Asymmetric Hydrogenation of Imines with Recyclable Chiral Frustrated Lewis Pair Catalyst

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Supplementary information

General

All reactions involving air or moisture-sensitive compounds were carried out under argon using standard Schlenk techniques or a glove box. Solvents for extraction and chromatography were technical grade and distilled prior to use. Solvents used in reactions were dried and distilled prior to use. Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. NMR experiments were performed on a Bruker AV300, AV400 or AV600 spectrometer. ^{1}H, ^{13}C NMR spectra are referenced to $SiMe_4$ or the residual solvent peak. ^{31}P, ^{11}B, ^{19}F NMR spectra were referenced externally to 85 % H_3PO_4 at 0 ppm, $BF_3.Et_2O$ at 0 ppm and CF_3CO_2H at -78.5 ppm relative to $CFCl_2$ at 0 ppm, respectively. Chemical shifts are given in ppm and spin-spin coupling constants, J, are given in Hz. Compound **10** has been studied by single crystal X-ray diffraction. Crystal data, parameters of collection and convergence results are listed in (Table 1). Intensity data were collected with a Bruker Smart APEX CCD (Mo-$K\alpha$ radiation, = 0.71073 Å, multilayer optics monochromator) area detector on a D8 goniometer in the ω scan mode. A temperature of 100(2) K was maintained for all data collections with the help of an Oxford Cryosystems Cryostream 800 cooler. Multi-scan absorption corrections were performed by SADABS.[1] The structures were solved by direct methods (SHELXS97) and refined by full matrix least-squares on $F2$ (SHELXL97).[2] Non-hydrogen atoms were assigned anisotropic displacement parameters, and H atoms were introduced in their idealized positions and refined using a riding model. The absolute configurations were confirmed by evaluation of the Flack parameter.[3] The enantiomeric excess was determined by HPLC using a chiral stationary phase column (Column, Chiralcel OD-H and AD-H) or by GC (Chirasil-Dex CB). All imines were prepared according to a general procedure.[4] Imines **11a-11h** and amines **12a-12h** are known compounds and their ^{1}H-NMR data matched the literature data. $(C_6F_5)_2BH$ was prepared according to literature methods.[5]

Preparation of 7:[6] A solution of 1,4-dibromobenzen (15.5 g, 65.7 mmol) in THF (10 ml), was slowly added to magnesium turnings (1.60 g, 65.7 mmol) in THF (50 ml) under an Argon atmosphere. After the initial reaction had subsided, the solution was heated for 30 min. A solution of *R*-(+)-Camphor (4.00 g, 26.3 mmol) in THF (10 ml) was added, and the reaction warmed overnight. The mixture was cooled in an ice/water bath and then quenched with saturated aqueous NH_4Cl (10 ml). The organic layer was separated and the aqueous phase was extracted with ether (3 × 30 ml). The organics were combined, dried (Na_2SO_4), and concentrated in vacuo. After removal of the solvent, the residue was purified through removal of unreacted camphor and biphenyl by Kugelrohr distillation (high vacuum, 80 °C). The residual oil was dissolved in 20 ml of pyridine, and the mixture was cooled in salt/ice bath (-10 °C). Thionyl chloride (1 ml) was slowly added by syringe, and the mixture stirred at 0 °C for 1 h. The reaction mixture was carefully diluted with water (0°C) and extracted with pentane (3 × 30 ml). The extract was washed with 10 % HCl, saturated $NaHCO_3$, and saturated aqueous NaCl. The combined organics were dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (eluent: pentane) to give **7** as a colorless solid in 45% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.74 (s, 3H), 0.79 (s, 3H), 0.99 (s, 3H), 1.00 (m, 1H), 1.19 (m, 1H), 1.60 (m, 1H), 1.86 (m, 1H), 2.30 (t, J = 3.8 Hz, 1H), 5.91 (d, J = 3.2 Hz, 1H), 7.25 (d, J= 8.0 Hz, 2H), 7.77 (t, J= 7.7 Hz, 2 H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 12.57, 19.60, 19.72, 25.61, 31.90, 51.68, 54.89, 57.18, 120.21, 128.26, 131.15, 132.46, 137.49, 148.76 ppm.

Preparation of 8: To a solution of **7** (1.5 g, 5.2 mmol) in THF (5 ml), *t*-BuLi (6.8 ml, 10.4 mmol) was slowly added at -78 °C under an Argon atmosphere. After 1 hour at -30 °C, di-*tert*-butylchlorophosphine (1.0 ml, 5.2 mmol) was added, stirred for 30 minutes at -78 °C, then warmed to room temperature, and stirred overnight. Subsequently, the THF was removed under vacuo, the residue washed with dry pentane (3 × 10 ml), and filtrated under Argon. Then the residual was washed with dry methanol (3 × 5 ml) to yield pure **5** in 60% yield as colorless powder.

^{1}H-NMR (400 MHz, C_6D_6): δ = 0.73 (s, 3H), 0.94 (s, 3H), 0.99 (s, 3H), 1.00 (m, 1H), 1.21 (d, J= 1.8, 9H), 1.24 (d, J= 2.0, 9H), 1.32 (m, 1H), 1.59 (m, 1H), 1.87 (m, 1H), 2.27 (t, J = 3.1 Hz, 1H), 5.96 (d, J = 3.9 Hz, 1H), 7.03 (d, J= 7.8 Hz, 2H), 7.33 (d, J= 8.8 Hz, 2 H) ppm.

^{13}C-NMR (75 MHz, Toluene-D_8): δ = 12.74, 19.75, 19.82, 25.98, 30.58, 30.73, 31.95, 32.18, 32.21, 52.10, 55.10, 57.24, 125.96, 126.05 (d, J_{P-C} = 8.5 Hz), 132.36, 135.51, 135.75, 136.7 139.44, 150.02 ppm.

^{31}P-NMR (400 MHz, C_6D_6): δ = 37.9 ppm.

