Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Asymmetric Hydroamination Catalyzed by a New Chiral Zirconium System: Reaction Scope and Mechanism

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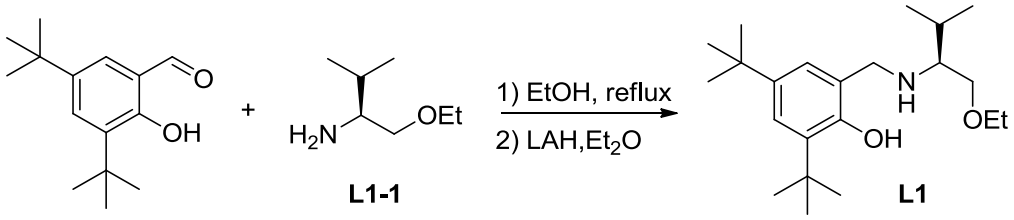
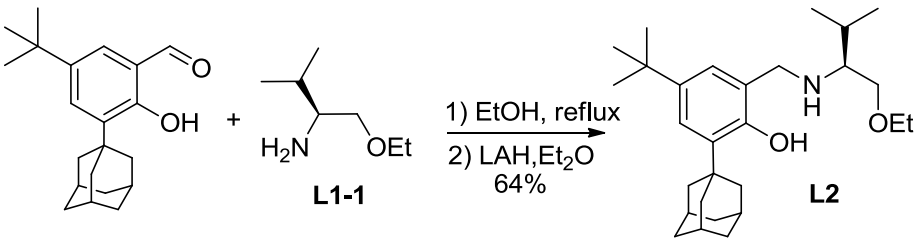
1. General Procedures

All manipulations of air- and moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques or drybox. ^{1}H NMR spectra were recorded on a Varian Mercury XL-300 MHz, Varian Mercury 400 MHz, Agilent Mercury 400 MHz or Agilent Mercury 600 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Mercury XL-75 MHz, Varian Mercury 100 MHz or Agilent Mercury 100 MHz spectrometer. Mass spectra were obtained using a HP5959A spectrometer, Finnigan Perkin-Elmer 241MC or Angilent 6224 LC/MS. Elemental analyses were performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry (CAS). Hexane, Et_2O, and toluene were purified by passing through a column of activated alumina and degassed with nitrogen by MBraun SPS system. C_6D_6, D_8-toluene and C_6D_5Br were degassed and distilled over CaH_2. Ferrocene as standard was recrystallized from petroleum ether. Substrates of hydroamination were prepared as described in the literature.[1] All aminoalkenes were distilled over CaH_2 under reduced pressure or under an argon atmosphere and stored in drybox. $ZrBn_4$ (Bn = $C_6H_5CH_2$), 4-*tert*-butyl-2-adamantanyl salicylaldehyde, and 4-*tert*-butyl-2-triphenylsilyl salicylaldehyde were synthesized according to the published procedures.[2-4]

2. Synthesis and Characterization of Ligands

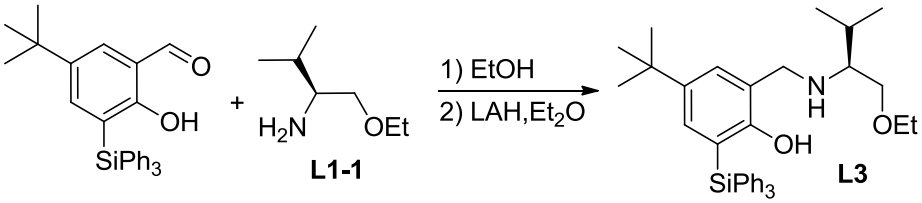


Preparation of Ligand (**L1**): An ethanol solution (40 mL) of 2,4-di-*tert*-butyl-salicylaldehyde (4.69 g, 20.0 mmol) and **L1-1** (2.62 g, 20.0 mmol) was refluxed for 6 h, and the resulting solution was concentrated in vacuo to give a yellow foam. Et_2O (30 mL) was added to dissolve the foam, and the solution was added dropwise to a stirring suspension of lithium aluminum hydride (1.02 g, 26.8 mmol) at 0 ℃. The stirring mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then quenched by addition of water (1.0 mL), 15% aqueous NaOH (1.0 mL) and water (3.0 mL), respectively. The precipitates were removed by filtration. Removal of the solvent gave a crude product which was purified by flash chromatography on silica gel (hexane/EtOAc 100/1 in V/V) to afford **L1** as a white foam (4.41 g, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (d, *J* = 2.1 Hz, 1H, Ar-*H*), 6.88 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 3.93 (ABd, *J* = 15.3 Hz, 1H, C*H*$_2$N), 3.98 (ABd, *J* = 15.3 Hz, 1H, C*H*$_2$N), 3.37-3.60 (m, 4H, C*H*$_2$O), 2.57 (m, 1H, C*H*-N), 1.95 (m, 1H, C*H*$(CH_3)_2$), 1.43 (s, 9H, C(C*H*$_3)_3$), 1.29 (s, 9H, C$(CH_3)_3$), 1.20 (t, *J* = 7.2 Hz, 3H, C*H*$_3$CH$_2$), 0.97 (t, *J* = 6.6 Hz, 6H, CH(C*H*$_3)_2$). ^{13}C NMR (75 M, $CDCl_3$): δ 154.7, 140.2, 135.9, 123.1, 122.8, 69.2, 66.7, 62.2, 51.7, 34.9, 34.1, 31.7, 29.6, 29.0, 19.1, 18.8, 15.2. IR (ν/cm^{-1}): 3314(w), 2953(s), 2895(m), 2869(m), 1476(s), 1433(s), 1235(s), 1107(s). Rotation: -5.9 °, c = 1.0 in EtOH. MS (EI, m/z): 349 (M^+). HRMS (EI) Calcd for $C_{22}H_{39}NO_2$: 349.2981; Found: 349.2980.

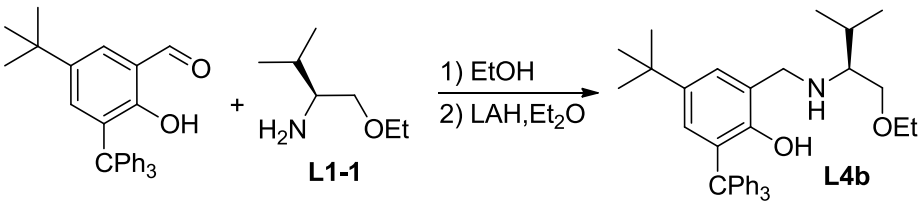


Preparation of Ligand (**L2**): Compound **L2** was prepared as a colorless oil from **L1-1** (0.67 g, 5.0 mmol) and 4-*tert*-butyl-2-adamantanyl salicylaldehyde (1.56 g, 5.0 mmol) in ethanol (20 mL)

using the same procedures as reported for **L1**: yield 1.37 g (64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (d, *J* = 1.5 Hz, 1H, Ar-*H*), 6.88 (s, 1H, Ar-*H*), 3.94 (s, 2H, C*H*$_2$N), 3.60-3.36 (m, 4H, C*H*$_2$OC*H*$_2$), 2.60-2.56 (m, 1H, C*H*N), 2.20-2.10 (m, 6H, CHC*H*$_2$), 2.09-2.06 (m, 3H, C*H*CH$_2$), 2.00-1.90 (m, 1H, CH(C*H*$_3$)$_2$), 1.83-1.73 (m, 6H), 1.29 (s, 9H, C(C*H*$_3$)$_3$), 1.20 (t, *J* = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 1.00-0.95 (m, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 140.4, 136.3, 123.0, 122.9, 122.8, 69.3, 66.7, 62.3, 51.8, 40.4, 37.2, 37.0, 34.2, 31.7, 29.2, 29.0 , 19.1, 18.7, 15.2. IR (ν/cm^{-1}): 2952 (s), 2902 (s), 2842 (s), 1479 (s), 1449 (w). Rotation: -2.80 °, c = 0.65 in EtOH. MS (ESI, m/z): 428.2 (M+H$^+$). HRMS (ESI) calcd for $C_{28}H_{46}NO_2$ (M+H$^+$): 428.3529; Found: 428.3532.

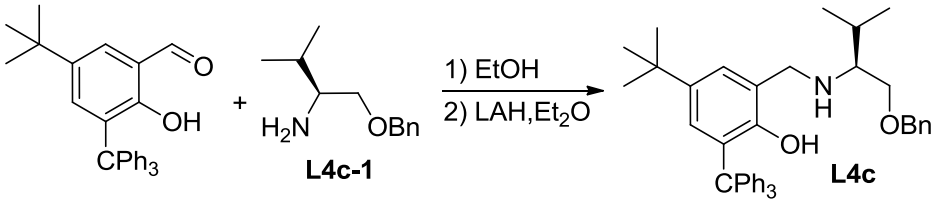


Preparation of Ligand (**L3**): Compound **L3** was prepared as a white solid from **L1-1** (131 mg, 1.0 mmol) and 4-*tert*-butyl-2-triphenylsilyl salicylaldehyde (437 mg, 1.0 mmol) in ethanol (15 mL) using the same procedures as reported for **L1**: yield 563 mg (100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 6.0 Hz, 6H, Ar-*H*), 7.63-7.30 (m, 9H, Ar-*H*), 7.08(s, 2H, Ar-*H*), 4.07 (ABd, *J* = 13.8 Hz, 1H, NC*H*$_2$), 3.96 (ABd, *J* = 13.8 Hz, 1H, NC*H*$_2$), 3.55-3.32 (m, 4H, (C*H*$_2$)$_2$O), 2.55-2.50 (m, 1H, NC*H*), 1.92-1.81 (m, 1H, (CH$_3$)$_2$C*H*), 1.16 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.12 (s, 9H, C(C*H*$_3$)$_3$), 0.90-0.85 (m, 6H, (C*H*$_3$)$_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.3, 140.7, 136.4, 135.4, 134.4, 129.0, 127.8, 127.4, 121.8, 119.4, 69.0, 66.6, 61.5, 51.0, 33.9, 31.4, 29.2, 19.2, 18.8, 15.1. IR (ν/cm^{-1}): 2957 (w), 2865 (w), 1591 (m), 1425 (m), 1103 (s). Rotation: -12.1 °, c = 0.55 in EtOH. MS (ESI, m/z): 552.2 (M+H$^+$). HRMS (ESI) calcd for $C_{36}H_{46}NO_2Si$ (M+H$^+$): 552.3298; Found: 552.3293.

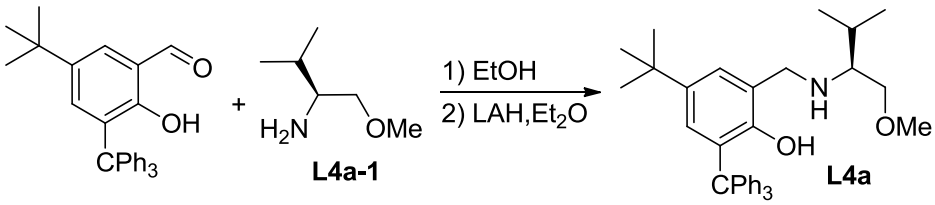


Preparation of Ligand (**L4b**): Compound **L4b** was prepared as a white solid from **L1-1** (262 mg, 2.0 mmol) and 4-*tert*-butyl-2-trityl salicylaldehyde (840 mg, 2.0 mmol) in ethanol (10 mL) using

the same procedures as reported for **L1**: yield 840 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.12 (m, 16H, Ar-*H*), 6.93 (s, 1H, Ar-*H*), 4.00 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 3.86 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 3.42-3.35 (m, 3H), 3.23 (dd, *J* = 9.6, 4.8 Hz, 1H, C*H*$_2$O), 2.32-2.28 (m, 1H, NC*H*), 1.72-1.62 (m, 1H, $(CH_3)_2$C*H*), 1.15-1.11 (m, 12H, C(C*H*$_3$)$_3$, OCH_2CH_3), 0.77-0.65 (m, 6H, (C*H*$_3$)$_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 146.2, 139.9, 133.4, 131.1, 127.6, 126.9, 125.2, 124.0, 122.9, 68.8, 66.6, 63.4, 60.8, 50.8, 34.0, 31.5, 29.3, 19.0, 18.7, 15.1. IR (ν/cm^{-1}): 3322 (w), 2958 (m), 2867 (m), 1599 (m), 1476 (m), 1444 (m), 1110 (s). Rotation: -11.5 °, c = 0.51 in EtOH. MS (ESI, m/z): 536.2 (M+H$^+$). HRMS (ESI) calcd for $C_{37}H_{46}NO_2$ (M+H$^+$): 536.3529; Found: 536.3533.

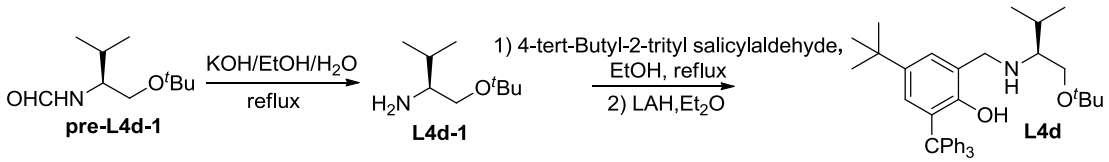


Preparation of Ligand (**L4c**): Compound **L4c** was prepared as a white solid from **L4c-1** (290 mg, 1.50 mmol) and 4-*tert*-butyl-2-trityl salicylaldehyde (632 mg, 1.50 mmol) in ethanol (10 mL) using the same procedures as reported for **L1**: yield 770 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.28 (m, 5H, Ar-*H*), 7.23-7.12 (m, 16H, Ar-*H*), 6.87 (s, 1H, Ar-*H*), 4.43 (ABd, *J* = 12.0 Hz, 2H, C*H*$_2$N), 3.96 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$O), 3.78 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$O), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H, C*H*$_2$O), 3.31 (dd, *J* = 9.6, 4.2 Hz, 1H, C*H*$_2$O), 2.28 (d, *J* = 5.1 Hz, 1H, NC*H*), 1.72-1.66 (m, 1H, $(CH_3)_2$C*H*), 1.14 (s, 9H, C(C*H*$_3$)$_3$), 0.73-0.70 (m, 6H, (C*H*$_3$)$_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 146.1, 139.9, 138.2, 133.4, 131.1, 128.4, 127.70, 127.66, 127.6, 126.8, 125.2, 124.1, 122.7, 73.3, 68.1, 63.4, 60.5, 50.5, 34.0, 31.5, 29.3, 19.1, 18.9. IR (ν/cm^{-1}): 3325(w), 2957 (m), 2865 (m), 1598 (m), 1476 (s), 1446 (s), 1259 (m), 1096 (s), 1030 (s). Rotation: 13.4 °, c = 0.445 in EtOH. MS (ESI, m/z): 598.2 (M+H$^+$). HRMS (ESI) calcd for $C_{42}H_{48}NO_2$ (M+H$^+$): 598.3685; Found: 598.3672.

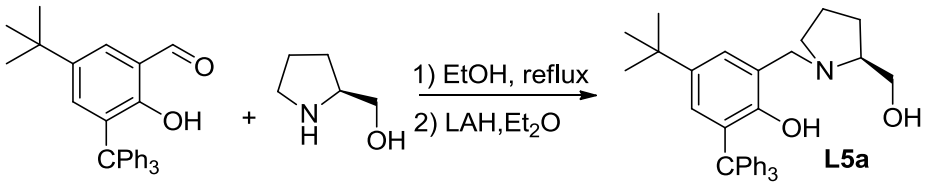


Preparation of Ligand (**L4a**): Compound **L4a** was prepared as a white solid from **L4a-1** (129

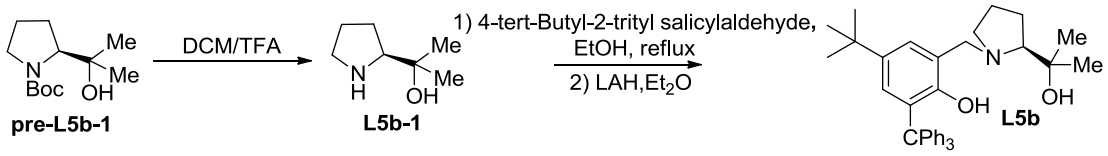
mg, 1.10 mmol) and 4-*tert*-butyl-2-trityl salicylaldehyde (468 mg, 1.1 mmol) in ethanol (10 mL) using the same procedures as reported for **L1**: yield 580 mg (100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15-7.6.99 (m, 16H, Ar-*H*), 6.84 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 3.90 (ABd, *J* = 13.8 Hz, 1H, C*H*$_2$N), 3.76 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 3.29-3.24 (m, 1H, C*H*$_2$O), 3.14 (s, 3H, C*H*$_3$O), 3.11-3.07 (m, 1H, C*H*$_2$O), 2.21-2.17 (m, 1H, NC*H*), 1.60-1.50 (m, 1H, $(CH_3)_2$C*H*), 1.07 (s, 9H, C(C*H*$_3$)$_3$), 0.62 (d, *J* = 6.9 Hz, 6H, (C*H*$_3$)$_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 146.1, 139.9, 133.4, 131.0, 127.6, 126.8, 125.2, 124.0, 122.7, 70.9, 63.4, 60.6, 58.9, 50.7, 34.0, 31.5, 29.3, 19.0, 18.8. IR (ν/cm^{-1}): 3309 (w), 2956 (m), 2871 (m), 1598 (m), 1475 (s), 1444 (s). Rotation: -18.4 °, c = 0.820 in EtOH. MS (ESI, m/z): 522.2 (M+H$^+$). HRMS (ESI) calcd for $C_{36}H_{44}NO_2$ (M+H$^+$): 522.3372; Found: 522.3383.



Preparation of Ligand (**L4d**): **Pre-L4d-1** (2.32 g, 5.0 mmol) was dissolved in ethanol and then 50% KOH solution was added. After the mixture refluxed for 13h, the mixture was extracted by 100 mL Et_2O. The organic layer was washed three times with brine and water. The organic layer was separated and dried by anhydrous $MgSO_4$, the solvent was evaporated and the residue was used for next reaction without further purification. And compound **L4d** was obtained from **L4d-1** and 4-*tert*-Butyl-2-trityl salicylaldehyde (1.26 g, 3.0 mmol) similarly to compound **L1** 0.65 g (39%). **Pre-L4d-1** was prepared according to the published procedures.[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11-7.22 (m, 16H, Ar-*H*), 6.91 (d, 1H, *J* = 1.8 Hz , Ar-*H*), 3.97 (ABd, *J* = 13.8 Hz, 1H, C*H*$_2$N), 3.84 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 3.37-3.33 (m, 1H, C*H*$_2$O), 3.30-3.20 (m, 1H, C*H*$_2$O), 2.27-2.26 (m, 1H, C*H*N), 1.73-1.70 (m, 1H, C*H*CH$_3$), 1.15 (s, 9 H, C(C*H*$_3$)$_3$), 1.11 (s, 9 H, C(C*H*$_3$)$_3$), 0.74-0.72 (m, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.4, 146.1, 139.8, 133.3, 131.1, 127.6, 126.8, 125.2, 123.9, 122.9, 72.6, 63.4, 60.9, 59.2, 50.6, 34.0, 31.5, 28.9, 27.4, 19.1, 18.8. IR (ν/cm^{-1}): 3086(w), 2958(s), 2869(m), 1598(m), 1475(s), 1444(s), 1258(s). Rotation: -13.3 °, c = 1.22 in EtOH. MS (ESI, m/z): 564.2 (M+H$^+$). HRMS (ESI) calcd for $C_{39}H_{50}NO_2$ (M+H$^+$): 564.3842; Found: 564.3835.

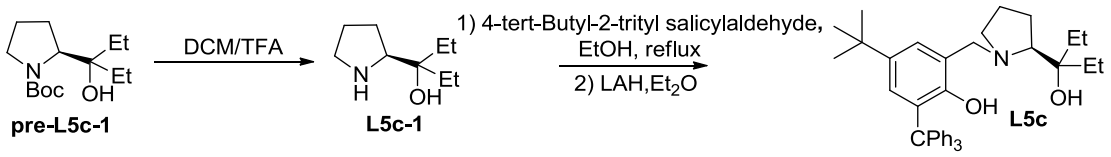


Preparation of Ligand (**L5a**): Compound **L5a** was prepared as a white solid from L-Prolinol (101 mg, 1.0 mmol) and 4-*tert*-Butyl-2-trityl salicylaldehyde (421 mg, 1.0 mmol) in ethanol (20 mL) using the same procedures as reported for **L1**: yield 506 mg (100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.23 (m, 16H, Ar-*H*), 6.91 (s, 1H, Ar-*H*), 3.84 (s, 2H, C*H*$_2$N), 3.07-2.89 (m, 3H), 2.57-2.52 (m, 1H, C*H*$_2$N), 2.32-2.30 (m, 1H, C*H*N), 1.87-1.82 (m, 1H, C*H*N), 1.65-1.55 (m, 3H, C*H*N), 1.15 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 145.9, 140.4, 133.2, 131.0, 127.5, 127.0, 125.4, 123.5, 122.4, 65.9, 63.9, 63.3, 59.4, 55.2, 34.0, 31.5, 27.7, 23.0. IR (ν/cm^{-1}): 3085(w), 2956(s), 2870 (m), 1474(s), 1444(s), 1257(m). Rotation: -19.8 °, c = 2.45 in EtOH. MS (ESI, *m*/*z*): 506.7 (M+H$^+$). HRMS (ESI) calcd for $C_{35}H_{40}NO_2$ (M+H$^+$): 506.3059; Found: 506.3069.

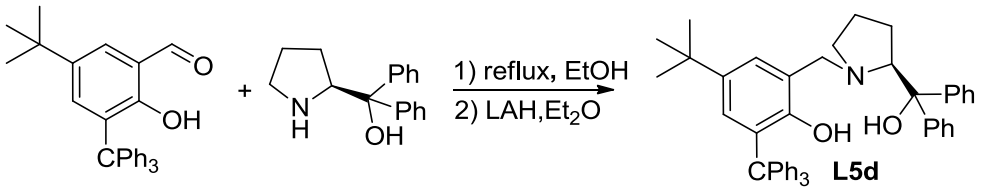


Preparation of Ligand (**L5b**): **Pre-L5b-1** (1.29 mmol, 296 mg) was dissolved in DCM (3 mL), and TFA was added in dropwise at ice bath. The mixture was stirred overnight, and then 15% NaOH solution was added to the pH 12. The mixture was extracted by DCM three times. The organic layer was combined and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue (**L5b-1)** was used for next reaction without further purification. And compound **L5b** was prepared as a colorless oil from **L5b-1** and 4-*tert*-Butyl-2-trityl salicylaldehyde (543 mg, 1.29 mmol) in ethanol (20 mL) using the same procedures as reported for **L1**: yield 350 mg (66%). **Pre-L5b-1** was prepared according to the published procedures.[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21-7.06 (m, 15H, Ar-*H*), 7.07 (d, *J* = 2.1 Hz, 1H, Ar-*H*), 6.89 (d, *J* = 2.1 Hz, 1H, Ar-*H*), 4.34 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 3.48 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 2.63-2.53 (m, 2H, C*H*$_2$N), 2.36-2.30 (m, 1H, C*H*N), 1.91-1.85 (m, 1H, C*H*$_2$N), 1.68-1.49 (m, 3H, C*H*$_2$N), 1.14 (s, 9H, C(C*H*$_3$)$_3$), 1.08 (s, 3H, C*H*$_3$), 0.97 (s, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 146.0, 140.1, 133.3, 131.1, 127.3, 126.9, 125.3, 123.8, 123.0, 73.7, 73.3, 63.4, 62.2, 54.5, 34.0, 31.5, 28.1, 27.9, 24.6, 24.1. IR (ν/cm^{-1}): 3055(w), 2957(s), 2865 (m), 1598(m), 1468(s), 1444(s), 1259(m). Rotation: -17.2 °, c = 0.71 in

EtOH. MS (ESI, *m*/*z*): 534.3 ($M+H^+$). HRMS (ESI) calcd for $C_{37}H_{43}NO_2$ ($M+H^+$): 534.3372; Found: 534.3353.

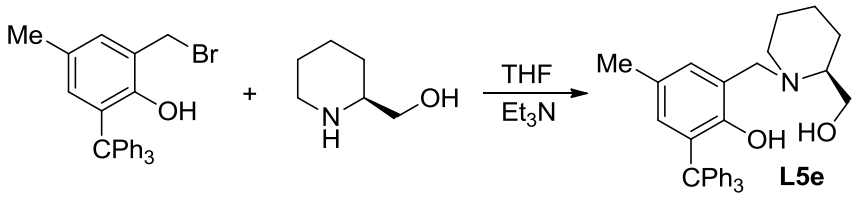


Preparation of Ligand (**L5c**): Compound **L5c** was prepared as a colorless oil from **Pre-L5c-1** (337 mg, 1.30 mmol) and 4-*tert*-Butyl-2-trityl salicylaldehyde (547 mg, 1.30 mmol) in ethanol (20 mL) using the same procedures as reported for **L5b**: yield 552 mg (75%). **Pre-L5c-1** was prepared according to the published procedures.[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13-6.99 (m, 16H, Ar-*H*), 6.80 (s, 1H, Ar-*H*), 4.13 (ABd, *J* = 13.5 Hz, 1H, C*H*$_2$N), 3.42 (ABd, *J* = 13.8 Hz, 1H, C*H*$_2$N), 2.70-2.65 (m ,1H, C*H*N), 2.49-2.42 (m, 1H, C*H*$_2$N), 2.35-2.28 (m ,1H, C*H*$_2$N), 1.77-1.11 (m, 8H), 1.06 (s, 9H, C(C*H*$_3$)$_3$), 0.73-0.64 (m, 6H, CH$_2$C*H*$_3$).^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6, 146.0, 140.0, 133.2, 131.1, 127.4, 126.9, 125.3, 123.8, 122.7, 76.3, 70.9, 63.4, 62.3, 54.0, 34.0, 31.5, 28.9, 27.1, 26.6, 24.0, 7.8, 7.5. IR (ν/cm^{-1}): 3590(w), 2961(m), 1599(m), 1465(s), 1445(s). Rotation: -39.3 °, c = 0.650 in EtOH. MS (ESI, *m*/*z*): 562.8 ($M+H^+$). HRMS (ESI) calcd for $C_{39}H_{48}NO_2$, ($M+H^+$): 562.3685; Found: 562.3675.

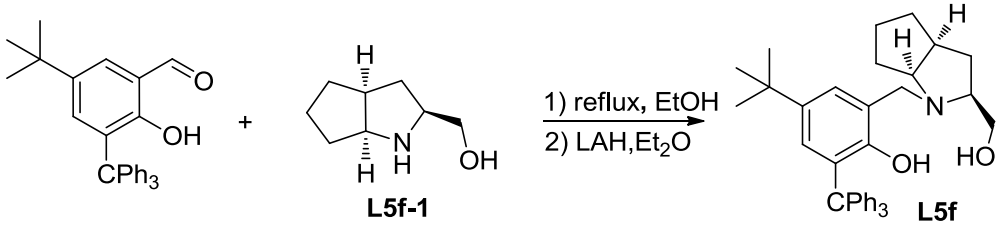


Preparation of Ligand (**L5d**): Compound **L5d** was prepared as a white solid from 2-(Diphenylhydroxymethyl) pyrrolidine (253 mg, 1.00 mmol) and 4-*tert*-Butyl-2-trityl salicylaldehyde (421 mg, 1.00 mmol) in ethanol (20 mL) using the same procedures as reported for **L1**: yield 274 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.39 (m, 4H, Ar-*H*), 7.34-6.98 (m, 22H, Ar-*H*), 6.79 (s, 1H, Ar-*H*), 3.80 (dd, *J* = 9.3, 3.9 Hz, 1H, C*H*$_2$N), 3.24-3.14 (m, 2H, C*H*$_2$N), 2.61-2.59 (1H, m, C*H*$_2$N), 2.31-2.22 (m, 1H, C*H*$_2$N), 2.00-1.93 (m, 1H, C*H*$_2$CH$_2$), 1.77-1.72 (m, 1H, C*H*$_2$CH$_2$), 1.60-1.50 (m, 1H, C*H*$_2$CH$_2$), 1.42-1.26 (m, 1H, C*H*$_2$CH$_2$), 1.10 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.0, 146.1, 145.9, 145.6, 140.3, 132.6, 131.1, 128.1, 128.0, 127.2, 127.0, 126.5, 125.9, 125.7, 125.6, 124.6, 123.5, 79.2, 72.0, 63.2, 59.8, 54.9, 33.9, 31.4, 29.4, 26.8,

24.1. IR (ν/cm^{-1}): 3515(m), 2956(m), 2927(m), 1478(s), 1442(s), 1207(m). 698 (vs). Rotation: 0.36 °, c = 1.1 in EtOH. HRMS calcd for $C_{47}H_{48}NO_2$ (M+H$^+$): 658.3685; Found: 658.3675.

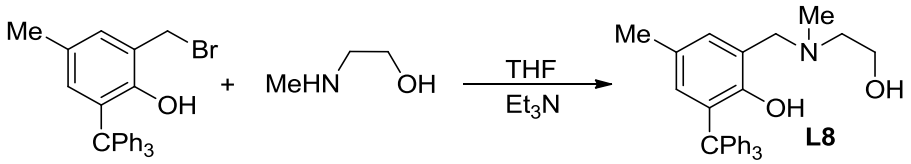


Preparation of Ligand (**L5e**): To a stirred solution of 2-(bromomethyl)-4-*tert*-Bu-6-trityl phenol (634 mg, 1.43 mmol) was added L-homoprolinol (164 mg, 1.43 mmol) in THF (30 mL). After complete dissolution, triethylamine (0.46 mL, 3.3 mmol) was added dropwise. A white solid formed immediately and the reaction stirred for 1.5h at room temperature. The precipitate was filtered off and solvent was evaporated. The residue was subjected to flash chromatography (PE:EA = 20:1 ~ 3:1, V/V). The yield was 0.60 mg (88%). 2-(bromomethyl)-4-*tert*-Bu-6-trityl phenol was prepared according to the published procedures.[7] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.12 (m, 15H, Ar-*H*), 6.85 (s, 1H, Ar-*H*), 6.75 (s, 1H, Ar-*H*), 4.20 (ABd, *J* = 15.1 Hz, 1H, C*H*$_2$N), 3.64-3.52 (m, 2H, C*H*$_2$O), 3.39 (ABd, *J* = 15.1 Hz, 1H, C*H*$_2$N), 2.66-2.62 (m, 1H, C*H*N), 2.28-2.24 (m, 1H, C*H*$_2$N), 2.16 (s, 3H, C*H*$_3$), 2.05-1.99 (m, 1H, C*H*$_2$N), 1.56-1.13 (m, 6H, C*H*$_2$C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 146.0, 134.0, 131.0, 130.3, 128.2, 126.9, 126.7, 125.3, 122.7, 63.1, 63.0, 62.3, 57.5, 51.2, 27.4, 24.4, 22.8, 20.9. IR (ν/cm^{-1}): 3552(w), 3497(w), 2933(m), 2857(w), 1595(s), 1462(s), 1443(s), 1241(m). 698 (vs). Rotation: -21.6 °, c = 0.96 in EtOH. HRMS (ESI) calcd for $C_{33}H_{36}NO_2$, (M+H$^+$): 478.2746; Found: 478.2747.



Preparation of Ligand (**L5f**): Compound **L5f** was prepared as a colorless oil from **L5f-1** (141 mg, 1.00 mmol) and 4-*tert*-Butyl-2-trityl salicylaldehyde (421 mg, 1.00 mmol) in ethanol (20 mL) using the same procedures as reported for **L1**: yield 472 mg (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.08 (m, 16H, Ar-*H*), 6.92 (s, 1H, Ar-*H*), 3.92 (ABd, *J* = 14.1 Hz, 1H, C*H*$_2$N), 3.74 (ABd, *J* =

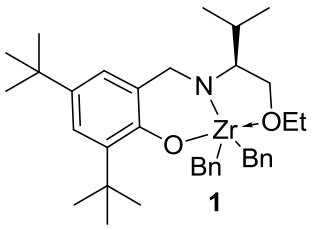
14.4 Hz, 1H, CH_2N), 3.26 (ABd, J = 12.3 Hz, 1H, CH_2O), 3.16 (ABd, J = 10.2 Hz, 1H, CH_2O), 3.03-2.99 (m, 1H, CHN), 2.56-2.43 (m, 2H, CHCH_2CH), 1.96-1.88 (m, 1H, CH_2CHCH_2), 1.43-1.19 (m, 7H), 1.15 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 145.7, 140.6, 133.2, 131.0, 128.4, 126.9, 125.3, 123.4, 122.9, 73.5, 69.1, 65.0, 63.3, 62.5, 58.8, 39.9, 34.9, 34.0, 32.6, 31.4, 24.4. IR (ν/cm^{-1}): 3055(w), 3085(w), 2951(m), 2862(m), 1598(m), 1476(s), 1445(s), 744(vs). 699 (vs). Rotation: -33.6 °, c = 0.500 in EtOH. MS (ESI, m/z): 546.7 (M+H$^+$). HRMS (ESI) calcd for $C_{38}H_{44}NO_2$, (M+H$^+$): 546.3372; Found: 546.3365.



Preparation of Ligand (**L8**): Compound **L8** was prepared as a white solid from 2-(bromomethyl)-4-*tert*-Butyl-6-trityl phenol (2.22 g, 5.0 mmol) and N-Me-ethanolamine (375 mg, 5.0 mmol) in THF (50 mL) using the same procedures as reported for **L5e**: yield 1.66 g (76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.14 (m, 15H, Ar-H), 6.91 (s, 1H, Ar-H), 6.75 (s, 1H, Ar-H), 5.23 (s, 1H, OH), 3.63 (s, 2H, CH_2N), 3.33 (t, J = 5.7 Hz, 2H, CH_2O), 2.28 (t, J = 5.7 Hz, 2H, CH_2N), 2.21 (s, 3H, Ph-CH_3), 2.17 (s, 3H, CH_3N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 145.9, 133.9, 131.0, 130.6, 128.4, 126.9, 126.7, 125.3, 122.1, 63.1, 61.9, 59.5, 57.3, 41.8, 20.9. IR (ν/cm^{-1}): 3543(w), 2919(w), 1491(s), 1450(s), 1248(s). HRMS (ESI) calcd for $C_{30}H_{32}NO_2$, (M+H$^+$): 438.2433; Found: 438.2422.

3. Synthesis and Characterization of Complexes

Preparation of Complex 1:



1

To a solution of $ZrBn_4$ (456 mg, 1.0 mmol) in toluene (20 mL) was added dropwise **L1** (350 mg, 1.0 mmol) in toluene (20 mL) at -78℃ over 1 h. After stirring for 3 h at room temperature, the solvent was removed to give a yellow solid that was washed with hexane. Recrystallization from toluene/hexane gave **1** as colorless crystals (335 mg, 54%). Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.58 (s, 1H, Ar-*H*), 7.38-7.28 (m, 2H, Ar-*H*), 7.24-7.22 (m, 3H, Ar-*H*), 7.13-7.05 (m, 3H, Ar-*H*), 6.88-6.80 (m, 3H, Ar-*H*), 4.45 (ABd, *J* = 16.2 Hz, 1H, C*H*$_2$-N), 4.16 (ABd, *J* = 15.9 Hz, 1H, C*H*$_2$-N), 3.62-3.51 (m, 1H, CH_3CH_2O), 3.36 (m, 1H, $CHCH_2O$), 3.26-3.21 (m, 1H, $CHCH_2O$), 2.99-2.88 (m, 1H, CH_3CH_2O), 2.62-2.59 (m, 1H, C*H*-N), 2.40 (ABd, *J* = 9.6 Hz, 1H, PhC*H*$_2$), 2.22-2.13 (m, 2H, PhC*H*$_2$), 1.79 (s, 9H, C(C*H*$_3$)$_3$), 1.70-1.64 (m, 1H, C*H*(CH$_3$)$_2$), 1.47 (s, 9H, C(C*H*$_3$)$_3$), 1.30 (ABd, *J* = 10.2 Hz, 1H, PhC*H*$_2$), 0.77-0.71 (m, 9H). ^{13}C NMR (100M, C_6D_6): δ 156.2, 149.0, 142.6, 142.0, 135.7, 131.5, 131.6, 128.5, 126.7, 126.2, 122.96, 122.90, 122.1, 120.6, 73.6, 71.9, 69.4, 60.2, 56.1, 55.6, 35.5, 34.5, 32.1, 30.6, 30.4, 20.2, 17.8, 12.9. Anal. Calcd for $C_{36}H_{51}NO_2Zr$ (**1**): C, 69.63; H, 8.28; N, 2.26. Found: C, 69.44; H, 8.39; N, 2.08.

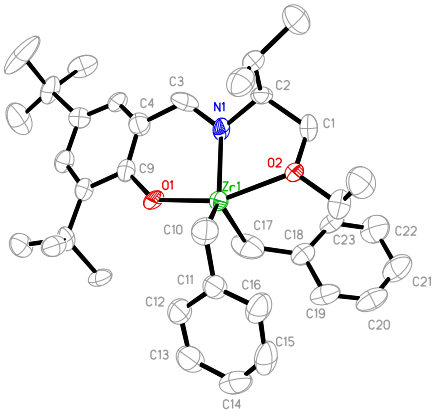
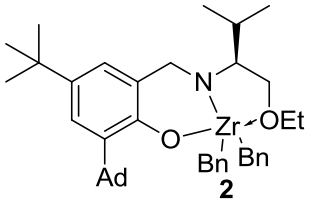


Figure S1. Molecular Structure of Complex **1**

Preparation of Complex 2:



2

Complex **2** was prepared as a white solid from ligand **L2** (214 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 135 mg (39%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6) : δ 7.49 (s, 1H, Ar-*H*), 7.30-7.19 (m, 3H, Ar-*H*), 7.09 (t, *J* = 7.2 Hz, 4H, Ar-*H*), 6.97 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.92-6.75 (m, 3H, Ar-*H*), 4.45 (ABd, *J* = 15.6 Hz, 1H, C*H*$_2$N), 4.10 (d, *J* = 15.9 Hz, 1H, C*H*$_2$N), 3.45-3.38 (m, 1H, C*H*$_2$O), 3.32-3.38 (m, 1H, C*H*$_2$O), 3.20-3.15 (m, 1H, C*H*$_2$O), 2.98-2.92 (m, 1H, C*H*$_2$O), 2.60-2.50 (m, 7H), 2.25-2.18 (m, 6H), 2.00-1.99 (m, 3H), 1.86-1.82 (m, 3H), 1.70-1.52 (m, 2H), 1.43 (s, 9H, C(C*H*$_3$)$_3$), 0.71-0.66 (m, 9H, CH_2CH_3, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 156.9, 148.0, 143.5, 142.1, 136.2, 131.8, 130.9, 128.9, 126.3, 126.2, 122.9, 122.5, 122.3, 121.0, 73.6, 71.9, 69.5, 60.1, 56.6, 56.0, 41.5, 37.8, 37.6, 34.6, 32.1, 30.8, 29.8, 20.2, 17.9, 13.0. Anal. Calcd for $C_{42}H_{57}NO_2Zr$ (**2**): C, 72.15; H, 8.22; N, 2.00. Found: C, 71.85; H, 8.42; N, 2.00.

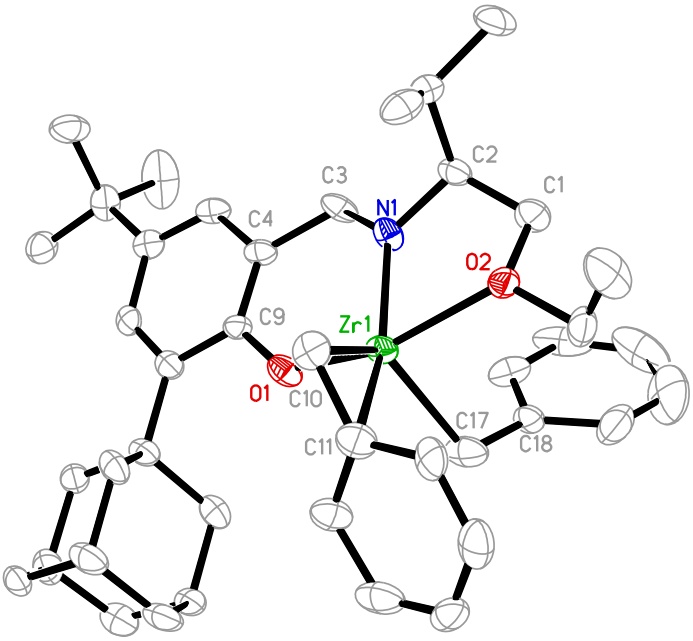
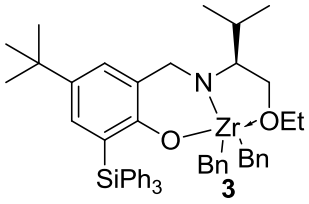


Figure S2. Molecular Structure of Complex **2**

Preparation of Complex 3:



3

Complex **3** was prepared as a white solid from ligand **L3** (276 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 265 mg (64%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.95-7.93 (m, 6H, Ar-*H*), 7.51 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 7.37 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 7.24-7.15 (m, 9H, Ar-*H*), 7.07-7.02 (m, 2H, Ar-*H*), 6.89-6.71 (m, 6H, Ar-*H*), 6.42 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 4.75 (ABd, *J* = 16.8 Hz, 1H, C*H*$_2$N), 4.04 (ABd, *J* = 16.8 Hz, 1H, C*H*$_2$N), 3.40-3.20 (m, 2H), 3.01-2.94 (m, 1H, C*H*$_2$O), 2.75 (dt, *J* = 6.0, 13.8 Hz, 1H, C*H*N), 2.47-2.44 (m, 1H), 1.86-1.78 (m, 2H, C*H*$_2$Ph), 1.69-1.58 (m, 1H, C*H*(CH$_3$)$_2$), 1.46 (ABd, *J* = 9.0 Hz, 1H, C*H*$_2$Ph), 1.40-1.20 (m, 10H, C(C*H*$_3$)$_3$, C*H*$_2$Ph), 0.75-0.68 (m, 6H, CH(C*H*$_3$)$_2$), 0.58 (t, *J* = 6.9 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 162.6, 150.0, 142.8, 140.9, 137.0, 136.2, 134.5, 131.7, 129.7, 128.2, 126.2, 125.8, 122.6, 120.3, 120.2, 73.6, 71.9, 69.2, 60.4, 56.8, 56.5, 34.4, 31.8, 31.4, 20.1, 18.2, 12.8. Anal. Calcd for $C_{50}H_{57}NO_2SiZr$ (**3**): C, 72.94; H, 6.98; N, 1.70. Found: C, 73.46; H, 6.54; N, 1.83.

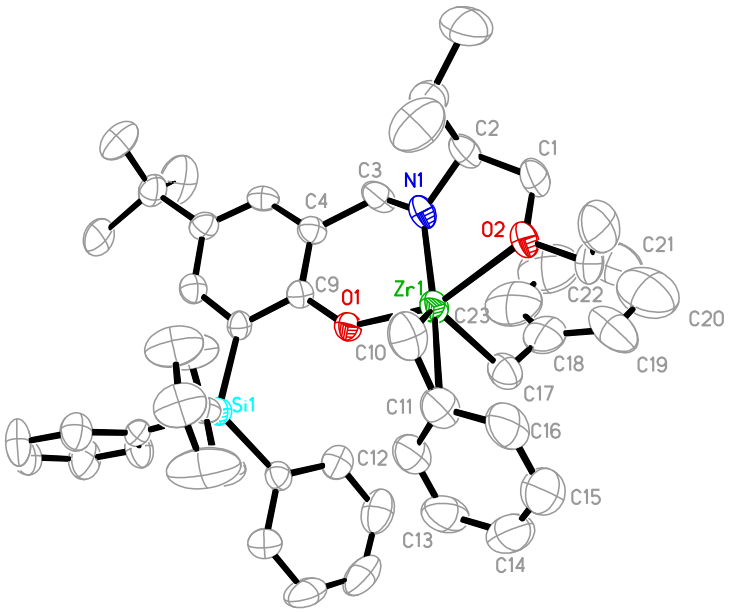
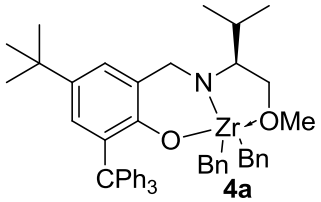


Figure S3. Molecular Structure of complex **3**

Preparation of Complex 4a:



4a

Complex **4a** was prepared as a white solid from ligand **L4a** (261 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1**: yield 228 mg (58%). Crystals suitable for X-ray analyses were grown from a toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 7.58 (d, *J* = 7.6 Hz, 6H, Ar-*H*), 7.34(d, *J* = 4.4 Hz, 2H, Ar-*H*), 7.15-7.07 (m, 8H, Ar-*H*), 7.00-6.93(m, 6H, Ar-*H*), 6.72 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.34 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 6.24 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 4.45 (d, *J* = 16.5 Hz, 1H, CH_2N), 4.16 (d, *J* = 16.5 Hz, 1H, CH_2N), 3.09-3.06 (m, 1H, CH_2O), 3.00 (m, 1H, CH_2O), 2.68 (s, 3H, OCH_3), 2.41-2.38 (m, 1H, C*H*N), 1.89 (ABd, *J* = 9.4 Hz, 1H, CH_2Ph), 1.67-1.60 (m, 2H), 1.46 (ABd, *J* = 10.7 Hz, 1H, CH_2Ph), 1.27 (s, 9H, C(CH_3)$_3$), 0.74 (ABd, *J* = 10.7 Hz, 1H, CH_2Ph), 0.68 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 0.61 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 155.7, 148.8, 141.8, 141.7, 134.5, 131.7, 131.2, 131.2, 128.4, 128.2, 127.9, 127.7, 126.7, 126.3, 125.8, 124.1, 122.4, 120.2, 77.8, 71.0, 64.4, 61.5, 60.0, 57.5, 56.9, 34.5, 31.8, 30.3, 20.2, 17.4. Anal. Calcd for $C_{50}H_{57}NO_2Zr$ (**4a**): C, 75.71; H, 6.99; N, 1.77. Found: C, 75.69; H, 7.16; N, 1.70.

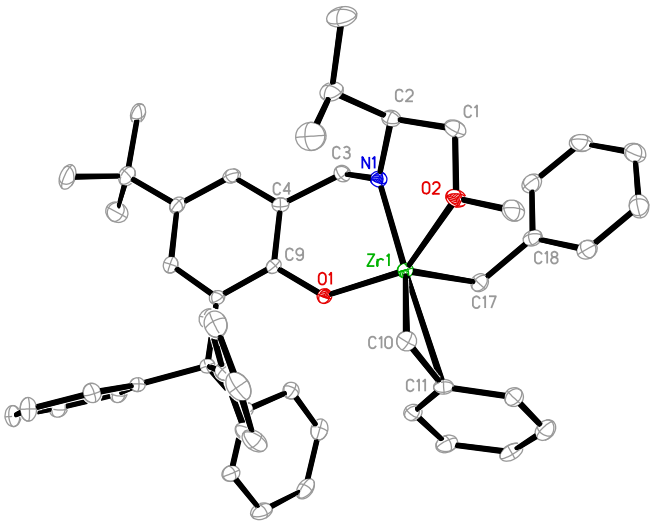
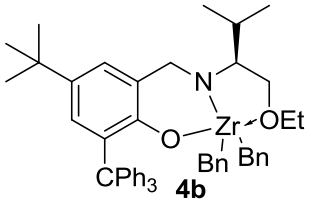


Figure S4. Molecular Structure of **4a**

Preparation of Complex 4b:



4b

Complex **4b** was prepared as a white solid from ligand **L4b** (268 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 230 mg (57%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.59 (d, *J* = 7.8 Hz, 6H, Ar-*H*), 7.37-7.32 (m, 2H, Ar-*H*), 7.18-7.10 (m, 3H, Ar-*H*), 7.14-7.05 (m, 5H, Ar-*H*), 7.02-6.95 (m, 6H, Ar-*H*), 6.72 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.40 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.27 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 4.53 (ABd, *J* = 16.4 Hz, 1H, C*H*$_2$N), 4.12 (ABd, *J* = 16.8 Hz, 1H, C*H*$_2$N), 3.41-3.35 (m, 1H, C*H*$_2$O), 3.21 (d, *J* = 8.4 Hz, 1H, C*H*$_2$O), 2.94-2.82 (m, 2H, C*H*$_2$O), 2.38-2.34 (m, 1H, C*H*N), 1.97 (ABd, *J* = 9.3 Hz, 1H, C*H*$_2$Ph), 1.74-1.59 (m, 2H), 1.45 (ABd, *J* = 10.8 Hz, 1H, C*H*$_2$Ph), 1.27 (s, 9H, C(C*H*$_3$)$_3$), 0.74-0.62 (m, 10H). ^{13}C NMR (75 MHz, C_6D_6): δ 155.7, 150.0, 147.0, 141.8, 141.3, 134.6, 131.7, 131.5, 131.2, 128.2, 127.9, 127.7, 126.30, 126.29, 125.8, 124.1, 122.5, 120.1, 73.0, 71.4, 69.2, 64.5, 60.6, 57.2, 56.9, 34.5, 31.8, 31.0, 20.3, 18.0, 12.9. Anal. Calcd for $C_{51}H_{57}NO_2Zr$ (**4b**): C, 75.88; H, 7.12; N, 1.74. Found: C, 75.37; H, 7.42; N, 1.73.

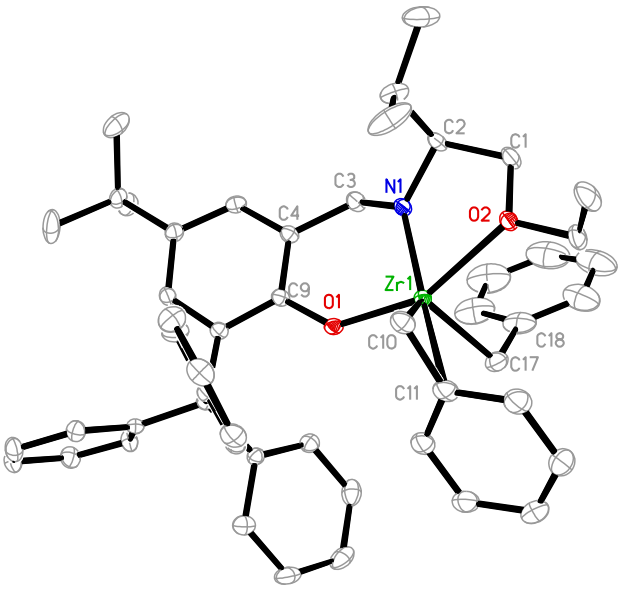
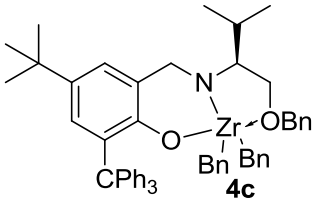


Figure S5. Molecular Structure of **4b**

Preparation of Complex 4c:



4c

Complex **4c** was prepared as a white solid from ligand **L4c** (299 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 113 mg (26%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.62 (d, *J* = 7.8 Hz, 6H, Ar-*H*), 7.37-7.34 (m, 2H, Ar-*H*), 7.19-7.17 (m, 2H, Ar-*H*), 7.14-7.10 (m, 3H, Ar-*H*), 7.08-6.95 (m, 14H, Ar-*H*), 6.76 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.50 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 6.41 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 4.76 (ABd, *J* = 12.9 Hz, 1H, C*H*$_2$N), 4.63 (ABd, *J* = 16.8 Hz, 1H, C*H*$_2$N), 4.06 (ABd, *J* = 16.8 Hz, 1H, C*H*$_2$O), 3.87 (ABd, *J* = 12.6 Hz, 1H, C*H*$_2$O), 3.36 (d, *J* = 8.4 Hz, 1H, C*H*$_2$O), 3.06-3.02 (m, 1H, C*H*$_2$O), 2.32-2.27 (m, 2H), 1.87 (ABd, *J* = 9.3 Hz, 1H, C*H*$_2$Ph), 1.66-1.56 (m, 2H), 1.27 (s, 9H, C(C*H*$_3$)$_3$), 0.84 (ABd, *J* = 11.1 Hz, 1H, C*H*$_2$Ph), 0.60-0.54 (m, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 156.0, 149.6, 141.9, 141.2, 134.6, 134.2, 131.7, 131.0, 129.4, 129.1, 129.0, 127.7, 126.5, 126.3, 126.1, 124.0, 122.7, 120.3, 75.5, 73.3, 71.8, 64.5, 60.9, 57.9, 57.0, 34.5, 32.1, 31.9, 20.1, 18.4. Anal. Calcd for $C_{56}H_{59}NO_2Zr$ (**4c**): C, 77.37; H, 6.84; N, 1.61. Found: C, 77.28; H, 7.04; N, 1.53.

