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ELECTRONIC SUPPORTING INFORMATION

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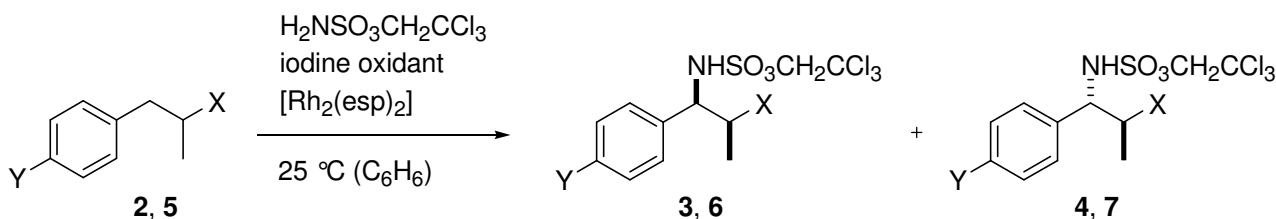
B E L O N G I N G T O T H E P A P E R

Acyclic Stereocontrol in the Catalytic C-H Amination of Benzylic
Methylene Groups.

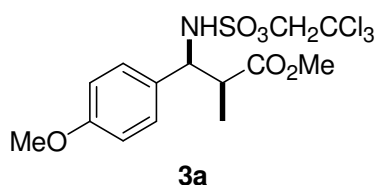
Anike Nörder, Pavel Herrmann, Eberhard Herdtweck, Thorsten Bach*

Preparation and Spectroscopic Data of the Products

- General procedure for C-H amination reactions:

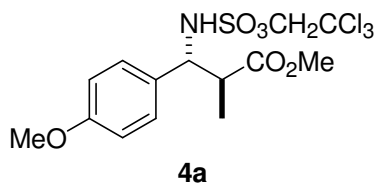


Following mainly an established protocol,^[1] the substrate **2** or **5** (1.0 mmol) was added to a solution of 114.2 mg $\text{H}_2\text{NSO}_3\text{CH}_2\text{CCl}_3$ (0.5 mmol) and 7.6 mg Rh_2esp_2 (10.0 μmol) in benzene (1.5 ml). The iodine oxidant (1.5 mmol) was then added portionwise over a period of 2 h and the mixture was stirred at 25°C for 16 h. The reaction was quenched by the addition of 5.0 ml CH_2Cl_2 and 5.0 ml of saturated aqueous solution of thiourea. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2×10 ml). The combined organic layers were washed with 0.5 M aqueous NaHCO_3 (20 ml), dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using the indicated solvent mixture (P = pentane).

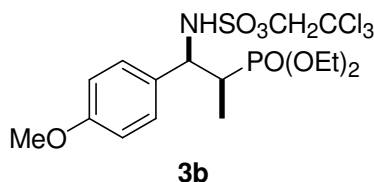


After flash chromatography (P:Et₂O = 6:4) of the crude product a diastereomeric mixture of **3a** and **4a** (81%, dr(**3a/4a**) = 82:18) was isolated as a pale brown solid.

R_f	0.24 (P:Et ₂ O = 6:4).
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.21 (d, ³ J = 7.2 Hz, 3 H), 3.05–3.13 (m, 1 H), 3.66 (s, 3 H), 3.81 (s, 3 H), 4.29–4.41 (m, 2 H), 4.66 (dd, ³ J = 8.9 Hz, ³ J = 6.0 Hz, 1 H), 6.15 (d, ³ J = 8.9 Hz, 1 H), 6.87–6.90 (m, 2 H), 7.18–7.23 (m, 2 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 14.3, 45.8, 52.6, 55.7, 60.8, 78.4, 93.7, 114.6 (2 C), 128.9 (2 C), 131.1, 160.0, 174.3.
HRMS (EI)	(C ₁₄ H ₁₈ Cl ₃ NO ₆ S ⁺): calc.: 432.9915; found: 432.9919.



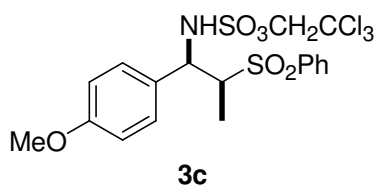
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.34 (d, ³ J = 7.1 Hz, 3 H), 2.88–2.95 (m, 1 H), 3.67 (s, 3 H), 3.81 (s, 3 H), 4.29–4.41 (m, 2 H), 4.60 (dd, ³ J = 8.7 Hz, ³ J = 5.7 Hz, 1 H), 6.40 (d, ³ J = 8.7 Hz, 1 H), 6.87–6.90 (m, 2 H), 7.18–7.23 (m, 2 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 16.0, 46.2, 52.7, 55.8, 61.2, 78.4, 93.7, 114.7 (2 C), 128.3 (2 C), 131.3, 159.9, 175.7.



After flash chromatography (P:EtOAc = 3:7) of the crude product **3b** (65%, dr(**3b**/**4b**) > 95:5) was isolated as a white solid.

R_f	0.26 (P:EtOAc = 3:7).
¹ H-NMR	(500 MHz, CDCl ₃): δ [ppm] = 1.09–1.14 (m, 6 H), 1.34 (<i>virt.</i> t, ³ J _{HH} ≈ ³ J _{HP} = 7.1 Hz, 3 H), 2.46–2.55 (m, 1 H), 3.79 (s, 3 H), 3.86–4.01 (m, 2 H), 4.08–4.16 (m, 2H), 4.37–4.41 (m, 2H), 4.70 (ddd, ³ J = 30.9 Hz, ³ J = 8.0 Hz, ³ J = 4.4 Hz, 1 H), 6.86 (d, ³ J = 8.7 Hz, 1 H), 7.31 (d, ³ J = 8.7 Hz, 2 H), 7.37 (d, ³ J = 8.0 Hz, 2 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 11.9 (d, ² J = 4.9 Hz), 16.2 (d, ³ J = 6.2 Hz), 16.6 (d, ³ J = 5.7 Hz), 37.7 (d, ¹ J = 138.1 Hz), 55.5, 59.3 (d, ² J = 4.0 Hz), 62.1 (d, ² J = 7.3 Hz), 62.5 (d, ² J = 6.4 Hz), 78.2, 93.6, 113.7 (2 C), 129.1 (2 C), 129.4 (d, ³ J = 6.0 Hz), 159.6.

HRMS (EI) (C₁₆H₂₅Cl₃NO₇PS⁺): calc.: 511.0149; found: 511.0167.



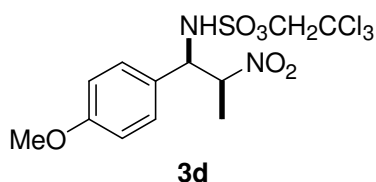
After flash chromatography (P:Et₂O = 1:1) of the crude product **3c** (56%, dr(**3c**/**4c**) > 95:5) was isolated as a pale yellow solid.

R_f 0.09 (P:Et₂O = 1:1).

¹H-NMR (360 MHz, CDCl₃): δ [ppm] = 1.26 (d, ³*J* = 7.2 Hz, 3 H), 3.39–3.46 (m, 1 H), 3.79 (s, 3 H), 4.53 (d, ²*J* = 10.8 Hz, 1 H), 4.56 (d, ²*J* = 10.8 Hz, 1 H), 5.07 (dd, ³*J* = 6.2 Hz, ³*J* = 3.2 Hz, 1 H), 6.49 (d, ³*J* = 6.2 Hz, 1 H), 6.87–6.91 (m, 2 H), 7.27–7.30 (m, 2 H), 7.57–7.63 (m, 2 H), 7.63–7.73 (m, 1 H), 7.90–7.93 (m, 2 H).

¹³C-NMR (90.6 MHz, CDCl₃): δ [ppm] = 10.3, 55.7, 58.4, 64.1, 78.8, 93.7, 114.5 (2 C), 128.1, 129.1 (2 C), 129.2 (2 C), 129.4 (2 C), 134.8, 137.9, 160.2.

HRMS (EI) (C₁₈H₂₀Cl₃NO₆S₂⁺): calc.: 514.9792; found: 514.9793.



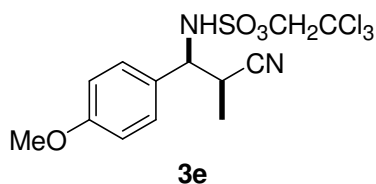
After flash chromatography (P:Et₂O = 6:4) of the crude product a diastereomeric mixture of **3d** and **4d** (63%, dr(**3d**/**4d**) = 91:9) was isolated as a pale yellow solid.

R_f 0.18 (P:Et₂O = 6:4).

¹H-NMR (360 MHz, CDCl₃): δ [ppm] = 1.62 (d, ³*J* = 6.8 Hz, 3 H), 3.80 (s, 3 H), 4.40 (d, ²*J* = 10.8 Hz, 1 H), 4.46 (d, ²*J* = 10.8 Hz, 1 H), 4.88 (dd, ³*J* = 8.8 Hz, ³*J* = 5.5 Hz, 1 H), 4.98 (dq, ³*J* = 6.8 Hz, ³*J* = 5.5 Hz, 1 H), 5.81 (d, ³*J* = 8.8 Hz, 1 H), 6.88–6.91 (m, 2 H), 7.14–7.19 (m, 2 H).

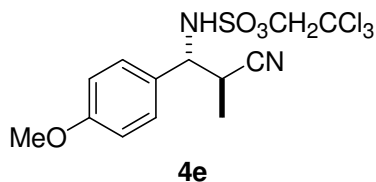
¹³C-NMR (90.6 MHz, CDCl₃): δ [ppm] = 15.8, 55.5, 60.7, 78.4, 85.5, 93.1, 114.9 (2 C), 126.2, 128.5 (2 C), 160.6.

HRMS (EI) (C₁₂H₁₅Cl₃N₂O₆S⁺): calc.: 419.9711; found: 419.9726.



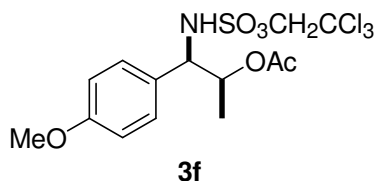
After flash chromatography (P:Et₂O = 6:4) of the crude product a diastereomeric mixture of **3e** and **4e** (86%, dr(**3e**/**4e**) = 80:20^{*}) was isolated as a pale yellow solid. The diastereoisomers were not completely separable by flash chromatography.

R_f	0.16 (P:Et ₂ O = 6:4).
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.20 (d, ³ J = 7.2 Hz, 3 H), 3.38–3.46 (m, 1 H), 3.81 (s, 3 H), 4.39 (d, ² J = 10.8 Hz, 1 H), 4.53 (d, ² J = 10.8 Hz, 1 H), 4.49–4.53 (m, 1 H), 5.76 (d, ³ J = 7.7 Hz, 1 H), 6.91–6.95 (m, 2 H), 7.32–7.36 (m, 2 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 15.3, 32.8, 55.5, 59.8, 78.4, 93.2, 114.8 (2 C), 120.2, 127.1, 128.7 (2 C), 160.5.
HRMS (EI)	(C ₁₃ H ₁₅ Cl ₃ N ₂ O ₄ S ⁺): calc.: 399.9813; found: 399.9815.



R_f	0.13 (P:Et ₂ O = 6:4).
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.43 (d, ³ J = 7.1 Hz, 3 H), 3.03–3.11 (m, 1 H), 3.81 (s, 3 H), 4.34 (d, ² J = 10.8 Hz, 1 H), 4.46 (d, ² J = 10.8 Hz, 1 H), 4.59 (dd, ³ J = 9.3 Hz, ³ J = 5.6 Hz, 1 H), 5.91 (d, ³ J = 9.3 Hz, 1 H), 6.92–6.93 (m, 2 H), 7.27–7.31 (m, 2 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 15.9, 33.8, 55.5, 60.3, 78.3, 93.1, 114.8 (2 C), 120.2, 127.9 (2 C), 129.1, 160.3.

^{*}The diastereomeric ratio of the purified mixture (see NMR spectra) was slightly different.



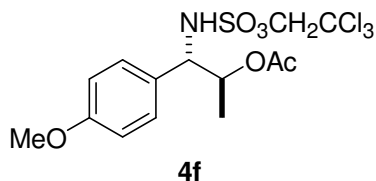
After flash chromatography (P:Et₂O = 6:4) of the crude product a diastereomeric mixture of **3f** and **4f** (40%, dr(**3f**/**4f**) = 86:14) was isolated as a pale yellow solid.

R_f 0.15 (P:Et₂O = 6:4).

¹H-NMR (360 MHz, CDCl₃): δ = 1.17 (d, ³*J* = 6.5 Hz, 3 H), 2.07 (s, 3 H), 3.81 (s, 3 H), 4.34 (d, ²*J* = 10.8 Hz, 1 H), 4.38 (d, ²*J* = 10.8 Hz, 1 H), 4.63 (dd, ³*J* = 8.0 Hz, ³*J* = 4.1 Hz, 1 H), 5.23 (dq, ³*J* = 6.5 Hz, ³*J* = 4.1 Hz, 1 H), 5.72 (d, ³*J* = 8.0 Hz, 1 H), 6.88–6.92 (m, 2 H), 7.22–7.25 (m, 2 H).

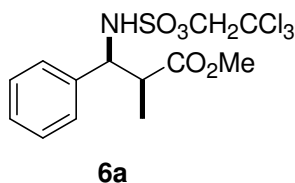
¹³C-NMR (90.6 MHz, CDCl₃): δ = 16.4, 21.3, 55.5, 61.5, 72.7, 78.3, 93.3, 114.3 (2 C), 128.2, 129.0 (2 C), 159.9, 170.9.

HRMS (EI) (C₁₄H₁₈Cl₃N₃O₆S⁺): calc.:432.9915; found:432.9909.



