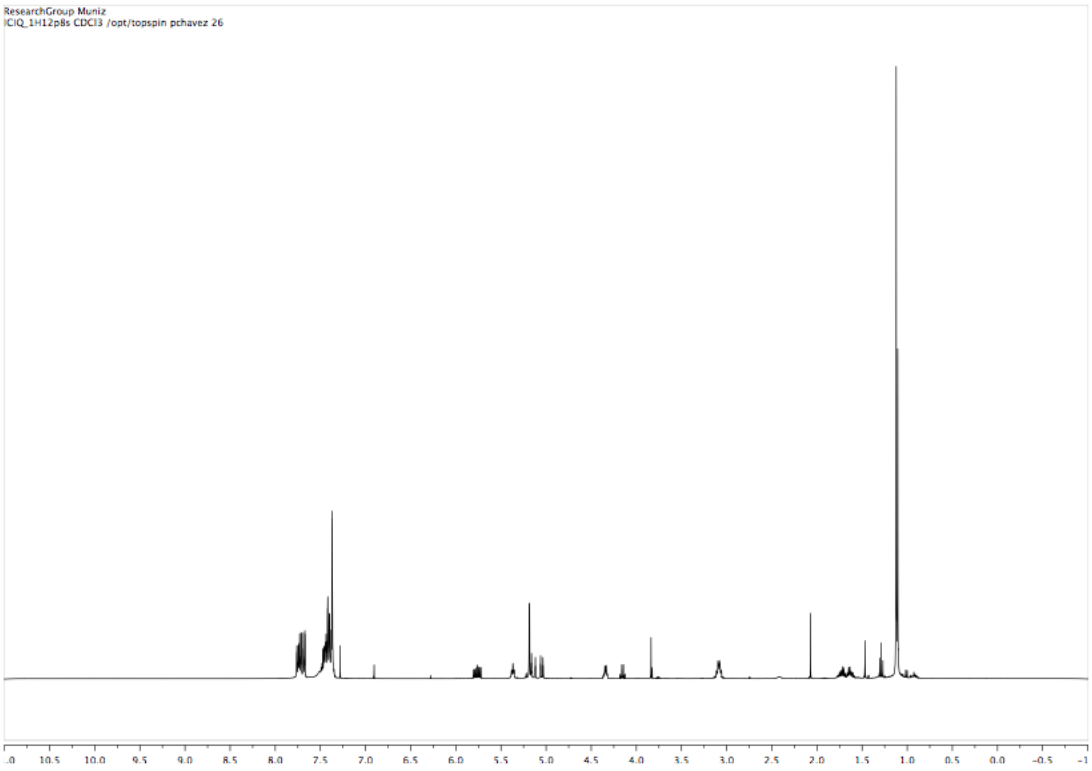
f1 (ppm)


O2
S
N
H
NHCO2Bn
TBDPSO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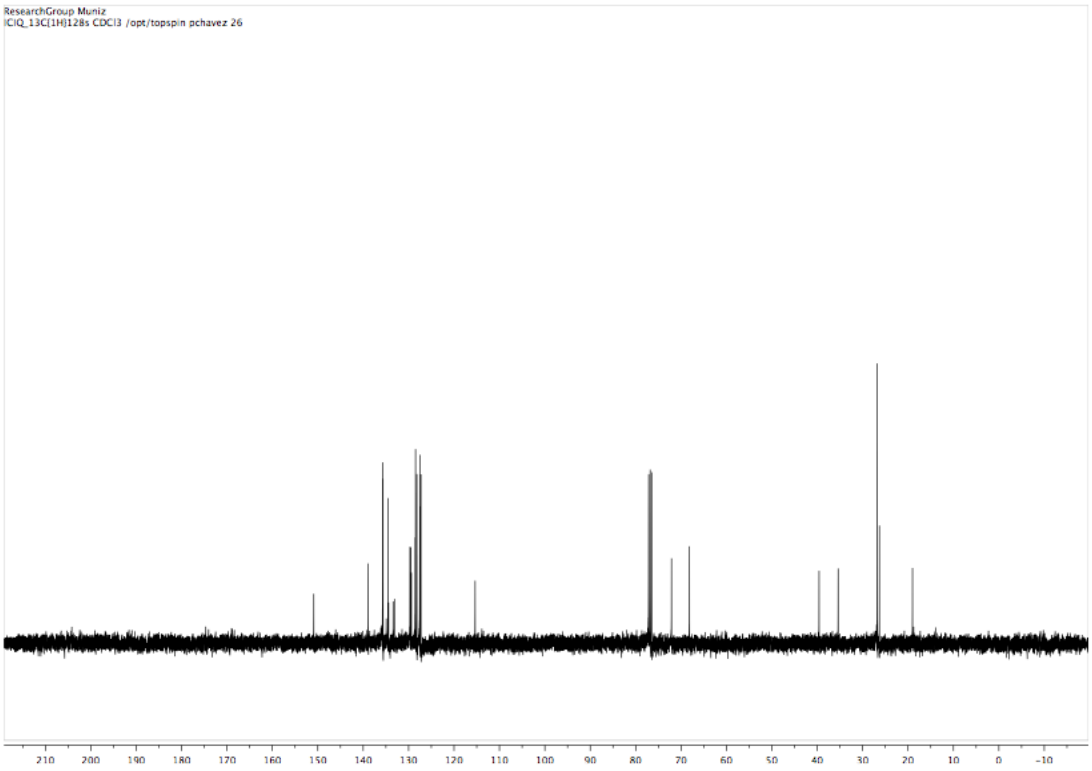
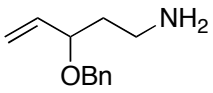
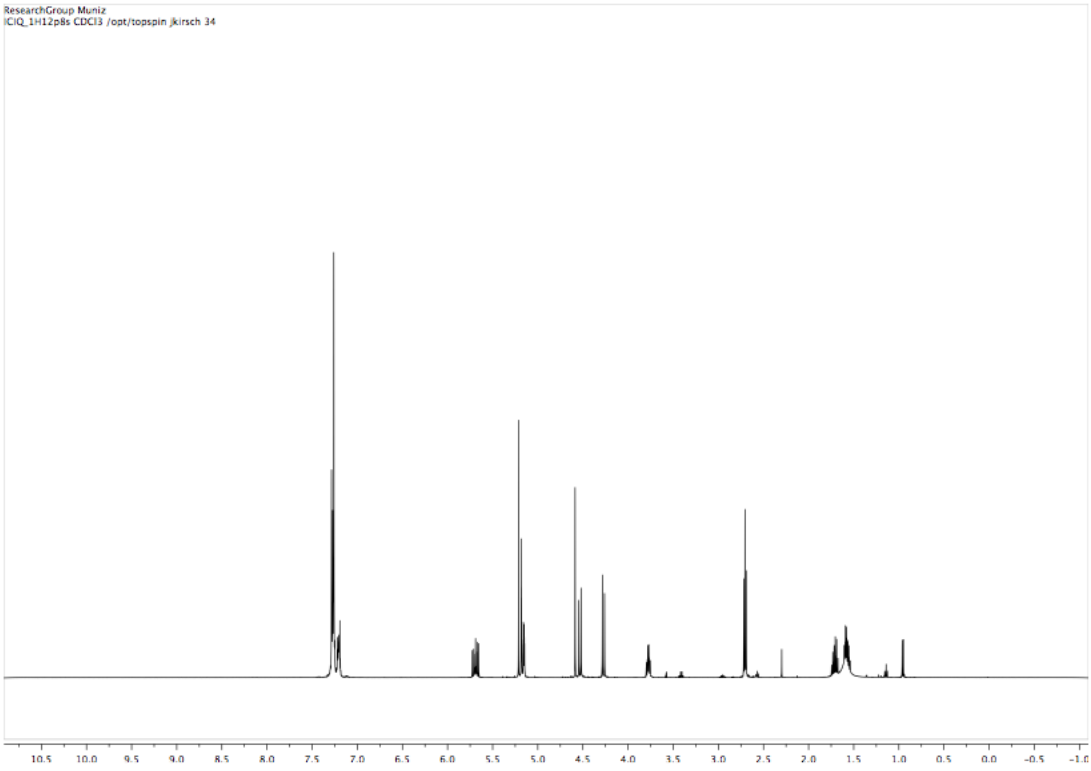

ResearchGroup Muniz
ICIQ_13C{1H}128s CDCl3 /opt/topspin pchavez 26


NH2
OBn


ResearchGroup Muniz
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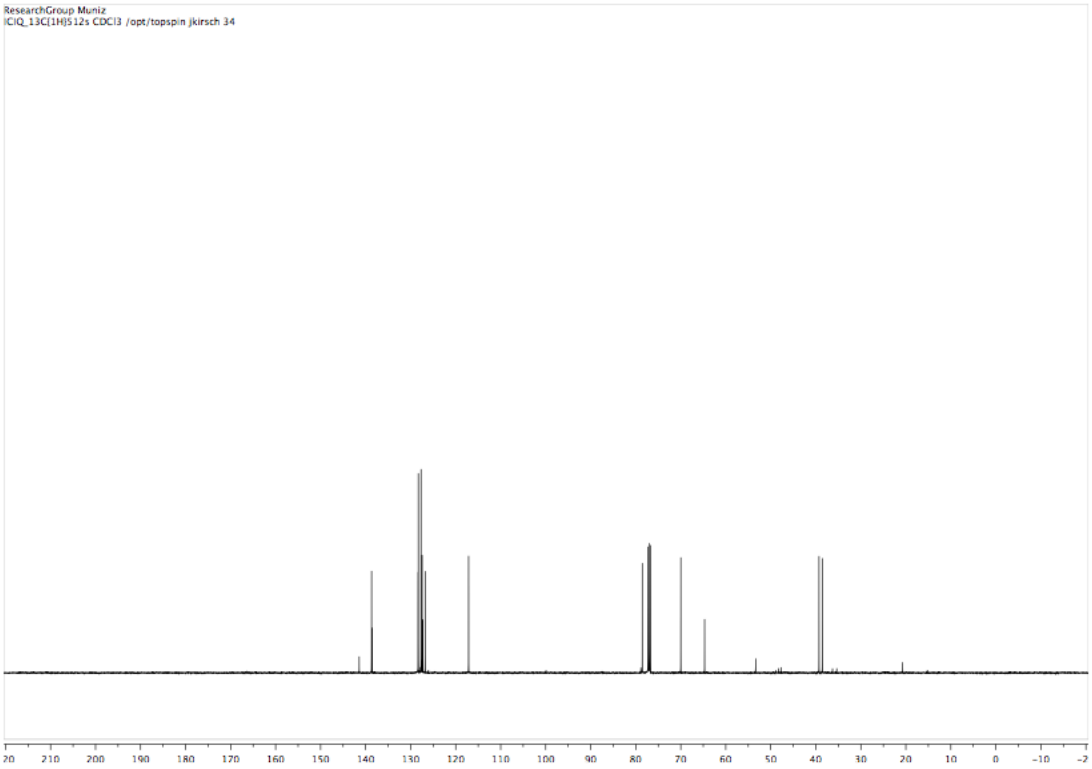
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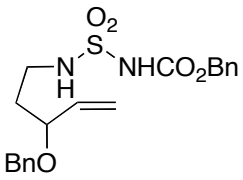
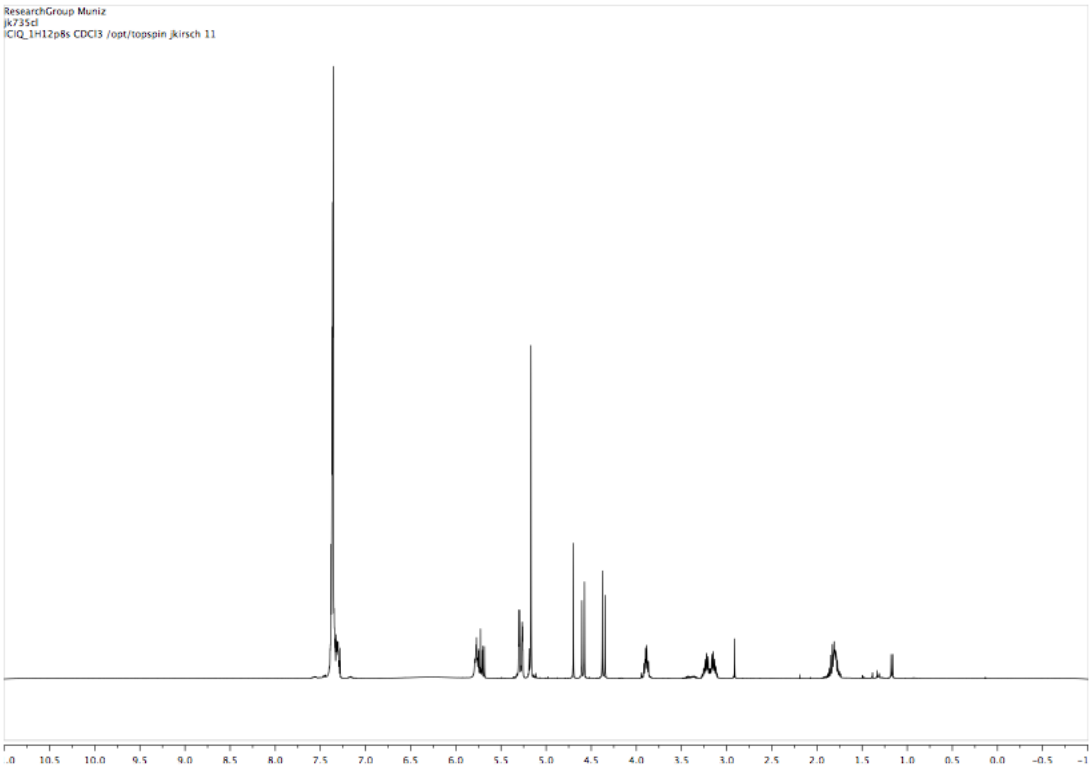

