Electronic Supporting Information

Design and Synthesis of Versatile Ligand Precursors Based on Phosphonium Ylides for Palladalactam Formation and Catalytic Investigation

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Experimental section

General information. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with standard procedures. Starting chemicals were purchased from commercial source and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 and 75.47 MHz, respectively, on a Bruker AV-300 spectrometer. Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. ESI-MS was carried out on a Finnigan/Thermo Quest MAT 95XL mass spectrometer.

Synthesis of 1a. A mixture of triethylphosphine (1.30 mL, 8.84 mmol) and 2-chloro-*N*-phenylacetamide (1.00 g, 5.89 mmol) in MeCN (25 mL) was placed in a Schlenk flask. The mixture was stirred at 80 °C for 16 h under a nitrogen atmosphere. After cooling and drying under vacuum, the resulting white solid was collected on a frit, washed with THF (50mL), and dried under vacuum. Yield: 1.42 g (84 %). Mp = 162.2–162.7 °C. ^{1}H NMR (DMSO–d_6): δ 1.12–1.23 (m, 9H, CH_3), 2.33–2.45 (m, 6H, CH_2), 3.98 (d, 2H, J = 15.0 Hz, C=O–CH_2), 7.08 (t, 1H, J = 9.0 Hz, Ph *H*), 7.32 (t, 2H, J = 9.0 Hz, Ph *H*), 7.68 (d, 2H, J = 3.0 Hz, Ph *H*), 11.68 (s, 1H, N*H*). ^{13}C{^{1}H} NMR (DMSO–d_6): δ 5.76 (d, J = 6.0 Hz, *C*H$_3$), 12.2 (d, J = 49.8 Hz, *C*H$_2$), 27.2 (d, J = 49.8 Hz, *C*H$_2$C=O), 119.7, 124.4, 129.2, 138.9 (quaternary *C*), 162.8 (d, J = 7.5 Hz, *C*=O). ^{31}P{^{1}H} NMR (DMSO–d_6): δ 38.3. HRMS (ESI) *m*/*z* calcd for $C_{14}H_{23}NOP$ $[M - Cl]^+$ 252.1517, found 252.1500.

Synthesis of 1b. The compound was prepared with a similar procedure to that of **1a**. A mixture of triphenylphosphine (1.85 g, 7.07 mmol) and 2-chloro-*N*-phenylacetamide (1.00 g, 5.89 mmol) were

used. Yield: 2.13 g (82 %). Mp = 284.2–284.8 °C. ^{1}H NMR (DMSO–d_6): δ 5.43 (d, 2H, J = 15.0 Hz, C=O–CH_2), 7.06 (t, 1H, J = 12.0 Hz, Ph *H*), 7.26 (t, 2H, J = 15.0 Hz, Ph *H*), 7.47 (t, 2H, J = 9.0 Hz, Ph *H*), 7.72–7.90 (m, 15H, Ph *H*), 11.53 (s, 1H, N*H*). ^{13}C{^{1}H} NMR (DMSO–d_6): δ 32.6 (d, J = 55.8 Hz, *C*H$_2$C=O), 119.1 (d, J = 88.2 Hz, quaternary *C*), 119.8, 124.6, 129.2, 130.4 (d, J = 15.0 Hz, PPh *C*), 134.3 (d, J = 15.0 Hz, PPh *C*), 135.3, 138.5 (quaternary *C*), 162.1 (d, J = 7.5 Hz, *C*=O). ^{31}P{^{1}H} NMR (DMSO–d_6): δ 21.8. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{23}NOP$ [M – Cl]$^+$ 396.1517, found 396.1490.

Synthesis of 1c. The compound was prepared with a similar procedure to that of **1a**. A mixture of tris(4-methoxyphenyl)phosphine (1.24 g, 3.53 mmol) and 2-chloro-*N*-phenylacetamide (0.50 g, 2.94 mmol) were used. Yield: 1.12 g (76 %). Mp = 183.8–184.3 °C. ^{1}H NMR ((DMSO–d_6): δ 3.87 (s, 9H, OCH_3), 5.12 (d, 2H, J = 15.0 Hz, CH_2C=O), 7.07 (t, 1H, J = 15.0 Hz, Ar *H* or Ph *H*), 7.25–7.30 (m, 8H, Ar *H* or Ph *H*), 7.47 (d, 2H, J = 9.0 Hz, Ar *H* or Ph *H*), 7.68–7.75 (m, 6H, Ar *H* or Ph *H*), 11.24 (s, 1H, N*H*). ^{13}C{^{1}H} NMR (DMSO–d_6): δ 33.3 (d, J = 60.3 Hz, *C*H$_2$C=O), 56.3 (O*C*H$_3$), 110.1 (d, J = 98.1 Hz, quaternary *C*), 116.1 (d, J = 15.0 Hz, PAr *C*) 119.8, 124.5, 129.2, 136.2 (d, J = 11.3 Hz, PAr *C*), 138.7 (quaternary *C*), 162.3 (d, J = 7.5 Hz, *C*=O), 164.4 (quaternary *C*). ^{31}P{^{1}H} NMR (DMSO–d_6): δ 19.6. HRMS (ESI) *m*/*z* calcd for $C_{29}H_{29}NO_4P$ [M – Cl]$^+$ 486.1834, found 486.1795.

Synthesis of 1d. The compound was prepared with a similar procedure to that of **1a**. A mixture of tricyclohexylphosphine (0.99 g, 3.53 mmol) and 2-chloro-*N*-phenylacetamide (0.50 g, 2.94 mmol) were used. Yield: 1.04 g (79 %). Mp = 286.1–286.8 °C. ^{1}H NMR ($CDCl_3$): δ 1.15–1.98 (m, 30H, Cy

H), 2.58 (m, 3H, Cy *H*), 4.03 (d, 2H, *J* = 12.0 Hz, CH_2C=O), 7.04 (t, 1H, *J* = 15.0 Hz, Ph *H*), 7.24 (t, 2H, *J* = 15.0 Hz, Ph *H*), 7.73 (d, 2H, *J* = 9.0 Hz, Ph *H*), 11.95 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.8 (d, *J* = 45.2 Hz, *C*H_2C=O), 25.3 (Cy *C*), 26.5 (d, *J* = 12.0 Hz, Cy *C*), 27.1 (d, *J* = 3.7 Hz, Cy *C*), 30.9 (d, *J* = 37.7 Hz, Cy *C*), 120.3, 124.4, 128.7, 138.1 (quaternary *C*), 162.0 (d, *J* = 3.7 Hz, *C*=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.4. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{41}NOP$ $[M - Cl]^+$ 414.2925, found 414.2901.

Synthesis of 1e. The compound was prepared with a similar procedure to that of **1a**. A mixture of triphenylphosphine (1.69 g, 6.46 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (1.0 g, 5.38 mmol) were used. Yield: 1.81 g (78 %). Mp = 224.7–225.5 °C. ^1H NMR (DMSO–d_6): δ 5.32 (d, 2H, *J* = 15.0 Hz, CH_2C=O), 6.64–6.70 (m, 1H, Ar *H*), 6.89–6.96 (m, 2H, Ar *H*), 7.52 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.73–7.92 (m, 15H, PPh *H*), 9.94 (s, 1H, N*H*), 10.13 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (DMSO–d_6): δ 32.4 (d, *J* = 52.8 Hz, *C*H_2C=O), 116.0, 118.9, 119.2 (d, *J* = 88.3 Hz, quaternary *C*), 122.6, 125.4 (quaternary *C*), 125.8, 130.5 (d, *J* = 15.0 Hz, PPh *C*), 134.2 (d, *J* = 7.5 Hz, PPh *C*), 135.3, 148.8 (quaternary *C*), 162.0 (d, *J* = 4.5 Hz, *C*=O). $^{31}P\{^1H\}$ NMR (DMSO–d_6): δ 21.8. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{23}NO_2P$ $[M - Cl]^+$ 412.1466, found 414.1488.

Synthesis of 1e′. A mixture of **1e** (1.82 g, 4.06 mmol) and $NaBF_4$ (2.23 g, 20.31 mmol) in MeCN (25 mL) was placed in a Schlenk flask. The mixture was heated to 50°C 48h. After cooling and dried under vacuum, the residual was extracted with DCM/H_2O twice. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a solid. Diethyl ether was added and the white

solid formed was collected on frit and dried under vacuum. Yield: 1.65 g (81 %). Mp = 175.6–176.1 °C. ^{1}H NMR (DMSO–d_6): δ 5.26 (d, 2H, J = 15.0 Hz, CH_2C=O), 6.68 (t, 1H, J = 12.0 Hz, Ar *H*), 6.86–6.96 (m, 2H, Ar *H*), 7.56 (d, 1H, J = 6.0 Hz, Ar *H*), 7.74–7.92 (m, 15H, PPh *H*), 9.83 (s, 1H, N*H*), 10.09 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (DMSO–d_6): δ 32.5 (d, J = 56.6 Hz, *C*H_2C=O), 115.6, 119.1 (d, J = 89.0 Hz, quaternary *C*), 119.2, 122.2, 125.5 (quaternary *C*), 125.7, 130.5 (d, J = 12.0 Hz, PPh *C*), 134.2 (d, J = 9.8 Hz, PPh *C*), 135.4, 148.2 (quaternary *C*), 161.9 (d, J = 4.5 Hz, *C*=O). ^{31}P{^{1}H} NMR (DMSO–d_6): δ 21.8. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{23}NO_2P$ [M – BF_4]$^+$ 412.1466, found 412.1449.

Synthesis of 2a. To a 20 mL Schlenk flask, $PdCl_2$ (0.06 g, 0.34 mmol), **1a** (0.10 g, 0.34 mmol), and K_2CO_3 (0.19 g, 1.38 mmol) were dissolved in pyridine (8 mL) under a nitrogen atmosphere. The solution stirred at room temperature for 12 h. After vacuum drying, the reside was extracted with DCM/H_2O twice. The extract was dried over anhydrous $MgSO_4$, then evaporated under vacuum to yield a solid. Diethyl ether was added, and the resulting yellow solid was collected on frit and dried under vacuum. Yield: 0.118 g (74%). Mp = 132.8–133.5 °C (dec.). Anal. Calc. for $C_{19}H_{26}ClN_2OPPd$: C, 48.50; H, 5.57; N, 5.95. Found: C, 48.37; H, 5.12; N, 5.48 %. ^{1}H NMR ($CDCl_3$): δ 1.33–1.44 (m, 9H, CH_3), 1.92 (d, 1H, J = 6.0 Hz, Pd–C*H*), 2.22–2.53 (m, 6H, CH_2), 6.82–7.00 (m, 5H, Ph *H*, Py *H*), 7.18 (t, 2H, J = 12.0 Hz, Ph *H*), 7.66 (t, 1H, J = 15.0 Hz, Py *H*), 8.50 (d, 2H, J = 6.0 Hz, Py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ –2.9 (d, J = 46.0 Hz, Pd–*C*H), 6.3 (d, J = 6.0 Hz, *C*H_3), 14.9 (d, J = 50.5 Hz, *C*H_2),

122.7, 124.2, 124.6 (Py *C*), 128.2, 137.5 (Py *C*), 142.6, 151.8 (Py *C*), 169.9 (d, *J* = 3.0 Hz, *C*=O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 39.5.

Synthesis of 2b. The compound was prepared using a similar procedure to that of **2a**. A mixture of $PdCl_2$ (0.04 g, 0.23 mmol), **1b** (0.10 g, 0.23 mmol), and K_2CO_3 (0.12 g, 0.92 mmol) were employed. MeOH was added and the resulting yellow solid was collected on a frit and dried under vacuum. Yield: 0.08 g (58 %). Mp = 177.1–177.9 °C (dec.). Anal. Calc. for $C_{31}H_{26}ClN_2OPPd$: C, 60.58; H, 4.26; N, 4.55. Found: C, 60.03; H, 4.50; N, 4.22 %. ^{1}H NMR (DMSO–d_6): δ 3.53 (d, 1H, *J* = 3.0 Hz, Pd–C*H*), 6.74 (t, 1H, *J* = 12.0 Hz, Ph *H*), 6.94 (t, 2H, *J* = 15.0 Hz, Ph *H*), 7.09 (t, 2H, *J* = 12.0 Hz, Ph *H*), 7.46–7.65 (m, 10H, Ph *H*), 7.88–8.03 (m, 7H, Ph *H*, Py *H*), 8.43 (d, 1H, *J* = 3.0 Hz, Py *H*), 8.45 (d, 2H, *J* = 6.0 Hz, Py *H*). $^{13}C\{^{1}H\}$ NMR (DMSO–d_6): δ 7.3 (d, *J* = 42.2 Hz, Pd–*C*H), 122.4, (d, *J* = 86.7 Hz, quaternary *C*), 124.3, 125.2, 125.9 (Py *C*), 127.4, 129.4 (d, *J* = 19.6 Hz, PPh *C*), 133.6, 134.2 (d, *J* = 10.5 Hz, PPh *C*), 139.9 (Py *C*), 153.4 (Py *C*), 166.8 (d, *J* = 4.5 Hz, *C*=O). $^{31}P\{^{1}H\}$ NMR (DMSO–d_6): δ 28.1.

Synthesis of 2c. The compound was prepared using a similar procedure to that of **2a**. A mixture of $PdCl_2$ (0.03 g, 0.19 mmol), **1c** (0.10 g, 0.19 mmol), and K_2CO_3 (0.10 g, 0.76 mmol) was employed. Diethyl ether was added and the resulting yellow solid was collected on a frit and dried under vacuum. Yield: 0.09 g (71 %). Mp = 261.7–262.2 °C. (dec.) Anal. Calc. for $C_{34}H_{32}ClN_2O_4PPd$: C, 57.94; H, 4.58; N, 3.97. Found: C, 57.68; H, 4.42; N, 4.47 %. ^{1}H NMR (DMSO–d_6): δ 3.78 (s, 9H, OCH_3), 3.83 (s, 1H, Pd–C*H*), 6.76 (t, 1H, *J* = 12.0 Hz, Ar *H* or Ph *H*), 6.97–7.18 (m, 9H, Ar *H* or Ph *H,* Py *H*), 7.43

(d, 2H, *J* = 12.0 Hz, Ar *H* or Ph *H*), 7.68 (t, 1H, *J* = 15.0 Hz, Py *H*), 7.82 (t, 7H, *J* = 21.0 Hz, Ar *H* or Ph *H*), 8.39 (d, 2H, *J* = 3.0 Hz, Py *H*). $^{13}C\{^{1}H\}$ NMR (DMSO–d_6): δ 9.2 (d, *J* = 46.0 Hz, Pd–*C*H), 56.0 (O*C*H_3), 113.9 (d, *J* = 94.3 Hz, quaternary *C*), 115.1 (d, *J* = 12.0 Hz, PAr *C*), 121.6, 124.3, 125.0 (Py *C*), 127.4, 135.0 (d, *J* = 11.3 Hz, PAr *C*), 137.3 (Py *C*), 144.8, 153.2 (Py *C*), 163.1 (d, *J* = 2.2 Hz, quaternary *C*), 167.4 (d, *J* = 3.7 Hz, *C*=O). $^{31}P\{^{1}H\}$ NMR (DMSO–d_6): δ 26.0.

Synthesis of 2d. The compound was prepared using a similar procedure to that of **2a**. A mixture of $PdCl_2$ (0.03 g, 0.22 mmol), **1d** (0.10 g, 0.22 mmol), and K_2CO_3 (0.12 g, 0.88 mmol) was employed. MeOH was added and the resulting yellow solid was collected on a frit and dried under vacuum. Yield: 0.08 g (63 %). Mp = 217.9–218.5 °C (dec.). Anal. Calc. for $C_{31}H_{44}ClN_2OPPd$: C, 58.84; H, 7.01; N, 4.42. Found: C, 59.30; H, 6.57; N, 4.65 %. ^{1}H NMR ($CDCl_3$): δ 1.18–1.33 (m, 10H, Cy *H*), 1.78–2.53 (m, 20H, Cy *H*), 2.57–2.65 (m, 1H, Pd–C*H*), 2.86 (q, 3H, *J* = 39.0 Hz, Cy *H*), 6.83–7.18 (m, 7H, Ph *H*, Py *H*), 7.64 (t, 1H, *J* = 12.0 Hz, Py *H*), 8.50 (d, 2H, *J* = 6.0 Hz, Py *H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ –8.1 (d, *J* = 38.4 Hz, Pd–*C*H), 26.1 (Cy *C*), 26.8 (d, *J* = 11.3 Hz, Cy *C*), 27.0 (d, *J* = 3.7 Hz, Cy *C*), 27.2 (d, *J* = 11.3 Hz, Cy *C*), 27.8 (d, *J* = 3.7 Hz, Cy *C*), 32.4 (d, *J* = 40.7 Hz, Cy *C*), 122.6, 124.3, 124.5, 128.2 (Py *C*), 137.3 (Py *C*), 142.4, 151.8 (Py *C*), 17.2 (d, *J* = 3.7 Hz, *C*=O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 35.5.

Synthesis of 2e. The compound was prepared with a similar procedure to that of **2a**. A mixture of $Pd(OAc)_2$ (0.05 g, 0.22 mmol), **1e** (0.10 g, 0.22 mmol), and NaOAc (0.07 g, 0.89 mmol) were used. MeOH was added and the yellow solid formed was collected on frit and dried under vacuum. Yield:

0.07 g (54 %). Mp = 176.2–176.8 °C (dec.). Anal. Calc. for $C_{31}H_{26}ClN_2O_2PPd$: C, 59.04; H, 4.15; N, 4.44. Found: C, 59.27; H, 4.63; N, 4.30 %. ^{1}H NMR (DMSO–d_6): δ 3.76 (d, 1H, *J* = 3.0 Hz, Pd–C*H*), 6.56 (d, 1H, *J* = 9.0 Hz, Ar *H*), 6.81 (t, 1H, *J* = 15.0 Hz, Ar *H*), 7.00 (d, 1H, *J* = 6.0 Hz, Ar *H*), 7.13 (t, 1H, *J* = 12.0 Hz, Ar *H*), 7.50–7.65 (m, 10H, Ph *H*), 7.90–8.03 (m, 7H, Ph *H*, Py *H*), 8.48 (s, 1H, Py *H*), 8.76 (d, 2H, *J* = 6.0 Hz, Py *H*), 9.43 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (DMSO–d_6): δ 7.0 (d, *J* = 46.0 Hz, Pd–*C*H), 117.8, 118.8, 122.6 (d, *J* = 86.0 Hz, quaternary *C*), 125.1, 125.3, 125.9 (Py *C*), 129.6 (d, *J* = 12.0 Hz, PPh *C*), 133.8, 134.1 (d, *J* = 10.5 Hz, PPh *C*), 139.9 (Py *C*), 149.6, 153.2, 153.4 (Py *C*), 167.0 (d, *J* = 3.7 Hz, *C*=O). ^{31}P{^{1}H} NMR (DMSO–d_6): δ 28.0.

Synthesis of 3b. To a 20 mL Schlenk flask, $PdCl_2$ (0.04 g, 0.23 mmol), **1b** (0.10 g, 0.23 mmol), and K_2CO_3 (0.12 g, 0.92 mmol) were dissolved in dry DMF (8 mL) under nitrogen atmosphere. The solution was allowed to stir at room temperature for 12 h. After drying under vacuum, the residual was extracted with DCM/H_2O twice. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a solid. MeOH was added and the yellow solid formed was collected on frit and dried under vacuum. Yield: 0.13 g (53 %). Mp = 235.8–236.3°C (dec.). Anal. Calc. for $C_{52}H_{42}Cl_2N_2O_2P_2Pd_2$: C, 58.31; H, 3.95; N, 2.61. Found：C, 58.08; H, 3.66; N, 2.79 %. ^{1}H NMR (DMSO–d_6): δ 3.27 (s, 1H, Pd–C*H*), 6.77 (t, 1H, *J* = 15.0 Hz, Ph *H*), 6.96 (t, 2H, *J* = 15.0 Hz, Ph *H*), 7.18 (d, 2H, *J* = 6.0 Hz, Ph *H*), 7.59–7.75 (m, 10H, Ph *H*), 7.96–8.03 (m, 5H, Ph *H*). ^{13}C{^{1}H} NMR (DMSO–d_6): δ 16.4 (d, *J* = 37.7 Hz, Pd–*C*H), 122.4, 122.5(d, *J* = 86.0 Hz, quaternary *C*), 123.1, 124.0,

127.6, 129.6 (d, *J* = 12.0 Hz, PPh *C*), 134.1, 135.1 (d, *J* = 9.0 Hz, PPh *C*), 165.2 (d, *J* = 4.5 Hz, *C*=O). $^{31}P\{^{1}H\}$ NMR (DMSO–d_6): δ 28.3.

Synthesis of 4e. The compound was prepared with a similar procedure to that of **2a**. A mixture of $Pd(OAc)_2$ (0.04 g, 0.20 mmol), **1e′** (0.10 g, 0.20 mmol), and NaOAc (0.06 g, 0.80 mmol) were used. THF was added and the white solid formed was collected on frit and dried under vacuum. Yield: 0.05 g (32 %). Mp = 192.6-193.4 °C (dec.). Anal. Calc. for $C_{36}H_{31}BF_4N_3O_2PPd$: C, 56.75; H, 4.10; N,5.51. Found： C, 56.68; H, 3.82; N, 5.63 %. ^{1}H NMR (DMSO–d_6): δ 3.87 (d, 1H, *J* = 3.0 Hz, Pd–C*H*), 6.14 (s, 1H, Ar *H*), 6.53 (d, 1H, *J* = 6.0 Hz, Ar *H*), 7.20 (t, 2H, *J* = 12.0 Hz, Ar *H*), 7.55–7.70 (m, 10H, Ph *H*), 7.97–8.07 (m, 9H, Ph *H*, Py *H*), 8.63 (d, 2H, *J* = 3.0 Hz, Py *H*), 9.02 (s, 1H, O*H*), 9.15 (d, 4H, *J* = 3.0 Hz, Py *H*). $^{13}C\{^{1}H\}$ NMR (DMSO–d_6): δ 7.2 (d, *J* = 46.0 Hz, Pd–*C*H), 117.9, 118.9, 122.4 (d, *J* = 86.0 Hz, quaternary *C*), 125.7, 126.2, 127.7 (Py *C*), 129.7 (d, *J* = 12.8 Hz, PPh *C*), 134.1 (d, *J* = 19.8 Hz, PAr *C*), 139.0, 141.3 (Py *C*), 150.4, 151.4 (Py *C*), 152.3, 167.2 (d, *J* = 2.2 Hz, *C*=O). $^{31}P\{^{1}H\}$ NMR (DMSO–d_6): δ 28.6.

X-ray structural determination. All the crystals suitable for X-ray structural determination were obtained by slow evaporation from the dichloromethane/hexane solvent combination. Structures of **2b**, **2e**, and **4e** were obtained from a Bruker APEX II diffractometer with a CCD area detector. Data acquisition was carried out at 150(2) K employing MoKα radiation (λ = 0.71073 Å) from a sealed X-ray tube. The unit cell parameters were refined using the least-squares method and the data acquisition and reduction were carried out using the Bruker APEX and SAINT software packages.[1] Absorption

corrections were performed using the multi-scan method implemented in SADABS.[2] Structures of **2a**, **2c**, **3d**, and **3b** were obtained using a Rigaku XtaLab Synerg DW X-ray diffractometer equipped with a MicroMax-007 HF microfocus rotating anode that generated CuKα radiation (λ = 1.54184 Å) and a HyPix-Arc 150° curved hybrid photon counting X-ray detector. The data acquisition and reduction were carried out using the CrysAlisPro 1.171.42.51a software.[3] Empirical absorption correction was performed using spherical harmonics implemented in SCALE3 ABSPACK.[3] The experiments were conducted at National Tsing Hua University, Hsinchu city, Taiwan

In the structural analysis of all the compounds, direct methods were initially used to solve the crystal structures. The obtained solutions were further refined using full-matrix least squares methods against F^2 with the SHELXL program.[4] Refinement of the non-hydrogen atoms was carried out using anisotropic refinement methods, taking into account the anisotropy of thermal motion. The positions of the hydrogen atoms were calculated and fixed at their respective calculated positions. Riding refinements were then performed for the hydrogen atoms. CCDC file numbers are 2340510 (**2a**), 2340511 (**2b**), 2340512 (**2c**), 2340513 (**2d**), 2340515 (**2e**), 2340516 (**3b**), and 2340517 (**4e**).

Computational studies. All calculations were carried out using the Gaussian 09W program.[5] For the metal complexes, geometry optimizations were carried out at the B3LYP[6]/LANL2DZ[7] level of theory, based on the coordinates from the X-ray structural data. Energy calculations were performed using the M06-L functional with def2-TZVP[8] basis sets. The natural bond orbital (NBO) analysis was performed using the NBO 3.1 program within Gaussian 09W.[9] Charge decomposition analysis (CDA)

was carried out using the Multiwfn 3.8 program based on M06-L/def2-TZVP levels of theory. To account for the solvent effects, the polarized continuum model (PCM) was employed to optimize all the geometries in pyridine solvent.[10] This model considers the influence of the solvent on the molecular structure and properties during the optimization process.