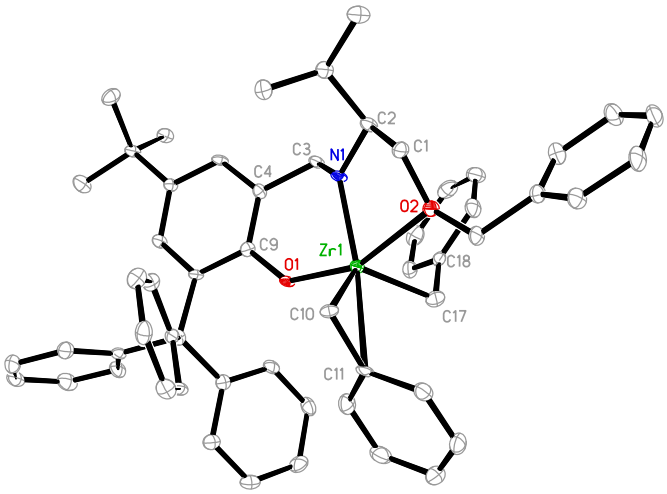
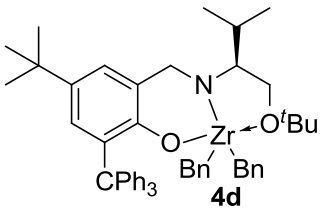


Figure S6. Molecular Structure of **4c**

Preparation of Complex 4d:



4d

Complex **4d** was prepared as a white solid from ligand **L4d** (282 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 450 mg (54%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 7.61 (d, *J* = 8.0 Hz, 6H, Ar-*H*), 7.20-7.19 (m, 2H, Ar-*H*), 7.14-7.05 (m, 8H, Ar-*H*), 7.00-6.89 (m, 4H, Ar-*H*), 6.76 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.63 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 4.23 (ABd, *J* = 16.4 Hz, 1H, C*H*$_2$O), 3.86 (ABd, *J* = 16.4 Hz, 1H, C*H*$_2$O), 3.40-3.38 (m, 2H, C*H*$_2$O), 2.45 (d, 1H, *J* = 5.2 Hz, C*H*N), 1.88-1.82 (m, 2H, C*H*$_2$Ph), 1.69-1.60 (m, 1H, C*H*(CH$_3$)$_2$), 1.46 (ABd, *J* = 10.4 Hz, 1H, C*H*$_2$Ph), 1.40 (ABd, *J* = 10.8 Hz, 1H, C*H*$_2$Ph), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 0.82 (s, 9H, C(C*H*$_3$)$_3$), 0.71 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.59 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 147.8, 147.1, 143.6, 141.7, 134.1, 131.8, 130.5, 129.7, 128.4, 128.2, 127.7, 127.2, 126.31, 126.28, 123.6, 121.8, 120.4, 83.7, 69.6, 67.5, 64.5, 59.0, 58.7, 58.3, 34.4, 31.8, 30.1, 27.4, 19.7, 17.5. Anal. Calcd for $C_{53}H_{61}NO_2Zr$ (**4d**): C, 76.21; H, 7.36; N, 1.68. Found: C, 76.19; H, 7.14; N, 1.64.

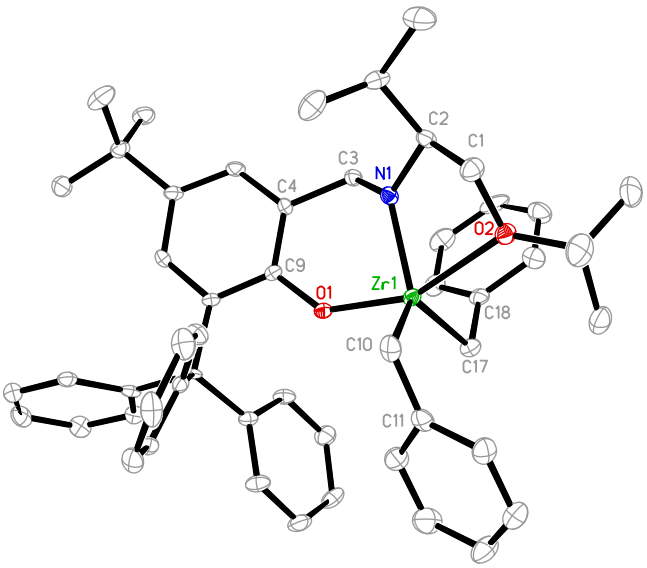
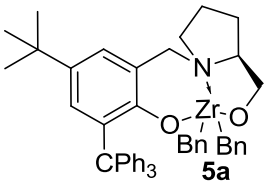


Figure S7. Molecular Structure of **4d**

Preparation of Complex 5a:



5a

Complex **5a** was prepared as a white solid from ligand **L5a** (253 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 206 mg (53%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 7.57-7.52 (m, 7H, Ar-*H*), 7.19-7.12 (m, 8H, Ar-*H*), 7.03-7.00 (m, 4H, Ar-*H*), 6.87 (d, *J* = 2.1 Hz, 1H, Ar-*H*), 6.81 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 6.65 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.42 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.34 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 3.98 (dd, *J* = 6.0, 11.2 Hz, 1H, C*H*$_2$O), 3.62 (dd, *J* = 6.4, 11.2 Hz, 1H, C*H*$_2$O), 2.79-2.74 (m, 2H, C*H*$_2$N), 2.64-2.63 (m, 1H, C*H*$_2$N), 2.52-2.46 (m, 1H, C*H*$_2$N), 2.33-2.24 (m, 2H), 1.69 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 1.34-1.18 (m, 15H). ^{13}C NMR (100M, C_6D_6): δ 156.8, 148.8, 140.6, 136.4, 134.5, 131.8, 131.6, 129.8, 129.0, 128.9, 128.2, 127.9, 127.8, 126.1, 125.5, 125.2, 124.0, 120.7, 74.0, 70.9, 64.3, 58.4, 57.1, 56.8, 47.9, 34.3, 31.8, 25.5, 21.8. Anal. Calcd for $C_{49}H_{51}NO_2Zr$ (**5a**): C, 75.73; H, 6.61; N, 1.80. Found: C, 75.41; H, 6.86; N, 1.56.

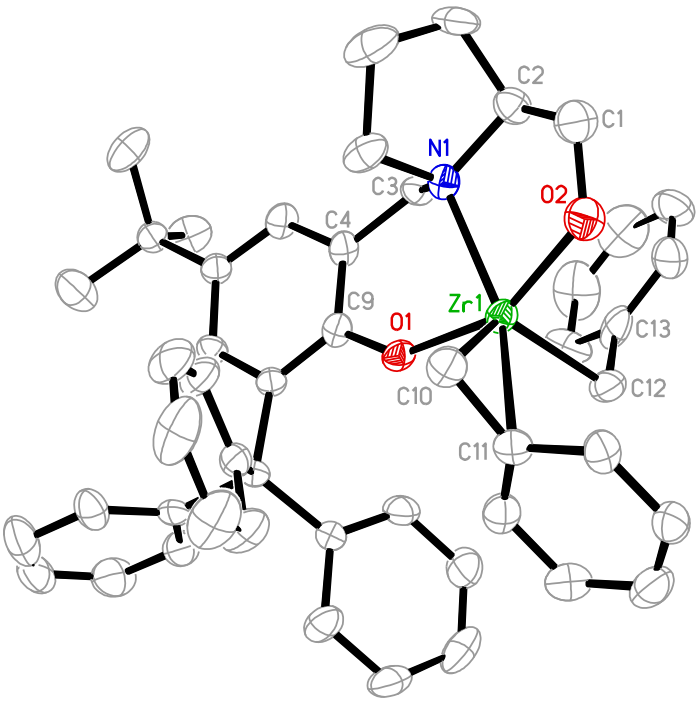
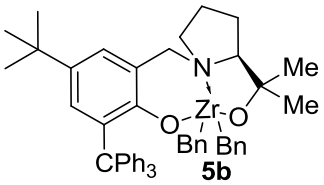


Figure S8. Molecular Structure of **5a**

Preparation of Complex 5b:



Complex **5b** was prepared as a white solid from ligand **L5b** (267 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 175 mg (43%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.59-7.55 (m, 7H, Ar-*H*), 7.22-7.11 (m, 8H, Ar-*H*), 7.05-7.03 (m, 4H, Ar-*H*), 6.92-6.88 (s, 1H, Ar-*H*), 6.81 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 6.66 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.52 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.38 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 2.94-2.83 (m, 2H, C*H*$_2$N), 2.67-2.62 (m, 2H, C*H*$_2$N), 2.56-2.49 (m, 1H, C*H*N), 2.33 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 1.64 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 1.50-1.31 (m, 6H), 1.22 (s, 9H, C(C*H*$_3$)$_3$), 1.03 (s, 3H, C*H*$_3$), 0.91 (s, 3H, C*H*$_3$). ^{13}C NMR (100M, C_6D_6): δ 157.0, 148.6, 140.5, 137.2, 134.7, 131.7, 131.3, 130.1, 129.5, 129.2, 128.4, 128.2, 127.9, 126.2, 125.6, 124.8, 123.7, 121.0, 83.2, 81.5, 64.3, 60.9, 56.9, 56.7, 45.7, 34.3, 31.8, 31.0, 27.6, 24.1, 22.3.Anal. Calcd for $C_{51}H_{55}NO_2Zr$ (**5b**): C, 76.07; H, 6.88; N, 1.74. Found: C, 75.21; H, 7.02; N, 1.42.

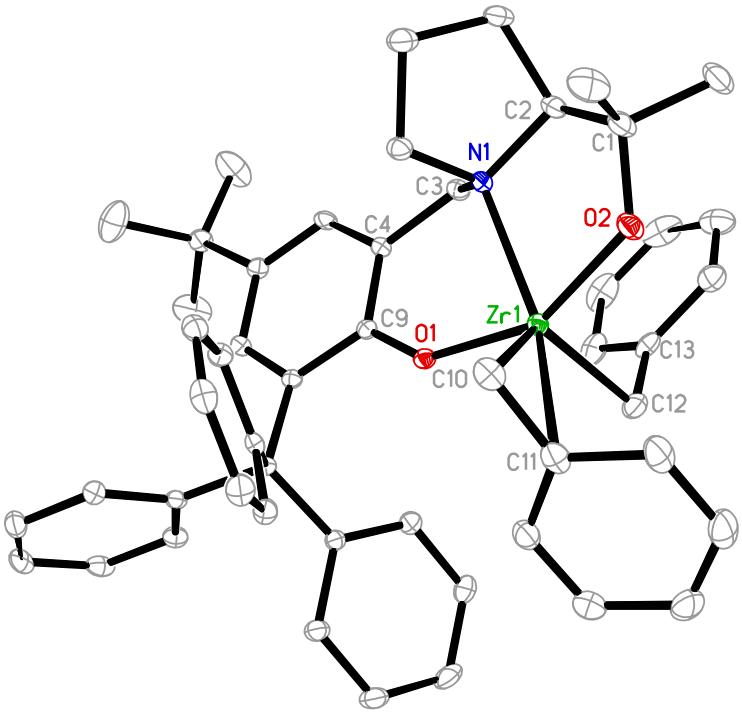
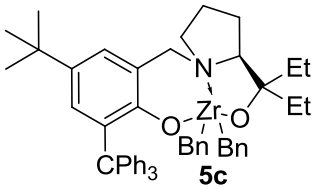


Figure S9. Molecular Structure of **5b**

Preparation of Complex 5c:



5c

Complex **5c** was prepared as a white solid from ligand **L5c** (281 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 285 mg (68%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.70-7.50 (m, 7H, Ar-*H*), 7.22-7.11 (m, 8H, Ar-*H*), 7.04-7.02 (m, 4H, Ar-*H*), 6.90-6.83 (m, 1H, Ar-*H*), 6.81 (t, *J* = 6.9 Hz, 2H, Ar-*H*), 6.67 (t, *J* = 6.6 Hz, 1H, Ar-*H*), 6.57 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.29 (d, *J* = 6.6 Hz, 2H, Ar-*H*), 2.94-2.89 (m, 2H, C*H*$_2$N), 2.74-2.69 (m, 2H, C*H*$_2$N), 2.50-2.46 (m, 1H, C*H*N), 2.21 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 1.62-1.34 (m, 9H), 1.34-1.10 (m, 11H), 0.95-0.93 (m, 3H, CH$_2$C*H*$_3$), 0.63 (t, *J* = 6.9 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, C_6D_6): δ 156.9, 148.1, 140.4, 138.1, 134.7, 131.7, 131.1, 130.0, 129.2, 129.0, 128.4, 126.1, 125.5, 125.0, 123,5, 121.1, 85.8, 83.4, 64.3, 61.0, 56.7, 56.2, 46.2, 34.3, 32.9, 31.8, 27.9, 24.8, 22.6, 9.3, 8.3. Anal. Calcd for $C_{53}H_{59}NO_2Zr$ (**5c**): C, 76.39; H, 7.14; N, 1.68. Found: C, 76.25; H, 7.10; N, 1.69.

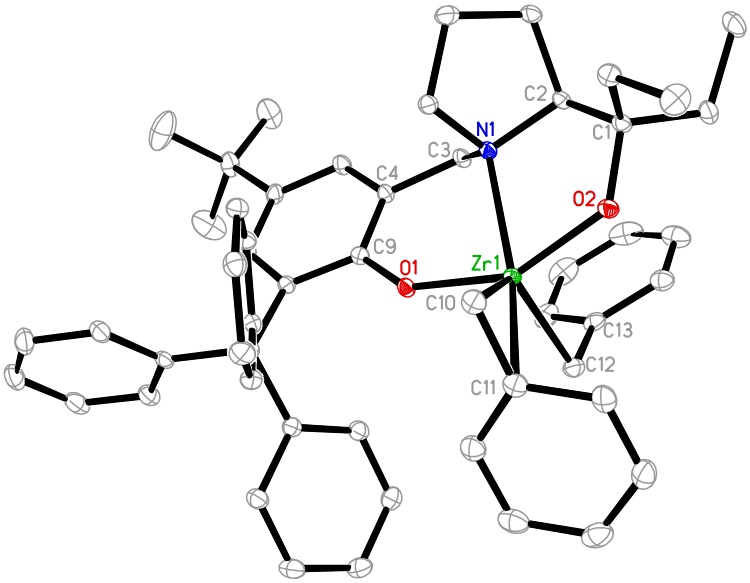
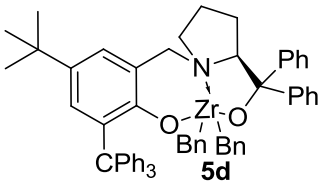


Figure S10. Molecular Structure of **5c**

Preparation of Complex 5d:



5d

Complex **5d** was prepared as a white solid from ligand **L5d** (329 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 293 mg (63%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.60-7.58 (m, 2H, Ar-*H*), 7.58-7.47 (m, 8H, Ar-*H*), 7.38-7.35 (m, 2H, Ar-*H*), 7.14-7.07 (m, 3H, Ar-*H*), 7.04-6.92 (m, 17H, Ar-*H*), 6.81-6.74 (m, 3H, Ar-*H*), 6.30-6.20 (m, 2H, Ar-*H*), 3.80-3.77 (m, 1H, C*H*N), 3.51 (ABd, *J* = 13.8 Hz, 1H, CH_2N), 3.08 (ABd, *J* = 14.7 Hz, 1H, CH_2N), 2.64-2.49 (m, 2H), 2.32 (ABd, *J* = 7.8 Hz, 1H, PhCH_2), 2.04 (ABd, *J* = 7.5 Hz, 1H, PhCH_2), 1.63 (ABd, *J* = 10.2 Hz, 1H, PhCH_2), 1.30-1.11 (m, 11H), 0.90-0.86 (m, 2H), 0.68 (ABd, *J* = 9.9 Hz, 1H, PhCH_2). ^{13}C NMR (75 MHz, C_6D_6): δ 157.3, 149.0, 147.3, 146.7, 141.7, 140.8, 134.5, 131.6, 130.3, 129.7, 129.3, 129.2, 129.1, 128.6, 128.2, 127.9, 127.8, 127.2, 126.43, 126.37, 126.3, 126.2, 125.60, 125.56, 123.6, 122.0, 87.9, 80.9, 64.0, 59.4, 58.8, 58.4, 50.6, 34.3, 31.7, 23.1, 21.2. Anal. Calcd for $C_{61}H_{59}NO_2Zr$ (**5d**): C, 78.83; H, 6.40; N, 1.51. Found: C, 78.82; H, 6.72; N, 1.21.

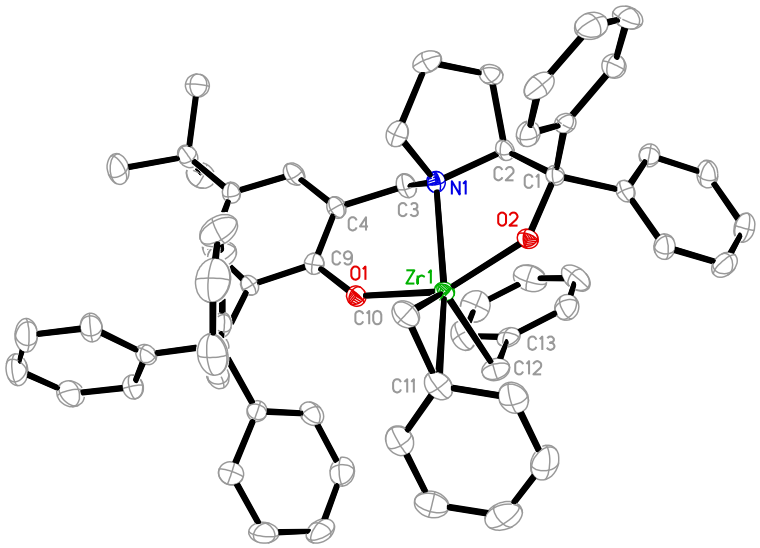
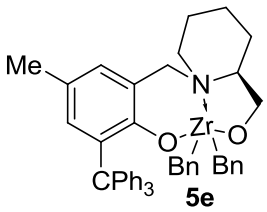


Figure S11. Molecular Structure of **5d**

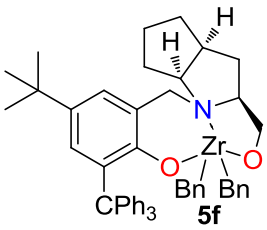
Preparation of Complex 5e:



5e

Complex **5e** was prepared as a white solid from ligand **L5e** (239 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 105 mg (28%)**.** ^{1}H NMR (400 MHz, C_6D_6): δ 7.53-7.51 (m, 6H, Ar-*H*), 7.30-7.29 (m, 1H, Ar-*H*), 7.20-7.13 (m, 8H, Ar-*H*), 7.04-7.01 (m, 5H, Ar-*H*), 6.85-6.81 (m, 2H, Ar-*H*), 6.66-6.59 (m, 4H, Ar-*H*), 6.41 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 4.28-4.25 (m, 1H, C*H*$_2$O), 3.80-3.77 (m, 1H, C*H*$_2$O), 3.51 (ABd, *J* = 14.4 Hz, 1H, C*H*$_2$N), 2.72 (ABd, *J* = 14.4 Hz, 1H, C*H*$_2$N), 2.54-2.52 (m, 1H, C*H*N), 2.46 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 2.36-2.34 (m, *2*H, C*H*$_2$N), 2.08 (s, 3H, C*H*$_3$), 1.66 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 1.34-1.32 (m, 2H), 1.24-1.21 (m, 2H), 1.12-1.07 (m, 2H), 0.81-0.78 (m, 1H, CH$_2$C*H*$_2$), 0.70-0.65 (m, 1H, CH$_2$C*H*$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 156.8, 148.7, 137.0, 135.2, 133.1, 131.7, 131.1, 130.0, 129.6, 129.0, 128.2, 127.94, 127.86, 127.3, 126.2, 123.9, 123.8, 121.0, 69.0, 65.3, 64.0, 57.7, 57.4, 55.6, 37.6, 21.1, 19.1, 18.2, 17.9. Anal. Calcd for $C_{47}H_{47}NO_2Zr$ (**5e**): C, 75.36; H, 6.32; N, 1.87. Found: C, 75.37; H, 6.40; N, 1.80.

Preparation of Complex 5f:

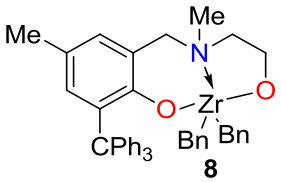


5f

Complex **5f** was prepared as a white solid from ligand **L5f** (273 mg, 0.5 mmol) and $ZrBn_4$ (228 mg, 0.5 mmol) using the same procedures as reported for complex **1:** yield 277 mg (68%)**.** ^{1}H NMR (400 MHz, C_6D_6): δ 7.61 (brs, 6H, Ar-*H*), 7.50 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.20-7.18 (m, 4H, Ar-*H*), 7.15-7.12 (m, 4H, Ar-*H*), 7.08-7.01 (m, 4H, Ar-*H*), 6.93-6.86 (m, 3H, Ar-*H*), 6.74-6.61 (m, 5H, Ar-*H*), 4.02-3.87 (m, 2H, C*H*$_2$O), 3.44-3.37 (m, 1H, C*H*N), 3.10-3.04 (m, 1H, C*H*N), 2.90 (ABd, *J* = 14.4 Hz, 1H, C*H*$_2$N), 2.70 (ABd, *J* = 14.4 Hz, 1H, C*H*$_2$N), 2.41 (ABd, *J* = 8.4 Hz, 1H, PhC*H*$_2$), 2.18-2.08 (m, 1H), 1.71-1.56 (m, 3H), 1.49-1.20 (m, 16H), 0.71-0.63 (m, 1H, C*H*CH$_2$). ^{13}C NMR (100 MHz, C_6D_6):

δ 157.1, 150.0, 140.7, 136.2, 134.8, 131.7, 131.0, 130.1, 130.0, 129.3, 128.6, 128.2, 127.9, 126.2, 125.7, 125.2, 124.3, 120.8, 76.8, 72.9, 68.6, 64.4, 61.6, 61.3, 58.0, 42.0, 34.4, 34.3, 32.2, 31.7, 31.5, 26.9. Anal. Calcd for $C_{52}H_{55}NO_2Zr$ (**5f**): C, 76.42; H, 6.78; N, 1.71. Found: C, 75.97; H, 6.86; N, 1.47.

Preparation of Complex 8:



8

Complex **8** was prepared as a white solid from ligand **L8** (438 mg, 1.0 mmol) and $ZrBn_4$ (456 mg, 1.0 mmol) using the same procedures as reported for complex **1**: yield 373 mg (53%)**.** Crystals suitable for X-ray analyses were grown from toluene/hexane solution as colorless crystals at room temperature. ^{1}H NMR (300 MHz, C_6D_6): δ 7.53-7.50 (m, 6H, Ar-*H*), 7.28 (s, 1H, Ar-*H*), 7.20-7.17 (m, 2H, Ar-*H*), 7.15-7.12 (m, 5H, Ar-*H*), 7.04-7.00 (m, 5H, Ar-*H*), 6.86-6.81 (m, 2H, Ar-*H*), 6.68-6.63 (m, 1H, Ar-*H*), 6.54-6.51 (m, 3H, Ar-*H*), 6.41 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 3.98-3.92 (m, 1H, C*H*$_2$O), 3.72-3.66 (m, 1H, C*H*$_2$O), 3.01 (ABd, *J* = 14.4 Hz, 1H, C*H*$_2$N), 2.66 (ABd, *J* = 14.1 Hz, 1H, C*H*$_2$N), 2.38 (ABd, *J* = 7.5 Hz, 1H, C*H*$_2$N), 2.27-2.17 (m, 1H, C*H*$_2$N), 2.08 (s, 3H, Ph-C*H*$_3$), 1.17-1.69 (m, 4H), 1.60 (ABd, *J* = 7.2 Hz, 1H, PhC*H*$_2$), 1.28 (ABd, *J* = 9.6 Hz, 1H, PhC*H*$_2$), 1.11 (ABd, *J* = 9.9 Hz, 1H, PhC*H*$_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 156.5, 148.4, 136.8, 135.3, 133.0, 131.6, 131.3, 129.8, 129.4, 129.3, 129.1, 128.6, 127.3, 126.2, 125.7, 123.9, 123.7, 121.0, 64.91, 64.88, 63.9, 63.4, 57.3, 34.9, 21.5, 21.0. Anal. Calcd for $C_{44}H_{43}NO_2Zr$ (**8**): C, 74.53; H, 6.11; N, 1.98. Found: C, 74.75; H, 6.22; N, 2.37.

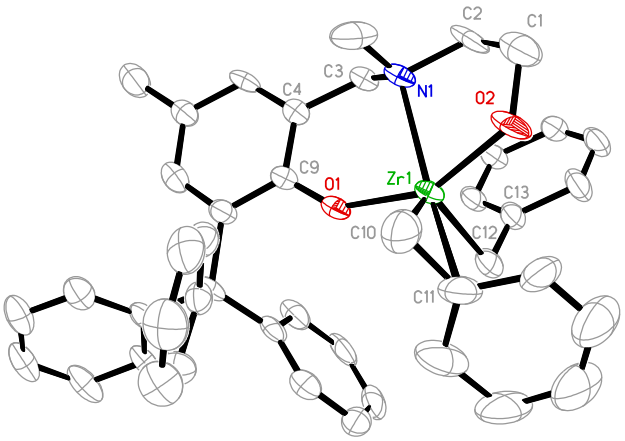
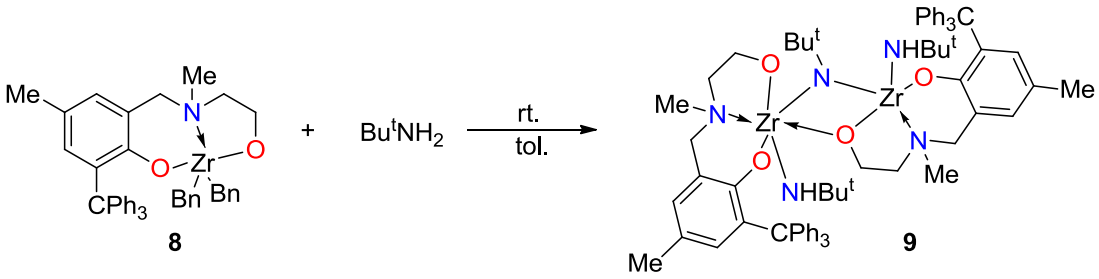


Figure S12. Molecular Structure of **8**

Preparation of Complex 9:



To a toluene solution (20 mL) of **8** (142 mg, 0.2 mmol) was added ^{t}BuNH$_2$ (73 mg, 1.0 mmol), and the mixture was stirred at room temperature for 5 h. Removal of the volatile molecules gave a crude product. Recrystallization from a mixed solvent of toluene and hexane afforded **9** as colorless crystals (56 mg, 44%). Crystals suitable for X-ray analyses were grown from toluene/hexane solution. The ^{13}C NMR spectrum was not available due to the very poor solubility. ^{1}H NMR (300 MHz, C_6D_6): δ 7.65-7.55 (m, 3H, Ar-*H*), 7.48-7.43 (m, 1H, Ar-*H*), 7.37-7.31 (m, 5H, Ar-*H*), 7.28-7.20 (m, 8H, Ar-*H*), 7.13-7.10 (m, 7H, Ar-*H*), 7.06-6.98 (m, 7H, Ar-*H*), 6.93 (s, 2H, Ar-*H*), 6.81 (s, 1H, Ar-*H*), 4.01-4.44 (m, 1H), 4.23-4.10 (m, 3H), 3.40 (s, 1H, N*H*), 3.34-3.28 (m, 1H), 3.10 (s, 1H, N*H*), 3.06-2.92 (m, 2H), 2.65-2.61 (m, 1H), 2.53 (s, 3H, Me), 2.25-2.24 (m, 1H), 2.17-2.14 (m, 1H), 2.21 (s, 3H, Me), 2.07 (s, 3H, Me), 1.68-1.64 (m, 2H), 1.61 (s, 3H, Me), 1.36 (s, 9H, *t*-Bu), 1.21 (s, 9H, *t*-Bu), 1.09 (s, 9H, *t*-Bu). Anal. Calcd for $C_{72}H_{87}N_5O_4Zr_2$ (**9**): C, 68.15; H, 6.91; N, 5.52. Found: C

68.00; H, 6.63; N, 5.09.

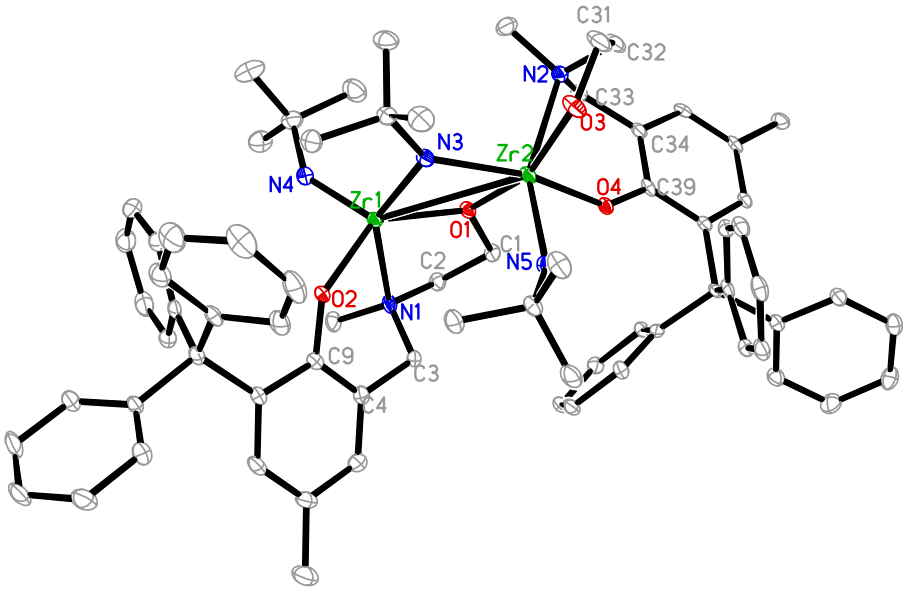


Figure S13. Molecular Structure of **9**

X-ray Structure Determination. Single crystals of **1-3**, **4a-d**, **5a-d, 8** and **9** were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. All data were collected at 293 K on a Bruker AXS D8 X-ray diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[8] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[9] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table S1.

CCDC1016330-1016342 (**1-3**, **4a, b, c, d, 5a, b, c, d, 8**, and **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Crystal Data and Summary of Data Collection and Refinement

Table S1. Crystal Data and Summary of Data Collection and Refinement

complex No.	**1**	**2**	**3**
empirical formula	$C_{36}H_{51}NO_2Zr$	$C_{42}H_{57}NO_2Zr$	$C_{50}H_{57}NO_2SiZr$
formula weight	621.00	699.11	823.28
crystal size (mm)	0.297×0.220×0.130	0.369×0.311×0.257	0.327×0.269×0.211
crystal system	Monoclinic	Trigonal	Orthorhombic
space group	$P2_1$	$P3_2$	$P2_12_12_1$
a, Å	10.820(6)	25.473(4)	10.472(1)
b, Å	11.235(7)	25.473(4)	20.727(2)
c, Å	15.074(9)	15.017(3)	21.297(2)
α, deg	90	90	90
β, deg	110.6(1)	90	90
γ, deg	90	120	90
V, $Å^3$	1714.7(17)	8439(2)	4622.8(7)
Z	2	9	4
D_{catcd}, Mg/m^3	1.203	1.238	1.183
radiation (λ), (Å)	Mo Ka (0.71073)	Mo Ka (0.71073)	Mo Ka (0.71073)
2θ range for data collection (deg)	1.44 to 27.00	1.60 to 26.49	1.91 to 25.50
absorption coefficient (mm^{-1})	0.350	0.328	0.301
F(000)	660	3348	1736
no. of obsd reflns	7112	22434	8583
no. of params reflns	371	1262	510
reflections collected / unique	10099 / 7112 [R(int) = 0.0635]	62219 / 22434 [R(int) = 0.0197]	24284 / 8583 [R(int) = 0.0858]
goodness-of-fit on F^2	0.830	1.211	0.827
R1 [I>2σ(I)] [a]	0.0636	0.0974	0.0510
wR1 [I>2σ(I)] [a]	0.1527	0.2550	0.0924

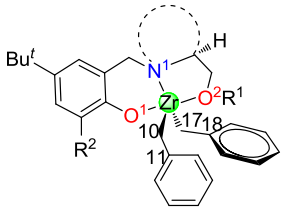
complex No.	**4a**	**4b**	**4c**
empirical formula	$C_{50}H_{55}NO_2Zr$	$C_{51}H_{56}NO_2Zr$	$C_{56}H_{59}NO_2Zr$
formula weight	793.17	807.20	869.26
crystal size (mm)	0.30×0.25×0.20	0.13×0.10×0.08	0.323×0.256×0.175
crystal system	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1$	$P2_12_12_1$	$P2_1$
a, Å	9.915(1)	9.970(2)	12.399(1)
b, Å	39.191(4)	20.770(4)	10.204(1)
c, Å	10.949(1)	20.886(4)	35.906(3)
α, deg	90	90	90
β, deg	93.596(2)	90	91.315(2)
γ, deg	90	90	90
V, Å^3	4246.1(7)	4325(1)	4541.2(7)
Z	4	4	4
D_{catcd}, Mg/m^3	1.241	1.238	1.271
radiation (λ), (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range for data collection (deg)	1.86 to 27.00	1.96 to 25.65	1.13 to 26.00
absorption coefficient (mm^{-1})	0.298	0.294	0.285
F(000)	1672	1736	1832
no. of obsd reflns	18179	3810	16208
no. of params reflns	1027	541	1100
reflections collected / unique	38003 / 18179 [R(int) = 0.0222]	14432 / 3810 R(int) = 0.0530]	34011 / 16208 [R(int) = 0.0242]
goodness-of-fit on F^2	1.092	1.064	1.150
R1 [I>2σ(I)] [a]	0.0333	0.0514	0.0513
wR1 [I>2σ(I)] [a]	0.0838	0.0920	0.1253

complex No.	**5a**	**5b**	**5c**
empirical formula	$C_{49}H_{51}NO_2Zr$	$C_{51}H_{55}NO_2Zr$	$C_{53}H_{59}NO_2Zr$
formula weight	777.13	805.18	833.23
crystal size (mm)	0.27×0.22×0.22	0.30×0.10×0.08	0.229×0.202×0.175
crystal system	Monoclinic	Orthorhombic	Orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å	10.249(4)	10.407(1)	10.505(1)
b, Å	10.086(4)	20.067(2)	20.145(2)
c, Å	20.139(8)	20.180(1)	20.793(2)
α, deg	90	90	90
β, deg	102.780(7)	90	90
γ, deg	90	90	90
V, Å^3	2030(1)	4214.4(5)	4400.3(6)
Z	2	4	4
D_{catcd}, Mg/m^3	1.271	1.269	1.258
radiation (λ), (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range for data collection (deg)	2.04 to 25.50	2.02 to 30.54	1.96 to 27.00
absorption coefficient (mm^{-1})	0.310	0.301	0.291
F(000)	816	1696	1760
no. of obsd reflns	6835	12891	9595
no. of params reflns	481	501	519
reflections collected / unique	13455 / 6835 [R(int) = 0.0407]	41831 / 12891 [R(int) = 0.0658]	34053 / 9595 [R(int) = 0.0356]
goodness-of-fit on F^2	1.009	0.980	1.065
R1 [I>2σ(I)] [a]	0.0405	0.0434	0.0326
wR1 [I>2σ(I)] [a]	0.1065	0.0876	0.0844

complex No.	**5d**	**8**	**9**
empirical formula	$C_{61}H_{59}NO_2Zr$	$C_{44}H_{43}NO_2Zr$	$C_{72}H_{87}NO_4Zr_2$
formula weight	929.31	709.01	1268.91
crystal size (mm)	0.25×0.15×0.05	0.08×0.04×0.03	0.12×0.05×0.03
crystal system	Orthorhombic	Monoclinic	Triclinic
space group	$P2_12_12_1$	C2/c	P-1
a, Å	9.986(1)	29.258(4)	12.065(2)
b, Å	10.263 (1)	24.694(4)	13.096(2)
c, Å	46.379(5)	23.148(3)	23.377(4)
α, deg	90	90	100.83(1)
β, deg	90	117.29(1)	93.01(1)
γ, deg	90	90	111.47(1)
V, Å^3	4753.2(8)	14862(4)	3346.3(9)
Z	4	16	2
D_{catcd}, Mg/m^3	1.299	1.268	1.259
radiation (λ), (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range for data collection (deg)	1.76 to 30.50	1.65 to 25.10	1.75 to 25.10
absorption coefficient (mm^{-1})	0.277	0.332	0.362
F(000)	1952	5920	1332
no. of obsd reflns	14461	13132	11728
no. of params reflns	589	857	748
reflections collected / unique	47013 / 14461 [R(int) = 0.0979]	48300 / 13132 [R(int) = 0.1208]	21203 / 11728 [R(int) = 0.0461]
goodness-of-fit on F^2	0.961	0.924	0.953
R1 [I>2σ(I)] [a]	0.0533	0.0789	0.0483
wR1 [I>2σ(I)] [a]	0.0810	0.1831	0.1250

componds No.	**4d**
empirical formula	$C_{53}H_{61}NO_2Zr$
formula weight	835.25
crystal size (mm)	0.20 x 0.16 x 0.04
crystal system	Monoclinic
space group	$P2_1$
a, Å	10.071(1)
b, Å	16.436(2)
c, Å	29.620(3)
α, deg	90
β, deg	91.340(2)
γ, deg	90
V, $Å^3$	4901.6(8)
Z	4
D_{catcd}, Mg/m^3	1.132
radiation (λ), (Å)	Mo Ka (0.71073)
2θ range for data collection (deg)	0.69 to 30.50
absorption coefficient (mm^{-1})	0.261
F(000)	1768
no. of obsd reflns	29501
no. of params reflns	1027
reflections collected / unique	48845 / 29501 [R(int) = 0.0716]
goodness-of-fit on F^2	0.922
R1 [I>2σ(I)] [a]	0.0637
wR1 [I>2σ(I)] [a]	0.1017

Table S2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1-8**



	1	**2** [a]	**3**	**4a** [b]	**4b**	**4c** [b]
Zr-O(1)	1.921(6)	1.948(8)	1.965(3)	1.973(2)	1.960(2)	1.962(3)
Zr-O(2)	2.246(6)	2.270(8)	2.258(3)	2.275(2)	2.257(2)	2.317(4)
Zr-N(1)	2.047(8)	2.057(8)	2.050(4)	2.044(2)	2.059(2)	2.058(4)
Zr-C(10)	2.316(10)	2.337(11)	2.277(6)	2.314(3)	2.296(3)	2.286(5)
Zr-C(11)	2.873(10)	2.713(10)	2.725(6)	2.759(3)	2.715(3)	2.728(6)
Zr-C(17)	2.285(13)	2.300(13)	2.257(5)	2.289(3)	2.300(3)	2.299(5)
Zr-C(18)	3.320(14)	3.218(12)	3.159(6)	3.127(3)	3.176(4)	3.077(6)
O(1)-Zr-N(1)	85.8(3)	86.3(3)	84.4(1)	86.1(1)	84.2(2)	85.1(2)
O(2)-Zr-N(1)	73.8(3)	73.1(3)	73.1(2)	71.1(1)	72.8(2)	73.3(1)
O(1)-Zr-O(2)	159.3(2)	159.1(3)	157.2(1)	146.4(1)	156.0(2)	158.3(1)
C(10)-Zr-C(17)	123.9(6)	127.8(4)	120.7(3)	119.7(1)	122.7(3)	124.6(2)
C(11)-C(10)-Zr	95.6(9)	87.4(6)	91.2(4)	91.0(2)	89.7(4)	90.6(3)
C(18)-C(17)-Zr	117.5(9)	113.8(8)	115.6(4)	109.9(2)	112.8(5)	107.0(4)

[a.] average values of three independent molecules in the unit cell. [b.] average values of two independent molecules in the unit cell.

	4d [b]	**5a**	**5b**	**5c**	**5d**	**8** [b]
Zr-O(1)	1.973(3)	2.008(4)	2.012(2)	2.011(1)	1.981(2)	2.001(5)
Zr-O(2)	2.343(3)	1.966(4)	1.975(2)	1.964(2)	1.966(2)	1.974(5)
Zr-N(1)	2.041(3)	2.328(4)	2.352(2)	2.350(2)	2.363(2)	2.379(5)
Zr-C(10)	2.278(5)	2.272(5)	2.287(3)	2.284(2)	2.265(3)	2.283(7)

Zr-C(11)	2.873(4)	2.666(4)	2.606(3)	2.610(2)	2.604(2)	2.657(7)
Zr-C(17)	2.314(4)	2.282(5)	2.280(3)	2.294(2)	2.280(3)	2.282(6)
Zr-C(18)	3.095(4)	3.015(5)	3.000(3)	3.005(2)	3.085(3)	3.003(7)
O(1)-Zr-N(1)	83.8(1)	77.5(1)	76.8(1)	76.6(1)	78.8(1)	77.8(2)
O(2)-Zr-N(1)	73.1(1)	74.3(2)	73.3(1)	73.0(1)	71.9(1)	73.8(2)
O(1)-Zr-O(2)	156.5(1)	151.7(1)	150.1(1)	149.5(1)	150.7(1)	150.6(2)
C(10)-Zr-C(17)	125.1(2)	124.8(2)	123.5(1)	122.8(1)	123.1(1)	120.9(3)
C(11)-C(10)-Zr	97.9(3)	88.8(3)	85.2(2)	85.3(1)	85.9 (2)	87.5(5)
C(18)-C(17)-Zr	107.5(3)	104.0(3)	103.9(2)	103.7(1)	108.2(2)	104.3(4)

[b.] average values of two independent molecules in the unit cell.

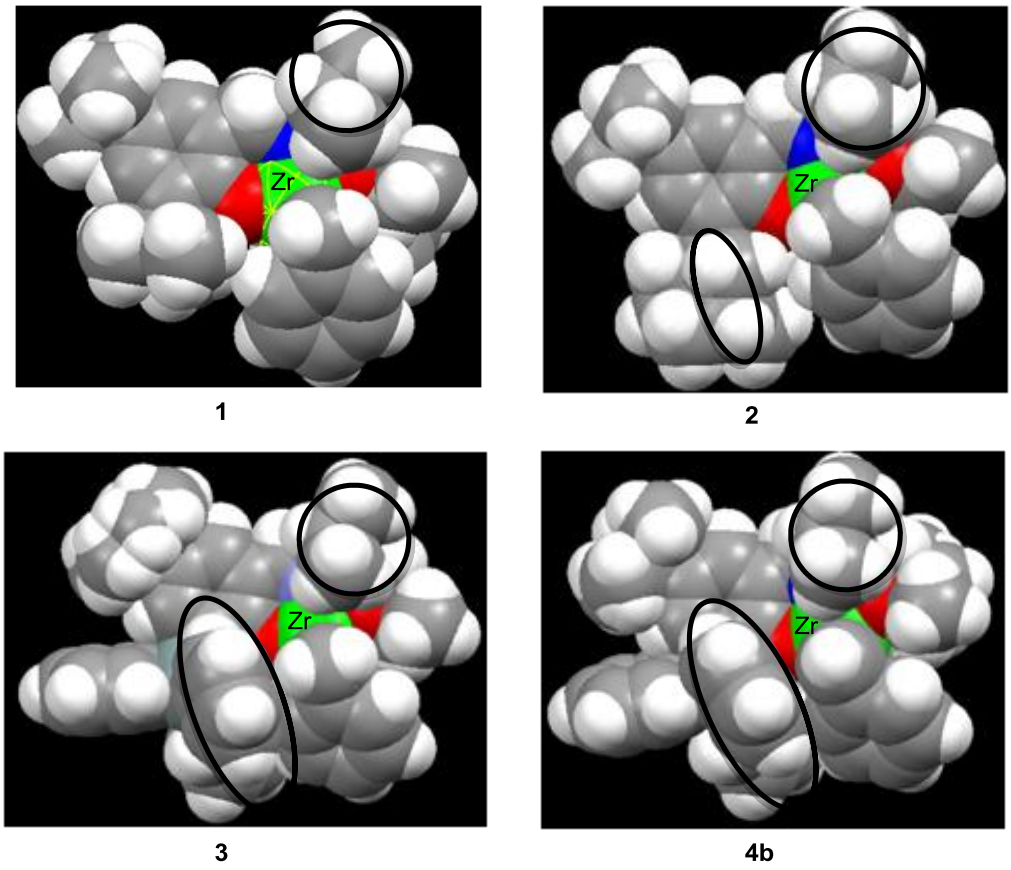
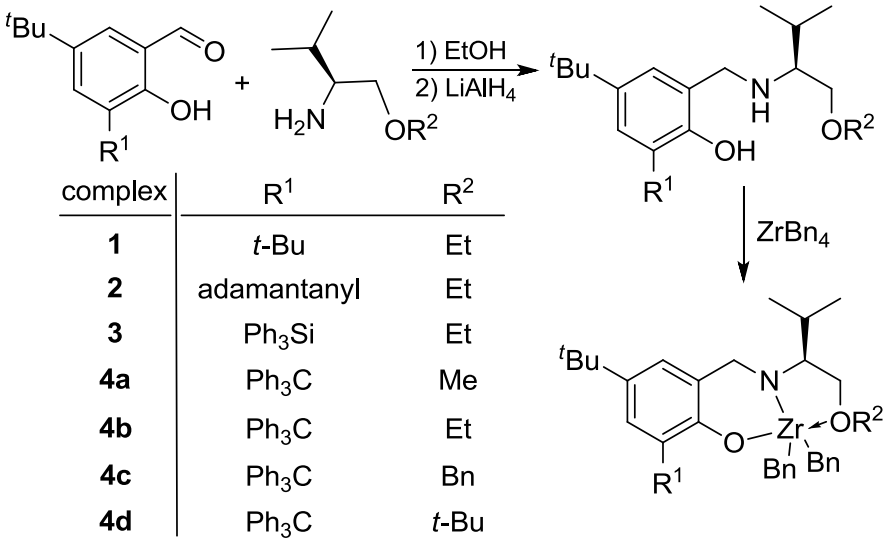


Figure S14. Space-filling Structures of Complexes **1**, **2**, **3**, **4b**

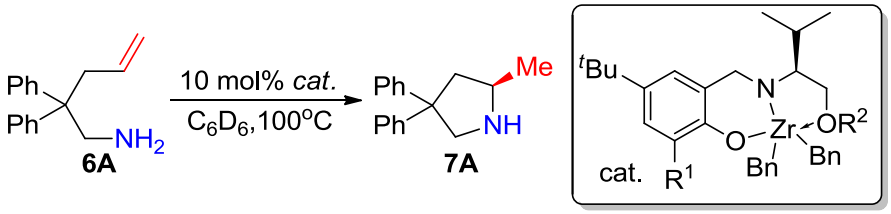
5. Ligand and Temperature Effects on Enantioselectivity



complex	R^1	R^2
1	*t*-Bu	Et
2	adamantanyl	Et
3	Ph_3Si	Et
4a	Ph_3C	Me
4b	Ph_3C	Et
4c	Ph_3C	Bn
4d	Ph_3C	*t*-Bu

Chart S1. New Zr Complexes **1**-**4**.

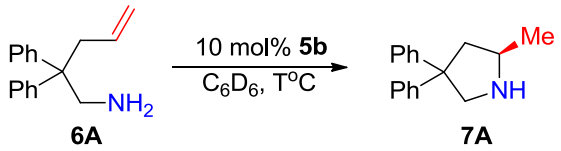
Table S3. Effect of R^1 and R^2 on Enantioselectivity



entry	cat.	R^1	R^2	time[a] (h)	ee [b] (%)
1	**1**	Bu^t	Et	4.0	27
2	**2**	adamantanyl	Et	8.5	28
3	**3**	Ph_3Si	Et	4.0	38
4	**4b**	Ph_3C	Et	2.0	56
5	**4a**	Ph_3C	Me	3.0	49
6	**4c**	Ph_3C	Bn	1.5	40
7	**4d**	Ph_3C	Bu^t	2.0	1

[a.] time for ≥ 95% conversion. [b] measured by chiral HPLC.

Table S4. Effects of Reaction Temperatures on Enantioselectivity



6A 7A

entry	temp. (°C)	time (h)	con. (%)	ee [a] (%)
1	115	4.5	95	84
2	100	4.5	94	89
3	85	11	92	92
4	80	14	90	93
5	70	19	95	94
6	55	29	93	94

[a] measured by chiral HPLC.

6. Procedure for Kinetics Experiments

A 5.00 mL stock standard solution in d_8-toluene containing aminoalkene substrate (1.778 g, 7.50 mmol) and Cp_2Fe (internal standard, 348.8 mg, 1.875 mmol) was prepared using a 5.0 mL volumetric flask. The concentration of substrate in the standard solution was 1.50 M, and that of internal standard Cp_2Fe was 0.375 M. At the same time, a standard solution of catalyst in d_8-toluene (387.9 mg, 0.3 mmol) was prepared using a 2.0 mL volumetric flask. Standard solutions of the substrate (1.50 M) and internal standard Cp_2Fe (0.375 M) in d_8-toluene were added to a Teflon-sealed J. Young NMR tube by a 50 μL microsyringe. And then a standard solution of the catalyst in d_8-toluene (0.15 M) was added to a J. Young NMR tube via a 50μL microsyringe. d_8-Toluene was added (150 μL) to bring a total volume to 500 μL. The NMR tube was inserted into a pre-heated NMR probe (600 MHz spectrometer) and was left to thermally equilibrate with the heated probe for five minutes before data acquisition was started. Each kinetic run was performed using four-scan experiments. The temperature of the probe was calibrated using tabulated chemical shifts of ethylene glycol at five-degree intervals. The product concentration was quantified by integration of the CH_2CH signal

of product relative to the signal of the internal standard Cp_2Fe. All errors on linear correlations were estimated from the standard error of the linear regression analysis performed using the Origin Linear Fit.

7. Supplementary Data.

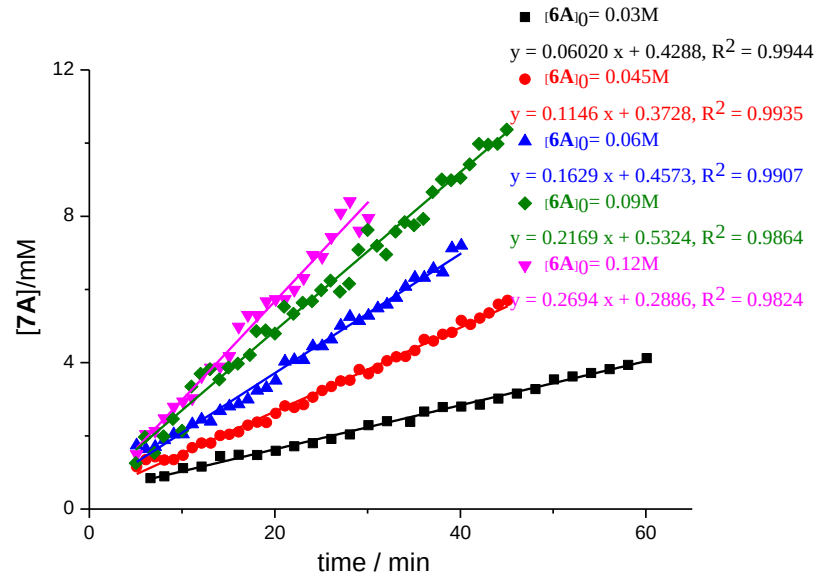


Figure S15. Plot of [**7A**] versus time in various $[\mathbf{6A}]_0$
Conditions for cyclization: $[\mathbf{6A}]_0$ = 0.03 - 0.12 M, $[\mathbf{5b}]_0$ = 6 mM, toluene-d_8, 60 ℃.

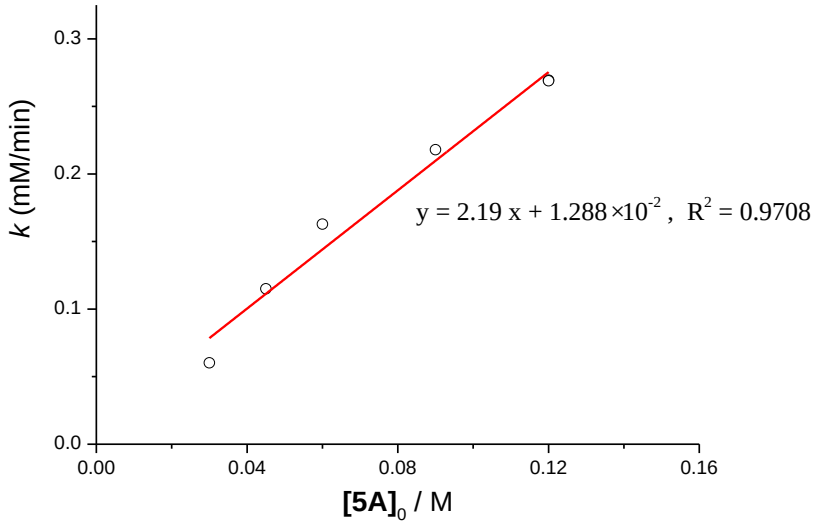


Figure S16. Plot of first-order k (mM min^{-1}) versus $[\mathbf{6A}]_0$ (M)
Conditions for cyclization: $[\mathbf{6A}]_0$ = 0.03 - 0.12 M, $[\mathbf{5b}]_0$ = 6 mM, toluene-d_8, 60 ℃.

