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Supporting Information

Coordination Chemistry of Cyclopropenylidene-Stabilized Phosphenium Cations: Synthesis and Reactivity of Pd and Pt Complexes

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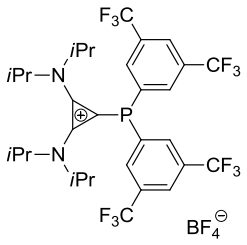
Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropiate drying agents and were transferred under Ar. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 600, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Column chromatography was performed on Merck 60 silica gel (40-63 µm). Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by UV.

All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received. Compounds **1a**-**f**, **3a**,**b**,**e**,**f**, [1] 2,3-bis(diisopropylamino)-1-chlorocyclopropenium tetrafluoroborate **2** [2], bis[3,5-bis(trifluoromethyl)phenyl]phosphine[3], 6-bromo-3-hydroxy-2-methoxynebzaldehyde **13**[4], 4-bromo-2,3-dimethoxy-1-benzyloxybenzene **18** [5], 6-bromoveratraldehyde **20** [6] and monosaccharide **25** [7] were prepared according to literature procedures.

Compound **1g**

A solution of bis[3,5-bis(trifluoromethyl)phenyl]phosphine (1 g, 2.18 mmol) in dry THF (15 mL) was cooled to -78 °C, then *n*-BuLi (1.6 M in hexane, 1.6 mL, 2.18 mmol) was added and the resulting mixture was stirred for 2 hours at this temperature. After this chlorocyclopropenium salt **2** (782 mg, 2.18 mmol) was added and the mixture allowed to warm up slowly to rt and further stirred at 60 °C for 2 days. After cooling to rt, the solvent was evaporated, the residue suspended in CH_2Cl_2 (20 mL) and washed with saturated aq. $NaBF_4$ solution (3 x 15 mL). Once dried over Na_2SO_4, the organic phase was concentrated and the residue purified by column chromatography (CH_2Cl_2/acetone: 9/1) affording the title compound as a pale yellow solid (653 mg, 38 %).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.11 (d, *J* = 6.8 Hz, 12H), 1.41 (d, *J* = 6.8 Hz, 12H), 3.48 (sept, *J* = 6.8 Hz, 2H), 4.16 (sept, *J* = 6.8 Hz, 2H), 7.93 (s, 2H), 7.95 (s, 2H), 8.02 (2H) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ = -26.9 ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -151.5, -151.5, -63.1 ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 20.8, 20.8, 21.2, 52.8, 54.6, 99.4 (d, *J* = 61.4 Hz), 122.7 (q, 273.3 Hz), 124.8-125.1 (m), 133.3 (dq, *J* = 34.3, 7.1 Hz), 133.6-134.1 (m), 134.3 (d, *J* = 15.4 Hz), 140.0 ppm.

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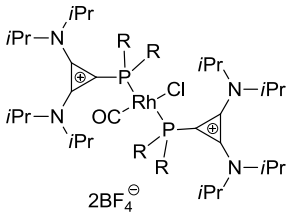
[6] S. Chandrasekhar, N. R. Reddy, Y. S. Rao, *Tetrahedron* **2006**, *62*, 12098.
[7] a) B. Dasari, S. Jogula, R. Borhade, S. Balasubramanian, G. Chandrasekhar, S. S. Kitambi, P. Arya, *Org. Lett*. **2013**, *15*, 432; b) R. R. Schmidt, M. Stumpp, *Liebigs Ann. Chem*. **1983**, 1249; c) R. R. Schmidt, J. Michel, M. Roos, *Liebigs Ann. Chem*. **1984**, 1343.

HRMS *calcd*. for $C_{31}H_{34}N_2F_{12}P^+$: 693.226254; *found* 693.226826.

IR $\tilde{\nu}$ = 681, 704, 845, 899, 1057, 1095, 1122, 1180, 1278, 1353, 1459, 1567, 1867, 2981 cm^{-1}.

Compound **3d**

Dry THF (2 mL) was added to a cooled (-20 °C) solid mixture of $[RhCl(CO)_2]_2$ (13 mg, 0.031 mmol) and phosphenium salt **1d** (67 mg, 0.12 mmol). The reaction mixture was allowed to warm to rt and then stirred for additional 30 minutes. After removal of the solvents *in vacuo*, the solid residue was washed with pentane (2 x 2 mL) and dried, affording the desired product as a yellow solid (76 mg, 99%).



R = *p*-(Me)C_6H_4

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 0.97 (d, *J* = 6.8 Hz, 24H), 1.34 (d, *J* = 6.8 Hz, 24H), 2.45 (s, 12H), 3.47 (sept, *J* = 7.0 Hz, 4H), 4.11 (sept, *J* = 7.0 Hz, 4H), 7.43 (d, *J* = 7.9 Hz, 8H), 8.00-8.10 (m, 8H) ppm.

^{31}P NMR (121 MHz, CD_2Cl_2) δ = 28.8 (d, *J* = 131.2 Hz) ppm.

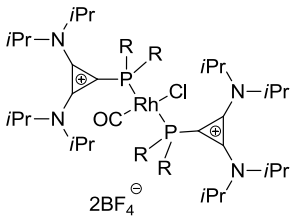
^{13}C NMR (75 MHz, CD_2Cl_2) δ = 21.1, 21.5, 21.6, 102.0 (d, *J* = 12.6 Hz), 125.1 (dd, *J* = 27.8, 26.5 Hz), 130.7 (t, *J* = 6.4 Hz), 136.0 (t, *J* = 7.9 Hz), 138.9 (d, *J* = 3.3 Hz), 144.6 (t, *J* = 1.3 Hz) ppm.

HRMS *calcd.* for $C_{59}H_{84}BClF_4N_4OP_2Rh^+$: 1151.488064; *found* 1151.491726.

IR $\tilde{\nu}$ = 664, 386, 807, 1031, 1094, 1149, 1189, 1357, 1375, 1455, 1554, 1866, 1969, 2969 cm^{-1}.

Compound **3g**

To a solution of the phosphenium salt **1g** (70 mg, 0.09 mmol) in CH_2Cl_2 (1.5 mL), $[RhCl(CO)_2]_2$ (8.7 mg,0.022 mmol) was added and the reaction mixture was stirred for 2 hours at rt. After removal of the solvents *in vacuo*, the solid residue was washed with pentane (2 x 1 mL) and dried, affording the desired product as a yellow solid (36 mg, 93%).



R = 3,5-di(CF_3)C_6H_3

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.06 (d, *J* = 6.9 Hz, 24H), 1.39 (d, *J* = 6.9 Hz, 24H), 3.49 (sept, *J* = 6.8 Hz, 4H), 4.20 (sept, *J* = 6.8 Hz, 4H), 8.21 (s, 4H), 9.02 (t, *J* = 5.8 Hz, 8H) ppm.

^{31}P NMR (162 MHz, CD_2Cl_2) δ = 25.0 (d, *J* = 136.5 Hz) ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -150.3, -150.2, -63.2 ppm.

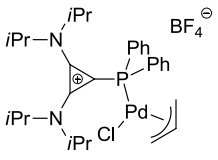
The sample decomposes during the ^{13}C NMR measurement.

MS: $[C_{63}H_{68}BClF_{28}N_4OP_2Rh]^+$: 1639.

IR $\tilde{\nu}$ = 681, 701, 901, 1051, 1095, 1121, 1181, 1278, 1354, 1457, 1561, 1863, 1991, 2981 cm^{-1}.

Compound **4a**

Dry THF (6 mL) was added to a cooled (-20 °C) solid mixture of allyl palladium chloride dimer (24 mg, 0.06 mmol) and compound **1a**, (66 mg, 0.13 mmol) and the thus obtained solution was stirred at this temperature for 30 min. After warming to rt, the solvents were removed *in vacuo*, affording the desired product as a white solid (89 mg, 98%).



^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.91-1.00 (m, 12H),1.40 (d, *J* = 7.0 Hz, 12H), 3.05 (d,

J = 12.3 Hz, 1H), 3.36 (sept, *J* = 7.0 Hz, 2H), 3.79-3.92 (m, 1H), 4.0-4.22 (m, 3H), 4.94-5.06 (m, 1H), 5.60-5.80 (m, 1H), 7.49-7.67 (m, 6H), 7.83-7.95 (m, 2H), 7.97-8.09 (m, 2H) ppm.

^{31}P NMR (121 MHz, $CDCl_3$) δ = 26.9 ppm.

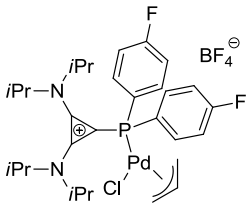
^{13}CNMR (100 MHz, $CDCl_3$) δ = 21.3, 21.3, 21.6, 53.1, 54.3, 58.9, 77.3, 118.2 (d, *J* = 5.6 Hz), 129.9 (d, *J* = 8.5 Hz), 130.0 (d, *J* = 8.8 Hz), 132.7 (brs), 135.4 (d, *J* = 15.9 Hz), 139.2 (d, *J* = 8.0 Hz) ppm.

HRMS *calcd*. for $C_{30}H_{43}N_2ClPPd^+$: 603.189045; *found* 603.189620.

IR $\tilde{\nu}$ = 699, 756, 1036, 1093, 1150, 1185, 1361, 1372, 1435, 1552, 1864, 2937, 2977 cm^{-1}.

Compound **4f**

Dry THF (4 mL) was added to a cooled (-20 ^{o}C) solid mixture of allyl palladium chloride dimer (18 mg, 0.05 mmol) and compound **1f**, (52 mg, 0.10 mmol) and the resulting solution was stirred at this temperature for 30 min. After warming to rt, the solvents were removed *in vacuo*, affording the desired product as a pale yellow solid (69 mg, 98%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.91-1.00 (m, 12H), 1.38 (d, *J* = 7.0 Hz, 12H), 3.07 (d, *J* = 12.0 Hz,1H), 3.41 (sept, *J* = 7.0 Hz, 2H), 3.79-3.90 (m, 1H), 4.05-4.20 (m, 3H), 4.91-5.02 (m, 1H), 5.67-5.81 (m, 1H), 7.24-7.37 (m, 4H), 7.79-7.90 (m, 2H), 7.92-8.04 (m, 2H) ppm.

^{31}P NMR (161 MHz, CD_2Cl_2) δ = 25.5 ppm.

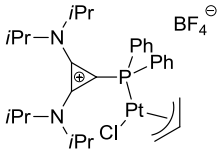
^{13}C NMR (100 MHz, CD_2Cl_2) δ = 21.2, 21.3, 21.6, 54.7 (brs), 60.2, 81.5 (d, *J* = 32.3 Hz), 100.8 (d, *J* = 21.3 Hz), 117.6 (ddd, *J* = 21.3, 13.1, 7.5 Hz), 119.0 (d, *J* = 5.2 Hz), 124.2 (dd, *J* = 48.7, 22.8 Hz), 137.8-138.3 (m), 138.9 (d, *J* = 7.7 Hz), 165.9 (dd, *J* = 255.6, 5.3 Hz) ppm.

HRMS *calcd*. for $C_{30}H_{41}N_2ClF_2PPd^+$: 639.170431; *found* 639.170937.

IR $\tilde{\nu}$ = 674, 817, 844, 891, 1008, 1031, 1044, 1079, 1148, 1163, 1230, 1359, 1496, 1548, 1586, 1854, 2987 cm^{-1}.

Compound **5a**

Dry THF (4 mL) was added to a cooled (-20 ^{o}C) solid mixture of allyl platinum chloride tetramer (35 mg, 0.03 mmol) and compound **1a**, (66 mg, 0.13 mmol) and the resulting solution was stirred at this temperature for 30 min. After warming to rt, the solvents were removed *in vacuo*, and the desired product was obtained as a pale yellow solid (95 mg, 94%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.87 (d, *J* = 7.0 Hz, 6H), 0.90 (d, *J* = 7.0 Hz, 6H), 1.38 (d, *J* = 6.9 Hz, 12H), 2.48 (dt, *J* = 25.8, 11.4 Hz, 1H), 3.11-3.28 (m, 1H), 3.44 (sept, *J* = 6.9 Hz, 2H), 3.77-3.88 (m, 1H), 4.05-4.20 (m, 2H), 4.60-4.68 (m, 1H), 4.98-5.24 (m, 1H), 7.54-7.66 (m, 6 H), 7.75-7.84 (m, 2H), 7.91-7.99 (m, 2H) ppm.

^{31}P NMR (161 MHz, CD_2Cl_2) δ = 31.8 ($^{1}J_{(Pt\text{-}P)}$ = 2188.0 Hz) ppm.

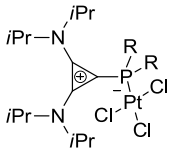
^{13}C NMR (100 MHz, CD_2Cl_2) δ = 20.9, 21.0, 21.7, 47.0 ($^{1}J_{(Pt\text{-}C)}$ = 108.7 Hz), 53.0, 54.9, 70.7 (d, *J* = 35.0, $^{1}J_{(Pt\text{-}C)}$ = 34.5 Hz), 100.2 (d, *J* = 32.3 Hz), 109.9 ($^{1}J_{(Pt\text{-}C)}$ = 24.8 Hz), 127.7 (d, *J* = 16.7 Hz), 128.3 (d, *J* = 17.3 Hz), 130.1 (d, *J* = 11.4 Hz), 130.1 (d, *J* = 11.9 Hz), 133.4 (d, *J* = 2.1 Hz), 133.5 (d, *J* = 2.1 Hz), 135.3 (d, *J* = 14.9 Hz), 135.5 (d, *J* = 15.0 Hz), 139.1 (d, *J* = 8.1 Hz) ppm.

HRMS *calcd*. for $C_{30}H_{43}C_{11}N_2PPt^+$: 692.248763; *found* 692.249285.

IR $\tilde{\nu}$ = 698, 754, 894, 998, 1033, 1048, 1094, 1149, 1184, 1203, 1355, 1376, 1437, 1454, 1550, 1866, 2938, 2980 cm^{-1}.

Compound **6d**

K_2PtCl_4 (43 mg, 0.103 mmol) was added to a solution of salt **1d** (51 mg, 0.094 mmol) in dry CH_3CN (3 mL) and the mixture was stirred at rt. After 1 day the solvents were evaporated and the residue was extracted with CH_2Cl_2 (5 x 2 mL). Removal of the solvents and recrystallization from CH_3CN/Et_2O gave the desired product as an orange solid (62 mg, 88%).



R = *p*-(Me)C_6H_4

^1H NMR (400 MHz, CD_2Cl_2) δ = 0.90 (d, *J* = 6.6 Hz, 12H), 1.32 (d, *J* = 6.7 Hz, 12H), 2.41 (s, 6H), 3.53 (sept, *J* = 6.7 Hz, 2H), 4.04 (sept, *J* = 6.7 Hz, 2H), 7.35 (dd, *J* = 7.9 Hz, 2.3 Hz, 4H), 8.16 (dd, *J* = 12.4 Hz, 8.1 Hz, 4H) ppm.

^{31}P NMR (162 MHz, CD_2Cl_2) δ = 3.0 ($^1J_{(Pt-P)}$ = 2000.8 Hz) ppm.

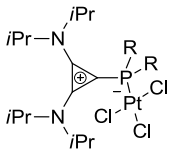
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.6, 21.6 (d, *J* = 1.4), 21.7, 52.2 (brs), 54.9 (brs), 101.9 (d, *J* = 42.0 Hz), 122.7 (d, *J* = 69.2 Hz), 129.9 (d, *J* = 12.3 Hz), 136.3 (d, *J* = 12.3 Hz), 138.2 (d, *J* = 8.0 Hz), 143.8 (d, *J* = 2.7 Hz).

HRMS *calcd*. for $C_{29}H_{42}N_2Cl_2PPt^+$: 714.210531; *found* 714.211157.

IR $\tilde{\nu}$ = 665, 678, 711, 814, 896, 1011, 1030, 1098, 1149, 1186, 1316, 1352, 1375, 1449, 1497, 1551, 1597, 1865, 2934, 2978 cm^{-1}.

Compound **6f**

K_2PtCl_4 (128 mg, 0.308 mmol) was added to a solution of salt **1f** (150 mg, 0.28 mmol) in dry CH_3CN (4 mL) and the mixture was stirred at rt. After 1 day the solvents were evaporated and the residue was extracted with CH_2Cl_2 (5 x 4 mL). Removal of the solvents and recrystallization from CH_3CN/Et_2O gave the desired product as a yellow solid (158 mg, 68%).



R = *p*-(F)C_6H_4

^1H NMR (400 MHz, CD_3CN) δ = 0.91 (d, *J* = 6.8 Hz, 12H), 1.30 (d, *J* = 7.0 Hz, 12H), 3.56 (sept, *J* = 6.7 Hz, 2H), 4.11 (sept, *J* = 6.7 Hz, 2H), 7.34 (dt, *J* = 8.9, 1.9 Hz, 4H), 8.31-8.40 (m, 4H) ppm.

^{31}P NMR (162 MHz, CD_3CN) δ = -0.01 ($^1J_{(Pt-P)}$ = 2016.8 Hz) ppm.

^{19}F NMR (282 MHz, CD_3CN) δ = -107.8 ppm.

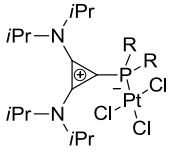
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 20.7, 21.7, 52.3 (brs), 100.3 (d, *J* = 43.7 Hz), 116.6 (dd, *J* = 21.6, 13.3 Hz), 121.8 (dd, *J* = 69.8, 3.4 Hz), 138.2 (d, *J* = 8.6 Hz), 138.8 (dd, *J* = 13.9, 8.9 Hz), 165.7 (dd, *J* = 255.7, 2.8 Hz) ppm.

HRMS *calcd*. for $C_{27}H_{36}Cl_4F_2N_2PPt^-$: 792.097748; *found* 792.098455.

IR $\tilde{\nu}$ = 685, 714, 815, 894, 1011, 1031, 1095, 1160, 1229, 1260, 1354, 1375, 1452, 1495, 1550, 1588, 1866, 2977 cm^{-1}.

Compound **6g**

K_2PtCl_4 (87 mg, 0.21 mmol) was added to a solution of salt **1g** (150 mg, 0.19 mmol) in dry CH_3CN (4 mL) and the mixture was stirred at rt. After 1 day the solvent was evaporated and the residue extracted with CH_2Cl_2 (3 x 3 mL). Removal of the solvent *in vacuo* afforded the desired product as a yellow solid (182 mg, 95%).



R = 3,5-di(CF_3)C_6H_3

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.98 (d, *J* = 6.8 Hz, 12H), 1.39 (d, *J* = 6.9 Hz, 12H), 3.61 (sept, *J* = 6.8 Hz, 2H), 4.16 (sept, *J* = 6.8 Hz, 2H), 8.16 (s, 2H), 8.70 (s, 2H), 8.73 (2H) ppm.

^{31}P NMR (121 MHz, CD_2Cl_2) δ = 3.11 ($^{1}J_{(Pt-P)}$ = 2037.3 Hz) ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -63.2 ppm.

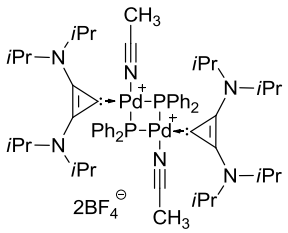
^{13}C NMR (101 MHz , CD_2Cl_2) δ = 20.7, 21.7, 55.5 (brs), 95.8 (d, *J* = 47.5 Hz), 122.9 (q, 273.3 Hz), 127.1-127.4 (m), 128.7 (d, *J* = 65.1 Hz), 132.9 (dq, *J* = 34.3, 11.8 Hz), 135.7-136.1 (m), 138.9 (d, *J* = 7.8 Hz) ppm.

HRMS *calcd*. for $C_{31}H_{34}Cl_4F_{12}N_2PPt^-$: 1028.066206; *found* 1028.067766.

IR $\tilde{\nu}$ = 680, 698, 845, 894, 910, 1031, 1096, 1120, 1179, 1276, 1354, 1455, 1560, 1865, 2983 cm^{-1}.

Compound **7a**

A mixture of the compound **1a** (77 mg, 0.15 mmol) and $Pd_2(dba)_3$ (70 mg, 0.076 mmol) was evacuated for 10 minutes, then CH_2Cl_2 (3 mL) was added under Ar and the suspension stirred at rt for 2 hours. After this time the solvent was removed *in vacuo* and the residue washed with Et_2O (4 x 2 mL). Recrystallization of the crude product from CH_3CN/Et_2O gave compound **7a** as a yellow solid (44 mg, 44%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.97 (brs, 24H), 1.10 (brs, 24H), 2.04 (s, 6H), 3.71 (sept, *J* = 6.7 Hz, 8H), 7.34-7.41 (m, 8H), 7.43-7.49 (m, 4H), 7.74-7.82 (m, 8H) ppm.

^{31}P NMR (162 MHz, CD_2Cl_2) δ = -130.6 ppm.

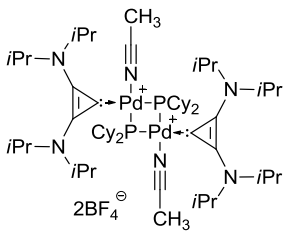
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 2.8, 21.7 (brs), 50.2 (brs), 51.8 (brs), 117.1, 129.1-129.4 (m), 130.7, 133.1-133.6 (m), 134.6-134.9 (m), 137.6, 148.2 ppm.

MS: $[C_{43}H_{54}B_2F_8N_4P_2Pd_2]^-$: 1075.

IR $\tilde{\nu}$ = 695, 745, 941, 1030, 1049, 1134, 1154, 1185, 1200, 1327, 1350, 1372, 1389, 1403, 1434, 1452, 1487, 1850, 2876, 2936, 2979 cm^{-1}.

Compound **7b**

A mixture of the compound **1b** (79 mg, 0.15 mmol) and $Pd_2(dba)_3$ (69 mg, 0.075 mmol) was evacuated for 10 minutes then CH_2Cl_2 (3 mL) was added under Ar and the suspension was stirred at rt for 2 hours. After removal of the solvents *in vacuo*, the residue was washed with Et_2O (4 x 2 mL) and recrystallized from CH_3CN/Et_2O to give compound **7b** as a yellow solid (33 mg, 38 %).



^{1}H NMR (400 MHz, CD_2Cl_2) = 1.14-1.65 (m, 70H), 1.71-2.10 (m, 20H), 2.25 (s, 6H), 2.28-2.38 (m, 2H) ppm.

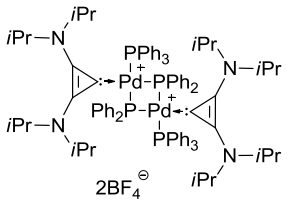
^{31}P NMR (162 MHz, CD_2Cl_2) δ = -104.6 ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.1 (brs), 22.4-22.8 (m), 26.5, 27.4-27.9 (m), 31.5, 33.6, 36.5, 51.0, 151.1 ppm.

MS: $[C_{44}H_{82}B_2F_8N_5PPd_2]^+$: 1099.

IR $\tilde{\nu}$ = 729, 849, 890, 1004, 1030, 1049, 1107, 1138, 1155, 1185, 1209, 1325, 1348, 1369, 1450, 1484, 1843, 2855, 2930, 2973 cm^{-1}.

Compound **8a**



A mixture of the compound **1a** (52 mg, 0.10 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) was evacuated for 10 minutes. After this time, toluene (4 mL) was then added under Ar and the suspension was stirred at 100 °C overnight. Then the solvents were removed *in vacuo* and the residue washed with Et_2O (4 x 2 mL). Recrystallization of the crude product from CH_2Cl_2/Et_2O, gave compound **8a** as a yellow solid (128 mg, 73%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.38 (brs, 12H), 0.67 (brs, 12H), 1.04 (d, *J* = 6.4 Hz, 12H), 1.11 (d, *J* = 6.0 Hz, 12H), 3.20 (sept, *J* = 6.3 Hz, 4H), 3.69 (sept, *J* = 6.3 Hz, 4H), 6.55-6.73 (m, 12H), 7.02-7.60 (m, 38H) ppm.

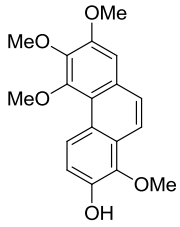
^{31}P NMR (162 MHz, CD_2Cl_2) δ = -168.9 (dd, $^2J_{(P\text{-}P\ trans)}$ = 213.3, $^2J_{(P\text{-}P\ cis)}$ = 108.8 Hz), 14.2 (dd, $^2J_{(P\text{-}P\ trans)}$ = 213.3, $^2J_{(P\text{-}P\ cis)}$ = 108.8 Hz) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.0, 22.4, 51.4 (brs), 128.7-129.3 (m), 129.6 (brs), 131.2, 131.5 (brs), 133.4-133.9 (m), 134.3 (brs), 147.8 ppm.

MS: $[C_{90}H_{106}BF_4N_4P_4Pd_2]^+$: 1665.

IR $\tilde{\nu}$ = 693, 739, 895, 999, 1031, 1049, 1088, 1151, 1185, 1318, 1345, 1372, 1433, 1451, 1488, 1841, 2976, 3058 cm^{-1}.

Compound **11**



A hot solution (80 °C) of alkyne **16** (40 mg, 127 µmol) in 2.5 mL dry dichloroethane was transferred to a Schlenk containing precatalyst **6g** (6.3 mg, 6 µmol, 5 mol%) and $Ag[SbF_6]$ (2.2 mg, 6 µmol, 5 mol%). After stirring for 10 minutes at this temperature, the mixture was filtered through silica, evaporated and the residue purified by flash chromatography (hexane:ethyl acetate 2:1). The sample thus obtained in 98% yield was 90 % pure by NMR. The analytically pure sample, was obtained by preparative HPLC separation.

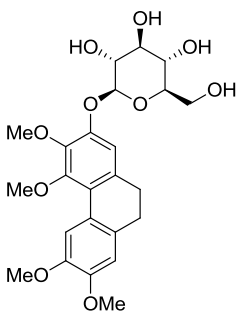
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.98 (s, 3H), 4.01 (s, 3H), 4.01 (s, 3H), 4.03 (s, 3H), 5.75 (s, 1H), 7.09 (s, 1H), 7.31 (d, *J* = 9.3 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.88 (d, *J* = 9.4 Hz, 1H), 9.24 (d, *J* = 9.4 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 56.0, 60.3, 61.3, 62.1, 105.5, 116.4, 119.5, 119.5, 124.3, 124.9, 126.5, 127.5, 128.9, 141.0, 143.2, 145.6, 152.0, 152.1 ppm.

HRMS *calcd.* for $C_{18}H_{18}O_5Na$: 337.104643; *found* 337.104323.

IR $\tilde{\nu}$ = 699, 716, 766, 780, 799,816, 837, 852, 899, 944, 978, 990, 1043, 1052, 1105, 1144, 1193, 1225, 1268, 1294,1322, 1341, 1353, 1392, 1433, 1475, 1574, 1608, 2838, 2931, 2960, 3009, 3451 cm^{-1}.

Compound **12**



Pd/C (10%) (46 mg, 0.043 mmol) was added to a suspension of compound **26** (180 mg, 0.22 mmol) in methanol/ethyl acetate mixture (2:1, 6 mL) and the mixture was stirred under a hydrogen atmosphere at rt for 24 hours. The mixture was then filtered over silica, concentrated and purified by column chromatography (CH_2Cl_2/MeOH 10:1) to afford compound **12** as a white solid (77 mg, 75%).

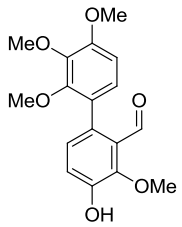
^{1}H NMR (600 MHz, CD_3OD) δ = 2.67-2.72 (m, 4H, 10-H, 11-H), 3.39 (dd, *J* = 9.6, 8.5 Hz, 1H, 4-H), 3.44 (ddd, *J* = 9.6, 5.8, 2.2 Hz, 1H, 5-H), 3.47 (dd, *J* = 9.5, 8.5 Hz, 1H, 3-H), 3.51 (dd, *J* = 9.2, 7.5 Hz, 1H, 2-H), 3.69 (dd, *J* = 12.1, 5.8 Hz, 1H, 6b-H), 3.73 (s, 3H, 22-H), 3.85 (s, 6H, 23-H, 24-H), 3.90 (dd, *J* = 12.1, 2.2 Hz, 1H, 6a-H), 3.92 (s, 3H, 21-H), 4.95 (d, *J* = 7.4 Hz, 1H, 1-H), 6.84 (s, 1H, 13-H), 6.90 (s, 1H, 8-H), 7.95 (s, 1H, 16-H) ppm.

