Electronic Supplementary Material (ESI) for ChemComm.

Structure and bonding of [(SIPr)AgX] complexes (X = Cl, Br, I and OTf)

Supporting Information

1. General Information

Unless otherwise stated, all manipulations were performed in air and solvents and materials were used as received from commercial sources without purification. Solvents were dried by passing through the columns of molecular sieves in a solvent purification system (Innovative Technology Inc.). ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F (376 Hz) spectra were recorded at 25 °C on Bruker Avance™ 400 spectrometers. Residual protic solvents were used as an internal standard ($CHDCl_2$, δ_H= 5.23 ppm, $CHCl_3$, δ_H= 7.26 ppm) and ^{13}C resonances were referenced to the deuterated carbon ($CHDCl_2$, δ_C = 54 ppm, $CDCl_3$, δ_C= 77 ppm). Chemical shifts (δ) are reported in ppm, and *J* values in Hz. Multiplicity is abbreviated to s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), sept (septet), and multiplet (m). Mass spectra (MS) were recorded at Imperial College London on Micromass Autospec Premier, Micromass LCT Premier, or VG Platform II spectrometers using EI, CI or ESI techniques. Infrared spectra were recorded using a Perkin Elmer 100 series FT-IR spectrometer, equipped with an ATR accessory. Single crystal X-ray diffraction was performed at Imperial College London using an Agilent Xcalibur 3 E diffractometer. Elemental analyses were performed by the Analytical Services at London Metropolitan University. The imidazolium salts SIMes·HCl,[1] SIPr·HCl,[2] SIPr·HBr,[3] SIPr·HBF_4,[4] and the NHC complex [(SIPr)AgCl][5] were synthesized according to published procedures.

2. Synthesis of Ag(I) NHC Complexes

General procedure for the synthesis of complexes 1 and 2:

[(SIPr)AgX] (X = Br, I for **1**, X = Cl for **2**) (0.1 mmol, 1.0 eq.), AgOTf (0.1 mmol, 1.0 eq.) were stirred in THF (0.5 mL) for 1 h. The resultant precipitate was removed by filtration through Celite. The residue was rinsed with another 1.0 mL of THF. The filtrate was removed *in vacuo* to give a colourless oil, which was triturated with Et_2O to give a white solid. X-ray diffraction quality single crystals were grown from CH_2Cl_2/hexane at 0 °C.

[(SIPr)AgOTf] (1).

Prepared according to the general procedure from [(SIPr)AgBr] (57.8 mg, 0.1 mmol) and AgOTf (25.7 mg). Yield: 44.7 mg (69%). White solid. ^{1}H NMR (CD_2Cl_2): δ = 7.48–7.44 (t, 2H), 7.30 (d, *J* = 7.8, 4H), 4.12 (s, 4H), 3.04 (sept, *J* = 6.9, 4H), 1.35 (d, *J* = 6.9, 12H), 1.31 (d, *J* = 6.9, 12H). ^{13}C NMR (CD_2Cl_2): δ = 146.7, 134.3, 130.0, 124.7, 54.1, 28.8, 25.0, 23.9. ^{19}F NMR (CD_2Cl_2): δ = -78.7. MS [ESI]: *m/z* (%) = 538.23 $[(SIPr)Ag(MeCN)]^+$ (100). Anal. Calc. for $C_{28}H_{38}AgF_3N_2O_3S$: C, 51.94; H, 5.92; N, 4.33%. Found: C, 50.49; H, 6.18; N, 4.24%.

$[(SIPr)_2Ag_2(\mu\text{-Cl})][OTf]$ (2).

Prepared according to the general procedure from [(SIPr)AgCl] (53.4 mg) and AgOTf (25.7 mg). Yield: 45.4 mg (88%). White solid. ^{1}H NMR ($CDCl_3$): δ = 7.45 (t, *J* = 7.8, 2H), 7.27 (d, *J* = 7.8, 4H), 4.13 (s, 4H), 3.01 (sept, *J* = 6.9, 4H), 1.35 (d, *J* = 6.9, 12H), 1.32 (d, *J* = 6.9, 12H). ^{13}C NMR ($CDCl_3$): δ = 205.4 [dd, $^{1}J(^{109}Ag, ^{13}C)$ = 310, $^{1}J(^{107}Ag, ^{13}C)$ = 268], 146.5, 134.1, 130.3, 124.8, 53.9 (d, *J* = 8.1), 28.9, 25.3, 24.1. ^{19}F NMR ($CDCl_3$): δ = 78.8. MS [ESI]: *m/z* (%) = 538.24 $[(SIPr)Ag(MeCN)]^+$ (100), 887.52 $[Ag(SIPr)_2]^+$ (31), 391.31 $[SIPr+H]^+$ (18), 1031.39 $[M\text{-}OTf]^+$ (9). Anal. Calc. for $C_{55}H_{76}Ag_2ClF_3N_4O_3S$: C, 55.91; H, 6.48; N, 4.74%. Found: C, 55.82; H, 6.38; N, 4.51%.

[(SIPr)AgBr] (3).[5]

A mixture of SIPr.HBr (0.47 g, 1.0 mmol, 2.0 eq.), Ag_2O (0.14 g, 0.6 mmol, 1.2 eq.) and CH_2Cl_2 (6.0 mL) were stirred at room temperature overnight. The resulting mixture was

filtered through Celite, and the solvent was removed *in vacuo*. The resulting white solid was recrystallized from CH_2Cl_2/hexane at 0 °C. Yield: 0.41 g (71%). ^{1}H NMR (CD_2Cl_2): δ = 7.48–7.44 (m, 2H), 7.29 (d, *J* = 7.8, 4H), 4.08 (s, 4H), 3.08 (sept, *J* = 6.9, 4H), 1.36 (d, *J* = 4.3, 12H), 1.34 (d, *J* = 4.3, 12H). ^{13}C NMR (CD_2Cl_2): δ = 209.9 [dd, $^1J(^{109}Ag, ^{13}C)$ = 249, $^1J(^{107}Ag, ^{13}C)$ = 216], 147.2, 135.0, 130.2, 125.0, 54.3 (d, *J* = 8.1), 29.16, 25.51, 24.13. MS [ESI]: *m/z* (%) = 538.22 $[(SIPr)Ag(MeCN)]^+$ (100). Anal. Calc. for $C_{27}H_{38}AgBrN_2$: C, 56.07; H, 6.62; N, 4.84%. Found: C, 55.93; H, 6.68; N, 4.87%.

[(SIPr)AgI] (4).
A mixture of SIPr.HBF_4 (47.8 mg, 0.1 mmol, 1.0 eq.), NaI (74.9 mg, 0.5 mmol, 5.0 eq.), Ag_2O (0.07 mmol, 16.2 mg, 0.7 eq.) and CH_2Cl_2 (2.5 mL) were stirred at room temperature overnight. The resulting mixture was filtered through Celite, and the solvent was removed *in vacuo*. The resulting white solid was recrystallized from CH_2Cl_2/hexane. Yield: 50.1 mg (80%). ^{1}H NMR ($CDCl_3$): δ = 7.43 (t, *J* = 7.8, 2H), 7.27 (d, *J* = 7.7, 4H), 4.09 (s, 4H), 3.09 (sept, *J* = 6.9, 4H), 1.37 (d, *J* = 2.4, 12H), 1.36 (d, *J* = 2.4, 12H). ^{13}C NMR ($CDCl_3$): δ = 210.8 [dd, $^1J(^{109}Ag, ^{13}C)$ = 207, $^1J(^{107}Ag, ^{13}C)$ = 238], 146.5, 134.3, 130.0, 124.6, 53.9 (d, *J* = 8.1), 28.8, 25.4, 24.1. MS [ESI]: *m/z* (%) = 650.35 (100). Anal. Calc. for $C_{27}H_{38}AgIN_2$: C, 51.86; H, 6.12; N, 4.48%. Found: C, 51.82; H, 6.06; N, 4.51%.

3. Crystal Data and Structure Refinement for Compounds 1-4

The X-ray crystal structure of 1

Crystal data for **1**: $C_{28}H_{38}AgF_3N_2O_3S$, M = 647.53, orthorhombic, $P2_12_12_1$ (no. 19), a = 12.9810(3), b = 13.4443(3), c = 17.5825(4) Å, V = 3068.51(13) Å^3, Z = 4, D_c = 1.402 g cm^{-3}, μ(Mo-Kα) = 0.773 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3E diffractometer; 5632 independent measured reflections (R_{int} = 0.0210), F^2 refinement,[X1] R_1(obs) = 0.0269, wR_2(all) = 0.0571, 5299 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 351 parameters. The absolute structure of **1** was determined by use of the Flack parameter [x = –0.013(14)]. CCDC 1400409.

The X-ray crystal structure of 2

Crystal data for **2**: $[C_{54}H_{76}Ag_2ClN_4](CF_3O_3S)\cdot 1.5(CH_2Cl_2)$, M = 1308.83, monoclinic, $P2_1/n$ (no. 14), a = 20.2292(6), b = 16.3318(4), c = 20.2255(7) Å, β = 111.277(4)°, V = 6226.6(3) Å^3, Z = 4, D_c = 1.396 g cm^{-3}, μ(Mo-Kα) = 0.886 mm^{-1}, T = 173 K, colourless blocky needles, Agilent Xcalibur 3E diffractometer; 12428 independent measured reflections (R_{int} = 0.0218), F^2 refinement,[X1] R_1(obs) = 0.0418, wR_2(all) = 0.1037, 9549 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 707 parameters. CCDC 1400410.

