Stereoselective Intermolecular C-H Amination Reactions

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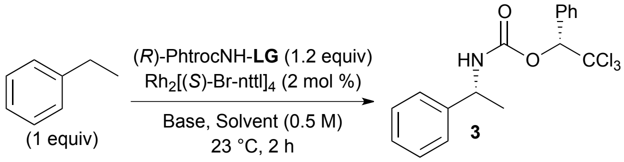
Supplementary Information

Table S1 Stereoselective C-H Amination of Ethyl Benzene with Chiral Reagent **1** and **2.**



Entry	LG	Base	Solvent	Crude dr[a]	Yield[b], dr[c]
1	OTs (**1**)	$K_2CO_{3\ \text{sat.}}$	PhF	9.0:1	50%, 50:1
2	OTs (**1**)	$K_2CO_{3\ \text{sat.}}$	^{i}PrOAc	8.5:1	65%, 8.6:1
3	OMs (**2**)	$K_2CO_{3\ \text{sat.}}$	^{i}PrOAc	8.2:1	43%, 86:1
4	OMs (**2**)	$K_2CO_{3\ \text{sat.}}$	EtOAc	8.1:1	47%, 25:1
5	OMs (**2**)	KOAc	EtOAc	7.7:1	58%, 54:1
6	OTs (**1**)	KOAc	EtOAc	7.3:1	60%, 9.4:1
7	OMs (**2**)	KOAc	^{i}PrOAc	9.0:1	57%, 16:1

[a] *R*,*R*:*S*,*R* ratio determined by HPLC on the crude material. [b] Isolated yield. [c] *R*,*R*:*S*,*R* ratio determined by HPLC on the purified material.

General Informations: (*R*)-1-Phenyl-2,2,2-trichloroethanol was prepared from trichloroacetophenone[1] by CBS reduction according to literature procedure.[2] $Rh_2(Br\text{-}nttl)_4$ was prepared according to literature.[3] Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, or aqueous potassium permanganate. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter at 589 nm. Data are reported as follows: $[\alpha]_{l}^{temp.}$, concentration (*c* g/100mL), and solvent. Infrared spectra were recorded on a Bruker FTIR spectrometer equipped with an ATR and are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. ^1H NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.26 ppm) or dimethylsulfoxide (2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) or dmso-D_6 (39.52 ppm) on the δ scale. Mass spectra were obtained on a LC-MSD TOF (ESI) Agilent Technologies high resolution from the Centre régional de spectrométrie de masse de l'Université de Montréal. High performance liquid chromatography (HPLC) analyses were performed on a Hewlett Packard 1100 Series quaternary gradient pump with diode-array detector interfaced with HP Chemstation software. Values for enantiomeric excess were determined using a chiral column. Data are reported as follows: column type, flow, solvent used, and retention time (t_r). Analytical supercritic fluid chromatography (SFC) and analytical supercritic fluid chromatography with mass spectroscopy (SFC-MS) were performed at the Laboratoire d'Analyse et de Séparation Chirale par SFC de l'Université de Montréal and Data are reported as follows: column type, eluent, flow rate, and retention time (t_r).

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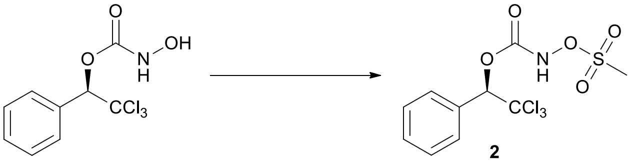
[1] Mellin-Morlière, C.; Aitken, D. J.; Bull, S. D.; Davies, S. G.; Husson, H.-P. *Tetrahedron: Asymmetry* **2001**, *12*, 149-155.

[2] a) Corey, E. J.; Bakshi, R. K. *Tetrahedron Lett.* **1990**, *31*, 611-614. b) Mathre, D. J.; Jones, T. K.; Xavier, L. C.; Blacklock, T. J.; Reamer, R. A.; Mohan, J. J.; Jones, E. T. T.; Hoogsteen, K.; Baum, M. W.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 751-762.

[3] Müller, P.; Ghanem, A. *Org. Lett.* **2004**, *6*, 4347-4350.

Synthesis of (*R*)-1-Phenyl-2,2,2-trichloroethyl-*N*-mesyloxycarbamate (2).

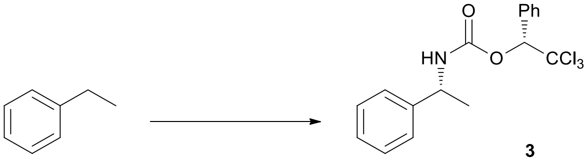
(*R*)-1-phenyl-2,2,2-trichloroethyl-*N*-hydroxycarbamate was prepared according to literature procedure.[4]



2

To a solution of (*R*)-1-phenyl-2,2,2-trichloroethyl-*N*-hydroxycarbamate (6.47 g, 22.7 mmol) in Et_2O (230 mL) at 0 °C was added dropwise methanesulfonyl chloride (1.76 mL, 22.7 mmol), then triethylamine (3.17 mL, 22.7 mmol). The resulting white suspension was stirred at 0 °C for 1 h. The mixture was quenched with H_2O and the resulting aqueous layer was extracted with ether (2 x 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude compound as yellowish oil. Purification by flash chromatography (25% Et_2O/Pentane), followed by recrystallization in $CHCl_3$/Hexanes, yields the desired *N*-mesyloxycarbamate **2** as a white solid (4.77g, 58%). The enantiomeric excess was determined to be 95% by SFC analysis using Chiracel ODH chiralpak column (25 cm, 30 °C, 15% MeOH at 150 bar, retention time: t_{minor} = 2.8 min, and t_{major} = 3.9 min.). R_f 0.57 (50% Et_2O/Pentane); mp 75 – 77 °C; $[\alpha]_D^{25}$ = - 14.2 (c 1.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s (br), 1H), 7.62-7.59 (m, 2H), 7.49-7.40 (m, 3H), 6.34 (s, 1H), 3.20 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.81, 131.74, 130.53, 129.67, 128.38, 98.63, 85.21, 36.73; IR (neat) 3485, 3177, 3034, 3015, 2962, 2935,1767, 1752, 1651, 1484, 1456, 1419, 1374, 1334, 1320, 1238, 1202, 1184, 1093, 1079, 1027; HMRS (ESI^+) calc. for $C_{10}H_{10}Cl_3NNaO_5S$ $[M+Na]^+$: 383.92375; found: 383.92393.

Typical Procedure for the Diastereoselective Amination of Benzylic C–H Bonds: Synthesis of (*R*)-2,2,2-trichloro-1-phenylethyl (*R*)-1-phenylethylcarbamate (3).



3

A solution of ethylbenzene (27 mg, 0.25 mmol), (*R*)-1-phenyl-2,2,2-trichloroethyl-*N*-mesyloxycarbamate (**2**) (109 mg, 0.30 mmol) and $Rh_2[(S)\text{-Br-nttl}]_4$ (9 mg, 2 mol%) in EtOAc (0.5 mL) was vigorously stirred at room temperature in an open 4 mL vial for 5 min. Potassium acetate (74 mg, 0.75 mmol) was then added. The resulting green heterogeneous reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then diluted with Et_2O (3 mL) and filtered on Celite®. The solid was washed with Et_2O (2 × 3 mL) and the filtrate was concentrated *in vacuo* to give the crude product in a 7.8:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 97/3 hexanes/iPrOH at 1mL/min., retention time: t_{minor} = 27.4 min. and t_{major} = 29.9 min.). Purification by flash chromatography (10% – 20% Et_2O/Pentane) produced a white solid (54 mg, 58%) as a 54:1 diastereomeric mixture. **R_f** 0.40 (20% Et_2O/Pentane); mp 62-64 °C; **$[\alpha]_D^{25}$** = +36.2 (c 1.4, $CHCl_3$). **^1H NMR** (400 MHz, DMSO, 110 °C) δ 7.79 (s (br), 1H), 7.59 – 7.65 (m, 2H), 7.43 – 7.37 (m, 3H), 7.33 – 7.22 (m, 4H), 7.21 – 7.14 (m, 1H), 6.23 (s, 1H), 4.79 – 4.67 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 153.22, 144.50, 133.61, 129.56, 129.42, 128.24, 127.89, 126.73, 125.69, 99.96, 81.95, 50.53, 22.86; **IR** (neat) 3322, 3032, 2929, 1713, 1586, 1495, 1453, 1378, 1343, 1281, 1236, 1202, 1146, 1063, 1027, 983 cm^{-1}; **HMRS** (ESI) calc. for $C_{17}H_{17}Cl_3NO_2$ $[M+H]^+$: 372.03194; found: 372.03203.

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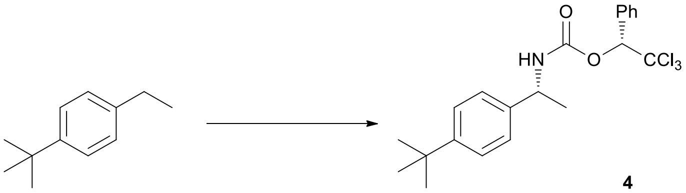
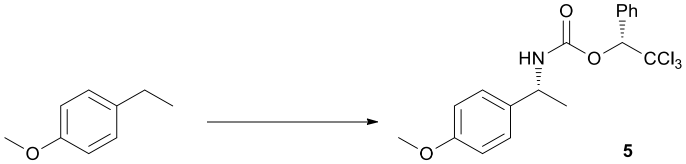
[4] Lebel, H.; Spitz, C.; Leogane, O.; Trudel, C.; Parmentier, M. *Org. Lett.* **2011**, *13*, 5460-5463.