O2
S
N
H
NHCO2Bn
BnO


ResearchGroup Muniz
jk735cl
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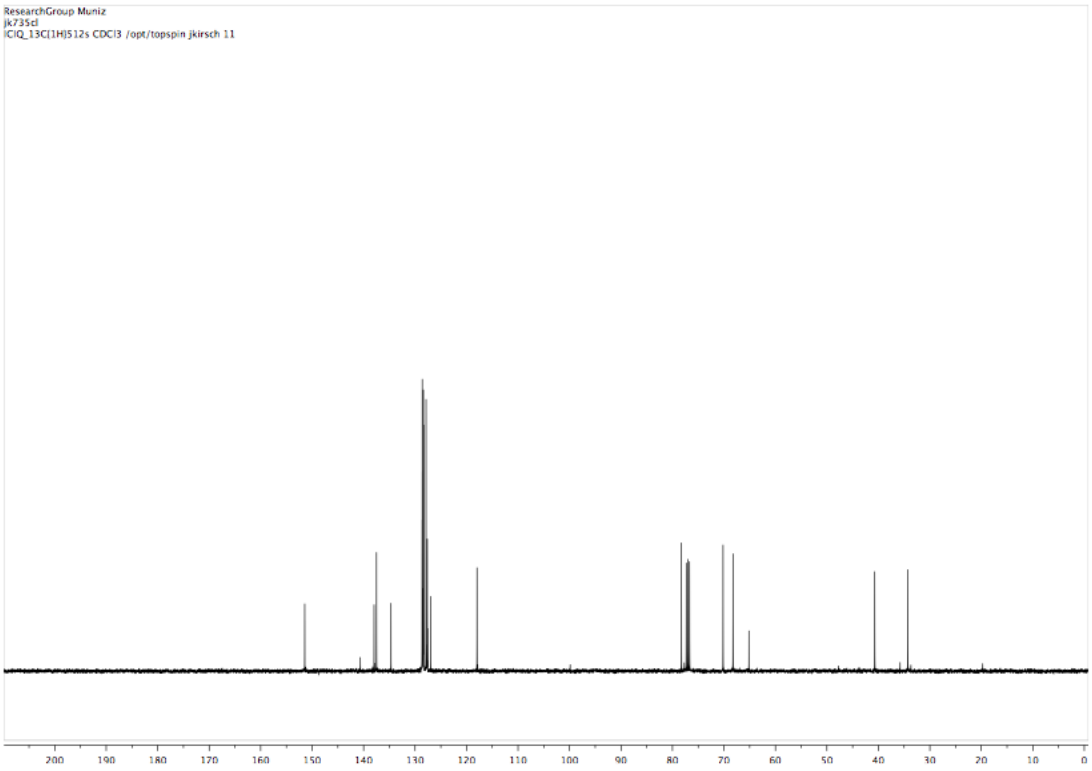
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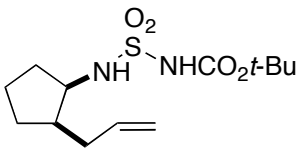
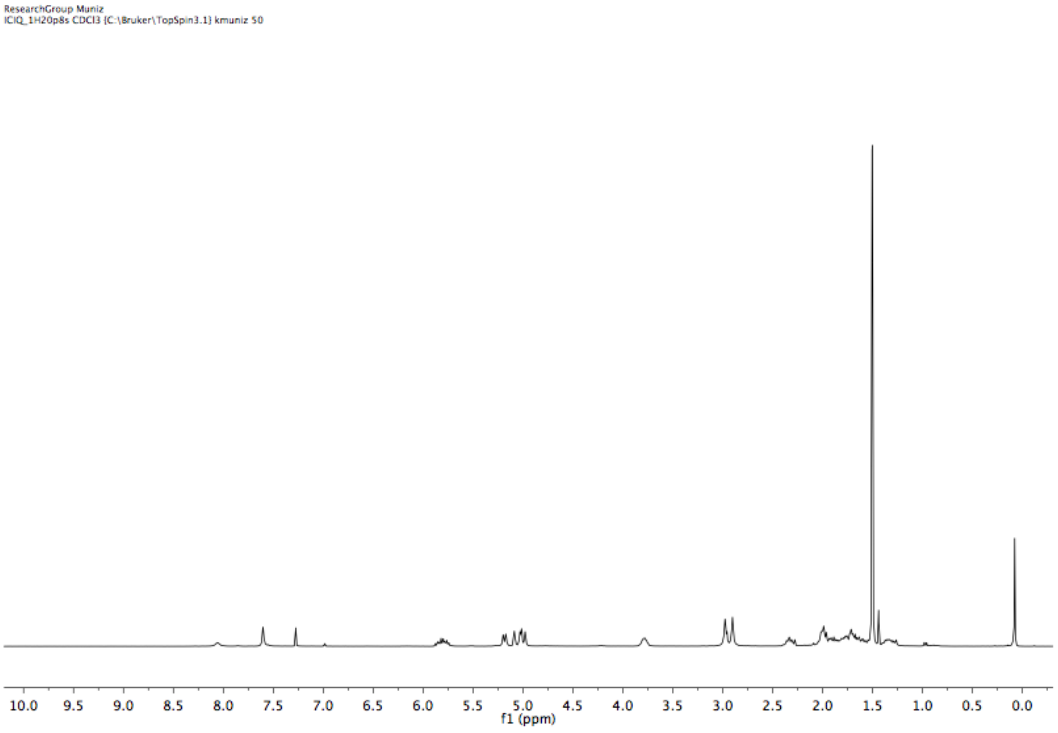

O2
S
NH
NHCO2t-Bu


ResearchGroup Muniz
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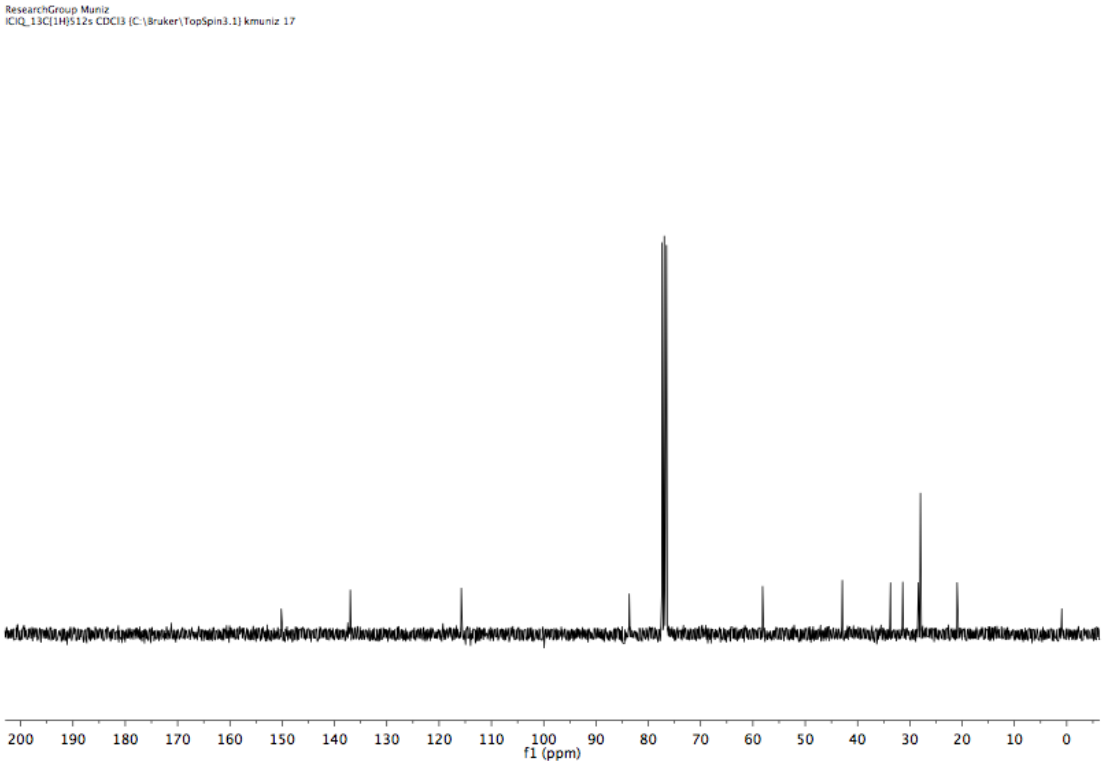
f1 (ppm)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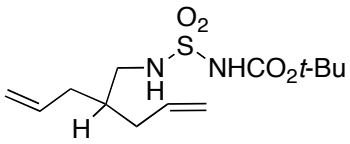
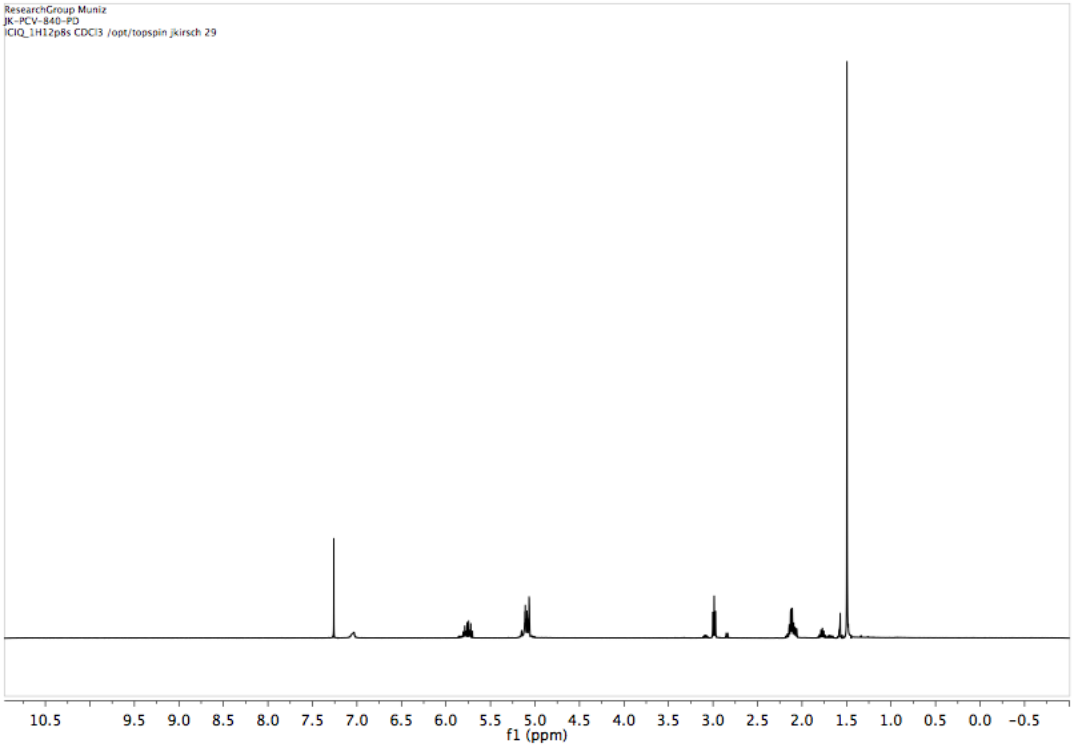
f1 (ppm)


O2
S
N
H
NHCO2t-Bu
H


ResearchGroup Muniz
JK-PCV-840-PD
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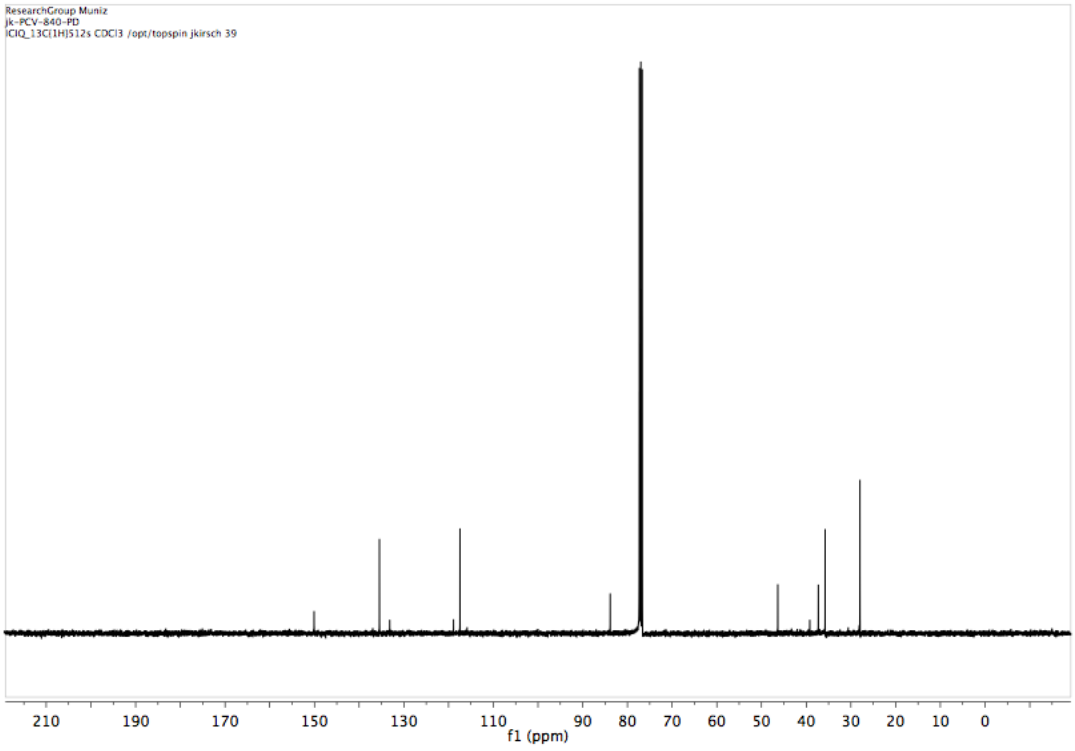
f1 (ppm)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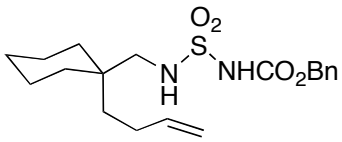
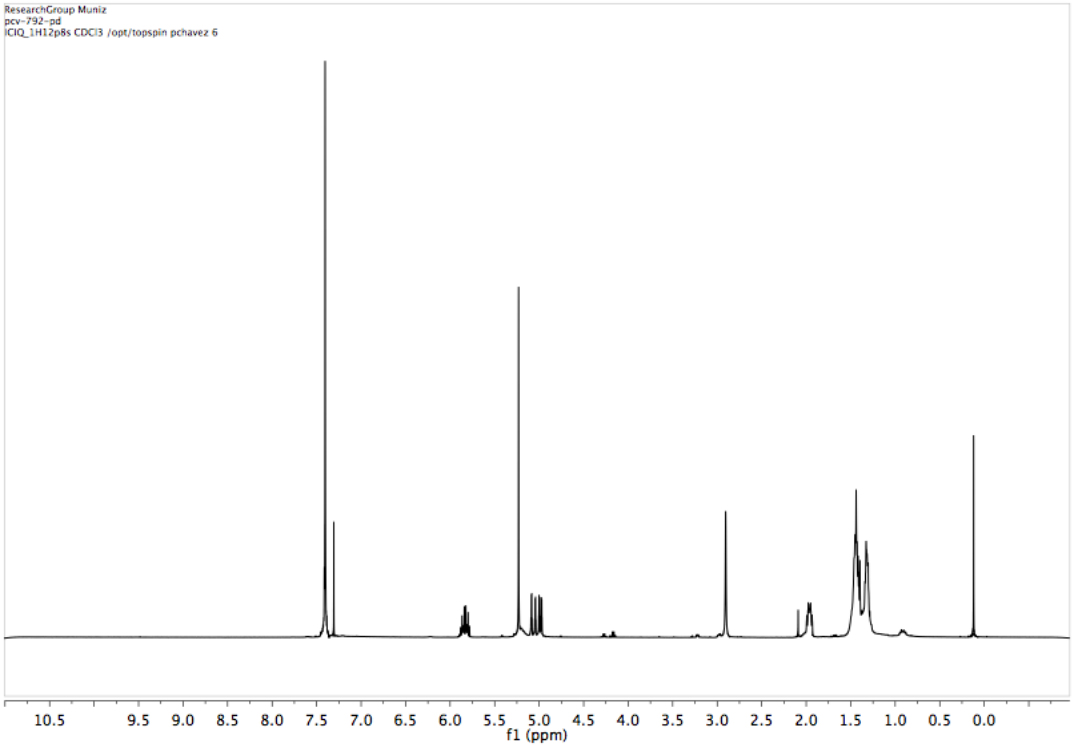
f1 (ppm)