The triflate anion in the structure of **2** was found to be disordered. Two orientations were identified of *ca*. 70 and 30% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The C(80)-based dichloromethane solvent molecule was also found to be disordered, and likewise two partial occupancy orientations were identified. However, both of these orientations were found to be unrealistically close to the minor (30%) occupancy orientation of the disordered triflate anion described above. The occupancy of the triflate is fixed by the charge balance requirements, so the combined occupancy of the two orientations of the disordered dichloromethane molecule cannot exceed 70%. For reasons of simplicity, and taking into account the thermal parameters, the combined occupancy of this disordered dichloromethane molecule was set to exactly 50%. Within this restriction, the two orientations were found to have

occupancies of *ca*. 36 and 14%. The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of 3

Crystal data for **3**: $C_{27}H_{38}AgBrN_2$, M = 578.37, orthorhombic, *Pccn* (no. 56), a = 10.94396(18), b = 12.5589(2), c = 19.9805(4) Å, V = 2746.19(8) Å^3, Z = 4 [C_S symmetry], D_c = 1.399 g cm^{-3}, μ(Mo-Kα) = 2.204 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3E diffractometer; 2964 independent measured reflections (R_{int} = 0.0212), F^2 refinement,[X1] R_1(obs) = 0.0287, wR_2(all) = 0.0644, 2295 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 147 parameters. CCDC 1400411.

The structure of **3** was found to have crystallographic C_S symmetry with the mirror plane passing though Br1, Ag1 and C1, and bisecting the N2–C1–N2A angle.

The X-ray crystal structure of 4

Crystal data for **4**: $C_{27}H_{38}AgIN_2{\cdot}CH_2Cl_2$, M = 710.29, monoclinic, $P2_1/c$ (no. 14), a = 10.7195(5), b = 19.0287(5), c = 16.2788(6) Å, β = 106.154(4)°, V = 3189.4(2) Å^3, Z = 4, D_c = 1.479 g cm^{-3}, μ(Mo-Kα) = 1.785 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3E diffractometer; 6338 independent measured reflections (R_{int} = 0.0207), F^2 refinement,[X1] R_1(obs) = 0.0369, wR_2(all) = 0.0685, 5184 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 316 parameters. CCDC 1400412.

Complex	**1**	**2**
CCDC no.	CCDC 1400409	CCDC 1400410
Formula	$C_{28}H_{38}AgF_3N_2O_3S$	$C_{54}H_{76}Ag_2ClN_4$, CF_3O_3S, 1.5(CH_2Cl_2)
Formula weight	647.53	1308.83
Temperature	173 K	173 K
Diffractometer, wavelength	Agilent Xcalibur 3 E, 0.71073 Å	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/n$

Unit cell dimensions	a = 12.9810(3) Å α = 90°	a = 20.2292(6) Å α = 90°
	b = 13.4443(3) Å β = 90°	b = 16.3318(4) Å β = 111.277(4)°
	c = 17.5825(4) Å γ = 90°	c = 20.2255(7) Å γ = 90°
Volume, Z	3068.51(13) $Å^3$, 4	6226.6(3) $Å^3$, 4
Density (calculated)	1.402 Mg/m^3	1.396 Mg/m^3
Absorption coefficient	0.773 mm^{-1}	0.886 mm^{-1}
F(000)	1336	2700
Crystal colour / morphology	Colourless blocks	Colourless blocky needles
Crystal size	0.67 x 0.44 x 0.23 mm^3	0.43 x 0.24 x 0.17 mm^3
θ range for data collection	2.470 to 28.170°	2.495 to 28.294°
Index ranges	$-16 \le h \le 9$, $-9 \le k \le 17$, $-15 \le l \le 22$	$-26 \le h \le 13$, $-21 \le k \le 12$, $-23 \le l \le 26$
Reflns collected / unique	7703 / 5632 [R(int) = 0.0210]	21593 / 12428 [R(int) = 0.0218]
Reflns observed [F>4σ(F)]	5299	9549
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.864 and 0.770	0.871 and 0.781
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5632 / 0 / 351	12428 / 95 / 707
Goodness-of-fit on F^2	1.031	1.026
Final R indices [F>4σ(F)]	R_1 = 0.0269, wR_2 = 0.0552	R_1 = 0.0418, wR_2 = 0.0923
R indices (all data)	R_1 = 0.0306, wR_2 = 0.0571	R1 = 0.0625, wR_2 = 0.1037
Largest diff. peak, hole	0.293, -0.340 $eÅ^{-3}$	1.157, -0.869 $eÅ^{-3}$
Mean and maximum shift/error	0.000 and 0.001	0.000 and 0.001

Complex	**3**	**4**
CCDC no.	CCDC 1400411	CCDC 1400412
Formula	$C_{27}H_{38}AgBrN_2$	$C_{27}H_{38}AgIN_2$, CH_2Cl_2
Formula weight	578.37	710.29
Temperature	173 K	173 K
Diffractometer, wavelength	Agilent Xcalibur 3 E, 0.71073 Å	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system, space group	Orthorhombic, Pccn	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 10.94396(18) Å α = 90°	a = 10.7195(5) Å α = 90°
	b = 12.5589(2) Å β = 90°	b = 19.0287(5) Å β = 106.154(4)°
	c = 19.9805(4) Å γ = 90°	c = 16.2788(6) Å γ = 90°
Volume, Z	2746.19(8) $Å^3$, 4	3189.4(2) $Å^3$, 4
Density (calculated)	1.399 Mg/m^3	1.479 Mg/m^3
Absorption coefficient	2.204 mm^{-1}	1.785 mm^{-1}
F(000)	1184	1424
Crystal colour / morphology	Colourless blocks	Colourless blocks
Crystal size	0.36 x 0.28 x 0.16 mm^3	0.70 x 0.38 x 0.12 mm^3
θ range for data collection	2.605 to 28.135°	2.605 to 28.274°
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 13$, $-18 \le l \le 24$	$-9 \le h \le 13$, $-18 \le k \le 25$, $-21 \le l \le 14$
Reflns collected / unique	14723 / 2964 [R(int) = 0.0212]	11647 / 6338 [R(int) = 0.0207]
Reflns observed [$F>4\sigma(F)$]	2295	5184
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.758 and 0.581	0.829 and 0.490
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2964 / 0 / 147	6338 / 0 / 316
Goodness-of-fit on F^2	1.029	1.046
Final R indices [$F>4\sigma(F)$]	$R_1 = 0.0287$, $wR_2 = 0.0580$	$R_1 = 0.0369$, $wR_2 = 0.0633$
R indices (all data)	$R_1 = 0.0435$, $wR_2 = 0.0644$	$R_1 = 0.0507$, $wR_2 = 0.0685$
Largest diff. peak, hole	0.401, -0.650 $eÅ^{-3}$	0.933, -0.777 $eÅ^{-3}$
Mean and maximum shift/error	0.000 and 0.000	0.000 and 0.002

Table S1. Bond lengths (Å) and angles (°) for 1

Ag(1)-C(1)	2.072(3)	C(1)-Ag(1)-O(31)	176.67(13)
Ag(1)-O(31)	2.137(2)	N(5)-C(1)-N(2)	108.5(3)
C(1)-N(5)	1.325(4)	N(5)-C(1)-Ag(1)	123.4(2)
C(1)-N(2)	1.335(4)	N(2)-C(1)-Ag(1)	128.1(2)
N(2)-C(6)	1.444(4)	C(1)-N(2)-C(6)	126.3(3)
N(2)-C(3)	1.476(4)	C(1)-N(2)-C(3)	112.5(3)
C(3)-C(4)	1.507(5)	C(6)-N(2)-C(3)	120.8(3)
C(4)-N(5)	1.478(4)	N(2)-C(3)-C(4)	102.8(3)
N(5)-C(18)	1.439(4)	N(5)-C(4)-C(3)	102.2(3)
C(6)-C(11)	1.388(5)	C(1)-N(5)-C(18)	125.7(3)
C(6)-C(7)	1.397(5)	C(1)-N(5)-C(4)	113.0(3)
C(7)-C(8)	1.391(5)	C(18)-N(5)-C(4)	120.7(3)
C(7)-C(12)	1.520(5)	C(11)-C(6)-C(7)	123.3(3)
C(8)-C(9)	1.382(6)	C(11)-C(6)-N(2)	117.7(3)
C(9)-C(10)	1.367(6)	C(7)-C(6)-N(2)	118.9(3)
C(10)-C(11)	1.397(6)	C(8)-C(7)-C(6)	117.3(4)
C(11)-C(15)	1.504(6)	C(8)-C(7)-C(12)	120.4(4)
C(12)-C(13)	1.506(6)	C(6)-C(7)-C(12)	122.3(3)
C(12)-C(14)	1.518(5)	C(9)-C(8)-C(7)	120.6(4)
C(15)-C(16)	1.524(6)	C(10)-C(9)-C(8)	120.6(4)
C(15)-C(17)	1.528(6)	C(9)-C(10)-C(11)	121.3(4)
C(18)-C(19)	1.390(5)	C(6)-C(11)-C(10)	116.9(4)
C(18)-C(23)	1.406(5)	C(6)-C(11)-C(15)	123.4(4)
C(19)-C(20)	1.390(5)	C(10)-C(11)-C(15)	119.8(4)
C(19)-C(24)	1.521(6)	C(13)-C(12)-C(14)	110.3(4)
C(20)-C(21)	1.380(6)	C(13)-C(12)-C(7)	110.9(4)
C(21)-C(22)	1.377(6)	C(14)-C(12)-C(7)	113.8(3)
C(22)-C(23)	1.393(5)	C(11)-C(15)-C(16)	112.3(4)
C(23)-C(27)	1.517(5)	C(11)-C(15)-C(17)	111.0(3)
C(24)-C(26)	1.510(6)	C(16)-C(15)-C(17)	110.0(4)
C(24)-C(25)	1.538(6)	C(19)-C(18)-C(23)	122.7(3)
C(27)-C(28)	1.525(6)	C(19)-C(18)-N(5)	119.4(3)
C(27)-C(29)	1.534(5)	C(23)-C(18)-N(5)	117.9(3)
S(30)-O(32)	1.427(3)	C(18)-C(19)-C(20)	117.6(4)
S(30)-O(33)	1.427(3)	C(18)-C(19)-C(24)	122.6(4)
S(30)-O(31)	1.467(2)	C(20)-C(19)-C(24)	119.8(4)
S(30)-C(30)	1.825(4)	C(21)-C(20)-C(19)	121.0(4)
C(30)-F(33)	1.315(5)	C(22)-C(21)-C(20)	120.5(4)
C(30)-F(31)	1.327(4)	C(21)-C(22)-C(23)	120.9(4)
C(30)-F(32)	1.331(5)	C(22)-C(23)-C(18)	117.3(4)
		C(22)-C(23)-C(27)	121.9(4)
		C(18)-C(23)-C(27)	120.8(3)
		C(26)-C(24)-C(19)	111.7(4)
		C(26)-C(24)-C(25)	111.0(4)
		C(19)-C(24)-C(25)	110.2(4)
		C(23)-C(27)-C(28)	110.9(3)
		C(23)-C(27)-C(29)	113.3(3)

