Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

SUPPORTING INFORMATION

Design, Synthesis, and Application of Tartaric Acid Derived *N*-Spiro Quaternary Ammonium Salts as Chiral Phase-Transfer Catalysts

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1. General Information:

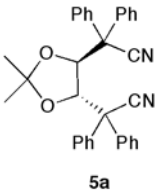
Melting points were measured on a Kofler melting point microscope (Reichert, Vienna). ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer using a TXI cryoprobe with z-gradient coil and on a Bruker Avance III 300 MHz spectrometer. Typical resolutions and chemical shift precisions were +/- 0.5 Hz for ^{1}H and +/- 0.8 Hz for ^{13}C. All NMR spectra were referenced on the solvent peak. High resolution mass spectra were obtained using an Agilent 6520 Q-TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer. All analyses were made in the positive ionization mode. Purine (exact mass for $[M+H]^+$ = 121.050873) and 1,2,3,4,5,6-hexakis(2,2,3,3-tetrafluoropropoxy)-1,3,5,2,4,6-triazatriphosphinane (exact mass for $[M+H]^+$ = 922.009798) were used for internal mass calibration. IR spectra were recorded on a Shimadzu IR Affinity-1 fourier transform infrared spectrometer. Optical rotations were recorded on a Perkin Elmer Polarimeter Model 241 MC. HPLC was performed using a Dionex Summit HPLC system with a Chiralcel OD-H (250 x 4.6 mm) chiral stationary phase. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were performed under an Ar-atmosphere. Starting TADDOLs are literature known compounds and were synthesised as described previously.[1]

[1] a) D. Seebach, A. B. Keck and A. Heckel, *Angew. Chem. Int. Ed.* 2001, **40**, 92; b) E. Weber, N. Dörpinghaus and C. Wimmer, *J. Org. Chem.* 1992, **57**, 6825; c) A. Voituriez and A. B. Charette, *Adv. Synth. Catal. 2006*, **348**, 2363; d) A. K. Beck, B. Bastani, D. A. Plattner, W. Petter, D. Seebach, H. Braunschweiger, P. Gysi and L. LaVecchia, *Chimia*, 1991, ***45***, 238.

2. Syntheses of Quaternary-Ammonium Salts:

Syntheses of dicyanides 5: $SOCl_2$ (3 eq.) was added to a solution of **2** in CH_2Cl_2 (14 mL / mmol **2**) and stirred at RT. A solution of Et_3N (5 eq.) in CH_2Cl_2 (7 mL / mmol **2**) was added dropwise over 30 min. The mixture was stirred for 1 h at RT, cooled to 5°C and $NaHCO_3$ (sat.) (20 mL / mmol **2**) was added. The biphasic mixture was vigorously stirred for 90 min, the layers separated, the organic phase was dried over Na_2SO_4 and evaporated to dryness. Crude **4** was directly dissolved in CH_2Cl_2 (14 mL / mmol **2**), cooled to 5°C and TMSCN (2.5 eq.) and $SnCl_4$ (25%) were added. The mixture was warmed to RT over 1 h and stirred for 12 h. After quenching with K_2CO_3 (sat.) the phases were separated and the organic phase washed twice with K_2CO_3 (sat.) and twice with brine (*Caution: aqueous phases may contain residual cyanide!*). After drying over Na_2SO_4 and evaporation to dryness the product was purified by column chromatography (heptanes:EtOAc = 5:1) to give dicyanides **5** in the reported yields.

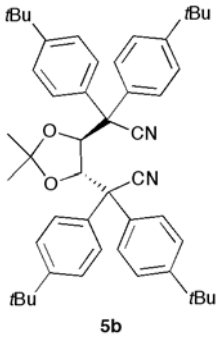
Dicyanide (*S*,*S*)-5a. Prepared from (*R*,*R*)-**2a** (4.71 g, 10.1 mmol) in 63% (3.08 g, 6.4 mmol).



5a

Grey solid. M.p.: decomp > 190 °C; $[\alpha]_D^{20}$ (c = 1.08, $CHCl_3$) = +52.9°; ^{1}H NMR (500 MHz, δ, DMSO-d6, 298 K): 1.41 (s, 6H), 5.58 (s, 2H), 6.99 (m, 6H), 7.16 (d, *J* = 7.5 Hz, 4H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.54 (d, *J* = 7.9 Hz, 4H) ppm; ^{13}C NMR (125 MHz, δ, DMSO-d6, 298 K): 28.1 (-CH_3), 57.2 (-*C*CN), 82.0 (-CH-), 112.0 (-$C(O)_2$-), 120.7 (-CN), 126.2 (ArC), 127.2 (ArC), 127.7 (ArC), 128.0 (ArC), 128.7 (ArC), 128.9 (ArC), 135.6 (ArC), 138.8 (ArC) ppm; IR (film): $\tilde{\nu}$ = 3061, 2986, 1599, 1494, 1450, 1369, 1232, 1220, 1178, 1161, 1083, 1033, 910, 875, 738 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{28}N_2O_2$: 485.2224 $[M+H]^+$; found: 485.2221.

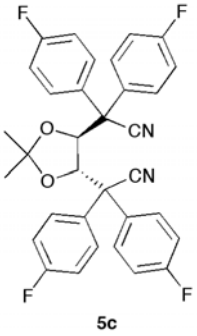
Dicyanide (*S*,*S*)-5b. Prepared from (*R*,*R*)-**2b** (2.0 g, 2.9 mmol) in 54% (1.11 g, 1.5 mmol).



5b

Light brown solid. M.p.: decomp > 185 °C; $[\alpha]_D^{20}$ (c = 1.43, $CHCl_3$) = -12.2°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.14 (s, 6H), 1.32 (s, 9H), 1.33 (s, 9H), 5.38 (s, 2H), 7.25-7.40 (m, 16H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 27.7 (-CH_3), 31.4 (-C(*C*H_3)$_3$), 31.5 (-C(*C*H_3)$_3$), 34.6 (-*C*$(CH_3)_3$), 34.7 (-*C*$(CH_3)_3$), 55.1 (-*C*CN), 81.8 (-CH-), 111.7 (-$C(O)_2$-), 120.7 (-CN), 125.4 (ArC), 126.0 (ArC), 127.6 (ArC), 128.4 (ArC), 134.8 (ArC), 135.3 (ArC), 150.9 (ArC), 151.1 (ArC) ppm; IR (film): $\tilde{\nu}$ = 2960, 2904, 2868, 1508, 1451, 1363, 1269, 1236, 1083, 1066, 1018, 825 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{49}H_{60}N_2O_2$: 726.4993 $[M+NH_4]^+$; found: 726.4987.

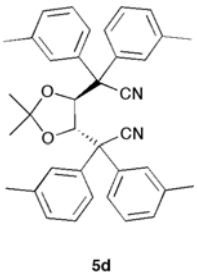
Dicyanide (*S*,*S*)-5c. Prepared from (*R*,*R*)-**2c** (9.2 g, 17.14 mmol) in 47% (4.48 g, 8.05 mmol).



5c

White foam. $[\alpha]_D^{20}$ (c = 1.55, $CHCl_3$) = +81.3°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.48 (s, 6H), 5.35 (s, 2H), 6.73 (t, *J* = 8.5 Hz, 4H), 7.02 (t, *J* = 8.5 Hz, 4H), 7.11 (m, 4H), 7.45 (m, 4H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 28.3 (-CH_3), 56.2 (-*C*CN), 82.6 (-CH-), 113.0 (-$C(O)_2$-), 115.8 (d, *J* = 22 Hz, ArC), 116.3 (d, *J* = 21 Hz, ArC), 120.7 (-CN), 128.8 (d, *J* = 8 Hz, ArC), 129.6 (d, *J* = 8 Hz, ArC), 132.2 (ArC), 134.4 (ArC), 161.2 (d, *J* = 12 Hz, ArC), 163.3 (d, *J* = 12 Hz, ArC) ppm; IR (film): $\tilde{\nu}$ = 3078, 2943, 1604, 1506, 1373, 1230, 1166, 1155, 1093, 1082, 1045, 827 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{24}F_4N_2O_2$: 595.1405 $[M+K]^+$; found: 595.1416.

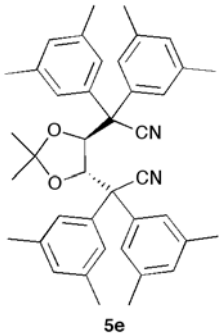
Dicyanide (*S*,*S*)-5d. Prepared from (*R*,*R*)-**2d** (2.2 g, 4.2 mmol) in 58% (1.36 g, 8.05 mmol).



5d

Light brown oily residue. $[\alpha]_D^{20}$ (c = 1.12, $CHCl_3$) = +50.0°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.49 (s, 6H), 2.13 (s, 6H), 2.32 (s, 6H), 5.49 (s, 2H), 6.76 (d, *J* = 7.3 Hz, 2H), 6.88 (m, 4H), 7.03 (t, *J* = 7.4 Hz, 4H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.27 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 21.6 ($ArCH_3$), 21.7 ($ArCH_3$), 28.1 (-CH_3), 57.1 (-*C*CN), 82.2 (-CH-), 111.4 (-$C(O)_2$-), 121.1 (-CN), 123.7 (ArC), 124.3 (ArC), 127.1 (ArC), 128.1 (ArC), 128.4 (ArC), 128.5 (ArC), 128.6 (ArC), 128.8 (ArC), 139.2 (ArC), 138.2 (ArC), 138.3 (ArC), 139.1 (ArC) ppm; IR (film): $\tilde{\nu}$ = 2985, 2924, 1604, 1489, 1456, 1382, 1373, 1242, 1172, 1066, 889, 746, 705, 688 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{37}H_{36}N_2O_2$: 579.2408 $[M+K]^+$; found: 579.2406.

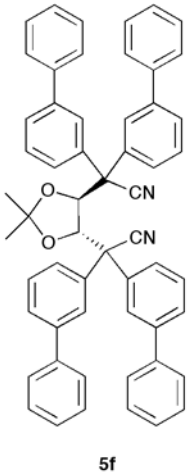
Dicyanide (*S*,*S*)-5e. Prepared from (*R*,*R*)-**2e** (2.0 g, 3.45 mmol) in 51% (1.05 g, 1.76 mmol).



5e

White oily residue. $[\alpha]_D^{20}$ (c = 1.6, $CHCl_3$) = +27.5°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.49 (s, 6H), 2.11 (s, 12H), 2.27 (s, 12H), 5.49 (s, 2H), 6.55 (s, 2H), 6.79 (s, 4H), 6.81 (s, 2H), 7.08 (s, 4H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 21.5 ($ArCH_3$), 21.6 ($ArCH_3$), 27.6 (-CH_3), 56.5 (-*C*CN), 81.4 (-CH-), 109.8 (-$C(O)_2$-), 121.3 (-CN), 123.9 (ArC), 124.5 (ArC), 129.3 (ArC), 129.5 (ArC), 136.0 (ArC), 138.0 (ArC (2x)), 139.7 (ArC) ppm; IR (film): $\tilde{\nu}$ = 2941, 2918, 1597, 1456, 1381, 1234, 1219, 1165, 1093, 1076, 1049, 864, 761, 746 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{41}H_{44}N_2O_2$: 597.3476 $[M+H]^+$; found: 579.3482.

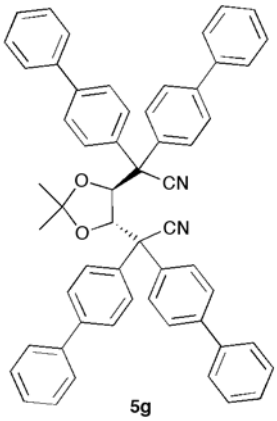
Dicyanide (*S*,*S*)-5f. Prepared from (*R*,*R*)-**2f** (0.72 g, 0.94 mmol) in 47% (0.35 g, 0.44 mmol).



5f

Light brown oily residue. $[\alpha]_D^{20}$ (c = 1.28, $CHCl_3$) = +41.1°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.60 (s, 6H), 5.77 (s, 2H), 6.76 (d, *J* = 7.3 Hz, 2H), 7.12-7.29 (m, 4H), 7.33-7.57 (m, 34H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 28.0 (-CH_3), 57.3 (-*C*CN), 82.2 (-CH-), 111.4 (-$C(O)_2$-), 120.9 (-CN), 125.2 (ArC), 125.5 (ArC), 126.2 (ArC), 126.5 (ArC), 126.8 (ArC), 127.0 (ArC), 127.2 (ArC), 127.4 (ArC), 127.7 (ArC), 128.9 (ArC), 129.0 (ArC), 129.1 (ArC), 129.6 (ArC), 136.7 (ArC), 139.8 (ArC), 140.0 (ArC), 140.7 (ArC), 141.6 (ArC), 141.8 (ArC) ppm; IR (film): $\tilde{\nu}$ = 3055, 3034, 1597, 1479, 1452, 1417, 1375, 1265, 1234, 1176, 1076, 887, 734, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{57}H_{44}N_2O_2$: 806.3741 $[M+NH_4]^+$; found: 806.3745.

Dicyanide (*S*,*S*)-5g. Prepared from (*R*,*R*)-**2g** (12.0 g, 15.6 mmol) using 5 eq. TMSCN and

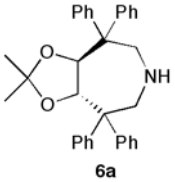


5g

1 eq. $SnCl_4$ in 59% (7.26 g, 9.2 mmol). Light brown solid. M.p.: decomp > 220 °C; $[\alpha]_D^{20}$ (c = 1.6, $CHCl_3$) = +104.6°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.65 (s, 6H), 5.68 (s, 2H), 7.24-7.36 (m, 14H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 4H), 7.65 (d, *J* = 8.8 Hz, 8H), 7.63 (d, *J* = 7.8 Hz, 4H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 28.0 (-CH_3), 56.6 (-*C*CN), 81.9 (-CH-), 111.2 (-$C(O)_2$-), 120.8 (-CN), 126.9 (ArC), 127.1 (ArC), 127.2 (ArC), 127.4 (ArC), 127.5 (ArC), 127.6 (ArC), 127.7 (ArC), 128.8 (ArC), 128.9 (ArC), 135.0 (ArC), 138.4 (ArC), 139.5 (ArC), 140.1 (ArC), 140.6 (ArC), 140.7 (ArC) ppm; IR (film): $\tilde{\nu}$ = 3055, 3030, 1485, 1409, 1373, 1234, 1159, 1076, 1006, 835, 742, 694 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{57}H_{44}N_2O_2$: 806.3741 $[M+NH_4]^+$; found: 806.3751.

Syntheses of *sec*-amines 6: A mixture of **5** and $LiAlH_4$ (20 eq.) in mesitylene (35 mL / mmol **5**) was refluxed for 30-45 min, cooled on an ice bath and carefully quenched with EtOAc first, followed by the addition of H_2O. After phase separation, the aqueous phase was extracted with EtOAc twice and the combined organic layers were washed with brine (3x). After drying over Na_2SO_4 and evaporation to dryness the product was purified by column chromatography (heptanes:EtOAc = 5:1) to give amines **6** in the reported yields.

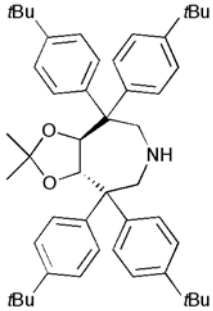
Amine (*S,S*)-6a. Prepared from (*S,S*)-**5a** (2.0 g, 4.1 mmol) in 37% (725 mg, 1.52 mmol).



6a

Grey solid. M.p.: 153-158°C; $[\alpha]_D^{20}$ (c = 4.04, $CHCl_3$) = -169.3°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.76 (s, 6H), 3.44 (d, *J* = 14.5 Hz, 2H), 3.79 (d, *J* = 14.5 Hz, 2H), 5.10 (s, 2H), 7.17-7.25 (m, 8H), 7.27-7.33 (m, 8H), 7.43 (d, *J* = 7.3 Hz, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 26.8 ($-CH_3$), 54.0 (Ar_2C-), 63.0 ($-CH_2N$-), 79.4 (-CH-), 109.3 ($-C(O)_2$-), 126.2 (ArC), 126.4 (ArC), 127.1 (ArC), 128.2 (ArC), 128.5 (ArC), 131.3 (ArC), 143.8 (ArC), 148.6 (ArC) ppm; IR (film): $\bar{\nu}$ = 3020, 2993, 2937, 2879, 1598, 1492, 1442, 1377, 1367, 1249, 1209, 1165, 1136, 1062, 1020, 873, 754, 738 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{33}NO_2$: 476.2584 $[M+H]^+$; found: 476.2580.

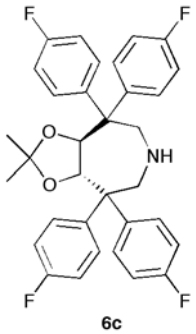
Amine (*S,S*)-6b. Prepared from (*S,S*)-**5b** (960 mg, 1.35 mmol) in 32% (303 mg, 0.43 mmol).



6b

Oily residue. $[\alpha]_D^{20}$ (c = 1.36, $CHCl_3$) = -122.7°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.70 (s, 6H), 1.31 (s, 18H), 1.32 (s, 18H), 3.39 (d, *J* = 14.2 Hz, 2H), 3.79 (d, *J* = 14.2 Hz, 2H), 5.10 (s, 2H), 7.20-7.27 (m, 8H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 26.8 ($-CH_3$), 31.4 ($-C(CH_3)_3$), 31.5 ($-C(CH_3)_3$), 34.4 ($-C(CH_3)_3$), 34.4 ($-C(CH_3)_3$), 53.3 (Ar_2C-), 63.1 ($-CH_2N$-), 79.4 (-CH-), 109.2 ($-C(O)_2$-), 123.8 (ArC), 125.0 (ArC), 128.0 (ArC), 130.7 (ArC), 140.7 (ArC), 145.6 (ArC), 148.5 (ArC), 149.0 (ArC) ppm; IR (film): $\bar{\nu}$ = 2960, 2902, 2870, 1508, 1458, 1361, 1269, 1242, 1215, 1168, 1072, 1016, 839, 754 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{49}H_{65}NO_2$: 700.5088 $[M+H]^+$; found: 700.5074.

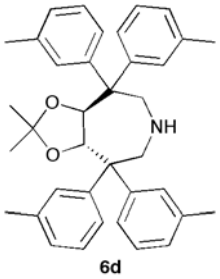
Amine (*S,S*)-6c. Prepared from (*S,S*)-**5c** (620 mg, 1.11 mmol) in 43% (261 mg, 8.05 mmol).



6c

White foam. $[\alpha]_D^{20}$ (c = 1.7, $CHCl_3$) = -146.1°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.79 (s, 6H), 1.83 (bs, 1H), 3.40 (d, *J* = 14.5 Hz, 2H), 3.71 (d, *J* = 14.5 Hz, 2H), 4.93 (s, 2H), 6.94 (t, *J* = 8.4 Hz, 4H), 6.99 (t, *J* = 8.7 Hz, 4H), 7.24 (t, *J* = 6.6 Hz, 4H), 7.40 (d, *J* = 6.7 Hz, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 26.9 ($-CH_3$), 52.8 (Ar_2C-), 63.3 ($-CH_2N$-), 79.5 (-CH-), 109.5 ($-C(O)_2$-), 113.9 (d, *J* = 21 Hz, ArC), 115.0 (d, *J* = 21 Hz, ArC), 129.9 (d, *J* = 8 Hz, ArC), 132.7 (d, *J* = 8 Hz, ArC), 139.1 (d, *J* = 4 Hz, ArC), 144.0 (d, *J* = 3 Hz, ArC), 160.5 (d, *J* = 46 Hz, ArC), 162.4 (d, *J* = 46 Hz, ArC) ppm; IR (film): $\bar{\nu}$ = 2987, 2933, 1600, 1504, 1371, 1244, 1161, 1072, 1016, 879, 827, 736 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{29}F_4NO_2$: 548.2207 $[M+H]^+$; found: 548.2213.

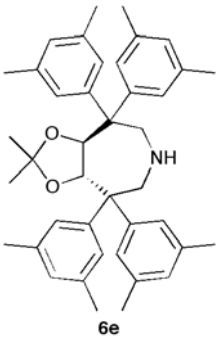
Amine (*S,S*)-6d. Prepared from (*S,S*)-**5d** (1.44 g, 2.66 mmol) in 31% (438 mg, 0.82 mmol).



