Electronic Supplementary Information for Dalton Transactions

C_2–Symmetric S/C/S ligands based on N-heterocyclic carbenes: a new ligand architecture for asymmetric catalysis

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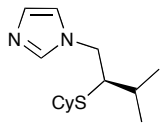
ELECTRONIC SUPPORTING INFORMATION

General experimental methods. Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica-gel (0.040-0.063 mm or 0.015-0.040 mm). Melting points were recorded in a metal block and are uncorrected. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. ^{1}H NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz; ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz or 125 MHz, with the solvent peak used as the internal reference. Coupling constants (*J* values) are given in Hz. (*R*)-2-(*tert*-Butylthio)-3-methylbutan-1-ol (**1b**),[1] (*R*)-2-phenylthio-3-methylbutan-1-ol[2] (**1c**), (*R*)-2-benzylsulfanyl-3-methylbutan-1-ol (**1d**)[2] and (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane (**2a**)[3] were prepared following previously described procedures. The enantiomeric excesses (ee's) were determined by HPLC using Chiralpak AS with *i*-PrOH/hexane mixtures as the eluent.

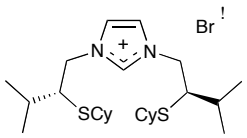
(*R*)-1-[2-(Cyclohexylthio)-3-methylbutyl]-1*H*-imidazole (3a)



1. (a) D. A. Evans, K. R. Campos, J. S. Tedrow, F. E. Michael and M. R. Gagné, *J. Am. Chem. Soc.* 2000, **122**, 7905.
(b) D. A. Cogan, G. Liu, K. Kim, B. J. Backes and J. A. Ellman, *J. Am. Chem. Soc.* 1998, **120**, 8011.
2. M. Marigo, T. C. Wabnitz, D. Fielenbach and K. A. Jørgensen, *Angew. Chem. Int. Ed.* 2005, **44**, 794.
3. A. Ros, D. Monge, M. Alcarazo, E. Álvarez, J. M. Lassaletta and R. Fernández, *Organometallics* 2006, **25**, 6039.

1*H*-Imidazole (166 mg, 2.44 mmol) was added to a solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane **2a** (323 mg, 1.22 mmol) in dry toluene (3 mL). The reaction mixture was stirred for 20 h at 80 °C and concentrated. The residue was diluted with CH_2Cl_2 (20 mL) and washed with saturated $NaHCO_3$ (2 × 10 mL). The organic layer was dried (Na_2SO_4), concentrated, and the resulting residue was purified by flash chromatography (1:15 MeOH-CH_2Cl_2) to afford **3a** (224 mg, 79%) as a yellow syrup. $[\alpha]_D^{20}$ +23.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (1H, s), 7.04 (1H, s), 6.95 (1H, s), 4.11 (1H, dd, *J* = 14.2, 6.3 Hz), 3.96 (1H, dd, *J* = 14.2, 8.5 Hz), 2.69 (1H, ddd, *J* = 8.5, 6.3, 3.4 Hz), 2.09-2.05 (1H, m), 1.87-1.81 (2H, m), 1.71-1.65 (3H, m), 1.56-1.49 (1H, m), 1.24-1.12 (5H, m), 1.03 (3H, d, *J* = 6.8 Hz), 0.93 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6, 129.2, 119.1, 52.9, 51.5, 44.4, 34.0, 33.8, 30.1, 25.9, 25.8, 25.6, 20.5, 17.5; MS (CI): *m/z* (%): 253 (34) [M^+], 252 (30), 185 (100), 171 (83), 129 (68), 89 (47), 83 (43), 69 (46); HRMS: *m/z*: calcd for $C_{14}H_{25}N_2S$: 253.1738; found: 253.1750.

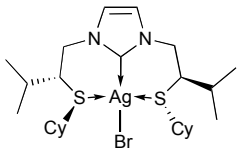
(*R*,*R*)-1,3-Bis[2-(cyclohexylthio)-3-methylbutyl]-3*H*-imidazol-1-ium bromide (4a)



A solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane (**2a**) (244 mg, 0.92 mmol) in dry toluene (2.2 mL) was added dropwise to a solution of **3a** (232 mg, 0.92 mmol) in dry toluene (2 mL) and the reaction mixture was refluxed for 2 d. The reaction mixture was concentrated and the residue was purified by flash chromatography (1:15 MeOH-CH_2Cl_2) to give **4a** (370 mg, 78%) as a white foam. $[\alpha]_D^{20}$ +3.3 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.65 (1H, s), 7.54 (2H, s), 4.71 (2H, dd, *J* = 14.0, 5.0 Hz), 4.10 (2H, dd, *J* = 14.0, 9.5 Hz), 3.00 (2H, q, *J* = 4.5 Hz), 2.42-2.35 (2H, m), 2.20-1.96 (2H, m), 1.92-1.85 (2H, m), 1.74-1.59 (8H, m), 1.54-1.50 (2H, m), 1.29-1.13 (8H, m), 1.07 (6H, d, *J* = 7.0 Hz), 0.97 (6H, d, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 122.5, 53.5, 52.2, 45.0, 34.0, 33.9, 30.7, 25.8, 25.7, 25.5, 20.3, 18.0;

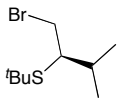
MS (CI): *m/z* (%): 437 (1) [M^+-Br], 253 (32), 185 (100), 171 (24), 129 (78), 83 (46), 69 (40); HRMS: *m/z*: calcd for $C_{25}H_{45}N_2S_2$: 437.3024; found: 437.3017.

Ag (I) S/NHC/S Complex 7a



Ag_2O (23 mg, 0.1 mmol) was added to a solution of **4a** (104 mg, 0.2 mmol) in dry CH_2Cl_2 (4 mL) and the mixture was stirred vigorously for 2 h in the dark. The reaction mixture was filtered through Celite and the solvent removed in vacuo to give **7a** (105 mg, 84%) as a white foam. $[\alpha]_D^{20}$ –27.7 (*c* 0.4 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (2H, s), 4.29 (2H, dd, *J* = 14.1, 6.6 Hz), 4.03 (2H, dd, *J* = 14.1, 8.7 Hz), 2.93-2.89 (2H, m), 2.36-2.32 (2H, m), 1.95-1.80 (4H, m), 1.79-1.60 (6H, m), 1.58-1.56 (2H, m), 1.31-1.10 (10H, m), 1.04 (6H, d, *J* = 6.6 Hz), 0.98 (6H, d, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.1, 121.8, 55.7, 53.5, 44.9, 34.1, 34.0, 30.3, 26.0, 25.8, 25.7, 20.4, 18.0; MS (CI): *m/z* (%): 580 (12), 545 (40), 543 (42), 501 (43), 499 (77), 185 (55), 129 (40), 83 (100), 69 (52), 61 (55); HRMS: *m/z*: calcd for $C_{25}H_{44}N_2S_2BrAg$: 622.1180; found: 622.1186.

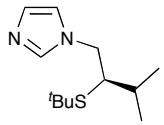
(*R*)-(1-Bromo-3-methylbutan-2-yl)(*tert*-butyl)sulfane (2b)



To a cooled (0 °C) solution of (*R*)-2-(*tert*-butylthio)-3-methylbutan-1-ol **1b** (640 mg, 3.63 mmol) in dry CH_2Cl_2 (20 ml) was added triphenylphosphine (1.150 g, 4.34 mmol) and carbon tetrabromide (1.454 g, 4.34 mmol) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 5 h, diluted with CH_2Cl_2 and washed with water. The organic layer was dried, filtered, concentrated and extracted with hexane. The hexane extract was concentrated to afford crude **2b**, which was used in the subsequent alkylation step without further purification. ^{1}H NMR (500 MHz,

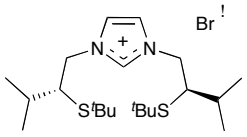
$CDCl_3$): δ 4.16-4.12 (1H, m), 3.06-2.98 (2H, m), 2.03 (1H, m), 1.31 (9H, s), 1.01 (3H, d, *J* = 6.5 Hz), 0.92 (3H, d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 64.5, 43.1, 34.9, 31.5, 30.7, 21.9, 16.4.

(*R*)-1-[2-(*tert*-Butylthio)-3-methylbutyl]-1*H*-imidazole (3b)



1*H*-Imidazole (171 mg, 2.51 mmol) was added to a solution of (*S*)-(1-bromo-3-methylbutan-2-yl)(*tert*-butyl)sulfane **2b** (300 mg, 1.25 mmol) in dry toluene (10 mL). The reaction mixture was stirred at 80 °C for 6 h and concentrated. The residue was diluted with CH_2Cl_2 (20 mL) and washed with saturated $NaHCO_3$ (2 × 10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated. Flash chromatography (1:20 MeOH-CH_2Cl_2) gave **3b** (151 mg, 53%) as a yellow oil. $[\alpha]_D^{20}$ +3.7 (*c* 0.75 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (1H, s), 7.01 (1H, s), 6.90 (1H, s), 4.05 (1H, dd, *J* = 14.4, 8.2 Hz), 3.98 (1H, dd, *J* = 14.4, 7.2 Hz), 2.67-2.63 (1H, m), 1.79-1.72 (1H, m), 1.19 (9H, s), 0.97 (3H, d, *J* = 6.8 Hz), 0.88 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 129.2, 119.0, 50.9, 50.1, 42.9, 31.0, 29.5, 20.1, 17.2; MS (EI): *m/z* (%): 226 (30) [M^+], 181 (22), 169 (23), 137 (35), 127 (25), 89 (43), 69 (100); HRMS: *m/z*: calcd for $C_{12}H_{22}N_2S$: 226.1504; found: 226.1503.

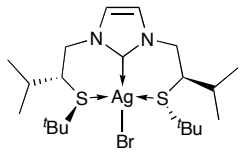
(*R*,*R*)-1,3-Bis[2-(*tert*-butylthio)-3-methylbutyl]-3*H*-imidazol-1-ium bromide (4b)



A solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(*tert*-butyl)sulfane **2b** (174 mg, 0.73 mmol) in dry toluene (6 mL) was added dropwise to a solution of **3b** (150 mg, 0.66 mmol) in dry toluene (4 mL) and the reaction mixture was refluxed for 7 d. The mixture was then concentrated and the

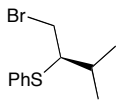
residue purified by flash chromatography (1:15 MeOH-CH_2Cl_2) to give **4b** (89 mg, 30%) as a yellow syrupe. $[\alpha]_D^{20}$ +2.7 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.85 (1H, s), 7.47 (2H, s), 4.65 (2H, dd, *J* = 14.0, 5.7 Hz), 4.08 (2H, dd, *J* = 14.0, 9.0 Hz), 3.13-3.05 (2H, m), 1.96-1.91 (2H, m), 1.17 (18H, s), 1.04 (6H, d, *J* = 6.5 Hz), 1.00 (6H, d, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 123.0, 53.2, 49.3, 43.8, 31.4, 31.0, 20.0, 29.7, 18.4; MS (CI): *m/z* (%): 385 (3) [M^+-Br], 227 (18), 159 (68), 137 (23), 103 (98), 89 (20), 69 (69), 57 (100); HRMS: *m/z*: calcd for $C_{21}H_{41}N_2S_2$: 385.2711; found: 385.2701.

Ag (I) S/NHC/S Complex (7b)



Ag_2O (23 mg, 0.1 mmol) was added to a solution of **4b** (104 mg, 0.2 mmol) in dry CH_2Cl_2 (4 mL) and the mixture was stirred vigorously for 5 h in the dark. The reaction mixture was filtered through Celite and the solvent removed in vacuo to give **7b** (108 mg, 95%) as a yellow foam. $[\alpha]_D^{20}$ –124.1 (*c* 1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (2H, s), 4.30 (2H, dd, *J* = 14.1, 7.1 Hz), 4.03 (2H, dd, *J* = 14.1, 8.1 Hz), 2.92 (2H, td, *J* = 7.7, 2.7 Hz), 1.87-1.84 (2H, m), 1.24 (18H, s), 1.04 (6H, d, *J* = 7.2 Hz), 1.02 (6H, d, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.1, 121.2, 54.3, 50.0, 42.9, 30.5, 29.8, 28.9, 18.9, 17.6; MS (CI): *m/z* (%): 493 (40), 491 (38), 449 (50), 447 (95), 390 (33), 159 (58), 103 (90), 69 (60), 57 (100); HRMS: *m/z*: calcd for $C_{21}H_{40}N_2S_2BrAg$: 570.0867; found: 570.0901.

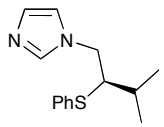
(*R*)-(1-Bromo-3-methylbutan-2-yl)(phenyl)sulfane (2c)



To a cooled (0 °C) solution of (*R*)-2-(phenyllthio)-3-methylbutan-1-ol **1c** (1.55 g, 7.9 mmol) in dry CH_2Cl_2 (43 mL) were added triphenylphosphine (2.52 g, 9.5 mmol) and carbon tetrabromide

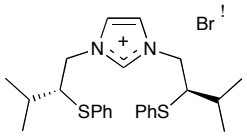
(3.18 g, 9.5 mmol) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 6 h, diluted with CH_2Cl_2 and washed with water. The organic layer was dried, filtered, concentrated and extracted with hexane. The hexane extract was concentrated to afford crude **2c** as a yellow oil, which was used in the subsequent alkylation step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.23 (5H, m), 4.12 (1H, ddd, *J* = 9.0, 6.0, 3.0 Hz), 3.49 (1H, dd, *J* = 14.0, 6.0 Hz), 3.33 (1H, dd, *J* = 14.0, 9.0 Hz), 2.21-2.13 (1H, m), 1.02 (3H, d, *J* = 7.0 Hz), 0.93 (3H, d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.2, 130.5, 129.4, 127.1, 63.1, 40.8, 31.3, 22.0, 16.7.