		C(28)-C(27)-C(29)	110.6(3)
		O(32)-S(30)-O(33)	117.15(17)
		O(32)-S(30)-O(31)	113.91(16)
		O(33)-S(30)-O(31)	113.57(16)
		O(32)-S(30)-C(30)	104.46(19)
		O(33)-S(30)-C(30)	104.16(17)
		O(31)-S(30)-C(30)	101.14(17)
		S(30)-O(31)-Ag(1)	124.53(15)
		F(33)-C(30)-F(31)	108.1(3)
		F(33)-C(30)-F(32)	107.7(4)
		F(31)-C(30)-F(32)	108.0(3)
		F(33)-C(30)-S(30)	112.0(3)
		F(31)-C(30)-S(30)	109.9(3)
		F(32)-C(30)-S(30)	111.0(3)

Table S2. Bond lengths (Å) and angles (°) for 2

Ag(1)-C(1)	2.078(3)	C(1)-Ag(1)-Cl(1)	175.40(9)
Ag(1)-Cl(1)	2.3507(9)	C(31)-Ag(2)-Cl(1)	169.17(9)
Ag(2)-C(31)	2.086(3)	Ag(1)-Cl(1)-Ag(2)	119.23(4)
Ag(2)-Cl(1)	2.3597(10)	N(5)-C(1)-N(2)	109.3(3)
C(1)-N(5)	1.324(4)	N(5)-C(1)-Ag(1)	121.9(2)
C(1)-N(2)	1.329(4)	N(2)-C(1)-Ag(1)	128.8(2)
N(2)-C(6)	1.443(4)	C(1)-N(2)-C(6)	125.0(3)
N(2)-C(3)	1.477(4)	C(1)-N(2)-C(3)	112.8(3)
C(3)-C(4)	1.538(5)	C(6)-N(2)-C(3)	122.2(3)
C(4)-N(5)	1.487(4)	N(2)-C(3)-C(4)	102.8(2)
N(5)-C(18)	1.440(4)	N(5)-C(4)-C(3)	101.5(2)
C(6)-C(11)	1.396(5)	C(1)-N(5)-C(18)	124.2(3)
C(6)-C(7)	1.403(5)	C(1)-N(5)-C(4)	113.4(3)
C(7)-C(8)	1.400(5)	C(18)-N(5)-C(4)	121.9(2)
C(7)-C(12)	1.514(5)	C(11)-C(6)-C(7)	122.9(3)
C(8)-C(9)	1.372(6)	C(11)-C(6)-N(2)	118.9(3)
C(9)-C(10)	1.370(6)	C(7)-C(6)-N(2)	118.1(3)
C(10)-C(11)	1.401(5)	C(8)-C(7)-C(6)	116.8(3)
C(11)-C(15)	1.514(5)	C(8)-C(7)-C(12)	120.2(3)
C(12)-C(14)	1.526(5)	C(6)-C(7)-C(12)	123.0(3)
C(12)-C(13)	1.528(5)	C(9)-C(8)-C(7)	121.4(4)
C(15)-C(17)	1.524(6)	C(10)-C(9)-C(8)	120.5(4)
C(15)-C(16)	1.525(5)	C(9)-C(10)-C(11)	121.3(4)
C(18)-C(23)	1.400(5)	C(6)-C(11)-C(10)	117.1(4)
C(18)-C(19)	1.404(5)	C(6)-C(11)-C(15)	123.5(3)
C(19)-C(20)	1.396(5)	C(10)-C(11)-C(15)	119.5(3)
C(19)-C(24)	1.517(5)	C(7)-C(12)-C(14)	111.8(3)
C(20)-C(21)	1.378(5)	C(7)-C(12)-C(13)	111.0(3)
C(21)-C(22)	1.377(5)	C(14)-C(12)-C(13)	110.1(4)
C(22)-C(23)	1.401(5)	C(11)-C(15)-C(17)	110.6(3)
C(23)-C(27)	1.523(5)	C(11)-C(15)-C(16)	111.6(3)
C(24)-C(25)	1.521(5)	C(17)-C(15)-C(16)	111.3(4)

C(24)-C(26)	1.525(5)	C(23)-C(18)-C(19)	122.8(3)
C(27)-C(28)	1.527(5)	C(23)-C(18)-N(5)	118.6(3)
C(27)-C(29)	1.527(5)	C(19)-C(18)-N(5)	118.6(3)
C(31)-N(32)	1.324(4)	C(20)-C(19)-C(18)	117.4(3)
C(31)-N(35)	1.332(4)	C(20)-C(19)-C(24)	119.8(3)
N(32)-C(36)	1.433(4)	C(18)-C(19)-C(24)	122.8(3)
N(32)-C(33)	1.482(4)	C(21)-C(20)-C(19)	120.8(3)
C(33)-C(34)	1.529(5)	C(22)-C(21)-C(20)	121.0(3)
C(34)-N(35)	1.473(4)	C(21)-C(22)-C(23)	120.9(3)
N(35)-C(48)	1.448(4)	C(18)-C(23)-C(22)	117.2(3)
C(36)-C(41)	1.399(5)	C(18)-C(23)-C(27)	123.1(3)
C(36)-C(37)	1.399(5)	C(22)-C(23)-C(27)	119.7(3)
C(37)-C(38)	1.396(5)	C(19)-C(24)-C(25)	112.2(3)
C(37)-C(42)	1.528(5)	C(19)-C(24)-C(26)	110.3(3)
C(38)-C(39)	1.382(6)	C(25)-C(24)-C(26)	110.8(3)
C(39)-C(40)	1.374(6)	C(23)-C(27)-C(28)	110.9(3)
C(40)-C(41)	1.390(5)	C(23)-C(27)-C(29)	111.3(3)
C(41)-C(45)	1.522(5)	C(28)-C(27)-C(29)	111.2(3)
C(42)-C(43)	1.517(6)	N(32)-C(31)-N(35)	109.3(3)
C(42)-C(44)	1.517(5)	N(32)-C(31)-Ag(2)	128.8(2)
C(45)-C(46)	1.532(6)	N(35)-C(31)-Ag(2)	121.7(2)
C(45)-C(47)	1.533(6)	C(31)-N(32)-C(36)	125.1(3)
C(48)-C(53)	1.393(5)	C(31)-N(32)-C(33)	112.4(3)
C(48)-C(49)	1.395(5)	C(36)-N(32)-C(33)	121.5(3)
C(49)-C(50)	1.396(5)	N(32)-C(33)-C(34)	101.7(3)
C(49)-C(54)	1.517(5)	N(35)-C(34)-C(33)	102.0(3)
C(50)-C(51)	1.372(6)	C(31)-N(35)-C(48)	123.7(3)
C(51)-C(52)	1.376(6)	C(31)-N(35)-C(34)	112.4(3)
C(52)-C(53)	1.391(5)	C(48)-N(35)-C(34)	123.6(3)
C(53)-C(57)	1.514(5)	C(41)-C(36)-C(37)	122.8(3)
C(54)-C(56)	1.511(6)	C(41)-C(36)-N(32)	119.3(3)
C(54)-C(55)	1.525(6)	C(37)-C(36)-N(32)	117.8(3)
C(57)-C(58)	1.530(6)	C(38)-C(37)-C(36)	117.6(3)
C(57)-C(59)	1.533(6)	C(38)-C(37)-C(42)	121.0(3)
S(60)-O(62)	1.394(4)	C(36)-C(37)-C(42)	121.3(3)
S(60)-O(63)	1.437(4)	C(39)-C(38)-C(37)	120.5(4)
S(60)-O(61)	1.462(5)	C(40)-C(39)-C(38)	120.5(4)
S(60)-C(60)	1.714(6)	C(39)-C(40)-C(41)	121.6(4)
C(60)-F(62)	1.350(6)	C(40)-C(41)-C(36)	116.9(4)
C(60)-F(63)	1.358(6)	C(40)-C(41)-C(45)	120.7(3)
C(60)-F(61)	1.370(6)	C(36)-C(41)-C(45)	122.4(3)
S(60')-O(61')	1.399(10)	C(43)-C(42)-C(44)	110.5(4)
S(60')-O(63')	1.480(10)	C(43)-C(42)-C(37)	110.9(3)
S(60')-O(62')	1.484(10)	C(44)-C(42)-C(37)	112.8(3)
S(60')-C(60')	1.672(11)	C(41)-C(45)-C(46)	112.1(3)
C(60')-F(63')	1.326(11)	C(41)-C(45)-C(47)	111.2(3)
C(60')-F(62')	1.334(11)	C(46)-C(45)-C(47)	110.2(4)
C(60')-F(61')	1.361(10)	C(53)-C(48)-C(49)	123.3(3)

