Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

for

Synthetic routes to [Au(NHC)(OH)] (NHC = N-heterocyclic carbene) complexes

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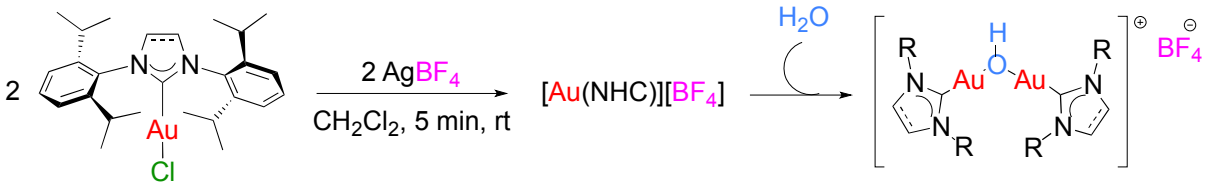
General considerations

Unless otherwise stated, all solvents and reagents were used as purchased and all reactions were performed under air. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were filtered through basic alumina in order to remove traces of HCl. NMR spectra were recorded on 400 and 300 MHz spectrometers at room temperature in CD_2Cl_2 or $CDCl_3$. Chemical shifts are given in parts per million (ppm) with respect to TMS. Elemental analysis was carried out by the analytical services of London Metropolitan University. CCDC 856432 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the synthesis of [{Au(NHC)}$_2$(μ-OH)][BF_4] complexes



$AgBF_4$ (40 mg, 0.20 mmol) was added to a stirred solution of [Au(NHC)Cl] (100 mg, 0.16 mmol) in dichloromethane (5 mL). The reaction mixture was stirred avoiding the presence of light at rt for 5 min and then filtered over celite into a separating funnel containing distilled water (10 mL). The mixture was shaken for 1 min. The organic phase was collected, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The resulting solid was dissolved in the minimum amount of CH_2Cl_2 (2 mL) and the product was precipitated by addition of 8 mL of pentane. The precipitate was collected by filtration, affording the corresponding [{Au(NHC)}$_2$(μ-OH)][BF_4] as a white powder.

Synthesis of [{Au(IPr)}$_2$(μ-OH)][BF_4] 3

Following the general procedure, 81% of a white powder was obtained. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.50 (t, *J* =7.8 Hz, 4H), 7.26 (s, 4H), 7.24 (d, *J* = 7.8 Hz, 8H), 2.39 (sept, *J* = 6.9 Hz, 8H), 1.19 (d, *J* = 6.9 Hz, 24H), 1.11 ppm (d, J = 6.9 Hz, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.6, 145.4, 133.6, 130.7, 124.2, 124.1, 28.6, 24.4, 23.8 ppm; ^{19}F NMR (185 MHz, $CDCl_3$): δ = -154.90, -154.85 ppm.

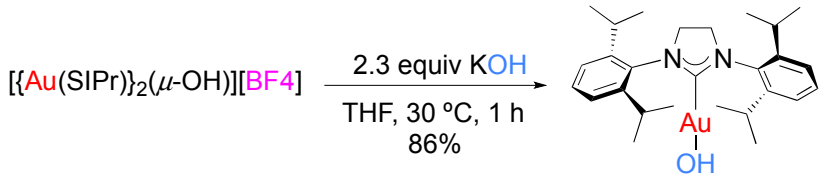
Synthesis of [{Au(SIPr)}$_2$(μ-OH)][BF_4] 5

Following the general procedure, 83% of a white powder was obtained. ^{1}H NMR (400 MHz; CD_2Cl_2): δ = 7.42 (t, *J* = 7.8 Hz, 4H), 7.19 (d, *J* = 7.8 Hz, 8H), 4.01 (s, 8H), 2.88 (sept, *J* = 6.9 Hz, 8H), 1.28 (d, *J* = 6.9 Hz, 24H), 1.16 (d, *J* = 6.8 Hz, 24H), 0.37 (s, 1H) ppm. ^{13}C NMR (101 MHz; CD_2Cl_2): δ = 186.1, 146.9, 134.1, 130.4, 124.9, 53.93, 53.80, 29.1, 25.2, 24.1 ppm.^{19}F NMR (376

MHz; CD_2Cl_2): δ = -154.09, -154.14 ppm. Anal. Calcd. for $C_{54}H_{77}Au_2BF_4N_4O$ (1278.95): C, 50.71; H, 6.07; N, 4.38. Found: C, 50.58; H, 6.00; N, 4.49.