^{13}C NMR (150 MHz, d^6-DMSO) δ = 28.5 (C11), 29.8 (C10), 55.4 (C24), 55.6 (C23), 60.3 (C22), 60.7 (C21), 60.8 (C6), 69.8 (C4), 73.4 (C2), 76.9 (C3), 77.2 (C5), 100.8 (C1), 111.1 (C16), 111.5 (C13), 111.5 (C8), 121.0 (C18), 124.3 (C17), 130.4 (C12), 133.4 (C9), 141.6 (C20), 146.8 (C15), 147.3 (C14), 149.4 (C7), 150.7 (C19) ppm.

HRMS *calcd.* for $C_{24}H_{30}O_{10}Na$: 501.173119; *found* 501.172265.

IR $\tilde{\nu}$ = 677, 724, 763, 781, 825, 884, 1002, 1023, 1046, 1145, 1185, 1215, 1242, 1261, 1290, 1306, 1345, 1376, 1398, 1413, 1453, 1484, 1512, 1546, 1568, 1649, 1864, 2851, 2907, 2927, 2975, 3380 cm^{-1}.

Compound **15**



A suspension of compounds **13** (1.40 g, 6.10 mmol), **14** (1.55 g, 7.30 mmol), $Pd(OAc)_2$ (68 mg, 0.30 mmol) and PPh_3 (80 mg, 0.30 mmol) in DMF/H_2O (10:1, 66 mL) mixture was stirred at 60 °C overnight. After removal of the solvents *in vacuo*, the residue was suspended in H_2O (40 mL) and extracted with EtOAc (3 x 50 mL). Once dried over Na_2SO_4, the organic phase was concentrated and purified by column chromatography (hexane/ethyl acetate 10:1) to afford the title compound as a white solid (1.30 g, 68 %).

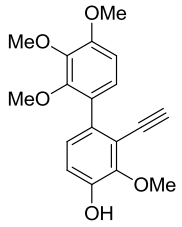
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.57 (s, 3H), 3.90 (s, 3H), 3.90 (s, 3H), 3.97 (s, 3H), 6.07 (s, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 9,84 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.2, 60.7, 61.2, 63.2, 107.5, 120.0, 125.2, 125.6, 127.2, 127.7, 134.5, 142.1, 146.6, 149.0, 151.3, 154.0, 191.4 ppm.

HRMS *calcd*. for $C_{17}H_{18}O_6Na$: 341.099561; *found* 341.099485.

IR $\tilde{\nu}$ = 705, 803, 827, 929, 986, 1002, 1032, 1088, 1127, 1163, 1176, 1213, 1275, 1403, 1426, 1442, 1474, 1591, 1698, 2843, 2953, 3398 cm^{-1}.

Compound **16**



Aldehyde **15** (1 g, 3.14 mmol), *Ohira-Bestmann* reagent (907 mg, 4.71 mmol) and K_2CO_3 (870 mg, 6.29 mmol) were stirred in MeOH (45 mL) at rt during 12 hours. After this time not consumed starting material could be observed by TLC, therefore more *Ohira-Bestmann* reagent (907 mg, 4.71 mmol) and K_2CO_3 (870 mg, 6.29 mmol) were added and the mixture was stirred 12 extra hours. After this time the solvents were removed *in vacuo*, the residue was suspended in H_2O (30 mL) and extracted with EtOAc (3 x 40 mL). Once dried over Na_2SO_4, the organic phase was concentrated and purified by column chromatography (hexane/ethyl acetate 20:1) to afford a mixture of compounds **16** and **17** which was separated by HPLC (MeOH/H_2O 60:40, flow rate 50 mL/min, $\tau_{\mathbf{16}}$ = 1.43 min, $\tau_{\mathbf{17}}$ = 1.76 min) (**16**: 510 mg, 52 %; **17**: 210 mg, 23 %).

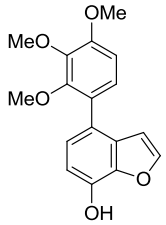
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.23 (s, 1H), 3.68 (s, 3H), 3.90 (s, 3H), 3.91 (s, 3H), 4.06 (s, 3H), 5.77 (s, 1H), 6.69 (d, *J* = 8.6, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.1, 61.1, 61.2, 61.5, 78.9, 85.1, 106.7, 115.4, 115.8, 125.7, 126.6, 127.1, 135.0, 142.2, 147.8, 148.7, 151.9, 153.4 ppm.

HRMS *calcd*. for $C_{18}H_{18}O_5Na$: 337.104644; *found* 337.104888.

IR $\tilde{\nu}$ = 670, 691, 789, 812, 827, 901, 925, 975, 999, 1010, 1038, 1091, 1125, 1230, 1272, 1290, 1329, 1411, 1433, 1462, 1484, 1576, 1599, 2827, 2934, 3279, 3370 cm^{-1}.

Compound **17**



Obtained as a side product during the synthesis of compound **16**.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.55 (s, 3H), 3.92 (s, 3H), 3.96 (s, 3H), 5.49 (s, 1H), 6.73 (d, *J* = 2.2 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 2.1 Hz, 1H) ppm.

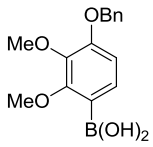
^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.2, 61.0, 61.3, 107.5, 108.0, 110.5, 124.2, 124.6, 125.6, 126.8, 128.6, 140.4, 142.6, 143.1, 144.7, 151.6, 153.1 ppm.

HRMS *calcd*. for $C_{17}H_{16}O_5Na$: 323.088998; *found* 323.088746.

IR $\tilde{\nu}$ = 681, 753, 780, 807, 826, 878, 911, 936,, 949, 1006, 1035, 1044, 1089, 1114, 1165, 1178, 1220, 1231, 1264, 1293, 1333, 1411,1436, 1460, 1481, 1593, 2839, 2941, 3266 cm^{-1}.

Compound **19**

Bromide **18** (1.312 g, 4.05 mmol) was solved in dry Et_2O (40 mL) and cooled to -78 °C. Then n-BuLi (2.5 M in hexane, 1.64 mL, 4.10 mmol) was added dropwise and the mixture stirred for 1.5 h at -78 °C. Subsequently trimethyl borate (1.37 mL, 12.15 mmol) was added and the resulting mixture allowed to warm to rt overnight. Then 2N HCl (24 mL) were added and the mixture was stirred for additional 2 h. After separation, the aqueous layer was extracted with MTBE and the combined organic layers were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (hexane/ethyl acetate 3:2) to yield a white solid (685 mg, 59 %).



^{1}H NMR (300 MHz, CD_3CN) δ = 3.82 (s, 3H), 3.95 (s, 3H), 5.14 (s, 2H), 6.30 (s, 2H), 6.86 (d, *J* = 8.4 Hz, 1H) 7.30-7.56 (m, 6H) ppm.

^{13}C NMR (75 MHz, CD_3CN) δ = 61.2, 62.3, 71.4, 110.5, 128.7, 129.0, 129.6, 131.8, 138.1, 142.5, 156.5, 160.0 ppm.

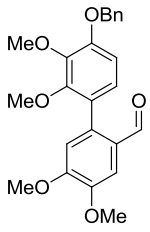
^{11}B NMR (128 MHz, CD_3CN) δ = 31 ppm.

HRMS *calcd*. for $C_{15}H_{17}O_5BNa$: 311.106123; *found* 311.105932.

IR $\tilde{\nu}$ = 665, 694, 742, 750, 774, 791, 803, 836, 879, 907, 926, 994, 1012, 1031, 1052, 1082, 1163, 1178, 1219, 1276, 1288, 1341, 1373, 1397, 1420, 1435, 1459, 1498, 1593, 2870, 2938, 2994, 3037, 3334 cm^{-1}.

Compound 21

Boronic acid **19** (411 mg, 1.43 mmol), bromide **20** (318 mg, 1.30 mmol), $Pd(PPh_3)_4$ (30 mg, 26 µmol) and Na_2CO_3 (275 mg, 2.60 mmol) were added to a microwave vessel and evacuated three times. Then a 1,4-dioxane/water mixture (3:2, 3.3 mL) was added and the vessel sealed quickly with a Teflon crim top. The suspension thus obtained was irradiated for 25 min at 120 °C and the resulting mixture extracted with ethyl acetate/H_2O. The organic layer was dried with Na_2SO_4 and evaporated obtaining a crude product that was purified by column



chromatography (hexane/ethyl acetate 2:1) to yield a light yellow oil (531 mg, 99 %).

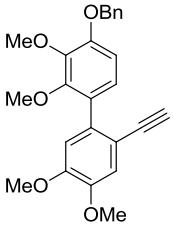
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.61 (s, 3H), 3.95 (s, 6H), 3.97 (s, 3H), 5.18 (s, 2H), 6.77-6.82 (m, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 7.31-7.50 (m, 5H), 7.52 (s, 1H), 9.71 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.2, 56.3, 61.0, 61.3, 71.1, 108.4, 109.4, 113.3, 124.7, 125.9, 127.3, 127.4, 128.2, 128.8, 136.9, 136.9, 142.8, 148.7, 151.7, 153.3, 153.4, 191.4 ppm.

HRMS *calcd*. for $C_{24}H_{24}O_6Na$: 431.146510; *found* 431.146724.

IR $\tilde{\nu}$ = 696, 718, 744, 807, 874, 909, 938, 985, 1013, 1062, 1081, 1093, 1143, 1201, 1215, 1249, 1288, 1350, 1413, 1394, 1461, 1488, 1514, 1595, 1676, 2768, 2846, 2936 cm^{-1}.

Compound **22**



Aldehyde **21** (717 mg, 1.76 mmol), *Ohira-Bestmann* reagent (506 mg, 2.63 mmol) and K_2CO_3 (486 mg, 3.52 mmol) were stirred in MeOH (27 mL) at rt overnight. Then, the solvents were removed *in vacuo* and the residue partitioned between CH_2Cl_2 and water. The combined organic layers were dried with Na_2SO_4, evaporated and the crude product was purified by column chromatography (hexane/ethyl acetate 2:1) to yield a transparent oil (594 mg, 83 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.92 (s, 1H), 3.71 (s, 3H), 3.88 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 5.16 (s, 2H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.84 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 7.07 (s, 1H), 7.30-7.52 (m, 5H) ppm.

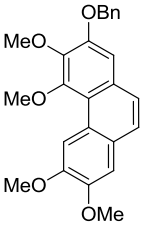
^{13}C NMR (101 MHz, $CDCl_3$) δ = 56.1, 56.1, 61.2, 61.3, 71.0, 78.3, 83.5, 108.8, 113.5, 113.7, 115.3, 125.7, 127.4, 127.6, 128.0, 128.6, 134.9, 137.2, 142.7, 147.7, 149.3, 151.8, 152.6 ppm.

HRMS *calcd.* for $C_{25}H_{24}O_5Na$: 427.151594; *found* 427.151708.

IR $\tilde{\nu}$ = 696, 726, 789, 862, 910, 975, 1014, 1063, 1093, 1145, 1211, 1248, 1291, 1346, 1385, 1411, 1461, 1488, 1516, 1561, 1599, 2100, 2843, 2936, 3278 cm^{-1}.

Compound **23**

A hot solution (80 °C) of alkyne **22** (59 mg, 0.15 mmol) in dry dichloroethane (3 mL) was transferred to a Schlenk containing precatalyst **6g** (7.3 mg, 7 µmol, 5 mol %) and $Ag[SbF_6]$ (2.5 mg, 7 µmol, 5 mol %). The mixture was stirred at this temperature overnight, then filtered through silica, evaporated and purified by column chromatography (hexane/ethyl acetate 2:1) to yield a light yellow solid (52 mg, 88 %).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.04 (s, 3H), 4.06 (s, 3H), 4.07 (s, 3H), 4.10 (s, 3H), 5.27 (s, 2H), 7.15 (s, 1H), 7.21 (s, 1H), 7.32-7.59 (m, 7H), 9.10 (s, 1H) ppm.

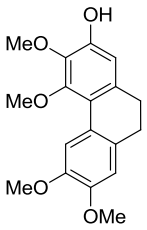
^{13}C NMR (101 MHz, $CDCl_3$) δ = 55.9, 56.0, 60.7, 61.5, 70.8, 107.2, 107.8, 108.2, 119.0, 124.5, 124.9, 126.2, 127.3, 127.5, 128.1, 128.8, 129.5, 137.0, 143.1, 148.3, 148.9, 151.1, 151.8 ppm.

HRMS *calcd.* for $C_{25}H_{24}O_5Na$: 427.151595; *found* 427.151595.

IR $\tilde{\nu}$ = 701, 712, 755, 777, 800, 833, 847, 861, 882, 918, 945, 974, 992, 1030, 1050, 1073, 1117, 1160, 1206, 1242, 1266, 1292, 1353, 1377, 1401, 1421, 1431, 1453, 1464, 1502, 1519, 1571, 1598, 1615, 2831, 2934 cm^{-1}.

Compound **24**

Phenanthrene **23** (120 mg, 0.30 mmol) and Pd/C (10 %) (64 mg, 0.06 mmol) were stirred in MeOH (3 mL) under an atmosphere of 30 bar H_2 for 2 days. After filtration through silica the crude was purified by column chromatography (hexane/ethyl acetate 2:1) to yield a light green solid (78 mg, 82 %).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.70 (s, 4H), 3.76 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 3.98 (s, 3H), 5.68 – 5.71 (m, 1H), 6.64 (s, 1H), 6.74 (s, 1H), 7.95 (s, 1H) ppm.

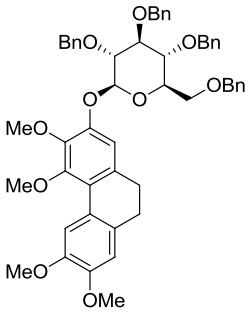
^{13}C NMR (101 MHz, $CDCl_3$) δ = 29.4, 30.4, 55.9, 56.2, 60.3, 61.4, 110.4, 111.0, 111.1, 120.4, 125.2, 130.6, 135.1, 139.2, 147.3, 147.4, 147.8, 150.6 ppm.

HRMS *calcd.* for $C_{18}H_{20}O_5Na$: 339.120295; *found* 339.120600.

IR $\tilde{\nu}$ = 682, 736, 782, 828, 146, 875, 889, 951, 963, 976, 1004, 1021, 1040, 1067, 1112, 1174, 1206, 1223, 1256, 1278, 1304, 1324, 1353, 1399, 1442, 1464, 1484, 1513 1589, 1611, 2840, 2931, 3005, 3238, 3414 cm^{-1}.

Compound **26**

A solution of **24** (50 mg, 0.16 mmol) and monosaccharide **25** (216 mg, 0.32 mmol) in dry CH_2Cl_2 (3 mL) was treated with freshly activated 4 Å molecular sieves and 0.5 mL of a 0.3 M solution of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at -20 °C. After stirring for 2 h at this temperature, $NaHCO_3$ (200 mg) was added and the mixture was stirred a few more minutes. After diluting with CH_2Cl_2 (10 mL) and filtration, the organic layer was washed with water, dried with Na_2SO_4 and evaporated. The crude was purified by column chromatography (hexane/ethyl acetate 3:1) to afford compound **26** as a white solid (125 mg, 93 %).



^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.49-2.79 (m, 4H), 3.61-3.86 (m, 9H), 3.86- 4.00 (m, 9H), 4.63-4.48 (m, 3H), 4.73-5.08 (m, 5H), 5.14-5.29 (m, 1H), 6.74 (s, 1H), 6.85 (s, 1H), 7.14-7.43 (m, 20H), 8.01 (s, 1H) ppm.

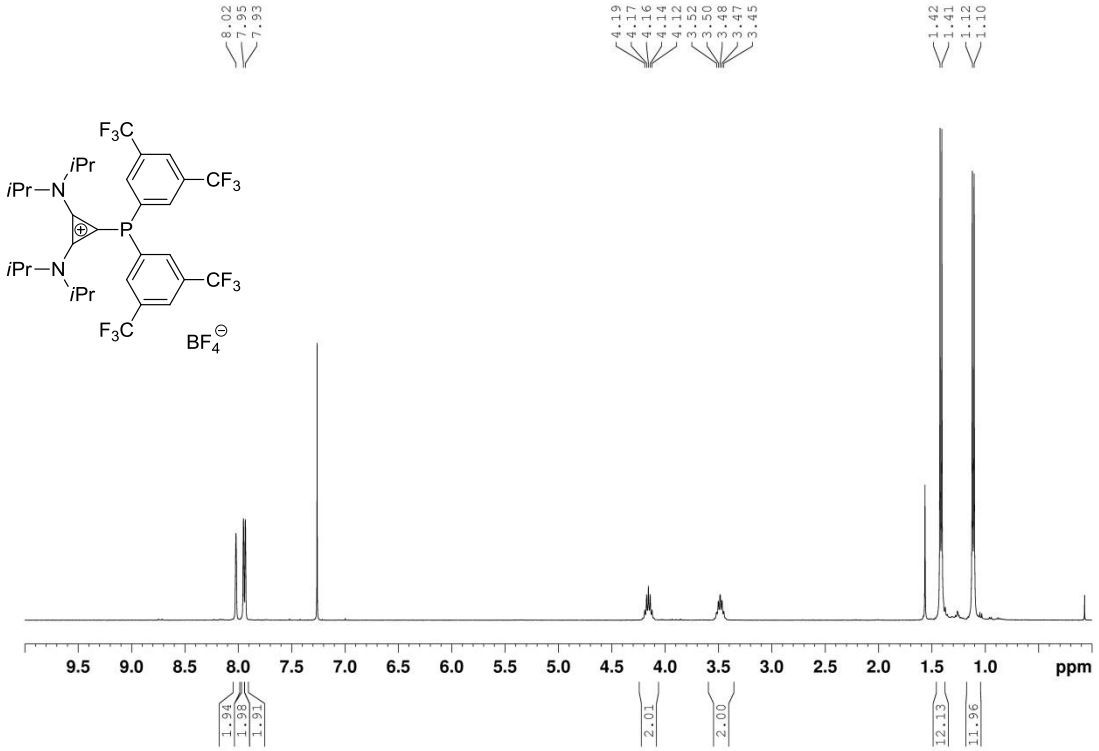
^{13}C NMR (75 MHz, $CDCl_3$) δ = 29.4, 30.5, 55.9, 56.2, 60.7, 61.4, 69.2, 73.6, 74.9, 75.1, 75.3, 75.8, 77.9, 82.1, 84.8, 102.5, 111.0, 111.4, 112.5, 122.9, 125.04, 127.7, 127.7, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.1, 128.4, 128.4, 128.4, 128.5, 128.5, 130.9, 134.5, 138.2, 138.2, 138.5, 138.7, 132.7, 147.3, 147.7, 149.5, 151.6 ppm.

HRMS *calcd*. for $C_{52}H_{54}O_{10}Na$: 861.360921; *found* 861.359548.

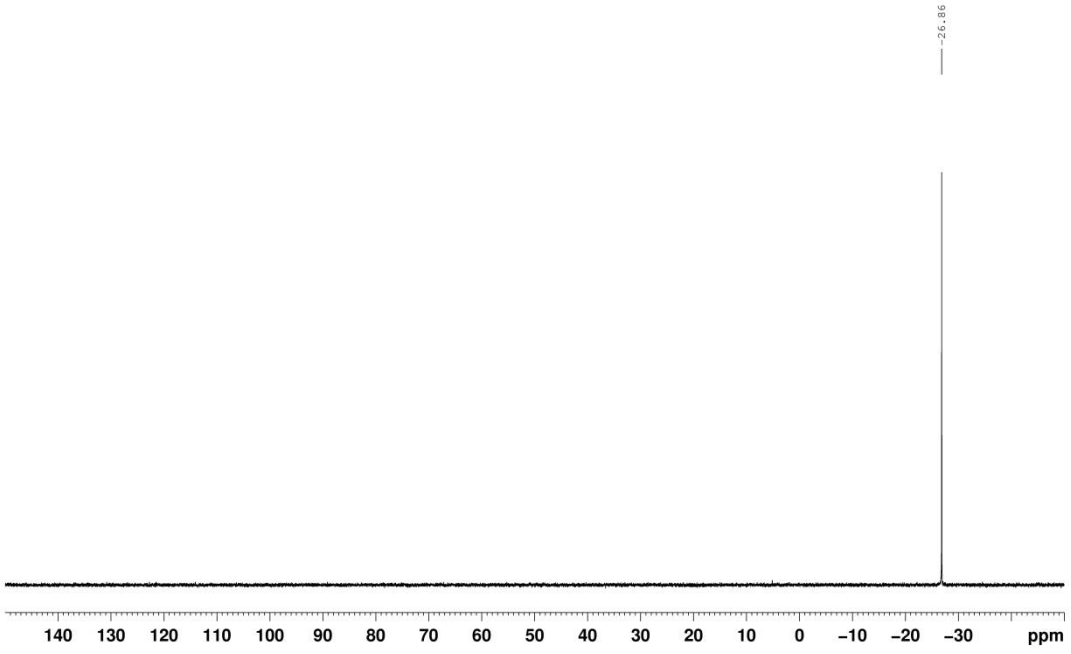
IR $\tilde{\nu}$ = 696, 735, 784, 829, 853, 872, 910, 1007, 1028, 1065, 1188, 1216, 1245, 1263, 1307, 1324, 1342, 1358, 1413, 1453, 1488, 1516, 1608, 1695, 1729, 2932, 3031, 3241, 3368 cm^{-1}.