C(70)-Cl(71)	1.729(5)	C(53)-C(48)-N(35)	119.2(3)
C(70)-Cl(72)	1.752(5)	C(49)-C(48)-N(35)	117.4(3)
C(80)-Cl(82)	1.728(10)	C(48)-C(49)-C(50)	116.9(4)
C(80)-Cl(81)	1.740(11)	C(48)-C(49)-C(54)	122.3(3)
C(85)-Cl(87)	1.739(15)	C(50)-C(49)-C(54)	120.7(4)
C(85)-Cl(86)	1.751(15)	C(51)-C(50)-C(49)	120.9(4)
		C(50)-C(51)-C(52)	120.9(4)
		C(51)-C(52)-C(53)	120.8(4)
		C(52)-C(53)-C(48)	117.1(4)
		C(52)-C(53)-C(57)	119.9(4)
		C(48)-C(53)-C(57)	122.9(3)
		C(56)-C(54)-C(49)	110.5(4)
		C(56)-C(54)-C(55)	111.9(4)
		C(49)-C(54)-C(55)	112.5(4)
		C(53)-C(57)-C(58)	112.5(4)
		C(53)-C(57)-C(59)	110.8(3)
		C(58)-C(57)-C(59)	109.6(3)
		O(62)-S(60)-O(63)	113.7(3)
		O(62)-S(60)-O(61)	116.4(4)
		O(63)-S(60)-O(61)	108.1(3)
		O(62)-S(60)-C(60)	106.7(3)
		O(63)-S(60)-C(60)	107.0(3)
		O(61)-S(60)-C(60)	104.2(3)
		F(62)-C(60)-F(63)	108.0(5)
		F(62)-C(60)-F(61)	103.7(5)
		F(63)-C(60)-F(61)	106.0(5)
		F(62)-C(60)-S(60)	114.4(4)
		F(63)-C(60)-S(60)	111.0(4)
		F(61)-C(60)-S(60)	113.1(4)
		O(61')-S(60')-O(63')	111.0(9)
		O(61')-S(60')-O(62')	113.9(8)
		O(63')-S(60')-O(62')	110.1(9)
		O(61')-S(60')-C(60')	110.9(7)
		O(63')-S(60')-C(60')	106.1(7)
		O(62')-S(60')-C(60')	104.3(6)
		F(63')-C(60')-F(62')	107.5(10)
		F(63')-C(60')-F(61')	100.2(10)
		F(62')-C(60')-F(61')	100.3(9)
		F(63')-C(60')-S(60')	115.8(8)
		F(62')-C(60')-S(60')	115.9(8)
		F(61')-C(60')-S(60')	114.9(7)
		Cl(71)-C(70)-Cl(72)	112.4(3)
		Cl(82)-C(80)-Cl(81)	112.9(7)
		Cl(87)-C(85)-Cl(86)	118.8(15)

Table S3. Bond lengths (Å) and angles (°) for 3

Ag(1)-C(1)	2.080(3)	C(1)-Ag(1)-Br(1)	180.0
Ag(1)-Br(1)	2.4077(4)	N(2A)-C(1)-N(2)	109.0(3)
C(1)-N(2A)[#]	1.323(2)	N(2A)-C(1)-Ag(1)	125.48(13)
C(1)-N(2)	1.323(2)	N(2)-C(1)-Ag(1)	125.48(13)
N(2)-C(4)	1.438(3)	C(1)-N(2)-C(4)	123.97(19)
N(2)-C(3)	1.476(3)	C(1)-N(2)-C(3)	113.25(18)
C(3)-C(3A)[#]	1.530(4)	C(4)-N(2)-C(3)	122.77(17)
C(4)-C(9)	1.392(3)	N(2)-C(3)-C(3A)[#]	102.21(11)
C(4)-C(5)	1.400(3)	C(9)-C(4)-C(5)	122.6(2)
C(5)-C(6)	1.386(3)	C(9)-C(4)-N(2)	119.1(2)
C(5)-C(10)	1.515(3)	C(5)-C(4)-N(2)	118.3(2)
C(6)-C(7)	1.372(4)	C(6)-C(5)-C(4)	117.6(2)
C(7)-C(8)	1.377(4)	C(6)-C(5)-C(10)	120.4(2)
C(8)-C(9)	1.393(3)	C(4)-C(5)-C(10)	121.9(2)
C(9)-C(13)	1.511(3)	C(7)-C(6)-C(5)	121.1(2)
C(10)-C(12)	1.523(4)	C(6)-C(7)-C(8)	120.3(2)
C(10)-C(11)	1.529(4)	C(7)-C(8)-C(9)	121.3(3)
C(13)-C(15)	1.525(4)	C(4)-C(9)-C(8)	117.1(2)
C(13)-C(14)	1.527(4)	C(4)-C(9)-C(13)	122.9(2)
		C(8)-C(9)-C(13)	120.0(2)
		C(5)-C(10)-C(12)	112.3(2)
		C(5)-C(10)-C(11)	110.2(2)
		C(12)-C(10)-C(11)	111.2(2)
		C(9)-C(13)-C(15)	111.5(2)
		C(9)-C(13)-C(14)	111.6(2)
		C(15)-C(13)-C(14)	110.6(2)

Symmetry transformations used to generate equivalent atoms:
[#] -x+3/2,-y+1/2,z

Table S4. Bond lengths (Å) and angles (°) for 4

Ag(1)-C(1)	2.094(3)	C(1)-Ag(1)-I(1)	177.34(9)
Ag(1)-I(1)	2.5743(3)	N(5)-C(1)-N(2)	109.1(3)
C(1)-N(5)	1.324(4)	N(5)-C(1)-Ag(1)	127.3(2)
C(1)-N(2)	1.326(4)	N(2)-C(1)-Ag(1)	123.6(2)
N(2)-C(6)	1.442(4)	C(1)-N(2)-C(6)	124.1(3)
N(2)-C(3)	1.487(4)	C(1)-N(2)-C(3)	113.3(3)
C(3)-C(4)	1.532(4)	C(6)-N(2)-C(3)	122.5(2)
C(4)-N(5)	1.480(4)	N(2)-C(3)-C(4)	101.7(2)
N(5)-C(18)	1.436(4)	N(5)-C(4)-C(3)	102.6(2)
C(6)-C(7)	1.387(5)	C(1)-N(5)-C(18)	125.7(3)
C(6)-C(11)	1.390(5)	C(1)-N(5)-C(4)	113.1(3)
C(7)-C(8)	1.396(5)	C(18)-N(5)-C(4)	120.9(2)
C(7)-C(12)	1.509(5)	C(7)-C(6)-C(11)	123.1(3)
C(8)-C(9)	1.384(6)	C(7)-C(6)-N(2)	118.5(3)
C(9)-C(10)	1.366(5)	C(11)-C(6)-N(2)	118.4(3)
C(10)-C(11)	1.397(5)	C(6)-C(7)-C(8)	117.4(3)

C(11)-C(15)	1.517(5)	C(6)-C(7)-C(12)	122.5(3)
C(12)-C(14)	1.525(5)	C(8)-C(7)-C(12)	120.0(3)
C(12)-C(13)	1.532(5)	C(9)-C(8)-C(7)	120.5(3)
C(15)-C(16)	1.521(5)	C(10)-C(9)-C(8)	120.8(3)
C(15)-C(17)	1.522(5)	C(9)-C(10)-C(11)	120.9(4)
C(18)-C(19)	1.395(5)	C(6)-C(11)-C(10)	117.4(3)
C(18)-C(23)	1.397(5)	C(6)-C(11)-C(15)	121.8(3)
C(19)-C(20)	1.388(5)	C(10)-C(11)-C(15)	120.8(3)
C(19)-C(24)	1.511(5)	C(7)-C(12)-C(14)	111.7(3)
C(20)-C(21)	1.369(5)	C(7)-C(12)-C(13)	111.2(3)
C(21)-C(22)	1.374(5)	C(14)-C(12)-C(13)	110.8(3)
C(22)-C(23)	1.395(5)	C(11)-C(15)-C(16)	112.2(3)
C(23)-C(27)	1.509(5)	C(11)-C(15)-C(17)	111.5(3)
C(24)-C(25)	1.518(5)	C(16)-C(15)-C(17)	110.5(3)
C(24)-C(26)	1.519(5)	C(19)-C(18)-C(23)	122.8(3)
C(27)-C(29)	1.528(5)	C(19)-C(18)-N(5)	118.5(3)
C(27)-C(28)	1.528(5)	C(23)-C(18)-N(5)	118.6(3)
C(30)-Cl(1)	1.721(5)	C(20)-C(19)-C(18)	117.1(3)
C(30)-Cl(2)	1.738(5)	C(20)-C(19)-C(24)	121.0(3)
		C(18)-C(19)-C(24)	121.8(3)
		C(21)-C(20)-C(19)	121.6(3)
		C(20)-C(21)-C(22)	120.3(3)
		C(21)-C(22)-C(23)	121.2(3)
		C(22)-C(23)-C(18)	117.0(3)
		C(22)-C(23)-C(27)	120.1(3)
		C(18)-C(23)-C(27)	122.9(3)
		C(19)-C(24)-C(25)	112.4(3)
		C(19)-C(24)-C(26)	111.2(3)
		C(25)-C(24)-C(26)	111.7(3)
		C(23)-C(27)-C(29)	111.6(3)
		C(23)-C(27)-C(28)	111.4(3)
		C(29)-C(27)-C(28)	110.7(3)
		Cl(1)-C(30)-Cl(2)	113.3(3)