O2
S
N
H
NHCO2Bn


ResearchGroup Muniz
pcv-792-pd
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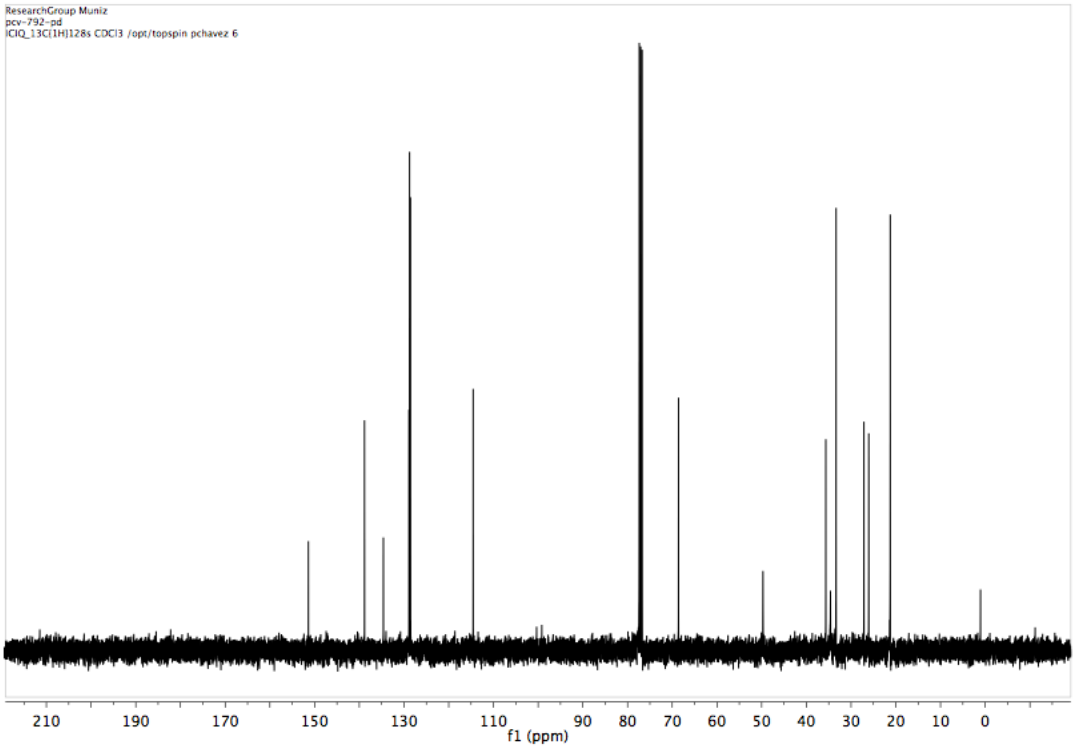
f1 (ppm)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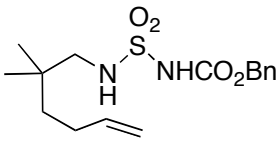
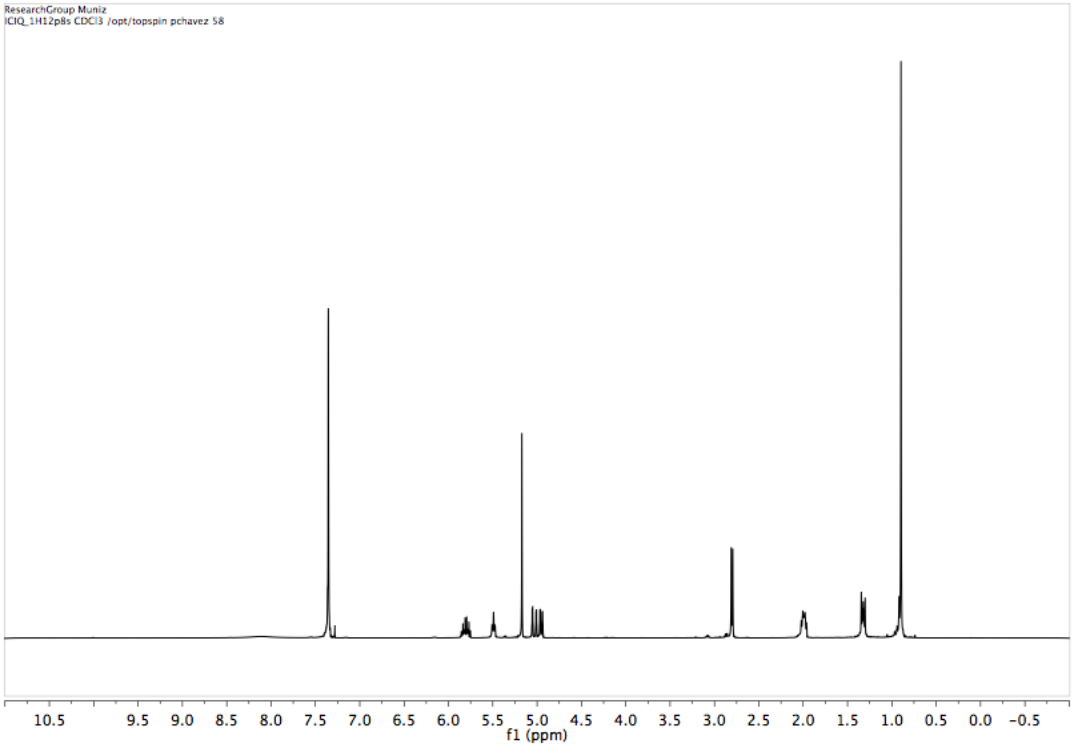
f1 (ppm)


O2
S
N
H
NHCO2Bn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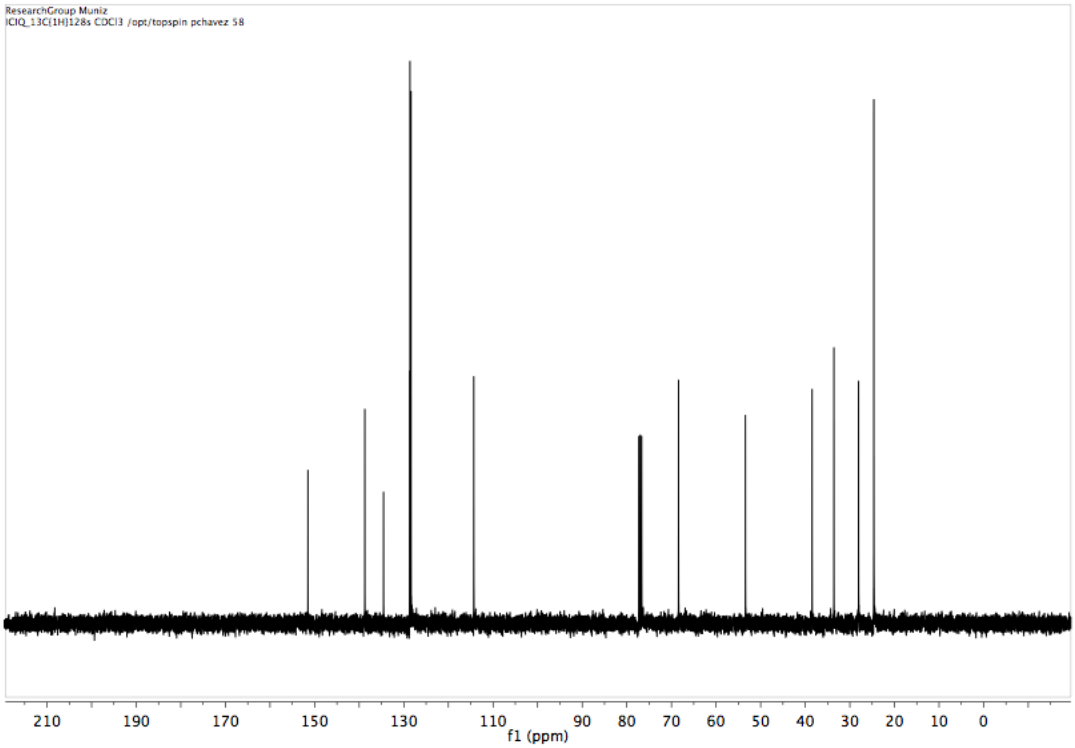
f1 (ppm)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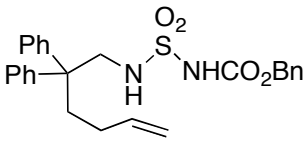
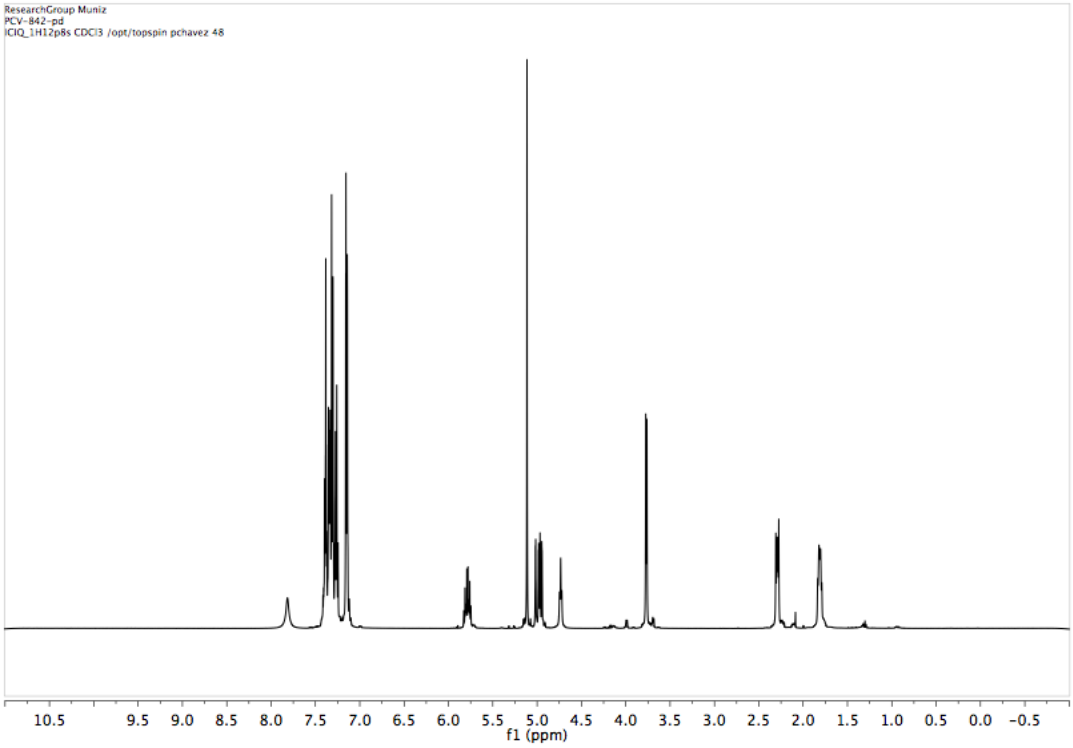
f1 (ppm)


O2
S
Ph
Ph
N
H
NHCO2Bn


ResearchGroup Muniz
PCV-842-pd
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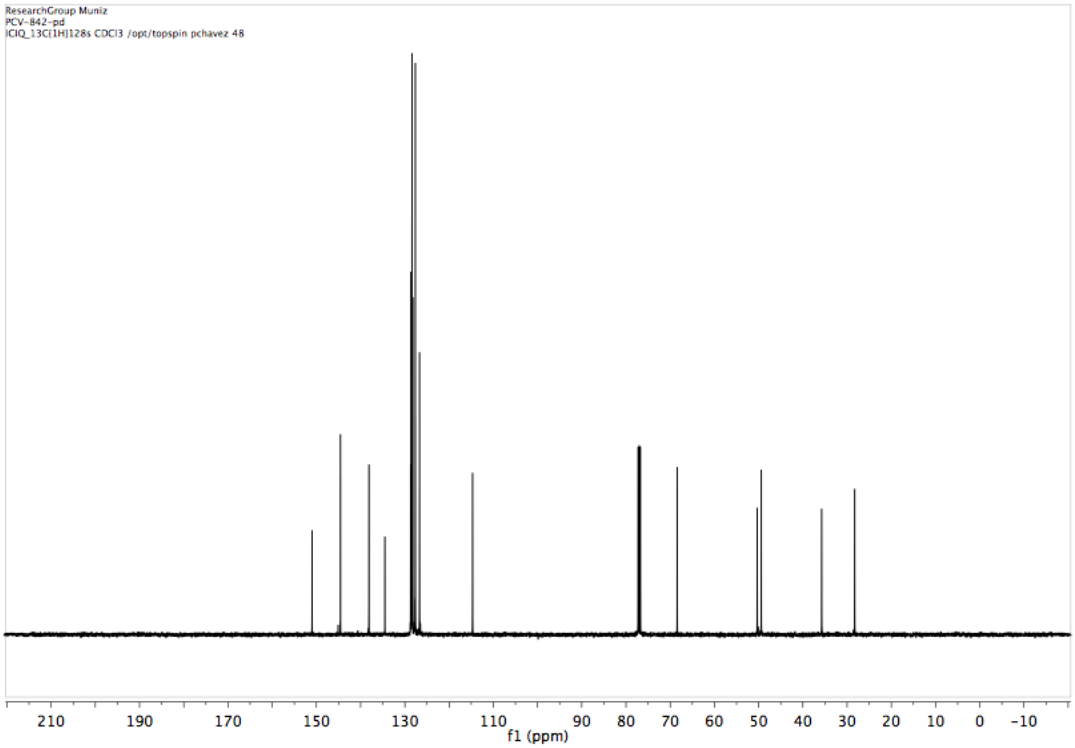
f1 (ppm)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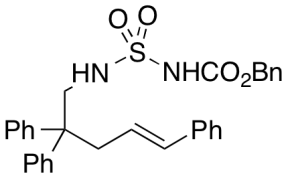
f1 (ppm)


O
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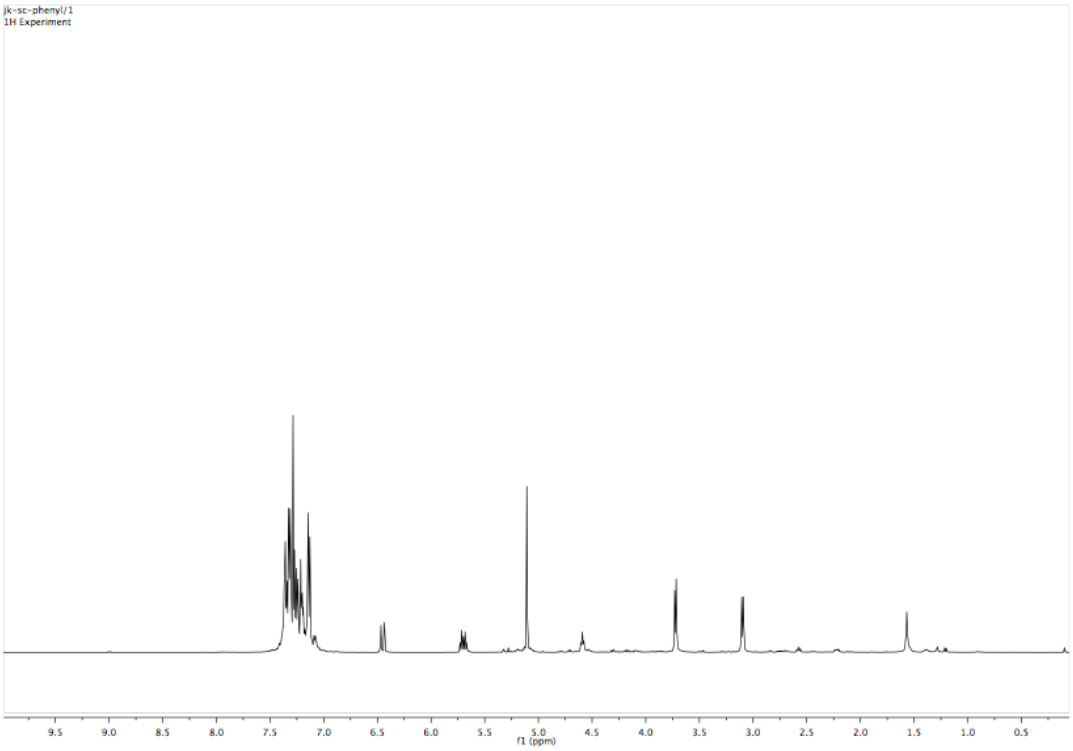
S
HN
NHCO2Bn
Ph
Ph
Ph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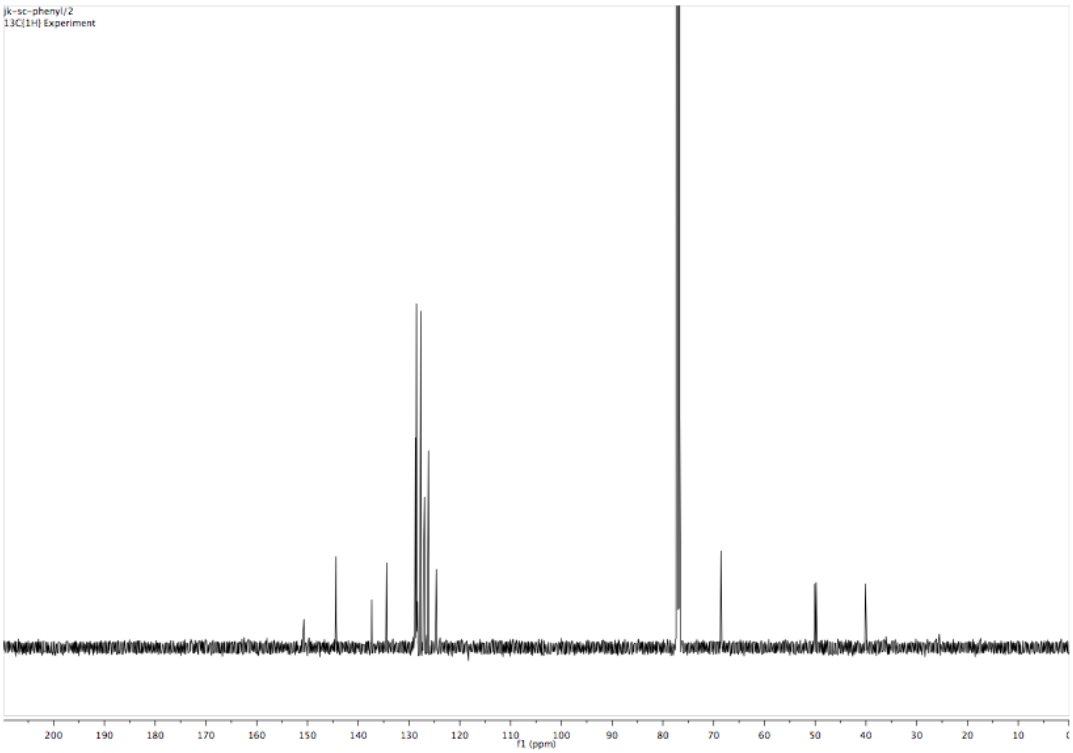
1H Experiment
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


jk-sc-phenyl/2
13C{1H} Experiment
200
190
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160
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140
130
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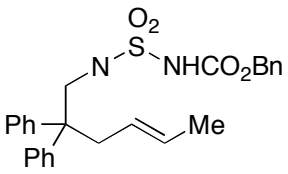
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