NMR spectra

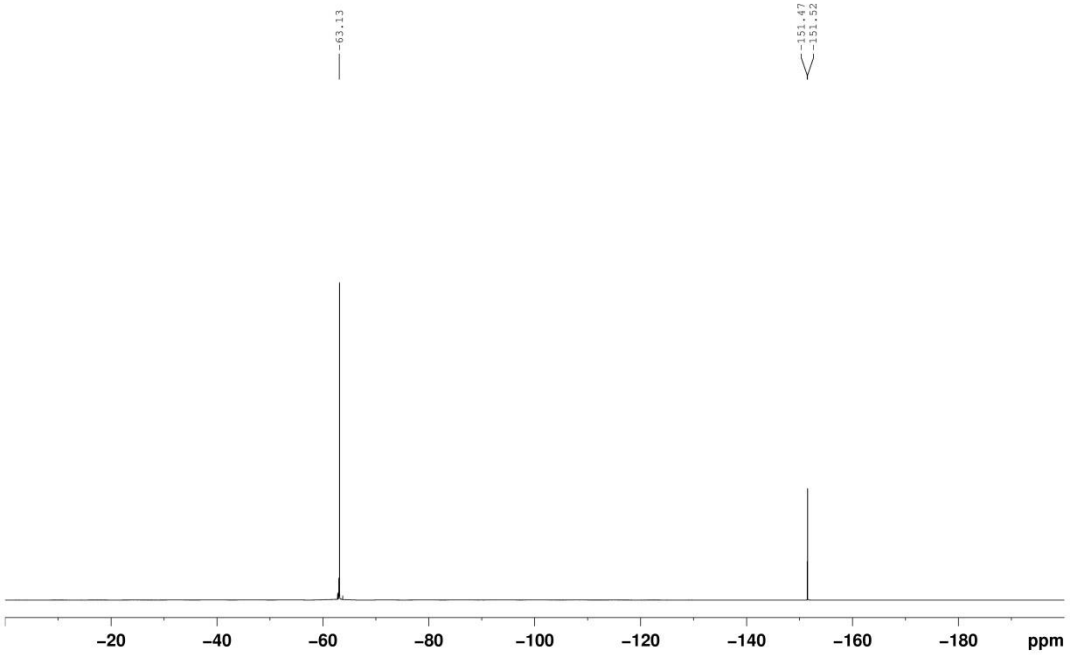
^{1}H NMR (400 MHz, $CDCl_3$) **1g**



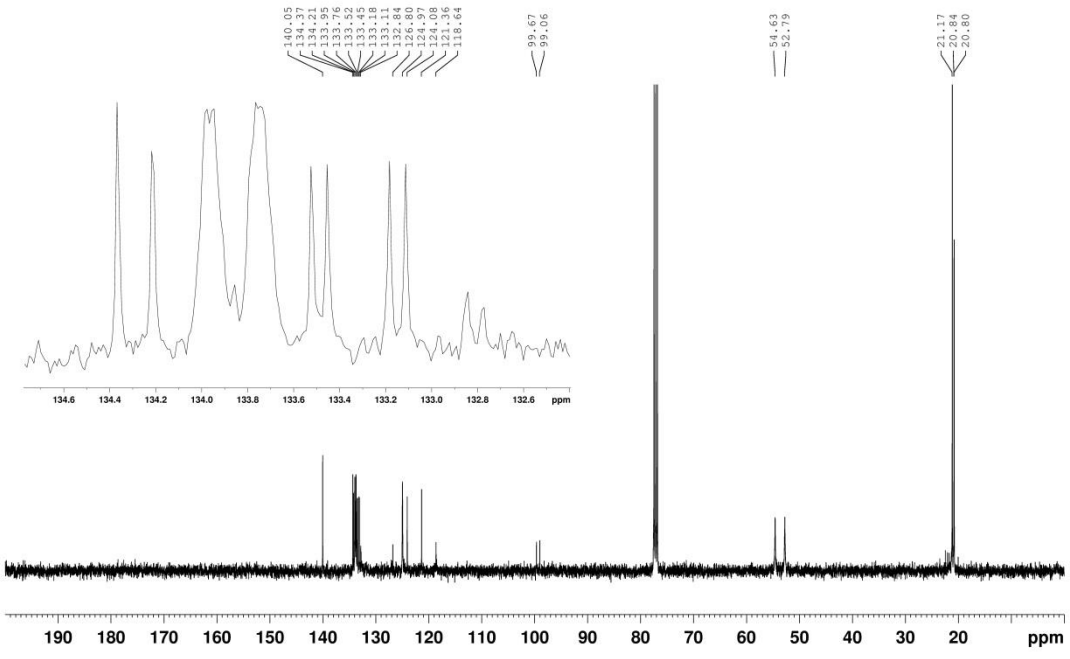
^{31}P NMR (162 MHz, $CDCl_3$) **1g**



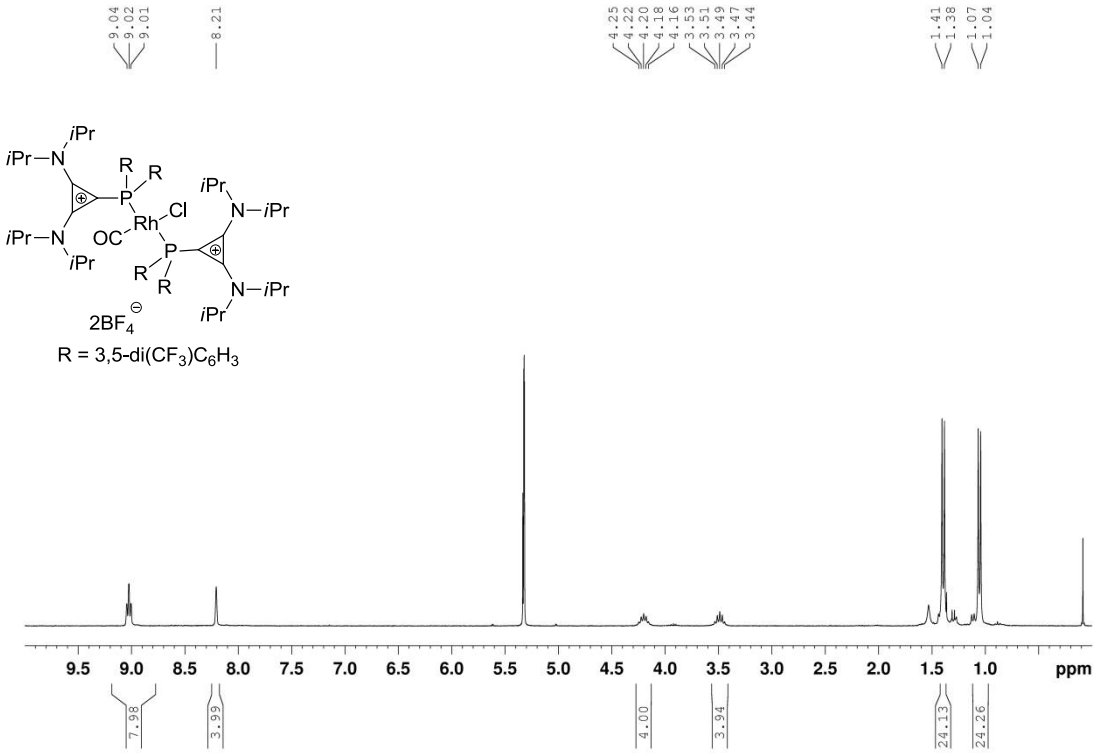
^{19}F NMR (282 MHz, CD_2Cl_2) **1g**



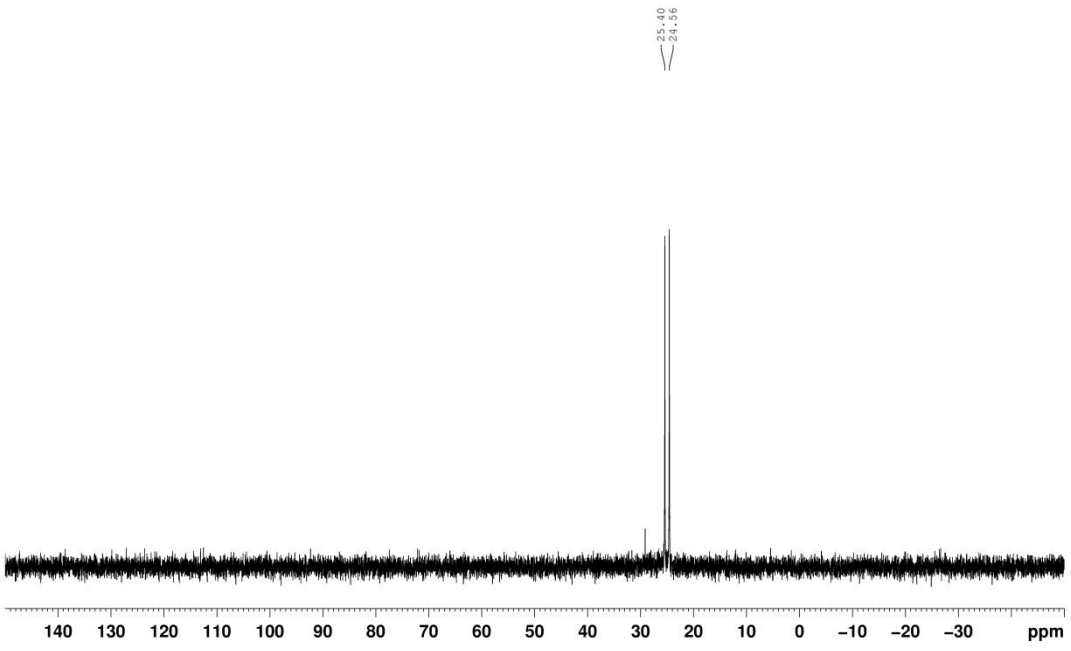
^{13}C NMR (101 MHz, $CDCl_3$) **1g**



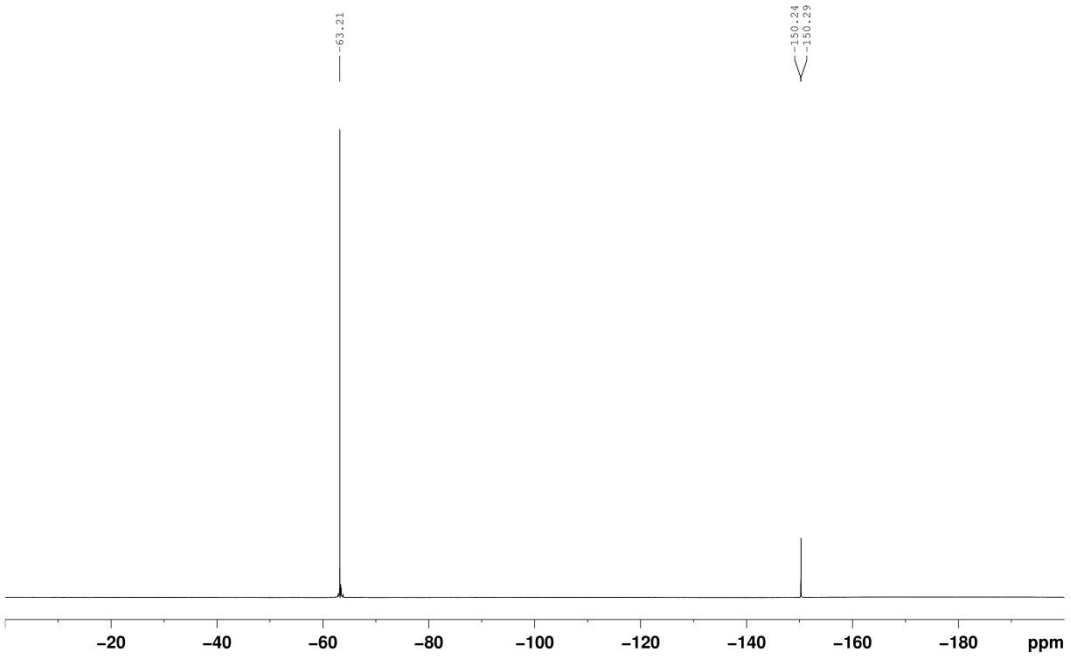
^{1}H NMR (400 MHz, $CDCl_3$) **3g**



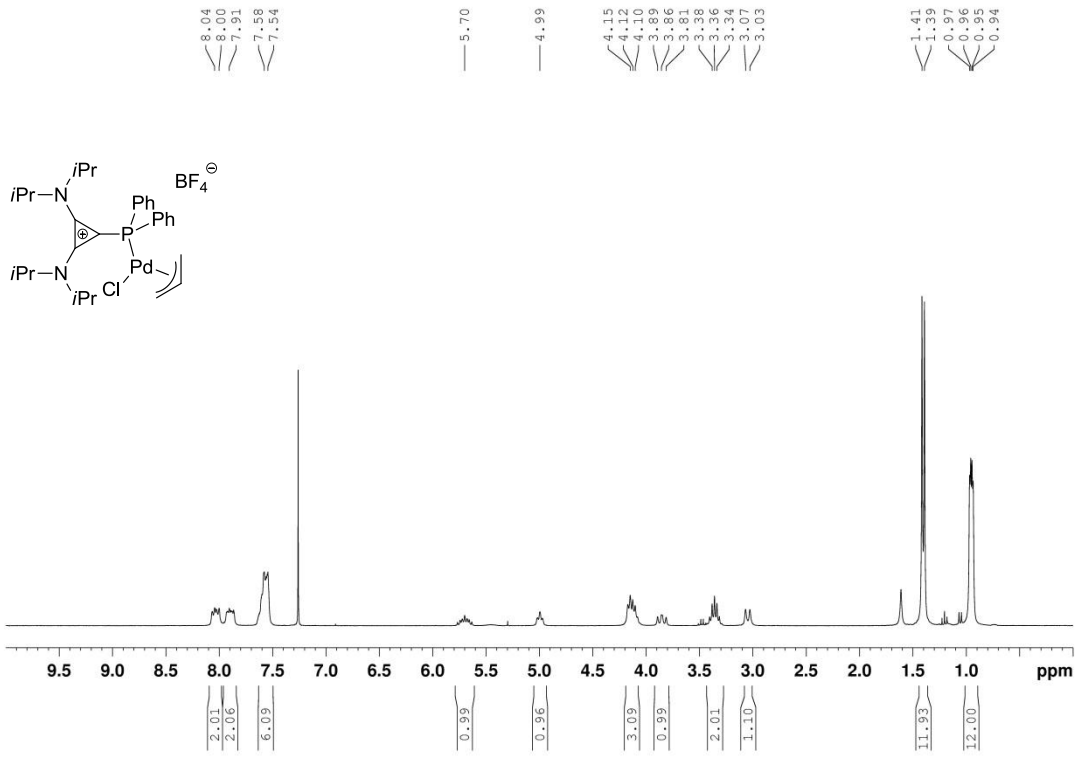
^{31}P NMR (162 MHz, CD_2Cl_2) **3g**



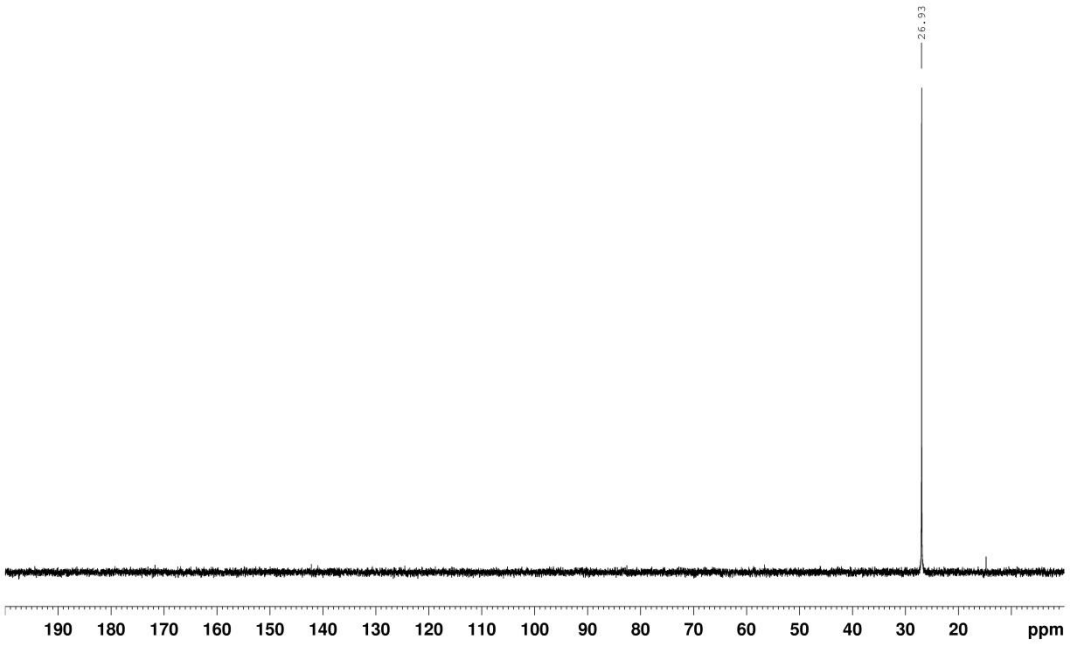
^{19}F NMR (282 MHz, CD_2Cl_2) **3g**



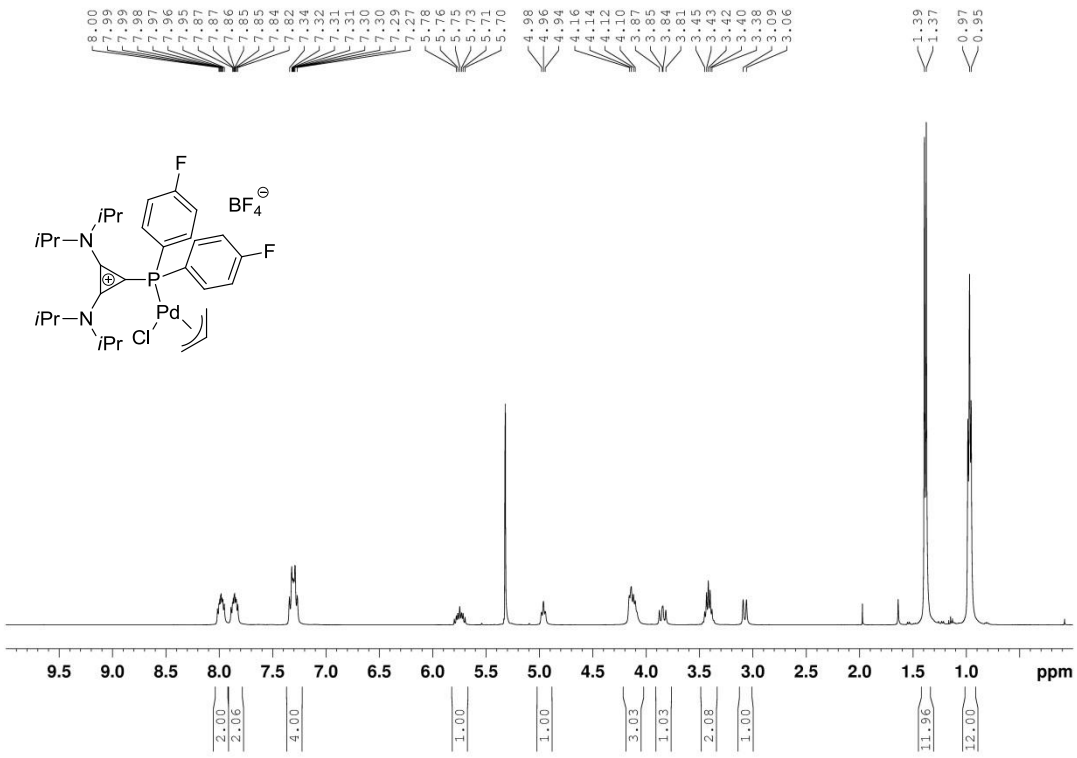
^{1}H NMR (300 MHz, $CDCl_3$) **4a**



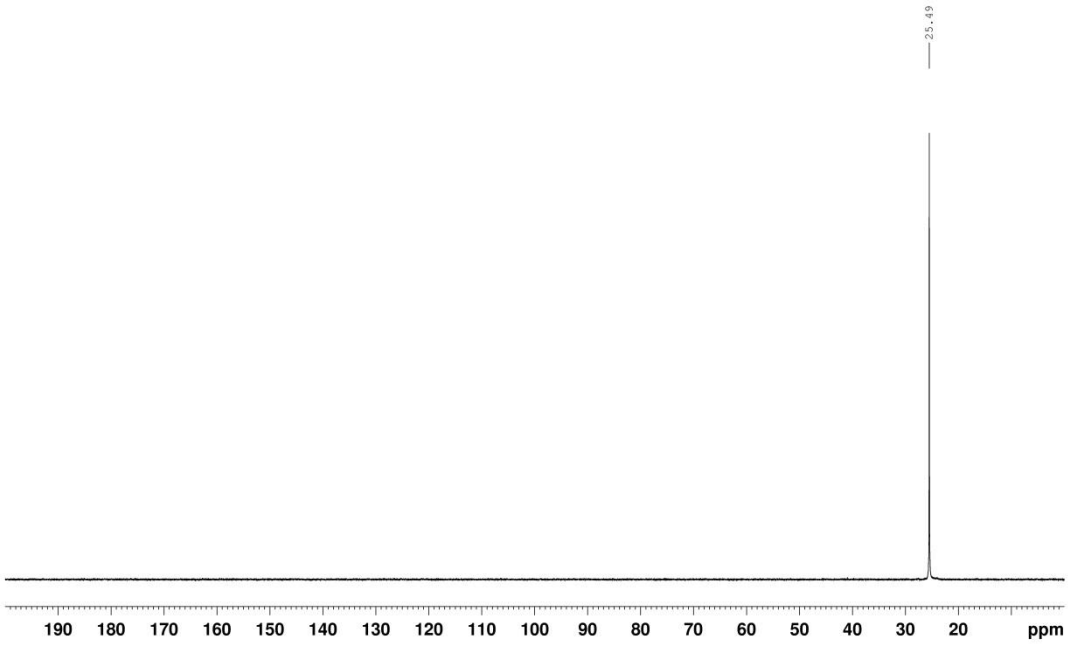
^{31}P NMR (121 MHz, $CDCl_3$) **4a**



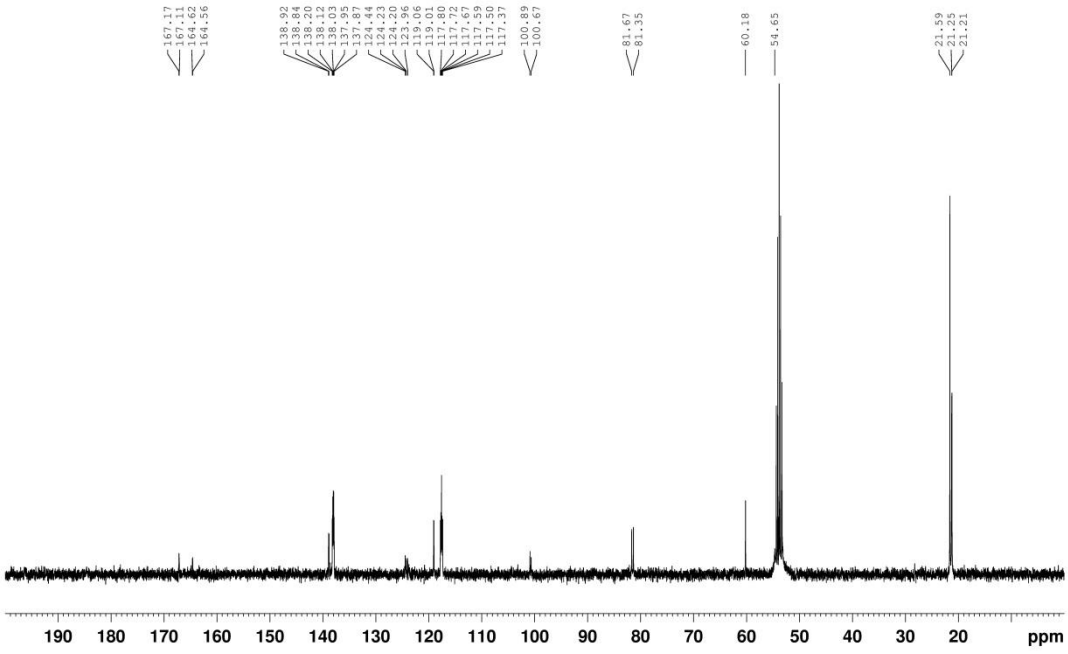
^{1}H NMR (400 MHz, CD_2Cl_2) **4f**



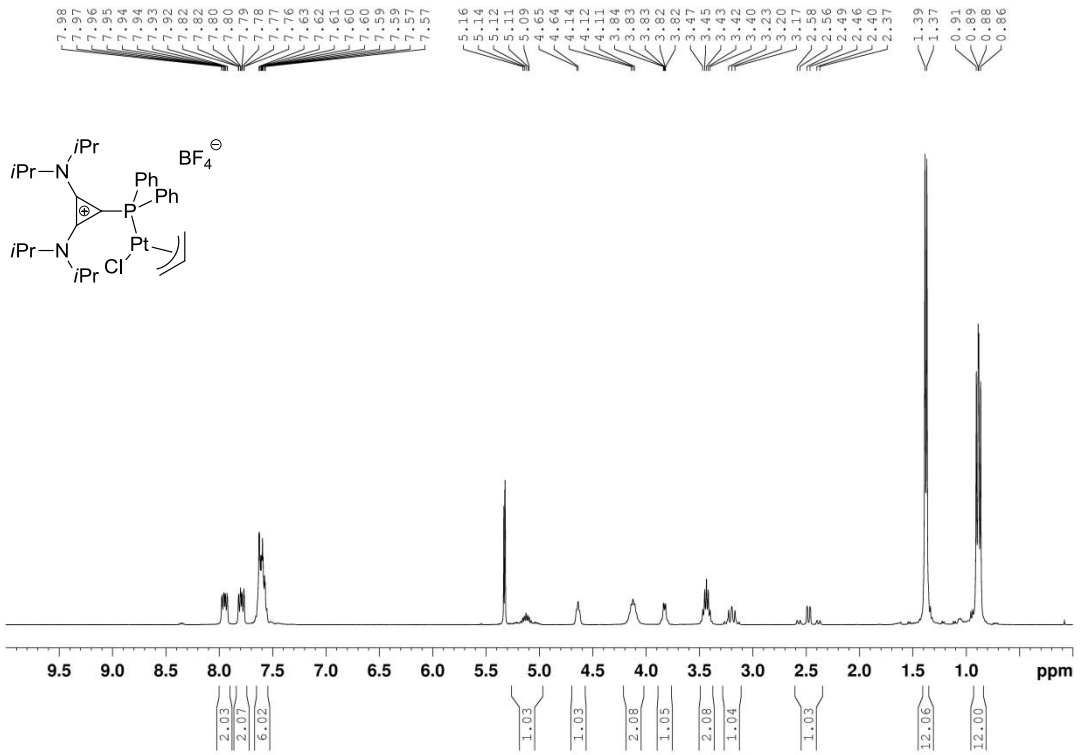
^{31}P NMR (161 MHz, CD_2Cl_2) **4f**



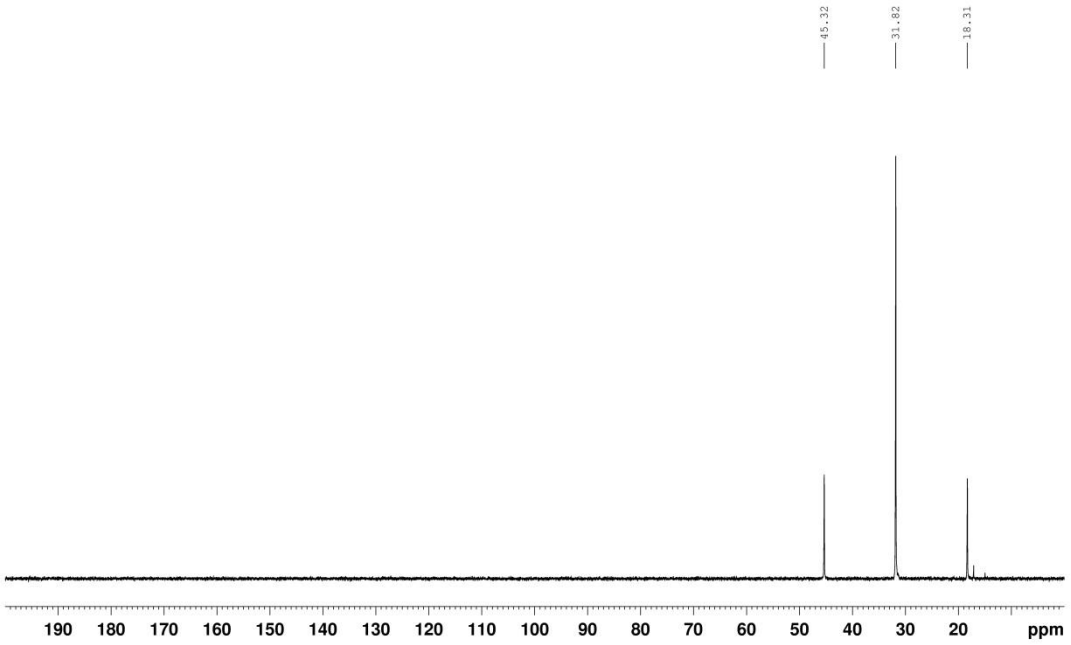
^{13}C NMR (100 MHz, CD_2Cl_2) **4f**



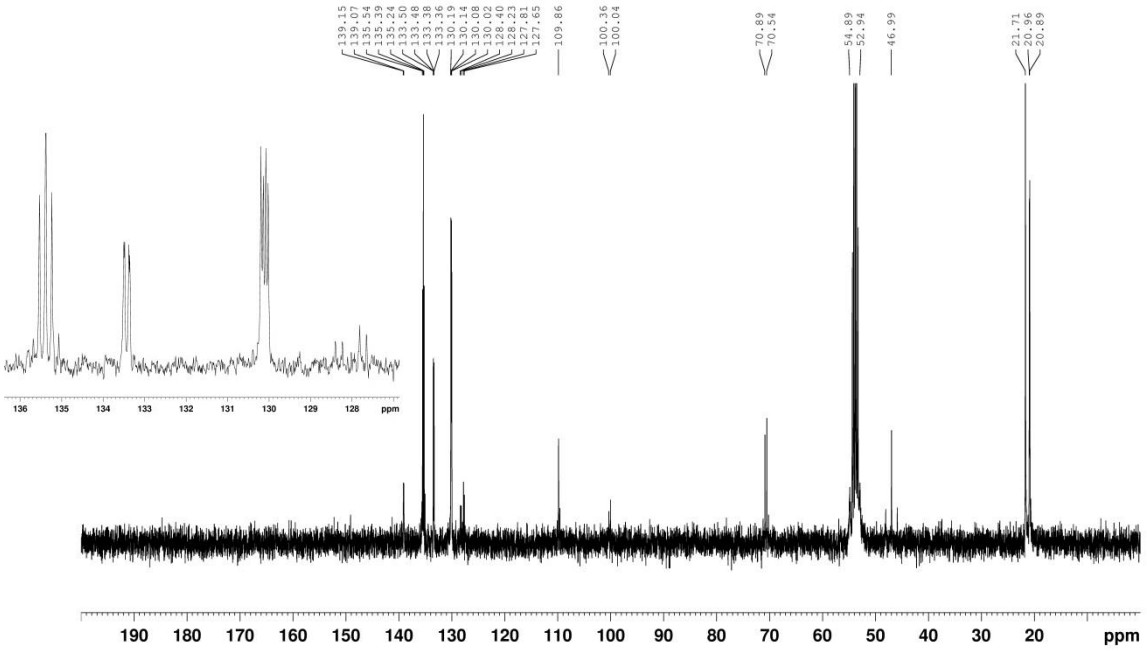
