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Supplementary information

Catalytic enantiocontrol over a non-classical carbocation

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Catalytic Enantiocontrol over a Non-Classical Carbocation

Supplementary Information

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1 Materials and Methods

1.1 General Information

Chemicals

Chemicals (Abcr, Acros Organics, Alfa Aesar, Apollo Scientific, Fluorochem, Manchester Organics, Oxchem Corporation, Sigma-Aldrich, TCI) were purchased as reagent grade and used without further purification unless otherwise stated. Et_3N was distilled over $LiAlH_4$ and stored under argon prior to use.

Solvents

Solvents (CH_2Cl_2, Et_2O, PhMe, THF) were dried by distillation from an appropriate drying agent in the technical department of the Max-Planck-Institut für Kohlenforschung and received in Schlenk flasks under argon[1]. Additional solvents (MeCN, DME, DMF, EtOAc, MeOH, PhH) were purchased from commercial suppliers and dried over molecular sieves.

Inert gas

Dry argon was purchased from Air Liquide with >99.5% purity.

Glassware

All non-aqueous reactions were performed in oven-dried (80 °C) or flame-dried glassware under Ar. Solvents were removed under reduced pressure at 40 °C using a rotary evaporator and drying under high vacuum (10^{-3} mbar).

Thin-layer chromatography

Thin-layer chromatography (TLC) was performed using pre-coated silica gel plastic sheets (Polygram SIL G/UV_{254}, 0.20 mm, with fluorescent indicator; Macherey-Nagel) or pre-coated reversed phase silica gel glass plates (Nano-SIL C18-100 UV_{254}, 0.20 mm, with fluorescent indicator; Macherey-Nagel), which were visualized under irradiation with UV light (λ = 254 or

366 nm), basic $KMnO_4$, and/or phosphomolybdic acid (PMA). $KMnO_4$ stain: aq NaOH (10 wt%, 1.25 mL), $KMnO_4$ (1.50 g), K_2CO_3 (10 g) in H_2O (200 mL); PMA stain: PMA (20 g) in EtOH (200 mL). Preparative thin-layer chromatography was performed on silica gel pre-coated glass plates SIL G-25 UV_{254} and SIL G-100 UV_{254} with 0.25 mm and 1.00 mm SiO_2 layers (Macherey-Nagel).

Column Chromatography

Column chromatography (CC) was carried out using Merck (60 Å, 230−400 mesh, particle size 0.040−0.063 mm) or VWR (40−63 μm) silica gel, using technical grade solvents. Elution was accelerated using compressed air. Automated column chromatography was conducted on a Biotage Isolera Spektra Four system, using SNAP Ultra HP-Sphere 25 μm cartridges or SNAP Ultra C18 HP-Sphere 25 μm reversed phase cartridges. Fractions containing a desired substance were combined and concentrated in vacuo, then redissolved in an appropriate solvent and filtered through cotton to remove silica residues. Solvent mixtures (mobile phase) are reported in terms of volume ratios (v/v). All reported yields refer to chromatographically and spectroscopically pure compounds.

Nomenclature

Nomenclature follows the suggestions proposed by the computer program ChemDraw Professional (15.0.0.106) of PerkinElmer.

Melting Points

Melting points (m.p.) were measured on a Büchi 540 Melting Point apparatus in open glass capillaries and are uncorrected.

IR Spectroscopy

IR spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer. The spectra were measured in the neat state on a UATR Two crystal plate. Selected absorption bands are

reported in wavenumbers (cm^{-1}). Intensities are reported as follows: br (broad), w (weak), m (medium) and s (strong).

Nuclear Magnetic Resonance Spectroscopy

^{1}H, ^{2}H, ^{13}C, ^{19}F, ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-600, AV-500, AV-400 or AV-300 spectrometer in a suitable deuterated solvent. The solvent employed and respective measuring frequencies (reported in MHz) are indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as universal reference of all nuclides and with two or one digits after the comma. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quadruplet), p (pentet), hept (heptet), m (multiplet), and b (broad). All spectra were recorded at 298 K unless otherwise noted and processed with MestReNova 11.0.2. Multiplicity and coupling constants are reported as observed. The residual solvent signal relative to tetramethylsilane was used as the internal reference in ^{1}H NMR and ^{2}H NMR spectra (e.g. $CHCl_3$ = 7.26 ppm)[2,3], which are reported as follows: chemical shift in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C, ^{19}F, ^{31}P NMR spectra were referenced according to Ξ-values (IUPAC recommendations 2008)[4] relative to the internal references set in ^{1}H NMR spectra (e.g. ^{13}C: Me_4Si, ^{19}F: CCl_3F, ^{31}P: H_3PO_4 each 0.00 ppm). All spectra are broadband decoupled unless otherwise noted.

Mass Spectrometry

Electron impact (EI, 70 eV) mass spectrometry was performed on a Thermo Fisher Scientific ISQ 7000 Single Quadrupole GC-MS system (LRMS), Thermo Fisher Scientific Q Exactive GC Orbitrap GC-MS/MS system (LRMS and HRMS) or Finnigan MAT 95 (LRMS and HRMS). Chemical ionization (CI) mass spectrometry was performed on a Thermo Fisher Scientific Q Exactive GC Orbitrap GC-MS/MS system (LRMS and HRMS). Electrospray ionization (ESI) was performed on a Thermo Finnigan LTQ-FT Ultra (LRMS and HRMS) or Thermo Fisher Scientific Q Exactive Plus Hybrid Quadrupol-Orbitrap (LRMS and HRMS). The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic mass units divided by elementary charge number (m/z).

Specific Rotations

Specific rotations $[\alpha]_D^T$ were measured on a Rudolph RA Autopol IV Automatic Polarimeter at the indicated temperature with a sodium lamp (sodium D line, λ = 589 nm). Measurements were performed in an acid resistant 1 mL cell (50 mm length) with concentrations (g/(100 mL)) reported in the corresponding solvent.

High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-20AD (SIL-20AC autosampler, DGU-20A5 degasser, CTO-20AC column oven, SPD-M20A diode array detector, CMB-20A controller) or Shimadzu LC-20AB (SIL-20AC HT autosampler, DGU-20A5 degasser, CTO-20AC column oven, SPD-M20A diode array detector) using Daicel columns with a chiral stationary phase. All solvents used were HPLC-grade solvents purchased from Sigma-Aldrich. The column employed and respective solvent mixtures are indicated for each experiment.

Preparative High Performance Liquid Chromatography

Preparative high performance liquid chromatography (Prep-HPLC) was performed on a Shimadzu LC-20AP (SIL-20A HT autosampler, CTO-20AC column over, SPD-20A diode array detector, FRC-10A fraction collector), Shimadzu LC-20AR (SIL-20A HT autosampler, CTO-20AC column over, SPD-20A diode array detector, FRC-10A fraction collector), Shimadzu LC-8A (CTO-10AC column over, SPD-10VP diode array detector, FRC-10A fraction collector, SCL-10AVP controller) or Agilent Technologies 1260 Preparative Binary Pump (G7157A autosampler, 1260 diode array detector WR, 1290 Prep FC, 1260 Prep Valve FC). All solvents used were HPLC-grade solvents purchased from Sigma-Aldrich. The column employed and respective solvent mixtures are indicated for each experiment.

Gas Chromatography

Gas chromatography (GC) analyses on a chiral stationary phase were performed on an Agilent Technologies 6890N, equipped with a 7683 automatic liquid sampler (split-mode capillary injection system, flame ionization detector (FID), helium carrier gas). GC method used for reaction monitoring (Macherey-Nagel Optima 5 column, 30 m, i.d. 0.32 mm, 0.25 μm): injector 250 °C, 50 °C 2 min (iso), 50–320 °C (15 °C/min), 320 °C 5 min (iso).

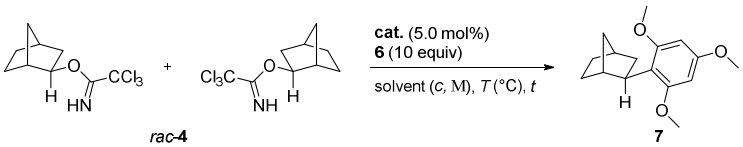
Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) analyses were performed on an Agilent Technologies 6890N G2577A, equipped with a Gerstel MPS (split-mode capillary injection system, helium carrier gas). GC-MS method used for reaction monitoring (Macherey-Nagel Optima 5 MS accent column, 30 m, i.d. 0.25 mm, 0.25 μm): injector 250 °C, 50 °C 5 min (iso), 50–340 °C (15 °C/min), 340 °C 5 min (iso).

Liquid Chromatography-Mass Spectrometry

Liquid chromatography-mass spectrometry (LCMS-IT-TOF) was performed on a Shimadzu LC-20AD. All solvents used were HPLC-grade solvents purchased from Sigma-Aldrich. The column employed, the respective solvent mixture, and the MS parameters are indicated for each experiment.

1.2 Evaluation of Diverse Chiral Brønsted Acid Catalysts



rac-**4** **7**

entry	catalyst	solvent (*c*, M)	yield (%)*	*T* (°C)	*t*	e.r.
1	**S1**	$CHCl_3$ (0.5)	n.d.†	25	1 h§	–
2	**S2**	$CHCl_3$ (0.5)	n.d.†	25	1 h§	–
3	**S3**	$CHCl_3$ (0.5)	n.d.†	25	1 h§	–
4	**S4**	$CHCl_3$ (0.5)	n.d.†	25	1 h§	–
5	**S5a**	$CHCl_3$ (0.5)	82	25	5 min	47:53
6	**S5b**	$CHCl_3$ (0.5)	69	25	20 min	58.5:41.5
7	**S5c**	$CHCl_3$ (0.5)	83	25	20 min	26:74
8	**S5d**#	$CHCl_3$ (0.5)	77	25	20 min	21:79
9	**S5e**#	$CHCl_3$ (0.5)	32	25	20 min	18:82
10	**S5f**#	$CHCl_3$ (0.5)	35	25	20 min	11.5:88.5
11	**S5f**#‖	PhMe (0.1)	24	–40	5 d	5:95
12	**3**	$CHCl_3$ (0.5)	92	25	5 min	87:13
13	**3**‖	PhMe (0.1)	93 (86)‡	–40	4 d	97:3

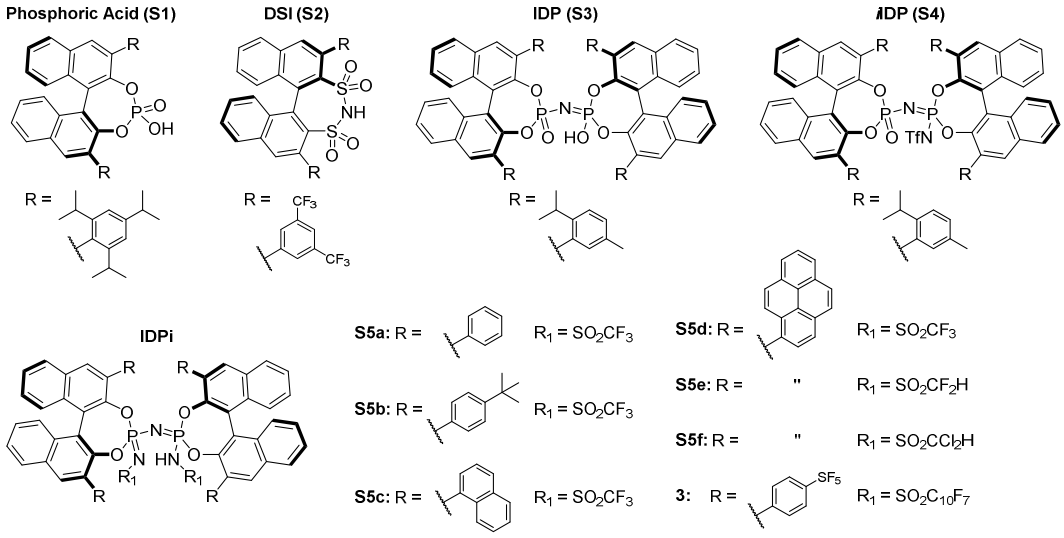
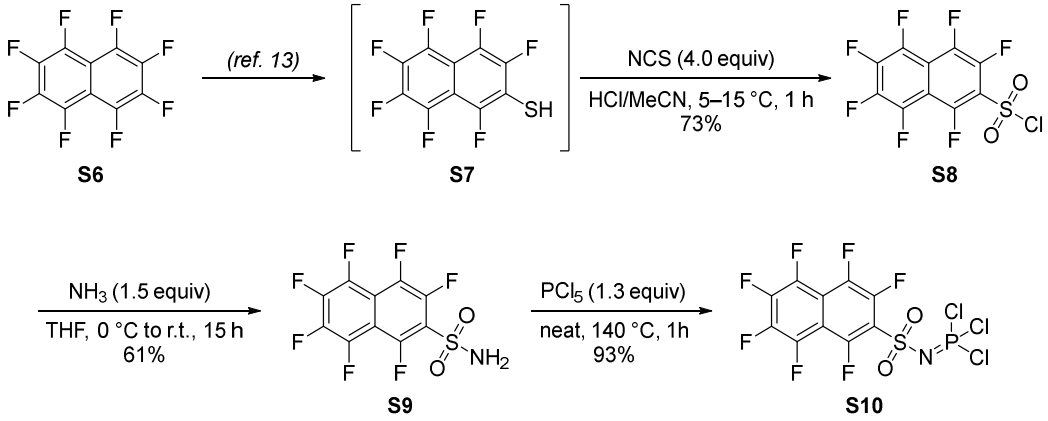


Table 1: A subset of catalysts[5-11] tested for the targeted transformation. Reactions were performed on a 0.025 mmol scale. All reactions reached complete conversion in the depicted reaction times.*Yields were determined by ^{1}H NMR using $CHPh_3$ as an internal standard. †Product was not detected by ^{1}H NMR. §Longer reaction times were not beneficial for the reactivity. ‖4Å Molecular sieves (MS) were added (200 mg/mmol). #Systematic substitution of the pyrene ring with electron withdrawing and donating groups was performed; however none to little influence on the yield and enantioselectivity was observed. ‡Isolated yield in parentheses.

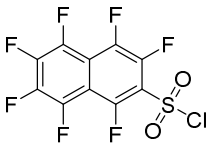
1.3 Supplementary Methods

1.3.1 Synthesis of sulfonylphosphorimidoyl trichloride reagents ($RSO_2N{=}PCl_3$)

((Perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride (S10)



*1,3,4,5,6,7,8-Heptafluoronaphthalene-2-sulfonyl chloride (**S8**)*[12]



N-Chlorosuccinimide (1.68 g, 12.6 mmol, 4.00 equiv) was added to a 1:5 mixture of 2.0 M $HCl_{(aq)}$ (0.4 mL)/MeCN (2 mL), then cooled to 5 °C. A solution of **S7**[13] (900 mg, 3.14 mmol, 1.00 equiv) in MeCN (1 mL) was added dropwise to the suspension, which was kept at <20 °C for 30 min. The resulting yellow solution was diluted with EtOAc (15 mL) and washed with brine (5x20 mL). The combined organic layers were dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by automated CC (spherical silica gel, EtOAc/hexanes 0:100 to 50:50) afforded compound **S8** (812 mg, 73%) as a colorless solid.

M.p. = 78–80 °C;

$\mathbf{R_f}$ = 0.39 (EtOAc/hexanes 10:90);

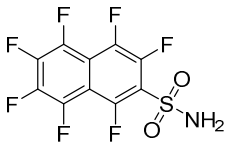
IR (neat) = 1647 (m), 1526 (w), 1485 (m), 1406 (s), 1392 (s), 1270 (m), 1186 (m), 1159 (m), 1186 (m), 1115 (m), 957 (s), 909 (s), 752 (w), 706 (w), 639 (m), 605 (m), 549 (s), 524 (m);

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 149.9, 144.3 (bs), 143.9–143.1 (m), 142.2 (bs), 141.8–140.6 (m), 140.2 (bs), 138.9 (t, *J* = 15.0 Hz), 121.2 (t, *J* = 14.8 Hz), 114.4, 107.6 (t, *J* = 12.9 Hz) (other signals not detected or observed);

^{19}F NMR (470 MHz, $CDCl_3$) δ −108.2 to −108.5 (m), −135.3 to −135.4 (m), −138.3 to −138.7 (m), −142.9 to −143.6 (m), −144.1 to −144.3 (m), −150.5 to −150.7 (m);

HRMS-EI (m/z): calculated for $C_{10}O_2Cl_1F_7S_1$ [$M^{+\cdot}$]: 351.9196, found: 351.9198.

*1,3,4,5,6,7,8-Heptafluoronaphthalene-2-sulfonamide (**S9**)*



In a flame-dried flask under Ar, **S8** (812 mg, 2.30 mmol, 1.00 equiv) was dissolved in THF (5 mL) and cooled to 0 °C. A freshly titrated solution of NH_3 (0.44 M in 1,4-dioxane, 7.8 mL, 3.45 mmol, 1.50 equiv) was added over 15 min to the solution. The reaction was allowed to slowly warm to r.t. and stirred for 15 h. The resulting yellow suspension was treated with 1.0 M $HCl_{(aq)}$ (10 mL) and extracted with EtOAc (3x15 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by automated CC (spherical silica gel, EtOAc/hexanes 0:100 to 70:30) afforded compound **S9** (470 mg, 61%) as an off-white solid[14].

M.p. = 200–202 °C;

R_f = 0.55 (EtOAc/hexanes 40:60);

IR (neat) = 3402 (br), 3290 (br), 1653 (s), 1530 (m), 1490 (m), 1398 (s), 1363 (s), 1264 (m), 1171 (s), 1159 (s), 1111 (m), 960 (s), 939 (m), 903 (s), 752 (w), 641 (w), 586 (s), 516 (m);

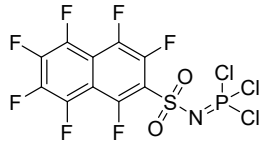
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.49 (s, 2H);

^{13}C NMR (151 MHz, DMSO-d_6) δ 149.8, 148.1, 143.7 (d, *J* = 14.6 Hz), 142.8, 142.0 (d, *J* = 14.6 Hz), 141.8–140.7 (m), 139.6 (t, *J* = 15.0 Hz), 137.9 (t, *J* = 15.4 Hz), 121.3 (t, *J* = 17.2 Hz), 112.0, 108.1–107.1 (m) (other signals not detected or observed);

^{19}F NMR (471 MHz, DMSO-d_6) δ −115.0 (dd, *J* = 75.0, 18.3 Hz), −137.7 to −137.9 (m), −143.7 to −144.1 (m), −147.1 (dt, *J* = 56.8, 16.6 Hz), −148.6 (dt, *J* = 56.2, 18.9 Hz), −151.2 (t, *J* = 20.3 Hz), −155.0 to −155.2 (m);

HRMS-ESI (m/z): calculated for $C_{10}H_1N_1O_2F_7S_1$ ([M−H]$^-$): 331.9622, found: 331.9622.

*((Perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride (**S10**)*[9]



In a flame-dried flask under Ar equipped with a magnetic stirring bar and connected to a trap containing $NaOH_{(s)}$, **S9** (532 mg, 1.60 mmol, 1.00 equiv) and PCl_5 (432 mg, 2.08 mmol, 1.30 equiv) were gradually heated to 140 °C. The resulting yellow solution was stirred at 140 °C for 45 min ($HCl_{(g)}$ evolution observed). The reaction was monitored by ^{1}H, ^{19}F and ^{31}P NMR to ensure full consumption of **S9**. Excess PCl_5 was removed by sublimation (1 atm, 120 °C). Subsequent sublimation (10^{-3} mbar, 150–160 °C) afforded compound **S10** (748 mg, 93%) as a colorless solid.

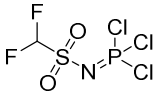
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6 (bs), 149.4 (bs), 144.6 (d, *J* = 15.4 Hz), 144.1–143.5 (m), 142.5 (t, *J* = 15.3 Hz), 142.2–141.5 (m), 140.4 (t, *J* = 15.3 Hz), 140.2–139.6 (m), 138.3 (t, *J* = 15.9 Hz) (other signals not detected or observed);

^{19}F NMR (471 MHz, $CDCl_3$) δ −111.4 (dd, *J* = 77.6, 18.8 Hz), −134.9 to −135.1 (m), −140.3 (dtt, *J* = 77.3, 16.7, 5.4 Hz), −144.4 to −144.6 (m), −145.7 (dtt, *J* = 58.6, 18.1, 4.8 Hz), −147.8 to −147.9 (m), −152.7 to −152.8 (m);

^{31}P NMR (203 MHz, $CDCl_3$) δ 8.1;

HRMS-CI (m/z): calculated for $C_{10}H_1N_1O_2Cl_3S_1F_7P_1$ ([M+H]$^+$): 467.8414, found: 467.8420.

((Difluoromethyl)sulfonyl)phosphorimidoyl trichloride (S11)



In a flame-dried flask under Ar equipped with a magnetic stirring bar and connected to a trap containing $NaOH_{(s)}$, difluoromethanesulfonamide (660 mg, 5.03 mmol, 1.00 equiv) and PCl_5 (1.36 g, 6.54 mmol, 1.30 equiv) were gradually heated to 80 °C. The resulting solution was stirred at 80 °C for 5 h ($HCl_{(g)}$ evolution observed). The reaction was monitored by ^{1}H, ^{19}F and ^{31}P NMR to ensure full consumption of difluoromethanesulfonamide. Excess PCl_5 was removed by sublimation (1 atm, 120 °C). Purification by bulb-to-bulb distillation (5 mbar, 130–150 °C) afforded **S11** (1.07 g, 80%) as a colorless liquid.

^{1}H NMR (501 MHz, $CDCl_3$) δ 6.18 (td, *J* = 53.8, 2.4 Hz, 1H);

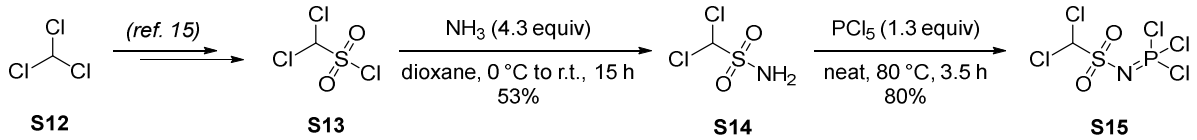
^{13}C NMR (126 MHz, $CDCl_3$) δ 113.2 (td, *J* = 282.2, 7.8 Hz);

^{19}F NMR (471 MHz, $CDCl_3$) δ −121.7 (d, *J* = 3.2 Hz);

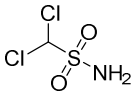
^{31}P NMR (203 MHz, $CDCl_3$) δ 13.3;

HRMS-ESI (m/z): calculated for $C_1H_2N_1O_2Cl_3S_1F_2P_1$ ($[M+H]^+$): 265.8578, found: 265.8580.

((Dichloromethyl)sulfonyl)phosphorimidoyl trichloride (S15)



*Dichloromethanesulfonamide (**S14**)*



In a flame-dried flask under Ar, a freshly titrated solution of NH_3 (0.44 M in 1,4-dioxane, 43.5 mL, 19.1 mmol, 4.28 equiv) was added to **S13**[15] (70% purity[I], 1.17 g,

[I] Inseparable chloromethanesulfonyl chloride is present from the previous step. This impurity was separated by CC at the sulfonamide stage (**S14**).

4.46 mmol, 1.00 equiv) at 0 °C. The suspension was warmed to r.t. and stirred for 15 h. The resulting suspension was filtered (filter paper) and concentrated under reduced pressure. Purification by automated CC (spherical silica gel, EtOAc/hexanes 7:93 to 60:40) afforded compound **S14** (558 mg, 76%) as a colorless solid.

M.p. = 79–82 °C;

$\mathbf{R}_f$ = 0.30 (EtOAc/hexanes 30:70);

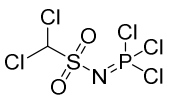
IR (neat) = 3388 (br), 3288 (br), 2982 (m), 1532 (m), 1341 (s), 1221 (m), 1196 (m), 1141 (s), 955 (m), 800 (s), 693 (m), 552 (m), 478 (s);

^{1}H NMR (501 MHz, $CDCl_3$) δ 6.33 (s, 1H), 5.17 (s, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 78.5;

HRMS-ESI (m/z): calculated for $C_1H_2Cl_2N_1O_2S_1$ ($[M-H]^-$): 161.9189, found: 161.9190.

*((Dichloromethyl)sulfonyl)phosphorimidoyl trichloride (**S15**)*



In a flame-dried flask under Ar equipped with a magnetic stirring bar and connected to a trap containing $NaOH_{(s)}$, **S14** (200 mg, 1.22 mmol, 1.00 equiv) and PCl_5 (330 mg, 1.58 mmol, 1.30 equiv) were gradually heated to 80 °C. The resulting solution was stirred at 80 °C for 3.5 h ($HCl_{(g)}$ evolution observed). The reaction was monitored by ^{1}H, ^{19}F and ^{31}P NMR to ensure full consumption of **S14**. Excess PCl_5 was removed by sublimation (1 atm, 120 °C). Purification by bulb-to-bulb distillation (10^{-3} mbar, 120–130 °C) afforded **S15** (290 mg, 79%) as a colorless viscous liquid.

^{1}H NMR (501 MHz, $CDCl_3$) δ 6.28 (d, J = 2.5 Hz, 1H);

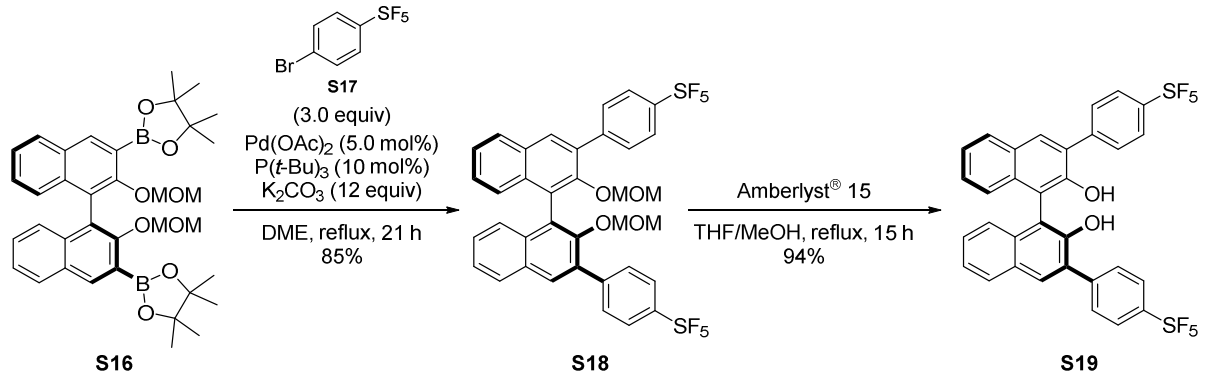
^{13}C NMR (126 MHz, $CDCl_3$) δ 79.2 (d, J = 9.2 Hz);

^{31}P NMR (203 MHz, $CDCl_3$) δ 10.9;

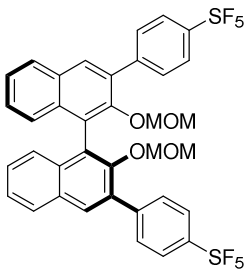
HRMS-ESI (m/z): calculated for $C_1H_2N_1O_2Cl_5S_1P_1$ ($[M+H]^+$): 297.7986, found: 297.7984.

1.3.2 Synthesis of 3,3′-substituted binaphthyl diols

(*S*)-3,3'-bis(4-(pentafluoro-λ^6-sulfanyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (S19)



(S)-((2,2'-Bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4,1-henylene))bis(pentafluoro-λ^6-sulfane) ***(S18)***



In a flask under Ar, (*S*)-2,2'-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**S16**)[16] (1.05 g, 1.67 mmol, 1.00 equiv) and (4-bromophenyl)pentafluoro-λ^6-sulfane (**S17**) (950 µL, 5.02 mmol, 3.00 equiv) were dissolved in a mixture of degassed DME (13 mL) and 2.0 M $K_2CO_{3(aq)}$ (10 mL, 20.1 mmol, 12.0 equiv). P(*t*-Bu)$_3$ (168 µL of a 1.0 M solution in PhMe, 0.168 mmol, 0.100 equiv) and $Pd(OAc)_2$ (18.8 mg, 0.084 mmol, 0.050 equiv) were added and the resulting mixture was heated to reflux for 21 h. The reaction mixture was cooled to r.t., exposed to air, diluted with H_2O (15 mL) and EtOAc (15 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3x15 mL). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by automated CC (spherical silica gel, CH_2Cl_2/hexanes 10:90 to 100:0) afforded compound **S18** (1.11 g, 85%) as a colorless solid.

M.p. = 216–217 °C;

R$_f$ = 0.33 (EtOAc/hexanes 10:90);

IR (neat) = 1390 (w), 1217 (w), 1184 (w), 1158 (m), 1099 (m), 1082 (w), 997 (m), 966 (m), 926 (w), 912 (w), 830 (s), 820 (s), 749 (s), 666 (m), 656 (m), 621 (w), 598 (m), 591 (m), 575 (w);

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.87 (s, 8H), 7.47 (ddd, *J* = 8.1, 6.6, 1.4 Hz, 2H), 7.37–7.28 (m, 4H), 4.41 (d, *J* = 5.9 Hz, 2H), 4.35 (d, *J* = 5.9 Hz, 2H), 2.38 (s, 6H);

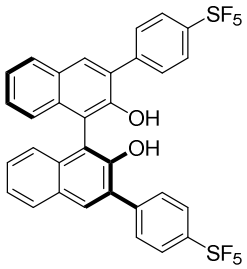
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (p, *J* = 17.1 Hz), 151.1, 142.5, 133.9, 133.5, 130.9, 130.7, 129.9, 128.1, 127.1, 126.5, 126.3, 126.1–125.8 (m), 125.7, 98.9, 56.0;

^{19}F NMR (471 MHz, $CDCl_3$) δ 84.6 (p, *J* = 149.7 Hz), 63.1 (d, *J* = 149.6 Hz), 63.0 (d, *J* = 150.0 Hz);

HRMS-ESI (m/z): calculated for $C_{36}H_{28}F_{10}O_4S_2Na_1$ ($[M+Na]^+$): 801.1162, found: 801.1159;

$[\alpha]_D^{25}$ = +100.00 (*c* 0.68, $CHCl_3$).

*(S)-3,3'-bis(4-(pentafluoro-λ^6-sulfanyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (**S19**)*



To a solution of **S18** (1.41 g, 1.81 mmol, 1.00 equiv) in THF/MeOH (1:1, 15 mL) was added Amberlyst® ion-exchange resin 15 (1.41 g). The reaction mixture was heated to reflux for 15 h, subsequently cooled to r.t., filtered (filter paper) and concentrated under reduced pressure. Purification by automated CC (spherical silica gel, EtOAc/hexanes 0:100 to 70:30) afforded compound **S19** (1.17 g, 94%) as a colorless crystalline solid.

M.p. = 159–166 °C;

R$_f$ = 0.55 (EtOAc/hexanes 20:80);

IR (neat) = 3520 (br), 1622 (w), 1603 (w), 1504 (w), 1444 (w), 1400 (w), 1360 (w), 1199 (w), 1171 (w), 1147 (w), 1129 (w), 1100 (m), 1065 (w), 831 (s), 824 (s), 750 (m), 739 (m), 664 (m), 657 (m), 598 (m), 589 (m), 482 (w);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.90–7.83 (m, 8H), 7.45 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H), 7.38 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.31 (s, 2H);

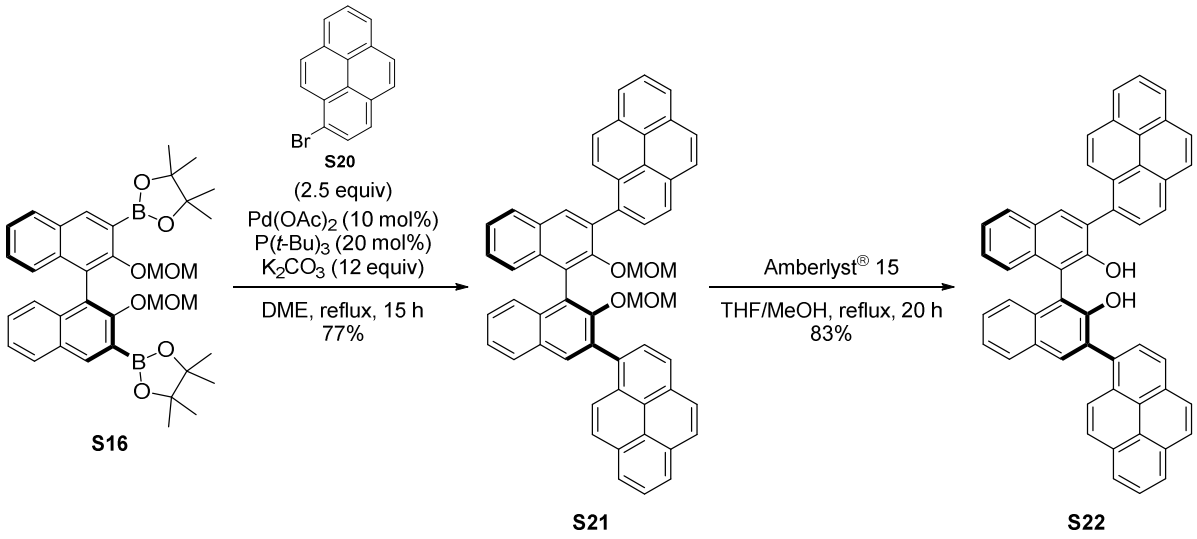
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3–152.9 (m), 150.0, 141.0, 133.1, 132.2, 129.9, 129.4, 128.8, 128.6, 128.2, 126.1–125.6 (m), 124.9, 124.0, 111.8;

^{19}F NMR (471 MHz, $CDCl_3$) δ 84.6 (p, *J* = 149.9 Hz), 63.0 (d, *J* = 149.9 Hz), 62.9 (d, *J* = 150.0 Hz); f

HRMS-ESI (m/z): calculated for $C_{32}H_{19}F_{10}O_2S_2$ ($[M-H]^-$): 689.0672, found: 689.0666;

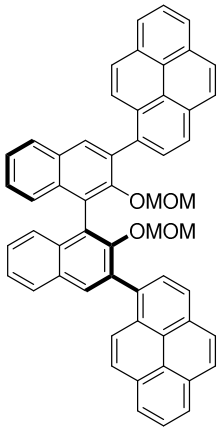
$[\alpha]_D^{25}$ = −44.80 (*c* 0.59, $CHCl_3$).

(*S*)-3,3'-di(pyren-1-yl)-[1,1'-binaphthalene]-2,2'-diol (S22)



*(S)-1,1'-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)dipyrene (**S21**)*

In a flask under Ar, (*S*)-2,2'-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**S16**)[16] (2.00 g, 3.19 mmol, 1.00 equiv) and 1-bromopyrene (**S20**) (2.24 g, 7.98 mmol, 2.50 equiv) were dissolved in a mixture of degassed



DME (50 mL) and 2.0 M $K_2CO_{3(aq)}$ (19 mL, 38.3 mmol, 12.0 equiv). P(*t*-Bu)$_3$ (639 µL of a 1.0 M solution in PhMe, 0.639 mmol, 0.200 equiv) and $Pd(OAc)_2$ (71.7 mg, 0.319 mmol, 0.100 equiv) were added and the resulting mixture was heated to reflux for 15 h. The reaction mixture was cooled to r.t., exposed to air, diluted with H_2O (20 mL) and CH_2Cl_2 (25 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3x25 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by CC (silica gel, EtOAc/hexanes 5:95 to 40:60) afforded compound **S21** (1.91 g, 77%) as an off-white solid (inseparable mixture of rotamers).

M.p. = 184–195 °C (decomposition);

R$_f$ = 0.27 (EtOAc/hexanes 10:90);

IR (neat) = 1424 (w), 1389 (w), 1200 (w), 1149 (m), 1101 (w), 1077 (w), 1062 (w), 997 (m), 972 (m), 911 (m), 844 (s), 830 (m), 818 (w), 804 (w), 750 (m), 720 (m), 684 (m), 668 (w), 627 (w), 518 (w);

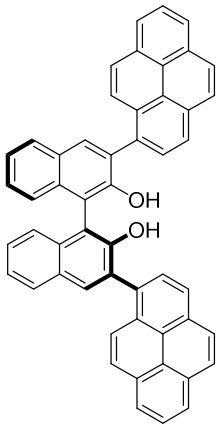
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.46–7.78 (m, 22H), 7.71–7.37 (m, 6H), 4.50–4.16 (m, 4H), 2.17–1.91 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.40, 152.30, 152.26, 152.19, 135.05, 134.97, 134.58, 134.50, 134.49, 134.46, 134.28, 134.18, 133.98, 133.96, 133.75, 132.56, 132.29, 132.09, 131.48, 131.40, 131.38, 131.18, 131.07, 131.03, 131.01, 130.99, 130.89, 130.76, 130.63, 130.61, 129.47, 129.39, 128.84, 128.77, 128.35, 128.15, 128.10, 128.03, 127.99, 127.97, 127.76, 127.74, 127.53, 127.49, 127.45, 127.42, 127.39, 127.01, 126.70, 126.66, 126.62, 126.59, 126.57, 126.53, 126.44, 126.39, 126.36, 126.07, 126.04, 125.98, 125.60, 125.56, 125.40, 125.37, 125.35, 125.26, 125.21, 125.09, 125.05, 125.03, 124.99, 124.97, 124.91, 124.79, 124.77, 124.73, 124.67, 124.50, 124.40, 98.63, 98.59, 98.51, 98.44, 55.83, 55.71, 55.52, 55.50;

HRMS-ESI (m/z): calculated for $C_{56}H_{38}O_4Na_1$ ($[M+Na]^+$): 797.2662, found: 797.2660;

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = −49.91 (*c* 0.55, $CHCl_3$).

*(S)-3,3'-di(pyren-1-yl)-[1,1'-binaphthalene]-2,2'-diol (**S22**)*



To a solution of **S21** (1.55 g, 2.00 mmol, 1.00 equiv) in THF/MeOH/$CHCl_3$ (30:15:10 mL) was added Amberlyst® ion-exchange resin 15 (1.55 g). The reaction mixture was heated to reflux for 20 h, subsequently cooled to r.t., filtered (filter paper) and concentrated under reduced pressure. Purification by CC (silica gel, EtOAc/hexanes 10:90 to 40:60) afforded compound **S22** (1.14 g, 83%) as an off-white solid (inseparable mixture of rotamers).

M.p. = 320–340 °C (decomposition);

$\mathbf{R}_f$ = 0.27 (EtOAc/hexanes 10:90);

IR (neat) = 3509 (br), 1384 (w), 1260 (w), 1243 (w), 1203 (w), 1188 (w), 1169 (w), 1143 (m), 1132 (w), 1101 (w), 844 (s), 831 (m), 818 (w), 778 (w), 751 (s), 712 (m), 692 (w), 682 (m), 666 (m), 625 (m);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.46–7.88 (m, 22H), 7.69–7.37 (m, 6H), 5.48–5.11 (m, 2H);

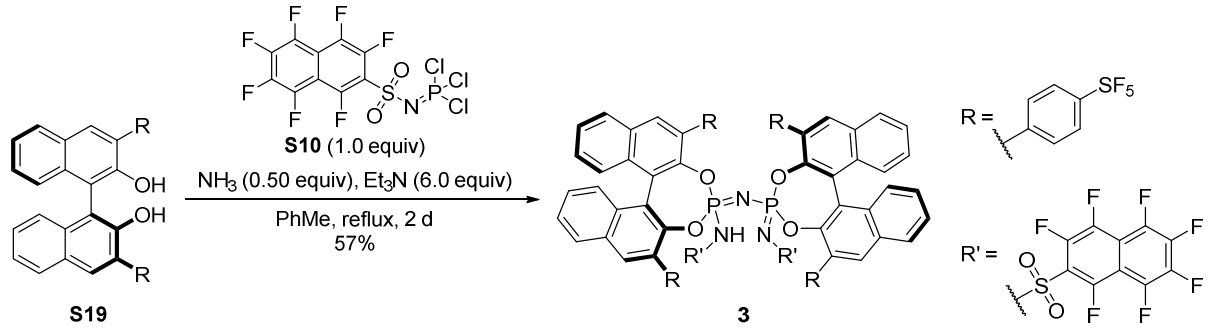
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.65, 150.64, 150.60, 133.65, 133.59, 133.55, 132.75, 132.66, 132.64, 132.58, 132.20, 132.14, 132.11, 132.05, 131.37, 131.35, 131.32, 131.29, 130.95, 130.90, 129.90, 129.84, 129.82, 129.73, 129.60, 129.56, 129.54, 129.52, 129.32, 129.24, 128.56, 128.46, 128.35, 128.31, 128.26, 128.05, 128.00, 127.95, 127.91, 127.83, 127.77, 127.48, 127.44, 127.41, 127.40, 127.37, 127.35, 126.15, 126.11, 126.06, 125.42, 125.37, 125.35, 125.31, 125.25, 125.22, 125.19, 125.17, 124.95, 124.91, 124.88, 124.85, 124.80, 124.78, 124.75, 124.73, 124.71, 124.68, 124.60, 124.57, 124.40, 124.39, 124.37, 124.33, 113.34, 113.10, 113.04;

HRMS-ESI (m/z): calculated for $C_{52}H_{29}O_2$ ($[M-H]^-$): 685.2173, found: 685.2174;

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +72.40 (*c* 1.00, $CHCl_3$).

1.3.3 Synthesis of imidodiphosphorimidate acids (IDPi)

_N_-((11b*S*)-4-(((11b*S*)-2,6-bis(4-(pentafluoro-λ^6-sulfanyl)phenyl)-4-(((perfluoronaphthalen-2-yl)sulfonyl)imino)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)imino)-2,6-bis(4-(pentafluoro-λ^6-sulfanyl)phenyl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-1,3,4,5,6,7,8-heptafluoronaphthalene-2-sulfonamide (3)



In a flame-dried flask under Ar, **S19** (500 mg, 0.724 mmol, 1.00 equiv) and **S10** (343 mg, 0.724 mmol, 1.01 equiv) were dissolved in PhMe (500 µL), then Et_3N (605 µL, 4.34 mmol, 6.00 equiv) was added and the yellow suspension was stirred at r.t. for 10 min. A freshly titrated solution of NH_3 (0.45 M in 1,4-dioxane, 804 µL, 0.362 mmol, 0.50 equiv) was added to the reaction mixture, which was stirred at r.t. for 10 min, then heated to reflux for 2 d. The reaction mixture was cooled to r.t., diluted with CH_2Cl_2 (10 mL), washed with 1.0 M HCl (10 mL) and brine (10 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by CC (silica gel, Et_2O/pentane 20:80 to 40:60) afforded a colorless solid, which was subjected to acidification. The solid was dissolved in CH_2Cl_2 (2.5 mL) and vigourously stirred with 6.0 M HCl (2.5 mL) at r.t. for 15 min, diluted with CH_2Cl_2 (10 mL) and washed with 6.0 M HCl (2x10 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3x5 mL). The combined organic layers were then dried under reduced pressure with PhMe (2x5 mL) to afford an off-white solid, which, upon recrystallization ($CHCl_3$/pentane), afforded compound **3** (438 mg, 57%) as colorless crystals.

M.p. = 242–300 °C (decomposition);

R_f = 0.28 (Et_2O/pentane 40:60);

IR (neat) = 1490 (m), 1411 (m), 1185 (m), 1151 (m), 1100 (w), 961 (m), 914 (w), 831 (s), 787 (m), 775 (w), 751 (m), 736 (m), 715 (w), 656 (m), 598 (m), 575 (s), 549 (w), 537 (w), 506 (w);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 2H), 8.03 (s, 2H), 7.97 (s, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.82–7.70 (m, 6H), 7.62–7.53 (m, 6H), 7.47 (ddd, *J* = 8.1, 6.6, 1.3 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.24–7.12 (m, 4H), 6.90–6.83 (m, 8H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5–152.5 (m), 150.5, 148.7, 143.7 (d, *J* = 14.4 Hz), 143.0 (t, *J* = 5.1 Hz), 142.6 (t, *J* = 5.5 Hz), 142.0 (d, *J* = 14.7 Hz), 141.8 (t, *J* = 14.8 Hz), 141.6–141.1 (m), 141.1–140.7 (m), 140.3–139.5 (m), 139.4–139.0 (m), 138.9, 138.4–137.9 (m), 138.1, 132.3, 132.1, 132.0, 131.8, 131.6, 131.4–131.1 (m), 129.7 (d, *J* = 27.8 Hz), 128.8, 128.4, 128.0, 127.6, 127.0 (d, *J* = 8.7 Hz), 126.7, 126.5–126.3 (m), 126.2, 125.4–124.8 (m), 123.6, 119.0–118.5 (m), 112.4–111.5 (m), 107.4–106.6 (m) (other signals not detected or observed);

^{19}F NMR (471 MHz, $CDCl_3$) δ 84.6 (p, *J* = 150.5), 84.3 (p, *J* = 149.9), 63.1 (d, *J* = 150.1 Hz), 62.7 (d, *J* = 149.5 Hz), −112.2 (dd, *J* = 77.1, 18.2 Hz), −133.6 (d, *J* = 18.2 Hz), −141.2 (dt, *J* = 78.4, 17.3 Hz), −143.9 (dt, *J* = 59.1, 17.1 Hz), −146.5 (dt, *J* = 58.6, 19.1 Hz), −148.3 to −148.9 (m), −153.3 to −153.6 (m);

^{31}P NMR (203 MHz, $CDCl_3$) δ −4.1;

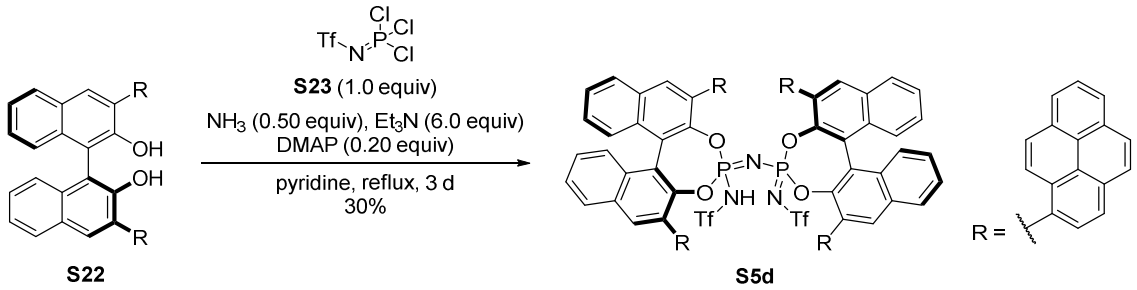
HRMS-ESI (m/z): calculated for $C_{84}H_{36}F_{34}N_3O_8P_2S_6$ ($[M-H]^-$): 2113.9765, found: 2113.9749;

$[\alpha]_D^{25}$ = +98.22 (*c* 0.90, $CHCl_3$);

LC-MS (50 mm Zorbax SB300-C8, 3.5 µm, 4.6 mm i.d., 1% TFA/MeCN 25:75, 1.0 mL/min, 4.7 MPa, 308 K, 254 nm): t_R = 3.27 min (>99% purity).

Crystallization by solvent layering (CH_2Cl_2/hexane, 1:1) afforded a single crystal suitable for X-ray analysis. For additional spectral and physical data for compound **3**, see section 1.4.3.

***N*-((11b*S*)-4-(((11b*S*)-2,6-di(pyren-1-yl)-4-(((trifluoromethyl)sulfonyl)imino)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)imino)-2,6-di(pyren-1-yl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-1,1,1-trifluoromethanesulfonamide (S5d)**



In a flame-dried flask under Ar, **S22** (595 mg, 0.866 mmol, 1.00 equiv) and **S23**[9] (246 mg, 0.866 mmol, 1.00 equiv) were dissolved in pyridine (1.5 mL), then Et_3N (724 µL, 5.20 mmol, 6.00 equiv) was added and the red suspension was stirred at r.t. for 5 min. A freshly titrated solution of NH_3 (0.35 M in 1,4-dioxane, 1.24 mL, 0.433 mmol, 0.50 equiv) was added to the reaction mixture, which was stirred at r.t. for 10 min. DMAP (21.2 mg, 0.173 mmol, 0.20 equiv) was added and the resulting orange suspension was heated to reflux for 3 d. The reaction mixture was cooled to r.t. and pyridine was removed by vacuum distillation. The residue was dissolved in CH_2Cl_2 (10 mL) and the solution was washed with 1.0 M HCl (10 mL) and brine (10 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by CC (silica gel, EtOAc/hexanes 0:100 to 5:95 then C18 spherical silica gel, MeCN/H_2O 40:60 to 90:10) afforded a solid, which was subjected to acidification. The solid was dissolved in CH_2Cl_2 (1 mL) and vigourously stirred with 6.0 M HCl (1 mL) at r.t. for 20 min, diluted with CH_2Cl_2 (10 mL) and washed with 6.0 M HCl (2x10 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3x5 mL). The combined organic layers were then dried under reduced pressure with PhMe (2x5 mL) and the residue washed with pentane to afford **S5d** as an olive-green solid (224 mg, 30%) (inseparable mixture of rotamers).

M.p. = 290–360 °C (decomposition);

R_f = 0.56 (EtOAc/hexanes 50:50);

IR (neat) = 3041 (br), 2922 (br), 1397 (w), 1315 (w), 1197 (s), 1184 (s), 1150 (m), 1134 (m), 1101 (m), 978 (w), 962 (m), 905 (m), 842 (s), 827 (w), 819 (w), 806 (w), 749 (m), 717 (m), 704 (m), 602 (m), 589 (w), 568 (m), 501 (m);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.54–7.42 (m), 7.40–7.30 (m), 7.28 (d, *J* = 9.1 Hz), 7.21 (d, *J* = 8.9 Hz), 7.17 (d, *J* = 9.2 Hz), 7.04 (d, *J* = 8.0 Hz), 6.76 (d, *J* = 8.1 Hz), 6.58 (d, *J* = 8.0 Hz), 6.51 (d, *J* = 7.9 Hz), 6.32 (d, *J* = 7.9 Hz), 6.19 (d, *J* = 7.9 Hz), 6.07 (d, *J* = 8.1 Hz), 5.86 (d, *J* = 8.1 Hz), 5.67 (d, *J* = 7.6 Hz), 5.25 (d, *J* = 9.4 Hz), 5.21 (d, *J* = 9.3 Hz) (for integration see copy of ^{1}H NMR spectrum);

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.62, 145.58, 145.54, 145.46, 145.38, 145.33, 145.30, 145.24, 144.21, 144.18, 144.14, 144.00, 143.94, 134.93, 134.70, 134.49, 134.37, 134.19, 134.17, 134.03, 133.54, 133.33, 133.15, 133.08, 132.83, 132.73, 132.61, 132.54, 132.49, 132.37, 132.26, 132.16, 131.97, 131.89, 131.75, 131.63, 131.45, 131.35, 131.25, 131.22, 131.17, 131.14, 130.99, 130.87, 130.71, 130.69, 130.65, 130.62, 130.57, 130.32, 130.25, 129.99, 129.59, 129.57, 129.43, 129.30, 129.28, 129.02, 128.93, 128.79, 128.69, 128.63, 128.33, 128.26, 128.07, 128.01, 127.98, 127.92, 127.86, 127.82, 127.76, 127.72, 127.65, 127.54, 127.47, 127.42, 127.38, 127.36, 127.34, 127.32, 127.21, 127.20, 127.17, 127.11, 127.08, 127.03, 126.96, 126.86, 126.82, 126.75, 126.69, 126.66, 126.64, 126.31, 126.25, 126.08, 126.01, 125.86, 125.83, 125.72, 125.64, 125.56, 125.45, 125.36, 125.26, 125.21, 125.02, 124.82, 124.75, 124.68, 124.63, 124.46, 124.45, 124.36, 124.30, 124.16, 124.13, 123.91, 123.87, 123.85, 123.73, 123.72, 123.68, 123.59, 123.51, 123.36, 123.34, 123.21, 123.19, 123.17, 122.98, 122.74, 121.19, 119.58, 117.44 (other signals not detected or observed);

^{19}F NMR (471 MHz, $CDCl_3$) δ −79.0, −79.5, −80.0, −80.9, −81.1, −81.5, −82.1;

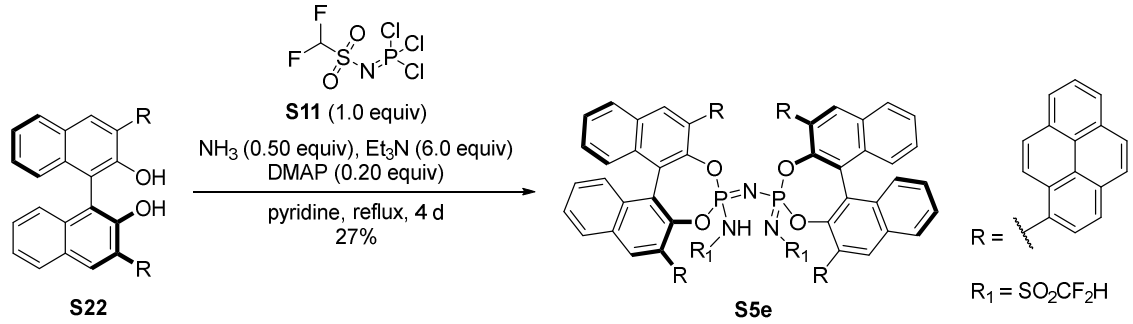
^{31}P NMR (203 MHz, $CDCl_3$) δ −4.7, −5.1, −5.5, −5.9, −6.0, −6.5;

HRMS-ESI (m/z): calculated for $C_{106}H_{56}F_6N_3O_8P_2S_2$ ($[M-H]^-$): 1738.2894, found: 1738.2910;

$[\alpha]_D^{25}$ = +210.00 (*c* 0.08, $CHCl_3$);

LC-MS (100 mm AdvanceBioRP mAb SB-C8, 3.5 µm, 4.6 mm i.d., 1% TFA/MeCN 35:65, 1.0 mL/min, 7.4 MPa, 308 K, 220 nm): t_R = 29.5 min (>95% purity).

***N*-((11b*S*)-4-(((11b*S*)-4-((difluoromethyl)sulfonamido)-2,6-di(pyren-1-yl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-ylidene)amino)-2,6-di(pyren-1-yl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-ylidene)-1,1-difluoromethanesulfonamide (S5e)**



In a flame-dried flask under Ar, **S22** (100 mg, 0.146 mmol, 1.00 equiv) and **S11** (38.8 mg, 0.146 mmol, 1.00 equiv) were dissolved in pyridine (300 µL), then Et_3N (122 µL, 0.874 mmol, 6.00 equiv) was added and the red suspension was stirred at r.t. for 5 min. A freshly titrated solution of NH_3 (0.35 M in 1,4-dioxane, 208 µL, 0.073 mmol, 0.50 equiv) was added to the reaction mixture, which was stirred at r.t. for 10 min. DMAP (3.56 mg, 0.029 mmol, 0.20 equiv) was added and the resulting red suspension was heated to reflux for 4 d. The reaction mixture was cooled to r.t. and pyridine was removed by vacuum distillation. The residue was dissolved in CH_2Cl_2 (8 mL). The solution was washed with 1.0 M HCl (10 mL) and brine (10 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by CC (silica gel, EtOAc/toluene 5:95 to 30:70, then C18 spherical silica gel, MeCN/H_2O 40:60 to 100:0) afforded a solid, which was subjected to acidification. The solid was dissolved in CH_2Cl_2 (1 mL) and vigourously stirred with 6.0 M HCl (1 mL) at r.t. for 10 min, diluted with CH_2Cl_2 (8 mL) and washed with 6.0 M HCl (2x5 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3x5 mL). The combined organic layers were then dried under reduced pressure with

PhMe (2x5 mL) and the residue washed with pentane to afford **S5e** as an olive-green solid (34.0 mg, 27%). (inseparable mixture of rotamers).

M.p. = 290–360 °C (decomposition);

$\mathbf{R}_f$ = 0.47 (EtOAc/hexanes 50:50);

IR (neat) = 3042 (br), 2924 (br), 1396 (w), 1382 (w), 1295 (w), 1244 (w), 1197 (m), 1184 (m), 1150 (m), 1134 (w), 1101 (m), 1080 (w), 978 (w), 962 (m), 914 (w), 900 (w), 843 (s), 828 (w), 819 (w), 750 (m), 717 (w), 704 (w), 623 (w), 542 (m), 506 (w);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47–7.46 (m), 7.44 (t, *J* = 7.7 Hz), 7.34 (t, *J* = 7.6 Hz), 7.29 (d, *J* = 9.1 Hz), 7.18 (d, *J* = 7.2 Hz), 7.14 (d, *J* = 8.9 Hz), 6.98–6.92 (m), 6.86 (d, *J* = 7.9 Hz), 6.80 (d, *J* = 7.9 Hz), 6.68 (dd, *J* = 12.8, 8.0 Hz), 6.52 (d, *J* = 7.9 Hz), 6.35 (d, *J* = 7.9 Hz), 6.32 (d, *J* = 7.9 Hz), 6.26–6.18 (m), 6.05 (d, *J* = 7.7 Hz), 5.99 (d, *J* = 7.8 Hz), 5.88 (d, *J* = 9.2 Hz), 5.78 (d, *J* = 8.0 Hz), 5.72 (d, *J* = 7.7 Hz), 5.55 (d, *J* = 9.2 Hz), 5.38 (d, *J* = 8.0 Hz), 3.51 (dt, *J* = 60.1, 53.8 Hz), 2.01 (dt, *J* = 99.3, 53.8 Hz) (for integration see copy of ^{1}H NMR spectrum);

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.66, 144.60, 144.37, 144.21, 144.14, 144.12, 144.05, 143.98, 143.75, 143.54, 143.48, 134.88, 134.59, 134.22, 134.17, 133.89, 133.81, 133.72, 133.66, 133.57, 133.33, 133.24, 133.13, 133.05, 132.90, 132.86, 132.75, 132.68, 132.54, 132.46, 132.35, 132.31, 132.28, 132.22, 132.18, 132.13, 131.91, 131.55, 131.48, 131.45, 131.41, 131.35, 131.32, 131.14, 131.06, 131.02, 130.95, 130.84, 130.77, 130.63, 130.53, 130.42, 130.35, 130.28, 130.19, 129.89, 129.84, 129.70, 129.65, 129.47, 129.11, 129.03, 128.97, 128.94, 128.88, 128.79, 128.76, 128.72, 128.68, 128.55, 128.45, 128.34, 128.23, 128.16, 128.11, 127.94, 127.89, 127.85, 127.80, 127.75, 127.70, 127.67, 127.61, 127.45, 127.36, 127.29, 127.26, 127.21, 127.18, 127.14, 127.11, 127.05, 127.01, 126.87, 126.66, 126.59, 126.54, 126.46, 126.35, 126.30, 126.25, 126.16, 126.06, 125.69, 125.63, 125.54, 125.49, 125.41, 125.33, 125.30, 125.23, 125.06, 124.88, 124.77, 124.74, 124.68, 124.59, 124.55, 124.51, 124.47, 124.43, 124.38, 124.32, 124.27, 124.23, 124.19, 124.14, 124.11, 123.85, 123.68, 123.63, 123.58, 123.30, 123.27, 123.15, 123.12, 122.82, 122.79, 122.75, 122.45, 121.60, 121.50, 113.32–108.43 (m) (other signals not detected or observed);

^{19}F NMR (282 MHz, $CDCl_3$) δ −120.46, −120.94, −121.03, −121.23, −121.72, −121.89, −121.98, −122.10, −122.18, −122.43, −122.54, −122.68, −122.82, −123.04, −123.32, −123.38, −123.46, −123.49, −123.77, −124.28, −124.69, −125.63;

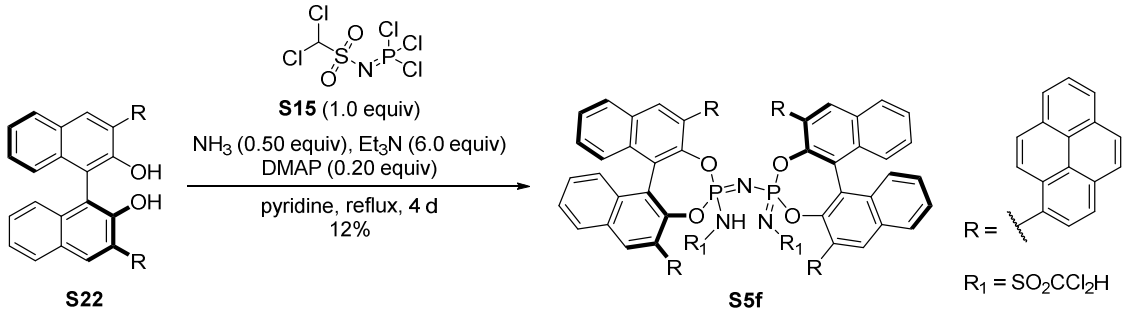
^{31}P NMR (122 MHz, $CDCl_3$) δ −5.4, −6.8, −7.6, −9.8, −10.7, −11.2, −12.1, −12.2, −12.4, −13.4;

HRMS-ESI (m/z): calculated for $C_{106}H_{58}F_4N_3O_8P_2S_2$ ($[M-H]^-$): 1702.3082, found: 1702.3096;

$[\alpha]_D^{25}$ = +158.78 (*c* 0.22, $CHCl_3$);

LC-MS (50 mm Zorbax SB300-C8, 3.5 μm, 4.6 mm i.d., 1% TFA/MeCN 25:75, 1.0 mL/min, 6.2 MPa, 308 K, 254 nm): t_R = 8.84 min (>96% purity).

1,1-Dichloro-*N*-((11b*S*)-4-(((11b*S*)-4-((dichloromethyl)sulfonamido)-2,6-di(pyren-1-yl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-ylidene)amino)-2,6-di(pyren-1-yl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-ylidene)methanesulfonamide (S5f)



In a flame-dried flask under Ar, **S22** (100 mg, 0.146 mmol, 1.00 equiv) and **S15** (43.6 mg, 0.146 mmol, 1.00 equiv) were dissolved in pyridine (300 μL), then Et_3N (122 μL, 0.874 mmol, 6.00 equiv) was added and the red suspension was stirred at r.t. for 5 min. A freshly titrated solution of NH_3 (0.40 M in 1,4-dioxane, 182 μL, 0.073 mmol, 0.50 equiv) was added to the reaction mixture, which was stirred at r.t. for 10 min. DMAP (3.56 mg, 0.029 mmol, 0.20 equiv) was added and the resulting red suspension was heated to reflux for 4 d. The reaction mixture was cooled to r.t. and pyridine was removed by vacuum distillation. The residue was dissolved in CH_2Cl_2 (8 mL). The solution was washed with 1.0 M HCl (10 mL) and brine (10 mL), dried

(Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by CC (silica gel, EtOAc/CH_2Cl_2/toluene 0:80:20 to 0:100:0 to 10:90:0, then C18 spherical silica gel, MeCN/H_2O 40:60 to 100:0) afforded a solid, which was subjected to acidification. The solid was dissolved in CH_2Cl_2 (1 mL) and vigourously stirred with 6.0 M HCl (1 mL) at r.t. for 10 min, diluted with CH_2Cl_2 (8 mL) and washed with 6.0 M HCl (2x5 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3x5 mL). The combined organic layers were then dried under reduced pressure with PhMe (2x5 mL) and the residue washed with pentane to afford **S5f** as an olive-green solid (15.0 mg, 12%). (inseparable mixture of rotamers).

M.p. = 270–360 °C (decomposition);

$\mathbf{R}_f$ = 0.50 (EtOAc/hexanes 50:50);

IR (neat) = 3050 (br), 2928 (br), 2852 (br), 1400 (w), 1290 (w), 1260 (w), 1244 (w), 1198 (m), 1182 (m), 1150 (m), 1101 (m), 977 (w), 962 (m), 910 (m), 898 (m), 843 (s), 827 (w), 818 (m), 805 (m), 798 (m), 750 (m), 717 (m), 703 (m), 683 (m), 577 (m), 554 (m), 504 (m);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44–7.39 (m), 7.32 (d, *J* = 8.9 Hz), 7.18 (d, *J* = 7.9 Hz), 7.14 (d, *J* = 7.7 Hz), 7.10 (d, *J* = 7.6 Hz), 7.06 (d, *J* = 9.2 Hz), 6.99 (t, *J* = 8.3 Hz), 6.85 (d, *J* = 7.9 Hz), 6.64 (d, *J* = 8.0 Hz), 6.54 (d, *J* = 7.9 Hz), 6.42 (d, *J* = 7.8 Hz), 6.38 (d, *J* = 7.9 Hz), 6.32 (d, *J* = 7.8 Hz), 6.28 (d, *J* = 7.9 Hz), 6.04 (d, *J* = 7.9 Hz), 4.45 (s), 4.35 (s), 3.35 (s), 3.07 (s), 1.50 (s), 1.43 (s) (for integration see copy of ^{1}H NMR spectrum);

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.93, 144.90, 144.23, 144.07, 144.04, 135.12, 134.77, 134.48, 134.14, 133.68, 133.48, 133.20, 133.16, 133.04, 133.00, 132.84, 132.77, 132.69, 132.65, 132.34, 132.29, 132.24, 132.04, 131.99, 131.92, 131.90, 131.79, 131.71, 131.45, 131.43, 131.40, 131.34, 131.30, 131.18, 131.15, 131.09, 131.03, 131.01, 130.98, 130.86, 130.84, 130.74, 130.72, 130.66, 130.57, 130.53, 130.49, 130.38, 130.32, 130.24, 130.13, 129.84, 129.74, 129.55, 129.02, 128.96, 128.93, 128.84, 128.79, 128.73, 128.70, 128.50, 128.39, 128.26, 128.22, 128.16, 128.00, 127.96, 127.90, 127.79, 127.72, 127.63, 127.58, 127.50, 127.38, 127.35, 127.27, 127.22, 127.16, 127.14, 127.08, 127.03, 126.94, 126.89, 126.86, 126.66, 126.61, 126.54, 126.36, 126.01, 125.87, 125.83, 125.78, 125.74, 125.69, 125.49, 125.45, 125.39, 125.32, 125.28, 125.21, 125.07, 124.96, 124.90,

124.86, 124.79, 124.73, 124.70, 124.58, 124.48, 124.42, 124.36, 124.32, 124.30, 124.11, 124.05, 123.94, 123.92, 123.86, 123.80, 123.66, 123.60, 123.52, 123.13, 123.06, 122.73, 122.63, 122.48, 121.55, 121.41 (other signals not detected or observed);

^{31}P NMR (203 MHz, $CDCl_3$) δ –10.9, –12.5, –13.1, –13.6, –14.2;

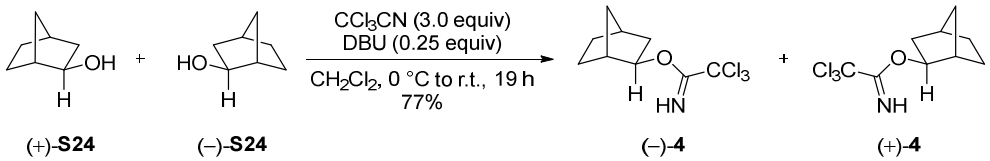
HRMS-ESI (m/z): calculated for $C_{106}H_{58}Cl_4N_3O_8P_2S_2$ ($[M-H]^-$): 1766.1900, found: 1766.1889;

$[\alpha]_D^{25}$ = +284.61 (*c* 0.13, $CHCl_3$);

LC-MS (50 mm Zorbax SB300-C8, 3.5 μm, 4.6 mm i.d., 1% TFA/MeCN 20:80, 1.0 mL/min, 5.6 MPa, 308 K, 254 nm): t_R = 4.37 min (>99% purity).

1.3.4 Synthesis of substrates

Exo-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate (_rac_-4)



(+)-**S24** (–)-**S24** (–)-**4** (+)-**4**

In a flame-dried flask under Ar, CCl_3CN (13.4 mL, 134 mmol, 3.00 equiv) was added to a solution of *exo*-norborneol (*rac*-**S24**) (5.00 g, 44.6 mmol, 1.00 equiv) in CH_2Cl_2 (80 mL) at 0 °C. DBU (1.66 mL, 11.1 mmol, 0.25 equiv) was added dropwise, the mixture stirred for 10 min at 0 °C, then warmed to r.t. and stirred for 19 h. The resulting dark brown mixture was concentrated under reduced pressure, purified by fractional distillation (5 mbar, b.p. = 106 °C) and filtered (cotton) to afford *rac*-**4** (8.80 g, 77%) as a colorless oil.

R_f = 0.28 (PhMe/pentane 50:50);

IR (neat) = 2960 (br), 2874 (w), 1656 (s), 1368 (w), 1319 (s), 1293 (m), 1079 (s), 1067 (s), 1041 (w), 988 (s), 866 (m), 839 (w), 817 (m), 791 (s), 764 (w), 701 (w), 648 (s), 492 (w);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.20 (bs, 1H), 4.76 (d, *J* = 6.8 Hz, 1H), 2.52 (d, 1H), 2.40–2.32 (m, 1H), 1.82 (ddd, *J* = 13.7, 6.9, 2.5 Hz, 1H), 1.66 (dp, *J* = 9.9, 1.9 Hz, 1H), 1.62–1.56 (m, 2H), 1.54–1.46 (m, 1H), 1.27–1.12 (m, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 92.0, 82.4, 40.9, 39.1, 35.3, 28.2, 24.0 (other signals not detected or observed);

HRMS-ESI (m/z): calculated for $C_9H_{12}N_1O_1Cl_3Na_1$ ($[M+Na]^+$): 277.9877, found: 277.9879;

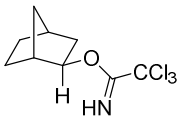
HPLC (Chiralcel® 150 mm OJ-3R, 3 µm, 4.6 mm i.d., MeOH/H_2O 80:20, 1.0 mL/min, 308 K, 210 nm): t_{R1} = 6.12 min, t_{R2} = 6.82 min;

Prep-HPLC (250 mm Chiralcel® OJ-H, 5 µm, 20 mm i.d., MeOH/H_2O 80:20, 20 mL/min, 20.9 MPa, 308 K, 210 nm): t_{R1} = 9.80 min, t_{R2} = 11.1 min.

Note: The enantiomers azeotrope with MeOH/H_2O. Therefore, the solvent mixture was saturated with NaCl and extracted with pentane (3x25 vol%); the combined organic layers were dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure to afford (−)-**4** and (+)-**4** as colorless oils.

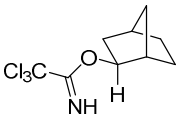
Absolute configuration of the single enantiomers was assigned on the basis of literature correlations[17,18], upon cleavage of the trichloroacetimidate group with *p*-TsOH[19] to obtain (+)-**S24** and (−)-**S24**.