(*R*)-1-[2-(Phenyl)-3-methylbutyl]-1*H*-imidazole (3c)



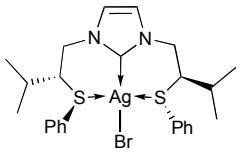
1*H*-Imidazole (381 mg, 5.6 mmol) was added to a solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(phenyl)sulfane **2c** (725 mg, 2.8 mmol) in dry toluene (15 mL). The reaction mixture was stirred at 80 °C for 16 h and concentrated. The residue was diluted with CH_2Cl_2 (20 mL) and washed with saturated $NaHCO_3$ (2 × 10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated. Flash chromatography (1:20 MeOH-CH_2Cl_2) gave **3c** (342 mg, 50%) as a yellow syrupe. $[\alpha]_D^{20}$ –12.0 (*c* 1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (1H, s), 7.24-7.17 (5H, m), 6.97 (1H, s), 6.82 (1H, s), 4.11 (1H, dd, *J* = 14.5, 7.0 Hz), 4.01 (1H, dd, *J* = 14.5, 7.5 Hz), 3.17-3.12 (1H, m), 1.93-1.84 (1H, m), 1.09 (3H, d, *J* = 7.0 Hz), 0.99 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 134.9, 132.2, 130.5, 129.2, 127.4, 119.2, 58.9, 49.8, 29.7, 20.6, 17.7; MS (CI): *m/z* (%): 247 (38) [M^++1], 246 (24) [M^+], 179 (63), 165 (26), 137 (22), 123 (100); HRMS: *m/z*: calcd for $C_{14}H_{19}N_2S$: 247.1269; found: 247.1266.

(*R*,*R*)-1,3-Bis[2-(phenylthio)-3-methylbutyl]-3*H*-imidazol-1-ium bromide (7c)



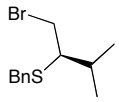
A solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(phenyl)sulfane **2c** (505 mg, 1.95 mmol) in dry toluene (5 mL) was added dropwise to a solution of **4c** (320 mg, 1.30 mmol) in dry toluene (5 mL) and the reaction mixture was refluxed for 7 d. The mixture was concentrated and the residue purified by flash chromatography (1:20 MeOH-CH_2Cl_2) to give **7c** (315 mg, 48%) as a yellow sirupe. $[\alpha]_D^{20}$ –5.7 (*c* 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.44 (1H, s), 7.31-7.13 (12H, m), 4.67 (2H, dd, *J* = 13.8, 3.8 Hz), 4.01 (2H, dd, *J* = 13.8, 9.8 Hz), 3.65-3.62 (2H, m), 2.11-2.04 (2H, m), 1.15 (6H, d, *J* = 6.7 Hz), 1.06 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 134.2, 130.8, 129.1, 127.0, 122.3, 56.8, 53.1, 30.5, 20.3, 18.3; MS (FAB): *m/z* (%): 425 (16) [M^+–Br], 123 (34), 95 (37), 81 (22), 69 (57), 57 (100); HRMS: *m/z*: calcd for $C_{25}H_{33}N_2S_2$: 425.2085; found: 425.2084.

Ag (I) S/NHC/S Complex 7c



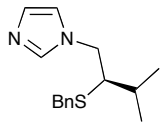
Ag_2O (23 mg, 0.1 mmol) was added to a solution of **4c** (101 mg, 0.2 mmol) in dry CH_2Cl_2 (4 mL) and the mixture was stirred vigorously for 5 h in the dark. The reaction mixture was filtered through Celite and the solvent removed in vacuo to give **7c** (115 mg, 94%) as a yellow foam. $[\alpha]_D^{20}$ –21.6 (*c* 0.35 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.16 (10H, m), 6.92 (2H, s), 4.30 (2H, dd, *J* = 14.1, 5.8 Hz), 3.98 (2H, dd, *J* = 14.1, 8.8 Hz), 3.45 (2H, ddd, *J* = 8.8, 5.8, 3.4 Hz), 2.01-1.95 (2H, m), 1.13 (6H, d, *J* = 6.8 Hz), 1.08 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.2, 134.6, 131.2, 129.1, 127.0, 121.7, 58.4, 54.5, 30.1, 20.2, 18.4; MS (FAB): *m/z* (%): 425 (39) [M^+-Ag-Br], 133 (19), 123 (100), 95 (37), 81 (10), 69 (20).

(*R*)-(1-Bromo-3-methylbutan-2-yl)(benzyl)sulfane (2d)



To a cooled (0 °C) solution of (*R*)-2-benzylsulfanyl-3-methylbutan-1-ol **1d** (1.0 g, 4.8 mmol) in dry CH_2Cl_2 (20 mL) were added triphenylphosphine (1.54 g, 5.7 mmol) and carbon tetrabromide (1.90 g, 5.7 mmol) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 3 h, diluted with CH_2Cl_2 and washed with water. The organic layer was dried, filtered, concentrated and extracted with hexane. The hexane extract was concentrated to afford crude **2d**, which was used in the subsequent alkylation step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (5H, m), 3.98 (1H, ddd, *J* = 8.4, 6.4, 3.0 Hz), 3.78-3.70 (2H, m), 2.95 (1H, dd, *J* = 14.0, 6.4 Hz), 2.88 (1H, dd, *J* = 14.0, 8.4 Hz), 2.04-2.00 (1H, m), 0.95 (3H, d, *J* = 6.8 Hz), 0.86 (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 128.9, 128.7, 127.4, 65.9, 63.8, 37.9, 37.1, 29.8, 16.7.

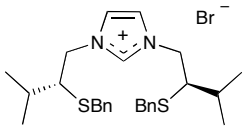
(*R*)-1-[2-(Benzylthio)-3-methylbutyl]-1*H*-imidazole (3d)



1*H*-Imidazole (286 mg, 4.2 mmol) was added to a solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(benzyl)sulfane **2d** (570 mg, 2.10 mmol) in dry toluene (10 mL). The reaction mixture was stirred at 80 °C for 40 h and concentrated. The residue was diluted with CH_2Cl_2 (20 mL) and washed with saturated $NaHCO_3$ (2 × 10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (1:20 MeOH-CH_2Cl_2) to afford **3d** (313 mg, 57%) as a orange oil. $[\alpha]_D^{20}$ −22.2 (*c* 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (1H, s), 7.29-7.17 (5H, m), 7.04 (1H, s), 6.83 (1H, s), 4.03 (1H, dd, *J* = 14.0, 6.8 Hz), 3.86 (1H, dd, *J* = 14.0, 8.2 Hz), 3.44 (1H, d, *J* = 13.2 Hz), 3.21 (1H, d, *J* = 13.2 Hz), 2.54-2.50 (1H, m), 1.78-1.70 (1H, m), 0.87 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7,

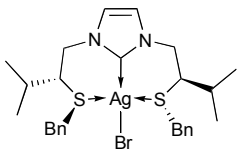
137.5, 129.7, 129.3, 128.4, 127.1, 119.1, 52.9, 50.8, 36.4, 29.6, 20.3, 17.3; MS (EI): *m/z* (%): 260 (25) [M^+], 179 (22), 169 (22), 137 (28), 91 (100), 82 (21); HRMS: *m/z*: calcd for $C_{15}H_{20}N_2S$: 260.1347; found: 260.1345.

(*R*,*R*)-1,3-Bis[2-(benzylthio)-3-methylbutyl]-3*H*-imidazol-1-ium bromide (4d)



A solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(benzyl)sulfane **2d** (570 mg, 2.1 mmol) in dry toluene (10 mL) was added dropwise to a solution of **3d** (313 mg, 1.20 mmol) in dry toluene (4 mL) and the reaction mixture was refluxed for 7 d. The mixture was then concentrated and the residue purified by flash chromatography (1:20 MeOH-CH_2Cl_2) to give **4d** (275 mg, 43%) as a white solid. M.p. 60–63 °C. $[\alpha]_D^{20}$ –20.4 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.13 (1H, s), 7.31-7.11 (12H, m), 4.53 (2H, dd, *J* = 14.0, 5.0 Hz), 3.97 (2H, dd, *J* = 14.0, 9.7 Hz), 3.63 (2H, d, *J* = 13.4 Hz), 3.55 (2H, d, *J* = 13.4 Hz), 2.89-2.86 (2H, m), 1.99-1.95 (2H, m), 1.01 (6H, d, *J* = 6.5 Hz), 0.96 (6H, d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 129.0, 128.6, 127.2, 121.9, 52.9, 52.7, 37.0, 30.6, 20.3, 18.0; MS (FAB): *m/z* (%): 453 (75) [M^+-Br], 237 (8), 193 (25), 137 (56), 102 (49), 91 (100); HRMS: *m/z*: calcd for $C_{27}H_{37}N_2S_2$: 453.2398; found: 453.2406.

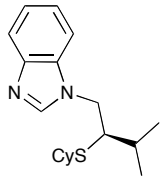
Ag (I) S/NHC/S Complex 7d



Ag_2O (23 mg, 0.1 mmol) was added to a solution of **4d** (107 mg, 0.2 mmol) in dry CH_2Cl_2 (4 mL) and the mixture was stirred vigorously for 5 h in the dark. The reaction mixture was filtered through Celite and the solvent removed in vacuo to give **7d** (118 mg, 92%) as a white foam. $[\alpha]_D^{20}$ –91.6 (*c* 1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.17 (10H, m), 6.85 (2H, s), 4.21

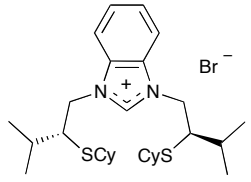
(2H, dd, *J* = 14.0, 5.8 Hz), 3.82 (2H, dd, *J* = 14.0, 9.1 Hz), 3.50 (2H, d, *J* = 13.4 Hz), 3.44 (2H, d, *J* = 13.4 Hz), 2.78-2.74 (2H, m), 1.90-1.86 (2H, m), 0.99 (6H, d, *J* = 6.8 Hz), 0.96 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.2, 137.8, 129.1, 128.5, 127.1, 121.5, 54.8, 53.7, 37.0, 30.3, 20.1, 18.2. MS (EI): *m/z* (%): 453 (56) [M^+-Ag-Br], 193 (22), 137 (73), 91 (100), 69 (24); HRMS: *m/z*: calcd for $C_{27}H_{37}N_2S_2$: 453.2398; found: 453.2423.

(*R*)-1-[2-(Cyclohexylthio)-3-methylbuty]-1*H*-benzo[d]imidazole (5)



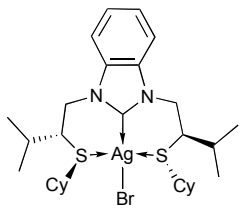
1*H*-Benzo[*d*]imidazole (1.06 g, 9.0 mmol) was added to a solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane **2a** (1.4 g, 4.5 mmol) in dry toluene (20 mL). The reaction mixture was stirred at 80 °C for 24 h, washed with saturated $NaHCO_3$ (2 × 10 mL), dried (Na_2SO_4), concentrated, and the resulting residue was purified by flash chromatography (1:40 MeOH-CH_2Cl_2) to give **5** (920 mg, 68%) as a yellow syrupe. $[\alpha]_D^{20}$ –36.5 (*c* 0.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (1H, s), 7.85-7.82 (1H, m), 7.41-7.36 (1H, m), 7.33-7.26 (2H, m), 4.43 (1H, dd, *J* = 14.4, 6.0 Hz), 4.19 (1H, dd, *J* = 14.4, 9.0 Hz), 2.93 (1H, ddd, *J* = 9.0, 6.0, 3.3 Hz), 2.00-1.85 (2H, m), 1.80-1.71 (1H, m), 1.66-1.42 (5H, m), 1.18-1.00 (4H, m), 1.09 (3H, d, *J* = 6.9 Hz), 1.06 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 133.6, 122.9, 122.1, 120.6, 109.3, 51.0, 49.5, 44.5, 33.9, 33.7, 30.7, 25.9, 25.8, 25.5, 20.4, 17.9; MS (EI): *m/z* (%): 302 (27), 171 (100), 132 (42), 89 (94), 83 (26), 55 (50); HRMS *m/z* calcd. for $C_{18}H_{26}N_2S$ 302.1817, found 302.1813.

(*R,R*)-1,3-Bis[2-(cyclohexylthio)-3-methylbutyl]-3*H*-benzo[d]imidazol-1-ium bromide (6)



A solution of (*R*)-(1-bromo-3-methylbutan-2-yl)(cyclohexyl)sulfane **2a** (1.4 g, 4.5 mmol) in dry toluene (5 mL) was added dropwise to a solution of **5** (920 mg, 3.05 mmol) in dry toluene (10 mL). The mixture was refluxed for 85 h, concentrated, and the residue was purified by flash chromatography (1:30 MeOH-CH_2Cl_2) to afford **6** (1.06 g, 61%) as a light brown foam and 300 mg (33%) of unreacted starting material **5**. Data for **6**: $[\alpha]_D^{20}$ +23.8 (*c* 0.8 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.47 (1H, s), 7.53 (2H, dd, *J* = 6.5, 3.0 Hz), 7.64 (2H, dd, *J* = 6.5, 3.0 Hz), 4.85 (2H, dd, *J* = 14.5, 6.5 Hz), 4.53 (2H, dd, *J* = 14.5, 9.0 Hz), 3.29 (2H, ddd, *J* = 9.0, 6.5, 3.3 Hz), 2.43-2.41 (2H, m), 2.01-1.98 (2H, m), 1.92-1.83 (3H, m), 1.68-1.62 (2H, m), 1.55-1.44 (7H, m), 1.24-1.18 (5H, m), 1.11 (6H, d, *J* = 6.5 Hz), 1.06 (6H, d, *J* = 6.5 Hz), 0.95-0.90 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 131.5, 126.9, 113.4, 51.4, 50.6, 44.7, 34.0, 33.9, 30.5, 25.7, 25.7, 25.5, 20.2, 18.0; MS (FAB): *m/z* (%): 487 (46) [M^+], 185 (37), 147 (28), 129 (100), 83 (55); HRMS: *m/z*: calcd for $C_{29}H_{47}N_2S_2$: 487.3181; found: 487.3165.