Preparation of 10: In a 100 ml Schlenk tube with a magnetic stirring bar, $(C_6F_5)_2BH$ (242.6 mg, 0.70 mmol) and **8** (0.70 mmol) were dissolved in pentane (5 ml) and stirred at 100°C to yield **9**, which was used without purification. The solution of **9** in pentane was degassed three times with freeze-pump-thaw cycles and refilled with H_2 (1 bar) at liquid nitrogen temperature. The reaction was allowed to stir at room temperature for 48 hours. The product precipitated during this time as a colorless solid. The supernatant was decanted and the residue was washed with pentane, then purified via column chromatography using silica and dichloromethane as eluent to yield pure **10** (40 % yield). Crystals suitable for X-ray diffraction were grown from a dichloromethane/pentane solution.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ = 0.62 (s, 3H), 0.91 (s, 3H), 1.13, (m, 1H), 1.38 (s, 3H),1.41 (m, 1H), 1.49 (d, J =1.6 Hz, 9H), 1.51 (d, J= 1.6 Hz, 9H), 1.59 (m, 1H), 1.68 (s, 1H), 1.89 (t, J= 8.7 Hz, 1H,), 1.96 (m, 1H), 2.85 (br, BH), 3.0 (d, J= 9.1 Hz, 1H), 5.71 (d, J_{P-H} = 477 Hz, PH), 7.38 (m, 2H), 7.49 (m, 2H) ppm.

^{13}C-NMR (150 MHz, CD_2Cl_2): δ = 14.57, 20.67, 21.99, 27.48, 28.75, 33.10, 34.50, 34.75, 50.29, 50.59, 51.43, 59.47, 107.45(d, J_{P-C} = 75.8 Hz), 132.06, 157.22 ppm. The carbon bonded to B atom and quaternary carbon of C_6F_5 ring was not observed;

^{31}P{^{1}H}-NMR (242 MHz, CD_2Cl_2): δ = 53.7;

^{19}F{^{1}H}-NMR (376 MHz, CD_2Cl_2): δ = −132.36 (d, J_{F-F} = 21.9 Hz, 2F), −132.83 (dm, J_{F-F} = 19.3 Hz, 2F), −165.73 (t, J_{F-F} = 23.4 Hz, 1F), −165.93 (t, J_{F-F} = 20.8 Hz, 1F), −167.61 (m, 2F), −167.82 (m, 2F) ppm.

^{11}B-NMR (96 MHz, CD_2Cl_2): $\delta = -19.3$ (d, $J_{B-H} = 81.6$ Hz)

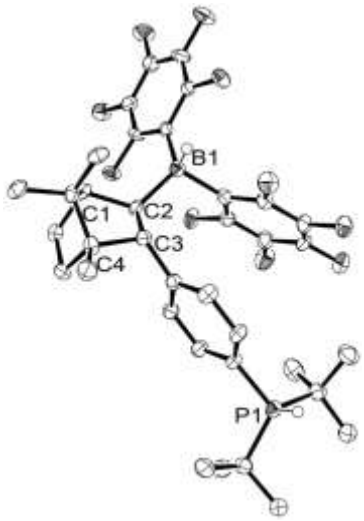


Fig. 1 Molecular structure of compound **10**in the crystal. Hydrogen atoms and solvent molecules were omitted for clarity except for the hydrogen atoms bonded to boron and phosphorus.

Table 1 Crystallographic Data

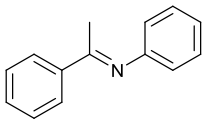
Compound reference	**10**
Chemical formula	$C_{30}H_{40}BF_{10}P$
Formula Mass	704.28
Crystal system	Monoclinic
a/Å	15.070(4)
b/Å	13.208(4)
c/Å	17.862(5)
α/°	90.00
β/°	97.089(8)
γ/°	90.00
V/Å^3	3528.1(18)
Temperature/K	100(2)
Space group	*P2(1)*
Z	2
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.233
No. of reflections measured	31922
No. of independent reflections	14422
R_{int}	0.0935
Final R_1 values ($I > 2\sigma(I)$)	0.0699
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1485
Final R_1 values (all data)	0.1082
Final $wR(F^2)$ values (all data)	0.1736
Goodness of fit on F^2	1.000
Flack parameter	-0.01(9)
CCDC number	

General procedure for the preparation of imines 11a-11h

Method A[4a]: To a solution of ketone (20 mmol) and aniline (24 mmol) in dry toluene (40 ml) 4 Å molecular sieves (20 ml) were added. After being heated to reflux overnight, the reaction mixture was filtered. Solvent was evaporated and the crude product was purified by Kugelrohr distillation, and subsequent crystallization in dry methanol.

Method B[4b]: To a solution of ketone (20 mmol), aniline (24 mmol), and triethylamine in dichloromethane (50 ml), $TiCl_4$ (10 mmol) in dichloromethane (15 ml) was added at 0°C. The reaction mixture was stirred for 30 minutes at 0°C and overnight at room temperature. The resulting suspension was quenched with saturated aqueous K_2CO_3 solution (60 ml), and then filtered through a Büchner-funnel. The water layer was extracted with ether (3 × 30 ml), and the combined organic layers were washed with brine. The solvent was evaporated, and the imine was recrystallized from ethanol.

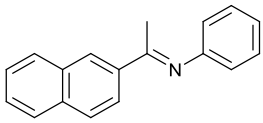
N-(1-Phenylethylidene)aniline 11a: Prepared according to method A from acetophenone and aniline, pale yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 6.82 (d, J = 7.3 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.42-7.54 (m, 3H), 8.00 (m, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.7, 119.4, 123.3, 127.2, 128.4, 129.0, 130.5, 139.5, 151.7 ppm.

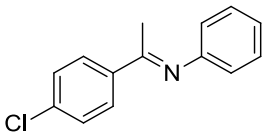
N-(1-(2-(Naphthyl)ethylidene)aniline 11b: Prepared according to method B from 2-acetonaphthone and aniline, yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 6.86 (d, J = 7.6 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.54 (m, 2H), 7.91 (m, 3H), 8.24 (d, J = 8.8 Hz, 1H), 8.36 (s, 1H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ =17.4, 119.5, 123.4, 124.3, 126.4, 127.2, 127.6, 127.7, 128.1, 129.0, 129.1, 132.9, 134.5, 136.8 ppm.

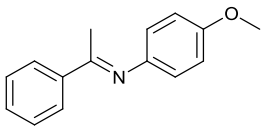
N-Phenyl-(1-(4-chlorophenyl)ethylidene)aniline 11c: Prepared according to method B from 4-chlorobenzaldehyde and aniline, yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 6.83 (d, J = 8.4 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.33–7.41 (m, 4H), 7.94 (d, J = 8.4 Hz, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.6, 119.3, 123.6, 128.5, 129.2, 136.7, 138.1, 151.6, 164.4 ppm.