*(1R,2R,4S)-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate ((−)-**4**)*

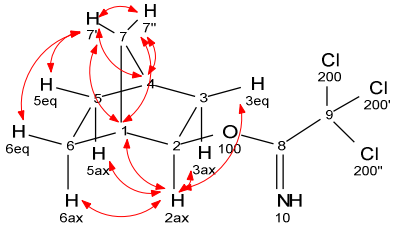


$[\alpha]_D^{25}$ = −9.90 (*c* 0.52, $CHCl_3$), **HPLC** (Chiralcel® 150 mm OJ-3R, 3 μm, 4.6 mm i.d., MeOH/H_2O 80:20, 1.0 mL/min, 308 K, 210 nm): t_{R1} = 6.12 min;

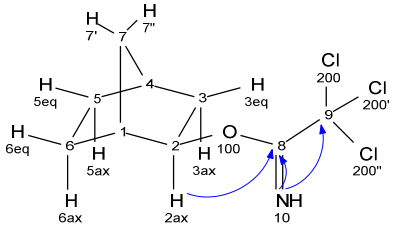
*(1S,2S,4R)-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate((+)-**4**)*



$[\alpha]_D^{25}$ = +9.06 (*c* 0.64, $CHCl_3$), **HPLC** (Chiralcel® 150 mm OJ-3R, 3 μm, 4.6 mm i.d., MeOH/H_2O 80:20, 1.0 mL/min, 308 K, 210 nm): t_{R2} = 6.82 min.



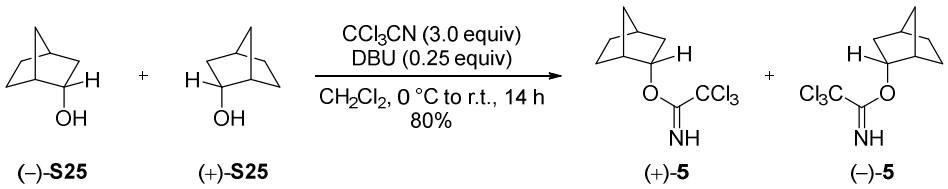
Important NOE connections



important HMBC crosspeaks

Assignments						Assignments					
Atom	**Chemical Shift**	**J**	**HSQC**	**HMBC**	**NOESY**	**Atom**	**Chemical Shift**	**J**	**HSQC**	**HMBC**	**NOESY**
1 C	40.85		1	3ax, 3eq, 4		**5eq H**	1.47		5	3, 4, 6	4, 5ax, 7'
H	2.5		1	2, 3, 4, 5	2ax, 6ax, 6eq, 7', 7"	**6 C**	23.97		6ax, 6eq	2ax, 4, 5eq, 7"	
2 C	82.37		2ax	1, 3eq, 4, 6ax, 6eq, 7'		**6ax H**	1.16		6	2	1, 2ax, 3ax, 6eq
2ax H	4.73	6.85(3ax)	2	4, 6, 7, 8	1, 3ax, 3eq, 5ax, 6ax	**6eq H**	1.58		6	2, 5	1, 6ax, 7'
3 C	39.15		3ax, 3eq	1, 5ax, 5eq, 7'		**7 C**	35.35		7', 7"	2ax, 3ax, 5ax	
3ax H	1.79	13.70(3eq), 6.85(2ax)	3	1, 5, 7	2ax, 4, 5ax, 6ax	**7' H**	1.21	9.90(7")	7	2, 3	1, 4, 5eq, 6eq, 7"
3eq H	1.56	13.70(3ax)	3	1, 2, 5	2ax, 3eq, 4	**7" H**	1.63	9.90(7')	7	5, 6	1, 4, 7'
4 C	35.35		4	1, 2ax, 5ax, 5eq		**8 C**	162.1			2ax, 10	
H	2.33		4	1, 2, 6	3ax, 3eq, 5ax, 5eq, 7', 7"	**9 C**	91.97			10	
5 C	28.22		5ax, 5eq	1, 3ax, 3eq, 6eq, 7"		**10 N**					
5ax H	1.14		5	3, 4, 7	2ax, 3ax, 4, 5eq	**H**	8.2			8, 9	

***Endo*-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate (*rac*-5)**



(–)-**S25** (+)-**S25** (+)-**5** (–)-**5**

In a flame-dried flask under Ar, CCl_3CN (2.39 mL, 23.8 mmol, 3.00 equiv) was added to a solution of *endo*-norborneol (*rac*-**S25**)[20] (890 mg, 7.93 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) at 0 °C. DBU (297 µL, 1.98 mmol, 0.25 equiv) was added dropwise, the mixture stirred for 10 min at 0 °C, then warmed to r.t. and stirred for 14 h. The resulting dark brown mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2 (20 mL), washed with 1.0 M HCl (15 mL), brine (15 mL) and dried (Na_2SO_4). Purification by bulb-to-bulb distillation (10^{-2} mbar, 50–60 °C) afforded *rac*-**5** (1.63 g, 80%) as colorless oil.

R_f = 0.36 (PhMe/pentane 50:50);

IR (neat) = 2957 (br), 2873 (w), 1658 (s), 1369 (w), 1321 (m), 1308 (m), 1290 (m), 1079 (s), 1014 (m), 992 (m), 883 (w), 848 (m), 834 (w), 792 (s), 693 (w), 647 (s), 534 (w), 523 (w);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.18 (bs, 1H), 5.19–4.84 (m, 1H), 2.67–2.63 (m, 1H), 2.29–2.24 (m, 1H), 2.10–2.02 (m, 1H), 1.96–1.89 (m, 1H), 1.66–1.53 (m, 1H), 1.45–1.31 (m, 4H), 1.14 (dt, *J* = 13.5, 3.5 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 80.4, 40.1, 37.4, 36.8, 36.4, 29.1, 21.0 (other signals not detected or observed);

HRMS-ESI (m/z): calculated for $C_9H_{13}N_1O_1Cl_3$ ($[M+H]^+$): 256.0057, found: 256.0057;

HPLC (Chiralpak® 150 mm AD-3R, 3 µm, 4.6 mm i.d., MeCN/H_2O 65:35, 1.0 mL/min, 298 K, 200 nm): t_{R1} = 7.47 min, t_{R2} = 8.70 min;

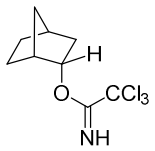
Prep-HPLC (250 mm Chiralpak® IA, 5 µm, 20 mm i.d., MeOH/H_2O 80:20, 15 mL/min, 21.2 MPa, 308 K, 220 nm): t_{R1} = 11.9 min, t_{R2} = 13.2 min; further prep-HPLC separation for second

fraction set (250 mm YMC-Pack PVA, 5 µm, 20 mm i.d., isohexane, 20 mL/min, 2.7 MPa, 308 K, 220 nm): t_{R2} = 9.36 min.

Note: The enantiomers azeotrope with MeOH/H_2O. Therefore, the solvent mixture was saturated with NaCl and extracted with pentane (3x25 vol%); the combined organic layers were dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure to afford (−)-**5** and (+)-**5** as colorless oils.

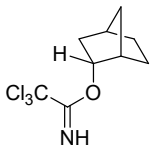
Absolute configuration of the single enantiomers was assigned on the basis of literature correlations[17,18], upon cleavage of the trichloroacetimidate group with *p*-TsOH[19] to obtain (+)-**S25** and (−)-**S25**.

*(1R,2S,4S)-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate ((+)-**5**)*

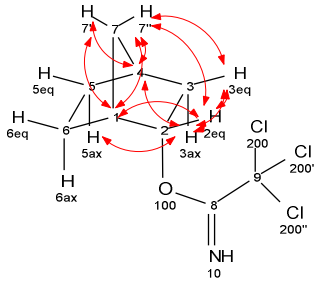


$[\alpha]_D^{25}$ = +8.00 (*c* 0.50, $CHCl_3$), **HPLC** (Chiralpak® 150 mm AD-3R, 3 µm, 4.6 mm i.d., MeCN/H_2O 65:35, 1.0 mL/min, 298 K, 200 nm): t_{R1} = 7.47 min;

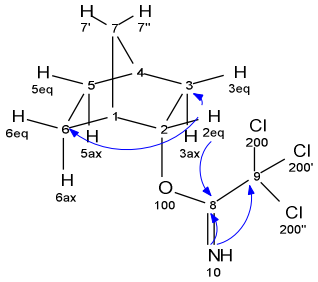
*(1S,2R,4R)-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate ((−)-**5**)*



$[\alpha]_D^{25}$ = −7.36 (*c* 0.43, $CHCl_3$), **HPLC** (Chiralpak® 150 mm AD-3R, 3 µm, 4.6 mm i.d., MeCN/H_2O 65:35, 1.0 mL/min, 298 K, 200 nm): t_{R2} = 8.70 min.



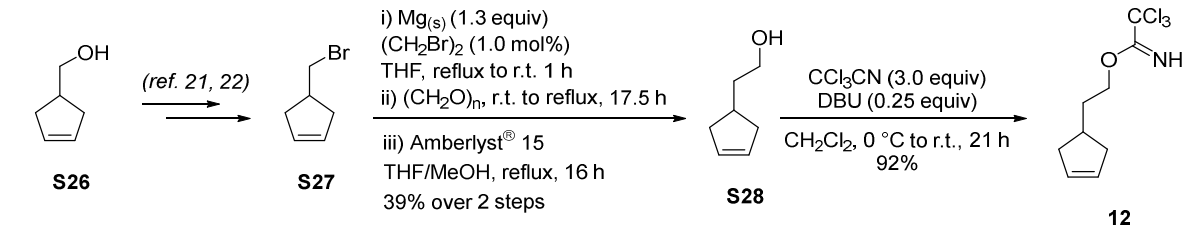
important NOE connections



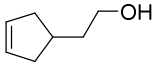
important HMBC crosspeaks

Assignments						Assignments					
Atom	**Chemical Shift**	**J**	**HSQC**	**HMBC**	**NOESY**	**Atom**	**Chemical Shift**	**J**	**HSQC**	**HMBC**	**NOESY**
1 C	40.09		1	3eq, 4, 6ax		**5eq H**	1.6		5	3, 4, 6	4
H	2.65		1	3, 4, 5	2eq, 6ax, 6eq, 7', 7''	**6 C**	21		6ax, 6eq	2eq, 4, 5eq	
2 C	80.42		2eq	3ax, 3eq, 4, 6ax		**6ax H**	1.41		6	1, 2, 5	1
2eq H	5.08	10.10(3eq)	2	3, 6, 8	1, 3ax, 3eq, 7''	**6eq H**	1.93		6		1
3 C	36.78		3ax, 3eq	1, 2eq, 5ax, 5eq		**7 C**	37.35		7', 7''	3ax, 5ax	
3ax H	1.14	13.40(3eq)	3	2, 4, 5, 7	2eq, 3eq, 4, 5ax	**7' H**	1.37		7		1, 4
3eq H	2.06	13.40(3ax), 10.10(2eq)	3	1, 2, 4, 5	2eq, 3ax, 4, 7''	**7'' H**	1.43		7		1, 2eq, 3eq, 4
4 C	36.42		4	1, 3ax, 3eq, 5eq		**8 C**	162.74			2eq, 10	
H	2.27		4	1, 2, 6	3ax, 3eq, 5ax, 5eq, 7', 7''	**9 C**	91.89			10	
5 C	29.12		5ax, 5eq	1, 3ax, 3eq, 6ax		**10 N**					
5ax H	1.36		5	3, 7	3ax, 4	**H**	8.19			8, 9	

2-(Cyclopent-3-en-1-yl)ethyl 2,2,2-trichloroacetimidate (12)



*2-(Cyclopent-3-en-1-yl)ethan-1-ol (**S28**)*



In a flame-dried flask under Ar, $(CH_2)Br_2$ (10.7 µL, 0.124 mmol, 0.010 equiv) was added to Mg turnings (392 mg, 16.1 mmol, 1.30 equiv) in THF (1.0 mL). The suspension was heated to reflux for 5 min. Heating was discontinued and a solution of **S27**[21,22] (2.00 g, 12.4 mmol, 1.00 equiv) in THF (7.5 mL) was added dropwise over 20 min, the mixture was heated to reflux for 1 h and subsequently cooled to r.t. Dried (30 mbar, 60 °C, 4 h) paraformaldehyde (1.12 g, 37.3 mmol, 3.00 equiv) was added in portions (exothermic reaction), the mixture stirred at r.t. for 16 h, heated to 80 °C for 1.5 h, and cooled to r.t. 1.0 M HCl (10 mL) was added dropwise at r.t. with stirring until gas evolution ceased, then the mixture was extracted with MTBE (3x15 mL), washed with brine (20 mL), dried (Na_2SO_4), filtered (silica gel) and concentrated under reduced pressure. The crude mixture was dissolved in MeOH (20 mL)/THF (20 mL) and heated to reflux with Amberlyst® ion-exchange resin 15 (800 mg) for 16 h. The mixture was diluted with CH_2Cl_2, filtered (filter paper) and concentrated under reduced pressure. Purification by CC (EtOAc/hexanes 5:95 to 40:60) afforded **S28** (545 mg, 39%) as a pale yellow oil[23].

R_f = 0.28 (EtOAc/hexanes 30:70);

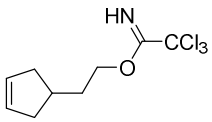
IR (neat) = 3321 (br), 3053 (w), 2924 (m), 2840 (m), 1440 (w), 1350 (w), 1082 (w), 1057 (s), 1040 (m), 1002 (m), 982 (w), 956 (w), 926 (m), 848 (w), 783 (w), 767 (w), 687 (s), 671 (s), 500 (w), 463 (w);

^{1}H NMR (501 MHz, $CDCl_3$) δ 5.93–5.41 (m, 2H), 3.67 (t, *J* = 6.8 Hz, 2H), 2.55–2.43 (m, 2H), 2.41–2.28 (m, 1H), 2.05–1.94 (m, 2H), 1.68 (q, *J* = 7.0 Hz, 2H), 1.43 (bs, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 129.8, 62.0, 39.4, 38.9, 34.1 (other signals not detected or observed);

HRMS-CI (m/z): calculated for $C_7H_{13}O_1$ ($[M+H]^+$): 113.0961, found: 113.0963.

*2-(cyclopent-3-en-1-yl)ethyl 2,2,2-trichloroacetimidate (**12**)*



In a flame-dried flask under Ar, CCl_3CN (402 µL, 4.01 mmol, 3.00 equiv) was added to a solution of **S28** (150 mg, 1.34 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 mL) at 0 °C. DBU (50.0 µL, 0.33 mmol, 0.25 equiv) was added dropwise, the mixture was stirred for 3 h at 0 °C, then warmed to r.t. and stirred for 18 h. The resulting dark brown mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2 (8 mL), washed with 1.0 M HCl (5 mL), brine (5 mL), dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by bulb-to-bulb distillation (10^{-2} mbar, 70–80 °C) afforded **12** (315 mg, 92%) as colorless oil.

R_f = 0.26 (PhMe/pentane 50:50);

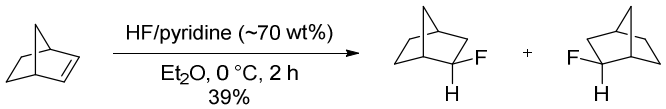
IR (neat) = 3345 (br), 2925 (br), 2842 (br), 1662 (m), 1470 (w), 1450 (w), 1389 (w), 1351 (w), 1305 (m), 1073 (m), 1028 (w), 993 (w), 928 (w), 854 (w), 794 (s), 717 (w), 690 (m), 646 (s);

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.24 (s, 1H), 5.68 (s, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.60–2.49 (m, 2H), 2.48–2.35 (m, 1H), 2.10–2.02 (m, 2H), 1.90 (q, *J* = 6.8 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 129.8, 91.6, 68.8, 38.8, 34.6, 34.4 (other signals not detected or observed);

HRMS-ESI (m/z): calculated for $C_9H_{13}N_1O_1Cl_3$ ($[M+H]^+$): 256.0057, found: 256.0058.

***Exo*-2-fluorobicyclo[2.2.1]heptane (*rac*-10)**



8 *rac*-**10**

In a polyethylene flask under Ar, a ca.70 wt% HF/pyridine solution (21.9 mL, 170 mmol, 8.00 equiv) was cooled to 0 °C for 35 min. Bicyclo[2.2.1]hept-2-ene (**8**) (2.00 g, 21.2 mmol, 1.00 equiv) in Et_2O (4.5 mL) was added over 25 min and the reaction mixture stirred for 1 h. Ice water (40 mL) was added dropwise at 0 °C and the mixture extracted with pentane (3x15 mL). The combined organic layers were washed with H_2O (2x30 mL), 0.05 M $H_2SO_{4\,(aq)}$ (3x20 mL), dried ($MgSO_4$), filtered (filter paper) and concentrated under reduced pressure (>500 mbar, 40 °C). Purification by sublimation (200 mbar, 60 °C) afforded *rac*-**10** as a volatile transparent colorless solid (950 mg, 39%)[24-26].

M.p. = 87–89 °C;

IR (neat) = 2961 (br), 2915 (w), 2874 (w), 1455 (w), 1437 (w), 1357 (w), 1176 (w), 1153 (w), 1073 (m), 1039 (w), 983 (s), 942 (w), 923 (w), 915 (w), 849 (m), 837 (m), 761 (w), 610 (w);

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.64–4.52 (m, 1H), 2.44–2.40 (m, 1H), 2.31–2.28 (m, 1H), 1.69–1.55 (m, 3H), 1.55–1.47 (m, 1H), 1.45–1.38 (m, 1H), 1.18–1.14 (m, 1H), 1.05–0.99 (m, 1H), 0.99–0.92 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 96.1 (d, *J* = 181.5 Hz), 42.0 (d, *J* = 19.5 Hz), 39.9 (d, *J* = 19.8 Hz), 34.8, 34.6 (d, *J* = 1.4 Hz), 27.9 (d, *J* = 1.4 Hz), 22.3 (d, *J* = 10.5 Hz);

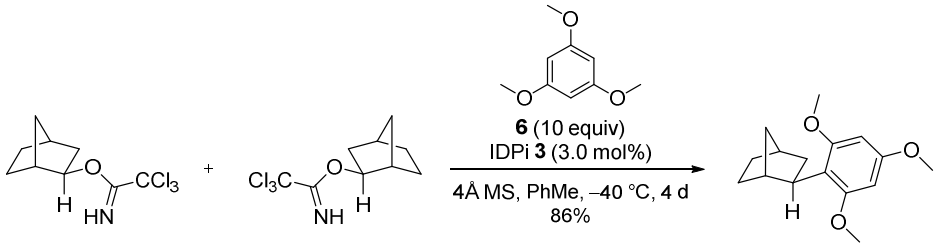
^{19}F NMR (471 MHz, $CDCl_3$) δ −160.2;

HRMS-EI (m/z): calculated for $C_7H_{11}F_1$ [$M^{+\cdot}$]: 114.0839, found: 114.0840.

1.3.5 Conversion of diverse substrates to enantioenriched product **7**

Note: product is depicted as the major enantiomer throughout; enantiomeric ratios are given for each individual case.

Synthesis of 2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane (7) from *rac*-4[II]



[Synthetic protocol I (**SP I**)[III]] In a flame-dried flask under Ar, IDPi **3** (12.7 mg, 6.00 µmol, 0.030 equiv), 1,3,5-trimethoxybenzene (**6**) (336 mg, 2.00 mmol, 10.0 equiv) and 4Å MS (40.0 mg, 200 mg/mmol) in PhMe (1.5 mL) were cooled to −40 °C. *rac*-**4** (51.3 mg, 0.200 mmol, 1.00 equiv) in PhMe (500 µL) was slowly added to the suspension and the mixture stirred at −40 °C for 4 d. Et_3N (27.8 µL, 0.200 mmol, 1.00 equiv) was added, the mixture was warmed to r.t. and concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (45.0 mg, 86%, e.r. = 97:3) as a colorless solid.

M.p. = 52–54 °C;

$\mathbf{R}_f$ = 0.30 (PhMe/pentane 50:50);

[II] Racemate was prepared similarly in 54% yield (0.70 mmol scale), using catalytic $NH(SO_2CF_3)_2$ (4.0 mol%) and **S16** (3.0 equiv) in $CHCl_3$ (0.80 M) at 25 °C.

[III] *Synthetic protocol I* (**SP I**) is referred to as *conditions a* in the text.

IR (neat) = 2943 (br), 1602 (m), 1584 (s), 1463 (m), 1453 (m), 1436 (w), 1416 (m), 1328 (m), 1230 (m), 1200 (s), 1183 (w), 1450 (m), 1142 (m), 1119 (s), 1113 (s), 1064 (m), 1033 (m), 962 (m), 949 (w), 806 (s);

^{1}H NMR (501 MHz, $CDCl_3$) δ 6.12 (s, 2H), 3.79 (s, 3H), 3.77 (s, 6H), 3.07 (t, *J* = 8.1 Hz, 1H), 2.32–2.28 (m, 1H), 2.28–2.23 (m, 1H), 1.98 (dp, *J* = 9.1, 2.0 Hz, 1H), 1.79–1.71 (m, 1H), 1.67–1.59 (m, 1H), 1.60–1.44 (m, 2H), 1.35–1.22 (m, 2H), 1.17–1.12 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 158.6, 115.7, 91.2, 55.6, 55.2, 42.1, 38.8, 38.3, 37.9, 36.8, 32.4, 28.6;

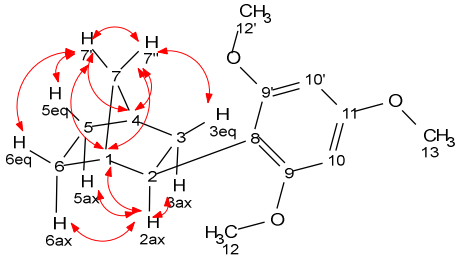
HRMS-ESI (m/z): calculated for $C_{16}H_{23}O_3$ ($[M+H]^+$): 263.1642, found: 263.1644;

$[\alpha]_D^{25}$ = −36.50 (*c* 0.40, $CHCl_3$);

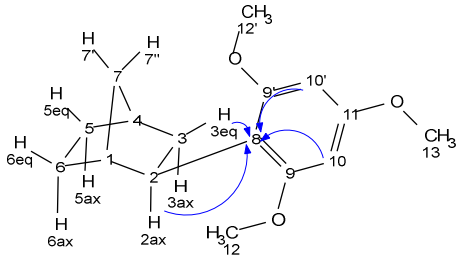
HPLC (Chiralpak® 150 mm AD-3R, 3 µm, 4.6 mm i.d., MeCN/H_2O 55:45, 1.0 mL/min, 298 K, 210 nm, or Chiralpak® 150 mm IB-3, 3 µm, 4.6 mm i.d., MTBE/*n*-heptane 10:90, 1.0 mL/min, 298 K, 220 nm): t_{R1} = 14.59 min, t_{R2} = 16.22 min, or t_{R1} = 5.32 min, t_{R2} = 6.18 min;

Prep-HPLC (250 mm Chiralpak® IB, 5 µm, 20 mm i.d., MTBE/*i*-hexane 10:90, 15 mL/min, 3.1 MPa, 298 K, 220 nm): t_{R1} = 10.8 min, t_{R2} = 11.9 min.

Both enantioenriched (e.r. = 97:3) and enantiopure (e.r. > 99.9) samples of compound **7** were used for crystallization by static vacuum sublimation (10^{-2} mbar, 48 °C). For additional spectral and physical data, see section 1.4.3.



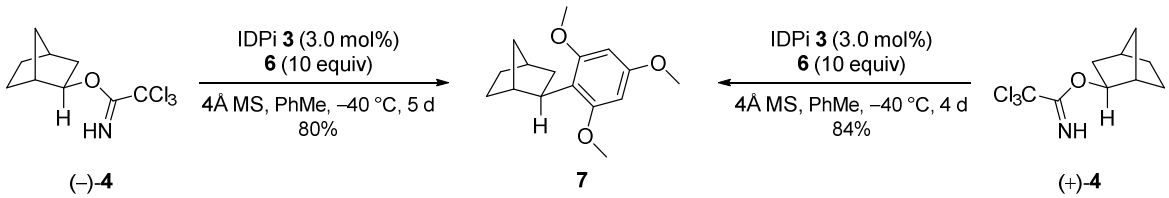
important NOE connections



important HMBC crosspeaks

Assignments						Assignments					
Atom	Chemical Shift	COSY	HSQC	HMBC	NOESY	Atom	Chemical Shift	COSY	HSQC	HMBC	NOESY
1 C	42.28		1	2ax, 3ax, 4, 6eq		7' H	1.15	1, 2ax, 3ax, 4, 7"	7		1, 4, 5eq, 6eq, 7"
H	2.3	4, 6ax, 6eq, 7', 7"	1	3, 4, 5	2ax, 6ax, 6eq, 7', 7"	7" H	1.98	1, 4, 5ax, 6aq, 7'	7		1, 3eq, 4, 7'
2 C	38.46		2ax	2ax, 3eq, 4, 6eq, 10, 10'		8 C	115.83			2ax, 3eq, 10, 10'	
2ax H	3.07	3ax, 3eq, 7', 10, 10'	2	1, 2, 3, 6, 7, 8, 9	1, 3ax, 5ax, 6ax	9 C	159.23			2ax, 10, 12	
3 C	38.96		3ax, 3eq	1, 2ax, 3ax, 5ax, 5eq		9' C	159.23			10', 12'	
3ax H	1.62	2ax, 3eq, 4, 7'	3	1, 3, 5, 7	2ax, 4, 5ax, 6ax	10 C	91.37		10	10'	
3eq H	1.74	2ax, 3ax, 4, 5eq	3	2, 4, 5, 8	4, 7"	H	6.12	2ax, 13	10	2, 8, 9, 10', 11	
4 C	36.93		4	1, 3eq, 4		10' C	91.37		10'	10	
H	2.26	1, 3ax, 3eq, 5eq, 7', 7"	4	1, 2, 4, 6	3ax, 3eq, 5ax, 5eq, 7', 7"	H	6.12	2ax, 13	10'	2, 8, 9', 10, 11	
5 C	28.76		5ax, 5eq	1, 3ax, 3eq, 6eq		11 C	158.77			10, 10', 13	
5ax H	1.25	5eq, 6ax, 6eq, 7"	5	3, 7	2ax, 3ax, 4, 5eq	12 C	55.77		12		
5eq H	1.55	3eq, 4, 5ax, 6ax, 6eq	5	3, 6	4, 5ax, 7'	H3	3.76		12	9	
6 C	32.58		6ax, 6eq	2ax, 4, 5eq		12' C	55.77		12'		
6ax H	1.31	1, 5ax, 5eq, 6eq, 7"	6	7	1, 2ax, 3ax, 6eq	H3	3.76		12'	9'	
6eq H	1.48	1, 5ax, 5eq, 6ax	6	1, 2, 5	1, 6ax, 7'	13 C	55.4		13		
7 C	38.08		7', 7"	2ax, 3ax, 5ax, 6ax		H3	3.79	10, 10'	13	11	

Synthesis of 7 from (-)-4 or (+)-4



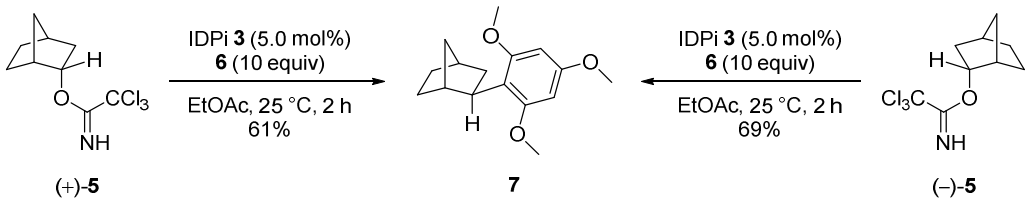
[(**SP I**)] In a flame-dried flask under Ar, IDPi **3** (6.35 mg, 3.00 µmol, 0.030 equiv), **6** (168 mg, 1.00 mmol, 10.0 equiv) and 4Å MS (20.0 mg, 200 mg/mmol) in PhMe (500 µL) were cooled to −40 °C. (−)-**4** or (+)-**4** (25.6 mg, 0.100 mmol, 1.00 equiv) in PhMe (500 µL) was slowly added to the suspension and the mixture was stirred at −40 °C for 5 d and 4 d, respectively. Et_3N (14.0 µL, 0.100 mmol, 1.00 equiv) was added, the mixture was warmed to r.t. and concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (21.0 mg, 80%, e.r. = 97:3 and 22.0 mg, 84%, e.r. = 97:3 respectively) as a colorless solid.

Synthesis of 7 from *rac*-5

[Synthetic protocol II (**SP II**)] In a flame-dried flask under Ar, IDPi **3** (10.6 mg, 5.00 µmol, 0.050 equiv) and **6** (168 mg, 1.00 mmol, 10.0 equiv) were dissolved in EtOAc (500 µL)[IV] and freshly prepared *rac*-**5** (25.6 mg, 0.100 mmol, 1.00 equiv) in EtOAc (500 µL) was added at 25 °C. The mixture was stirred for 2 h, subsequently treated with Et_3N (14.0 µL, 0.100 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (18.0 mg, 69%, e.r. = 88:12) as a colorless solid.

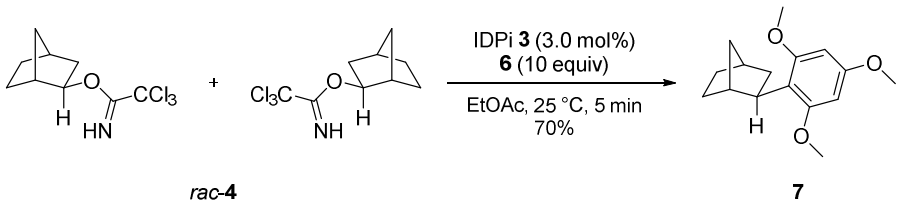
[IV] The reaction did not proceed in PhMe or other aromatic, chlorinated and ethereal organic solvents.

Synthesis of 7 from (-)-5 or (+)-5



[(**SP II**)] In a flame-dried flask under Ar, IDPi **3** (10.6 mg, 5.00 µmol, 0.050 equiv) and **6** (168 mg, 1.00 mmol, 10.0 equiv) were dissolved in EtOAc (500 µL) and freshly prepared (+)-**5** or (−)-**5** (25.6 mg, 0.100 mmol, 1.00 equiv) in EtOAc (500 µL) was added at 25 °C. The mixture was stirred for 2 h, subsequently treated with Et_3N (14.0 µL, 0.100 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (16.0 mg, 61%, e.r. = 87.5:12.5 and 18.0 mg, 69%, e.r. = 88:12 respectively) as a colorless solid.

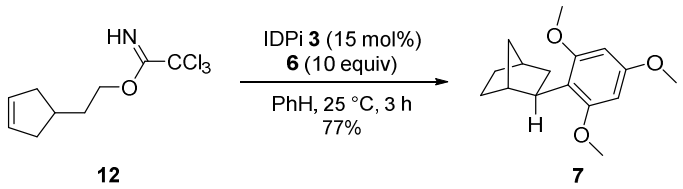
Synthesis of 7 from *rac*-4[V]



[(**SP II**)] In a flame-dried flask under Ar, IDPi **3** (6.35 mg, 3.00 µmol, 0.030 equiv) and **6** (168 mg, 1.00 mmol, 10.0 equiv) were dissolved in EtOAc (500 µL) and *rac*-**4** (25.6 mg, 0.100 mmol, 1.00 equiv) in EtOAc (500 µL) was added at 25 °C. The mixture was stirred for 5 min, subsequently treated with Et_3N (14.0 µL, 0.100 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (18.3 mg, 70%, e.r. = 88:12) as a colorless solid.

[V] The experiment was devised to compare the reactivity of *rac*-**4** to that of *rac*-**5**.

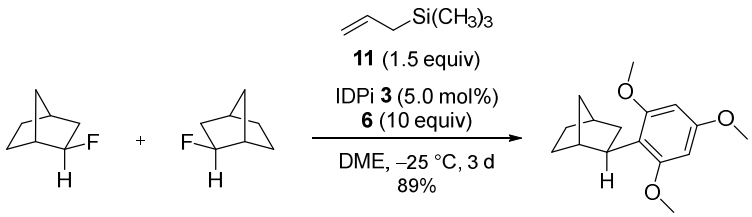
Synthesis of 7 from 2-(cyclopent-3-en-1-yl)ethyl 2,2,2-trichloroacetimidate (12)



12 **7**

[Synthetic protocol III (**SP III**)] In a flame-dried flask under Ar, IDPi **3** (31.7 mg, 15.0 µmol, 0.150 equiv) and **6** (168 mg, 1.00 mmol, 10.0 equiv) were dissolved in PhH (100 µL) and **12** (25.6 mg, 0.100 mmol, 1.00 equiv) in PhH (100 µL) was added at 25 °C. The mixture was stirred for 3 h, subsequently treated with Et_3N (14.0 µL, 0.100 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (20.1 mg, 77%, e.r. = 87:13) as a colorless solid.

Synthesis of 7 from *exo*-2-fluorobicyclo[2.2.1]heptane (*rac*-10)



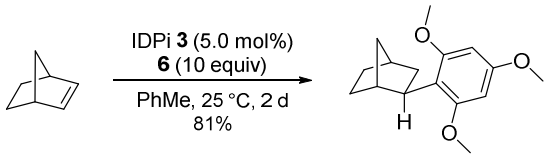
rac-**10** **7**

[Synthetic protocol IV (**SP IV**)] In a flame-dried flask under Ar, allyltrimethylsilane (**11**) (35.7 µL, 0.225 mmol, 1.50 equiv)[VI] was added at r.t. to a solution of IDPi **3** (15.9 mg, 7.50 µmol, 0.050 equiv) and **6** (252 mg, 1.50 mmol, 10.0 equiv) in 1,2-dimethoxyethane (DME, 300 µL). The solution was stirred at r.t. for 5 min, and then cooled to −25 °C. A solution of *rac*-**10** (25.6 mg, 0.100 mmol, 1.00 equiv) in DME (300 µL) was slowly added to the bright pink suspension

[VI] In the absence of allyltrimethylsilane (**11**) a racemic product is obtained, presumably due to the background reaction promoted by the HF by-product.

and the mixture stirred at −25 °C for 3 d[VII]. Et_3N (20.9 µL, 0.150 mmol, 1.00 equiv) was added, the mixture was warmed to r.t. and concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (35.0 mg, 89%, e.r. = 92:8) as a colorless solid.

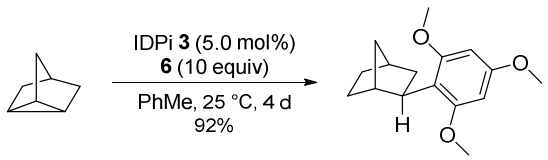
Synthesis of 7 from bicyclo[2.2.1]hept-2-ene (8)



8 **7**

[Synthetic protocol V (**SP V**)] In a flame-dried flask under Ar, IDPi **3** (15.9 mg, 7.50 µmol, 0.050 equiv) and **6** (252 mg, 1.50 mmol, 10.0 equiv) were dissolved in PhMe (1 mL) and sublimed (1 atm, 47 °C) bicyclo[2.2.1]hept-2-ene (**8**) (14.1 mg, 0.150 mmol, 1.00 equiv) in PhMe (500 µL) was added at 25 °C. The mixture was stirred for 2 d[VII], subsequently treated with Et_3N (20.9 µL, 0.150 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (32.0 mg, 81%, e.r. = 92:8) as a colorless solid.

Synthesis of 7 from tricyclo[2.2.1.0^{2,6}]heptane (9)



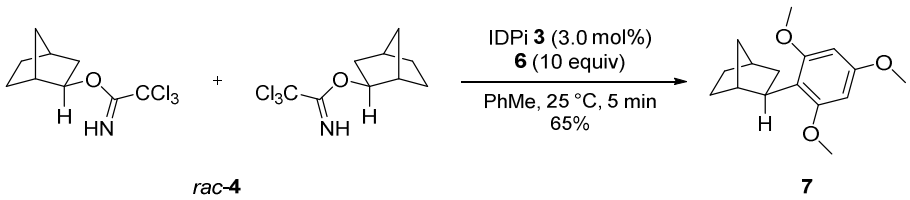
9 **7**

[(**SP V**)] In a flame-dried flask under Ar, IDPi **3** (15.9 mg, 7.50 µmol, 0.050 equiv) and **6** (252 mg, 1.50 mmol, 10.0 equiv) were dissolved in PhMe (1 mL) and tricyclo[2.2.1.0^{2,6}]heptane (**9**)[27]

[VII] Consumption of *rac*-**10**, **8** and **9** was monitored by GC/GC-MS analysis.

(90% purity[VIII], 15.7 mg, 0.150 mmol, 1.00 equiv) in PhMe (500 µL) was added at 25 °C. The mixture was stirred for 4 d[VII], subsequently treated with Et_3N (20.9 µL, 0.150 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/pentane 10:90 to 30:70) afforded **7** (39.0 mg, 92%, e.r. = 92:8) as a colorless solid.

Synthesis of 7 from *rac*-4[IX]



rac-**4** **7**

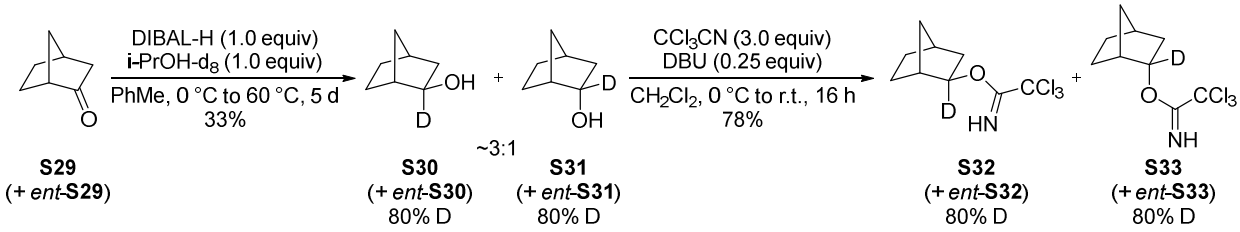
[(**SP V**)] In a flame-dried flask under Ar, IDPi **3** (6.35 mg, 3.00 µmol, 0.030 equiv) and **6** (168 mg, 1.00 mmol, 10.0 equiv) were dissolved in PhMe (500 µL) and *rac*-**4** (25.6 mg, 0.100 mmol, 1.00 equiv) in PhMe (500 µL) was added at 25 °C. The mixture was stirred for 5 min, subsequently treated with Et_3N (14.0 µL, 0.100 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/hexanes 10:90 to 30:70) afforded **7** (17.0 mg, 65%, e.r. = 92:8) as a colorless solid.

[VIII] Residual solvent is present.

[IX] The experiment was devised to compare the reactivity of *rac*-**4** to that of bicyclo[2.2.1]hept-2-ene (**8**) and tricyclo[2.2.1.$0^{2,6}$]heptane (**9**).

1.3.6 Synthesis of deuterium-labelled substrate analogues

Deuterium-labelled analogues of *exo*- and *endo*-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate (C_2-D *exo*-4, S32 and C_2-D *endo*-5, S33)

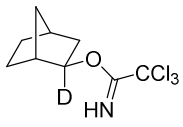


In a flame-dried flask under Ar, *i*-PrOH-d_8 (365 µL, 4.77 mmol, 1.05 equiv) was added over 80 min to a solution of DIBAL-H (4.54 mL of a 1.0 M solution in PhMe, 4.54 mmol, 1.00 equiv) at 0 °C. The solution was warmed to r.t. and added via cannula to a solution of *rac*-bicyclo[2.2.1]heptan-2-one (**S29**) (500 mg, 4.54 mmol, 1.00 equiv) in PhMe (10 mL) at r.t. The solution was subsequently heated to 60 °C for 5 d. Et_2O (10 mL) and 3.0 M HCl (5 mL) were added and the mixture was stirred for 15 min. The organic phase was separated and washed with 3.0 M NaOH (10 mL). The aqueous layer was extracted with Et_2O (3×15 mL) and the combined organic phases were washed with brine, dried (Na_2SO_4), filtered (filter paper) and concentrated under reduced pressure. Purification by automated CC (spherical silica gel, EtOAc/hexanes 5:95 to 60:40) afforded a mixture of the alcohols (*exo*/*endo* 3:1, 80% D incorporation, 170 mg, 33%, see copy of ^{1}H NMR spectra), which was converted without further purification[28]. In a flame-dried flask under Ar, CCl_3CN (359 µL, 3.58 mmol, 3.00 equiv) was added to a solution of **S30** and **S31** (135 mg, 1.19 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 mL) at 0 °C. DBU (44. 6 µL, 0.300 mmol, 0.250 equiv) was added dropwise, the mixture stirred for 10 min at 0 °C, then warmed to r.t. and stirred for 16 h. The resulting dark brown mixture was concentrated under reduced pressure and purified by bulb-to-bulb distillation (10^{-2} mbar, 50–60 °C) to afford a mixture of **S32** (C_2-D *exo*-**4**) and **S33** (C_2-D *endo*-**5**) (240 mg, 78%). Prep-HPLC separation afforded enantiomerically pure **S32** and *ent*-**S32** (80% D incorporation at C_2-$D_{(endo)}$ and C_3-$D_{(exo/endo)}$, for ratios see copy of ^{2}H NMR spectrum) and a racemic mixture of **S33** and *ent*-**S33** (80% D incorporation at C_2-$D_{(exo)}$ and C_3-$D_{(exo/endo)}$, for ratios see copy of ^{2}H NMR spectrum).

Note: As the products exist as isotopic mixtures, the absolute configuration of the deuterated analogues was not assigned.

HPLC (Chiralcel® 150 mm OJ-3R, 3 μm, 4.6 mm i.d., MeCN/H_2O 65:35, 1.0 mL/min, 298 K, 210 nm): t_{R1} = 4.97 min, t_{R2} = 5.24 min, t_{R3} = 5.63 min;

Prep-HPLC (250 mm Chiralcel® OJ-H, 5 μm, 20 mm i.d., MeCN/H_2O 60:40, 18 mL/min, 16.7 MPa, 298 K, 210 nm): t_{R1} = 11.68 min, t_{R2} = 12.38 min, t_{R3} = 13.48 min.



S32 or ***ent*-S32**

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 2.53–2.43 (m, 1H), 2.38–2.26 (m, 1H), 1.82–1.75 (m, 1H), 1.63 (dp, *J* = 9.9, 2.0 Hz, 1H), 1.61–1.54 (m, 2H), 1.52–1.44 (m, 1H), 1.23–1.19 (m, 1H), 1.18–1.10 (m, 2H);

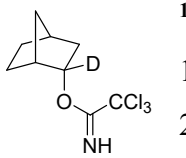
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 92.0, 82.4, 82.2–81.8 (t, $^1J_{CD}$ = 24.0 Hz), 40.9, 40.8, 39.2, 39.0, 35.4–35.3 (m), 35.3, 28.2, 24.0, 23.9 (other signals not detected or observed);

^{2}H NMR (92 MHz, $CDCl_3$) δ 4.74, 1.78, 1.56 (for integration see copy of ^{2}H NMR spectrum);

LRMS-CI (%D, **S32**): D_1 = 77.3±5.4%, D_0 = 24.1z±5.4%, (%D, *ent*-**S32**): D_1 = 78.2±5.2%, D_0 = 23.0±5.2%;

HRMS-CI (m/z): calculated for $C_9H_{12}N_1O_1Cl_3D_1$ ($[M+H]^+$): 257.0120, found: 257.0120;

HPLC: t_{R2} = 5.24 min, t_{R3} = 5.63 min.



S33 + ***ent*-S33**

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 2.67–2.62 (m, 1H), 2.28–2.24 (m, 1H), 2.10–2.00 (m, 1H), 1.96–1.89 (m, 1H), 1.66–1.56 (m, 1H), 1.45–1.39 (m, 2H), 1.38–1.33 (m, 2H), 1.19–1.08 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 91.9, 80.4, 80.2–79.8 (t, $^1J_{CD}$ = 23.9 Hz), 40.1 (m), 40.0 (m), 37.4–37.2 (m), 36.8, 36.6, 36.5–36.4 (m), 36.3–36.3 (m), 29.1, 29.1, 21.0, 21.0. (other signals not detected or observed);

^{2}H NMR (92 MHz, $CDCl_3$) δ 5.09, 2.06, 1.14 (for integration see copy of ^{2}H NMR spectrum);

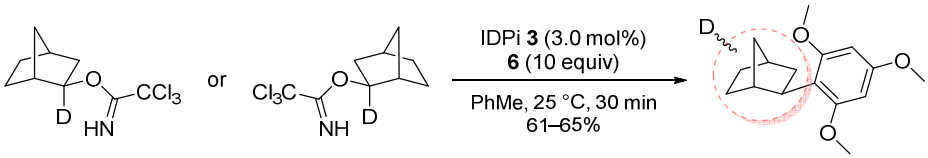
LRMS-CI (%D, **S33** and *ent*-**S33**): D_1 = 72.9±4.4%, D_0 = 15±4.4%, D_2 = 11±4.4%, D_3 = 2.7 ±4.4%;

HRMS-CI (m/z): calculated for $C_9H_{12}N_1O_1Cl_3D_1$ ($[M+H]^+$): 257.0120, found: 257.0120;

HPLC: t_{R1} = 4.97 min.

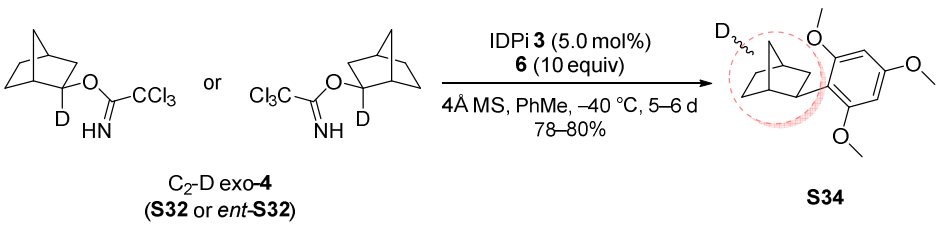
Synthesis of deuterium-labelled analogues of 7 for deuterium distribution analyses

*Synthesis of **S34** from C_2-D exo-**4** (**S32** or ent-**S32**) (25 °C)*



[(**SP V**)] In a flame-dried flask under Ar, IDPi **3** (3.17 mg, 1.50 µmol, 0.030 equiv) and **6** (84.1 mg, 0.500 mmol, 10.0 equiv) were dissolved in PhMe (250 µL) and enantiomerically pure **S32** or *ent*-**S32** (12.9 mg, 0.050 mmol, 1.00 equiv) in PhMe (250 µL) was added at 25 °C. The mixture was stirred for 30 min, subsequently treated with Et_3N (7.00 µL, 0.050 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/pentane 10:90 to 30:70) afforded a mixture of deuterium-labelled product analogues (**S34**) (8.50 mg, 65% or 8.00 mg, 61%) as a colorless solid. Further analysis is shown in section 2.1.3.

*Synthesis of **S34** from C_2-D exo-**4** (**S32** or ent-**S32**) (−40 °C)*



[(**SP I**)] In a flame-dried flask under Ar, IDPi **3** (5.29 mg, 2.50 µmol, 0.050 equiv), **6** (84.1 mg, 0.500 mmol, 10.0 equiv) and 4Å MS (10.0 mg, 200 mg/mmol) in PhMe (250 µL) were cooled to −40 °C. Enantiomerically pure **S32** or *ent*-**S32** (12.9 mg, 0.050 mmol, 1.00 equiv) in PhMe (250 µL) was slowly added to the suspension and the mixture stirred at −40 °C for 5 or 6 d. Et_3N (7.00 µL, 0.050 mmol, 1.00 equiv) was added, the mixture was warmed to r.t. and concentrated under reduced pressure. Purification by CC (silica gel, PhMe/pentane 10:90 to 30:70) afforded a mixture of deuterium-labelled product analogues (**S34**) (10.5 mg, 80% or 10.2 mg, 78%) as a colorless solid. Further analysis is shown in section 2.1.3.

*Synthesis of **S34** from C_2-D endo-**5** (**S33** and ent-**S33**) (25 °C)*

C_2-D *endo*-**5** (**S33** + *ent*-**S33**)

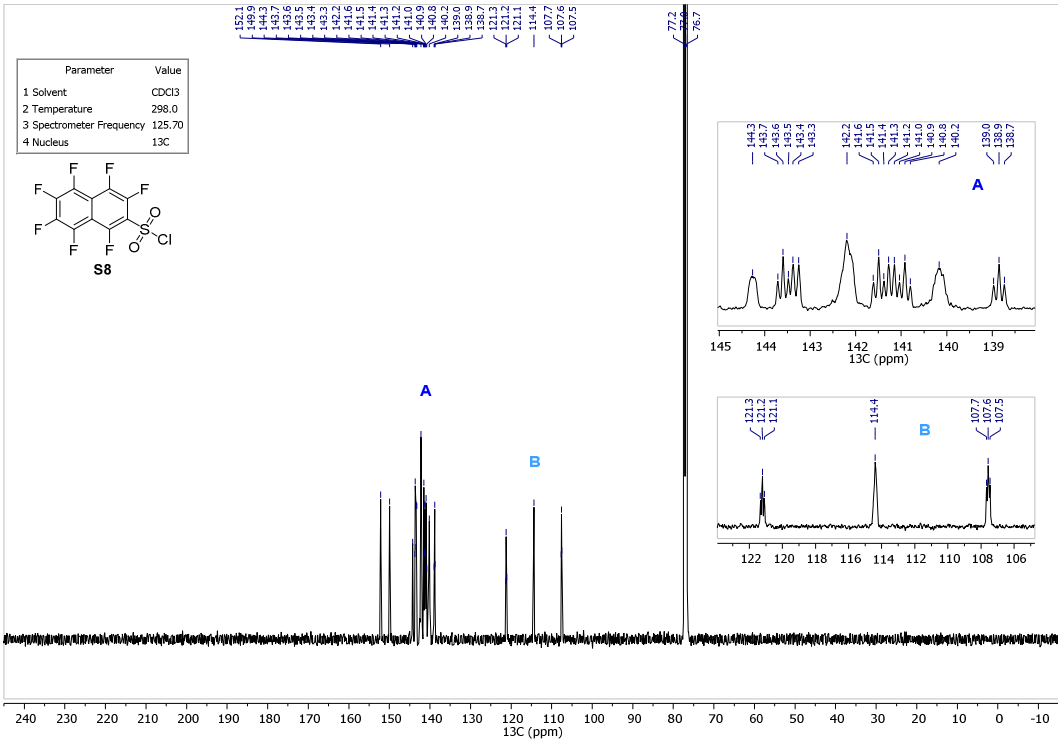
S34

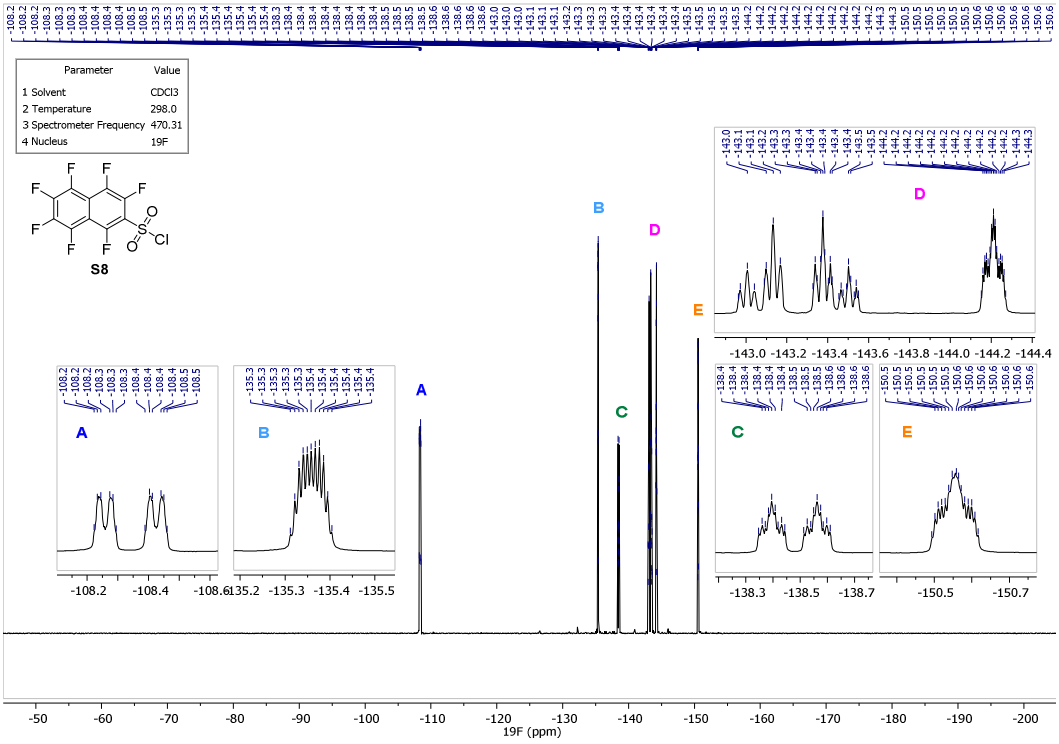
[(**SP II**)] In a flame-dried flask under Ar, IDPi **3** (5.29 mg, 2.50 µmol, 0.050 equiv) and **6** (84.1 mg, 0.500 mmol, 10.0 equiv) were dissolved in EtOAc (250 µL) and a racemic mixture of **S33** and *ent*-**S33** (12.9 mg, 0.050 mmol, 1.00 equiv) in EtOAc (250 µL) was added at 25 °C. The mixture was stirred for 15 h, subsequently treated with Et_3N (7.00 µL, 0.050 mmol, 1.00 equiv) and then concentrated under reduced pressure. Purification by CC (silica gel, PhMe/pentane 10:90 to 30:70) afforded a mixture of deuterium-labelled product analogues (**S34**) (9.10 mg, 69%) as a colorless solid. Further analysis is shown in section 2.1.3.

1.4 Supplementary Data

1.4.1 Copies of NMR spectra

Imidodiphosphorimidate acids and intermediates thereof

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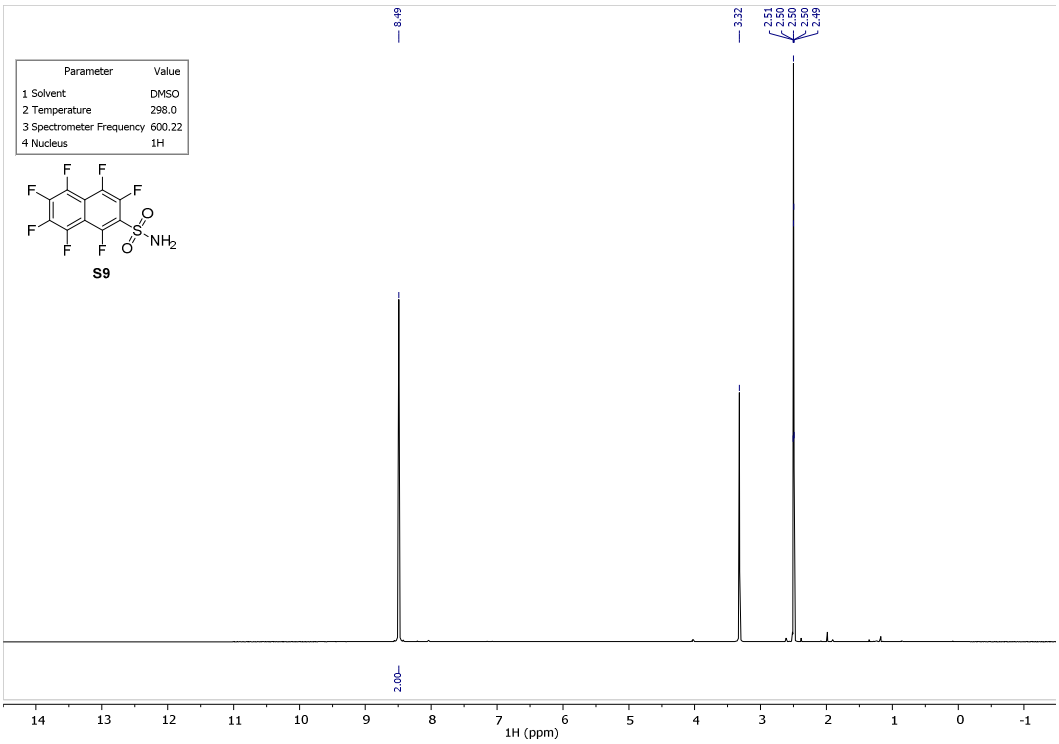
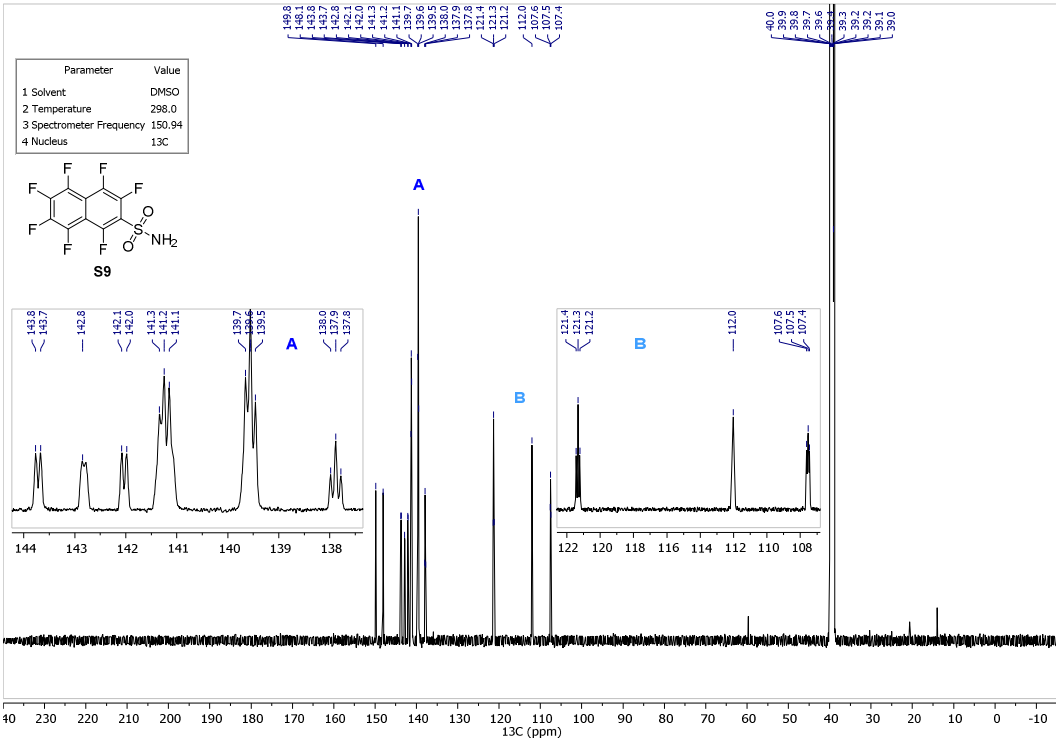
4 Nucleus 19F
S8
A
B
C
D
E
19F (ppm)


Parameter Value
1 Solvent DMSO
2 Temperature 298.0
3 Spectrometer Frequency 600.22
4 Nucleus 1H
S9
8.49
3.32
2.51
2.50
2.50
2.50
2.49
2.00
1H (ppm)


Parameter Value
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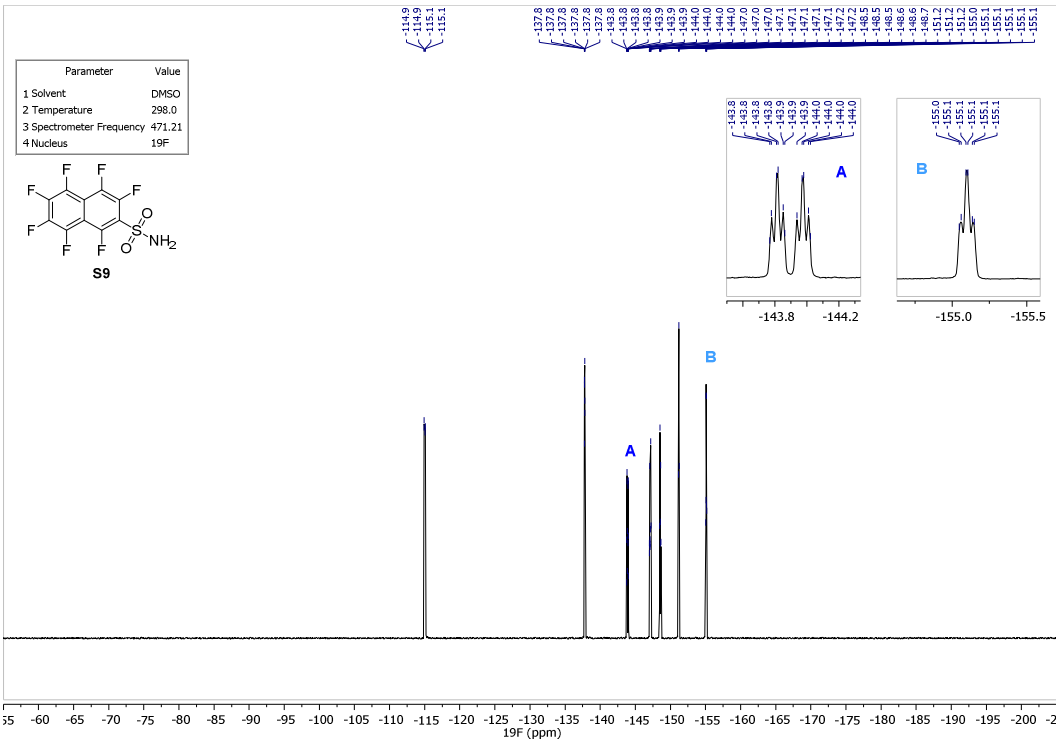
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
S9
A
B
13C (ppm)


Parameter Value
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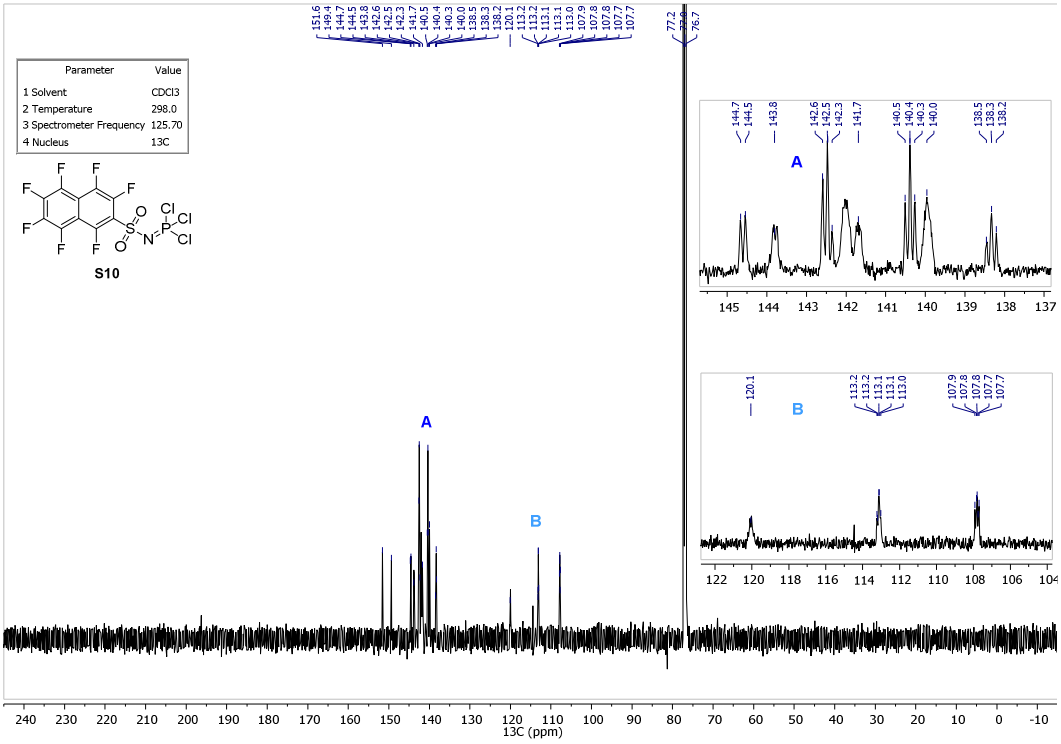
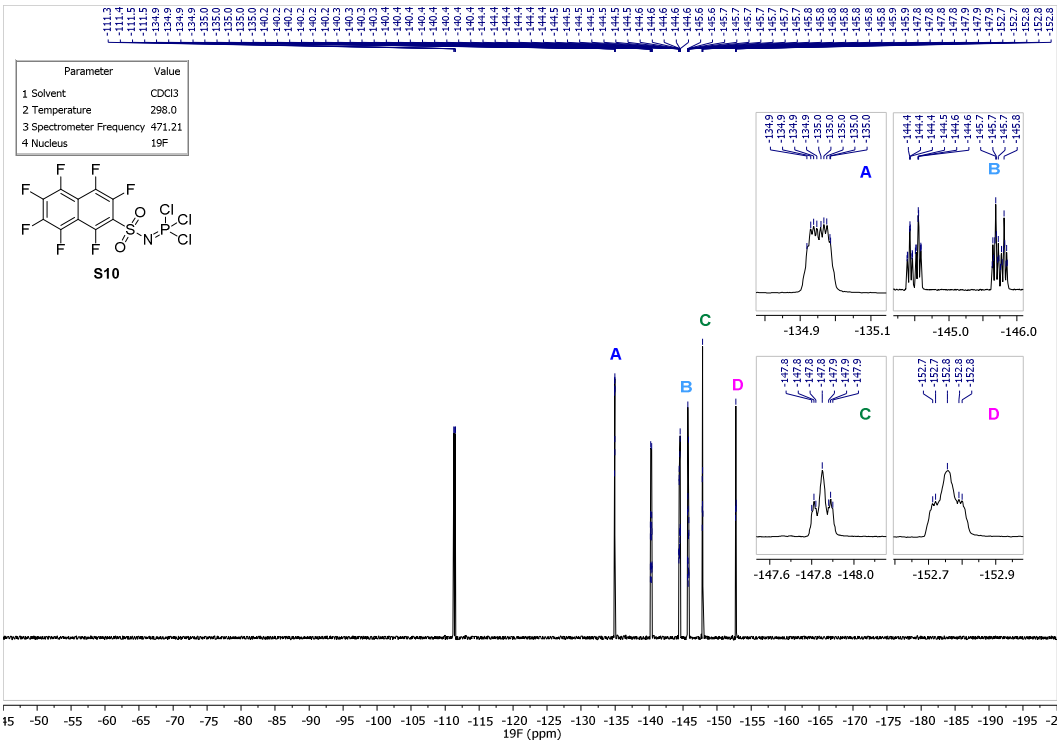
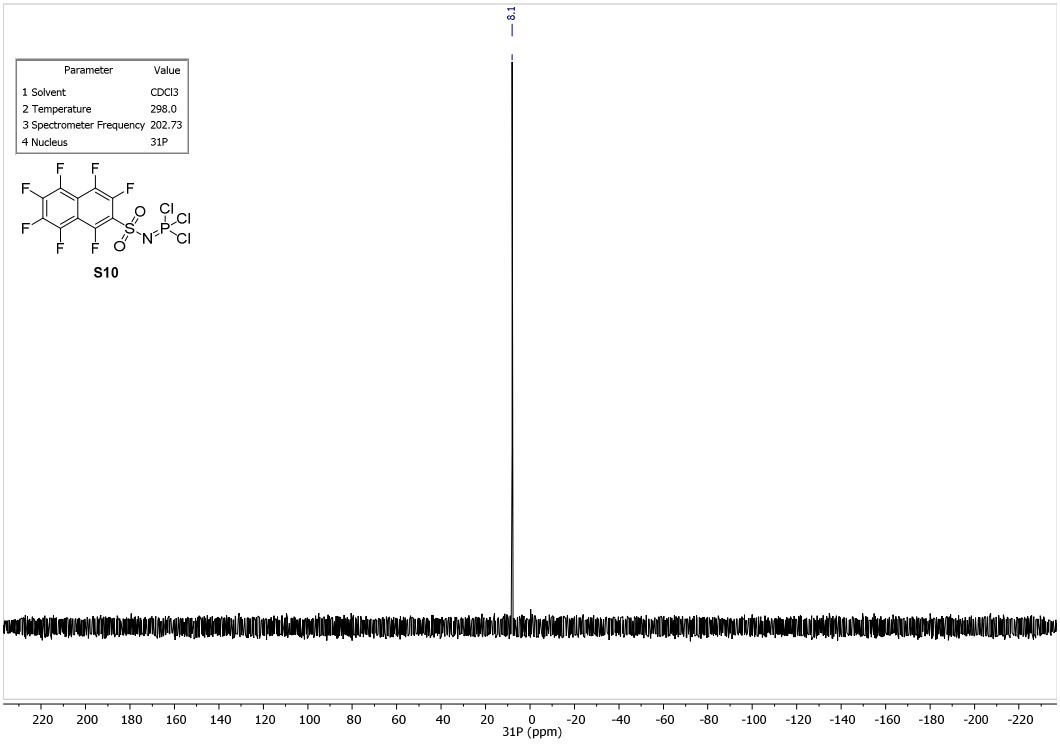
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
S9
A
B
19F (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.70
4 Nucleus 13C
S10
A
B
13C (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
S10
A
B
C
D
19F (ppm)


8.1
Parameter Value
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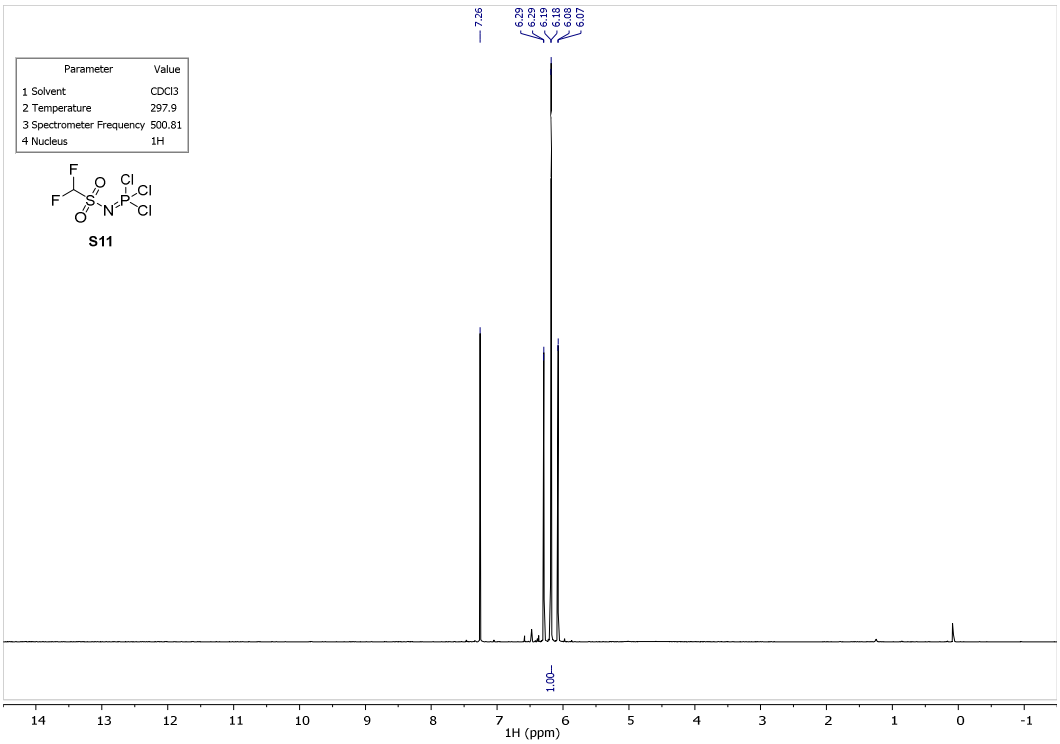
S10
220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220
31P (ppm)