^{1}H NMR (400 MHz, CD_2Cl_2) **5a**



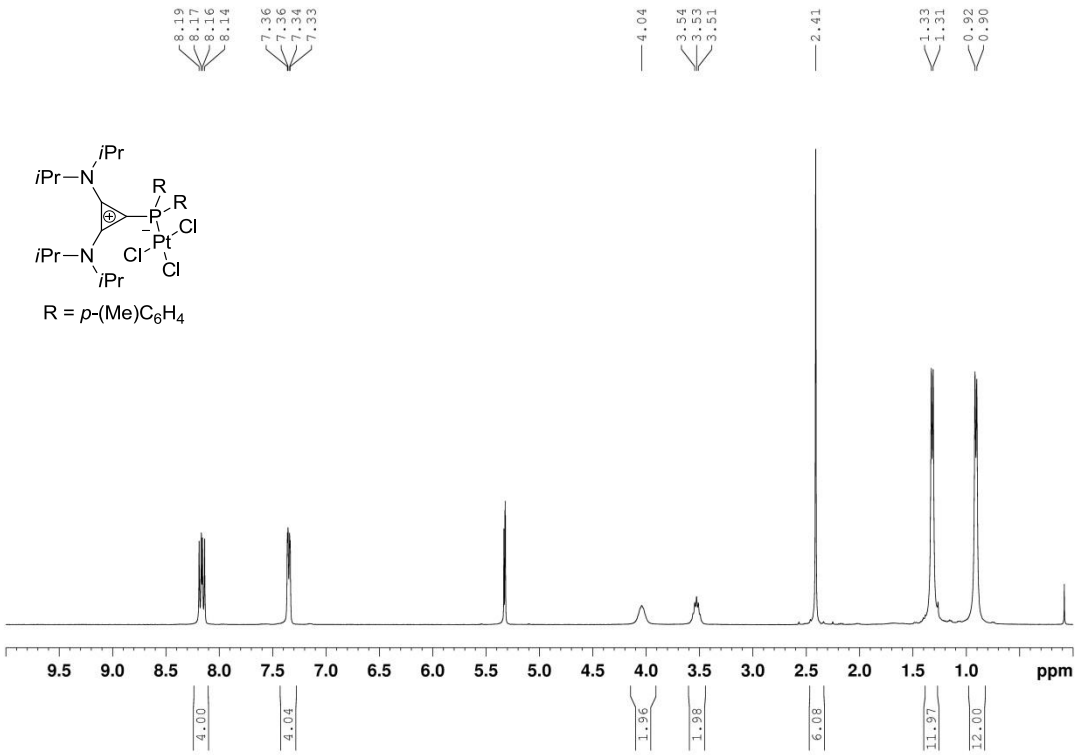
^{31}P NMR (161 MHz, CD_2Cl_2) **5a**



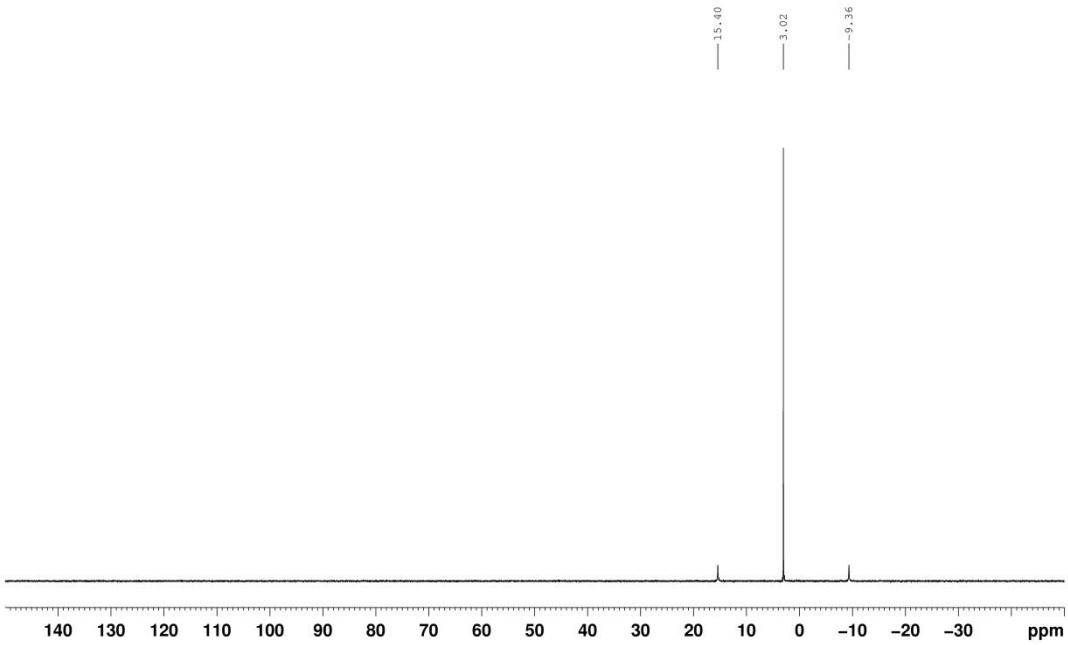
^{13}C NMR (100 MHz, CD_2Cl_2) **5a**



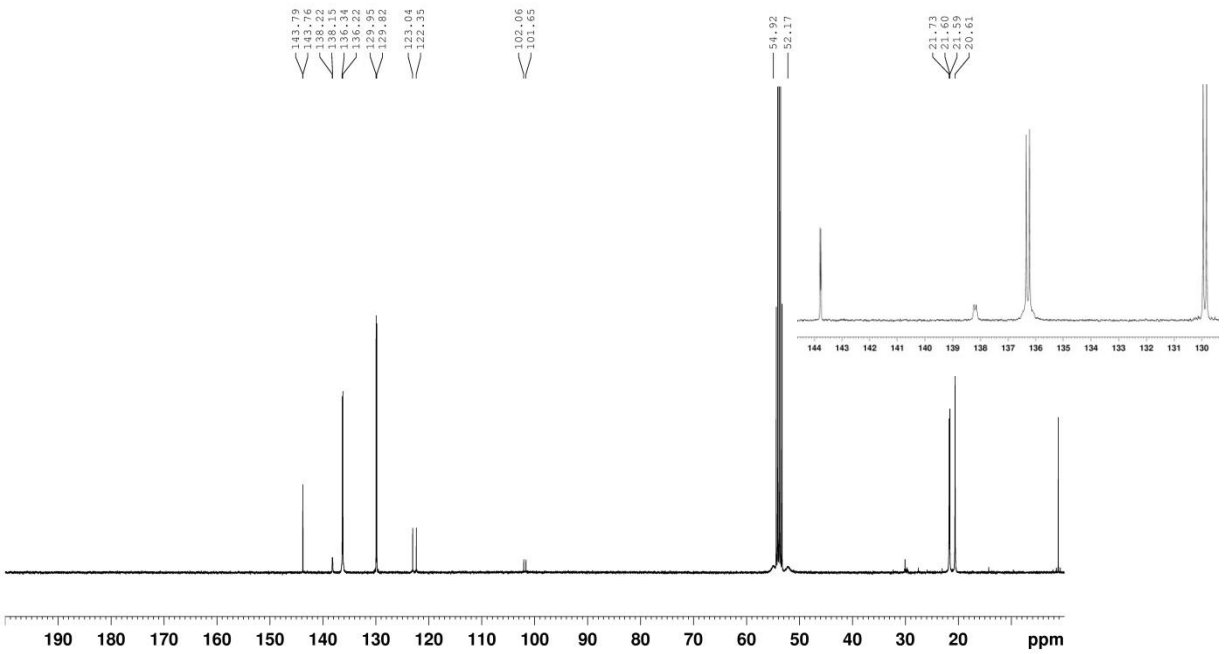
^{1}H NMR (400 MHz, CD_2Cl_2) **6d**



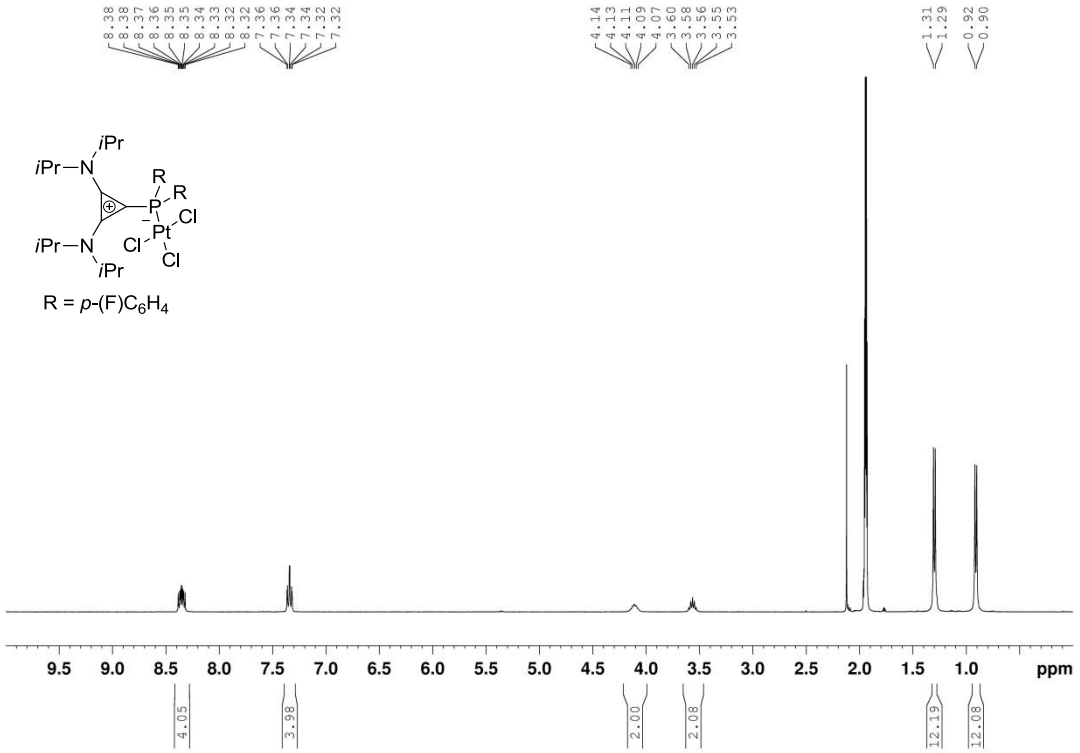
^{31}P NMR (162 MHz, CD_2Cl_2) **6d**



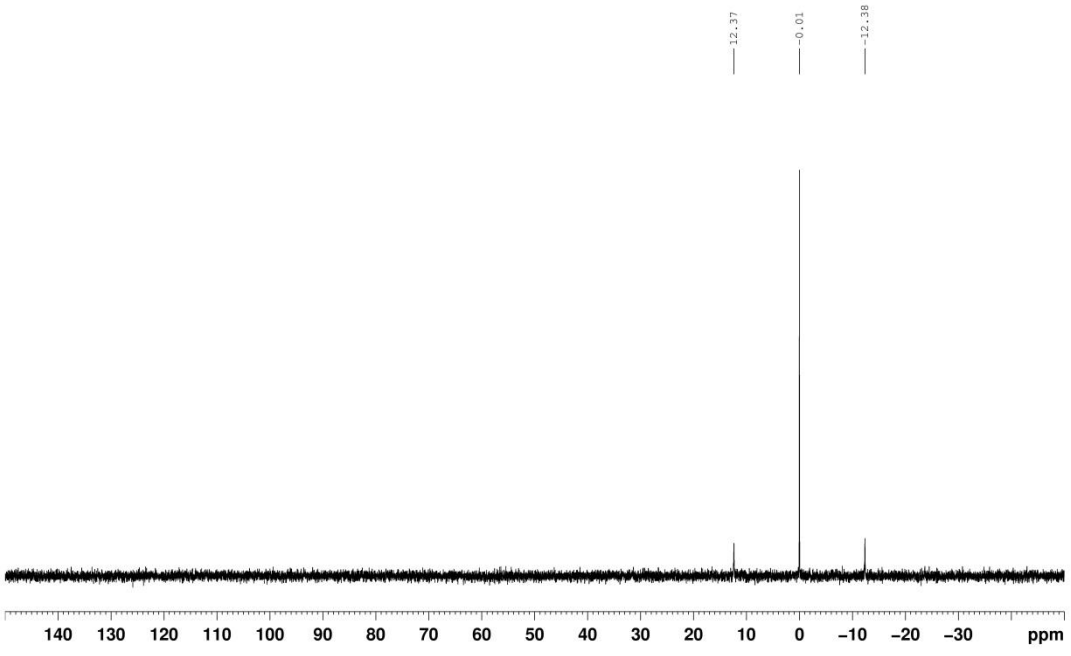
^{13}C NMR (101 MHz, CD_2Cl_2) **6d**



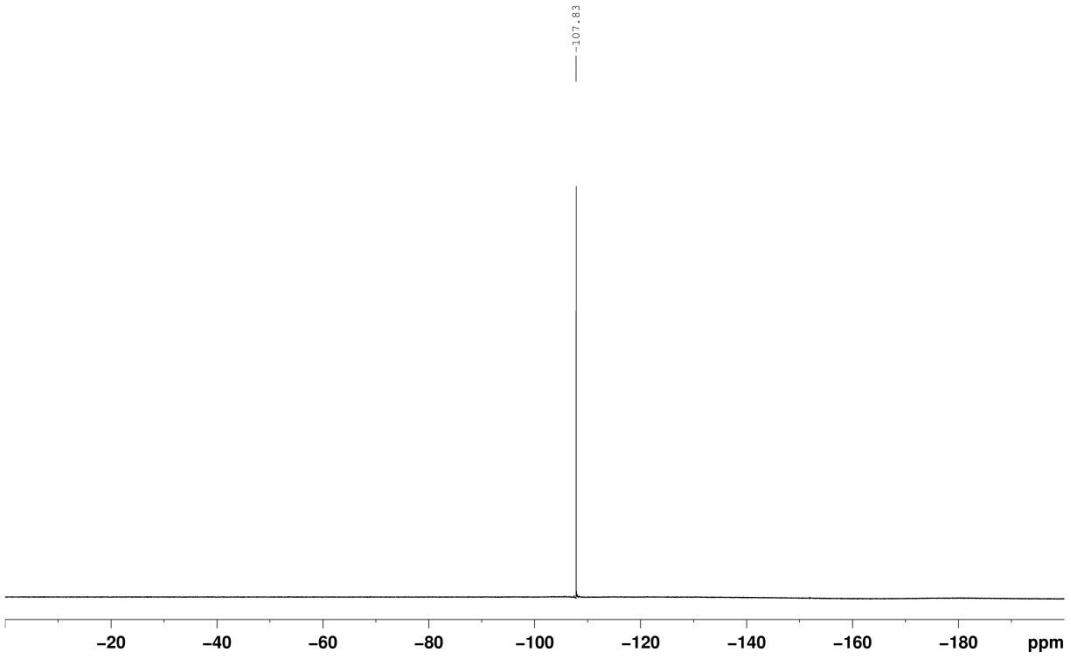
^{1}H NMR (400 MHz, CD_3CN) **6f**



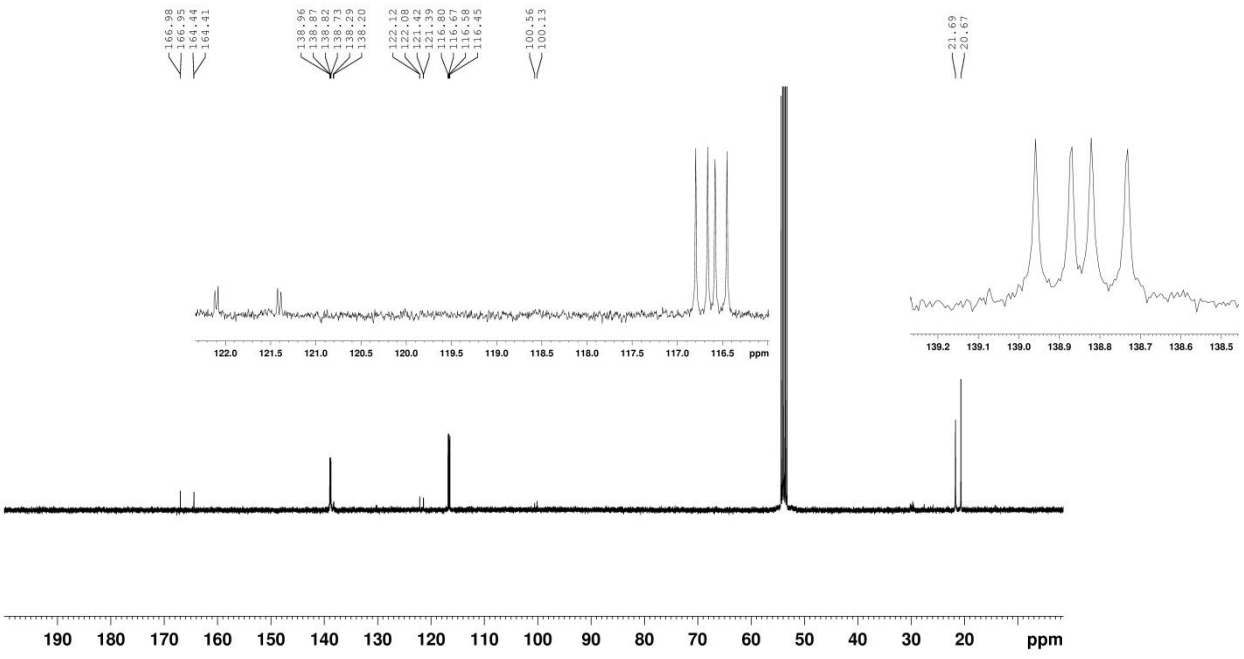
^{31}P NMR (162 MHz, CD_3CN) **6f**



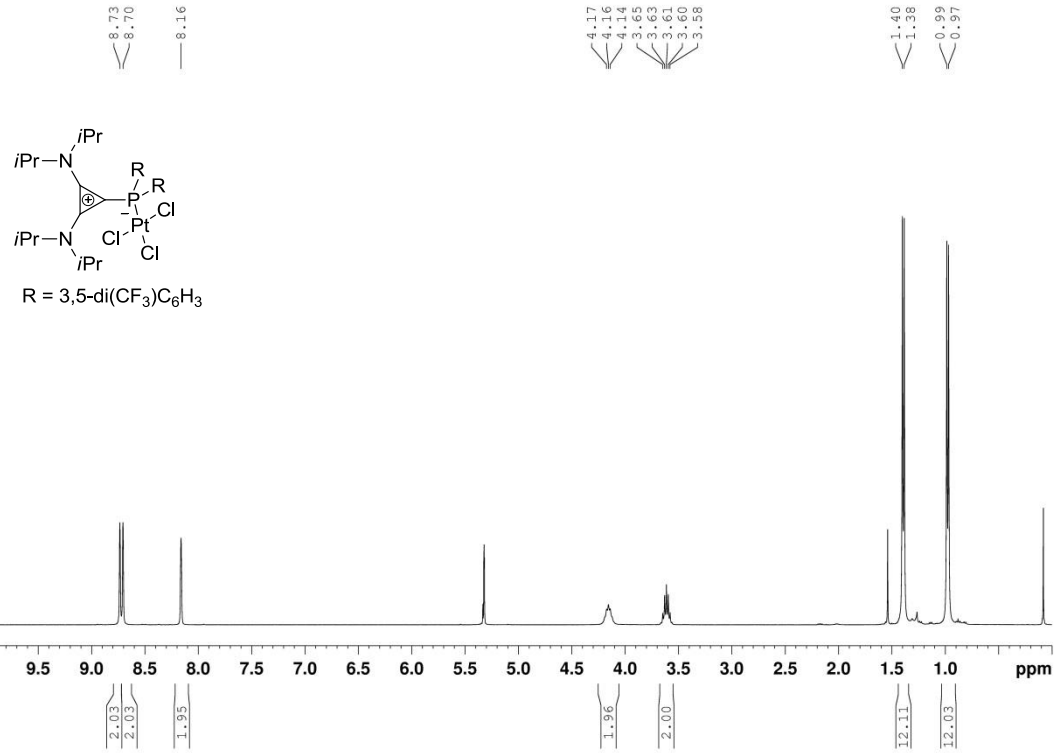
^{19}F NMR (282 MHz, CD_3CN) **6f**



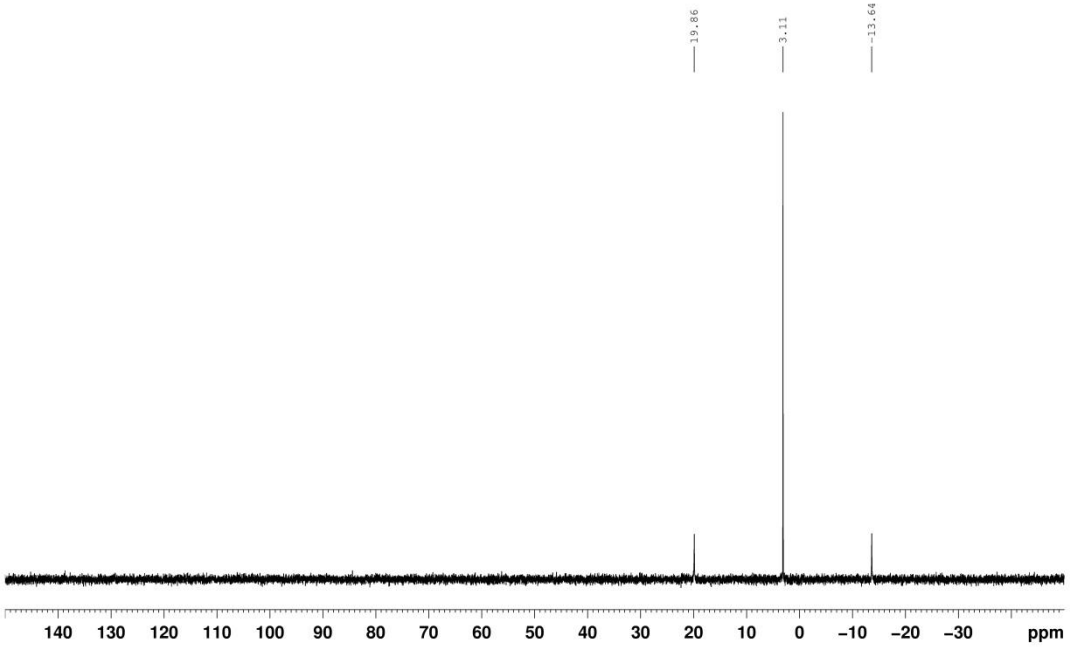
^{13}C NMR (101 MHz, CD_2Cl_2) **6f**



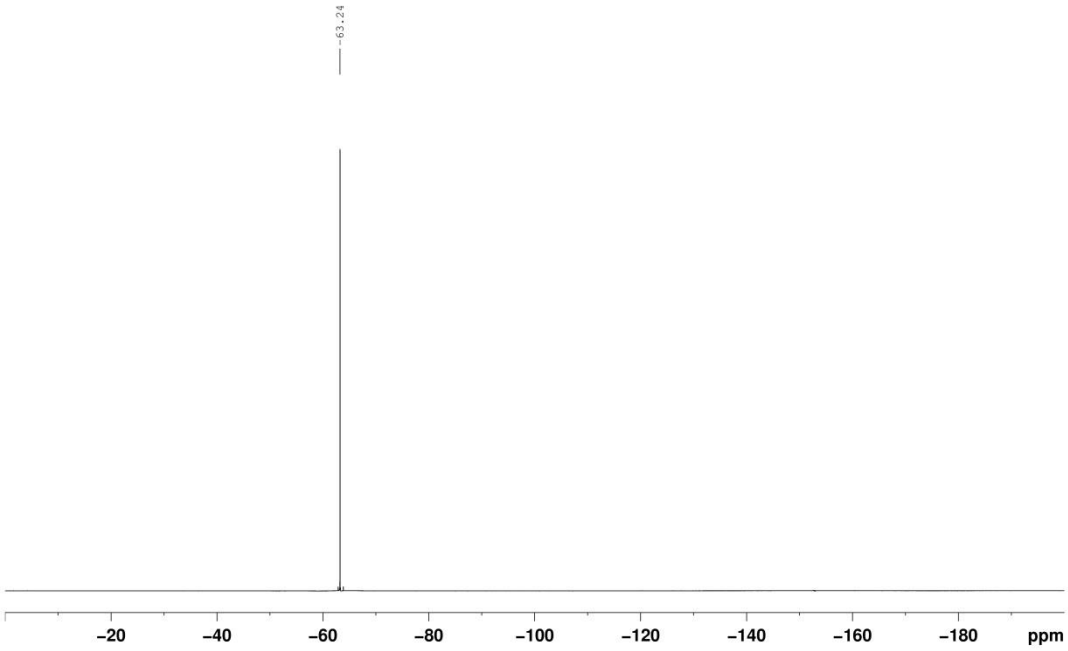
^{1}H NMR (400 MHz, CD_2Cl_2) **6g**



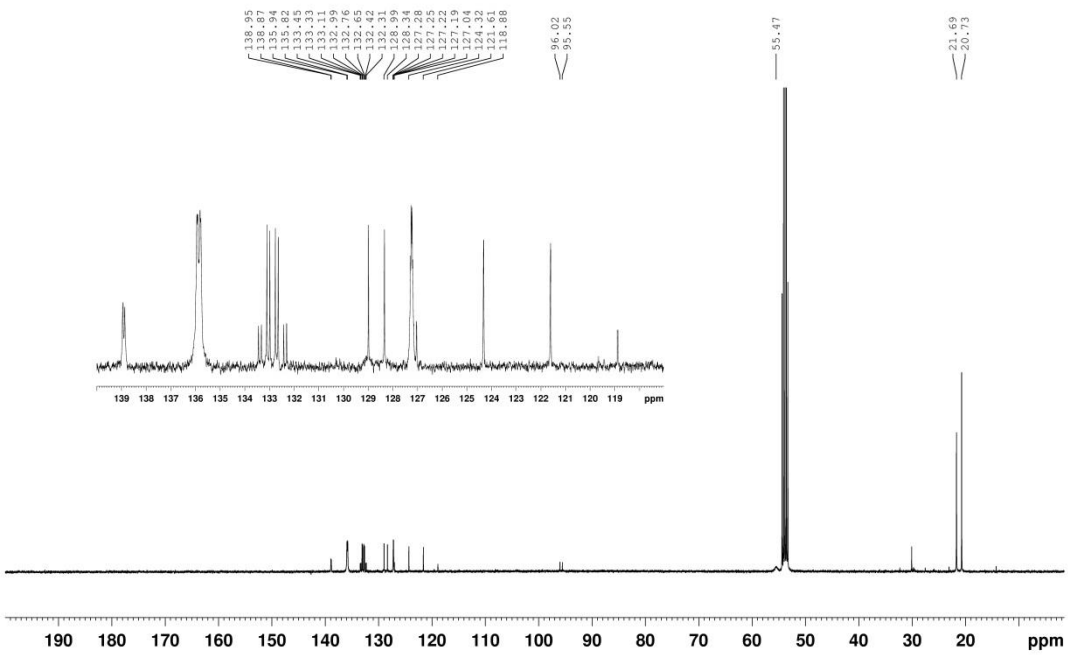
^{31}P NMR (121 MHz, CD_2Cl_2) **6g**



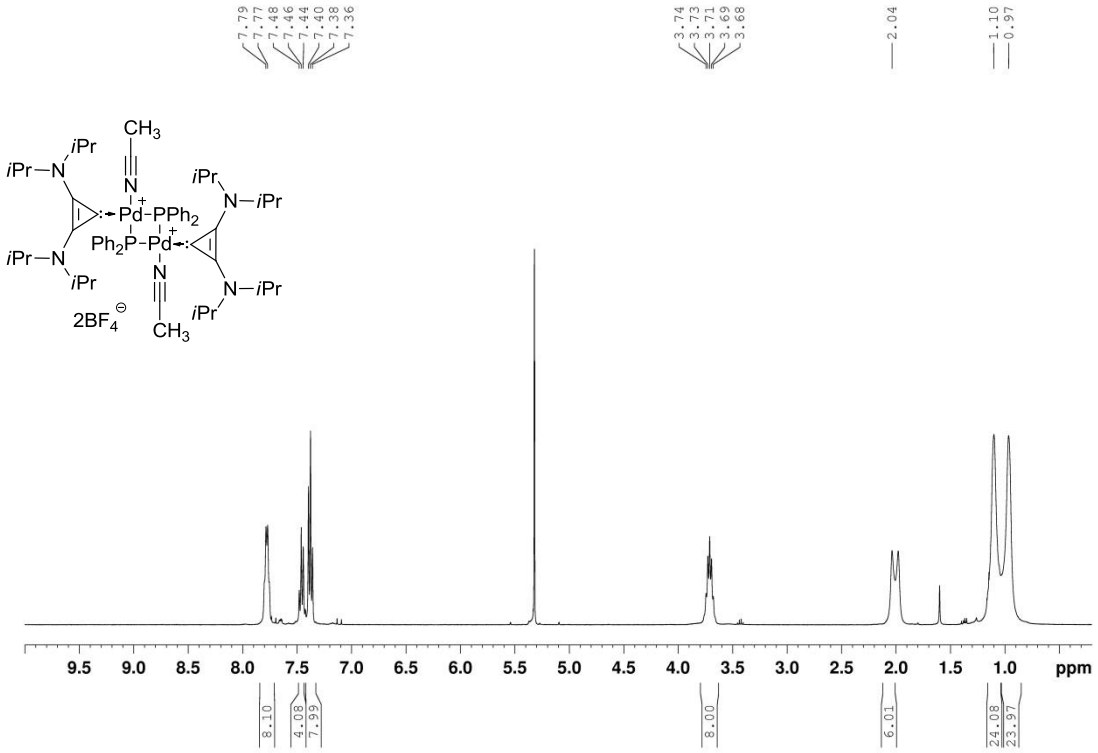
^{19}F NMR (282 MHz, CD_2Cl_2) **6g**



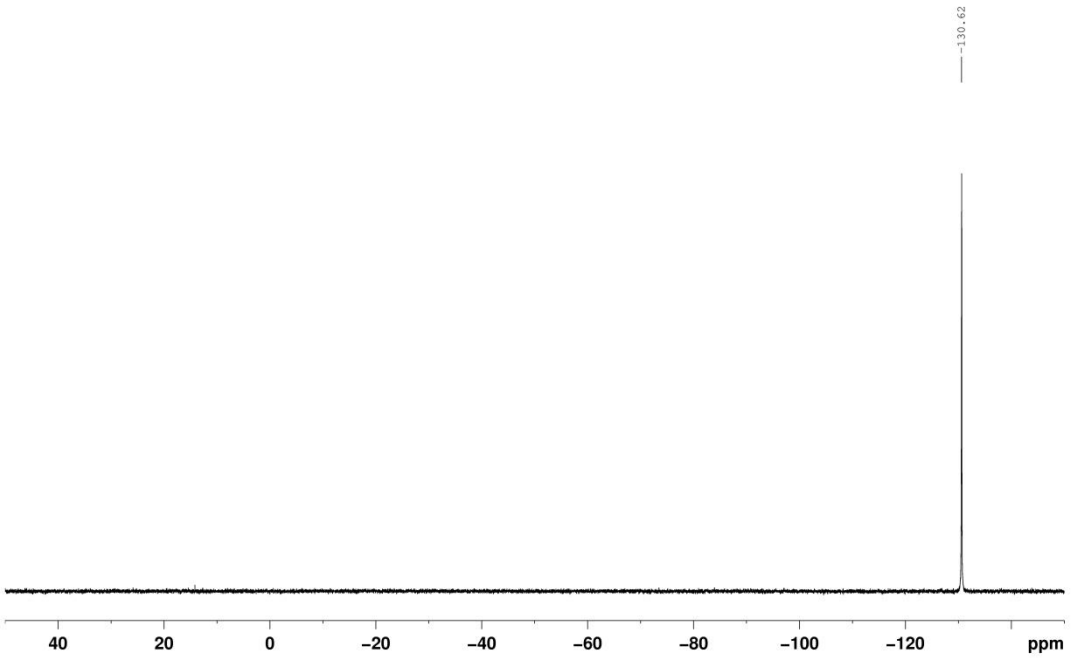