6d

Oily residue. $[\alpha]_D^{20}$ (c = 1.5, $CHCl_3$) = -101.9°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.82 (s, 6H), 2.31 (s, 6H), 2.33 (s, 6H), 3.41 (d, *J* = 14.4 Hz, 2H), 3.77 (d, *J* = 14.4 Hz, 2H), 5.08 (s, 2H), 7.00-7.17 (m, 7H), 7.17-7.27 (m, 7H), 7.30 (d, *J* = 7.7 Hz, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 21.8 ($ArCH_3$), 21.9 ($ArCH_3$), 26.8 ($-CH_3$), 53.9 (Ar_2C-), 62.9 ($-CH_2N$-), 79.6 (-CH-), 109.2 ($-C(O)_2$-), 125.5 (ArC), 126.9 (ArC), 127.1 (ArC), 127.9 (ArC), 129.1 (ArC), 132.3 (ArC), 136.3 (ArC), 137.5 (ArC), 143.6 (ArC), 148.5 (ArC) ppm; IR (film): $\tilde{\nu}$ = 2922, 1602, 1487, 1454, 1377, 1367, 1244, 1215, 1172, 1072, 1039, 883, 779, 752, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{37}H_{42}NO_2$: 532.3210 $[M+H]^+$; found: 532.3209.

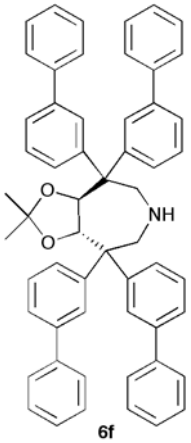
Amine (*S,S*)-6e. Prepared from (*S,S*)-**5e** (865 mg, 1.45 mmol) in 30% (266 mg, 0.435 mmol).



6e

Oily residue. $[\alpha]_D^{20}$ (c = 0.5, $CHCl_3$) = -80.8°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.83 (s, 6H), 2.26 (s, 24 H), 3.36 (d, *J* = 14.7 Hz, 2H), 3.72 (d, *J* = 14.7 Hz, 2H), 4.99 (s, 2H), 6.85 (s, 4H), 6.87 (s, 4H), 7.06 (s, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 21.5 ($ArCH_3$), 21.6 ($ArCH_3$), 26.7 ($-CH_3$), 53.0 (Ar_2C-), 62.3 ($-CH_2N$-), 79.6 (-CH-), 108.9 ($-C(O)_2$-), 126.1 (ArC), 127.8 (ArC), 127.9 (ArC), 128.7 (ArC), 136.1 (ArC), 137.2 (ArC), 137.3 (ArC), 137.9 (ArC) ppm; IR (film): $\tilde{\nu}$ = 3020, 2993, 2937, 2879, 1598, 1492, 1442, 1377, 1367, 1249, 1209, 1165, 1136, 1062, 1020, 873, 754, 738 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{41}H_{49}NO_2$: 588.3836 $[M+H]^+$; found: 588.3834.

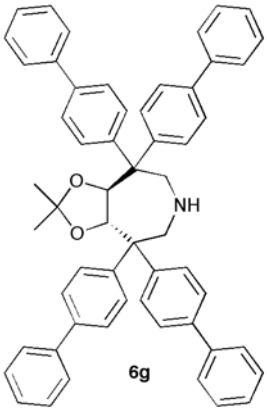
Amine (*S,S*)-6f. Prepared from (*S,S*)-**5f** (483 mg, 0.61 mmol) in 29% (138 g, 0.18 mmol).



6f

Oily residue. $[\alpha]_D^{20}$ (c = 1.15, $CHCl_3$) = -44.9°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.84 (s, 6H), 3.59 (d, *J* = 14.6 Hz, 2H), 3.86 (d, *J* = 14.6 Hz, 2H), 5.32 (s, 2H), 7.26-7.36 (m, 10H), 7.39-7.51 (m, 18H), 7.55 (d, *J* = 7.7 Hz, 4H), 7.67 (s, 2H), 7.89 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 26.9 ($-CH_3$), 54.2 (Ar_2C-), 63.3 ($-CH_2N$-), 80.0 (-CH-), 109.4 ($-C(O)_2$-), 125.2 (ArC), 125.4 (ArC), 127.1 (ArC), 127.3 (ArC), 127.4 (ArC), 127.5 (ArC), 127.6 (ArC), 128.6 (ArC), 128.8 (ArC), 128.9 (ArC), 129.9 (ArC), 130.5 (ArC), 139.9 (ArC), 141.0 (ArC), 141.6 (ArC) 141.7 (ArC), 144.3 (ArC), 149.0 (ArC) ppm; IR (film): $\tilde{\nu}$ = 3030, 2968, 1597, 1477, 1460, 1409, 1369, 1263, 1244, 1216, 1172, 1072, 877, 766, 734 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{57}H_{49}NO_2$: 780.3836 $[M+H]^+$; found: 780.3842.

Amine (*S*,*S*)-6g. Prepared from (*S*,*S*)-**5g** (2.13 g, 2.7 mmol) in 30% (631 mg, 0.81 mmol).

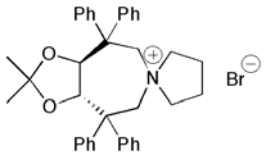


6g

White foam. $[\alpha]_D^{20}$ (c = 1.14, $CHCl_3$) = -143.4°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.86 (s, 6H), 3.54 (d, *J* = 14.5 Hz, 2H), 3.89 (d, *J* = 14.5 Hz, 2H), 5.21 (s, 2H), 7.31-7.34 (m, 4H), 7.41-7.44 (m, 12H), 7.51-7.64 (m, 20H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 27.0 ($-CH_3$), 53.7 (Ar_2C-), 63.1 ($-CH_2N$-), 79.7 (-CH-), 109.6 ($-C(O)_2$-), 125.7 (ArC), 126.9 (ArC), 127.1 (ArC), 127.2 (ArC), 127.3 (ArC), 127.4 (ArC), 128.8 (ArC), 128.9 (ArC), 131.7 (ArC), 139.0 (ArC), 139.1 (ArC), 140.9 (ArC), 141.0 (ArC), 142.8 (ArC), 147.6 (ArC) ppm; IR (film): $\bar{\nu}$ = 3028, 2983, 1732, 1598, 1485, 1369, 1240, 1215, 1166, 1072, 1006, 831, 763, 742 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{57}H_{49}NO_2$: 818.3395 $[M+K]^+$; found: 818.3376.

Syntheses of quaternary ammonium salts 3: A mixture of **6**, dibromoalkane (4 eq.), and K_2CO_3 (4 eq.) in acetonitrile (60 mL / mmol **6**) was refluxed for 2 days. The inorganic salts were filtered off, the solvent evaporated and the residue purified by column chromatography (CH_2Cl_2:MeOH = 10:1) to obtain ammonium salts **3** in the reported yields. Unreacted starting material **6** (25-45%) could easily be recovered reused again.

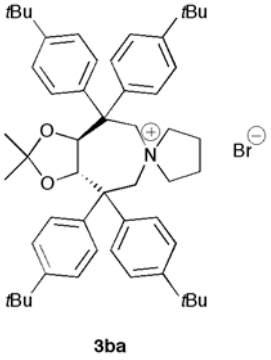
Ammonium salt (*S*,*S*)-3aa. Prepared from (*S*,*S*)-**6a** (201 mg, 0.42 mmol) and



3aa

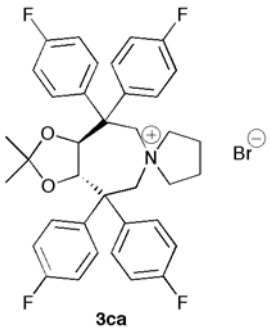
1,4-dibromobutane in 62% (160 mg, 0.26 mmol). White solid. M.p.: 154-157°C; $[\alpha]_D^{20}$ (c = 1.66, $CHCl_3$) = -73.7°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.6 (s, 6H), 0.91 (bm, 2H), 1.38 (bm, 2H), 3.50 (bm, 2H), 3.72 (bm, 2H), 4.86 (bm, 2H), 5.46 (bm, 2H), 5.47 (s, 2H), 7.19-7.22 (m, 2H), 7.29-7.33 (m, 6H), 7.41-7.45 (m, 8H), 7.89 (bs, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 19.7 ($-CH_2$-), 25.0 ($-CH_3$), 52.2 (Ar_2C-), 65.8 ($-CH_2N^+$-), 69.7 ($-CH_2N^+$-), 78.3 (-CH-), 110.1 ($-C(O)_2$-), 126.9 (ArC), 127.2 (ArC), 127.9 (ArC), 128.1 (ArC), 128.3 (ArC), 130.4 (ArC), 138.5 (ArC), 144.1 (ArC) ppm; IR (film): $\bar{\nu}$ = 3055, 2991, 2937, 1496, 1444, 1382, 1249, 1213, 1076, 1056, 869, 729 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{37}H_{40}NO_2^+$: 530.3054 $[M^+]$; found: 530.3052.

Ammonium salt (*S,S*)-3ba. Prepared from (*S,S*)-**6b** (52 mg, 0.074 mmol) and 1,4-dibromobutane in 65% (40 mg, 0.048 mmol). Oily residue. $[\alpha]_D^{20}$ (c = 0.38, $CHCl_3$) = -55.3°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.72 (s, 6H), 1.08 (bm, 2H), 1.24 (s, 18H), 1.28 (s, 18H), 1.46 (bm, 2H), 3.58-3.70 (m, 4H), 4.86 (bm, 2H), 5.28 (bm, 2H), 5.39 (s, 2H), 7.26-7.41 (m, 12H), 7.72 (bs, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 20.5 (-CH_2-), 25.6 (-CH_3), 31.4 (-C(CH_3)$_3$) 34.6 (-*C*(CH_3)$_3$) 52.1 (Ar_2*C*-), 66.5 (-CH_2N^+-), 70.5 (-CH_2N^+-), 78.9 (-CH-), 110.6 (-$C(O)_2$-), 125.4 (ArC), 125.8 (ArC), 128.2 (ArC), 130.2 (ArC), 136.3 (ArC), 141.5 (ArC), 150.3 (ArC), 150.6 (ArC) ppm; IR (film): $\tilde{\nu}$ = 2962, 2868, 1458, 1363, 1271, 1249, 1209, 1101, 1076, 1055, 831, 754 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{53}H_{72}NO_2^+$: 754.5558 [M^+]; found: 754.5568.



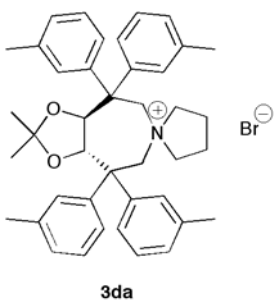
3ba

Ammonium salt (*S,S*)-3ca. Prepared from (*S,S*)-**6c** (128 mg, 0.333 mmol) and 1,4-dibromobutane in 51% (115 mg, 0.17 mmol). White solid. M.p.: 142-144°C; $[\alpha]_D^{20}$ (c = 0.8, $CHCl_3$) = -40.0°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.81 (s, 6H), 1.04 (bm, 2H), 1.53 (bm, 2H), 3.49-3.66 (m, 4H), 4.86 (bm, 2H), 5.32 (s, 2H), 5.51 (bm, 2H), 6.85-7.05 (m, 4H), 7.11-7.15 (m, 4H), 7.54 (m, 4H), 7.93 (bs, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 20.5 (-CH_2-), 25.7 (-CH_3), 52.2 (Ar_2*C*-), 66.3 (-CH_2N^+-), 70.5 (-CH_2N^+-), 79.0 (-CH-), 110.9 (-$C(O)_2$-), 115.6 (d, *J* = 21 Hz, ArC), 116.0 (d, *J* = 21 Hz, ArC), 130.4 (ArC), 132.9 (ArC), 134.4.2 (ArC), 140.2 (ArC), 161.1 (d, *J* = 51 Hz, ArC), 163.0 (d, *J* = 51 Hz, ArC) ppm; IR (film): $\tilde{\nu}$ = 2991, 1602, 1510, 1382, 1238, 1166, 1078, 1014, 835 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{37}H_{36}F_4NO_2^+$: 602.2677 [M^+]; found: 602.2682.



3ca

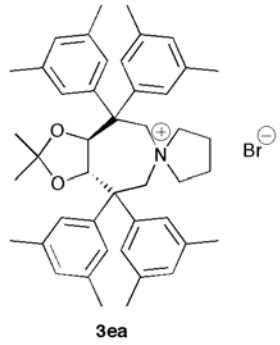
Ammonium salt (*S,S*)-3da. Prepared from (*S,S*)-**6d** (73 mg, 0.137 mmol) and 1,4-dibromobutane in 49% (45 mg, 0.067 mmol). Colourless oily residue. $[\alpha]_D^{20}$ (c = 1.17, $CHCl_3$) = -68.1°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.79 (s, 6H), 1.29 (bm, 2H), 1.63 (bm, 2H), 2.33 (s, 6H), 2.39 (s, 6H), 3.45 (m, 2H), 3.66 (m, 2H), 4.89 (d, *J* = 12.8 Hz, 2H), 5.16 (d, *J* = 12.8 Hz, 2H), 5.41 (s, 2H), 7.04-7.10 (m, 4H), 7.21-7.30 (m, 8H), 7.51 (m, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 20.4 (-CH_2-), 21.7 ($ArCH_3$), 21.9 ($ArCH_3$), 25.7 (-CH_3), 52.7 (Ar_2*C*-), 66.5



3da

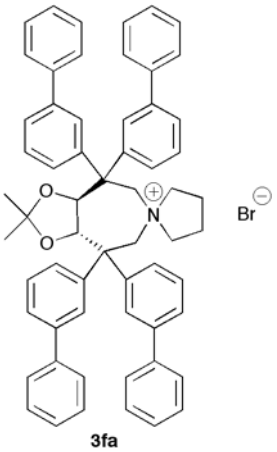
(-CH_2N^+-), 70.5 (-CH_2N^+-), 78.9 (-CH-), 110.7 (-$C(O)_2$-), 125.6 (ArC), 127.7 (ArC), 128.3 (ArC (2x)), 128.5 (ArC), 128.7 (ArC), 129.3 (ArC), 131.5 (ArC), 137.9 (ArC), 138.4 (ArC), 139.1 (ArC), 144.6 (ArC) ppm; IR (film): $\bar{\nu}$ = 3039, 2989, 1602, 1489, 1456, 1375, 1265, 1251, 1213, 1168, 1078, 877, 854, 788, 731 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{41}H_{48}NO_2^+$: 586.3680 [M^+]; found: 586.3684.

Ammonium salt (*S*,*S*)-3ea. Prepared from (*S*,*S*)-**6e** (70 mg, 0.119 mmol) and 1,4-dibromobutane in 57% (49 mg, 0.068 mmol). Colourless oily residue. $[\alpha]_D^{20}$ (c = 1.2, $CHCl_3$) = -69.0°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.83 (s, 6H), 1.34 (m, 2H), 1.64 (m, 2H), 2.30 (s, 12H), 2.33 (s, 12H), 3.48 (m, 2H), 3.60 (m, 2H), 4.76 (d, *J* = 14.0 Hz, 2H), 5.01 (d, *J* = 14.0 Hz, 2H), 5.39 (s, 2H), 6.87 (s, 2H), 6.89 (s, 2H), 7.09 (s, 4H), 7.26 (bs, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 20.5 (-CH_2-), 21.6 ($ArCH_3$), 21.8 ($ArCH_3$), 26.0 (-CH_3), 52.5 (Ar_2C-), 66.7 (-CH_2N^+-), 70.2 (-CH_2N^+-), 78.6 (-CH-), 111.0 (-$C(O)_2$-), 126.4 (ArC), 128.2 (ArC), 129.3 (ArC), 129.4 (ArC), 137.6 (ArC), 138.3 (ArC), 139.3 (ArC), 144.0 (ArC) ppm; IR (film): $\bar{\nu}$ = 2966, 2918, 1724, 1597, 1456, 1375, 1265, 1251, 1211, 1166, 1072, 912, 850, 731 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{45}H_{56}NO_2^+$: 642.4306 [M^+]; found: 642.4301.



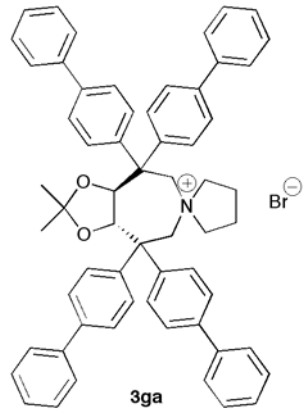
3ea

Ammonium salt (*S*,*S*)-3fa. Prepared from (*S*,*S*)-**6f** (131 mg, 0.168 mmol) and 1,4-dibromobutane in 58% (49 mg, 0.096 mmol). White foam. $[\alpha]_D^{20}$ (c = 0.9, $CHCl_3$) = -80.7°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.80 (bs, 6H), 0.95 (bm, 2H), 1.36 (bm, 2H), 3.48-3.95 (m, 4H), 5.08 (bs, 2H), 5.69 (bm, 4H), 7.22-8.27 (m, 36H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 20.3 (-CH_2-), 25.8 (-CH_3), 53.2 (Ar_2C-), 66.8 (-CH_2N^+-), 70.5 (-CH_2N^+-), 79.3 (-CH-), 110.9 (-$C(O)_2$-), 126.3 (ArC), 126.5 (ArC), 126.9 (ArC), 127.4 (ArC), 127.6 (ArC), 127.7 (ArC), 128.2 (ArC), 129.0 (ArC), 129.1 (ArC), 129.4 (ArC), 129.8 (ArC), 139.8 (ArC), 140.3 (ArC), 140.9 (ArC), 141.1 (ArC), 141.3 (ArC), 145.5 (ArC) ppm; IR (film): $\bar{\nu}$ = 3032, 1597, 1481, 1450, 1373, 1249, 1213, 1157, 1072, 758 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{61}H_{56}NO_2^+$: 834.4306 [M^+]; found: 834.4314.

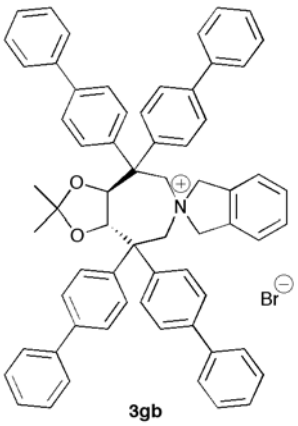


3fa

Ammonium salt (*S,S*)-3ga. Prepared from (*S,S*)-**6g** (134 mg, 0.172 mmol) and 1,4-dibromobutane in 57% (108 mg, 0.118 mmol). White solid. M.p.: 163-168°C; $[\alpha]_D^{20}$ (c = 0.74, $CHCl_3$) = -57.4°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.89 (s, 6H), 1.24 (b, 2H), 1.62 (b, 2H), 3.57 (bm, 2H), 3.77 (bm, 2H), 5.03 (bm, 2H), 5.44 (bm, 2H), 5.64 (s, 2H), 7.31-7.41 (m, 8H), 7.46 (t, *J* = 7.2 Hz, 4H), 7.52-7.62 (m, 12H), 7.67 (d, *J* = 7.8 Hz, 4H), 7.74 (d, *J* = 7.5 Hz, 4H), 7.97 (bs, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 20.7 ($-CH_2-$), 25.8 ($-CH_3$), 52.6 (Ar_2C-), 66.8 ($-CH_2N^+-$), 70.6 ($-CH_2N^+-$), 79.2 (-CH-), 110.9 ($-C(O)_2-$), 127.0 (ArC (2x)), 127.1 (ArC), 127.5 (ArC), 127.7 (ArC), 127.8 (ArC), 129.0 (ArC (2x)), 129.1 (ArC), 131.3 (ArC), 138.1 (ArC), 139.9 (ArC), 140.0 (ArC), 140.1 (ArC), 140.3 (ArC), 143.6 (ArC) ppm; IR (film): $\bar{\nu}$ = 3028, 2931, 1736, 1487, 1371, 1247, 1213, 1161, 1078, 1006, 837, 765, 740, 696 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{61}H_{56}NO_2^+$: 834.4306 [M^+]; found: 834.4317.

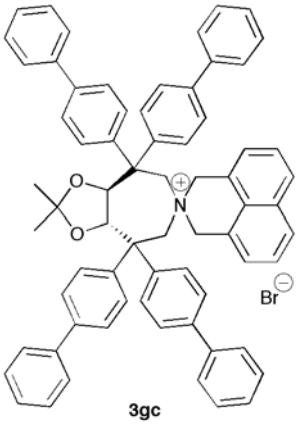


3ga



3gb

Ammonium salt (*S,S*)-3gb.[2] Prepared from (*S,S*)-**6g** (56 mg, 0.072 mmol) and dibromoxylene in 60% (42 mg, 0.043 mmol). Oily residue. $[\alpha]_D^{20}$ (c = 1.69, $CHCl_3$) = -32.4°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.92 (bs, 6H), 4.70-5.10 (bm, 4H), 5.42-5.90 (bm, 4H), 5.61 (bs, 2H), 7.23-8.16 (m, 40H) ppm; HRMS (ESI): *m/z* calcd for $C_{65}H_{56}NO_2^+$: 882.4306 [M^+]; found: 882.4320.