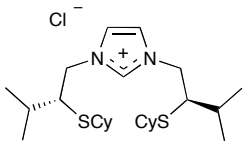
Ag (I) S/NHC/S Complex 8



Ag_2O (23 mg, 0.1 mmol) was added to a solution of **6** (113 mg, 0.2 mmol) in dry CH_2Cl_2 (4 mL) and the mixture was stirred vigorously for 2 h in the dark. The reaction mixture was then filtered through Celite and the solvent removed *in vacuo* to afford **8** (122 mg, 84%) as a light brown foam. $[\alpha]_D^{20}$ +35.5 (*c* 0.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (2H, dd, *J* = 6.0, 3.0 Hz), 7.45 (2H, dd, *J* = 6.0, 3.0 Hz), 4.59 (2H, dd, *J* = 14.4, 7.2 Hz), 4.45 (2H, dd, *J* = 14.4, 7.2 Hz), 3.20-3.15 (2H, m), 2.43-2.32 (2H, m), 1.97-1.82 (4H, m), 1.75-1.47 (9H, m), 1.30-1.16 (9H, m), 1.10 (6H, d, *J* = 6.6 Hz), 1.08 (6H, d, *J* = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.7, 134.0, 124.1, 111.7, 52.6, 52.6, 44.7, 34.0, 30.1, 25.8, 25.7, 25.6, 20.5, 18.1; MS (CI): *m/z* (%): 595 (35), 593

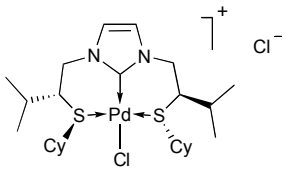
(34), 549 (45), 303 (43), 185 (100), 129 (51), 83 (61); HRMS: *m/z*: calcd for $C_{29}H_{46}N_2S_2BrAg$: 672.1337; found: 672.1329.

(*R,R*)-1,3-Bis(2-(cyclohexylthio)-3-methylbutyl)-3H-imidazol-1-ium chloride (9)



To a solution of **4a** (600 mg, 1.16 mmol) in MeOH (25 mL), was added Dowex® 22 (Cl) exchange anion resin (2.5 g). The reaction mixture was stirred until the starting material was consumed (TLC). The mixture was then filtered and concentrated. The resulting residue was dissolved in CH_2Cl_2, dried (Na_2SO_4) and concentrated to yield **9** (530 mg, 97%) as a white foam. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.85 (s, 1H), 7.52 (s, 2H), 4.72 (dd, 2H, *J* = 14.0, 5.2 Hz), 4.11 (dd, 2H, *J* = 14.0, 9.6 Hz), 2.97 (m, 2H), 2.36 (m, 2H), 2.04-1.94 (m, 2H), 1.92-1.85 (m, 2H), 1.74-1.59 (m, 6H), 1.54-1.48 (m, 2H), 1.28-1.13 (m, 10H), 1.06 (d, 6H, *J* = 6.4 Hz), 0.96 (d, 6H, *J* = 6.8 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.9, 122.3, 53.6, 52.5, 45.1, 34.1, 33.9, 30.9, 25.9, 25.8, 25.5, 20.3, 18.0. $[\alpha]^{20}_D$= + 5.8 (*c* 1.0, $CHCl_3$). HRMS *m/z* calcd. for $C_{25}H_{45}N_2S_2$ 437.3024, found 437.3020.

Palladium complex 10



Method A: To a solution of **9** (56 mg, 0.11mmol) in dry DMF (2.2 mL) was added $PdCl_2$ (19.6 mL, 0.11 mmol) and the reaction mixture was refluxed overnight under an argon atmosphere. The mixture was concentrated and the residue was purified by flash chromatography (1:10 MeOH-CH_2Cl_2) to afford **10** as a yellow syrupe. Trituration with diethyl ether gave **10** (64 mg, 96%) as a light yellow powder.

Method B: To a solution of **9** (96 mg, 0.2 mmol) in dry CH_2Cl_2 (4 mL) was added Ag_2O (22 mg, 0.1 mmol) and the reaction mixture was vigorously stirred for 1 h in the dark. $[PdCl_2(CH_3CN)_2]$ (52 mg, 0.2 mmol) was then added and the reaction mixture was stirred at rt overnight. The mixture was filtered through Celite and concentrated. The resulting residue was purified by flash chromatography (1:10 MeOH-CH_2Cl_2) to afford **10** as a yellow syrupe. Trituration with diethyl ether gave **10** as light yellow powder (105 mg, 86%). X-Ray quality crystals were grown by slow diffusion of hexane into a solution of **10** in CH_2Cl_2. M.p. = 124-126 °C (dec.). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.35 (s, 2H), 5.31 (d, 2H, *J* = 12.5 Hz), 3.93 (t, 2H, *J* = 12.5 Hz), 2.94 (d, 2H, *J* = 10.0 Hz), 2.89 (t, 2H, *J* = 12.5 Hz), 2.37-2.30 (m, 2H), 2.13-2.08 (m, 2H), 1.92-1.76 (m, 10H), 1.69-1.64 (m, 2H), 1.59-1.51 (m, 2H), 1.35-1.28 (m, 4H), 1.26 (d, 6H, *J* = 7.0 Hz), 1.23 (d, 6H, *J* = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 150.0, 124.0, 54.5, 52.0, 36.2, 33.1, 31.6, 26.9, 26.7, 24.7, 19.8, 19.5. $[\alpha]^{20}_D$ = –95.2 (*c* 1.4, $CHCl_3$). m/z (FAB) 577 (5, M^+ –Cl), 459 (22), 129 (100). HRMS *m/z* calcd. for $C_{25}H_{44}N_2S_2ClPd$ (M^+-Cl) 577.1669, found 577.1711.

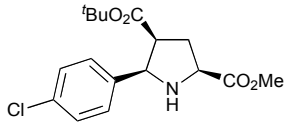
General procedure for the catalytic cycloaddition reaction

To a suspension of imino glycinate **11**-**16** (0.15 mmol) and the catalyst (7.5×10^{-3} μmol, 5 mol%) in Et_2O (0.25 mL) was added ^{i}Pr_2EtN (3 μL, 0.015 mmol, 10 mol%) and the mixture was stirred in dark for 1 h at –25 °C. Then, *tert*-butyl acrylate (27 μL, 0.18 mmol) was added and the mixture was stirred at this temperature for 3 d. The solvent was then removed in vacuo and the residue was purified by flash chromatography (1:1 Et_2O-hexane) to yield the product **22**-**27**.

Compounds **22-25** and **27** had spectral and analytical data in good agreement with those previously reported in the literature.[4]

[4] C. Chen, X. Li and Stuart L. Schreiber, *J. Am. Chem. Soc.*, 2003, **125**, 10174.

***tert*-Butyl (2*R*,4*R*,5*S*)-2-methoxycarbonyl-5-(4-chlorophenyl)pyrrolidin-4-carboxylate (26)**

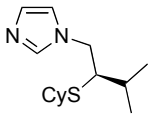


Following the general procedure described above, compound **26** (36 mg, 70%) was obtained as a white solid in 80% ee [Chiralpak AS, 90:10 hexane: *i*-PrOH, flow = 1 mL/min, T = 30 °C; t_r = 5.7 min (major), t_r = 12.9 min (minor)]. M.p. = 78–80 °C; $[\alpha]_D^{20}$ –12.3 (*c* 0.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.29 (4H, m), 2.20-1.96 (1H, d, *J* = 7.9 Hz), 3.92 (1H, t, *J* = 8.4 Hz), 3.82 (3H, s), 3.25 (1H, q, *J* = 7.8 Hz), 2.56 (1H, br s), 2.48-2.27 (2H, m), 1.07 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 171.6, 138.0, 133.1, 128.7, 128.2, 80.9, 64.8, 59.8, 52.3, 50.1, 33.9, 27.6; MS (CI): *m/z* (%): 340 (18) [M^++1], 339 (9) [M^+], 284 (100), 282 (43), 224 (31), 211 (30), 151 (15); HRMS: *m/z*: calcd for $C_{17}H_{23}ClNO_4$: 340.3016; found: 340.3017.

Enantiomeric excesses of cycloadducts **22-27** were determined by HPLC on a Chiralpak AS column using 90:10 hexane: *i*-PrOH as eluent, flow = 1 mL/min and T = 30 °C. Data for **22:** t_r = 5.2 min (major), t_r = 8.1 min (minor). Data for **23**: t_r = 4.8 min (major), t_r = 24.8 min (minor). Data for **24**: t_r = 13.7 min (major), t_r = 16.6 min (minor). Data for **25**: t_r = 6.1 min (major), t_r = 12.8 min (minor). Data for **26**: t_r = 5.7 min (major), t_r = 12.9 min (minor). Data for **27**: t_r = 6.7 min (major), t_r = 12.4 min (minor).

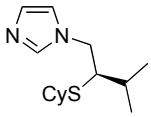
NMR SPECTRA

^{1}H NMR ($CDCl_3$, 500 MHz)



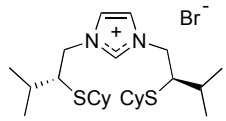
3a

^{13}C NMR ($CDCl_3$, 125 MHz)



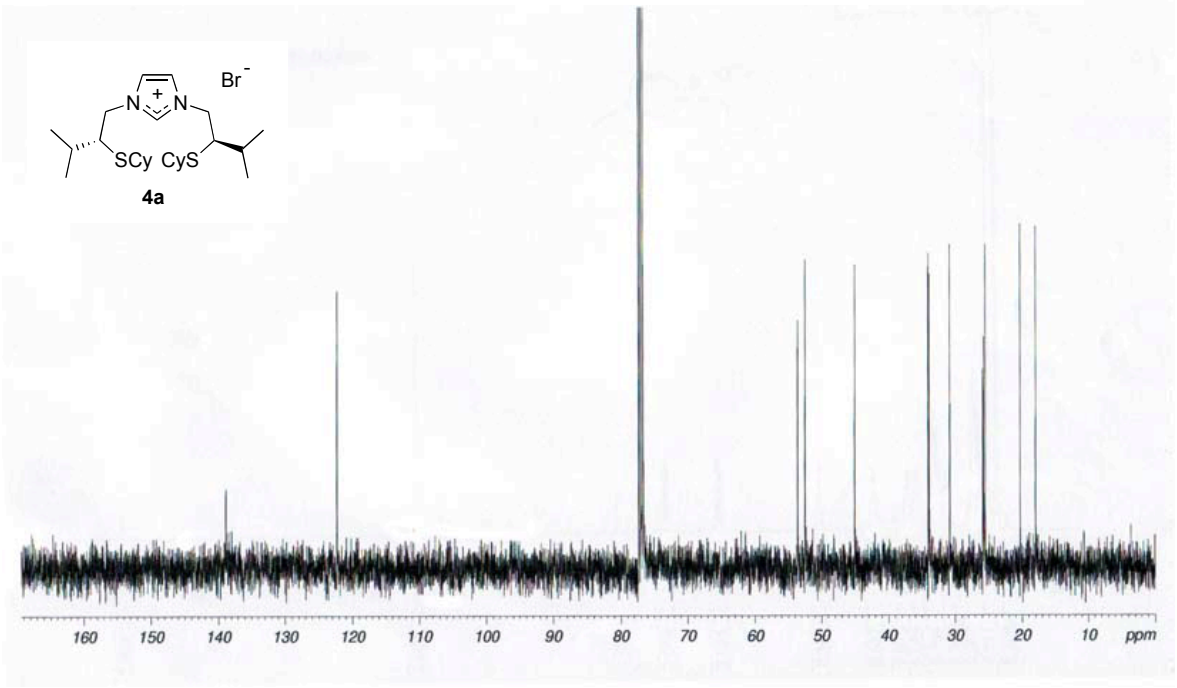
3a

^{1}H NMR ($CDCl_3$, 500 MHz)



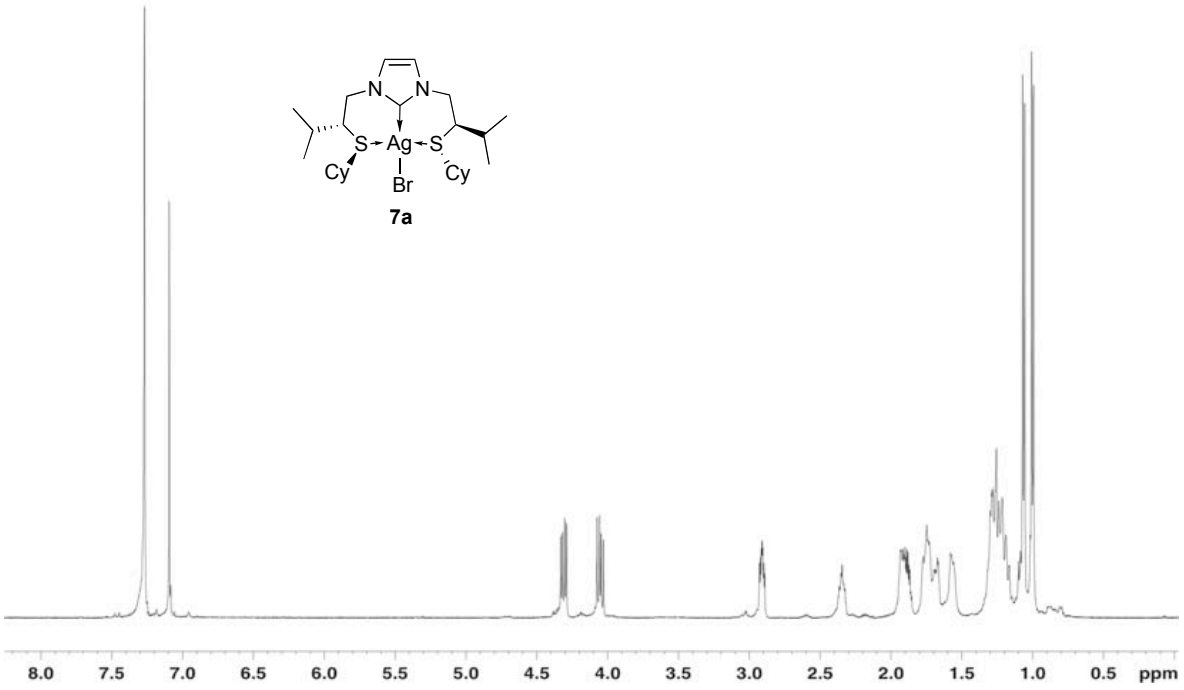
4a

^{13}C NMR ($CDCl_3$, 125 MHz)