7.26
6.29
6.28
6.19
6.18
6.08
6.07
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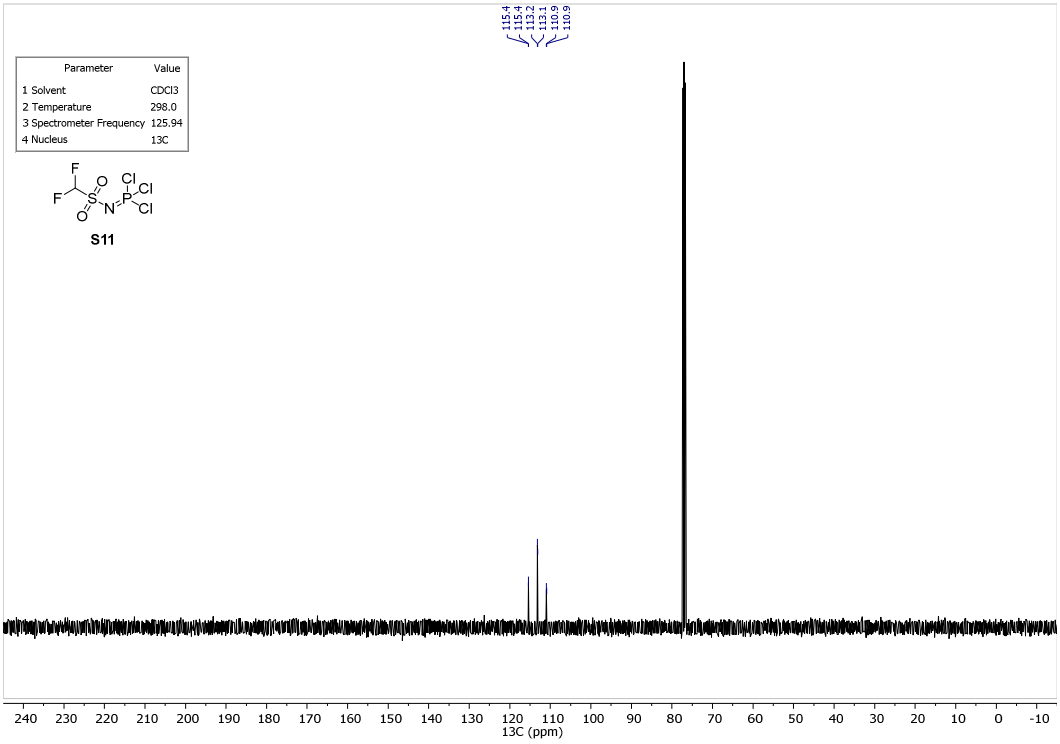
3 Spectrometer Frequency 500.81
4 Nucleus 1H
S11
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
1H (ppm)


115.4
115.4
113.2
113.1
110.9
110.9
Parameter Value
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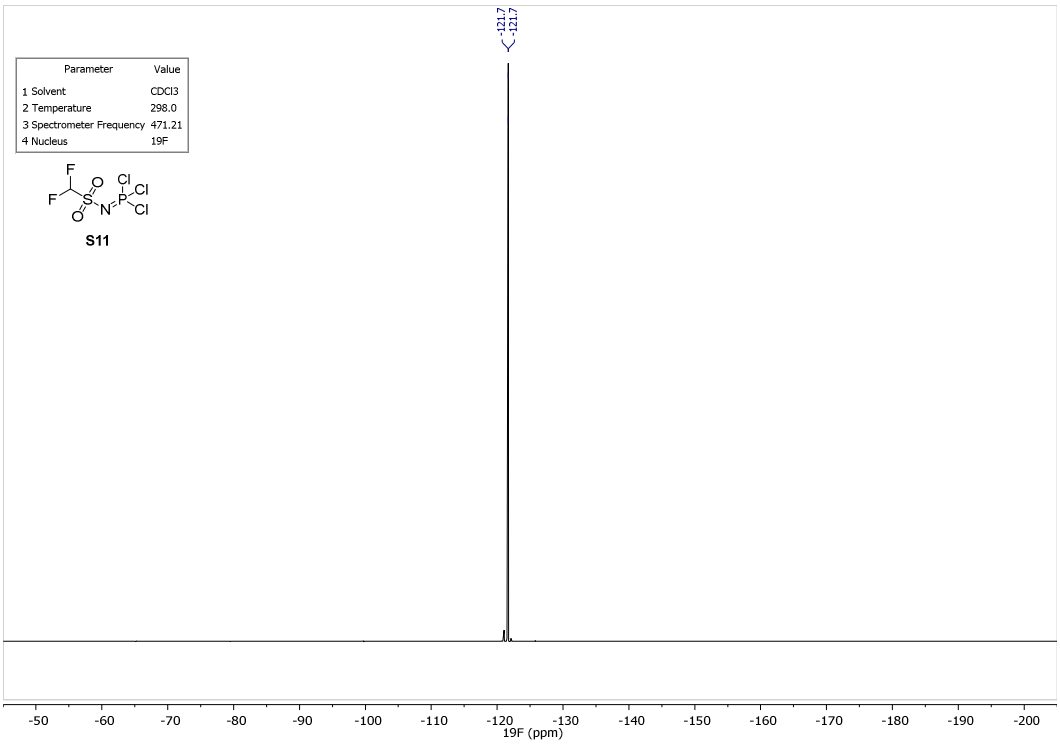
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
S11
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


-121.7
-121.7
Parameter Value
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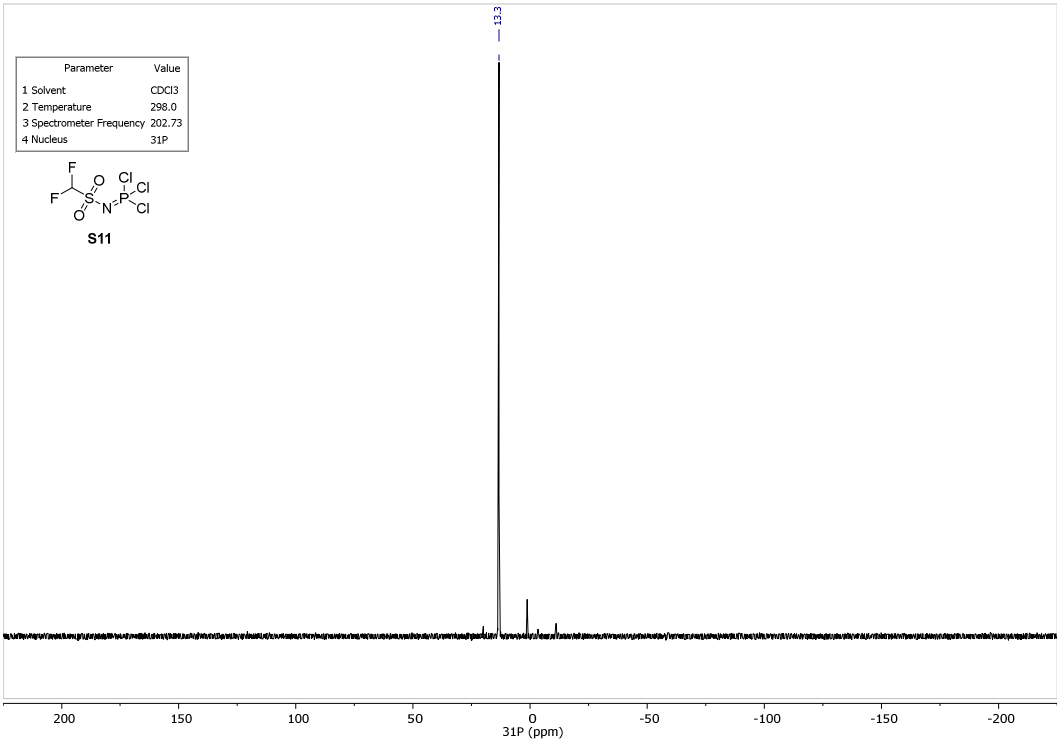
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
S11
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
19F (ppm)


13.3
Parameter Value
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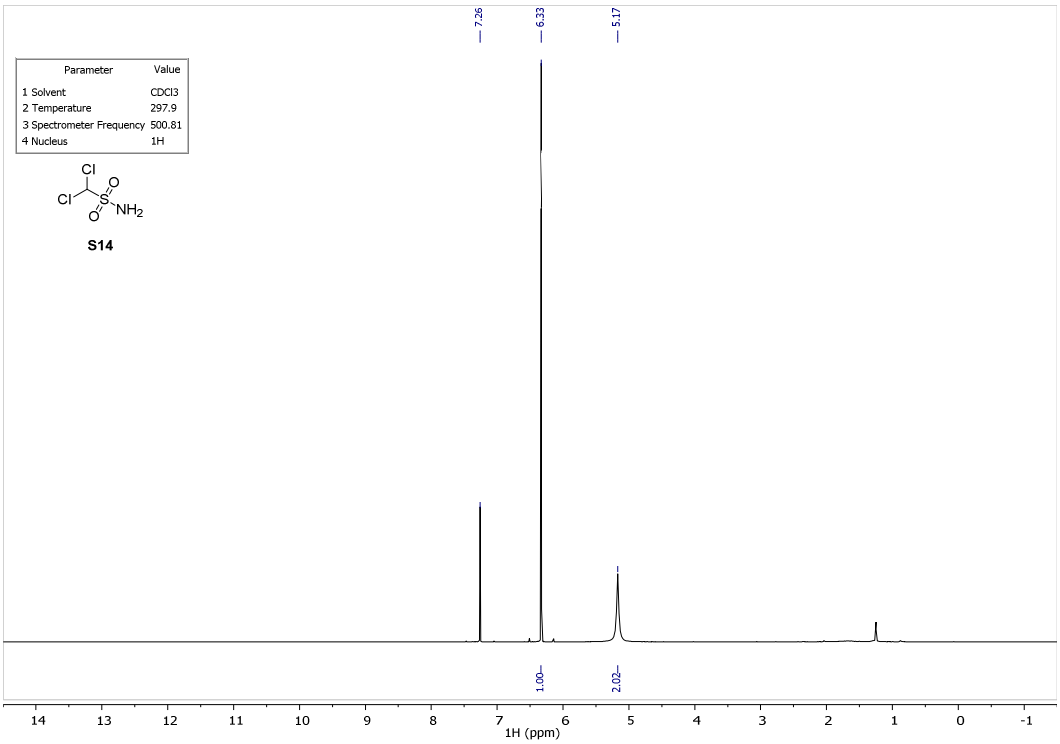
2 Temperature 298.0
3 Spectrometer Frequency 202.73
4 Nucleus 31P
F
F
O
S
O
N
P
Cl
Cl
Cl
200
150
100
50
0
-50
-100
-150
-200
31P (ppm)

S11


7.26
6.33
5.17
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3 Spectrometer Frequency 500.81
4 Nucleus 1H
Cl
Cl
O
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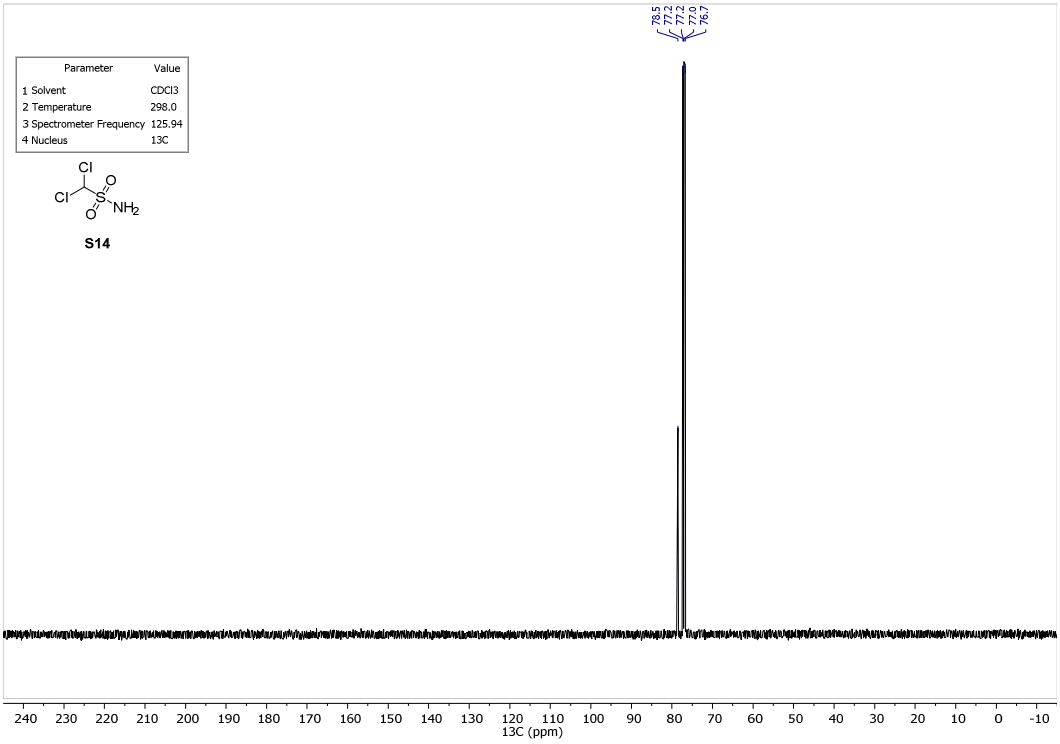
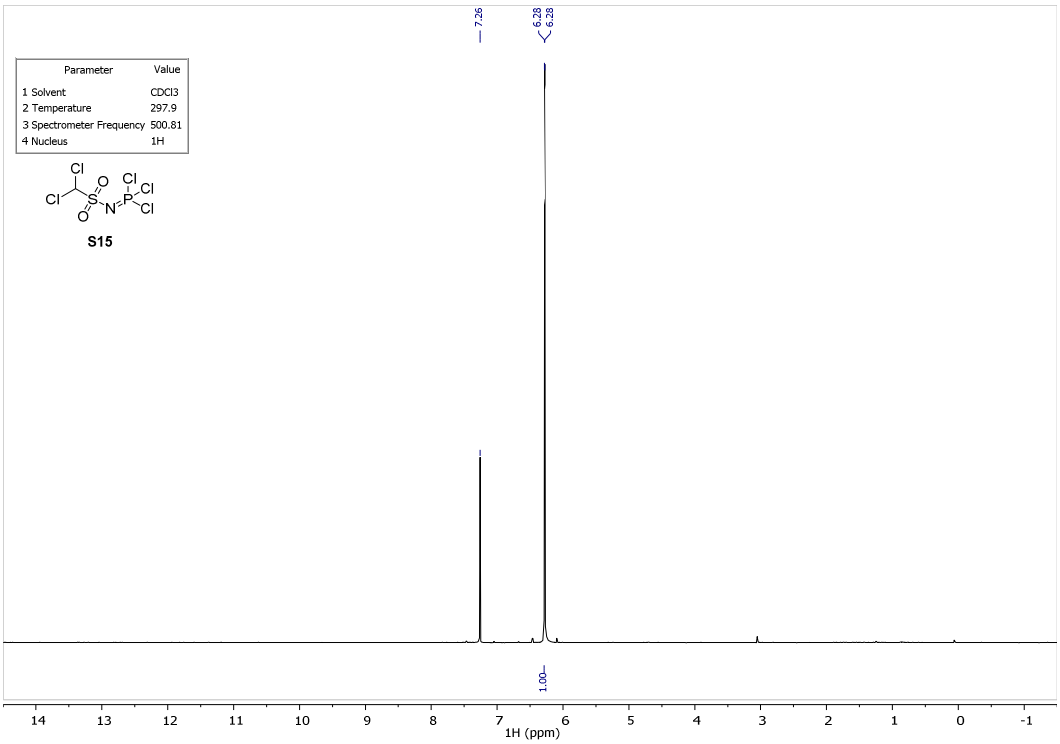
O
NH2
1.00
2.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
1H (ppm)

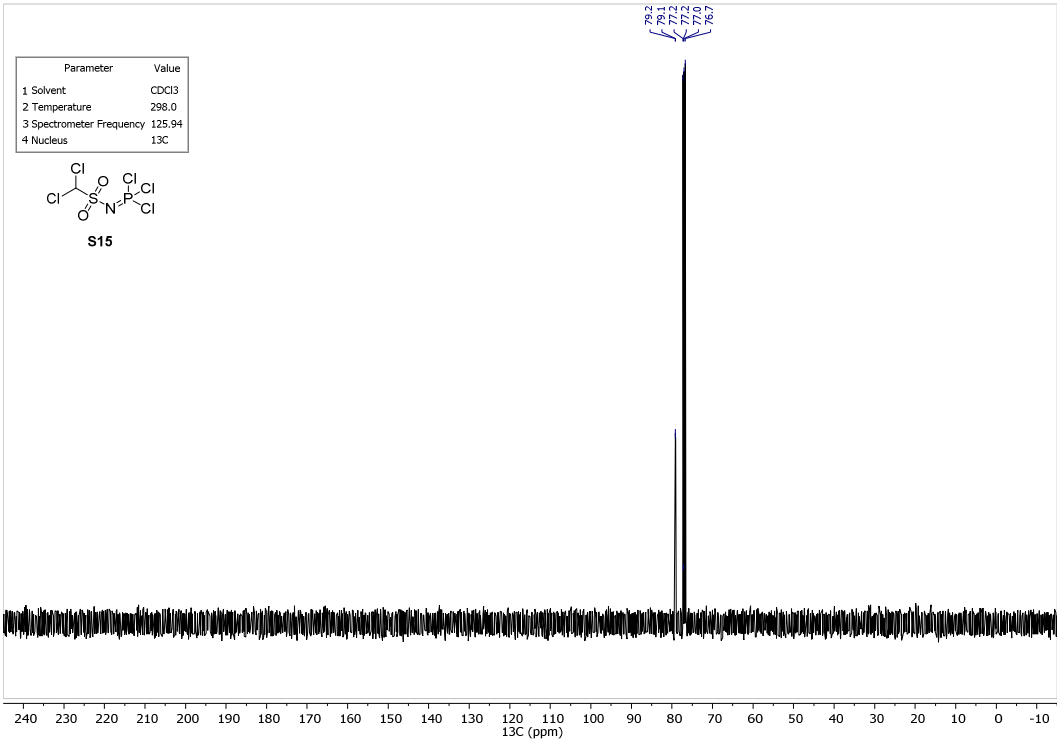
S14

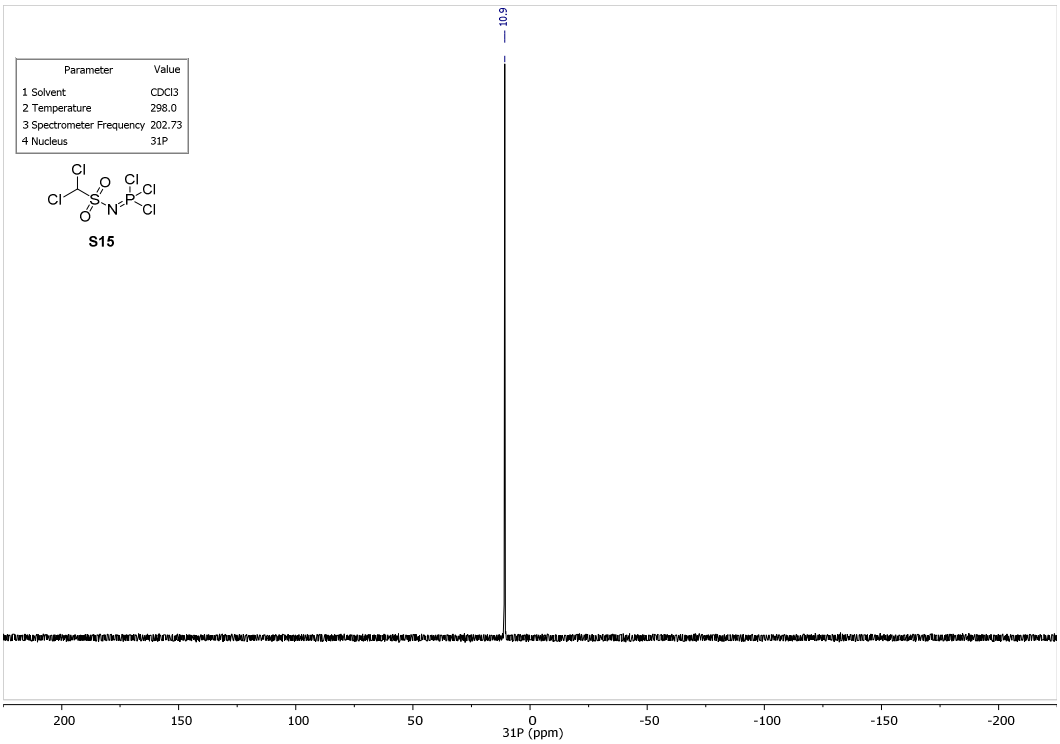

78.5
77.2
77.2
77.0
76.7
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
Cl
Cl
O
S
O
NH2
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

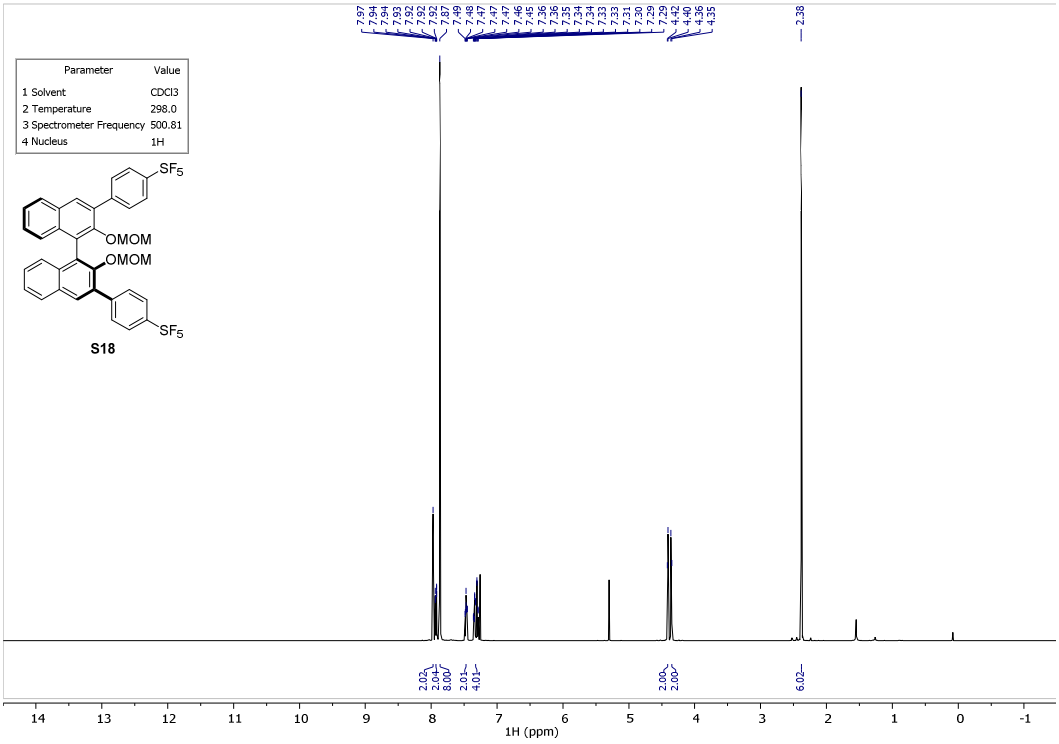
S14

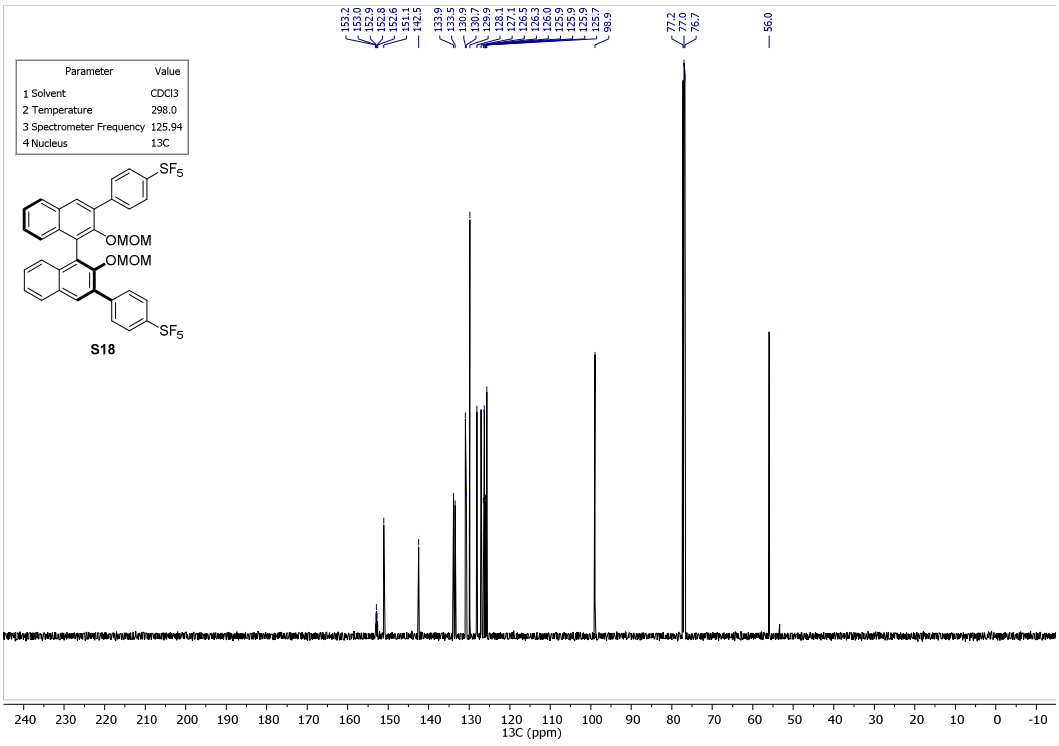

7.26
6.28
6.28
Parameter Value
1 Solvent CDCl3
2 Temperature 297.9
3 Spectrometer Frequency 500.81
4 Nucleus 1H
Cl
Cl
O
S
O
N
Cl
P
Cl
Cl
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
1H (ppm)

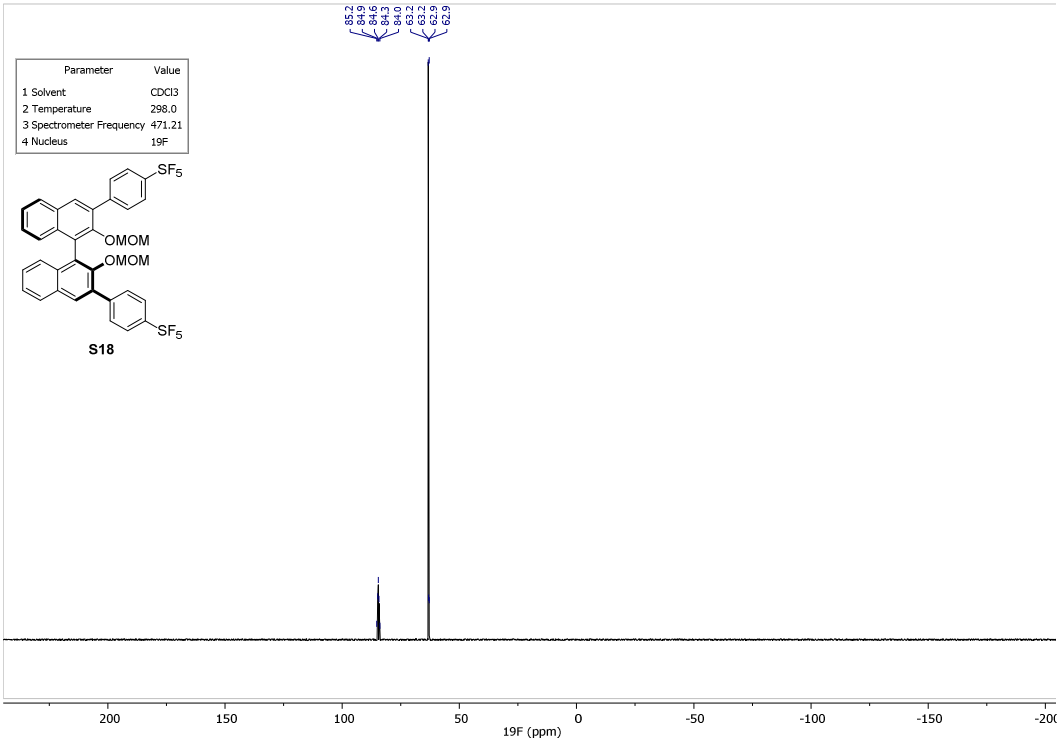
S15

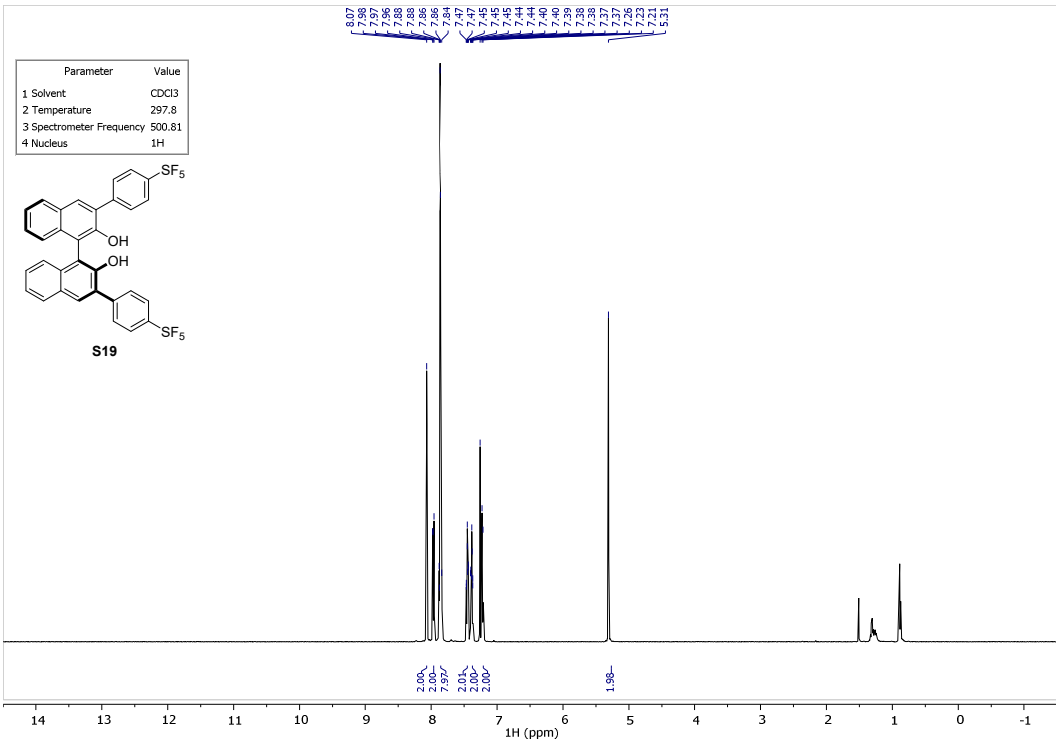

79.2
79.1
77.2
77.1
77.0
76.7
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
S15
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

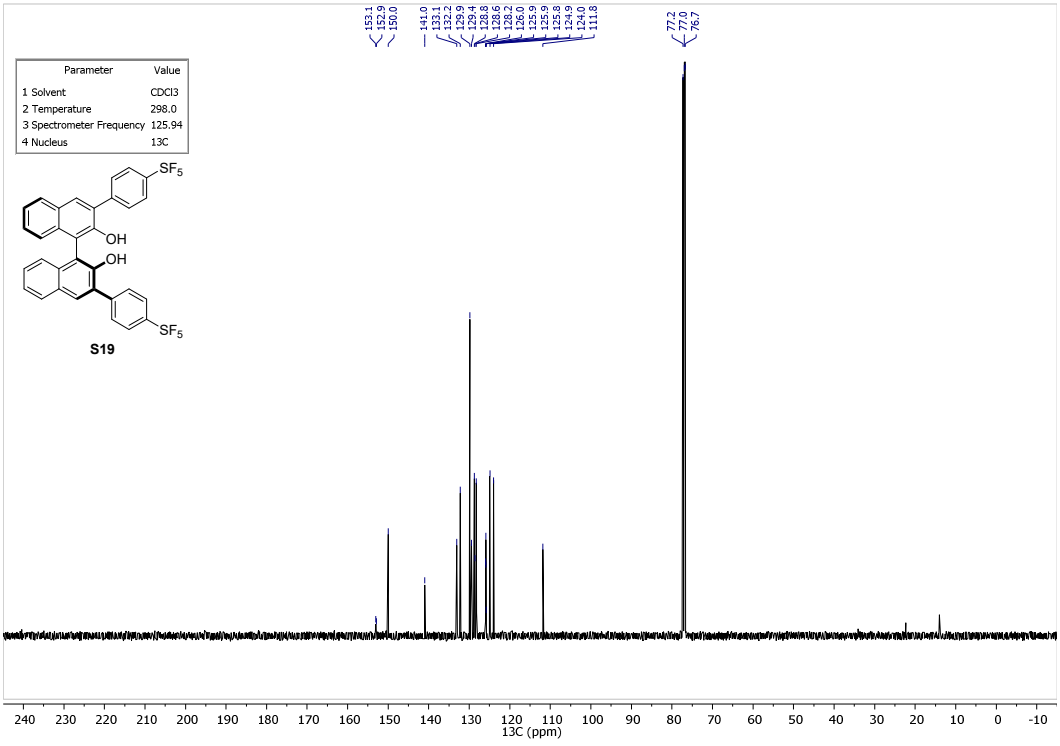

10.9
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 202.73
4 Nucleus 31P
S15
200 150 100 50 0 -50 -100 -150 -200
31P (ppm)

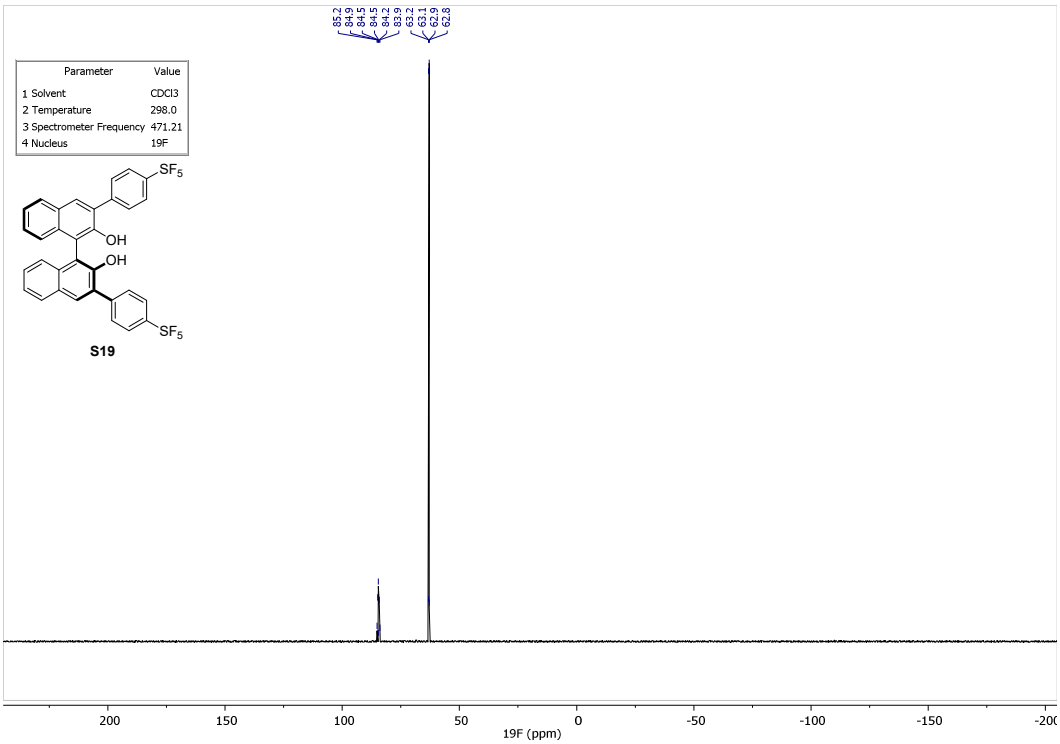

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
SF5
OMOM
OMOM
SF5
S18
1H (ppm)

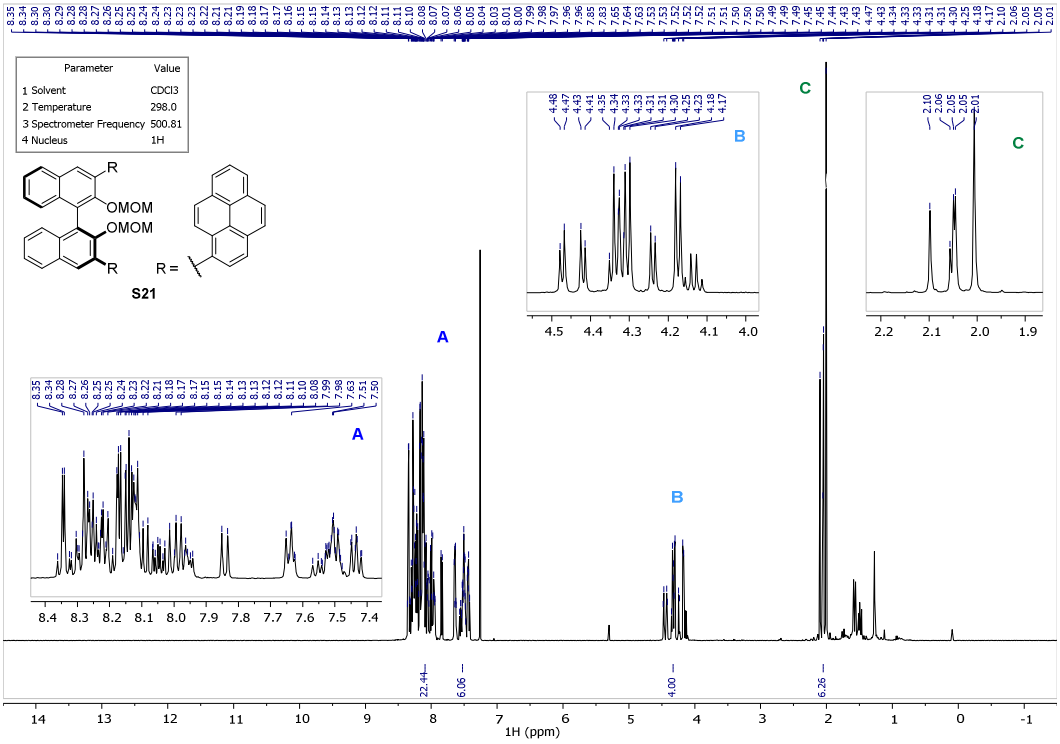

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
SF5
OMOM
OMOM
SF5
S18
13C (ppm)

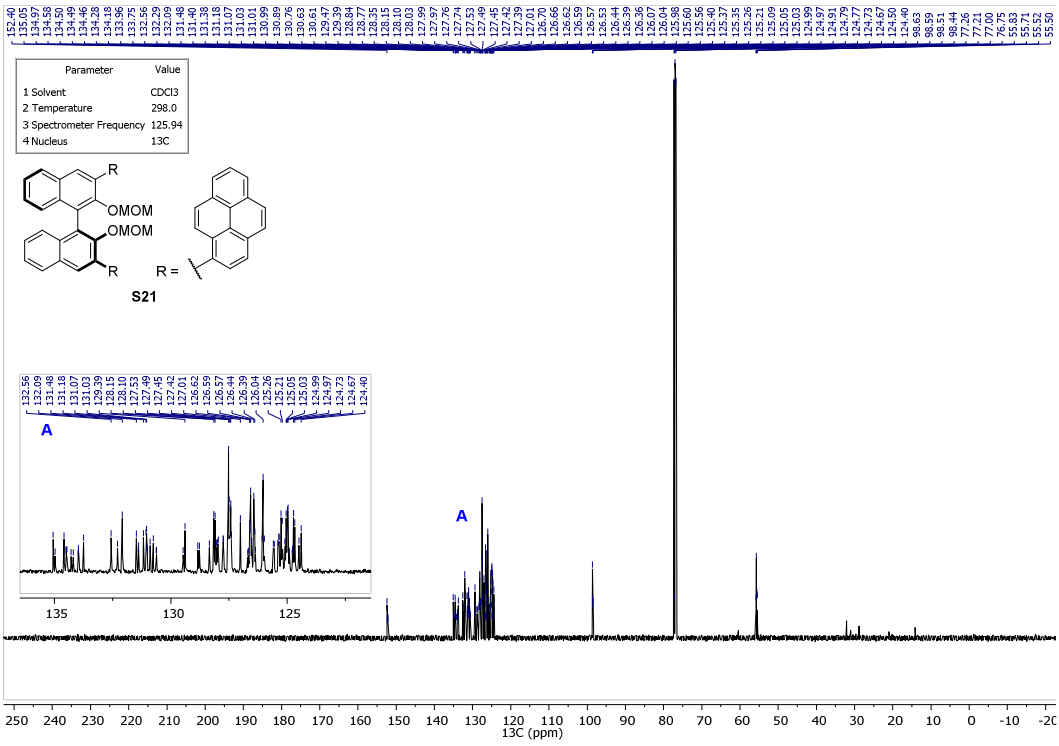

85.2
84.9
84.6
84.3
84.0
63.2
63.2
63.0
62.9
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
SF5
OMOM
OMOM
SF5
S18
200
150
100
50
0
-50
-100
-150
19F (ppm)

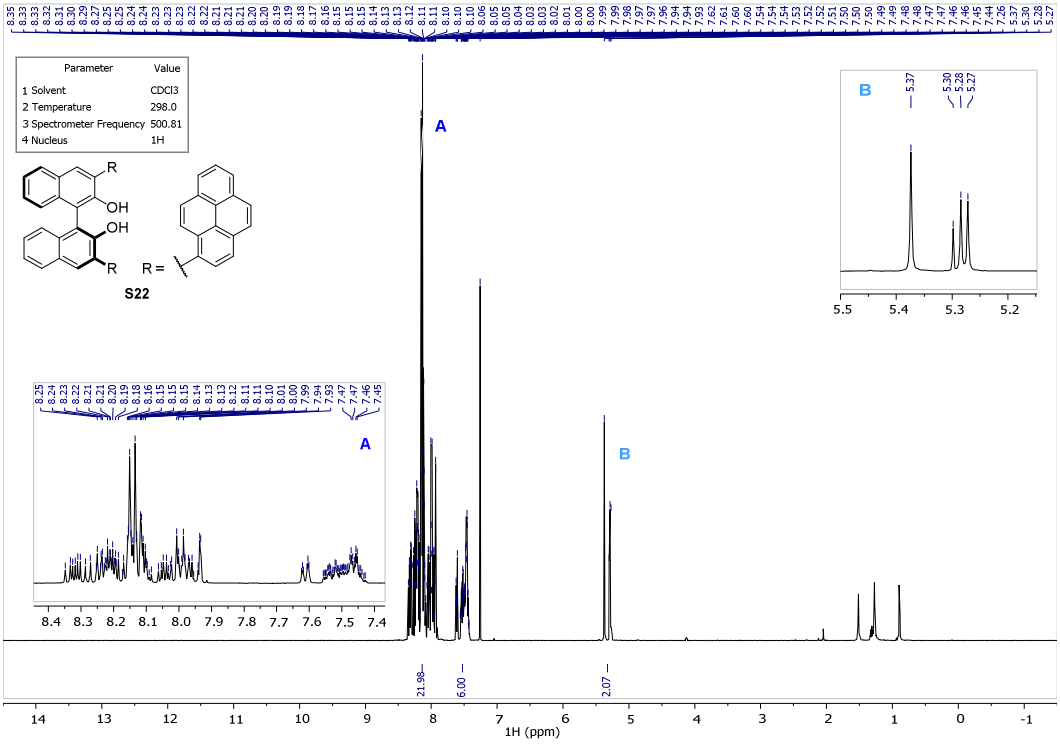

8.07
7.98
7.97
7.96
7.88
7.88
7.86
7.86
7.84
7.47
7.47
7.45
7.45
7.45
7.44
7.44
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.26
7.23
7.21
5.31
Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Spectrometer Frequency 500.81
4 Nucleus 1H
SF5
OH
OH
SF5
S19
2.00
2.00
7.97
2.01
2.00
2.00
1.98
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
1H (ppm)

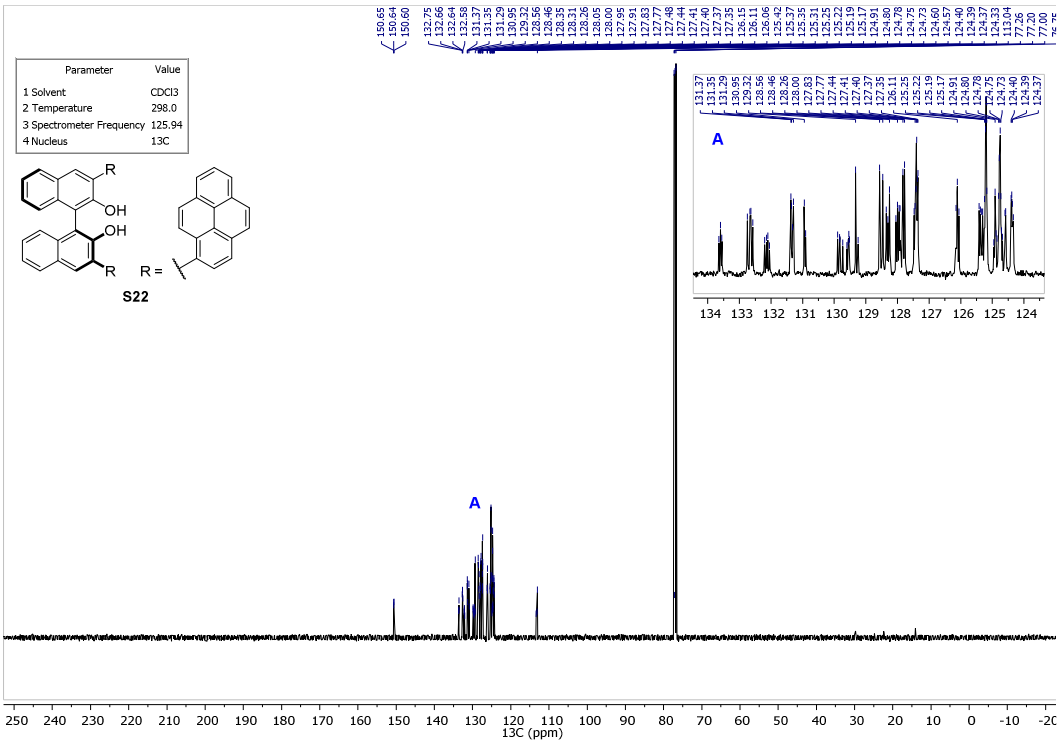

153.1
152.9
150.0
141.0
133.1
132.2
129.9
129.4
128.8
128.6
128.2
126.0
125.9
125.9
125.8
124.9
124.0
111.8
77.2
77.0
76.7
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
SF5
OH
OH
SF5
S19
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

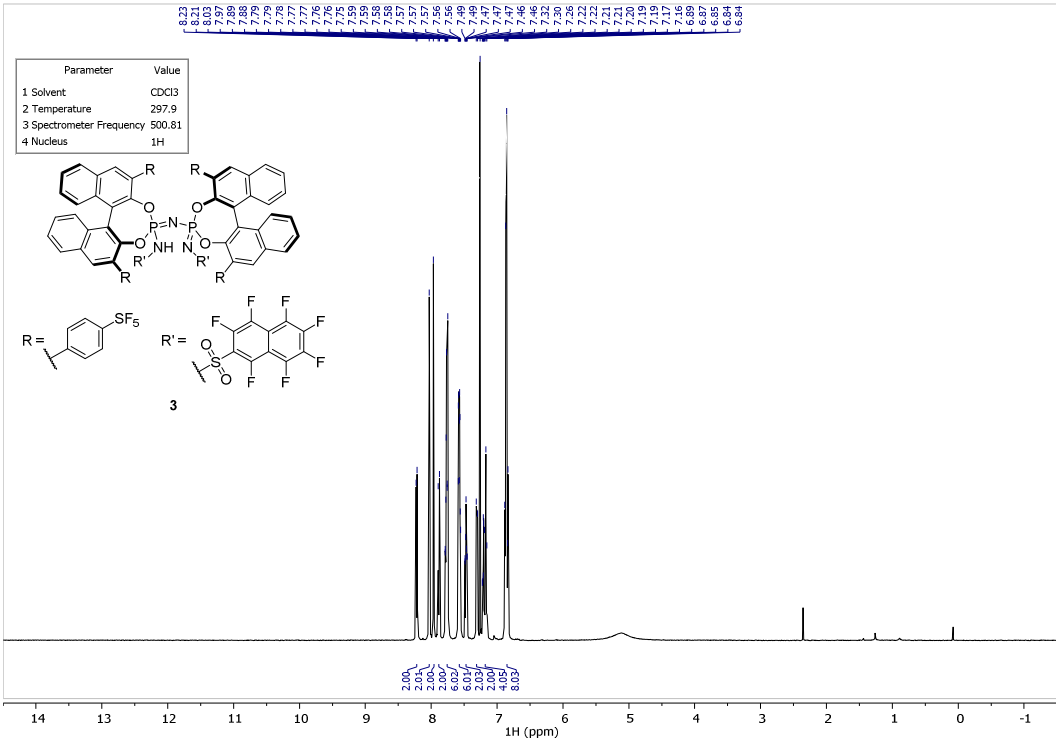

85.2
84.9
84.5
84.5
84.2
83.9
63.2
63.1
62.9
62.8
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
SF5
OH
OH
SF5
S19
200 150 100 50 0 -50 -100 -150 -200
19F (ppm)

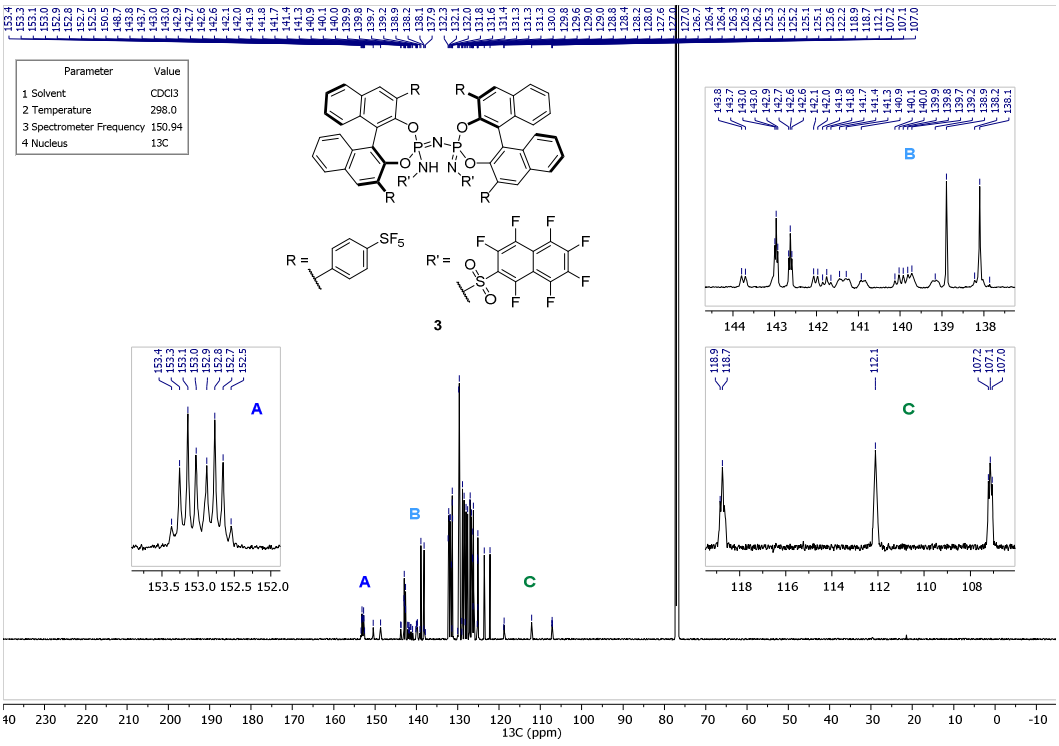

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
R
OMOM
OMOM
R
R =
S21
A
B
C
22.44
6.06
4.00
6.26
1H (ppm)

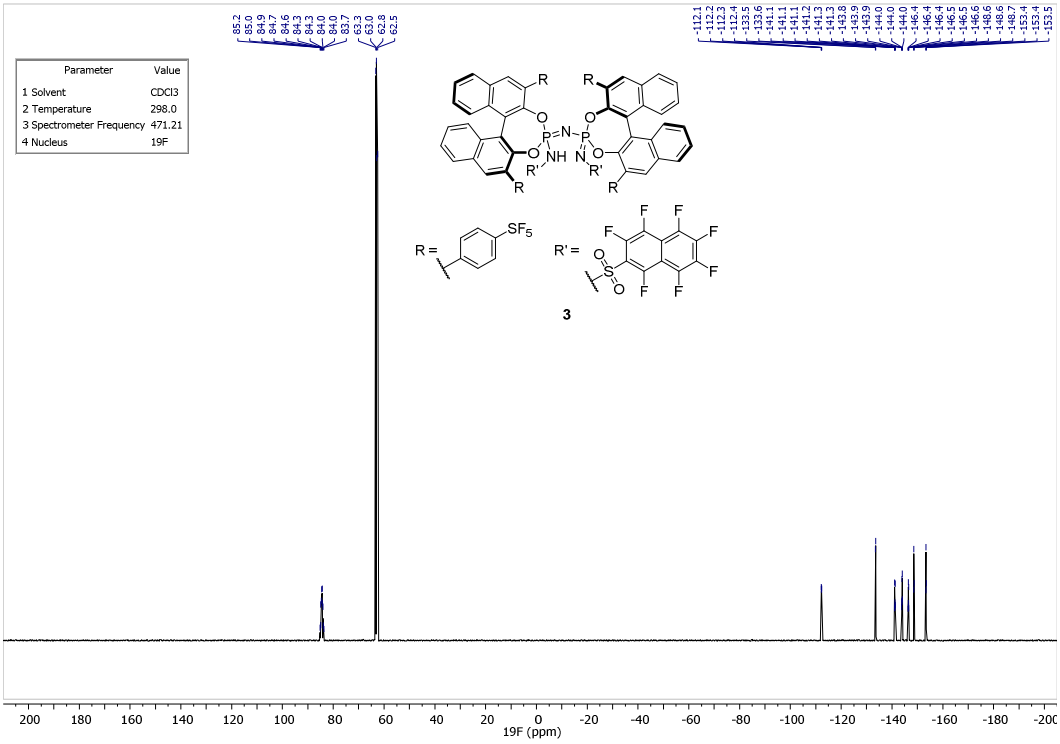

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
R
OMOM
OMOM
R
R =
S21
A
13C (ppm)

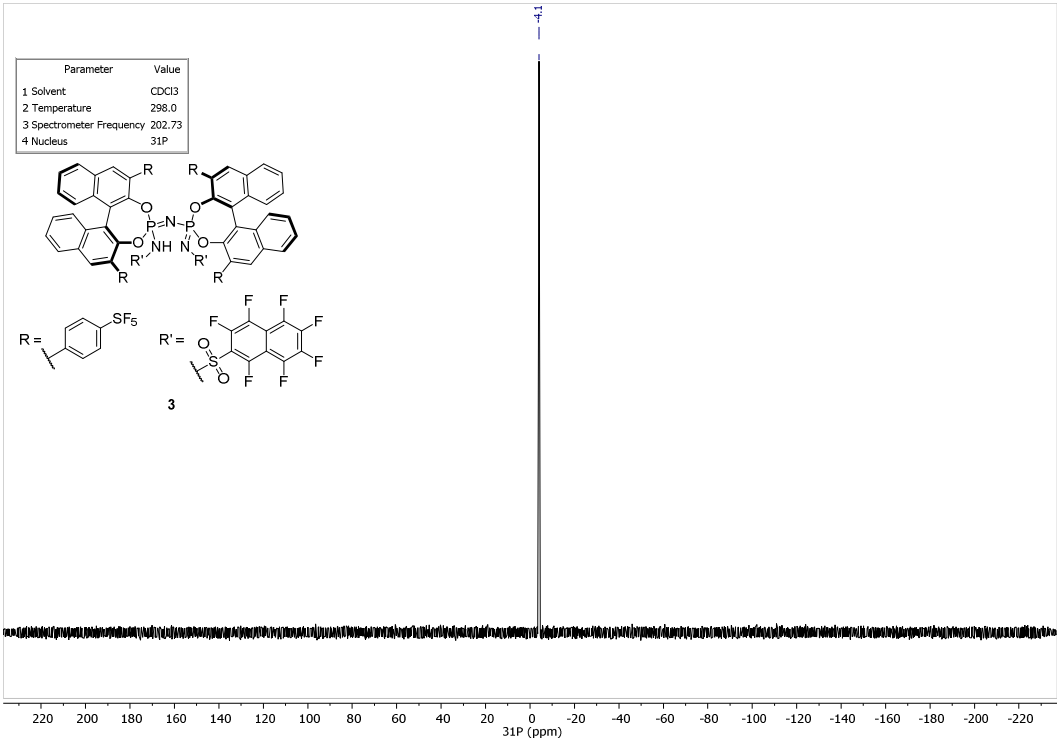

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
R
OH
OH
R
R =
S22
A
B
21.98
6.00
2.07
1H (ppm)

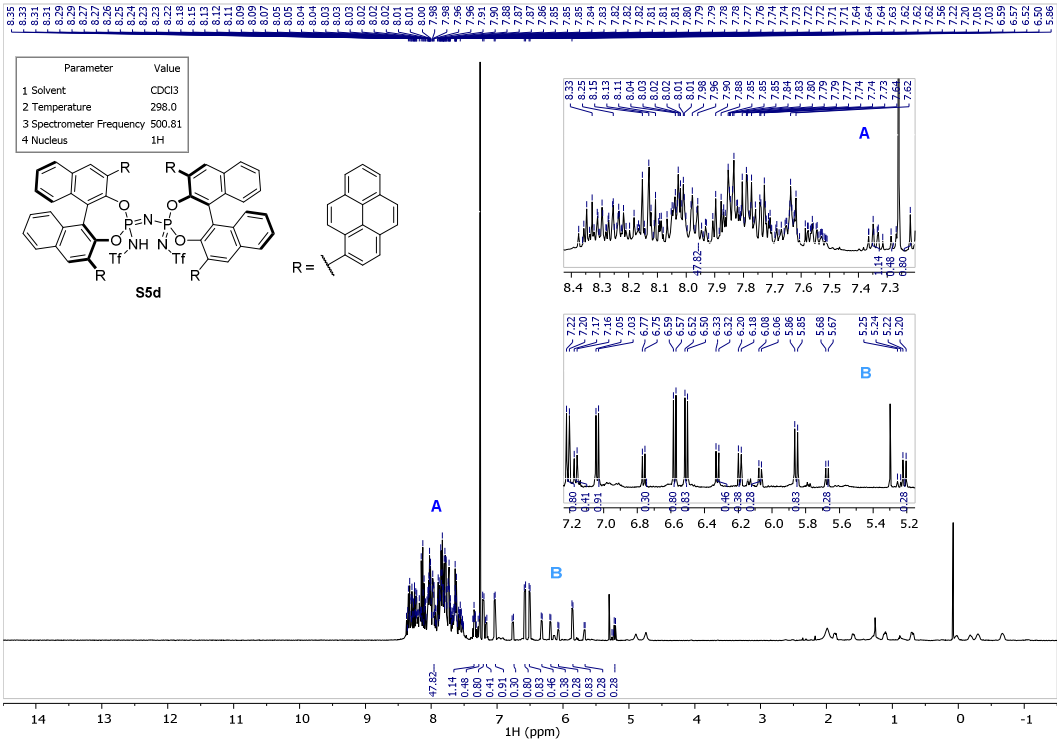

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
R
OH
OH
R
R =
S22
A
13C (ppm)

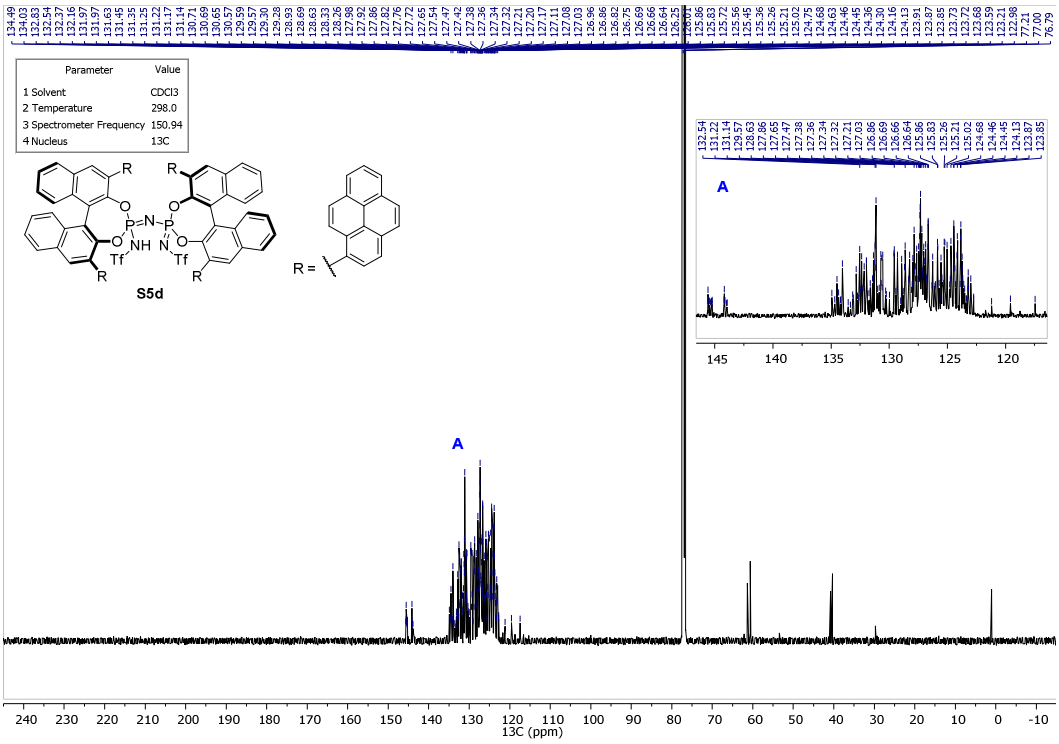

Parameter Value
1 Solvent CDCl3
2 Temperature 297.9
3 Spectrometer Frequency 500.81
4 Nucleus 1H
R =
R' =
3
1H (ppm)

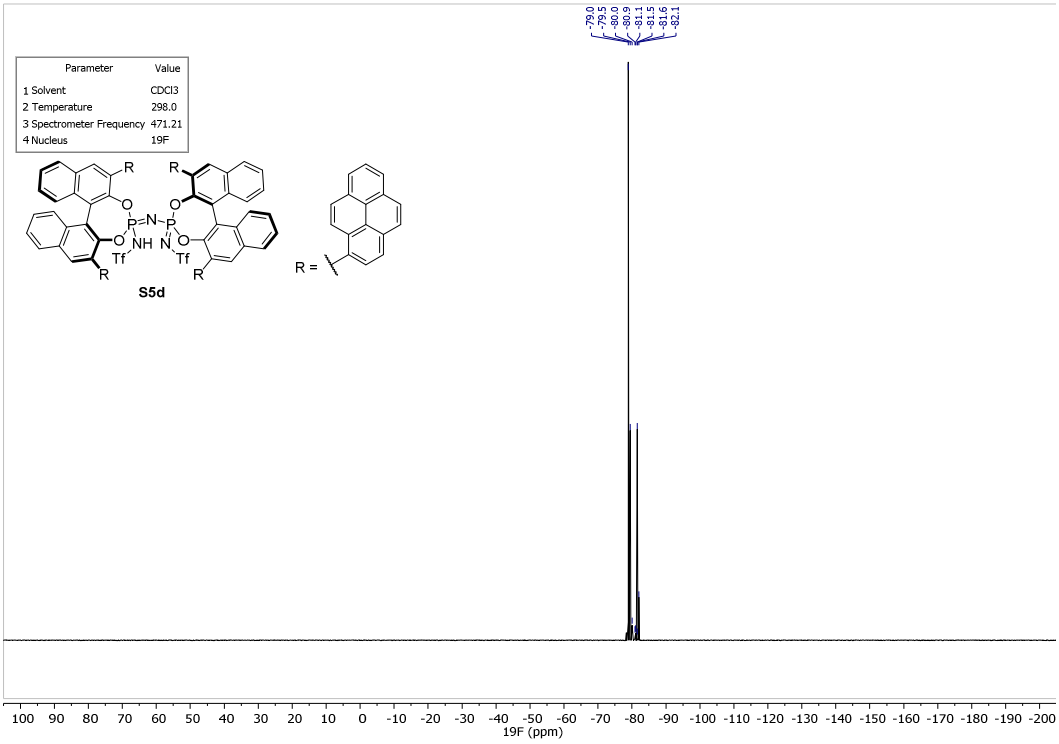

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
R =
R' =
3
A
B
C
13C (ppm)

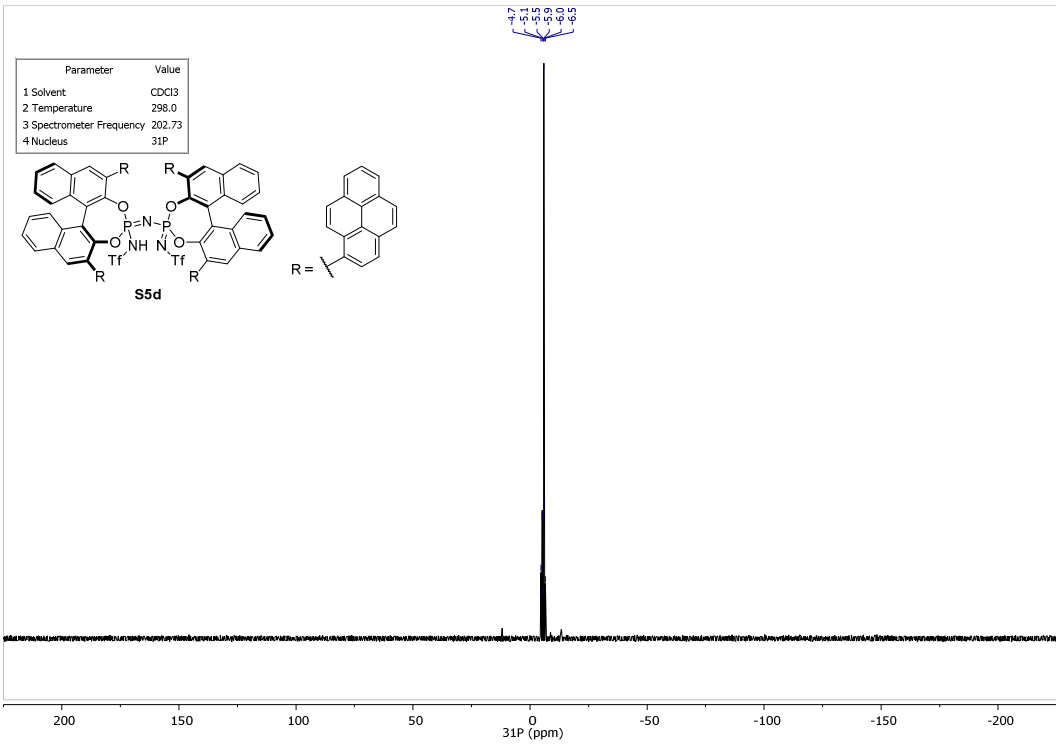

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
R =
R' =
3
19F (ppm)

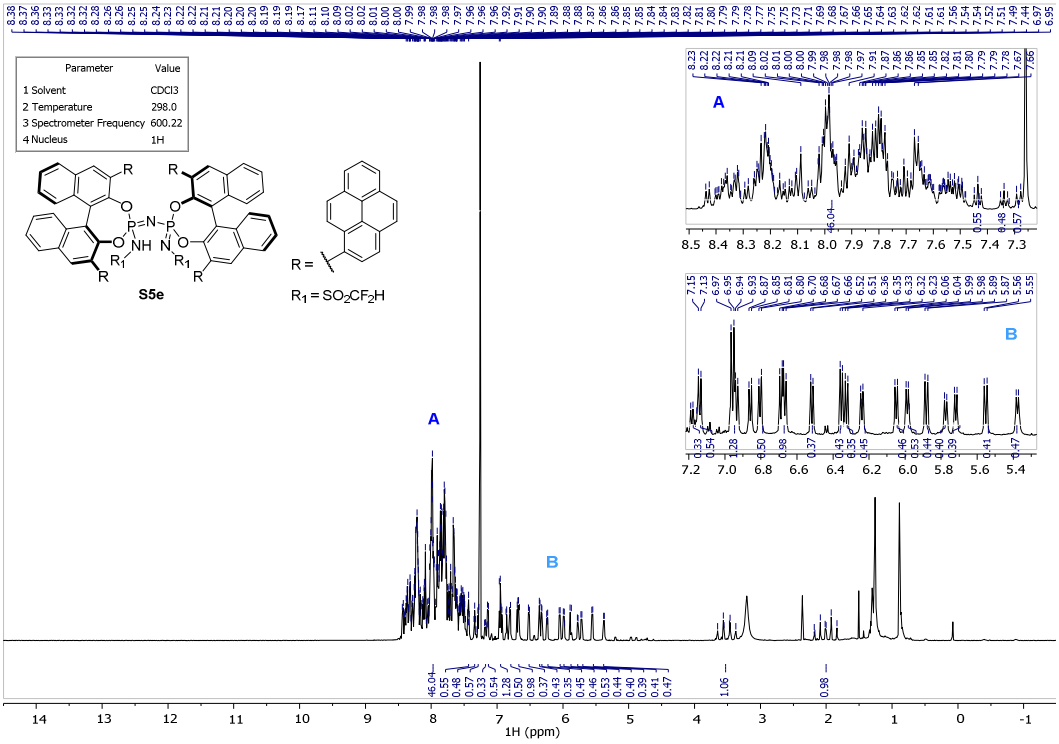

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 202.73
4 Nucleus 31P
R =
R' =
3
31P (ppm)