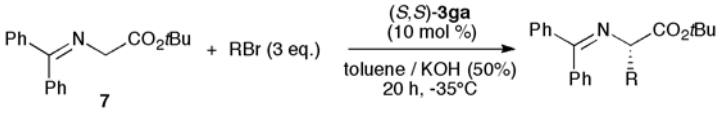


3gc

Ammonium salt (*S,S*)-3gc.[2] Prepared from (*S,S*)-**6g** (56 mg, 0.072 mmol) and dibromonapthalene in 49% (35 mg, 0.035 mmol). Oily residue. $[\alpha]_D^{20}$ (c = 1.58, $CHCl_3$) = -9.4°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.89 (bs, 6H), 4.80-5.40 (bm, 4H), 5.50-5.90 (bm, 4H), 5.72 (bs, 2H), 7.02-8.16 (m, 42H) ppm; HRMS (ESI): *m/z* calcd for $C_{69}H_{58}NO_2^+$: 932.4462 [M^+]; found: 932.4466.

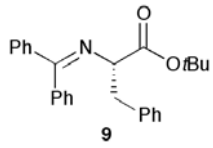
[2] ^{1}H NMR-signals were much broader than in the case of the pyrrolidine-based ammonium salts and no meaningful 13C spectra could be obtained. Thus an unambiguous proof was just possible by means of HRMS. As **3gb** and **3gc** turned out to be not useful as PTCs, no further attempts to overcome this analytical limitation were undertaken.

3. Asymmetric α-Alkylation:



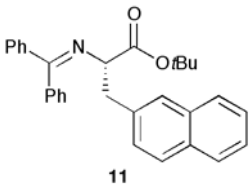
General procedure for the phase-transfer catalysed α-alkylation of glycine Schiff base 7: Reactions were usually carried out using 0.2 – 1 mmol **7**. A mixture of **7** and catalyst **3ga** (10 mol%) in toluene (6.5 mL / mmol **7**) was cooled to 0°C. KOH (50%) (2 mL / mmol **7**) was added and the vigorously stirred mixture (>1200 rpm) cooled to -35°C (Ar-atmosphere). After addition of the electrophile (3 eq.) the biphasic mixture was stirred for 20 h at -35°C. After extraction with CH_2Cl_2 / H_2O the combined organic phases were dried over Na_2SO_4, evaporated to dryness and purified by column chromatography. The alkylation products were isolated using heptanes:EtOAc = 15:1 as eluent whereas the catalyst could be recovered in >85% by flushing with CH_2Cl_2:MeOH = 10:1. The catalyst could be reused several times without any decrease in yield or enantioselectivity.

***(S)*-9.** Obtained in 81% yield and with 87% *ee* upon reacting **7** with benzylbromide (**8**).



Analytical data are in full accordance with those reported in literature.[3] $[\alpha]_D^{20}$ (c = 1.53, $CHCl_3$) = -125.7°; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.43 (s, 9H), 3.11-3.23 (m, 2H), 4.10 (dd, *J* = 9.0, 4.2 Hz, 1H), 6.59 (d, *J* = 6.6 Hz, 2H), 7.03-7.40 (m, 11H), 7.61 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 28.0, 39.6, 68.0, 81.2, 126.2, 127.7, 127.9, 128.0, 128.1, 128.3, 128.8, 129.9, 130.1, 136.4, 138.4, 139.6, 170.3, 170.9 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{27}NO_2$: 386.2115 $[M+H]^+$; found: 386.2113.

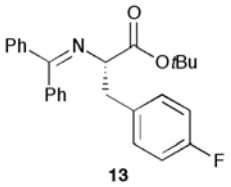
***(S)*-11.** Obtained in 83% yield and 76% *ee* upon reacting **7** with **10**. Analytical data are in full accordance with those reported in literature.[3,4] $[\alpha]_D^{20}$ (c = 0.3, $CHCl_3$) = -139.0°; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.49 (s, 9H), 3.32-3.48 (m, 2H), 4.28 (dd, *J* = 8.7, 3.9 Hz, 1H), 6.57 (d, *J* = 6.9 Hz, 2H), 7.18-7.81 (m, 15H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 28.1, 39.8, 67.9, 81.4, 125.3, 125.8, 127.5, 127.6, 127.7, 128.0, 128.1, 128.2, 128.4, 128.8, 130.1, 132.1,



[3] a) E. J. Corey, F. Xu and M. C. Noe, *J. Am. Chem. Soc.*, 1997, **119**, 12414. b) T. Ooi, M. Kameda and K. Maruoka, *J. Am. Chem. Soc.* 1999, **121**, 6519.
[4] J. H. Lee, M. S. Yoo, J. H. Jung, S. Jew, H. Park and B. S. Jeong, *Tetrahedron* 2007, **62**, 7906.

133.5, 135.9, 136.3, 170.5, 170.9 ppm; HRMS (ESI): *m/z* calcd for $C_{30}H_{29}NO_2$: 436.2271 $[M+H]^+$; found: 436.2269.

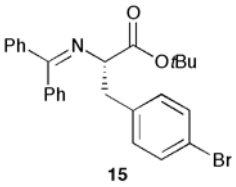
***(S)*-13.** Obtained in 80% yield and 85% *ee* upon reacting **7** with **12**. Analytical data are in full



13

accordance with those reported in literature.[3,4] $[\alpha]_D^{20}$ (c = 2.36, $CHCl_3$) = -153.2°; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.42 (s, 9H), 3.08-3.22 (m, 2H), 4.08 (m, 1H), 6.69 (d, *J* = 6.6 Hz, 2H), 6.89 (t, *J* = 8.6 Hz, 2H), 7.04 (m, 2H), 7.27-7.40 (m, 6H), 7.59 (d, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 28.0, 38.7, 67.8, 81.2, 114.8 (d, *J* = 21 Hz), 127.6, 128.0, 128.1, 128.3, 128.7, 130.2, 131.2 (d, *J* = 8 Hz), 134.1 (d, *J* = 3 Hz), 136.3, 139.4, 161.6 (d, *J* = 243 Hz), 170.4, 170.7 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{26}FNO_2$: 404.2020 $[M+H]^+$; found: 404.2036.

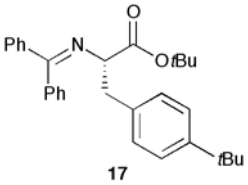
***(S)*-15.** Obtained in 79% yield and 80% *ee* upon reacting **7** with **14**. Analytical data are in full



15

accordance with those reported in literature.[5] $[\alpha]_D^{20}$ (c = 1.09, $CHCl_3$) = -110.1°; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.47 (s, 9H), 3.10-3.23 (m, 2H), 4.11 (dd, *J* = 8.1, 4.5 Hz, 1H), 6.70 (d, *J* = 6.6 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 7.28-7.62 (m, 8H), 7.60 (d, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 28.1, 39.0, 67.6, 81.4, 120.1, 127.6, 128.0, 128.2, 128.4, 128.7, 130.3, 131.1, 131.6, 136.2, 137.5, 139.4, 170.5, 170.6 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{26}BrNO_2$: 464.1220 $[M+H]^+$; found: 464.1221.

***(S)*-17.** Obtained in 79% yield and 93% *ee* upon reacting **7** with **16**. Analytical data are in full



17

accordance with those reported in literature.[4,6] $[\alpha]_D^{20}$ (c = 1.28, $CHCl_3$) = -132.0°; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.32 (s, 9H), 1.47 (s, 9H), 3.15-3.25 (m, 2H), 4.09 (dd, *J* = 9.0, 4.2 Hz, 1H), 6.55 (d, *J* = 6.6 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 7.21-7.44 (m, 8H), 7.61 (d, *J* = 7.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 28.0, 31.5, 34.4, 39.0, 68.2, 81.1, 125.0, 127.7, 127.9, 128.0, 128.1, 128.8, 129.6, 130.1, 135.3, 136.4, 139.7, 149.1, 170.1, 171.0 ppm; HRMS (ESI): *m/z* calcd for $C_{30}H_{35}NO_2$: 442.2741 $[M+H]^+$; found: 442.2740.

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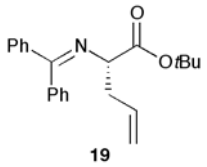
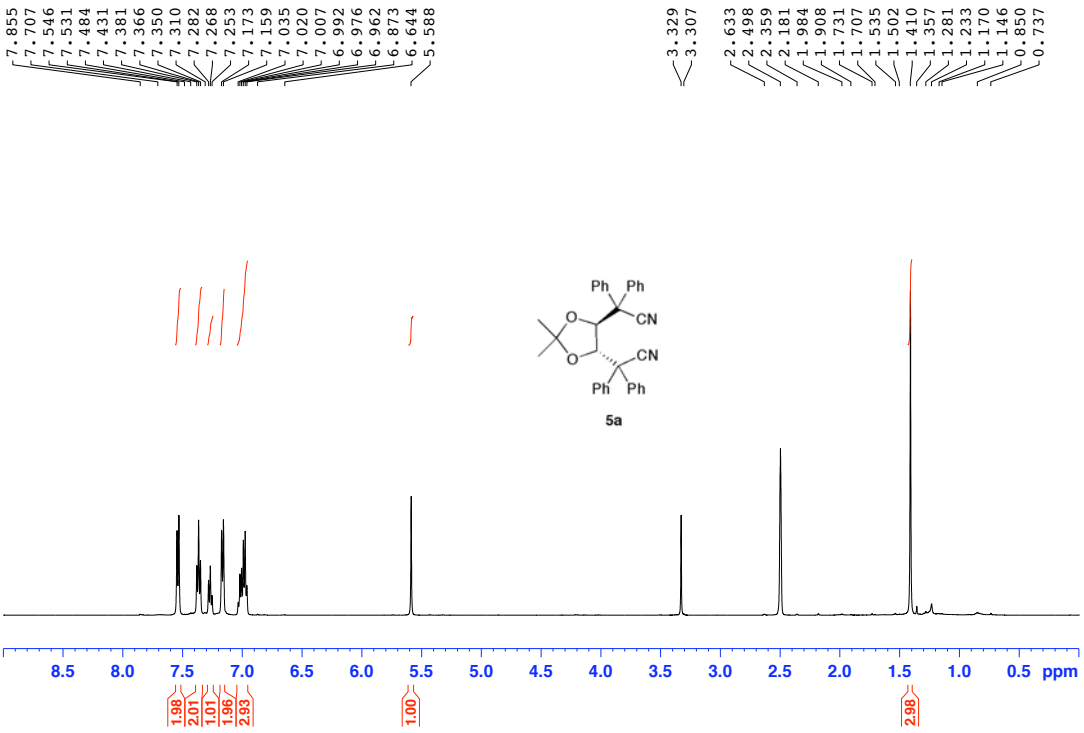
5 Y. Arakawa, N. Haraguchi and S. Itsuno, *Angew. Chem. Int. Ed.*, 2008, **47**, 8232.
6 S. Jew, B.-S. Jeong, M.-S. Yoo, H. Huh and H. Park, *Chem. Commun.*, 2001, 1244.

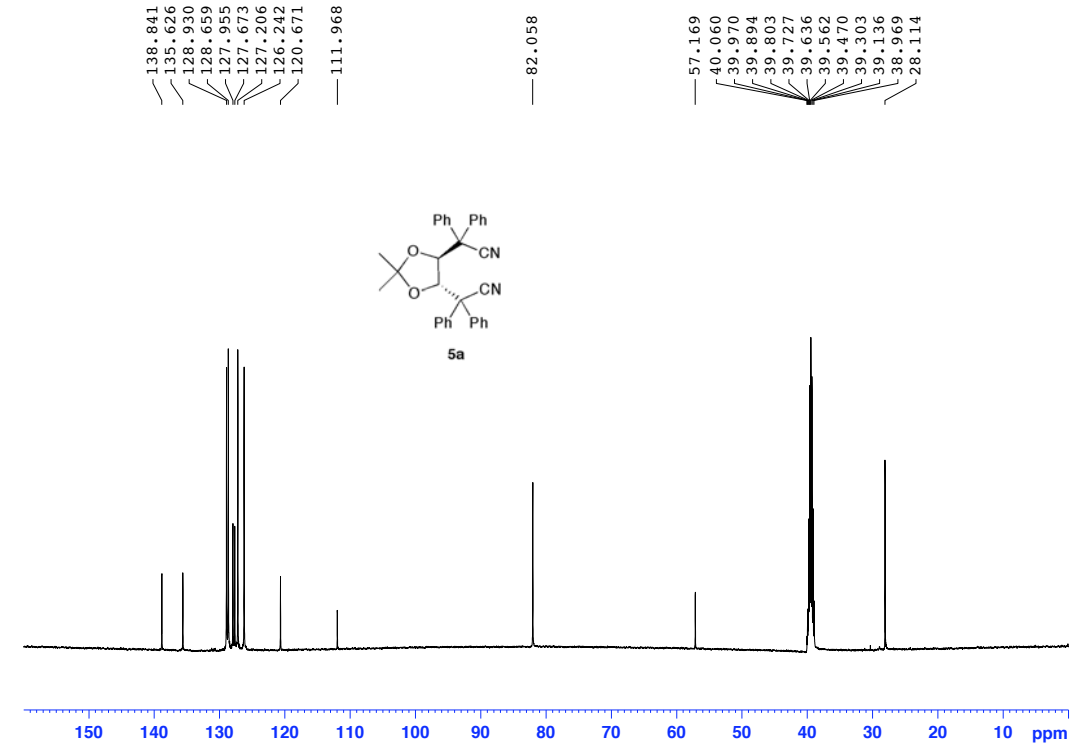
***(S)*-19.** Obtained in 71% yield and 78% *ee* upon reacting **7** with **18**. Analytical data are in full accordance with those reported in literature.[3,4] $[\alpha]_D^{20}$ (c = 1.22, $CHCl_3$) = -71.3°; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.44 (s, 9H), 2.56-2.71 (m, 2H), 4.00 (m, 1H), 5.00-5.10 (m, 2H), 5.65-5.79 (m, 1H), 7.19 (m, 2H), 7.30-7.79 (m, 6H), 7.66 (d, *J* = 7.9 Hz, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 28.1, 38.2, 65.9, 81.0, 117.3, 127.9, 128.0, 128.4, 128.5, 128.8, 130.2, 134.7, 136.7, 139.7, 170.1, 170.9 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{25}NO_2$: 336.1958 $[M+H]^+$; found: 336.1959.

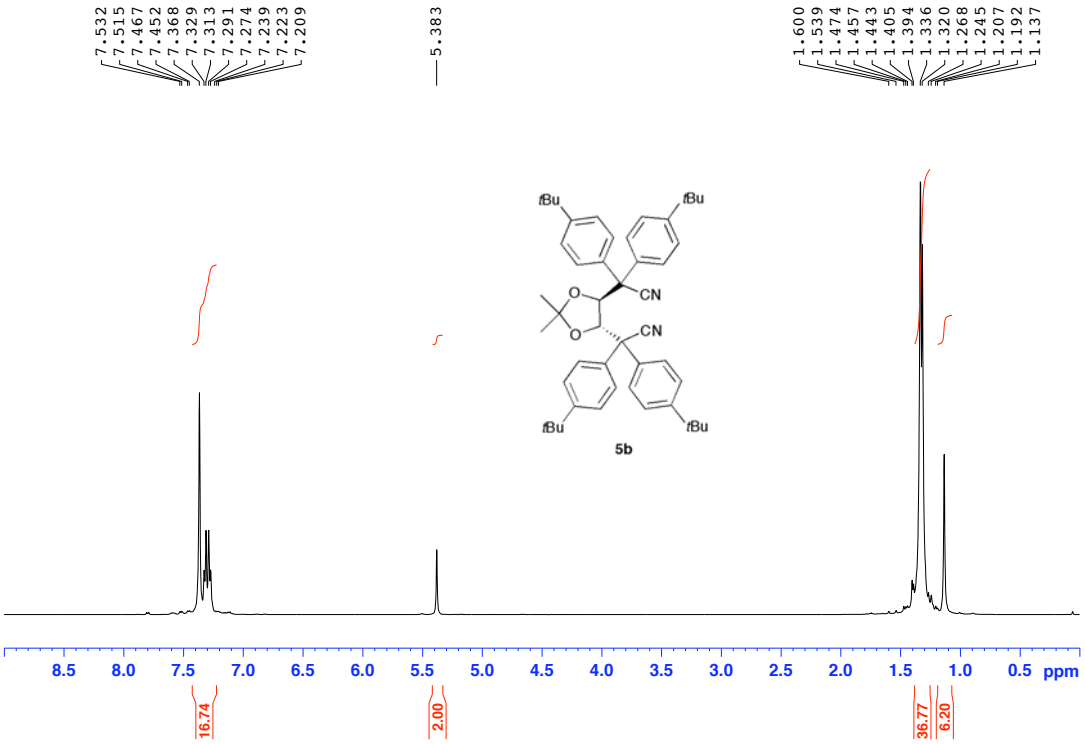


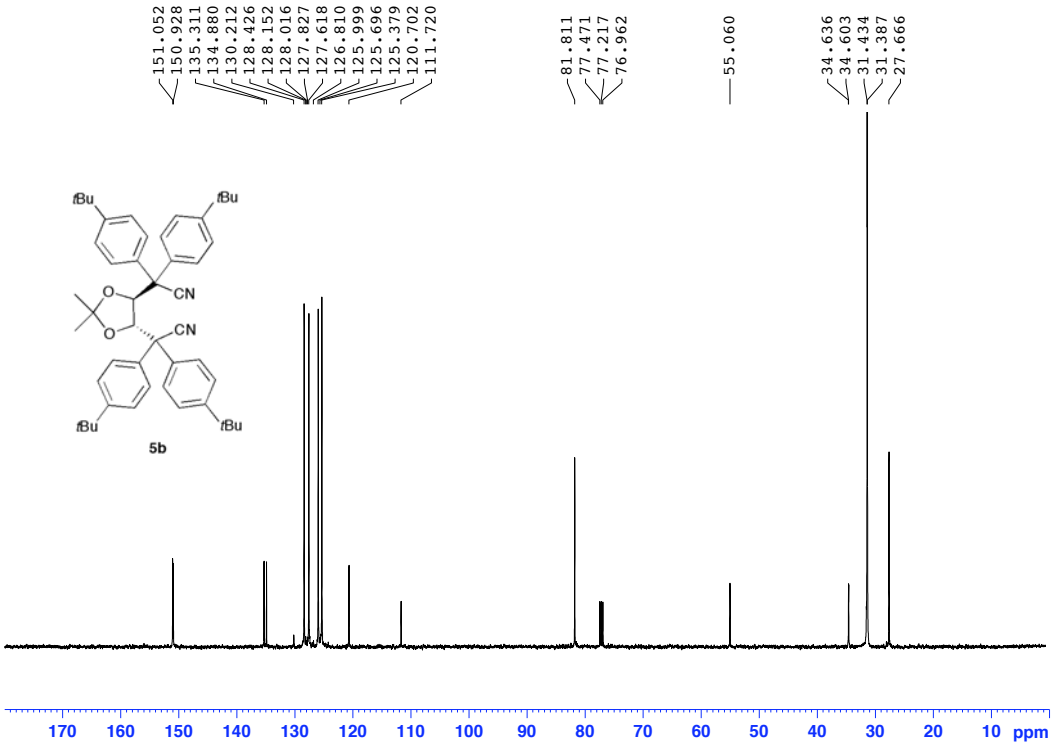
19

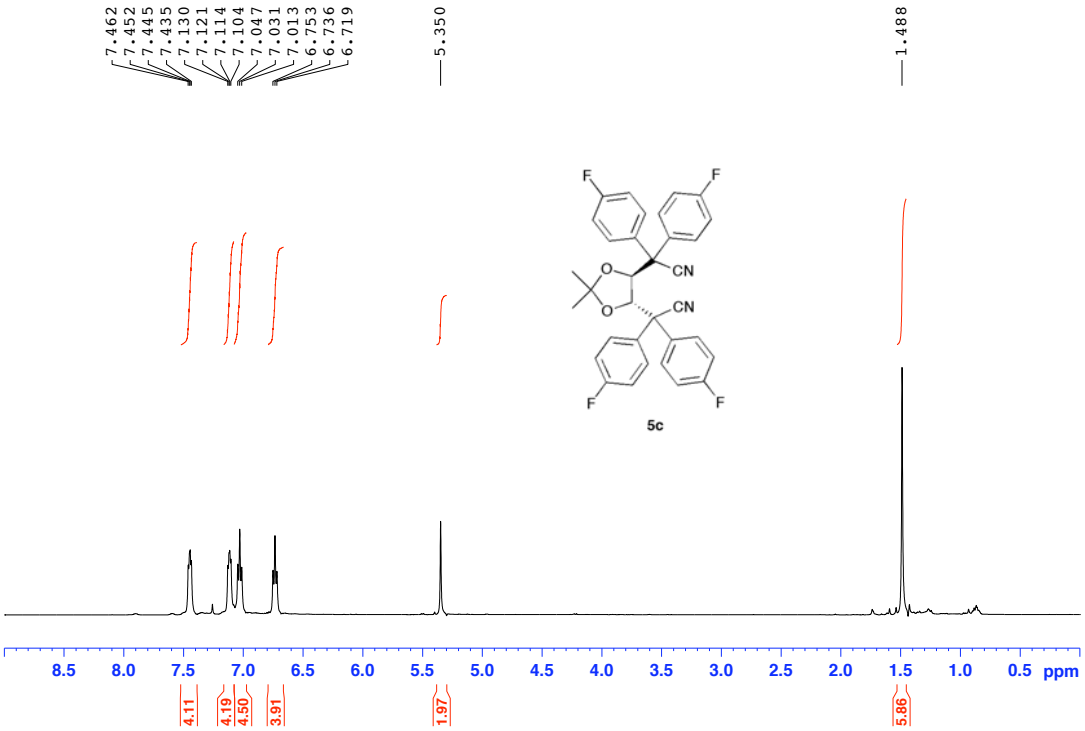
4. NMR Spectra of New Compounds:

