Electronic Supplementary Material (ESI) for Green Chemistry

Efficient catalytic hydrogenation of levulinic acid: a key step in biomass conversion

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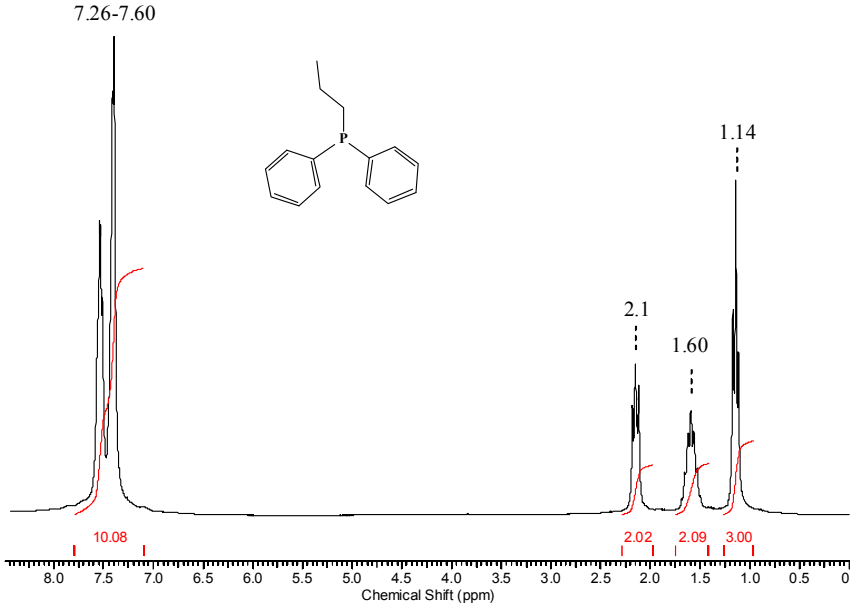
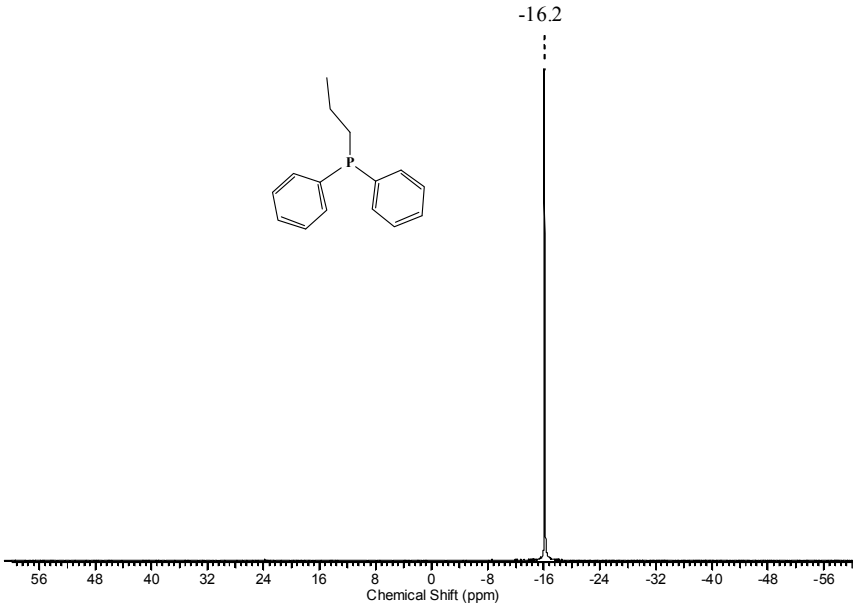
Supporting Information

Propyl-diphenylphosphine (P3)

Starting materials: Propyl bromide (23g, 190 mmol) in 50 mL diethyl ether, magnesium (5g, 210 mmol), $ClPPh_2$ (38g, 170 mmol) in 100 mL Et_2O, distilled water for washing 3x10 mL. **P3** was isolated as a colorless liquid (27 g, yield: 70%) by distillation at 120°C/0.1 mmHg. ^{1}H–NMR (in $CDCl_3$): δ 1.14 (t, 3 H), 1.6 (t, 2 H), 2.1 (t, 2 H),7.26 – 7.60 (m, 10H) ^{31}P–NMR: -16.2 (s). ^{13}C-NMR: 15.7 (d, J_{P-C} = 13.3 Hz), 19.2 (d, J_{P-C} = 16.5 Hz), 30.3 (d, J_{P-C} = 11.1 Hz), 128.1 (d, J_{P-C} = 5.7 Hz), 128.3 (s), 132.5 (d, J_{P-C} = 17.9 Hz), 138.8 (d, J_{P-C} = 13.3 Hz).



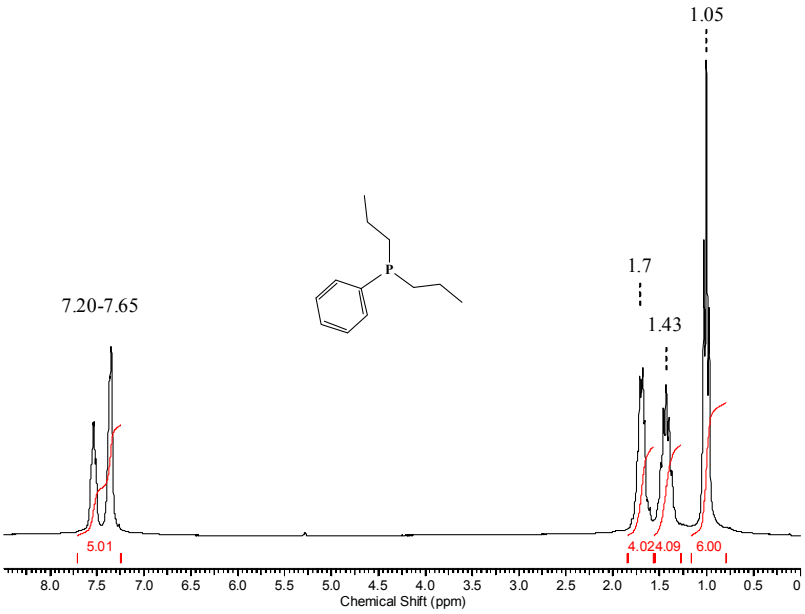
^{1}H-NMR spectrum of Propy-diphenylphosphine (P3)



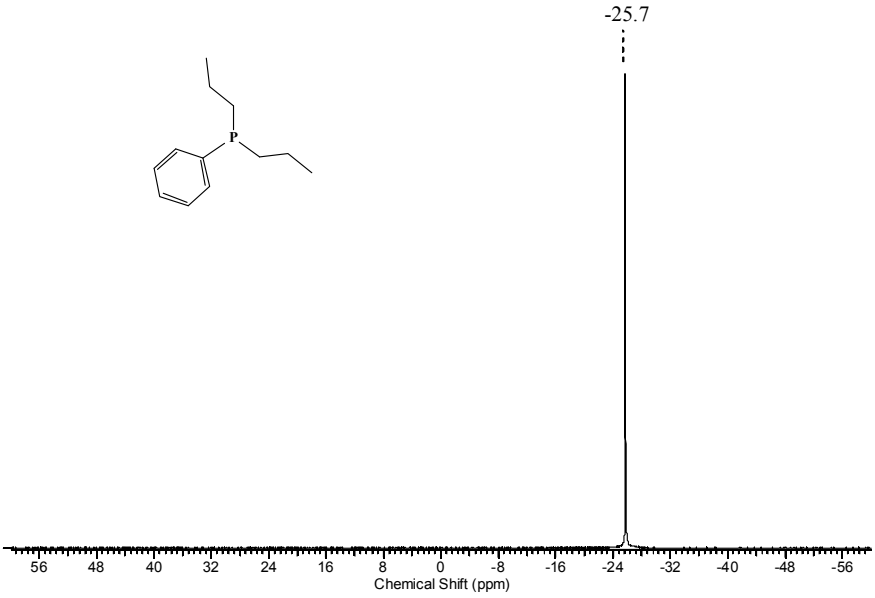
^{31}P-NMR spectrum of Propy-diphenylphosphine (P3)

Dipropyl-phenylphosphine (P4)

Starting materials: Propyl bromide (46g, 370 mmol) in 100 mL diethyl ether, magnesium (510g, 420 mmol), Cl_2PPh (30g, 170 mmol) in 100 mL diethyl ether, distilled water for washing, 3x10 mL. **P4** was isolated as a colorless liquid (20.9 g, yield: 63%) by distillation at 92-93°C/0.1 mmHg. ^{1}H–NMR (in $CDCl_3$): δ 1.05 (t, 6 H), 1.43 (t, 4 H), 1.7 (t, 4 H),7.20 – 7.65 (m, 5H) ^{31}P–NMR: -25.7 (s). ^{13}C-NMR: 15.9 (d, J_{P-C} = 12.4 Hz), 19.4 (d, J_{P-C} = 14.2 Hz), 30.6 (d, J_{P-C} = 10.5 Hz), 128.2 (d, J_{P-C} = 6.9 Hz), 128.6 (s), 132.3 (d, J_{P-C} = 18.3 Hz), 139.1 (d, J_{P-C} = 15.1 Hz).