^{13}C NMR (101 MHz , CD_2Cl_2) **6g**



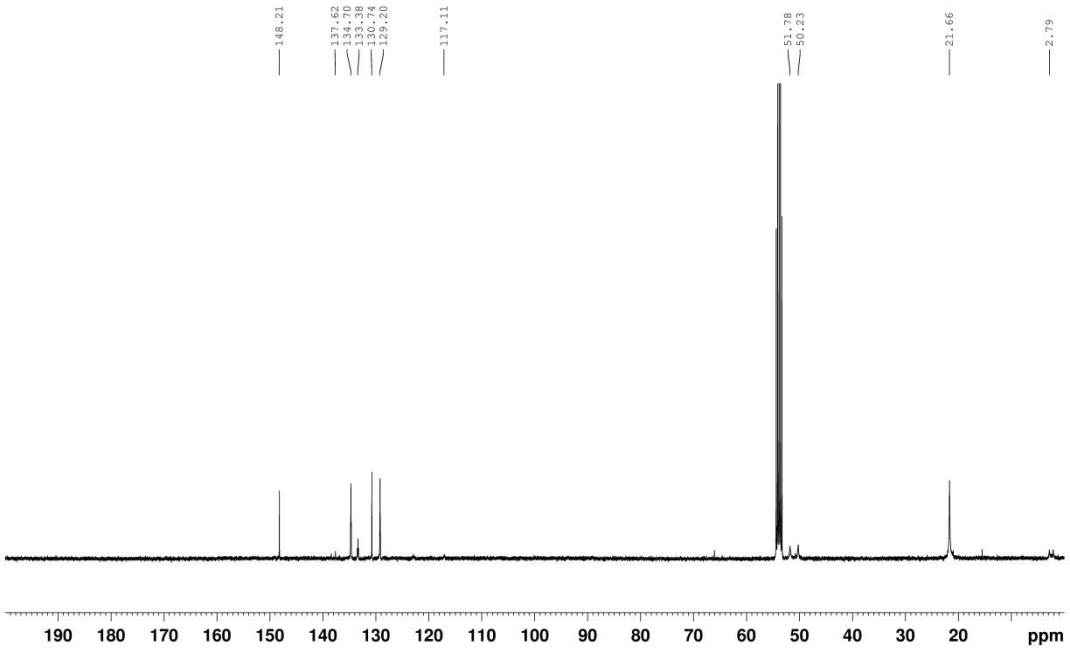
^{1}H NMR (400 MHz, CD_2Cl_2) **7a**



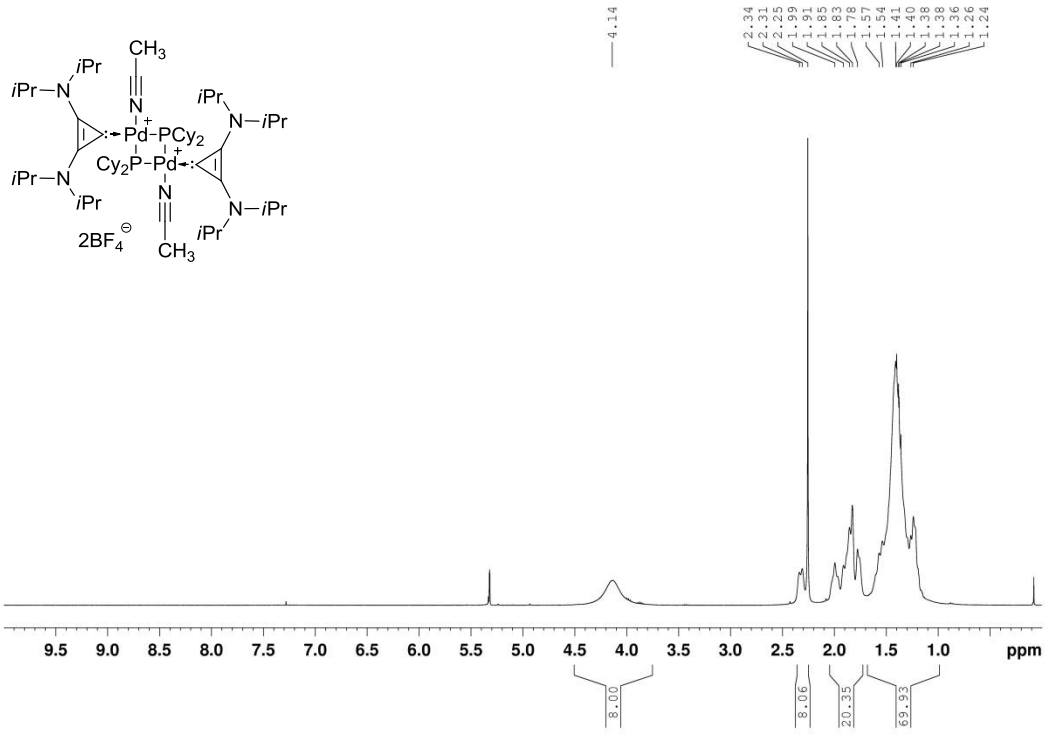
^{31}P NMR (162 MHz, CD_2Cl_2) **7a**



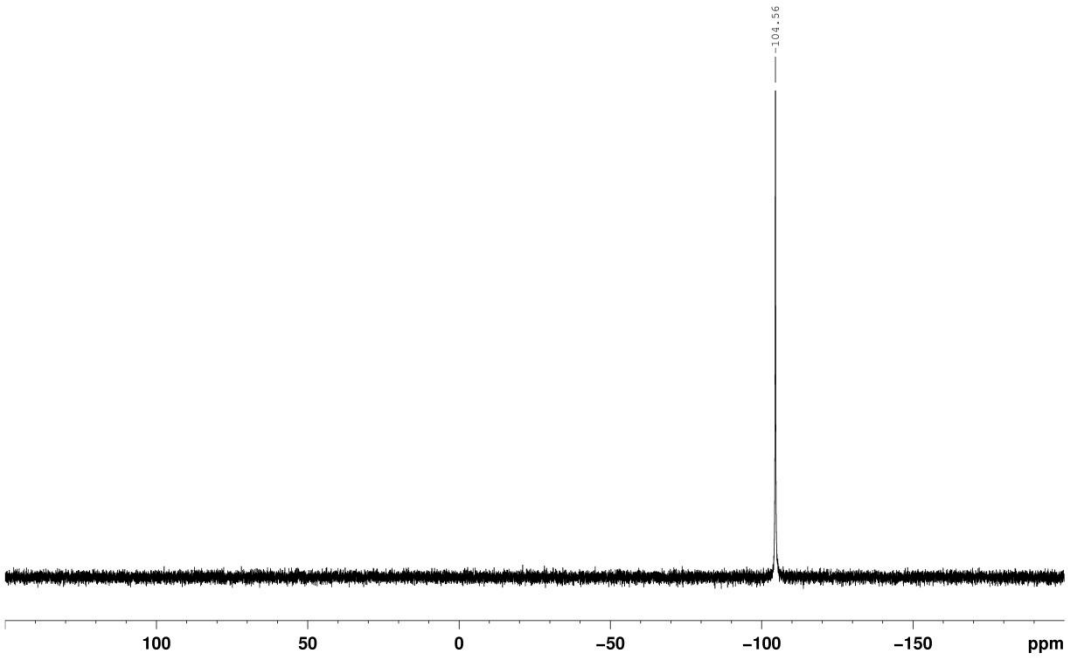
^{13}C NMR (101 MHz, CD_2Cl_2) **7a**



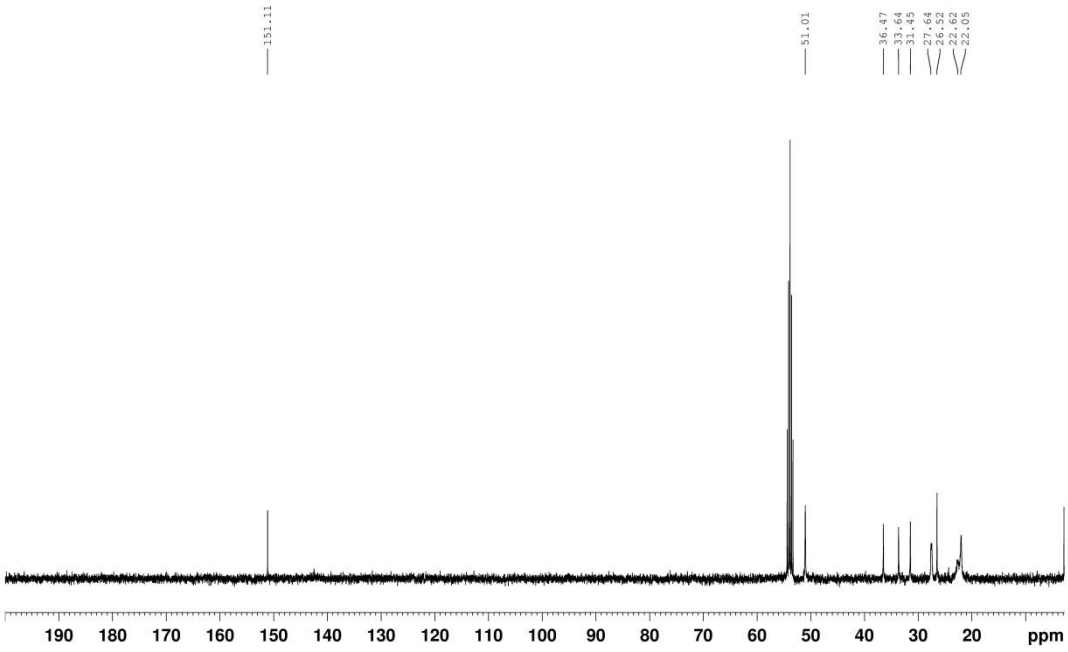
^{1}H NMR (400 MHz, CD_2Cl_2) **7b**



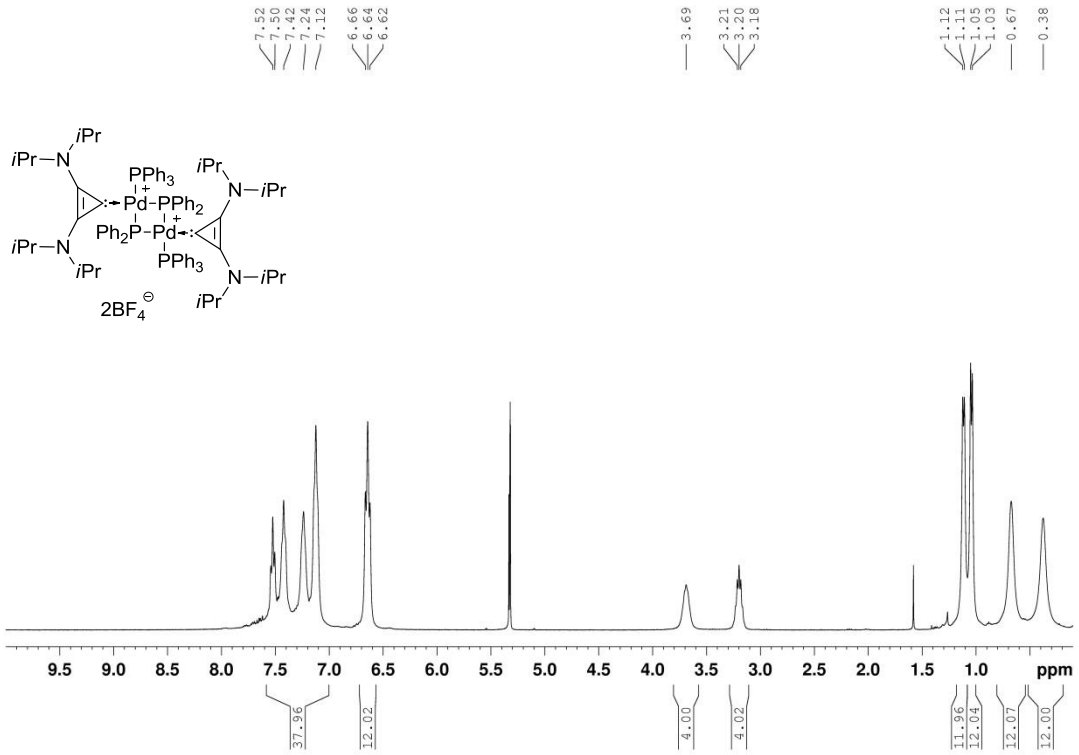
^{31}P NMR (162 MHz, CD_2Cl_2) **7b**



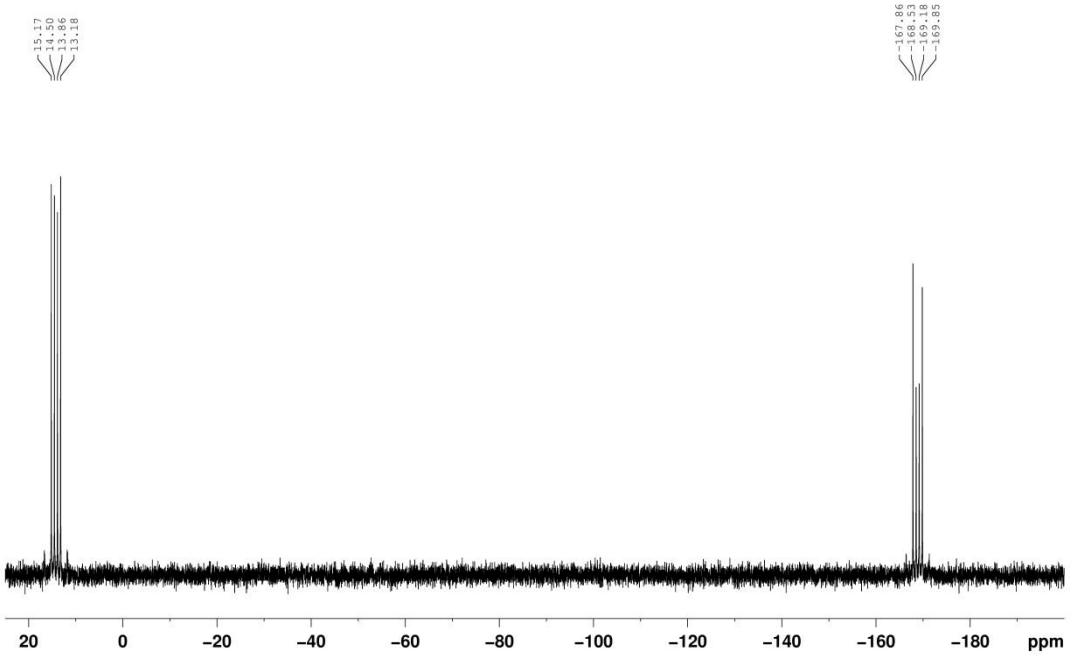
^{13}C NMR (101 MHz, CD_2Cl_2) **7b**



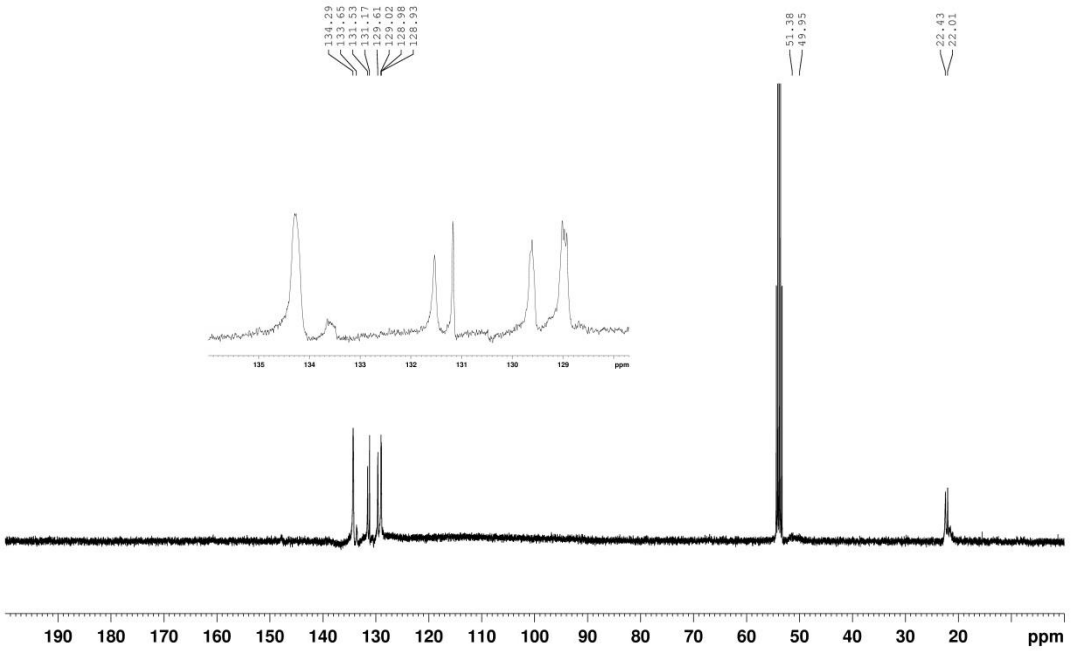
^{1}H NMR (400 MHz, CD_2Cl_2) **8a**



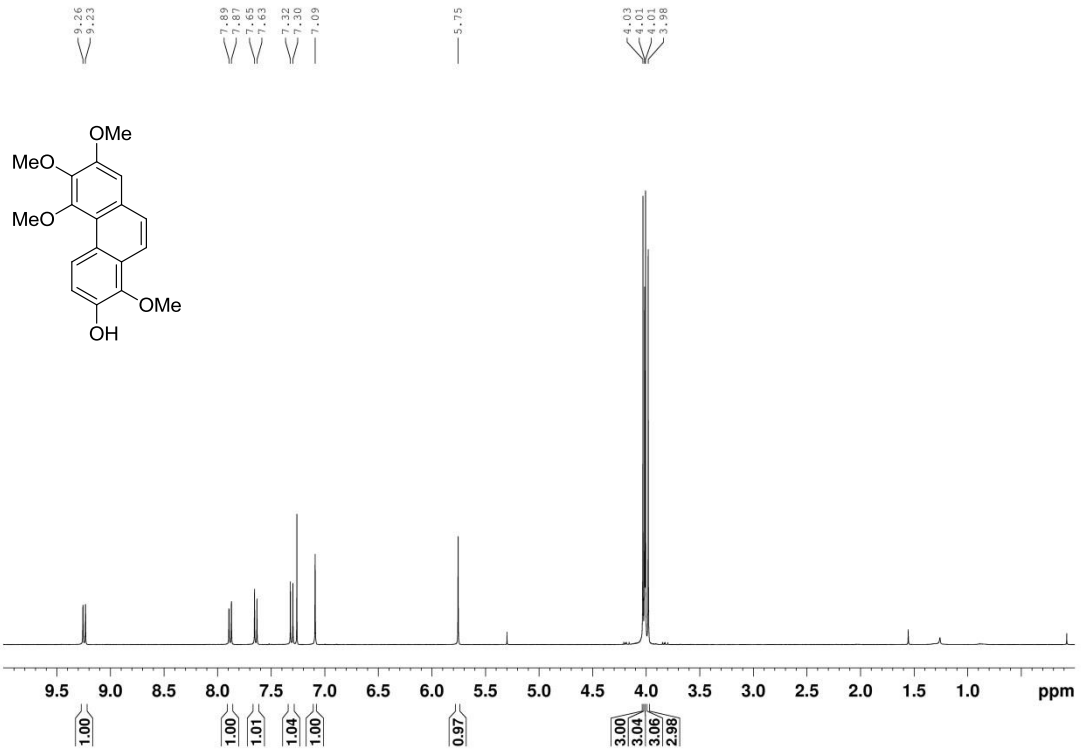
^{31}P NMR (162 MHz, CD_2Cl_2) **8a**



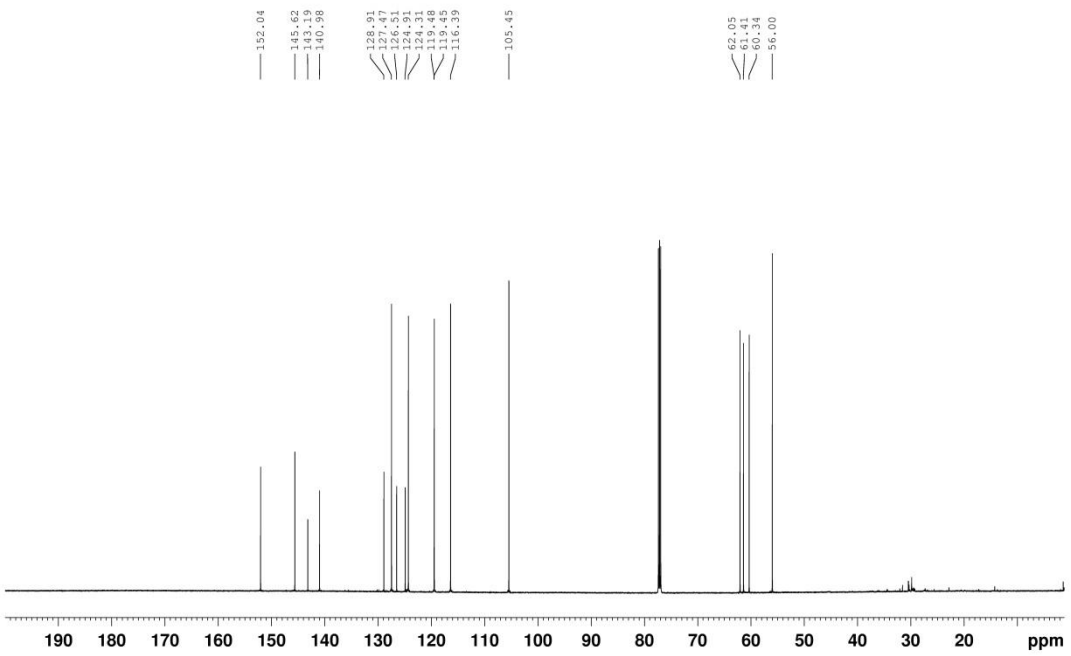
^{13}C NMR (101 MHz, CD_2Cl_2) **8a**



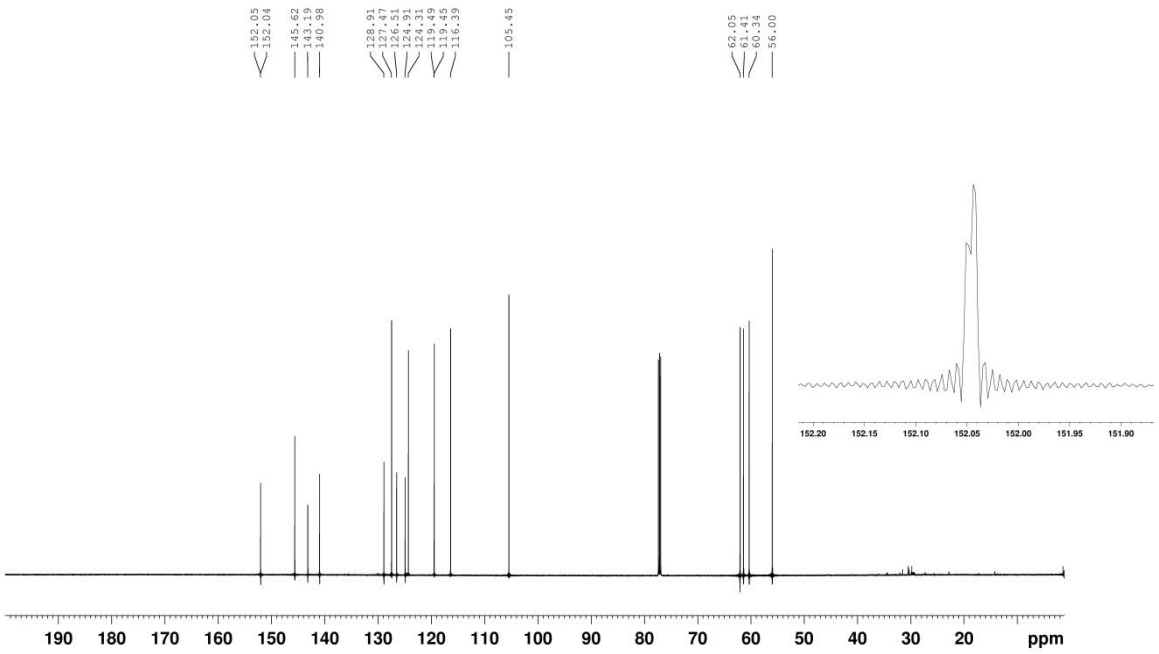
^{1}H NMR (400 MHz, $CDCl_3$) **11**



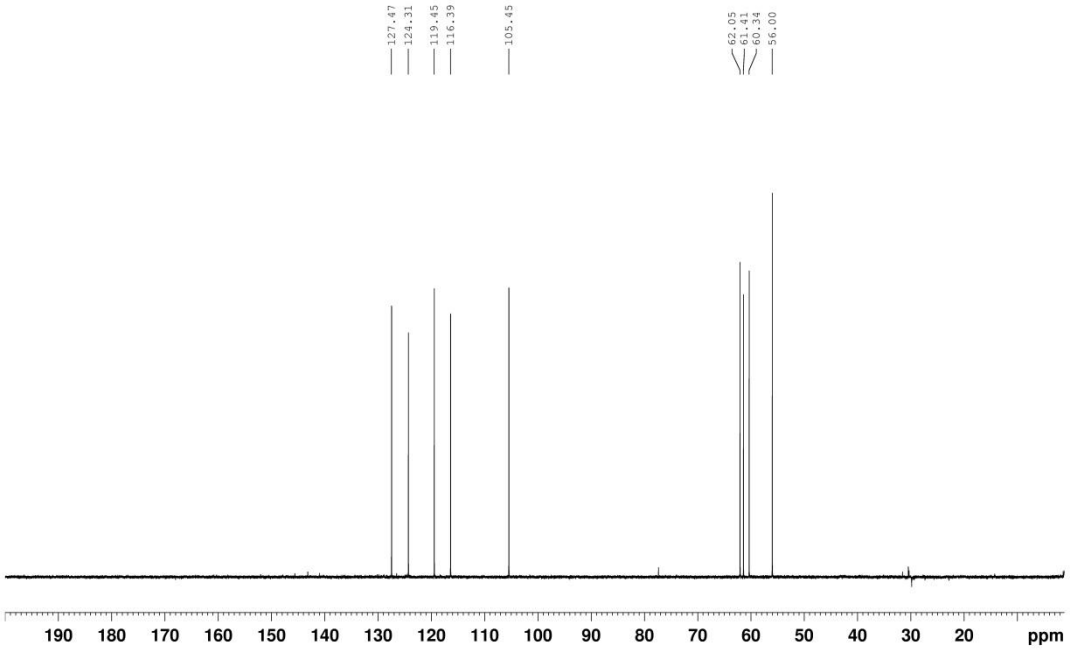
^{13}C NMR (151 MHz, $CDCl_3$, LB = 0.8) **11**



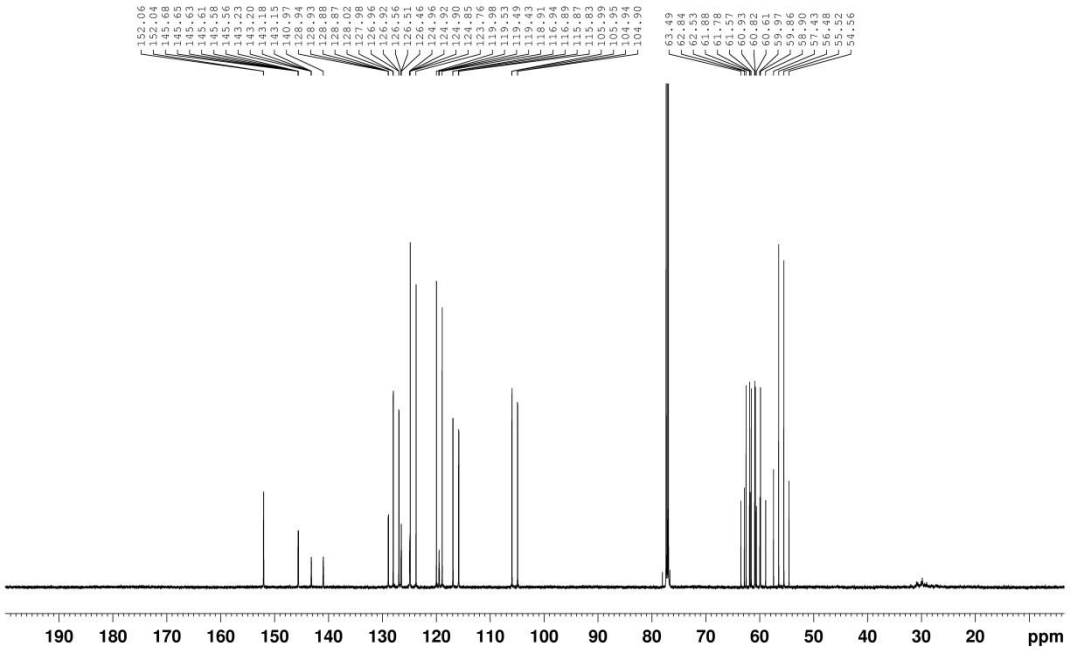
^{13}C NMR (151 MHz, $CDCl_3$, LB = 0.0) **11**



