Metal-Free Diamination of Alkenes
Employing Halide Catalysis

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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$_3$ $\delta$ = 7.26 and 77.0 ppm, acetone-d$_6$ $\delta$ = 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$_2$O (0.5% HCO$_2$H) 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:


Acrylates:


Sulfamides:


**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, CH₂Ph, tBu) 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 MgSO₄ 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$_3$) $\delta$ = 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$_3$) $\delta$ = 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$_2$NaO$_4$S [M+Na]$^+$: 287.1041; found: 287.1053.

**Benzyl N-((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$_3$) $\delta$ = 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$_3$) $\delta = 150.8, 138.8, 135.7, 135.6, 134.5, 129.7, 129.5, 129.4, 128.5, 128.4, 128.1, 127.5, 127.4, 127.3, 115.3, 72.1, 68.1, 39.5, 35.4, 26.7, 19.0. IR (cm$^{-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$_2$NaO$_5$Si [M+Na]$^+$: 575.2012; found: 575.2007.

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

\[ \text{O} \text{Bn} \text{NH}_2 \]

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$_2$O at 0$^\circ$C 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 -10$^\circ$C until a bright white solid appeared. MgSO$_4$ was then added, the reaction mixture was stirred during 5 minutes, filtrated and washed with CH$_2$Cl$_2$. After evaporation under reduced pressure the product was obtained as yellow oil in 87% yield.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.30 – 7.22$ (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$_3$) $\delta = 138.7, 128.3, 127.7, 127.4, 126.7, 117.1, 78.6, 70.0, 39.3, 38.6$. 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\(_3\)) \(\delta = 7.40 - 7.27\) (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\(_3\)) \(\delta = 151.4, 137.9, 137.5, 134.7, 128.6, 128.4, 128.3, 128.3, 127.8, 127.6, 126.9, 117.9, 78.2, 70.2, 68.2, 40.7, 34.3.\) 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\(_2\)NaO\(_5\)S [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\(_3\)) \(\delta = 7.03\) (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\(_3\)) \(\delta = 150.1, 135.4(2x), 117.4, 83.8, 46.3, 37.3, 35.7(2x), 27.9.\) IR (cm\(^{-1}\)): 3283, 3228, 2980, 2931,
1702, 1641, 1440, 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_{2}NaO_{4}S [M+Na]^+: 327.1354; found: 327.1368.

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

![Structural formula of 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\(_3\)) \(\delta = 7.42 – 7.38\) (m, 5H), 5.83 (ddt, \(J = 16.8, 10.1, 6.6\) Hz, 1H), 5.23 (s, 2H), 5.06 (dd, \(J = 16.8, 3.4, 1.5\) 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\(_3\)) \(\delta = 151.3, 138.8, 134.6, 128.8, 128.7, 128.5, 114.5, 68.6, 49.7, 35.6, 34.6, 33.3, 27.1, 26.0, 21.2\). 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_{2}NaO_{4}S [M+Na]^+: 403.1667; found: 403.1657.

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

![Structural formula of 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\(_3\)) \(\delta = 8.07\) (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$_2$NaO$_4$S [M+Na]$^+$: 363.1354; found: 363.1367.

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

![Chemical Structure](image)

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$_2$NaO$_4$S [M+Na]$^+$: 487.1667; found: 487.1683.
2,2,2-Trichloro-N-(2,2-diphenylpent-4-enylcarbamoyl)ethanamide 5e

![Chemical structure](image)

Obtained as a white solid. Mp. 151°C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.91$ (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): $\delta = 161.6, 151.4, 144.8, 133.4, 128.3, 127.8, 126.6, 118.7, 49.8, 47.1, 41.9$. IR (cm$^{-1}$): $\approx$ 3448, 3319, 3234, 3087, 3060, 2933, 1717, 1704, 1539, 1469, 1237, 853. HRMS-ESI-TOF $m/z$ calculated for C$_{20}$H$_{19}$Cl$_3$N$_2$O$_2$: 424.0512, found: 424.0504.