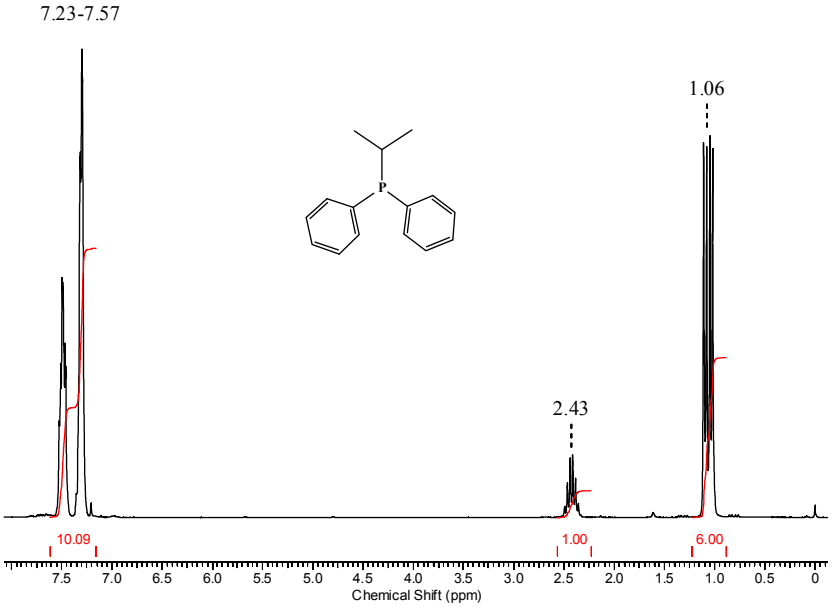
^{1}H-NMR spectrum of dipropy-phenylphosphine (P4)



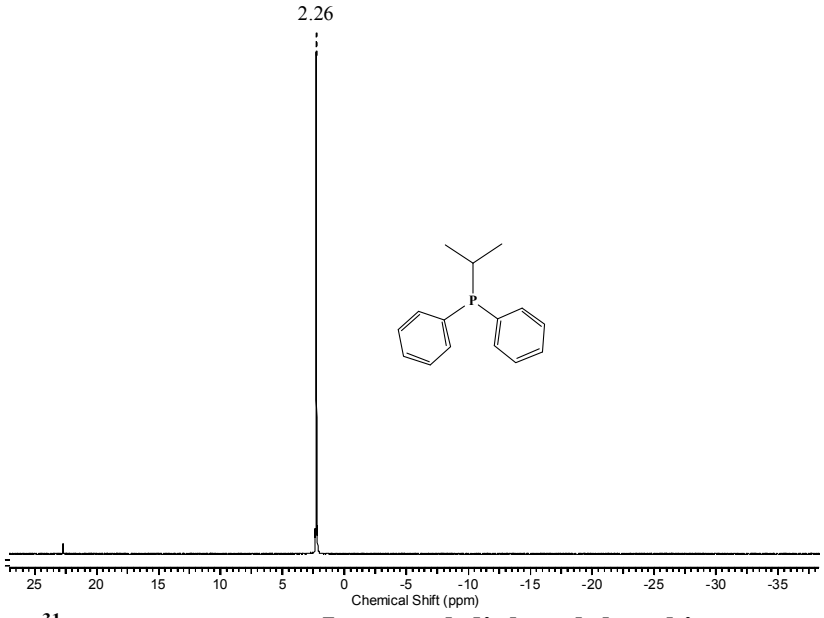
^{31}P-NMR spectrum of dipropy-phenylphosphine (P4)

Isopropyl-diphenylphosphine (P7)

Starting materials: Isopropyl chloride (5.52g, 70.4 mmol) in 30 mL diethyl ether, magnesium (1.87 g, 78 mmol), $ClPPh_2$ (14.04, 63.7 mmol) in 40 mL diethyl ether, distilled water for washing, 3x10 mL. **P7** was isolated as a colorless liquid (7.1 g, yield: 48%) by distillation at 130-132°C/0.1 mmHg. ^{1}H–NMR (in $CDCl_3$): δ 1.06 (dd, 6 H), 2.43 (h, 1 H), 7.23 – 7.57 (m, 10H) ^{31}P–NMR: 2.26 (s). ^{13}C-NMR: 19.6 (d, J_{P-C} = 17.9 Hz), 24.9 (d, J_{P-C} = 8.27 Hz), 128.2 (d, J_{P-C} = 6.9 Hz), 128.5 (s), 133.4 (d, J_{P-C} = 18.8 Hz), 137.5 (d, J_{P-C} = 13.8 Hz).



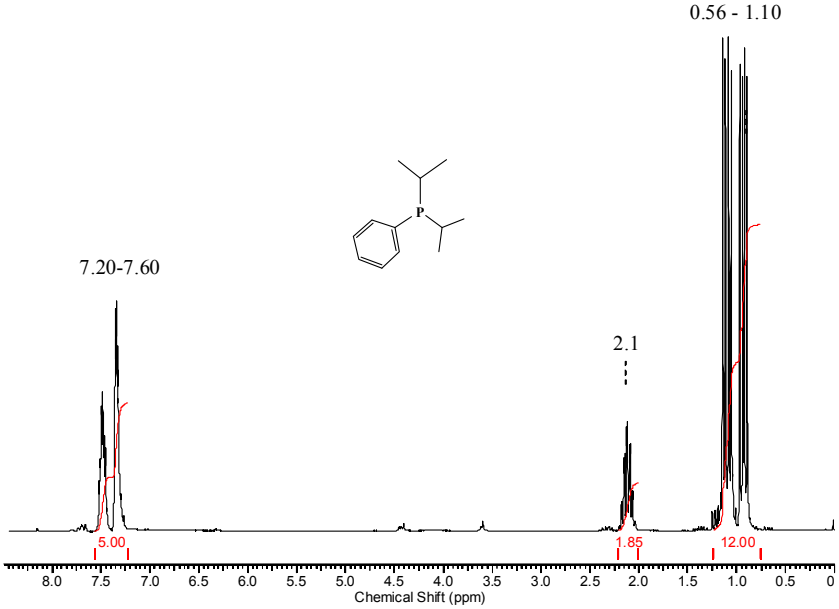
^{1}H-NMR spectrum of Isopropyl-diphenylphosphine (P7)



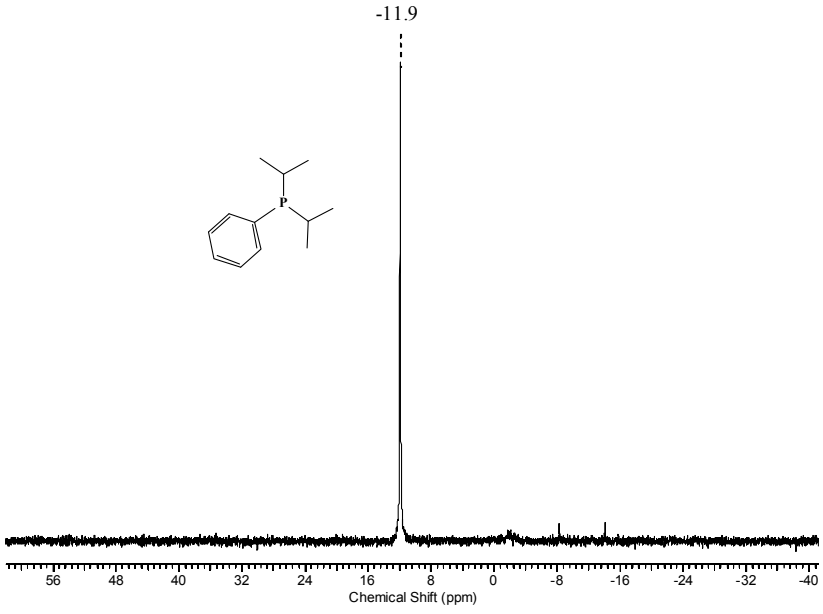
^{31}P-NMR spectrum of Isopropyl-diphenylphosphine (P7)

Diisopropyl-phenylphosphine (P8)

Isopropyl chloride (11.4 g, 155.8 mmol) in 100 mL diethyl ether, magnesium (3.74g, 155.8 mmol), Cl_2PPh (11.9g, 152.5 mmol) in 125 mL diethyl ether, distilled water for washing 3x10 mL. **P4** was isolated as a colorless liquid (2.7 g, yield: 7%), by distillation at 138-139°C/0.1 mmHg, ^{1}H–NMR (in $CDCl_3$): δ 0.56-1.10 (dd, 6 H), 2.10 (hd, 1 H), 7.20 – 7.60 (m, 10H) ^{31}P–NMR: 11.9 (s). ^{13}C-NMR: 19.2 (d, J_{P-C} = 16.07 Hz), 22.2 (d, J_{P-C} = 5.5 Hz), 129.2 (d, J_{P-C} = 7.1 Hz), 126.5 (s), 131.1 (d, J_{P-C} = 16.1 Hz), 138.1 (d, J_{P-C} = 18.3 Hz).