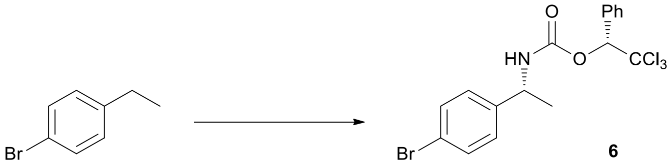
4

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-*tert*-butylphenyl)ethylcarbamate (4). The title compound was prepared from 1-*tert*-butyl-4-ethylbenzene (37 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **4** was obtained as a 12:1 diastereomeric mixture (determined by HPLC analysis using WELCO 25 cm column, 95/5 hexanes/iPrOH at 1mL/min., retention time: t_{major} = 7.5 min. and t_{minor} = 9.4 min.). Purification by flash chromatography (10% – 20% Et_2O/Pentane) produced a white solid (73 mg, 70%) as a >99:1 diastereomeric mixture. **R_f** 0.37 (toluene); **$[\alpha]_D^{23}$** = +51.0 (c 0.9, $CHCl_3$); **mp** 103-104 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.74 (s (br), 1H) 7.66 – 7.57 (m, 2H), 7.45 – 7.37 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.24 (s, 1H), 4.78 – 4.64 (m, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, DMSO) δ 153.21, 149.02, 141.41, 133.60, 129.55, 129.45, 127.90, 125.41, 124.98, 100.01, 81.86, 50.18, 34.10, 31.13, 22.81; **IR** (neat) 3331, 2960, 2868, 1717, 1498, 1454, 1378, 1343, 1269, 1236, 1201, 1110, 1085, 1063, 1017, 985, cm^{-1}; **HMRS** (ESI) calc. for $C_{21}H_{25}Cl_3NO_2$ $[M+H]^+$: 428.09454; found: 428.09401.



5

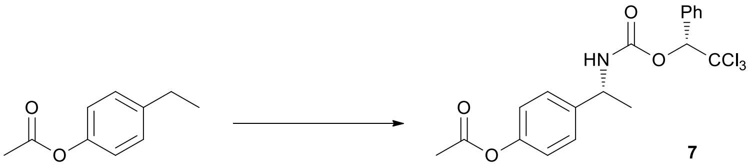
(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-methoxyphenyl)ethylcarbamate (5). The title compound was prepared from 4-ethylanisole (34 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine 5 was obtained as a 11:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 97/3 hexanes/iPrOH at 1mL/min., retention time: t_{major} = 36.7 min. and t_{minor} = 48.7 min.). Purification by flash chromatography (20% Et_2O/pentane) produced a white solid (63.5 mg, 64%) as a 18:1 diastereomeric mixture. **R_f** 0.34 (25% Et_2O/Pentane); **$[\alpha]_D^{23}$** = +50.2 (c 5.0, $CHCl_3$); **mp** 75-77 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.70 (s (br), 1H), 7.66 – 7.58 (m, 2H), 7.44 – 7.37 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.24 (s, 1H), 4.76 – 4.62 (m, 1H), 3.73 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 158.06, 153.15, 136.44, 133.62, 129.55, 129.44, 127.89, 126.90, 113.59, 100.00, 81.87, 55.00, 49.95, 22.85; **IR** (neat) 3331, 2954, 2836, 1715, 1612, 1586, 1511, 1454, 1377, 1343, 1287, 1240, 1178, 1146, 1084, 1061 cm^{-1}; **HMRS** (ESI) calc. for $C_{18}H_{19}Cl_3NO_3$ $[M+H]^+$: 402.04250; found: 402.04244.



6

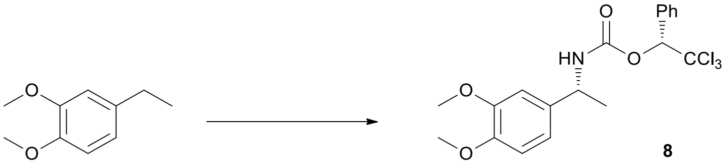
(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-bromophenyl)ethylcarbamate (6). The title compound was prepared from 1-bromo-4-ethylbenzene (44.6 mg, 0.24 mmol) following the typical procedure. The desired crude benzylic amine **6** was obtained as a 9.1:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 96/4 hexanes/iPrOH at 1mL/min., retention time: t_{major} = 21.6 min. and t_{minor} = 38.9 min.). Purification by flash chromatography (20% Et_2O/Pentane) produced a white solid (81.7 mg, 74%) as a >99:1 diastereomeric mixture. **R_f** 0.34 (100% toluene); **$[\alpha]_D^{23}$** = +37.8 (c 5.3, $CHCl_3$); **mp** 157-159 °C; **^{1}H**

NMR (400 MHz, DMSO, 110 °C) δ 7.85 (s (br), 1H), 7.65 – 7.58 (m, 2H), 7.47 – 7.37 (m, 5H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.22 (s, 1H), 4.71 (p, *J* = 7.1 Hz, 1H), 1.43 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.41, 141.90, 133.33, 131.90, 129.79, 129.73, 128.00, 127.85, 121.46, 99.91, 83.34, 50.70, 22.26; **IR** (neat) 3421, 3327, 3037, 2975, 1714, 1489, 1454, 1379, 1339, 1305, 1240, 1204, 1150, 1110, 1083, 1066, 1009 cm^{-1}; **HMRS** (ESI) calc. for $C_{17}H_{16}BrCl_3NO_2$ $[M+H]^+$: 449.94245; found: 449.94255.



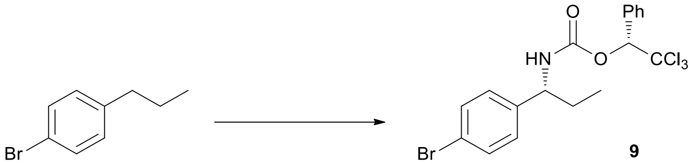
7

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-acetoxyphenyl)ethylcarbamate (7). The title compound was prepared from 4-ethylphenyl acetate (41 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **7** was obtained as a 10:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 97/3 hexanes/iPrOH at 1mL/min., retention time: t_{minor} = 46.7 min. and t_{major} = 50.5 min.). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (10% – 20% EtOAc/Hexanes) produced a slightly yellow solid (86 mg, 80%) as a 11:1 diastereomeric mixture. **R_f** 0.24 (100% $CHCl_3$); **$[\alpha]_D^{23}$** = +31.6 (c 2.5, $CHCl_3$); **mp** 69-70 °C; Major diastereoisomer: **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.84 (s (br), 1H), 7.64 – 7.59 (m, 2H), 7.43 – 7.39 (m, 3H), 7.34 – 7.28 (m, 2H), 7.04 – 6.98 (m, 2H), 6.23 (s, 1H), 4.74 (m, 1H), 2.23 (s, 3H), 1.44 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, CDCl3) δ 170.34, 154.15, 150.75, 140.97, 134.10, 130.46, 128.69, 128.03, 122.62, 116.28, 100.66, 84.03, 78.28, 77.85, 77.43, 51.35, 22.85, 21.94; **IR** (neat) 3337, 3032, 2962, 2924, 2852, 1722, 1598, 1504, 1451, 1372, 1340, 1300, 1197, 1062, 1015, 913 cm^{-1}; **HMRS** (ESI) calc. for $C_{19}H_{22}Cl_3N_2O_4$ $[M+NH_4]^+$: 447.06397; found: 447.06413.



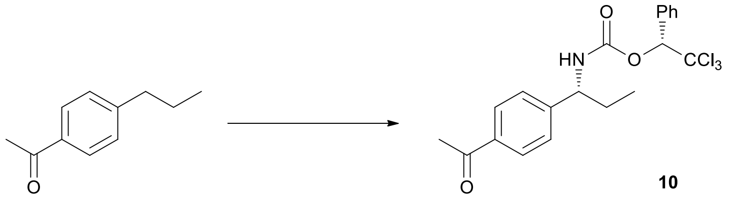
8

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(3,4-dimethoxyphenyl)ethylcarbamate (8). The title compound was prepared from 1,2-dimethoxy-4-ethylbenzene (42 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **8** was obtained as a 18:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 93/7 hexanes/iPrOH at 1mL/min., retention time: t_{major} = 34.2 min. and t_{minor} = 53.0 min.). A drop of pyridine (~20 μL) is added to the crude product, followed by purification by flash chromatography (20% – 30% EtOAc/Hexanes) produced a white solid (89 mg, 82%) as a 43:1 diastereomeric mixture. **R_f** 0.37 (30% EtOAc/Hexanes); **$[\alpha]_D^{23}$** = +32.5 (c 5.1, $CHCl_3$); **mp** 106-108 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.70 – 7.59 (m, 3H), 7.45 – 7.36 (m, 3H), 6.94 – 6.89 (m, 1H), 6.88 – 6.79 (m, 2H), 6.24 (s, 1H), 4.73 – 4.61 (m, 1H), 3.73 (s, 1H), 3.70 (s, 1H), 1.43 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.43, 149.16, 148.50, 133.50, 129.72, 129.69, 127.93, 117.99, 114.52, 111.29, 109.70, 99.94, 83.25, 56.02, 55.91, 50.88, 22.07; **IR** (neat) 3338, 3010, 2957, 2935, 2837, 1718, 1594, 1514, 1453, 1419, 1376, 1343, 1255, 1231, 1201, 1168, 1141, 1086, 1064, 1025 cm^{-1}; **HMRS** (ESI) calc. for $C_{19}H_{20}Cl_3NNaO_4$ $[M+Na]^+$: 454.03501; found: 454.03587.



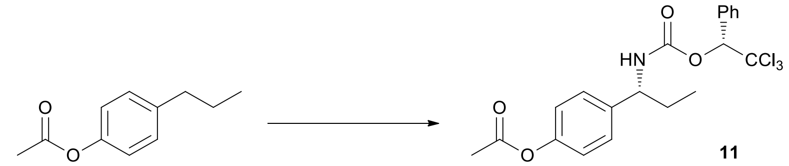
9

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-bromophenyl)propylcarbamate (9). The title compound was prepared from 1-bromo-4-propylbenzene (50 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **9** was obtained as a 5.1:1 diastereomeric mixture (determined by SFC-MS analysis using Chiracel-ADH chiralpak column 25 cm, 25 °C, 8% *i*PrOH at 150 bars, retention time: t_{major} = 25.9 min., t_{minor} = 32.5 min.). Purification by flash chromatography (50% $CHCl_3$/pentane) produced a colorless sticky oil (73 mg, 63%) as a >99:1 diastereomeric mixture. $\mathbf{R}_f$ 0.21 (50% $CHCl_3$/pentane); $[\alpha]_D^{23}$ = +47.2 (c 2.4, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.73 (s (br), 1H), 7.65 – 7.58 (m, 2H), 7.46 – 7.38 (m, 5H), 7.29 – 7.21 (m, 2H), 6.23 (s, 1H), 4.54 – 4. 42 (m, 1H), 1.87 – 1.68 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.72, 140.86, 133.33, 131.87, 129.75, 128.31, 127.99, 121.44, 100.02, 83.33, 56.82, 29.51, 10.73; **IR** (neat) 3421, 3332, 3035, 2967, 2934, 2876, 1718, 1590, 1490, 1455, 1408, 1380, 1342, 1276, 1226, 1201, 1074, 1033, 1010, 978 cm^{-1}; **HMRS** (ESI) calc. for $C_{18}H_{18}BrCl_3NO_2$ $[M+H]^+$: 463.95810; found: 463.95862.