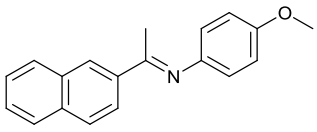
N-(1-phenylethylidene)-4-methoxyaniline 11d: Prepared according to method B from acetophenone and 4-methoxyaniline, yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 3.82 (s, 3H), 6.76 (d, J = 8.7 Hz, 2H), 6.92 (t, J = 8.7 Hz, 2H), 7.10 (m, 2H), 7.45 (m, 3H), 7.97 (m, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.4, 55.5, 114.3, 120.8, 127.1, 128.4, 130.4, 139.7, 144.8, 156.0, 165.8 ppm.

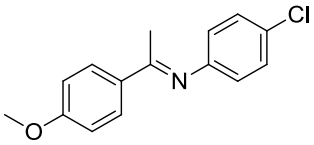
N-(1-(2-(Naphthyl)ethylidene)-4-methoxyaniline 11e: Prepared according to method B from 2-acetonaphthone and 4-methoxyaniline, yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 3.84 (s, 3H), 6.83 (d, J = 9.1 Hz, 2H), 6.95 (d, J = 9.1 Hz, 2H), 7.54 (m, 2H), 7.85-8.00 (m, 3H), 8.24 (d, J = 8.7 Hz, 1H), 8.34 (s, 1H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.3, 55.5, 114.3, 120.8, 124.3, 126.3, 127.1, 127.6, 127.8, 128.0, 128.9, 133.0, 134.4, 137.2, 144.9, 156.1, 165.5 ppm.

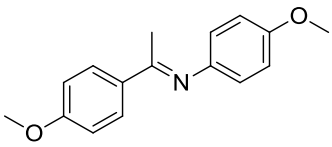
N-[1-(4-chlorophenyl)ehylidene]-p-anisidine 11f: Prepared according to method A from 4-methoxyacetophenone and 4-chloroaniline, yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 3.71 (s, 3H), 6.62 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 9.2 Hz, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.16, 55.47, 114.04, 120.79, 128.51, 129.28, 136.43, 138.18, 144.47, 156.12, 164.6 ppm.

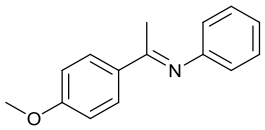
N-[1-(4-Methoxy)phenyl]ethylidene-4-methoxyaniline 11g: Prepared according to method A from 4-methoxyacetophenone and 4-methoxyaniline, yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 6.74 (m¸ 2 H), 6.95 (m, 2 H), 6.94 (m, 2 H), 7.94 (m, 2 H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.2, 55.4, 55.5, 113.5, 114.1, 120.8, 128.6, 132.3, 144.8, 156.12, 164.38 ppm.

N-(1-(4-Methoxyphenyl)ethylidene)aniline 11h: Prepared according to method B from 4-methoxyacetophenone and aniline, pale yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 3.87 (s, 3H), 6.80 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.8 Hz, 1H), 7.08 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.9 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.2, 55.4, 113.6, 119.7, 123.1, 128.8, 128.9, 132.2, 151.9, 161.6, 164.6 ppm.

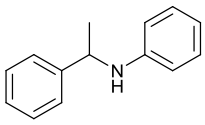
General procedure for the catalytic hydrogenation of imines 12a-12h

Under an argon atmosphere, imine (0.5 mmol), catalyst **10** (2.0 mol %), and 1 ml toluene were transferred to a stainless steel autoclave. The autoclave was purged three times with hydrogen and finally pressurized to 25 bar. The reaction mixture was stirred at 65°C for the indicated period of time, and then the hydrogen gas was released. Entry 9, 0.5 mol% catalyst was mixed with (2.0 mmol) imine **11h**. The conversion of the substrate was determined by ^{1}H NMR spectroscopy of the crude reaction mixture, and the product was purified by chromatography with pentane/ethyl acetate (10/1). The enantiomeric excess was determined by HPLC using a chiral stationary phase column (Column, Chiralcel OD-H, and AD-H) or by GC (Chirasil-Dex CB).

Procedure for catalyst recycling experiments

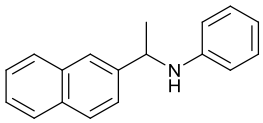
Under an argon atmosphere catalyst **10** (2.5 mol %), imine **11g** (1.42 mmol), and 1 ml toluene were transferred to a stainless steel autoclave. The autoclave was purged three times with hydrogen and finally pressurized to 25bar. The reaction mixture was stirred at 65°C for 24 hours, and then the hydrogen gas was released. Afterwards, 5 ml of pentane were added, the colorless precipitate separated from the supernatant solution, and retransferred to the autoclave for subsequent hydrogenation experiment.

N-(1-phenylethyl)amine 12a (*R*):[8] Conversion: 70%, determined by ^{1}H-NMR.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.52 (d, J = 6.7 Hz, 3H), 3.43 (brs, 1H), 4.48 (q, J = 6.7 Hz, 1H), 6.52 (m, 2H), 6.65 (m, 1H), 7.04-7.14 (m, 2H), 7.18-7.40 (m, 5H); isolated yield: 63%. The enantiomers were analyzed by GC using a Chirasil-Dex CB, 25 m × 0.25mm, H_2 2.0 ml/min, 100°C for 5min, 5°C/min to 160°C, 160°C for 15 min, FID temperature 250°C; Major enantiomer: t_r = 19.46 min, minor enantiomer: t_r = 19.32 min; 72% ee (*R*).

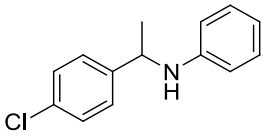
N-(1-(2-Naphthyl)ethyl)amine 12b (−):[9] Conversion: 51%, determined by ^{1}H-NMR.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.62 (d, J = 6.5 Hz, 3H), 4.23 (brs, 1H), 4.67 (q, J = 6.5 Hz, 1H), 6.5-6.63 (m, 2H), 6.67 (t, J = 7.3 Hz), 7.11 (t, J = 7.9 Hz, 2H), 7.40-7.58 (m, 3H), 7.72-7.92 (m, 4H);); isolated yield: 32%.