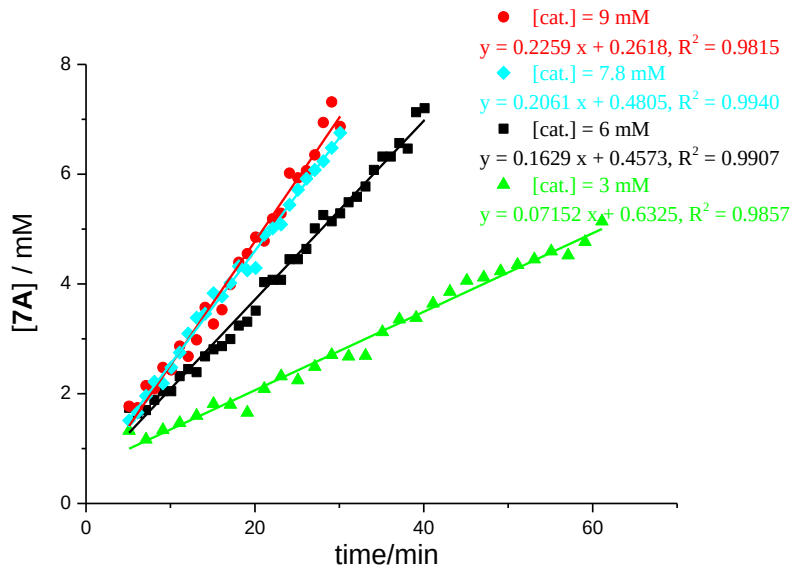


Figure S17. Plot of [**7A**] versus time (min) in various [cat.]
Conditions for cyclization: [**6A**]$_0$ = 0.06 M, [**5b**]$_0$ = 3-9 mM, toluene-d_8, 60 ℃.

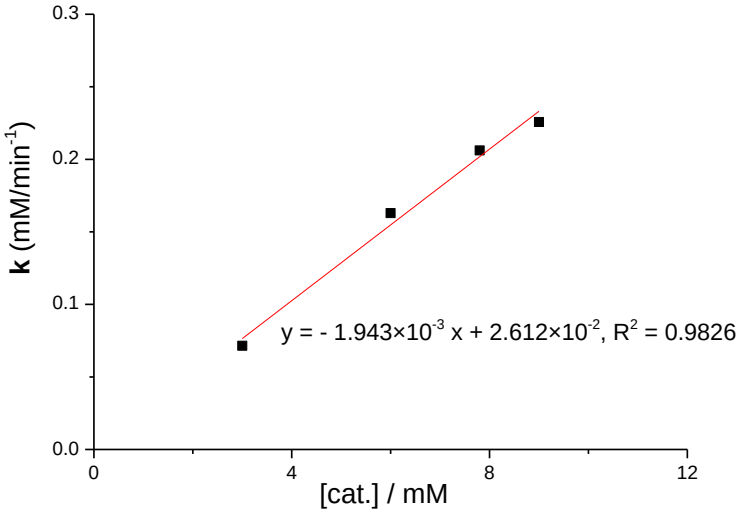


Figure S18. Plot of first-order k (mM min^{-1}) versus [cat.] (mM)
Conditions for cyclization: [**6A**]$_0$ = 0.06 M, [**5b**]$_0$ = 3-9 mM, toluene-d_8, 60 ℃.

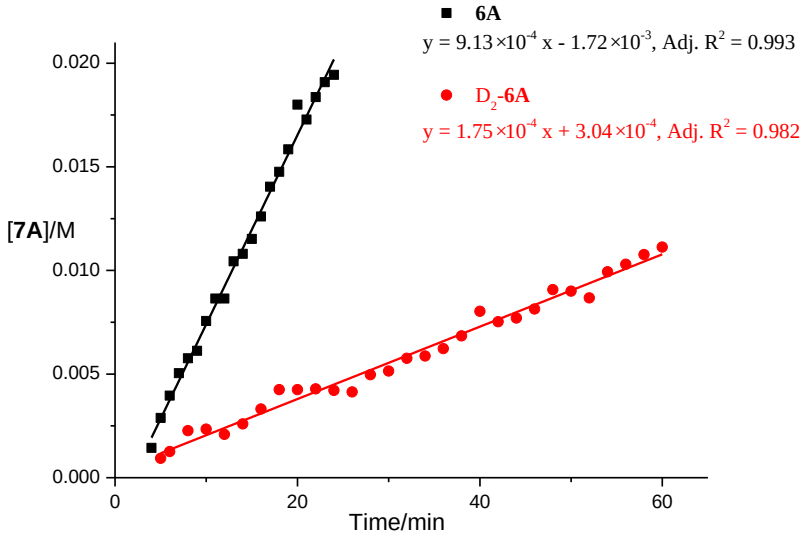


Figure S19. Kinetic Isotope Effect for the **6A**/d_2-**6A**
Conditions for cyclization: [**6A**]$_0$ = 0.15 M, [**5b**]$_0$ = 18 mM, toluene-d_8, 60 ℃.

In the presence of catalyst **5b**, the cyclization of *N*-deuterated **6A** was much slower than for the proteo counterpart **6A**, giving the *k* (H)/ *k* (D) = (9.12 E-4/ 1.75 E-4) = 5.2 at 60 °C, toluene-*d8* (Figure S19).

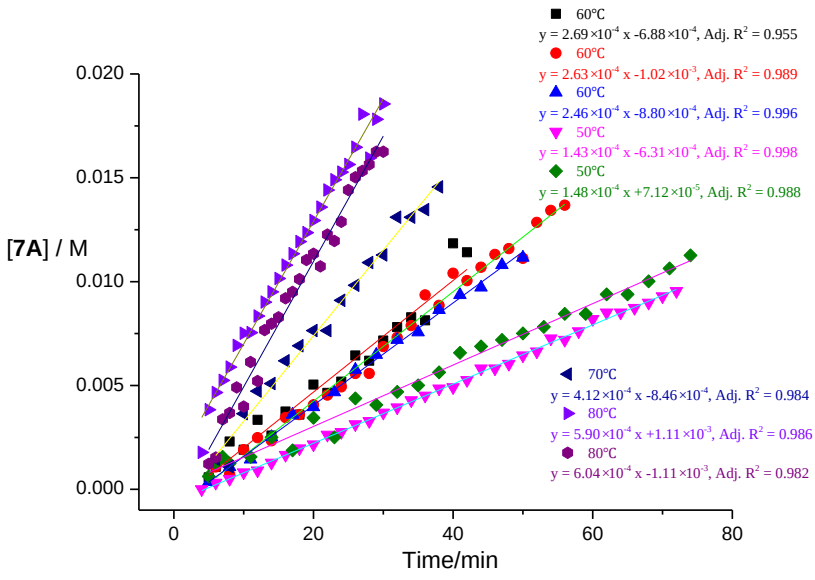


Figure S20. Plot of [**7A**] versus Time/min at ten-degree intervals from 50 ℃ to 80 ℃ in toluene-d_8.
Conditions for cyclization: [**6A**]$_0$ = 0.15 M, [**5b**]$_0$ = 6 mM.

In order to obtain parameters for the Eyring analysis, the temperature was converted from Celsius to Kelvin, and the *k* values were converted from units of min^{-1} to s^{-1}.

Table S5. Parameters for Eyring analysis.

Entry	Temp.(°C) [a]	Temp. (K) [b]	*k* (M/min)	*k* (M/s)	1/T (K^{-1})	Ln(K_{obs}/T)
1	50	323.05	1.43E-04	2.38E-06	0.003095	-18.7282
2	50	323.05	1.48E-04	2.46E-06	0.003095	-18.6914
3	60	332.77	2.69E-04	4.48E-06	0.003005	-18.1241
4	60	332.77	2.63E-04	4.39E-06	0.003005	-18.1437
5	60	332.77	2.46E-04	4.11E-06	0.003005	-18.2105
6	70	343.04	4.12E-04	6.87E-06	0.002915	-17.7264
7	80	353.85	5.90E-04	9.83E-06	0.002826	-17.399
8	80	353.85	6.04E-04	1.01E-05	0.002826	-17.3756

[a] Setting Temperature. [b] Actual temperature measured by NMR spectrometer, ±0.1 K.

Plotting 1/*T* versus ln(*k*/*T*) and performing a least-squares linear regression analysis gave:

y = - (4843.9 ±235.9) x - (3.66±0.70), Adj. R^2 = 0.984 (errors from standard error of regression)

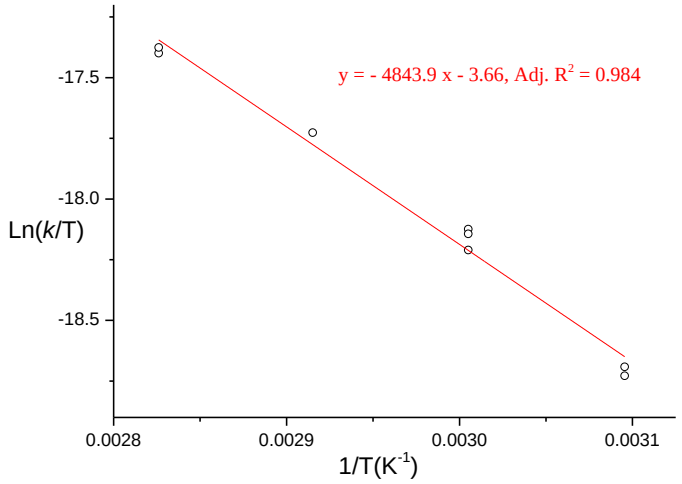


Figure S21. Eyring plot for the cyclization of **6A**.

Conditions for cyclization: [**6A**] $_0$ = 0.15 M, [**5b**]$_0$ = 6 mM in toluene-d_8.

From the Eyring equation: $\ln(k/T) = -\Delta H^{\neq}/RT + \Delta S^{\neq}/R + \ln(k_B/h)$

$-\Delta H^{\neq}/R$ = -4843.9 ±235.9 , *R* = 1.98588 cal K^{-1} mol^{-1},

Therefore, $\Delta H^{\neq}$ = 9.9±0.3 kcal mol^{-1}

$\Delta S^{\neq}/R + \ln(k_B/h) = -3.66 \pm 0.70$, $\ln(k\mathrm{B}/h) = 23.76$

Therefore, $\Delta S^{\neq} = -53.4 \pm 0.9$ cal mol^{-1} K^{-1}。

Table S6. Linear regression statistics on Eyring analysis

Regression Statistics	
Number of Points	8
Degrees of Freedom	6
Residual Sum of Squares	0.02659
Pearson's r	-0.99296
Adj. R-Square	0.98363

ANOVA

	DF	*Sum of Squares*	*Mean Square*	*F Value*	*Prob>F*
Model	1	1.86815	1.86815	421.52762	8.68381E-7
Error	6	0.02659	0.00443		
Total	7	1.89474			

ee of **5b** (%)	ee of **7A** (%)
0	3
20	11
40	41
60	54
80	69
100	94

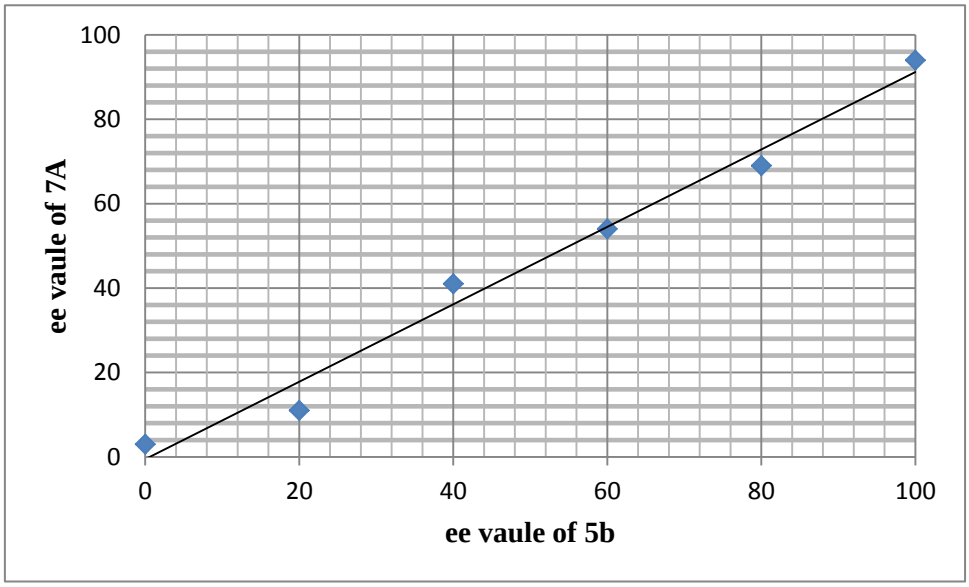
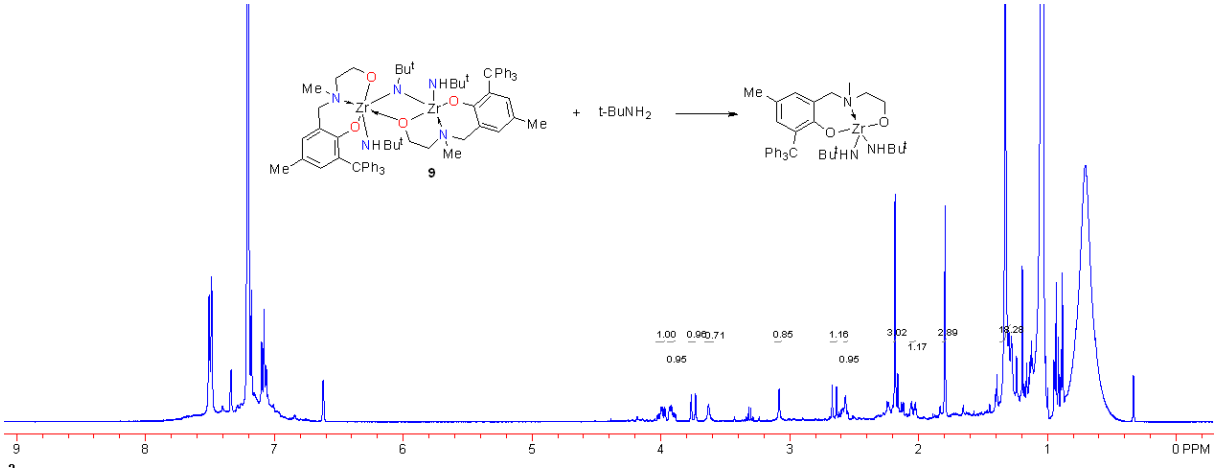
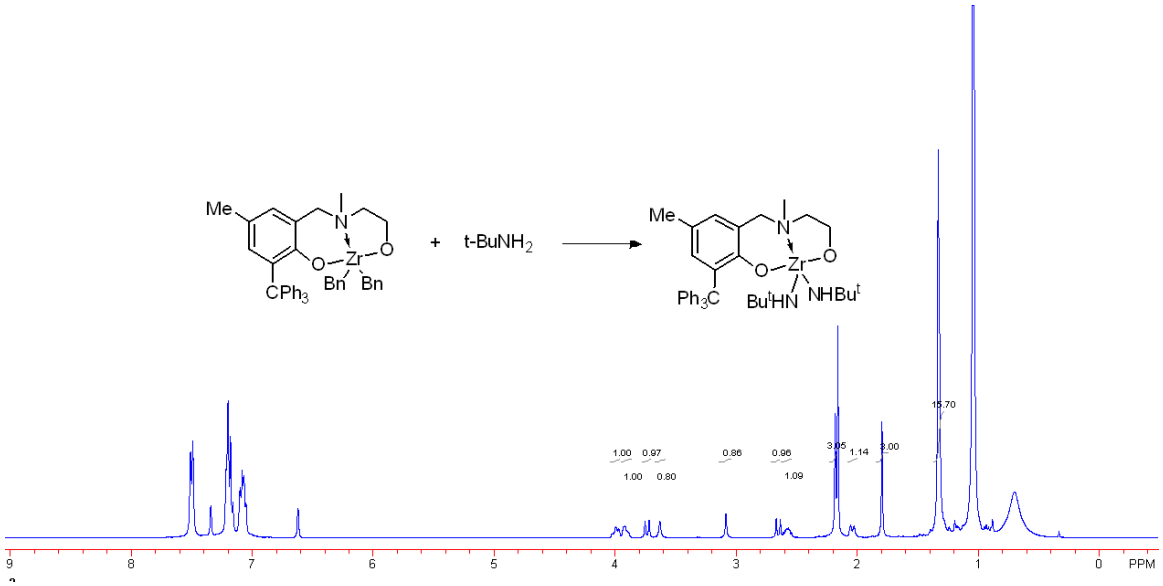


Figure S22. Plot of *ee* values of **5b** versus *ee* values of **7A**
Conditions: [**5b**] = 0.02 M and [**6A**] = 0.2 M in 0.5 mL of C_6D_6.

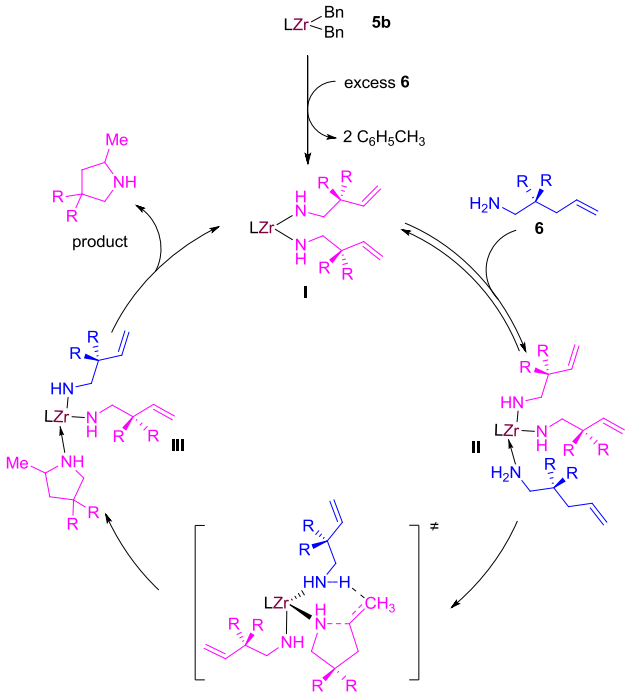
Scheme **S1**. Reaction of Complex **9** with excess *t*-$BuNH_2$ at 85°C in d_6-Benzene.



Scheme **S2**. Reaction of Complex **8** with 5 equiv of t-$BuNH_2$ at 85°C in d_6-Benzene.



Scheme **S3**. Rate equation derived from Steady State Approximation.



Since the rate-determining step is from **II** to **III**, the rate equation is: rate = k[**II**].

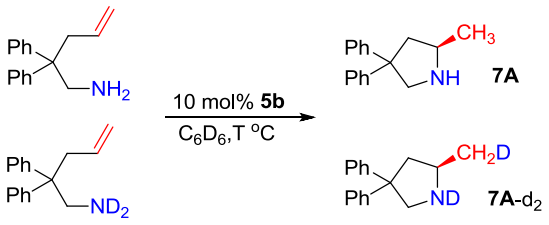
Since the conversion from **I** to **II** is reversible, [**II**]=k'[**I**][**6**].

∴ rate = kk'[**I**][**6**].

Since the conversion from **5b** to **I** is irreversible, ∴ [**I**] = [**5b**]

∴ rate = kk'[**5b**][**6**] = k_{obs}[**5b**][**6**].

Table **S7**. Isotopic substitution effects on the reaction enantioselectivity.



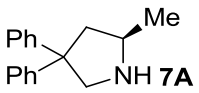
temp	% ee **7A**-d_2	% ee **7A**
70 °C	97	94
100 °C	94	89
115 °C	89	84

8. HPLC analysis of Hydroamination Products

General procedure for NMR scale intramolecular hydroamination of aminoalkene. In a dry-box, the desired aminoalkene substrate (0.2 mmol), internal standard ferrocene (0.1 mmol, 18.6 mg), zirconium complex (0.02 mmol, 10 mol%), 500 mg C_6D_6 were added to a Teflon-sealed J. Young NMR tube. The reaction proceeded at desired temperature, which were frequently monitored by ^{1}H NMR. The racemic samples were prepared by hydroamination of the corresponding aminoalkenes in the presence of 10 mol% $Zr(NMe_2)_4$.

HPLC analysis. The enantiomeric excess of chiral pyrrolidines (**7A**, **7G**) was determined by chiral HPLC and the other pyrrolidines (**7B**, **7C**, **7D**, **7E, 7F**) were determined by the analysis of their tosyl derivatized products.

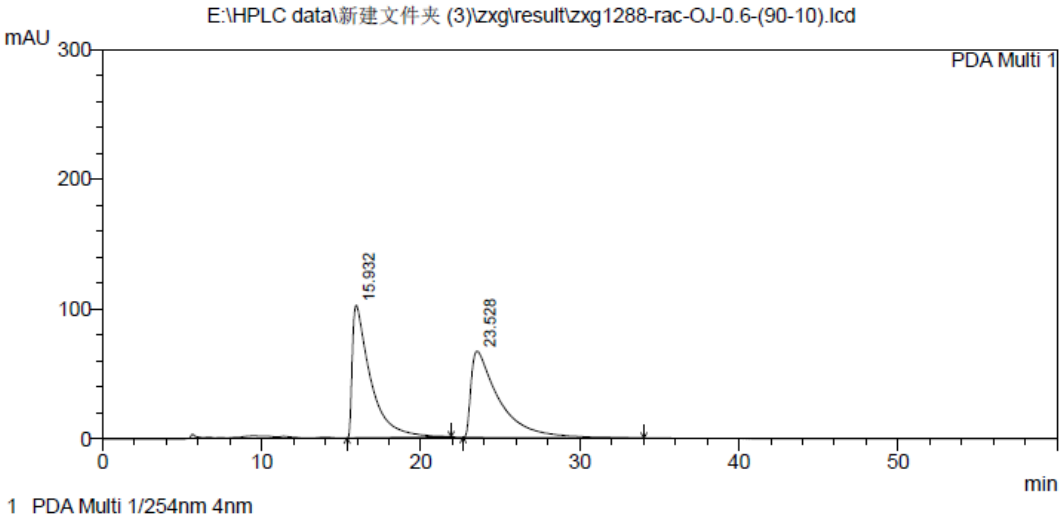
Typical procedure for derivatization: 4-Toluenesulfonyl chloride (120 mg) was added to a CH_2Cl_2 solution of reaction mixture and triethylamine (0.2 mL) at room temperature. The resultant mixture was stirred for 2 h at room temperature, and then the volatile materials were removed by rotary evaporation, giving a white solid which was purified by flash chromatography on silica gel (PE:EA=25:1).



7A

Heated at 70 ℃ for 19 h to give **7A**: 40 mg, 84%, ee: 94% (Chiralcel O*J*, 10/90 *i*PrOH/Hexane, 0.6 mL/min, 234 nm; tr (major) = 13.93 min, tr (minor) = 22.02 min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23-7.06 (m, 10H), 3.70 (ABd, *J* = 11.4 Hz, 1H), 3.47 (ABd, *J* = 11.4 Hz, 1H), 3.32-3.25 (m, 1H), 2.66 (dd, J_1 = 6.9 Hz, J_2 = 11.4 Hz), 2.07 (br, 1 H, obscured by water residue in $CDCl_3$, N*H*), 1.95 (dd, *J* = 9.3 Hz, 12.6 Hz, 1H), 1.12 (d, *J* = 6.3 Hz, 3H). Rotation: -44.2 °, c = 2.0 in EtOH.

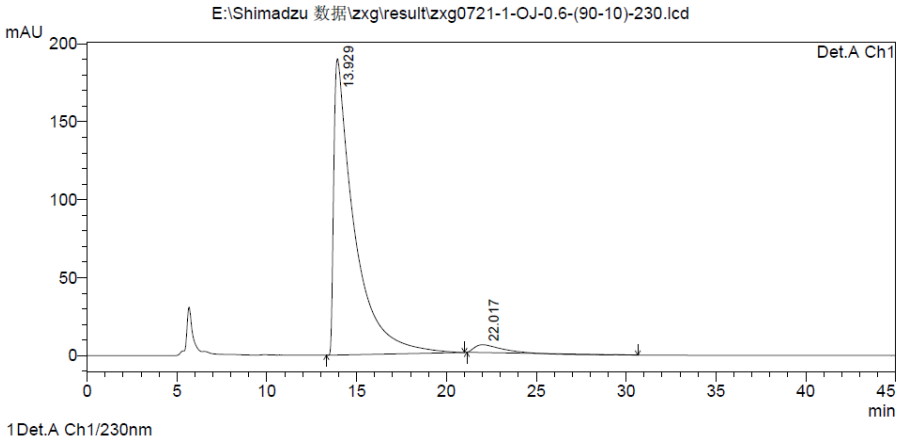
<Chromatogram>



PeakTable

PDA Ch1 254nm 4nm

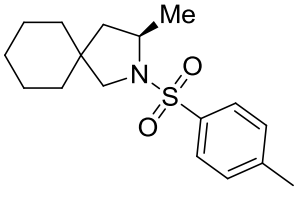
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.932	8118964	102113	50.029	60.634
2	23.528	8109649	66295	49.971	39.366
Total		16228613	168408	100.000	100.000



PeakTable

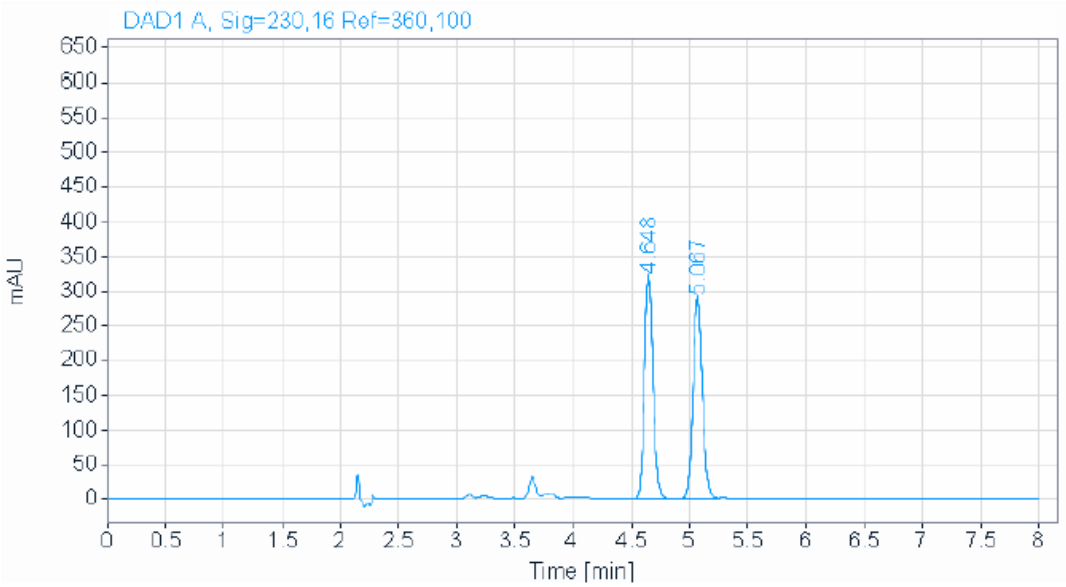
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.929	15055218	189963	97.037	97.464
2	22.017	459634	4943	2.963	2.536
Total		15514853	194907	100.000	100.000



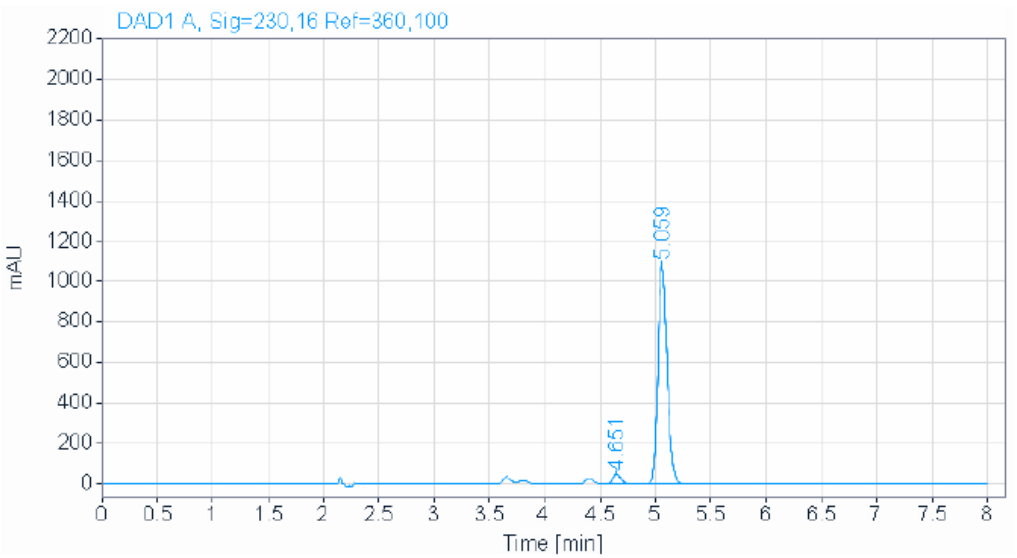
(N-Ts-**7B**)

Heated at 70 ℃ for 21 h, followed by reaction with TsCl to give N-Ts-**7B**: 59.4 mg, 97%, ee: 93% (Chiralcel OJ-H, 90/10 N_2/CO_2, 1.5 MPa, 230 nm; tr (minor) = 4.7 min, tr (major) = 5.1 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.30 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 3.60-3.51 (m, 1H, CH_3CHN), 3.24 (ABd, *J* = 10.4 Hz, 1H, CH_2N), 3.14 (ABd, *J* = 10.8 Hz, 1H, CH_2N), 2.42(s, CH_3, Ar-CH_3), 1.80 (dd, J_1 = 7.2 Hz, J_2 = 12.8 Hz, 1H), 1.42-1.12 (m, 12H), 0.85-0.77 (m, 1H), 0.71-0.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 134.8, 129.4, 127.4, 58.7, 55.1, 47.0, 40.9, 36.5, 34.1, 25.8, 23.6, 22.8, 22.7, 21.5. IR (ν/cm^{-1}): 2924(m), 2853(w), 1598(w), 1337(s), 1155(s). 658 (s). Rotation: -20.7 °, c = 3.0 in EtOH. HRMS (ESI) calcd for $C_{17}H_{26}NO_2S$, ($M+H^+$): 308.1679; Found: 308.1677.



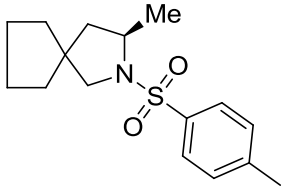
Signal: DAD1 A, Sig=230,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
4.648	BB	0.0786	1628.5398	318.6733	49.9934
5.067	BV	0.0869	1628.9717	288.2773	50.0066
		Sum	3257.5115		



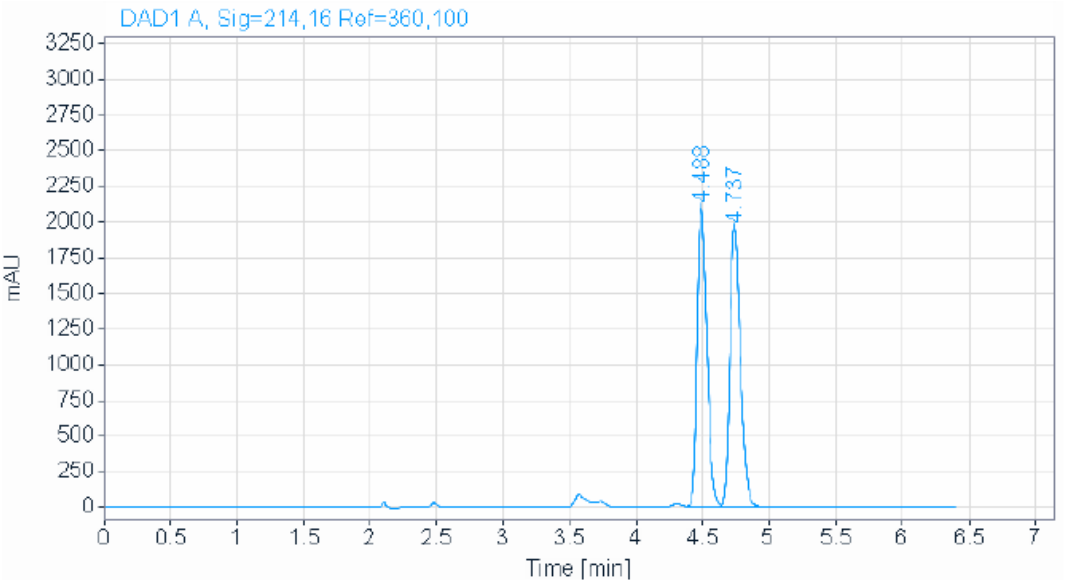
Signal: DAD1 A, Sig=230, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
4.651	VB	0.0797	236.2276	46.1372	3.6097
5.059	BB	0.0897	6308.0537	1086.8413	96.3903
		Sum	6544.2813		



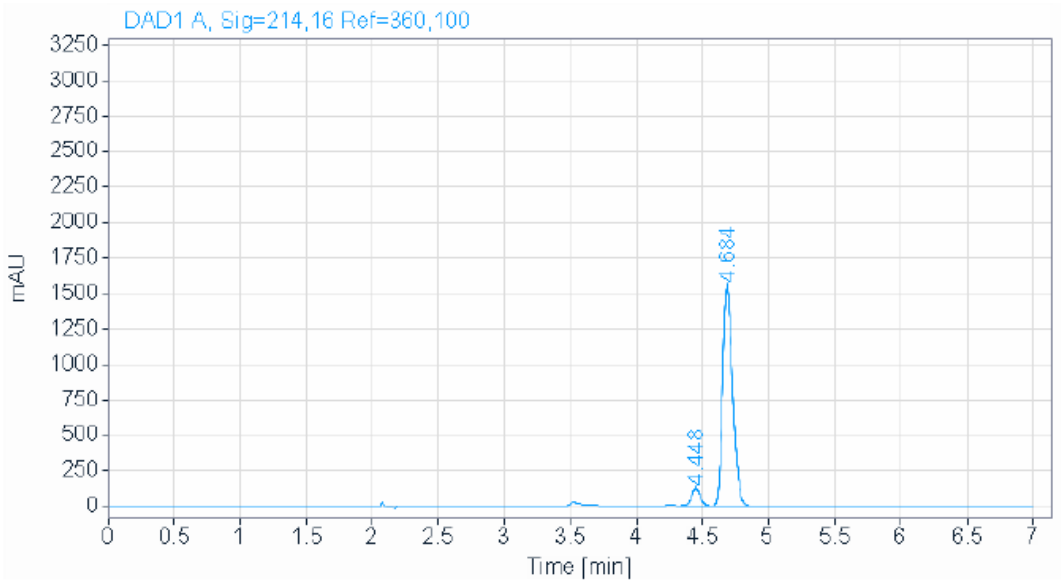
(N-Ts-**7C**)

Heated at 85 ℃ for 72 h, followed by reaction with TsCl to give N-Ts-**7C:** 53.2 mg, 91%, ee: 87% (Chiralcel OJ-H, 90/10 N_2/CO_2, 1.5 MPa, 230 nm; tr (minor) = 4.4 min, tr (major) = 4.7 min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.31 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 3.66-3.55 (m, 1H, CH_3CHN), 3.26 (ABd, *J* = 10.2 Hz, 1H, CH_2N), 3.07 (ABd, *J* = 9.9 Hz, 1H, NCH_2), 2.43(s, CH_3, Ar-CH_3), 1.85-1.78 (m, 1H), 1.63-1.40 (m, 10H), 1.06-0.85 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.1, 134.9, 129.4, 127.4, 59.9, 56.1, 48.3, 46.6, 36.52, 36.49, 24.4, 24.2, 22.7, 21.4. IR (ν/cm^{-1}): 2952(m), 2861(w), 1333(s), 1154(s). 659 (s). Rotation: -19.7 °, c = 2.5 in EtOH. HRMS (ESI) calcd for $C_{16}H_{24}NO_2S$, ($M+H^+$): 294.1522; Found: 294.1520.



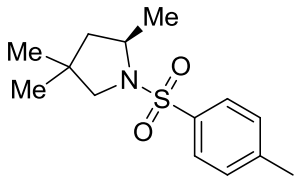
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
4.488	BV	0.0794	10726.2539	2105.4753	49.6740
4.737	VB	0.0858	10867.0293	1957.1085	50.3260
		Sum	21593.2832		



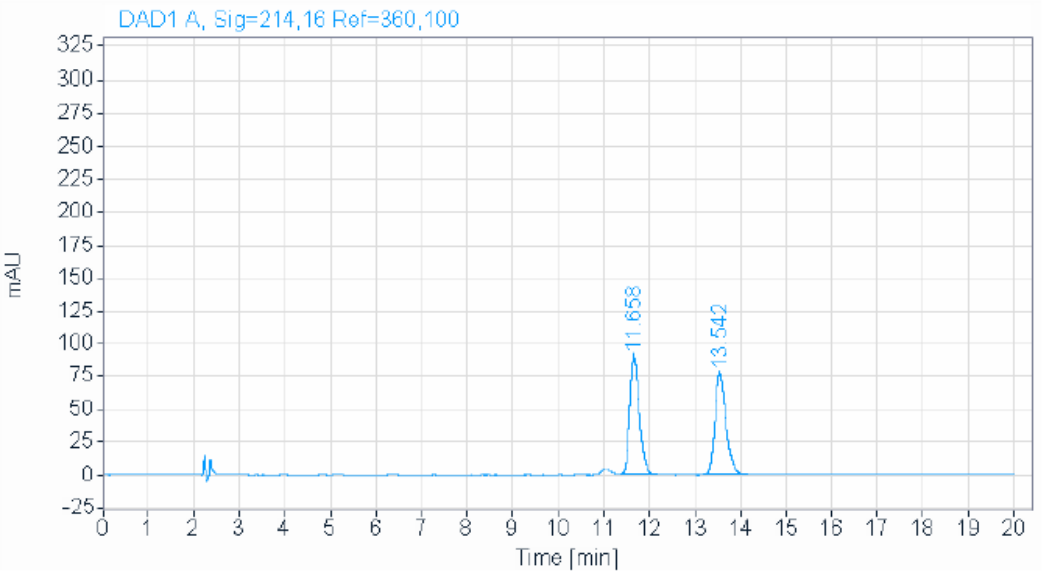
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
4.448	VV	0.0762	594.0263	119.1694	6.6896
4.684	VB	0.0825	8285.7656	1545.5056	93.3104
		Sum	8879.7919		



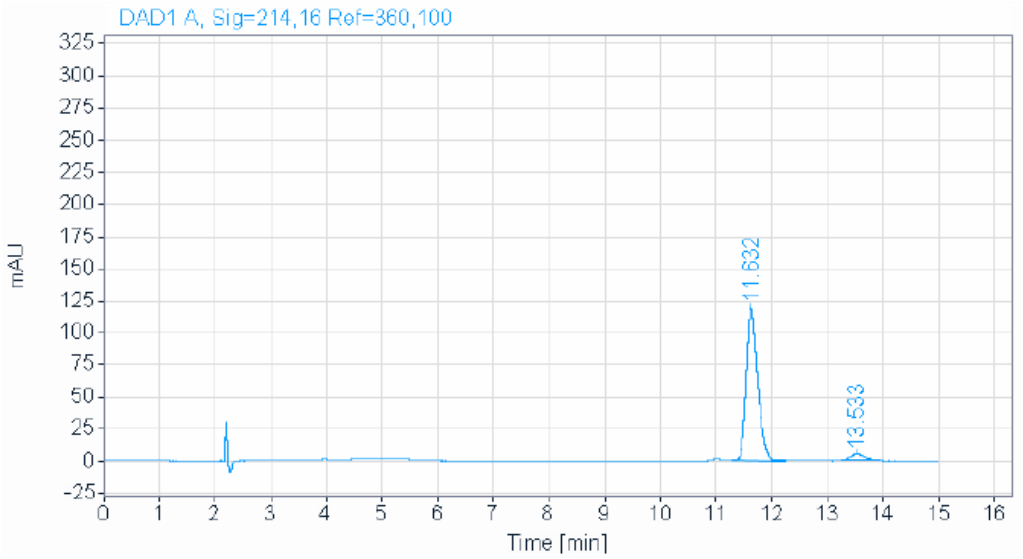
(N-Ts-**7D**)

Heated at 85 ℃ for 120 h, followed by reaction with TsCl to give N-Ts-**7D**: 51.0 mg, 96%, ee: 89% (Chiralcel AD-H, 95/5 N_2/CO_2, 1.5 MPa, 214 nm; tr (major) = 11.6 min, tr (minor) = 13.5 min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.31 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 3.71-3.59 (m, 1H, CH_3CHN), 3.17 (ABd, *J* = 10.2 Hz, 1H, CH_2N), 3.07 (ABd, *J* = 10.2 Hz, 1H, NCH_2), 2.43(s, CH_3, Ar-CH_3), 1.77-1.70 (m, 1H), 1.44-1.37 (m, 4H), 1.04 (s, 3H, CH_3), 0.55 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.0, 135.0, 129.4, 127.3, 61.4, 55.9, 48.8, 37.0, 26.5, 25.8, 22.7, 21.4. IR (ν/cm^{-1}): 2965(m), 2885(w), 1326(s), 1152(s). 659 (s). Rotation: -30.8 °, c = 1.7 in EtOH. HRMS (ESI) calcd for $C_{14}H_{22}NO_2S$, ($M+H^+$): 268.1366; Found: 268.1366.



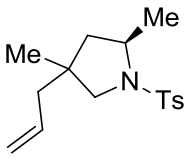
Signal: DAD1 A, Sig=214, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
11.658	BB	0.2212	1288.0347	88.8306	49.8780
13.542	BB	0.2591	1294.3381	76.2170	50.1220
		Sum	2582.3728		



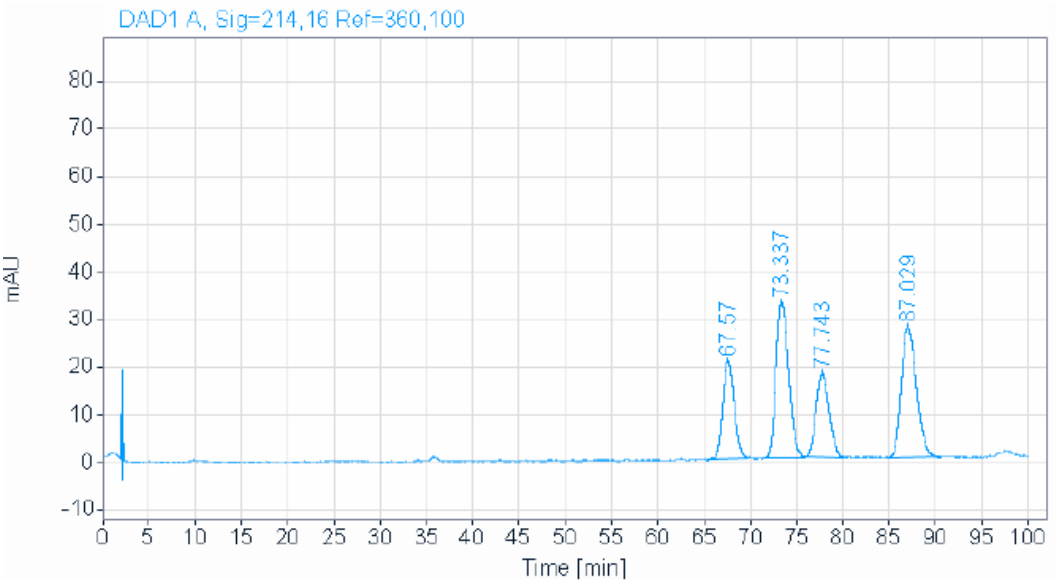
Signal: DAD1 A, Sig=214, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
11.632	BB	0.2153	1707.7028	119.8208	94.5537
13.533	BB	0.2153	98.3644	6.0319	5.4463
		Sum	1806.0672		



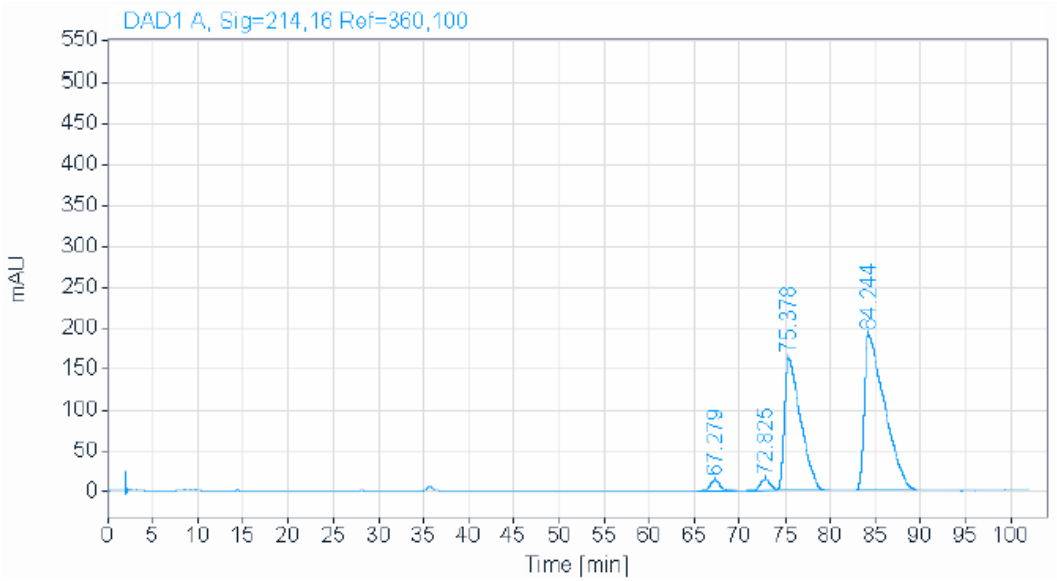
(N-Ts-**7E**)

Heated at 85 ℃ for 89 h, followed by reaction with TsCl to give N-Ts-**7E**: 51.9 mg, 89%. ee: 90%, 93%, dr=1.2:1 (Chiralcel IC, 95/5 N_2/CO_2, 1.7 MPa, 214 nm; tr (minor) = 67.3 min, tr (major) = 75.4 min; tr (minor) = 72.8 min, tr (major) = 84.2 min).For a mixture of cis- and trans- isomers ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2 H, Ar-*H*), 7.31 (d, *J* = 6.6 Hz, 2 H, Ar-*H*), 5.76-5.49 (m, 1 H, CH_2=C*H*), 5.05-4.78 (m, 2 H, CH_2=CH), 3.69-3.58 (m, 1 H, C*H*N), 3.25-3.04 (m, 2 H, NCH_2), 2.43(s, 3 H, Ar-CH_3), 2.07 (d, *J* = 7.2 Hz, 1 H), 1.90-1.83 (m, 0.5 H), 1.67-1.59 (m, 1.5H), 1.48-1.29 (m, 4 H), 1.03 (s, 1.4H, CH_3), 0.49 (s, 1.3 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2(143.1), 135.14(135.11), 134.2(134.0), 129.49(129.47), 127.41(127.40), 118.0(117.9), 60.0(59.8), 55.58(55.56), 47.05(46.51), 44.3(42.7), 40.2(40.1), 24.0(23.2), 22.8(22.6), 21.49(21.47). IR (ν/cm^{-1}): 2964(m), 2928(m), 2875(w), 1344(s), 1335(s),1155(s). 657 (s). Rotation: -11.7 °, c = 3.0 in EtOH. HRMS (ESI) calcd for $C_{16}H_{24}NO_2S$, ($M+H^+$): 294.1522; Found: 294.1524.



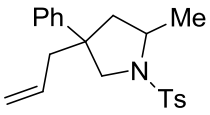
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
67.570	MM R	1.3747	1724.1978	20.2618	17.9493
73.337	MM R	1.5231	3076.5605	32.6234	32.0277
77.743	MM R	1.5782	1711.6000	17.4349	17.8182
87.029	MM R	1.8032	3093.5752	27.1522	32.2048
		Sum	9605.9335		



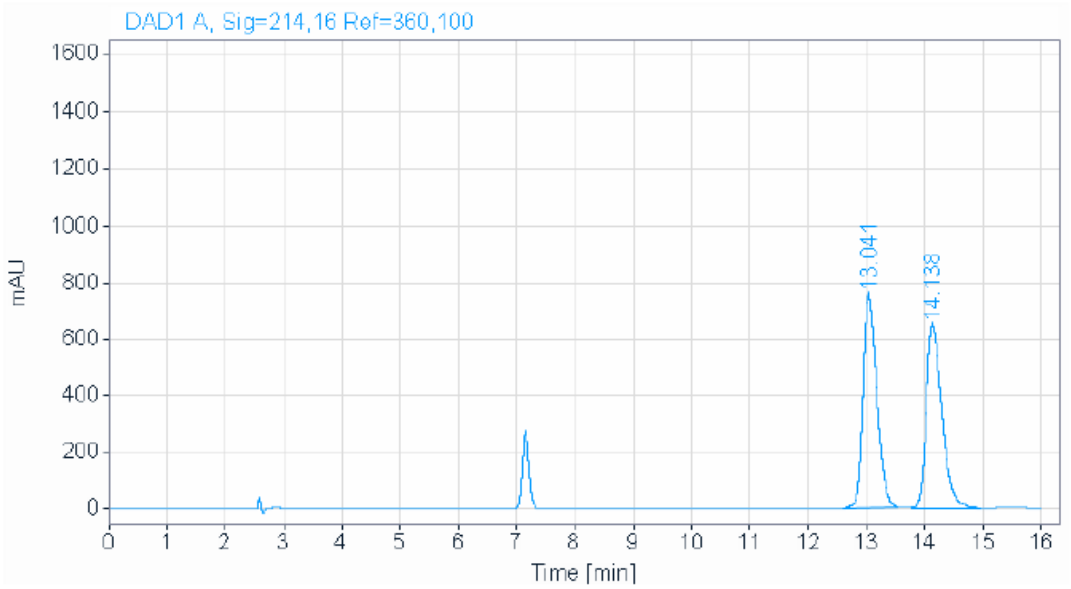
Signal: DAD1 A, Sig=214, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
67.279	MM R	1.3131	1025.4575	12.3733	1.9549
72.825	MF R	1.3143	1159.7544	14.1931	2.2109
75.378	FM R	2.0653	20469.5332	162.6545	39.0219
84.244	BB R	1.8152	29801.7793	190.2420	56.8123
		Sum	52456.5244		



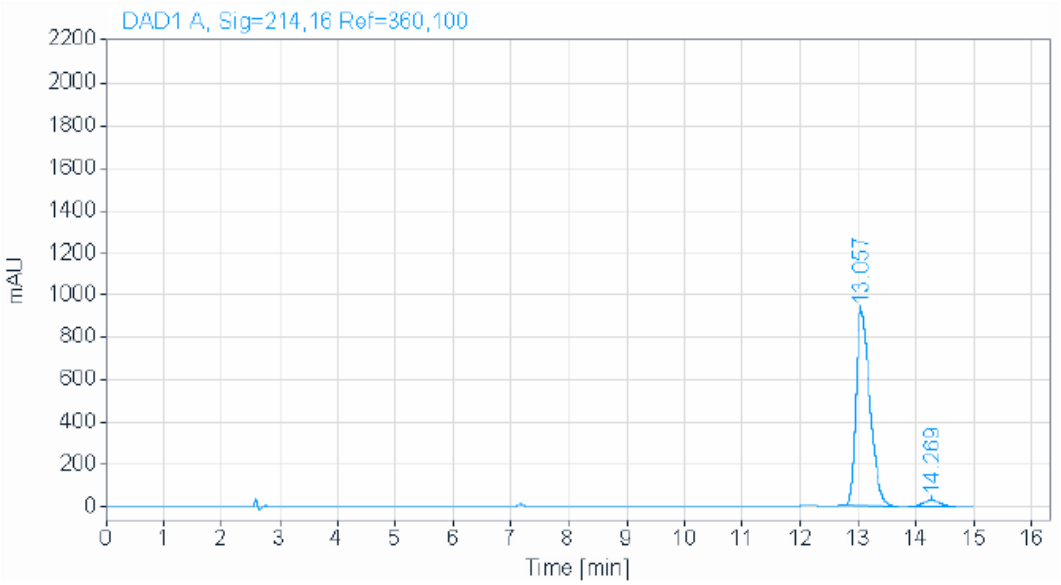
(N-Ts-**7F**)

Heated at 70 ℃ for 24 h, followed by reaction with TsCl to give N-Ts-**7F**: 64.8 mg, 91%, dr=1.7:1. For one of the isomer A ee value: 92% (Chiralcel OJ-H, 95/5 N_2/CO_2, 1.3 MPa, 214 nm; tr (major) = 13.1 min, tr (minor) = 14.3 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.4 Hz, 2 H, Ar-*H*), 7.34-7.06 (m, 5 H, Ar-*H*), 7.05 (d, *J* = 7.2 Hz, 2 H, Ar-*H*), 5.25-5.15 (m, 1H, CH_2CH), 4.87-4.84 (m, 1H, CH_2CH), 4.66-4.62 (m, 1H, CH_2CH), 3.89-3.83 (m, 1H, C*H*N), 3.75 (ABd, *J* = 10.4 Hz, 1 H, CH_2N), 3.57 (ABd, *J* = 10.4 Hz, 1 H, CH_2N), 2.43-2.35 (m, 4H, CH_3, CH_2N), 1.99-1.94 (m, 1H), 1.84-1.77 (m, 2H), 1.36 (d, *J* = 6.0 Hz, 3H, CH_3CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 143.3, 136.1, 133.4, 129.6, 128.2, 127.2, 126.5, 126.4, 118.1, 57.9, 55.1, 47.9, 44.0, 43.4, 22.3, 21.5. IR (ν/cm^{-1}): 2965(m), 2924(m), 2875(w), 1335(s), 1157(s), 662(s). Rotation: 15.3 °, c = 2.0 in EtOH. HRMS (ESI) calcd for $C_{21}H_{26}NO_2S$, ($M+H^+$): 356.1679; Found: 356.1682.