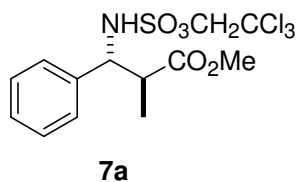
¹H-NMR (250 MHz, CDCl₃): δ [ppm] = 1.18–1.21 (m, 3 H), 2.11 (s, 3 H), 3.80 (s, 3 H), 4.24 (d, ²*J* = 10.8 Hz, 1 H), 4.29 (d, ²*J* = 10.8 Hz, 1 H), 4.40–4.49 (m, 1 H), 5.10–5.18 (m, 1 H), 5.64 (d, ³*J* = 8.0 Hz, 1 H), 6.88–6.92 (m, 2 H), 7.22–7.25 (m, 2 H).

¹³C-NMR (90.6 MHz, CDCl₃): δ [ppm] = 17.9, 21.3, 55.5, 63.2, 72.4, 78.2, 99.7, 114.6 (2 C), 128.3, 128.5 (2 C), 160.0, 171.4.

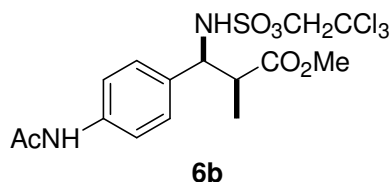


Compounds **6a** and **7a** were obtained from ester **5a**. After flash chromatography (P:EtOAc = 8:1) of the crude product a diastereomeric mixture of **6a** and **7a** (43%, dr(**6a**/**7a**) = 78:22) was isolated as a colorless oil.

R_f	0.14 (P:Et ₂ O = 8:1).
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.20 (d, ³ J = 7.2 Hz, 3 H), 3.04–3.12 (m, 1 H), 3.63 (s, 3 H), 4.28 (d, ² J = 10.8 Hz, 1 H), 4.32 (d, ² J = 10.8 Hz, 1 H), 4.71 (dd, ³ J = 9.0 Hz, ³ J = 6.0 Hz, 1 H), 6.28 (d, ³ J = 9.0 Hz, 1 H), 7.25–7.37 (m, 5 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 16.9, 45.2, 52.3, 60.9, 78.2, 93.3, 127.4 (2 C), 128.7, 128.9 (2 C), 137.7, 173.9.



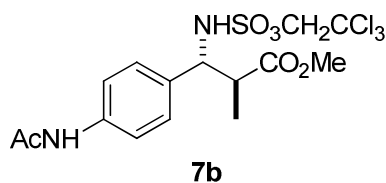
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.33 (d, ³ J = 7.1 Hz, 3 H), 2.89–2.97 (m, 1 H), 3.65 (s, 3 H), 4.42 (d, ² J = 11.0 Hz, 1 H), 4.46 (d, ² J = 11.0 Hz, 1 H), 4.63 (dd, ³ J = 8.9 Hz, ³ J = 5.7 Hz, 1 H), 6.54 (d, ³ J = 8.9 Hz, 1 H), 7.25–7.37 (m, 5 H).
¹³ C-NMR	(90.6 MHz, CDCl ₃): δ [ppm] = 16.0, 45.6, 52.4, 61.3, 78.1, 93.3, 126.6 (2 C), 128.5, 129.0 (2 C), 139.1, 175.4.



Compounds **6b** and **7b** were obtained from ester **5b**. After flash chromatography (P:EtOAc = 1:1) of the crude product a diastereomeric mixture of **6b** and **7b** (50%, dr(**6b**/**7b**) = 78:22) was isolated as a pale white solid.

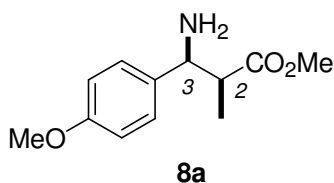
R_f	0.12 (P:EtOAc = 1:1).
¹ H-NMR	(360 MHz, CDCl ₃): δ [ppm] = 1.19 (d, ³ J = 7.2 Hz, 3 H), 2.18 (s, 3 H), 3.03–3.11 (m, 1 H), 3.64 (s, 3 H), 4.35 (d, ² J = 10.8 Hz, 1 H), 4.40 (d, ² J = 10.8 Hz, 1 H), 4.68 (dd, ³ J = 8.9 Hz, ³ J = 6.0 Hz, 1 H), 6.36 (d, ³ J = 8.9 Hz, 1 H), 7.21–7.25 (m, 3 H), 7.48 (d, ³ J = 8.5 Hz, 2 H).
¹³ C-NMR	(90.6 MHz, DMSO- <i>d</i> ₆): δ [ppm] = 14.3, 24.0, 45.8, 51.6, 60.3, 77.1, 93.5, 118.8 (2 C), 127.5 (2 C), 134.1, 138.9, 168.3, 173.1.

HRMS (EI) (C₁₅H₁₉Cl₃N₂O₆S⁺): calc.:460.0024; found: 460.0019.



¹H-NMR (360 MHz, CDCl₃): δ [ppm] = 1.35 (d, ³J = 7.2 Hz, 3 H), 2.18 (s, 3 H), 2.89–2.92 (m, 1 H), 3.64 (s, 3 H), 4.39 (s, 2 H), 4.59–4.63 (m, 1 H), 6.57 (d, ³J = 9.4 Hz, 1 H), 7.21–7.25 (m, 3 H), 7.48 (d, ³J = 8.5 Hz, 2 H).

● Cleavage of the Tces Protecting Group



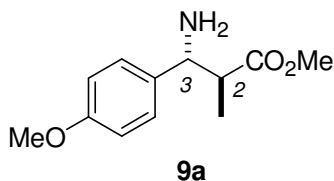
The Tces-protecting group of **3a** and **4a** was cleaved following the protocol of Du Bois^[2]. After flash chromatography (CH₂Cl₂:MeOH = 40:1) of the crude product a diastereomeric mixture of the free amines **8a** and **9a** (60%, dr = 82:18) was isolated as a yellow oil.

HPLC t_R = 24.9/30.1 min.

R_f 0.13 (CH₂Cl₂:MeOH = 40:1).

¹H-NMR (360 MHz, CDCl₃): δ [ppm] = 1.17 (d, ³J = 7.0 Hz, 3 H), 2.63–2.78 (m, 1 H), 3.58 (s, 3 H), 3.80 (s, 3 H), 4.23 (d, ³J = 6.1 Hz, 1 H), 6.84–6.89 (m, 2 H), 7.18–7.26 (m, 2 H).

¹³C-NMR (90.6 MHz, CDCl₃): δ [ppm] = 12.4, 47.6, 51.7, 55.4, 57.0, 113.8 (2 C), 127.8 (2 C), 135.9, 158.8, 175.7.

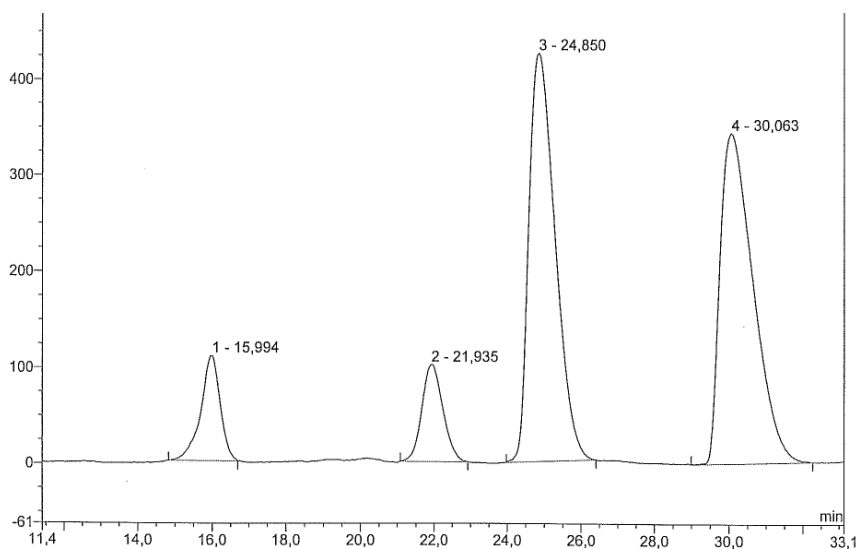


HPLC t_R = 16.0/21.9 min.

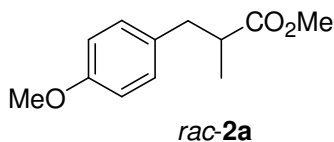
$^1\text{H-NMR}$ (360 MHz, CDCl_3): δ [ppm] = 0.94 (d, $^3J = 7.1$ Hz, 3 H), 1.57 (s, br., 2 H), 2.60–2.67 (m, 1 H), 3.72 (s, 3 H), 3.80 (s, 3 H), 3.98 (d, $^3J = 9.9$ Hz, 1 H), 6.83–6.89 (m, 2 H), 7.14–7.26 (m, 2 H).

Literature data for the parent phenyl substituted β -aminoester show a coupling constant between H-2 and H-3 of $^3J = 5.9$ Hz for the *syn*-diastereomer^[3a] and $^3J = 9.5$ Hz for the *anti*-diastereomer.^[3b] The major diastereomer **8a** of the CH-insertion exhibits a coupling constant of $^3J = 6.1$ Hz and the minor diastereomer **9a** of $^3J = 9.9$ Hz. A comparison of our NMR-data with the literature data^[3] thus confirms the assignment based on the X-ray crystal structure analysis.

HPLC-trace from the racemic mixture of the diastereomers **8a** and **9a** (chiral stationary phase: Daicel Chiralcel OJ-H, 250×4.6 mm, mobile phase: MeOH, flow rate: 1.0 ml/min).

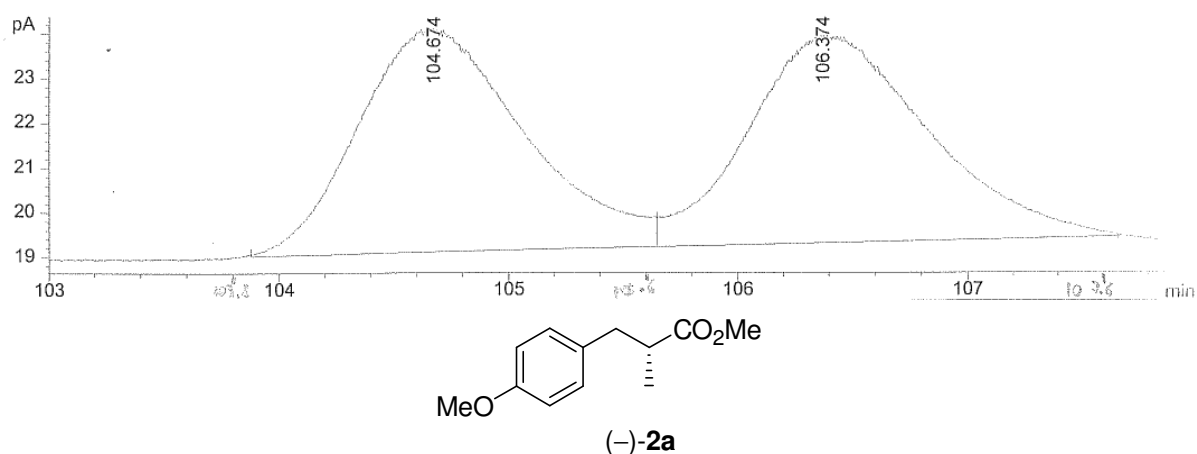


- Retention of the absolute configuration in the course of C-H amination



GC $t_R = 104.7/106.4$ min

Compound *rac-2a* is literature known. The spectroscopic data of our synthetic material were in accord with the literature.^[4] GC-trace of *rac-2a*

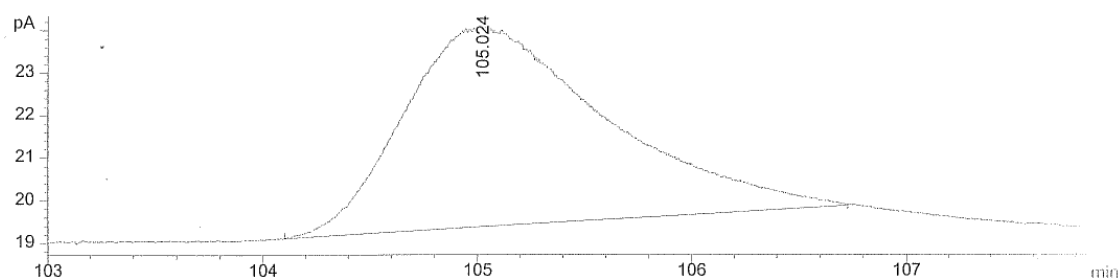


The substrate **(-)-2a** was prepared according to the procedure described in the literature.^[5] The *ee* was established by chiral GC (Agilent β -Dex 325 column, 20% permethylated β -cyclodextrin (2,3-dimethyl-6-TBDMS- β -cyclodextrin, 1 min 60 °C, 20 K/min to 123 °C, 125 min at 123 °C, 30 °C/min to 220 °C, 4 min 220 °C).

$[\alpha]_D^{20}$ -33 (c = 0.23, in CHCl₃).