Table S1. Crystallographic data

	2a	**2b**	**2c**	**2e**
empirical formula	$C_{19}H_{26}ClN_2OPPd$	$C_{31}H_{25}ClN_2OPPd\cdot CH_2Cl_2$	$C_{34}H_{32}ClN_2O_4PPd$	$C_{31}H_{26}ClN_2O_2PPd\cdot CH_2Cl_2$
formula weight	471.24	699.28	705.43	716.28
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	20.8409(6)	13.0545(11)	17.4769(2)	12.9136(11)
b, Å	9.6630(2)	14.5057(12)	10.10810(10)	18.0641(15)
c, Å	21.7185(6)	16.7574(14)	17.5375(3)	13.3406(11)
α, deg	90	90	90	90
β, deg	114.714(3)	100.750(5)	98.1770(10)	99.507(4)
γ, deg	90	90	90	90
V, Å^3	3973.2(2)	3117.6(5)	3066.65(7)	3069.3(4)
T, K	100(2)	150(2)	100(2)	150(2)
Z	8	4	4	4
F(000)	1920	1412	1440	1448
no. of unique data	3553	6818	6031	6705
no. of params refined	230	361	391	378
R_1[a] [$I > 2\sigma I$]	0.0349	0.0449	0.0320	0.0459
wR_2[b] (all data)	0.1090	0.1307	0.1045	0.1186

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$

Table S2. Crystallographic data

	3b	**3d**	**4e**
empirical formula	$C_{26}H_{21}ClNOPPd$	$C_{26}H_{39}ClNOPPd$	$C_{36}H_{31}N_3O_2PPd\cdot BF_4$
formula weight	536.26	554.40	761.82
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	14.2817(11)	9.87687(19)	13.6635(12)
b, Å	9.8382(8)	19.9674(4)	10.8979(10)
c, Å	17.6371(12)	14.8230(3)	23.520(2)
α, deg	90	90	90
β, deg	104.783(7)	103.5669(19)	105.835(4)
γ, deg	90	90	90
V, Å^3	2396.1(3)	2841.74(10)	3369.3(5)
T, K	100(2)	100(2)	150(2)
Z	4	4	4
F(000)	1080	1152	1544
no. of unique data	4538	5079	7355
no. of params refined	281	281	433
$R_1{}^a$ [$I > 2\sigma I$]	0.0371	0.0454	0.0393
$wR_2{}^b$ (all data)	0.0999	0.1950	0.0913

$^a R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$

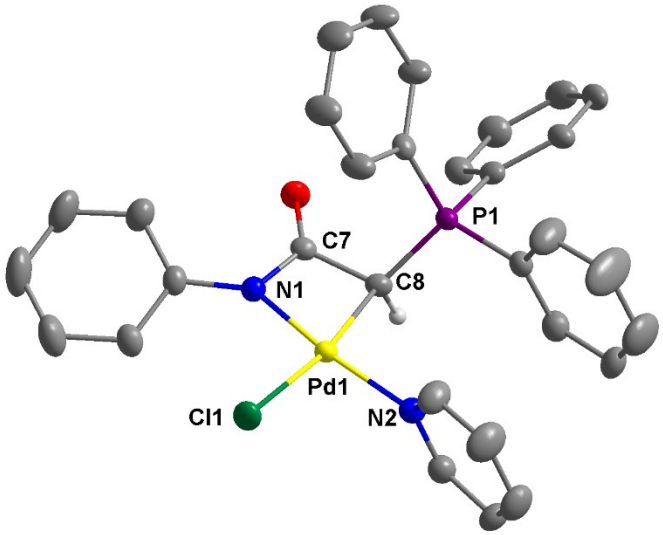


Figure S1. Thermal ellipsoid plot of **2b** (50% probability). Hydrogen atoms except that on C8 are omitted for clarity. Selected bond distances (Å) and angles (º): Pd1—C8, 2.068(4); Pd1—Cl1, 2.3624(10); Pd1—N1, 2.022(3); Pd1—N2, 2.045(3); C8—Pd1—N1, 67.12(13); N1—Pd1—Cl1, 103.28(9); Cl1—Pd1—N2, 86.14(9); N2—Pd1—C8, 103.52(14); N1—Pd1—N2, 170.31(12); C8—Pd1—Cl1, 170.26(11).

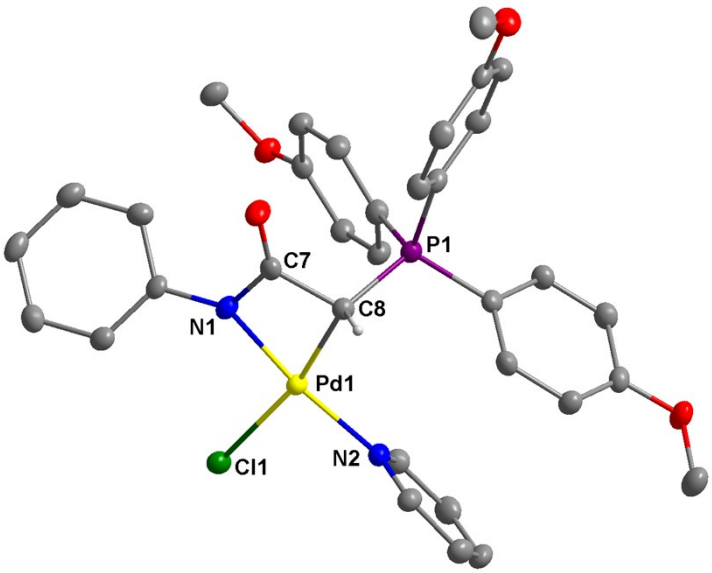


Figure S2. Thermal ellipsoid plot of **2c** (50% probability). Hydrogen atoms except that on C8 are omitted for clarity. Selected bond distances (Å) and angles (º): Pd1—C8, 2.082(3); Pd1—Cl1,

2.3649(6); Pd1—N1, 2.007(2); Pd1—N2, 2.058(2); C8—Pd1—N1, 66.99(10); N1—Pd1—Cl1, 100.79(7); Cl1—Pd1—N2, 86.56(6); N2—Pd1—C8, 105.81(10); N1—Pd1—N2, 172.55(9); C8—Pd1—Cl1, 166.54(7).

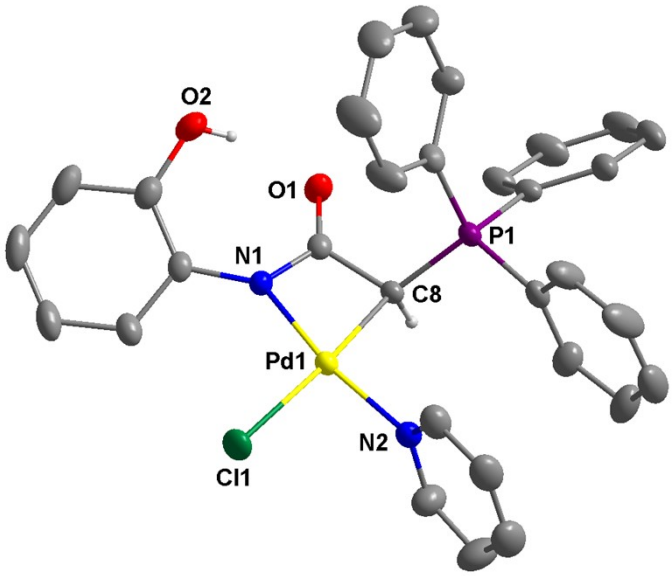


Figure S3. Thermal ellipsoid plot of **2e** (50% probability). Hydrogen atoms except that on C8 and O2 are omitted for clarity. Selected bond distances (Å) and angles (º): Pd1—C8, 2.051(3); Pd1—Cl1, 2.3735(9); Pd1—N1, 2.035(3); Pd1—N2, 2.031(3); C8—Pd1—N1, 67.23(12); N1—Pd1—Cl1, 106.43(8); Cl1—Pd1—N2, 84.10(9); N2—Pd1—C8, 102.17(13); N1—Pd1—N2, 169.39(12); C8—Pd1—Cl1, 172.15(10).

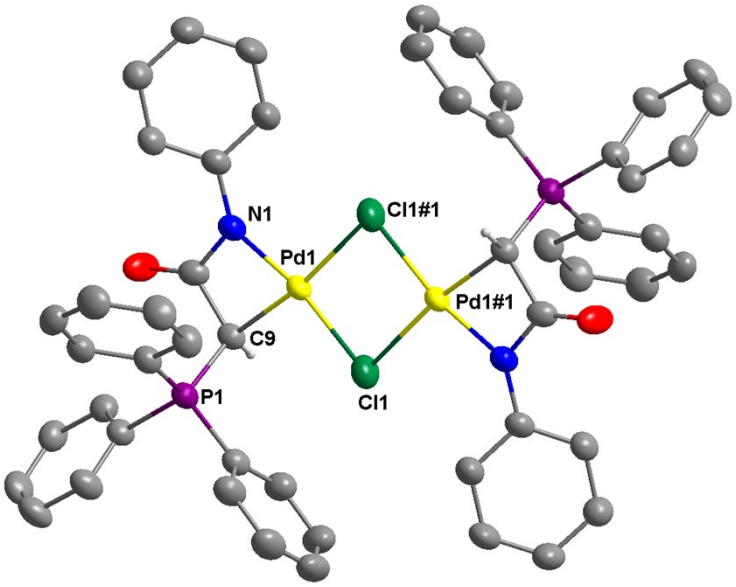


Figure S4. Thermal ellipsoid plot of **3b** (50% probability). Hydrogen atoms except that on C9 are omitted for clarity. Selected bond distances (Å) and angles (º): Pd1—C9, 2.053(3); Pd1—N1, 2.017(3); Pd1—Cl1, 2.3536(10); Pd1—Cl1#1, 2.3948(9); Cl1#1—Pd1—N1, 103.44(9); N1—Pd1—C9, 67.34(13); C9—Pd1—Cl1, 103.07(10); Cl1—Pd1—Cl#1, 86.21(4); N1—Pd1—Cl1, 170.24(9); Cl1#1—Pd1—C9, 170.48(10). Symmetry code #1: 1 – x, 1 – y, 1 – z.□

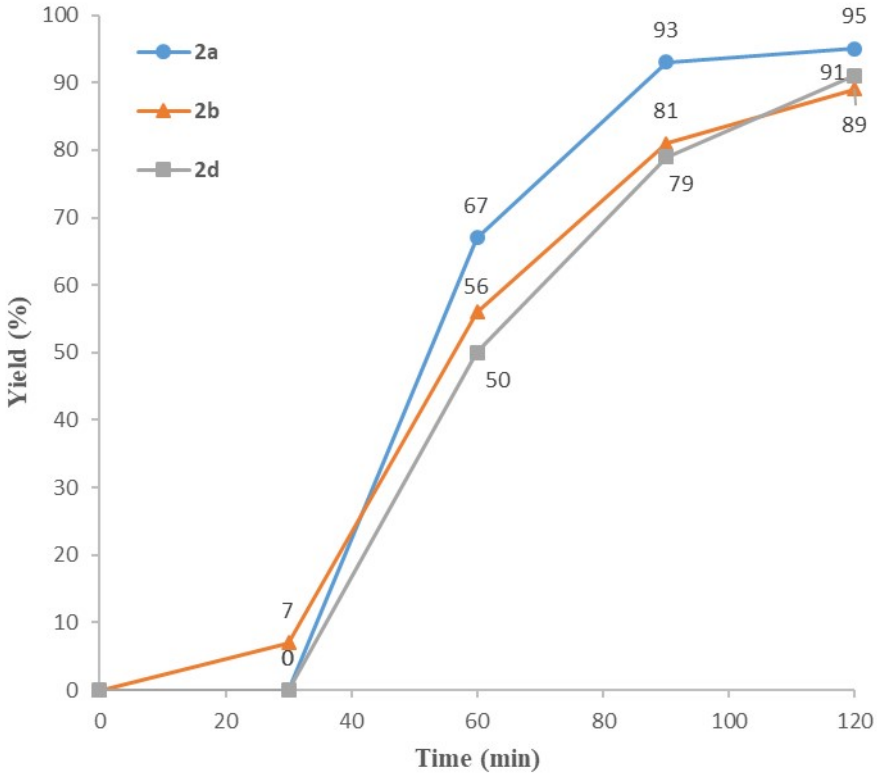


Figure S5. Time-yield curves of the Mizoroki-Heck coupling reaction between 4-chloroacetophenone and styrene catalyzed by complexes **2a**, **2b**, and **2d**.

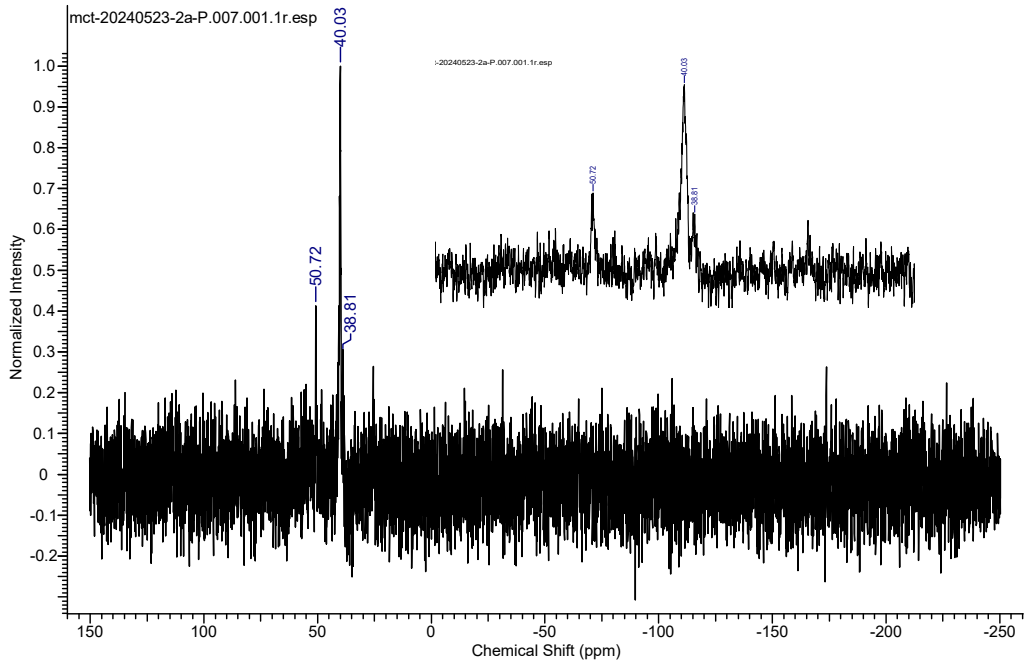


Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of catalytic solution of complex **2a** in DMSO-d_6, post-heating at 140°C for 30 Minutes, without substrates. The spectrum displays a signal from complex **2a** at 40.03 ppm, a peak at 50.72 ppm attributed to an oxidized product, and an additional peak at 38.81 ppm linked to an active palladium(0) species.

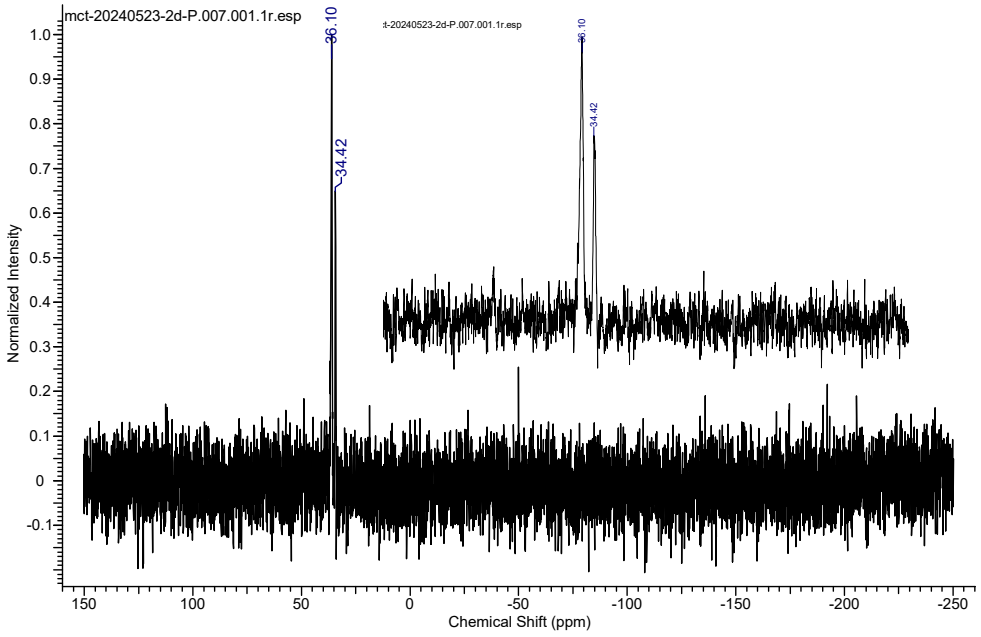


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of catalytic solution of complex **2d** in DMSO-d_6, post-heating at 140°C for 30 Minutes, without substrates. The spectrum displays a signal from complex **2d** at 36.10 ppm and an additional peak at 34.42 ppm linked to an active palladium(0) species.