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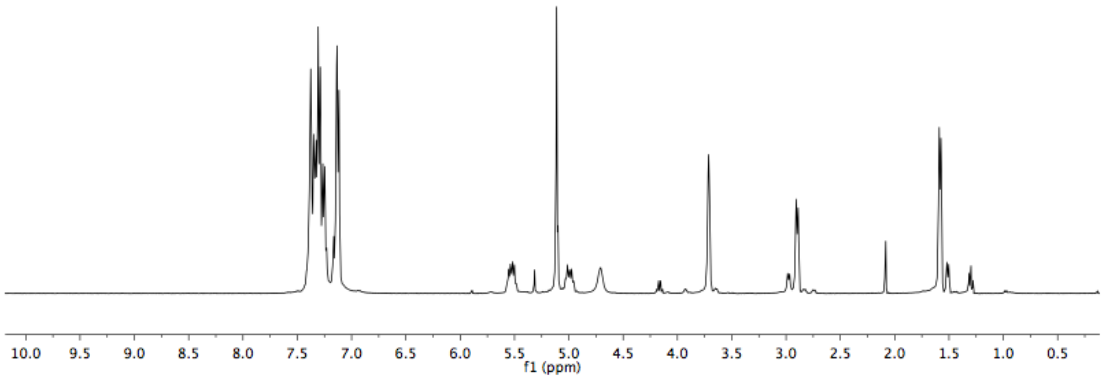

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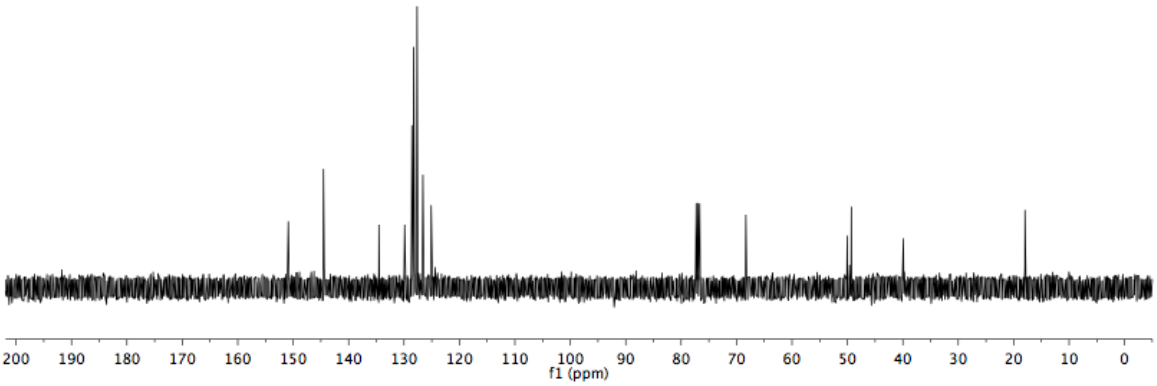
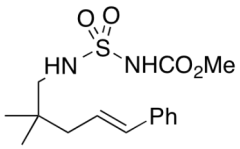
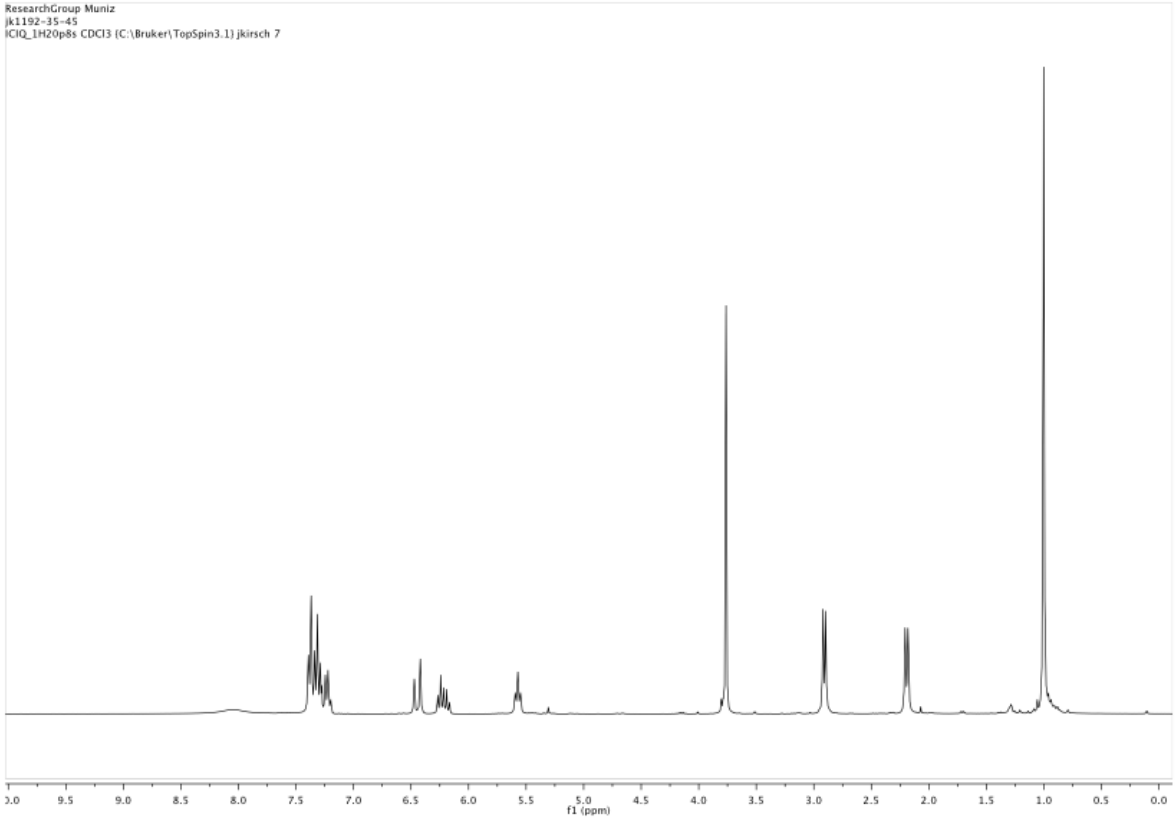



O
O
S
HN
NHCO2Me
Ph


ResearchGroup Muniz
jk1192-35-45
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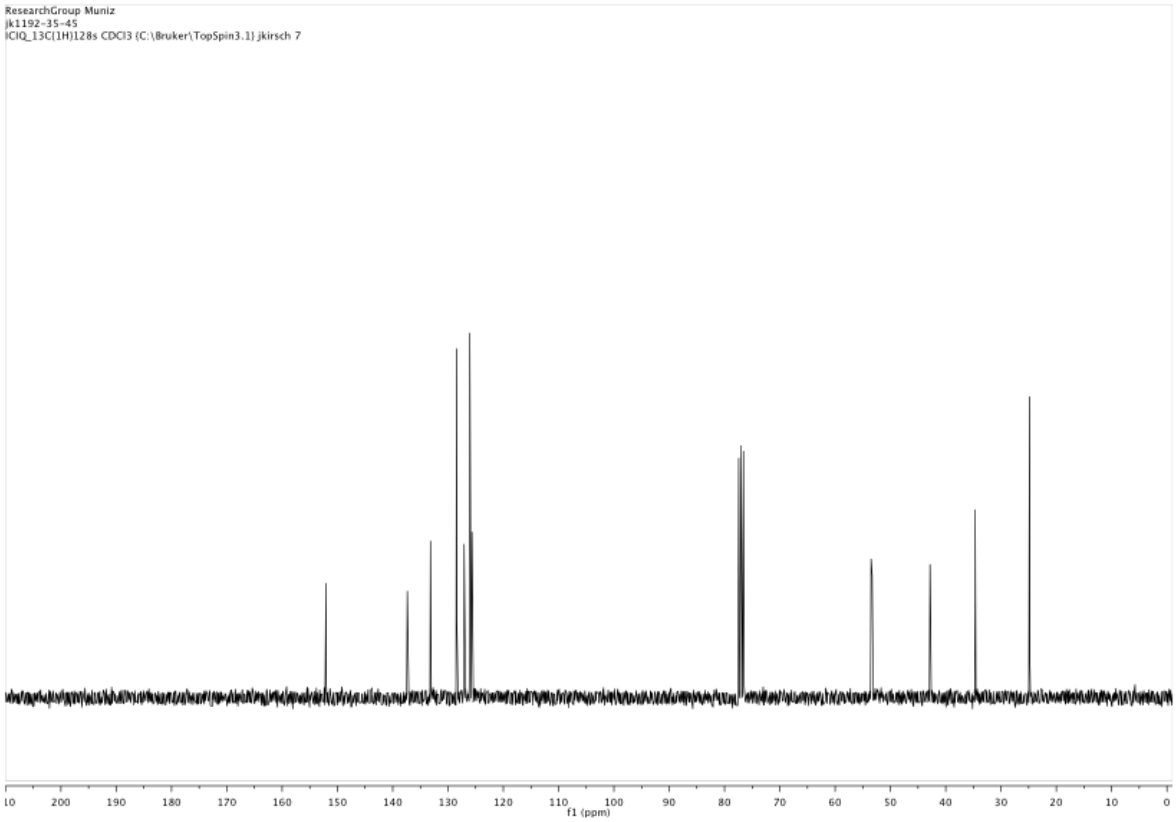
f1 (ppm)


ResearchGroup Muniz
jk1192-35-45
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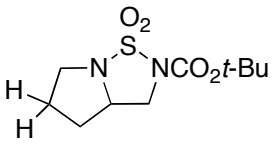
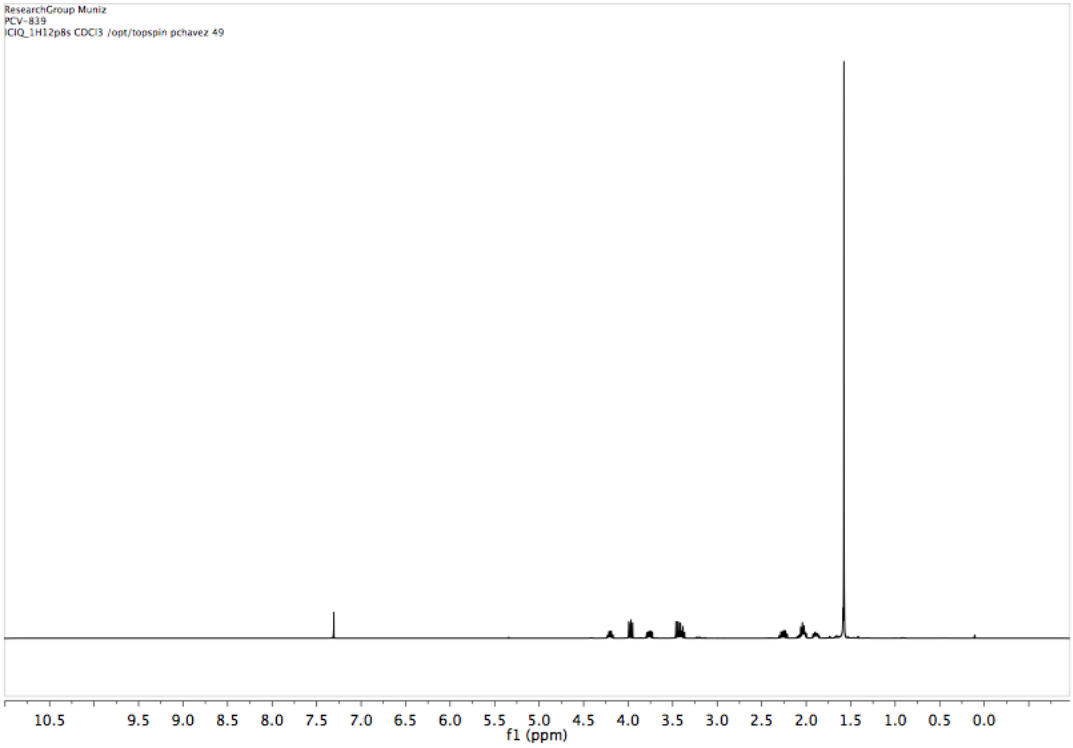
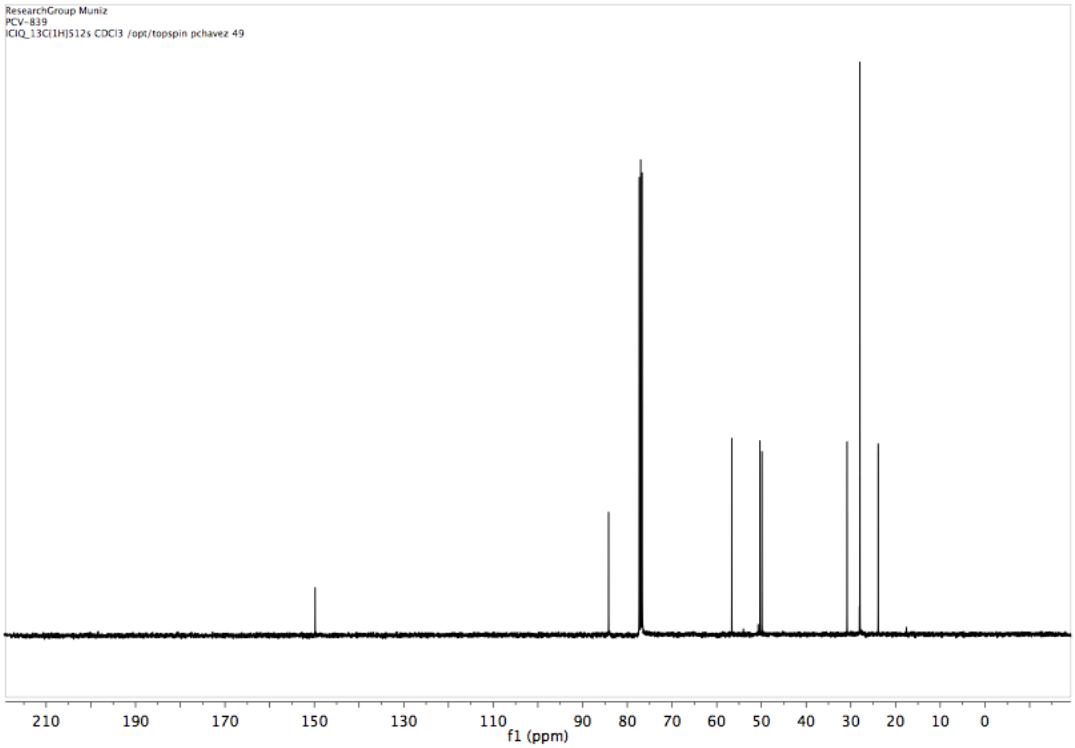
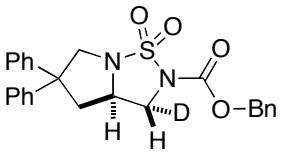
f1 (ppm)