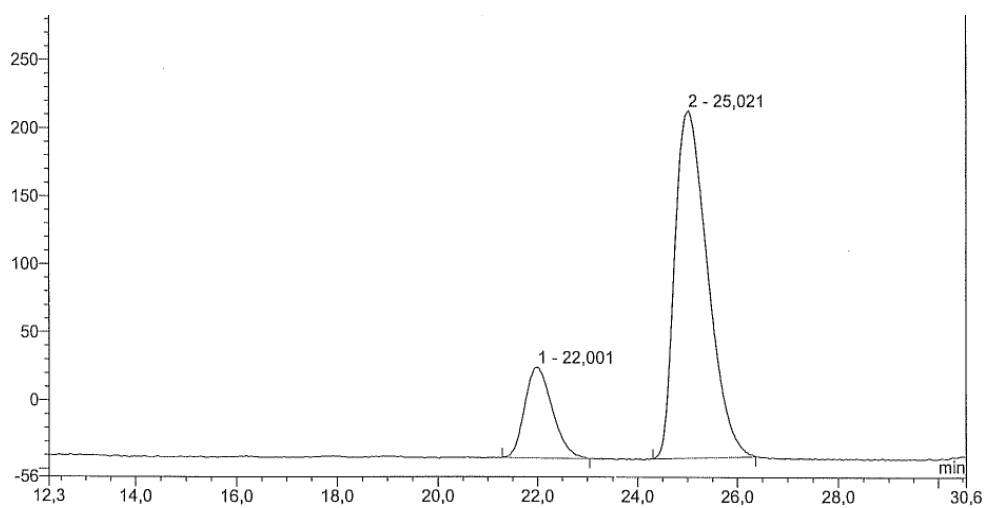
GC t_R = 105.0 min

GC-trace of **(-)-2a**



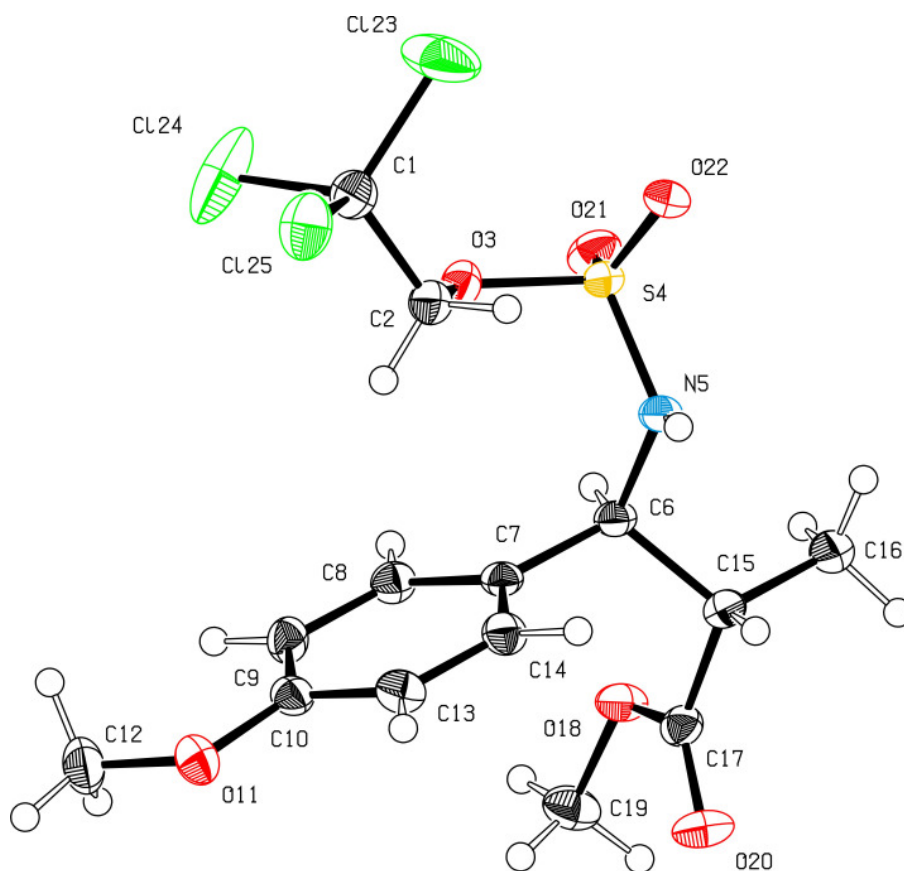
The C-H amination reaction with **(-)-2a** was carried out following the general procedure. The product was obtained as a diastereomeric mixture of **3a** and **4a** (dr(**3a/4a**) = 82:18). The *ee* of **3a**, **4a** was established by chiral HPLC after deprotection of the Tces-group.^[2] Both diastereomers **8a**, **9a** were enantiomerically pure according to HPLC analysis (chiral stationary phase: Daicel Chiralcel OJ-H, 250 × 4.6 mm, mobile phase: MeOH, flow rate: 1.0 ml/min).

HPLC-trace of the enantiomerically pure diastereomers **8a** and **9a** (t_R = 22.0/25.0 min.)



Crystal Structure Determination

Compound 3a



Molecular Formula:	C ₁₄ H ₁₈ Cl ₃ N O ₆ S
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.13 × 0.15 × 0.48 mm
Molecular Weight:	434.71 a.m.u.
F ₀₀₀ :	896
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic <i>P</i> 2 ₁ /c (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9877 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 2.03° < θ < 25.40°; Mo(Kα ⁻); λ = 71.073 pm <i>a</i> = 1015.19(5) pm <i>b</i> = 1033.66(6) pm β = 99.174(3)° <i>c</i> = 1870.36(9) pm <i>V</i> = 1937.58(18) · 10 ⁶ pm ³ ; <i>Z</i> = 4; <i>D</i> _{calc} = 1.490 g cm ⁻³ ; Mos. = 0.78
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 60 kV; 50 mA; λ = 71.073 pm; Mo(Kα ⁻)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	2.03° < θ < 25.40°; h: -12/12, k: -12/12, l: -22/22
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 9 runs; 4891 films / scaled: 9 runs; 4891 films φ- and ω-movement; Increment: Δφ/Δω = 0.50°; dx = 60.0 mm
LP - Correction:	Yes ^[7]

Intensity Correction	No/Yes; during scaling ^[7]
Absorption Correction:	Multi-scan; during scaling; $\mu = 0.610 \text{ mm}^{-1}$ ^[7]
	Correction Factors: $T_{\min} = 0.6238$ $T_{\max} = 0.7452$
Reflection Data:	54055 reflections were integrated and scaled
	2185 reflections systematic absent and rejected
	51870 reflections to be merged
	3570 independent reflections
	0.037 R_{int} : (basis F_o^2)
	3570 independent reflections (all) were used in refinements
	3313 independent reflections with $I_o > 2\sigma(I_o)$
	99.9 % completeness of the data set
	233 parameter full-matrix refinement
	15.3 reflections per parameter
Solution:	Direct Methods ^[8] ; Difference Fourier syntheses
Refinement Parameters:	In the asymmetric unit:
	25 Non-hydrogen atoms with anisotropic displacement parameters
	1 Hydrogen atoms with isotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 95, 98, 99, 100 \text{ pm}$). Isotropic displacement parameters were calculated from the parent carbon atom ($U_{\text{H}} = 1.2/1.5 U_{\text{C}}$). The hydrogen atoms were included in the structure factor calculations but not refined.
Hydrogen Atoms:	H□N refined freely
Atomic Form Factors:	For neutral atoms and anomalous dispersion ^[9]
Extinction Correction:	no
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a*P)^2 + b*P$ with a: 0.0458; b: 4.1519; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2*F_c^2]/3$
Shift/Err:	Less than 0.001 in the last cycle of refinement:
Resid. Electron Density:	+1.68 $e_0/\text{\AA}^3$; -1.55 $e_0/\text{\AA}^3$
R1:	$\Sigma(F_o - F_c)/\Sigma F_o $
$[F_o > 4\sigma(F_o)$; N=3313]:	= 0.0461
[all reflctns; N=3570]:	= 0.0498
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$
$[F_o > 4\sigma(F_o)$; N=3313]:	= 0.1122
[all reflctns; N=3570]:	= 0.1164
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO-NV})]^{1/2}$ = 1.058
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$

Table S1 – Bond Distances (Angstrom) for: **Compound 3a**

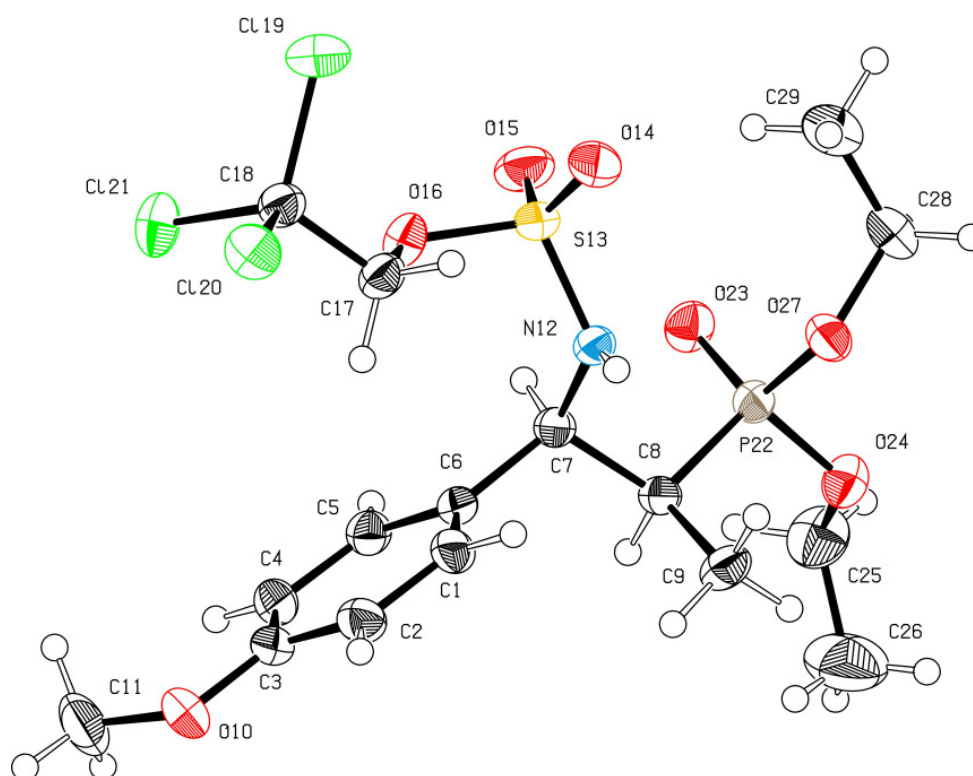
C123	C1	1.759 (3)	C10	C13	1.396 (4)
C124	C1	1.751 (3)	C13	C14	1.383 (4)
C125	C1	1.772 (3)	C15	C16	1.536 (4)
S4	O3	1.6061 (18)	C15	C17	1.515 (3)
S4	O21	1.417 (2)	C2	H21	0.9900
S4	O22	1.4254 (19)	C2	H22	0.9900
S4	N5	1.597 (2)	C6	H61	1.0000
O3	C2	1.429 (3)	C8	H81	0.9500
O11	C10	1.369 (3)	C9	H91	0.9500
O11	C12	1.420 (4)	C12	H121	0.9800

O18	C17	1.322(4)	C12	H122	0.9800
O18	C19	1.451(4)	C13	H131	0.9500
O20	C17	1.214(3)	C14	H141	0.9500
N5	C6	1.481(3)	C15	H151	1.0000
N5	H5	0.79(3)	C15	H151	1.0000
C1	C2	1.520(4)	C16	H161	0.9800
C6	C15	1.546(3)	C16	H162	0.9800
C6	C7	1.514(3)	C16	H163	0.9800
C7	C8	1.383(3)	C19	H191	0.9800
C7	C14	1.402(3)	C19	H192	0.9800
C8	C9	1.394(4)	C19	H193	0.9800
C9	C10	1.388(4)			

Table S2 – Bond Angles (Degrees) for: **Compound 3a**

O3	-S4	-O21	101.70(11)	O3	-C2	-H21	110.00
O3	-S4	-O22	108.33(10)	O3	-C2	-H22	110.00
O3	-S4	-N5	107.92(11)	C1	-C2	-H21	110.00
O21	-S4	-O22	121.53(12)	C1	-C2	-H22	110.00
O21	-S4	-N5	109.68(12)	H21	-C2	-H22	108.00
O22	-S4	-N5	106.99(11)	N5	-C6	-H61	108.00
S4	-O3	-C2	119.20(17)	C7	-C6	-H61	108.00
C10	-O11	-C12	117.9(2)	C15	-C6	-H61	108.00
C17	-O18	-C19	116.6(2)	C7	-C8	-H81	119.00
S4	-N5	-C6	120.30(16)	C9	-C8	-H81	119.00
S4	-N5	-H5	113(2)	C8	-C9	-H91	120.00
C6	-N5	-H5	117(2)	C10	-C9	-H91	120.00
C123	-C1	-C124	110.35(17)	O11	-C12	-H121	109.00
C124	-C1	-C125	108.46(15)	O11	-C12	-H122	109.00
C123	-C1	-C125	108.01(17)	O11	-C12	-H123	109.00
C123	-C1	-C2	110.87(19)	H121	-C12	-H122	109.00
C125	-C1	-C2	108.1(2)	H121	-C12	-H123	109.00
C124	-C1	-C2	110.9(2)	H122	-C12	-H123	110.00
O3	-C2	-C1	109.3(2)	C10	-C13	-H131	120.00
N5	-C6	-C7	112.76(19)	C14	-C13	-H131	120.00
N5	-C6	-C15	106.75(17)	C7	-C14	-H141	120.00
C7	-C6	-C15	112.83(17)	C13	-C14	-H141	120.00
C6	-C7	-C8	119.9(2)	C6	-C15	-H151	108.00
C8	-C7	-C14	118.6(2)	C16	-C15	-H151	108.00
C6	-C7	-C14	121.49(19)	C17	-C15	-H151	108.00
C7	-C8	-C9	121.6(2)	C15	-C16	-H161	110.00
C8	-C9	-C10	119.1(2)	C15	-C16	-H162	110.00
O11	-C10	-C9	124.7(3)	C15	-C16	-H163	109.00
O11	-C10	-C13	115.2(2)	H161	-C16	-H162	109.00
C9	-C10	-C13	120.1(2)	H161	-C16	-H163	109.00
C10	-C13	-C14	120.1(2)	H162	-C16	-H163	109.00
C7	-C14	-C13	120.5(2)	O18	-C19	-H191	109.00
C6	-C15	-C17	109.81(19)	O18	-C19	-H192	109.00
C16	-C15	-C17	109.8(2)	O18	-C19	-H193	109.00
C6	-C15	-C16	111.97(19)	H191	-C19	-H192	110.00
O20	-C17	-C15	124.1(3)	H191	-C19	-H193	109.00
O18	-C17	-O20	123.8(2)	H192	-C19	-H193	109.00
O18	-C17	-C15	112.1(2)				