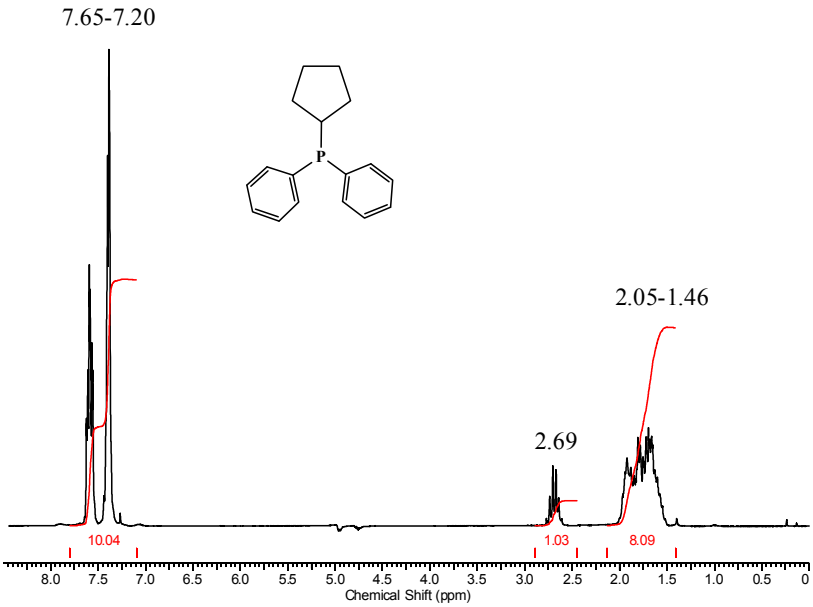
^{1}H-NMR spectrum of Diisopropyl-phenylphosphine (P8)



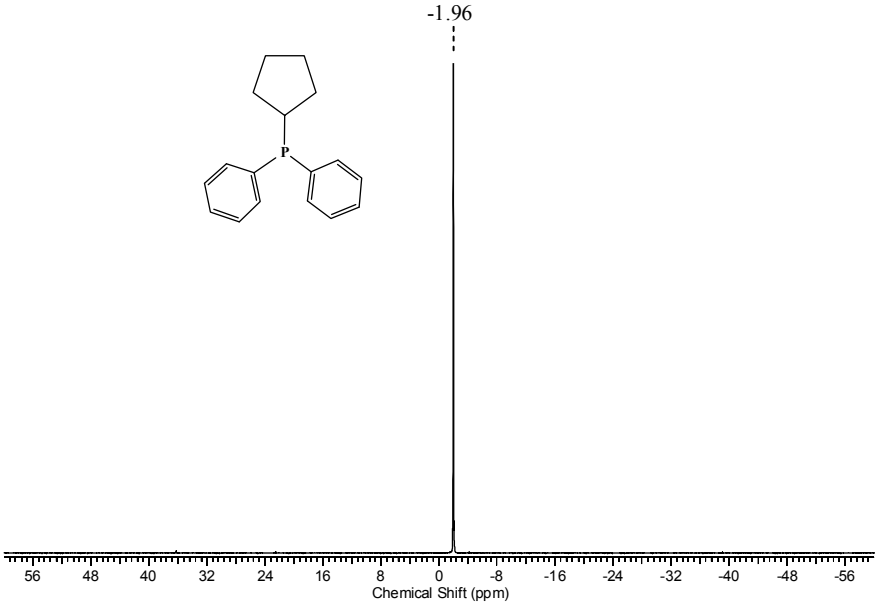
^{31}P-NMR spectrum of Diisopropyl-phenylphosphine (P8)

Cyclopentyl-diphenylphosphine (P9)

Starting materials: Cyclopentyl chloride (6.51g, 62.3 mmol) in 50 mL diethyl ether, magnesium (1.66 g, 68.5 mmol), $ClPPh_2$ (12.5, 56.5 mmol) in 50 mL diethyl ether, distilled water for washing, 3x10 mL. **P9** was isolated as a colorless liquid (10.46 g, yield: 72%) by distillation at 200-202°C/0.1 mmHg. ^{1}H–NMR (in $CDCl_3$): δ 1.46 – 2.80 (m, 9 H), 7.20 – 7.65 (m, 10H) ^{31}P–NMR: -1.96 (s). ^{13}C-NMR: 26.9 (d, J_{P-C} = 7.8 Hz), 31.8 (d, J_{P-C} = 20.2 Hz), 36.3 (d, J_{P-C} = 8.2 Hz), 128.7 (d, J_{P-C} = 6.9 Hz), 128.9 (s), 133.7 (d, J_{P-C} = 18.3 Hz), 139.5 (d, J_{P-C} = 13.8 Hz).



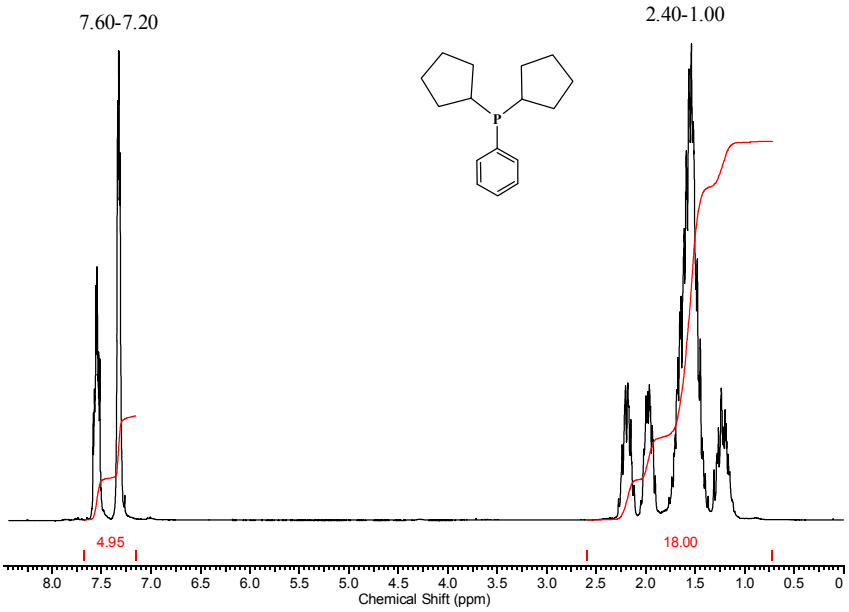
^{1}H-NMR spectrum of Cyclopentyl-diphenylphosphine (P9)



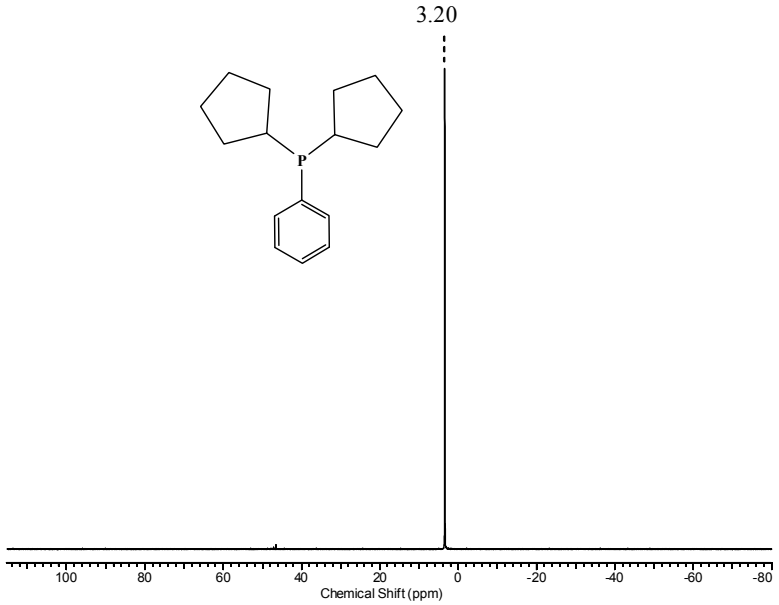
^{31}P-NMR spectrum of Cyclopentyl-diphenylphosphine (P9)

