

## Supporting Information

### Scalable and Highly Diastereo- and Enantioselective Catalytic Diels–Alder Reaction of $\alpha,\beta$ -Unsaturated Methyl Esters

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## General Information and Instrumentation

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. For all reactions under argon, dried and degassed solvents were used. Dry argon was purchased from Air Liquide with >99.5% purity. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds. Nomenclature follows the suggestions proposed by the computer program ChemBioDraw of CBD/Cambridgesoft. The enantiomeric ratios were determined by HPLC or GC analysis employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures. The diastereomeric ratios were determined by HPLC analysis or <sup>1</sup>H NMR analysis and specified in the individual experiment.

Thin-layer chromatography (TLC) was performed using silica gel pre-coated plastic sheets (Polygram SIL G/UV254, 0.2 mm, with fluorescent indicator; Macherey-Nagel), which were visualized with a UV lamp (254 or 366 nm) and/or phosphomolybdic acid (PMA) stain and/or permanganate stain. Preparative thin-layer chromatography (PrepTLC) was performed on silica gel pre-coated glass plates SIL G-25 UV254 and SIL G-100 UV254 with 0.25 mm and 1.0 mm SiO<sub>2</sub> layers (Macherey-Nagel). Flash column chromatography was performed on Merck silica gel (60, particle size 0.040-0.063 mm). <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>31</sup>P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500, AV-400 or DPX-300 spectrometer in a suitable deuterated solvent. The employed solvents and respective measuring frequencies are indicated for each experiment. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quadruplet), p (pentet), hept (heptet), m (multiplet), and br (broad). All spectra were recorded at 298 K unless otherwise noted, processed with Bruker TOPSPIN or MestReNova suits of programs, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane was used as the internal reference in <sup>1</sup>H and <sup>13</sup>C NMR spectra (e.g. CDCl<sub>3</sub> = 7.26 ppm for <sup>1</sup>H, 77.160 ppm for <sup>13</sup>C), and are reported as follows: chemical shift in ppm (multiplicity, coupling constant *J* in Hz, number of protons). All spectra are broadband decoupled unless otherwise noted. Electron impact (EI) mass spectrometry (MS) was performed on a Finnigan MAT 8200 (70 eV) or MAT 8400 (70 eV) spectrometer. Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker ESQ 3000 spectrometer. High resolution mass spectrometry (HRMS) was performed on a Finnigan MAT 95 (EI) or Bruker APEX III FTMS (7T magnet, ESI). The ionization method and mode of detection employed is indicated for the respective experiment. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AD liquid chromatograph (SIL-20AC auto sampler, CMB-20A communication bus module, DGU-20A5 degasser, CTO-20AC column oven, SPD-M20A diode array detector), Shimadzu LC-20AB liquid chromatograph (SIL-20ACHT auto sampler, DGU-20A5 degasser, CTO-20AC column oven, SPD-M20A diode array detector), or Shimadzu LC-20AB liquid chromatograph (reversed phase, SIL-20ACHT auto sampler, CTOS3 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 the respective solvent mixture is indicated for each experiment. Optical rotations were measured on an Autopol IV automatic polarimeter (Rudolph Research Analytical) at 589 nm (sodium D line), 25 °C. Data are reported as: [α]<sub>D</sub><sup>t</sup>, concentration (c in g/100 mL), and in the corresponding solvent.

If available,  $\alpha,\beta$ -unsaturated methyl esters have been purchased from commercial sources and the *E/Z* ratios were >99:1 unless otherwise stated. Other  $\alpha,\beta$ -unsaturated methyl esters have been prepared as described previously with *E/Z* ratios of >99:1.<sup>1</sup>

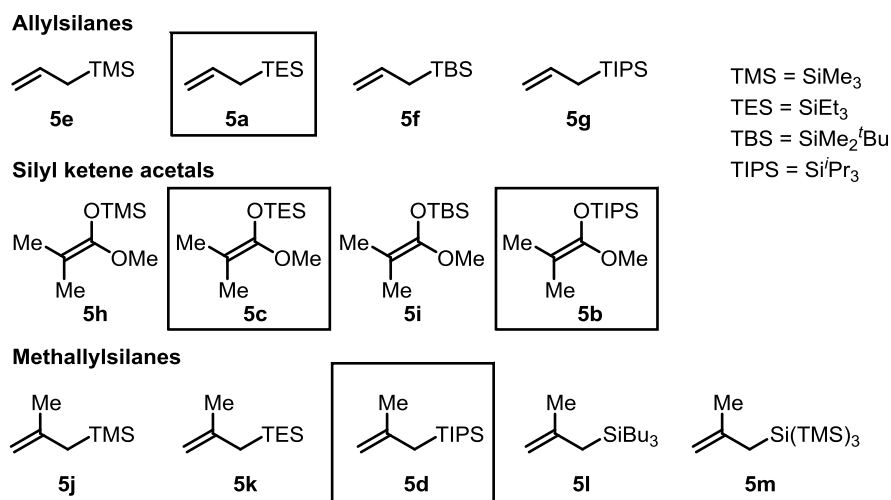
### **Purification and storage of dienes**

1,3-Cyclopentadiene was prepared by pyrolysis of dicyclopentadiene<sup>2</sup> and was stored in a Schlenk flask under argon at  $-78\text{ }^{\circ}\text{C}$ .

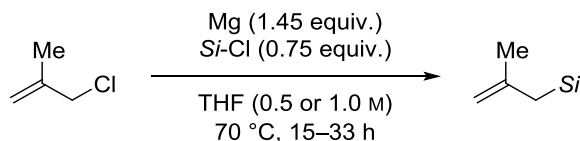
For the reaction optimization with dienes other than 1,3-cyclopentadiene, the dienes were used as received. The effect of diene purification was investigated as described in the corresponding section. For the isolation experiments, purified dienes were used. The commercial dienes were purified as follows: the dienes were washed several times with 1M NaOH, water and brine to remove the inhibitor (mostly BHT = 3,5-di-*tert*-butyl-4-hydroxytoluol). The dienes were then dried over  $\text{MgSO}_4$ , subsequently distilled under argon from  $\text{NaBH}_4$  and stored in a Schlenk flask under argon at  $-20\text{ }^{\circ}\text{C}$ .<sup>3</sup>

## Synthesis and Characterization of Silylating Reagents

The following silylating reagents have been tested during the reaction development. Reagents **5a-d** were found optimal for individual combinations of substrate and catalyst.



Allylsilanes **5e**, **5a**, **5f** and **5g** were purchased from commercial sources and used without further purification. Silyl ketene acetals (SKA) **5h**, **5c**, **5l**, **5b** were synthesized and purified as described previously.<sup>1</sup> Methallylsilane **5j** was purchased from commercial sources and used without further purification. Methallylsilanes **5k**, **5d**, **5l**, **5m** were synthesized and purified according to a slightly modified literature procedure<sup>4</sup> and stored in Schlenk flasks under argon in a fridge at 5 °C.



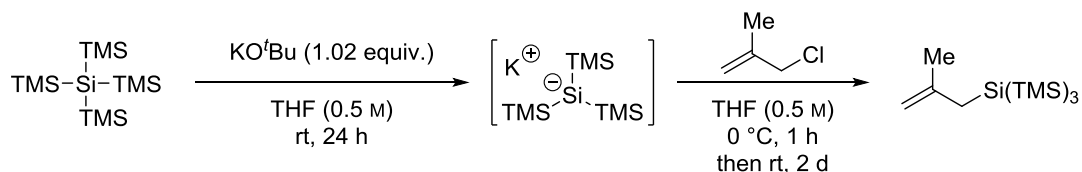
**triethyl(2-methylallyl)silane (5k):** To a 50 mL two-neck Schlenk-flask under argon equipped with a magnetic stirring bar and a reflux condenser was added magnesium (705 mg, 29.0 mmol). The apparatus was evacuated and purged with argon three times. Then, THF (2.00 mL) was added and to the resulting suspension was added one grain of iodine to initiate the reaction. A solution of 3-chloro-2-methylpropene (1.97 mL, 1.81 g, 20.0 mmol) and triethylsilyl chloride (2.52 mL, 2.26 g, 15.0 mmol) in THF (13.0 mL) was added dropwise using a syringe pump over 35 min (total volume 17.5 mL, 20 mL syringe, diameter 20 mm, pump rate: 0.50 mL · min<sup>-1</sup>) to the reaction mixture under reflux (NOTE: a color change from yellow to a cloudy/turbid colorless suspension was immediately visible upon addition of the methallylchloride/silyl chloride solution). After the addition was complete, the reaction mixture was heated under reflux for an additional 33 h at 75 °C (oil bath temperature). The formed colorless precipitate was filtrated off and the residue was extracted with hexane (2 × 50 mL). The combined filtrate and extracts were concentrated under reduced pressure and triethyl(2-methylallyl)silane **5k** was obtained by distillation under reduced pressure (bp 48–52 °C at 3.3–5.3 mbar) as a colorless oil (1.80 g, 10.6 mmol, 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.61–4.56 (m, 1H), 4.53–4.48 (m, 1H), 1.73 (s, 3H), 1.56 (s, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (mixture of rotamers) 144.2, 144.1, 108.3, 108.3, 25.4, 25.4, 23.3, 23.3, 7.5, 7.5, 3.7, 3.7;

<sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) δ 5.4; HRMS (CI, ammonia) calculated for C<sub>10</sub>H<sub>26</sub>NSi<sup>+</sup> [M+NH<sub>4</sub>]<sup>+</sup>: 188.1829; found: 188.1828.

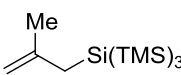
**triisopropyl(2-methylallyl)silane (5d):** Magnesium (881 mg, 36.3 mmol) was transferred to a 100 mL two-neck round-bottom flask under argon equipped with a magnetic stirring bar and a reflux condenser. Anhydrous THF (3.75 mL) and a small amount of iodine were added to initiate the reaction and the orange suspension was heated to 80 °C (oil bath temperature). Then, a solution of 3-chloro-2-methylpropene (2.46 mL, 2.26 g, 25.0 mmol) and triisopropyl chloride (4.01 mL, 3.62 g, 18.8 mmol) in THF (13.5 mL) was added dropwise using a syringe pump over 40 min (total volume 20 mL, 20 mL syringe, diameter 20 mm, pump rate: 0.50 mL · min<sup>-1</sup>) to the reaction mixture at reflux (NOTE: a color change from yellow to colorless was observed; formation of a colorless off-white precipitate was also observed during the addition) and reaction mixture was heated under reflux for an additional 28 h after the addition was complete. After cooling of the reaction mixture to room temperature, the precipitate was filtered off and the residue was extracted with hexane (2 × 50 mL). Triisopropyl(2-methylallyl)silane **5d** was obtained by distillation (Vigreux column, 7 cm) under reduced pressure (bp 85–87 °C at 12.6 mbar) as a colorless oil (3.91 g, 18.7 mmol, 98%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.63–4.59 (m, 2H), 1.79 (app t, *J* = 1.1 Hz, 3H), 1.67–1.62 (m, 2H), 1.11–1.02 (m, 21H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.6, 109.5, 25.8, 20.9, 18.9, 11.7; <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) δ 4.6; HRMS (CI, ammonia) calculated for C<sub>13</sub>H<sub>29</sub>Si<sup>+</sup> [M+H]<sup>+</sup>: 213.2033; found: 213.2032.

**tributyl(2-methylallyl)silane (5l):** To a 50 mL two-neck Schlenk-flask under argon equipped with a magnetic stirring bar and a reflux condenser was added magnesium (705 mg, 29.0 mmol). The apparatus was evacuated and purged with argon three times. Then, THF (2.00 mL) was added and to the resulting suspension was added one crystal of iodine to initiate the reaction. A solution of 3-chloro-2-methylpropene (1.97 mL, 1.81 g, 20.0 mmol) and triethylsilyl chloride (2.52 mL, 2.26 g, 15.0 mmol) in THF (13.0 mL) was added dropwise using a syringe pump over 35 min (total volume 17.5 mL, 20 mL syringe, diameter 20 mm, pump rate: 0.50 mL min<sup>-1</sup>) to the reaction mixture under reflux (NOTE: a color change from yellow to a cloudy/turbid colorless suspension was immediately visible upon addition of the methylchloride/silyl chloride solution). After the addition was complete, the reaction mixture was heated under reflux for an additional 33 h at 75 °C (oil bath temperature). The formed colorless precipitate was filtered off and the residue was extracted with *iso*-hexane (2 × 50 mL). The combined filtrate and extracts were concentrated under reduced pressure and tributylsilyl(2-methylallyl)silane **5l** was obtained by distillation under reduced pressure (bp 104–107 °C at 3.3 mbar) as a colorless oil (2.73 g, 10.7 mmol, 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.58 (dq, *J* = 2.8, 1.4 Hz, 1H), 4.49 (dq, *J* = 2.0, 0.9 Hz, 1H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.55 (d, *J* = 1.0 Hz, 2H), 1.37–1.24 (m, 12H), 0.89 (t, *J* = 7.1 Hz, 9H), 0.61–0.48 (m, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.2, 108.4, 27.0, 26.2, 25.5, 24.3, 13.9, 12.5; <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) δ 1.7; HRMS (EI) calculated for C<sub>16</sub>H<sub>34</sub>Si: 254.2430; found: 254.2428.

Tris(trimethylsilyl)silylmethylsilane **5m** was prepared according to a slightly modified procedure reported in the literature.<sup>5</sup>

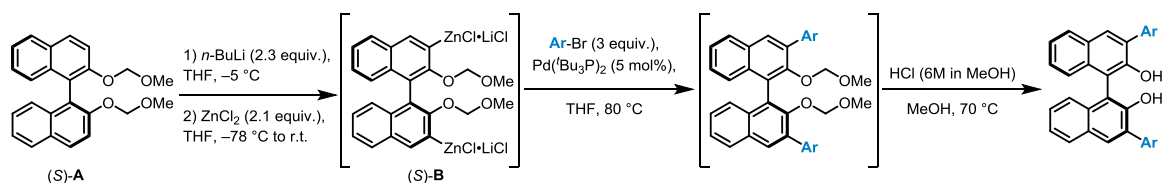


**1,1,1,3,3,3-hexamethyl-2-(2-methylallyl)-2-(trimethylsilyl)trisilane (5m):**

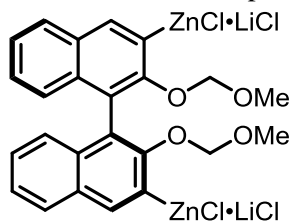
 Tetrakis(trimethylsilyl)silane (160 mg, 0.50 mmol, 1.0 equiv.) was transferred to a 10 mL Schlenk-tube under argon and KO<sup>t</sup>Bu (1.0 M solution in THF, 58.2 mg, 0.52 mL, 0.52 mmol, 1.04 equiv.) was added at r.t.. The solution was stirred for 24 h at r.t. (NOTE: slow color change from colorless to yellow-orange was observed), then the solution of tris(trimethylsilyl)potassium was cooled to 0 °C and 3-chloro-2-methyl-1-propene (2.4 mL, 24 mmol) was added. The mixture was stirred for 1 h at 0° C, the ice bath was removed and the reaction was further stirred at r.t. (2 d), then treated at 0 °C with sat. aq. NH<sub>4</sub>Cl (0.5 mL). The organic layer was separated and the aqueous layer was extracted with Et<sub>2</sub>O (2 × 5 mL). The combined extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was filtered through a short pad of silica (using pentane as eluent), to afford **5m** as a white waxy solid (134.2 mg, 0.44 mmol, 89%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.60 (s, 1H), 4.56 (s, 1H), 1.79 (s, 2H), 1.76 (s, 3H), 0.19 (s, 27H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.2, 109.0, 25.0, 18.6, 1.3; HRMS (EI) calculated for C<sub>13</sub>H<sub>34</sub>Si<sub>4</sub>: 302.1732; found: 302.1727. The analytical data was in agreement with the data reported in the literature.<sup>5</sup>

## Synthesis and Characterization of Catalysts

### Synthesis of BINOL derivatives

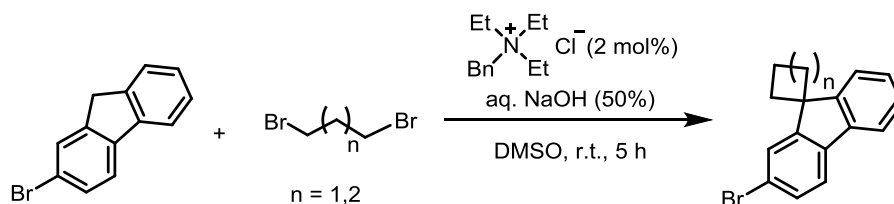


#### 3,3'-zincated MOM-protected BINOL (S)-B:



To a solution of MOM-protected BINOL (S)-A (5.92 g, 15.8 mmol) in THF (40 mL) under argon at  $-5\text{ }^\circ\text{C}$ ,  $n\text{-BuLi}$  in hexane (2.45 M, 22.6 mL, 55.3 mmol, 3.5 equiv.) was added over a period of 5 min (NOTE: The temperature was kept between  $-10\text{ }^\circ\text{C}$  and  $-5\text{ }^\circ\text{C}$  during the addition. The color changed from light yellow to deep red). The reaction was stirred between  $-10\text{ }^\circ\text{C}$  and  $-5\text{ }^\circ\text{C}$  for 4 h, during which the color changed from deep red to red-brownish. Then, the reaction mixture was cooled to  $-78\text{ }^\circ\text{C}$  and a solution of  $\text{ZnCl}_2$  in THF (0.96 M, 34.7 mL, 33.2 mmol, 2.1 equiv.) was added over a period of 20 min. The dry-ice bath was removed and the reaction was allowed to warm up to r.t. and stirred for additional 45 min, during which the color changed from red-brownish to light yellow. Then, the solvent was removed from the reaction vessel under reduced pressure by using a cooling trap with liquid nitrogen (NOTE: A voluminous foam results). Upon dryness, the organozinc compound was afforded as a pale yellow solid and dried on high vacuum overnight. A stock solution (0.27 M) in THF under argon was prepared (54 mL total volume) and stored in a fridge at  $-20\text{ }^\circ\text{C}$ . The concentration was determined through deuterium incorporation after treatment with  $\text{D}_2\text{O}$  as analyzed by  $^1\text{H-NMR}$  ( $\sim 93\%$ ) with respect to the total volume and the initial molarity of (S)-A (15.8 mmol).

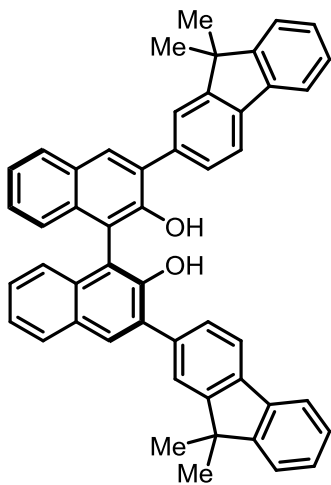
### Representative procedure for derivatization of 2-bromo-9H-fluorene:



**2'-bromospiro[cyclopentane-1,9'-fluorene]:** Following a reported procedure,<sup>6</sup> aq. NaOH (50%, 8.8 mL, 110 mmol, 5.5 equiv.) was added dropwise to the mixture of 2-bromo-9H-fluorene (4.90 g, 20.0 mmol, 1.0 equiv.) and benzyltriethylammonium chloride (91.1 g, 0.4 mmol, 2 mol%) in DMSO (20 mL) under argon at r.t. (NOTE: rapid color change from yellow to red). After the subsequent addition of 1,4-dibromobutane (2.4 mL, 20.0 mmol, 1.0 equiv.) (NOTE: color change from red to beige), the reaction was stirred for 5 hours at r.t.. Then, water (100 mL) and toluene (100 mL) were added and the organic layer was separated, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes) to yield 2'-bromospiro[cyclopentane-1,9'-fluorene] as a light yellow solid (3.70 g, 12.4 mmol, 62%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.63 (m, 1H), 7.59 – 7.52 (m, 2H), 7.47 – 7.39 (m, 2H), 7.35 – 7.29 (m, 2H), 2.19 – 2.04 (m, 8H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.51, 154.07, 138.65, 138.58, 129.91, 128.01, 127.04, 126.43, 123.02, 121.25, 121.06, 119.77, 57.94, 39.83, 27.07; HRMS (GC-EI) calculated for C<sub>15</sub>H<sub>11</sub>Br: 298.0357; found: 298.0356.

**2'-bromospiro[cyclobutane-1,9'-fluorene]:** Prepared according to the representative procedure on a 30 mmol scale for to give the title compound as a colorless viscous oil (3.0 g, 10.6 mmol, 35%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, J = 1.7 Hz, 1H), 7.76 (dt, J = 7.7, 0.9 Hz, 1H), 7.64 (dt, J = 7.2, 1.0 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.46 (dd, J = 8.0, 1.8 Hz, 1H), 7.39 (td, J = 7.4, 1.3 Hz, 1H), 7.34 (td, J = 7.4, 1.2 Hz, 1H), 2.72 – 2.57 (m, 4H), 2.48 – 2.34 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.5, 152.0, 138.5, 138.4, 130.2, 128.1, 127.3, 126.3, 122.9, 121.4, 121.0, 119.7, 52.1, 33.3, 17.1; HRMS (GC-EI): calculated for C<sub>16</sub>H<sub>13</sub>Br: 284.0195; found: 284.0193.

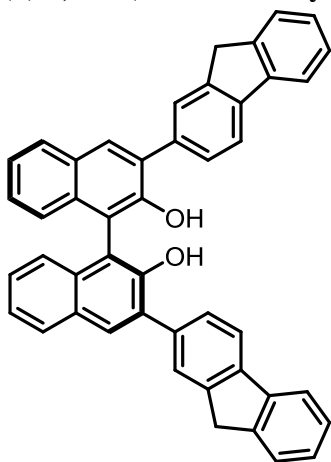
**Representative procedure for Negishi cross-coupling reactions and subsequent MOM-deprotections: (*S*)-3,3'-bis(9,9-dimethyl-9H-fluoren-2-yl)-[1,1'-binaphthalene]-2,2'-diol**



In a 2-neck flask under argon, 2-bromo-9,9-dimethyl-9H-fluorene (2.46 g, 9.0 mmol) and Pd(*t*Bu<sub>3</sub>P)<sub>2</sub> (77 mg, 0.15 mmol) were dissolved in THF (60 mL). Then, a solution of organozinc BINOL (*S*)-**B** in THF (0.27 M, 11.1 mL, 3.0 mmol) was added at r.t. under stirring and the resulting reaction mixture was refluxed under argon for 18 h. The cooled reaction mixture was treated with sat. aq. NH<sub>4</sub>Cl (30 mL) and extracted with MTBE (3 × 50 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was dissolved in MeOH or dioxane (30 mL), HCl in MeOH (12 mL, 1.25 M, 15 mmol) was added and the reaction solution was refluxed overnight. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (Hex/EtOAc 20:1→10:1) to give the title compound as an off-white solid (1.46 g, 72% over two steps). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.10 (s, 2H),

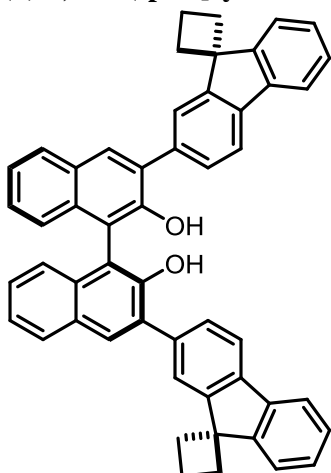
7.96 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 1.4 Hz, 2H), 7.79 – 7.76 (m, 2H), 7.73 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.41 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H), 7.38 – 7.32 (m, 6H), 7.28 (d, *J* = 8.5 Hz, 2H), 5.47 (s, 2H), 1.55 (s, 12H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.1, 154.0, 150.3, 139.1, 139.0, 136.5, 133.2, 131.4, 131.2, 129.7, 128.7, 128.6, 127.6, 127.4, 127.2, 124.5, 124.5, 124.1, 122.8, 120.3, 120.2, 112.8, 47.2, 27.4; HRMS (ESI) calculated for C<sub>50</sub>H<sub>37</sub>O<sub>2</sub> (M-H)<sup>-</sup>: 669.2799; found 669.2805.

**(*S*)-3,3'-di(9H-fluoren-2-yl)-[1,1'-binaphthalene]-2,2'-diol:** Prepared according to the



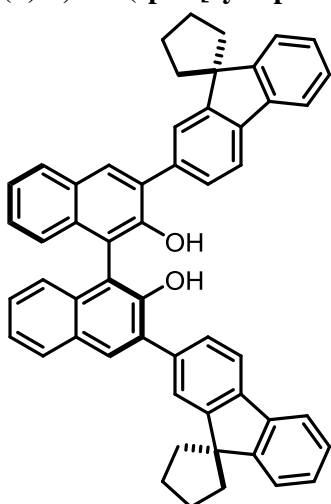
representative procedure on a 3 mmol scale for (*S*)-**B** with 2-bromo-9H-fluorene (2.57 g, 10.5 mmol) to give the title compound as an off-white solid (1.10 g, 59% over two steps). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.10 (s, 2H), 7.98 – 7.93 (m, 4H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.85 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.77 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.58 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.42 (ddt, *J* = 8.5, 7.4, 1.5 Hz, 4H), 7.38 – 7.32 (m, 4H), 7.29 (dd, *J* = 8.5, 1.2 Hz, 2H), 5.46 (s, 2H), 3.99 (s, 4H).; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.3, 143.7, 141.5, 141.5, 136.0, 133.1, 131.4, 131.1, 129.7, 128.6, 128.5, 127.4, 127.0, 127.0, 126.4, 125.2, 124.5, 124.5, 120.2, 120.0, 112.7, 37.2; HRMS (ESI) calculated for C<sub>46</sub>H<sub>29</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 613.2173; found: 613.2170.

**(S)-3,3'-di(spiro[cyclobutane-1,9'-fluoren]-2'-yl)-[1,1'-binaphthalene]-2,2'-diol:** Prepared



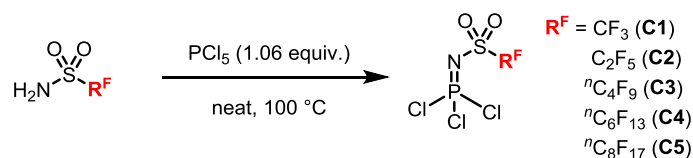
according to the representative procedure on a 3 mmol scale for (S)-**B** with 2'-bromospiro[cyclobutane-1,9'-fluorene] (3.0 g, 10.6 mmol) to give the title compound as an off-white solid (1.66 g, 80% over two steps).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 – 8.13 (m, 4H), 8.00 (d,  $J = 8.0$  Hz, 2H), 7.88 – 7.80 (m, 4H), 7.79 – 7.72 (m, 4H), 7.48 – 7.42 (m, 2H), 7.42 – 7.36 (m, 6H), 7.34 (d,  $J = 8.4$  Hz, 2H), 5.55 (s, 2H), 2.83 – 2.72 (m, 4H), 2.73 – 2.64 (m, 4H), 2.45 (p,  $J = 9.0, 8.5$  Hz, 4H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8, 152.7, 150.3, 139.2, 139.1, 136.8, 133.2, 131.4, 131.2, 129.7, 128.7, 128.6, 127.9, 127.4, 127.2, 124.6, 124.5, 124.2, 122.8, 119.8, 119.7, 112.8, 77.4, 52.2, 33.4, 33.4, 17.2.; **HRMS** (ESI) calculated for  $\text{C}_{52}\text{H}_{37}\text{O}_2$   $[\text{M-H}]^-$ : 693.2799; found: 693.2800.

**(S)-3,3'-di(spiro[cyclopentane-1,9'-fluoren]-2'-yl)-[1,1'-binaphthalene]-2,2'-diol:** Prepared



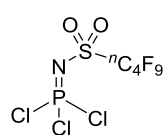
according to the representative procedure on a 3.5 mmol scale for (S)-**B** with 2'-bromospiro[cyclopentane-1,9'-fluorene] (3.1 g, 10.4 mmol) to give the title compound as an off-white solid (2.11 g, 84% over two steps).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 2H), 8.04 – 7.98 (m, 2H), 7.89 (d,  $J = 1.5$  Hz, 2H), 7.86 (d,  $J = 7.8$  Hz, 2H), 7.79 (dd,  $J = 6.6, 1.8$  Hz, 2H), 7.76 (dd,  $J = 7.8, 1.6$  Hz, 2H), 7.52 (dd,  $J = 6.7, 1.8$  Hz, 2H), 7.45 (ddd,  $J = 8.1, 6.7, 1.3$  Hz, 2H), 7.41 – 7.34 (m, 6H), 7.30 (d,  $J = 8.4$  Hz, 2H), 5.61 (s, 2H), 2.24 – 2.14 (m, 16H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.69, 154.63, 150.34, 139.18, 139.06, 136.73, 133.14, 131.22, 129.64, 128.48, 128.37, 127.72, 127.18, 126.83, 124.33, 124.31, 124.29, 123.01, 119.75, 119.56, 112.87, 57.89, 39.91, 39.87, 26.96; **HRMS** (ESI) calculated for  $\text{C}_{52}\text{H}_{37}\text{O}_2$   $[\text{M-H}]^-$ : 693.2799; found: 693.2800.

## Synthesis of phosphorimidoyl trichlorides



The syntheses of ((trifluoromethyl)sulfonyl)phosphorimidoyl trichloride<sup>7</sup> **C1**, ((perfluoroethyl)sulfonyl)phosphorimidoyl trichloride<sup>8</sup> **C2** have been described previously. 1,1,2,2,3,3,4,4,4 nonafluoro-*n*-butanesulfonamide was synthesized as reported in the literature<sup>9</sup> and purified by recrystallization from toluene. 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulfonamide and 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide were purchased from commercial sources and recrystallized twice from toluene to removed impurities of branched perfluoroalkylsulfonamides.

### Representative procedure: ((Perfluoro-*n*-butyl)sulfonyl)phosphorimidoyl trichloride (**C3**)



In a Schlenk flask under Argon equipped with a magnetic stirring bar connected to a two-neck flask containing NaOH pellets and a vacuum pump in this order, a mixture of sulfonamide (2.50 g, 8.36 mmol, 1.0 equiv) and  $\text{PCl}_5$  (1.84 g, 8.86 mmol, 1.06 equiv) was heated to 100 °C under Argon for 1 h. The reaction was monitored by  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR to ensure full consumption of sulfonamide.

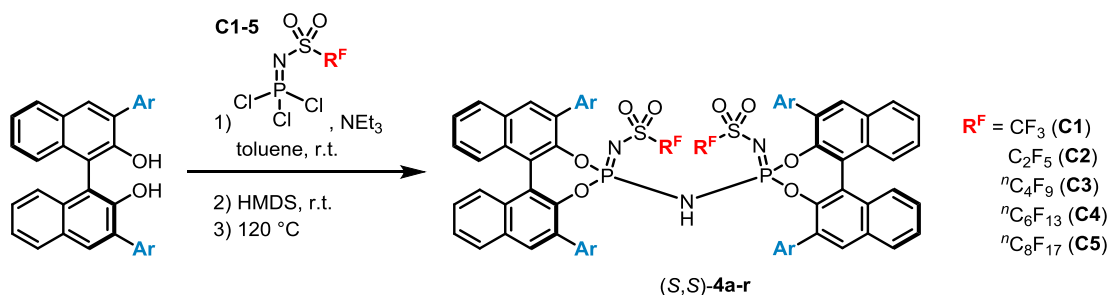
Removal of the excess amount of  $\text{PCl}_5$  by prolonged evacuation in vacuum afforded the title compound in quantitative yield as colorless oil, which was stored in a Schlenk flask under argon.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -81.1 (t,  $J = 10.1$  Hz, 3F), -112.6 (t,  $J = 14.2$  Hz, 2F), -120.7 – -121.6 (m, 2F), -125.8 – -126.7 (m, 2F);  $^{31}\text{P}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  17.0; HRMS (CI [DE] *i*-butane) calculated for  $\text{C}_4\text{H}_1\text{N}_1\text{O}_2\text{Cl}_3\text{F}_9\text{P}_1\text{S}_1$  [M+H]: 433.8387; found: 433.8390.

**((Perfluoro-*n*-hexyl)sulfonyl)phosphorimidoyl trichloride (**C4**):** Obtained as a colorless oil, which became a solid upon storage in a fridge at 4 °C.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.7 (t,  $J = 9.9$  Hz, 3F), -111.9 (tdt,  $J = 12.3, 6.7, 3.3$  Hz, 2F), -120.0 (ddt,  $J = 19.6, 14.2, 6.6$  Hz, 2F), -121.7 (p,  $J = 13.9$  Hz, 2F), -122.4 – -122.9 (m, 2F), -126.1 (ttt,  $J = 13.1, 6.7, 6.1, 3.0$  Hz, 2F);  $^{31}\text{P}$  NMR (203 MHz,  $\text{CDCl}_3$ )  $\delta$  15.3; HRMS (CI [DE] *i*-butane) calculated for  $\text{C}_6\text{H}_1\text{N}_1\text{O}_2\text{Cl}_3\text{F}_{13}\text{P}_1\text{S}_1$  [M+H]: 533.8318; found: 533.8321.

**((Perfluoro-*n*-octyl)sulfonyl)phosphorimidoyl trichloride (**C5**):** Obtained as a colorless solid.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.7 (t,  $J = 9.8$  Hz, 3F), -111.9 (t,  $J = 15.4$  Hz, 2F), -119.6 – -120.4 (m, 2F), -121.3 – -121.5 (m, 2F), -121.5 – -121.7 (m, 2F), -121.7 – -122.0 (m, 2F), -122.4 – -122.9 (m, 2F), -125.8 – -126.3 (m, 2F);  $^{31}\text{P}$  NMR (203 MHz,  $\text{CDCl}_3$ )  $\delta$  15.3; HRMS (CI [DE] *i*-butane) calculated for  $\text{C}_8\text{H}_1\text{N}_1\text{O}_2\text{Cl}_3\text{F}_{17}\text{P}_1\text{S}_1$  [M+H]: 633.8260; found: 633.8255.

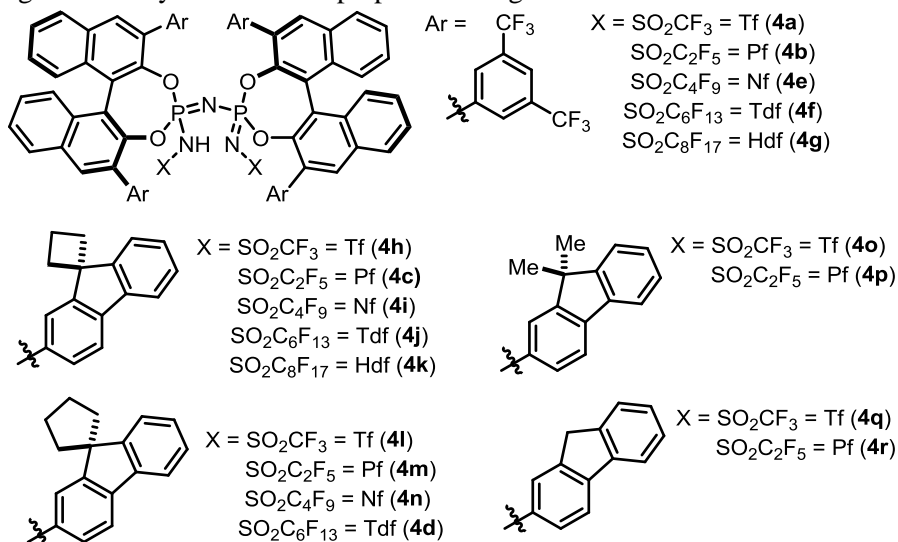
NOTE:  $^{13}\text{C}$  spectra could not be obtained due to very low signal intensity.

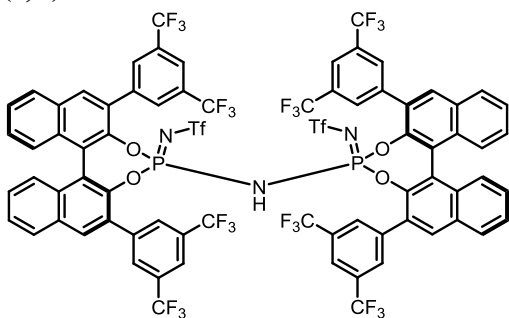
## General Procedure for IDPi Synthesis



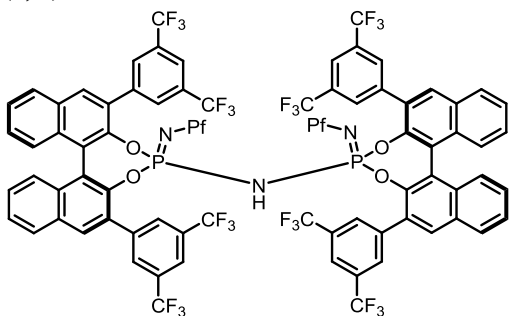
An improved protocol for the synthesis of imidodiphosphorimidate Brønsted acids was applied.<sup>7</sup> In a Schlenk tube under argon, a suspension of 3,3'-substituted (*S,S*)-BINOL (1.05 mmol, 2.1 equiv.) in toluene (2.5 mL) was treated with phosphorimidoyl trichloride **C1-5** (1.05 mmol, 2.1 equiv.) and then  $\text{NEt}_3$  (1.12 mL, 8.0 mmol, 16 equiv.). The reaction mixture was stirred for 15 min at r.t., until neat hexamethyldisilazane (HMDS, 104  $\mu\text{L}$ , 0.5 mmol, 1 equiv.) was added dropwise. The reaction mixture was stirred for additional 15 min at r.t., the Schlenk tube was subsequently sealed and heated to 120 °C for 3 days. After cooling to r.t., aq. HCl (10%) was added and the mixture was extracted with DCM or  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine, dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (hexane/MTBE 90:10→80:20→70:30→60:40→50:50 and/or 0.5–5% EtOAc in DCM) to afford the desired product as a salt. The corresponding IDPi Brønsted acids (*S,S*)-**4a-r** were obtained after acidification in DCM or  $\text{Et}_2\text{O}$  with aq. HCl (6 M) and evaporation of the solvent followed by drying under high vacuum as typically off-white solids.

The following IDPi catalysts have been prepared during the course of this work:

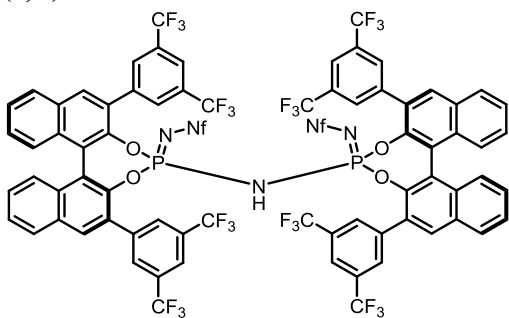


**(S,S)-4a:**

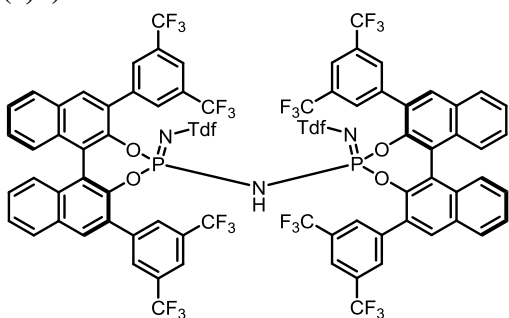
Prepared according to the general procedure on a 1.0 mmol scale (with respect to HMDS) and purified by column chromatography (first: hexane/Et<sub>2</sub>O 80:20 → 70:30 → 60:40 → 50:50; second: DCM/EtOAc 99:1 → 98:2 → 97:3 → 96:4 → 95:5). Off-white solid (914 mg, 0.51 mmol, 51%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.19 – 8.04 (m, 4H), 7.98 – 7.89 (m, 4H), 7.86 (s, 4H), 7.82 – 7.70 (m, 4H), 7.68 – 7.57 (m, 6H), 7.38 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 7.33 (s, 4H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.66 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.7 (t, *J* = 5.6 Hz), 141.6 (t, *J* = 4.9 Hz), 138.0, 137.7, 133.3, 132.5, 132.3, 132.2, 132.2, 132.1, 132.1, 132.0, 132.0, 131.9, 131.8, 131.7, 131.5, 131.3, 130.8, 130.5, 130.0, 129.9, 129.9, 129.5, 129.3, 128.8, 128.1, 127.4, 127.3, 126.7, 126.4, 126.3, 124.2, 124.1, 123.7, 122.1, 121.9, 121.3, 120.1, 119.9, 119.8, 117.5 (other signals not detected or observed); <sup>19</sup>F NMR (280 MHz, CDCl<sub>3</sub>) δ -62.5 (s, 12F), -63.1 (s, 12F), -79.0 (s, 6F); <sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>) δ -15.4; HRMS (ESI) calculated for C<sub>74</sub>H<sub>32</sub>N<sub>3</sub>O<sub>8</sub>F<sub>30</sub>P<sub>2</sub>S<sub>2</sub> (M-H)<sup>-</sup>: 1786.0633; found: 1786.0641.

**(S,S)-4b:**

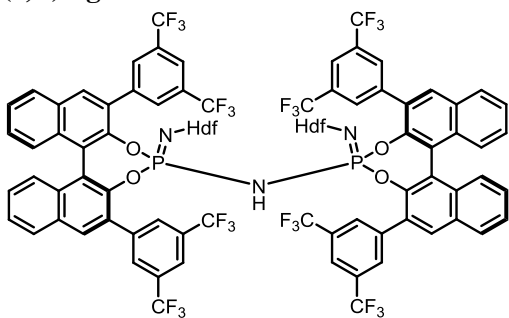
Prepared according to the general procedure on a 0.33 mmol scale (with respect to HMDS) and purified by column chromatography (first: hexane/Et<sub>2</sub>O 80:20 → 70:30 → 60:40 → 50:50; second: DCM/EtOAc 99:1 → 98:2 → 97:3 → 96:4 → 95:5). Off-white solid (329 mg, 0.174 mmol, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.07 (t, *J* = 4.0 Hz, 4H), 7.96 – 7.88 (m, 4H), 7.86 (s, 2H), 7.83 (s, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.73 (ddd, *J* = 8.3, 5.9, 2.0 Hz, 2H), 7.64 (s, 4H), 7.63 – 7.59 (m, 2H), 7.38 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 2H), 7.32 (s, 4H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.64 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.7 (t, *J* = 5.3 Hz), 141.9 (t, *J* = 5.1 Hz), 138.2, 137.9, 133.3, 132.3, 132.2, 132.1, 132.0, 132.0, 131.9, 131.8, 131.8, 131.7, 131.5, 131.4, 131.2, 130.9, 130.7, 129.9, 129.9, 129.5, 129.3, 128.7, 128.0, 127.3, 127.2, 126.8, 126.4, 126.3, 124.3, 124.1, 123.7, 122.1, 122.0, 122.0, 121.9, 121.9, 121.6, 119.9, 119.8, 118.5, 118.3, 118.0, 116.2, 116.0, 115.7, 111.5, 111.1 (other signals not detected or observed); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -62.5 (s, 12F), -63.1 (s, 12F), -79.1 (s, 6F), -117.0 (s, 4F); <sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>) δ -14.7; HRMS (ESI) calculated for C<sub>76</sub>H<sub>32</sub>N<sub>3</sub>O<sub>8</sub>P<sub>2</sub>S<sub>2</sub>F<sub>34</sub> (M-H)<sup>-</sup>: 1886.0569; found: 1886.0573.

**(S,S)-4e:**

Prepared according to the general procedure on a 0.255 mmol scale (with respect to HMDS) and purified by column chromatography (first: hexane/MTBE 90:10 → 80:20 → 70:30 → 60:40 → 50:50 → 40:60 → 30:70; second: DCM/EtOAc 99:1 → 98:2 → 97:3). Off-white solid (369 mg, 0.177 mmol, 69%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (s, 2H), 8.10 (d,  $J = 8.2$  Hz, 2H), 7.96 – 7.89 (m, 4H), 7.86 (s, 2H), 7.83 – 7.77 (m, 4H), 7.73 (ddd,  $J = 8.4, 5.3, 2.7$  Hz, 2H), 7.67 – 7.59 (m, 6H), 7.39 (ddd,  $J = 8.2, 6.9, 1.0$  Hz, 2H), 7.33 (s, 4H), 7.17 (d,  $J = 8.6$  Hz, 2H), 6.65 (s, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4 (t,  $J = 5.3$  Hz), 141.7 (t,  $J = 5.0$  Hz), 138.2, 137.4, 133.3, 132.5, 132.4, 132.2, 132.2, 132.2, 132.1, 132.0, 132.0, 132.0, 131.9, 131.7, 131.6, 131.2, 130.7, 130.5, 129.9, 129.4, 129.4, 128.8, 128.1, 127.4, 127.3, 127.3, 126.7, 126.4, 126.2, 124.2, 124.1, 123.8, 122.2, 122.2, 122.1, 121.9, 121.9, 121.7, 119.9, 119.7, 116.0 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.5 (s, 12F), -63.35 (s, 12F), -80.98 (t,  $J = 10.1$  Hz, 6F), -112.47 (d,  $J = 261.2$  Hz, 2F), -113.30 (d,  $J = 264.6$  Hz, 2F), -120.91 (s, 4F), -125.87 (d,  $J = 296.8$  Hz, 2F), -126.71 (d,  $J = 297.4$  Hz, 2F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.1; **HRMS** (ESI) calculated for  $\text{C}_{80}\text{H}_{32}\text{F}_{42}\text{N}_3\text{O}_8\text{P}_2\text{S}_2$  (M-H) $^-$ : 2086.0441; found: 2086.0427.

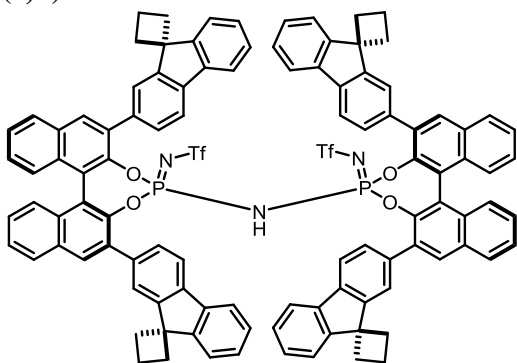
**(S,S)-4f:**

Prepared according to the general procedure on a 0.174 mmol scale (with respect to HMDS), purified by column chromatography (first: hexane/MTBE 90:10 → 80:20 → 70:30 → 60:40 → 50:50 → 40:60 → 30:70; second: DCM/EtOAc 99:1 → 98:2) and acidified in  $\text{Et}_2\text{O}$  instead of DCM. Off-white solid (237 mg, 0.104 mmol, 60%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (s, 2H), 8.10 (d,  $J = 8.2$  Hz, 2H), 7.96 – 7.88 (m, 4H), 7.86 (s, 2H), 7.82 – 7.76 (m, 4H), 7.73 (ddd,  $J = 8.4, 5.4, 2.5$  Hz, 2H), 7.66 – 7.58 (m, 6H), 7.39 (ddd,  $J = 8.3, 6.8, 1.3$  Hz, 2H), 7.33 (s, 4H), 7.17 (d,  $J = 8.5$  Hz, 2H), 6.65 (s, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4 (t,  $J = 5.6$  Hz), 141.7 (t,  $J = 4.6$  Hz), 138.2, 137.4, 133.3, 132.5, 132.4, 132.2, 132.2, 132.2, 132.1, 132.0, 132.0, 132.0, 131.9, 131.7, 131.6, 131.2, 130.7, 130.5, 129.9, 129.4, 129.4, 128.8, 128.1, 127.3, 127.3, 126.7, 126.4, 126.2, 124.2, 124.1, 123.8, 122.3, 122.2, 122.2, 122.2, 122.2, 122.0, 121.9, 121.9, 121.8, 121.8, 121.8, 121.7, 119.9, 119.7 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6 (s, 12F), -63.4 (s, 12F), -81.0 (t,  $J = 9.6$  Hz, 6F), -112.3 (d,  $J = 256.1$  Hz, 2F), -113.2 (d,  $J = 259.1$  Hz, 2F), -120.1 (d,  $J = 61.2$  Hz, 4F), -122.1 (s, 4F), -123.0 (s, 4F), -126.4 (d,  $J = 13.6$  Hz, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -15.1; **HRMS** (ESI) calculated for  $\text{C}_{84}\text{H}_{32}\text{F}_{50}\text{N}_3\text{O}_8\text{P}_2\text{S}_2$  (M-H) $^-$ : 2286.0313; found: 2286.0296.

**(S,S)-4g:**

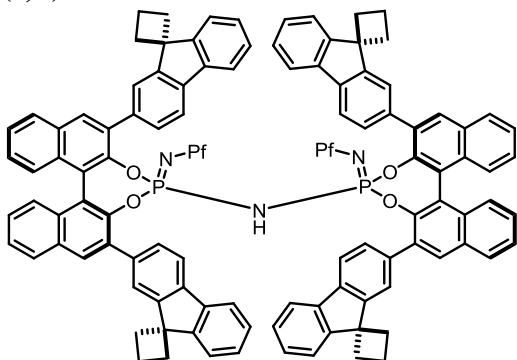
Prepared according to the general procedure on a 0.236 mmol scale (with respect to HMDS), purified by column chromatography (first: hexane/MTBE 90:10 → 80:20 → 70:30 → 60:40 → 50:50 → 40:60 → 30:70; second: DCM/EtOAc 99.5:0.5 → 99:1 → 98:2) and acidified in Et<sub>2</sub>O instead of DCM. Off-white solid (85 mg, 0.034 mmol, 15%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.96 – 7.88 (m, 4H), 7.85 (s, 2H), 7.82 – 7.76 (m, 4H), 7.73 (ddd, *J* = 8.3, 5.8, 2.1 Hz, 2H), 7.67 –

7.59 (m, 6H), 7.39 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 7.33 (s, 4H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.65 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.5 (t, *J* = 5.0 Hz), 141.8 (t, *J* = 5.3 Hz), 138.2, 137.5, 133.3, 132.5, 132.4, 132.2, 132.2, 132.2, 132.1, 132.0, 131.9, 131.9, 131.8, 131.7, 131.6, 131.2, 130.7, 130.5, 129.9, 129.9, 129.9, 129.4, 129.3, 128.8, 128.1, 127.3, 126.7, 126.4, 126.3, 124.2, 124.1, 123.8, 122.2, 122.2, 122.1, 122.1, 121.9, 121.8, 121.8, 121.8, 119.9, 119.8 (other signals not detected or observed); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -62.6 (s, 12F), -63.4 (s, 12F), -80.9 (t, *J* = 10.0 Hz, 6F), -112.3 (d, *J* = 258.7 Hz, 2F), -113.2 (d, *J* = 260.5 Hz, 2F), -120.0 (d, *J* = 51.2 Hz, 4F), -121.1 – -122.8 (m, 12F), -122.9 (s, 4F), -126.3 (s, 4F); <sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>) δ -14.8; HRMS (ESI) calculated for C<sub>88</sub>H<sub>32</sub>F<sub>58</sub>N<sub>3</sub>O<sub>8</sub>P<sub>2</sub>S<sub>2</sub> (M-H)<sup>-</sup>: 2486.0186; found: 2486.0164.

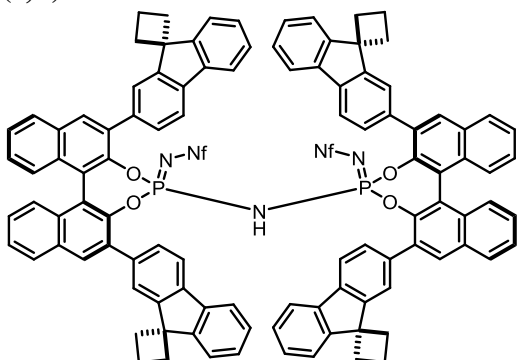
**(S,S)-4h:**

Prepared according to the general procedure on a 0.15 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 20:1 → 9:1 → 4:1 → 2:1). Off-white solid (112 mg, 0.064 mmol, 43%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.14 – 8.05 (m, 6H), 7.93 – 7.82 (m, 4H), 7.82 – 7.79 (m, 4H), 7.70 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 7.66 – 7.62 (m, 2H), 7.62 – 7.58 (m, 4H), 7.50 (dd, *J* = 8.1, 5.7 Hz, 4H), 7.41 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 2H), 7.33 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.30 (td, *J* = 7.5, 1.1 Hz, 2H), 7.26 – 7.15 (m, 10H), 6.55 (d, *J* = 8.0 Hz,

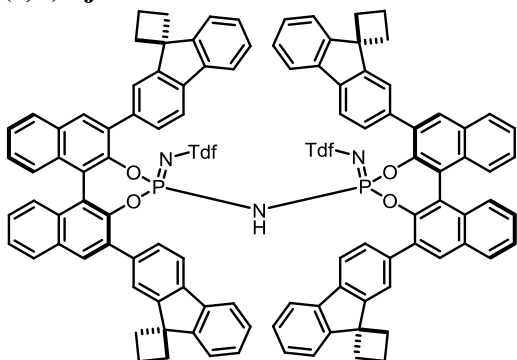
2H), 6.44 (dd, *J* = 7.9, 1.6 Hz, 2H), 6.09 (dd, *J* = 7.9, 1.6 Hz, 2H), 2.84 – 2.76 (m, 2H), 2.68 – 2.53 (m, 8H), 2.42 – 2.33 (m, 8H), 2.29 – 2.15 (m, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 153.0, 152.9, 152.5, 151.9, 144.0 (t, *J* = 5.0 Hz), 143.1 (t, *J* = 5.0 Hz), 139.5, 139.0, 138.8, 138.6, 135.1, 135.0, 134.5, 134.4, 132.3, 132.0, 132.0, 131.9, 131.8, 131.4, 129.1, 128.9, 128.9, 128.7, 128.1, 127.6, 127.4, 127.3, 127.1, 127.0, 126.9, 126.7, 126.6, 124.1, 123.6, 122.6, 122.5, 121.9, 120.1, 119.8, 119.2, 118.7, 118.3, 117.5, 52.1, 52.1, 33.7, 33.1, 32.8, 32.7, 17.1 (other signals not detected or observed); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.3 (s, 6F); <sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>) δ -16.6; HRMS (ESI) calculated for C<sub>106</sub>H<sub>72</sub>N<sub>3</sub>O<sub>8</sub>F<sub>6</sub>P<sub>2</sub>S<sub>2</sub> (M-H)<sup>-</sup>: 1754.4146; found: 1754.4158.

**(S,S)-4c:**

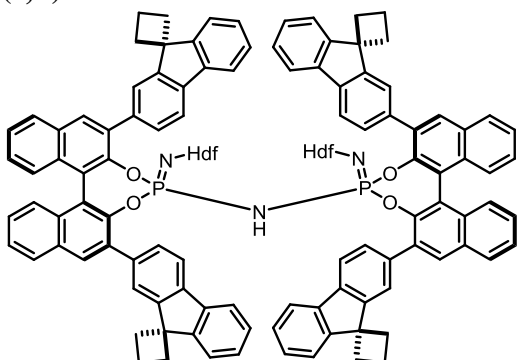
Prepared according to the general procedure on a 0.071 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 10:1 → 4:1 → 2:1 → 1:1). Off-white solid (95 mg, 0.051 mmol, 72%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (s, 2H), 8.06 (dd,  $J = 8.4, 5.8$  Hz, 4H), 7.92 – 7.84 (m, 4H), 7.83 – 7.77 (m, 4H), 7.71 (ddd,  $J = 8.3, 6.9, 1.3$  Hz, 2H), 7.66 – 7.63 (m, 2H), 7.59 (ddd,  $J = 8.2, 6.6, 1.3$  Hz, 2H), 7.56 (d,  $J = 1.6$  Hz, 2H), 7.53 (dt,  $J = 7.6, 0.9$  Hz, 2H), 7.47 – 7.43 (m, 2H), 7.40 (ddd,  $J = 8.5, 6.7, 1.3$  Hz, 2H), 7.35 (d,  $J = 7.9$  Hz, 2H), 7.31 – 7.27 (m, 4H), 7.25 – 7.19 (m, 4H), 7.19 – 7.16 (m, 2H), 7.09 (s, 2H), 6.49 (d,  $J = 8.0$  Hz, 2H), 6.38 (dd,  $J = 8.0, 1.6$  Hz, 2H), 6.33 (dd,  $J = 7.9, 1.6$  Hz, 2H), 2.84 – 2.76 (m, 2H), 2.67 – 2.52 (m, 8H), 2.41 – 2.23 (m, 13H), 2.18 – 2.11 (m, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 153.0, 152.4, 151.9, 144.1 (t,  $J = 5.0$  Hz), 143.0 (t,  $J = 5.0$  Hz), 139.7, 139.1, 138.8, 138.6, 135.1, 135.1, 134.5, 134.2, 132.3, 132.1, 131.9, 131.8, 131.7, 131.5, 129.3, 129.0, 128.9, 128.9, 128.1, 127.5, 127.3, 127.1, 127.0, 126.9, 126.8, 126.7, 126.5, 124.0, 123.6, 122.5, 122.4, 121.8, 119.9, 119.2, 118.7, 118.3, 52.1, 52.1, 33.5, 33.0, 32.8, 17.1, 17.0 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.0 (s, 6F), -114.8 – -116.8 (m, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -17.5; **HRMS** (ESI) calculated for  $\text{C}_{108}\text{H}_{72}\text{N}_3\text{O}_8\text{F}_{10}\text{P}_2\text{S}_2$  (M-H): 1854.4082; found: 1854.4089.

**(S,S)-4i:**

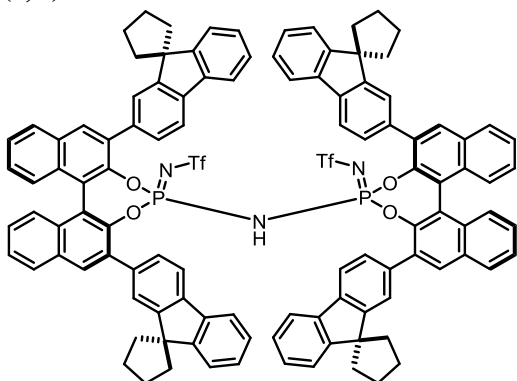
Prepared according to the general procedure on a 0.076 mmol scale (with respect to HMDS) and purified by column chromatography (first: hexane/MTBE 9:1 → 4:1 → 2:1 → 1:1). Off-white solid (99 mg, 0.048 mmol, 67%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (s, 2H), 8.06 (d,  $J = 8.3$  Hz, 2H), 8.03 (dd,  $J = 8.6, 1.3$  Hz, 2H), 7.88 (td,  $J = 5.9, 5.2, 1.4$  Hz, 4H), 7.81 (d,  $J = 1.6$  Hz, 2H), 7.77 (d,  $J = 7.5$  Hz, 2H), 7.72 (ddd,  $J = 8.3, 6.8, 1.3$  Hz, 2H), 7.67 – 7.64 (m, 2H), 7.60 – 7.54 (m, 6H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.40 – 7.35 (m, 4H), 7.32 – 7.27 (m, 4H), 7.24 (dd,  $J = 7.4, 1.3$  Hz, 2H), 7.20 (td,  $J = 7.5, 1.2$  Hz, 4H), 7.05 (s, 2H), 6.60 (dd,  $J = 7.9, 1.6$  Hz, 2H), 6.55 (d,  $J = 8.0$  Hz, 2H), 6.34 (dd,  $J = 7.9, 1.6$  Hz, 2H), 2.81 – 2.74 (m, 2H), 2.69 – 2.54 (m, 8H), 2.38 – 2.21 (m, 12H), 2.17 – 2.08 (m, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 152.9, 152.3, 152.1, 144.2 (t,  $J = 5.0$  Hz), 143.1 (t,  $J = 5.0$  Hz), 139.7, 139.1, 138.9, 138.6, 135.1, 135.0, 134.4, 133.9, 132.3, 132.1, 131.8, 131.7, 131.3, 129.5, 129.1, 128.9, 128.7, 128.1, 127.4, 127.3, 127.3, 127.1, 127.0, 126.8, 126.6, 126.5, 123.8, 123.7, 123.6, 122.4, 121.8, 119.8, 119.3, 118.7, 118.3, 52.1, 52.0, 33.2, 33.1, 32.7, 17.1, 17.0 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.0 (t,  $J = 10.1$  Hz, 3F), -111.0 – -112.6 (m, 2F), -121.1 (q,  $J = 11.1$  Hz, 2F), -125.1 – -126.9 (m, 2F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.8; **HRMS** (ESI) calculated for  $\text{C}_{112}\text{H}_{72}\text{N}_3\text{O}_8\text{F}_{18}\text{P}_2\text{S}_2$  (M-H): 2054.3954; found: 2054.3944.

**(S,S)-4j:**

Prepared according to the general procedure on a 0.5 mmol scale (with respect to HMDS) and purified by column chromatography (first: hexane/MTBE 9:1 → 4:1 → 2:1 → 1:1). Off-white solid (205 mg, 0.091 mmol, 64%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10 (s, 2H), 8.07 (d,  $J = 8.3$  Hz, 2H), 8.04 – 8.00 (m, 2H), 7.91 – 7.84 (m, 4H), 7.81 (d,  $J = 1.6$  Hz, 2H), 7.76 (d,  $J = 7.5$  Hz, 2H), 7.72 (ddd,  $J = 8.2, 6.8, 1.3$  Hz, 2H), 7.63 (d,  $J = 7.5$  Hz, 2H), 7.58 (ddd,  $J = 8.2, 5.9, 2.1$  Hz, 2H), 7.56 – 7.51 (m, 4H), 7.42 – 7.37 (m, 6H), 7.30 (d,  $J = 7.4$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.23 (td,  $J = 7.4, 1.2$  Hz, 2H), 7.21 – 7.18 (m, 2H), 7.18 – 7.15 (m, 2H), 7.07 (s, 2H), 6.60 (d,  $J = 8.0$  Hz, 4H), 6.37 (dd,  $J = 7.9, 1.6$  Hz, 2H), 2.83 – 2.73 (m, 2H), 2.68 – 2.52 (m, 8H), 2.38 – 2.22 (m, 12H), 2.18 – 2.08 (m, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 152.9, 152.3, 152.1, 144.2 (t,  $J = 5.0$  Hz), 143.1 (t,  $J = 5.0$  Hz), 139.7, 139.1, 139.0, 138.6, 135.1, 134.9, 134.3, 134.0, 132.3, 132.1, 131.8, 131.7, 131.3, 129.4, 129.1, 128.9, 128.7, 128.1, 127.4, 127.3, 127.1, 127.0, 126.8, 126.6, 126.5, 126.5, 123.8, 123.7, 123.6, 122.4, 122.4, 122.0, 119.7, 119.2, 118.7, 118.4, 52.1, 52.0, 33.2, 33.1, 33.1, 32.6, 17.1, 17.0 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (t,  $J = 9.7$  Hz, 6F), -110.4 – -112.6 (m, 4F), -120.1 (dt,  $J = 32.4, 14.4$  Hz, 4F), -121.8 (p,  $J = 13.1$  Hz, 4F), -122.6 – -123.2 (m, 4F), -126.2 (t,  $J = 14.6$  Hz, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.8; **HRMS** (ESI) calculated for  $\text{C}_{116}\text{H}_{72}\text{N}_3\text{O}_8\text{F}_{26}\text{P}_2\text{S}_2$  (M-H) $^-$ : 2254.3827; found: 2254.3809.

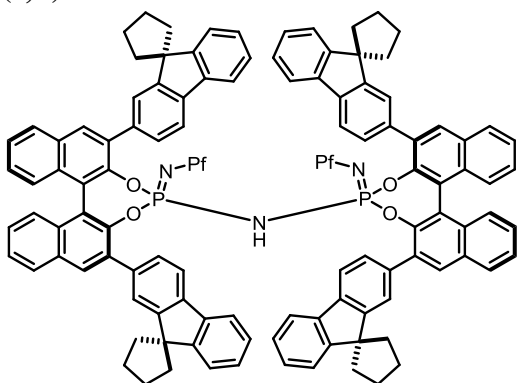
**(S,S)-4k:**

Prepared according to the general procedure on a 0.22 mmol scale (with respect to HMDS) and purified by column chromatography (first: hexane/MTBE 9:1 → 4:1 → 2:1 → 1:1; second: DCM/EtOAc 99.5:0.5 → 99:1 → 98:2). Off-white solid (50 mg, 0.02 mmol, 9%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11 (s, 2H), 8.05 (dd,  $J = 20.2, 8.3$  Hz, 4H), 7.88 (d,  $J = 8.1$  Hz, 4H), 7.82 (s, 2H), 7.80 – 7.69 (m, 4H), 7.64 (d,  $J = 7.5$  Hz, 2H), 7.61 – 7.51 (m, 6H), 7.39 (q,  $J = 8.3$  Hz, 6H), 7.30 (dd,  $J = 17.3, 7.4$  Hz, 4H), 7.24 – 7.14 (m, 6H), 7.08 (s, 2H), 6.61 (dd,  $J = 8.2, 3.0$  Hz, 4H), 6.39 (d,  $J = 7.9$  Hz, 2H), 2.85 – 2.75 (m, 2H), 2.71 – 2.51 (m, 8H), 2.40 – 2.23 (m, 12H), 2.19 – 2.10 (m, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 152.9, 152.3, 152.1, 144.2 (t,  $J = 5.0$  Hz), 143.1 (t,  $J = 5.0$  Hz), 139.7, 139.1, 139.0, 138.6, 135.1, 134.8, 134.3, 134.0, 132.3, 132.1, 131.9, 131.8, 131.7, 131.3, 129.5, 129.1, 128.9, 128.7, 128.1, 127.4, 127.3, 127.1, 127.0, 126.8, 126.6, 126.5, 126.5, 123.8, 123.7, 122.4, 122.4, 122.0, 119.7, 119.3, 118.7, 118.4, 52.1, 52.0, 33.3, 33.1, 33.1, 32.6, 17.1, 17.0 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (t,  $J = 9.8$  Hz, 6F), -110.5 – -112.8 (m, 4F), -120.1 (p,  $J = 12.8, 11.4$  Hz, 4F), -121.6 (m, 4F), -121.8 – -122.3 (m, 8F), -122.8 (dd,  $J = 22.3, 11.9$  Hz, 4F), -126.1 (t,  $J = 14.2$  Hz, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.7; **HRMS** (ESI) calculated for  $\text{C}_{120}\text{H}_{72}\text{N}_3\text{O}_8\text{F}_{34}\text{P}_2\text{S}_2$  (M-H) $^-$ : 2454.3699; found: 2454.3676.

**(S,S)-4l:**

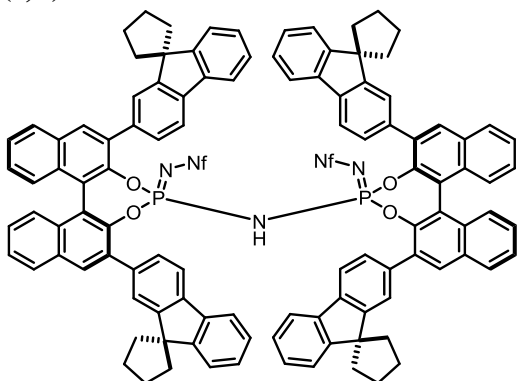
Prepared according to the general procedure on a 0.066 mmol scale (with respect to HMDS) and purified by column chromatography (5% EtOAc, 20% DCM, 75% hexanes). Off-white solid (106 mg, 0.058 mmol, 88%).  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.12 (s, 2H), 8.08 (t,  $J = 8.1$  Hz, 4H), 7.86 (t,  $J = 7.5$  Hz, 2H), 7.80 (d,  $J = 8.5$  Hz, 2H), 7.69 (dd,  $J = 8.5$ , 6.9 Hz, 2H), 7.61 (ddd,  $J = 8.1$ , 6.3, 1.5 Hz, 2H), 7.58 – 7.52 (m, 4H), 7.47 – 7.43 (m, 4H), 7.43 – 7.36 (m, 6H), 7.34 (dt,  $J = 7.0$ , 3.0 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.23 – 7.17 (m, 6H), 7.16 (s, 2H), 6.68 (d,  $J = 7.9$  Hz, 2H), 6.51 (dd,  $J = 7.9$ , 1.6 Hz, 2H), 6.30 –

6.22 (m, 2H), 2.22 (qd,  $J = 10.6$ , 9.1, 5.4 Hz, 2H), 2.17 – 1.91 (m, 22H), 1.88 – 1.60 (m, 8H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  154.82, 154.75, 154.47, 153.79, 139.53, 138.85, 138.82, 138.64, 134.96, 134.52, 134.39, 133.87, 132.15, 131.78, 131.56, 131.36, 129.13, 128.67, 128.54, 128.43, 127.76, 127.48, 127.30, 126.84, 126.81, 126.77, 126.54, 126.41, 123.85, 123.65, 123.27, 122.85, 122.72, 121.87, 119.66, 119.11, 118.69, 118.24, 57.89, 57.77, 39.94, 39.84, 39.04, 38.87, 26.94, 26.73, 26.57, 26.41 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -78.7 (s, 6F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -16.9; **HRMS** (ESI) calculated for  $\text{C}_{110}\text{H}_{80}\text{N}_3\text{O}_8\text{F}_6\text{P}_2\text{S}_2$  (M-H) $^-$ : 1810.4772; found: 1810.4779.

**(S,S)-4m:**

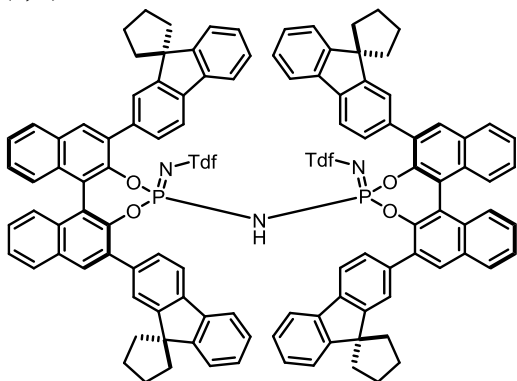
Prepared according to the general procedure on a 0.25 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 20:1  $\rightarrow$  9:1  $\rightarrow$  4:1  $\rightarrow$  2:1). Off-white solid (238 mg, 0.124 mmol, 50%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (q,  $J = 8.3$  Hz, 6H), 7.86 – 7.81 (m, 4H), 7.68 (ddd,  $J = 8.3$ , 6.8, 1.3 Hz, 2H), 7.58 (ddd,  $J = 8.2$ , 6.4, 1.5 Hz, 2H), 7.54 (d,  $J = 7.5$  Hz, 2H), 7.51 (d,  $J = 1.6$  Hz, 2H), 7.43 – 7.37 (m, 8H), 7.31 (ddd,  $J = 7.9$ , 4.9, 2.1 Hz, 4H), 7.25 – 7.14 (m, 10H), 7.02 (s, 2H), 6.59 (d,  $J = 8.0$  Hz, 2H), 6.47 (dd,  $J = 8.0$ , 1.6 Hz, 2H), 6.30 (dd,  $J = 7.9$ , 1.7 Hz, 2H), 2.29 – 2.19

(m, 2H), 2.13 – 1.95 (m, 22H), 1.86 – 1.69 (m, 8H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 155.2, 154.6, 154.2, 144.3 (t,  $J = 5.0$  Hz), 143.3 (t,  $J = 5.0$  Hz), 140.2, 139.5, 139.3, 138.9, 135.3, 134.7, 134.5, 132.5, 132.3, 132.2, 132.0, 132.0, 131.8, 129.5, 129.1, 128.9, 128.2, 127.7, 127.5, 127.4, 127.3, 127.3, 127.1, 127.0, 126.7, 126.7, 124.1, 124.0, 123.8, 123.1, 123.0, 122.0, 120.3, 119.6, 119.0, 118.7, 58.2, 58.2, 40.4, 40.0, 39.3, 27.3, 27.1, 26.9 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.9 (s, 6F), -114.8 – -116.5 (m, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -17.3; **HRMS** (ESI) calculated for  $\text{C}_{112}\text{H}_{80}\text{N}_3\text{O}_8\text{F}_{10}\text{P}_2\text{S}_2$  (M-H) $^-$ : 1910.4708; found: 1910.4713.

**(S,S)-4n:**

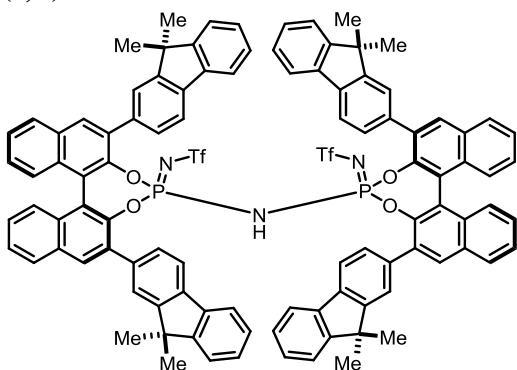
Prepared according to the general procedure on a 0.086 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 20:1 → 9:1 → 4:1 → 2:1). Off-white solid (57 mg, 0.027 mmol, 32%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.98 – 7.92 (m, 4H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.60 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 2H), 7.49 (ddd, *J* = 7.7, 6.1, 2.0 Hz, 4H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.30 – 7.25 (m, 4H), 7.25 – 7.21 (m, 4H), 7.17 – 7.12 (m, 4H), 7.12 – 7.07 (m, 6H), 6.88 (s, 2H), 6.50 (t, *J* = 7.8 Hz, 4H),

6.33 (dd, *J* = 7.9, 1.6 Hz, 2H), 2.07 – 1.86 (m, 24H), 1.75 – 1.68 (m, 2H), 1.66 – 1.48 (m, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 154.8, 154.4, 153.9, 144.3 (t, *J* = 5.0 Hz), 143.1 (t, *J* = 5.0 Hz), 140.0, 139.3, 139.1, 138.7, 135.1, 135.0, 134.3, 133.9, 132.3, 132.1, 131.8, 131.7, 131.7, 131.3, 129.5, 128.8, 128.6, 127.8, 127.3, 127.1, 127.0, 126.7, 126.5, 126.4, 126.3, 124.0, 123.6, 123.4, 122.9, 122.6, 121.7, 120.0, 119.3, 118.7, 118.4, 58.1, 57.9, 39.7, 39.6, 39.3, 39.0, 27.1, 26.8, 26.6, 26.5 (other signals not detected or observed); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -80.9 (t, *J* = 10.1 Hz, 6F), -110.9 – -112.7 (m, 4F), -121.0 (q, *J* = 10.7 Hz, 4F), -125.2 – -126.9 (m, 4F); <sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>) δ -16.7; HRMS (ESI) calculated for C<sub>116</sub>H<sub>80</sub>N<sub>3</sub>O<sub>8</sub>F<sub>18</sub>P<sub>2</sub>S<sub>2</sub> (M-H)<sup>-</sup>: 2110.4580; found: 2110.4574.

**(S,S)-4d:**

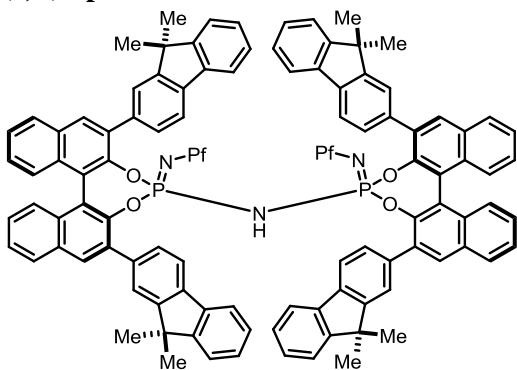
Prepared according to the general procedure on a 0.12 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 10:1 → 5:1 → 2:1 → 1:1). Off-white solid (141 mg, 0.061 mmol, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.04 (d, *J* = 7.2 Hz, 4H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.84 (t, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.56 (ddd, *J* = 15.3, 6.4, 1.9 Hz, 4H), 7.51 (d, *J* = 1.6 Hz, 2H), 7.41 (dd, *J* = 11.6, 7.7 Hz, 4H), 7.37 – 7.34 (m, 4H), 7.32 – 7.29 (m, 4H), 7.23 (d, *J* = 1.5 Hz, 2H), 7.22 – 7.13 (m, 8H), 6.99 (s, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 7.9 Hz,

2H), 6.45 (dd, *J* = 8.0, 1.6 Hz, 2H), 2.16 – 1.93 (m, 24H), 1.82 – 1.75 (m, 2H), 1.73 – 1.63 (m, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 154.8, 154.4, 153.9, 144.2 (t, *J* = 5.0 Hz), 143.1 (t, *J* = 5.0 Hz), 139.9, 139.3, 139.1, 138.7, 135.0, 134.3, 134.0, 132.3, 132.1, 131.8, 131.7, 131.7, 131.3, 129.4, 128.9, 128.5, 127.8, 127.3, 127.1, 127.1, 127.0, 126.7, 126.5, 126.4, 126.3, 124.0, 123.6, 123.4, 122.9, 122.6, 121.8, 119.9, 119.3, 118.7, 118.4, 58.1, 57.9, 39.7, 39.7, 39.3, 39.0, 27.1, 26.7, 26.6, 26.5 (other signals not detected or observed); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -80.8 (t, *J* = 10.0 Hz, 6F), -110.5 – -113.0 (m, 4F), -120.0 (dt, *J* = 48.6, 14.6 Hz, 4F), -121.4 – -122.1 (m, 4F), -122.6 – -123.2 (m, 4F), -125.9 – -126.5 (m, 4F); <sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>) δ -16.6; HRMS (ESI) calculated for C<sub>120</sub>H<sub>80</sub>N<sub>3</sub>O<sub>8</sub>F<sub>26</sub>P<sub>2</sub>S<sub>2</sub> (M-H)<sup>-</sup>: 2310.4452; found: 2310.4438.

**(S,S)-4o:**

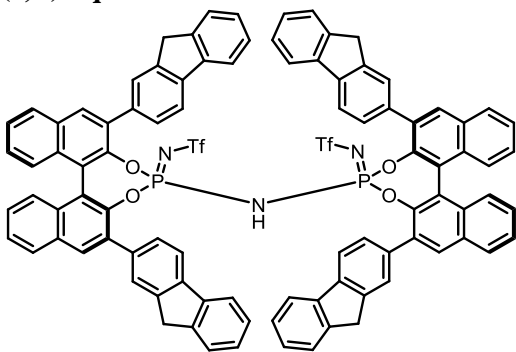
Prepared according to the general procedure on a 0.5 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 9:1 → 4:1 → 2:1 → 1:1). Off-white solid (557 mg, 0.325 mmol, 65%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 – 8.02 (m, 6H), 7.89 – 7.82 (m, 4H), 7.70 (ddd,  $J = 8.2, 6.8, 1.2$  Hz, 2H), 7.62 – 7.56 (m, 4H), 7.50 (d,  $J = 1.4$  Hz, 2H), 7.45 – 7.41 (m, 4H), 7.41 – 7.37 (m, 6H), 7.31 – 7.27 (m, 4H), 7.24 – 7.23 (m, 2H), 7.23 – 7.18 (m, 6H), 7.08 (s, 2H), 6.73 (d,  $J = 7.9$  Hz, 2H), 6.62 (dd,  $J = 8.0, 1.6$  Hz, 2H), 6.25 (dd,  $J = 7.9, 1.7$  Hz, 2H), 1.50 (s, 6H), 1.42 (s, 6H), 1.26 (s,

6H), 1.22 (s, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.3, 154.2, 153.9, 153.7, 144.1 (t,  $J = 5.0$  Hz), 142.9 (t,  $J = 5.0$  Hz), 139.4, 138.8, 138.8, 138.6, 134.9, 134.8, 134.3, 134.2, 132.2, 132.2, 131.9, 131.8, 131.5, 129.2, 129.0, 128.8, 128.7, 127.7, 127.6, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 123.8, 123.6, 123.5, 122.6, 122.5, 121.8, 120.4, 119.8, 119.2, 119.1, 47.1, 47.1, 27.6, 27.1, 27.0, 26.6 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.2 (s, 6F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.8; **HRMS** (ESI) calculated for  $\text{C}_{102}\text{H}_{72}\text{N}_3\text{O}_8\text{F}_6\text{P}_2\text{S}_2$  (M-H) $^-$ : 1706.4146; found: 1706.4162.

**(S,S)-4p:**

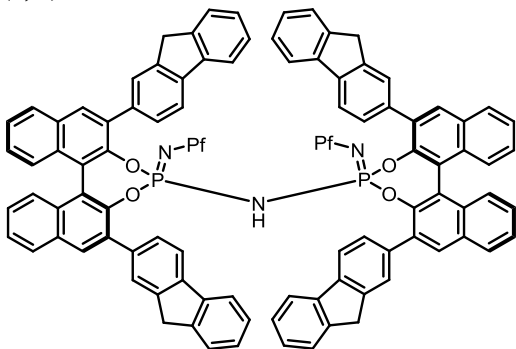
Prepared according to the general procedure on a 0.10 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 20:1 → 9:1 → 4:1 → 2:1). Off-white solid (62 mg, 0.034 mmol, 34%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 – 8.01 (m, 6H), 7.89 – 7.83 (m, 4H), 7.71 (ddd,  $J = 8.4, 6.8, 1.3$  Hz, 2H), 7.61 – 7.56 (m, 4H), 7.50 (d,  $J = 1.6$  Hz, 2H), 7.45 (d,  $J = 7.9$  Hz, 2H), 7.42 – 7.37 (m, 6H), 7.33 (ddd,  $J = 20.0, 5.8, 3.3$  Hz, 4H), 7.28 – 7.26 (m, 1H), 7.25 (d,  $J = 1.2$  Hz, 1H), 7.24 – 7.18 (m, 8H), 6.99 (s, 2H), 6.69 (d,  $J = 8.0$  Hz, 2H), 6.57 (dd,  $J = 7.9, 1.6$  Hz, 2H), 6.43 (dd,  $J = 7.9, 1.6$

Hz, 2H), 1.51 (s, 6H), 1.45 (s, 6H), 1.26 (s, 6H), 1.18 (s, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.3, 154.2, 153.9, 153.8, 144.2 (t,  $J = 5.0$  Hz), 143.2 (t,  $J = 5.0$  Hz), 139.5, 138.9, 138.8, 138.5, 134.9, 134.3, 134.1, 132.3, 132.2, 131.9, 131.8, 131.7, 131.6, 129.3, 128.9, 127.7, 127.5, 127.3, 127.3, 127.1, 127.0, 126.9, 126.7, 126.5, 123.7, 123.7, 123.6, 122.5, 122.4, 121.8, 120.4, 119.8, 119.2, 119.0, 47.2, 47.1, 29.9, 27.6, 27.1, 26.6, 22.6 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.9 (s, 6F), -114.9 – -116.4 (m, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -17.3; **HRMS** (ESI) calculated for  $\text{C}_{104}\text{H}_{72}\text{N}_3\text{O}_8\text{F}_{10}\text{P}_2\text{S}_2$  (M-H) $^-$ : 1806.4082; found: 1806.4084.

**(*S,S*)-4q:**

Prepared according to the general procedure on a 0.076 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 9:1 → 4:1 → 2:1 → 1:1). Off-white solid (42 mg, 0.026 mmol, 34%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11 (d,  $J = 8.1$  Hz, 2H), 8.03 (d,  $J = 8.5$  Hz, 2H), 8.00 (s, 2H), 7.94 – 7.84 (m, 4H), 7.78 – 7.68 (m, 4H), 7.62 – 7.55 (m, 4H), 7.53 (d,  $J = 7.9$  Hz, 2H), 7.50 – 7.43 (m, 4H), 7.42 – 7.36 (m, 4H), 7.31 – 7.26 (m, 2H), 7.25 – 7.22 (m, 4H), 7.21 – 7.17 (m, 2H), 7.14 (d,  $J = 7.9$  Hz, 2H), 7.09 (d,  $J = 13.9$  Hz, 4H),

6.95 (s, 2H), 6.73 (d,  $J = 7.8$  Hz, 2H), 6.55 (d,  $J = 7.9$  Hz, 2H), 3.75 (d,  $J = 21.9$  Hz, 2H), 3.53 – 3.33 (m, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 143.6, 143.1, 142.9, 141.7, 141.2, 141.2, 134.8, 134.0, 133.9, 133.6, 132.1, 131.9, 131.9, 131.8, 130.9, 129.1, 128.9, 128.6, 128.5, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.6, 126.5, 126.4, 126.2, 125.1, 124.8, 123.5, 121.6, 120.2, 119.9, 119.0, 118.9, 36.9, 36.3 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.6 (s, 6F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.8; **HRMS** (ESI) calculated for  $\text{C}_{94}\text{H}_{56}\text{N}_3\text{O}_8\text{F}_6\text{P}_2\text{S}_2$  (M-H) $^-$ : 1594.2894; found: 1594.2910.

**(*S,S*)-4r:**

Prepared according to the general procedure on a 0.048 mmol scale (with respect to HMDS) and purified by column chromatography (hexane/MTBE 9:1 → 4:1 → 2:1 → 1:1). Off-white solid (47 mg, 0.028 mmol, 58%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (d,  $J = 8.4$  Hz, 2H), 8.03 (d,  $J = 8.2$  Hz, 2H), 7.99 (s, 2H), 7.93 – 7.86 (m, 4H), 7.80 – 7.72 (m, 4H), 7.59 (ddd,  $J = 8.1, 6.6, 1.3$  Hz, 2H), 7.55 (dd,  $J = 7.8, 5.3$  Hz, 4H), 7.52 (d,  $J = 7.3$  Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.42 – 7.39 (m, 2H), 7.37 (d,  $J = 7.3$  Hz, 2H), 7.30 (td,  $J = 7.4, 1.2$  Hz, 2H), 7.26 – 7.24

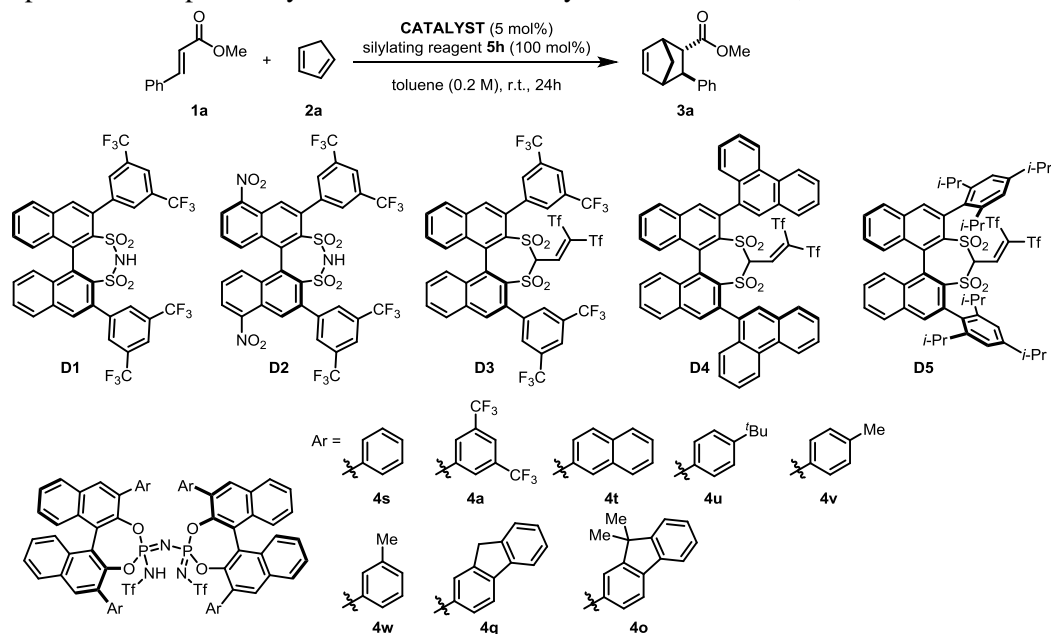
(m, 2H), 7.20 (td,  $J = 7.4, 1.2$  Hz, 2H), 7.15 (s, 2H), 7.08 – 7.03 (m, 4H), 7.00 (s, 2H), 6.72 (d,  $J = 7.8$  Hz, 2H), 6.59 (d,  $J = 7.9$  Hz, 2H), 3.76 (d,  $J = 21.9$  Hz, 2H), 3.54 – 3.36 (m, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2 (t,  $J = 5.0$  Hz), 143.8, 143.6, 143.1, 142.9, 141.7, 141.3, 141.2, 134.8, 133.9, 133.7, 132.1, 132.1, 131.9, 131.7, 131.0, 129.2, 128.9, 128.6, 128.4, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 126.6, 126.5, 126.4, 126.4, 126.1, 125.1, 124.8, 123.5, 121.5, 120.3, 119.8, 119.0, 118.9, 36.8, 36.4 (other signals not detected or observed);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.3 (s, 6F), -116.3 (d,  $J = 50.1$  Hz, 4F);  $^{31}\text{P NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -17.1; **HRMS** (ESI) calculated for  $\text{C}_{96}\text{H}_{56}\text{N}_3\text{O}_8\text{F}_{10}\text{P}_2\text{S}_2$  (M-H) $^-$ : 1694.2830; found: 1694.2849.

## Reaction Development

### Optimization for Dienophiles

**Table S1.** Initial Catalyst screening

Initial catalyst screening experiments were performed on an analytical scale (0.02 mmol) in argonated GC-vial at r.t. with commercial SKA **5h** (1 equiv.) as the silylating reagent for the specified period of time. The reaction mixtures were analyzed by  $^1\text{H}$  NMR and the desired product was isolated by preparative TLC. Chiral DSIs (**D1** and **D2**) and C–H acids (**D3–5**) gave either insufficient reactivity or no enantioselectivity. IDPi catalyst **4a** and **4o**, however, both catalyzed the reaction with high efficiency and promising enantioselectivity. Further, the reaction conditions were optimized independently with **4a** and 3-fluorenyl-substituted IDPis, such as **4o**.

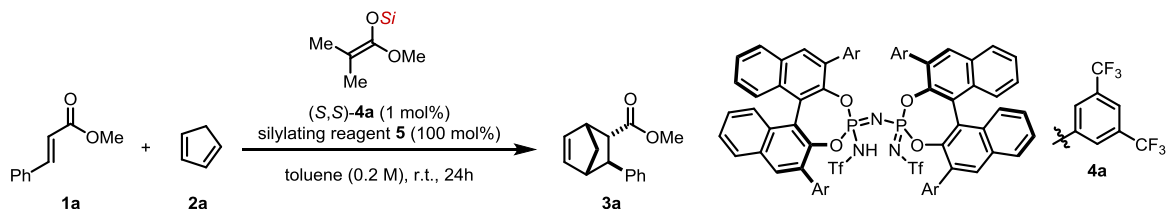


entry	CATALYST	conv.(%) <sup>a</sup>	e.r. <sub>endo</sub> <sup>b</sup>	d.r. (endo/exo) <sup>b</sup>
1	<b>D1</b>	traces	/	/
2	<b>D2</b>	60%	50:50	1:1
3 <sup>d</sup>	<b>D3</b>	(traces of product) <sup>c</sup>	52.5:47.5	26:1
4	<b>D4</b>	>99%	51:49	9:1
5	<b>D5</b>	82%	n.d.	n.d.
6	<b>4s</b>	71%		
7	<b>4a</b>	>99%	85:15	11:1
8	<b>4t</b>	(traces of product) <sup>c</sup>	26.5:73.5	10:1
9	<b>4u</b>	>99%	25:75	6:1
10	<b>4v</b>	>99%	54:46	8:1
11	<b>4w</b>	>99%	73:27	11:1
12	<b>4q</b>	>99%	74:26	7:1
13	<b>4o</b>	>99%	85:15	8:1

<sup>a</sup>Determined by  $^1\text{H}$  NMR analysis. <sup>b</sup>Determined by HPLC on a chiral stationary phase. <sup>c</sup>Mukaiyama-Michael adduct was the major product. <sup>d</sup>-40 °C.

**Table S2.** Screening of silyl groups with **4a**.<sup>a</sup>

The influence of the silyl group on conversion and stereoselectivity was tested by employing various silyl ketene acetal (SKA) reagents. The triethylsilyl (TES) group gave the best result.

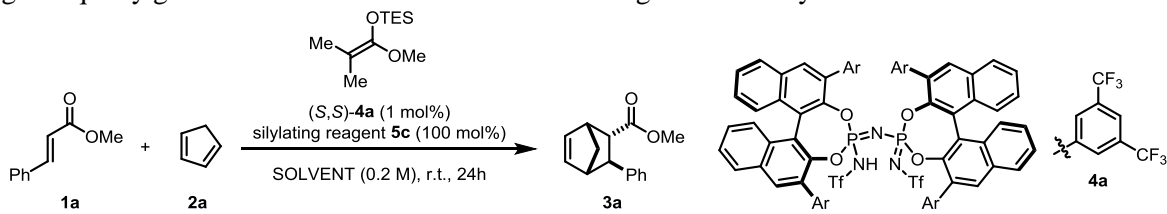


entry	SiR <sub>3</sub>	conv.(%) <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	TMS ( <b>5h</b> )	90%	86.5:13.5	82:18	11:1
2	TES ( <b>5c</b> )	>99%	88:12	86.5:13.5	9:1
3	TBS ( <b>5i</b> )	>95%	87.5:12.5	83.5:16.5	11:1
4	TIPS ( <b>5b</b> )	>99%	87:13	87:13	6:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 5 equiv. of CP **2a**. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

**Table S3.** Screening of solvents with **4a**.<sup>a</sup>

The influence of the solvent was evaluated and many non-protic, apolar solvents were found to give equally good results. Toluene was chosen due to good solubility of reactants and substrates.



entry	SOLVENT	conv.(%) <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	Et <sub>2</sub> O	>99%	86.75:13.25	84.5:15.5	9:1
2	MTBE	38%	79.5:20.5	n.d.	2.6:1
3	1,4-dioxane	>95%	85.5:14.5	82.75:17.25	9:1
4	TMS <sub>2</sub> O	>99%	89.75:10.25	87.5:12.5	8:1
5	CH <sub>2</sub> Cl <sub>2</sub>	>95%	72:28	69:31	8.5:1
6	CHCl <sub>3</sub>	90%	81.25:18.75	77.5:22.5	7:1
7	CCl <sub>4</sub>	>95%	89.75:10.25	87.5:12.5	8:1
8	EtOAc	70%	82.25:17.75	75.5:24.4	7:1
9	MeCN	36%	52.5:47.5	50:50	1:1
10	benzene	>95%	87.25:12.75	84.75:15.25	8:1
11	toluene	>95%	88:12	86:14	8:1
12	<i>o</i> -xylene	>95%	88.5:11.5	86.75:13.25	9:1
13	<i>m</i> -xylene	>95%	87.75:12.25	86.75:13.25	9:1
14	<i>p</i> -xylene	>95%	88.5:11.5	87.25:12.75	9:1
15	mesitylene	>95%	87.75:12.25	87:13	9:1
16	<i>n</i> -hexane	>99%	90:10	89:11	9:1
17	cyclohexane	>99%	89.75:10.25	89:11	10:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 5 equiv. of CP **2a**. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

**Table S4.** Evaluation of other silylating reagent with **4a**.<sup>a</sup>

We found that lowering the temperature to  $-40^{\circ}\text{C}$  gave excellent enantio- and diastereoselectivity for product **3a**, however, the use of SKA **5c** in high quantities caused the formation of Mukaiyama–Michael side products. Thus, allylsilane **5a** was tested as an alternative reagent to silylate the catalyst. Reagent loadings of as low as 10 mol% of **5a** were found to be sufficient to activate the catalyst and fully prevent side product formation. However, the reaction time for reaching full conversion of **1a** was very long (6 days).

entry	silylating reagent	conv.(%) <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	<b>5c</b> (100 mol%)	>99% <sup>d</sup>	96.75:3.25	n.d.	22:1
2	<b>5a</b> (100 mol%)	>99% <sup>e</sup>	97:3	94.5:5.5	22:1
3	<b>5a</b> (50 mol%)	>95% <sup>e</sup>	97:3	n.d.	20:1
4	<b>5a</b> (30 mol%)	>99% <sup>e</sup>	96.75:3.25	95.5:4.5	21:1
5	<b>5a</b> (20 mol%)	>99% <sup>e</sup>	97:3	95.5:4.5	19:1
6	<b>5a</b> (10 mol%)	>99% <sup>e</sup>	96.75:3.25	94.25:5.75	21:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 5 equiv. of CP **2a**. <sup>b</sup>Determined by  $^1\text{H}$  NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase. <sup>d</sup>24 h reaction time, Mukaiyama–Michael adduct is the major product. <sup>e</sup>6d reaction time.

**Table S5.** Evaluation of concentration effects at r.t. with **4a**.<sup>a</sup>

We tested the effect of concentration on the reaction at r.t. and detected only small deviations in stereoselectivities, but a strong deceleration with dilution.

entry	concentration	conv.(%) <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	1M	>99%	86.5:13.5	85.25:14.75	8:1
2	0.5M	>99%	87:13	85.25:14.75	8:1
3	0.2M	>95%	87.5:12.5	85:15	8:1
4	0.1M	93%	87.5:12.5	84.25:15.75	8:1
5	0.05M	78%	87.75:12.25	82:18	7:1
6	0.025M	47%	87.5:12.5	74.5:25.5	6:1
7	0.01M	10%	88.75:11.25	n.d.	3:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 5 equiv. of CP **2a**. <sup>b</sup>Determined by  $^1\text{H}$  NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

**Table S6.** Evaluation of concentration effects at low temperature with **4a**.<sup>a</sup>

A study on concentration effects was repeated with silylating agent **5a** at decreased temperature ( $-40^{\circ}\text{C}$ ) and the reaction time to achieve full conversion was evaluated. At 1M concentration, the reaction completed within 24 h using 1 mol% catalyst. For these optimal conditions, we derived a corresponding general procedure for the catalytic, asymmetric Diels–Alder reaction (vide infra).

entry	concentration	reaction time <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	0.2M	6d	97:3	93.25:6.75	21:1
2	0.4M	2d	96.75:3.25	96:4	20:1
3	1M	<24h	96.5:3.5	95.5:4.5	19:1
4	2M	<24h	95.5:4.5	95.25:4.75	17:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 10 equiv. of CP **2a**. <sup>b</sup>for the reaction to reach full conversion.

<sup>c</sup>Determined by HPLC on a chiral stationary phase.

**Table S7.** Screening of silyl groups with **4o**.<sup>a</sup>

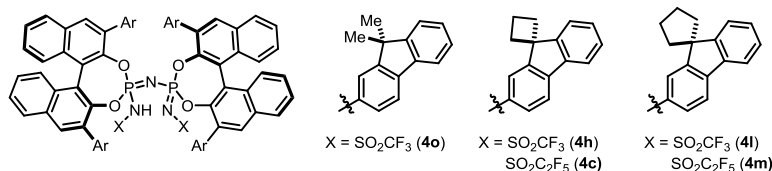
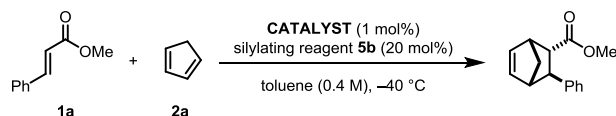
For the second catalyst lead structure **4o**, the influence of the silyl group on conversion and stereoselectivity was re-evaluated. In this case, the triisopropylsilyl (TIPS) group was found optimal. In addition, only small amounts of Mukaiyama-Michael side products were detected with SKA **5b**.

entry	SiR <sub>3</sub>	conv.(%) <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	TMS ( <b>5h</b> )	83%	85.75:14.25	86.5:13.5	7.5:1
2	TES ( <b>5c</b> )	>99%	87.5:12.5	86.75:13.25	7.5:1
3	TBS ( <b>5i</b> )	76%	86.25:13.75	85:15	9:1
4	TIPS ( <b>5b</b> )	>99%	88.25:11.75	88.25:11.75	5.5:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 10 equiv. of CP **2a**. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

**Table S8.** Screening of other 3-fluorenyl-derived IDPi catalysts.<sup>a</sup>

Although promising results were obtained with **4o**, reactivity was significantly lower than with **4a**. Thus, we tested more 3-fluorenyl-derived IDPi catalysts including the corresponding inner-core modified derivatives (X = SO<sub>2</sub>CF<sub>3</sub>, SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>) to achieve higher reactivity and/or enantioselectivity. We found that using corresponding cyclobutyl-derivatives **4h** and **4c** resulted in increased stereinduction, while the latter was significantly more active due to the inner-core modification (X = SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>). Product **3a** was isolated in 90% yield after 12 h of reaction time (entry 3). These conditions were used in a corresponding general procedure for the catalytic, asymmetric Diels–Alder reaction (vide infra).



entry	CATALYST	conv.(%) <sup>b</sup>	e.r. <sub>endo</sub> <sup>c</sup>	e.r. <sub>exo</sub> <sup>c</sup>	d.r. (endo/exo) <sup>c</sup>
1	<b>4o</b>	84% (64h)	94.75:5.25	95.5:4.5	7:1
2	<b>4h</b>	92% (64h)	97:3	92:8	12:1
3 <sup>d</sup>	<b>4c</b>	>99% (<12h)	97.5:2.5	91.5:8.5	16:1
4	<b>4l</b>	89% (64h)	95:5	95.75:4.25	7:1
5	<b>4m</b>	>99% (64h)	97:3	94.75:5.25	12.5:1

<sup>a</sup>Reactions were performed on a 0.02 mmol scale and 10 equiv. of CP **2a**. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis after the specified reaction time. <sup>c</sup>Determined by HPLC on a chiral stationary phase. <sup>d</sup>at 1M concentration using 5 equiv. of CP **2a**.

## Optimization for Dienes

### General procedure for the screening experiments:

The experiments were conducted on a 0.08 mmol or 0.1 mmol scale. An oven-dried 2.0 mL screw-cap glass vial was charged with the corresponding (*S,S*)-IDPi catalyst (0.8  $\mu\text{mol}$  or 1.0  $\mu\text{mol}$ , 1 mol%) and the appropriate  $\alpha,\beta$ -unsaturated methyl ester (0.08 mmol or 0.1 mmol). A Teflon-coated magnetic stirring bar was added, the vial was closed with a screw-cap containing a PTFE/rubber septum and sealed with parafilm. The reaction vial was evacuated and purged with argon (3  $\times$ ). The silyl donor (30–50 mol%) was transferred to the reaction mixture and the reaction mixture was stirred for 5 min at r.t.. Then, the diene was transferred to the reaction vial and the colorless solution was stirred at the indicated temperature for the specified reaction time until sufficient conversion was observed. The reaction was monitored by TLC and  $^1\text{H}$  NMR spectroscopy and treated with triethylamine. The desired Diels–Alder product was obtained by preparative TLC.

**Table S9.** Catalyst screening<sup>a</sup>

**4a**

**4c**

**5a**

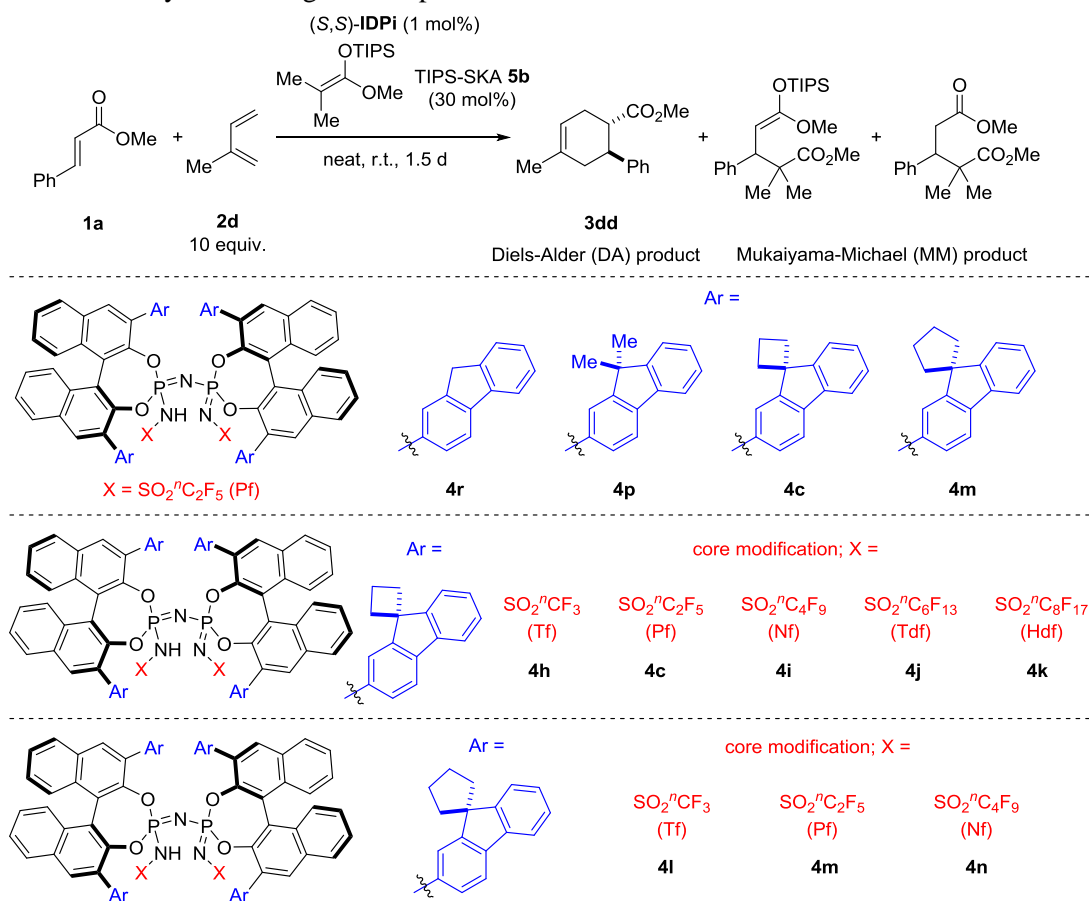
**5b**

entry	catalyst	silyl donor	conversion(%) <sup>b</sup>	ratio <sup>b</sup> 3:[MM]	e.r. <sup>c</sup> <b>3bb</b> or <b>3dd</b>
diene substrate: isoprene ( <b>2d</b> )					
1	<b>4a</b>	<b>5a</b>	24	n.a.	67.4:32.6
2	<b>4c</b>	<b>5b</b>	34	15:85	95.3:4.7
diene substrate: 2,3-dimethylbuta-1,3-diene ( <b>2b</b> )					
3	<b>4a</b>	<b>5a</b>	16	n.a.	51.4:48.6
4	<b>4c</b>	<b>5b</b>	34	10:90	78.3:21.7

<sup>a</sup>Reactions were performed on a 0.08 mmol scale with 50 mol% of **5a** or 30 mol% of **5b** and 1 mol% of catalyst for 1.75 d and quenched with 1.1 equiv. of  $\text{NEt}_3$ . <sup>b</sup>Determined by  $^1\text{H}$  NMR analysis; n.a.: not applicable. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

An initial catalyst screening (Table S9) of representative examples of both catalyst families used for the dienophile scope indicated that 3-fluorenyl-derived IDPi (**4c**) provided the Diels–Alder products with higher enantiomeric ratios for both dienes compared to the more acidic trifluoromethylphenyl derivative (**4a**). Therefore, further IDPi catalyst derivatives of the 3-fluorenyl substitution family with different core modifications and substituents in the 3,3'-position of the BINOL backbone were investigated (Table S10).

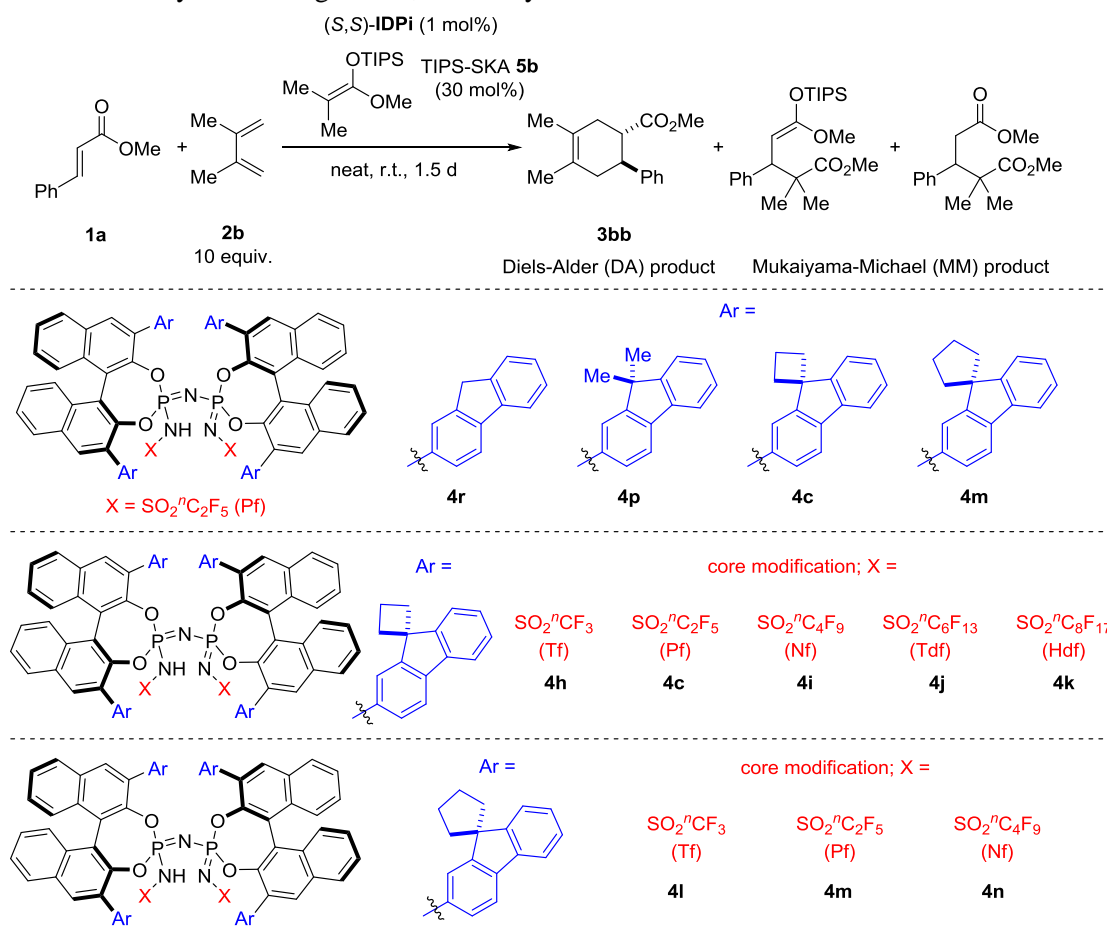
**Table S10.** Catalyst screening with isoprene<sup>a</sup>



diene substrate: isoprene ( <b>2d</b> )				
entry	catalyst	conversion (%) <sup>b</sup>	ratio <sup>b</sup> <b>3dd</b> : <b>[MM]</b>	e.r. <sup>c</sup> <b>3dd</b>
1	<b>4r</b>	35	18:82	54.6:45.4
2	<b>4p</b>	28	6:94	91.9:8.1
3	<b>4c</b>	34	21:79	94.3:5.7
4	<b>4m</b>	34	40:60	96.7:3.3
5 <sup>d</sup>	<b>4h</b>	34	4:96	94.4:5.6
6 <sup>e</sup>	<b>4c</b>	43	17:83	95.1:4.9
7 <sup>e</sup>	<b>4i</b>	61	21:79	95.2:4.8
8 <sup>e</sup>	<b>4j</b>	63	27:73	95.5:4.5
9 <sup>e</sup>	<b>4k</b>	64	21:79	96.8:3.2
10 <sup>d</sup>	<b>4l</b>	34	25:75	95.3:4.7
11 <sup>e</sup>	<b>4m</b>	34	40:60	96.7:3.3
12	<b>4n</b>	37	42:58	97.2:2.8

<sup>a</sup>Reactions were performed on a 0.08 mmol scale with 30 mol% of SKA and 1 mol% of catalyst for 1.5 d and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase. <sup>d</sup>3.5 days reaction time. <sup>e</sup>50 mol% TIPS-SKA (**5b**) were used.

**Table S11.** Catalyst screening with 2,3-dimethylbutadiene<sup>a</sup>

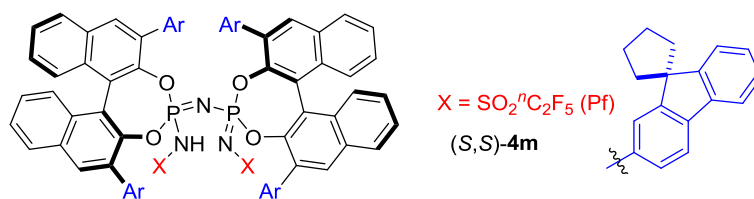
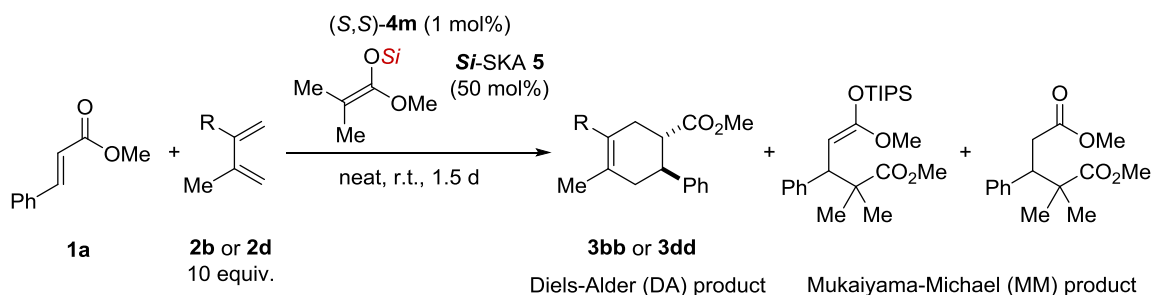


diene substrate: 2,3-dimethylbuta-1,3-diene ( <b>2b</b> )				
entry	catalyst	conversion (%) <sup>b</sup>	ratio <sup>b</sup> <b>3bb</b> : <b>[MM]</b>	e.r. <sup>c</sup> <b>3bb</b>
1	<b>4r</b>	56	31:69	55.4:44.6
2	<b>4p</b>	37	2:98	84.3:15.7
3	<b>4c</b>	44	22:78	78.3:21.7
4	<b>4m</b>	52	24:76	93.6:6.4
5 <sup>d</sup>	<b>4h</b>	32	5:95	89.4:10.6
6 <sup>e</sup>	<b>4c</b>	35	10:90	75.6:24.4
7 <sup>e</sup>	<b>4i</b>	57	20:80	92.7:7.3
8 <sup>e</sup>	<b>4j</b>	55	22:78	92.7:7.3
9 <sup>e</sup>	<b>4k</b>	62	18:82	92.3:7.7
10 <sup>d</sup>	<b>4l</b>	36	18:82	92.7:7.3
11	<b>4m</b>	52	24:76	93.6:6.4
12	<b>4n</b>	50	14:86	95.2:4.8

<sup>a</sup>Reactions were performed on a 0.08 mmol scale with 30 mol% of SKA and 1 mol% of catalyst for 1.5 d and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase. <sup>d</sup>3.5 days reaction time. <sup>e</sup>50 mol% TIPS-SKA (**5b**) were used.

Increasing the size of the 3-fluorenyl substituent from 9H-fluorenyl to 3-cyclopentylfluorenyl proved to be beneficial for the enantiomeric ratio with both tested dienes (**2b** and **2d**, see Table S10, entries 1–4, and Table S11, entries 1–4). Inner-core modifications bearing longer perfluoroalkyl substituents provided an improvement in both reactivity and selectivity towards the desired Diels–Alder product, while maintaining or slightly improving the enantiomeric ratio (Tables S10 and S11, entries 5–12). The IDP*i* catalysts bearing 3-cyclopentylfluorenyl substituents were identified as the best catalyst system for both dienes. With this catalyst subgroup in hand, the effect of the silyl group on both enantioselectivity and conversion was investigated. Changing the silyl group from the initially used TIPS group to TMS, TES or TBS was found to be deleterious for conversion, chemo- and enantioselectivity (Table S12).

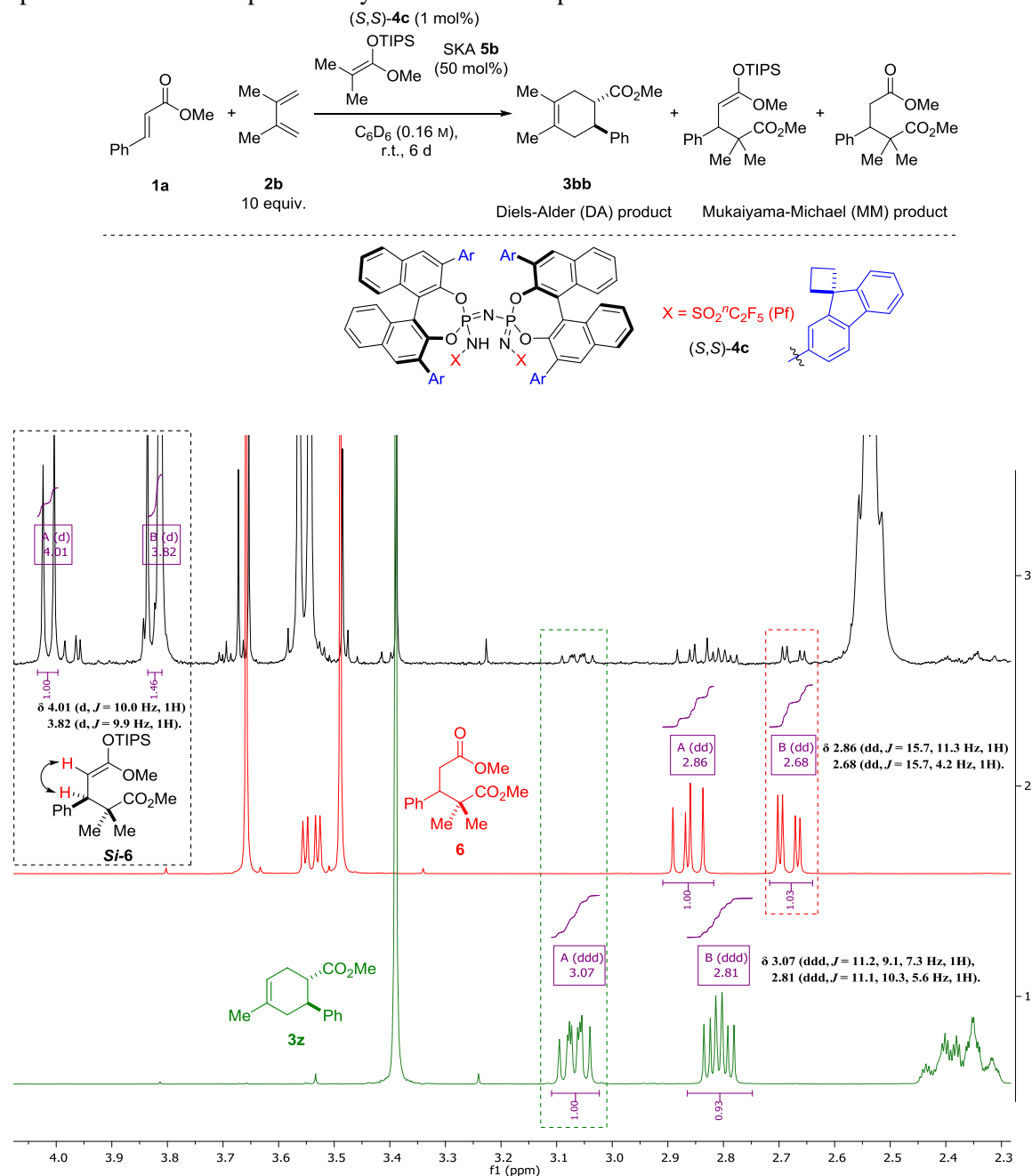
**Table S12.** Screening of silyl groups with silyl ketene acetals (SKA) as activators<sup>a</sup>



entry	SKA 5	conversion (%) <sup>b</sup>	ratio <sup>b</sup> <b>3</b> : <b>[MM]</b>	e.r. <sup>c</sup> <b>3bb</b> or <b>3dd</b>
diene substrate: isoprene ( <b>2d</b> )				
1	<b>TMS-SKA (5h)</b>	37	5:95	90.3:9.7
2	<b>TES-SKA (5c)</b>	51	7:93	94.4:5.6
3	<b>TBS-SKA (5i)</b>	28	3:97	94.3:5.7
4	<b>TIPS-SKA (5b)</b>	53	15:85	96.7:3.3
diene substrate: 2,3-dimethylbuta-1,3-diene ( <b>2b</b> )				
5	<b>TMS-SKA (5h)</b>	49	4:96	78.8:21.2
6	<b>TES-SKA (5c)</b>	49	5:96	86.4:13.6
7	<b>TBS-SKA (5i)</b>	44	1:99	91.4:6.6
8	<b>TIPS-SKA (5b)</b>	56	11:89	94.4:5.6

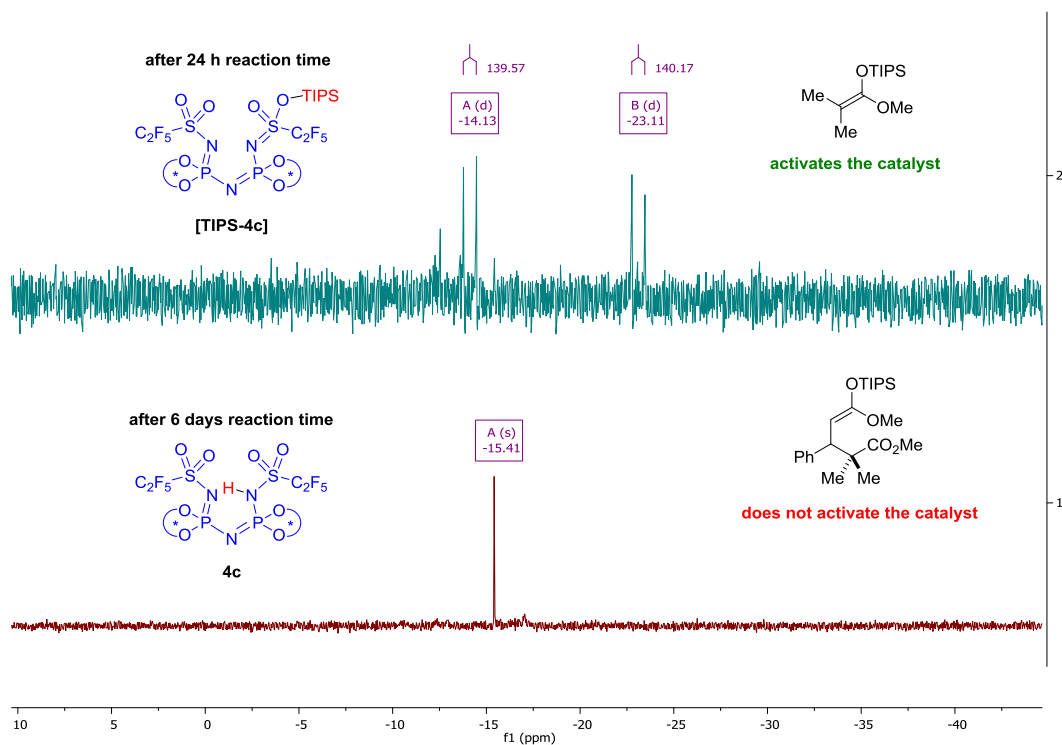
<sup>a</sup>Reactions were performed on a 0.08 mmol scale with 50 mol% of SKA and 1 mol% of catalyst for 1.5 d and quenched with 1.1 equiv. of  $\text{NEt}_3$ . <sup>b</sup>Determined by  $^1\text{H}$  NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

In contrast to Diels–Alder reactions with cyclopentadiene, using SKAs as silylating reagents with less reactive dienes is the competing Mukaiyama–Michael reaction and the corresponding product is usually observed as the major product species in the crude reaction mixture (Figure S1). In addition, incomplete conversion was observed, even after prolonged reaction times suggesting deactivation of the catalyst. In order to clarify this issue, a mixture of **1a** (0.08 mmol), **2b** (0.8 mmol, 10 equiv.), SKA **5b** (24 μmol, 30 mol%) and IDPi catalyst **4c** (0.8 μmol, 1 mol%) was dissolved in 0.5 mL C<sub>6</sub>D<sub>6</sub> and transferred to a 5 mm NMR tube under argon. <sup>1</sup>H and <sup>31</sup>P NMR spectra were collected periodically until full consumption of SKA **5b** was observed.



**Figure S1.** Representative <sup>1</sup>H NMR spectra of the reaction mixture described above (upper spectrum), the purified Mukaiyama–Michael product (middle spectrum) and the purified Diels–Alder product. The proton signals chosen for integration to determine the conversion are highlighted in the dashed boxes.

The  $^{31}\text{P}$  NMR spectra indicate complete silylation long as **5b** is present in the reaction mixture. However, as the sub-stoichiometric amount of silylating reagent **5b** is gradually consumed in the competing Mukaiyama–Michael reaction, deactivation of the catalyst due to slow hydrolysis occurs. Consequently, the formed silylated Mukaiyama–Michael product does not silylate (or significantly slower than silyl ketene acetal **5b**) the IDPi catalyst as suggested by the  $^{31}\text{P}$  NMR spectrum of the reaction mixture after 6 days (Figure S2).



**Figure S2.** Stacked  $^{31}\text{P}$  NMR spectra of the reaction mixture after 24 h reaction time and 6 days reaction time using 30 mol% of **5b** as silylating reagent.

## Screening of methallylsilanes as silyl donors

Due to the observed competing Mukaiyama–Michael reaction with silyl ketene acetals as silylating reagents, allylsilanes and (2-methallyl)silanes were tested as alternative silyl donors for the activation of 3-fluorenyl-derived IDPi's.

**Table S13.** Screening of (2-methallyl)silanes as silylating reagents.<sup>a</sup>

entry	<i>Si</i> -(2-methallyl)silane	conversion (%) <sup>b</sup>	remaining silyl <i>Si</i> -(2-methallyl)silane	e.r. <sup>c</sup>
1	<b>TMS (5j)</b>	8	14	75:25
2	<b>TES (5k)</b>	16	20	86:14
3	<b>SiBu<sub>3</sub> (5l)</b>	24	19	76:24
4	<b>TIPS (5d)</b>	22	20	96:4
5	<b>Si(TMS)<sub>3</sub> (5m)</b>	8	36	94:6

<sup>a</sup>Reactions were performed on a 0.1 mmol scale with 50 mol% of (2-methallyl)silanes **5** and 1 mol% of catalyst (*S,S*)-**4d** for 3 d and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

**Table S14.** Screening of allylsilanes and (2-methallyl)silanes as silylating reagents.<sup>a</sup>

entry	catalyst	silylating reagent	conversion (%) <sup>b</sup>	e.r. <sup>c</sup>
1	<b>4n</b>	<b>5g</b>	~ 5	n.d.
2	<b>4d</b>	<b>5g</b>	~ 5	n.d.
3 <sup>d</sup>	<b>4n</b>	<b>5g</b>	8	93.9:6.1
4	<b>4n</b>	<b>5d</b>	12	94.1:5.9
5	<b>4d</b>	<b>5d</b>	13	94.5:5.5

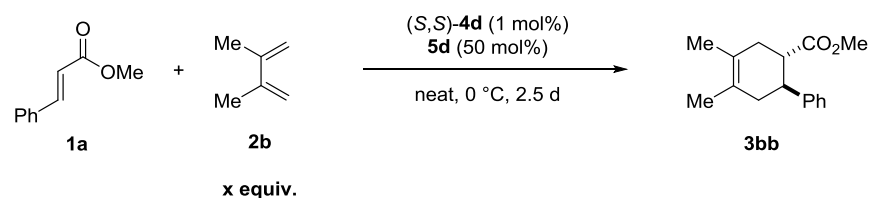
<sup>a</sup>Reactions were performed on a 0.1 mmol scale with 20 mol% of silylating reagent and 1 mol% of IDPi catalyst for 3 d and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase; n.d.: not determined. <sup>d</sup>3.75 d reaction time using 50 mol% **5g**.

Several (2-methallyl)silanes bearing different silyl groups were prepared and used in the enantioselective Diels–Alder reactions in order to investigate the effect of the silyl group on conversion and enantioselectivity. In consistency with the results obtained with silyl ketene acetals, the TIPS group delivered the desired Diels–Alder product with an excellent enantiomeric ratio (96:4; Table S13, entry 4). A direct comparison between allylsilanes and (2-methallyl)silanes indicated an accelerated silylation of the catalyst with (2-methallyl)silanes, thus resulting in a shorter induction/dormant period of the catalytic system (Table S14).