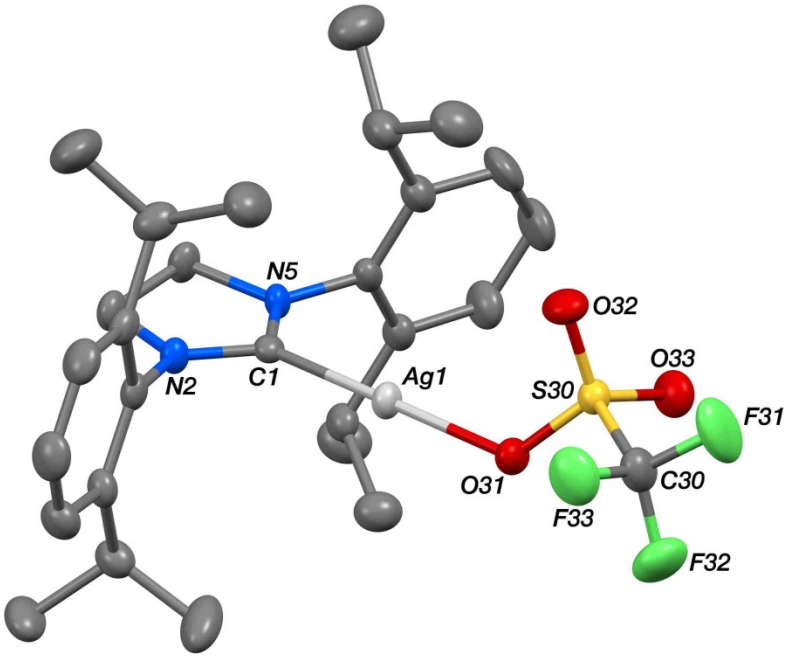

Fig. S1 The crystal structure of **1** (50% probability ellipsoids).

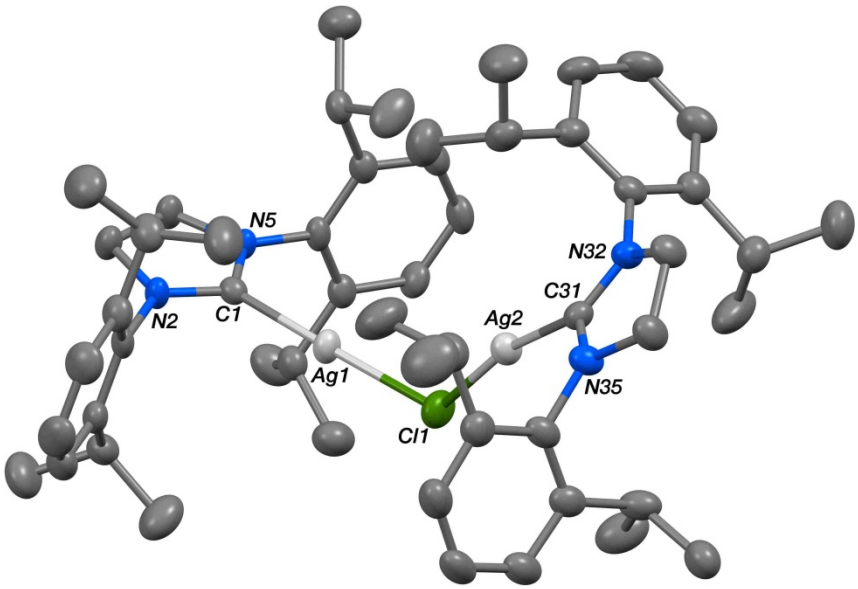

Fig. S2 The crystal structure of **2** (50% probability ellipsoids).

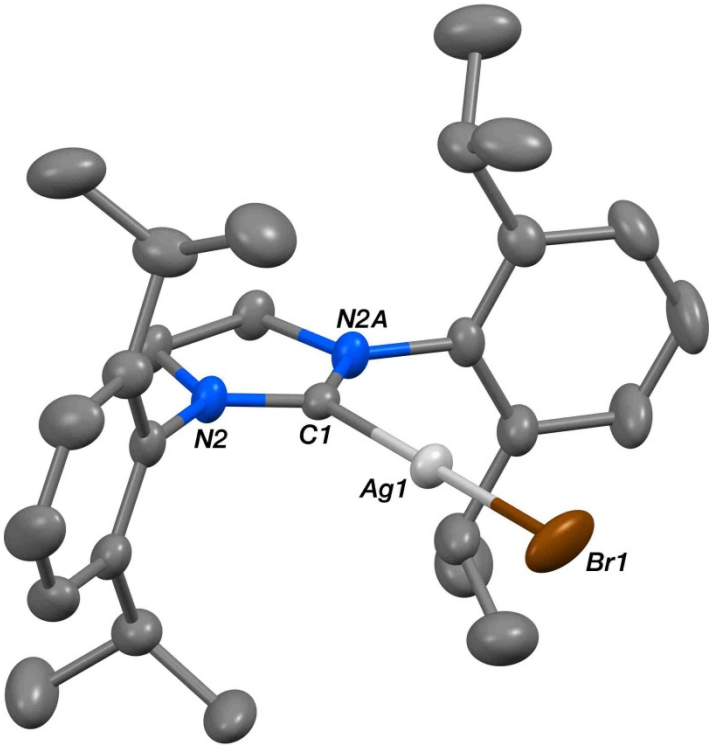

Fig. S3 The crystal structure of the C_S symmetry complex **3** (50% probability ellipsoids).

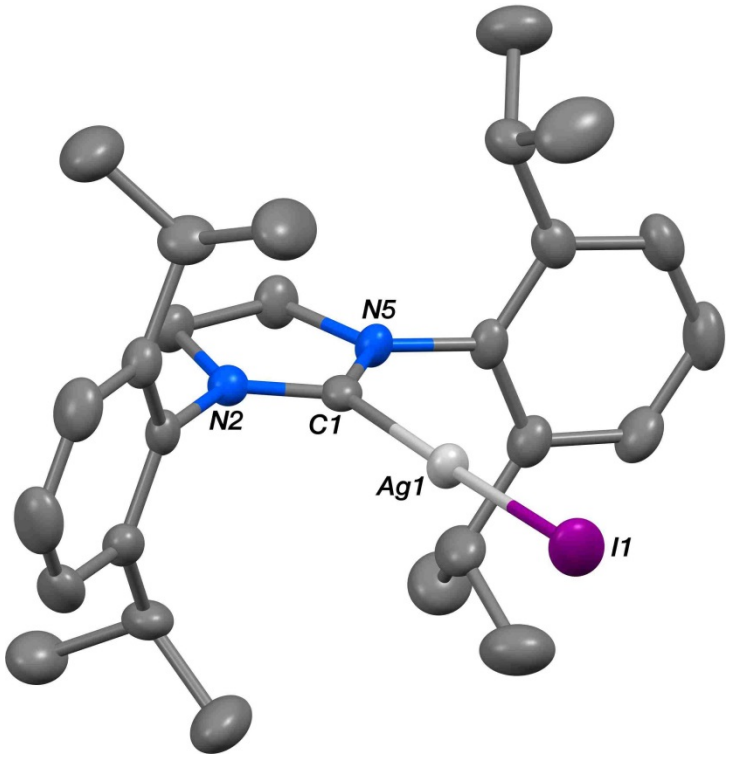

Fig. S4 The crystal structure of **4** (50% probability ellipsoids).

4. Computational details

The geometry of all four complexes were initially optimised in the gas phase using the Gaussian 09[6] suite on the Imperial College HPC cluster. The B3PW91 density functional was found to afford the closest prediction of experimental values than WB97XD and M06L. A triple zeta electron core potential Def2TZVP basis set[7] was employed on all atoms. Bond Energy Decomposition Analysis[8] (BEDA) was performed using Amsterdam Density Functional (ADF) programme package 2014 on the Slater HPC NSCCS Cluster with the geometry optimized with PW91 functional and a triple-ζ quality basis set augmented by two polarization functions (TZ2P). Scalar relativistic effects were also considered for Ag using the zero-order regular approximation (ZORA).[9] Natural Orbitals for Chemical Valence (NOCV) bond analysis was implemented on the M-C bond between SIPr and AgX fragments.