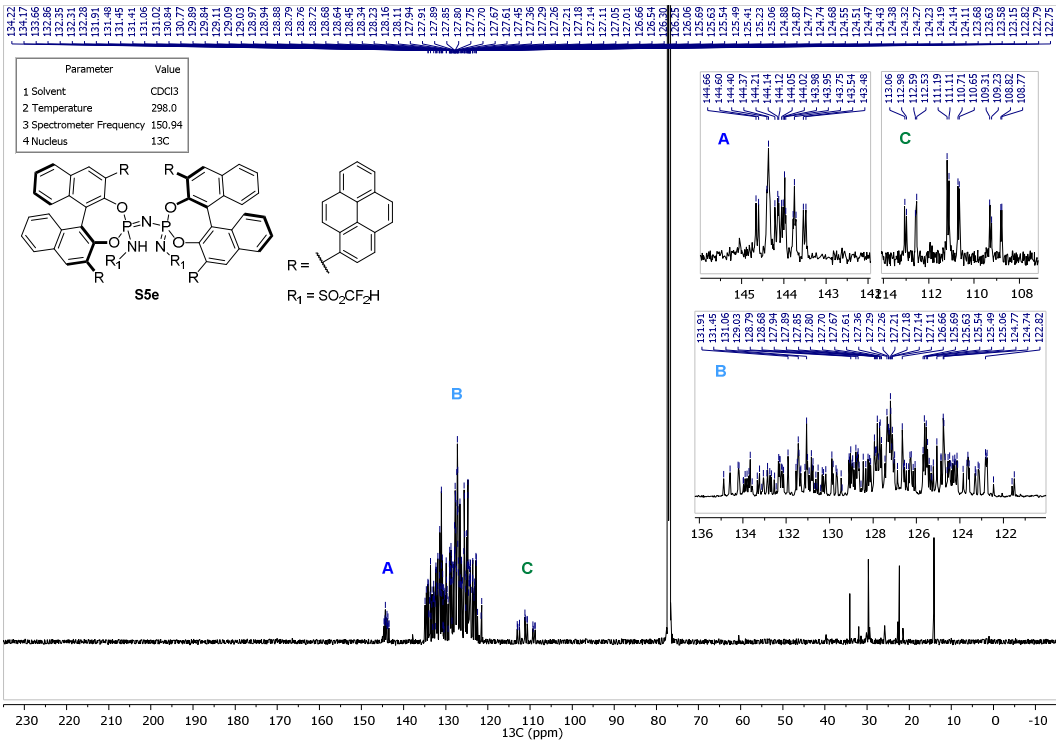

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
S5d
R =
A
B
1H (ppm)

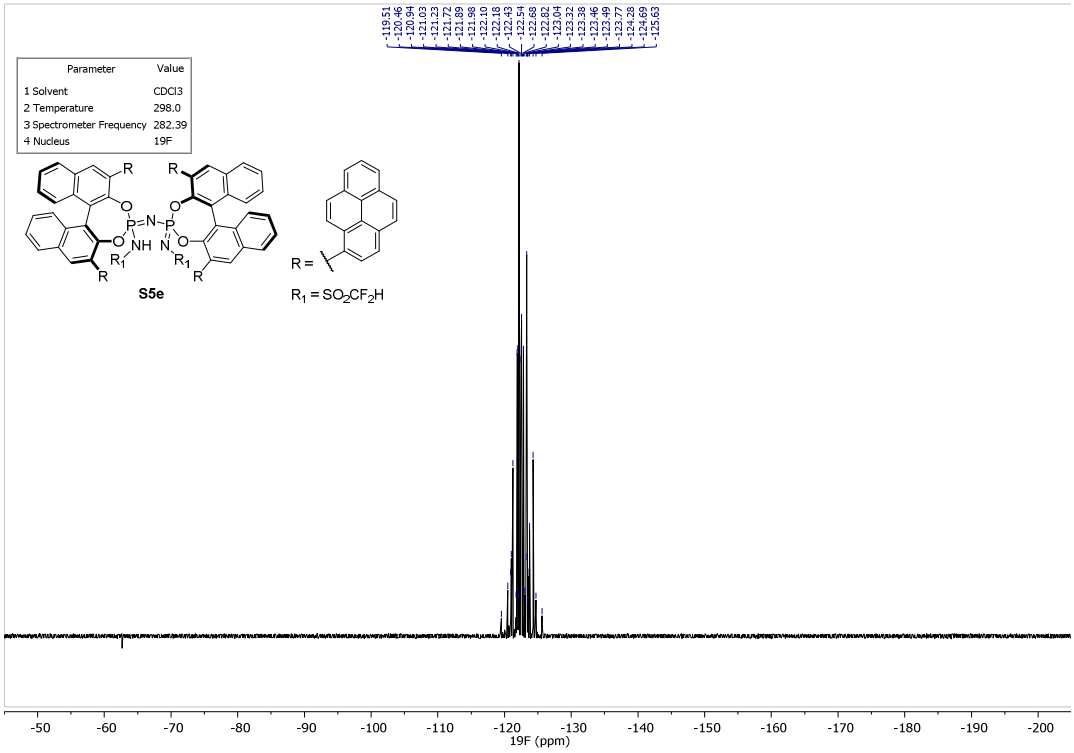

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
S5d
R =
A
13C (ppm)

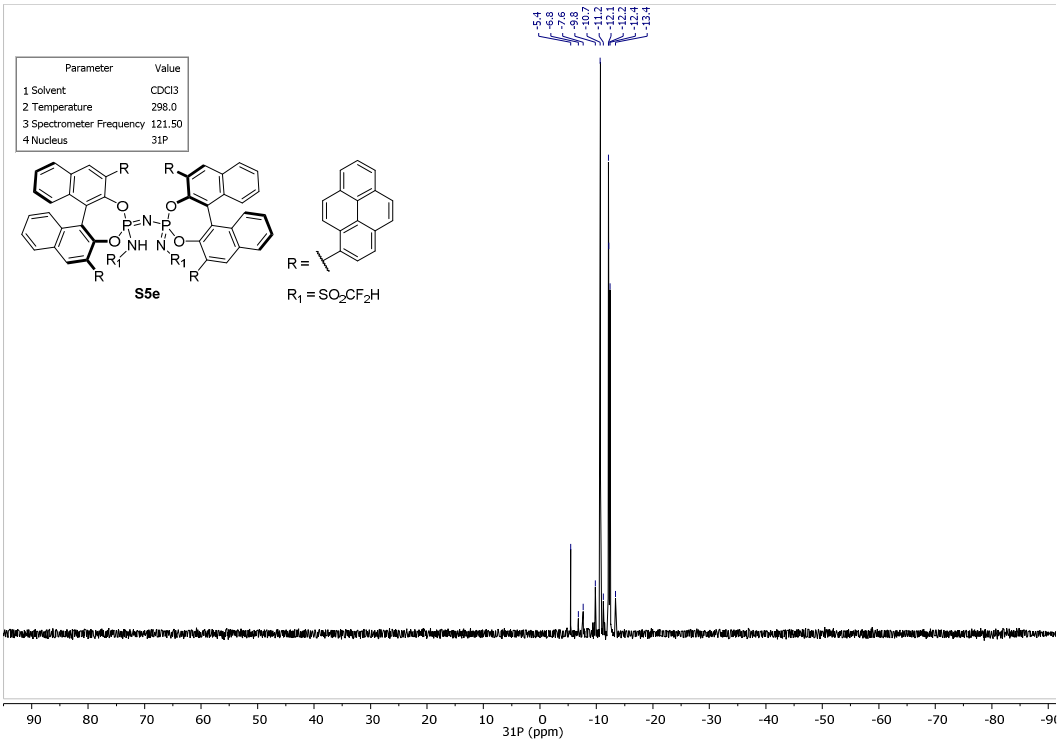

-79.0
-79.5
-80.0
-80.9
-81.1
-81.5
-81.6
-82.1
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
R
O
P=N-P
O NH N O
Tf Tf
R R
S5d
R =
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
19F (ppm)

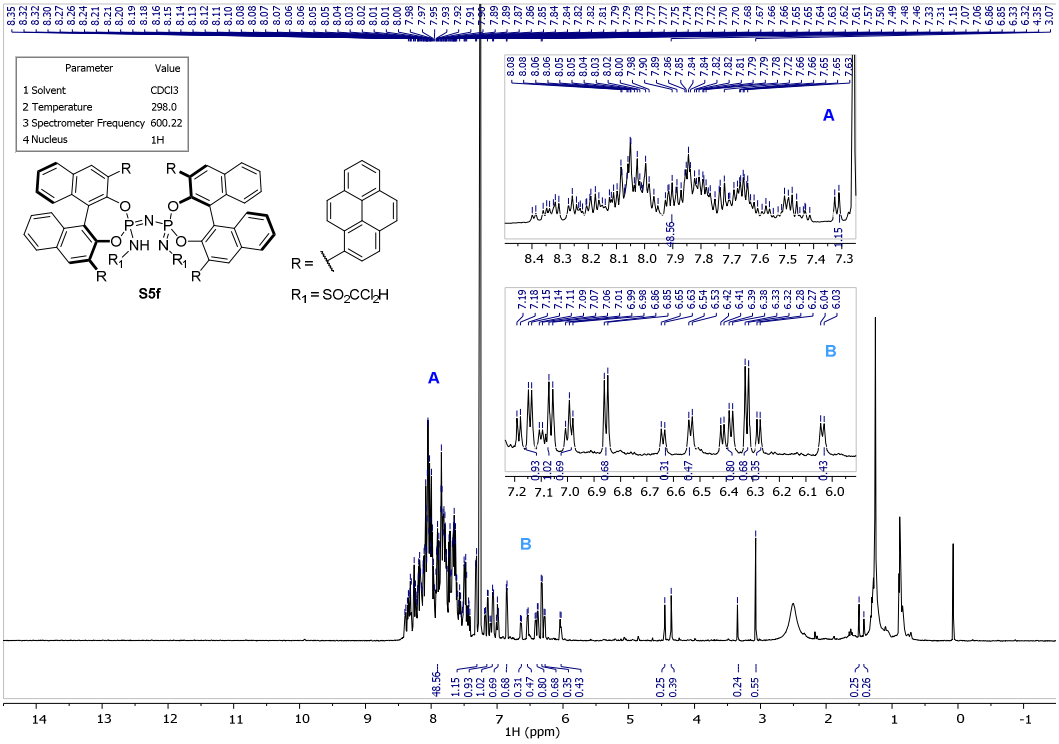

-4.7
-5.1
-5.5
-5.9
-6.0
-6.5
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 202.73
4 Nucleus 31P
R
O
P=N-P
O NH N O
Tf Tf
R R
S5d
R =
200 150 100 50 0 -50 -100 -150 -200
31P (ppm)

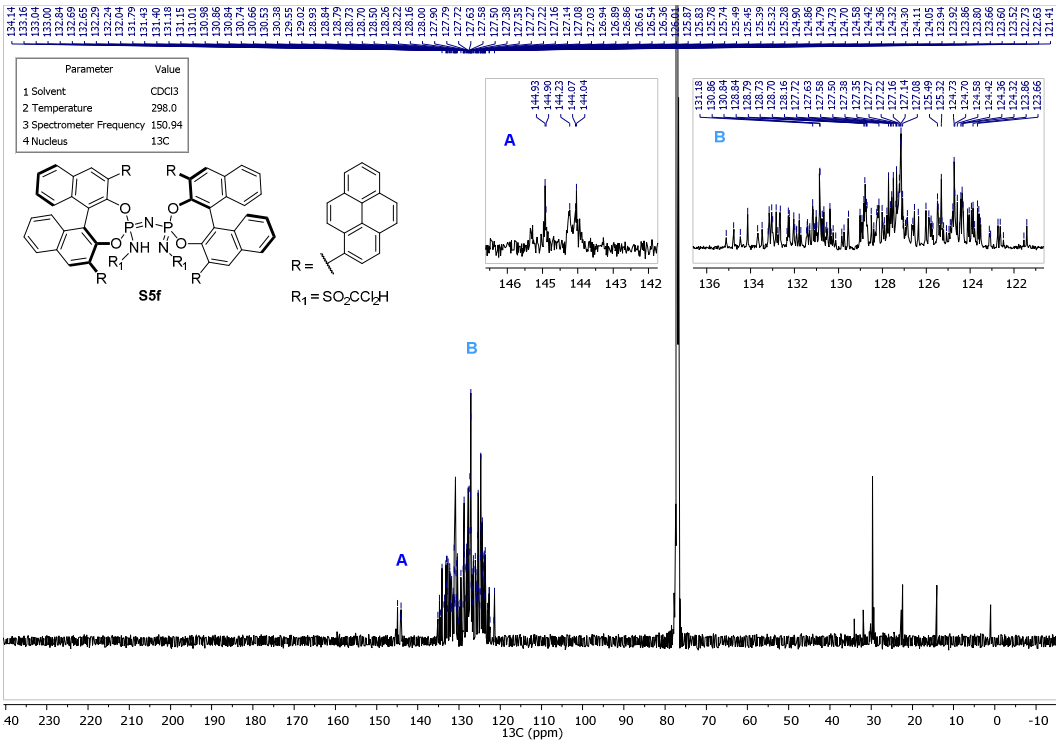

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 600.22
4 Nucleus 1H
S5e
R =
R1 = SO2CF2H
A
B
1H (ppm)

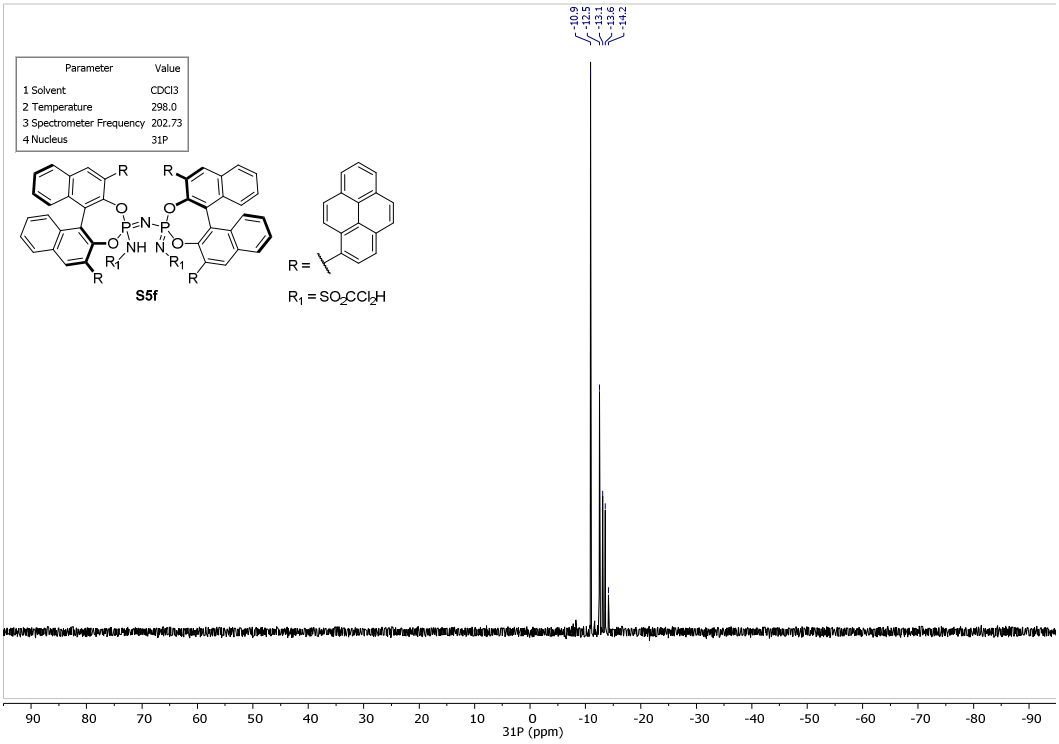

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
S5e
R =
R1 = SO2CF2H
A
B
C
13C (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 282.39
4 Nucleus 19F
S5e
R =
R1 = SO2CF2H
19F (ppm)

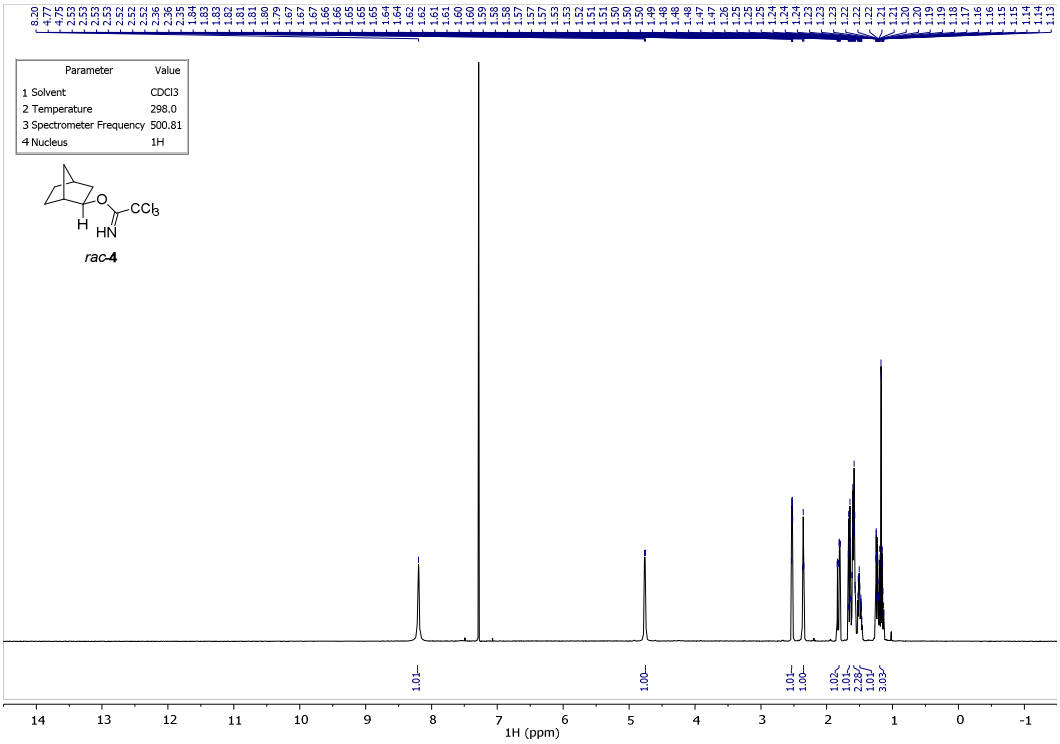

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 121.50
4 Nucleus 31P
S5e
R =
R1 = SO2CF2H
31P (ppm)

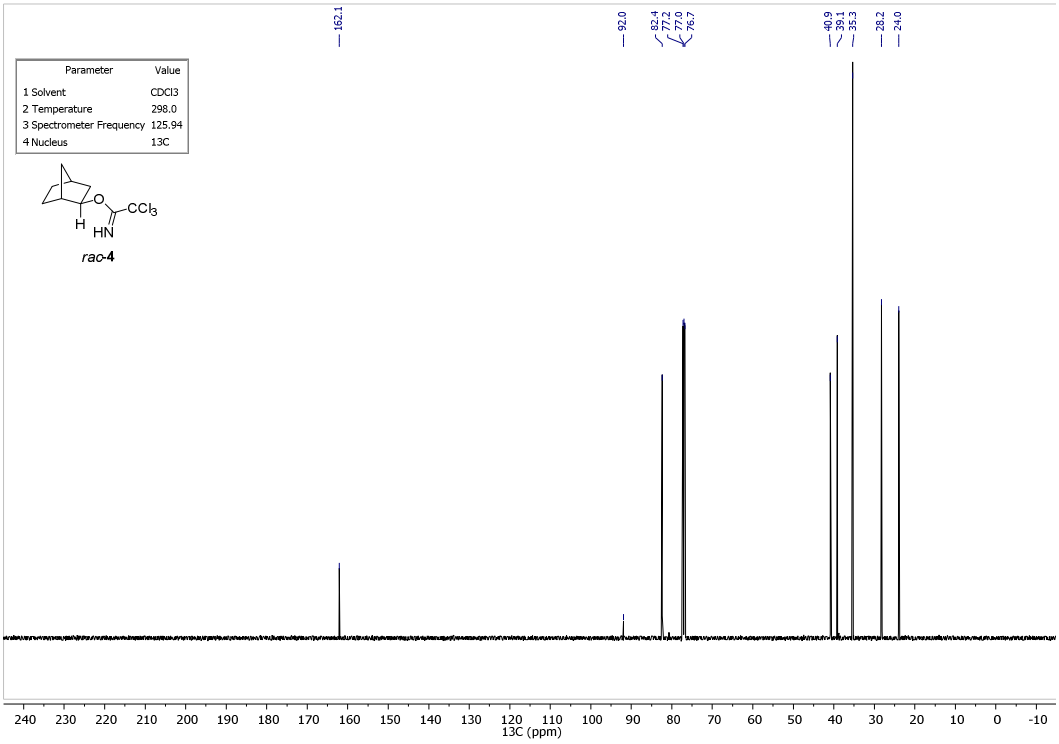

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 600.22
4 Nucleus 1H
S5f
R =
R1 = SO2CCl2H
A
B
1H (ppm)

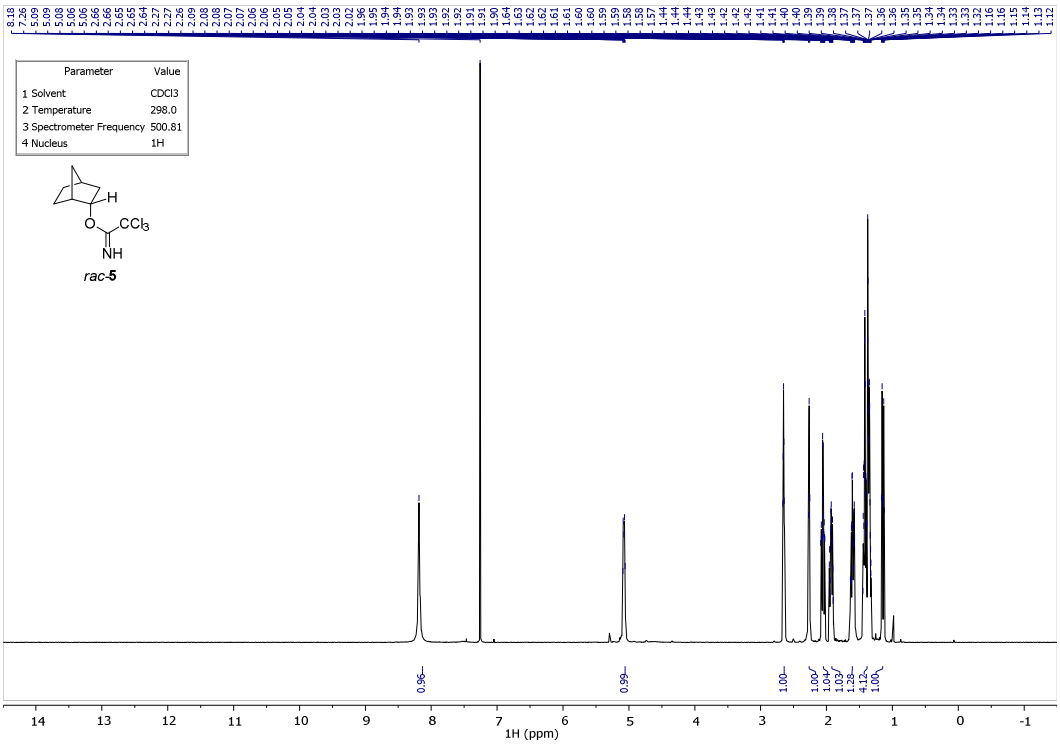

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
S5f
R =
R1 = SO2CCl2H
A
B
13C (ppm)

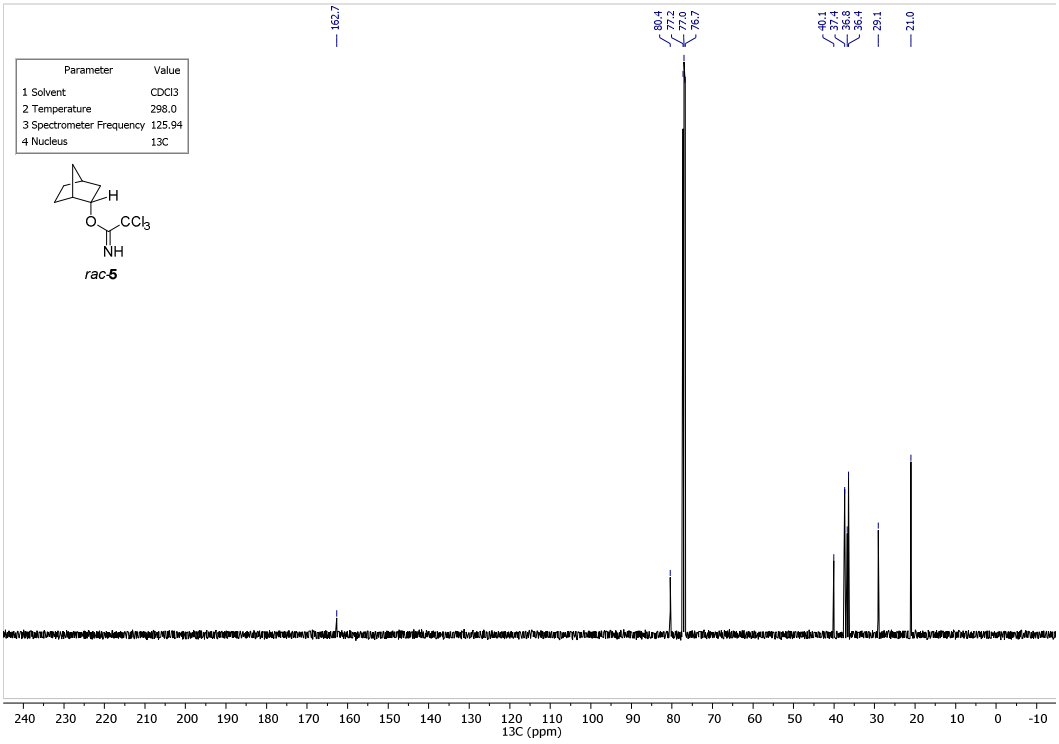


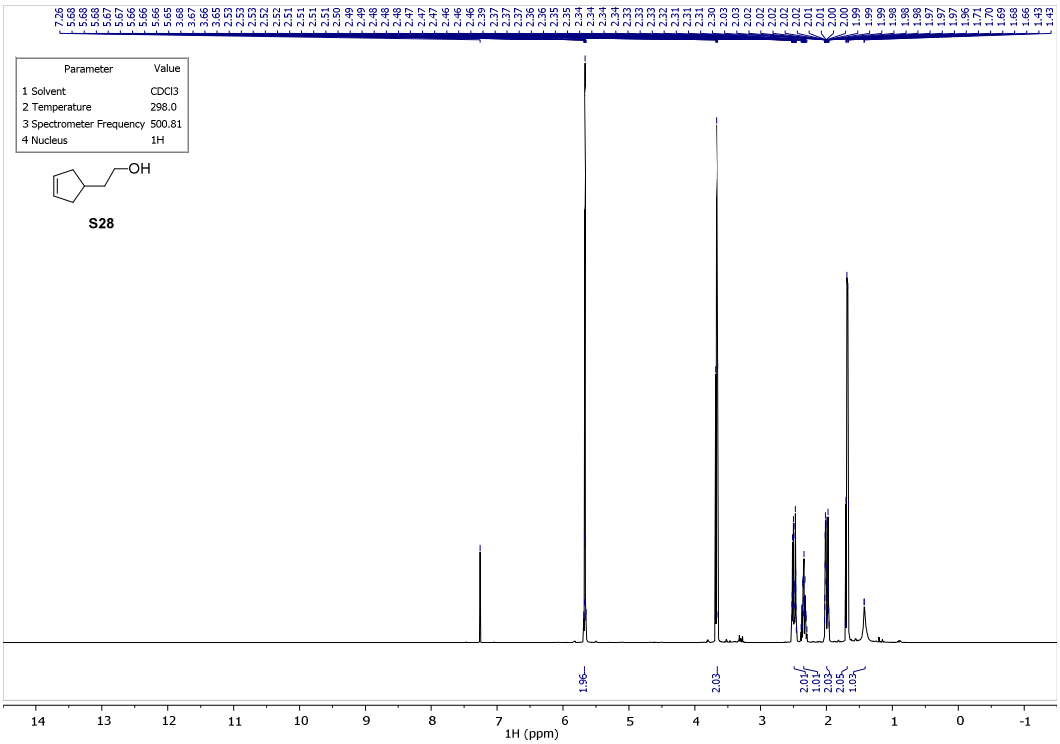
Substrates and intermediates thereof

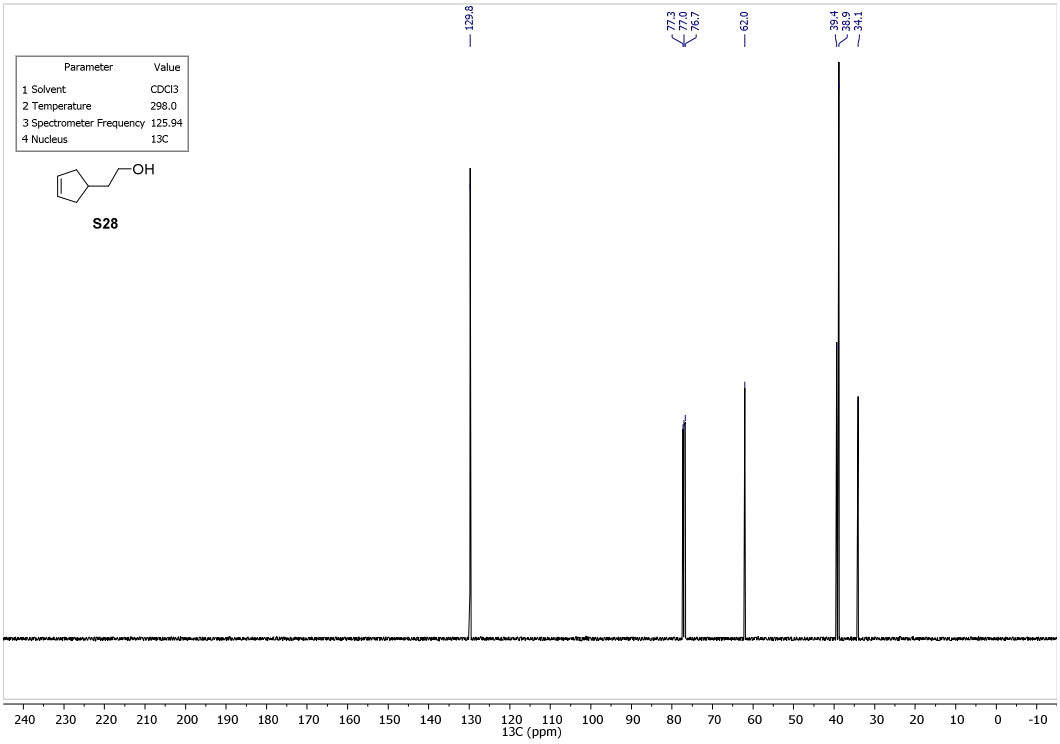


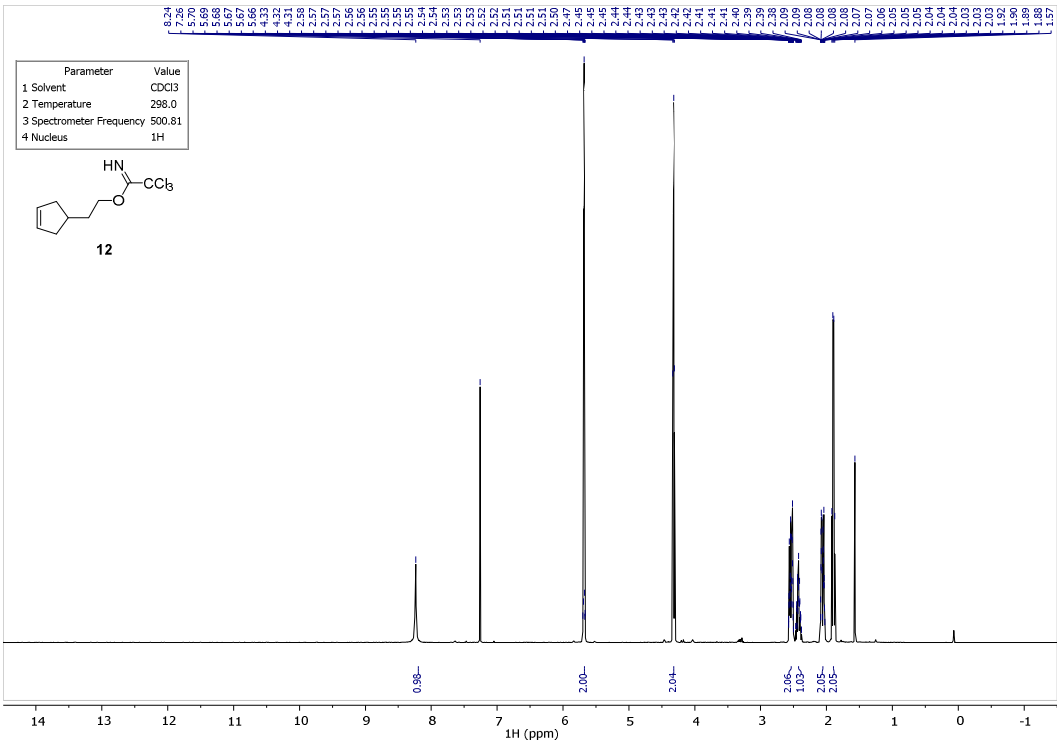

162.1
92.0
82.4
77.2
77.0
76.7
40.9
39.1
35.3
28.2
24.0
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
O
CCl3
H
HN
rac-4
13C (ppm)

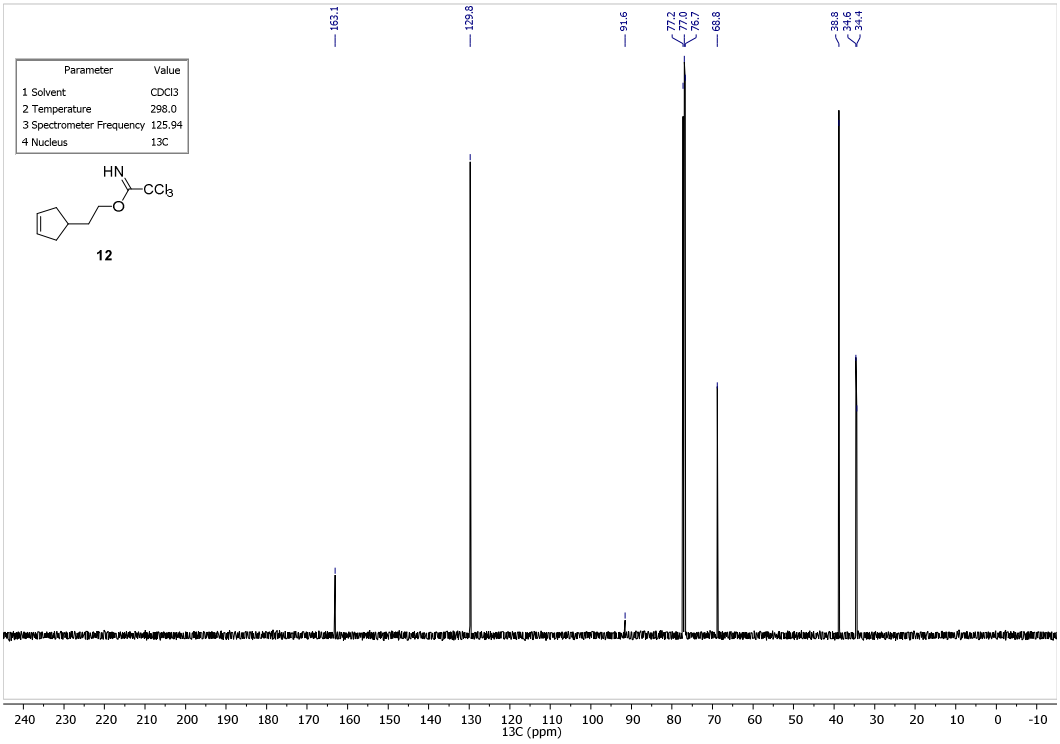

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
H
O
CCl3
NH
rac-5
0.96
0.99
1.00
1.00
1.04
1.03
1.28
4.12
1.00
1H (ppm)

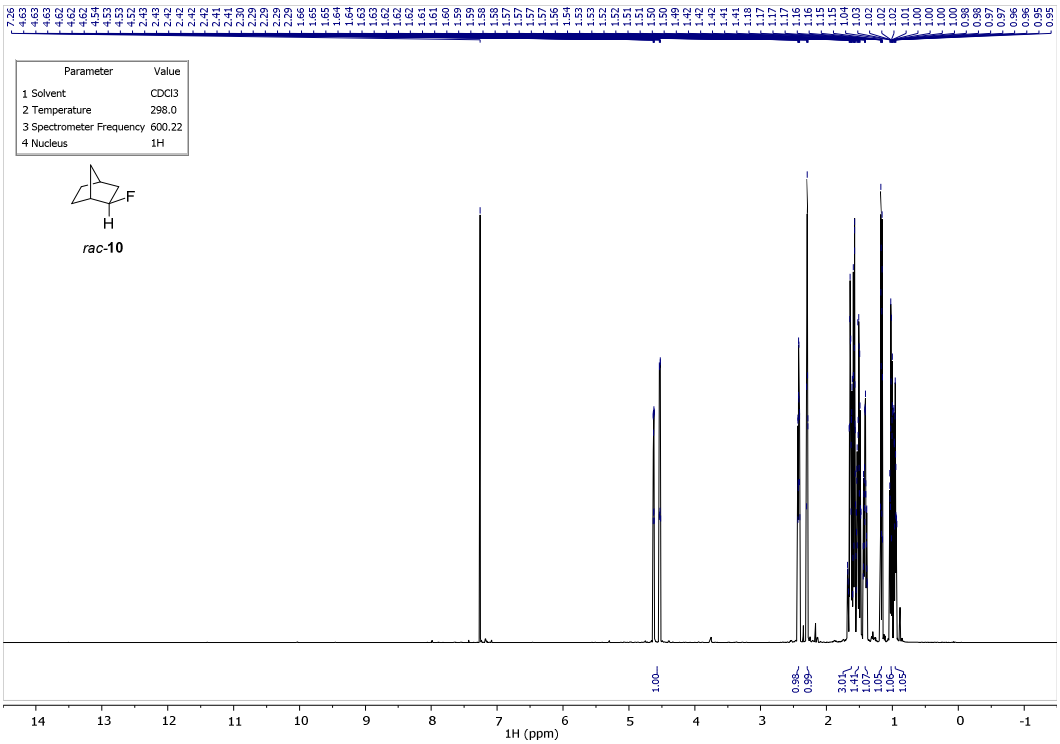

162.7
80.4
77.2
77.0
76.7
40.1
37.4
36.8
36.4
29.1
21.0
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
H
O
CCl3
NH
rac-5
13C (ppm)

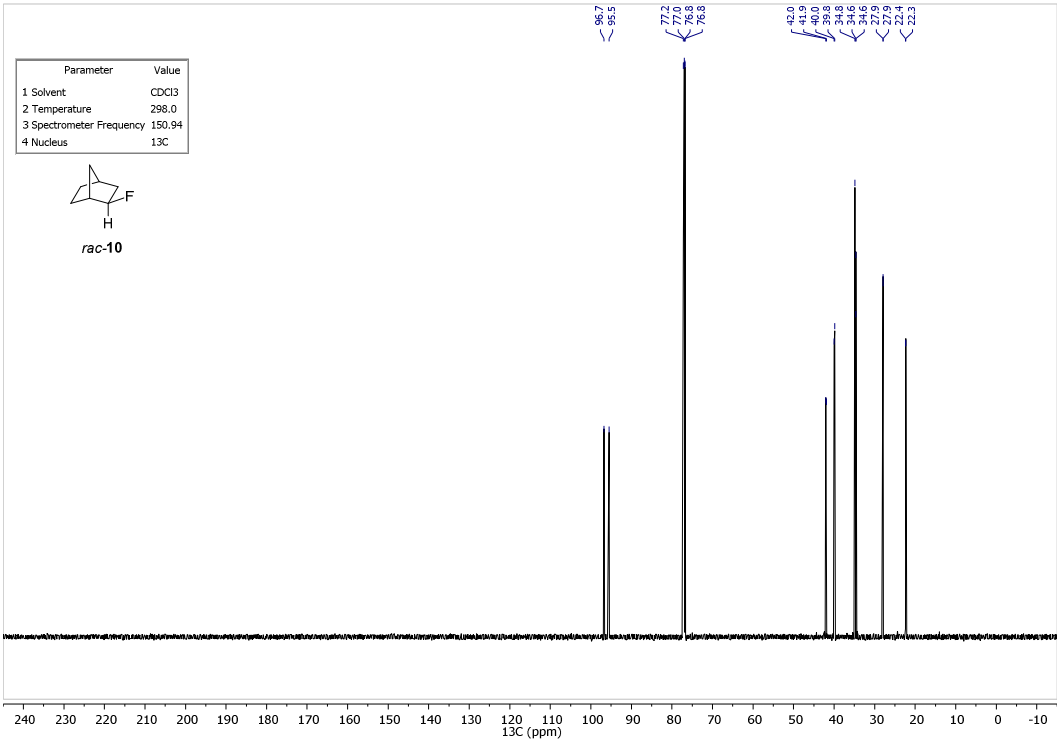

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
OH
S28
1.96
2.03
2.01
1.01
2.05
2.15
1.03
1H (ppm)

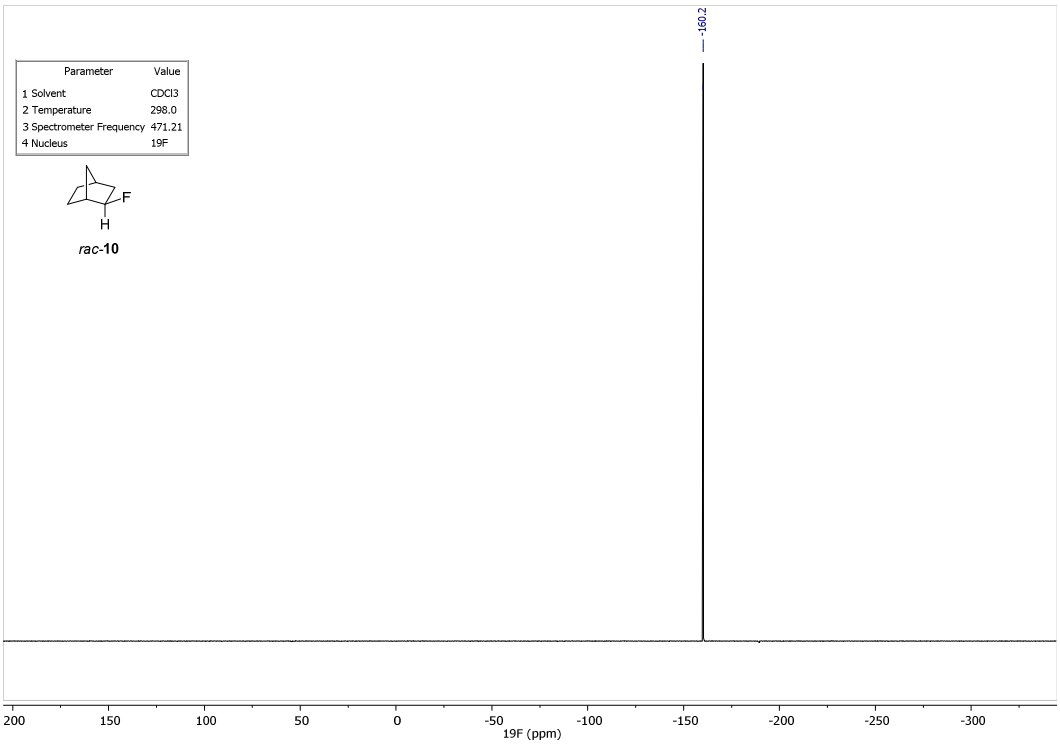

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
OH
S28
129.8
77.3
77.0
76.7
62.0
39.4
38.9
34.1
13C (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 500.81
4 Nucleus 1H
HN
CCl3
O
12
0.98
2.00
2.04
2.06
1.03
2.05
2.05
1H (ppm)

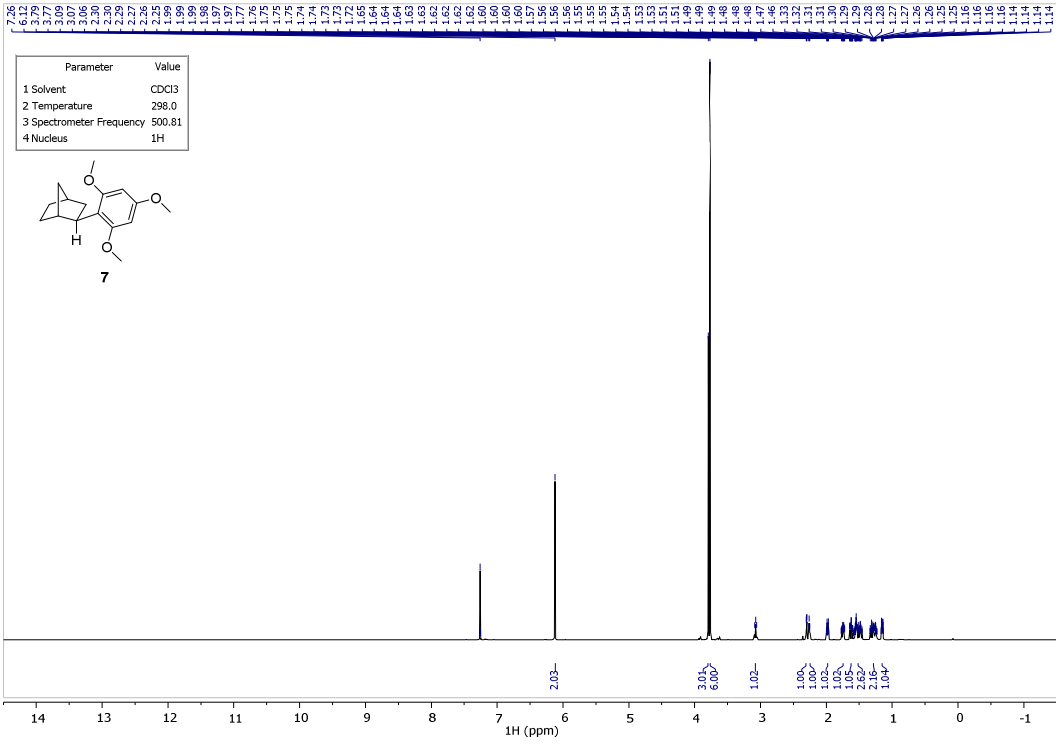

163.1
129.8
91.6
77.2
77.0
76.7
68.8
38.8
34.6
34.4
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 125.94
4 Nucleus 13C
HN
CCl3
O
12
13C (ppm)

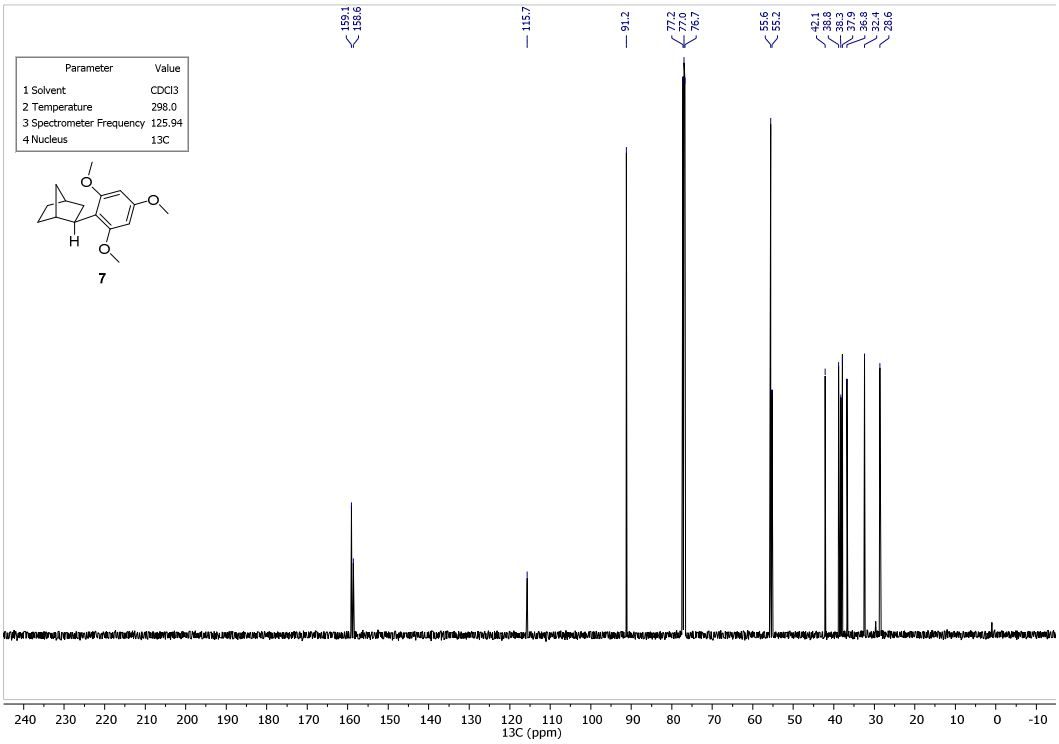

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 600.22
4 Nucleus 1H
F
H
rac-10
1.00
0.98
0.99
3.01
1.41
1.07
1.05
1.06
1.05
1H (ppm)


96.7
95.5
77.2
77.0
76.8
76.8
42.0
41.9
40.0
38.8
34.8
34.6
34.6
27.9
27.9
22.4
22.3
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
F
H
rac-10
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

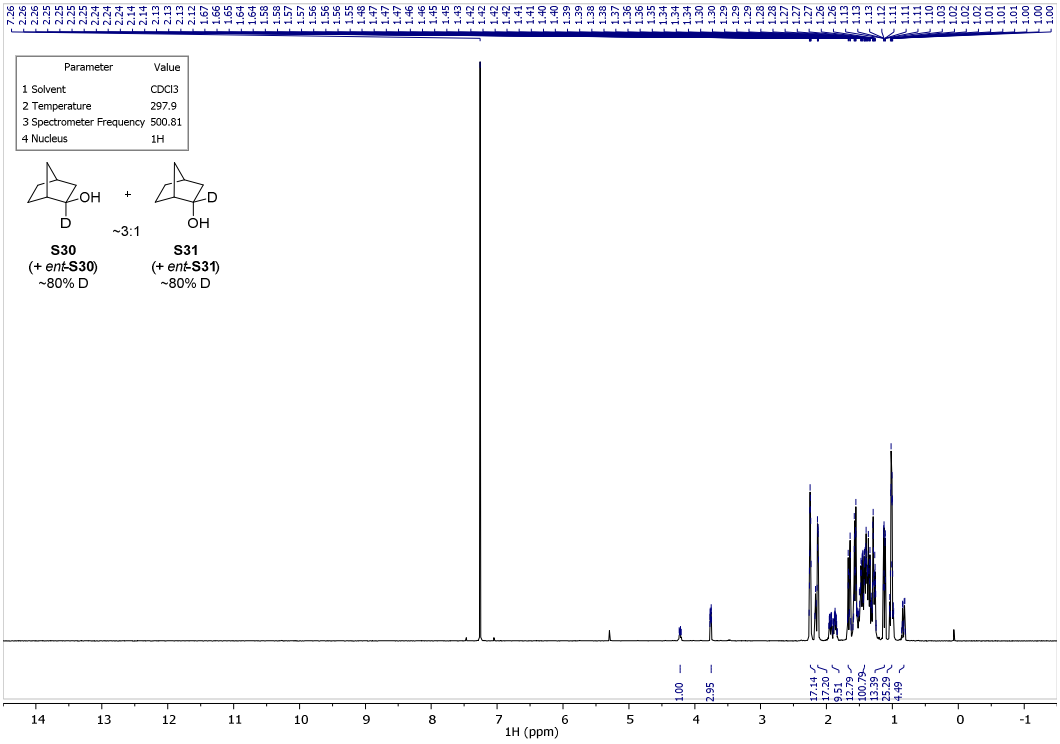

-160.2
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 471.21
4 Nucleus 19F
F
H
rac-10
200 150 100 50 0 -50 -100 -150 -200 -250 -300
19F (ppm)

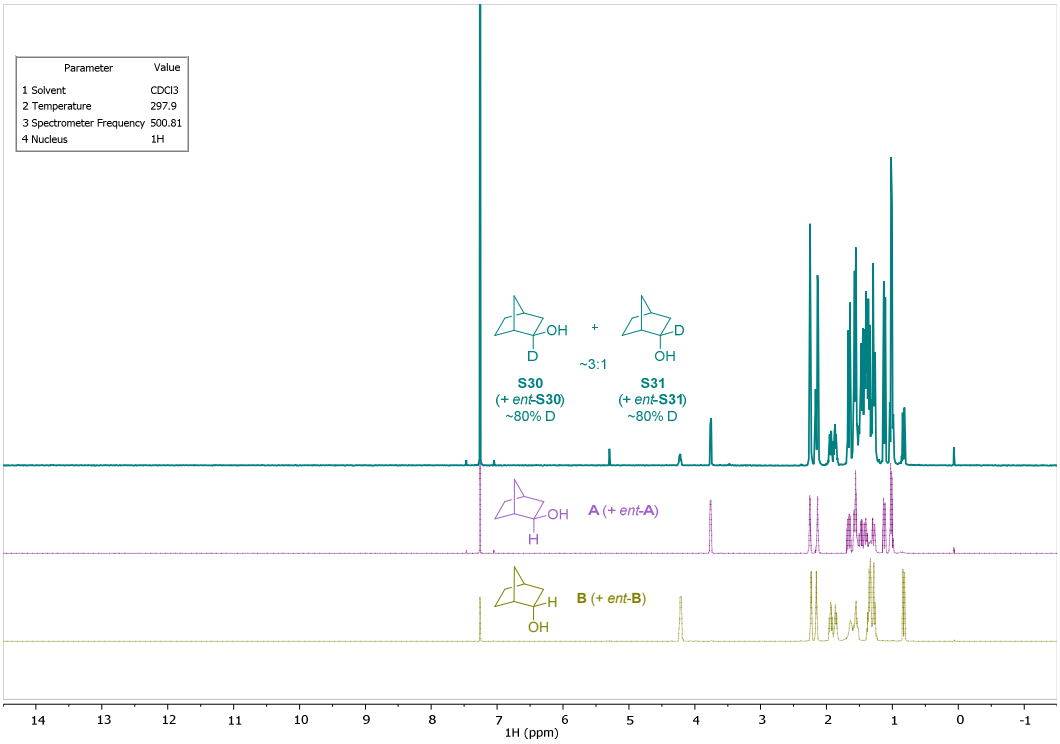
Product 7 (*exo*-2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane)

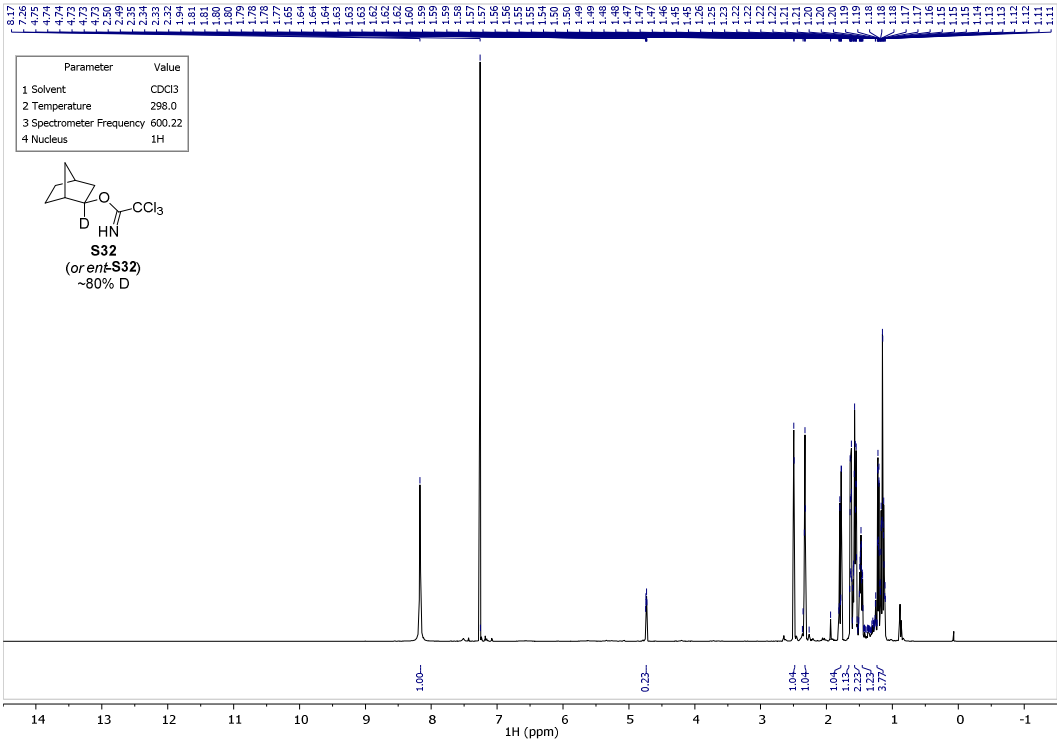


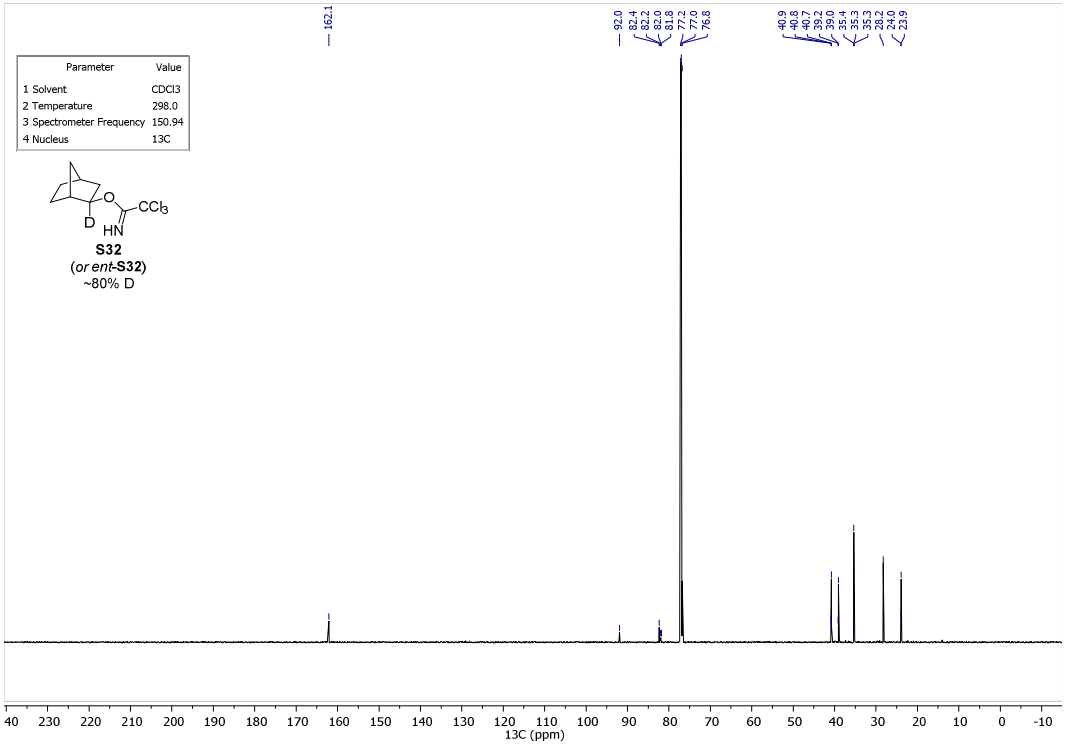


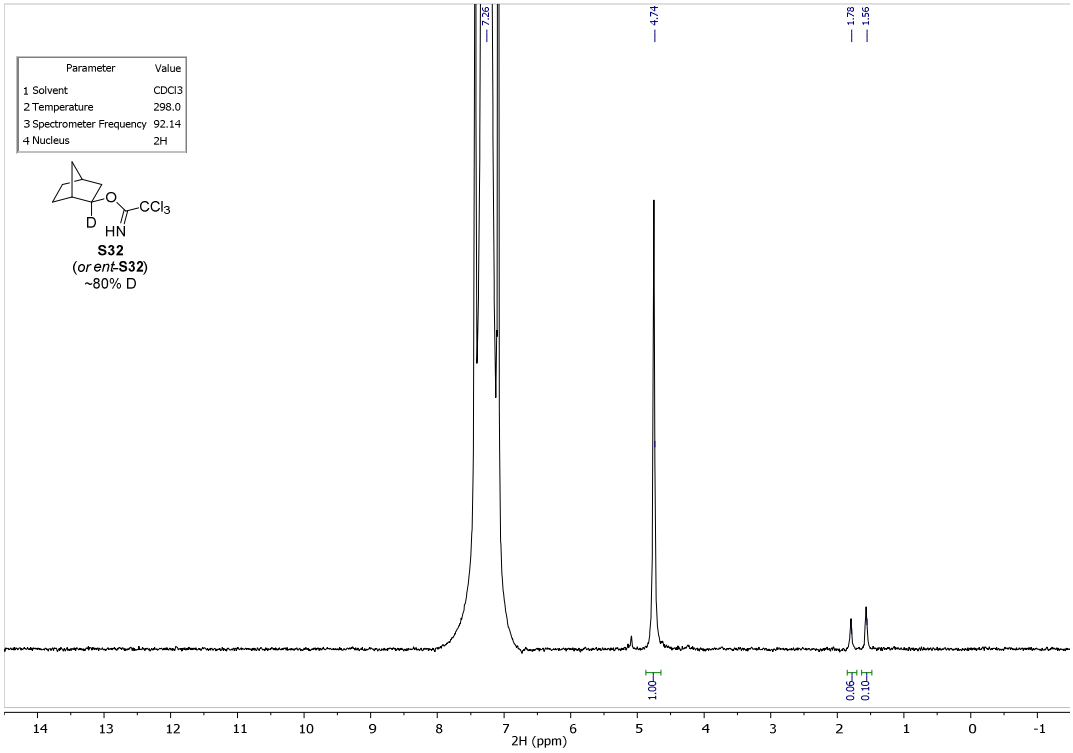
Deuterium-labelled analogues

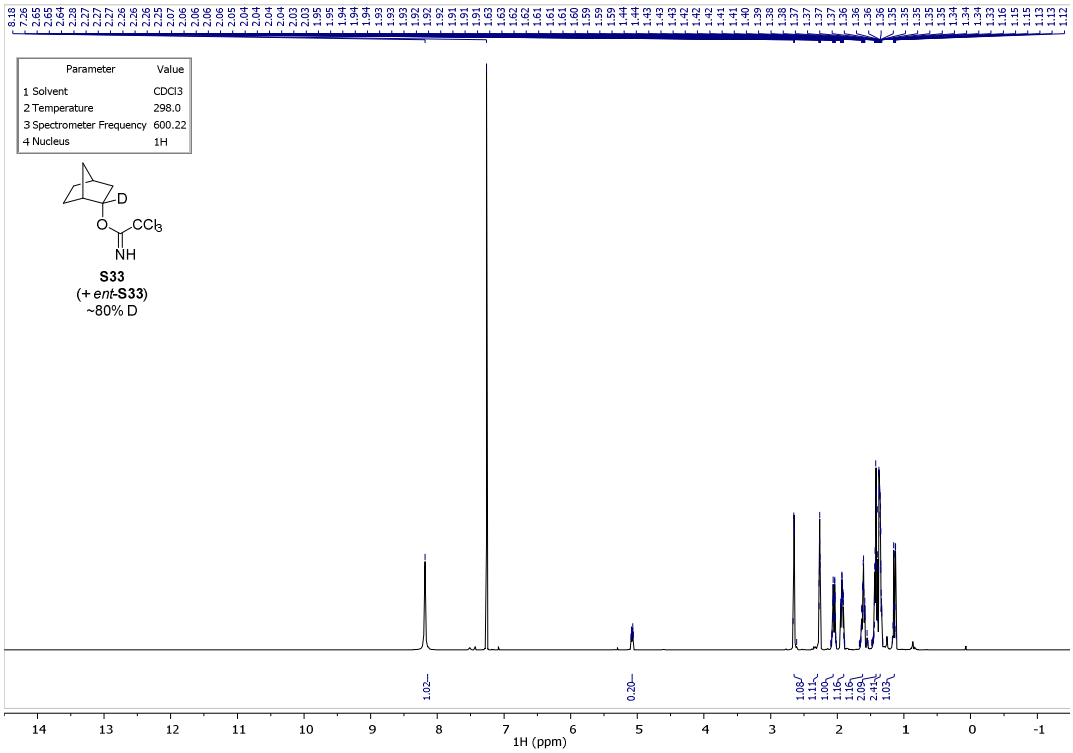


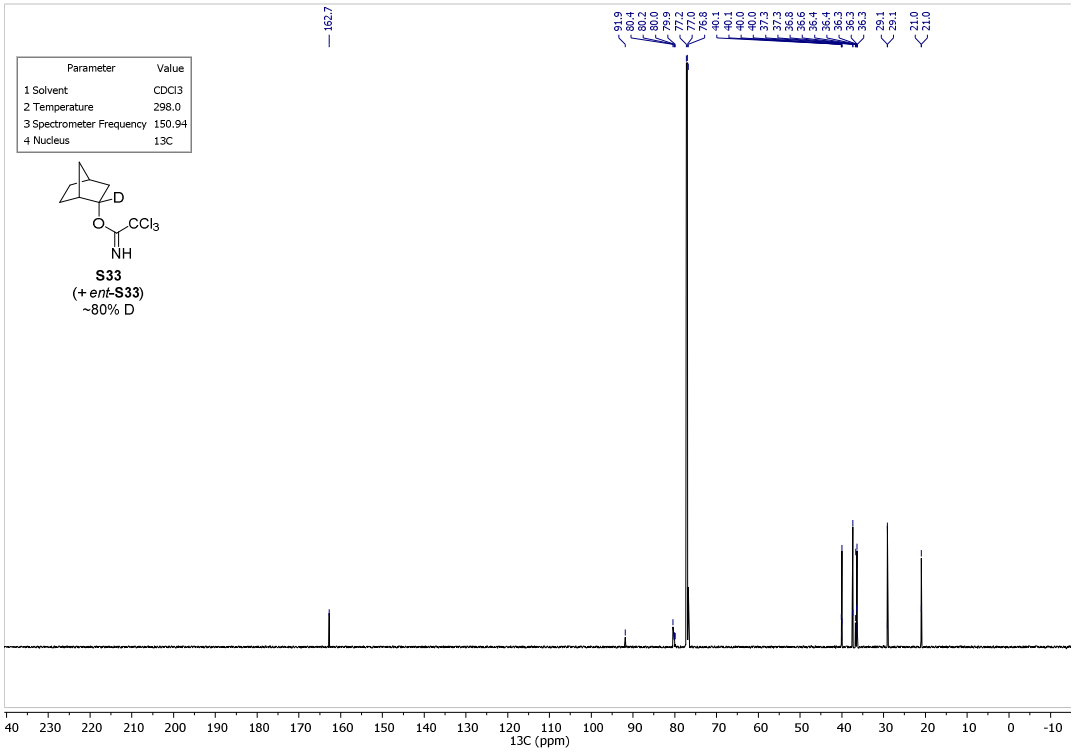


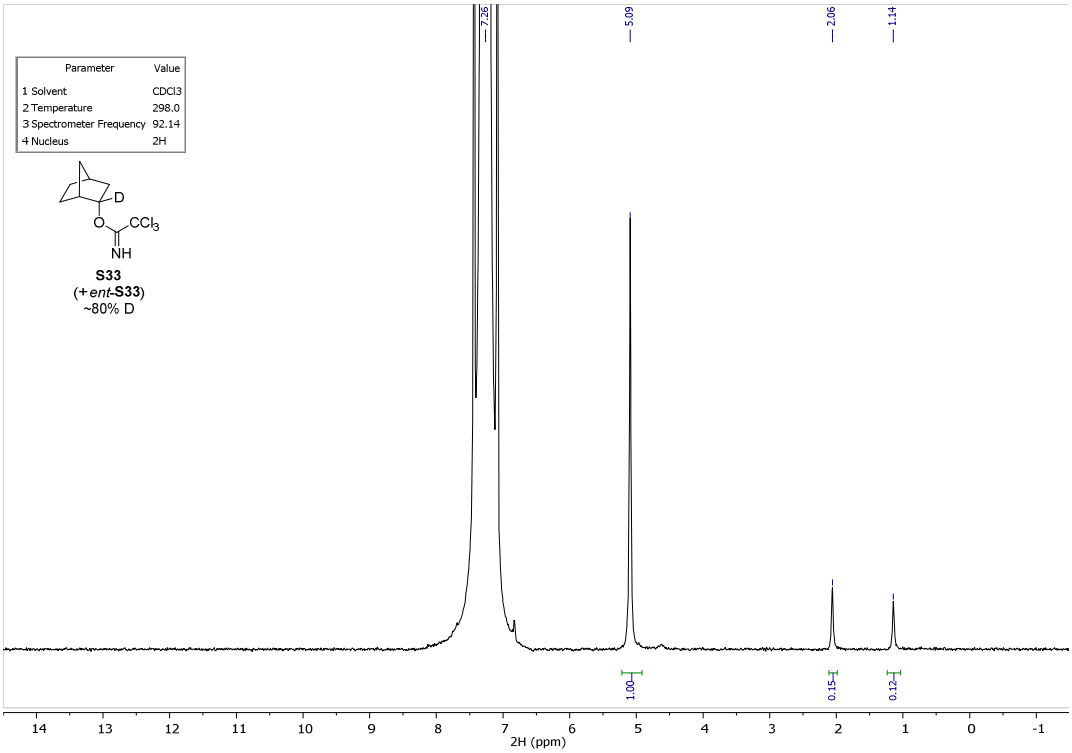

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 600.22
4 Nucleus 1H
CCl3
D
HN
S32
(ent-S32)
~80% D
1H (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
CCl3
D
HN
S32
(ent-S32)
~80% D
13C (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 92.14
4 Nucleus 2H
D
O
CCl3
HN
S32
(or ent-S32)
~80% D
7.26
4.74
1.78
1.56
1.00
0.06
0.10
2H (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 600.22
4 Nucleus 1H
D
O
CCl3
NH
S33
(+ ent-S33)
~80% D
1.02
0.20
1H (ppm)

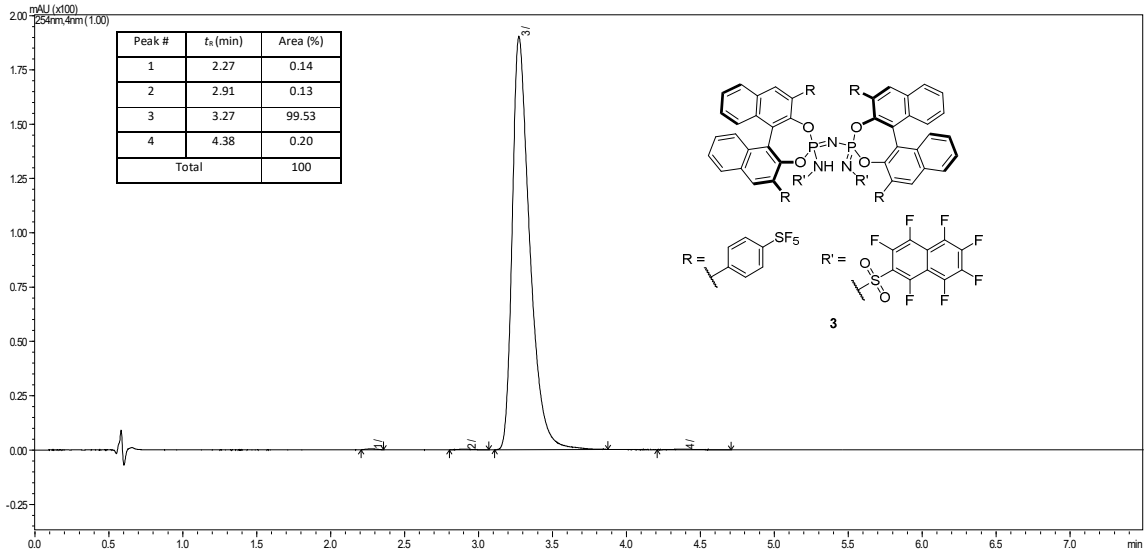

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 150.94
4 Nucleus 13C
D
O
CCl3
NH
S33
(+ent-S33)
~80% D
162.7
91.9
80.4
80.2
80.0
79.9
77.2
77.0
76.8
40.1
40.1
40.0
40.0
37.3
37.3
36.8
36.6
36.4
36.4
36.3
36.3
36.3
29.1
29.1
21.0
21.0
13C (ppm)

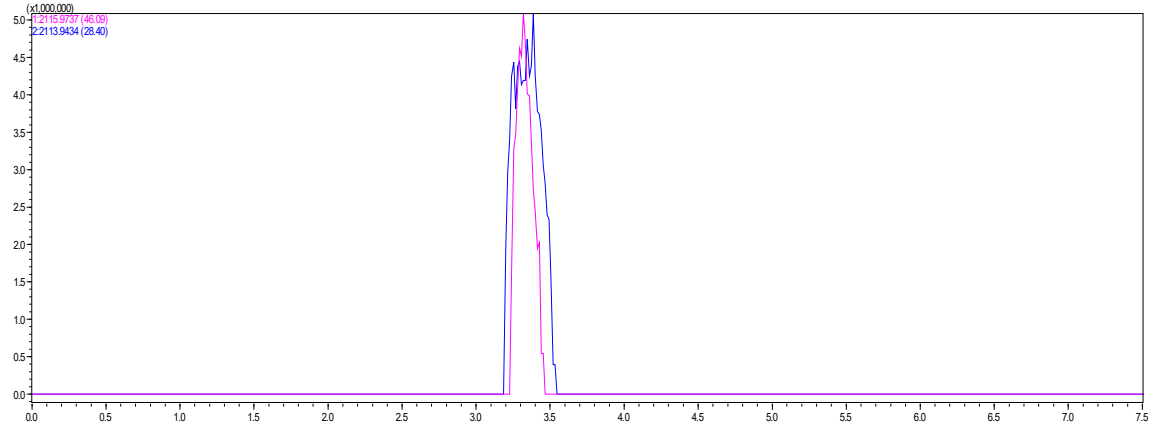

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Spectrometer Frequency 92.14
4 Nucleus 2H
D
O
CCl3
NH
S33
(+ent-S33)
~80% D
7.26
5.09
2.06
1.14
1.00
0.15
0.12
2H (ppm)

1.4.2 Copies of HPLC traces

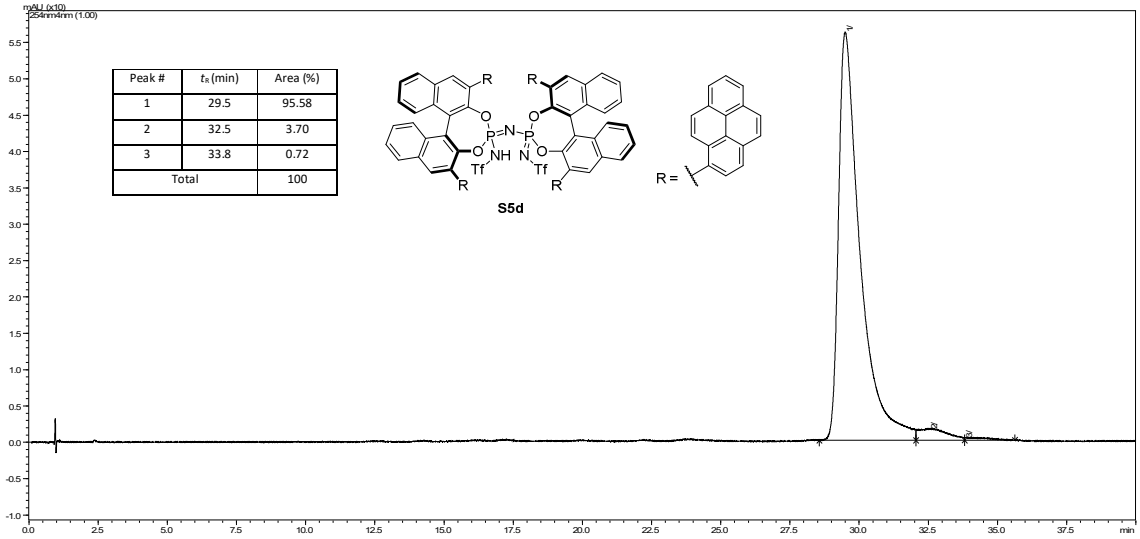
Imidodiphosphorimidate acids

LC-MS (50 mm Zorbax SB300-C8, 3.5 µm, 4.6 mm i.d.): 1% TFA/MeCN 25:75, 1.0 mL/min, 4.7 MPa, 308 K, 254 nm.