### Screening of concentration effects

As the reaction was conducted under neat conditions, we expected a concentration on effect stereoselectivity and conversion with different equivalents of diene. In general, lower concentrations resulted in an increased enantiomeric ratio of Diels–Alder product **3x**, whereas higher conversion was observed at 0.02 M concentration (corresponding to 4 equiv. of diene, see Table S15). Thus, in the preparative scale experiments, either 4 or 5 equivalents of the diene were used to achieve an acceptable balance of conversion and enantioselectivity.

**Table S15.** Screening of different concentrations.<sup>a</sup>

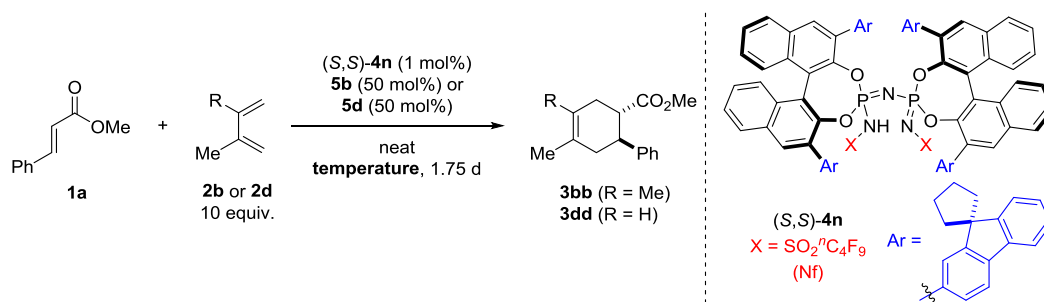


entry	<b>2b</b> /equiv.	concentration (M)	conversion (%) <sup>b</sup>	e.r. <sup>c</sup>
1	2	0.044	7	92.4:7.6
2	3	0.029	19	93.5:6.5
3	4	0.022	24	94.7:5.3
4	5	0.018	17	95.3:4.7
5	10	0.009	14	95.9:4.1

<sup>a</sup>Reactions were performed on a 0.1 mmol scale with 50 mol% of **5d** and 1 mol% of catalyst (*S,S*)-**4d** for 2.5 d and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

## Temperature screening

**Table S16.** Screening of different reaction temperatures.<sup>a</sup>



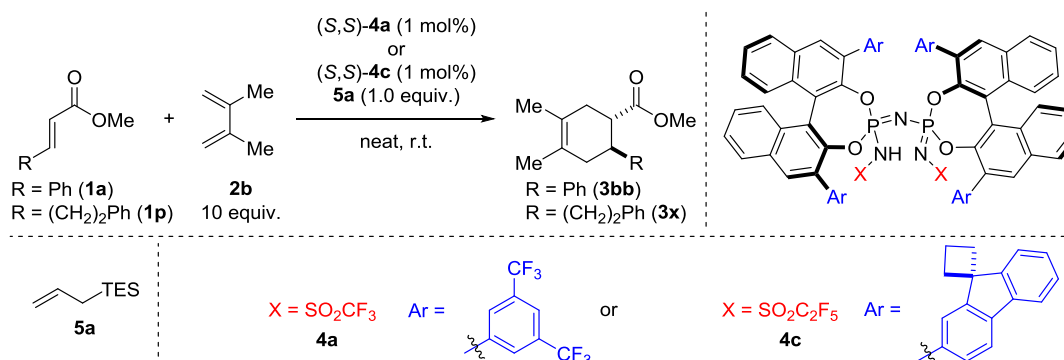
entry	diene	silyl donor	temperature(°C)	conversion(%) <sup>b</sup>	e.r. <sup>c</sup>
1	<b>2b</b>	<b>5b</b>	40	6	92:8
2 <sup>d</sup>	<b>2b</b>	<b>5d</b>	60	12	62:38
3	<b>2d</b>	<b>5b</b>	40	5	95:5
4 <sup>d</sup>	<b>2d</b>	<b>5d</b>	60	10	79:21

<sup>a</sup>Reactions were performed on a 0.1 mmol scale with 50 mol% of **5d** and 1 mol% of catalyst (*S,S*)-**4n** for 1.75 d and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase. <sup>d</sup>8.5 d reaction time.

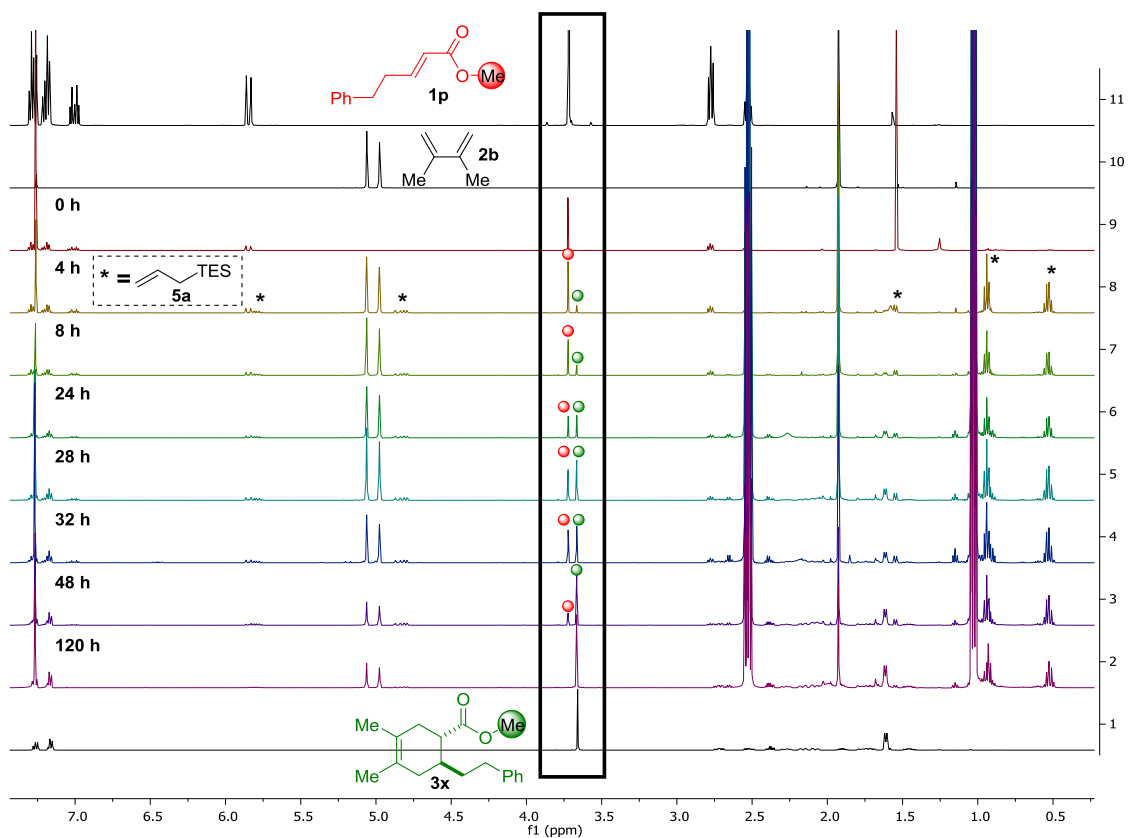
We tested if increasing the temperature (40 °C and 60 °C) would improve the conversion of the Diels–Alder reaction with catalyst (*S,S*)-**4n**, however surprisingly found that this proved to be detrimental for both conversion and enantioselectivity (Table S16). In contrast, for the preparation of racemates using HNTf<sub>2</sub> as catalyst this effect was not observed and increasing temperatures usually provided full conversion of the starting materials.

## Preliminary kinetic studies

A possible explanation accounting for these results could involve a deactivation pathway with IDPi catalysts at increased temperatures. Therefore, we followed the course of the catalytic enantioselective Diels–Alder reaction at r.t. over time with substrates **1a** and **1p** and 2,3-dimethylbutadiene **2b** (see below). One member of each catalyst family was chosen to compare both electronic and steric effects.

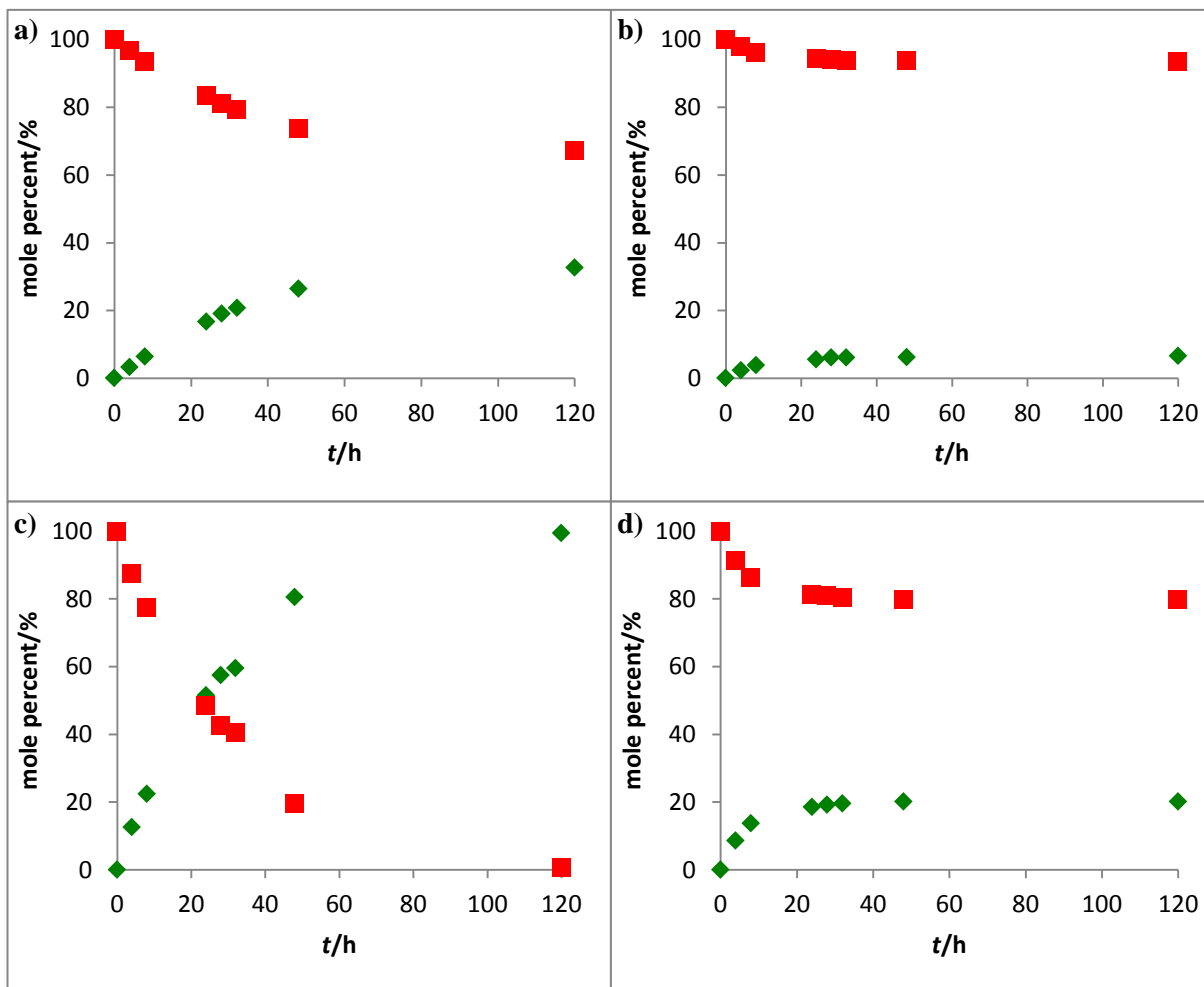


To an oven dried 2 mL screw-cap glass vial were added the IDPi catalyst (1.43 mg, 0.80  $\mu\text{mol}$ , 1.0 equiv.) and the appropriate  $\alpha,\beta$ -unsaturated methyl ester (80  $\mu\text{mol}$ , 1.0 equiv.). A Teflon-coated magnetic stirring bar was added, the vial was sealed, evacuated and purged with argon ( $3 \times$ ). Allyltriethylsilane (16  $\mu\text{L}$ , 80  $\mu\text{mol}$ , 1.0 equiv.) and 2,3-dimethyl-1,3-butadiene (91  $\mu\text{L}$ , 0.8 mmol, 10 equiv.) were transferred to the reaction vial and the resulting pale yellow solution was stirred at 25  $^{\circ}\text{C}$ . At the indicated time, a 5  $\mu\text{L}$  aliquot was taken, quenched with triethylamine (12  $\mu\text{L}$ , 1 equiv.), dissolved in 0.5 mL  $\text{CDCl}_3$  and the conversion of the reaction was determined by  $^1\text{H}$  NMR spectroscopy (integration of the methoxy groups of starting material and product; see Figure S3 with representative stacked  $^1\text{H}$  NMR spectra depicted below).



**Figure S3.** Stacked  $^1\text{H}$  NMR spectra of starting materials, the kinetic study ( $^1\text{H}$  NMR spectra from each collected data point) and the Diels–Alder product **3x**.

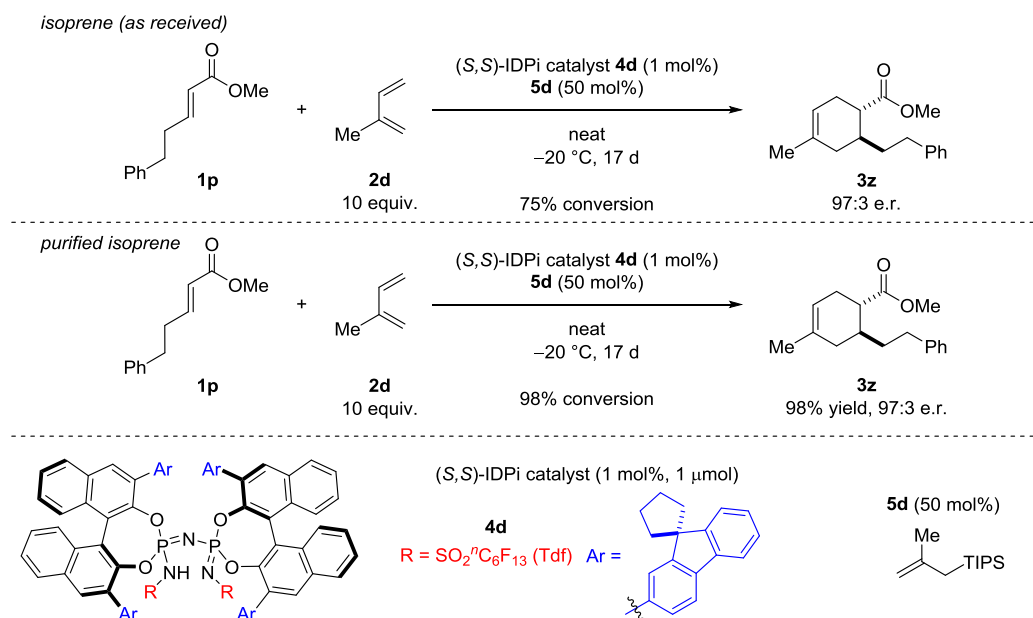
With (*S,S*)-**4a**, higher conversions were observed than with (*S,S*)-**4c** for both substrates, however full conversion was only obtained with substrate **1p** (see plots in Figure S4a-d). In all other cases, the reaction stopped after a certain amount of time and only partial conversion was obtained. These preliminary kinetic data suggests that catalyst inhibition or deactivation for certain substrates and catalyst combinations is indeed an inhibitory pathway.



**Figure S4.** a) Preliminary kinetic data obtained for the reaction of dienophile **1a** with catalyst (*S,S*)-**4a**. b) Reaction of dienophile **1a** with catalyst (*S,S*)-**4c**. c) Reaction of dienophile **1p** with catalyst (*S,S*)-**4a**. d) Reaction of dienophile **1p** with catalyst (*S,S*)-**4c**.

## Effect of diene purification

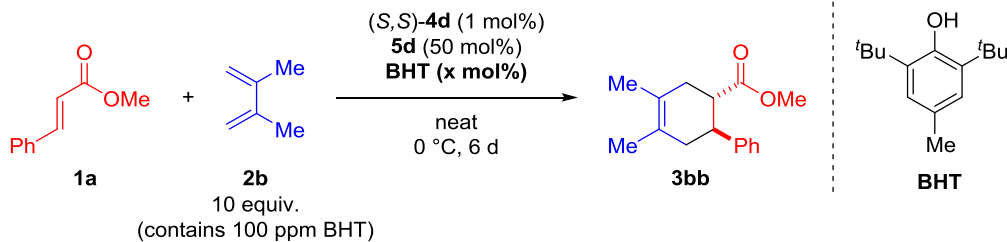
We tested the influence of diene purification and in particular inhibitory additives to conversion and stereoselectivity of the catalytic asymmetric Diels–Alder reaction. Comparison experiments were conducted according to the described general procedure with purified isoprene (as described in the general information) and commercially supplied material.



Although the use of commercially supplied isoprene in the catalytic asymmetric Diels–Alder reaction is possible, it is recommended to purify each diene using the typical purification procedure. This is particularly important in case of low catalyst loadings (1 mol% and below) as small amounts of impurities significantly affect the performance of the IDPi catalyst, as demonstrated in the comparison experiment above. Using 1 mol% of (*S,S*)-IDPi catalyst **4d** essentially full conversion to the desired Diels–Alder product **3z** was observed after 17 d with purified isoprene, whereas commercially supplied isoprene provided **3z** in 75% conversion after the same reaction time. The enantiomeric ratio remained the same regardless of the diene purity.

## Effect of inhibitory additives

As most dienes contain inhibitors, the effect of the inhibitor on both conversion and enantioselectivity was evaluated by the deliberate addition of BHT (butylhydroxytoluene, 2,6-di-*tert*-butyl-4-methylphenol) to the reaction mixture.



additionally added BHT/mol%	conversion after 24 h/% <sup>b</sup>	conversion after 6 d/% <sup>b</sup>	e.r. <sup>c</sup>
0	12.5	21.5	95.5:4.5
1	12.5	21.0	96:4
10	12.8	23.6	96:4

<sup>a</sup>Reactions were performed on a 0.2 mmol scale with 50 mol% of silylating reagent **5d** and 1 mol% IDPi catalyst (S,S)-**4d** for the indicated time and quenched with 1.1 equiv. of NEt<sub>3</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

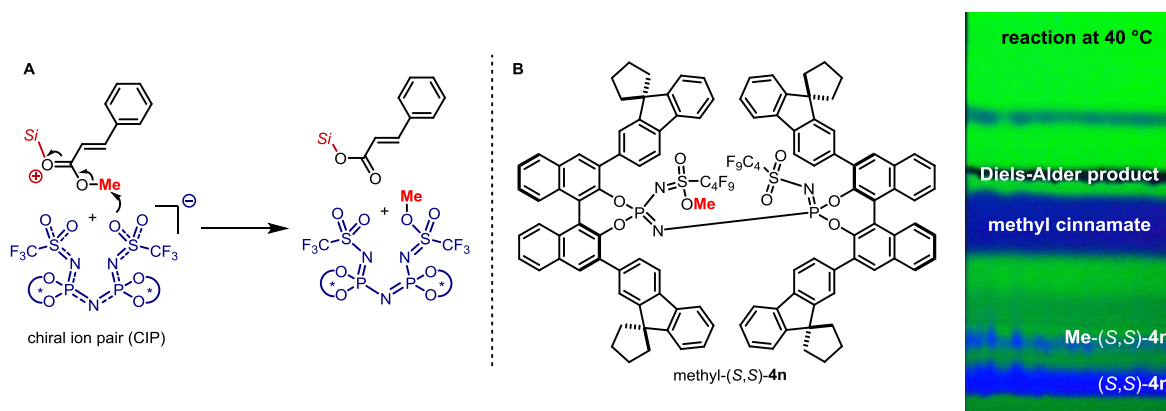
No detrimental effect of the inhibitor on conversion and enantioselectivity in the catalytic asymmetric Diels–Alder reaction was observed.

## Methylation of the catalyst

In consequence to these preliminary kinetic studies, we carefully re-examined reactions at higher temperature than r.t. (Table S16). Upon isolation of the Diels–Alder product by preparative TLC, we detected a less polar IDPi derivative in significant amounts (Figure S5B). This compound was identified as the methylated IDPi (methyl-*[S,S]*-**4n**) by HRMS (see below).

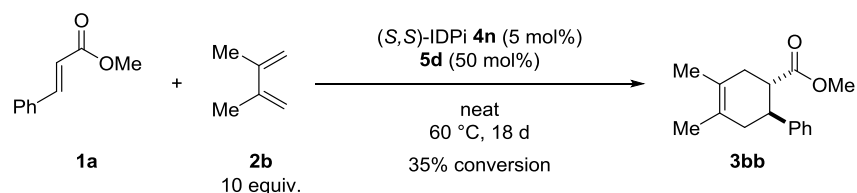
In further studies at various temperatures, we qualitatively observed increasing catalyst methylation with higher temperatures. We reason that this inhibitory pathway, at least partially, accounts for the observed low conversions at r.t. and rationalize it via collapse of the chiral ion pair (CIP) consisting of silylated substrate and chiral counteranion (Figure S5A). Thus, methyl cinnamate **1a** acts as a methyl group donor to give a silyl ester side product. The nucleophilic atom of the IDPi anion (oxygen or nitrogen atom of the sulfonyl group) remains unclear to this point.

For catalyst derivatives with longer perfluoroalkyl groups as inner-modifications, we qualitatively observed less catalyst methylation. For IDPi **4d** (X = SO<sub>2</sub>C<sub>6</sub>F<sub>13</sub>) essentially no methylation was detected  $\leq 0$  °C. We therefore reason that the stability of the chiral ion pair depends not only on the reaction temperature, but also on the nucleophilicity of the chiral counteranion and on methyl ester substrate. For the optimized conditions, we selected 3 mol% of IDPi **4d** (X = SO<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 0 °C as reaction temperature and 3 equiv. of diene (see general procedures), for which we obtained full conversion with both substrates after 3.5 to 5.5 days.



**Figure S5.** **A** Proposed methylation pathway of IDPi catalysts; **B** Qualitative analysis of a representative preparative TLC plate (silica gel; hexane/EtOAc 19:1, one elution, 254 nm) indicating catalyst methylation at 40 °C.

### Catalyst methylation at 60 °C



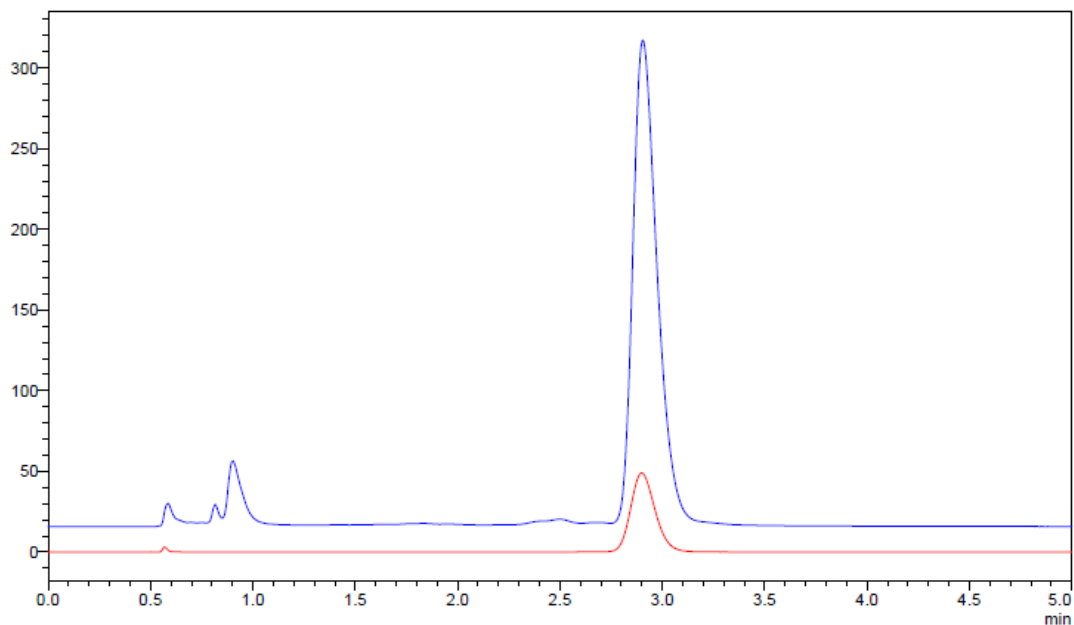
(*S,S*)-IDPi catalyst **4n** (10.6 mg, 5.00  $\mu$ mol, 5 mol%) and methyl (*E*)-cinnamate (16.2 mg, 0.10 mmol, 1.0 equiv.) were transferred to an oven-dried 2 mL pressure glass vial. A Teflon-coated magnetic stirring bar was added, the vial was sealed with a pressure cap, evacuated and purged with argon (3  $\times$ ). Then, triisopropyl(2-methylallyl)silane **5d** (10.6 mg, 11.7  $\mu$ L, 0.05 mmol, 50 mol%) was added to the solids and the mixture was stirred at room temperature for 5 min. After the elapsed time, 2,3-dimethyl-1,3-butadiene **2b** (82.1 mg, 113  $\mu$ L, 1.00 mmol, 10 equiv.) was transferred to the vial and the resulting pale yellow solution was placed inside a pre-heated aluminum block at 60 °C and stirred for 18 days at this temperature until TLC and  $^1\text{H}$  NMR analysis indicated complete consumption of (*S,S*)-IDPi catalyst **4n**. After cooling to room temperature, the reaction mixture was directly transferred onto a 20  $\times$  20 cm glass plate coated with 0.25 mm silica gel. Purification by preparative TLC (*iso*-hexane/ethyl acetate 19:1, two elutions) afforded the methylated IDPi catalyst as a pale yellow solid in 84% purity (by HPLC,  $^{31}\text{P}$  NMR; the corresponding *i*IDP, imino-imidodiphosphate, was identified as major impurity by LC-MS and HRMS). A sequential purification by preparative HPLC afforded the methylated IDPi **Me-4n** (5.20 mg, 2.45  $\mu$ mol, 49% yield) as a colorless solid (>99% purity, HPLC).

$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -13.00 (d,  $J$  = 119.7 Hz), -16.30 (d,  $J$  = 120.7 Hz); HRMS (ESI) calculated for  $\text{C}_{117}\text{H}_{83}\text{F}_{18}\text{N}_3\text{O}_8\text{P}_2\text{S}_2\text{Na}$  ( $\text{M}+\text{Na}$ ) $^+$ : 2148.4702; found: 2148.4734; HPLC (50 mm Zorbax SB300-C8, 3.5  $\mu$ m, 4.6 mm i.D.,  $\text{CH}_3\text{CN}/0.1\%$  TFA in  $\text{H}_2\text{O}$ , 1.0 mL/min, 3.5 MPa, 308 K): 254 nm:  $t_{\text{R}(1)}$  = 2.90 min.

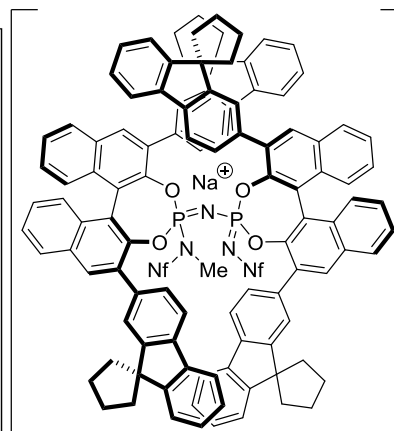
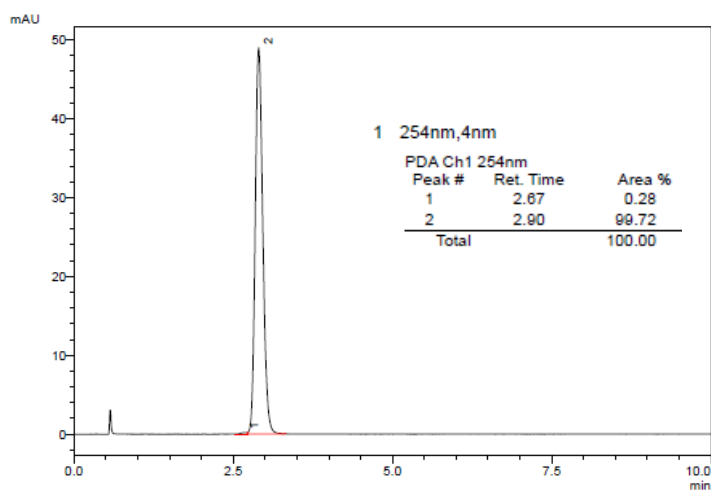
NOTE:  $^1\text{H}$  and  $^{13}\text{C}$  spectra could not be obtained due to insufficient material.

Data1 : \* C:\LabSolutions\Data\Data 1\Turberg\TUM-TA-232-01-02.lcd  
 Data2 : C:\LabSolutions\Data\Data 1\Turberg\TUM-TA-232-01-10G-01.lcd  
 mV

50 mm Eclipse Plus C18 1.8  $\mu$ m, 4.6 mm i.D.  
 Acetonitril/Wasser + 0.1% TFA = 95:5  
 1.0 mL/min, 308 K, 254 nm



5  $\mu$ L TUM-TA-232-01-10 gesamt  
 50 mm Zorbax 300SB-C8 3.5  $\mu$ m, 4.6 mm i.D.  
 Acetonitril/0.1% in Wasser= 95:5  
 1.0 mL/min, 3.5 MPa, 308 K  
 254 nm

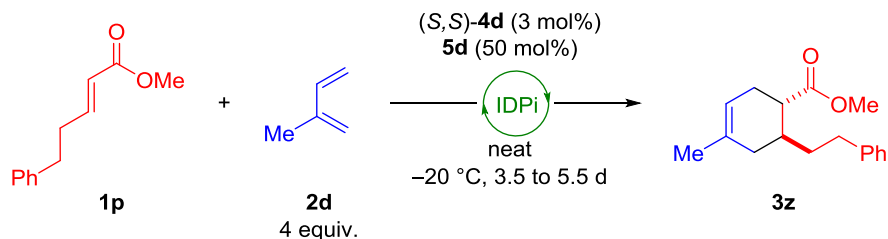


**Me-4n**

Exact Mass: 2148.47016

**HRMS** (ESI) calculated for  $C_{117}H_{83}F_{18}N_3O_8P_2S_2Na$  ( $M+Na$ )<sup>+</sup>: 2148.4702; found: 2148.4734.

## Recyclability of the IDPi catalyst



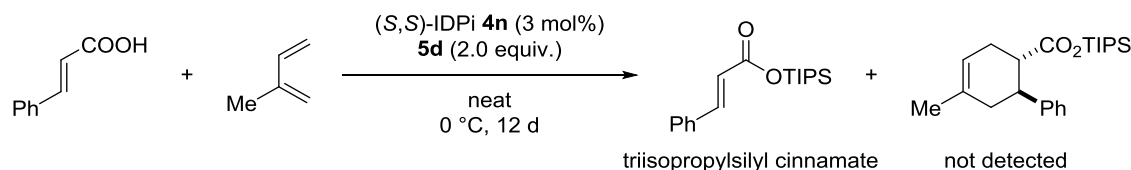
An oven-dried 2.0 mL screw-cap glass vial was charged with  $(S,S)\text{-4d}$  (13.9 mg, 6  $\mu\text{mol}$ , 3 mol%) and methyl (*E*)-5-phenylpent-2-enoate **1p** (0.2 mmol, 38.0 mg). A Teflon-coated magnetic stirring bar was added, the vial was closed with a screw-cap containing a PTFE/rubber septum and sealed with parafilm. Then, the reaction vial was evacuated, purged with argon (3  $\times$ ) and subsequently placed into an aluminum block submerged in a dry-ice/isopropanol bath at  $-77\text{ }^{\circ}\text{C}$ . Isoprene **2c** (0.8 mmol, 80  $\mu\text{L}$ , 4 equiv.) was transferred to the reaction vial and the colorless solution was kept at this temperature for 5 min. After the elapsed time, triisopropyl(2-methyl)silane (**5d**, 23  $\mu\text{L}$ , 0.1 mmol, 50 mol%) was added to the reaction mixture to initiate the reaction. Then, the vial was placed into an aluminum block in a cryostat at  $-20\text{ }^{\circ}\text{C}$  and stirred at this temperature for the indicated time. Purification by column chromatography on silica gel (*iso*-hexane  $\rightarrow$  *iso*-hexane/ethyl acetate 19:1) afforded the title compound as a colorless oil (51.6 mg, 0.20 mmol, 99% yield). The enantiomeric ratio was determined by HPLC on a chiral stationary phase. The regioisomeric ratio was determined by  $^1\text{H}$  NMR spectroscopy. The catalyst was recovered by elution with ethyl acetate. Fractions containing salts of the IDPi catalyst were concentrated under reduced pressure, dichloromethane (15 mL) and aq. HCl (6 M) were added and the biphasic mixture was vigorously stirred (1000 rpm) for 30 min at room temperature. The organic phase was separated and the aqueous phase was extracted with dichloromethane (2  $\times$  10 mL). The combined organic layers were washed with aq. HCl (6 M) and concentrated under reduced pressure. Repeated co-evaporation of remaining water and drying under reduced pressure ( $1.0 \times 10^{-3}$  mbar) afforded the protonated IDPi catalyst  $(S,S)\text{-4d}$  as a pale yellow solid. No erosion in regio- and enantioselectivity was observed over five runs with the same catalyst after recovery and acidification.

entry/cycle <sup>a</sup>	reaction time/d	recovered catalyst after acidification	yield/%	r.r. <sup>b</sup>	e.r. <sup>c</sup>
1	3.5	99% (13.8 mg, 5.9 $\mu\text{mol}$ , 3 mol%)	99	>50:1	96.5:3.5
2	3.5	89% (12.4 mg, 5.4 $\mu\text{mol}$ , 2.7 mol%)	99	>50:1	97:3
3	4.5	87% (12.1 mg, 5.2 $\mu\text{mol}$ , 2.6 mol%)	99	>50:1	97:3
4	5	84% (11.6 mg, 5.0 $\mu\text{mol}$ , 2.5 mol%)	99	>50:1	96.5:3.5
5	5.5	77% (10.7 mg, 4.6 $\mu\text{mol}$ , 2.3 mol%)	99	>50:1	97:3

<sup>a</sup>Reactions were performed on a 0.2 mmol scale with 50 mol% of silylating reagent **5d** and the indicated amount of catalyst  $(S,S)\text{-4d}$  for the indicated time and quenched with 1.1 equiv. of  $\text{NEt}_3$ . <sup>b</sup>Determined by  $^1\text{H}$  NMR analysis. <sup>c</sup>Determined by HPLC on a chiral stationary phase.

## Control experiment using (*E*)-cinnamic acid as dienophile

In order to prevent methylation of the IDPi catalyst, it was tested if carboxylic acids could potentially be used as dienophiles. We conducted a control experiment with an excess of the silylating reagent as protic functionalities are typically converted into their silylated analogs under the silylium Lewis acidic conditions.



(*S,S*)-IDPi catalyst **4n** (12.7 mg, 6  $\mu$ mol, 3 mol%) and (*E*)-cinnamic acid (29.6 mg, 0.20 mmol, 1.0 equiv.) were transferred to an oven-dried 2 mL screw-cap glass vial. A Teflon-coated magnetic stirring bar was added, the vial was closed with a screw-cap containing a PTFE/silicone septum, sealed with parafilm, evacuated and purged with argon (3  $\times$ ). Triisopropyl(2-methylallyl)silane (85 mg, 94  $\mu$ L, 0.40 mmol, 2.0 equiv.) was transferred to the vial and the mixture was stirred for 5 min at room temperature (colorless suspension  $\rightarrow$  pale yellow suspension). After the elapsed time, the vial was submerged into an ice/acetone bath (1:1 mixture) at  $-10$  °C and stirred for 10 min at this temperature. Then, isoprene (54.5 mg, 80  $\mu$ L, 0.80 mmol, 4 equiv.) was added, the vial was placed in an aluminum block inside a cryostat at 0 °C and the resulting pale orange solution was stirred at this temperature for 12 d.

Indeed, a quantitative conversion of cinnamic acid to its corresponding triisopropyl silyl ester was observed both optically by dissolving of cinnamic acid and via  $^1\text{H}$  NMR. However, no formation of the Diels–Alder products was detected. We hypothesize that unfavorable interaction of the silylated triisopropylester with the IDPi silylium Lewis acid prevents productive catalysis towards the Diels–Alder products.

triisopropylsilyl cinnamate

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J$  = 15.9 Hz, 1H), 7.58–7.51 (m, 2H), 7.43–7.34 (m, 3H), 6.45 (d,  $J$  = 15.8 Hz, 1H), 1.38 (hept,  $J$  = 7.4 Hz, 3H), 1.13 (d,  $J$  = 7.5 Hz, 18H). HRMS (ESI+) calculated for  $\text{C}_{18}\text{H}_{29}\text{O}_2\text{Si}^+$  [ $\text{M}+\text{H}^+$ ]: 305.1931; found: 305.1931.

## Diene scope

We explored the diene scope with two representative dienophiles **1a** and **1p** in combination with 2,3-dimethylbutadiene **2b**, *trans*-pentadiene **2c**, isoprene **2d** and cyclohexadiene **2e**. Isolated products were characterized below. Methyl cinnamate reacted very slowly with *trans*-pentadiene and cyclohexadiene (<20% conversion after 4d). We found that the reactivity of the dienes in IDPi catalyzed Diels–Alder reactions did not follow the determined order in all cases, while the expected order of reactivity was observed in non-enantioselective Diels–Alder reactions with  $\text{TMS-NTf}_2$  as the catalyst. Diels–Alder reactions of 1,3-butadiene proceeded with low conversions using  $\text{TMS-NTf}_2$ , thus asymmetric catalytic variants represent a subject of future work.

## General Procedures

### Catalytic, Asymmetric Diels-Alder Reactions

#### Procedure A: Catalyst activation with allylsilanes

A 4 mL vial with a septum lid was charged with a magnetic stirrer bar, the appropriate  $\alpha,\beta$ -unsaturated ester (0.2 mmol) and (*S,S*)-**4a** (2  $\mu\text{mol}$ , 3.6 mg, 1 mol%) under argon. The reagents were dissolved in dry toluene (0.2 mL) and triethylallylsilane **5a** (40  $\mu\text{mol}$ , 8  $\mu\text{L}$ , 20 mol%) was added. The reaction mixture was stirred at r.t. for 5 min, subsequently cooled to the appropriate temperature and cyclopentadiene was added (1 mmol, 84  $\mu\text{L}$ , 5 equiv.). Some parafilm was wrapped around the lid to seal the vial and the reaction was stirred at the appropriate temperature until TLC or NMR analysis indicated full consumption of the starting material. The reaction was then treated with a mixture of methanol/triethylamine (5:1, 50  $\mu\text{L}$ ) and diluted with hexanes, which caused precipitation of eventual cyclopentadiene polymers. The reaction mixture was filtered through cotton directly onto an equilibrated silica flash column and elution with the specified solvent mixture afforded the pure Diels-Alder products.

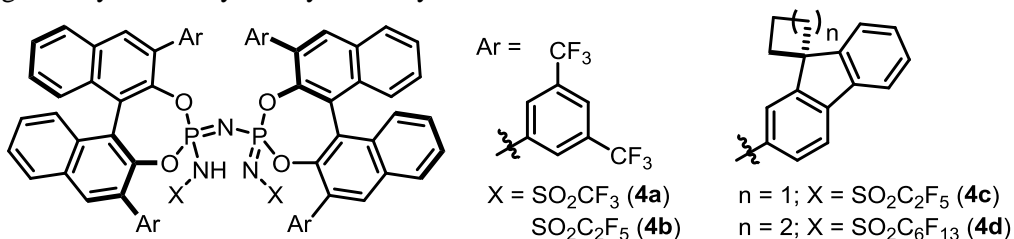
#### Procedure B: Catalyst activation with silyl ketene acetals

A 4 mL vial with a septum lid was charged with a magnetic stirrer bar, the appropriate  $\alpha,\beta$ -unsaturated ester (0.2 mmol) and (*S,S*)-**4c** (2  $\mu\text{mol}$ , 3.7 mg, 1 mol%) under argon. The reagents were dissolved in dry toluene (0.2 mL) and the reaction mixture was cooled to the appropriate temperature. Then, silyl ketene acetal **5b** (40  $\mu\text{mol}$ , 12  $\mu\text{L}$ , 20 mol%) and cyclopentadiene (1 mmol, 84  $\mu\text{L}$ , 5 equiv.) were added in this order. The following steps were identical to those described in procedure A.

#### Procedure C: Neat reaction conditions

A 4 mL vial with a septum lid was charged with a magnetic stirrer bar, the appropriate  $\alpha,\beta$ -unsaturated ester (0.2 mmol) and (*S,S*)-**4a-c** (2  $\mu\text{mol}$ , 1 mol%) under argon. The sealed vial was cooled to the appropriate temperature and cyclopentadiene (2 mmol, 180  $\mu\text{L}$ , 10 equiv.) was added. The reaction was stirred for 10 min to correctly adjust the temperature, before silylating agent **5a-d** (40  $\mu\text{mol}$ , 20 mol%) was added. The following steps were identical to those described in procedure A.

NOTE: We found that catalysts with highly fluorinated 3,3'-substituents, such as **4a** and **4b**, generally tend to be more active, however also cause a certain level of cyclopentadiene polymerization. These catalysts can be activated with both, silyl ketene acetals or allyl silanes with the exception of triisopropylallylsilane reacting very sluggishly with these IDPi acids. With catalysts possessing 3-fluorene-derived 3,3'-substituents, such as **4c**, cyclopentadiene polymerization is significantly suppressed or not detected at all depending on the reaction temperature. These IDPi derivatives are conveniently activated with silyl ketene acetals, while they generally react only slowly with allyl silanes.



**Procedure D:** Reactions with alternative dienes at 0 °C

An oven-dried 2.0 mL screw-cap glass vial was charged with (*S,S*)-**4d** (13.9 mg, 6 μmol, 3 mol%) and the appropriate α,β-unsaturated methyl ester (0.2 mmol). A Teflon-coated magnetic stirring bar was added, the vial was closed with a screw-cap containing a PTFE/silicone septum and sealed with parafilm. The reaction vial was evacuated, purged with argon (3 ×) and subsequently placed into an aluminum block submerged in an ice/acetone bath at -10 °C. The diene was transferred to the reaction vial and the colorless solution was kept at this temperature for 5 min. After the elapsed time, triisopropyl(2-methylallyl)silane (**5d**, 23 μL, 0.1 mmol, 50 mol%) was added to the reaction mixture to initiate the reaction. Then, the vial was placed into an aluminum block in a cryostat at 0 °C and stirred at this temperature for the indicated time. The reaction was monitored by TLC and <sup>1</sup>H NMR spectroscopy and quenched with triethylamine (5 μL, 0.2 equiv.).

**Procedure E:** Reactions with alternative dienes at -20 °C and -40 °C

An oven-dried 2.0 mL screw-cap glass vial was charged with (*S,S*)-**4d** (13.9 mg, 6 μmol, 3 mol%) and the appropriate α,β-unsaturated methyl ester (0.2 mmol). A Teflon-coated magnetic stirring bar was added, the vial was closed with a screw-cap containing a PTFE/silicone septum and sealed with parafilm. Then, the reaction vial was evacuated, purged with argon (3 ×) and subsequently placed into an aluminum block submerged in a dry-ice/isopropanol bath at -77 °C. The diene was transferred to the reaction vial and the colorless solution was kept at this temperature for 5 min. After the elapsed time, triisopropyl(2-methylallyl)silane (**5d**, 23 μL, 0.1 mmol, 50 mol%) was added to the reaction mixture to initiate the reaction. Then, the vial was placed into an aluminum block in a cryostat at the indicated temperature and stirred at this temperature for the indicated time.

## Preparation of racemic Diels-Alder Products

### Procedure A: with HNTf<sub>2</sub> as catalyst using Schlenk technique

In a flame-dried Schlenk flask, appropriate  $\alpha,\beta$ -unsaturated ester (8 mmol) and trimethylallylsilane (0.8 mmol, 0.13 mL, 10 mol%) were dissolved in dry DCM (8 mL) under argon. The reaction solution was cooled to -78 °C and a stock solution of HNTf<sub>2</sub> (0.2 M in DCM, 40  $\mu$ L, 8  $\mu$ mol, 0.1 mol%) was added. Then, cyclopentadiene (40 mmol, 3.4 mL, 5 equiv.) was added and the reaction mixture was warmed up to 0 °C. Upon completion of the reaction indicated by TLC (typically within a few hours), the reaction was quenched with triethylamine (0.5 mL) and diluted with hexanes. Precipitated cyclopentadiene polymers were removed by filtration through celite and subsequent column chromatography on silica gel gave the racemic Diels-Alder products.

NOTE: This procedure was used for sensitive substrates such as methyl acrylate and methyl crotonate, which are prone to decomposition or polymerization. Higher amounts of silylating reagent were necessary in some cases to prevent extensive cyclopentadiene polymerization.

### Procedure B: with HNTf<sub>2</sub> as catalyst in a vial

In a 4 mL vial with a septum lid with a magnetic stirrer bar, the appropriate  $\alpha,\beta$ -unsaturated ester (0.2 mmol) was dissolved in dry toluene (0.2 mL) under argon. Trimethylallylsilane (0.1 mmol, 15  $\mu$ L, 50 mol%) and a stock solution of HNTf<sub>2</sub> (0.2 M in DCM, 10  $\mu$ L, 2  $\mu$ mol, 1 mol%) was added in this order at r.t.. Then, cyclopentadiene (1 mmol, 84  $\mu$ L, 5 equiv.) was added and the reaction mixture was stirred at r.t. until TLC indicated complete reaction (typically within a few hours). Triethylamine (10  $\mu$ L) was added and the solvent was removed under reduced pressure. The residue oil was diluted with methanol and the precipitated cyclopentadiene polymers were filtered off through cotton. Concentration under reduced pressure gave the crude racemic Diels-Alder product, which were used for analytics without further purification.

### Procedure C: thermal Diels-Alder reaction

A microwave reaction vial was charged with the appropriate unsaturated ester (0.2 mmol) and cyclopentadiene (2.4 mmol, 0.2 mL). The vial was sealed and heated to 120 °C overnight. Racemic Diels-Alder products were obtained after purification of the crude material by preparative TLC.

NOTE: Under these conditions, the exo-cycloadduct is typically the major diastereomer.

## Characterization of Products

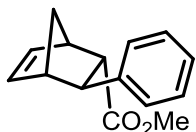
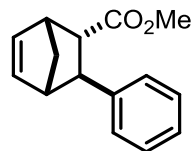
**methyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3a):** Prepared according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), (*E*)-methyl cinnamate (**1a**, 0.20 mmol, 32 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40$   $^{\circ}$ C for 12 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1 $\rightarrow$ 1:1) as a colorless oil (42 mg, 92%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $[\alpha]_{\text{D}}^{25} = +127.1$  (*c* 0.65, CHCl<sub>3</sub>); **HPLC** Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 90/10, 1 mL/min, 25  $^{\circ}$ C, 220 nm,  $t_{\text{R}}$  (major, *endo*) = 7.6 min,  $t_{\text{R}}$  (major, *exo*) = 8.8 min,  $t_{\text{R}}$  (minor, *exo*) = 9.5 min,  $t_{\text{R}}$  (minor, *endo*) = 11.9 min; e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 96.5:3.5, d.r. (*endo/exo*) = 26:1.

The performance of catalysts **4a-c** was compared at a reaction temperature of  $-40$   $^{\circ}$ C and a reaction time of 12 hours following the appropriate procedure A or B respectively:

entry	catalyst	silyl group	procedure	yield (%)	e.r. <sub>endo</sub>	e.r. <sub>exo</sub>	d.r. (endo/exo)
1	<b>4a</b>	TES	A	92	97:3	96.5:3.5	26:1
2	<b>4b</b>	TES	A	90	95.5:4.5	95:5	19:1
3	<b>4c</b>	TIPS	B	90	97.5:2.5	91.5:8.5	16:1

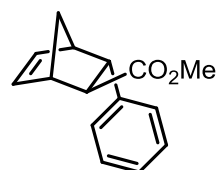
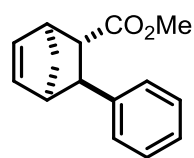
An enantioenriched mixture of *endo/exo* diastereomers (d.r. 9:1, e.r.<sub>endo</sub> = 95.5:4.5, e.r.<sub>exo</sub> = 95:5) was separated by preparative HPLC and the pure diastereomers were characterized as followed:

*endo*-diastereomer: **methyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3a<sub>endo</sub>):**



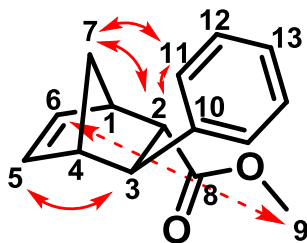
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 – 7.18 (m, 1H), 6.42 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.12 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.67 (s, 3H), 3.32 – 3.25 (m, 1H), 3.11 (dd, *J* = 5.0, 1.8 Hz, 1H), 3.07 – 3.03 (m, 1H), 3.01 (dd, *J* = 5.0, 3.6 Hz, 1H), 1.81 – 1.76 (dm, *J* = 8.7 Hz, 1H), 1.61 – 1.55 (dm, *J* = 8.7 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  175.0, 144.4, 139.2, 134.7, 128.6, 127.6, 126.2, 77.4, 77.2, 76.9, 52.2, 51.9, 48.5, 47.6, 47.3, 46.4;  $[\alpha]_{\text{D}}^{25} = +114.8$  (*c* 0.77, CHCl<sub>3</sub>) for e.r.<sub>endo</sub> = 95.5:4.5, d.r. (*endo/exo*) = >99:1; Lit.:<sup>10</sup>  $[\alpha]_{\text{D}}^{20} = +126.8$  (*c* 0.401, CHCl<sub>3</sub>) for e.r.<sub>endo</sub> = 98.5:1.5, d.r. (*endo/exo*) = 99:1; **HRMS** (ESI) calculated for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup>: 251.1042; found 251.1044.

*exo*-diastereomer: **methyl (1*S*,2*S*,3*S*,4*R*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3a<sub>exo</sub>):**



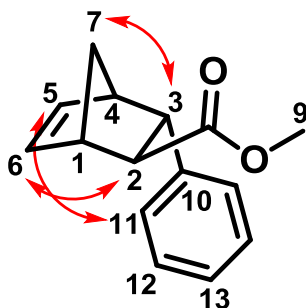
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.23 (m, 2H), 7.21 – 7.15 (m, 3H), 6.31 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.03 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.72 (s, 3H), 3.70 (dd, *J* = 5.3, 3.5 Hz, 1H), 3.20 – 3.13 (m, 2H), 2.52 (dd, *J* = 5.3, 1.8 Hz, 1H), 1.90 (dm, *J* = 8.6 Hz, 1H), 1.56 (dm, *J* = 8.6 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  176.2, 143.2, 136.7, 136.1, 128.2, 128.0, 127.9, 126.3, 77.4, 77.2, 76.9, 52.1, 50.6, 48.8, 48.4, 48.2, 48.1;  $[\alpha]_{\text{D}}^{25} = +247.5$  (*c* 0.54, CHCl<sub>3</sub>) for e.r.<sub>exo</sub> = 95:5, d.r. (*endo/exo*) = <1:99; **HRMS** (ESI) calculated for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup>: 251.1042; found 251.1043.

**Table S17.** Peak table for methyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**3a<sub>endo</sub>**). Red arrows and circles indicate the characteristic NOESY signals for the assignment of stereochemistry.



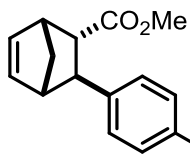
Atom	$\delta$	J	COSY	HSQC	HMBC	NOESY
<b>C1</b>	46,40			1	1, 2, 4, 5, 6, 7', 7''	
<b>H1</b>	3,289	m	6, 7', 7''	1	1, 4, 5	2, 6, 7', 7''
<b>C2</b>	52,15			2	2, 4, 7''	
<b>H2</b>	3,005	dd 3.6(H1), 5.0(H3)	3, 4	2	1, 2, 3, 6, 8, 10	1, 7', 9, 11
<b>C3</b>	47,65			3	2, 3, 7'', 11	
<b>H3</b>	3,113	dd 5.0(H2), 1.8(H7'' anti)	2, 7'', 11	3	3, 4, 5, 7, 8, 10, 11	5, 9, 11
<b>C4</b>	48,49			4	1, 3, 4, 5, 6, 7', 7''	
<b>H4</b>	3,042	m	2, 5, 7', 7''	4	1, 2, 4, 6	5, 7', 7'', 11
<b>C5</b>	139,24			5	1, 3, 5, 6, 7'	
<b>H5</b>	6,424	dd 3.1(H4), 5.6(H6)	4, 6	5	1, 4, 5, 6, 7	3, 4, H7''
<b>C6</b>	134,70			6	2, 4, 5, 6, 7'	
<b>H6</b>	6,122	dd 2.8(H1), 5.6(H5)	1, 5	6	1, 4, 5, 6, 7	1, 9, H7''
<b>C7</b>	47,32			7', 7''	3, 5, 6, 7', 7''	
<b>H7' syn</b>	1,786	dm 8.7(H7'' anti)	1, 4, 7''	7	1, 4, 5, 6, 7	1, 2, 4, 11
<b>H7'' anti</b>	1,579	dm 8.7(H7' syn)	1, 3, 4, 7'	7	1, 2, 3, 4, 7, 8	1, 4, 5, 6
<b>C8</b>	174,96				2, 3, 7'', 9	
<b>C9</b>	51,87			9	9	
<b>H9</b>	3,672	s		9	8, 9	2, 3, 6
<b>C10</b>	144,38				2, 3, 12	
<b>C11</b>	127,61			11	3, 11, 13	
<b>H11</b>	7,328	m	3	11	3, 11, 13	2, 3, 4, 7'
<b>C12</b>	128,60			12	12	
<b>H12</b>	7,308	m		12	10, 12	
<b>C13</b>	126,19			13	11	
<b>H13</b>	7,200	m		13	11	

**Table S18.** Peak table for methyl (1*S*,2*S*,3*S*,4*R*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**3a<sub>exo</sub>**). Red arrows and circles indicate the characteristic NOESY signals for the assignment of stereochemistry.



Atom	$\delta$	J	COSY	HSQC	HMBC	NOESY
<b>C1</b>	48,24			1	1, 2, 4, 5, 6, 7'	
<b>H1</b>	3,149	m	6, 7', 7''	1	1, 3, 4, 5	2, 6, 7', 7''
<b>C2</b>	50,57			2	2, 3, 4, 5, 7''	
<b>H2</b>	2,520	dd 5.3(3), 1.8(7''anti)	3, 7''	2	1, 2, 3, 6, 7, 8, 10	1, 6, 11
<b>C3</b>	48,85			3	1, 2, 3, 6, 7', 7'', 11	
<b>H3</b>	3,702	dd 3.5(4), 5.3(2)	2, 4, 11	3	2, 3, 4, 5, 8, 10, 11	4, 7, 11
<b>C4</b>	48,41			4	1, 3, 4, 5, 6, 7'	
<b>H4</b>	3,180	m	3, 5, 7', 7''	4	1, 2, 4, 6	3, 5, 7', 7'', 11
<b>C5</b>	136,06			5	1, 3, 5, 6, 7', 7''	
<b>H5</b>	6,026	dd 2.9(4), 5.6(6)	4, 6, 7'	5	1, 2, 4, 5, 6, 7	4, 7'', 11
<b>C6</b>	136,73			6	2, 4, 5, 6, 7', 7''	
<b>H6</b>	6,314	dd 3.2(1), 5.6(5)	1, 5, 7'	6	1, 3, 4, 5, 6, 7	1, 2, 7''
<b>C7</b>	48,11			7', 7''	2, 5, 6, 7', 7''	
<b>H7' syn</b>	1,897	dm 8.6(7''anti)	1, 4, 5, 6, 7''	7	1, 3, 4, 5, 6, 7	1, 3, 4
<b>H7'' anti</b>	1,557	dm 8.6(7'syn)	1, 2, 4, 7'	7	2, 3, 5, 6, 7, 10	1, 4, 5, 6
<b>C8</b>	176,21				2, 3, 9	
<b>C9</b>	52,05			9	9	
<b>H9</b>	3,716	s		9	8, 9	
<b>C10</b>	143,17				2, 3, 7'', 12	
<b>C11</b>	127,97			11	3, 11, 13	
<b>H11</b>	7,178	m	3	11	3, 11, 13	2, 3, 4, 5
<b>C12</b>	128,18			12	12	
<b>H12</b>	7,255	m		12	10, 12	
<b>C13</b>	126,29			13	11	
<b>H13</b>	7,176	m		13	11	

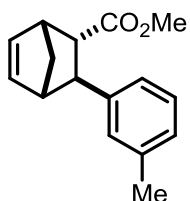
**methyl (1*R*,2*S*,3*S*,4*S*)-3-(*p*-tolyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3b):** Prepared



according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(*p*-tolyl)acrylate (**1b**, 0.20 mmol, 35.4 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40^\circ\text{C}$  for 48 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1 $\rightarrow$ 1:1) as a colorless oil (48 mg, 99%). The enantiomeric ratios

were determined by HPLC on a chiral stationary phase. The diastereomeric ratio was determined by  $^1\text{H NMR}$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 8.1$  Hz, 2H), 7.12 (d,  $J = 7.9$  Hz, 2H), 6.42 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.12 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.67 (s, 3H), 3.28 (dtq,  $J = 4.1, 2.2, 1.1$  Hz, 1H), 3.07 (dd,  $J = 5.1, 1.7$  Hz, 1H), 3.03 – 2.97 (m, 2H), 2.33 (s, 3H), 1.78 (dt,  $J = 8.6, 1.5$  Hz, 1H), 1.56 (dq,  $J = 8.7, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 141.3, 139.2, 135.7, 134.6, 129.3, 127.5, 52.1, 51.8, 48.7, 47.4, 47.3, 46.3, 21.1; **HRMS** (EI) calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_2$ : 242.1301; found 242.1301;  $[\alpha]_{\text{D}}^{25} = +118.5$  ( $c$  0.53,  $\text{CHCl}_3$ ); **HPLC** (Heartcut) 1. 50 mm Zorbax Eclipse PAH, 4.6 mm, methanol/water – gradient 50 % B - 5' - 80 % B - 5' - 80% - 1' - 100% B, 1.0 mL/min, 38.5 MPa, 308 K, 220 nm; 2. 150mm Chiralcel OJ-3R, 4.6 mm, methanol, 1.0 mL/min, 298 K, 17.7 MPa, 220 nm;  $t_{\text{R}}$  (major, *exo*) = 5.3 min,  $t_{\text{R}}$  (major, *endo*) = 5.5 min,  $t_{\text{R}}$  (minor, *exo*) = 7.0 min,  $t_{\text{R}}$  (minor, *endo*) = 9.5 min; e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 96:4, d.r. (*endo/exo*) = 20:1.

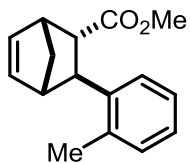
**methyl (1*R*,2*S*,3*S*,4*S*)-3-(*m*-tolyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3c):** Prepared



according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(*m*-tolyl)acrylate (**1c**, 0.20 mmol, 35.9 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40^\circ\text{C}$  for 48 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (44 mg, 89%). The enantiomeric and diastereomeric ratios were

determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (t,  $J = 7.5$  Hz, 1H), 7.16 – 7.10 (m, 2H), 7.02 (d,  $J = 7.4$  Hz, 1H), 6.42 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.12 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.67 (s, 3H), 3.32 – 3.25 (m, 1H), 3.08 (dd,  $J = 5.1, 1.8$  Hz, 1H), 3.05 – 2.98 (m, 2H), 2.35 (s, 3H), 1.79 (dt,  $J = 8.8, 1.5$  Hz, 1H), 1.57 (dq,  $J = 8.7, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 144.3, 139.3, 138.1, 134.6, 128.5, 128.5, 126.9, 124.5, 52.0, 51.8, 48.6, 47.6, 47.4, 46.4, 21.7; **HRMS** (EI) calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_2$ : 242.1301; found 242.1302;  $[\alpha]_{\text{D}}^{25} = +128.1$  ( $c$  0.51,  $\text{CHCl}_3$ ); **HPLC** Daicel Chiralcel OJ-3R, MeOH/ $\text{H}_2\text{O}$  = 90/10, 1 mL/min,  $25^\circ\text{C}$ , 220 nm,  $t_{\text{R}}$  (major, *endo*) = 7.7 min,  $t_{\text{R}}$  (minor, *exo*) = 9.5 min,  $t_{\text{R}}$  (major, *exo*) = 10.6 min,  $t_{\text{R}}$  (minor, *endo*) = 11.8 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 98:2, d.r. (*endo/exo*) = 17:1.

**methyl (1*R*,2*S*,3*S*,4*S*)-3-(*o*-tolyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3d):** Prepared



according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(*o*-tolyl)acrylate (**1d**, 0.20 mmol, 36.0 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40^\circ\text{C}$  for 48 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1 $\rightarrow$ 1:1) as a colorless oil (43 mg, 87%). The enantiomeric and

diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.27 (m, 1H), 7.21 – 7.16 (m, 2H), 7.18 – 7.09 (m, 2H), 6.47 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.10 (dd,  $J = 5.6, 2.8$  Hz, 1H), 3.64 (s, 3H), 3.30 (dddt,  $J = 4.0, 3.2, 2.3, 1.1$  Hz, 1H), 3.20 (dd,  $J = 5.2, 1.7$  Hz, 1H), 3.12 (dd,  $J = 5.1, 3.6$  Hz, 1H), 2.84 (dq,  $J = 3.2, 1.6$  Hz, 1H), 2.32 (s, 3H), 1.85 (dt,  $J = 8.7, 1.5$  Hz, 1H), 1.55 (dd,  $J = 8.8, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.1, 142.0, 139.1, 137.2, 134.2, 130.7, 126.2, 126.1, 125.5, 51.8, 49.6, 49.5, 47.2, 46.8, 44.6, 20.4; **HRMS** (EI) calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_2$ : 242.1301; found 242.1302;  $[\alpha]_{\text{D}}^{25} = +150.3$  ( $c$  0.64,  $\text{CHCl}_3$ ); **HPLC** (Heartcut) 1. 50 mm Eclipse Plus C18, 3.0 mm, methanol/water – gradient 50% B - 5' - 70 % B - 5' - 70 % B - 1' - 100% B, 0.5 mL/min, 34.8 MPa, 308 K, 220 nm; 2. 150 mm Chiralcel OJ3R, 4.6 mm, methanol/water = 90:10, 1.0 mL/min, 25.6 MPa, 308 K, 220 nm;  $t_{\text{R}}$  (minor, *exo*) =

4.2 min,  $t_R$  (major, *exo*) = 4.9 min,  $t_R$  (minor, *endo*) = 5.7 min,  $t_R$  (major, *endo*) = 6.1 min; e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = >50:1.

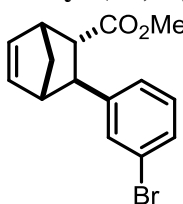
**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3e)**: Prepared according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(4-bromophenyl)acrylate (**1e**, 0.20 mmol, 48.5 mg) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-40$  °C for 24 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1→2:1→1:1) as a colorless oil (60 mg, 97%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. **HPLC** Daicel Chiralcel OJ-3R, MeCN/H<sub>2</sub>O = 60/40, 1 mL/min, 25 °C, 220 nm,  $t_R$  (major, *exo*) = 8.9 min,  $t_R$  (major, *endo*) = 9.7 min,  $t_R$  (minor, *exo*) = 10.5 min,  $t_R$  (minor, *endo*) = 12.3 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 97.5:2.5, d.r. (*endo/exo*) = 16:1;  $[\alpha]_D^{25}$  = +102.2 (*c* 0.64, CHCl<sub>3</sub>).

An enantioenriched mixture of *endo/exo* diastereomers (d.r. 17:1, e.r.<sub>endo</sub> = 95.5:4.5, e.r.<sub>exo</sub> = 91:9) was separated by preparative HPLC on a chiral stationary phase to give optically pure diastereomers, which were characterized as followed:

*endo*-diastereomer: **methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3e<sub>endo</sub>)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.39 (m, 2H), 7.22 – 7.17 (m, 2H), 6.40 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.12 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.67 (s, 3H), 3.33 – 3.26 (m, 1H), 3.05 (dd, *J* = 5.0, 1.8 Hz, 1H), 3.03 – 2.96 (m, 1H), 2.92 (dd, *J* = 5.0, 3.6 Hz, 1H), 1.72 (d, *J* = 8.8 Hz, 1H), 1.58 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  174.7, 143.5, 139.1, 134.9, 131.6, 129.4, 120.0, 52.4, 52.0, 48.2, 47.3, 47.2, 46.3;  $[\alpha]_D^{25}$  = +101.1 (*c* 0.73, CHCl<sub>3</sub>); **HRMS** (ESI) calculated for C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>BrNa (M+Na)<sup>+</sup>: 329.0148; found 329.0151.

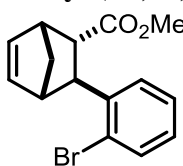
*exo*-diastereomer: **methyl (1*S*,2*S*,3*S*,4*R*)-3-(4-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3e<sub>exo</sub>)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.33 (m, 1H), 7.07 – 7.01 (m, 1H), 6.31 (dd, *J* = 5.7, 3.1 Hz, 1H), 5.99 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.71 (s, 2H), 3.64 (dd, *J* = 5.3, 3.4 Hz, 1H), 3.16 – 3.14 (m, 1H), 3.14 – 3.11 (m, 0H), 2.44 (dd, *J* = 5.3, 1.7 Hz, 1H), 1.86 (dtt, *J* = 8.7, 1.6, 0.7 Hz, 1H), 1.56 (dq, *J* = 8.7, 1.7 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  175.9, 142.2, 137.0, 135.8, 131.2, 129.7, 120.1, 52.1, 50.7, 48.4, 48.2, 48.2;  $[\alpha]_D^{25}$  = +260.2 (*c* 0.625, CHCl<sub>3</sub>); **HRMS** (ESI) calculated for C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>BrNa (M+Na)<sup>+</sup>: 329.0148; found 329.0151.

**methyl (1*R*,2*S*,3*S*,4*S*)-3-(3-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3f):** Prepared



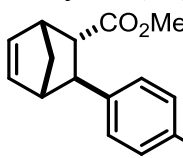
according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(3-bromophenyl)acrylate (**1f**, 0.20 mmol, 48.4 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40$   $^{\circ}$ C for 48 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (57 mg, 92%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 2.0$  Hz, 1H), 7.33 (dt,  $J = 8.0, 1.4$  Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 (t,  $J = 7.8$  Hz, 1H), 6.40 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.12 (dd,  $J = 5.6, 2.8$  Hz, 1H), 3.68 (s, 3H), 3.33 – 3.26 (m, 1H), 3.07 (dd,  $J = 5.1, 1.8$  Hz, 1H), 3.02 (dq,  $J = 3.2, 1.5$  Hz, 1H), 2.95 (dd,  $J = 5.0, 3.6$  Hz, 1H), 1.74 (dt,  $J = 8.8, 1.5$  Hz, 1H), 1.59 (dq,  $J = 8.8, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.6, 146.9, 139.0, 134.9, 130.6, 130.1, 129.3, 126.4, 122.8, 52.3, 52.0, 48.2, 47.3, 47.3, 46.4; **HRMS** (EI) calculated for  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{Br}$ : 306.0250; found 306.0245;  $[\alpha]_{\text{D}}^{25} = +104.1$  ( $c$  0.58,  $\text{CHCl}_3$ ); **HPLC** Daicel Chiralpak AD-3R, MeOH/ $\text{H}_2\text{O} = 80/20$ , 1 mL/min, 25  $^{\circ}$ C, 220 nm,  $t_{\text{R}}$  (minor, *exo*) = 14.6 min,  $t_{\text{R}}$  (minor, *endo*) = 15.8 min,  $t_{\text{R}}$  (major, *endo*) = 18.3 min,  $t_{\text{R}}$  (major, *exo*) = 20.6 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 97.5:2.5, d.r. (*endo/exo*) = 15:1.

**methyl (1*R*,2*S*,3*S*,4*S*)-3-(2-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3g):** Prepared



according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(2-bromophenyl)acrylate (**1g**, 0.20 mmol, 48.2 mg) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-40$   $^{\circ}$ C for 24 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1 $\rightarrow$ 1:1) as a colorless oil (43 mg, 70%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.32 (dd,  $J = 7.9, 1.7$  Hz, 1H), 7.28 (td,  $J = 7.7, 1.2$  Hz, 1H), 7.08 (td,  $J = 7.7, 1.8$  Hz, 1H), 6.49 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.14 (dd,  $J = 5.6, 2.8$  Hz, 1H), 3.64 (s, 3H), 3.38 (dd,  $J = 5.2, 1.7$  Hz, 1H), 3.31 (dddt,  $J = 4.1, 3.3, 2.4, 1.1$  Hz, 1H), 3.14 (dd,  $J = 5.2, 3.6$  Hz, 1H), 2.93 – 2.88 (m, 1H), 1.71 (dddd,  $J = 8.8, 2.2, 1.4, 0.6$  Hz, 1H), 1.52 (dq,  $J = 8.8, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.6, 142.6, 138.8, 134.6, 133.5, 127.8, 127.5, 127.4, 126.4, 51.9, 50.0, 49.1, 48.3, 46.7, 46.6; **HRMS** (ESI) calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Br}$  ( $\text{M}+\text{H}^+$ ): 307.0328; found 307.0329;  $[\alpha]_{\text{D}}^{25} = +95.6$  ( $c$  0.55,  $\text{CHCl}_3$ ); **HPLC** (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 3.0 mm, methanol/water – gradient 60% - 5' - 90% B, 0.5 mL/min, 38.5 MPa, 308 K; 2. 150 mm 3-CelluCoat RP, 4.6 mm, methanol/water – gradient 70% - 5' - 90% B, 1.0 mL/min, 35.3 MPa, 298 K;  $t_{\text{R}}$  (major, *endo*) = 10.4 min,  $t_{\text{R}}$  (minor, *endo*) = 10.7 min,  $t_{\text{R}}$  (*exo*) = 39.6 min,  $t_{\text{R}}$  (*exo*) = 39.8 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = 47:1.

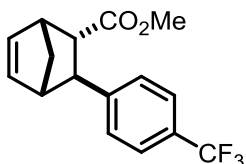
**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-fluorophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3h):** Prepared



according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(4-fluorophenyl)acrylate (**1h**, 0.20 mmol, 36.5 mg) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-40$   $^{\circ}$ C for 24 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (49 mg, 98%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.23 (m, 2H), 7.04 – 6.95 (m, 2H), 6.41 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.12 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.67 (s, 3H), 3.32 – 3.26 (m, 1H), 3.07 (d,  $J = 4.7$  Hz, 1H), 3.00 (dq,  $J = 3.3, 1.7$  Hz, 1H), 2.93 (dd,  $J = 5.1, 3.5$  Hz, 1H), 1.74 (dt,  $J = 8.7, 1.5$  Hz, 1H), 1.59 (dq,  $J = 8.7, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 162.4, 160.4, 140.1, 140.0, 139.1, 134.8, 129.0, 128.9, 115.4, 115.2, 52.5, 51.9, 48.4, 47.2, 47.0, 46.3; **HRMS** (ESI) calculated for  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{FNa}$  ( $\text{M}+\text{Na}^+$ ): 269.0948; found 269.0948;  $[\alpha]_{\text{D}}^{25} = +103.3$  ( $c$  0.79,  $\text{CHCl}_3$ ); **HPLC** Daicel Chiralcel OJ-3R, MeOH/ $\text{H}_2\text{O} = 90/10$ , 1 mL/min, 25  $^{\circ}$ C, 220 nm,  $t_{\text{R}}$  (major, *endo*) = 6.1 min,  $t_{\text{R}}$  (major, *exo*) =

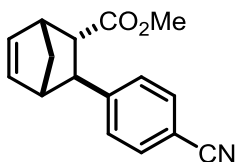
6.9 min,  $t_R$  (minor, *exo*) = 7.3 min,  $t_R$  (minor, *endo*) = 8.9 min; e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 95.5:4.5, d.r. (*endo/exo*) = 18:1.

**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3i):**



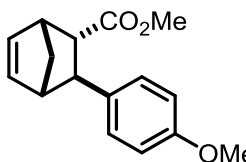
Prepared according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu$ mol, 3.6 mg, 1 mol%), methyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (**1i**, 0.20 mmol, 45.9 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40$   $^{\circ}$ C for 48 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1 $\rightarrow$ 1:1) as a colorless oil (58 mg, 98%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 8.1 Hz, 2H), 7.44 (d,  $J$  = 8.1 Hz, 2H), 6.43 (dd,  $J$  = 5.7, 3.2 Hz, 1H), 6.14 (dd,  $J$  = 5.6, 2.8 Hz, 1H), 3.68 (s, 3H), 3.32 (s, 1H), 3.16 (d,  $J$  = 4.8 Hz, 1H), 3.06 (dt,  $J$  = 3.3, 1.7 Hz, 1H), 2.96 (dd,  $J$  = 5.1, 3.6 Hz, 1H), 1.74 (dt,  $J$  = 8.8, 1.5 Hz, 1H), 1.62 (dq,  $J$  = 8.8, 1.8 Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 148.6, 139.0, 135.0, 127.9, 125.5 (q,  $J$  = 3.7 Hz), 52.4, 52.0, 48.1, 47.6, 47.3, 46.4;  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4; **HRMS** (ESI) calculated for  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_3\text{Na}$  ( $\text{M}+\text{Na}$ ) $^+$ : 319.0916; found 319.0919;  $[\alpha]_D^{25}$  = +93.1 ( $c$  0.64,  $\text{CHCl}_3$ ); **HPLC** Daicel Chiralcel OJ-3R, MeOH/ $\text{H}_2\text{O}$  = 75/25, 1 mL/min, 25  $^{\circ}$ C, 220 nm,  $t_R$  (major, *exo*) = 20.7 min,  $t_R$  (major, *endo*) = 21.9 min,  $t_R$  (minor, *exo*) = 24.0 min,  $t_R$  (minor, *endo*) = 29.6 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 98.5:1.5, d.r. (*endo/exo*) = 12:1.

**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-cyanophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3j):**



Prepared according to procedure A with catalyst (*S,S*)-**4b** (6  $\mu$ mol, 11.3 mg, 3 mol%), methyl (*E*)-3-(4-cyanophenyl)acrylate (**1j**, 0.20 mmol, 37.8 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at  $-40$   $^{\circ}$ C for 3 days. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 2:1 $\rightarrow$ 1:1 $\rightarrow$ 1:2 $\rightarrow$ 1:4) as a colorless wax (48 mg, 94%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.57 (m, 2H), 7.46 – 7.41 (m, 2H), 6.41 (dd,  $J$  = 5.7, 3.2 Hz, 1H), 6.14 (dd,  $J$  = 5.7, 2.8 Hz, 1H), 3.68 (s, 3H), 3.32 (dddd,  $J$  = 4.6, 2.7, 2.0, 1.1 Hz, 1H), 3.15 (dd,  $J$  = 5.2, 1.9 Hz, 1H), 3.06 (dq,  $J$  = 3.1, 1.5 Hz, 1H), 2.92 (dd,  $J$  = 5.1, 3.6 Hz, 1H), 1.70 (dddd,  $J$  = 8.8, 2.2, 1.4, 0.6 Hz, 1H), 1.62 (dq,  $J$  = 8.9, 1.8 Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 150.2, 138.9, 135.1, 132.4, 128.4, 119.1, 110.1, 52.5, 52.1, 47.9, 47.8, 47.3, 46.4; **HRMS** (ESI) calculated for  $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}$  ( $\text{M}+\text{Na}$ ) $^+$ : 276.0995; found 276.0997;  $[\alpha]_D^{25}$  = +125.8 ( $c$  0.48,  $\text{CHCl}_3$ ); **HPLC** (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 3.0 mm, methanol/water – gradient 40% - 5' - 60% B, 0.5 mL/min, 308 K, 32.7 MPa; 2. 150 mm AmyCoat RP, 4.6 mm, methanol/water = 90:10, 1.0 mL/min, 298 K, 21.0 MPa, 220 nm;  $t_R$  (major, *exo*) = 12.5 min,  $t_R$  (minor, *exo*) = 13.5 min,  $t_R$  (minor, *endo*) = 36.2 min,  $t_R$  (major, *endo*) = 24.8 min; e.r.<sub>endo</sub> = 95:5, e.r.<sub>exo</sub> = 64.5:35.5, d.r. (*endo/exo*) = 13:1.

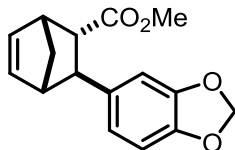
**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3k):**



Prepared according to procedure A with catalyst (*S,S*)-**4a** (6  $\mu$ mol, 10.8 mg, 3 mol%), methyl (*E*)-3-(4-methoxyphenyl)acrylate (**1k**, 0.20 mmol, 38.3 mg), triethylallylsilane (0.1 mmol, 20  $\mu$ L, 50 mol%) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-20$   $^{\circ}$ C for 2 days. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 2:1 $\rightarrow$ 1:1) as a colorless oil (50 mg, 97%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.21 (m, 2H), 6.88 – 6.83 (m, 2H), 6.41 (dd,  $J$  = 5.7, 3.2 Hz, 1H), 6.11 (dd,  $J$  = 5.7, 2.8 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 3.27 (ddd,  $J$  = 4.0, 3.1, 2.2, 1.1 Hz, 1H), 3.04 (dd,  $J$  = 5.1, 1.8 Hz, 1H), 2.98 (dq,  $J$  = 3.3, 1.7 Hz, 1H), 2.95 (dd,  $J$  = 5.0, 3.6 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.56 (dq,  $J$  = 8.7, 1.8 Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 158.0, 139.2, 136.4, 134.6, 128.5, 114.0, 55.4, 52.3, 51.8, 48.7, 47.3, 47.0, 46.3; **HRMS** (ESI) calculated for  $\text{C}_{16}\text{H}_{19}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 259.1329; found

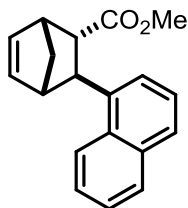
259.1333;  $[\alpha]_D^{25} = +112.6$  (*c* 0.57,  $\text{CHCl}_3$ ); **HPLC** Daicel Chiralcel OJ-3R,  $\text{MeCN}/\text{H}_2\text{O} = 70/30$ , 1 mL/min, 25 °C, 220 nm,  $t_R$  (major, *exo*) = 4.4 min,  $t_R$  (major, *endo*) = 4.9 min,  $t_R$  (minor, *exo*) = 5.4 min,  $t_R$  (major, *endo*) = 6.6 min; e.r.<sub>endo</sub> = 95:5, e.r.<sub>exo</sub> = n.d., d.r. (*endo/exo*) = 12:1.

**methyl (1R,2S,3S,4S)-3-(benzo[d][1,3]dioxol-5-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3l):**



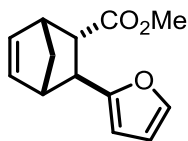
Prepared according to procedure A with catalyst (*S,S*)-**4a** (6  $\mu\text{mol}$ , 10.8 mg, 3 mol%), methyl (*E*)-3-(benzo[d][1,3]dioxol-5-yl)acrylate (**1l**, 0.20 mmol, 41.6 mg), triethylallylsilane (0.1 mmol, 20  $\mu\text{L}$ , 50 mol%) and cyclopentadiene (2 mmol, 180  $\mu\text{L}$ ) at -20 °C for 2 days. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 2:1→1:1) as a colorless oil (51 mg, 94%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.84 (d, *J* = 1.6 Hz, 1H), 6.77 (ddd, *J* = 8.1, 1.7, 0.7 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.39 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.10 (dd, *J* = 5.7, 2.8 Hz, 1H), 5.92 (s, 2H), 3.67 (s, 3H), 3.26 (dddt, *J* = 4.2, 3.2, 2.4, 1.2 Hz, 1H), 3.02 (dd, *J* = 5.0, 1.8 Hz, 1H), 2.97 (dq, *J* = 3.2, 1.6 Hz, 1H), 2.91 (dd, *J* = 5.0, 3.5 Hz, 1H), 1.75 (ddd, *J* = 9.5, 1.9, 1.2 Hz, 1H), 1.60 – 1.55 (m, 1H); **<sup>13</sup>C NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.9, 147.8, 145.9, 139.2, 138.4, 134.7, 120.2, 108.3, 101.0, 52.6, 51.9, 48.6, 47.5, 47.3, 46.3; **HRMS** (ESI) calculated for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Na}$  ( $\text{M}+\text{Na}$ )<sup>+</sup>: 295.0941; found 295.0940;  $[\alpha]_D^{25} = +102.3$  (*c* 0.58,  $\text{CHCl}_3$ ); **HPLC** Kromasil AmyCoat RP,  $\text{MeOH}/\text{H}_2\text{O} = 85/15$ , 1 mL/min, 25 °C, 254 nm,  $t_R$  (minor, *exo*) = 11.6 min,  $t_R$  (minor, *endo*) = 13.2 min,  $t_R$  (major, *endo*) = 18.8 min,  $t_R$  (minor, *exo*) = 22.2 min; e.r.<sub>endo</sub> = 96:4, e.r.<sub>exo</sub> = 91:9, d.r. (*endo/exo*) = 15:1.

**methyl (1R,2S,3S,4S)-3-(naphthalen-1-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3m):**



Prepared according to procedure A with catalyst (*S,S*)-**4a** (2  $\mu\text{mol}$ , 3.6 mg, 1 mol%), methyl (*E*)-3-(naphthalen-1-yl)acrylate (**1m**, 0.20 mmol, 42.4 mg) and cyclopentadiene (1 mmol, 90  $\mu\text{L}$ ) at -40 °C for 48 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1→2:1) as a colorless oil (55 mg, 99%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.51 (dddd, *J* = 17.8, 8.0, 6.8, 1.4 Hz, 2H), 7.47 – 7.42 (m, 2H), 6.60 (dd, *J* = 5.7, 3.1 Hz, 1H), 6.19 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.80 (dd, *J* = 5.1, 1.1 Hz, 1H), 3.66 (s, 3H), 3.34 (dtd, *J* = 3.6, 1.8, 0.9 Hz, 1H), 3.21 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.08 (dt, *J* = 3.3, 1.7 Hz, 1H), 1.88 (d, *J* = 8.7 Hz, 1H), 1.63 (dq, *J* = 8.7, 1.8 Hz, 1H); **<sup>13</sup>C NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2, 139.9, 138.9, 134.6, 134.1, 132.7, 128.9, 127.1, 126.1, 125.7, 125.4, 124.2, 122.8, 51.9, 49.8, 49.8, 47.8, 47.0, 43.9; **HRMS** (ESI) calculated for  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{Na}$  ( $\text{M}+\text{Na}$ )<sup>+</sup>: 301.1199; found 301.1200;  $[\alpha]_D^{25} = +89.8$  (*c* 0.53,  $\text{CHCl}_3$ ); **HPLC** (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu\text{m}$ , 3.0 mm, methanol/water – gradient 60% - 5' - 90% B, 0.5 mL/min, 37.0 MPa, 308 K; 2. 150 mm 3-AmyCoat RP, 4.6 mm, acetonitrile/water = 50:50, 1.0 ml/min, 18.6 MPa, 298 K, 220 nm;  $t_R$  (*exo*) = 15.0 min,  $t_R$  (*exo*) = 16.1 min,  $t_R$  (major, *endo*) = 36.2 min,  $t_R$  (minor, *endo*) = 37.5 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = >50:1.

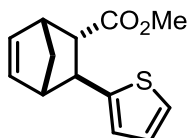
**methyl (1R,2S,3S,4S)-3-(furan-2-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3n):**



Prepared according to procedure A with catalyst (*S,S*)-**4b** (6  $\mu\text{mol}$ , 11.3 mg, 3 mol%), methyl (*E*)-3-(furan-2-yl)acrylate (**1n**, 0.20 mmol, 30.4 mg) and cyclopentadiene (2 mmol, 180  $\mu\text{L}$ ) at -40 °C for 14 hours. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1→2:1→1:1) as an orange oil (39 mg, 89%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.30 (m, 1H), 6.34 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.29 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.10 – 6.05 (m, 2H), 3.65 (s, 3H), 3.29 – 3.26 (m, 1H), 3.11 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.06 (dd, *J* = 5.0, 1.8 Hz, 1H), 3.01 – 2.98 (m, 1H), 1.74 (dt, *J* = 8.6, 1.6 Hz, 1H), 1.51 (dq, *J* = 8.7, 1.8 Hz, 1H); **<sup>13</sup>C NMR**

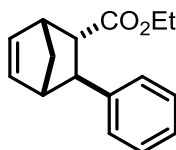
**NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 157.7, 141.3, 138.3, 134.4, 110.3, 105.0, 51.9, 49.8, 48.6, 47.7, 46.0, 41.9; **HRMS** (EI) calculated for C<sub>13</sub>H<sub>14</sub>O<sub>3</sub> (M): 218.0937; found 218.0937;  $[\alpha]_D^{25} = +120.0$  (*c* 0.42, CHCl<sub>3</sub>); **HPLC** (Heartcut) 1. 50 mm YMC Triart C18 ExRS, 3.0 mm, methanol/water – gradient 50 % B - 5` - 70 % B - 5` - 70% - 1` - 100% B, 0.5 mL/min, 58.7 MPa, 308 K, 220 nm; 2. 150mm Chiralcel OJ-3R, 4.6 mm, methanol/water = 90:10, 1.0 mL/min, 298 K, 26.5 MPa, 220 nm;  $t_R$  (major, *exo*) = 4.7 min,  $t_R$  (minor, *exo*) = 5.0 min,  $t_R$  (major, *endo*) = 5.0 min,  $t_R$  (minor, *endo*) = 6.6 min; e.r.<sub>endo</sub> = 94:6, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = >50:1.

**methyl (1R,2S,3S,4S)-3-(thiophen-2-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3o):** Prepared



according to procedure A with catalyst (*S,S*)-**4b** (6  $\mu$ mol, 11.3 mg, 3 mol%), methyl (*E*)-3-(thiophen-2-yl)acrylate (**1o**, 0.20 mmol, 34.3 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at -40 °C for 3 days. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 2:1→1:1→1:2) as a colorless oil (43 mg, 90%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.90 (dt, *J* = 3.5, 1.1 Hz, 1H), 6.38 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.11 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.67 (s, 3H), 3.33 – 3.25 (m, 2H), 3.07 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.01 (ddq, *J* = 3.2, 1.6, 0.8 Hz, 1H), 1.83 (dtt, *J* = 9.0, 1.5, 0.7 Hz, 1H), 1.60 (dq, *J* = 8.9, 1.8 Hz, 1H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 148.7, 138.5, 134.5, 126.9, 123.8, 123.3, 53.6, 51.9, 50.7, 47.6, 46.1, 43.9; **HRMS** (ESI) calculated for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>SNa (M+Na)<sup>+</sup>: 257.0607; found 257.0606;  $[\alpha]_D^{25} = +117.7$  (*c* 0.53, CHCl<sub>3</sub>); **HPLC** Daicel Chiralcel OJ-3R, MeCN/H<sub>2</sub>O = 40/60, 1 mL/min, 25 °C, 220 nm,  $t_R$  (minor, *exo*) = 35.6 min,  $t_R$  (major, *endo*) = 38.2 min,  $t_R$  (minor, *endo*) = 42.9 min,  $t_R$  (minor, *exo*) = 45.1 min; e.r.<sub>endo</sub> = 94:6, e.r.<sub>exo</sub> = 90:10, d.r. (*endo/exo*) = >50:1.

**ethyl (1R,2S,3S,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate:** Prepared according to

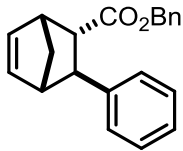


procedure B with catalyst (*S,S*)-**4d** (2  $\mu$ mol, 3.7 mg, 1 mol%), silyl ketene acetal **5b** (0.04 mmol, 12  $\mu$ L, 20 mol%), ethyl (*E*)-cinnamate (0.20 mmol, 35.7 mg) and cyclopentadiene (1 mmol, 90  $\mu$ L) at -40 °C for 7 days. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1→2:1) as a colorless oil (49 mg, 99%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.28 (m, 4H), 7.23 – 7.18 (m, 1H), 6.43 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.12 (dd, *J* = 5.7, 2.8 Hz, 1H), 4.13 (p, *J* = 7.1 Hz, 2H), 3.29 (tdq, *J* = 3.1, 2.2, 1.1 Hz, 1H), 3.12 (dd, *J* = 5.2, 1.8 Hz, 1H), 3.05 (dt, *J* = 3.3, 1.7 Hz, 1H), 2.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 1.79 (dt, *J* = 8.6, 1.5 Hz, 1H), 1.60 – 1.56 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  174.4, 144.5, 139.2, 134.6, 128.6, 127.6, 126.1, 60.5, 52.4, 48.4, 47.5, 47.3, 46.4, 14.5; **HRMS** (ESI) calculated for C<sub>16</sub>H<sub>19</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 243.1380; found 243.1384;  $[\alpha]_D^{25} = +89.0$  (*c* 0.54, CHCl<sub>3</sub>); **HPLC** Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 90/10, 1 mL/min, 25 °C, 220 nm,  $t_R$  (major, *endo*) = 8.7 min,  $t_R$  (minor, *exo*) = 10.2 min,  $t_R$  (major, *exo*) = 10.8 min,  $t_R$  (minor, *endo*) = 12.0 min; e.r.<sub>endo</sub> = 88:12, e.r.<sub>exo</sub> = 82:18, d.r. (*endo/exo*) = 14:1.

The performance of catalysts **4a** and **4c** was compared at a reaction temperature of -40 °C and a reaction time of 7 days following the appropriate procedure A or B respectively:

entry	catalyst	procedure	yield (%)	d.r. (endo:exo)	e.r. (endo)	e.r. (exo)
1	<b>4a</b>	A	99	15:1	73.5:26.5	75:25
2	<b>4c</b>	B	99	14:1	88:12	82:18

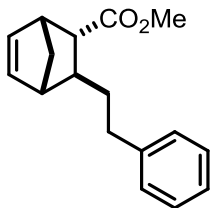
**benzyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate**: Prepared according to procedure B with catalyst (*S,S*)-**4d** (2 μmol, 3.7 mg, 1 mol%), silyl ketene acetal **5b** (0.04 mmol, 12 μL, 20 mol%), benzyl (*E*)-cinnamate (0.20 mmol, 47.7 mg) and cyclopentadiene (1 mmol, 90 μL) at -40 °C for 3 weeks. The conversion was determined by <sup>1</sup>H-NMR to be approx. 10% and isolation of the product for stereochemical analysis was performed by preparative TLC. The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.42–7.13 (m, 10H), 6.42 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.06 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.11 (q, *J* = 12.4, 6.9 Hz, 2H), 3.32 (s, 1H), 3.15 (dd, *J* = 7.3, 2.0 Hz, 2H), 3.05 (dd, *J* = 4.9, 3.6 Hz, 2H), 1.89 (d, *J* = 8.6 Hz, 1H), 1.80 (d, *J* = 8.7 Hz, 2H), 1.61–1.55 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.2, 144.4, 139.3, 136.8, 134.6, 128.7, 128.6, 128.2, 128.0, 127.6, 126.2, 66.6, 52.4, 48.5, 47.7, 47.4, 46.6; HRMS (ESI) calculated for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup>: 327.1354; found 327.1355; HPLC Daicel Chiralcel OJ-3R, MeOH/MeCN/H<sub>2</sub>O = 45/45/10, 1 mL/min, 25 °C, 220 nm, t<sub>R</sub> (major, *endo*) = 6.2 min, t<sub>R</sub> (major, *exo*) = 6.5 min, t<sub>R</sub> (minor, *endo*) = 8.3 min, t<sub>R</sub> (minor, *exo*) = 14.5 min; e.r.<sub>endo</sub> = 84:16, e.r.<sub>exo</sub> = 80:20, d.r. (*endo/exo*) = 32:1.



The performance of catalysts **4a** and **4c** was compared at a reaction temperature of -40 °C and a reaction time of 3 weeks following the appropriate procedure A or B respectively:

entry	catalyst	procedure	conversion (%)	d.r. (endo:exo)	e.r. (endo)	e.r. (exo)
1	<b>4a</b>	A	<5	21:1	58.5:41.5	57.5:42.5
2	<b>4c</b>	B	10	32:1	84:16	80:20

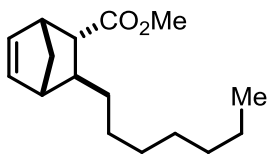
**methyl (1*R*,2*S*,3*S*,4*S*)-3-phenethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**3p**)**: Prepared according to procedure B with catalyst (*S,S*)-**4a** (2 μmol, 3.6 mg, 1 mol%), silyl ketene acetal **5c** (0.04 mmol, 10 μL, 20 mol%), methyl (*E*)-5-phenylpent-2-enoate **1p** (0.20 mmol, 38.4 mg) and cyclopentadiene (1 mmol, 90 μL) at -80 °C for 30 h. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1→2:1) as a colorless oil (46 mg, 89%). The enantiomeric and diastereomeric ratios were determined by HPLC on a chiral stationary phase. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.26 (dd, *J* = 5.7, 3.1 Hz, 1H), 6.01 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.64 (s, 3H), 3.15 – 3.12 (m, 1H), 2.77 – 2.67 (m, 2H), 2.67 – 2.63 (m, 1H), 2.49 (t, *J* = 3.8 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.80 – 1.73 (m, 1H), 1.56 – 1.52 (m, 1H), 1.46 (dq, *J* = 8.8, 1.7 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 175.2, 142.6, 138.6, 133.7, 128.4, 128.4, 125.9, 51.6, 51.4, 47.2, 46.6, 46.0, 43.7, 38.2, 35.2; HRMS (EI) calculated for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>: 256.1458; found 256.1457; [α]<sub>D</sub><sup>25</sup> = +83.2 (c 0.62, CHCl<sub>3</sub>); HPLC Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 90/10, 1 mL/min, 25 °C, 220 nm, t<sub>R</sub> (major, *endo*) = 6.7 min, t<sub>R</sub> (major, *exo*) = 7.2 min, t<sub>R</sub> (minor, *exo*) = 7.7 min, t<sub>R</sub> (minor, *endo*) = 8.5 min; e.r.<sub>endo</sub> = 96.5:3.5, e.r.<sub>exo</sub> = 97:3, d.r. (*endo/exo*) = 10:1.



The performance of catalysts **4a** and **4c** was compared at a reaction temperature of -80 °C and a reaction time of 24 hours following procedure B:

entry	catalyst	silyl group	yield (%)	d.r. (endo:exo)	e.r. (endo)	e.r. (exo)
1	<b>4a</b>	TES	89	10:1	96.5:3.5	97:3
2	<b>4c</b>	TIPS	(46% conv.)	5:1	98:2	92:8

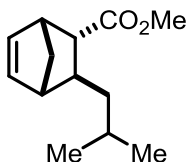
**methyl (1*R*,2*S*,3*S*,4*S*)-3-heptylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3q):** Prepared according



to procedure B with catalyst (*S,S*)-**4a** (4  $\mu$ mol, 7.2 mg, 1 mol%), silyl ketene acetal **5c** (0.08 mmol, 20  $\mu$ L, 20 mol%), methyl (*E*)-dec-2-enoate **1q** (0.40 mmol, 77.5 mg) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-80$   $^{\circ}$ C for 30 h. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil

(84 mg, 80%). The enantiomeric and diastereomeric ratios were determined by GC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.24 (dd,  $J = 5.7, 3.1$  Hz, 1H), 5.97 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.61 (s, 3H), 3.09 (tdd,  $J = 3.9, 2.7, 1.6$  Hz, 1H), 2.58 (h,  $J = 1.6$  Hz, 1H), 2.40 (dd,  $J = 4.5, 3.5$  Hz, 1H), 1.74 – 1.69 (m, 1H), 1.52 – 1.19 (m, 14H), 0.89 – 0.85 (m, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 138.7, 133.5, 51.6, 51.3, 47.0, 46.6, 45.9, 43.8, 36.2, 32.0, 29.9, 29.4, 28.8, 22.8, 14.2; **HRMS** (EI) calculated for  $\text{C}_{16}\text{H}_{26}\text{O}_2$ : 250.1927; found 250.1925;  $[\alpha]_{\text{D}}^{25} = +68.8$  ( $c$  0.63,  $\text{CHCl}_3$ ); **GC** column: BGB 176/BGB 15 G 618, 30.0 m, temperature: 230 140 60 MIN ISO 9/MIN 220 2 MIN ISO 350, gas: 0.50 bar  $\text{H}_2$ , sample size: 1.0  $\mu$ L,  $t_{\text{R}}$  (minor, *exo*) = 53.63 min,  $t_{\text{R}}$  (major, *exo*) = 56.83 min,  $t_{\text{R}}$  (minor, *endo*) = 58.37 min,  $t_{\text{R}}$  (major, *endo*) = 59.78 min; e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 98.5:1.5, d.r. (*endo/exo*) = 19:1.

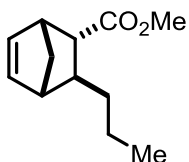
**methyl (1*R*,2*S*,3*S*,4*S*)-3-isobutylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3r):** Prepared



according to procedure B with catalyst (*S,S*)-**4a** (4  $\mu$ mol, 7.2 mg, 1 mol%), silyl ketene acetal **5c** (0.08 mmol, 20  $\mu$ L, 20 mol%), methyl (*E*)-5-methylhex-2-enoate **1r** (0.44 mmol, 64.1 mg, *E/Z* 96:4) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-80$   $^{\circ}$ C for 30 h. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (77 mg, 85%). The enantiomeric and diastereomeric ratios were determined by

GC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.25 (dd,  $J = 5.7, 3.2$  Hz, 1H), 5.97 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.61 (s, 3H), 3.12 – 3.05 (m, 1H), 2.54 (dq,  $J = 3.4, 1.7$  Hz, 1H), 2.40 (dd,  $J = 4.5, 3.5$  Hz, 1H), 1.83 (tdd,  $J = 7.8, 4.5, 1.7$  Hz, 1H), 1.63 (dp,  $J = 13.2, 6.5$  Hz, 1H), 1.51 (dt,  $J = 8.7, 1.5$  Hz, 1H), 1.41 (dq,  $J = 8.7, 1.7$  Hz, 1H), 1.38 – 1.21 (m, 2H), 0.91 (d,  $J = 3.1$  Hz, 3H), 0.89 (d,  $J = 3.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 138.7, 133.5, 51.6, 51.4, 47.4, 46.6, 46.1, 45.7, 41.4, 27.0, 23.2, 22.8; **HRMS** (EI) calculated for  $\text{C}_{13}\text{H}_{20}\text{O}_2$ : 208.1458; found 208.1457;  $[\alpha]_{\text{D}}^{25} = +69.5$  ( $c$  0.57,  $\text{CHCl}_3$ ); **GC** column: BGB 176/BGB 15 G 618, 30.0 m, temperature: 230 110 50 MIN ISO 9/MIN 220 3 MIN ISO 350, gas: 0.60 bar  $\text{H}_2$ , sample size: 1.0  $\mu$ L,  $t_{\text{R}}$  (minor, *exo*) = 25.49 min,  $t_{\text{R}}$  (major, *exo*) = 28.01 min,  $t_{\text{R}}$  (major, *endo*) = 28.79 min,  $t_{\text{R}}$  (minor, *endo*) = 29.38 min; e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = n.d., d.r. (*endo/exo*) = 23:1.

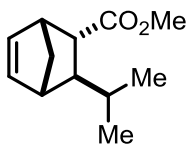
**methyl (1*R*,2*S*,3*S*,4*S*)-3-propylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3s):** Prepared according



to procedure B with catalyst (*S,S*)-**4a** (4  $\mu$ mol, 7.2 mg, 1 mol%), silyl ketene acetal **5c** (0.08 mmol, 20  $\mu$ L, 20 mol%), methyl (*E*)-hex-2-enoate **1s** (0.44 mmol, 57 mg, *E/Z* 98:2) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-80$   $^{\circ}$ C for 30 h. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (64 mg, 76%). The enantiomeric and diastereomeric ratios were determined by GC on a chiral stationary phase.  $^1\text{H}$

**NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.24 (dd,  $J = 5.7, 3.2$  Hz, 1H), 5.97 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.61 (s, 3H), 3.11 – 3.06 (m, 1H), 2.57 (dq,  $J = 3.3, 1.6$  Hz, 1H), 2.40 (dd,  $J = 4.5, 3.5$  Hz, 1H), 1.73 (tdd,  $J = 6.7, 4.6, 1.8$  Hz, 1H), 1.53 – 1.30 (m, 6H), 0.93 – 0.88 (m, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 138.7, 133.5, 51.6, 51.2, 47.0, 46.6, 45.9, 43.5, 38.5, 21.9, 14.4; **HRMS** (EI) calculated for  $\text{C}_{12}\text{H}_{18}\text{O}_2$ : 194.1301; found 194.1302;  $[\alpha]_{\text{D}}^{25} = +79.7$  ( $c$  0.65,  $\text{CHCl}_3$ ); **GC** column: G-TA 0.25 G/448, 30.0 m, temperature: 230 80 30 MIN ISO 9/MIN 170 2 MIN ISO 350, gas: 0.90 bar  $\text{H}_2$ , sample size: 1.0  $\mu$ L,  $t_{\text{R}}$  (minor, *exo*) = 23.89 min,  $t_{\text{R}}$  (major, *exo*) = 24.68 min,  $t_{\text{R}}$  (major, *endo*) = 26.09 min,  $t_{\text{R}}$  (minor, *endo*) = 28.72 min; e.r.<sub>endo</sub> = 96.5:3.5, e.r.<sub>exo</sub> = 99:1, d.r. (*endo/exo*) = 21:1.

**methyl (1R,2S,3S,4S)-3-isopropylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3t):** Prepared



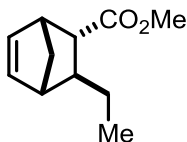
according to procedure C with catalyst (*S,S*)-**4c** (4  $\mu$ mol, 7.4 mg, 1 mol%), silyl ketene acetal **5c** (0.16 mmol, 40  $\mu$ L, 40 mol%), methyl (*E*)-4-methylpent-2-enoate **1t** (0.42 mmol, 56 mg, *E/Z* 97:3) and cyclopentadiene (4 mmol, 340  $\mu$ L) at  $-60$   $^{\circ}$ C for 48 h. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (80 mg, 98%). The enantiomeric and diastereomeric ratios were determined by GC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.27 (dd,  $J = 5.7, 3.2$  Hz, 1H), 5.94 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.62 (s, 3H), 3.11 (dddt,  $J = 4.1, 3.3, 2.4, 1.2$  Hz, 1H), 2.77 (dq,  $J = 3.4, 1.7$  Hz, 1H), 2.52 (t,  $J = 3.8$  Hz, 1H), 1.49 – 1.36 (m, 4H), 0.99 (d,  $J = 6.0$  Hz, 3H), 0.94 (d,  $J = 6.2$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 139.2, 133.4, 51.6, 51.4, 49.7, 46.8, 46.4, 45.2, 33.1, 22.3, 22.0; **HRMS** (ESI) calculated for  $\text{C}_{12}\text{H}_{19}\text{O}_2$  ( $\text{M}+\text{H}^+$ ): 195.1380; found 195.1381;  $[\alpha]_{\text{D}}^{25} = +48.9$  ( $c$  0.56,  $\text{CHCl}_3$ ); **GC** column: G-TA 0.25 G/448, 30.0 m, temperature: 230 80 25 MIN ISO g/MIN 170 3 MIN ISO 350, gas: 0.90 bar  $\text{H}_2$ , sample size: 1.0  $\mu$ L,  $t_{\text{R}}$  (major, *exo*) = 19.59 min,  $t_{\text{R}}$  (minor, *exo*) = 20.12 min,  $t_{\text{R}}$  (major, *endo*) = 21.25 min,  $t_{\text{R}}$  (minor, *endo*) = 22.63 min; e.r.<sub>endo</sub> = 95.5:4.5, e.r.<sub>exo</sub> = 92:8, d.r. (*endo/exo*) = 9:1.

The stereoselectivity for **3t** was optimized by comparing catalysts and reactions conditions:

entry	catalyst	temp.	silyl group	yield	d.r. (endo:exo)	e.r. <sub>endo</sub>	e.r. <sub>exo</sub>
1	<b>4a</b>	$-20^{\circ}\text{C}$	TES	(19% conv.) <sup>a,b</sup>	3.7:1	84:16	89:11
2	<b>4c</b>	$-20^{\circ}\text{C}$	TIPS	(93% conv.) <sup>b</sup>	1.3:1	92.5:7.5	92:8
3	<b>4c</b>	$-40^{\circ}\text{C}$	TES	(70% conv.) <sup>c,d</sup>	3.1:1	94.5:5.5	90:10
4	<b>4c</b>	$-60^{\circ}\text{C}$	TES	98% <sup>d,e</sup>	9:1	95.5:4.5	92:8

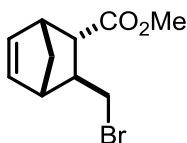
<sup>a</sup>extensive cyclopentadiene polymerization was observed. <sup>b</sup>18 h reaction time. <sup>c</sup>12 h reaction time. <sup>d</sup>The reaction was performed neat with 10 eq. of cyclopentadiene. <sup>e</sup>48 h reaction time.

**methyl (1R,2S,3S,4S)-3-ethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3u):** Prepared according to



procedure B with catalyst (*S,S*)-**4a** (4  $\mu$ mol, 7.2 mg, 1 mol%), silyl ketene acetal **5c** (0.08 mmol, 20  $\mu$ L, 20 mol%), methyl (*E*)-pent-2-enoate **1u** (0.41 mmol, 49 mg, *E/Z* 98:2) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-80$   $^{\circ}$ C for 30 h. The product was obtained as a diastereomeric mixture after column chromatography (pentane/DCM 4:1 $\rightarrow$ 2:1) as a colorless oil (56 mg, 76%). The enantiomeric and diastereomeric ratios were determined by GC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.24 (dd,  $J = 5.7, 3.1$  Hz, 1H), 5.97 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.61 (s, 3H), 3.09 (dp,  $J = 5.1, 1.7$  Hz, 1H), 2.60 (h,  $J = 1.6$  Hz, 1H), 2.40 (dd,  $J = 4.5, 3.5$  Hz, 1H), 1.64 (tdd,  $J = 7.6, 4.5, 1.7$  Hz, 1H), 1.57 – 1.39 (m, 4H), 0.96 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 138.7, 133.6, 51.6, 51.1, 46.6, 46.5, 45.9, 45.7, 28.9, 13.2; **HRMS** (EI) calculated for  $\text{C}_{11}\text{H}_{16}\text{O}_2$ : 180.1145; found 180.1146;  $[\alpha]_{\text{D}}^{25} = +75.5$  ( $c$  0.54,  $\text{CHCl}_3$ ); **GC** column: BGB 176/BGB 15 G 618, 30.0 m, temperature: 230 100 40 MIN ISO 9/MIN 220 3 MIN ISO 350, gas: 0.50 bar  $\text{H}_2$ , sample size: 1.0  $\mu$ L,  $t_{\text{R}}$  (minor, *exo*) = 24.70 min,  $t_{\text{R}}$  (major, *exo*) = 27.41 min,  $t_{\text{R}}$  (minor, *endo*) = 27.90 min,  $t_{\text{R}}$  (major, *endo*) = 28.34 min; e.r.<sub>endo</sub> = 95.5:4.5, e.r.<sub>exo</sub> = 97.5:2.5, d.r. (*endo/exo*) = 16:1.

**methyl (1R,2S,3S,4S)-3-(bromomethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3v):** Prepared



according to procedure B with catalyst (*S,S*)-**4a** (4  $\mu$ mol, 7.2 mg, 1 mol%), silyl ketene acetal **5c** (0.08 mmol, 20  $\mu$ L, 20 mol%), methyl (*E*)-4-bromobut-2-enoate **1v** (0.40 mmol, 84 mg, *E/Z* 96:4, >80% purity, freshly distilled) and cyclopentadiene (2 mmol, 180  $\mu$ L) at  $-80$   $^{\circ}$ C for 30 h. NOTE: After full conversion, the reaction was treated with a mixture of hexane/triethylamine(5:1, 50  $\mu$ L) and a drop of water. The standard treatment resulted in product decomposition. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1 $\rightarrow$ 2:1) as

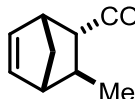
a colorless oil (81 mg, 88%). The enantiomeric and diastereomeric ratios were determined by GC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.28 (dd,  $J = 5.7, 3.2$  Hz, 1H), 6.04 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.64 (s, 3H), 3.56 (dd,  $J = 9.9, 7.2$  Hz, 1H), 3.40 (dd,  $J = 9.9, 8.8$  Hz, 1H), 3.21 – 3.18 (m, 1H), 2.86 (dt,  $J = 3.4, 1.7$  Hz, 1H), 2.54 (dd,  $J = 4.7, 3.6$  Hz, 1H), 2.26 (dddd,  $J = 8.7, 7.1, 4.7, 1.4$  Hz, 1H), 1.53 – 1.46 (m, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 138.3, 134.4, 51.9, 51.0, 46.5, 46.5, 46.3, 46.2, 37.2; **HRMS** (ESI) calculated for  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{BrNa}$  ( $\text{M}+\text{Na}$ ) $^+$ : 266.9991; found 266.9994;  $[\alpha]_{\text{D}}^{25} = +36.1$  ( $c$  0.62,  $\text{CHCl}_3$ ); **GC** column: LIPODEX E G644, 25.0 m, temperature: 230 110 45 MIN ISO 8/MIN 220 3 MIN ISO350, gas: 0.40 bar  $\text{H}_2$ , sample size: 1.0  $\mu\text{L}$ ,  $t_{\text{R}}$  (minor, *exo*) = 24.35 min,  $t_{\text{R}}$  (major, *exo*) = 25.52 min,  $t_{\text{R}}$  (major, *endo*) = 30.81 min,  $t_{\text{R}}$  (minor, *endo*) = 31.89 min; e.r.<sub>endo</sub> = 87:13, e.r.<sub>exo</sub> = 90:10, d.r. (*endo/exo*) = 48:1.

The stereoselectivity for **3v** with catalysts **4a** and **4c** was compared following procedure B:

entry	catalyst	temp.	silyl group	yield	d.r. (endo:exo)	e.r. <sub>endo</sub>	e.r. <sub>exo</sub>
1	<b>4a</b>	-80°C	TES	98% <sup>a</sup>	48:1	87:13	90:10
2	<b>4c</b>	-80°C → -60°C	TES	(66% conv.) <sup>b,c</sup>	1.2:1	95:5	74:26

<sup>a</sup>30 h reaction time. <sup>b</sup>The reaction was performed neat with 10 eq. of cyclopentadiene. <sup>c</sup>The reaction was set up at -80 °C, warmed up to -60 °C after 18 h due to insufficient conversion, and stopped after 5d at -60 °C.

**methyl (1R,2R,3S,4S)-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3w):** Prepared



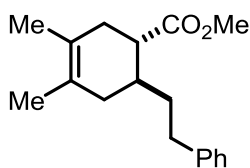
according to procedure C with catalyst (*S,S*)-**4c** (2  $\mu\text{mol}$ , 3.7 mg, 0.5 mol%), silyl ketene acetal **5c** (0.08 mmol, 20  $\mu\text{L}$ , 20 mol%), methyl crotonate **1w** (0.41 mmol, 41.5 mg) and cyclopentadiene (4 mmol, 340  $\mu\text{L}$ ) at -80 °C for 18 h. The product was obtained as a diastereomeric mixture after column chromatography (hexane/DCM 4:1→2:1) as a colorless oil (52 mg, 78%). The enantiomeric and diastereomeric ratios were determined by GC on a chiral stationary phase.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.26 (dd,  $J = 5.7, 3.2$  Hz, 1H), 5.98 (dd,  $J = 5.7, 2.8$  Hz, 1H), 3.61 (s, 3H), 3.10 (dh,  $J = 3.4, 1.6$  Hz, 1H), 2.46 (td,  $J = 3.3, 1.6$  Hz, 1H), 2.36 (dd,  $J = 4.5, 3.5$  Hz, 1H), 1.82 (qdd,  $J = 6.8, 4.5, 1.7$  Hz, 1H), 1.57 – 1.49 (m, 1H), 1.42 (dq,  $J = 8.7, 1.8$  Hz, 1H), 1.17 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.3, 138.8, 133.4, 52.5, 51.6, 49.0, 46.1, 46.0, 38.0, 21.1; **HRMS** (EI) calculated for  $\text{C}_{10}\text{H}_{14}\text{O}_2$ : 166.0988; found 166.0986;  $[\alpha]_{\text{D}}^{25} = +112.4$  ( $c$  0.64,  $\text{CHCl}_3$ ); **GC** column: BGB 176/BGB 15 G 618, 30.0 m, temperature: 230 85 60 MIN ISO 9/MIN 220 3 MIN ISO 350, gas: 0.50 bar  $\text{H}_2$ , sample size: 1.0  $\mu\text{L}$ ,  $t_{\text{R}}$  (minor, *exo*) = 28.93 min,  $t_{\text{R}}$  (major, *exo*) = 31.23 min,  $t_{\text{R}}$  (minor, *endo*) = 32.42 min,  $t_{\text{R}}$  (major, *endo*) = 34.90 min; e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 95:5, d.r. (*endo/exo*) = >50:1.

The stereoselectivity for **3w** was optimized by comparing catalysts and reactions conditions following procedure B:

entry	catalyst	temp.	silyl group	yield	d.r. (endo:exo)	e.r. <sub>endo</sub>	e.r. <sub>exo</sub>
1	<b>4a</b>	-80°C	TES	(full conv.) <sup>a</sup>	26:1	85.5:14.5	92.5:7.5
2	<b>4a</b>	-100°C	TES	(>95% conv.) <sup>a</sup>	38:1	88.5:12.5	93.75:6.25
3	<b>4c</b>	-80°C	TIPS	(18% conv.) <sup>a</sup>	5:1	96.5:3.5	95:5
4	<b>4c</b>	-100°C	TIPS	(<5%) <sup>a</sup>	n.d.	n.d.	n.d.
5	<b>4c</b>	-80°C	TMS	(>95% conv.) <sup>a,b</sup>	5:1	93.5:6.5	94.5:5.5
6	<b>4c</b>	-80°C	TES	(full conv.) <sup>a,b</sup>	21:1	97:3	95:5
7	<b>4c</b>	-80°C	TBS	(full conv.) <sup>a,b</sup>	26:1	95:5	94.5:5.5
8	<b>4c</b>	-80°C	TIPS	(59% conv.) <sup>a,b</sup>	6:1	96:4	95:5
9	<b>4c</b>	-80°C	TES	78% <sup>b,c</sup>	>50:1	97:3	95:5

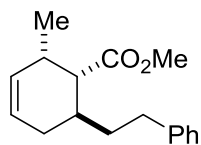
<sup>a</sup>24 h reaction time. <sup>b</sup>The reaction was performed neat with 10 eq. of cyclopentadiene. <sup>c</sup>18 h reaction time and 0.5 mol% of **4d**.

**methyl (1*S*,6*S*)-3,4-dimethyl-6-phenethylcyclohex-3-ene-1-carboxylate (3x):** Prepared



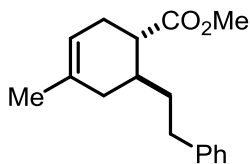
according to procedure E with catalyst (*S,S*)-**4d** (6  $\mu$ mol, 13.9 mg, 3 mol%), triisopropyl(2-methylallyl)silane **5d** (0.1 mmol, 23  $\mu$ L, 50 mol%), methyl (*E*)-5-phenylpent-2-enoate **1p** (0.2 mmol, 38.0 mg) and 2,3-dimethyl-1,3-butadiene **2b** (0.8 mmol, 91  $\mu$ L, 4 equiv.) at  $-20$   $^{\circ}$ C for 3.5 days. Purification by column chromatography on silica gel (hexane  $\rightarrow$  hexane/EtOAc 19:1) afforded the title compound as a colorless oil (44.8 mg, 0.17 mmol, 82%). The enantiomeric ratio was determined by HPLC on a chiral stationary phase.  **$^1$ H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.26 (m, 2H), 7.22–7.14 (m, 3H), 3.67 (s, 3H), 2.73 (ddd,  $J = 13.6, 11.0, 5.1$  Hz, 1H), 2.53 (ddd,  $J = 13.7, 10.9, 6.0$  Hz, 1H), 2.39 (td,  $J = 10.3, 5.2$  Hz, 1H), 2.32–2.25 (m, 1H), 2.18 (dd,  $J = 17.1, 5.3$  Hz, 1H), 2.10 (dd,  $J = 17.0, 5.2$  Hz, 1H), 1.96–1.88 (m, 1H), 1.83–1.77 (m, 1H), 1.73 (dddd,  $J = 13.4, 11.0, 6.0, 3.8$  Hz, 1H), 1.63 (s, 3H), 1.62 (s, 3H), 1.47 (dddd,  $J = 13.4, 10.9, 9.1, 5.1$  Hz, 1H);  **$^{13}$ C NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 142.6, 128.4, 128.4, 125.8, 124.6, 123.7, 51.6, 46.5, 36.9, 36.2, 35.9, 35.0, 33.0, 19.1, 18.7; **HRMS** (EI) calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_2$ : 272.1771; found: 272.1771;  $[\alpha]_{\text{D}}^{25} = +82.0$  ( $c$  0.49,  $\text{CHCl}_3$ ); **HPLC** Daicel Chiralcel IC-3R, MeOH/ $\text{H}_2\text{O}$  = 80:20, 1 mL/min, 25  $^{\circ}$ C, 220 nm,  $t_{\text{R}}$  (major) = 12.1 min,  $t_{\text{R}}$  (minor) = 14.3 min; e.r. = 92:8.

**methyl (1*R*,2*S*,6*S*)-2-methyl-6-phenethylcyclohex-3-ene-1-carboxylate (3y):** Prepared according



to procedure D with catalyst (*S,S*)-**4d** (6  $\mu$ mol, 13.9 mg, 3 mol%), triisopropyl(2-methylallyl)silane **5d** (0.1 mmol, 23  $\mu$ L, 50 mol%), methyl (*E*)-5-phenylpent-2-enoate **1p** (0.2 mmol, 38.0 mg) and (*E*)-1,3-pentadiene **2c** (0.8 mmol, 80  $\mu$ L, 4 equiv.) at 0  $^{\circ}$ C for 16 days. The title compound was obtained as a diastereomeric mixture after purification by column chromatography on silica gel (hexane  $\rightarrow$  hexane/EtOAc 19:1) as a colorless oil (27.1 mg, 0.11 mmol, 52%). The enantiomeric ratios were determined by HPLC on a chiral stationary phase. The diastereomeric ratio was determined by  $^1$ H NMR spectroscopy.  **$^1$ H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.26 (m, 2H), 7.21–7.15 (m, 3H), 5.69–5.60 (m, 2H), 3.67 (s, 3H), 2.72 (ddd,  $J = 13.6, 11.3, 5.2$  Hz, 1H), 2.63–2.48 (m, 3H), 2.40–2.32 (m, 1H), 2.07–1.98 (m, 1H), 1.92 (dddd,  $J = 13.2, 11.2, 6.0, 3.3$  Hz, 1H), 1.82–1.75 (m, 1H), 1.43 (dddd,  $J = 13.2, 10.9, 9.5, 5.2$  Hz, 1H), 0.93 (d,  $J = 7.0$  Hz, 3H);  **$^{13}$ C NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.7, 142.6, 131.3, 128.5, 128.4, 125.8, 124.8, 51.3, 49.3, 36.4, 33.1, 31.5, 30.4, 29.8, 17.5; **HRMS** (EI) calculated for  $\text{C}_{17}\text{H}_{22}\text{O}_2$ : 258.1614; found: 258.1617;  $[\alpha]_{\text{D}}^{25} = +28.3$  ( $c$  0.85,  $\text{CHCl}_3$ ); **HPLC** (2D-Separation) 1. 50 mm Eclipse Plus C18 1.8  $\mu$ m, 4.6 mm, methanol/water gradient 80% – 3' – 100% methanol, 1.0 mL/min, 46.4 MPa, 308 K, 220 nm,  $t_{\text{R}}$  (*endo*) = 2.94 min,  $t_{\text{R}}$  (*exo*) = 2.80 min; 2. 150 mm Amycoat RP, 4.6 mm, acetonitrile/water 50:50, 1.0 ml/min, 20.6 MPa, 298 K, 220 nm.;  $t_{\text{R}}$  (major, *endo*) = 12.7 min,  $t_{\text{R}}$  (minor, *endo*) = 22.0 min,  $t_{\text{R}}$  (major, *exo*) = 16.9 min,  $t_{\text{R}}$  (minor, *exo*) = 12.0 min; e.r.<sub>*endo*</sub> = 69:31, e.r.<sub>*exo*</sub> = 81:19, d.r. (*endo/exo*) = 6:1.

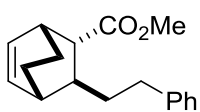
**methyl (1*S*,6*S*)-4-methyl-6-phenethylcyclohex-3-ene-1-carboxylate (3z):** Prepared according to



procedure E with catalyst (*S,S*)-**4d** (6  $\mu$ mol, 13.9 mg, 3 mol%), triisopropyl(2-methylallyl)silane **5d** (0.1 mmol, 23  $\mu$ L, 50 mol%), methyl (*E*)-5-phenylpent-2-enoate **1p** (0.2 mmol, 38.0 mg) and isoprene **2d** (0.8 mmol, 80  $\mu$ L, 4 equiv.) at  $-20$   $^{\circ}$ C for 3.5 days. Purification by column chromatography on silica gel (hexane  $\rightarrow$  hexane/ethyl acetate 19:1) afforded the title compound as a colorless oil (51.6 mg, 0.20 mmol, 99%).

The enantiomeric ratio was determined by HPLC on a chiral stationary phase. The regioisomeric ratio was determined by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.26 (m, 2H), 7.22–7.13 (m, 3H), 5.37 (ddq,  $J = 4.1, 2.9, 1.5$  Hz, 1H), 3.68 (s, 3H), 2.74 (ddd,  $J = 13.6, 11.0, 5.1$  Hz, 1H), 2.55 (ddd,  $J = 13.6, 10.8, 6.0$  Hz, 1H), 2.36 (td,  $J = 9.7, 5.3$  Hz, 1H), 2.32–2.25 (m, 1H), 2.24–2.15 (m, 2H), 1.98 (qdd,  $J = 9.6, 5.4, 3.9$  Hz, 1H), 1.80–1.71 (m, 2H), 1.70–1.65 (m, 3H), 1.50 (dddd,  $J = 13.4, 10.9, 9.1, 5.1$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 142.5, 133.0, 128.5, 128.4, 125.9, 118.9, 51.6, 45.5, 36.2, 35.5, 35.1, 32.9, 28.7, 23.6; HRMS (EI) calculated for  $\text{C}_{17}\text{H}_{22}\text{O}_2$ : 258.1614; found: 258.1616;  $[\alpha]_{\text{D}}^{25} = +86.1$  ( $c$  0.60,  $\text{CHCl}_3$ ); HPLC Daicel Chiralcel IC-3R, MeOH/ $\text{H}_2\text{O} = 70:30$ , 1 mL/min, 25  $^{\circ}$ C, 220 nm,  $t_{\text{R}}$  (major) = 31.8 min,  $t_{\text{R}}$  (minor) = 36.2 min; e.r. = 97:3; r.r. (*para/meta*) > 50:1.

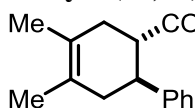
**methyl (1*R*,2*S*,3*S*,4*S*)-3-phenethylbicyclo[2.2.2]oct-5-ene-2-carboxylate (3aa):** Prepared



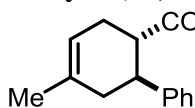
according to procedure D with catalyst (*S,S*)-**4d** (6  $\mu$ mol, 13.9 mg, 3 mol%), triisopropyl(2-methylallyl)silane **5d** (0.1 mmol, 23  $\mu$ L, 50 mol%), methyl (*E*)-5-phenylpent-2-enoate **1p** (0.2 mmol, 38.0 mg) and cyclohexa-1,3-diene **2e** (0.8 mmol, 76  $\mu$ L, 4 equiv.) at 0  $^{\circ}$ C for 4 days. The title compound was

obtained as a diastereomeric mixture after purification by column chromatography on silica gel (hexane  $\rightarrow$  hexane/EtOAc 19:1) as a colorless oil (54.0 mg, 0.20 mmol, 99%). The enantiomeric ratios were determined by HPLC on a chiral stationary phase. The diastereomeric ratio was determined by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.26 (m, 2H), 7.21–7.17 (m, 3H), 6.42 (ddd,  $J = 8.2, 6.7, 1.3$  Hz, 1H), 6.16 (ddd,  $J = 7.8, 6.3, 1.1$  Hz, 1H), 3.64 (s, 3H), 2.90–2.84 (m, 1H), 2.67 (ddd,  $J = 13.6, 10.6, 5.5$  Hz, 1H), 2.58 (ddd,  $J = 13.7, 10.8, 5.5$  Hz, 1H), 2.52–2.48 (m, 1H), 2.10 (dd,  $J = 5.7, 2.1$  Hz, 1H), 1.90 (dddd,  $J = 9.6, 7.4, 5.8, 2.0$  Hz, 1H), 1.88–1.78 (m, 1H), 1.72 (dtdd,  $J = 20.4, 13.0, 4.7, 2.1$  Hz, 2H), 1.52 (dddd,  $J = 12.3, 9.8, 4.5, 2.4$  Hz, 1H), 1.32 (tt,  $J = 12.4, 3.9$  Hz, 1H), 1.14–1.07 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0, 142.6, 136.6, 131.3, 128.4, 128.4, 125.9, 51.8, 51.1, 40.3, 37.1, 34.6, 33.4, 33.2, 25.6, 18.4; HRMS (EI) calculated for  $\text{C}_{18}\text{H}_{22}\text{O}_2$ : 279.1614; found: 270.1613;  $[\alpha]_{\text{D}}^{25} = +17.5$  ( $c$  1.0,  $\text{CHCl}_3$ ); HPLC (2D separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 4.6 mm, methanol/water 75:25, 1.0 mL/min, 51.1 MPa, 308 K, 220 nm,  $t_{\text{R}}$  (*endo*) = 2.93 min,  $t_{\text{R}}$  (*exo*) = 3.69 min; 2. 150 mm Chiralcel OJ-3R, 4.6 mm, methanol/water 80:20, 1.0 ml/min, 33.6 MPa, 298 K, 220 nm;  $t_{\text{R}}$  (major, *endo*) = 27.4 min,  $t_{\text{R}}$  (minor, *endo*) = 35.6 min,  $t_{\text{R}}$  (major, *exo*) = 29.5 min,  $t_{\text{R}}$  (minor, *exo*) = 38.2 min; e.r.<sub>*endo*</sub> = 98.5:1.5, e.r.<sub>*exo*</sub> = 92.5:7.5, d.r. (*endo/exo*) = 13:1.

**methyl (1*S*,6*S*)-3,4,6-trimethylcyclohex-3-ene-1-carboxylate (3bb):** Prepared according to procedure D with catalyst (*S,S*)-**4d** (6  $\mu$ mol, 13.9 mg, 3 mol%), triisopropylmethallylsilane **5d** (0.1 mmol, 23.4  $\mu$ L, 50 mol%), methyl (*E*)-cinnamate **1a** (0.2 mmol, 32.4 mg) and 2,3-dimethyl-1,3-butadiene **2b** (1 mmol, 113  $\mu$ L, 5 equiv.) at 0 °C for 5.5 days. Purification by column chromatography on silica gel (hexane→hexane/EtOAc 19:1) afforded the title compound as a colorless oil (26.8 mg, 0.11 mmol, 55%). The enantiomeric ratio was determined by HPLC on a chiral stationary phase. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.29–7.26 (m, 2H), 7.23–7.15 (m, 3H), 3.39 (s, 3H), 3.02 (ddd, *J* = 11.6, 9.8, 6.8 Hz, 1H), 2.86 (ddd, *J* = 11.5, 10.7, 5.2 Hz, 1H), 2.46–2.38 (m, 1H), 2.25–2.21 (m, 1H), 2.21–2.15 (m, 2H), 1.69–1.66 (m, 3H), 1.66–1.63 (m, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  175.8, 144.2, 128.5, 127.5, 126.6, 125.4, 123.8, 51.4, 47.0, 43.7, 40.2, 35.6, 18.8, 18.7; **HRMS** (EI) calculated for C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>: 244.1458; found: 244.1457; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +77.4 (*c* 0.78, CHCl<sub>3</sub>); **HPLC** Daicel Chiralcel OD-3R, MeOH/H<sub>2</sub>O = 80:20, 1 mL/min, 25 °C, 220 nm, *t*<sub>R</sub> (major) = 10.7 min, *t*<sub>R</sub> (minor) = 12.2 min; e.r. = 96:4.