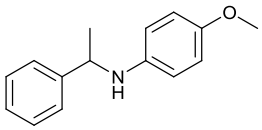
The enantiomers were analyzed by HPLC using a Chiralcel AD-H (n-heptane/2-propanol = 98/2, flow rate=0.5 ml/min, wavelength=240 nm); major enantiomer: t_r = 15.92 min, minor enantiomer: t_r = 14.20 min; 76 % ee (−)

N-Phenyl-1-(4-chlorophenyl)ethylamine 12c (−):[10] Conversion: 33%, determined by ^{1}H-NMR.



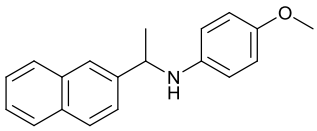
^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.52 (d, J = 6.9 Hz, 3H) 4.13 (bs, 1H), 4.48 (dd, J = 6.6 and 13.2 Hz, 1H), 6.51 (d, J = 7.8 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 7.07–7.12 (m, 2H), 7.24–7.35 (m, 4H). The enantiomers were analyzed by HPLC using a Chiralcel OD-H (heptanes/iPrOH: 98/2, flow rat=0.5 mL/min, wavelength=240 nm); major enantiomer: t_r = 27.56 min. minor enantiomer t_r = 24.58 min 72 % ee (−)

N-(1-phenylethyl)-4-methoxyamine 12d (*R*):[9] Conversion: >99%, determined by ^{1}H-NMR.



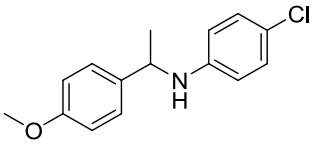
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.50 (d, J = 6.8 Hz, 3H), 3.69 (s, 3H), 3.78 (brs, 1H), 4.41 (q, J = 6.8 Hz, 1H), 6.47 (m, 2H), 6.69 (m, 2H), 7.17-7.42 (m, 5H); isolated yield: 95%. The enantiomers were analyzed by HPLC using a Chiracel OD-H (n-heptane/2-propanol = 99/1, flow rate=0.5ml/min, wavelength=240 nm); major enantiomer: t_r = 34.73 min, minor enantiomer: t_r = 30.59 min; 73 % ee (*R*).

N-(1-(2-Naphthyl)ethyl)-4-methoxyamine 12e (+):[11] Conversion: >99%, determined by ^{1}H-NMR.



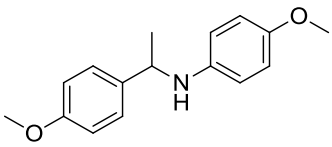
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, J = 6.7 Hz, 3H), 3.58 (s, 3H), 3.79 (brs, 1H), 4.48 (q, J = 6.7 Hz, 1H), 6.36-6.64 (m, 4H), 7.26-7.46 (m, 3H), 7.64-7.78 (m, 4H); isolated yield: 94%. The enantiomers were analyzed by HPLC using a Chiralcel OD-H (n-heptane/2-propanol = 98/2, flow rate=0.5ml/min, wavelength=240 nm); major enantiomer: t_r = 31.51 min, minor enantiomer: t_r = 38.77 min; 76% ee (+).

N-(4-Methoxyphenyl)-N-(1-(4-chlorophenyl)ethyl)amine 12f (+):[7] Conversion: 70%, determined by ^{1}H-NMR.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.36 (d, J = 6.75 Hz, 3H), 3.59 (s, 3H), 4.07 (brs, 1H), 4.32 (q, J = 6.8 Hz, 1H), 6.32 (d, J = 9.1 Hz, 2H), 6.66 (d, J = 9.6 Hz, 2H), 7.12 (m, 4H); isolated yield 51%. The enantiomers were analyzed by HPLC using a Chiralcel OD-H (heptanes/iPrOH: 95/5, flow rate=0.5 mL/min, wavelength=250 nm); major enantiomer: t_r = 21.99 min, minor enantiomer t_r = 27.05 min; 72% ee (+).

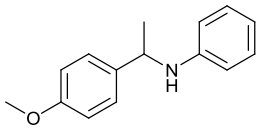
4-methoxy-N-(1-(4-methoxyphenyl)ethyl)amine 12g (+):[12] Conversion: >99%, determined by ^{1}H-NMR.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.39 (d, J= 5.10, 3 H), 3.73 (s, 3 H),3.81 (s, 3 H), 3.82 (brs, 1H), 4.42 (q, J = 6.7 Hz, 1H), 6.53 (d, J = 6.8 Hz, 2 H), 6.75 (d, J = 6.2 Hz,2 H), 6.90 (d, J = 7.8 Hz), 7.33 (d, J = 8.7 Hz); isolated yield 95%. The enantiomers were analyzed by HPLC using a

Chiralcel OD-H (heptanes/iPrOH: 97/3, flow rate=0.5 mL/min, wavelength=220 nm); major enantiomer: t_r = 21.88 min, minor enantiomer t_r = 25.23 min; 76 % ee (+).

N-(1-(4-methoxyphenyl)ethyl)amine 12h (−):[10] Conversion: >99%, determined by ^{1}H-NMR.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.51 (d, J = 6.7 Hz, 3H), 3.80 (s, 3H), 4.07 (brs, 1H), 4.46 (q, J = 6.7 Hz, 1H), 6.54 (d, J = 7.6 Hz, 2H), 6.66 (t, J = 6.7 Hz, 1H), 6.87 (m, 2H), 7.11 (m, 2H), 7.30 (m, 2H); isolated yield: 95 %.

The enantiomers were analyzed by HPLC using a Chiracel OD-H (n-heptane/2-propanol = 99/1, flow rate=0.5ml/min, wavelength=240 nm); major enantiomer: t_r = 22.87 min, minor enantiomer: t_r = 20.56 min; 70 % ee (−).