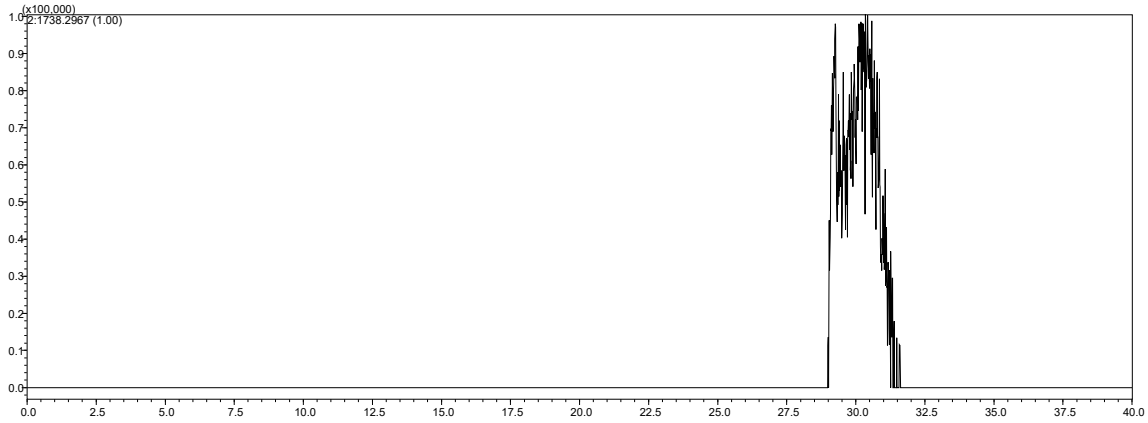


LC-MS (100 mm AdvanceBioRP mAb SB-C8, 3.5 μm, 4.6 mm i.d.): 1% TFA/MeCN 35:65, 1.0 mL/min, 7.4 MPa, 308 K, 220 nm.

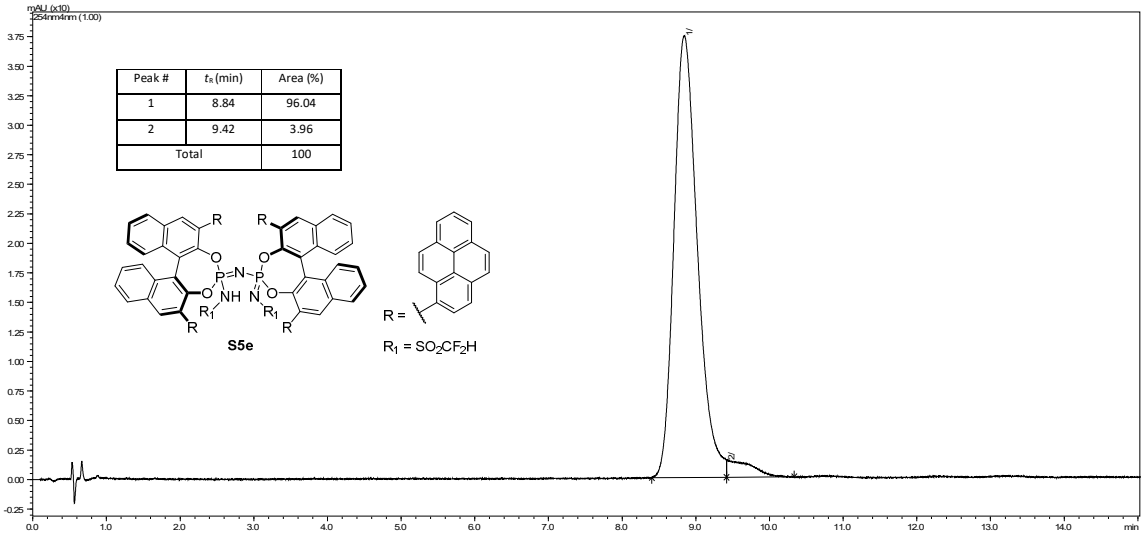


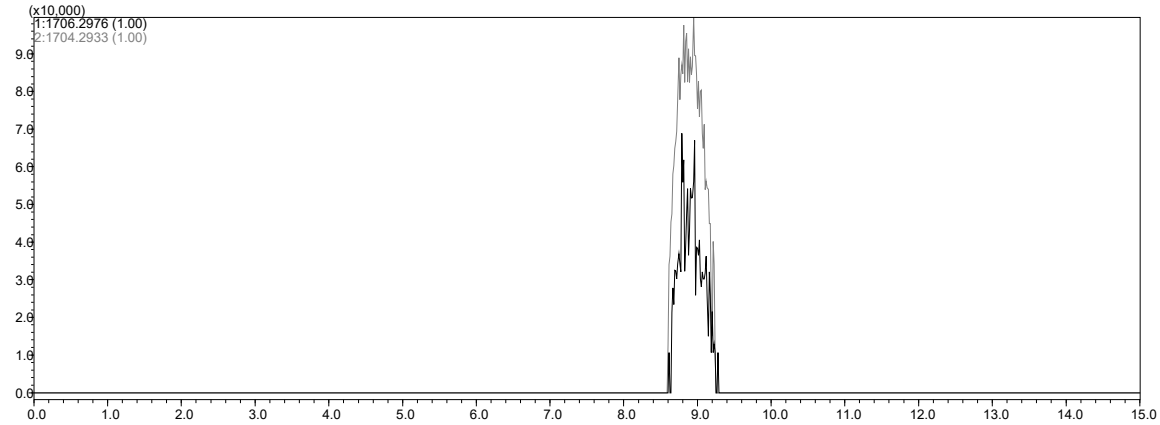
Peak #	t_R (min)	Area (%)
1	29.5	95.58
2	32.5	3.70
3	33.8	0.72
Total		100

S5d

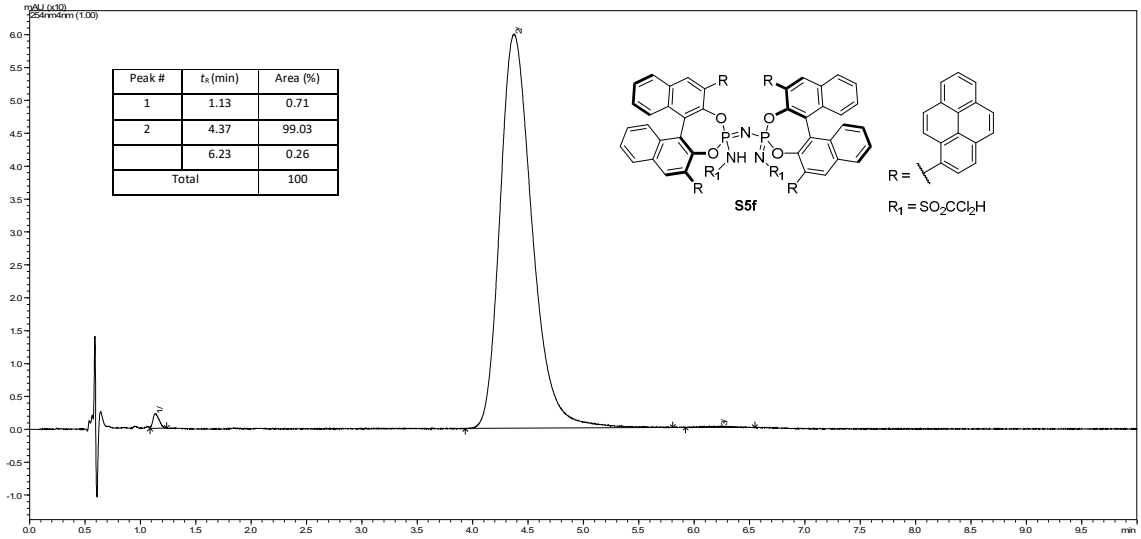


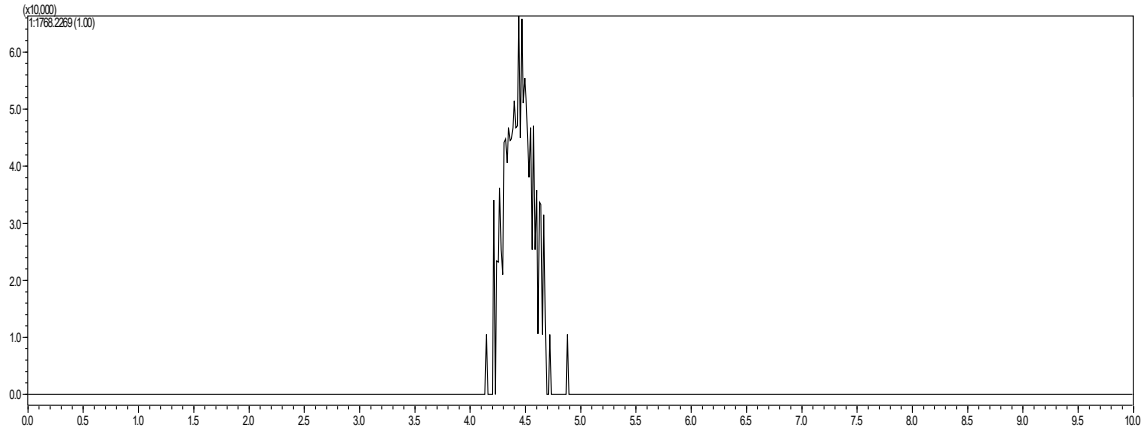
LC-MS (50 mm Zorbax SB300-C8, 3.5 µm, 4.6 mm i.d.): 1% TFA/MeCN 25:75, 1.0 mL/min, 6.2 MPa, 308 K, 254 nm.





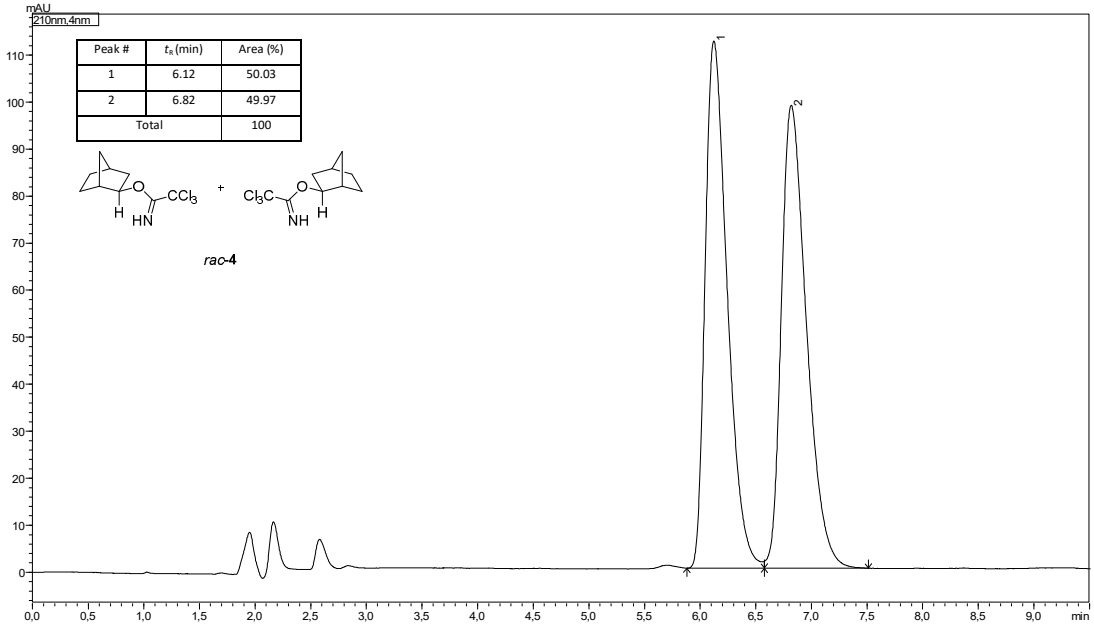
LC-MS (50 mm Zorbax SB300-C8, 3.5 μm, 4.6 mm i.d.): 1% TFA/MeCN 20:80, 1.0 mL/min, 5.6 MPa, 308 K, 254 nm.

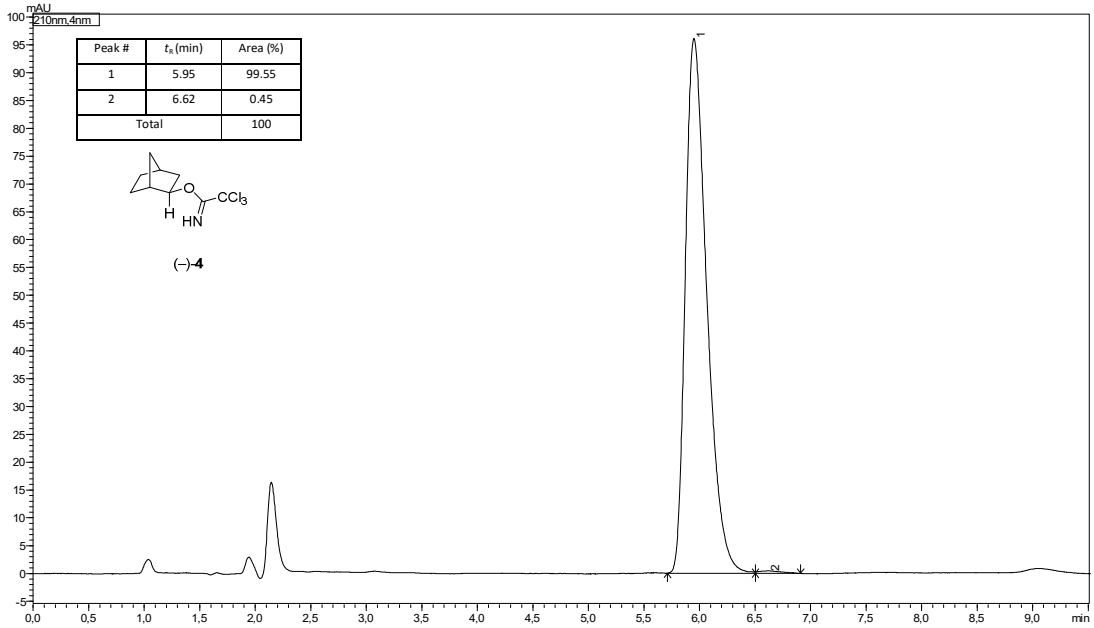


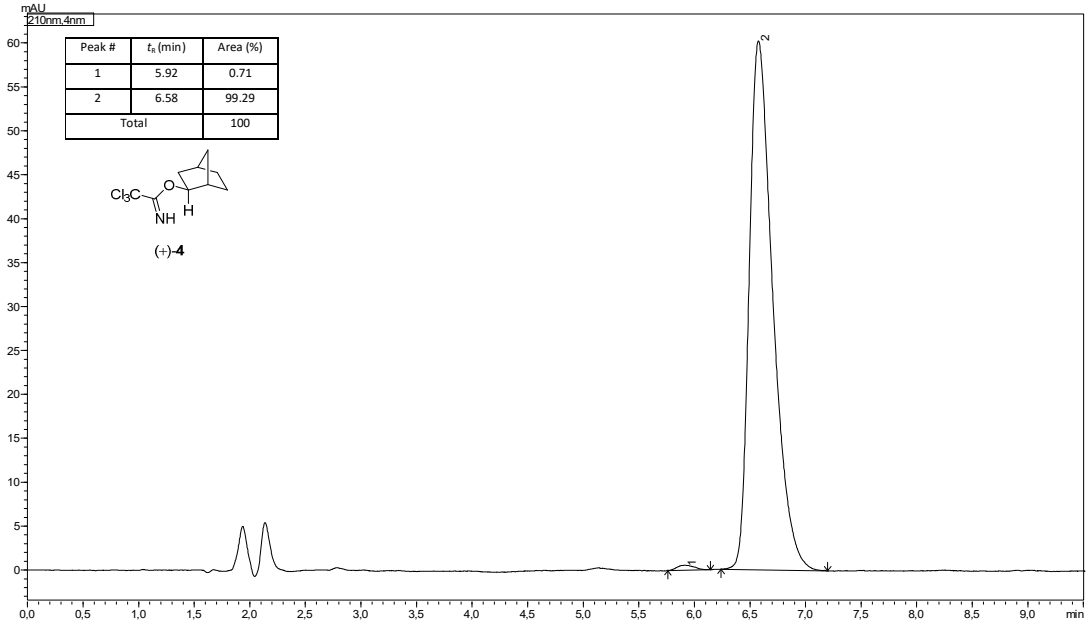


***Exo*-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate (4)**

HPLC (Chiralcel® 150 mm OJ-3R, 3 μm, 4.6 mm i.d.): MeOH/H_2O 80:20, 1.0 mL/min, 308 K, 210 nm.

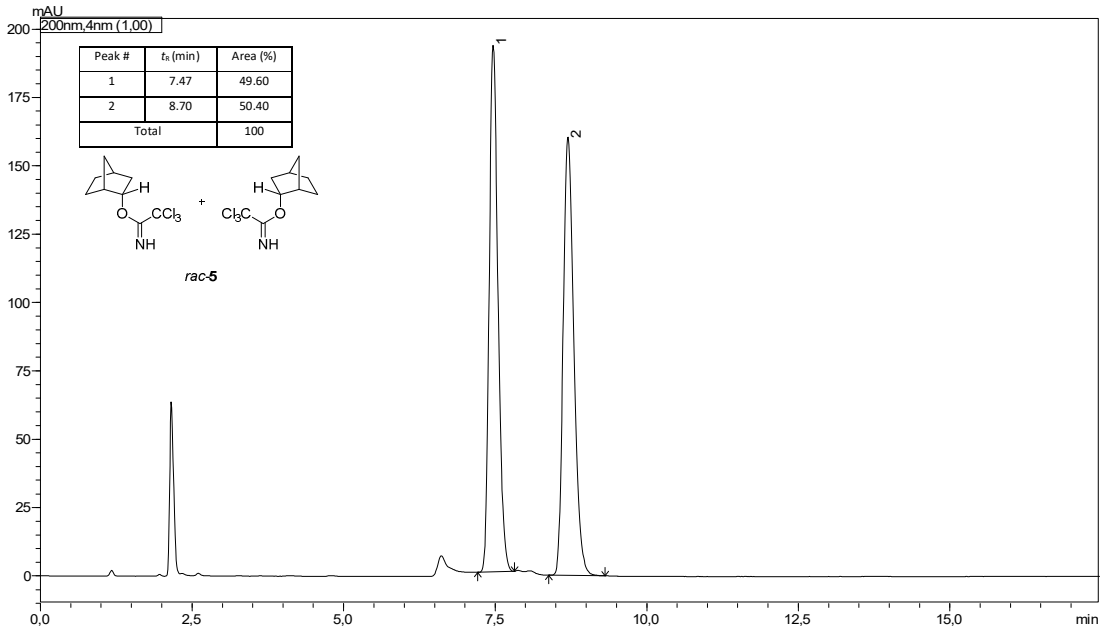


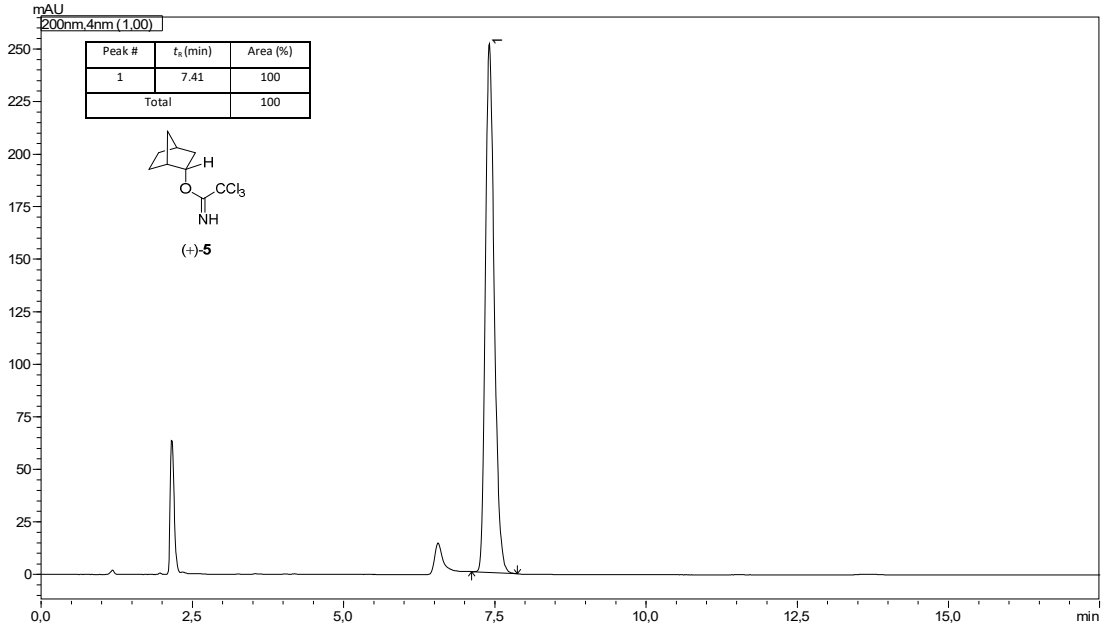


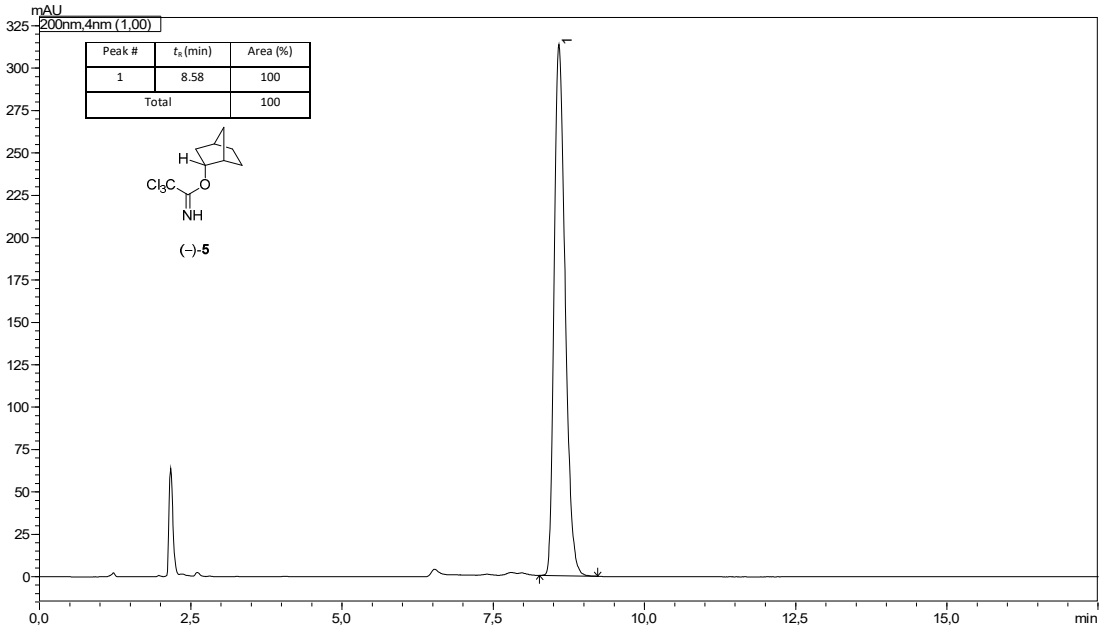


***Endo*-bicyclo[2.2.1]heptan-2-yl 2,2,2-trichloroacetimidate (5)**

HPLC (Chiralpak® 150 mm AD-3R, 3 µm, 4.6 mm i.d.): MeCN/H_2O 65:35, 1.0 mL/min, 298 K, 200 nm.

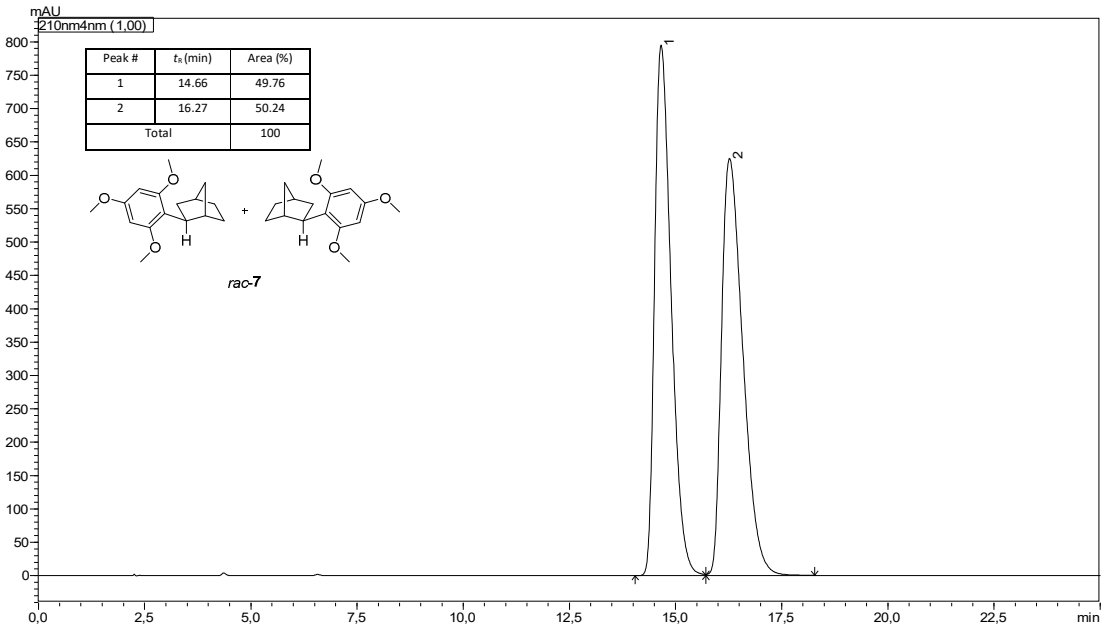


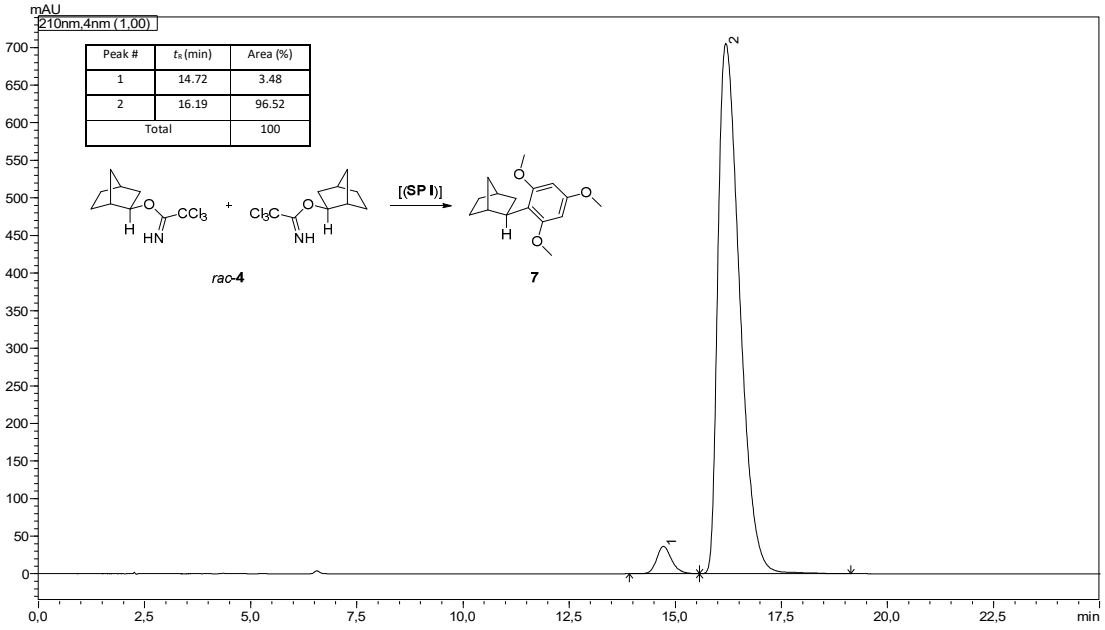

mAU
200nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 7.41 | 100
Total | | 100
H
O
CCl_3
NH
(+)-5
250
225
200
175
150
125
100
75
50
25
0
0,0
2,5
5,0
7,5
10,0
12,5
15,0
min

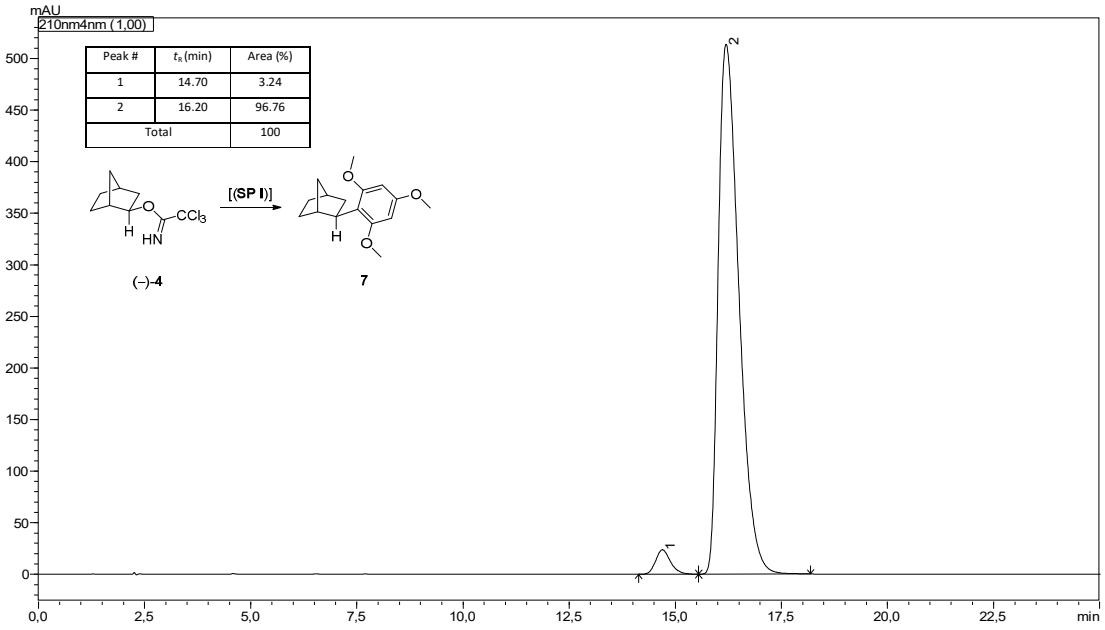

mAU
200nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 8.58 | 100
Total | | 100
H
Cl_3C
O
NH
(–)-5
325
300
275
250
225
200
175
150
125
100
75
50
25
0
0,0
2,5
5,0
7,5
10,0
12,5
15,0
min

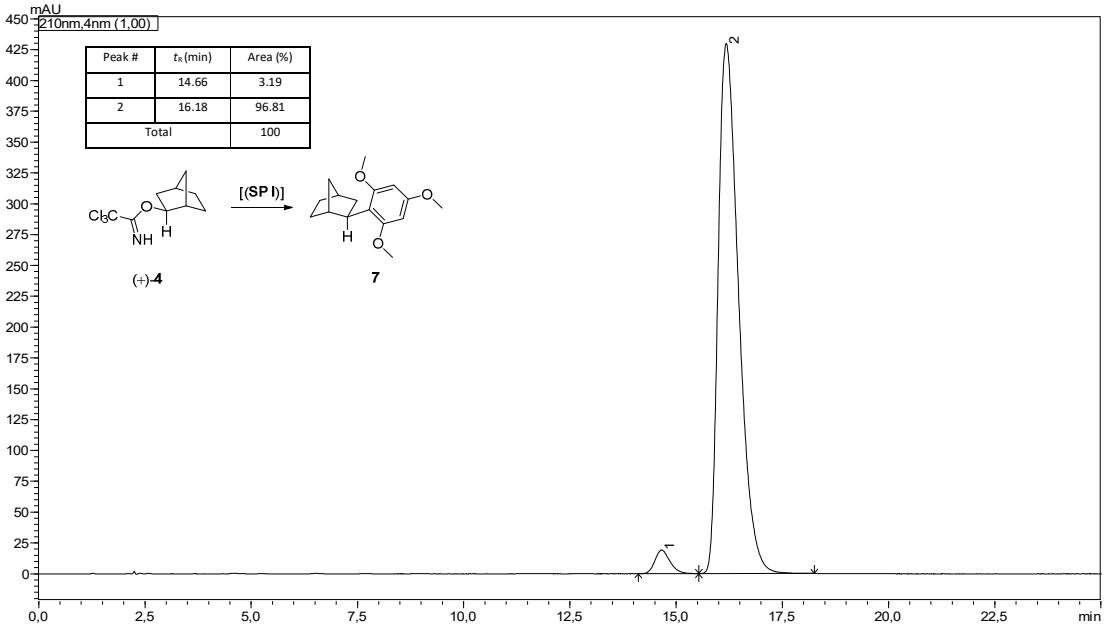
Exo-2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane (7)

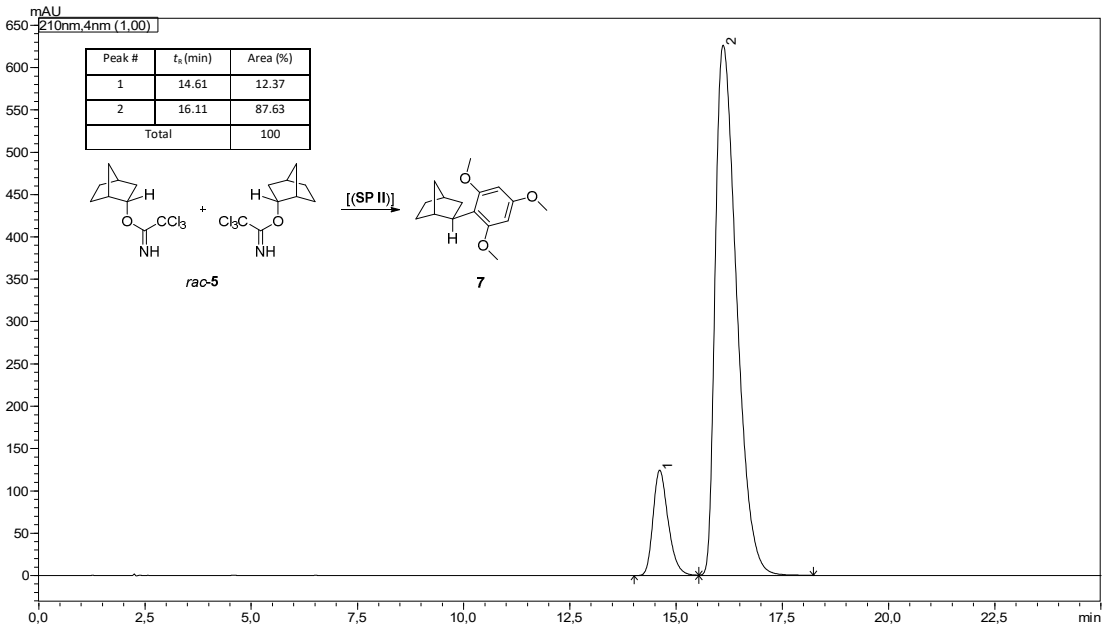
HPLC (Chiralpak® 150 mm AD-3R, 3 μm, 4.6 mm i.d.): MeCN/H_2O 55:45, 1.0 mL/min. 298 K, 210 nm.

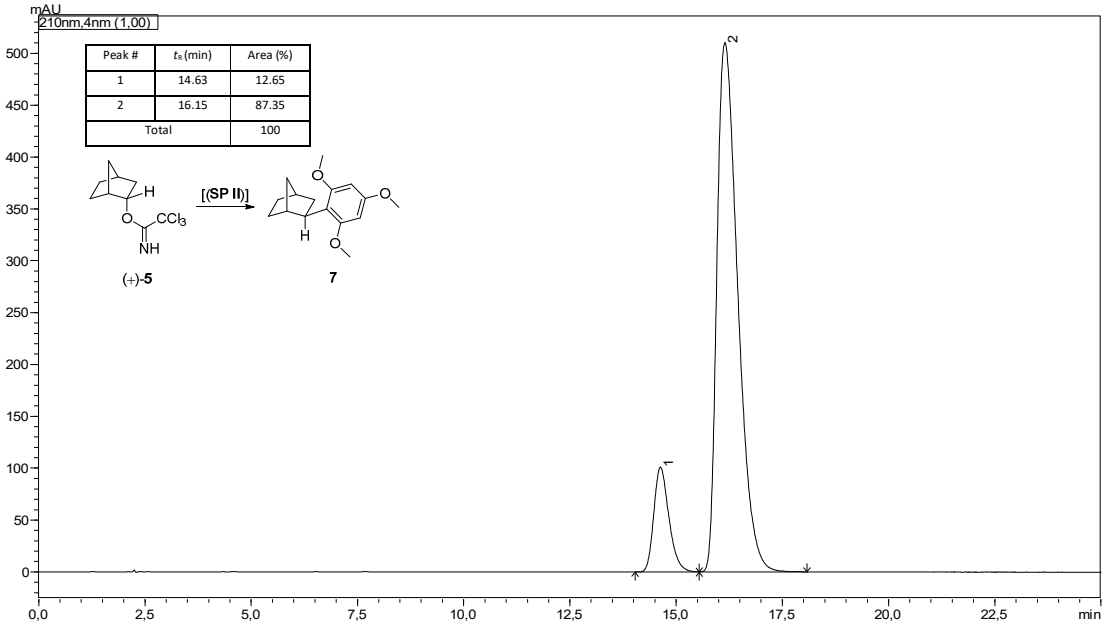


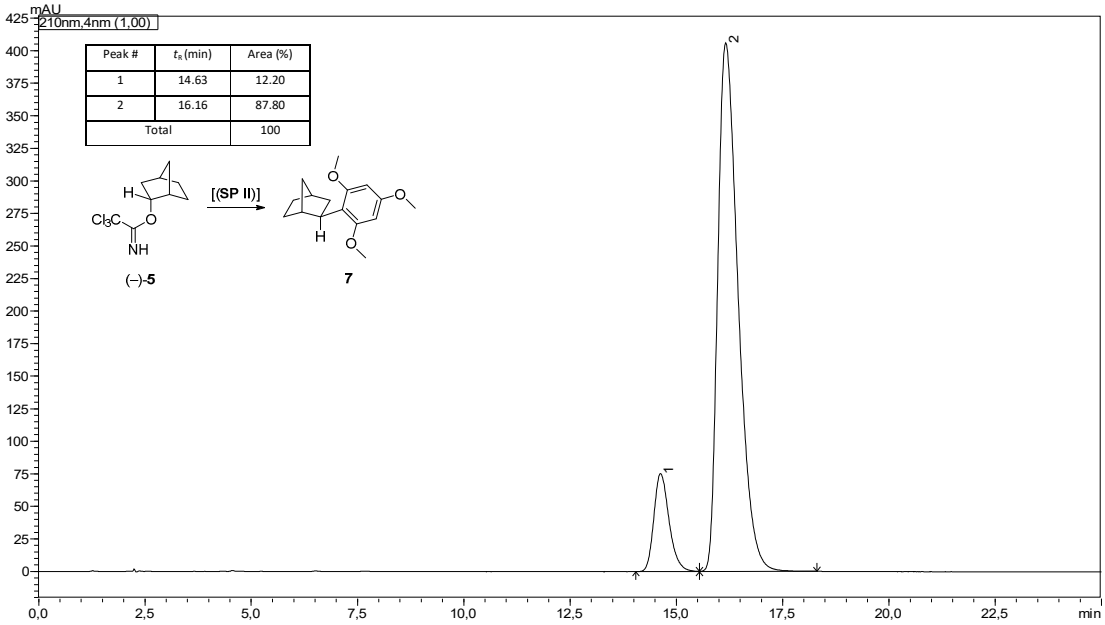


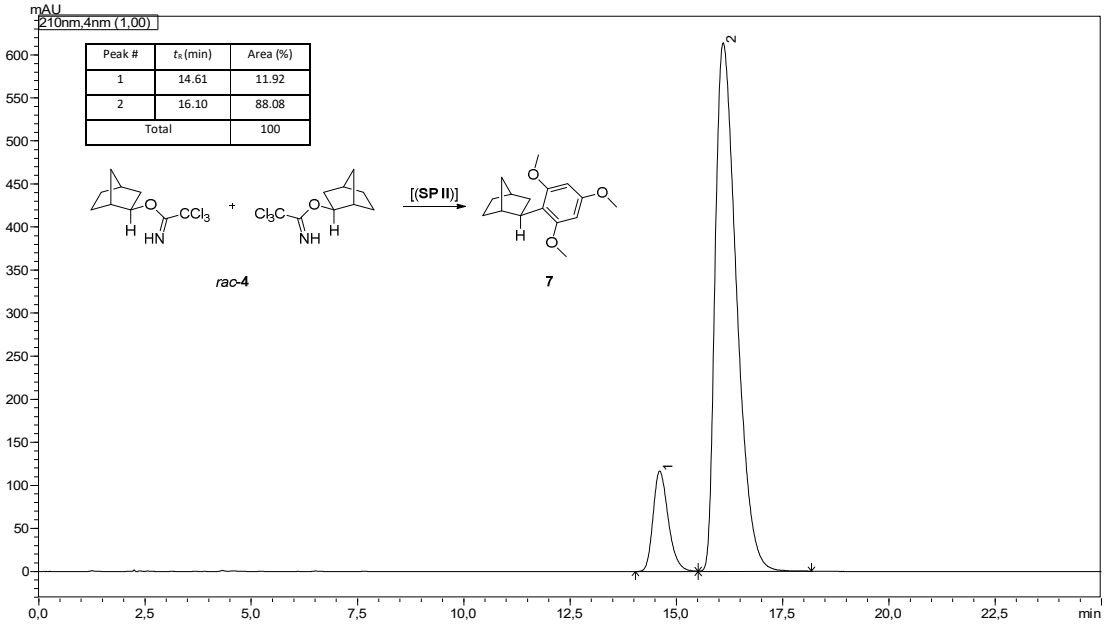

mAU
210nm4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.70 | 3.24
2 | 16.20 | 96.76
Total | | 100
[(SP I)]
(–)-4
7
1
2
min

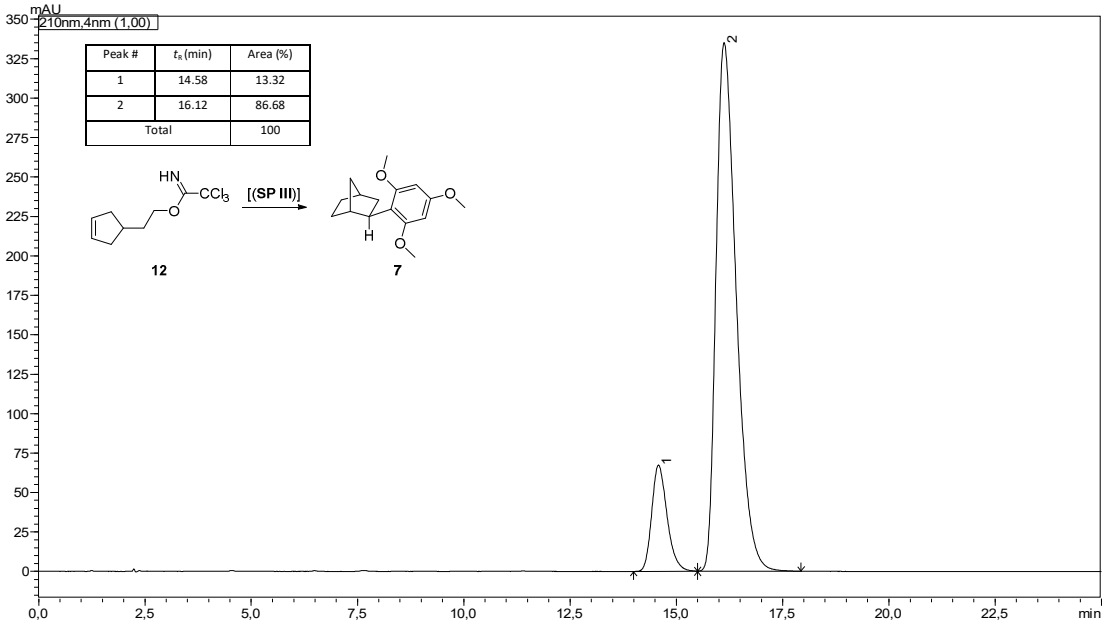

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.66 | 3.19
2 | 16.18 | 96.81
Total | | 100
[(SP I)]
(+)-4
7
1
2
min

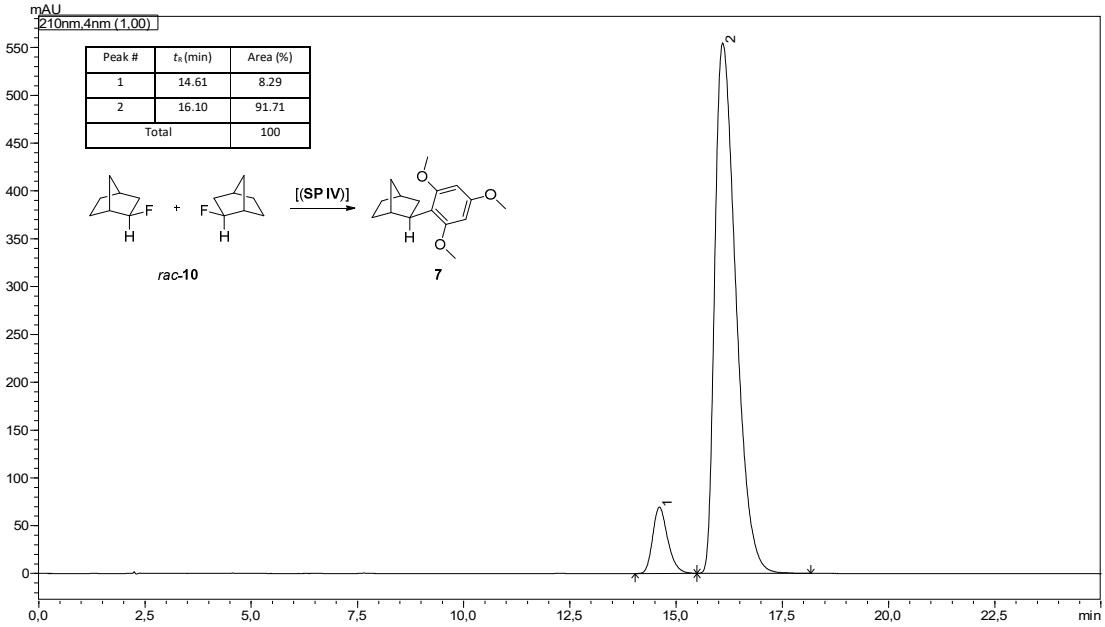

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.61 | 12.37
2 | 16.11 | 87.63
Total | | 100
[(SP II)]
rac-5
7
1
2
min

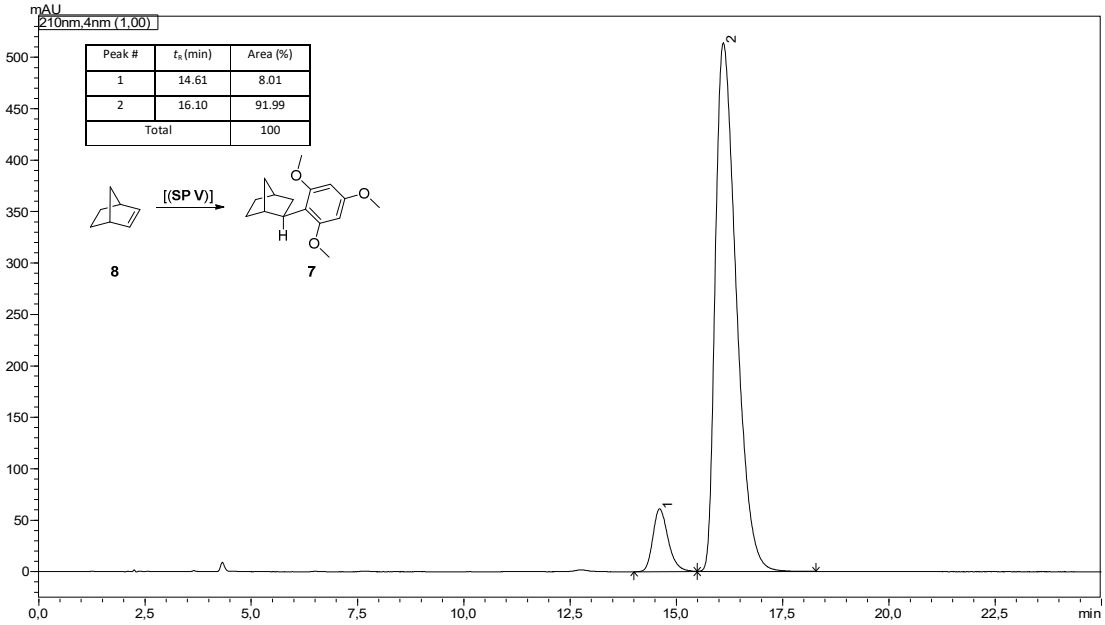

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.63 | 12.65
2 | 16.15 | 87.35
Total | | 100
[(SP II)]
(+)-5
7
1
2
min

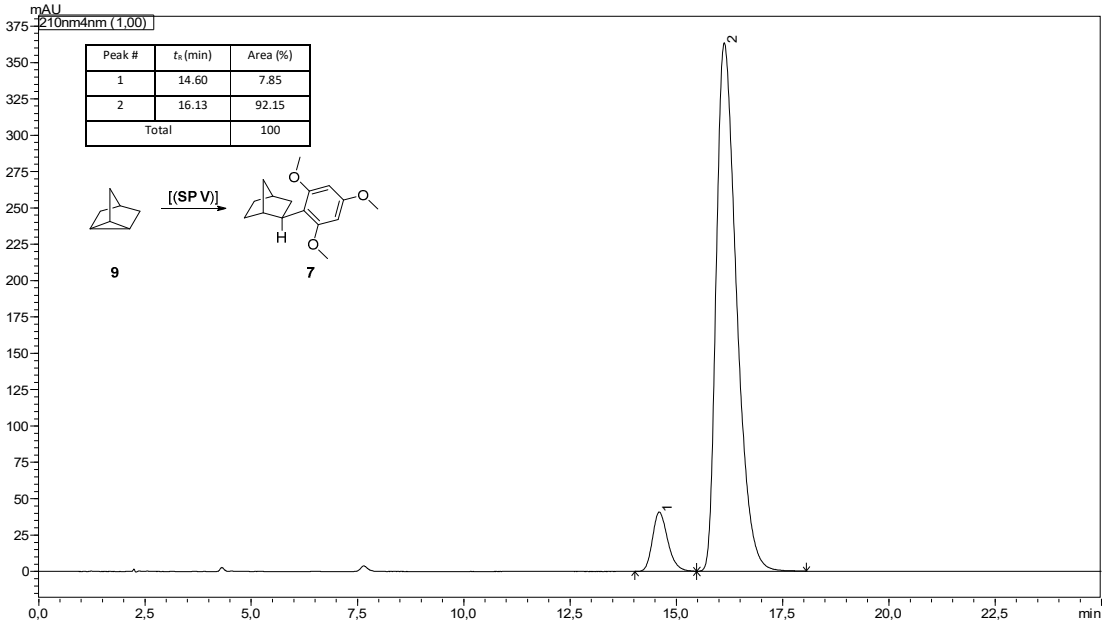

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.63 | 12.20
2 | 16.16 | 87.80
Total | | 100
[(SP II)]
(–)-5
7
1
2
min

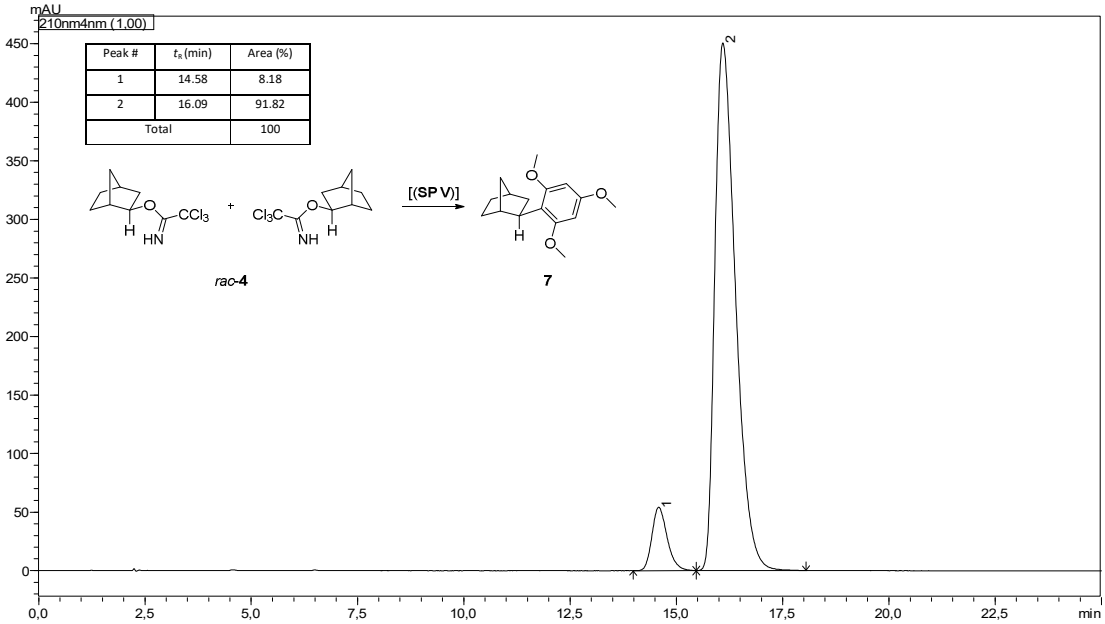

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.61 | 11.92
2 | 16.10 | 88.08
Total | | 100
[(SP II)]
rac-4
7
1
2
min


mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.58 | 13.32
2 | 16.12 | 86.68
Total | | 100
HN
CCl3
O
[(SP III)]
12
7
H
O
1
2
0,0
2,5
5,0
7,5
10,0
12,5
15,0
17,5
20,0
22,5
min

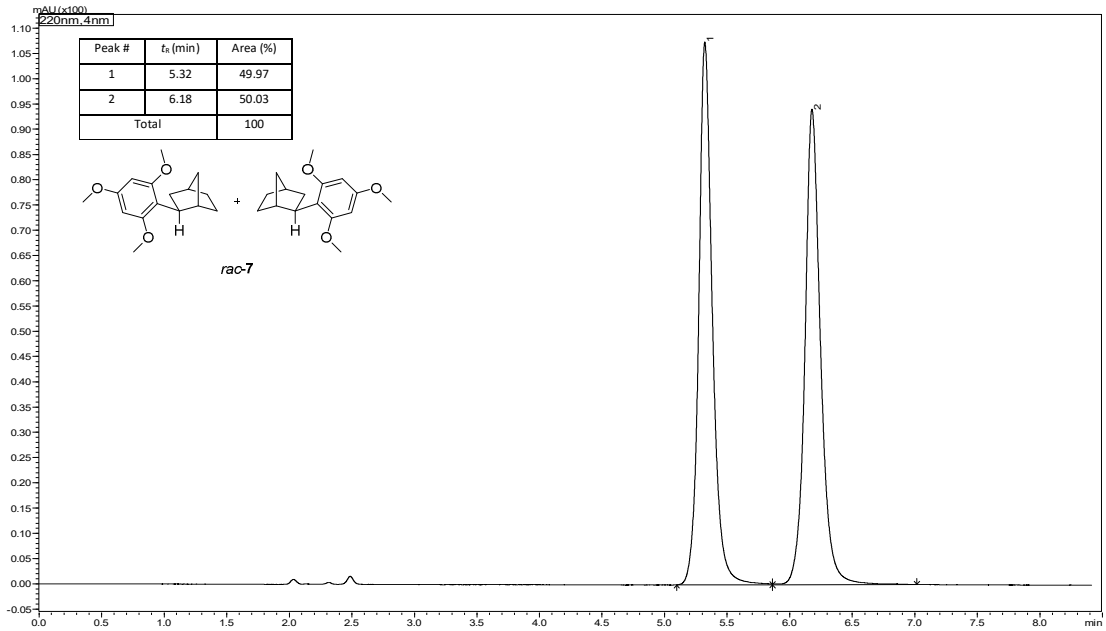

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.61 | 8.29
2 | 16.10 | 91.71
Total | | 100
F
H
+
[(SP IV)]
rac-10
7
O
1
2
0,0
2,5
5,0
7,5
10,0
12,5
15,0
17,5
20,0
22,5
min

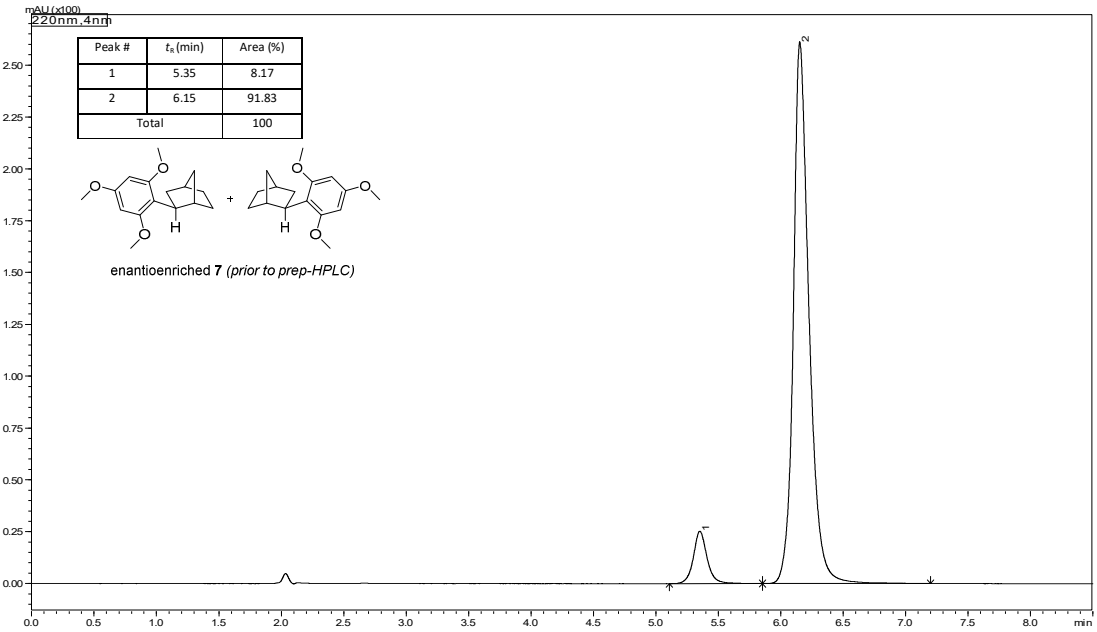

mAU
210nm,4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.61 | 8.01
2 | 16.10 | 91.99
Total | | 100
[(SP V)]
8
7
1
2
min

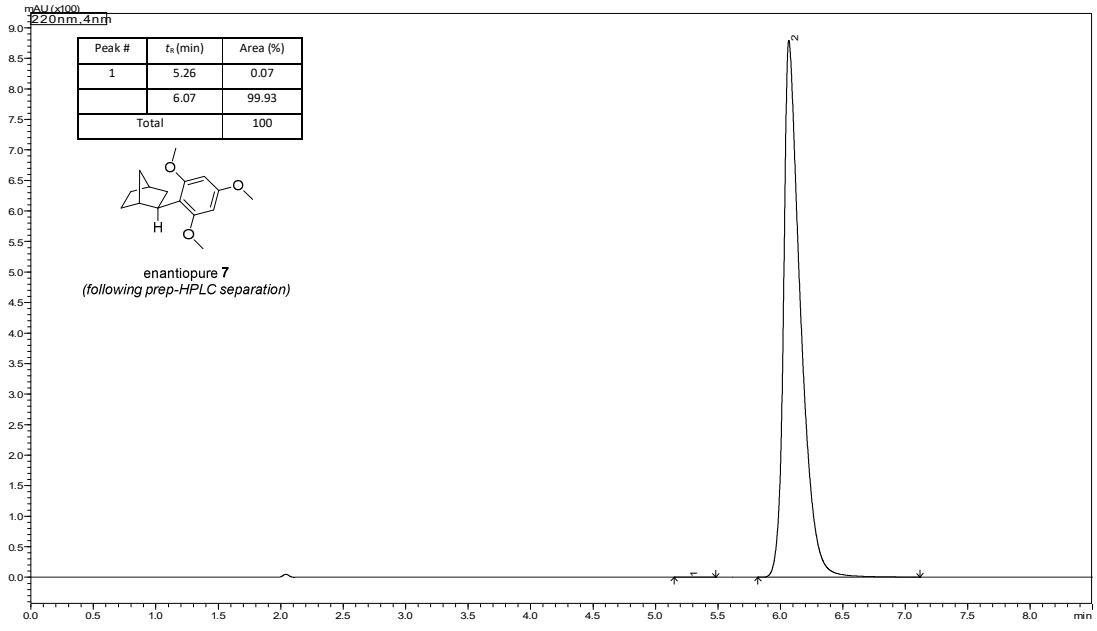

mAU
210nm4nm (1,00)
Peak # | t_R (min) | Area (%)
1 | 14.60 | 7.85
2 | 16.13 | 92.15
Total | | 100
[(SP V)]
9
7
1
2
min



HPLC (Chiralpak® 150 mm IB-3, 3 µm, 4.6 mm i.d.): MTBE/*n*-heptane 10:90, 1.0 mL/min, 298 K, 220 nm (before and after prep-HPLC).