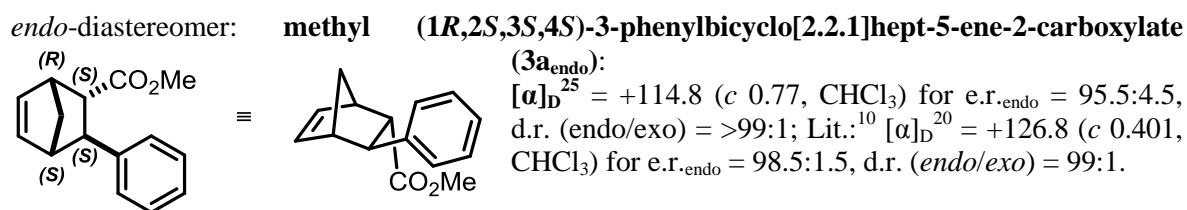
**methyl (1*S*,2*S*)-5-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (3dd):** Prepared according to procedure D with catalyst (*S,S*)-**4d** (6  $\mu$ mol, 13.9 mg, 3 mol%), triisopropyl(2-methallyl)silane **5d** (0.1 mmol, 23  $\mu$ L, 50 mol%), methyl (*E*)-cinnamate **1a** (0.2 mmol, 32.7 mg) and isoprene **2d** (1 mmol, 100  $\mu$ L, 5 equiv.) at 0 °C for 5.5 days. Purification by column chromatography on silica gel (hexane → hexane/EtOAc 19:1) afforded the title compound as a colorless oil (32.4 mg, 0.14 mmol, 71%). The enantiomeric ratio was determined by HPLC on a chiral stationary phase. The regioisomeric ratio was determined by <sup>1</sup>H NMR spectroscopy. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32–7.24 (m, 2H), 7.24–7.15 (m, 3H), 5.45 (ddq, *J* = 5.9, 3.3, 1.6 Hz, 1H), 3.39 (s, 3H), 3.07 (ddd, *J* = 11.2, 9.1, 7.3 Hz, 1H), 2.81 (ddd, *J* = 11.1, 10.3, 5.6 Hz, 1H), 2.45–2.37 (m, 1H), 2.33 (dddd, *J* = 15.6, 6.9, 3.6, 1.7 Hz, 1H), 2.20 (d, *J* = 8.0 Hz, 2H), 1.70 (dt, *J* = 2.7, 1.3 Hz, 3H). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  175.9, 144.2, 133.8, 128.5, 127.5, 126.6, 119.0, 51.4, 46.2, 43.3, 38.4, 29.5, 23.3; **HRMS** (EI) calculated for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>: 230.1301; found: 230.1303; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +74.1 (*c* 0.95, CHCl<sub>3</sub>); **HPLC** Daicel Chiralcel OD-3R, MeOH/H<sub>2</sub>O = 75:25, 1 mL/min, 25 °C, 220 nm, *t*<sub>R</sub> (major) = 13.7 min, *t*<sub>R</sub> (minor) = 15.4 min; e.r. = 98:2; r.r. (*para/meta*) > 50:1.



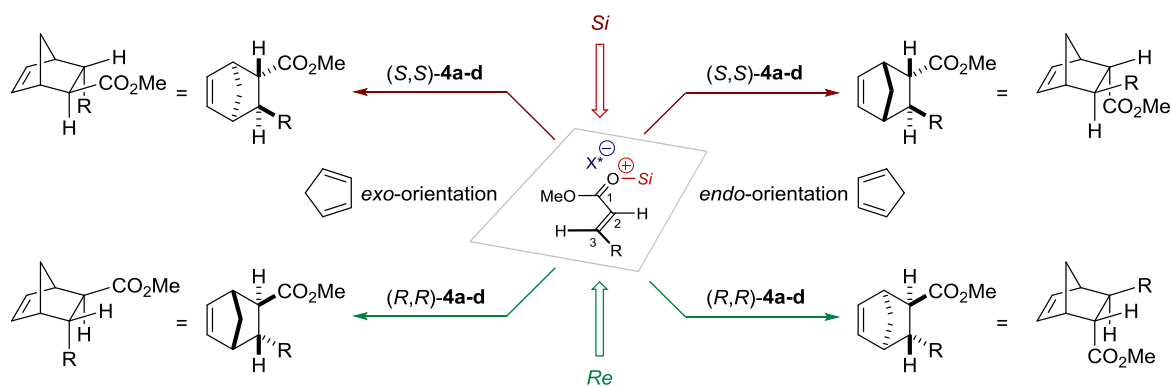
## Stereochemical Assignment

The assignment of endo- and exo-diastereomers for product **3a** was conducted by  $^1\text{H}$  and NOESY NMR analysis and comparison of spectroscopic data with literature data. The major diastereomer in catalyzed Diels–Alder reactions was generally assigned as the endo-diastereomer.

The absolute configuration of **3a<sub>endo</sub>** was determined by comparing the optical rotation with reported value available in literature. All other endo-products were assigned by analogy.

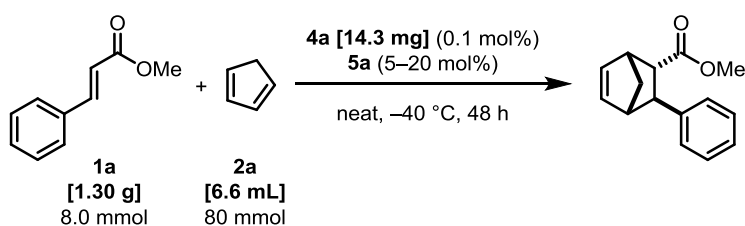


We rationalize the enantioinduction of the Diels–Alder reactions by steric shielding of the enantiotopic faces by the chiral anion in the approach of the diene. A detailed stereochemical model is depicted below. The *Si*- and *Re*-faces are defined according to the priority on C-2. With IDPi catalysts (*S,S*)-**4a-d**, the diene approaches from the *Si*-face in either the endo- or exo-orientation. The absolute configuration of the minor exo-diastereomer is assigned accordingly.



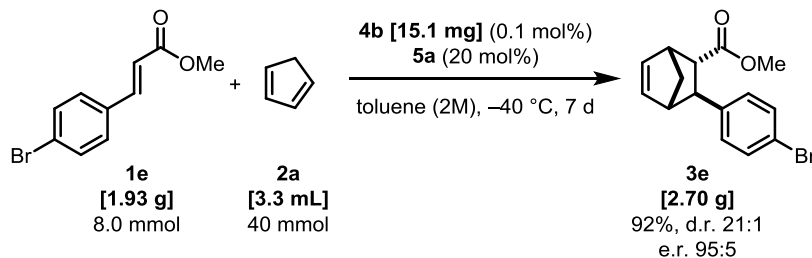
## Scale-Up Experiments

Following a modified procedure C, a 15 mL vial was charged with (*E*)-methyl cinnamate (**1a**, 8 mmol, 1.3 g), (*S,S*)-**4a** (8  $\mu$ mol, 14.3 mg, 0.1 mol%) and a magnetic stirrer bar. The vial was sealed with a screw-cap containing a PTFE/rubber septum and was either evacuated by purged with argon (3  $\times$ ) or left under air. After addition of triethylallylsilane **5a** (320  $\mu$ mol, 20 mol%) at r.t., the vial was cooled in a cryostat at  $-40$   $^{\circ}$ C under stirring for 10 min. Then, neat cyclopentadiene (80 mmol, 6.6 mL) was added via a syringe, the cap sealed with parafilm. After 48 h, TLC indicated full conversion. Work-up and purification was performed as described before. In case of entry 3, a flame-dried Schlenk flask under argon was used in combination with 5 mol% triethylallylsilane **5a** (80  $\mu$ L).



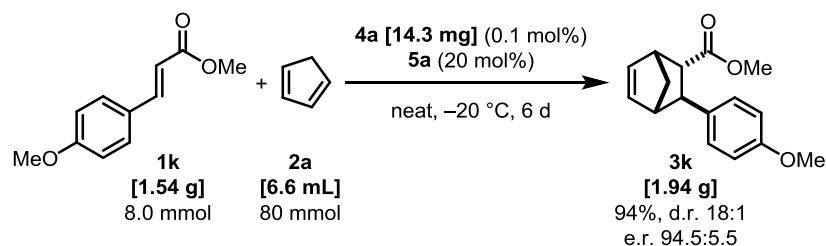
entry	container	atmosphere	loading <b>5a</b>	yield (%)	e.r. <sub>endo</sub>	d.r. (endo/exo)
1	vial	argon	20 mol%	97	96.25:3.75	21:1
2	vial	air	20 mol%	99	96:4	22:1
3	Schlenk	argon	5 mol%	94	96:4	21:1

Following a modified procedure A, a 15 mL vial was charged with methyl (*E*)-3-(4-bromophenyl)acrylate (**1e**, 8 mmol, 48.5 mg), (*S,S*)-**4b** (8  $\mu$ mol, 15.1 mg, 0.1 mol%) and a magnetic stirrer bar. The vial was sealed with a screw-cap containing a PTFE/rubber septum and was either evacuated by purged with argon (3  $\times$ ). Dry toluene (4 mL) and triethylallylsilane **5a** (320  $\mu$ mol, 20 mol%) were added at r.t. and the reaction was cooled to  $-40$   $^{\circ}$ C. Then, neat cyclopentadiene (40 mmol, 3.3 mL) was added via a syringe, the cap sealed with parafilm. After 7 days, TLC indicated full conversion. Work-up and purification was performed as described before. Product **3e** was isolated in 92% yield (2.70 g, e.r.<sub>endo</sub> = 95:5, d.r. [*endo/exo*] = 21:1).

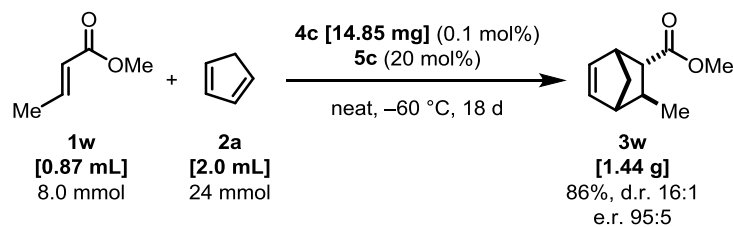


NOTE: Attempts to perform this example under neat conditions at  $-40$   $^{\circ}$ C or  $-20$   $^{\circ}$ C resulted in extensive polymerization of cyclopentadiene and consequently very low conversion, presumably due to the very low solubility of **1e** in cyclopentadiene.

Following a modified procedure C, a 15 mL vial was charged with methyl (*E*)-3-(4-methoxyphenyl)acrylate (**1k**, 8 mmol, 1.54 g), (*S,S*)-**4a** (8  $\mu$ mol, 14.3 mg, 0.1 mol%) and a magnetic stirrer bar. The vial was sealed with a screw-cap containing a PTFE/rubber septum and was either evacuated by purged with argon (3  $\times$ ). After addition of triethylallylsilane **5a** (320  $\mu$ mol, 20 mol%) at r.t., the vial was cooled in a cryostat at  $-20$   $^{\circ}$ C under stirring for 10 min. Then, neat cyclopentadiene (80 mmol, 6.6 mL) was added via a syringe, the cap sealed with parafilm. After 6 days, TLC indicated full conversion. Work-up and purification was performed as described before. Product **3k** was isolated in 94% yield (1.94 g, e.r.<sub>endo</sub> = 94.5:5.5, d.r. [*endo/exo*] = 18:1).



Following a modified procedure C, a 15 mL vial was charged with *S,S*-**4c** (8  $\mu$ mol, 14.9 mg, 0.1 mol%) and a magnetic stirrer bar. The vial was sealed with a screw-cap containing a PTFE/rubber septum and was either evacuated by purged with argon (3  $\times$ ). The vial was cooled in a cryostat at  $-60$   $^{\circ}$ C. Then, neat cyclopentadiene (24 mmol, 2.0 mL) was added via a syringe followed by silyl ketene acetal **5c** (400  $\mu$ L, 20 mol%) and methyl crotonate **1w** (8 mmol, 0.87 mL) in this order. The cap was sealed with parafilm and the reaction mixture was stirred at  $-60$   $^{\circ}$ C for 18 days, after which  $^1$ H NMR analysis indicated full conversion. Work-up and purification was performed as described before. Product **3w** was isolated in 86% yield (1.44 g, e.r.<sub>endo</sub> = 95:5, d.r. [*endo/exo*] = 16:1).



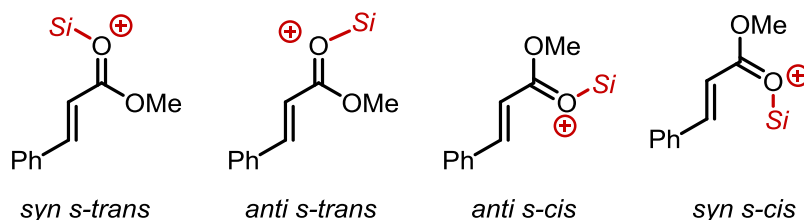
## Computational Studies

### Computational Details

All calculations presented in this paper were carried out with the development version of the ORCA suite of programs based on version 4.0.<sup>11</sup> All molecular geometries were optimized in the gas-phase using the PBE functional<sup>12</sup> in conjunction with the D3 version of Grimme's dispersion correction with Becke-Johnson damping function,<sup>13</sup> using the resolution of identity approximation. The def2-SVP basis set was used for all atoms with matching auxiliary basis.<sup>14</sup> In all cases, a fine integration grid (grid7) was used. Analytic frequency calculations were performed to verify the nature of all stationary points (minima and transition states) and to calculate free energies and enthalpies at 233 K by using the rigid-rotor harmonic oscillator (RRHO) approximation, as implemented in ORCA, combined with B3LYP-D3(BJ)/def2-TZVP single-point energies.<sup>15</sup> Single-point energies taking into account solvation effects (toluene) were also carried out via the conductor like polarizable continuum model (C-PCM)<sup>16</sup> at B3LYP-D3(BJ)/def2-TZVP level. The gas phase electronic energies were also refined using single-point DLPNO-CCSD(T)/def2-TZVP<sup>17</sup> calculations with NormalPNO settings and tighten TCutPairs threshold ( $10^{-5}$ ). Solvation, entropy and thermal corrections were kept at DFT level. This protocol is denoted as (DLPNO-CCSD(T) + C-PCM(toluene))/PBE-D3(BJ)/def2-SVP.

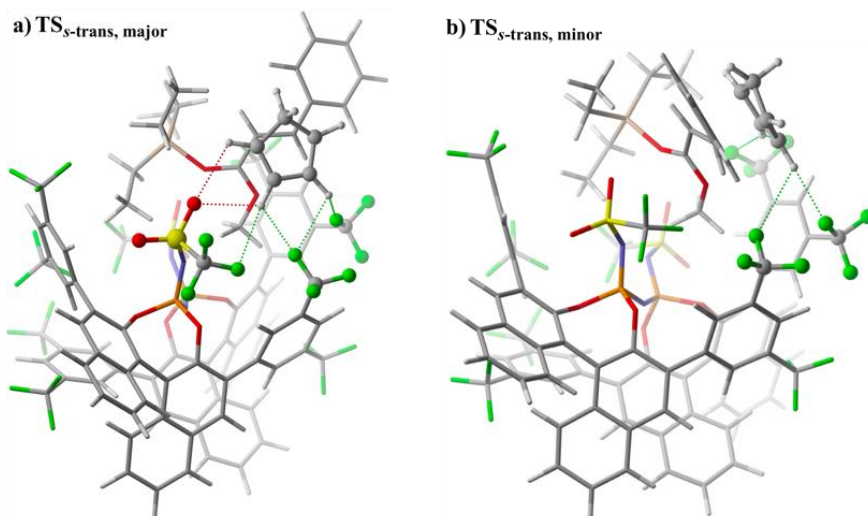
### Conformational sampling

Due to the conformational flexibility of the substrate and the catalyst, two different strategies were used to localize the most stable transition states (TS) for both enantiomers. First, the conformers of the silylated methyl cinnamate **1a** (Figure S6) together with different conformers of the (*S,S*)-**4a** counteranion (18 different conformers located by scanning the rotation of the SO<sub>2</sub>CF<sub>3</sub> and 3,5-trifluoromethylphenyl substituents) were used to explore several structures for the chiral ion pair (CIP). Although, this particular type of catalyst has a highly delocalized negative charge, the electrostatic potential map (see Fig. 4 in the manuscript) evidenced that the negative region is confined into a chiral pocket adopted by the anion. Consequently, the electrostatic interaction with the cationic substrate can be highly directional. In total, 9 CIP were found and used as a starting point for the endo-attack of cyclopentadiene on both faces of the silylated-**1a**. 16 different transition states were located: 9 for the favoured and 7 for the disfavoured enantiomer.



**Figure S6.** Conformational possibilities for the silylated methyl cinnamate silylated-**1a**: the carbonyl group can be placed either *s-trans* or *s-cis* to the olefin, while the silyl group is bonded *syn* or *anti* to the ester fragment. The *anti s-trans* conformation is often most stable.<sup>18</sup>

The two lowest-lying TS leading to both enantiomers of the endo-cycloadduct have *s-trans* conformation of silylated-**1a** (Figure S7). Both transition states originate from the same CIP and have different non-classical C-H...O and C-H...F hydrogen bonds assisting the cyclopentadiene addition. As visualized in Fig S7, the TS<sub>*s-trans*</sub> structure leading to the favoured enantiomer has two stabilizing C-H...O hydrogen bonds between an oxygen atom of the SO<sub>2</sub>CF<sub>3</sub> group of the catalyst and the C-H groups of the cyclopentadiene (2.506 Å and 2.651 Å), that are lacked in the other TS. Thus, these interactions allow the discrimination of both TSs, guiding to the high enantioselectivity.



**Figure S7.** Close-up of the non-classical C-H...O (dotted red lines) and C-H...F (dotted green lines) hydrogen bonds assisting the cyclopentadiene attack for both enantiodetermining TS structures. Distances shorter than 3 Å are shown.

### Cartesian coordinates and electronic energies

Cartesian coordinates (in Å) and electronic energies (in a. u.) of all the stationary points discussed in the text. Calculations reported at PBE-D3(BJ)/def2-SVP level.

#### 1a (methyl cinnamate)

E = -536.508893432386

C	3.167405	-2.240044	0.596801
C	1.981376	-1.605171	0.411591
C	1.843926	-0.192442	0.004229
O	0.773230	0.371700	-0.162589
H	1.013776	-2.109466	0.554478
H	4.083181	-1.648838	0.428754
O	3.045638	0.428984	-0.173839
C	2.964095	1.798471	-0.571692
H	2.424154	2.402321	0.186271
H	4.005626	2.152713	-0.673705
H	2.425539	1.902030	-1.536002
C	3.372916	-3.632402	0.997605
C	4.697031	-4.113447	1.138768
C	2.305867	-4.529262	1.252985
C	4.949780	-5.437448	1.519809
H	5.535935	-3.427079	0.943362
C	2.557912	-5.850591	1.633261
H	1.266415	-4.183954	1.151328
C	3.880339	-6.311482	1.768626
H	5.987215	-5.789774	1.623366
H	1.715883	-6.532261	1.827227
H	4.074148	-7.352569	2.068202

### Cyclopentadiene

E = -193.710286707175

C	0.448150	-0.593955	-0.134747
C	1.810381	-0.544452	-0.134769
C	2.244175	0.858213	-0.134861
C	1.147724	1.668099	-0.134886
H	-0.179379	-1.495363	-0.134688
H	2.490591	-1.408233	-0.134730
H	3.293261	1.187182	-0.134898
H	1.138630	2.766391	-0.134948
C	-0.087365	0.810865	-0.134813
H	-0.735921	1.011391	-1.019477
H	-0.735864	1.011480	0.749872

### Catalyst [Si-X\*]

E = -8593.59563547091

P	0.960999	-1.153585	-0.218729
O	2.458345	-0.776130	0.366389
O	0.583893	-2.472576	0.715302
C	3.375817	-1.743024	0.750989
C	4.535292	-1.916061	-0.064318
C	5.486628	-2.832886	0.362922
C	5.301909	-3.618123	1.533549
C	6.274197	-4.582263	1.931894
C	6.065303	-5.392145	3.036687
C	4.859477	-5.277100	3.776507
C	3.898746	-4.340146	3.422743
C	4.097982	-3.465583	2.314043
C	3.141968	-2.459398	1.923828
C	1.905467	-2.202303	2.712819
C	1.951955	-1.856939	4.112918
C	3.175318	-1.604085	4.803244
C	3.180796	-1.281385	6.153111
C	1.966669	-1.217223	6.886564
C	0.759661	-1.434582	6.240498
C	0.716471	-1.725455	4.844990
C	-0.521905	-1.902372	4.170273
C	-0.581243	-2.179291	2.807902
C	0.653748	-2.286936	2.093911
C	4.680057	-1.183472	-1.344010
H	6.406311	-2.968982	-0.226017
H	7.191815	-4.678589	1.331211
H	6.822275	-6.134549	3.330658
H	4.680038	-5.941988	4.634738
H	2.965805	-4.273308	3.998277
H	4.121223	-1.659438	4.251449
H	4.137798	-1.083453	6.658928
H	1.986759	-0.990129	7.963326

H	-0.191344	-1.374921	6.789627
H	-1.455085	-1.838636	4.750690
C	-1.890134	-2.462489	2.163660
C	4.391989	0.189173	-1.438837
C	4.510261	0.860259	-2.664708
C	4.924778	0.179613	-3.814654
C	5.194152	-1.196663	-3.729957
C	5.071476	-1.873466	-2.511608
C	-3.008529	-1.639854	2.417661
C	-4.276880	-2.003065	1.941493
C	-4.455022	-3.194798	1.218381
C	-3.345523	-4.006435	0.950750
C	-2.068461	-3.634904	1.400626
H	4.060556	0.741526	-0.552676
H	5.016957	0.711339	-4.771158
H	5.229621	-2.959100	-2.474662
H	-2.881220	-0.710340	2.989636
H	-5.449837	-3.487915	0.859692
H	-1.208242	-4.285860	1.193021
N	0.097042	0.092469	0.260552
P	-0.829657	1.271438	-0.144636
O	-0.580860	2.608007	0.787425
O	-2.356150	0.830150	0.282293
C	-0.654460	2.370508	2.164071
C	0.572597	2.258013	2.887748
C	0.485381	1.943248	4.240119
C	-0.765588	1.728497	4.881345
C	-0.829586	1.405488	6.268817
C	-2.043286	1.142835	6.884291
C	-3.243375	1.189434	6.127426
C	-3.220019	1.538770	4.784267
C	-1.990408	1.839792	4.126448
C	-1.917824	2.216850	2.735632
C	-3.136309	2.435766	1.903691
C	-4.135678	3.401562	2.289333
C	-3.973105	4.278611	3.402245
C	-4.963921	5.186647	3.747281
C	-6.167684	5.264243	2.999022
C	-6.345132	4.447124	1.894277
C	-5.338694	3.515848	1.502214
C	-5.492762	2.716887	0.337459
C	-4.502398	1.841085	-0.090123
C	-3.325096	1.731731	0.711294
C	1.885418	2.520886	2.243025
H	1.405628	1.865143	4.838750
H	0.111644	1.353710	6.835136
H	-2.078451	0.889590	7.954650
H	-4.204055	0.953731	6.609338
H	-4.156389	1.576052	4.215002
H	-3.043720	4.238664	3.985828
H	-4.811100	5.856800	4.606543
H	-6.948998	5.982707	3.288374

H	-7.263228	4.512271	1.290290
H	-6.423917	2.800476	-0.243295
C	-4.675450	1.057798	-1.339522
C	2.073608	3.665647	1.442464
C	3.336343	3.966591	0.907898
C	4.427391	3.123748	1.152078
C	4.246066	1.978815	1.946807
C	2.988520	1.674327	2.487343
C	-5.130519	1.699282	-2.512637
C	-5.358112	0.965031	-3.683781
C	-5.148378	-0.423894	-3.710643
C	-4.665132	-1.055988	-2.559861
C	-4.420559	-0.325576	-1.385938
H	1.232596	4.347117	1.259430
H	5.411097	3.358310	0.724783
H	2.856643	0.765751	3.091381
H	-5.272658	2.788077	-2.514715
H	-5.320911	-1.000715	-4.629075
H	-4.028743	-0.841933	-0.501040
N	0.854198	-1.482464	-1.775686
N	-0.709511	1.800484	-1.685680
S	1.570587	-2.762279	-2.500459
O	1.982973	-2.392837	-3.867497
O	2.499871	-3.509621	-1.618159
S	-1.408206	3.042324	-2.336712
O	-1.442469	2.776837	-3.877576
O	-2.678859	3.572746	-1.822495
C	-0.185219	4.497751	-2.309296
C	0.084339	-3.913509	-2.715387
F	0.060166	4.811809	-1.036532
F	0.938843	4.157465	-2.930487
F	-0.757125	5.529011	-2.930925
F	-0.535481	-4.086301	-1.539035
F	0.515044	-5.096393	-3.165684
F	-0.782408	-3.396430	-3.599354
C	5.456834	1.123419	2.246431
C	3.509783	5.234484	0.097508
C	4.156439	2.324505	-2.699343
C	5.554345	-1.939910	-4.994875
F	6.167651	0.855366	1.122976
F	5.124873	-0.063928	2.807646
F	6.297792	1.751187	3.103652
F	2.943023	6.290446	0.734563
F	2.916395	5.151979	-1.118351
F	4.811276	5.529245	-0.107079
F	5.079852	3.086427	-2.053581
F	2.968338	2.541680	-2.073611
F	4.051255	2.808288	-3.958829
F	6.605110	-1.348376	-5.622626
F	5.893691	-3.225840	-4.757446
F	4.525959	-1.942103	-5.875789
C	-3.517957	-5.324570	0.221152

C	-5.496642	-1.163381	2.242254
C	-4.356264	-2.534332	-2.557889
C	-5.742088	1.662053	-4.966677
F	-6.130398	2.938594	-4.765014
F	-4.685541	1.693632	-5.831812
F	-6.744250	1.017430	-5.606310
F	-5.227462	-3.225653	-1.776527
F	-4.418625	-3.077217	-3.795755
F	-3.114888	-2.756025	-2.068326
F	-5.172477	0.076660	2.690550
F	-6.272067	-0.998616	1.140533
F	-6.275027	-1.738578	3.189125
F	-2.994396	-5.299506	-1.024267
F	-4.821886	-5.666328	0.107287
F	-2.889929	-6.322961	0.891602
Si	-0.759352	1.392062	-4.852283
C	-1.647022	-0.162653	-4.286425
H	-2.540062	0.156444	-3.710948
H	-0.984306	-0.684976	-3.564362
C	-1.281334	2.037692	-6.540429
H	-2.387951	2.129365	-6.532592
H	-1.049037	1.244204	-7.284325
C	1.099560	1.333158	-4.629228
H	1.323213	1.009218	-3.592211
H	1.537719	2.343736	-4.755993
C	1.691800	0.334067	-5.640994
H	2.793223	0.275661	-5.550066
H	1.327691	-0.695864	-5.457373
H	1.461526	0.613737	-6.690323
C	-2.058774	-1.095614	-5.436201
H	-2.549791	-2.009715	-5.051078
H	-2.768408	-0.599505	-6.129626
H	-1.183021	-1.428909	-6.029796
C	-0.619062	3.366932	-6.929831
H	-0.973144	3.728257	-7.916696
H	-0.841191	4.160157	-6.186930
H	0.484837	3.273205	-6.990262

**CIP (s-trans)**

E = -9130.13585176186

P	0.953790	-0.466206	-0.632019
O	2.438547	-0.291037	0.072043
O	0.534429	-1.990269	-0.104793
C	3.335325	-1.350123	0.045352
C	4.435593	-1.283402	-0.862139
C	5.332463	-2.343742	-0.856387
C	5.161869	-3.467388	-0.000530
C	6.079222	-4.558947	-0.026588
C	5.887256	-5.672636	0.775826
C	4.756887	-5.740664	1.631771

C	3.850021	-4.691743	1.689317
C	4.031032	-3.521605	0.895438
C	3.119495	-2.407910	0.923994
C	1.925846	-2.377332	1.814361
C	2.038091	-2.442258	3.247827
C	3.297514	-2.395406	3.915409
C	3.369346	-2.417632	5.300878
C	2.188505	-2.519054	6.083391
C	0.948227	-2.558290	5.463899
C	0.836000	-2.491231	4.043612
C	-0.432915	-2.475252	3.400615
C	-0.553105	-2.355220	2.019094
C	0.651282	-2.248843	1.254498
C	4.565428	-0.133446	-1.787681
H	6.200989	-2.320140	-1.532141
H	6.941841	-4.502318	-0.708441
H	6.601472	-6.508955	0.742320
H	4.594388	-6.635280	2.251710
H	2.974093	-4.760481	2.348726
H	4.214334	-2.309570	3.317263
H	4.350675	-2.352030	5.793714
H	2.260219	-2.559081	7.180781
H	0.024781	-2.629145	6.058007
H	-1.339783	-2.569413	4.017176
C	-1.887003	-2.438614	1.367156
C	4.356689	1.181497	-1.328481
C	4.400018	2.262513	-2.218312
C	4.701208	2.063386	-3.571208
C	4.926855	0.756604	-4.032115
C	4.845068	-0.336088	-3.154804
C	-2.988036	-1.727716	1.883363
C	-4.274732	-1.929877	1.354049
C	-4.483252	-2.835176	0.304980
C	-3.387365	-3.535631	-0.222362
C	-2.099062	-3.331614	0.292262
H	4.128377	1.360294	-0.270484
H	4.731183	2.914783	-4.262756
H	4.936062	-1.360025	-3.541561
H	-2.837606	-1.012855	2.705516
H	-5.489340	-2.990768	-0.103012
H	-1.250900	-3.890926	-0.124737
N	0.074164	0.629742	0.074132
P	-0.741223	1.969700	-0.113011
O	-0.500846	2.943549	1.206246
O	-2.324543	1.490833	0.101919
C	-0.698060	2.328355	2.438069
C	0.454280	1.929501	3.186091
C	0.238927	1.215784	4.361572
C	-1.068564	0.879401	4.807824
C	-1.268858	0.107505	5.990246
C	-2.542629	-0.267205	6.390274
C	-3.669713	0.126106	5.621382

C	-3.511940	0.913666	4.489580
C	-2.216241	1.320855	4.054064
C	-2.007662	2.102651	2.861548
C	-3.145325	2.632177	2.059822
C	-4.118864	3.521735	2.641030
C	-3.991862	4.042919	3.962701
C	-4.947323	4.901057	4.488163
C	-6.078134	5.281983	3.719628
C	-6.220865	4.810046	2.424150
C	-5.251686	3.936099	1.850911
C	-5.379048	3.468231	0.513116
C	-4.417553	2.655495	-0.066068
C	-3.282389	2.282440	0.715309
C	1.829904	2.316069	2.780704
H	1.099809	0.906744	4.973644
H	-0.384324	-0.195613	6.570012
H	-2.682357	-0.872497	7.298742
H	-4.678205	-0.196633	5.919320
H	-4.389417	1.209410	3.900811
H	-3.115132	3.767000	4.564319
H	-4.822051	5.295313	5.507929
H	-6.830886	5.960183	4.148636
H	-7.083540	5.111434	1.809913
H	-6.262700	3.761957	-0.073839
C	-4.577695	2.139989	-1.453960
C	2.116151	3.632692	2.358280
C	3.440148	4.037887	2.135144
C	4.498651	3.132559	2.294033
C	4.218615	1.815484	2.686985
C	2.896826	1.406063	2.926482
C	-4.502117	3.001261	-2.567382
C	-4.671058	2.490430	-3.863168
C	-4.935874	1.127211	-4.070126
C	-4.998586	0.269846	-2.964843
C	-4.816144	0.769194	-1.664502
H	1.298834	4.355957	2.235341
H	5.532561	3.455609	2.121889
H	2.690290	0.370174	3.232384
H	-4.258796	4.060490	-2.413064
H	-5.070414	0.731566	-5.085703
H	-4.859429	0.091860	-0.801064
N	0.958025	-0.492981	-2.229455
N	-0.449358	2.800952	-1.450698
S	1.320082	-1.656487	-3.279211
O	1.083084	-1.113169	-4.639601
O	2.555369	-2.421427	-3.002648
S	-1.198521	4.175969	-1.880458
O	-1.397636	4.200215	-3.348503
O	-2.326467	4.564438	-0.992954
C	0.124668	5.480617	-1.532711
C	-0.084963	-2.934581	-3.072288
F	0.554826	5.359529	-0.270902

F	1.159066	5.353272	-2.372267
F	-0.425323	6.690547	-1.697733
F	0.257820	-3.887263	-2.199021
F	-0.329521	-3.508415	-4.262290
F	-1.205703	-2.323014	-2.648404
C	5.343546	0.825418	2.874939
C	3.718305	5.488754	1.799501
C	4.070551	3.632667	-1.678784
C	5.273193	0.518630	-5.482105
F	6.558745	1.412083	2.823544
F	5.327926	-0.143882	1.916858
F	5.248357	0.185576	4.068799
F	3.261798	6.298540	2.790546
F	3.102979	5.881509	0.662388
F	5.040656	5.732391	1.656765
F	5.027203	4.069944	-0.815623
F	2.903724	3.600372	-0.989877
F	3.953893	4.559025	-2.655128
F	6.609749	0.383038	-5.662321
F	4.694752	-0.610408	-5.960939
F	4.871142	1.548566	-6.275222
C	-3.618174	-4.605616	-1.267558
C	-5.443862	-1.173889	1.941068
C	-5.177654	-1.215066	-3.152714
C	-4.459618	3.371836	-5.071534
F	-4.514079	4.681633	-4.779617
F	-3.237998	3.124864	-5.635114
F	-5.377861	3.119001	-6.039448
F	-6.148722	-1.715370	-2.352491
F	-5.482509	-1.550441	-4.427980
F	-4.027805	-1.882680	-2.836149
F	-5.527515	-1.343969	3.282929
F	-5.328338	0.168335	1.724803
F	-6.623783	-1.557413	1.406599
F	-3.592713	-5.839898	-0.705495
F	-2.667985	-4.602409	-2.237579
F	-4.817188	-4.474093	-1.884823
C	-1.521960	-0.067702	-5.543297
H	-1.473223	-1.085878	-7.462713
O	-2.046453	-0.100212	-4.351374
O	-0.797169	0.935559	-5.851610
C	-1.640928	0.911169	-3.387854
H	-0.564481	0.787717	-3.177625
H	-2.235994	0.689419	-2.489133
H	-1.850933	1.921746	-3.776959
Si	0.297774	1.635333	-7.072209
C	0.622874	3.299514	-6.271321
H	-0.360985	3.749006	-6.013700
H	1.076527	3.963367	-7.041202
C	1.807754	0.528670	-7.161570
H	2.171166	0.418425	-6.119493
H	2.582841	1.124739	-7.694140

C	-0.705936	1.704544	-8.670264
H	-0.755706	0.679548	-9.100199
H	-0.076518	2.280933	-9.386393
C	1.510863	3.222889	-5.018777
H	1.046921	2.604020	-4.225287
H	1.675853	4.224892	-4.579823
H	2.501427	2.783982	-5.249565
C	1.651382	-0.861867	-7.787353
H	2.634621	-1.370837	-7.844748
H	1.232963	-0.827739	-8.815339
H	1.003179	-1.502974	-7.158008
C	-2.107065	2.322660	-8.565299
H	-2.599522	2.385781	-9.556876
H	-2.077512	3.345871	-8.141138
H	-2.769874	1.729713	-7.903828
H	-2.785885	-2.235117	-4.886893
C	-2.879327	-3.468214	-6.658040
C	-3.506630	-4.500022	-5.913168
C	-2.635933	-3.672344	-8.040025
C	-3.877099	-5.698903	-6.531504
H	-3.687190	-4.349675	-4.837815
C	-3.009566	-4.869855	-8.653480
H	-2.150212	-2.884236	-8.634582
C	-3.630846	-5.885491	-7.901490
H	-4.359126	-6.493338	-5.942777
H	-2.817045	-5.020112	-9.726232
H	-3.922263	-6.827852	-8.389641
C	-1.842160	-1.163882	-6.430919
C	-2.510768	-2.256397	-5.952276

**RC (*s*-trans, major)**

E = -9323.86539073144

P	0.849311	-0.815285	-0.739578
O	2.354885	-0.317630	-0.247771
O	0.698099	-2.250175	0.074271
C	3.400110	-1.208667	-0.034261
C	4.559891	-1.078804	-0.863338
C	5.590062	-1.992190	-0.677848
C	5.514900	-3.029708	0.290433
C	6.562425	-3.986606	0.431770
C	6.475082	-5.006475	1.366096
C	5.324088	-5.111378	2.190090
C	4.293196	-4.188206	2.085605
C	4.361111	-3.113558	1.150548
C	3.311891	-2.134740	1.010029
C	2.153558	-2.120064	1.948492
C	2.324664	-1.978769	3.371711
C	3.588810	-1.700726	3.970061
C	3.708504	-1.547492	5.344030
C	2.577301	-1.702239	6.188381

C	1.332493	-1.963981	5.635928
C	1.163807	-2.072885	4.223469
C	-0.125006	-2.252957	3.648244
C	-0.314326	-2.314473	2.269990
C	0.856912	-2.228295	1.449012
C	4.692122	0.020059	-1.851322
H	6.502291	-1.902734	-1.287247
H	7.441367	-3.902331	-0.225889
H	7.288693	-5.740870	1.462506
H	5.244540	-5.935539	2.914996
H	3.403279	-4.289376	2.721407
H	4.469736	-1.582826	3.326024
H	4.689537	-1.303090	5.777478
H	2.689596	-1.605858	7.278861
H	0.445444	-2.075519	6.277217
H	-0.990638	-2.339179	4.322168
C	-1.664734	-2.480479	1.672320
C	4.354855	1.342877	-1.511354
C	4.501535	2.377694	-2.448756
C	4.973084	2.113936	-3.739663
C	5.298884	0.792873	-4.086066
C	5.173458	-0.241651	-3.150856
C	-2.795107	-1.874651	2.262084
C	-4.076671	-2.069445	1.720523
C	-4.258348	-2.845922	0.566632
C	-3.137639	-3.441566	-0.027923
C	-1.859663	-3.277932	0.522463
H	3.960491	1.568148	-0.512015
H	5.055728	2.922739	-4.477584
H	5.391110	-1.274513	-3.450358
H	-2.674424	-1.234069	3.147390
H	-5.258988	-2.991534	0.140046
H	-1.008416	-3.779956	0.048734
N	-0.156034	0.227889	-0.119098
P	-0.975339	1.555320	-0.364734
O	-0.637133	2.671871	0.816041
O	-2.540524	1.114450	-0.005936
C	-0.740899	2.227889	2.129080
C	0.464641	2.022226	2.870106
C	0.353210	1.467055	4.141664
C	-0.907022	1.119731	4.700870
C	-1.004610	0.526177	5.993972
C	-2.234368	0.159788	6.519576
C	-3.418972	0.383867	5.769328
C	-3.361412	0.999628	4.526991
C	-2.113194	1.391991	3.959769
C	-2.011326	2.008564	2.661108
C	-3.217773	2.430734	1.899484
C	-4.151464	3.364521	2.479009
C	-3.914208	4.024095	3.722019
C	-4.838341	4.915887	4.246798
C	-6.047871	5.194642	3.558314

C	-6.298166	4.590198	2.336645
C	-5.361867	3.680201	1.764503
C	-5.592110	3.085207	0.494117
C	-4.661896	2.245746	-0.100213
C	-3.456311	1.956097	0.607136
C	1.783816	2.503506	2.385601
H	1.260139	1.313705	4.746039
H	-0.077184	0.357987	6.560850
H	-2.295056	-0.305866	7.514890
H	-4.392589	0.067076	6.171571
H	-4.282547	1.168570	3.955392
H	-2.977454	3.831176	4.261595
H	-4.626244	5.417678	5.202897
H	-6.774856	5.900076	3.987818
H	-7.221465	4.812486	1.779396
H	-6.529109	3.310392	-0.037841
C	-4.969433	1.649116	-1.433932
C	1.919139	3.816434	1.884352
C	3.189450	4.356208	1.637743
C	4.342806	3.583882	1.837120
C	4.211440	2.264585	2.293659
C	2.943754	1.725866	2.569846
C	-4.854410	2.421394	-2.606264
C	-5.250306	1.887798	-3.842398
C	-5.786970	0.596120	-3.923417
C	-5.887272	-0.181171	-2.760312
C	-5.475449	0.337258	-1.521517
H	1.024394	4.434874	1.728022
H	5.333872	4.009060	1.638512
H	2.852066	0.695869	2.942894
H	-4.439788	3.435534	-2.543725
H	-6.130745	0.202286	-4.889690
H	-5.574021	-0.265268	-0.608907
N	0.633861	-1.185907	-2.276126
N	-0.782772	2.242731	-1.799765
S	1.429609	-2.084431	-3.346803
O	0.651571	-2.074559	-4.608364
O	2.889826	-1.859620	-3.396408
S	-1.547594	3.579783	-2.296661
O	-1.919194	3.440036	-3.726714
O	-2.560659	4.109457	-1.345234
C	-0.163058	4.866257	-2.251236
C	1.274419	-3.866747	-2.711299
F	0.351231	4.921019	-1.017918
F	0.804531	4.561151	-3.127711
F	-0.680154	6.058677	-2.570831
F	2.094310	-4.060472	-1.670500
F	1.609897	-4.703574	-3.699274
F	0.009437	-4.130671	-2.329179
C	5.437435	1.415613	2.533356
C	3.301545	5.812978	1.237291
C	4.103390	3.774464	-2.043061

C	5.645273	0.472284	-5.519211
F	6.583923	2.080246	2.278960
F	5.435894	0.300687	1.750200
F	5.494968	0.979466	3.819126
F	2.796364	6.609572	2.215935
F	2.607613	6.091775	0.112122
F	4.584055	6.188358	1.035089
F	5.014092	4.334880	-1.201487
F	2.918228	3.757517	-1.383550
F	3.973884	4.603520	-3.101404
F	6.344711	1.472916	-6.107048
F	6.374104	-0.660530	-5.630858
F	4.517305	0.294636	-6.265233
C	-3.282297	-4.223725	-1.311114
C	-5.275676	-1.416264	2.366882
C	-6.397680	-1.595205	-2.880213
C	-5.064939	2.669437	-5.121778
F	-4.821685	3.972608	-4.910307
F	-4.016848	2.167257	-5.844352
F	-6.155578	2.571295	-5.923674
F	-6.792920	-2.108198	-1.692783
F	-7.447780	-1.683559	-3.737124
F	-5.433754	-2.424848	-3.373279
F	-5.220716	-1.475785	3.717613
F	-5.364231	-0.093811	2.034353
F	-6.436980	-1.988806	1.977232
F	-4.553688	-4.630848	-1.528527
F	-2.488811	-5.315784	-1.335338
F	-2.926224	-3.450954	-2.378671
C	-2.416014	-0.391197	-5.579624
C	-3.118356	-0.738774	-6.792629
C	-4.356298	-1.322822	-6.750766
C	-3.691227	-4.236300	-6.848959
C	-2.004037	-3.705465	-5.366651
C	-3.399253	-4.108304	-5.516977
C	-1.433820	-3.583791	-6.602361
H	-2.132230	-4.849411	-8.226697
H	-0.389840	-3.308189	-6.797450
H	-1.498330	-3.521567	-4.412816
H	-4.091760	-4.265712	-4.679366
H	-4.652723	-4.532350	-7.289162
C	-2.451588	-3.950972	-7.647276
H	-2.607446	-3.159262	-8.415092
H	-2.643964	-0.430333	-7.733193
O	-2.963150	-0.767766	-4.454287
O	-1.343619	0.303658	-5.529996
C	-2.346528	-0.357760	-3.209175
H	-2.257780	0.742507	-3.186071
H	-3.019570	-0.726483	-2.420678
H	-1.341818	-0.810169	-3.116632
Si	-0.169607	1.155912	-6.593986
C	0.795223	2.177342	-5.368554

H	1.479119	2.822535	-5.967006
H	0.061519	2.863675	-4.897658
C	-1.174611	2.231442	-7.785650
H	-0.595480	2.268626	-8.736333
H	-2.121556	1.709365	-8.042461
C	0.835682	-0.210781	-7.406817
H	1.819502	0.257499	-7.638614
H	1.048296	-0.953344	-6.606404
C	1.557183	1.396827	-4.295069
H	2.336070	0.733609	-4.719484
H	2.051351	2.086416	-3.585756
H	0.866872	0.775843	-3.698194
C	-1.474204	3.652137	-7.277673
H	-2.091979	4.214316	-8.007490
H	-2.017682	3.641261	-6.313619
H	-0.541925	4.230596	-7.118836
C	0.247642	-0.882112	-8.654130
H	0.947186	-1.629601	-9.081914
H	-0.691435	-1.424125	-8.421736
H	0.020247	-0.150361	-9.457420
H	-4.749571	-1.578550	-5.756143
C	-5.254846	-1.559391	-7.871695
C	-6.556957	-2.048285	-7.597359
C	-4.897648	-1.303396	-9.218942
C	-7.469922	-2.275324	-8.632869
H	-6.841268	-2.244390	-6.551413
C	-5.810034	-1.536241	-10.252243
H	-3.896277	-0.915273	-9.459087
C	-7.097729	-2.024488	-9.964157
H	-8.478303	-2.650041	-8.402707
H	-5.519365	-1.332610	-11.293882
H	-7.813033	-2.204738	-10.780716

### **RC (s-trans, minor)**

E = -9323.86377638752

P	0.782125	-0.681975	-0.895618
O	2.283797	-0.463960	-0.227388
O	0.373791	-2.173283	-0.293596
C	3.189966	-1.514993	-0.137781
C	4.355473	-1.463892	-0.962403
C	5.254923	-2.517160	-0.875493
C	5.026254	-3.633507	-0.025589
C	5.935288	-4.731400	0.012572
C	5.681983	-5.840411	0.804397
C	4.496850	-5.894957	1.583353
C	3.599409	-4.836434	1.579919
C	3.841956	-3.670263	0.796154
C	2.936426	-2.549205	0.763165
C	1.734456	-2.501209	1.640644
C	1.844840	-2.576585	3.073823

C	3.100926	-2.547197	3.749304
C	3.165286	-2.616280	5.133632
C	1.980588	-2.751167	5.905748
C	0.743788	-2.764442	5.278925
C	0.639314	-2.641254	3.861414
C	-0.625845	-2.562211	3.218399
C	-0.747907	-2.397713	1.839649
C	0.464146	-2.362763	1.077285
C	4.578368	-0.335904	-1.897348
H	6.169149	-2.495614	-1.487916
H	6.839892	-4.685250	-0.613328
H	6.388391	-6.683854	0.819565
H	4.282679	-6.787235	2.190841
H	2.680391	-4.898438	2.178228
H	4.022704	-2.449540	3.160795
H	4.144434	-2.567712	5.632796
H	2.046799	-2.834953	7.001002
H	-0.183180	-2.850136	5.865437
H	-1.531520	-2.626905	3.839909
C	-2.088781	-2.283110	1.207450
C	4.427002	0.996738	-1.471786
C	4.638015	2.055862	-2.366504
C	5.009846	1.809469	-3.693403
C	5.142862	0.481089	-4.128123
C	4.928962	-0.583963	-3.241187
C	-3.120492	-1.597016	1.882166
C	-4.421673	-1.558628	1.356353
C	-4.716230	-2.175318	0.133039
C	-3.689175	-2.838432	-0.557475
C	-2.391854	-2.902453	-0.027756
H	4.127420	1.208505	-0.437067
H	5.150203	2.644082	-4.392054
H	4.965986	-1.619748	-3.603500
H	-2.905396	-1.084943	2.830983
H	-5.736274	-2.152963	-0.271297
H	-1.615666	-3.456117	-0.568478
N	-0.137523	0.404711	-0.231064
P	-0.766763	1.851063	-0.323265
O	-0.291912	2.767795	0.977404
O	-2.378970	1.579247	-0.009356
C	-0.457363	2.182443	2.228438
C	0.703594	1.718437	2.923272
C	0.505708	1.034588	4.120327
C	-0.792927	0.799554	4.647602
C	-0.978672	0.069624	5.858657
C	-2.250516	-0.189617	6.346235
C	-3.388302	0.283231	5.640265
C	-3.238984	1.035685	4.483729
C	-1.944814	1.323655	3.958182
C	-1.748063	2.076116	2.744613
C	-2.885635	2.735322	2.050127
C	-3.702607	3.696425	2.748700

C	-3.374481	4.187964	4.047423
C	-4.187234	5.111627	4.688836
C	-5.370497	5.589570	4.067289
C	-5.706449	5.148678	2.796976
C	-4.884874	4.210543	2.106821
C	-5.207794	3.766527	0.795250
C	-4.379612	2.906681	0.090214
C	-3.188185	2.436191	0.719314
C	2.083215	2.053531	2.489185
H	1.377574	0.684958	4.693790
H	-0.086724	-0.294775	6.389062
H	-2.381002	-0.763348	7.276394
H	-4.398907	0.052719	6.008443
H	-4.124914	1.396726	3.947088
H	-2.455328	3.838021	4.536556
H	-3.906389	5.482338	5.686272
H	-6.009443	6.317881	4.588789
H	-6.610615	5.524644	2.293654
H	-6.135288	4.125567	0.323803
C	-4.810139	2.426736	-1.257205
C	2.410229	3.366589	2.086774
C	3.749206	3.742202	1.904858
C	4.781920	2.807752	2.070752
C	4.458947	1.490407	2.429365
C	3.122600	1.113581	2.636973
C	-4.543207	3.158914	-2.427453
C	-5.074095	2.734455	-3.657626
C	-5.885539	1.593715	-3.736792
C	-6.149607	0.861387	-2.567732
C	-5.611562	1.270752	-1.338843
H	1.614273	4.112699	1.958384
H	5.827511	3.107536	1.929058
H	2.882599	0.081916	2.931482
H	-3.924886	4.063988	-2.365038
H	-6.328568	1.292852	-4.696482
H	-5.848207	0.716504	-0.422466
N	0.729142	-0.801064	-2.497208
N	-0.457770	2.647398	-1.678806
S	1.361355	-1.958692	-3.429891
O	1.214744	-1.534964	-4.841572
O	2.644665	-2.539954	-2.975409
S	-1.091821	4.088425	-2.064789
O	-1.367606	4.141360	-3.517998
O	-2.133379	4.568930	-1.114863
C	0.346405	5.284796	-1.763750
C	0.148383	-3.415424	-3.275848
F	0.867159	5.070008	-0.549435
F	1.302617	5.144238	-2.690870
F	-0.134042	6.532743	-1.824516
F	0.454315	-4.197873	-2.235224
F	0.207575	-4.147353	-4.398484
F	-1.108030	-2.956535	-3.121113

C	5.546586	0.462654	2.635665
C	4.068281	5.198698	1.636197
C	4.414043	3.462472	-1.870137
C	5.506599	0.196385	-5.566006
F	6.783254	0.998423	2.559983
F	5.481327	-0.532489	1.709138
F	5.433709	-0.138227	3.849633
F	3.723032	5.958849	2.709263
F	3.385748	5.687332	0.577838
F	5.385530	5.400015	1.410597
F	5.377064	3.836654	-0.985616
F	3.226531	3.555998	-1.224131
F	4.412480	4.371515	-2.870389
F	6.842425	0.035435	-5.728357
F	4.913064	-0.934438	-6.021417
F	5.128009	1.210625	-6.389892
C	-4.003829	-3.460958	-1.899073
C	-5.512019	-0.843080	2.119289
C	-7.039979	-0.355454	-2.646543
C	-4.736891	3.500802	-4.915200
F	-4.534624	4.807652	-4.686350
F	-3.590803	3.006996	-5.485297
F	-5.706322	3.382469	-5.855306
F	-7.451850	-0.769584	-1.422833
F	-8.141406	-0.121602	-3.393812
F	-6.396630	-1.413209	-3.218134
F	-5.466344	-1.118613	3.443524
F	-5.401053	0.514093	1.998181
F	-6.745034	-1.169519	1.672527
F	-3.214481	-4.527977	-2.174241
F	-3.821290	-2.564579	-2.911998
F	-5.287231	-3.877390	-1.973429
C	-1.472828	-0.479695	-5.558949
C	-1.423750	-1.624994	-6.430490
C	-2.028869	-2.801052	-6.081653
C	-4.761551	-2.326394	-7.233837
C	-4.367840	-0.076981	-6.920868
C	-4.901166	-1.305565	-6.334076
C	-3.898673	-0.342033	-8.177530
H	-4.827984	-1.902509	-9.365357
H	-3.455720	0.382207	-8.874140
H	-4.336461	0.899963	-6.421165
H	-5.320432	-1.387534	-5.322394
H	-5.062666	-3.372684	-7.093211
C	-4.143508	-1.790352	-8.491987
H	-3.220363	-2.341790	-8.779489
H	-0.785719	-1.530024	-7.317560
O	-2.259135	-0.552203	-4.516100
O	-0.796145	0.593967	-5.727262
C	-2.212821	0.502231	-3.519967
H	-1.219125	0.483612	-3.037353
H	-3.009565	0.250108	-2.800522

H	-2.384529	1.487857	-3.986758
Si	0.398547	1.340125	-6.837893
C	0.870394	2.822414	-5.800205
H	-0.055798	3.330490	-5.454697
H	1.399316	3.545255	-6.461343
C	1.886232	0.242150	-7.167654
H	2.312986	-0.037447	-6.184698
H	2.607236	0.965975	-7.615725
C	-0.590275	1.710725	-8.402237
H	-1.022581	0.752470	-8.767530
H	0.157981	2.003130	-9.173532
C	1.741755	2.440294	-4.593273
H	1.219476	1.735006	-3.916055
H	2.005246	3.329648	-3.992725
H	2.685520	1.957161	-4.911036
C	1.771509	-1.009476	-8.043849
H	2.777659	-1.383820	-8.323020
H	1.210579	-0.832646	-8.986563
H	1.278640	-1.828986	-7.484419
C	-1.676390	2.786646	-8.267483
H	-2.211702	2.952165	-9.225449
H	-1.245549	3.760686	-7.958613
H	-2.432019	2.520575	-7.503653
H	-2.598751	-2.812773	-5.142133
C	-1.897347	-4.081216	-6.759156
C	-2.426166	-5.230615	-6.121557
C	-1.221654	-4.239906	-7.994345
C	-2.288921	-6.496553	-6.701216
H	-2.925873	-5.113204	-5.147083
C	-1.091807	-5.504806	-8.574919
H	-0.784647	-3.363863	-8.496669
C	-1.625721	-6.636728	-7.931819
H	-2.695264	-7.380946	-6.188018
H	-0.562277	-5.614407	-9.533098
H	-1.516673	-7.631449	-8.389710

TS (s-trans, major)

E = -9323.85434826665

P	0.852586	-0.809522	-0.742533
O	2.355070	-0.307852	-0.246114
O	0.699581	-2.239985	0.079168
C	3.400858	-1.199314	-0.035668
C	4.556977	-1.072828	-0.870230
C	5.584116	-1.991042	-0.690349
C	5.508819	-3.029854	0.276514
C	6.550846	-3.994110	0.409060
C	6.461935	-5.016194	1.340825
C	5.315539	-5.115312	2.171950
C	4.290662	-4.184500	2.076887
C	4.359824	-3.108429	1.143602
C	3.314629	-2.124759	1.009222
C	2.158958	-2.107100	1.950733
C	2.332458	-1.965767	3.373716
C	3.598762	-1.693929	3.970219
C	3.721144	-1.541906	5.344104
C	2.590247	-1.689840	6.190013
C	1.343268	-1.944817	5.639366
C	1.172364	-2.054603	4.227329
C	-0.117648	-2.233679	3.654391
C	-0.307735	-2.299955	2.276781
C	0.861639	-2.214551	1.453434
C	4.687477	0.025589	-1.858743
H	6.493679	-1.905083	-1.304133
H	7.426430	-3.914295	-0.253643
H	7.270715	-5.756835	1.429900
H	5.234646	-5.941186	2.894710
H	3.404162	-4.280970	2.718194
H	4.479388	-1.580218	3.324949
H	4.704223	-1.303761	5.776405
H	2.704657	-1.594147	7.280301
H	0.456533	-2.051882	6.281836
H	-0.982916	-2.317519	4.329061
C	-1.655994	-2.477804	1.679022
C	4.343838	1.347680	-1.521722
C	4.487145	2.381149	-2.460846
C	4.963037	2.117548	-3.750206
C	5.296680	0.797696	-4.093175
C	5.173313	-0.235758	-3.156556
C	-2.792126	-1.870251	2.254887
C	-4.070064	-2.080714	1.709908
C	-4.242094	-2.875234	0.566726
C	-3.114669	-3.473546	-0.012500
C	-1.840715	-3.293302	0.540767
H	3.947128	1.573731	-0.523544
H	5.042825	2.925456	-4.489422
H	5.396725	-1.267909	-3.454225

H	-2.678842	-1.216292	3.131438
H	-5.239760	-3.031691	0.137117
H	-0.983927	-3.796354	0.078329
N	-0.157581	0.235640	-0.137049
P	-0.980774	1.560857	-0.388052
O	-0.646621	2.678998	0.792501
O	-2.544758	1.113621	-0.029739
C	-0.754013	2.237771	2.105852
C	0.449527	2.033077	2.850767
C	0.334059	1.479614	4.122682
C	-0.927981	1.133284	4.678393
C	-1.029110	0.539747	5.971242
C	-2.260327	0.173815	6.493761
C	-3.442912	0.398919	5.740613
C	-3.381895	1.014481	4.498316
C	-2.132055	1.405700	3.933819
C	-2.026176	2.019763	2.634165
C	-3.230853	2.437223	1.866592
C	-4.168022	3.371701	2.439030
C	-3.933604	4.040275	3.677726
C	-4.860502	4.933466	4.195380
C	-6.069975	5.204326	3.503581
C	-6.317843	4.590120	2.286264
C	-5.379017	3.678210	1.721621
C	-5.608587	3.069936	0.457344
C	-4.675606	2.229515	-0.130987
C	-3.466499	1.953687	0.576909
C	1.770243	2.513320	2.369413
H	1.238811	1.326696	4.730451
H	-0.103023	0.371350	6.540410
H	-2.323665	-0.291942	7.488874
H	-4.417727	0.082964	6.140510
H	-4.301393	1.183939	3.924309
H	-2.996626	3.853250	4.219207
H	-4.650657	5.442557	5.148180
H	-6.799110	5.911137	3.927142
H	-7.241293	4.805759	1.726772
H	-6.548026	3.284535	-0.074581
C	-4.987568	1.607171	-1.452579
C	1.906289	3.824249	1.863162
C	3.176961	4.364289	1.619185
C	4.330327	3.593807	1.825427
C	4.198522	2.276121	2.286631
C	2.930330	1.737510	2.560918
C	-4.857402	2.343374	-2.646911
C	-5.247636	1.774419	-3.869198
C	-5.789342	0.482968	-3.916528
C	-5.910117	-0.255333	-2.730912
C	-5.508168	0.299281	-1.504586
H	1.011654	4.441109	1.700282
H	5.321723	4.019157	1.628598
H	2.838455	0.708900	2.937731

H	-4.434625	3.355618	-2.612946
H	-6.120397	0.059958	-4.875296
H	-5.622128	-0.273150	-0.574722
N	0.646700	-1.197153	-2.277101
N	-0.785035	2.244673	-1.822830
S	1.435527	-2.104129	-3.341294
O	0.627759	-2.152956	-4.584409
O	2.887391	-1.846507	-3.437975
S	-1.560670	3.573875	-2.326206
O	-1.928382	3.428856	-3.755801
O	-2.580708	4.095721	-1.377734
C	-0.184805	4.869576	-2.281698
C	1.338304	-3.875547	-2.665314
F	0.328041	4.931796	-1.047769
F	0.785656	4.567965	-3.155843
F	-0.709357	6.057678	-2.605260
F	2.160907	-4.025751	-1.620401
F	1.699784	-4.723306	-3.635945
F	0.079238	-4.171035	-2.281831
C	5.424559	1.428994	2.532600
C	3.288807	5.820068	1.214874
C	4.081673	3.776867	-2.058590
C	5.651112	0.475793	-5.524008
F	6.571336	2.094464	2.281778
F	5.427601	0.312742	1.750986
F	5.477542	0.994776	3.819197
F	2.788676	6.619094	2.194214
F	2.589995	6.096724	0.092326
F	4.570748	6.193992	1.006526
F	4.990643	4.343770	-1.219351
F	2.897273	3.755687	-1.398255
F	3.947389	4.602106	-3.119153
F	6.342613	1.481166	-6.112769
F	6.392265	-0.650111	-5.628309
F	4.528352	0.283169	-6.273655
C	-3.242790	-4.278733	-1.281686
C	-5.275114	-1.427248	2.345085
C	-6.426439	-1.669133	-2.811487
C	-5.059394	2.510116	-5.175479
F	-4.726067	3.800050	-5.010785
F	-4.074708	1.918280	-5.917893
F	-6.183667	2.462111	-5.933941
F	-6.836208	-2.143386	-1.612391
F	-7.466801	-1.781953	-3.675810
F	-5.459493	-2.519345	-3.265842
F	-5.234197	-1.491651	3.696028
F	-5.357839	-0.103600	2.016634
F	-6.433173	-1.996386	1.941024
F	-4.509694	-4.693969	-1.508996
F	-2.446111	-5.369699	-1.277360
F	-2.873458	-3.526306	-2.360228
C	-2.336006	-0.557484	-5.501664

C	-2.911927	-1.082027	-6.694079
C	-4.200836	-1.691126	-6.680623
C	-3.842185	-3.703077	-6.757787
C	-2.021030	-3.625571	-5.342247
C	-3.390628	-3.949842	-5.433380
C	-1.566156	-3.246114	-6.608754
H	-2.371347	-4.683066	-7.955681
H	-0.535364	-2.942334	-6.832212
H	-1.427291	-3.578136	-4.423292
H	-4.033349	-4.214435	-4.583694
H	-4.803185	-4.080737	-7.137290
C	-2.599227	-3.642059	-7.621454
H	-2.666960	-3.023662	-8.535592
H	-2.454994	-0.746189	-7.632652
O	-2.917999	-0.896095	-4.371624
O	-1.321359	0.232696	-5.439835
C	-2.380055	-0.377657	-3.133043
H	-2.356235	0.725291	-3.170423
H	-3.062454	-0.738948	-2.348707
H	-1.355392	-0.762866	-2.974817
Si	-0.220841	1.073597	-6.571620
C	0.757319	2.153308	-5.406049
H	1.422970	2.784866	-6.038216
H	0.028015	2.845163	-4.937055
C	-1.306056	2.070797	-7.762150
H	-0.789465	2.073409	-8.748345
H	-2.255698	1.517479	-7.929708
C	0.836523	-0.259847	-7.391661
H	1.840011	0.209013	-7.508265
H	0.987262	-1.051206	-6.624630
C	1.548242	1.407897	-4.327434
H	2.320610	0.734632	-4.748727
H	2.055690	2.119589	-3.650039
H	0.874012	0.801747	-3.697054
C	-1.605379	3.508212	-7.304565
H	-2.281614	4.021934	-8.018017
H	-2.085680	3.534228	-6.307942
H	-0.677879	4.111558	-7.234793
C	0.371147	-0.838850	-8.733892
H	1.089120	-1.588856	-9.125226
H	-0.611760	-1.347768	-8.655677
H	0.265820	-0.054148	-9.511247
H	-4.690377	-1.684244	-5.696691
C	-5.158991	-1.527529	-7.804998
C	-6.537496	-1.709609	-7.546227
C	-4.762185	-1.195456	-9.119064
C	-7.487372	-1.565171	-8.565608
H	-6.861796	-1.964996	-6.524134
C	-5.712229	-1.055709	-10.139819
H	-3.699777	-1.025705	-9.350951
C	-7.077749	-1.240559	-9.868795
H	-8.555491	-1.703723	-8.339956

H -5.383374 -0.790873 -11.156114  
H -7.821639 -1.125207 -10.671215

TS (s-trans, minor)

E = -9323.85080394122

P 0.776751 -0.690212 -0.895570  
O 2.281820 -0.480484 -0.232949  
O 0.370059 -2.184837 -0.299919  
C 3.183125 -1.535620 -0.149562  
C 4.344127 -1.487824 -0.980268  
C 5.242873 -2.541831 -0.895300  
C 5.019447 -3.653604 -0.038139  
C 5.932267 -4.748140 0.003659  
C 5.687450 -5.851344 0.806093  
C 4.506392 -5.903687 1.591402  
C 3.604745 -4.848672 1.583519  
C 3.839288 -3.687485 0.789887  
C 2.932050 -2.567676 0.754872  
C 1.730974 -2.516497 1.633708  
C 1.841287 -2.587300 3.067142  
C 3.097196 -2.553789 3.742826  
C 3.161289 -2.614760 5.127599  
C 1.976506 -2.746404 5.900190  
C 0.739912 -2.764598 5.273055  
C 0.635640 -2.648492 3.854893  
C -0.629421 -2.570110 3.211665  
C -0.751693 -2.406218 1.832786  
C 0.460549 -2.375596 1.070405  
C 4.570654 -0.357715 -1.911704  
H 6.154632 -2.522082 -1.511472  
H 6.833721 -4.702922 -0.626864  
H 6.397876 -6.691337 0.825416  
H 4.299311 -6.791255 2.208179  
H 2.689451 -4.908876 2.187603  
H 4.018940 -2.458100 3.153926  
H 4.140201 -2.561616 5.626826  
H 2.042440 -2.822981 6.996025  
H -0.187109 -2.847053 5.859931  
H -1.534806 -2.633172 3.833649  
C -2.092903 -2.284653 1.201900  
C 4.431225 0.974266 -1.479991  
C 4.655094 2.035616 -2.369113  
C 5.027865 1.791647 -3.696068  
C 5.147146 0.464007 -4.137192  
C 4.920115 -0.602985 -3.256281  
C -3.122182 -1.602219 1.884552  
C -4.424687 -1.557175 1.362896  
C -4.723385 -2.162660 0.135334  
C -3.699082 -2.820243 -0.564107  
C -2.400132 -2.891687 -0.038930

H	4.132032	1.184251	-0.444830
H	5.177052	2.627969	-4.390928
H	4.947101	-1.637136	-3.623980
H	-2.904409	-1.098298	2.837031
H	-5.744755	-2.136430	-0.265305
H	-1.626672	-3.441862	-0.587422
N	-0.135765	0.394235	-0.214546
P	-0.768511	1.837919	-0.320522
O	-0.298698	2.762056	0.977170
O	-2.382259	1.567440	-0.008938
C	-0.461338	2.177235	2.228662
C	0.700596	1.713920	2.922180
C	0.504662	1.030945	4.119941
C	-0.793073	0.796635	4.649661
C	-0.976450	0.069554	5.862711
C	-2.247268	-0.188251	6.353597
C	-3.386409	0.283036	5.648813
C	-3.239378	1.032458	4.489953
C	-1.946275	1.319081	3.961074
C	-1.751406	2.069348	2.745831
C	-2.889535	2.725954	2.049687
C	-3.706278	3.688857	2.745890
C	-3.377071	4.184362	4.042827
C	-4.188128	5.111610	4.681092
C	-5.370915	5.589162	4.058330
C	-5.708519	5.143566	2.790100
C	-4.888593	4.201670	2.103152
C	-5.212724	3.752949	0.793572
C	-4.384116	2.891978	0.090381
C	-3.191399	2.424177	0.719061
C	2.079412	2.047925	2.485059
H	1.377463	0.681446	4.692009
H	-0.083440	-0.293250	6.392295
H	-2.375819	-0.759344	7.285612
H	-4.396257	0.053928	6.020003
H	-4.126324	1.392680	3.954367
H	-2.458097	3.834982	4.532599
H	-3.906097	5.485748	5.676837
H	-6.008082	6.321003	4.577046
H	-6.612365	5.518936	2.285657
H	-6.141045	4.109724	0.321958
C	-4.818434	2.407792	-1.254272
C	2.406643	3.361398	2.084446
C	3.745476	3.735681	1.899039
C	4.777441	2.799578	2.059913
C	4.453992	1.481806	2.416395
C	3.117849	1.106193	2.627573
C	-4.540063	3.127438	-2.429683
C	-5.080170	2.704275	-3.656303
C	-5.911300	1.577105	-3.725243
C	-6.182496	0.853795	-2.552452
C	-5.636255	1.262573	-1.327161

H	1.610941	4.108591	1.960468
H	5.822858	3.098376	1.915286
H	2.877168	0.074227	2.920455
H	-3.907372	4.023086	-2.373321
H	-6.368414	1.281239	-4.679848
H	-5.878951	0.717197	-0.407041
N	0.712529	-0.792370	-2.495200
N	-0.458887	2.629392	-1.678485
S	1.321738	-1.936654	-3.458726
O	1.164377	-1.482169	-4.858779
O	2.601733	-2.539457	-3.022942
S	-1.088269	4.068957	-2.073360
O	-1.364901	4.115069	-3.527316
O	-2.129455	4.559506	-1.127826
C	0.356063	5.260055	-1.782061
C	0.086657	-3.373759	-3.334731
F	0.879041	5.048802	-0.568158
F	1.308007	5.108520	-2.711507
F	-0.117885	6.510338	-1.847964
F	0.348668	-4.163100	-2.285829
F	0.165590	-4.102420	-4.455623
F	-1.165717	-2.891981	-3.213425
C	5.541127	0.452114	2.615400
C	4.065271	5.191929	1.630248
C	4.440828	3.442197	-1.868277
C	5.508547	0.184463	-5.576631
F	6.778154	0.986608	2.537030
F	5.471350	-0.539855	1.685812
F	5.432035	-0.152742	3.827796
F	3.716167	5.953183	2.701350
F	3.386456	5.679565	0.569018
F	5.383199	5.393247	1.408863
F	5.402942	3.806270	-0.978325
F	3.251384	3.543398	-1.226685
F	4.450425	4.354819	-2.865205
F	6.846370	0.045337	-5.744969
F	4.930840	-0.954846	-6.029382
F	5.110636	1.193302	-6.398144
C	-4.022000	-3.427697	-1.910255
C	-5.512837	-0.846049	2.132600
C	-7.094126	-0.347192	-2.625600
C	-4.737093	3.457232	-4.920499
F	-4.511317	4.761063	-4.703938
F	-3.605955	2.938355	-5.497874
F	-5.716471	3.347388	-5.854163
F	-7.483960	-0.772913	-1.400152
F	-8.208658	-0.085538	-3.344837
F	-6.482512	-1.407971	-3.229473
F	-5.459658	-1.121955	3.456154
F	-5.407950	0.511645	2.011027
F	-6.747355	-1.176536	1.691859
F	-3.225785	-4.481776	-2.209763

F	-3.863393	-2.513834	-2.912709
F	-5.302757	-3.856052	-1.976289
C	-1.550087	-0.398458	-5.649526
C	-1.675189	-1.471038	-6.579202
C	-2.367855	-2.664176	-6.212267
C	-4.227224	-2.448928	-6.968283
C	-4.344960	-0.158086	-6.731940
C	-4.773823	-1.388284	-6.192334
C	-3.583572	-0.411027	-7.878401
H	-4.698975	-1.855406	-8.968666
H	-3.117755	0.355248	-8.512690
H	-4.480327	0.828618	-6.274636
H	-5.321654	-1.513235	-5.249123
H	-4.602305	-3.480664	-6.897011
C	-3.812513	-1.833202	-8.289625
H	-2.986530	-2.336642	-8.823885
H	-0.993024	-1.442713	-7.436415
O	-2.304867	-0.464974	-4.574107
O	-0.793431	0.633922	-5.780380
C	-2.155515	0.539860	-3.539470
H	-1.156131	0.424760	-3.081937
H	-2.951681	0.316623	-2.809455
H	-2.262446	1.556277	-3.956862
Si	0.424748	1.356095	-6.858698
C	0.939060	2.810437	-5.798329
H	0.024434	3.344664	-5.460938
H	1.502579	3.523670	-6.441061
C	1.867911	0.206272	-7.214914
H	2.322847	-0.055114	-6.239768
H	2.597290	0.882077	-7.720194
C	-0.515436	1.818703	-8.431571
H	-0.906862	0.883849	-8.891400
H	0.259428	2.181091	-9.144654
C	1.775943	2.384674	-4.582898
H	1.219490	1.687993	-3.925081
H	2.059558	3.257016	-3.966896
H	2.707460	1.874675	-4.893081
C	1.660613	-1.073740	-8.031381
H	2.635770	-1.517683	-8.318066
H	1.088133	-0.904489	-8.968657
H	1.134529	-1.836506	-7.424384
C	-1.624946	2.865384	-8.263446
H	-2.129853	3.091099	-9.225339
H	-1.222632	3.820595	-7.869987
H	-2.401394	2.539130	-7.544321
H	-2.666712	-2.707621	-5.156101
C	-1.972739	-3.991872	-6.754355
C	-2.349610	-5.148211	-6.033822
C	-1.229985	-4.155146	-7.943683
C	-2.007055	-6.425553	-6.493255
H	-2.897930	-5.032036	-5.085401
C	-0.887675	-5.434124	-8.404551

H	-0.888402	-3.275840	-8.510523
C	-1.278495	-6.574237	-7.684744
H	-2.302966	-7.312130	-5.912344
H	-0.300852	-5.539935	-9.329472
H	-1.005819	-7.577076	-8.046247

**P (s-trans, major)**

E = -9323.89299227211

P	0.855760	-0.748004	-0.718468
O	2.367142	-0.277711	-0.224982
O	0.698538	-2.199059	0.063907
C	3.399922	-1.189886	-0.038819
C	4.544237	-1.077698	-0.890910
C	5.561180	-2.010927	-0.727900
C	5.485080	-3.050905	0.237600
C	6.517452	-4.027510	0.355321
C	6.427595	-5.051031	1.285303
C	5.290067	-5.139264	2.129927
C	4.274641	-4.196846	2.049288
C	4.345210	-3.119185	1.117882
C	3.310457	-2.123114	0.998020
C	2.156031	-2.102588	1.940456
C	2.329211	-1.970011	3.363889
C	3.596673	-1.708492	3.962139
C	3.718406	-1.561714	5.336644
C	2.585085	-1.703282	6.180495
C	1.336936	-1.948238	5.627781
C	1.167317	-2.054564	4.215324
C	-0.122279	-2.226977	3.639534
C	-0.311847	-2.284946	2.261313
C	0.858781	-2.197263	1.440411
C	4.670685	0.020253	-1.879807
H	6.463755	-1.935244	-1.353239
H	7.386223	-3.955593	-0.317132
H	7.228746	-5.801203	1.362686
H	5.208584	-5.966000	2.851650
H	3.394955	-4.284448	2.701144
H	4.478049	-1.597417	3.317341
H	4.702492	-1.331924	5.771181
H	2.698585	-1.610399	7.271113
H	0.448485	-2.050307	6.268738
H	-0.988618	-2.312133	4.312567
C	-1.660162	-2.457420	1.662670
C	4.331654	1.343324	-1.541071
C	4.460622	2.374372	-2.484462
C	4.921983	2.107822	-3.778655
C	5.252959	0.787482	-4.122656
C	5.140566	-0.243909	-3.182678
C	-2.797258	-1.865258	2.252208
C	-4.075963	-2.077780	1.710237

C	-4.247619	-2.857312	0.556728
C	-3.118579	-3.435185	-0.040303
C	-1.844141	-3.254785	0.511108
H	3.948773	1.571854	-0.538251
H	4.992256	2.914038	-4.520778
H	5.359159	-1.276557	-3.482444
H	-2.685529	-1.223127	3.137625
H	-5.246369	-3.017786	0.131818
H	-0.986728	-3.744787	0.036436
N	-0.136790	0.292983	-0.073611
P	-0.983382	1.597196	-0.365949
O	-0.682959	2.734204	0.803036
O	-2.549651	1.137283	-0.030897
C	-0.788270	2.284656	2.115591
C	0.415286	2.071176	2.857618
C	0.298039	1.505144	4.123724
C	-0.964568	1.153662	4.674885
C	-1.065724	0.545671	5.961006
C	-2.297086	0.174570	6.479500
C	-3.479521	0.408079	5.728812
C	-3.418279	1.034284	4.491768
C	-2.168482	1.431265	3.931525
C	-2.060687	2.054292	2.636190
C	-3.263946	2.458258	1.858576
C	-4.214782	3.383875	2.421970
C	-3.992864	4.060969	3.658298
C	-4.931152	4.947645	4.166465
C	-6.140117	5.201990	3.467467
C	-6.377090	4.577185	2.253342
C	-5.426488	3.671686	1.698277
C	-5.646103	3.048634	0.439356
C	-4.700636	2.216787	-0.141422
C	-3.487184	1.965623	0.569625
C	1.737752	2.543957	2.374892
H	1.202176	1.343561	4.730110
H	-0.139700	0.370032	6.528194
H	-2.360695	-0.302355	7.469291
H	-4.454396	0.088680	6.125817
H	-4.337689	1.206860	3.918541
H	-3.056541	3.885808	4.205008
H	-4.731184	5.464337	5.117281
H	-6.878114	5.904063	3.883415
H	-7.300924	4.778938	1.689367
H	-6.589072	3.242913	-0.094135
C	-5.011761	1.563237	-1.449179
C	1.880383	3.850950	1.860587
C	3.153277	4.380916	1.606548
C	4.302581	3.604663	1.813246
C	4.164281	2.290976	2.284183
C	2.893844	1.761626	2.565978
C	-4.856552	2.254669	-2.667429
C	-5.234575	1.641654	-3.872973

C	-5.786237	0.354337	-3.879745
C	-5.942546	-0.334752	-2.669438
C	-5.554829	0.262156	-1.459163
H	0.989106	4.472469	1.697247
H	5.295907	4.022373	1.609638
H	2.797230	0.734687	2.946585
H	-4.422220	3.262789	-2.664920
H	-6.098970	-0.101427	-4.829218
H	-5.693266	-0.270969	-0.509721
N	0.630712	-1.079497	-2.262100
N	-0.773719	2.251698	-1.812539
S	1.338108	-1.970719	-3.391089
O	0.428987	-2.013067	-4.564899
O	2.772394	-1.693368	-3.611228
S	-1.562811	3.553738	-2.361506
O	-1.909040	3.364091	-3.792103
O	-2.604598	4.083359	-1.441772
C	-0.206451	4.870597	-2.334606
C	1.316642	-3.749442	-2.732530
F	0.307701	4.954434	-1.103054
F	0.766161	4.571896	-3.207788
F	-0.748768	6.046627	-2.671780
F	2.198743	-3.886910	-1.734858
F	1.646671	-4.575967	-3.731568
F	0.088714	-4.078318	-2.287320
C	5.386456	1.438057	2.529537
C	3.271562	5.832286	1.188983
C	4.054352	3.769724	-2.080419
C	5.592080	0.465288	-5.557119
F	6.536399	2.101459	2.287859
F	5.389405	0.327254	1.739572
F	5.432490	0.994589	3.812889
F	2.785451	6.643434	2.165205
F	2.564071	6.102643	0.069965
F	4.553866	6.195711	0.965556
F	4.968908	4.341862	-1.251802
F	2.876080	3.746360	-1.409403
F	3.906266	4.591487	-3.142647
F	6.309815	1.454981	-6.141102
F	6.299296	-0.680548	-5.673105
F	4.461006	0.312188	-6.304257
C	-3.249948	-4.209563	-1.330124
C	-5.282100	-1.439751	2.358432
C	-6.503424	-1.734411	-2.718224
C	-5.020642	2.311439	-5.210161
F	-4.650713	3.597518	-5.105716
F	-4.042685	1.654126	-5.912821
F	-6.135876	2.257031	-5.977728
F	-6.843449	-2.200970	-1.493268
F	-7.607690	-1.803516	-3.503275
F	-5.601701	-2.607188	-3.246273
F	-5.227991	-1.504443	3.708749

F	-5.382643	-0.115616	2.032312
F	-6.437503	-2.020370	1.964595
F	-4.500752	-4.687068	-1.520659
F	-2.397381	-5.257400	-1.385037
F	-2.960708	-3.409199	-2.394361
C	-2.158308	-0.749011	-5.395953
C	-2.525080	-1.610548	-6.552028
C	-4.018700	-2.060967	-6.586647
C	-3.879926	-3.625268	-6.855402
C	-2.095064	-3.807686	-5.394982
C	-3.380814	-4.198951	-5.543023
C	-1.727214	-2.996164	-6.618659
H	-2.257113	-4.713883	-7.903142
H	-0.650798	-2.854422	-6.809796
H	-1.456658	-3.917226	-4.511639
H	-4.011399	-4.688607	-4.788321
H	-4.801025	-4.063445	-7.280577
C	-2.593119	-3.678613	-7.701292
H	-2.655542	-3.113517	-8.654597
H	-2.258585	-1.041707	-7.461663
O	-2.738846	-1.033497	-4.274413
O	-1.335212	0.218296	-5.442189
C	-2.378103	-0.287210	-3.081353
H	-2.424902	0.794260	-3.291960
H	-3.109853	-0.593944	-2.319894
H	-1.348788	-0.571845	-2.792732
Si	-0.257542	1.032390	-6.652930
C	0.692361	2.194329	-5.547758
H	1.339672	2.801362	-6.222040
H	-0.046722	2.895396	-5.108303
C	-1.436834	1.908227	-7.844455
H	-0.968765	1.871800	-8.853553
H	-2.365380	1.302417	-7.929595
C	0.824739	-0.308197	-7.424355
H	1.833185	0.158980	-7.494286
H	0.944238	-1.101202	-6.654000
C	1.511488	1.524808	-4.439741
H	2.262274	0.810392	-4.829786
H	2.049254	2.282851	-3.841279
H	0.853211	0.980703	-3.738484
C	-1.778613	3.356482	-7.456838
H	-2.517417	3.792131	-8.159541
H	-2.205245	3.424532	-6.438106
H	-0.878482	4.003210	-7.478431
C	0.416340	-0.879380	-8.788187
H	1.141042	-1.641600	-9.139648
H	-0.577425	-1.372711	-8.765821
H	0.365841	-0.093375	-9.569225
H	-4.458627	-1.941536	-5.579912
C	-4.916326	-1.331962	-7.563613
C	-6.291165	-1.235712	-7.254762
C	-4.472320	-0.773109	-8.778873

C	-7.186001	-0.581424	-8.112199
H	-6.661729	-1.688082	-6.320145
C	-5.365874	-0.121848	-9.643891
H	-3.411154	-0.833496	-9.065355
C	-6.724285	-0.016369	-9.311406
H	-8.249501	-0.507781	-7.838643
H	-4.991923	0.312821	-10.583250
H	-7.420663	0.505928	-9.984287

**P (s-trans, minor)**

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O	0.498982	-2.239353	-0.159551
C	3.299020	-1.597749	-0.104107
C	4.438578	-1.594533	-0.964334
C	5.321444	-2.661736	-0.875145
C	5.104428	-3.743009	0.022144
C	5.992938	-4.857259	0.064906
C	5.752471	-5.929427	0.909780
C	4.602186	-5.927857	1.741335
C	3.725863	-4.851843	1.733996
C	3.954882	-3.723589	0.892552
C	3.064817	-2.591033	0.846756
C	1.891020	-2.495132	1.757754
C	2.037782	-2.499290	3.189194
C	3.310364	-2.448785	3.830538
C	3.408247	-2.434736	5.214662
C	2.241399	-2.502879	6.021852
C	0.989185	-2.541322	5.427260
C	0.851023	-2.507381	4.007633
C	-0.428998	-2.466657	3.391368
C	-0.586790	-2.378944	2.008952
C	0.609265	-2.378167	1.218704
C	4.672153	-0.486279	-1.921315
H	6.214320	-2.676388	-1.518663
H	6.870551	-4.853231	-0.599993
H	6.442153	-6.786592	0.927951
H	4.397981	-6.790512	2.393468
H	2.833493	-4.870631	2.374090
H	4.217181	-2.395621	3.213876
H	4.399761	-2.369123	5.686818
H	2.334014	-2.516674	7.118410
H	0.076413	-2.580884	6.040288
H	-1.317264	-2.502812	4.039331
C	-1.940856	-2.322201	1.399756
C	4.628889	0.854925	-1.496978
C	4.889652	1.894357	-2.402893
C	5.195537	1.616862	-3.740186
C	5.213530	0.281216	-4.173621

C	4.952578	-0.763290	-3.275887
C	-3.005177	-1.702618	2.090081
C	-4.309693	-1.728168	1.571282
C	-4.578095	-2.342522	0.341394
C	-3.519291	-2.928295	-0.367602
C	-2.220094	-2.934426	0.155499
H	4.383064	1.088352	-0.452578
H	5.370547	2.437247	-4.448158
H	4.903354	-1.800375	-3.633121
H	-2.816007	-1.189653	3.043485
H	-5.598863	-2.369840	-0.058633
H	-1.420903	-3.429375	-0.407185
N	0.005008	0.347201	-0.049965
P	-0.759022	1.716147	-0.243063
O	-0.397185	2.731532	1.015785
O	-2.352413	1.333834	0.055700
C	-0.540364	2.184371	2.286541
C	0.641427	1.809092	2.998712
C	0.477126	1.174007	4.226288
C	-0.808834	0.898862	4.764455
C	-0.955738	0.223081	6.011760
C	-2.211781	-0.079430	6.514755
C	-3.372230	0.291603	5.785473
C	-3.262709	0.984900	4.588114
C	-1.986393	1.317972	4.046083
C	-1.828741	2.015556	2.793756
C	-2.998158	2.549329	2.043067
C	-3.902217	3.481622	2.669955
C	-3.650433	4.058213	3.950892
C	-4.546551	4.949408	4.523136
C	-5.741872	5.309519	3.847378
C	-6.004765	4.787426	2.591043
C	-5.095799	3.881943	1.970014
C	-5.333636	3.378739	0.662286
C	-4.422834	2.553807	0.019719
C	-3.237650	2.171050	0.717542
C	2.006053	2.158545	2.528087
H	1.364871	0.890900	4.811739
H	-0.045505	-0.062237	6.559664
H	-2.311818	-0.608452	7.474631
H	-4.369291	0.027555	6.167763
H	-4.166797	1.265408	4.034097
H	-2.724003	3.801116	4.481757
H	-4.323055	5.387354	5.507618
H	-6.447041	6.013141	4.314514
H	-6.915647	5.074150	2.043005
H	-6.255196	3.672433	0.136976
C	-4.721032	2.087202	-1.367891
C	2.304239	3.463892	2.079980
C	3.632542	3.848512	1.842340
C	4.680374	2.931798	2.012280
C	4.385752	1.622811	2.419659

C	3.060431	1.234733	2.673460
C	-4.462573	2.930908	-2.464666
C	-4.820331	2.527845	-3.760563
C	-5.462620	1.302166	-3.976461
C	-5.736812	0.466405	-2.883505
C	-5.357712	0.848042	-1.586073
H	1.494628	4.197041	1.962404
H	5.717794	3.240202	1.836816
H	2.841175	0.208343	3.001370
H	-3.964405	3.894433	-2.295531
H	-5.751641	1.000093	-4.991400
H	-5.578319	0.196964	-0.730142
N	0.710943	-0.826820	-2.376655
N	-0.502478	2.470956	-1.633856
S	1.345536	-1.888816	-3.414867
O	1.377234	-1.265038	-4.757830
O	2.518452	-2.647321	-2.923181
S	-1.107726	3.918141	-2.032526
O	-1.402022	3.948926	-3.486426
O	-2.122313	4.448105	-1.082679
C	0.378468	5.068253	-1.800491
C	-0.023155	-3.181321	-3.592845
F	0.950815	4.830374	-0.614518
F	1.279010	4.887018	-2.775397
F	-0.054917	6.333098	-1.838707
F	-0.100431	-3.953136	-2.500626
F	0.240888	-3.947562	-4.656876
F	-1.204684	-2.563089	-3.780048
C	5.497390	0.620503	2.622610
C	3.933152	5.292271	1.491686
C	4.753672	3.317268	-1.918641
C	5.496075	-0.021265	-5.625806
F	6.721221	1.180232	2.517071
F	5.437807	-0.388291	1.708205
F	5.419409	0.034051	3.845134
F	3.414682	6.123857	2.432461
F	3.397839	5.662365	0.307930
F	5.263130	5.530107	1.429534
F	5.631651	3.594989	-0.917907
F	3.510183	3.529869	-1.419022
F	4.961386	4.221519	-2.900041
F	6.824255	-0.132755	-5.871962
F	4.917294	-1.178992	-6.023420
F	5.026973	0.964571	-6.439009
C	-3.783987	-3.494945	-1.741423
C	-5.438501	-1.062486	2.322788
C	-6.522375	-0.796542	-3.145628
C	-4.459690	3.378100	-4.953951
F	-4.236501	4.660872	-4.640810
F	-3.329982	2.896710	-5.562299
F	-5.434172	3.343726	-5.905391
F	-6.628624	-1.583196	-2.049557

F	-7.782226	-0.507142	-3.554872
F	-5.963415	-1.544824	-4.135517
F	-5.340848	-1.249918	3.659527
F	-5.448836	0.286796	2.111690
F	-6.648201	-1.522853	1.930906
F	-2.878444	-4.431261	-2.101231
F	-3.731651	-2.502098	-2.678622
F	-5.010460	-4.056787	-1.839690
C	-1.853889	-0.105892	-5.841302
C	-2.334282	-0.960490	-6.968430
C	-3.319473	-2.105569	-6.582790
C	-4.449567	-1.941724	-7.687796
C	-4.398646	0.370636	-7.549318
C	-5.206211	-0.685460	-7.298116
C	-3.107894	-0.184504	-8.127477
H	-4.284982	-1.126774	-9.744438
H	-2.464345	0.521494	-8.680283
H	-4.580082	1.426734	-7.311785
H	-6.182265	-0.679486	-6.793226
H	-5.047560	-2.859403	-7.826791
C	-3.641290	-1.417110	-8.891829
H	-2.848565	-2.108623	-9.240448
H	-1.409451	-1.367425	-7.422459
O	-2.524409	-0.158890	-4.735913
O	-0.838867	0.651406	-5.909275
C	-2.038811	0.579071	-3.571945
H	-1.049838	0.175743	-3.283134
H	-2.786812	0.382553	-2.788320
H	-1.964860	1.653735	-3.809819
Si	0.517972	1.430247	-6.813048
C	1.113894	2.661228	-5.537700
H	0.238876	3.258056	-5.197655
H	1.781734	3.372870	-6.075330
C	1.768220	0.125137	-7.323450
H	2.366240	-0.138683	-6.430963
H	2.454526	0.670005	-8.012075
C	-0.251613	2.243615	-8.331703
H	-0.564980	1.449946	-9.045595
H	0.621707	2.730850	-8.824603
C	1.828971	2.039760	-4.331055
H	1.158858	1.377522	-3.752678
H	2.188085	2.822281	-3.638409
H	2.699796	1.433241	-4.641036
C	1.245059	-1.162251	-7.972405
H	2.079748	-1.769814	-8.377022
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H	-2.279242	2.796704	-7.681527
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C	-2.724667	-3.496358	-6.501177
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## P

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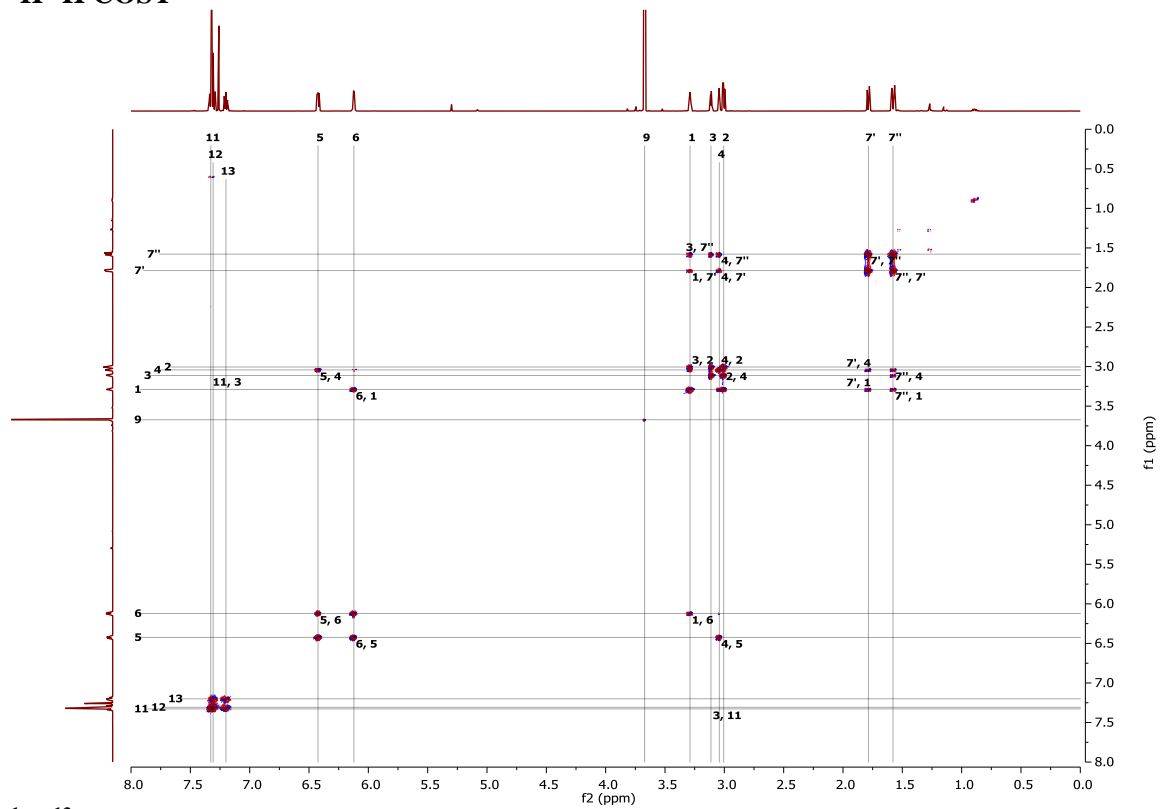
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C	0.873125	3.520456	-1.178612
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C	1.829322	5.383142	2.612484
C	1.798796	6.763764	2.906469
C	2.470885	4.530515	3.535234
C	2.391120	7.277371	4.068420
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C	3.065521	5.038784	4.700643
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C	3.030591	6.414633	4.972453
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H	3.557124	4.349809	5.404546
H	3.494365	6.812245	5.887868

## References

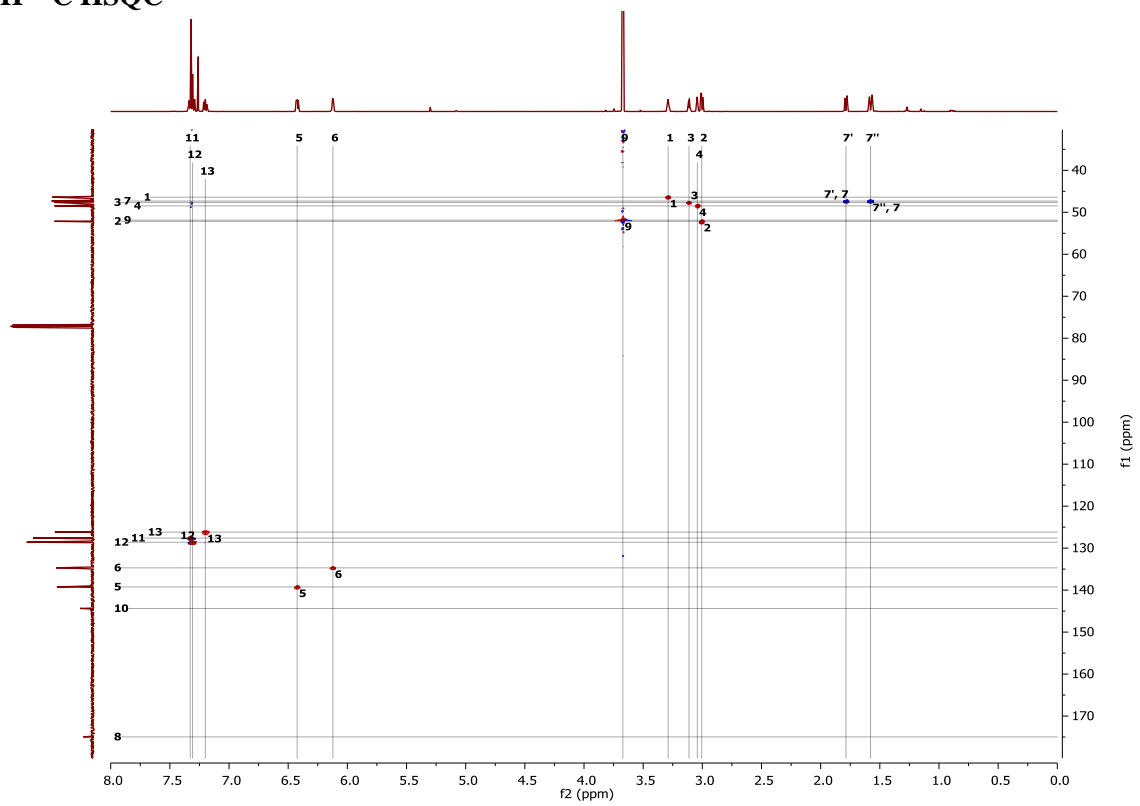
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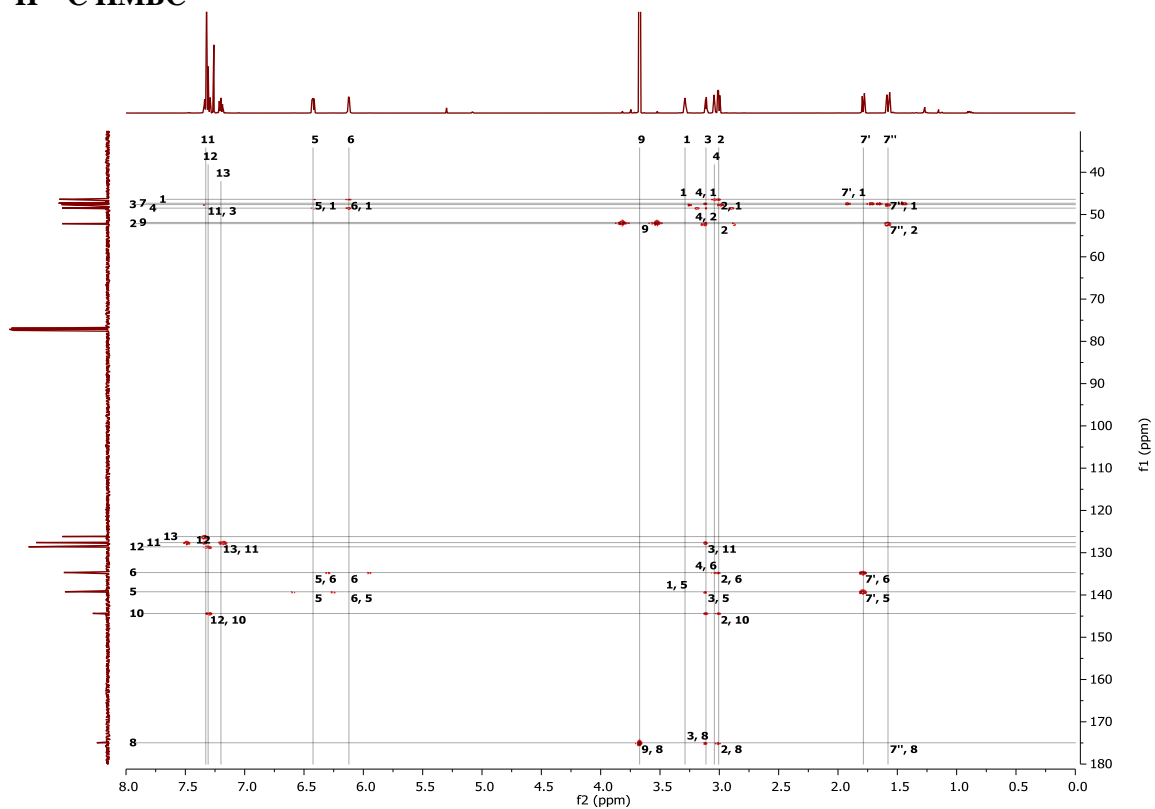
# $^1\text{H}$ - $^1\text{H}$ COSY



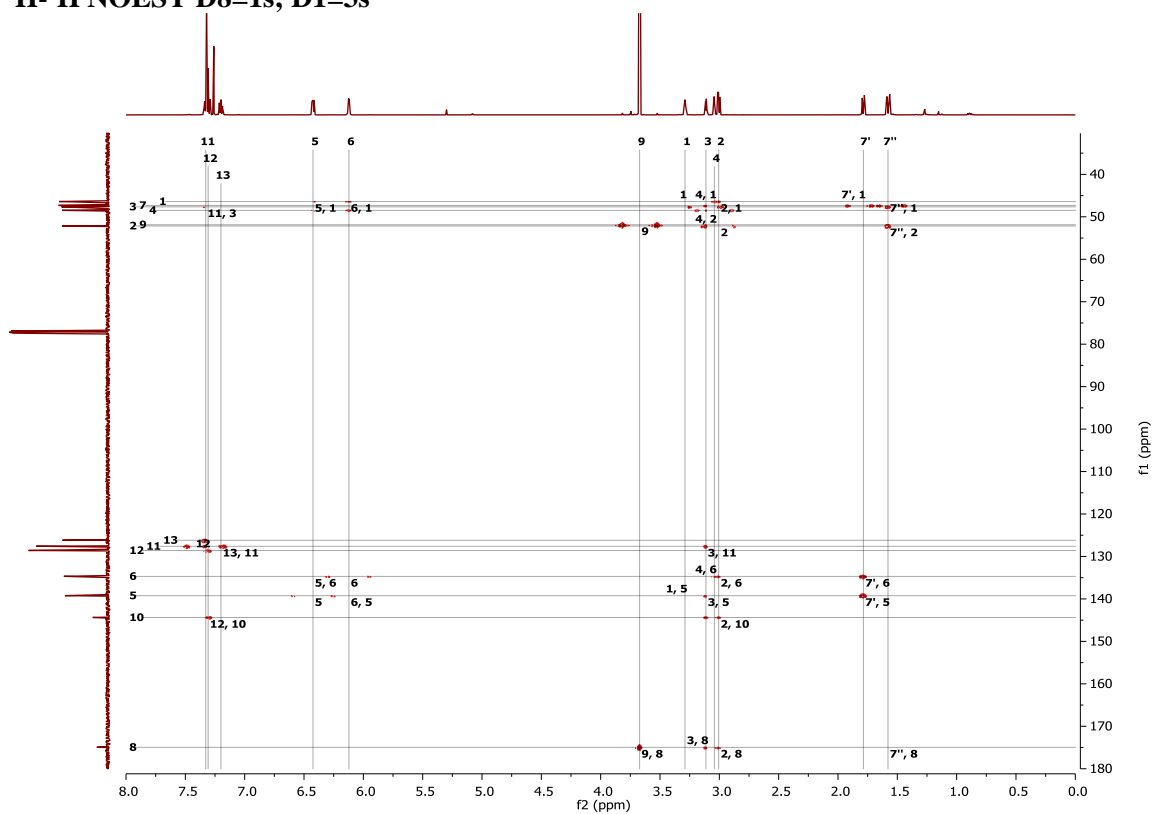
# $^1\text{H}$ - $^{13}\text{C}$ HSQC



**$^1\text{H}$ - $^{13}\text{C}$  HMBC**

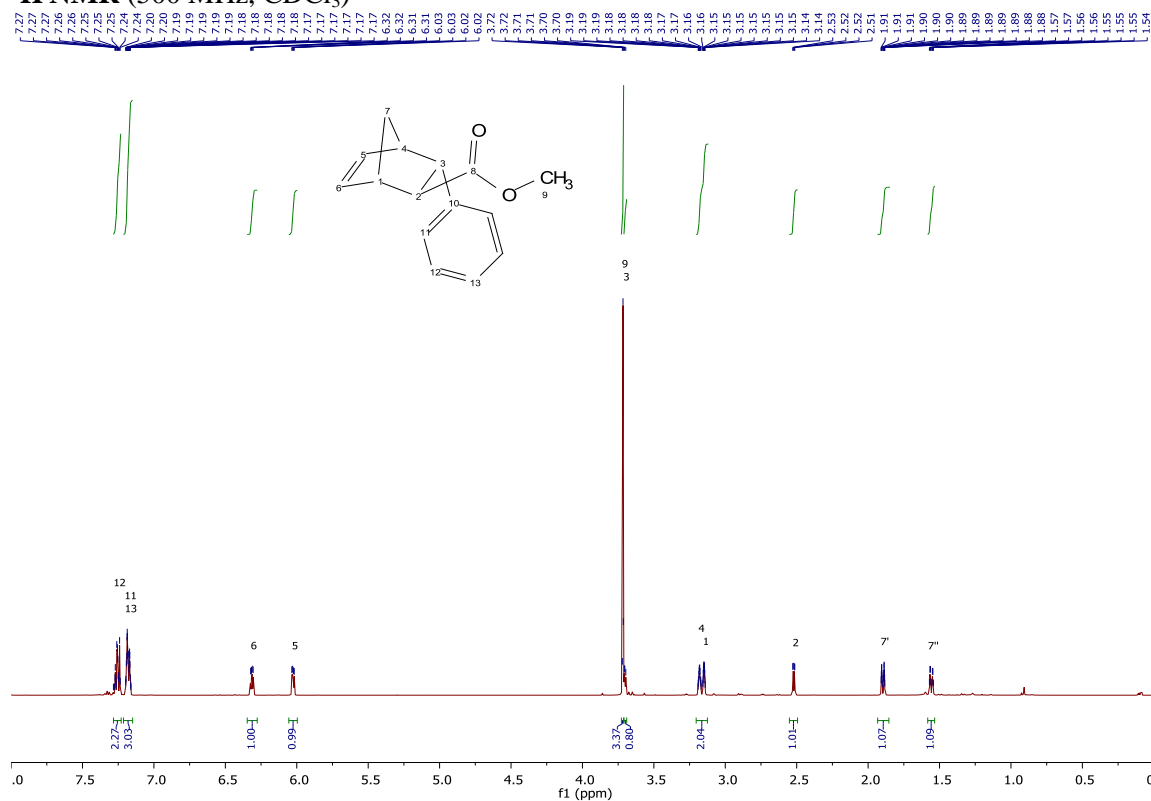


**$^1\text{H}$ - $^1\text{H}$  NOESY D8=1s; D1=3s**

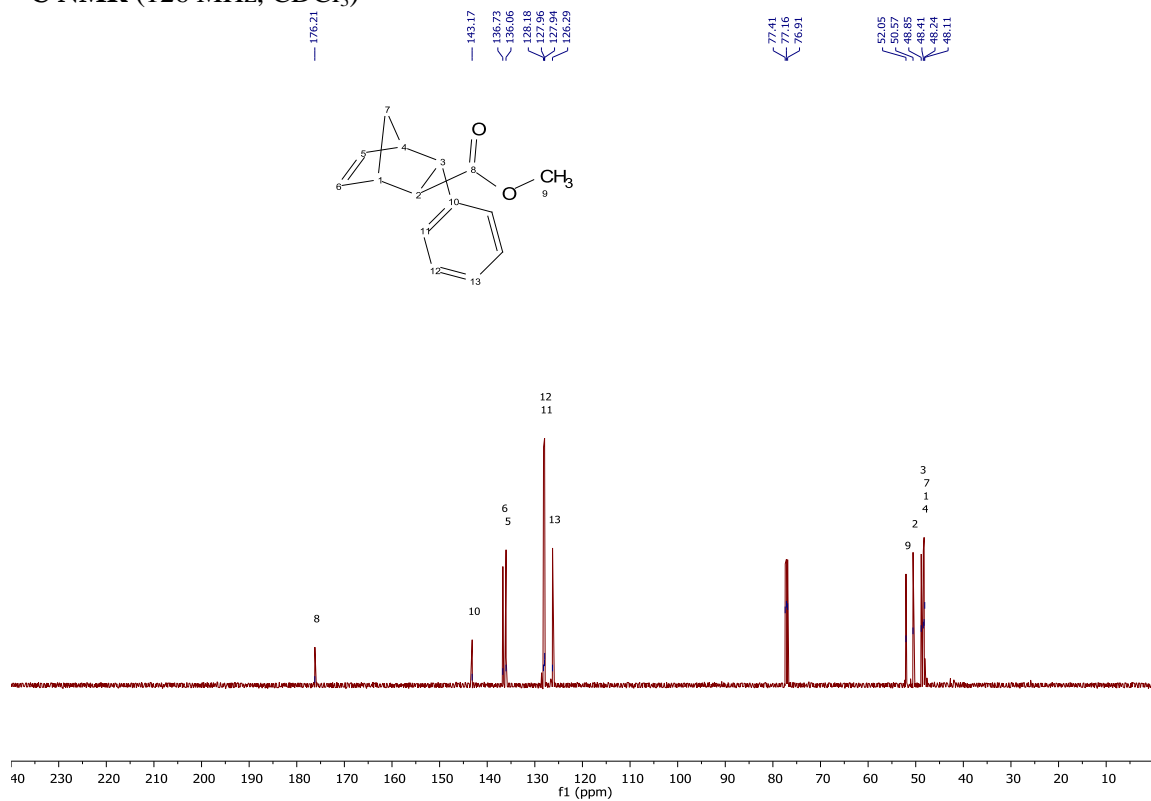


**methyl (1*S*,2*S*,3*S*,4*R*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3a<sub>exo</sub>)**

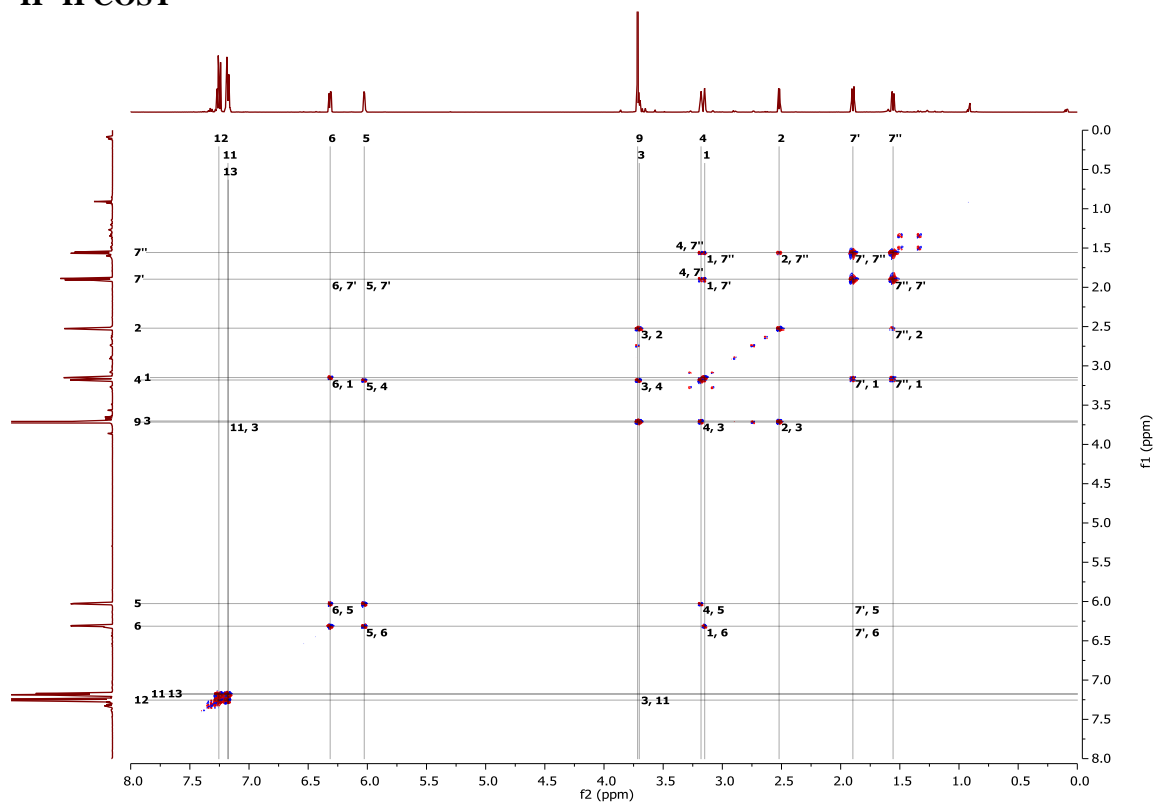
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



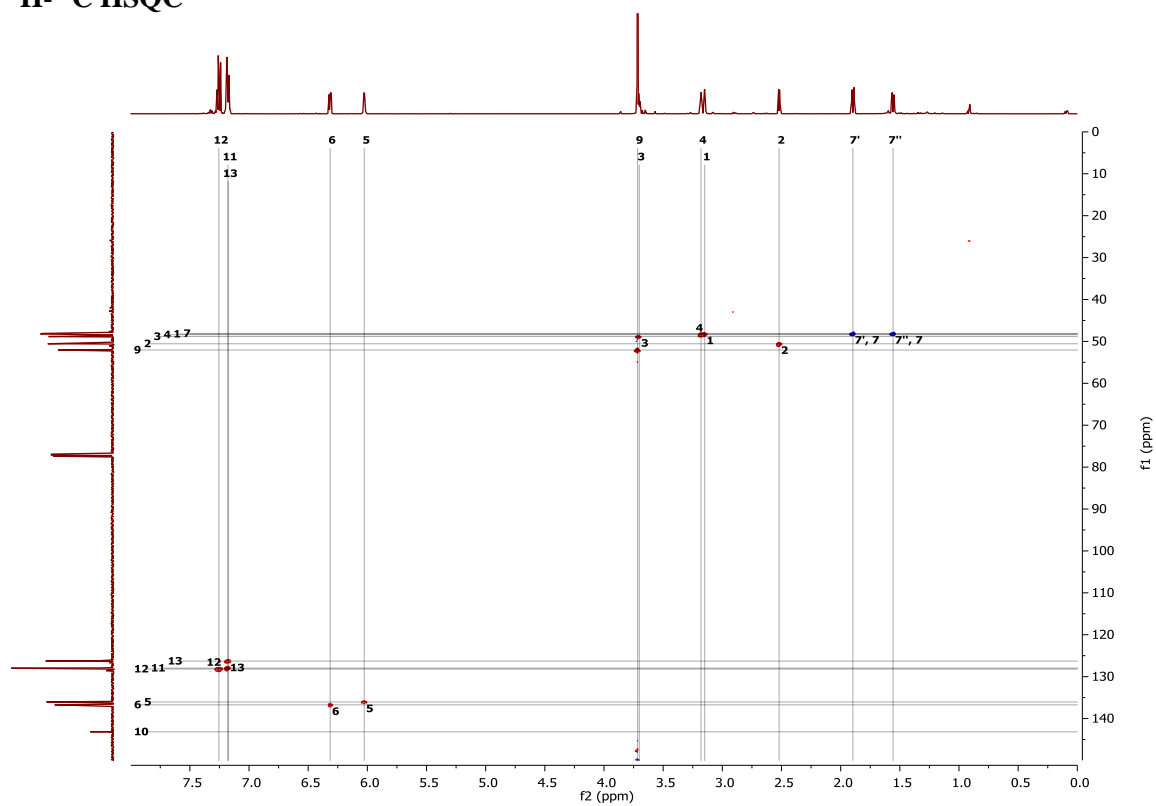
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



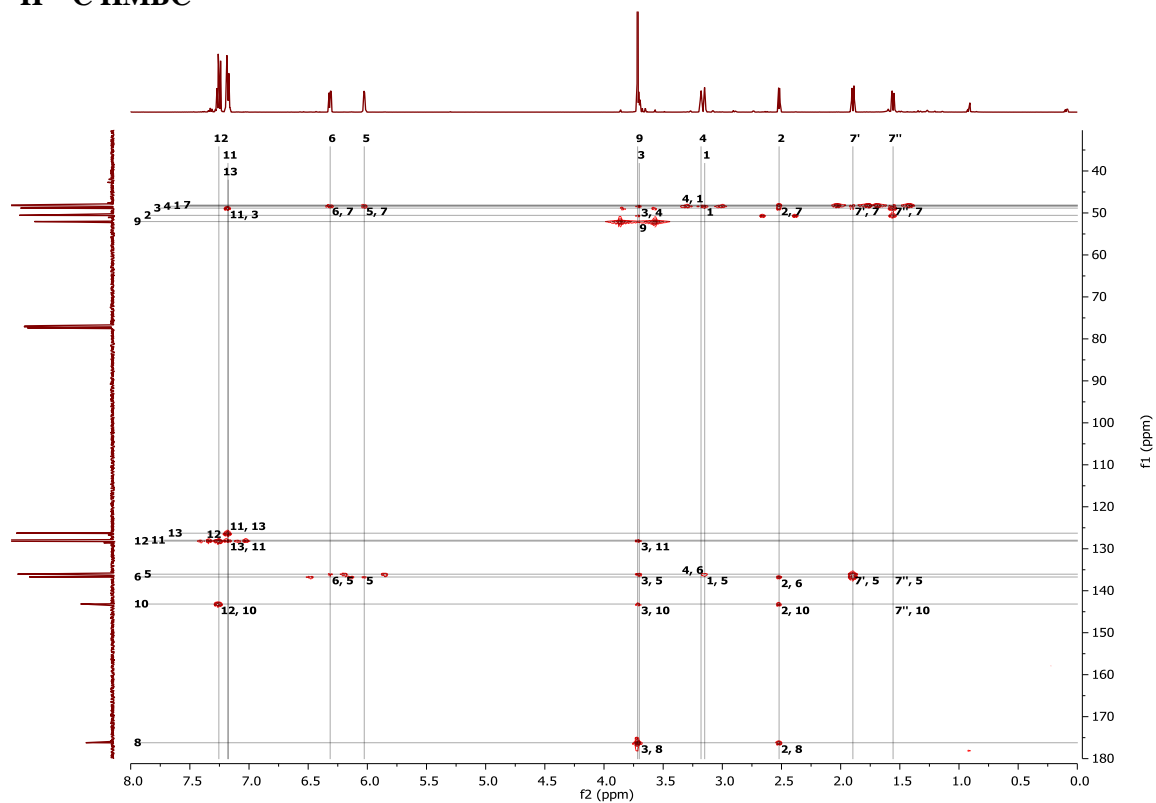
# $^1\text{H}$ - $^1\text{H}$ COSY



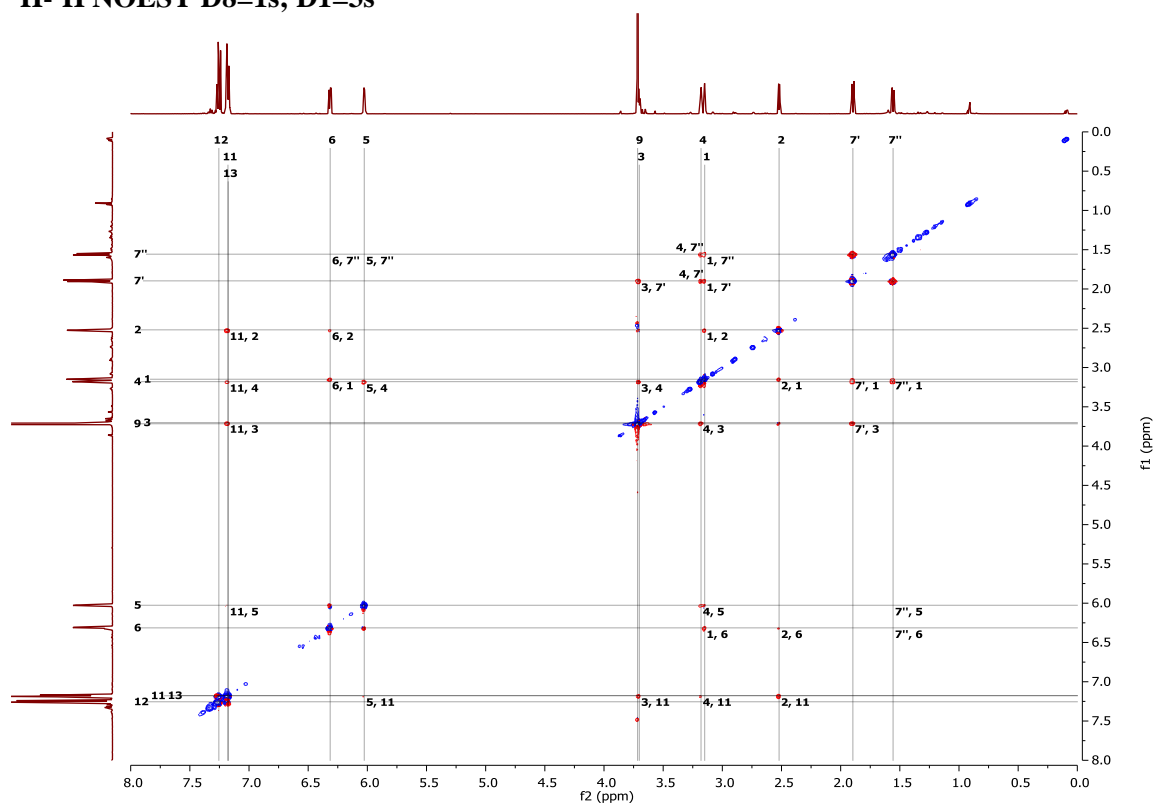
# $^1\text{H}$ - $^{13}\text{C}$ HSQC



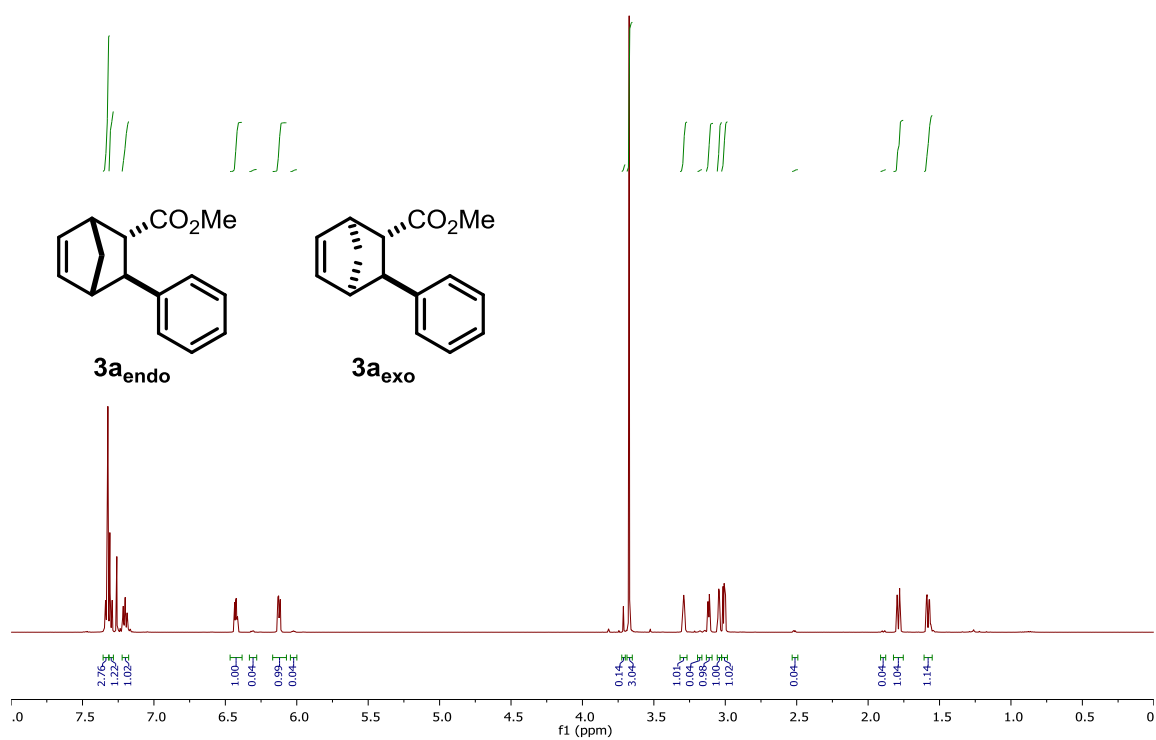
# $^1\text{H}$ - $^{13}\text{C}$ HMBC



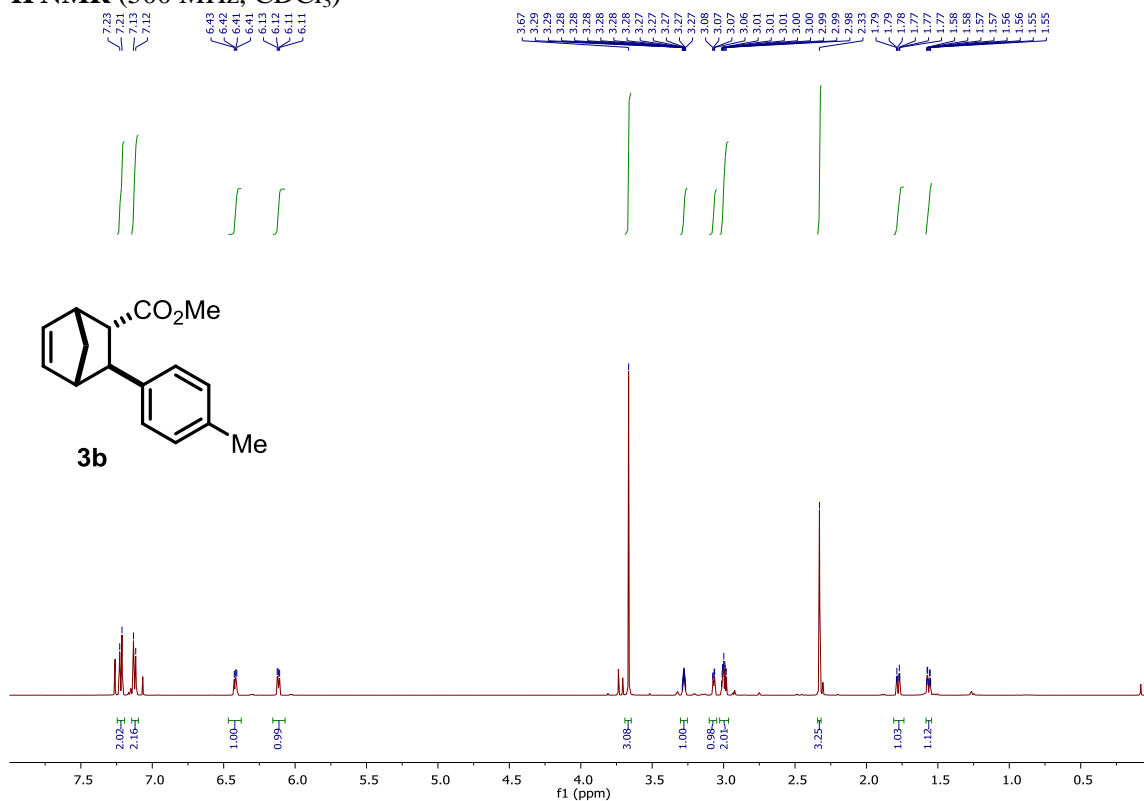
# $^1\text{H}$ - $^1\text{H}$ NOESY D8=1s; D1=3s