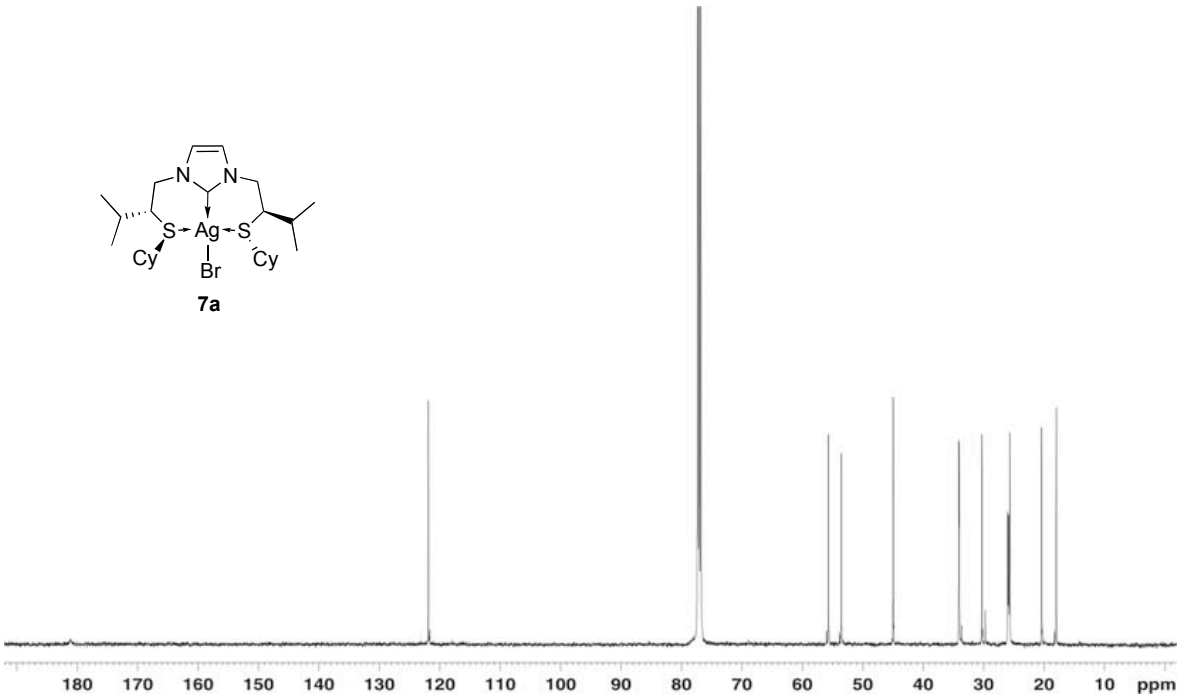
4a

^{1}H-RMN ($CDCl_3$, 500 MHz)



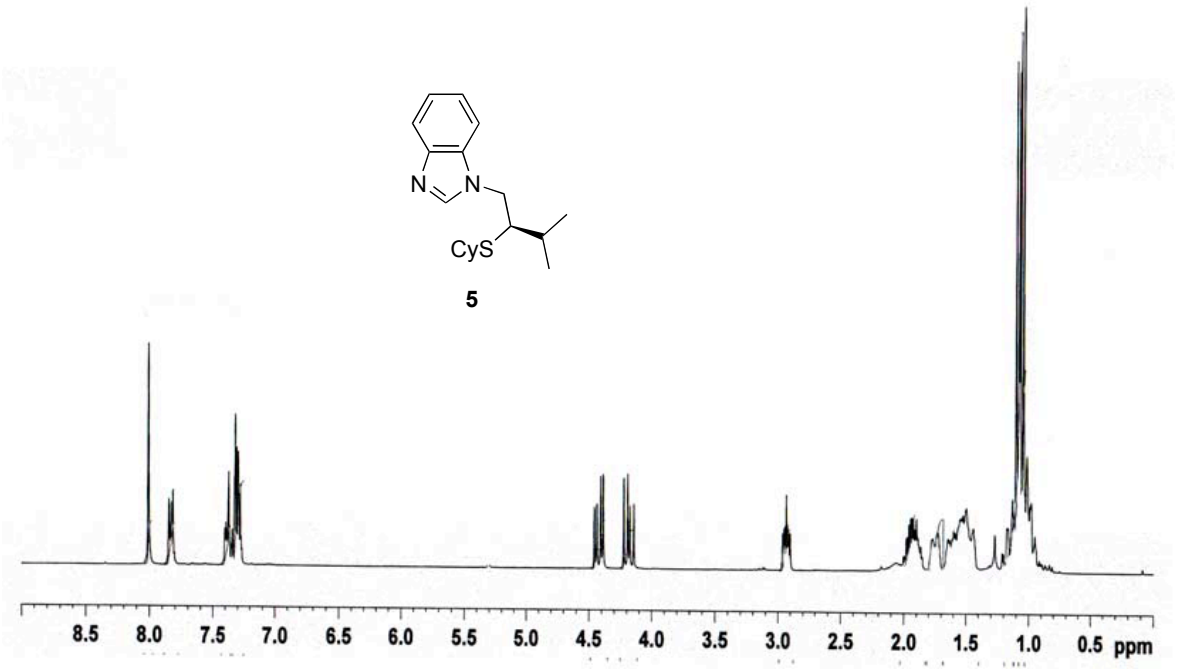
7a

^{13}C NMR ($CDCl_3$, 125 MHz)



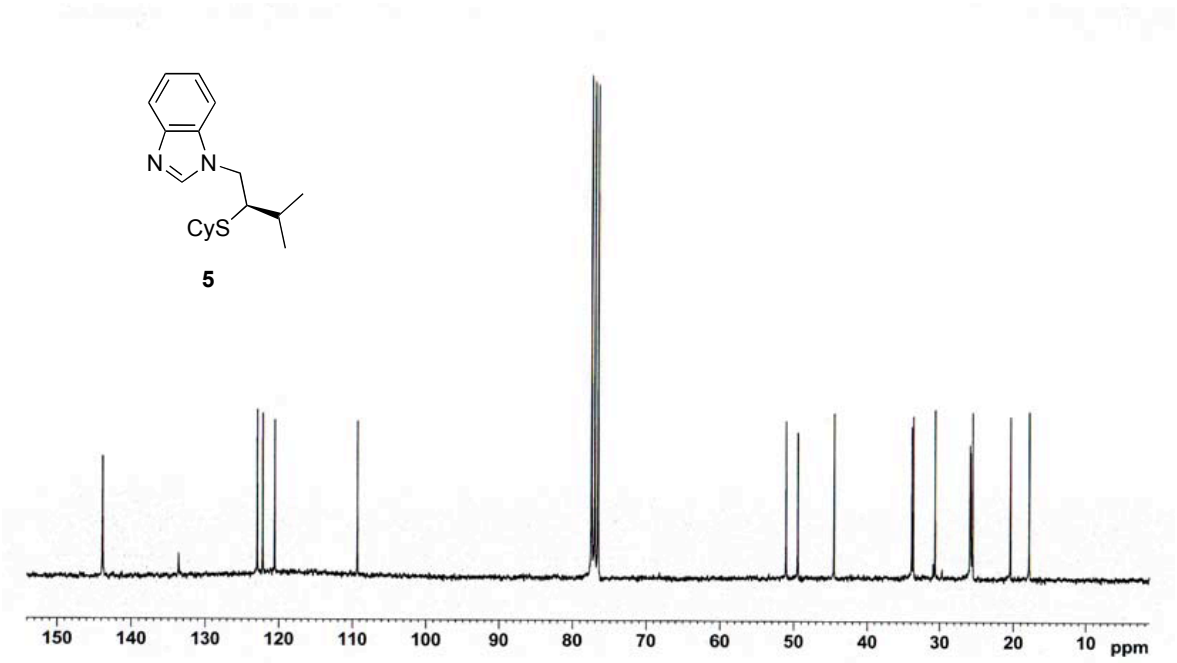
7a

$_1$H-RMN ($CDCl_3$, 300 MHz)



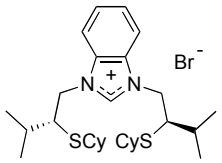
5

^{13}C NMR ($CDCl_3$, 75 MHz)



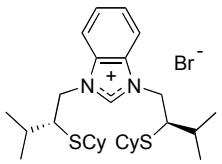
5

^{1}H NMR ($CDCl_3$, 500 MHz)



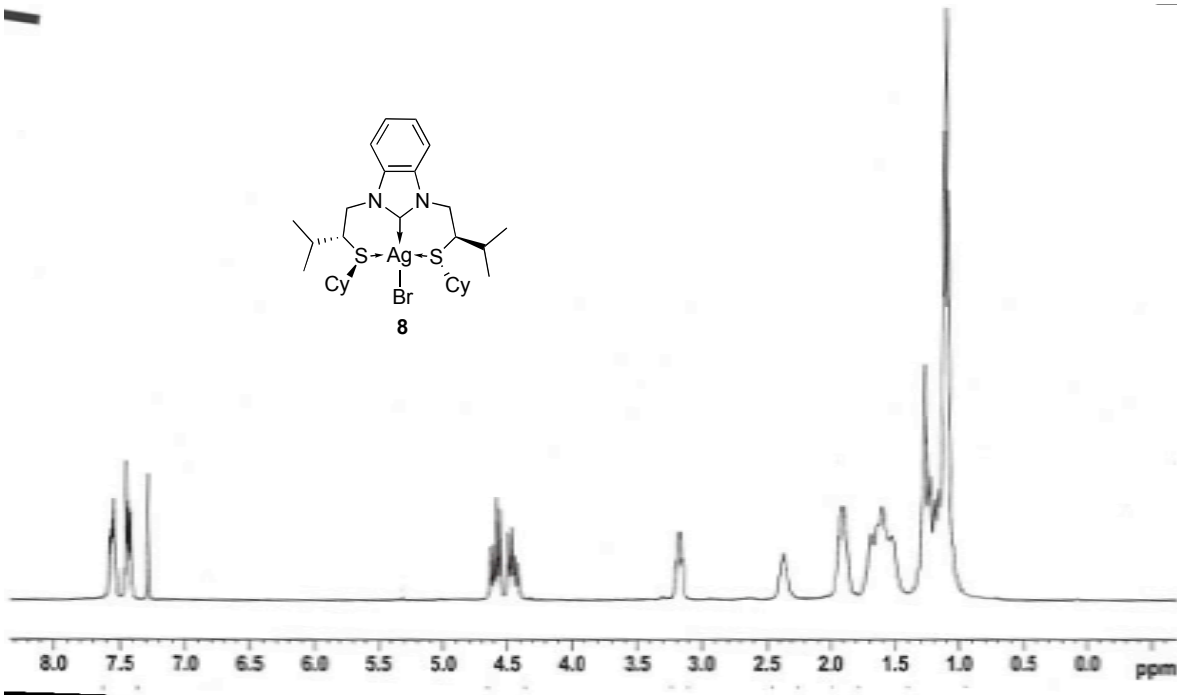
6

^{13}C NMR ($CDCl_3$, 125 MHz)



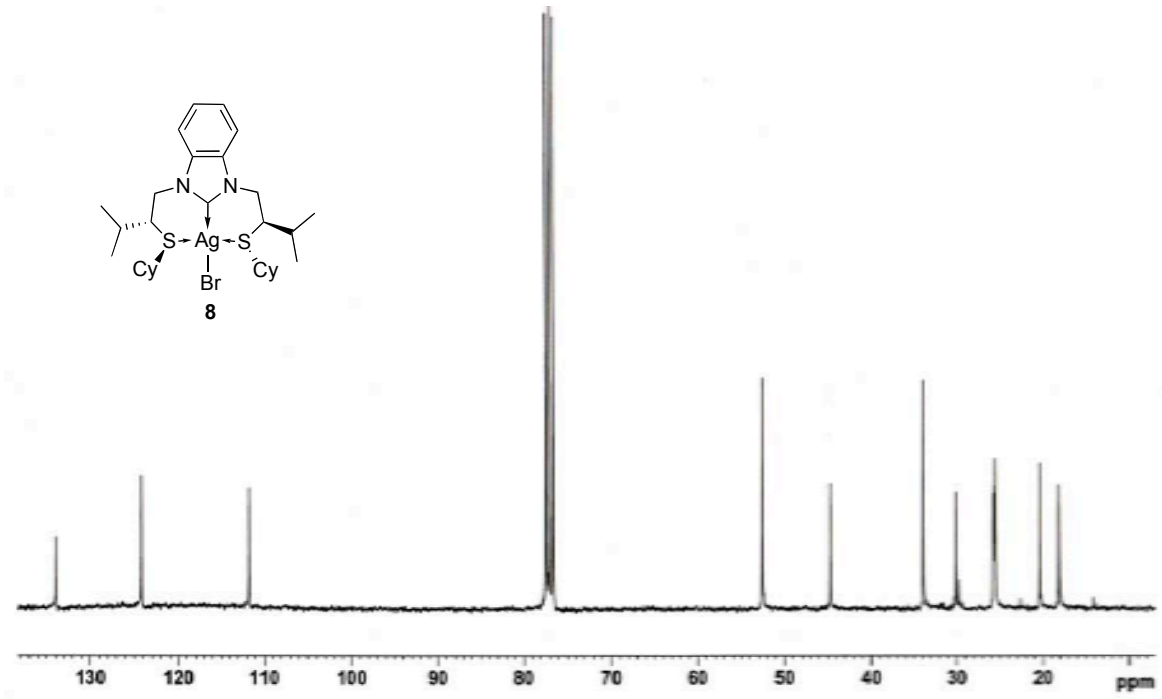
6

^{1}H NMR ($CDCl_3$, 300 MHz)



