Supplementary data for

The first example of solid phase synthesis of pincer palladium complexes

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Experimental details

All manipulations were carried out without taking precautions to exclude air and moisture unless otherwise noted. Dichloromethane and acetonitrile were distilled from P_2O_5. The starting ligands were obtained as described previously (see ref. 28). NMR spectra were recorded on Bruker Avance-300 and Bruker Avance-400 spectrometers, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H and ^{13}C) or externally to H_3PO_4 (^{31}P). IR spectra were recorded on a "Magna-IR750" Fourier spectrometer (Nicolet), resolution 2 cm^{-1}, 128 scans. Raman spectra were recorded with a LabRAM Jobin-Yvon Raman spectrometer with an exciting He-Ne laser line of 632.8 nm.

DCS-30 TA Mettler instrument was used to capture the heating traces from 298 K up to 600 K. The scanning rate was 5 K/min. The Al pans were used. Each DSC sample weighed 10~15 mg. The matrix-assisted laser desorption/ionization (MALDI) mass spectrometry data were obtained on an Autoflex II instrument of the Bruker company (resolution FWHM 18000), equipped by a nitrogen laser with working wavelength 337 nm for ionization and time-of-flight mass-analyzer working in reflectron regime. The accelerating potential was 20 KV. The registration of the spectra was performed in the positive ions mode. The final spectrum represents the sum of 300 spectra obtained for different points of a sample (matrix-free or anthracene or dithranol as a matrix). All powder XRD measurements were carried out by Bruker D8 advance diffractometer at ambient temperature in the 2θ range 5-60°.

NCA calculations were performed in Gaussian 03 program[1] on DFT level of theory using PBE[2] functional, cc-pVTZ-pp[3] basis set for Pd atoms and 6-311G(d,p)[4] for the other ones.

Table S1. Selected data of IR and Raman spectra of the ligands **1a-d**, intermediate complexes **2a-d** and pincer derivatives **3a-d**.

Compound	$\nu_{(Pd-Cl+Pd-S)}$, cm^{-1}		$\nu_{P=S}$, cm^{-1}		ν (benzothiazole), cm^{-1}	
	IR	Raman	IR	Raman	IR	Raman
1a	-	-	628(m)	630(w)	1435(s)[a], 1507(w), 1585(w)	1435(m), 1510(s), 1593(m)
1b	-	-	633(w) 649(m)	633(m) 648(w)	1439(s)[a], 1529(s), 1580(w)	1441(w), 1528(m), 1570(sh)
1c	-	-	640(m)	639(m)	1436(s)[a], 1463(w), 1505(m), 1580(m)	1466(m), 1506(s), 1589(w)
1d	-	-	629(m) 613(m)	628(w) 614(w)	1437(s)[a], 1510(m), 1589(m)	1436(m), 1512(s), 1591(m)
2a	297(w), 332(m), 345(m)	301(s) 331(w)	596(s)	594(w)	1436(s)[a], 1502(w), 1585(w)	1440(m), 1504(s), 1590(m)
2b	315(m) 337(m)	296(s) 312(sh) 331(vw)	593(m) 619(w)	587(w) 615(w)	1439(m)[a], 1444(m), 1528(s), 1573(w)	1444(br, w), 1523(m), 1510(sh), 1570(m)
2c	295(w) 335(m)	298(m) 335(w)	622(m) 609(m)	624(w)	1437(s)[a], 1456(w), 1471(w), 1480(w), 1509(w), 1581(m)	1444(m), 1485(s), 1504(m), 1580(m)
2d	305(m) 337(m)	297(m) 332(w)	588(m)	n/o	1436(s)[a], 1481(m), 1512(w), 1584(w)	1428(m), 1440(sh), 1491(s), 1510(sh), 1575(m), 1590(sh)
3a	330(m), 340(m)	280(w) 317(w) 332(vw)	601(m)	604(w)	1415(m), 1434(m)[a], 1546(m)	1418(s), 1478(s), 1550(m)
3b	-	311(w) 332(w)	607(m) 623(w)	604(w) 624(w)	1437(m)[a], 1448(m), 1515(m), 1560(w)	1449(w), 1516(m), 1561(m)
3c	-	286(w) 333(m)	633(m)	632(w)	1435(m)[a], 1446(w), 1457(w), 1488(w), 1580(w)	1446(m), 1487(s), 1581(m)
3d		296 (w) 333(m)	606(m)	605(m)	1427(m), 1435(m)[a], 1491(w), 1575(w)	1427(s), 1488(s), 1576(s)

[a] may be attributed to P-C(phenyl) vibrations

Full description of IR and Raman spectral data for ligands 1a-d

1a. IR (KBr, ν/cm^{-1}): 495(w), 515(s), 614(m), 628(m), 641(m), 659(m), 680(m), 696(s), 714(s), 725(m), 742(m), 754(m), 787(w), 999(m), 1098(s), 1234(w), 1312(m), 1409(m), 1435(s), 1457(w), 1478(m), 1507(w), 1585(w), 1700(w), 3051(w). Far IR (nujol, ν/cm^{-1}): 256(w), 337(w), 440(m), 449(w), 496(m), 515(s). Raman (solid, Δν/cm^{-1}): 191(w), 243(w), 255(w), 630(w), 639(m), 661(w), 712(m), 1002(s), 1018(w), 1078(m), 1123(w), 1184(w), 1237(s), 1435(m), 1467(m), 1510(s), 1576(m), 1593(m), 3058(m).

1b. IR (KBr, ν/cm^{-1}): 515(m), 633(w), 649(m), 693(m), 717(m), 751(m), 764(w), 1098(m), 1210(m), 1229(s), 1247(m), 1411(m), 1439(s), 1529(s), 1580(w), 1599(w), 3054(w). Raman (solid, Δν/cm^{-1}): 183(w), 239(w), 266(w), 503(w), 614(w), 633(m), 648(w), 705(w), 999(s), 1030(w), 1098(w), 1246(w), 1283(w), 1441(w), 1528(m), 1570(sh), 1586(m), 3055(m).

1c. IR (KBr, ν/cm^{-1}): 491(m), 506(s), 640(m), 687(m), 717(m), 728(s), 757(m), 791(m), 846(m), 857(m), 893(m), 910(s), 1107(m), 1161(m), 1174(m) 1238(m), 1254(m), 1313(w), 1436(s), 1463(w), 1505(m), 1580(m), 1605(w), 3028(w), 3051(w), 3064(w). Raman (solid, Δν/cm^{-1}): 213(w), 242(m), 341(w), 506(w), 639(m), 664(w), 711(m), 1002(s), 1068(w), 1129(w), 1238(m), 1295(w), 1435(m), 1466(m), 1506(s), 1559(w), 1589(m), 1607(m), 3066(m).

1d. IR (KBr, ν/cm^{-1}): 483(w), 510(m), 613(m), 629(m), 690(m), 717(s), 753(m), 936(s), 1018(w), 1105(m), 1197(w), 1260(w), 1279(w), 1304(m), 1372(w), 1437(s), 1463(m), 1486(s), 1510(m), 1589(m), 1606(m), 2922(w), 3055(w), 3201(m). Raman (solid, Δν/cm^{-1}): 240(w), 363(w), 506(w), 601(w), 614(w), 628(w), 710(w), 999(s), 1031(w), 1070(w), 1127(m), 1199(w), 1246(m), 1260(m), 1282(w), 1375(w), 1436(m), 1465(w), 1487(m), 1512(s), 1591(m), 1609(m), 3052(w).

IR and Raman spectral data and MALDI mass spectrometry data for complexes 2a-d

2a. IR (KBr, ν/cm^{-1}): 496(w), 512(m), 596(s), 619(w), 643(w), 687(s), 696(s), 718(m), 742(m), 768(m), 1004(w), 1101(s), 1242(w), 1400(w), 1436(s), 1458(w), 1481(w), 1502(w), 1585(w), 1700(w), 2920(w), 3053(w). Far IR (nujol, ν/cm^{-1}): 297(w), 332(m), 345(m), 362(m), 373(w), 422(w), 449(m), 477(m), 496(s), 511(s), 523(s). Raman (solid, Δν/cm^{-1}): 205(w), 233(w), 301(s), 331(w), 364(w), 594(w), 645(w), 666(w), 710(w), 1002(m), 1018(w), 1030(w), 1079(w), 1101(w), 1132(w), 1249(s), 1282(w), 1326(w), 1403(w), 1440(m), 1504(s), 1565(w), 1590(m), 1598(m), 3067(w). MALDI-MS (matrix-free), m/z: 743 [L-4H+9Cl], 707 [L-3H+8Cl], 673 [L-2H+7Cl], 639 [L-H+6Cl], 605 [L+5Cl], 568 [(L-2H)PdCl], 534 [(L-H)Pd], 498 [L+2Cl], 464 [L+H+Cl], 430 [L+3H], 315 [$Ph_2P(S)C_6H_4CN$-4H].

2b. IR (KBr, ν/cm^{-1}): 512(m), 593(m), 619(w), 689(m), 719(m), 750(m), 1103(m), 1194(m), 1245(m), 1278(m), 1421(m), 1439(m), 1444(m), 1471(m), 1528(s), 1573(w), 1591(w), 1724(w), 2851(w), 2922(w), 3059(w). Far IR (nujol, ν/cm^{-1}): 315(m), 337(m), 354(m), 364(w), 418(w), 445(w), 484(m), 503(m), 512(m), 533(m), 540 (w). Raman (solid, Δν/cm^{-1}): 241(w), 296(s), 312(sh), 331(vw), 364(w), 505(w), 587(w), 615(w), 666(w), 711(w), 998(s), 1027(m), 1102(w), 1243(w), 1287(w), 1444(br, w), 1510(sh), 1523(m), 1570(m), 1586(m), 3062(m). MALDI-MS (matrix-free), m/z: 887 [2L+H], 669 [2L-$Ph_2P(S)$], 584 [(L-2H)PdCl], 548 [(L-

H)Pd], 514 [L+2Cl], 480 [L+H+Cl], 446 [L+3H], 403[L+H+Cl-Ph], 330 [$Ph_2P(S)C_6H_4OCN$-5H].