Signal: DAD1 A, Sig=214,16 Ref=360,100

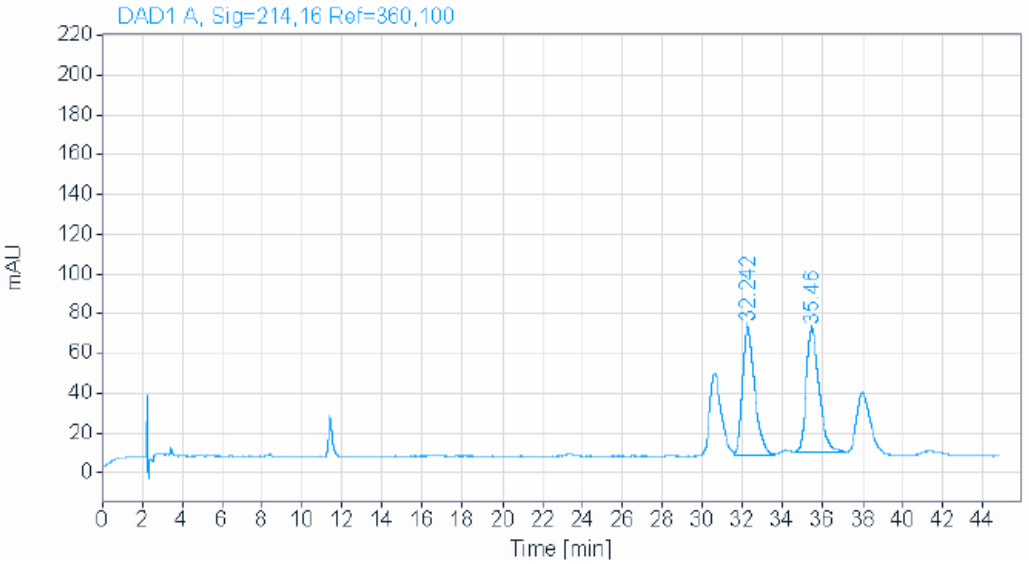
RT [min]	Type	Width [min]	Area	Height	Area%
13.041	MM R	0.2623	12402.1201	749.6440	50.7656
14.138	VB	0.2865	12028.0527	645.0943	49.2344
		Sum	24430.1729		



Signal: DAD1 A, Sig=214,16 Ref=360,100

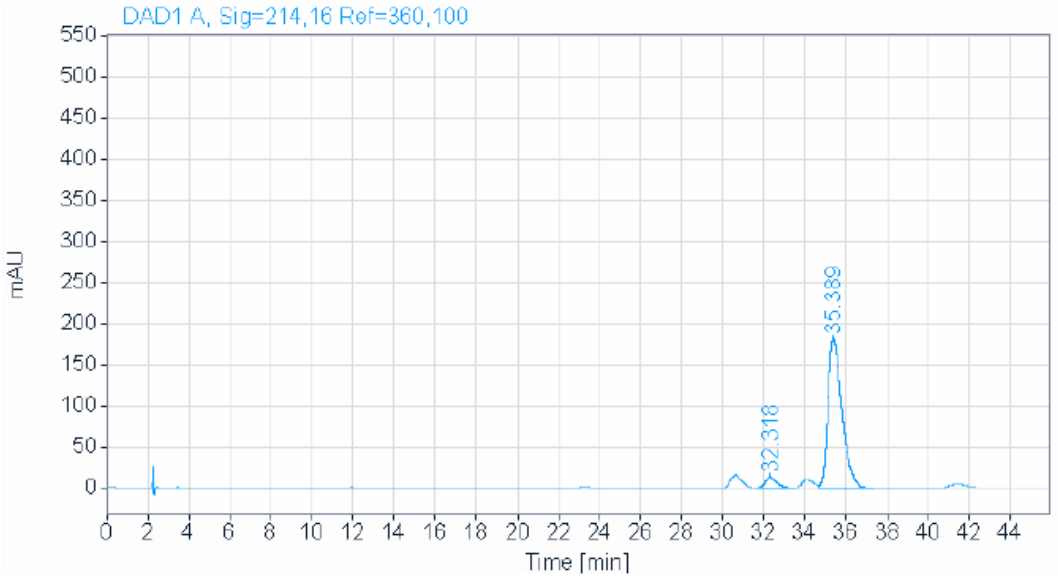
RT [min]	Type	Width [min]	Area	Height	Area%
13.057	MM R	0.2784	15579.4180	926.0387	96.6548
14.269	MM R	0.2816	539.2034	31.4341	3.3452
		Sum	16118.6213		

For another isomer **B**, ee: 88 % (Chiralcel AD-H, 95/5 N_2/CO_2, 1.5 MPa, 214 nm; tr (minor) = 32.3 min, tr (major) = 35.4 min). Mixture of isomer A and isomer B: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.1 Hz, 2 H, Ar-*H*), 7.22-7.12 (m, 5 H, Ar-*H*), 7.00-6.97 (m, 2 H, Ar-*H*), 5.39-5.26 (m, 1H, CH_2=C*H*), 4.98-4.93 (m, 2H, CH_2=CH), 3.77 (ABd, *J* = 9.9 Hz, 1H, CH_2N), 3.59-3.48 (m, 1H, C*H*N), 3.37 (ABd, *J* = 9.9 Hz, 1 H, CH_2N), 2.52 (d, *J* = 7.2 Hz, 2 H, CH_2CH=CH_2), 2.37-2.28 (m, 4H, CH_3, CH_2N), 1.92-1.86 (m, 1H), 1.54 (d, *J* = 6.6 Hz, 3H, CH_3CH).For a mixture of isomer A and isomer B ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1(144.2), 143.1(143.3), 133.8(136.1), 129.5(133.4), 129.4(129.6), 127.5(128.2), 127.0(127.2), 126.21(126.5), 126.17(126.4), 118.3(118.1), 59.3(57.9), 55.2(55.1), 47.92(47.86), 45.6(44.0), 43.6(43.4), 23.2(22.3), 21.4(21.5).



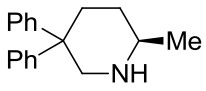
Signal: DAD1 A, Sig=214, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
32.242	VB	0.5407	2709.6060	64.1658	49.2385
35.460	BB	0.5520	2793.4175	61.8422	50.7615
		Sum	5503.0234		



Signal: DAD1 A, Sig=214, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
32.318	MM R	0.6487	528.2576	13.0832	5.7559
35.389	MM R	0.7658	8649.4043	182.1060	94.2441
		Sum	9177.6619		



7G

Heated at 130 ℃ for 2 h to give **7G**: 45.7 mg, 91%, ee: 66% (Chiralcel OD-H, 2/98 *i*PrOH/Hexane, 0.4 mL/min, 230 nm; tr (major) = 18.43 min, tr (minor) = 31.52 min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.31 (m, 4H, Ph-*H*), 7.25-7.09 (m, 6H, Ph-*H*), 3.91 (dd, *J* = 3.0 Hz, 13.5 Hz, 1H), 3.11 (d, *J* = 13.5 Hz, 1H), 2.83-2.67 (m, 2H), 2.22 (dt, *J* = 3.6 Hz, 13.2 Hz, 1H), 1.67-1.60 (m, 2H), 1.48 (brs, 1H), 1.22-1.08 (m, 1H), 1.01 (d, *J* = 6.3 Hz, 3H, C*H*$_3$CH).

2011-12-2 20:14:4

==== Shimadzu LCsolution Analysis Report ====

E:\Shimadzu 数据\zxg\result\zxg0745-rac-OD-H-0.4-(98-2)-214.lcd

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Sample ID	:
Vail #	: 1
Injection Volume	: 2 uL
Data File Name	: zxg0745-rac-OD-H-0.4-(98-2)-214.lcd
Method File Name	: OD-H-98-2-0.4-214.lcm
Batch File Name	: 1.lcb
Report File Name	: Default.lcr
Data Acquired	: 2011-12-2 19:35:21
Data Processed	: 2011-12-2 20:12:22

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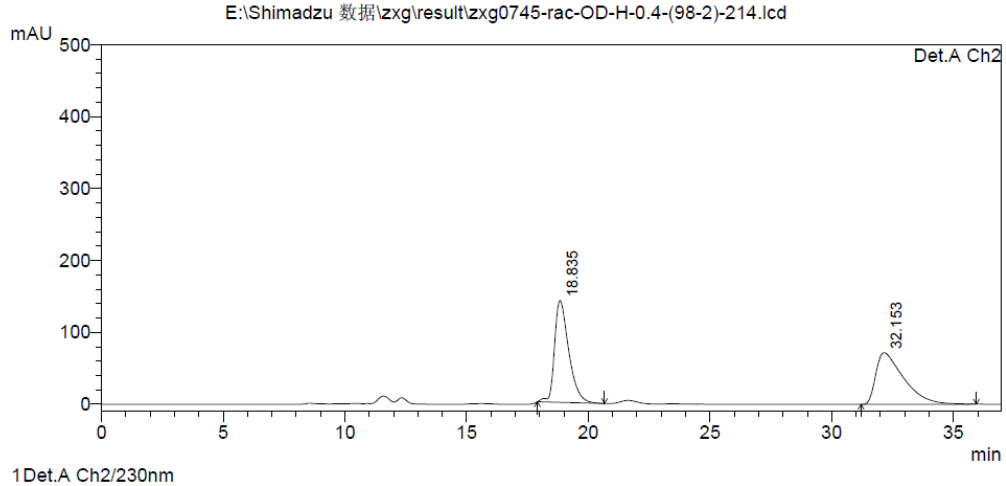

1Det.A Ch2/230nm

PeakTable

Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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2	32.153	5694520	71845	49.746	33.669
Total		11447271	213385	100.000	100.000

==== Shimadzu LCsolution Analysis Report ====

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Method File Name	: 98-2-0.4-214.lcm
Batch File Name	: xh-batch-1.lcb
Report File Name	: Default.lcr
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Data Processed	: 2012-6-14 15:12:44

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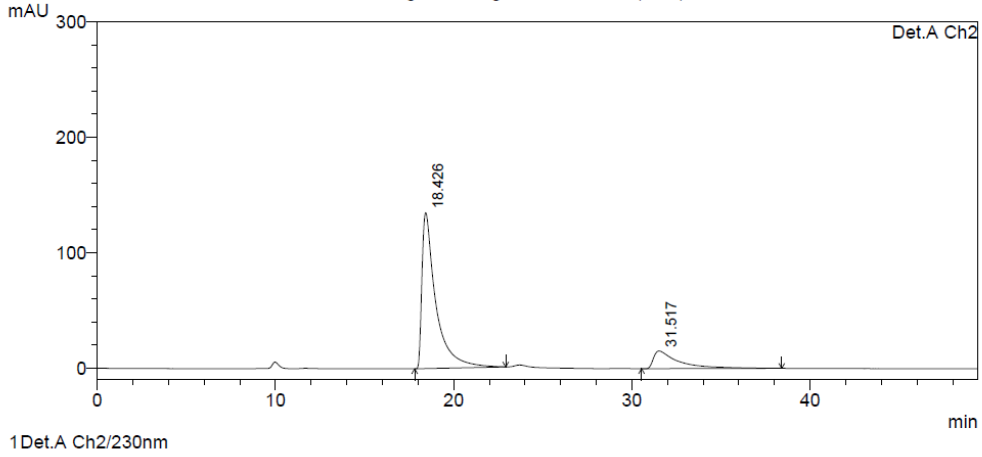

1Det.A Ch2/230nm

PeakTable

Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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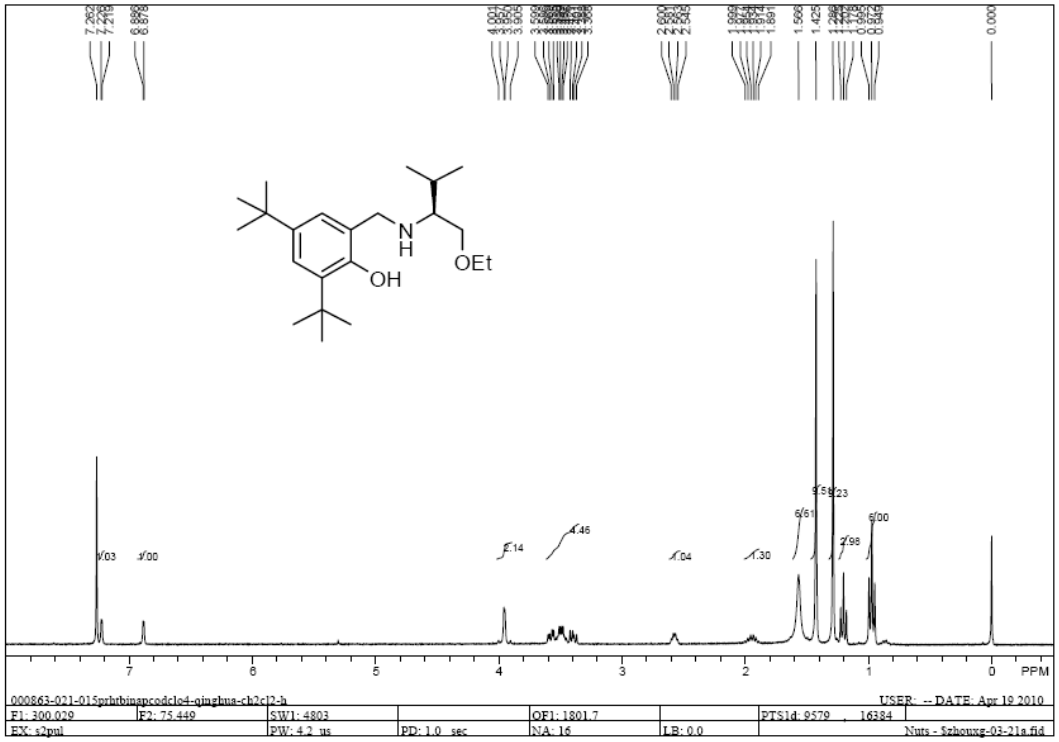
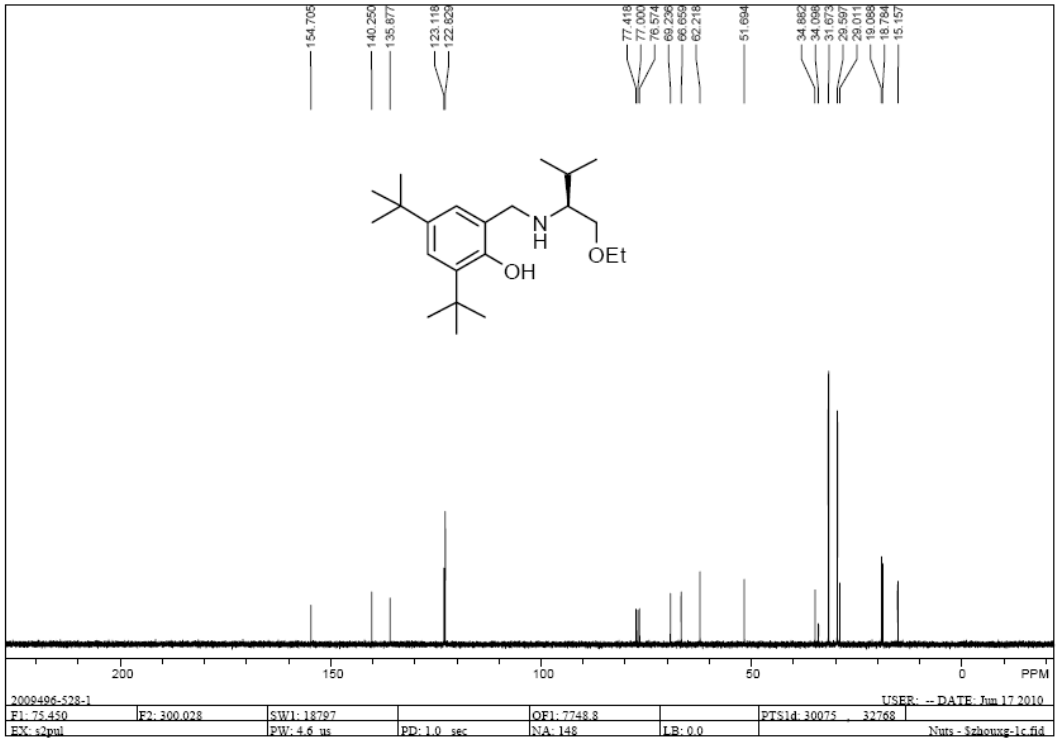
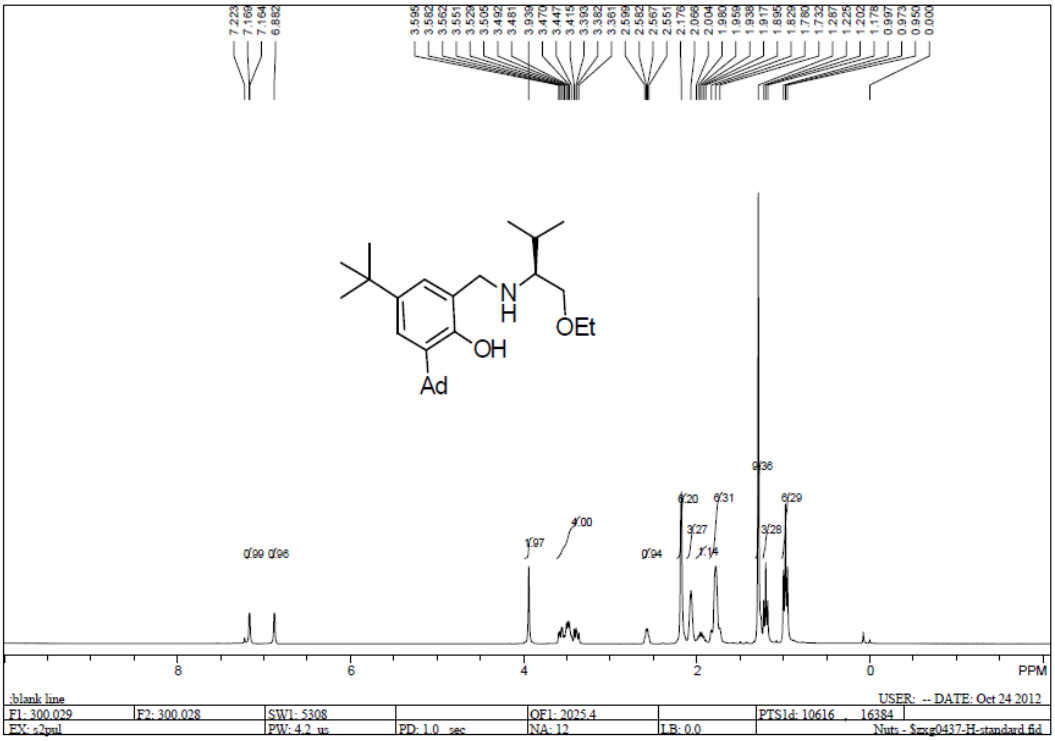
9. NMR Spectra of New Compounds and the Products



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3.415
3.393
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OH
Ad
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6.20
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6.29
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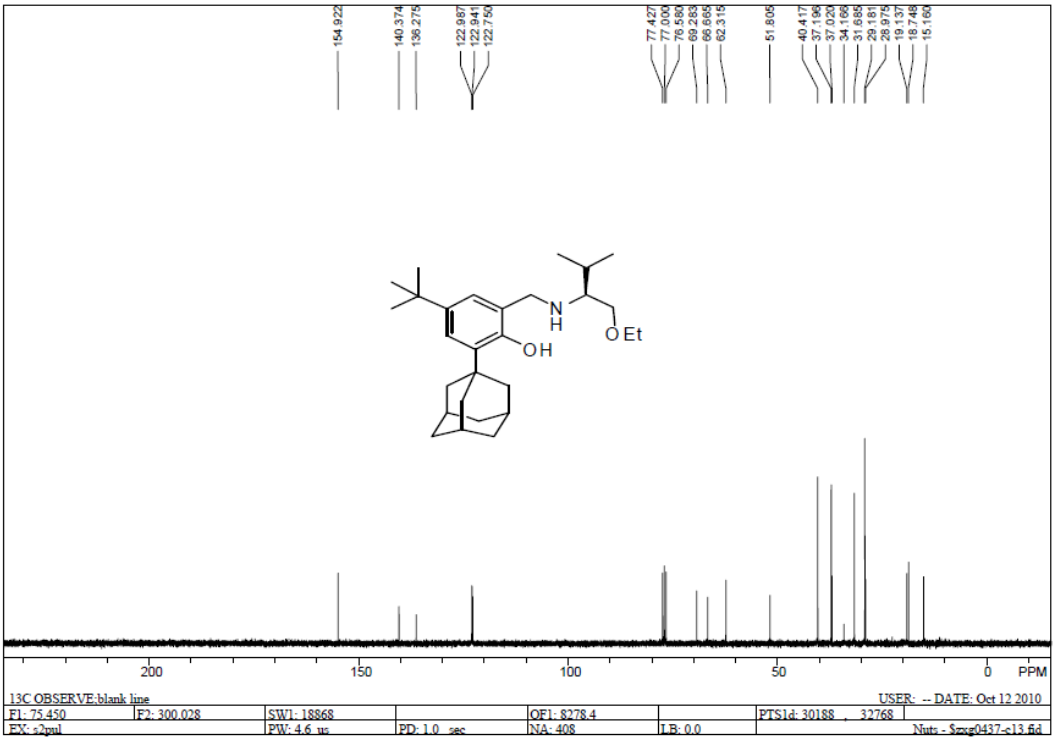
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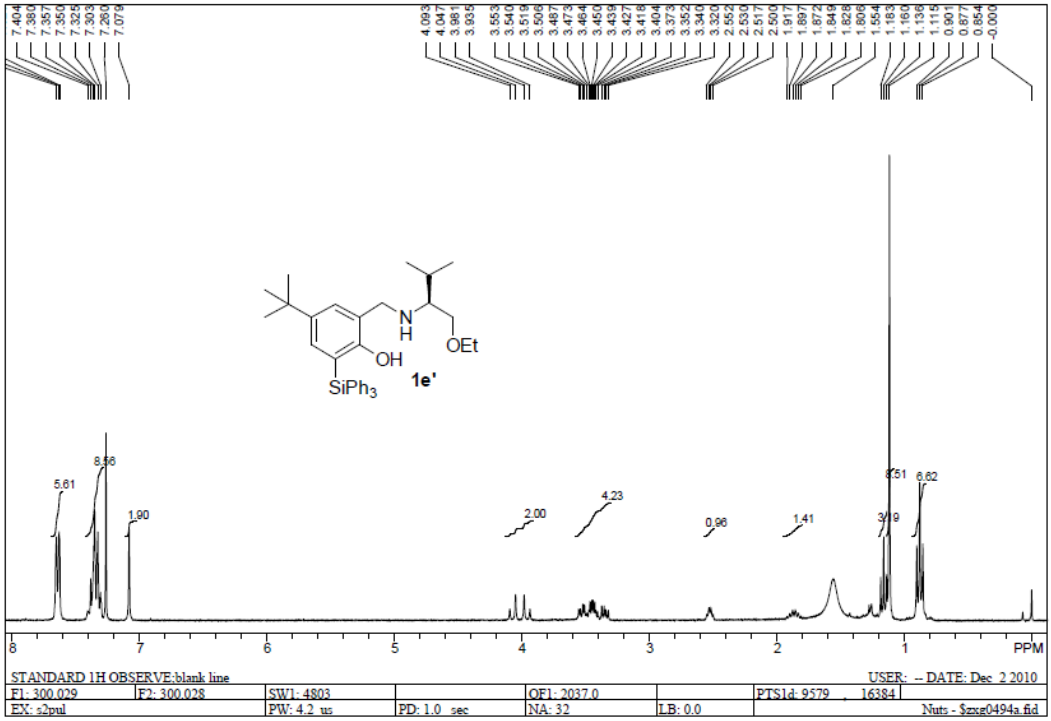
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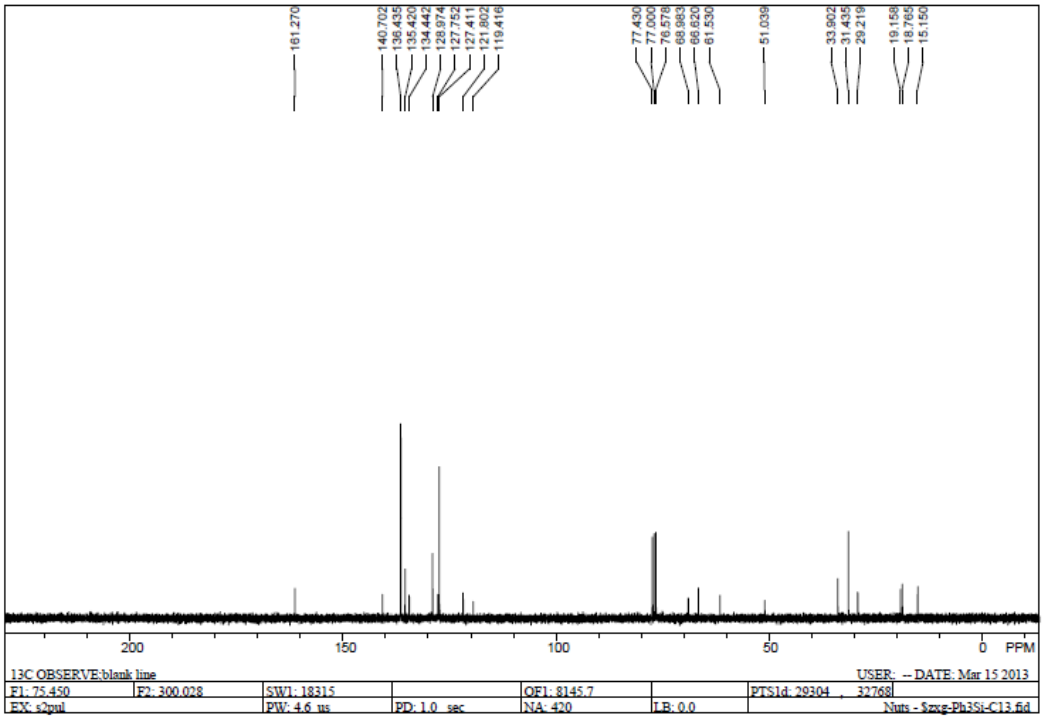
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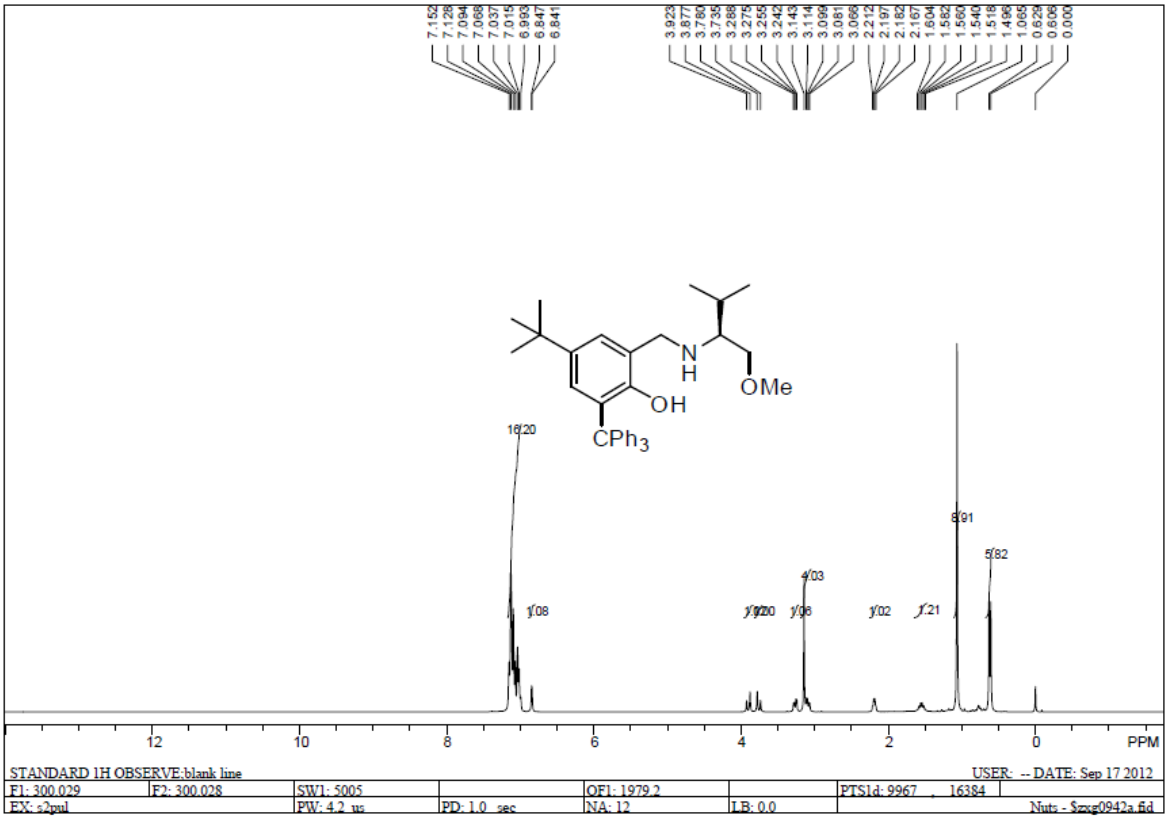
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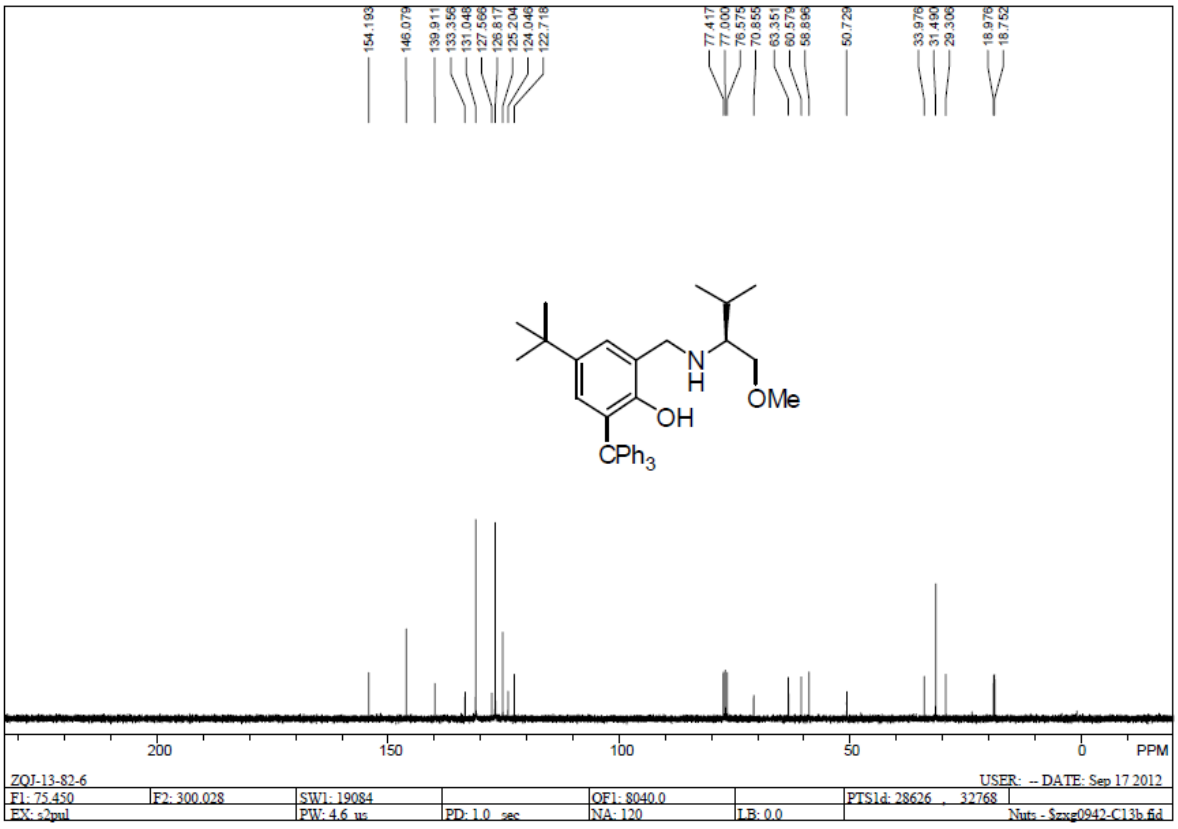
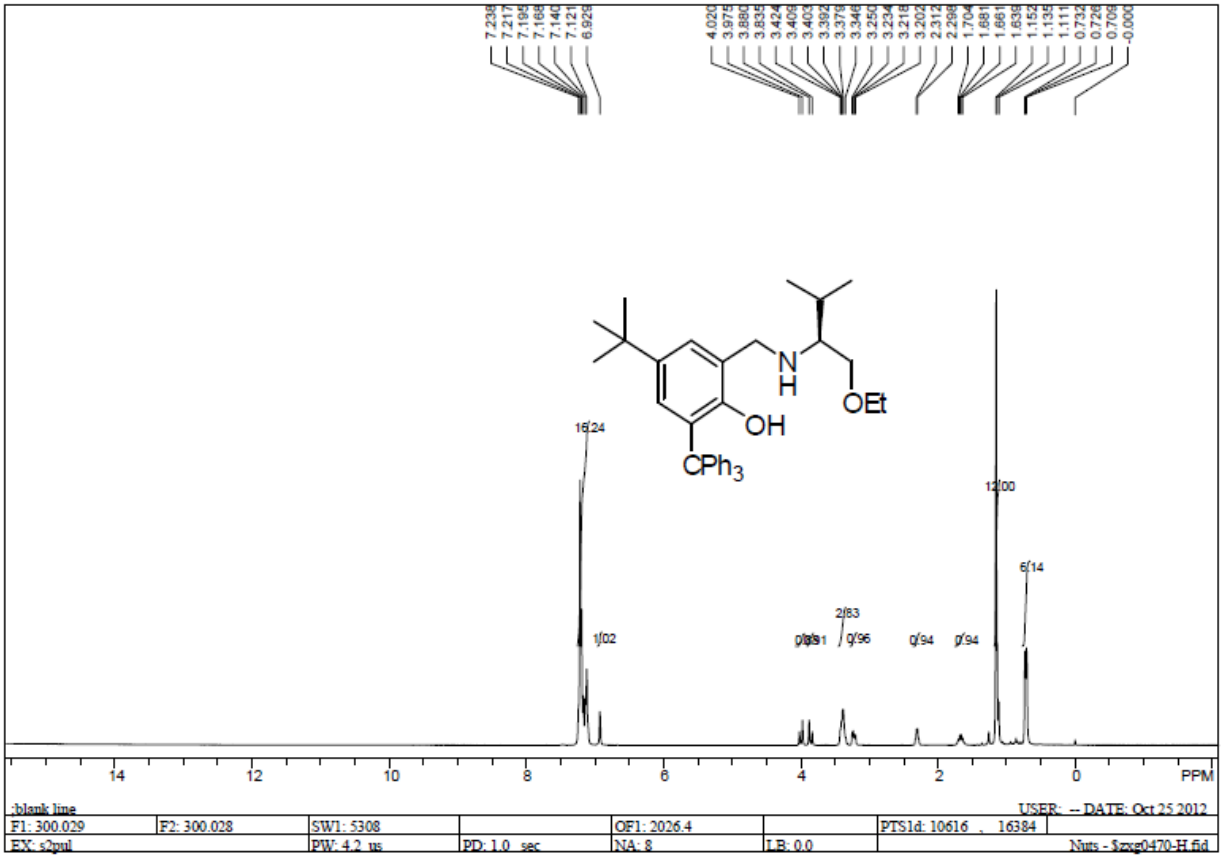
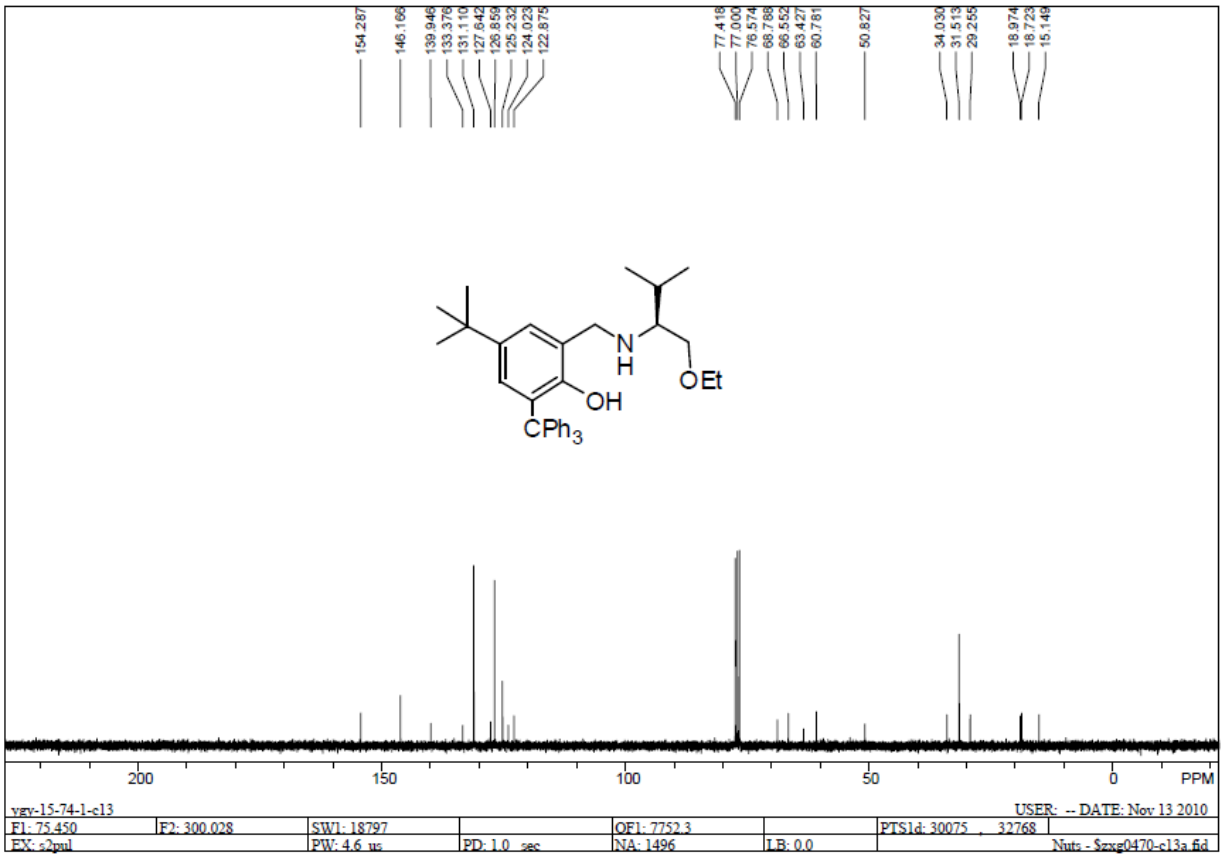
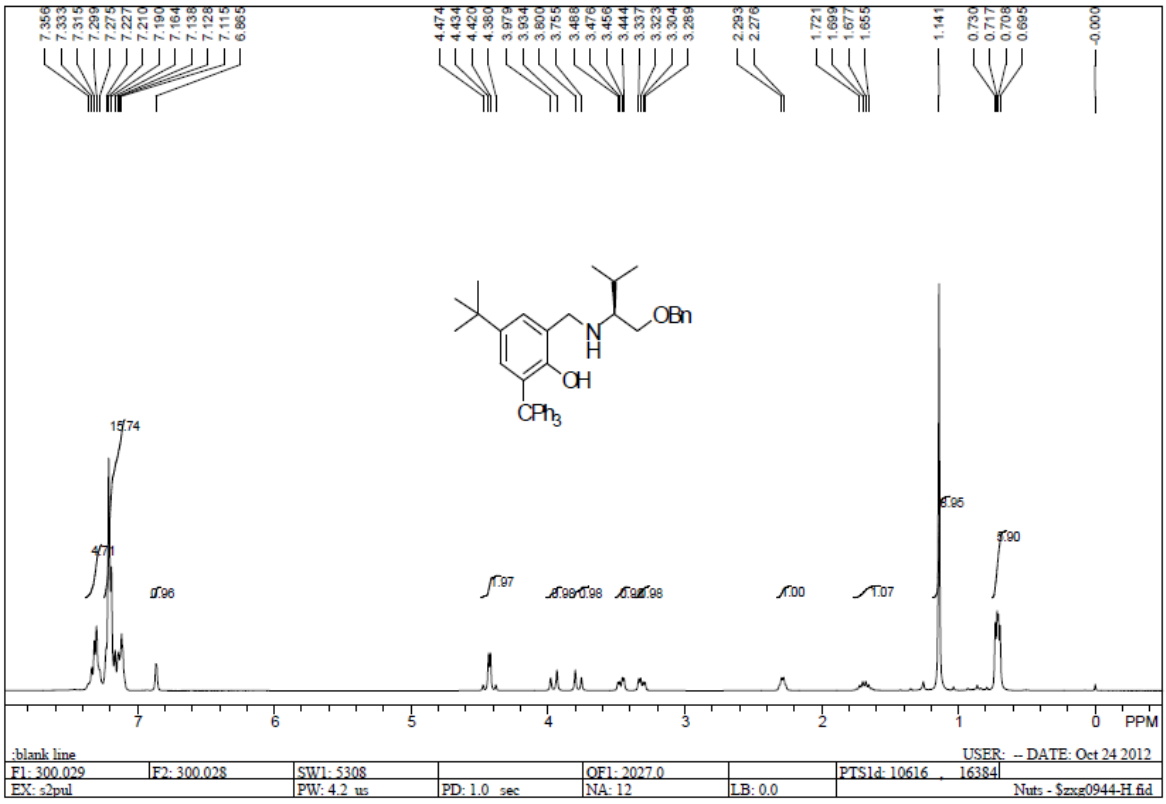
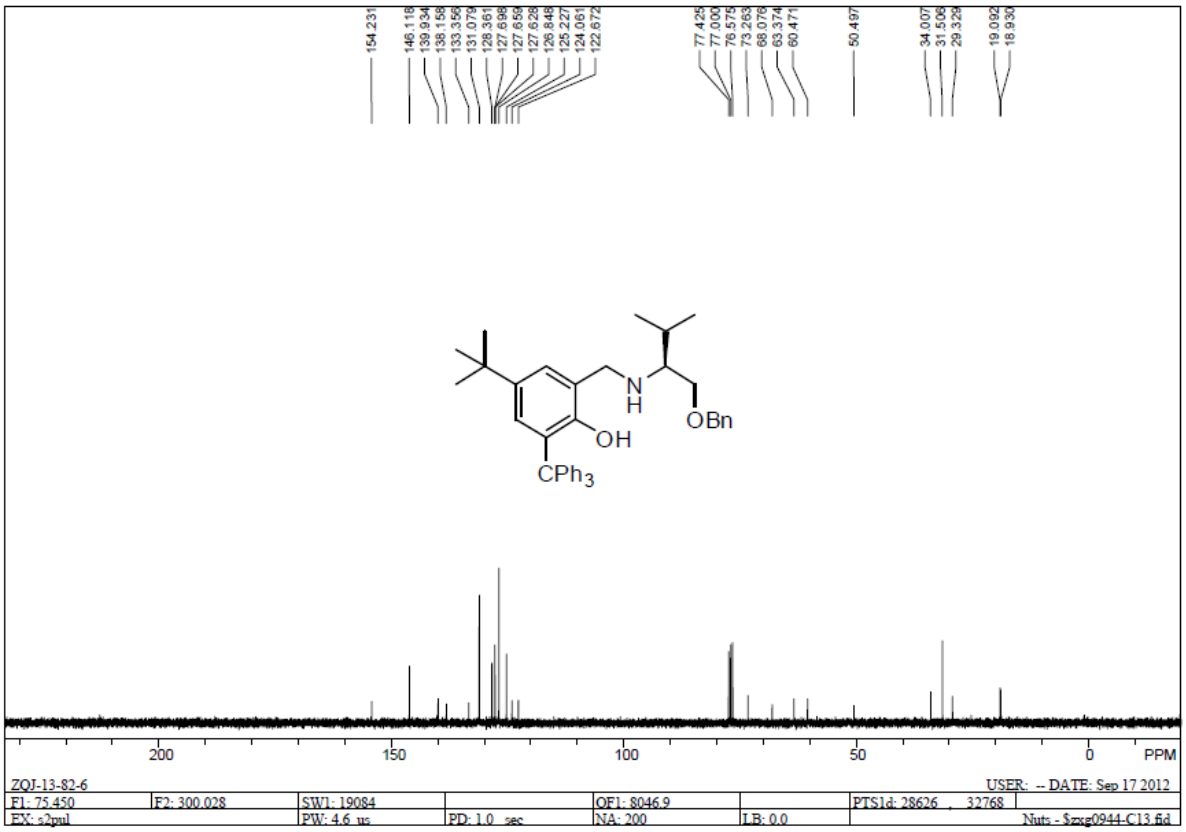
LB: 0.0
Nuts - $zxg0942a.fid

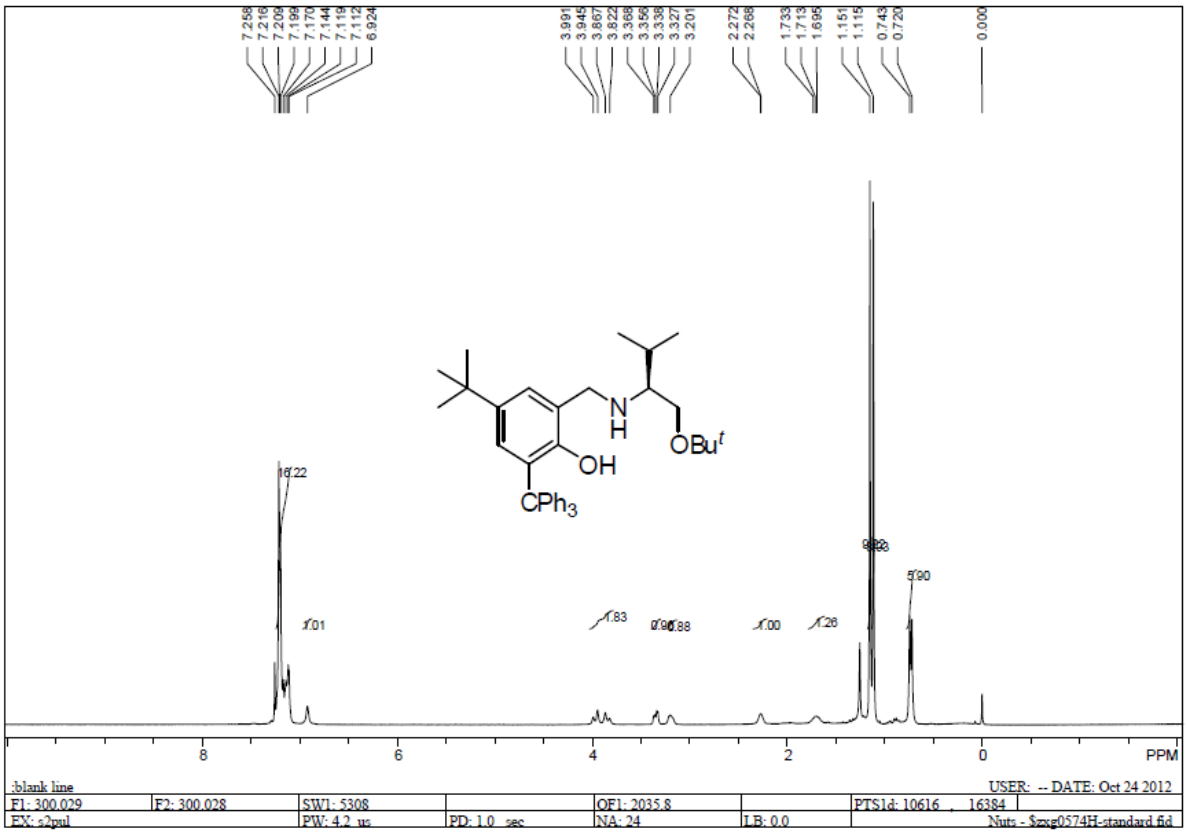

154.193
146.079
139.911
133.356
131.048
127.566
126.817
125.204
124.046
122.718
77.417
77.000
76.575
70.855
63.351
60.579
58.896
50.729
33.976
31.490
29.306
18.976
18.752
OH
CPh3
OMe
200
150
100
50
0
PPM
ZQJ-13-82-6
USER: -- DATE: Sep 17 2012
F1: 75.450
F2: 300.028
SW1: 19084
OF1: 8040.0
PTS1d: 28626 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 120
LB: 0.0
Nuts - $zxg0942-C13b.fid

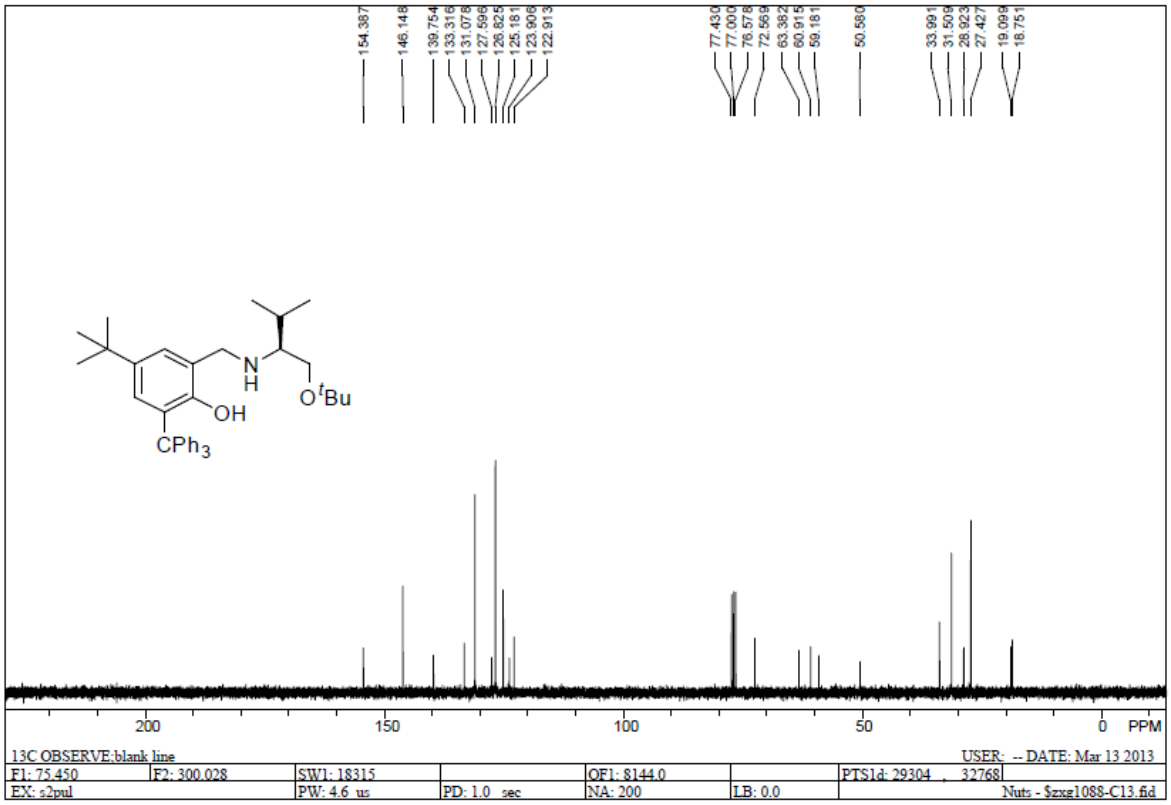

7.238
7.217
7.195
7.168
7.140
7.121
6.928
4.020
3.975
3.880
3.835
3.424
3.406
3.403
3.392
3.376
3.346
3.250
3.234
3.218
3.202
2.312
2.298
1.704
1.681
1.661
1.639
1.152
1.135
1.111
0.732
0.726
0.706
-0.000
N
H
OEt
OH
CPh3
16.24
12.00
6.14
2.83
1.02
0.96
0.94
0.94
14
12
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Oct 25 2012
F1: 300.029
F2: 300.028
SW1: 5308
OF1: 2026.4
PTS1d: 10616 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $zxg0470-H.fid