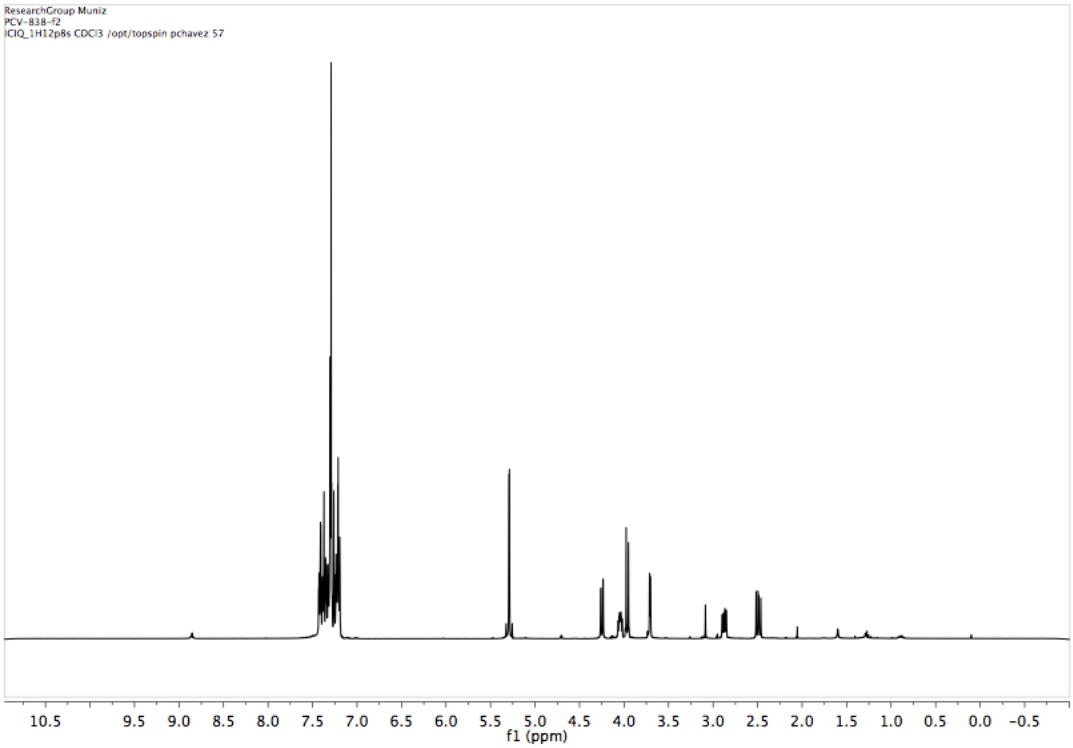
Spectral characterization of diamination products

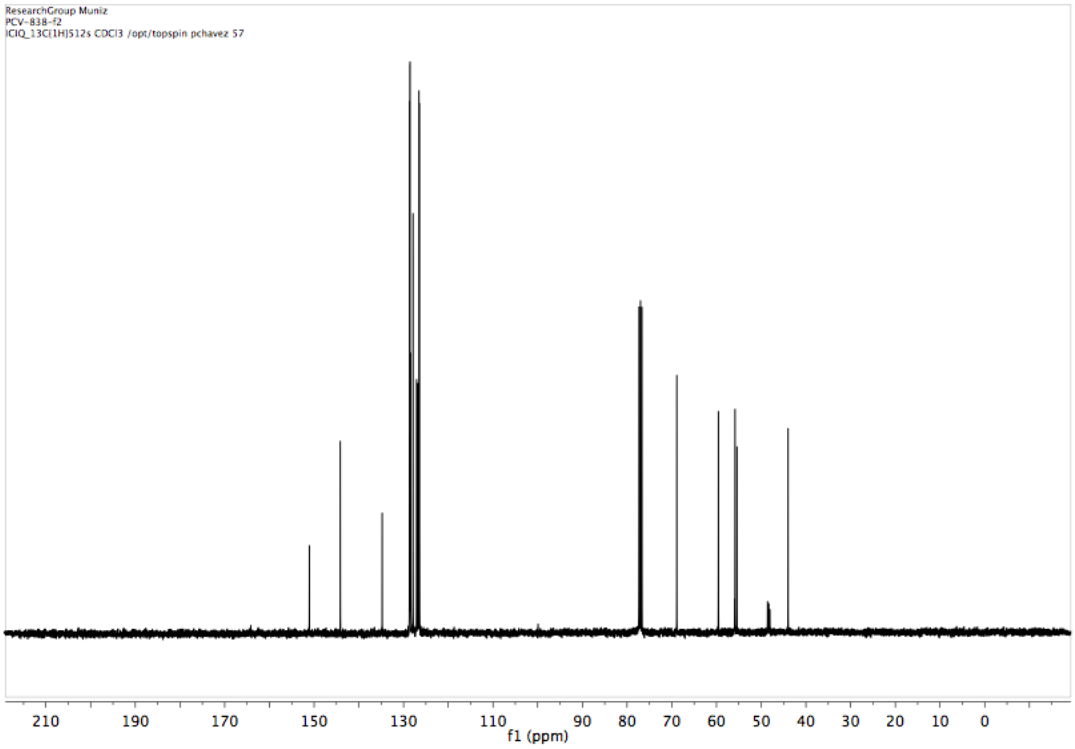

O2
S
N
NCO2t-Bu
H
H

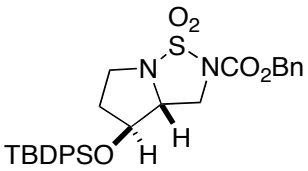

ResearchGroup Muniz
PCV-839
ICIQ_1H12p8s CDCl3 /opt/topspin pchavez 49
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

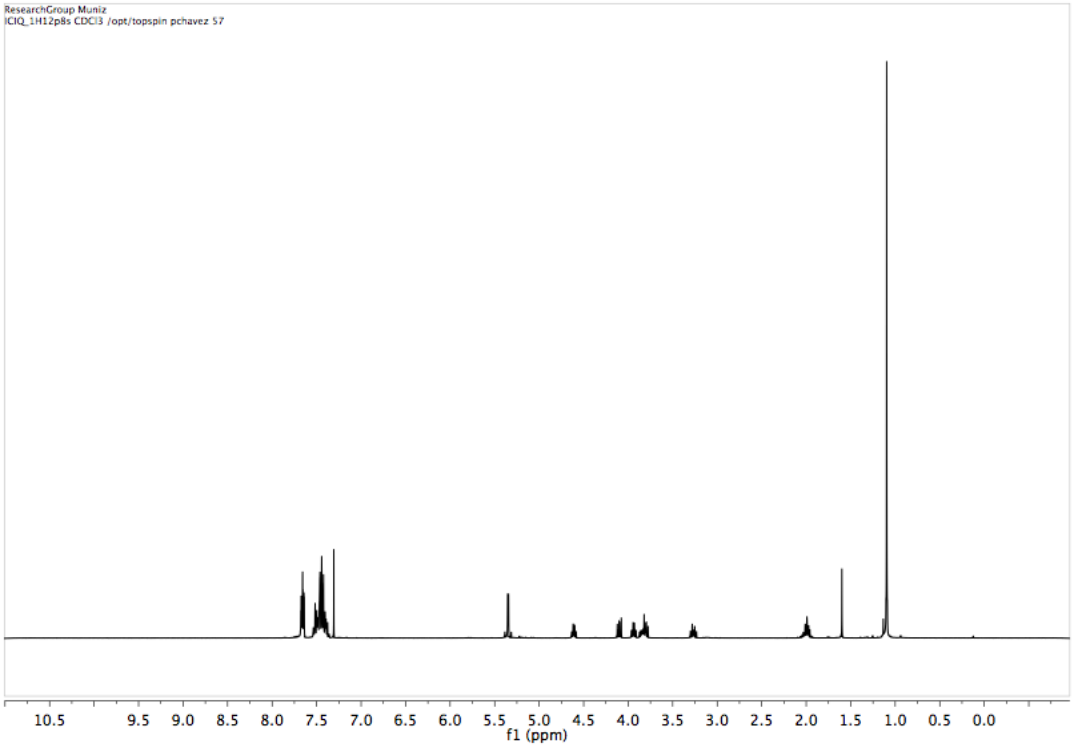

ResearchGroup Muniz
PCV-839
ICIQ_13C{1H}512s CDCl3 /opt/topspin pchavez 49
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

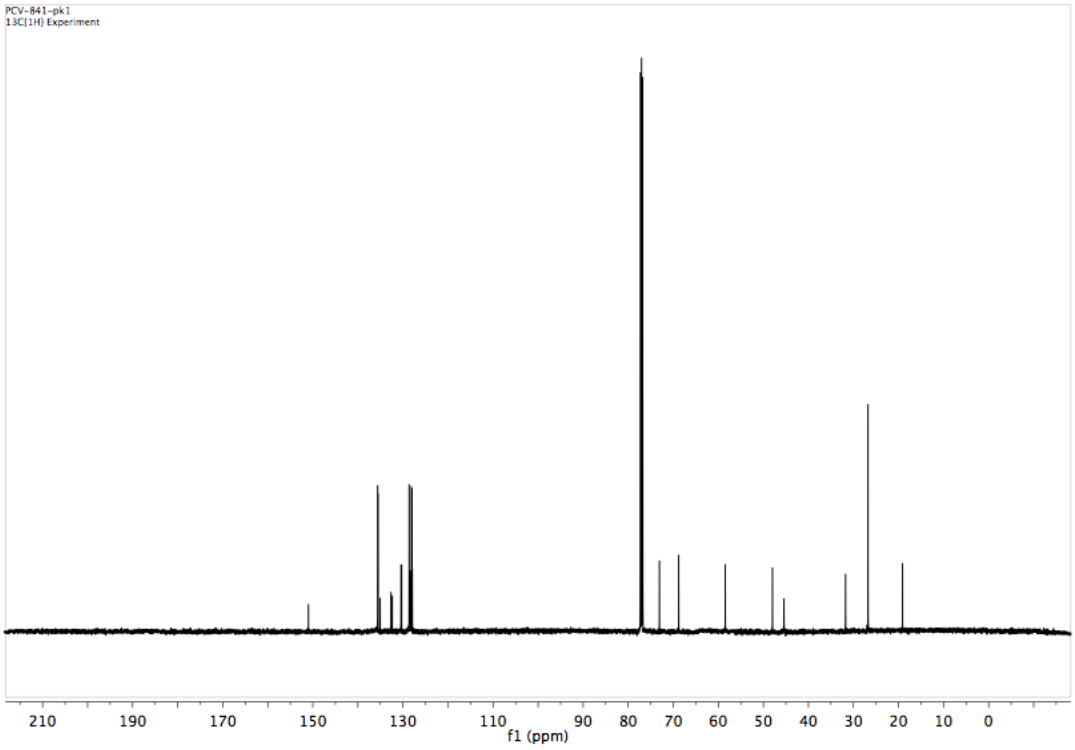

O
O
S
N
N
O
Ph
Ph
D
O–Bn
H
H

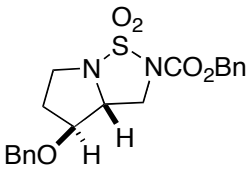

ResearchGroup Muniz
PCV-838-f2
ICIQ_1H12pBs CDCl3 /opt/topspin pchavez 57
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

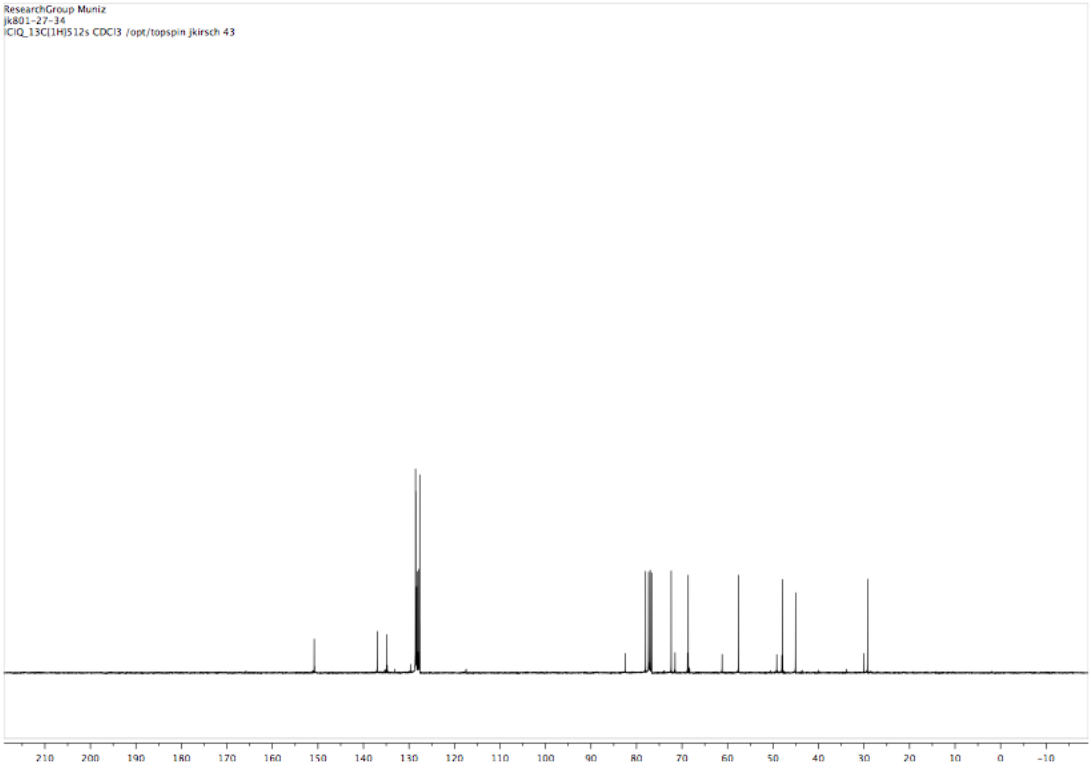

ResearchGroup Muniz
PCV-838-f2
ICIQ_13C{1H}512s CDCl3 /opt/topspin pchavez 57
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

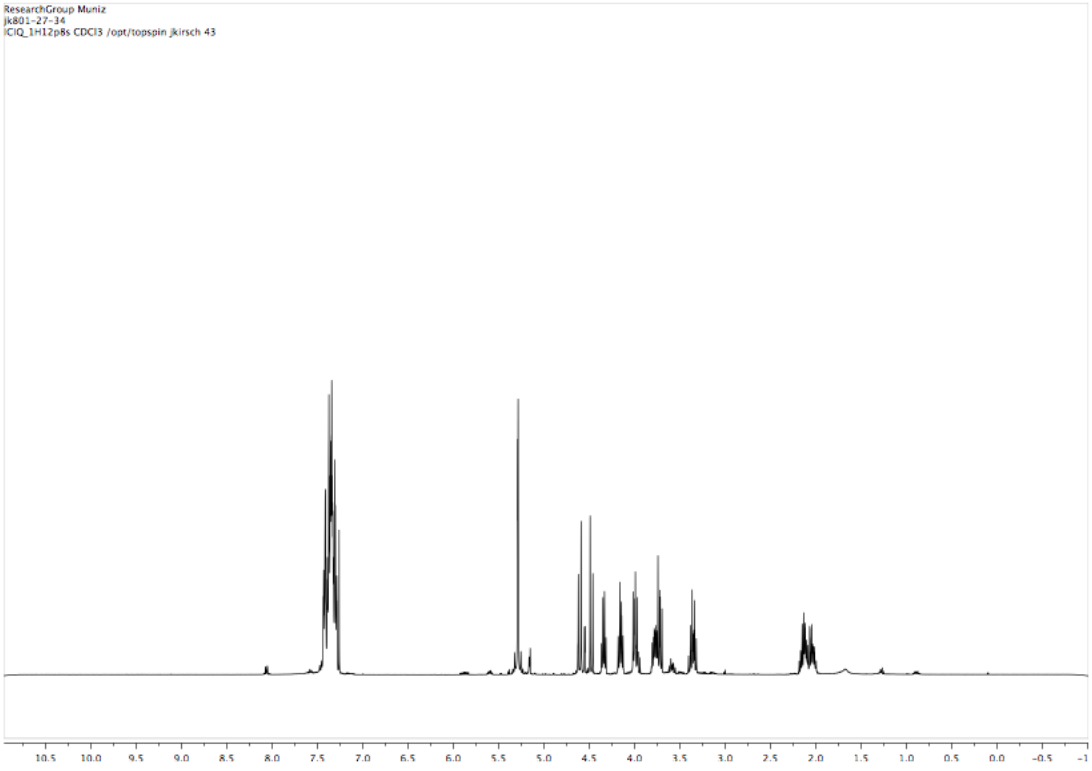

O2
S
N
NCO2Bn
H
TBDPSO
H

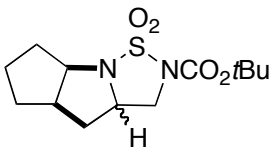

ResearchGroup Muniz
ICIQ_1H12p8s CDCl3 /opt/topspin pchavez 57
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