2c. IR (KBr, ν/cm^{-1}): 508(m), 609(m), 622(m), 688(m), 711(s), 727(m), 759(m), 911(w), 948(s), 1106(m), 1114(m), 1161(m), 1179(m), 1255(m), 1437(s), 1456(w), 1471(w), 1480(w), 1509(w), 1581(m), 2853(w), 2923(w), 3056(w). Far IR (nujol, ν/cm^{-1}): 295(w), 335(m), 352(m), 358(w), 365(m), 429(w), 458(w), 490(m), 510(s), 517(m), (547(m). Raman (solid, Δν/cm^{-1}): 237(w), 298(m), 335(w), 367(w), 508(m), 599(w), 615(w), 624(w), 642(w), 711(w), 999(s), 1020(m), 1183(w), 1244(m), 1270(w), 1420(m), 1444(m), 1485(s), 1504(m), 1580(m), 3058(m). MALDI-MS (matrix-free), m/z: 671 [2L-$Ph_2P(S)H$], 584 [(L-2H)PdCl], 548 [(L-H)Pd], 516 [L+2H+2Cl], 476 [L-2H+Cl], 446 [L+3H], 415 [L-S].

2d: IR (KBr, ν/cm^{-1}): 489(w), 508(w), 588(m), 623(w), 689(m), 703(m), 723(m), 754(m), 942(w), 1106(m), 1190(w), 1294(w), 1374(w), 1436(s), 1456(m), 1481(m), 1512(w), 1584(w), 1603(w), 3054(w). Far IR (nujol, ν/cm^{-1}): 305(m), 337(m), 448(w), 490(m), 508(m). Raman (solid, Δν/cm^{-1}): 213(w), 297(m), 332(w), 374(w), 509(m), 618(w), 650(w), 712(w), 1000(m), 1019(m), 1104(w), 1133(w), 1180(w), 1246(m), 1272(m), 1428(m), 1440(sh), 1491(s), 1510(sh), 1575(m), 1590(sh), 3061(w). MALDI-MS (matrix-free), m/z: 879 [2L-5H], 617 [L+5Cl], 547 [(L-H)Pd], 509 [L-2H+2Cl], 475 [L-H+Cl], 441 [L-H], 409 [L-H-S].

IR and Raman spectral data and MALDI mass spectrometry data for SCN pincer complexes 3a-d

[2-(1,3-Benzothiazol-2-yl)-6-(diphenylthiophosphoryl)phenyl]palladium chloride, 3a. IR (KBr, ν/cm^{-1}): 518(s), 591 (w), 601(m), 618 (w), 692(m), 704(m), 718(m), 732(m), 748(m), 761(s), 996(w), 1038(m), 1101(m), 1272(w), 1319(w), 1394(m), 1415(m), 1434(m), 1475(w), 1511(w), 1546(m), 1600(w), 2852(w), 2926(w), 3043(w), 3061(w). Far IR (nujol, ν/cm^{-1}): 254(w), 279(m), 314(w), 330(w), 340(w), 361(m), 431(m), 449(m), 472(w), 482(w), 519(s). Raman (solid, Δν/cm^{-1}): 173(w), 201(w), 245(w), 280(w), 317(w), 332(vw), 362(w), 509(w), 395(w), 593(w), 604(w), 712(w), 999(m), 1019(w), 1029(m), 1083(w), 1102(w), 1137(m), 1155(w), 1253(m), 1276(m), 1396(m), 1418(s), 1449(m), 1461(w), 1478(s), 1550(m), 1564(w), 1577(m).

[2-(1,3-Benzothiazol-2-yloxy)-6-(diphenylthiophosphoryl)phenyl]palladium chloride, 3b. IR (KBr, ν/cm^{-1}): 517(s), 562(m), 607(m), 623(w), 671(m), 692(s), 707(s), 720(m), 755(s), 996(w), 1059(w), 1107(m), 1147(w), 1159(m), 1192(m), 1234(m), 1272(s), 1289(s), 1400(m), 1437(m), 1448(m), 1458(w), 1515(m), 1560(w), 1593(w), 2856(w), 2925(w), 3040(w), 3432(w). Raman (solid, Δν/cm^{-1}): 172(w), 244(m), 311(w), 332(w), 346(w), 365(s), 509(w), 563(w),

604(w), 624(w), 667(w), 712(w), 997(s), 1030(m), 1110(w), 1159(w), 1233(m), 1449(w), 1516(m), 1561(m), 1587(m), 2911(w), 3056(m).

{2-(1,3-Benzothiazol-2-yl)-6-[(diphenylthiophosphoryl)oxy]phenyl}palladium chloride, 3c. IR (KBr, ν/cm^{-1}): 492(m), 515(m), 633(m), 692(s), 719(s), 756(s), 782(w), 798(w), 952(s), 962(m), 1106(s), 1119(s), 1164(m), 1198(s), 1270(m), 1298(m), 1412(m), 1435(m), 1446(w), 1457(w), 1488(w), 1580(w), 2854(w), 2925(w), 3081(w), 3438(w). Raman (solid, Δν/cm^{-1}): 186(m), 241(m), 286(w), 333(m), 367(w), 510(m), 632(w), 598(w), 612(w), 712(w), 997(m), 1019(w), 1136(w), 1248(m), 1269(w), 1421(w), 1446(m), 1487(s), 1581(m), 3050(w).

{2-(1,3-Benzothiazol-2-yl)-6-[(diphenylthiophosphoryl)amino]phenyl}palladium chloride, 3d. IR (KBr, ν/cm^{-1}): 512(m), 606(m), 623(m), 690(m), 710(s), 724(m), 754(m), 760(m), 951(m), 1115(m), 1273(m), 1303(m), 1373(s), 1427(m), 1435(m), 1458(m), 1491(w), 1575(w), 2922(w), 3095(w), 3142(m), 3430(w). Raman (solid, Δν/cm^{-1}): 210(w), 244(m), 296(w), 333(m), 371(w), 507(m), 605(m), 645(w), 711(w), 999(m), 1020(m), 1100(w), 1133(w), 1179(w), 1250(s), 1272(m), 1372(w), 1427(s), 1446(m), 1456(w), 1488(s), 1576(s), 3056(w).