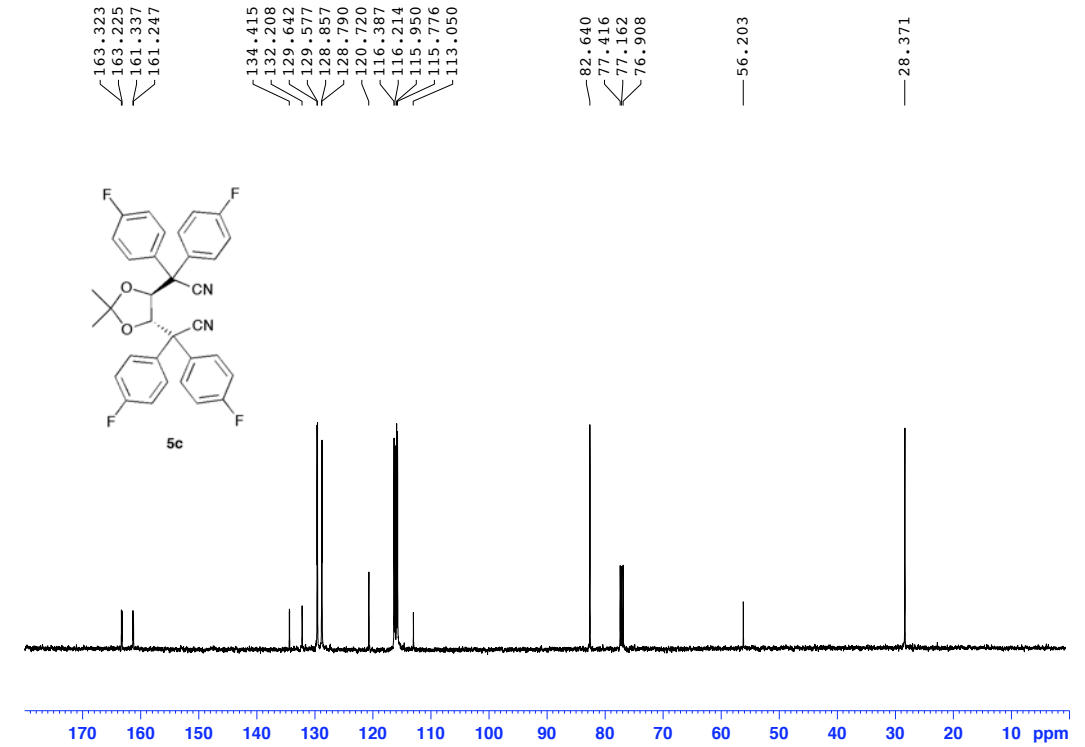


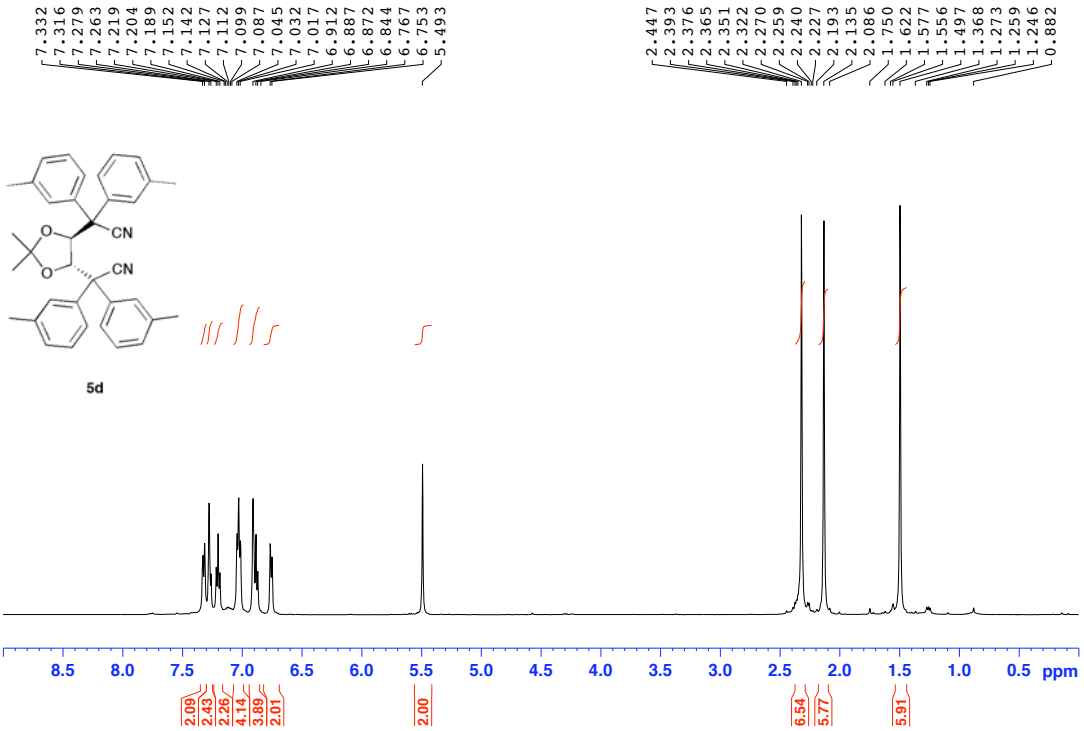


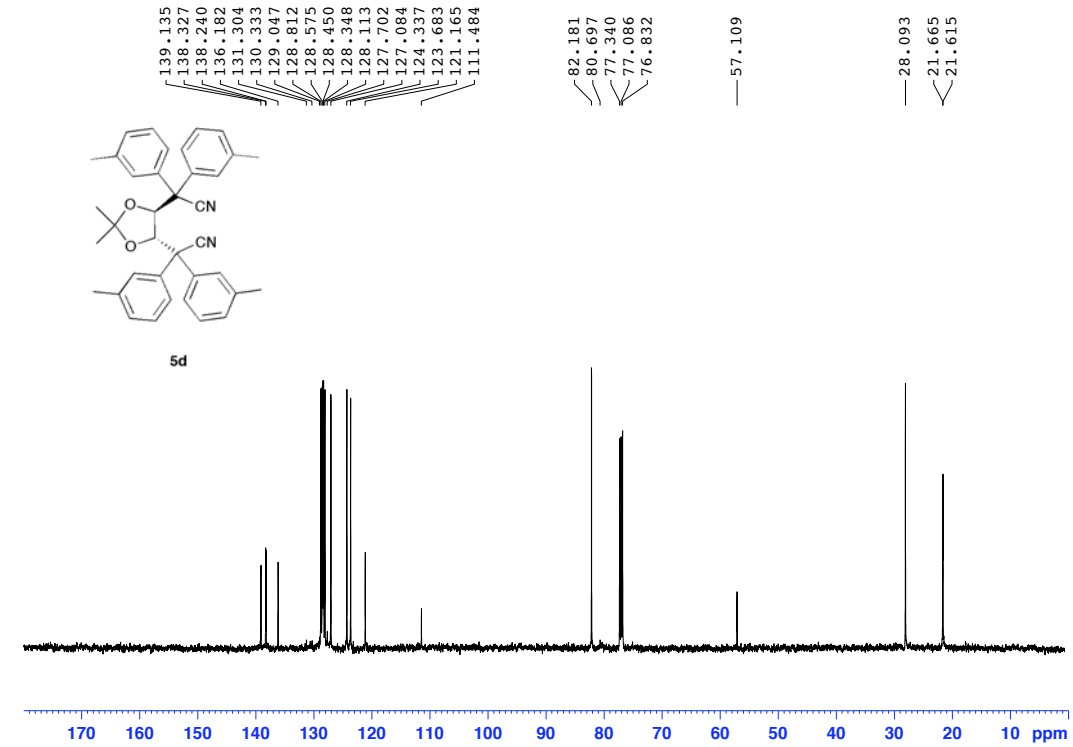


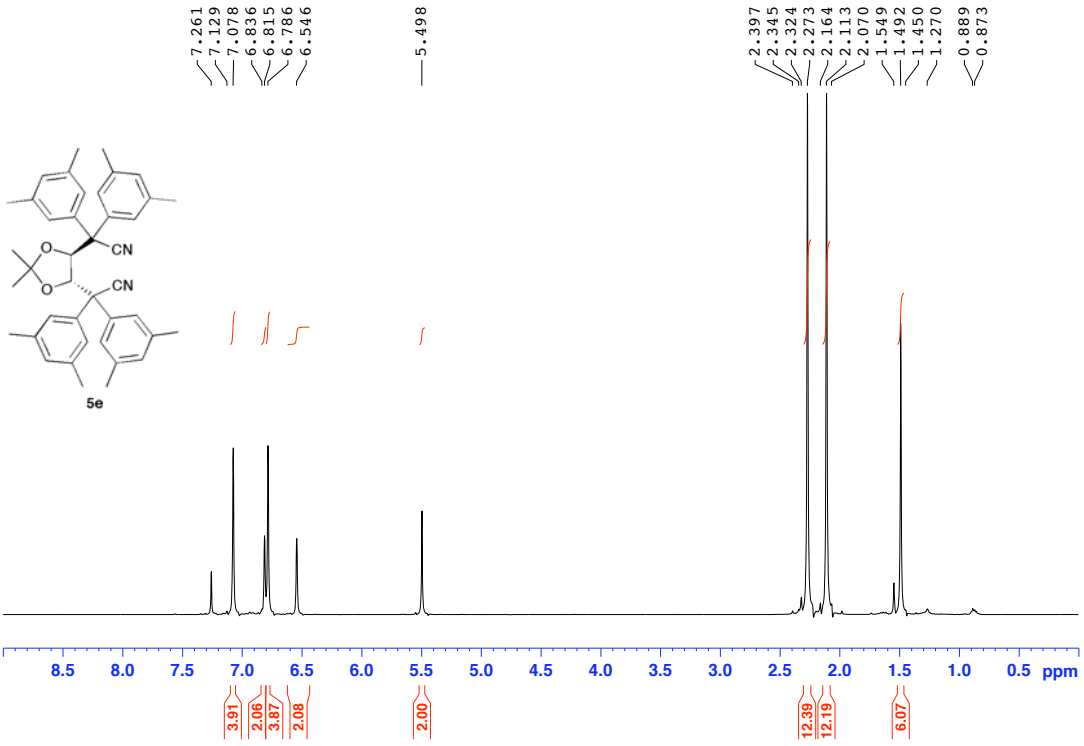


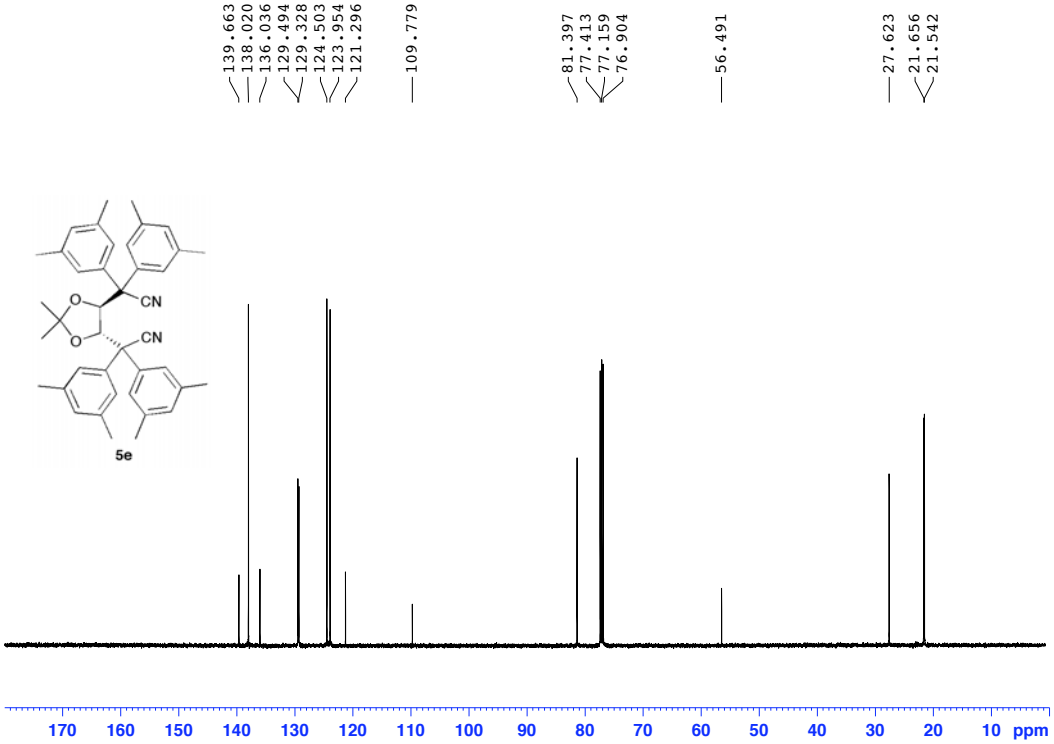


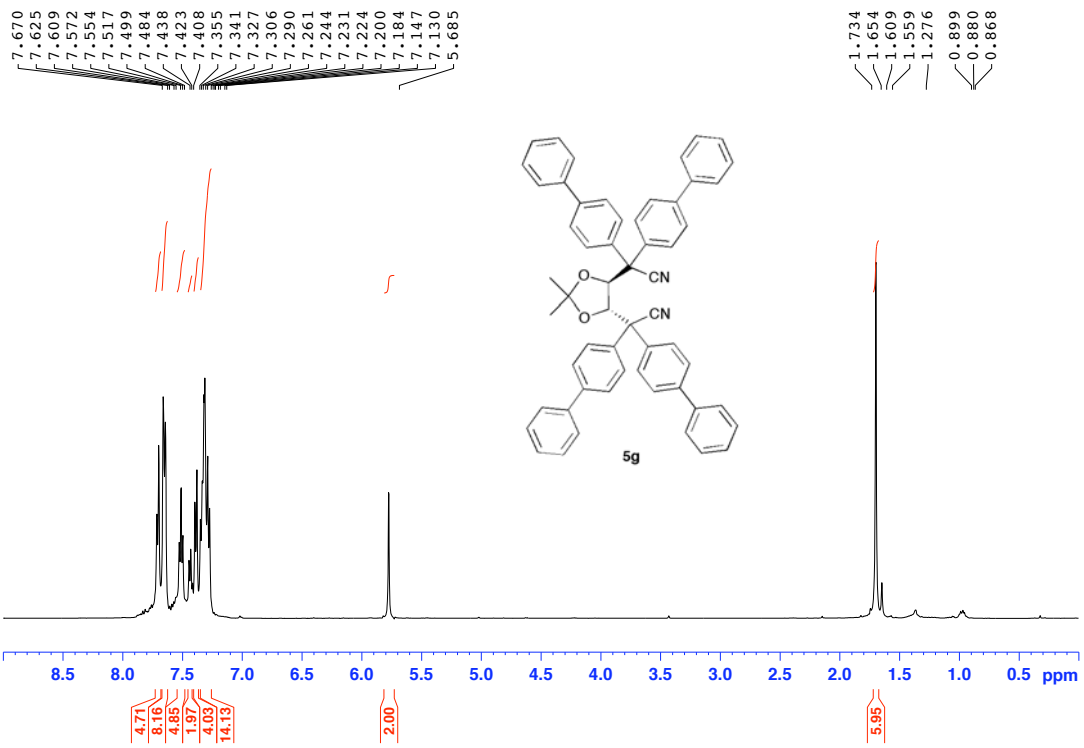








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7.572
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7.484
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7.423
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7.341
7.327
7.306
7.290
7.261
7.244
7.231
7.224
7.200
7.184
7.147
7.130
5.685
1.734
1.654
1.609
1.559
1.276
0.899
0.880
0.868
CN
CN
O
O
5g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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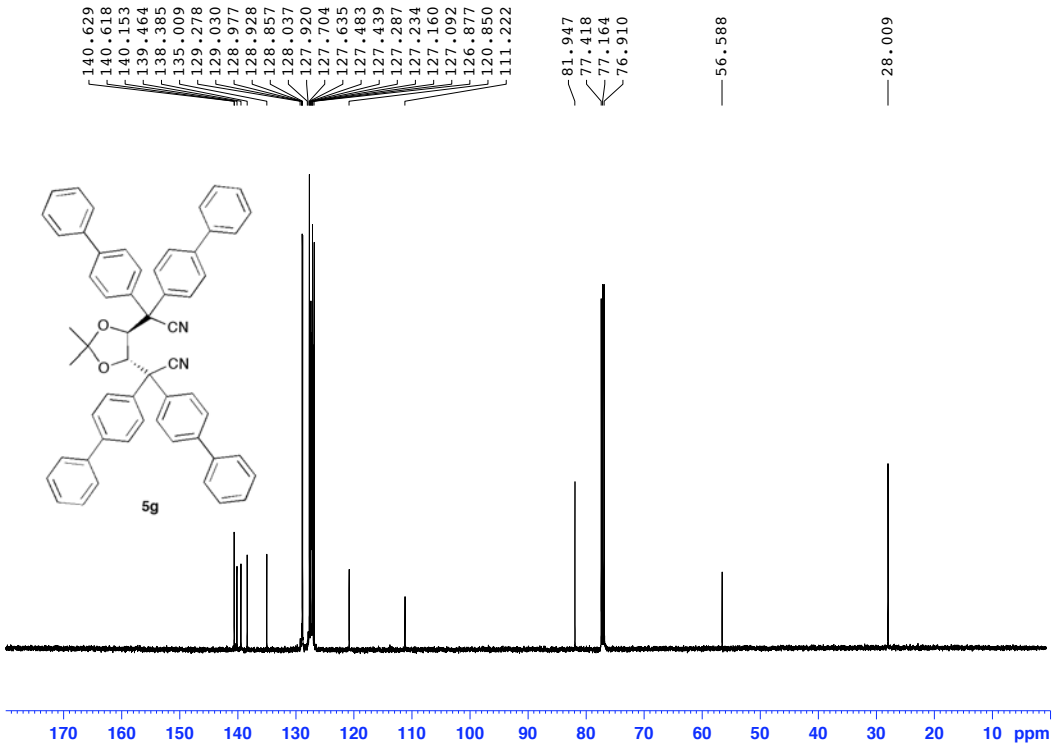