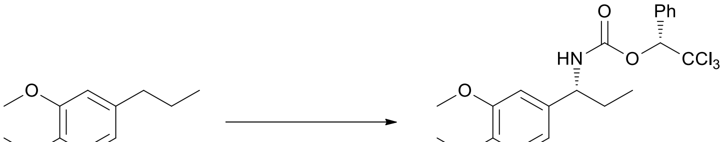
10

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-acetylphenyl)propylcarbamate (10). The title compound was prepared from 4-propylacetophenone (40 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **10** was obtained as a 6.6:1 diastereomeric mixture (determined by SFC-MS analysis using Chiracel-ADH chiralpak column 25 cm, 25 °C, 5% MeOH at 150 bars, retention time: t_{major} = 18.3 min., t_{minor} = 20.2 min.). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (10% – 20% EtOAc/Hexanes) produced a colorless sticky oil that solidifies on standing (73 mg, 68%) as a 7.4:1 diastereomeric mixture. $\mathbf{R}_f$ 0.28 (20% EtOAc/hexanes); $[\alpha]_D^{23}$ = +6.1 (c 3.1, $CHCl_3$); **mp** 31-32 °C; Major diastereomer: **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.88 – 7.80 (m, 2H), 7.68 – 7.57 (m, 3H), 7.45 – 7.38 (m, 5H), 6.62 (s (br), 1H), 6.26 – 6.17 (m, 1H), 4.62 – 4. 51 (m, 1H), 2.54 – 2.51 (m, 3H), 1.90 – 1.70 (m, 2H), 0.95 – 0.83 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.75, 153.75, 136.49, 133.29, 129.73, 128.89, 127.98, 126.72, 99.76, 83.36, 57.12, 29.60, 26.74, 10.71; **IR** (neat) 3326, 3062, 3034, 2967, 2936, 2874, 2845, 1720, 1674, 1607, 1573, 1522, 1455, 1415, 1360, 1342, 1305, 1267, 1229, 1201, 1145, 1085, 1070, 1033, 1016, 976 cm^{-1}; **HMRS** (ESI) calc. for $C_{20}H_{21}Cl_3NO_3$ $[M+H]^+$: 428.05815; found: 428.05811.



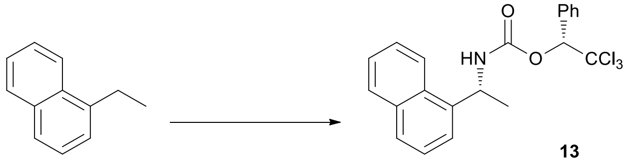
11

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(4-acetoxyphenyl)propylcarbamate (11). The title compound was prepared from 4-propylphenyl acetate (44 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **11** was obtained as a 10:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 97/3 hexanes/iPrOH at 1mL/min., retention time: t_{minor} = 39.8 min. and t_{minor} = 47.9 min.). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (100% $CHCl_3$) produced a colorless wax that solidifies on standing (64 mg, 58%) as a 12:1 diastereomeric mixture. **R*f*** 0.22 (100% $CHCl_3$); **[α]$_D$^{23}** = +24.2 (c 3.6, $CHCl_3$); **mp** 32-34 °C; Major diastereomer: **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.71 (s (br), 1H), 7.65 – 7.61 (m, 2H), 7.44 – 7.38 (m, 3H), 7.34 – 7.29 (m, 2H), 7.05 – 6.99 (m, 2H), 6.24 (s, 1H), 4.55 – 4. 46 (m, 1H), 2.27 – 2.19 (m, 3H), 1.89 – 1.68 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.60, 153.76, 150.02, 139.29, 133.37, 129.75, 128.03, 127.98, 127.68, 121.85, 100.07, 83.28, 56.78, 29.53, 21.25, 10.81; **IR** (neat) 3495, 3342, 3065, 3035, 3012, 2966, 2934, 2875, 1723, 1597, 1507, 1455, 1422, 1370, 1343, 1279, 1196, 1086, 1073, 1033, 1016, 976 cm^{-1}; **HMRS** (ESI) calc. for $C_{20}H_{21}Cl_3NO_4$ [M+H]$^+$: 444.05307; found: 444.05375.



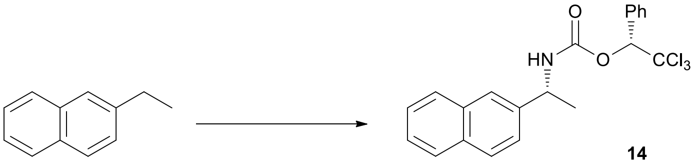
12

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(3,4-dimethoxyphenyl)propylcarbamate (12). The title compound was prepared from 1,2-dimethoxy-4-propylbenzene (45 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **12** was obtained as a 8.0:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 93/7 hexanes/iPrOH at 1mL/min., retention time: t_{major} = 36.1 min. and t_{minor} = 54.0 min.). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (15-20% EtOAc/Hexanes) produced a slightly yellow oil that solidifies on standing (66 mg, 59%) as a 8.5:1 diastereomeric mixture. **R*f*** 0.23 (20% EtOAc/Hexanes); **[α]$_D$^{23}** = +12.6 (c 2.7, $CHCl_3$); **mp** 52-54 °C; Major diastereomer: **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.68 – 7.57 (m, 3H), 7.44 – 7.38 (m, 3H), 6.95 – 6.90 (m, 1H), 6.87 – 6.79 (m, 2H), 6.25 (s, 1H), 4.47 – 4. 38 (m, 1H), 3.73 (s, 3H), 3.72 (s, 1H), 1.84 – 1.70 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.74, 149.19, 148.51, 134.35, 133.48, 129.75, 128.02, 127.94, 118.54, 111.33, 110.06, 100.08, 83.53, 57.16, 56.03, 55.99, 29.50, 10.88; **IR** (neat) 3342, 3034, 2963, 2935, 2876, 2836, 1729, 1593, 1515, 1455, 1420, 1379, 1342, 1263, 1233, 1202, 1165, 1143, 1086, 1076, 1028, 978 cm^{-1}; **HMRS** (ESI) calc. for $C_{20}H_{23}Cl_3NO_4$ [M+H]$^+$: 446.06872; found: 446.06877.



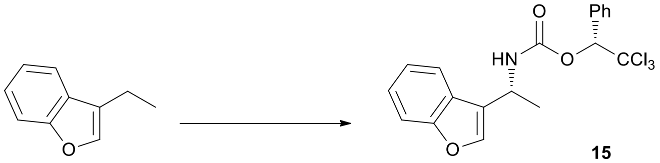
13

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(naphthalen-1-yl)ethylcarbamate (13). The title compound was prepared from 1-ethylnaphthalene (39 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **13** was obtained as a 39:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 93/7 hexanes/iPrOH at 1mL/min., retention time: t_{minor} = 25.5 min. and t_{major} = 29.5 min.). Purification by flash chromatography (10 – 20% Et_2O/pentane) produced a white solid (76 mg, 72%) as a 95:1 diastereomeric mixture. **R*f*** 0.35 (20% Et_2O/pentane); **[α]$_D$^{23}** = –11.9 (c 2.1, $CHCl_3$); **mp** 110-111 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 8.15 – 8.06 (m, 1H), 8.00 (s (br), 1H), 7.92 – 7.86 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.35 (m, 4H), 6.23 (s, 1H), 5.60 – 5.49 (m, 1H), 1.59 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 153.21, 140.33, 133.63, 133.27, 129.97, 129.53, 129.36, 128.66, 127.86, 127.24, 126.19, 125.60, 125.43, 122.81, 122.01, 99.90, 82.12, 46.79, 22.14; **IR** (neat) 3330, 3039, 2929, 1716, 1598, 1498, 1454, 1377, 1336, 1289, 1236, 1146, 1086, 1064, 1028, 980, 908, 821, 798, 777, 733, 698 cm-1; **HMRS** (ESI) calc. for $C_{21}H_{19}Cl_3NO_2$ $[M+H]^+$: 422.04759; found: 422.04798.



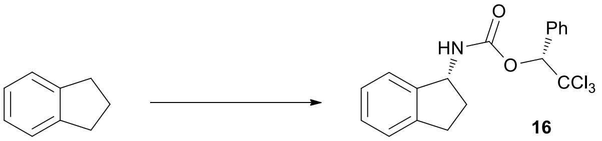
14

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(naphthalen-2-yl)ethylcarbamate (14). The title compound was prepared from 2-ethylnaphthalene (39 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **14** was obtained as a 15:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD chiralpak 25 cm column, 93/7 hexanes/iPrOH at 1mL/min., retention time: t_{major} = 32.1 min. and t_{minor} = 40.6 min.). Purification by flash chromatography (10 – 20% Et_2O/pentane) produced a white solid (77 mg, 73%) as a >99:1 diastereomeric mixture. $\mathbf{R}_f$ 0.35 (20% Et_2O/pentane); $[\alpha]_D^{23}$ = +64.7 (c 0.9, $CHCl_3$); **mp** 78-80 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.92 (s (br), 1H), 7.85 – 7.73 (m, 4H), 7.67 – 7.60 (m, 2H), 7.50 – 7.43 (m, 3H), 7.42 – 7.37 (m, 3H), 6.24 (s, 1H), 4.96 – 4.86 (m, 1H), 1.54 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 153.29, 141.92, 133.62, 132.72, 132.04, 129.54, 129.38, 127.95, 127.87, 127.55, 127.45, 126.16, 125.66, 124.50, 123.74, 99.90, 82.04, 50.66, 22.57; **IR** (neat) 3327, 3055, 2972, 1714, 1601, 1497, 1454, 1379, 1328, 1294, 1271, 1229, 1201, 1084, 1062, 1024, 987, 950, 908, 856, 818, 785, 733, 697 cm-1; **HMRS** (ESI) calc. for $C_{21}H_{19}Cl_3NO_2$ $[M+H]^+$: 422.04759; found: 422.04871.