Compound 3b



Molecular Formula:	$C_{16}H_{25}Cl_3NO_7P_2S$
Crystal Color / Shape	Colorless needle
Crystal Size	Approximate size of crystal fragment used for data collection: $0.10 \times 0.18 \times 0.76$ mm
Molecular Weight:	512.76 a.m.u.
F_{000} :	1064
Systematic Absences:	$h0l: l \neq 2n; 0k0: k \neq 2n$
Space Group:	Monoclinic $P 2_1/c$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9026 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $1.84^\circ < \theta < 25.39^\circ$; $Mo(K\alpha)$; $\lambda = 71.073$ pm $a = 1144.76(5)$ pm $b = 1743.30(7)$ pm $\beta = 104.311(2)^\circ$ $c = 1201.45(5)$ pm $V = 2323.28(17) \cdot 10^6$ pm ³ ; $Z = 4$; $D_{calc} = 1.466$ g cm ⁻³ ; Mos. = 0.63
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 60 kV; 50 mA; $\lambda = 71.073$ pm; $Mo(K\alpha)$
Temperature:	$(-100 \pm 1)^\circ C$; (173 ± 1) K
Measurement Range:	$1.84^\circ < \theta < 25.39^\circ$; h: -13/13, k: -21/21, l: -13/14
Measurement Time:	2×5 s per film
Measurement Mode:	measured: 12 runs; 5945 films / scaled: 12 runs; 5945 films ϕ - and ω -movement; Increment: $\Delta\phi/\Delta\omega = 0.50^\circ$; dx = 60.0 mm
LP - Correction:	Yes ^[7]
Intensity Correction	No/Yes; during scaling ^[7]
Absorption Correction:	Multi-scan; during scaling; $\mu = 0.589$ mm ⁻¹ ^[7]
Reflection Data:	Correction Factors: $T_{min} = 0.4309$ $T_{max} = 0.7452$ 59121 reflections were integrated and scaled

	1574	reflections systematic absent and rejected
	57547	reflections to be merged
	4160	independent reflections
	0.059	R_{int} : (basis F_o^2)
	4160	independent reflections (all) were used in refinements
	3802	independent reflections with $I_o > 2\sigma(I_o)$
	97.3 %	completeness of the data set
	270	parameter full-matrix refinement
	15.4	reflections per parameter
Solution:	Direct Methods ^[8] ; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	29	Non-hydrogen atoms with anisotropic displacement parameters
	1	Hydrogen atoms with isotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 95, 98, 99, 100$ pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_{\text{H}} = 1.2/1.5 U_{\text{C}}$). The hydrogen atoms were included in the structure factor calculations but not refined.	
Hydrogen Atoms:	H□N refined freely	
Atomic Form Factors:	For neutral atoms and anomalous dispersion ^[9]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P$ with a: 0.0506; b: 1.1049; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2 \cdot F_c^2]/3$	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	$+0.50 \text{ e}_0/\text{\AA}^3$; $-0.28 \text{ e}_0/\text{\AA}^3$	
R1:	$\Sigma(F_o - F_c)/\Sigma F_o $	
$[F_o > 4\sigma(F_o)$; N=3802]:		= 0.0328
[all refltns; N=4160]:		= 0.0353
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
$[F_o > 4\sigma(F_o)$; N=3802]:		= 0.0880
[all refltns; N=4160]:		= 0.0900
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2}$	
		= 1.023
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$	

Table S3 – Bond Distances (Angstrom) for: **Compound 3b**

C119	–C18	1.7799 (18)	C17	–C18	1.512 (3)
C120	–C18	1.7672 (19)	C25	–C26	1.486 (4)
C121	–C18	1.7654 (19)	C28	–C29	1.472 (3)
S13	–O14	1.4209 (14)	C1	–H11	0.9500
S13	–O15	1.4166 (15)	C2	–H21	0.9500
S13	–O16	1.6012 (14)	C4	–H41	0.9500
S13	–N12	1.5947 (16)	C5	–H51	0.9500
P22	–O23	1.4668 (14)	C7	–H71	1.0000
P22	–O24	1.5783 (14)	C8	–H81	1.0000
P22	–O27	1.5623 (14)	C9	–H91	0.9800
P22	–C8	1.8047 (18)	C9	–H92	0.9800
O10	–C3	1.366 (2)	C9	–H93	0.9800
O10	–C11	1.427 (3)	C11	–H111	0.9800
O16	–C17	1.432 (2)	C11	–H112	0.9800
O24	–C25	1.454 (3)	C11	–H113	0.9800

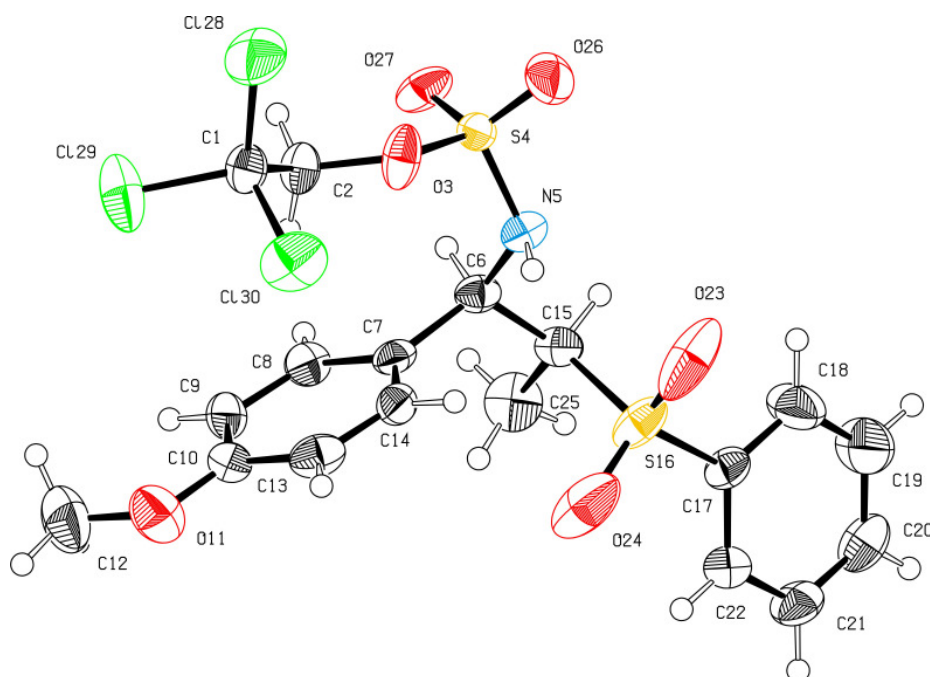
O27	-C28	1.456(2)	C17	-H171	0.9900
N12	-C7	1.474(2)	C17	-H172	0.9900
N12	-H12	0.79(2)	C25	-H251	0.9900
C1	-C2	1.384(3)	C25	-H252	0.9900
C1	-C6	1.396(2)	C26	-H261	0.9800
C2	-C3	1.389(3)	C26	-H262	0.9800
C3	-C4	1.381(3)	C26	-H263	0.9800
C4	-C5	1.393(3)	C28	-H281	0.9900
C5	-C6	1.382(2)	C28	-H282	0.9900
C6	-C7	1.519(2)	C29	-H291	0.9800
C7	-C8	1.549(2)	C29	-H292	0.9800
C8	-C9	1.531(3)	C29	-H293	0.9800

Table S4 Bond Angles (Degrees) for: **Compound 3b**

O14	-S13	-O15	121.81(8)	C5	-C4	-H41	120.00
O14	-S13	-O16	108.11(8)	C4	-C5	-H51	119.00
O14	-S13	-N12	107.04(9)	C6	-C5	-H51	119.00
O15	-S13	-O16	101.80(8)	N12	-C7	-H71	107.00
O15	-S13	-N12	109.92(9)	C6	-C7	-H71	107.00
O16	-S13	-N12	107.33(8)	C8	-C7	-H71	107.00
O23	-P22	-O24	113.34(8)	P22	-C8	-H81	106.00
O23	-P22	-O27	115.50(8)	C7	-C8	-H81	106.00
O23	-P22	-C8	112.45(8)	C9	-C8	-H81	106.00
O24	-P22	-O27	102.65(8)	C8	-C9	-H91	109.00
O24	-P22	-C8	106.92(8)	C8	-C9	-H92	109.00
O27	-P22	-C8	105.04(8)	C8	-C9	-H93	109.00
C3	-O10	-C11	116.90(16)	H91	-C9	-H92	109.00
S13	-O16	-C17	118.12(12)	H91	-C9	-H93	109.00
P22	-O24	-C25	121.01(13)	H92	-C9	-H93	109.00
P22	-O27	-C28	121.41(13)	O10	-C11	-H111	109.00
S13	-N12	-C7	121.16(13)	O10	-C11	-H112	110.00
S13	-N12	-H12	111.8(16)	O10	-C11	-H113	109.00
C7	-N12	-H12	119.1(15)	H111	-C11	-H112	109.00
C2	-C1	-C6	120.72(16)	H111	-C11	-H113	110.00
C1	-C2	-C3	120.39(17)	H112	-C11	-H113	109.00
O10	-C3	-C2	115.62(17)	O16	-C17	-H171	110.00
C2	-C3	-C4	119.63(17)	O16	-C17	-H172	110.00
O10	-C3	-C4	124.75(17)	C18	-C17	-H171	110.00
C3	-C4	-C5	119.40(17)	C18	-C17	-H172	110.00
C4	-C5	-C6	121.87(17)	H171	-C17	-H172	108.00
C5	-C6	-C7	119.52(16)	O24	-C25	-H251	110.00
C1	-C6	-C5	117.97(16)	O24	-C25	-H252	110.00
C1	-C6	-C7	122.51(15)	C26	-C25	-H251	110.00
C6	-C7	-C8	112.62(13)	C26	-C25	-H252	110.00
N12	-C7	-C8	109.16(14)	H251	-C25	-H252	108.00
N12	-C7	-C6	113.58(14)	C25	-C26	-H261	109.00
P22	-C8	-C9	112.73(12)	C25	-C26	-H262	109.00
P22	-C8	-C7	110.37(11)	C25	-C26	-H263	110.00
C7	-C8	-C9	115.51(15)	H261	-C26	-H262	109.00
O16	-C17	-C18	107.96(15)	H261	-C26	-H263	109.00
C119	-C18	-C120	108.99(10)	H262	-C26	-H263	110.00
C120	-C18	-C121	109.74(10)	O27	-C28	-H281	110.00
C120	-C18	-C17	107.45(13)	O27	-C28	-H282	109.00
C121	-C18	-C17	110.95(13)	C29	-C28	-H281	110.00
C119	-C18	-C17	110.58(13)	C29	-C28	-H282	110.00
C119	-C18	-C121	109.11(10)	H281	-C28	-H282	108.00
O24	-C25	-C26	109.2(2)	C28	-C29	-H291	109.00
O27	-C28	-C29	110.72(19)	C28	-C29	-H292	109.00
C2	-C1	-H11	120.00	C28	-C29	-H293	109.00
C6	-C1	-H11	120.00	H291	-C29	-H292	110.00
C1	-C2	-H21	120.00	H291	-C29	-H293	110.00

C3	-C2	-H21	120.00	H292	-C29	-H293	109.00
C3	-C4	-H41	120.00	.	.	.	no

Compound 3c



Molecular Formula:	C ₁₈ H ₂₀ Cl ₃ N O ₆ S ₂
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.48 × 0.58 × 0.58 mm
Molecular Weight:	516.84 a.m.u.
F ₀₀₀ :	1064
Systematic Absences:	0kl: k+l≠2n; h0l: h≠2n; 00l: l≠2n
Space Group:	Orthorhombic <i>P na</i> 2 ₁ (I.T.-No.: 33)
Cell Constants:	Least-squares refinement of 9915 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 4.34° < θ < 65.84°; Cu(Kα); λ = 154.180 pm <i>a</i> = 1167.61(4) pm <i>b</i> = 2038.79(7) pm <i>c</i> = 937.47(3) pm <i>V</i> = 2231.66(13) · 10 ⁶ pm ³ ; <i>Z</i> = 4; <i>D</i> _{calc} = 1.538 g cm ⁻³ ; Mos. = 0.81
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 40 kV; 30 mA; λ = 154.180 pm; Cu(Kα)
Temperature:	(20±1) °C; (293±1) K
Measurement Range:	4.34° < θ < 65.84°; h: -13/13, k: -21/24, l: -10/11
Measurement Time:	2 × 7.50 s per film
Measurement Mode:	measured: 14 runs; 3507 films / scaled: 14 runs; 3507 films φ- and ω-movement; Increment: Δφ/Δω = 1.00°; dx = 35.0 mm
LP - Correction:	Yes ^[7]
Intensity Correction	No/Yes; during scaling ^[7]
Absorption Correction:	Multi-scan; during scaling; μ = 5.787 mm ⁻¹ ^[7]
Reflection Data:	Correction Factors: T _{min} = 0.4505 T _{max} = 0.7526 33301 reflections were integrated and scaled 1419 reflections systematic absent and rejected