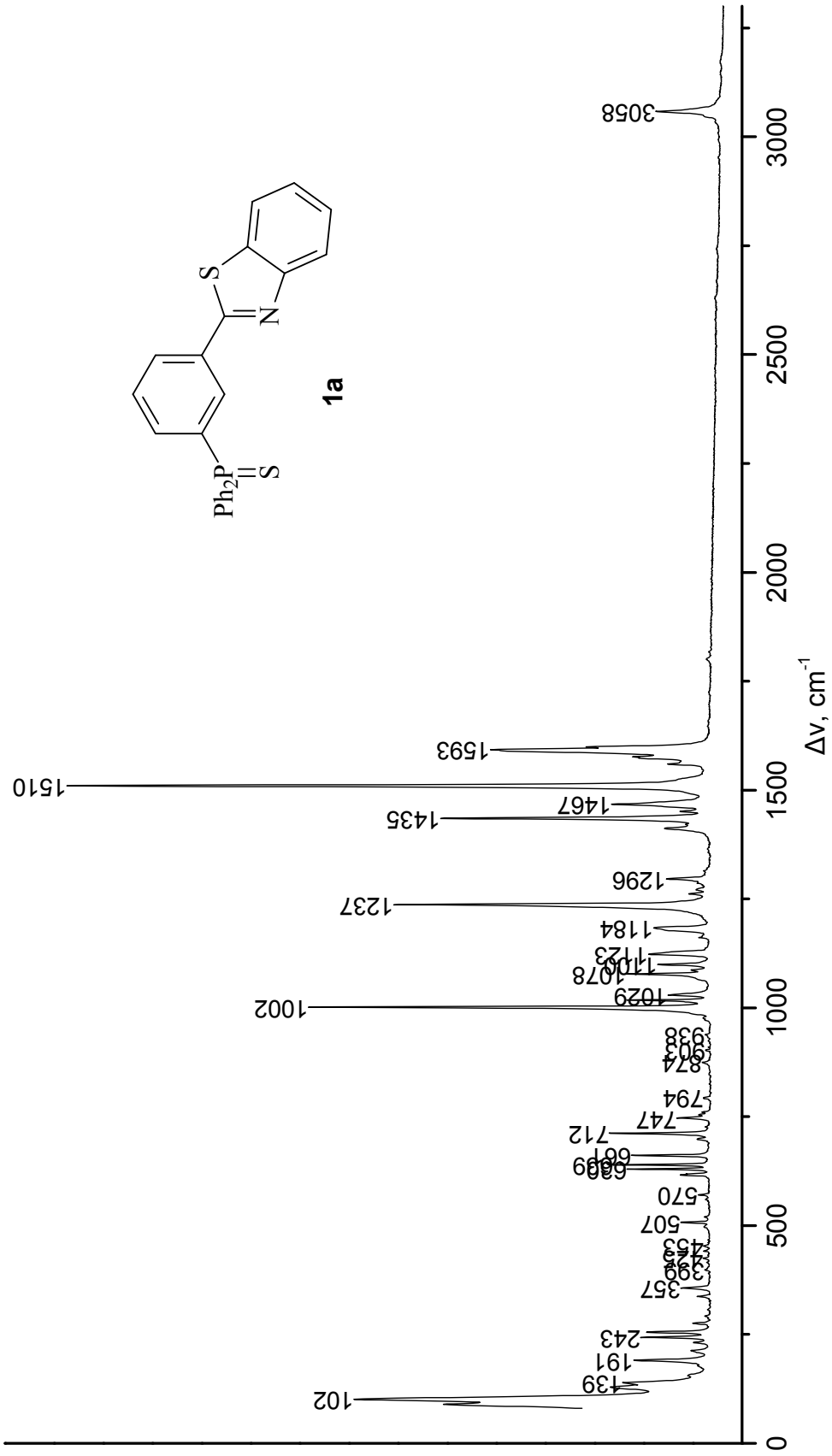

Fig. 1S. Raman spectra of ligand **1a**

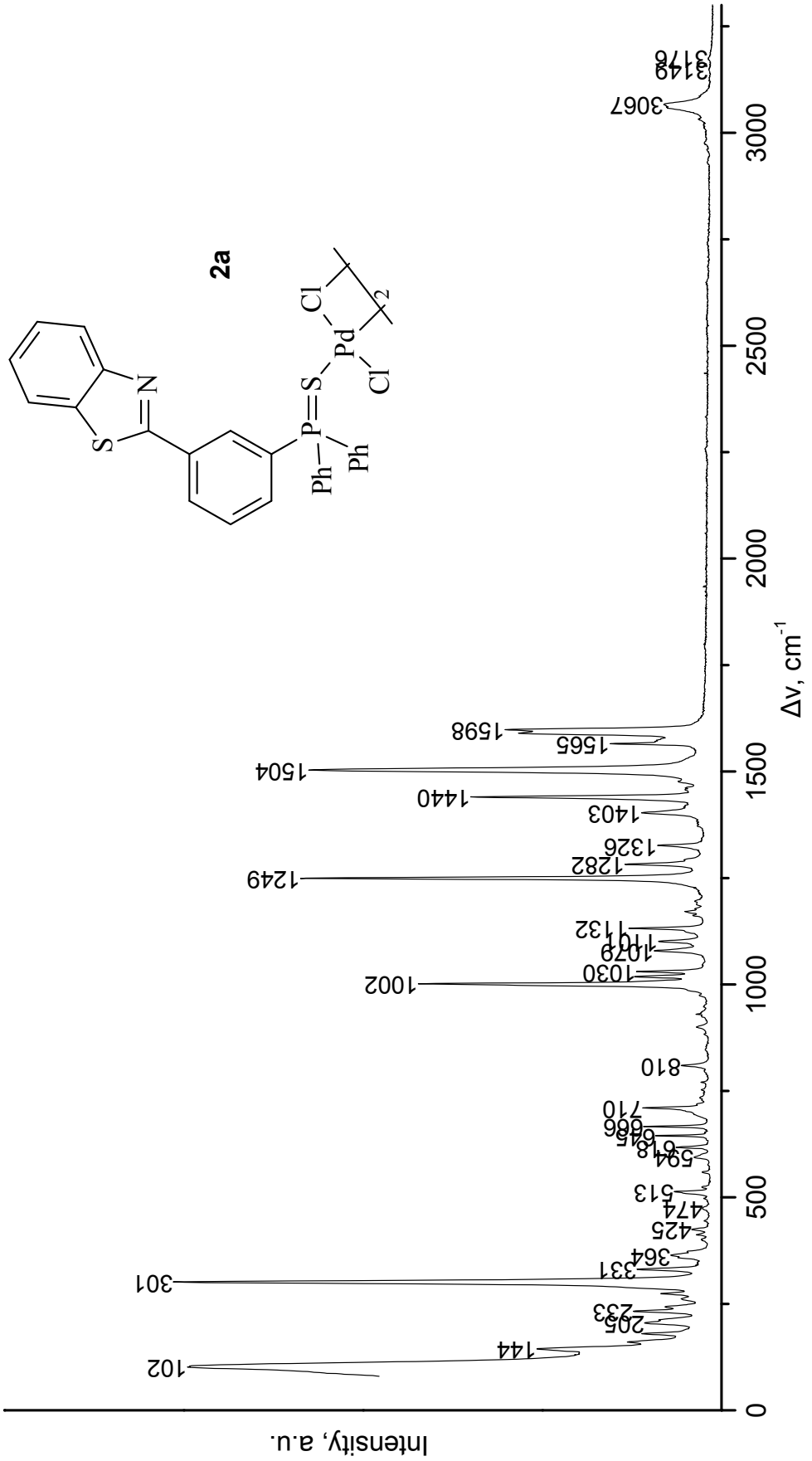

Fig. 2S. Raman spectra of complex **2a**

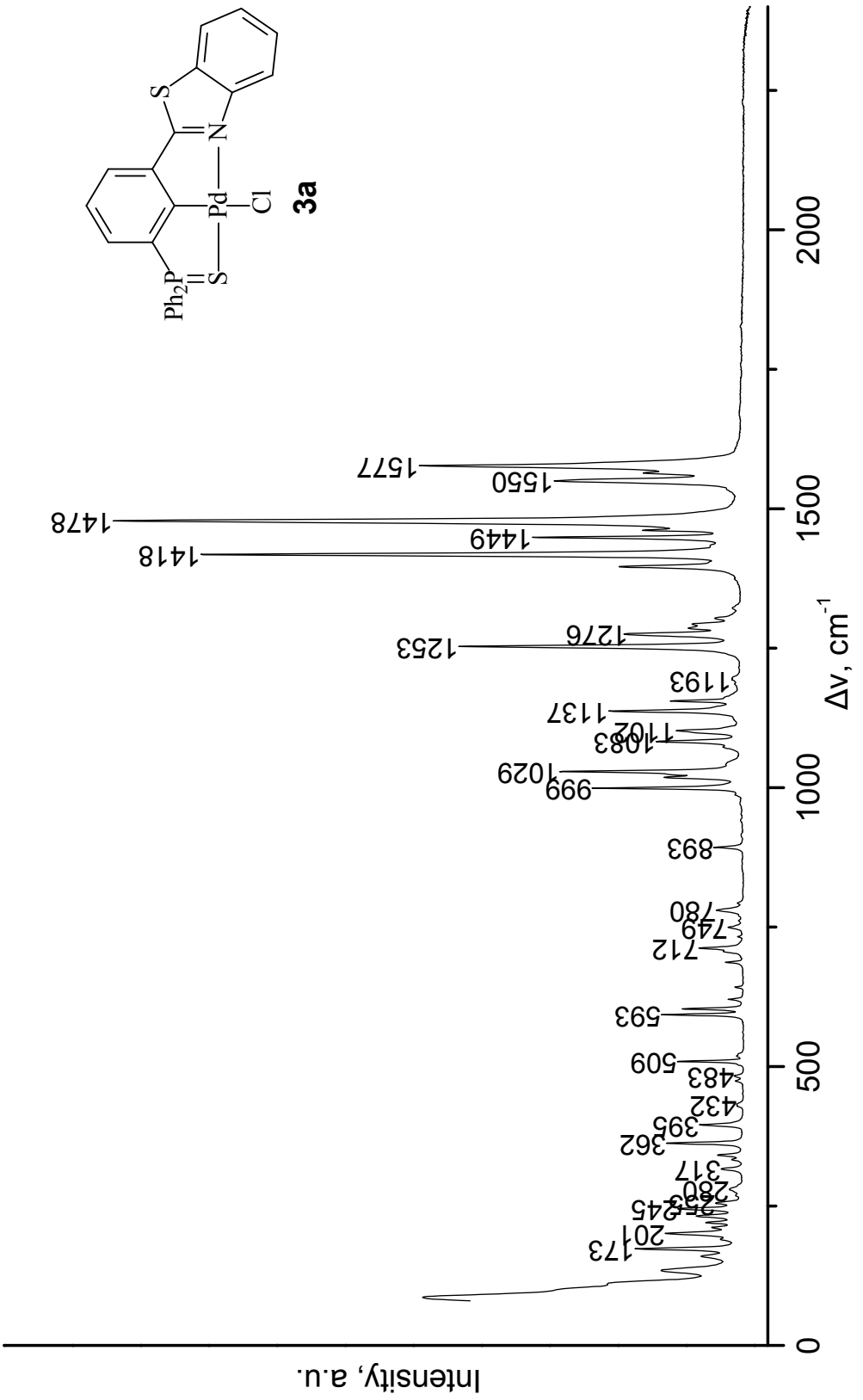

Fig. 3S. Raman spectra of pincer complex **3a**