15

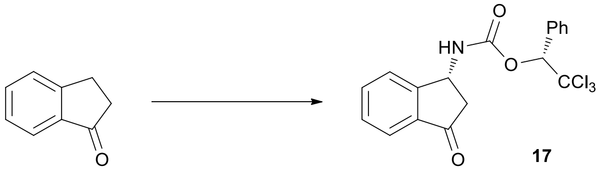
(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-1-(benzofuran-3-yl)ethylcarbamate (15). The title compound was prepared from 2-ethylbenzofurane (37 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **15** was obtained as a 17:1 diastereomeric mixture (determined by HPLC analysis using Chiracel AD-H chiralpak 25 cm column, 95/5 hexanes/iPrOH at 1mL/min., retention time: t_{minor} = 22.0 min. and t_{major} = 24.2 min.). Purification by flash chromatography (10 – 20% Et2O/pentane) produced a colorless oil that solidifies on standing (61 mg, 59%) as a 47:1 diastereomeric mixture. $\mathbf{R}_f$ 0.52 (100% $CHCl_3$); $[\alpha]_D^{23}$ = +19.3 (c 2.1, $CHCl_3$); **mp** 35-36 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.86 (s (br), 1H), 7.73 (s, 1H), 7.62 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.31 – 7.23 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.28 (s, 1H), 5.04 – 4.94 (m, 1H), 1.59 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.80, 153.57, 141.49, 133.49, 129.72, 128.05, 126.22, 124.84, 122.94, 122.50, 120.24, 111.80, 99.82, 83.59, 43.28, 20.56; **IR** (neat) 3404, 3332, 3118, 3064, 3036, 2977, 2953, 2875, 1720, 1584, 1502, 1453, 1379, 1334, 1300, 1279, 1221, 1199, 1151, 1105, 1061, 1028, 1011 cm-1; **HMRS** (ESI) calc. for $C_{19}H_{16}Cl_3NNaO_3$ $[M+Na]^+$: 434.0088; found: 434.01006.



16

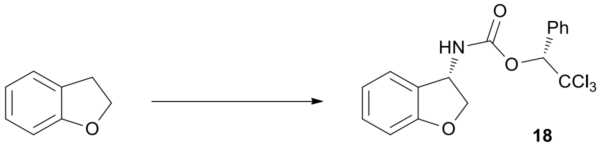
(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-2,3-dihydro-1H-inden-1-ylcarbamate (16). The title compound was prepared from indane (31 mg, 0.26 mmol) following the typical procedure. The desired crude benzylic amine **16** was obtained as a 13:1 diastereomeric mixture (determined by HPLC analysis using Chiracel-AD chiralpak 25 cm column, 97/3 hexane/*i*-PrOH at 1 mL/min, retention time: t_{minor} = 17.6 min, and t_{major} = 22.1 min). Purification by flash chromatography (15% Et_2O/pentane) produced a white solid (70.0 mg, 70%) as a 14:1 diastereomeric mixture. **R_f** 0.35 (100% toluene); **$[\alpha]_D^{23}$** = +27.1 (c 4.4, $CHCl_3$); **mp** 101-102 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.79 – 7.56 (m, 3H), 7.49 – 7.37 (m, 3H), 7.27 – 7.15 (m, 2H), 7.15 – 7.03 (m, 2H), 6.32 (s, 1H), 5.14 – 4.99 (m, 1H), 3.04 – 2.94 (m, 1H), 2.86 – 2.74 (m, 1H), 2.48 – 2.38 (m, 1H), 2.04 – 1.90 (m, 1H); **^{13}C NMR** (100 MHz, DMSO) δ 154.04, 143.63, 142.73, 133.66, 129.61, 129.49, 127.94, 127.50, 126.32, 124.56, 123.55, 99.92, 82.12, 55.95, 32.38, 29.60; **IR** (neat) 3323, 3037, 2949, 2850, 1712, 1504, 1455, 1378, 1343, 1287, 1228, 1201, 1137, 1088, 1058, 1023 cm^{-1}; **HMRS** (ESI) calc. for $C_{18}H_{17}Cl_3NO_2$ $[M+H]^+$: 384.03194; found: 384.03225.

Gram Scale Procedure: Indane (641 mg, 5.42 mmol), (*R*)-1-phenyl-2,2,2-trichloroethyl-*N*-mesyloxycarbamate (**2**) (2.36 g, 6.51 mmol) and $Rh_2[(S)\text{-Br-nttl}]_4$ (10 mg, 0.005 mmol) were dissolved in EtOAc (11 mL) in an open 20 mL vial equipped with a magnetic stirrer. Potassium acetate (1.60 g, 16.3 mmol) was added portion wise to the stirred solution. After 20 min, the green solution turned to pale yellow and another portion of rhodium dimer (10 mg, 0.005 mmol) was added. After an additional 20 min, another portion of rhodium dimer (10 mg, 0.005 mmol) was added. After three more hours, the reaction mixture was diluted with Et_2O (4 mL). Celite® was added to the reaction mixture and it was filtered on a Celite® plug. The plug was washed with Et_2O (3 x 4 mL) and the filtrate was concentrated under vacuum. MeOH (6 mL), pyridine (50 μL) and Celite® were added to the foamy solid. The heterogeneous mixture was filtered on a Celite® plug, the solids washed with MeOH (2 x 2 mL) and the filtrate partially concentrated to a volume of about 4 mL. The desired benzylic amine **16** (1.24 g, 59%) was obtained as an off-white solid after crystallization at -15 °C and as a 15:1 diastereomeric mixture determined by HPLC analysis using Chiracel-AD chiralpak 25 cm column, 97/3 hexane/*i*-PrOH at 1 mL/min, retention time: t_{minor} = 18.6 min, and t_{major} = 23.5 min).



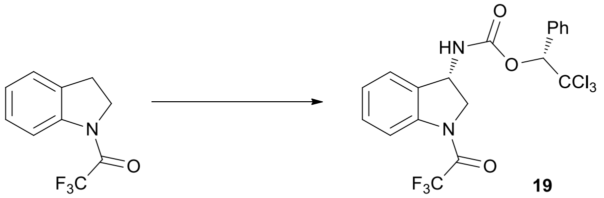
17

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-2,3-dihydro-1H-inden-1-ylcarbamate (17). The title compound was prepared from 1-indanone (33 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **17** was obtained as a 7.0:1 diastereomeric mixture (determined by HPLC analysis using Chiracel-AS chiralpak 25 cm column, 90/10 hexane/i-PrOH at 1 mL/min, retention time: t_{minor} = 13.1 min, and t_{major} = 20.0 min). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (20% acetone/pentane) produced a yellow sticky oil (79 mg, 80%) as a 14:1 diastereomeric mixture. **R_f** 0.24 (20% acetone/pentane); **$[\alpha]_D^{23}$** = –17.3 (c 4.8, $CHCl_3$); **mp** 77-80 °C. Major diastereomer: **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.69 – 7.63 (m, 3H), 7.58 (s (br), 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.40 (m, 4H), 6.31 (s, 1H), 5.33 – 5.22 (m, 1H), 3.10 (dd, *J* = 18.6, 7.8 Hz, 1H), 2.64 (dd, *J* = 18.4, 3.6 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.74, 152.97, 136.87, 135.63, 133.27, 129.93, 129.76, 129.70, 128.11, 128.04, 126.00, 123.69, 99.67, 83.71, 49.70, 45.08; **IR** (neat) 3494, 3326, 3034, 3014, 2955, 2924, 2861, 1705, 1603, 1518, 1464, 1455, 1372, 1337, 1276, 1234, 1202, 1182, 1128, 1088, 1049, 1022, 948 cm^{-1}; **HMRS** (ESI) calc. for $C_{18}H_{15}Cl_3NO_2$ $[M+H]^+$: 398.01120; found: 398.00995.



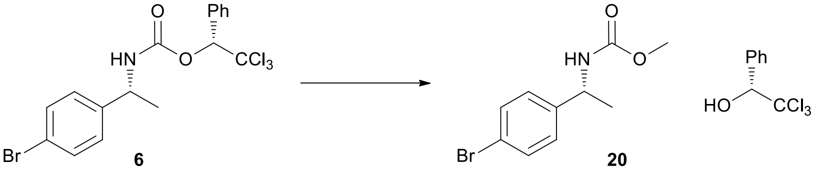
18

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*S*)-2,3-dihydrobenzofuran-3-ylcarbamate (18). The title compound was prepared from dihydrobenzofurane (30 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **18** was obtained as a 28:1 diastereomeric mixture (determined by HPLC analysis using Chiracel-ADH chiralpak 25 cm column, 97/3 hexane/i-PrOH at 1 mL/min, retention time: t_{major} = 28.4 min, and t_{minor} = 33.6 min). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (15% Et_2O/pentane) produced a white solid (90 mg, 93%) as a 46:1 diastereomeric mixture. **R_f** 0.17 (20% Et_2O/pentane); **$[\alpha]_D^{23}$** = 26.4 (c 3.7, $CHCl_3$); **mp** 145-146 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.99 (s (br), 1H), 7.68 – 7.57 (m, 2H), 7.50 – 7.37 (m, 3H), 7.26 – 7.15 (m, 2H), 6.89 – 6.76 (m, 2H), 6.31 (s, 1H), 5.40 – 5.30 (m, 1H), 4.72 – 4.65 (m, 1H), 4.34 (dd, *J* = 9.8, 5.3 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.46, 153.66, 133.27, 130.83, 129.89, 129.79, 128.08, 125.53, 125.34, 121.34, 110.69, 99.73, 83.57, 77.91, 53.69; **IR** (neat) 3329, 3064, 3037, 2955, 2890, 1721, 1599, 1508, 1481, 1460, 1373, 1336, 1320, 1291, 1232, 1202, 1171, 1137, 1067, 1017, 970, 937 cm^{-1}; **HMRS** (ESI) calc. for $C_{17}H_{15}Cl_3NO_2$ $[M+H]^+$: 386.01120; found: 386.01049.