8.16
4.85
1.97
4.03
14.13
2.00
5.95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128.928
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128.037
127.920
127.704
127.635
127.483
127.439
127.287
127.234
127.160
127.092
126.877
120.850
111.222
81.947
77.418
77.164
76.910
56.588
28.009
CN
CN
O
O
5g
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150
140
130
120
110
100
90
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70
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50
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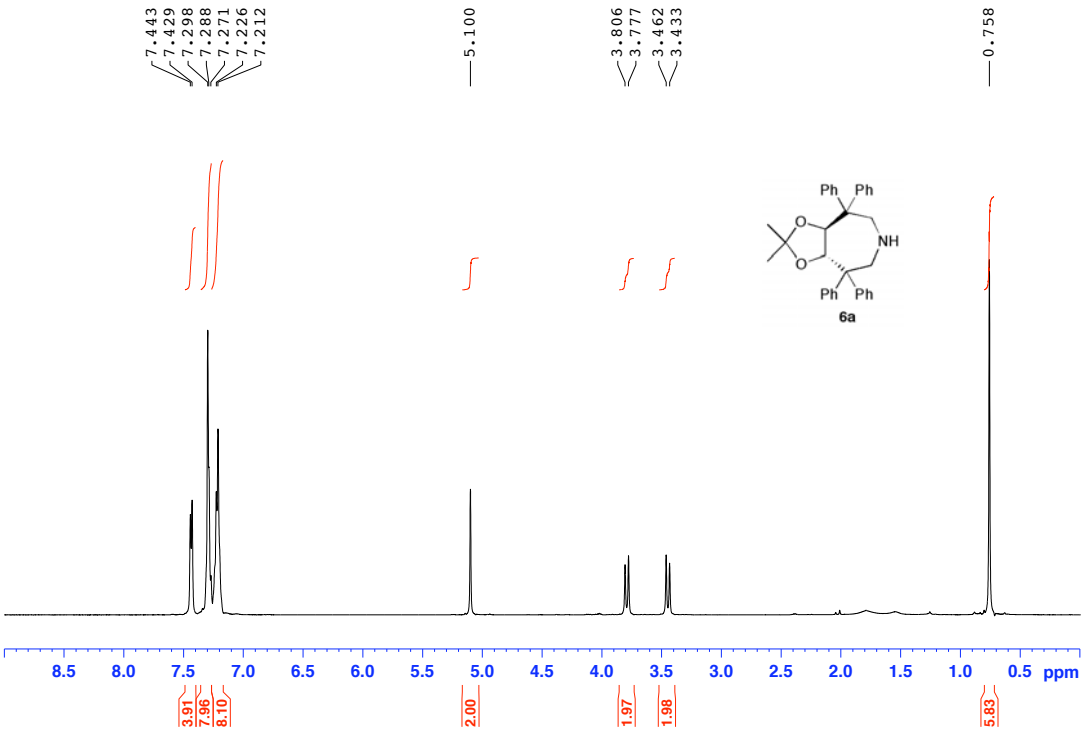
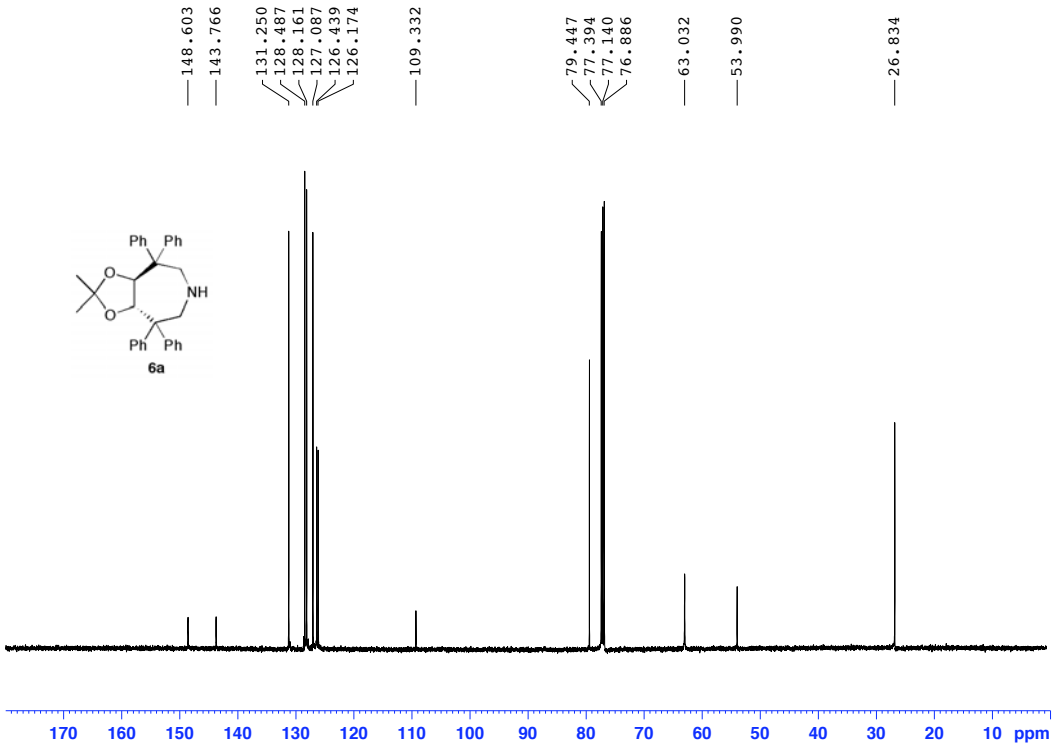
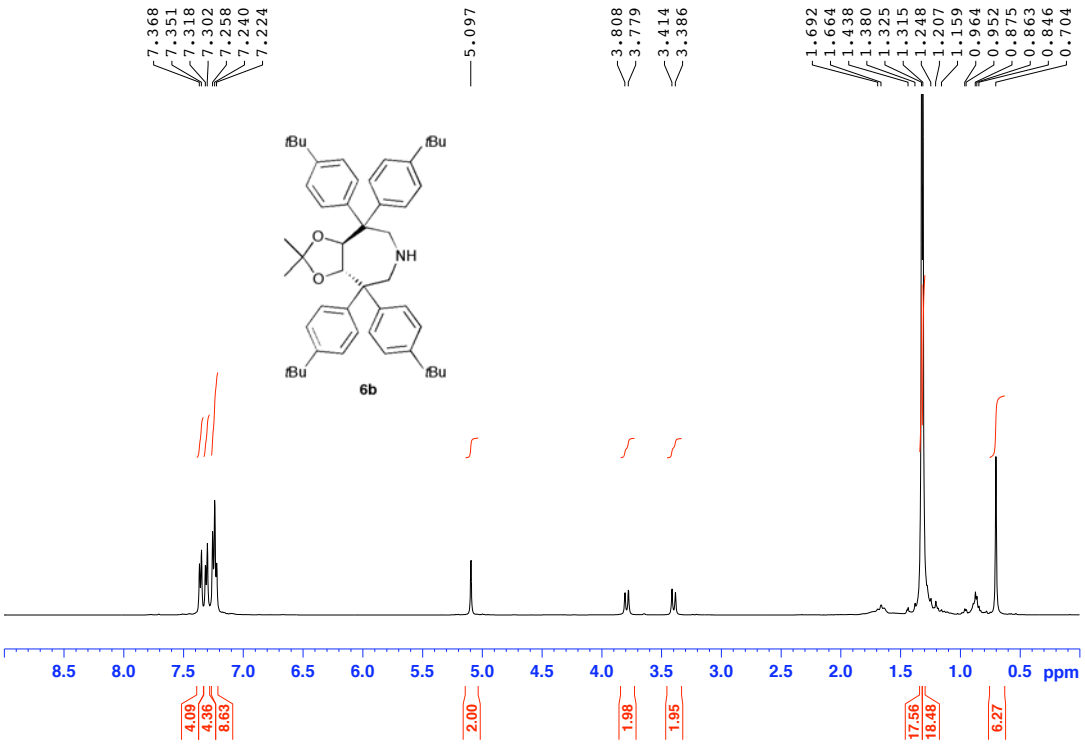
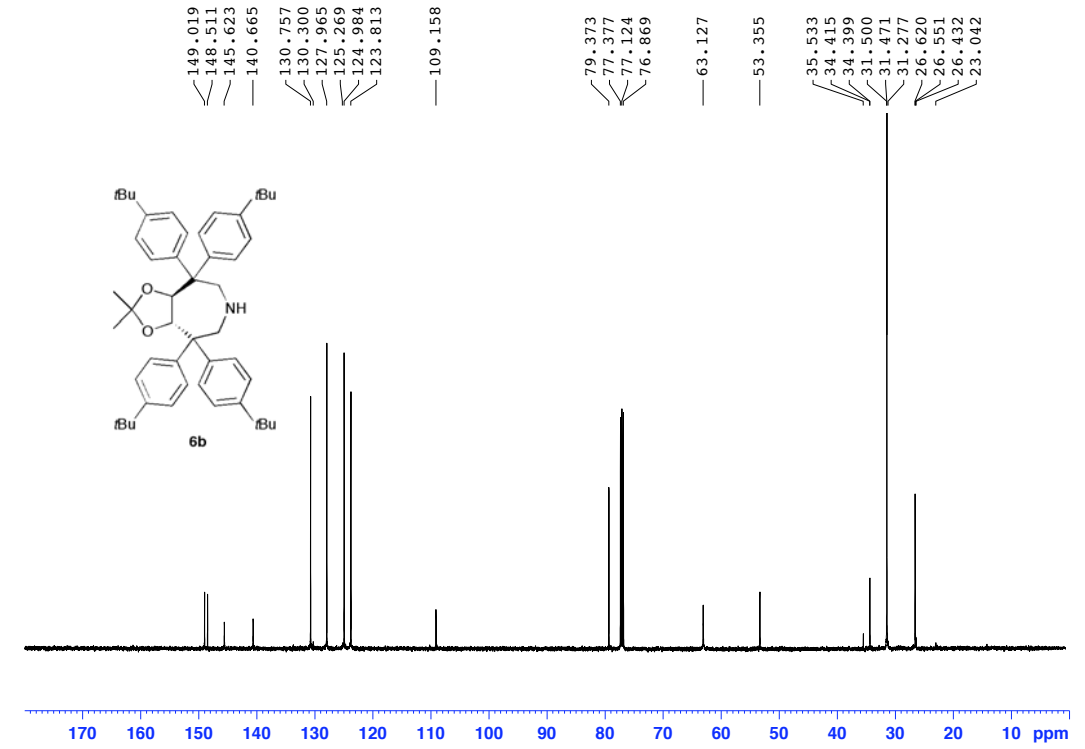
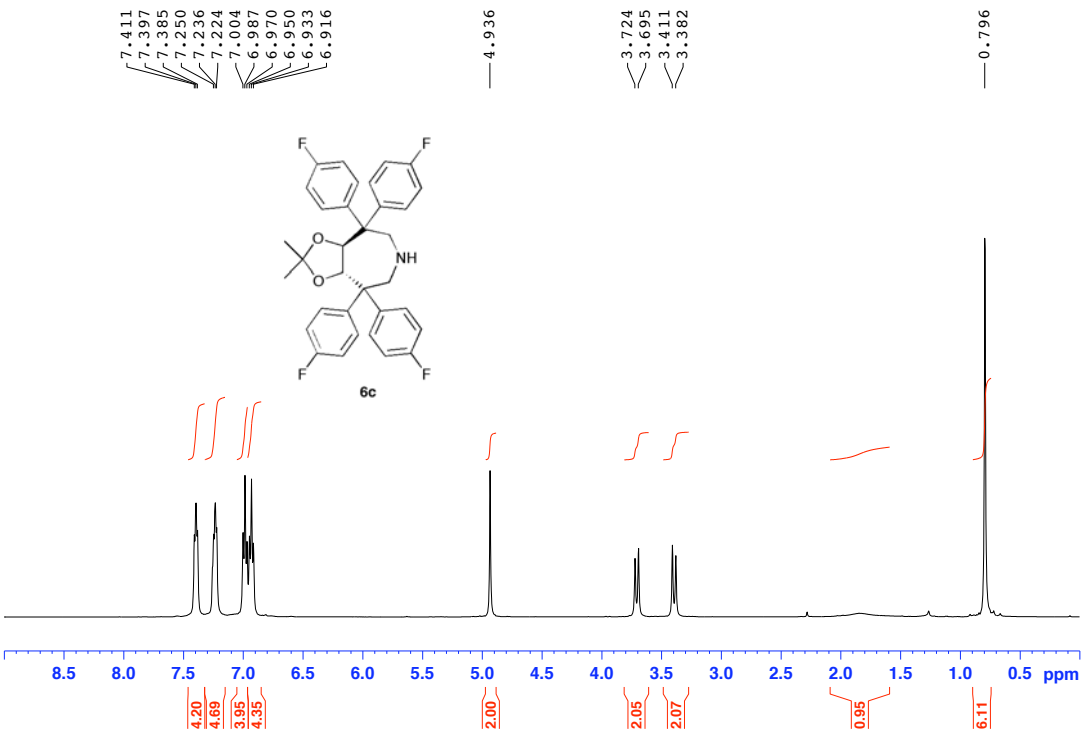
30
20
10
ppm