Synthesis of [Au(SIPr)(OH)] 4

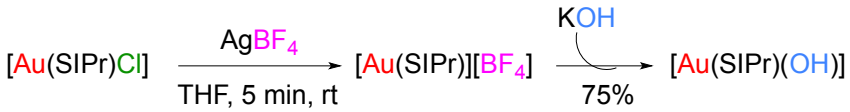
General procedure A



5 **4**

KOH (10 mg, 178 µmol) was added to a stirred solution of [{Au(NHC)}$_2$(μ-OH)][BF_4] **5** (100 mg, 78 µmol) in THF (3 mL). The reaction mixture was stirred for 1 h at 30 ºC, then filtered over celite and concentrated under vacuum. The resulting solid was dissolved in 2 mL of THF and the product was precipitated by addition of 8 mL of pentane. The precipitate was collected by filtration, affording **4** in 86% yield as a white powder.

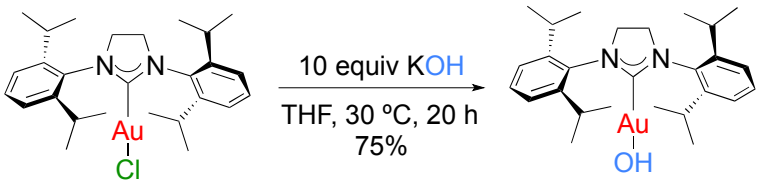
General procedure B



6 **4**

$AgBF_4$ (40 mg, 0.20 mmol) was added to a stirred solution of [Au(SIPr)Cl] **6** (100 mg, 0.16 mmol) in THF (3 mL). The reaction mixture was stirred avoiding the presence of light at rt for 5 min and then filtered over celite. KOH (10 mg, 178 µmol) was then added. The reaction was stirred for 1.5 h at 30 ºC, filtered over celite and concentrated under vacuum. The resulting solid was dissolved in 2 mL of THF and the product was precipitated by addition of 10 mL of pentane. The precipitate was collected by filtration, affording **4** in 75% yield as a white powder.