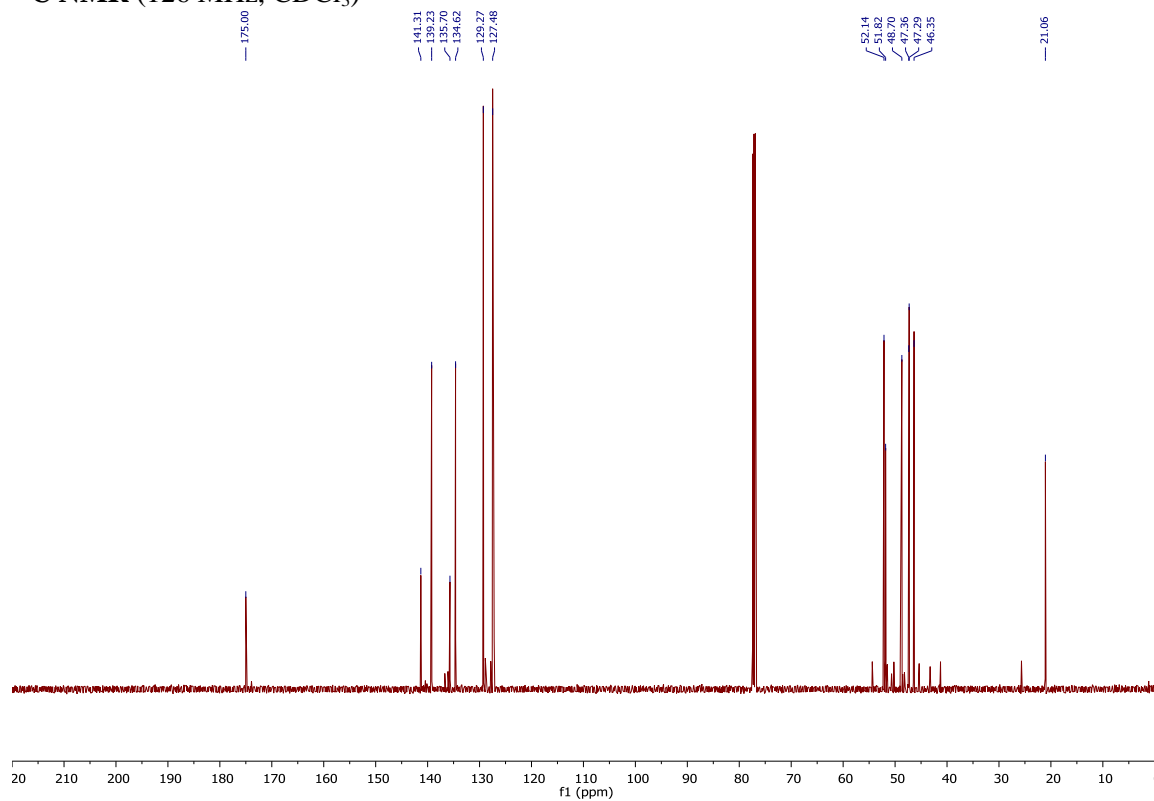
**3a<sub>endo</sub>** and **3a<sub>exo</sub>** (d.r. 26:1)  
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)



**methyl (1*R*,2*S*,3*S*,4*i*)-3-(*p*-tolyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3b):**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

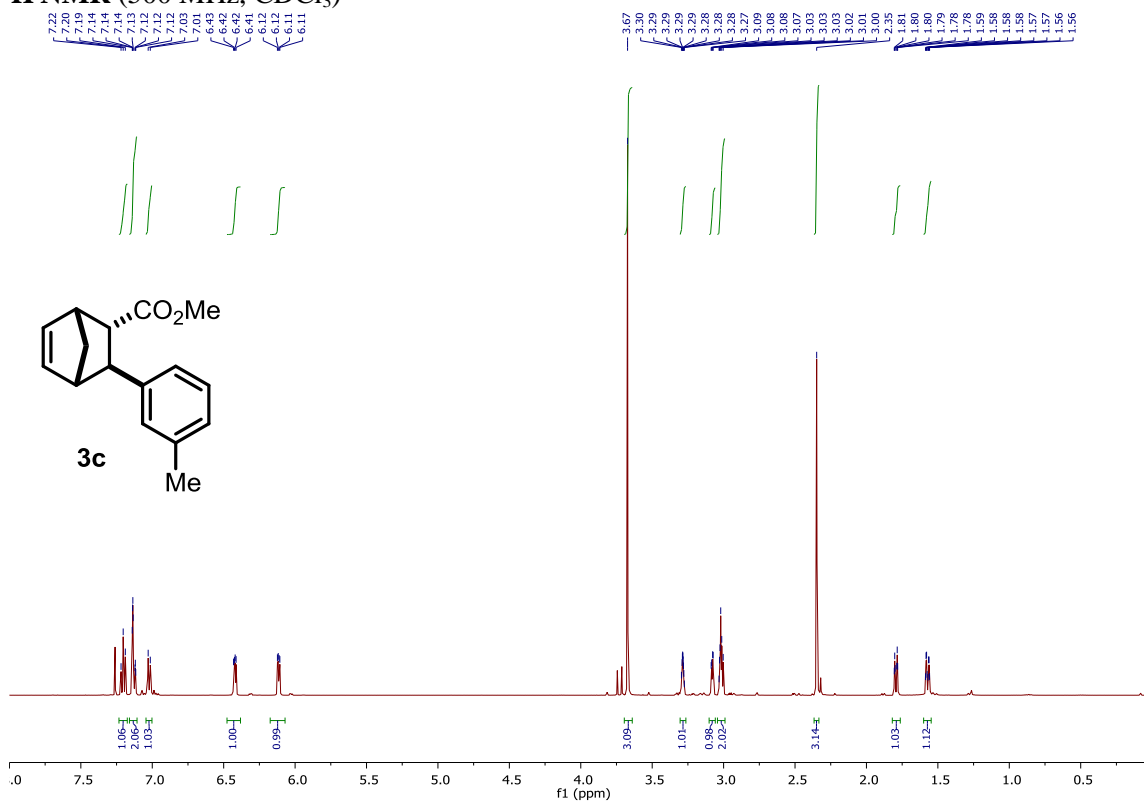


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

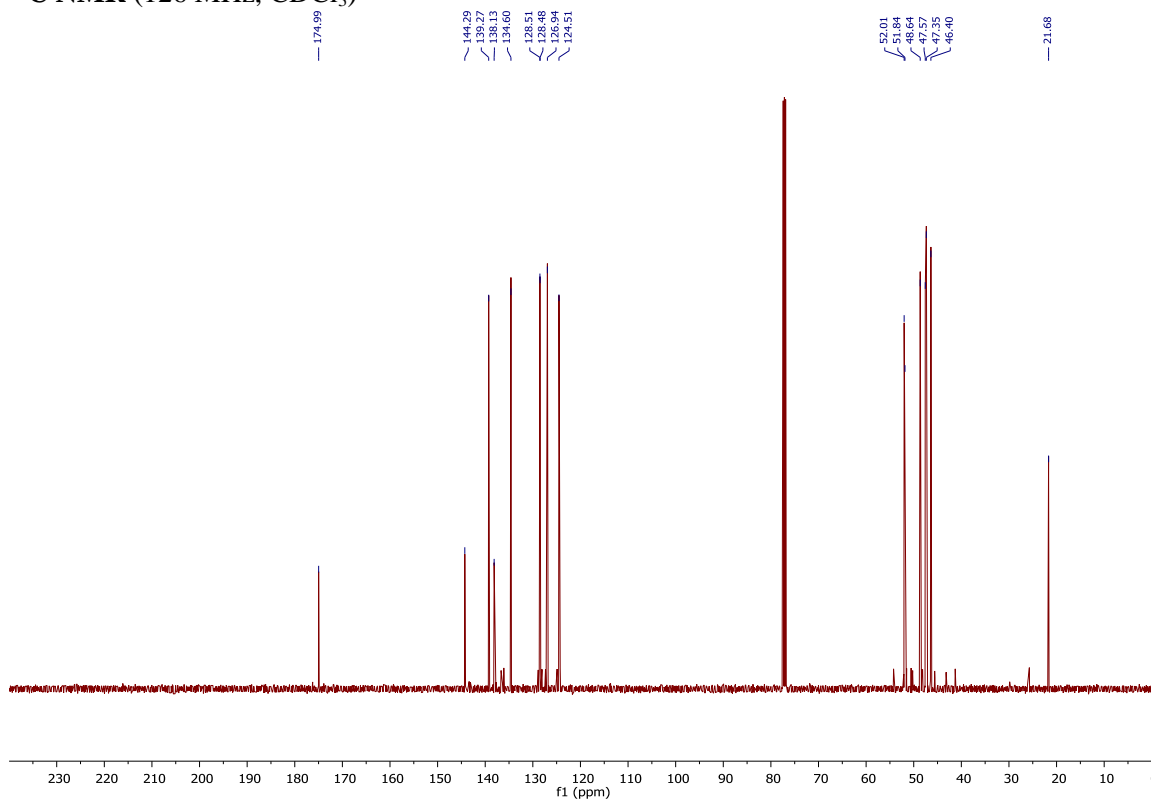


**methyl (1*R*,2*S*,3*S*,4*S*)-3-(*m*-tolyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3c):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

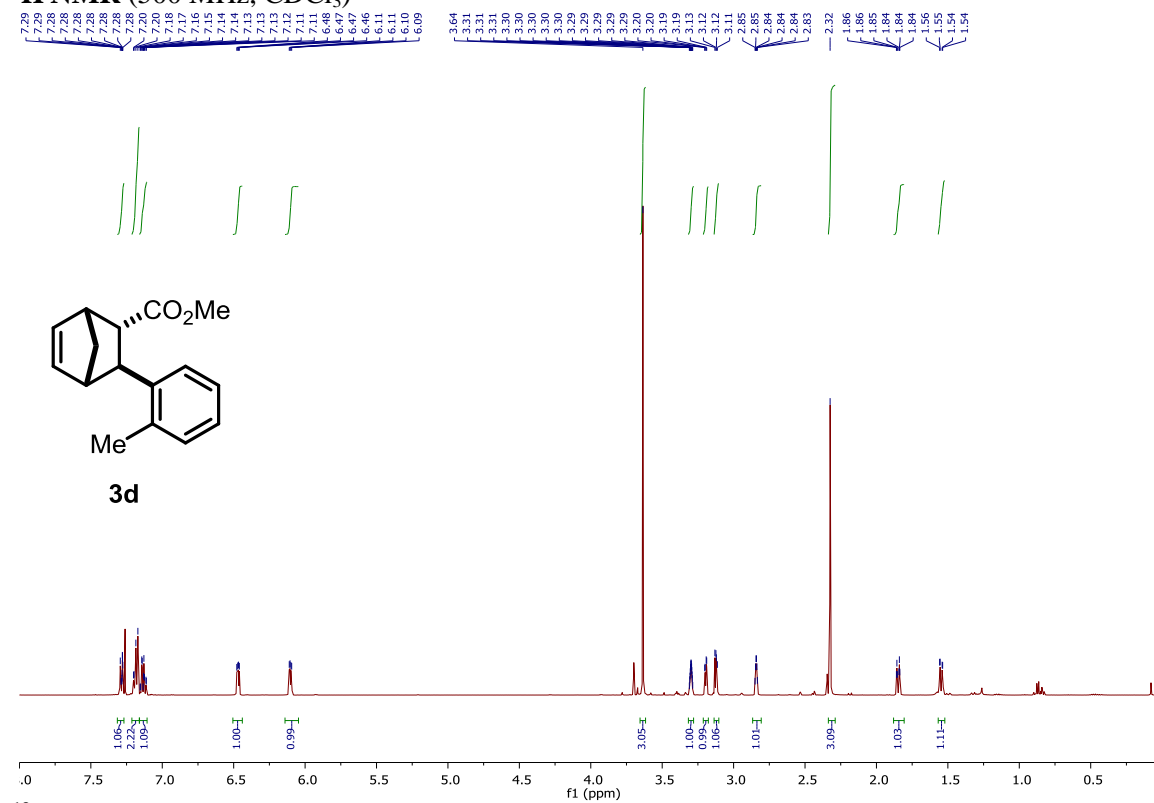


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

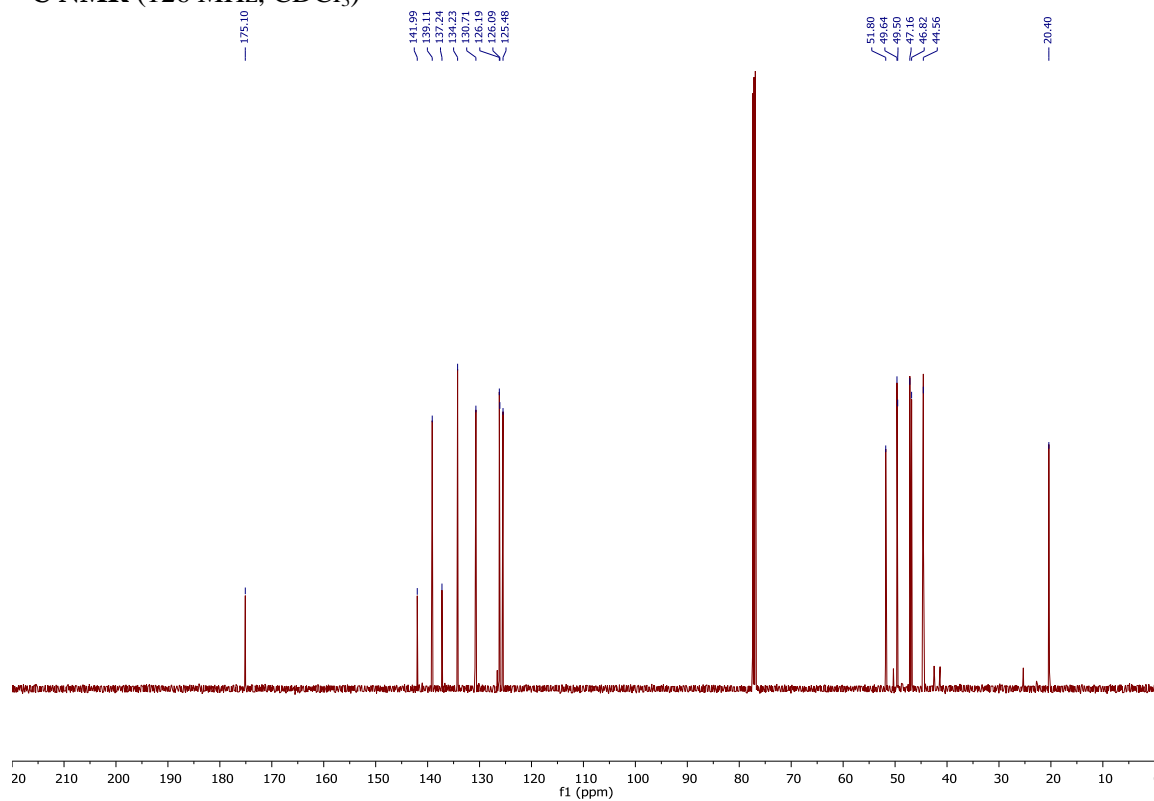


methyl (1*R*,2*S*,3*S*,4*S*)-3-(*o*-tolyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**3d**):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

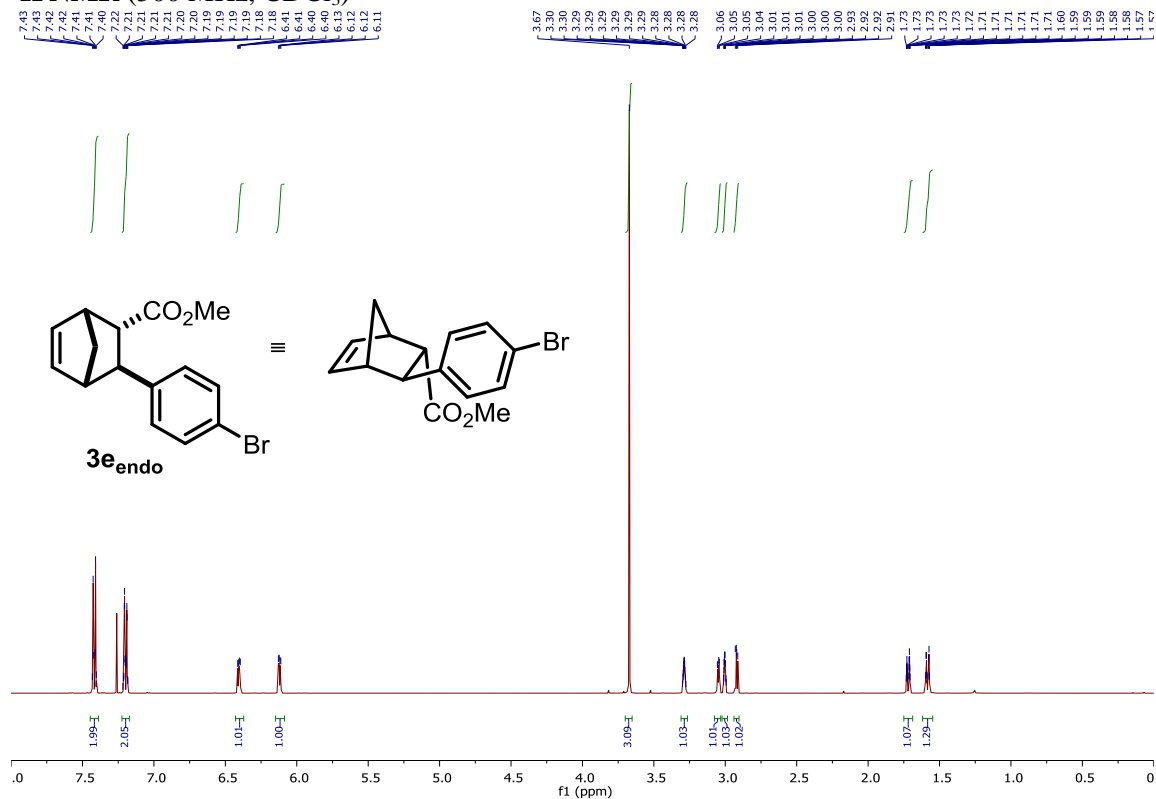


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

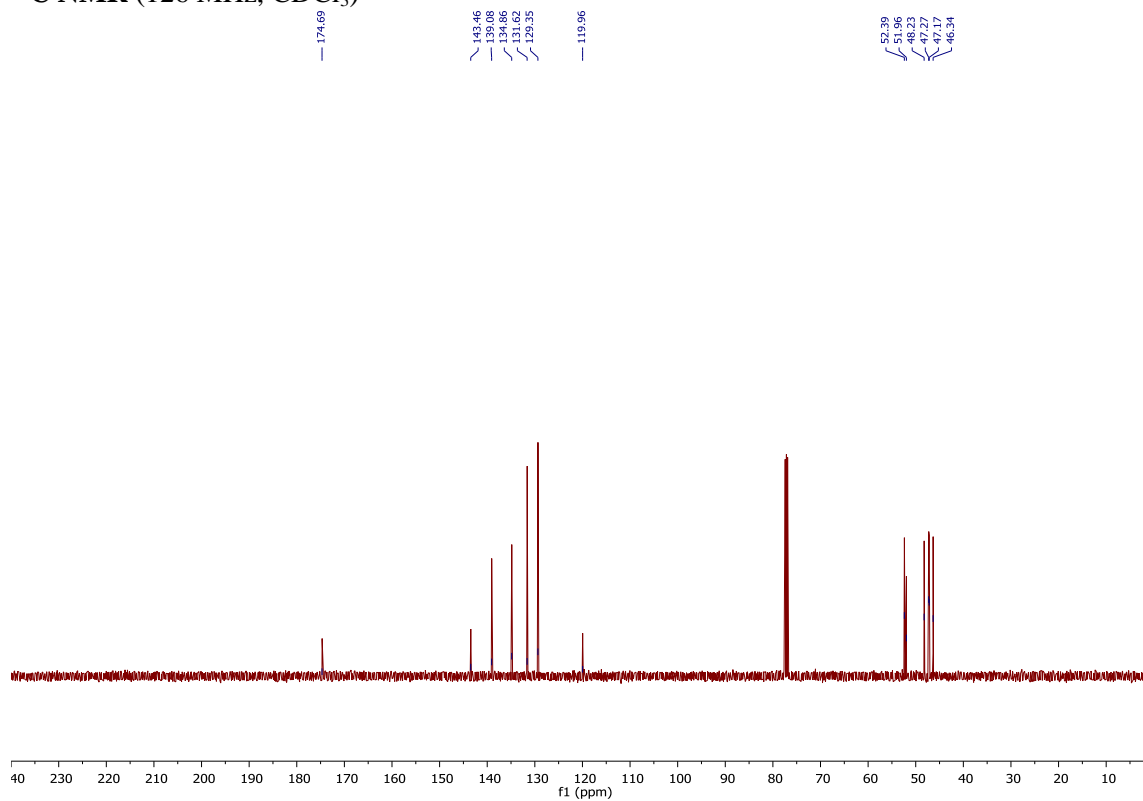


methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**3e<sub>endo</sub>**):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

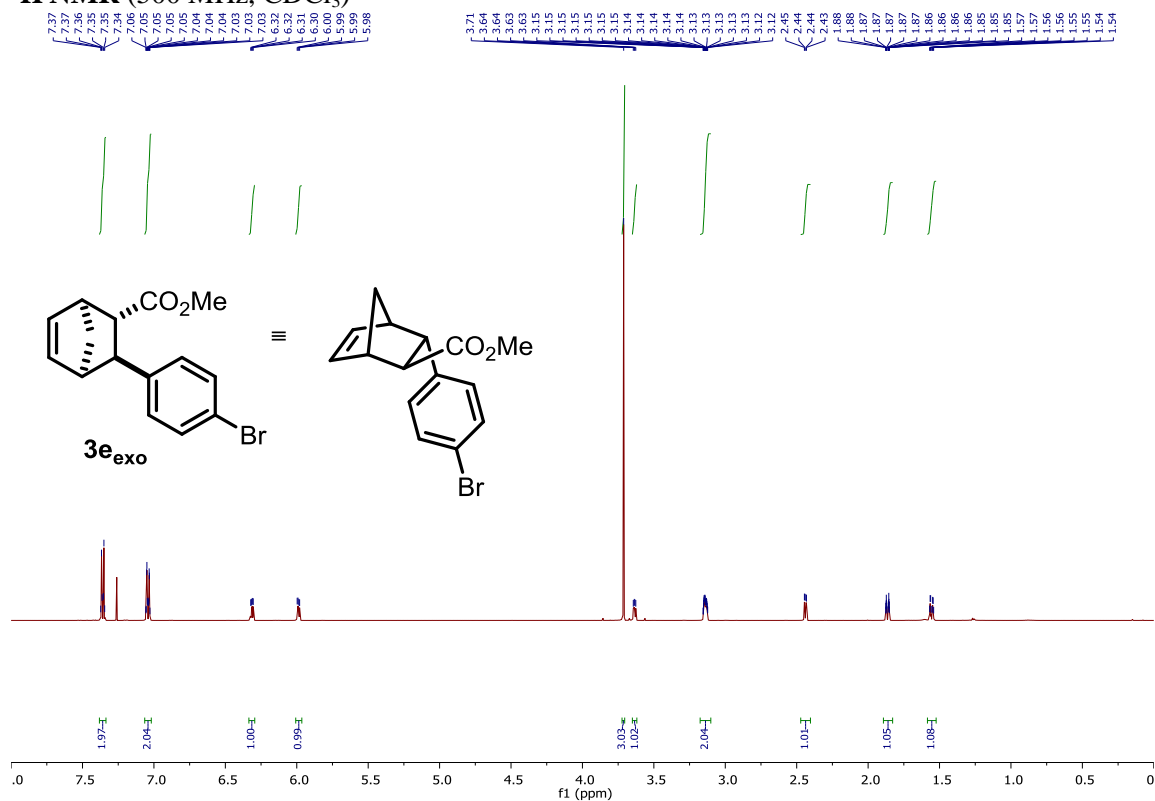


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

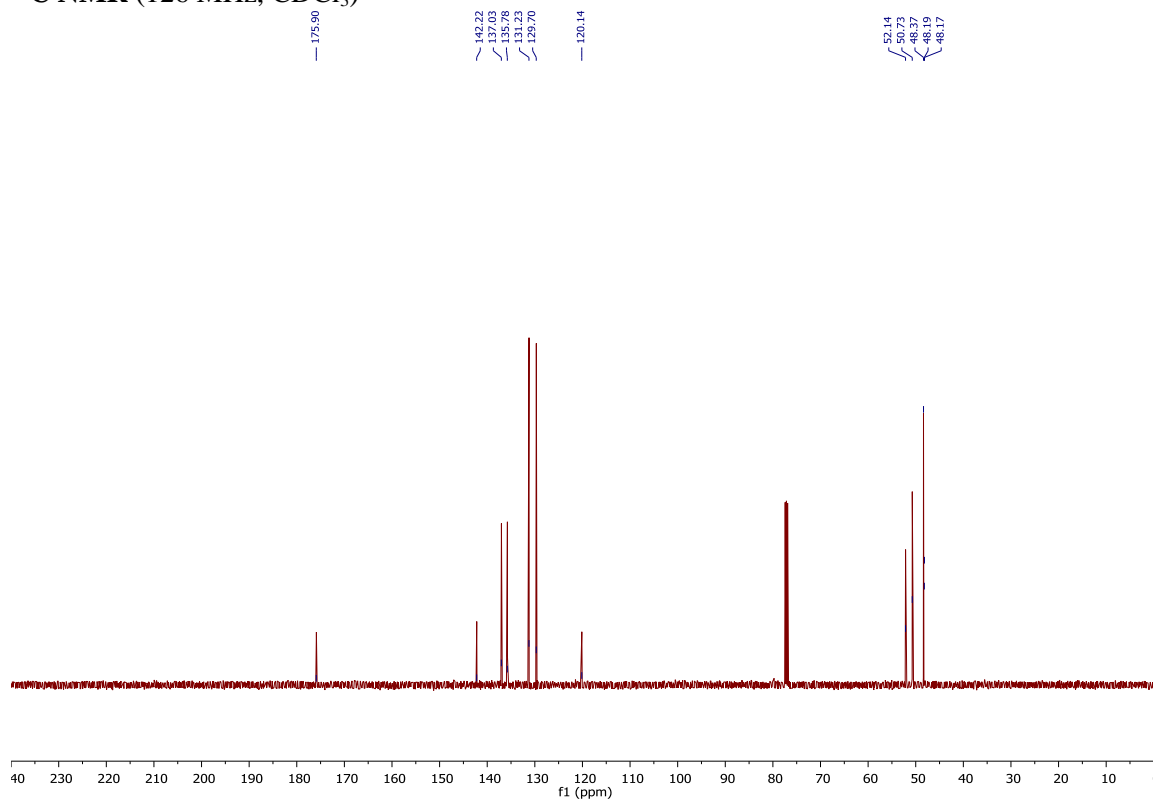


methyl (1*S*,2*S*,3*S*,4*R*)-3-(4-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**3e<sub>exo</sub>**):

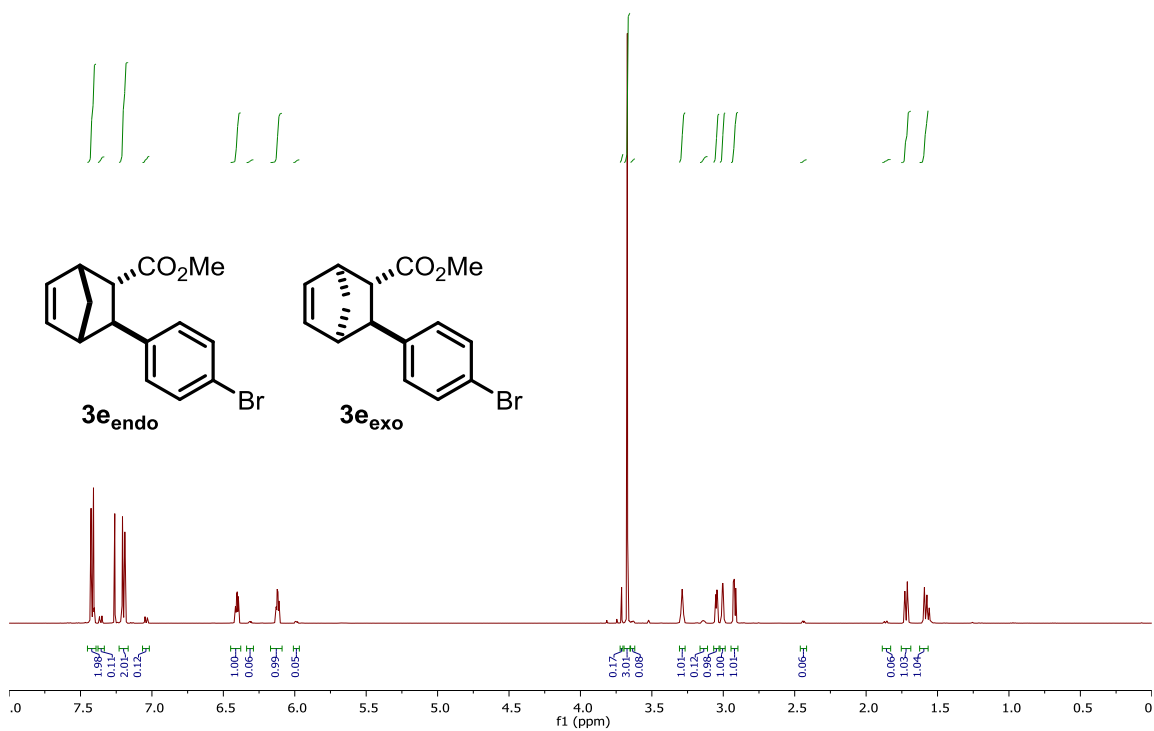
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



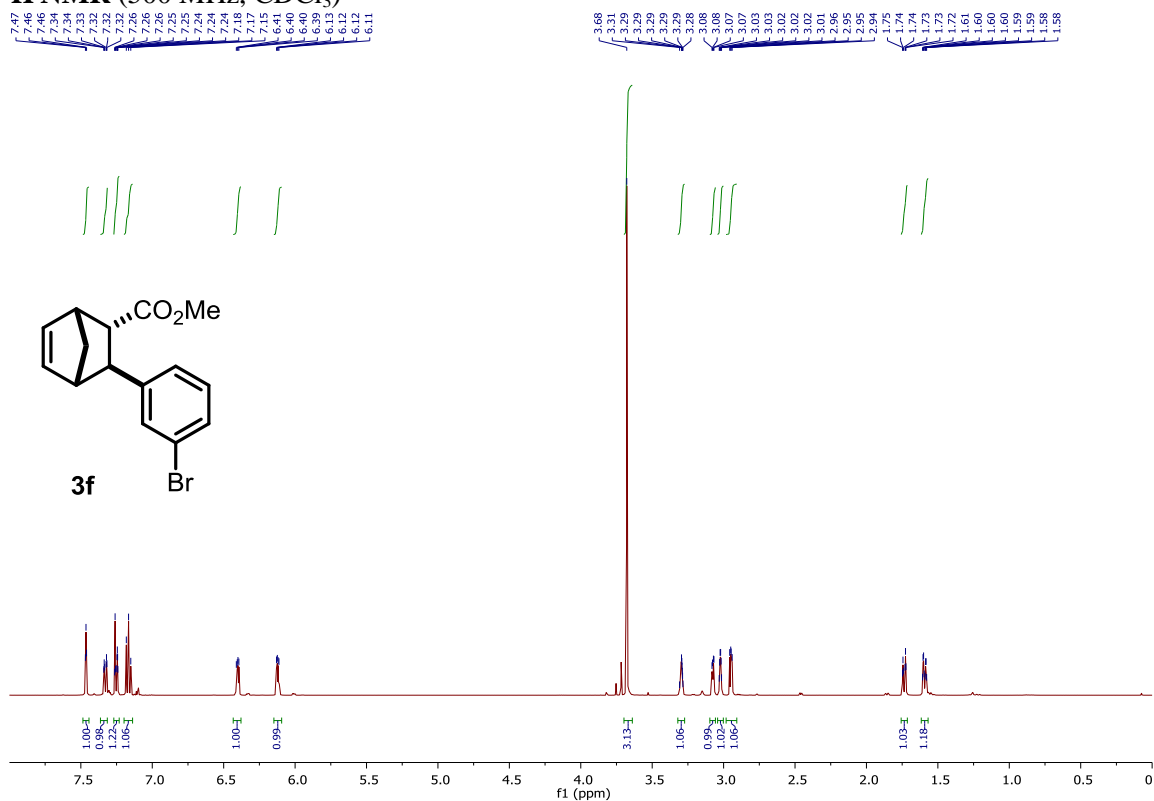
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



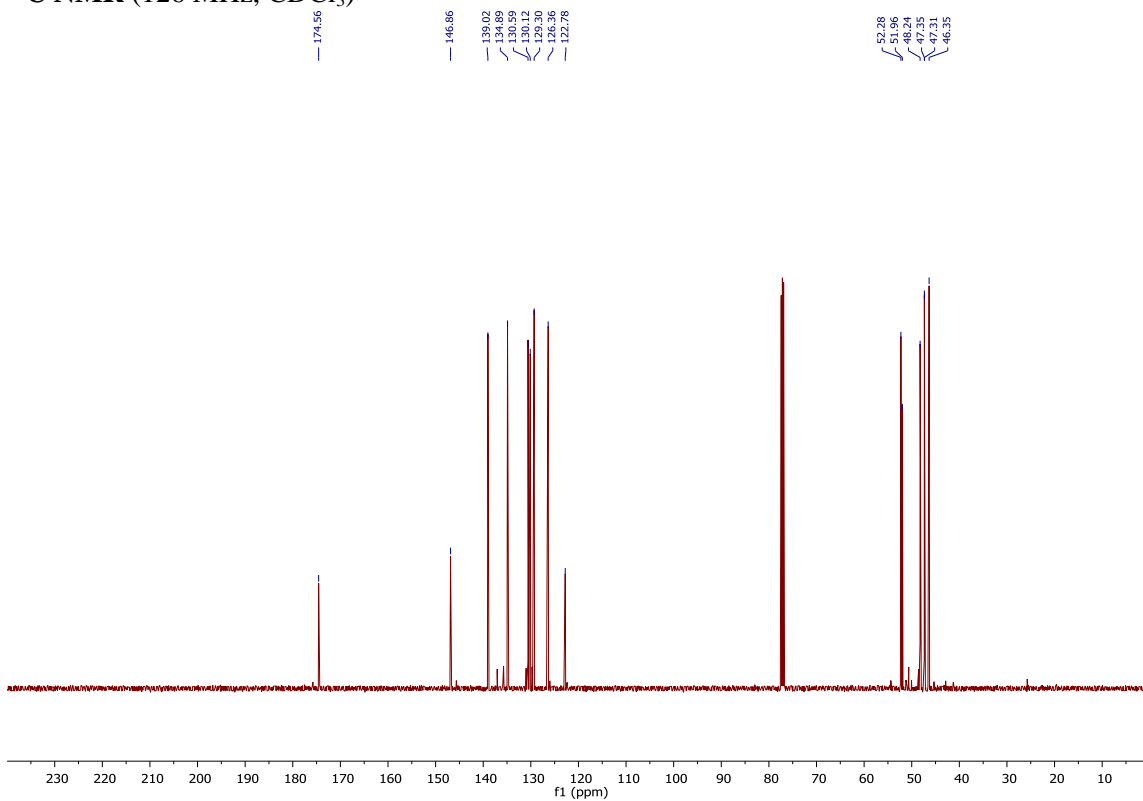
**3e<sub>endo</sub>** and **3e<sub>exo</sub>** (d.r. 16:1)  
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)



**methyl (1R,2S,3S,4S)-3-(3-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3f):**  
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

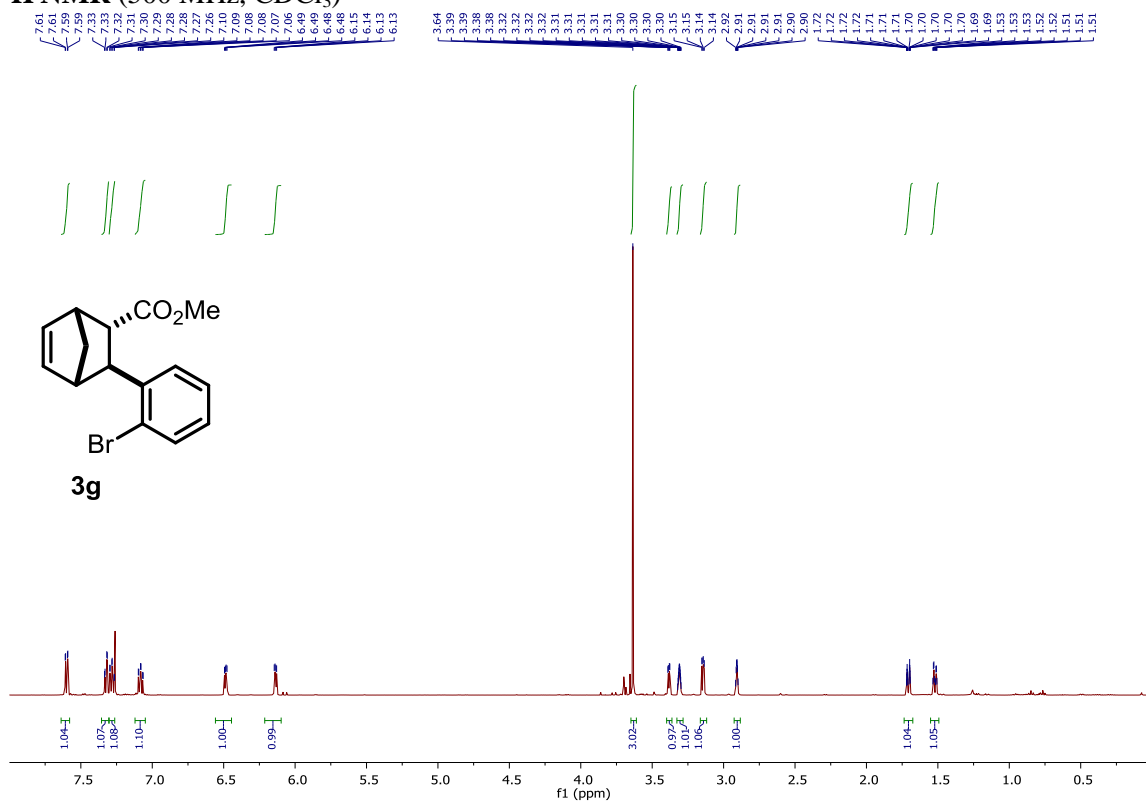


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

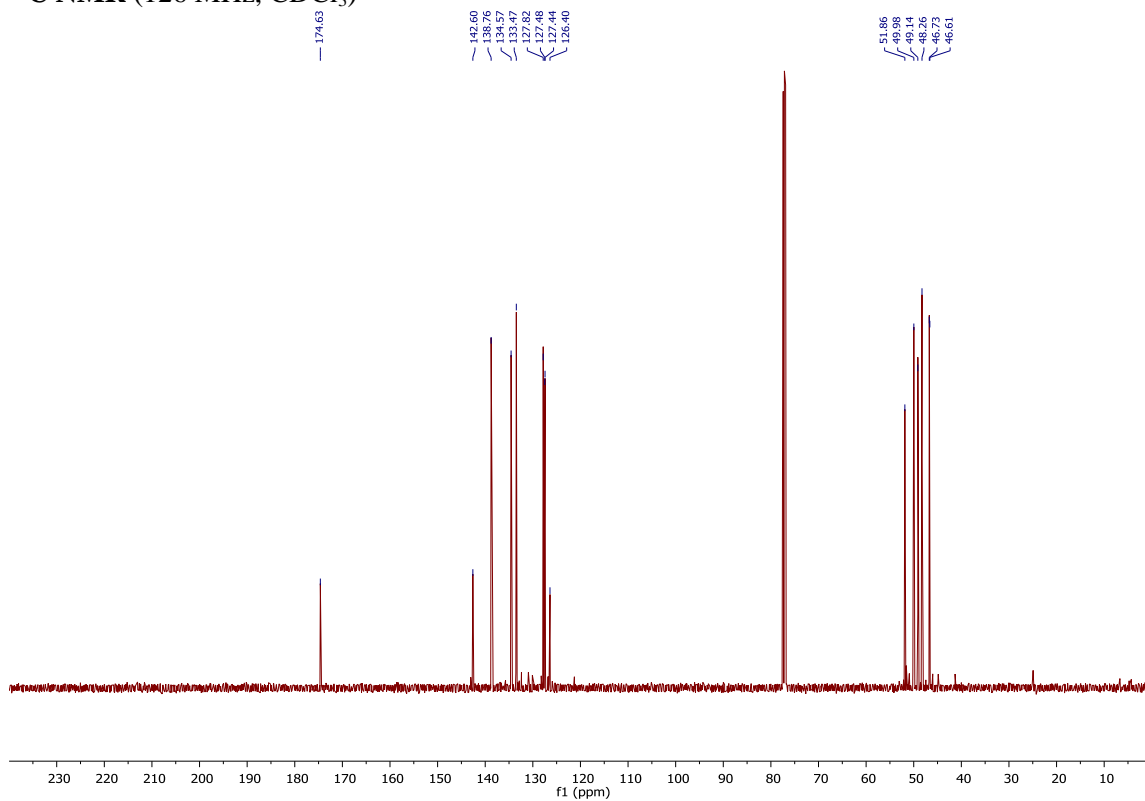


**methyl (1*R*,2*S*,3*S*,4*S*)-3-(2-bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3g):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

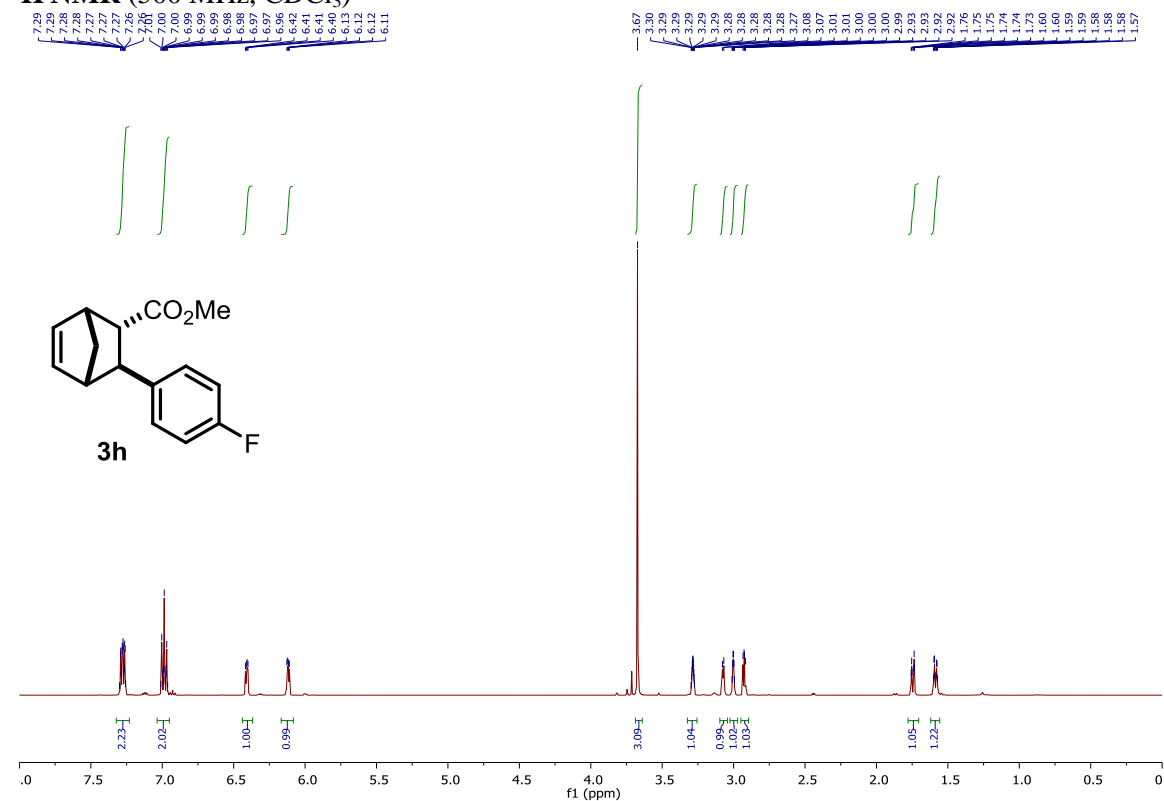


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

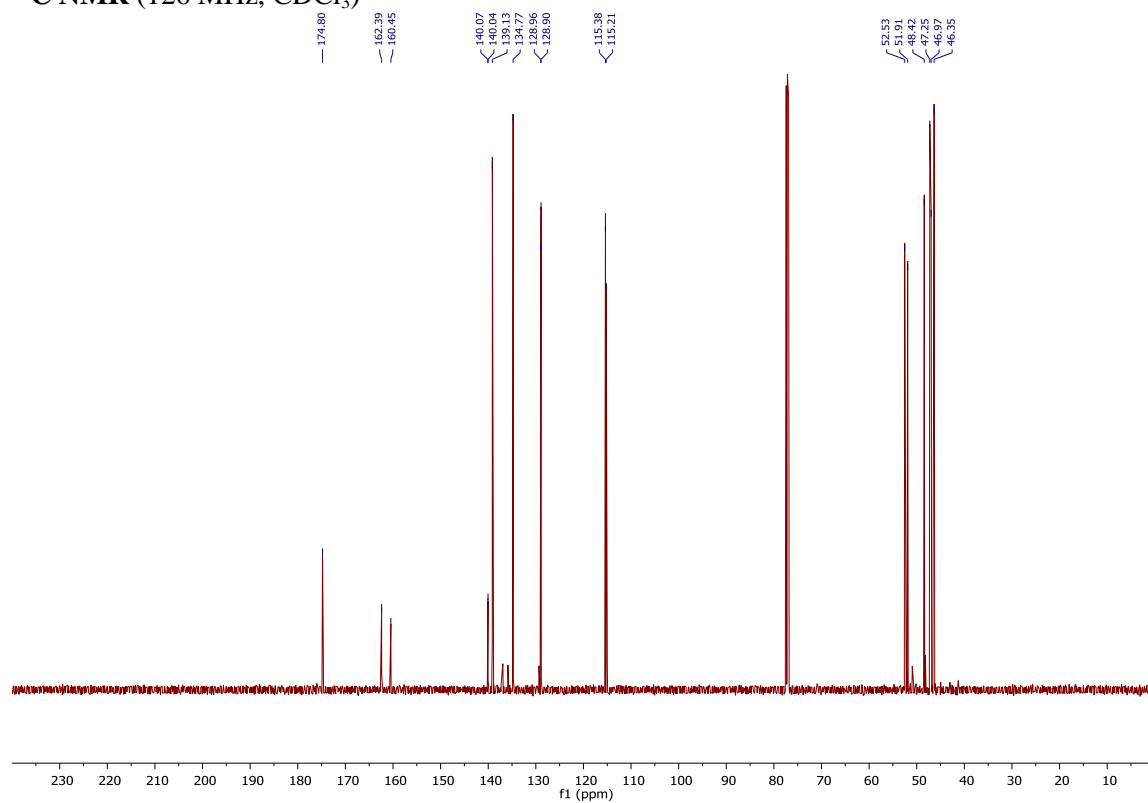


**methyl (1R,2S,3S,4S)-3-(4-fluorophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3h):**

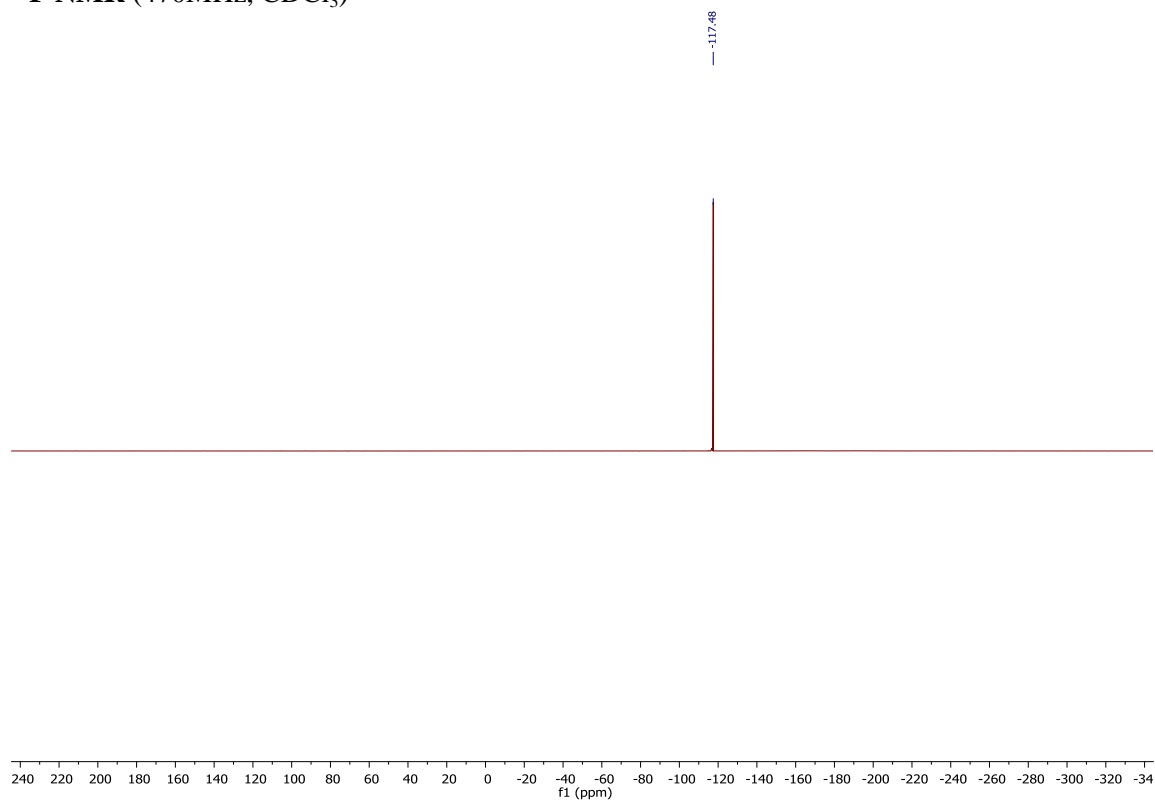
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

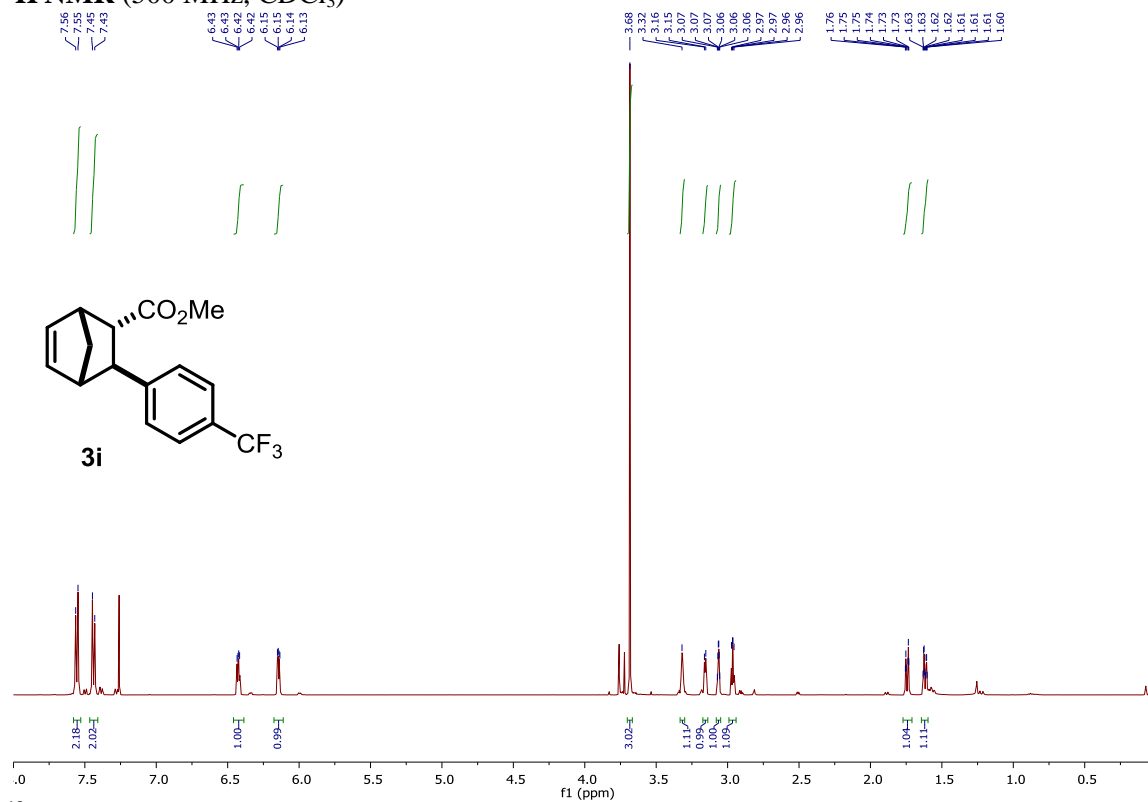


$^{19}\text{F}$  NMR (470MHz,  $\text{CDCl}_3$ )

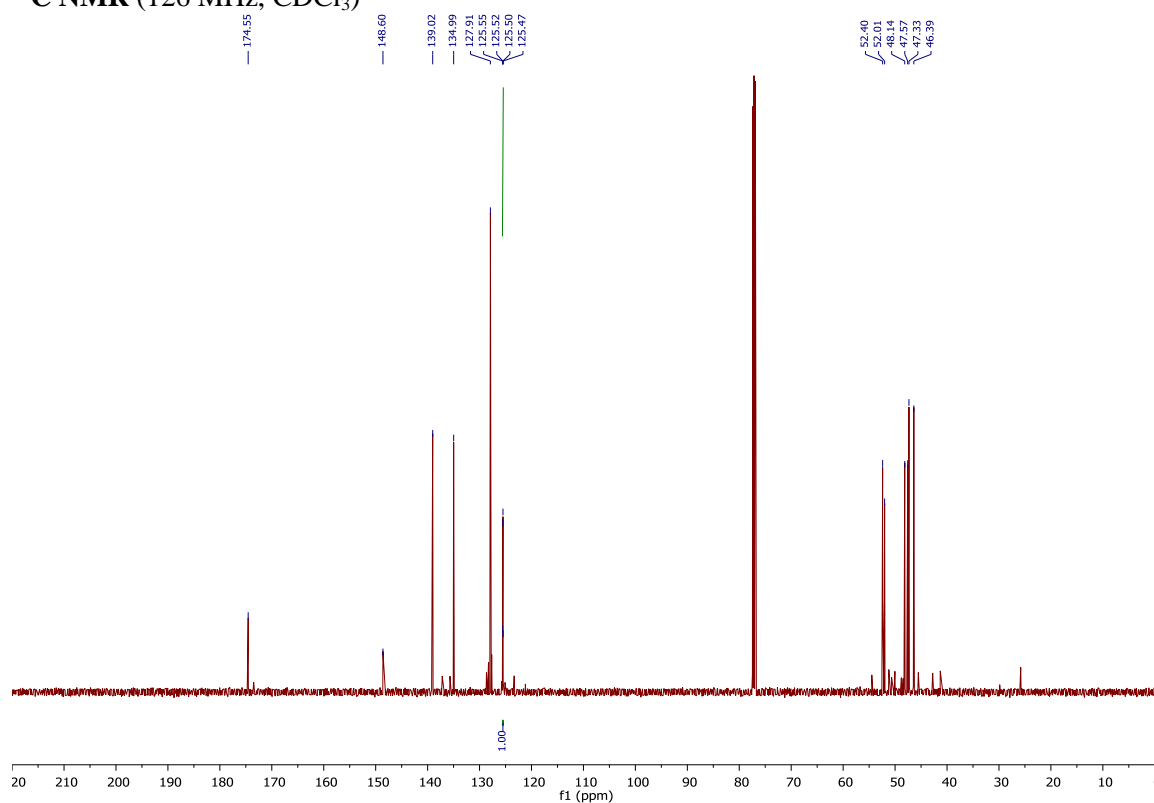


**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate**  
**(3i):**

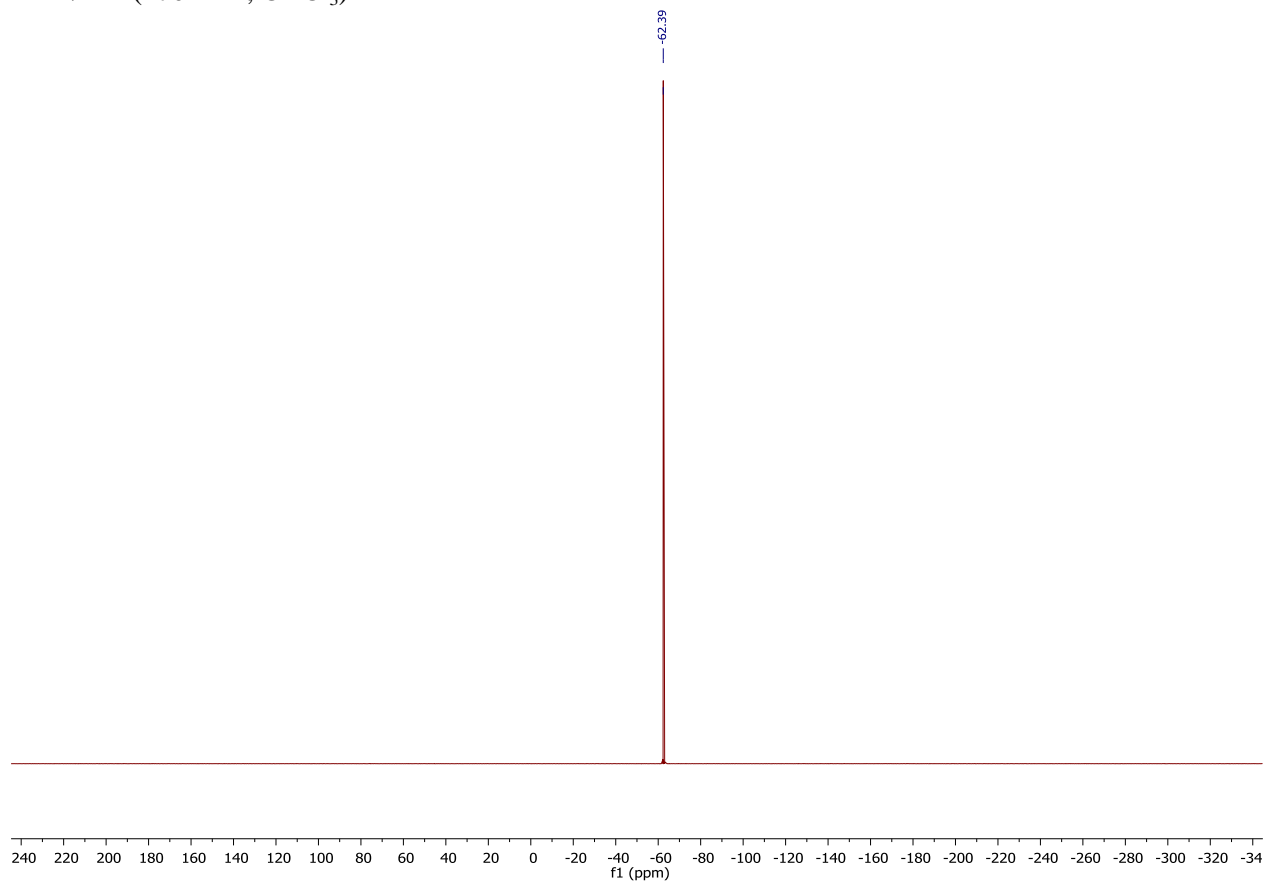
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



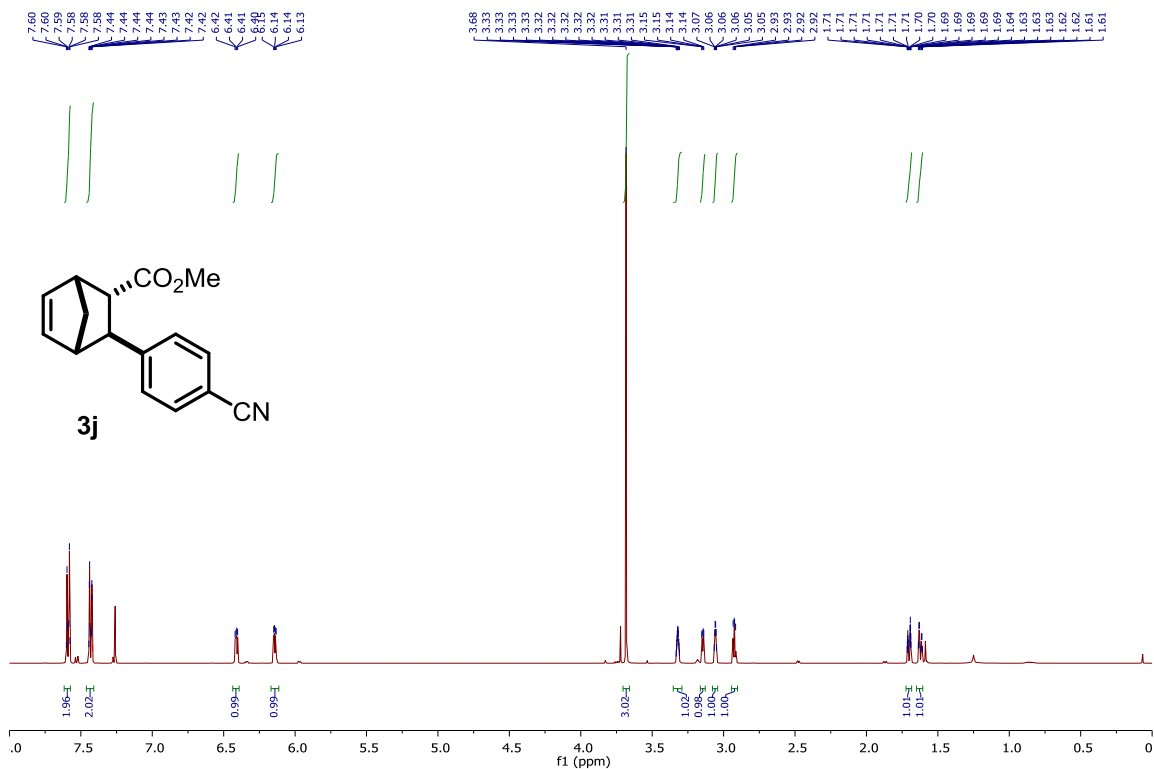
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



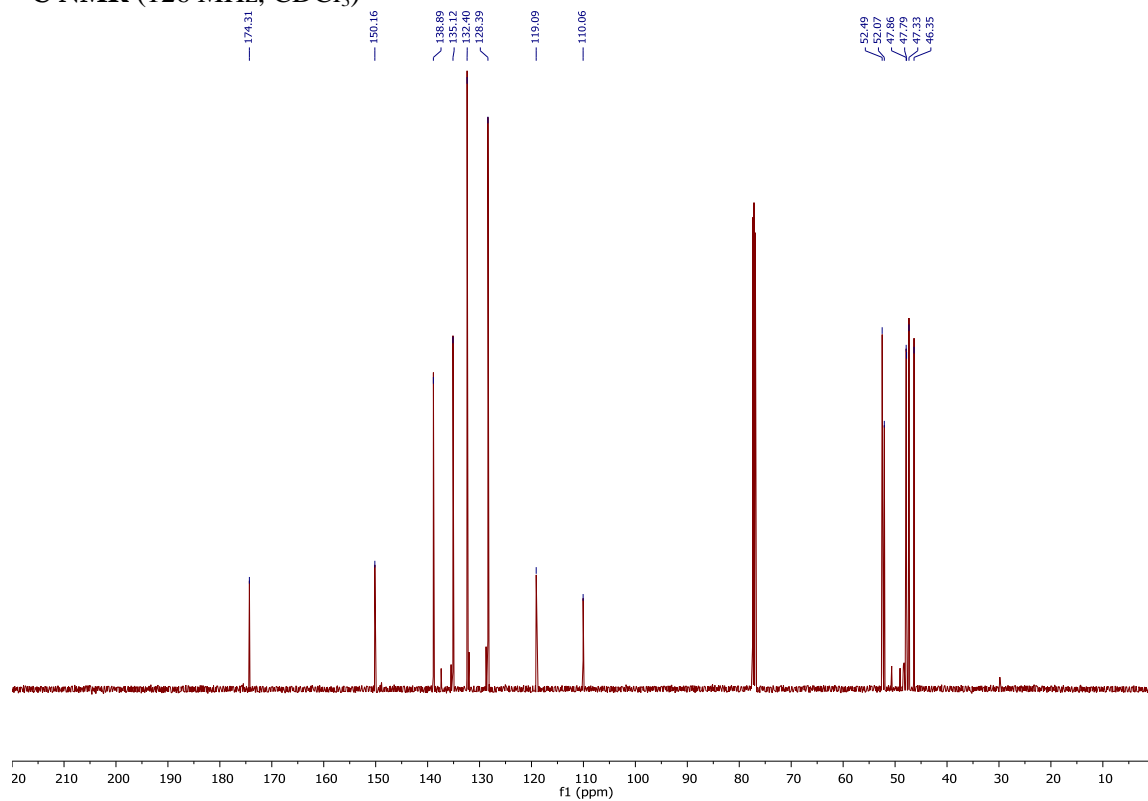
$^{19}\text{F}$  NMR (470MHz,  $\text{CDCl}_3$ )



**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-cyanophenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3j):**  
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

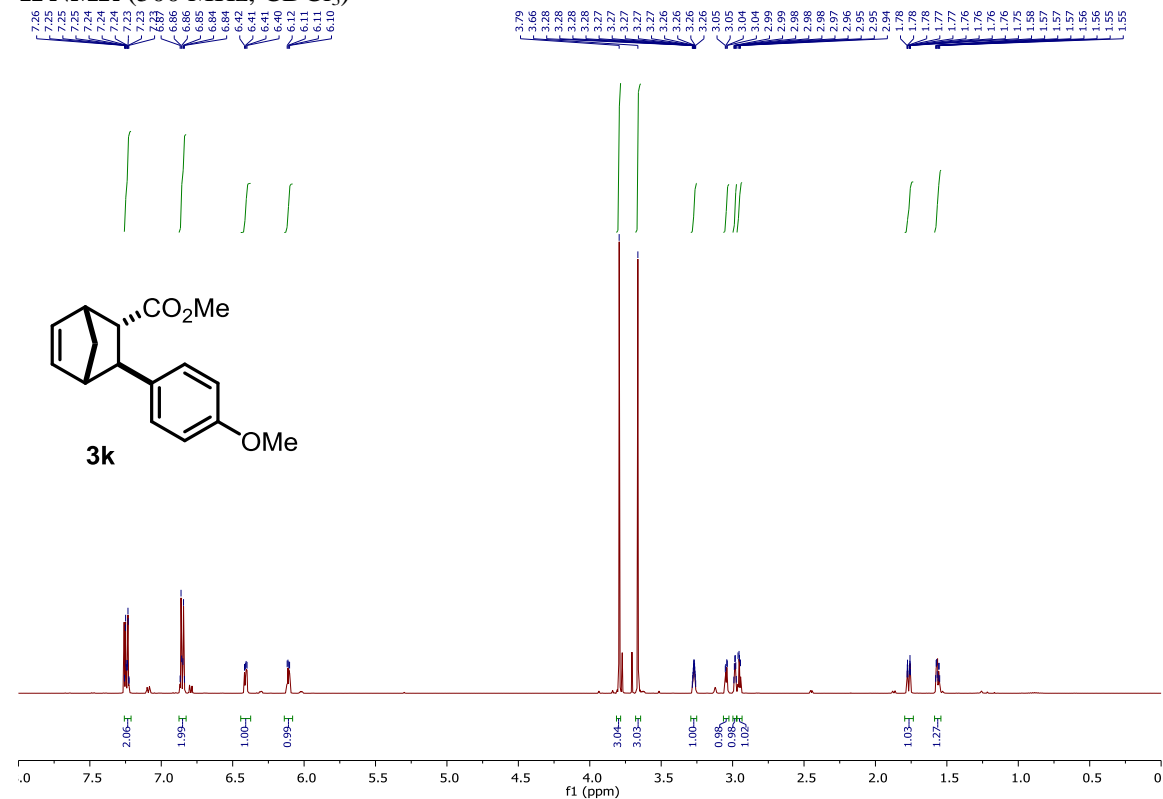


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

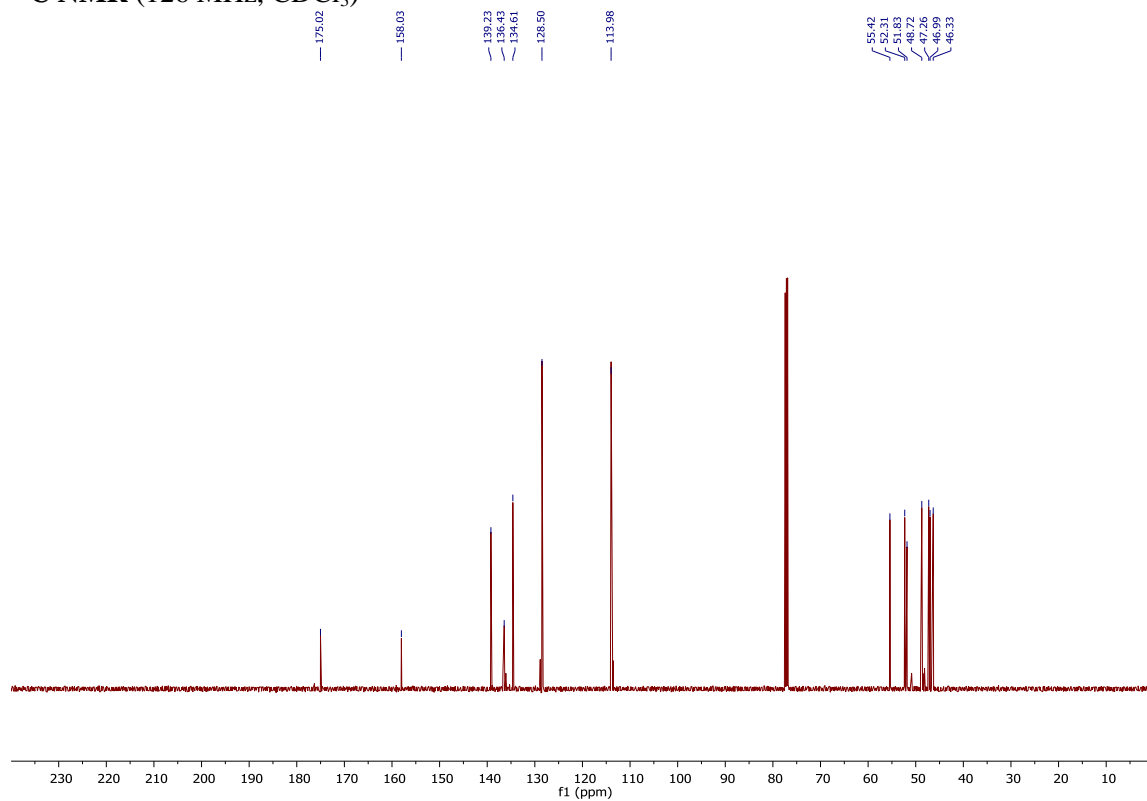


**methyl (1*R*,2*S*,3*S*,4*S*)-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3k):**

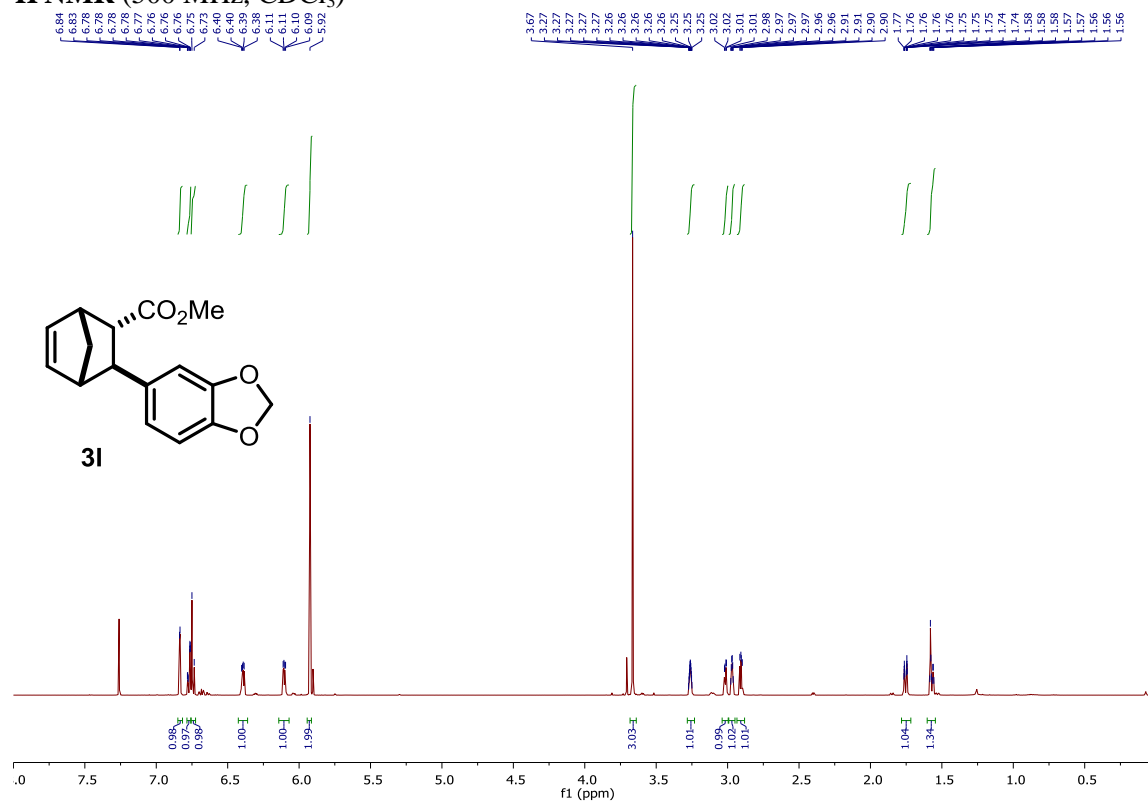
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



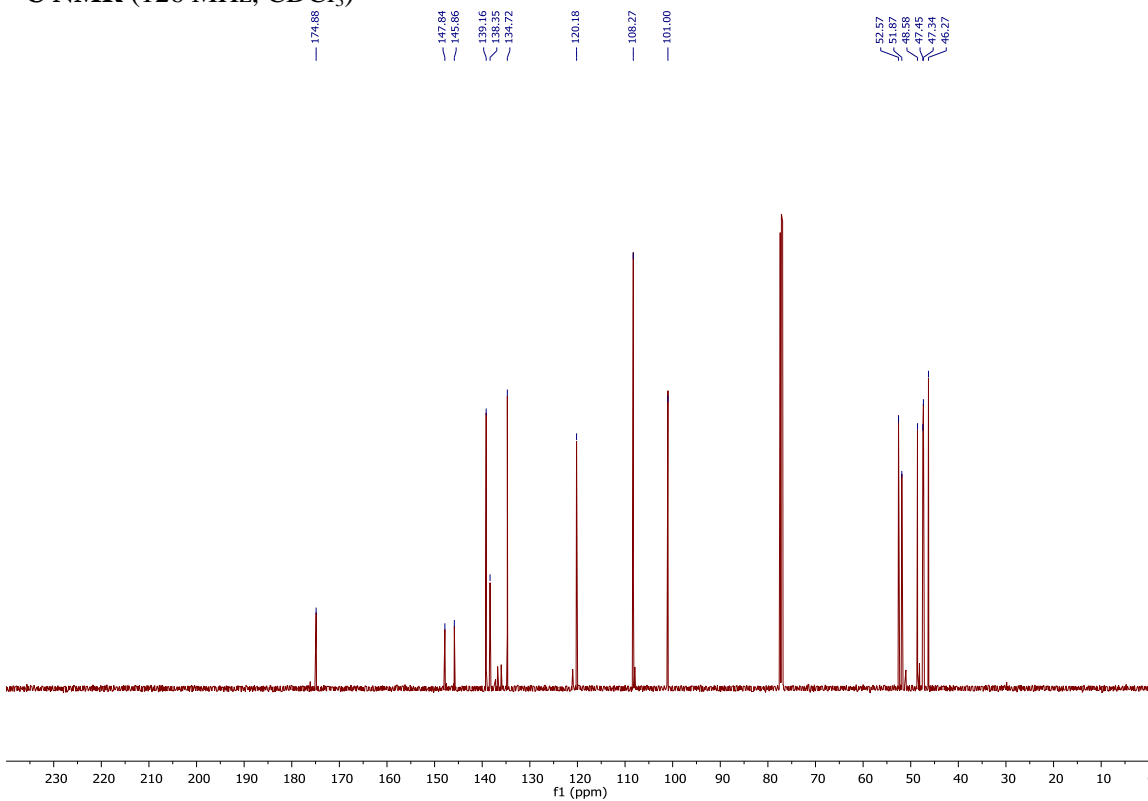
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



**methyl (1*R*,2*S*,3*S*,4*S*)-3-(benzo[d][1,3]dioxol-5-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (31):**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

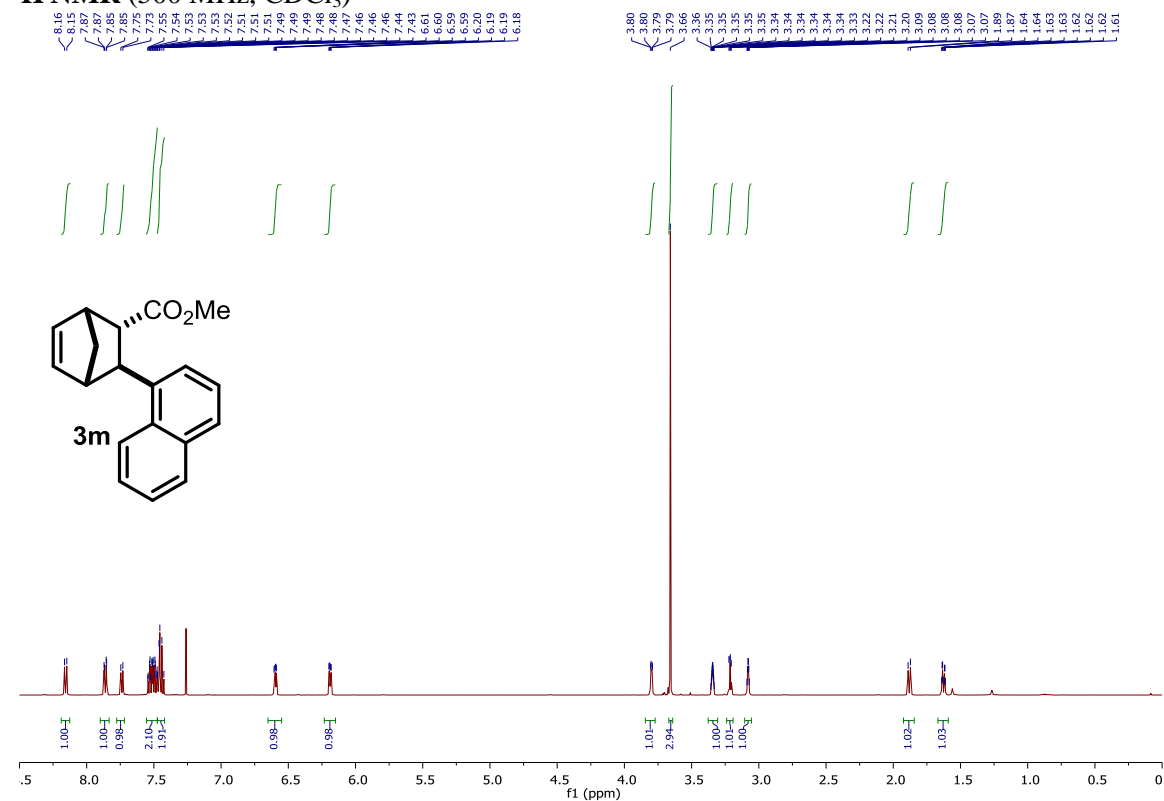


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

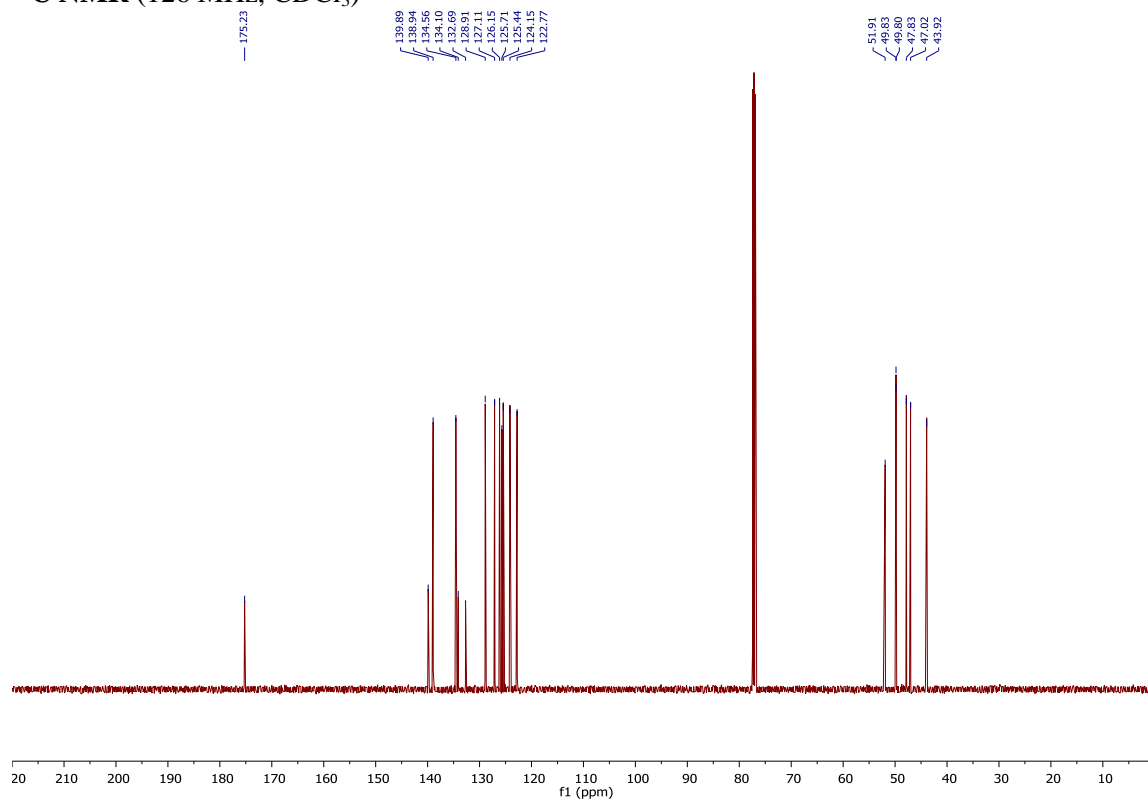


**methyl (1*R*,2*S*,3*S*,4*S*)-3-(naphthalen-1-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3m):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

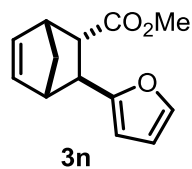
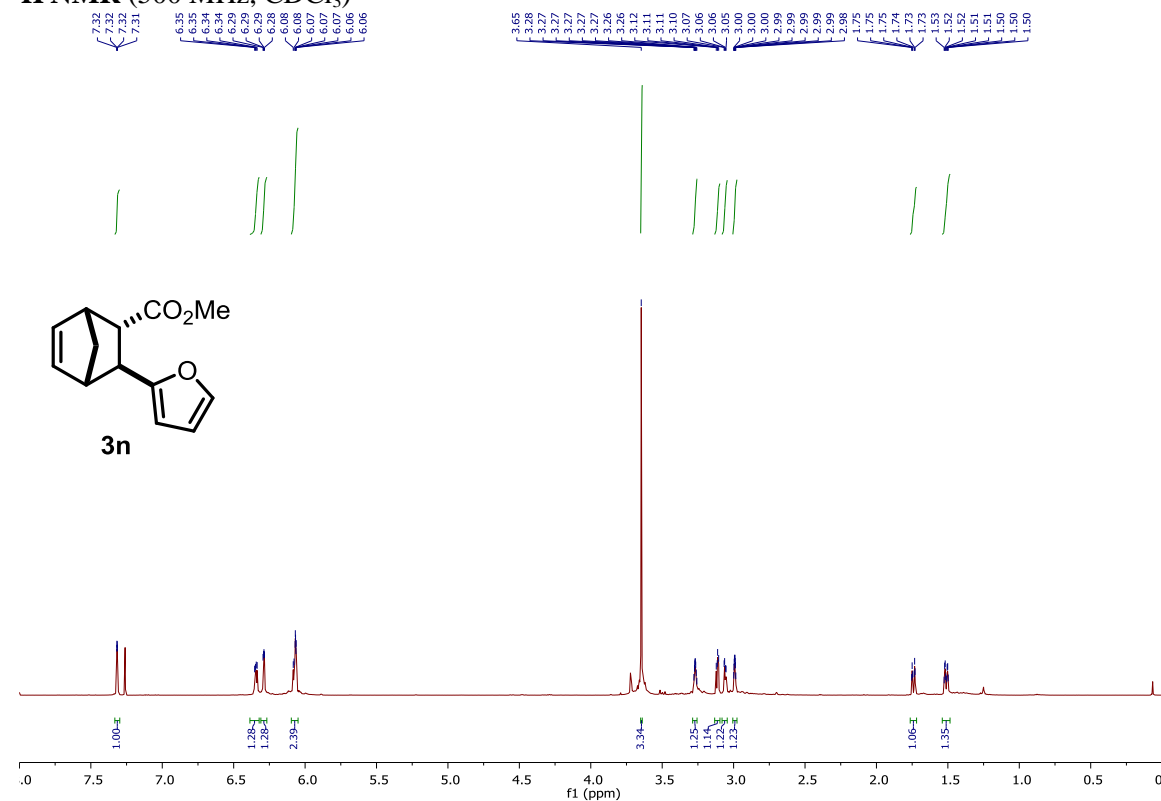


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

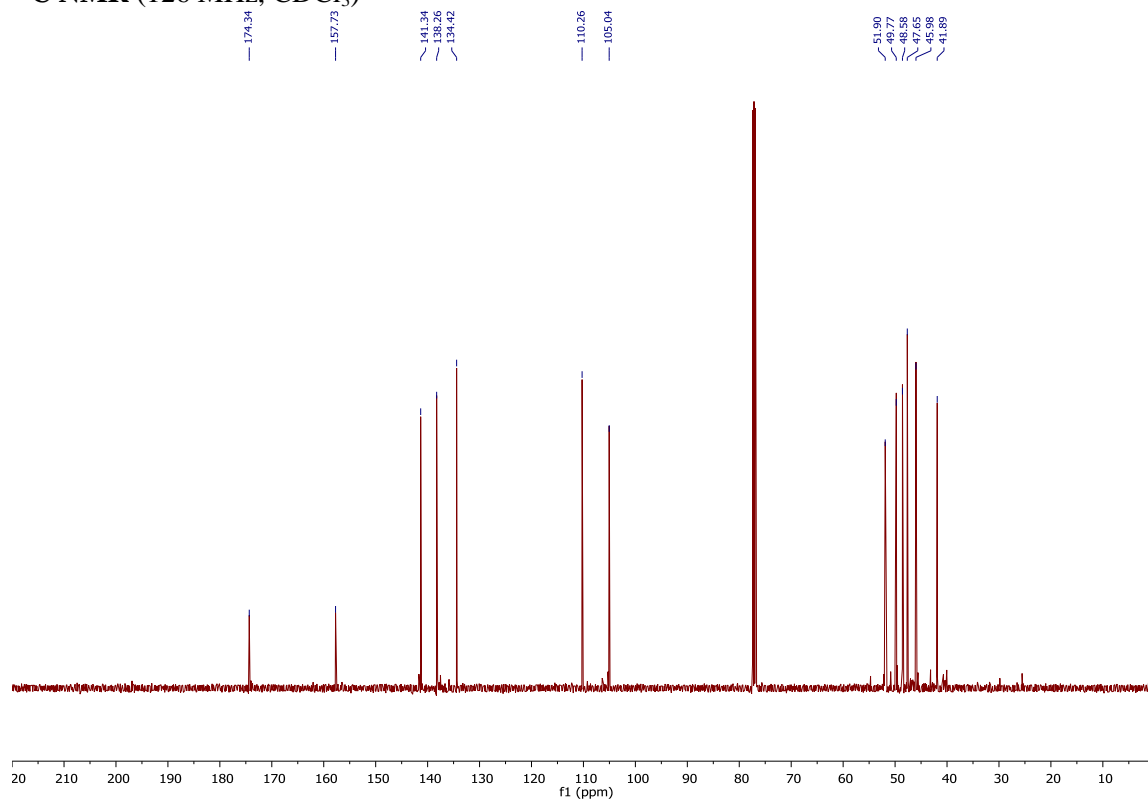


methyl (1*R*,2*S*,3*S*,4*S*)-3-(furan-2-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**3n**):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

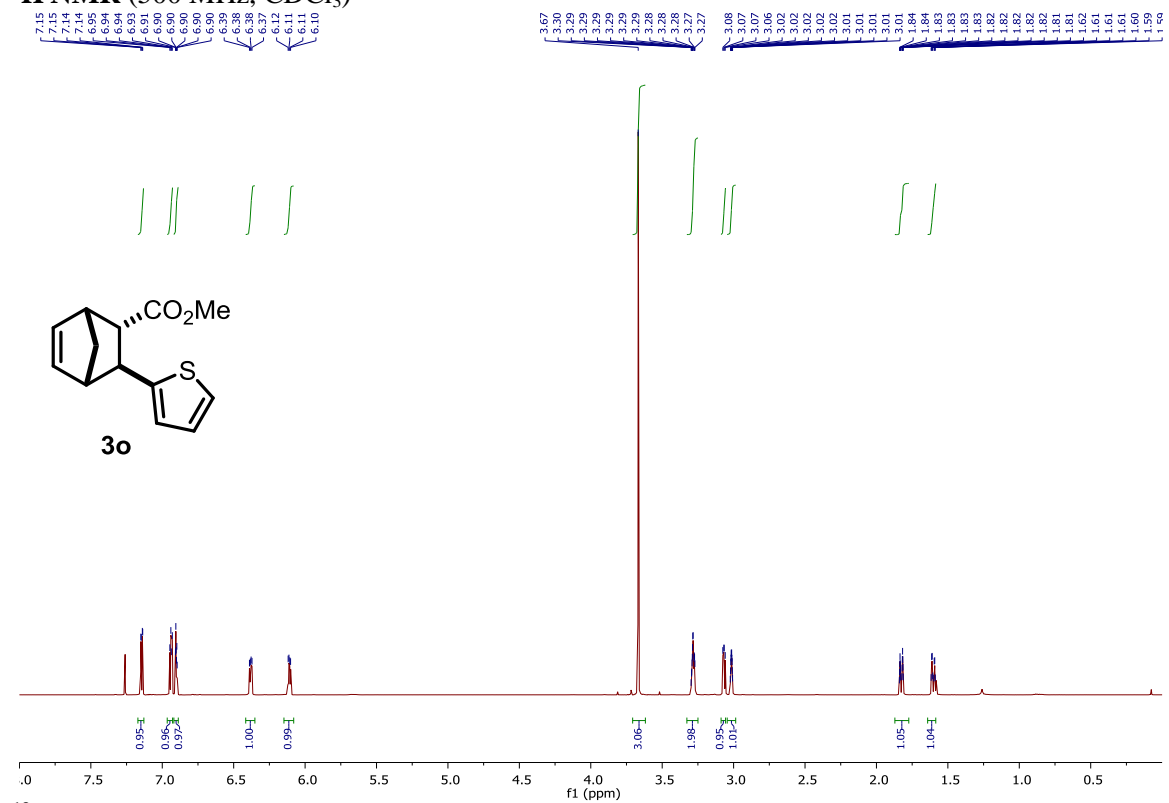


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

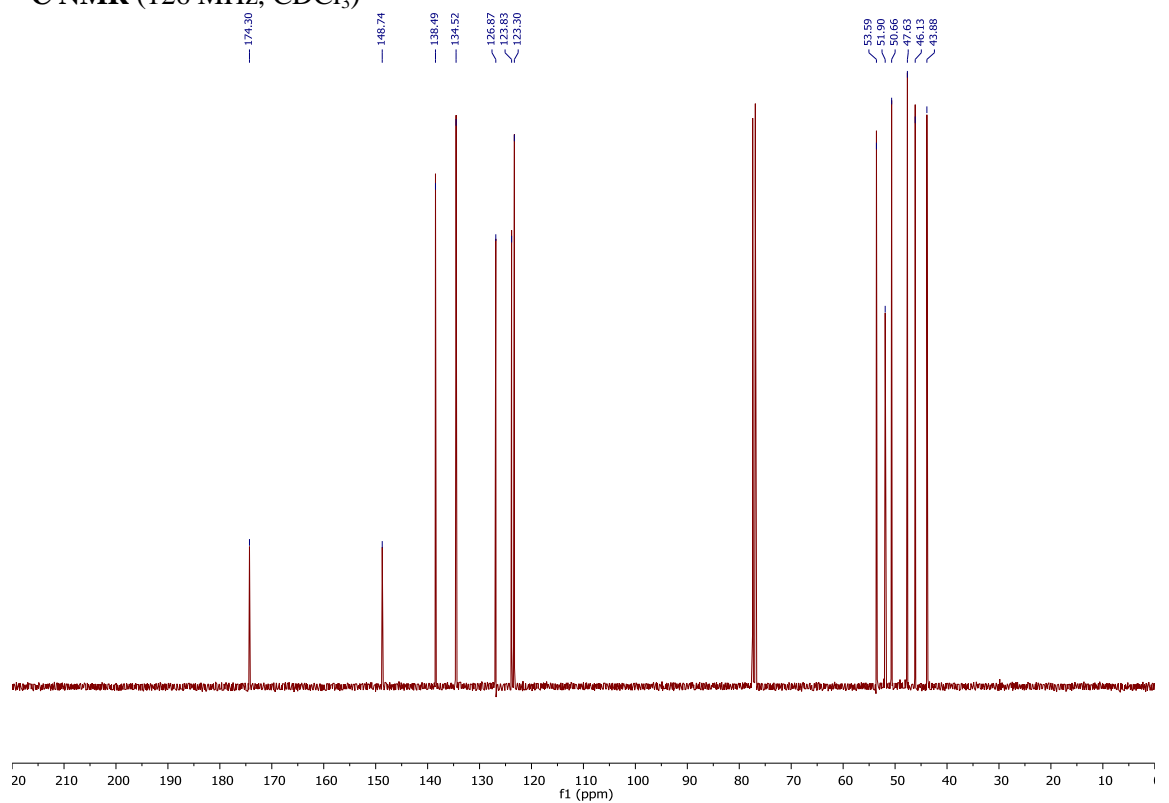


**methyl (1*R*,2*S*,3*S*,4*S*)-3-(thiophen-2-yl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (3o):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

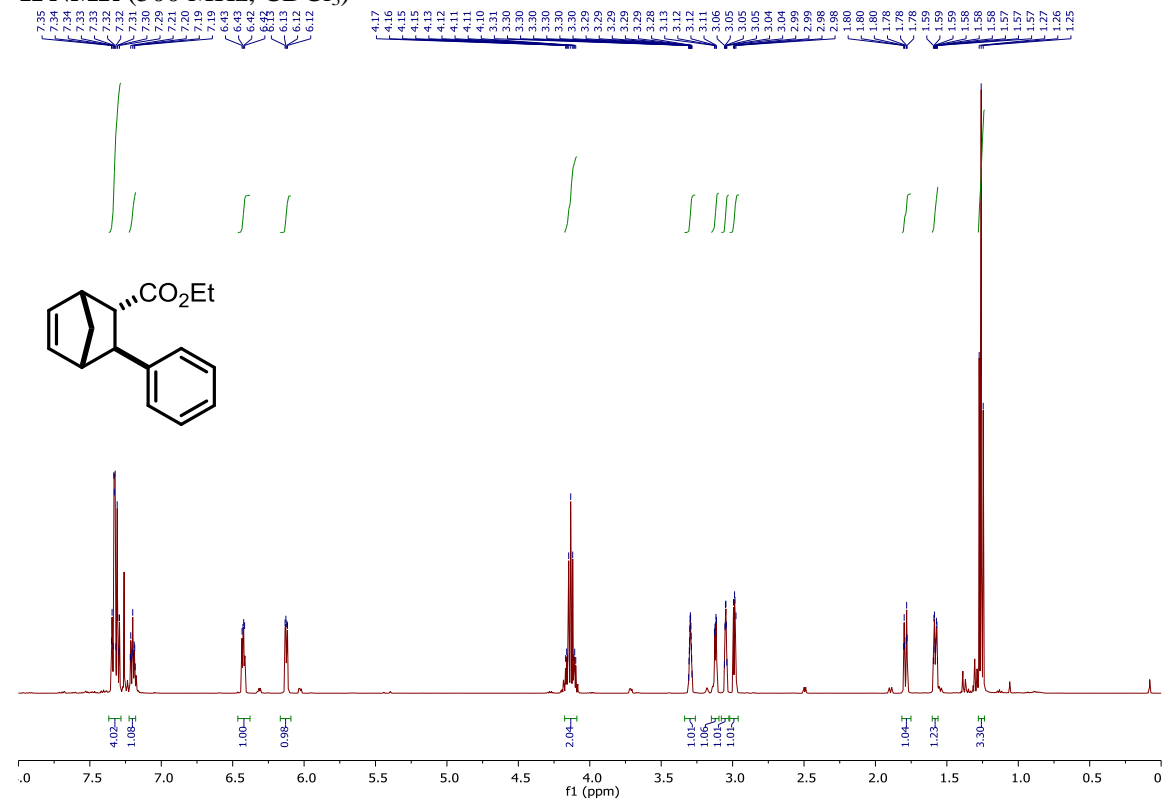


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

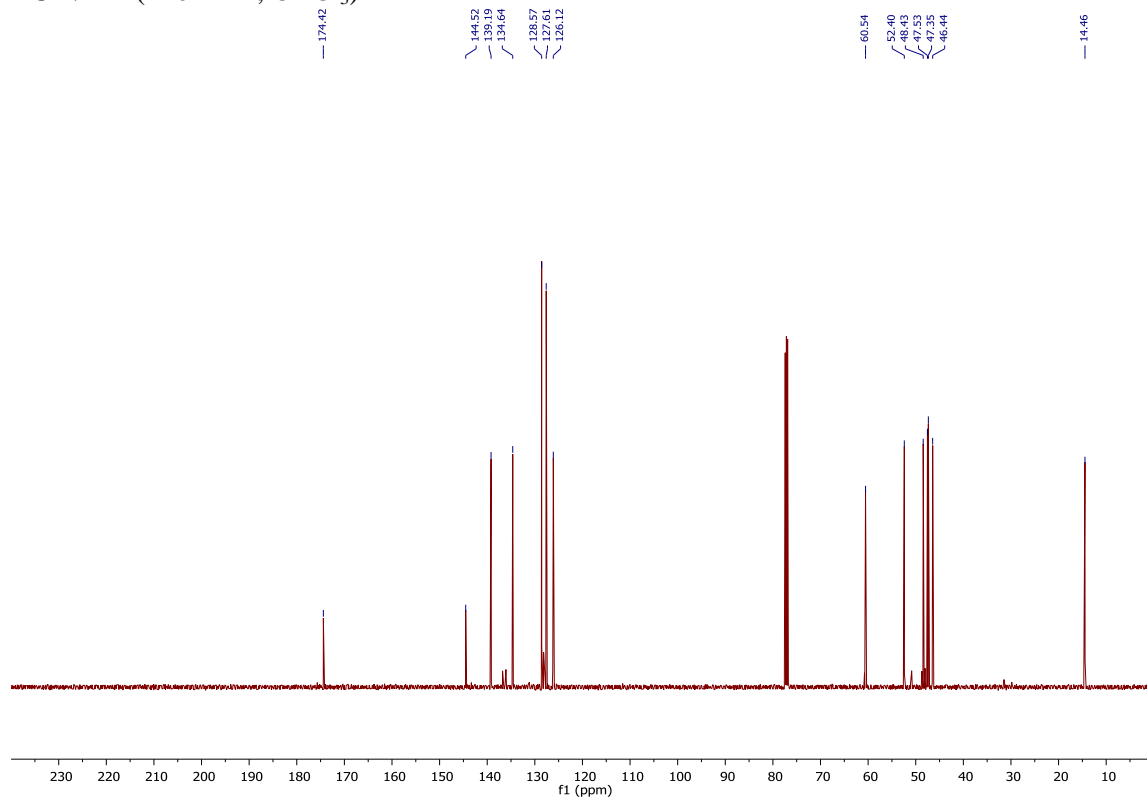


ethyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

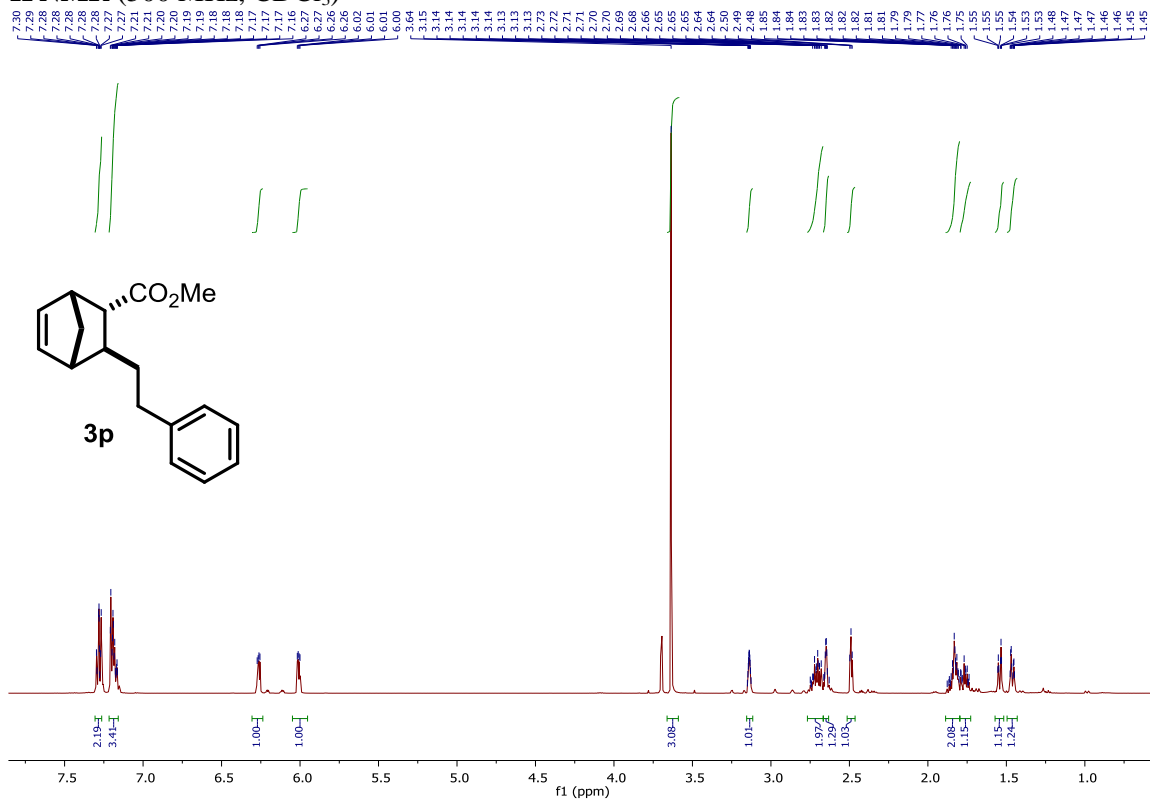


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

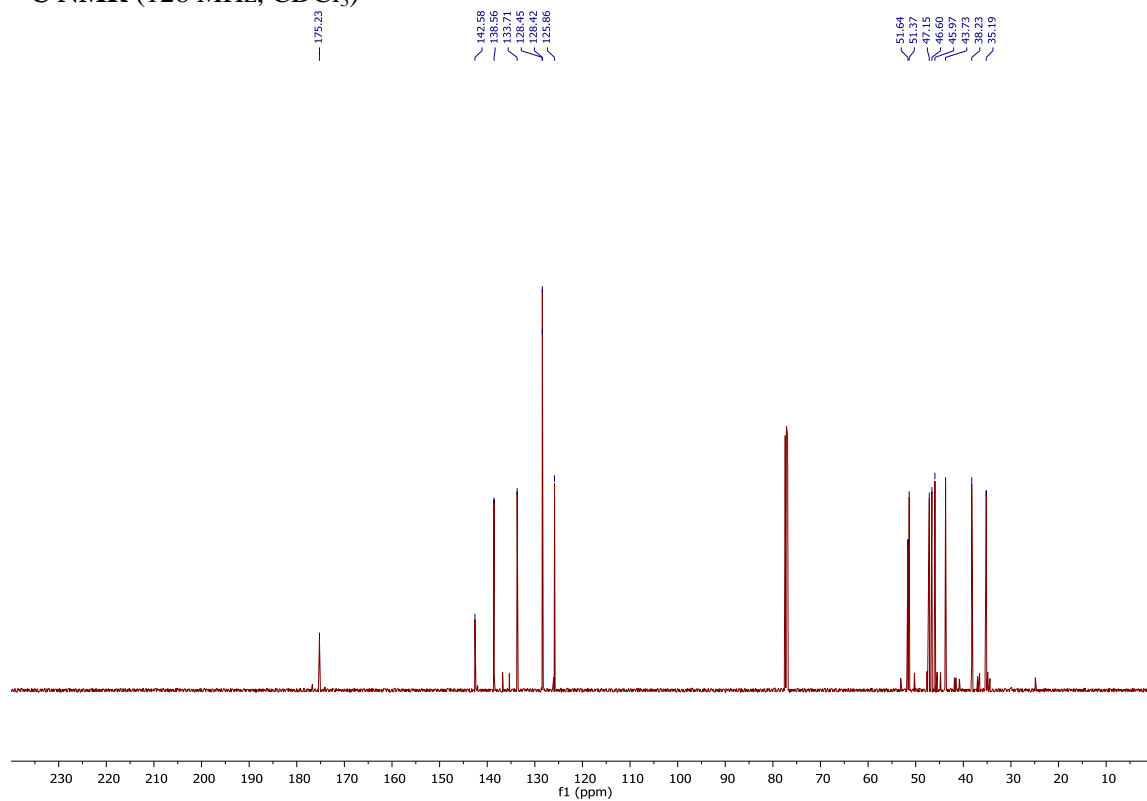


**methyl (1*R*,2*S*,3*S*,4*S*)-3-phenethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3p):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

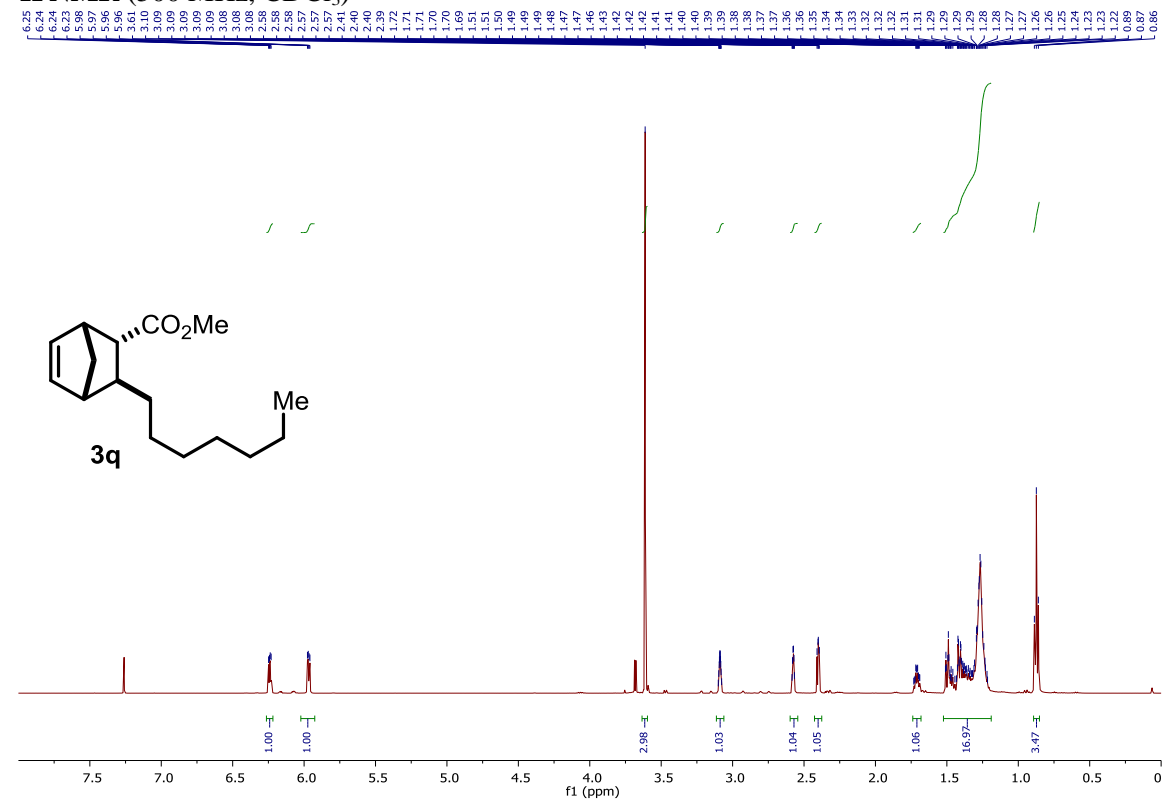


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

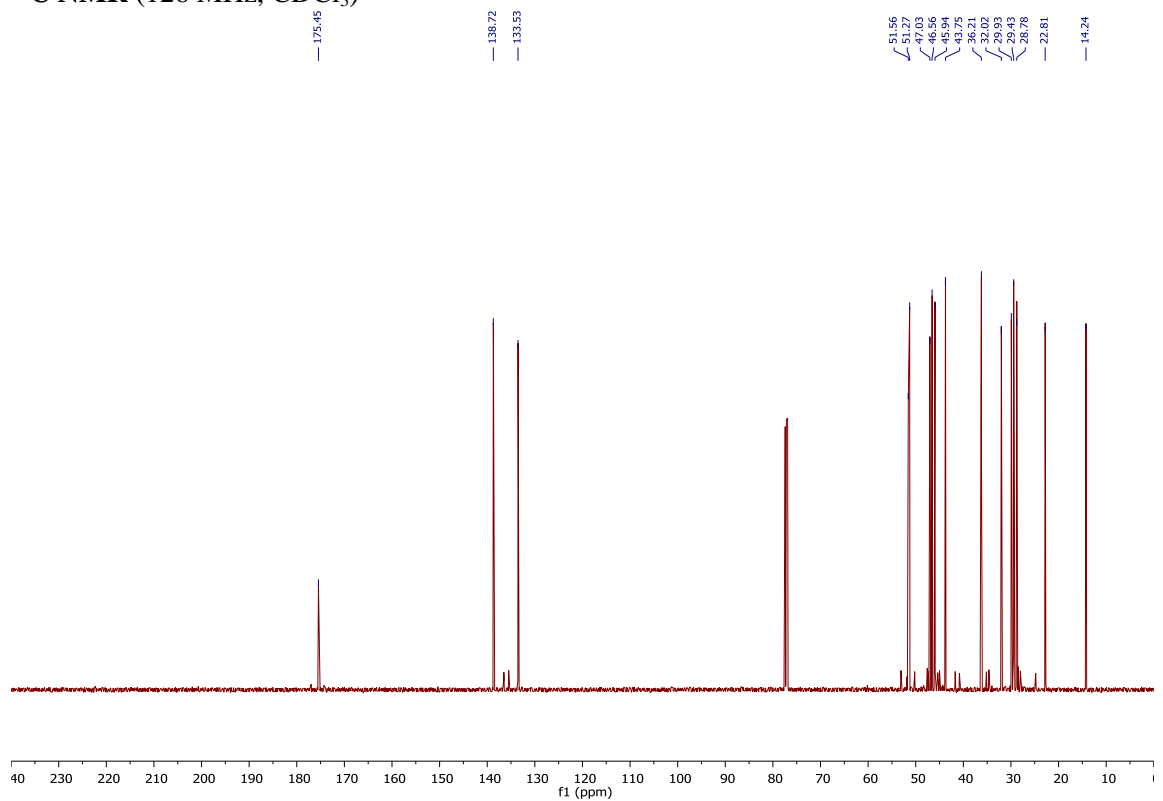


**methyl (1*R*,2*S*,3*S*,4*S*)-3-heptylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3q):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

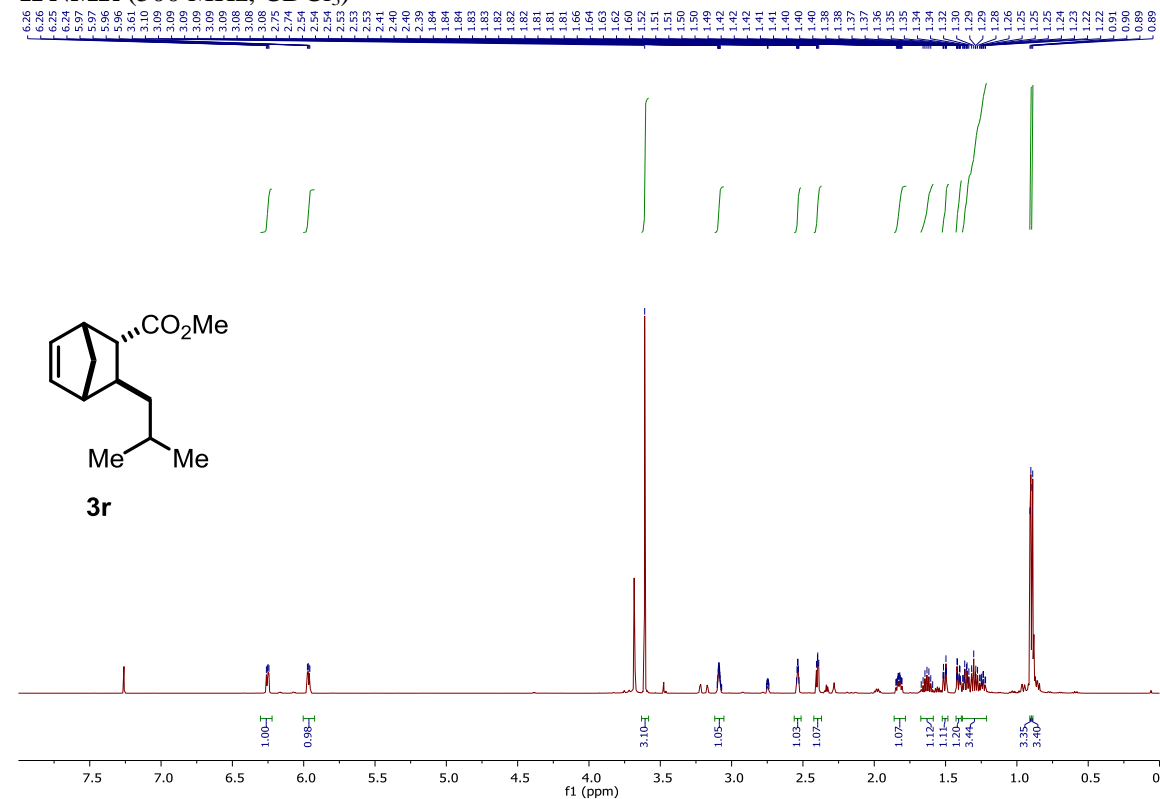


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

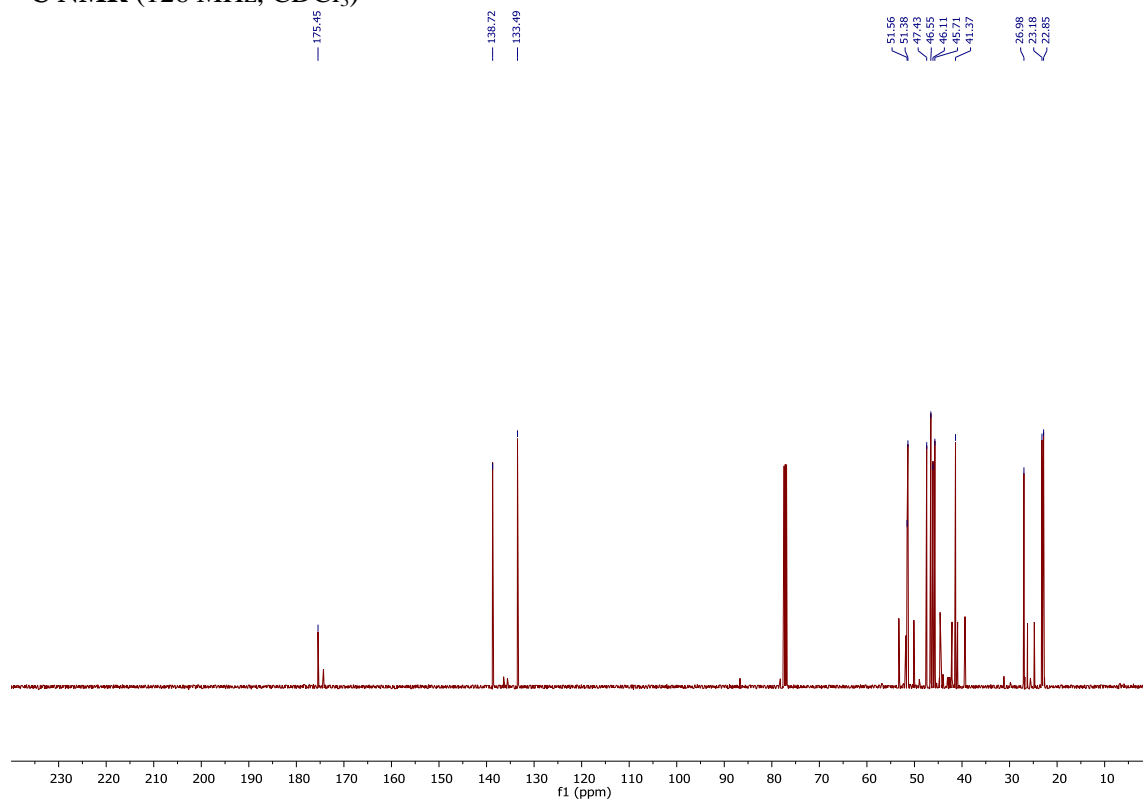


**methyl (1*R*,2*S*,3*S*,4*S*)-3-isobutylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3r):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

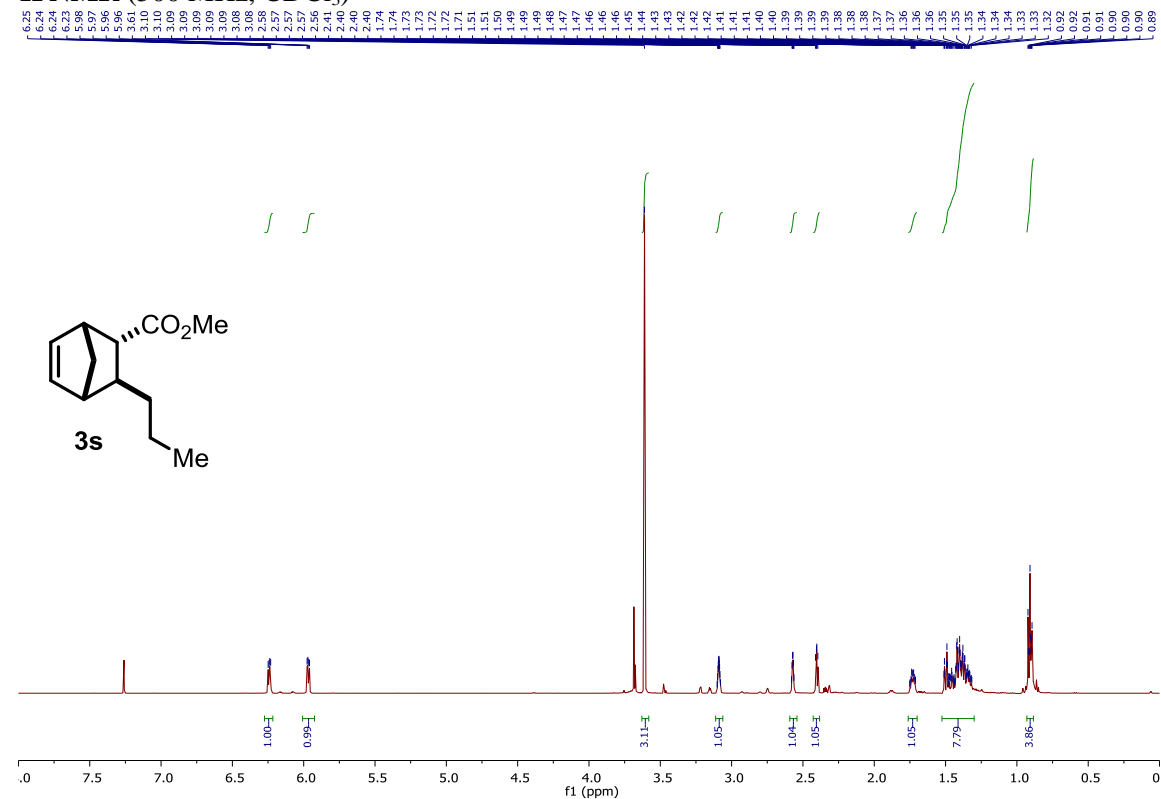


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

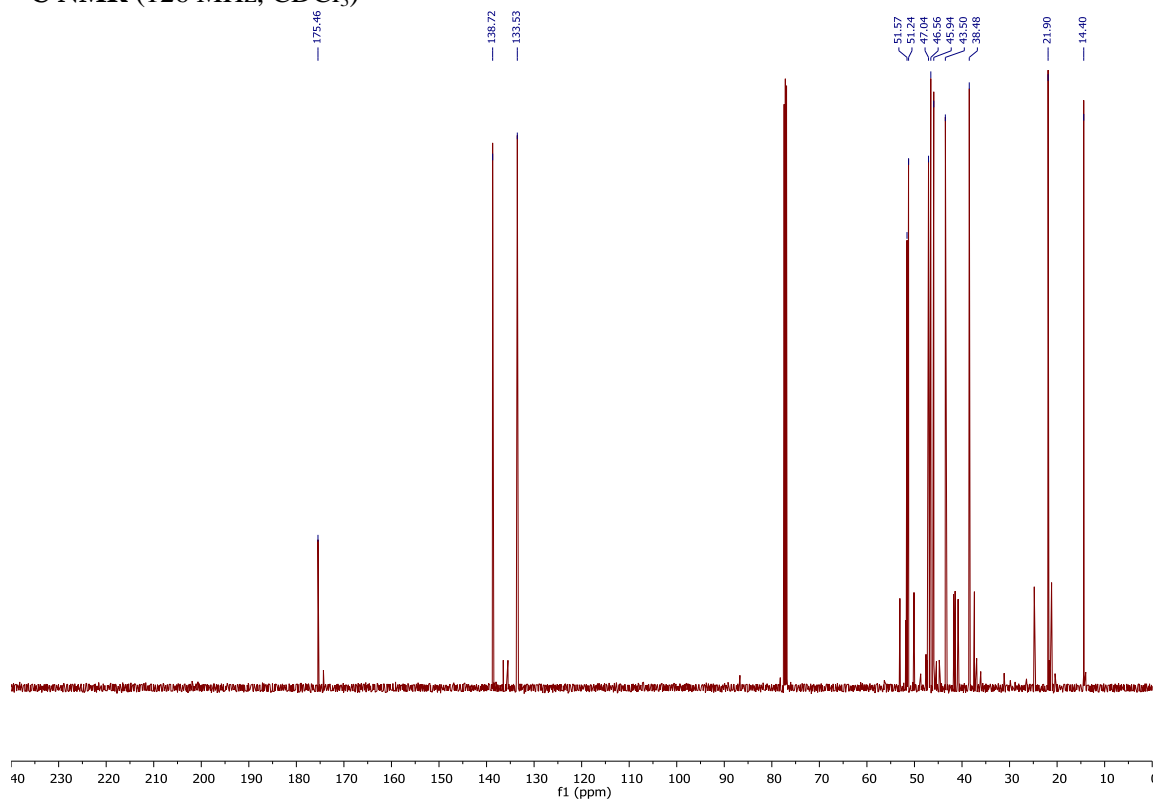


**methyl (1R,2S,3S,4S)-3-propylbicyclo[2.2.1]hept-5-ene-2-carboxylate (3s):**

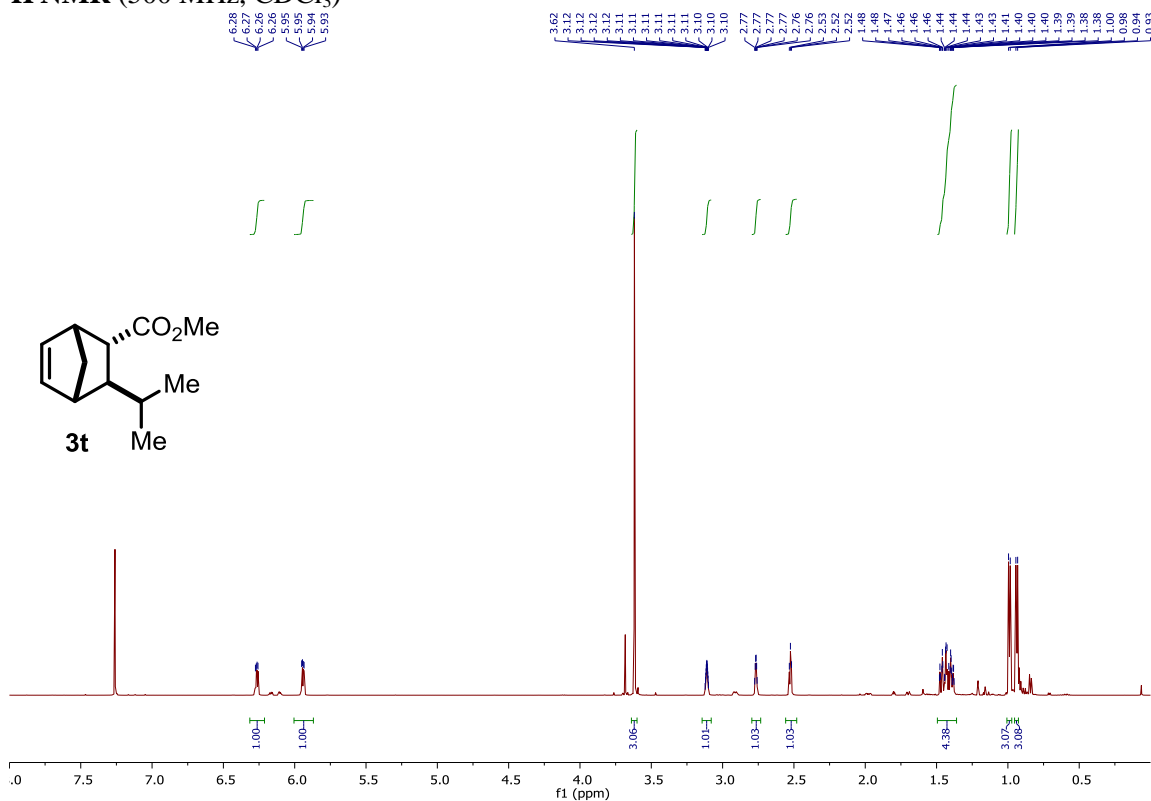
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