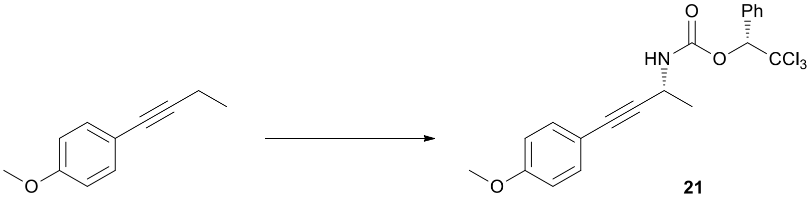
(*R*)-1-Phenyl-2,2,2-trichloroethyl (*S*)-1-(2,2,2-trifluoroacetyl)indolin-3-ylcarbamate (19). The title compound was prepared from indoline *N*-trifluoroacetamide (54 mg, 0.25 mmol) following the typical procedure. The desired crude benzylic amine **19** was obtained as a 7.0:1 diastereomeric mixture (determined by HPLC analysis using Chiracel-ADH chiralpak 25 cm column, 97/3 hexane/i-PrOH at 1 mL/min, retention time: t_{minor} = 35.4 min, and t_{major} = 38.1 min). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (20% Et_2O/pentane) produced a white solid (90 mg, 75%) as a 52:1 diastereomeric mixture. **R_f** 0.17 (20% Et_2O/pentane); **$[\alpha]_D^{23}$** = -0.46 (c 2.9, $CHCl_3$); **mp** 111-112 °C; **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 8.18 (s (br), 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.47 – 7.37 (m, 4H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.31 (s, 1H), 5.41 – 5.32 (m, 1H), 4.64 – 4.53 (m, 1H), 4.14 (dd, *J* = 11.4, 4.7 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.61, 153.79, 141.81, 133.04, 130.64, 129.98, 129.73, 128.11, 126.61, 125.21, 118.40, 117.88, 114.07, 99.58, 83.76, 55.48, 51.99; **IR** (neat) 3330, 3068, 3034, 2956, 1734, 1690, 1602, 1513, 1485, 1464, 1437, 1368, 1324, 1253, 1202, 1144, 1085, 1065, 1025, 945 cm^{-1}; **HMRS** (ESI) calc. for $C_{19}H_{18}Cl_3F_3N_3O_3$ $[M+NH_4]^+$: 498.03604; found: 498.03634.

Deprotection of Benzylic Amine 6.



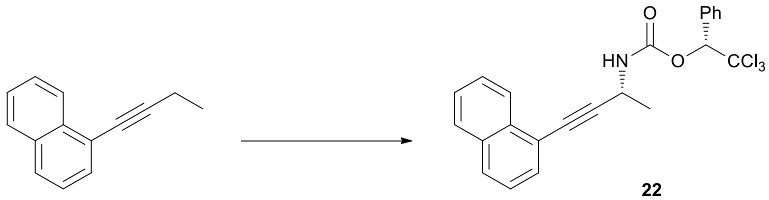
(*R*)-Methyl 1-(4-bromophenyl)ethylcarbamate (20) A 2.2 M butyl lithium solution in hexanes (0.43 mL, 0.95 mmol) was added dropwise to ice cold methanol (2 mL). After 15 min, a solution of carbamate **6** (285 mg; 0.63 mmol) in MeOH (4.3 mL) was added to the methanolate at 0 °C under argon. The yellow reaction mixture was then allowed to warm up to room temperature and stirred for 72 h The desired carbamate protected amine was obtained as a white solid (124 mg, 76%) after chromatography on silica gel (20 – 30% Et_2O/pentane) in an enantiomeric purity of 91% ee (determined by HPLC analysis using Chiracel-AD chiralpak column 25 cm, 96/4 hexanes/*i*PrOH at 1 mL/min, retention time: t_{major} = 13.7 min. and t_{minor} = 16.5 min). $\mathbf{R_f}$ 0,10 (20% Et_2O/pentane); $[\alpha]_D^{23}$ = +64.4 (c 2.7, $CHCl_3$); **mp** 88-90 °C; **^{1}H NMR** (400 MHz, DMSO, 80 °C) δ 7.54 – 7.42 (m, 3H), 7.30 – 7.24 (m, 2H), 4.64 (p, *J* = 7.1 Hz, 1H), 3.52 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.29, 142.89, 131.86, 127.81, 121.24, 52.33, 50.37, 22.53; **IR** (neat) 3348, 2984, 2945, 2925, 2851, 1684, 1527, 1488, 1456, 1408, 1373, 1342, 1307, 1293, 1254, 1197, 1156, 1116, 1096, 1068, 1010 cm^{-1}; **HMRS** (ESI) calc. for $C_{10}H_{13}BrNO_2$ $[M+H]^+$: 258.01242; found: 258.01120.

Typical Procedure for the Diastereoselective Amination of Propargylic C–H Bonds: Synthesis of ((*R*)-1-phenyl-2,2,2-trichloroethyl (*R*)-4-(4-methoxyphenyl)but-3-yn-2-ylcarbamate (21).



21

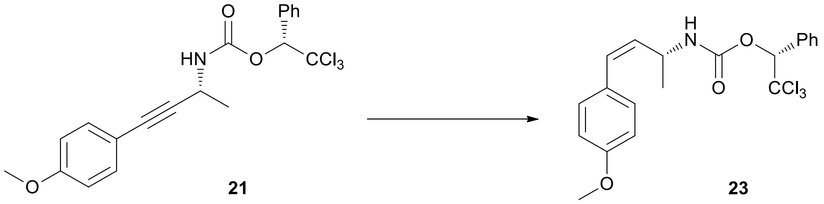
A solution of 1-(4-methoxyphenyl)but-1-yne (40 mg, 0.25 mmol), (*R*)-1-phenyl-2,2,2-trichloroethyl-*N*-mesyloxycarbamate (**2**) (109 mg, 0.30 mmol) and $Rh_2[(S)\text{-Br-nttl}]_4$ (9 mg, 2 mol%) in EtOAc (0.5 mL) was vigorously stirred at room temperature in an open 4 mL vial for 5 min. Potassium acetate (74 mg, 0.75 mmol) was then added. The resulting green heterogeneous reaction mixture was stirred at room temperature for 15 min. before an extra 0.2 mL of EtOAc was added (to ease the stirring). After 1h45, the reaction mixture was then diluted with Et_2O (3 mL) and filtered on Celite® plug. The solid was washed with Et_2O (2 × 3 mL) and the filtrate was concentrated *in vacuo* to give the crude product in a 27:1 diastereomeric mixture (determined by HPLC analysis using Chiracel-ADH chiralpak 25 cm column, 97/3 hexane/i-PrOH at 1 mL/min, retention time: t_{major} = 37.5 min., and t_{minor} = 48.6 min.). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (10 – 20% Et_2O/pentane) produced a sticky oil that solidifies on standing (53 mg, 50%) as a >99:1 diastereomeric mixture. $\mathbf{R_f}$ 0.29 (20% Et_2O/Pentane); $[\alpha]_D^{23}$ = +86.4 (c 1.1, MeOH); **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.83 (s (br), 1H), 7.70 – 7.65 (m, 2H), 7.45 – 7.40 (m, 3H), 7.30 – 7.25 (m, 2H), 6.92 – 6.87 (m, 2H), 6.30 (s, 1H), 4.65 – 4.55 (m, 1H), 3.78 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.85, 153.15, 133.38, 133.30, 129.83, 129.80, 128.02, 114.56, 114.05, 99.91, 87.34, 83.39, 82.99, 55.41, 40.22, 23.05; **IR** (neat) 3416, 3341, 3037, 2980, 2955, 2935, 2837, 1733, 1606, 1509, 1454, 1377, 1334, 1289, 1246, 1202, 1174, 1087, 1071, 1028, 941 cm^{-1}; **HMRS** (ESI) calc. for $C_{20}H_{19}Cl_3NO_3$ $[M+H]^+$: 426.0425; found: 426.0425.



22

(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*)-4-(naphtalen-1-yl)but-3-yn-2-ylcarbamate (22). The title compound was prepared from 1-(1-naphtyl)but-1-yne (45 mg, 0.25 mmol) following the typical procedure. The desired crude propargylic amine **22** was obtained as a 7.0:1 diastereomeric mixture (determined by HPLC analysis using Chiracel-ADH chiralpak 25 cm column, 97/3 hexane/i-PrOH at 1 mL/min, retention time: t_{major} = 23.4 min., and t_{minor} = 25.3 min.). A drop of pyridine (~20 μL) was added to the crude product. Purification by flash chromatography (5 – 15% Et_2O/pentane) produced a yellow sticky oil that solidifies on standing (63 mg, 57%) as a 52:1 diastereomeric mixture. **R$_f$** 0.38 (20% Et_2O/Pentane); **$[\alpha]_D^{23}$** = +58.5 (c 1.1, MeOH); **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 8.24 – 8.17 (m, 1H), 8.05 (s (br), 1H), 7.95 – 7.89 (m, 2H), 7.73 – 7.67 (m, 2H), 7.61 – 7.57 (m, 1H), 7.57 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H),7.43 – 7.39 (m, 3H) 6.34 (s, 1H), 4.84 – 4.74 (m, 1H), 1.60 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.23, 133.39, 133.24, 130.77, 129.82, 129.35, 129.13, 128.43, 128.05, 127.96, 126.99, 126.56, 126.06, 125.25, 120.08, 99.89, 93.63, 83.51, 81.22, 40.43, 23.09; **IR** (neat) 3420, 3326, 3060, 3036, 3013, 2981, 2954, 2933, 1717, 1586, 1496, 1453, 1395, 1378, 1333, 1294, 1275, 1216, 1201, 1157, 1110, 1084, 1066, 1053, 1022, 933 cm^{-1}; **HMRS** (ESI) calc. for $C_{23}H_{19}Cl_3NO_2$ $[M+H]^+$: 446.04759; found: 446.04588.