Dicyclopentyl-phenylphosphine (P10)

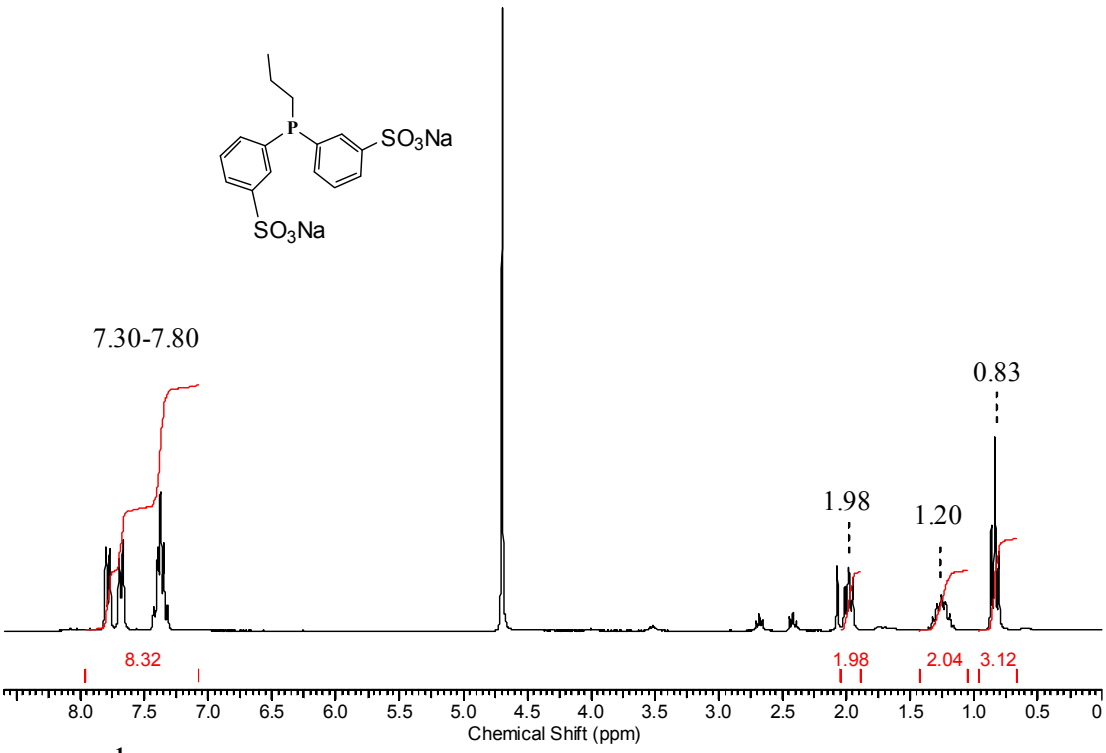
Starting materials: Cyclopentyl chloride (16.43, 157.2 mmol) in in 100 mL diethyl ether, magnesium (3.96g, 163.1mmol), Cl_2PPh (12.5g, 69.8 mmol) in 100 mL diethyl ether, distilled water for washing, 3x10 mL. **P10** was isolated as a colorless liquid (8.92 g, yield: 51%) by distillation at 174-175°C/0.1 mmHg. ^{1}H–NMR (in $CDCl_3$): δ 1.0 – 2.4 (m) (cyclopentyl 18 H), 7.2 – 7.6 (m, 5H) ^{31}P–NMR: 3.20 (s). ^{13}C-NMR: δ 26.1 (d, J_{P-C} = 6.9 Hz), 27.0 (d, J_{P-C} = 7.8 Hz), 31.3 (s), 31.4 (d, J_{P-C} = 30.1 Hz), 37.4 (d, J_{P-C} = 9.6 Hz), 128.2 (d, J_{P-C} = 7.3 Hz), 128.9 (s), 134.2 (d, J_{P-C} = 18.3 Hz), 138.7 (d, J_{P-C} = 14.7 Hz)



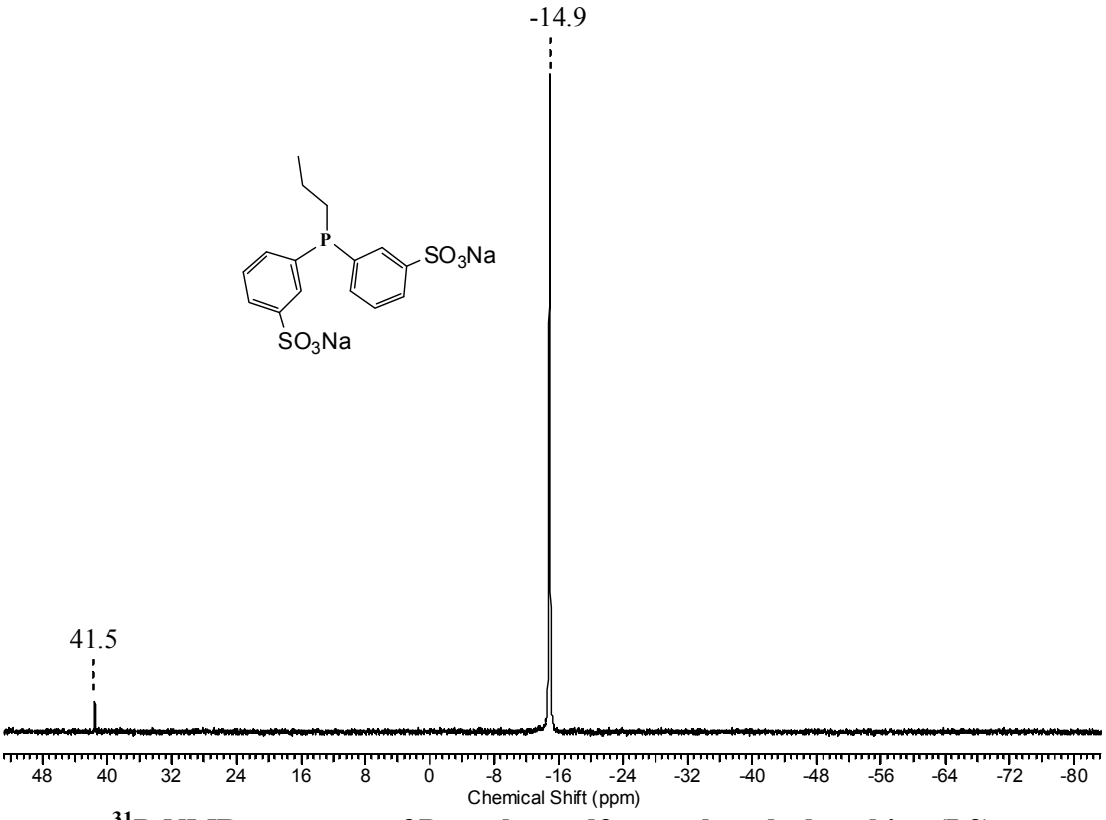
^{1}H-NMR spectrum of Dicyclopentyl-phenylphosphine (P10)