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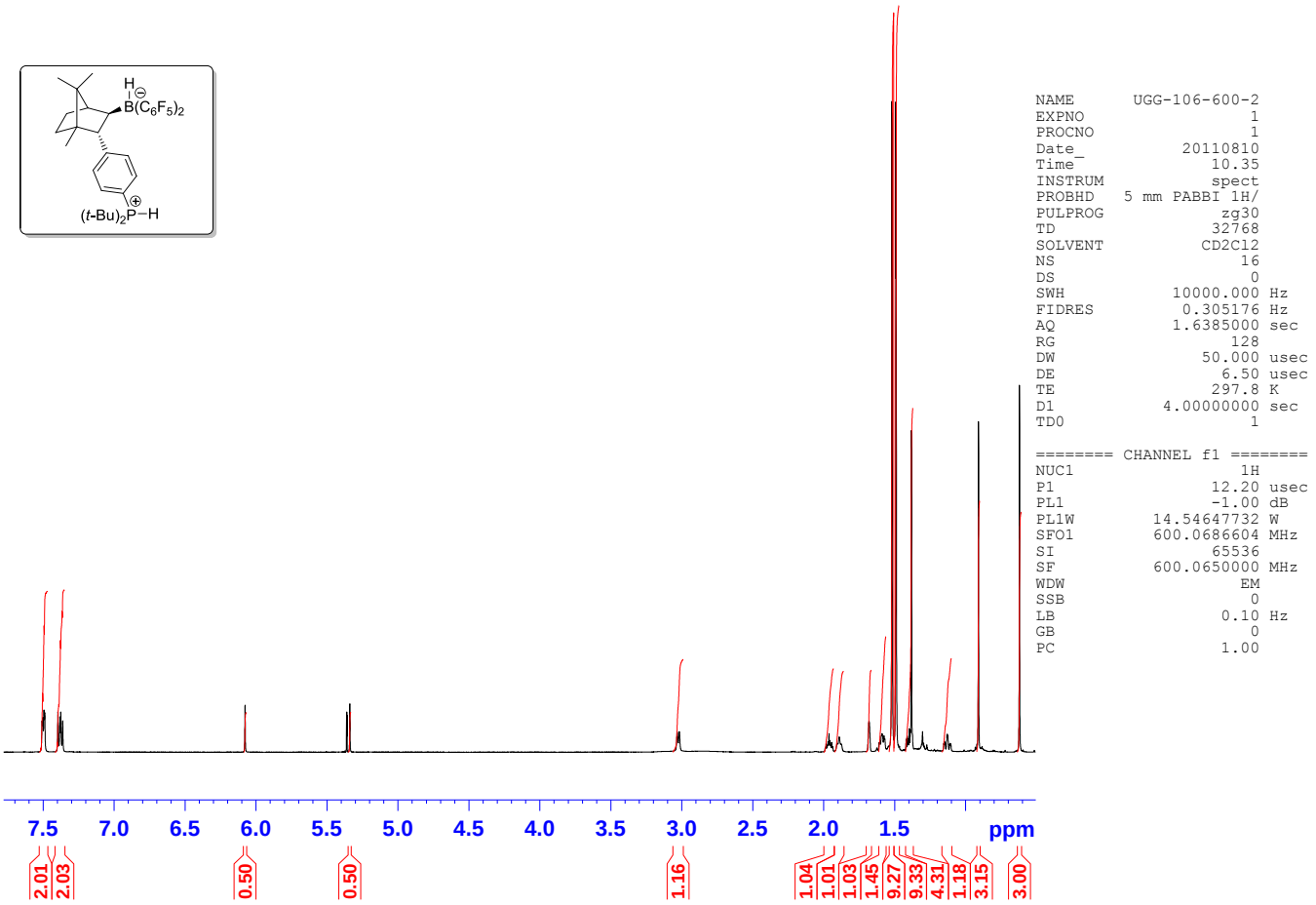