Reduction of Propargylic Amine 21



(*R*)-1-Phenyl-2,2,2-trichloroethyl (*R*,*Z*)-4-(4-methoxyphenyl)but-3-en-2-ylcarbamate (23). Quinoline (0.39 mL, 3.31 mmol) followed by Lindlar catalyst (5% of Pd on $CaCO_3$, lead poisoned, 33 mg) were added to a stirred solution of propargylic amine **21** (140 mg, 0.33 mmol) in EtOAc (3.3 mL). The reaction vessel was then flushed twice with H_2 and the reaction mixture was stirred at room temperature under H_2 (1 atm) for 5 h, then filtered through a plug of Celite®. The plug was rinsed with EtOAc (3 x 2 mL) and the solution was concentrated under reduced pressure. Allylic amine **23** was obtained as a colorless oil (129 mg, 92%) after purification by flash chromatography (10 – 20% Et_2O/pentane). **R$_f$** 0.34 (20% Et_2O/Pentane); **$[\alpha]_D^{23}$** = –137.4 (c 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO, 110 °C) δ 7.65 – 7.59 (m, 2H), 7.46 – 7.37 (m, 3H), 7.35 (s (br), 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 11.5 Hz, 1H), 6.25 (s, 1H), 5.55 (dd, *J* = 11.6, 9.3 Hz, 1H), 4.69 – 4.57 (m, 1H), 3.77 (s, 3H), 1.27 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.96, 153.21, 133.59, 131.00, 130.39, 130.08, 129.82, 129.68, 128.86, 127.97, 113.99, 100.03, 83.13, 55.37, 45.75, 22.16; **IR** (neat) 3341, 3063, 3034, 3008, 2952, 2934, 2858, 2836, 1719, 1608, 1585, 1510, 1453, 1378, 1343, 1299, 1242, 1201, 1176, 1088, 1063, 1030, 991, 938 cm^{-1}; **HMRS** (ESI) calc. for $C_{20}H_{21}Cl_3NO_3$ $[M+H]^+$: 428.05815; found: 428.05708.

CRYSTAL AND MOLECULAR STRUCTURE OF

C20 H22 Cl6 N2 O11 S2 COMPOUND (hele47)

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Structure solved and refined in the laboratory of X-ray diffraction Université de Montréal by Francine Bélanger.

Table 1. Crystal data and structure refinement for C20 H22 Cl6 N2 O11 S2.

Identification code	hele47
Empirical formula	C20 H22 Cl6 N2 O11 S2
Formula weight	743.22
Temperature	100K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 18.1577(8) Å α = 90° b = 5.7280(2) Å β = 114.835(2)° c = 15.9994(8) Å γ = 90°
Volume	1510.15(12)Å^3
Z	2
Density (calculated)	1.634 g/cm^3
Absorption coefficient	7.004 mm^{-1}
F(000)	756
Crystal size	0.18 x 0.02 x 0.01 mm
Theta range for data collection	3.04 to 70.72°
Index ranges	$-22 \le h \le 22$, $-6 \le k \le 6$, $-19 \le \ell \le 19$
Reflections collected	20459
Independent reflections	2695 [R$_{int}$ = 0.066]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9324 and 0.6464
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2695 / 1 / 196
Goodness-of-fit on F^2	1.105
Final R indices [I>2sigma(I)]	R$_1$ = 0.0527, wR$_2$ = 0.1267
R indices (all data)	R$_1$ = 0.0537, wR$_2$ = 0.1281
Absolute structure parameter	0.06(2)

Largest diff. peak and hole 0.789 and -0.516 e/Å^3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for C20 H22 Cl6 N2 O11 S2.

U_{eq} is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U_{eq}
Cl(1)	6900(1)	-584(2)	5595(1)	28(1)
Cl(2)	6748(1)	-37(2)	7305(1)	34(1)
Cl(3)	7268(1)	3834(2)	6542(1)	30(1)
C(1)	8202(2)	-119(6)	7220(2)	18(1)
C(2)	7326(2)	769(7)	6688(2)	21(1)
O(2)	8486(2)	794(5)	8140(2)	21(1)
C(3)	8746(2)	-839(7)	8819(2)	21(1)
O(3)	8795(2)	-2891(5)	8714(2)	25(1)
N(3)	8895(2)	317(7)	9635(2)	22(1)
O(4)	9387(1)	-1033(5)	10416(2)	23(1)
S(5)	8863(1)	-2076(2)	10945(1)	26(1)
O(5)	8174(2)	-3258(7)	10302(2)	38(1)
O(6)	9470(2)	-3314(7)	11677(2)	43(1)
C(7)	8568(2)	443(9)	11345(3)	35(1)
C(8)	8781(2)	549(6)	6805(2)	18(1)
C(9)	9200(2)	2660(7)	7018(2)	21(1)
C(10)	9754(2)	3168(8)	6653(2)	23(1)
C(11)	9898(2)	1591(8)	6090(2)	26(1)
C(12)	9479(2)	-503(8)	5869(3)	30(1)
C(13)	8923(2)	-1028(8)	6233(2)	26(1)
O(7)	10000	4129(8)	10000	31(1)

Table 3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for C20 H22 Cl6 N2 O11 S2.

	x	y	z	U_{eq}
H(1)	8187	-1861	7254	21
H(3)	9000(40)	1610(160)	9700(40)	49(18)
H(7A)	8236	1426	10821	53
H(7B)	9052	1312	11750	53
H(7C)	8253	1	11689	53
H(9)	9107	3749	7412	25
H(10)	10036	4616	6793	27
H(11)	10286	1939	5852	31
H(12)	9570	-1580	5471	36
H(13)	8640	-2472	6087	31
H(7)	9560(40)	4840(130)	9450(40)	55(17)

Table 4. Anisotropic parameters ($Å^2 \times 10^3$) for $C_{20}H_{22}Cl_6N_2O_{11}S_2$.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Cl(1)	25(1)	21(1)	25(1)	0(1)	-1(1)	-4(1)
Cl(2)	24(1)	38(1)	44(1)	-1(1)	19(1)	-8(1)
Cl(3)	20(1)	14(1)	47(1)	1(1)	7(1)	0(1)
C(1)	20(2)	12(2)	18(1)	0(1)	5(1)	-3(1)
C(2)	17(2)	14(2)	29(2)	-1(1)	6(1)	-2(1)
O(2)	25(1)	20(1)	17(1)	0(1)	7(1)	-3(1)
C(3)	12(1)	27(2)	22(2)	2(1)	5(1)	-2(1)
O(3)	26(1)	19(2)	23(1)	1(1)	3(1)	0(1)
N(3)	23(2)	21(2)	18(1)	6(1)	5(1)	-2(1)
O(4)	17(1)	30(2)	18(1)	3(1)	2(1)	1(1)
S(5)	24(1)	30(1)	22(1)	5(1)	8(1)	0(1)
O(5)	34(2)	40(2)	38(2)	-2(1)	13(1)	-15(2)
O(6)	39(2)	56(2)	31(1)	21(2)	13(1)	15(2)
C(7)	29(2)	42(3)	30(2)	0(2)	10(2)	1(2)
C(8)	14(1)	19(2)	17(1)	1(1)	3(1)	0(1)
C(9)	15(1)	23(2)	21(1)	-4(1)	4(1)	0(1)
C(10)	19(2)	23(2)	23(2)	-1(1)	6(1)	-4(1)
C(11)	20(2)	39(2)	20(2)	-2(2)	9(1)	-4(2)
C(12)	35(2)	32(2)	26(2)	-9(2)	16(2)	-4(2)
C(13)	27(2)	21(2)	28(2)	-1(2)	10(1)	-2(2)
O(7)	31(2)	18(2)	32(2)	0	2(2)	0

Table 5. Bond lengths [Å] and angles [°] for C20 H22 Cl6 N2 O11 S2

Cl(1)-C(2)	1.766(4)	CL1-C(2)-CL3	109.1(2)
Cl(2)-C(2)	1.776(3)	C(1)-C(2)-CL2	108.7(2)
Cl(3)-C(2)	1.768(4)	CL1-C(2)-CL2	108.72(19)
C(1)-O(2)	1.438(4)	CL3-C(2)-CL2	108.4(2)
C(1)-C(8)	1.511(4)	C(3)-O(2)-C(1)	115.0(3)
C(1)-C(2)	1.542(5)	O(3)-C(3)-O(2)	125.8(3)
O(2)-C(3)	1.359(5)	O(3)-C(3)-N(3)	127.3(4)
C(3)-O(3)	1.196(5)	O(2)-C(3)-N(3)	106.8(3)
C(3)-N(3)	1.385(5)	C(3)-N(3)-O(4)	111.7(3)
N(3)-O(4)	1.421(4)	N(3)-O(4)-S(5)	111.5(2)
O(4)-S(5)	1.629(2)	O(5)-S(5)-O(6)	120.3(2)
S(5)-O(5)	1.414(3)	O(5)-S(5)-O(4)	109.19(16)
S(5)-O(6)	1.416(3)	O(6)-S(5)-O(4)	101.09(16)
S(5)-C(7)	1.751(5)	O(5)-S(5)-C(7)	110.4(2)
C(8)-C(13)	1.385(5)	O(6)-S(5)-C(7)	111.2(2)
C(8)-C(9)	1.392(5)	O(4)-S(5)-C(7)	102.85(19)
C(9)-C(10)	1.391(5)	C(13)-C(8)-C(9)	119.7(3)
C(10)-C(11)	1.376(6)	C(13)-C(8)-C(1)	118.9(3)
C(11)-C(12)	1.385(6)	C(9)-C(8)-C(1)	121.4(3)
C(12)-C(13)	1.394(5)	C(10)-C(9)-C(8)	119.7(3)
		C(11)-C(10)-C(9)	120.5(4)
O(2)-C(1)-C(8)	110.0(3)	C(10)-C(11)-C(12)	120.0(3)
O(2)-C(1)-C(2)	106.8(3)	C(11)-C(12)-C(13)	119.8(4)
C(8)-C(1)-C(2)	114.9(3)	C(8)-C(13)-C(12)	120.3(4)
C(1)-C(2)-CL1	108.8(2)		
C(1)-C(2)-CL3	113.0(2)		

Table 6. Torsion angles [°] for $C_{20} H_{22} Cl_6 N_2 O_{11} S_2$.

