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Highly (regio)selective hydroformylation of olefins using self-assembling phosphines

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Supporting Information – Table of Contents

SI-A: General information

Air- and moisture-sensitive syntheses were performed under argon atmosphere. Chemicals were purchased from Aldrich, TCI or ABCR. Unless otherwise noted, all commercial reagents were used without further purification.

Products were characterized by 1H NMR, 13C NMR, and HRMS spectroscopy. 1H and 13C NMR spectra were recorded on Bruker Avance 300 (300 MHz) or 400 (400M) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent: references for CDCl3 were 7.26 ppm (1H-NMR) and 77.16 ppm (13C-NMR). 13C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), and m (multiplet).

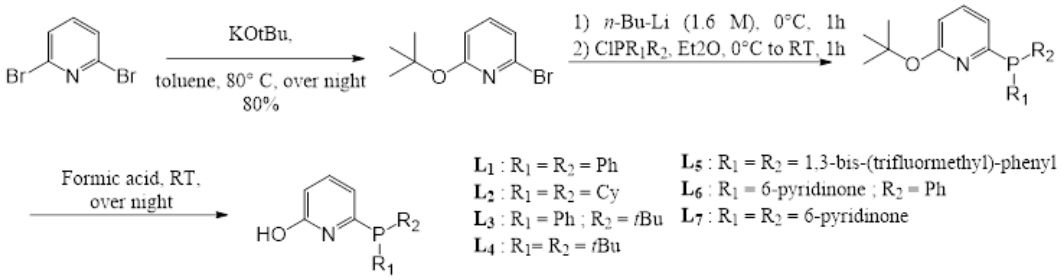
For GC analyses, HP 6890 chromatograph with a 29 m HP5 column was used. Linear to branched ratios were determined by GC analysis of the crude reaction mixture.

ESI (electrospray ionization) high resolution mass spectra were recorded on an Agilent Technologies 6210 TOF.

Solid-state IR data were collected on a Bruker Alpha FT-IR-Spectrometer.

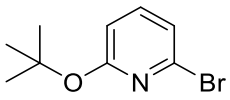
Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by intrinsic phasing (SHELXT: Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2019: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations.

SI-B: General procedure for the synthesis of ligands L1-L7



Supplementary Figure 1. General method for the synthesis of ligands **L1-L7**

2-tert-Butoxy-6-bromo-pyridine (b)



Synthesis was performed as previously reported by Breit et al. (*J. Am. Chem. Soc*. **2003**, *125*, 6608-6609, *J. Am. Chem. Soc*. **2011**, *133*, 964–975). To a solution of 10.00 g 2,6-dibromo-pyridine (42.21 mmol, 1.0 eq) in 100 ml toluene was added 7.11 g potassium-tert-butylate (63.32 mmol, 1.2 eq). The mixture was heated at 80°C overnight. After this time, it was cooled to room temperature and was filtered through celite. The filtrate was concentrated in a rotary evaporator and distillated (110°C, reduced pressure). 2-Tert-butoxy-6-bromo-pyridine was obtained as colorless liquid. (7.77 g, 80%).

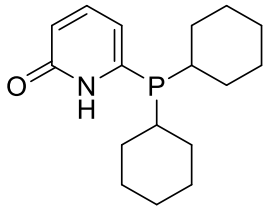
^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 7.33 (t, J = 7.79 Hz, 1H), 6.97 (d, J = 7.55 Hz, 1H), 6.24 (d, J= 8.13 Hz, 1H), 1.58 (s, 9H).

6-Diphenylphosphanyl-1H-pyridin-2-one (6-DPPon) (L1)

Synthesis was performed as previously reported by Breit et al. (*J. Am. Chem. Soc*. **2003**, *125*, 6608-6609, *J. Am. Chem. Soc*. **2011**, *133*, 964–975). 2-Tert-butoxy-6-bromo-pyridine (0.52 ml, 3.04 mmol) was dissolved in 18 ml of Et_2O and 1.6 M *n*-BuLi (2ml, 3.19 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C 1 hour and then stirred at room temperature for 30 minutes. A solution of chlorodiphenylphosphine in 3 ml of Et_2O was added at 0°C and reaction mixture was stirred an hour at room temperature. Then, 10ml of water was added, the organic phase was extracted with Et_2O (4x6ml)and Na_2SO_4 was added for drying. It was filtrated and evaporated. 2-Tert-butoxy-6-diphenylphosphanyl-pyridine was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.43-7.29 (m, 11H), 6.77 (ddd, J = 7.11, 3.11, 0.87 Hz, 1H), 6.50 (dt, J = 8.29, 0.73 Hz, 1H), 1.35 (s, 9H). ^{31}P (300 MHz, $CDCl_3$, ppm) -2.62. This product was no isolated. It was dissolved in concentrated formic acid (11 ml) and stirred overnight at room temperature. After this time, distilled water (22 ml) was added. The organic phase was extracted with DCM (3 x 10ml). It was washed with a mixture of 1.5ml FA and 4.5ml of H_2O and Na_2SO_4 was added. Solution was filtrated via cannula and dried under vacuum giving a white solid/yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 7.45-7.34 (m, 11H), 6.58 (d, J = 9.17, 1.10Hz, 1H), 6.21 (ddd, J = 6.76, 3.94, 1.09 Hz, 1H). ^{31}P (300 MHz, $CDCl_3$, ppm) -8.99. It was recrystallized from acetone (5ml) and washed several times (4x5ml). Product was obtained as white crystals (520mg, 61%). In the washes there were more crystals, but they were not isolated.