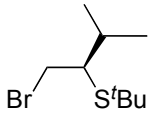
8

^{13}C NMR ($CDCl_3$, 75 MHz)



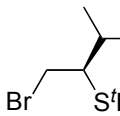
8

^{1}H NMR ($CDCl_3$, 400 MHz)



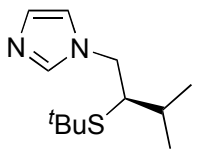
2b

^{13}C NMR ($CDCl_3$, 100 MHz)



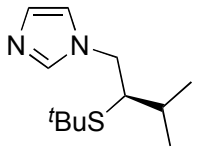
2b

^{1}H NMR ($CDCl_3$, 400 MHz)



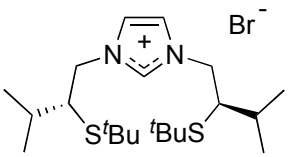
3b

^{13}C NMR ($CDCl_3$, 100 MHz)



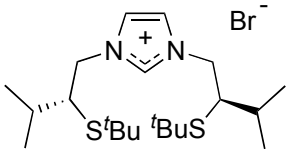
3b

^{1}H NMR ($CDCl_3$, 500 MHz)



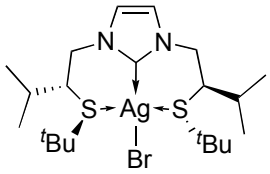
4b

^{13}C NMR ($CDCl_3$, 125 MHz)



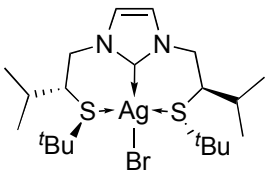
4b

^{1}H NMR ($CDCl_3$, 500 MHz)



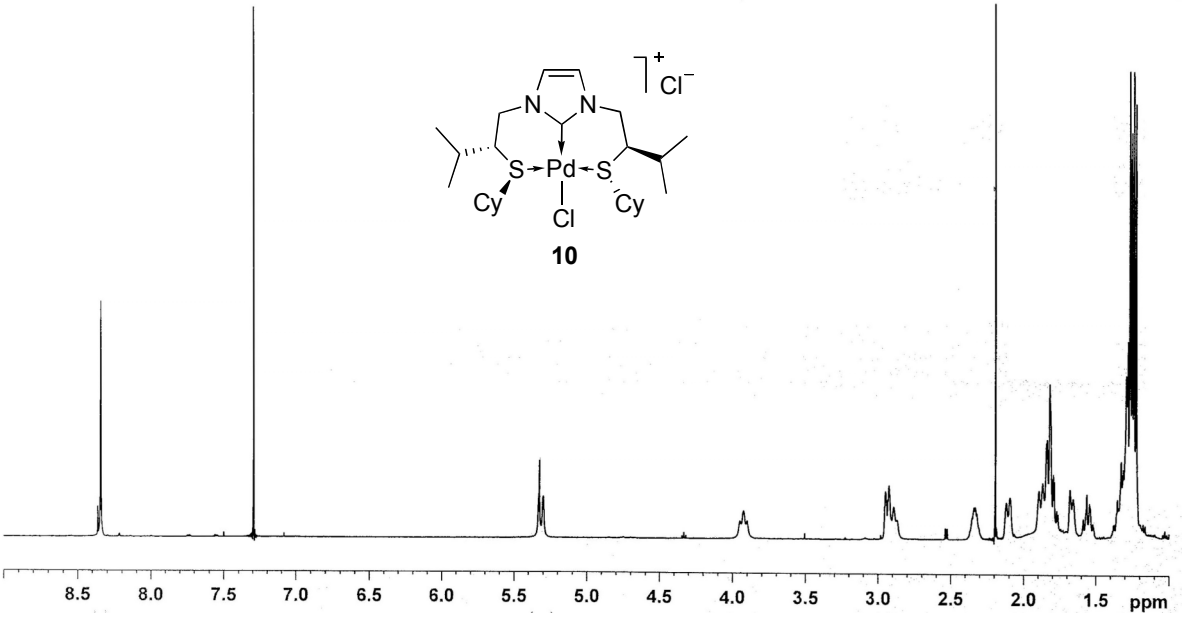
7b

^{13}C NMR ($CDCl_3$, 125 MHz)



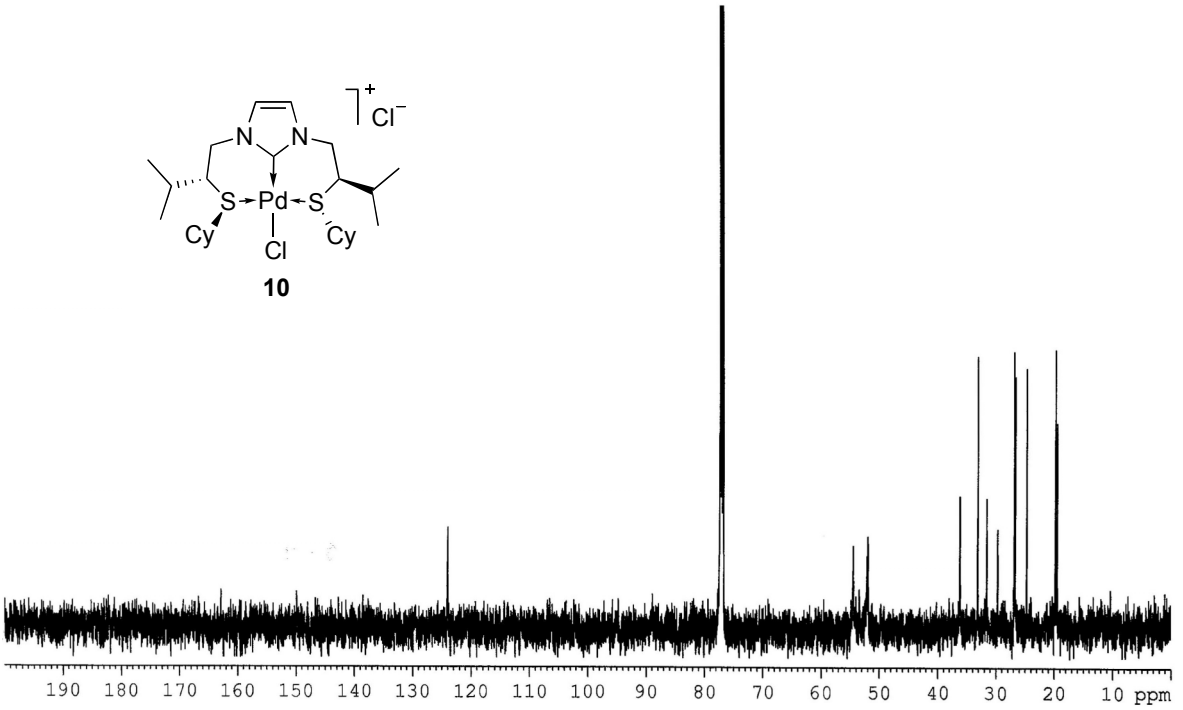
7b

^{1}H NMR ($CDCl_3$, 500 MHz)



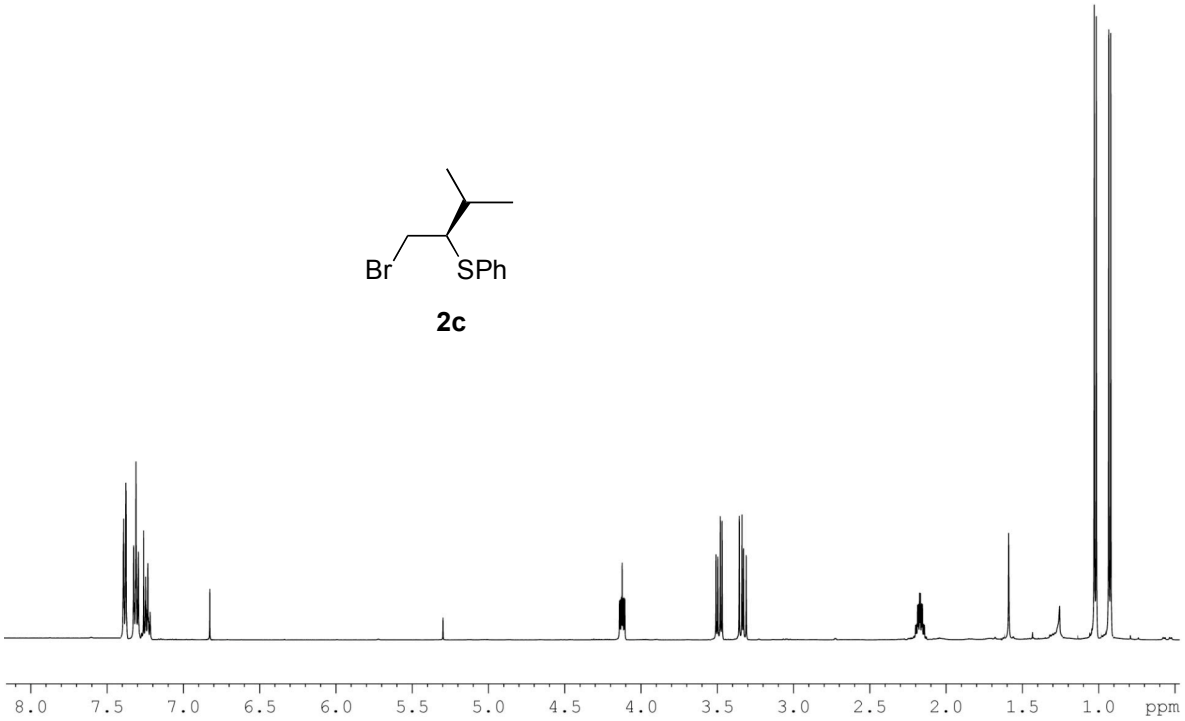
10

^{13}C NMR ($CDCl_3$, 125 MHz)



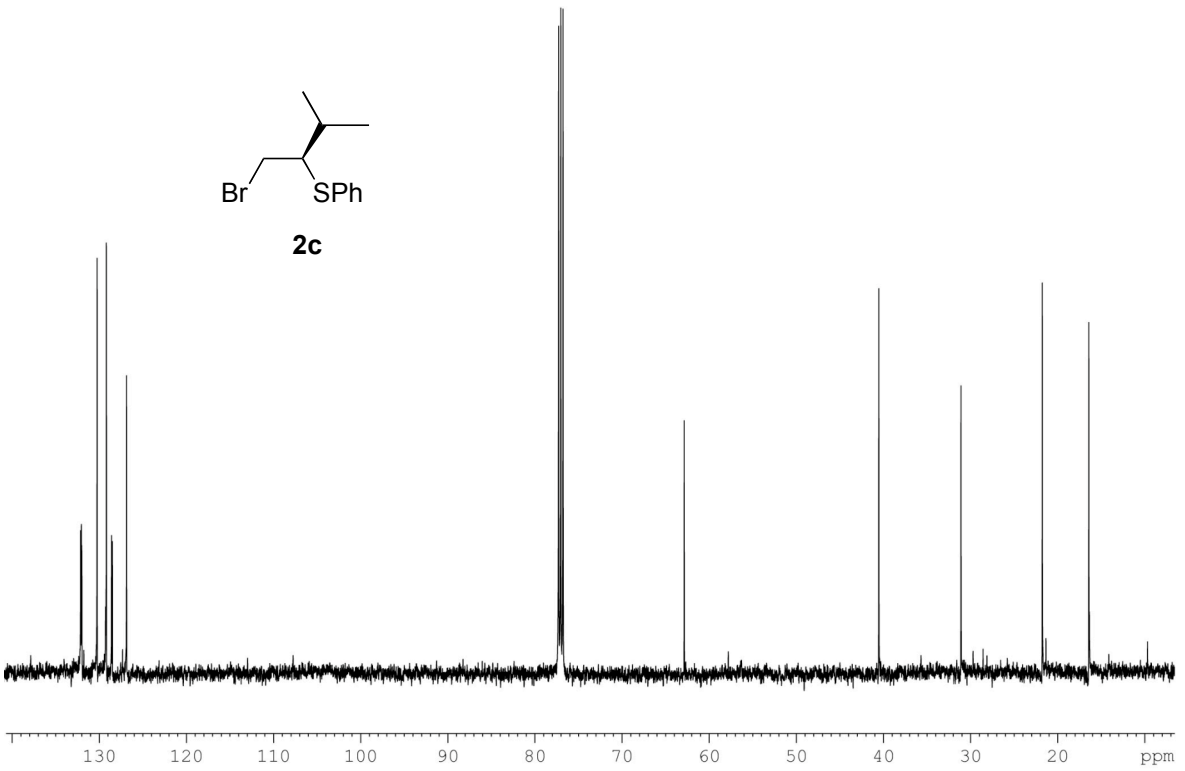
10

^{1}H NMR ($CDCl_3$, 500 MHz)