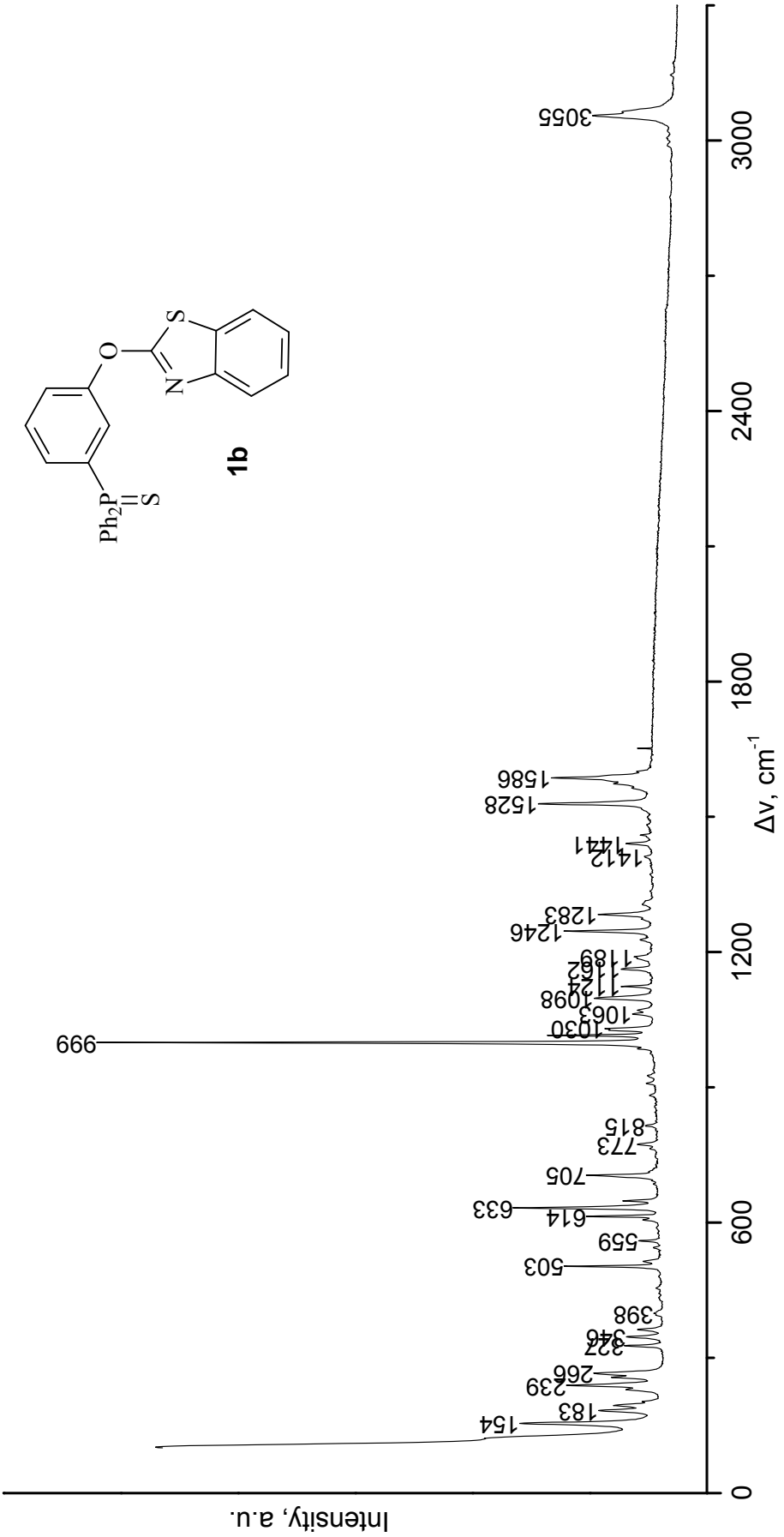

Fig. 4S. Raman spectra of ligand **1b**

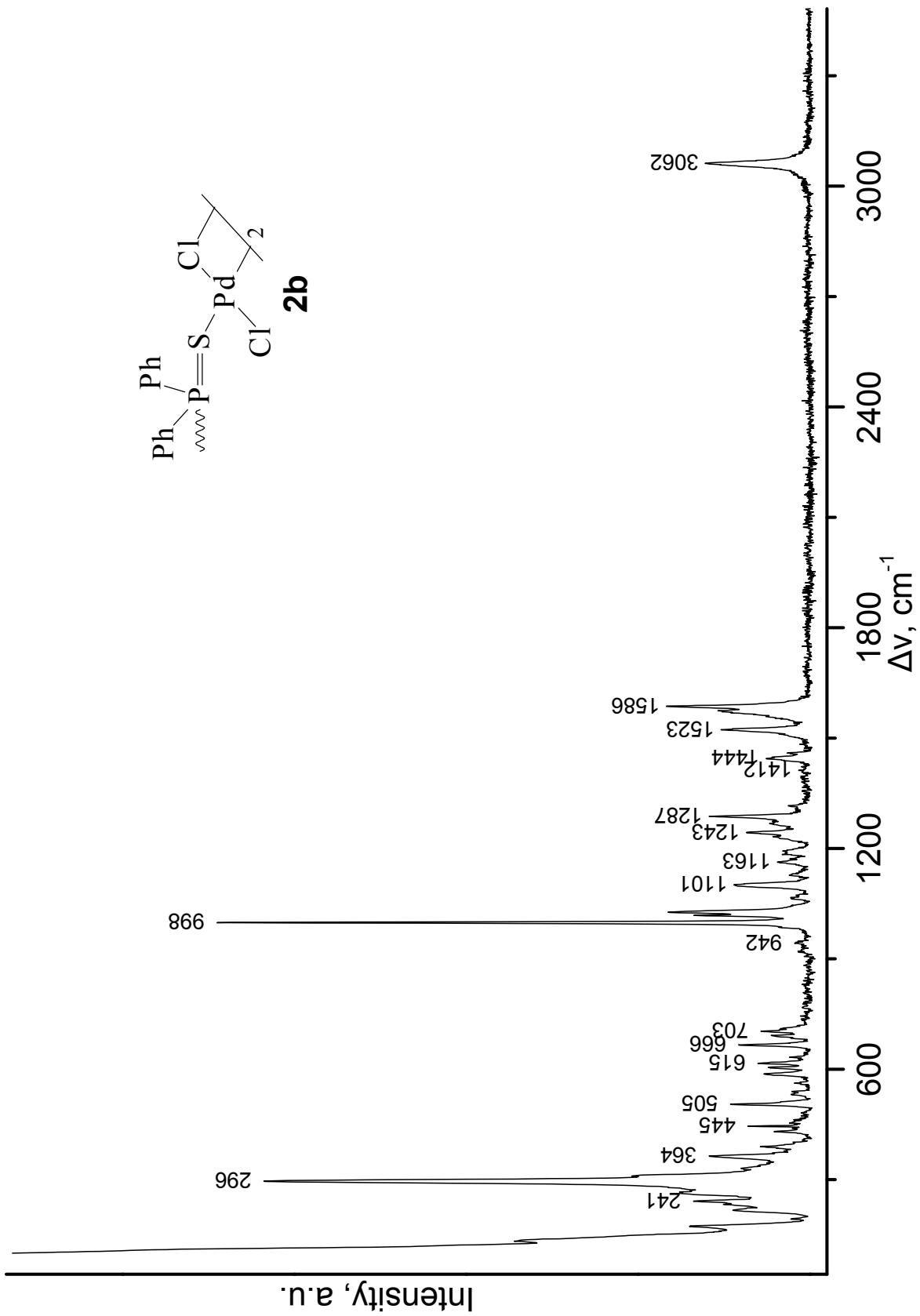

Fig. 5S. Raman spectra of complex **2b**

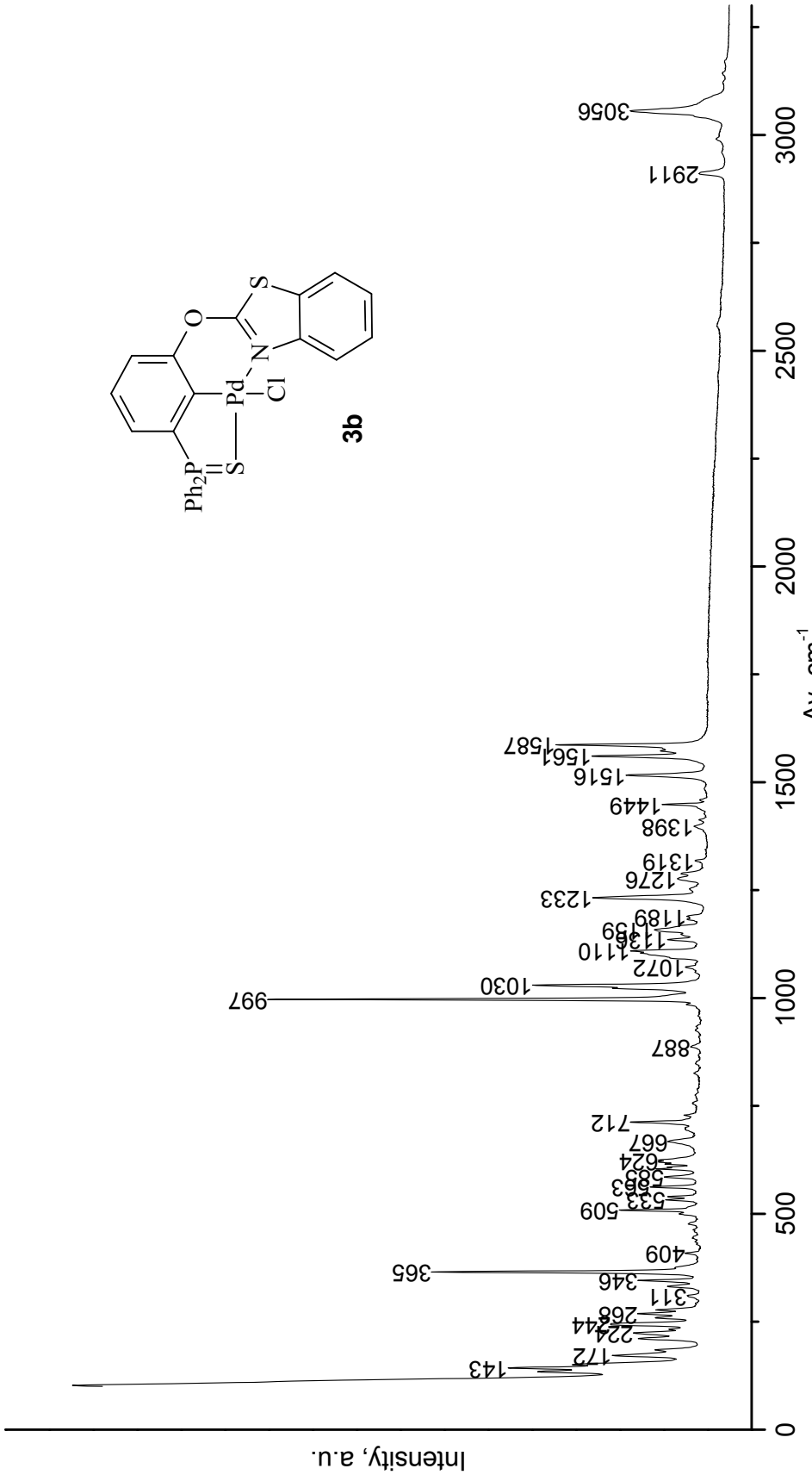

Fig. 6S. Raman spectra of pincer complex **3b**