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

![Chemical structure](image)

Obtained as a white solid. Mp. 165°C. $^1$H NMR (500 MHz, CDCl$_3$), $\delta = 7.39 - 7.06$ (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$_3$), $\delta = 150.7, 144.4, 137.4, 134.5, 134.4, 128.8, 128.7, 128.5, 128.4, 128.4, 127.7, 127.2, 127.0, 126.2, 124.6, 68.6, 50.1, 49.8, 40.1$. 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$_2$NaO$_4$S [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$_3$), $\delta$ = 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$_3$) $\delta$ = 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$_2$NaO$_4$S [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$_3$), $\delta$ = 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$_3$) $\delta$ = 150.9, 144.5, 129.9, 128.7, 128.6, 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$_2$NaO$_4$S [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$_2$O$_4$S: 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)$_2$ (177 mg, 0.55 mmol, 1.1 eq.), NaOAc (41 mg, 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$_2$S$_2$O$_3$ solution (2 mL) and brine (5 mL) and extracted with CH$_2$Cl$_2$ (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$_4$Cl and extracted with EtOAc several times. The combined organic layers were dried over Mg$_2$SO$_4$. 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:**

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 (1.82 g, 22.2 mol, 2.0 equiv) and alkene \( 1a \) (5 g, 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\(_4\)Cl and extracted with EtOAc (4 x 75 mL). The combined organic layers were dried over Mg\(_2\)SO\(_4\) 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 (4.53 g, 91%).
Characterization of diamination products

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

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

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<td>Independent reflections</td>
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anti-Benzyl-5,5-diphenyl-3-deuteriumtetrahydropyrrolo[1,2-b][1,2,5]thiadiazole-2(3H)-carboxylate 1,1-dioxide trans-2c-d

![Chemical Structure](image)

Obtained as a white solid in 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.44 – 7.16$ (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 (dd, $J = 12.3$, 6.2, 1.3 Hz, 1H), 2.49 (dd, $J = 12.3$, 8.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 151.1$, 144.2 (2x), 134.8, 128.7, 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, $J_{C-D} = 22.3$), 44.0. IR (cm$^{-1}$): 3059, 3030, 2954, 2896, 1728, 1597, 1495, 1447, 1363, 1292, 1169, 1025, 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$_2$NaO$_4$S [M+Na]$^+$: 472.1417; found: 472.1431.

anti-Benzyl 4-((tert-butyldiphenylsilyl)oxy)tetrahydropyrrolo[1,2-b][1,2,5]thiadiazole-2(3H)-carboxylate 1,1-dioxide 2j

![Chemical Structure](image)

Obtained as a white solid in 75% yield.

Mp. 98$^\circ$C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.69 – 7.63$ (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$_3$) $\delta = 150.9$, 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, 973, 931, 851, 821, 740, 698, 626, 574, 561, 503. MS (ESI-TOF): \textit{m/z} (%): 573.2 [M+Na]\(^+\) (100). HRMS-ESI-TOF \textit{m/z} calculated for C\(_{29}\)H\(_{34}\)N\(_{2}\)O\(_5\)SSi [M+Na]\(^+\): 573.1855; found: 573.1841.

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

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

Obtained as a colorless wax in 71% yield.

Mp. 113°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.45 - 7.28\) (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\(_3\)) \(\delta = 150.81, 136.97, 134.91, 128.56, 128.50, 128.30, 128.15, 127.82, 127.63, 78.01, 72.38, 68.64, 57.60, 47.89, 45.05, 29.22\). 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 \textit{m/z} calculated for C\(_{20}\)H\(_{22}\)N\(_2\)NaO\(_5\)S [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:

\begin{center}
\includegraphics[width=0.5\textwidth]{coupling.png}
\end{center}
†tert-Butyl octahydro-2H-cyclopenta[4,5]pyrrolo[1,2-b][1,2,5]thiadiazole-2-carboxylate 1,1-dioxide 2l


**Major**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 4.34$-$4.27$ (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$_3$) $\delta = 149.3$, 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$_3$) $\delta = 4.08$-$3.92$ (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$_3$) $\delta = 149.7$, 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(3H)-carboxylate 1,1-dioxide 2m

Obtained as a white solid in 82% yield.

Mp. 77°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 5.77$ – 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$_3$) $\delta$ = 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$_2$O$_4$S [M+Na]$^+$: 325.1198; found: 325.1209.

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

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Z

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(7H)-carboxylate 1,1-dioxide 4a

Obtained as a white solid in 89% yield.

Mp. 82°C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 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$_3$) $\delta$ = 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, 1303, 1054, 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$_2$NaO$_4$S [M+Na]$^+$: 401.1511; found: 401.1513.