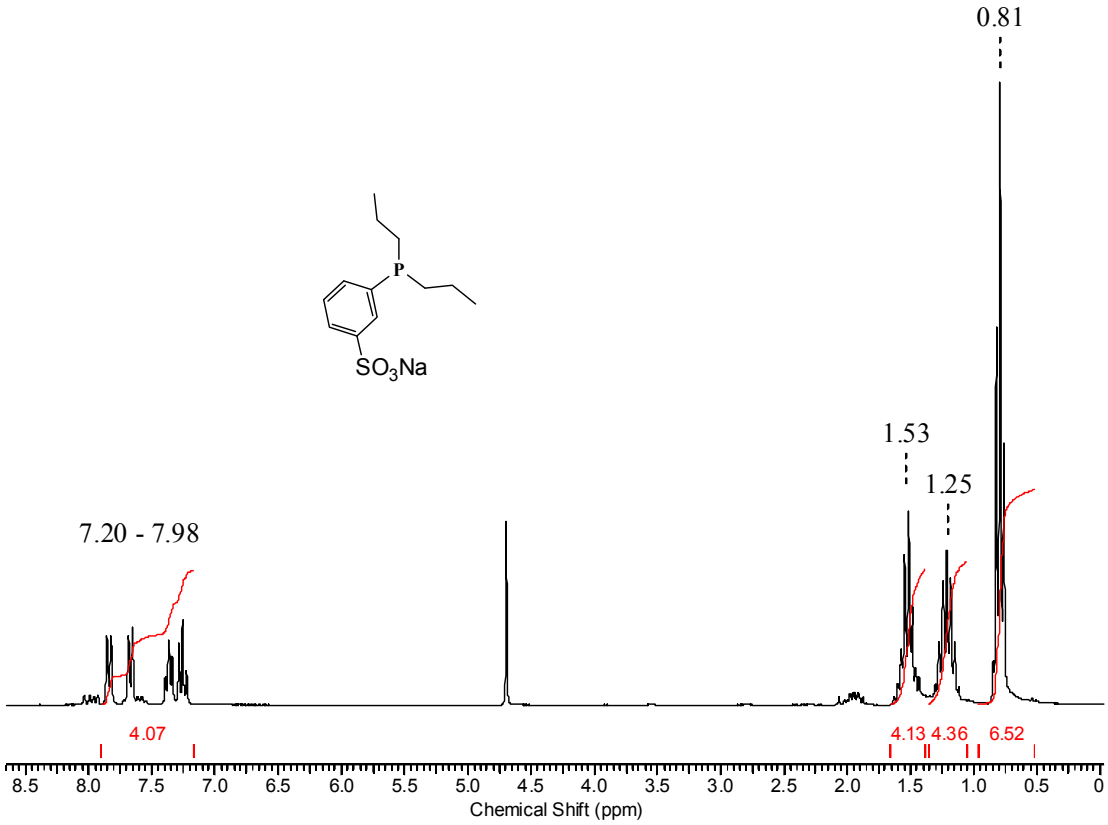
^{31}P-NMR spectrum of Dicyclopentyl-phenylphosphine (P10)



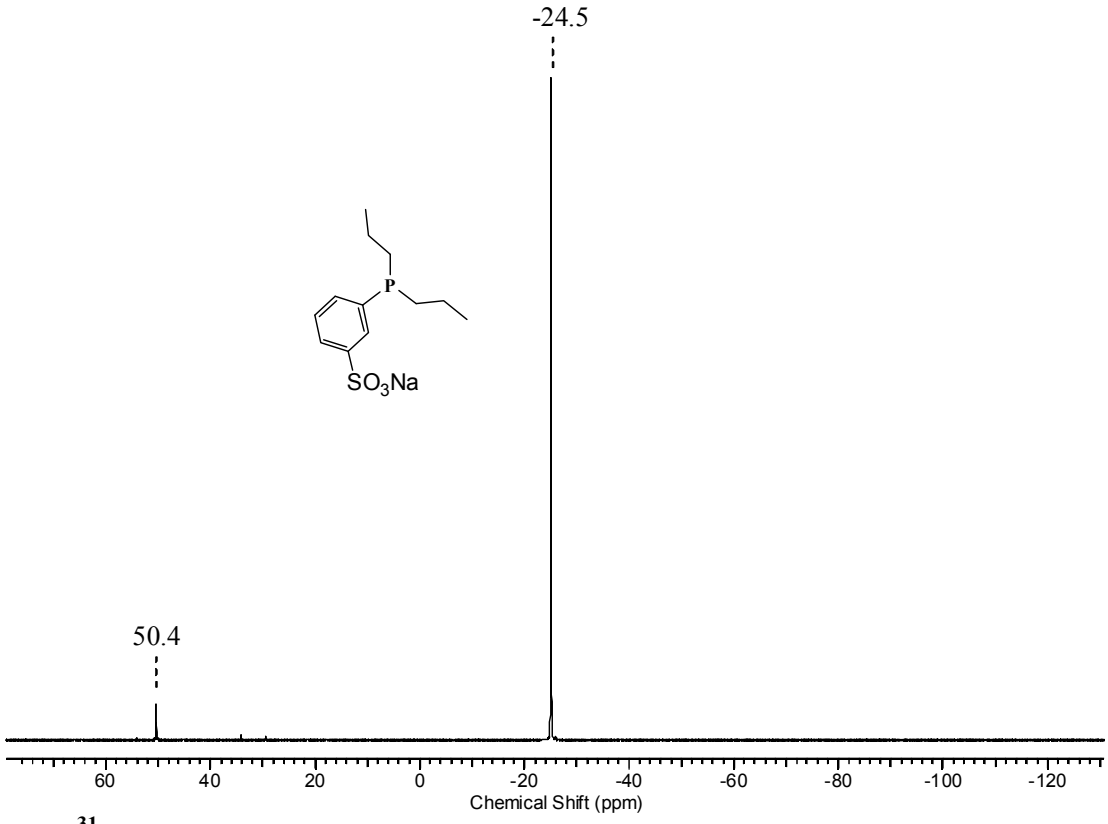
^{1}H-NMR spectrum of Propyl-*m*-sulfonatophenyl-phosphine (L3)



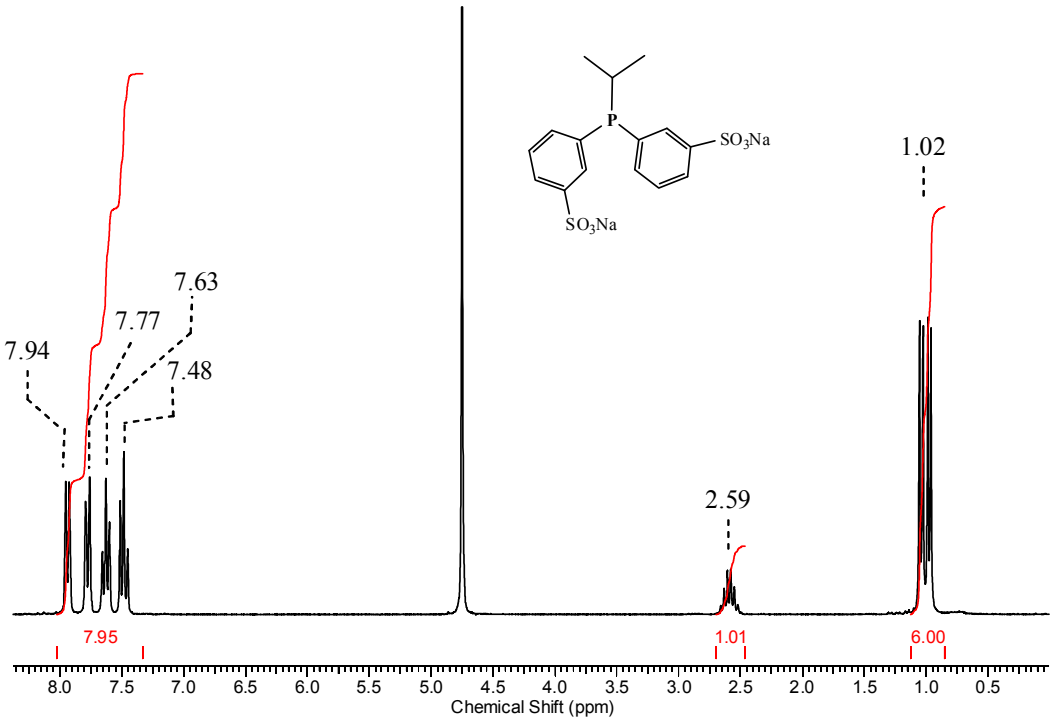
^{31}P-NMR spectrum of Propyl-*m*-sulfonatophenyl-phosphine (L3)