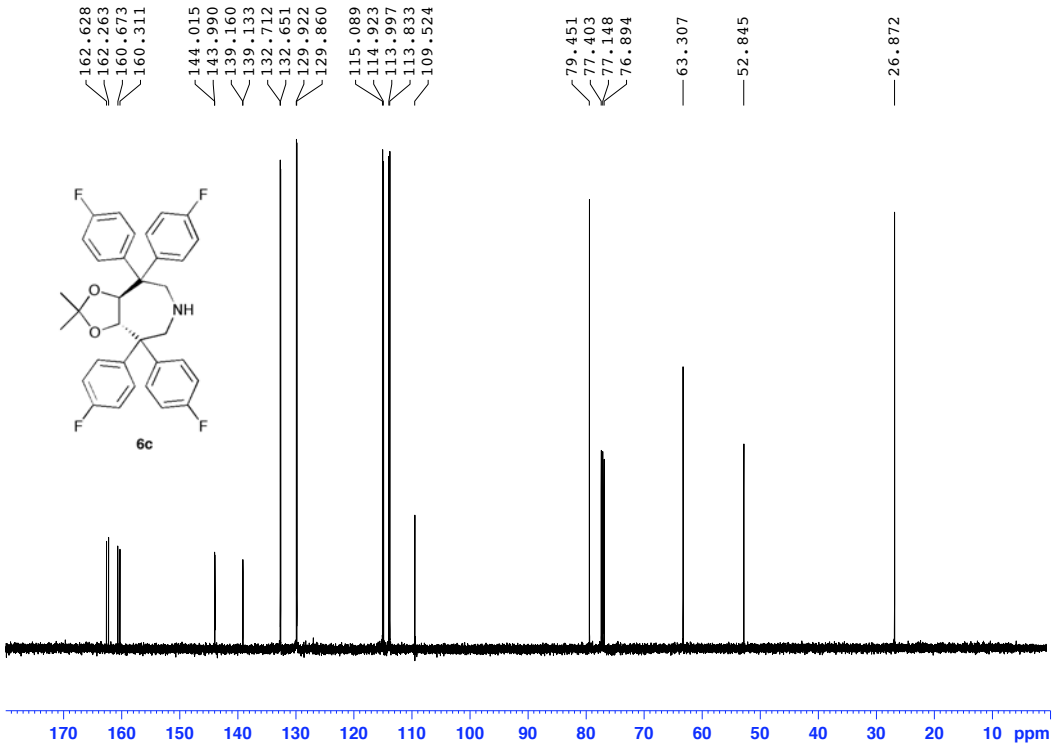


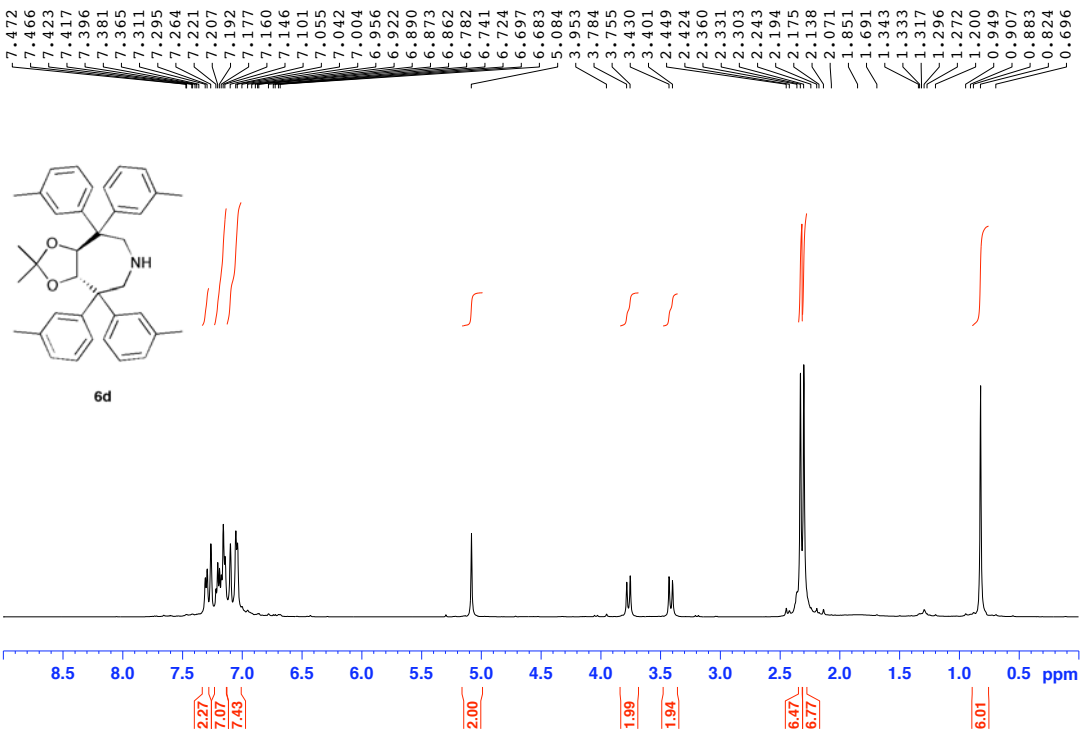


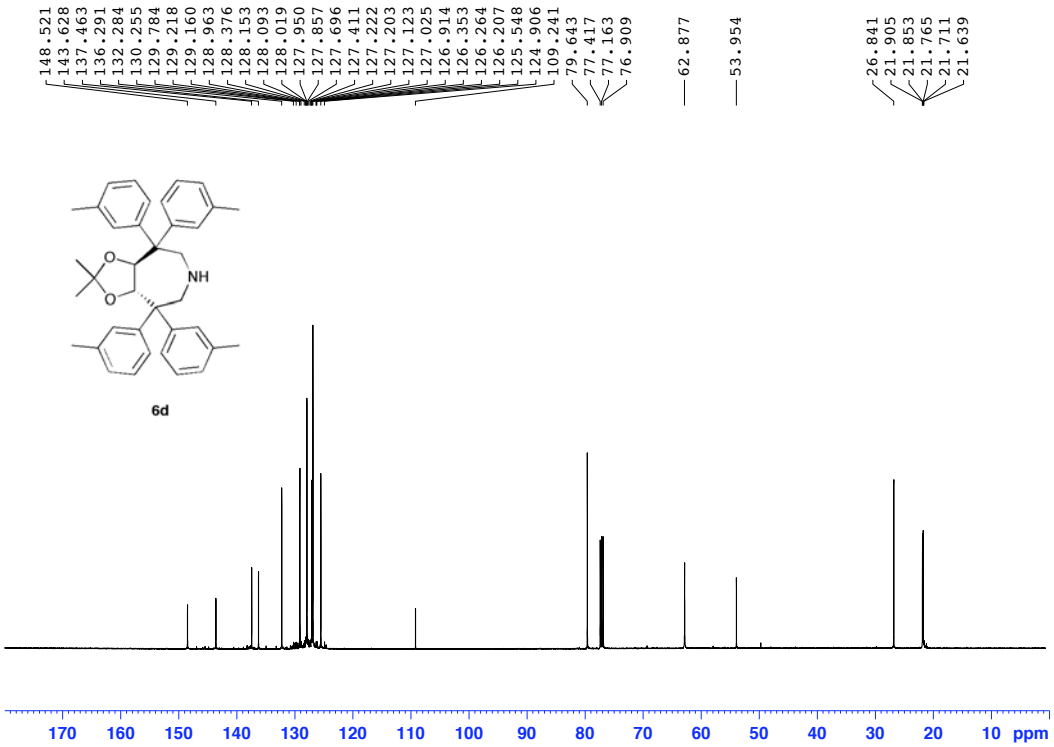


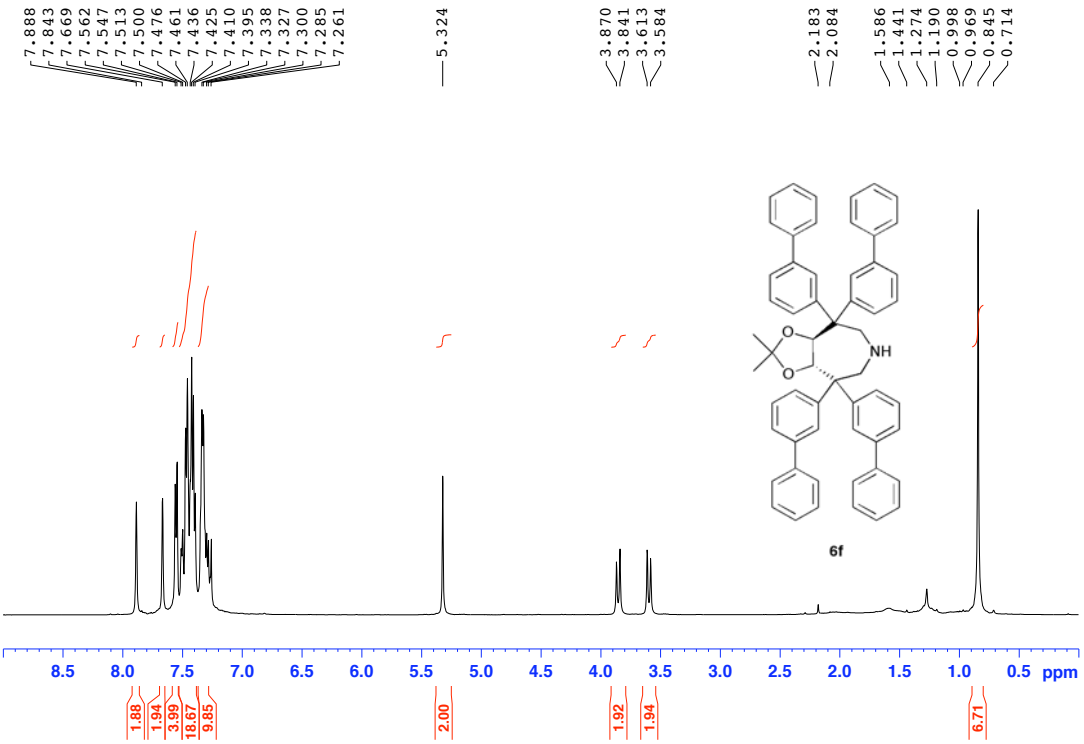


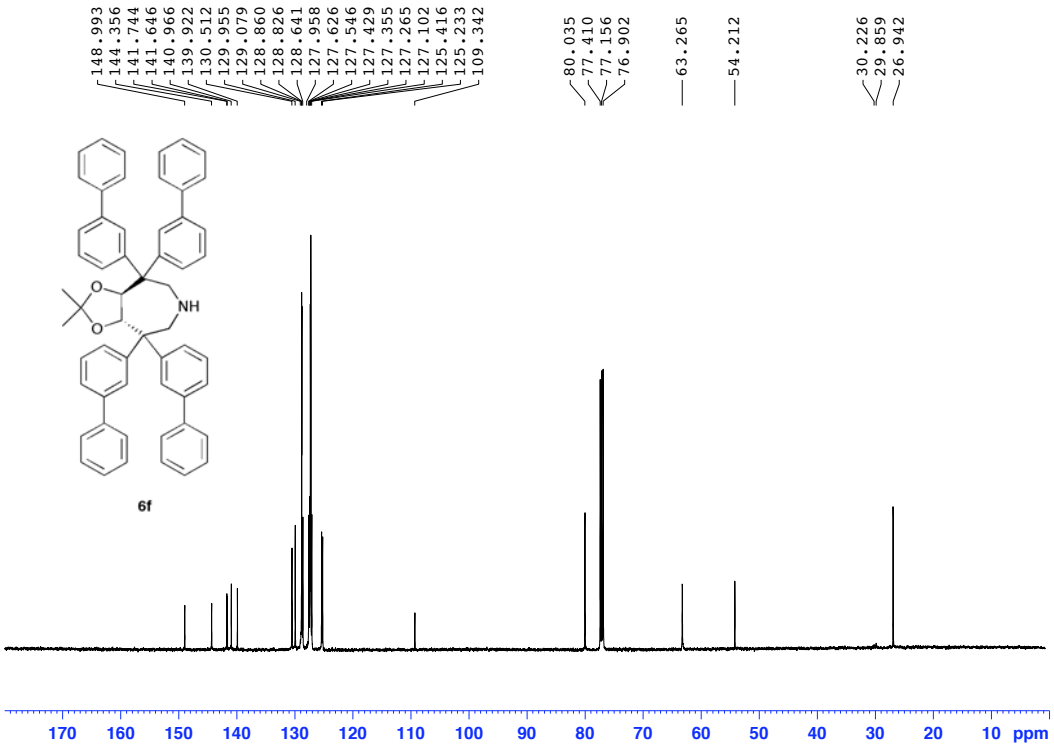


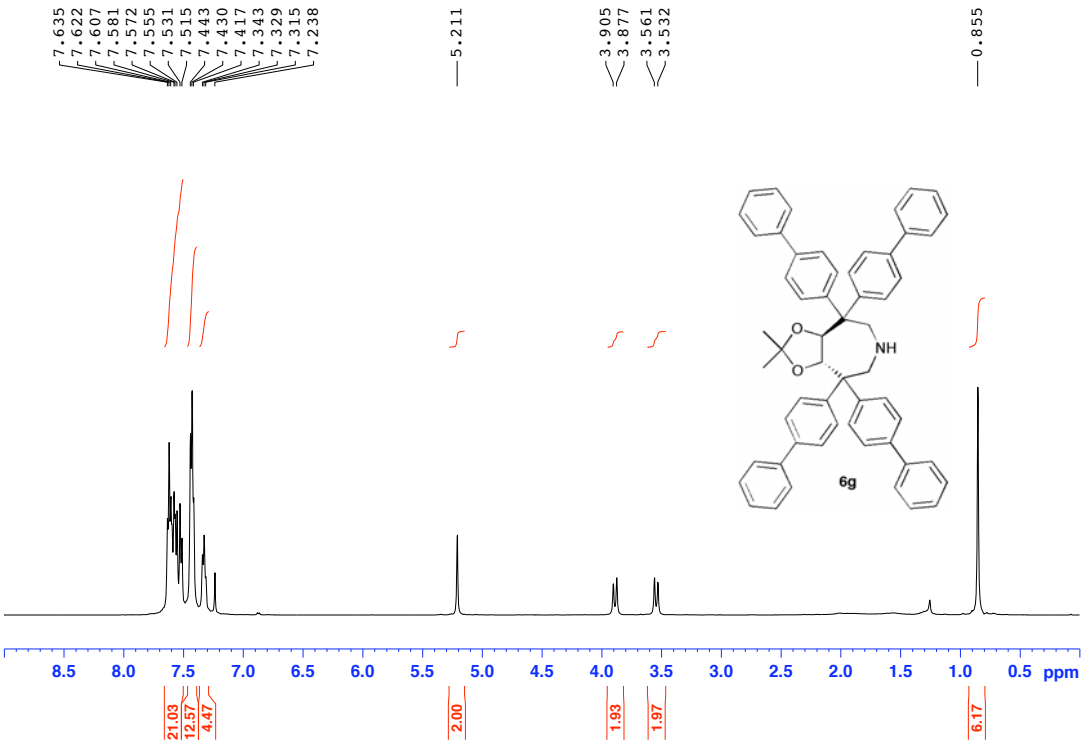


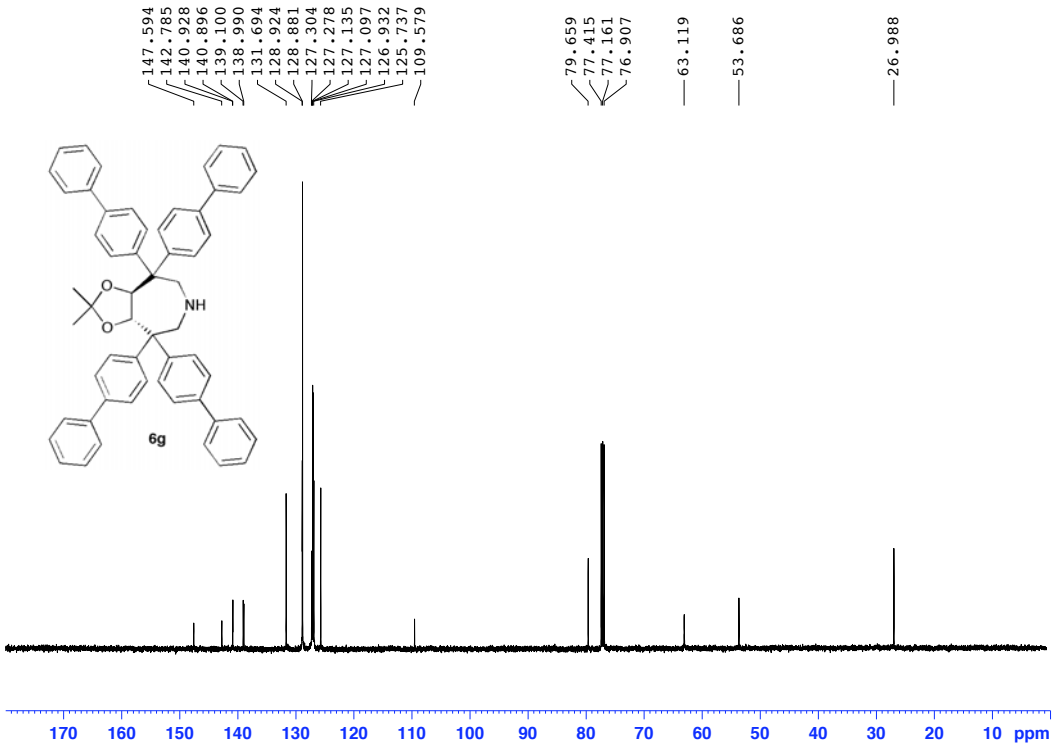


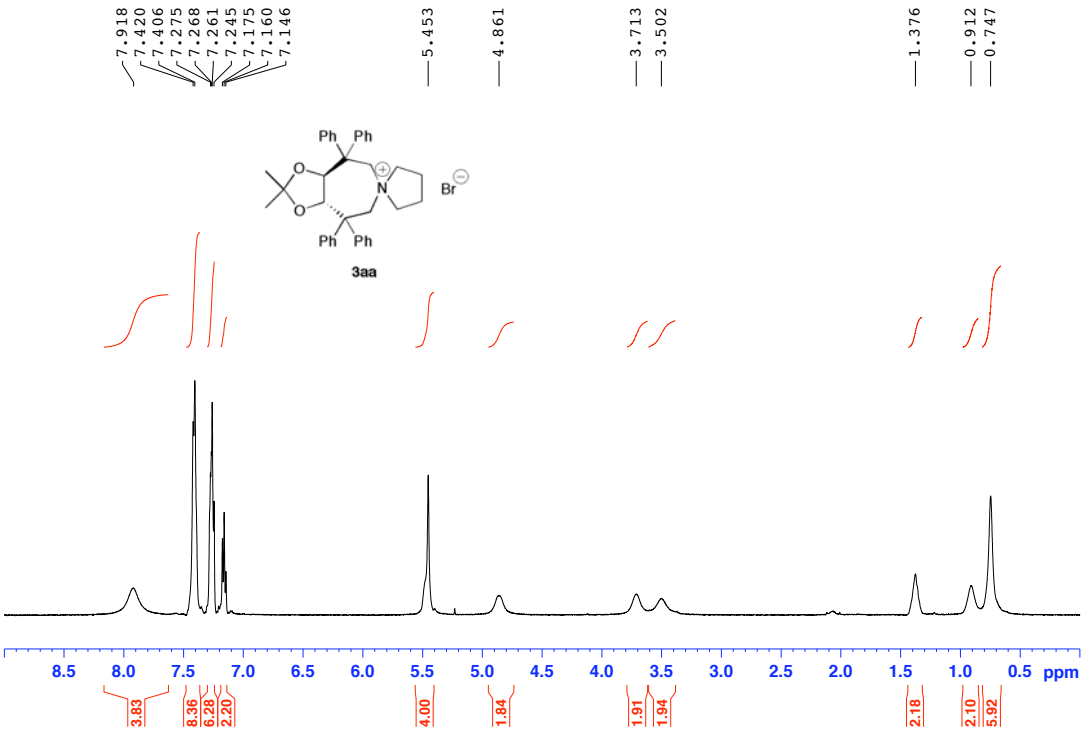


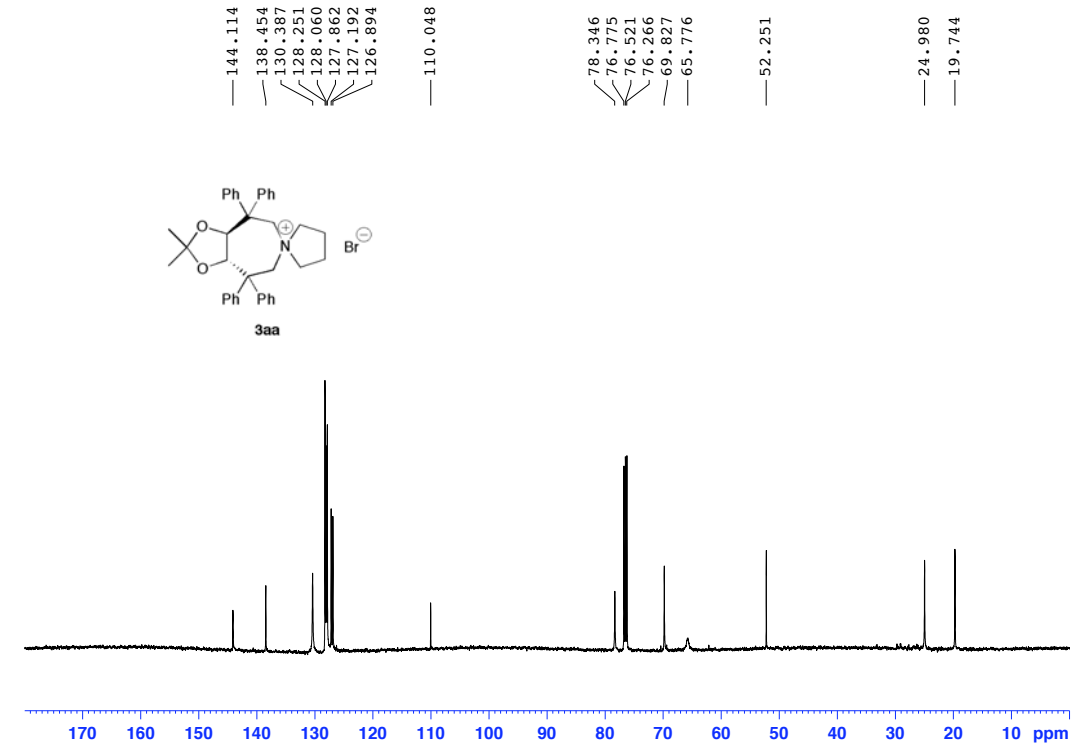


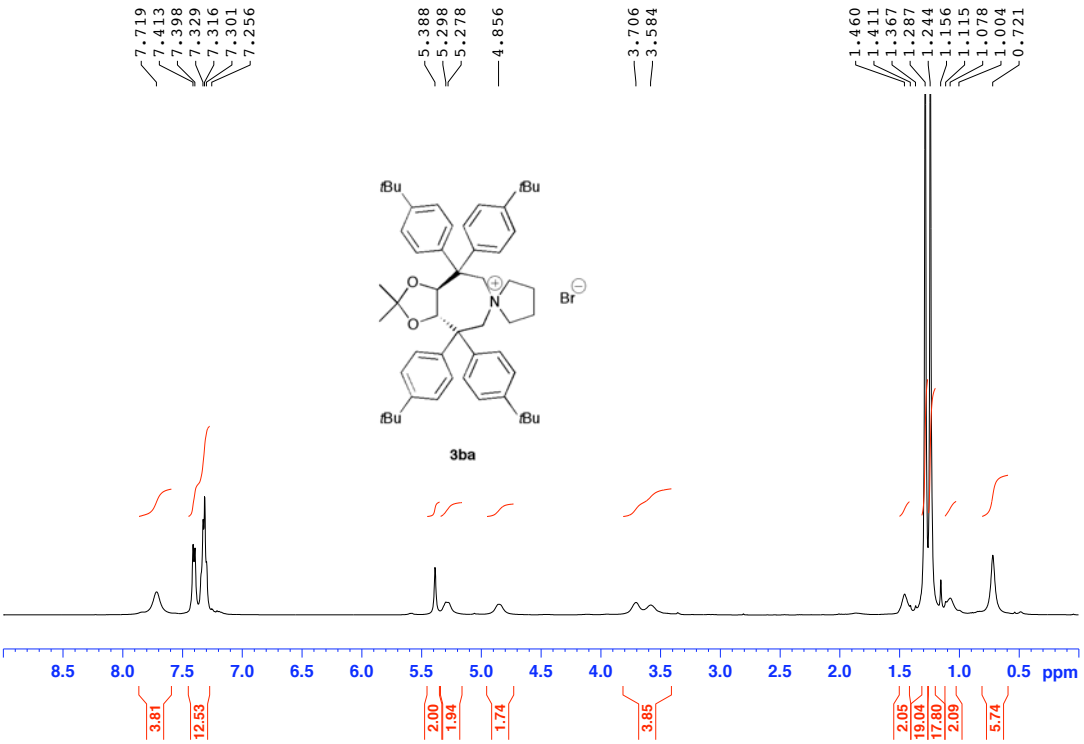


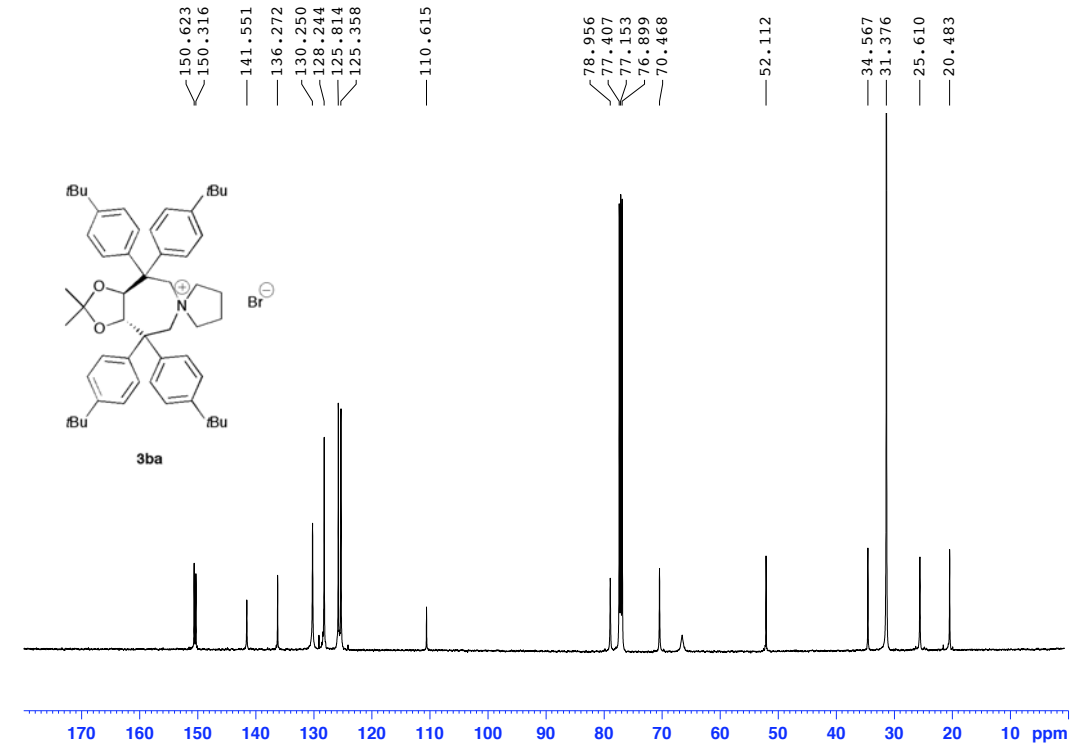


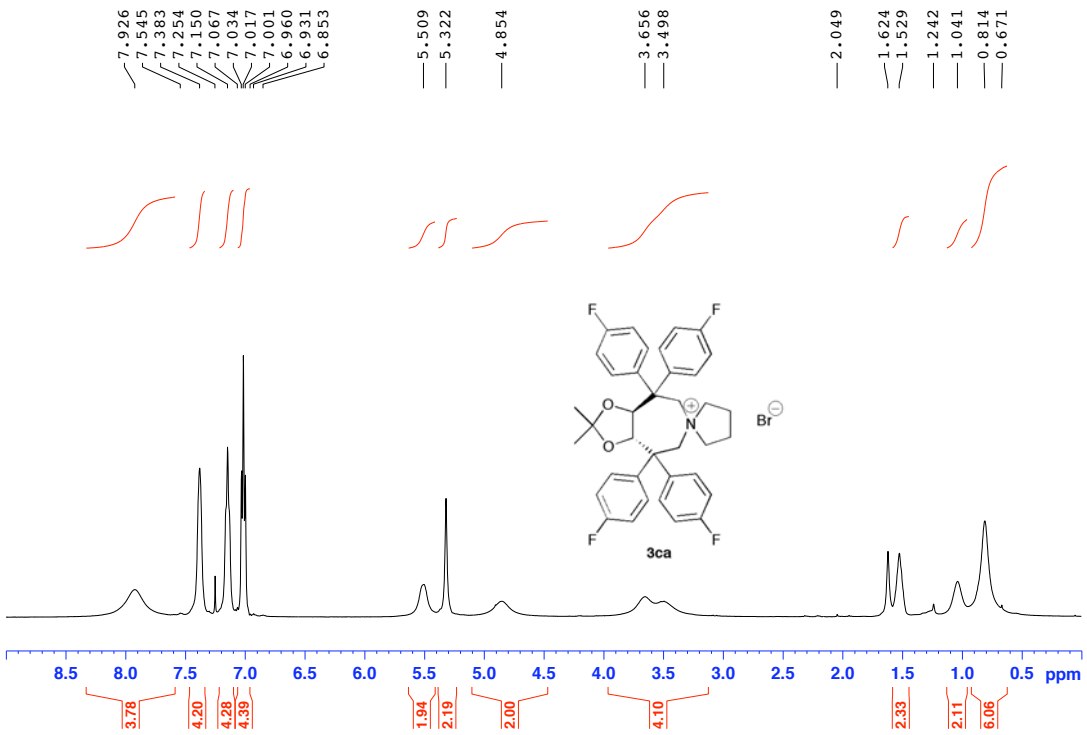


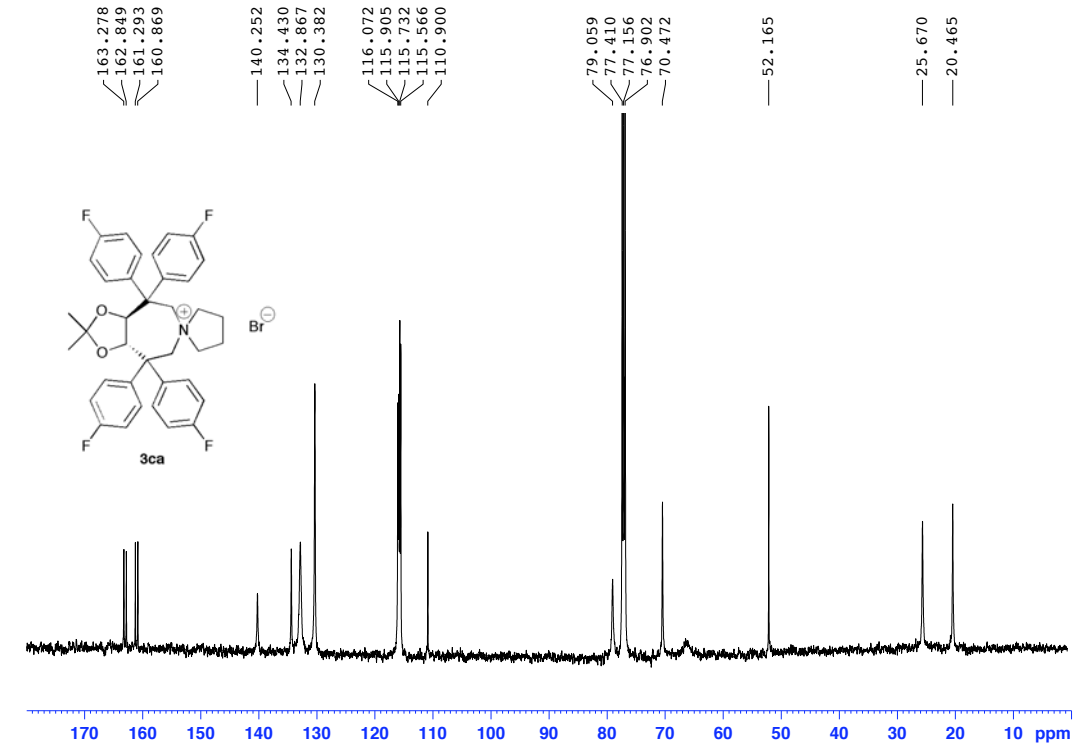


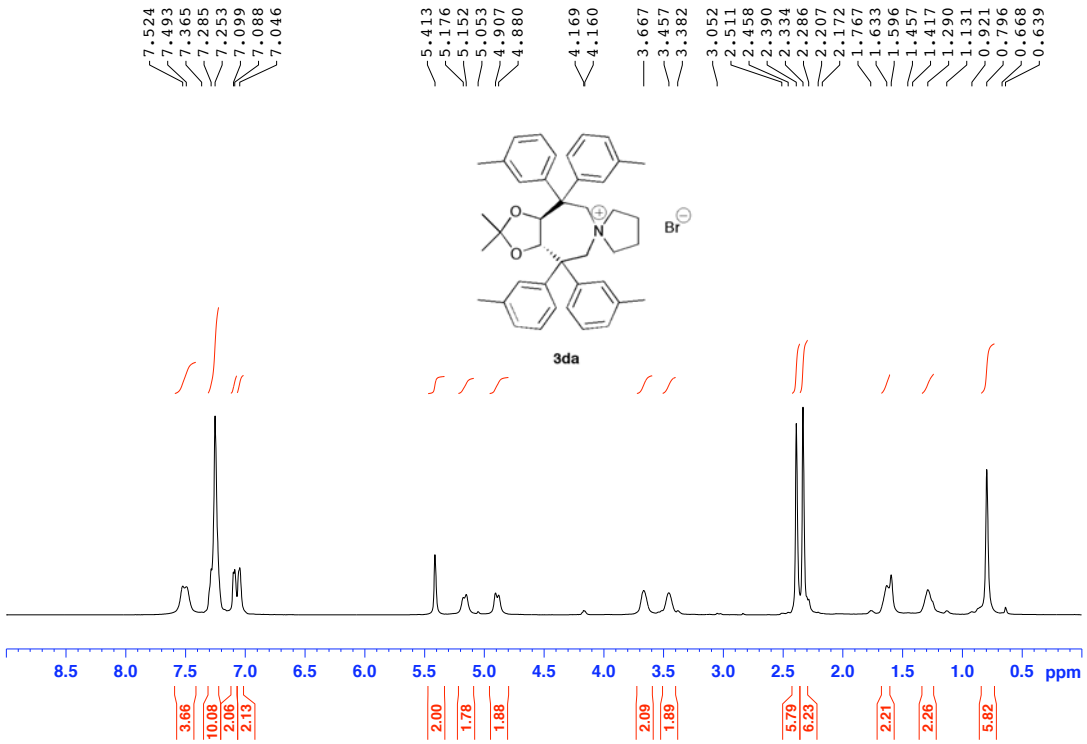


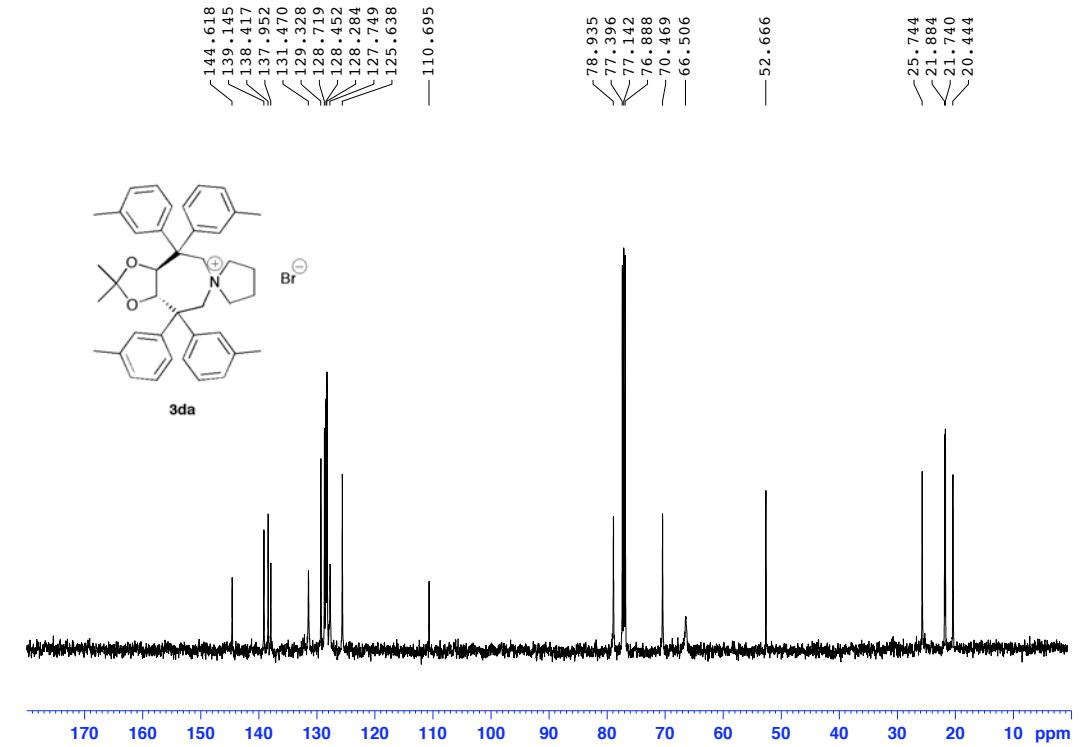


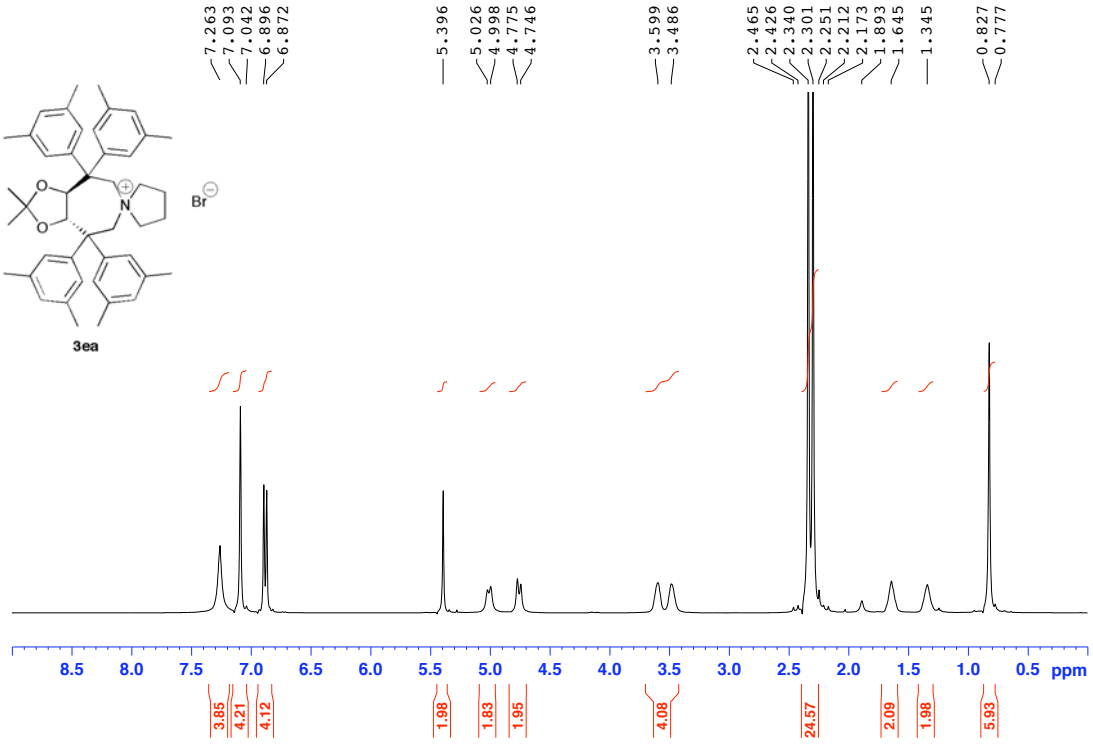


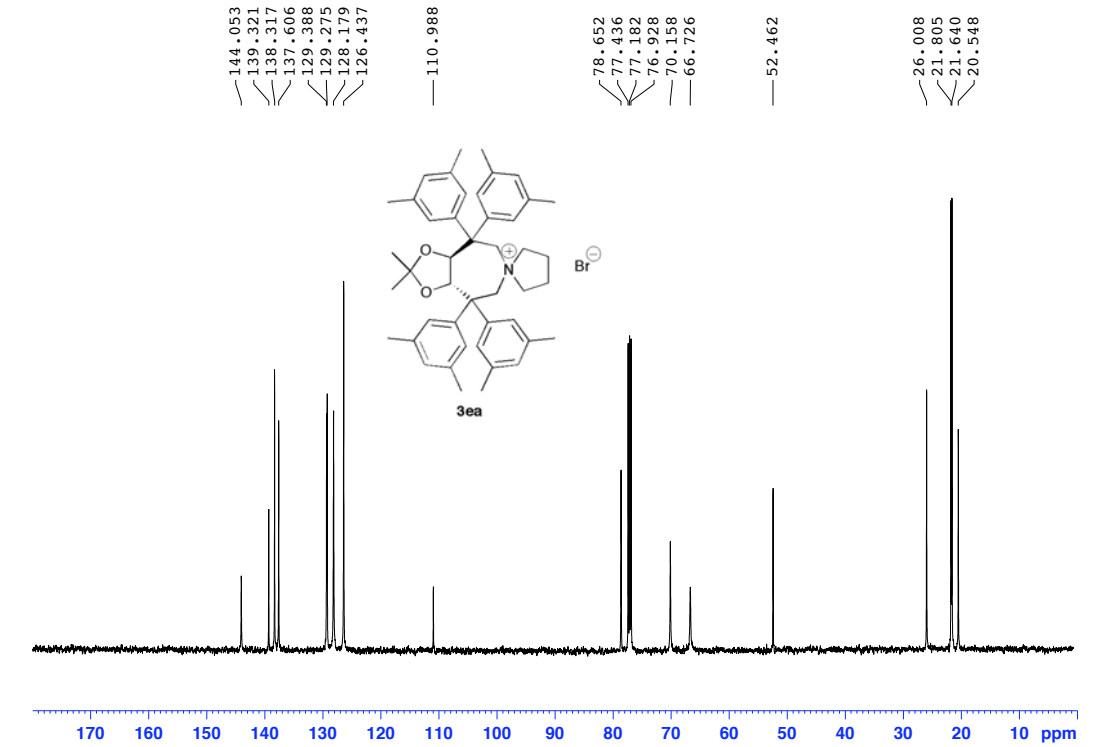


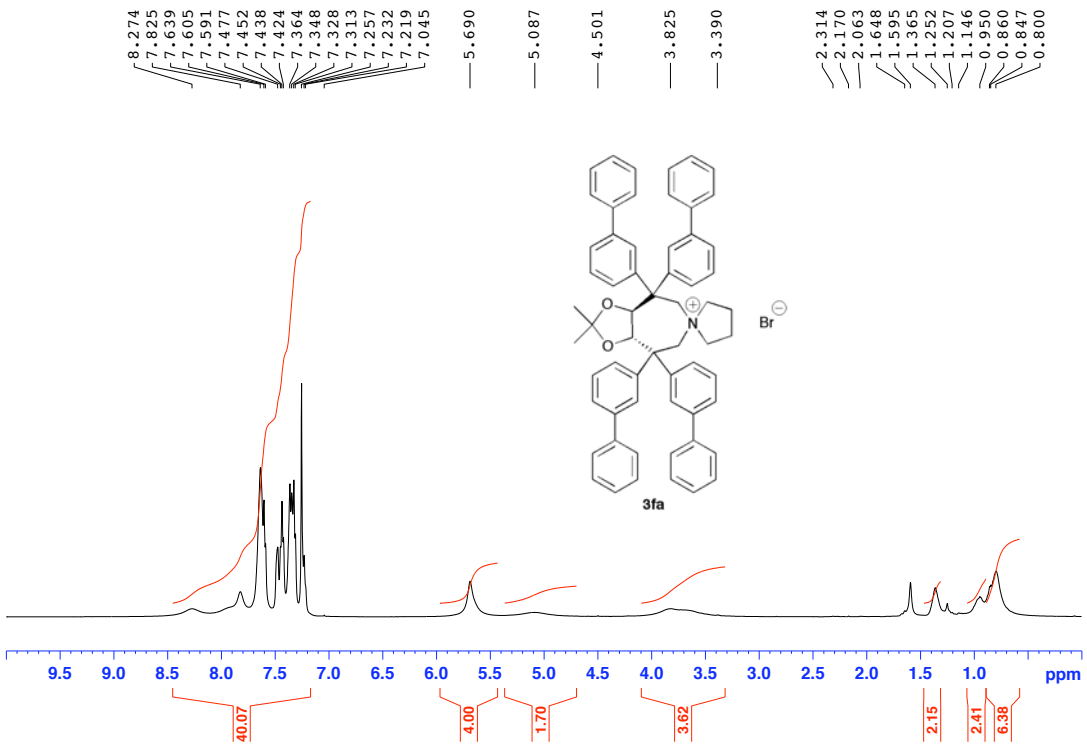


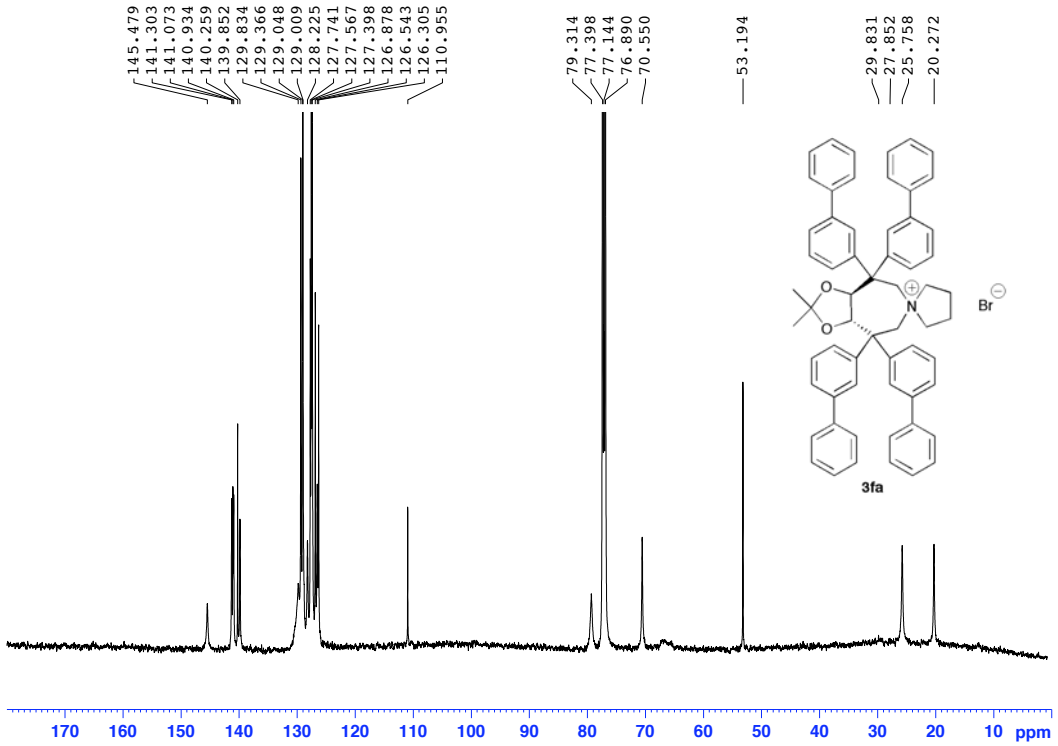


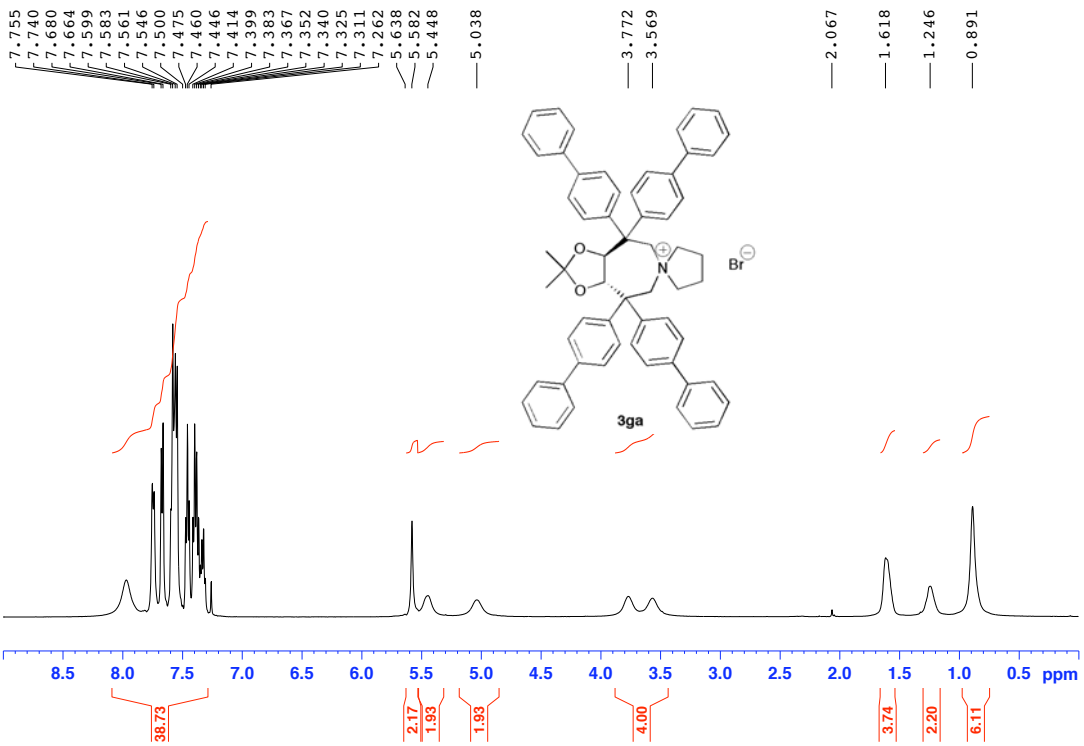


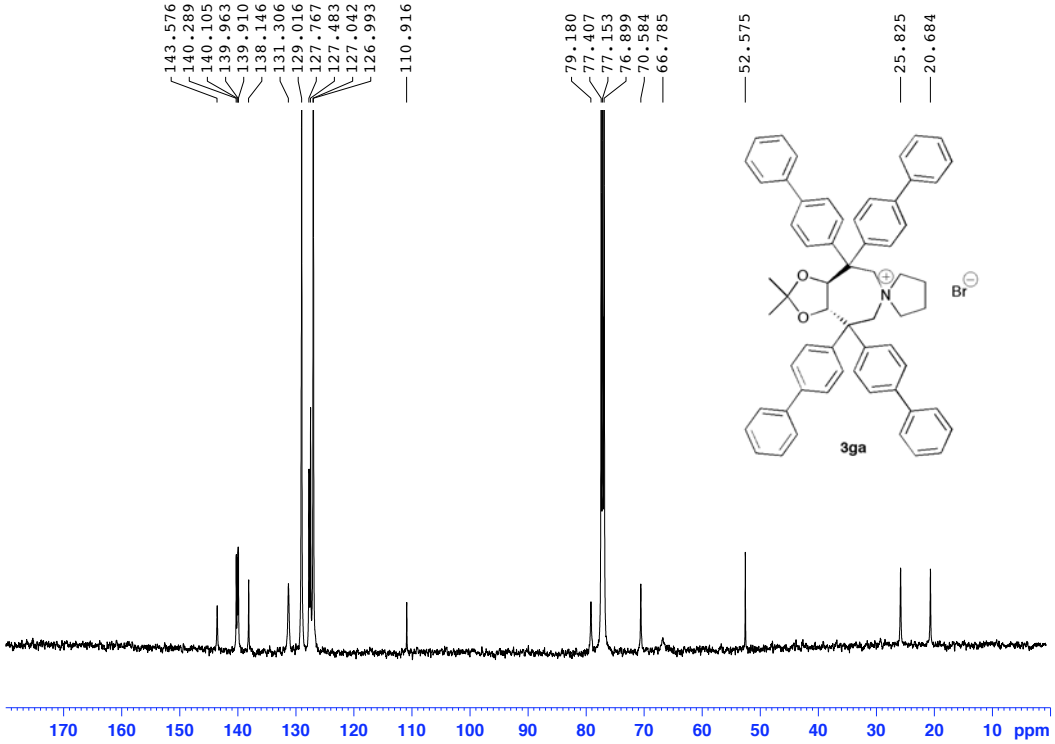












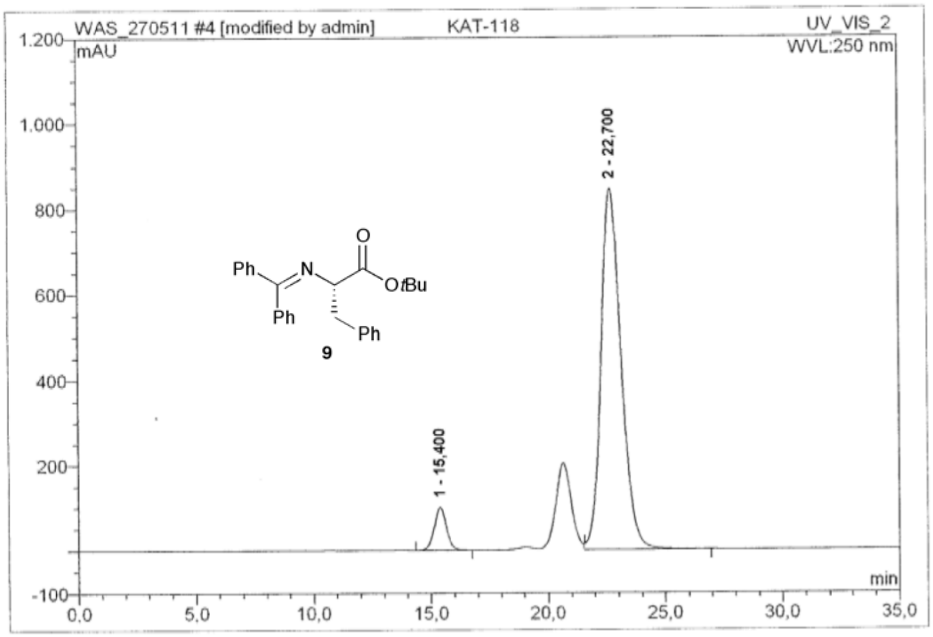
5. HPLC-chromatograms (chiral stationary phase):

Operator:admin Timebase:Summit_1 Sequence:WAS_270511

27.5.2011 12:06 PM

4 KAT-118

Sample Name:	**KAT-118**	*Injection Volume:*	**10,0**
Vial Number:	**RA4**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**TEST**	*Bandwidth:*	**n.a.**
Quantif. Method:	**default**	*Dilution Factor:*	**1,0000**
Recording Time:	**27.5.2011 11:03**	*Sample Weight:*	**1,0000**
Run Time (min):	**35,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15,40	n.a.	100,827	60,198	6,68	n.a.	BMB
2	22,70	n.a.	845,136	841,177	93,32	n.a.	MB*
Total:			945,963	901,375	100,00	0,000	

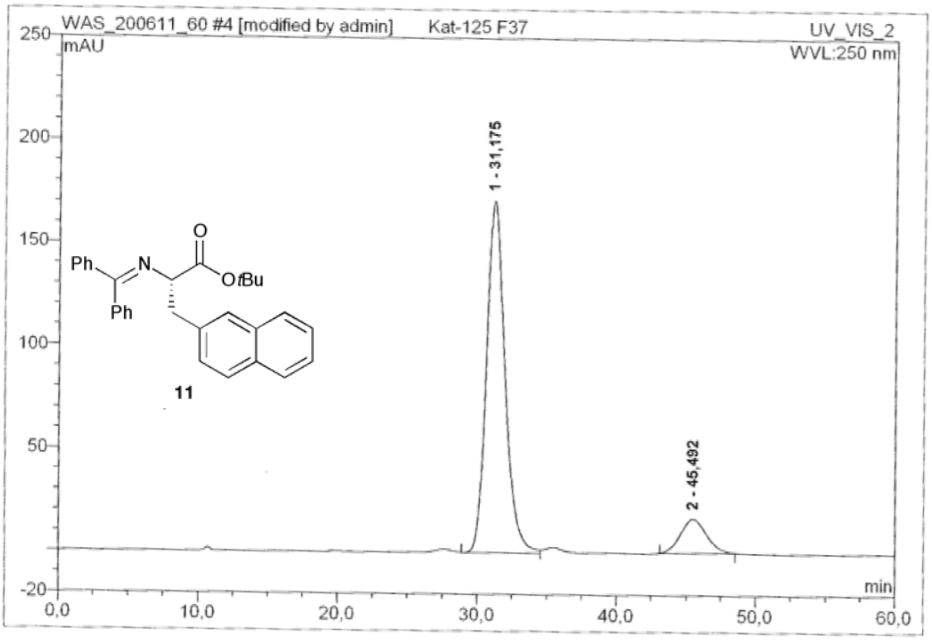
ee = 86.7 %