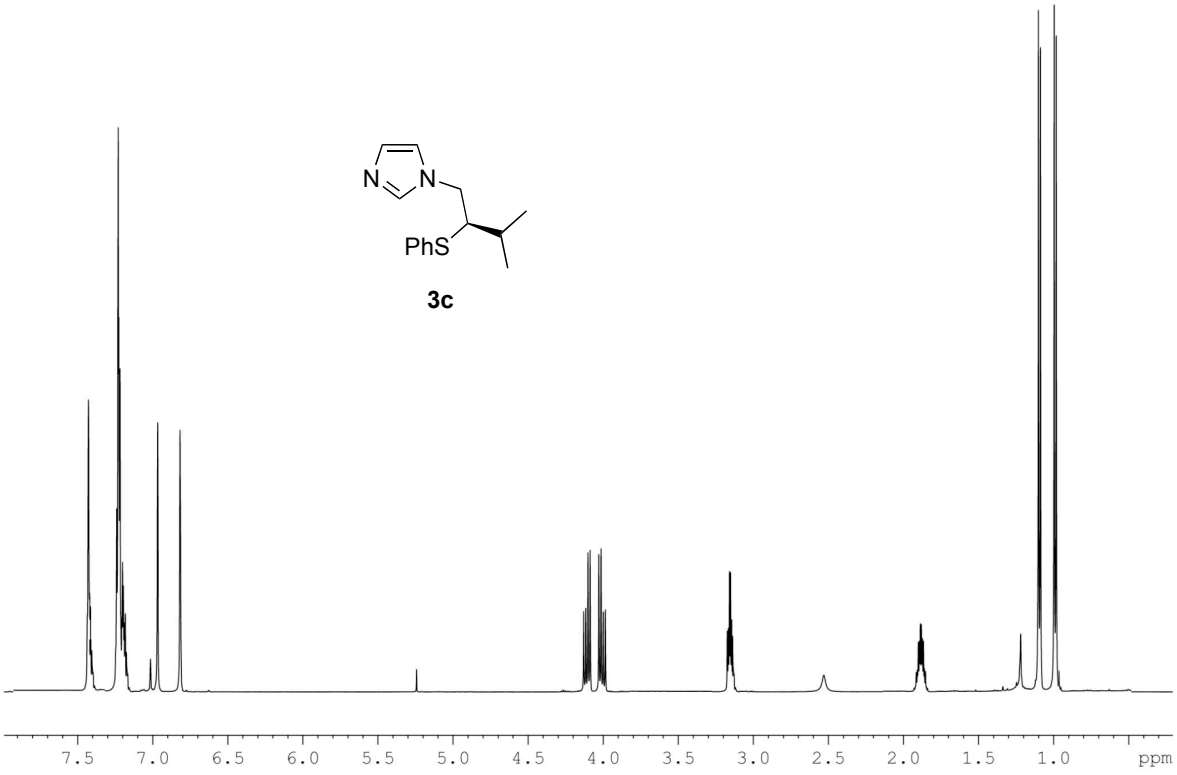
2c

^{13}C NMR ($CDCl_3$, 125 MHz)



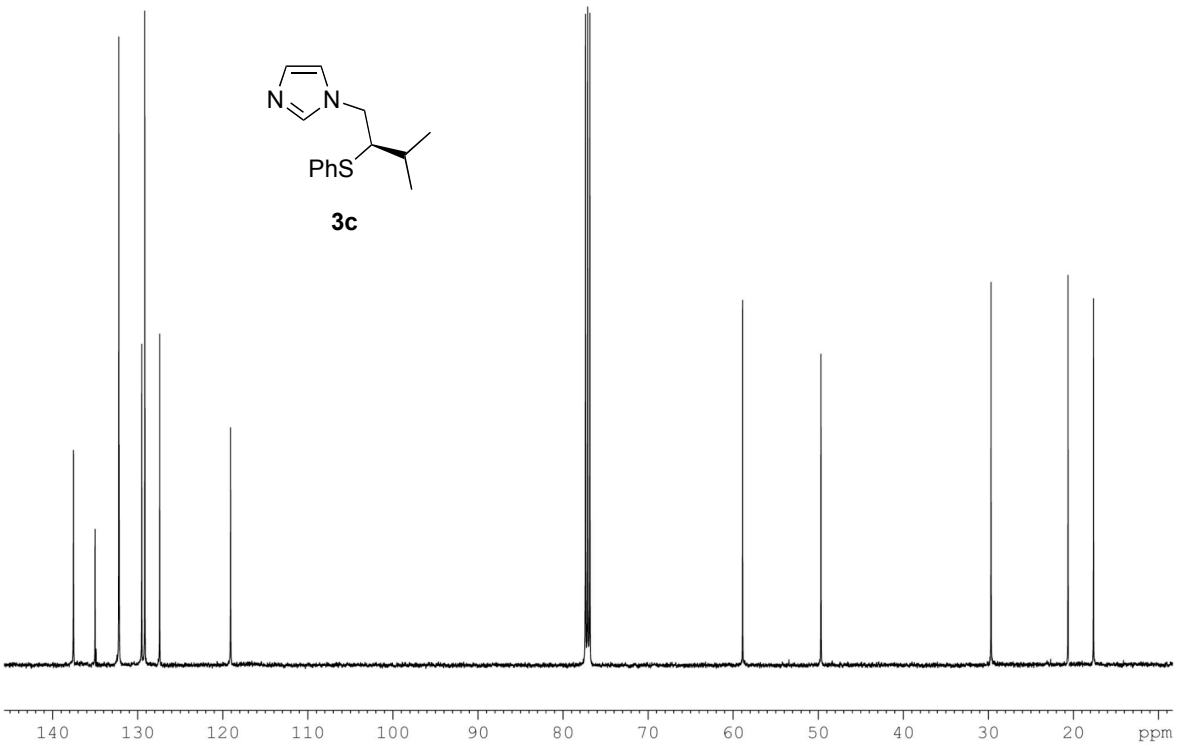
2c

^{1}H NMR ($CDCl_3$, 500 MHz)



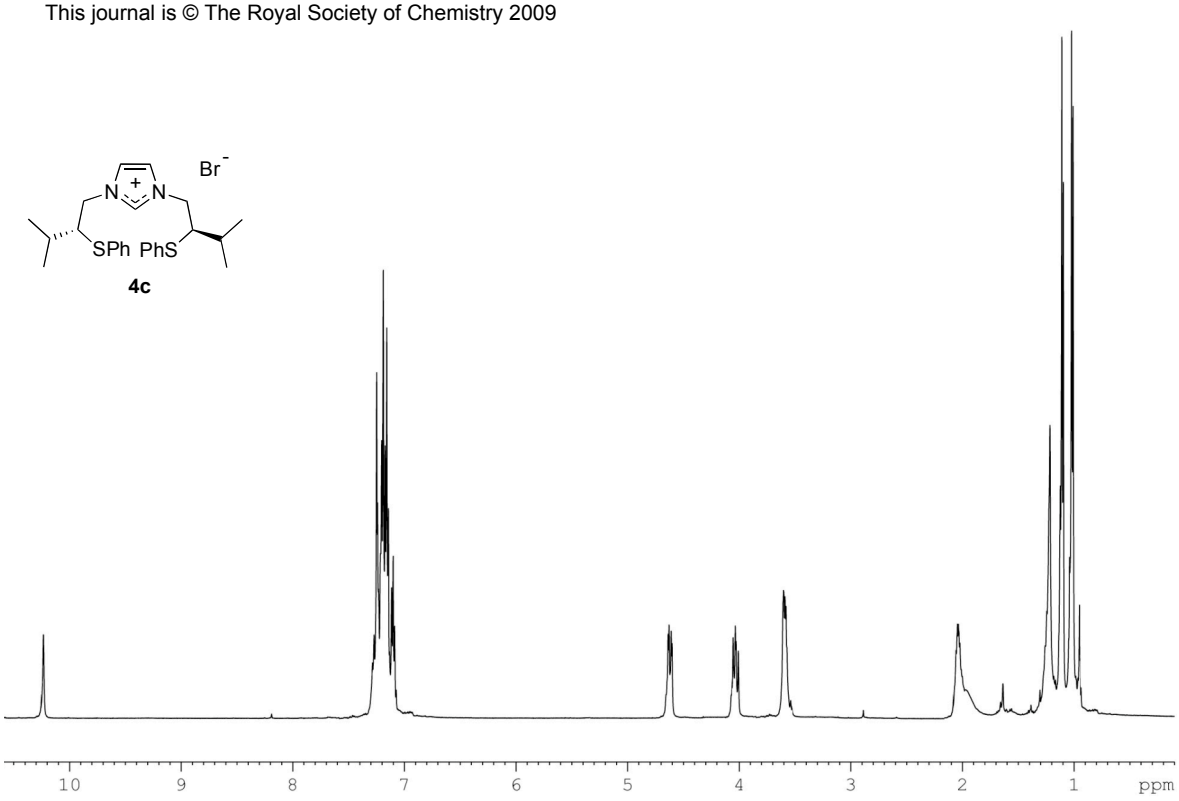
3c

^{13}C NMR ($CDCl_3$, 125 MHz)

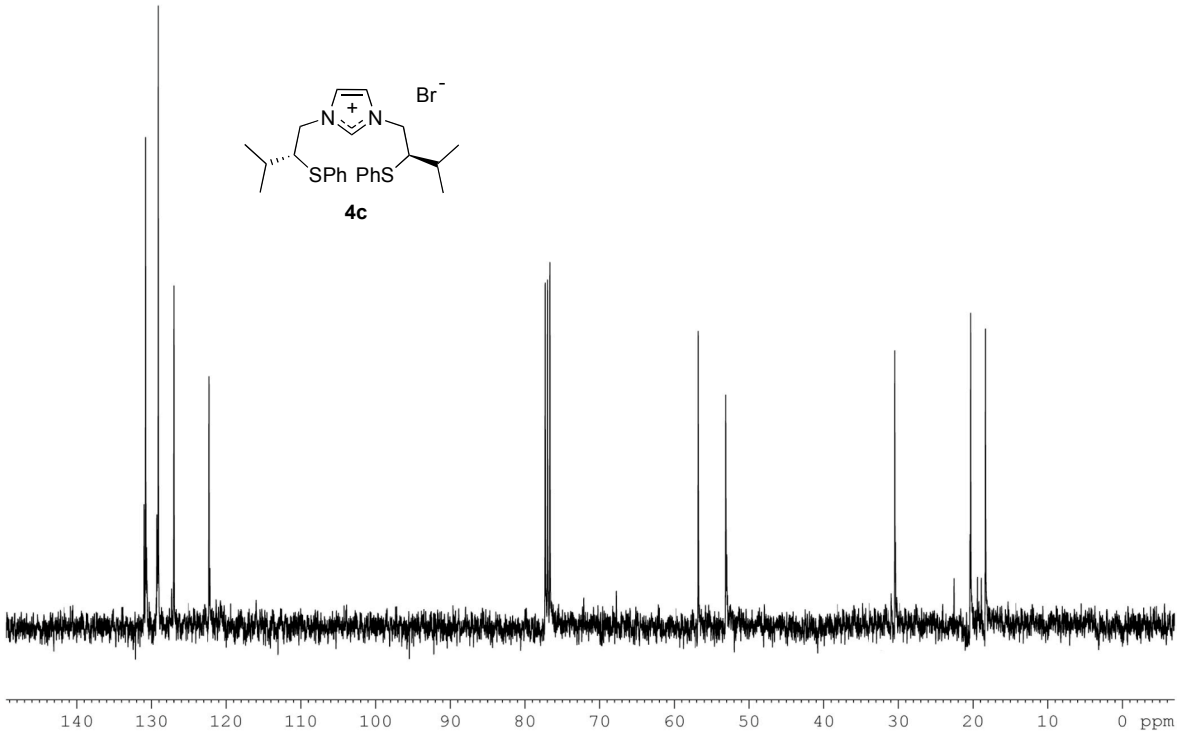


3c

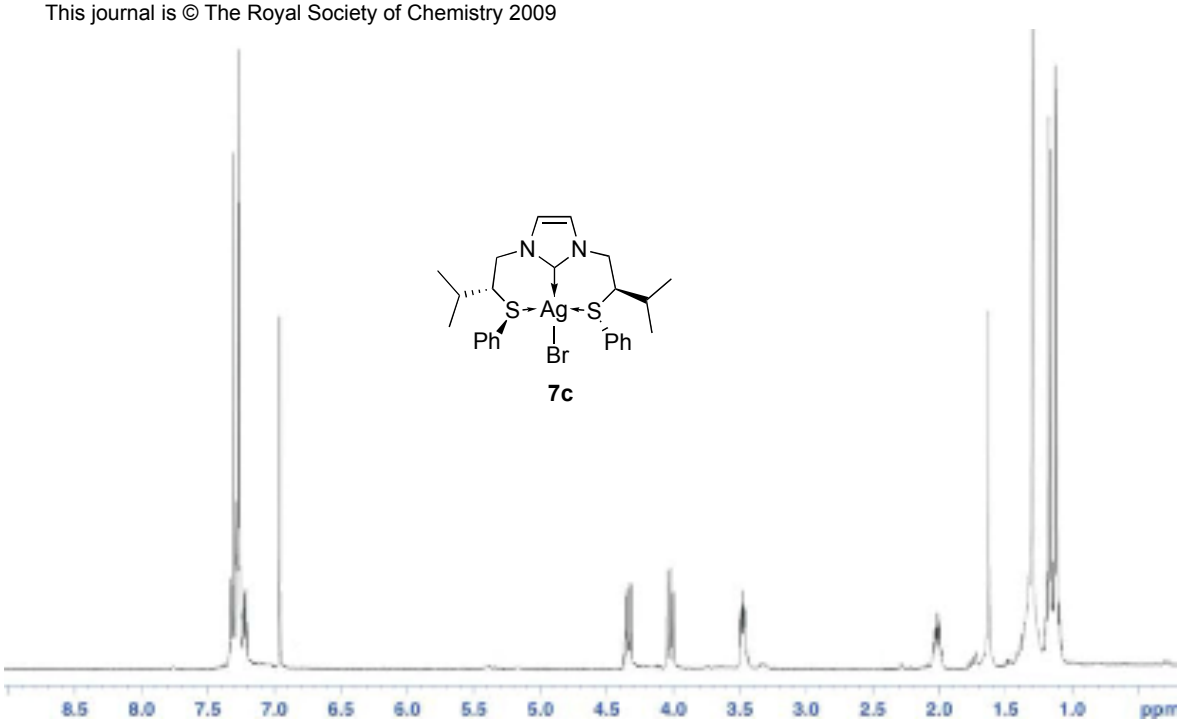
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 125 MHz)