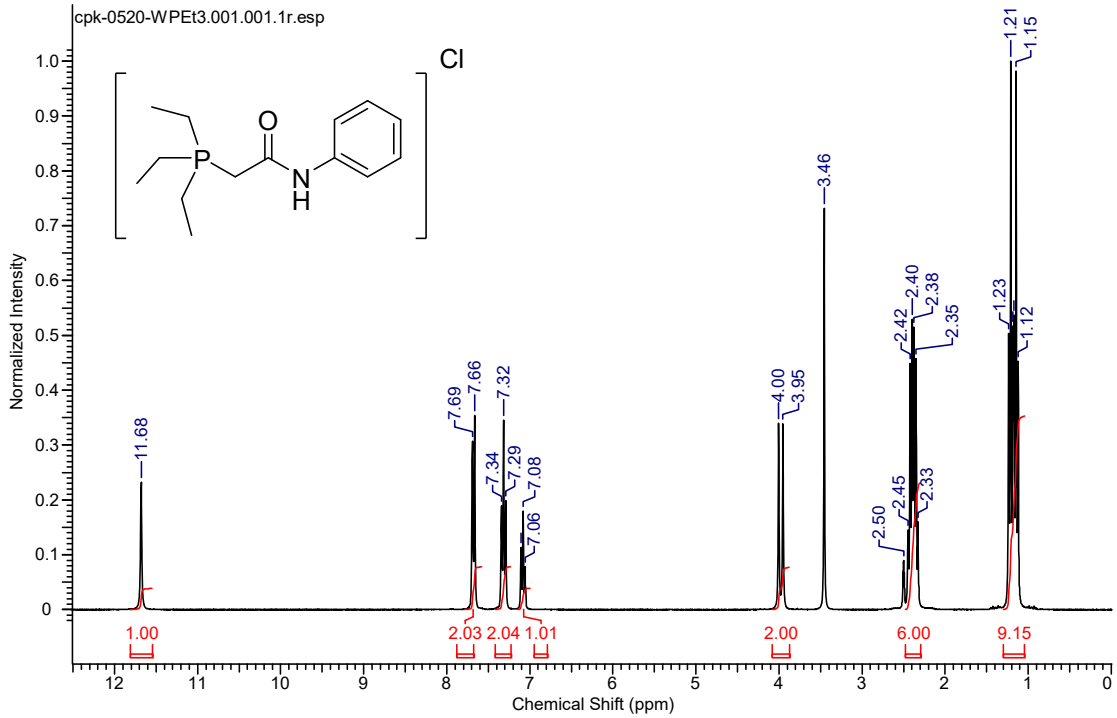


Figure S8. ^{1}H NMR spectrum of **1a**

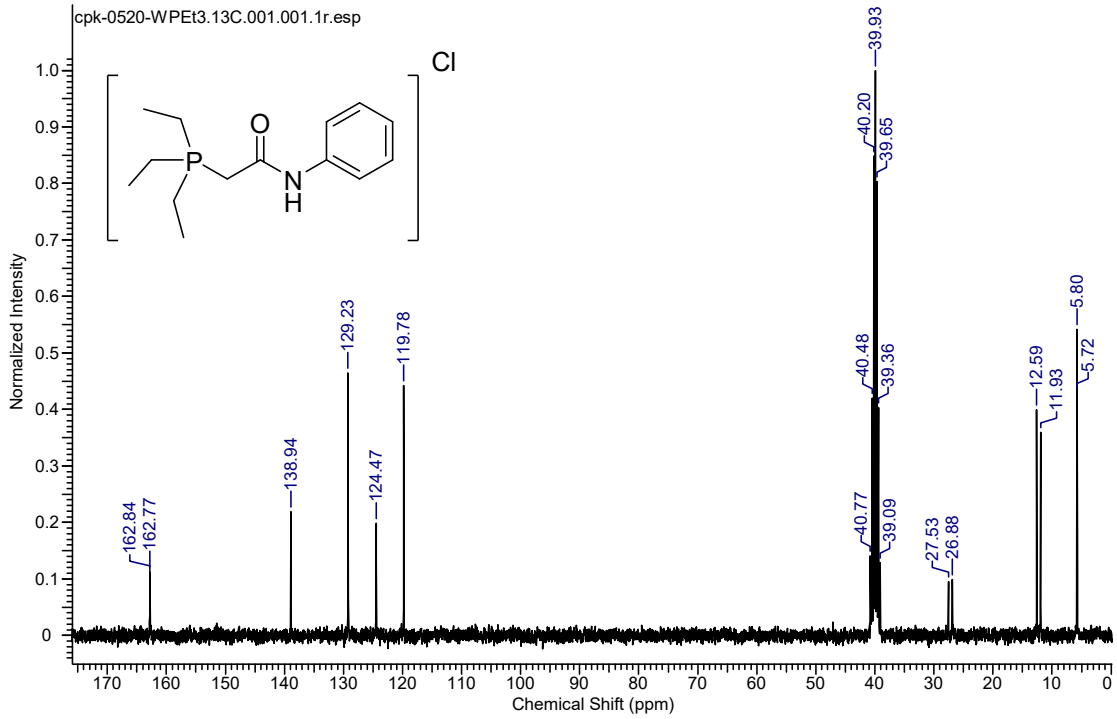


Figure S9. ^{13}C{^{1}H} NMR spectrum of **1a**

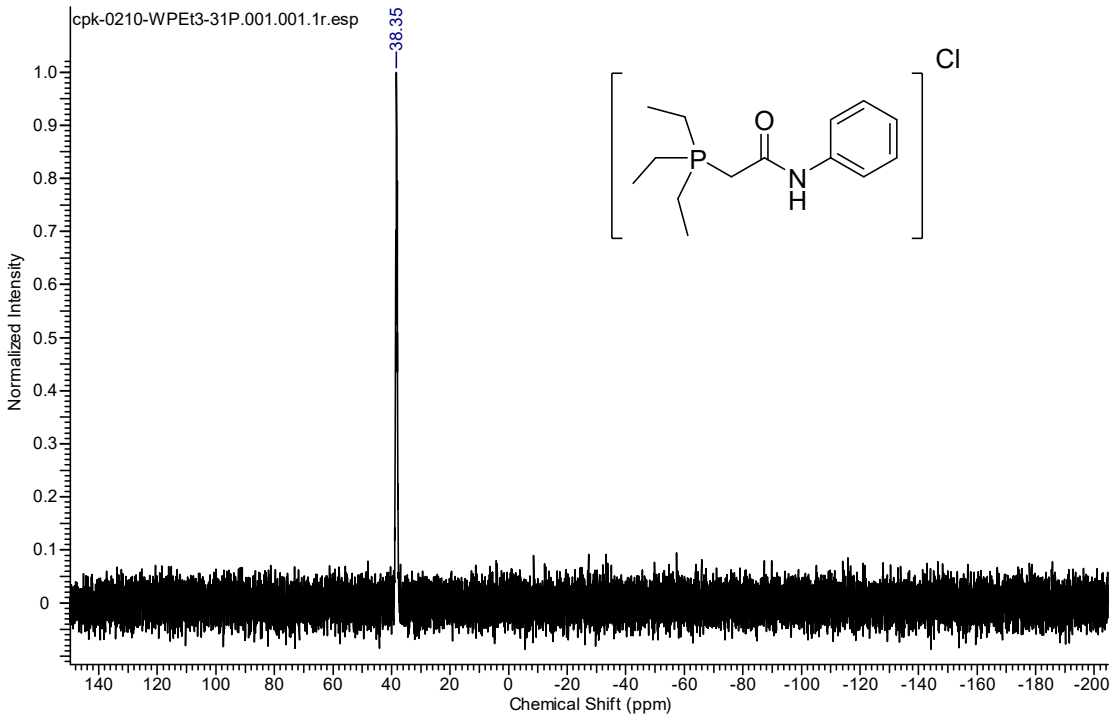


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **1a**

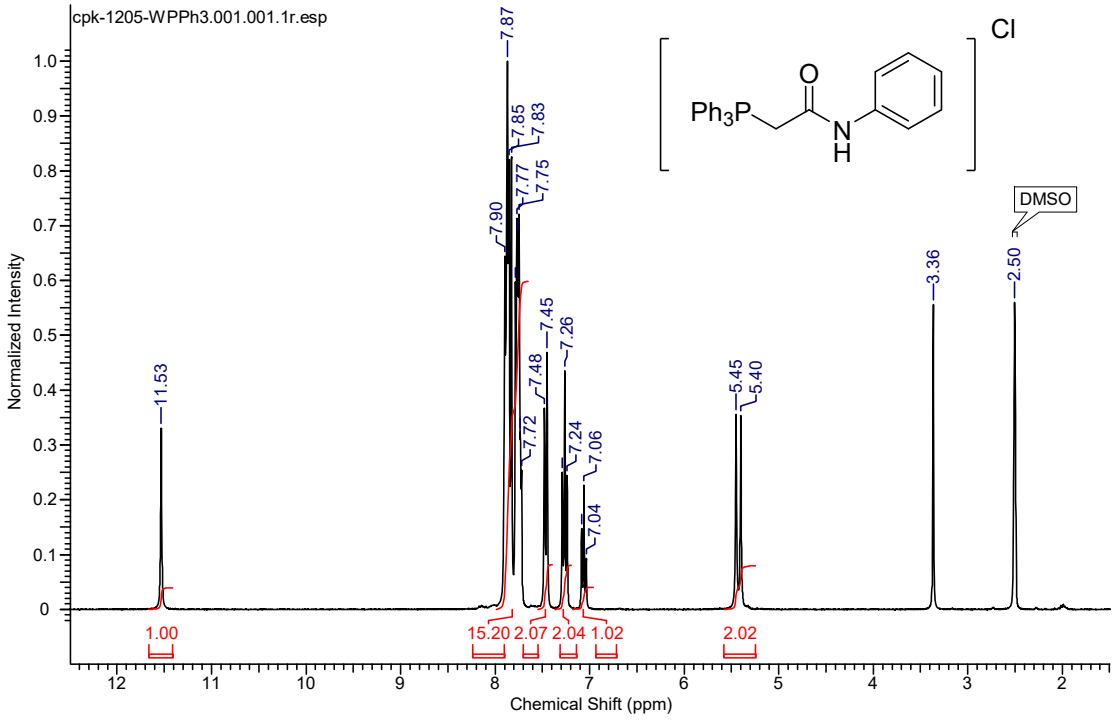


Figure S11. ^{1}H NMR spectrum of **1b**

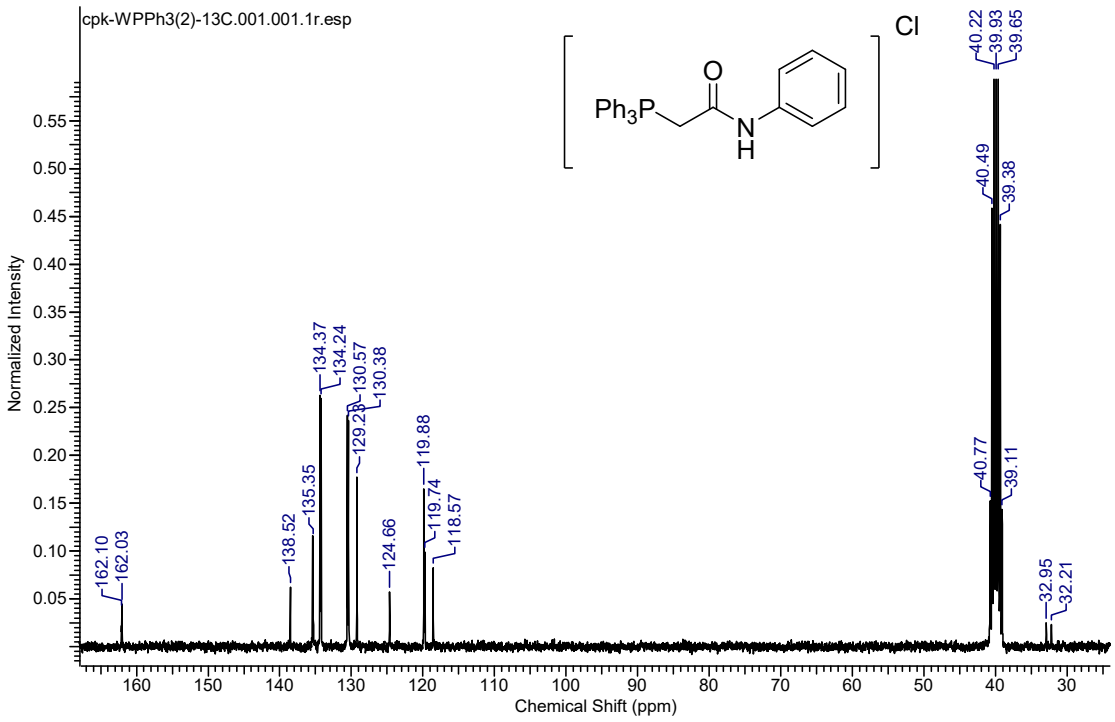


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **1b**

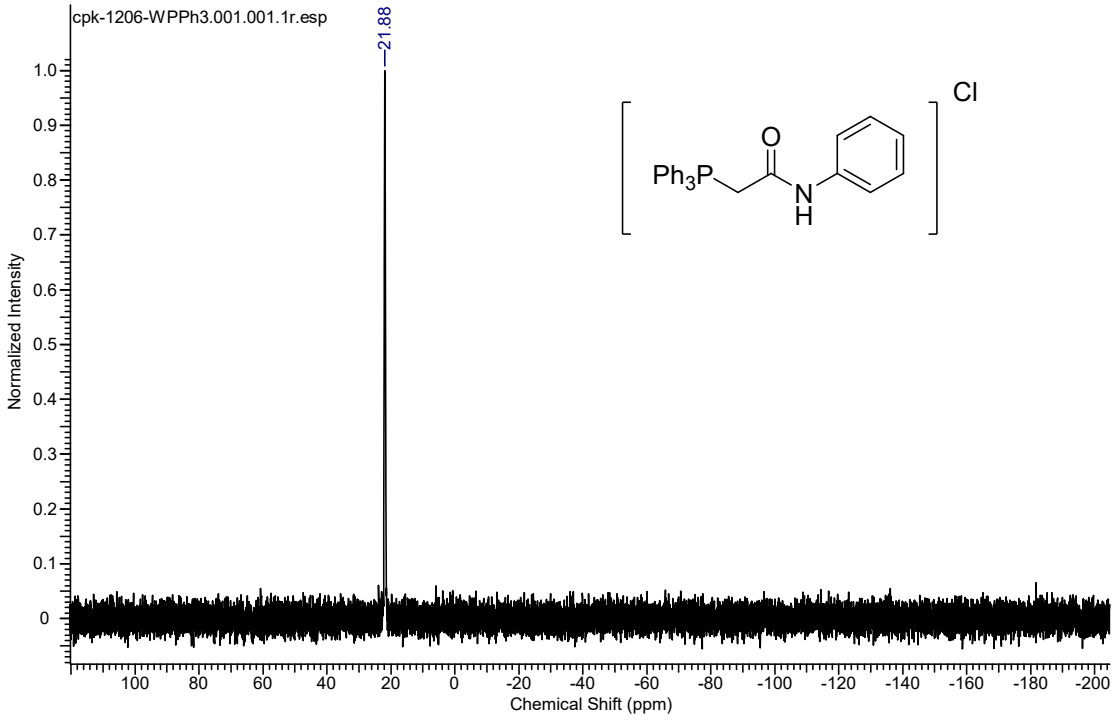


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **1b**

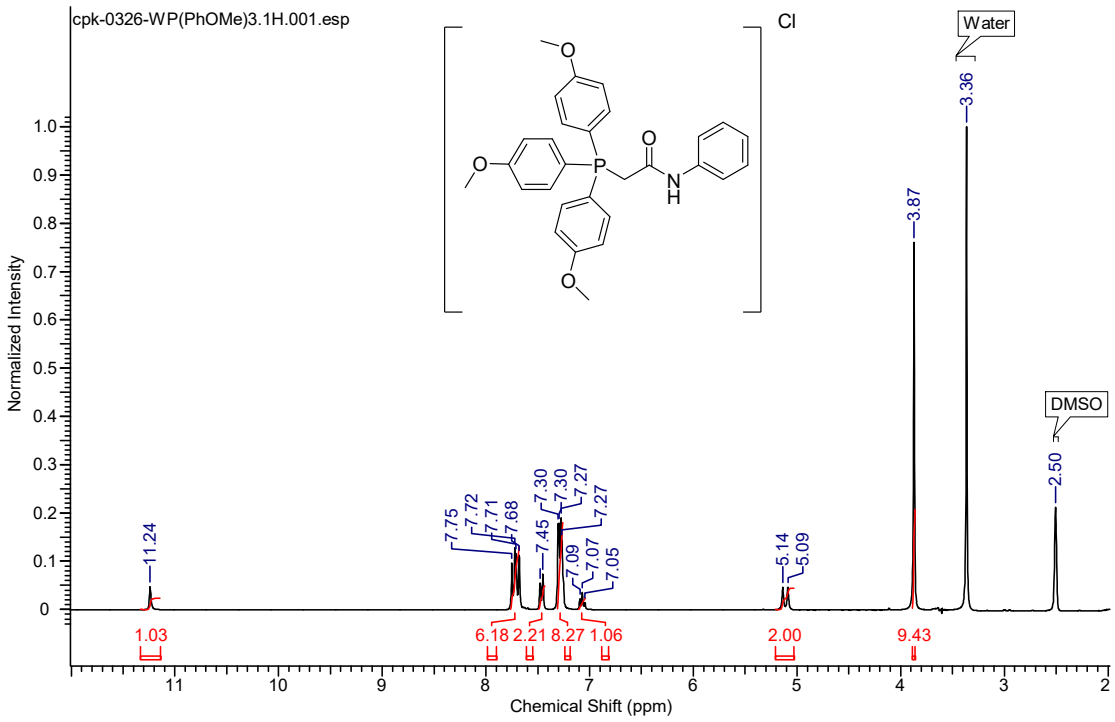


Figure S14. ^{1}H NMR spectrum of **1c**

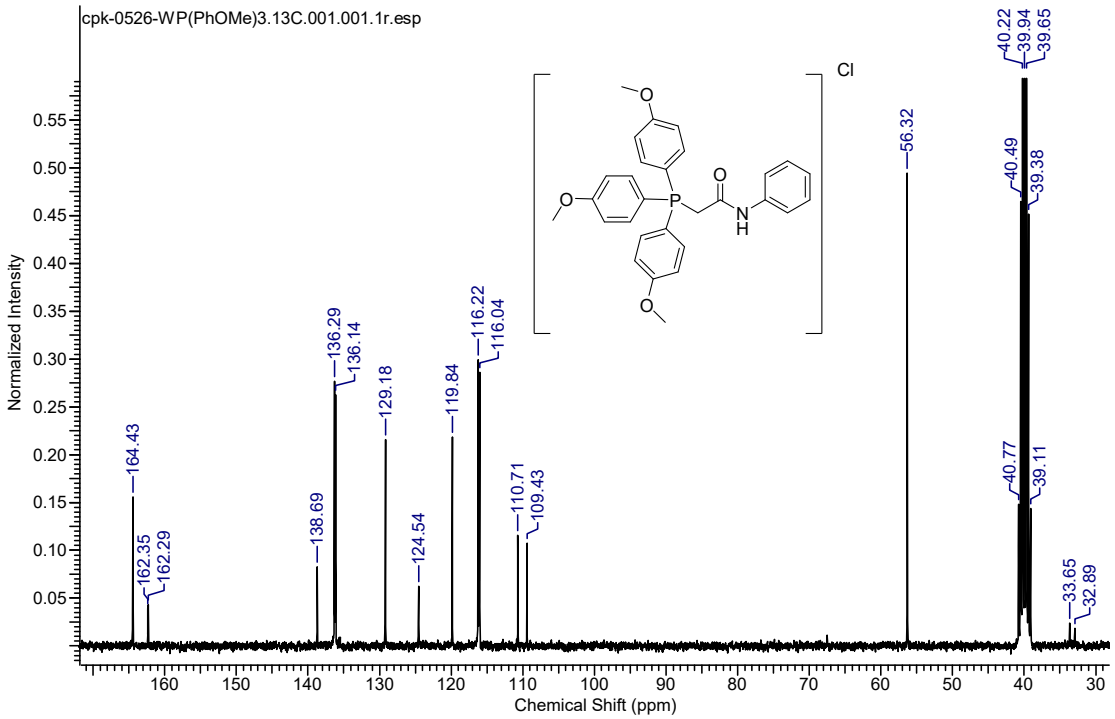


Figure S15. ^{13}C{^{1}H} NMR spectrum of **1c**

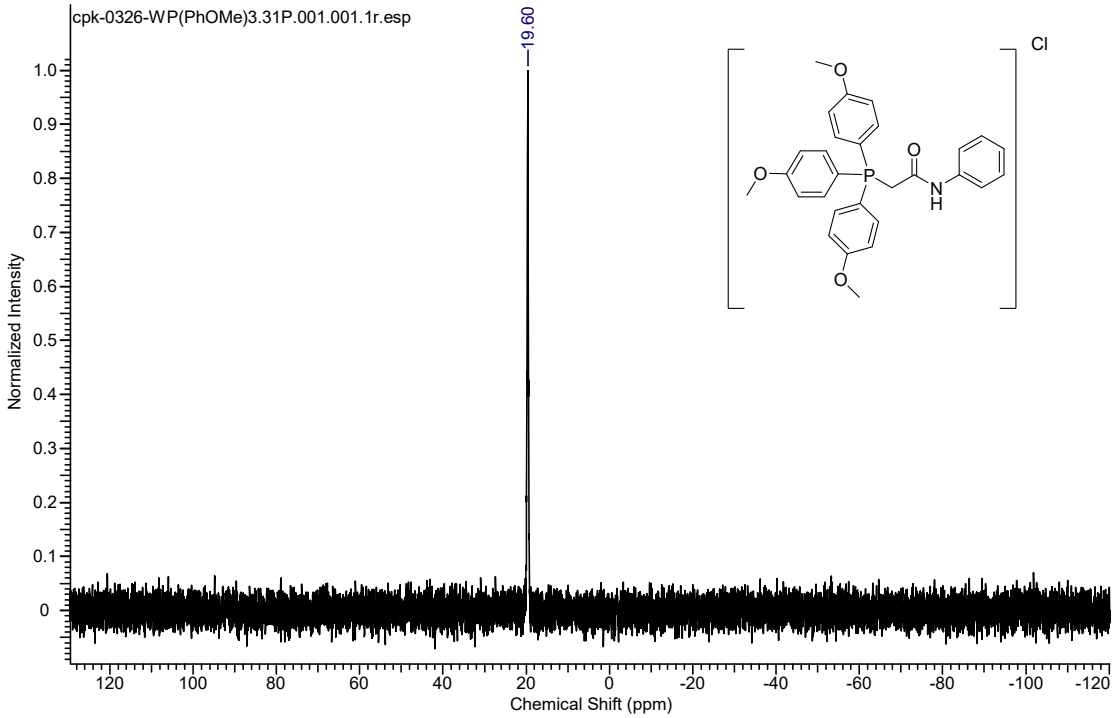


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **1c**

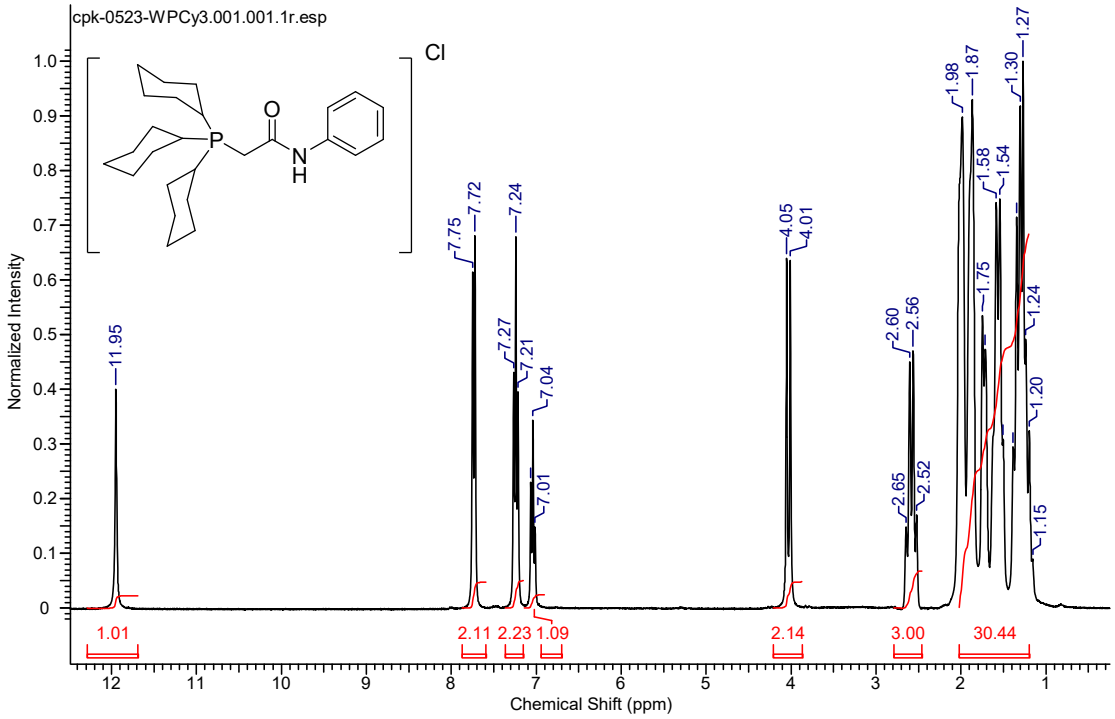


Figure S17. ^{1}H NMR spectrum of **1d**

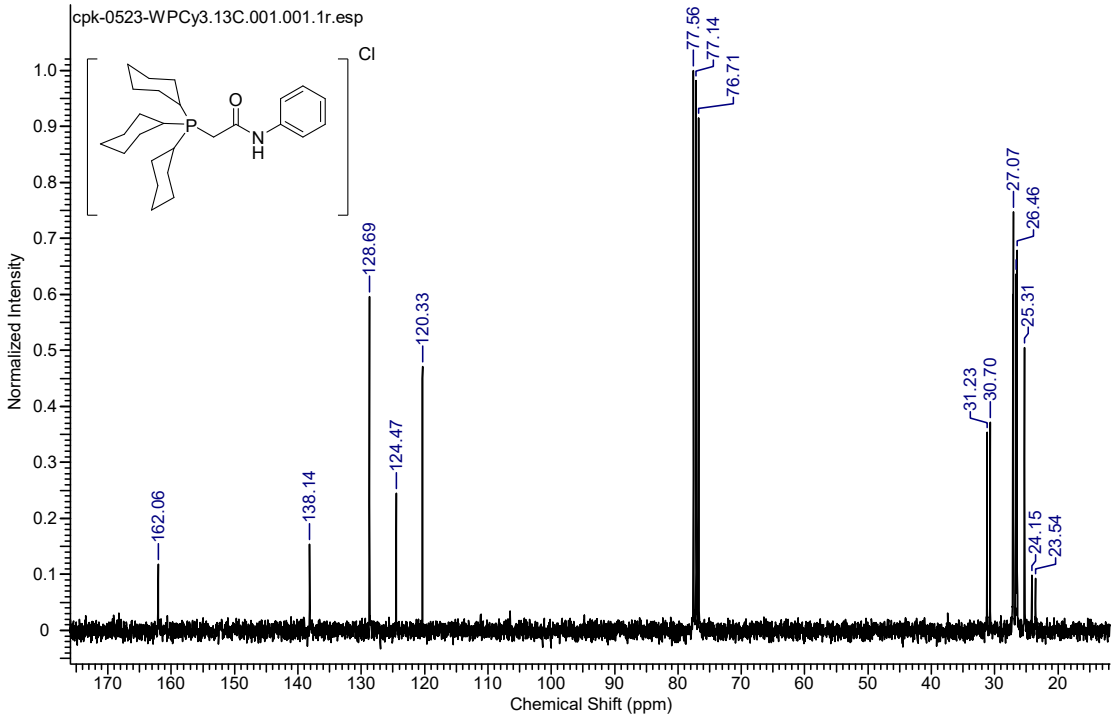