Rueckl/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR10 Build 2818 (166959)

4 Kat-125 F37

Sample Name:	**Kat-125 F37**	*Injection Volume:*	**10,0**
Vial Number:	**RA4**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**TEST_60**	*Bandwidth:*	**n.a.**
Quantif. Method:	**default**	*Dilution Factor:*	**1,0000**
Recording Time:	**20.6.2011 16:03**	*Sample Weight:*	**1,0000**
Run Time (min):	**60,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	31,18	n.a.	170,699	263,984	88,03	n.a.	M *
2	45,49	n.a.	16,625	35,881	11,97	n.a.	BMB*
Total:			187,323	299,865	100,00	0,000	

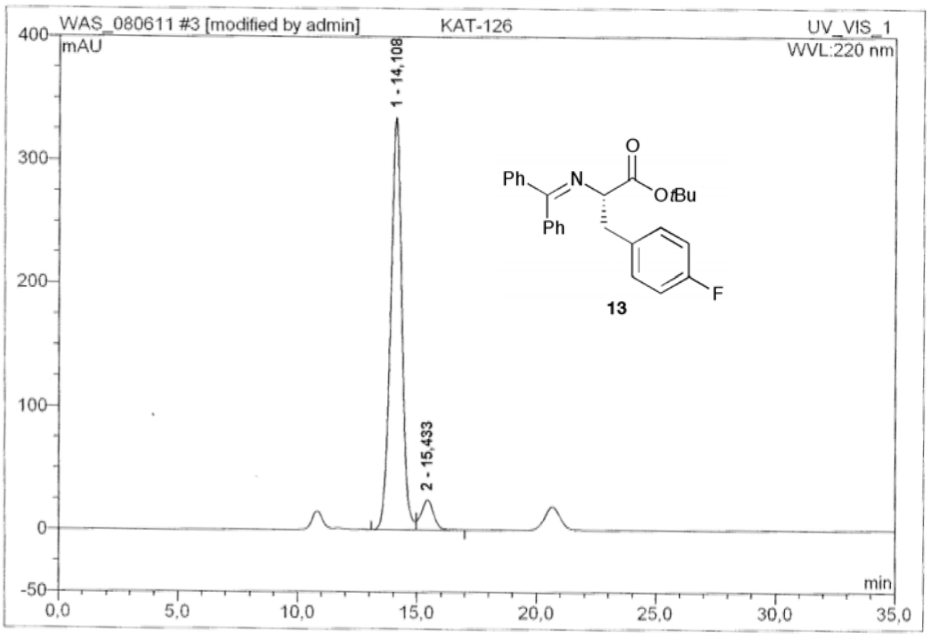
ee = 76,06%

Operator:admin Timebase:Summit_1 Sequence:WAS_080611

Page 1-1
14.6.2011 10:51 AM

3 KAT-126

Sample Name:	**KAT-126**	*Injection Volume:*	**10,0**
Vial Number:	**RA3**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**TEST**	*Bandwidth:*	**n.a.**
Quantif. Method:	**default**	*Dilution Factor:*	**1,0000**
Recording Time:	**8.6.2011 15:47**	*Sample Weight:*	**1,0000**
Run Time (min):	**35,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14,11	n.a.	334,205	181,739	92,53	n.a.	M *
2	15,43	n.a.	24,374	14,676	7,47	n.a.	MB*
Total:			358,579	196,415	100,00	0,000	

ee = +85,06 %

Rueckl/Integration

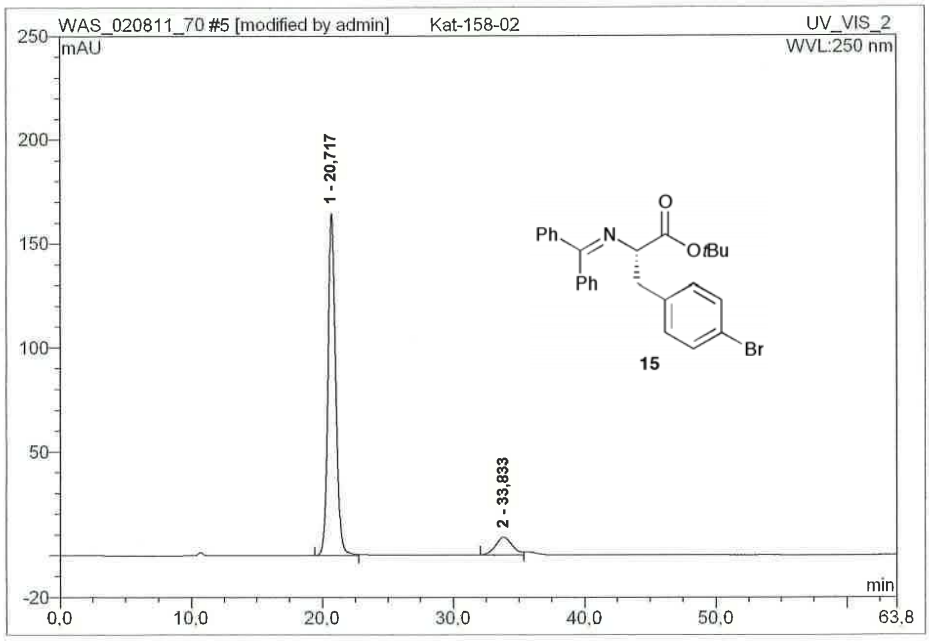
Chromeleon (c) Dionex 1996-2006
Version 6.80 SR10 Build 2818 (166959)

Operator:admin Timebase:Summit_1 Sequence:WAS_020811_70

Page 1-1
8.8.2011 11:42 AM

5 Kat-158-02

Sample Name:	**Kat-158-02**	*Injection Volume:*	**10,0**
Vial Number:	**RA5**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**TEST_70**	*Bandwidth:*	**n.a.**
Quantif. Method:	**default**	*Dilution Factor:*	**1,0000**