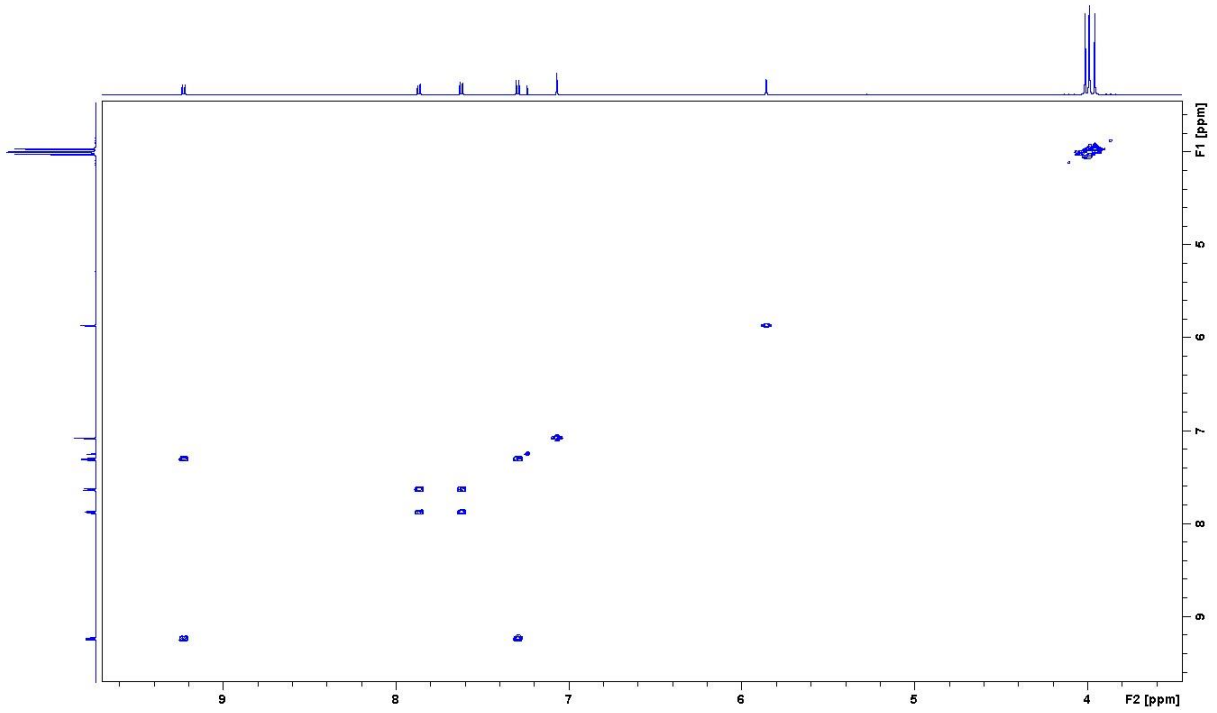
^{13}C NMR - DEPT (151 MHz, $CDCl_3$) **11**



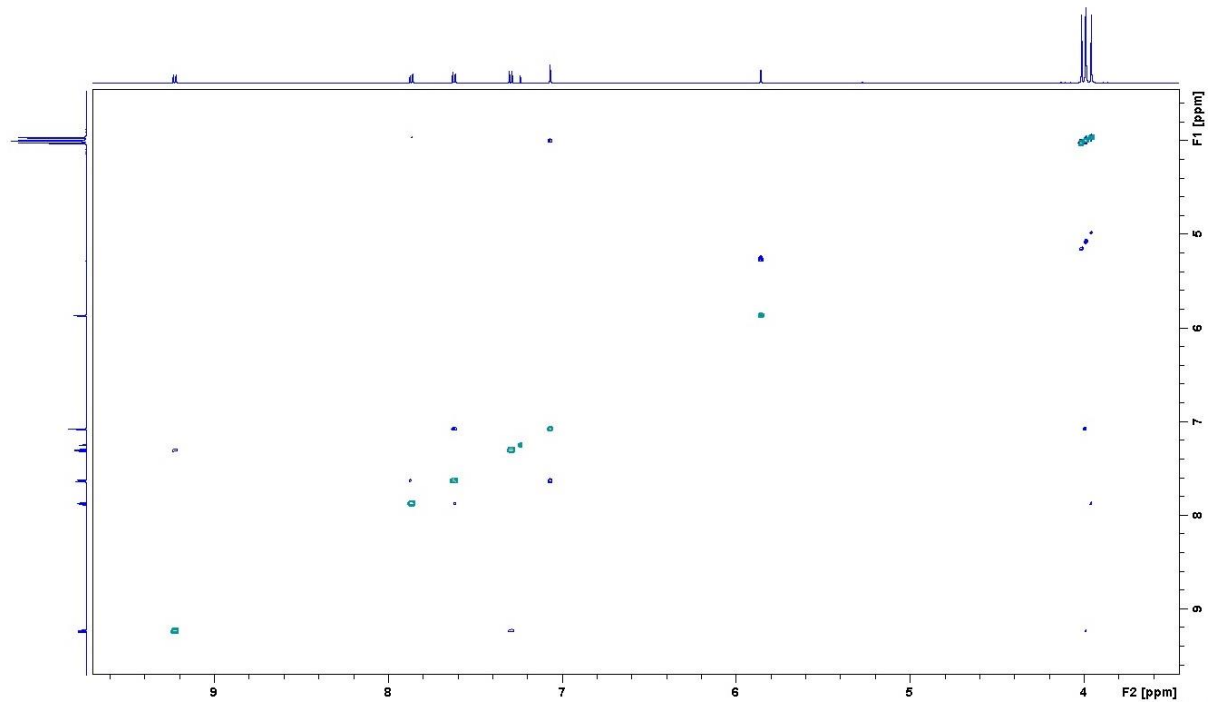
^{13}C NMR – GATED (151 MHz, $CDCl_3$) **11**



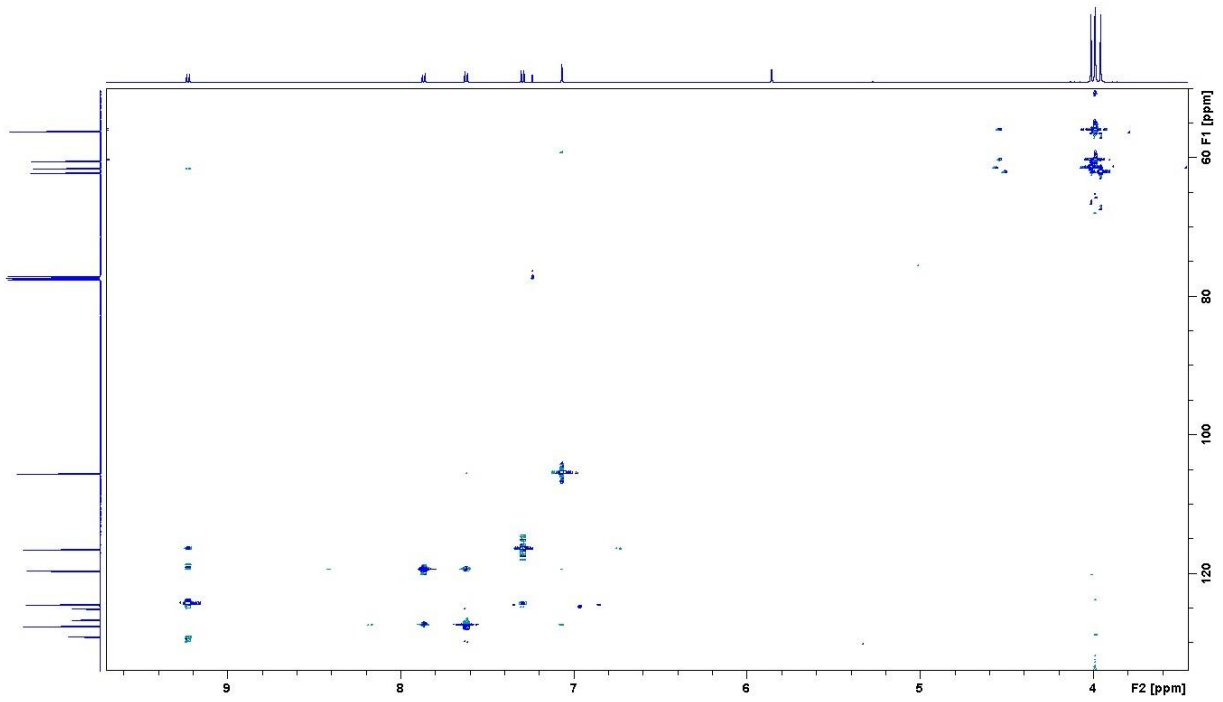
^{13}C NMR - COSY (151 MHz, $CDCl_3$) **11**



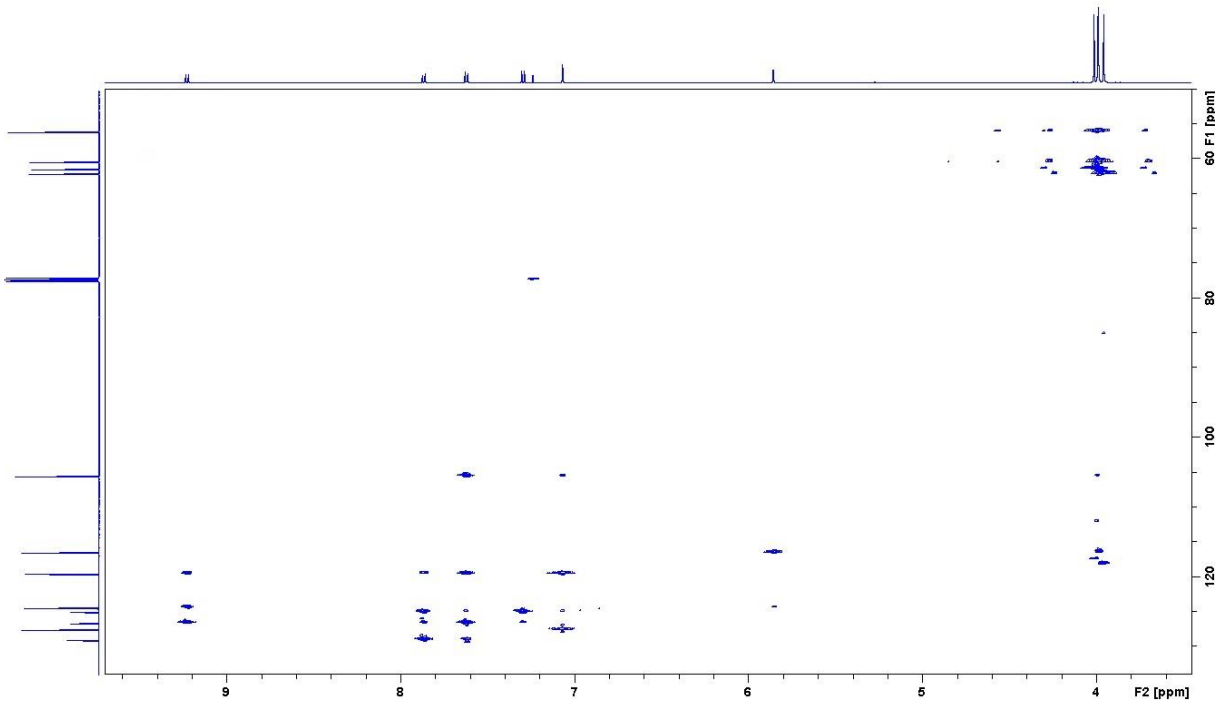
^{13}C NMR - NOESY (151 MHz, $CDCl_3$) **11**



^{13}C NMR - HSQC (151 MHz, $CDCl_3$) **11**

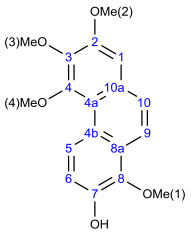


^{13}C NMR - HMQC (151 MHz, $CDCl_3$) **11**

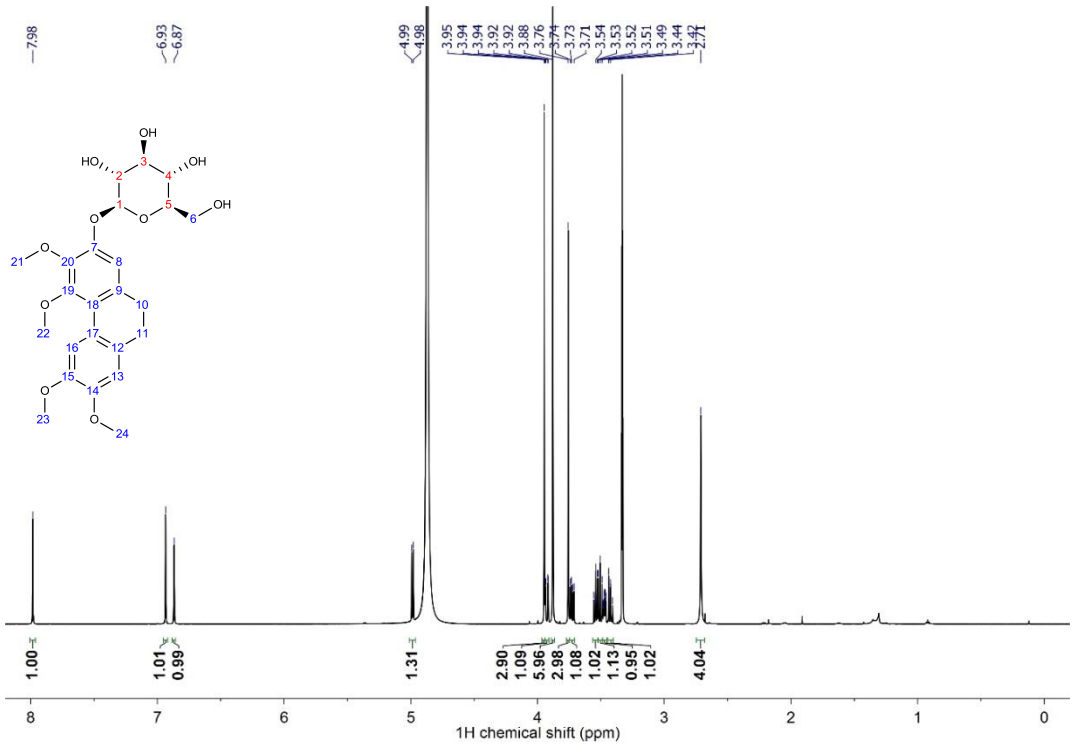


Carbon nr.	Synthetic sample	Natural sample*
1	105.5	105.3
2	152.0	148.0
3	143.2	143.1
4	152.1	151.9
4a	119.5	119.4
4b	124.9	124.8
5	124.3	124.2
6	116.4	116.2
7	145.6	145.5
8	141.0	140.8
8a	126.5	126.4
9	119.5	119.3
10	127.5	127.3
10a	128.9	128.4
OMe(2)	56.0	55.9
OMe(4)	60.3	60.2
OMe(3)	61.4	61.2
OMe(1)	62.1	61.9

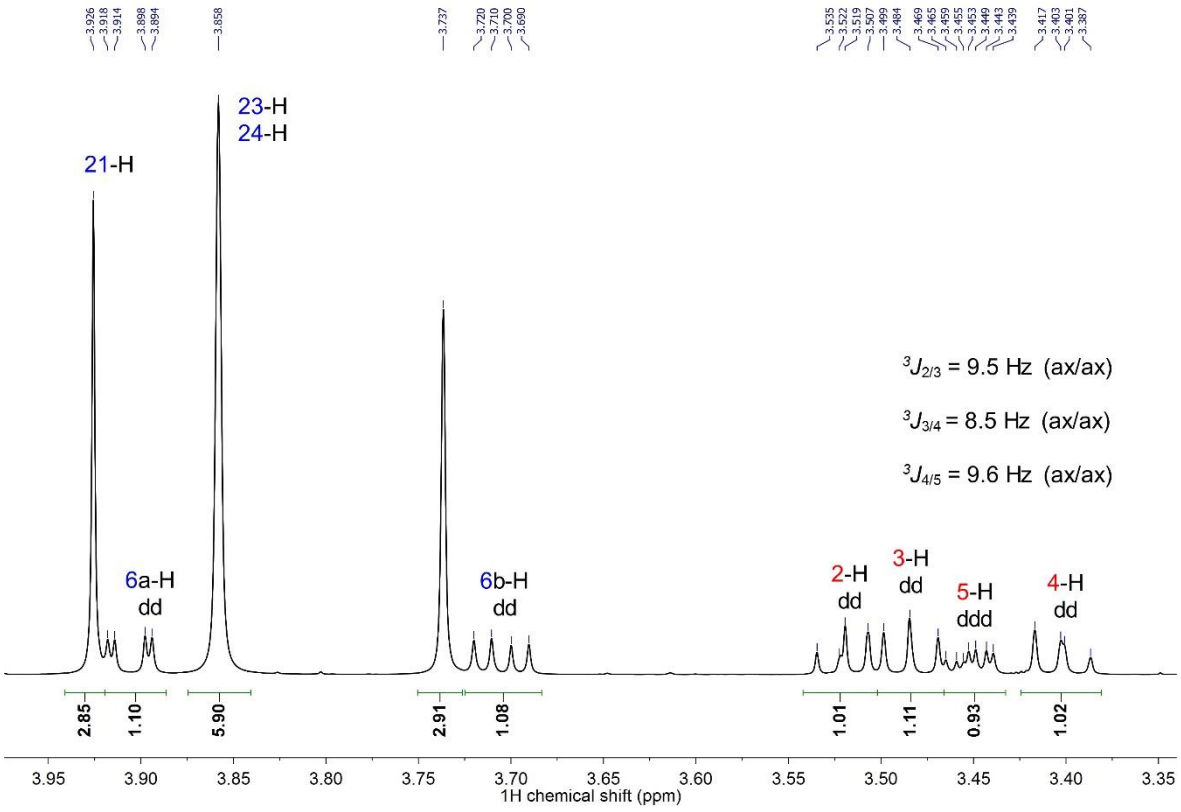
* A. Kovács, P. Forgo, I. Zupkó, B. Réthy, G. Falkay, P. Szabó, J. Hohmann, *Phytochemistry* **2007**, *68*, 687.



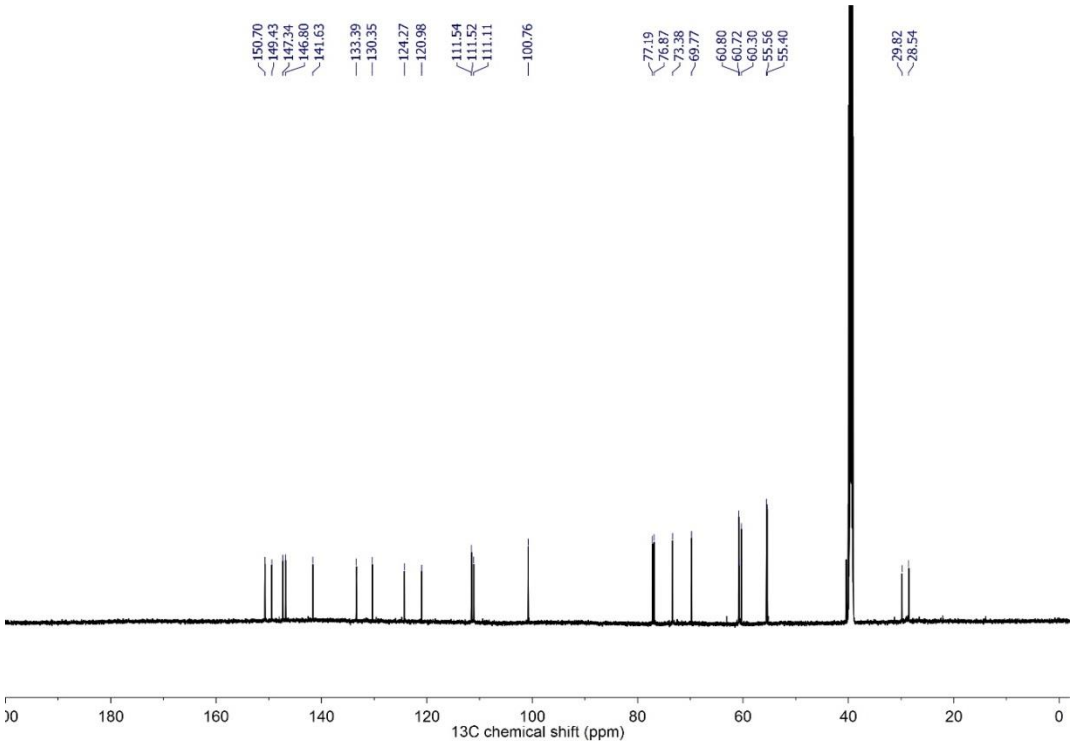
^{1}H NMR (600 MHz, CD_3OD) **12**



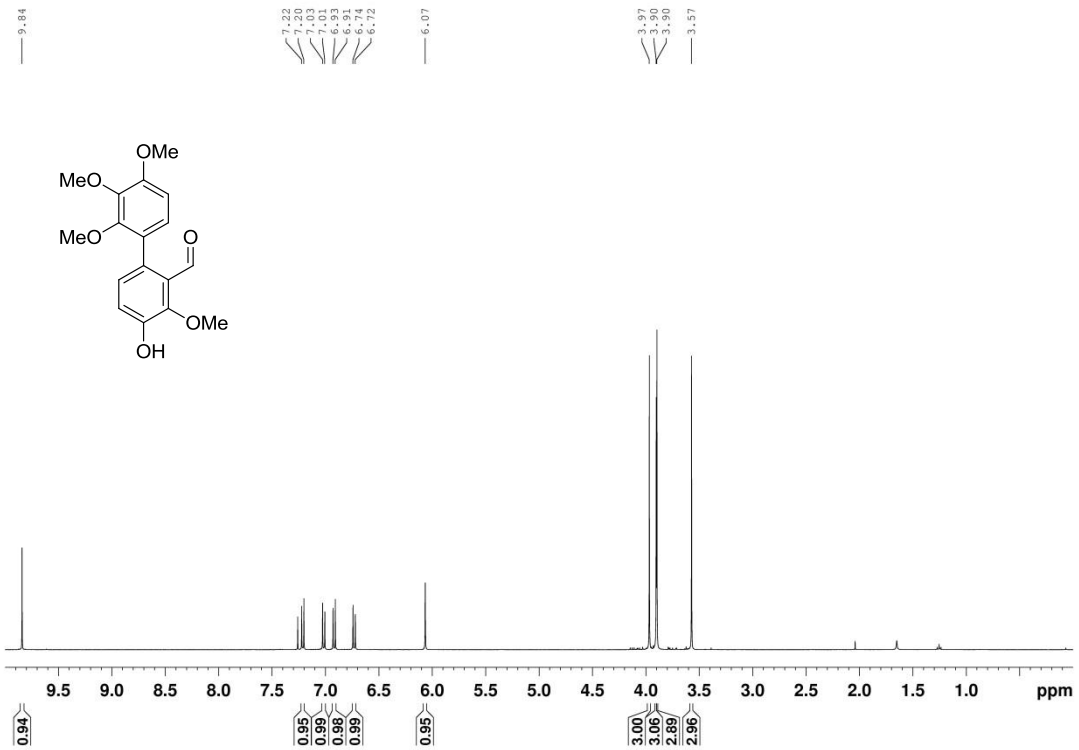
^{1}H NMR (600 MHz, CD_3OD) **12** (3.35 – 3.95 ppm)