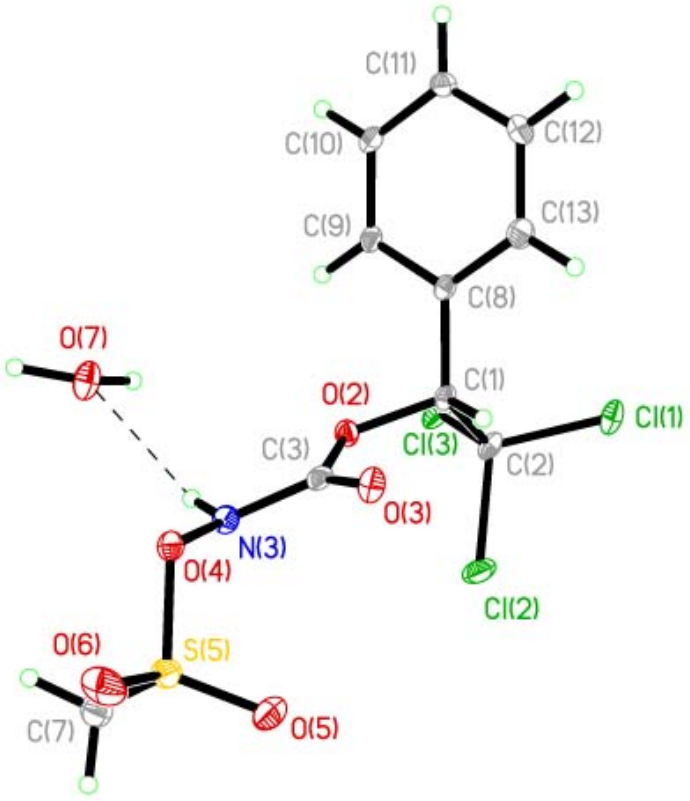
O(2)-C(1)-C(2)-CL1	-172.9(2)
C(8)-C(1)-C(2)-CL1	64.9(4)
O(2)-C(1)-C(2)-CL3	65.7(3)
C(8)-C(1)-C(2)-CL3	-56.6(4)
O(2)-C(1)-C(2)-CL2	-54.7(3)
C(8)-C(1)-C(2)-CL2	-176.9(2)
C(8)-C(1)-O(2)-C(3)	-111.2(3)
C(2)-C(1)-O(2)-C(3)	123.5(3)
C(1)-O(2)-C(3)-O(3)	4.1(5)
C(1)-O(2)-C(3)-N(3)	-172.5(3)
O(3)-C(3)-N(3)-O(4)	20.7(5)
O(2)-C(3)-N(3)-O(4)	-162.8(3)
C(3)-N(3)-O(4)-S(5)	-107.0(3)
N(3)-O(4)-S(5)-O(5)	52.3(3)
N(3)-O(4)-S(5)-O(6)	-179.9(3)
N(3)-O(4)-S(5)-C(7)	-64.9(3)
O(2)-C(1)-C(8)-C(13)	143.6(3)
C(2)-C(1)-C(8)-C(13)	-95.9(4)
O(2)-C(1)-C(8)-C(9)	-33.5(4)
C(2)-C(1)-C(8)-C(9)	87.0(4)
C(13)-C(8)-C(9)-C(10)	0.2(5)
C(1)-C(8)-C(9)-C(10)	177.2(3)
C(8)-C(9)-C(10)-C(11)	-0.7(5)
C(9)-C(10)-C(11)-C(12)	1.2(6)
C(10)-C(11)-C(12)-C(13)	-1.2(6)
C(9)-C(8)-C(13)-C(12)	-0.2(5)
C(1)-C(8)-C(13)-C(12)	-177.4(3)
C(11)-C(12)-C(13)-C(8)	0.8(6)

Table 7. Bond lengths [Å] and angles [°] related to the hydrogen bonding for C20 H22 Cl6 N2 O11 S2.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N(3)-H(3)	O(7)	0.76(9)	2.21(8)	2.856(5)	143(6)
O(7)-H(7)	O(3)#1	0.99(6)	1.91(7)	2.855(4)	159(6)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z



ORTEP view of the C20 H22 Cl6 N2 O11 S2 compound with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

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Université de Montréal

CRYSTAL AND MOLECULAR STRUCTURE OF

C21 H18 Cl3 N O2 COMPOUND (hele48)

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Structure solved and refined in the laboratory of X-ray diffraction Université de Montréal by Francine Bélanger.

Table 1. Crystal data and structure refinement for C21 H18 Cl3 N O2.

Identification code	hele48
Empirical formula	C21 H18 Cl3 N O2
Formula weight	422.71
Temperature	100K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 24.7313(8) Å α = 90° b = 8.5903(3) Å β = 90.2928(17)° c = 11.4980(4) Å γ = 90°
Volume	2442.71(14)$Å^3$
Z	4
Density (calculated)	1.149 g/cm^3
Absorption coefficient	3.504 mm^{-1}
F(000)	872
Crystal size	0.07 x 0.04 x 0.02 mm
Theta range for data collection	3.57 to 70.95°
Index ranges	$-30 \leq h \leq 30$, $-9 \leq k \leq 10$, $-14 \leq \ell \leq 13$
Reflections collected	18084
Independent reflections	4185 [R_{int} = 0.067]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9323 and 0.7086
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4185 / 1 / 250
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R_1 = 0.0558, wR_2 = 0.1418
R indices (all data)	R_1 = 0.0598, wR_2 = 0.1457
Absolute structure parameter	0.14(2)
Largest diff. peak and hole	0.406 and -0.364 $e/Å^3$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for C21 H18 Cl3 N O2.

U_{eq} is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U_{eq}
Cl(1)	3282(1)	-117(1)	6115(1)	33(1)
Cl(2)	3881(1)	1947(1)	4631(1)	36(1)
Cl(3)	4445(1)	-24(1)	6241(1)	42(1)
C(1)	3834(1)	2404(4)	6956(3)	20(1)
C(2)	3856(1)	1098(5)	6029(3)	25(1)
O(2)	3870(1)	1613(3)	8048(2)	20(1)
C(3)	4098(1)	2470(4)	8937(3)	16(1)
O(3)	4294(1)	3744(3)	8788(2)	22(1)
N(3)	4083(1)	1664(4)	9930(2)	20(1)
C(4)	4298(1)	2347(4)	10994(3)	21(1)
C(5)	4498(2)	1046(6)	11785(3)	38(1)
C(6)	3892(1)	3373(4)	11615(3)	19(1)
C(7)	3351(1)	3140(6)	11495(4)	36(1)
C(8)	2974(2)	4051(7)	12093(5)	55(2)
C(9)	3136(2)	5242(6)	12774(4)	39(1)
C(10)	3689(1)	5568(4)	12923(3)	22(1)
C(11)	3869(2)	6828(5)	13628(3)	32(1)
C(12)	4404(2)	7112(6)	13774(4)	46(1)
C(13)	4789(2)	6169(6)	13240(4)	47(1)
C(14)	4630(1)	4949(6)	12543(3)	33(1)
C(15)	4075(1)	4616(4)	12350(3)	19(1)
C(16)	3340(1)	3440(4)	6901(3)	20(1)
C(17)	2900(2)	3124(6)	7607(3)	32(1)
C(18)	2444(2)	4068(8)	7557(4)	50(1)
C(19)	2424(2)	5323(6)	6785(4)	45(1)
C(20)	2862(2)	5624(5)	6095(4)	38(1)
C(21)	3318(2)	4694(5)	6148(3)	30(1)

Table 3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for C21 H18 Cl3 N O2.

	x	y	z	U_{eq}
H(1)	4163	3072	6868	24
H(3)	3925(19)	610(70)	10050(40)	41(13)
H(4)	4616	3007	10783	25
H(5A)	4197	349	11970	57
H(5B)	4644	1493	12504	57
H(5C)	4782	457	11388	57
H(7)	3226	2339	10992	43
H(8)	2599	3827	12018	66
H(9)	2875	5867	13157	47
H(11)	3612	7477	14000	38
H(12)	4518	7962	14244	55
H(13)	5163	6371	13358	56
H(14)	4897	4317	12185	40
H(17)	2911	2263	8125	39
H(18)	2145	3859	8049	60
H(19)	2110	5959	6738	54
H(20)	2852	6482	5574	46
H(21)	3619	4918	5665	37

Table 4. Anisotropic parameters ($Å^2 \times 10^3$) for $C21\ H18\ Cl3\ N\ O2$.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