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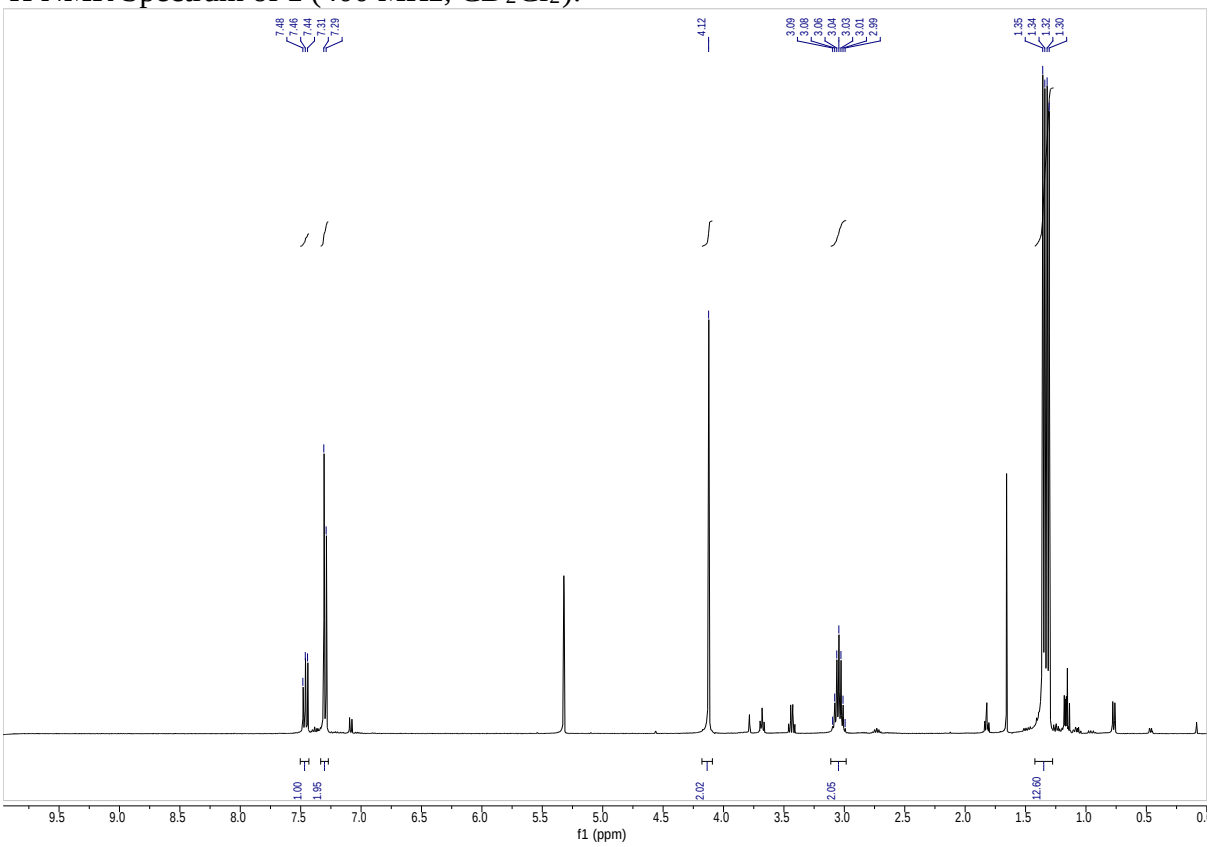
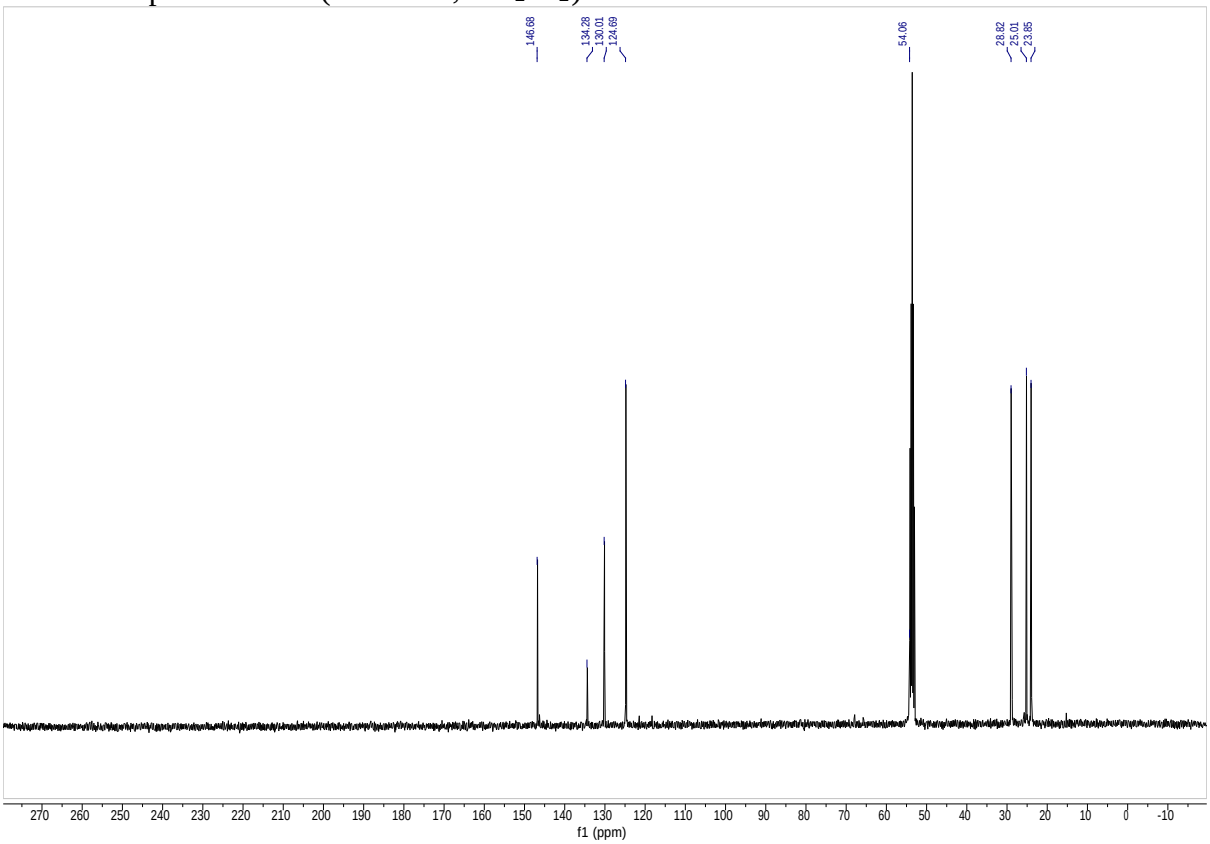
6. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

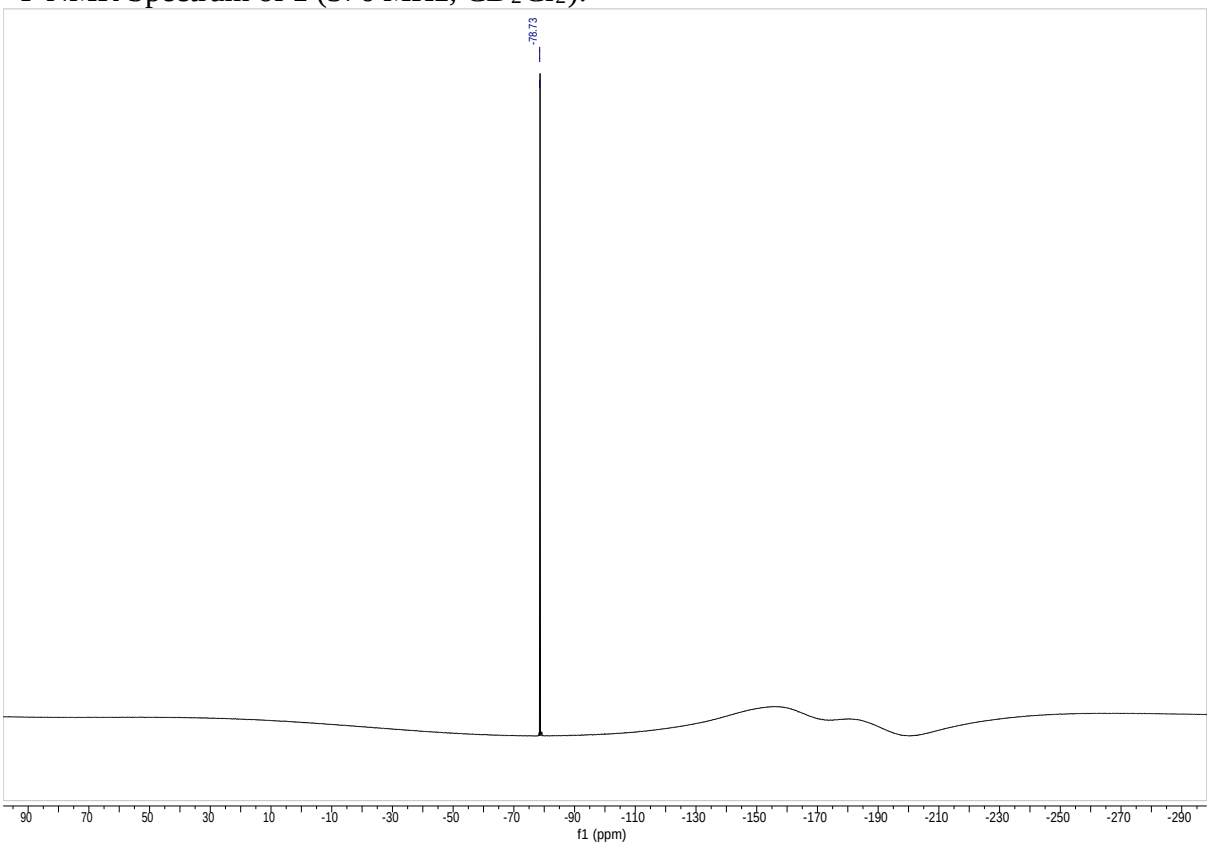
^{1}H NMR Spectrum of **1** (400 MHz, CD_2Cl_2):