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **1d**

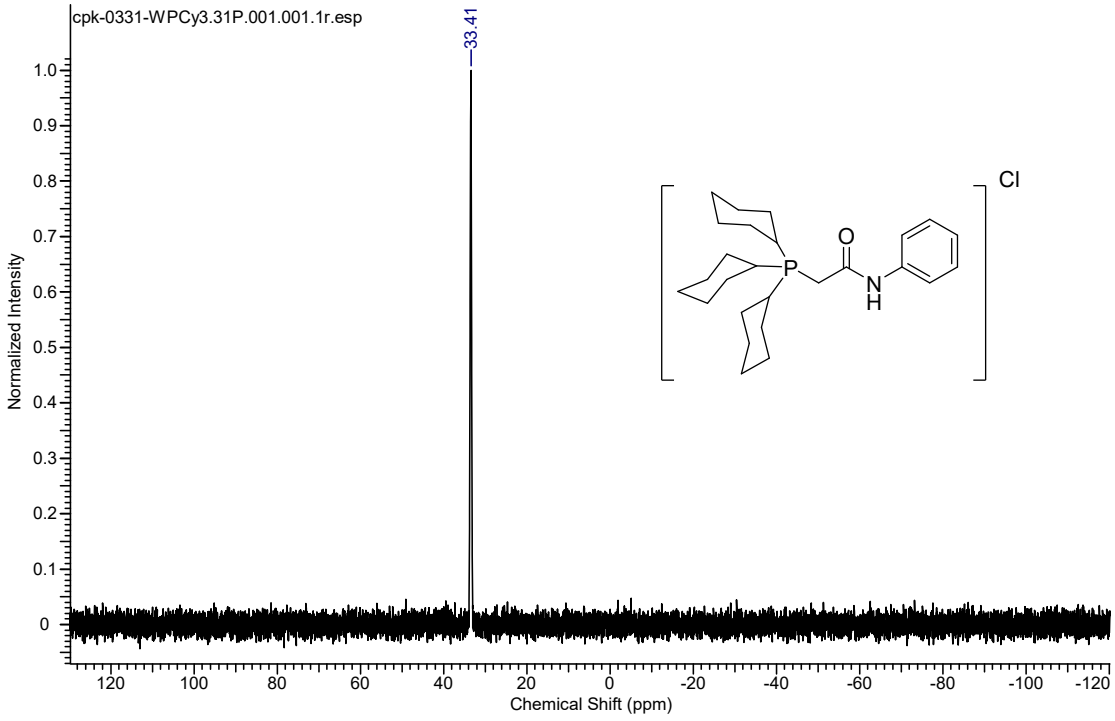


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **1d**

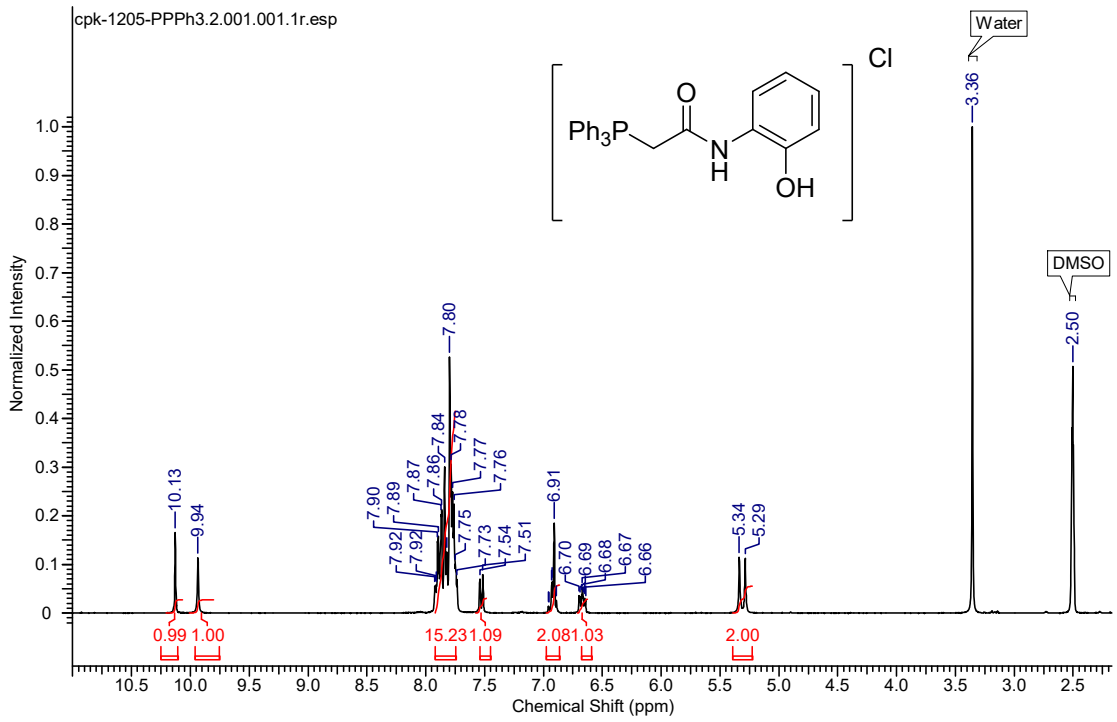


Figure S20. ^{1}H NMR spectrum of **1e**

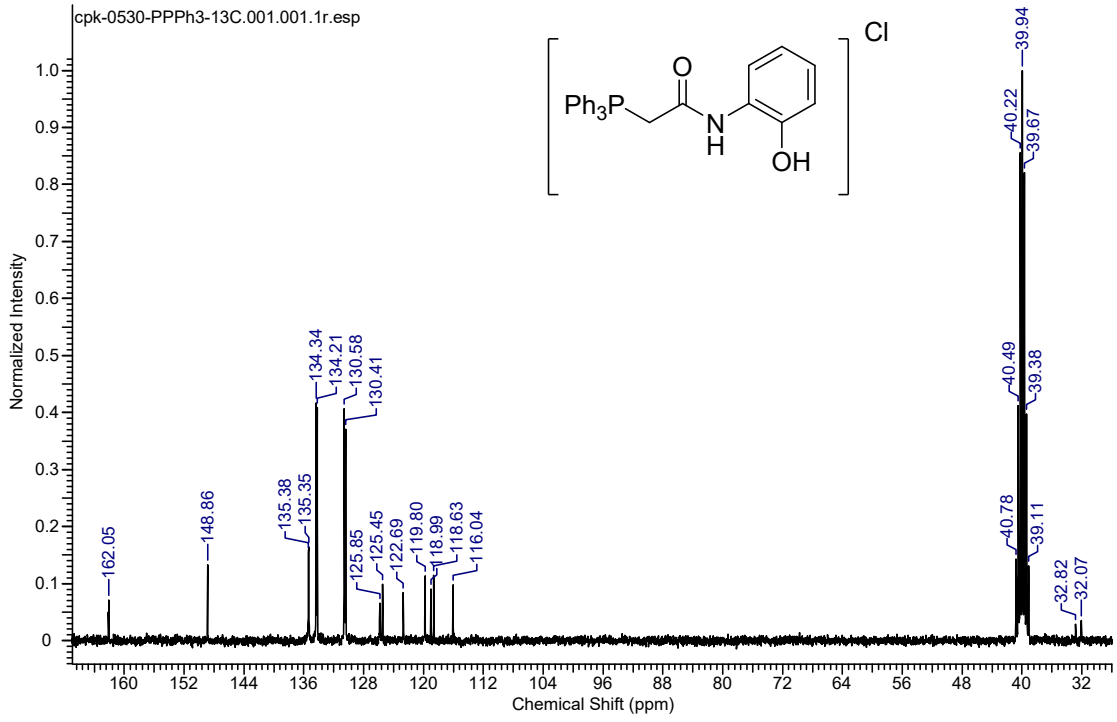


Figure S21. ^{13}C{^{1}H} NMR spectrum of **1e**

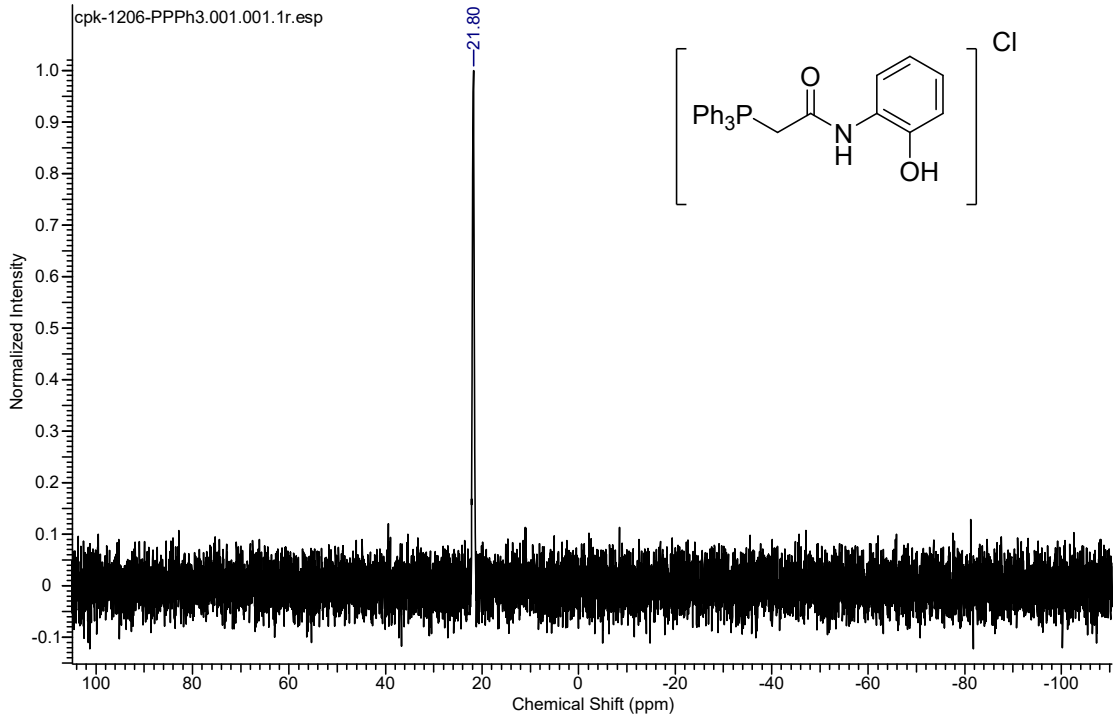


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **1e**

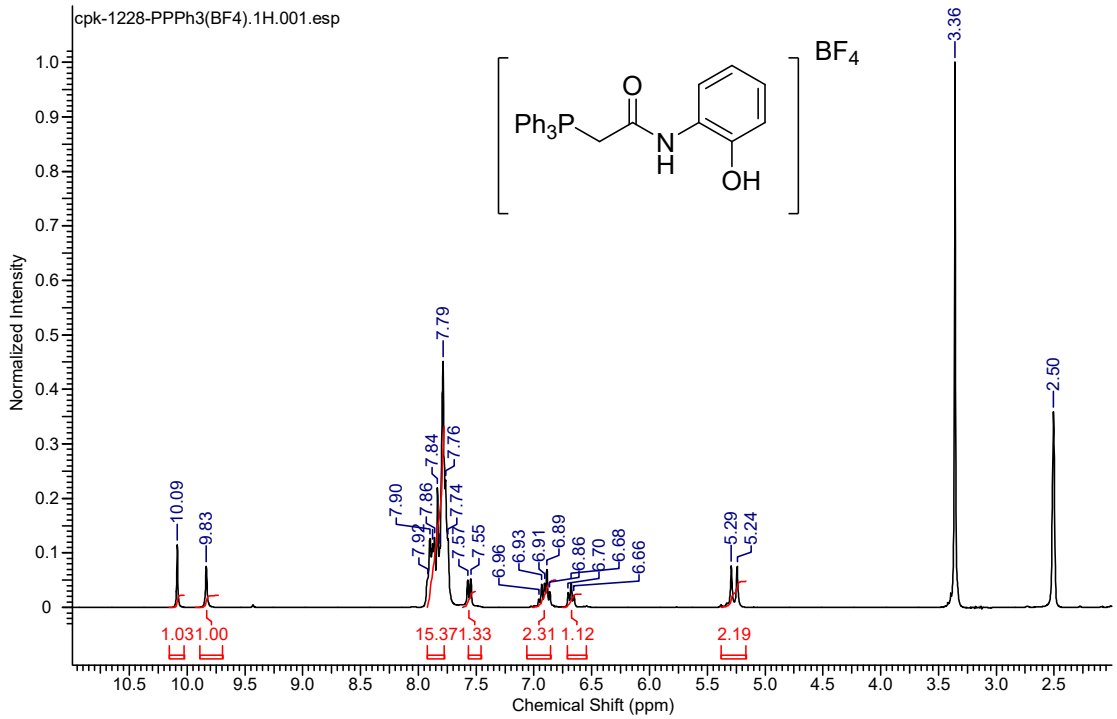


Figure S23. ^{1}H NMR spectrum of **1e′**

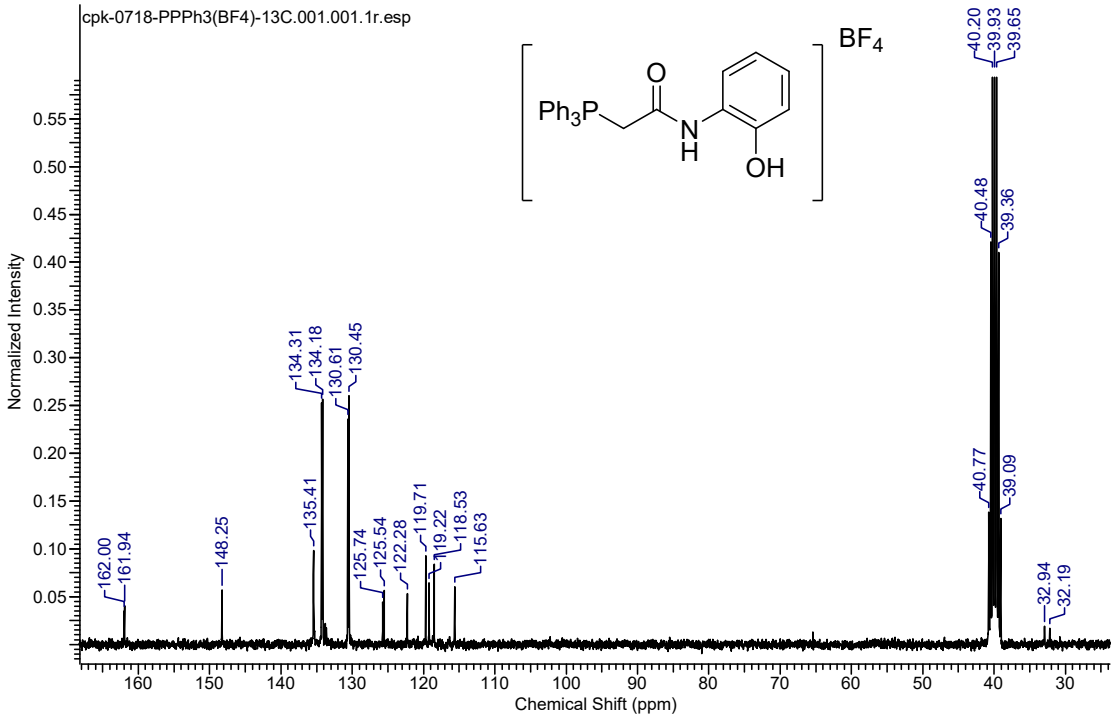


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **1e′**

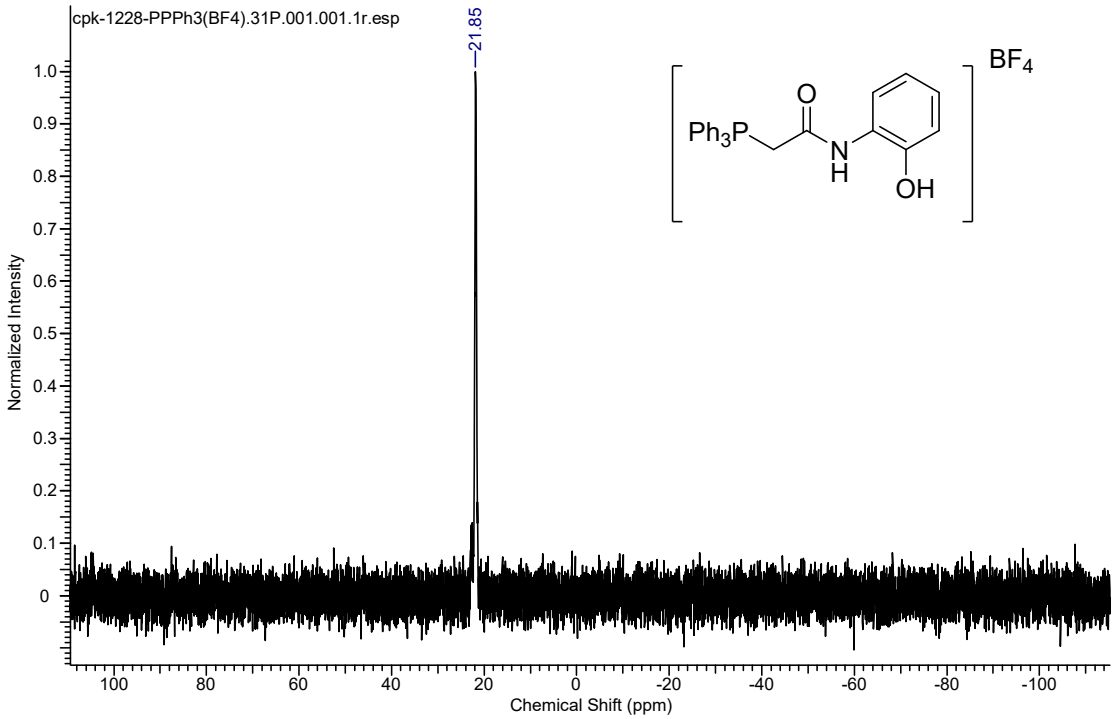


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **1e′**

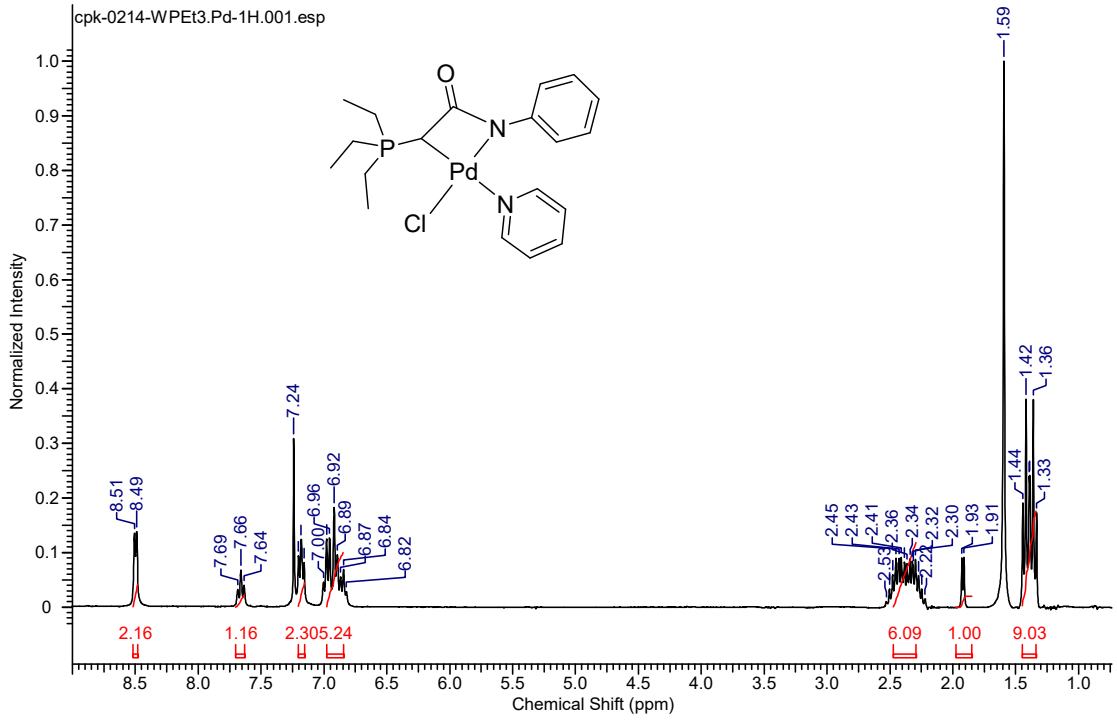


Figure S26. ^{1}H NMR spectrum of **2a**

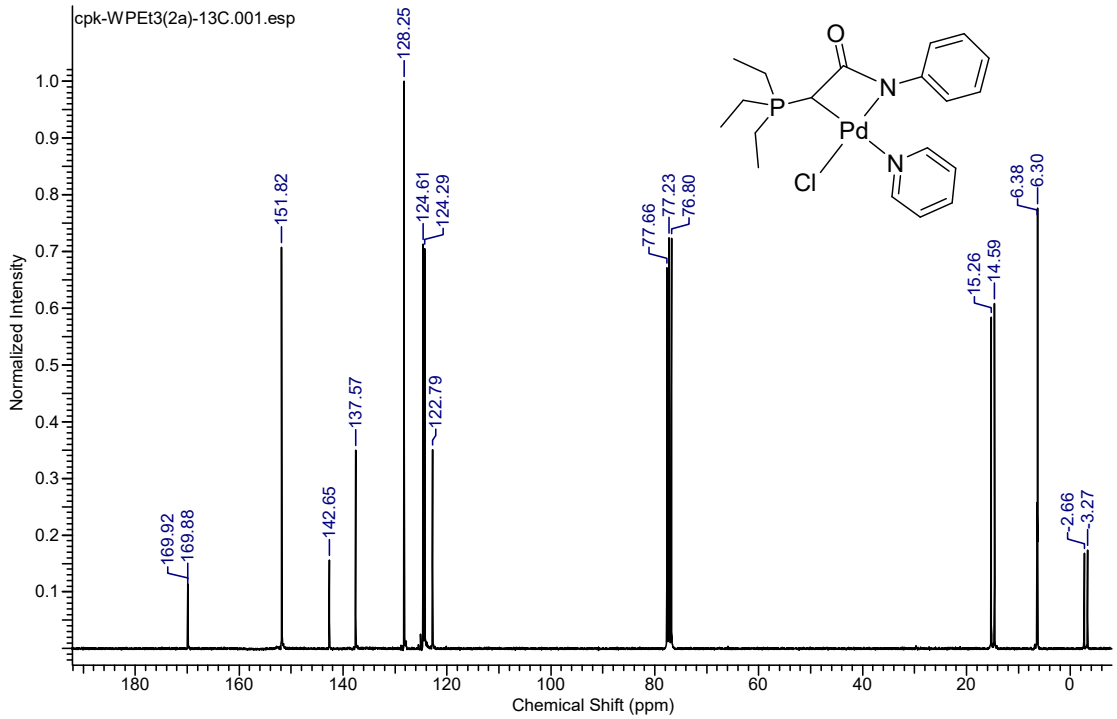


Figure S28. ^{13}C{^{1}H} NMR spectrum of **2a**

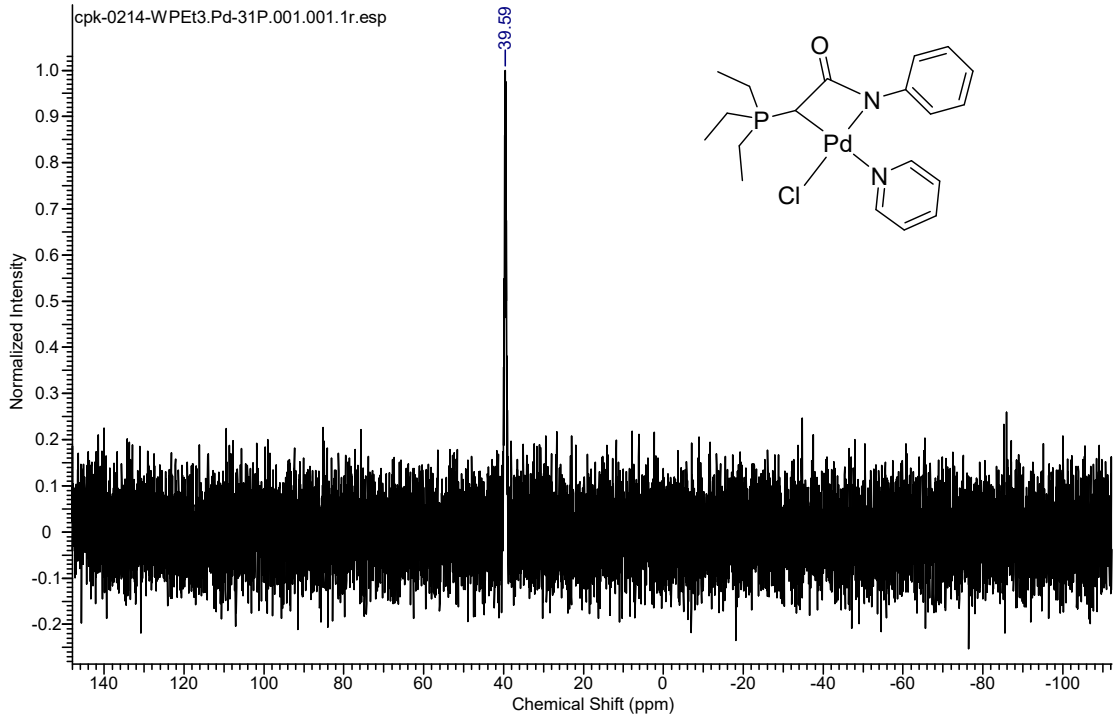


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of **2a**