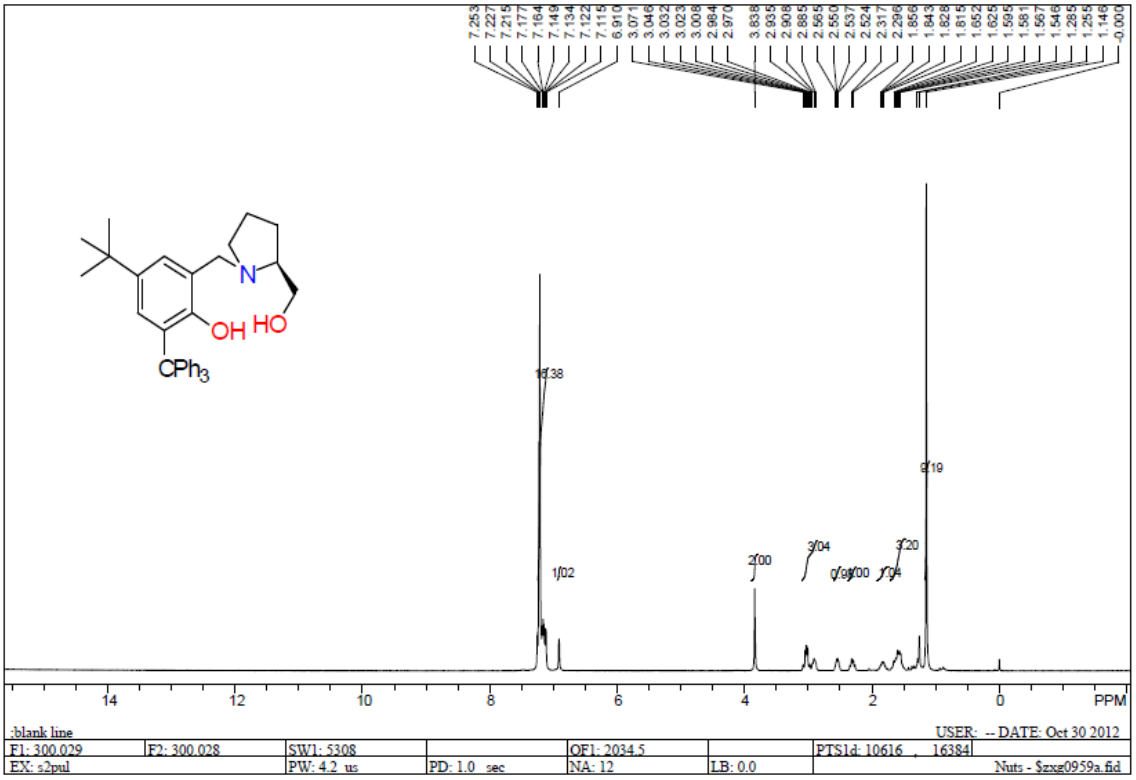

154.287
146.166
139.946
133.376
131.110
127.642
126.859
125.232
124.023
122.875
77.418
77.000
76.574
68.788
66.552
63.427
60.781
50.827
34.030
31.513
29.255
18.974
18.723
15.149
N
H
OEt
OH
CPh3
200
150
100
50
0
PPM
vgv-15-74-1-c13
USER: -- DATE: Nov 13 2010
F1: 75.450
F2: 300.028
SW1: 18797
OF1: 7752.3
PTS1d: 30075 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 1496
LB: 0.0
Nuts - $zxg0470-c13a.fid

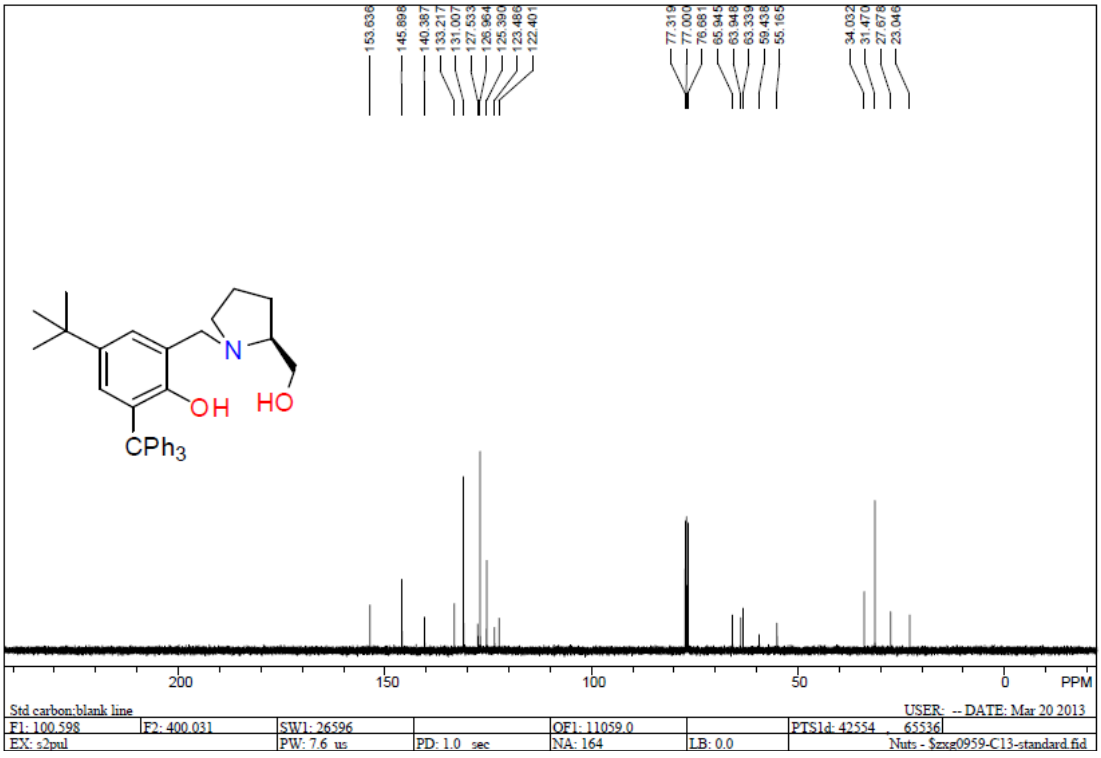

7.356
7.333
7.315
7.299
7.275
7.227
7.210
7.190
7.164
7.138
7.128
7.115
6.865
4.474
4.434
4.420
4.380
3.979
3.934
3.800
3.755
3.488
3.476
3.456
3.444
3.337
3.323
3.304
3.289
2.293
2.276
1.721
1.699
1.677
1.655
1.141
0.730
0.717
0.708
0.695
-0.000
OBn
N
H
OH
CPh3
15.74
4.71
0.96
1.97
0.98
0.98
0.98
1.00
1.07
8.95
9.90
7
6
5
4
3
2
1
0
PPM
:blank line
USER: -- DATE: Oct 24 2012
F1: 300.029
F2: 300.028
SW1: 5308
OF1: 2027.0
PTS1d: 10616 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - $zxg0944-H.fid


154.231
146.118
139.934
138.158
133.356
131.079
128.361
127.698
127.659
127.628
126.848
125.227
124.061
122.872
77.425
77.000
76.575
73.263
68.976
63.374
60.471
50.497
34.007
31.506
29.329
19.092
18.930
OBn
N
H
OH
CPh3
200
150
100
50
0
PPM
ZQJ-13-82-6
USER: -- DATE: Sep 17 2012
F1: 75.450
F2: 300.028
SW1: 19084
OF1: 8046.9
PTS1d: 28626 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 200
LB: 0.0
Nuts - $zxg0944-C13.fid


7.258
7.216
7.206
7.199
7.170
7.144
7.119
7.112
6.924
3.991
3.945
3.867
3.822
3.368
3.356
3.338
3.327
3.201
2.272
2.268
1.733
1.713
1.695
1.151
1.115
0.743
0.720
0.000
OBu^t
OH
CPh3
16.22
1.01
1.83
0.96
0.88
1.00
1.26
9.28
5.90
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Oct 24 2012
F1: 300.029
F2: 300.028
SW1: 5308
OF1: 2035.8
PTS1d: 10616 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 24
LB: 0.0
Nuts - $zxg0574H-standard.fid


154.387
146.148
139.754
133.316
131.078
127.596
126.825
125.181
123.906
122.913
77.430
77.000
76.578
72.569
63.382
60.915
59.181
50.580
33.991
31.509
28.923
27.427
19.099
18.751
O^tBu
OH
CPh3
200
150
100
50
0
PPM
13C OBSERVE:blank line
USER: -- DATE: Mar 13 2013
F1: 75.450
F2: 300.028
SW1: 18315
OF1: 8144.0
PTS1d: 29304 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 200
LB: 0.0
Nuts - $zxg1088-C13.fid


7.253
7.227
7.215
7.177
7.164
7.149
7.134
7.122
7.115
6.910
3.071
3.046
3.032
3.023
3.008
2.984
2.970
3.838
2.935
2.908
2.885
2.565
2.550
2.537
2.524
2.317
2.296
1.856
1.843
1.828
1.815
1.652
1.625
1.595
1.581
1.567
1.546
1.285
1.255
1.146
-0.000
N
OH
HO
CPh3
1.38
1.02
2.00
3.04
3.20
9.19
14
12
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Oct 30 2012
F1: 300.029
F2: 300.028
SW1: 5308
OF1: 2034.5
PTS1d: 10616 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - $zxg0959a.fid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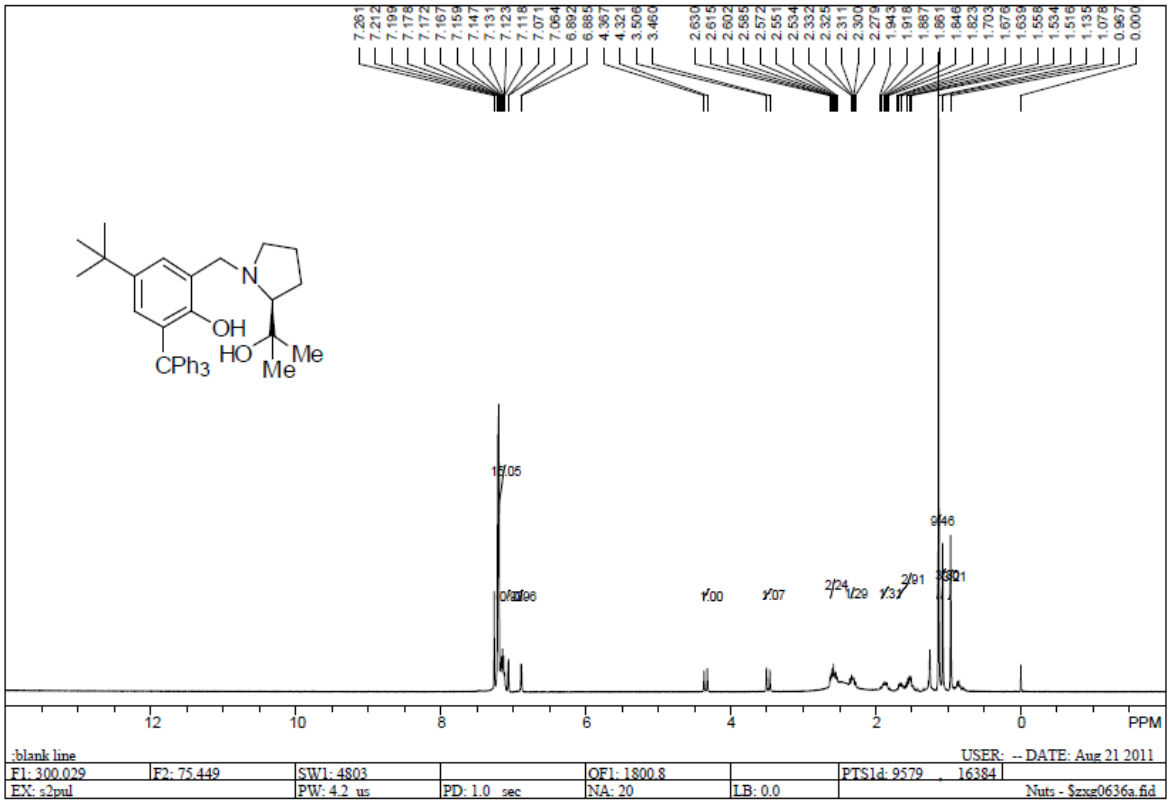
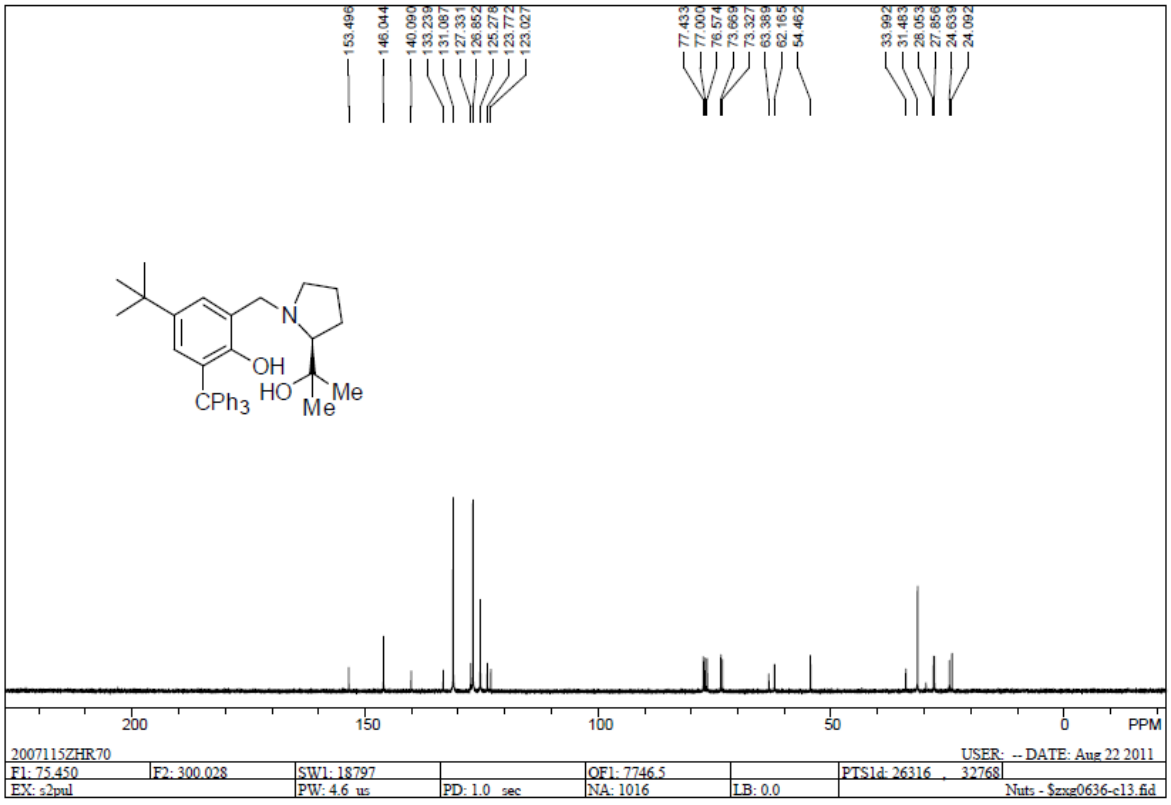
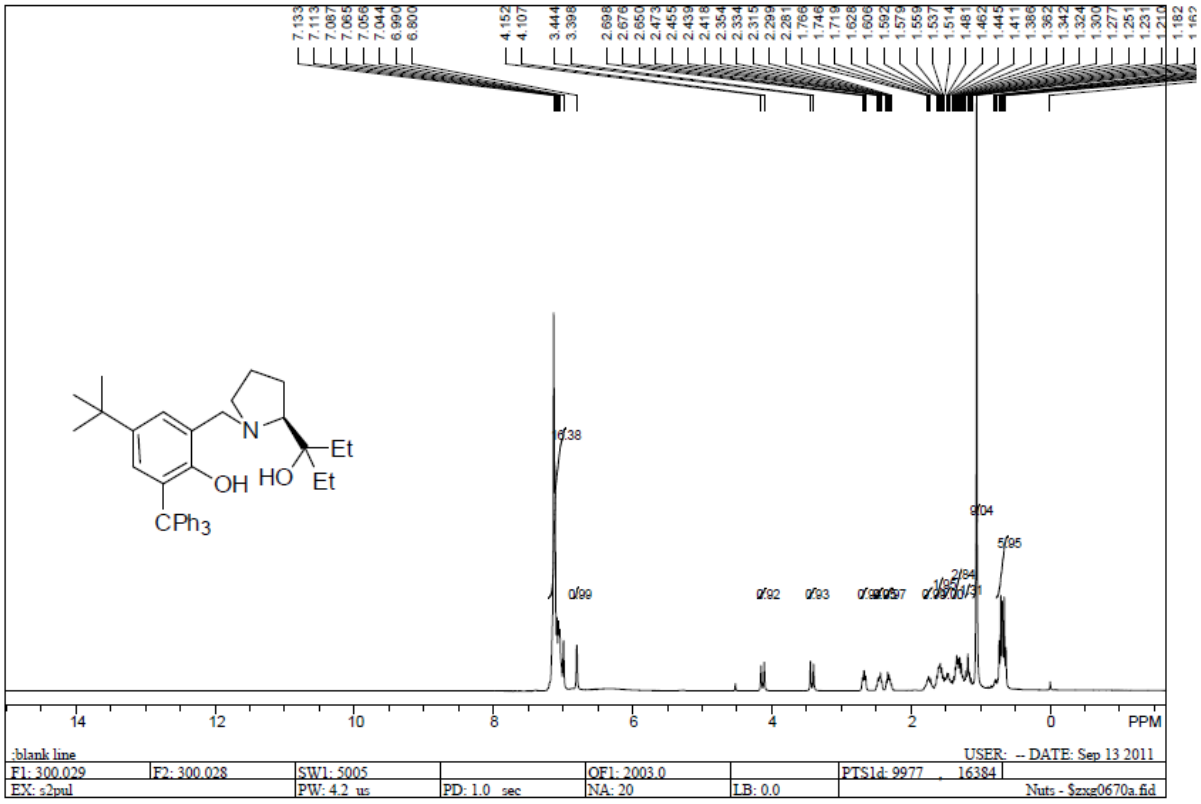
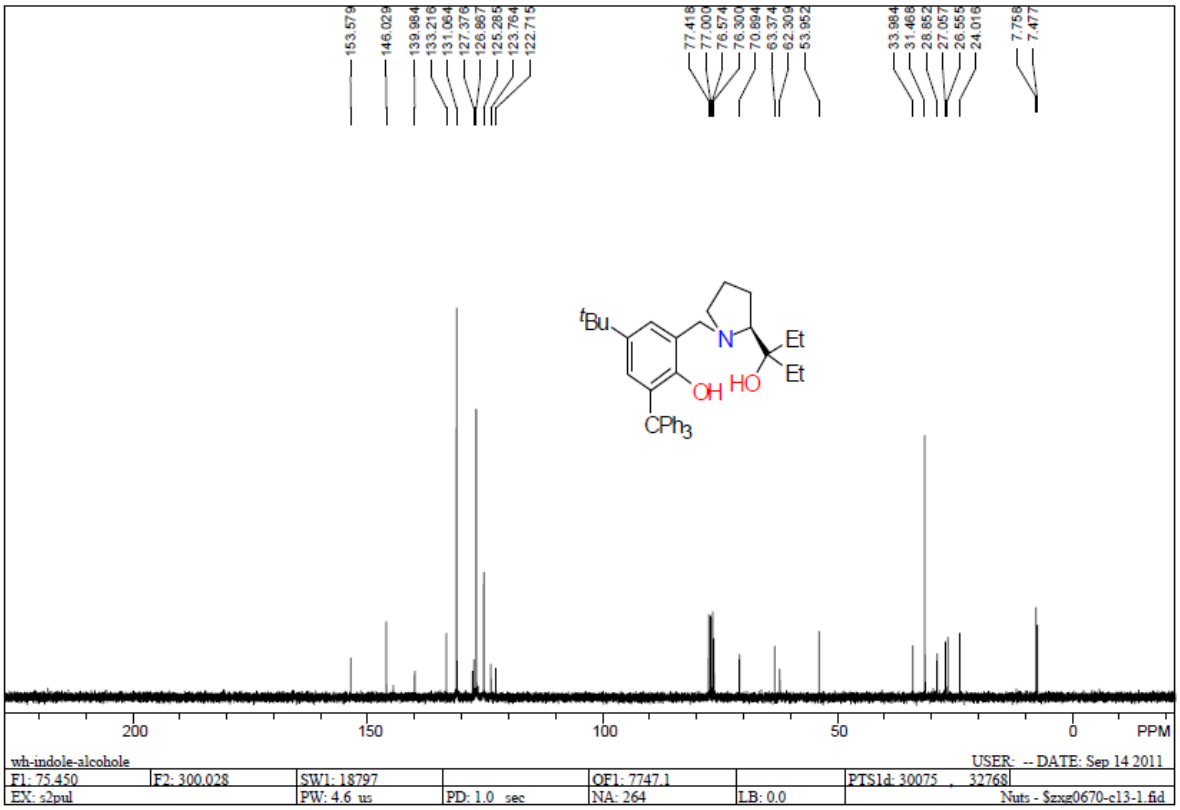
145.898
140.387
133.217
131.007
127.533
126.964
125.390
123.486
122.401
77.319
77.000
76.681
65.945
63.948
63.339
59.438
55.165
34.032
31.470
27.678
23.046
N
OH
HO
CPh3
200
150
100
50
0
PPM
Std carbon:blank line
USER: -- DATE: Mar 20 2013
F1: 100.598
F2: 400.031
SW1: 26596
OF1: 11059.0
PTS1d: 42554 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 164
LB: 0.0
Nuts - $zxg0959-C13-standard.fid


7.261
7.212
7.199
7.178
7.172
7.167
7.159
7.147
7.131
7.123
7.118
7.071
7.064
6.892
6.885
4.367
4.321
3.506
3.460
2.630
2.615
2.602
2.585
2.572
2.551
2.534
2.332
2.325
2.311
2.300
2.279
1.943
1.918
1.887
1.861
1.846
1.823
1.703
1.676
1.639
1.558
1.534
1.516
1.135
1.078
0.967
0.000
N
OH
HO
Me
Me
CPh3
15.05
9.46
1.00
1.07
2.24
1.29
3.31
2.91
3.21
12
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Aug 21 2011
F1: 300.029
F2: 75.449
SW1: 4803
OF1: 1800.8
PTS1d: 9579 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $zxg0636a.fid


153.496
146.044
140.090
133.239
131.087
127.331
126.852
125.278
123.772
123.027
77.433
77.000
76.574
73.669
73.327
63.389
62.165
54.462
33.992
31.483
28.053
27.856
24.639
24.092
N
OH
HO
Me
Me
CPh3
200
150
100
50
0
PPM
2007115ZHR70
USER: -- DATE: Aug 22 2011
F1: 75.450
F2: 300.028
SW1: 18797
OF1: 7746.5
PTS1d: 26316 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 1016
LB: 0.0
Nuts - $zxg0636-c13.fid


7.133
7.113
7.087
7.065
7.056
7.044
6.990
6.800
4.152
4.107
3.444
3.398
2.698
2.676
2.650
2.473
2.455
2.439
2.418
2.354
2.334
2.315
2.299
2.281
1.766
1.746
1.719
1.628
1.606
1.592
1.579
1.559
1.537
1.514
1.481
1.462
1.445
1.411
1.386
1.362
1.342
1.324
1.300
1.277
1.251
1.231
1.210
1.182
N
Et
HO
Et
OH
CPh3
6.38
9.04
5.95
0.99
0.92
0.93
PPM
:blank line
USER: -- DATE: Sep 13 2011
F1: 300.029
F2: 300.028
SW1: 5005
OF1: 2003.0
PTS1d: 9977 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $zxg0670a.fid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139.984
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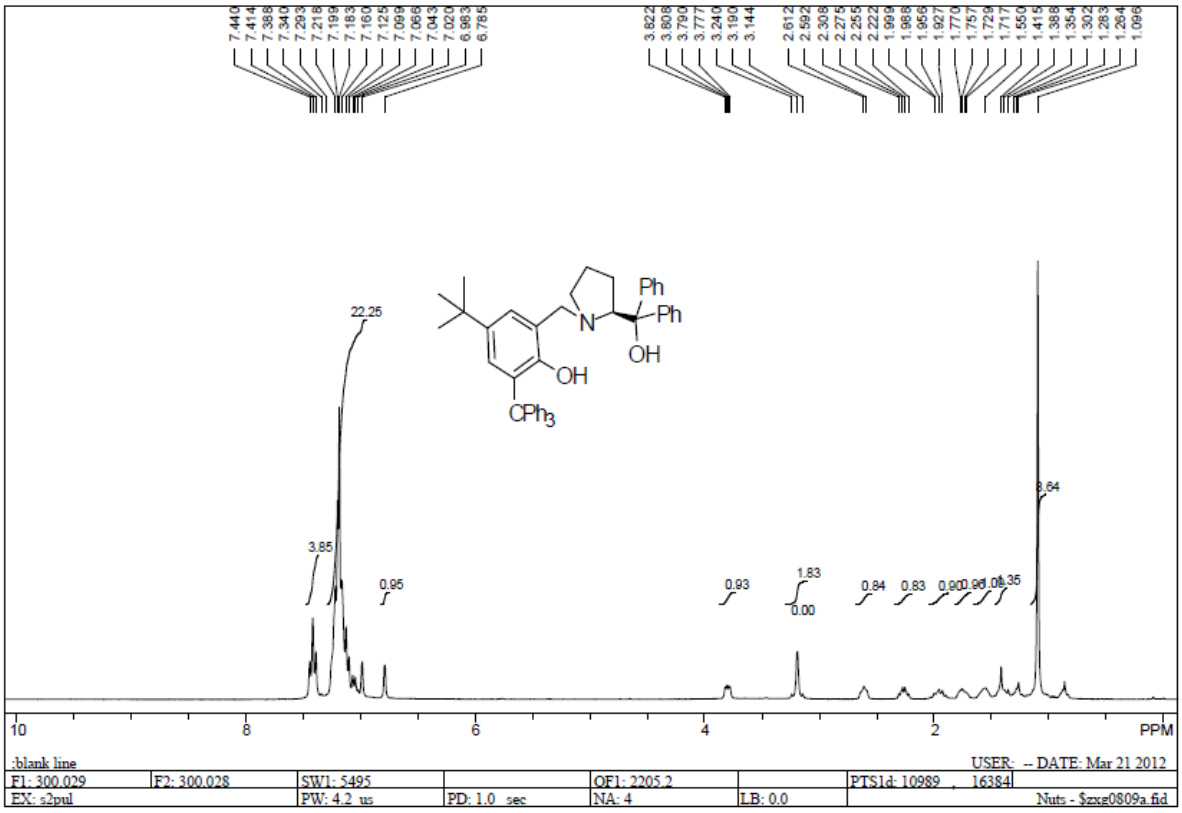
127.376
126.867
125.285
123.764
122.715
77.418
77.000
76.574
76.300
70.894
63.374
62.309
53.952
33.984
31.468
28.852
27.057
26.555
24.016
7.758
7.477
tBu
N
Et
Et
OH
HO
CPh3
PPM
wh-indole-alcohole
USER: -- DATE: Sep 14 2011
F1: 75.450
F2: 300.028
SW1: 18797
OF1: 7747.1
PTS1d: 30075 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 264
LB: 0.0
Nuts - $zxg0670-c13-1.fid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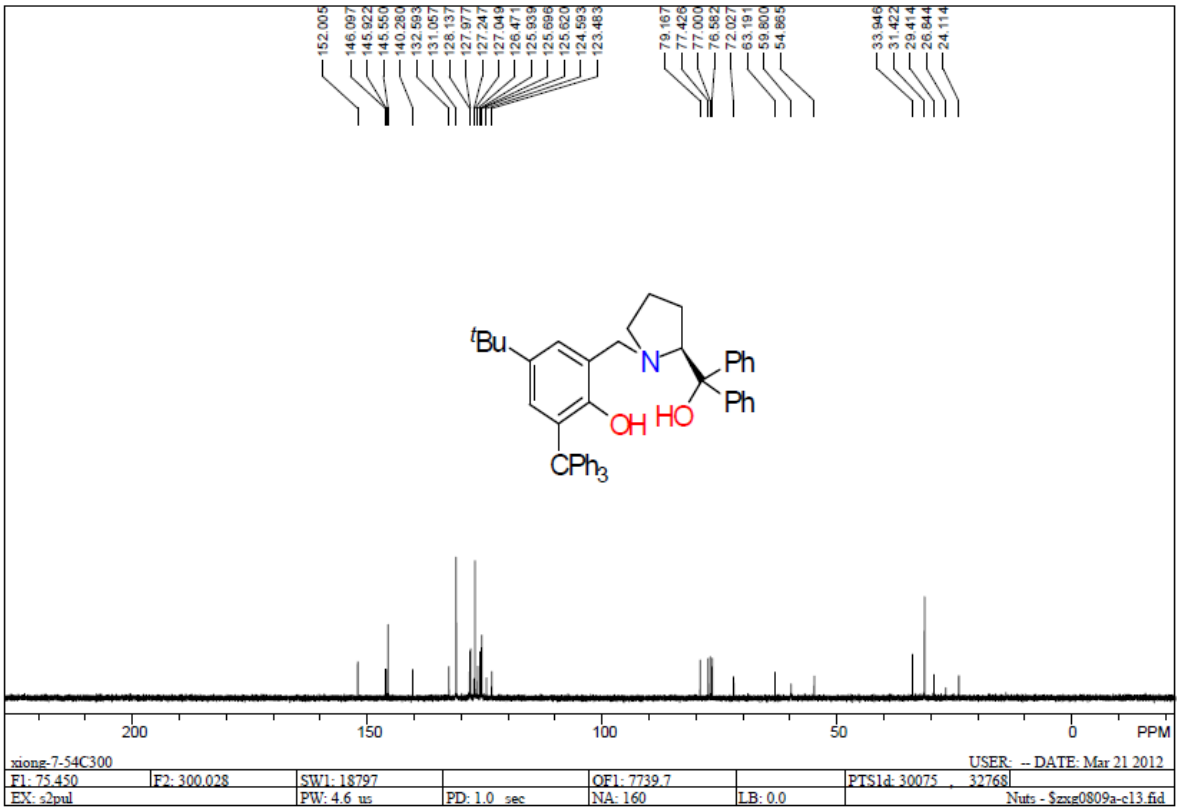
7.414
7.388
7.340
7.293
7.218
7.199
7.183
7.160
7.125
7.099
7.066
7.043
7.020
6.983
6.785
3.822
3.808
3.790
3.777
3.240
3.190
3.144
2.612
2.592
2.308
2.275
2.255
2.222
1.999
1.988
1.956
1.927
1.770
1.757
1.729
1.717
1.550
1.415
1.388
1.354
1.302
1.283
1.264
1.066
Ph
Ph
OH
N
OH
CPh3
22.25
3.85
0.95
0.93
1.83
0.00
0.84
0.83
0.90
0.96
1.08
1.35
9.64
10
8
6
4
2
PPM
:blank line
USER: -- DATE: Mar 21 2012
F1: 300.029
F2: 300.028
SW1: 5495
OF1: 2205.2
PTS1d: 10989 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 4
LB: 0.0
Nuts - $zxg0809a.fid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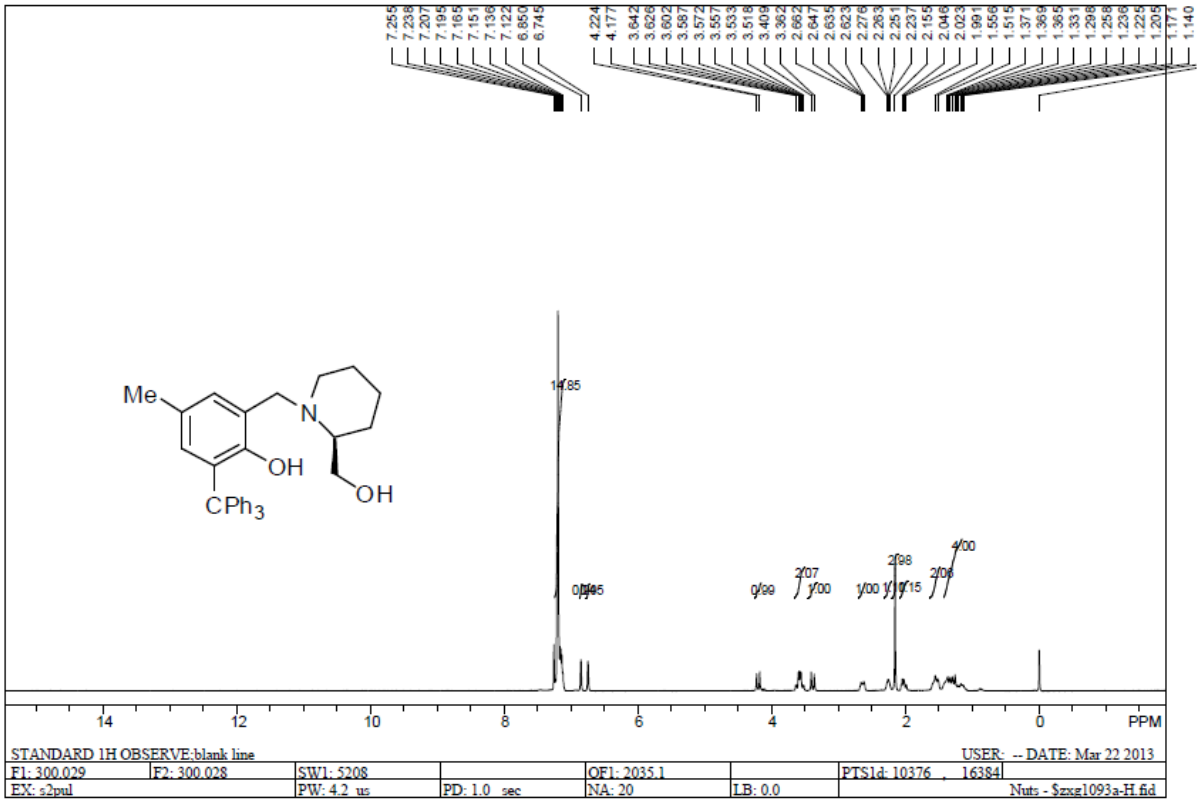
146.097
145.922
145.550
140.280
132.593
131.057
128.137
127.977
127.247
127.049
126.471
125.939
125.696
125.620
124.593
123.483
79.167
77.426
77.000
76.582
72.027
63.191
59.800
54.865
33.946
31.422
29.414
26.844
24.114
tBu
N
Ph
Ph
OH
HO
CPh3
200
150
100
50
0
PPM
xiong-7-54C300
USER: -- DATE: Mar 21 2012
F1: 75.450
F2: 300.028
SW1: 18797
OF1: 7739.7
PTS1d: 30075 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 160
LB: 0.0
Nuts - $zxg0809a-c13.fid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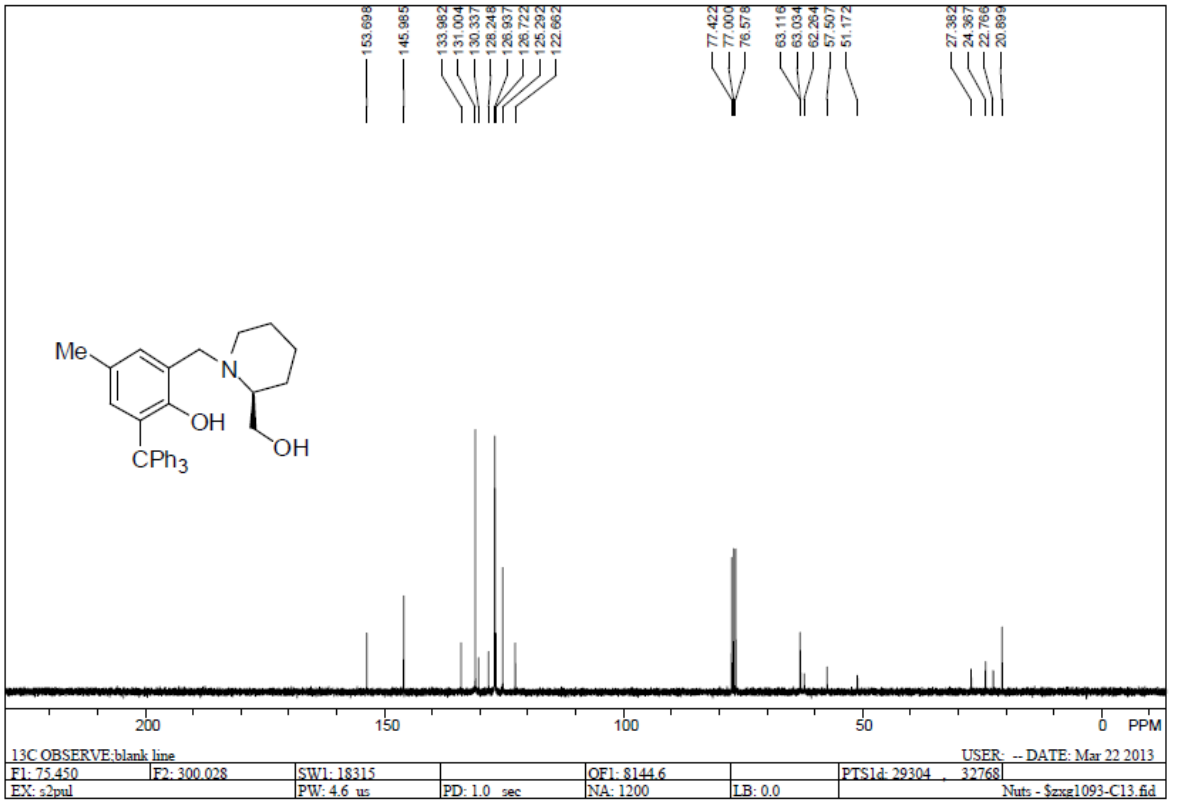
7.207
7.195
7.165
7.151
7.136
7.122
6.850
6.745
4.224
4.177
3.642
3.626
3.602
3.587
3.572
3.557
3.533
3.518
3.409
3.362
2.662
2.647
2.635
2.623
2.276
2.263
2.251
2.237
2.155
2.046
2.023
1.991
1.556
1.515
1.371
1.369
1.365
1.331
1.298
1.258
1.236
1.225
1.205
1.171
1.140
Me
N
OH
OH
CPh3
14.85
0.99
2.07
3.00
1.00
1.15
2.08
2.98
4.00
14
12
10
8
6
4
2
0
PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Mar 22 2013
F1: 300.029
F2: 300.028
SW1: 5208
OF1: 2035.1
PTS1d: 10376 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $zxg1093a-H.fid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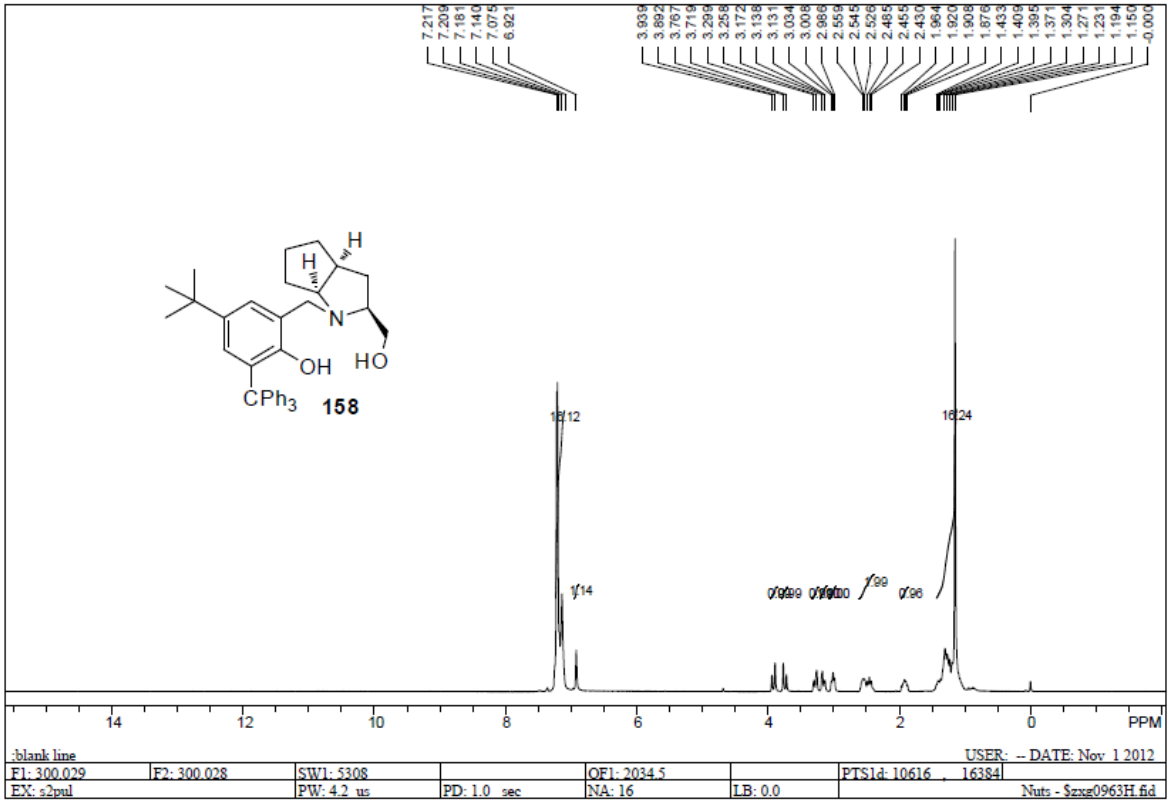
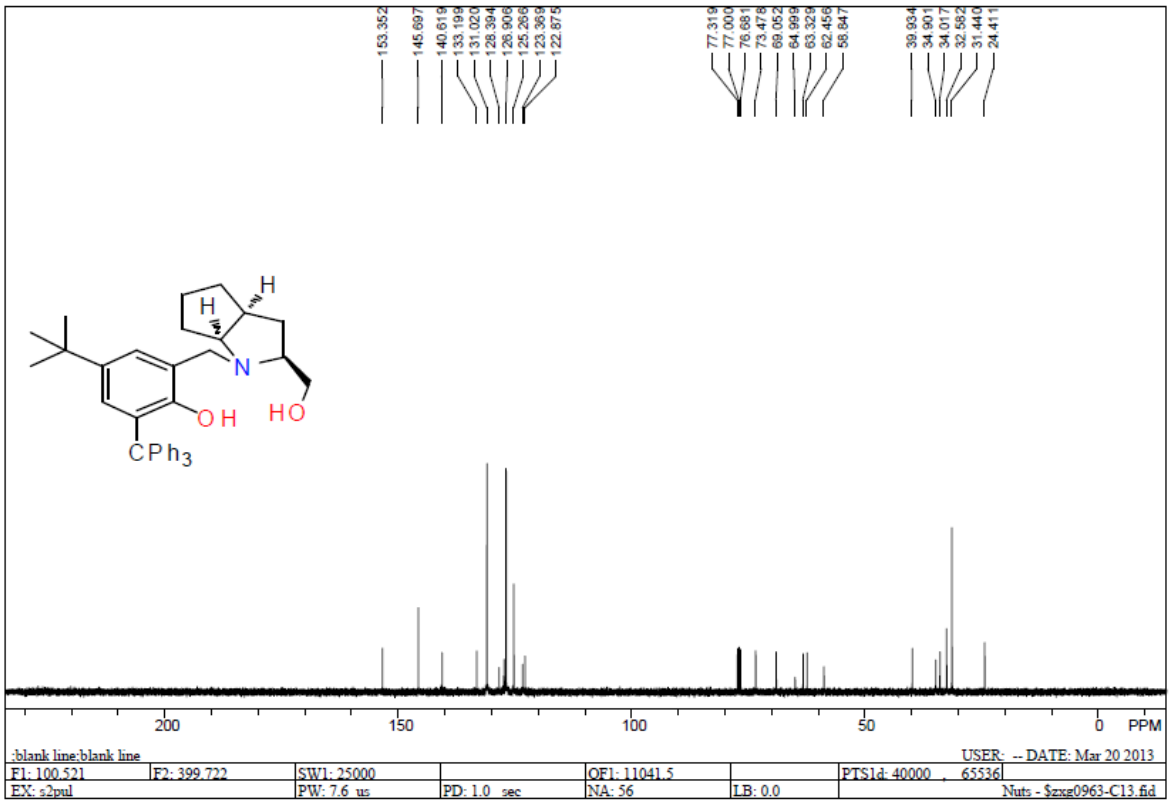
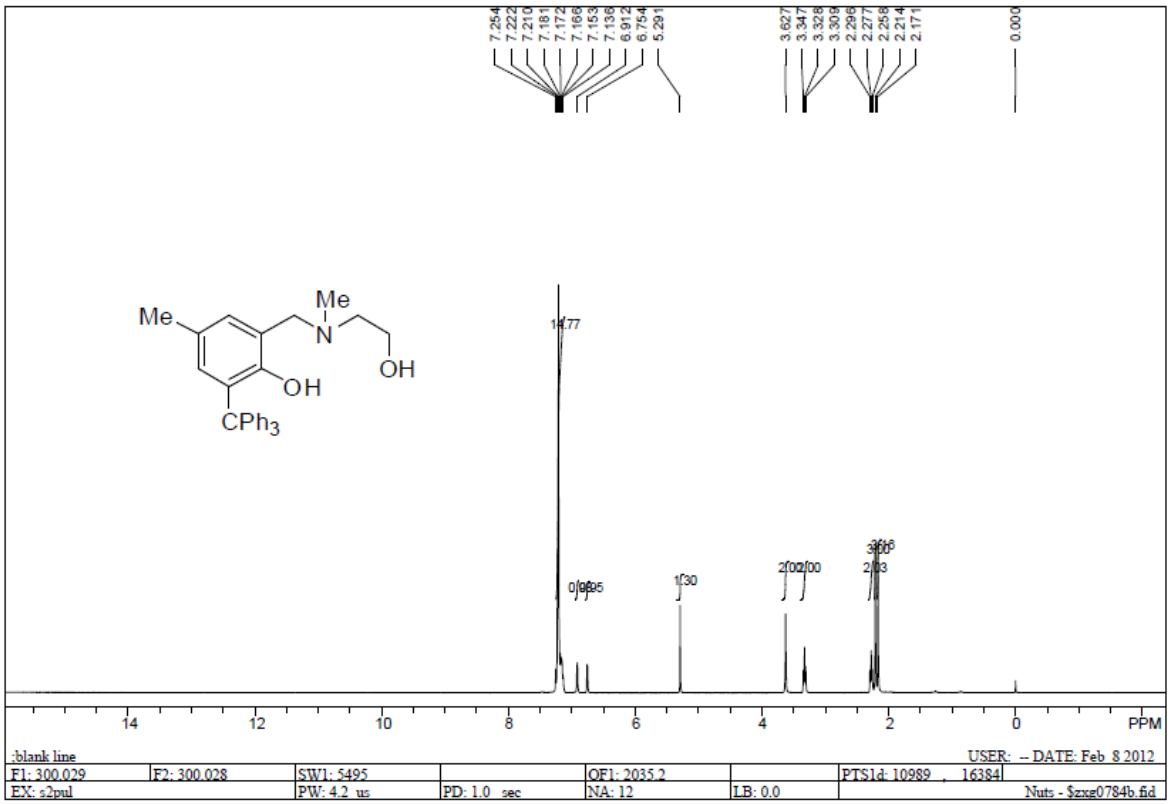
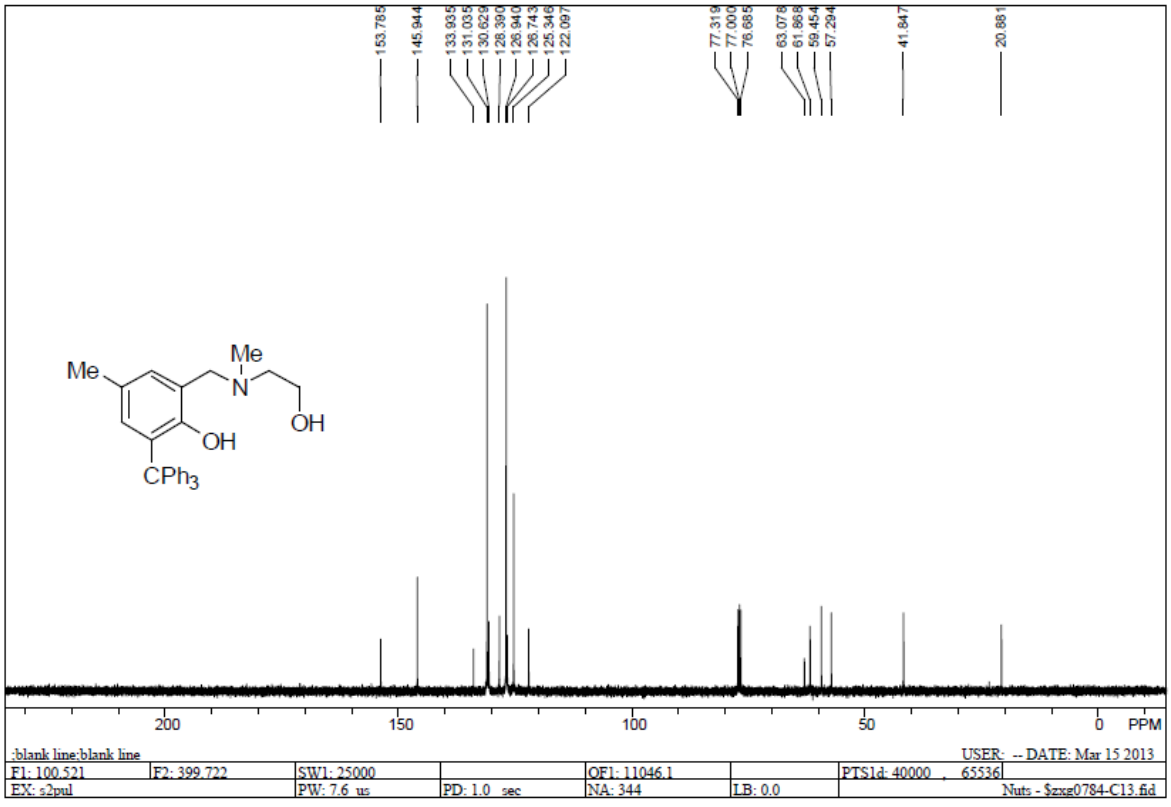
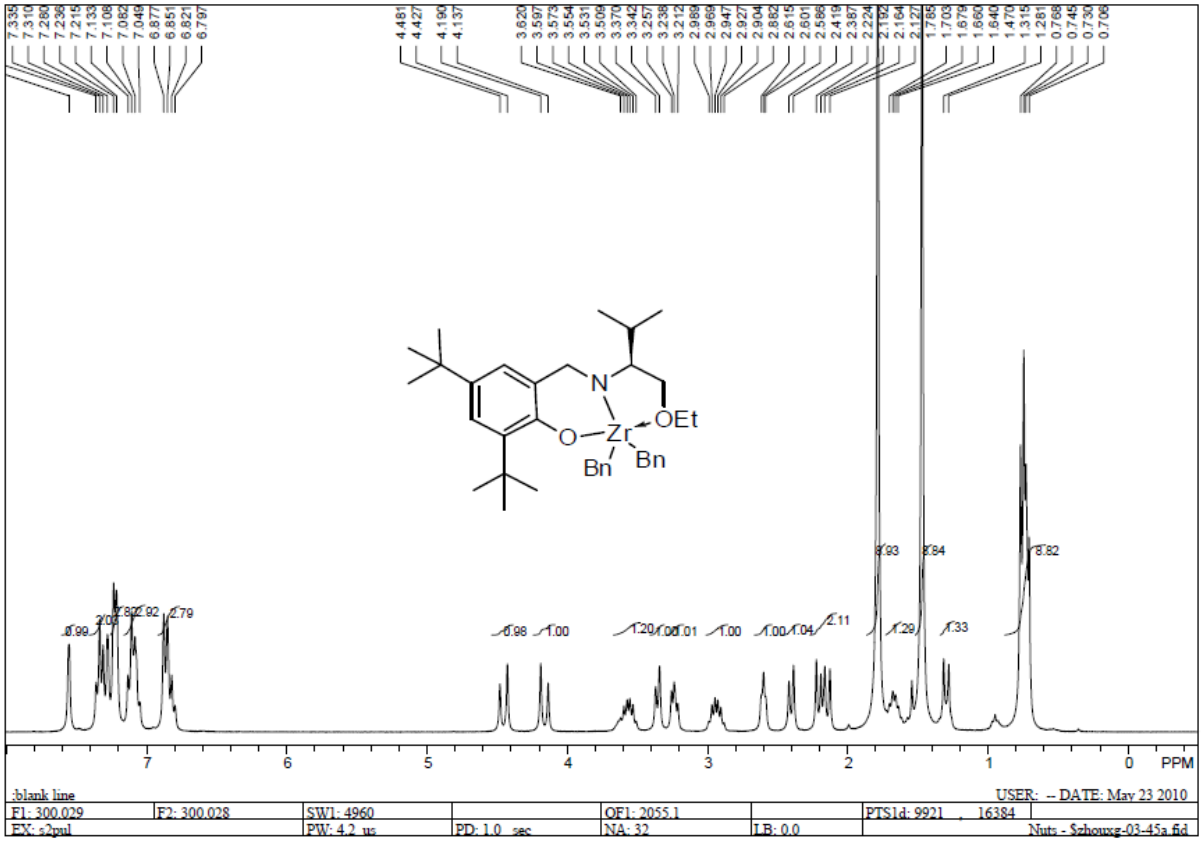
130.337
128.248
126.937
126.722
125.292
122.662
77.422
77.000
76.578
63.116
63.034
62.264
57.507
51.172
27.382
24.367
22.766
20.899
Me
N
OH
OH
CPh3
200
150
100
50
0
PPM
13C OBSERVE;blank line
USER: -- DATE: Mar 22 2013
F1: 75.450
F2: 300.028
SW1: 18315
OF1: 8144.6
PTS1d: 29304 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 1200
LB: 0.0
Nuts - $zxg1093-C13.fid