	31882	reflections to be merged
	3744	independent reflections
	0.045	R_{int} : (basis F_o^2)
	3744	independent reflections (all) were used in refinements
	3589	independent reflections with $I_o > 2\sigma(I_o)$
	96.8 %	completeness of the data set
	274	parameter full-matrix refinement
	13.7	reflections per parameter
Solution:	Direct Methods ^[8] ; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	30	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 93, 96, 97, 98$ pm; $d_{\text{N-H}} = 90$ pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_{\text{H}} = 1.2/1.5 U_{\text{C}}$, $U_{\text{H}} = 1.2 U_{\text{N}}$). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion ^[9]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P$ with a: 0.0530; b: 4.1168; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2 \cdot F_c^2]/3$	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	+0.55 $e_0/\text{\AA}^3$; -0.39 $e_0/\text{\AA}^3$	
R1:	$\Sigma(F_o - F_c)/\Sigma F_o $	
	$[F_o > 4\sigma(F_o)$; N=3589]:	= 0.0482
	$[\text{all reflctns}$; N=3744]:	= 0.0513
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
	$[F_o > 4\sigma(F_o)$; N=3589]:	= 0.1238
	$[\text{all reflctns}$; N=3744]:	= 0.1270
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2}$	
		= 1.086
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$ The correct enantiomere is proved by synthesis Twin refinement (twin operation: inversion) BASF = 0.42(2)	

Table S5 – Bond Distances (Angstrom) for: **Compound 3c**

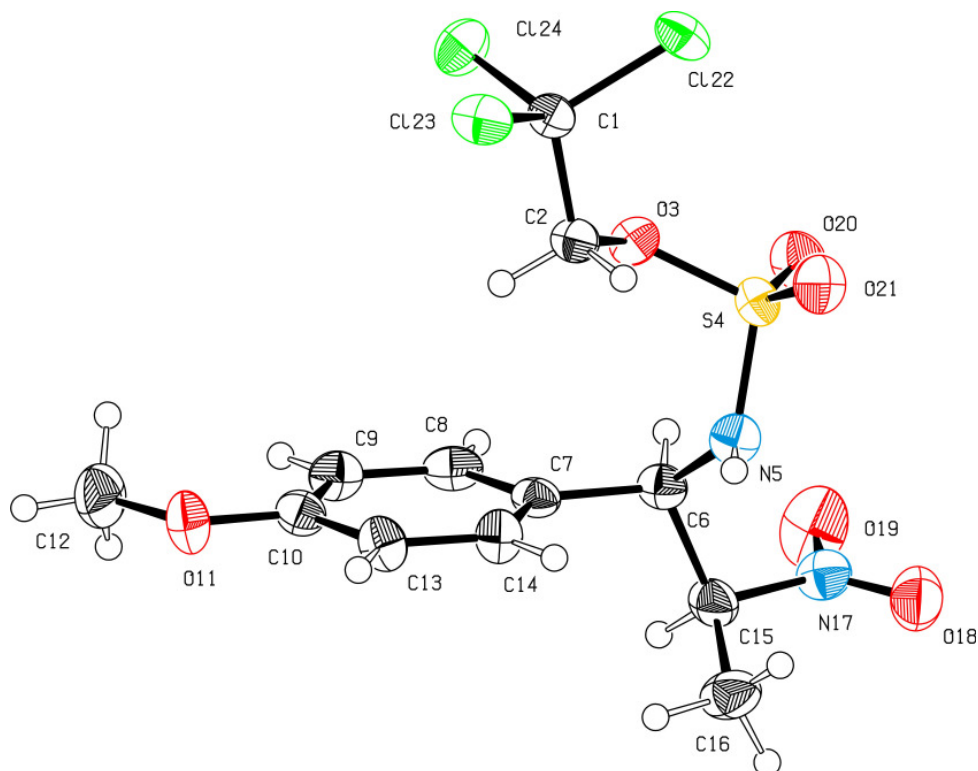
C128	-C1	1.739 (5)	C17	-C22	1.374 (6)
C129	-C1	1.760 (5)	C17	-C18	1.371 (8)
C130	-C1	1.773 (5)	C18	-C19	1.389 (9)
S4	-O3	1.585 (3)	C19	-C20	1.349 (9)
S4	-O26	1.395 (4)	C20	-C21	1.355 (7)
S4	-O27	1.402 (3)	C21	-C22	1.371 (6)
S4	-N5	1.587 (4)	C2	-H21	0.9700
S16	-O23	1.415 (6)	C2	-H22	0.9700
S16	-O24	1.426 (6)	C6	-H61	0.9800
S16	-C15	1.802 (5)	C8	-H81	0.9300
S16	-C17	1.758 (4)	C9	-H91	0.9300
O3	-C2	1.415 (6)	C12	-H121	0.9600
O11	-C10	1.334 (6)	C12	-H122	0.9600
O11	-C12	1.435 (8)	C12	-H123	0.9600
N5	-C6	1.457 (6)	C13	-H131	0.9300

N5	-H5	0.9000	C14	-H141	0.9300
C1	-C2	1.510(6)	C15	-H151	0.9800
C6	-C15	1.560(6)	C18	-H181	0.9300
C6	-C7	1.516(6)	C19	-H191	0.9300
C7	-C14	1.372(7)	C20	-H201	0.9300
C7	-C8	1.385(6)	C21	-H211	0.9300
C8	-C9	1.391(6)	C22	-H221	0.9300
C9	-C10	1.369(7)	C25	-H251	0.9600
C10	-C13	1.414(7)	C25	-H252	0.9600
C13	-C14	1.388(7)	C25	-H253	0.9600
C15	-C25	1.498(7)			

Table S6 Bond Angles (Degrees) for: **Compound 3c**

O3	-S4	-O26	102.5(2)	C19	-C20	-C21	120.1(4)
O3	-S4	-O27	108.55(18)	C20	-C21	-C22	121.2(4)
O3	-S4	-N5	108.34(19)	C17	-C22	-C21	118.7(4)
O26	-S4	-O27	120.9(2)	O3	-C2	-H21	110.00
O26	-S4	-N5	107.8(2)	O3	-C2	-H22	110.00
O27	-S4	-N5	108.2(2)	C1	-C2	-H21	110.00
O23	-S16	-O24	120.7(3)	C1	-C2	-H22	110.00
O23	-S16	-C15	106.7(3)	H21	-C2	-H22	109.00
O23	-S16	-C17	107.4(2)	N5	-C6	-H61	105.00
O24	-S16	-C15	108.8(3)	C7	-C6	-H61	105.00
O24	-S16	-C17	107.3(2)	C15	-C6	-H61	105.00
C15	-S16	-C17	104.9(2)	C7	-C8	-H81	119.00
S4	-O3	-C2	120.0(3)	C9	-C8	-H81	119.00
C10	-O11	-C12	117.3(5)	C8	-C9	-H91	120.00
S4	-N5	-C6	122.8(3)	C10	-C9	-H91	120.00
S4	-N5	-H5	106.00	O11	-C12	-H121	109.00
C6	-N5	-H5	106.00	O11	-C12	-H122	109.00
C128	-C1	-C2	112.6(3)	O11	-C12	-H123	109.00
C129	-C1	-C130	109.8(3)	H121	-C12	-H122	109.00
C129	-C1	-C2	106.5(3)	H121	-C12	-H123	109.00
C130	-C1	-C2	110.6(3)	H122	-C12	-H123	110.00
C128	-C1	-C129	109.6(2)	C10	-C13	-H131	120.00
C128	-C1	-C130	107.8(3)	C14	-C13	-H131	121.00
O3	-C2	-C1	107.2(4)	C7	-C14	-H141	119.00
N5	-C6	-C15	109.6(4)	C13	-C14	-H141	118.00
N5	-C6	-C7	114.1(3)	S16	-C15	-H151	107.00
C7	-C6	-C15	117.1(4)	C6	-C15	-H151	107.00
C6	-C7	-C14	123.6(4)	C25	-C15	-H151	107.00
C8	-C7	-C14	116.7(4)	C17	-C18	-H181	121.00
C6	-C7	-C8	119.5(4)	C19	-C18	-H181	121.00
C7	-C8	-C9	122.1(4)	C18	-C19	-H191	120.00
C8	-C9	-C10	120.6(4)	C20	-C19	-H191	120.00
O11	-C10	-C9	126.0(4)	C19	-C20	-H201	120.00
C9	-C10	-C13	118.6(4)	C21	-C20	-H201	120.00
O11	-C10	-C13	115.5(4)	C20	-C21	-H211	119.00
C10	-C13	-C14	119.0(4)	C22	-C21	-H211	119.00
C7	-C14	-C13	123.0(4)	C17	-C22	-H221	121.00
S16	-C15	-C6	113.6(3)	C21	-C22	-H221	121.00
S16	-C15	-C25	112.3(3)	C15	-C25	-H251	109.00
C6	-C15	-C25	110.6(4)	C15	-C25	-H252	110.00
S16	-C17	-C18	120.7(4)	C15	-C25	-H253	109.00
C18	-C17	-C22	120.8(4)	H251	-C25	-H252	109.00
S16	-C17	-C22	118.5(3)	H251	-C25	-H253	109.00
C17	-C18	-C19	118.6(5)	H252	-C25	-H253	109.00
C18	-C19	-C20	120.6(6)				

Compound 3d



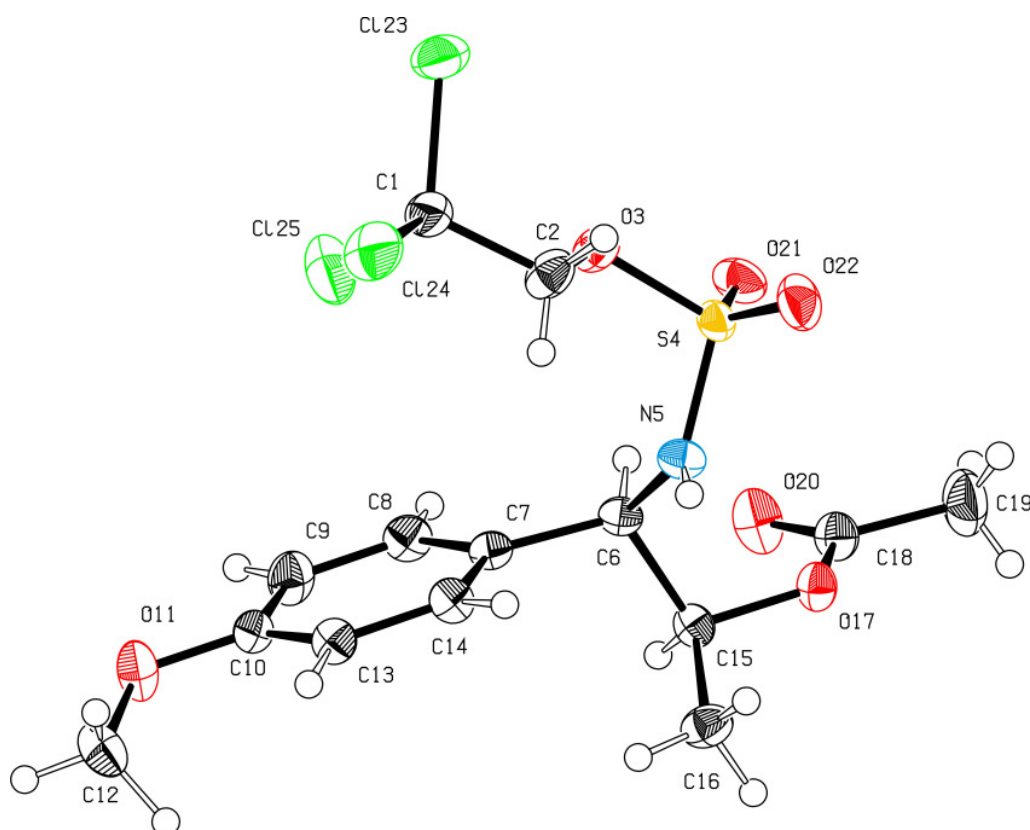
Molecular Formula:	C ₁₂ H ₁₅ Cl ₃ N ₂ O ₆ S
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.05 × 0.25 × 0.43 mm
Molecular Weight:	421.68 a.m.u.
F ₀₀₀ :	864
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic <i>P</i> 2 ₁ /c (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9971 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 2.08° < θ < 25.32°; Mo(Kα ⁻); λ = 71.073 pm <i>a</i> = 919.97(4) pm <i>b</i> = 1959.83(8) pm β = 95.769(2)° <i>c</i> = 981.97(4) pm <i>V</i> = 1761.51(13) · 10 ⁶ pm ³ ; <i>Z</i> = 4; <i>D</i> _{calc} = 1.590 g cm ⁻³ ; Mos. = 0.78
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(Kα ⁻)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	2.08° < θ < 25.32°; h: -11/11, k: -23/23, l: -11/11
Measurement Time:	2 × 10 s per film
Measurement Mode:	measured: 6 runs; 2748 films / scaled: 6 runs; 2748 films φ- and ω-movement; Increment: Δφ/Δω = 0.50°; dx = 35.0 mm
LP - Correction:	Yes ^[7]
Intensity Correction	No/Yes; during scaling ^[7]
Absorption Correction:	Multi-scan; during scaling; μ = 0.669 mm ⁻¹ ^[7] Correction Factors: T _{min} = 0.6678 T _{max} = 0.7452
Reflection Data:	54684 reflections were integrated and scaled 1200 reflections systematic absent and rejected

C1	-C2	1.520(4)	C15	-H151	1.0000
C6	-C7	1.516(4)	C16	-H161	0.9800
C6	-C15	1.544(5)	C16	-H162	0.9800
C7	-C14	1.403(4)	C16	-H163	0.9800
C7	-C8	1.383(4)			