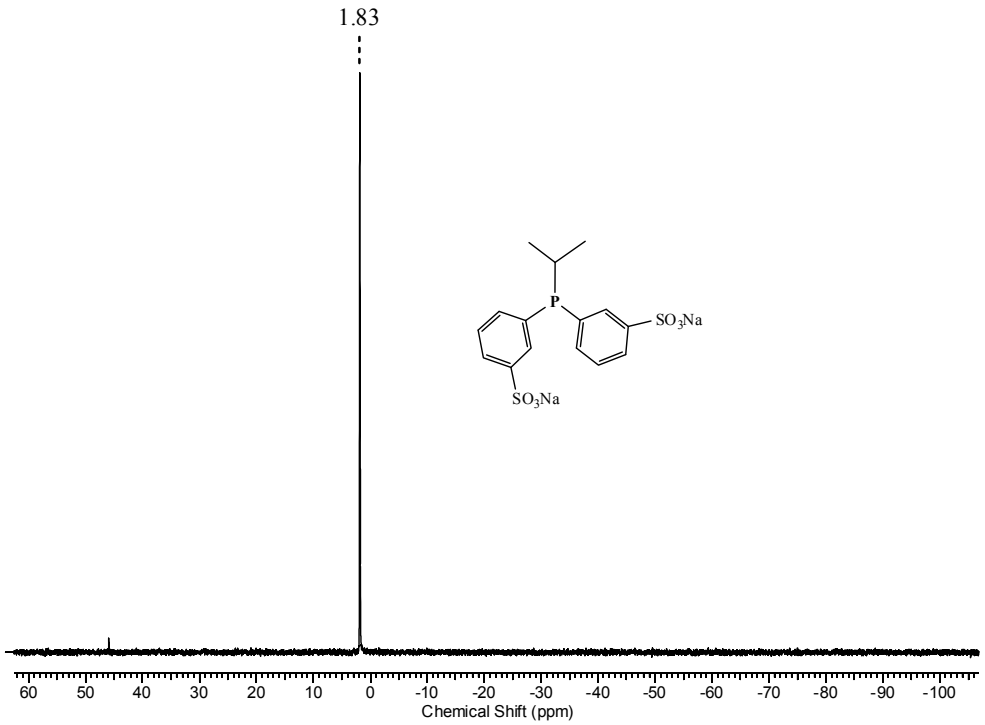
^{1}H-NMR spectrum of dipropyl-bis(*m*-sulfonatophenyl)phosphine (L4)



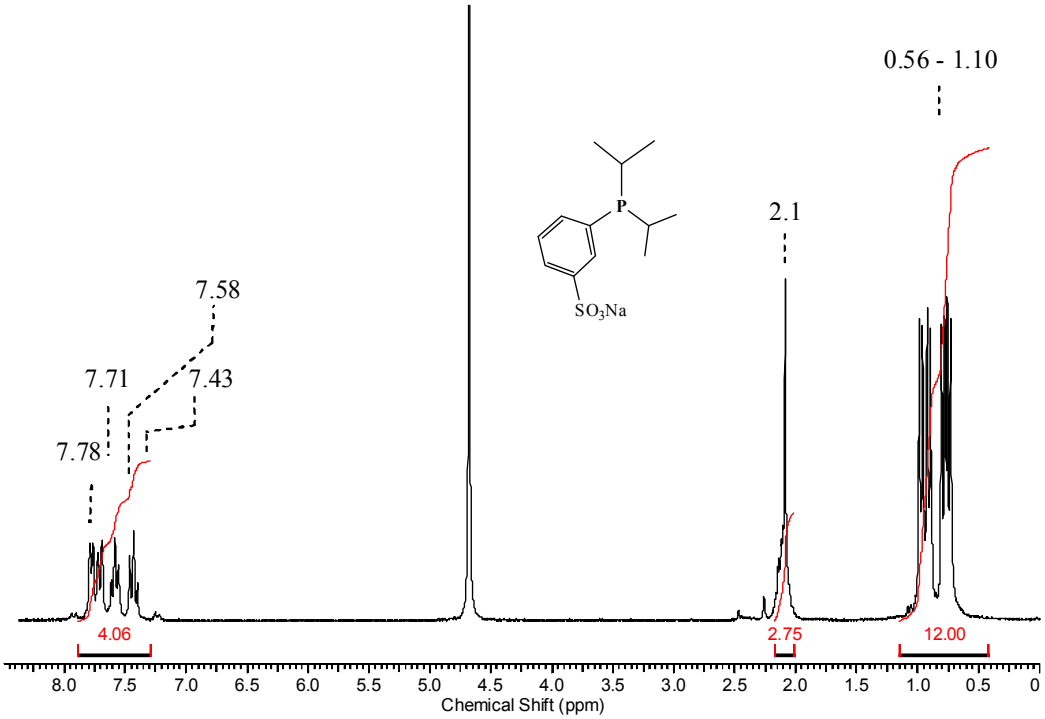
^{31}P-NMR spectrum of dipropyl-bis(*m*-sulfonatophenyl)phosphine (L4)



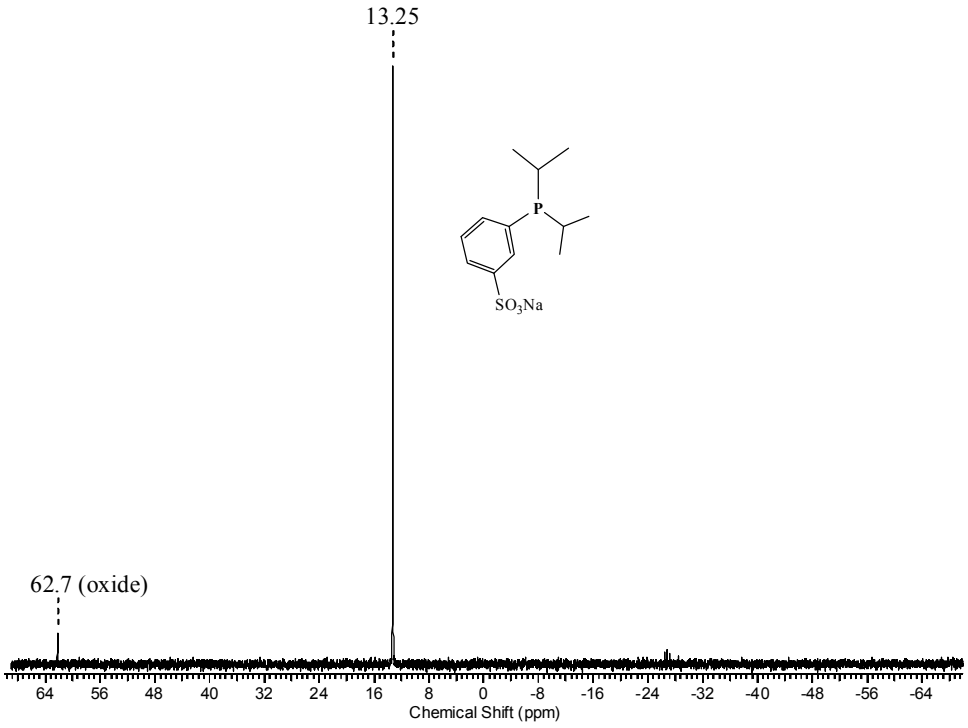
^{1}H-NMR spectrum of Isopropyl-bis(m-sulfonatophenyl)phosphine (L7)



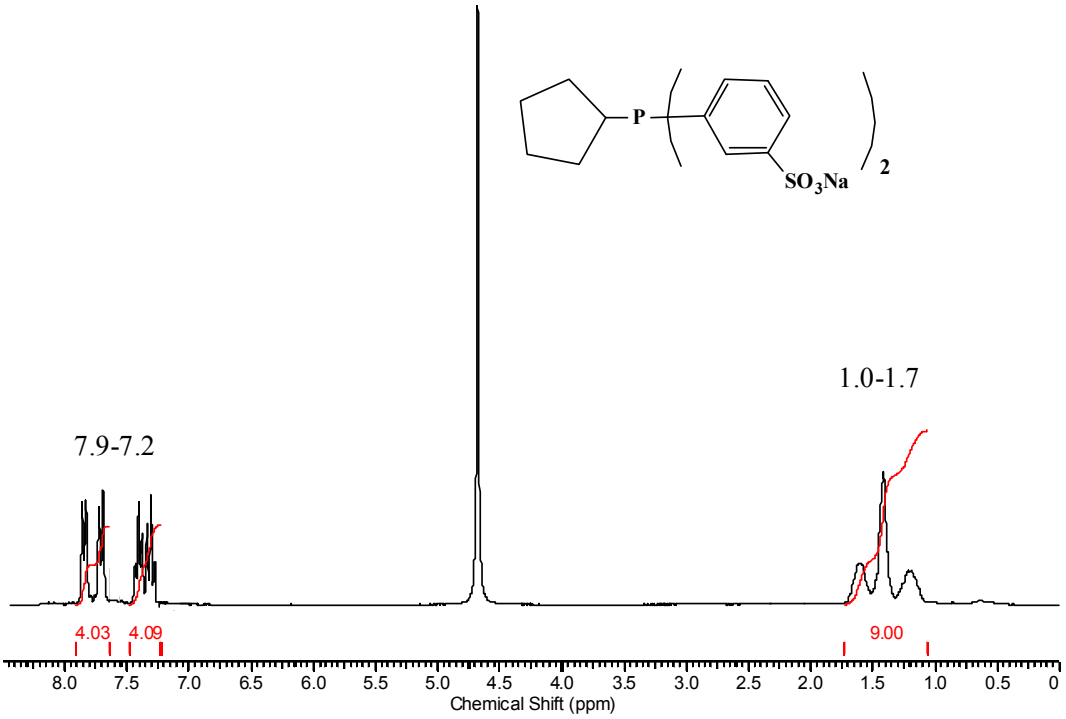
^{31}P-NMR spectrum of Isopropyl-bis(m-sulfonatophenyl)phosphine (L7)