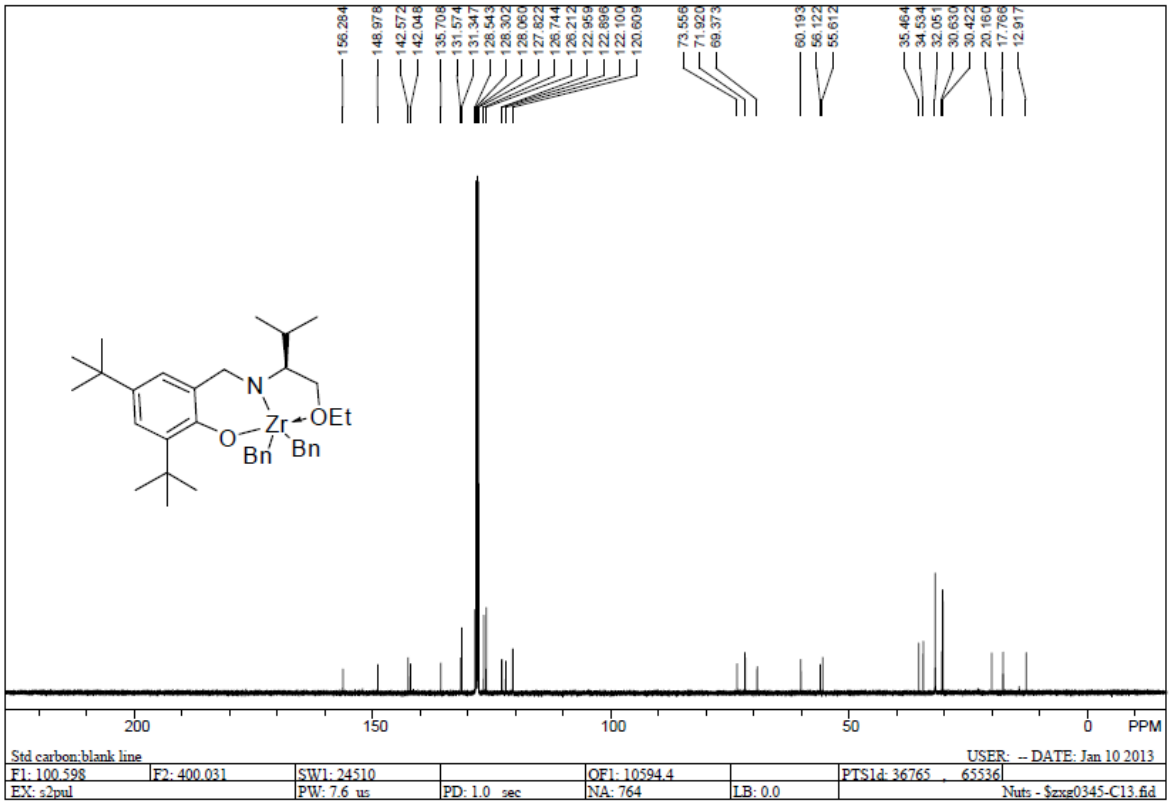

7.217
7.209
7.181
7.140
7.075
6.921
3.939
3.892
3.767
3.719
3.299
3.258
3.172
3.138
3.131
3.034
3.008
2.986
2.559
2.545
2.526
2.485
2.455
2.430
1.964
1.920
1.908
1.676
1.433
1.409
1.395
1.371
1.304
1.271
1.231
1.194
1.150
-0.000
H
H
N
OH
HO
CPh3
158
16.12
16.24
1.14
0.99
0.96
14
12
10
8
6
4
2
0
PPM
;blank line
USER: -- DATE: Nov 1 2012
F1: 300.029
F2: 300.028
SW1: 5308
OF1: 2034.5
PTS1d: 10616 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $zxg0963H.fid

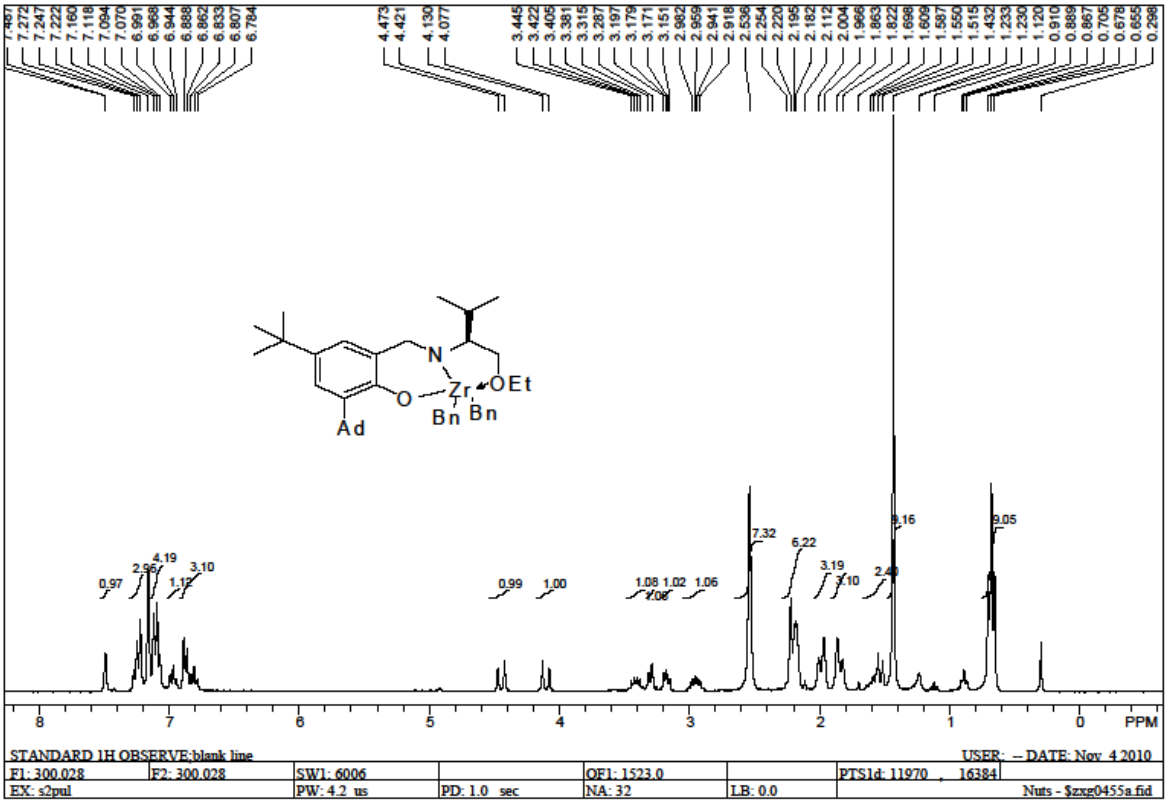

153.352
145.697
140.619
133.199
131.020
128.394
126.906
125.266
123.369
122.875
77.319
77.000
76.681
73.478
69.052
64.999
63.329
62.456
58.847
39.934
34.901
34.017
32.582
31.440
24.411
H
H
N
OH
HO
CPh3
200
150
100
50
0
PPM
;blank line;blank line
USER: -- DATE: Mar 20 2013
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11041.5
PTS1d: 40000 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 56
LB: 0.0
Nuts - $zxg0963-C13.fid

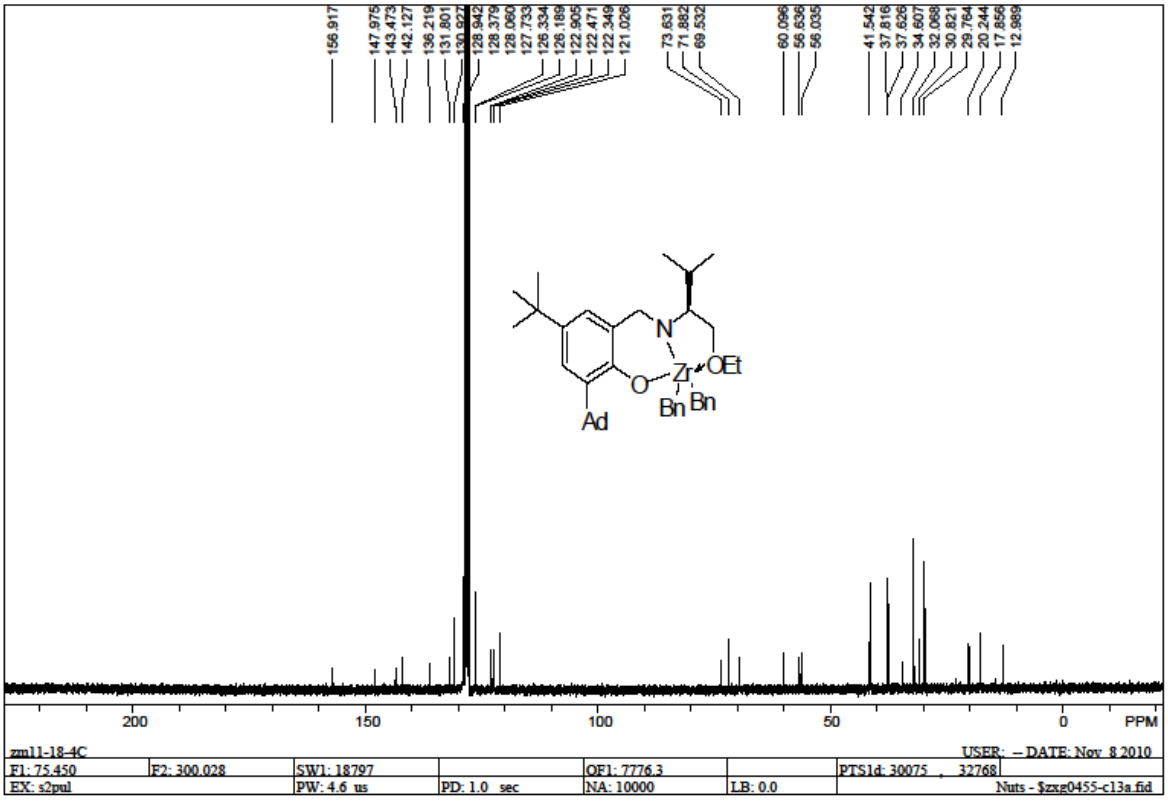

7.254
7.222
7.210
7.181
7.172
7.166
7.153
7.136
6.912
6.754
5.291
3.627
3.347
3.328
3.309
2.296
2.277
2.258
2.214
2.171
0.000
Me
N
OH
OH
CPh3
14.77
1.30
2.02
2.00
2.03
14
12
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Feb 8 2012
F1: 300.029
F2: 300.028
SW1: 5495
OF1: 2035.2
PTS1d: 10989 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - $zxg0784b.fid

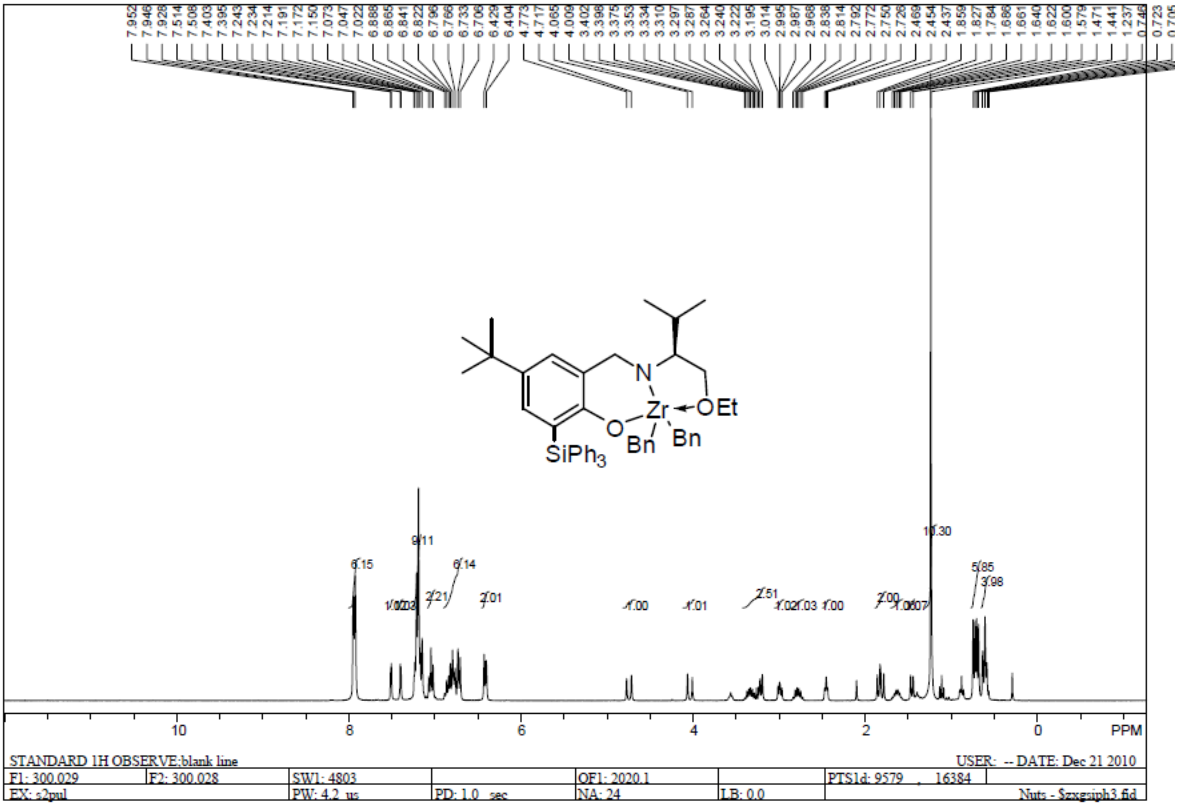

153.785
145.944
133.935
131.035
130.629
128.390
128.040
126.743
125.346
122.097
77.319
77.000
76.685
63.078
61.868
59.454
57.294
41.847
20.881
Me
N
OH
OH
CPh3
200
150
100
50
0
PPM
:blank line:blank line
USER: -- DATE: Mar 15 2013
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11046.1
PTS1d: 40000 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 344
LB: 0.0
Nuts - $zxg0784-C13.fid

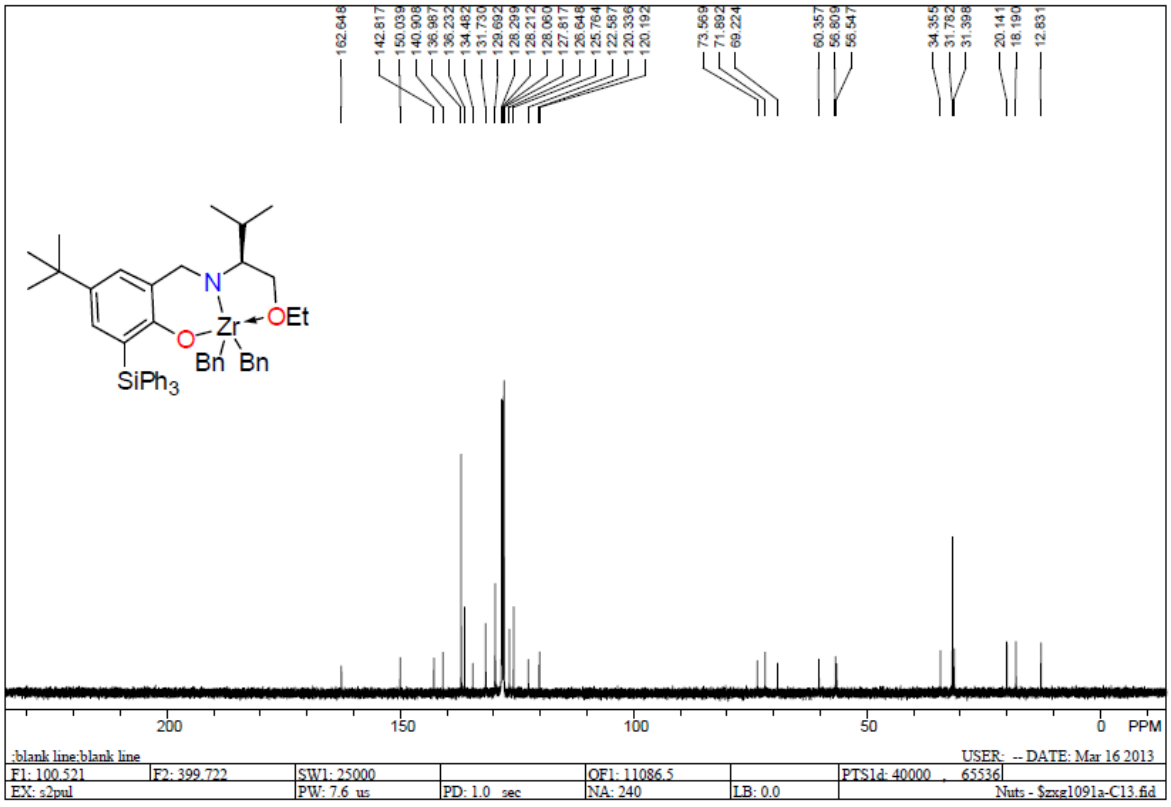

7.335 7.310 7.280 7.236 7.215 7.133 7.106 7.082 7.049 6.877 6.851 6.821 6.797
4.481 4.427 4.190 4.137
3.620 3.597 3.573 3.554 3.531 3.509 3.370 3.342 3.257 3.238 3.212 2.989 2.969 2.947 2.927 2.904 2.882 2.615 2.601 2.586 2.419 2.387 2.224 2.182 2.164 2.127
1.785 1.703 1.679 1.660 1.640 1.470 1.315 1.281 0.768 0.745 0.730 0.706
N
O
Zr
OEt
Bn
Bn
8.99 2.08 7.82 7.92 2.79
0.98 1.00
1.20 0.00 1.01 1.00 1.00 1.04 2.11
8.93 8.84 1.29 1.33 8.82
7 6 5 4 3 2 1 0 PPM
:blank line
USER: -- DATE: May 23 2010
F1: 300.029 F2: 300.028 SW1: 4960 OF1: 2055.1 PTS1d: 9921 , 16384
EX: s2pul PW: 4.2 us PD: 1.0 sec NA: 32 LB: 0.0 Nuts - $zhouxg-03-45a.fid

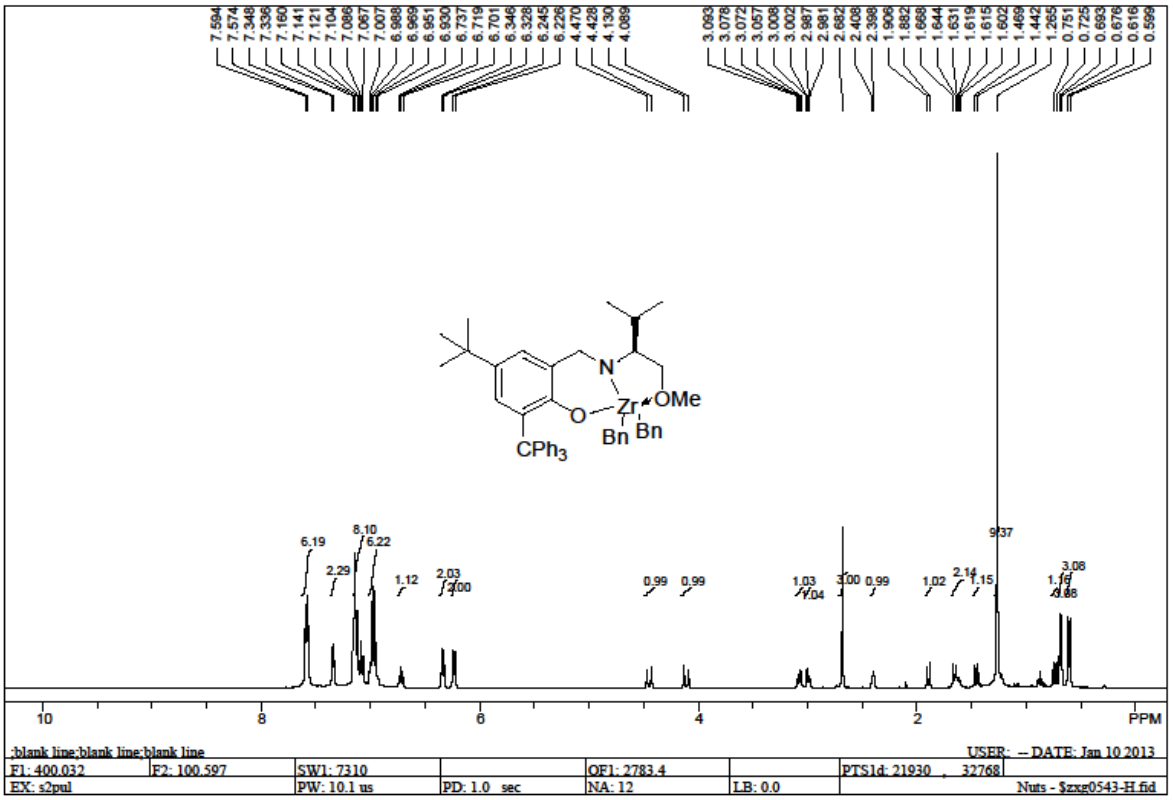

156.284 148.978 142.572 142.048 135.708 131.574 131.347 128.543 128.302 128.060 127.822 126.744 126.212 122.959 122.898 122.100 120.609
73.556 71.920 69.373
60.193 58.122 55.612
35.464 34.534 32.051 30.630 30.422 20.160 17.766 12.917
N
O
Zr
OEt
Bn
Bn
200 150 100 50 0 PPM
Std carbon:blank line
USER: -- DATE: Jan 10 2013
F1: 100.598 F2: 400.031 SW1: 24510 OF1: 10594.4 PTS1d: 36765 , 65536
EX: s2pul PW: 7.6 us PD: 1.0 sec NA: 764 LB: 0.0 Nuts - $zxg0345-C13.fid

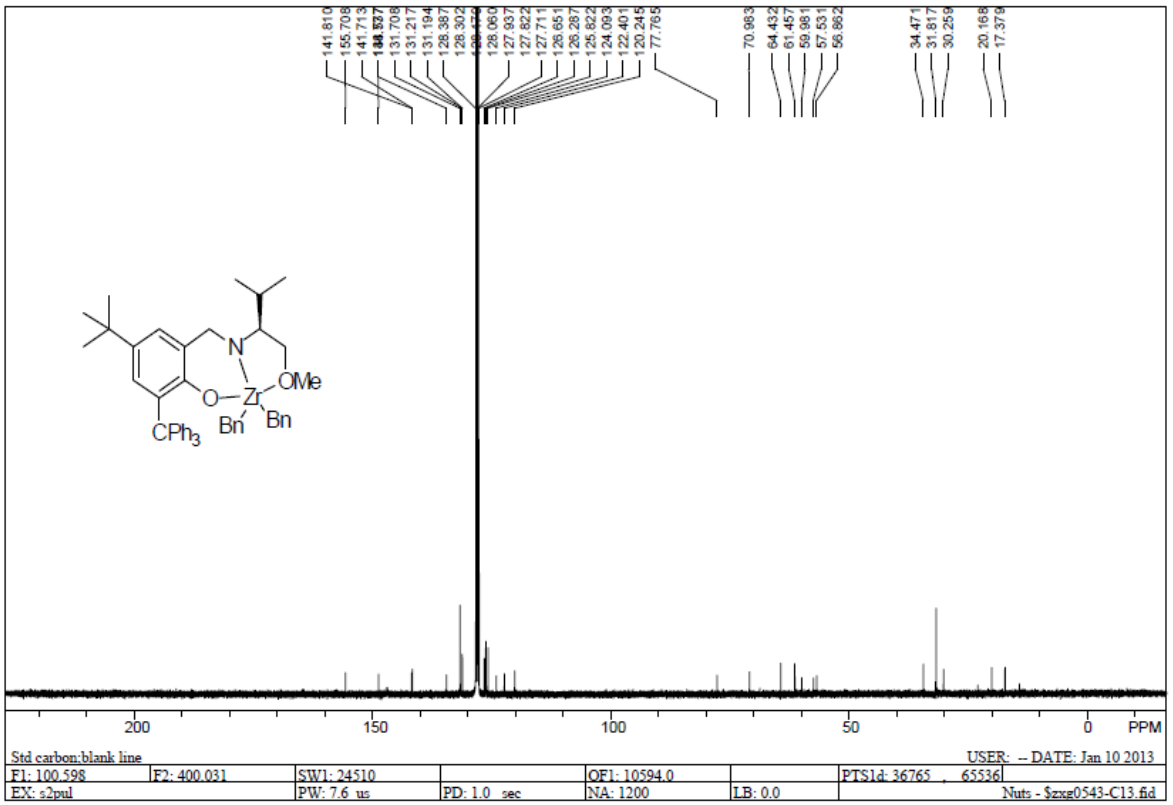

N
Zr
OEt
O
Bn Bn
Ad
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 4 2010
F1: 300.028 F2: 300.028 SW1: 6006 OF1: 1523.0 PTS1d: 11970 , 16384
EX: s2pul PW: 4.2 us PD: 1.0 sec NA: 32 LB: 0.0 Nuts - $zxg0455a.fid
PPM

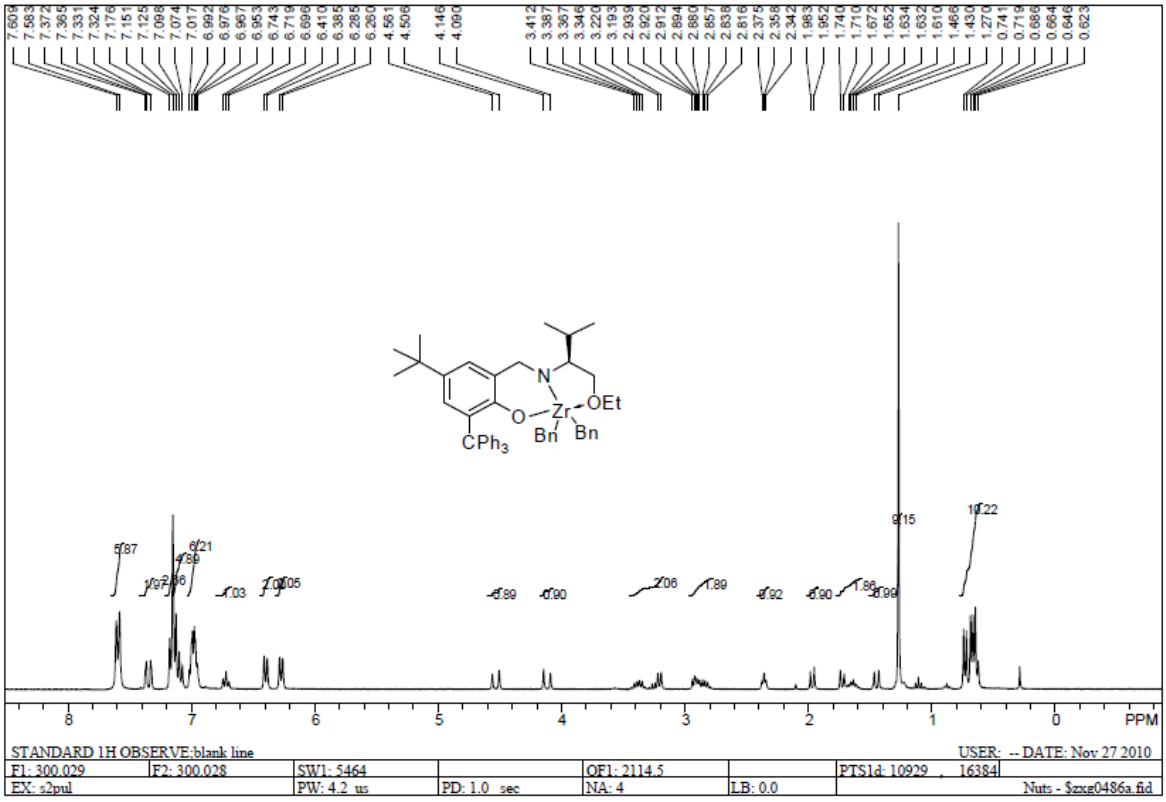

N
Zr
OEt
O
Bn Bn
Ad
zm11-18-4C
USER: -- DATE: Nov 8 2010
F1: 75.450 F2: 300.028 SW1: 18797 OF1: 7776.3 PTS1d: 30075 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 10000 LB: 0.0 Nuts - $zxg0455-c13a.fid
PPM

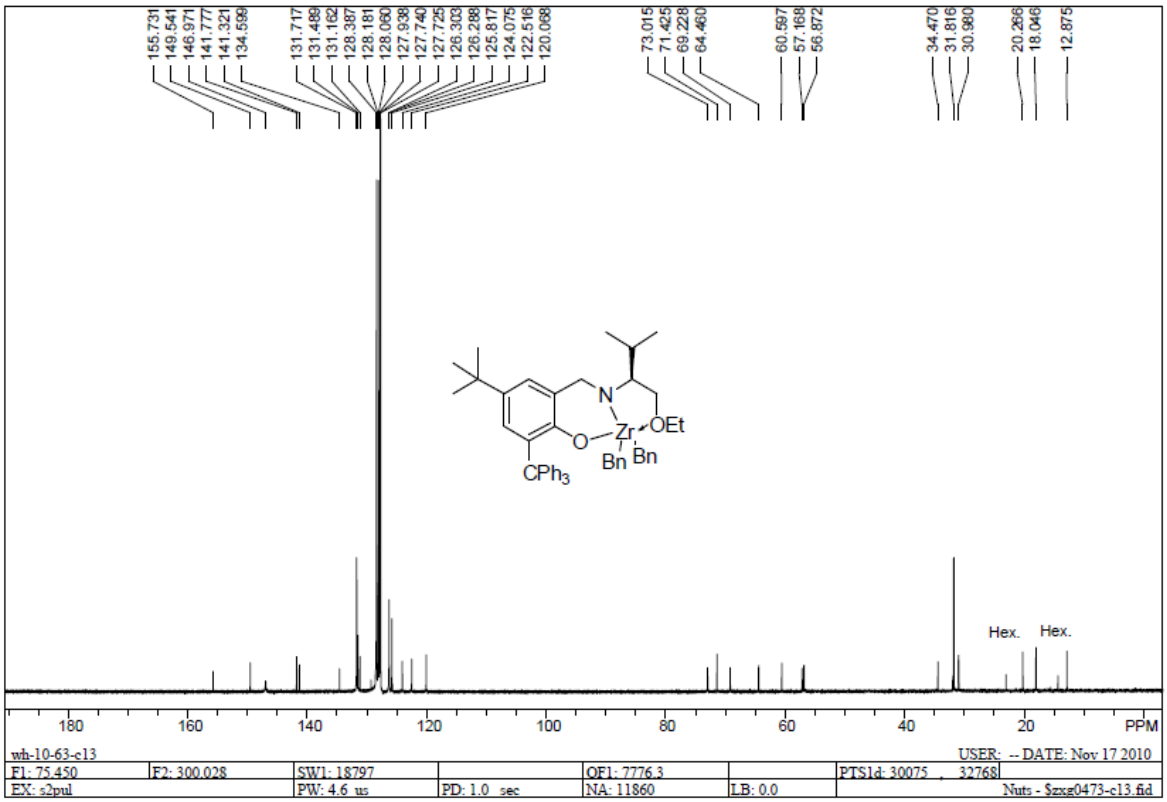

N
Zr
OEt
O
Bn
Bn
SiPh3
6.15
9.11
6.14
2.21
2.01
1.00
1.01
2.51
1.02
1.03
1.00
2.00
1.00
10.30
5.85
3.98
10
8
6
4
2
0
PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Dec 21 2010
F1: 300.029
F2: 300.028
SW1: 4803
OF1: 2020.1
PTS1d: 9579 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 24
LB: 0.0
Nuts - $zxgsiph3.fid

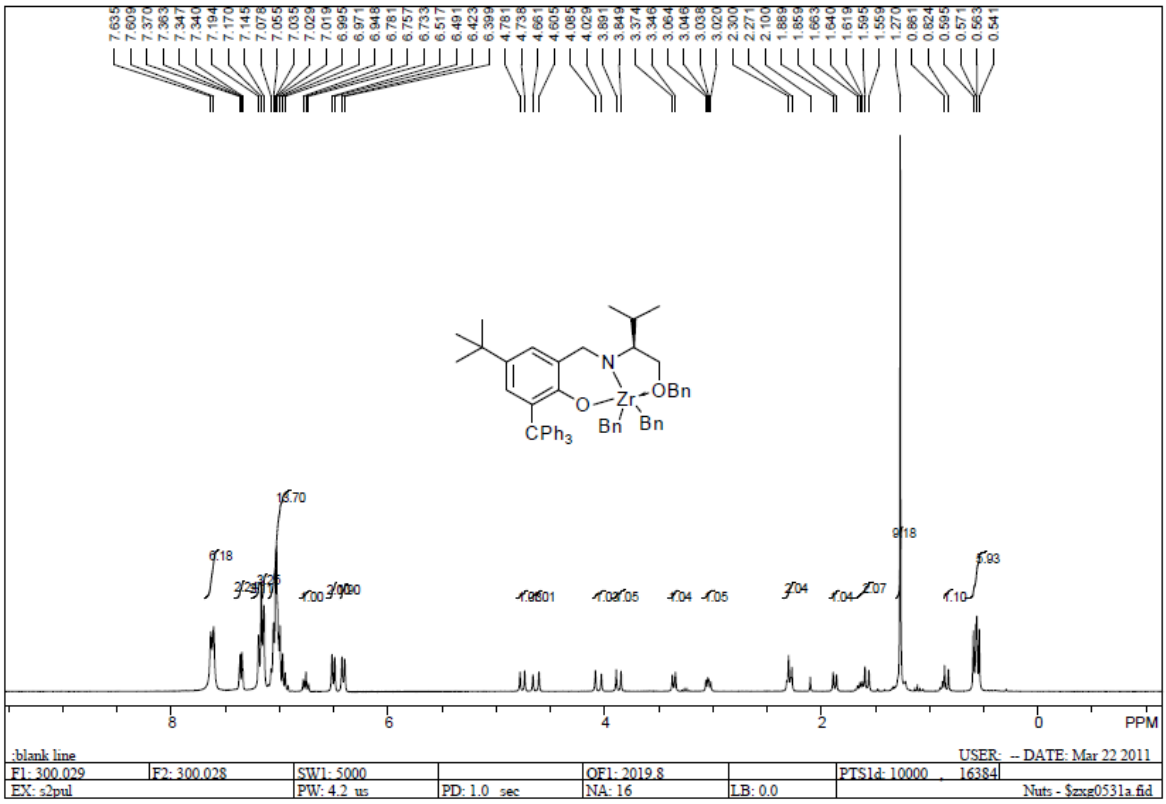

N
Zr
OEt
O
Bn
Bn
SiPh3
200
150
100
50
0
PPM
;blank line;blank line
USER: -- DATE: Mar 16 2013
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11086.5
PTS1d: 40000 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 240
LB: 0.0
Nuts - $zxgz1091a-C13.fid

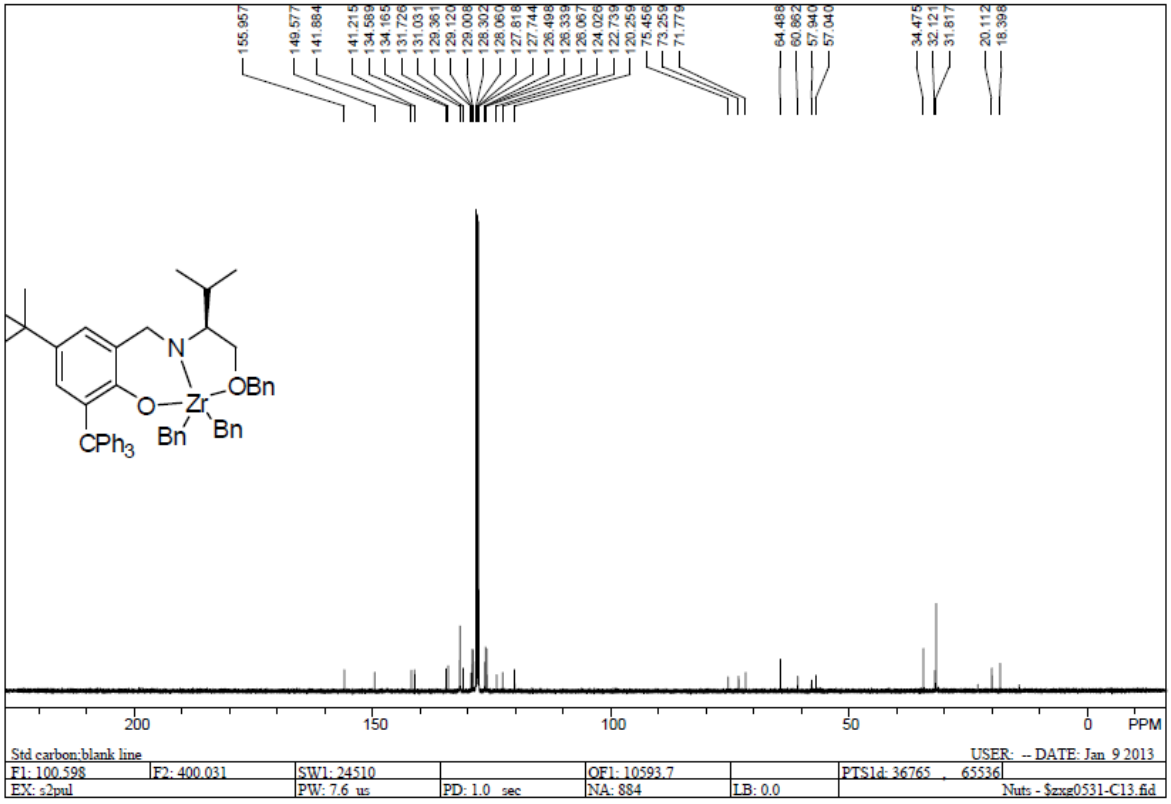

7.594 7.574 7.348 7.336 7.160 7.141 7.121 7.104 7.086 7.067 7.007 6.988 6.969 6.951 6.930 6.737 6.719 6.701 6.346 6.328 6.245 6.226 4.470 4.428 4.130 4.089
3.093 3.078 3.072 3.057 3.008 3.002 2.987 2.981 2.682 2.408 2.398 1.906 1.882 1.668 1.644 1.631 1.619 1.615 1.602 1.469 1.442 1.265 0.751 0.725 0.693 0.676 0.616 0.599
N
O
Zr
OMe
Bn Bn
CPh3
6.19 2.29 8.10 6.22 1.12 2.03 2.00 0.99 0.99 1.03 1.04 3.00 0.99 1.02 2.14 1.15 9.37 3.08
10 8 6 4 2 PPM
;blank line;blank line;blank line
USER: -- DATE: Jan 10 2013
F1: 400.032 F2: 100.597 SW1: 7310 OF1: 2783.4 PTS1d: 21930 , 32768
EX: s2pul PW: 10.1 us PD: 1.0 sec NA: 12 LB: 0.0 Nuts - $zxg0543-H.fid

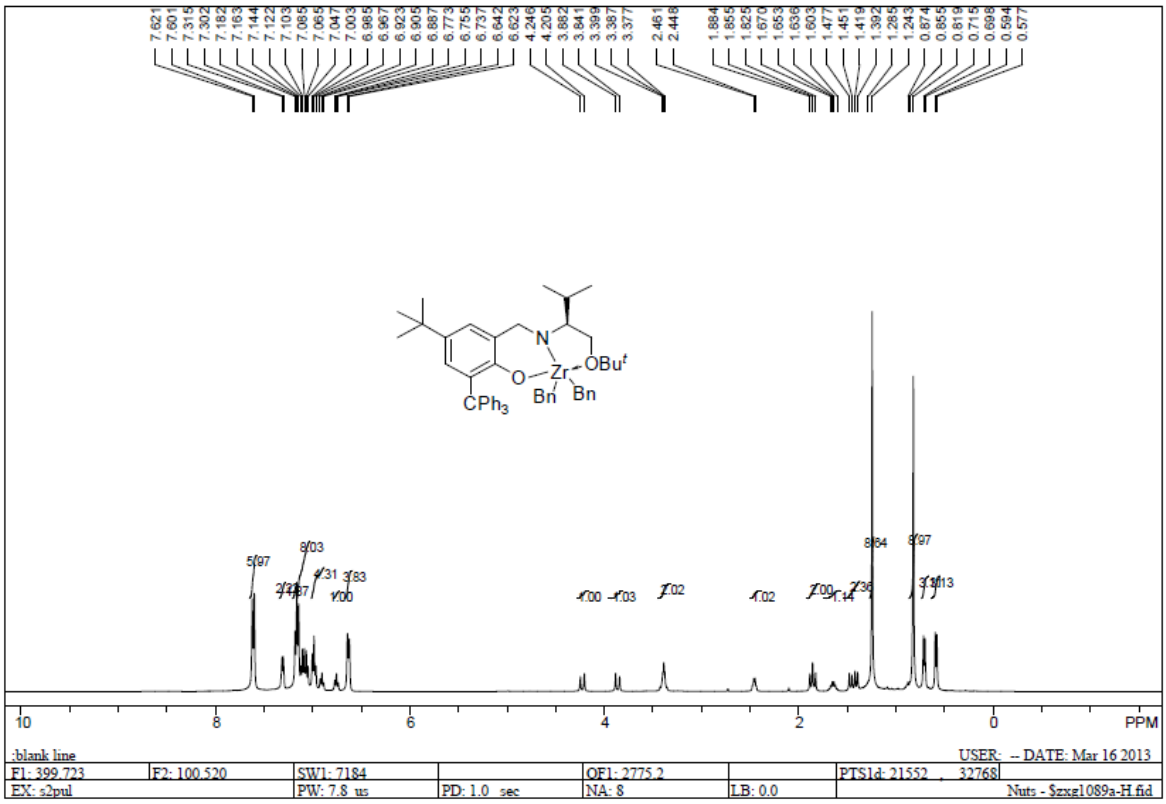

141.810 155.708 141.713 131.708 131.217 131.194 128.387 128.302 128.060 127.937 127.822 127.711 126.651 126.287 125.822 124.093 122.401 120.245 77.765
70.983 64.432 61.457 59.981 57.531 56.862
34.471 31.817 30.259 20.168 17.379
N
O
Zr
OMe
Bn Bn
CPh3
200 150 100 50 0 PPM
Std carbon;blank line
USER: -- DATE: Jan 10 2013
F1: 100.598 F2: 400.031 SW1: 24510 OF1: 10594.0 PTS1d: 36765 , 65536
EX: s2pul PW: 7.6 us PD: 1.0 sec NA: 1200 LB: 0.0 Nuts - $zxg0543-C13.fid

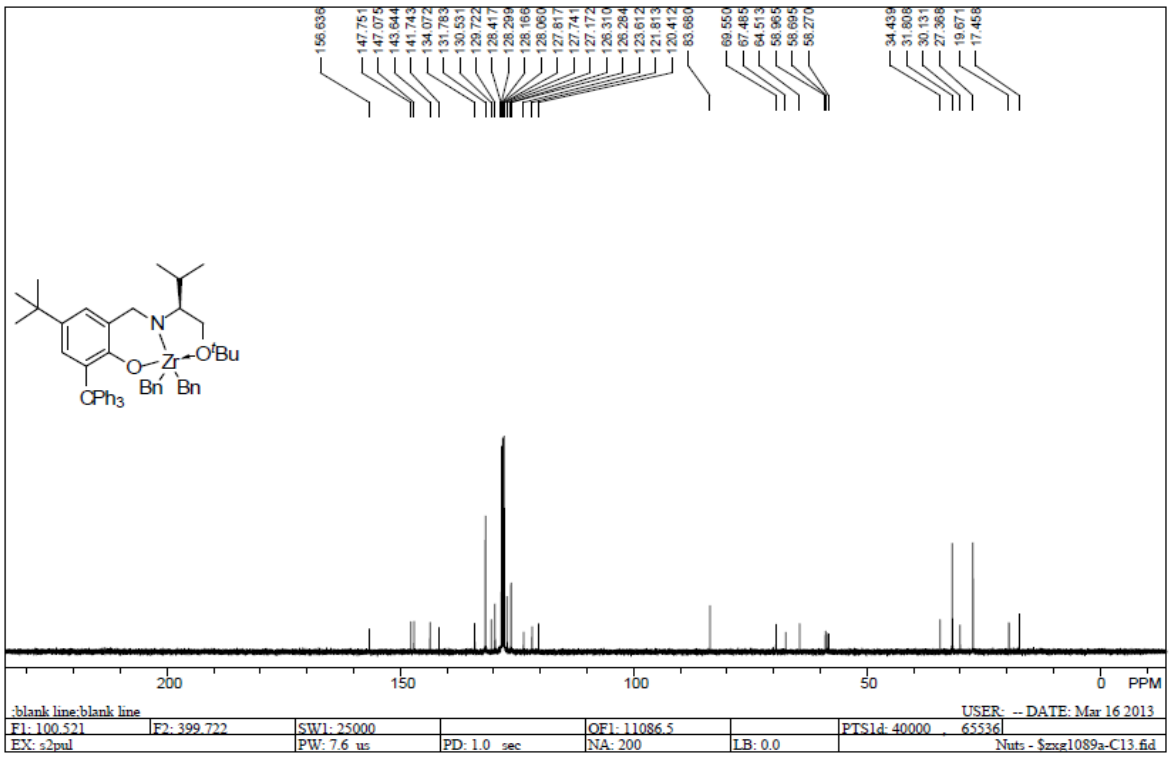

7.609 7.583 7.372 7.365 7.331 7.324 7.176 7.151 7.125 7.098 7.074 7.017 6.992 6.976 6.967 6.953 6.743 6.719 6.696 6.410 6.385 6.285 6.260 4.561 4.508 4.146 4.090 3.412 3.387 3.367 3.346 3.220 3.193 2.939 2.920 2.912 2.894 2.880 2.857 2.838 2.816 2.375 2.358 2.342 1.983 1.952 1.740 1.710 1.672 1.652 1.634 1.632 1.610 1.466 1.430 1.270 0.741 0.719 0.686 0.664 0.646 0.623
N
O
Zr
OEt
Bn Bn
CPh3
5.87 6.21 4.89 2.06 1.03 1.05 6.89 6.90 2.06 1.89 6.92 6.90 1.86 8.99 9.15 10.22
8 7 6 5 4 3 2 1 0 PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 27 2010
F1: 300.029 F2: 300.028 SW1: 5464 OF1: 2114.5 PTS1d: 10929 , 16384
EX: s2pul PW: 4.2 us PD: 1.0 sec NA: 4 LB: 0.0 Nuts - $zxg0486a.fid

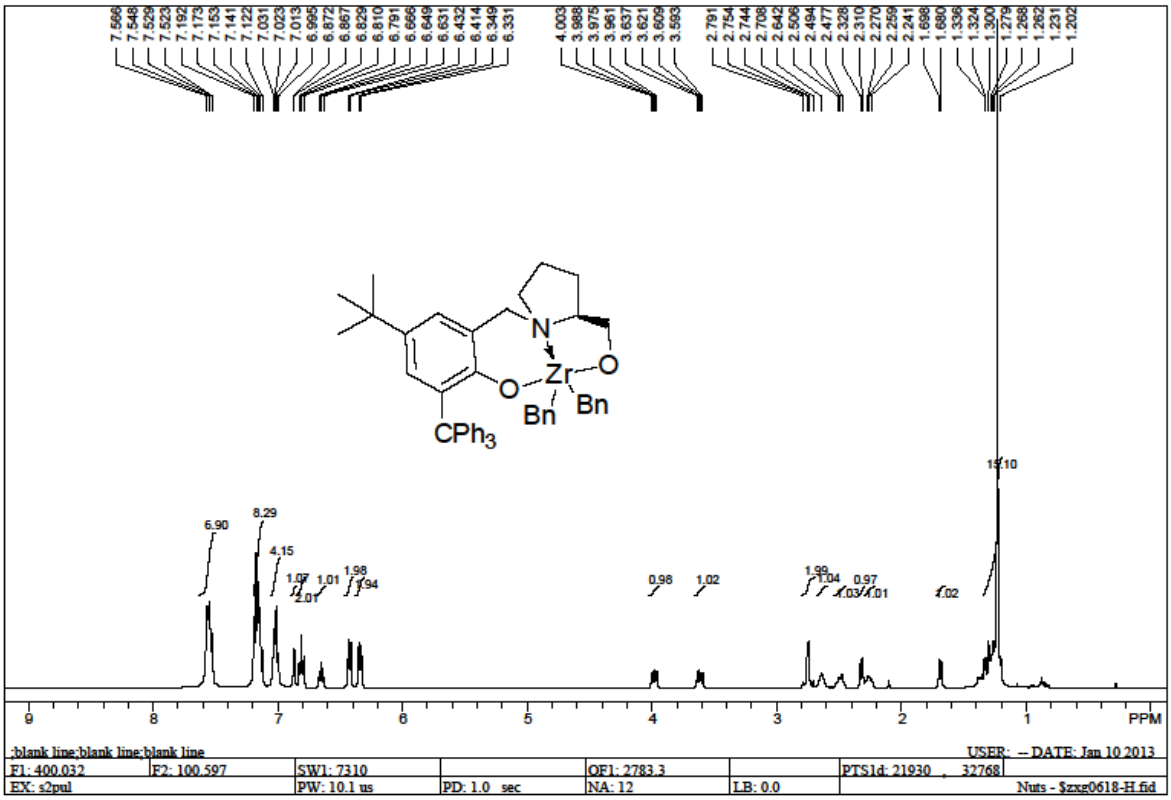

155.731 149.541 146.971 141.777 141.321 134.599 131.717 131.489 131.162 128.387 128.181 128.060 127.938 127.740 127.725 126.303 126.288 125.817 124.075 122.516 120.068
73.015 71.425 69.228 64.460 60.597 57.168 56.872 34.470 31.816 30.980 20.266 18.046 12.875
N
O
Zr
OEt
Bn Bn
CPh3
Hex. Hex.
180 160 140 120 100 80 60 40 20 PPM
wh-10-63-c13
USER: -- DATE: Nov 17 2010
F1: 75.450 F2: 300.028 SW1: 18797 OF1: 7776.3 PTS1d: 30075 , 32768
EX: s2pul PW: 4.6 us PD: 1.0 sec NA: 11860 LB: 0.0 Nuts - $zxg0473-c13.fid

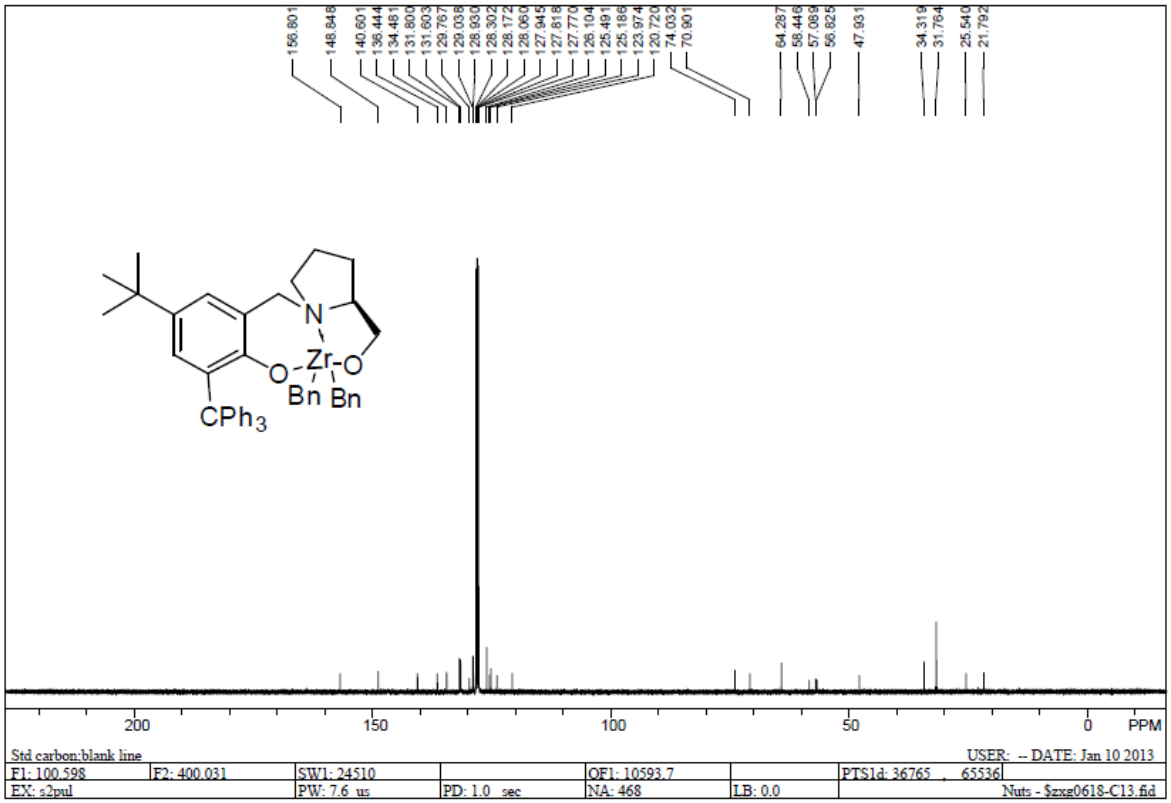

7.635
7.609
7.370
7.363
7.347
7.340
7.194
7.170
7.145
7.078
7.055
7.029
7.019
6.995
6.971
6.948
6.781
6.757
6.733
6.517
6.491
6.423
6.399
4.781
4.738
4.661
4.605
4.085
4.029
3.891
3.849
3.374
3.346
3.064
3.046
3.038
3.020
2.300
2.271
2.100
1.889
1.859
1.663
1.640
1.619
1.595
1.559
1.270
0.861
0.824
0.595
0.571
0.563
0.541
N
O
Zr
OBn
Bn
Bn
CPh3
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Mar 22 2011
F1: 300.029
F2: 300.028
SW1: 5000
OF1: 2019.8
PTS1d: 10000 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $zxg0531a.fid