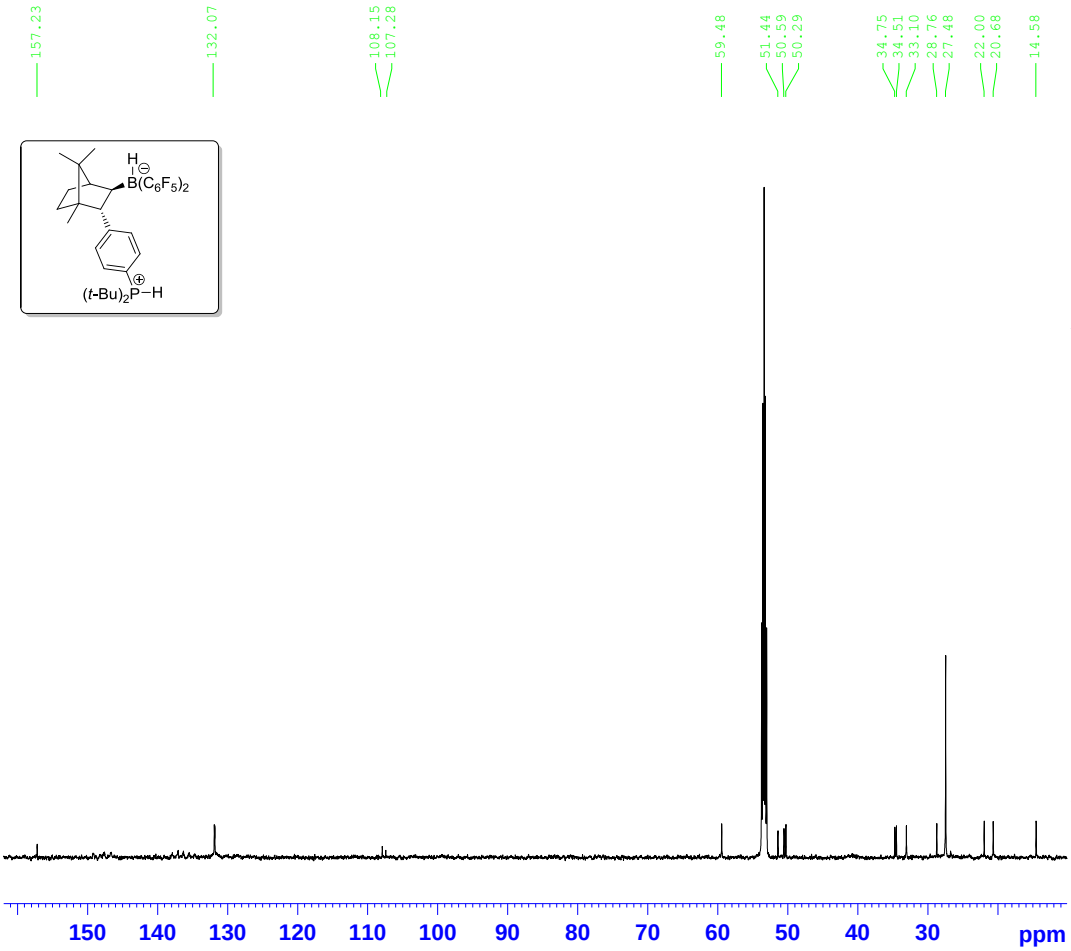


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PROCNO                 1
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INSTRUM            spect
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PULPROG          zgpg30
TD                32768
SOLVENT           CD2Cl2
NS                 4096
DS                    4
SWH           40983.605 Hz
FIDRES         1.250720 Hz
AQ            0.3998318 sec
RG                26008
DW               12.200 usec
DE               17.43 usec
TE               299.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                16.20 usec
PL1                0.00 dB
PL1W        85.40413666 W
SFO1       150.9045709 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.27 dB
PL13               20.00 dB
PL2W        14.54647732 W
PL12W        0.21664955 W
PL13W        0.11554678 W
SFO2       600.0678800 MHz
SI                32768
SF         150.8864640 MHz
WDW                  EM
SSB                   0
LB                 5.00 Hz
GB                    0
PC                 1.00
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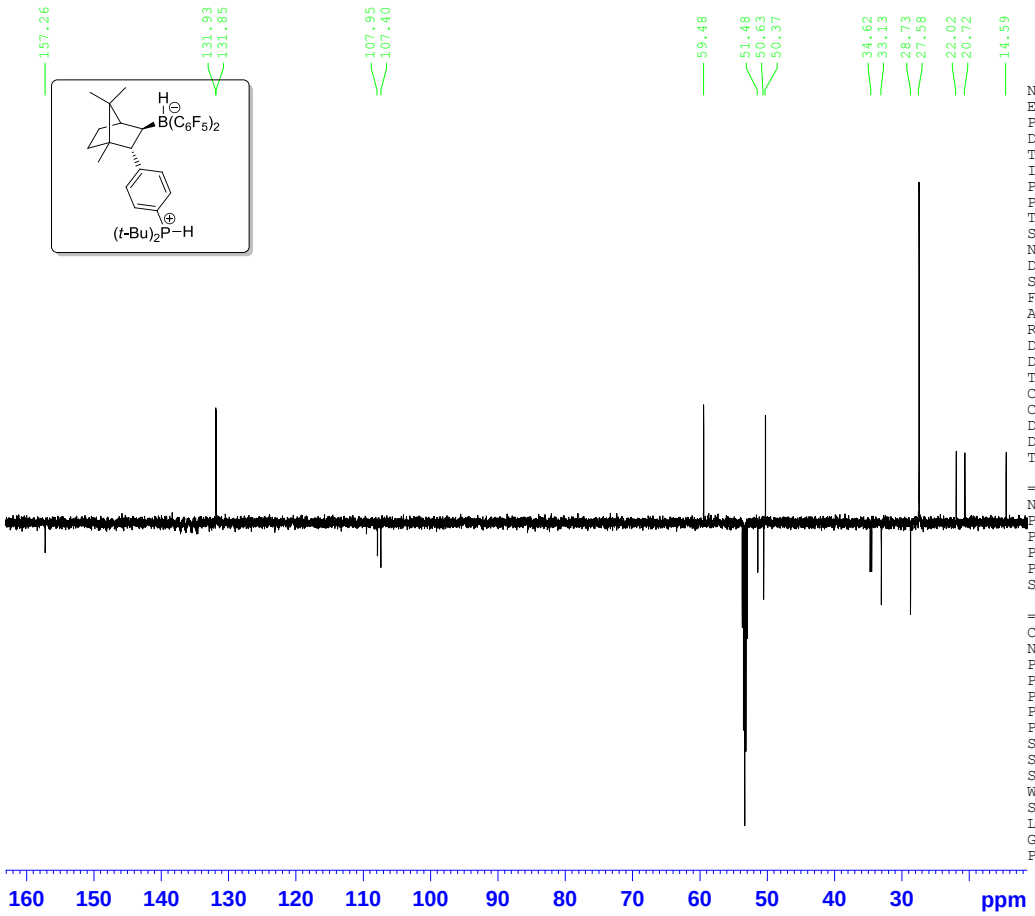


```
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EXPNO                  5
PROCNO                 1
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Time               13.29
INSTRUM            spect
PROBHD   5 mm PABBI 1H/
PULPROG             jmod
TD                 65536
SOLVENT           CD2Cl2
NS                   1024
DS                      4
SWH           35971.223 Hz
FIDRES         0.548877 Hz
AQ            0.9110143 sec
RG                  26008
DW                13.900 usec
DE                 6.50 usec
TE                299.1 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
D20           0.00689655 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 16.20 usec
P2                 32.40 usec
PL1                 0.00 dB
PL1W         85.40413666 W
SFO1        150.9015534 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.27 dB
PL2W         14.54647732 W
PL12W         0.21664955 W
SFO2        600.0674003 MHz
SI                 32768
SF          150.8864640 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
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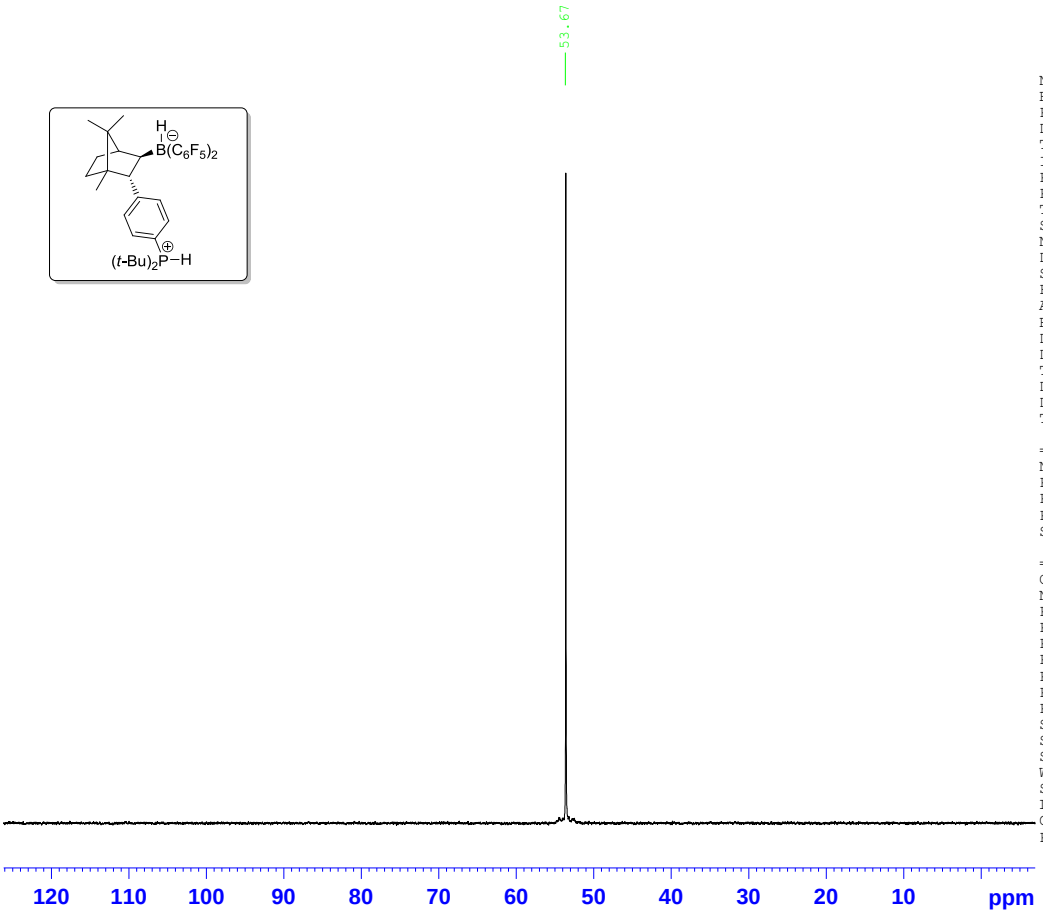