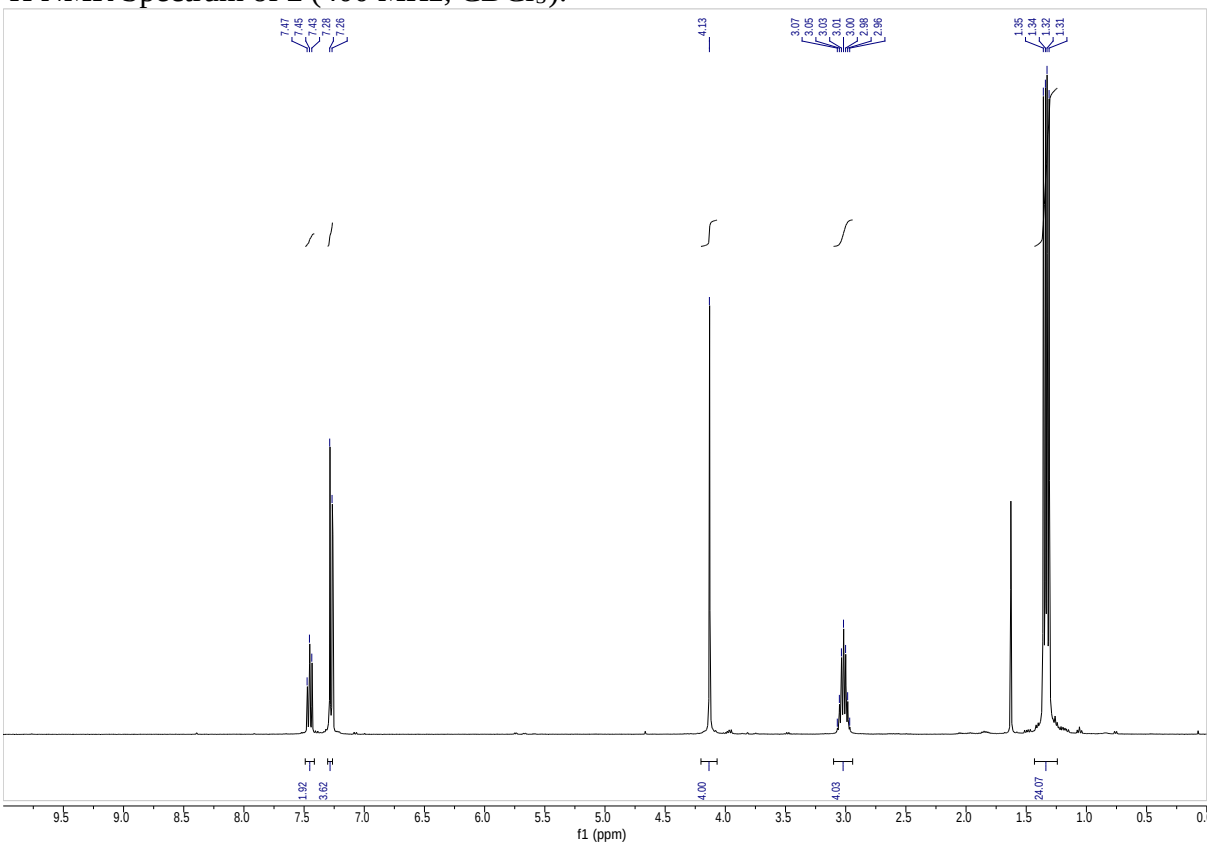
^{13}C NMR Spectrum of **1** (101 MHz, CD_2Cl_2):



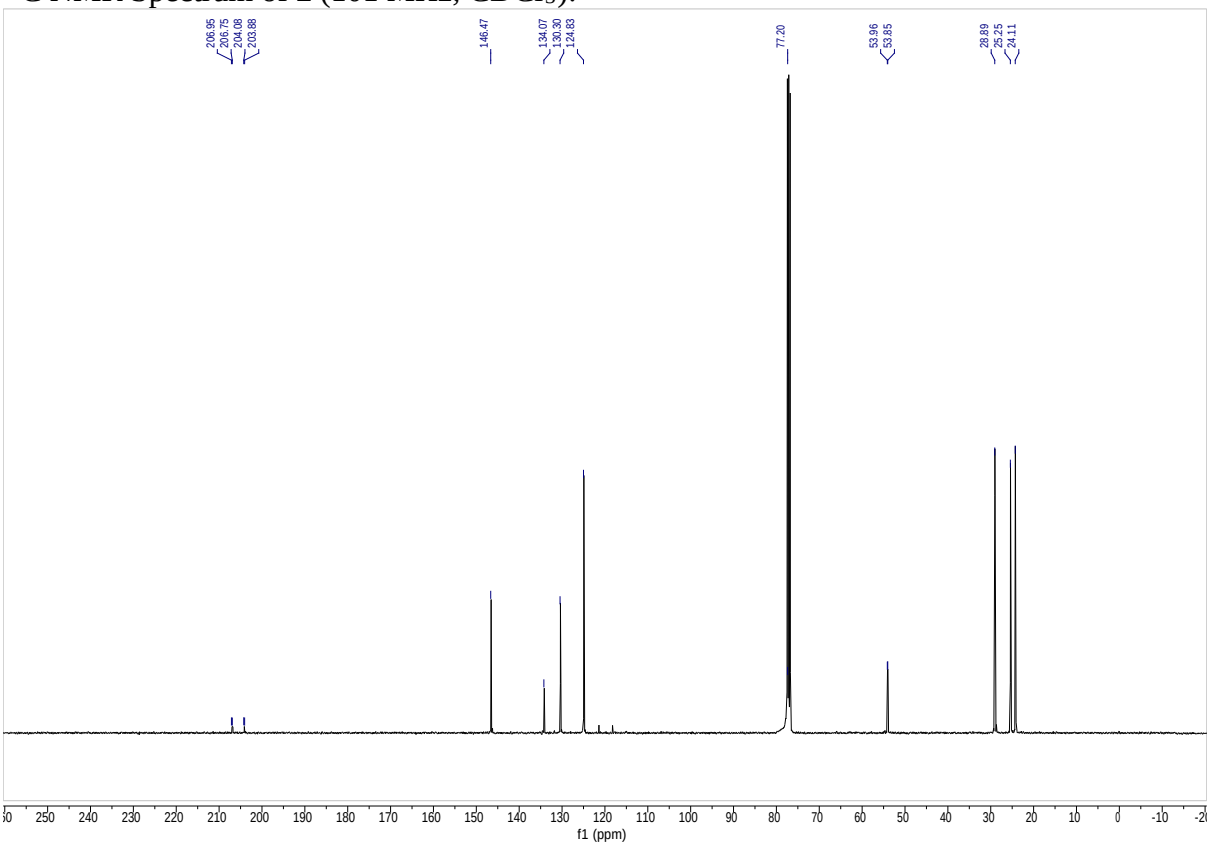
^{19}F NMR Spectrum of **1** (376 MHz, CD_2Cl_2):



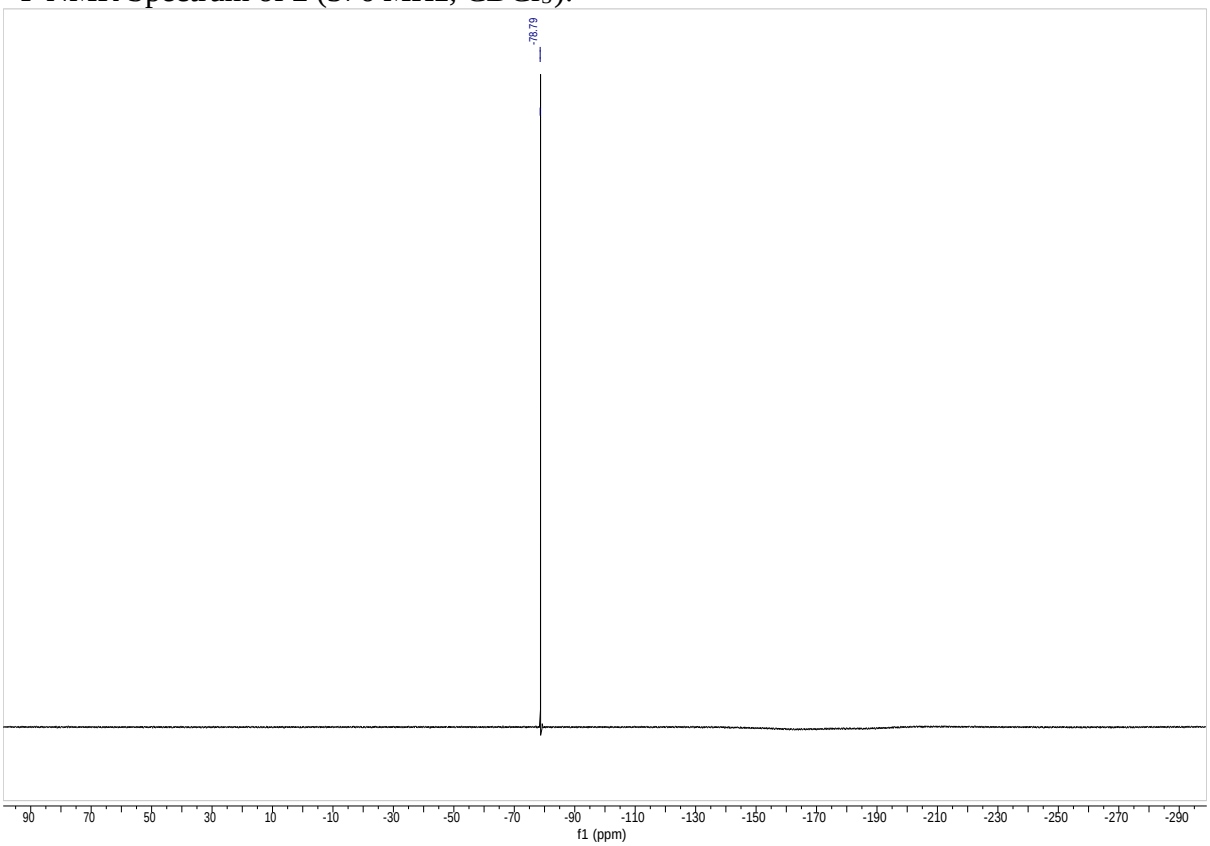
^{1}H NMR Spectrum of **2** (400 MHz, $CDCl_3$):