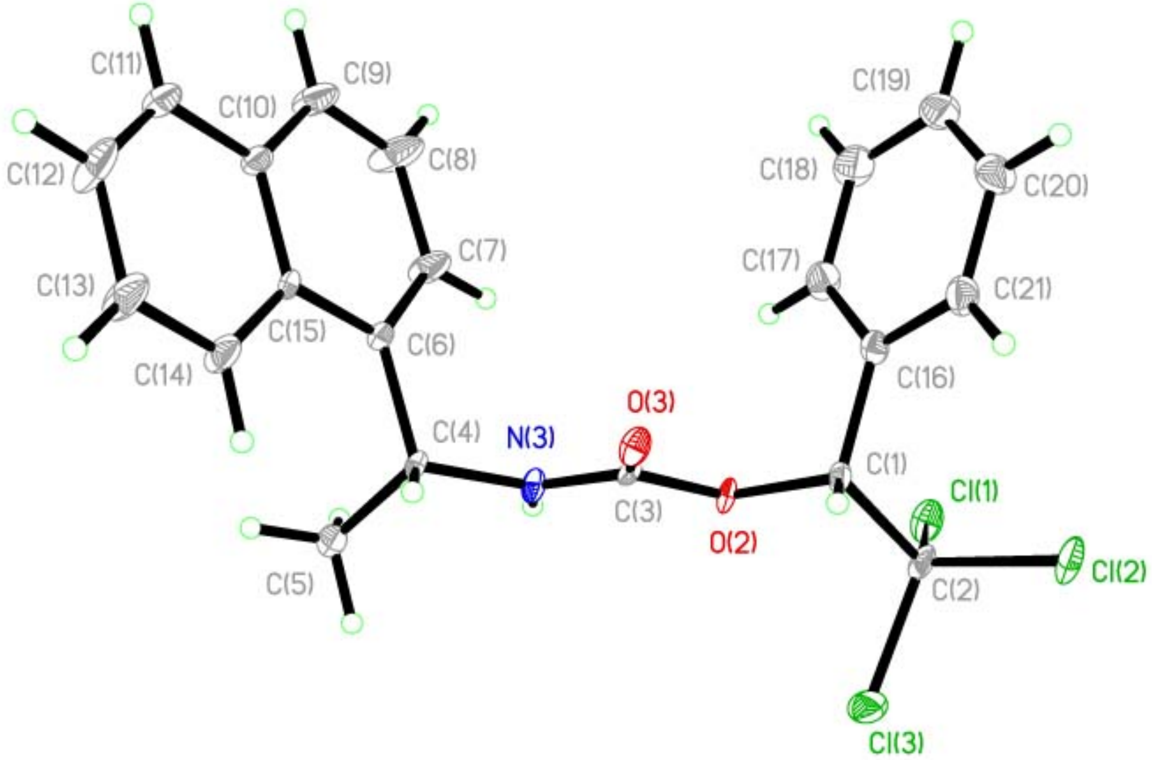
	U11	U22	U33	U23	U13	U12
Cl(1)	38(1)	35(1)	25(1)	-8(1)	-3(1)	-13(1)
Cl(2)	41(1)	53(1)	13(1)	-3(1)	4(1)	-7(1)
Cl(3)	36(1)	54(1)	36(1)	-22(1)	-8(1)	17(1)
C(1)	19(1)	29(2)	12(1)	-2(1)	-2(1)	0(1)
C(2)	25(2)	36(2)	14(2)	-13(2)	-2(1)	-4(2)
O(2)	27(1)	25(1)	7(1)	-3(1)	0(1)	-4(1)
C(3)	17(1)	20(2)	11(1)	-3(1)	3(1)	3(1)
O(3)	25(1)	24(1)	18(1)	-4(1)	1(1)	-9(1)
N(3)	27(1)	19(2)	13(1)	-4(1)	-3(1)	-5(1)
C(4)	23(2)	27(2)	13(1)	-9(1)	-2(1)	5(1)
C(5)	51(2)	41(3)	22(2)	-7(2)	-6(2)	23(2)
C(6)	22(2)	22(2)	13(2)	-2(1)	2(1)	3(1)
C(7)	16(2)	48(3)	45(2)	-24(2)	6(2)	-2(2)
C(8)	18(2)	67(4)	81(4)	-45(3)	8(2)	-3(2)
C(9)	25(2)	44(3)	50(2)	-20(2)	10(2)	3(2)
C(10)	27(2)	23(2)	17(2)	-2(1)	4(1)	5(1)
C(11)	35(2)	34(2)	26(2)	-8(2)	8(1)	7(2)
C(12)	45(2)	53(3)	40(2)	-30(2)	9(2)	-19(2)
C(13)	28(2)	60(3)	52(3)	-39(3)	1(2)	-9(2)
C(14)	24(2)	43(2)	32(2)	-23(2)	-1(1)	-2(2)
C(15)	23(2)	26(2)	8(1)	-2(1)	1(1)	4(1)
C(16)	17(2)	25(2)	18(2)	-1(1)	-3(1)	-4(1)
C(17)	25(2)	45(2)	26(2)	6(2)	6(1)	-2(2)
C(18)	20(2)	91(4)	39(2)	-6(3)	3(2)	13(2)
C(19)	31(2)	65(4)	39(2)	-11(2)	-8(2)	19(2)
C(20)	51(2)	26(2)	39(2)	-2(2)	-11(2)	7(2)
C(21)	40(2)	29(2)	22(2)	3(2)	0(2)	1(2)

Table 5. Bond lengths [Å] and angles [°] for C21 H18 Cl3 N O2

Cl(1)-C(2)	1.765(4)
Cl(2)-C(2)	1.766(4)
Cl(3)-C(2)	1.763(4)
C(1)-O(2)	1.430(4)
C(1)-C(16)	1.514(4)
C(1)-C(2)	1.549(4)
O(2)-C(3)	1.379(4)
C(3)-O(3)	1.210(4)
C(3)-N(3)	1.336(4)
N(3)-C(4)	1.455(4)
C(4)-C(6)	1.516(4)
C(4)-C(5)	1.522(5)
C(6)-C(7)	1.359(5)
C(6)-C(15)	1.433(5)
C(7)-C(8)	1.401(6)
C(8)-C(9)	1.348(6)
C(9)-C(10)	1.405(5)
C(10)-C(15)	1.421(4)
C(10)-C(11)	1.422(5)
C(11)-C(12)	1.356(6)
C(12)-C(13)	1.394(6)
C(13)-C(14)	1.375(6)
C(14)-C(15)	1.420(5)
C(16)-C(21)	1.382(5)
C(16)-C(17)	1.386(5)
C(17)-C(18)	1.392(6)
C(18)-C(19)	1.397(8)
C(19)-C(20)	1.371(7)
C(20)-C(21)	1.384(6)
O(2)-C(1)-C(16)	111.2(2)
O(2)-C(1)-C(2)	104.9(3)
C(16)-C(1)-C(2)	115.3(3)
C(1)-C(2)-CL3	109.3(2)
C(1)-C(2)-CL1	111.1(2)
CL3-C(2)-CL1	109.5(2)
C(1)-C(2)-CL2	109.2(3)
CL3-C(2)-CL2	108.60(18)
CL1-C(2)-CL2	109.15(18)
C(3)-O(2)-C(1)	114.8(2)
O(3)-C(3)-N(3)	127.1(3)
O(3)-C(3)-O(2)	122.8(3)
N(3)-C(3)-O(2)	110.1(3)
C(3)-N(3)-C(4)	119.8(3)
N(3)-C(4)-C(6)	113.0(3)
N(3)-C(4)-C(5)	108.8(3)
C(6)-C(4)-C(5)	111.1(3)
C(7)-C(6)-C(15)	118.4(3)
C(7)-C(6)-C(4)	121.3(3)
C(15)-C(6)-C(4)	120.3(3)
C(6)-C(7)-C(8)	121.7(4)
C(9)-C(8)-C(7)	120.8(4)
C(8)-C(9)-C(10)	120.6(4)
C(9)-C(10)-C(15)	118.9(3)
C(9)-C(10)-C(11)	121.5(3)
C(15)-C(10)-C(11)	119.6(3)
C(12)-C(11)-C(10)	120.7(3)
C(11)-C(12)-C(13)	120.5(4)
C(14)-C(13)-C(12)	120.4(4)
C(13)-C(14)-C(15)	121.2(4)
C(14)-C(15)-C(10)	117.6(3)
C(14)-C(15)-C(6)	122.9(3)
C(10)-C(15)-C(6)	119.5(3)
C(21)-C(16)-C(17)	119.4(3)
C(21)-C(16)-C(1)	120.8(3)
C(17)-C(16)-C(1)	119.7(3)
C(16)-C(17)-C(18)	120.0(4)
C(17)-C(18)-C(19)	120.1(4)
C(20)-C(19)-C(18)	119.2(4)
C(19)-C(20)-C(21)	120.8(4)
C(16)-C(21)-C(20)	120.4(4)

Table 6. Torsion angles [°] for C21 H18 Cl3 N O2.

O(2)-C(1)-C(2)-CL3	-55.7(3)
C(16)-C(1)-C(2)-CL3	-178.4(2)
O(2)-C(1)-C(2)-CL1	65.2(3)
C(16)-C(1)-C(2)-CL1	-57.5(4)
O(2)-C(1)-C(2)-CL2	-174.4(2)
C(16)-C(1)-C(2)-CL2	62.9(3)
C(16)-C(1)-O(2)-C(3)	-82.7(3)
C(2)-C(1)-O(2)-C(3)	152.0(2)
C(1)-O(2)-C(3)-O(3)	-5.8(4)
C(1)-O(2)-C(3)-N(3)	176.3(2)
O(3)-C(3)-N(3)-C(4)	2.8(5)
O(2)-C(3)-N(3)-C(4)	-179.4(3)
C(3)-N(3)-C(4)-C(6)	84.9(4)
C(3)-N(3)-C(4)-C(5)	-151.3(3)
N(3)-C(4)-C(6)-C(7)	26.6(5)
C(5)-C(4)-C(6)-C(7)	-96.0(4)
N(3)-C(4)-C(6)-C(15)	-153.5(3)
C(5)-C(4)-C(6)-C(15)	83.9(4)
C(15)-C(6)-C(7)-C(8)	-1.9(7)
C(4)-C(6)-C(7)-C(8)	178.0(5)
C(6)-C(7)-C(8)-C(9)	3.0(9)
C(7)-C(8)-C(9)-C(10)	-1.8(9)
C(8)-C(9)-C(10)-C(15)	-0.4(7)
C(8)-C(9)-C(10)-C(11)	179.3(5)
C(9)-C(10)-C(11)-C(12)	179.1(4)
C(15)-C(10)-C(11)-C(12)	-1.2(6)
C(10)-C(11)-C(12)-C(13)	-0.3(7)
C(11)-C(12)-C(13)-C(14)	0.9(8)
C(12)-C(13)-C(14)-C(15)	0.0(8)
C(13)-C(14)-C(15)-C(10)	-1.4(6)
C(13)-C(14)-C(15)-C(6)	178.9(4)
C(9)-C(10)-C(15)-C(14)	-178.3(4)
C(11)-C(10)-C(15)-C(14)	2.0(5)
C(9)-C(10)-C(15)-C(6)	1.4(5)
C(11)-C(10)-C(15)-C(6)	-178.3(3)
C(7)-C(6)-C(15)-C(14)	179.4(4)
C(4)-C(6)-C(15)-C(14)	-0.5(5)
C(7)-C(6)-C(15)-C(10)	-0.3(5)
C(4)-C(6)-C(15)-C(10)	179.9(3)
O(2)-C(1)-C(16)-C(21)	157.0(3)
C(2)-C(1)-C(16)-C(21)	-83.8(4)
O(2)-C(1)-C(16)-C(17)	-23.5(4)
C(2)-C(1)-C(16)-C(17)	95.7(4)
C(21)-C(16)-C(17)-C(18)	-0.2(6)
C(1)-C(16)-C(17)-C(18)	-179.7(4)
C(16)-C(17)-C(18)-C(19)	0.9(7)
C(17)-C(18)-C(19)-C(20)	-1.1(7)
C(18)-C(19)-C(20)-C(21)	0.7(7)
C(17)-C(16)-C(21)-C(20)	-0.2(6)
C(1)-C(16)-C(21)-C(20)	179.3(4)
C(19)-C(20)-C(21)-C(16)	0.0(6)



ORTEP view of the C21 H18 Cl3 N O2 compound with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

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