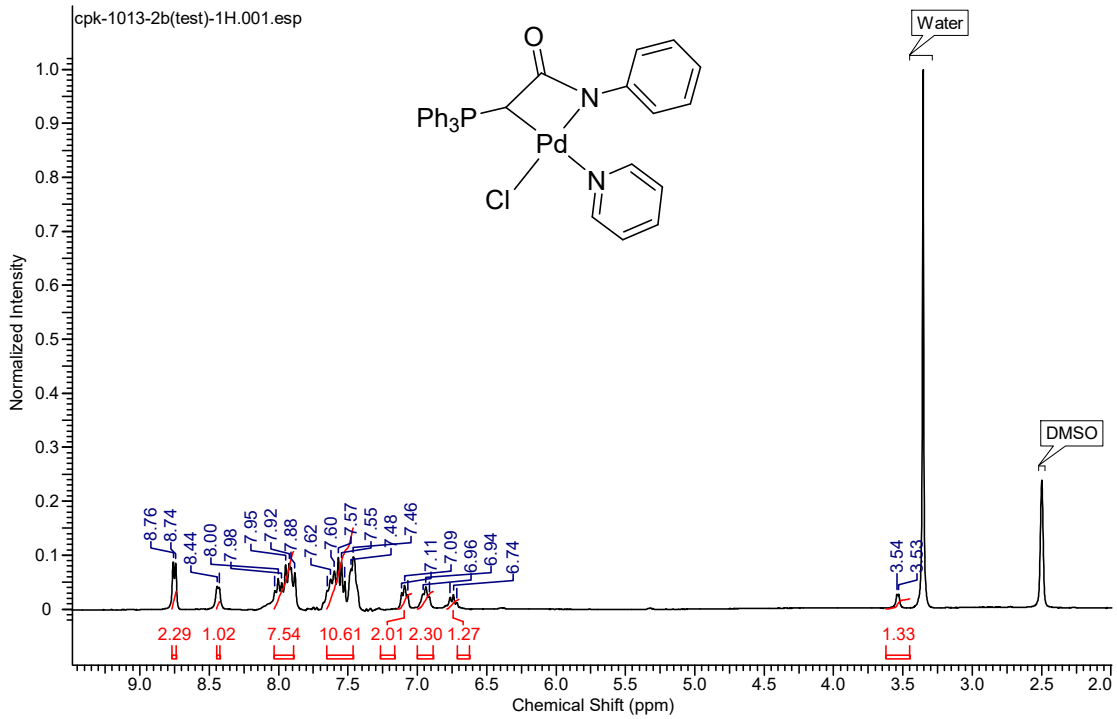


Figure S30. ^{1}H NMR spectrum of **2b**

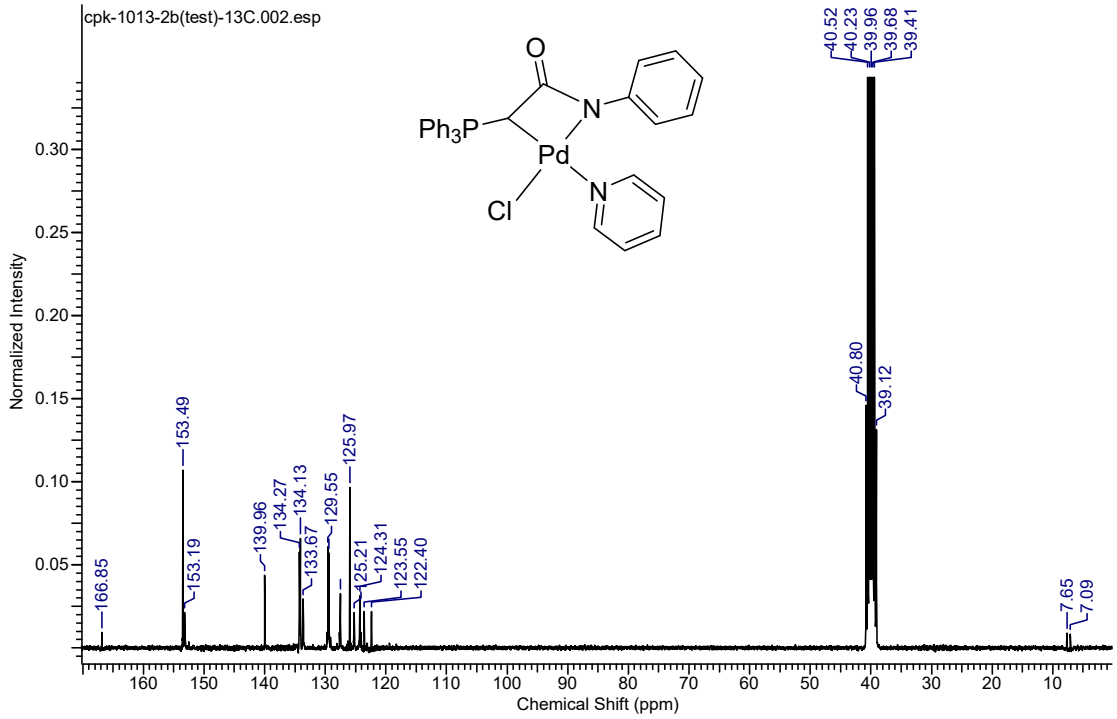


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **2b**

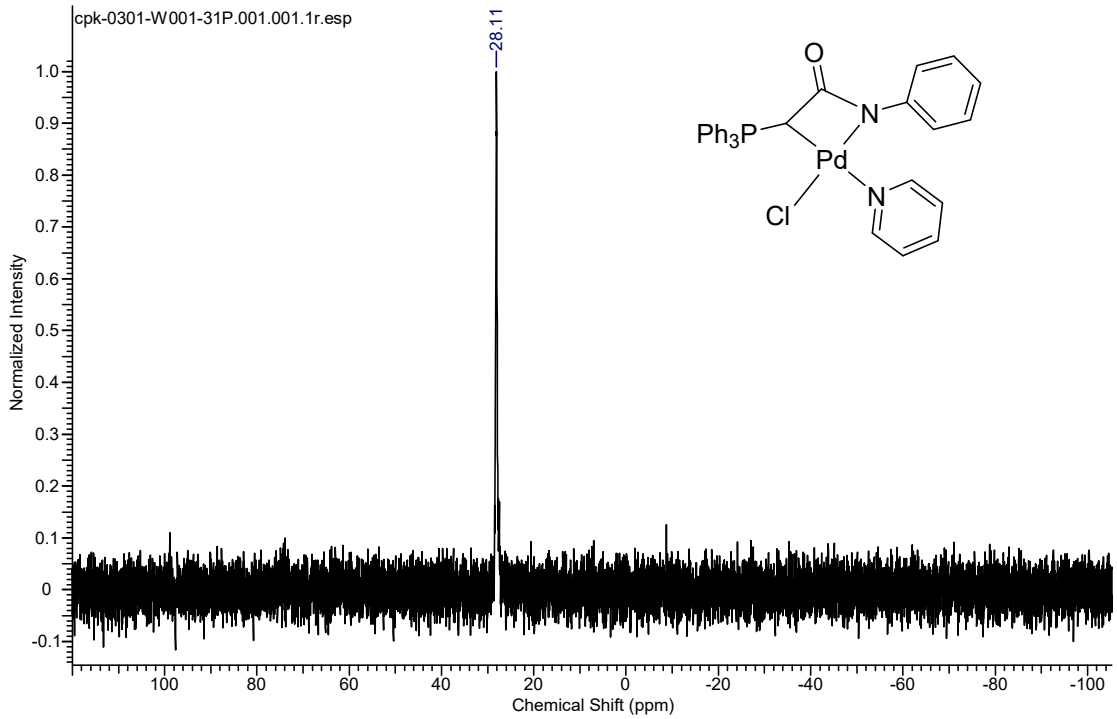


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of **2b**

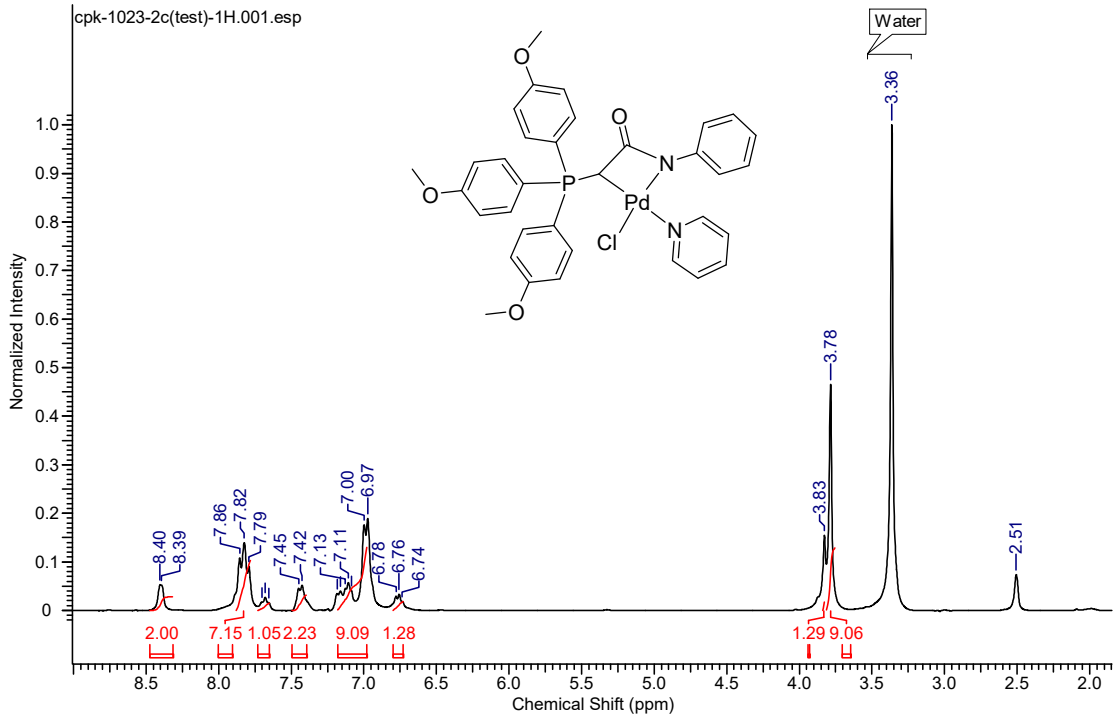


Figure S33. ^{1}H NMR spectrum of **2c**

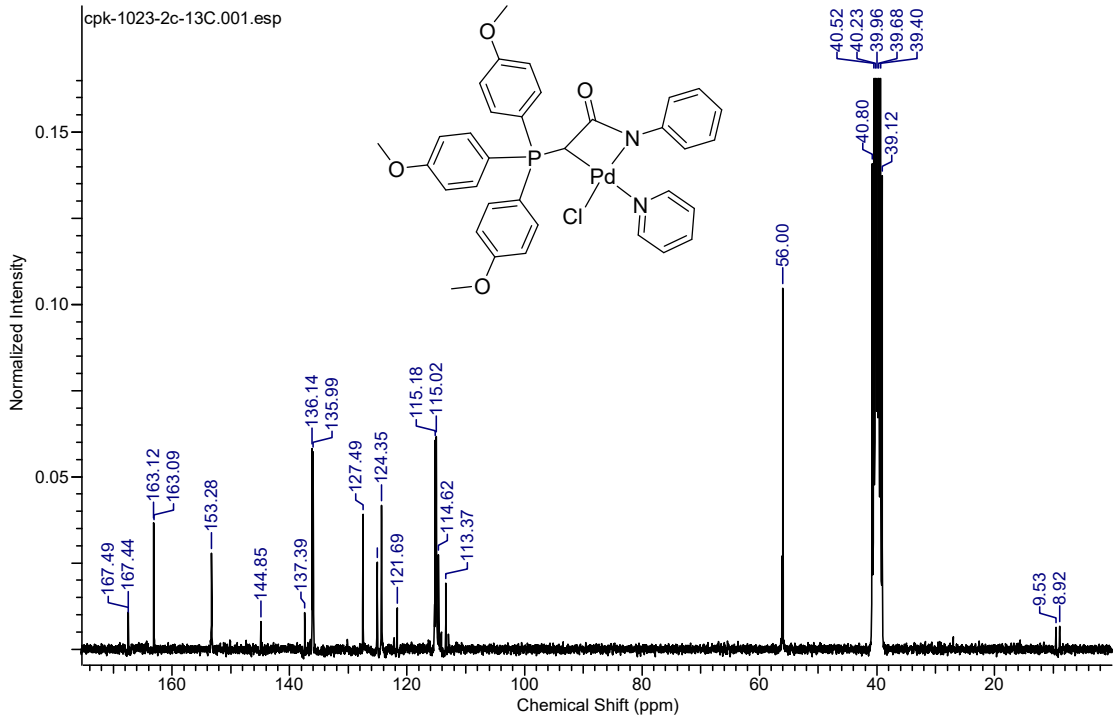


Figure S34. ^{13}C{^{1}H} NMR spectrum of **2c**

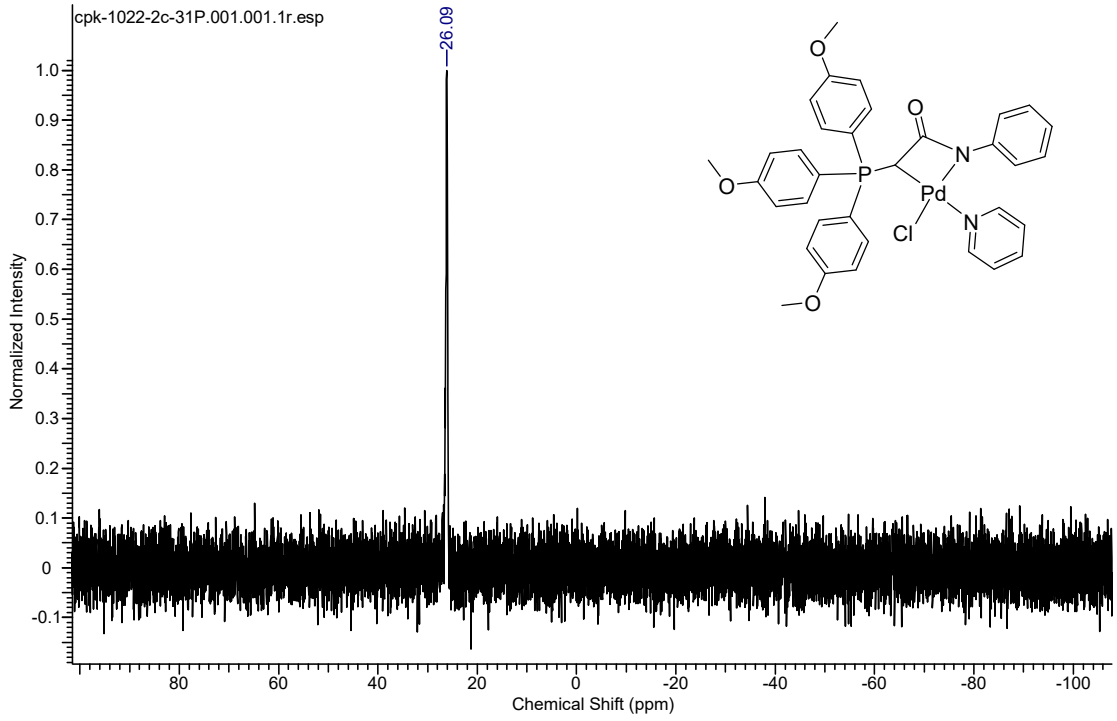


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of **2c**

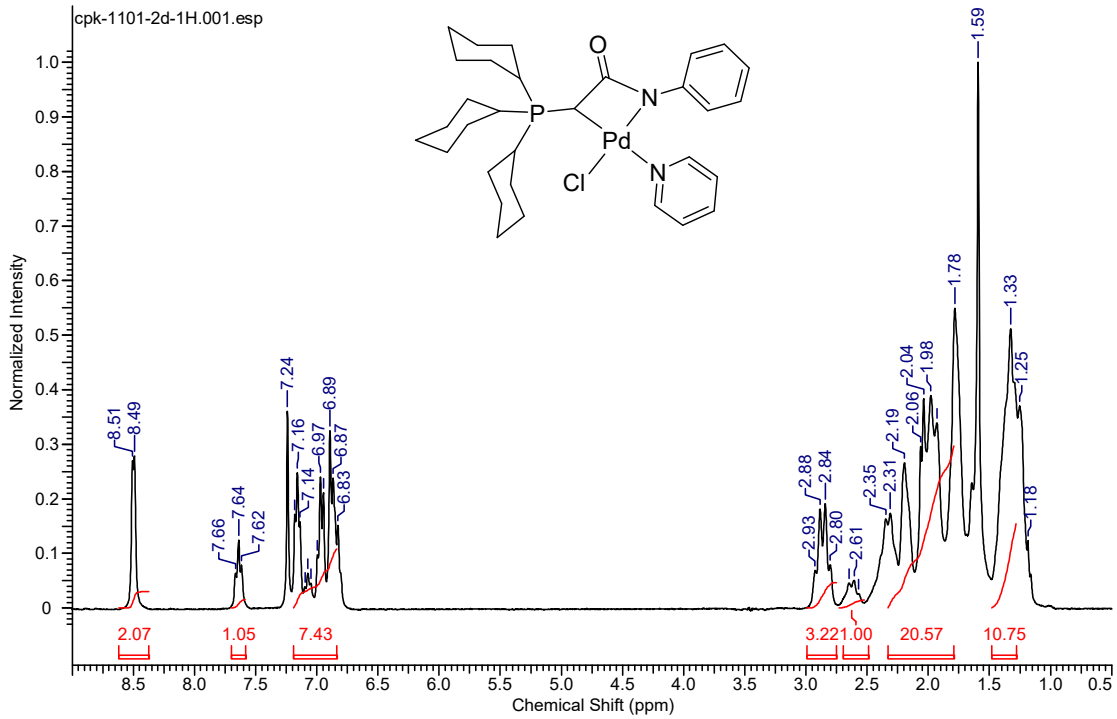


Figure S36. ^{1}H NMR spectrum of **2d**

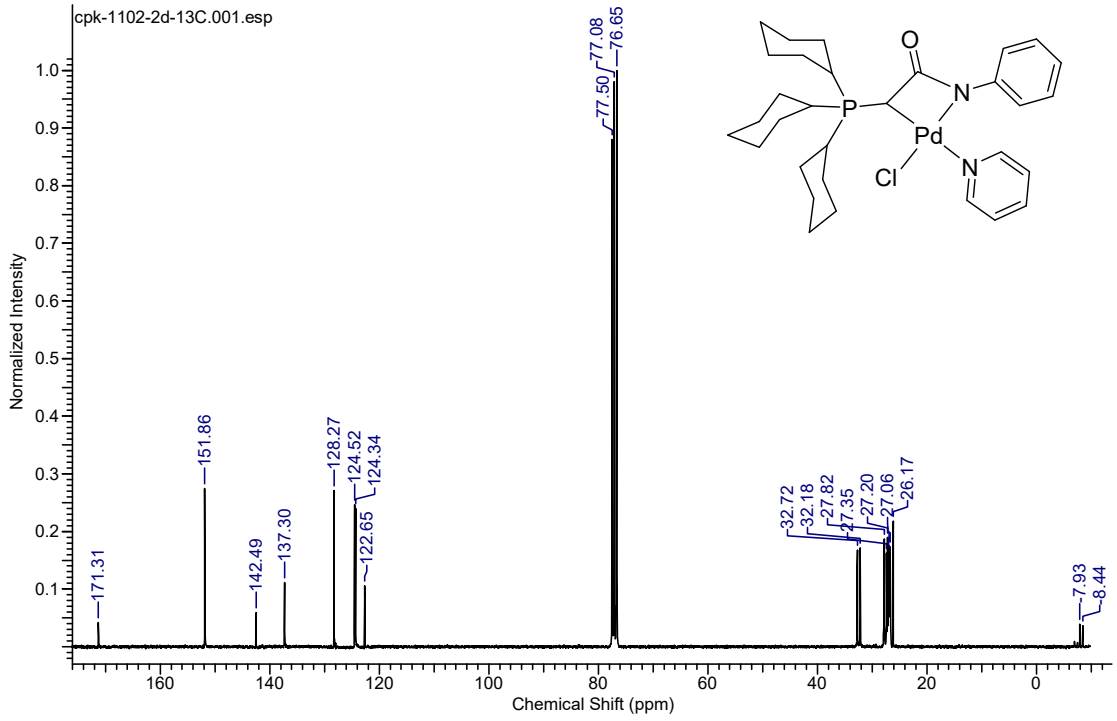


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **2d**

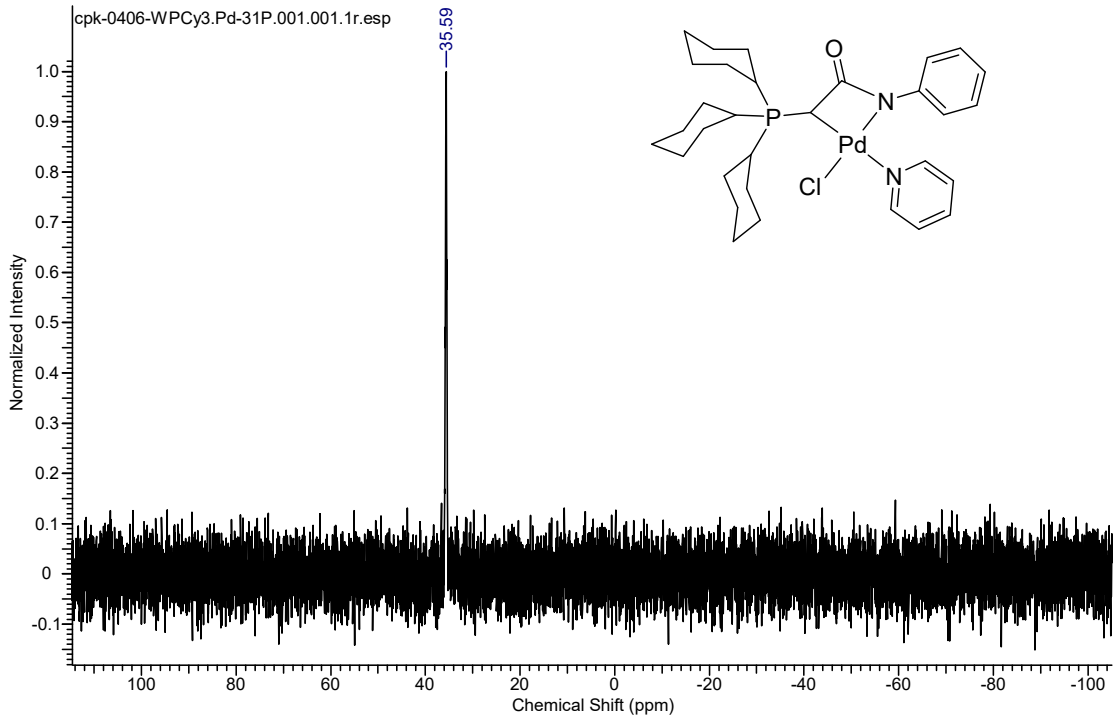


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of **2d**

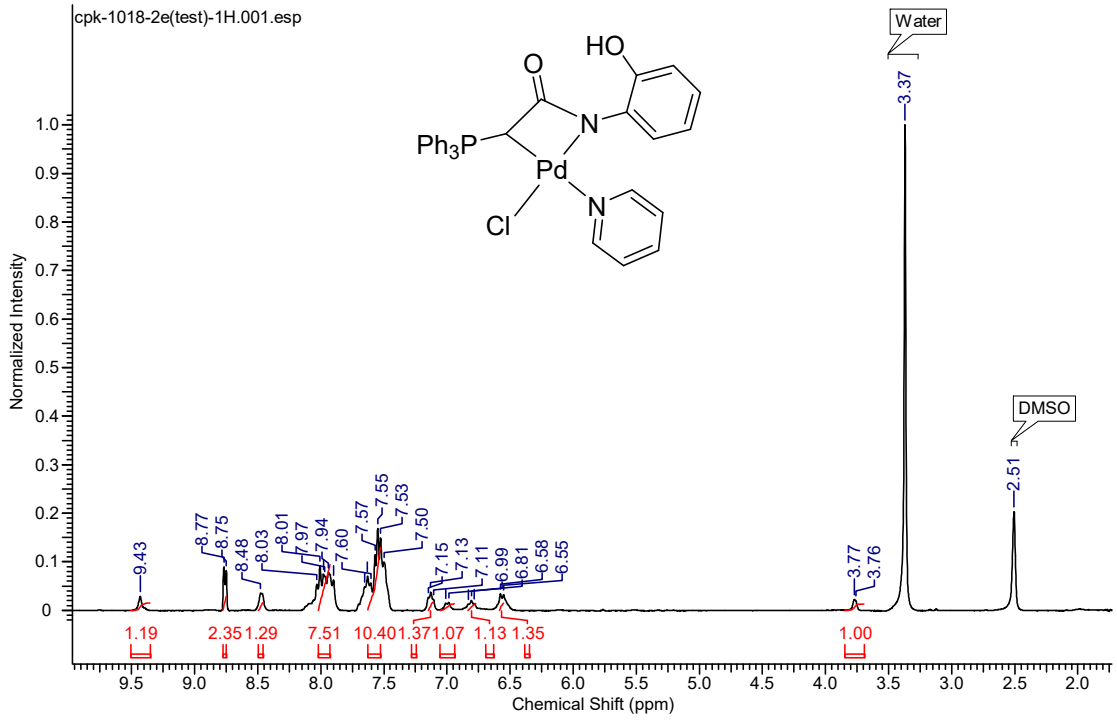


Figure S39. ^{1}H NMR spectrum of **2e**

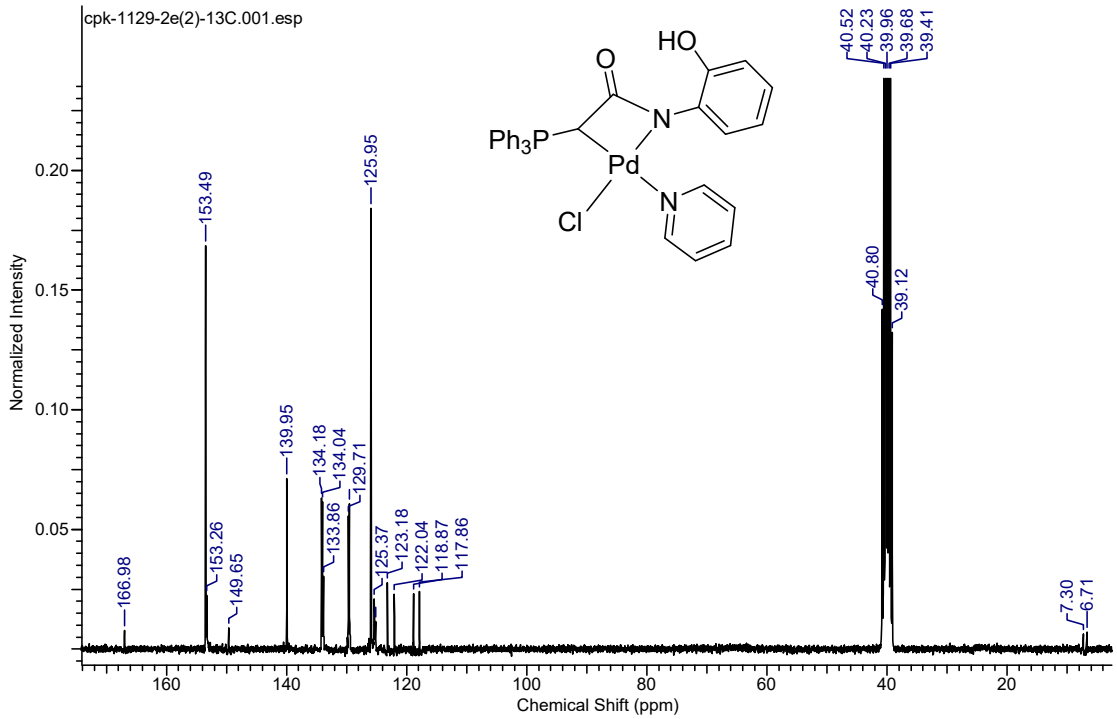