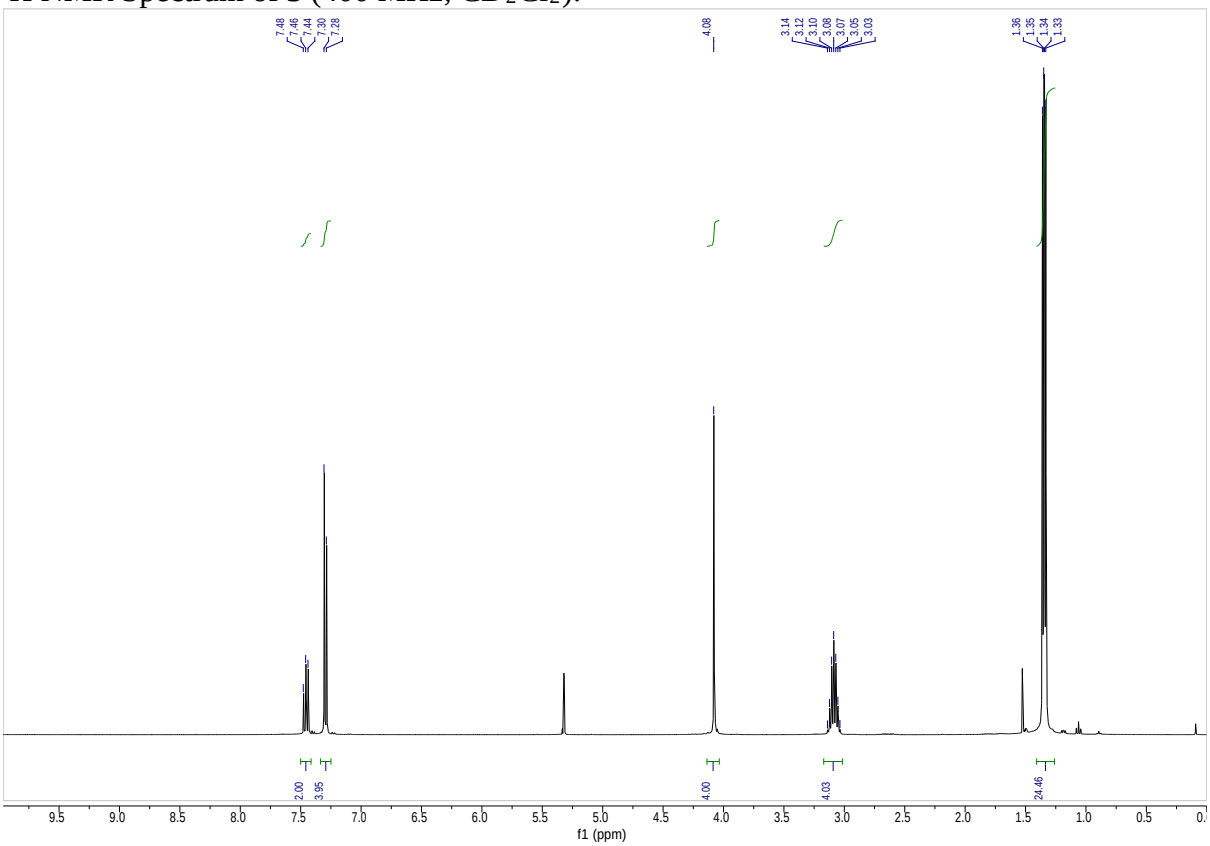
^{13}C NMR Spectrum of **2** (101 MHz, $CDCl_3$):



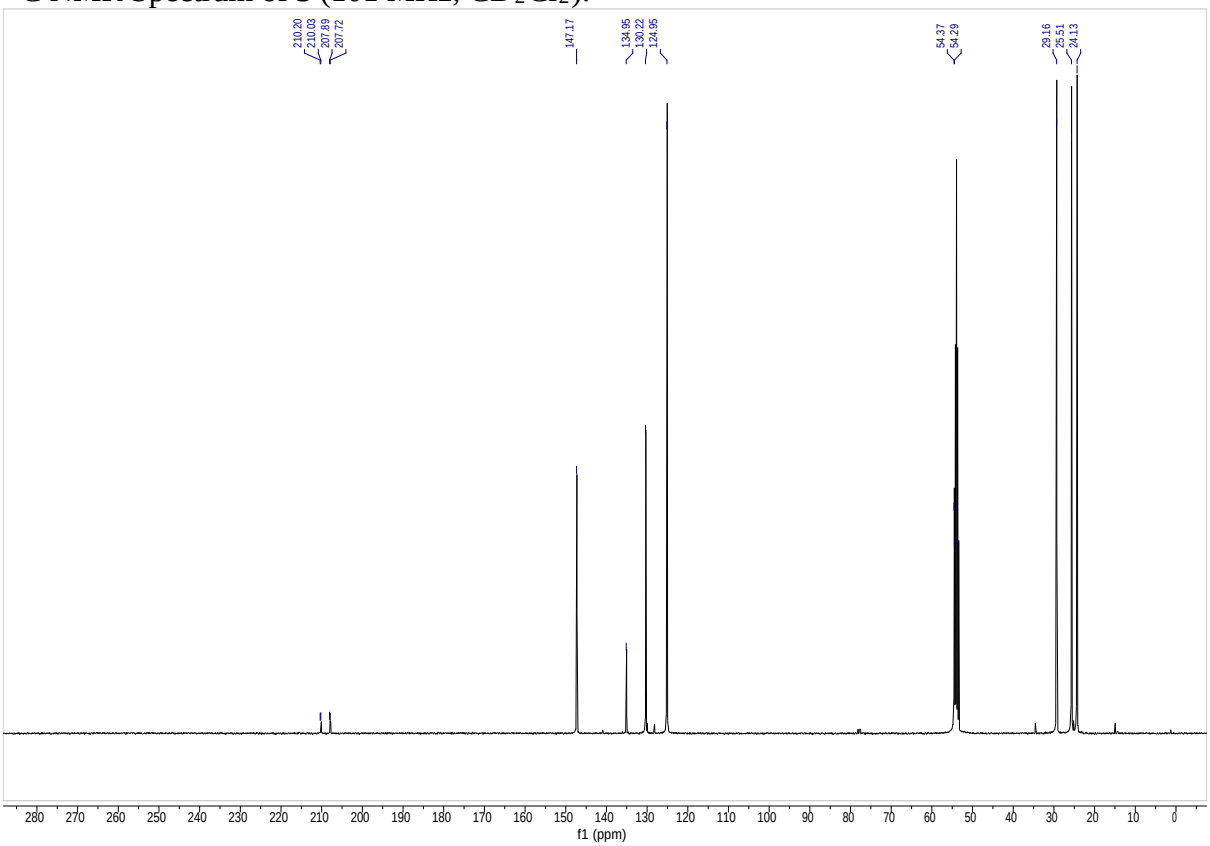
^{19}F NMR Spectrum of **2** (376 MHz, $CDCl_3$):



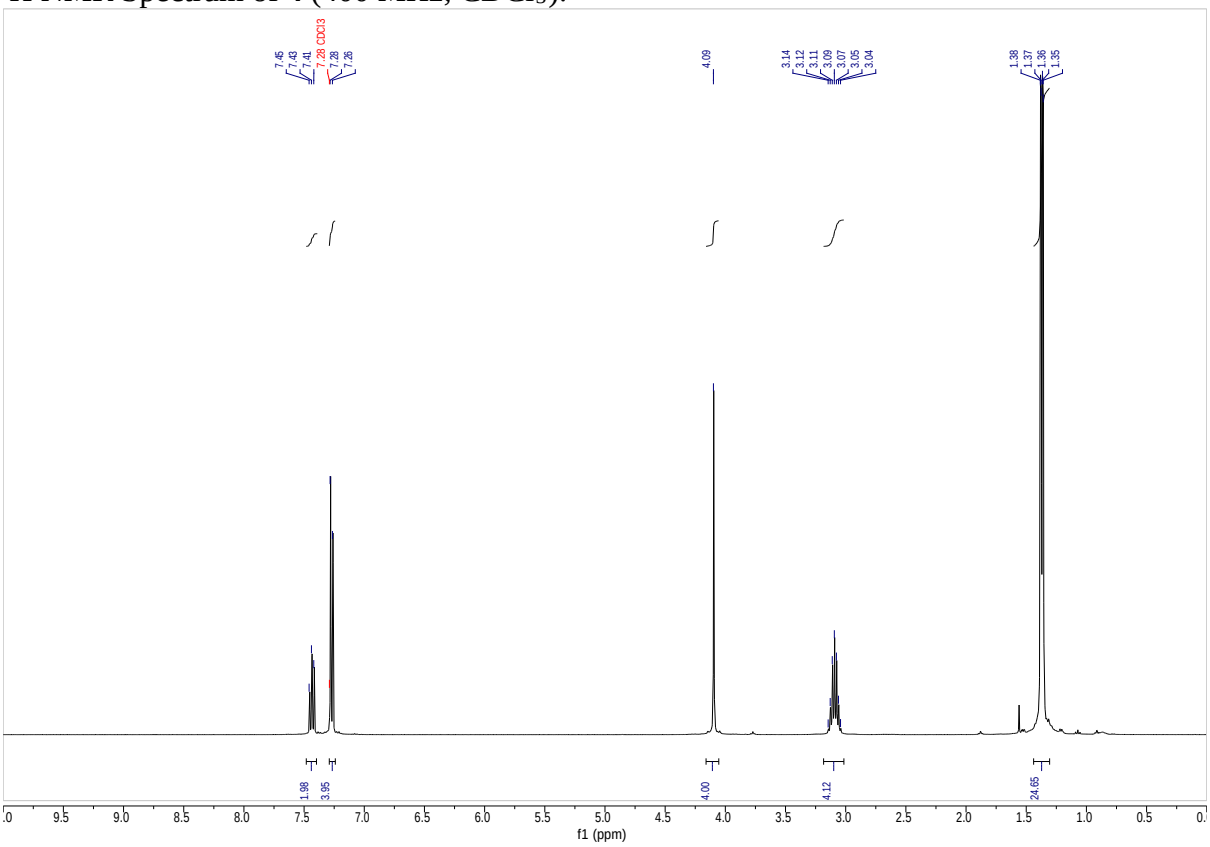
^{1}H NMR Spectrum of **3** (400 MHz, CD_2Cl_2):



^{13}C NMR Spectrum of **3** (101 MHz, CD_2Cl_2):



^{1}H NMR Spectrum of **4** (400 MHz, $CDCl_3$):



^{13}C NMR Spectrum of **4** (101 MHz, $CDCl_3$):