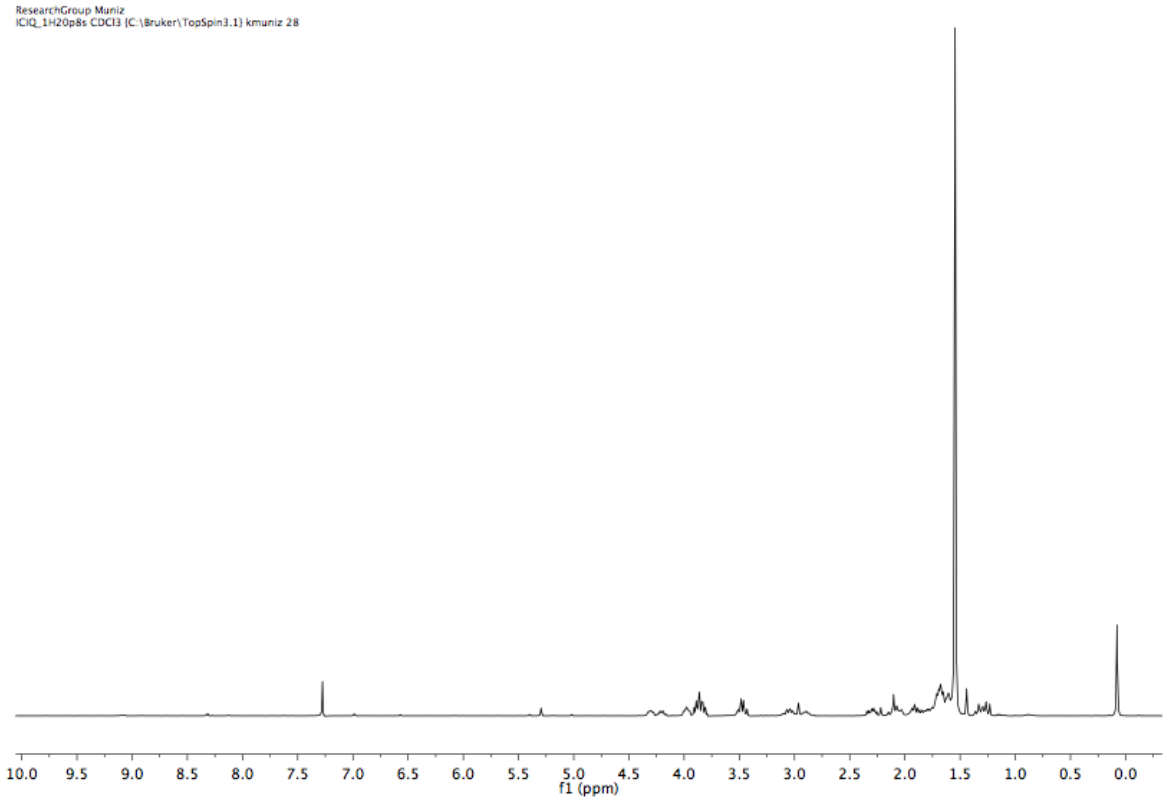

PCV-841-pk1
13C{1H} Experiment
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

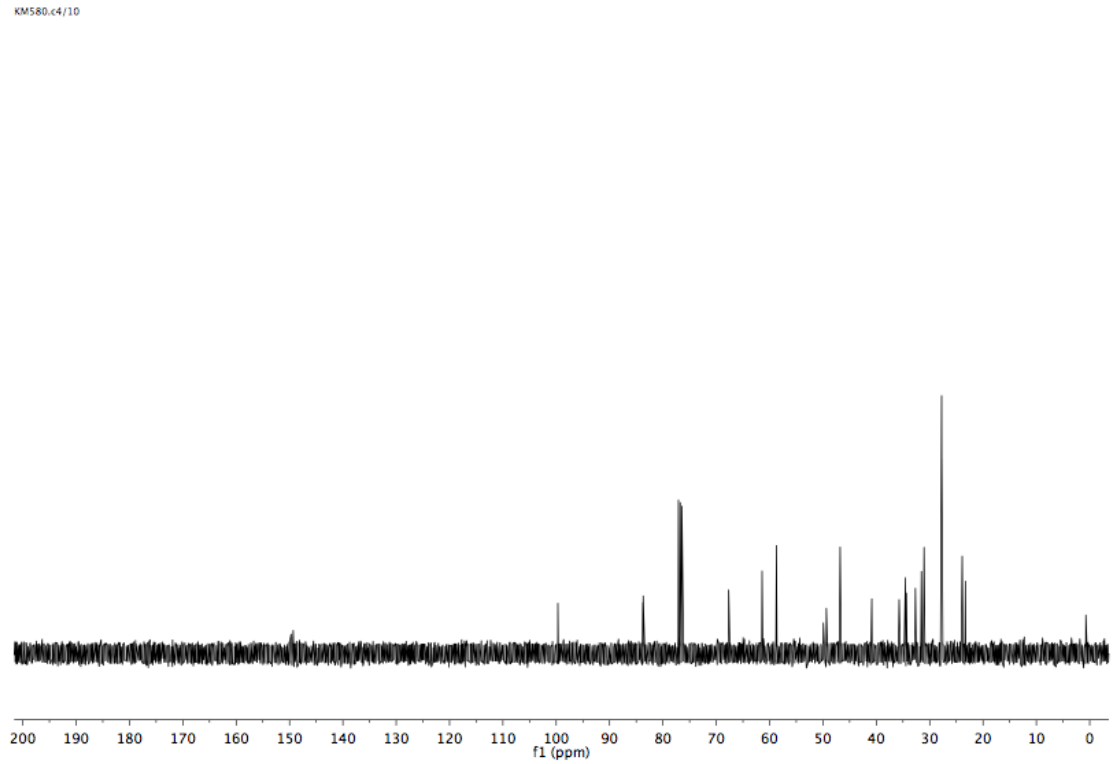

O2
S
N
NCO2Bn
BnO
H
H

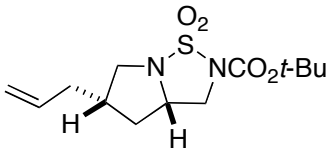

ResearchGroup Muniz
jk801-27-34
ICIQ_13C{1H}512s CDCl3 /opt/topspin jkirsch 43


ResearchGroup Muniz
jk801-27-34
ICIQ_1H12p8s CDCl3 /opt/topspin jkirsch 43

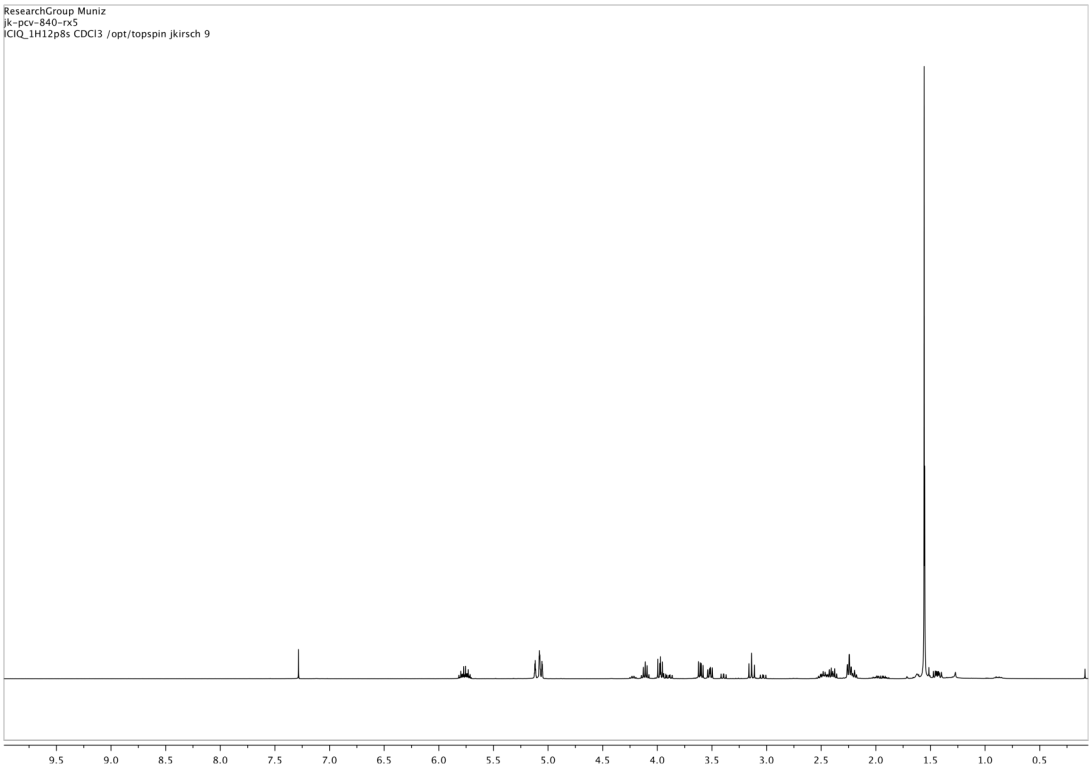

O2
S
N
NCO2tBu
H

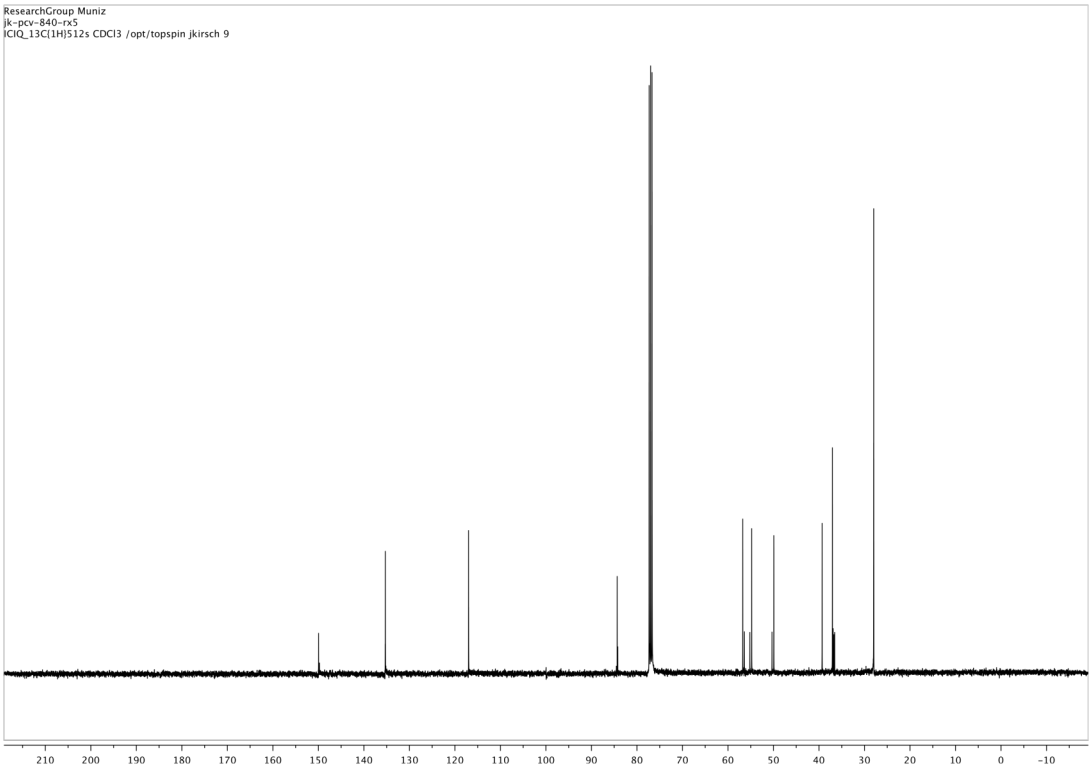

ResearchGroup Muniz
ICIQ_1H20p8s CDCl3 (C:\Bruker\TopSpin3.1) kmuniz 28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

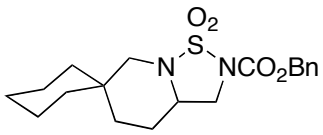

KM580.c4/10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

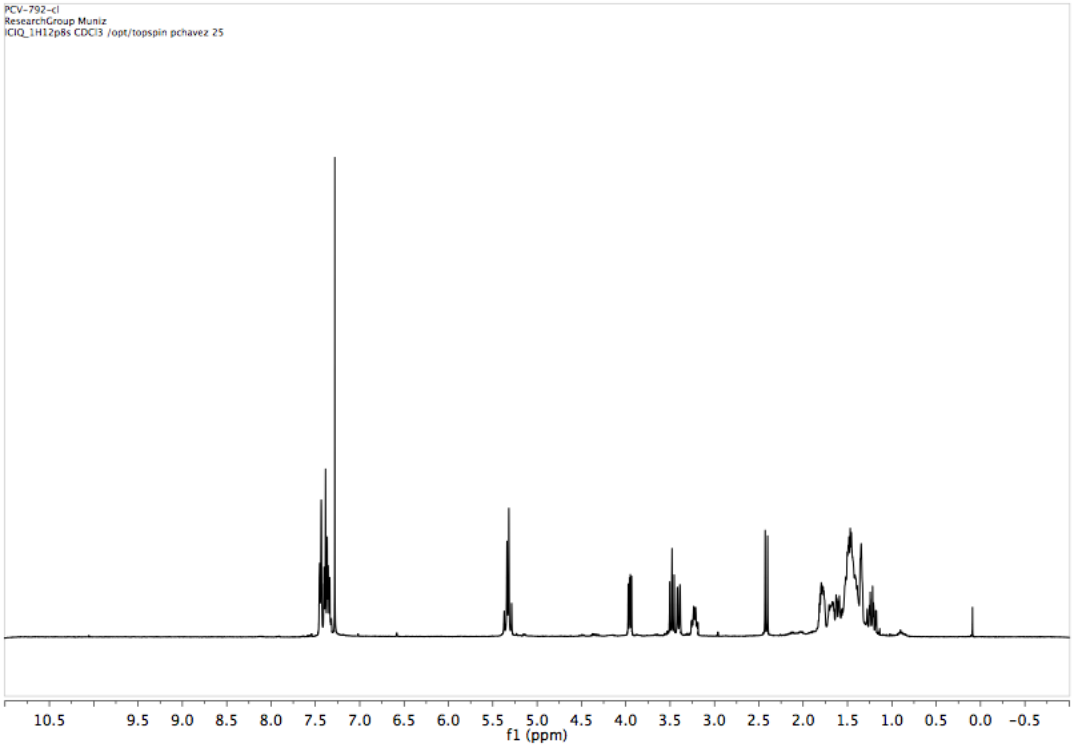

O2
S
N
NCO2t-Bu
H
H

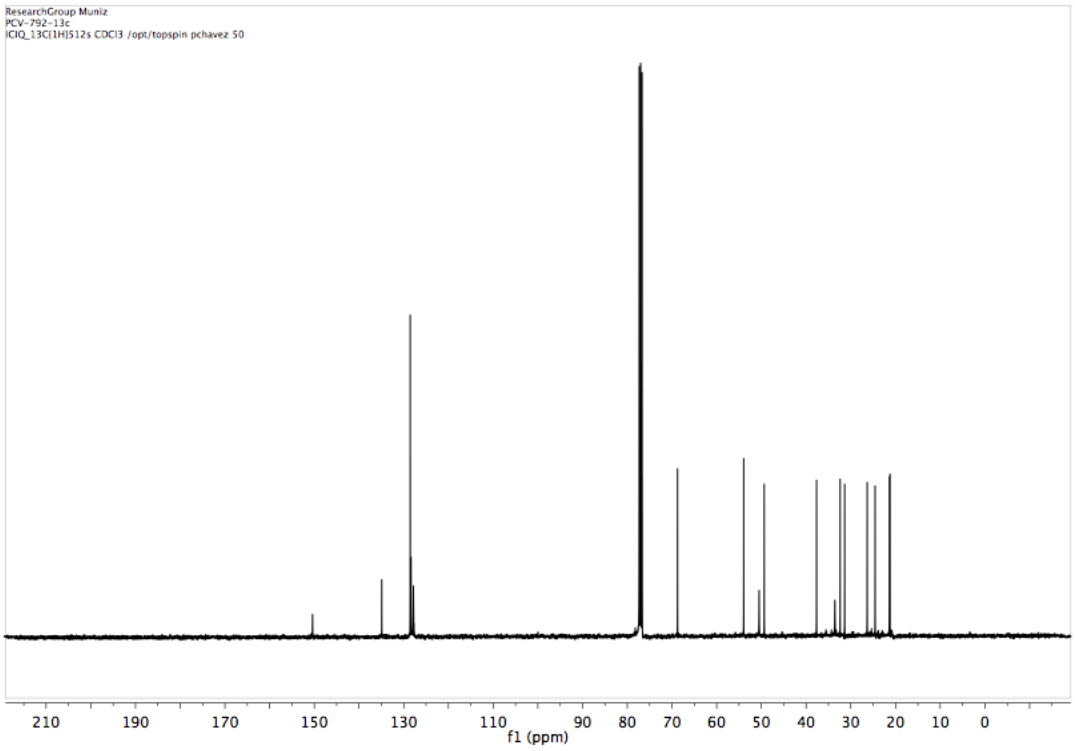
(3.5:1 d.r.)