Figure S40. ^{13}C{^{1}H} NMR spectrum of **2e**

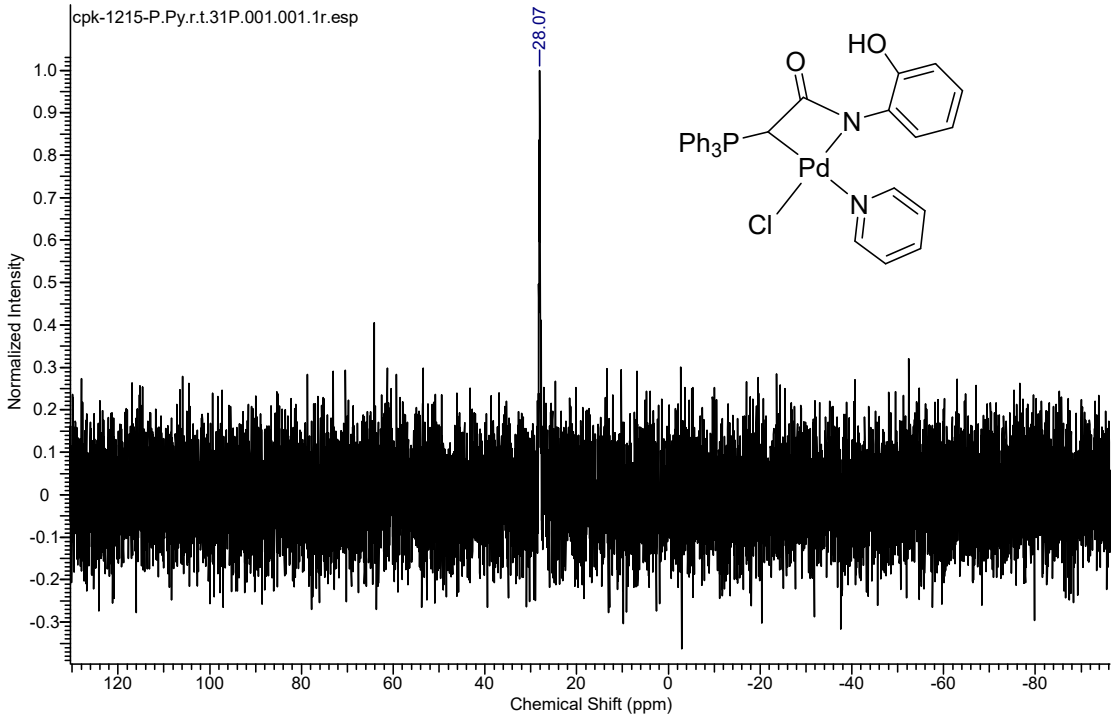


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of **2e**

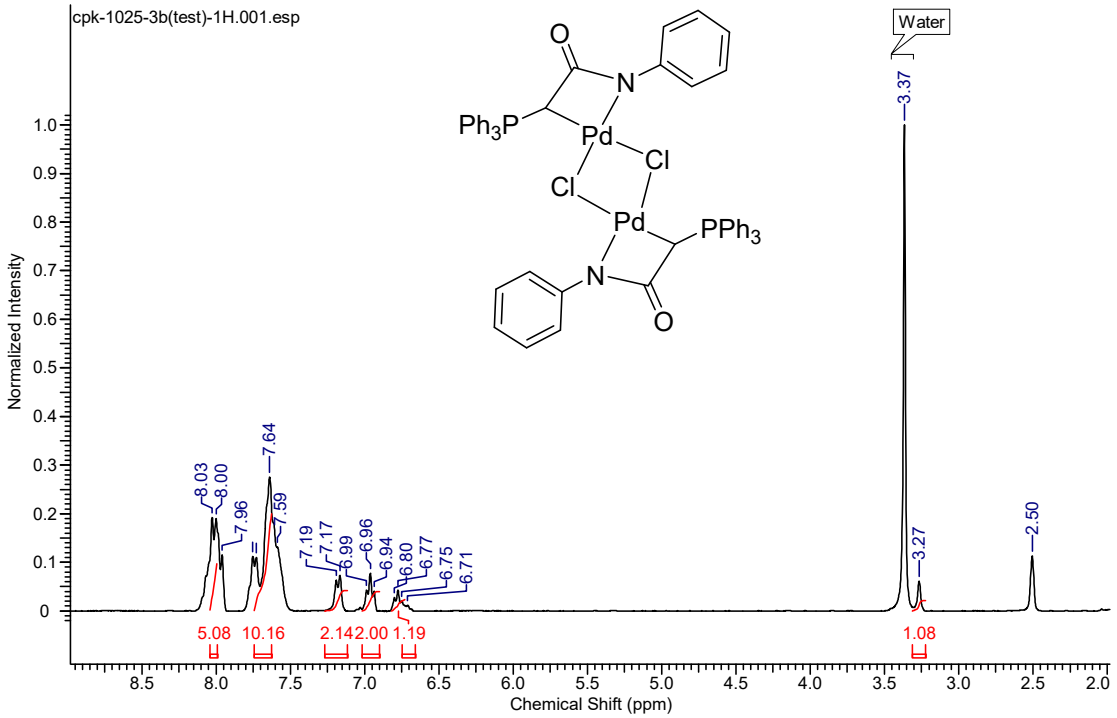


Figure S42. ^{1}H NMR spectrum of **3b**

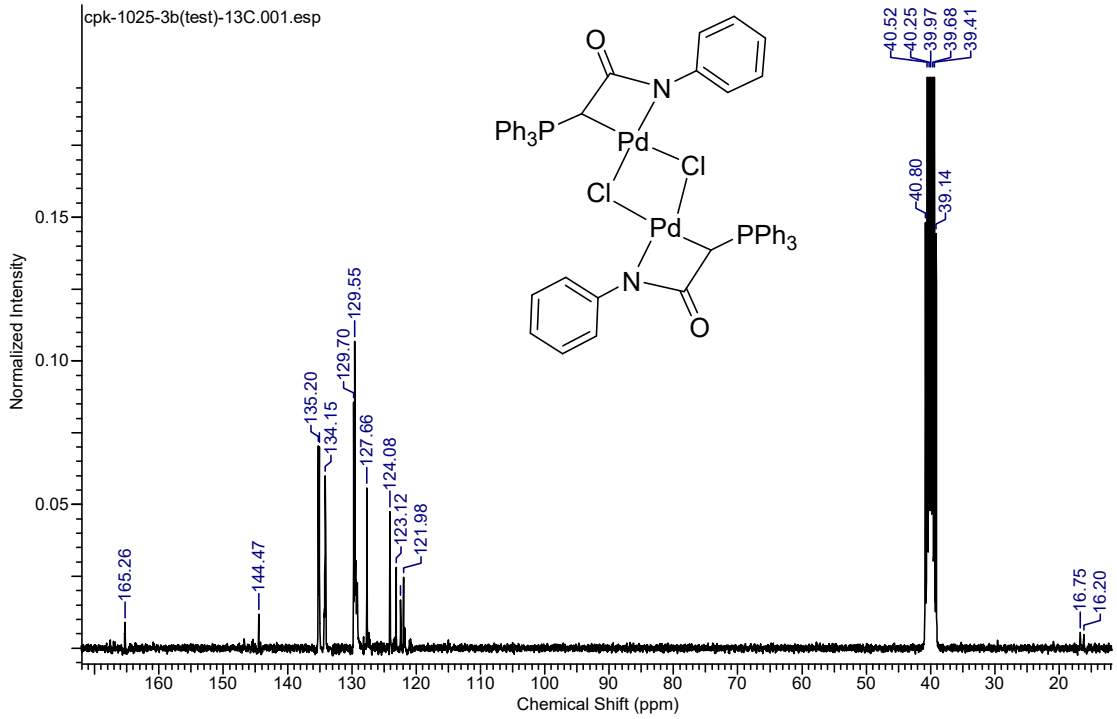


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **3b**

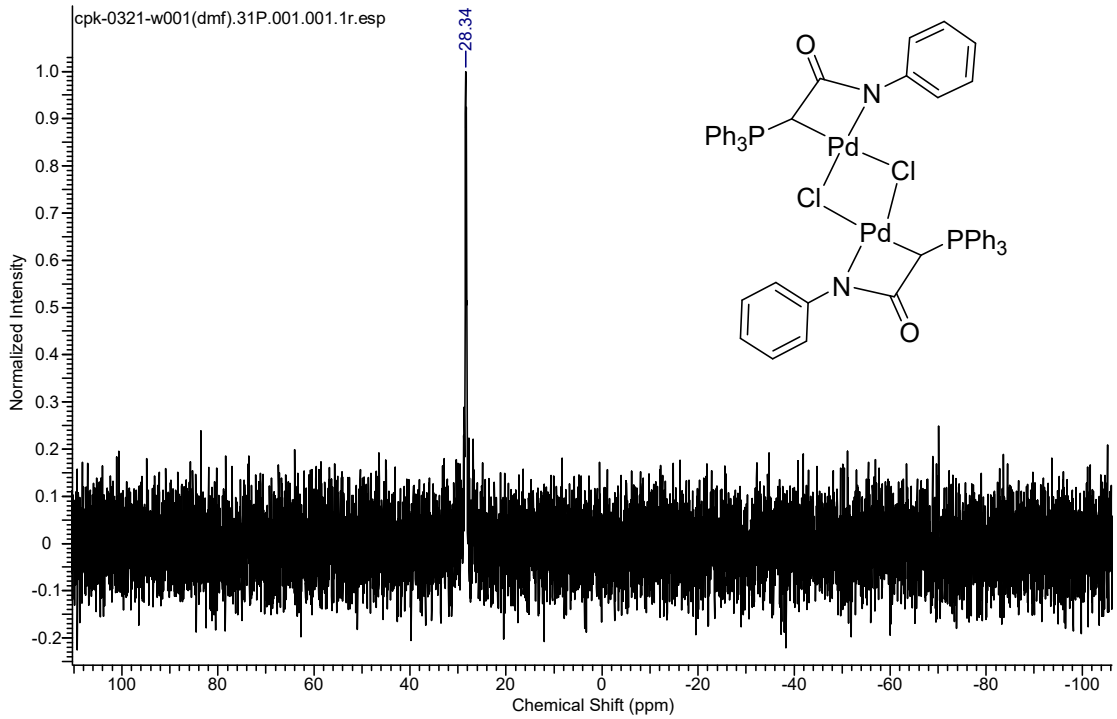


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum of **3b**

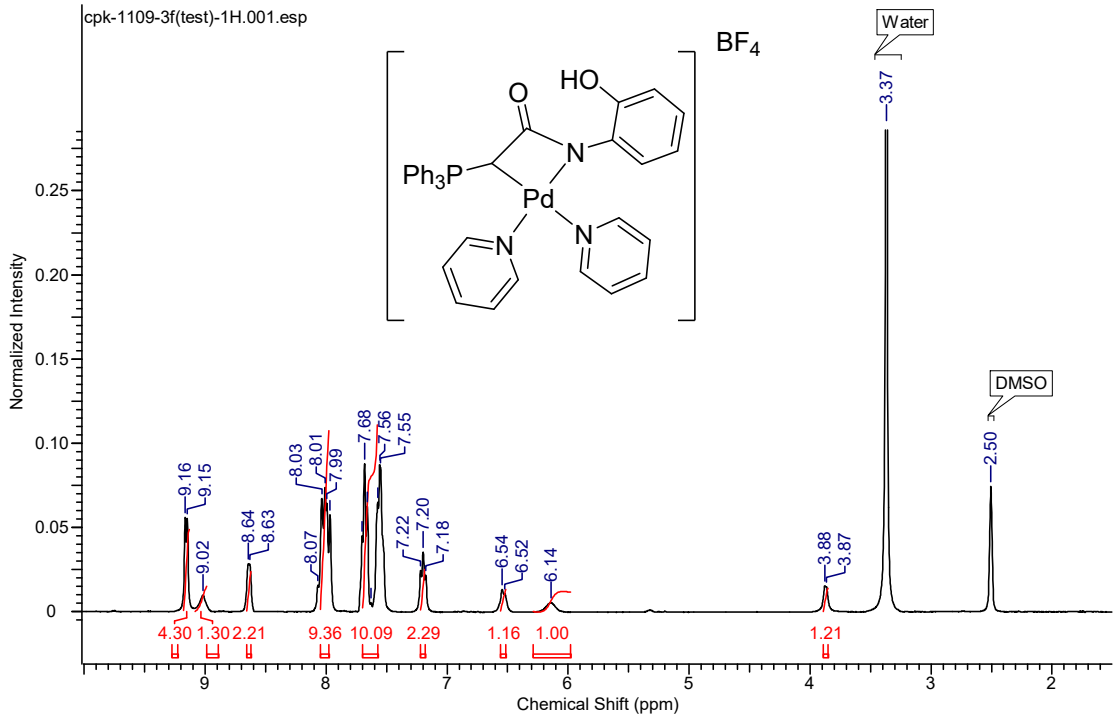


Figure S425 ^{1}H NMR spectrum of **4e**

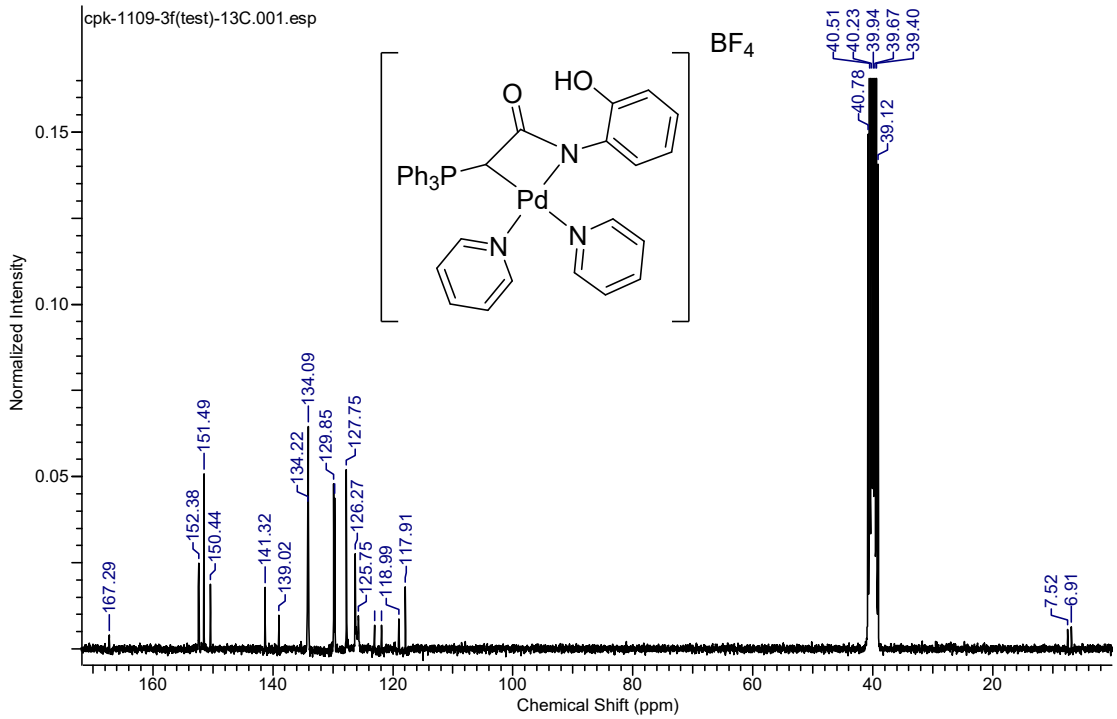


Figure S43. ^{13}C{^{1}H} NMR spectrum of **4e**

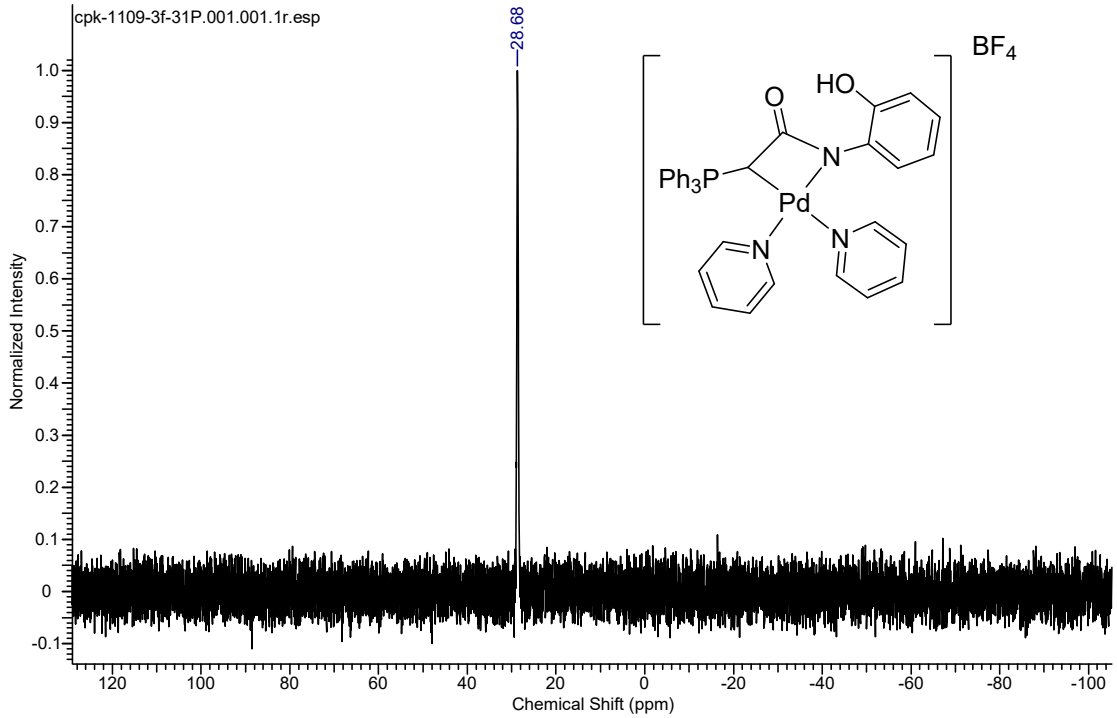


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of **4e**

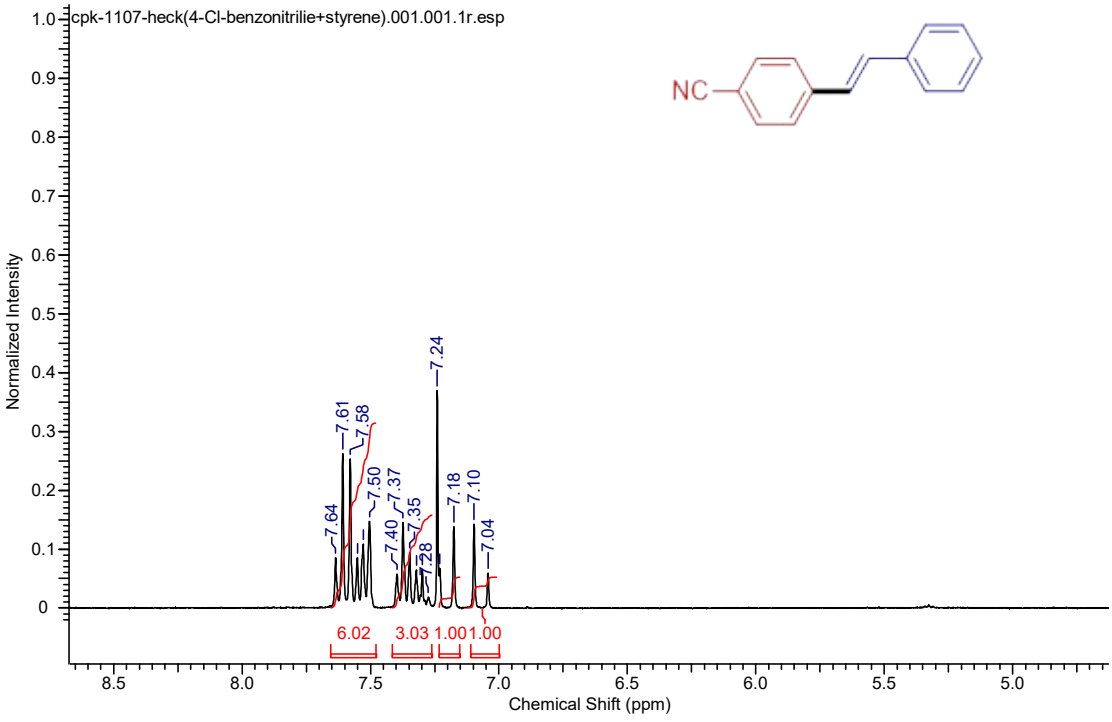


Figure S47. ^{1}H NMR spectrum of (*E*)-4-styrylbenzonitrile

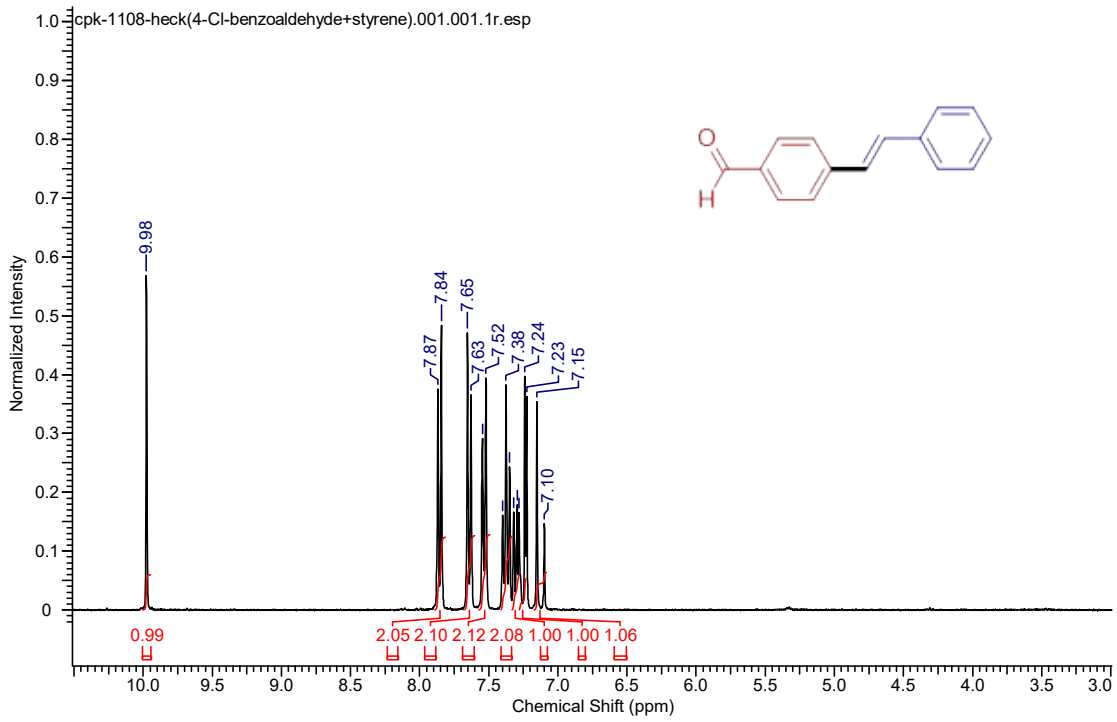


Figure S48. ^{1}H NMR spectrum of (*E*)-4-styrylbenzonitrile

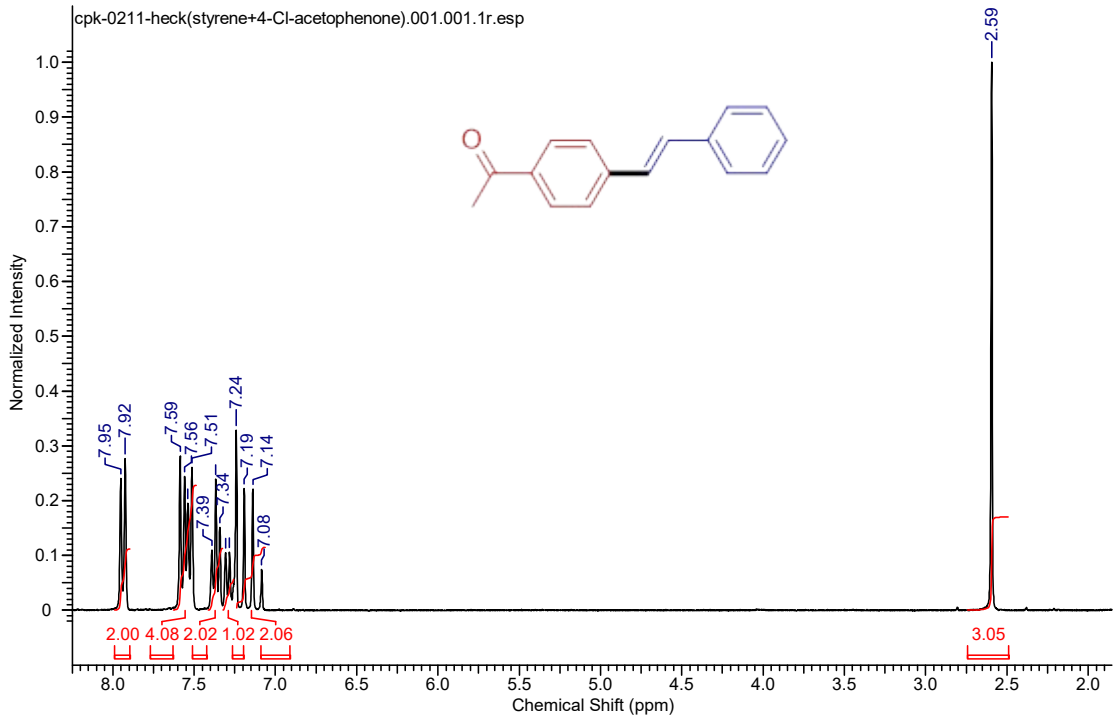
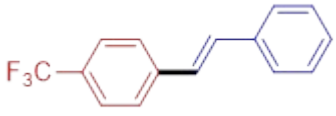