```
NAME       UGG-106-600-2
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PROCNO                 1
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Time              10.39
INSTRUM           spect
PROBHD   5 mm PABBI 1H/
PULPROG         zgpg30
TD               32768
SOLVENT          CD2Cl2
NS                  128
DS                    2
SWH           72992.703 Hz
FIDRES         2.227561 Hz
AQ            0.2245176 sec
RG              23170.5
DW                6.850 usec
DE                6.50 usec
TE                298.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 31P
P1                20.00 usec
PL1               -2.00 dB
PL1W        98.33247375 W
SFO1       242.9337650 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -1.00 dB
PL12              17.27 dB
PL13              20.00 dB
PL2W        14.54647732 W
PL12W        0.21664955 W
PL13W        0.11554678 W
SFO2       600.0686604 MHz
SI               65536
SF         242.9107640 MHz
WDW                 EM
SSB                  0
LB                5.00 Hz
GB                   0
PC                1.00
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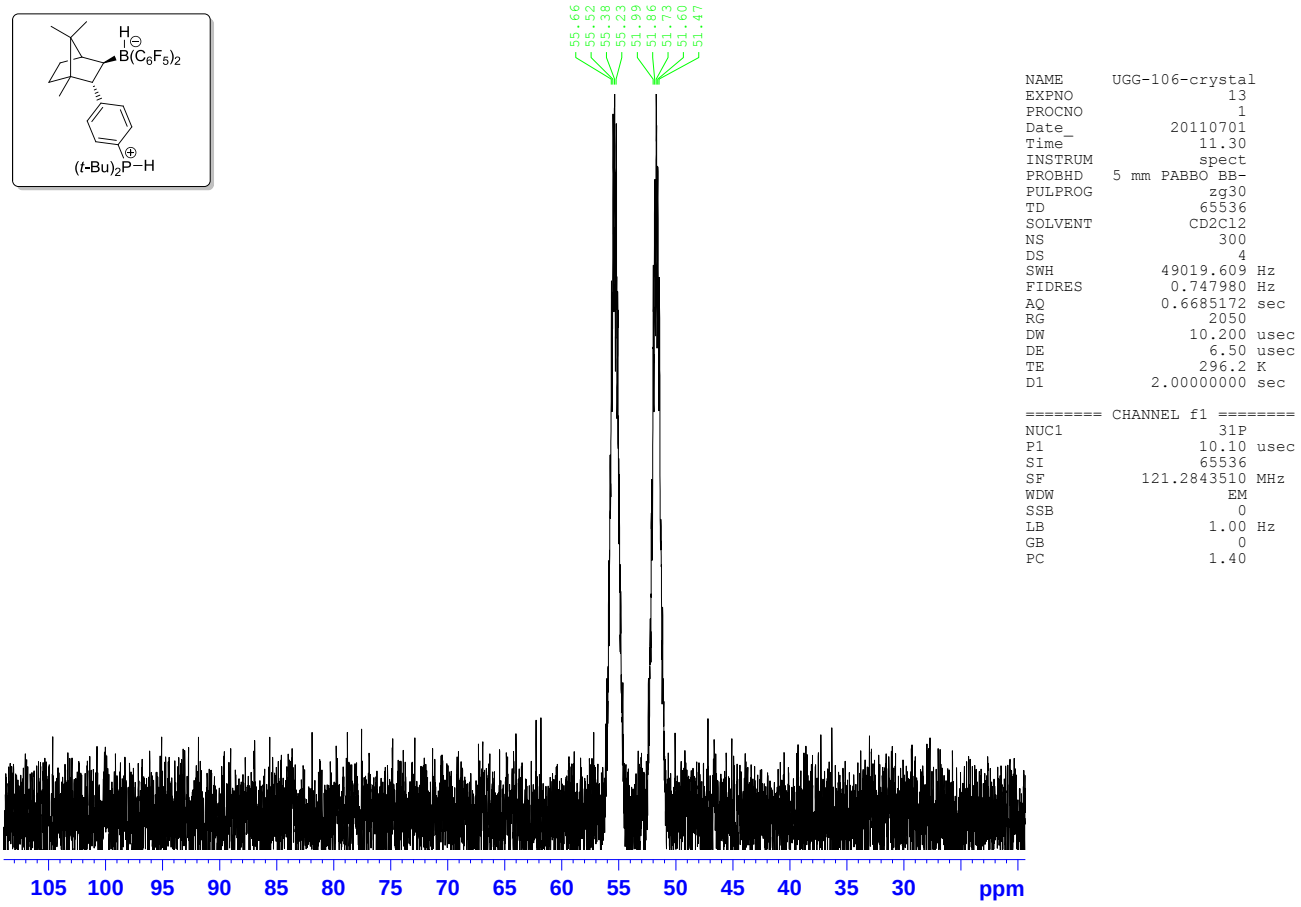