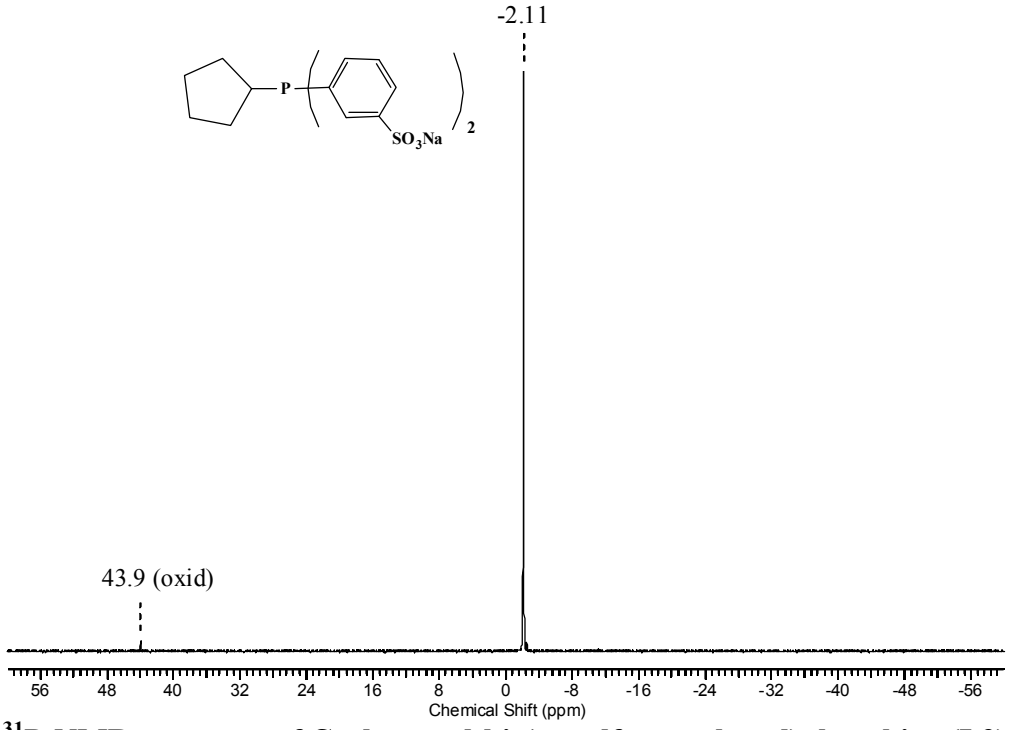
^{1}H-NMR spectrum of Diisopropyl-m-sulfonatophenyl-phosphine (L8)



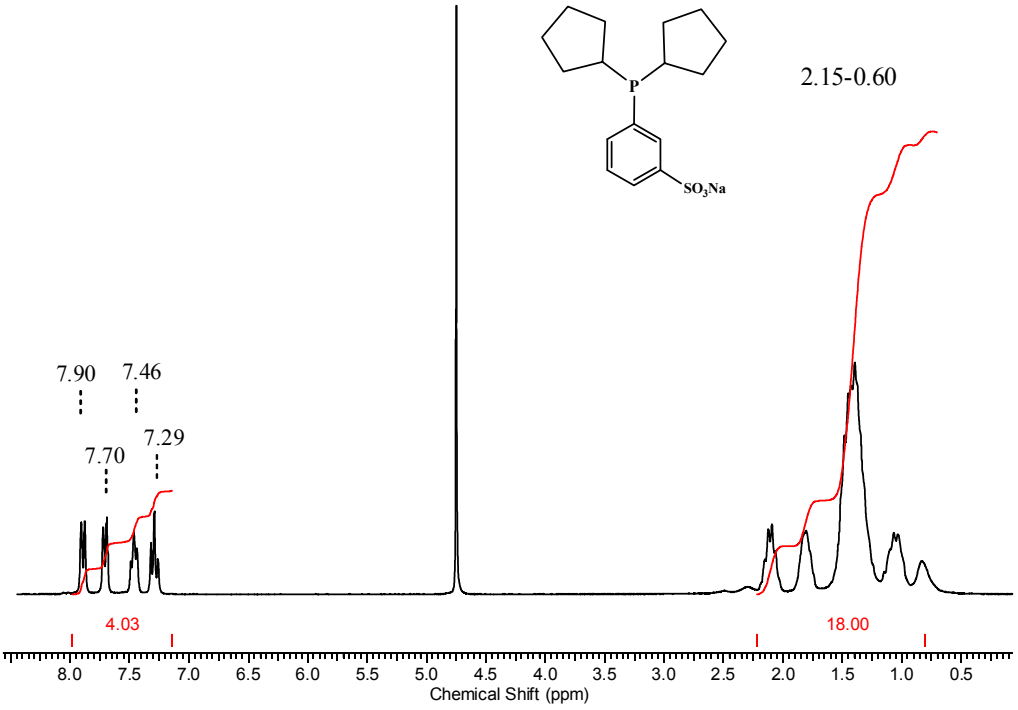
^{31}P-NMR spectrum of Diisopropyl-m-sulfonatophenyl-phosphine (L8)



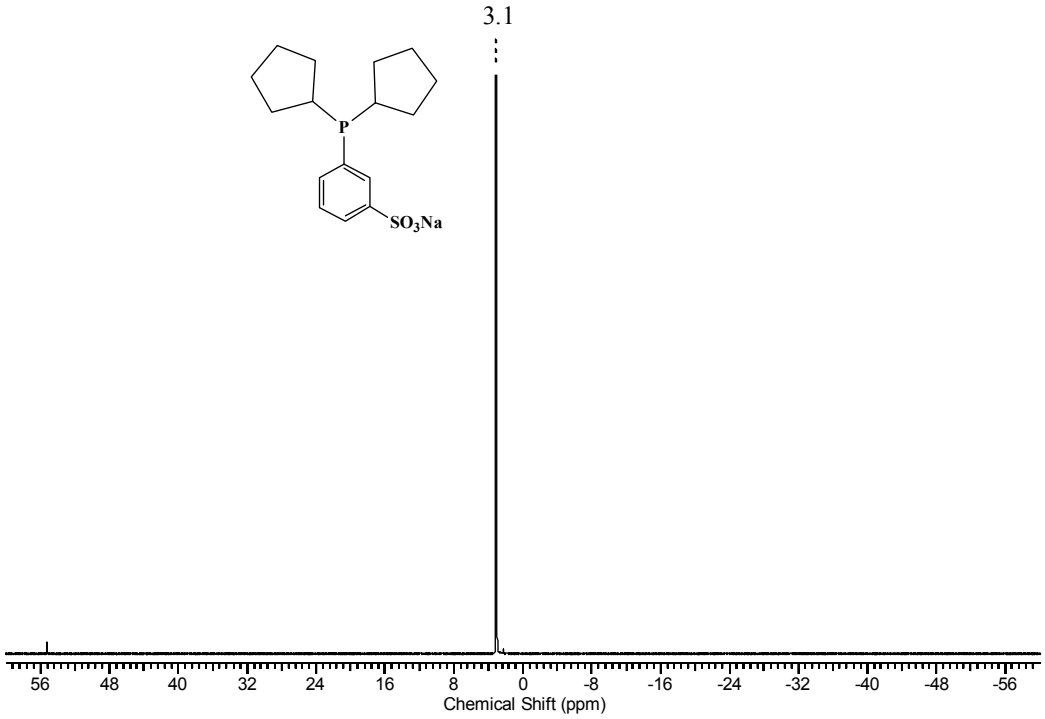
^{1}H-NMR spectrum of Cyclopentyl-bis(m-sulfonatophenyl)phosphine (L9)



^{31}P-NMR spectrum of Cyclopentyl-bis(m-sulfonatophenyl)phosphine (L9)



^{1}H-NMR spectrum of Dicyclopentyl-*m*-sulfonatophenyl-phosphine (L10)



^{31}P-NMR spectrum of Dicyclopentyl-*m*-sulfonatophenyl-phosphine (L10)

IR and NMR data of the nickel-complexes of non-sulfonated ligands

$[(Me)P(C_6H_5)_2]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 11.2 , IR (ν(CO), CH_2Cl_2): 2068.3 (w), 1992.9 (vs); ^{31}P NMR (δ, THF:H_2O): , IR (ν(CO), THF:H_2O): 2066.6 (w), 1994.6 (vs)

$[(Me)_2P(C_6H_5)]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): -5.5 , IR (ν(CO), CH_2Cl_2): 2066.7 (w), 1990.1 (vs); ^{31}P NMR (δ, THF:H_2O): -5.2 , IR (ν(CO), THF:H_2O): 2064.8 (w), 1991.2 (vs)

$[PrP(C_6H_5)_2]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 23.3 , IR (ν(CO), CH_2Cl_2): 2067.3,
^{31}P NMR (δ, THF:H_2O): 23.5 , IR (ν(CO), THF:H_2O): 2065.8 (w), 1992.3 (ws).