Figure S49. ^{1}H NMR spectrum of (*E*)-1-(4-styrylphenyl)ethanone



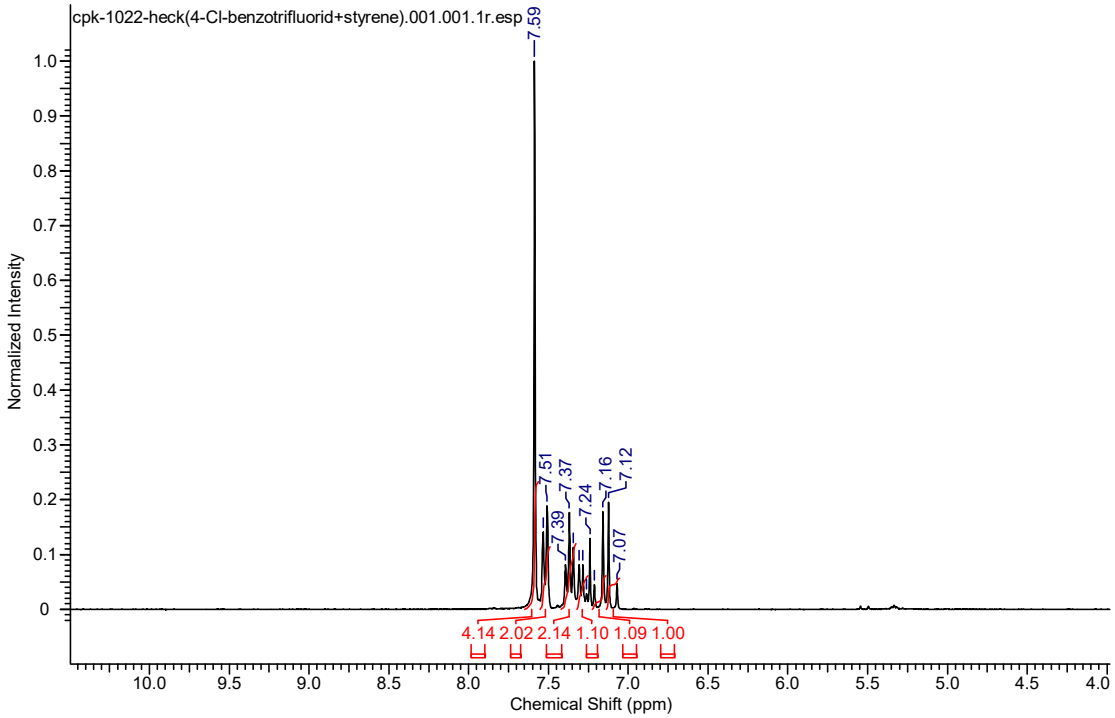


Figure S50. ^{1}H NMR spectrum of (E)-1-styryl-4-(trifluoromethyl)benzene

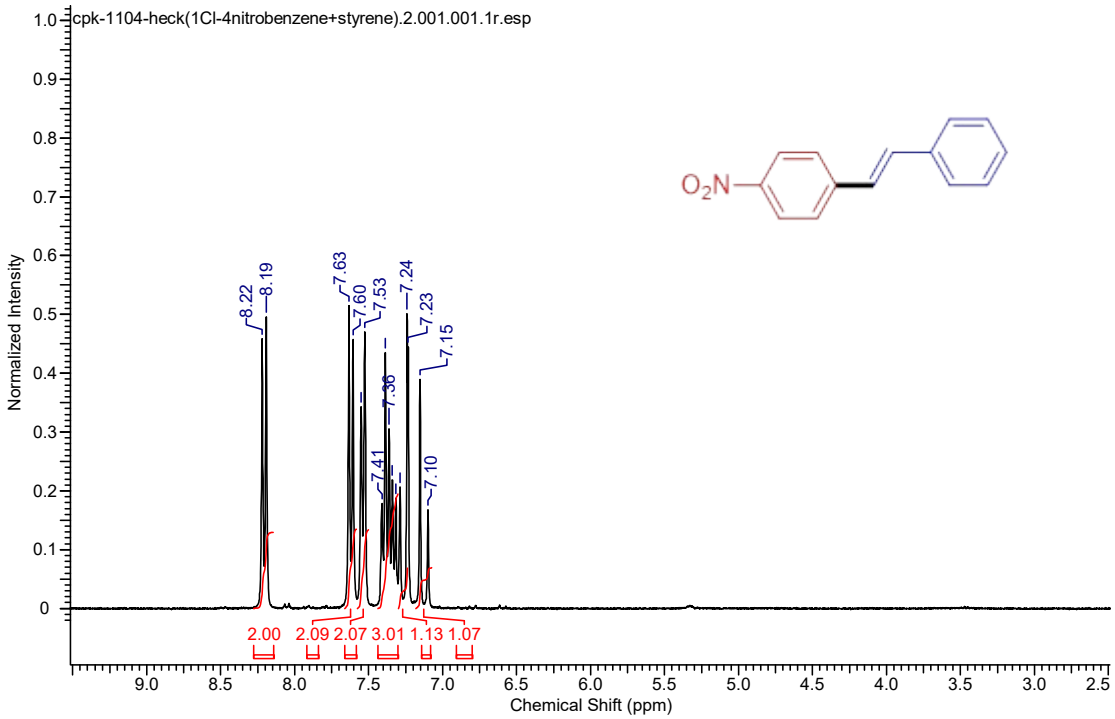


Figure S51. ^{1}H NMR spectrum of (*E*)-1-nitro-4-styrylbenzene

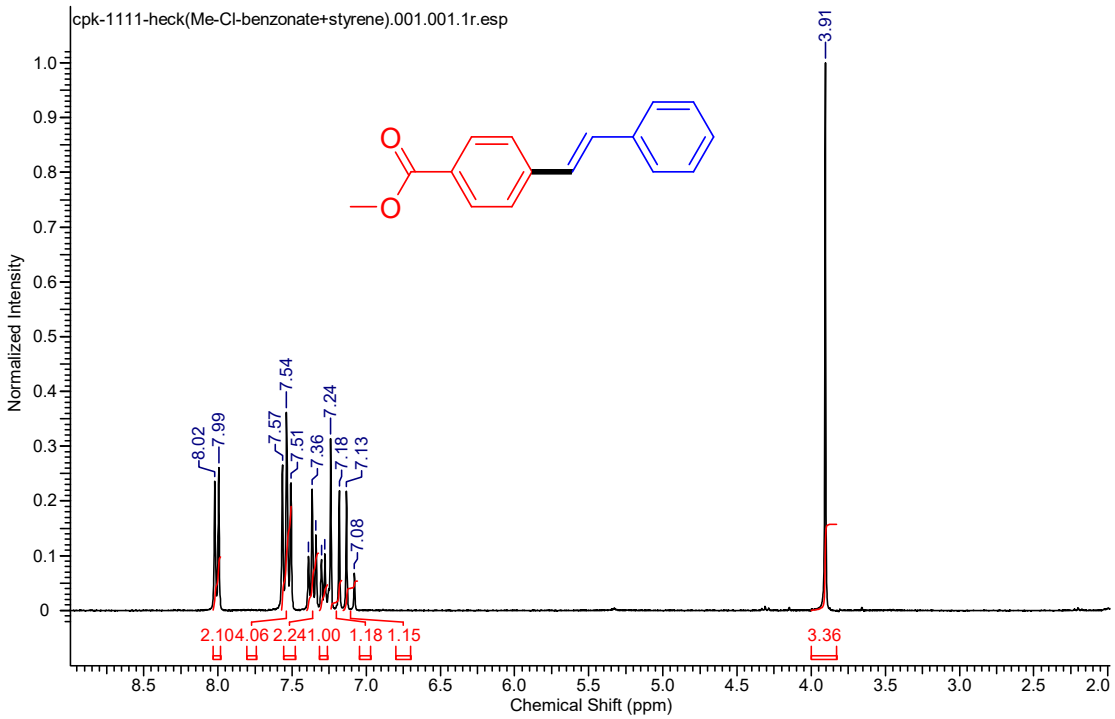


Figure S52. ^{1}H NMR spectrum of (*E*)-methyl-4-styrylbenzoate

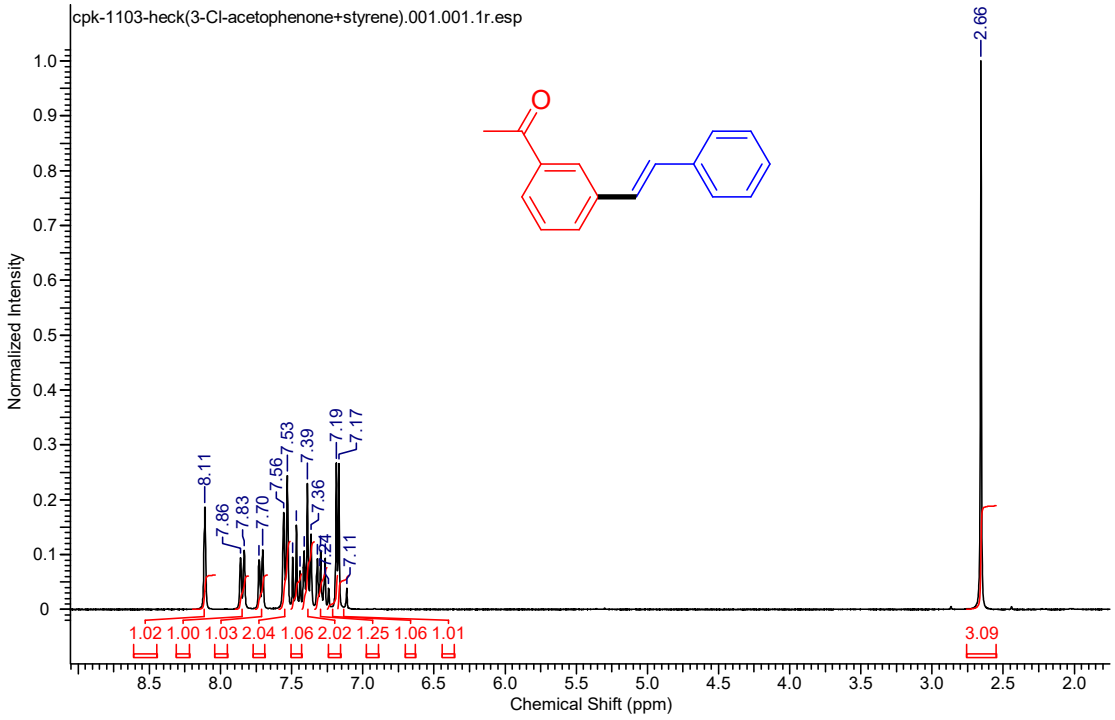


Figure S53. ^{1}H NMR spectrum of (*E*)-1-(3-styrylphenyl)ethanone

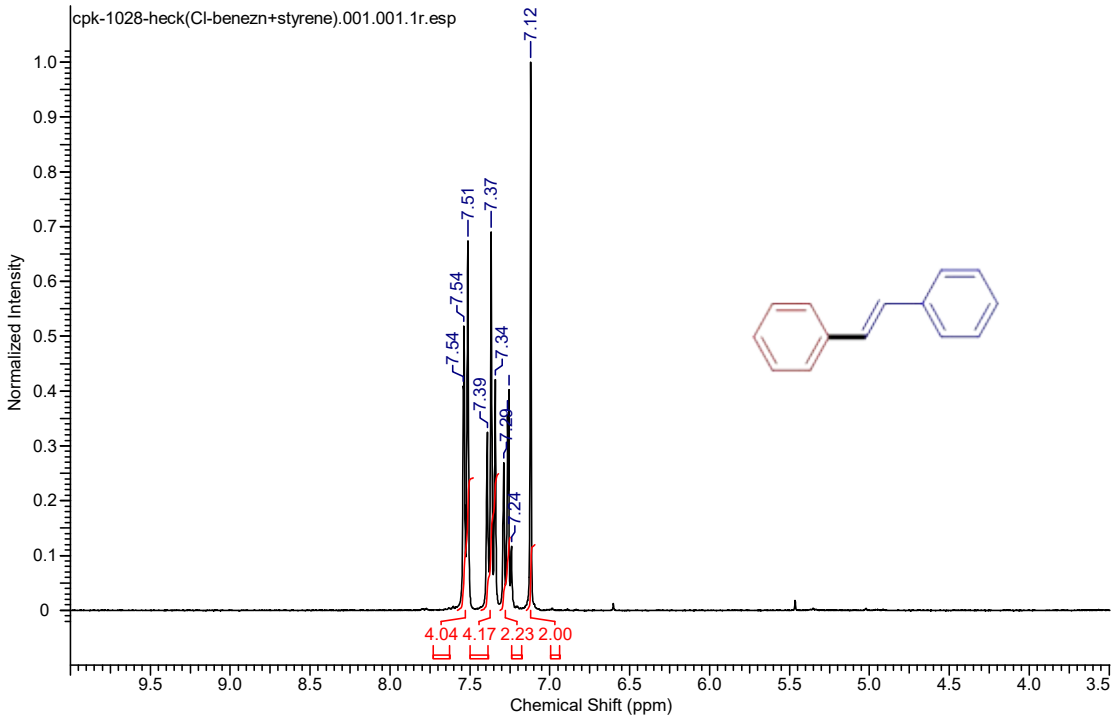


Figure S54. ^{1}H NMR spectrum of (*E*)-1,2-diphenylethene

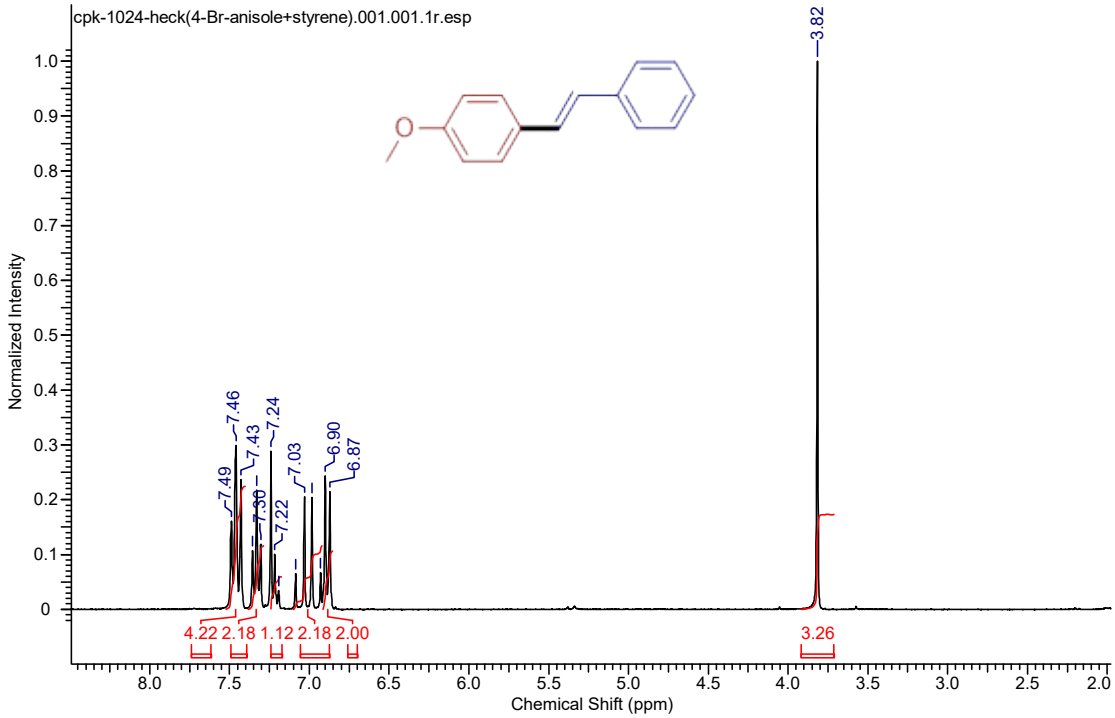


Figure S55. ^{1}H NMR spectrum of (*E*)-1-methoxy-4-styrylbenzene

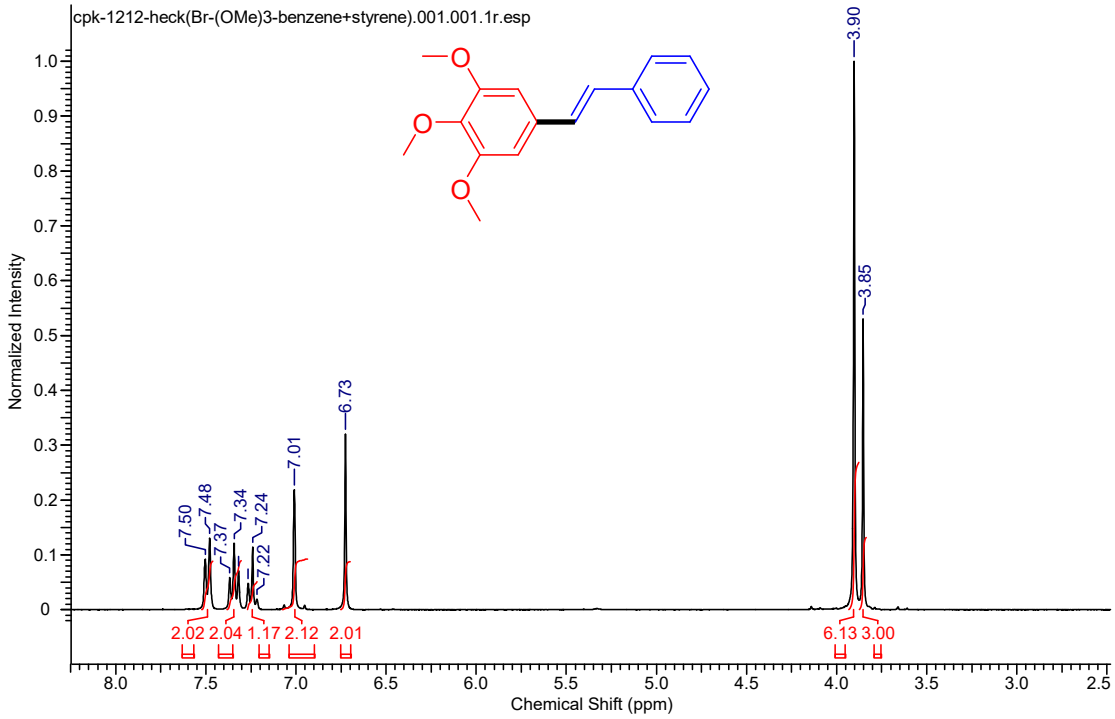


Figure S56. ^{1}H NMR spectrum of 1,2,3-trimethoxy-5-[(1*E*)-2-phenylethenyl]benzene