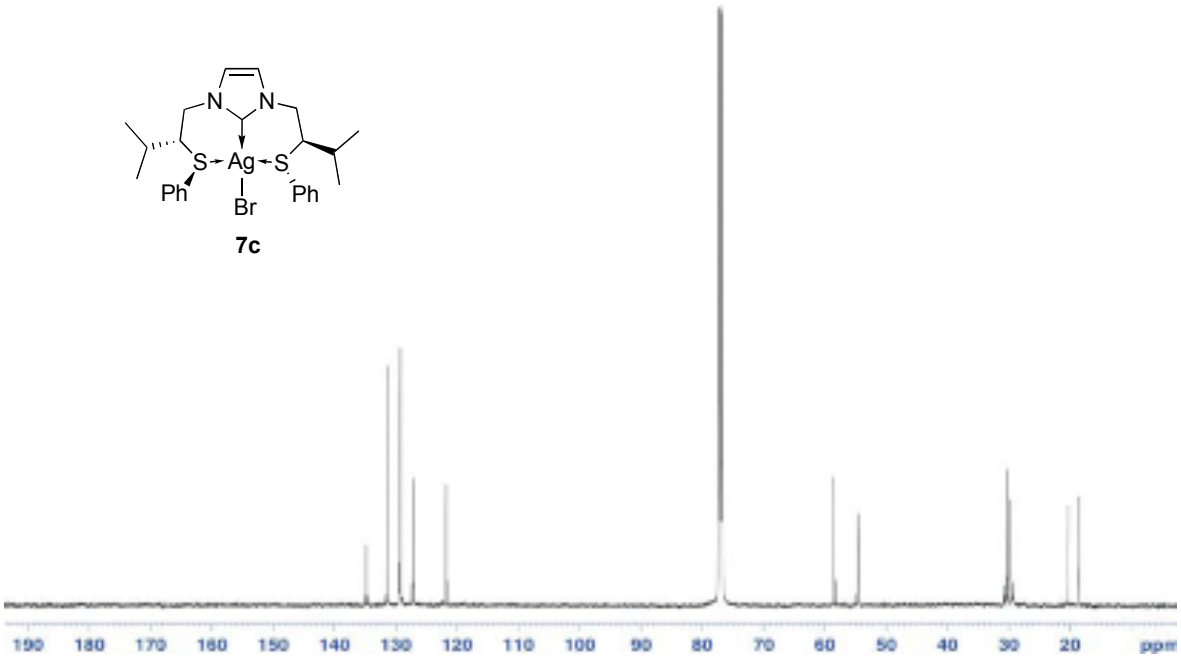


^{1}H NMR ($CDCl_3$, 500 MHz)



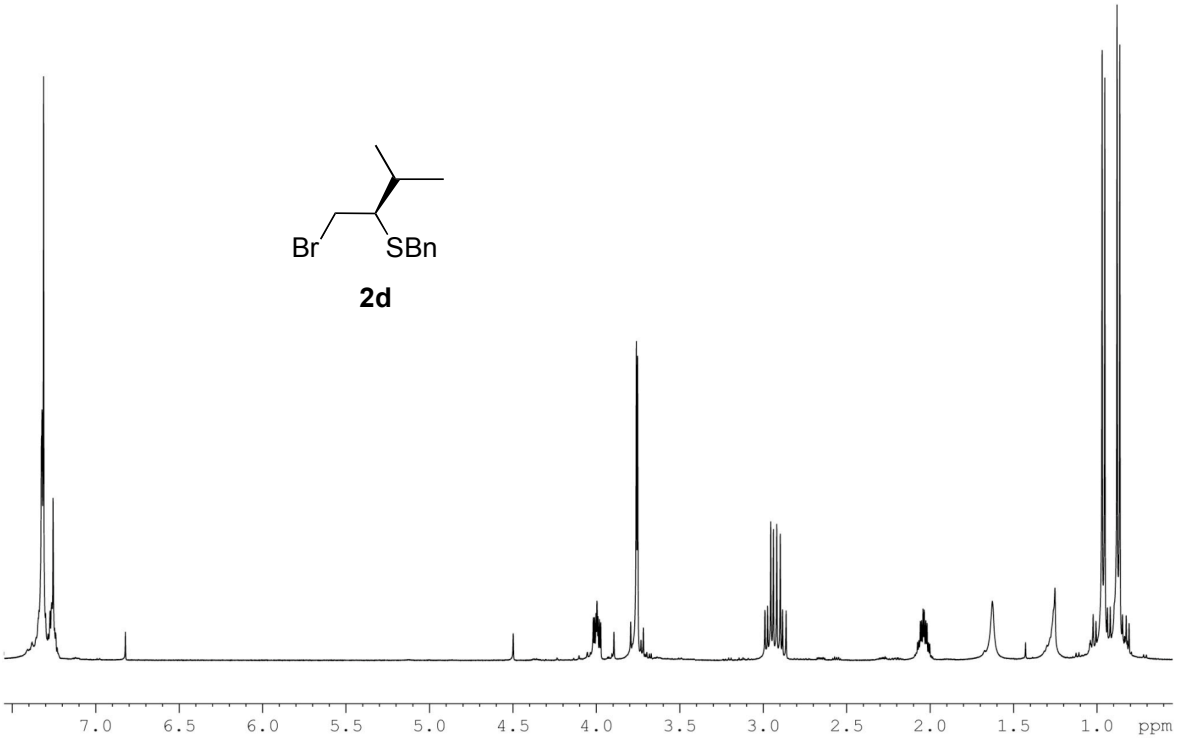
7c

^{13}C NMR ($CDCl_3$, 125 MHz)



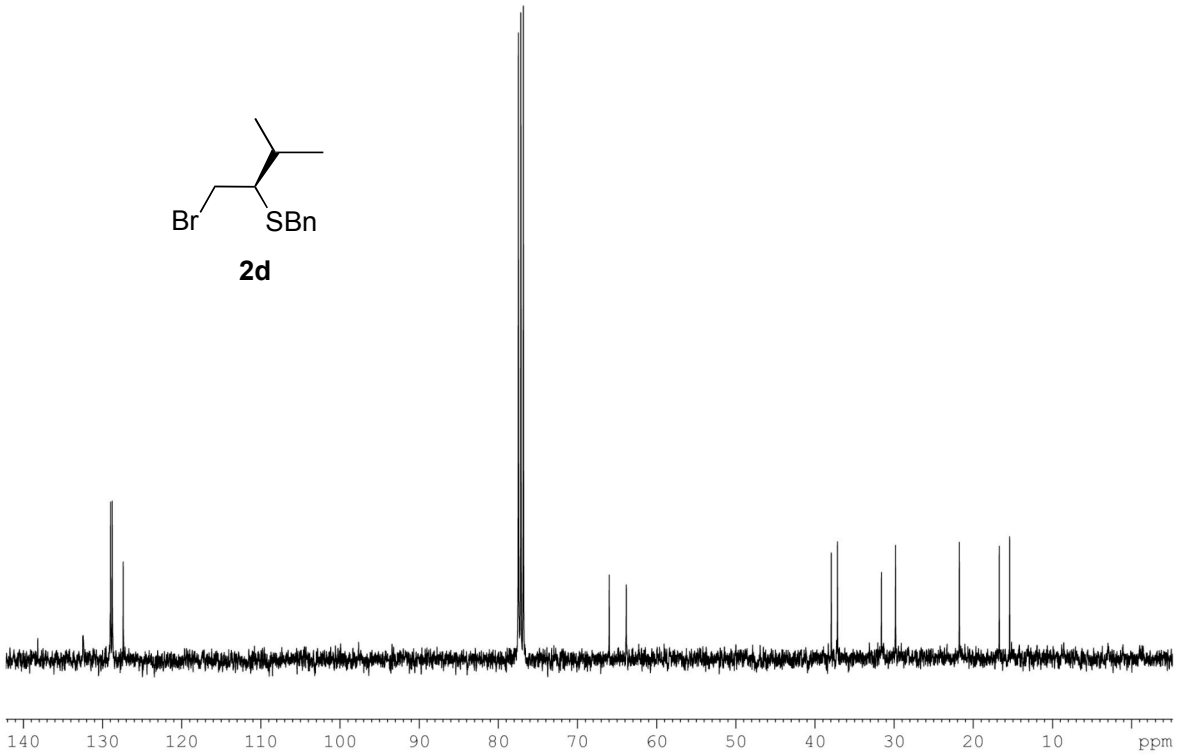
7c

^{1}H NMR ($CDCl_3$, 400 MHz)



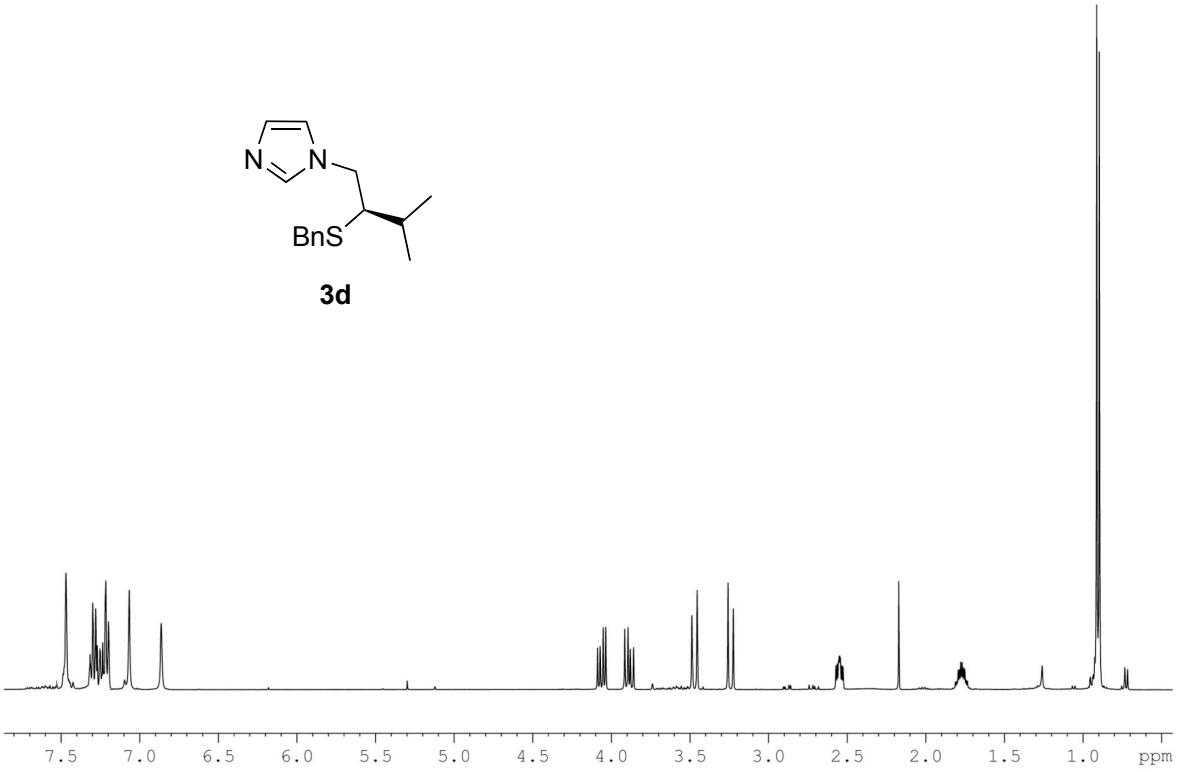
2d

^{13}C NMR ($CDCl_3$, 100 MHz)



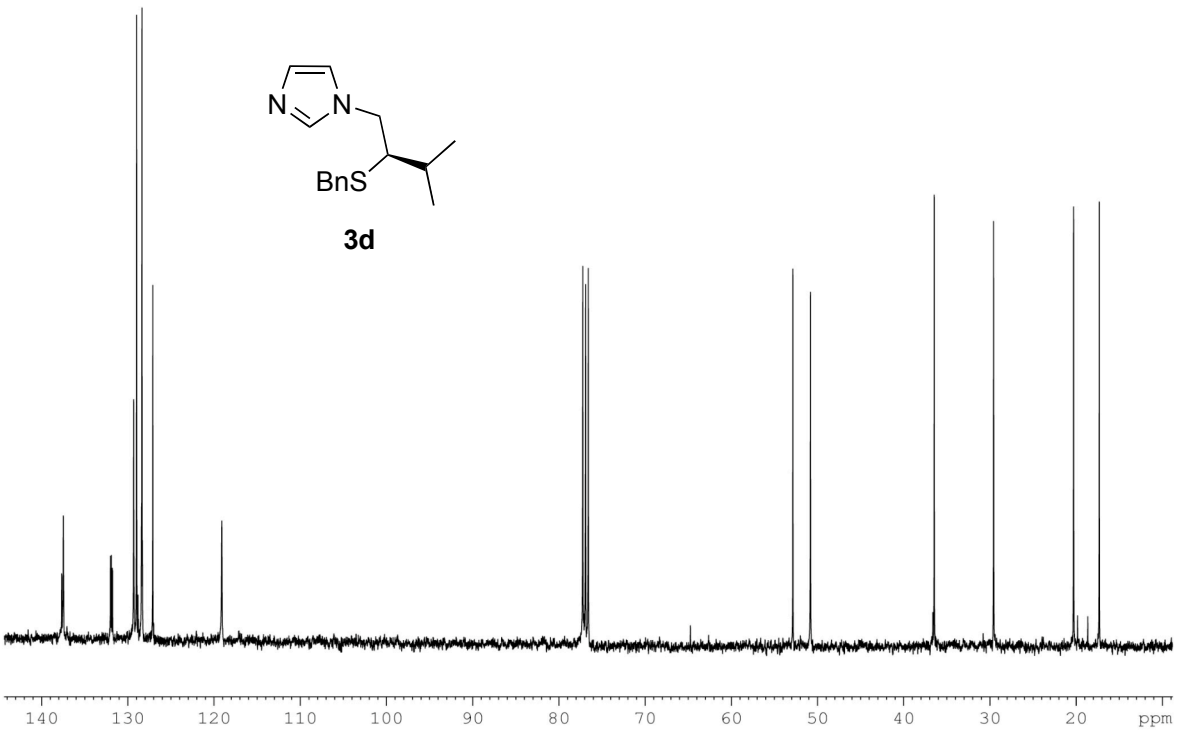
2d

^{1}H NMR ($CDCl_3$, 400 MHz)