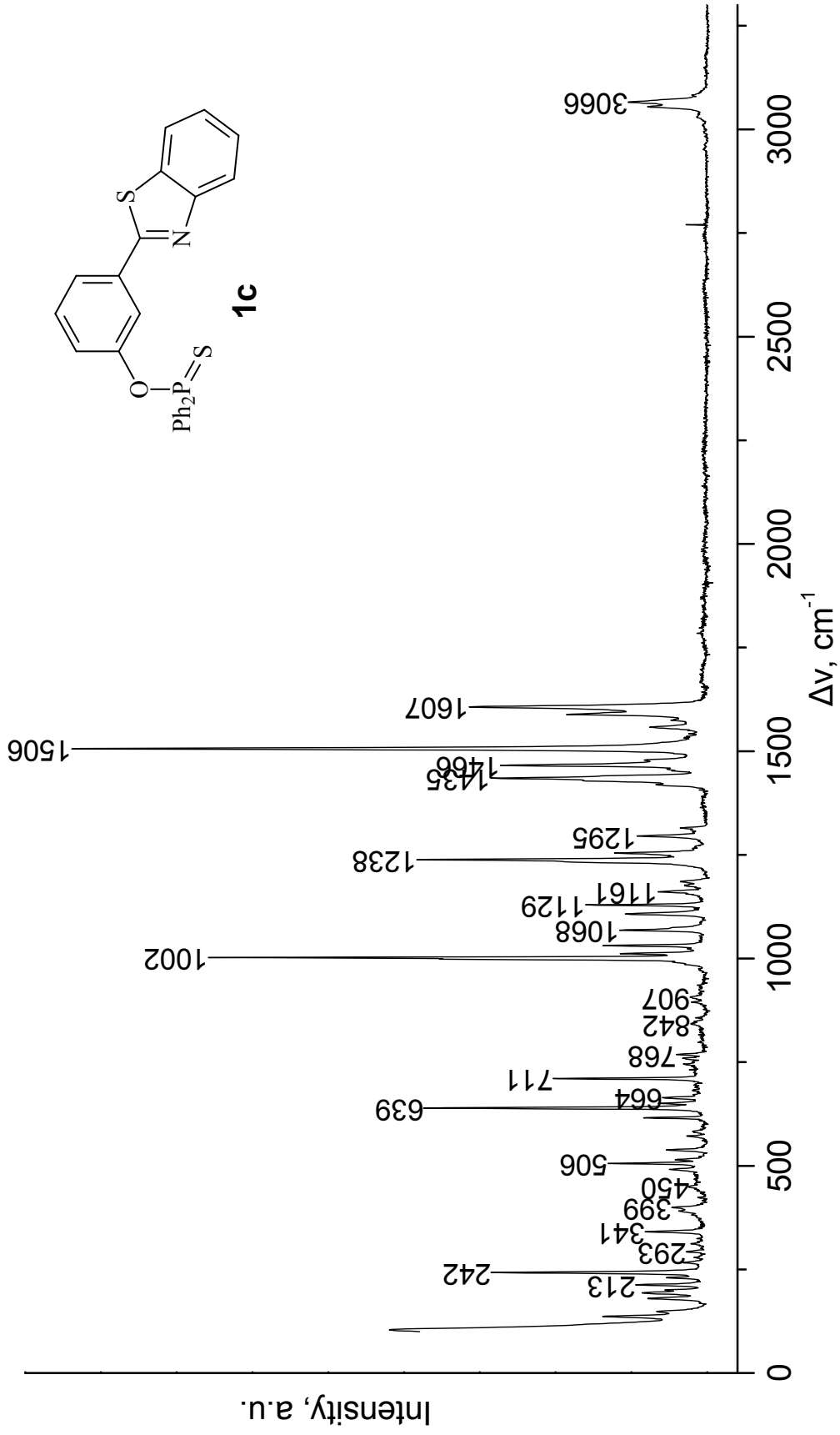

Fig. 7S. Raman spectra of ligand **1c**

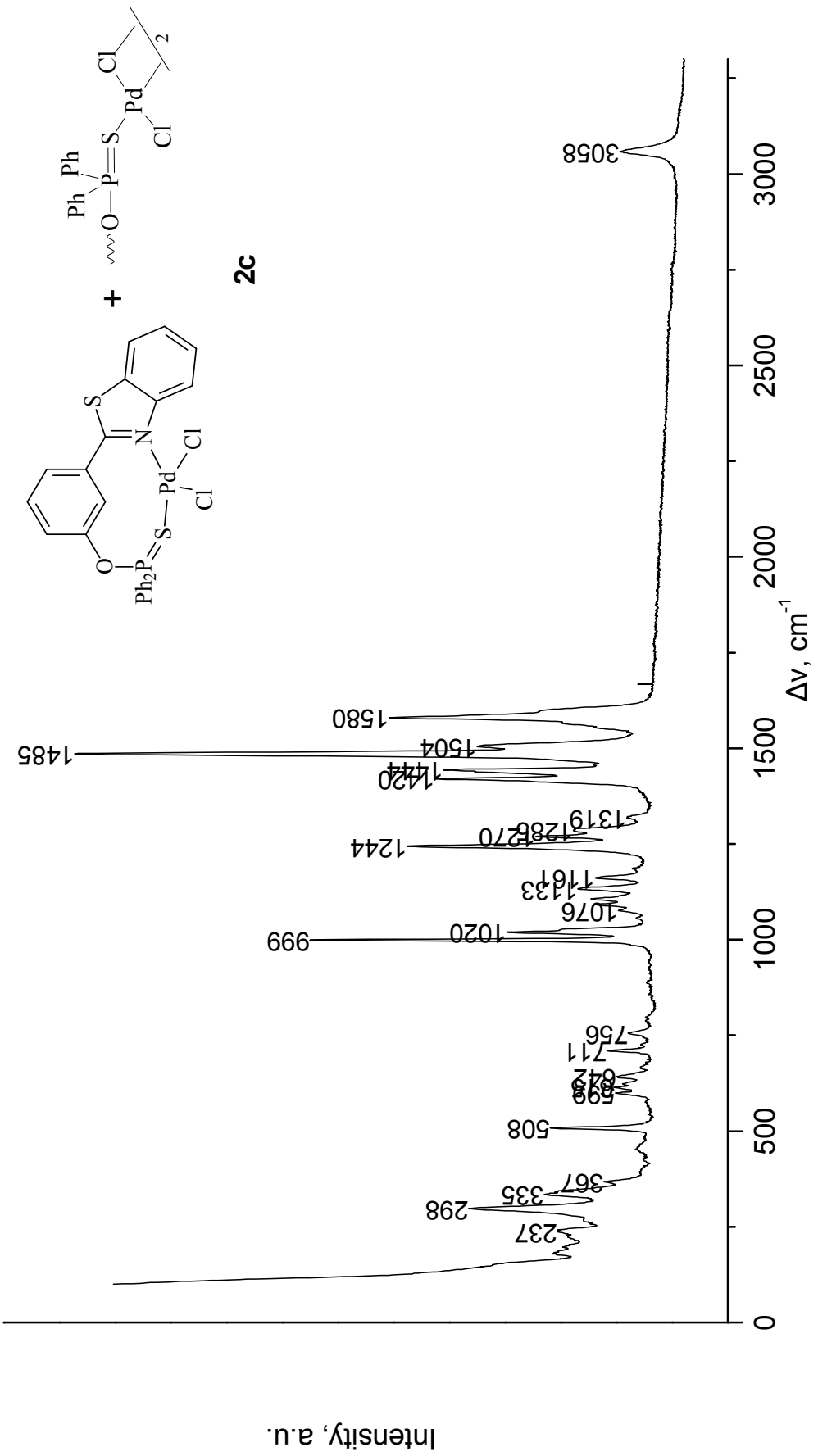

Fig. 8S. Raman spectra of complex **2c**

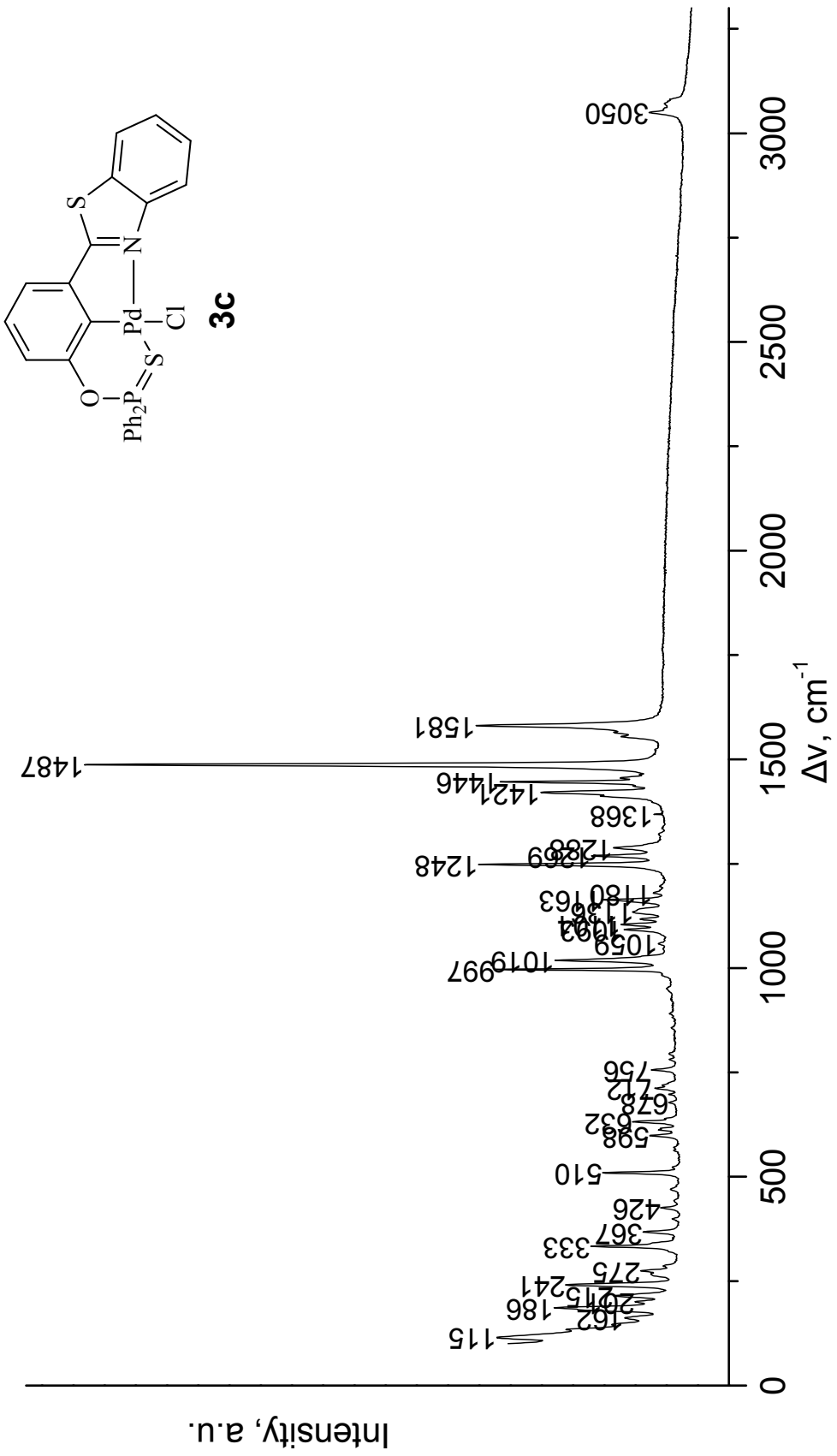

Fig. 9S. Raman spectra of pincer complex **3c**