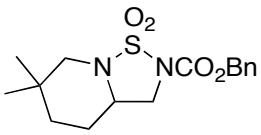

ResearchGroup Muniz
jk-pcv-840-rx5
ICIQ_1H12p8s CDCl3 /opt/topspin jkirsch 9
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

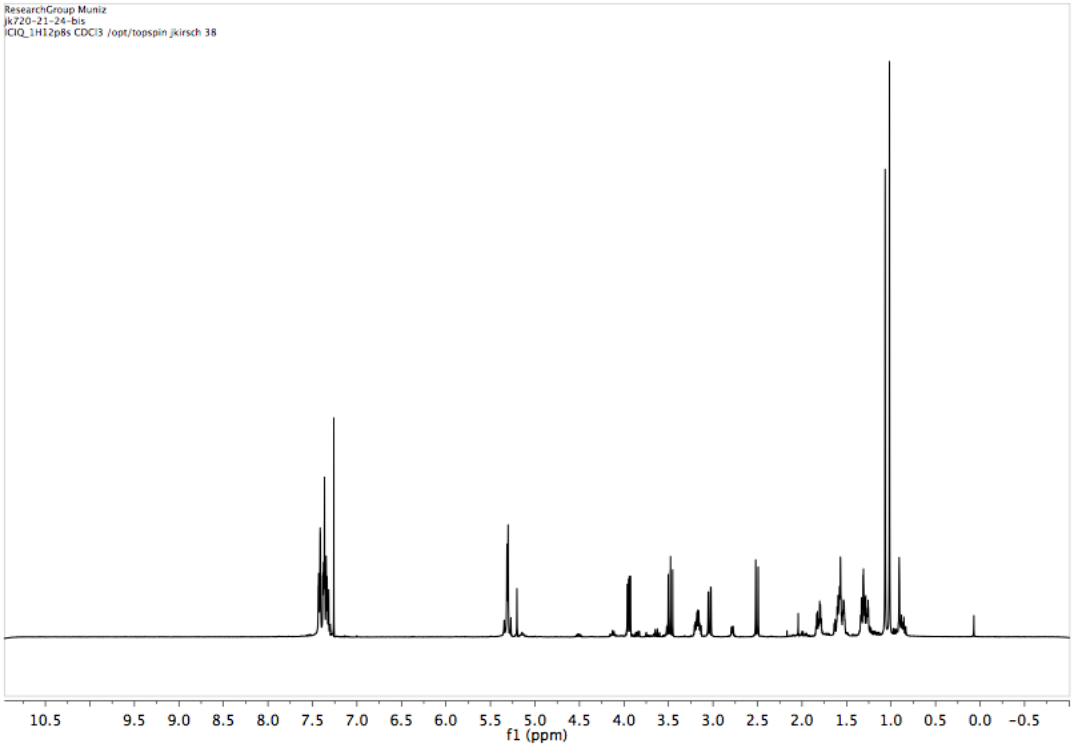

ResearchGroup Muniz
jk-pcv-840-rx5
ICIQ_13C{1H}512s CDCl3 /opt/topspin jkirsch 9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

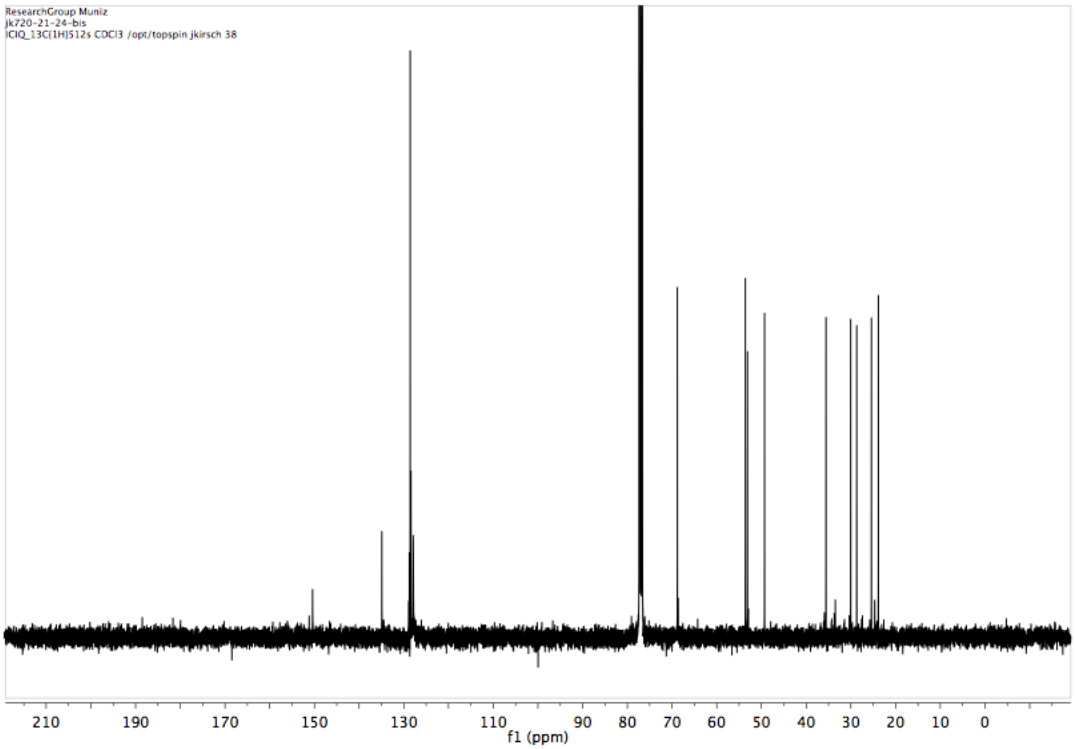

O2
S
N
NCO2Bn

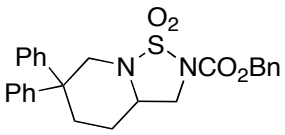

PCV-792-cl
ResearchGroup Muniz
ICIQ_1H12p8s CDCl3 /opt/topspin pchavez 25
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

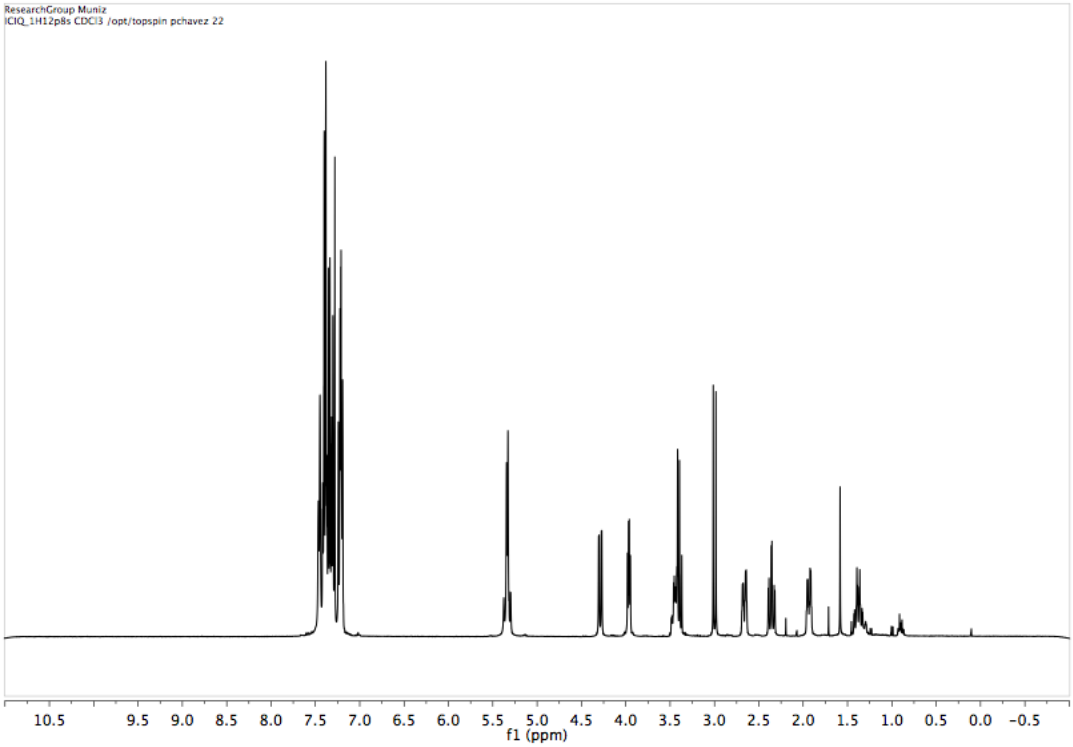

ResearchGroup Muniz
PCV-792-13c
ICIQ_13C{1H}512s CDCl3 /opt/topspin pchavez 50
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

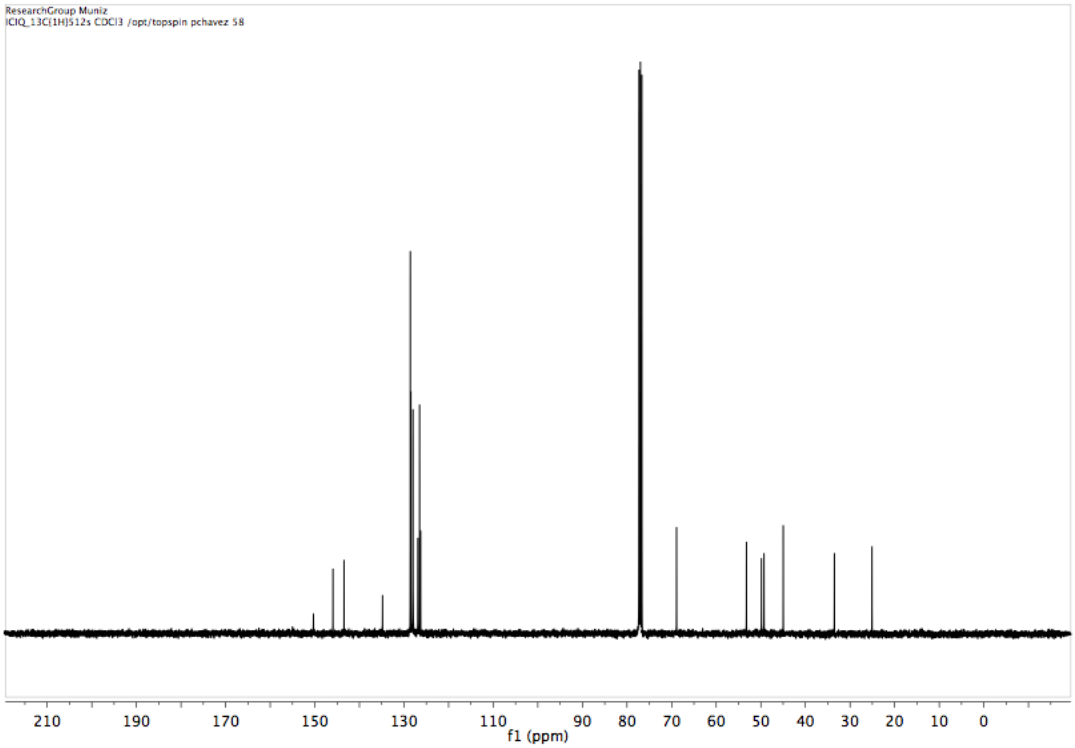

O2
S
N
NCO2Bn

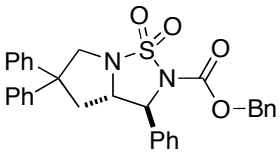

ResearchGroup Muniz
jk720-21-24-bis
ICIQ_1H12p8s CDCl3 /opt/topspin jkirsch 38
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

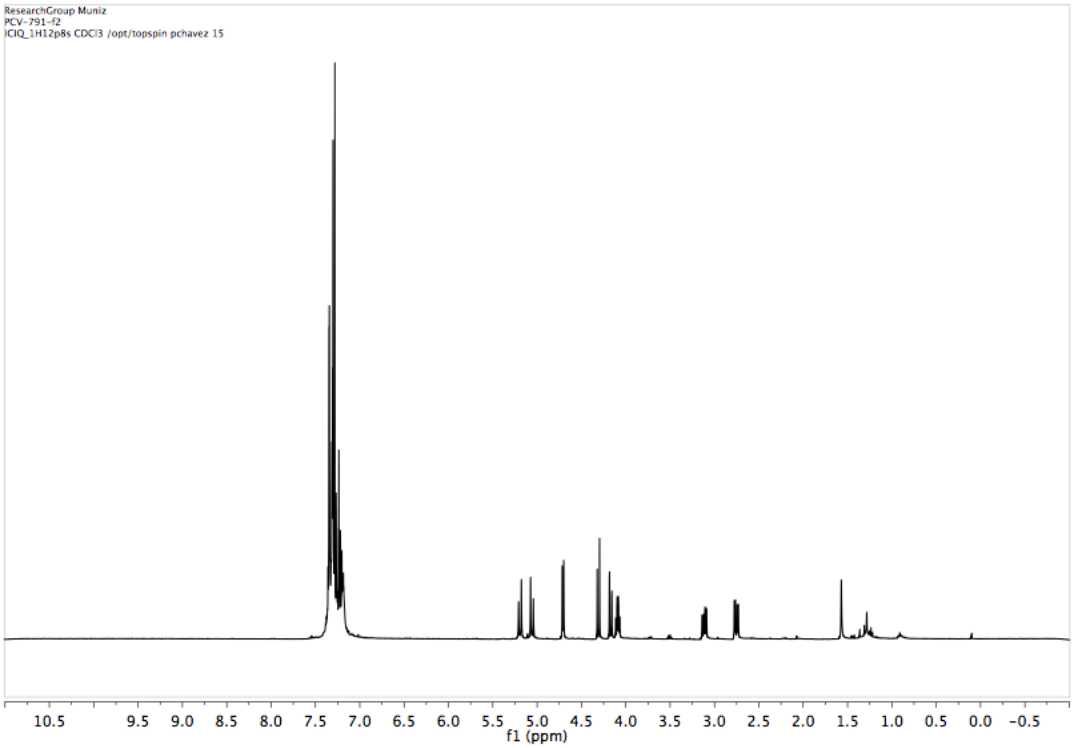

ResearchGroup Muniz
jk720-21-24-bis
ICIQ_13C{1H}512s CDCl3 /opt/topspin jkirsch 38
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