Table S8 Bond Angles (Degrees) for: **Compound 3d**

O3	-S4	-O20	102.10(13)	C6	-C15	-C16	116.9(3)
O3	-S4	-O21	109.68(14)	N17	-C15	-C6	106.9(3)
O3	-S4	-N5	107.02(13)	N17	-C15	-C16	111.7(3)
O20	-S4	-O21	122.17(15)	O3	-C2	-H21	110.00
O20	-S4	-N5	109.58(15)	O3	-C2	-H22	110.00
O21	-S4	-N5	105.51(15)	C1	-C2	-H21	110.00
S4	-O3	-C2	118.97(17)	C1	-C2	-H22	110.00
C10	-O11	-C12	117.8(2)	H21	-C2	-H22	108.00
S4	-N5	-C6	120.3(2)	N5	-C6	-H61	107.00
O18	-N17	-O19	123.9(3)	C7	-C6	-H61	107.00
O18	-N17	-C15	119.9(3)	C15	-C6	-H61	107.00
O19	-N17	-C15	116.2(3)	C7	-C8	-H811	119.00
S4	-N5	-H5	114(2)	C9	-C8	-H811	119.00
C6	-N5	-H5	118(2)	C8	-C9	-H91	120.00
C122	-C1	-C123	109.01(16)	C10	-C9	-H91	120.00
C123	-C1	-C124	110.08(15)	O11	-C12	-H121	109.00
C123	-C1	-C2	106.8(2)	O11	-C12	-H122	109.00
C124	-C1	-C2	111.0(2)	O11	-C12	-H123	109.00
C122	-C1	-C2	111.2(2)	H121	-C12	-H122	110.00
C122	-C1	-C124	108.74(16)	H121	-C12	-H123	109.00
O3	-C2	-C1	108.5(2)	H122	-C12	-H123	109.00
N5	-C6	-C7	113.9(2)	C10	-C13	-H131	120.00
C7	-C6	-C15	112.2(3)	C14	-C13	-H131	120.00
N5	-C6	-C15	109.4(2)	C7	-C14	-H141	120.00
C6	-C7	-C14	123.2(3)	C13	-C14	-H141	120.00
C8	-C7	-C14	118.1(3)	N17	-C15	-H151	107.00
C6	-C7	-C8	118.8(3)	C6	-C15	-H151	107.00
C7	-C8	-C9	122.2(3)	C16	-C15	-H151	107.00
C8	-C9	-C10	119.1(3)	C15	-C16	-H161	110.00
O11	-C10	-C9	124.7(3)	C15	-C16	-H162	109.00
C9	-C10	-C13	119.9(3)	C15	-C16	-H163	109.00
O11	-C10	-C13	115.3(2)	H161	-C16	-H162	109.00
C10	-C13	-C14	120.4(3)	H161	-C16	-H163	109.00
C7	-C14	-C13	120.4(3)	H162	-C16	-H163	109.00

Compound 3f



Molecular Formula:	C ₁₄ H ₁₈ Cl ₃ N O ₆ S
Crystal Color / Shape	Colorless column
Crystal Size	Approximate size of crystal fragment used for data collection: 0.18 × 0.25 × 0.64 mm
Molecular Weight:	434.71 a.m.u.
F ₀₀₀ :	896
Systematic Absences:	0kl: k+l≠2n; h0l: h≠2n; 00l: l≠2n
Space Group:	Orthorhombic <i>P na</i> 2 ₁ (I.T.-No.: 33)
Cell Constants:	Least-squares refinement of 9455 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.80° < θ < 25.34°; Mo(Kα ⁻); λ = 71.073 pm <i>a</i> = 2266.16(14) pm <i>b</i> = 641.70(3) pm <i>c</i> = 1330.06(8) pm <i>V</i> = 1934.17(19) · 10 ⁶ pm ³ ; <i>Z</i> = 4; <i>D</i> _{calc} = 1.493 g cm ⁻³ ; Mos. = 068
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(Kα ⁻)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	1.80° < θ < 25.34°; h: -27/27, k: -7/7, l: -16/16
Measurement Time:	2 × 2.50 s per film
Measurement Mode:	measured: 9 runs; 3960 films / scaled: 9 runs; 3960 films φ- and ω-movement; Increment: Δφ/Δω = 0.50°; dx = 35.0 mm
LP - Correction:	Yes ^[7]
Intensity Correction	No/Yes; during scaling ^[7]
Absorption Correction:	Multi-scan; during scaling; μ = 0.611 mm ⁻¹ ^[7]

	Correction Factors:	$T_{\min} = 0.6671$	$T_{\max} = 0.7452$
Reflection Data:	88334	reflections were integrated and scaled	
	6212	reflections systematic absent and rejected	
	82122	reflections to be merged	
	3526	independent reflections	
	0.035	R_{int} : (basis F_o^2)	
	3526	independent reflections (all) were used in refinements	
	3489	independent reflections with $I_o > 2\sigma(I_o)$	
	99.9 %	completeness of the data set	
	298	parameter full-matrix refinement	
	11.8	reflections per parameter	
Solution:	Direct Methods ^[8] ; Difference Fourier syntheses		
Refinement Parameters:	In the asymmetric unit:		
	25	Non-hydrogen atoms with anisotropic displacement parameters	
	18	Hydrogen atoms with isotropic displacement parameters	
Hydrogen Atoms:	All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters.		
Atomic Form Factors:	For neutral atoms and anomalous dispersion ^[9]		
Extinction Correction:	no		
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P$ with a: 0.0328; b: 0.4010; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2 \cdot F_c^2]/3$		
Shift/Err:	Less than 0.001 in the last cycle of refinement:		
Resid. Electron Density:	$+0.19 \text{ e}^-/\text{\AA}^3$; $-0.17 \text{ e}^-/\text{\AA}^3$		
R1:	$\Sigma(F_o - F_c)/\Sigma F_o $		
$[F_o > 4\sigma(F_o)$; N=3489]:	= 0.0186		
[all reflctns; N=3526]:	= 0.0188		
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$		
$[F_o > 4\sigma(F_o)$; N=3489]:	= 0.0512		
[all reflctns; N=3526]:	= 0.0515		
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2/(\text{NO} - \text{NV})]^{1/2}$		
	= 1.054		
Flack's Parameter :	$x = -0.00(3)$		
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$		
	The correct enantiomere is proved by Flack's Parameter.		

Table S9 – Bond Distances (Angstrom) for: **Compound 3f**

C123	-C1	1.7650 (17)	C10	-C13	1.394 (2)
C124	-C1	1.780 (2)	C13	-C14	1.395 (2)
C125	-C1	1.7747 (18)	C15	-C16	1.515 (2)
S4	-O3	1.6045 (11)	C18	-C19	1.493 (3)
S4	-O21	1.4223 (12)	C2	-H21	0.89 (2)
S4	-O22	1.4257 (12)	C2	-H22	0.98 (2)
S4	-N5	1.5911 (14)	C6	-H61	0.959 (19)
O3	-C2	1.437 (2)	C8	-H81	0.867 (19)
O11	-C10	1.3626 (18)	C9	-H91	0.92 (2)
O11	-C12	1.426 (2)	C12	-H121	0.96 (2)
O17	-C15	1.4628 (18)	C12	-H122	1.07 (3)
O17	-C18	1.3301 (17)	C12	-H123	0.97 (3)
O20	-C18	1.2079 (19)	C13	-H131	1.01 (2)
N5	-C6	1.4629 (19)	C14	-H141	0.950 (19)
N5	-H5	0.811 (19)	C15	-H151	0.973 (18)
C1	-C2	1.511 (2)	C16	-H161	0.930 (19)

C6	-C15	1.540(2)	C16	-H162	0.87(2)
C6	-C7	1.5202(19)	C16	-H163	0.97(2)
C7	-C8	1.396(2)	C19	-H191	0.88(3)
C7	-C14	1.3905(19)	C19	-H192	1.00(4)
C8	-C9	1.381(2)	C19	-H193	0.85(4)
C9	-C10	1.393(2)			

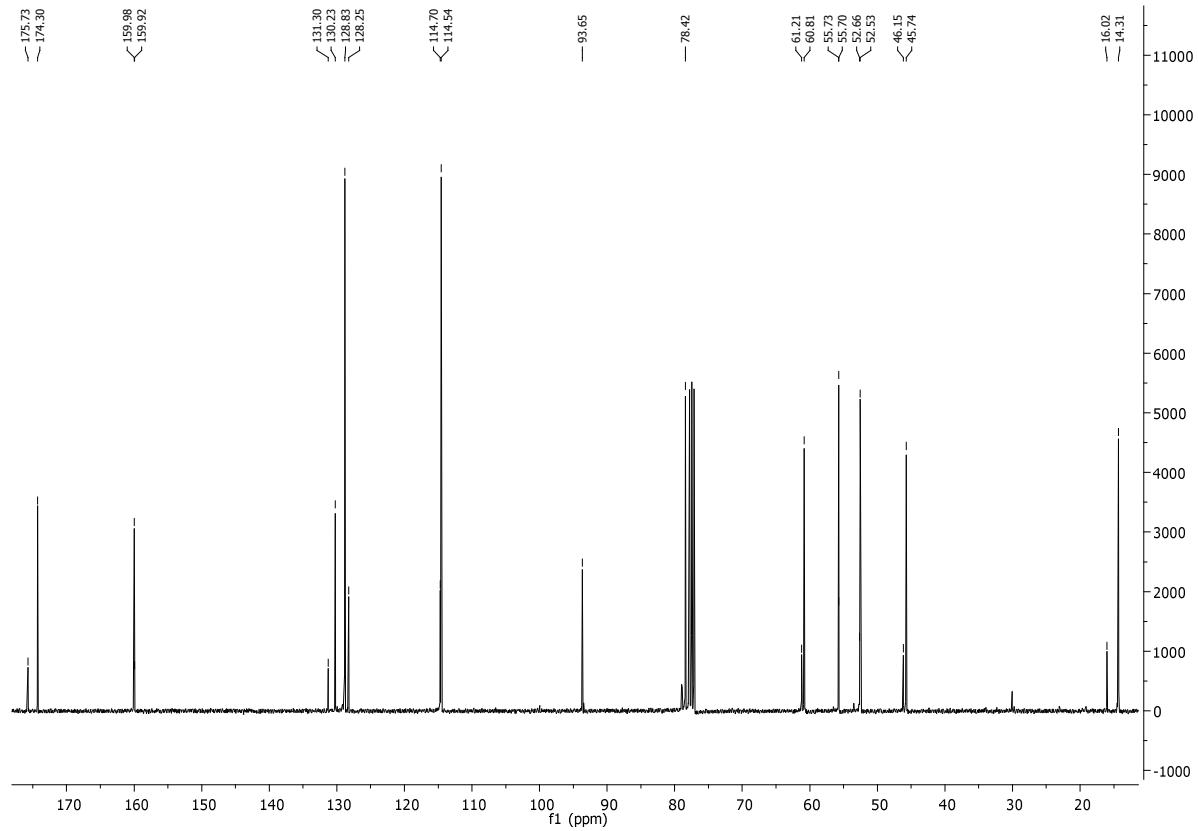
Table S10 Bond Angles (Degrees) for: **Compound 3f**