Recording Time:	**2.8.2011 15:33**	*Sample Weight:*	**1,0000**
Run Time (min):	**63,78**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20,72	n.a.	164,284	111,687	89,91	n.a.	BM *
2	33,83	n.a.	8,471	12,529	10,09	n.a.	BM *
Total:			172,755	124,216	100,00	0,000	

ee = 79,8 %

Rueckl/Integration

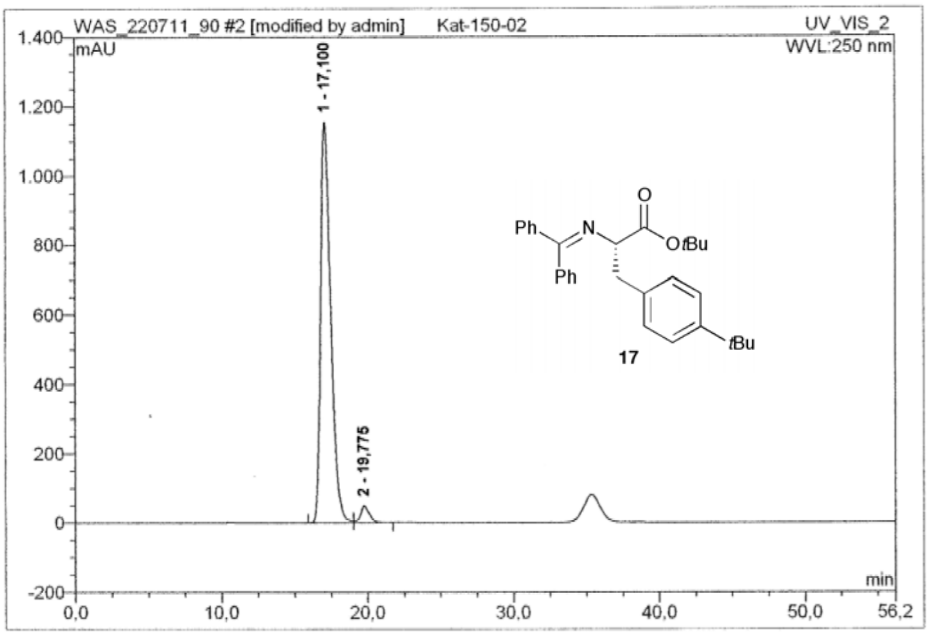
Chromeleon (c) Dionex 1996-2006
Version 6.80 SR10 Build 2818 (166959)

Operator:admin Timebase:Summit_1 Sequence:WAS_220711_90

Page 1-1
22.7.2011 12:20 PM

2 Kat-150-02

Sample Name:	**Kat-150-02**	*Injection Volume:*	**10,0**
Vial Number:	**RA2**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**TEST_90**	*Bandwidth:*	**n.a.**
Quantif. Method:	**default**	*Dilution Factor:*	**1,0000**
Recording Time:	**22.7.2011 11:13**	*Sample Weight:*	**1,0000**
Run Time (min):	**56,23**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17,10	n.a.	1154,567	926,532	96,41	n.a.	BM
2	19,78	n.a.	49,449	34,452	3,59	n.a.	MB
Total:			1204,016	960,984	100,00	0,000	

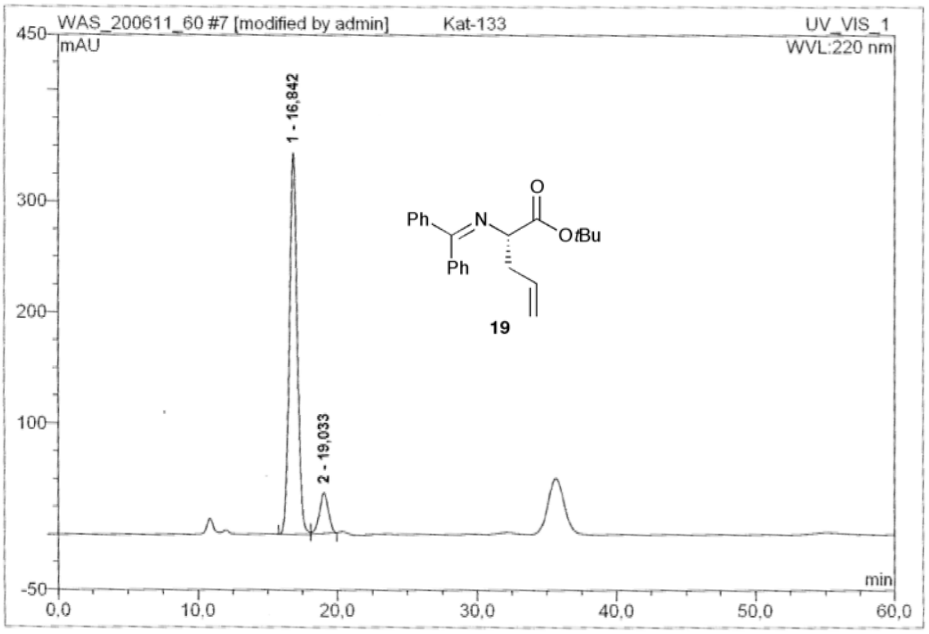
ee = 92,82 %

Rueckl/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR10 Build 2818 (166959)

7 Kat-133

Sample Name:	**Kat-133**	*Injection Volume:*	**10,0**
Vial Number:	**RA7**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**TEST_60**	*Bandwidth:*	**n.a.**
Quantif. Method:	**default**	*Dilution Factor:*	**1,0000**
Recording Time:	**20.6.2011 19:08**	*Sample Weight:*	**1,0000**
Run Time (min):	**60,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,84	n.a.	342,709	223,644	89,21	n.a.	BM *
2	19,03	n.a.	36,504	27,059	10,79	n.a.	MB*
Total:			379,213	250,702	100,00	0,000	

ee = 78,4%