General procedure C



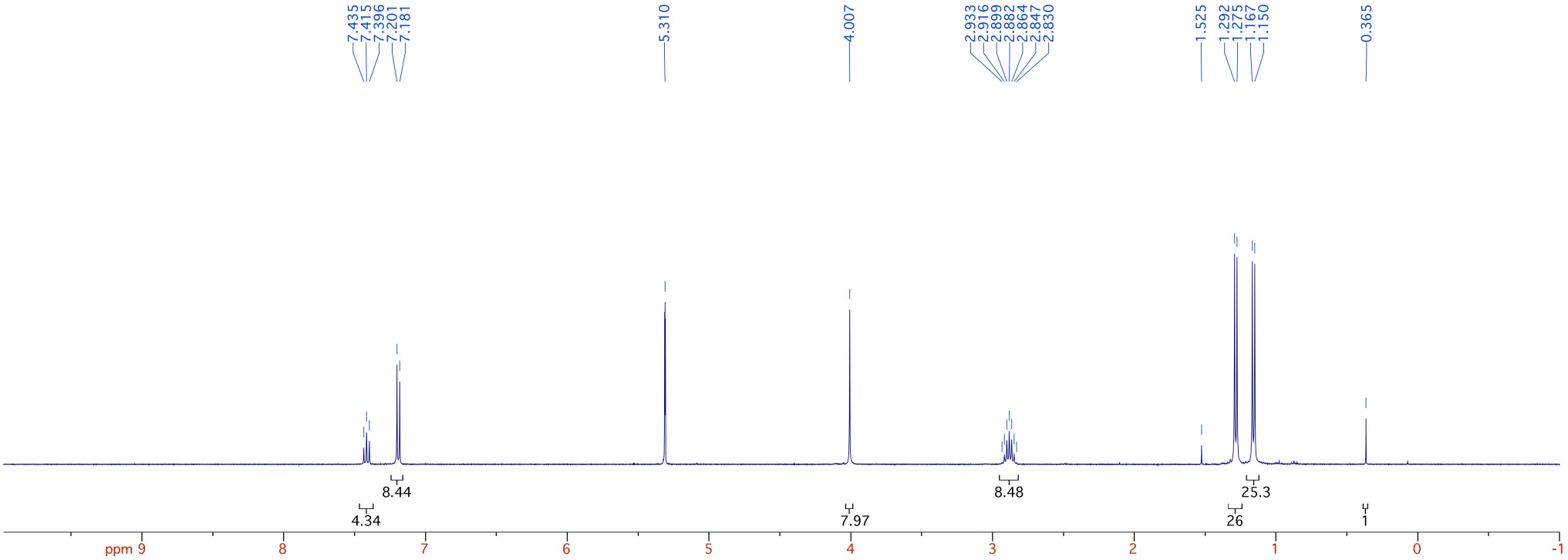
6 **4**

KOH (90 mg, 1.6 mmol) was added to a stirred solution of [Au(SIPr)Cl] **6** (100 mg, 0.16 mmol) in THF (3 mL). The reaction mixture was stirred for 20 h at 30 ºC, then filtered over celite and concentrated under vacuum. The resulting solid was dissolved in 2 mL of THF and the product was

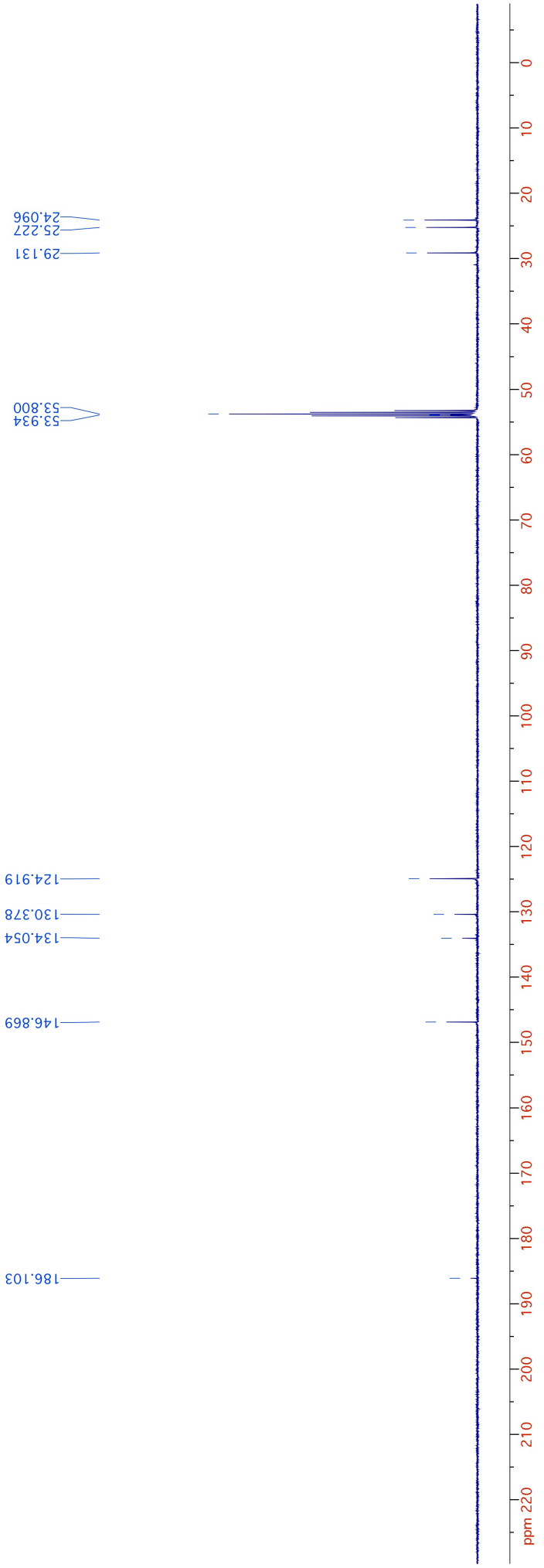
precipitated by addition of 10 mL of pentane. The precipitate was collected by filtration, affording **4** as a white powder in 75% yield. ^{1}H NMR (400 MHz; CD_2Cl_2): δ = 7.45 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 4H), 3.99 (s, 4H), 3.06 (sept, *J* = 6.9 Hz, 4H), 1.41 (d, *J* = 6.8 Hz, 12H), 1.33 (d, *J* = 6.9 Hz, 12H), -0.71 (br, 1H) ppm. ^{13}C NMR (101 MHz; CD_2Cl_2): δ = 193.5, 147.2, 135.0, 130.0, 124.8, 53.7, 29.2, 25.1, 24.2 ppm. Anal. Calcd. for $C_{27}H_{39}AuN_2O$ (604.58): C, 53.64; H, 6.50; N, 4.63. Found: C, 53.50; H, 6.36; N, 4.48.