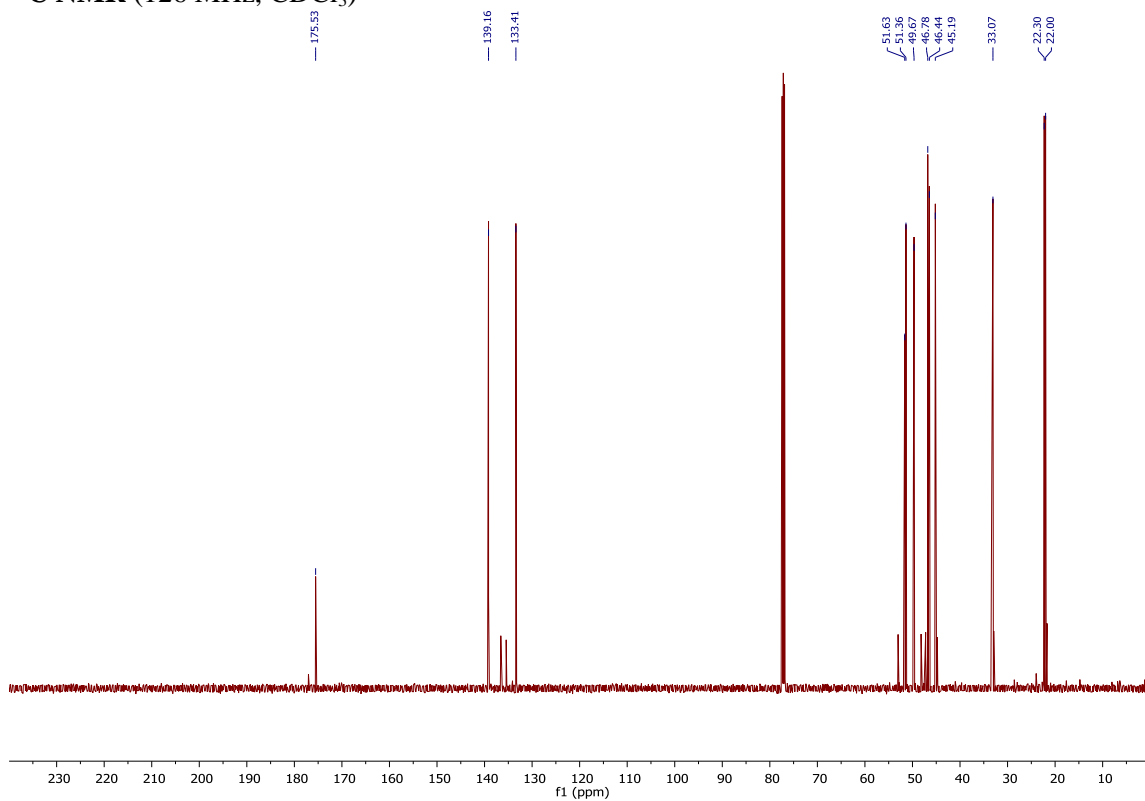
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



methyl (1*R*,2*S*,3*S*,4*S*)-3-isopropylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**3t**):  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



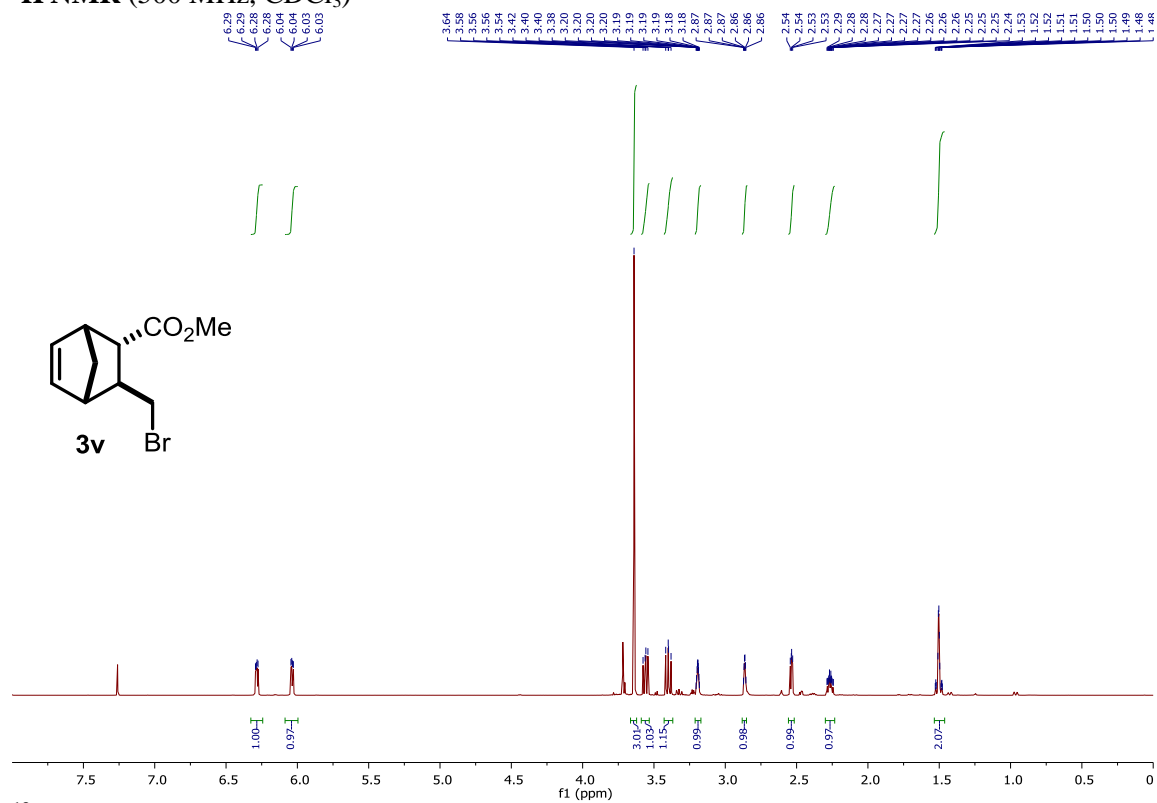
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



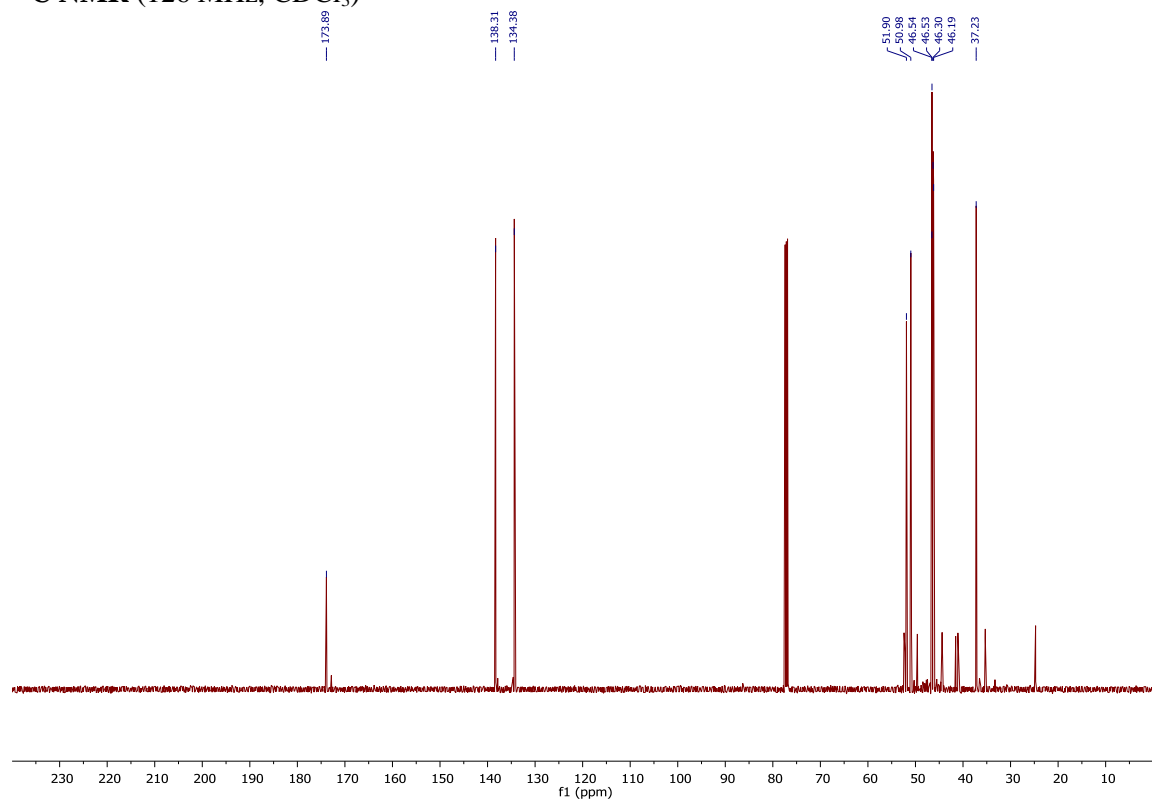


methyl (1*R*,2*S*,3*S*,4*S*)-3-(bromomethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**3v**):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

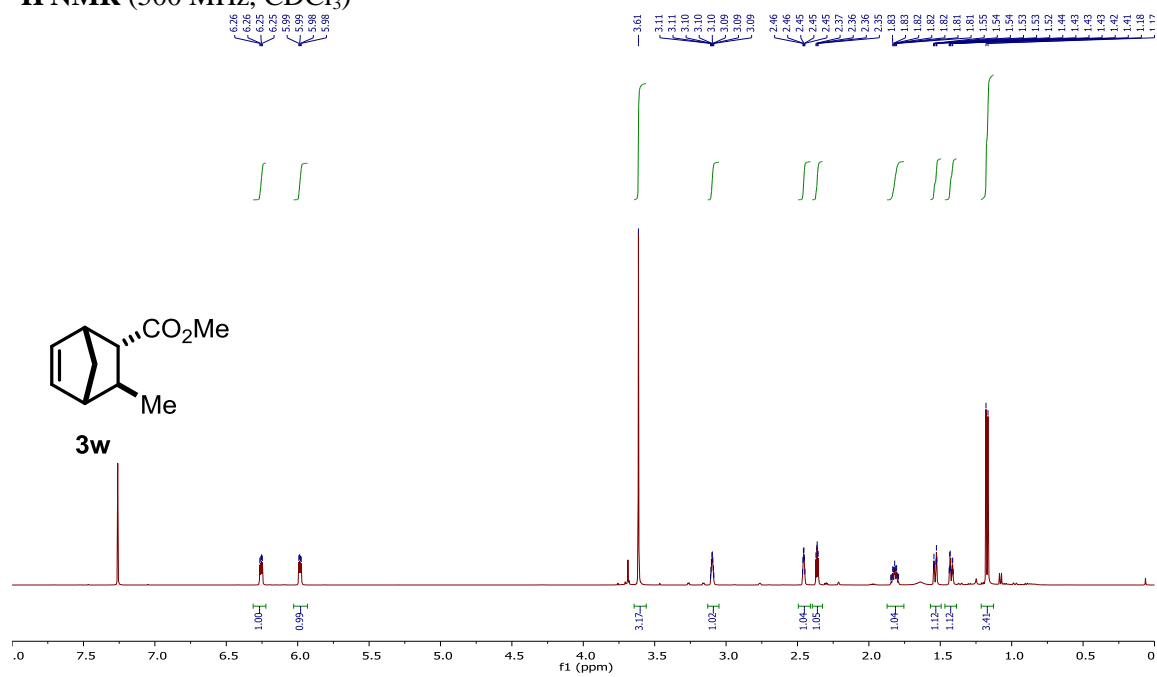


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

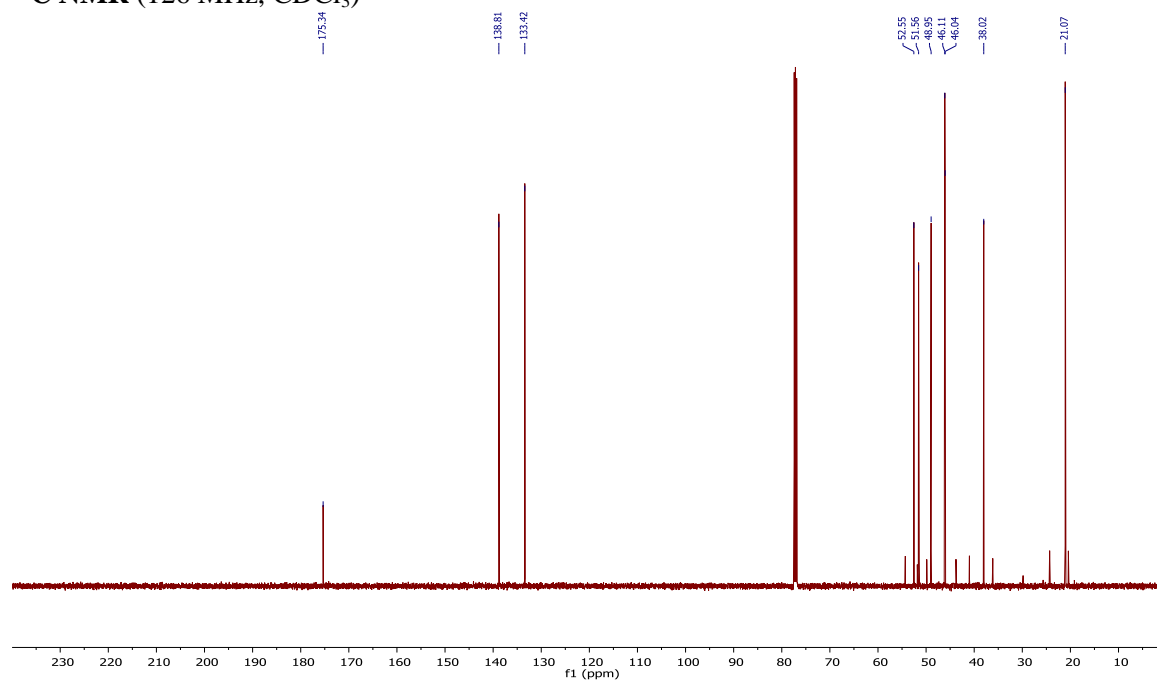


methyl (1*R*,2*R*,3*S*,4*S*)-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**3w**):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



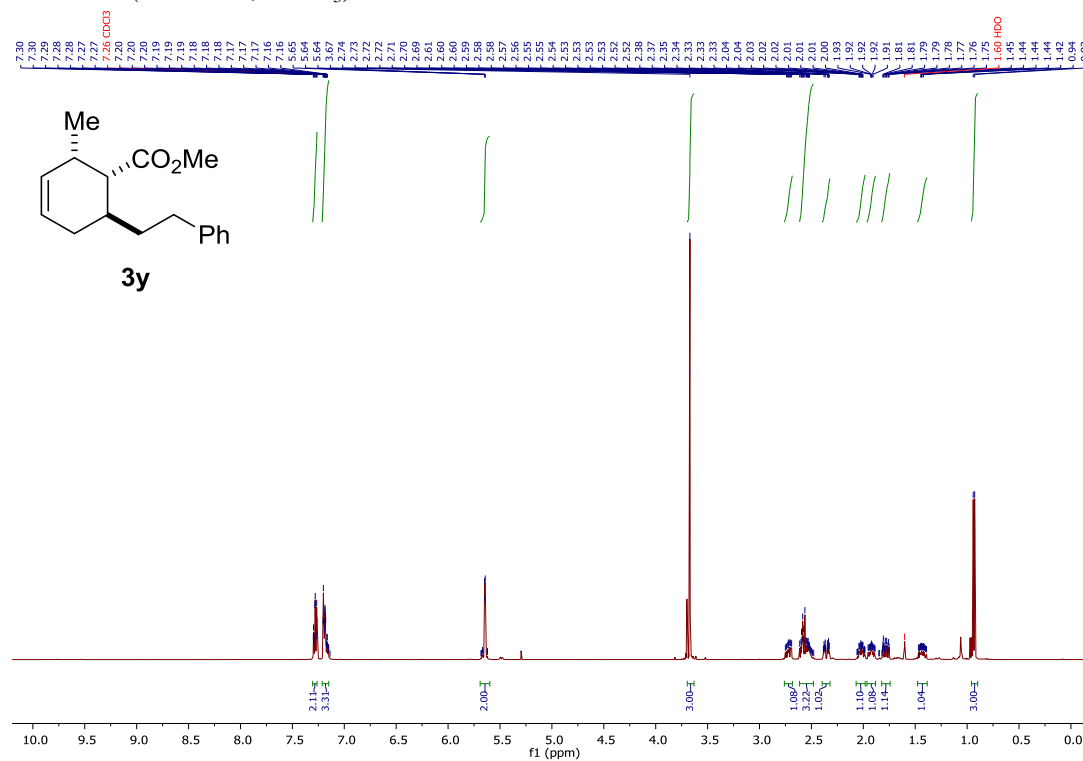
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



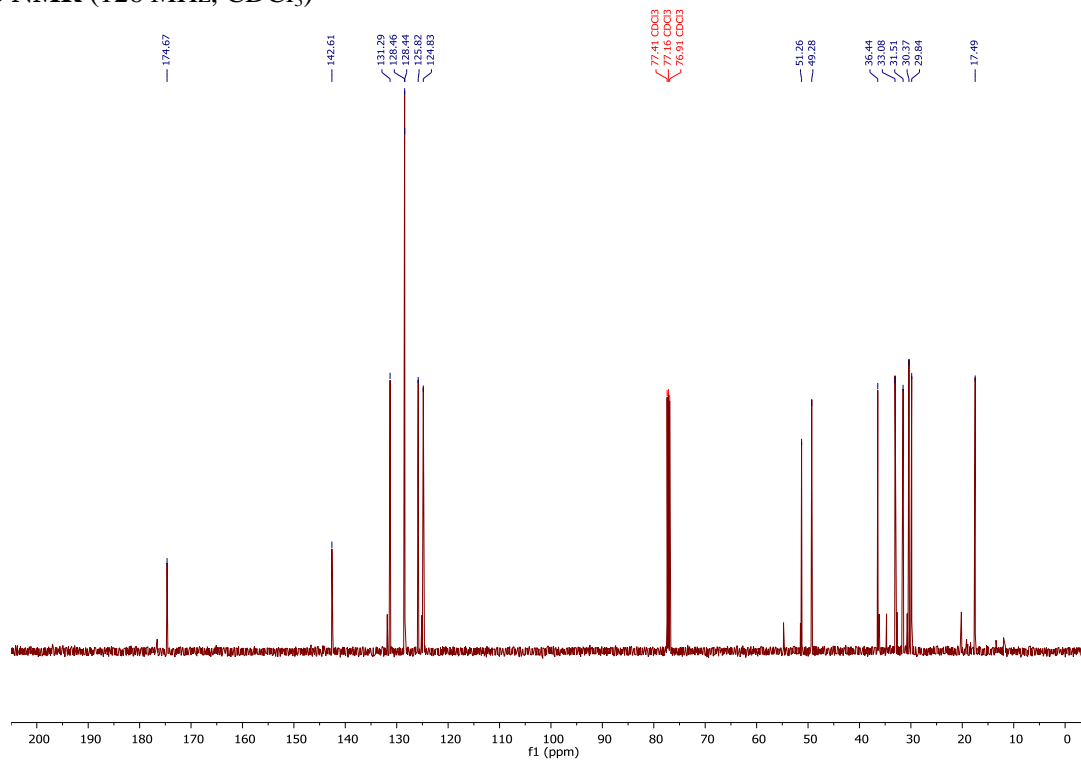


**methyl (1*R*,2*S*,6*S*)-2-methyl-6-phenethylcyclohex-3-ene-1-carboxylate (3y):**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

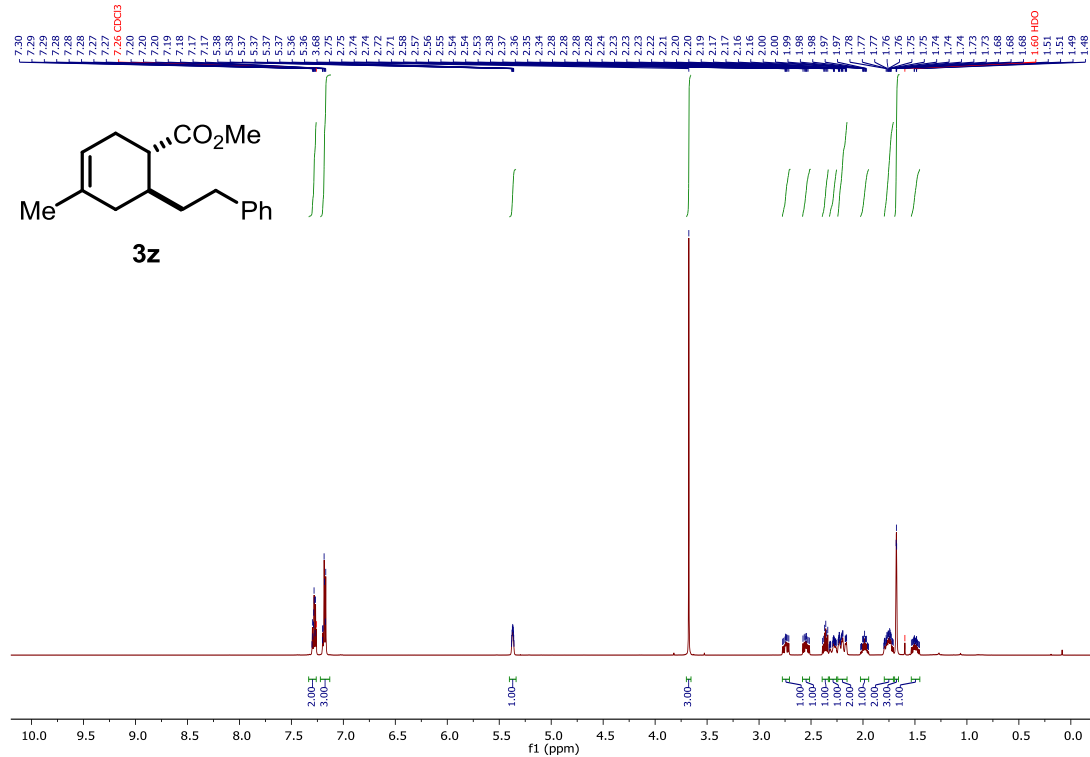


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

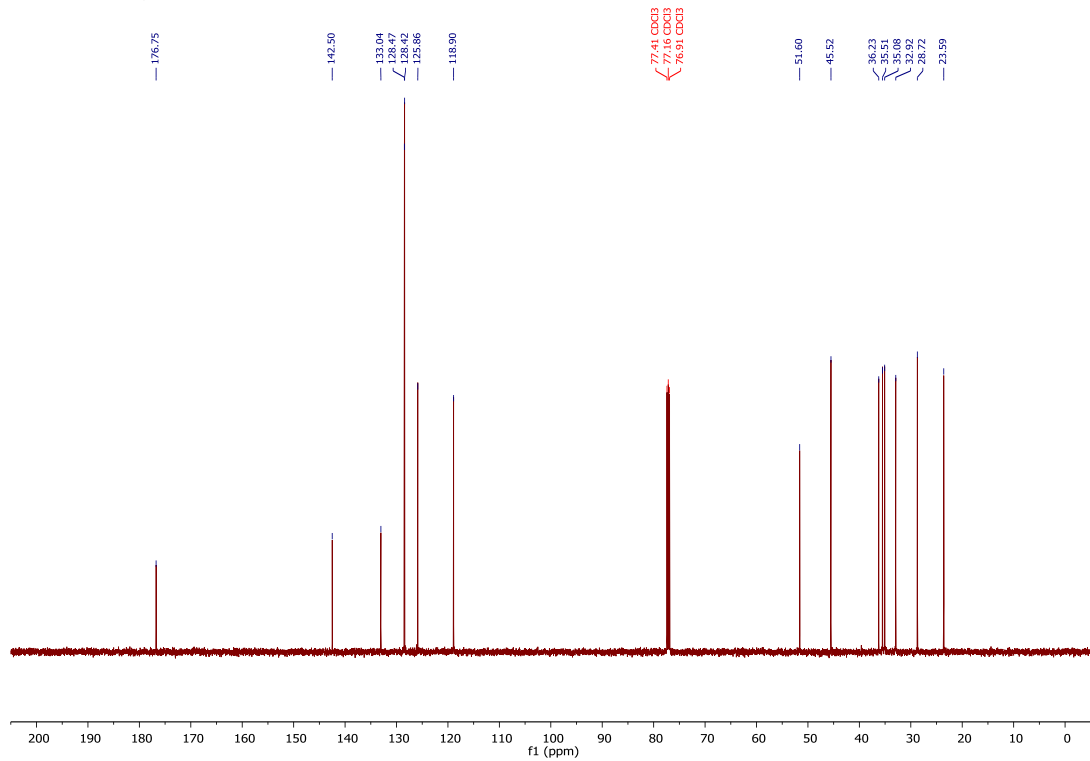


**methyl (1*S*,6*S*)-4-methyl-6-phenethylcyclohex-3-ene-1-carboxylate (3z):**

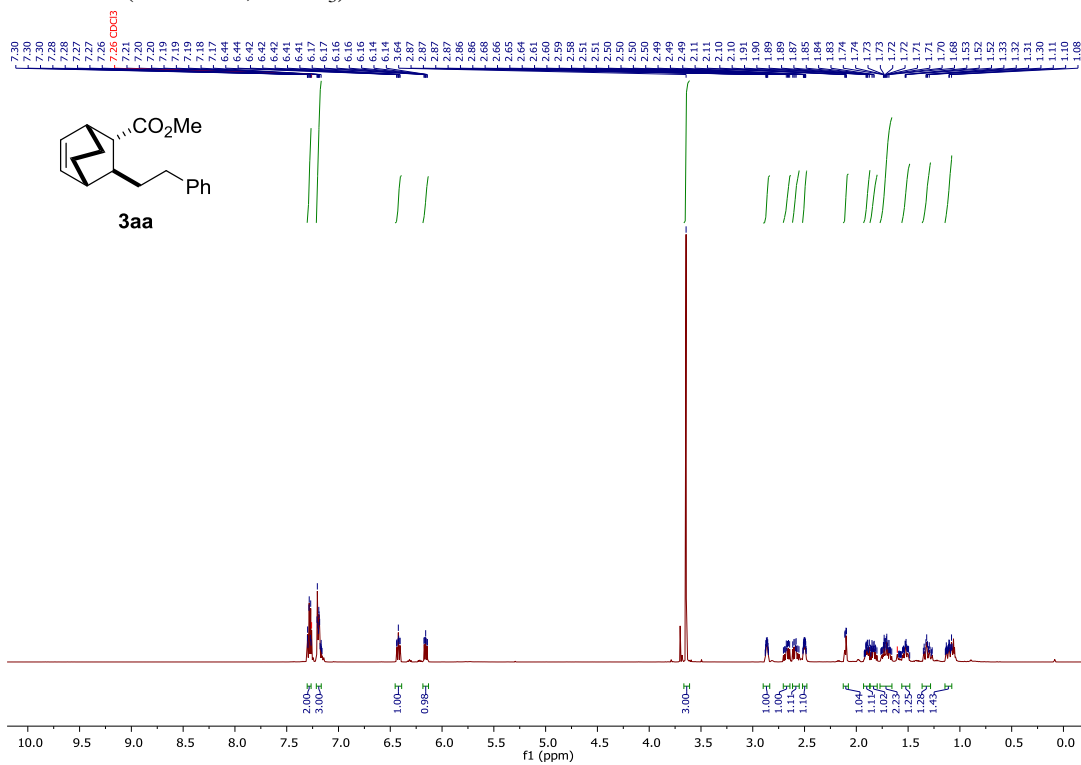
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



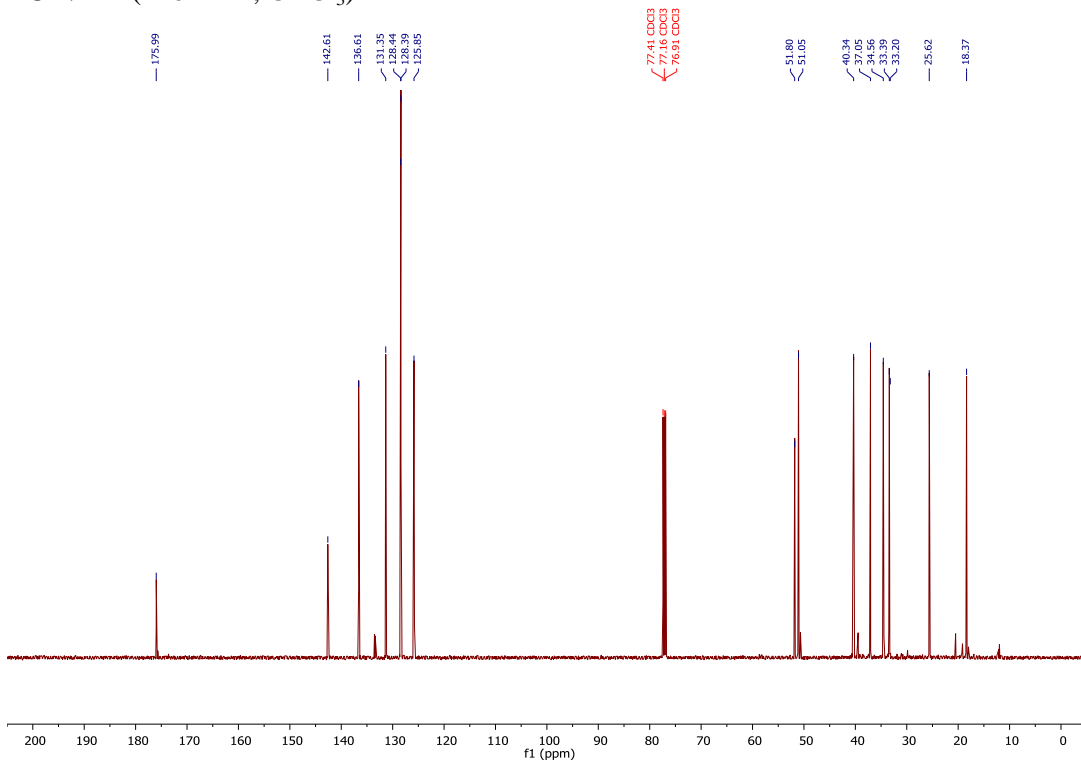
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



**methyl (1*R*,2*S*,3*S*,4*S*)-3-phenethylbicyclo[2.2.2]oct-5-ene-2-carboxylate (3aa):**  
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

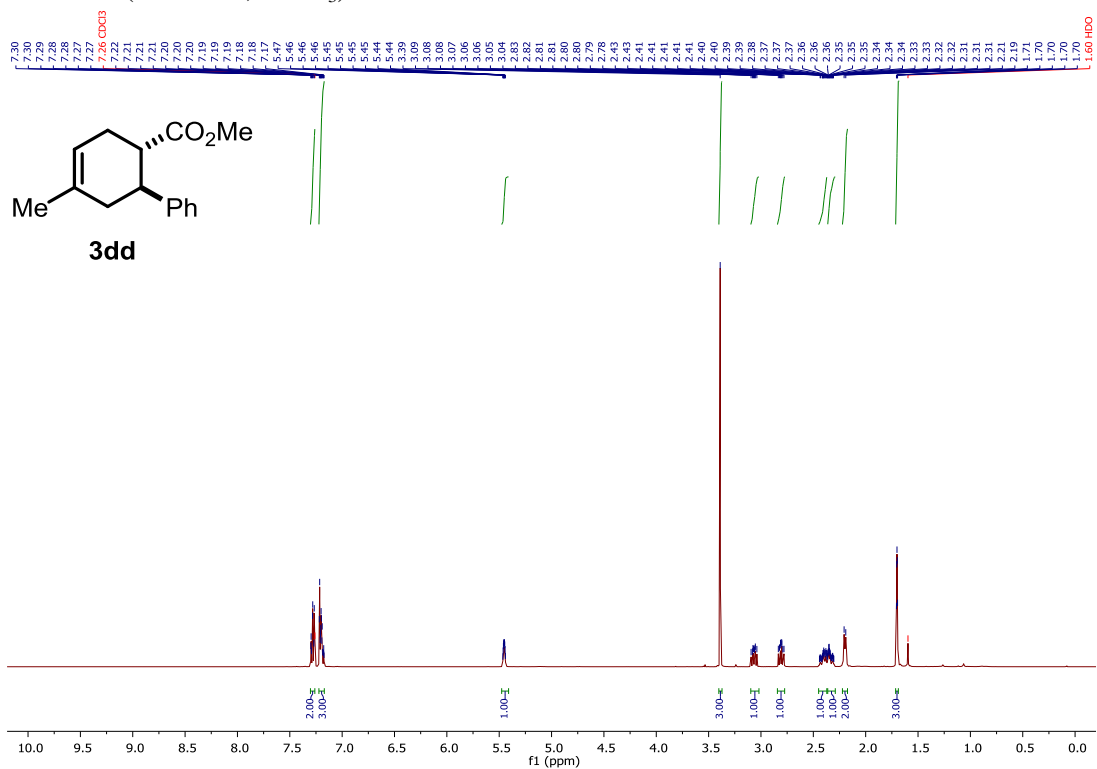


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

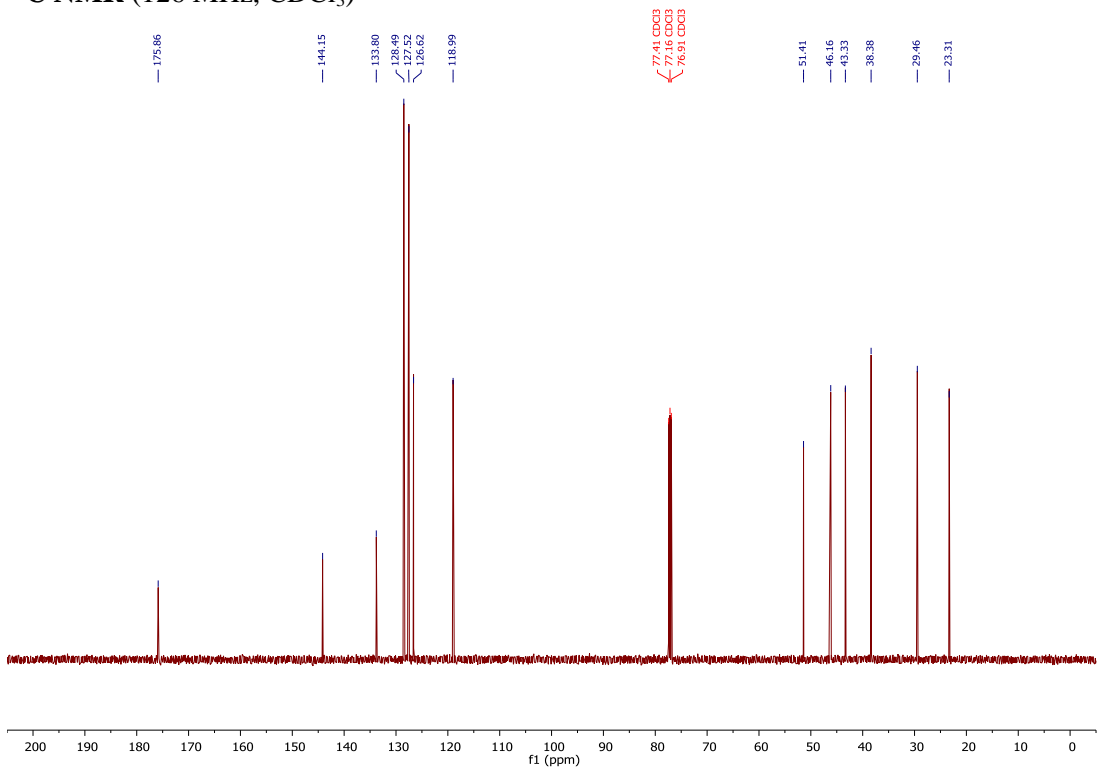




**methyl (1*S*,2*S*)-5-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (3dd):**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

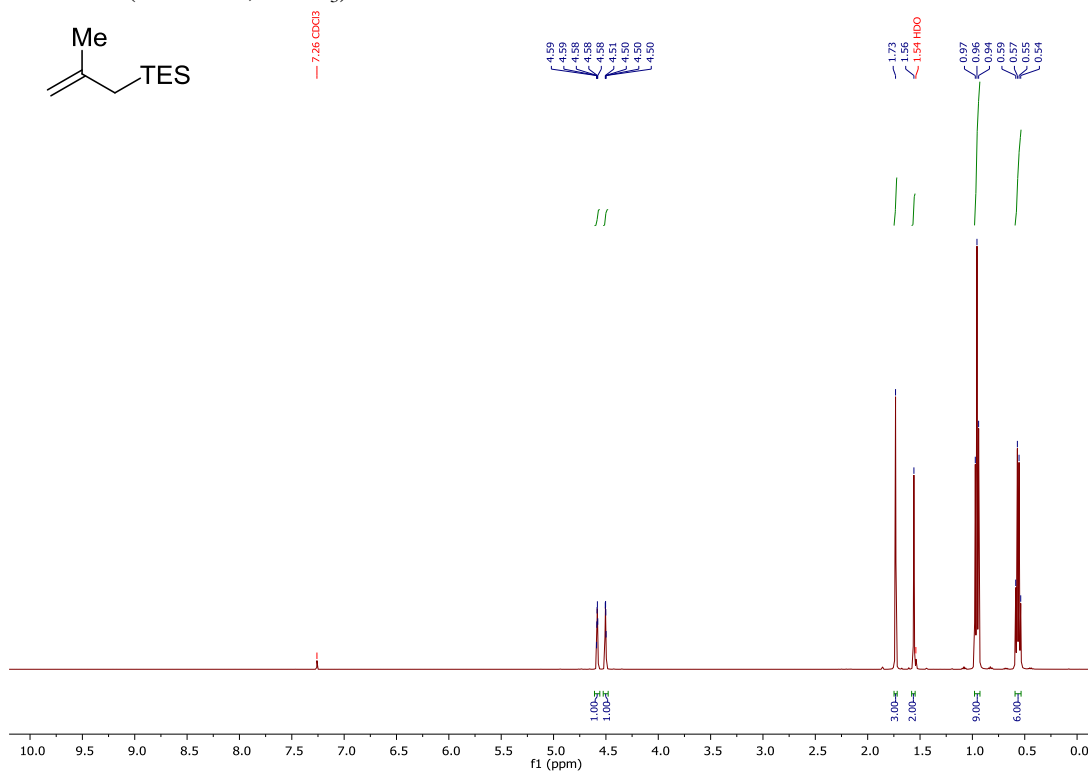
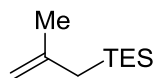


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

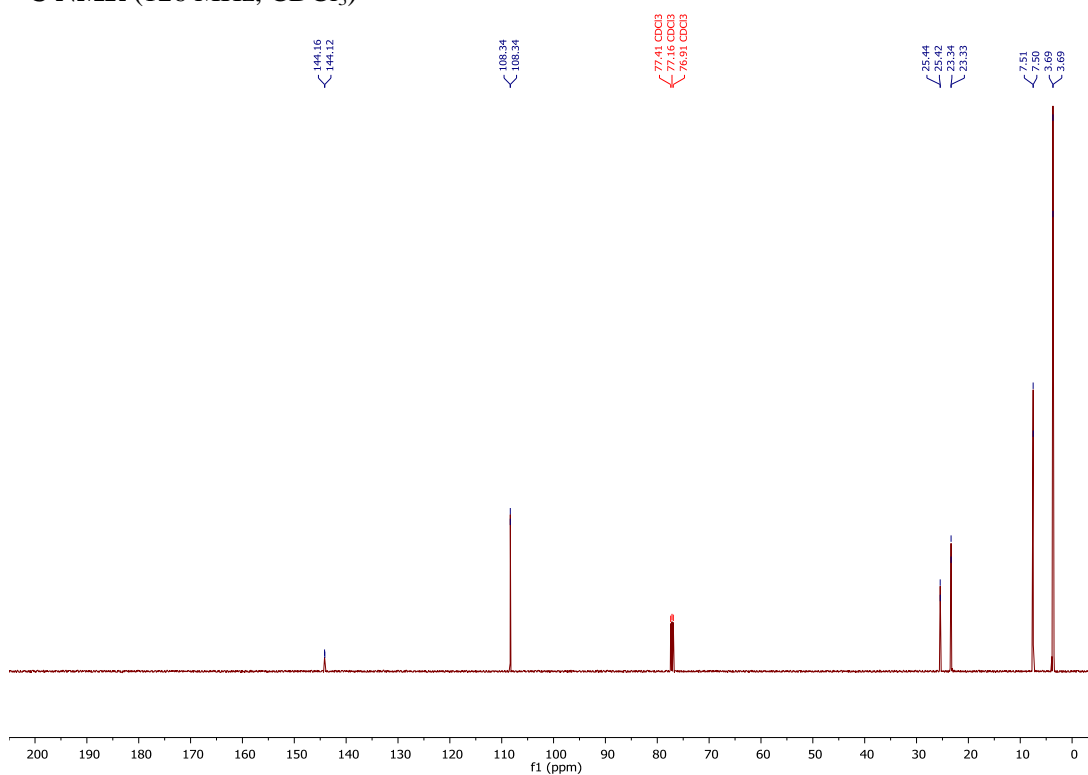


triethyl(2-methylallyl)silane (5k):

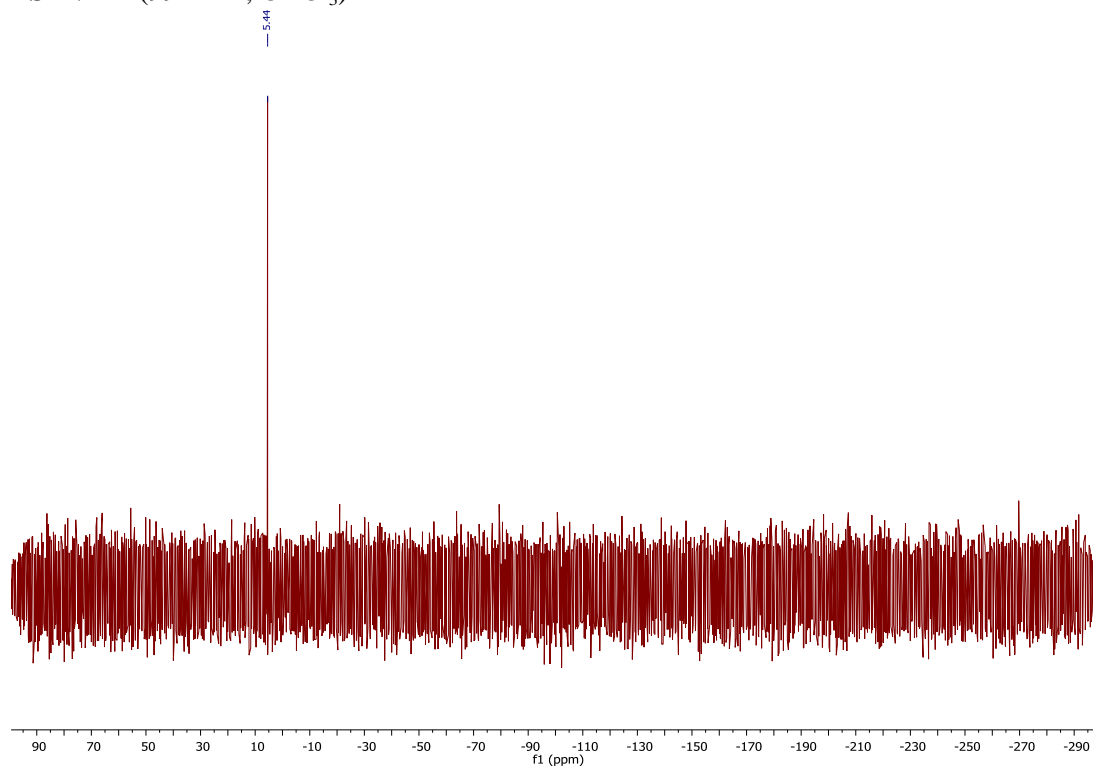
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )

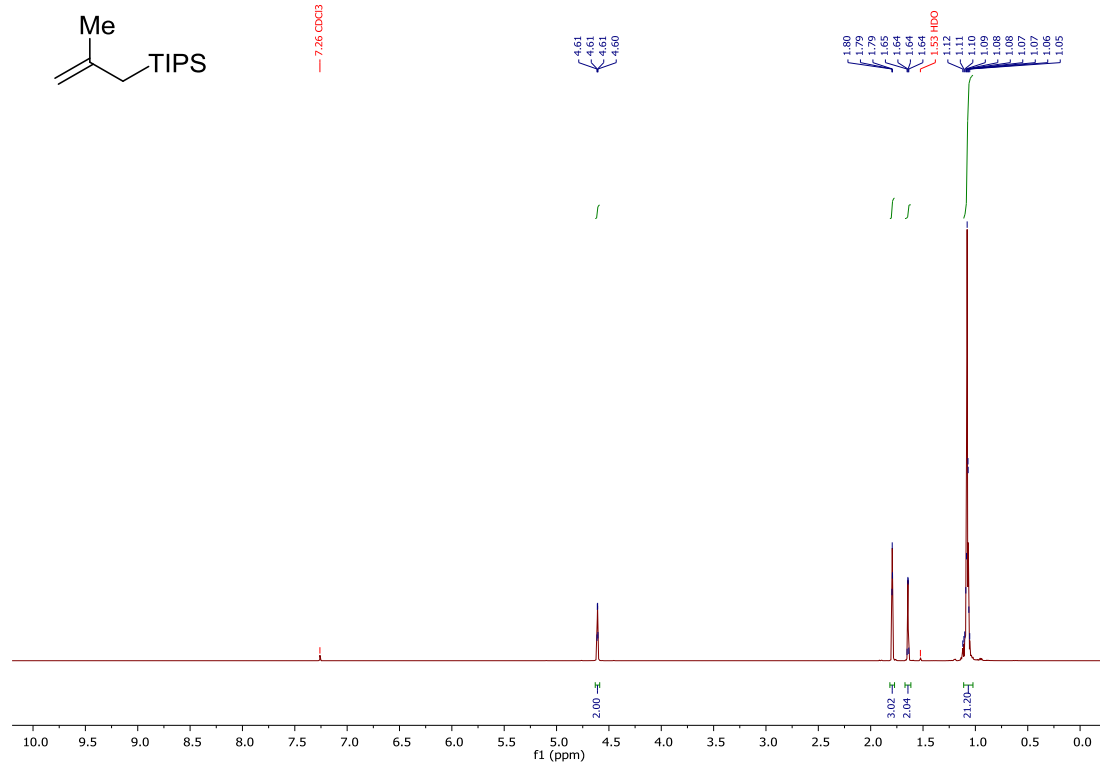


$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )

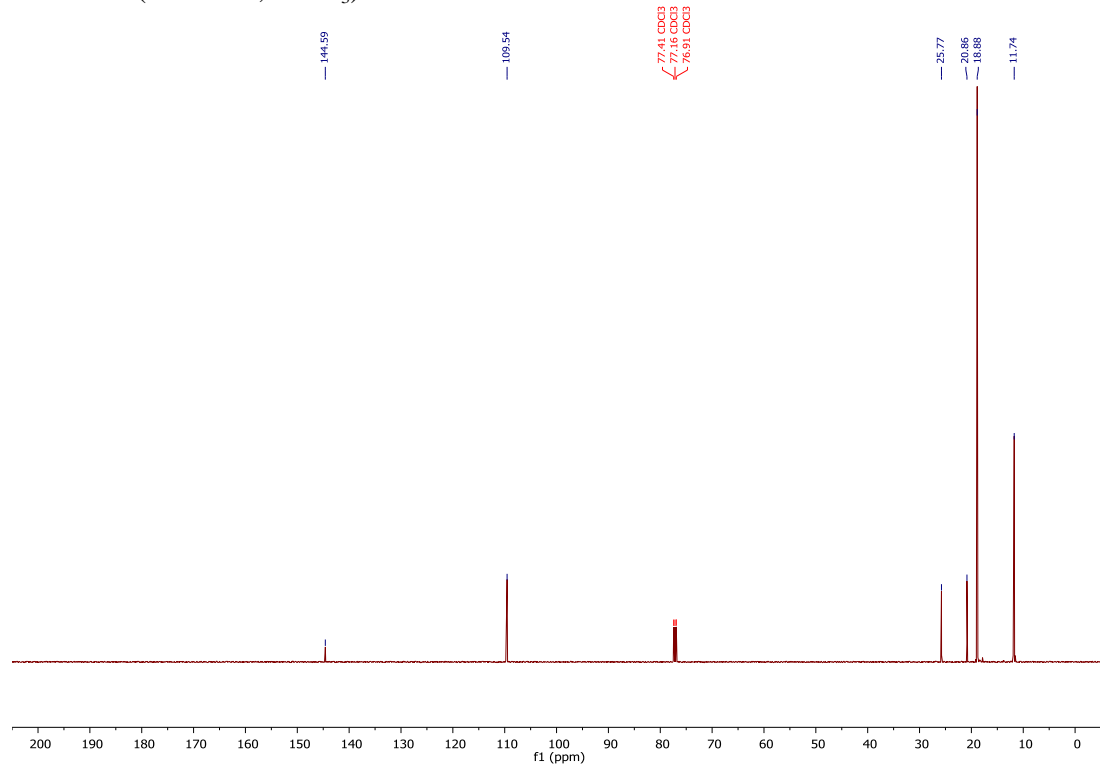


**triisopropyl(2-methylallyl)silane (5d):**

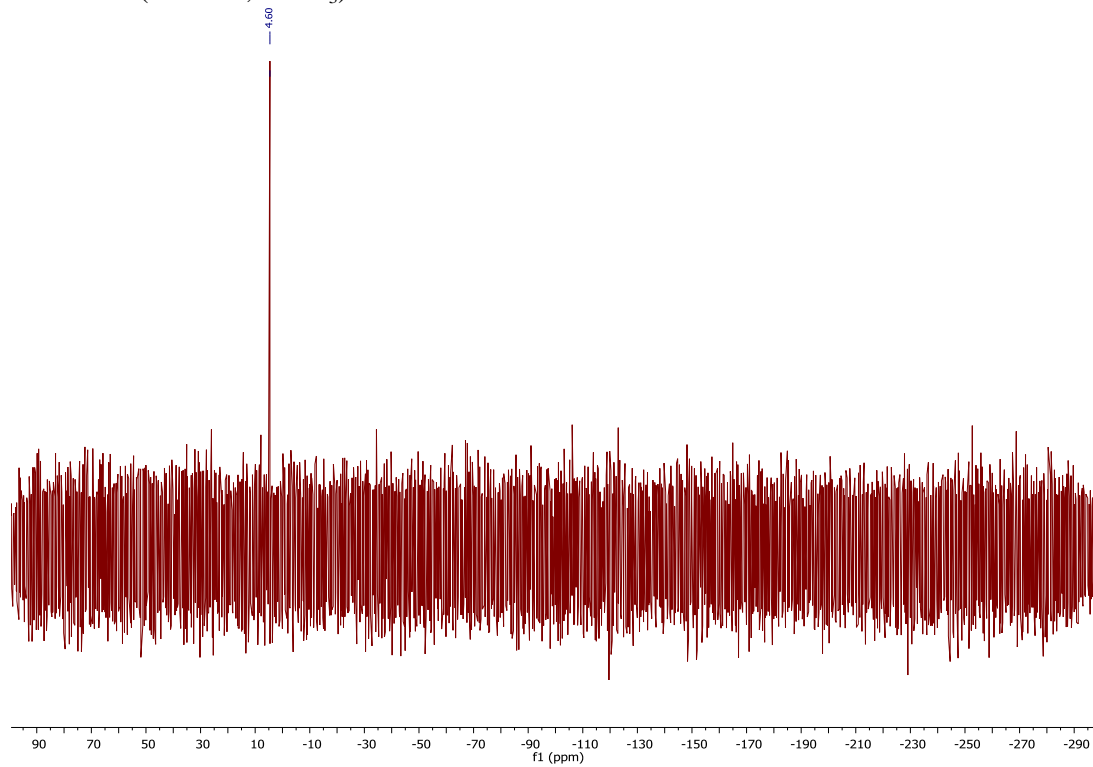
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



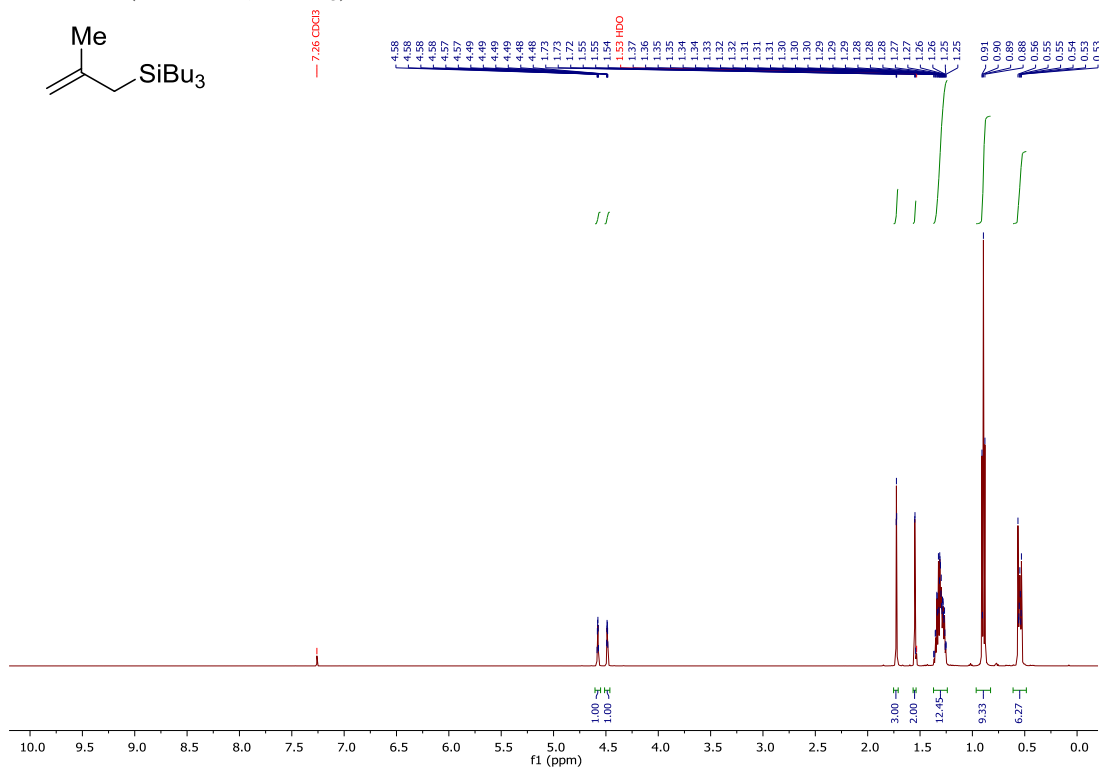
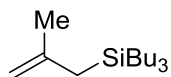
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



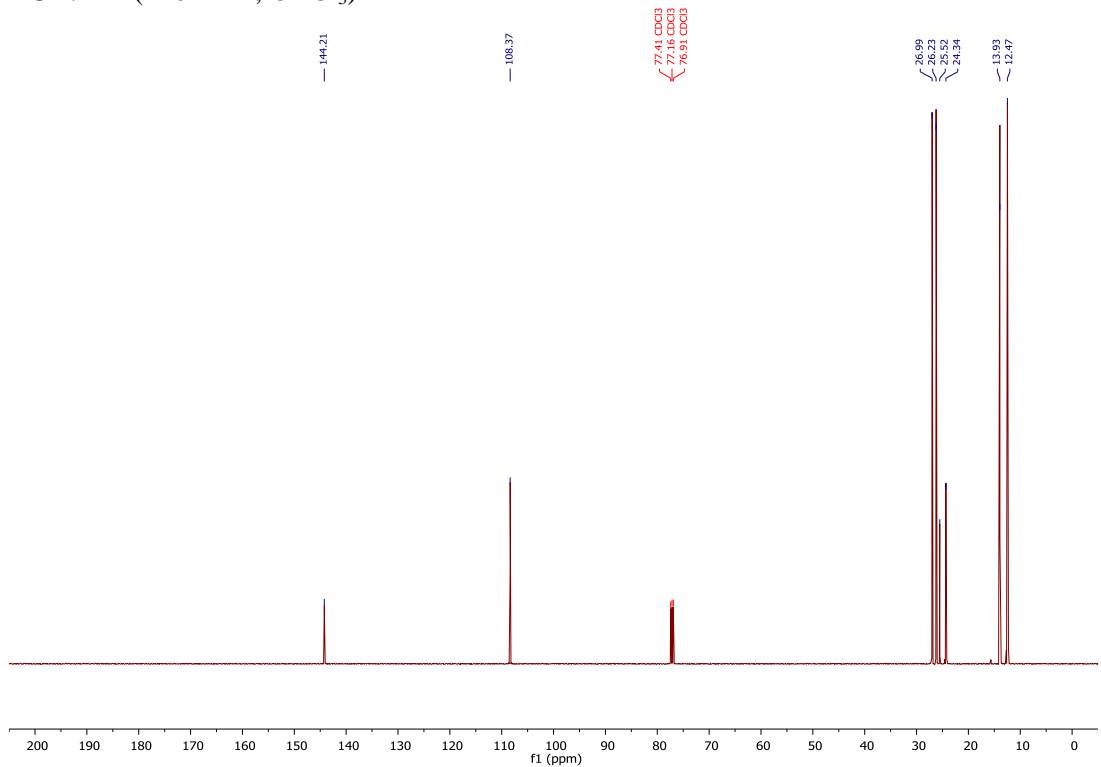
$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )



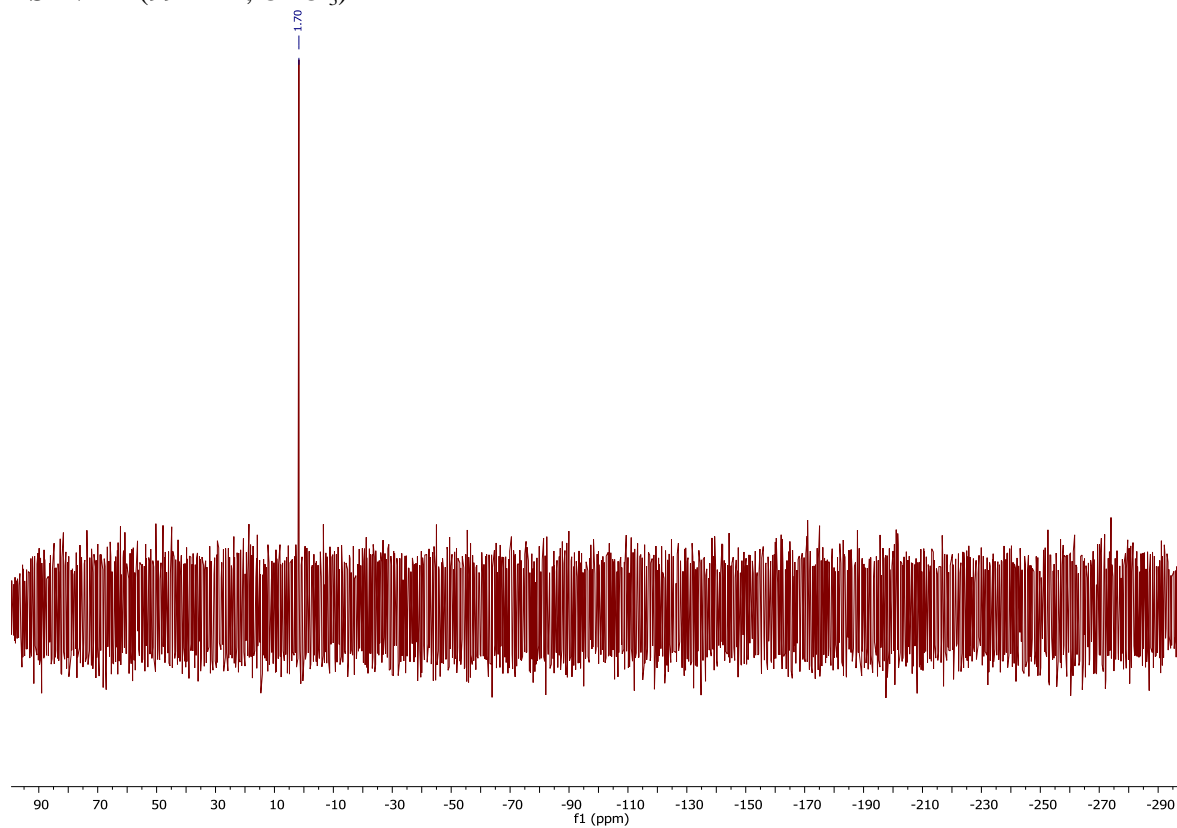
tributyl(2-methylallyl)silane (5I):  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



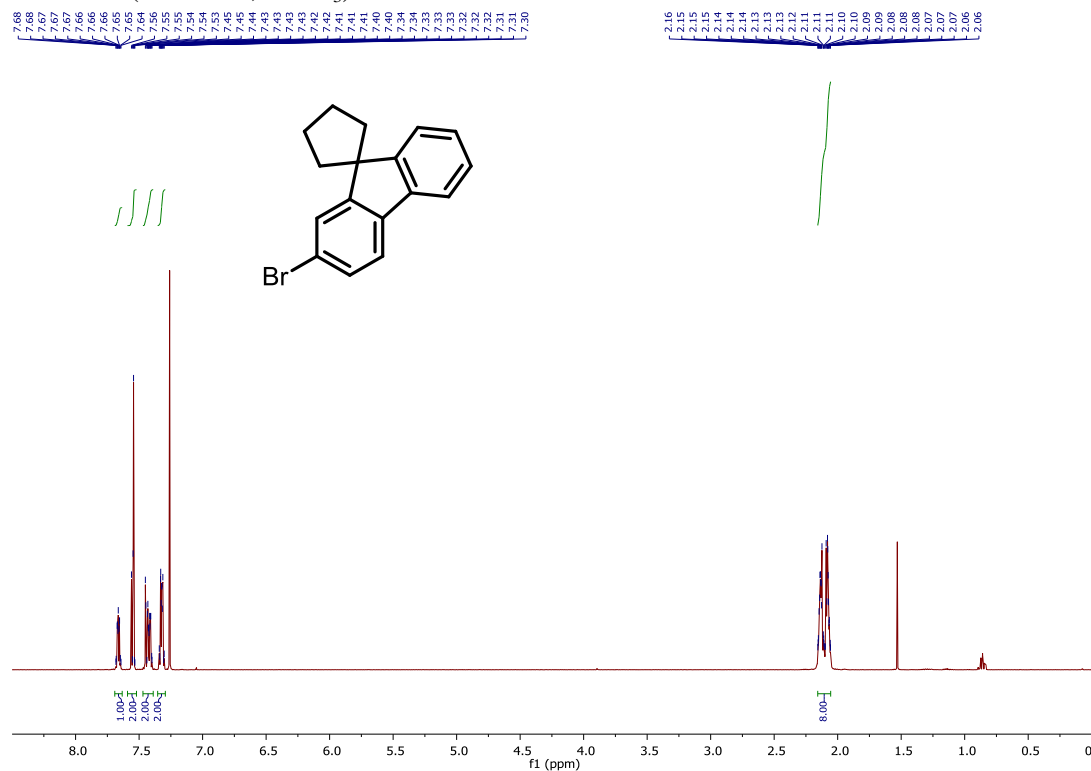
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



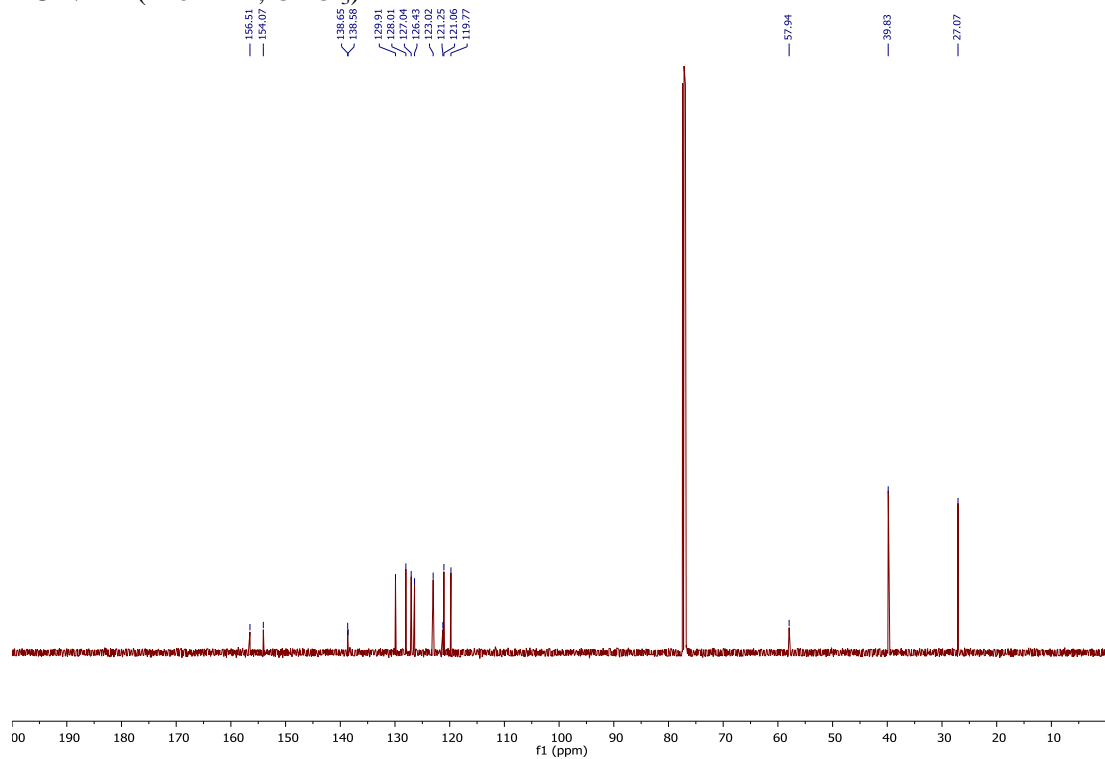
$^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )



**2'-bromospiro[cyclopentane-1,9'-fluorene]:**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

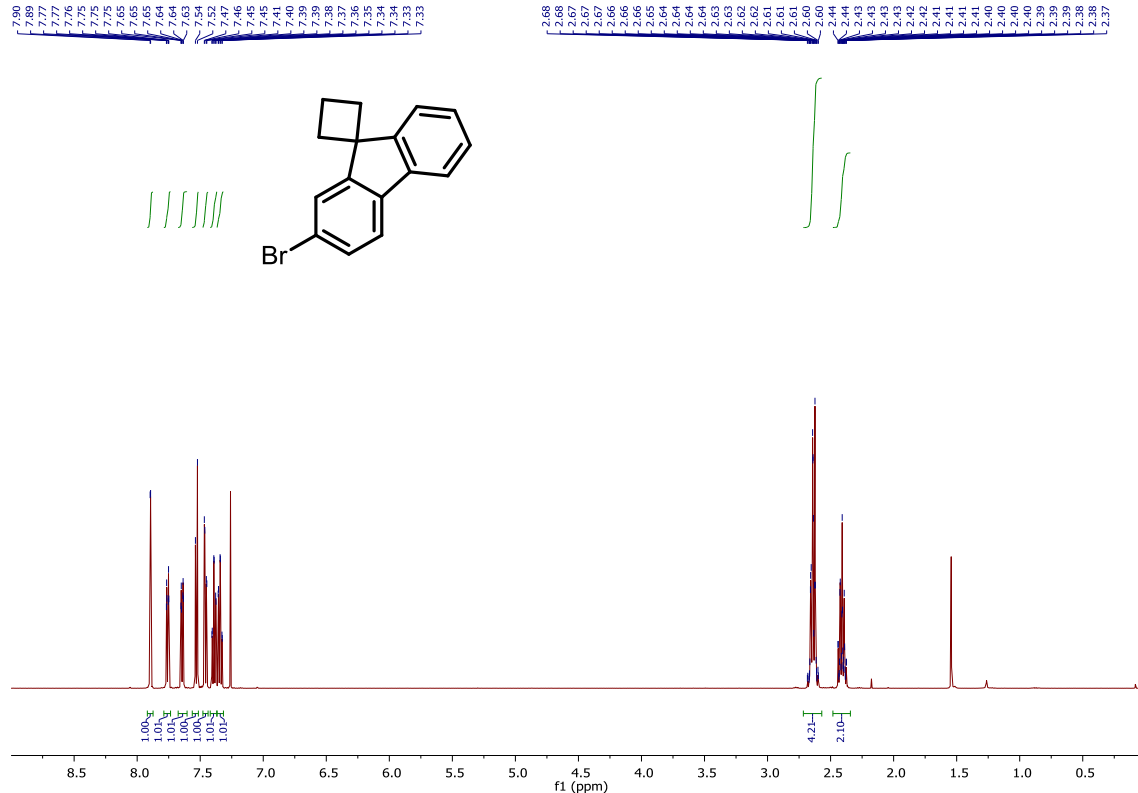


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

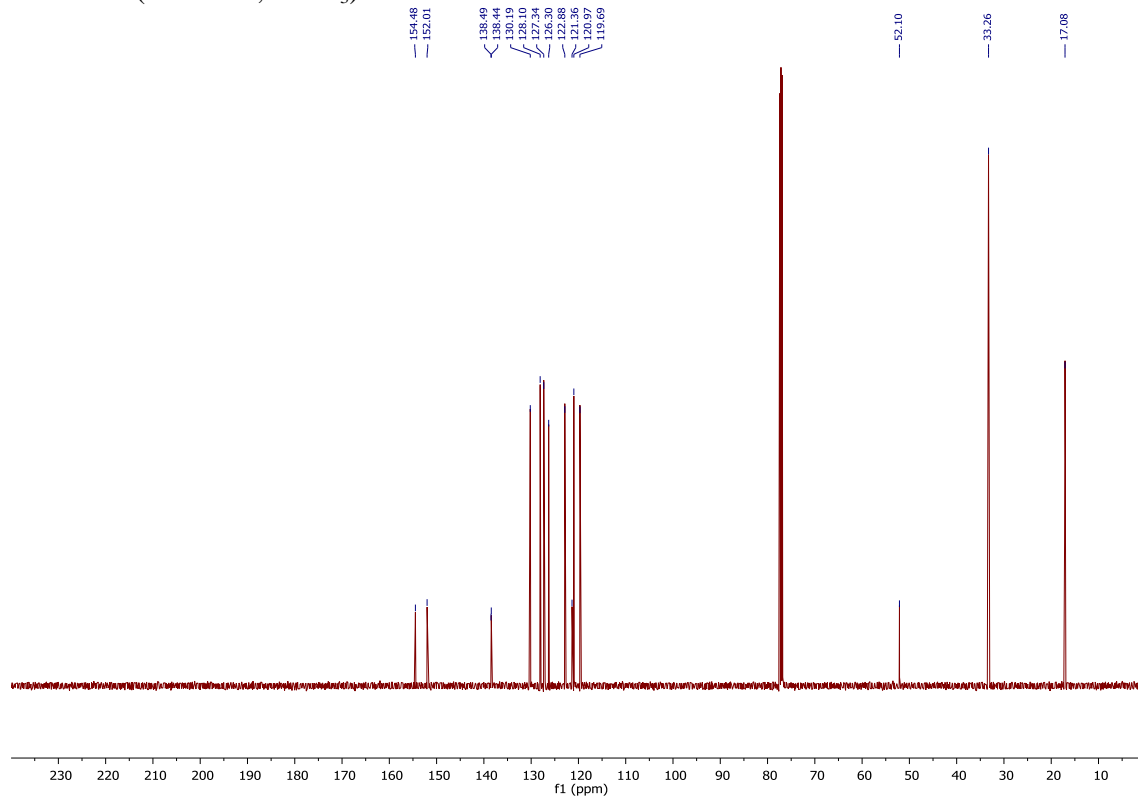


## 2'-bromospiro[cyclobutane-1,9'-fluorene]:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

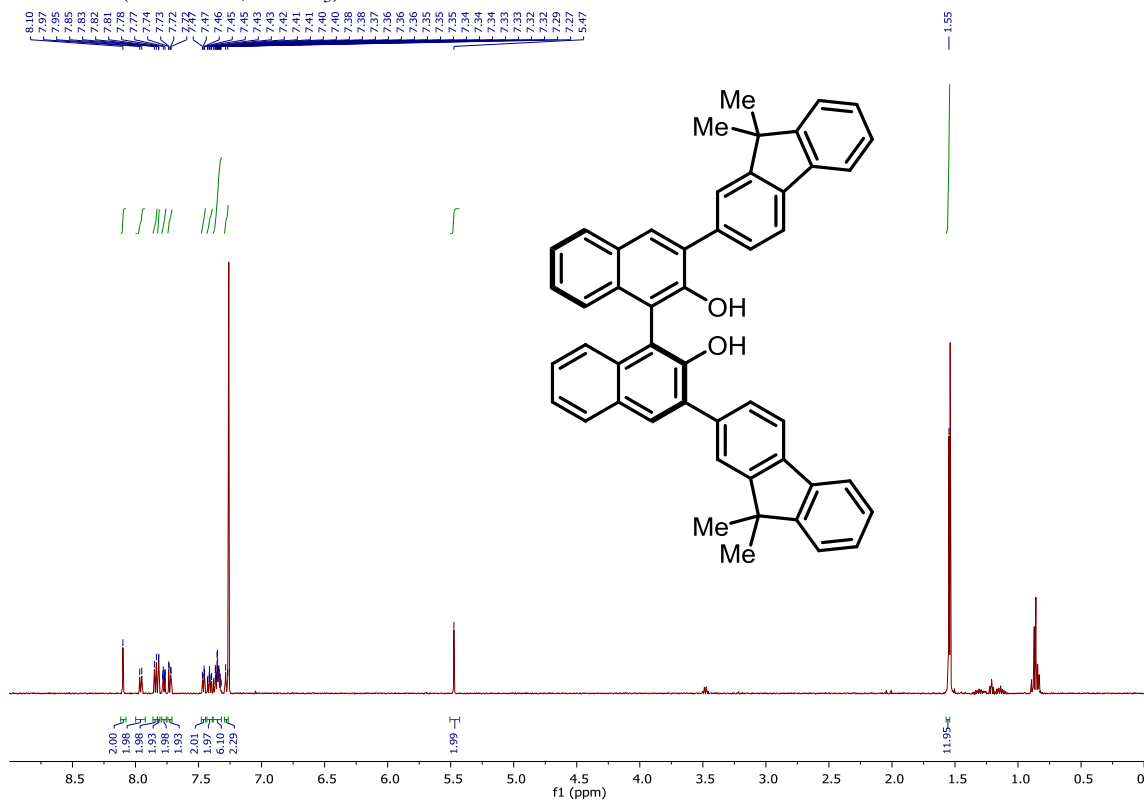


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )

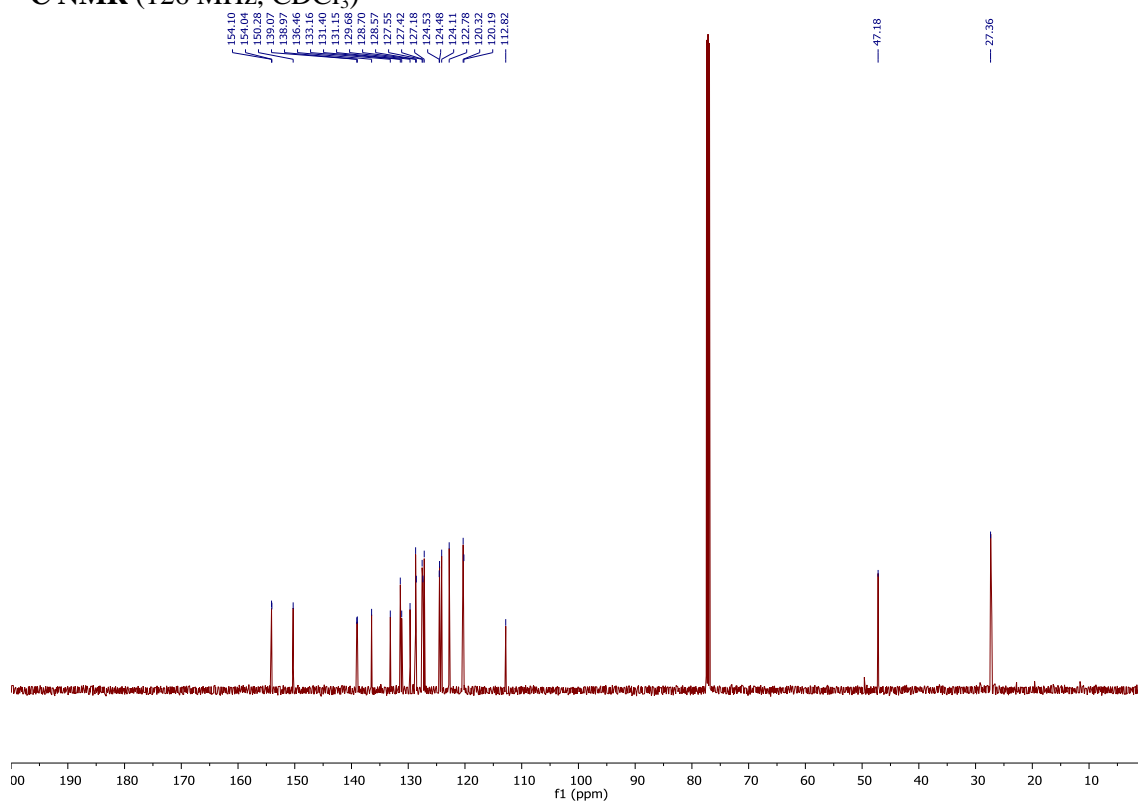


**(S)-3,3'-bis(9,9-dimethyl-9H-fluoren-2-yl)-[1,1'-binaphthalene]-2,2'-diol:**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



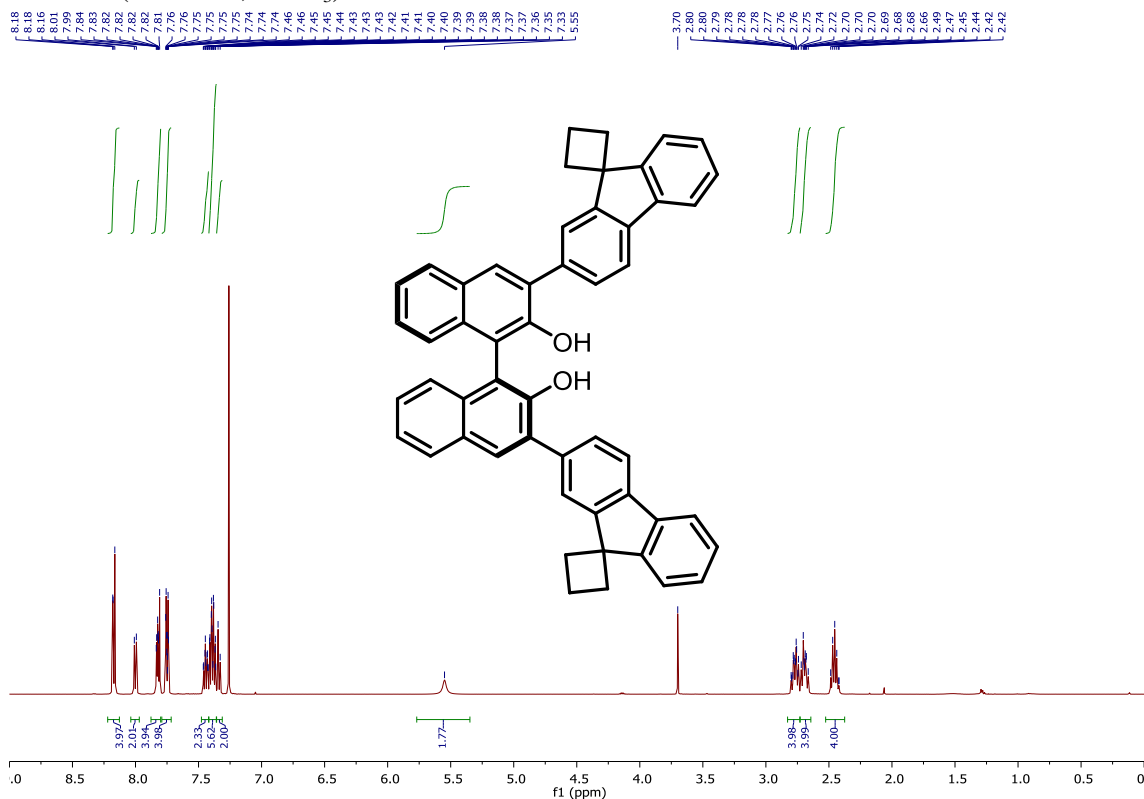
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



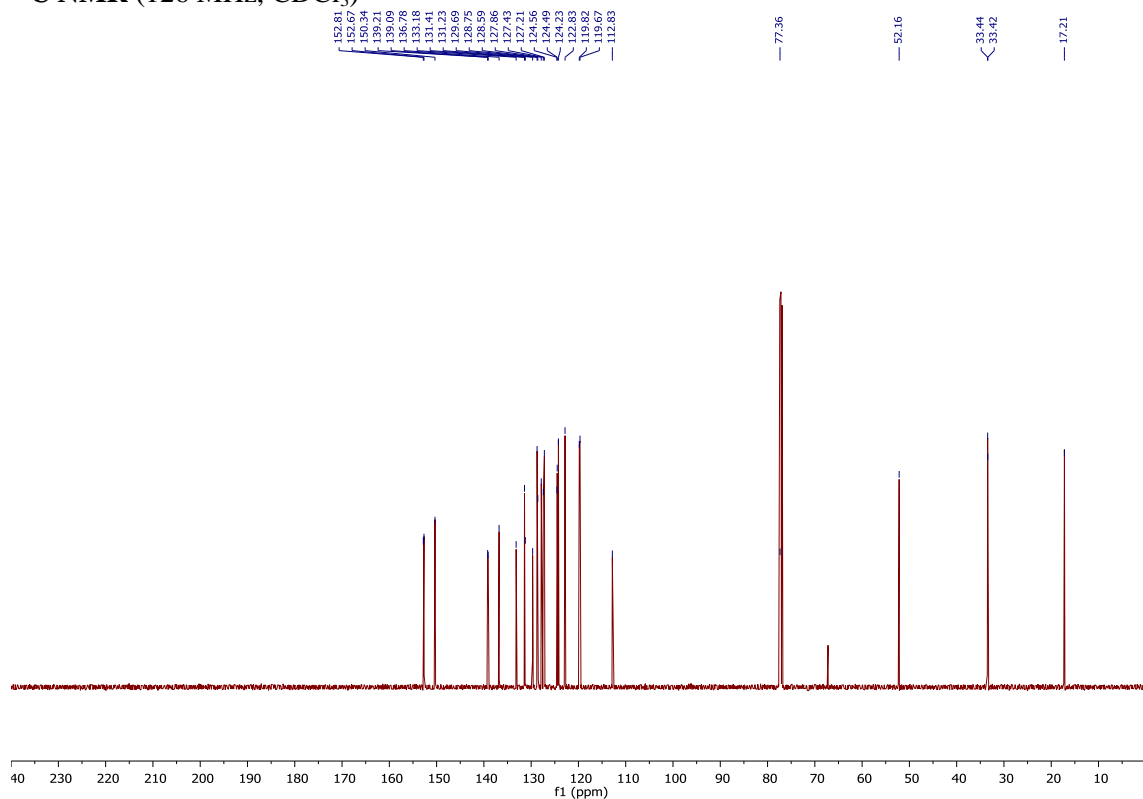


**(S)-3,3'-di(spiro[cyclobutane-1,9'-fluoren]-2'-yl)-[1,1'-binaphthalene]-2,2'-diol:**

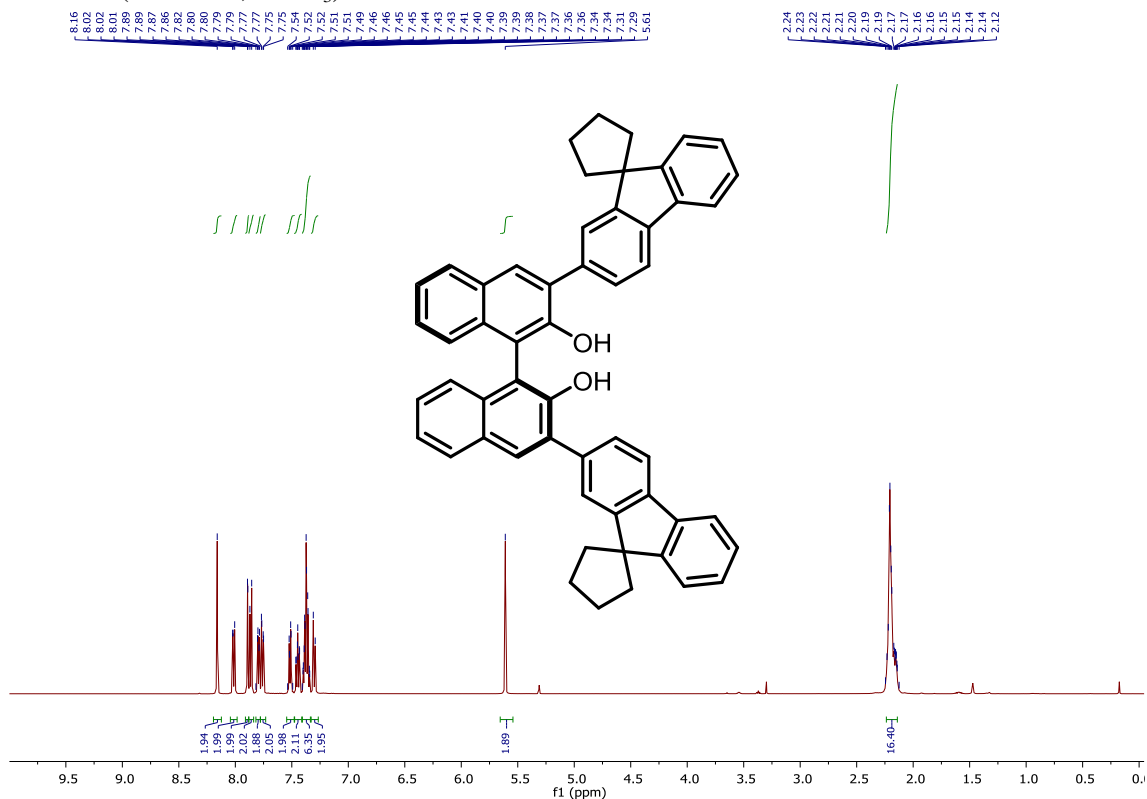
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



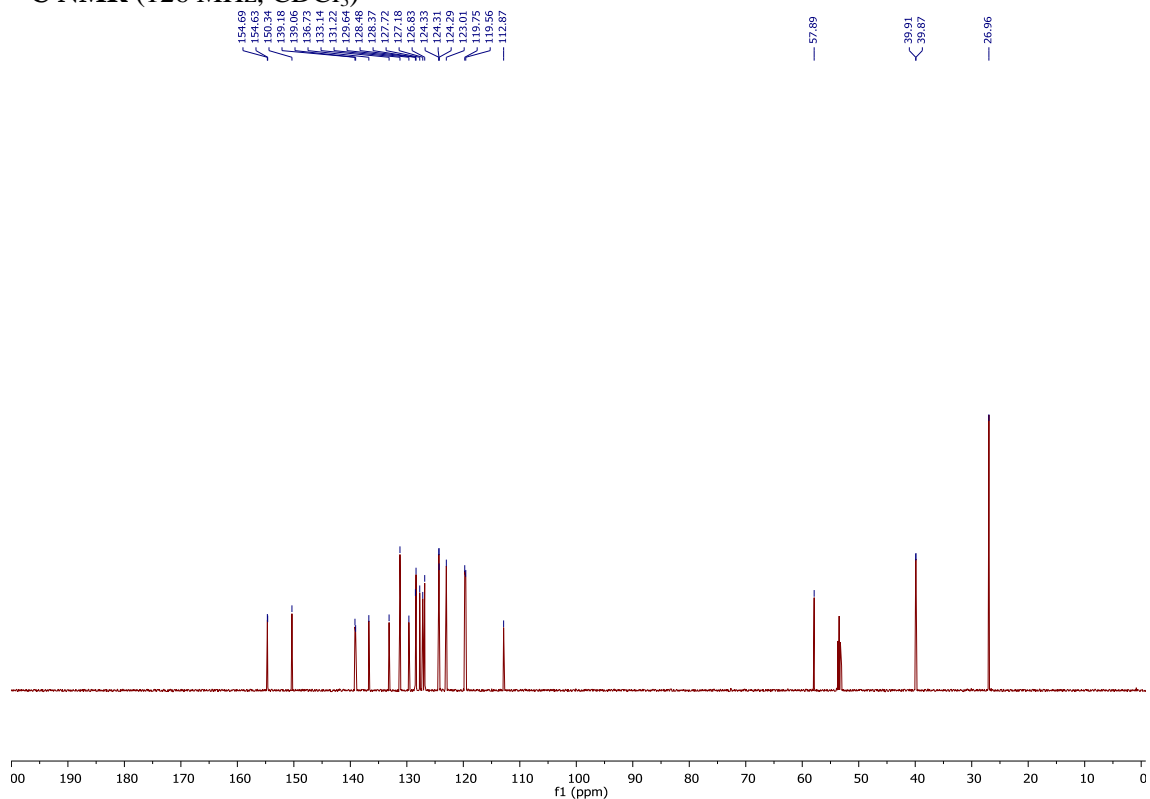
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



**(S)-3,3'-di(spiro[cyclopentane-1,9'-fluoren]-2'-yl)-[1,1'-binaphthalene]-2,2'-diol:**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



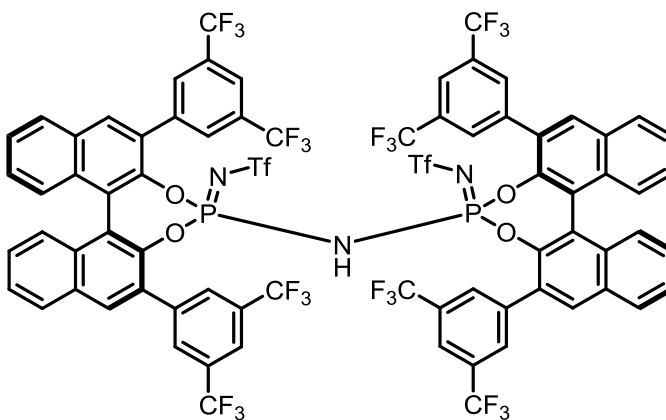
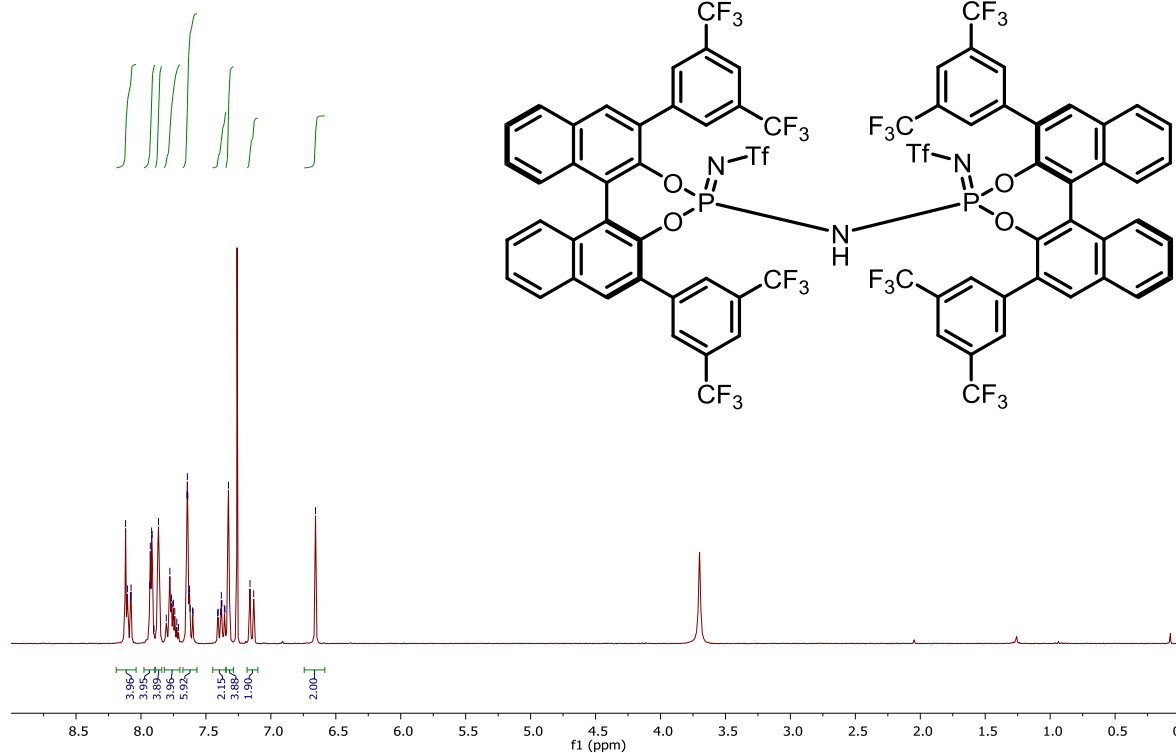
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



(*S,S*)-4a

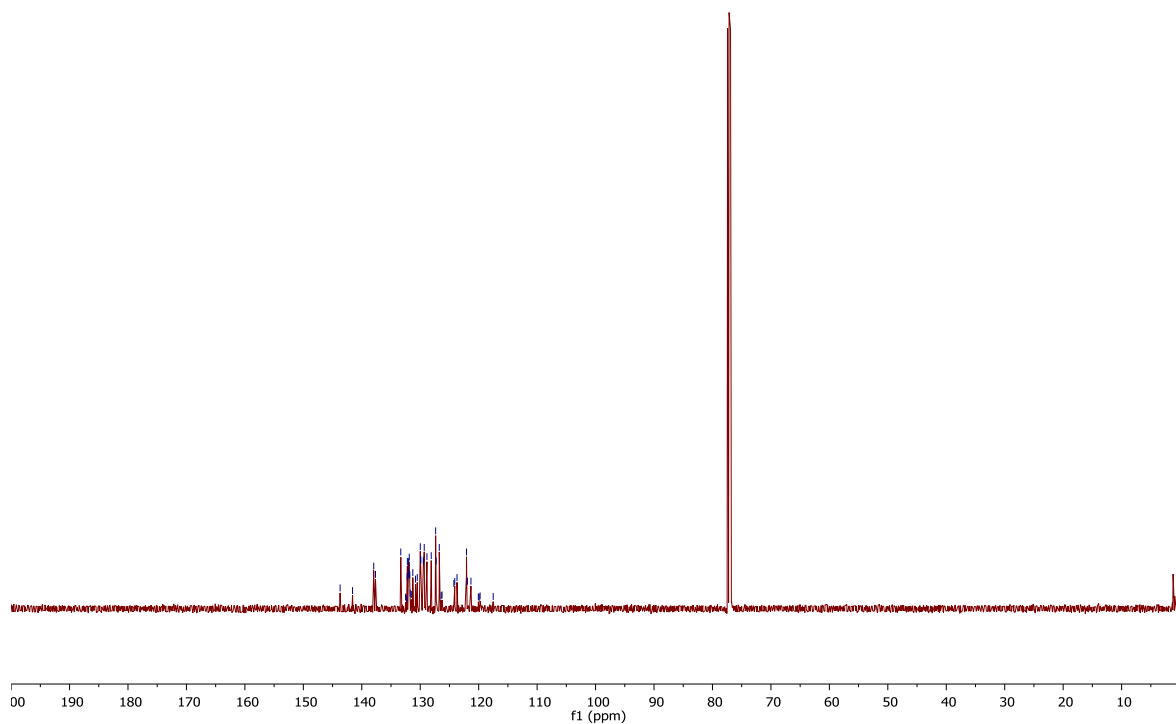
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

8.12, 8.10, 8.08, 7.98, 7.93, 7.93, 7.92, 7.91, 7.90, 7.88, 7.81, 7.78, 7.77, 7.76, 7.75, 7.75, 7.72, 7.72, 7.71, 7.65, 7.65, 7.64, 7.64, 7.63, 7.63, 7.60, 7.60, 7.41, 7.41, 7.41, 7.41, 7.38, 7.38, 7.38, 7.36, 7.35, 7.33, 7.33, 7.13, 7.13, 6.66

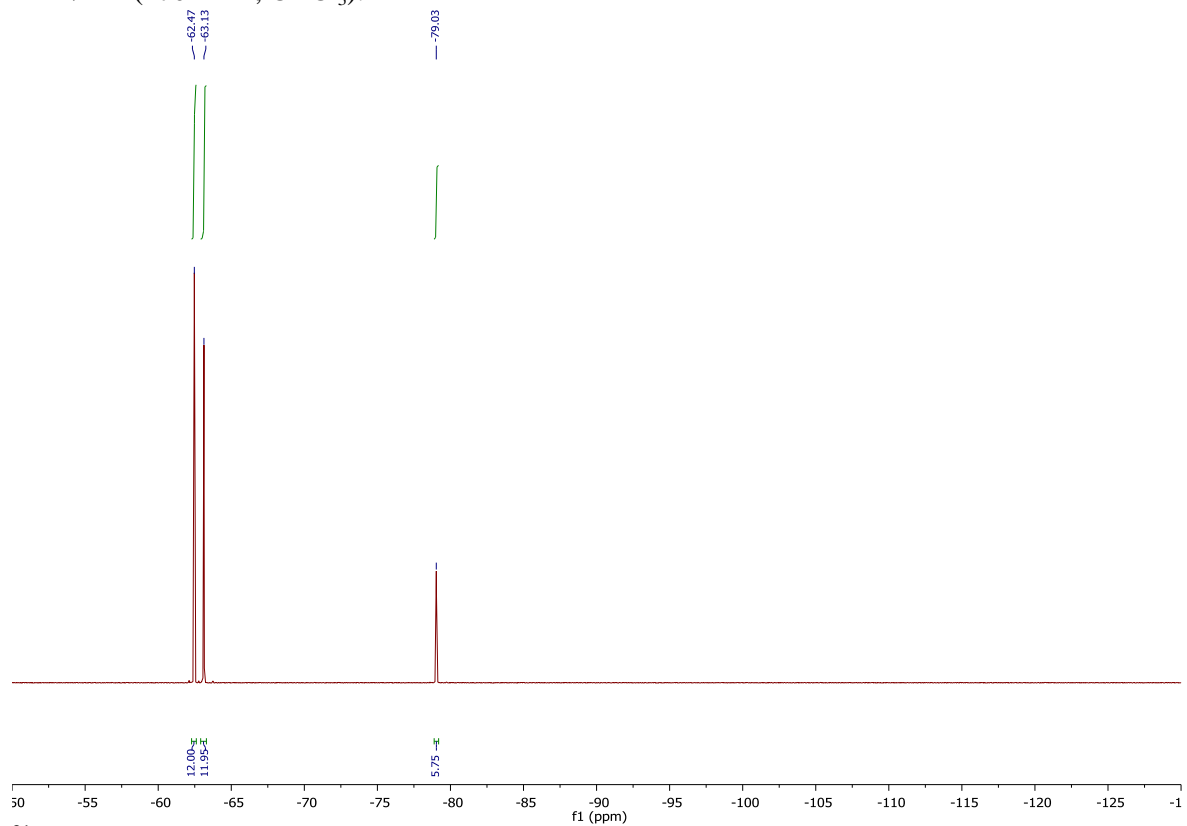


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

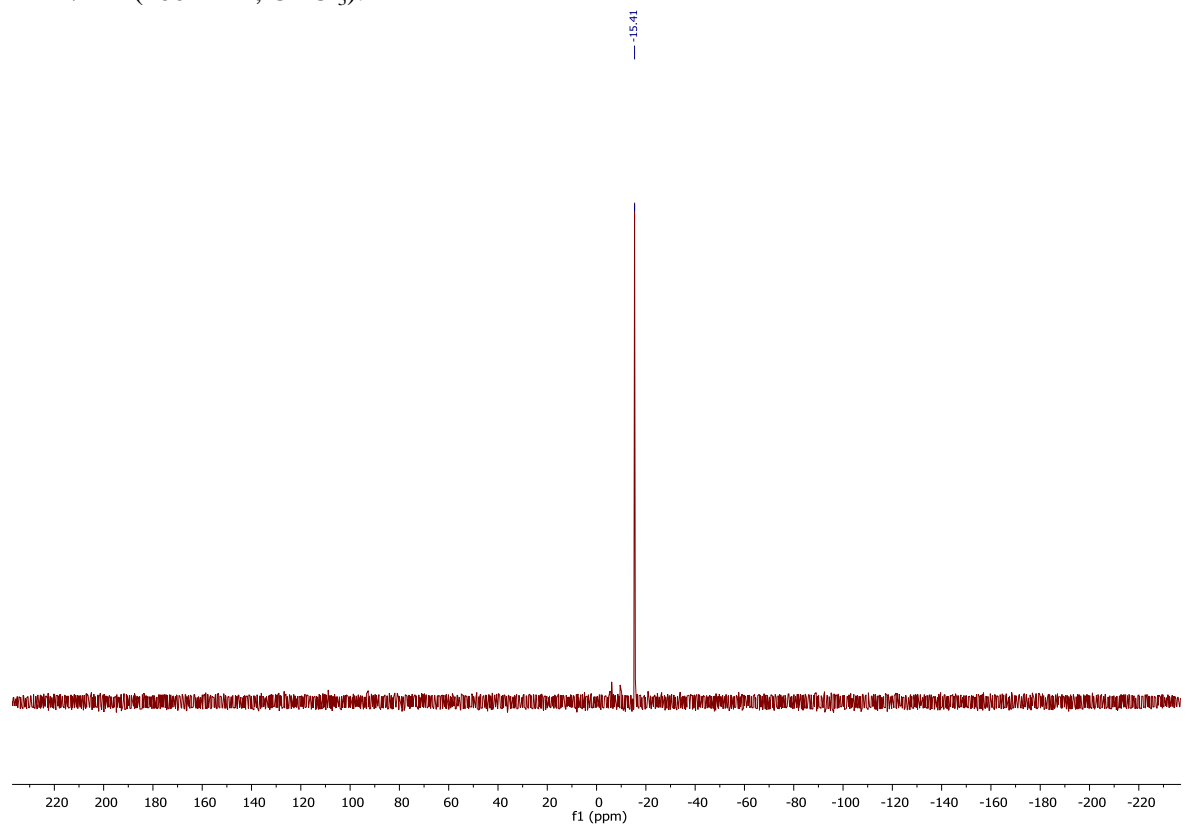
143.71, 141.58, 141.56, 137.65, 133.33, 132.51, 132.32, 132.24, 132.08, 132.05, 131.99, 131.97, 131.88, 131.70, 131.52, 131.27, 130.80, 130.51, 129.91, 129.91, 129.47, 129.31, 128.85, 128.85, 127.36, 127.28, 126.74, 126.41, 126.27, 126.27, 124.40, 124.40, 123.71, 122.08, 121.83, 121.32, 121.32, 120.06, 119.76, 119.76, 117.52



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



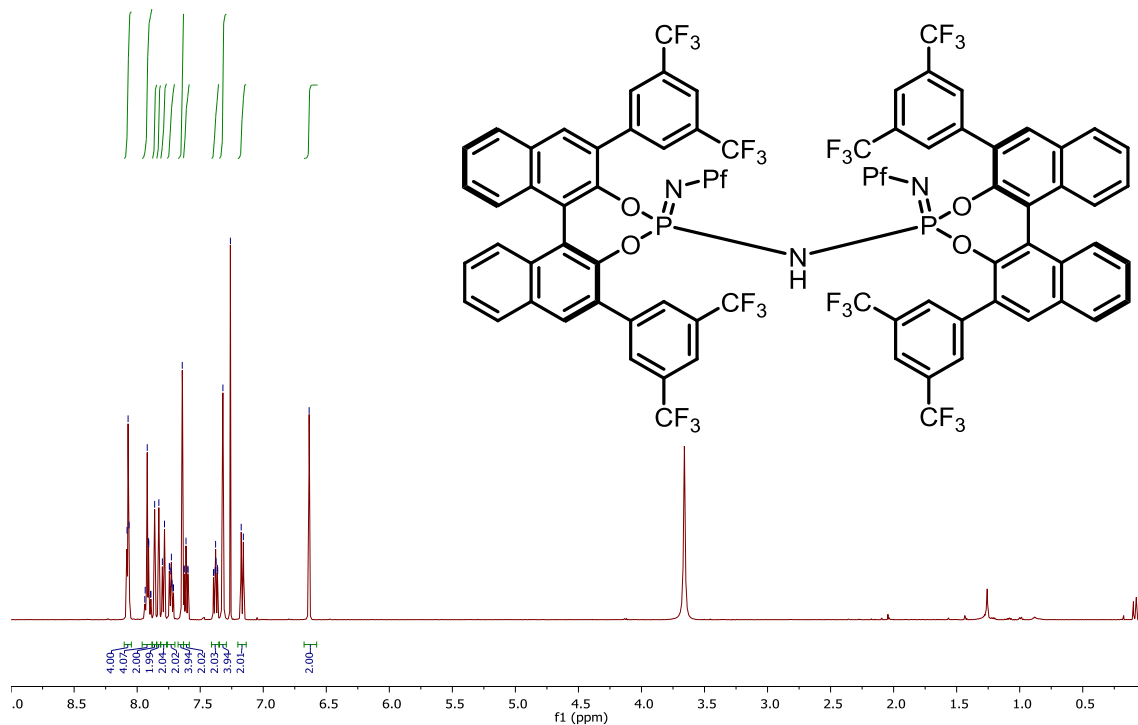
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



**(S,S)-4b**

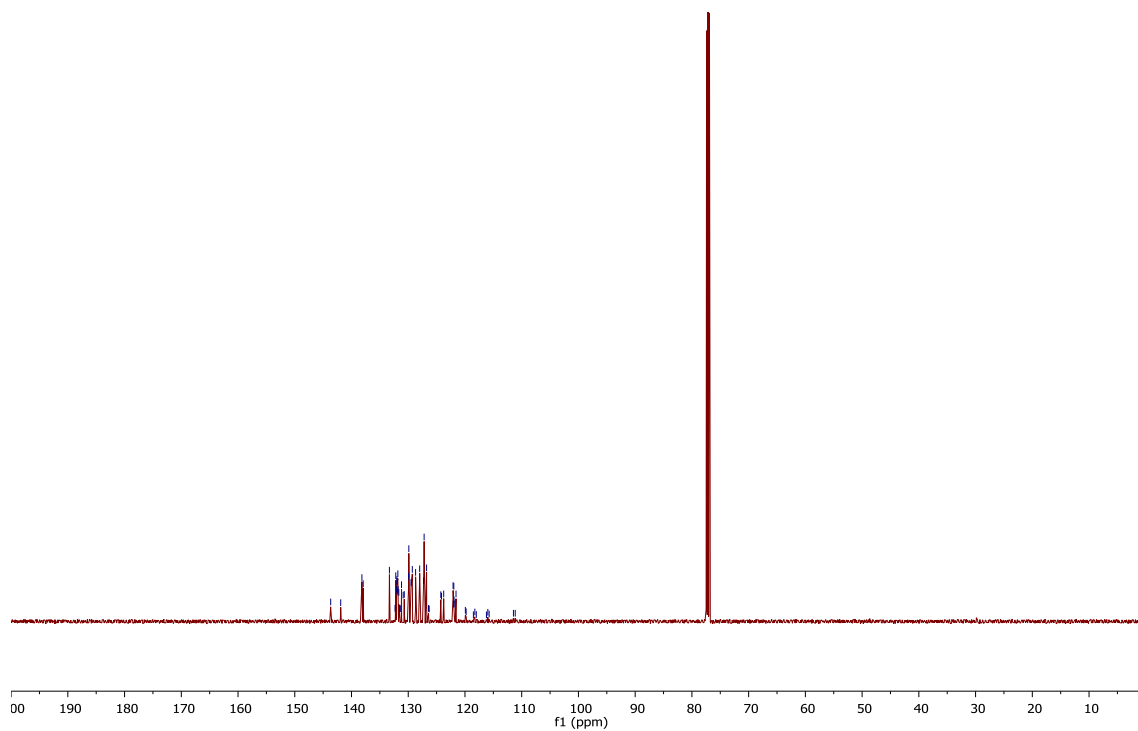
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

8.08, 8.07, 8.04, 7.94, 7.94, 7.92, 7.91, 7.91, 7.89, 7.89, 7.86, 7.83, 7.80, 7.80, 7.74, 7.74, 7.73, 7.73, 7.72, 7.72, 7.71, 7.64, 7.63, 7.63, 7.60, 7.60, 7.39, 7.39, 7.38, 7.38, 7.37, 7.37, 7.36, 7.36, 7.32, 7.32, 7.17, 7.17, 6.64

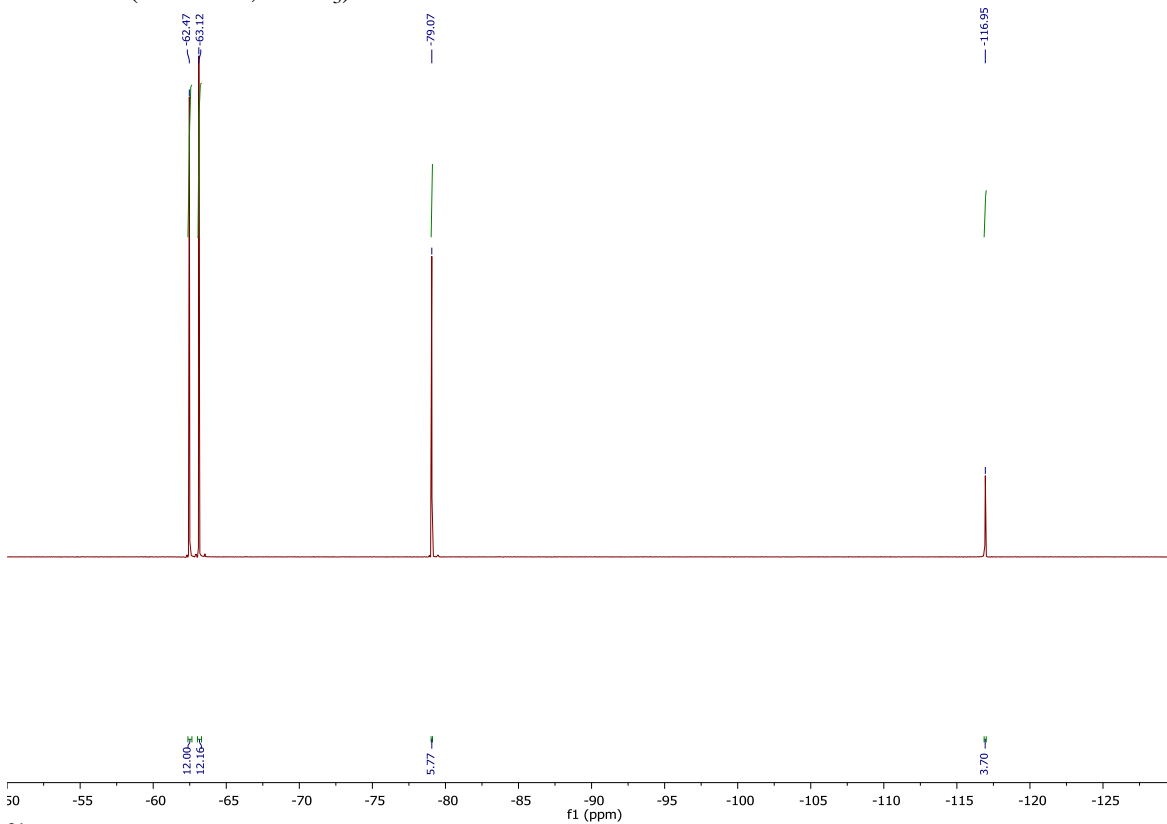


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

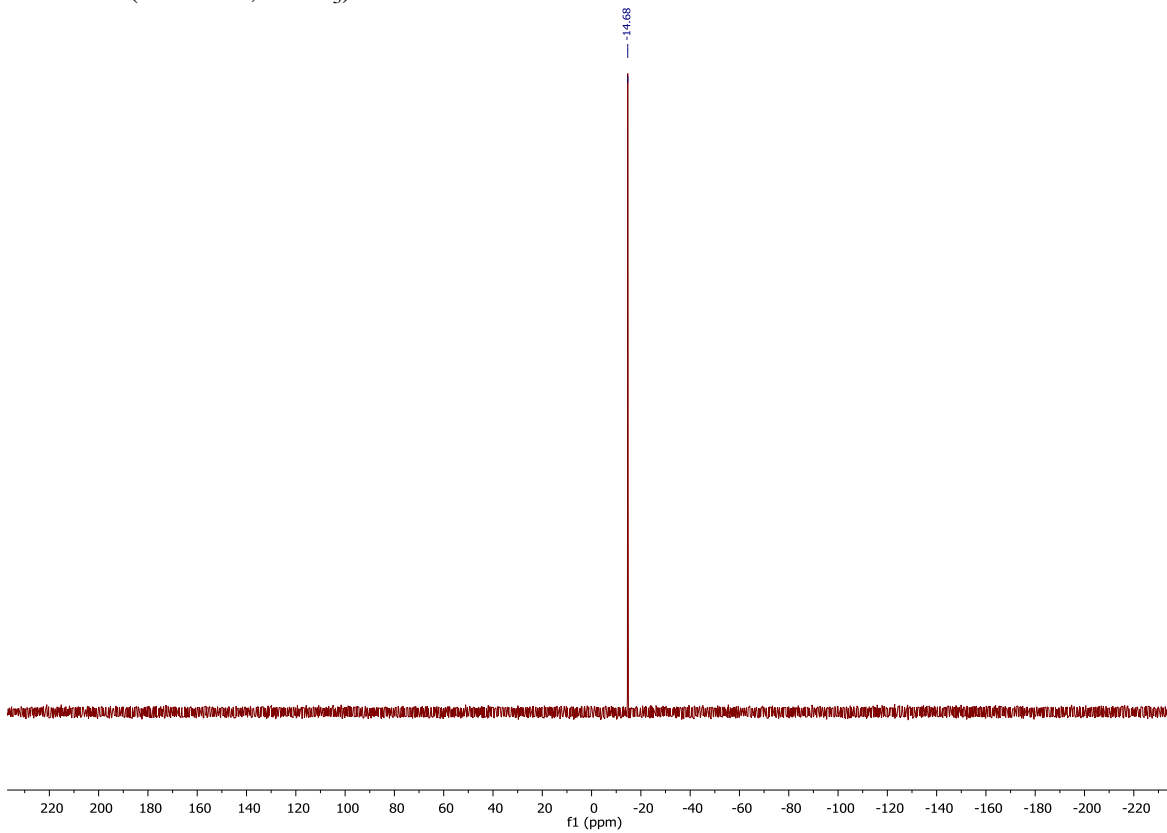
143.67, 141.90, 138.16, 137.94, 133.32, 133.32, 132.20, 132.05, 132.00, 131.98, 131.98, 131.83, 131.79, 131.66, 131.52, 131.46, 131.18, 130.89, 130.70, 129.93, 129.89, 129.89, 129.28, 128.70, 127.98, 127.30, 127.30, 126.77, 126.42, 126.31, 124.26, 124.14, 122.75, 122.09, 122.04, 121.97, 121.93, 121.93, 121.58, 119.93, 119.80, 118.51, 118.51, 118.00, 116.22, 115.97, 115.74, 111.46, 111.14



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):

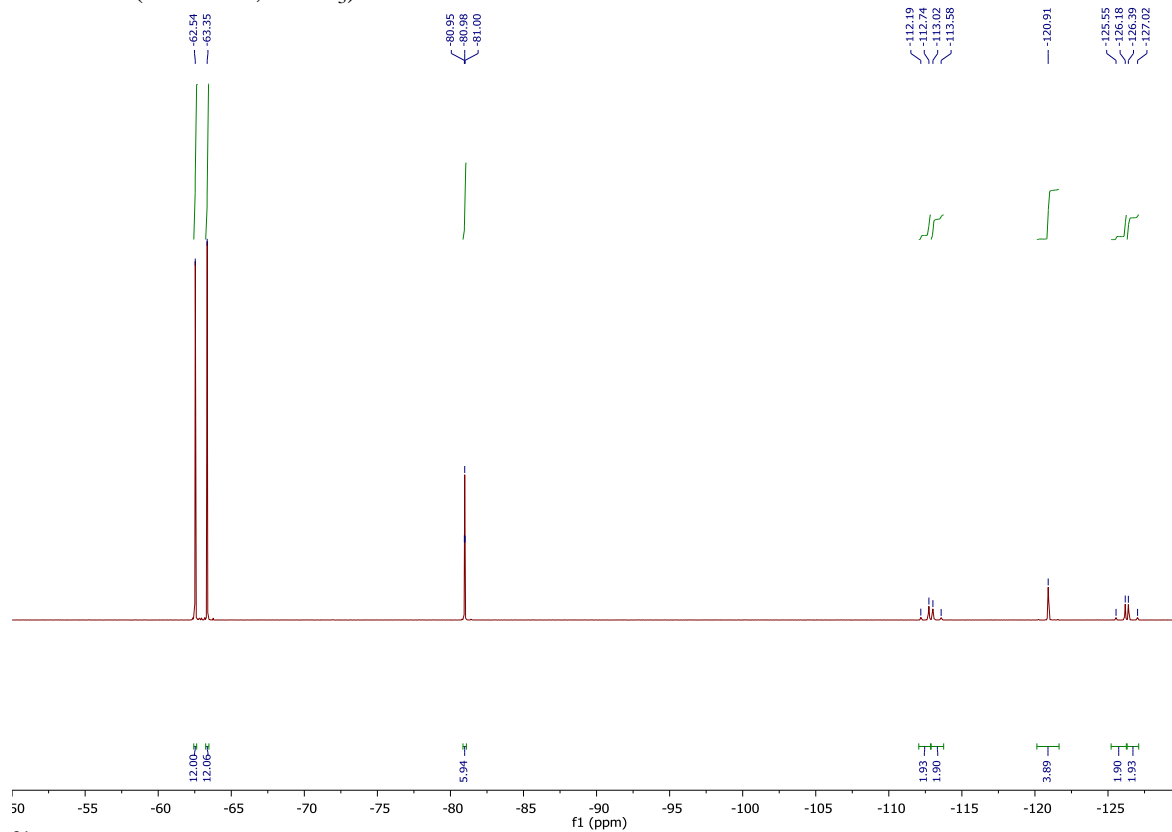


$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):

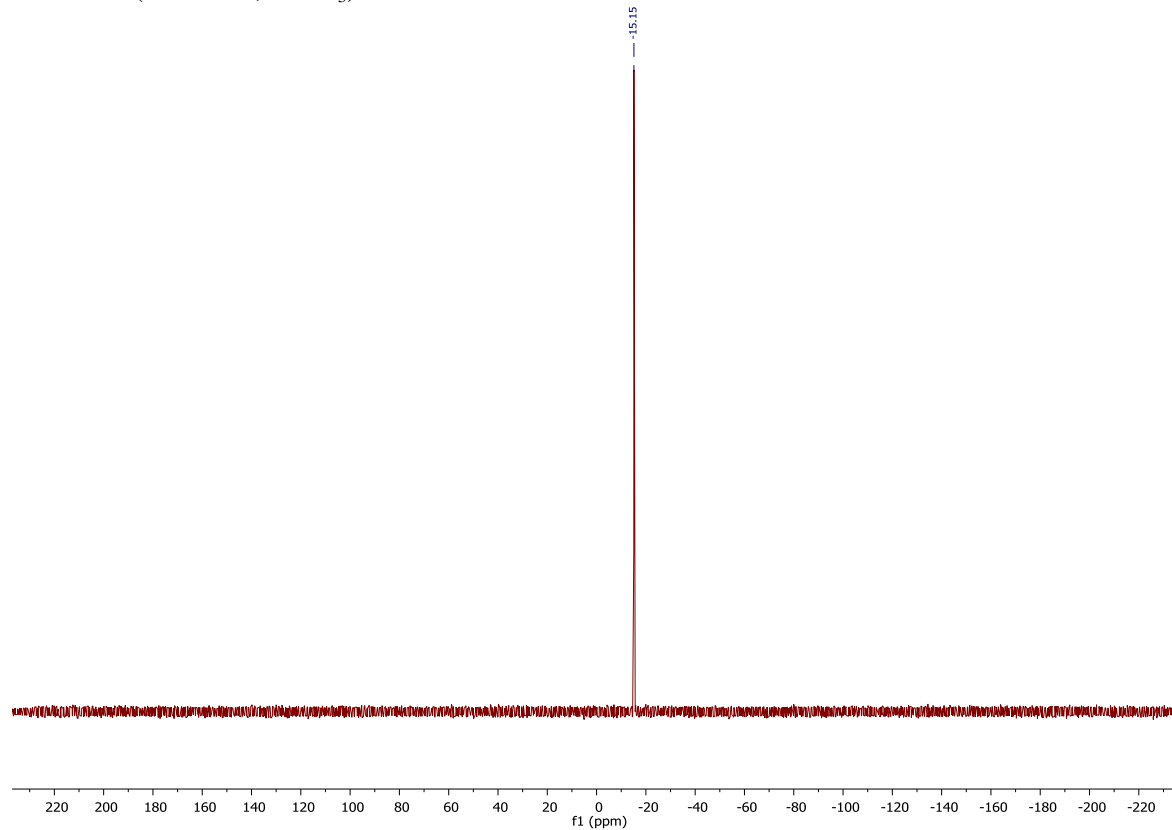




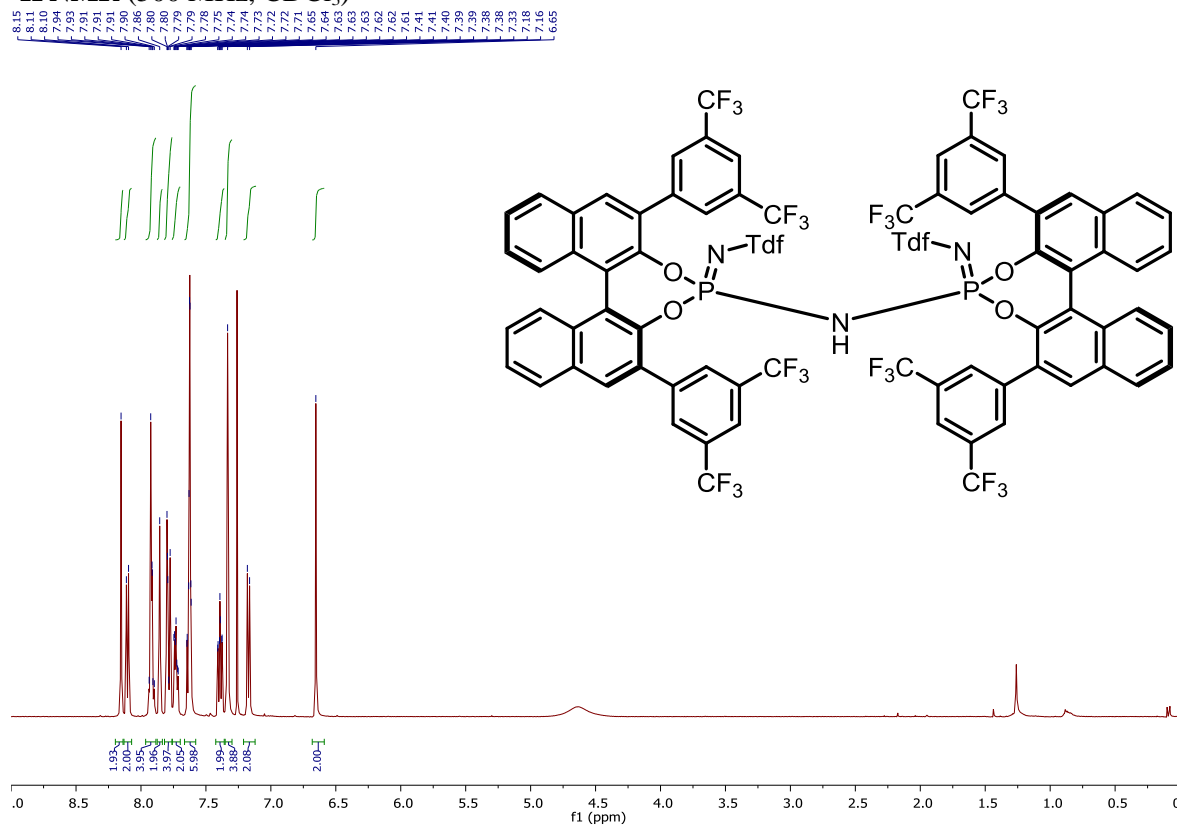
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



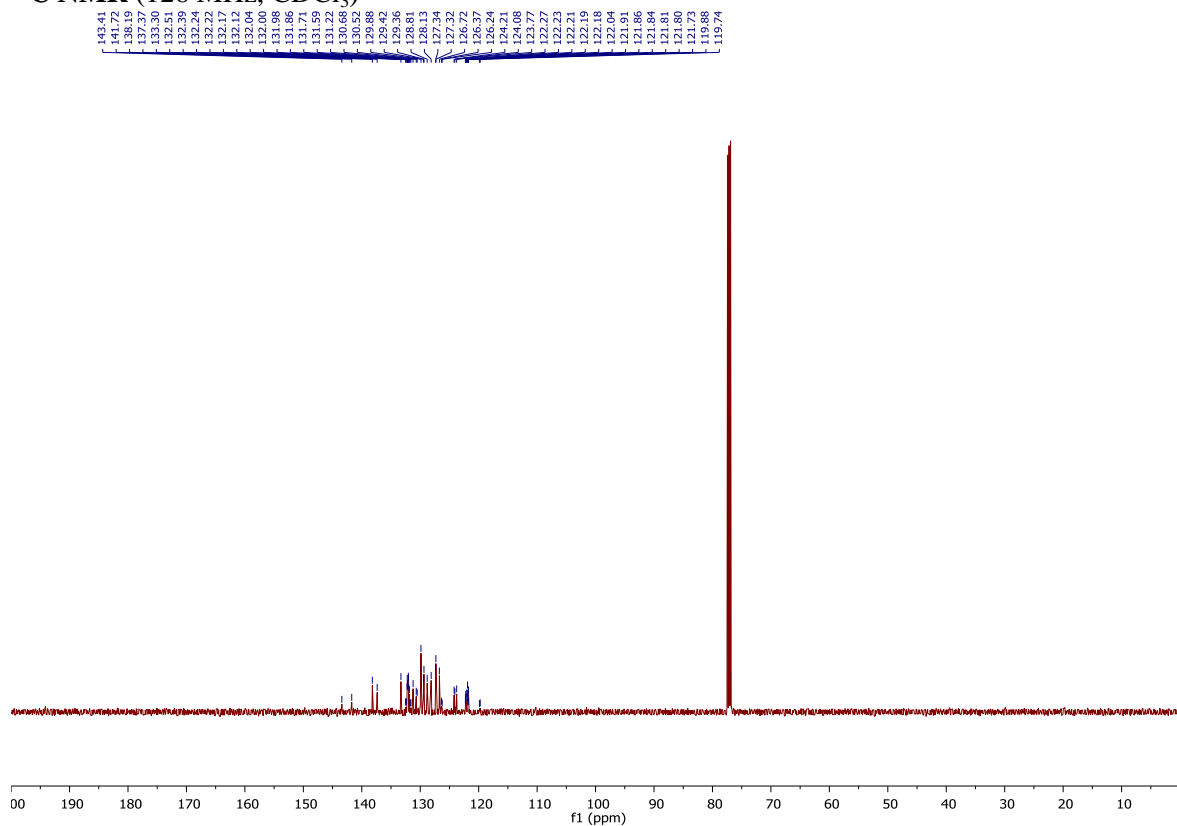
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



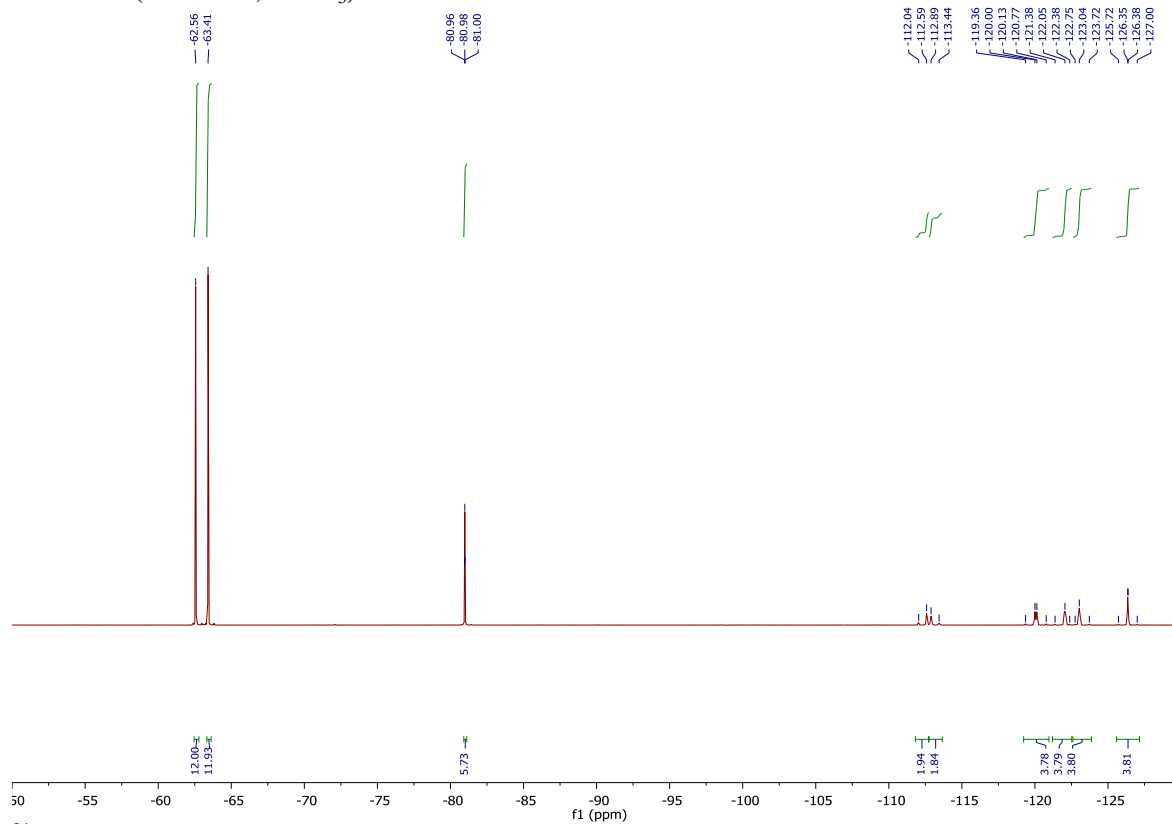
(*S,S*)-4f  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