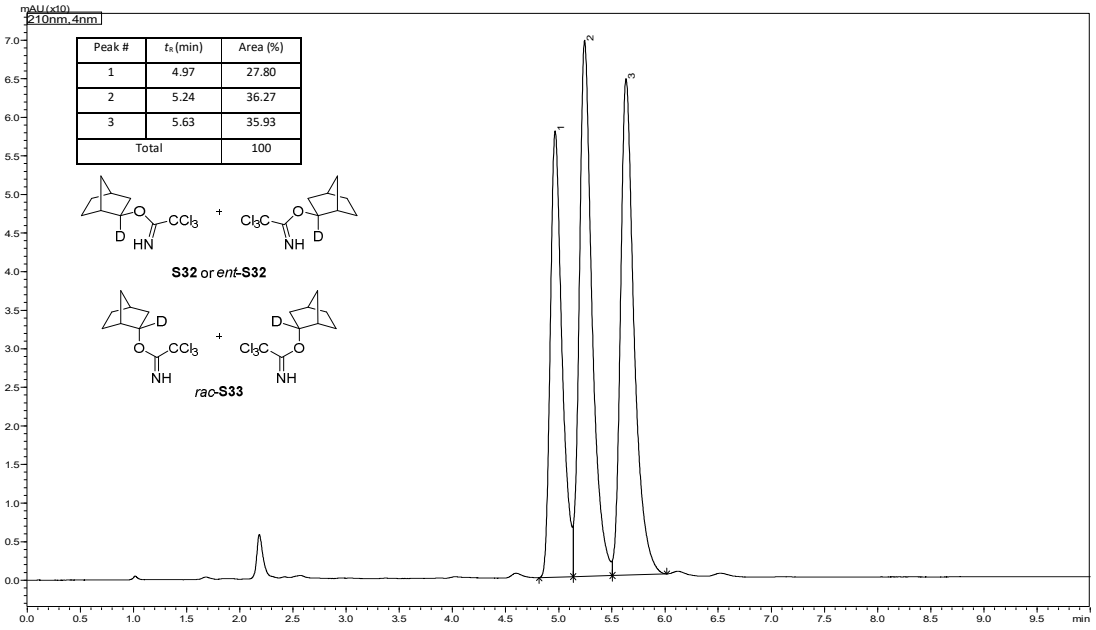


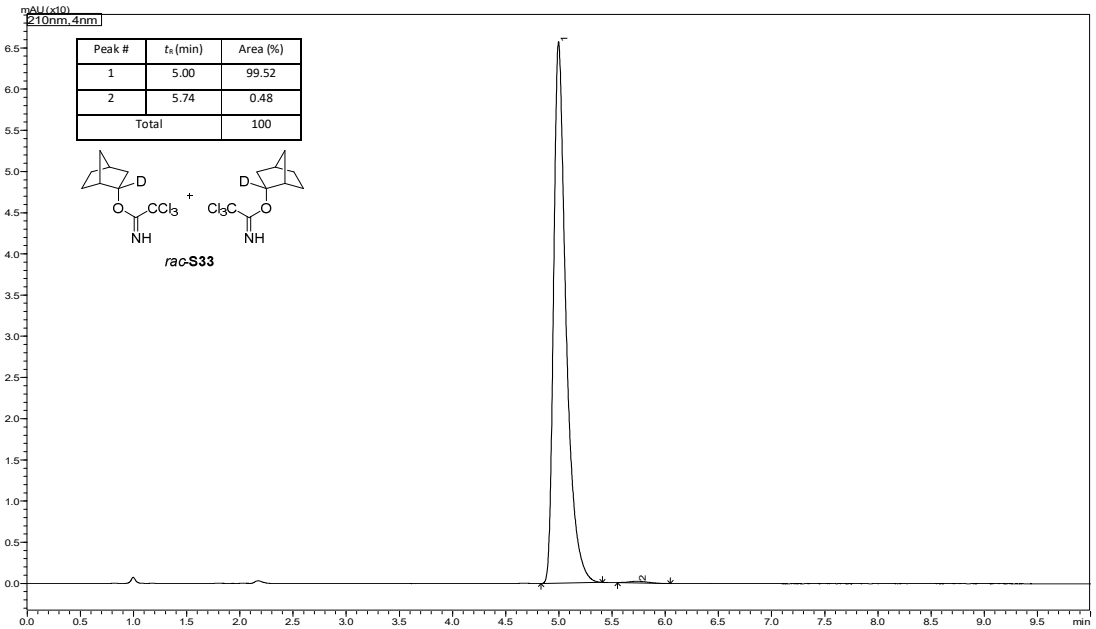

mAU (x100)
220nm,4nm
Peak # | t_R (min) | Area (%)
1 | 5.35 | 8.17
2 | 6.15 | 91.83
Total | | 100
enantioenriched **7** *(prior to prep-HPLC)*
min

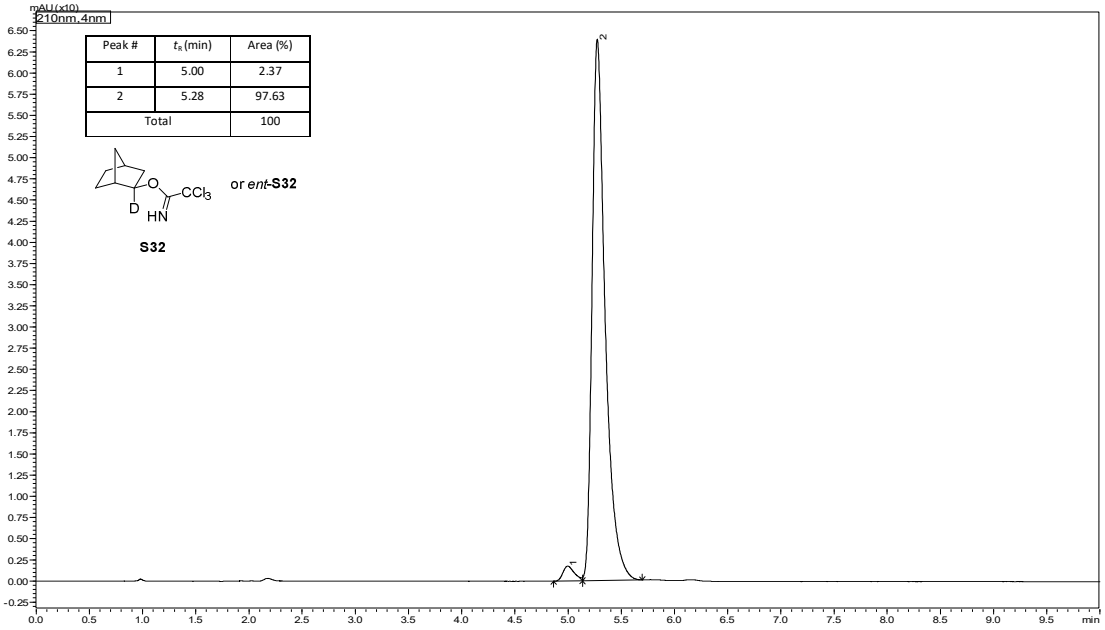

mAU (x100)
220nm,4nm
Peak # | t_R (min) | Area (%)
1 | 5.26 | 0.07
| 6.07 | 99.93
Total | | 100
enantiopure **7**
(following prep-HPLC separation)
min

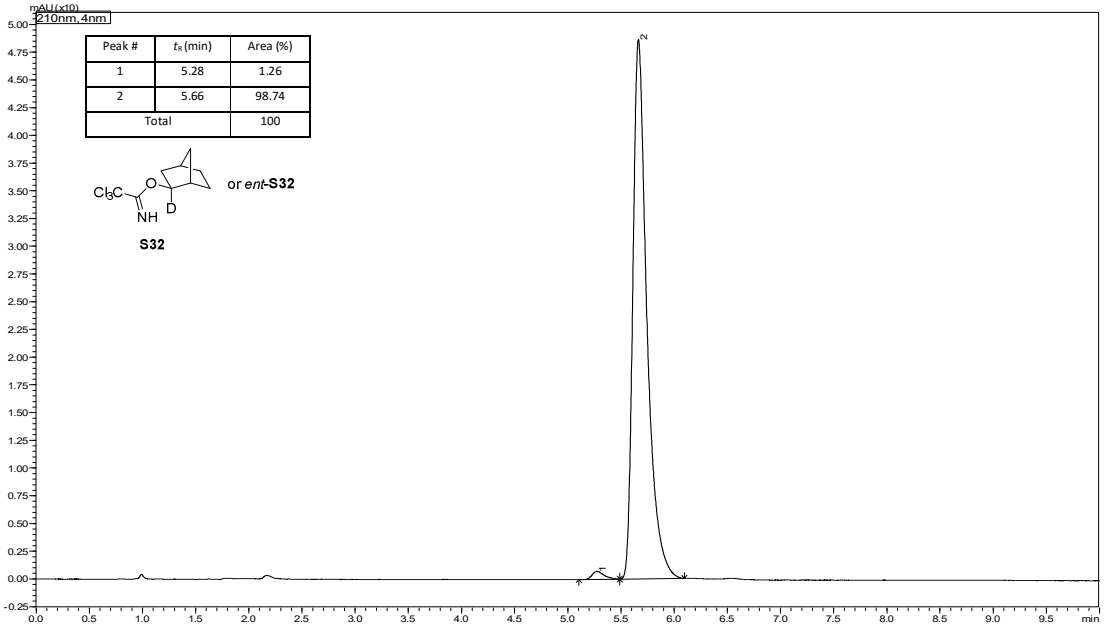
Deuterium-labelled analogues of 4 and 5 (S32 and S33)

HPLC (Chiralcel® 150 mm OJ-3R, 3 µm, 4.6 mm i.d.): MeCN/H_2O 65:35, 1.0 mL/min, 298 K, 210 nm.






mAU(x10)
210nm,4nm
Peak # | t_R(min) | Area (%)
1 | 5.00 | 2.37
2 | 5.28 | 97.63
Total | | 100
or *ent*-**S32**
S32
min


mAU(x10)
210nm,4nm
Peak # | t_R(min) | Area (%)
1 | 5.28 | 1.26
2 | 5.66 | 98.74
Total | | 100
or *ent*-**S32**
S32
min

1.4.3 X-Ray data

Determination of the crystal structure of IDPi 3 by X-ray crystallography

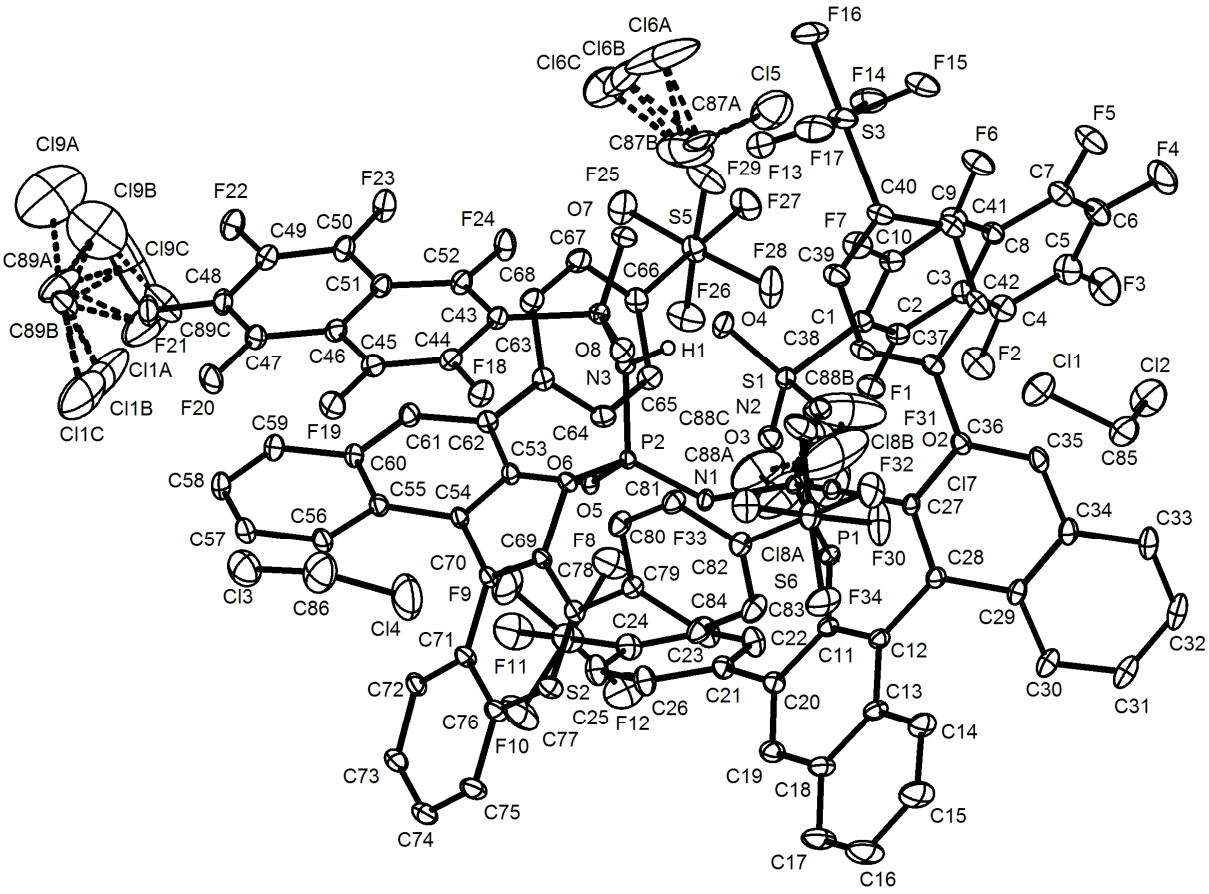
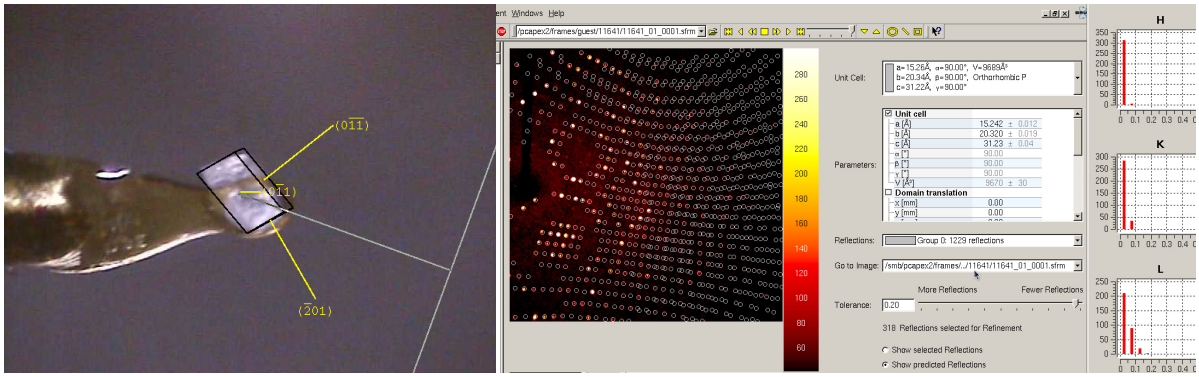


Figure 1. The molecular structure of IDPi **3**·CH_2Cl_2. Disordered dichloromethane molecules are shown with dashed bonds. H atoms have been removed for clarity.

X-ray crystal structure analysis of IDPi 3: $C_{89}H_{41}Cl_{10}F_{34}N_3O_8P_2S_6$, M_r = 2535.05 g · mol^{-1}, colorless block, crystal size 0.120 x 0.228 x 0.317 mm^3, orthorhombic, space group $P2_12_12_1$ [19], a = 15.246(2) Å, b = 20.350(3) Å, c = 31.210(4) Å, V = 9683(2) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.739 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.575 mm^{-1}, analytical absorption correction (T_{min} = 0.93251, T_{max} = 0.97219), Bruker AXS Enraf-Nonius Mach3 Kappa diffractometer with an IμS X-ray source and APEX-II detector, 1.867 < θ < 36.390°, 386775 measured reflections, 47128

independent reflections, 41336 reflections with $I > 2\sigma(I)$, $R_{int} = 0.054$. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0440$ [$I > 2\sigma(I)$], $wR_2 = 0.1236$, 1477 parameters. The absolute structure parameter has been determined as −0.001(8) via anomalous dispersion (Parsons' method, 17505 quotients).

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. **CCDC-Number: 1948386**.



INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.44	710	716	99.2	12.64	56.42	65.01	0.0243	0.0143
2.44 - 1.63	1660	1661	99.9	12.85	23.23	59.65	0.0307	0.0148
1.63 - 1.29	2371	2371	100.0	12.72	13.23	52.41	0.0362	0.0162
1.29 - 1.12	2486	2486	100.0	11.86	11.07	45.84	0.0410	0.0180
1.12 - 1.02	2338	2338	100.0	10.89	6.73	36.54	0.0510	0.0222
1.02 - 0.95	2273	2273	100.0	10.04	4.38	28.46	0.0643	0.0285
0.95 - 0.89	2554	2554	100.0	9.41	3.58	23.72	0.0747	0.0340
0.89 - 0.85	2133	2133	100.0	8.94	2.94	20.18	0.0865	0.0404
0.85 - 0.81	2601	2601	100.0	8.45	2.60	17.20	0.0959	0.0468
0.81 - 0.78	2296	2296	100.0	8.06	2.32	15.39	0.1066	0.0537
0.78 - 0.75	2677	2677	100.0	7.73	2.24	14.07	0.1128	0.0580
0.75 - 0.73	1988	1988	100.0	7.41	1.95	12.35	0.1267	0.0672
0.73 - 0.71	2277	2277	100.0	7.15	1.86	11.52	0.1361	0.0733
0.71 - 0.69	2535	2535	100.0	6.91	1.66	10.11	0.1514	0.0832
0.69 - 0.67	2835	2835	100.0	6.60	1.51	9.01	0.1652	0.0946
0.67 - 0.65	3224	3224	100.0	6.33	1.25	7.51	0.1963	0.1151
0.65 - 0.64	1773	1773	100.0	6.08	1.04	6.40	0.2325	0.1384
0.64 - 0.63	1853	1853	100.0	5.95	0.97	5.97	0.2444	0.1505
0.63 - 0.62	1977	1977	100.0	5.75	0.91	5.39	0.2620	0.1648
0.62 - 0.60	4624	4707	98.2	5.02	0.82	4.55	0.2853	0.2044
0.70 - 0.60	17566	17649	99.5	5.93	1.12	6.65	0.2122	0.1346
Inf - 0.60	47185	47275	99.8	8.19	4.80	19.82	0.0531	0.0339

B-level alert: PLAT934_ALERT_3_B Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers . 3

Several low-angle reflections were shadowed by the beam stop and removed from the dataset before the final refinement cycles. The crystal structure contains disordered and non-disordered dichloromethane solvate. The H atom on N3 was located on a difference Fourier synthesis and refined with U(H) = 1.2 U(N). The poor agreement between Fo^2 and Fc^2 for several reflections (see below) may be a result of the inability to model the electron density in the disordered solvent region of the crystal. In addition, diffracted intensities were collected with a high redundancy. This may have resulted in artificially low esd values and correspondingly high error/esd values.

```
Most Disagreeable Reflections (* if suppressed or used for Rfree).
 Error/esd is calculated as sqrt(wD^2/<wD^2>) where w is given by the weight
 formula, D = Fo^2-Fc^2 and <> refers to the average over all reflections.

     h    k    l      Fo^2          Fc^2    Error/esd  Fc/Fc(max)  Resolution(A)

     8    0    0       1429.61        362.22      12.98       0.031       1.91
     2    0   11       1347.49        347.89      12.86       0.031       2.66
     5    0    6        278.54          0.95      12.30       0.002       2.63
     4    4   15        406.54         93.33       9.56       0.016       1.72
```

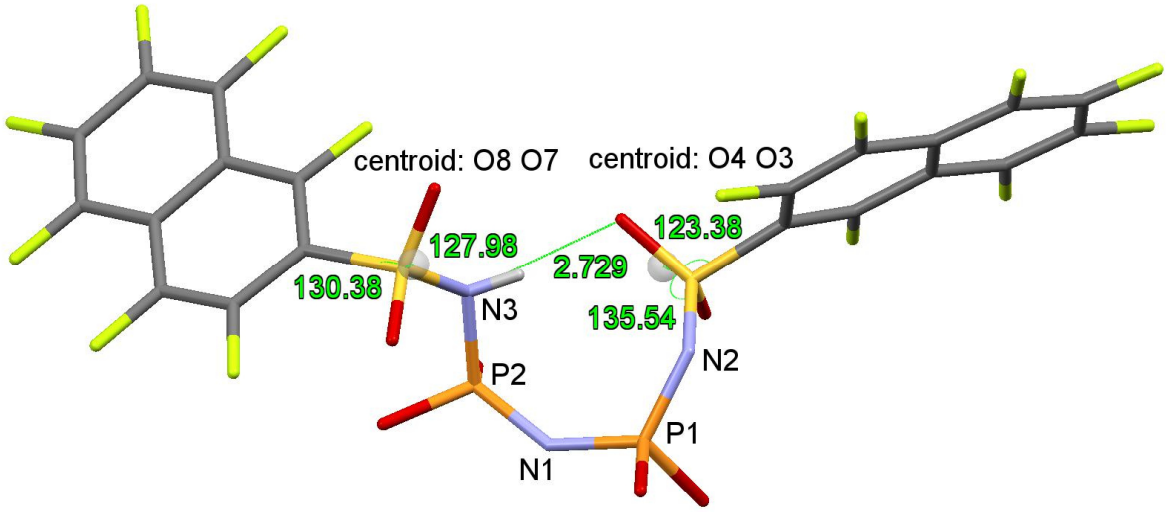


Figure 2. The geometry of the (heptafluoronaphth-2-yl)-sulfonyl-disubstituted imidophosphorimidate moiety in IDPi **3**. The white spheres represent the centroids of the respective O atoms of the sulfonyl groups.

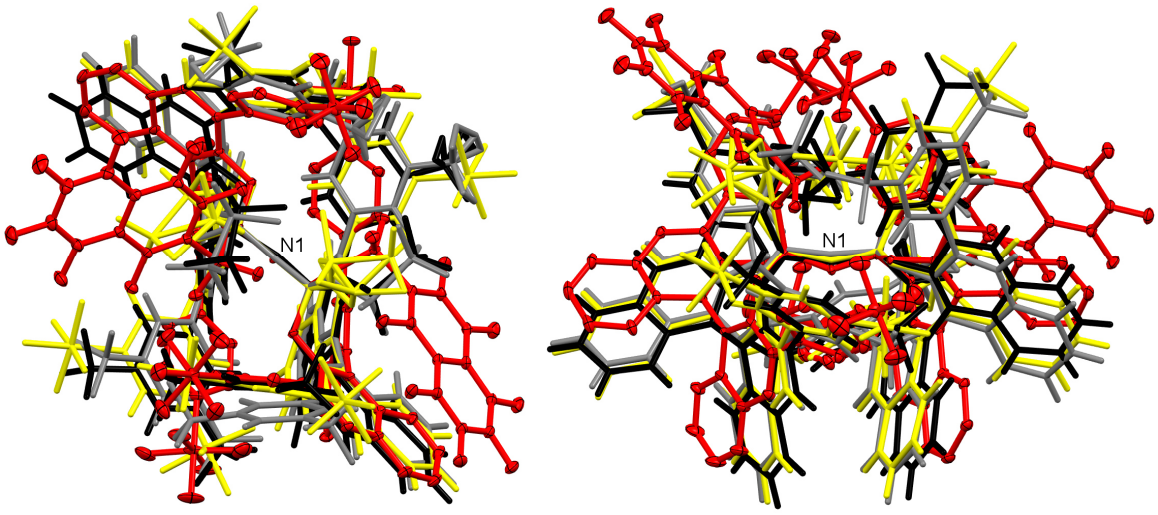


Figure 3. Top and side views showing the overlay of the –P(O_2)–N1–P(O_2)– moiety of IDPi **3** (red) with similar moieties in the published crystal structures with the CSD refcodes AWAHIR (two independent molecules, black and grey)[9] and SEFWAE (yellow)[29]. H atoms have been removed for clarity.

Table 2. Crystal data and structure refinement of IDPi 3

Identification code	11641	
Empirical formula	$C_{89}\ H_{41}\ Cl_{10}\ F_{34}\ N_3\ O_8\ P_2\ S_6$	
Color	colorless	
Formula weight	2535.05 g · mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$, (no. 19)	
Unit cell dimensions	a = 15.246(2) Å	α = 90°.
	b = 20.350(3) Å	β = 90°.
	c = 31.210(4) Å	γ = 90°.
Volume	9683(2) Å^3	
Z	4	
Density (calculated)	1.739 Mg · m^{-3}	
Absorption coefficient	0.575 mm^{-1}	
F(000)	5048 e	
Crystal size	0.317 x 0.228 x 0.120 mm^3	
θ range for data collection	1.867 to 36.390°.	
Index ranges	$-25 \le h \le 25, -33 \le k \le 33, -52 \le l \le 52$	
Reflections collected	386775	
Independent reflections	47128 [R_{int} = 0.0540]	
Reflections with $I > 2\sigma(I)$	41336	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97219 and 0.93251	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	47128 / 0 / 1477	
Goodness-of-fit on F^2	1.046	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0440	wR^2 = 0.1164
R indices (all data)	R_1 = 0.0545	wR^2 = 0.1236
Absolute structure parameter	−0.001(8)	
Extinction coefficient	0	
Largest diff. peak and hole	1.409 and −1.142 e·Å^{-3}	

Table 3. Bond lengths [Å] and angles [°] for IDPi 3

C(1)-C(2)	1.368(3)	C(1)-C(10)	1.412(3)
C(1)-S(1)	1.779(2)	C(2)-F(1)	1.337(3)
C(2)-C(3)	1.424(3)	C(3)-C(4)	1.406(3)
C(3)-C(8)	1.427(3)	C(4)-F(2)	1.348(3)
C(4)-C(5)	1.363(3)	C(5)-F(3)	1.334(3)
C(5)-C(6)	1.400(4)	C(6)-F(4)	1.329(3)
C(6)-C(7)	1.363(4)	C(7)-F(5)	1.333(3)
C(7)-C(8)	1.418(3)	C(8)-C(9)	1.409(3)
C(9)-F(6)	1.339(3)	C(9)-C(10)	1.362(3)
C(10)-F(7)	1.334(2)	C(11)-C(12)	1.378(3)
C(11)-O(1)	1.401(2)	C(11)-C(20)	1.414(3)
C(12)-C(13)	1.433(3)	C(12)-C(28)	1.483(3)
C(13)-C(14)	1.422(3)	C(13)-C(18)	1.424(3)
C(14)-C(15)	1.376(4)	C(14)-H(14)	0.9500
C(15)-C(16)	1.421(4)	C(15)-H(15)	0.9500
C(16)-C(17)	1.356(4)	C(16)-H(16)	0.9500
C(17)-C(18)	1.427(3)	C(17)-H(17)	0.9500
C(18)-C(19)	1.418(3)	C(19)-C(20)	1.379(3)
C(19)-H(19)	0.9500	C(20)-C(21)	1.483(3)
C(21)-C(22)	1.395(3)	C(21)-C(26)	1.395(3)
C(22)-C(23)	1.395(3)	C(22)-H(22)	0.9500
C(23)-C(24)	1.386(4)	C(23)-H(23)	0.9500
C(24)-C(25)	1.385(4)	C(24)-S(2)	1.806(2)
C(25)-C(26)	1.394(3)	C(25)-H(25)	0.9500
C(26)-H(26)	0.9500	C(27)-C(28)	1.381(3)
C(27)-O(2)	1.406(2)	C(27)-C(36)	1.421(3)
C(28)-C(29)	1.434(3)	C(29)-C(34)	1.421(3)
C(29)-C(30)	1.422(3)	C(30)-C(31)	1.371(3)
C(30)-H(30)	0.9500	C(31)-C(32)	1.413(4)
C(31)-H(31)	0.9500	C(32)-C(33)	1.373(4)
C(32)-H(32)	0.9500	C(33)-C(34)	1.416(3)

C(33)-H(33)	0.9500	C(34)-C(35)	1.416(3)
C(35)-C(36)	1.381(3)	C(35)-H(35)	0.9500
C(36)-C(37)	1.486(3)	C(37)-C(38)	1.401(3)
C(37)-C(42)	1.402(3)	C(38)-C(39)	1.388(3)
C(38)-H(38)	0.9500	C(39)-C(40)	1.388(3)
C(39)-H(39)	0.9500	C(40)-C(41)	1.391(3)
C(40)-S(3)	1.804(2)	C(41)-C(42)	1.390(3)
C(41)-H(41)	0.9500	C(42)-H(42)	0.9500
C(43)-C(52)	1.375(3)	C(43)-C(44)	1.414(3)
C(43)-S(4)	1.779(2)	C(44)-F(18)	1.330(3)
C(44)-C(45)	1.368(3)	C(45)-F(19)	1.331(2)
C(45)-C(46)	1.408(3)	C(46)-C(47)	1.419(3)
C(46)-C(51)	1.433(3)	C(47)-F(20)	1.332(3)
C(47)-C(48)	1.363(3)	C(48)-F(21)	1.327(3)
C(48)-C(49)	1.402(3)	C(49)-F(22)	1.331(3)
C(49)-C(50)	1.364(3)	C(50)-F(23)	1.332(3)
C(50)-C(51)	1.422(3)	C(51)-C(52)	1.415(3)
C(52)-F(24)	1.337(2)	C(53)-C(54)	1.379(3)
C(53)-O(5)	1.409(2)	C(53)-C(62)	1.421(3)
C(54)-C(55)	1.433(3)	C(54)-C(70)	1.490(3)
C(55)-C(60)	1.419(3)	C(55)-C(56)	1.424(3)
C(56)-C(57)	1.376(3)	C(56)-H(56)	0.9500
C(57)-C(58)	1.406(4)	C(57)-H(57)	0.9500
C(58)-C(59)	1.374(4)	C(58)-H(58)	0.9500
C(59)-C(60)	1.422(3)	C(59)-H(59)	0.9500
C(60)-C(61)	1.417(3)	C(61)-C(62)	1.381(3)
C(61)-H(61)	0.9500	C(62)-C(63)	1.488(3)
C(63)-C(64)	1.391(3)	C(63)-C(68)	1.402(3)
C(64)-C(65)	1.393(3)	C(64)-H(64)	0.9500
C(65)-C(66)	1.389(3)	C(65)-H(65)	0.9500
C(66)-C(67)	1.393(3)	C(66)-S(5)	1.798(2)
C(67)-C(68)	1.385(3)	C(67)-H(67)	0.9500
C(68)-H(68)	0.9500	C(69)-C(70)	1.375(3)

C(69)-C(78)	1.413(3)	C(69)-O(6)	1.415(2)
C(70)-C(71)	1.436(3)	C(71)-C(76)	1.419(3)
C(71)-C(72)	1.424(3)	C(72)-C(73)	1.378(3)
C(72)-H(72)	0.9500	C(73)-C(74)	1.418(4)
C(73)-H(73)	0.9500	C(74)-C(75)	1.365(3)
C(74)-H(74)	0.9500	C(75)-C(76)	1.415(3)
C(75)-H(75)	0.9500	C(76)-C(77)	1.420(3)
C(77)-C(78)	1.380(3)	C(77)-H(77)	0.9500
C(78)-C(79)	1.481(3)	C(79)-C(80)	1.391(3)
C(79)-C(84)	1.392(3)	C(80)-C(81)	1.387(3)
C(80)-H(80)	0.9500	C(81)-C(82)	1.387(3)
C(81)-H(81)	0.9500	C(82)-C(83)	1.385(3)
C(82)-S(6)	1.800(2)	C(83)-C(84)	1.390(3)
C(83)-H(83)	0.9500	C(84)-H(84)	0.9500
C(85)-Cl(2)	1.754(3)	C(85)-Cl(1)	1.762(3)
C(85)-H(85A)	0.9900	C(85)-H(85B)	0.9900
C(86)-Cl(4)	1.757(4)	C(86)-Cl(3)	1.767(4)
C(86)-H(86A)	0.9900	C(86)-H(86B)	0.9900
C(87A)-Cl(5)	1.697(16)	C(87A)-Cl(6B)	1.742(12)
C(87A)-Cl(6A)	1.830(16)	C(87A)-Cl(6C)	2.140(15)
C(87B)-Cl(6B)	1.69(3)	C(87B)-Cl(5)	1.84(2)
C(87B)-Cl(6C)	1.93(3)	C(87B)-Cl(6A)	2.00(3)
C(88A)-C(88C)	1.22(2)	C(88A)-Cl(8A)	1.686(9)
C(88A)-Cl(7)	1.780(11)	C(88A)-Cl(8B)	1.815(12)
C(88A)-C(88B)	1.86(6)	C(88B)-C(88C)	0.65(6)
C(88B)-Cl(8B)	1.27(5)	C(88B)-Cl(7)	2.00(4)
C(88C)-Cl(8B)	1.14(3)	C(88C)-Cl(7)	1.80(2)
C(88C)-Cl(8A)	1.86(3)	C(89A)-Cl(9B)	1.549(19)
C(89A)-Cl(9C)	1.73(2)	C(89A)-Cl(1B)	1.779(15)
C(89A)-Cl(9A)	1.913(16)	C(89A)-Cl(1C)	1.965(13)
C(89A)-Cl(1A)	1.99(2)	C(89B)-Cl(1B)	1.50(3)
C(89B)-Cl(1C)	1.640(19)	C(89B)-Cl(9B)	1.782(19)
C(89B)-Cl(9C)	1.82(2)	C(89B)-Cl(1A)	1.90(3)

C(89B)-Cl(9A)	2.223(18)	C(89C)-Cl(9C)	0.87(4)
C(89C)-Cl(9B)	1.71(3)	C(89C)-Cl(1B)	1.84(2)
Cl(1A)-Cl(9C)	1.06(4)	Cl(1A)-Cl(1B)	1.428(19)
Cl(1A)-Cl(9B)	1.838(12)	Cl(1A)-Cl(1C)	2.153(16)
Cl(1B)-Cl(1C)	0.748(14)	Cl(1B)-Cl(9C)	2.16(3)
Cl(6A)-Cl(6B)	1.107(10)	Cl(6A)-Cl(6C)	2.174(13)
Cl(6B)-Cl(6C)	1.127(9)	Cl(8A)-Cl(8B)	1.205(13)
Cl(9A)-Cl(9B)	0.996(9)	Cl(9A)-Cl(9C)	1.82(4)
Cl(9B)-Cl(9C)	0.85(4)	F(8)-S(2)	1.585(2)
F(9)-S(2)	1.588(2)	F(10)-S(2)	1.590(2)
F(11)-S(2)	1.5811(19)	F(12)-S(2)	1.597(2)
F(13)-S(3)	1.5847(19)	F(14)-S(3)	1.5858(19)
F(15)-S(3)	1.595(2)	F(16)-S(3)	1.5874(18)
F(17)-S(3)	1.5867(19)	F(25)-S(5)	1.5781(18)
F(26)-S(5)	1.5949(19)	F(27)-S(5)	1.5832(16)
F(28)-S(5)	1.5849(19)	F(29)-S(5)	1.581(2)
F(30)-S(6)	1.5829(19)	F(31)-S(6)	1.5893(18)
F(32)-S(6)	1.5868(17)	F(33)-S(6)	1.5869(17)
F(34)-S(6)	1.5900(19)	N(1)-P(2)	1.5351(18)
N(1)-P(1)	1.5747(17)	N(2)-S(1)	1.5701(19)
N(2)-P(1)	1.5753(18)	N(3)-S(4)	1.6478(18)
N(3)-P(2)	1.6497(17)	N(3)-H(1)	0.8587
O(1)-P(1)	1.5912(15)	O(2)-P(1)	1.5875(16)
O(3)-S(1)	1.4355(18)	O(4)-S(1)	1.4549(18)
O(5)-P(2)	1.5808(16)	O(6)-P(2)	1.5721(15)
O(7)-S(4)	1.4240(17)	O(8)-S(4)	1.4232(17)
C(2)-C(1)-C(10)	117.69(19)	C(2)-C(1)-S(1)	123.01(16)
C(10)-C(1)-S(1)	119.26(15)	F(1)-C(2)-C(1)	120.55(19)
F(1)-C(2)-C(3)	116.54(18)	C(1)-C(2)-C(3)	122.91(19)
C(4)-C(3)-C(2)	123.0(2)	C(4)-C(3)-C(8)	119.1(2)
C(2)-C(3)-C(8)	117.78(19)	F(2)-C(4)-C(5)	117.4(2)
F(2)-C(4)-C(3)	121.3(2)	C(5)-C(4)-C(3)	121.3(2)

F(3)-C(5)-C(4)	120.3(2)	F(3)-C(5)-C(6)	120.0(2)
C(4)-C(5)-C(6)	119.8(2)	F(4)-C(6)-C(7)	120.4(2)
F(4)-C(6)-C(5)	118.6(2)	C(7)-C(6)-C(5)	120.9(2)
F(5)-C(7)-C(6)	118.5(2)	F(5)-C(7)-C(8)	120.6(2)
C(6)-C(7)-C(8)	120.8(2)	C(9)-C(8)-C(7)	123.4(2)
C(9)-C(8)-C(3)	118.56(19)	C(7)-C(8)-C(3)	118.0(2)
F(6)-C(9)-C(10)	118.2(2)	F(6)-C(9)-C(8)	120.53(19)
C(10)-C(9)-C(8)	121.26(19)	F(7)-C(10)-C(9)	119.06(19)
F(7)-C(10)-C(1)	119.26(19)	C(9)-C(10)-C(1)	121.67(19)
C(12)-C(11)-O(1)	117.94(17)	C(12)-C(11)-C(20)	124.00(19)
O(1)-C(11)-C(20)	118.06(18)	C(11)-C(12)-C(13)	118.35(18)
C(11)-C(12)-C(28)	119.45(18)	C(13)-C(12)-C(28)	122.19(18)
C(14)-C(13)-C(18)	118.9(2)	C(14)-C(13)-C(12)	122.4(2)
C(18)-C(13)-C(12)	118.65(19)	C(15)-C(14)-C(13)	120.4(2)
C(15)-C(14)-H(14)	119.8	C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	120.2(3)	C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9	C(17)-C(16)-C(15)	120.6(2)
C(17)-C(16)-H(16)	119.7	C(15)-C(16)-H(16)	119.7
C(16)-C(17)-C(18)	120.7(2)	C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6	C(19)-C(18)-C(13)	120.0(2)
C(19)-C(18)-C(17)	120.9(2)	C(13)-C(18)-C(17)	119.0(2)
C(20)-C(19)-C(18)	121.5(2)	C(20)-C(19)-H(19)	119.3
C(18)-C(19)-H(19)	119.3	C(19)-C(20)-C(11)	117.42(19)
C(19)-C(20)-C(21)	121.40(19)	C(11)-C(20)-C(21)	121.17(19)
C(22)-C(21)-C(26)	119.0(2)	C(22)-C(21)-C(20)	120.62(19)
C(26)-C(21)-C(20)	120.3(2)	C(21)-C(22)-C(23)	120.8(2)
C(21)-C(22)-H(22)	119.6	C(23)-C(22)-H(22)	119.6
C(24)-C(23)-C(22)	118.9(2)	C(24)-C(23)-H(23)	120.6
C(22)-C(23)-H(23)	120.6	C(25)-C(24)-C(23)	121.6(2)
C(25)-C(24)-S(2)	118.87(18)	C(23)-C(24)-S(2)	119.53(19)
C(24)-C(25)-C(26)	118.9(2)	C(24)-C(25)-H(25)	120.5
C(26)-C(25)-H(25)	120.5	C(25)-C(26)-C(21)	120.8(2)
C(25)-C(26)-H(26)	119.6	C(21)-C(26)-H(26)	119.6

C(28)-C(27)-O(2)	117.80(17)	C(28)-C(27)-C(36)	123.78(18)
O(2)-C(27)-C(36)	118.43(17)	C(27)-C(28)-C(29)	118.65(18)
C(27)-C(28)-C(12)	120.11(17)	C(29)-C(28)-C(12)	121.02(18)
C(34)-C(29)-C(30)	118.86(19)	C(34)-C(29)-C(28)	118.35(19)
C(30)-C(29)-C(28)	122.6(2)	C(31)-C(30)-C(29)	120.3(2)
C(31)-C(30)-H(30)	119.8	C(29)-C(30)-H(30)	119.8
C(30)-C(31)-C(32)	121.0(2)	C(30)-C(31)-H(31)	119.5
C(32)-C(31)-H(31)	119.5	C(33)-C(32)-C(31)	119.7(2)
C(33)-C(32)-H(32)	120.2	C(31)-C(32)-H(32)	120.2
C(32)-C(33)-C(34)	120.9(2)	C(32)-C(33)-H(33)	119.5
C(34)-C(33)-H(33)	119.5	C(35)-C(34)-C(33)	120.8(2)
C(35)-C(34)-C(29)	119.93(19)	C(33)-C(34)-C(29)	119.2(2)
C(36)-C(35)-C(34)	122.20(19)	C(36)-C(35)-H(35)	118.9
C(34)-C(35)-H(35)	118.9	C(35)-C(36)-C(27)	116.59(19)
C(35)-C(36)-C(37)	120.53(18)	C(27)-C(36)-C(37)	122.74(18)
C(38)-C(37)-C(42)	118.06(19)	C(38)-C(37)-C(36)	122.61(18)
C(42)-C(37)-C(36)	119.32(19)	C(39)-C(38)-C(37)	121.04(19)
C(39)-C(38)-H(38)	119.5	C(37)-C(38)-H(38)	119.5
C(38)-C(39)-C(40)	119.2(2)	C(38)-C(39)-H(39)	120.4
C(40)-C(39)-H(39)	120.4	C(39)-C(40)-C(41)	121.4(2)
C(39)-C(40)-S(3)	119.56(18)	C(41)-C(40)-S(3)	118.97(16)
C(42)-C(41)-C(40)	118.5(2)	C(42)-C(41)-H(41)	120.8
C(40)-C(41)-H(41)	120.8	C(41)-C(42)-C(37)	121.7(2)
C(41)-C(42)-H(42)	119.2	C(37)-C(42)-H(42)	119.2
C(52)-C(43)-C(44)	117.74(19)	C(52)-C(43)-S(4)	118.64(16)
C(44)-C(43)-S(4)	123.52(16)	F(18)-C(44)-C(45)	117.58(19)
F(18)-C(44)-C(43)	121.32(19)	C(45)-C(44)-C(43)	121.1(2)
F(19)-C(45)-C(44)	118.2(2)	F(19)-C(45)-C(46)	120.1(2)
C(44)-C(45)-C(46)	121.73(19)	C(45)-C(46)-C(47)	123.4(2)
C(45)-C(46)-C(51)	118.38(19)	C(47)-C(46)-C(51)	118.3(2)
F(20)-C(47)-C(48)	118.4(2)	F(20)-C(47)-C(46)	120.8(2)
C(48)-C(47)-C(46)	120.8(2)	F(21)-C(48)-C(47)	120.8(2)
F(21)-C(48)-C(49)	118.2(2)	C(47)-C(48)-C(49)	120.9(2)

F(22)-C(49)-C(50)	120.8(2)	F(22)-C(49)-C(48)	118.8(2)
C(50)-C(49)-C(48)	120.4(2)	F(23)-C(50)-C(49)	118.8(2)
F(23)-C(50)-C(51)	120.57(19)	C(49)-C(50)-C(51)	120.6(2)
C(52)-C(51)-C(50)	123.32(19)	C(52)-C(51)-C(46)	117.75(19)
C(50)-C(51)-C(46)	118.91(19)	F(24)-C(52)-C(43)	118.55(19)
F(24)-C(52)-C(51)	118.15(19)	C(43)-C(52)-C(51)	123.26(19)
C(54)-C(53)-O(5)	119.14(17)	C(54)-C(53)-C(62)	123.63(18)
O(5)-C(53)-C(62)	117.15(16)	C(53)-C(54)-C(55)	118.33(18)
C(53)-C(54)-C(70)	120.46(17)	C(55)-C(54)-C(70)	121.19(17)
C(60)-C(55)-C(56)	118.73(19)	C(60)-C(55)-C(54)	119.04(18)
C(56)-C(55)-C(54)	122.2(2)	C(57)-C(56)-C(55)	120.2(2)
C(57)-C(56)-H(56)	119.9	C(55)-C(56)-H(56)	119.9
C(56)-C(57)-C(58)	120.9(2)	C(56)-C(57)-H(57)	119.6
C(58)-C(57)-H(57)	119.6	C(59)-C(58)-C(57)	120.2(2)
C(59)-C(58)-H(58)	119.9	C(57)-C(58)-H(58)	119.9
C(58)-C(59)-C(60)	120.4(2)	C(58)-C(59)-H(59)	119.8
C(60)-C(59)-H(59)	119.8	C(61)-C(60)-C(55)	119.42(18)
C(61)-C(60)-C(59)	121.2(2)	C(55)-C(60)-C(59)	119.4(2)
C(62)-C(61)-C(60)	122.17(19)	C(62)-C(61)-H(61)	118.9
C(60)-C(61)-H(61)	118.9	C(61)-C(62)-C(53)	116.99(18)
C(61)-C(62)-C(63)	119.80(18)	C(53)-C(62)-C(63)	123.10(18)
C(64)-C(63)-C(68)	119.09(19)	C(64)-C(63)-C(62)	121.21(19)
C(68)-C(63)-C(62)	119.55(19)	C(63)-C(64)-C(65)	120.8(2)
C(63)-C(64)-H(64)	119.6	C(65)-C(64)-H(64)	119.6
C(66)-C(65)-C(64)	118.9(2)	C(66)-C(65)-H(65)	120.5
C(64)-C(65)-H(65)	120.5	C(65)-C(66)-C(67)	121.35(19)
C(65)-C(66)-S(5)	119.75(17)	C(67)-C(66)-S(5)	118.90(17)
C(68)-C(67)-C(66)	119.0(2)	C(68)-C(67)-H(67)	120.5
C(66)-C(67)-H(67)	120.5	C(67)-C(68)-C(63)	120.8(2)
C(67)-C(68)-H(68)	119.6	C(63)-C(68)-H(68)	119.6
C(70)-C(69)-C(78)	125.18(18)	C(70)-C(69)-O(6)	117.25(17)
C(78)-C(69)-O(6)	117.55(17)	C(69)-C(70)-C(71)	117.49(18)
C(69)-C(70)-C(54)	120.41(17)	C(71)-C(70)-C(54)	122.00(17)

C(76)-C(71)-C(72)	118.34(18)	C(76)-C(71)-C(70)	118.80(18)
C(72)-C(71)-C(70)	122.80(19)	C(73)-C(72)-C(71)	120.4(2)
C(73)-C(72)-H(72)	119.8	C(71)-C(72)-H(72)	119.8
C(72)-C(73)-C(74)	120.6(2)	C(72)-C(73)-H(73)	119.7
C(74)-C(73)-H(73)	119.7	C(75)-C(74)-C(73)	120.0(2)
C(75)-C(74)-H(74)	120.0	C(73)-C(74)-H(74)	120.0
C(74)-C(75)-C(76)	120.6(2)	C(74)-C(75)-H(75)	119.7
C(76)-C(75)-H(75)	119.7	C(75)-C(76)-C(71)	119.9(2)
C(75)-C(76)-C(77)	119.7(2)	C(71)-C(76)-C(77)	120.37(19)
C(78)-C(77)-C(76)	121.3(2)	C(78)-C(77)-H(77)	119.4
C(76)-C(77)-H(77)	119.4	C(77)-C(78)-C(69)	116.79(18)
C(77)-C(78)-C(79)	121.26(19)	C(69)-C(78)-C(79)	121.95(18)
C(80)-C(79)-C(84)	119.7(2)	C(80)-C(79)-C(78)	120.65(19)
C(84)-C(79)-C(78)	119.68(19)	C(81)-C(80)-C(79)	120.4(2)
C(81)-C(80)-H(80)	119.8	C(79)-C(80)-H(80)	119.8
C(82)-C(81)-C(80)	119.0(2)	C(82)-C(81)-H(81)	120.5
C(80)-C(81)-H(81)	120.5	C(83)-C(82)-C(81)	121.7(2)
C(83)-C(82)-S(6)	119.82(17)	C(81)-C(82)-S(6)	118.47(17)
C(82)-C(83)-C(84)	118.7(2)	C(82)-C(83)-H(83)	120.7
C(84)-C(83)-H(83)	120.7	C(83)-C(84)-C(79)	120.6(2)
C(83)-C(84)-H(84)	119.7	C(79)-C(84)-H(84)	119.7
Cl(2)-C(85)-Cl(1)	111.92(16)	Cl(2)-C(85)-H(85A)	109.2
Cl(1)-C(85)-H(85A)	109.2	Cl(2)-C(85)-H(85B)	109.2
Cl(1)-C(85)-H(85B)	109.2	H(85A)-C(85)-H(85B)	107.9
Cl(4)-C(86)-Cl(3)	110.1(2)	Cl(4)-C(86)-H(86A)	109.6
Cl(3)-C(86)-H(86A)	109.6	Cl(4)-C(86)-H(86B)	109.6
Cl(3)-C(86)-H(86B)	109.6	P(2)-N(1)-P(1)	140.42(13)
S(1)-N(2)-P(1)	123.63(12)	S(4)-N(3)-P(2)	127.11(11)
S(4)-N(3)-H(1)	108.5	P(2)-N(3)-H(1)	108.5
C(11)-O(1)-P(1)	116.95(13)	C(27)-O(2)-P(1)	118.29(12)
C(53)-O(5)-P(2)	120.10(13)	C(69)-O(6)-P(2)	114.85(12)
N(1)-P(1)-N(2)	119.66(10)	N(1)-P(1)-O(2)	105.51(9)
N(2)-P(1)-O(2)	109.07(9)	N(1)-P(1)-O(1)	108.67(9)

N(2)-P(1)-O(1)	108.95(9)	O(2)-P(1)-O(1)	103.81(8)
N(1)-P(2)-O(6)	114.10(9)	N(1)-P(2)-O(5)	108.91(9)
O(6)-P(2)-O(5)	105.78(8)	N(1)-P(2)-N(3)	118.23(9)
O(6)-P(2)-N(3)	101.02(8)	O(5)-P(2)-N(3)	107.89(9)
O(3)-S(1)-O(4)	115.99(11)	O(3)-S(1)-N(2)	112.93(10)
O(4)-S(1)-N(2)	111.54(11)	O(3)-S(1)-C(1)	109.06(10)
O(4)-S(1)-C(1)	104.90(10)	N(2)-S(1)-C(1)	100.96(10)
F(11)-S(2)-F(8)	87.93(11)	F(11)-S(2)-F(9)	87.57(13)
F(8)-S(2)-F(9)	90.17(13)	F(11)-S(2)-F(10)	87.04(12)
F(8)-S(2)-F(10)	174.94(10)	F(9)-S(2)-F(10)	90.14(14)
F(11)-S(2)-F(12)	88.15(13)	F(8)-S(2)-F(12)	89.71(13)
F(9)-S(2)-F(12)	175.72(11)	F(10)-S(2)-F(12)	89.61(14)
F(11)-S(2)-C(24)	179.43(13)	F(8)-S(2)-C(24)	92.58(11)
F(9)-S(2)-C(24)	92.69(11)	F(10)-S(2)-C(24)	92.45(11)
F(12)-S(2)-C(24)	91.59(11)	F(13)-S(3)-F(14)	90.16(11)
F(13)-S(3)-F(17)	89.67(11)	F(14)-S(3)-F(17)	175.32(10)
F(13)-S(3)-F(16)	87.65(11)	F(14)-S(3)-F(16)	87.60(11)
F(17)-S(3)-F(16)	87.72(11)	F(13)-S(3)-F(15)	175.31(10)
F(14)-S(3)-F(15)	89.82(11)	F(17)-S(3)-F(15)	89.97(12)
F(16)-S(3)-F(15)	87.67(11)	F(13)-S(3)-C(40)	92.25(10)
F(14)-S(3)-C(40)	91.85(10)	F(17)-S(3)-C(40)	92.82(10)
F(16)-S(3)-C(40)	179.44(13)	F(15)-S(3)-C(40)	92.44(11)
O(8)-S(4)-O(7)	120.62(11)	O(8)-S(4)-N(3)	110.15(10)
O(7)-S(4)-N(3)	105.37(10)	O(8)-S(4)-C(43)	108.17(10)
O(7)-S(4)-C(43)	109.27(11)	N(3)-S(4)-C(43)	101.60(10)
F(25)-S(5)-F(29)	90.25(12)	F(25)-S(5)-F(27)	87.87(10)
F(29)-S(5)-F(27)	87.76(10)	F(25)-S(5)-F(28)	175.12(10)
F(29)-S(5)-F(28)	89.98(13)	F(27)-S(5)-F(28)	87.26(10)
F(25)-S(5)-F(26)	89.42(12)	F(29)-S(5)-F(26)	175.46(10)
F(27)-S(5)-F(26)	87.71(10)	F(28)-S(5)-F(26)	89.97(13)
F(25)-S(5)-C(66)	92.54(10)	F(29)-S(5)-C(66)	92.49(10)
F(27)-S(5)-C(66)	179.52(12)	F(28)-S(5)-C(66)	92.32(10)
F(26)-S(5)-C(66)	92.05(10)	F(30)-S(6)-F(32)	87.86(10)

F(30)-S(6)-F(33)	175.38(10)	F(32)-S(6)-F(33)	87.52(9)
F(30)-S(6)-F(31)	90.51(12)	F(32)-S(6)-F(31)	87.79(10)
F(33)-S(6)-F(31)	89.30(10)	F(30)-S(6)-F(34)	90.13(13)
F(32)-S(6)-F(34)	87.82(10)	F(33)-S(6)-F(34)	89.71(11)
F(31)-S(6)-F(34)	175.54(10)	F(30)-S(6)-C(82)	92.34(10)
F(32)-S(6)-C(82)	179.79(12)	F(33)-S(6)-C(82)	92.28(9)
F(31)-S(6)-C(82)	92.27(10)	F(34)-S(6)-C(82)	92.11(10)

Determination of the absolute configuration of 2-(2,4,6-trimethoxyphenyl)-bicyclo[2.2.1]heptane (7) in the sample

The absolute configuration of the sample of 2-(2,4,6-trimethoxyphenyl)-bicyclo[2.2.1]heptane (**7**) was determined using anomalous dispersion of X-rays. Four different crystals were investigated: crystals 1–3 were grown from a sample with e.r. = 97:3 and crystal 4 from a sample with e.r. > 99.9 (for crystallization details, see section 1.3.5). Three belong to one crystal form with two independent molecules in the asymmetric unit (crystals 1, 2, and 4) and one (crystal 3) is a different polymorph with five independent molecules in the asymmetric unit (one partially disordered over two positions with a refined occupancy of 0.785(7):0.215(7)). Figure 4 shows a superposition of the 8 independent molecules (one molecule in crystal 3 was disordered over two positions) in the two polymorphs. Absolute structure indicators and final R_1 indexes [$I > 2\sigma(I)$] are given in Table 4. Of the four crystals studied, none appeared to be of a different configuration or of a racemate.

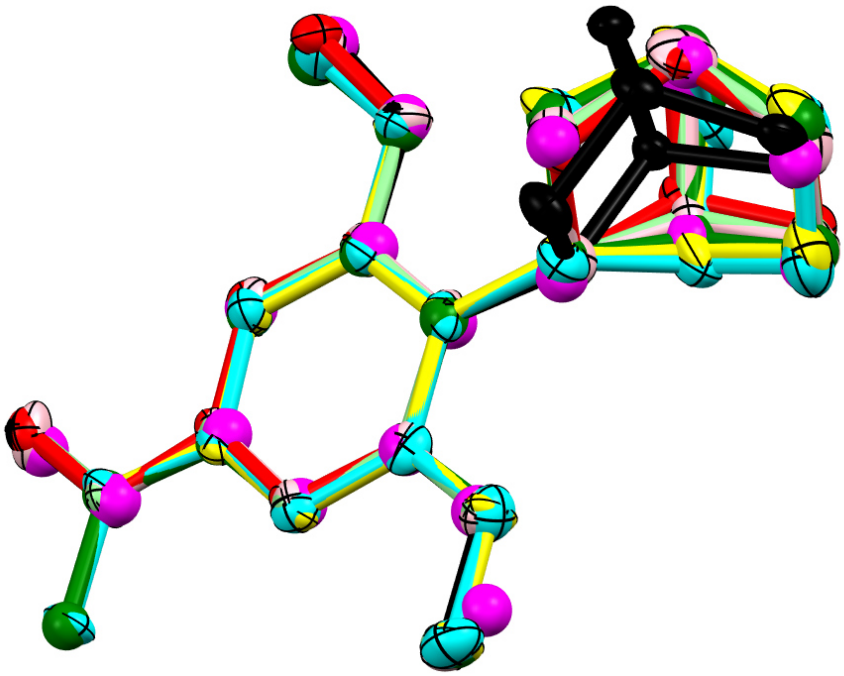


Figure 4. Superposition of the 8 independent molecules using the Mercury structure overlay function[30]. The red and black structures represent the two conformations in crystal 4. The green and magenta structures represent respectively the major and minor components of the disorded molecule in crystal 3.

Crystal (identification code)	Parsons parameter[31] (*SHELXL*)	Friedel pair coverage	Quotients [(I+)−(I−)]/ [(I+)+(I−)][1]	R_1 [$I > 2\sigma(I)$]	Flack parameter[32] (*SHELXL*)	Hooft parameter[33] (*PLATON*)
1 (11948)	0.13(22)	0.917	1523	0.0547	−0.02(35)	0.04(18)
2 (11954)	−0.15(14)	0.868	1567	0.0443	−0.24(26)	−0.15(11)
3 (11955)	0.11(13)	0.700	3514	0.0773	0.08(29)	0.14(9)
4 (12370)	0.03(4)	0.875	1964	0.0271	0.00(17)	0.02(3)

Table 4. Comparison of absolute configuration indicators for the four crystals that were investigated.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. **CCDC-Numbers: 2021275 for 1, 1948044 for 2, 1948043 for 3 and 2021276 for 4**.

Single crystal structure analysis of 7, crystal 1

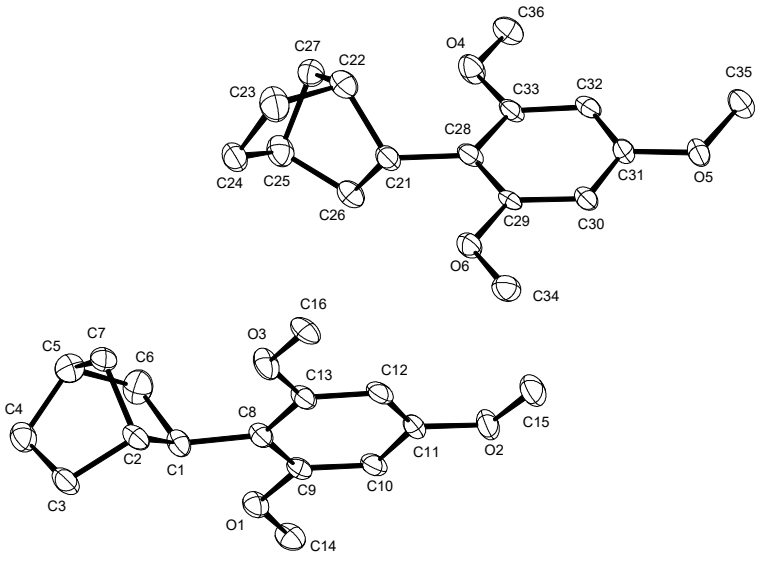
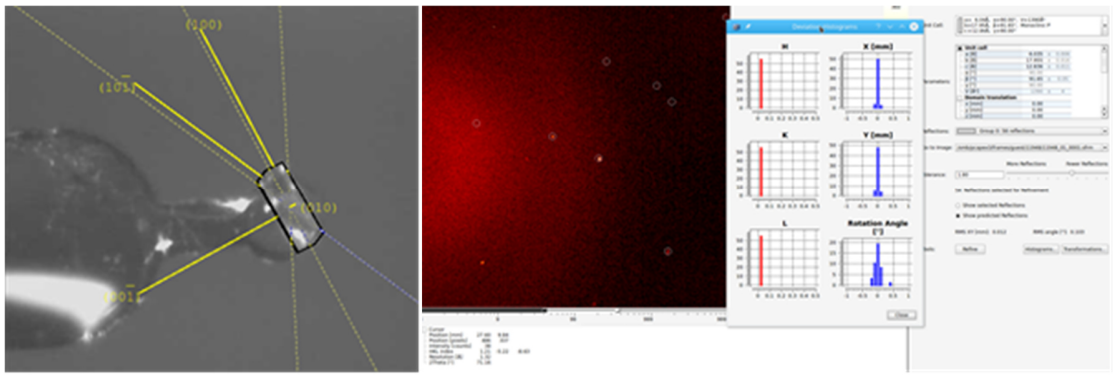


Figure 5. The molecular structure of 2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane, showing the two independent molecules in the asymmetric unit. H atoms have been removed for clarity.

X-ray crystal structure analysis of 7, crystal 1 (11948)**:** $C_{16}H_{22}O_3$, M_r = 262.33 g · mol^{-1}, colorless prism, crystal size 0.171 x 0.071 x 0.060 mm^3, monoclinic, space group $P2_1$ [4], a = 6.0319(3) Å, b = 17.9502(9) Å, c = 12.8415(6) Å, β = 91.722(3) °, V = 1389.77(12) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.254 g · cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 0.681 mm^{-1}, analytical absorption correction (T_{min} = 0.90471, T_{max} = 0.96256), Bruker AXS Enraf-Nonius Mach3 Proteum diffractometer with a FR591 rotating anode X-ray source and APEX-II detector, 6.016 < θ < 72.008 °, 46374 measured reflections, 5143 independent reflections, 3879 reflections with $I > 2\sigma(I)$, R_{int} = 0.1582. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0564 [$I > 2\sigma(I)$], wR_2 = 0.1602, 374 parameters, 1 restraint. The absolute structure parameter has been determined as 0.13(22) via anomalous dispersion (Parsons' method, 1523 quotients).



INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.29	78	86	90.7	2.87	260.22	12.68	0.0396	0.0697
3.29 - 2.24	181	183	98.9	2.97	68.21	12.92	0.0475	0.0731
2.24 - 1.77	263	263	100.0	5.91	62.90	17.20	0.0596	0.0531
1.77 - 1.55	255	255	100.0	5.79	32.96	15.60	0.0749	0.0573
1.55 - 1.41	266	270	98.5	5.21	26.74	13.10	0.0856	0.0652
1.41 - 1.31	263	263	100.0	4.75	20.87	11.52	0.1040	0.0725
1.31 - 1.23	247	255	96.9	9.64	19.90	13.67	0.1431	0.0648
1.23 - 1.16	295	306	96.4	13.85	32.76	18.24	0.1302	0.0448
1.16 - 1.12	213	216	98.6	13.52	25.39	14.96	0.1250	0.0523
1.12 - 1.07	286	300	95.3	12.80	17.83	13.89	0.1665	0.0605
1.07 - 1.03	271	281	96.4	12.31	16.24	11.22	0.1665	0.0689
1.03 - 0.99	310	334	92.8	12.81	11.72	10.66	0.2326	0.0803
0.99 - 0.97	193	200	96.5	12.19	8.55	7.63	0.2956	0.1204
0.97 - 0.94	292	314	93.0	11.62	7.85	7.75	0.3046	0.1178
0.94 - 0.92	228	246	92.7	11.37	5.75	6.54	0.3602	0.1542

0.92 - 0.90	227	241	94.2	11.09	6.17	6.54	0.3607	0.1474
0.90 - 0.87	369	412	89.6	9.81	3.94	4.78	0.4104	0.2143
0.87 - 0.86	137	146	93.8	6.61	3.45	3.24	0.4338	0.3716
0.86 - 0.84	330	368	89.7	2.22	3.55	1.60	0.3809	0.6762
0.84 - 0.82	322	365	88.2	2.08	2.79	1.35	0.4604	0.8087
0.82 - 0.81	125	197	63.5	1.15	3.23	1.38	0.3426	0.7546
0.91 - 0.81	1406	1617	87.0	5.06	3.72	2.95	0.3950	0.4638
Inf - 0.81	5151	5501	93.6	8.37	22.20	9.83	0.1461	0.0845

B-level alert: PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.955

Owing to its small size, the crystal diffracted poorly at high angles and the intensities of the reflections could not be satisfactorily integrated. Please see above table for the complete intensity statistics of the data set.

Table 5. Crystal data and structure refinement of crystal 1

Identification code	11948	
Empirical formula	$C_{16}H_{22}O_3$	
Color	colorless	
Formula weight	262.33 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1$, (No. 4)	
Unit cell dimensions	a = 6.0319(3) Å	$\alpha = 90°$.
	b = 17.9502(9) Å	$\beta = 91.722(3)°$.
	c = 12.8415(6) Å	$\gamma = 90°$.
Volume	1389.77(12) $Å^3$	
Z	4	
Density (calculated)	1.254 $Mg \cdot m^{-3}$	
Absorption coefficient	0.681 mm^{-1}	
F(000)	568 e	
Crystal size	0.171 x 0.071 x 0.060 mm^3	
θ range for data collection	6.016 to 72.008°.	
Index ranges	$-7 \le h \le 7, -21 \le k \le 22, -15 \le l \le 15$	
Reflections collected	46374	
Independent reflections	5143 [R_{int} = 0.1582]	
Reflections with $I > 2\sigma(I)$	3879	

Completeness to θ = 67.679°	95.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.96256 and 0.90471	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5143 / 1 / 374	
Goodness-of-fit on F^2	1.023	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0564	wR^2 = 0.1397
R indices (all data)	R_1 = 0.0909	wR^2 = 0.1602
Absolute structure parameter	0.13(22)	
Extinction coefficient	0.0103(17)	
Largest diff. peak and hole	0.327 and −0.290 e $Å^{-3}$	

Table 6. Bond lengths [Å] and angles [°] for crystal 1

O(1)-C(9)	1.380(5)	O(1)-C(14)	1.427(5)
O(2)-C(11)	1.368(5)	O(2)-C(15)	1.419(5)
O(3)-C(13)	1.371(5)	O(3)-C(16)	1.425(5)
C(1)-C(8)	1.511(6)	C(1)-C(2)	1.560(6)
C(1)-C(6)	1.563(6)	C(2)-C(3)	1.531(6)
C(2)-C(7)	1.548(6)	C(3)-C(4)	1.552(7)
C(4)-C(5)	1.530(7)	C(5)-C(6)	1.533(7)
C(5)-C(7)	1.538(7)	C(8)-C(13)	1.393(6)
C(8)-C(9)	1.413(6)	C(9)-C(10)	1.378(6)
C(10)-C(11)	1.394(6)	C(11)-C(12)	1.396(6)
C(12)-C(13)	1.406(6)	O(4)-C(33)	1.364(5)
O(4)-C(36)	1.429(5)	O(5)-C(31)	1.380(5)
O(5)-C(35)	1.430(6)	O(6)-C(29)	1.383(5)
O(6)-C(34)	1.426(6)	C(21)-C(28)	1.509(6)
C(21)-C(26)	1.546(7)	C(21)-C(22)	1.580(7)
C(22)-C(27)	1.515(7)	C(22)-C(23)	1.534(7)
C(23)-C(24)	1.562(7)	C(24)-C(25)	1.534(7)
C(25)-C(26)	1.522(7)	C(25)-C(27)	1.545(7)
C(28)-C(33)	1.402(6)	C(28)-C(29)	1.403(6)
C(29)-C(30)	1.394(6)	C(30)-C(31)	1.384(7)

C(31)-C(32)	1.388(7)	C(32)-C(33)	1.405(6)
C(9)-O(1)-C(14)	117.8(4)	C(11)-O(2)-C(15)	118.0(4)
C(13)-O(3)-C(16)	119.6(4)	C(8)-C(1)-C(2)	120.9(4)
C(8)-C(1)-C(6)	113.7(4)	C(2)-C(1)-C(6)	102.3(4)
C(3)-C(2)-C(7)	99.1(4)	C(3)-C(2)-C(1)	106.2(4)
C(7)-C(2)-C(1)	103.8(4)	C(2)-C(3)-C(4)	103.6(4)
C(5)-C(4)-C(3)	103.1(4)	C(4)-C(5)-C(6)	109.1(4)
C(4)-C(5)-C(7)	102.2(4)	C(6)-C(5)-C(7)	100.5(4)
C(5)-C(6)-C(1)	103.2(4)	C(5)-C(7)-C(2)	94.4(4)
C(13)-C(8)-C(9)	115.5(4)	C(13)-C(8)-C(1)	126.4(4)
C(9)-C(8)-C(1)	118.1(4)	C(10)-C(9)-O(1)	122.5(4)
C(10)-C(9)-C(8)	123.0(4)	O(1)-C(9)-C(8)	114.5(4)
C(9)-C(10)-C(11)	119.4(4)	O(2)-C(11)-C(10)	115.0(4)
O(2)-C(11)-C(12)	124.4(4)	C(10)-C(11)-C(12)	120.6(4)
C(11)-C(12)-C(13)	118.0(4)	O(3)-C(13)-C(8)	115.5(4)
O(3)-C(13)-C(12)	121.0(4)	C(8)-C(13)-C(12)	123.5(4)
C(33)-O(4)-C(36)	119.4(3)	C(31)-O(5)-C(35)	117.7(4)
C(29)-O(6)-C(34)	118.4(3)	C(28)-C(21)-C(26)	117.1(4)
C(28)-C(21)-C(22)	119.2(4)	C(26)-C(21)-C(22)	101.1(3)
C(27)-C(22)-C(23)	99.6(4)	C(27)-C(22)-C(21)	105.1(4)
C(23)-C(22)-C(21)	105.1(4)	C(22)-C(23)-C(24)	102.3(4)
C(25)-C(24)-C(23)	103.1(4)	C(26)-C(25)-C(24)	109.8(4)
C(26)-C(25)-C(27)	99.6(4)	C(24)-C(25)-C(27)	101.8(4)
C(25)-C(26)-C(21)	103.7(4)	C(22)-C(27)-C(25)	94.6(4)
C(33)-C(28)-C(29)	115.7(4)	C(33)-C(28)-C(21)	124.2(4)
C(29)-C(28)-C(21)	120.0(4)	O(6)-C(29)-C(30)	121.6(4)
O(6)-C(29)-C(28)	115.6(4)	C(30)-C(29)-C(28)	122.8(4)
C(31)-C(30)-C(29)	118.6(4)	O(5)-C(31)-C(30)	114.3(4)
O(5)-C(31)-C(32)	123.7(4)	C(30)-C(31)-C(32)	122.0(4)
C(31)-C(32)-C(33)	117.4(4)	O(4)-C(33)-C(28)	114.7(4)
O(4)-C(33)-C(32)	121.9(4)	C(28)-C(33)-C(32)	123.4(4)

Single crystal structure analysis of 7, crystal 2

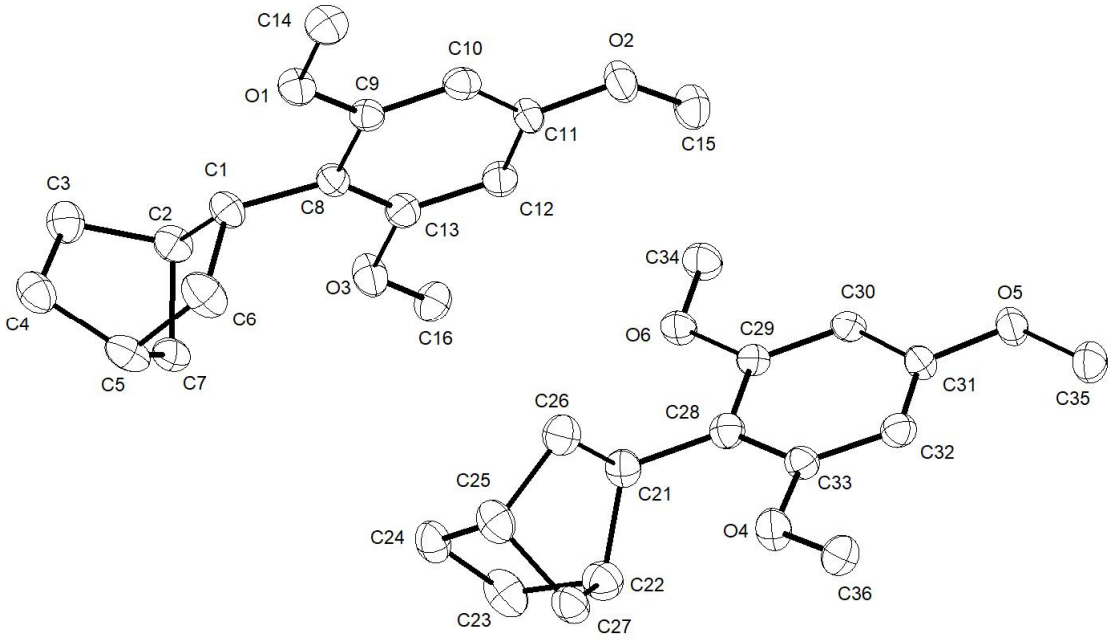
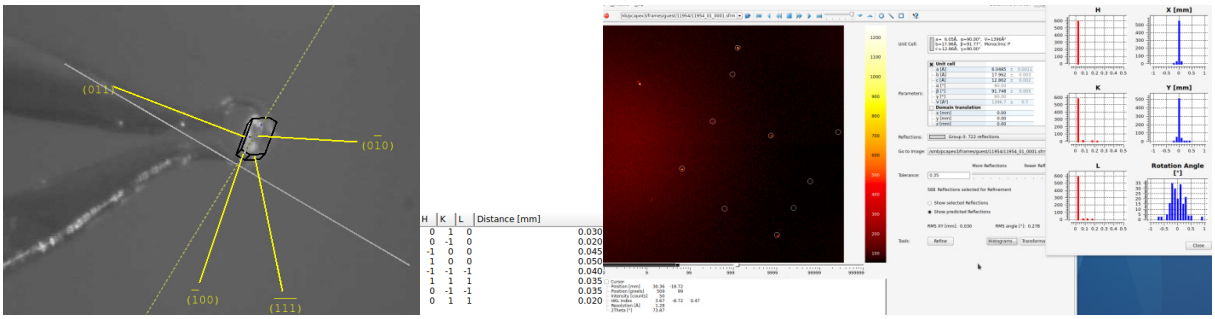


Figure 6. The molecular structure of 2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane, crystal 2.