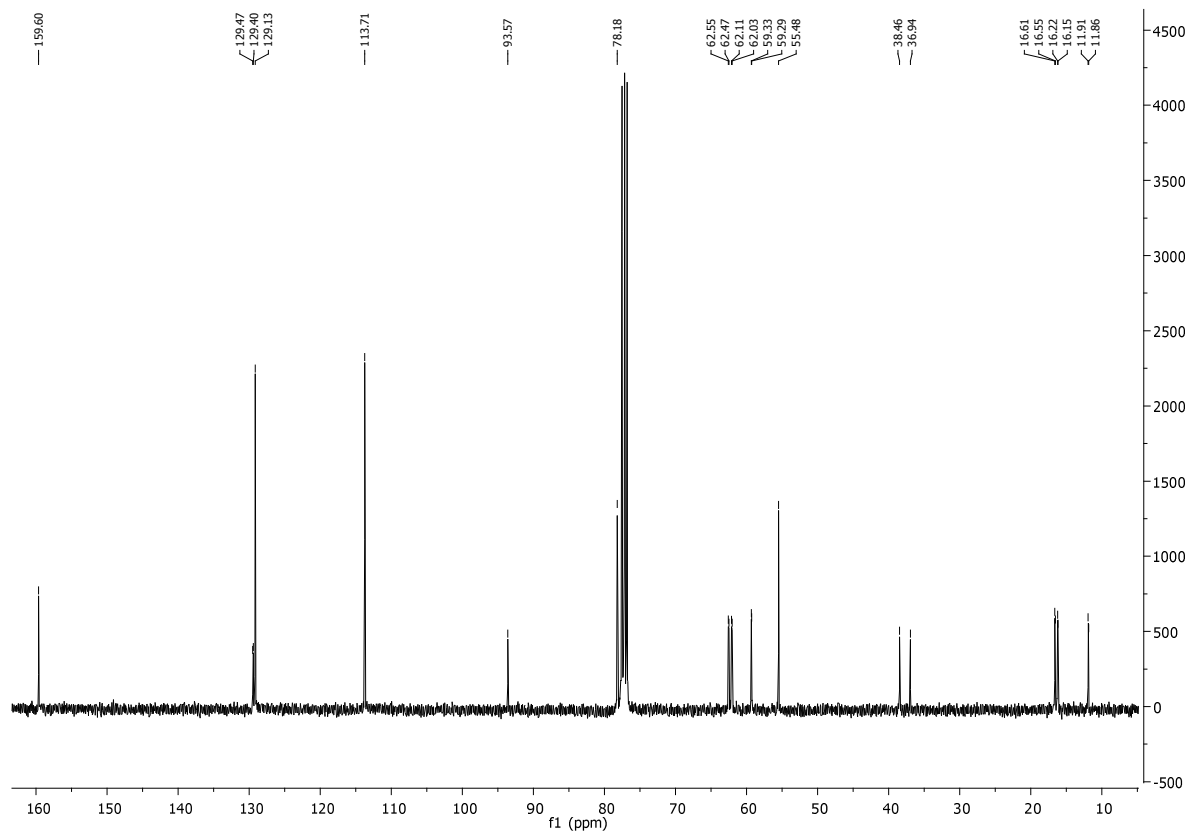
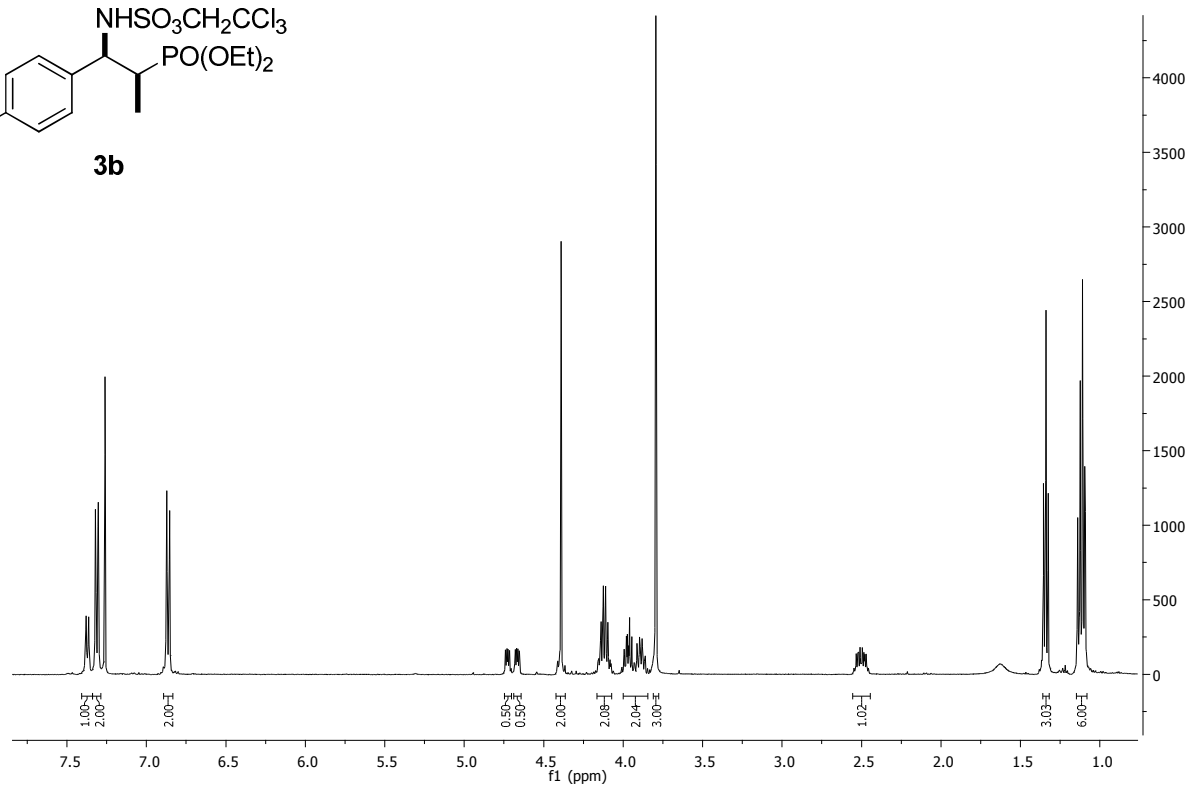
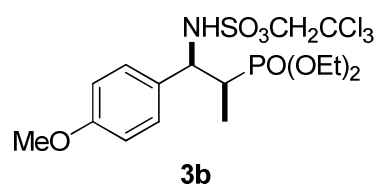
O3	-S4	-O21	102.67(7)	O3	-C2	-H21	111.0(13)
O3	-S4	-O22	107.04(7)	O3	-C2	-H22	108.3(11)
O3	-S4	-N5	106.45(6)	C1	-C2	-H21	109.2(13)
O21	-S4	-O22	121.91(7)	C1	-C2	-H22	108.5(13)
O21	-S4	-N5	110.25(7)	H21	-C2	-H22	112.1(18)
O22	-S4	-N5	107.45(7)	N5	-C6	-H61	104.7(11)
S4	-O3	-C2	114.82(10)	C7	-C6	-H61	111.2(11)
C10	-O11	-C12	118.04(13)	C15	-C6	-H61	105.3(11)
C15	-O17	-C18	117.00(12)	C7	-C8	-H81	119.5(12)
S4	-N5	-C6	122.56(10)	C9	-C8	-H81	119.3(12)
S4	-N5	-H5	116.4(13)	C8	-C9	-H91	120.2(14)
C6	-N5	-H5	120.3(13)	C10	-C9	-H91	119.3(13)
C123	-C1	-C124	109.43(10)	O11	-C12	-H121	107.1(12)
C124	-C1	-C125	110.02(9)	O11	-C12	-H122	110.7(14)
C123	-C1	-C125	109.30(10)	O11	-C12	-H123	114.9(14)
C123	-C1	-C2	111.72(12)	H121	-C12	-H122	111(2)
C125	-C1	-C2	110.27(13)	H121	-C12	-H123	106.5(18)
C124	-C1	-C2	106.05(13)	H122	-C12	-H123	106(2)
O3	-C2	-C1	107.72(14)	C10	-C13	-H131	119.2(12)
N5	-C6	-C7	114.99(11)	C14	-C13	-H131	120.6(12)
N5	-C6	-C15	109.08(11)	C7	-C14	-H141	119.7(11)
C7	-C6	-C15	111.06(11)	C13	-C14	-H141	119.0(11)
C6	-C7	-C8	118.79(12)	O17	-C15	-H151	108.8(10)
C8	-C7	-C14	117.97(13)	C6	-C15	-H151	107.5(9)
C6	-C7	-C14	123.11(12)	C16	-C15	-H151	110.5(10)
C7	-C8	-C9	121.30(14)	C15	-C16	-H161	111.9(13)
C8	-C9	-C10	120.47(15)	C15	-C16	-H162	113.1(14)
O11	-C10	-C9	115.88(13)	C15	-C16	-H163	112.4(12)
O11	-C10	-C13	125.13(12)	H161	-C16	-H162	108.2(17)
C9	-C10	-C13	118.98(13)	H161	-C16	-H163	105.9(18)
C10	-C13	-C14	119.98(12)	H162	-C16	-H163	105.0(18)
C7	-C14	-C13	121.24(13)	C18	-C19	-H191	108.0(18)
O17	-C15	-C16	105.14(12)	C18	-C19	-H192	114(2)
C6	-C15	-C16	115.97(11)	C18	-C19	-H193	111(2)
O17	-C15	-C6	108.72(11)	H191	-C19	-H192	112(3)
O20	-C18	-C19	125.36(15)	H191	-C19	-H193	114(3)
O17	-C18	-O20	122.54(14)	H192	-C19	-H193	98(3)
O17	-C18	-C19	112.10(15)				

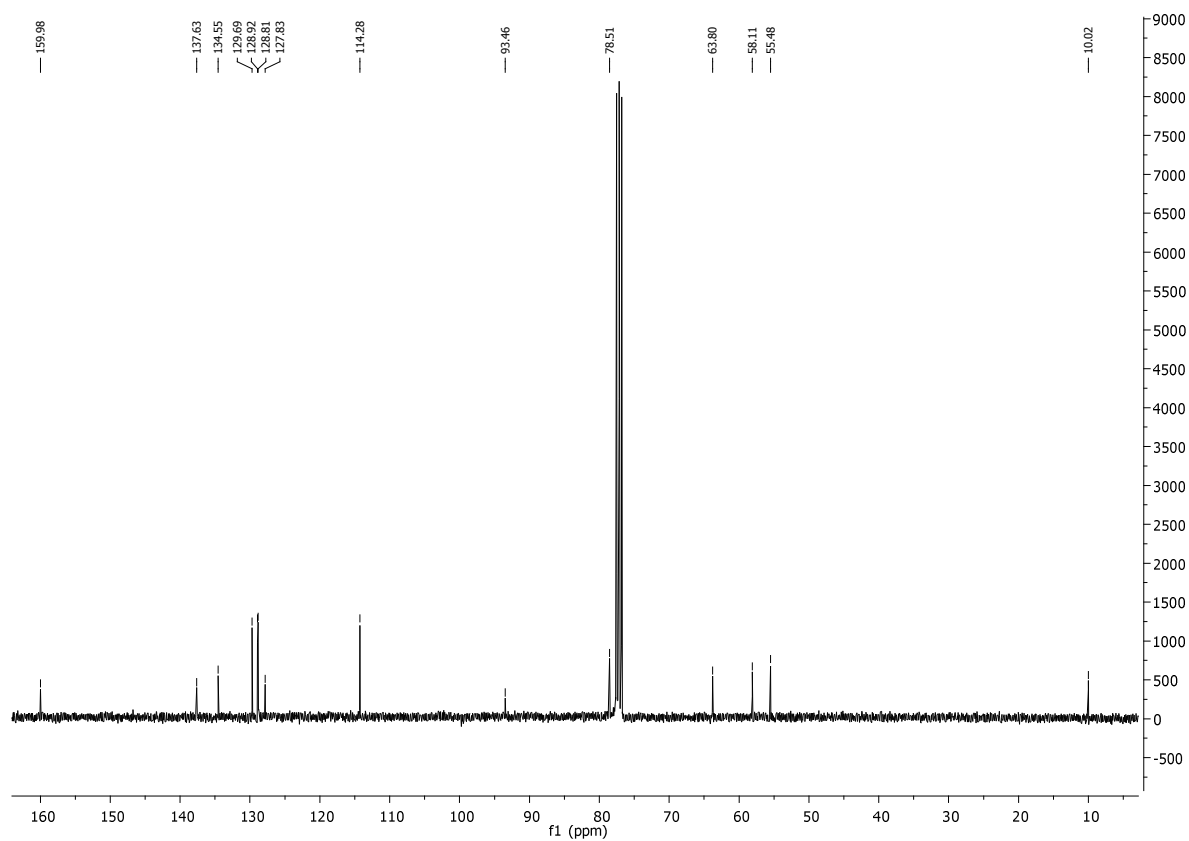
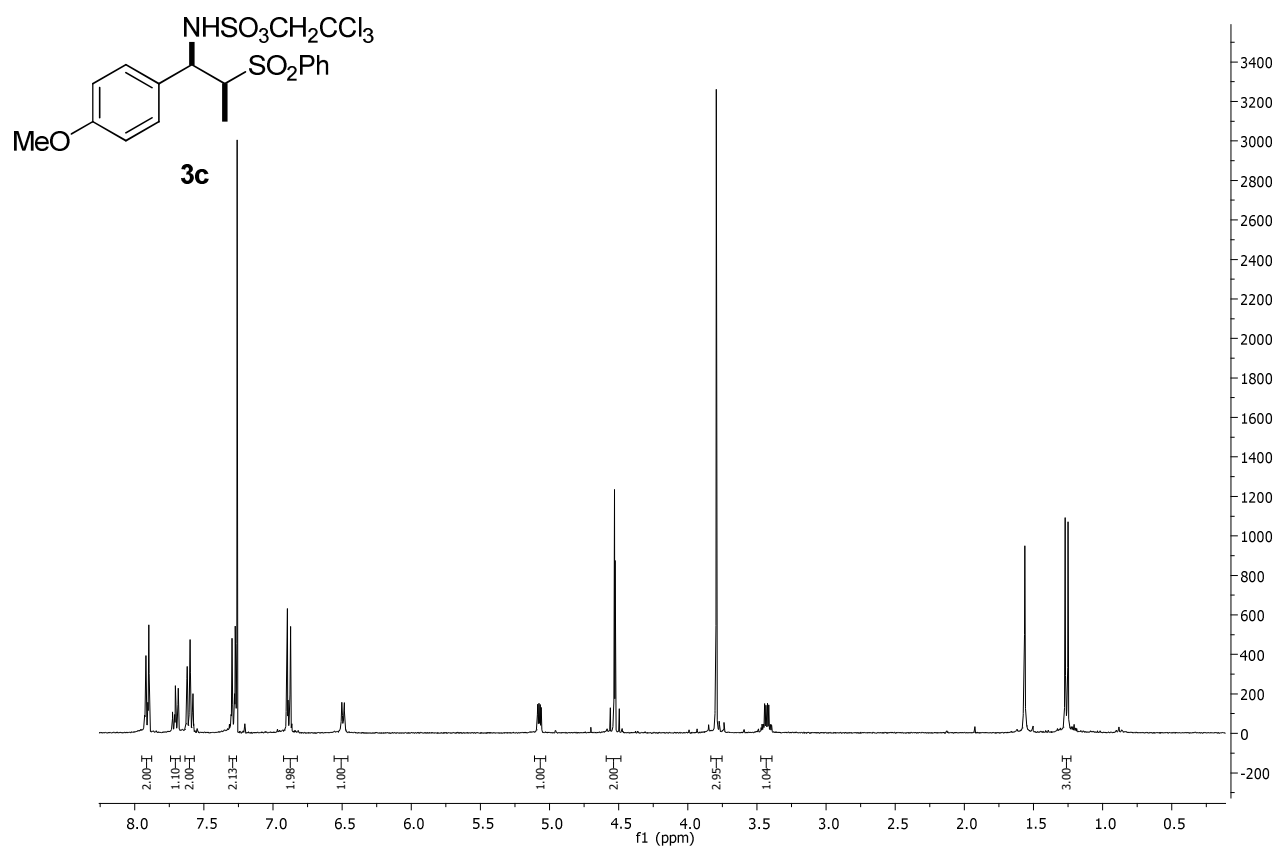
The crystallographic data (without structural factors) of the compounds described in this publication (see also supporting information) were deposited as "supplementary publication no. CCDC-774428 (**3a**), CCDC-774429 (**3b**), CCDC-774430 (**3c**), CCDC-774431 (**3d**) and CCDC-774432 (**3f**)" at the Cambridge Crystallographic Data Centre. Copies can be obtained free of charge at the following address in the U.K.: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