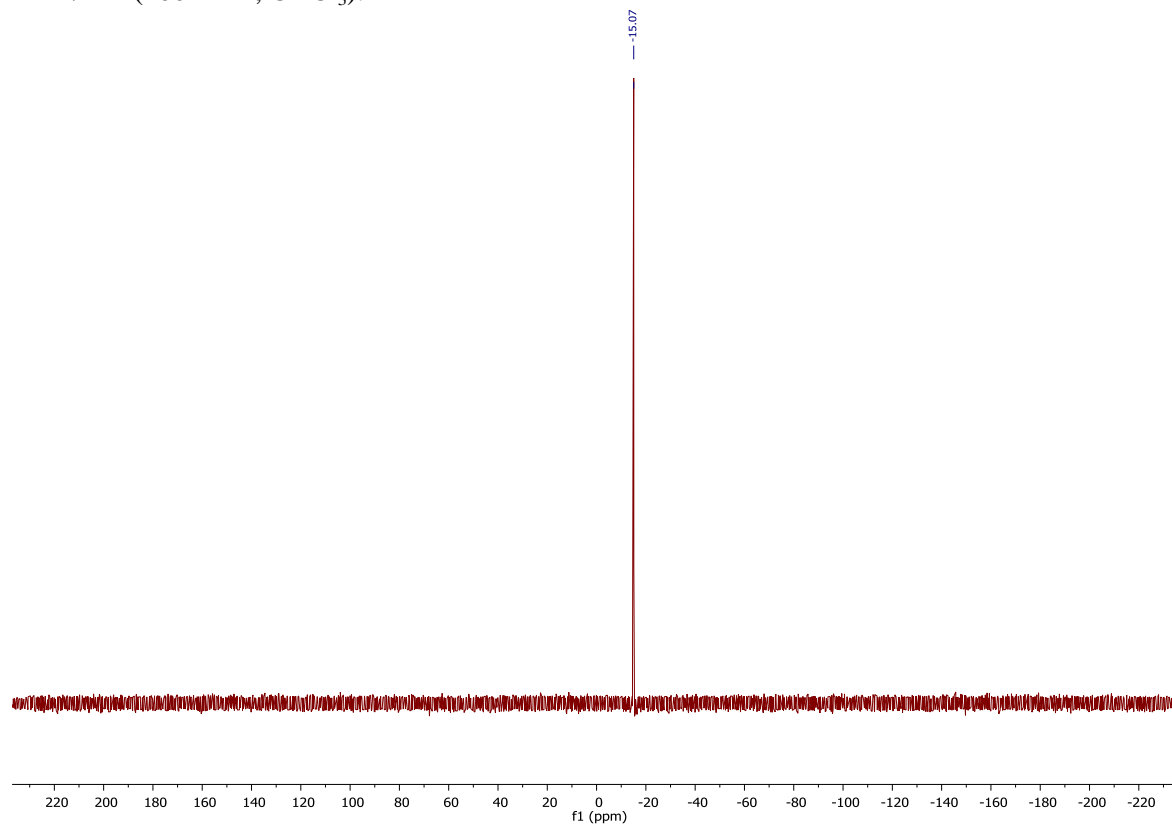
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



**<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):**

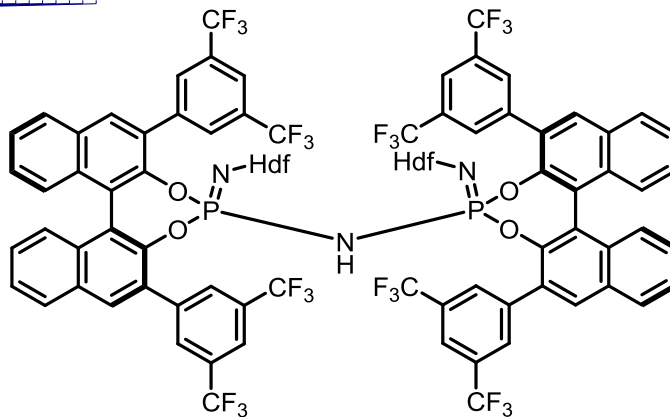
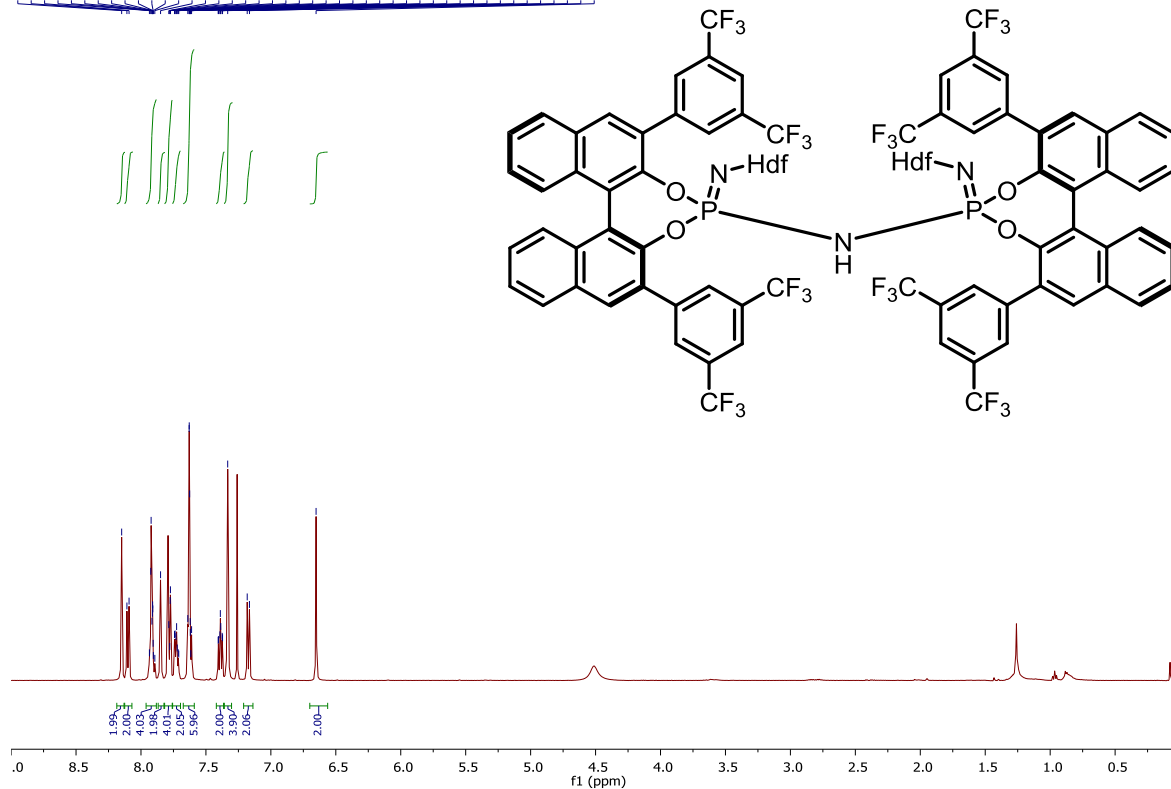


**<sup>31</sup>P NMR (200 MHz, CDCl<sub>3</sub>):**



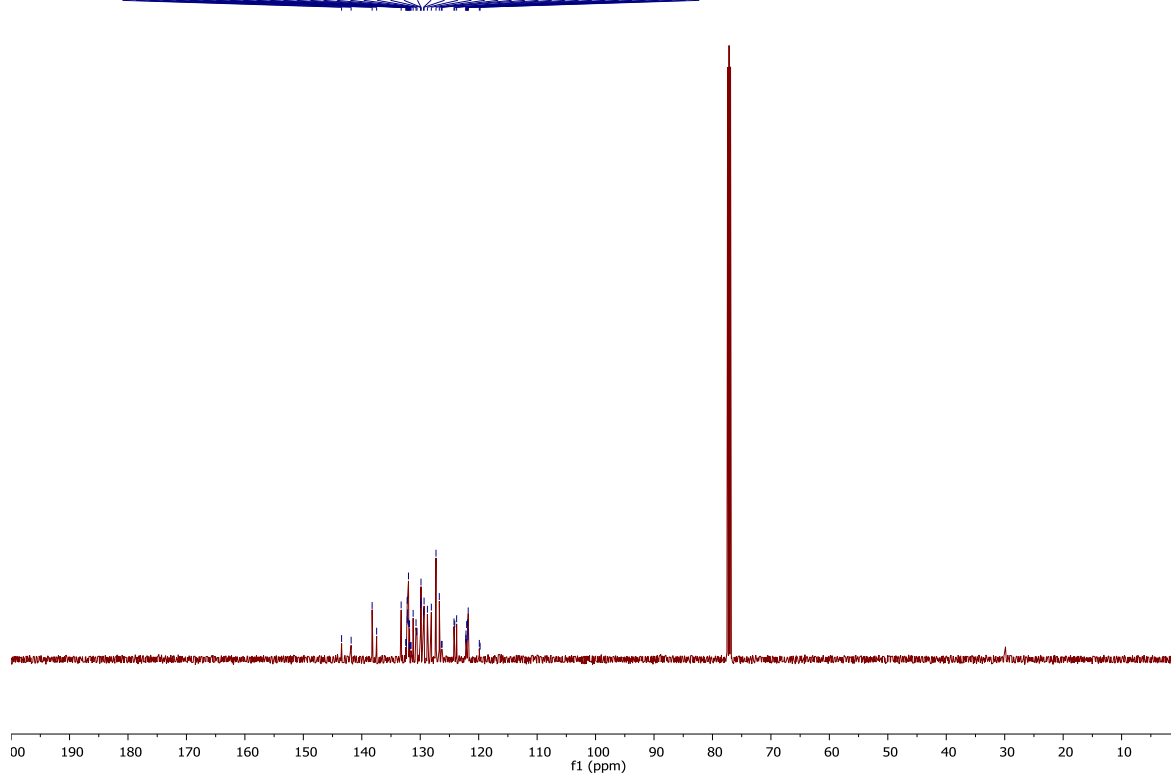
**(S,S)-4g**  
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

8.15, 8.11, 8.09, 7.92, 7.92, 7.92, 7.91, 7.91, 7.91, 7.91, 7.90, 7.89, 7.89, 7.85, 7.85, 7.79, 7.79, 7.77, 7.77, 7.74, 7.74, 7.74, 7.73, 7.73, 7.73, 7.72, 7.72, 7.72, 7.71, 7.71, 7.71, 7.64, 7.64, 7.63, 7.63, 7.63, 7.62, 7.62, 7.62, 7.61, 7.61, 7.61, 7.41, 7.41, 7.41, 7.39, 7.39, 7.39, 7.39, 7.37, 7.37, 7.37, 7.37, 7.37, 7.18, 7.18, 7.16, 6.65

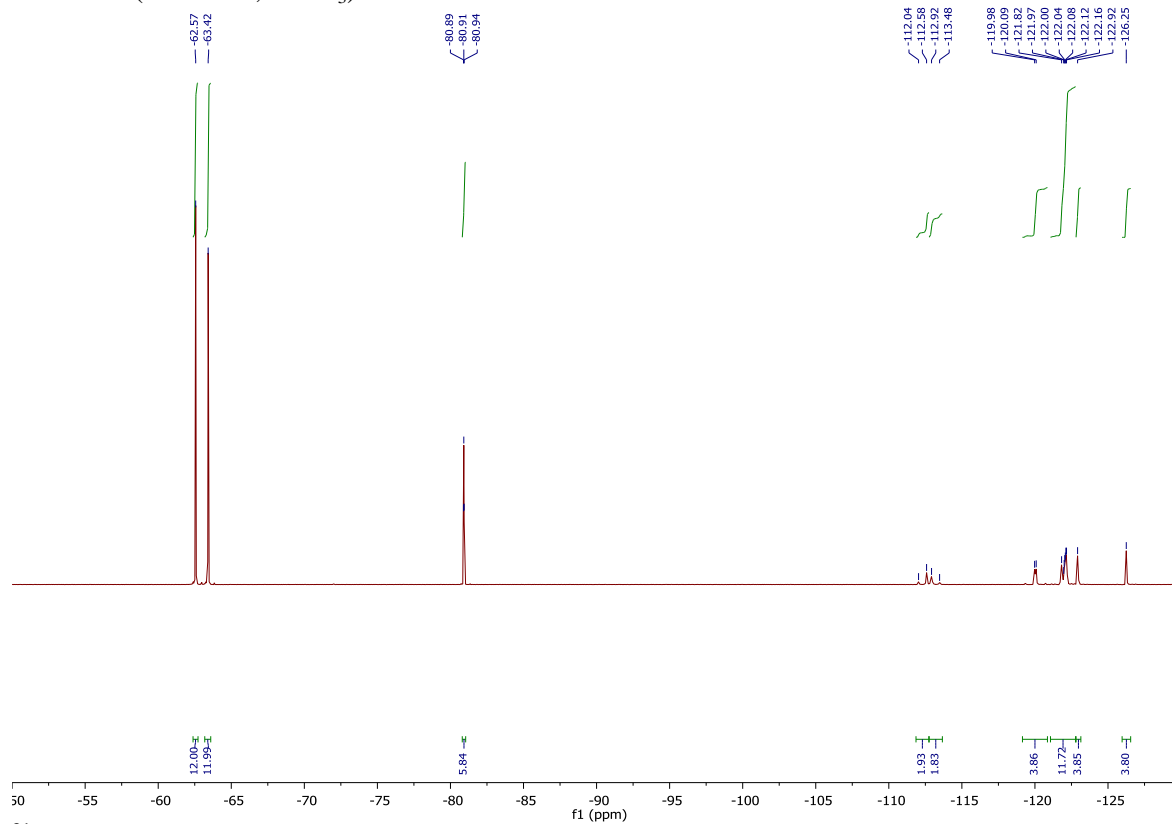


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

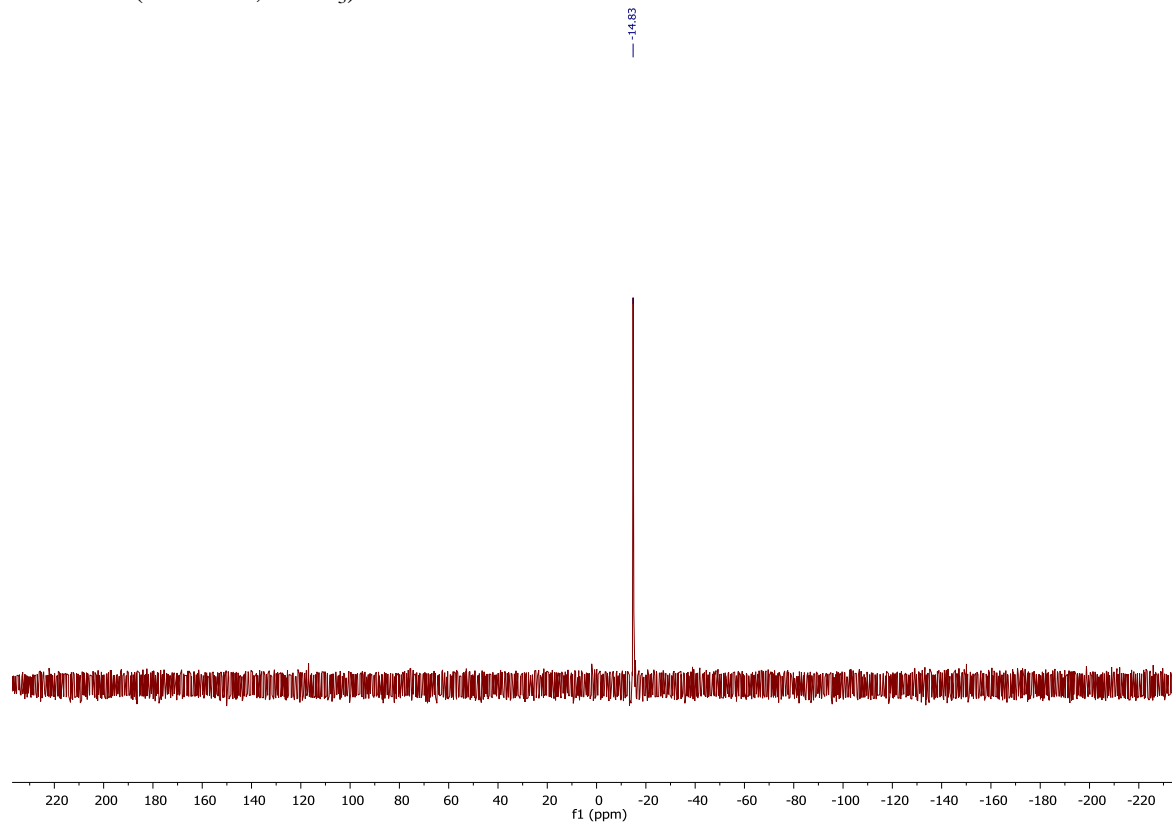
163.65, 161.82, 138.23, 137.46, 133.26, 132.48, 132.36, 132.21, 132.15, 132.10, 132.01, 131.95, 131.95, 131.83, 131.68, 131.56, 131.21, 131.21, 130.72, 129.91, 129.91, 129.89, 129.87, 129.43, 129.34, 129.34, 129.10, 128.10, 127.30, 126.73, 126.39, 126.26, 126.26, 126.26, 124.69, 124.69, 123.77, 122.19, 122.17, 122.15, 122.15, 122.15, 121.83, 121.83, 121.82, 121.79, 121.79, 119.89, 119.76



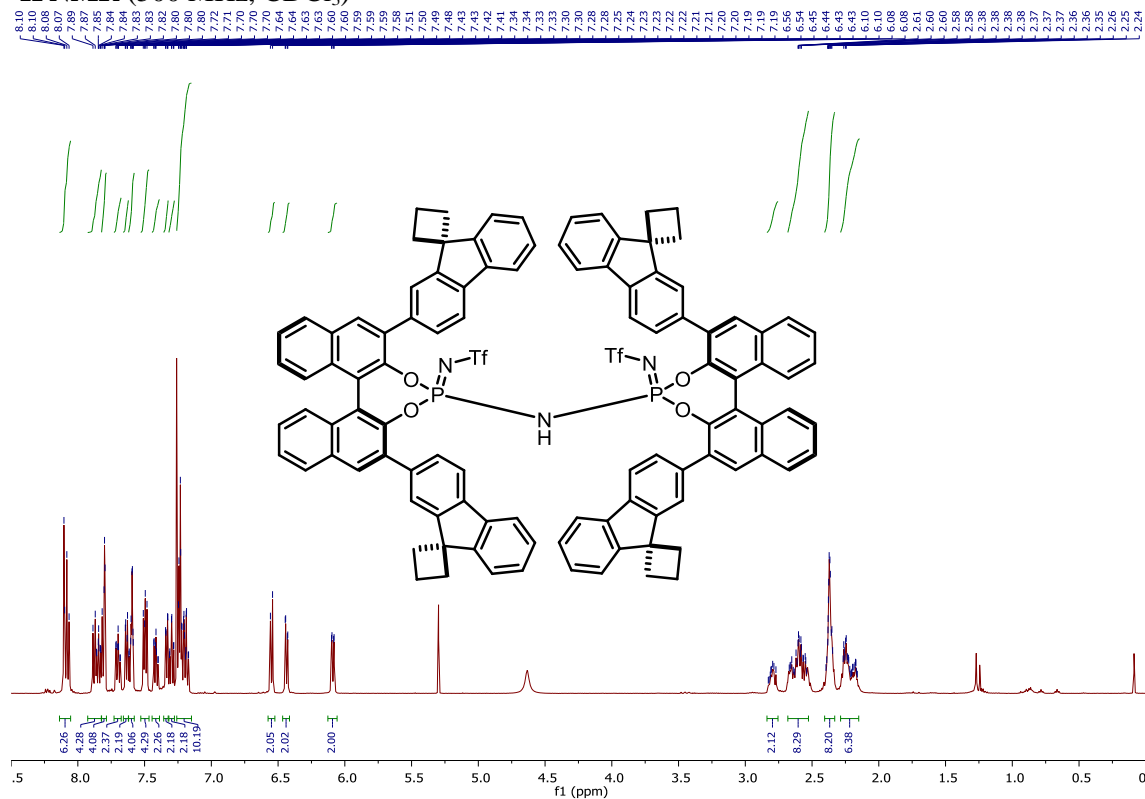
**$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):**



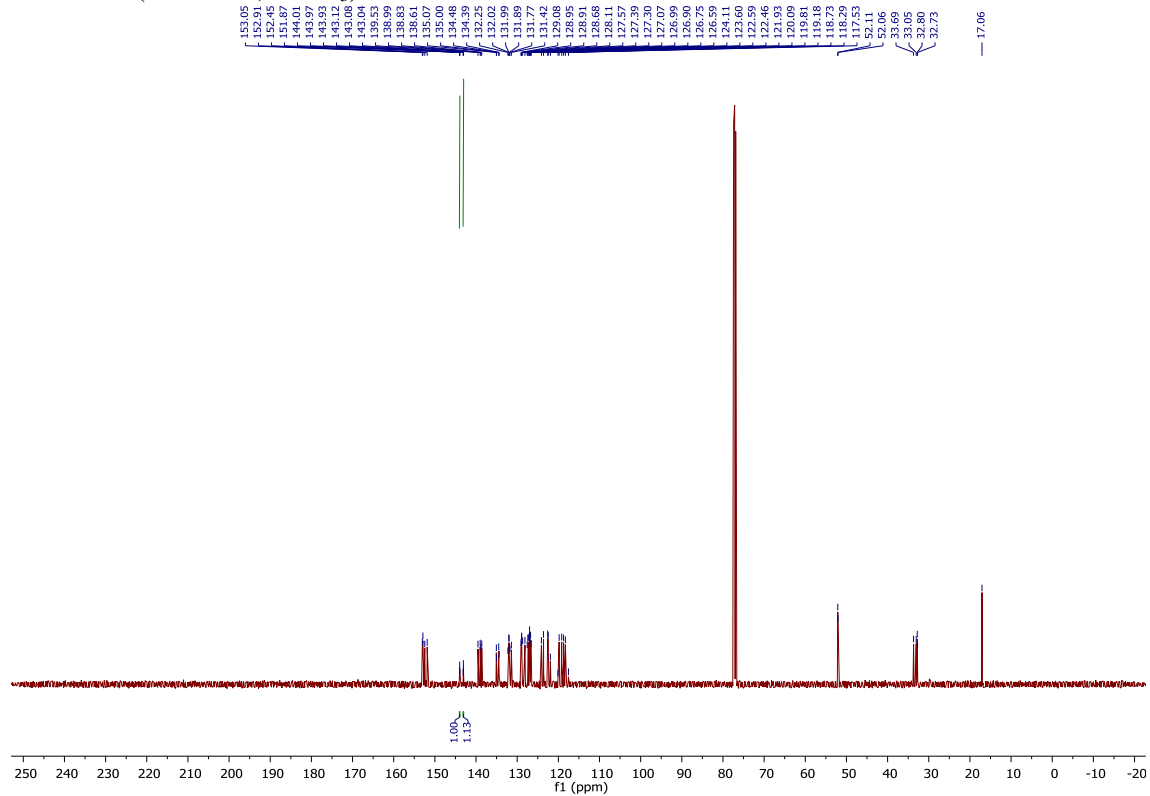
**$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):**



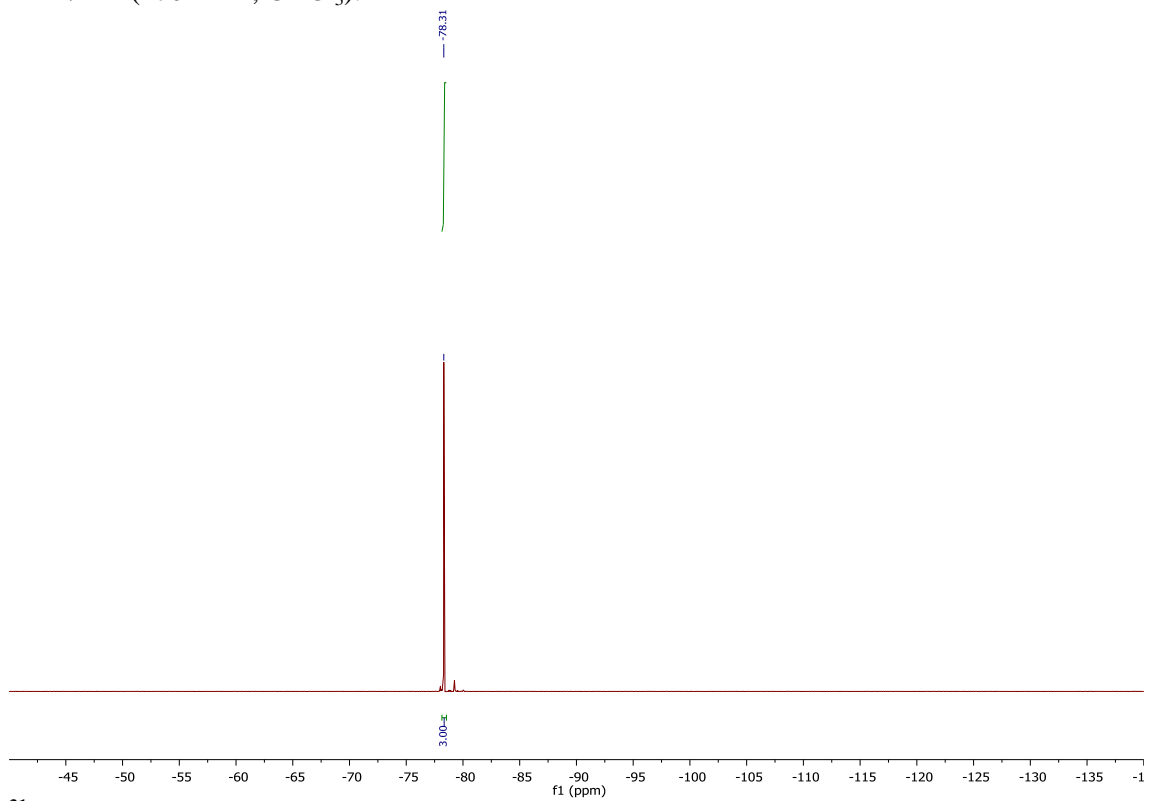
**(S,S)-4h**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



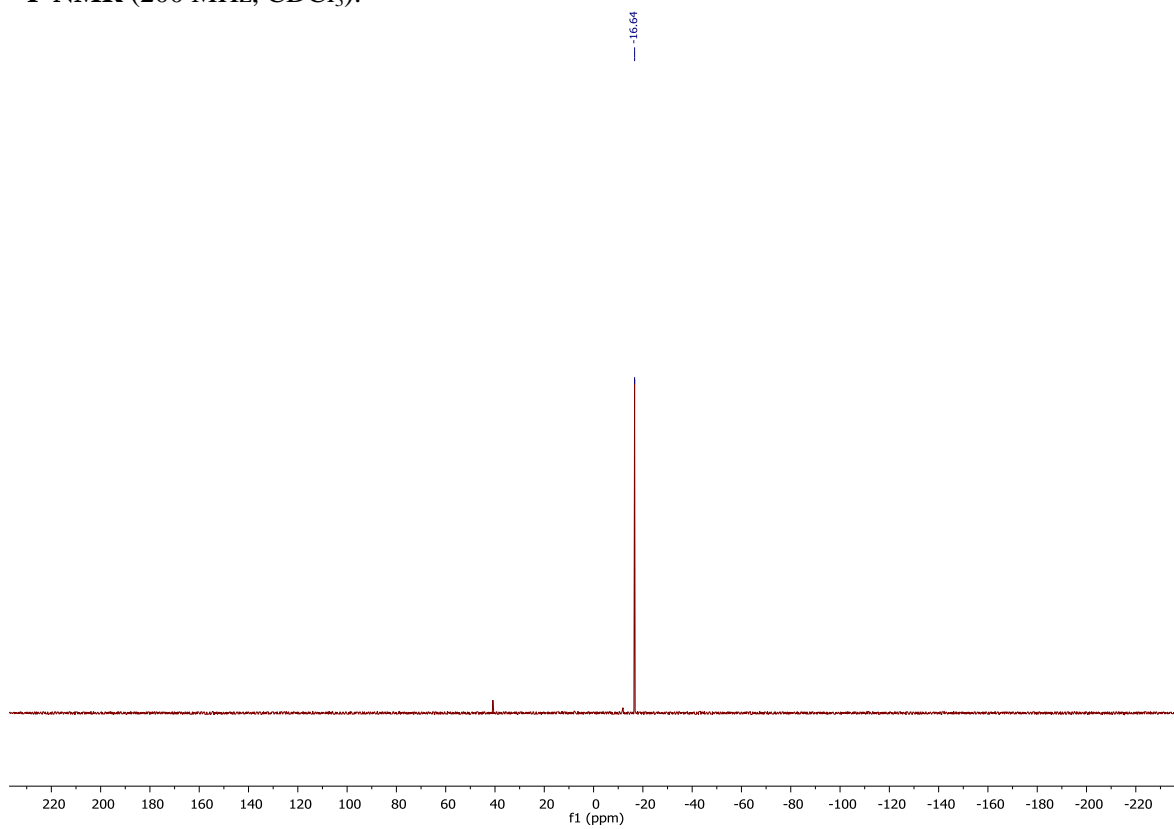
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



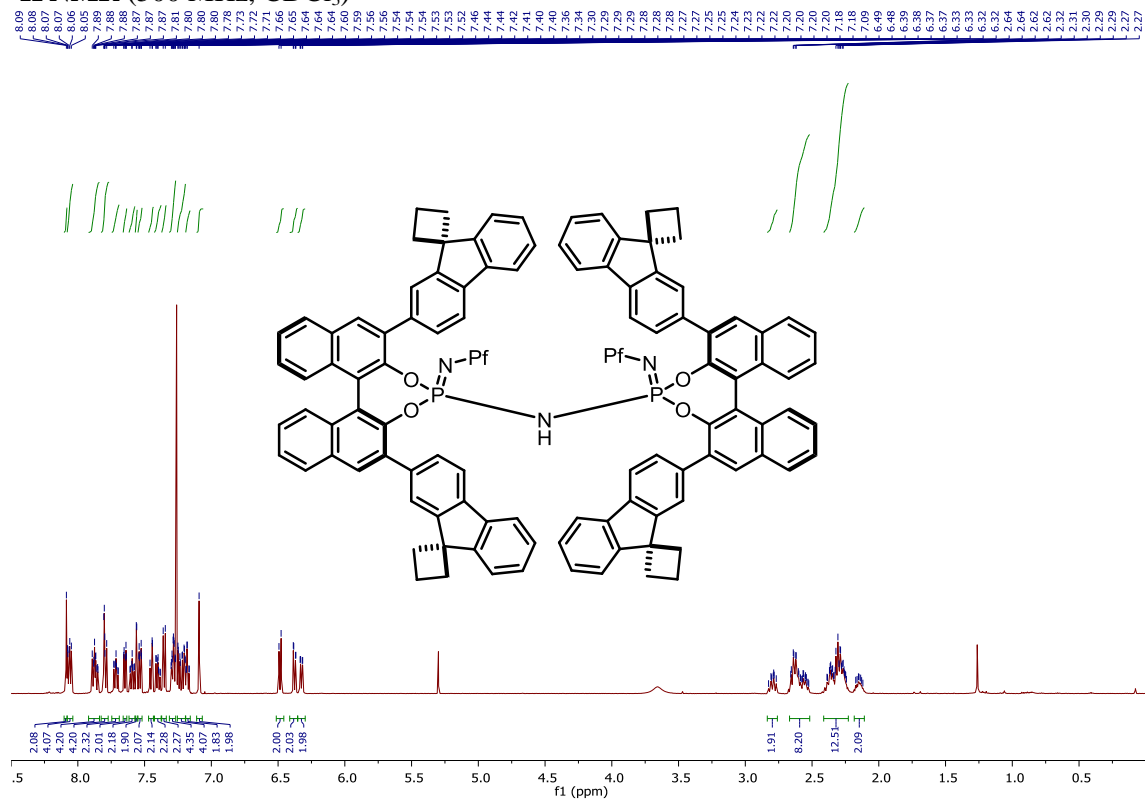
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



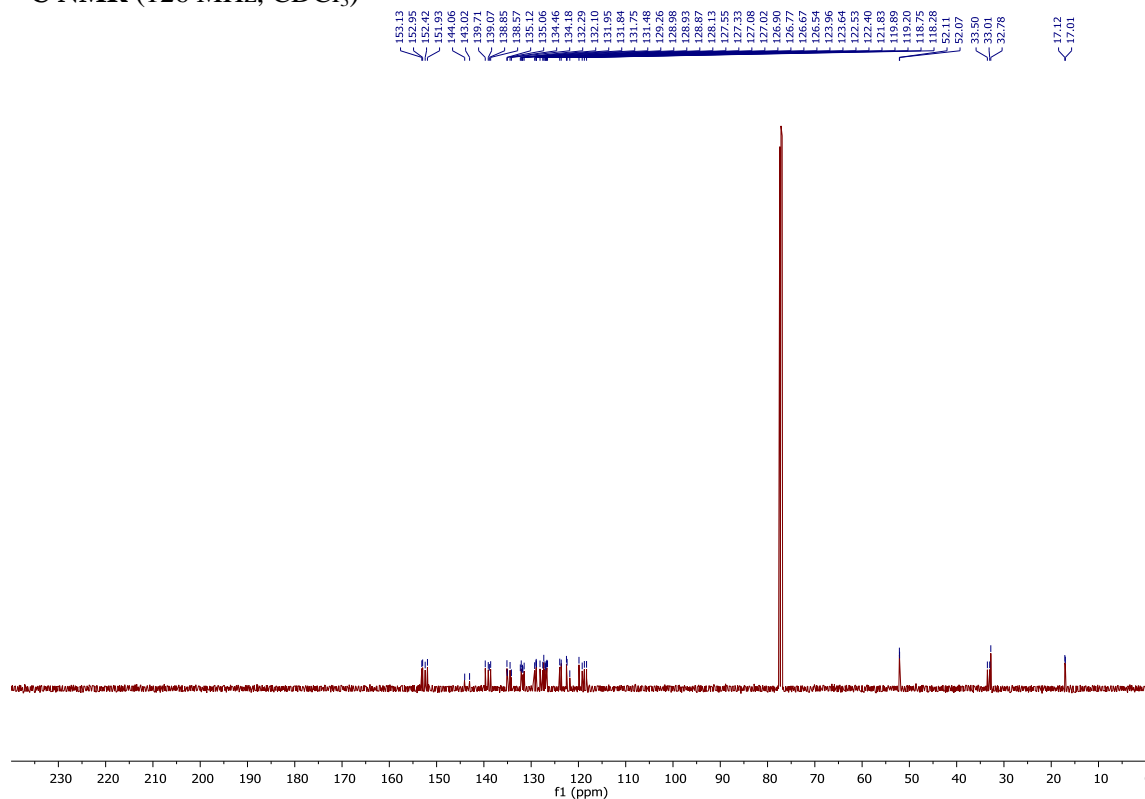
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



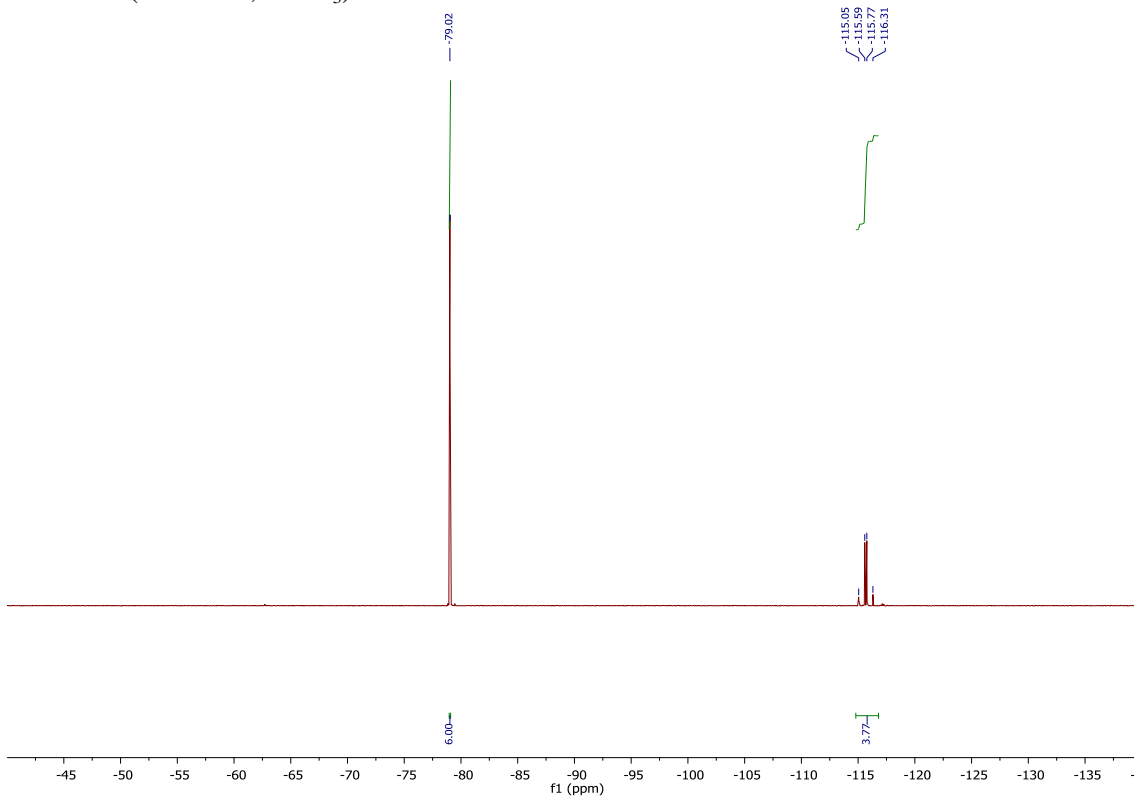
**(S,S)-4c**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



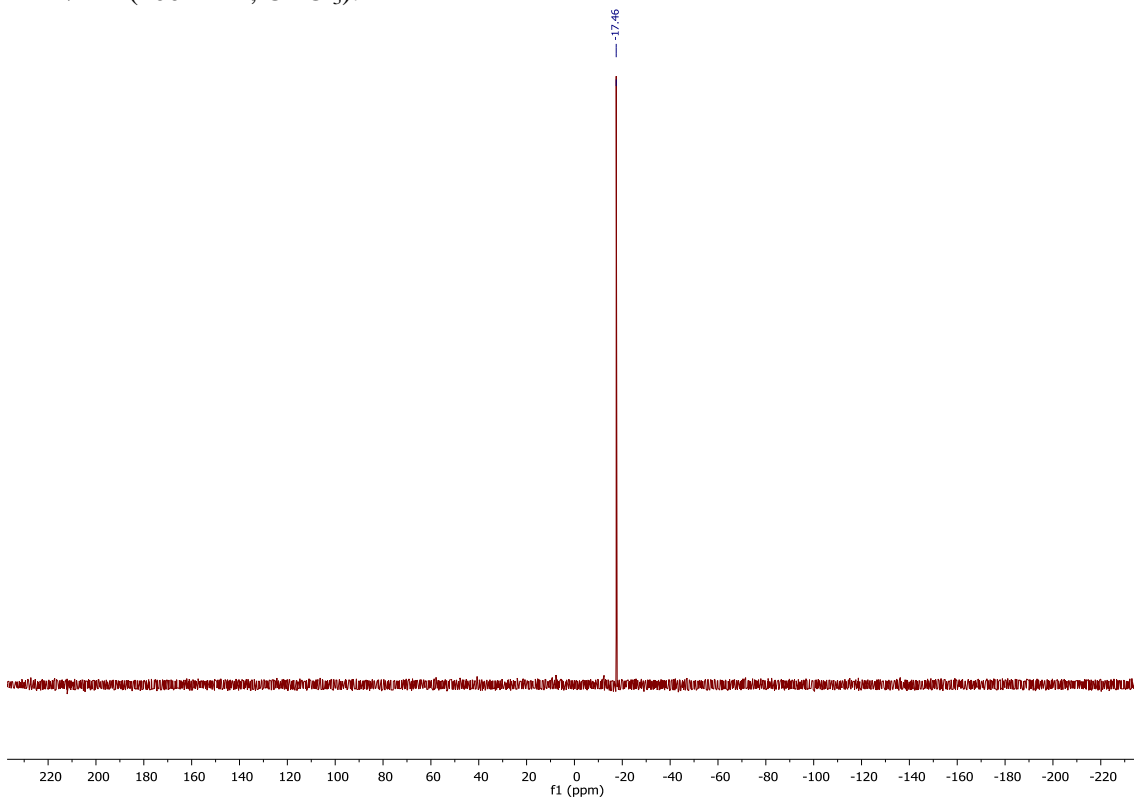
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



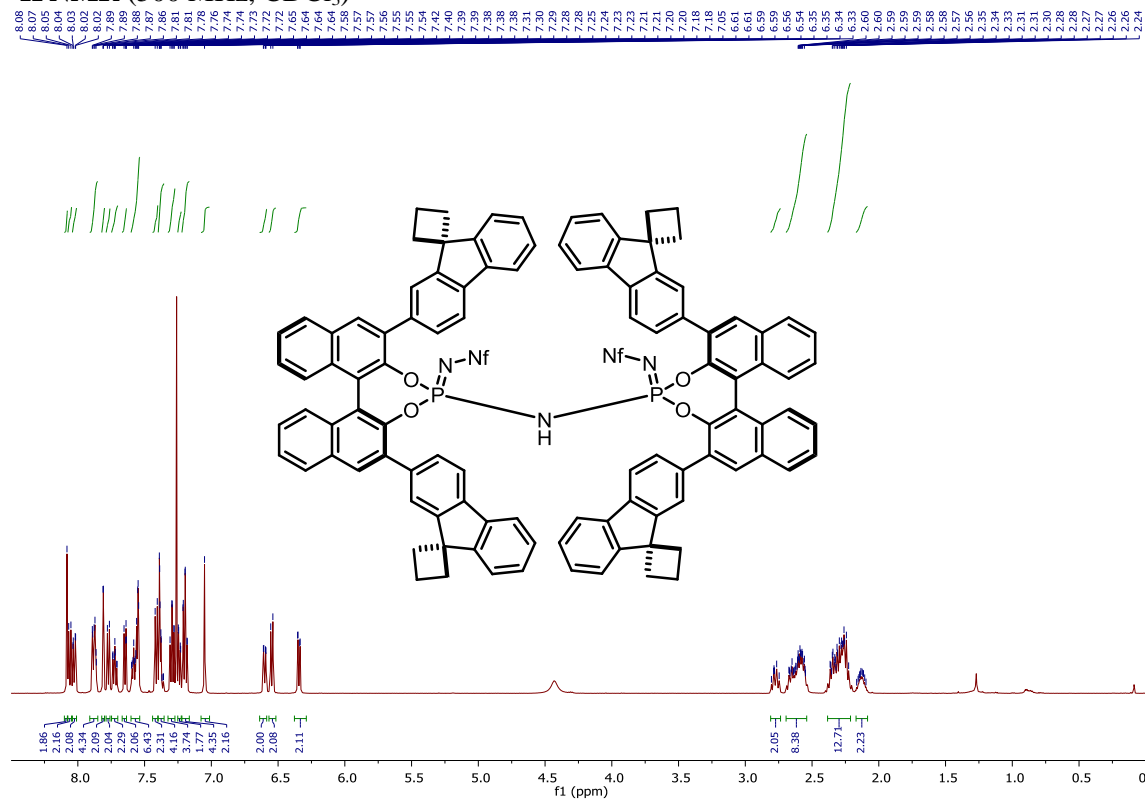
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



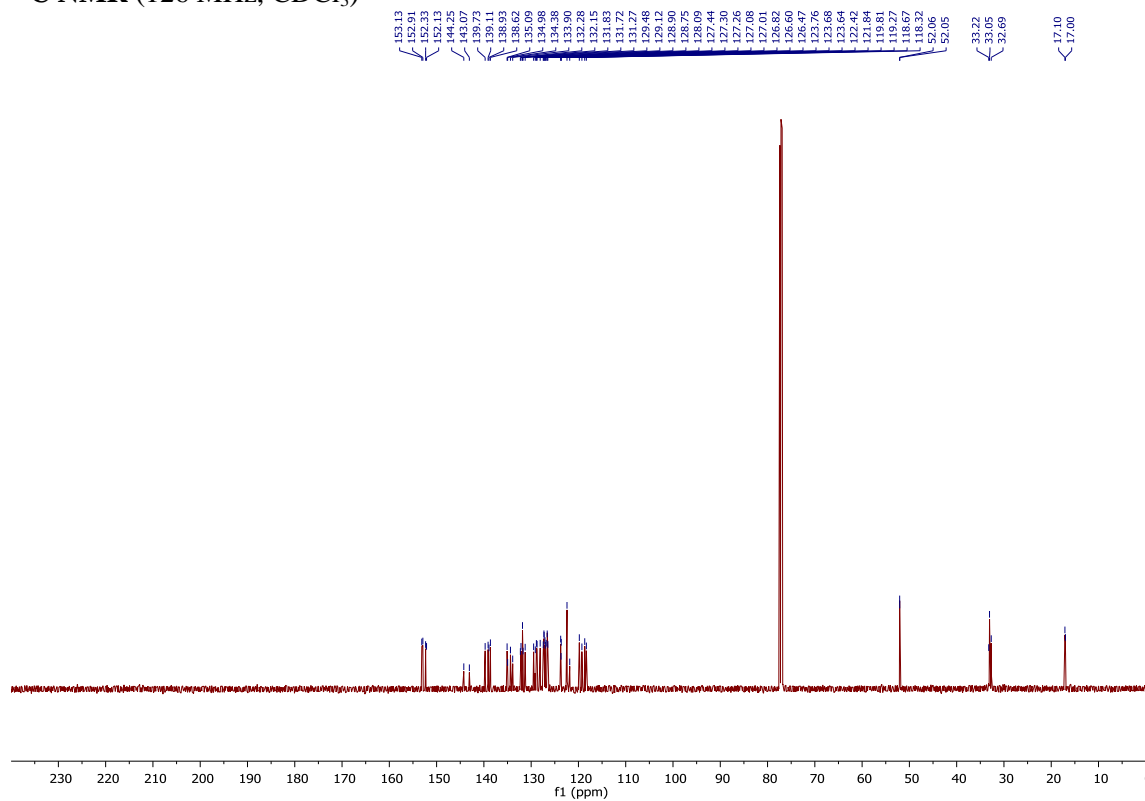
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



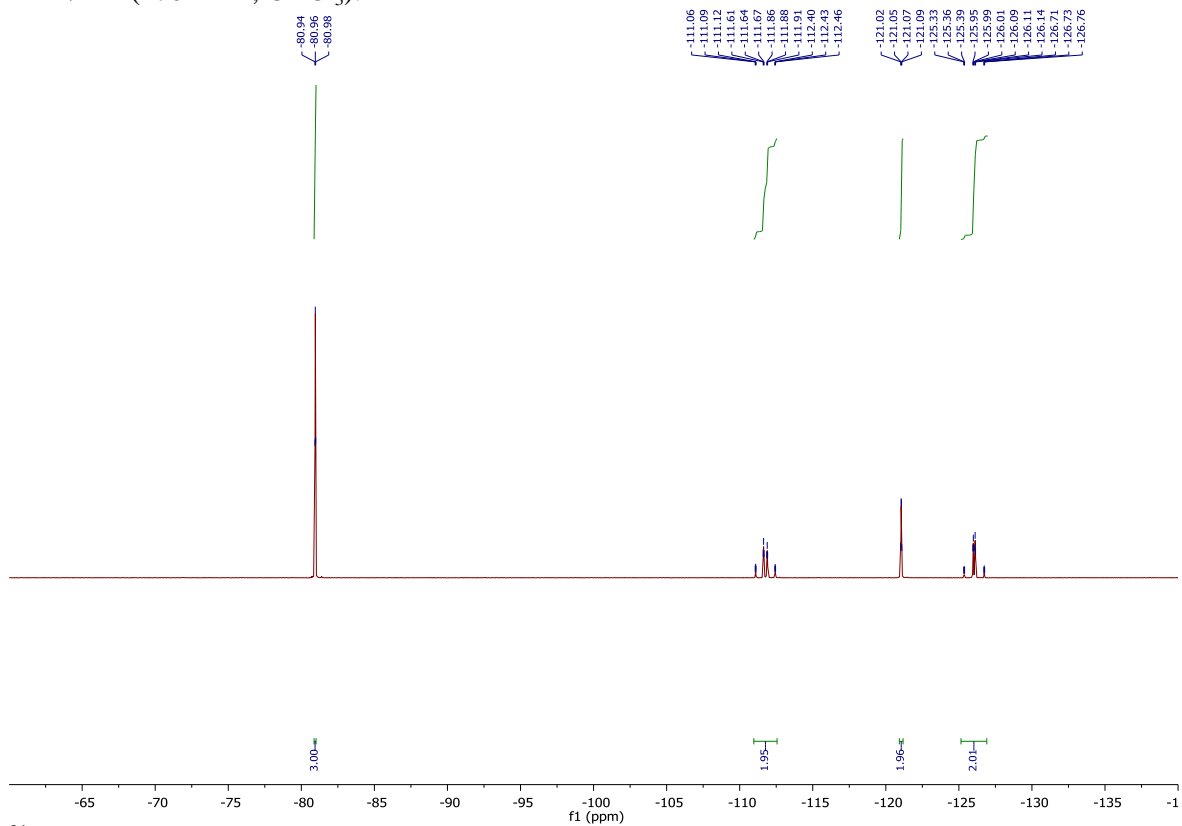
**(S,S)-4i**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



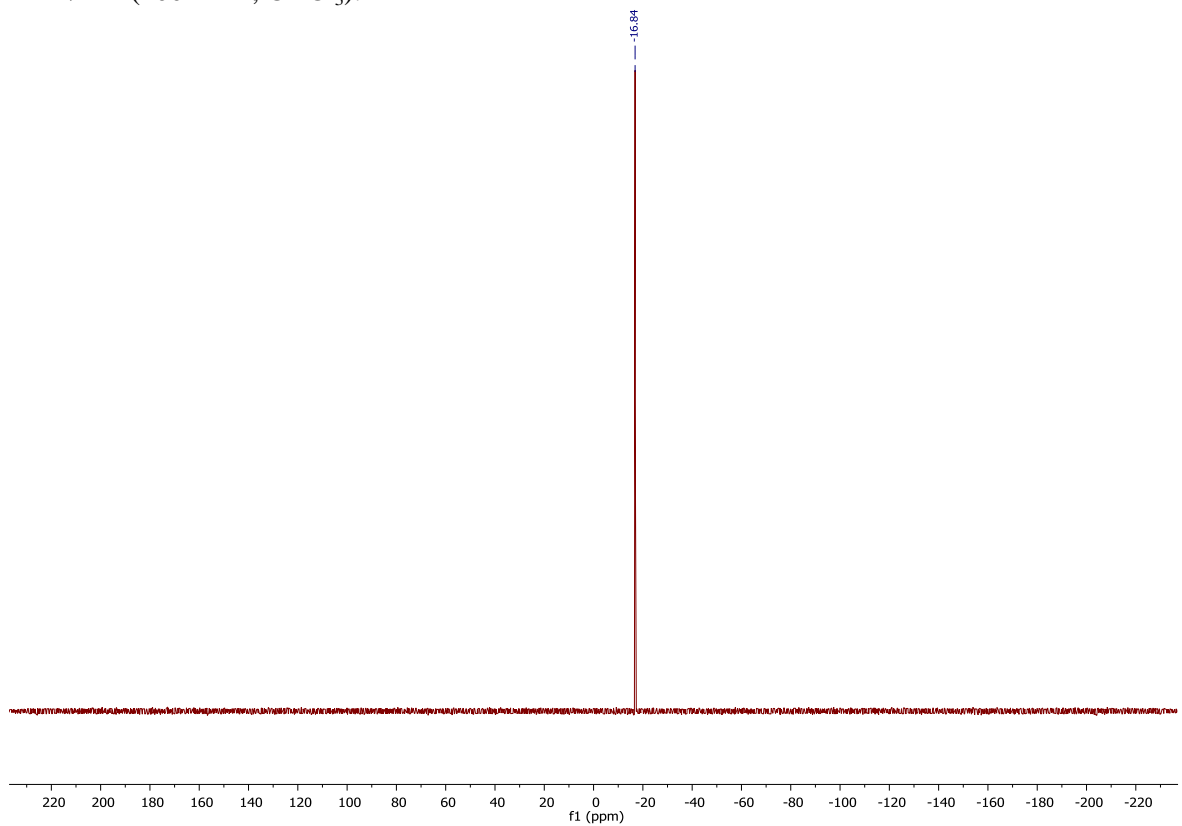
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



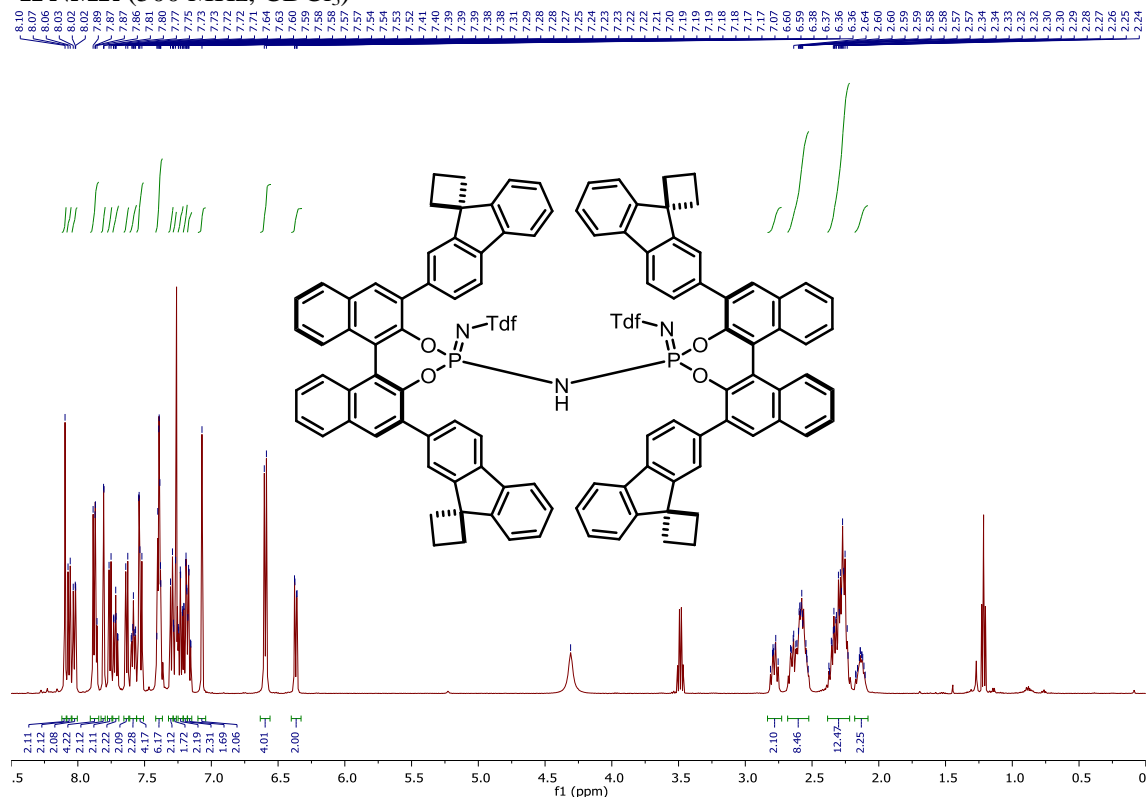
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



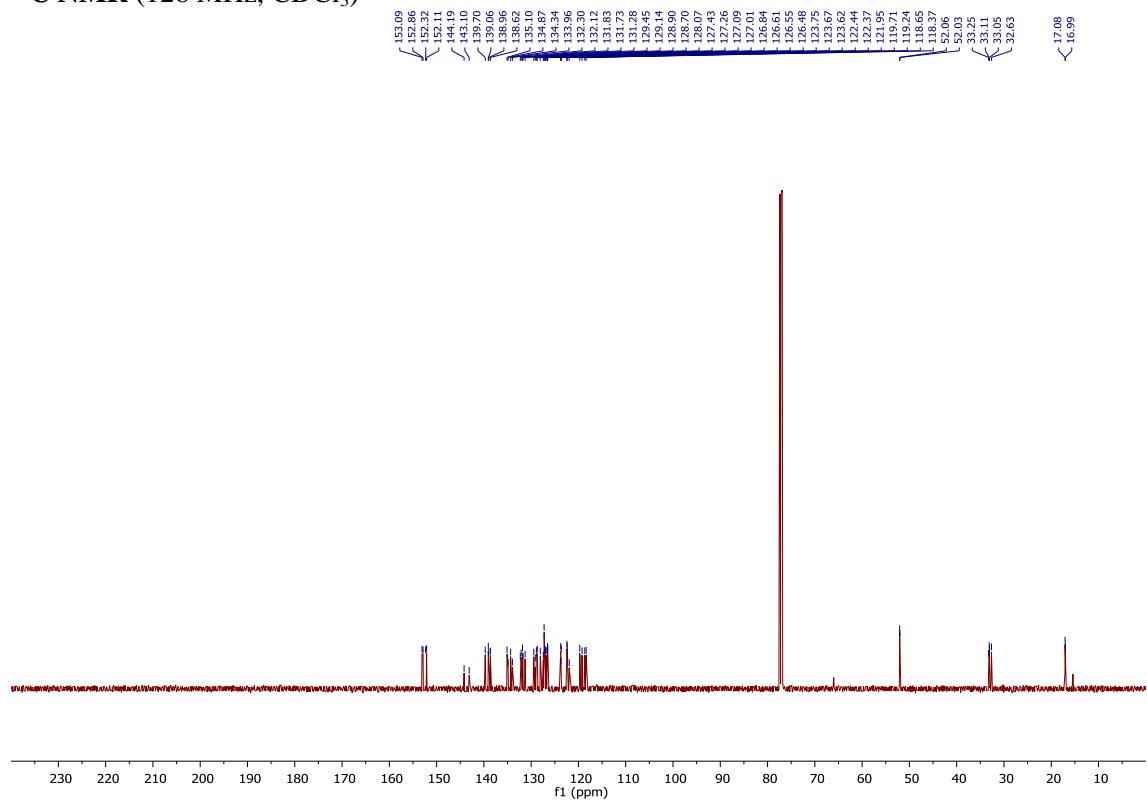
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



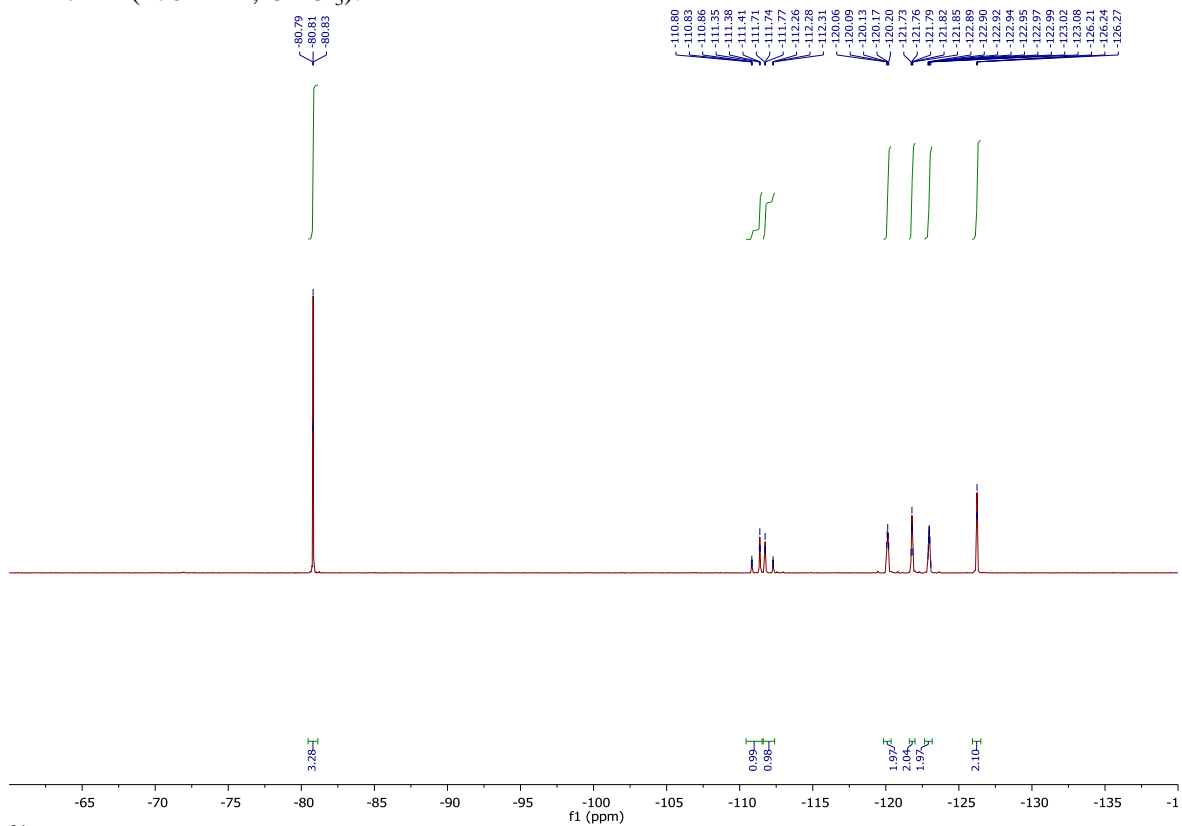
**(S,S)-4j**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



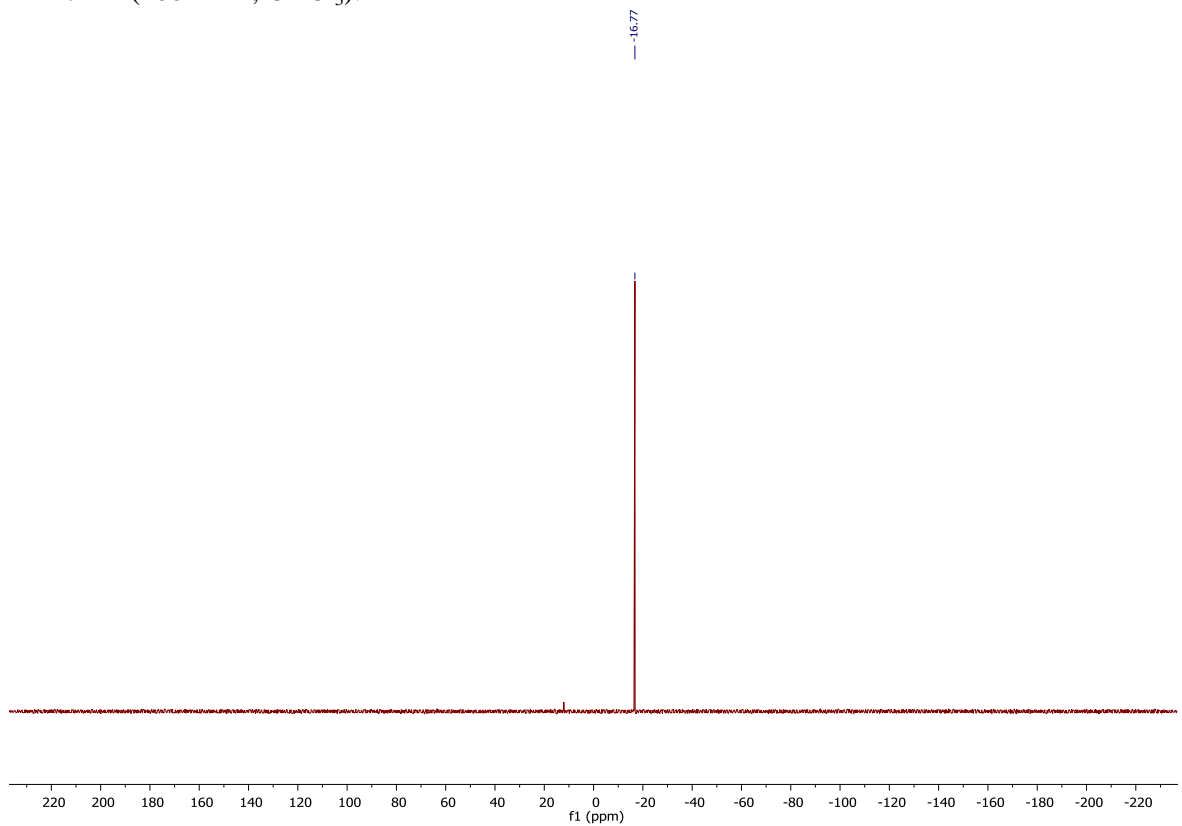
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):

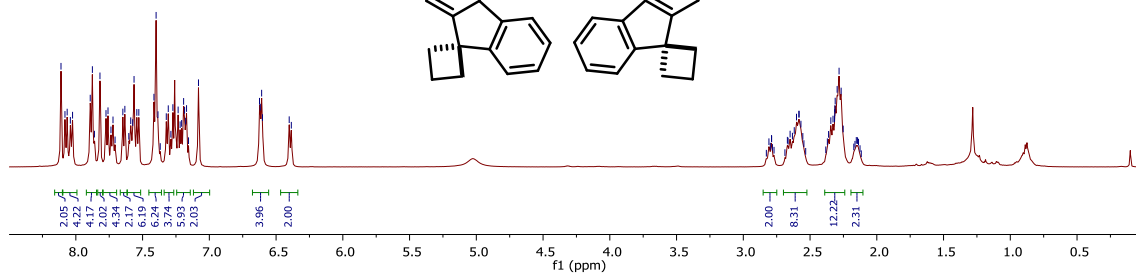
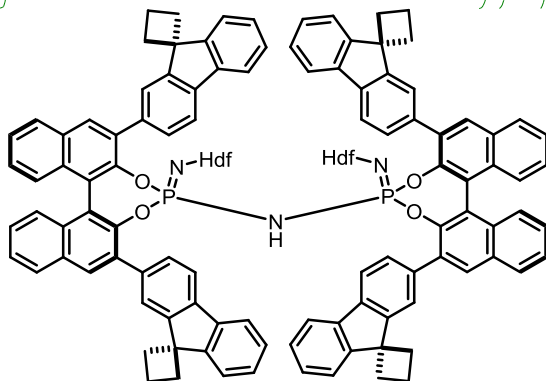


$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



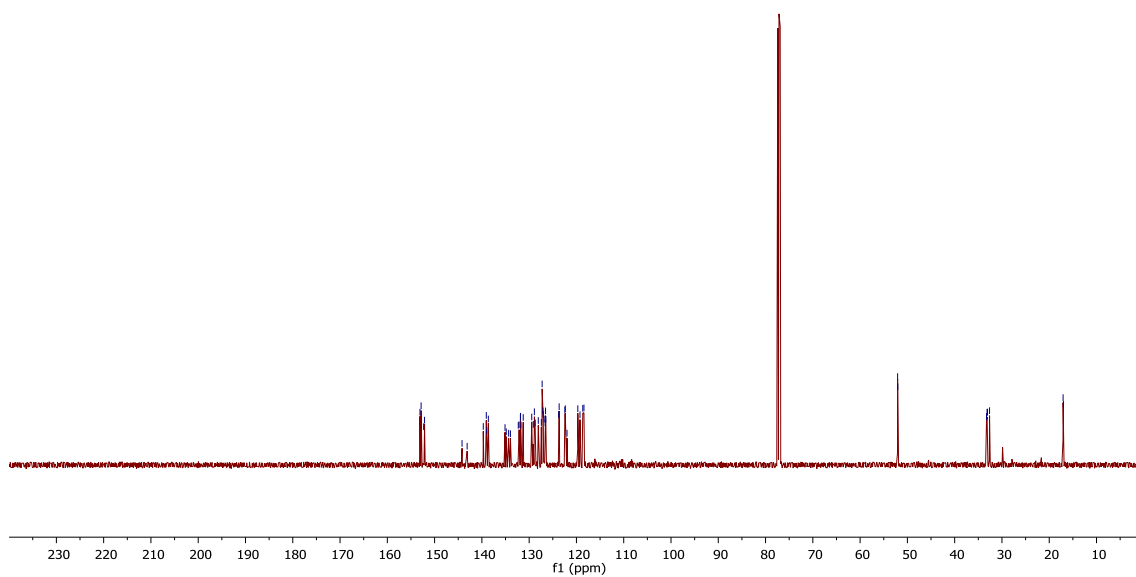
**(S,S)-4k**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

8.11, 8.08, 8.04, 8.02, 7.89, 7.88, 7.86, 7.77, 7.76, 7.74, 7.72, 7.71, 7.65, 7.63, 7.60, 7.59, 7.57, 7.54, 7.53, 7.41, 7.40, 7.37, 7.33, 7.31, 7.29, 7.27, 7.22, 7.21, 7.19, 7.19, 7.19, 7.17, 7.16, 7.08, 7.08, 6.62, 6.62, 6.61, 6.60, 6.40, 6.39, 6.38, 6.35, 2.80, 2.79, 2.79, 2.78, 2.69, 2.67, 2.66, 2.65, 2.62, 2.62, 2.58, 2.58, 2.57, 2.55, 2.53, 2.37, 2.37, 2.34, 2.34, 2.33, 2.32, 2.32, 2.31, 2.30, 2.28, 2.27, 2.27, 2.16, 2.15, 2.14, 2.14, 2.12, 2.12

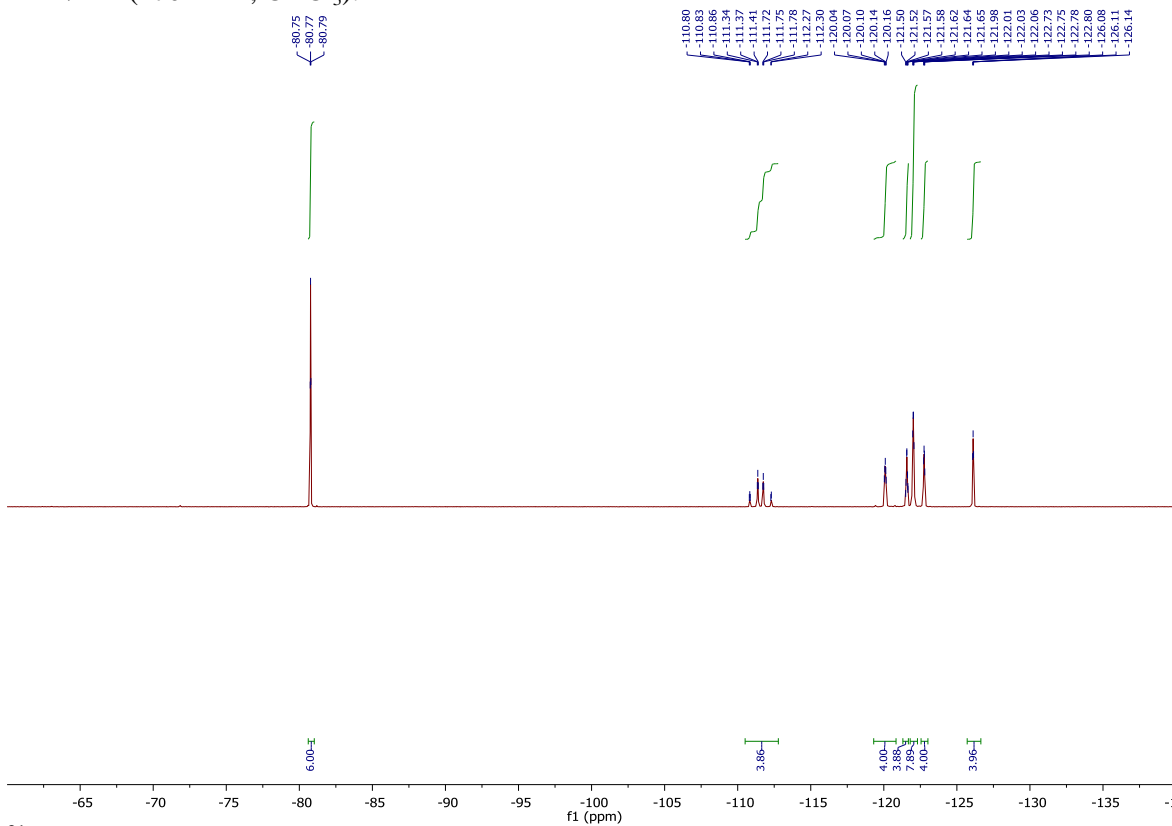


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

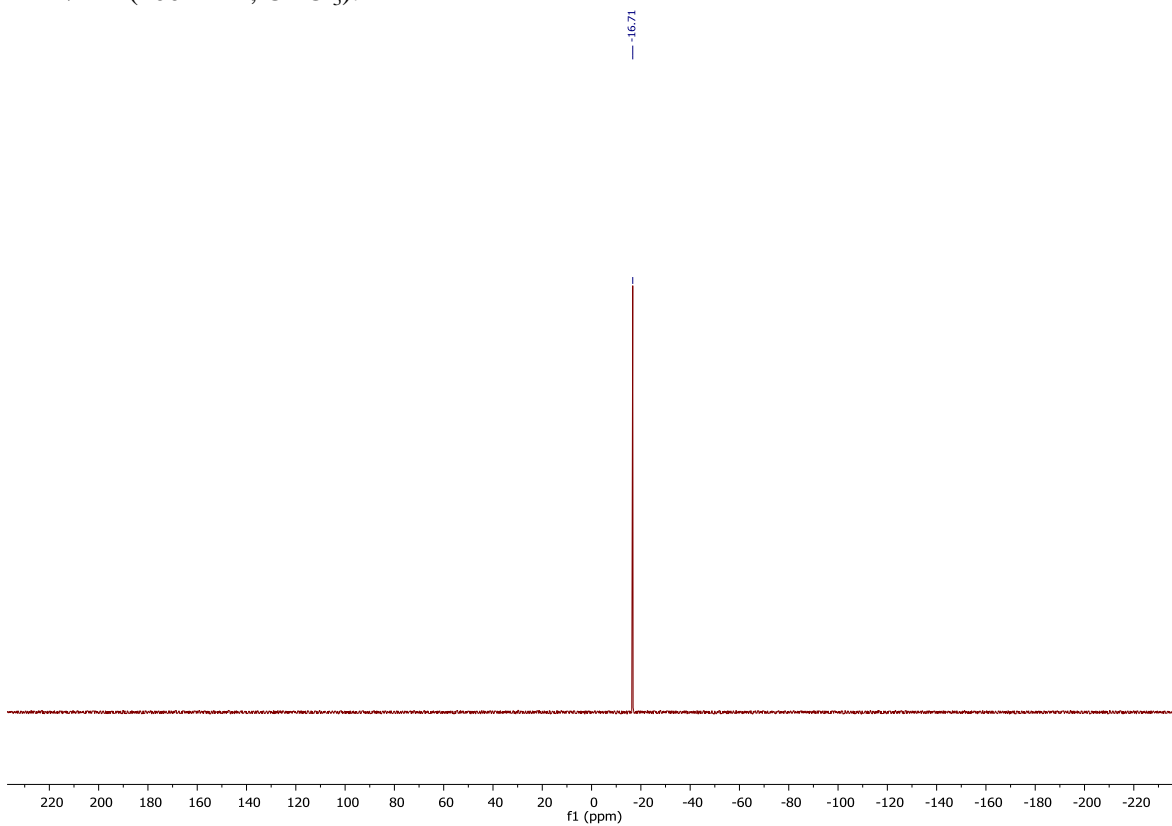
153.09, 152.85, 152.71, 152.12, 144.20, 143.12, 138.71, 138.07, 138.06, 138.64, 135.11, 134.85, 134.34, 134.34, 132.13, 132.30, 131.86, 131.86, 131.76, 131.26, 129.45, 128.90, 128.90, 128.73, 128.07, 127.43, 127.26, 127.09, 127.01, 127.01, 126.61, 126.53, 126.48, 123.75, 123.64, 122.44, 122.36, 121.99, 118.71, 118.25, 118.25, 118.41, 118.41, 52.07, 52.03, 33.27, 33.16, 33.06, 32.62, 17.07, 17.00



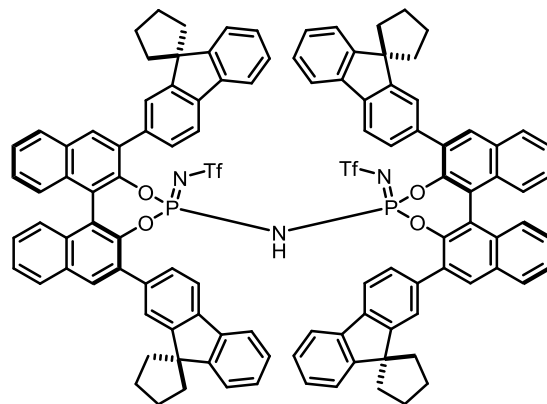
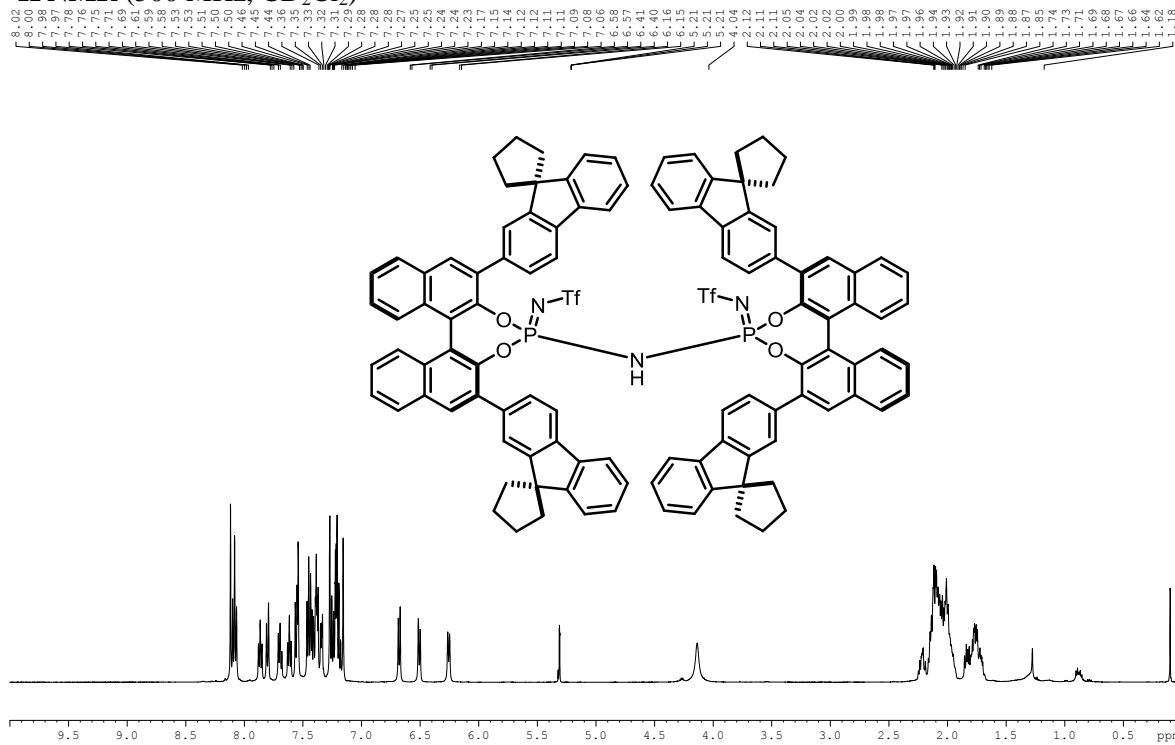
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



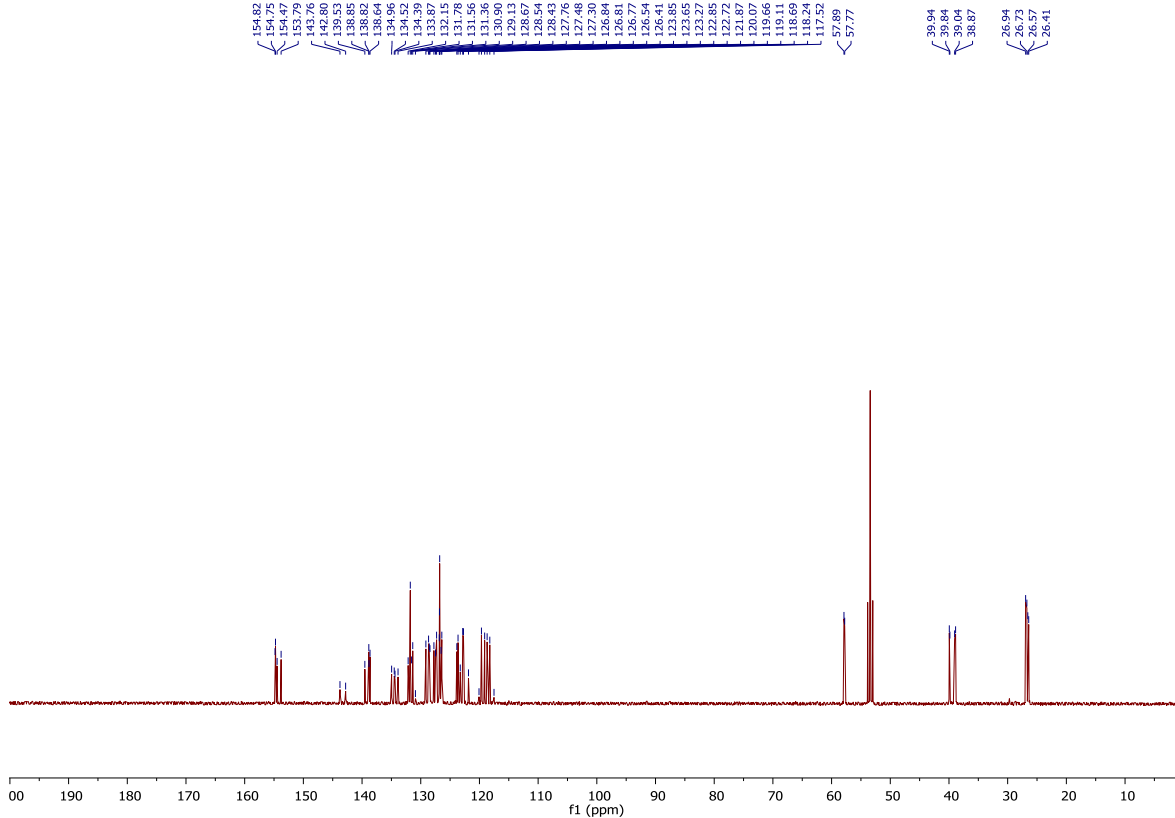
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



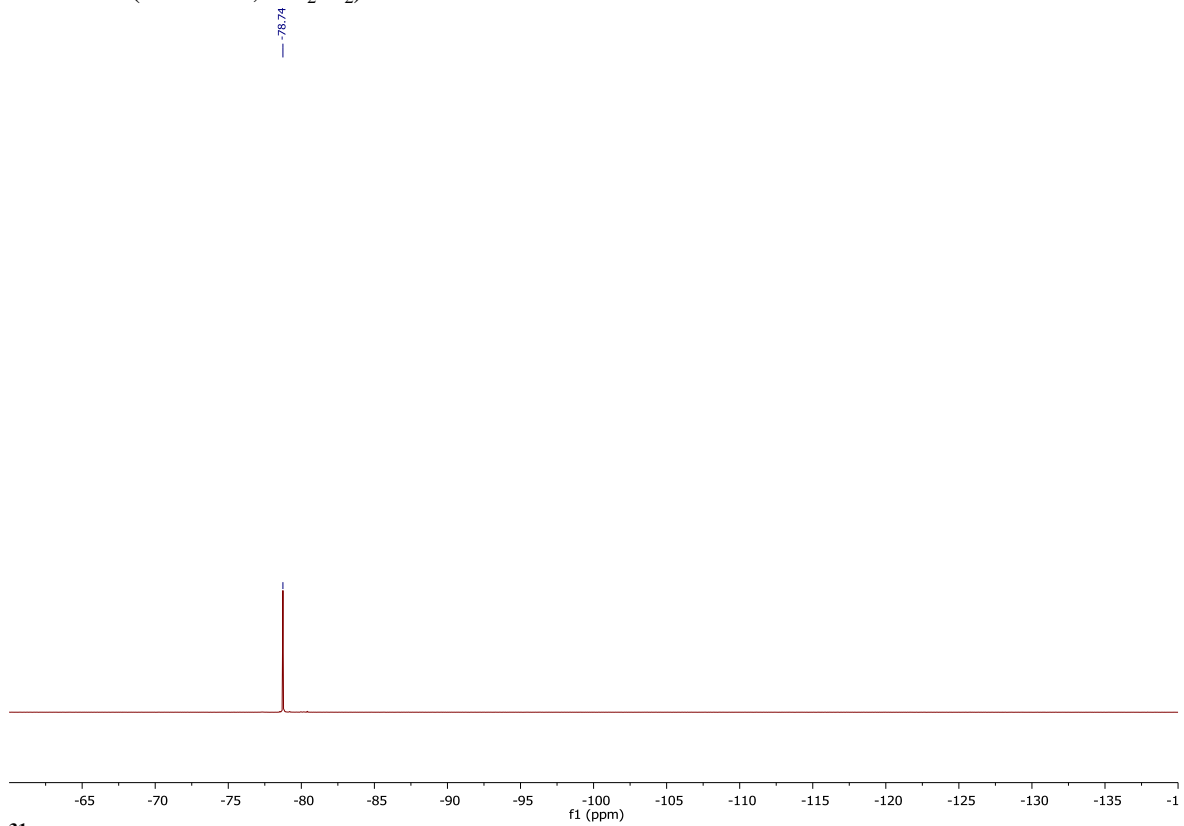
**(S,S)-4l**  
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



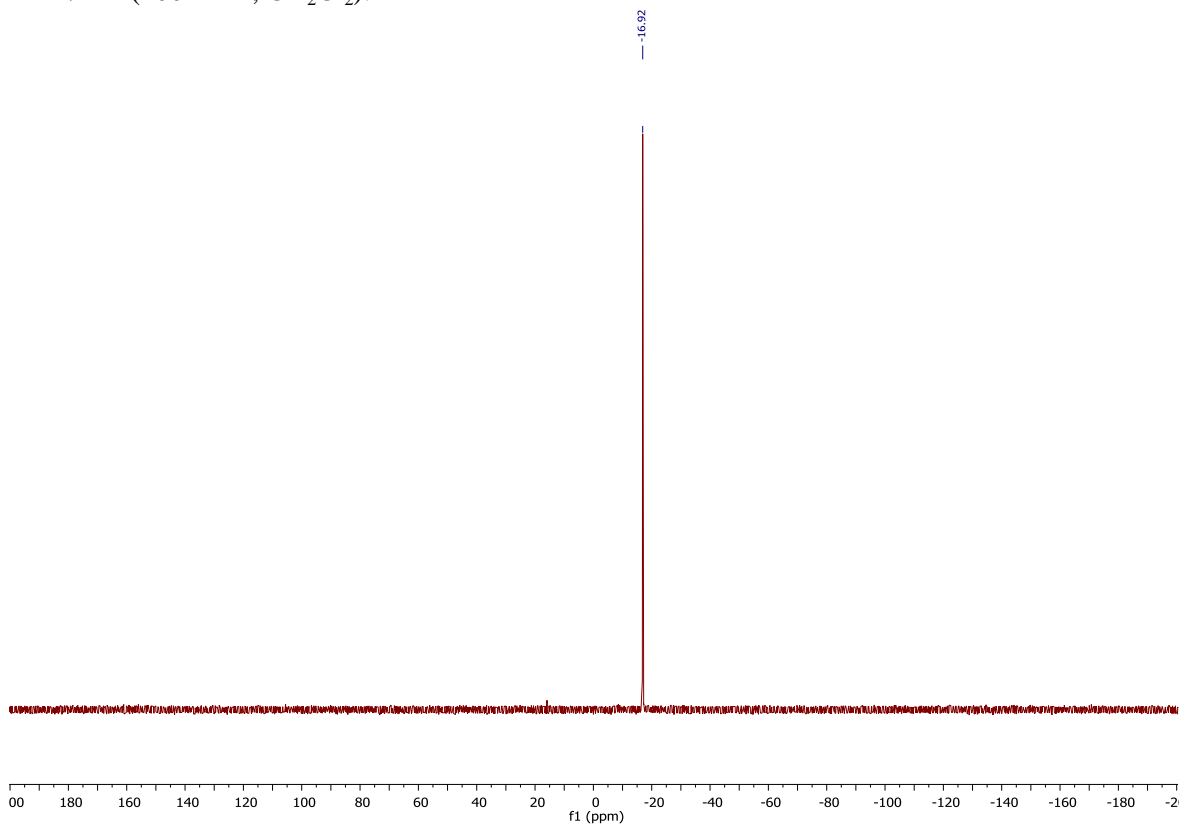
<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



$^{19}\text{F}$  NMR (470 MHz,  $\text{CD}_2\text{Cl}_2$ ):

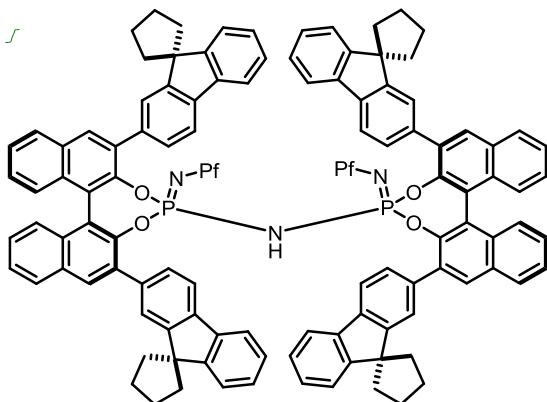
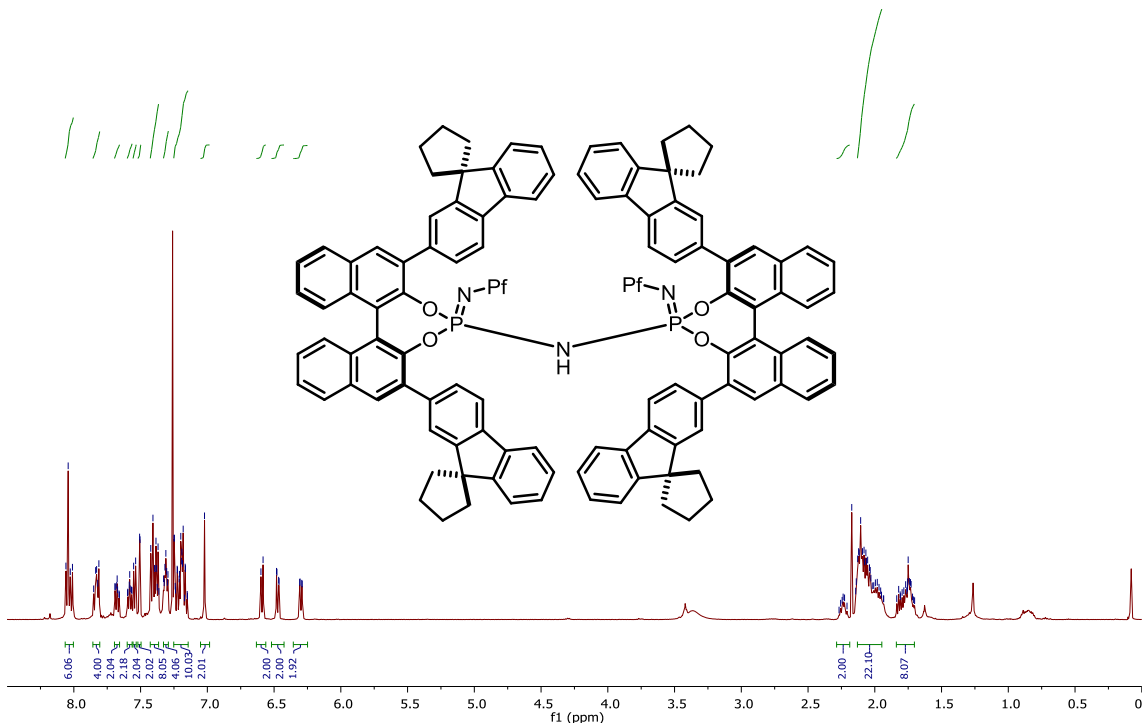


$^{31}\text{P}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ ):



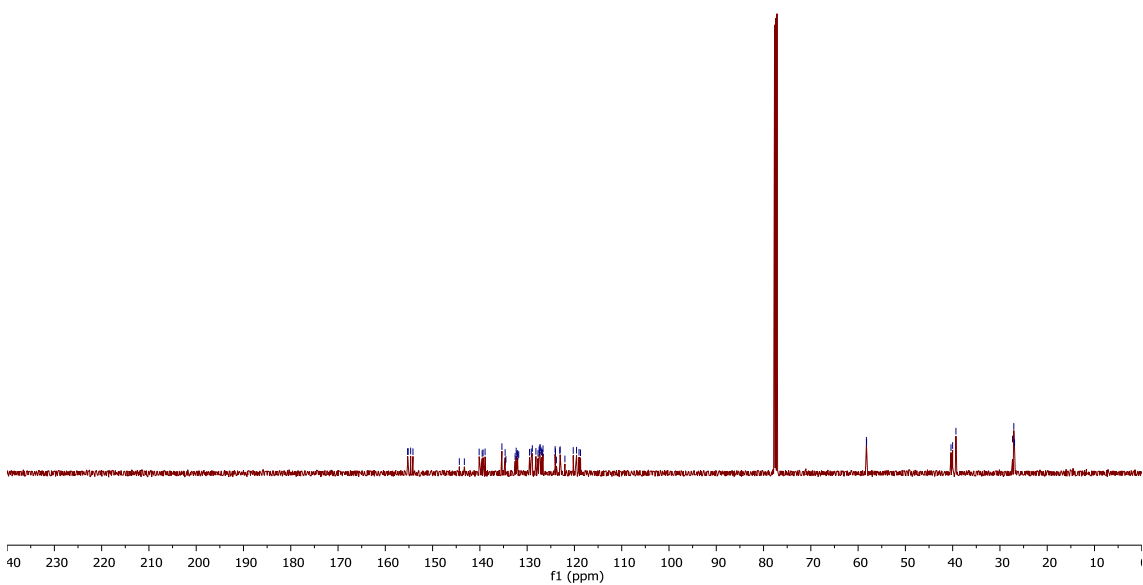
**(S,S)-4m**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

8.06, 8.04, 8.03, 7.95, 7.94, 7.884, 7.82, 7.81, 7.769, 7.668, 7.598, 7.58, 7.555, 7.54, 7.51, 7.49, 7.47, 7.41, 7.39, 7.38, 7.38, 7.38, 7.37, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.30, 7.29, 7.29, 7.25, 7.25, 7.24, 7.23, 7.22, 7.21, 7.21, 7.20, 7.19, 7.19, 7.19, 7.19, 7.16, 7.02, 6.60, 6.38, 6.31, 6.29, 6.29, 6.29, 2.17, 2.14, 2.14, 2.13, 2.12, 2.11, 2.09, 2.08, 2.07, 2.07, 2.06, 2.05, 2.04, 2.04, 2.03, 2.02, 2.01, 2.00, 2.00, 1.98, 1.97, 1.77, 1.76, 1.75, 1.75, 1.73, 1.73

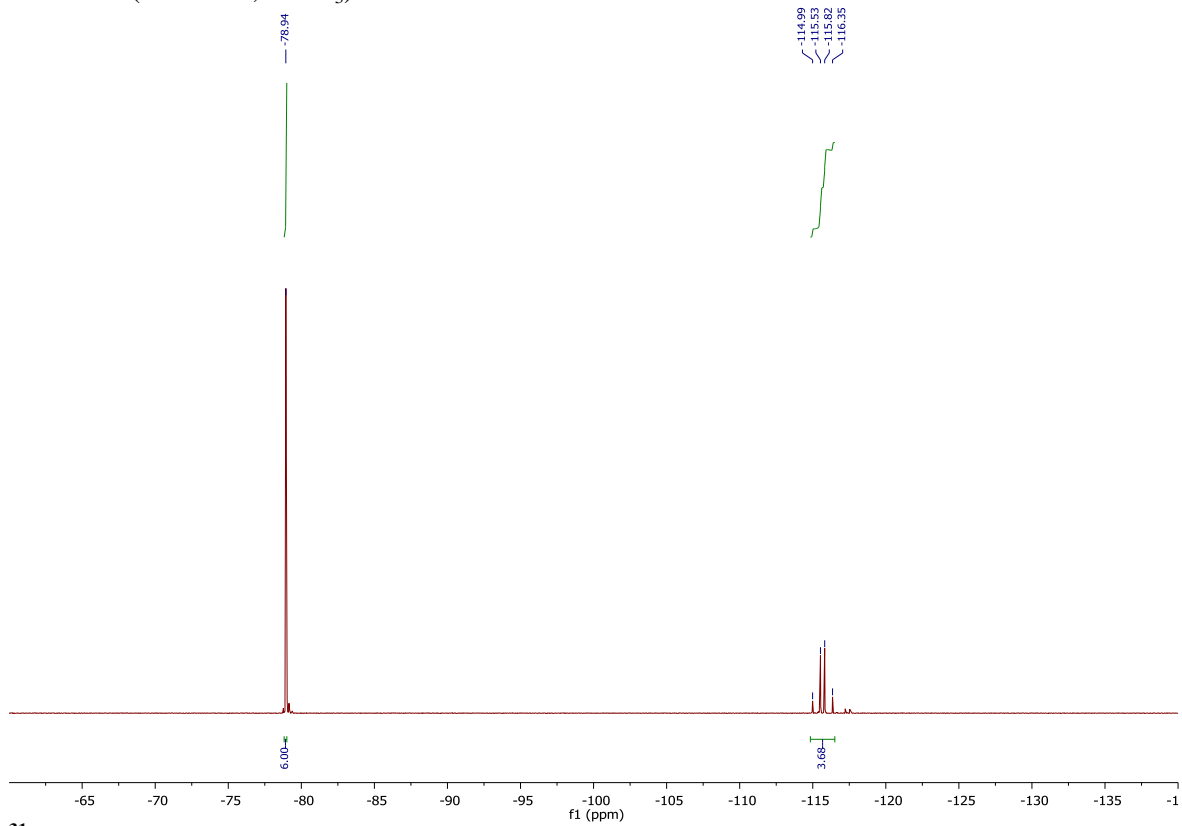


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

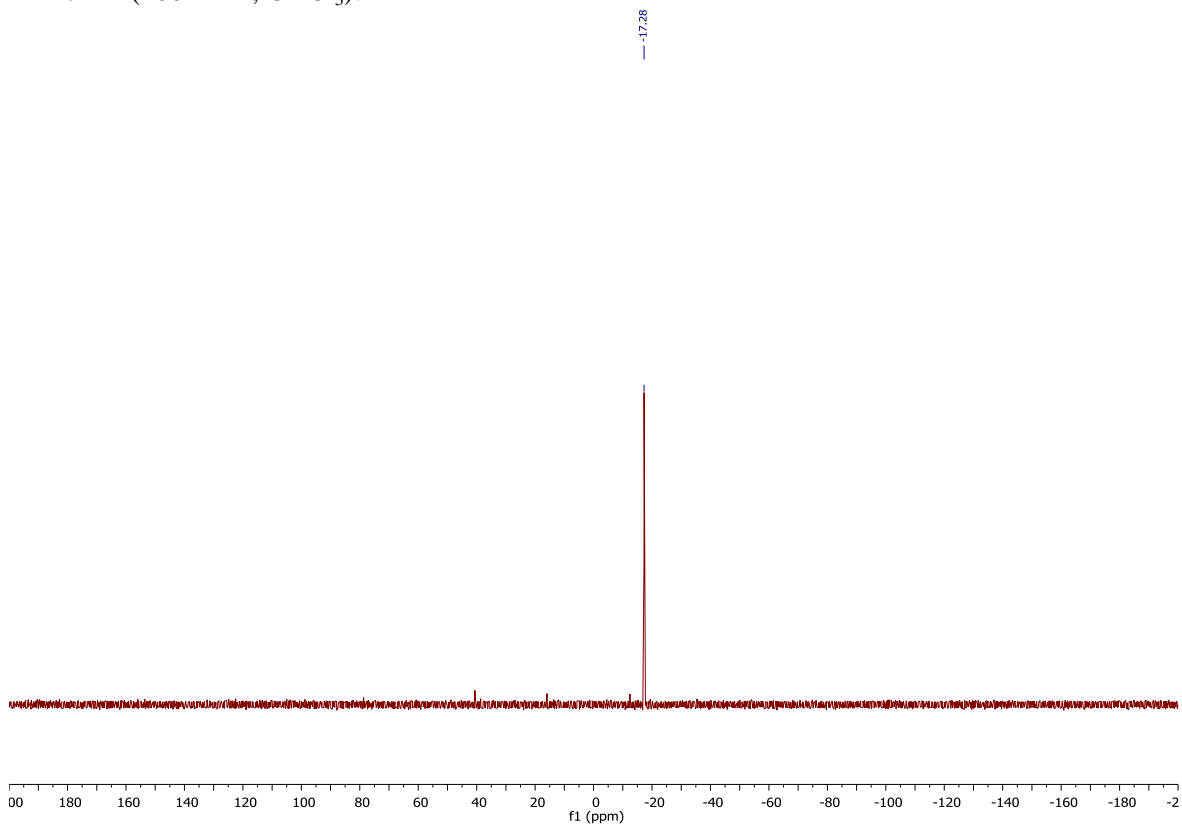
155.29, 155.17, 154.64, 154.15, 144.35, 143.28, 142.15, 139.51, 138.90, 138.34, 138.06, 137.85, 137.54, 132.32, 132.19, 132.02, 132.02, 131.79, 131.79, 129.49, 129.13, 128.91, 128.75, 127.71, 127.47, 127.36, 127.28, 127.26, 127.26, 126.95, 126.95, 126.74, 126.65, 124.09, 124.09, 123.82, 123.82, 123.09, 123.02, 122.01, 122.01, 118.75, 119.03, 118.53, 118.53, 118.71, 58.25, 38.21, 38.21, 39.03, 40.01, 39.31, 27.34, 27.07, 26.91



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):

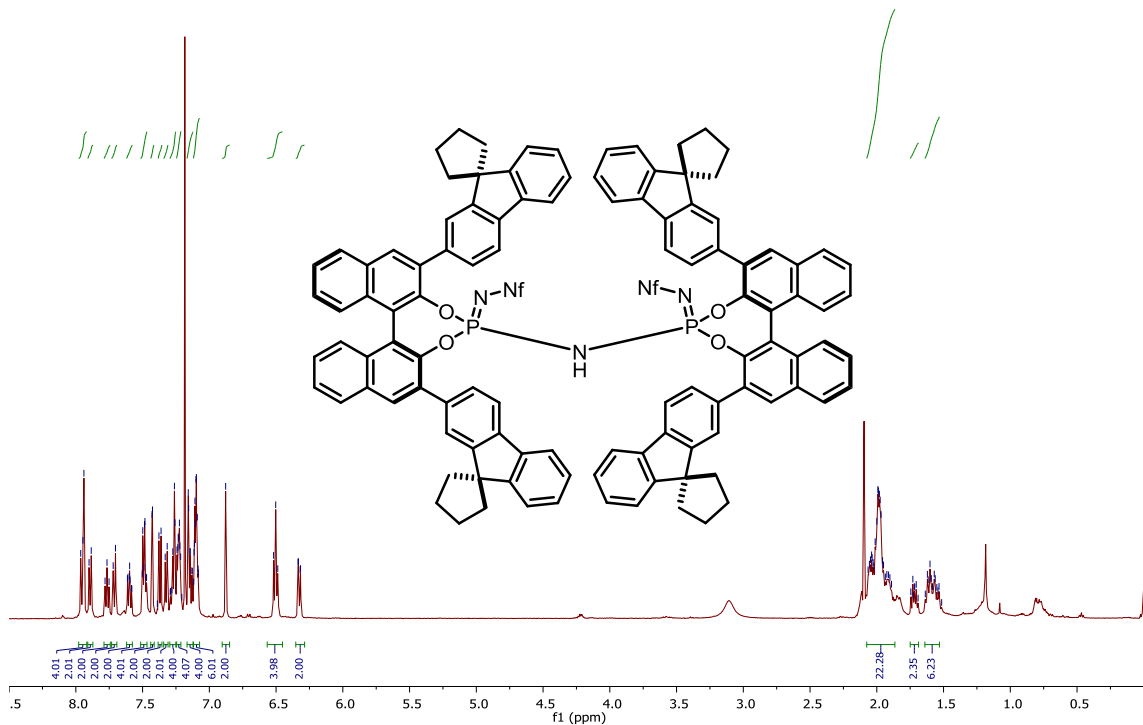


$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



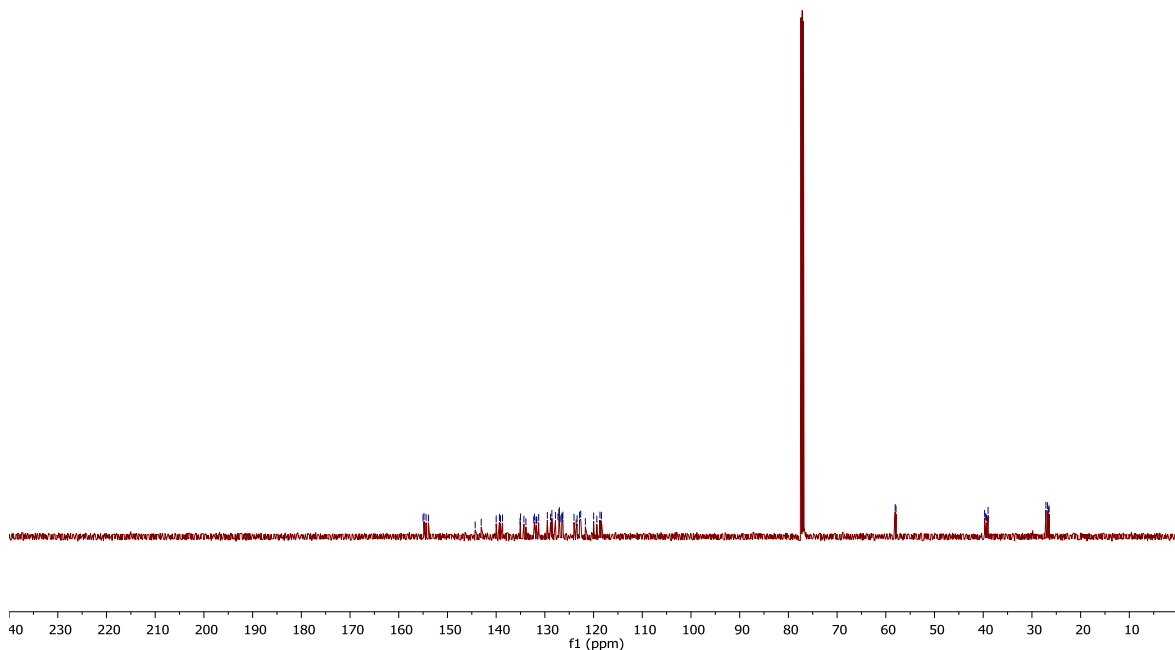
**(S,S)-4n**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

7.96, 7.95, 7.94, 7.93, 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56

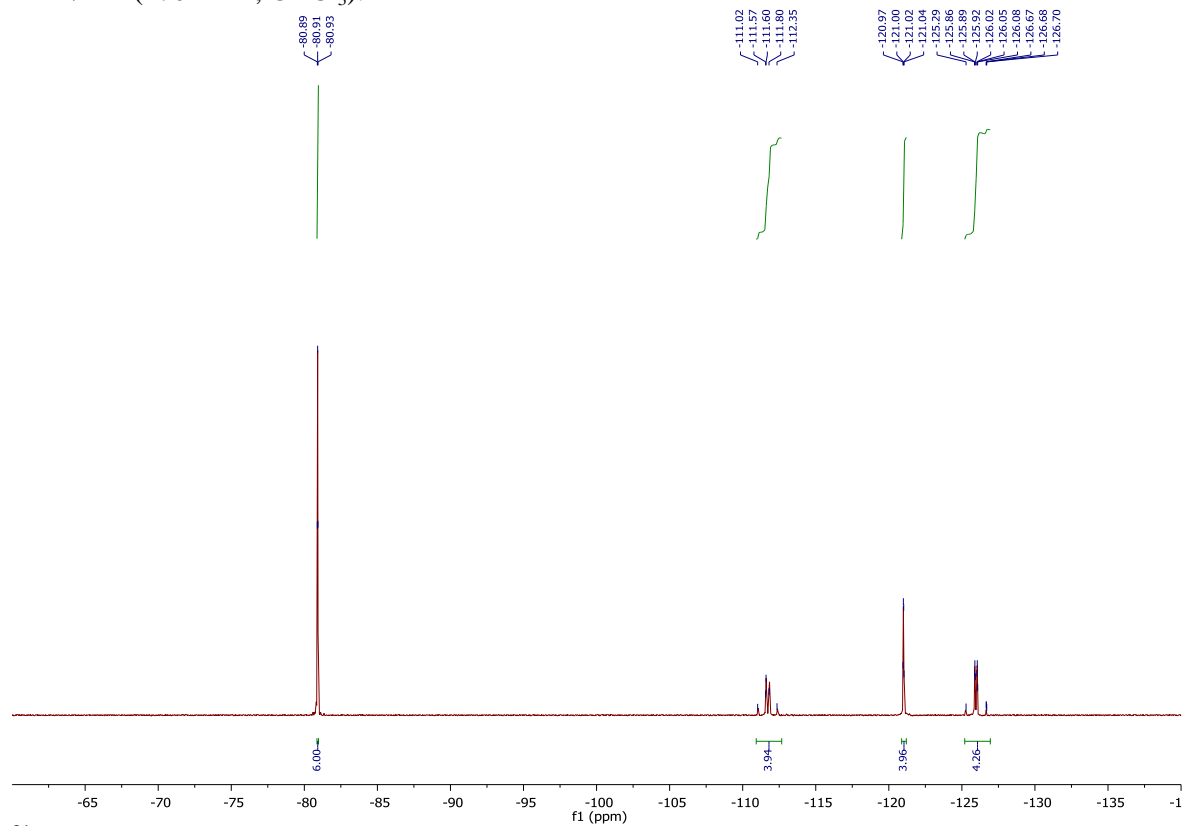


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

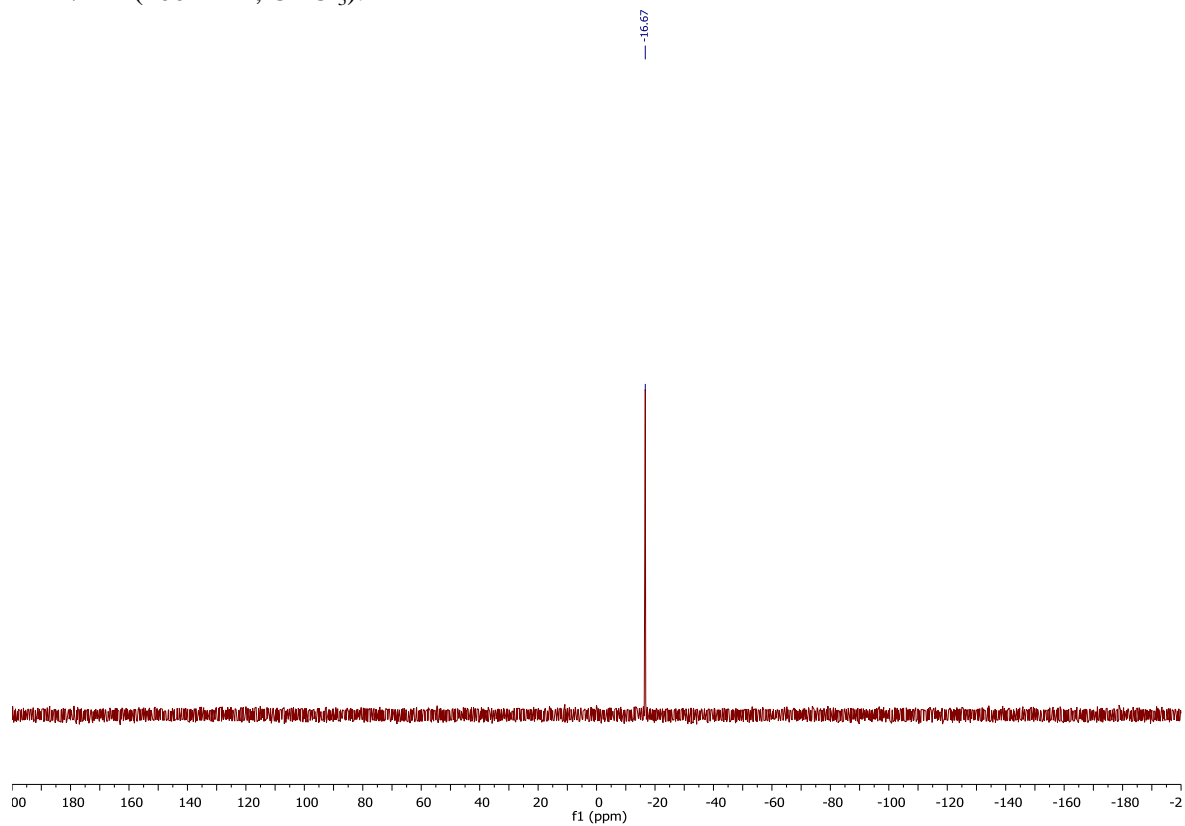
155.02, 154.82, 154.39, 153.91, 144.31, 143.67, 139.99, 139.33, 138.12, 138.69, 138.09, 138.00, 138.00, 133.90, 132.28, 132.14, 131.81, 131.76, 131.66, 131.27, 129.49, 128.83, 128.56, 127.84, 127.79, 127.12, 127.03, 126.71, 126.52, 126.42, 126.02, 124.02, 123.39, 122.88, 122.64, 119.93, 119.99, 118.69, 118.39, 98.08, 39.71, 39.57, 39.34, 39.01, 27.13, 26.76, 26.57, 26.48



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):

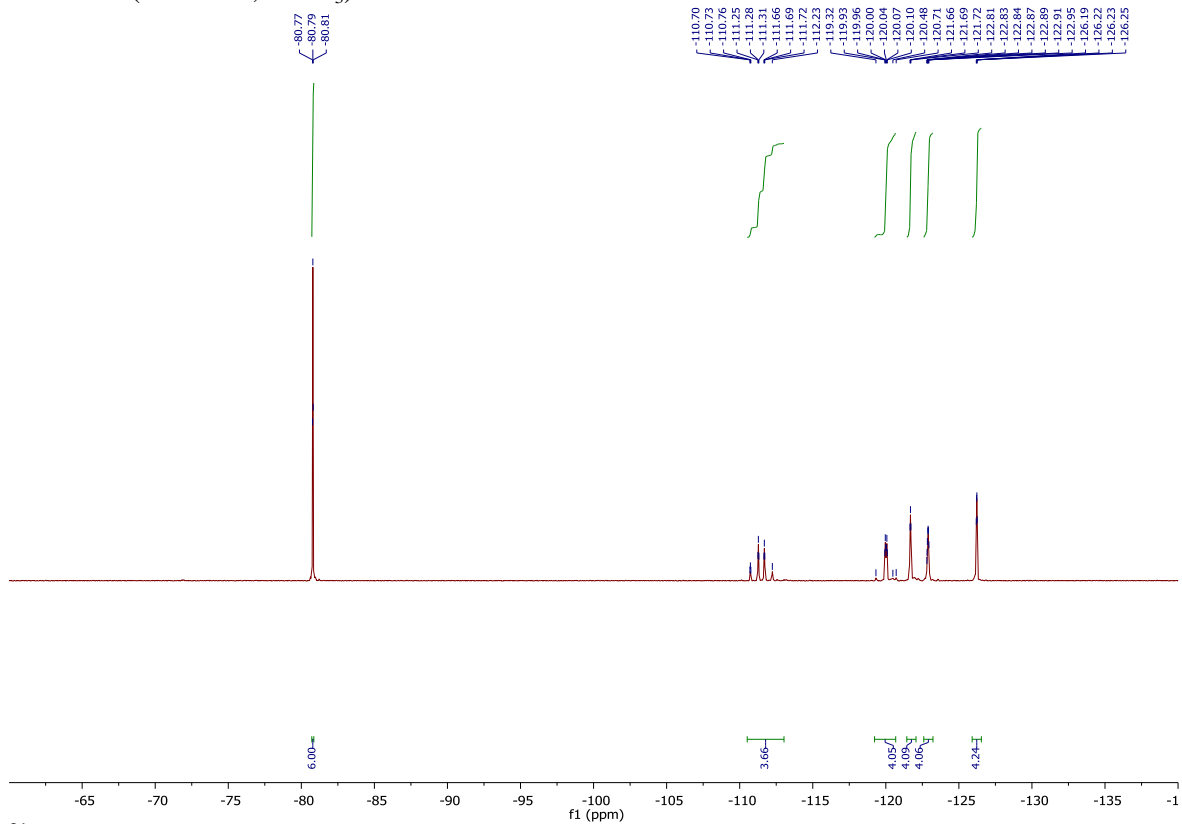


$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):

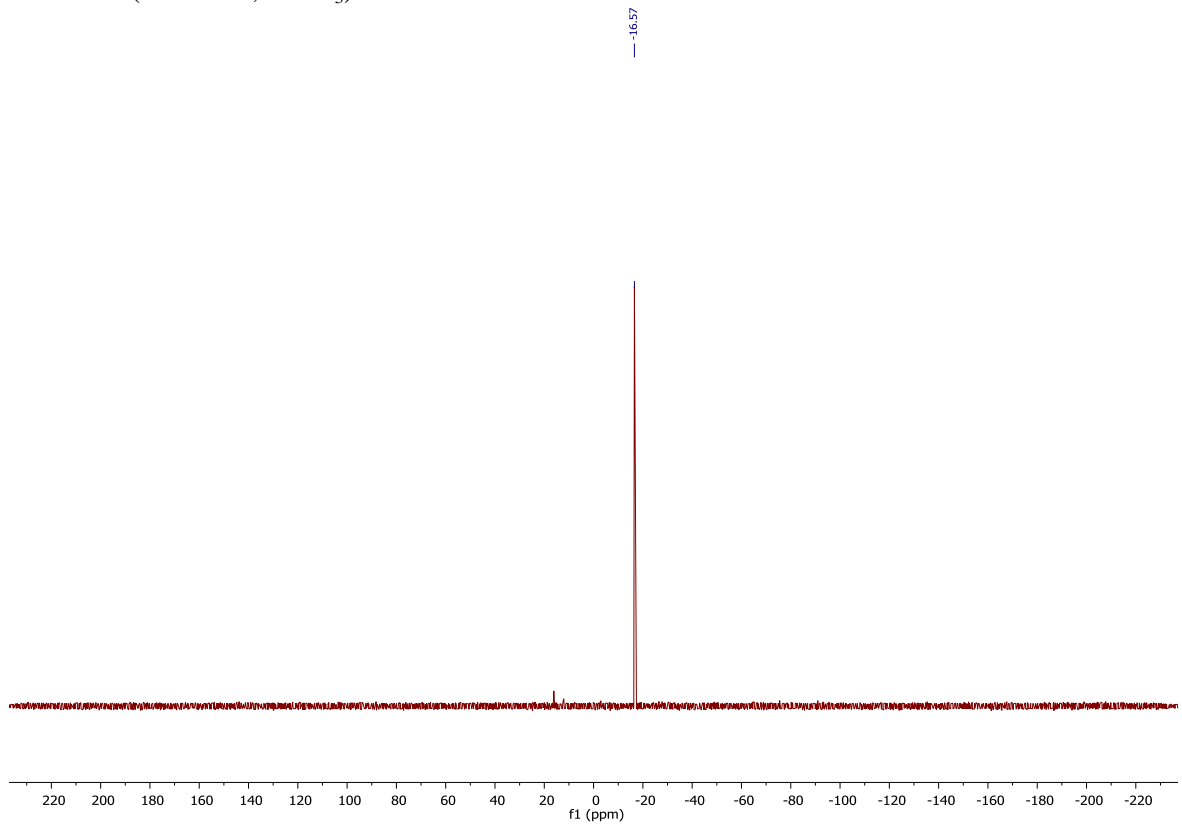




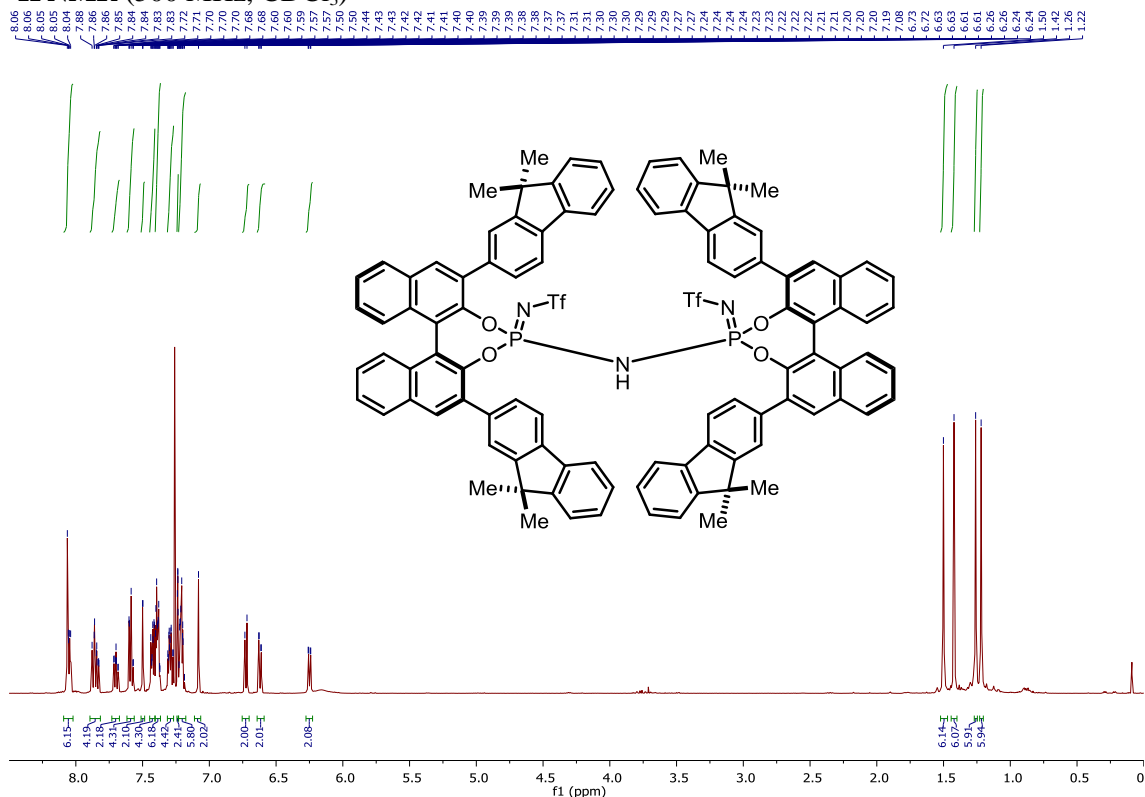
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



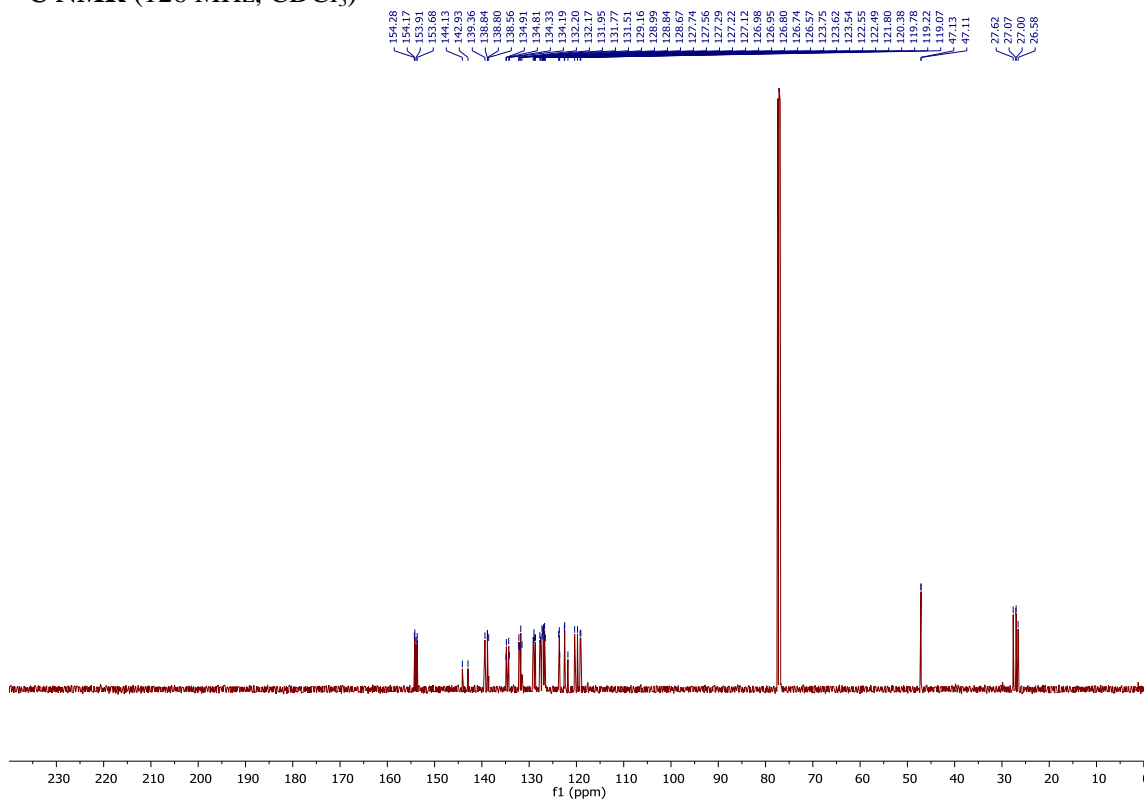
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