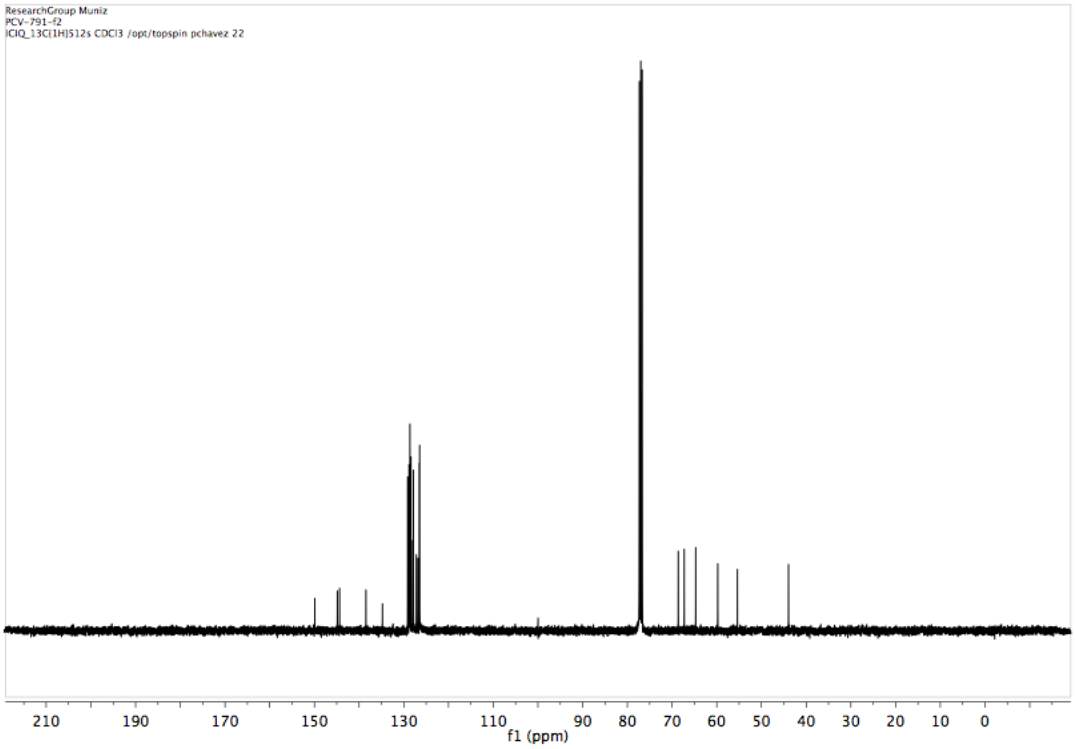

O2
S
Ph
Ph
N
NCO2Bn

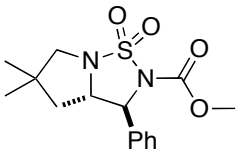

ResearchGroup Muniz
ICIQ_1H12p8s CDCl3 /opt/topspin pchavez 22
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

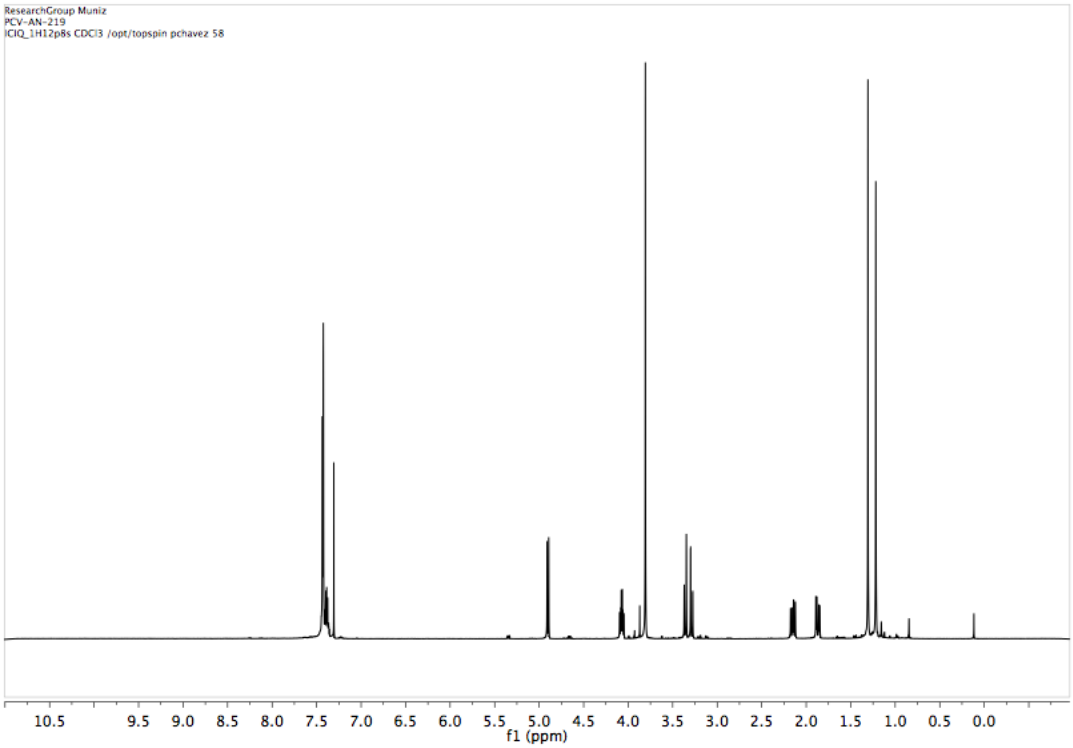

ResearchGroup Muniz
ICIQ_13C{1H}512s CDCl3 /opt/topspin pchavez 58
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

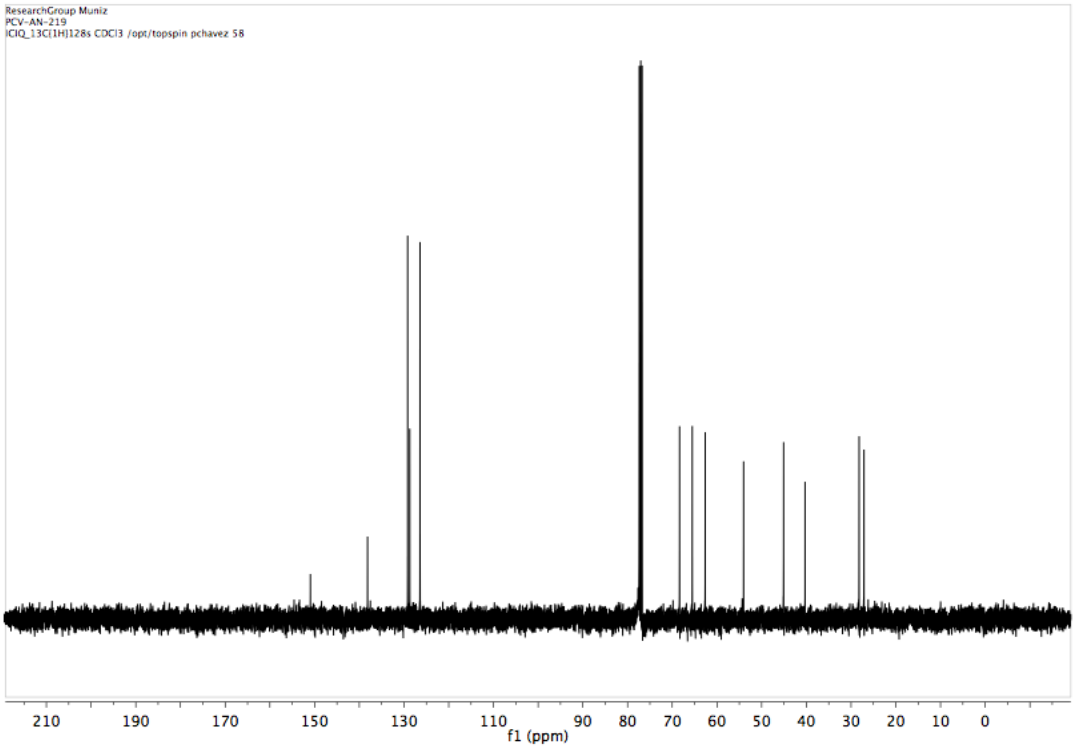

O
O
S
N
N
O
Ph
Ph
O–Bn
Ph

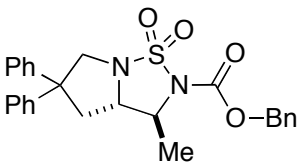

ResearchGroup Muniz
PCV-791-f2
ICIQ_1H12pBs CDCl3 /opt/topspin pchavez 15
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


ResearchGroup Muniz
PCV-791-f2
ICIQ_13C{1H}512s CDCl3 /opt/topspin pchavez 22
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

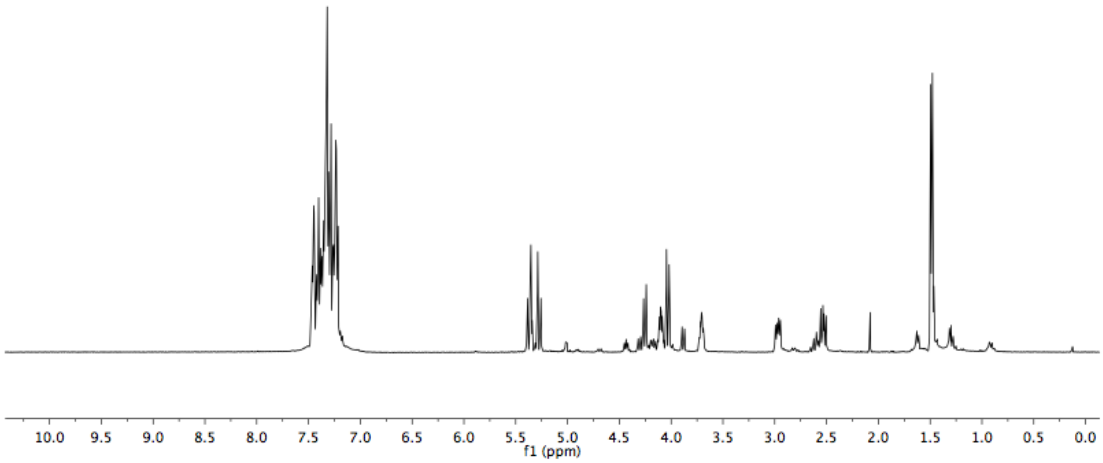

O
O
N
S
N
O
O
Ph


ResearchGroup Muniz
PCV-AN-219
ICIQ_1H12p8s CDCl3 /opt/topspin pchavez 58
10.5 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
f1 (ppm)

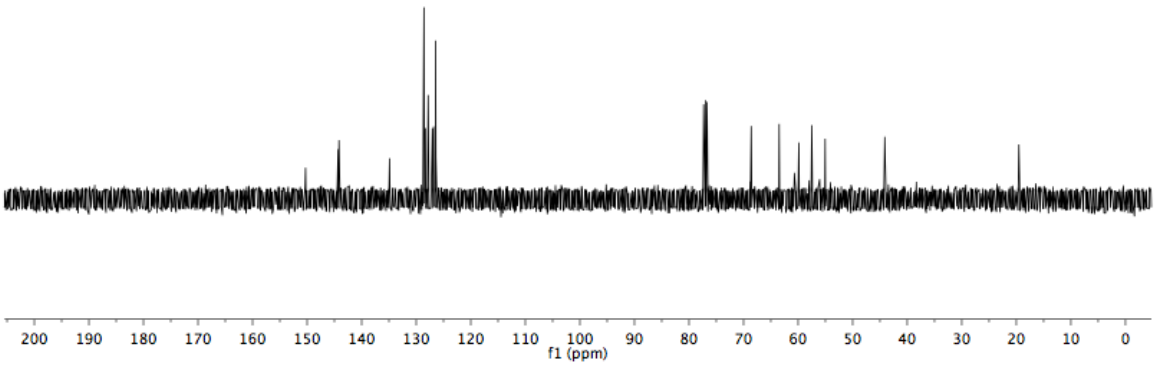

ResearchGroup Muniz
PCV-AN-219
ICIQ_13C{1H}128s CDCl3 /opt/topspin pchavez 58
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

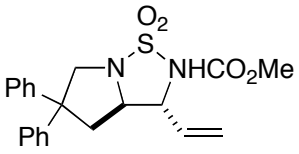


km581.col1/10

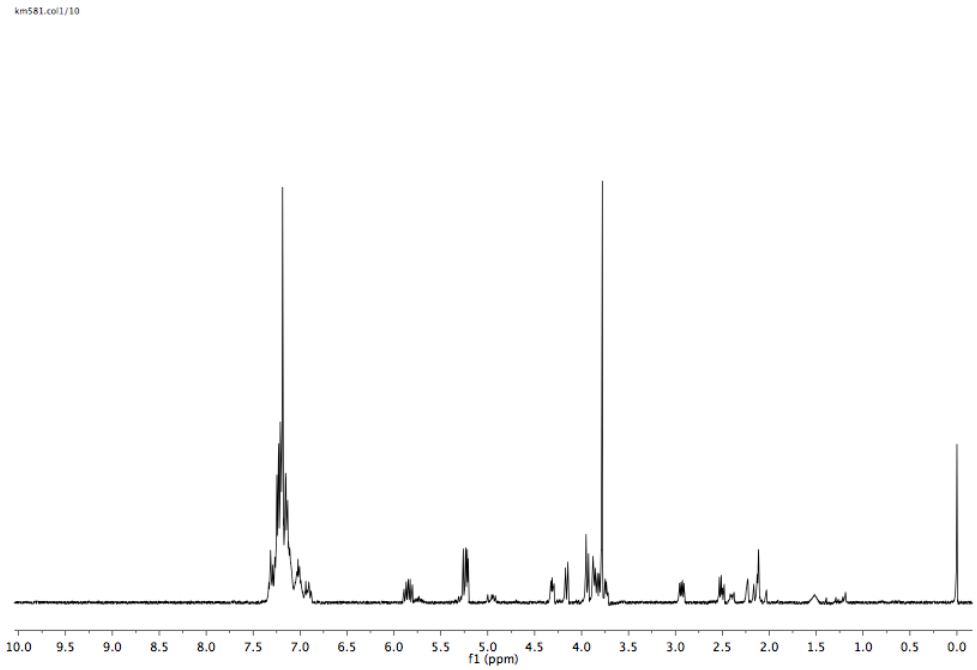


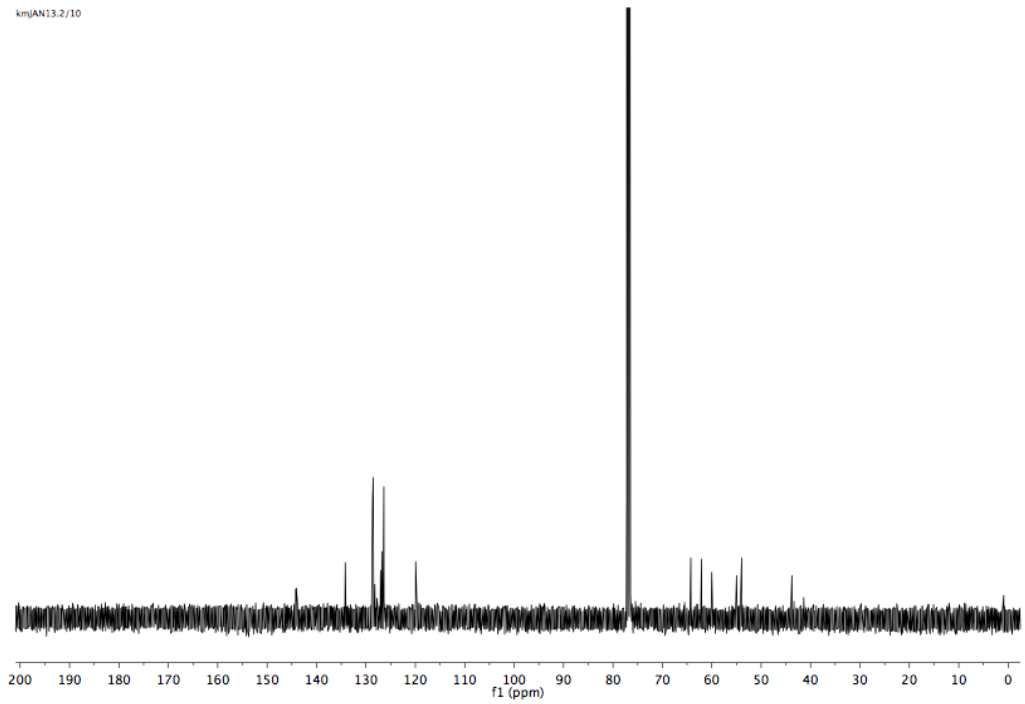
km581.col2/10




O2
S
N
NHCO2Me
Ph
Ph

***trans*-8d**


km581.col1/10
10.0 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
f1 (ppm)


kmJAN13.2/10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)