Benzyl 6,6-dimethylhexahydro-2H-[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$_3$) $\delta$ = 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$_3$) $\delta$ = 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, 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$_{2}$NaO$_{4}$S [M+Na]$^+$: 361.1198; found: 361.1212.

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

Obtained as a white solid in 97% yield.  
Mp. 131$^\circ$C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 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$_3$) $\delta$ = 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$_{2}$NaO$_{4}$S [M+Na]$^+$: 485.1511; found: 485.1507.
Table S-3. Crystal data and structure refinement for compound 4c.

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Reflections collected            17043  
Independent reflections         5087 \[R\mathrm{int} = 0.0416\] 
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 eÅ^{-3}
6,6-Diphenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one 6e

Obtained in 80% isolated yield.

Mp. 83° C. 1H NMR (400 MHz, CDCl3): 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 (pqrst, 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). 13C -NMR (100 MHz, CDCl3): 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 C18H18N2O: 278.1419, found: 278.1422.

trans-6,6-Diphenyl-2-tosyl-1-vinyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-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. Na2SO3 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 MgSO4, 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.

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

![Structure of 8a]

Obtained as a white solid in 87% yield.

Mp. 167°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 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, $J = 10.4$, 0.8 Hz, 1H), 2.78 (dd, $J = 12.9$, 5.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 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$_2$NaO$_4$S [M+Na]$^+$: 547.1667; found: 547.1680.

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

![Structure of 8b]

Obtained as a white solid in 65% yield.

Mp. 147°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 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$_2$O$_4$S [M+Na]$^+$: 347.1041; found: 347.1055.

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

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<th>Identification code</th>
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</tr>
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<td>Empirical formula</td>
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<td>Temperature</td>
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Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2(1)/n
Unit cell dimensions
\[ a = 5.8032(8) \text{ Å} \quad a = 90.00 \degree. \]
\[ b = 20.518(3) \text{ Å} \quad b = 97.101(4) \degree. \]
\[ c = 12.8411(17) \text{ Å} \quad g = 90.00 \degree. \]
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 \(\leq h \leq 7\), -28 \(\leq k \leq 28\), -17 \(\leq l \leq 17\)
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)]
\[ R1 = 0.0349, \quad wR2 = 0.0869 \]
R indices (all data)
\[ R1 = 0.0435, \quad wR2 = 0.0908 \]
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(3H)-carboxylate 1,1-dioxide 8c

Obtained as a colorless solid in 85% yield.

Mp. 80°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 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$_3$) $\delta$ = 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$_2$NaO$_4$S [M+Na]$^+$: 485.1511; found: 485.1522.

trans-Methyl 6,6-diphenyl-1-vinyltetrahydro-1H-pyrrolo[1,2-c]sulfoximadazole-2(3H)-carboxylate 8d

A pyrex tube equipped with a stirrer bar is charged with substrate (1.0 eq.), Bu$_4$NI (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$_2$SO$_3$ 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): $\delta = 7.10$-$7.34$ (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): $\delta = 150.84$, 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): $\nu$ [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-1H-pyrrolo[1,2-c]sulfoximidazole-2(3H)-carboxylate 8d’**

Mp. 71ºC. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.08$-$7.32$ (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): $\delta = 150.82$, 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): $\nu$ [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.

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32
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<td>Largest diff. peak and hole</td>
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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$_2$SO$_3$ 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 acetate, 2/1, v/v) gives the product as a colorless solid (137 mg, 87%).

Mp. 61°C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.65$ (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$_3$): $\delta = 144.3$, 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


A representative example is as follows:

**Direct complete deprotection of sulfamide 2c**

\[
\begin{align*}
\text{LiAlH}_4 & \quad \text{Et}_2\text{O, reflux} \\
& \quad \text{Et}_2\text{O, reflux} \\
& \quad \text{LiAlH}_4
\end{align*}
\]

Lithium aluminium hydride (0.3 mmol, 3eq.) is suspended in 4mL dry Et\(_2\)O, 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\(_2\)O and then 0.07 mL NaOH (15% aqueous solution) are added carefully. After stirring for 10 min additional 0.2 mL of H\(_2\)O are added, the mixture is filtered over MgSO\(_4\) and washed with Et\(_2\)O (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\(_2\)Cl\(_2\) (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.
Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2012
Spectral characterization of diamination products
Electronic Supplementary Material (ESI) for Chemical Science
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Electronic Supplementary Material (ESI) for Chemical Science
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trans-8d