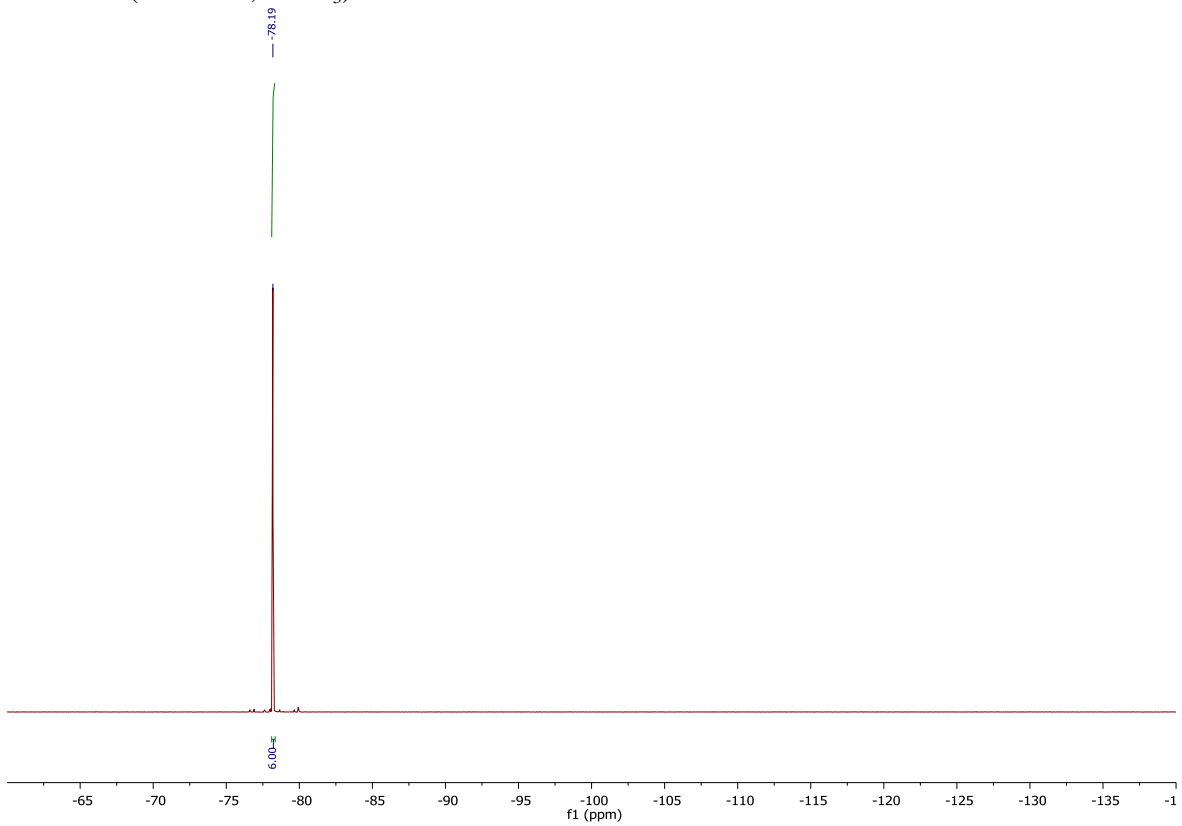
**(S,S)-4o**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



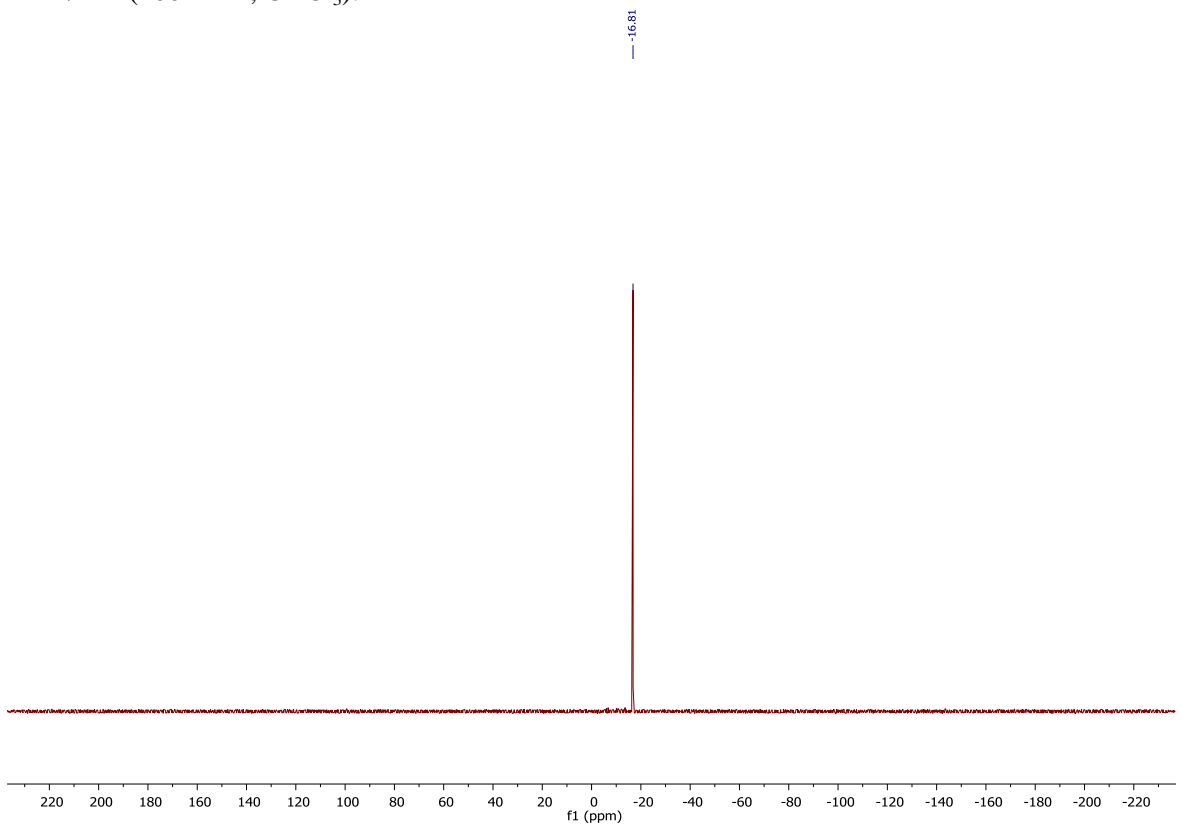
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



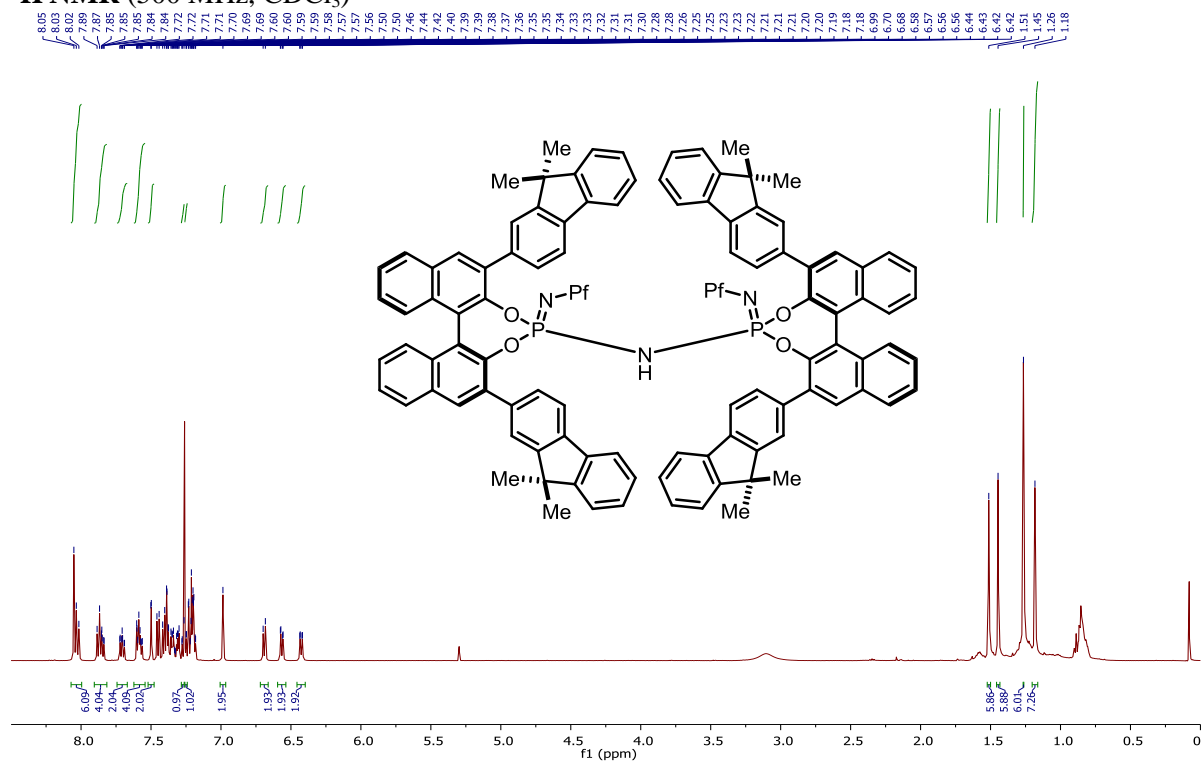
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



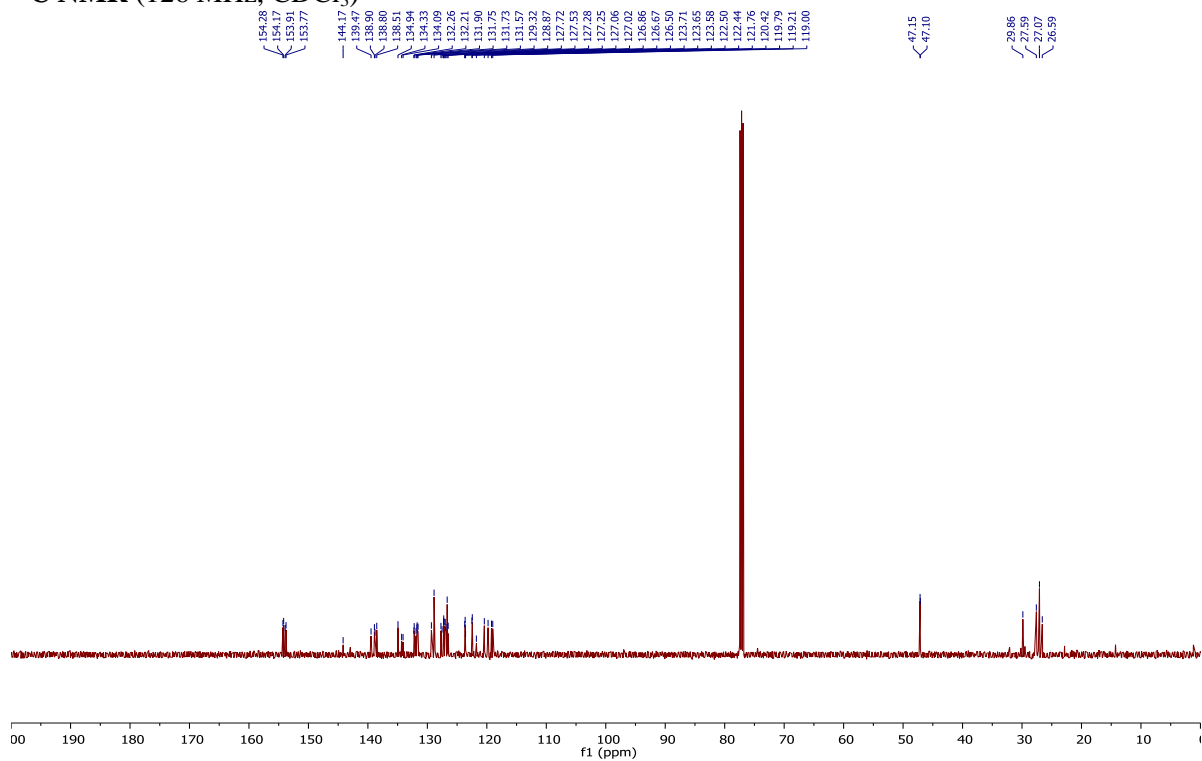
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



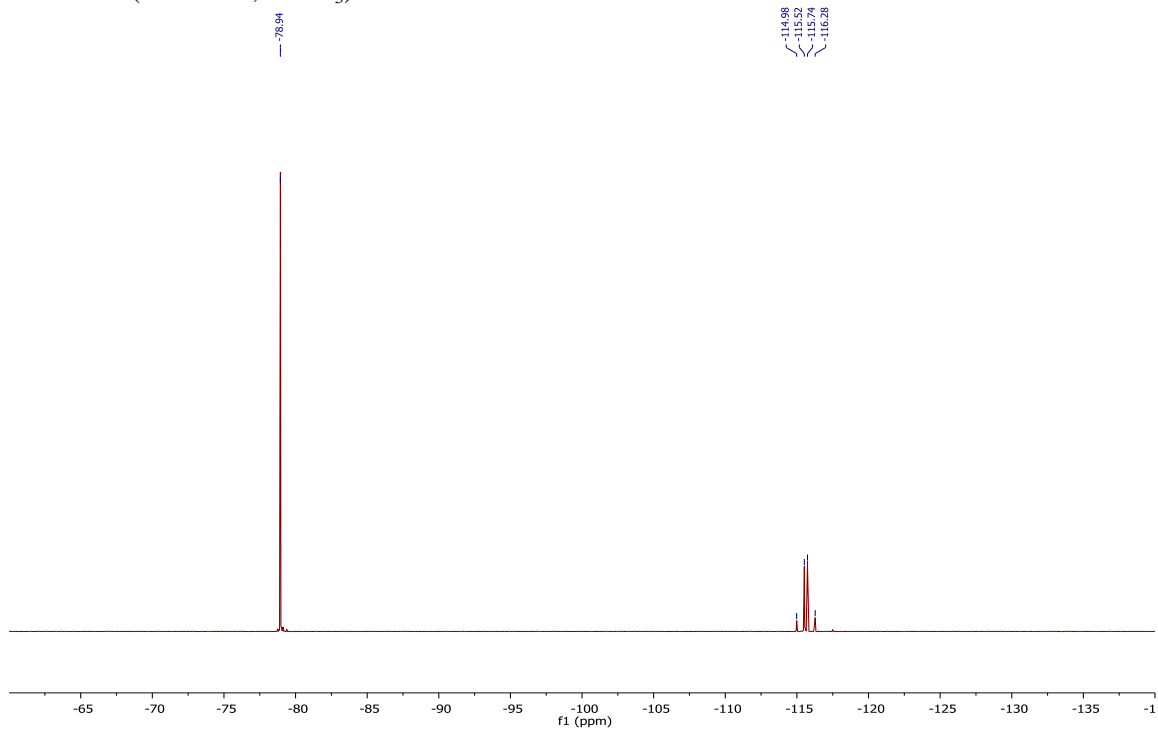
**(S,S)-4p**  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



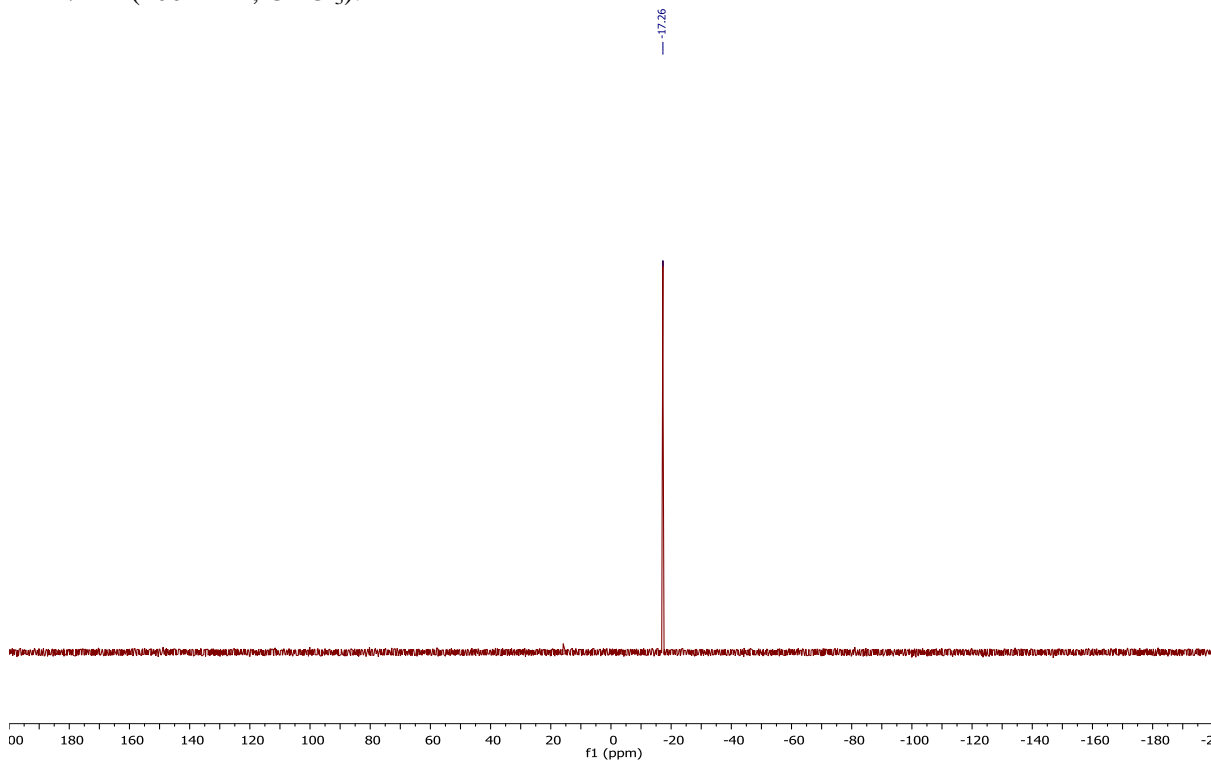
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):

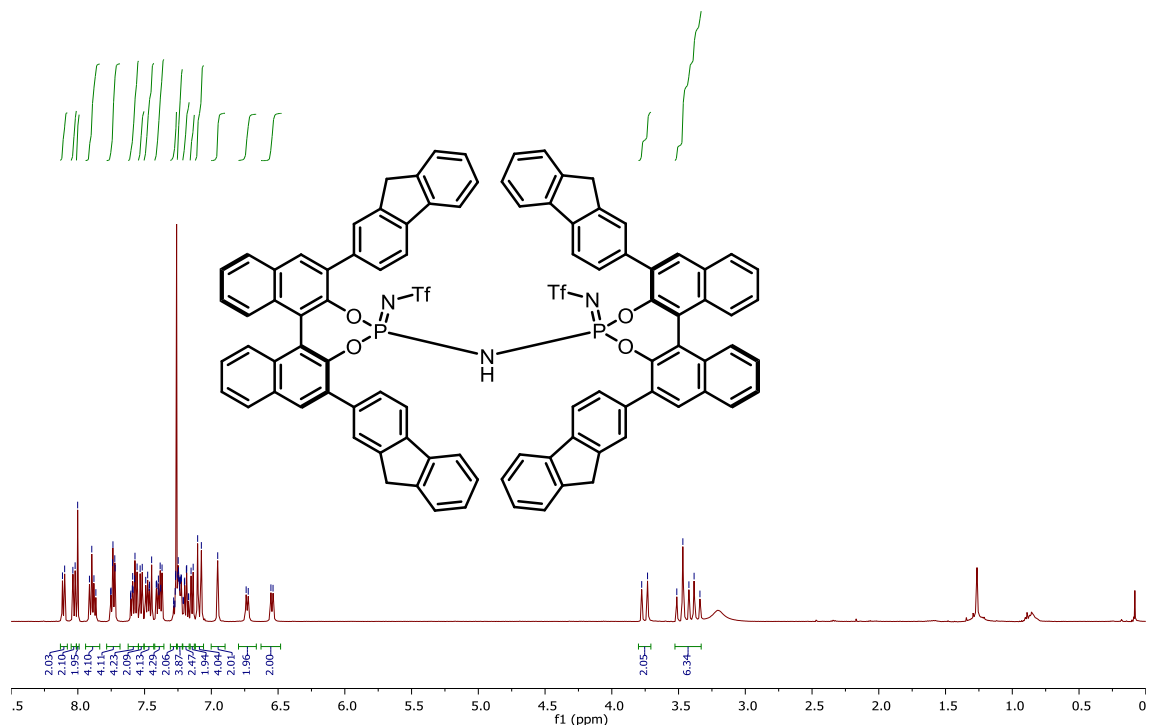


$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



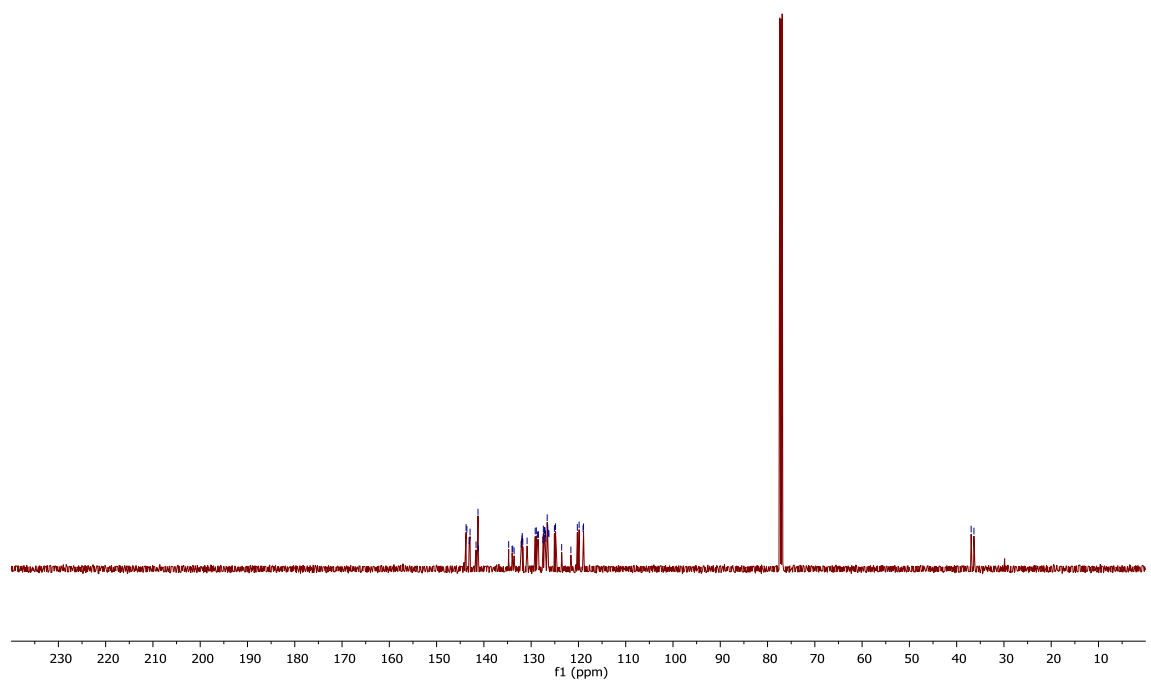
**(S,S)-4q**  
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

8.12, 8.10, 8.09, 8.08, 8.00, 7.91, 7.90, 7.88, 7.87, 7.85, 7.75, 7.74, 7.74, 7.74, 7.72, 7.61, 7.60, 7.59, 7.59, 7.58, 7.57, 7.56, 7.55, 7.53, 7.49, 7.48, 7.48, 7.47, 7.46, 7.45, 7.44, 7.41, 7.40, 7.40, 7.39, 7.38, 7.38, 7.37, 7.37, 7.28, 7.28, 7.28, 7.27, 7.27, 7.25, 7.25, 7.25, 7.25, 7.25, 7.25, 7.24, 7.24, 7.23, 7.23, 7.23, 7.22, 7.22, 7.21, 7.21, 7.21, 7.20, 7.20, 7.19, 7.18, 7.17, 7.17, 7.15, 7.15, 7.14, 7.14, 7.10, 7.10, 7.07, 6.95, 6.95, 6.94, 6.94, 6.94, 6.55, 6.54, 3.78, 3.78, 3.51, 3.51, 3.47, 3.42, 3.38, 3.34

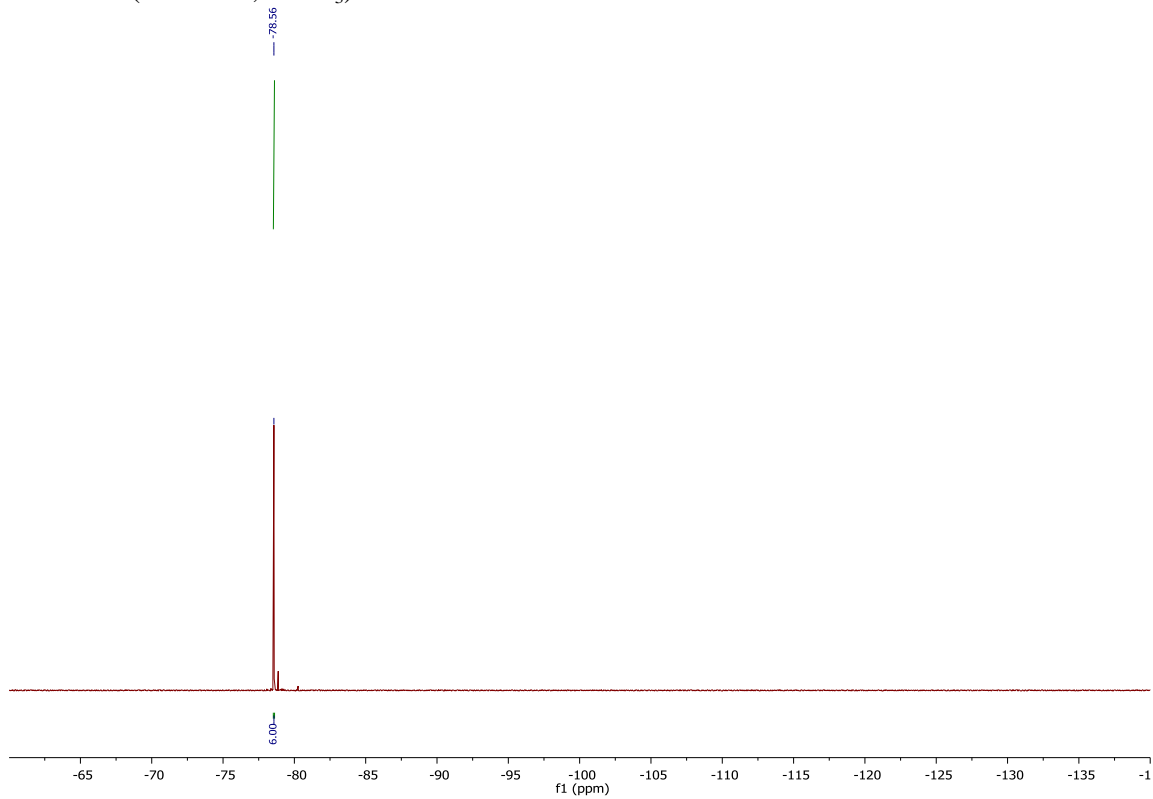


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

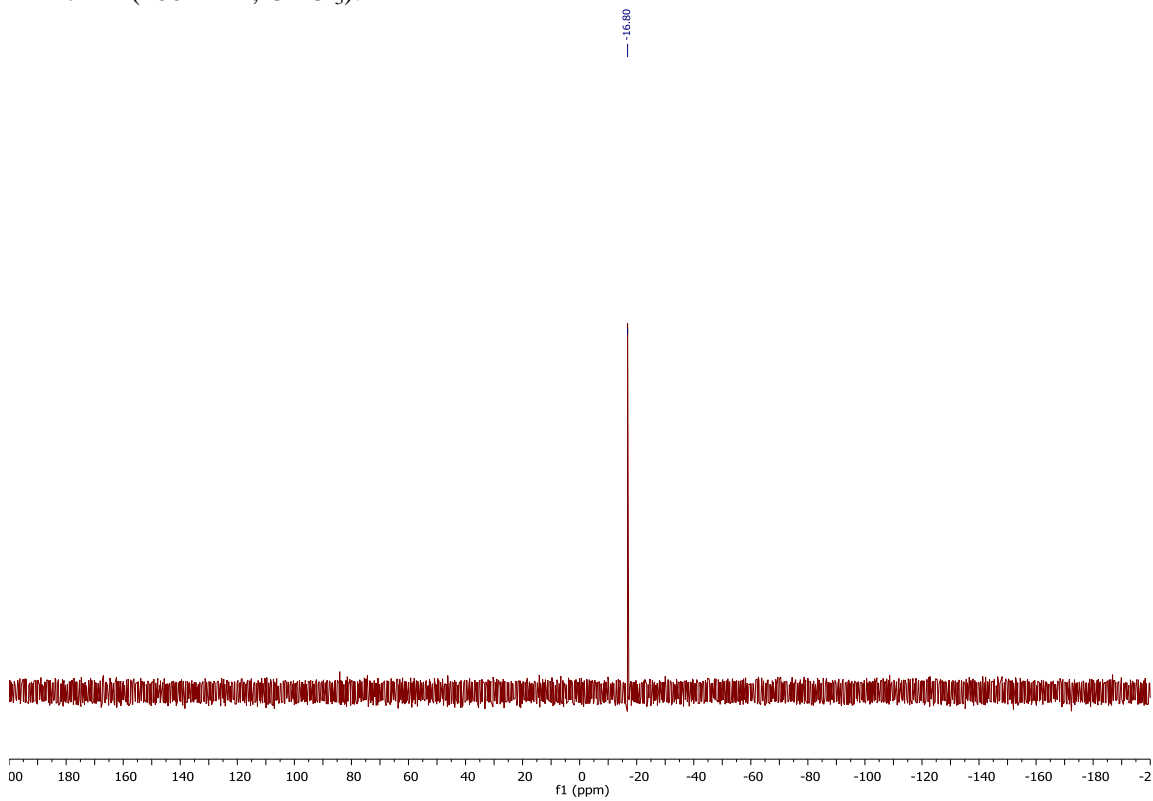
143.76, 143.60, 143.13, 142.93, 141.66, 141.52, 141.17, 134.75, 134.04, 133.89, 133.91, 133.91, 131.93, 131.89, 131.77, 131.77, 130.86, 130.86, 128.91, 128.63, 128.47, 127.51, 127.46, 127.26, 127.18, 127.08, 126.98, 126.90, 126.90, 126.50, 126.38, 126.24, 126.24, 125.09, 125.09, 121.55, 121.60, 120.23, 119.86, 118.92, 118.92, 36.04, 36.35



$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):

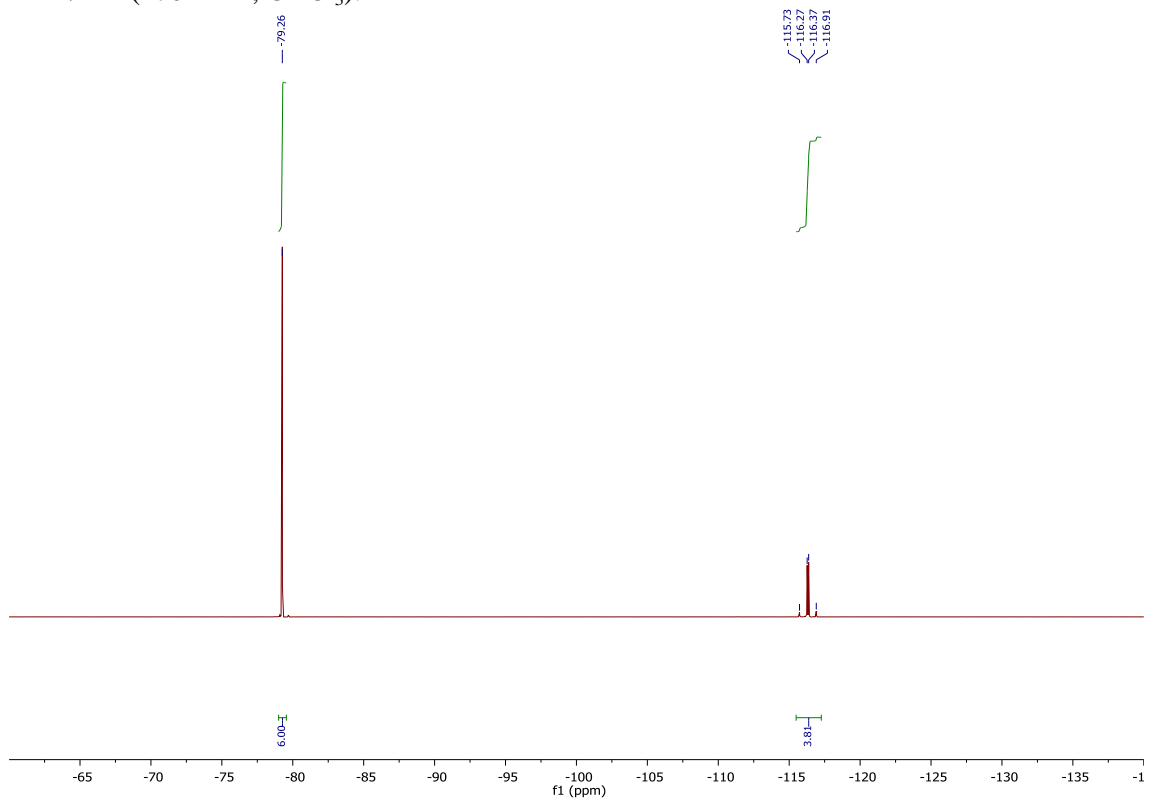


$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):

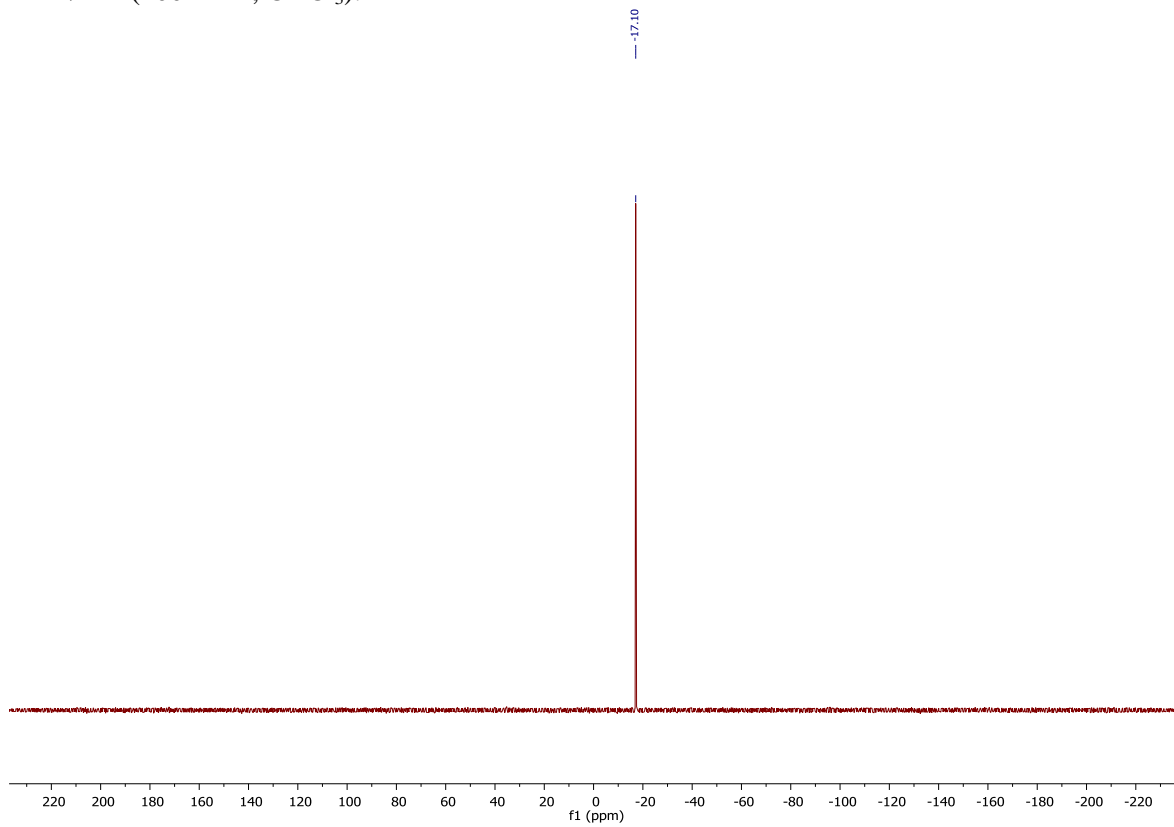




$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):



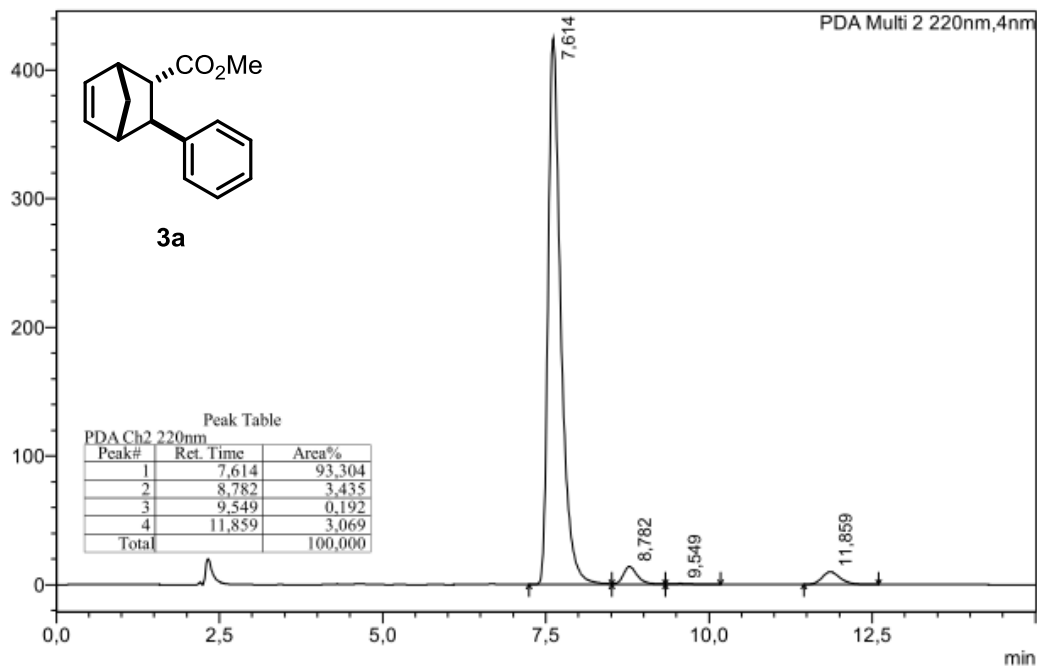
$^{31}\text{P}$  NMR (200 MHz,  $\text{CDCl}_3$ ):



## HPLC Traces

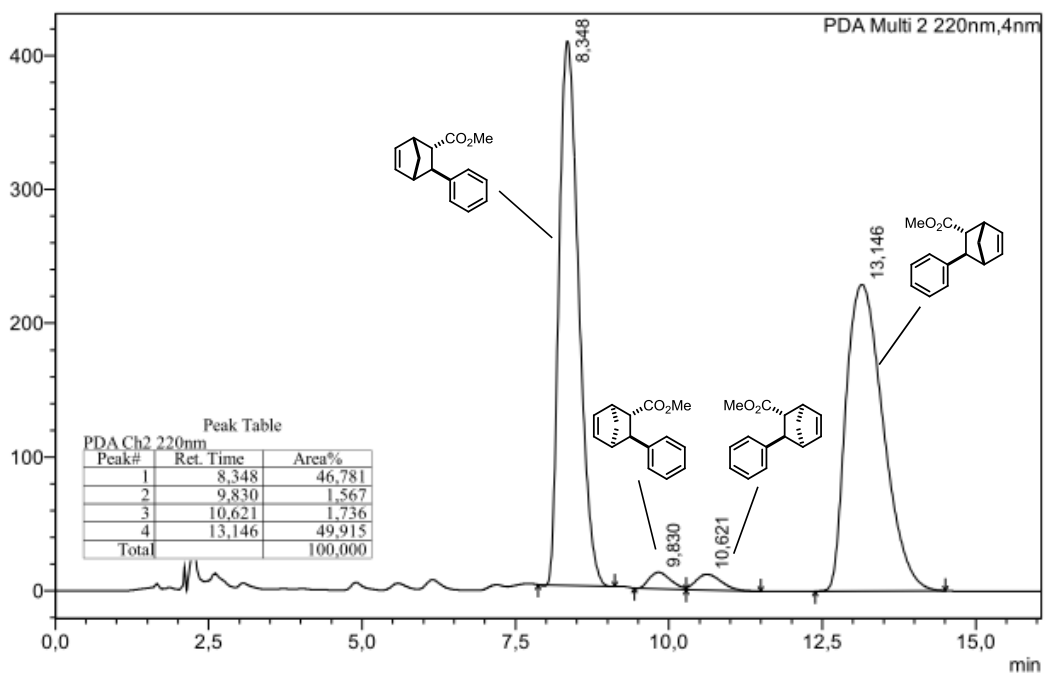
Enantioenriched sample of **3a**:

e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 96.5:3.5, d.r. (*endo*/*exo*) = 26:1.  
mAU



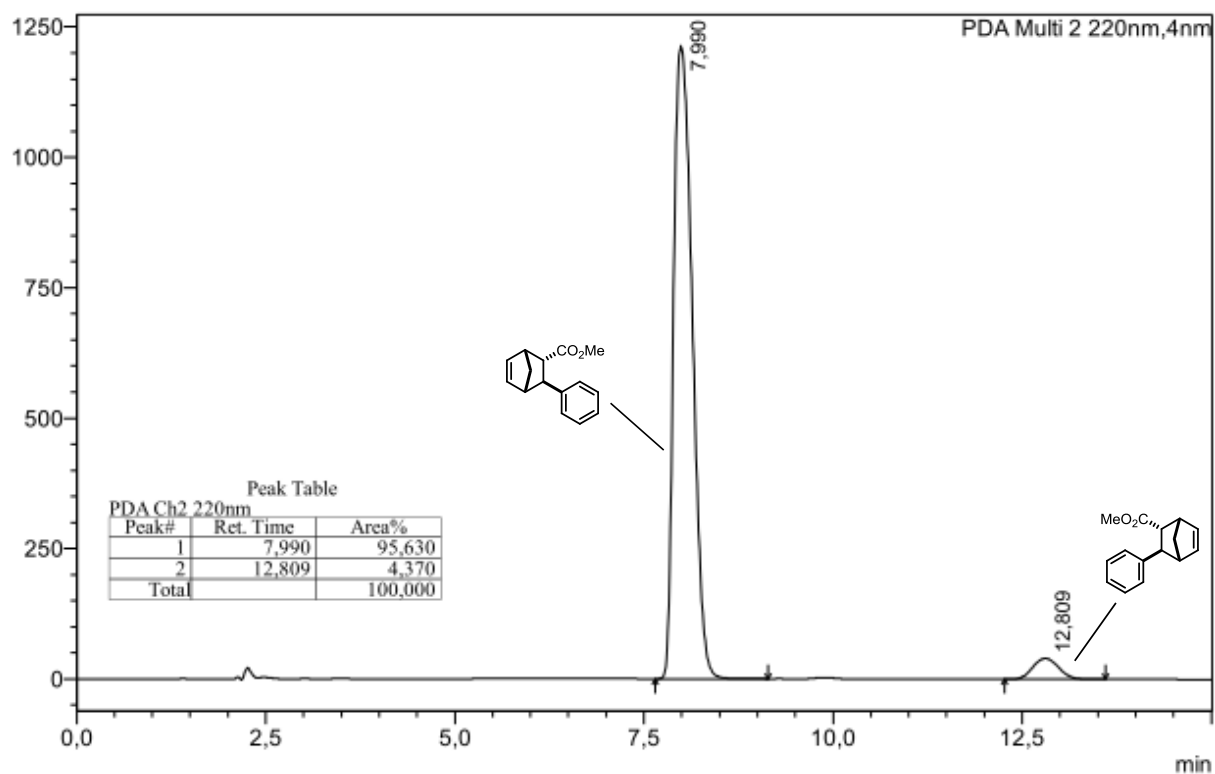
*rac*-**3a**: Daicel Chiralcel OJ-3R, methanol/water = 90/10, 1 mL/min. The racemic sample was prepared with procedure B.

mAU



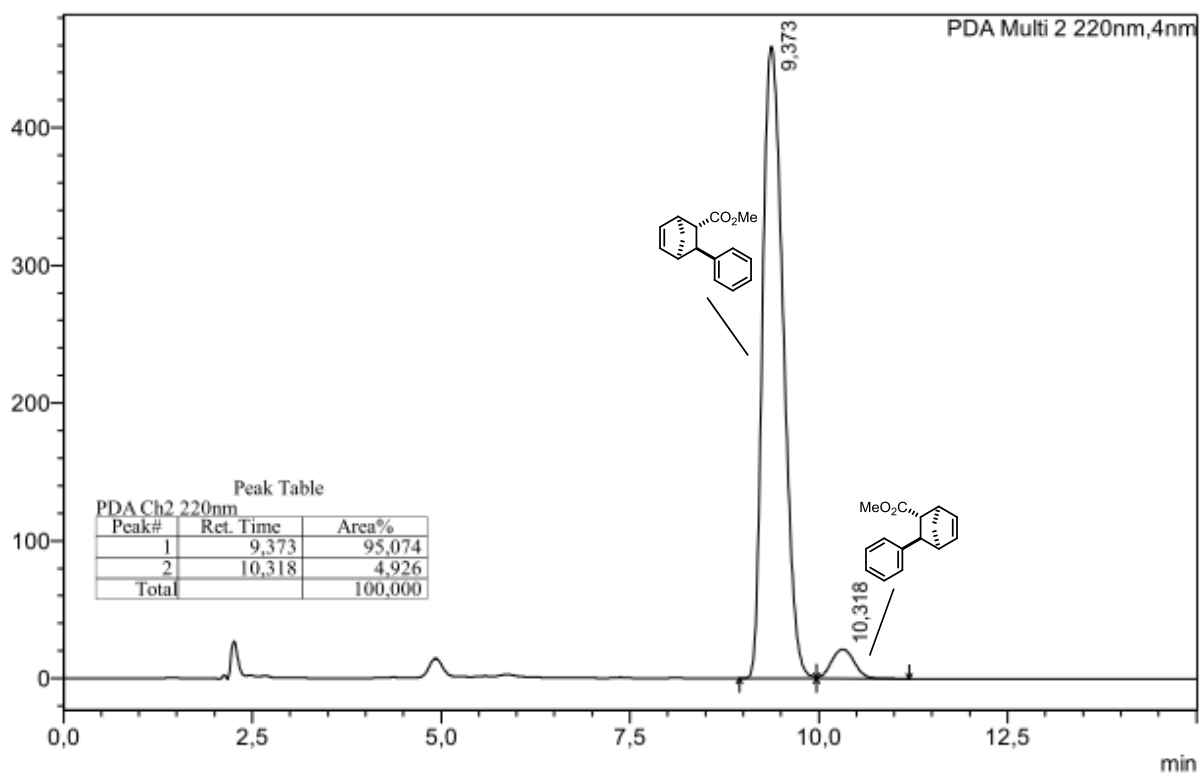
Enantioenriched, diastereomerically pure sample of **3a<sub>endo</sub>** (e.r. = 95.5:4.5):

mAU

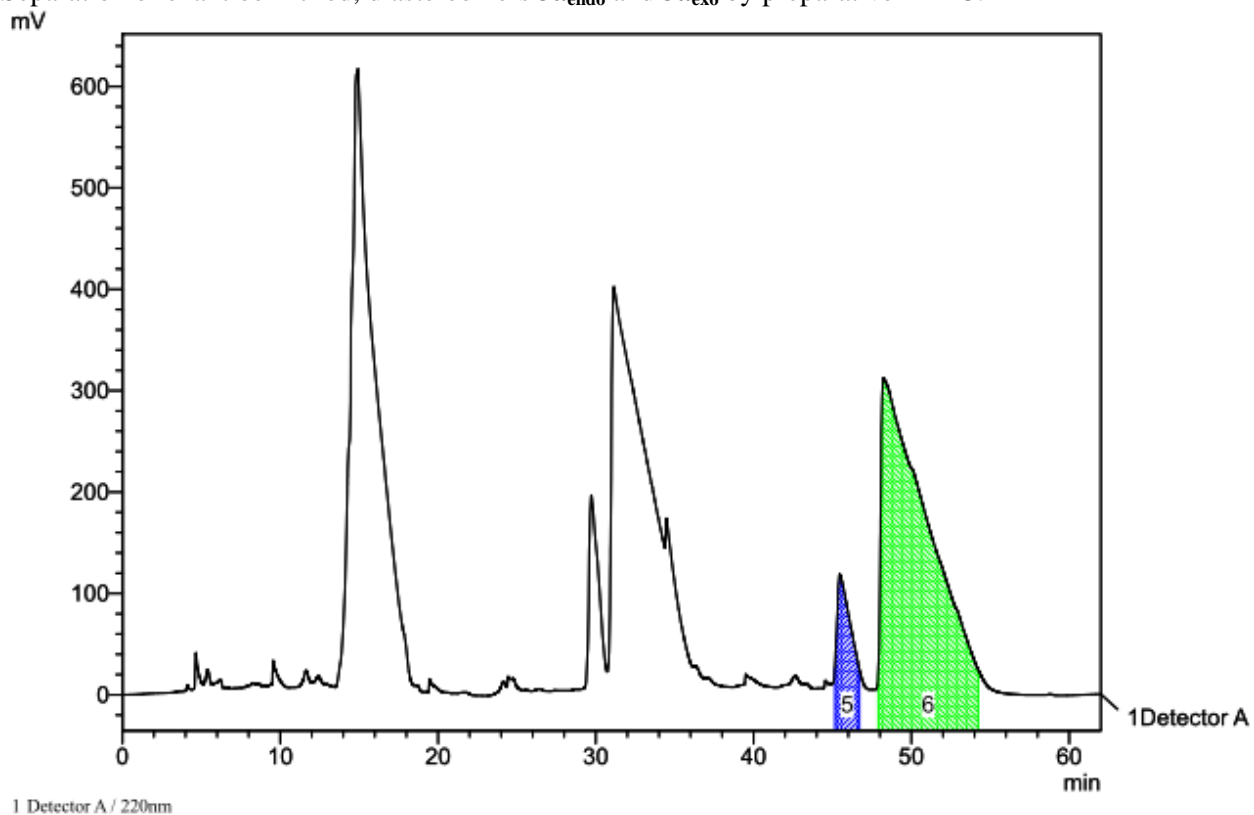


Enantioenriched, diastereomerically pure sample of **3a<sub>exo</sub>** (e.r. = 95:5):

mAU



Separation of enantioenriched, diastereomers **3a<sub>endo</sub>** and **3a<sub>exo</sub>** by preparative HPLC:



Injection volume: 300  $\mu$ L (15-20 mg)

250 mm MultoKrom 100Si, 3  $\mu$ m, 20 mm; *iso*-hexane/2-propanol = 99.9:0.1; 15.0 ml/min,

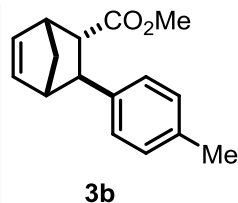
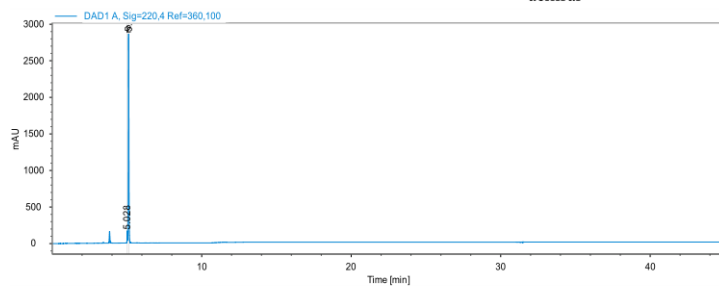
8.1 MPa, 308 K; UV, 220 nm, 0.5 mm.

Enantioenriched sample of **3b**:

$e.r._{endo} = 97:3$ ,  $e.r._{exo} = 96:4$ ,  $d.r. (endo/exo) = 20:1$ .

<sup>1</sup>D chromatogram(s)

achiral



Sampling table (<sup>1</sup>D)

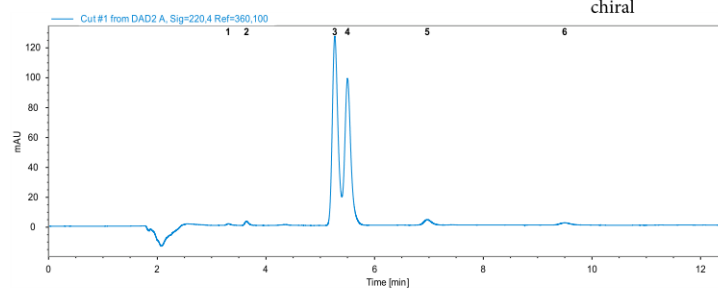
achiral

Cut group	Cut #	<sup>1</sup> D Cut start [min]	<sup>1</sup> D Ret. time [min]	<sup>1</sup> D Duration [min]	Trigger	<sup>1</sup> D Run start [min]
	1	5.00	5.028	0.04	Time	5.08
	2	5.11	5.111	0.04	Time	19.88

1. Diastereomer

Cut# : 1

chiral

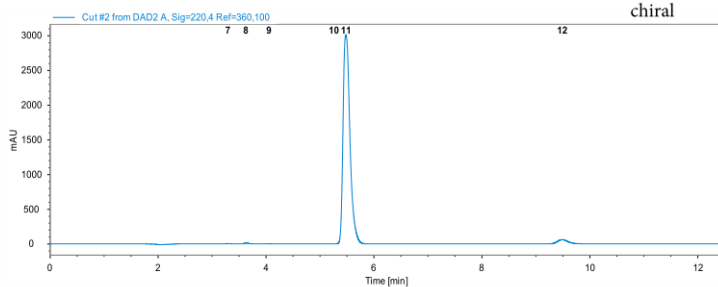


Signal: DAD2 A, Sig=220.4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	3.310	5.537 <b>5.537</b>	0.076	1.056	0.709	
2	1	3.641	13.602 <b>13.602</b>	0.075	2.728	0.695	
3	1	5.266	909.334 <b>909.334</b>	0.110	126.562	0.773	1. D 1. E
4	1	5.501	766.315 <b>766.315</b>	0.118	98.242	0.802	2. D 1. E
5	1	6.970	36.106 <b>36.106</b>	0.132	3.648	0.805	1. D 2. E
6	1	9.499	18.937 <b>18.937</b>	0.158	1.443	0.797	2. D 2. E

Cut# : 2 2. Diastereomer

chiral

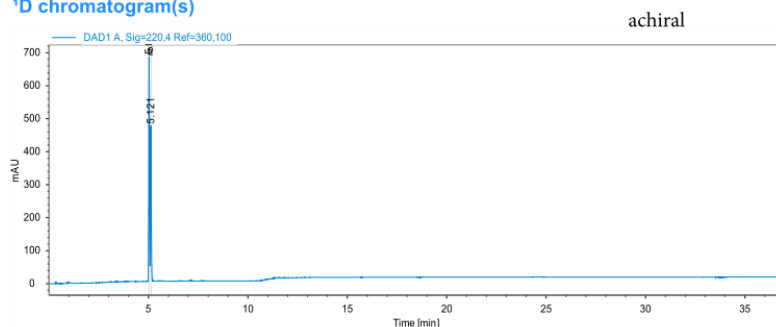


Signal: DAD2 A, Sig=220.4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
7	2	3.303	16.191 <b>16.191</b>	0.076	3.134	0.760	
8	2	3.635	63.554 <b>63.554</b>	0.075	12.856	0.715	
9	2	4.057	10.202 <b>10.202</b>	0.088	1.727	0.774	
10	2	5.256	6.332 <b>6.332</b>	0.081	1.188	1.358	1. D 1. E
11	2	5.479	26665.684 <b>26665.684</b>	0.136	3013.039	0.655	2. D 1. E
12	2	9.488	847.145 <b>847.145</b>	0.212	60.882	0.777	2. D 2. E

*rac-3b*: (Heartcut) 1. 50 mm Zorbax Eclipse PAH, 4.6 mm, methanol/water – gradient 50 % B - 5` - 80 % B - 5` - 80% - 1` - 100% B, 1.0 mL/min, 38.5 MPa, 308 K, 220 nm; 2. 150mm Chiralcel OJ-3R, 4.6 mm, methanol, 1.0 mL/min, 298 K, 17.7 MPa, 220 nm. The racemic sample was prepared with procedure C.

**'D chromatogram(s)**

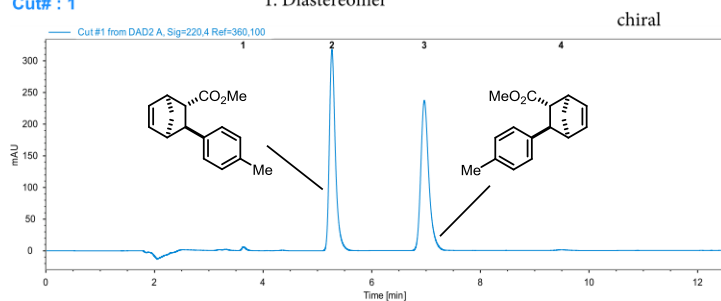


**Sampling table ('D)**

Cut group	Cut #	'D Cut start [min]	'D Ret. time [min]	'D Duration [min]	Trigger 'D Run start [min]
	1	5.00	5.030	0.04	Time 5.08
	2	5.11	5.121	0.04	Time 19.89

**Cut# : 1**

**1. Diastereomer**

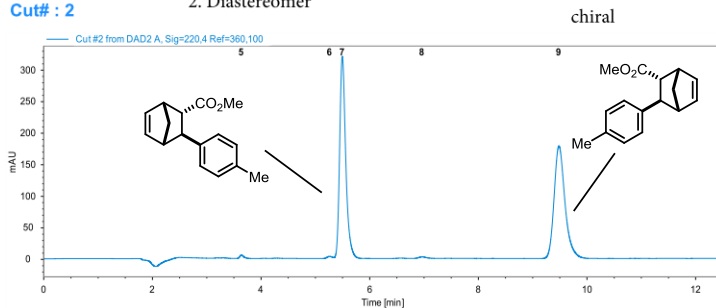


Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	3.638	30.012	0.078	5.784	0.640
			<b>30.012</b>			
2	1	5.267	2449.171	0.117	317.435	0.698
			<b>2449.171</b>			
3	1	6.968	2418.769	0.155	236.731	0.737
			<b>2418.769</b>			
4	1	9.494	14.549	0.168	1.037	0.649
			<b>14.549</b>			

**Cut# : 2**

**2. Diastereomer**



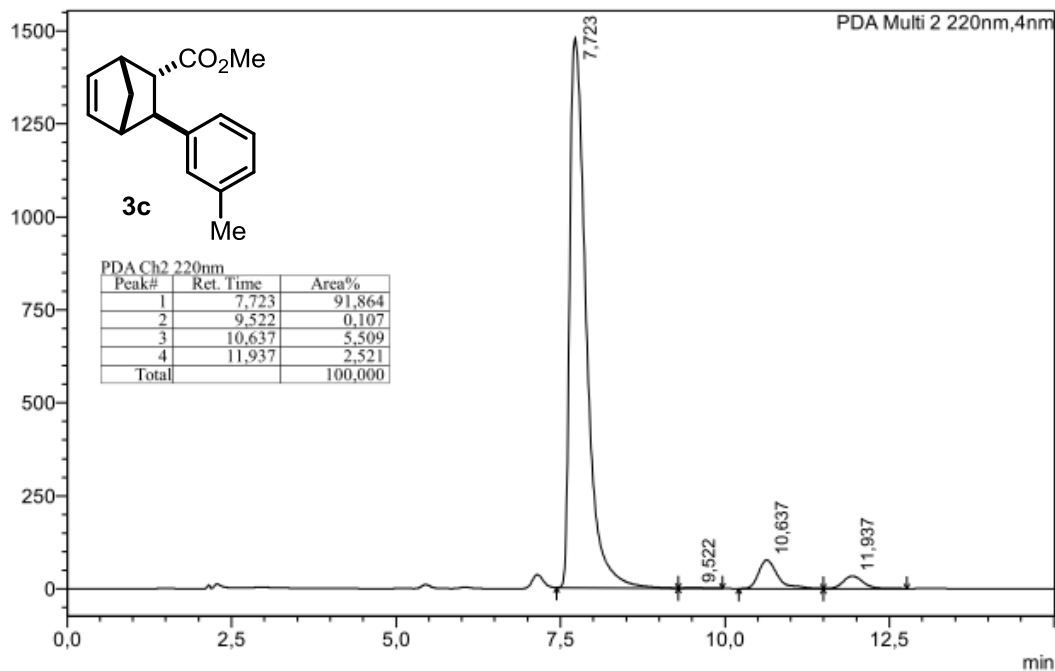
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
5	2	3.637	25.813	0.074	5.238	0.702
			<b>25.813</b>			
6	2	5.263	22.266	0.101	3.410	0.979
			<b>22.266</b>			
7	2	5.496	2491.483	0.118	320.234	0.725
			<b>2491.483</b>			
8	2	6.964	24.772	0.147	2.522	0.734
			<b>24.772</b>			
9	2	9.484	2472.736	0.210	178.464	0.756
			<b>2472.736</b>			

Enantioenriched sample of **3c**:

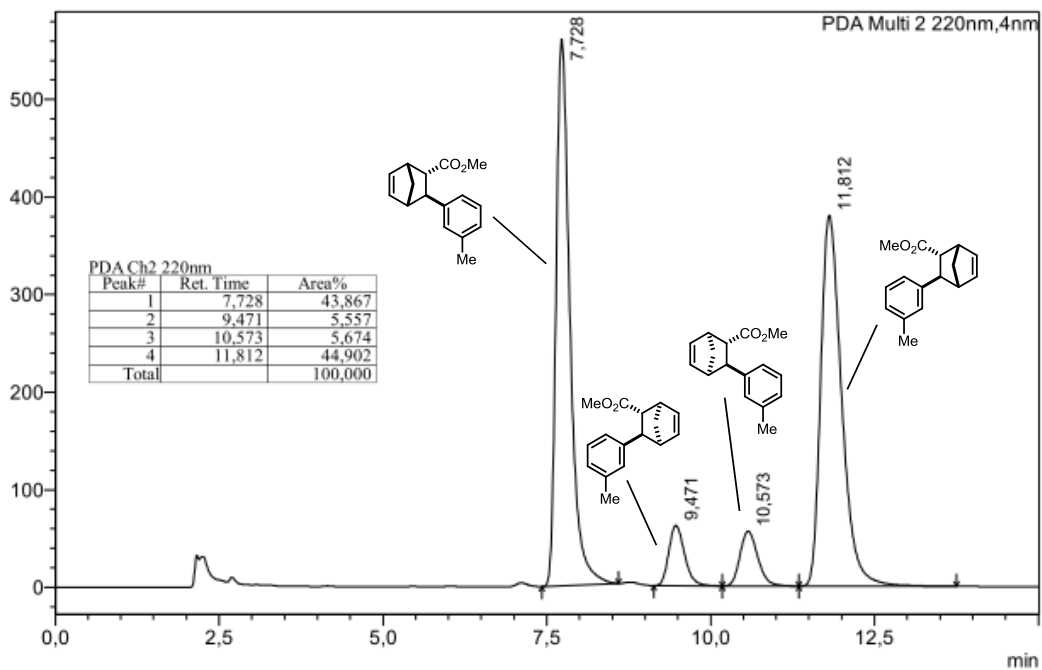
e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 98:2, d.r. (*endo/exo*) = 17:1.

mAU



*rac*-**3c**: Daicel Chiralcel OJ-3R, methanol/water = 90/10, 1 mL/min. The racemic sample was prepared with procedure B.

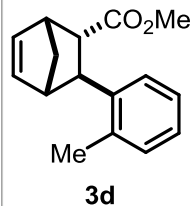
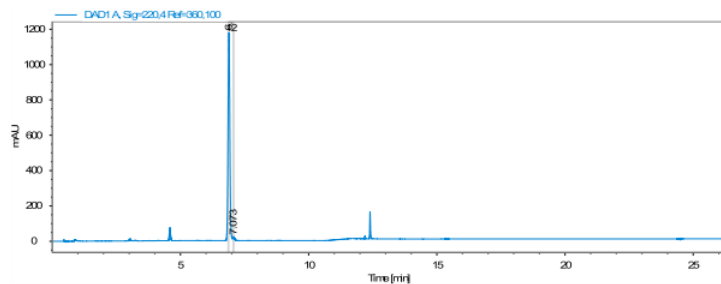
mAU



Enantioenriched sample of **3d**:

e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = >50:1.

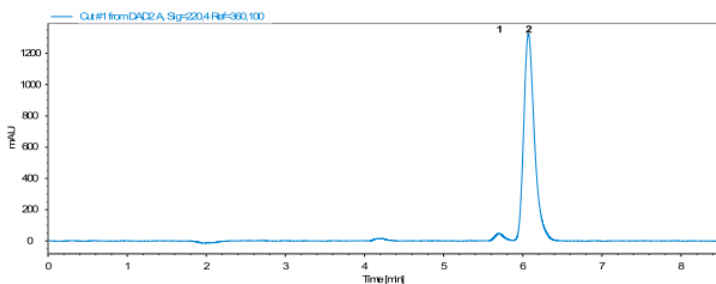
<sup>1</sup>D chromatogram(s)



Sampling table (<sup>1</sup>D)

Cut group	Cut #	'D Cut start [min]	'D Ret. time [min]	'D Duration [min]	Trigger	'D Run start [min]
	1	6.83	6.892	0.08	Time	6.96
	2	7.03	7.073	0.08	Time	17.77

Cut# : 1 . Diastereomer

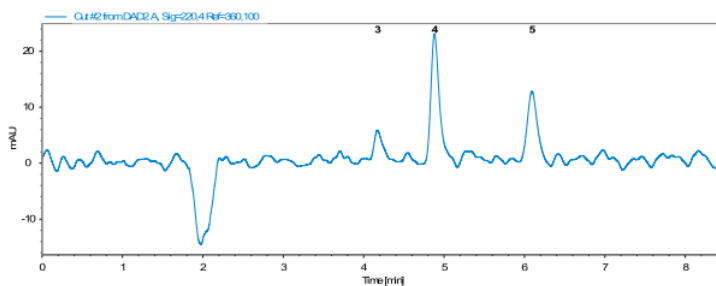


Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	5.698	388.529 <b>388.529</b>	0.126	47.160	0.753	1. Enantiomer
2	1	6.071	12540.852 <b>12540.852</b>	0.143	1325.139	0.718	2. Enantiomer

ee = 94.0 %

Cut# : 2 2. Diastereomer



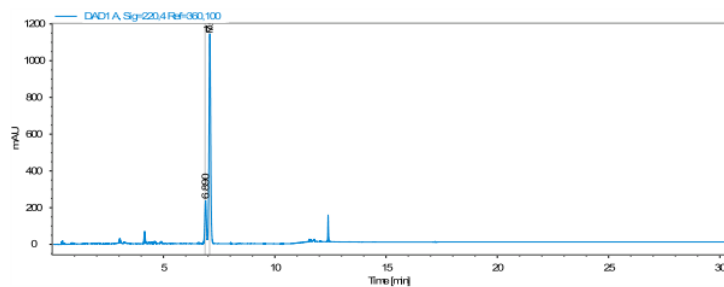
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
3	2	4.171	62.787 <b>62.787</b>	0.137	6.454	0.514	1. Enantiomer
4	2	4.880	189.789 <b>189.789</b>	0.119	23.716	0.634	2. Enantiomer
5	2	6.092	116.935 <b>116.935</b>	0.136	12.929	0.786	

ee = 50.3 %

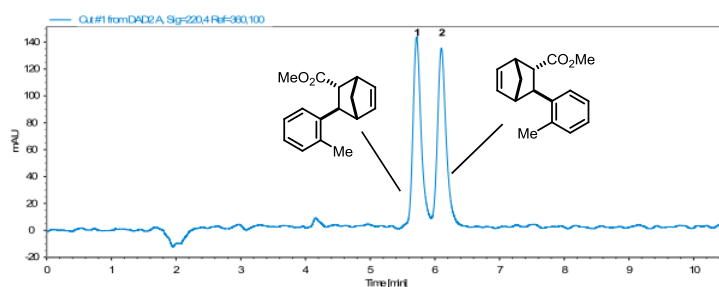
*rac*-**3d**: (Heartcut) 1. 50 mm Eclipse Plus C18, 3.0 mm, methanol/water – gradient 50% B - 5` - 70 % B - 5` - 70 % B - 1` - 100% B, 0.5 mL/min, 34.8 MPa, 308 K, 220 nm; 2. 150 mm Chiralcel OJ3R, 4.6 mm, methanol/water = 90:10, 1.0 mL/min, 25.6 MPa, 308 K, 220 nm. The racemic sample was prepared with procedure C.

**1**<sup>D</sup> chromatogram(s)



Cut# : 1

1. Diastereomer

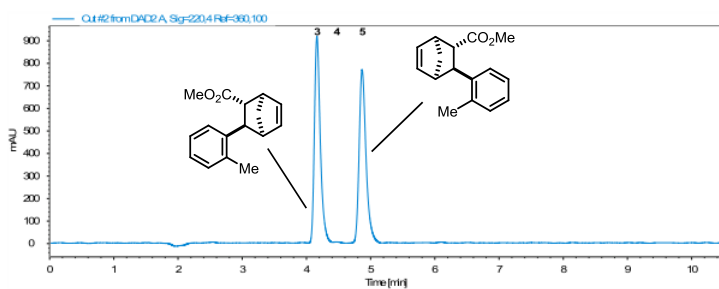


Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	5.718	1275.571	0.135	142.360	0.755	1. Enantiomer
2	1	6.101	1276.023	0.143	133.684	0.753	2. Enantiomer

Cut# : 2

2. Diastereomer



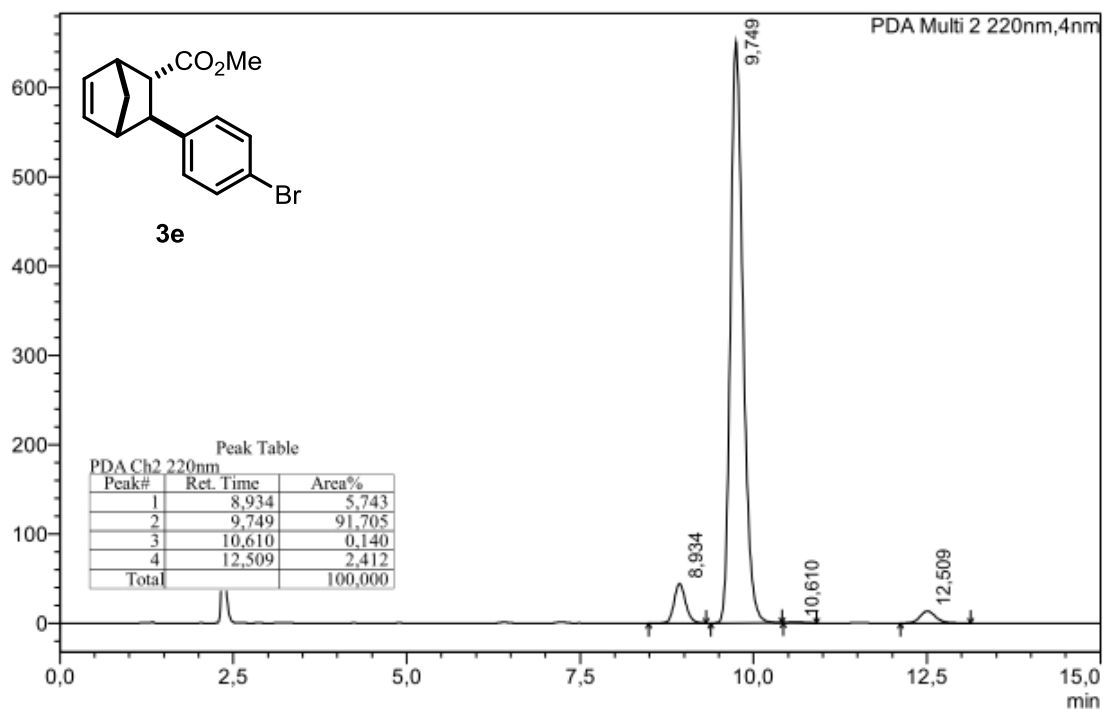
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
3	2	4.164	5855.409	0.096	917.521	0.694	1. Enantiomer
4	2	4.467	34.987	0.113	4.979	0.678	
5	2	4.868	5757.587	0.113	768.996	0.711	2. Enantiomer

Enantioenriched sample of **3e**:

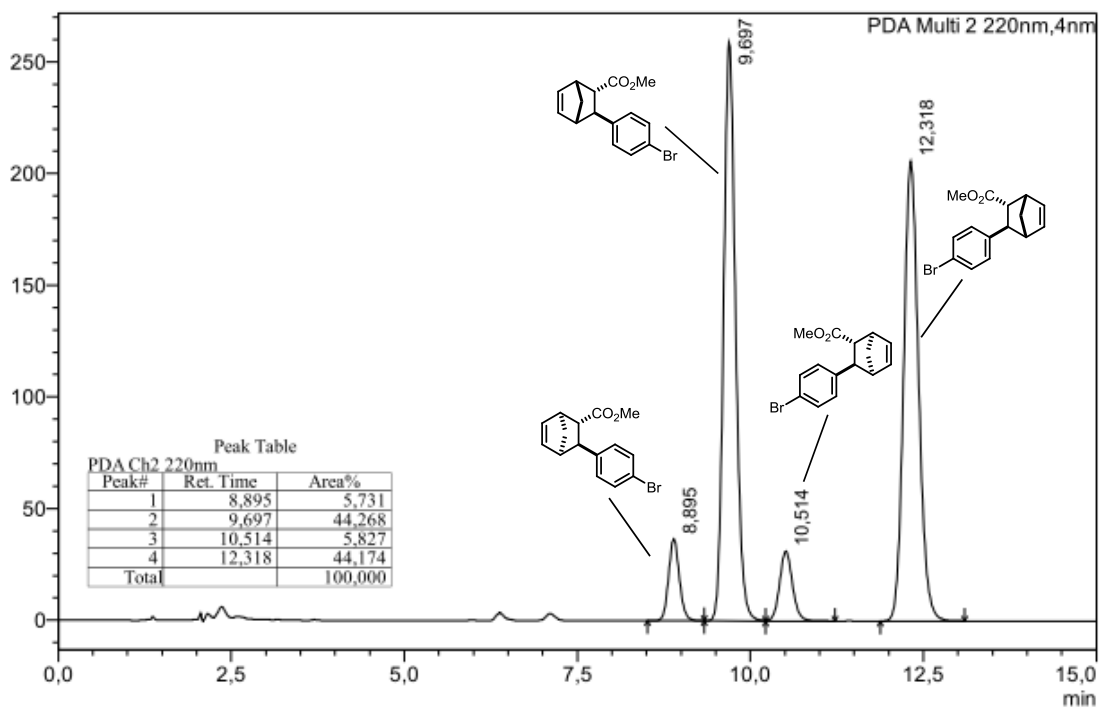
e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 97.5:2.5, d.r. (*endo/exo*) = 16:1.

mAU

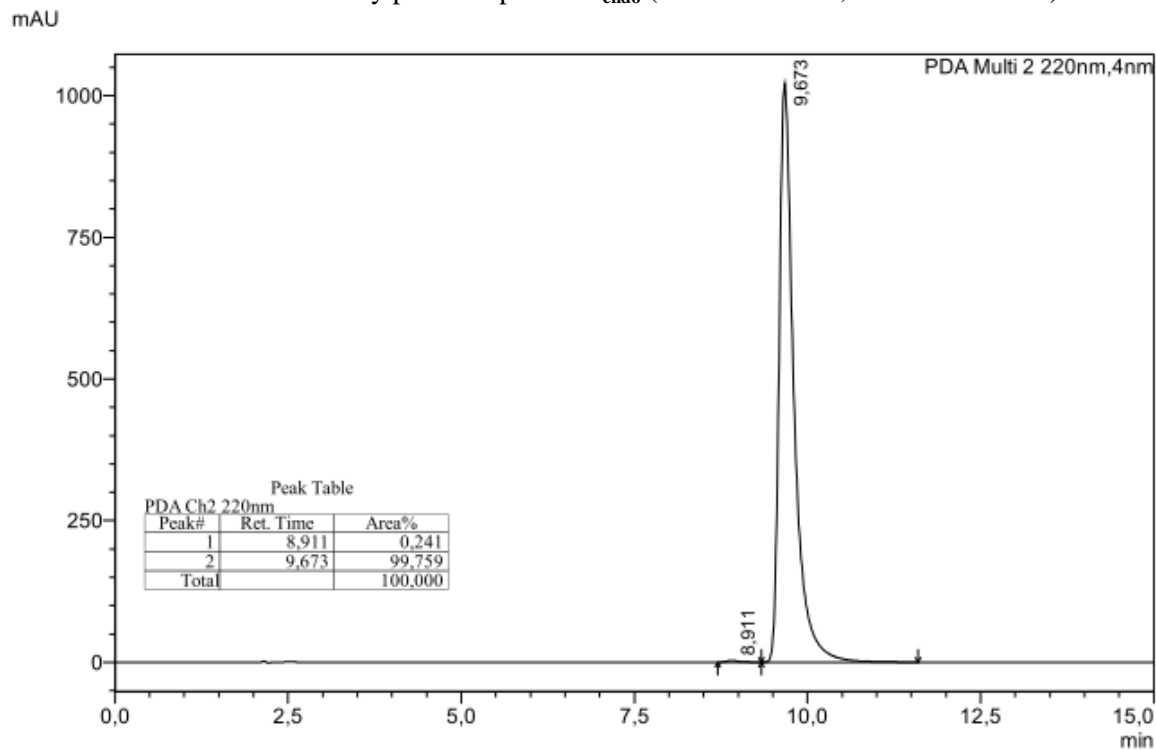


*rac*-**3e**: Daicel Chiralcel OJ-3R, acetonitrile/water = 60/40, 1 mL/min. The racemic sample was prepared with procedure B.

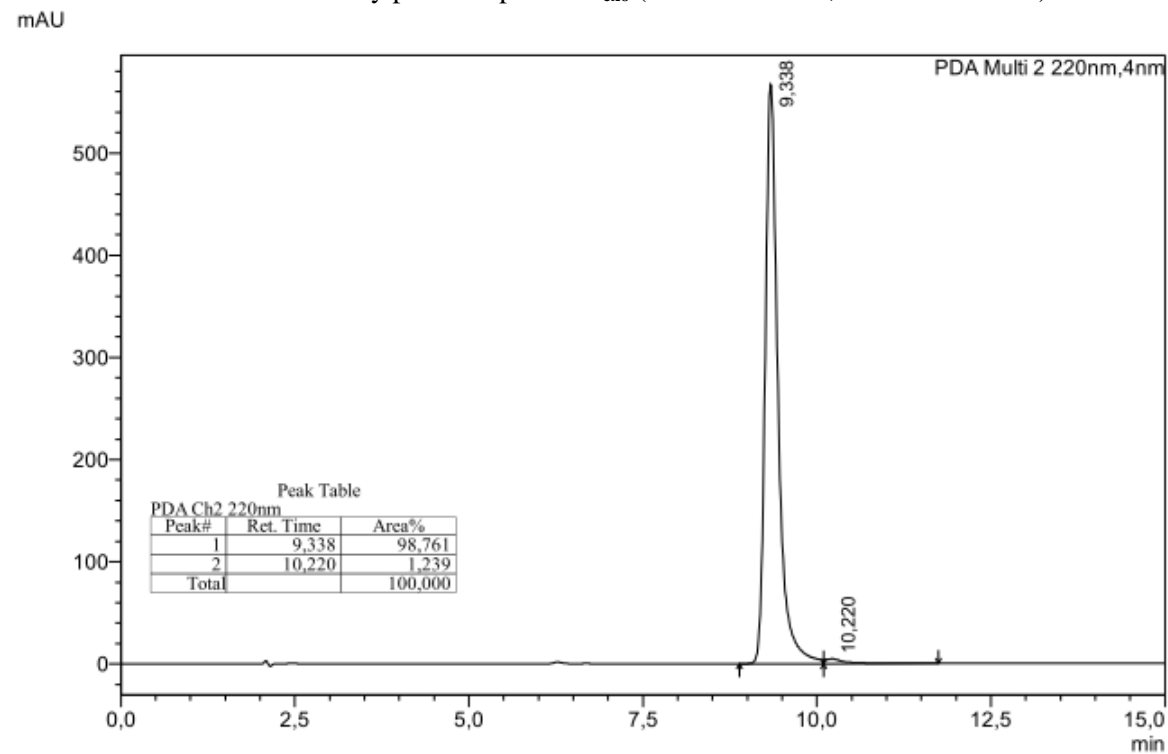
mAU



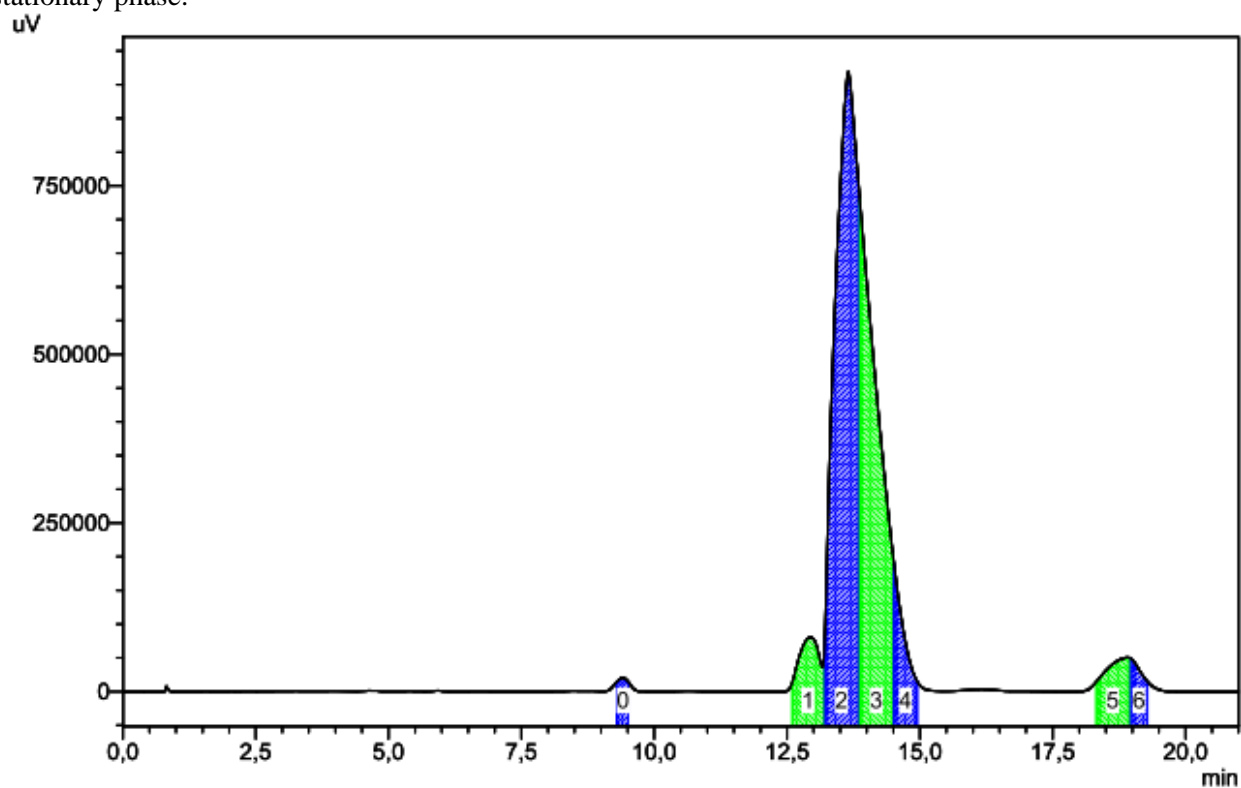
Enantio- and diastereomerically pure sample of **3e<sub>endo</sub>** (e.r. = >99.5:0.5, d.r. = 99.75:0.25):



Enantio- and diastereomerically pure sample of **3e<sub>exo</sub>** (e.r. = >99.5:0.5, d.r. = 98.75:1.25):



Separation of enantiomers and diastereomers of  $3e_{\text{endo}}$  and  $3e_{\text{exo}}$  by preparative HPLC on a chiral stationary phase:



Injection volume: 75  $\mu\text{L}$  (10 mg)

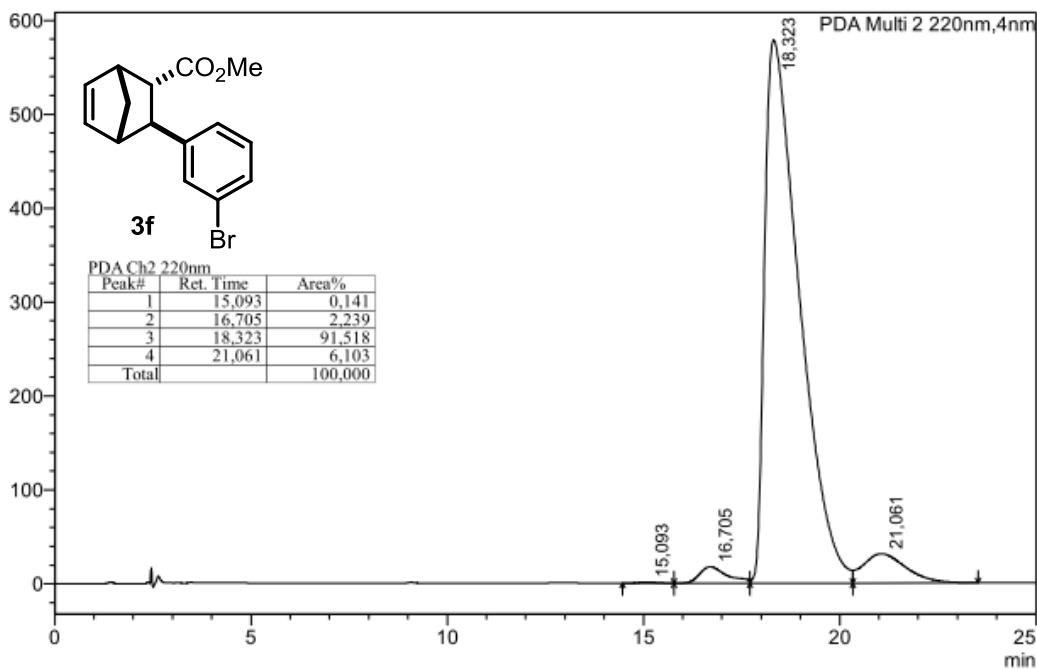
CHIRALPAK OJ, 5 $\mu\text{m}$ , 250x20 mm; acetonitrile/water = 60:40; 20.0 ml/min, 11.3 MPa, 308 K;

UV, 220 nm, 0.5 mm.

Enantioenriched sample of **3f**:

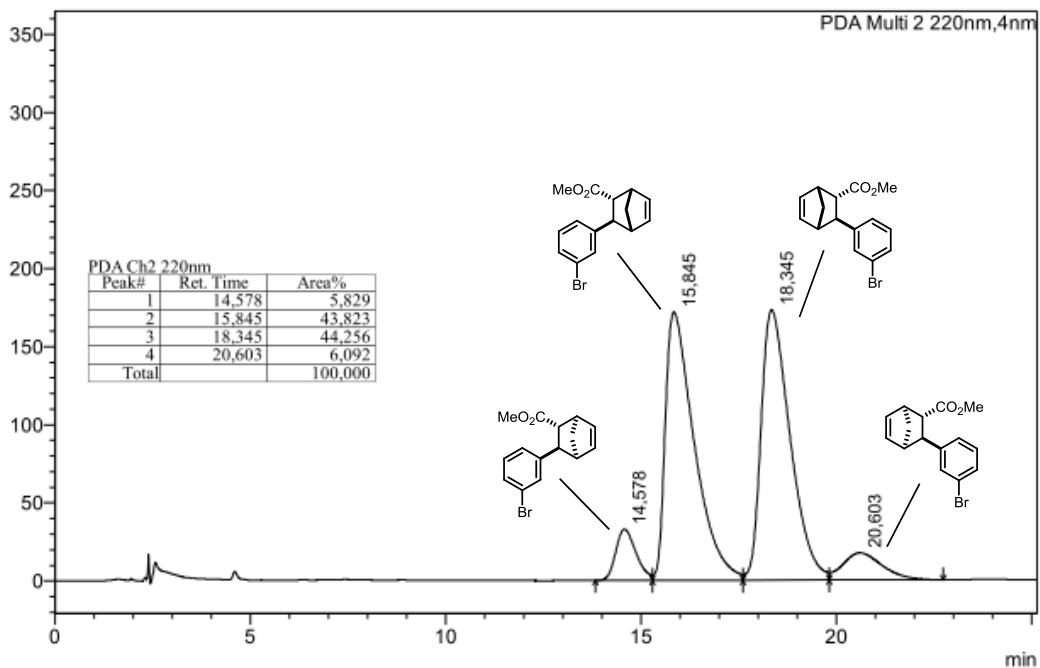
e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 97.5:2.5, d.r. (*endo/exo*) = 15:1.

mAU



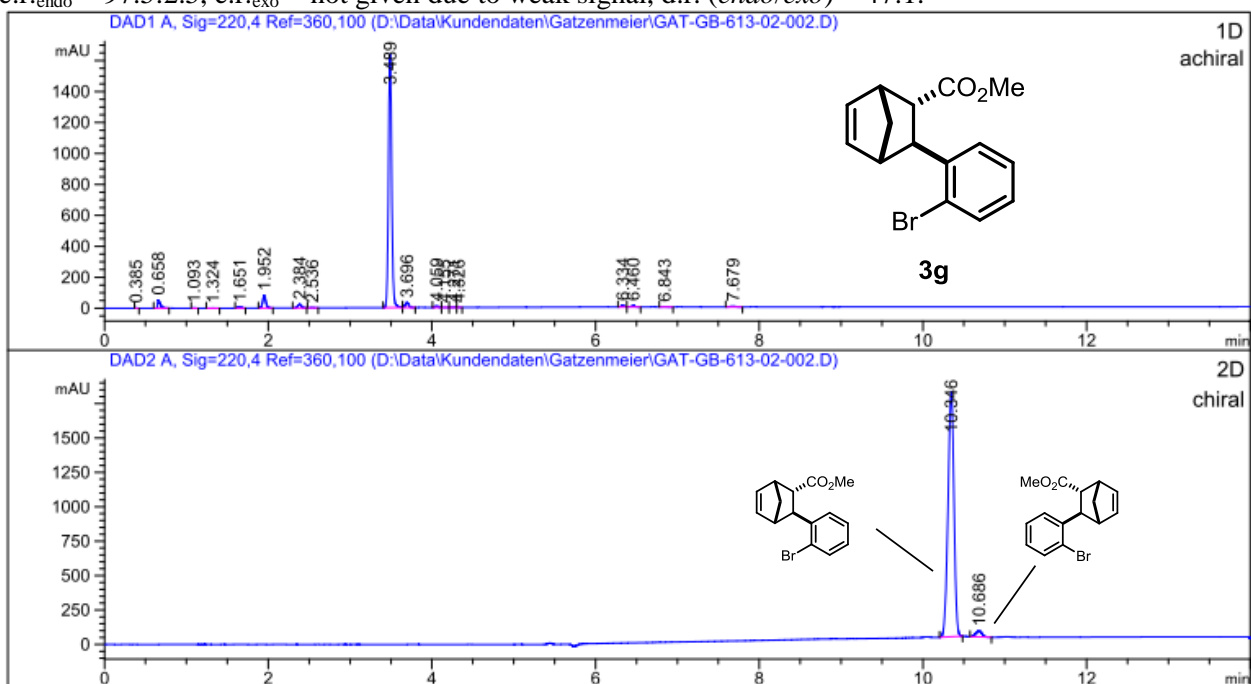
*rac*-**3f**: Daicel Chiralpak AD-3R, MeOH/H<sub>2</sub>O = 80/20, 1 mL/min. The racemic sample was prepared with procedure B.

mAU



Enantioenriched sample of **3g**:

e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = 47:1.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	achiral
1	0.385	VB	0.0182	1.75949	1.42518	0.0345	
2	0.658	BB	0.0329	117.98016	52.64093	2.3163	
3	1.093	BB	0.0295	2.74547	1.40649	0.0539	
4	1.324	BB	0.0499	1.70687	4.09642e-1	0.0335	
5	1.651	BB	0.0413	23.00131	8.58473	0.4516	
6	1.952	BB	0.0412	216.78537	80.96581	4.2562	
7	2.384	BB	0.0460	69.56708	23.17639	1.3658	
8	2.536	BB	0.0439	5.83819	1.98102	0.1146	
9	3.489	BV	0.0417	4453.63086	1638.41223	87.4383	1. Diastereomer
10	3.696	VB	0.0437	93.88791	32.27446	1.8433	2. Diastereomer
11	4.059	BV	0.0389	25.51735	10.03910	0.5010	
12	4.155	VV	0.0463	1.81610	5.79064e-1	0.0357	
13	4.271	VV	0.0426	4.72428	1.67896	0.0928	
14	4.326	VV	0.0353	2.26992	9.52786e-1	0.0446	
15	6.334	BV	0.0396	22.58567	8.60488	0.4434	
16	6.460	VB	0.0451	24.28718	7.96896	0.4768	
17	6.843	BB	0.0465	3.59163	1.14686	0.0705	
18	7.679	BB	0.0682	21.75821	4.91204	0.4272	

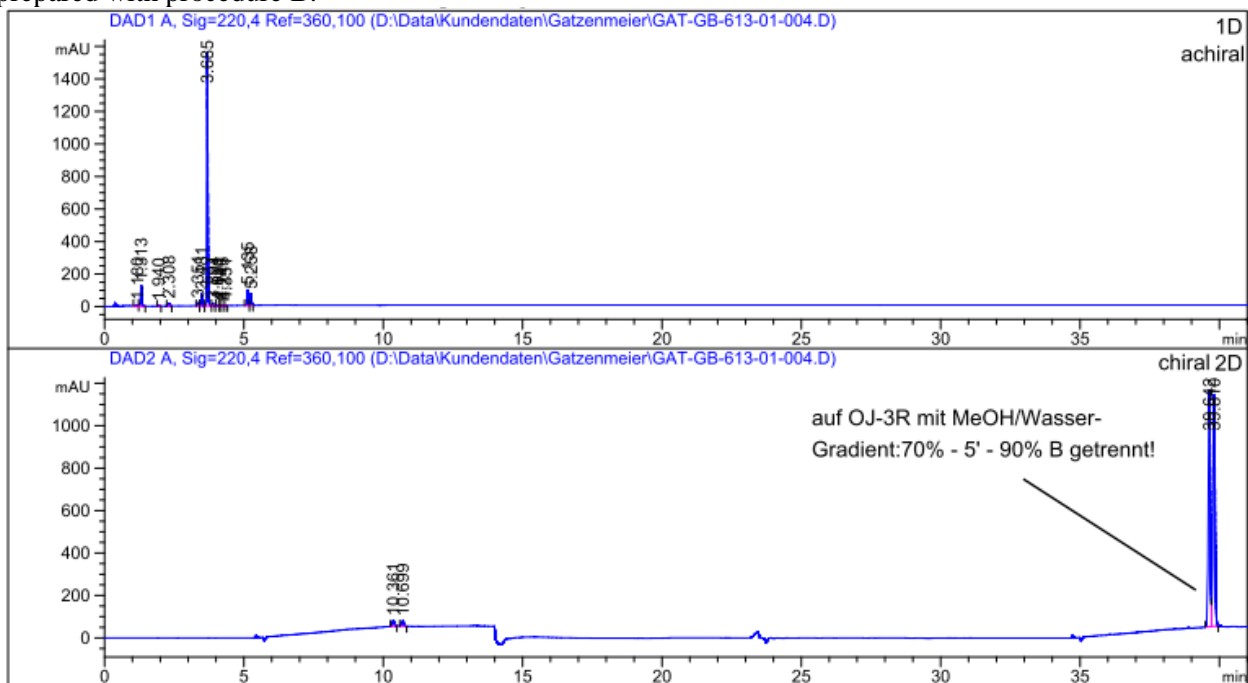
Totals : 5093.45305 1877.15954

Signal 2: DAD2 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	chiral
1	10.346	BB	0.0783	8998.46094	1778.42188	97.5573	1. Enantiomer/1. Diastereomer
2	10.686	BB	0.0821	225.30823	42.70459	2.4427	2. Enantiomer/1. Diastereomer

Totals : 9223.76917 1821.12646

*rac-3g*: (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 3.0 mm, methanol/water – gradient 60% - 5' - 90% B, 0.5 mL/min, 38.5 MPa, 308 K; 2. 150 mm 3-CelluCoat RP, 4.6 mm, methanol/water – gradient 70% - 5' - 90% B, 1.0 ml/min, 35.3 MPa, 298 K, 220 nm. The racemic sample was prepared with procedure B.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	achiral
1	1.180	BV	0.0928	64.12762	8.82427	1.1633	
2	1.313	VB	0.0467	390.39883	126.78525	7.0819	
3	1.940	BB	0.0438	6.91031	2.45985	0.1254	
4	2.308	VB	0.0522	55.38831	16.28692	1.0048	
5	3.351	BV	0.0479	54.11137	17.46093	0.9816	
6	3.481	VV	0.0436	198.95468	70.13082	3.6091	1. Diastereomer
7	3.685	VV	0.0424	4253.32422	1556.82874	77.1561	2. Diastereomer
8	3.894	VB	0.0441	25.97373	8.89396	0.4712	dr = 1:21
9	4.051	BV	0.0441	15.03858	5.15073	0.2728	
10	4.140	VV	0.0443	4.93774	1.67989	0.0896	
11	4.245	VV	0.0459	13.39829	4.48114	0.2430	
12	4.351	VB	0.0393	4.04191	1.55400	0.0733	
13	5.135	BV	0.0394	244.59335	95.53503	4.4370	
14	5.258	VV	0.0388	181.42403	72.26519	3.2911	

Totals : 5512.62298 1988.33670

Signal 2: DAD2 A, Sig=220,4 Ref=360,100

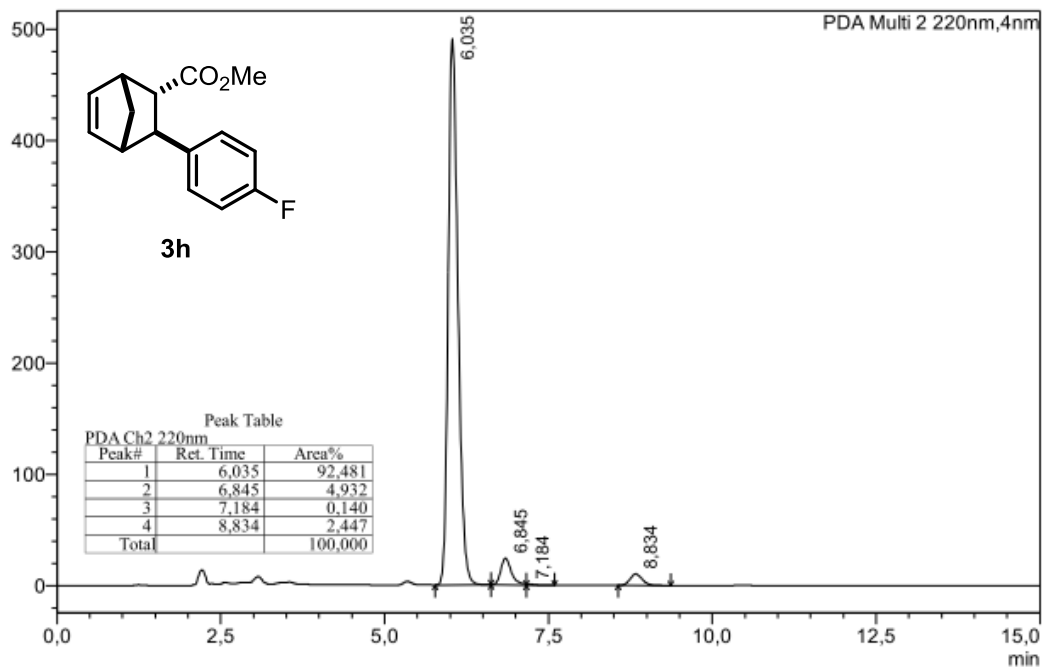
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	chiral
1	10.361	BB	0.0780	135.90913	26.54230	1.1853	1. Enantiomer/ 1. Diastereomer
2	10.699	BB	0.0821	130.91170	24.28997	1.1417	2. Enantiomer/ 1. Diastereomer
3	39.642	BV	0.0779	5602.76904	1114.56848	48.8613	1. Enantiomer/ 2. Diastereomer
4	39.810	VB	0.0796	5597.09863	1091.89404	48.8118	2. Enantiomer/ 2. Diastereomer

Totals : 1.14667e4 2257.29480

Enantioenriched sample of **3h**:

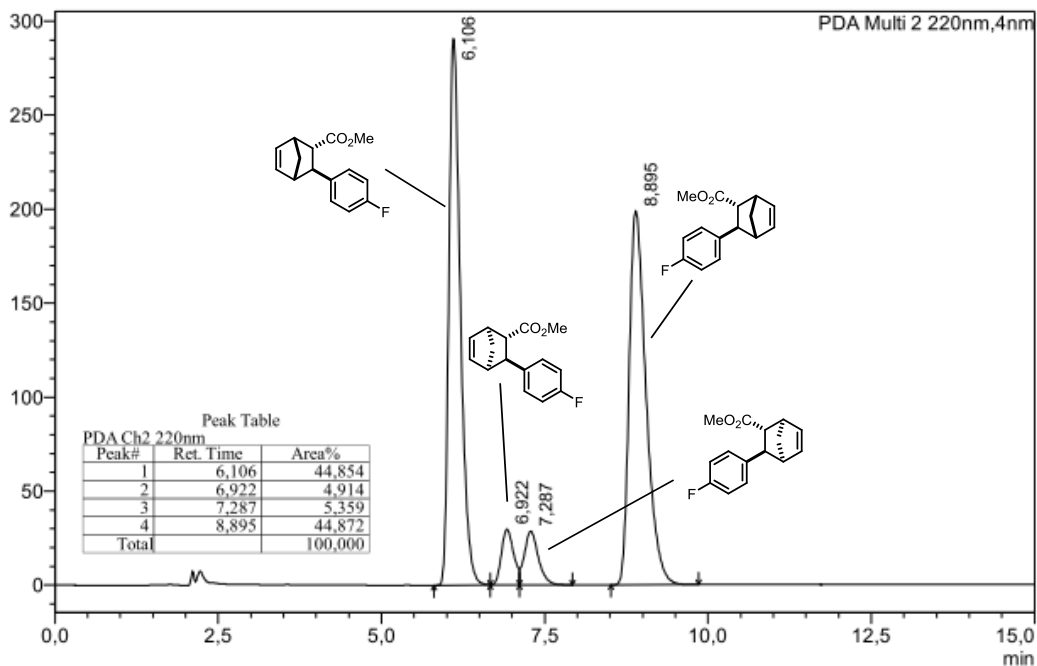
e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 95.5:4.5, d.r. (*endo/exo*) = 18:1.

mAU



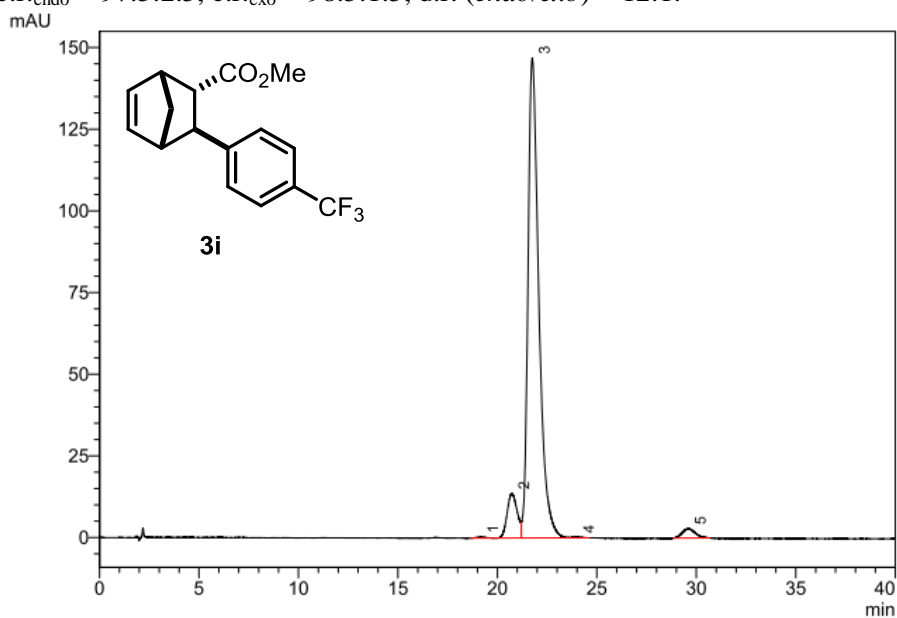
*rac*-**3h**: Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 90/10, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure B.

mAU



Enantioenriched sample of **3i**:

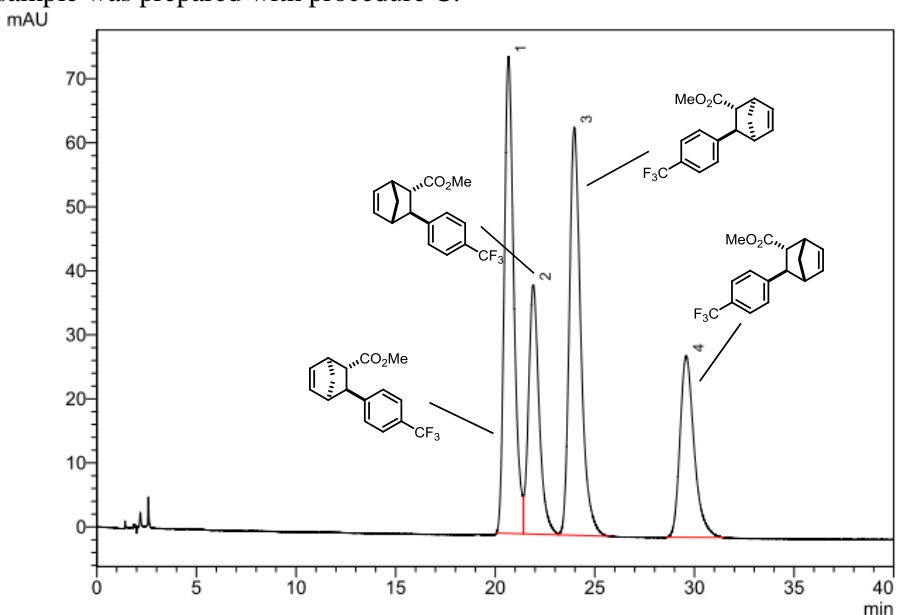
e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 98.5:1.5, d.r. (*endo/exo*) = 12:1.



1 220nm,4nm

Peak #	Ret. Time	Area %	Name	
1	19.16	0.14		
2	20.73	7.79	1E/1D	ee 1. D = 97.2 %
3	21.75	89.86	1E/2D	
4	23.99	0.11	2E/1D	ee 2. D = 95.4 %
5	29.60	2.10	2E/2D	
Total		100.00		

*rac*-**3i**: Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 75/25, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure C.

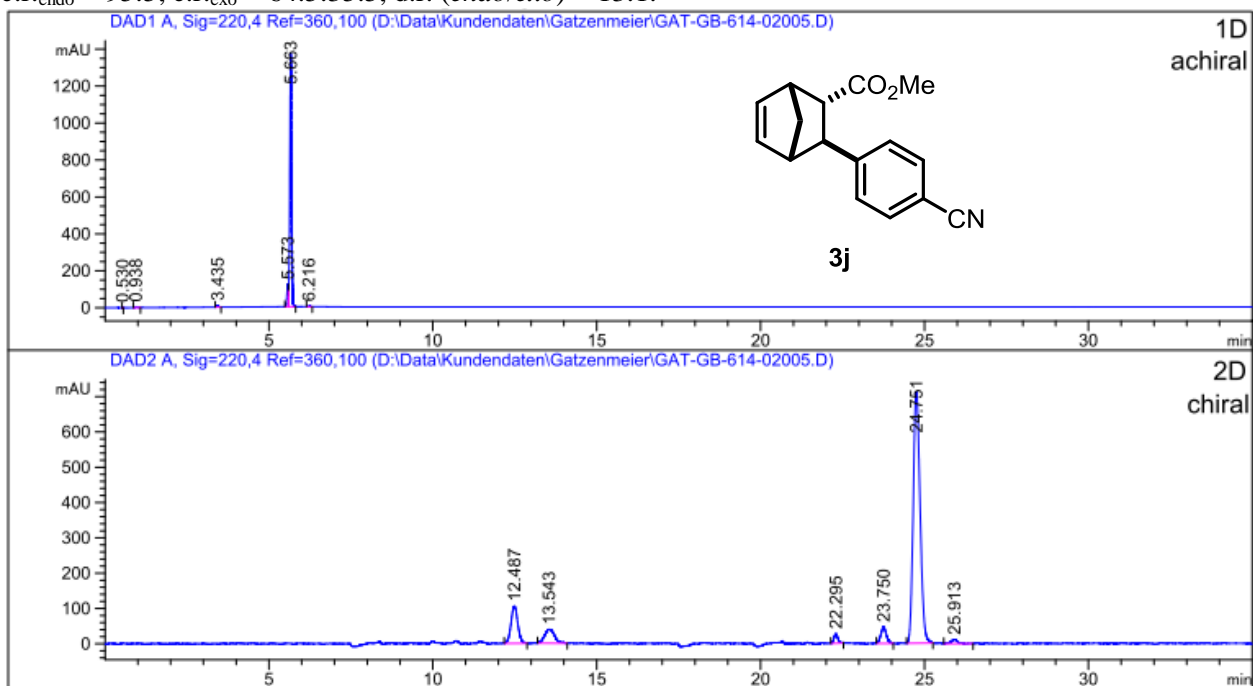


1 220nm,4nm

Peak #	Ret. Time	Area %	Name
1	20.67	31.58	1E/1D
2	21.91	18.31	1E/2D
3	23.97	32.34	2E/1D
4	29.59	17.77	2E/2D
Total		100.00	

Enantioenriched sample of **3j**:

$e.r._{endo} = 95:5$ ,  $e.r._{exo} = 64.5:35.5$ ,  $d.r. (endo/exo) = 13:1$ .



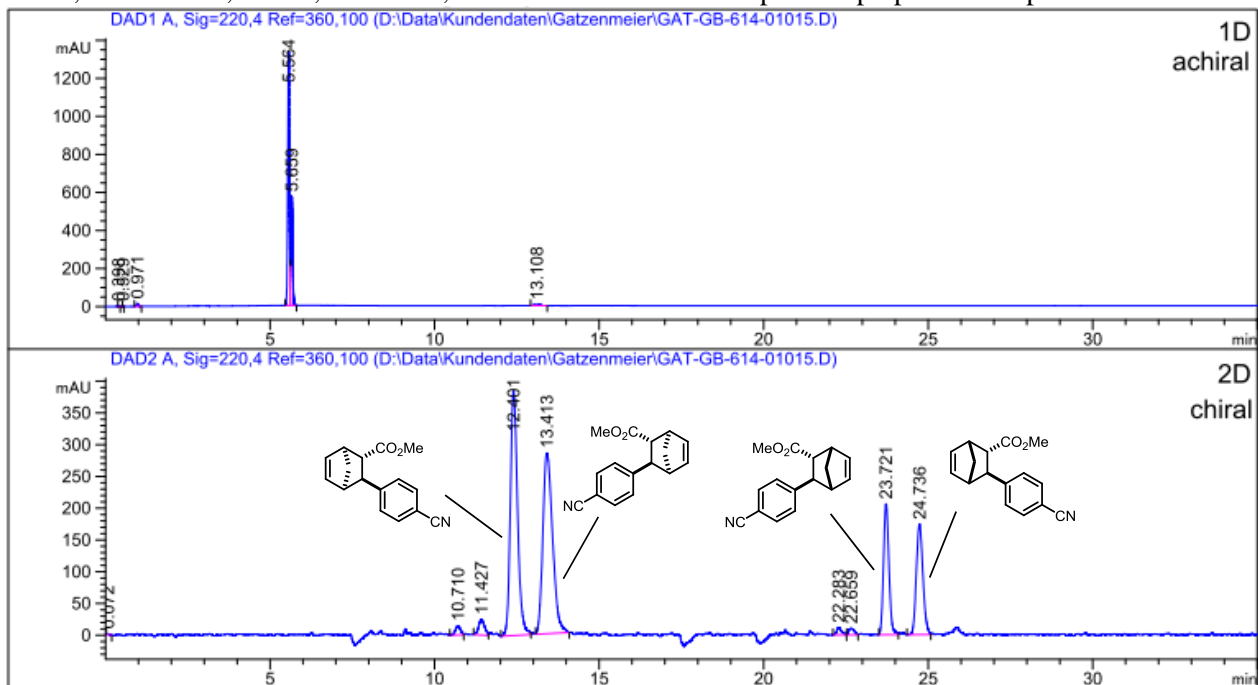
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	achiral
1	0.530	VB	0.0201	5.82296	4.22848	0.1099	
2	0.938	BB	0.0831	25.57858	4.41291	0.4827	
3	3.435	BB	0.0601	32.30696	8.44227	0.6097	
4	5.573	BV	0.0458	362.57318	119.96786	6.8423	1. Diastereomer
5	5.663	VB	0.0549	4863.15820	1370.83923	91.7755	2. Diastereomer
6	6.216	BB	0.0685	9.53076	2.11979	0.1799	
Totals :				5298.97064	1510.01055		dr = 13:1

Signal 2: DAD2 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	chiral
1	12.487	BB	0.2202	1509.73071	105.00599	11.0273	1E/1D
2	13.543	BB	0.2787	833.91565	39.12630	6.0911	2E/1D
3	22.295	BB	0.1288	225.42531	27.01975	1.6465	
4	23.750	BB	0.1733	542.03735	46.57364	3.9591	1E/2D
5	24.751	BB	0.2246	1.04024e4	711.44122	75.9809	2E/2D
6	25.913	BB	0.2328	177.30058	11.63223	1.2950	
Totals :				1.36908e4	940.79914		ee = 28.8%
							ee = 90.1%

*rac-3j*: (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 3.0 mm, methanol/water – gradient 40% - 5' - 60% B, 0.5 mL/min, 308 K, 32.7 MPa; 2. 150 mm AmyCoat RP, 4.6 mm, methanol/water = 90:10, 1.0 mL/min, 298 K, 21.0 MPa, 220 nm. The racemic sample was prepared with procedure C.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	achiral
1	0.398	VB	0.0362	6.62569	2.47670	0.0985	
2	0.529	VB	0.0191	5.03267	3.88542	0.0749	
3	0.971	BB	0.0688	62.84029	14.02658	0.9346	
4	5.564	BV	0.0530	4573.91260	1334.89063	68.0282	1. Diastereomer
5	5.659	VB	0.0538	1999.43408	572.14551	29.7378	2. Diastereomer
6	13.108	BB	0.1540	75.70598	5.82903	1.1260	

Totals : 6723.55131 1933.25386

Signal 2: DAD2 A, Sig=220,4 Ref=360,100

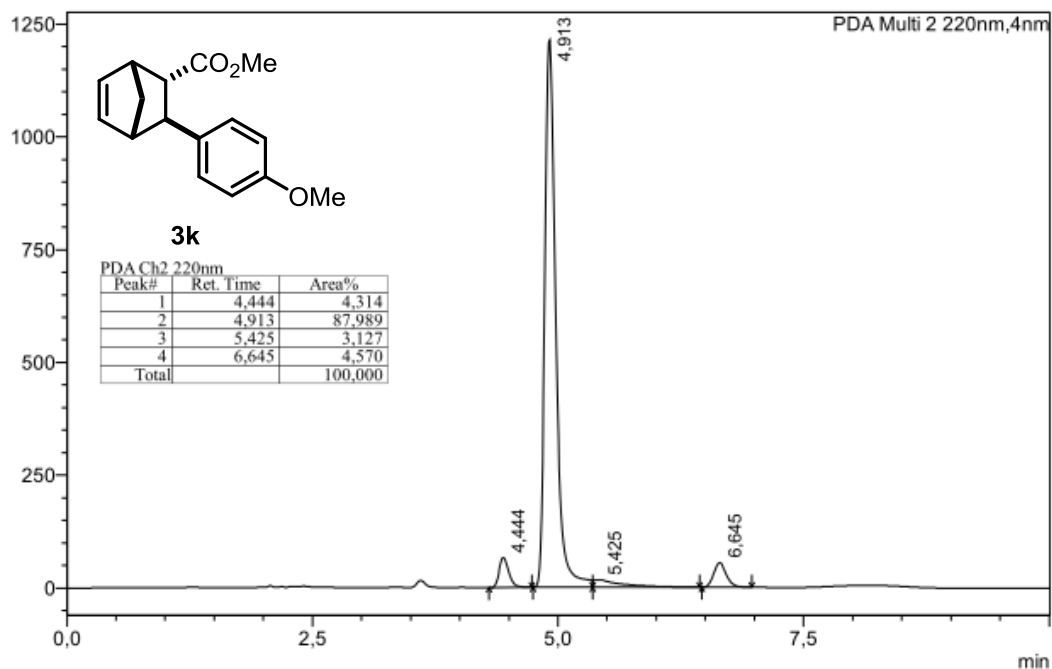
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	chiral
1	0.072	BB	0.0674	5.35692	1.20415	0.0312	
2	10.710	VV	0.1550	153.90506	14.36459	0.8957	
3	11.427	BV	0.1859	307.07565	24.72403	1.7871	
4	12.401	VB	0.2355	5856.17041	384.97626	34.0808	1E/1D
5	13.413	BB	0.3077	5843.07764	284.39651	34.0046	2E/1D
6	22.283	BV	0.1477	117.07733	11.50369	0.6813	
7	22.659	VV	0.1687	115.56059	9.86023	0.6725	
8	23.721	BB	0.1767	2360.26025	205.93506	13.7358	1E/2D
9	24.736	VV	0.2180	2424.73315	173.57298	14.1111	2E/2D

Totals : 1.71832e4 1110.53751

Enantioenriched sample of **3k**:

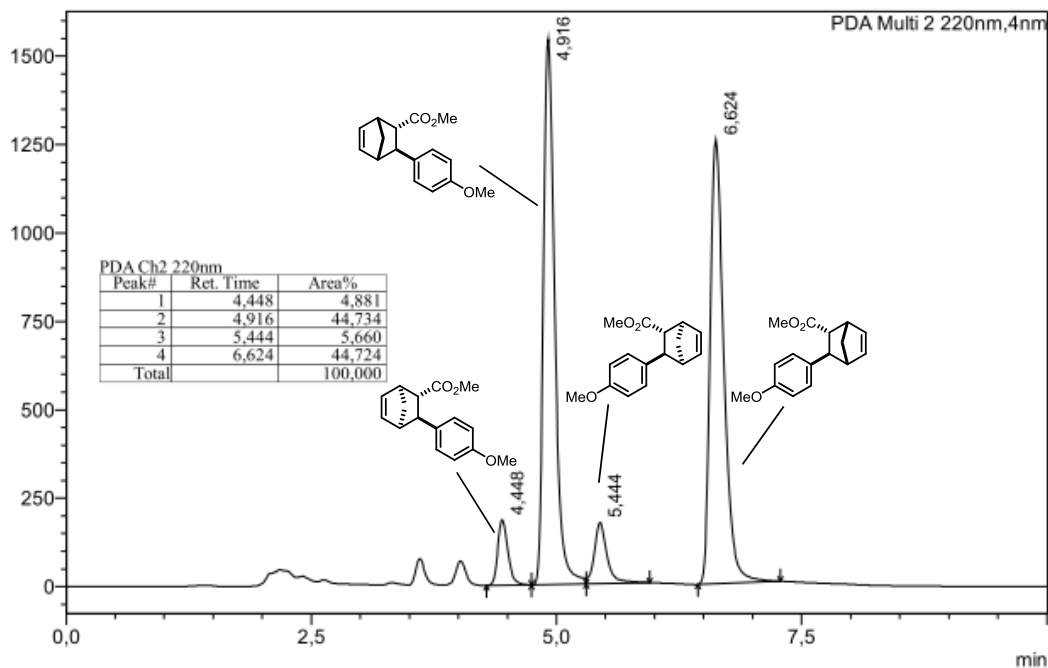
e.r.<sub>endo</sub> = 95:5, e.r.<sub>exo</sub> = not given due to signal overlap, d.r. (*endo/exo*) = 12:1.

mAU



*rac*-**3k**: Daicel Chiralcel OJ-3R, MeCN/H<sub>2</sub>O = 70/30, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure B.

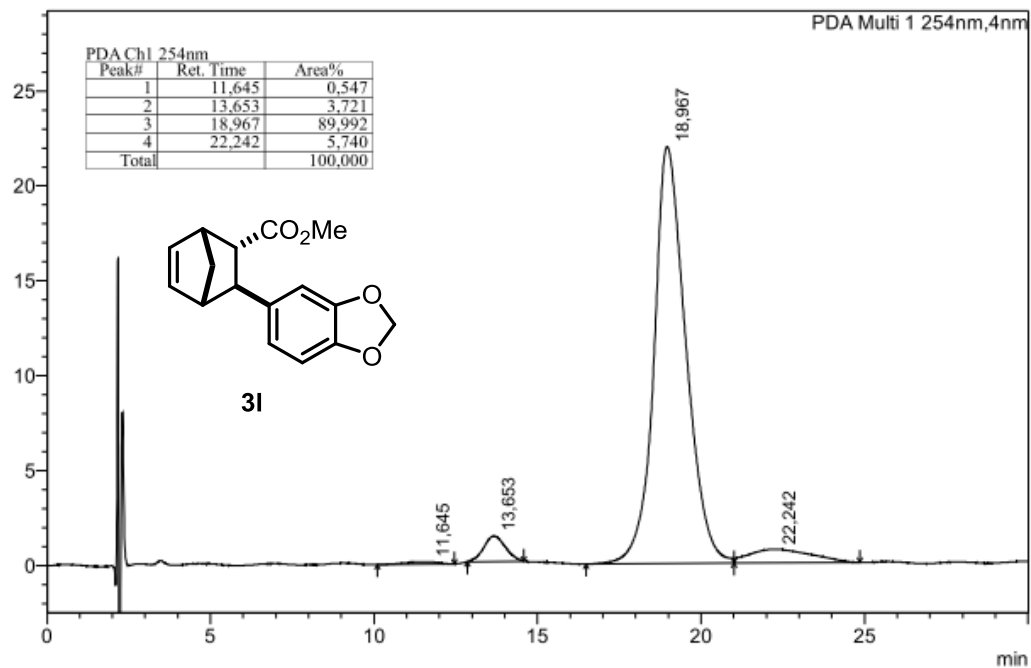
mAU



Enantioenriched sample of **3l**:

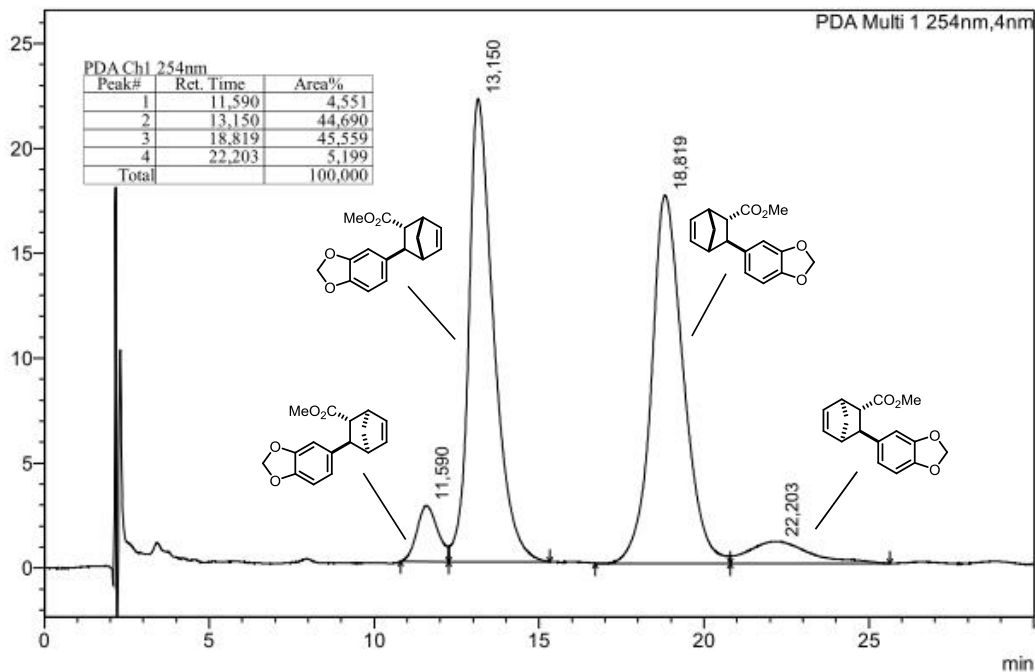
e.r.<sub>endo</sub> = 96:4, e.r.<sub>exo</sub> = 91:9, d.r. (*endo*/*exo*) = 15:1.

mAU



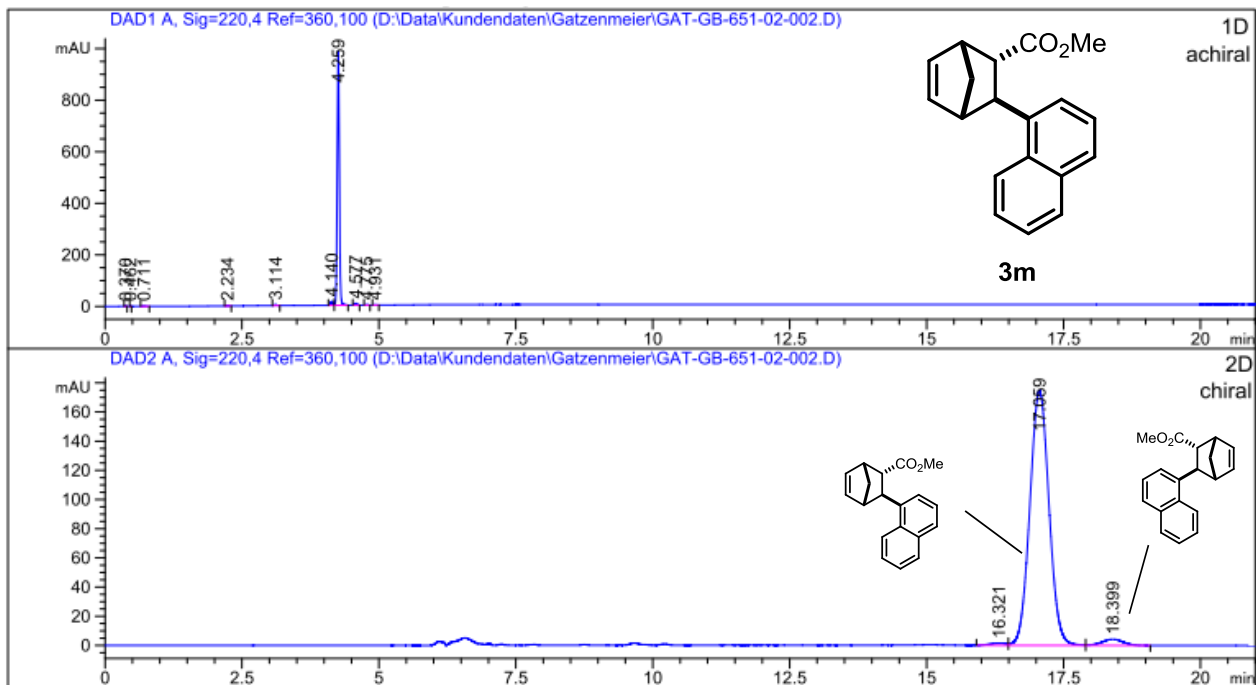
*rac*-**3l**: Kromasil AmyCoat RP, MeOH/H<sub>2</sub>O = 85/15, 1 mL/min, 25 °C, 254 nm. The racemic sample was prepared with procedure B.

mAU



Enantioenriched sample of **3m**:

e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = >50:1.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	achiral
1	0.370	BB	0.0191	1.54699	1.21911	0.0560	
2	0.462	BV	0.0128	1.29569	1.46706	0.0469	
3	0.711	BB	0.0495	3.75342	9.16757e-1	0.1359	
4	2.234	BB	0.0384	4.24640	1.50447	0.1537	
5	3.114	BB	0.0457	10.08386	3.29929	0.3650	
6	4.140	BV	0.0407	40.52106	15.26381	1.4669	1. Diastereomer
7	4.259	VB	0.0420	2677.62036	984.37939	96.9310	2. Diastereomer
8	4.577	BB	0.0394	17.88769	7.04697	0.6475	
9	4.775	BB	0.0363	3.81870	1.54568	0.1382	
10	4.931	BB	0.0319	1.62445	6.40134e-1	0.0588	

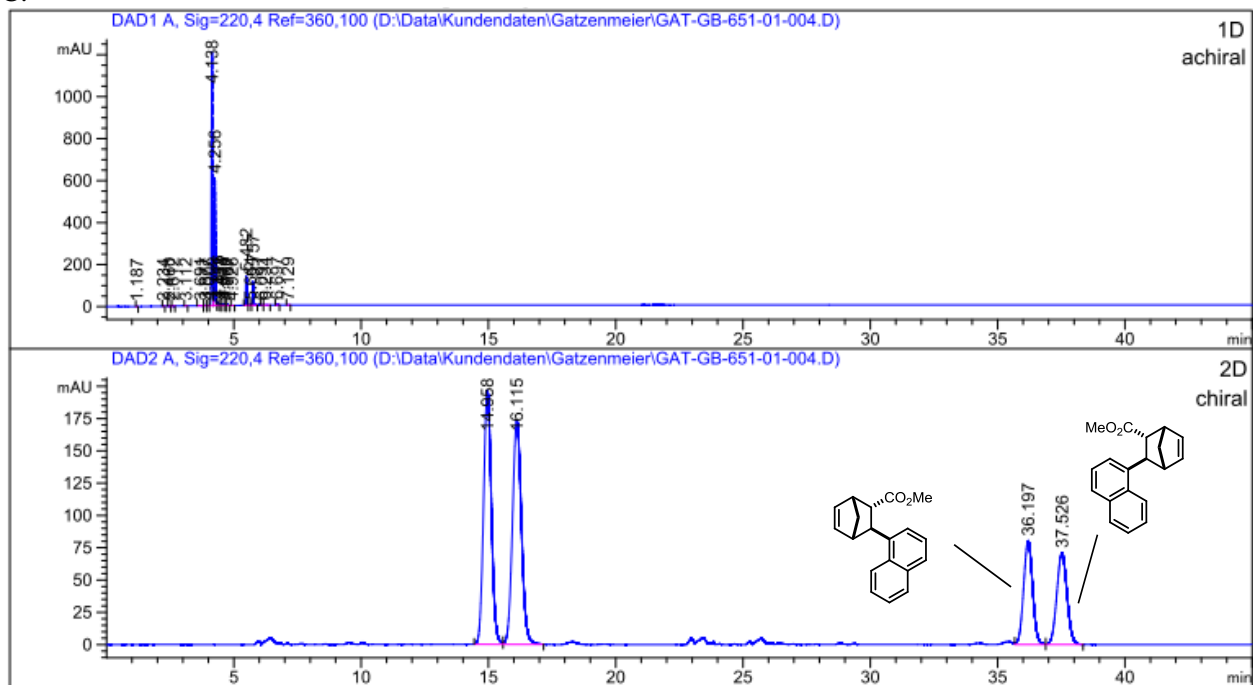
Totals : 2762.39863 1017.28266

Signal 2: DAD2 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	chiral
1	16.321	BV	0.2556	29.74233	1.43614	0.6775	
2	17.059	VB	0.3796	4245.97217	174.67932	96.7213	1. Enantiomer/2. Diastereomer
3	18.399	BB	0.3864	114.19006	4.21055	2.6012	2. Enantiomer/2. Diastereomer

Totals : 4389.90456 180.32601

*rac-3m*: (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 3.0 mm, methanol/water – gradient 60% - 5' - 90% B, 0.5 mL/min, 37.0 MPa, 308 K; 2. 150 mm 3-AmyCoat RP, 4.6 mm, acetonitrile/water = 50:50, 1.0 ml/min, 18.6 MPa, 298 K, 220 nm. The racemic sample was prepared with procedure C.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	achiral
1	1.187	BB	0.0311	1.50795	7.00113e-1	0.0265	
2	2.234	BB	0.0329	1.45922	5.50752e-1	0.0257	
3	2.460	BB	0.0401	8.18418	3.04856	0.1439	
4	2.612	BB	0.0459	7.57040	2.54862	0.1331	
5	3.112	BB	0.0460	4.05950	1.29623	0.0714	
6	3.691	BB	0.0688	8.08943	1.66858	0.1422	
7	3.877	BV	0.0478	7.36245	2.38073	0.1295	
8	4.006	VV	0.0439	4.55907	1.56701	0.0802	
9	4.138	VV	0.0412	3232.22681	1206.76367	56.8370	1. Diastereomer
10	4.256	VV	0.0415	1643.44861	608.02271	28.8992	2. Diastereomer
11	4.376	VV	0.0440	34.14941	11.55140	0.6005	
12	4.452	VV	0.0427	10.35534	3.52866	0.1821	
13	4.571	VV	0.0487	26.75994	7.96906	0.4706	
14	4.650	VB	0.0423	5.61421	1.99974	0.0987	
15	4.767	BB	0.0469	7.40984	2.44083	0.1303	
16	4.926	BB	0.0459	1.72854	5.61466e-1	0.0304	
17	5.482	BV	0.0404	359.66974	138.22304	6.3246	
18	5.664	VV	0.0566	6.91026	1.72844	0.1215	
19	5.757	VB	0.0408	296.37125	110.51096	5.2115	
20	6.091	BB	0.0454	1.94403	6.39965e-1	0.0342	
21	6.234	BB	0.0970	5.78649	7.41706e-1	0.1018	
22	6.697	BB	0.0528	8.48359	2.45722	0.1492	
23	7.129	BB	0.0586	3.18730	8.43151e-1	0.0560	
Totals :				5686.83754	2111.74261		

dr = 1:2

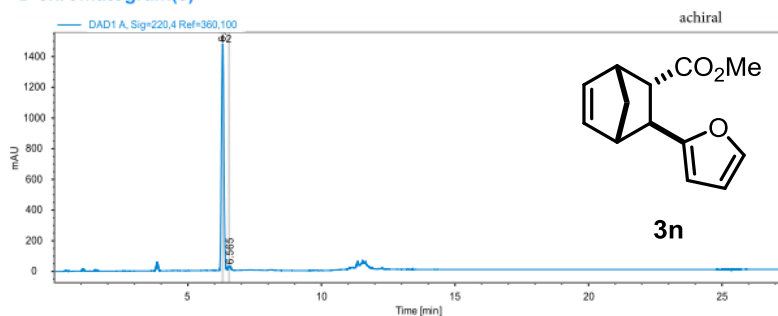
Signal 2: DAD2 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	chiral
1	14.958	BV	0.3334	4198.98291	196.44382	33.8493	1. Enantiomer/1. Diastereomer
2	16.115	VB	0.3793	4246.25000	173.66313	34.2303	2. Enantiomer/1. Diastereomer
3	36.197	VV	0.3848	1975.63879	80.35578	15.9262	1. Enantiomer/2. Diastereomer
4	37.526	VB	0.4345	1984.06116	70.90605	15.9941	2. Enantiomer/2. Diastereomer
Totals :				1.24049e4	521.36878		

Enantioenriched sample of **3n**:

e.r.<sub>endo</sub> = 94:6, e.r.<sub>exo</sub> = not given due to weak signal, d.r. (*endo/exo*) = >50:1.