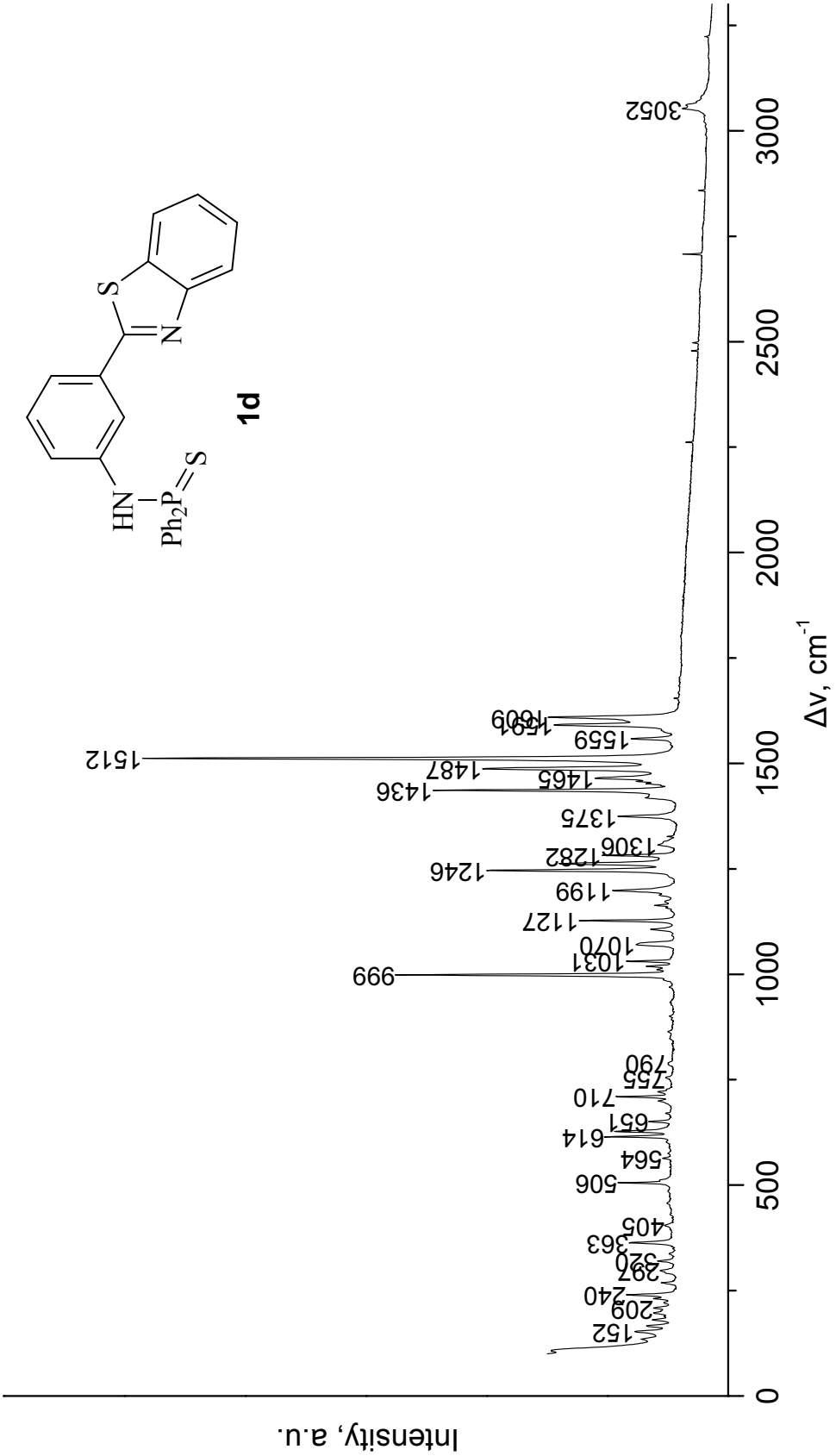

Fig. 10S. Raman spectra of ligand **1d**

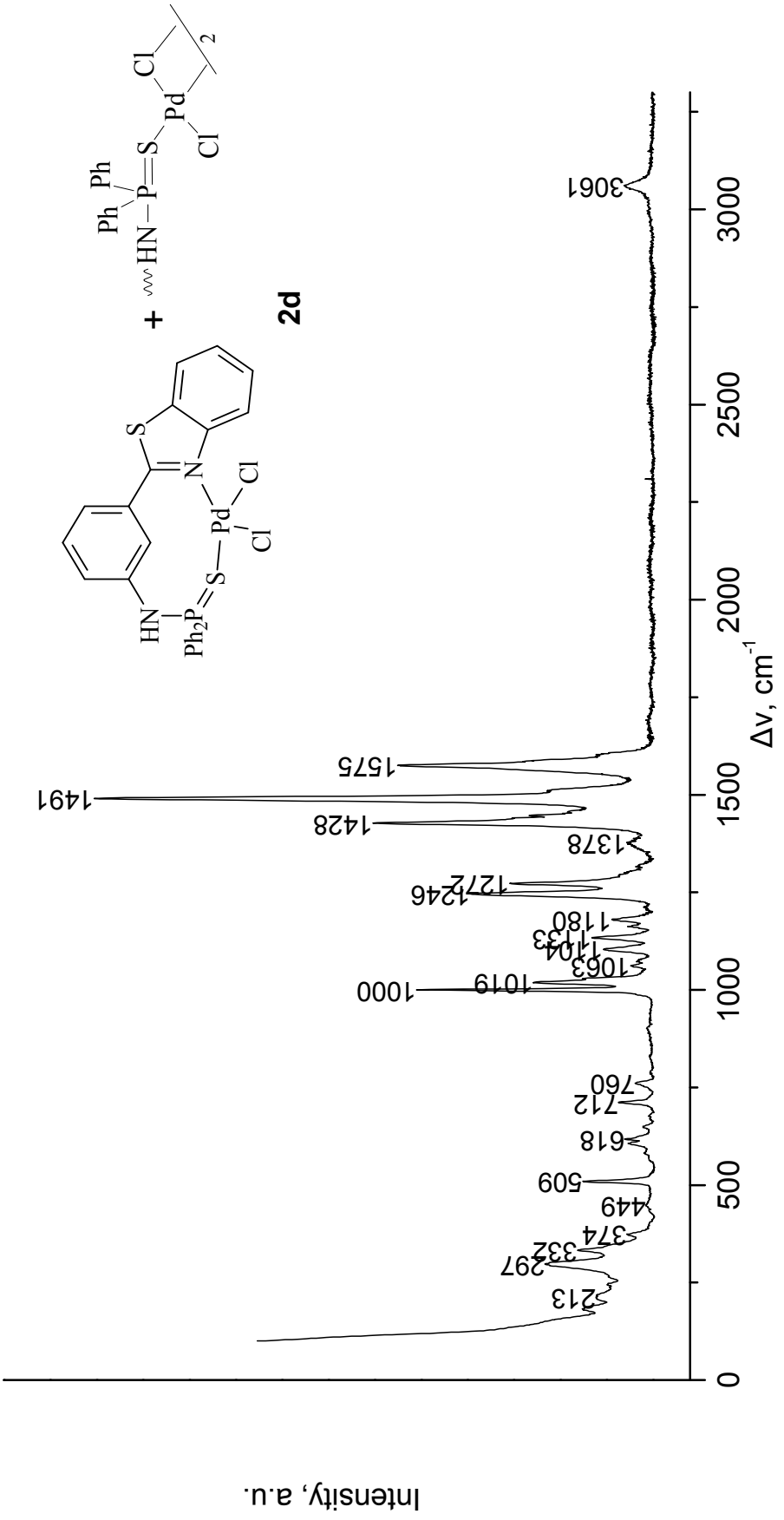

Fig. 11S. Raman spectra of complex **2d**

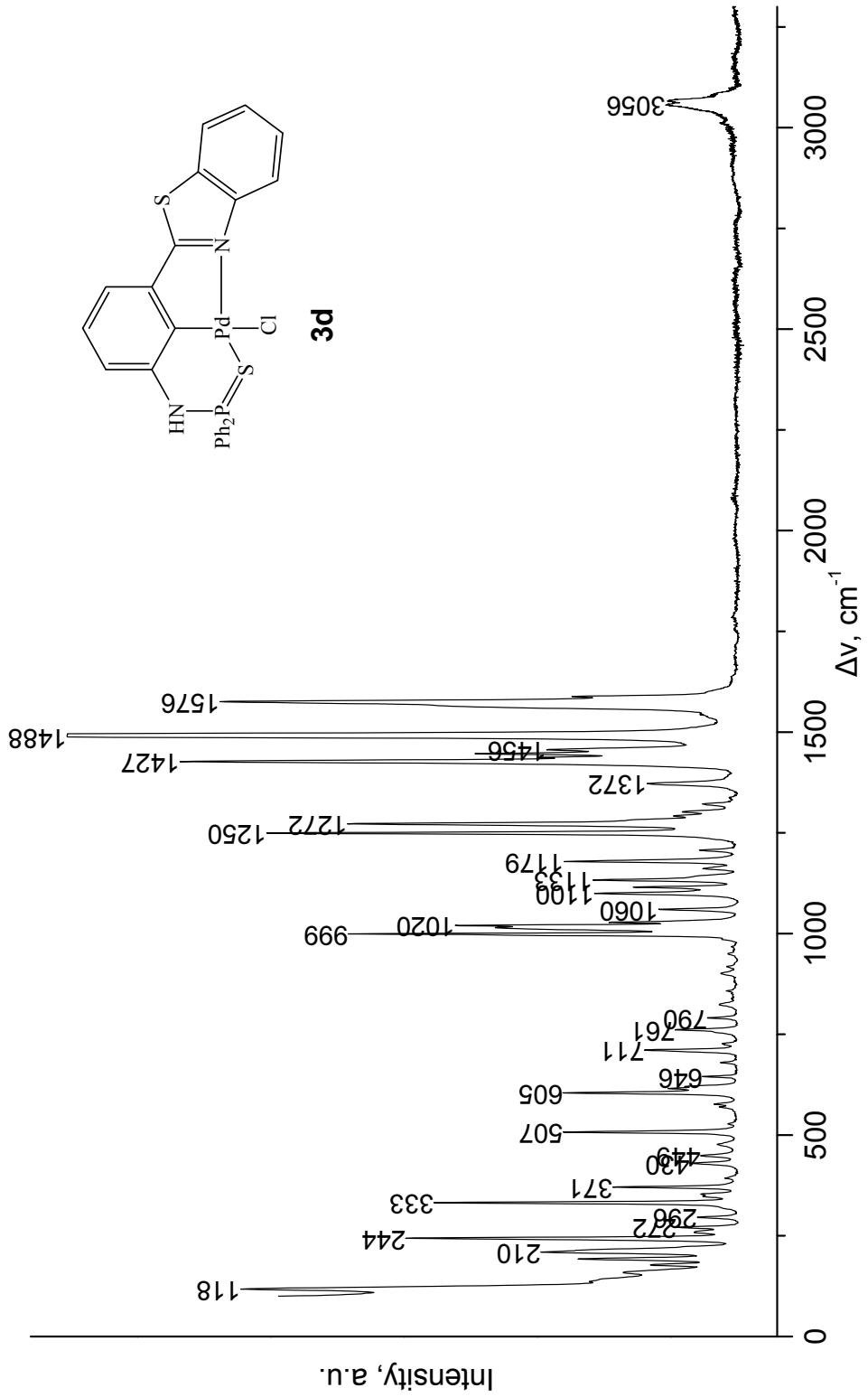

Fig. 12S. Raman spectra of pincer complex **3d**