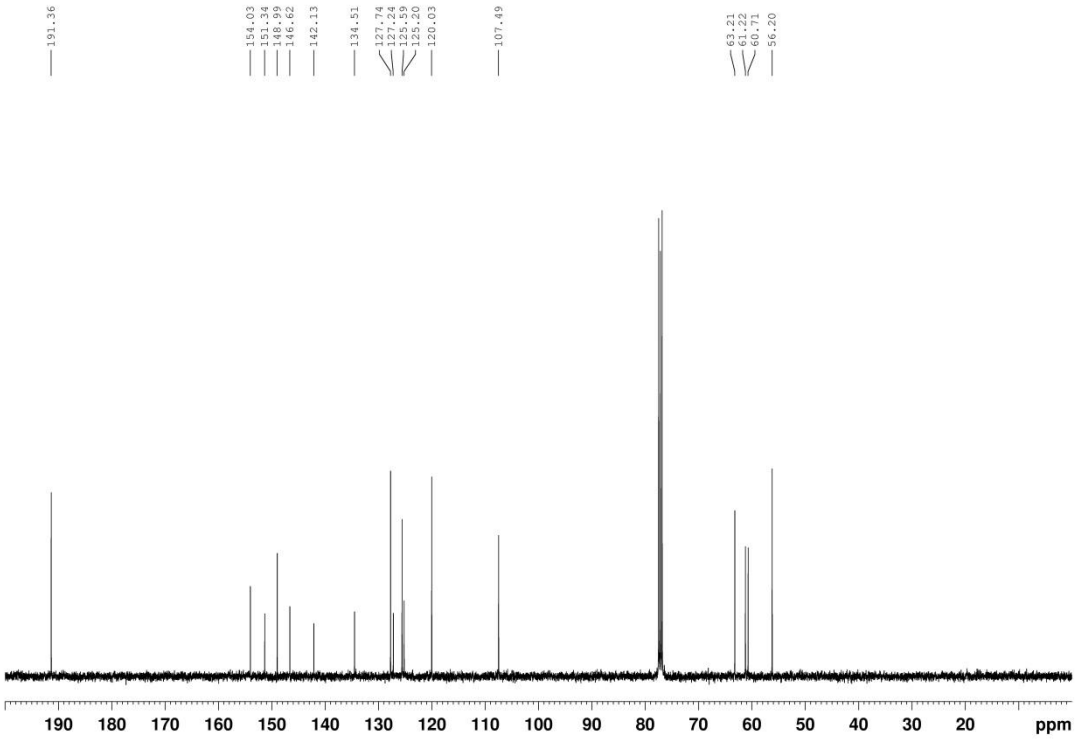
^{13}C NMR (150 MHz, d^6-DMSO) **12**



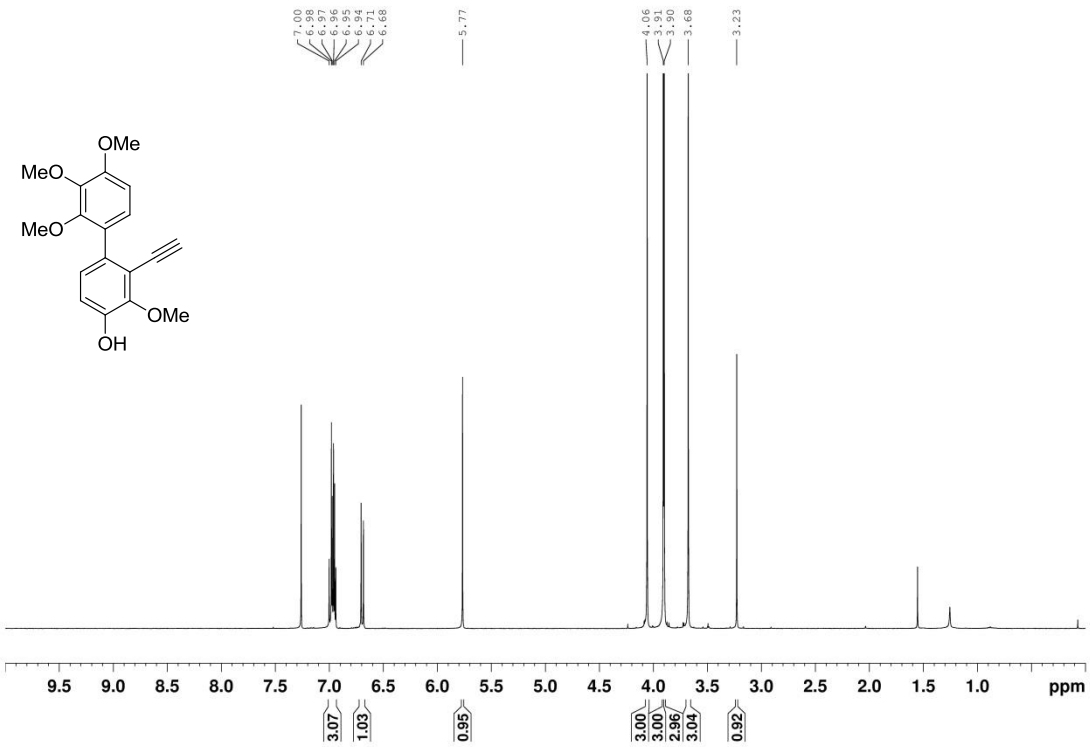
^{1}H NMR (400 MHz, $CDCl_3$) **15**



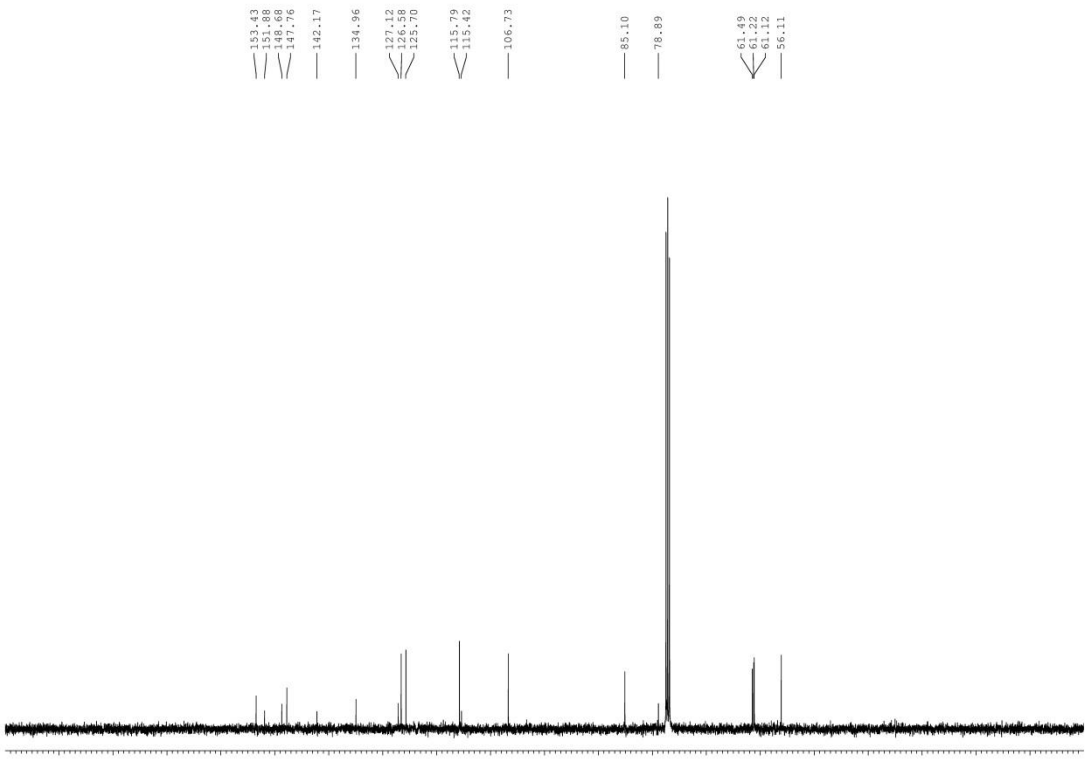
^{13}C NMR (101 MHz, $CDCl_3$) **15**



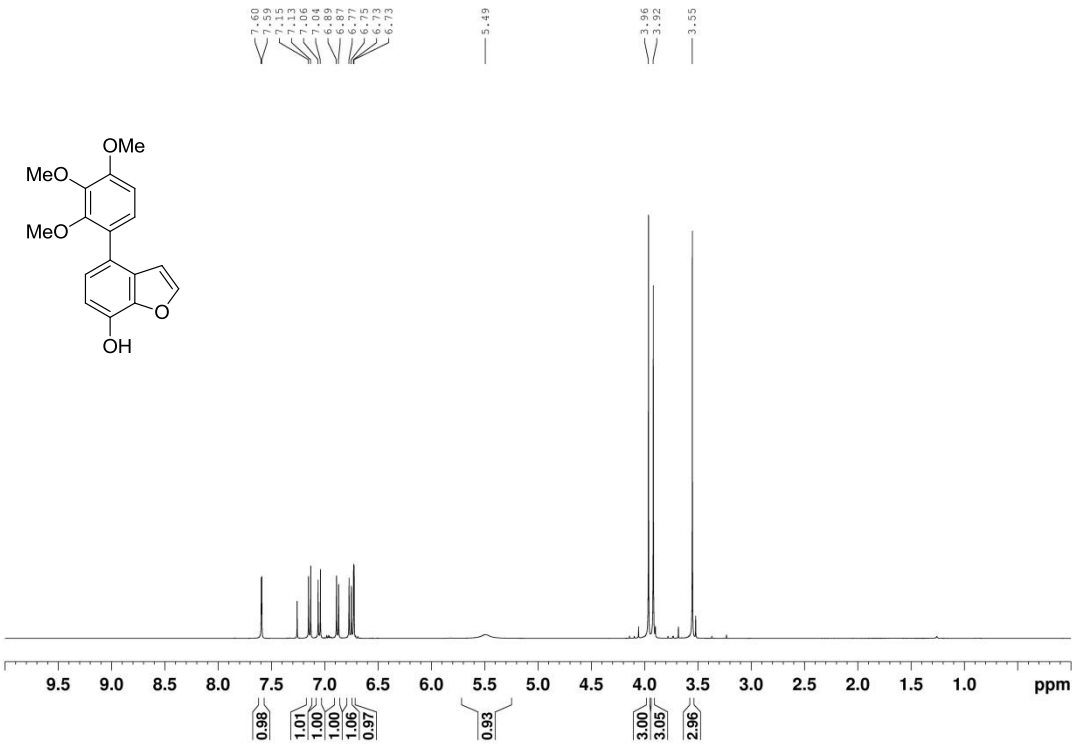
^{1}H NMR (400 MHz, $CDCl_3$) **16**



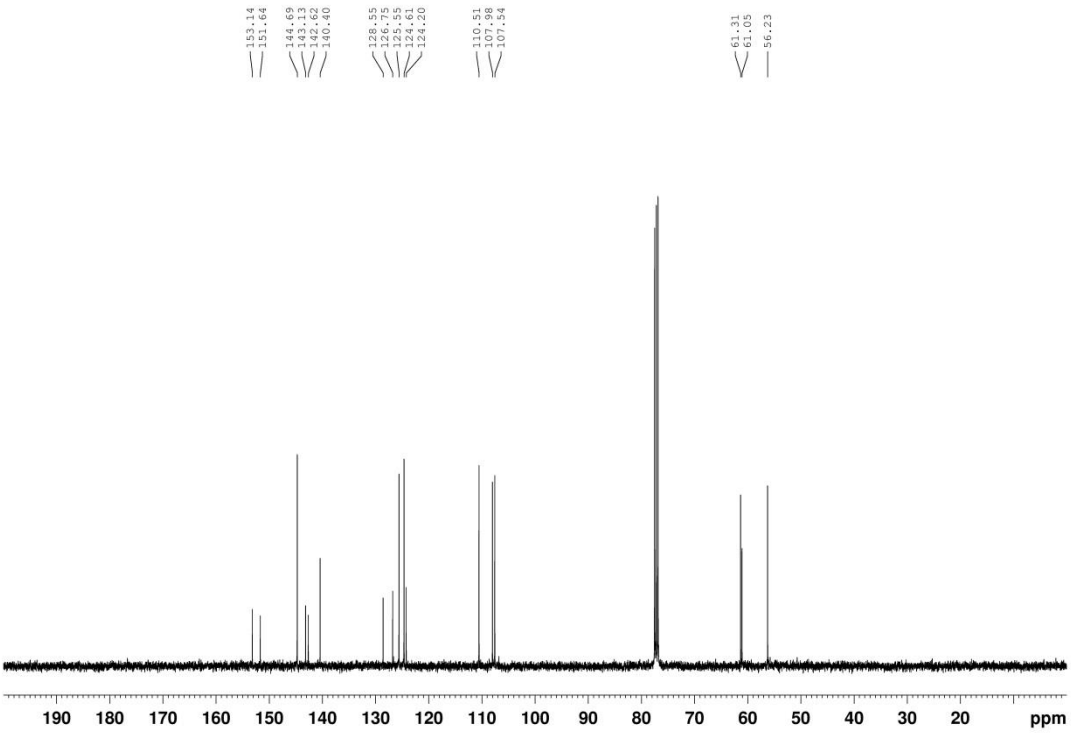
^{13}C NMR (101 MHz, $CDCl_3$) **16**



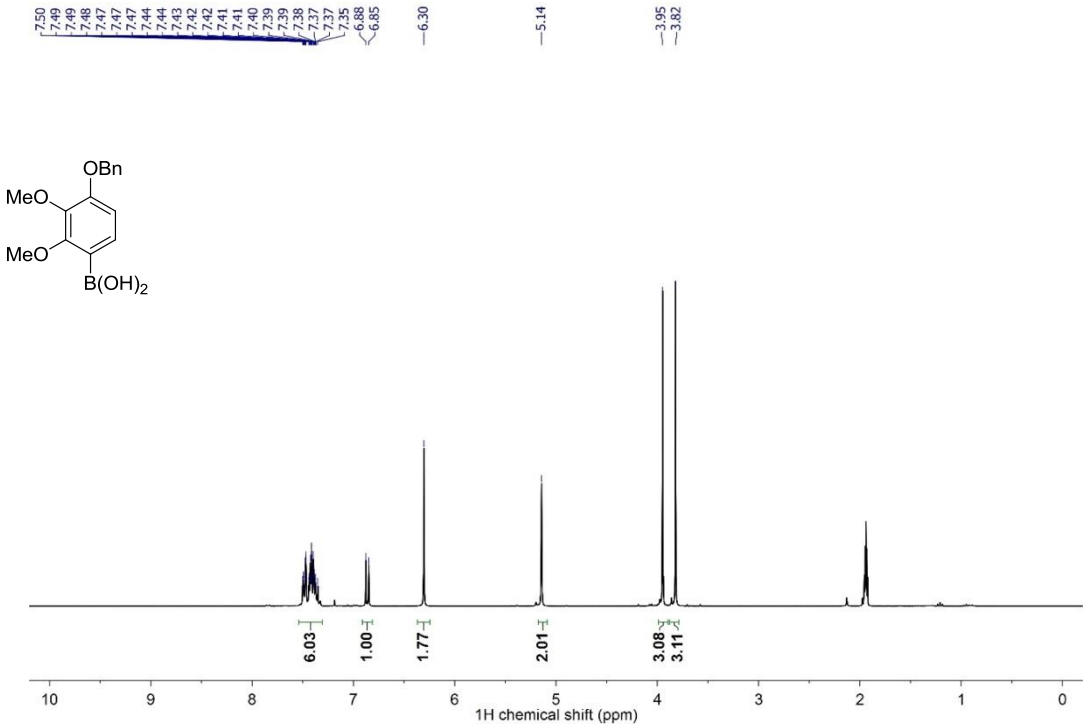
^{1}H NMR (400 MHz, $CDCl_3$) **17**



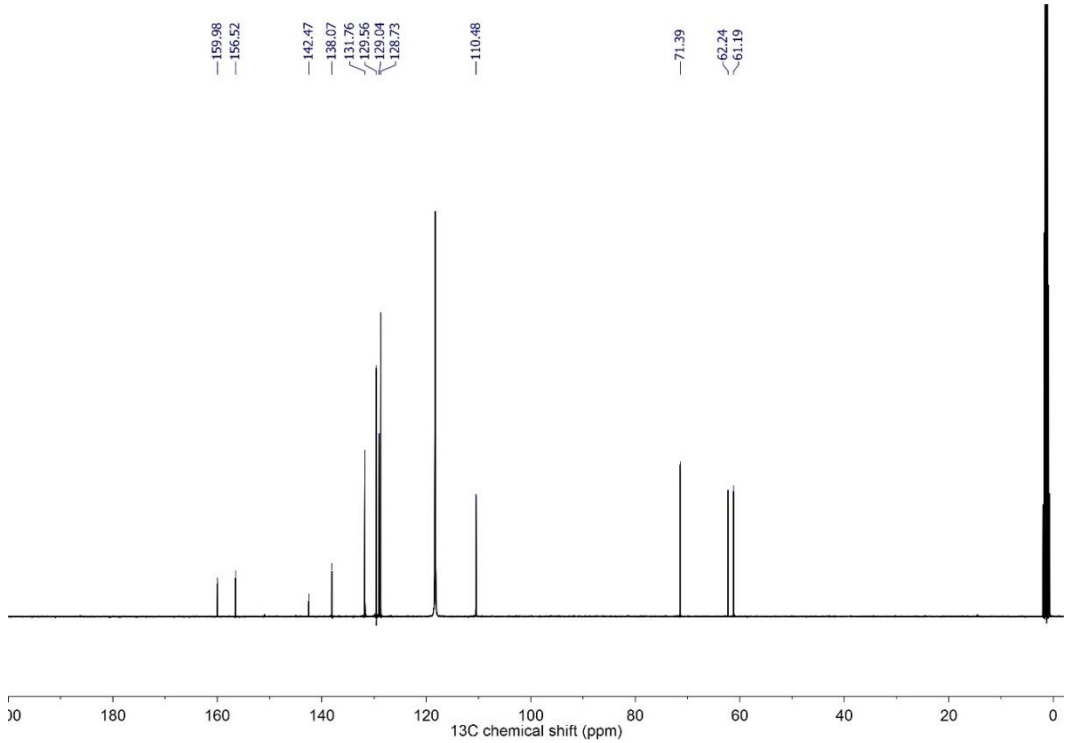
^{13}C NMR (101 MHz,$CDCl_3$) **17**



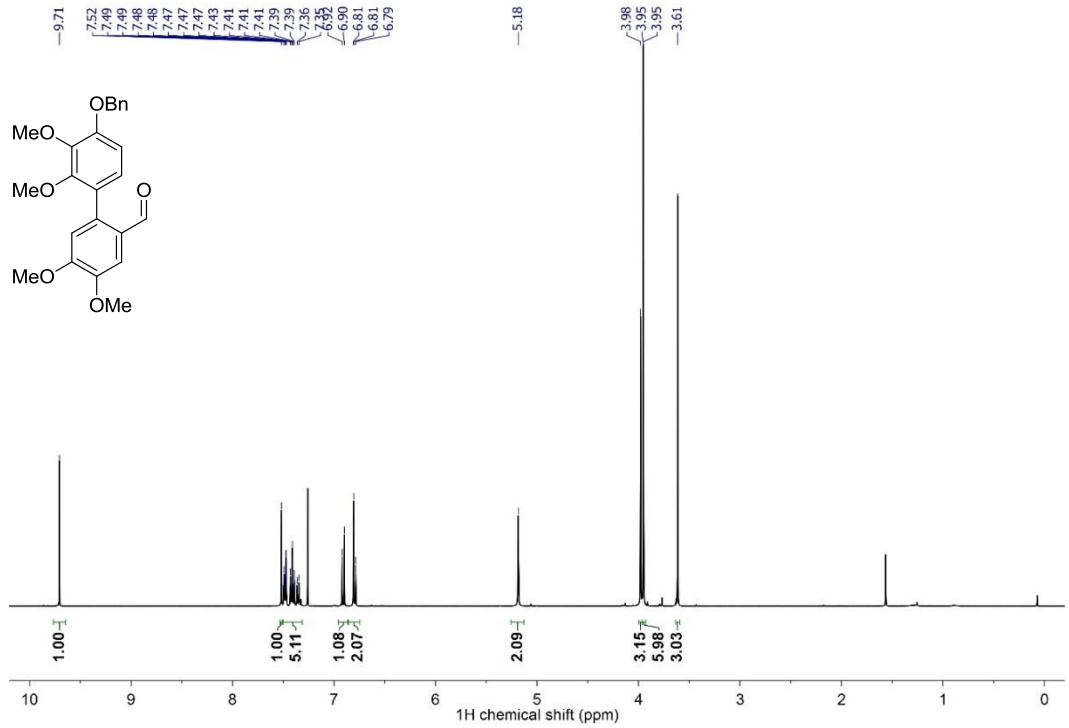
^{1}H NMR (300 MHz, CD_3CN) **19**



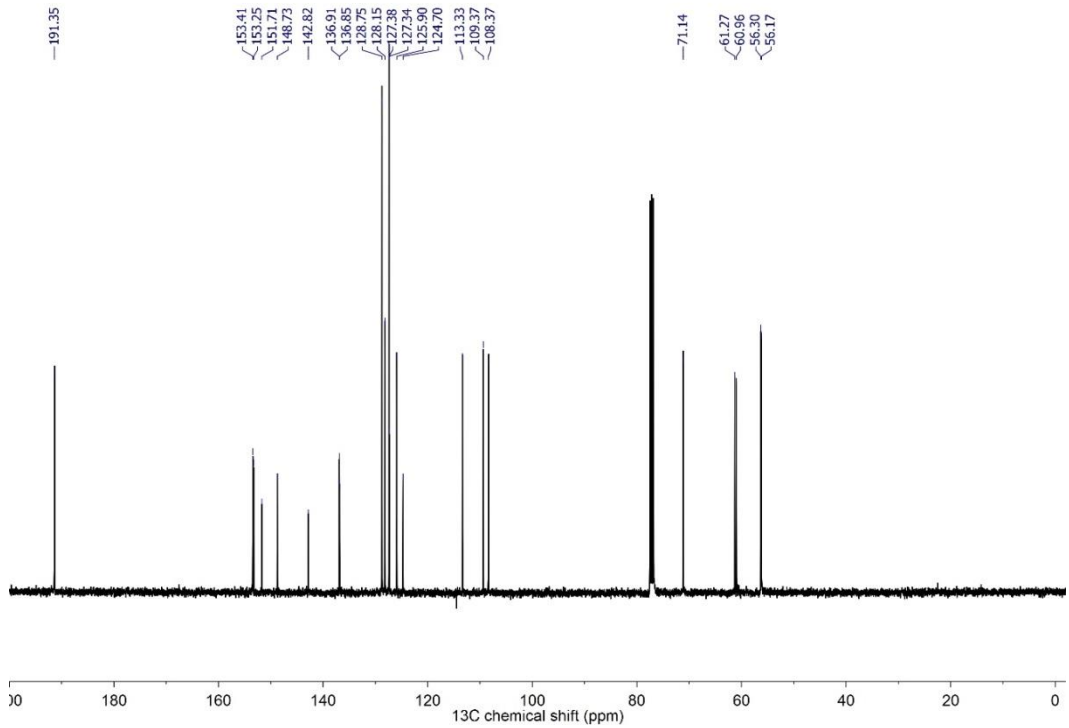
^{13}C NMR (75 MHz, CD_3CN) **19**



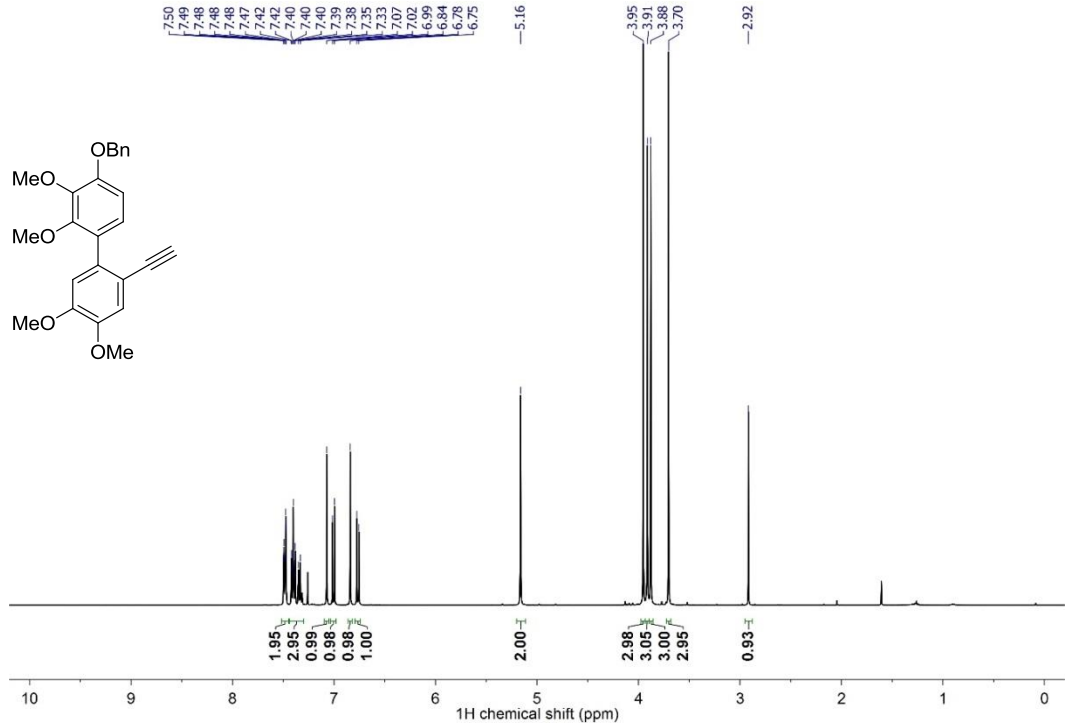
^{1}H NMR (400 MHz, $CDCl_3$) **21**



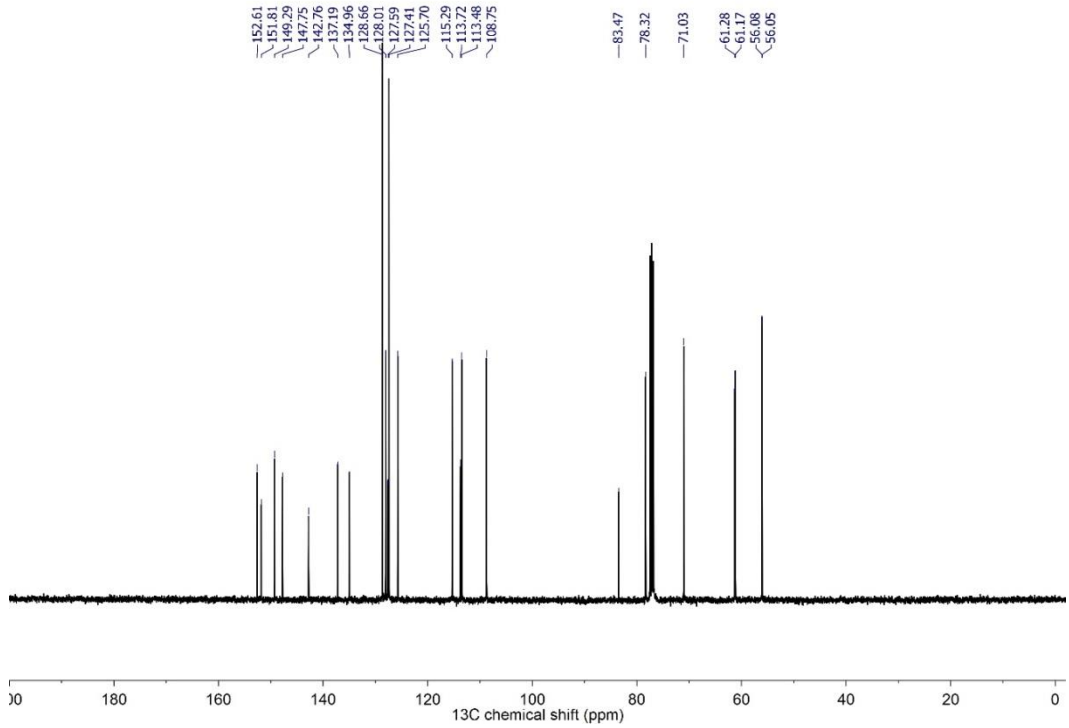
^{13}C NMR (101 MHz, $CDCl_3$) **21**



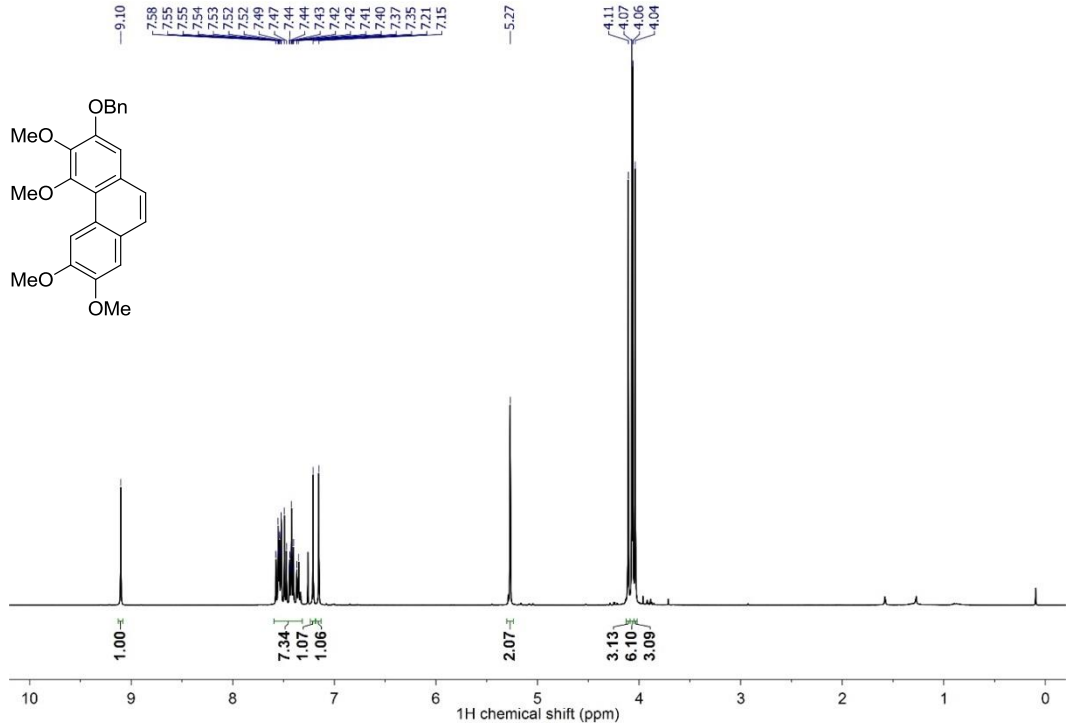
^{1}H NMR (400 MHz, $CDCl_3$) **22**



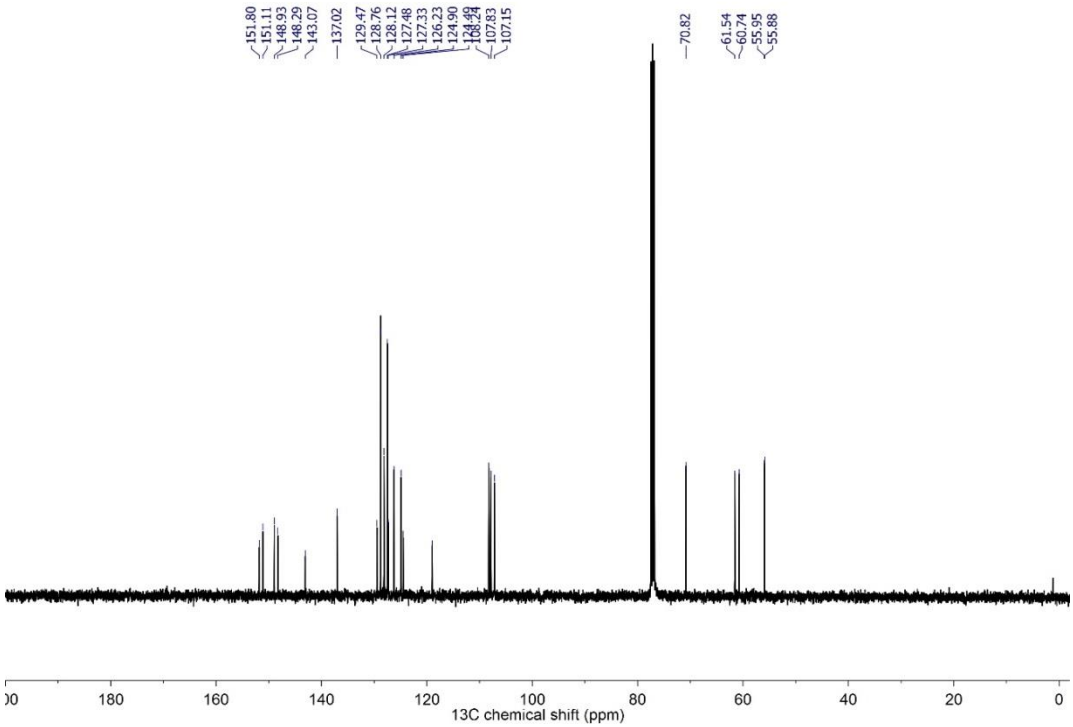
^{13}C NMR (101 MHz, $CDCl_3$) **22**



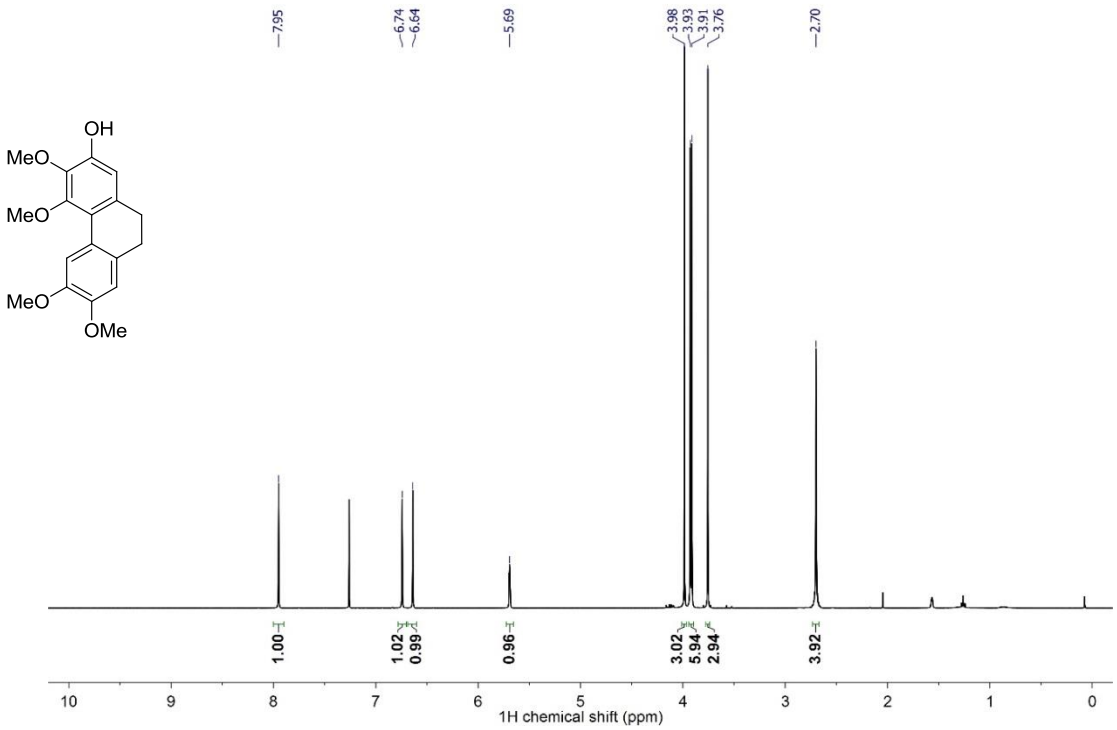
^{1}H NMR (400 MHz, $CDCl_3$) **23**



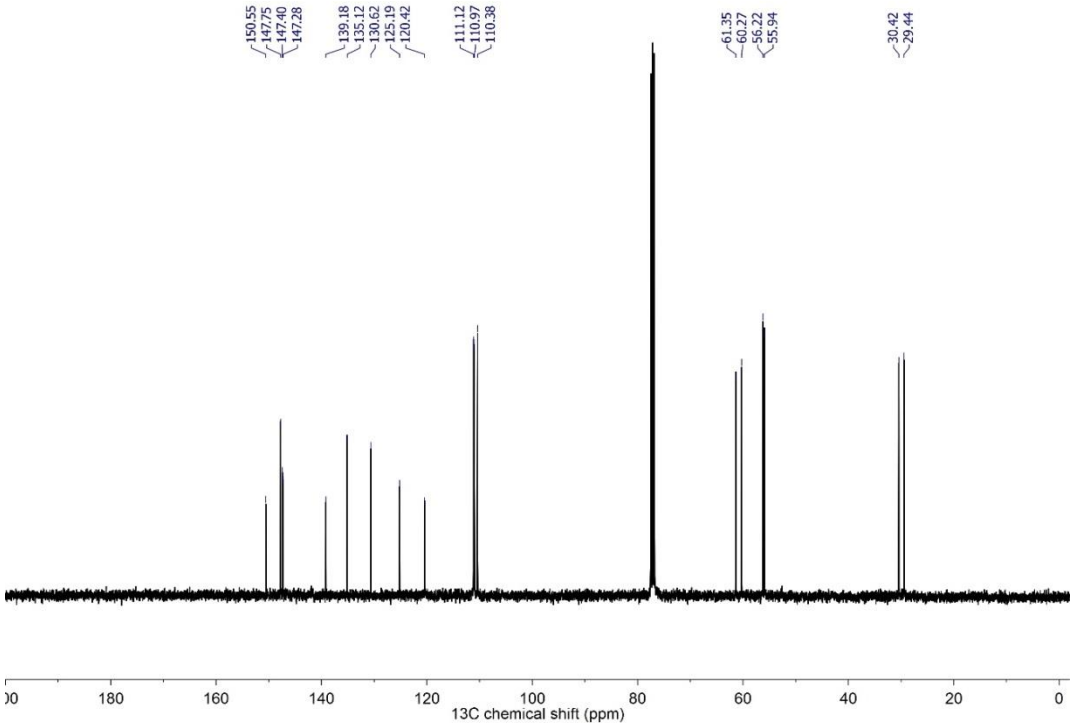
^{13}C NMR (101 MHz, $CDCl_3$) **23**



^{1}H NMR (400 MHz, $CDCl_3$) **24**

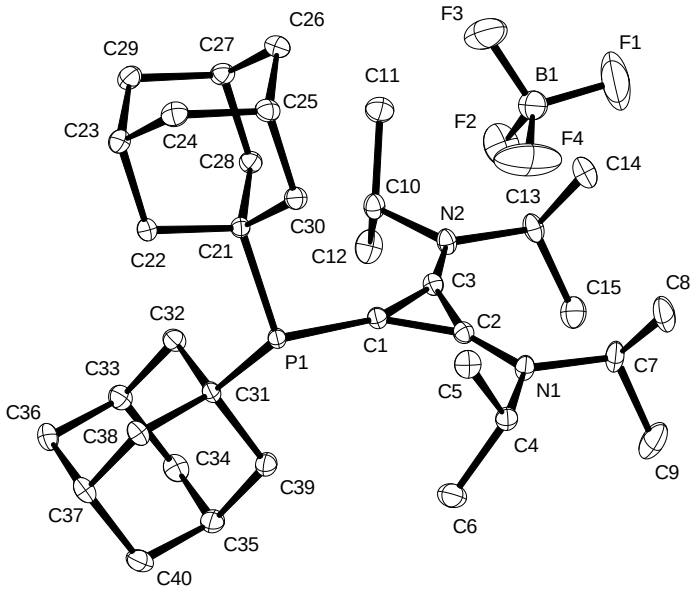


^{13}C NMR (101 MHz, $CDCl_3$) **24**



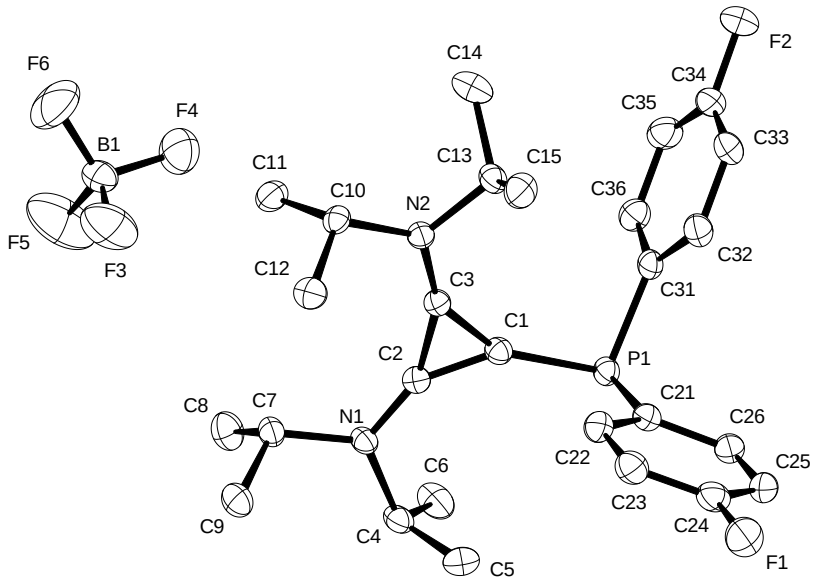
X-ray Structures

Compound **1c**



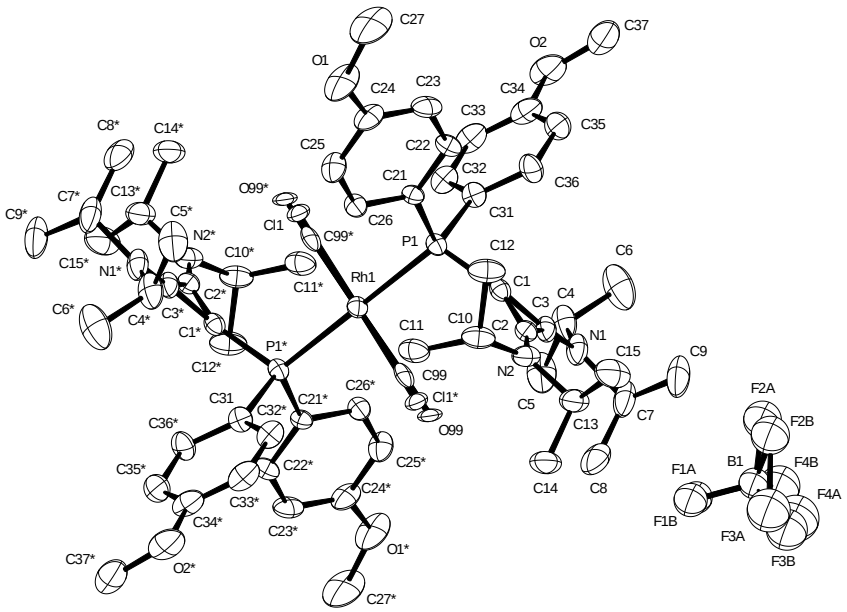
Empirical formula	$C_{35}H_{54}BF_4N_2P$	
Color	pale yellow	
Formula weight	620.58 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 10.6538(11) Å	α = 90°.
	b = 25.582(3) Å	β= 90.245(2)°.
	c = 12.4815(13) Å	γ = 90°.
Volume	3401.7(6) Å^3	
Z	4	
Density (calculated)	1.212 Mg · m^{-3}	
Absorption coefficient	0.129 mm^{-1}	
F(000)	1336 e	
Crystal size	0.06 x 0.05 x 0.02 mm^3	
θ range for data collection	1.59 to 29.49°.	
Index ranges	$-14 \le h \le 14$, $-35 \le k \le 35$, $-17 \le l \le 17$	
Reflections collected	88571	
Independent reflections	9480 [R_{int} = 0.0390]	
Reflections with I>2σ (I)	8047	
Completeness to θ = 29.49°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.00 and 0.91	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9480 / 0 / 396	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2σ (I)]	R_1 = 0.0453	wR^2 = 0.1276
R indices (all data)	R_1 = 0.0546	wR^2 = 0.1381
Largest diff. peak and hole	1.042 and -0.532 e · Å^{-3}	

Compound **1f**



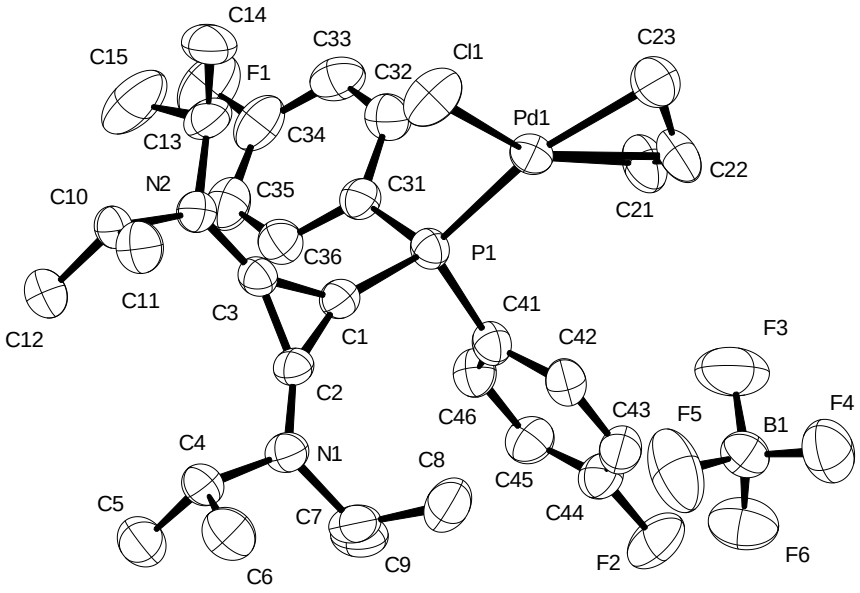
Empirical formula	$C_{27}H_{36}BF_6N_2P$	
Color	colorless	
Formula weight	544.36 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 9.9783(2) Å	α = 90°.
	b = 18.3382(6) Å	β= 100.866(2)°.
	c = 15.6515(4) Å	γ = 90°.
Volume	2812.63(13) Å^3	
Z	4	
Density (calculated)	1.286 Mg · m^{-3}	
Absorption coefficient	0.156 mm^{-1}	
F(000)	1144 e	
Crystal size	0.10 x 0.07 x 0.05 mm^3	
θ range for data collection	3.04 to 31.59°.	
Index ranges	$-14 \le h \le 14$, $-26 \le k \le 26$, $-23 \le l \le 23$	
Reflections collected	45554	
Independent reflections	9392 [R_{int} = 0.0722]	
Reflections with I>2σ (I)	5892	
Completeness to θ = 31.59°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.99 and 0.74	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9392 / 0 / 342	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2σ (I)]	R_1 = 0.0629	wR^2 = 0.1299
R indices (all data)	R_1 = 0.1161	wR^2 = 0.1532
Largest diff. peak and hole	0.596 and -0.452 e · Å^{-3}	

Compound **3e**



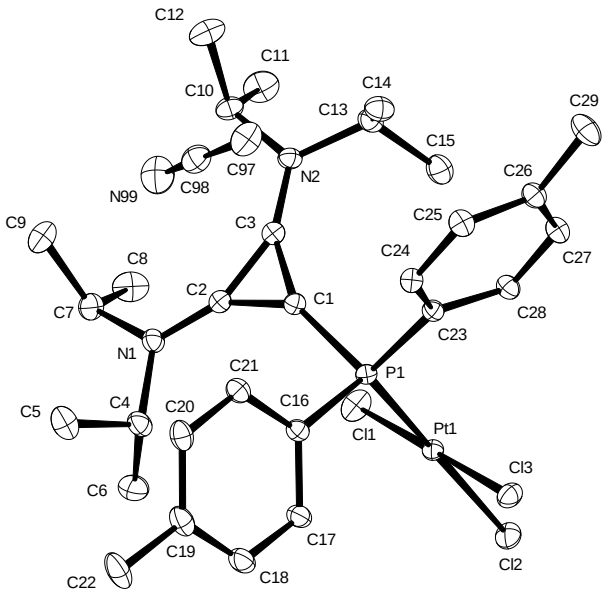
Empirical formula	$C_{59}H_{84}B_2ClF_8N_4O_5P_2Rh$	
Color	yellow	
Formula weight	1303.22 g · mol^{-1}	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 15.9294(2) Å	α = 90°.
	b = 13.9444(2) Å	β= 117.81°.
	c = 16.2976(2) Å	γ = 90°.
Volume	3201.96(7) Å^3	
Z	2	
Density (calculated)	1.352 Mg · m^{-3}	
Absorption coefficient	0.430 mm^{-1}	
F(000)	1360 e	
Crystal size	0.27 x 0.25 x 0.14 mm^3	
θ range for data collection	2.95 to 33.19°.	
Index ranges	-24 ≤ h ≤ 24, -21≤ k ≤ 21, -25≤ l ≤ 25	
Reflections collected	76251	
Independent reflections	12234 [R_{int} = 0.0431]	
Reflections with I>2σ (I)	9762	
Completeness to θ = 33.19°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12234 / 0 / 386	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2σ (I)]	R_1 = 0.0575	wR^2 = 0.1541
R indices (all data)	R_1 = 0.0728	wR^2 = 0.1653
Largest diff. peak and hole	1.742 and -1.167 e · Å^{-3}	

Compound **4f**



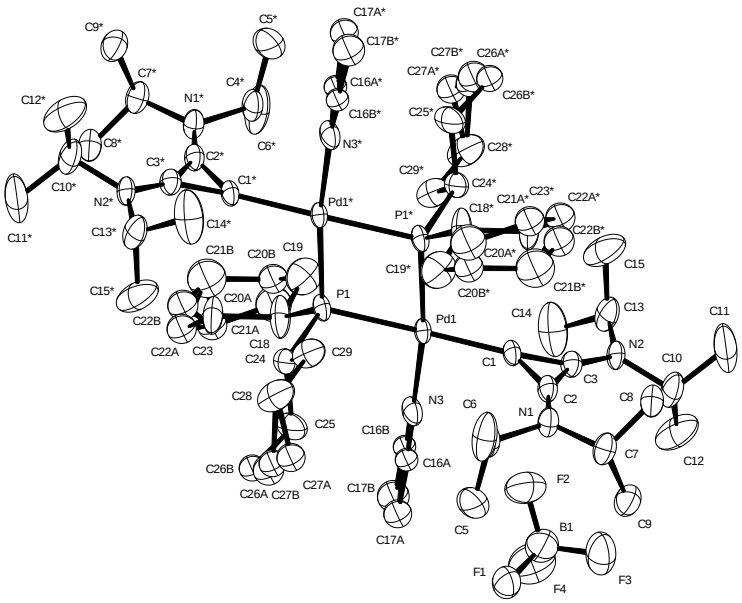
Empirical formula	$C_{30}H_{42}BClF_6N_2PPd$	
Color	yellow	
Formula weight	728.29 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca, (no. 61)	
Unit cell dimensions	a = 15.8827(7) Å	α = 90°.
	b = 11.0550(5) Å	β= 90°.
	c = 36.5987(16) Å	γ = 90°.
Volume	6426.1(5) Å^3	
Z	8	
Density (calculated)	1.506 Mg · m^{-3}	
Absorption coefficient	0.769 mm^{-1}	
F(000)	2984 e	
Crystal size	0.30 x 0.17 x 0.12 mm^3	
θ range for data collection	3.16 to 33.19°.	
Index ranges	$-24 \le h \le 24$, $-17 \le k \le 16$, $-56 \le l \le 56$	
Reflections collected	80403	
Independent reflections	12270 [R_{int} = 0.0797]	
Reflections with I>2σ (I)	6885	
Completeness to θ = 33.19°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.99 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12270 / 0 / 388	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2σ (I)]	R_1 = 0.0805	wR^2 = 0.2271
R indices (all data)	R_1 = 0.1359	wR^2 = 0.2741
Extinction coefficient	0.0024(4)	
Largest diff. peak and hole	2.663 and -2.813 e · Å^{-3}	

Compound **6d**



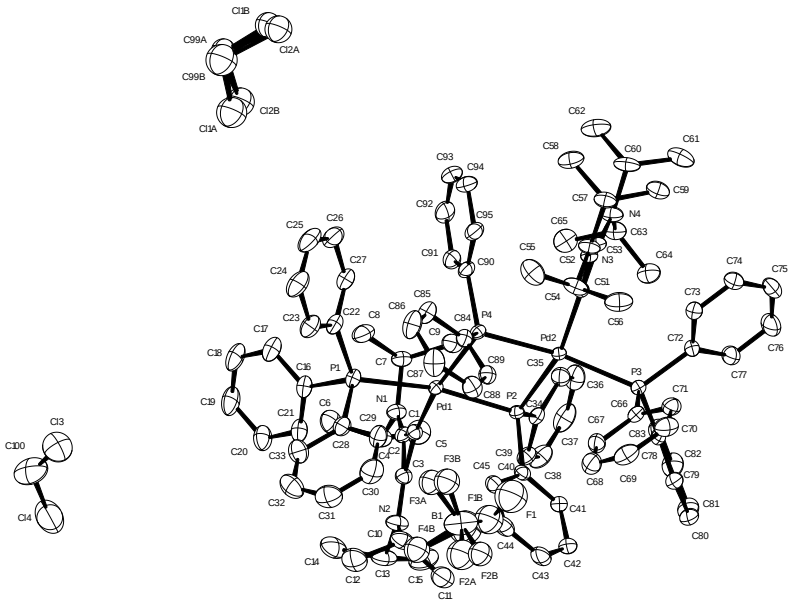
Empirical formula	$C_{29}H_{42}Cl_3N_2PPt \cdot CH_3CN$	
Color	yellow	
Formula weight	792.11 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	Pbca, (no. 61)	
Unit cell dimensions	a = 15.4474(15) Å	α = 90°.