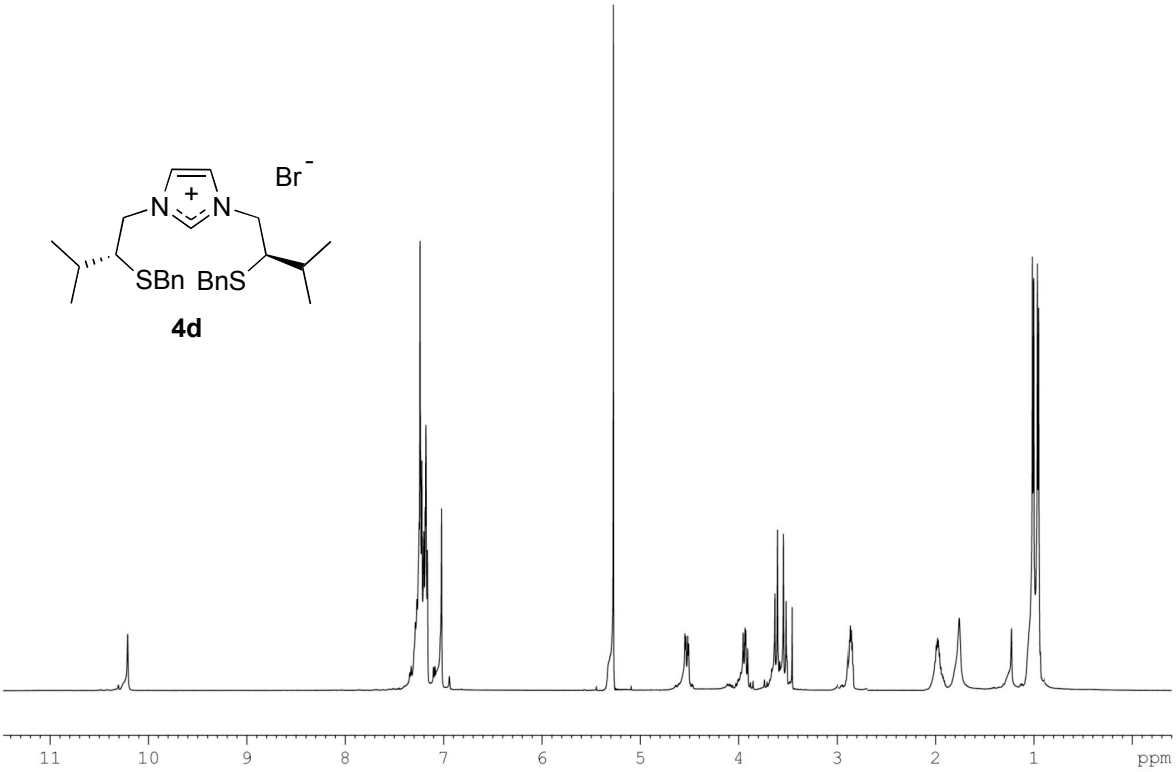
3d

^{13}C NMR ($CDCl_3$, 100 MHz)

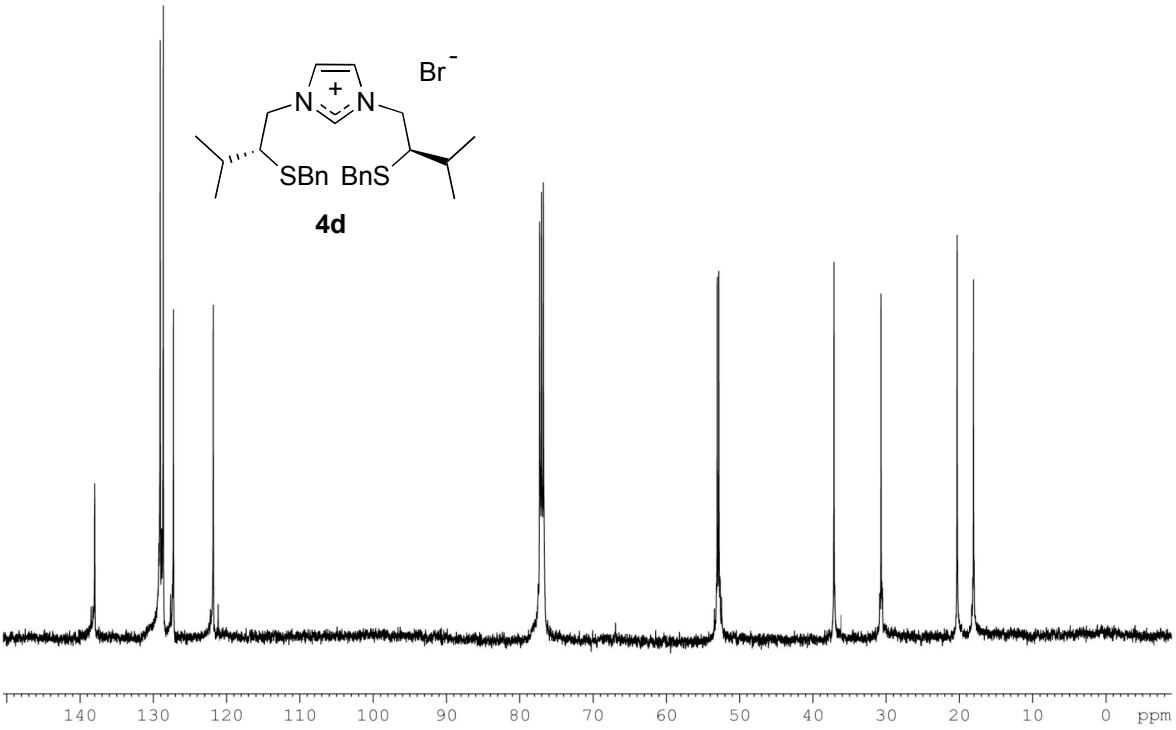


3d

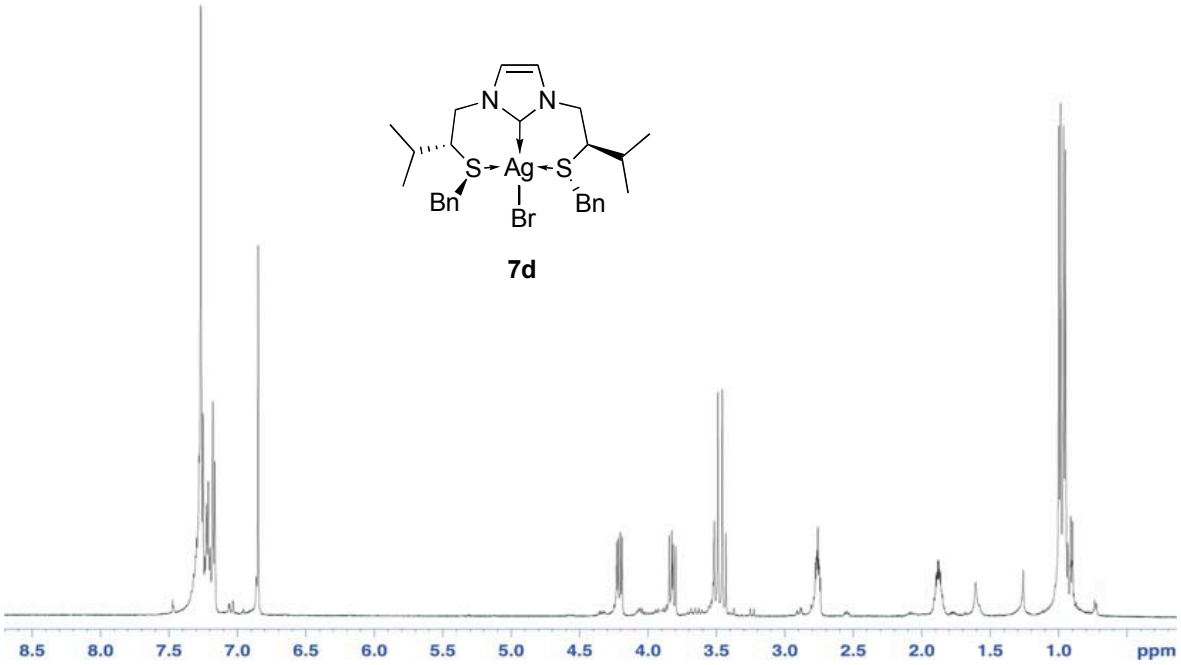
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 125 MHz)

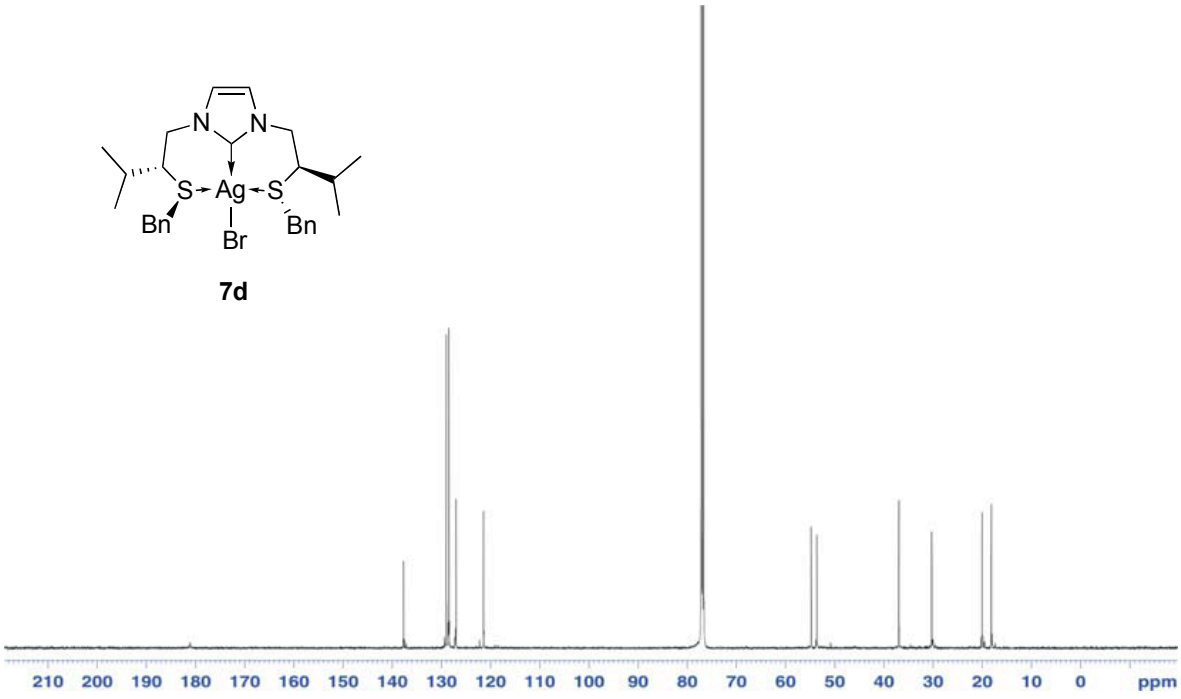


^{1}H NMR ($CDCl_3$, 500 MHz)



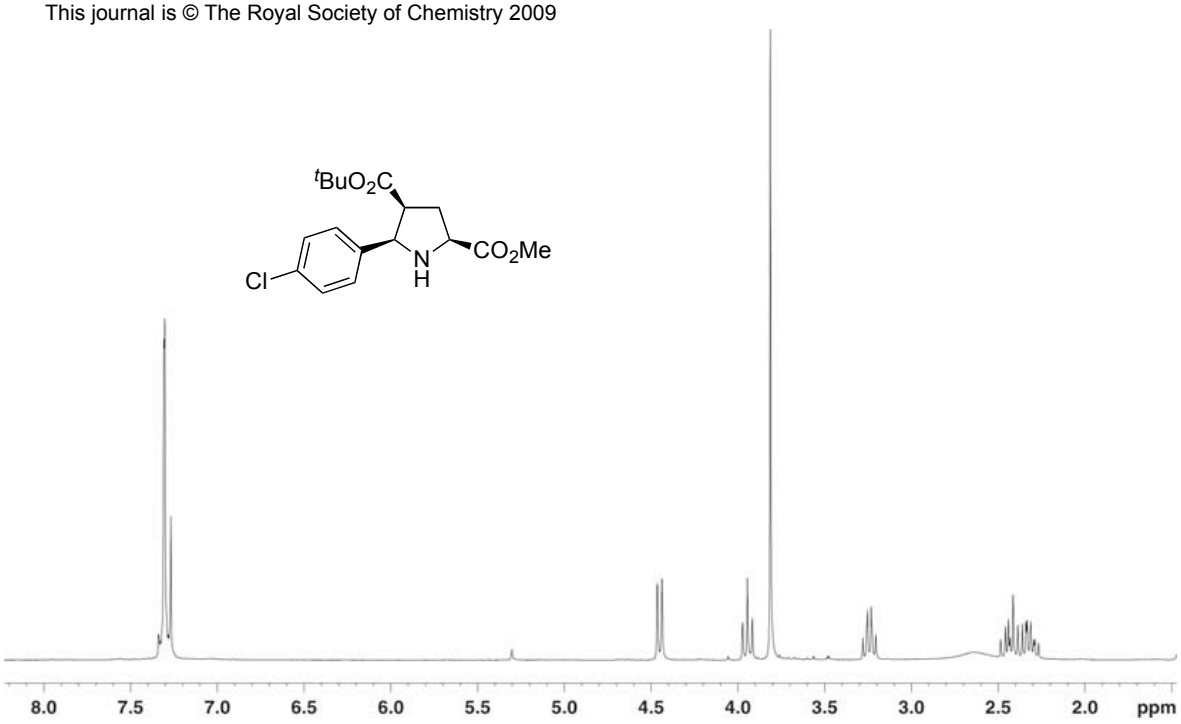
7d

^{13}C NMR ($CDCl_3$, 125 MHz)



7d

^{1}H NMR ($CDCl_3$, 300 MHz)



^{13}C NMR ($CDCl_3$, 75 MHz)