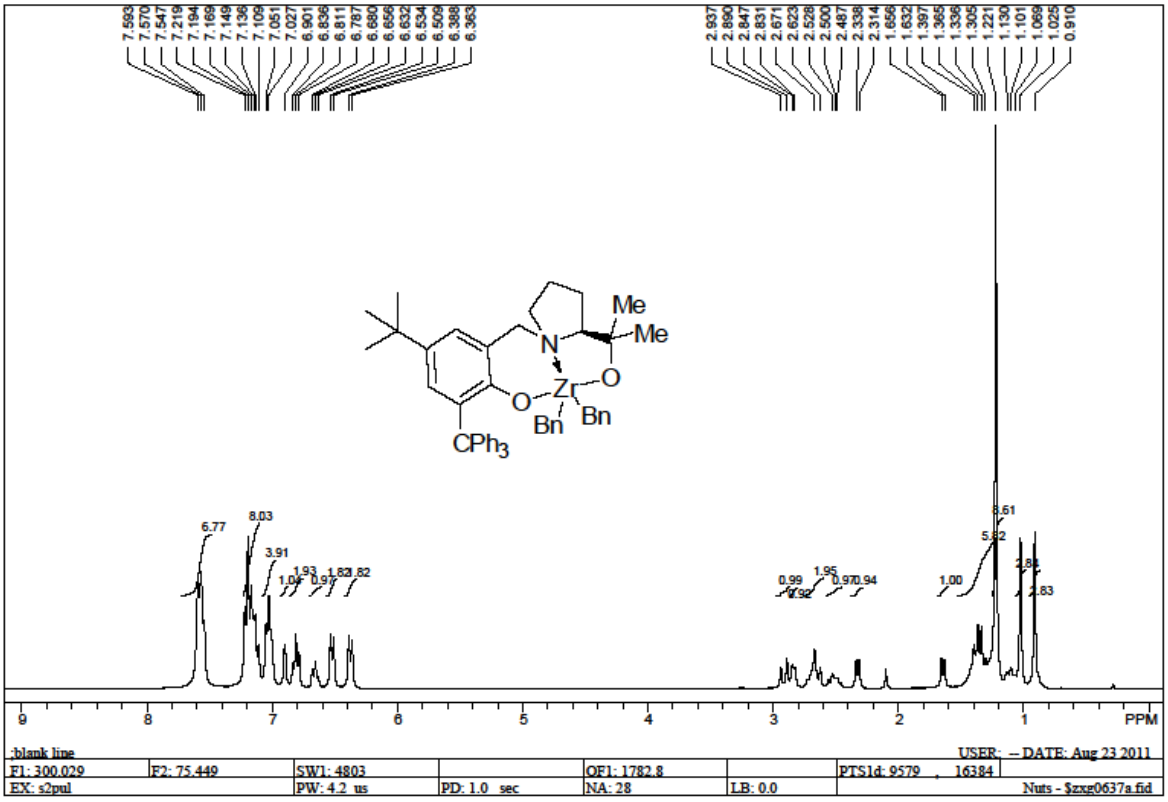

155.957
149.577
141.884
141.215
134.589
134.165
131.726
131.031
129.361
129.120
129.008
128.302
128.060
127.818
127.744
126.498
126.339
126.067
124.026
122.739
120.259
75.456
73.259
71.779
64.488
60.882
57.940
57.040
34.475
32.121
31.817
20.112
18.398
N
O
Zr
OBn
Bn
Bn
CPh3
200
150
100
50
0
PPM
Std carbon:blank line
USER: -- DATE: Jan 9 2013
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10593.7
PTS1d: 36765 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 884
LB: 0.0
Nuts - $zxg0531-C13.fid

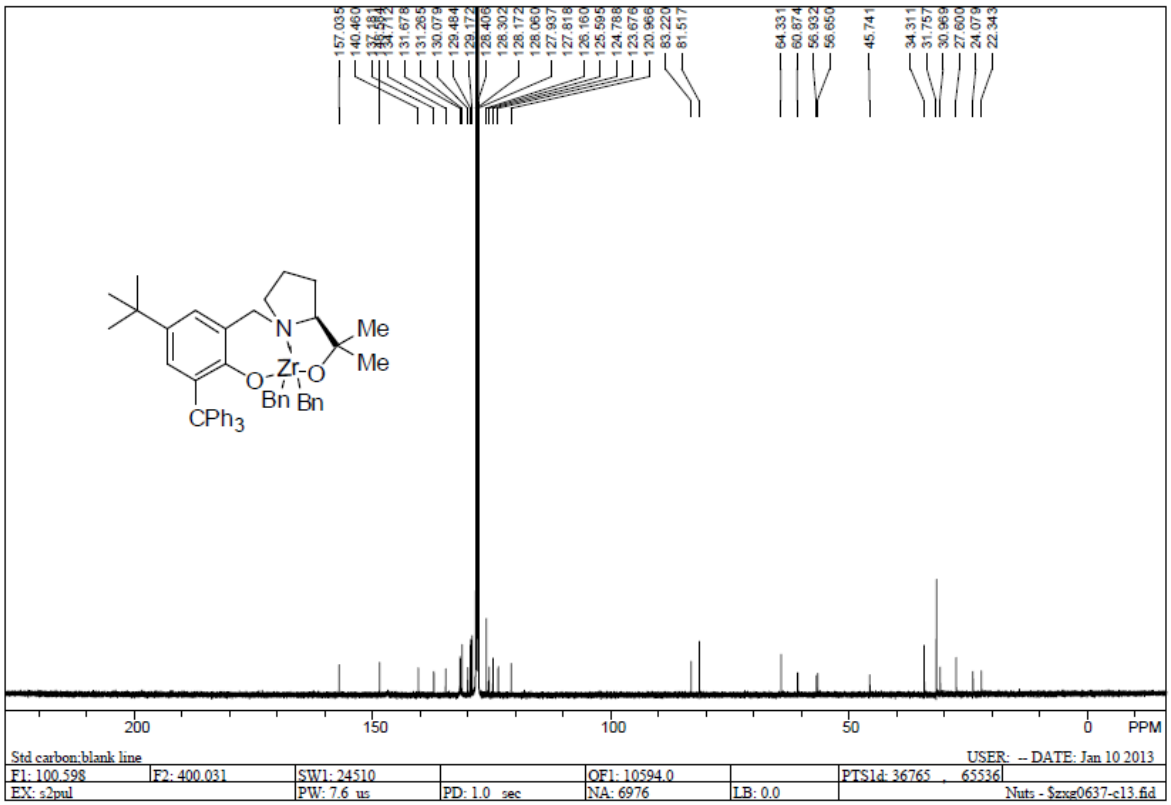

7.621
7.601
7.315
7.302
7.182
7.163
7.144
7.122
7.103
7.065
7.065
7.047
7.003
6.985
6.967
6.923
6.905
6.887
6.773
6.755
6.737
6.642
6.623
4.246
4.205
3.882
3.841
3.399
3.387
3.377
2.461
2.448
1.884
1.855
1.825
1.670
1.653
1.636
1.603
1.477
1.451
1.419
1.392
1.285
1.243
0.874
0.855
0.819
0.715
0.698
0.594
0.577
N
Zr
O
OBu^t
Bn
Bn
CPh$_3$
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Mar 16 2013
F1: 399.723
F2: 100.520
SW1: 7184
OF1: 2775.2
PTS1d: 21552 , 32768
EX: s2pul
PW: 7.8 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $zxg1089a-H.fid

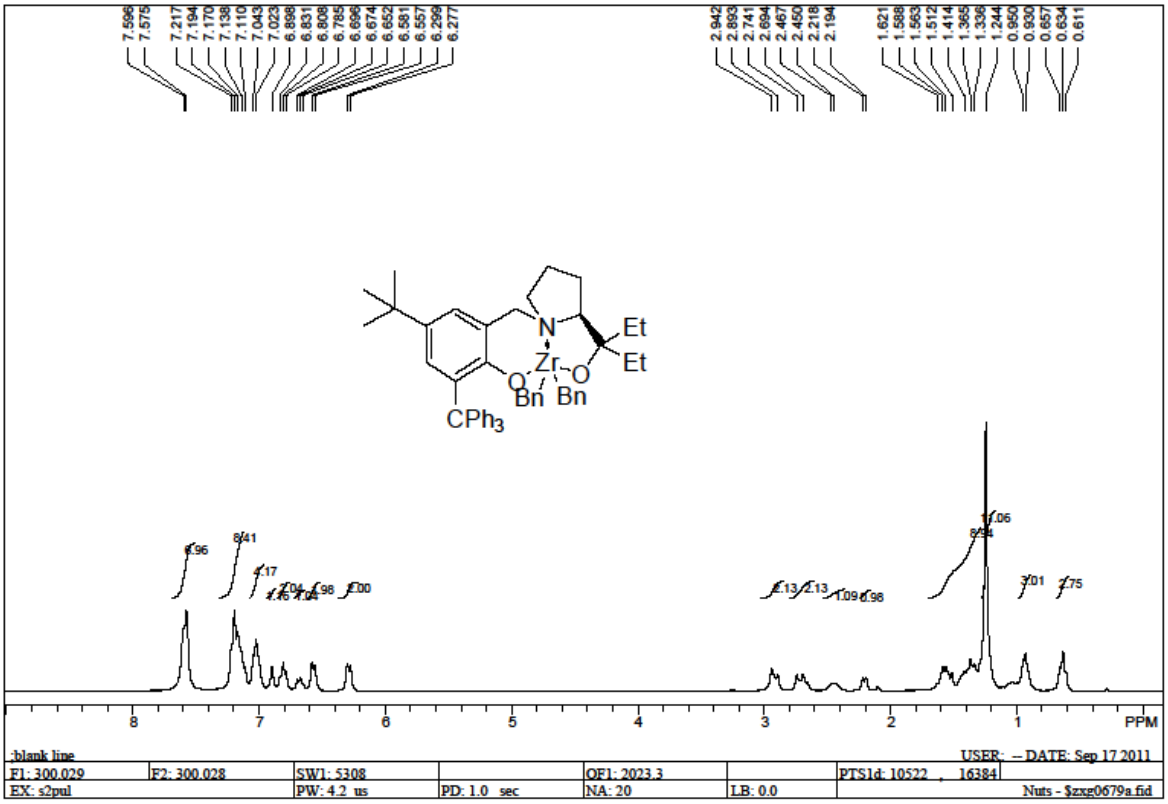

156.636
147.751
147.075
143.644
141.743
134.072
131.783
130.531
129.722
128.417
128.299
128.166
128.060
127.817
127.741
127.172
126.310
126.284
123.612
121.813
120.412
83.680
69.550
67.485
64.513
58.965
58.695
58.270
34.439
31.806
30.131
27.368
19.671
17.458
N
Zr
O
O^{t}Bu
Bn
Bn
CPh$_3$
200
150
100
50
0
PPM
:blank line;blank line
USER: -- DATE: Mar 16 2013
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11086.5
PTS1d: 40000 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 200
LB: 0.0
Nuts - $zxg1089a-C13.fid

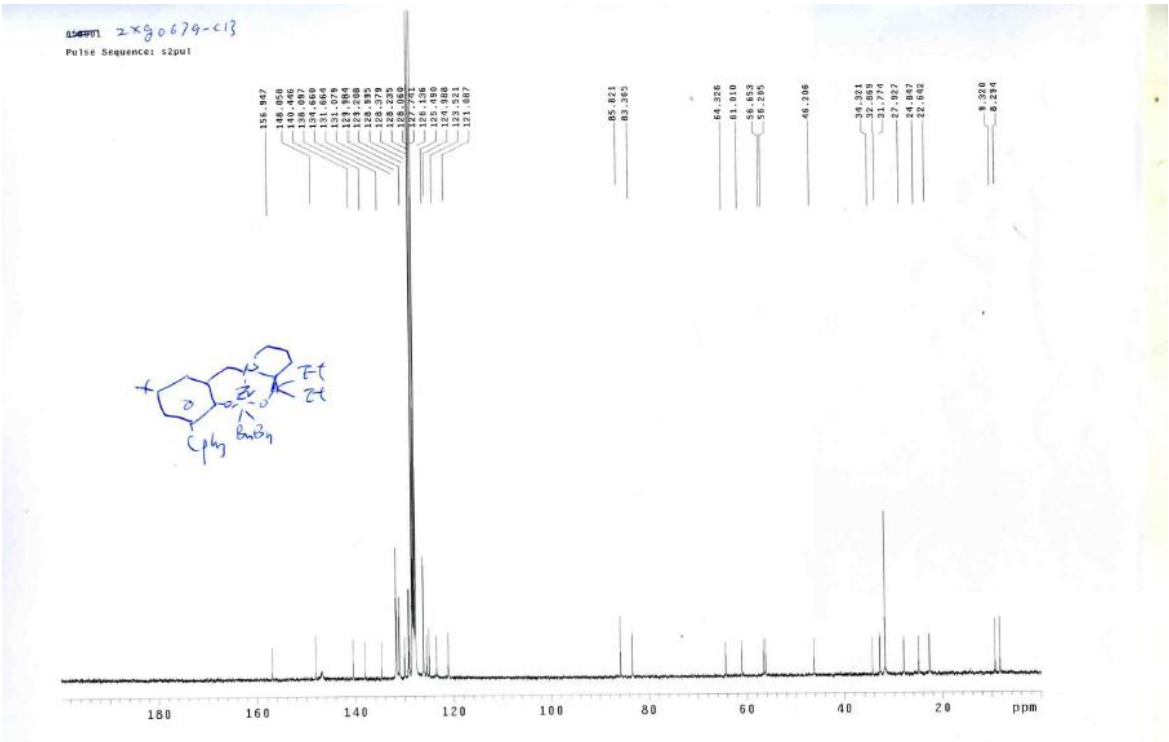

7.566 7.548 7.529 7.523 7.192 7.173 7.153 7.141 7.122 7.031 7.023 7.013 6.995 6.872 6.867 6.829 6.810 6.791 6.666 6.649 6.631 6.432 6.414 6.349 6.331
4.003 3.988 3.975 3.961 3.637 3.621 3.609 3.593
2.791 2.754 2.744 2.708 2.642 2.506 2.494 2.477 2.328 2.310 2.270 2.259 2.241 1.698 1.680 1.336 1.324 1.300 1.279 1.268 1.262 1.231 1.202
N
Zr
O
O
Bn
Bn
CPh3
6.90
8.29
4.15
1.07
1.01
1.98
1.94
2.01
0.98
1.02
1.99
1.04
0.97
1.03
1.01
1.02
19.10
9 8 7 6 5 4 3 2 1 PPM
;blank line;blank line;blank line
USER: -- DATE: Jan 10 2013
F1: 400.032 F2: 100.597 SW1: 7310 OF1: 2783.3 PTS1d: 21930 , 32768
EX: s2pul PW: 10.1 us PD: 1.0 sec NA: 12 LB: 0.0 Nuts - $zxg0618-H.fid

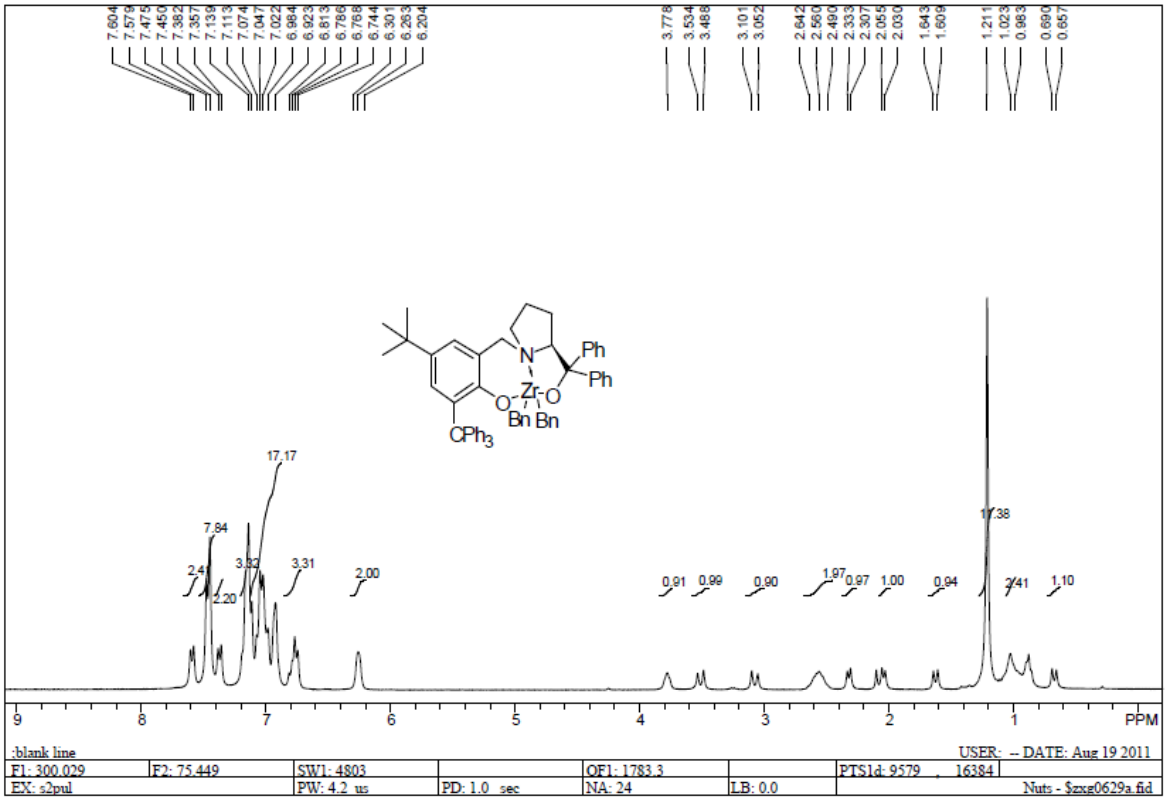

156.801 148.848 140.601 138.444 134.481 131.800 131.603 129.767 129.038 128.930 128.302 128.172 128.060 127.945 127.818 127.770 126.104 125.491 125.186 123.974 120.720 74.032 70.901
64.287 58.445 57.089 56.825
47.931
34.319 31.764 25.540 21.792
N
Zr
O
O
Bn
Bn
CPh3
200 150 100 50 0 PPM
Std carbon;blank line
USER: -- DATE: Jan 10 2013
F1: 100.598 F2: 400.031 SW1: 24510 OF1: 10593.7 PTS1d: 36765 , 65536
EX: s2pul PW: 7.6 us PD: 1.0 sec NA: 468 LB: 0.0 Nuts - $zxg0618-C13.fid

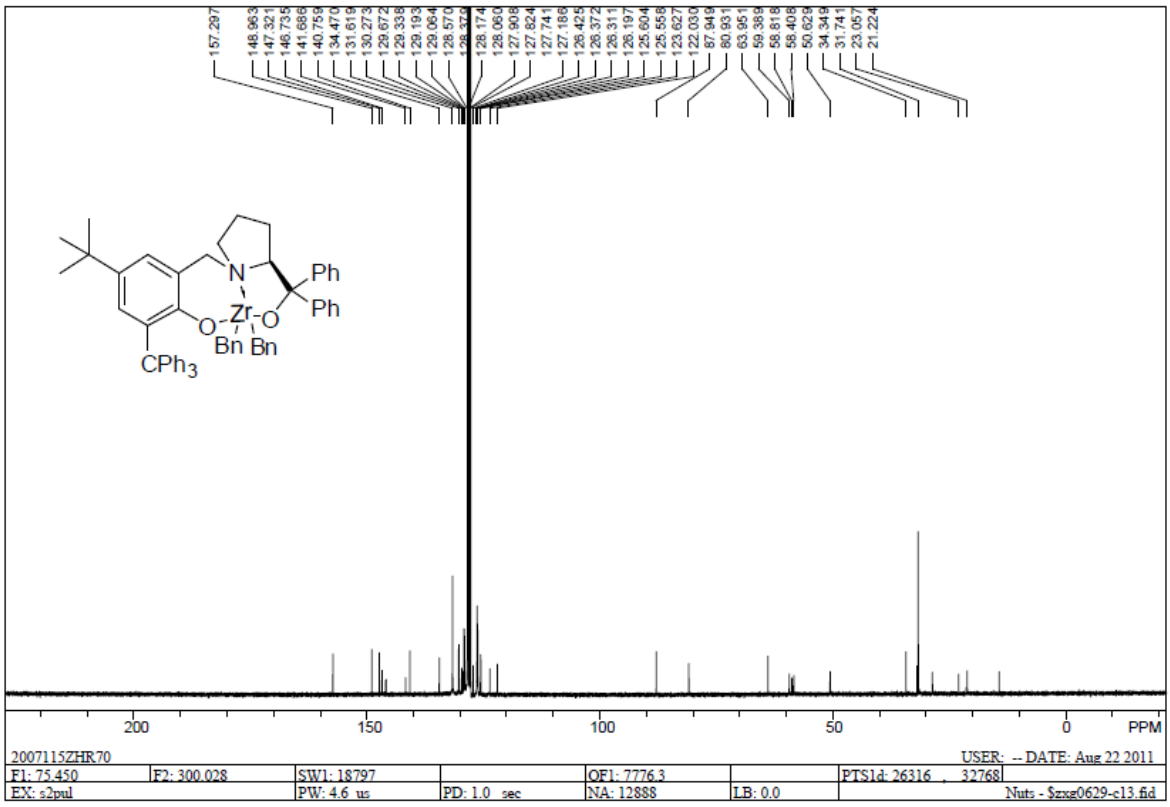

7.593 7.570 7.547 7.219 7.194 7.169 7.149 7.136 7.109 7.051 7.027 6.901 6.836 6.811 6.787 6.680 6.656 6.632 6.534 6.509 6.388 6.363
2.937 2.890 2.847 2.831 2.671 2.623 2.528 2.500 2.487 2.338 2.314 1.656 1.632 1.397 1.365 1.336 1.305 1.221 1.130 1.101 1.069 1.025 0.910
Me
Me
N
Zr
O
O
Bn
Bn
CPh3
6.77
8.03
3.91
1.93
1.82
1.82
0.99
1.95
0.97
0.94
1.00
3.61
5.32
2.84
2.83
9 8 7 6 5 4 3 2 1 PPM
:blank line
USER: -- DATE: Aug 23 2011
F1: 300.029 F2: 75.449 SW1: 4803 OF1: 1782.8 PTS1d: 9579 16384
EX: s2pul PW: 4.2 us PD: 1.0 sec NA: 28 LB: 0.0 Nuts - $zxg0637a.fid

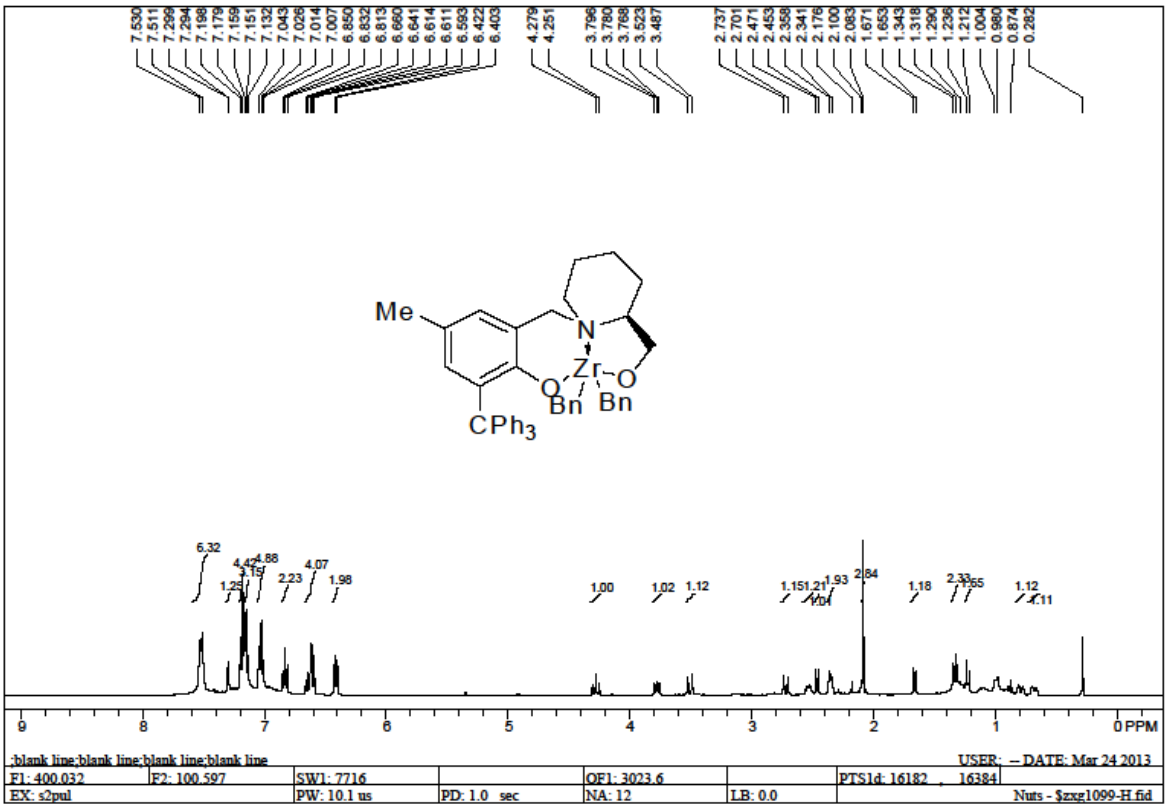

157.035 140.460 131.678 131.285 130.079 129.484 129.172 128.406 128.302 128.172 128.060 127.937 127.818 126.160 125.595 124.788 123.676 120.966 83.220 81.517
64.331 60.874 56.932 56.650 45.741 34.311 31.757 30.969 27.600 24.079 22.343
N
Me
Me
Zr
O
O
Bn
Bn
CPh3
200 150 100 50 0 PPM
Std carbon:blank line
USER: -- DATE: Jan 10 2013
F1: 100.598 F2: 400.031 SW1: 24510 OF1: 10594.0 PTS1d: 36765 65536
EX: s2pul PW: 7.6 us PD: 1.0 sec NA: 6976 LB: 0.0 Nuts - $zxg0637-c13.fid

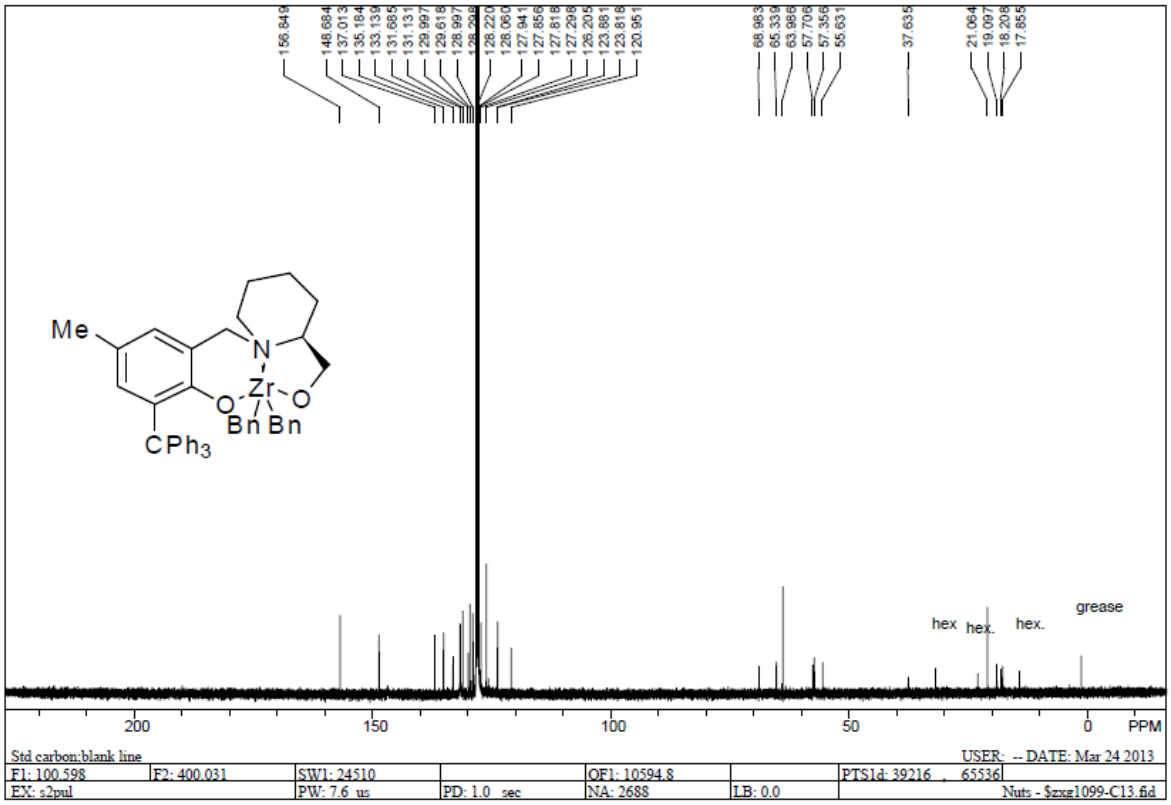

7.596
7.575
7.217
7.194
7.170
7.138
7.110
7.043
7.023
6.898
6.831
6.808
6.785
6.696
6.674
6.652
6.581
6.557
6.299
6.277
2.942
2.893
2.741
2.694
2.457
2.450
2.218
2.194
1.621
1.588
1.563
1.512
1.414
1.365
1.336
1.244
0.950
0.930
0.657
0.634
0.611
N
Et
Et
Zr
O
O
Bn
Bn
CPh3
8.96
8.41
4.17
2.04
1.98
2.00
2.13
2.13
1.09
0.98
17.06
8.94
3.01
2.75
8
7
6
5
4
3
2
1
PPM
:blank line
USER: -- DATE: Sep 17 2011
F1: 300.029
F2: 300.028
SW1: 5308
OF1: 2023.3
PTS1d: 10522 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $zxg0679a.fid

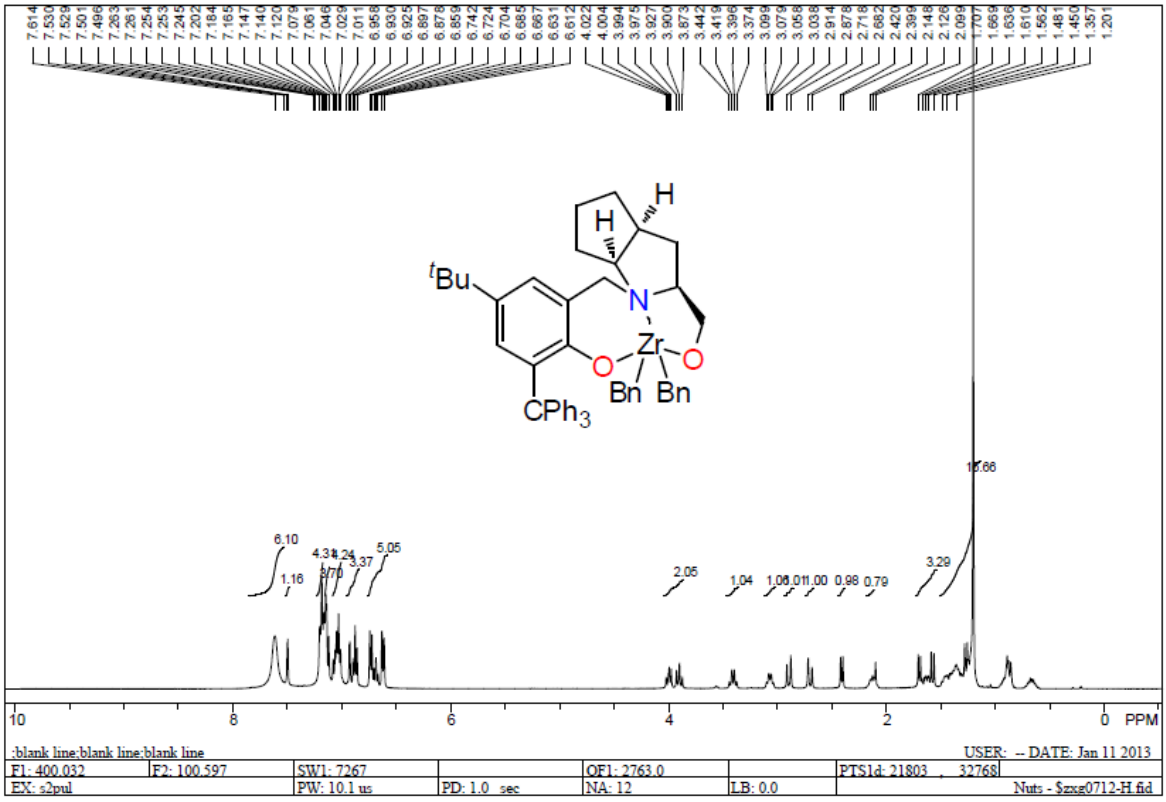

zxg0679-c13
Pulse Sequence: s2pul
156.947
148.058
140.446
136.097
134.660
131.666
131.079
129.984
129.208
128.995
128.239
128.235
128.060
127.741
126.136
125.480
124.388
123.521
121.087
85.821
83.365
64.326
61.010
56.653
56.285
46.206
34.381
33.858
31.774
27.922
24.867
22.642
9.300
8.244
180
160
140
120
100
80
60
40
20
ppm

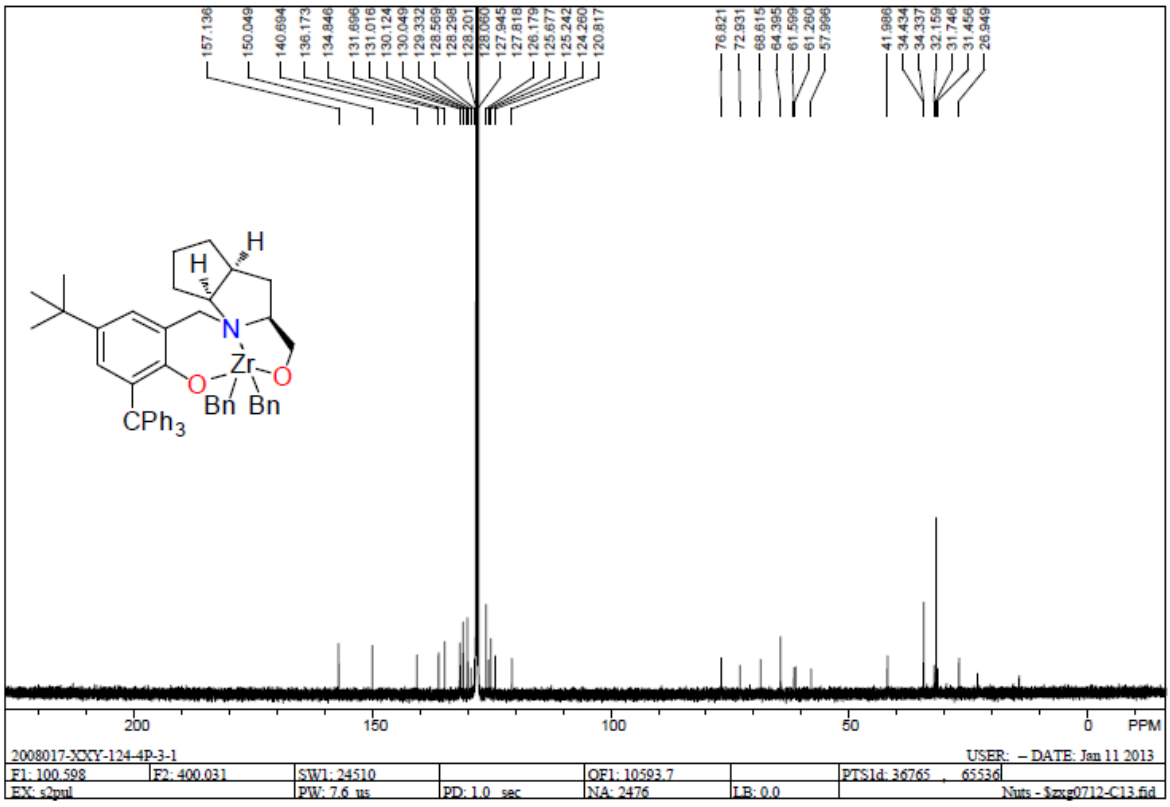

7.604
7.579
7.475
7.450
7.382
7.357
7.139
7.113
7.074
7.047
7.022
6.984
6.923
6.813
6.786
6.768
6.744
6.301
6.283
6.204
3.778
3.534
3.488
3.101
3.052
2.642
2.560
2.490
2.333
2.307
2.055
2.030
1.643
1.609
1.211
1.023
0.983
0.690
0.657
Ph
Ph
N
Zr
O
O
Bn Bn
CPh3
17.17
7.84
2.41
2.20
3.32
3.31
2.00
17.38
0.91
0.99
0.90
1.97
0.97
1.00
0.94
2.41
1.10
9
8
7
6
5
4
3
2
1
PPM
:blank line
USER: -- DATE: Aug 19 2011
F1: 300.029
F2: 75.449
SW1: 4803
OF1: 1783.3
PTS1d: 9579 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 24
LB: 0.0
Nuts - $zxg0629a.fid

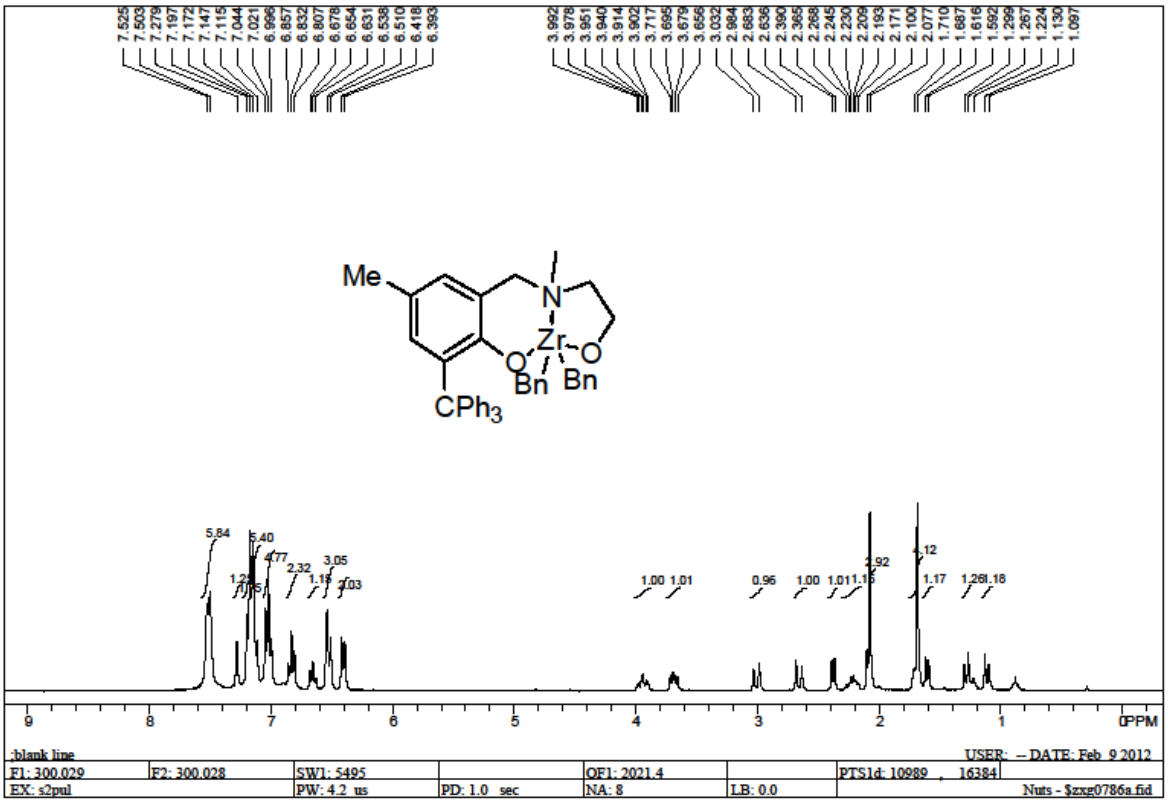

157.297
148.963
147.321
146.735
141.686
140.759
134.470
131.619
130.273
129.672
129.338
129.193
129.064
128.570
128.374
128.174
128.060
127.908
127.824
127.741
127.186
126.425
126.372
126.311
126.197
125.604
125.558
123.627
122.030
87.949
80.931
63.951
59.389
58.818
58.408
50.629
34.349
31.741
23.057
21.224
Ph
Ph
N
Zr
O
O
Bn Bn
CPh3
200
150
100
50
0
PPM
2007115ZHR70
USER: -- DATE: Aug 22 2011
F1: 75.450
F2: 300.028
SW1: 18797
OF1: 7776.3
PTS1d: 26316 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 12888
LB: 0.0
Nuts - $zxg0629-c13.fid

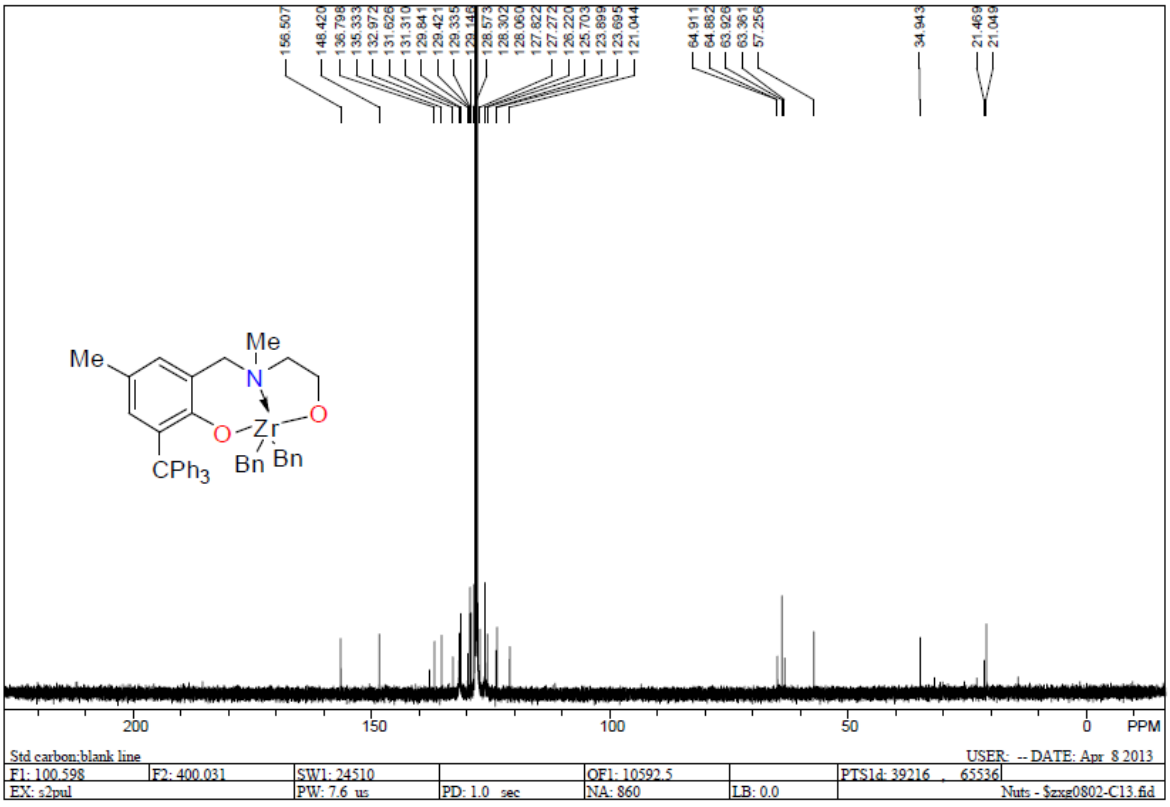

7.530
7.511
7.299
7.294
7.198
7.179
7.159
7.151
7.132
7.043
7.026
7.014
7.007
6.850
6.832
6.813
6.660
6.641
6.614
6.611
6.593
6.422
6.403
4.279
4.251
3.796
3.780
3.768
3.523
3.487
2.737
2.701
2.471
2.453
2.358
2.341
2.176
2.100
2.083
1.671
1.653
1.343
1.318
1.290
1.236
1.212
1.004
0.980
0.874
0.282
Me
N
Zr
O
O
Bn Bn
CPh3
6.32
4.42
4.88
3.15
1.25
2.23
4.07
1.98
1.00
1.02
1.12
1.15
1.21
1.93
2.84
1.18
2.33
1.55
1.12
1.11
9
8
7
6
5
4
3
2
1
0 PPM
;blank line;blank line;blank line;blank line
USER: -- DATE: Mar 24 2013
F1: 400.032
F2: 100.597
SW1: 7716
OF1: 3023.6
PTS1d: 16182 , 16384
EX: s2pul
PW: 10.1 us
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - $zxg1099-H.fid

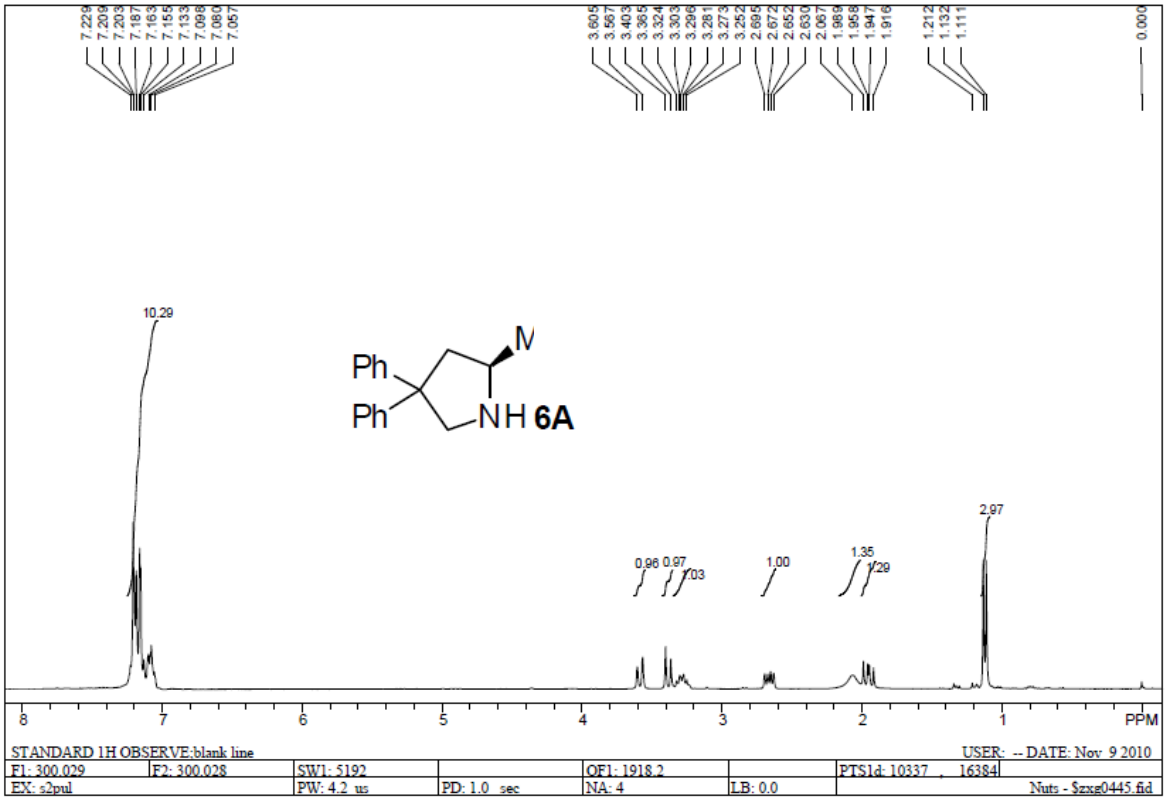

156.849
148.684
137.013
135.184
133.139
131.685
131.131
129.997
129.618
128.997
128.298
128.220
128.060
127.941
127.856
127.818
127.298
126.205
123.881
123.818
120.951
68.983
65.339
63.986
57.706
57.356
55.631
37.635
21.064
19.097
18.208
17.855
Me
N
Zr
O
O
Bn Bn
CPh3
hex
hex.
hex.
grease
200
150
100
50
0 PPM
Std carbon;blank line
USER: -- DATE: Mar 24 2013
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10594.8
PTS1d: 39216 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 2688
LB: 0.0
Nuts - $zxg1099-C13.fid

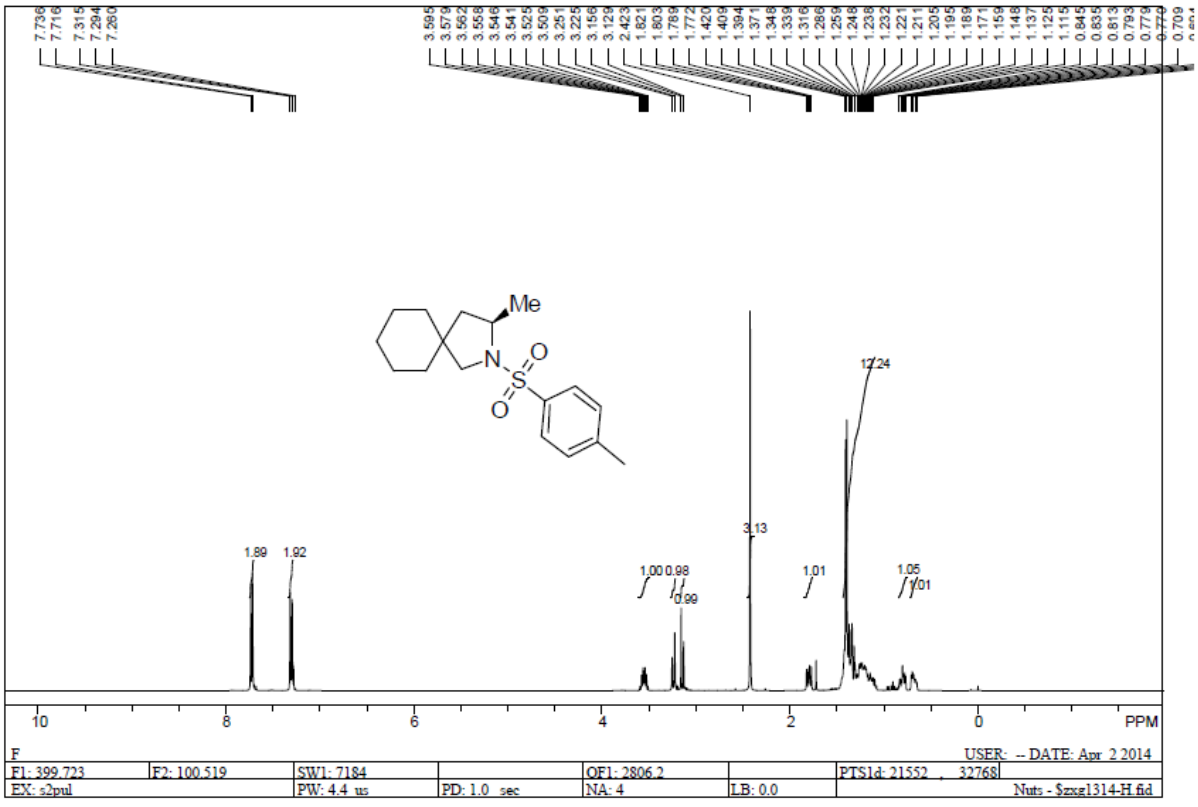

tBu
H
H
N
Zr
O
O
Bn Bn
CPh3
6.10
1.16
4.34
4.24
3.70
3.37
5.05
2.05
1.04
1.06
1.01
1.00
0.98
0.79
3.29
15.66
10
8
6
4
2
0 PPM
:blank line:blank line:blank line
USER: -- DATE: Jan 11 2013
F1: 400.032 F2: 100.597 SW1: 7267 OF1: 2763.0 PTS1d: 21803 , 32768
EX: s2pul PW: 10.1 us PD: 1.0 sec NA: 12 LB: 0.0 Nuts - $zxg0712-H.fid