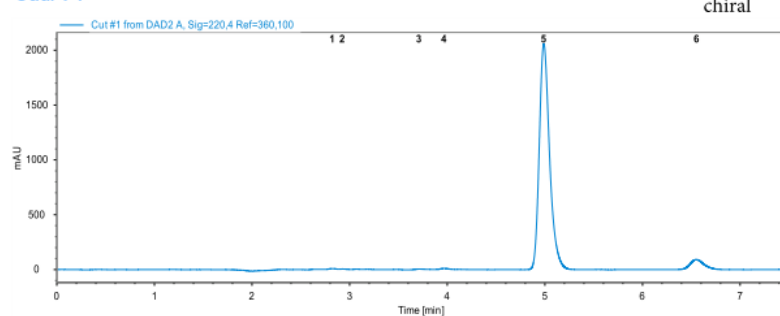
'D chromatogram(s)



Sampling table ('D)

Cut group	Cut #	'D Cut start [min]	'D Ret. time [min]	'D Duration [min]	Trigger	'D Run start [min]	
	1	6.26	6.302	0.08	Time	6.39	1. Diastereomer
	2	6.50	6.565	0.08	Time	16.20	2. Diastereomer

Cut# : 1

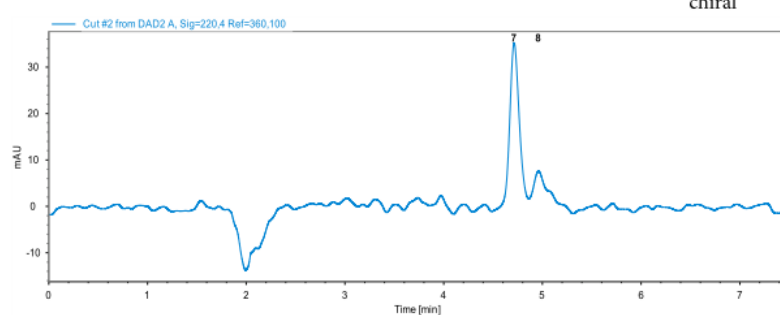


Signal: DAD2 A, Sig=220,4 Ref=360,100

1. Diastereomer

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	2.825	35.594 35.594	0.071	7.670	0.832	
2	1	2.929	18.844 18.844	0.066	4.307	0.715	
3	1	3.714	53.164 53.164	0.110	6.650	0.475	
4	1	3.968	82.317 82.317	0.101	11.865	0.831	
5	1	4.989	15121.091 15121.091	0.112	2059.331	0.732	1. Enantiomer
6	1	6.553	905.792 905.792	0.152	90.943	0.795	2. Enantiomer

Cut# : 2



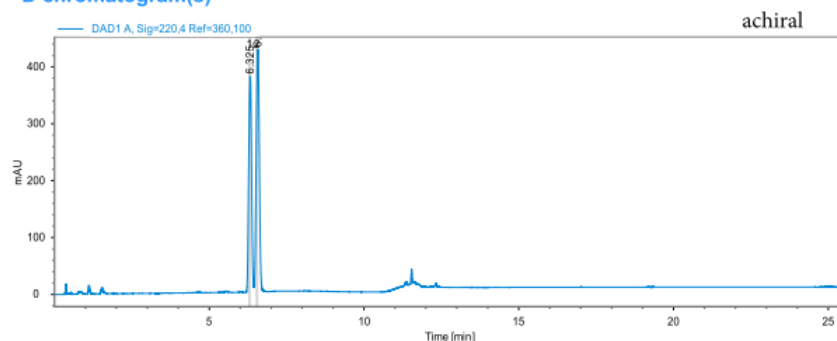
Signal: DAD2 A, Sig=220,4 Ref=360,100

2. Diastereomer

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
7	2	4.714	255.195 255.195	0.106	36.269	0.825	1. Enantiomer
8	2	4.961	105.619 105.619	0.163	8.863	0.440	2. Enantiomer

*rac*-**3n**: (Heartcut) 1. 50 mm YMC Triart C18 ExRS, 3.0 mm, methanol/water – gradient 50 % B - 5` - 70 % B - 5` - 70% - 1` - 100% B, 0.5 mL/min, 58.7 MPa, 308 K, 220 nm; 2. 150mm Chiralcel OJ-3R, 4.6 mm, methanol/water = 90:10, 1.0 mL/min, 298 K, 26.5 MPa, 220 nm. The racemic sample was prepared with procedure C.

**'D chromatogram(s)**



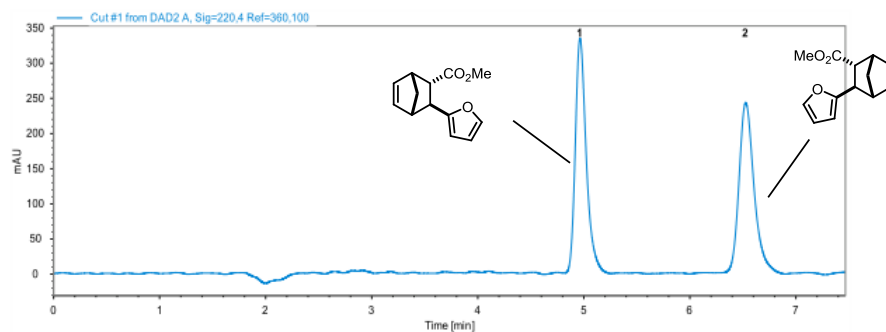
**Sampling table ('D)**

Cut group	Cut #	'D Cut start [min]	'D Ret. time [min]	'D Duration [min]	Trigger	'D Run start [min]	
	1	6.26	6.325	0.08	Time	6.39	1. Diastereomer
	2	6.50	6.572	0.08	Time	16.19	2. Diastereomer

**Cut# : 1**

1. Diastereomer

chiral



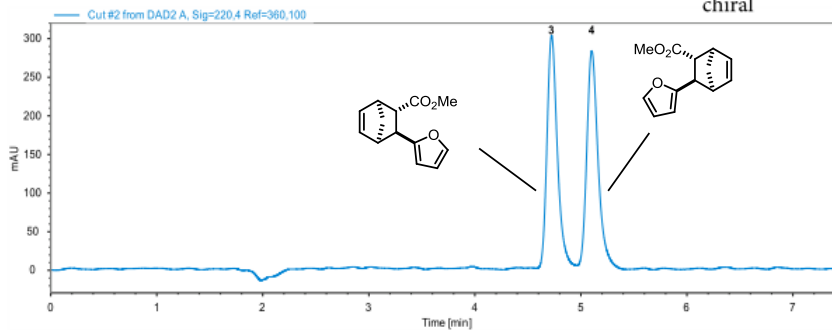
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	4.964	2398.888 <b>2398.888</b>	0.109	334.442	0.704	1. Enantiomer
2	1	6.527	2398.820 <b>2398.820</b>	0.149	242.789	0.745	2. Enantiomer

**Cut# : 2**

2. Diastereomer

chiral



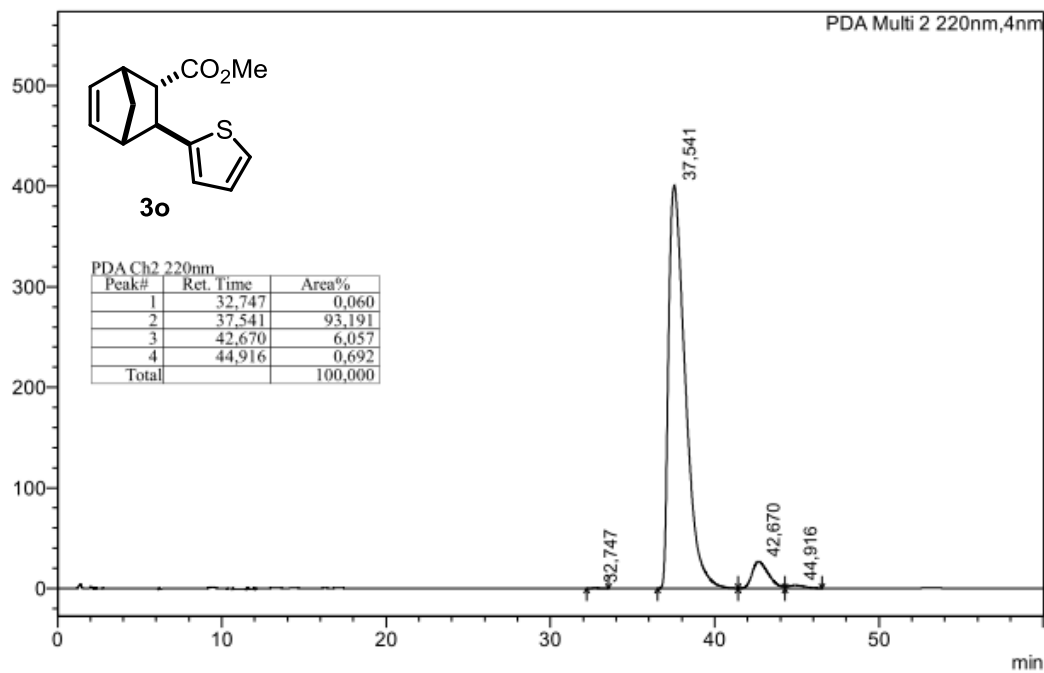
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
3	2	4.724	2061.119 <b>2061.119</b>	0.104	301.746	0.736	1. Enantiomer
4	2	5.103	2104.210 <b>2104.210</b>	0.113	282.360	0.739	2. Enantiomer

Enantioenriched sample of **3o**:

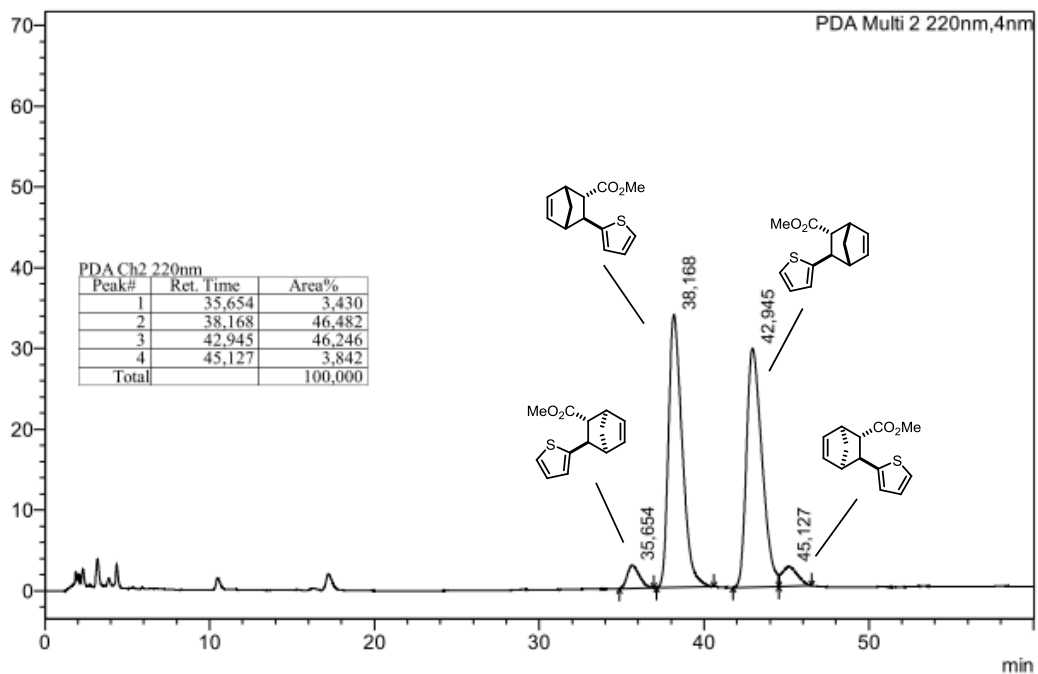
e.r.<sub>endo</sub> = 94:6, e.r.<sub>exo</sub> = 90:10, d.r. (*endo/exo*) = >50:1.

mAU



*rac-3o*: Daicel Chiralcel OJ-3R, MeCN/H<sub>2</sub>O = 40/60, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure B.

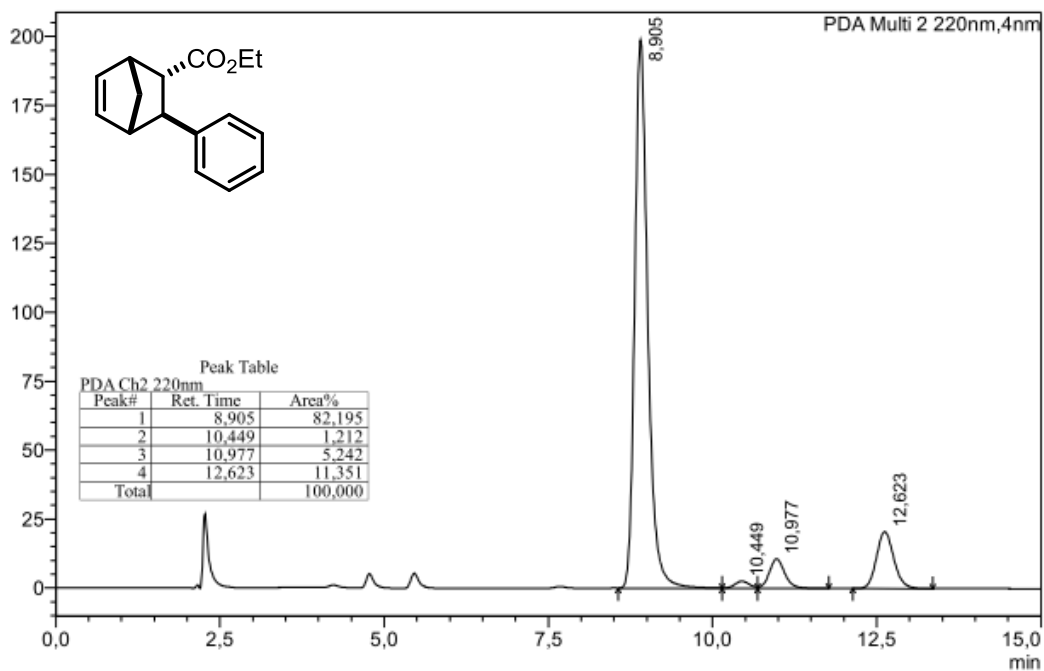
mAU



Enantioenriched sample of **ethyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate**:

e.r.<sub>endo</sub> = 88:12, e.r.<sub>exo</sub> = 82:18, d.r. (*endo*/*exo*) = 14:1.

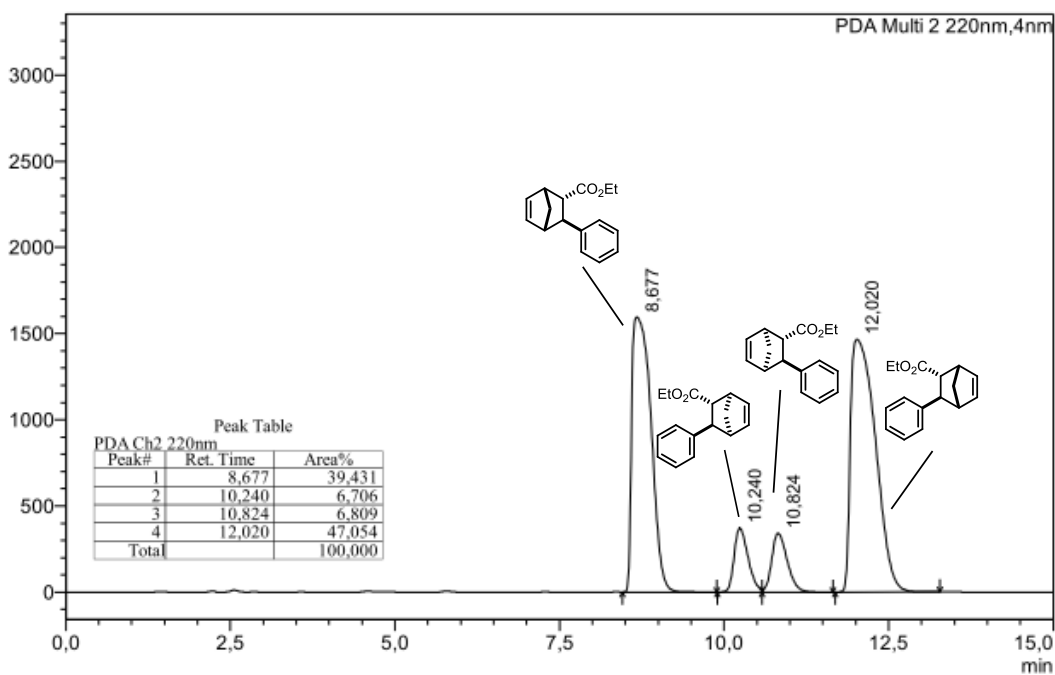
mAU



*rac*-ethyl (1*R*,2*S*,3*S*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate:

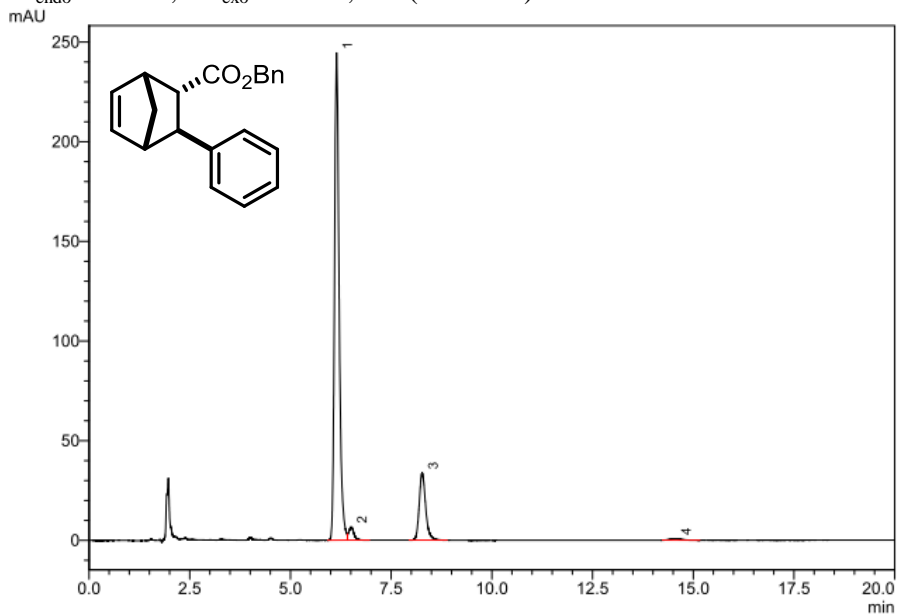
Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 90/10, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure B.

mAU



Enantioenriched sample of **benzyl (1R,2S,3S,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate**:

e.r.<sub>endo</sub> = 84:16, e.r.<sub>exo</sub> = 80:20, d.r. (*endo/exo*) = 32:1.



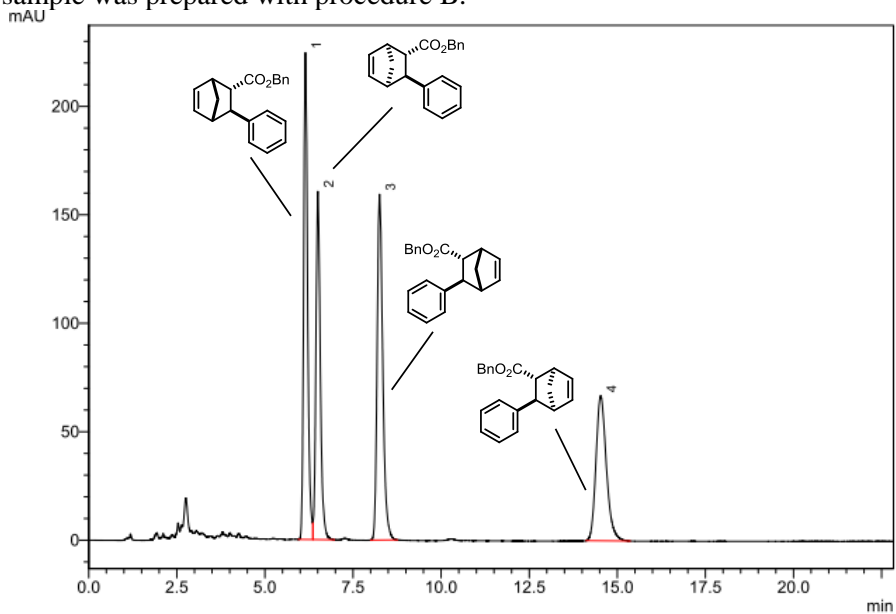
1 220nm,4nm

Peak #	Ret. Time	Area %	Name
1	6.15	81.48	1. Diastereomer 1. Enantiomer
2	6.51	2.43	2. Diastereomer 1. Enantiomer
3	8.27	15.50	1. Diastereomer 2. Enantiomer
4	14.55	0.60	2. Diastereomer 2. Enantiomer
Total		100.00	

= 68.0 % ee
   
 = 60.4 % ee

*rac*-benzyl (1R,2S,3S,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate:

Daicel Chiralcel OJ-3R, MeOH/MeCN/H<sub>2</sub>O = 45/45/10, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure B.



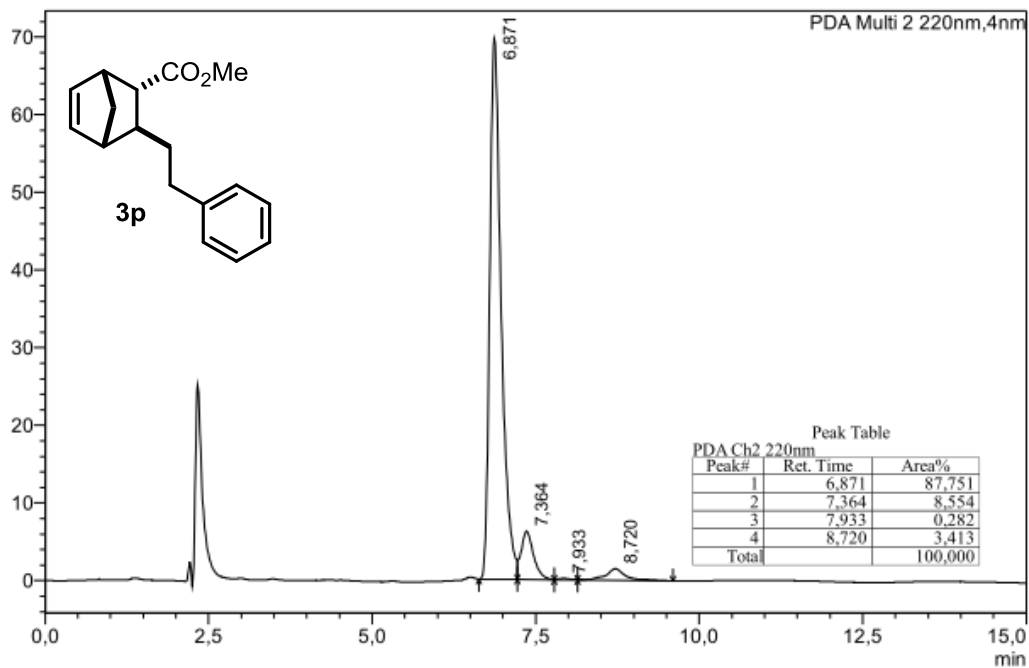
1 220nm,4nm

Peak #	Ret. Time	Area %	Name
1	6.15	27.86	1. Diastereomer 1. Enantiomer
2	6.50	22.27	2. Diastereomer 1. Enantiomer
3	8.25	28.10	1. Diastereomer 2. Enantiomer
4	14.53	21.78	2. Diastereomer 2. Enantiomer
Total		100.00	

Enantioenriched sample of **3p**:

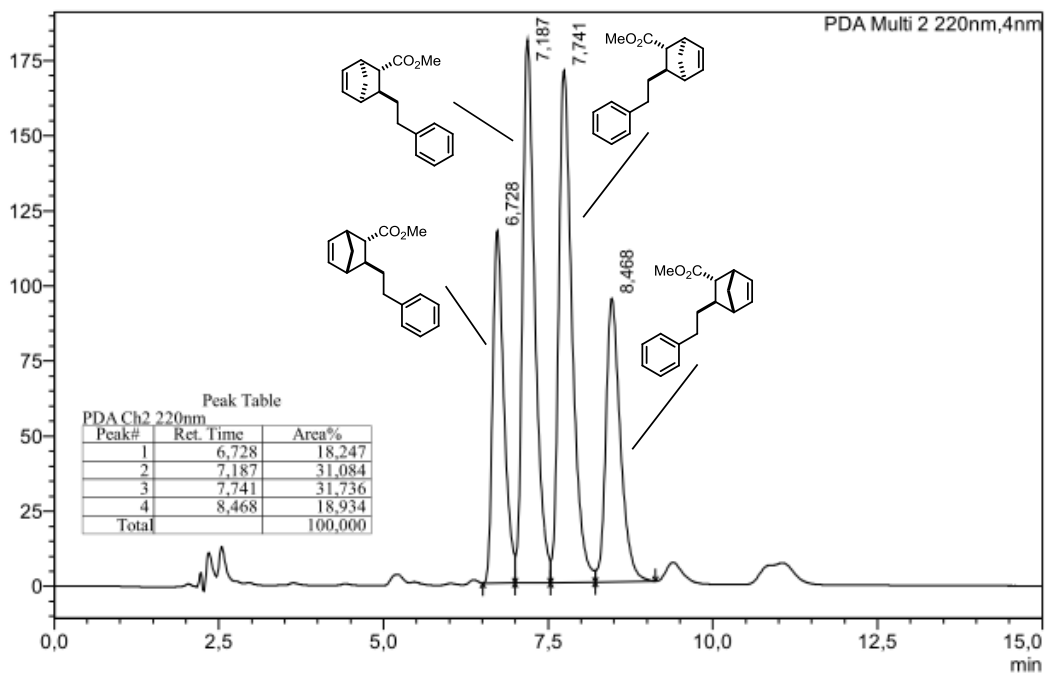
e.r.<sub>endo</sub> = 96.5:3.5, e.r.<sub>exo</sub> = 97:3, d.r. (*endo*/*exo*) = 10:1.

mAU



*rac*-**3p**: Daicel Chiralcel OJ-3R, MeOH/H<sub>2</sub>O = 90/10, 1 mL/min, 25 °C, 220 nm. The racemic sample was prepared with procedure C.

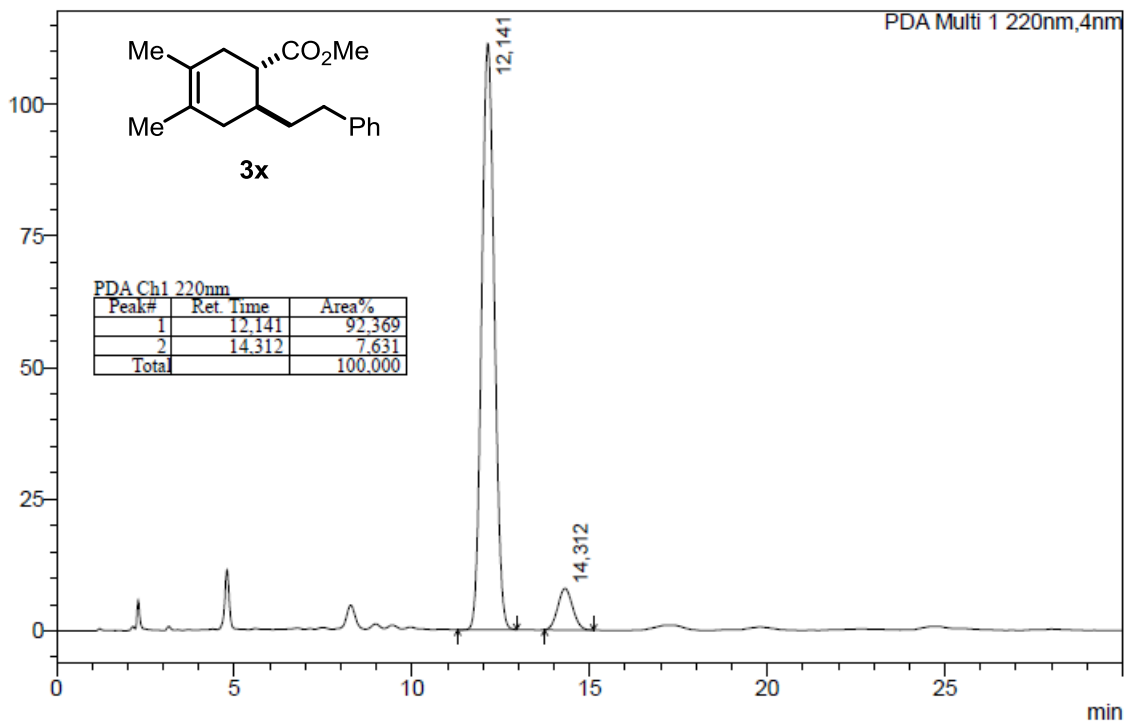
mAU



Enantioenriched sample of **3x**:

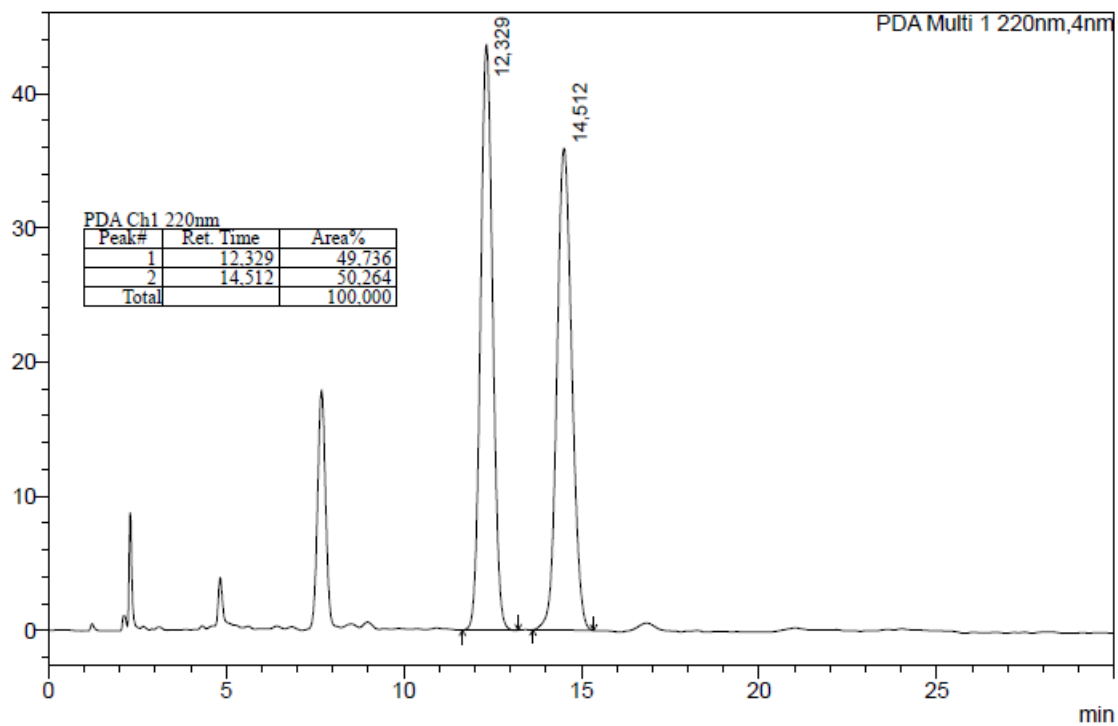
e.r. = 92:8.

mAU



*rac*-**3x**: Daicel Chiralcel IC-3R, MeOH/H<sub>2</sub>O = 80:20, 1 mL/min, 25 °C, 220 nm.

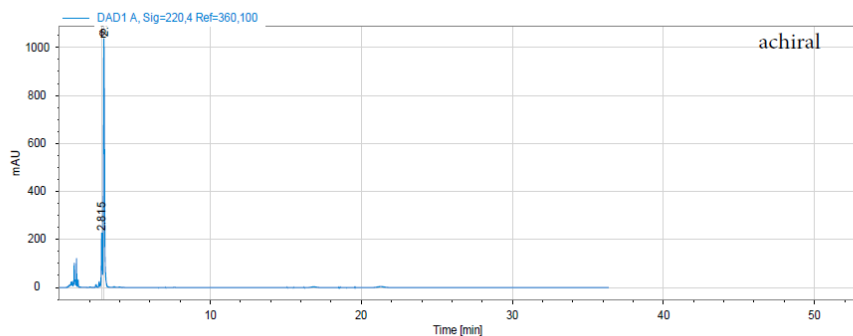
mAU



Enantioenriched sample of **3y**:

e.r.<sub>endo</sub> = 69:31, e.r.<sub>exo</sub> = 81:19, d.r. (*endo/exo*) = 6:1.

#### <sup>1</sup>D chromatogram(s)



#### Sampling table (<sup>1</sup>D)

Cut group	Cut #	<sup>1</sup> D Cut start [min]	<sup>1</sup> D Ret. time [min]	<sup>1</sup> D Duration [min]	Trigger	<sup>1</sup> D Run start [min]
	1	2.80	2.815	0.04	Time	2.84
	2	2.94	2.959	0.04	Time	28.75

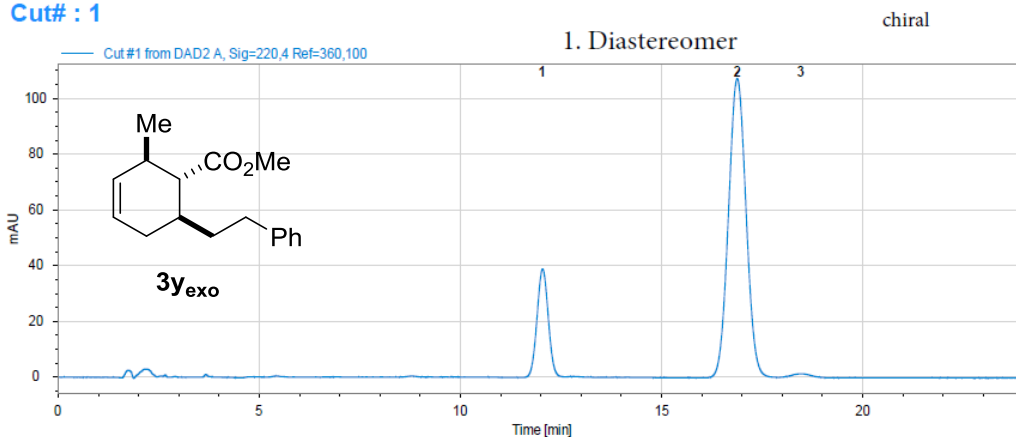
#### Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

chiral

Component	<sup>1</sup> D Sampling range [min]	Ret.Time <sup>1</sup> D [min]	Area	Area%	
1	2.80 - 2.84	12.043	751.299	2.574	1. Diastereomer 1. Enantiomer
2	2.80 - 2.84	16.883	3249.026	11.130	1. Diastereomer 2. Enantiomer
3	2.80 - 2.84	18.468	45.320	0.155	
4	2.94 - 2.98	8.761	21.189	0.073	
5	2.94 - 2.98	12.742	16521.346	56.598	2. Diastereomer 1. Enantiomer
6	2.94 - 2.98	16.879	58.129	0.199	
7	2.94 - 2.98	22.027	8544.605	29.271	2. Diastereomer 2. Enantiomer

Cut# : 1

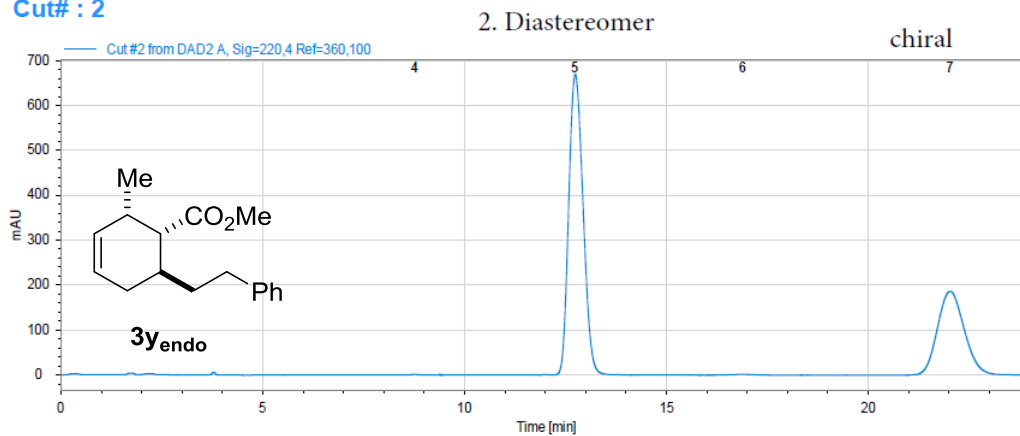


Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	12.043	751.299 <b>751.299</b>	0.250	38.830	0.943	1. Enantiomer
2	1	16.883	3249.026 <b>3249.026</b>	0.415	107.304	0.972	2. Enantiomer
3	1	18.468	45.320 <b>45.320</b>	0.394	1.347	0.903	

ee = 62.4 %

Cut# : 2



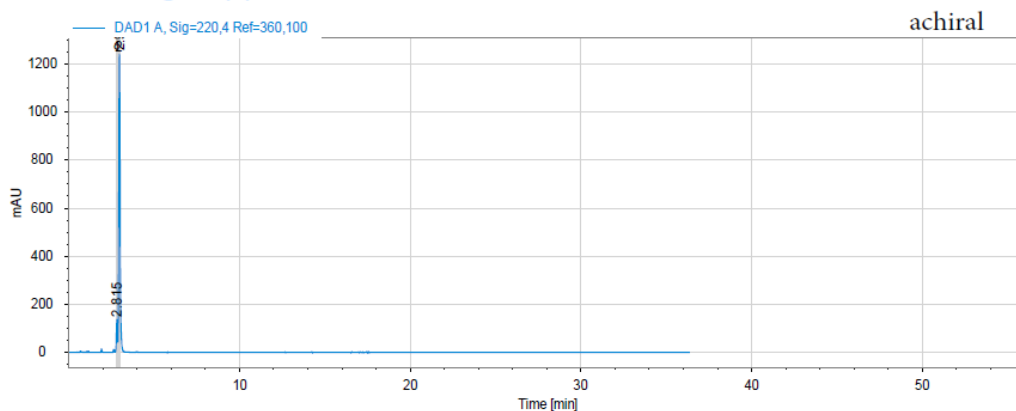
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
4	2	8.761	21.189 <b>21.189</b>	0.150	1.670	0.963	
5	2	12.742	16521.346 <b>16521.346</b>	0.373	669.616	0.802	1. Enantiomer
6	2	16.879	58.129 <b>58.129</b>	0.356	1.920	1.021	
7	2	22.027	8544.605 <b>8544.605</b>	0.546	186.427	0.856	2. Enantiomer

ee = 31.8 %

*rac-3y*: (2D-Separation) 1. 50 mm Eclipse Plus C18 1.8  $\mu\text{m}$ , 4.6 mm, methanol/water gradient 80% – 3' – 100% MeOH, 1.0 mL/min, 46.4 MPa, 308 K, 220 nm,  $t_R$  (*endo*) = 2.94 min,  $t_R$  (*exo*) = 2.80 min; 2. 150 mm Amycoat RP, 4.6 mm, acetonitrile/water 50:50, 1.0 ml/min, 20.6 MPa, 298 K, 220 nm. The racemic sample was prepared with procedure B. The major diastereomer was assigned to be the endo-product.

### <sup>1</sup>D chromatogram(s)



### Sampling table (<sup>1</sup>D)

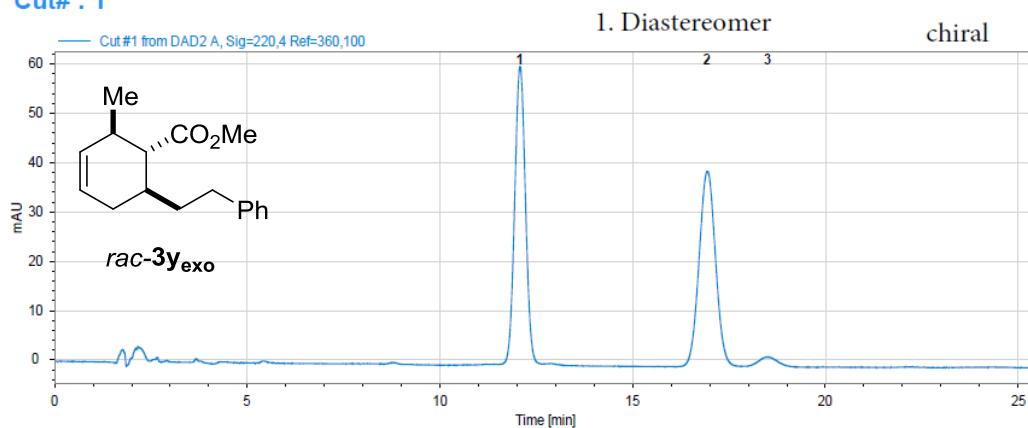
Cut group	Cut #	<sup>1</sup> D Cut start [min]	<sup>1</sup> D Ret. time [min]	<sup>1</sup> D Duration [min]	Trigger	<sup>2</sup> D Run start [min]
	1	2.80	2.815	0.04	Time	2.84
	2	2.94	2.960	0.04	Time	30.65

### Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	<sup>1</sup> D Sampling range [min]	Ret.Time <sup>2</sup> D [min]	Area	Area%	chiral
1	2.80 - 2.84	12.078	1165.488	3.126	1. Diastereomer 1. Enantiomer
2	2.80 - 2.84	16.942	1168.363	3.134	1. Diastereomer 2. Enantiomer
3	2.80 - 2.84	18.503	67.140	0.180	
4	2.94 - 2.98	3.787	37.170	0.100	
5	2.94 - 2.98	12.784	16486.652	44.218	2. Diastereomer 1. Enantiomer
6	2.94 - 2.98	16.477	38.338	0.103	
7	2.94 - 2.98	21.987	18321.785	49.140	2. Diastereomer 2. Enantiomer

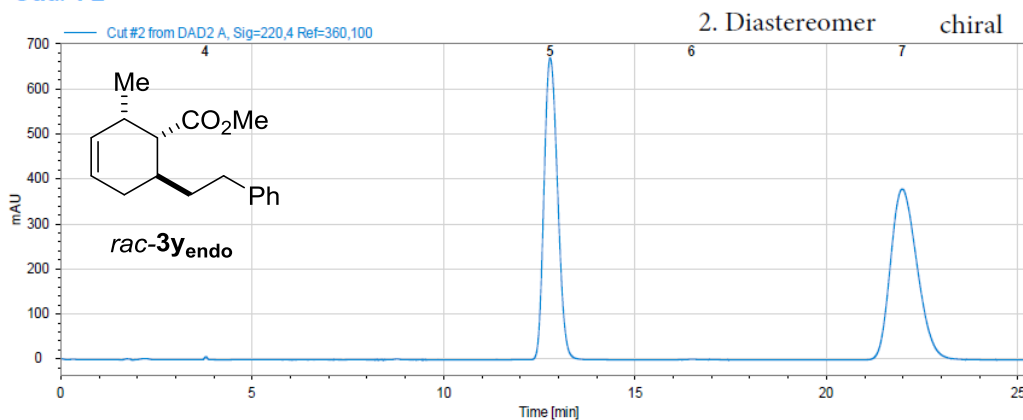
Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	12.078	1165.488 <b>1165.488</b>	0.281	60.370	0.966	1. Enantiomer
2	1	16.942	1168.363 <b>1168.363</b>	0.351	39.578	1.013	2. Enantiomer
3	1	18.503	67.140 <b>67.140</b>	0.395	2.005	0.877	

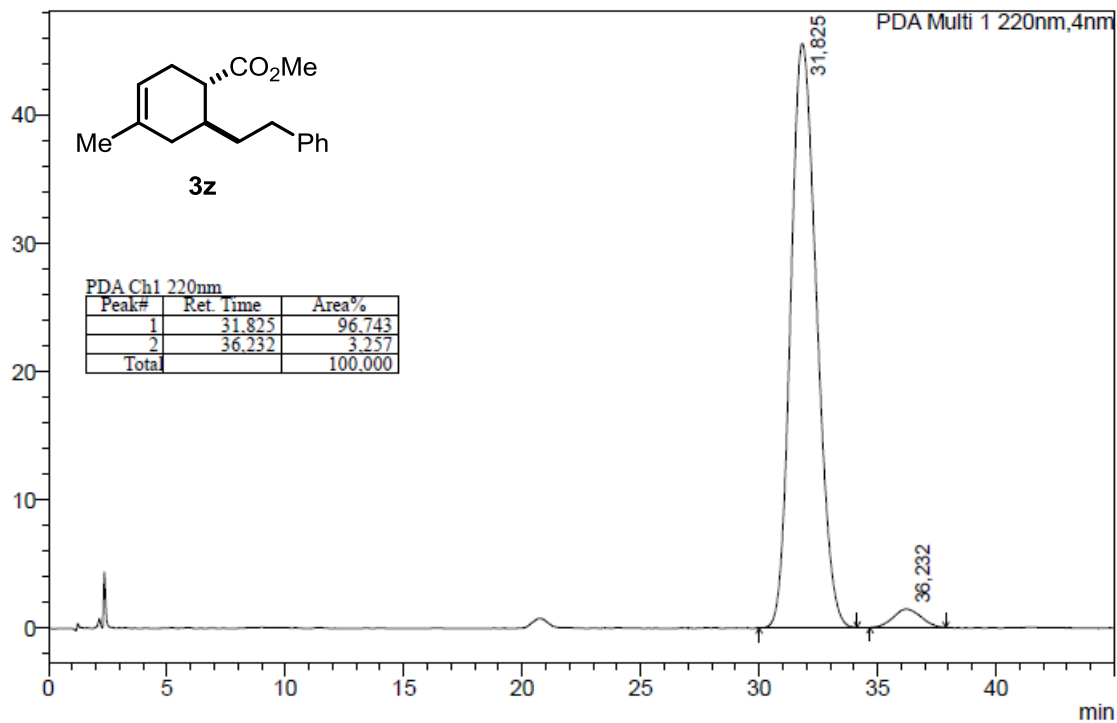
Cut# : 2



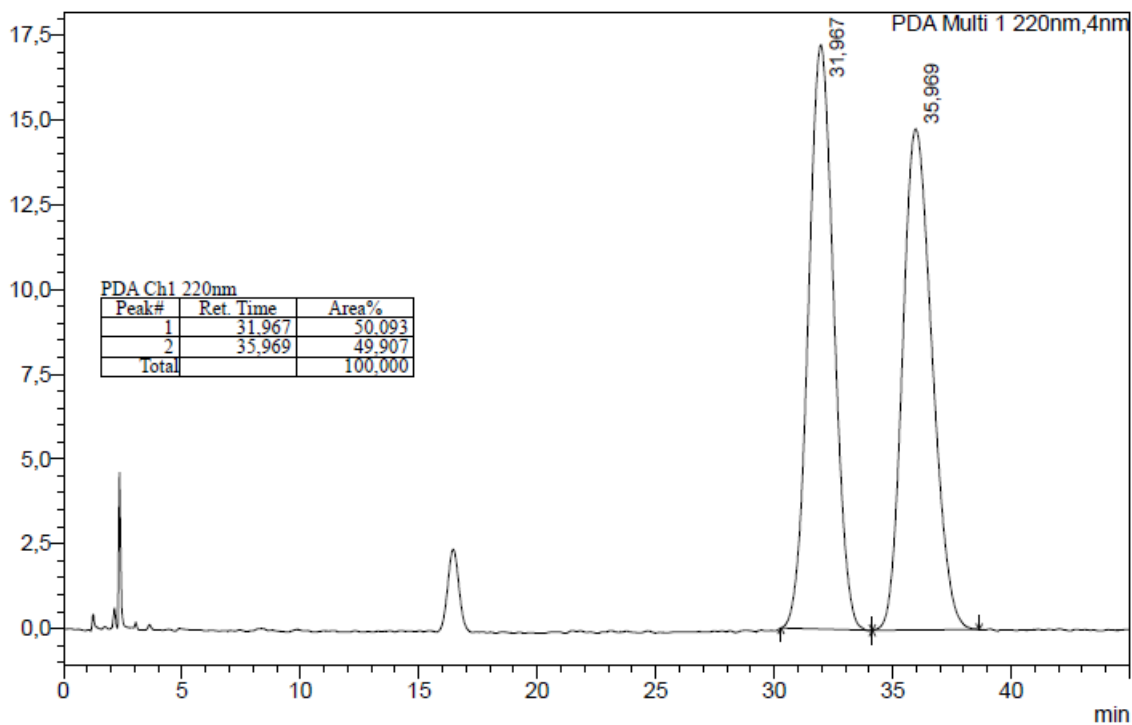
Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
4	2	3.787	37.170 <b>37.170</b>	0.083	6.899	0.947	
5	2	12.784	16486.652 <b>16486.652</b>	0.374	670.481	0.791	1. Enantiomer
6	2	16.477	38.338 <b>38.338</b>	0.383	1.171	0.636	
7	2	21.987	18321.785 <b>18321.785</b>	0.566	379.295	0.780	2. Enantiomer

Enantioenriched sample of **3z**:  
e.r. = 97:3; r.r. (*para/meta*) > 50:1.  
mAU

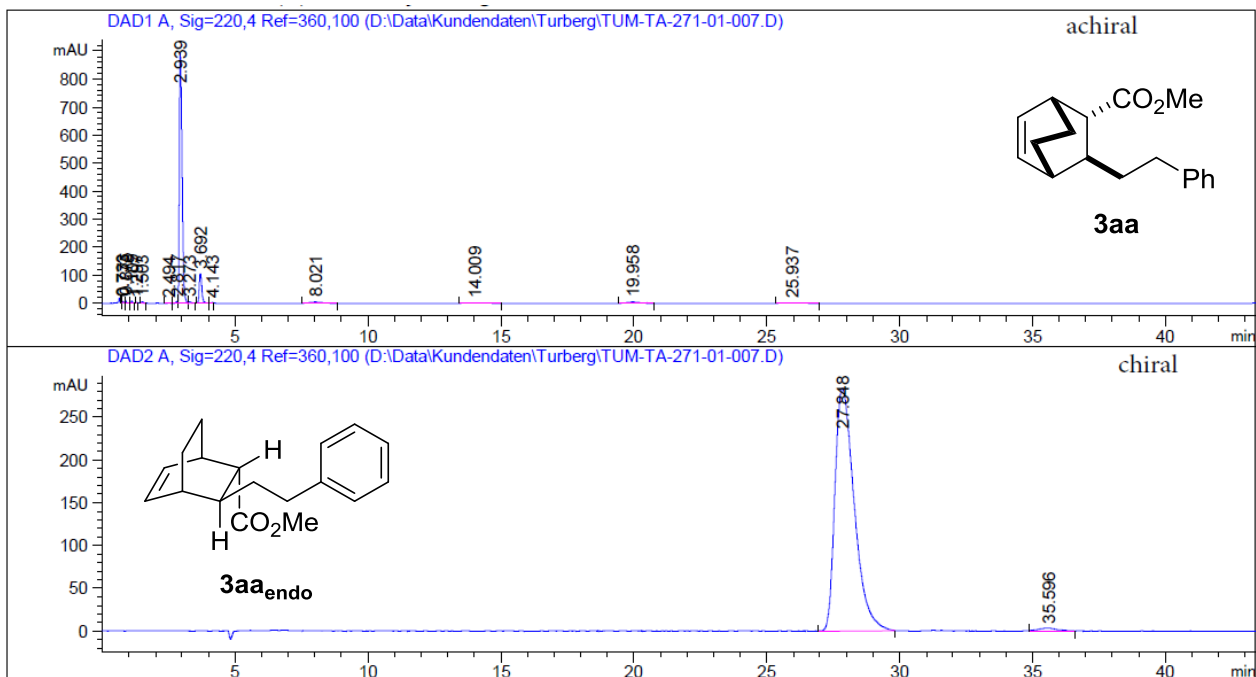


*rac*-**3z**: Daicel Chiralcel IC-3R, MeOH/H<sub>2</sub>O = 70:30, 1 mL/min, 25 °C, 220 nm.  
mAU



Enantioenriched sample of **3aa**:

$e.r._{endo} = 98.5:1.5$ ,  $e.r._{exo} = 92.5:7.5$ ,  $d.r. (endo/exo) = 13:1$ .



chiral

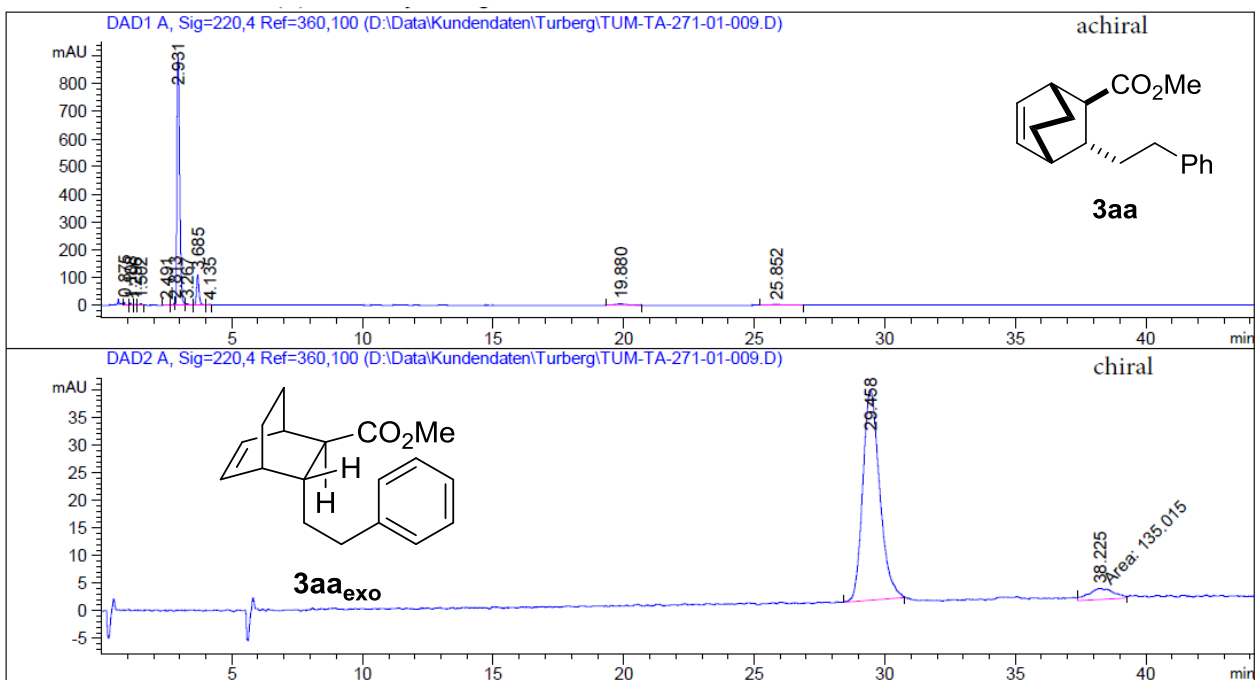
Signal 2: DAD2 A, Sig=220,4 Ref=360,100

1. Diastereomer

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
1	27.848	BB	0.5918	1.43283e4	283.64984	98.6854	1. Enantiomer
2	35.596	VV	0.6700	190.86609	3.34616	1.3146	2. Enantiomer

ee = 97.4 %

Totals : 1.45191e4 286.99600



Signal 2: DAD2 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
1	29.458	BB	0.5280	1711.58411	37.99856	92.6885	1. Enantiomer
2	38.225	MM	1.1053	135.01486	2.03589	7.3115	2. Enantiomer

ee = 85.4 %

Totals : 1846.59897 40.03445

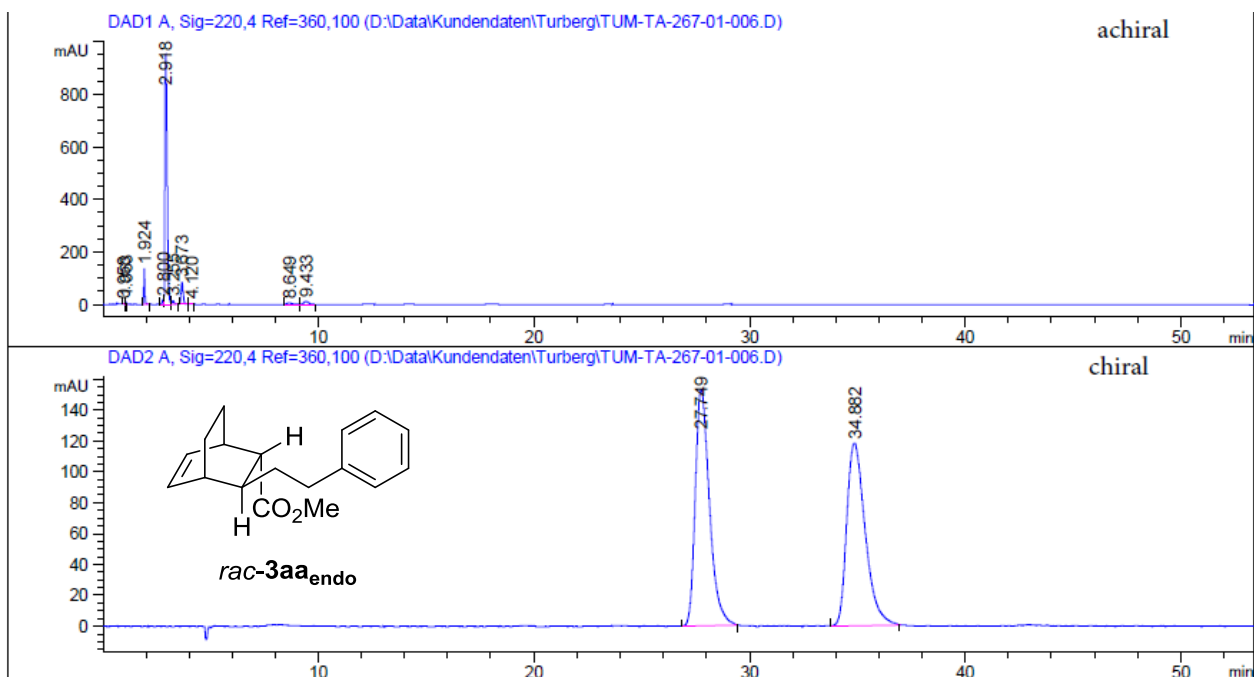
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
1	0.875	VV	0.0268	17.36311	9.96850	0.2264	
2	1.108	VB	0.0347	20.76262	8.88980	0.2708	
3	1.296	BV	0.0405	6.41228	2.45634	0.0836	
4	1.502	VV	0.0830	28.88373	5.61605	0.3767	
5	2.491	BV	0.0728	9.63442	1.96141	0.1256	
6	2.813	VV	0.0542	26.89859	7.60936	0.3508	
7	2.931	VV	0.1168	6573.22510	904.28802	85.7224	1. Diastereomer
8	3.267	VB	0.1017	34.16027	4.90871	0.4455	
9	3.685	BV	0.0992	725.09039	108.16921	9.4560	2. Diastereomer
10	4.135	VBA	0.0839	9.50229	1.76325	0.1239	
11	19.880	BB	0.3652	130.95526	4.20610	1.7078	
12	25.852	BB	0.5014	85.14802	1.99112	1.1104	

achiral

Totals : 7668.03609 1061.82787

*rac-3aa*: (2D-Separation) 1. 50 mm Eclipse PAH 1.8  $\mu$ m, 4.6 mm, methanol/water 75:25, 1.0 mL/min, 51.1 MPa, 308 K, 220 nm,  $t_R$  (*endo*) = 2.93 min,  $t_R$  (*exo*) = 3.69 min; 2. 150 mm Chiralcel OJ-3R, 4.6 mm, methanol/water 80:20, 1.0 mL/min, 33.6 MPa, 298 K, 220 nm. The racemic sample was prepared with procedure B.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

achiral

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
1	0.958	VV	0.0318	6.32877	2.91723	0.0751	
2	1.063	VV	0.0336	25.35197	11.33634	0.3007	
3	1.924	BB	0.0561	498.07574	136.45403	5.9087	
4	2.800	VV	0.0590	69.10846	17.91934	0.8198	
5	2.918	VV	0.1016	6897.98633	951.74323	81.8306	1. Diastereomer
6	3.255	VB	0.1027	89.26076	12.98814	1.0589	2. Diastereomer
7	3.673	BV	0.1058	566.25397	82.23016	6.7175	
8	4.120	VBA	0.0957	18.78285	3.14450	0.2228	
9	8.649	BB	0.2253	95.12035	5.51183	1.1284	
10	9.433	BB	0.2225	163.32018	10.88691	1.9375	

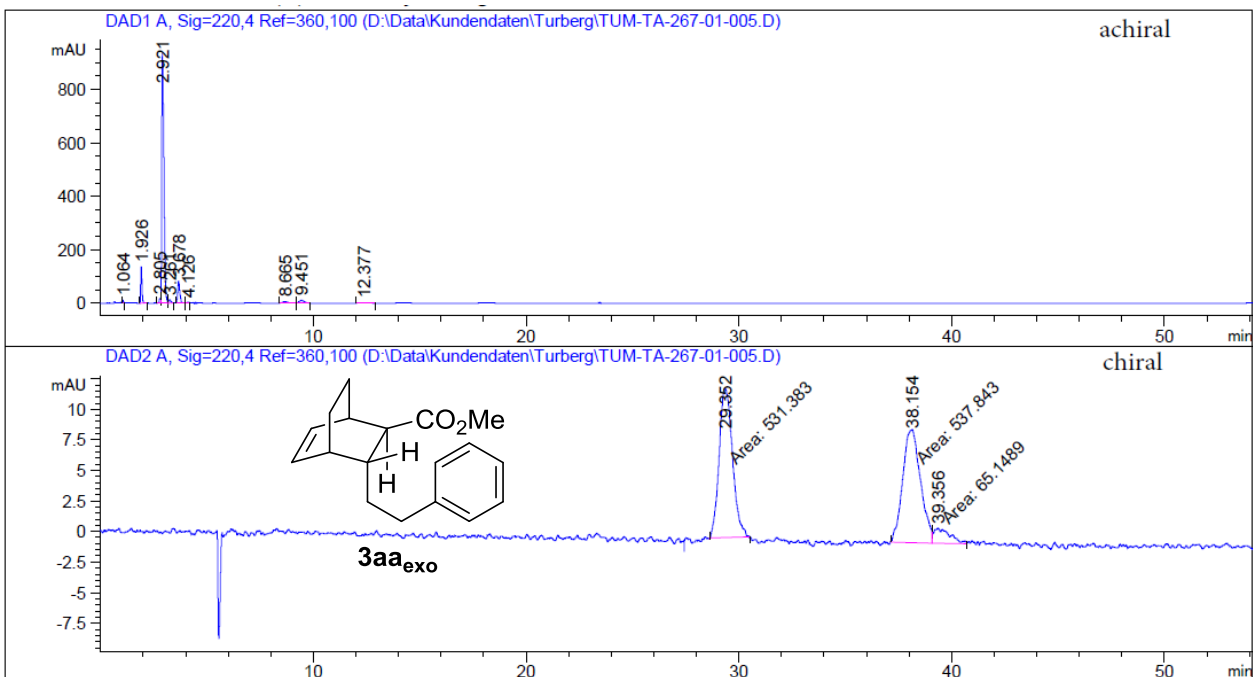
Totals : 8429.58938 1235.13169

Signal 2: DAD2 A, Sig=220,4 Ref=360,100

chiral

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	1. Diastereomer
1	27.749	VB	0.5453	7009.80957	153.20244	49.8684	1. Enantiomer
2	34.882	VB	0.7069	7046.81250	118.30661	50.1316	2. Enantiomer

Totals : 1.40566e4 271.50905



Signal 2: DAD2 A, Sig=220,4 Ref=360,100

2. Diastereomer

chiral

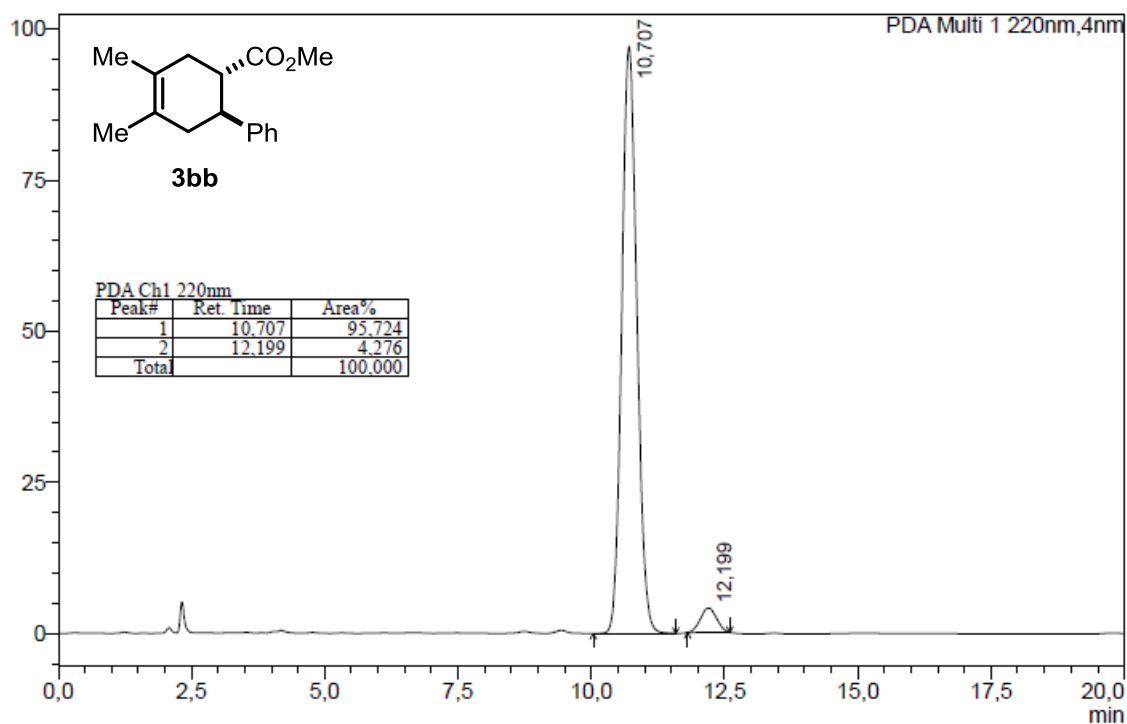
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	1. Diastereomer
1	29.352	MM	0.7267	531.38312	12.18673	46.8437	1. Enantiomer
2	38.154	MF	0.9689	537.84344	9.25179	47.4132	2. Enantiomer
3	39.356	FM	0.8635	65.14893	1.25748	5.7432	

Totals : 1134.37550 22.69600

Enantioenriched sample of **3bb**:

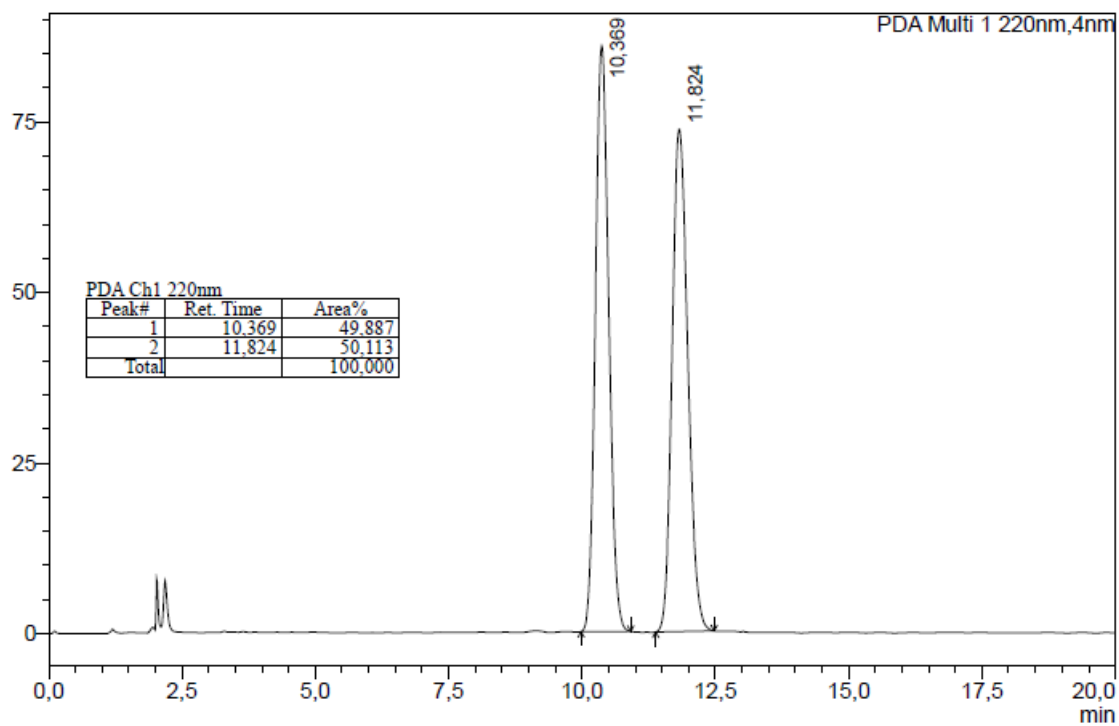
e.r. = 96:4.

mAU



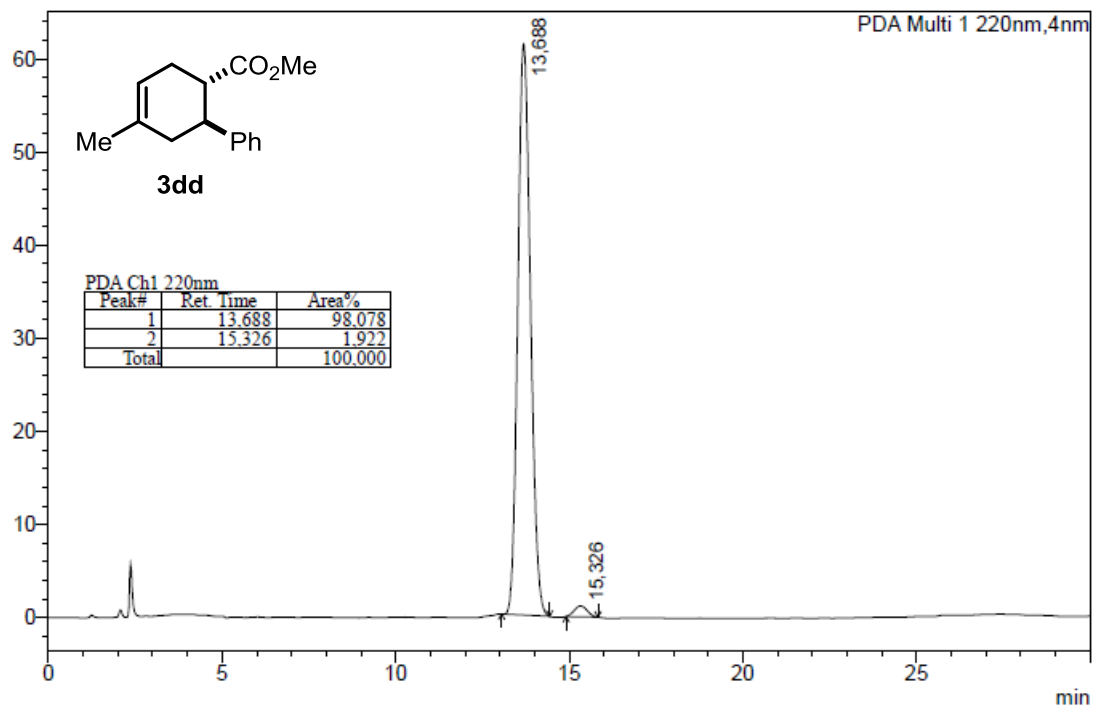
*rac*-**3bb**: Daicel Chiralcel OD-3R, MeOH/H<sub>2</sub>O = 80:20, 1 mL/min, 25 °C, 220 nm.

mAU



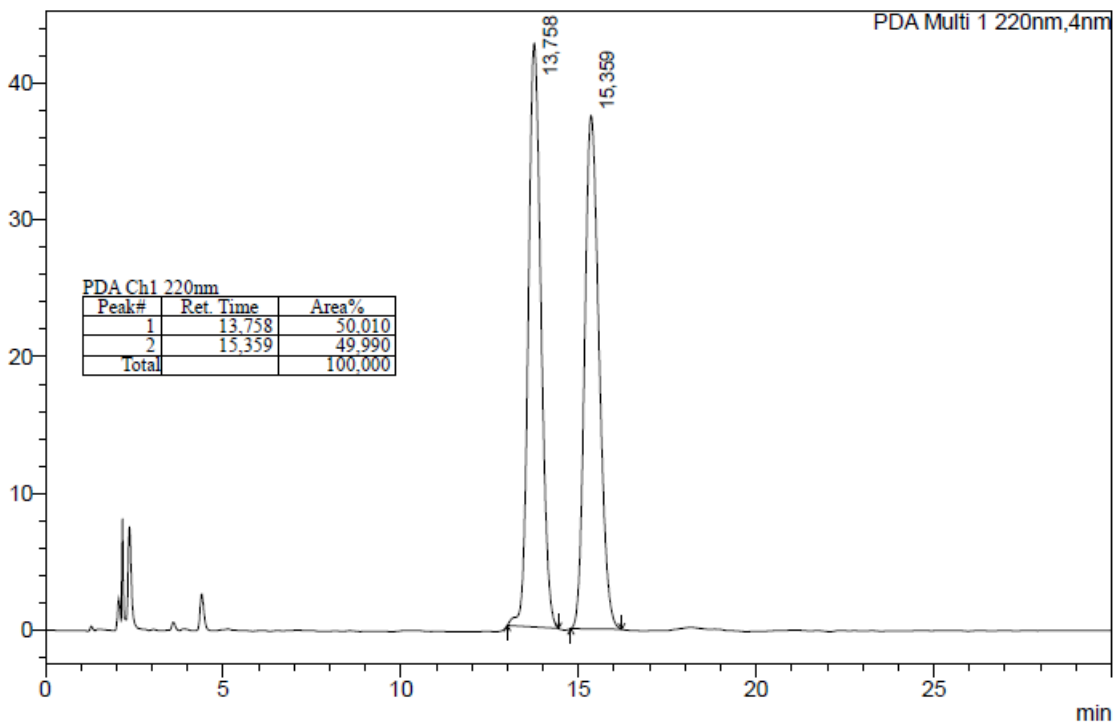
Enantioenriched sample of **3dd**:  
e.r. = 98:2; r.r. (*para/meta*) > 50:1.

mAU



*rac*-**3dd**: Daicel Chiralcel OD-3R, MeOH/H<sub>2</sub>O = 75:25, 1 mL/min, 25 °C, 220 nm.

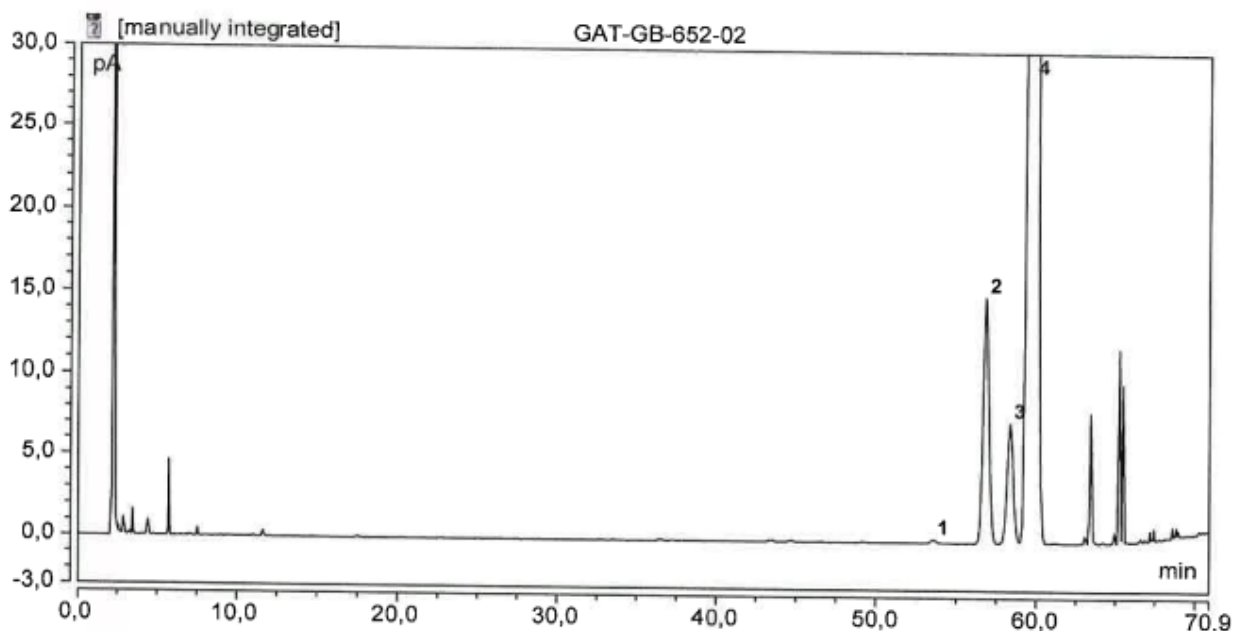
mAU



# GC Traces

Enantioenriched sample of **3q**:

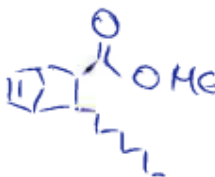
e.r.<sub>endo</sub> = 97.5:2.5, e.r.<sub>exo</sub> = 98.5:1.5, d.r. (endo/exo) = 19:1.



Sample: **GAT-GB-652-02**  
 Sequenz: **4453 GAT-GB RO**  
 Sequenz date: **27.03.18**

Instrument: **GC\_313**  
 Measured: **28.03.18 11:06**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

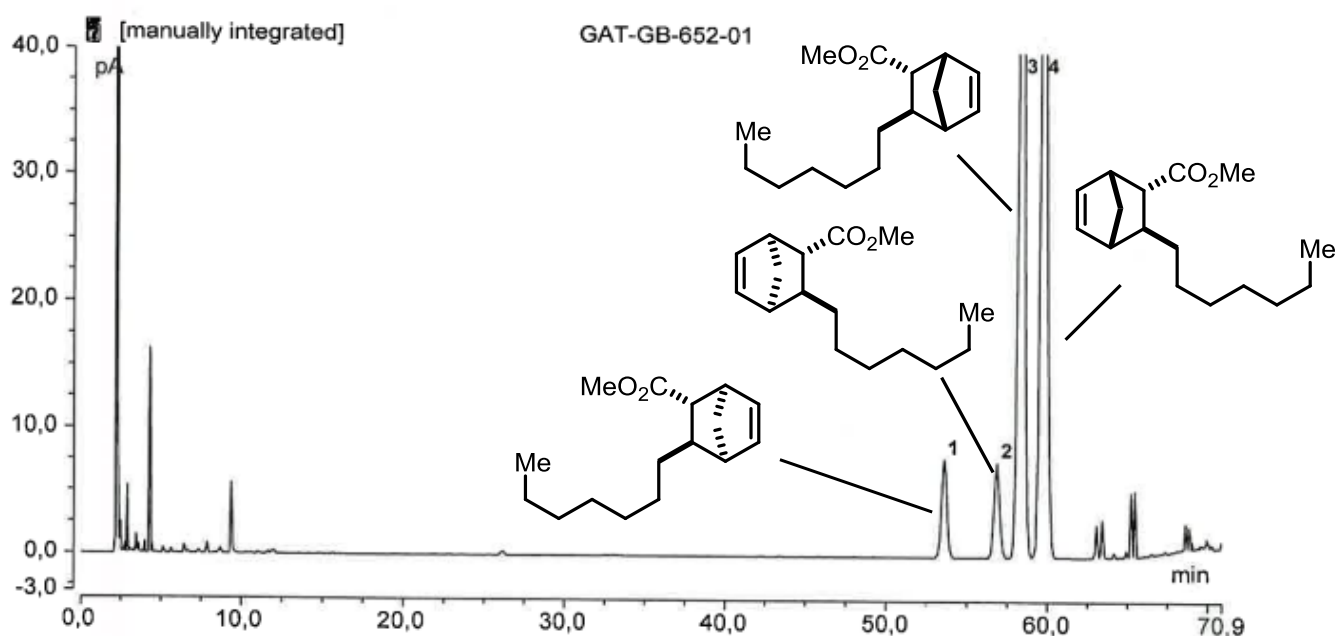
No.	Ret.Time min	area-% %	Peak Name
1	53,63	0,06	
2	56,83	4,76	
3	58,37	2,47	
4	59,78	92,70	



Instrument parameters:

Column: 30,0 m BGB 176/BGB 15 G 618  
 Temperature: 230 140 60 MIN ISO 9/MIN 220 2 MIN ISO 350  
 Gas: 0,50 bar H2  
 Sample size: 1,0 µL

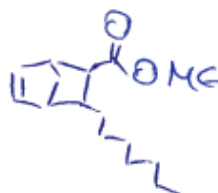
*rac*-3q: The racemic sample was prepared with procedure B.



Sample: **GAT-GB-652-01**  
 Sequenz: **4453 GAT-GB RO**  
 Sequenz date: **27.03.18**

Instrument: **GC\_313**  
 Measured: **27.03.18 14:29**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	53,61	4,98	
2	56,87	4,86	
3	58,39	44,83	
4	59,72	45,32	

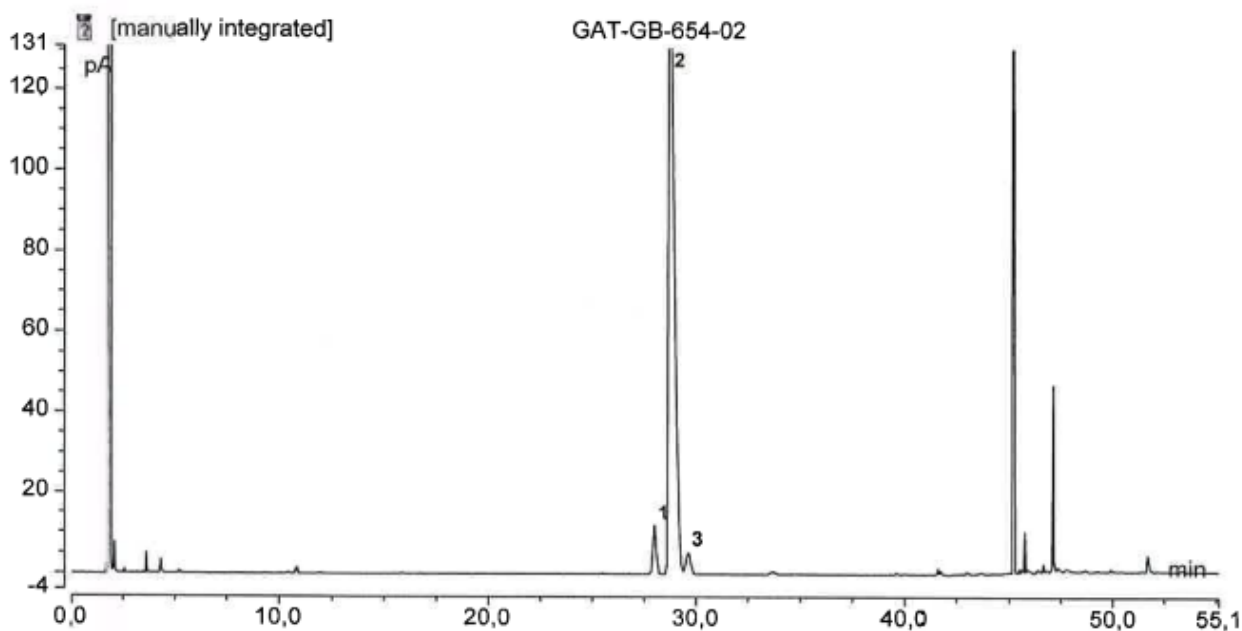


Instrument parameters:

Column: 30,0 m BGB 176/BGB 15 G 618  
 Temperature: 230 140 60 MIN ISO 9/MIN 220 2 MIN ISO 350  
 Gas: 0,50 bar H2  
 Sample size: 1,0 µL

Enantioenriched sample of **3r**:

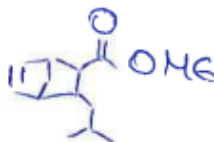
e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = n.d., d.r. (*endo/exo*) = 23:1.



Sample: GAT-GB-654-02  
Sequenz: 4455 GAT-GB RO  
Sequenz date: 26.03.18

Instrument: GC\_313  
Measured: 28.03.18 10:05  
Processing M.: MPI  
Report-File: Übersichtsanalyse

No.	Ret.Time min	area-% %	Peak Name
1	28,01	4,12	
2	28,73	93,20	
3	29,63	2,68	

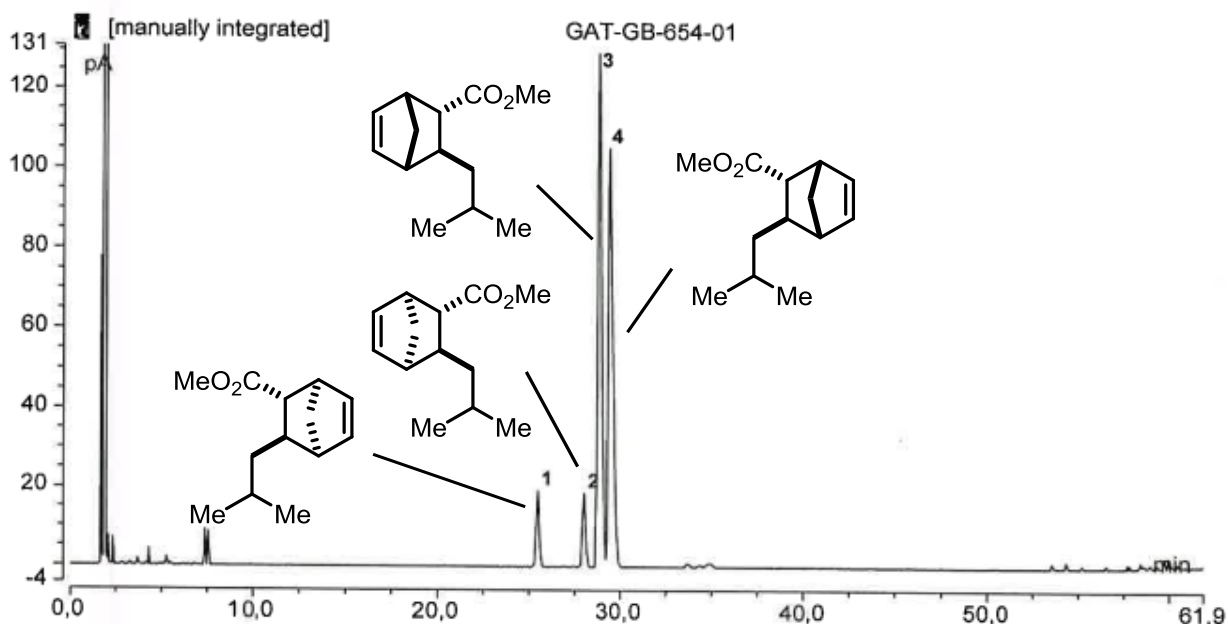


Instrument parameters:

Column: 30,0 m BGB 176/BGB 15 G 618  
Temperature: 230 110 35 MIN ISO 9/MIN 220 3 MIN ISO 350  
Gas: 0,60 bar H2  
Sample size: 1,0 µL

Handwritten signature or initials.

**rac-3r:** The racemic sample was prepared with procedure B.

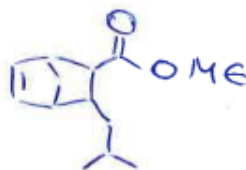


Sample:  
Sequenz:  
Sequenz date:

**GAT-GB-654-01**  
**4455 GAT-GB RO**  
**26.03.18**

Instrument: **GC\_313**  
Measured: **27.03.18 07:38**  
Processing M.: **MPI**  
Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	25,49	5,03	
2	28,01	5,04	
3	28,79	44,99	
4	29,38	44,93	

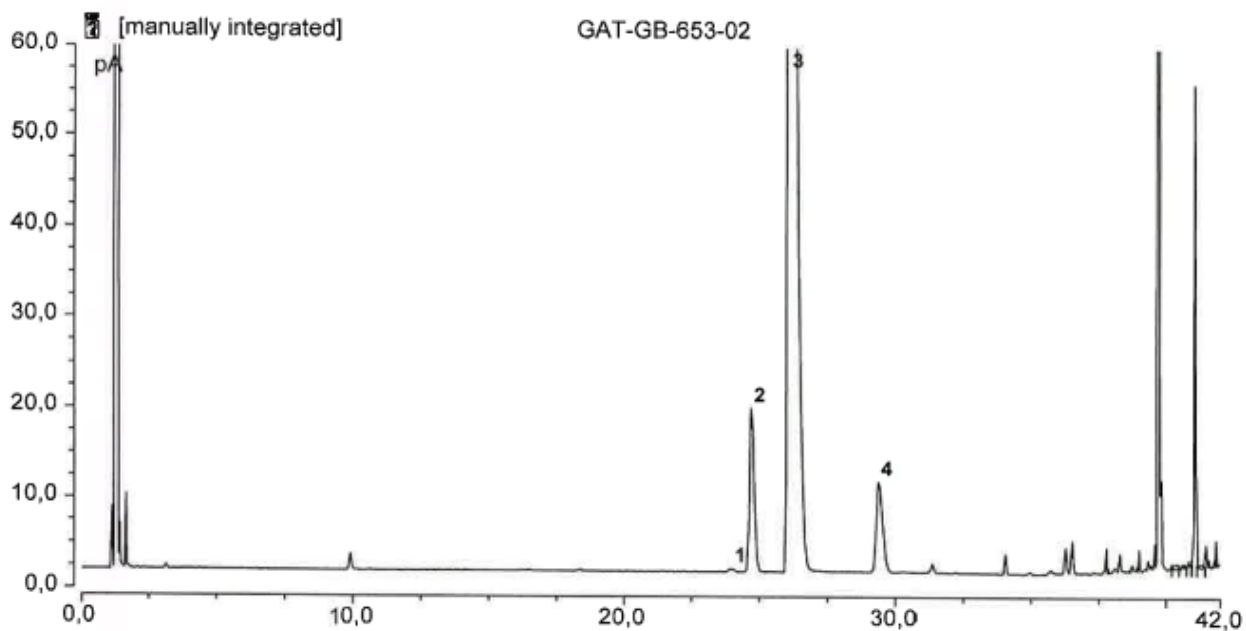


Instrument parameters:

Column: 30,0 m BGB 176/BGB 15 G 618  
Temperature: 230 110 50 MIN ISO 9/MIN 220 3 MIN ISO 350  
Gas: 0,60 bar H2  
Sample size: 1,0 µL

Enantioenriched sample of **3s**:

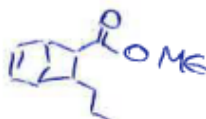
e.r.<sub>endo</sub> = 96.5:3.5, e.r.<sub>exo</sub> = 99:1, d.r. (*endo/exo*) = 21:1.



Sample: **GAT-GB-653-02**  
Sequenz: **4454 GAT-GB RO**  
Sequenz date: **27.03.18**

Instrument: **GC\_112**  
Measured: **27.03.18 14:14**  
Processing M.: **MPI**  
Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	23,96	0,04	
2	24,71	4,52	
3	26,06	91,97	
4	29,40	3,46	

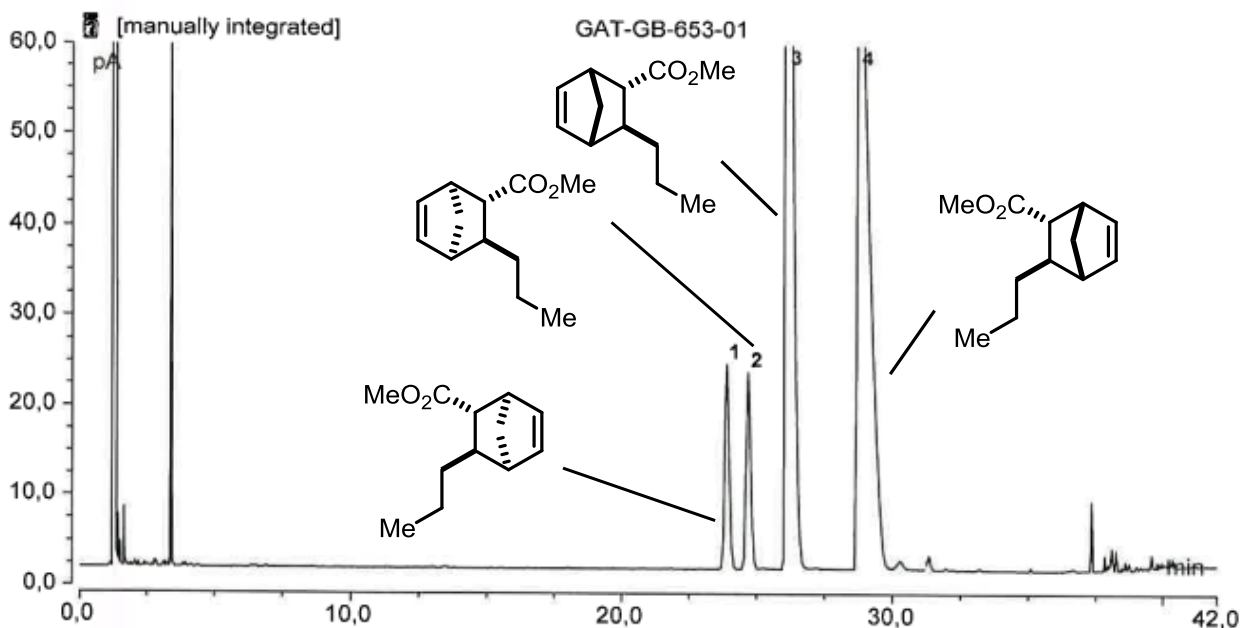


Instrument parameters:

Column: 30,0 m G-TA 0,25/?df ; G/448  
Temperature: 230 80 30 MIN ISO 9/MIN 170 2 MIN ISO 350  
Gas: 0,90 bar Hydrogen  
Sample size: 1,0 µL

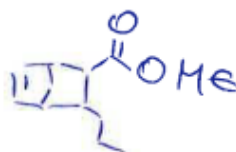
RO

*rac-3s*: The racemic sample was prepared with procedure B.



Sample: **GAT-GB-653-01** Instrument: **GC\_112**  
 Sequenz: **4454 GAT-GB RO** Measured: **27.03.18 10:12**  
 Sequenz date: **27.03.18** Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

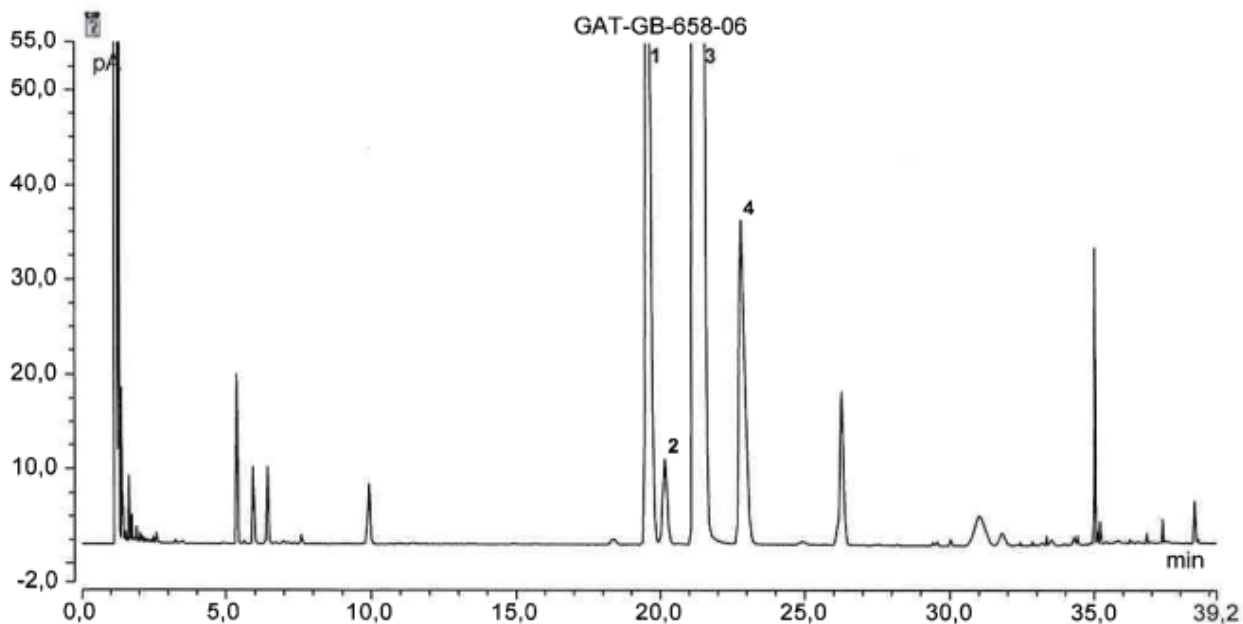
No.	Ret. Time min	area-% %	Peak Name
1	23,89	4,99	
2	24,68	5,03	
3	26,09	44,99	
4	28,72	44,99	



Instrument parameters:  
 Column: 30,0 m G-TA 0,25/?df ; G/448  
 Temperature: 230 80 30 MIN ISO 9/MIN 170 2 MIN ISO 350  
 Gas: 0,90 bar Hydrogen  
 Sample size: 1,0 µL

Enantioenriched sample of **3t**:

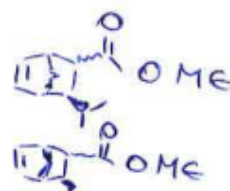
e.r.<sub>endo</sub> = 95.5:4.5, e.r.<sub>exo</sub> = 92:8, d.r. (endo/exo) = 9:1.



Sample: **GAT-GB-658-06**  
 Sequenz: **4640 GAT-GB RO**  
 Sequenz date: **14.05.18**

Instrument: **GC\_112**  
 Measured: **14.05.18 09:33**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	19,57	9,37	$\left. \begin{array}{l} \text{EXO} \\ \text{ENDO} \end{array} \right\} \begin{array}{l} \text{[Structure 1]} \\ \text{[Structure 2]} \end{array}$
2	20,17	0,81	
3	21,45	85,80	
4	22,81	4,02	

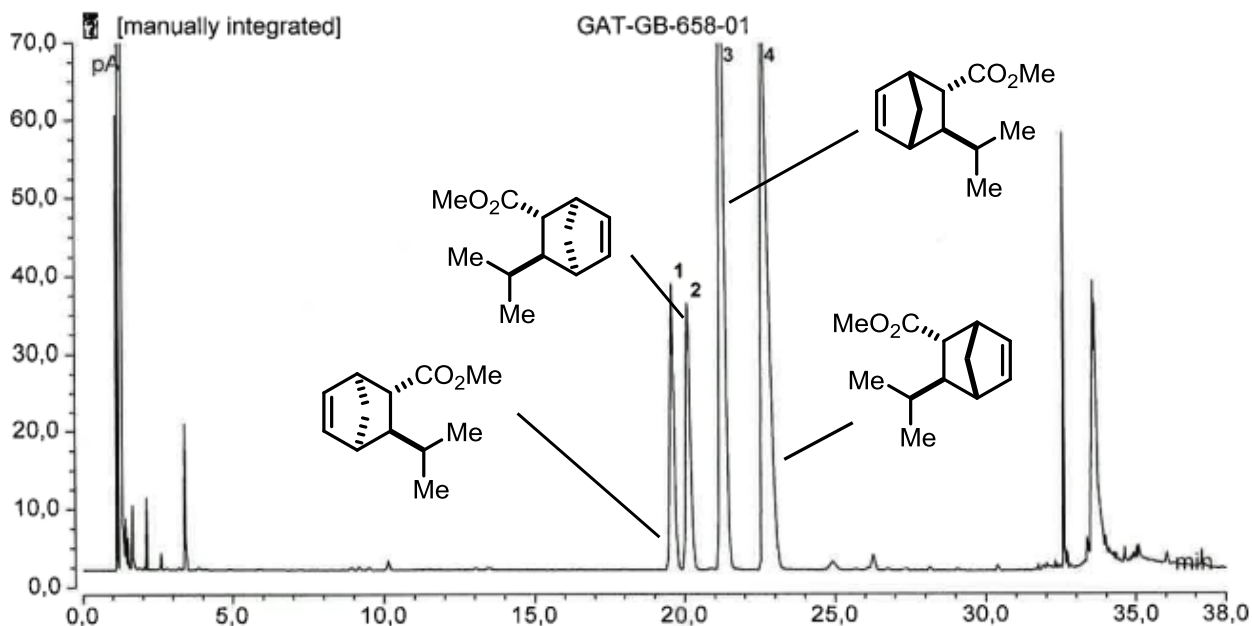


Instrument parameters:

Column: 30,0 m G-TA 0,25/?df ; G/448  
 Temperature: 230 80 25 MIN ISO 8/MIN 170 3 MIN ISO 350  
 Gas: 0,90 bar Hydrogen  
 Sample size: 1,0 µL

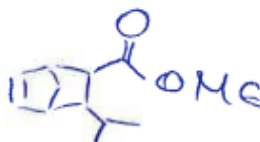
Handwritten signature or initials.

**rac-3t:** The racemic sample was prepared with procedure B.



Sample: **GAT-GB-658-01** Instrument: **GC\_112**  
 Sequenz: **4458 GAT-GB RO** Measured: **26.03.18 10:53**  
 Sequenz date: **26.03.18** Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

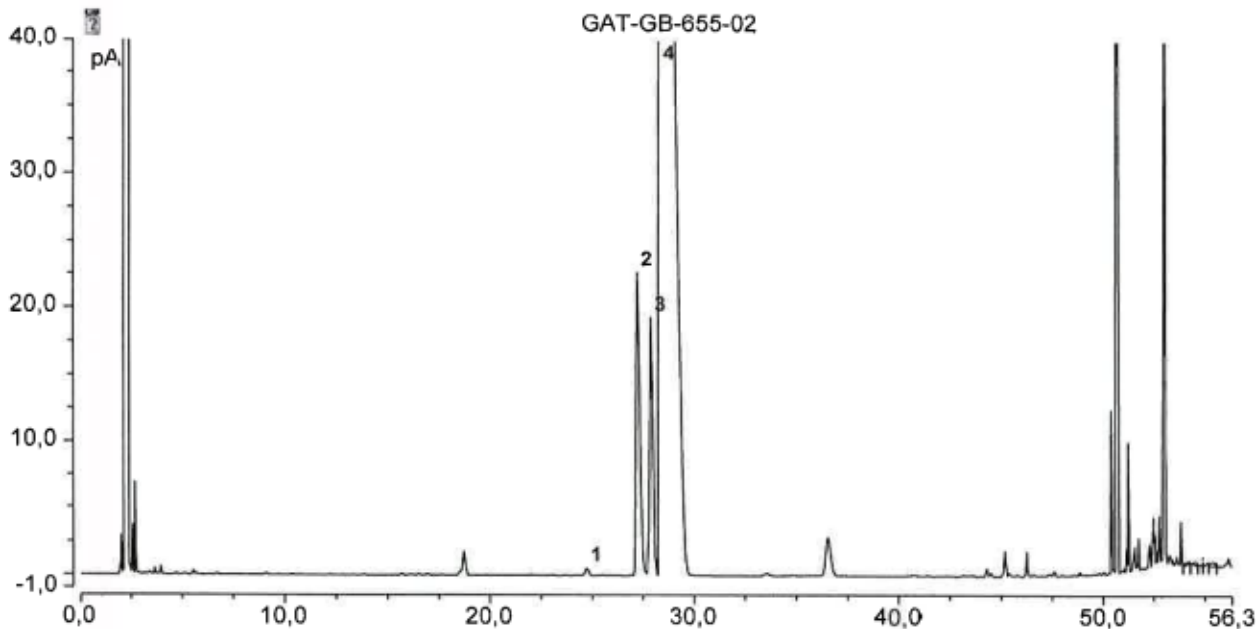
No.	Ret. Time min	area-% %	Peak Name
1	19,59	10,89	
2	20,12	10,85	
3	21,25	39,15	
4	22,63	39,12	



Instrument parameters:  
 Column: 30,0 m G-TA 0,25/?df ; G/448  
 Temperature: 230 80 25 MIN ISO 9/MIN 170 3 MIN ISO 350  
 Gas: 0,90 bar Hydrogen  
 Sample size: 1,0 µL

Enantioenriched sample of **3u**:

$e.r._{endo} = 95.5:4.5$ ,  $e.r._{exo} = 97.5:2.5$ , d.r. (*endo/exo*) = 16:1.



Sample: **GAT-GB-655-02**  
Sequenz: **4456 GAT-GB RO**  
Sequenz date: **23.03.18**

Instrument: **GC\_313**  
Measured: **28.03.18 07:40**  
Processing M.: **MPI**  
Report-File: **Übersichtsanalyse**

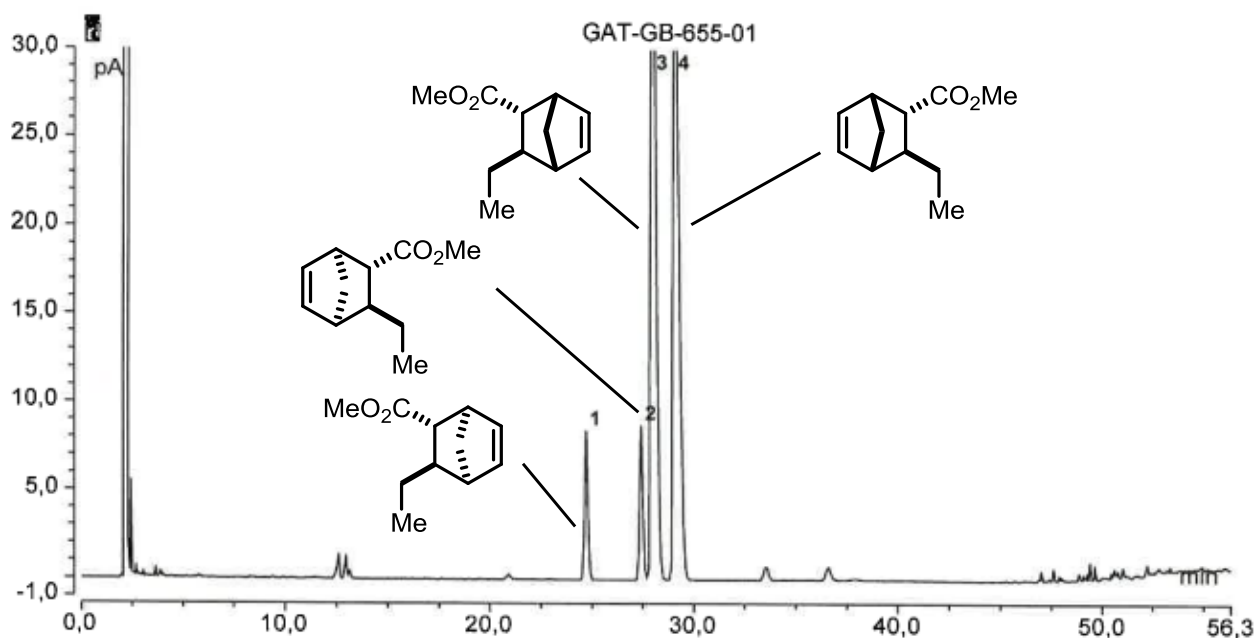
No.	Ret.Time min	area-% %	Peak Name
1	24,74	0,14	
2	27,24	5,61	
3	27,90	4,34	
4	28,34	89,91	



Instrument parameters:

Column: 30,0 m BGB 176/BGB !5 G 618  
Temperature: 230 100 40 MIN ISO 9/MIN 220 3 MIN ISO 350  
Gas: 0,50 bar H2  
Sample size: 1,0 µL

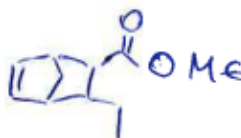
*rac*-**3u**: The racemic sample was prepared with procedure B.



Sample: **GAT-GB-655-01**  
 Sequenz: **4456 GAT-GB RO**  
 Sequenz date: **23.03.18**

Instrument: **GC\_313**  
 Measured: **23.03.18 09:05**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	24,70	5,45	
2	27,41	5,55	
3	27,93	44,54	
4	29,02	44,46	

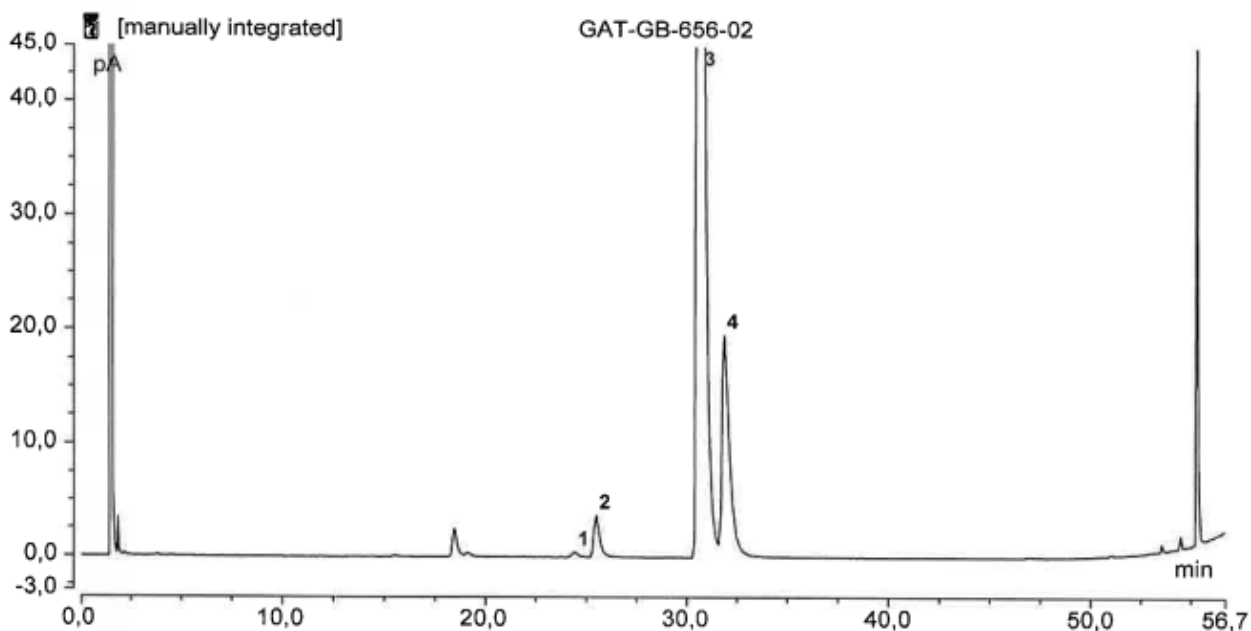


Instrument parameters:

Column: 30,0 m BGB 176/BGB I5 G 618  
 Temperature: 230 100 40 MIN ISO 9/MIN 220 3 MIN ISO 350  
 Gas: 0,50 bar H2  
 Sample size: 1,0 µL

Enantioenriched sample of **3v**:

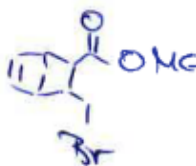
e.r.<sub>endo</sub> = 87:13, e.r.<sub>exo</sub> = 90:10, d.r. (*endo/exo*) = 48:1.



Sample: **GAT-GB-656-02**  
Sequenz: **4457 GAT-GB RO**  
Sequenz date: **23.03.18**

Instrument: **GC\_212**  
Measured: **28.03.18 10:42**  
Processing M.: **MPI**  
Report-File: **Übersichtsanalyse**

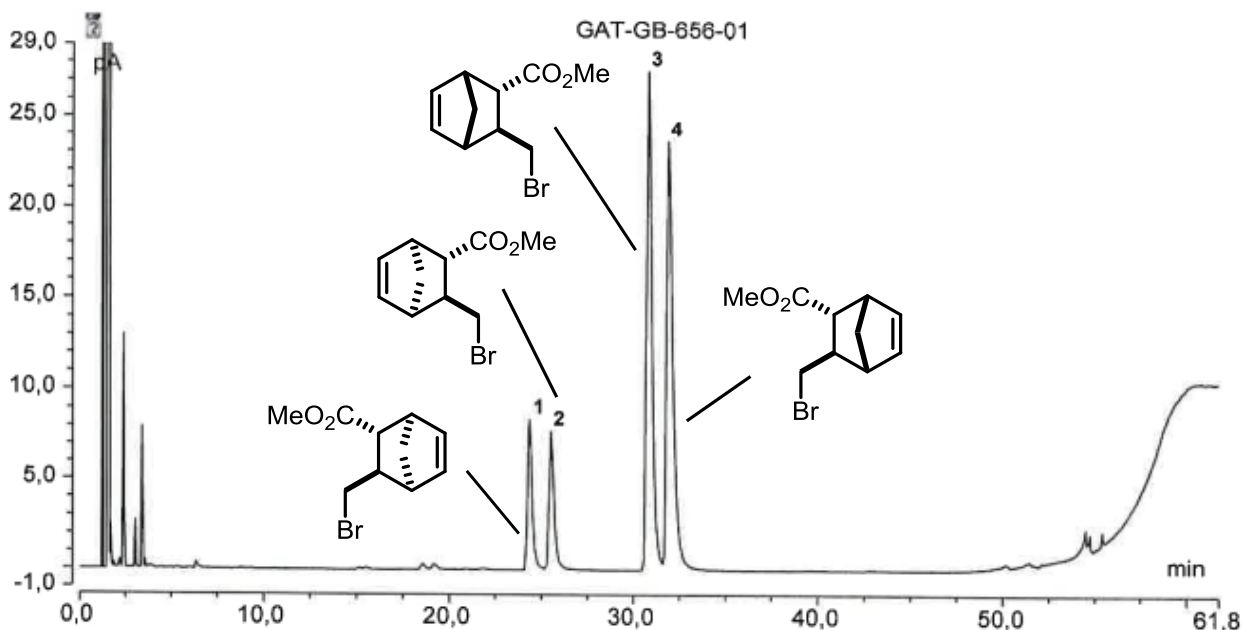
No.	Ret.Time min	area-% %	Peak Name
1	24,41	0,21	
2	25,49	1,82	
3	30,69	85,22	
4	31,87	12,75	



Instrument parameters:

Column: 25,0 m LIPODEX E G 644  
Temperature: 230 110 45 MIN ISO 8/MIN 220 3 MIN ISO350  
Gas: 0,40 bar H2  
Sample size: 1,0 µL

*rac-3v*: The racemic sample was prepared with procedure B.



Sample: **GAT-GB-656-01**  
 Sequenz: **4457 GAT-GB RO**  
 Sequenz date: **23.03.18**

Instrument: **GC\_212**  
 Measured: **23.03.18 09:28**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

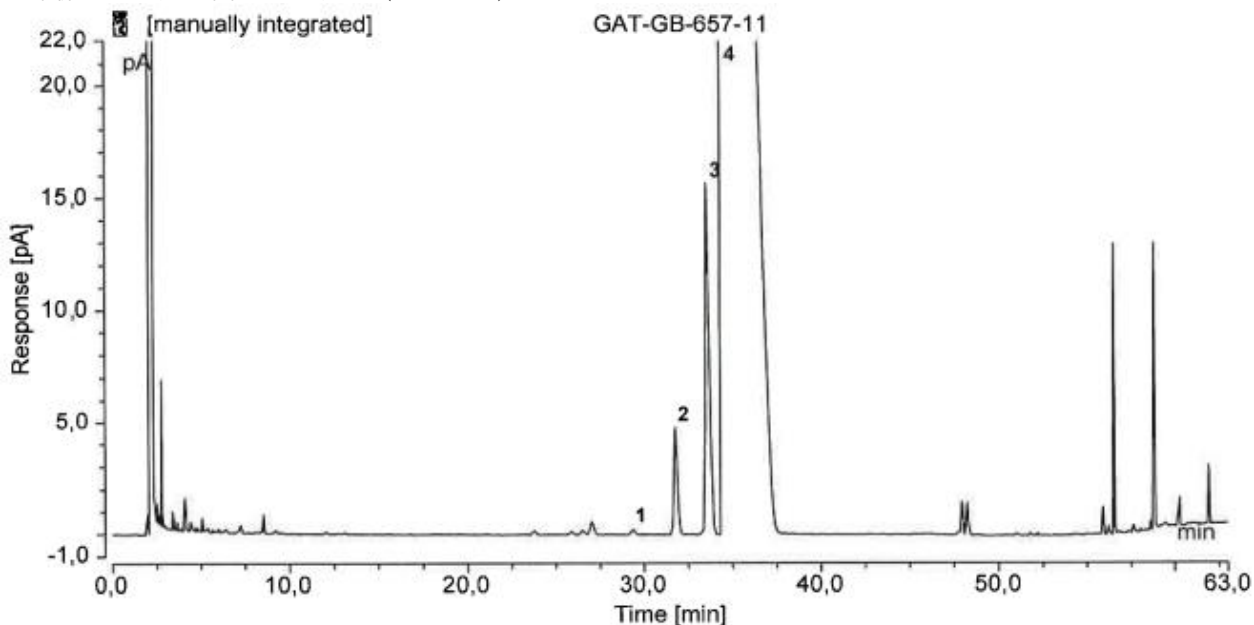
No.	Ret.Time min	area-% %	Peak Name
1	24,35	10,10	
2	25,52	10,21	
3	30,81	39,46	
4	31,89	40,23	

Instrument parameters:  
 Column: 25,0 m LIPODEX E G 644  
 Temperature: 230 110 45 MIN ISO 8/MIN 220 3 MIN ISO350  
 Gas: 0,40 bar H2  
 Sample size: 1,0 µL

*Handwritten signature*

Enantioenriched sample of **3w**:

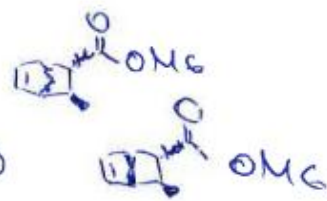
e.r.<sub>endo</sub> = 97:3, e.r.<sub>exo</sub> = 95:5, d.r. (endo/exo) = >50:1.



Sample: **GAT-GB-657-11**  
 Sequenz: **4532 GAT-GB RO**  
 Sequenz date: **10.04.18**

Instrument: **GC\_313**  
 Measured: **10.04.18 14:12**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	29,37	0,04	EXO
2	31,77	0,80	
3	33,56	2,92	
4	34,41	96,24	ENDO

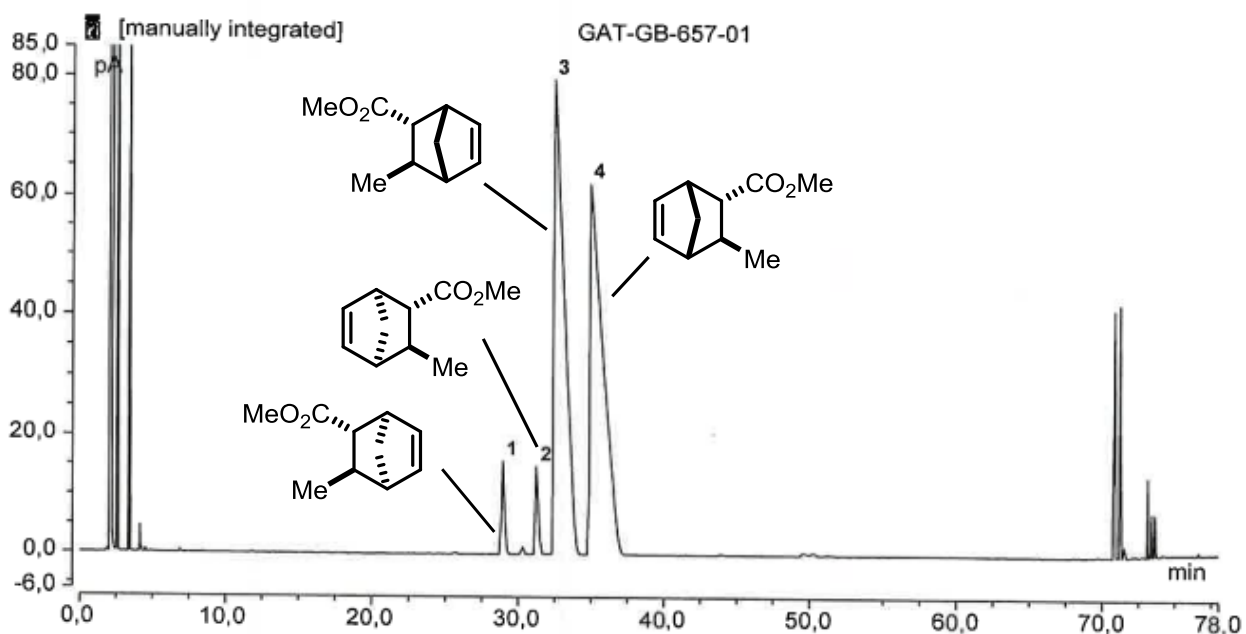


Instrument parameters:  
 Column: 30,0 m BGb 176/BGB 15 G 618  
 Temperature: 230 85 45 MIN ISO 9/Min 220 3 MI ISO 350  
 Gas: 0,50 bar H2  
 Sample size: 1,0 µL

(4497)

R<sub>0</sub>

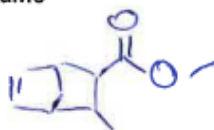
*rac-3w*: The racemic sample was prepared with procedure A.



Sample: **GAT-GB-657-01**  
 Sequenz: **4376 GAT-GB RO**  
 Sequenz date: **20.02.18**

Instrument: **GC\_313**  
 Measured: **20.02.18 12:18**  
 Processing M.: **MPI**  
 Report-File: **Übersichtsanalyse**

No.	Ret.Time min	area-% %	Peak Name
1	28,93	2,68	
2	31,23	2,63	
3	32,42	47,40	
4	34,90	47,29	



Instrument parameters:  
 Column: 30,0 m BGB176/BGB 15 G 618  
 Temperature: 230 85 60 MIN ISO 9/MIN 220 3 MIN ISO 350  
 Gas: 0,50 bar H2  
 Sample size: 1,0 µL

*Ro*