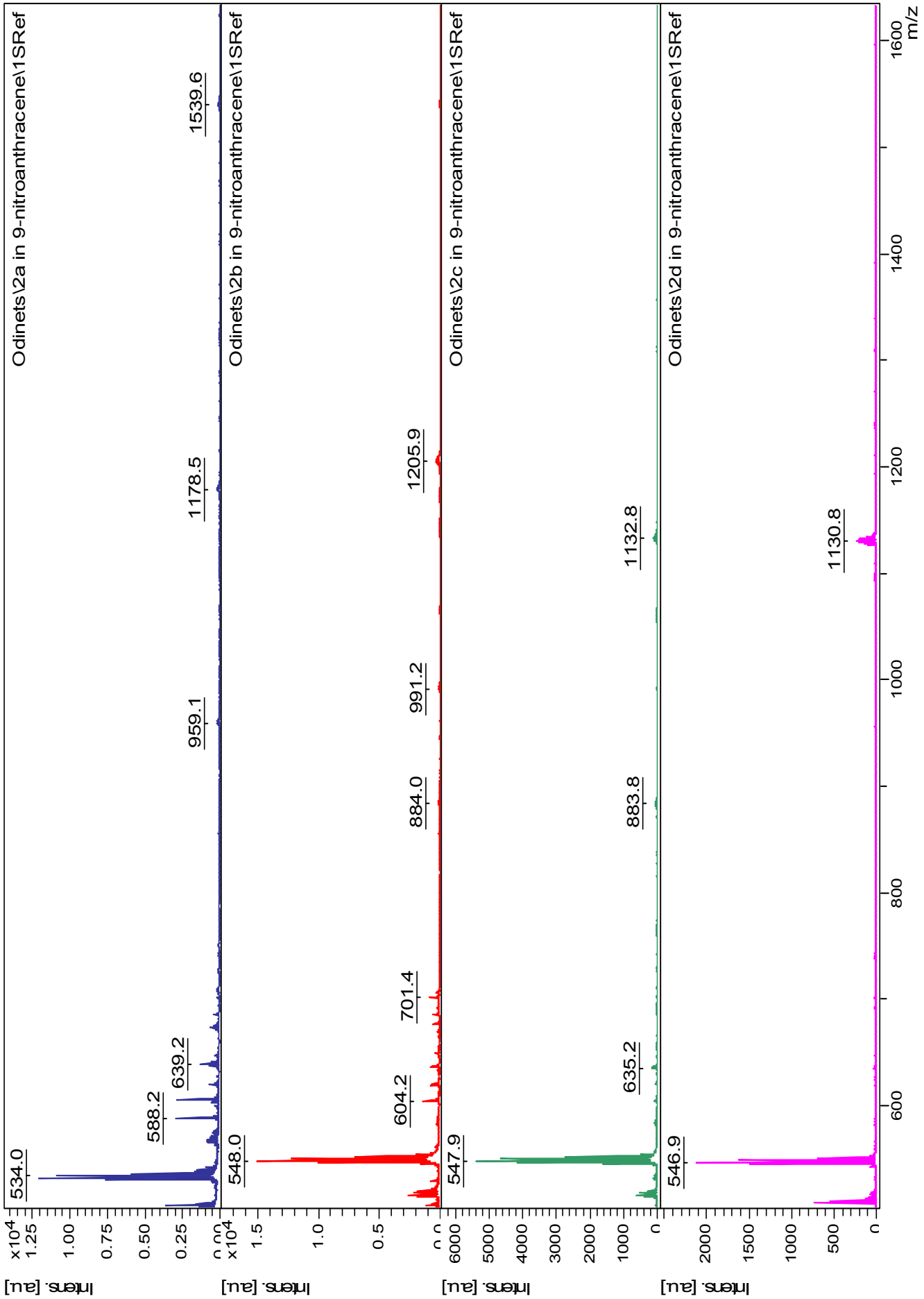

Fig. 13S. MALDI(+)-MS spectra of intermediate complexes **2a-d** (9-nitroanthracene matrix).

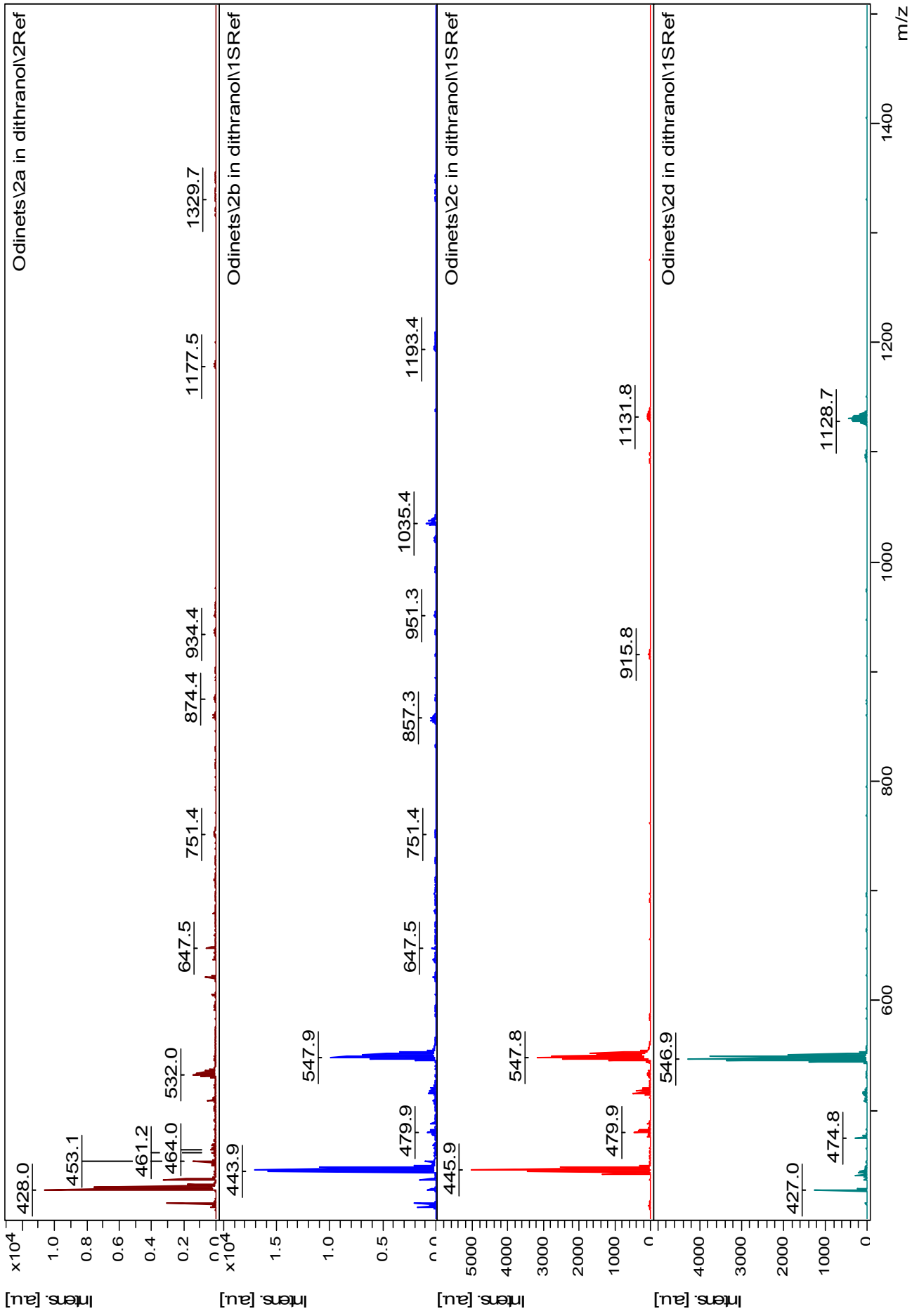

Fig. 14S. MALDI(+)-MS spectra of intermediate complexes **2a-d** (dithranol matrix).