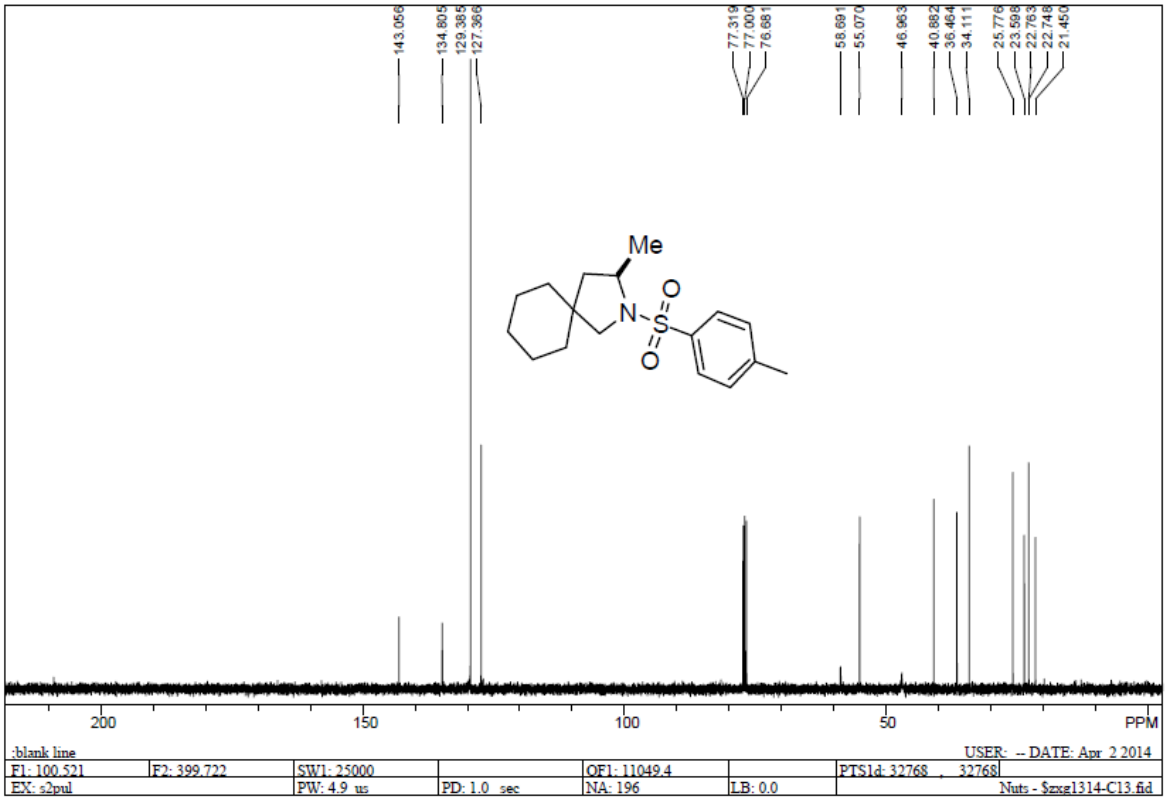

157.136
150.049
140.694
136.173
134.846
131.696
131.016
130.124
130.049
129.332
128.569
128.298
128.201
128.060
127.945
127.818
126.179
125.677
125.242
124.260
120.817
76.821
72.931
68.615
64.395
61.599
61.260
57.996
41.986
34.434
34.337
32.159
31.746
31.456
26.949
H
H
N
Zr
O
O
Bn Bn
CPh3
200
150
100
50
0 PPM
2008017-XXY-124-4P-3-1
USER: -- DATE: Jan 11 2013
F1: 100.598 F2: 400.031 SW1: 24510 OF1: 10593.7 PTS1d: 36765 , 65536
EX: s2pul PW: 7.6 us PD: 1.0 sec NA: 2476 LB: 0.0 Nuts - $zxg0712-C13.fid

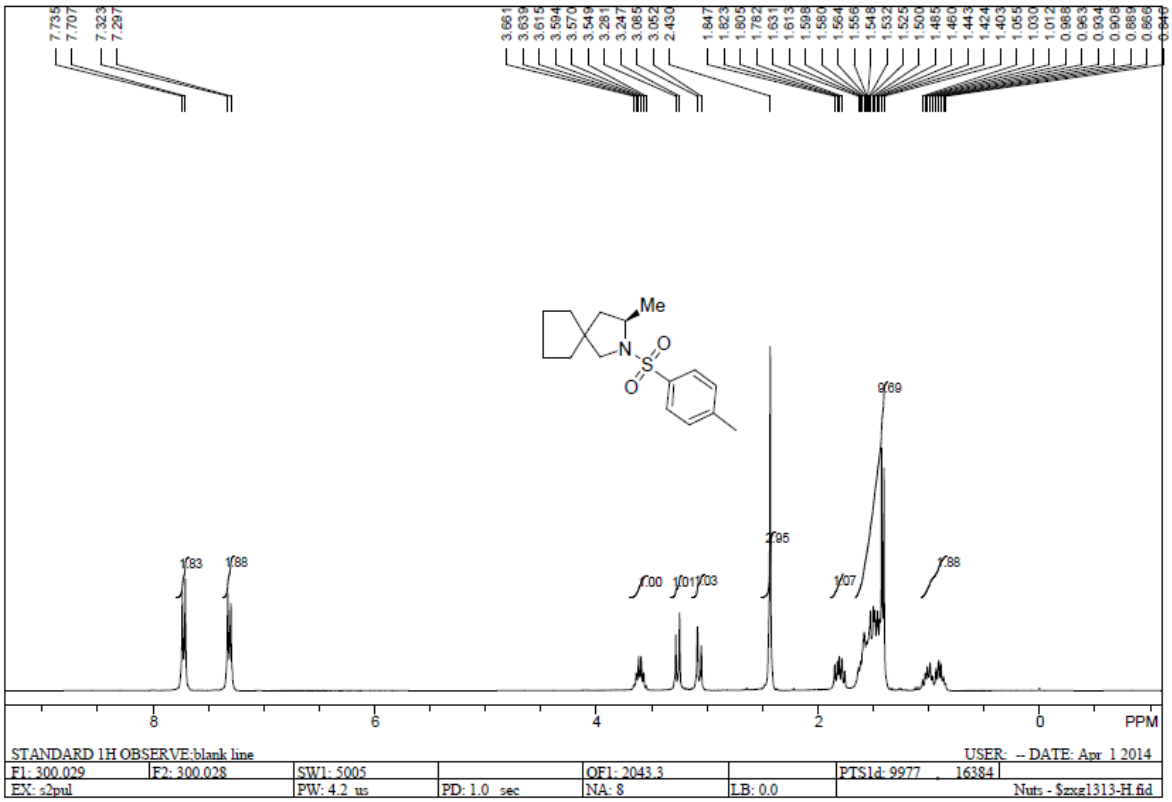

Me
N
Zr
O
O
Bn
Bn
CPh3
:blank line
USER: -- DATE: Feb 9 2012
F1: 300.029
F2: 300.028
SW1: 5495
OF1: 2021.4
PTS1d: 10989 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $zxg0786a.fid

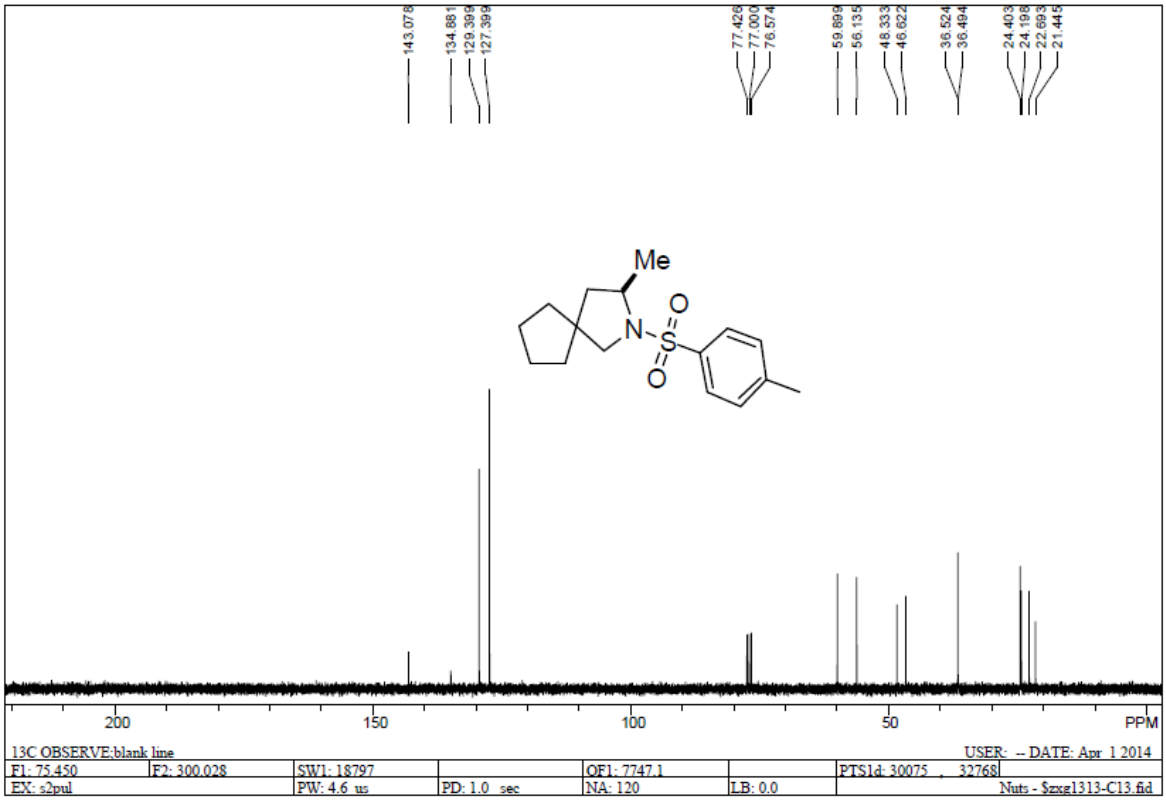

Me
Me
N
O
O
Zr
Bn
Bn
CPh3
Std carbon:blank line
USER: -- DATE: Apr 8 2013
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10592.5
PTS1d: 39216 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 860
LB: 0.0
Nuts - $zxg0802-C13.fid

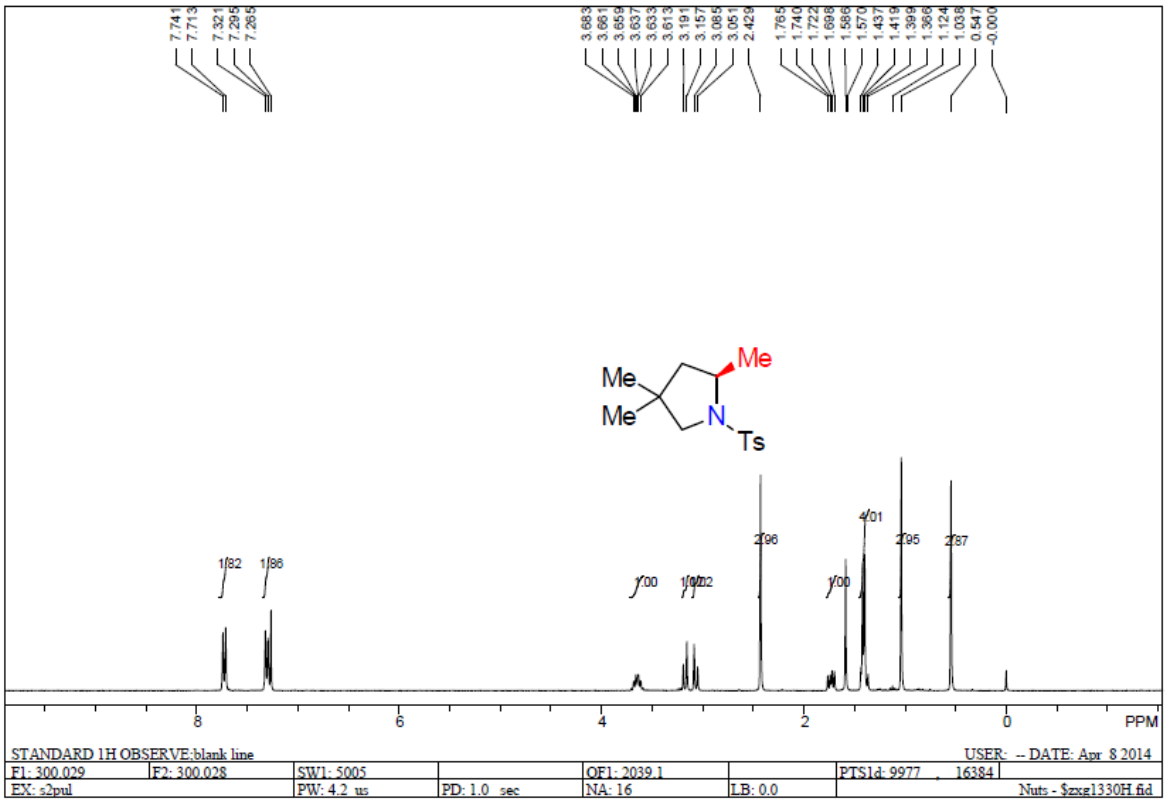

7.229
7.209
7.203
7.187
7.163
7.155
7.133
7.098
7.060
7.057
3.605
3.567
3.403
3.365
3.324
3.303
3.296
3.281
3.273
3.252
2.695
2.672
2.652
2.630
2.067
1.989
1.958
1.947
1.916
1.212
1.132
1.111
0.000
10.29
Ph
Ph
NH
6A
0.96
0.97
1.03
1.00
1.35
1.29
2.97
8
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Nov 9 2010
F1: 300.029
F2: 300.028
SW1: 5192
OF1: 1918.2
PTS1d: 10337 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 4
LB: 0.0
Nuts - $zxg0445.fid


7.736
7.716
7.315
7.294
7.260
3.595
3.579
3.562
3.558
3.546
3.541
3.525
3.509
3.251
3.225
3.156
3.129
2.423
1.821
1.803
1.789
1.772
1.420
1.409
1.394
1.371
1.348
1.339
1.316
1.286
1.259
1.248
1.238
1.232
1.221
1.211
1.205
1.195
1.189
1.171
1.159
1.148
1.137
1.125
1.115
0.845
0.835
0.813
0.793
0.779
0.709
Me
N
S
O
O
1.89
1.92
1.00
0.98
0.99
3.13
1.01
12.24
1.05
1.01
10
8
6
4
2
0
PPM
F
USER: -- DATE: Apr 2 2014
F1: 399.723
F2: 100.519
SW1: 7184
OF1: 2806.2
PTS1d: 21552 , 32768
EX: s2pul
PW: 4.4 us
PD: 1.0 sec
NA: 4
LB: 0.0
Nuts - $zxg1314-H.fid


143.056
134.805
129.385
127.366
77.319
77.000
76.681
58.691
55.070
46.963
40.882
36.464
34.111
25.776
23.598
22.763
22.748
21.450
Me
N
S
O
O
200
150
100
50
PPM
:blank line
USER: -- DATE: Apr 2 2014
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11049.4
PTS1d: 32768 , 32768
EX: s2pul
PW: 4.9 us
PD: 1.0 sec
NA: 196
LB: 0.0
Nuts - $zxg1314-C13.fid


7.735
7.707
7.323
7.297
3.661
3.639
3.615
3.594
3.570
3.549
3.281
3.247
3.085
3.052
2.430
1.847
1.823
1.805
1.782
1.631
1.613
1.598
1.580
1.564
1.548
1.532
1.525
1.500
1.485
1.460
1.443
1.424
1.403
1.055
1.030
1.012
0.988
0.963
0.934
0.908
0.889
0.869
0.840
Me
N
S
O
O
1.83
1.88
2.00
2.01
2.03
2.95
3.07
9.69
1.88
8
6
4
2
0
PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Apr 1 2014
F1: 300.029
F2: 300.028
SW1: 5005
OF1: 2043.3
PTS1d: 9977 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $zxg1313-H.fid


143.078
134.681
129.399
127.399
77.426
77.000
76.574
59.899
56.135
48.333
46.622
36.524
36.494
24.403
24.198
22.693
21.445
Me
N
S
O
O
200
150
100
50
PPM
13C OBSERVE:blank line
USER: -- DATE: Apr 1 2014
F1: 75.450
F2: 300.028
SW1: 18797
OF1: 7747.1
PTS1d: 30075 , 32768
EX: s2pul
PW: 4.6 us
PD: 1.0 sec
NA: 120
LB: 0.0
Nuts - $zxg1313-C13.fid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7.321
7.295
7.285
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3.659
3.637
3.633
3.613
3.191
3.157
3.085
3.051
2.429
1.765
1.740
1.722
1.698
1.586
1.570
1.437
1.419
1.399
1.366
1.124
1.038
0.547
-0.000
Me
Me
N
Ts
1.82
1.86
2.96
4.01
2.95
2.87
8
6
4
2
0
PPM
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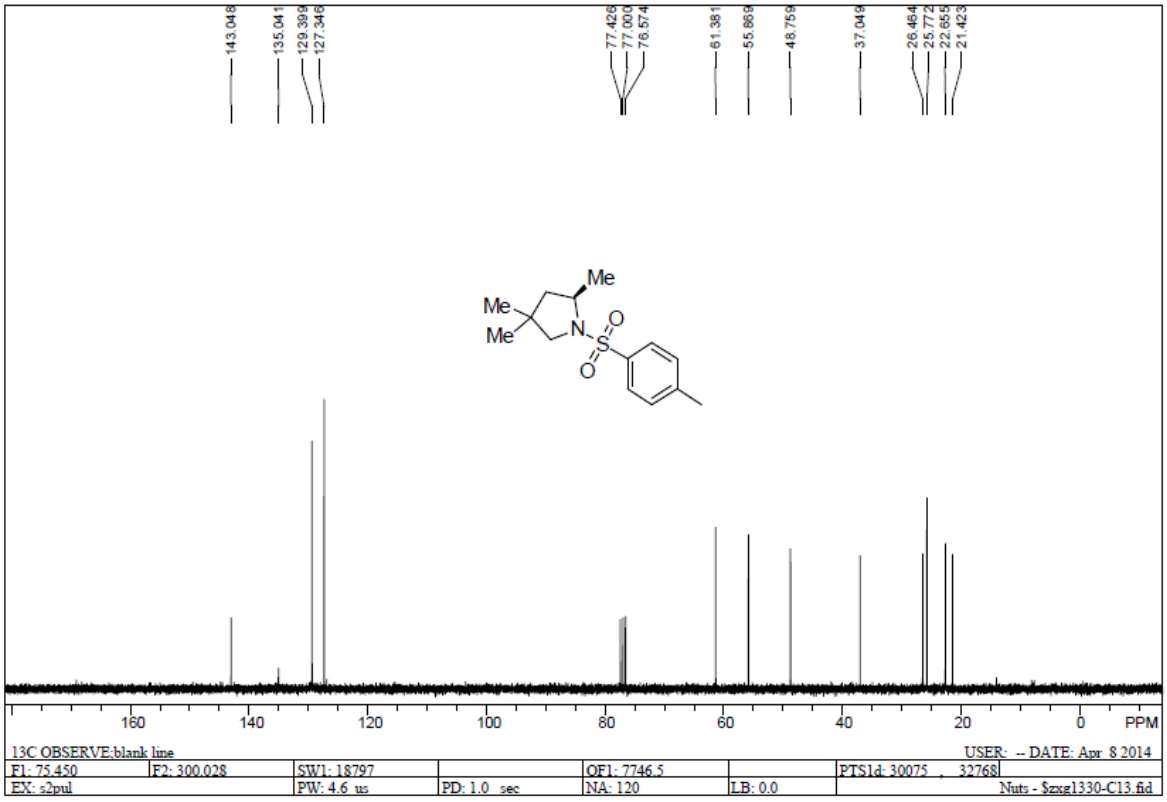
USER: -- DATE: Apr 8 2014
F1: 300.029
F2: 300.028
SW1: 5005
OF1: 2039.1
PTS1d: 9977 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $zxg1330H.fid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135.041
129.399
127.346
77.426
77.000
76.574
61.381
55.869
48.759
37.049
26.464
25.772
22.655
21.423
Me
Me
Me
N
S
O
O
160
140
120
100
80
60
40
20
0
PPM
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F2: 300.028
SW1: 18797
OF1: 7746.5
PTS1d: 30075 , 32768
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PW: 4.6 us
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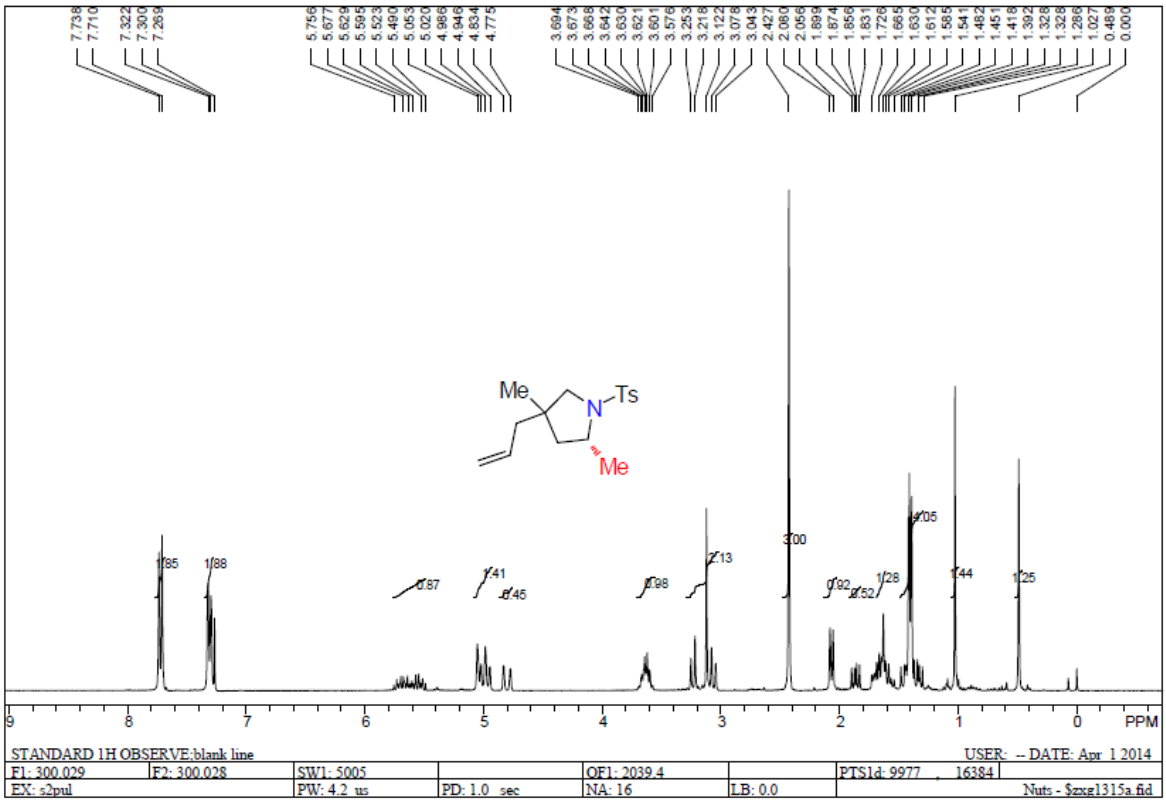
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7.710
7.322
7.300
7.269
5.756
5.677
5.629
5.595
5.523
5.490
5.053
5.020
4.986
4.946
4.834
4.775
3.694
3.673
3.668
3.642
3.630
3.621
3.601
3.576
3.253
3.218
3.122
3.078
3.043
2.427
2.060
2.056
1.899
1.874
1.856
1.831
1.728
1.665
1.630
1.612
1.585
1.541
1.482
1.451
1.418
1.392
1.328
1.328
1.286
1.027
0.489
0.000
Me
N
Ts
Me
1.85
1.88
0.87
1.41
0.45
0.98
2.13
3.00
0.92
0.52
1.28
4.05
1.44
1.25
9
8
7
6
5
4
3
2
1
0
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Apr 1 2014
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F2: 300.028
SW1: 5005
OF1: 2039.4
PTS1d: 9977 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA: 16
LB: 0.0
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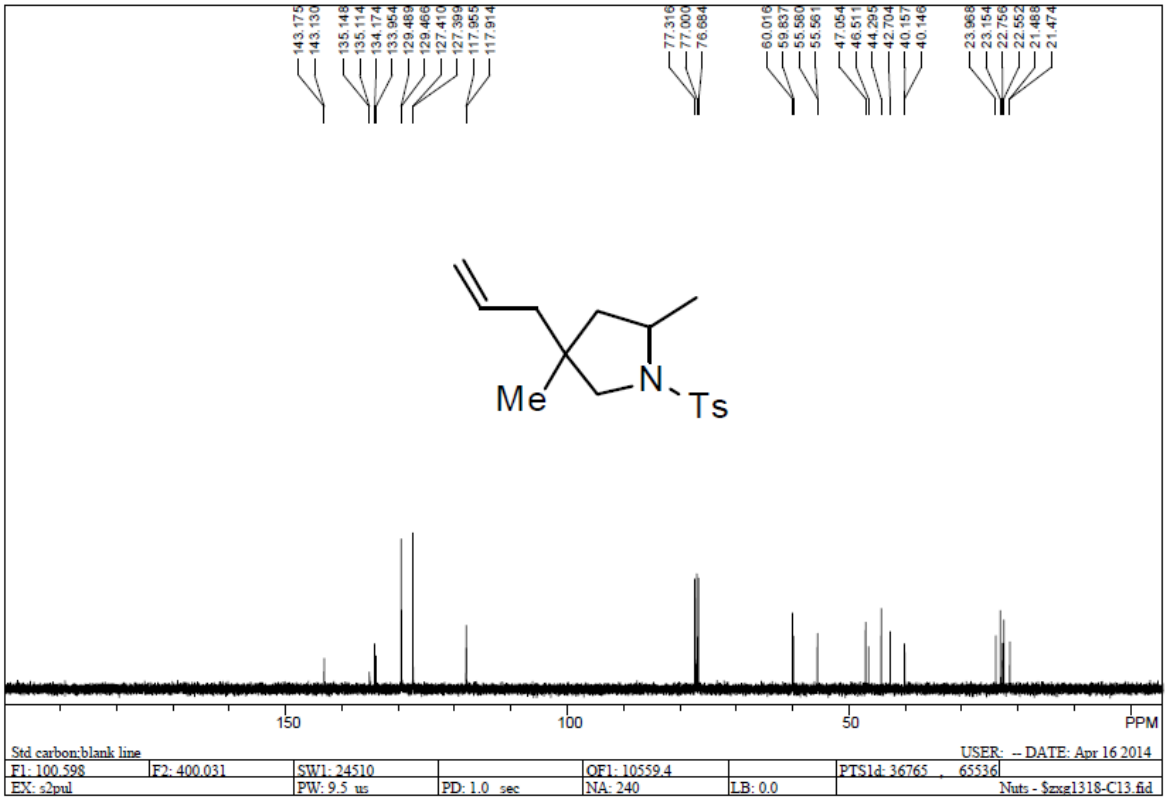
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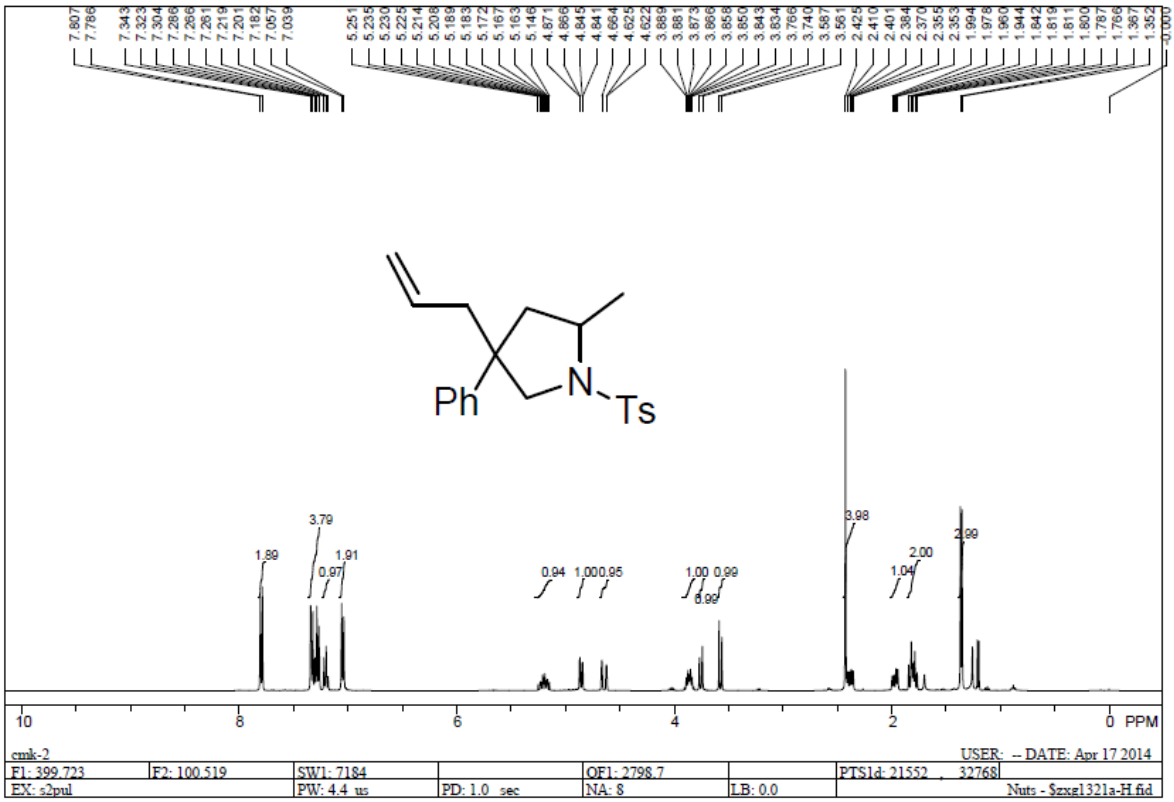
143.130
135.148
135.114
134.174
133.954
129.489
129.466
127.410
127.399
117.955
117.914
77.316
77.000
76.684
60.016
59.837
55.580
55.561
47.054
46.511
44.295
42.704
40.157
40.146
23.968
23.154
22.756
22.552
21.488
21.474
Me
N
Ts
150
100
50
PPM
Std carbon:blank line
USER: -- DATE: Apr 16 2014
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10559.4
PTS1d: 36765 , 65536
EX: s2pul
PW: 9.5 us
PD: 1.0 sec
NA: 240
LB: 0.0
Nuts - $zxg1318-C13.fid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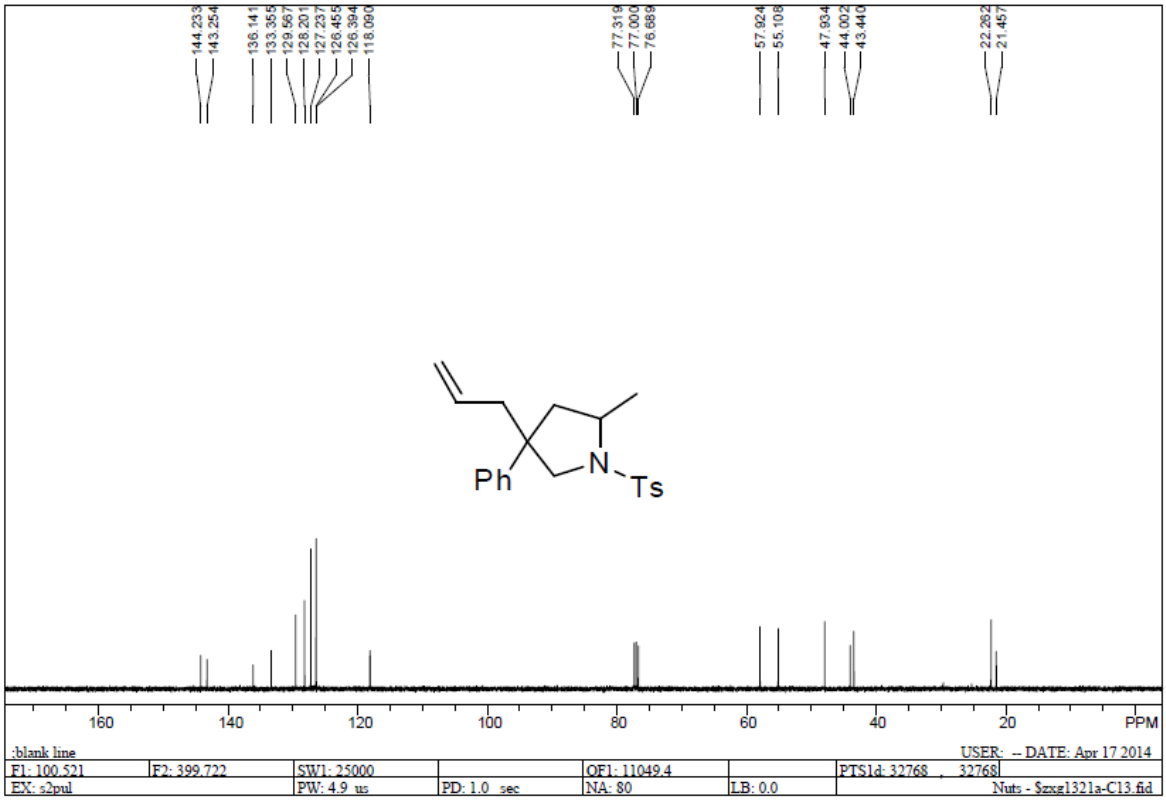
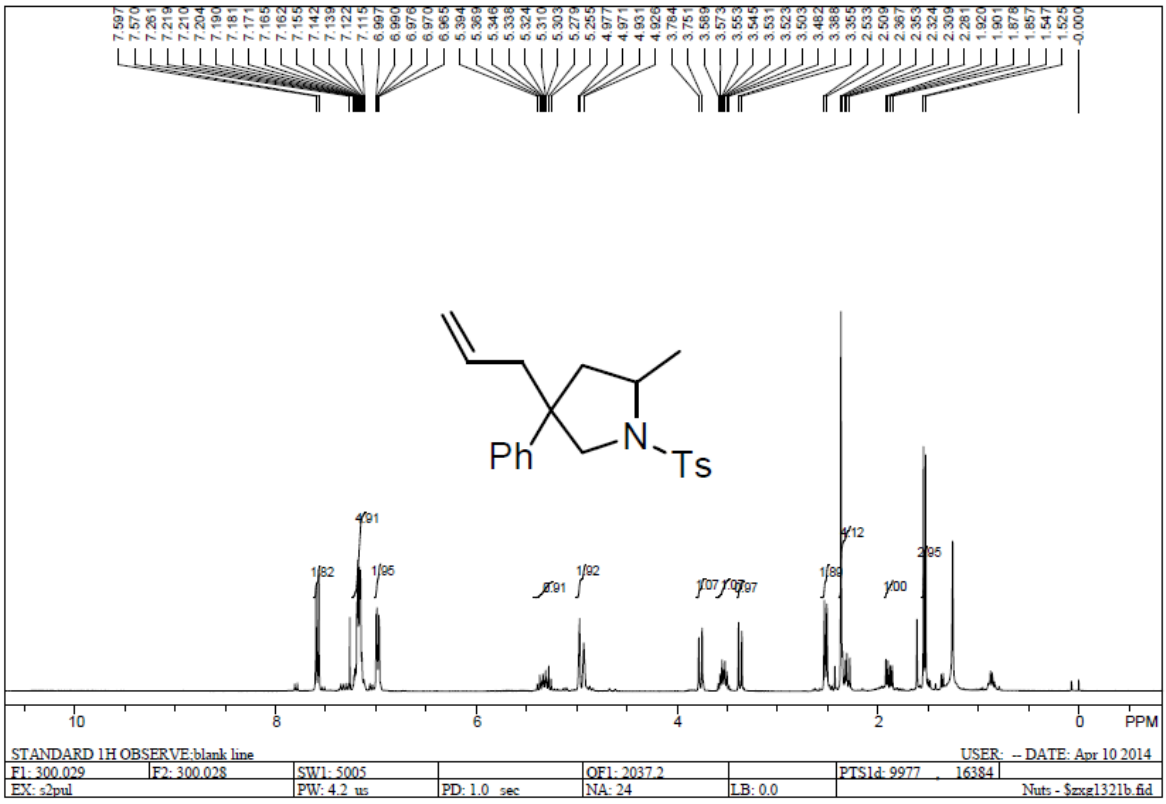
7.786
7.343
7.323
7.304
7.286
7.266
7.261
7.219
7.201
7.182
7.057
7.039
5.251
5.235
5.230
5.225
5.214
5.208
5.189
5.183
5.172
5.167
5.163
5.148
4.871
4.866
4.845
4.841
4.664
4.625
4.622
3.889
3.881
3.873
3.866
3.858
3.850
3.843
3.834
3.766
3.740
3.587
3.561
2.425
2.410
2.401
2.384
2.370
2.355
2.353
1.994
1.978
1.960
1.944
1.842
1.819
1.811
1.800
1.787
1.766
1.367
1.352
-0.000
Ph
N
Ts
1.89
3.79
1.91
0.97
0.94
1.00
0.95
1.00
0.99
0.99
3.98
1.04
2.00
2.99
10
8
6
4
2
0 PPM
cmk-2
USER: -- DATE: Apr 17 2014
F1: 399.723
F2: 100.519
SW1: 7184
OF1: 2798.7
PTS1d: 21552 , 32768
EX: s2pul
PW: 4.4 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $zxg1321a-H.fid


144.233
143.254
136.141
133.355
129.567
128.201
127.237
126.455
126.394
118.090
77.319
77.000
76.689
57.924
55.108
47.934
44.002
43.440
22.262
21.457
Ph
N
Ts
160
140
120
100
80
60
40
20
PPM
:blank line
USER: -- DATE: Apr 17 2014
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11049.4
PTS1d: 32768 , 32768
EX: s2pul
PW: 4.9 us
PD: 1.0 sec
NA: 80
LB: 0.0
Nuts - $zxg1321a-C13.fid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7.570
7.261
7.219
7.210
7.204
7.190
7.181
7.171
7.165
7.162
7.155
7.142
7.139
7.122
7.115
6.997
6.990
6.976
6.970
6.965
5.394
5.369
5.346
5.338
5.324
5.310
5.303
5.279
5.255
4.977
4.971
4.931
4.926
3.784
3.751
3.589
3.573
3.553
3.545
3.531
3.523
3.503
3.482
3.388
3.355
2.553
2.509
2.367
2.353
2.324
2.309
2.281
1.920
1.901
1.678
1.857
1.547
1.525
-0.000
Ph
N
Ts
4.91
1.82
1.95
0.91
1.92
1.07
1.07
0.97
1.88
3.12
1.00
2.95
10
8
6
4
2
0
PPM
STANDARD 1H OBSERVE;blank line
USER: -- DATE: Apr 10 2014
F1: 300.029
F2: 300.028
SW1: 5005
OF1: 2037.2
PTS1d: 9977 , 16384
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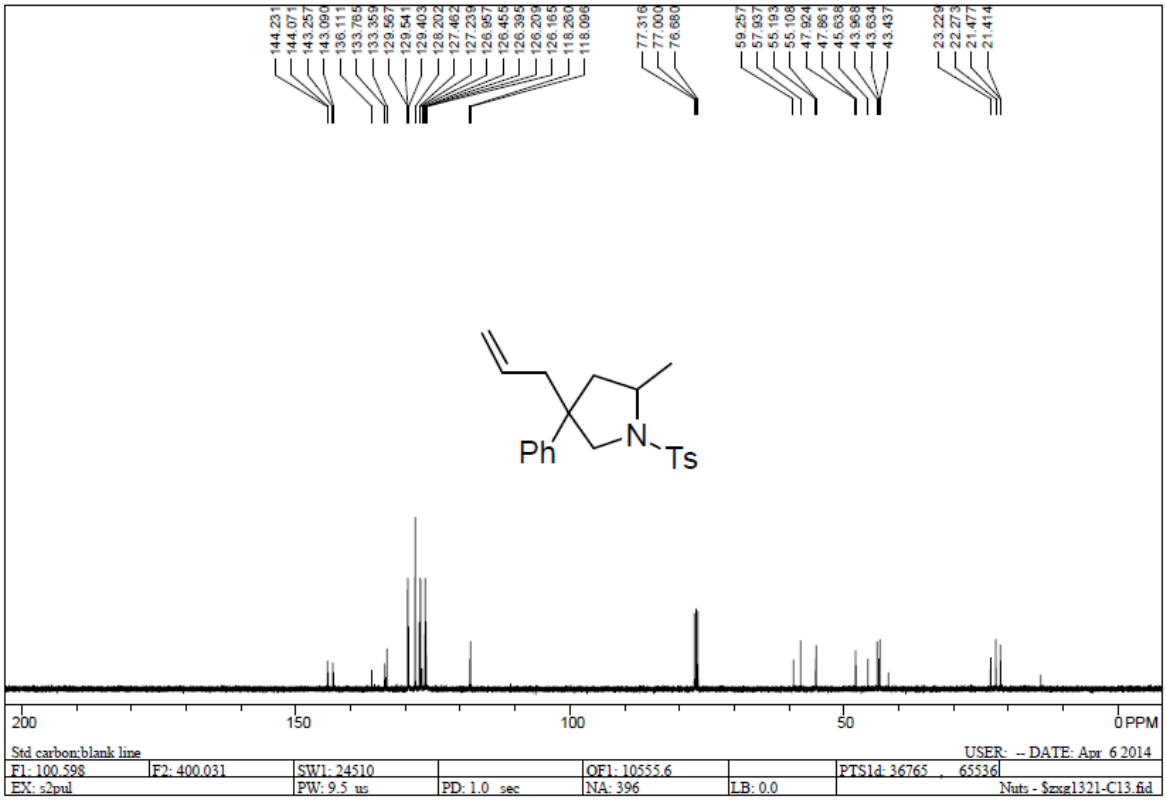
PW: 4.2 us
PD: 1.0 sec
NA: 24
LB: 0.0
Nuts - $zxg1321b.fid


144.231
144.071
143.257
143.090
136.111
133.765
133.359
129.567
129.541
129.403
128.202
127.462
127.239
126.957
126.455
126.395
126.209
126.165
118.260
118.096
77.316
77.000
76.680
59.257
57.937
55.193
55.108
47.924
47.861
45.638
43.968
43.634
43.437
23.229
22.273
21.477
21.414
Ph
N
Ts
200
150
100
50
0 PPM
Std carbon:blank line
USER: -- DATE: Apr 6 2014
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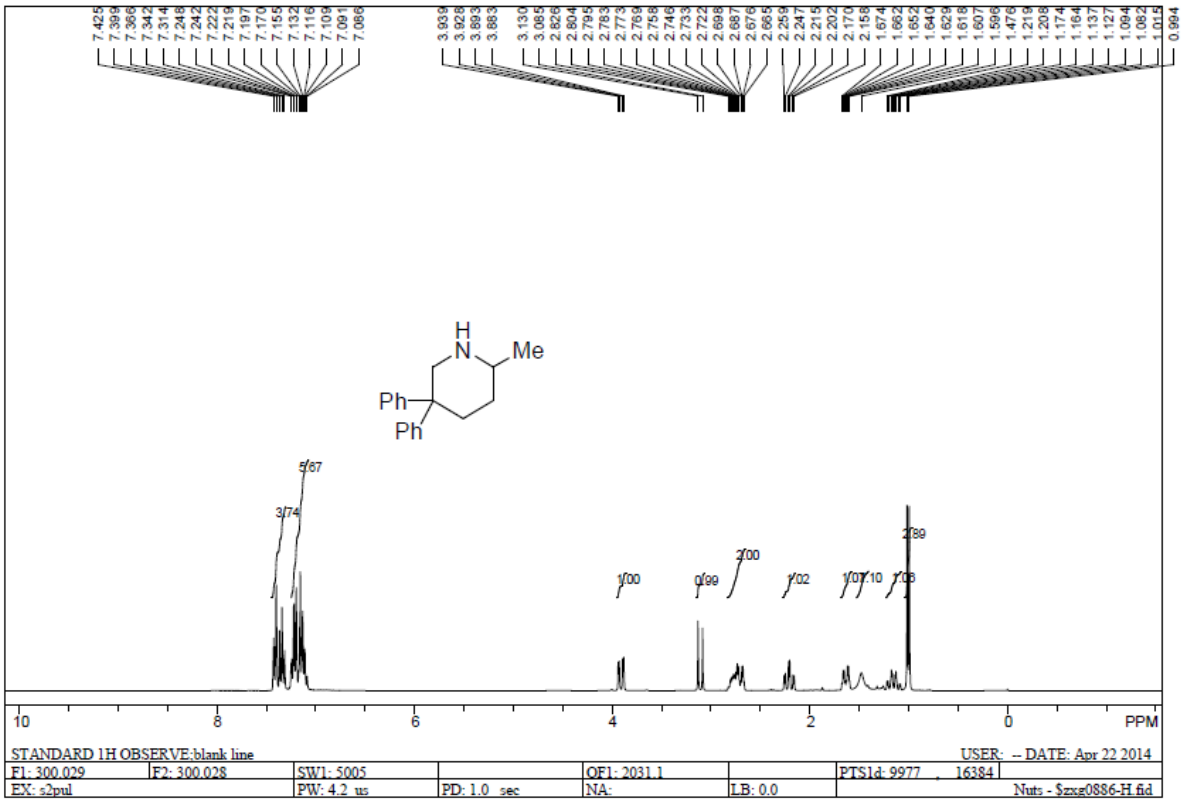
F2: 400.031
SW1: 24510
OF1: 10555.6
PTS1d: 36765 , 65536
EX: s2pul
PW: 9.5 us
PD: 1.0 sec
NA: 396
LB: 0.0
Nuts - $zxg1321-C13.fid


7.425
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7.314
7.248
7.242
7.222
7.219
7.197
7.170
7.155
7.132
7.116
7.109
7.091
7.086
3.939
3.928
3.893
3.883
3.130
3.085
2.826
2.804
2.795
2.783
2.773
2.769
2.758
2.746
2.733
2.722
2.698
2.687
2.676
2.665
2.259
2.247
2.215
2.202
2.170
2.158
1.674
1.662
1.652
1.640
1.629
1.618
1.607
1.596
1.476
1.219
1.208
1.174
1.164
1.137
1.127
1.094
1.082
1.015
0.994
H
N
Me
Ph
Ph
5.67
3.74
1.00
0.99
2.00
1.02
1.07
1.10
1.08
2.89
10
8
6
4
2
0
PPM
STANDARD 1H OBSERVE:blank line
USER: -- DATE: Apr 22 2014
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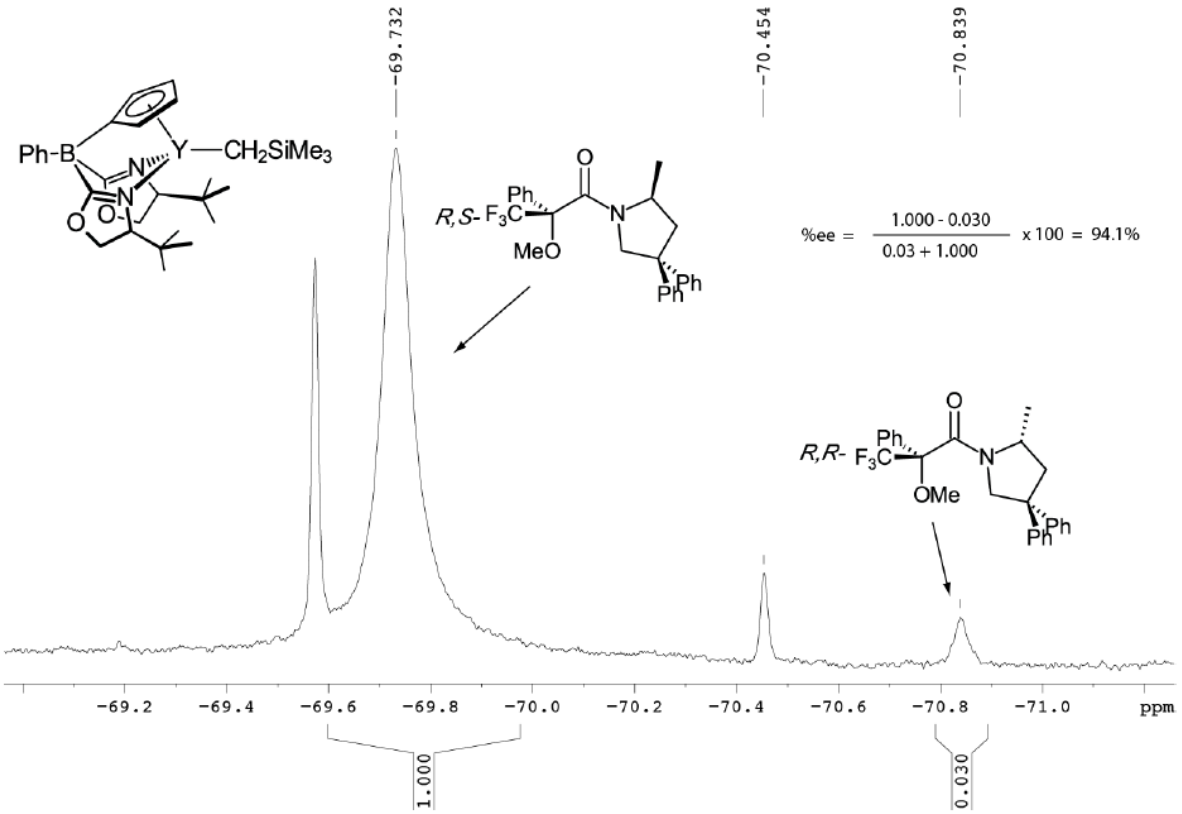
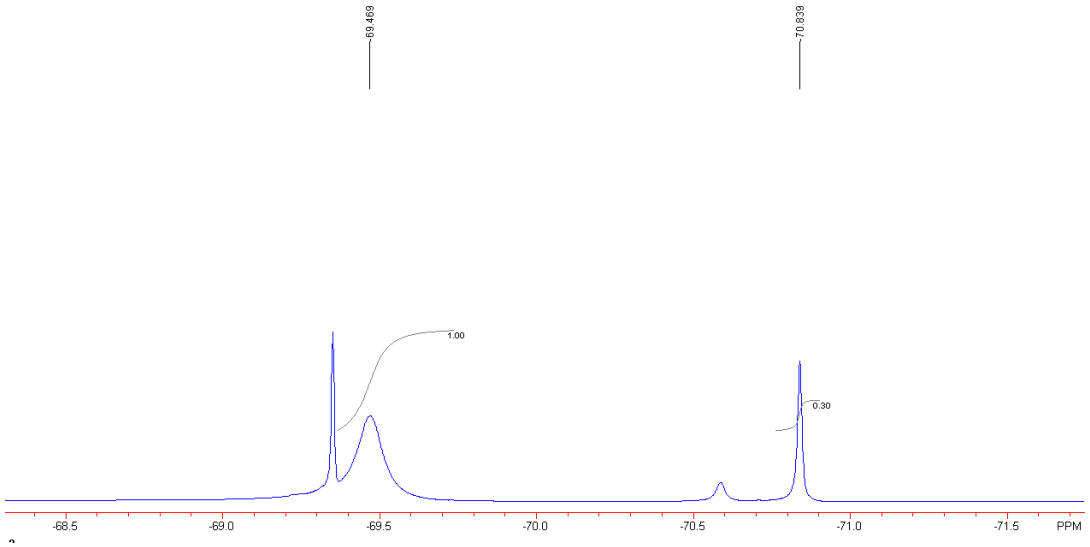
SW1: 5005
OF1: 2031.1
PTS1d: 9977 , 16384
EX: s2pul
PW: 4.2 us
PD: 1.0 sec
NA:
LB: 0.0
Nuts - $zxg0886-H.fid

Figure S23 Sadow reported ^{19}F NMR (376 MHz, $CDCl_3$, 60 ℃) spectrum of (R)-Mosher amide derivative of 2-methyl-4,4-diphenylpyrrolidine (**7A**) from stereoselective hydroamination obtained after treatment with (S)-Mosher chloride.[10]



The reported absolute configuration of **6A** is S.[10]

Figure S24 ^{19}F NMR (450 MHz, $CDCl_3$, 60 ℃) spectrum of (S)-Mosher amide derivative of **7A** from stereoselective hydroamination obtained after treatment with (R)-Mosher chloride in our condition.



Comparisons between two spectra suggested that the absolute configuration of **7A** is R in our system.

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