NMR SPECTRA

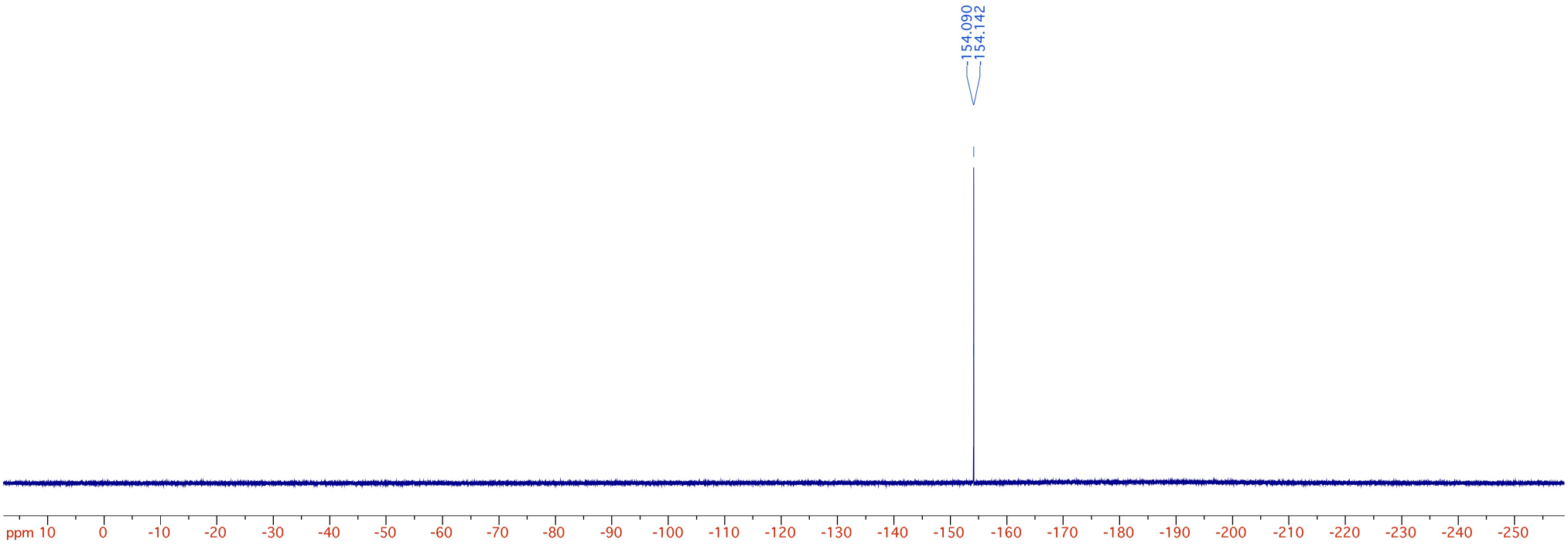
^{1}H NMR complex 5



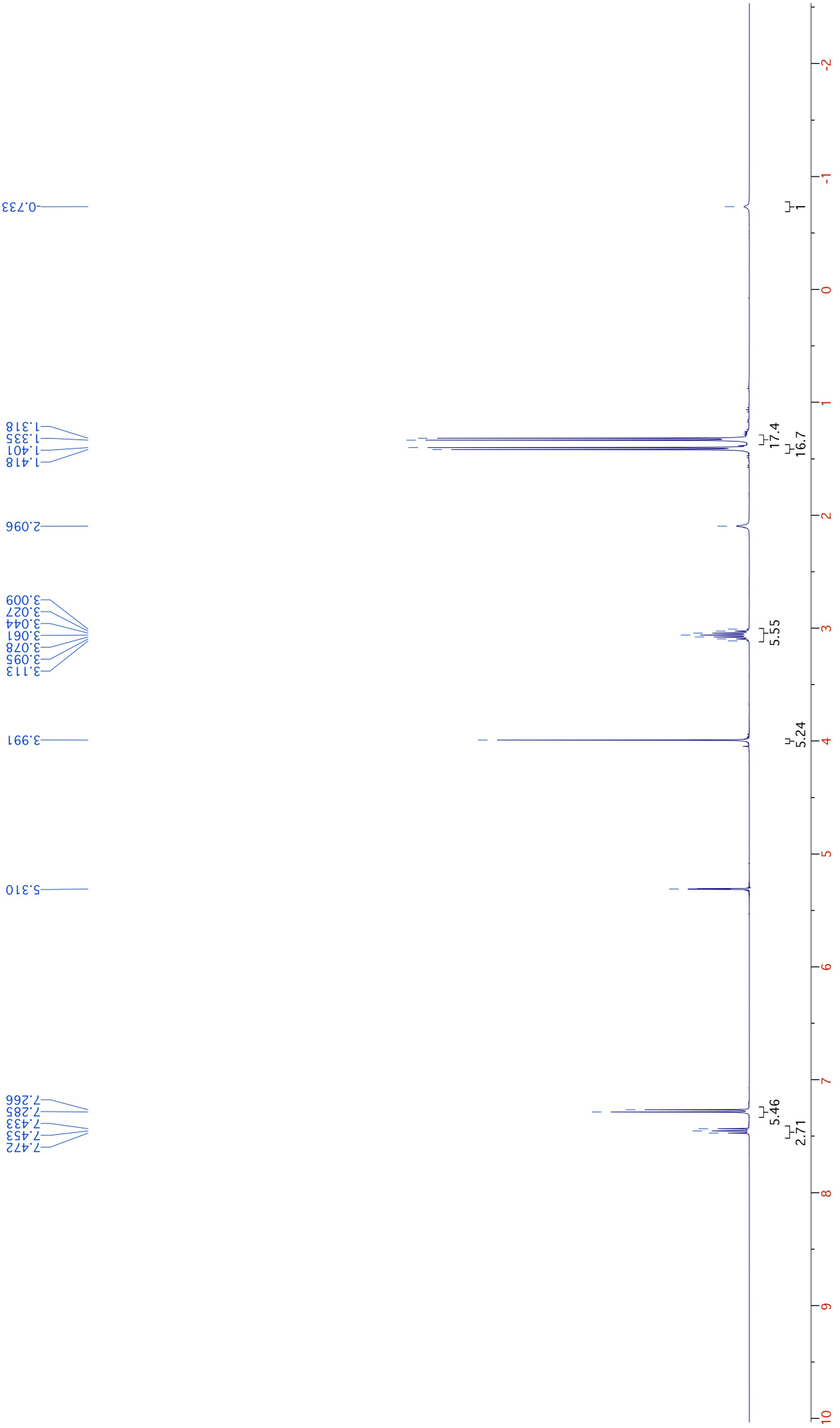
^{13}C NMR complex 5



^{19}F NMR complex 5



^{1}H NMR complex 4



^{13}C NMR complex 4