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PROCNO                  1
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Time                11.30
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT           CD2Cl2
NS                    300
DS                      4
SWH             49019.609 Hz
FIDRES          0.747980 Hz
AQ              0.6685172 sec
RG                   2050
DW                 10.200 usec
DE                  6.50 usec
TE                 296.2 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                  31P
P1                 10.10 usec
SI                  65536
SF           121.2843510 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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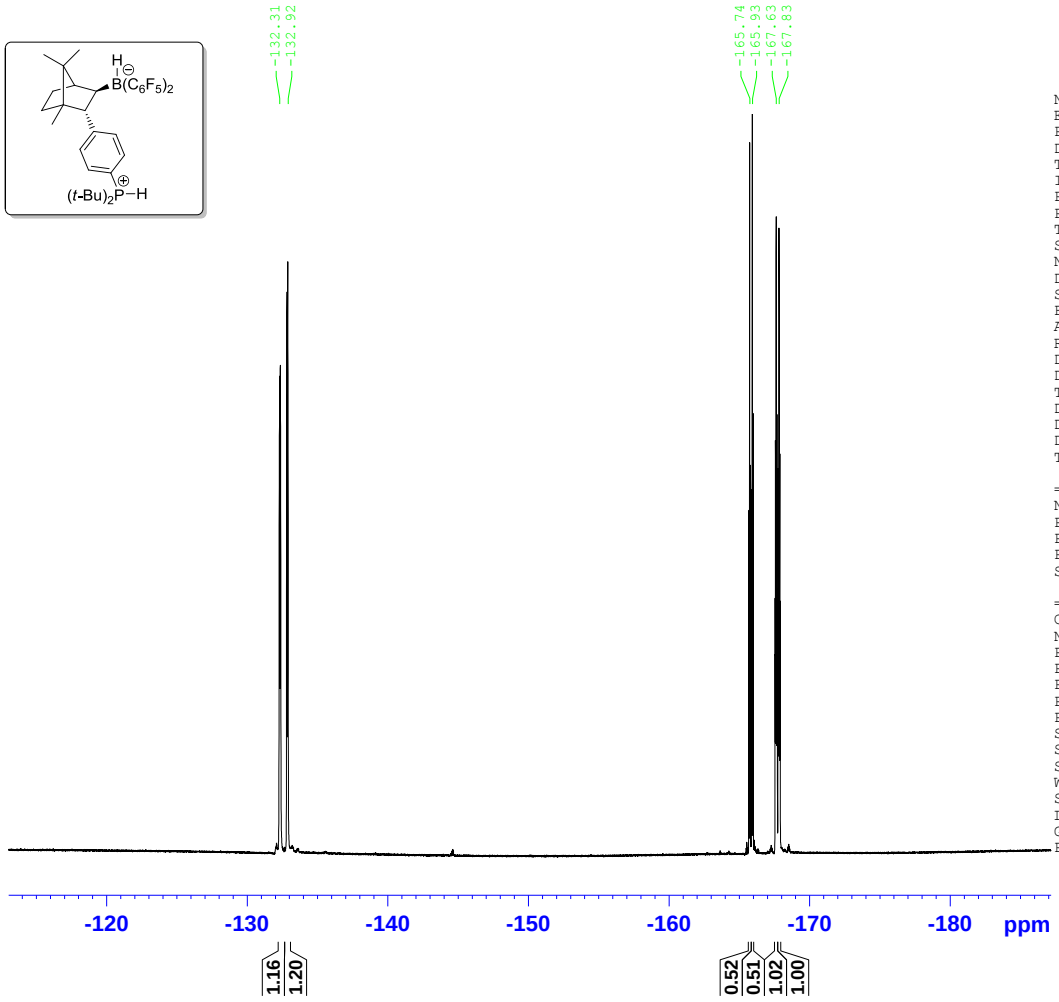


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PROCNO                   1
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Time                 14.39
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG          zgfhigqn
TD                 131072
SOLVENT           CD2Cl2
NS                    128
DS                      4
SWH             89285.711 Hz
FIDRES          0.681196 Hz
AQ              0.7340532 sec
RG                   2050
DW                5.600 usec
DE                6.50 usec
TE                296.7 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   19F
P1                  13.75 usec
PL1                 -4.00 dB
PL1W          16.53108215 W
SFO1          376.4983502 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -4.00 dB
PL12                14.50 dB
PL2W          26.12163353 W
PL12W          0.36897787 W
SFO2          400.1716007 MHz
SI                   65536
SF            376.5360040 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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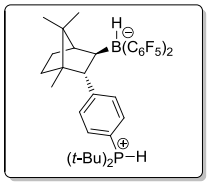

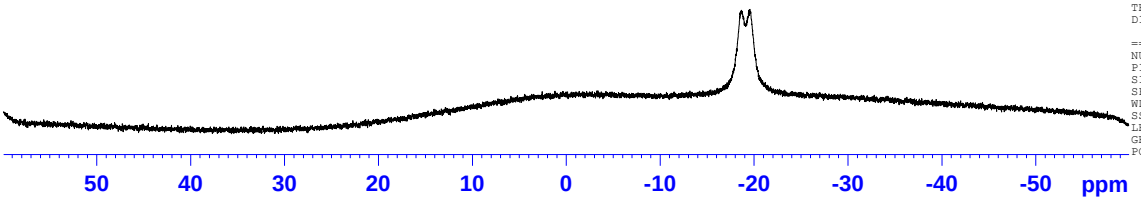


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PROCNO                  1
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INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG                zg
TD                  32768
SOLVENT           CD2Cl2
NS                    200
DS                      4
SWH             11520.737 Hz
FIDRES          0.351585 Hz
AQ              1.4221812 sec
RG                   1030
DW                43.400 usec
DE                 6.50 usec
TE                296.2 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                  11B
P1                 13.90 usec
SI                  32768
SF           96.1267950 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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