X-ray crystal structure analysis of 7, **crystal 2** (11954): C_{16} H_{22} O_3, M_r = 262.33 g · mol^{-1}, colorless prism, crystal size 0.137 x 0.102 x 0.061 mm^3, monoclinic, space group $P2_1$ [4], a = 6.0400(4) Å, b = 17.9375(10) Å, c = 12.8404(7) Å, β = 91.770(3) °, V = 1390.50(14) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.253 g · cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 0.680 mm^{-1}, analytical absorption correction (T_{min} = 0.94562, T_{max} = 0.97541), Bruker AXS Enraf-Nonius Mach3 Proteum diffractometer with a FR591 rotating anode X-ray source and APEX II detector, 4.931 < θ < 72.226 °, 43201 measured reflections, 5278 independent reflections, 3956 reflections with $I > 2\sigma(I)$, R_{int} = 0.1366. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0443 [$I > 2\sigma(I)$], wR_2 = 0.1125, 374 parameters, 1 restraint. The absolute structure parameter has been determined as −0.16(14) via anomalous dispersion (Parsons' method, 1567 quotients).



INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.09	80	99	80.8	2.93	270.33	24.50	0.0357	0.0370
3.09 - 2.12	184	209	88.0	3.28	65.36	24.91	0.0387	0.0372
2.12 - 1.73	270	273	98.9	6.01	58.96	29.21	0.0408	0.0329
1.73 - 1.51	267	268	99.6	5.72	30.70	23.31	0.0457	0.0409
1.51 - 1.38	273	274	99.6	4.93	23.29	18.65	0.0594	0.0477
1.38 - 1.28	278	282	98.6	4.38	18.32	15.29	0.0760	0.0611
1.28 - 1.20	269	275	97.8	11.96	22.02	20.10	0.1390	0.0453
1.20 - 1.15	241	245	98.4	12.73	28.23	21.00	0.1235	0.0404
1.15 - 1.10	273	279	97.8	12.34	21.31	17.90	0.1384	0.0481
1.10 - 1.06	259	266	97.4	11.81	15.29	14.58	0.1665	0.0566
1.06 - 1.02	280	287	97.6	11.10	14.46	13.48	0.1693	0.0622
1.02 - 0.99	251	257	97.7	11.91	11.17	11.75	0.2387	0.0763
0.99 - 0.96	298	303	98.3	11.63	8.46	9.06	0.3015	0.0987
0.96 - 0.93	337	348	96.8	10.50	6.74	7.66	0.3784	0.1225
0.93 - 0.91	217	223	97.3	10.40	6.07	7.70	0.3606	0.1260
0.91 - 0.89	260	267	97.4	9.82	5.57	6.77	0.3293	0.1338
0.89 - 0.87	257	266	96.6	9.12	3.61	5.05	0.4364	0.1909
0.87 - 0.85	315	331	95.2	3.93	3.39	2.15	0.4904	0.5760
0.85 - 0.84	174	186	93.5	2.18	3.18	1.38	0.4918	0.7893
0.84 - 0.82	351	368	95.4	2.14	2.86	1.11	0.5254	0.8626
0.82 - 0.81	155	213	72.8	1.19	2.23	0.94	0.4797	1.1396
0.91 - 0.81	1512	1631	92.7	4.78	3.54	2.98	0.4009	0.5017
Inf - 0.81	5289	5519	95.8	7.84	20.80	12.73	0.1316	0.0692

Table 7. Crystal data and structure refinement for crystal 2

Identification code	11954	
Empirical formula	$C_{16}\ H_{22}\ O_3$	
Color	colorless	
Formula weight	262.33 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1$, (No. 4)	
Unit cell dimensions	a = 6.0400(4) Å	$\alpha = 90°$.
	b = 17.9375(10) Å	$\beta = 91.770(3)°$.
	c = 12.8404(7) Å	$\gamma = 90°$.
Volume	1390.50(14) $Å^3$	
Z	4	
Density (calculated)	1.253 $Mg \cdot m^{-3}$	
Absorption coefficient	0.680 mm^{-1}	
F(000)	568 e	
Crystal size	0.137 x 0.102 x 0.061 mm^3	
θ range for data collection	4.931 to 72.226°.	
Index ranges	$-7 \le h \le 7, -22 \le k \le 22, -15 \le l \le 15$	
Reflections collected	43201	
Independent reflections	5278 [R_{int} = 0.1366]	
Reflections with $I > 2\sigma(I)$	3956	
Completeness to θ = 67.679°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97541 and 0.94562	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5278 / 1 / 374	
Goodness-of-fit on F^2	1.019	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0443	wR^2 = 0.1035
R indices (all data)	R_1 = 0.0689	wR^2 = 0.1125
Absolute structure parameter	−0.15(14)	
Extinction coefficient	0.0069(9)	
Largest diff. peak and hole	0.292 and −0.236 $e \cdot Å^{-3}$	

Table 8. Bond lengths [Å] and angles [°] for crystal 2

O(4)-C(33)	1.367(4)	O(4)-C(36)	1.431(4)
O(5)-C(31)	1.375(4)	O(5)-C(35)	1.426(4)
O(6)-C(29)	1.379(4)	O(6)-C(34)	1.429(4)
C(21)-C(22)	1.566(5)	C(21)-C(26)	1.552(5)
C(21)-C(28)	1.517(5)	C(22)-C(23)	1.530(5)
C(22)-C(27)	1.521(5)	C(23)-C(24)	1.557(5)
C(24)-C(25)	1.542(5)	C(25)-C(26)	1.521(5)
C(25)-C(27)	1.539(5)	C(28)-C(29)	1.404(5)
C(28)-C(33)	1.399(4)	C(29)-C(30)	1.391(5)
C(30)-C(31)	1.394(5)	C(31)-C(32)	1.379(5)
C(32)-C(33)	1.398(4)	O(1)-C(9)	1.382(4)
O(1)-C(14)	1.432(4)	O(2)-C(11)	1.366(4)
O(2)-C(15)	1.423(4)	O(3)-C(13)	1.375(4)
O(3)-C(16)	1.425(4)	C(1)-C(2)	1.565(4)
C(1)-C(6)	1.558(5)	C(1)-C(8)	1.507(5)
C(2)-C(3)	1.523(5)	C(2)-C(7)	1.544(5)
C(3)-C(4)	1.552(5)	C(4)-C(5)	1.527(5)
C(5)-C(6)	1.526(5)	C(5)-C(7)	1.537(5)
C(8)-C(9)	1.416(5)	C(8)-C(13)	1.394(4)
C(9)-C(10)	1.373(5)	C(10)-C(11)	1.396(5)
C(11)-C(12)	1.389(5)	C(12)-C(13)	1.399(5)
C(33)-O(4)-C(36)	119.1(3)	C(31)-O(5)-C(35)	117.2(3)
C(29)-O(6)-C(34)	118.0(3)	C(26)-C(21)-C(22)	101.5(3)
C(28)-C(21)-C(22)	120.0(3)	C(28)-C(21)-C(26)	116.6(3)
C(23)-C(22)-C(21)	105.7(3)	C(27)-C(22)-C(21)	104.6(3)
C(27)-C(22)-C(23)	99.6(3)	C(22)-C(23)-C(24)	102.4(3)
C(25)-C(24)-C(23)	103.3(3)	C(26)-C(25)-C(24)	109.6(3)
C(26)-C(25)-C(27)	99.3(3)	C(27)-C(25)-C(24)	101.7(3)
C(25)-C(26)-C(21)	103.4(3)	C(22)-C(27)-C(25)	94.8(3)
C(29)-C(28)-C(21)	120.3(3)	C(33)-C(28)-C(21)	123.9(3)

C(33)-C(28)-C(29)	115.8(3)	O(6)-C(29)-C(28)	115.5(3)
O(6)-C(29)-C(30)	122.0(3)	C(30)-C(29)-C(28)	122.5(3)
C(29)-C(30)-C(31)	119.0(3)	O(5)-C(31)-C(30)	114.1(3)
O(5)-C(31)-C(32)	124.9(3)	C(32)-C(31)-C(30)	121.1(3)
C(31)-C(32)-C(33)	118.4(3)	O(4)-C(33)-C(28)	114.5(3)
O(4)-C(33)-C(32)	122.3(3)	C(32)-C(33)-C(28)	123.2(3)
C(9)-O(1)-C(14)	117.7(3)	C(11)-O(2)-C(15)	118.1(3)
C(13)-O(3)-C(16)	119.2(3)	C(6)-C(1)-C(2)	101.8(3)
C(8)-C(1)-C(2)	121.1(3)	C(8)-C(1)-C(6)	114.3(3)
C(3)-C(2)-C(1)	106.6(3)	C(3)-C(2)-C(7)	99.4(3)
C(7)-C(2)-C(1)	103.6(3)	C(2)-C(3)-C(4)	103.5(3)
C(5)-C(4)-C(3)	103.1(3)	C(4)-C(5)-C(7)	102.3(3)
C(6)-C(5)-C(4)	108.7(3)	C(6)-C(5)-C(7)	100.2(3)
C(5)-C(6)-C(1)	103.9(3)	C(5)-C(7)-C(2)	94.4(3)
C(9)-C(8)-C(1)	118.0(3)	C(13)-C(8)-C(1)	126.5(3)
C(13)-C(8)-C(9)	115.4(3)	O(1)-C(9)-C(8)	114.4(3)
C(10)-C(9)-O(1)	122.6(3)	C(10)-C(9)-C(8)	123.0(3)
C(9)-C(10)-C(11)	119.3(3)	O(2)-C(11)-C(10)	115.0(3)
O(2)-C(11)-C(12)	124.6(3)	C(12)-C(11)-C(10)	120.5(3)
C(11)-C(12)-C(13)	118.5(3)	O(3)-C(13)-C(8)	115.2(3)
O(3)-C(13)-C(12)	121.5(3)	C(8)-C(13)-C(12)	123.3(3)

Single crystal structure analysis of 7, crystal 3

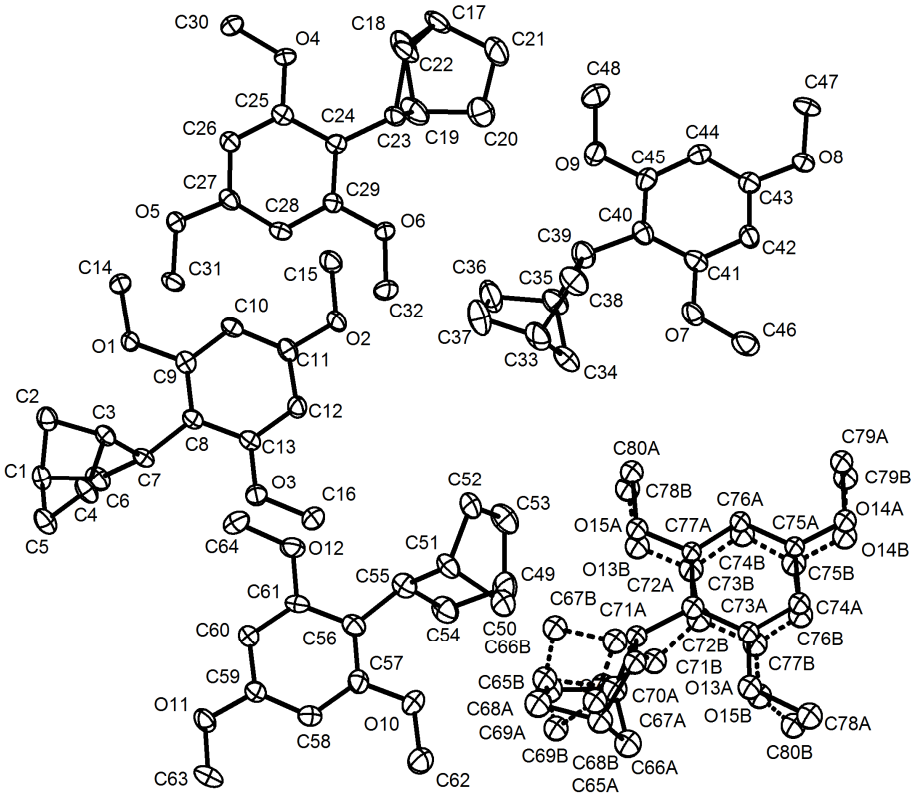
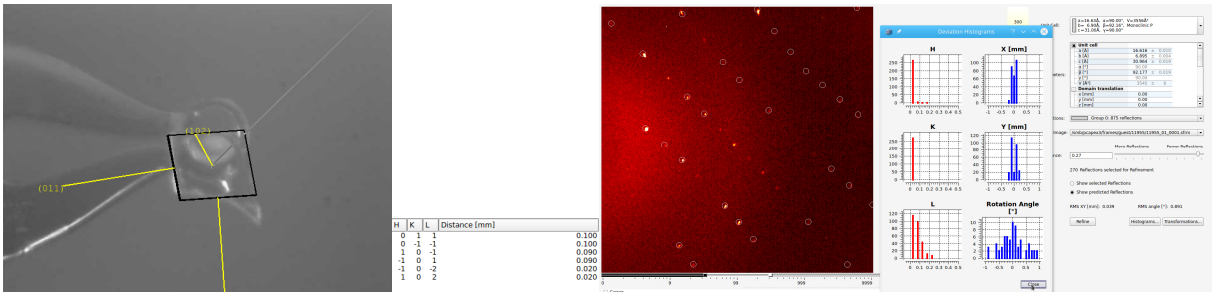


Figure 7. The molecular structure of 2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane, crystal 3. One molecule is disordered over two positions (dashed lines indicate the 21.7% minor component). H atoms have been removed for clarity.

X-ray crystal structure analysis of 7, crystal 3 (11955): C_{16} H_{22} O_3, M_r = 262.33 g · mol^{-1}, colorless plate, crystal size 0.040 x 0.201 x 0.238 mm^3, monoclinic, space group $P2_1$ [4], a = 16.6412(7) Å, b = 6.8948(3) Å, c = 30.9074(14) Å, β = 92.160(2) °, V = 3543.7(3) Å^3, T = 100(2) K, Z = 10, D_{calc} = 1.229 g · cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 0.667 mm^{-1}, analytical absorption correction (T_{min} = 0. 88477, T_{max} = 0. 97426), Bruker AXS Enraf-Nonius Mach3 Proteum diffractometer with a FR591 rotating anode X-ray source and APEX II detector, 1.430 < θ < 72.524°, 140382 measured reflections, 12569 independent reflections, 9807 reflections with $I > 2\sigma(I)$, R_{int} = 0.0755. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0773 [$I > 2\sigma(I)$], wR_2 = 0.2377, 838 parameters, 2

restraints. The absolute structure parameter has been determined as 0.114(133) via anomalous dispersion using 3514 quotients (Parsons' method).



INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.35	194	196	99.0	9.55	21.93	16.15	0.0438	0.0528
3.35 - 2.25	441	443	99.5	9.76	6.61	17.42	0.0376	0.0472
2.25 - 1.80	622	622	100.0	11.04	4.81	18.37	0.0421	0.0455
1.80 - 1.58	648	649	99.8	10.29	3.39	16.82	0.0420	0.0543
1.58 - 1.43	636	636	100.0	9.53	1.76	14.59	0.0569	0.0520
1.43 - 1.33	609	610	99.8	8.53	1.32	13.26	0.0799	0.0619
1.33 - 1.25	663	674	98.4	8.77	1.36	12.92	0.0811	0.0650
1.25 - 1.18	697	697	100.0	16.52	1.82	16.55	0.0623	0.0477
1.18 - 1.13	570	601	94.8	15.08	2.10	16.55	0.0585	0.0480
1.13 - 1.09	579	619	93.5	14.18	1.23	14.80	0.0793	0.0508
1.09 - 1.05	699	705	99.1	14.18	0.97	13.63	0.0953	0.0573
1.05 - 1.01	747	747	100.0	14.15	1.10	13.38	0.0898	0.0577
1.01 - 0.98	548	636	86.2	13.60	0.68	12.18	0.1861	0.0697
0.98 - 0.95	657	848	77.5	11.39	0.71	12.00	0.1831	0.0691
0.95 - 0.92	735	885	83.1	11.24	0.49	10.00	0.2143	0.0803
0.92 - 0.90	519	613	84.7	10.91	0.38	9.28	0.2416	0.0905
0.90 - 0.88	632	720	87.8	11.13	0.36	8.53	0.2424	0.0939
0.88 - 0.86	612	721	84.9	7.96	0.22	5.30	0.3286	0.1884
0.86 - 0.84	710	930	76.3	2.28	0.24	2.11	0.4252	0.5089
0.84 - 0.82	721	940	76.7	2.21	0.23	2.09	0.4253	0.5224
0.82 - 0.81	334	603	55.4	1.06	0.18	1.66	0.4207	0.6978
0.91 - 0.81	3279	4233	77.5	5.19	0.26	4.41	0.2956	0.3207
Inf - 0.81	12573	14095	89.2	9.96	1.75	11.69	0.0731	0.0632

There are five molecules in the asymmetric unit, four with full occupancy and one disordered over two positions with refined occupancy of 0.785(7):0.215(7). The atomic displacement parameters of all atoms of the minor component were restrained to be equal and two similar C–C bond lengths in the norbornyl group were restrained to be equal with an effective standard deviation of 0.01. All molecules in the asymmmetric unit have the same chirality.

Table 9. Crystal data and structure refinement for crystal 3

Identification code	11955	
Empirical formula	$C_{16}\ H_{22}\ O_3$	
Color	colorless	
Formula weight	262.33 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1$, (No. 4)	
Unit cell dimensions	a = 16.6412(7) Å	$\alpha = 90°$.
	b = 6.8948(3) Å	$\beta = 92.160(2)°$.
	c = 30.9074(14) Å	$\gamma = 90°$.
Volume	3543.7(3) $Å^3$	
Z	10	
Density (calculated)	1.229 $Mg \cdot m^{-3}$	
Absorption coefficient	0.667 mm^{-1}	
F(000)	1420 e	
Crystal size	0.238 x 0.201 x 0.040 mm^3	
θ range for data collection	1.430 to 72.524°.	
Index ranges	$-20 \le h \le 20, -8 \le k \le 7, -37 \le l \le 38$	
Reflections collected	140382	
Independent reflections	12569 [R_{int} = 0.0755]	
Reflections with $I > 2\sigma(I)$	9807	
Completeness to θ = 67.679°	97.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97426 and 0.88477	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12569 / 2 / 838	
Goodness-of-fit on F^2	1.098	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0773	wR^2 = 0.2159
R indices (all data)	R_1 = 0.1026	wR^2 = 0.2377
Absolute structure parameter	0.11(13)	
Extinction coefficient	0	
Largest diff. peak and hole	0.569 and −0.471 $e \cdot Å^{-3}$	

Table 10. Bond lengths [Å] and angles [°] for crystal 3

C(1)-C(6)	1.528(7)	C(1)-C(5)	1.531(7)
C(1)-C(2)	1.540(7)	C(2)-C(3)	1.547(6)
C(3)-C(7)	1.542(7)	C(3)-C(4)	1.548(6)
C(4)-C(5)	1.564(7)	C(6)-C(7)	1.568(7)
C(7)-C(8)	1.524(5)	C(8)-C(9)	1.392(6)
C(8)-C(13)	1.407(6)	C(9)-O(1)	1.372(5)
C(9)-C(10)	1.402(6)	C(10)-C(11)	1.382(6)
C(11)-O(2)	1.364(5)	C(11)-C(12)	1.392(6)
C(12)-C(13)	1.395(6)	C(13)-O(3)	1.365(5)
C(14)-O(1)	1.432(5)	C(15)-O(2)	1.431(5)
C(16)-O(3)	1.419(5)	C(17)-C(18)	1.515(8)
C(17)-C(22)	1.536(7)	C(17)-C(21)	1.536(7)
C(18)-C(19)	1.522(8)	C(19)-C(20)	1.537(8)
C(19)-C(23)	1.555(7)	C(20)-C(21)	1.549(9)
C(22)-C(23)	1.569(7)	C(23)-C(24)	1.520(6)
C(24)-C(25)	1.410(6)	C(24)-C(29)	1.410(5)
C(25)-O(4)	1.373(5)	C(25)-C(26)	1.387(6)
C(26)-C(27)	1.393(6)	C(27)-O(5)	1.362(5)
C(27)-C(28)	1.385(6)	C(28)-C(29)	1.395(6)
C(29)-O(6)	1.367(5)	C(30)-O(4)	1.432(5)
C(31)-O(5)	1.433(5)	C(32)-O(6)	1.423(5)
C(33)-C(37)	1.521(8)	C(33)-C(38)	1.534(8)
C(33)-C(34)	1.560(9)	C(34)-C(35)	1.538(7)
C(35)-C(36)	1.502(7)	C(35)-C(39)	1.571(8)
C(36)-C(37)	1.524(9)	C(38)-C(39)	1.540(7)
C(39)-C(40)	1.506(6)	C(40)-C(41)	1.409(6)
C(40)-C(45)	1.411(6)	C(41)-O(7)	1.373(5)
C(41)-C(42)	1.390(6)	C(42)-C(43)	1.395(6)
C(43)-O(8)	1.364(5)	C(43)-C(44)	1.369(6)
C(44)-C(45)	1.395(6)	C(45)-O(9)	1.365(5)
C(46)-O(7)	1.420(6)	C(47)-O(8)	1.437(5)

C(48)-O(9)	1.437(5)	C(49)-C(50)	1.513(9)
C(49)-C(54)	1.537(8)	C(49)-C(53)	1.551(8)
C(50)-C(51)	1.555(7)	C(51)-C(52)	1.517(7)
C(51)-C(55)	1.557(7)	C(52)-C(53)	1.528(8)
C(54)-C(55)	1.561(7)	C(55)-C(56)	1.534(6)
C(56)-C(57)	1.395(6)	C(56)-C(61)	1.403(6)
C(57)-O(10)	1.362(5)	C(57)-C(58)	1.409(6)
C(58)-C(59)	1.382(6)	C(59)-O(11)	1.367(5)
C(59)-C(60)	1.384(6)	C(60)-C(61)	1.385(6)
C(61)-O(12)	1.380(5)	C(62)-O(10)	1.425(5)
C(63)-O(11)	1.421(5)	C(64)-O(12)	1.425(5)
C(65A)-C(66A)	1.498(11)	C(65A)-C(70A)	1.539(9)
C(65A)-C(69A)	1.543(10)	C(66A)-C(67A)	1.492(9)
C(67A)-C(68A)	1.513(12)	C(67A)-C(71A)	1.547(10)
C(68A)-C(69A)	1.583(11)	C(70A)-C(71A)	1.544(9)
C(71A)-C(72A)	1.529(10)	C(72A)-C(77A)	1.399(10)
C(72A)-C(73A)	1.410(10)	C(73A)-O(13A)	1.371(8)
C(73A)-C(74A)	1.411(10)	C(74A)-C(75A)	1.405(9)
C(75A)-O(14A)	1.350(7)	C(75A)-C(76A)	1.389(9)
C(76A)-C(77A)	1.372(9)	C(77A)-O(15A)	1.367(8)
C(78A)-O(13A)	1.526(9)	C(79A)-O(14A)	1.453(7)
C(80A)-O(15A)	1.424(8)	C(65B)-C(66B)	1.31(4)
C(65B)-C(69B)	1.60(3)	C(65B)-C(70B)	1.61(4)
C(66B)-C(67B)	1.63(3)	C(67B)-C(71B)	1.55(4)
C(67B)-C(68B)	1.59(3)	C(68B)-C(69B)	1.43(4)
C(70B)-C(71B)	1.68(4)	C(71B)-C(72B)	1.47(4)
C(72B)-C(73B)	1.33(4)	C(72B)-C(77B)	1.42(4)
C(73B)-O(13B)	1.36(3)	C(73B)-C(74B)	1.50(4)
C(74B)-C(75B)	1.38(4)	C(75B)-C(76B)	1.33(4)
C(75B)-O(14B)	1.39(3)	C(76B)-C(77B)	1.30(4)
C(77B)-O(15B)	1.29(3)	C(78B)-O(13B)	1.44(3)
C(79B)-O(14B)	1.40(3)	C(80B)-O(15B)	1.08(3)

C(6)-C(1)-C(5)	110.1(4)	C(6)-C(1)-C(2)	101.4(4)
C(5)-C(1)-C(2)	101.1(4)	C(1)-C(2)-C(3)	93.7(3)
C(7)-C(3)-C(2)	104.9(4)	C(7)-C(3)-C(4)	106.1(4)
C(2)-C(3)-C(4)	99.8(3)	C(3)-C(4)-C(5)	101.5(4)
C(1)-C(5)-C(4)	104.2(4)	C(1)-C(6)-C(7)	102.4(4)
C(8)-C(7)-C(3)	119.3(4)	C(8)-C(7)-C(6)	117.3(4)
C(3)-C(7)-C(6)	102.6(3)	C(9)-C(8)-C(13)	116.2(4)
C(9)-C(8)-C(7)	124.6(4)	C(13)-C(8)-C(7)	119.2(3)
O(1)-C(9)-C(8)	116.1(3)	O(1)-C(9)-C(10)	120.8(4)
C(8)-C(9)-C(10)	123.1(4)	C(11)-C(10)-C(9)	118.5(4)
O(2)-C(11)-C(10)	124.9(4)	O(2)-C(11)-C(12)	114.3(4)
C(10)-C(11)-C(12)	120.9(4)	C(11)-C(12)-C(13)	119.1(4)
O(3)-C(13)-C(12)	121.9(4)	O(3)-C(13)-C(8)	115.8(3)
C(12)-C(13)-C(8)	122.3(4)	C(18)-C(17)-C(22)	101.5(4)
C(18)-C(17)-C(21)	102.3(5)	C(22)-C(17)-C(21)	109.3(4)
C(17)-C(18)-C(19)	95.1(4)	C(18)-C(19)-C(20)	100.4(4)
C(18)-C(19)-C(23)	103.0(5)	C(20)-C(19)-C(23)	106.2(5)
C(19)-C(20)-C(21)	103.4(5)	C(17)-C(21)-C(20)	102.6(4)
C(17)-C(22)-C(23)	102.1(4)	C(24)-C(23)-C(19)	116.7(4)
C(24)-C(23)-C(22)	118.0(4)	C(19)-C(23)-C(22)	102.7(4)
C(25)-C(24)-C(29)	115.3(4)	C(25)-C(24)-C(23)	125.3(4)
C(29)-C(24)-C(23)	119.3(4)	O(4)-C(25)-C(26)	121.4(4)
O(4)-C(25)-C(24)	115.7(4)	C(26)-C(25)-C(24)	122.9(4)
C(25)-C(26)-C(27)	119.2(4)	O(5)-C(27)-C(28)	124.6(4)
O(5)-C(27)-C(26)	114.9(4)	C(28)-C(27)-C(26)	120.5(4)
C(27)-C(28)-C(29)	119.1(4)	O(6)-C(29)-C(28)	122.3(4)
O(6)-C(29)-C(24)	114.8(3)	C(28)-C(29)-C(24)	122.8(4)
C(37)-C(33)-C(38)	108.1(5)	C(37)-C(33)-C(34)	100.3(5)
C(38)-C(33)-C(34)	100.3(4)	C(35)-C(34)-C(33)	94.5(4)
C(36)-C(35)-C(34)	101.0(4)	C(36)-C(35)-C(39)	107.2(5)
C(34)-C(35)-C(39)	101.6(4)	C(35)-C(36)-C(37)	104.0(5)
C(33)-C(37)-C(36)	104.7(4)	C(33)-C(38)-C(39)	104.4(5)
C(40)-C(39)-C(38)	119.4(4)	C(40)-C(39)-C(35)	116.5(4)

C(38)-C(39)-C(35)	102.9(4)	C(41)-C(40)-C(45)	115.4(4)
C(41)-C(40)-C(39)	126.9(4)	C(45)-C(40)-C(39)	117.7(4)
O(7)-C(41)-C(42)	120.7(4)	O(7)-C(41)-C(40)	116.1(4)
C(42)-C(41)-C(40)	123.2(4)	C(41)-C(42)-C(43)	118.1(4)
O(8)-C(43)-C(44)	124.0(4)	O(8)-C(43)-C(42)	114.3(4)
C(44)-C(43)-C(42)	121.7(4)	C(43)-C(44)-C(45)	118.9(4)
O(9)-C(45)-C(44)	121.8(4)	O(9)-C(45)-C(40)	115.5(4)
C(44)-C(45)-C(40)	122.7(4)	C(50)-C(49)-C(54)	100.9(4)
C(50)-C(49)-C(53)	100.9(5)	C(54)-C(49)-C(53)	109.1(5)
C(49)-C(50)-C(51)	94.9(4)	C(52)-C(51)-C(50)	98.3(4)
C(52)-C(51)-C(55)	105.5(4)	C(50)-C(51)-C(55)	104.3(4)
C(51)-C(52)-C(53)	104.1(5)	C(52)-C(53)-C(49)	103.2(4)
C(49)-C(54)-C(55)	102.9(5)	C(56)-C(55)-C(51)	118.0(4)
C(56)-C(55)-C(54)	116.8(4)	C(51)-C(55)-C(54)	102.3(4)
C(57)-C(56)-C(61)	116.0(4)	C(57)-C(56)-C(55)	125.6(4)
C(61)-C(56)-C(55)	118.3(4)	O(10)-C(57)-C(56)	115.7(4)
O(10)-C(57)-C(58)	121.6(4)	C(56)-C(57)-C(58)	122.6(4)
C(59)-C(58)-C(57)	118.4(4)	O(11)-C(59)-C(58)	124.3(4)
O(11)-C(59)-C(60)	114.7(4)	C(58)-C(59)-C(60)	121.0(4)
C(59)-C(60)-C(61)	119.1(4)	O(12)-C(61)-C(60)	121.2(4)
O(12)-C(61)-C(56)	116.1(4)	C(60)-C(61)-C(56)	122.8(4)
C(9)-O(1)-C(14)	118.7(3)	C(11)-O(2)-C(15)	117.5(3)
C(13)-O(3)-C(16)	118.1(3)	C(25)-O(4)-C(30)	118.2(3)
C(27)-O(5)-C(31)	117.3(3)	C(29)-O(6)-C(32)	118.4(3)
C(41)-O(7)-C(46)	118.1(3)	C(43)-O(8)-C(47)	117.3(3)
C(45)-O(9)-C(48)	118.6(4)	C(57)-O(10)-C(62)	118.0(4)
C(59)-O(11)-C(63)	117.9(3)	C(61)-O(12)-C(64)	118.3(3)
C(66A)-C(65A)-C(70A)	100.5(6)	C(66A)-C(65A)-C(69A)	104.9(6)
C(70A)-C(65A)-C(69A)	108.6(6)	C(67A)-C(66A)-C(65A)	94.2(6)
C(66A)-C(67A)-C(68A)	99.8(6)	C(66A)-C(67A)-C(71A)	106.0(6)
C(68A)-C(67A)-C(71A)	107.2(6)	C(67A)-C(68A)-C(69A)	103.2(7)
C(65A)-C(69A)-C(68A)	99.2(6)	C(65A)-C(70A)-C(71A)	102.5(5)
C(72A)-C(71A)-C(70A)	117.7(6)	C(72A)-C(71A)-C(67A)	116.6(6)

C(70A)-C(71A)-C(67A)	100.8(5)	C(77A)-C(72A)-C(73A)	115.1(7)
C(77A)-C(72A)-C(71A)	119.6(6)	C(73A)-C(72A)-C(71A)	125.3(6)
O(13A)-C(73A)-C(72A)	115.1(6)	O(13A)-C(73A)-C(74A)	121.9(6)
C(72A)-C(73A)-C(74A)	122.9(6)	C(75A)-C(74A)-C(73A)	118.6(6)
O(14A)-C(75A)-C(76A)	125.4(5)	O(14A)-C(75A)-C(74A)	115.4(5)
C(76A)-C(75A)-C(74A)	119.3(6)	C(77A)-C(76A)-C(75A)	120.4(6)
O(15A)-C(77A)-C(76A)	122.5(5)	O(15A)-C(77A)-C(72A)	113.9(6)
C(76A)-C(77A)-C(72A)	123.6(6)	C(73A)-O(13A)-C(78A)	115.4(5)
C(75A)-O(14A)-C(79A)	116.6(5)	C(77A)-O(15A)-C(80A)	117.7(5)
C(66B)-C(65B)-C(69B)	106(3)	C(66B)-C(65B)-C(70B)	100(2)
C(69B)-C(65B)-C(70B)	100(2)	C(65B)-C(66B)-C(67B)	101(2)
C(71B)-C(67B)-C(68B)	105(2)	C(71B)-C(67B)-C(66B)	101(2)
C(68B)-C(67B)-C(66B)	97.1(18)	C(69B)-C(68B)-C(67B)	105.3(19)
C(68B)-C(69B)-C(65B)	105(2)	C(65B)-C(70B)-C(71B)	103(2)
C(72B)-C(71B)-C(67B)	115(2)	C(72B)-C(71B)-C(70B)	123(2)
C(67B)-C(71B)-C(70B)	99.1(18)	C(73B)-C(72B)-C(77B)	119(3)
C(73B)-C(72B)-C(71B)	126(3)	C(77B)-C(72B)-C(71B)	112(3)
C(72B)-C(73B)-O(13B)	121(3)	C(72B)-C(73B)-C(74B)	120(3)
O(13B)-C(73B)-C(74B)	119(2)	C(75B)-C(74B)-C(73B)	113(2)
C(76B)-C(75B)-C(74B)	126(3)	C(76B)-C(75B)-O(14B)	115(2)
C(74B)-C(75B)-O(14B)	119(2)	C(77B)-C(76B)-C(75B)	120(3)
O(15B)-C(77B)-C(76B)	122(3)	O(15B)-C(77B)-C(72B)	117(3)
C(76B)-C(77B)-C(72B)	121(3)	C(73B)-O(13B)-C(78B)	123(2)
C(75B)-O(14B)-C(79B)	121(2)	C(80B)-O(15B)-C(77B)	138(3)

Single crystal structure analysis of 7, crystal 4

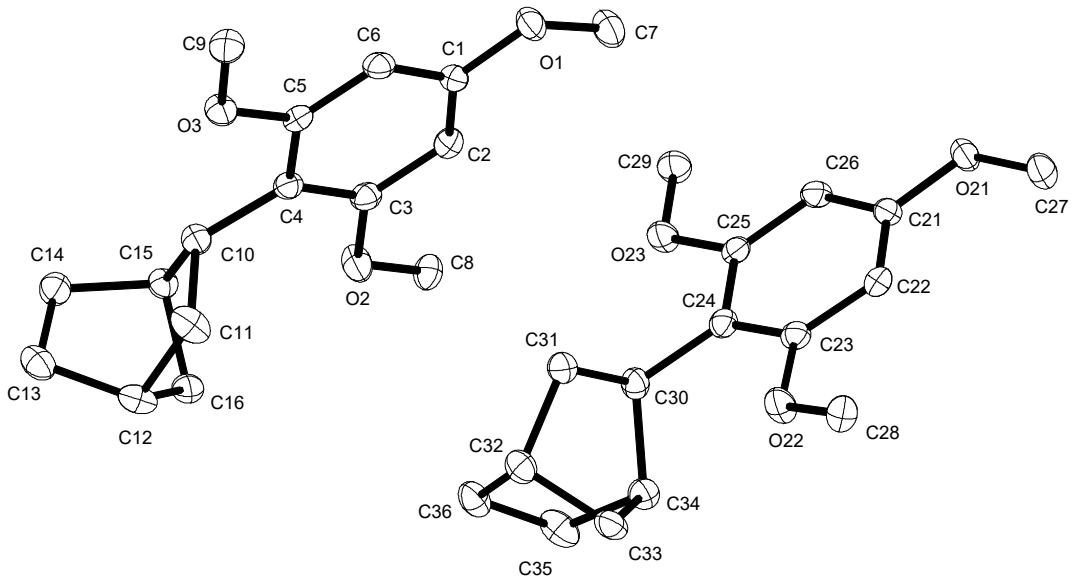
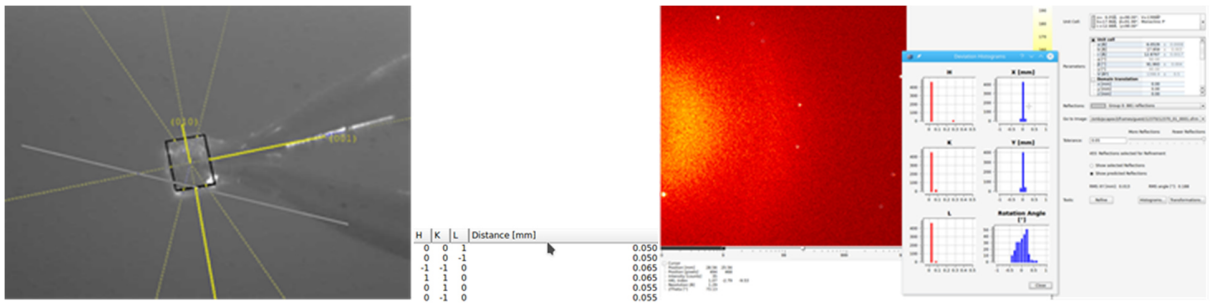


Figure 8. The molecular structure of the two independent molecules in the asymmetric unit of 2-(2,4,6-trimethoxyphenyl)bicyclo[2.2.1]heptane. H atoms have been removed for clarity.

X-ray crystal structure analysis of 7, crystal 4 (12370): C_{16} H_{22} O_3, M_r = 262.33 g · mol^{-1}, colorless prism, crystal size 0.177 x 0.111 x 0.100 mm^3, monoclinic, space group $P2_1$ [4], a = 6.0445(5) Å, b = 17.9421(14) Å, c = 12.8422(10) Å, β = 91.951(3) °, V = 1391.94(19) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.252 g · cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 0.680 mm^{-1}, analytical absorption correction (T_{min} = 0.91538, T_{max} = 0.94267), Bruker AXS Enraf-Nonius Mach3 Proteum diffractometer with a FR591 rotating anode X-ray source and APEX II detector, 3.443 < θ < 66.591°, 49095 measured reflections, 4607 independent reflections, 4332 reflections with $I > 2\sigma(I)$, R_{int} = 0.0338. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0271 [$I > 2\sigma(I)$], wR_2 = 0.0831, 349 parameters, 1 restraint. The absolute structure parameter has been determined as 0.026(37) via anomalous dispersion using 1964 quotients (Parsons' method).



INTENSITY STATISTICS FOR DATASET (Friedel pairs not averaged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.45	77	79	97.5	9.23	273.79	77.20	0.0330	0.0108
3.45 - 2.28	178	178	100.0	9.41	76.21	79.53	0.0283	0.0111
2.28 - 1.80	254	254	100.0	10.24	70.25	84.31	0.0302	0.0111
1.80 - 1.56	265	265	100.0	9.90	34.52	77.19	0.0252	0.0116
1.56 - 1.42	249	249	100.0	9.30	27.58	70.09	0.0282	0.0129
1.42 - 1.33	240	242	99.2	7.89	21.05	60.10	0.0339	0.0143
1.33 - 1.24	278	283	98.2	6.92	19.55	56.55	0.0368	0.0157
1.24 - 1.17	281	287	97.9	15.49	29.04	92.68	0.0259	0.0101
1.17 - 1.13	200	210	95.2	14.56	25.22	85.71	0.0238	0.0100
1.13 - 1.08	273	282	96.8	14.37	19.00	81.32	0.0245	0.0115
1.08 - 1.04	256	272	94.1	13.14	14.99	72.45	0.0283	0.0121
1.04 - 1.01	226	237	95.4	12.39	13.59	69.13	0.0322	0.0138
1.01 - 0.98	265	280	94.6	11.66	12.42	62.06	0.0516	0.0207
0.98 - 0.95	260	293	88.7	10.59	8.77	54.79	0.0680	0.0185
0.95 - 0.93	224	250	89.6	10.16	8.43	55.71	0.0692	0.0163
0.93 - 0.90	314	352	89.2	9.76	7.27	52.75	0.0829	0.0342
0.90 - 0.88	245	284	86.3	8.68	5.58	45.85	0.0924	0.0418
0.88 - 0.86	248	279	88.9	6.72	3.92	30.73	0.1497	0.1157
0.86 - 0.84	293	365	80.3	1.69	2.32	3.53	0.2303	0.7045
0.84 - 0.82	291	367	79.3	1.56	1.45	2.99	0.2613	0.9238
0.82 - 0.81	128	274	46.7	0.70	1.25	2.26	0.3842	1.0420
0.91 - 0.81	1319	1700	77.6	4.12	3.34	20.35	0.1136	0.2784
Inf - 0.81	5045	5582	90.4	8.95	23.32	57.46	0.0338	0.0224

Table 11. Crystal data and structure refinement for crystal 4

Identification code	12370	
Empirical formula	$C_{16}\ H_{22}\ O_3$	
Color	colorless	
Formula weight	262.33 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1$, (No. 4)	
Unit cell dimensions	a = 6.0445(5) Å	$\alpha = 90°$.
	b = 17.9421(14) Å	$\beta = 91.951(3)°$.
	c = 12.8422(10) Å	$\gamma = 90°$.
Volume	1391.94(19) $Å^3$	
Z	4	
Density (calculated)	1.252 $Mg \cdot m^{-3}$	
Absorption coefficient	0.680 mm^{-1}	
F(000)	568 e	
Crystal size	0.177 x 0.111 x 0.100 mm^3	
θ range for data collection	3.443 to 66.591°.	
Index ranges	$-7 \le h \le 7, -21 \le k \le 21, -14 \le l \le 12$	
Reflections collected	49095	
Independent reflections	4607 [R_{int} = 0.0338]	
Reflections with $I > 2\sigma(I)$	4332	
Completeness to θ = 66.592°	96.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.94267 and 0.91538	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4607 / 1 / 349	
Goodness-of-fit on F^2	1.117	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0271	wR^2 = 0.0723
R indices (all data)	R_1 = 0.0422	wR^2 = 0.0831
Absolute structure parameter	0.03(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.237 and −0.247 $e \cdot Å^{-3}$	

Table 12. Bond lengths [Å] and angles [°] for crystal 4

O(3)-C(5)	1.377(3)	O(3)-C(9)	1.427(3)
O(23)-C(25)	1.378(3)	O(23)-C(29)	1.428(3)
O(21)-C(21)	1.372(3)	O(21)-C(27)	1.423(3)
O(2)-C(3)	1.368(3)	O(2)-C(8)	1.423(3)
O(22)-C(23)	1.366(3)	O(22)-C(28)	1.427(3)
O(1)-C(1)	1.372(3)	O(1)-C(7)	1.423(3)
C(22)-H(22)	0.9500	C(22)-C(21)	1.387(3)
C(22)-C(23)	1.397(3)	C(3)-C(4)	1.396(3)
C(3)-C(2)	1.405(3)	C(25)-C(24)	1.405(3)
C(25)-C(26)	1.390(3)	C(5)-C(4)	1.412(3)
C(5)-C(6)	1.384(3)	C(4)-C(10)	1.516(3)
C(6)-H(6)	0.9500	C(6)-C(1)	1.390(3)
C(2)-H(2)	0.9500	C(2)-C(1)	1.389(3)
C(21)-C(26)	1.392(3)	C(23)-C(24)	1.397(3)
C(15)-H(15)	1.0000	C(15)-C(16)	1.541(3)
C(15)-C(14)	1.534(3)	C(15)-C(10)	1.557(3)
C(24)-C(30)	1.516(3)	C(26)-H(26)	0.9500
C(32)-H(32)	1.0000	C(32)-C(33)	1.523(3)
C(32)-C(36)	1.539(3)	C(32)-C(31)	1.537(3)
C(27)-H(27A)	0.9800	C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800	C(34)-H(34)	1.0000
C(34)-C(30)	1.570(3)	C(34)-C(33)	1.537(3)
C(34)-C(35)	1.537(3)	C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800	C(7)-H(7C)	0.9800
C(12)-H(12)	1.0000	C(12)-C(16)	1.539(3)
C(12)-C(13)	1.533(4)	C(12)-C(11)	1.533(3)
C(30)-H(30)	1.0000	C(30)-C(31)	1.560(3)
C(29)-H(29A)	0.9800	C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800	C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800	C(9)-H(9C)	0.9800
C(33)-H(33A)	0.9900	C(33)-H(33B)	0.9900

C(16)-H(16A)	0.9900	C(16)-H(16B)	0.9900
C(14)-H(14A)	0.9900	C(14)-H(14B)	0.9900
C(14)-C(13)	1.551(3)	C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900	C(10)-H(10)	1.0000
C(10)-C(11)	1.563(3)	C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800	C(28)-H(28C)	0.9800
C(36)-H(36A)	0.9900	C(36)-H(36B)	0.9900
C(36)-C(35)	1.560(3)	C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800	C(8)-H(8C)	0.9800
C(11)-H(11A)	0.9900	C(11)-H(11B)	0.9900
C(31)-H(31A)	0.9900	C(31)-H(31B)	0.9900
C(35)-H(35A)	0.9900	C(35)-H(35B)	0.9900

C(5)-O(3)-C(9)	117.99(17)	C(25)-O(23)-C(29)	118.33(17)
C(21)-O(21)-C(27)	117.53(18)	C(3)-O(2)-C(8)	119.55(17)
C(23)-O(22)-C(28)	119.28(17)	C(1)-O(1)-C(7)	118.02(17)
C(21)-C(22)-H(22)	120.8	C(21)-C(22)-C(23)	118.3(2)
C(23)-C(22)-H(22)	120.8	O(2)-C(3)-C(4)	115.68(19)
O(2)-C(3)-C(2)	121.51(19)	C(4)-C(3)-C(2)	122.81(19)
O(23)-C(25)-C(24)	115.77(19)	O(23)-C(25)-C(26)	121.67(19)
C(26)-C(25)-C(24)	122.6(2)	O(3)-C(5)-C(4)	114.70(19)
O(3)-C(5)-C(6)	122.51(18)	C(6)-C(5)-C(4)	122.79(19)
C(3)-C(4)-C(5)	115.99(19)	C(3)-C(4)-C(10)	126.19(19)
C(5)-C(4)-C(10)	117.82(19)	C(5)-C(6)-H(6)	120.5
C(5)-C(6)-C(1)	118.95(19)	C(1)-C(6)-H(6)	120.5
C(3)-C(2)-H(2)	120.8	C(1)-C(2)-C(3)	118.34(19)
C(1)-C(2)-H(2)	120.8	O(21)-C(21)-C(22)	124.5(2)
O(21)-C(21)-C(26)	114.54(19)	C(22)-C(21)-C(26)	120.98(19)
O(22)-C(23)-C(22)	122.10(19)	O(22)-C(23)-C(24)	114.74(18)
C(24)-C(23)-C(22)	123.16(19)	O(1)-C(1)-C(6)	114.61(19)
O(1)-C(1)-C(2)	124.3(2)	C(2)-C(1)-C(6)	121.11(19)
C(16)-C(15)-H(15)	115.0	C(16)-C(15)-C(10)	104.07(18)
C(14)-C(15)-H(15)	115.0	C(14)-C(15)-C(16)	99.84(17)

C(14)-C(15)-C(10)	106.20(17)	C(10)-C(15)-H(15)	115.0
C(25)-C(24)-C(30)	120.00(19)	C(23)-C(24)-C(25)	115.96(19)
C(23)-C(24)-C(30)	124.04(19)	C(25)-C(26)-C(21)	118.96(19)
C(25)-C(26)-H(26)	120.5	C(21)-C(26)-H(26)	120.5
C(33)-C(32)-H(32)	114.5	C(33)-C(32)-C(36)	102.58(18)
C(33)-C(32)-C(31)	99.95(18)	C(36)-C(32)-H(32)	114.5
C(31)-C(32)-H(32)	114.5	C(31)-C(32)-C(36)	109.31(19)
O(21)-C(27)-H(27A)	109.5	O(21)-C(27)-H(27B)	109.5
O(21)-C(27)-H(27C)	109.5	H(27A)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27C)	109.5	H(27B)-C(27)-H(27C)	109.5
C(30)-C(34)-H(34)	115.2	C(33)-C(34)-H(34)	115.2
C(33)-C(34)-C(30)	104.44(17)	C(35)-C(34)-H(34)	115.2
C(35)-C(34)-C(30)	105.53(19)	C(35)-C(34)-C(33)	99.39(17)
O(1)-C(7)-H(7A)	109.5	O(1)-C(7)-H(7B)	109.5
O(1)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
C(16)-C(12)-H(12)	114.6	C(13)-C(12)-H(12)	114.6
C(13)-C(12)-C(16)	102.62(18)	C(13)-C(12)-C(11)	108.7(2)
C(11)-C(12)-H(12)	114.6	C(11)-C(12)-C(16)	100.27(18)
C(24)-C(30)-C(34)	119.93(19)	C(24)-C(30)-H(30)	106.0
C(24)-C(30)-C(31)	116.18(18)	C(34)-C(30)-H(30)	106.0
C(31)-C(30)-C(34)	101.78(16)	C(31)-C(30)-H(30)	106.0
O(23)-C(29)-H(29A)	109.5	O(23)-C(29)-H(29B)	109.5
O(23)-C(29)-H(29C)	109.5	H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5	H(29B)-C(29)-H(29C)	109.5
O(3)-C(9)-H(9A)	109.5	O(3)-C(9)-H(9B)	109.5
O(3)-C(9)-H(9C)	109.5	H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5	H(9B)-C(9)-H(9C)	109.5
C(32)-C(33)-C(34)	94.67(17)	C(32)-C(33)-H(33A)	112.8
C(32)-C(33)-H(33B)	112.8	C(34)-C(33)-H(33A)	112.8
C(34)-C(33)-H(33B)	112.8	H(33A)-C(33)-H(33B)	110.3
C(15)-C(16)-H(16A)	112.9	C(15)-C(16)-H(16B)	112.9
C(12)-C(16)-C(15)	94.15(17)	C(12)-C(16)-H(16A)	112.9

C(12)-C(16)-H(16B)	112.9	H(16A)-C(16)-H(16B)	110.3
C(15)-C(14)-H(14A)	111.1	C(15)-C(14)-H(14B)	111.1
C(15)-C(14)-C(13)	103.21(18)	H(14A)-C(14)-H(14B)	109.1
C(13)-C(14)-H(14A)	111.1	C(13)-C(14)-H(14B)	111.1
C(12)-C(13)-C(14)	103.08(18)	C(12)-C(13)-H(13A)	111.1
C(12)-C(13)-H(13B)	111.1	C(14)-C(13)-H(13A)	111.1
C(14)-C(13)-H(13B)	111.1	H(13A)-C(13)-H(13B)	109.1
C(4)-C(10)-C(15)	120.98(17)	C(4)-C(10)-H(10)	106.4
C(4)-C(10)-C(11)	113.83(18)	C(15)-C(10)-H(10)	106.4
C(15)-C(10)-C(11)	101.96(17)	C(11)-C(10)-H(10)	106.4
O(22)-C(28)-H(28A)	109.5	O(22)-C(28)-H(28B)	109.5
O(22)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5	H(28B)-C(28)-H(28C)	109.5
C(32)-C(36)-H(36A)	111.1	C(32)-C(36)-H(36B)	111.1
C(32)-C(36)-C(35)	103.18(18)	H(36A)-C(36)-H(36B)	109.1
C(35)-C(36)-H(36A)	111.1	C(35)-C(36)-H(36B)	111.1
O(2)-C(8)-H(8A)	109.5	O(2)-C(8)-H(8B)	109.5
O(2)-C(8)-H(8C)	109.5	H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5	H(8B)-C(8)-H(8C)	109.5
C(12)-C(11)-C(10)	103.32(17)	C(12)-C(11)-H(11A)	111.1
C(12)-C(11)-H(11B)	111.1	C(10)-C(11)-H(11A)	111.1
C(10)-C(11)-H(11B)	111.1	H(11A)-C(11)-H(11B)	109.1
C(32)-C(31)-C(30)	102.62(17)	C(32)-C(31)-H(31A)	111.2
C(32)-C(31)-H(31B)	111.2	C(30)-C(31)-H(31A)	111.2
C(30)-C(31)-H(31B)	111.2	H(31A)-C(31)-H(31B)	109.2
C(34)-C(35)-C(36)	102.30(18)	C(34)-C(35)-H(35A)	111.3
C(34)-C(35)-H(35B)	111.3	C(36)-C(35)-H(35A)	111.3
C(36)-C(35)-H(35B)	111.3	H(35A)-C(35)-H(35B)	109.2

2 Supplementary Text

2.1 NMR Kinetic and Mechanistic Studies

2.1.1 NMR kinetic studies

Sample preparation

In an oven-dried (80 °C, overnight) NMR tube under Ar equipped with a J. Young valve, IDPi **3** (3.0–5.0 mol%) and 1,3,5-trimethoxybenzene (**6**) (0.500 mmol, 10.0 equiv) were dissolved in anhydrous PhMe-d_8 (500 µL) and the mixture was cooled to −50 °C. Substrate **4** (0.050 mmol, 1.00 equiv) was added as a solution in PhMe-d_8 and the sample was quickly transferred to the NMR spectrometer, which was precooled to −50 °C. After rapidly (<2 min) warming the sample to −35 °C, the kinetic measurement was started.

Note: excess nucleophile was not completely soluble at low temperatures, thus a heterogeneous effect cannot be excluded.

Overview

From the ^{1}H NMR data a concentration profile was generated (Figure 9) showing the independent reaction rates of *rac*-**4**, (−)-**4** and (+)-**4**. In all cases, the baseline was optimized to the H_{2ax} signal in the starting material.

When averaging the individual enantiomers, the resulting curve overlapped with the measurement made for *rac*-**4** at the initial stage of the reaction, however at higher conversion a difference could be observed. Due to the complexity of the systems, this difference will not be discussed further.

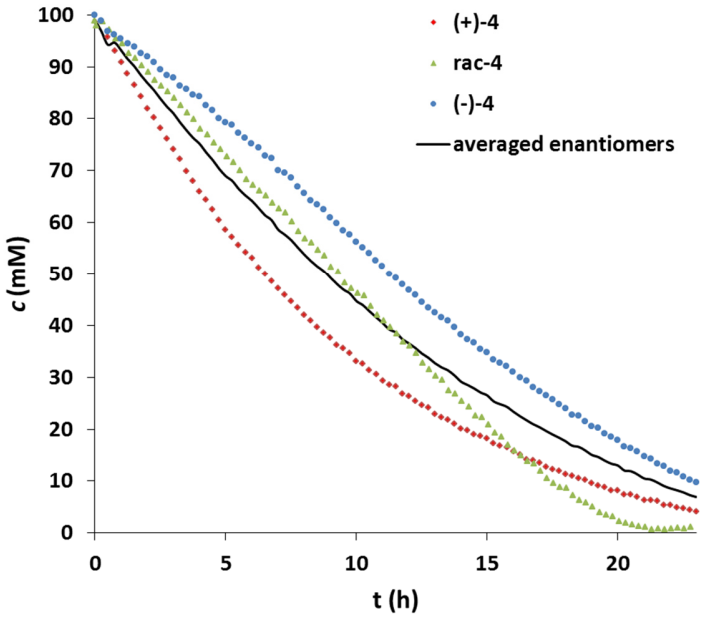


Figure 9: Concentration plots obtained from ^{1}H NMR reaction monitoring of the H_{2ax} signal during the reaction of *rac*-**4**, (−)-**4** and (+)-**4** with 5.0 mol% catalyst loading.

Reaction of *rac*-4 to 7

The reaction was monitored by ^{1}H (Figure 10) and ^{31}P NMR (Figure 11). The starting material decayed linearly, according to pseudo-zero-order kinetics. ^{31}P NMR revealed that the catalyst is present as a complex with the substrate until high conversion is reached (signal visible from a chemical shift of >0.5 ppm; for additional details see section 2.1.2). Additionally, a broad ^{31}P NMR signal at −2 ppm was observed, and its δ value was comparable to the chemical shift of the free catalyst. Furthermore, an impurity was detected at 3 ppm during the course of the reaction; however, its profile remained unaltered before and after reaching full conversion, with no evident engagement in the transformation of interest. This signal was only present in the ^{31}P NMR of the racemic reaction and was likely associated with a small (<2%) impurity in the racemic starting material.

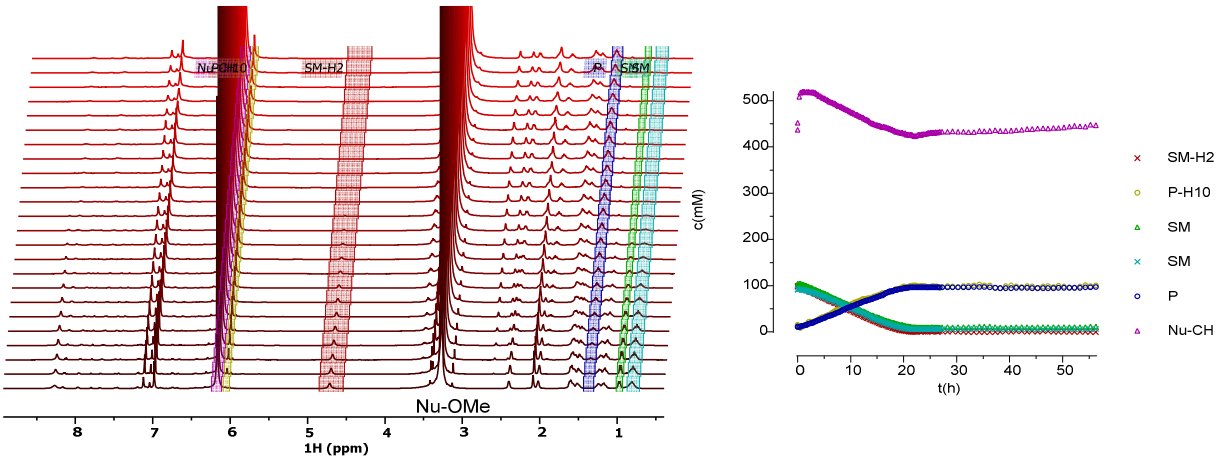


Figure 10: Left: ^{1}H NMR spectra recorded at different time points (every 2 h from t = 0); Right: concentration plots derived from the integration of ^{1}H NMR signals of starting material, product and nucleophile.

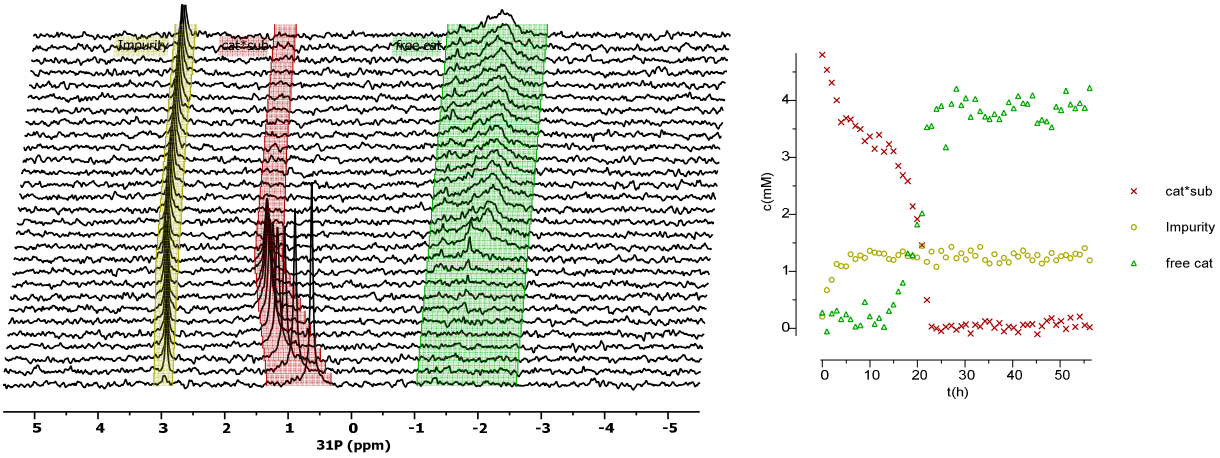


Figure 11: Left: ^{31}P NMR spectra recorded at different time points (every 2 h from t = 0); Right: concentration plots derived from the integration of ^{31}P NMR signals representing either free or substrate-bound catalyst.

Reaction of (+)-4 to 7

The reaction profile for (+)-**4**, as monitored by ^{1}H NMR, showed an exponential trend, in contrast to the linear decay observed in the reaction of *rac*-**4** (Figure 12). Nevertheless, in analogy to the reaction of *rac*-**4**, the catalyst-substrate complex at 1.5 ppm could be detected by

^{31}P NMR (Figure 13). Notably, the broad ^{31}P NMR signal at −2 ppm, likely corresponding to the free catalyst, was detected at an earlier stage of the reaction.

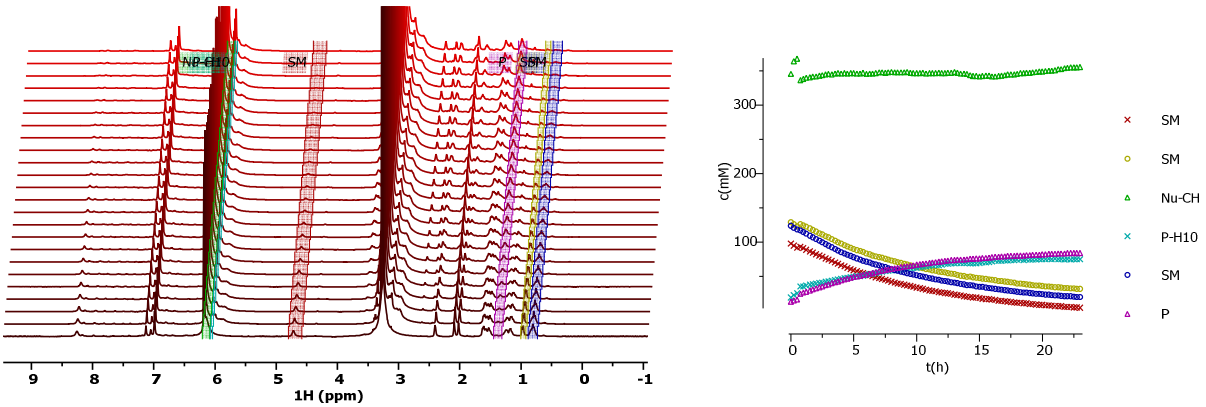


Figure 12: Left: ^{1}H NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{1}H NMR signals of starting material, product and nucleophile.

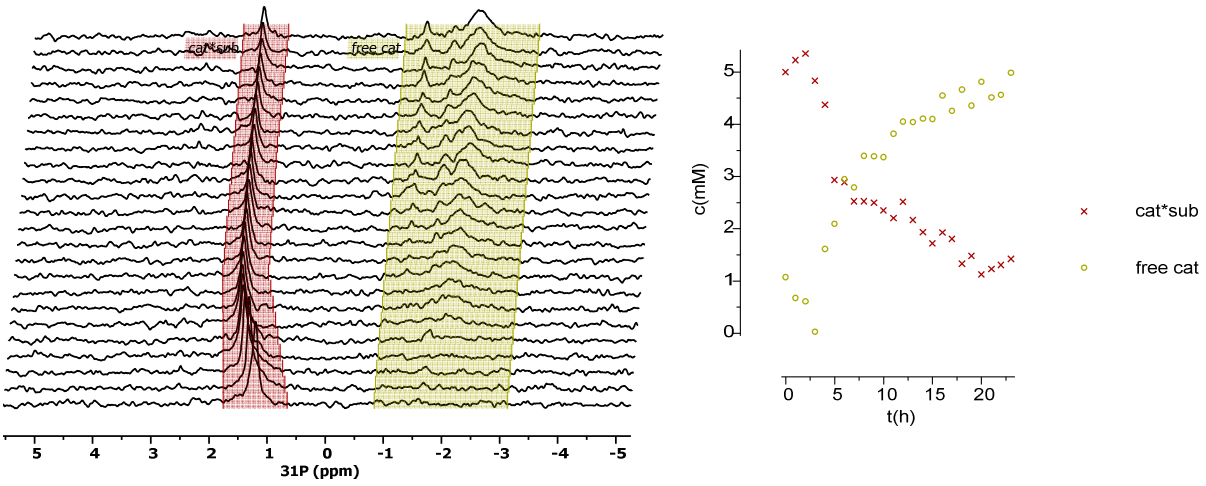


Figure 13: Left: ^{31}P NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{31}P NMR signals representing either free or substrate-bound catalyst.

Reaction of (−)-4 to 7

The reaction profile for (−)-**4**, as monitored by ^{1}H NMR, showed a linear decay of the starting material until high conversion was reached, similar to what was observed for *rac*-**4**, albeit with a

slower rate (Figure 14). Similar to previous cases, a signal at 1.5 ppm in the ^{31}P NMR indicates the formation of the catalyst-substrate complex (Figure 15). The unbound catalyst signal at −2 ppm could also be detected, but it appeared to be broader than in the reactions described above.

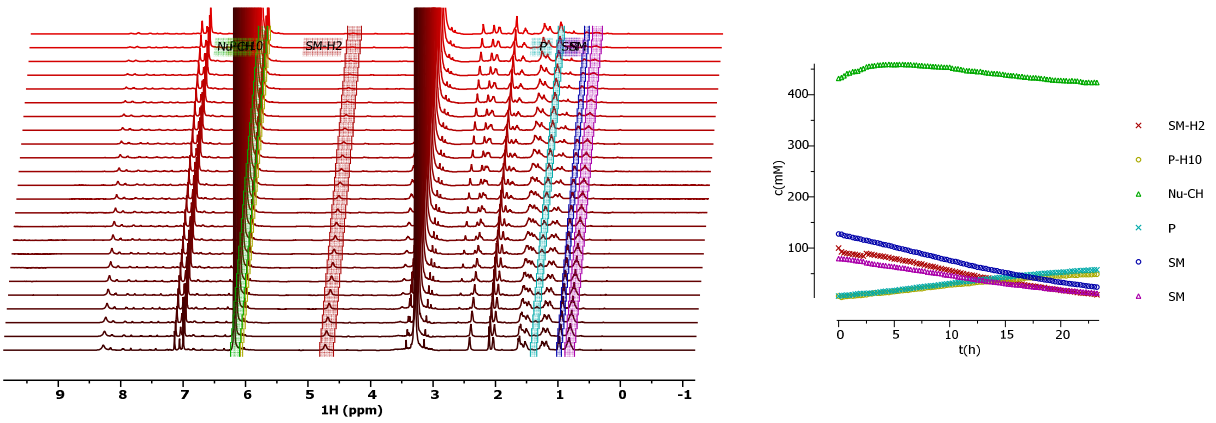


Figure 14: Left: ^{1}H NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{1}H NMR signals of starting material, product and nucleophile.

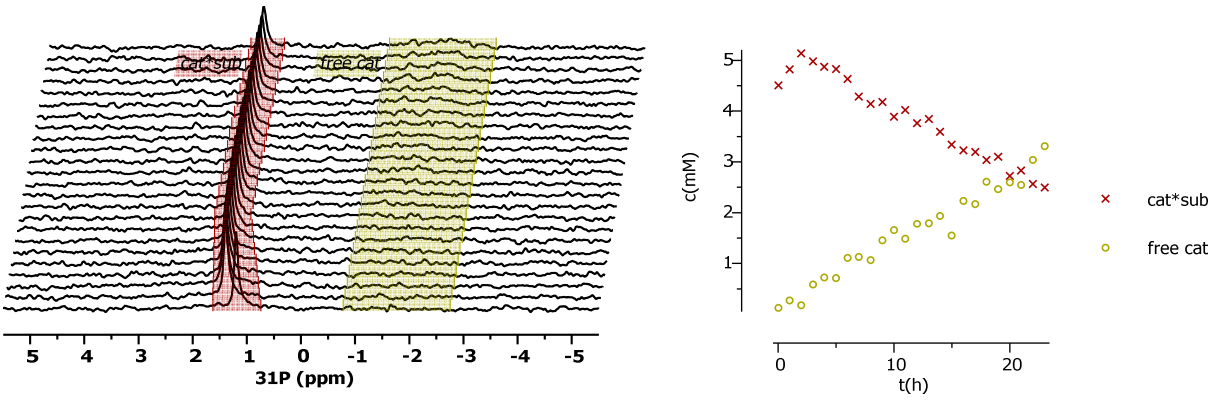


Figure 15: Left: ^{31}P NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{31}P NMR signals representing either free or substrate-bound catalyst.

Reaction of *rac*-4 to 7 with lower catalyst loading

The reaction of *rac*-**4** in the presence of 3.0 mol% of IDPi **3** showed a reaction profile comparable to that of the reaction conducted with 5 mol% of IDPi **3**, as monitored by ^{1}H NMR (Figure 16). As expected, the rate of the reaction decreased, with a linear decay of the starting

material until high conversion was reached. ^{31}P NMR (Figure 17) showed characteristic signals as described above, i.e., a catalyst-starting material complex at 1.5 ppm and the formation of unbound catalyst species when higher conversion was reached. A higher relative amount of the catalyst side-product (δ 3 ppm) could also be observed.