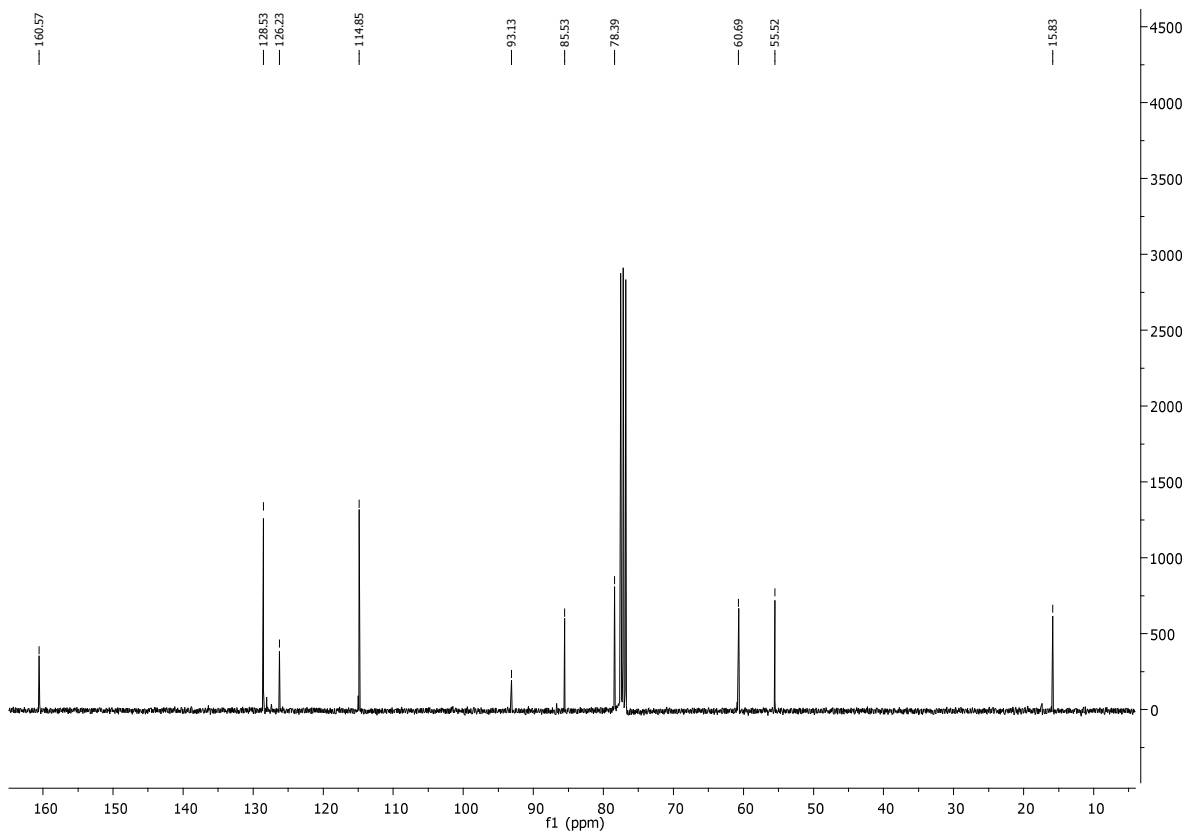
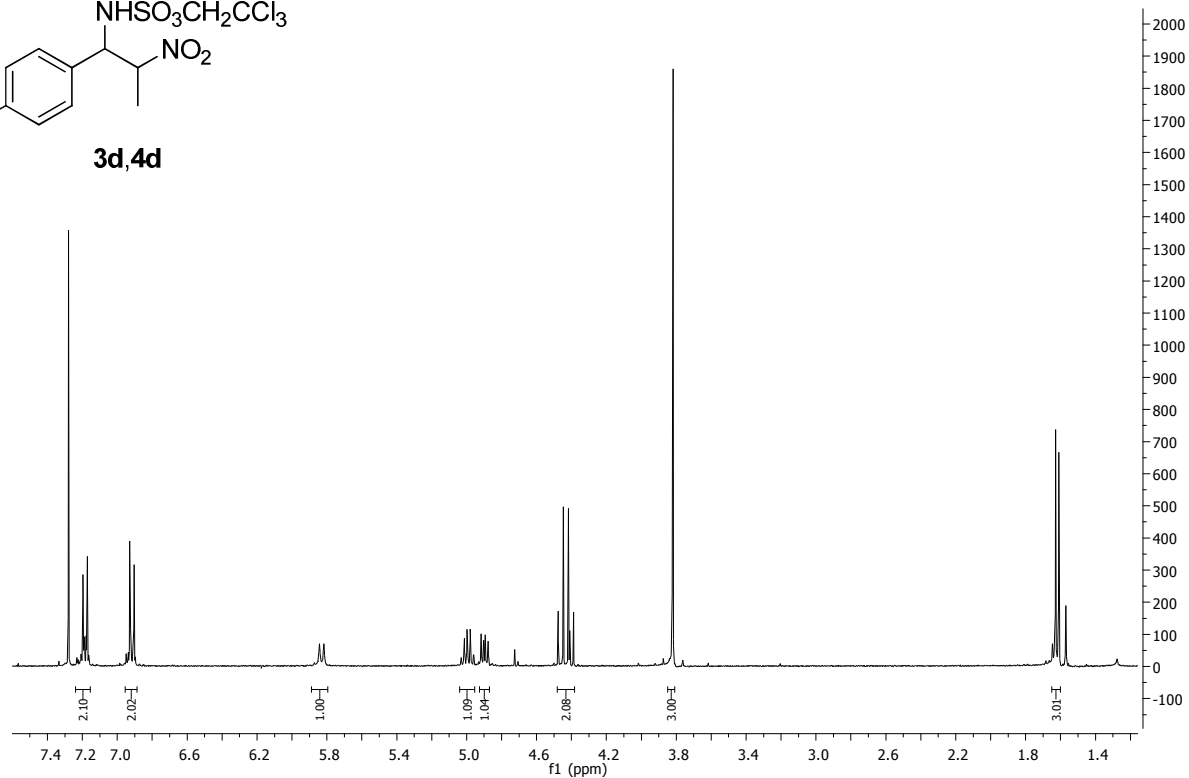
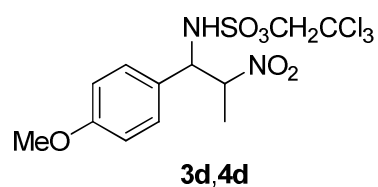
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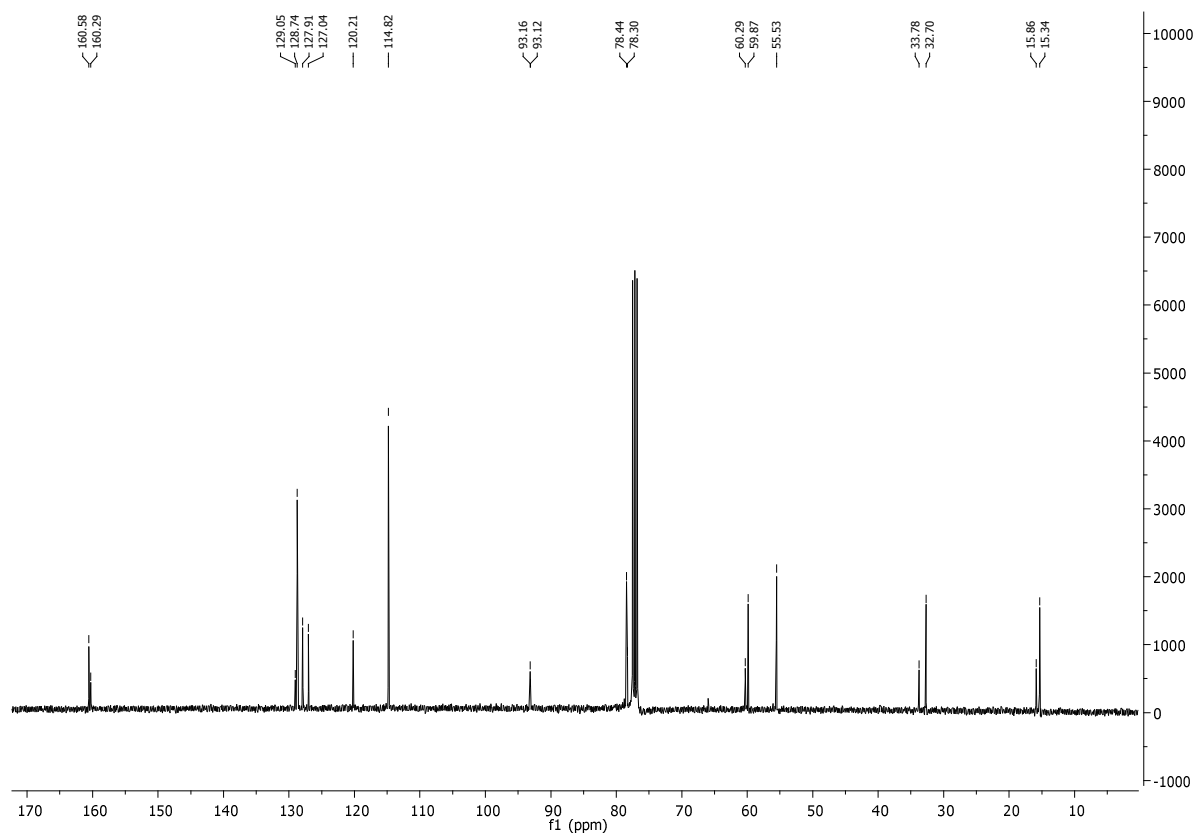
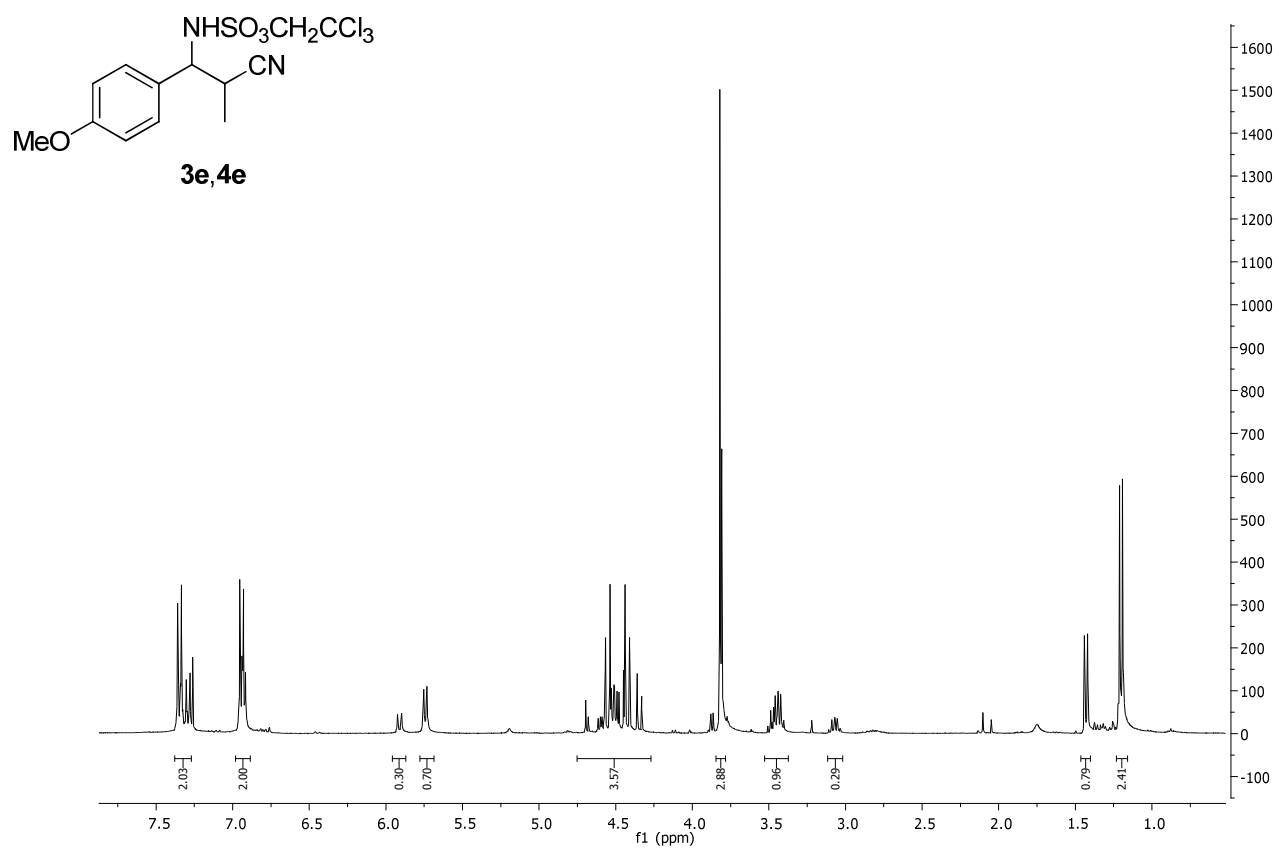
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The diastereomeric ratio in the ¹H-NMR is slightly different from the d.r. of the crude mixture.