$[Pr_2P(C_6H_5)]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 18.5 , IR (ν(CO), CH_2Cl_2): 2064.9,
^{31}P NMR (δ, THF:H_2O): 18.8, IR (ν(CO), THF:H_2O): 2063.6 (w), 1987.6 (ws).

$[BuP(C_6H_5)_2]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 23.8, IR (ν(CO), CH_2Cl_2): 2067.1 (w), 1997.1 (vs); 1998.2
^{31}P NMR (δ, THF:H_2O): 24.0, IR (ν(CO), THF:H_2O): 2065.64 (w), 1995.8 (vs).

$[(Bu_2)P(C_6H_5)]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 18.7, IR (ν(CO), CH_2Cl_2): 2064.6 (w), 1997.4 (vs); ^{31}P NMR (δ, THF:H_2O): 19.8, IR (ν(CO), THF:H_2O): 2063.6 (w), 1986.6(vs).

$[^{i}PrP(C_6H_5)_2]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2):, 41.5 IR (ν(CO), CH_2Cl_2): 2067.2 (w), 1991.8 (ws); ^{31}P NMR (δ, THF:H_2O): 42.0, IR (ν(CO), THF:H_2O): 2065.6 (w), 1991.1 (ws).

$[^{i}Pr_2P(C_6H_5)]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 50.4, IR (ν(CO), CH_2Cl_2): 2063.7 (v), 1986.1 (vs); ^{31}P NMR (δ, THF:H_2O): 52.4, IR (ν(CO), THF:H_2O): 2062.3 (w), 1985.9 (vs).

$[CpP(C_6H_5)_2]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 38.8 , IR (ν(CO), CH_2Cl_2): 2066.6 (w), 1990.6 (vs); ^{31}P NMR (δ, THF:H_2O): , IR (ν(CO), THF:H_2O): 2065.1 (w), 1990.1 (vs).

$[(Cp)_2P(C_6H_5)]Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 45.5 , IR (ν(CO), CH_2Cl_2): 2063.2 (w), 1985.6 (vs); ^{31}P NMR (δ, THF:H_2O):, IR (ν(CO), THF:H_2O): 2061.9 (vw 1985.3 (vs).

$(PPh_3)Ni(CO)_3$:
^{31}P NMR (δ, CH_2Cl_2): 31.7, IR (ν(CO), CH_2Cl_2): 2069.5 (w), 1995.6 (vs); ^{31}P NMR (δ, THF:H_2O): 32.2, IR (ν(CO), THF:H_2O): 2068.1 (w), 1997.8 (vs)

^{31}P-NMR and IR data of the nickel-complexes of sulfonated ligands

$[(Me)P(C_6H_4$-*m*-$SO_3Na)_2]Ni(CO)_3$: 12.4 ppm, 2067.9 (w), 1994.3 (vs)

$[(Me)_2P(C_6H_4$-*m*-$SO_3Na)]Ni(CO)_3$: -4.1 ppm, 2065.2 (w), 1987.8 (vs)

$[PrP(C_6H_4$-*m*-$SO_3Na)_2]Ni(CO)_3$: 15.8 ppm, 2066.8 (w), 1988.9 (vs)

$[Pr_2P(C_6H_4\text{-}m\text{-}SO_3Na)]Ni(CO)_3$: 9.8 ppm, 2063.4 (w), 1986.3 (vs)

$[BuP(C_6H_4\text{-}m\text{-}SO_3Na)_2]Ni(CO)_3$: 25.3 ppm, 2066.9 (w), 1988.9 (vs)

$[(Bu_2)P(C_6H_4\text{-}m\text{-}SO_3Na)]Ni(CO)_3$: 20.9 ppm, 2063.2 (w), 1985.9 (vs)

$[^iPrP(C_6H_4\text{-}m\text{-}SO_3Na)_2]Ni(CO)_3$: 43.5 ppm, 2066.4 (w), 1992.3 (vs)

$[^iPr_2P(C_6H_4\text{-}m\text{-}SO_3Na)]Ni(CO)_3$: 2061.9 (w), 1985.2 (vs)

$[CpP(C_6H_4\text{-}m\text{-}SO_3Na)_2]Ni(CO)_3$: 39.6 ppm, 2065.9 (w), 1987.3 (vs)

$[(Cp)_2P(C_6H_4\text{-}m\text{-}SO_3Na)]Ni(CO)_3$: 47.5 ppm, 2061.5 (w), 1984.2 (vs)

$[TPPTS]Ni(CO)_3$: 32.2 ppm, 2070.1 (w), 1993.7 (vs)

^{31}P-NMR data of the palladium-complexes of non-sulfonated ligands

$MeP(C_6H_5)_2]_2PdCl_2$: Trans Isomer: 13.9 ppm

$[Me_2P(C_6H_5)]_2PdCl_2$: Trans Isomer: 2.6 ppm

$[PrP(C_6H_5)_2]_2PdCl_2$: Trans Isomer: 16.3 ppm

$[Pr_2P(C_6H_5)]_2PdCl_2$: Trans Isomer: 10.5 ppm

$[BuP(C_6H_5)_2]_2PdCl_2$: Trans Isomer: 17.4 ppm

$[Bu_2P(C_6H_5)]_2PdCl_2$: Trans Isomer: 11.2 ppm

$[^iPrP(C_6H_5)_2]_2PdCl_2$: Trans Isomer: 31.4 ppm

$[^iPr_2P(C_6H_5)]_2PdCl_2$: Trans Isomer: 37.4 ppm

$[CpP(C_6H_5)_2]_2PdCl_2$: Trans Isomer: 27.9 ppm

$[Cp_2P(C_6H_5)]_2PdCl_2$:Trans Isomer: 25.1 ppm

^{31}P-NMR data of the palladium-complexes of sulfonated ligands

$MeP(C_6H_4\text{-}m\text{-}SO_3Na)_2]_2PdCl_2$: Trans Isomer: 14.7; Cis Isomer: 35.90

$[Me_2P(C_6H_4\text{-}m\text{-}SO_3Na)]_2PdCl_2$: Trans Isomer: 9.2; could not be detected

$[PrP(C_6H_4\text{-}m\text{-}SO_3Na)_2]_2PdCl_2$: Trans Isomer: 19.1.; Cis Isomer.: 31.91

$[Pr_2P(C_6H_4\text{-}m\text{-}SO_3Na)]_2PdCl_2$: Trans Isomer: 16.4 Cis Isomer: not detectable

$[BuP(C_6H_4\text{-}m\text{-}SO_3Na)_2]_2PdCl_2$: Trans Isomer: 20.1; Cis Isomer: 34.34

$[Bu_2P(C_6H_4\text{-}m\text{-}SO_3Na)]_2PdCl_2$: Trans Isomer. 11.8 ; Cis Isomer: 23.27.

$[^iPrP(C_6H_4\text{-}m\text{-}SO_3Na)_2]_2PdCl_2$: Trans Isomer: 33.18; Cis Isomer.: 43.4.

$[^iPr_2P(C_6H_4\text{-}m\text{-}SO_3Na)]_2PdCl_2$: Trans Isomer: 38.4; Cis Isomer.: 42.9

$[CpP(C_6H_4\text{-}m\text{-}SO_3Na)_2]_2PdCl_2$: Trans Isomer: 28.1.; Cis Isomer: 38.97.

$[Cp_2P(C_6H_4\text{-}m\text{-}SO_3Na)]_2PdCl_2$:Trans Isomer: 30.3.; Cis Isomer: 34.65.

$[TPPTS]_2PdCl_2$: Trans Isomer: 26.2. Cis Isomer: 34.3.