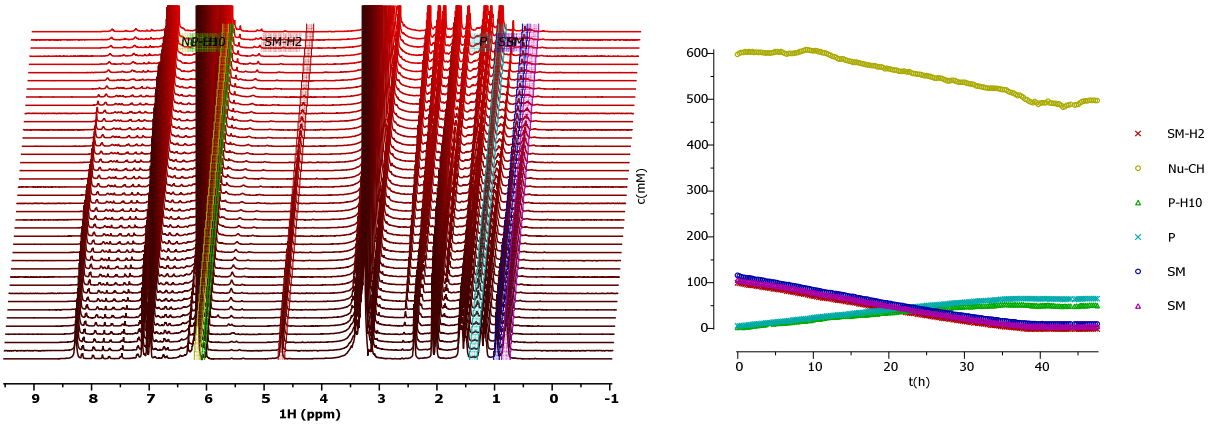


Figure 16: Left: ^{1}H NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{1}H NMR signals of starting material, product and nucleophile.

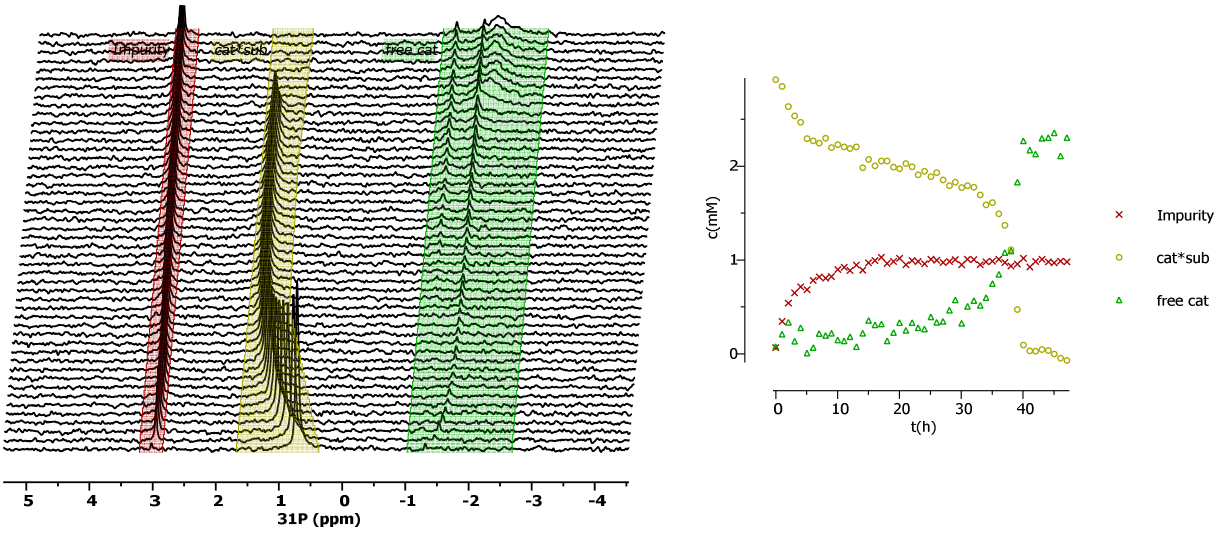


Figure 17: Left: ^{31}P NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{31}P NMR signals representing either free or substrate-bound catalyst.

To investigate the order in catalyst, reactions of *rac*-**4** were conducted in the presence of either 3.0 or 5.0 mol% catalyst loading and analyzed using the normalized time scale method by Burés[34]. An overview of various concentration profiles normalized for different assumed orders in catalyst is shown in Figure 18a–e. The optimal overlap was found with a 1.25th-order in catalyst, which was unexpected. This discrepancy could be explained by taking into consideration the catalyst degradation side-product detected by ^{31}P NMR (δ 3 ppm). We therefore fitted the formation of the catalyst degradation product to a first-order reaction (Figure 19) in order to get the effective catalyst concentration over time. This information was then used to generate a normalized time scale analysis based on the effective catalyst loading, as shown in Figure 18f[35,36]. Owing to this method by Burés, curves for the different loadings consistently overlapped by assuming a first-order dependency on catalyst concentration.

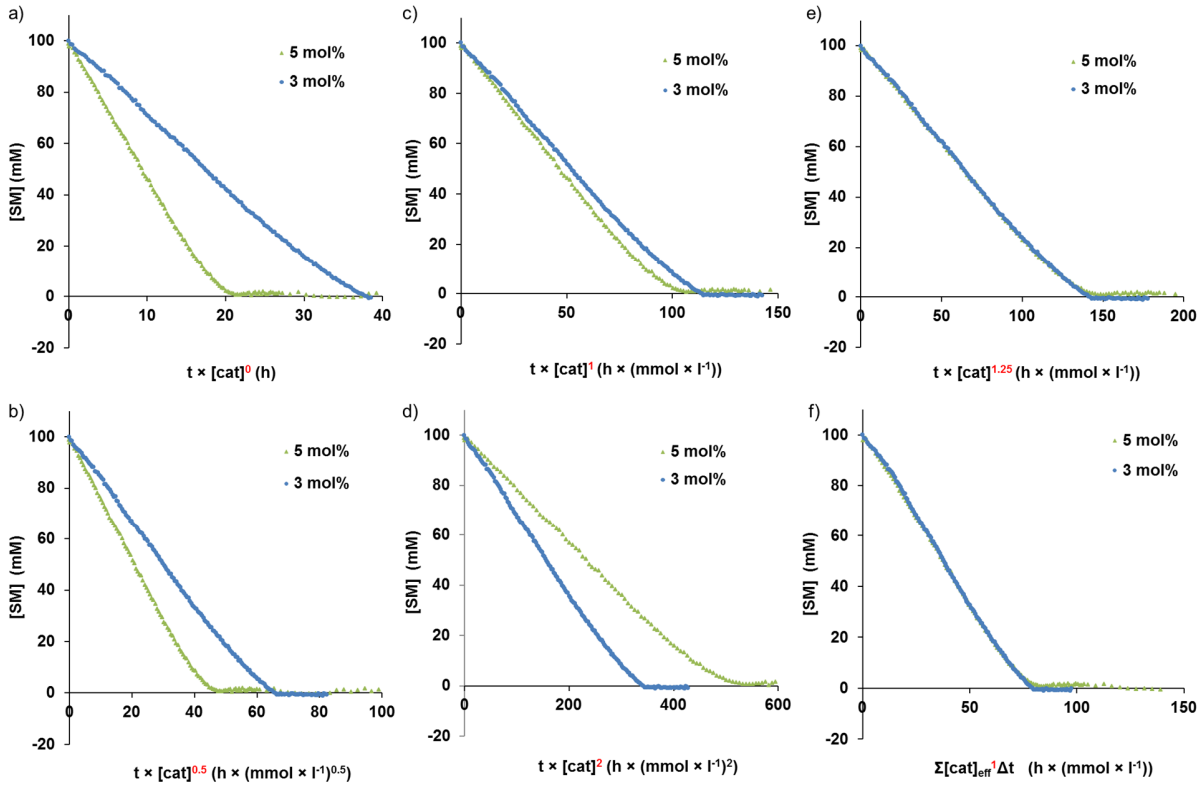


Figure 18: Concentration plots of the starting material decay with time-normalized x-axes to different catalyst orders; a) zero-order; b) half-order; c); first-order d) second-order; e) 1.25th-order; f) time-normalized to the effective catalyst concentration in solution.

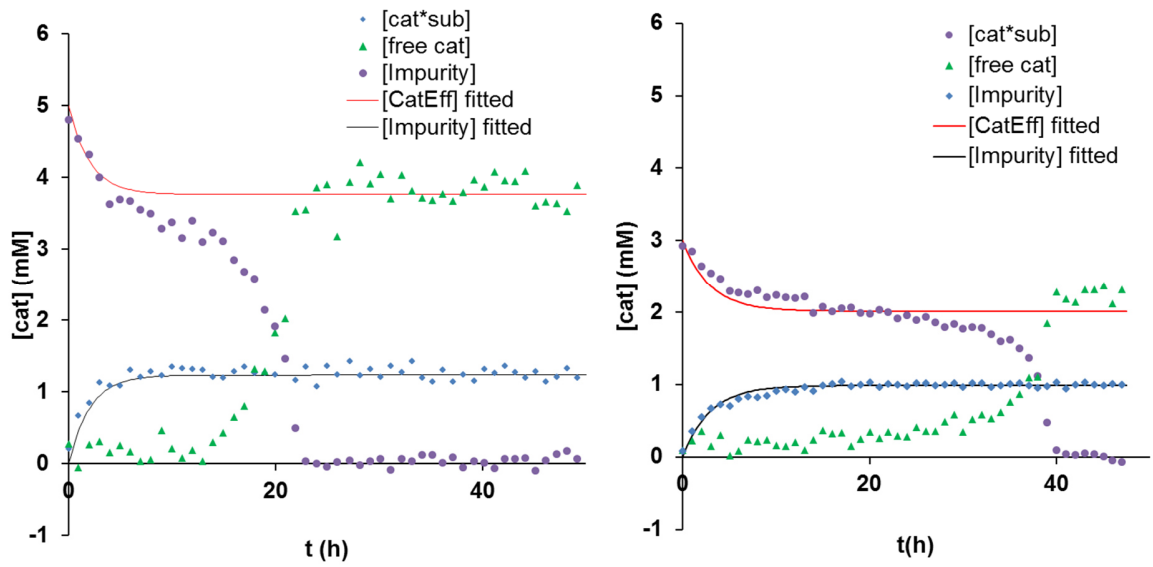


Figure 19: Change of effective catalyst concentration during the reaction of *rac*-**4**.

Reaction of *rac*-4 in the absence of nucleophile 6

In contrast to the reactions conducted in the presence of **6**, the rate of starting material decay was considerably slower in the absence of nucleophile. Indeed, only 60% of *rac*-**4** was converted after 60 h at −35 °C; whereas, full conversion of *rac*-**4** was achieved at the same point in time in the presence of 10 equivalents of **6**. The influence of the nucleophile on the reaction rate is therefore considerable, and might be associated with a different polarity of the reaction medium. In particular, in the absence of nucleophile, ^{31}P NMR showed the catalyst-substrate complex (δ 1.5 ppm) as the predominant species (Figure 20). ^{1}H NMR analysis revealed the existence of side-reactions that could also be observed in 1:1 complexation studies, as will be discussed later in this chapter (section 2.1.2) (Figure 21). Various side-products could be detected, including norbornene (**8**), nortricyclene (**9**), bis(2-norbornyl) ether (**S35**), and 2-norbornyl trichloroacetamide (**S36**) (Figure 22), which could not be observed in comparable concentrations in the presence of 10 equivalents of nucleophile. No evidence for the formation of a cationic species, which was long-lived enough to be spectroscopically characterized by NMR, could be collected. Rapid conversion of a short-lived cationic intermediate to the aforementioned side-products can instead be hypothesized.

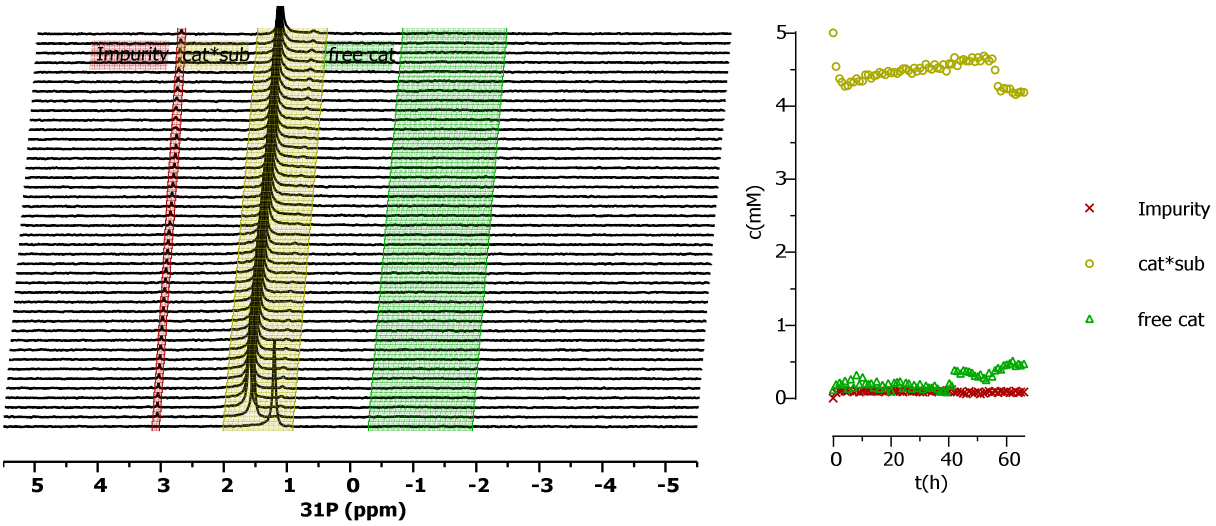


Figure 20: Left: ^{31}P NMR spectra recorded at different time points (every 2 h from t = 0); Right: concentration plots derived from the integration of ^{31}P NMR signals representing either free or substrate-bound catalyst.

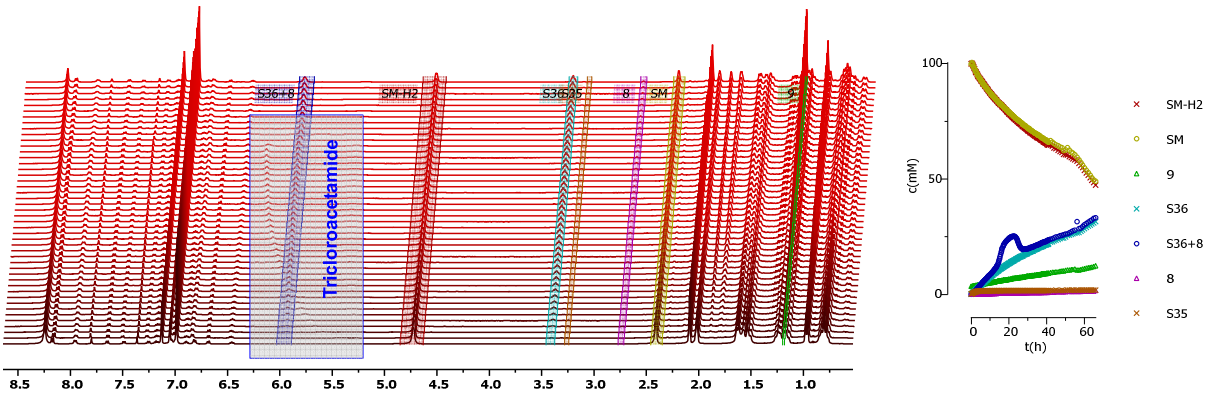


Figure 21: ^{1}H NMR spectra recorded at different time points (every 1 h from t = 0); Right: concentration plots derived from the integration of ^{1}H NMR signals of starting material and various side-products.

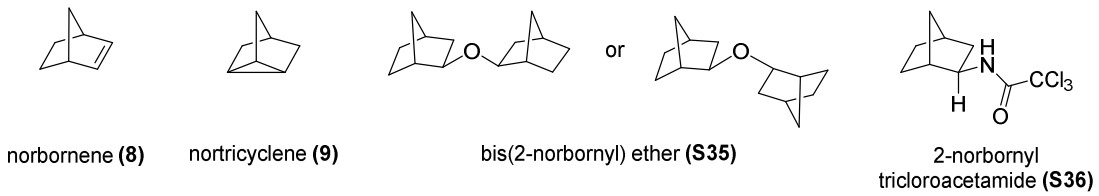


Figure 22: Products detected in the absence of nucleophile.

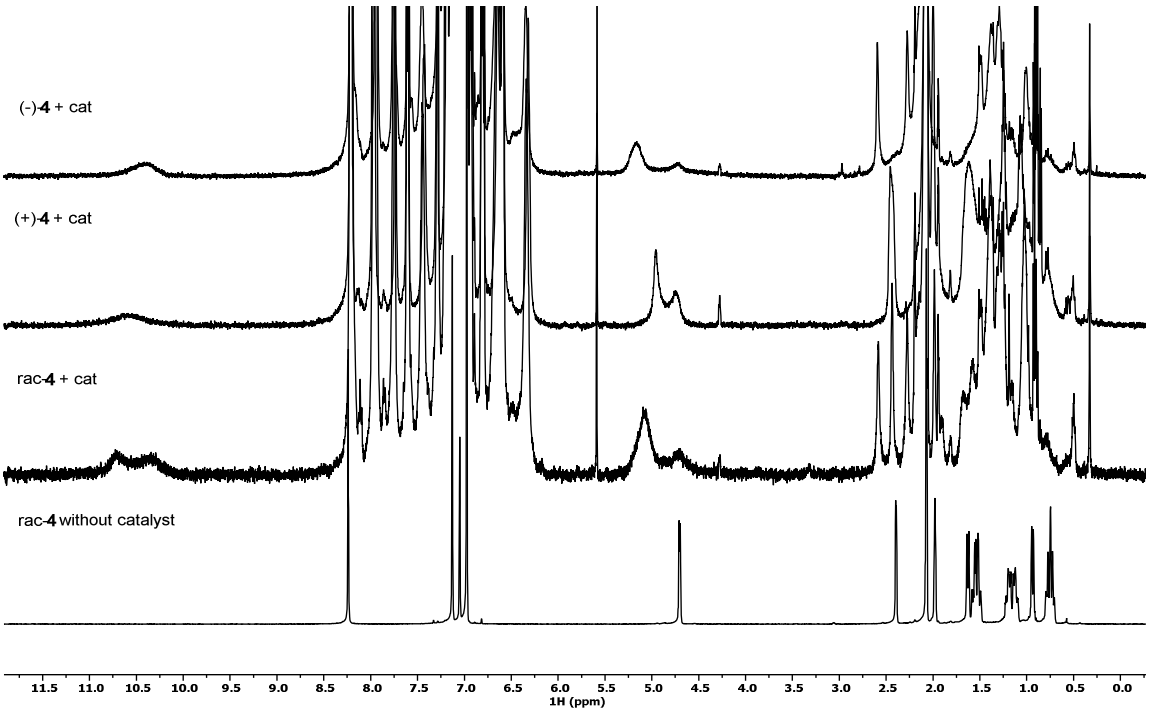
2.1.2 Interaction of various substrates and IDPi **3**

Sample preparation

In an oven-dried (80 °C, overnight) NMR tube under Ar equipped with a J. Young valve, IDPi **3** (5.00–10.0 mg, 2.10–4.70 µmol) and additives (if required) were dissolved in anhydrous PhMe-d_8 and the solution was cooled to the appropriate temperature. An equimolar amount of substrate (2.10–4.70 µmol) was added as a solution in PhMe-d_8 (total amount of solvent: 500 µL). The sample was quickly transferred to the NMR spectrometer and the measurement was started.

Interaction with *rac*-4, (−)-4 and (+)-4

The interaction of the racemic or enantiopure substrate with the catalyst was studied by ^{1}H NMR at −60 °C (Figure 23). Slowly increasing the temperature resulted in the detection of side-products, as depicted in Figure 22.



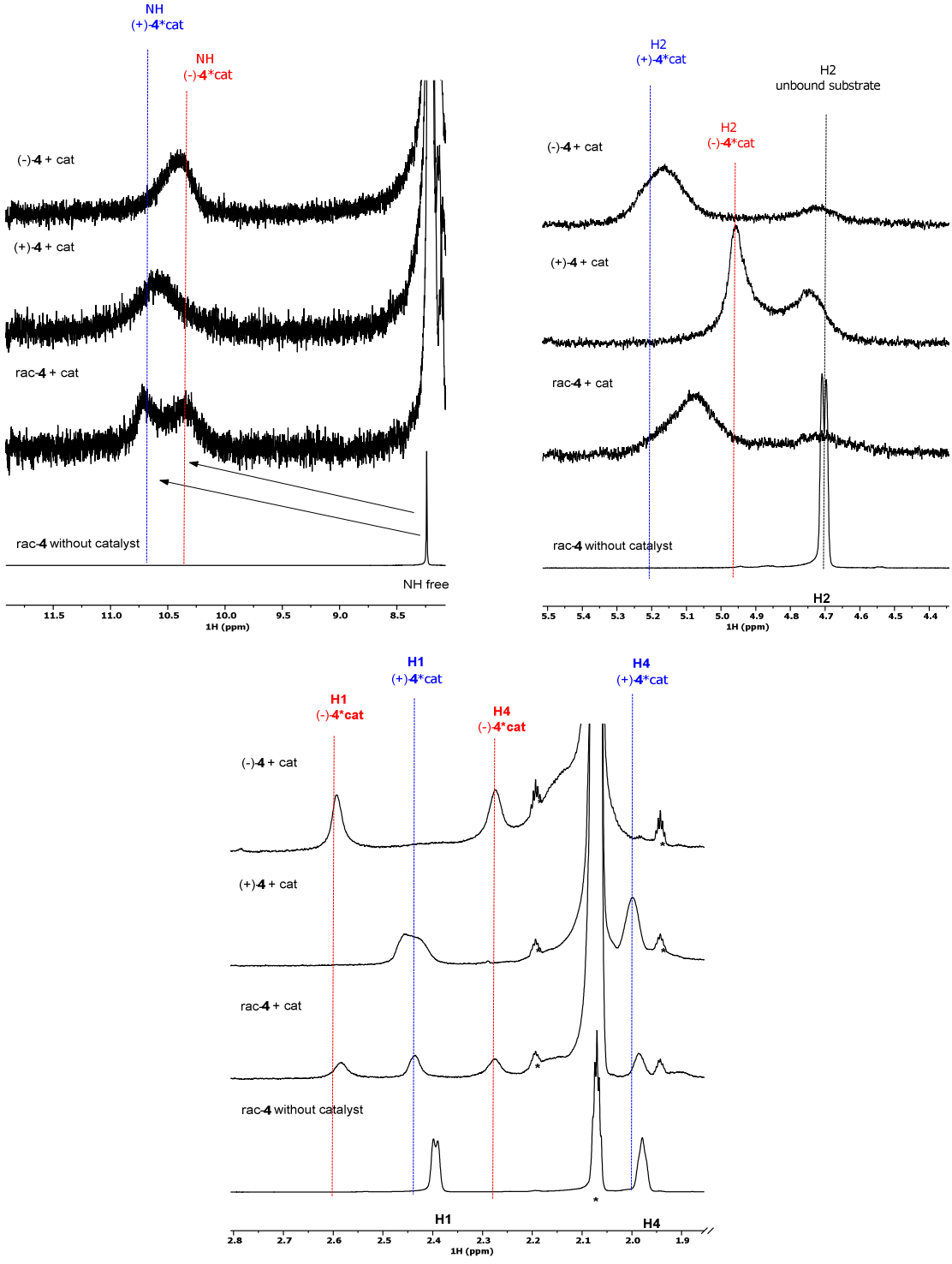


Figure 23: ^{1}H NMR spectra obtained at –60 °C for *rac*-**4**, (−)-**4** and (+)-**4** in the absence and presence of IDPi **3**.

^{31}P NMR analysis revealed that addition of the substrate to the catalyst shifted the ^{31}P NMR signal by approximately 3.5 ppm towards higher frequencies, comparable to the δ values observed for organic and inorganic salts of IDPi catalysts. Differences in the peak shape for *rac*-**4** and the single enantiomers were observed, as shown in Figure 24.

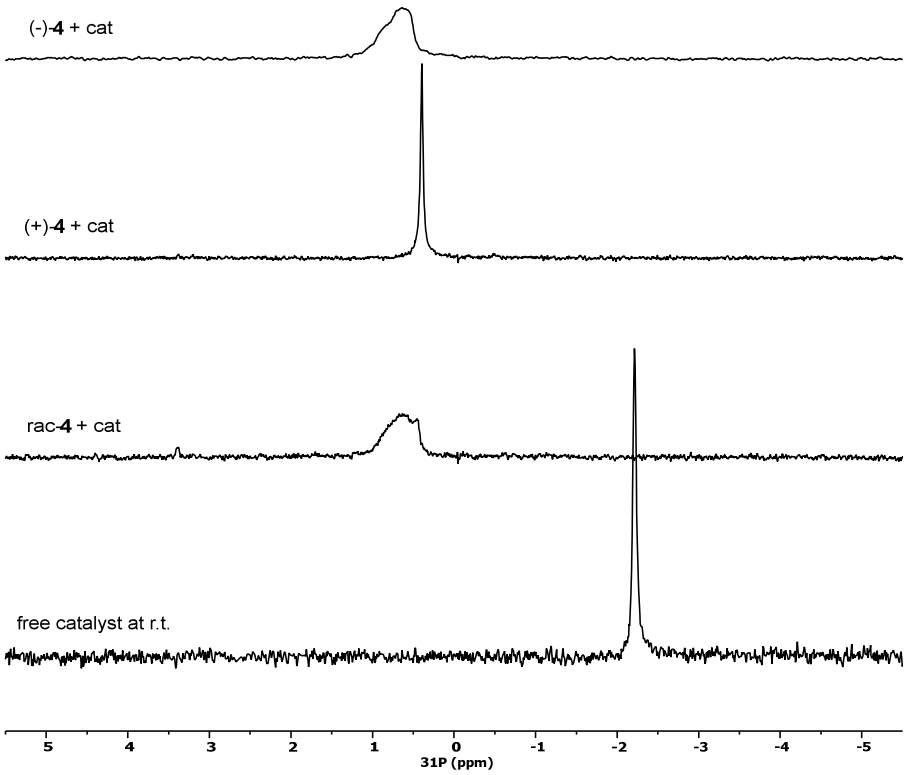


Figure 24: ^{31}P NMR spectra obtained at −60 °C for a 1:1 mixture of IDPi **3** with *rac*-**4**, (−)-**4** and (+)-**4** and comparison with the free catalyst.

Interaction with 8

Next, we evaluated the reaction between norbornene (**8**) and IDPi **3**, seeking to identify ionic or covalent adducts. Thus, an equimolar mixture of the two components was investigated by NMR spectroscopy. No changes in the chemical shifts of the norbornene signals could be detected by ^{1}H NMR upon mixing of the two components at room temperature (Figure 25). The course of the reaction was hence monitored over time, until the formation of nortricyclene, *exo*-norbornyl alcohol and bis(2-norbornyl) ether (due to the presence of traces of water in solution) was observed.

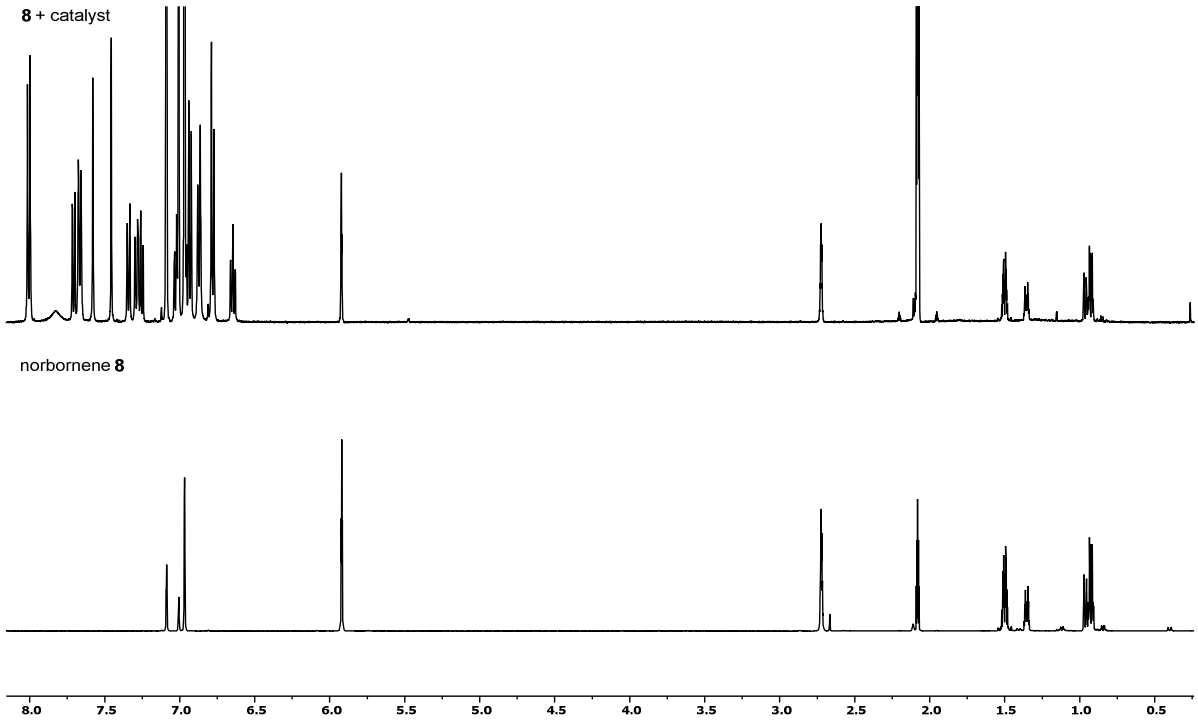


Figure 25: ^{1}H NMR spectra of norbornene and a 1:1 mixture of norbornene/IDPi **3** at room temperature.

Interaction with *rac*-10 in the presence of allyltrimethylsilane 11

In attempt to detect the formation of cationic or covalent intermediates, we also investigated an equimolar mixture of IDPi **3** with *rac*-**10** in the presence of allyltrimethylsilane (**11**) at −50 °C. An excess of allyltrimethylsilane was required to consume residual water and to observe a completely silylated catalyst species, which appeared in the ^{31}P NMR spectrum with two characteristic sharp doublets at −1.2 and −4.1 ppm (Figure 26). As a consequence for the formation of a "silylium" Lewis acid species upon protodesilylation of allyltrimethylsilane, in situ generation of propene could be detected by ^{1}H NMR. In contrast to the studies with **4**, no changes in the chemical shift of the signals relative to *rac*-**10** were detected.

The mixture was warmed to −30 °C in the spectrometer and, after 18 h, formation of nortricyclene (**9**) and fluorotrimethylsilane (TMS–F) was exclusively observed (Figure 27).

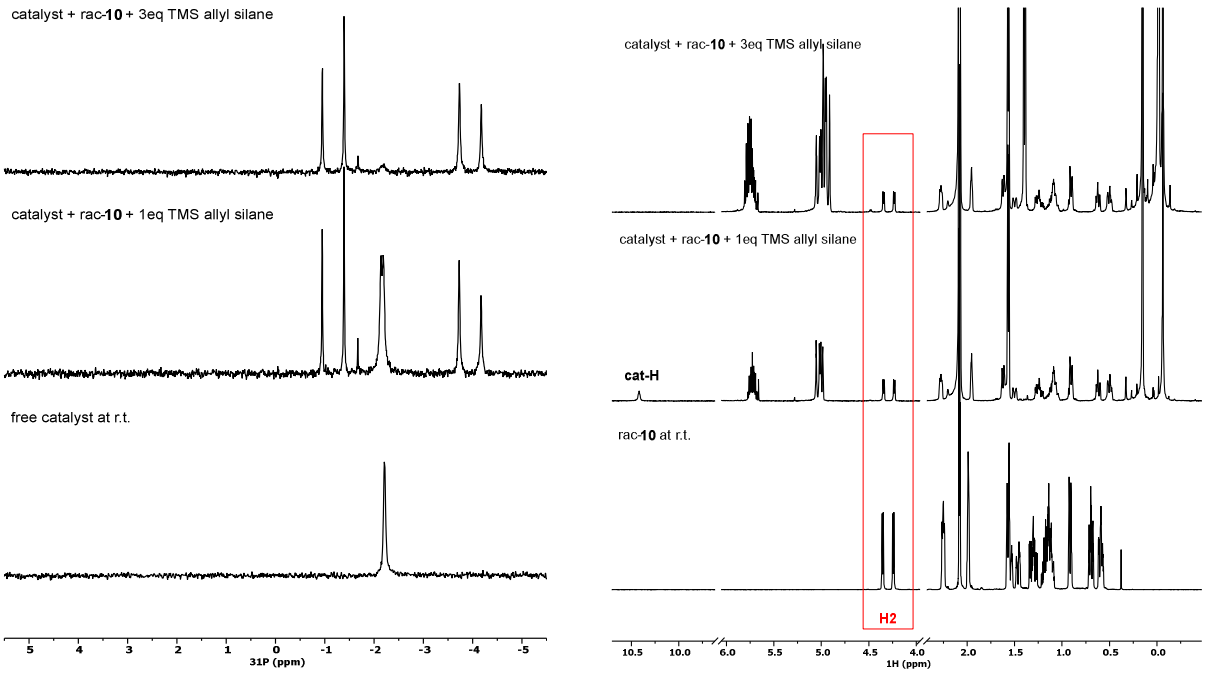


Figure 26: Left: ^{31}P NMR spectra of IDPi **3** in the presence of *rac*-**10** and various equivalents of allyltrimethylsilane **(11)**, Right: ^{1}H spectra of *rac*-**10** in the presence of IDPi **3** and various equivalents of **11**.

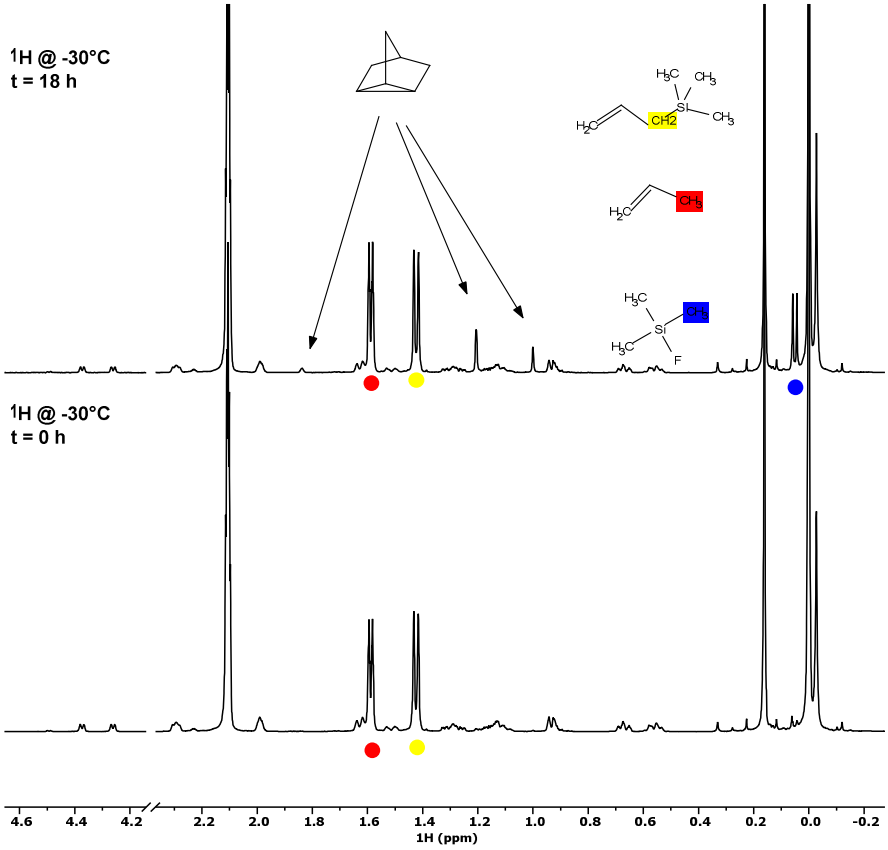


Figure 27: Excerpt of the ^{1}H NMR spectrum at different time points showing the formation of TMS–F and nortricyclene (**9**).

2.1.3 Deuterium studies

Methods

^{2}H NMR spectra were measured on a Bruker Avance III 600 MHz NMR spectrometer equipped with the lock coil of a standard TCI CryoProbe (^{1}H, ^{13}C, ^{15}N) with a cryogenically cooled preamplifier on the lock channel. The latter was crucial for obtaining good signal-to-noise ratio (SNR) with short acquisition times and a standard NMR probe. During the measurement, the ^{2}H lock was off. The acquired ^{2}H-NMR were baseline corrected with a multiple point baseline correction in MestReNova 12.0.3 and the individual signals were fitted with a fixed Lorentzian/Gaussian of 0.33.

Overview

Relative distributions of ^{2}H in product mixture **S34** for the reaction of **S32** (or *ent*-**S32**) and **S33** at 25 °C are shown in Figure 28 (for related experiments, see section 1.3.6).

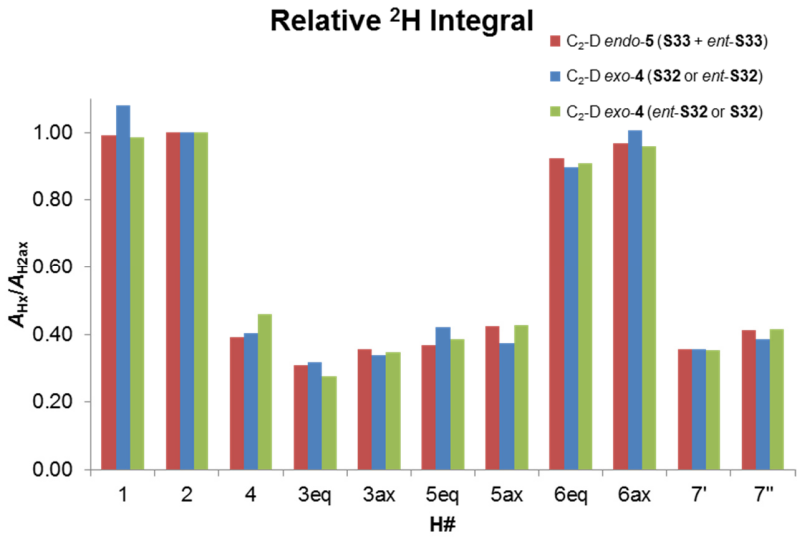


Figure 28: ^{2}H Integral distribution obtained for product **S34** after line shape fitting. Reactions of C_2-D *exo*-**4** (**S32** or *ent*-**S32**) and C_2-D *endo*-**5** (**S33** and *ent*-**S33**) were conducted at 25 °C. The data were normalized to the peak area of H_{2ax}.

Relative distributions of ^{2}H in product mixture **S34** for the reaction of **S32** or *ent*-**S32** at 25 °C and –40 °C are shown in Figure 29 and 30 (for related experiments, see section 1.3.6).

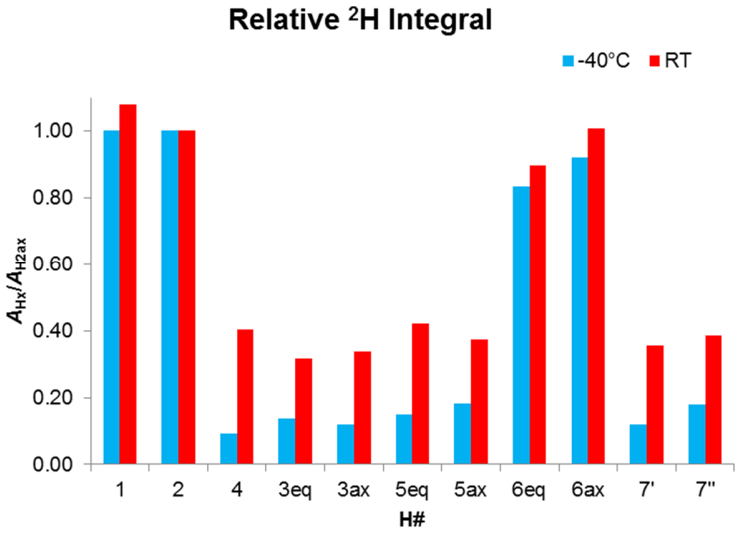


Figure 29: ^{2}H Integral distribution obtained for product **S34** after line shape fitting. Reactions of **S32** or *ent*-**S32** were conducted at 25 °C and −40 °C. The data were normalized to the peak area of H_{2ax}.

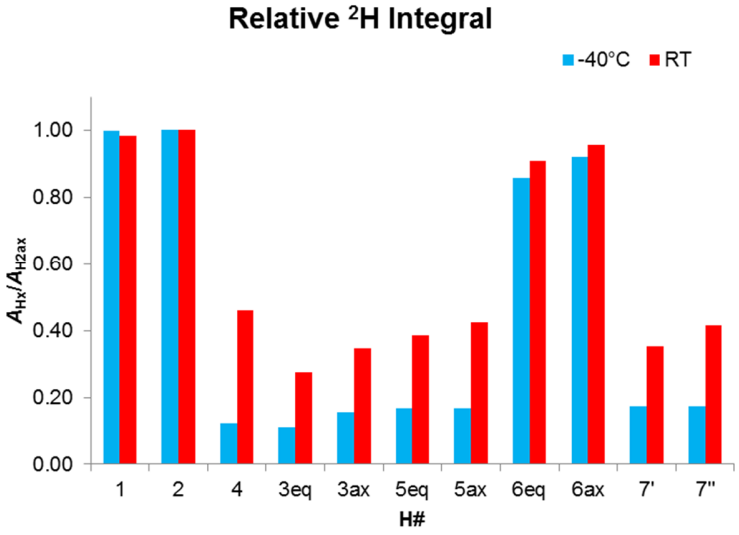


Figure 30: ^{2}H Integral distribution obtained for product **S34** after line shape fitting. Reactions of *ent*-**S32** or **S32** were conducted at 25 °C and −40 °C. The data were normalized to the peak area of H_{2ax}.

Data for individual reactions

*Reaction of **S33** and ent-**S33** (C_2-D endo-**5**) at 25 °C*

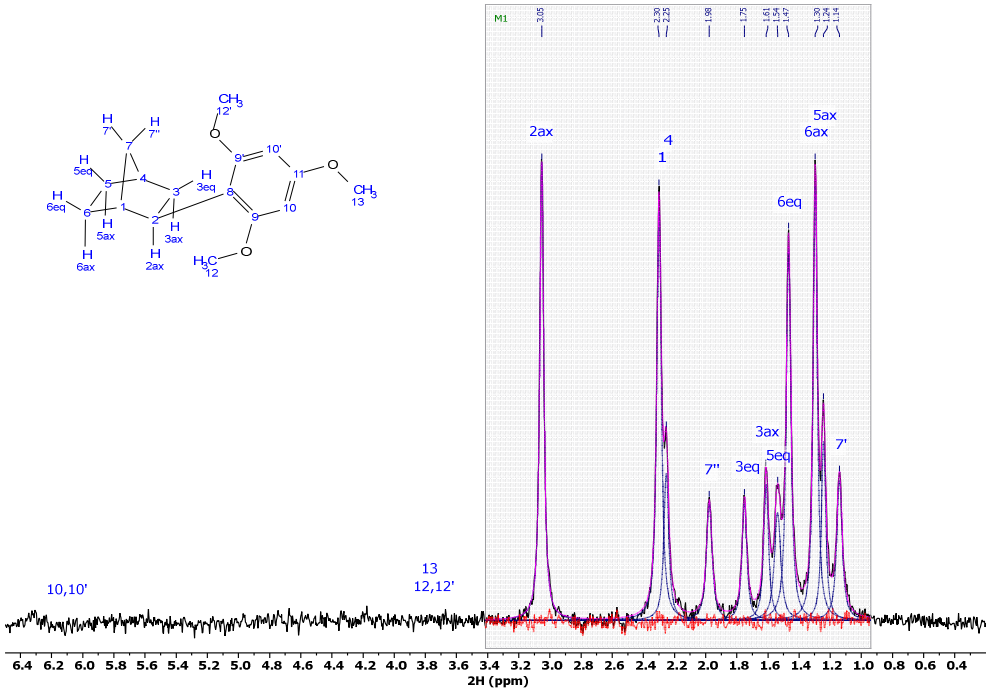


Figure 31: ^{2}H NMR spectrum with fitted peaks. **Grey box** = fitting region; **black lines** = experimental data; **blue lines** = individual fitted peaks; **magenta lines** = sum of the fitted peaks; **red lines** = residual. Blue numbers indicate the structural assignment of protonated product **7**, which was used as reference for the assignment of the deuterated analogues.

#	ppm	Assignment	Height	Width(Hz)	L/G	Area	Relative
1	2.299	1	576.58	3.2	0.33	12216.6	0.99
2	3.053	2	648.42	2.8	0.33	12321.3	1.00
3	2.253	4	207.41	3.5	0.33	4815.2	0.39
4	1.751	3eq	165.36	3.4	0.33	3798.5	0.31
5	1.612	3ax	191.86	3.4	0.33	4379.1	0.36
6	1.538	5eq	152.21	4.4	0.33	4518.4	0.37
7	1.243	5ax	252.8	3.1	0.33	5219.5	0.42
8	1.467	6eq	522.11	3.3	0.33	11372.5	0.92
9	1.296	6ax	613.49	2.9	0.33	11914.6	0.97
10	1.977	7'	165.17	4	0.33	4392.3	0.36
11	1.141	7"	197.76	3.8	0.33	5078.4	0.41

Table 13: Line shape parameters obtained after fitting.

*Reaction of **S32** or ent-**S32** (C_2-D exo-**4**) at 25 °C*

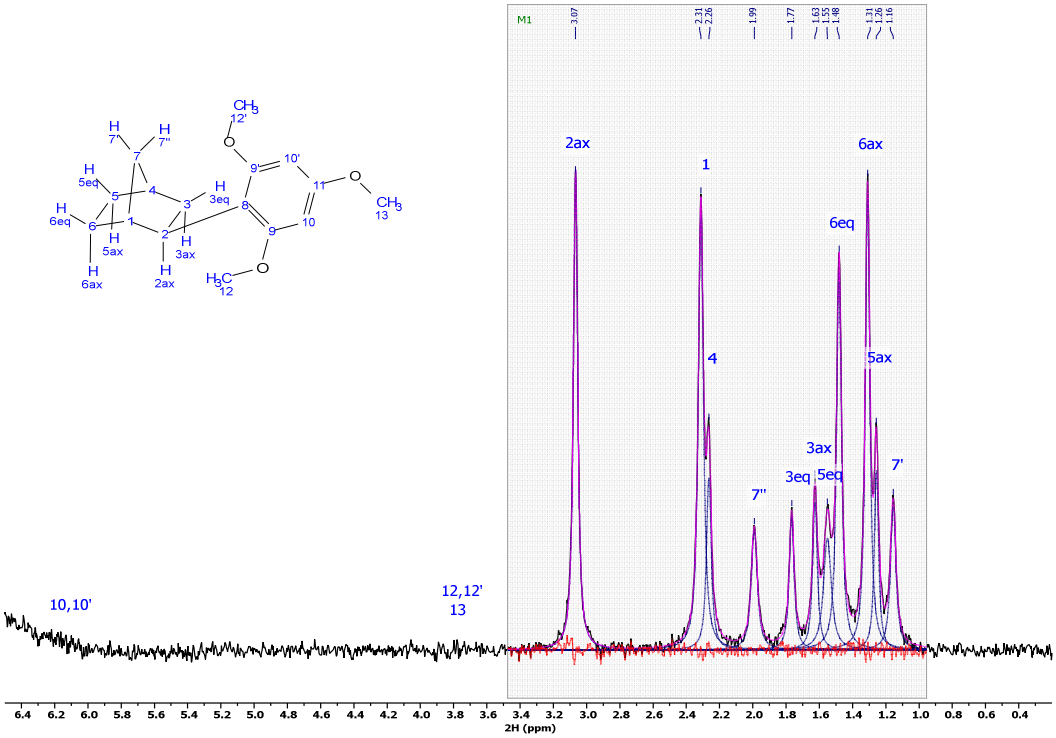


Figure 32: ^{2}H NMR spectrum with fitted peaks. **Grey box** = fitting region; **black lines** = experimental data; **blue lines** = individual fitted peaks; **magenta lines** = sum of the fitted peaks; **red lines** = residual. Blue numbers indicate the structural assignment of protonated product **7**, which was used as reference for the assignment of the deuterated analogues.

#	ppm	Assignment	Height	Width(Hz)	L/G	Area	Relative
1	2.313	1	1003.63	3.4	0.33	22711.1	1.08
2	3.066	2	1107.83	2.8	0.33	21042.1	1.00
3	2.264	4	398.59	3.2	0.33	8459.9	0.40
4	1.766	3eq	307.1	3.3	0.33	6675.1	0.32
5	1.626	3ax	340.62	3.1	0.33	7127.0	0.34
6	1.551	5eq	257.8	5.1	0.33	8840.2	0.42
7	1.256	5ax	416.12	2.8	0.33	7839.3	0.37
8	1.481	6eq	871.37	3.2	0.33	18886.4	0.90
9	1.31	6ax	1040.64	3.1	0.33	21200.8	1.01
10	1.991	7'	276.91	4.0	0.33	7485.4	0.36
11	1.155	7''	330.11	3.7	0.33	8087.2	0.38

Table 14: Line shape parameters obtained after fitting.

*Reaction of **S32** or ent-**S32** (C_2-D exo-**4**) at −40 °C*

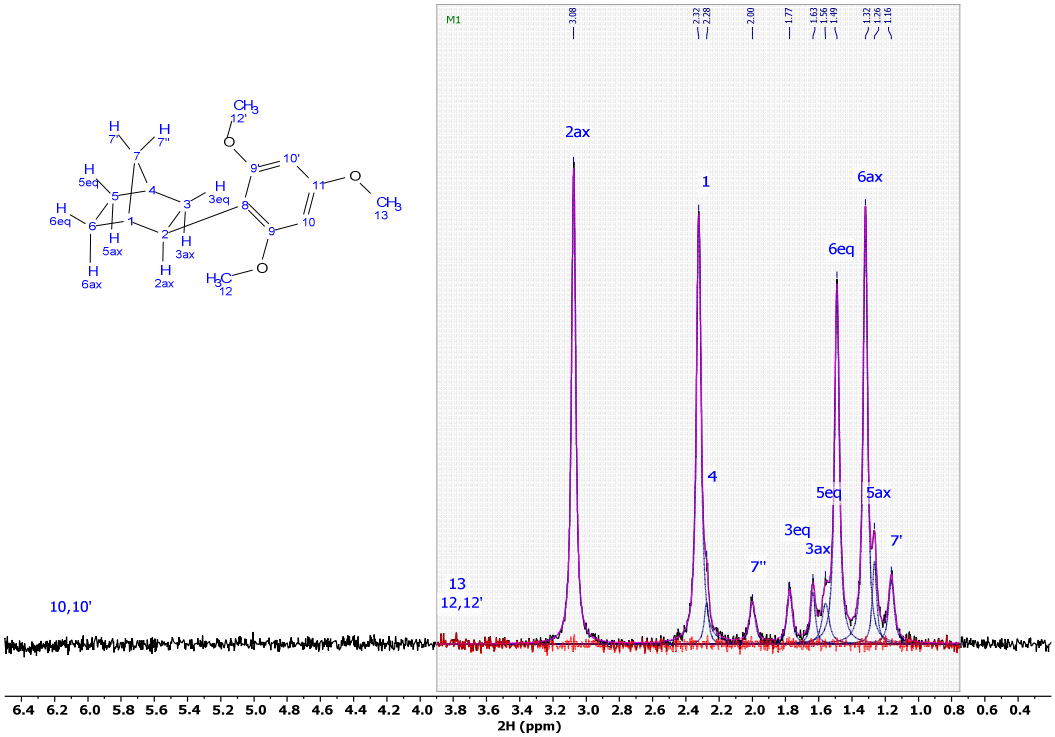


Figure 33: ^{2}H NMR spectrum with fitted peaks. **Grey box** = fitting region; **black lines** = experimental data; **blue lines** = individual fitted peaks; **magenta lines** = sum of the fitted peaks; **red lines** = residual. Blue numbers indicate the structural assignment of protonated product **7**, which was used as reference for the assignment of the deuterated analogues.

#	ppm	Assignment	Height	Width(Hz)	L/G	Area	Relative
1	2.322	1	2507.84	3.1	0.33	51272.9	1.00
2	3.075	2	2788.2	2.8	0.33	51194.1	1.00
3	2.276	4	241.14	3	0.33	4804.1	0.09
4	1.775	3eq	302.88	3.5	0.33	6984.6	0.14
5	1.635	3ax	303.97	3	0.33	6154.8	0.12
6	1.559	5eq	238.46	4.8	0.33	7584.7	0.15
7	1.264	5ax	485.89	2.9	0.33	9363.9	0.18
8	1.490	6eq	2062.41	3.1	0.33	42659.7	0.83
9	1.319	6ax	2521.36	2.8	0.33	47148.8	0.92
10	2.000	7'	238.18	3.8	0.33	6076.6	0.12
11	1.163	7"	374.34	3.6	0.33	9102.7	0.18

Table 15: Line shape parameters obtained after fitting.

*Reaction of ent-**S32** or **S32** (C_2-D exo-**4**) at 25 °C*

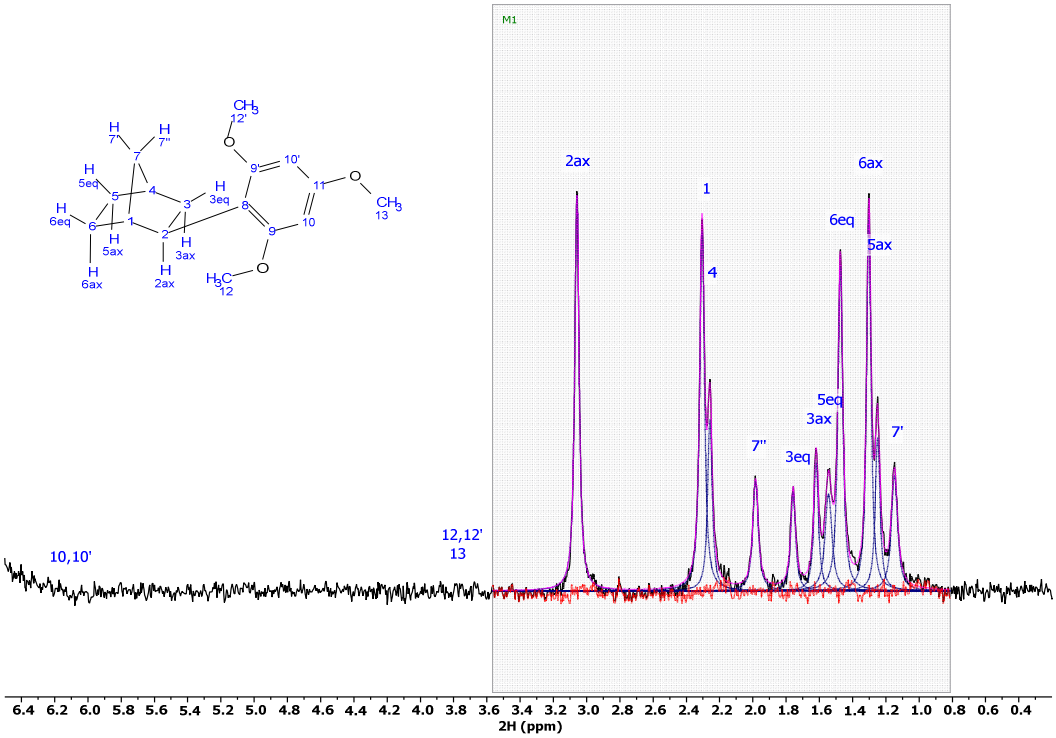


Figure 34: ^{2}H NMR spectrum with fitted peaks. **Grey box** = fitting region; **black lines** = experimental data; **blue lines** = individual fitted peaks; **magenta lines** = sum of the fitted peaks; **red lines** = residual. Blue numbers indicate the structural assignment of protonated product **7**, which was used as reference for the assignment of the deuterated analogues.

#	ppm	Assignment	Height	Width(Hz)	L/G	Area	Relative
1	2.305	1	713.4	3.1	0.33	14756.5	0.98
2	3.058	2	784.05	2.9	0.33	14993.6	1.00
3	2.258	4	339.27	3	0.33	6893.8	0.46
4	1.758	3eq	196.32	3.1	0.33	4125.5	0.28
5	1.620	3ax	254.46	3.1	0.33	5192.3	0.35
6	1.545	5eq	192.38	4.5	0.33	5767.4	0.38
7	1.249	5ax	304.06	3.1	0.33	6382.2	0.43
8	1.474	6eq	644.45	3.2	0.33	13626.8	0.91
9	1.302	6ax	741.73	2.9	0.33	14363.2	0.96
10	1.984	7'	217.51	3.7	0.33	5306.2	0.35
11	1.148	7"	228.5	4.1	0.33	6243.1	0.42

Table 16: Line shape parameters obtained after fitting.

*Reaction of ent-**S32** or **S32** (C_2-D exo-**4**) at −40 °C*

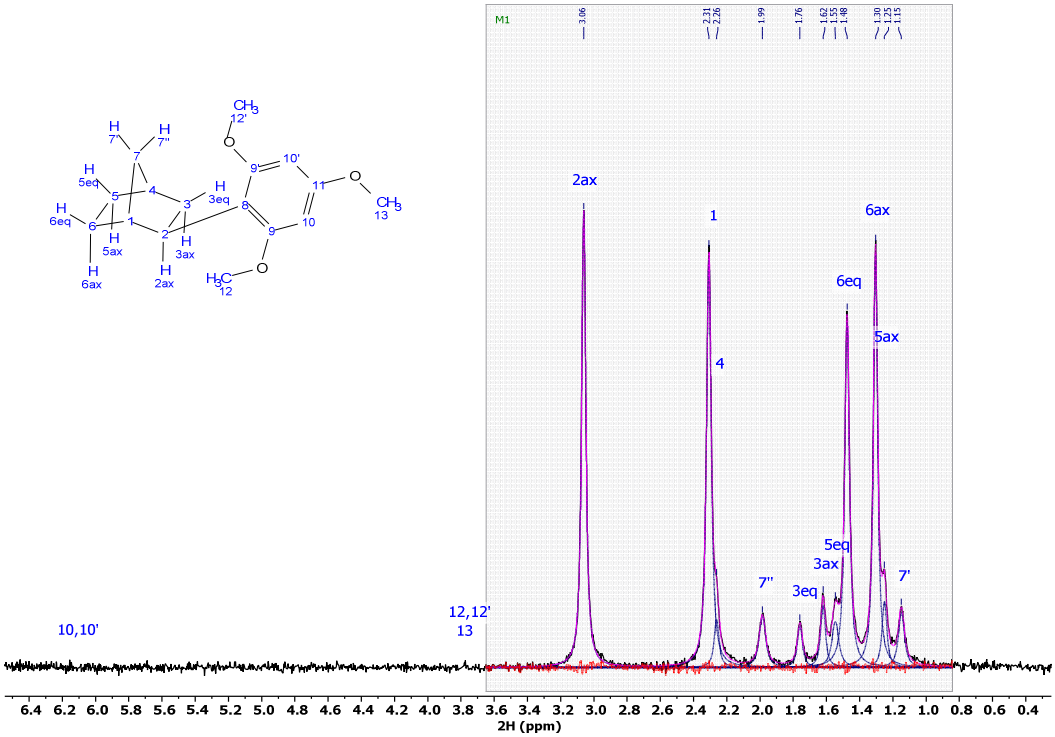


Figure 35: ^{2}H NMR spectrum with fitted peaks. **Grey box** = fitting region; **black lines** = experimental data; **blue lines** = individual fitted peaks; **magenta lines** = sum of the fitted peaks; **red lines** = residual. Blue numbers indicate the structural assignment of protonated product **7**, which was used as reference for the assignment of the deuterated analogues.

#	ppm	Assignment	Height	Width(Hz)	L/G	Area	Relative
1	2.308	1	3611.65	3.1	0.33	73989.9	1.00
2	3.061	2	4028.18	2.8	0.33	74186.3	1.00
3	2.261	4	424.84	3.2	0.33	9101.1	0.12
4	1.76	3eq	364.94	3.4	0.33	8207.5	0.11
5	1.62	3ax	546.88	3.2	0.33	11541.5	0.16
6	1.546	5eq	405.1	4.6	0.33	12425.0	0.17
7	1.251	5ax	582.95	3.2	0.33	12316.9	0.17
8	1.476	6eq	3045.76	3.1	0.33	63587.9	0.86
9	1.304	6ax	3647.89	2.8	0.33	68366.5	0.92
10	1.985	7'	448.66	4.3	0.33	12877.6	0.17
11	1.148	7"	483.14	4	0.33	12863.6	0.17

Table 17: Line shape parameters obtained after fitting.

2.2 Computational Methods

An exhaustive conformational analysis for the ion pairs of the anion of catalyst **3** with the 2-norbornyl cation was performed with xtb (version 5.8) employing GFN2-xTB[37] by simulated annealing molecular dynamics (MD) simulations in the gas phase. Multiple association geometries were randomly chosen to reassure that the optimal ion pair was located. These were then subjected to the MD simulations. The lower energy structures (in a 0–3 kcal mol^{-1} range) were further optimized utilizing density functional theory (DFT). Geometry optimizations were carried out with Gaussian 16[38] employing the PBE functional including Grimme's D3 dispersion correction[39] with Becke-Johnson damping[40] in conjunction with a double-ζ basis set (def2-SVP)[41]. A full computational analysis is in progress but is extremely time-consuming because solvent effects will have to be taken into account as well. These results will be reported in due course.

Cartesian coordinates (in Å) of the ion pair depicted in Figure 4e of the manuscript:

C	-3.477970000	1.054502000	2.725215000
C	-4.079073000	-0.014759000	3.379424000
C	-5.499523000	-0.174295000	3.418300000
C	-6.135288000	-1.286455000	4.045819000
C	-7.520860000	-1.401048000	4.061502000
C	-8.326044000	-0.401863000	3.463723000
C	-7.742045000	0.698770000	2.849972000
C	-6.327929000	0.831576000	2.785155000
C	-5.687437000	1.904516000	2.103924000
C	-4.306605000	2.010353000	2.076899000
C	-2.766710000	-2.549052000	0.659726000
C	-3.905689000	-2.503941000	-0.148497000
C	-4.358263000	-3.731718000	-0.756822000
C	-5.428235000	-3.786870000	-1.699605000
H	-5.930838000	-2.859078000	-1.996327000
C	-5.807921000	-4.987657000	-2.282405000
H	-6.622773000	-4.995954000	-3.021494000
C	-5.145549000	-6.197845000	-1.947141000
H	-5.461830000	-7.144312000	-2.410399000
C	-4.088667000	-6.177382000	-1.051437000

H	-3.550361000	-7.104111000	-0.798693000
C	-3.655693000	-4.956031000	-0.452798000
C	-2.509818000	-4.924883000	0.388640000
H	-1.986955000	-5.869890000	0.601023000
C	-2.022417000	-3.739506000	0.932660000
C	-0.747224000	-3.705345000	1.692940000
C	-0.568612000	-2.905324000	2.843926000
H	-1.384216000	-2.278266000	3.222314000
C	0.659533000	-2.875066000	3.515552000
H	0.779184000	-2.237240000	4.400093000
C	1.714821000	-3.661266000	3.037067000
C	1.570928000	-4.474413000	1.907777000
H	2.404094000	-5.083653000	1.538639000
C	0.341858000	-4.482917000	1.240796000
H	0.245774000	-5.080933000	0.323254000
C	-3.814946000	-0.122278000	-0.927134000
C	-4.565262000	-1.194555000	-0.424990000
C	-5.977305000	-1.006563000	-0.221956000
C	-6.800685000	-1.969352000	0.432811000
H	-6.338841000	-2.879467000	0.839394000
C	-8.166585000	-1.763962000	0.566585000
H	-8.782055000	-2.512246000	1.088775000
C	-8.776020000	-0.587660000	0.054218000
H	-9.858894000	-0.436194000	0.172538000
C	-7.996630000	0.384769000	-0.550928000
H	-8.449598000	1.319895000	-0.913106000
C	-6.586574000	0.214028000	-0.686919000
C	-5.773450000	1.236050000	-1.243161000
H	-6.267828000	2.147613000	-1.607882000
C	-4.385371000	1.126982000	-1.334431000
C	-3.580253000	2.268117000	-1.847798000
C	-4.048696000	3.586282000	-1.627730000
H	-4.924376000	3.750703000	-0.984630000
C	-3.408552000	4.695869000	-2.187066000
H	-3.801004000	5.706546000	-2.019641000
C	-2.261771000	4.489360000	-2.965387000
C	-1.724076000	3.211393000	-3.149528000
H	-0.799477000	3.048605000	-3.717295000
C	-2.386310000	2.110621000	-2.590782000
H	-1.964569000	1.116563000	-2.768773000
C	3.598065000	-1.118801000	0.478220000
C	4.138833000	-2.070339000	-0.398464000
C	5.568075000	-2.121894000	-0.558207000

C	6.208820000	-2.932769000	-1.541127000
H	5.590466000	-3.490861000	-2.257544000
C	7.592418000	-3.017270000	-1.603818000
H	8.065517000	-3.641661000	-2.375810000
C	8.402553000	-2.297645000	-0.685388000
H	9.497895000	-2.378782000	-0.739188000
C	7.810526000	-1.456488000	0.243702000
H	8.429425000	-0.855428000	0.928290000
C	6.390726000	-1.326526000	0.317070000
C	5.777605000	-0.422467000	1.223754000
H	6.428877000	0.155820000	1.895043000
C	4.393514000	-0.254751000	1.299152000
C	3.819329000	0.752068000	2.232793000
C	2.575196000	0.595840000	2.891644000
H	1.931944000	-0.263176000	2.676751000
C	2.143678000	1.507583000	3.864950000
H	1.173205000	1.345648000	4.353247000
C	2.965752000	2.593223000	4.186832000
C	4.171730000	2.821819000	3.511097000
H	4.792137000	3.695462000	3.746225000
C	4.578255000	1.909985000	2.532747000
H	5.507563000	2.110857000	1.983589000
C	2.142597000	-2.594556000	-1.810643000
C	3.244659000	-3.049544000	-1.082763000
C	3.427227000	-4.474122000	-0.939859000
C	4.431673000	-5.054416000	-0.108623000
H	5.095674000	-4.400964000	0.468671000
C	4.546270000	-6.431323000	0.021293000
H	5.316667000	-6.849123000	0.686293000
C	3.670336000	-7.301273000	-0.679634000
H	3.777569000	-8.391174000	-0.574648000
C	2.668962000	-6.771375000	-1.477198000
H	1.966290000	-7.432630000	-2.007674000
C	2.506088000	-5.359773000	-1.612281000
C	1.415728000	-4.821571000	-2.349247000
H	0.723793000	-5.517004000	-2.848307000
C	1.186259000	-3.451232000	-2.440999000
C	-0.033283000	-2.915216000	-3.097208000
C	-0.013012000	-1.754792000	-3.902042000
H	0.921782000	-1.210360000	-4.074681000
C	-1.187540000	-1.257739000	-4.479023000
H	-1.150303000	-0.345154000	-5.086640000
C	-2.391155000	-1.937969000	-4.259855000

C	-2.447226000	-3.098378000	-3.480480000
H	-3.395515000	-3.622083000	-3.313378000
C	-1.267597000	-3.572310000	-2.897792000
H	-1.321813000	-4.452446000	-2.241125000
F	-3.332942000	-0.943509000	3.980443000
F	-5.424962000	-2.257760000	4.624995000
F	-8.110655000	-2.459619000	4.619308000
F	-9.650893000	-0.551937000	3.460947000
F	-8.547432000	1.608966000	2.293710000
F	-6.407823000	2.826766000	1.448448000
F	-3.765666000	3.023752000	1.395508000
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F	3.231981000	-1.997494000	4.154760000
F	4.772915000	-3.583660000	4.662148000
F	4.145794000	-3.334011000	2.490850000
F	-1.382905000	5.117717000	-5.221146000
F	0.034622000	5.414285000	-3.409687000
F	-1.535075000	6.829312000	-2.417706000
F	-0.794057000	7.204200000	-4.533970000
F	-2.942053000	6.530883000	-4.240923000
F	0.965401000	3.910765000	4.955254000
F	2.980133000	5.054568000	4.684980000
F	2.079285000	4.743200000	6.748131000
F	3.983911000	3.626641000	6.217216000
F	1.977038000	2.487785000	6.485201000
F	-3.522551000	0.267718000	-4.666927000
F	-3.245441000	-1.161472000	-6.478431000
F	-5.316549000	-0.713530000	-5.652171000
F	-4.468656000	-2.798792000	-5.367891000
F	-4.734665000	-1.369173000	-3.554185000
N	-0.152644000	-1.023650000	-0.293037000
N	-1.435405000	1.105700000	0.975487000
N	1.562357000	1.125530000	-0.791608000
O	-2.311750000	-1.360325000	1.210357000
O	-2.449054000	-0.296070000	-1.092817000
O	-0.983374000	0.267033000	3.403185000
O	-1.455560000	2.708313000	2.915820000
O	2.221926000	-1.058347000	0.622468000
O	1.949836000	-1.222809000	-1.900407000
P	-1.474746000	-0.320999000	0.237195000
P	1.291200000	-0.450500000	-0.598071000
S	-1.678343000	1.280721000	2.573698000

S	3.326260000	-3.620705000	3.898265000
S	-1.486205000	5.917761000	-3.797351000
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S	-3.933016000	-1.290471000	-4.997071000
S	1.779542000	1.803535000	-2.257795000
C	3.512510000	1.349538000	-2.616008000
O	0.923481000	1.231677000	-3.323065000
C	3.873227000	0.433577000	-3.638059000
C	4.510002000	1.818327000	-1.764910000
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F	7.940488000	-0.847108000	-3.953370000
F	9.159152000	1.875186000	-0.314241000
F	9.805967000	0.109565000	-2.265142000
O	1.756759000	3.274824000	-2.077450000
C	0.871656000	4.251797000	2.002308000
C	1.785895000	3.834186000	1.011368000
H	0.339772000	3.579936000	2.689332000
C	0.985540000	5.751030000	2.178757000
C	2.502395000	5.047289000	0.464527000
H	2.065055000	2.788094000	0.809871000
C	0.140580000	4.160497000	0.408938000
C	1.412405000	6.109358000	0.741929000
H	0.040118000	6.222489000	2.508352000
H	1.767949000	5.953841000	2.937914000
H	3.416404000	5.210755000	1.075886000
H	2.783901000	4.928006000	-0.596896000
C	0.215982000	5.601592000	-0.087158000
H	-0.788055000	3.730662000	0.844267000
H	0.424027000	3.399306000	-0.359281000
H	1.712272000	7.157884000	0.566850000
H	-0.713212000	6.159747000	0.132769000
H	0.400002000	5.638678000	-1.173439000

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