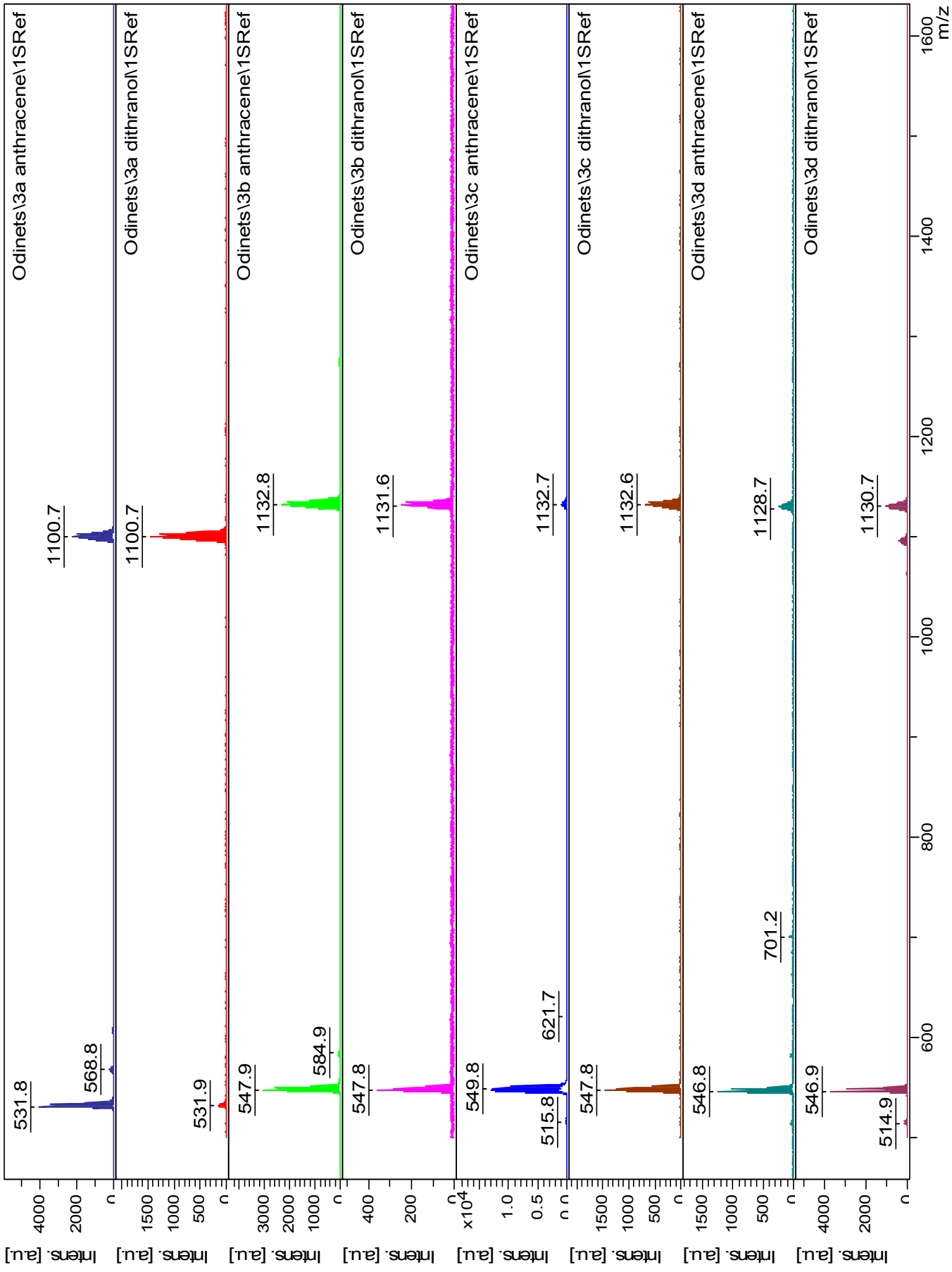

Fig. 15S. MALDI(+)-MS spectra of the pincer complexes **3a-d** (9-nitroanthracene and dithranol matrix).

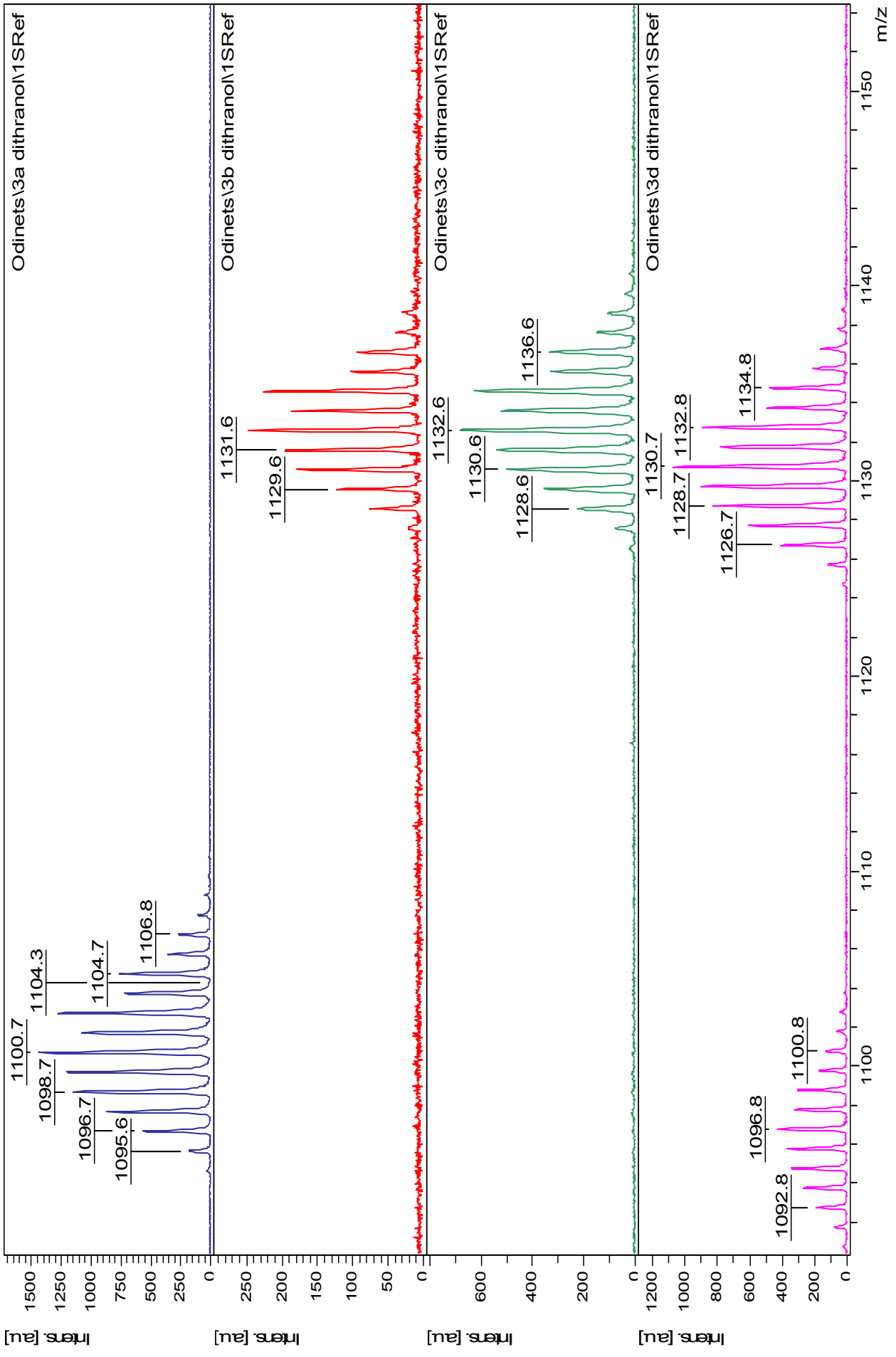

Fig. 16S. Ionic bimetallic palladacycles in the MALDI(+)-MS spectra of the pincer complexes **3a-d** (dithranol matrix)

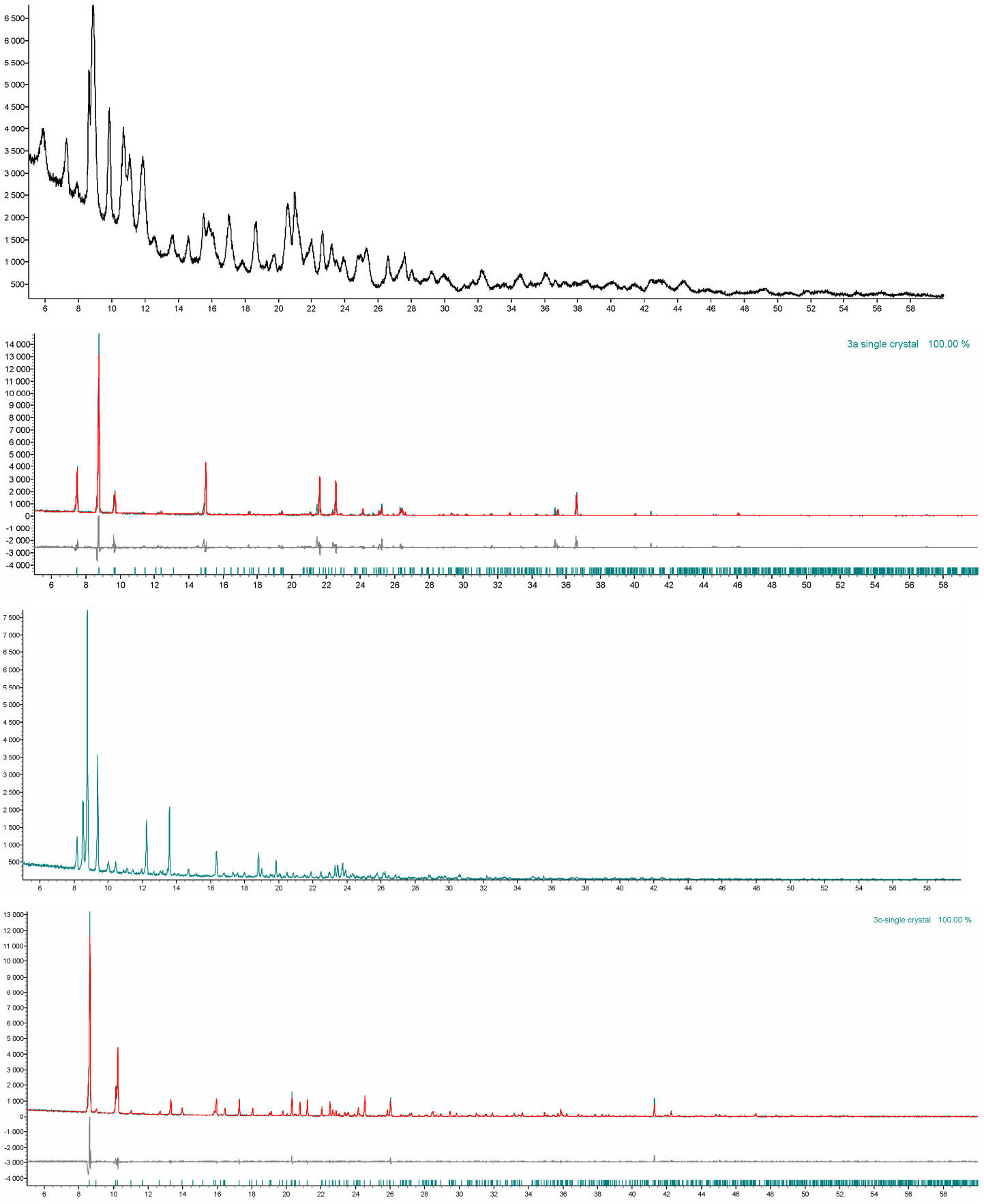

Fig 17S. The XRD diffraction pattern of complexes (from top to bottom) **2c**, **3a** and **3c**. Red line correspond to the theoretical XRD pattern calculated from the single crystal data.

References for Supporting information

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