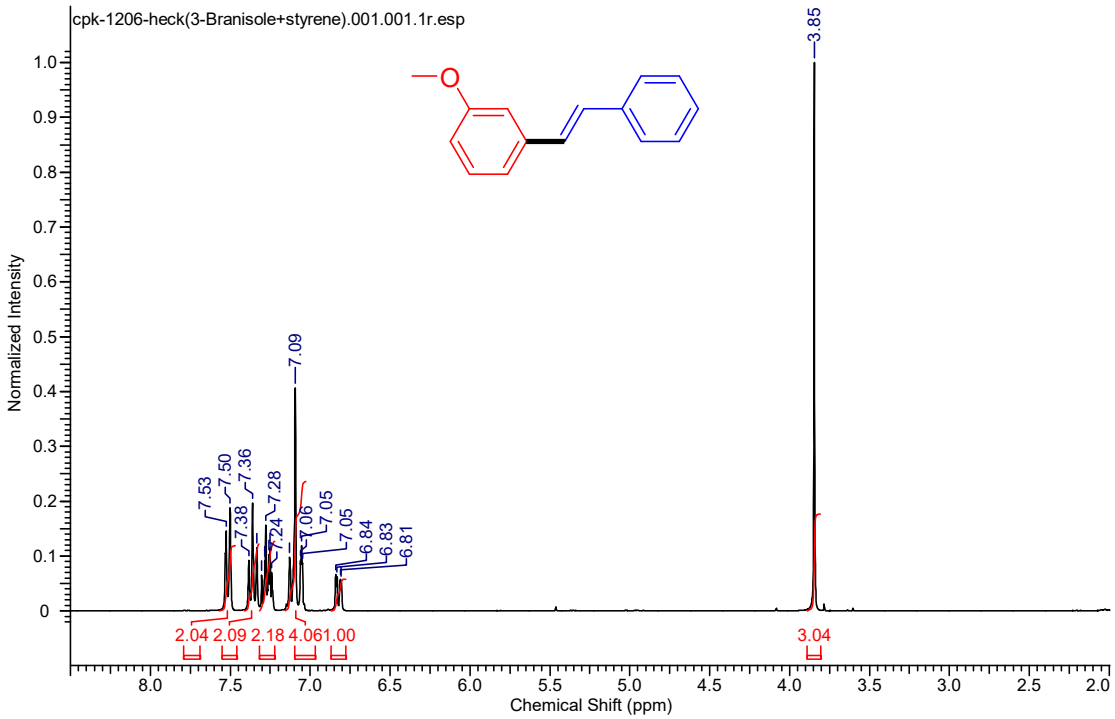


Figure S57. ^{1}H NMR spectrum of (*E*)-1-methoxy-3-styrylbenzene

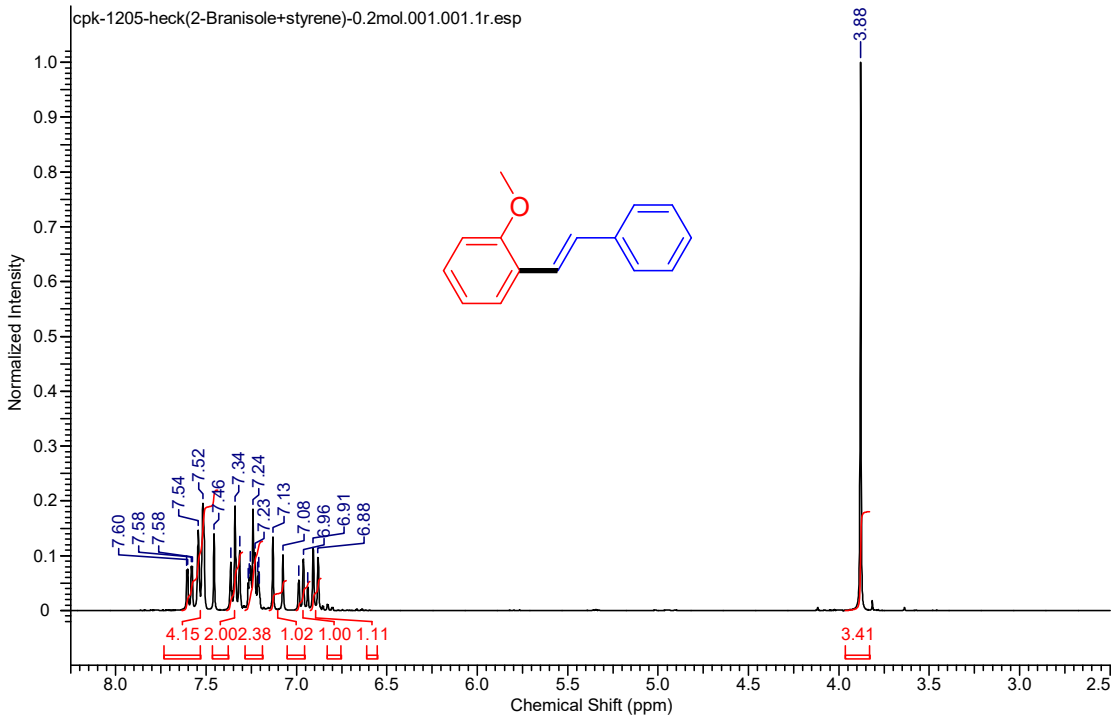


Figure S58. ^{1}H NMR spectrum of (*E*)-1-methoxy-2-styrylbenzene

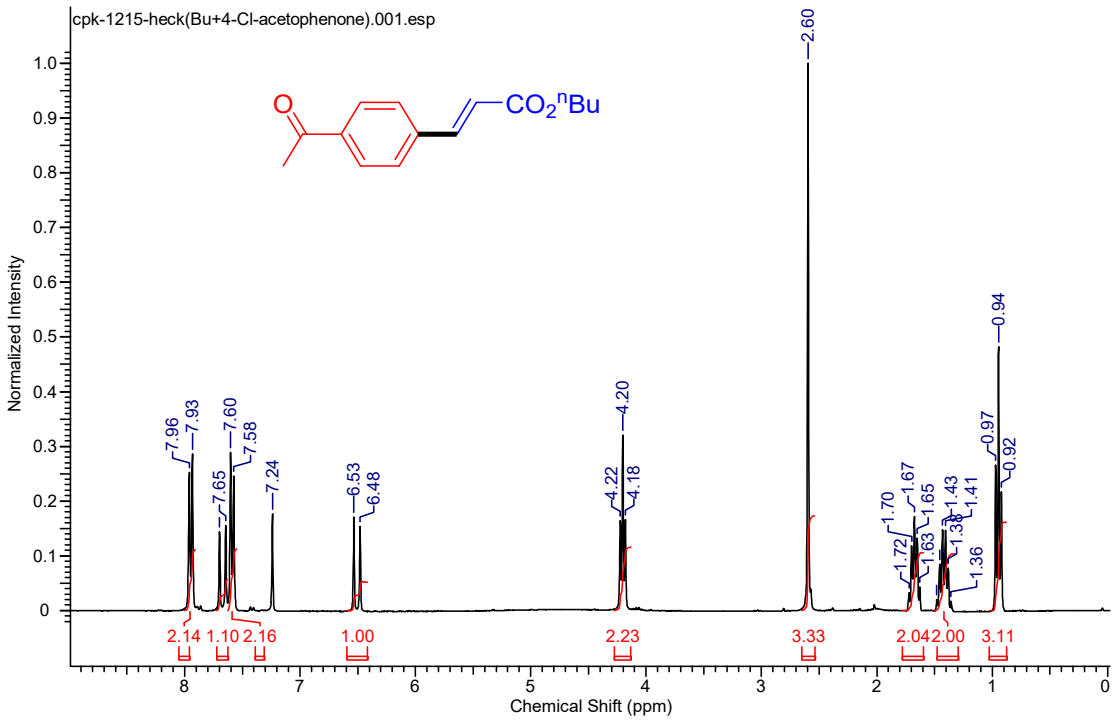


Figure S59. ^{1}H NMR spectrum of (*E*)-butyl-3-(4-acetylphenyl)acrylate

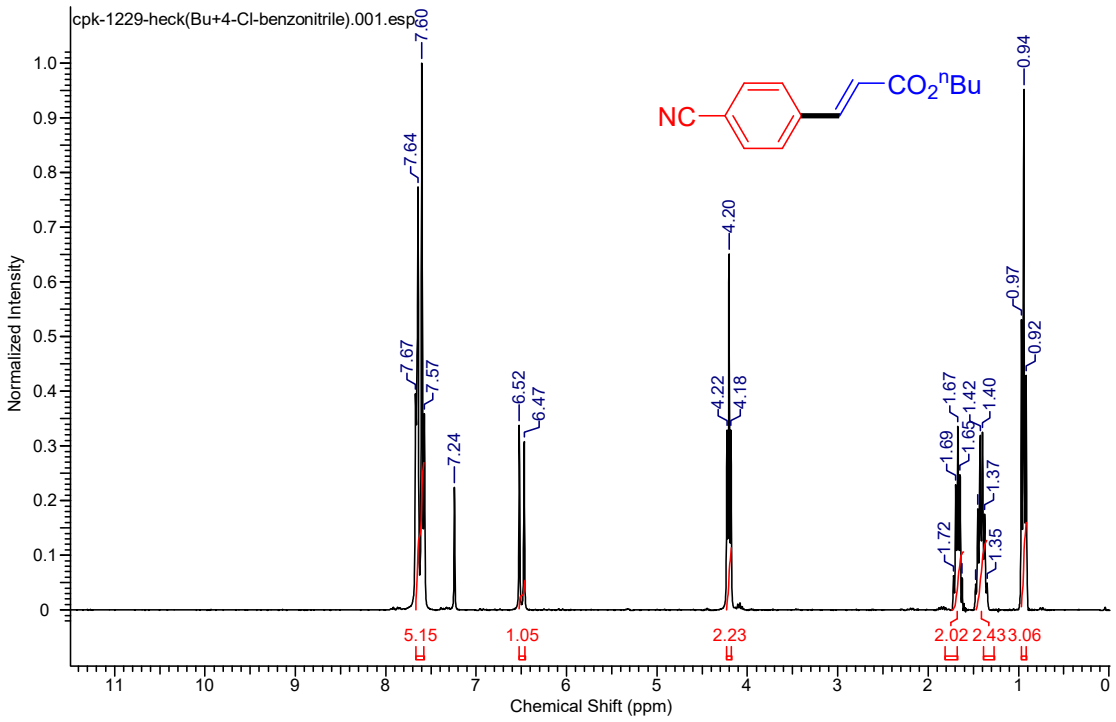


Figure S60. ^{1}H NMR spectrum of (*E*)-butyl 3-(4-cyanophenyl)acrylate

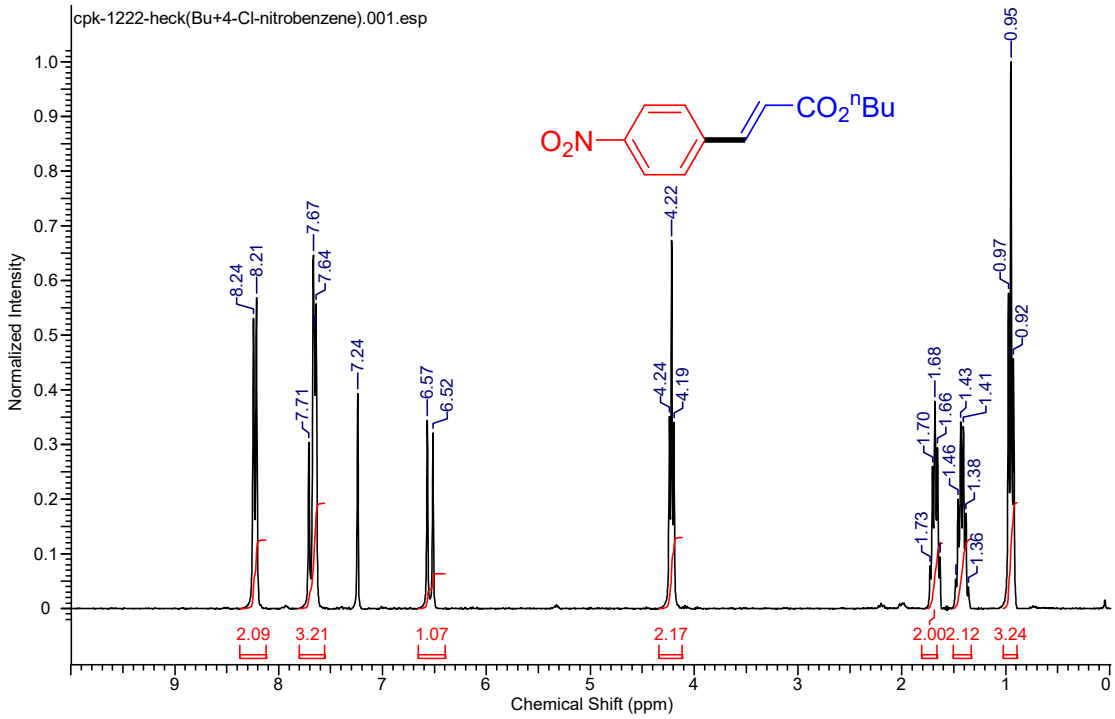


Figure S61. ^{1}H NMR spectrum of (*E*)-butyl 3-(4-nitrophenyl)acrylate

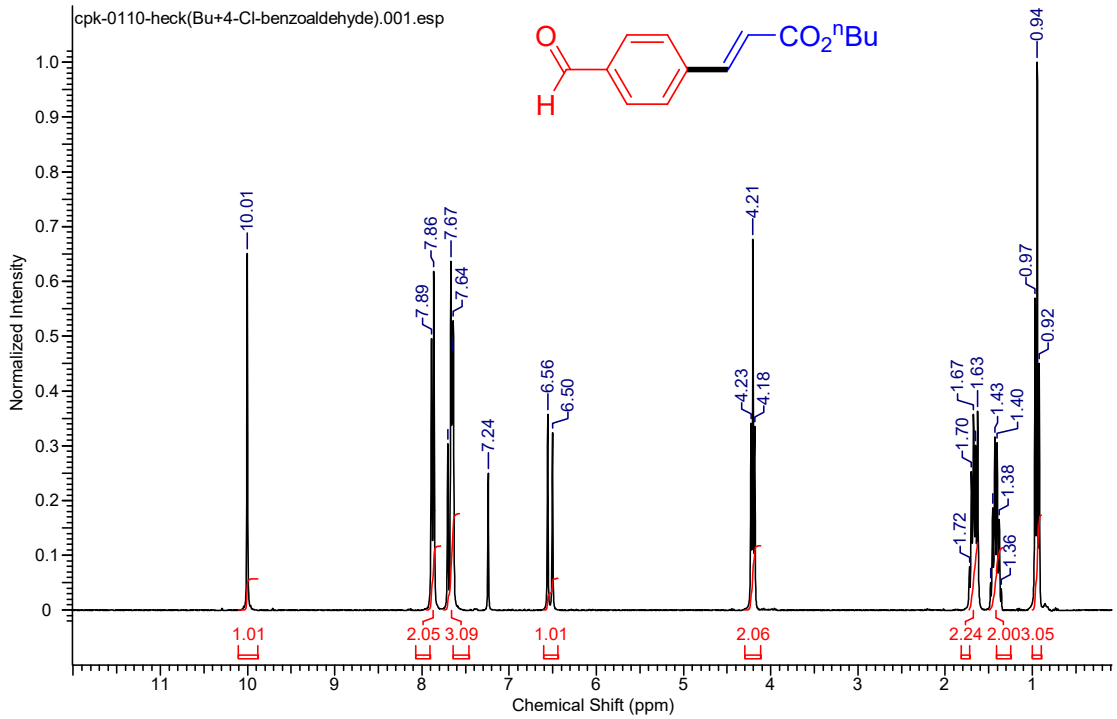


Figure S62. ^{1}H NMR spectrum of butyl (*E*)-3-(4-formylphenyl)-2-propenoate

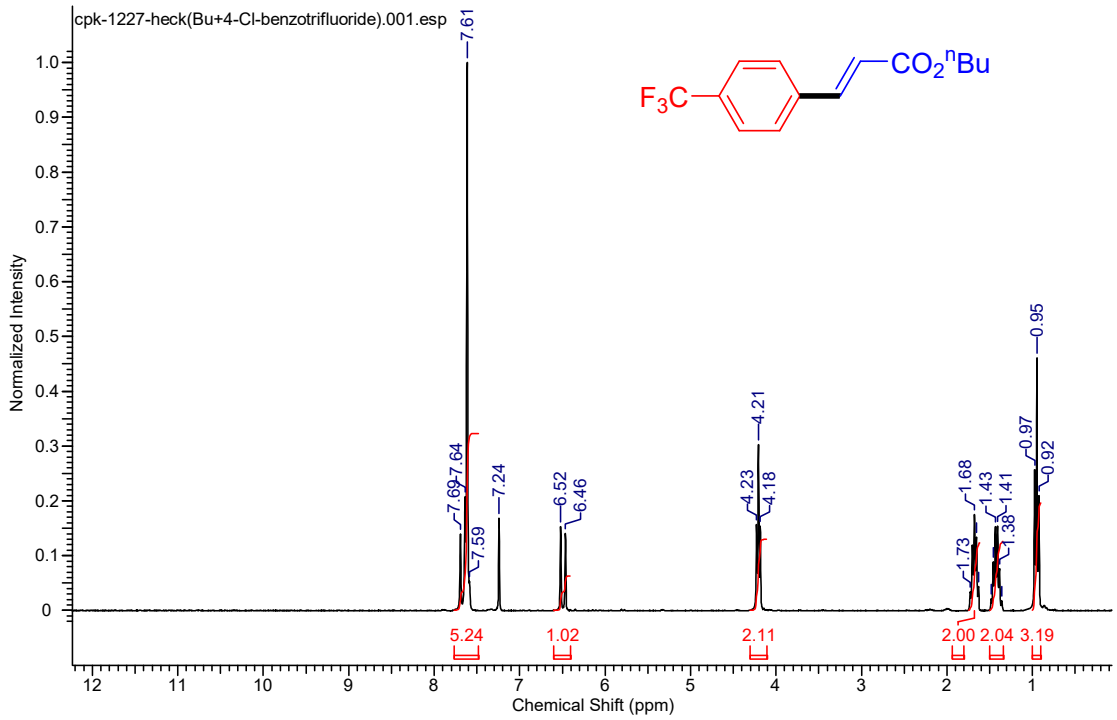


Figure S63. ^{1}H NMR spectrum of butyl (2*E*)-3-[4-(trifluoromethyl)phenyl]-2-propenoate

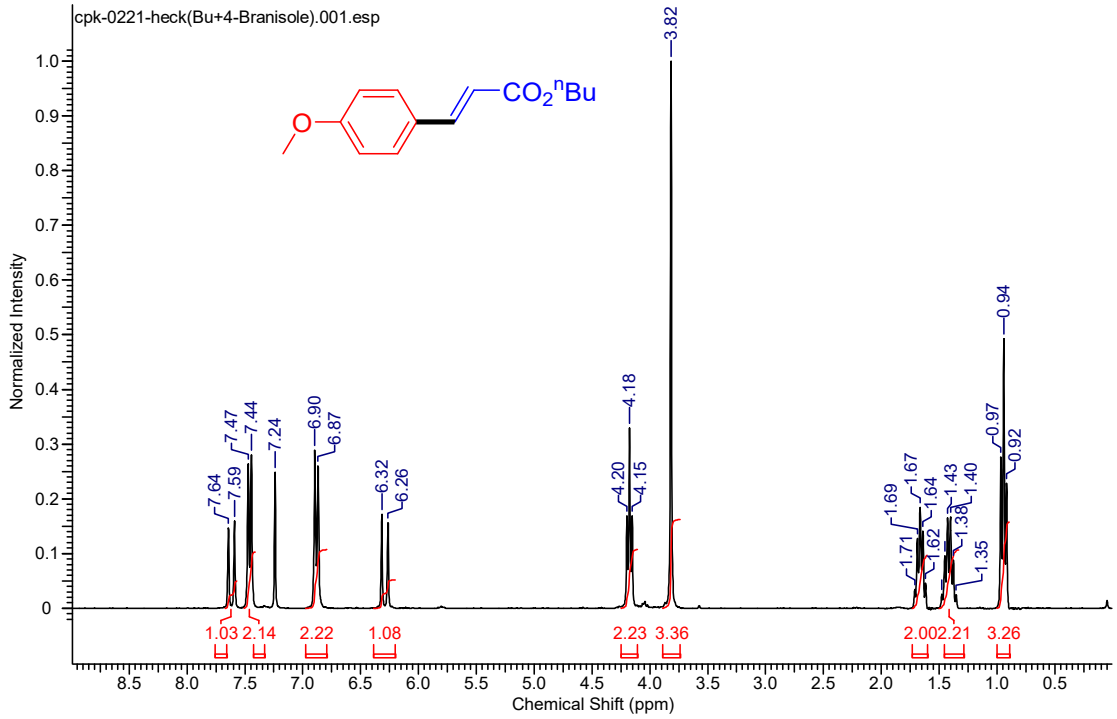


Figure S64. ^{1}H NMR spectrum of (*E*)-butyl 3-(4-methoxyphenyl)acrylate

^{1}H NMR data of catalytic products

(*E*)-4-Styrylbenzonitrile.[11] ^{1}H NMR ($CDCl_3$): δ 7.07 (d, 1H, *J* = 18.0 Hz, C*H*), 7.20 (d, 1H, *J* = 15.0 Hz, C*H*), 7.28–7.40 (m, 3H, Ar *H*), 7.50-7.64 (m, 6H, Ar *H*).

(*E*)-4-Styrylbenzaldehyde.[12] ^{1}H NMR ($CDCl_3$): δ 7.12 (d, 1H, *J* = 15.0 Hz, C*H*), 7.25 (d, 1H, *J* = 15.0 Hz, C*H*), 7.30 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.38 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.53 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.64 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.85 (d, 2H, *J* = 9.0 Hz, Ar *H*), 9.98 (s, 1H, CO*H*).

(*E*)-1-(4-Styrylphenyl)ethenone.[13] ^{1}H NMR ($CDCl_3$): δ 2.59 (s, 3H, CH_3), 7.11 (d, 1H, *J* = 18.0 Hz, C*H*), 7.22 (d, 1H, *J* = 18.0 Hz, C*H*), 7.29 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.37 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.51–7.59 (m, 4H, Ar *H*), 7.93 (d, 2H, *J* = 9.0 Hz, Ar *H*).

(*E*)-1-Styryl-4-(trifluoromethyl)benzene.[11] ^{1}H NMR ($CDCl_3$): δ 7.09 (d, 1H, *J* = 15.0 Hz, C*H*), 7.18 (d, 1H, *J* = 15.0 Hz, C*H*), 7.26–7.31 (m, 1H, Ar *H*), 7.37 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.51–7.59 (m, 6H, Ar *H*).

(*E*)-1-Nitro-4-styrylbenzene.[11] ^{1}H NMR ($CDCl_3$): δ 7.12 (d, 1H, *J* = 15.0 Hz, C*H*), 7.26 (d, 1H, *J* =

18.0 Hz, C*H*), 7.32–7.41 (m, 3H, Ar *H*), 7.54 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.61 (d, 2H, *J* = 9.0 Hz, Ar *H*), 8.20 (d, 2H, *J* = 9.0 Hz, Ar *H*).

(*E*)-Methyl-4-styrylbenzoate.[14] ^{1}H NMR ($CDCl_3$): δ 3.91 (s, 3H, CH_3), 7.10 (d, 1H, *J* = 15.0 Hz, C*H*), 7.21 (d, 1H, *J* = 21.0 Hz, C*H*), 7.29 (d, 1H, *J* = 6.0 Hz, Ar *H*), 7.36 (t, 2H, *J* = 9.0 Hz, Ar *H*), 7.54 (t, 4H, *J* = 9.0 Hz, Ar *H*), 8.00 (t, 2H, *J* = 9.0 Hz, Ar *H*).

(*E*)-1-(3-Styrylphenyl)ethenone.[15] ^{1}H NMR ($CDCl_3$): δ 2.66 (s, 3H, CH_3), 7.14 (d, 1H, *J* = 18.0 Hz, C*H*), 7.21 (d, 1H, *J* = 15.0 Hz, C*H*), 7.26–7.32 (m, 1H, Ar *H*), 7.39 (t, 2H, *J* = 15.0 Hz, Ar *H*), 7.47 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.54 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.71 (d, 1H, *J* = 9.0 Hz, Ar *H*), 7.84 (d, 1H, *J* = 9.0 Hz, Ar *H*), 8.11 (s, 1H, Ar *H*).

(*E*)-1,2-Diphenylethene.[11] ^{1}H NMR ($CDCl_3$): δ 7.12 (s, 2H, C*H*), 7.24–7.29 (m, 2H, *J* = 9.0 Hz, Ph *H*), 7.37 (t, 4H, *J* = 6.0 Hz, Ph *H*), 7.54 (d, 4H, *J* = 9.0 Hz, Ph *H*).

(*E*)-1-Methoxy-4-styrylbenzene.[11] ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 3H, CH_3), 6.88 (d, 2H, *J* = 9.0 Hz, C*H*), 6.93–7.09 (m, 2H, Ar *H*), 7.19–7.24 (m, 1H, Ar *H*), 7.33 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.43–7.49 (m, 4H, Ar *H*).

1,2,3-Trimethoxy-5-[(1*E*)-2-phenylethenyl]benzene.[16] ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 3H, CH_3), 3.90 (s, 6H, CH_3), 6.73 (s, 2H, C*H*), 7.01 (s, 2H, Ar *H*), 7.22–7.27 (m, 1H, Ar *H*), 7.34 (t, 2H, *J* = 15.0 Hz, Ar *H*), 7.49 (d, 2H, *J* = 6.0 Hz, Ar *H*).

(*E*)-1-Methoxy-3-styrylbenzene. [17] ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 3H, CH_3), 6.81-6.84 (m, 1H, C*H*), 7.05–7.13 (m, 4H, C*H*, Ar *H*), 7.24–7.30 (m, 2H, Ar *H*), 7.36 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.51(d, 2H, *J* = 9.0 Hz, Ar *H*).

(*E*)-1-Methoxy-2-styrylbenzene.[18] ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 3H, CH_3), 6.89 (d, 1H, *J* = 9.0 Hz, C*H*) , 6.96 (t, 1H, *J* = 6.0 Hz, Ar *H*), 7.10 (d, 1H, *J* = 15.0 Hz, C*H*), 7.21–7.27 (m, 2H, Ar *H*), 7.34 (t, 2H, *J* = 6.0 Hz, Ar *H*), 7.46-7.61 (m, 4H, Ar *H*).

(*E*)-Butyl-3-(4-acetylphenyl)acrylate.[19] ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, *J* = 9.0 Hz, CH_3), 1.42 (sext, 2H, *J* = 6.0 Hz, CH_2), 1.67 (quint, 2H, *J* = 6.0 Hz, CH_2), 2.60 (s, 3H, CH_3), 4.20 (t, 2H, *J* = 6.0 Hz, CH_2), 6.50 (d, 1H, *J* = 15.0 Hz, C*H*), 7.59 (d, 2H, *J* = 6.0 Hz, Ar *H*), 7.67 (d, 1H, *J* = 15.0 Hz, C*H*), 7.94 (d, 2H, *J* = 9.0 Hz, Ar *H*).

(*E*)-Butyl 3-(4-cyanophenyl)acrylate.[20] ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, *J* = 9.0 Hz, CH_3), 1.41 (sext, 2H, *J* = 6.0 Hz, CH_2), 1.67 (quint, 2H, *J* = 6.0 Hz, CH_2), 4.20 (t, 2H, *J* = 6.0 Hz, CH_2), 6.49 (d, 1H, *J* =

15.0 Hz, C*H*), 7.57-7.67 (m, 5H, C*H*, Ar *H*).

(*E*)-Butyl 3-(4-nitrophenyl)acrylate.[21] ^{1}H NMR ($CDCl_3$): δ 0.95 (t, 3H, *J* = 9.0 Hz, CH_3), 1.42 (sext, 2H, *J* = 6.0 Hz, CH_2), 1.63-1.72 (m, 2H, CH_2), 4.22 (t, 2H, *J* = 6.0 Hz, CH_2), 6.54 (d, 1H, *J* = 15.0 Hz, C*H*), 7.64–7.71 (m, 3H, C*H*, Ar *H*), 8.22 (d, 2H, *J* = 9.0 Hz, Ar *H*).

Butyl (*E*)-3-(4-formylphenyl)-2-propenoate.[22] ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, *J*= 9.0 Hz, CH_3), 1.41 (sext, 2H, *J* = 6.0 Hz, CH_2), 1.60 (quint, 2H, *J* = 6.0Hz, CH_2), 4.21 (t, 2H, *J* = 6.0 Hz, CH_2), 6.53 (d, 1H, *J* = 18.0 Hz, C*H*), 7.64–7.71 (m, 3H, C*H*, Ar *H*), 7.87 (d, 2H, *J* = 9.0 Hz, Ar *H*), 10.01 (s, 1H, CO*H*).

Butyl (2*E*)-3-[4-(trifluoromethyl)phenyl]-2-propenoate.[20] ^{1}H NMR ($CDCl_3$): δ 0.95 (t, 3H, *J* = 9.0 Hz, CH_3), 1.42 (sext, 2H, *J* = 6.0 Hz, CH_2), 1.68 (quint, 2H, *J* = 6.0 Hz, CH_2), 4.21 (t, 2H, *J* = 6.0 Hz, CH_2), 6.49 (d, 1H, *J* = 18.0 Hz, C*H*), 7.59–7.69 (m, 5H, C*H*, Ar *H*).

(*E*)-Butyl 3-(4-methoxyphenyl)acrylate.[23] ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, *J* = 9.0 Hz, CH_3), 1.41 (sext, 2H, *J* = 6.0 Hz, CH_2), 1.67 (quint, 2H, *J* = 6.0 Hz, CH_2), 3.82 (s, 3H, CH_3), 4.18 (t, 2H, *J* = 9.0 Hz, CH_2), 6.29 (d, 1H, *J* = 18.0 Hz, C*H*), 6.88 (d, 2H, *J* = 9.0 Hz, Ar *H*), 7.45 (t, 2H, *J* = 9.0 Hz, Ar *H*), 7.61 (d, 1H, *J* = 15.0 Hz, C*H*).

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