	b = 17.4383(17) Å	β= 90°.
	c = 24.944(2) Å	γ = 90°.
Volume	6719.3(11) Å^3	
Z	8	
Density (calculated)	1.566 Mg · m^{-3}	
Absorption coefficient	4.487 mm^{-1}	
F(000)	3168 e	
Crystal size	0.30 x 0.12 x 0.11 mm^3	
θ range for data collection	1.63 to 33.76°.	
Index ranges	$-24 \le h \le 24$, $-27 \le k \le 27$, $-38 \le l \le 38$	
Reflections collected	407730	
Independent reflections	13448 [R_{int} = 0.0892]	
Reflections with I>2σ (I)	11540	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.71 and 0.19	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13448 / 0 / 363	
Goodness-of-fit on F^2	1.188	
Final R indices [I>2σ (I)]	R_1 = 0.0274	wR^2 = 0.0617
R indices (all data)	R_1 = 0.0380	wR^2 = 0.0707
Largest diff. peak and hole	2.573 and -1.662 e · Å^{-3}	

Compound **7b**



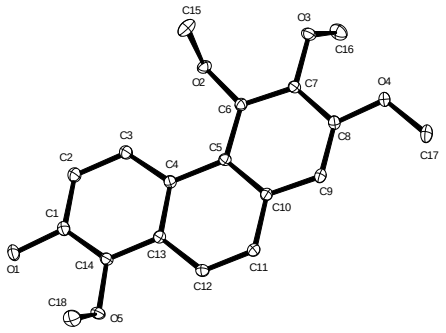
Empirical formula	$C_{29}H_{53}BF_4N_3PPd$	
Color	colourless	
Formula weight	667.92 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	a = 11.910(2) Å	α = 99.923(4)°.
	b = 12.072(2) Å	β= 105.144(5)°.
	c = 14.873(4) Å	γ = 109.581(3)°.
Volume	1863.6(7) $Å^3$	
Z	2	
Density (calculated)	1.190 $Mg \cdot m^{-3}$	
Absorption coefficient	0.580 mm^{-1}	
F(000)	700 e	
Crystal size	0.140 x 0.120 x 0.070 mm^3	
θ range for data collection	1.48 to 29.13°.	
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-20 \le l \le 20$	
Reflections collected	41584	
Independent reflections	10043 [R_{int} = 0.1654]	
Reflections with I>2σ (I)	7830	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.96 and 0.92	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10043 / 0 / 355	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2σ (I)]	R_1 = 0.0735	wR^2 = 0.1938
R indices (all data)	R_1 = 0.0891	wR^2 = 0.2040
Largest diff. peak and hole	1.630 and -1.807 $e \cdot Å^{-3}$	

Compound **8a**



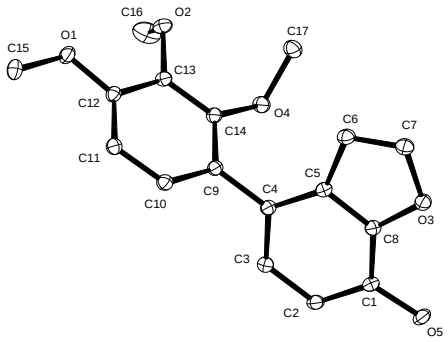
Empirical formula	2 ($C_{90}H_{106}N_4P_4Pd_2 \cdot BF_4^-$) · 3 CH_2Cl_2	
Color	orange	
Formula weight	3589.35 g · mol^{-1}	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	$P\bar{1}$, (no. 2)	
Unit cell dimensions	a = 14.9923(14) Å	α = 88.907(8)°.
	b = 15.0686(12) Å	β= 85.865(10)°.
	c = 24.293(3) Å	γ = 84.908(6)°.
Volume	5451.7(9) $Å^3$	
Z	1	
Density (calculated)	1.093 Mg · m^{-3}	
Absorption coefficient	0.506 mm^{-1}	
F(000)	1860 e	
Crystal size	0.26 x 0.22 x 0.21 mm^3	
θ range for data collection	2.73 to 27.50°.	
Index ranges	$-19 \le h \le 19$, $-19 \le k \le 19$, $-31 \le l \le 31$	
Reflections collected	108051	
Independent reflections	25020 [R_{int} = 0.0321]	
Reflections with I>2σ (I)	20928	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.87 and 0.80	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25020 / 0 / 1011	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2σ (I)]	R_1 = 0.0431	wR^2 = 0.1267
R indices (all data)	R_1 = 0.0523	wR^2 = 0.1333
Largest diff. peak and hole	1.870 and -1.576 e · $Å^{-3}$	

Compound **11**



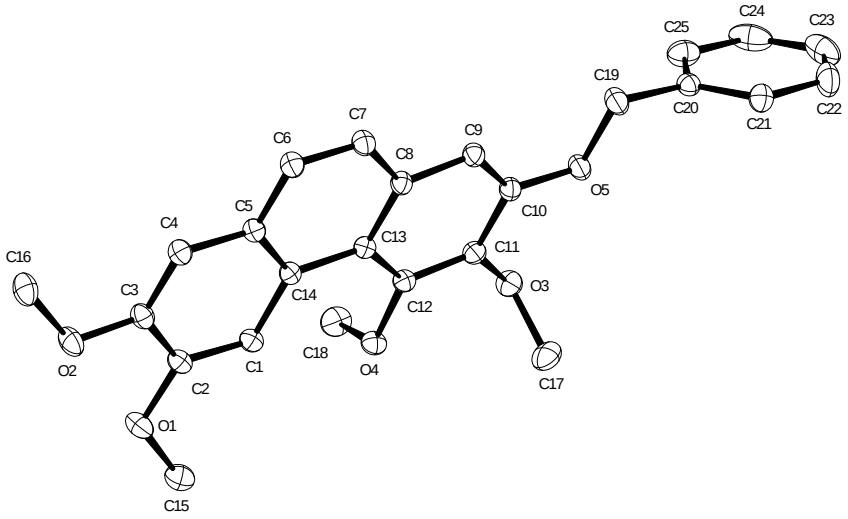
Empirical formula	$C_{18}H_{18}O_5$	
Color	yellow	
Formula weight	314.32 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	$P2_12_12_1$, (no. 19)	
Unit cell dimensions	a = 7.6876(5) Å	α = 90°.
	b = 11.3305(7) Å	β= 90°.
	c = 17.3270(8) Å	γ = 90°.
Volume	1509.26(15) Å^3	
Z	4	
Density (calculated)	1.383 Mg · m^{-3}	
Absorption coefficient	0.101 mm^{-1}	
F(000)	664 e	
Crystal size	0.42 x 0.37 x 0.20 mm^3	
θ range for data collection	2.90 to 33.06°.	
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 17$, $-26 \le l \le 26$	
Reflections collected	40870	
Independent reflections	5698 [R_{int} = 0.0265]	
Reflections with I>2σ (I)	5125	
Completeness to θ = 27.50°	99.4 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5698 / 0 / 213	
Goodness-of-fit on F^2	1.211	
Final R indices [I>2σ (I)]	R_1 = 0.0375	wR^2 = 0.1009
R indices (all data)	R_1 = 0.0484	wR^2 = 0.1099
Largest diff. peak and hole	0.4 and -0.3 e·Å^{-3}	

Compound **17**



Empirical formula	$C_{17}H_{16}O_5$	
Color	colourless	
Formula weight	300.30 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	$P2_1/c$, (no. 14)	
Unit cell dimensions	a = 11.1834(12) Å	α = 90°.
	b = 12.5326(13) Å	β= 106.040(3)°.
	c = 10.6579(11) Å	γ = 90°.
Volume	1435.6(3) Å^3	
Z	4	
Density (calculated)	1.389 Mg·m^{-3}	
Absorption coefficient	0.103 mm^{-1}	
F(000)	632 e	
Crystal size	0.24 x 0.08 x 0.07 mm^3	
θ range for data collection	2.50 to 35.46°.	
Index ranges	$-18 \le h \le 18$, $-20 \le k \le 20$, $-17 \le l \le 17$	
Reflections collected	126675	
Independent reflections	6504 [R_{int} = 0.0511]	
Reflections with I>2σ (I)	5349	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6504 / 0 / 203	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2σ (I)]	R_1 = 0.0367	wR^2 = 0.0997
R indices (all data)	R_1 = 0.0485	wR^2 = 0.1089
Largest diff. peak and hole	0.6 and -0.3 e·Å^{-3}	

Compound **23**



Empirical formula	$C_{25}H_{24}O_5$	
Color	colorless	
Formula weight	404.44 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	$Pna2_1$, (no. 33)	
Unit cell dimensions	a = 17.595(3) Å	α = 90°.
	b = 7.4401(11) Å	β= 90°.
	c = 15.723(2) Å	γ = 90°.
Volume	2058.3(5) Å^3	
Z	4	
Density (calculated)	1.305 Mg · m^{-3}	
Absorption coefficient	0.090 mm^{-1}	
F(000)	856 e	
Crystal size	0.41 x 0.10 x 0.08 mm^3	
θ range for data collection	2.315 to 35.633°.	
Index ranges	$-28 \le h \le 28$, $-12 \le k \le 12$, $-25 \le l \le 25$	
Reflections collected	72147	
Independent reflections	9448 [R_{int} = 0.0589]	
Reflections with I>2σ (I)	8085	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9448 / 1 / 275	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2σ (I)]	R_1 = 0.0429	wR^2 = 0.1069
R indices (all data)	R_1 = 0.0586	wR^2 = 0.1190
Absolute structure parameter	0.3(3)	
Largest diff. peak and hole	0.413 and -0.273 e · Å^{-3}	