^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 8.52 (s, 1H), 7.45-7.30 (m, 11H), 6.49 (ddd, J = 9.25, 1.08 0.47Hz, 1H), 6.27 (dt, J = 6.39, 1.13 Hz, 1H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) = 163.97, 146.25, 140.26, 133.94, 132.80, 130.21, 129.31, 121.11, 113.54. ^{31}P (300 MHz, $CDCl_3$, ppm) = -9.25 (100%). HR-MS (ESI-TOF) calculated for $C_{17}H_{14}PON$ [M] 279.0813, found [M+H(1)]: 280.0891, [M+Na(23)]: 302.0705.

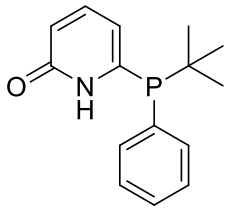
6-Dicyclohexylphosphanyl-1H-pyridin-2-one (L2)



2-Tert-butoxy-6-bromo-pyridine (2.62 ml, 15.21 mmol) was dissolved in 40 ml of Et_2O and 1.6 M *n*-BuLi (9.98 ml, 15.97 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 hour and after that time, it was stirred at room temperature for 30 minutes giving a yellow/orange suspension. A solution of chlorodicyclohexylphosphine in 10 ml of Et_2O was added at 0°C and stirred an hour at room temperature. Color turned orange/brown. Then, 30ml of water was added and the organic phase was extracted with Et_2O (3x20ml). Na_2SO_4 was added and the suspension was washed with Et_2O (3x5ml). It was filtrated and evaporated. 2-Tert-butoxy-6-dicyclohexylphosphanyl-pyridine was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 7.40 (dt, 7.79, 2.39 Hz, 1H), 7.06 (s, broad signal, 1H), 6.53 (d, J = 8.26, 0.73 Hz, 1H), 1.60 (s, 9H), ^{31}P (300 MHz, $CDCl_3$, ppm) = -8.38. This product was no isolated. It was dissolved in concentrated formic acid (56 ml) and stirred overnight at room temperature. After this time, distilled water (112 ml) was added. The organic phase was extracted with DCM (6 x 20ml). It was washed with a mixture of 3ml FA and 12ml of H_2O and Na_2SO_4 was added. The solution was filtrated via cannula, dried over Na_2SO_4 and filtrated again (DCM 2 x 5ml) and dried under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 7.36 (dt, J = 6.58, 1.30Hz, 1H), 6.53 (td, J = 9.15, 1.05 Hz, 1H), 6.21 (dt, J = 6.31, 1.08 Hz, 1H). ^{31}P (300 MHz, $CDCl_3$, ppm) = 3.77 (94%). It was recrystallized from acetone (10ml) and washed several times (5 x 5ml, 2 x 10ml). Product was obtained as a white powder (1.91 g, 43%). Washes from recrystallization were concentrated under vacuum and let overnight in the freezer. After this time, they were filtrated with a cannula and washed several times with cold acetone (2 x 10ml, 1 x 5ml). 0.68 g were obtained with a final yield of 58%.

^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 9.84 (s, 1H), 7.35 (dd, J = 7.94, 1.44Hz 1H), 6.55 (td, J = 9.23, 1.11Hz, 1H), 6.38 (dt, J = 6.27, 1.13 Hz, 1H). ^{13}C NMR = (300 MHz, $CDCl_3$, ppm) = 164.93, 145.87, 140.09, 121.29, 115.41, 32.55, 30.33, 29.39, 27.03, 26.82, 26.27, 113.54. ^{31}P = (300 MHz, $CDCl_3$, ppm) 3.58. HR-MS (ESI-TOF) calculated for $C_{17}H_{26}PON$ [M] 291.1752, found [M+H(1)]: 292.1830,[M+Na(23)]: 314.1644.

6-(*tert*-Butyl)-phenylphosphanyl-1H-pyridin-2-one (L3)

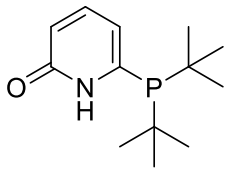


2-Tert-butoxy-6-bromo-pyridine (1.87ml, 10.86 mmol) was dissolved in 27 ml of Et_2O and 1.6 M *n*-BuLi (7.13 ml, 11.41 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 hour and after that time, it was stirred at room

temperature for 30 minutes. A solution of (tert-butyl)-chloro-phenylphosphine (2.15 ml, 11.41 mmol) in 6 ml of Et_2O was added at 0°C and stirred an hour at room temperature. Then, 19ml of water was added and the organic phase was extracted with Et_2O (3 x 15ml), Na_2SO_4 was added (washed with 2 x 5 ml of Et_2O) and it was filtrated and evaporated giving a yellow oil. 2-Tert-butoxy-6-(tert-butyl)-phenylphosphanyl-pyridine was obtained. ^1H NMR (300 MHz, $CDCl_3$, ppm) 7.66 (dt, J = 7.54, 1.69Hz, 1H), 7.43-7.29 (m, 5H), 7.03 (t, J = 5.99Hz, 1H), 6.53 (d, J = 8.40Hz, 1H), 1.60 (s, 9H). ^{31}P (300 MHz, $CDCl_3$, ppm) = 18.95. This product was no isolated. It was dissolved in concentrated formic acid (40 ml) and stirred overnight at room temperature. After this time, distilled water (80 ml) was added. The organic phase was extracted with DCM (4 x 20ml). It was washed with a mixture of 2.5 ml FA and 10 ml of H_2O and Na_2SO_4 was added. The solution was filtrated via cannula and dried over Na_2SO_4 then under vacuum. ^1H NMR (300 MHz, $CDCl_3$, ppm) = 7.62-7.55 (m, 2H), 7.48-7.38 (m, 4H), 6.61-6.55 (m, 2H). ^{31}P (300 MHz, $CDCl_3$, ppm) = 14.57. It was recrystallized from acetone (5ml) and washed several times (4x5ml). Product was obtained as a white powder (1.23mg, 32%). Washes were concentrated and let in the freezer overnight. After that, they were filtered and washed several times with cold acetone giving 0.500 g (total yield of 61%).

^1H NMR (300 MHz, $CDCl_3$, ppm) = 9.05 (s, 1H), 7.60-7.52 (m, 2H), 7.43-7.37 (m, 3H), 7.33 (dt, J = 8.06, 2.05 Hz, 1H), 6.49-6.42 (m, 2H). ^{13}C NMR = (300 MHz, $CDCl_3$, ppm) = 163.71, 146.41, 140.08, 135.02, 131.97, 130.30, 129.14, 120.68, 113.44, 31.78, 28.68. ^{31}P = (300 MHz, $CDCl_3$, ppm) 14.51 (100%). HR-MS (ESI-TOF) calculated for $C_{15}H_{18}PON$ [M] 259.1126, found [M+H(1)]: 260.1204,[M+Na(23)]: 282.1018.

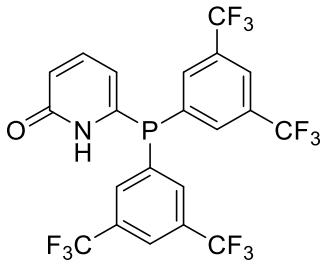
6-Di-*tert*-butylphosphanyl-1H-pyridin-2-one (L4)



2-Tert-butoxy-6-bromo-pyridine (1.80ml, 10.44 mmol) was dissolved in 30 ml of Et_2O and 1.6 M *n*-BuLi (6.85 ml, 10.96 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 hour and after that time, it was stirred at room temperature for 30 minutes. A solution of di-tert-butylchlorophosphine in 4 ml of Et2O was added at 0°C and stirred an hour at room temperature. Then, 15ml of water were added and the organic phase was extracted with Et_2O (3x10ml, 1x5ml). Na_2SO_4 was added and the suspension was filtrated and evaporated. 2-Tert-butoxy-6-di-tert-butyl-phosphanyl-pyridine was obtained. ^1H NMR (400 MHz, $CDCl_3$, ppm) = 7.41 (dt, J = 7.72, 2.28Hz, 1H), 7.20 (dt, J = 8.15, 0.87Hz, 1H), 6.58 (td, J = 8.33, 1.17Hz, 1H), 1.59 (s, 9H), 1.25 (s, 9H), 1.22 (s, 9H). ^{31}P (400 MHz, $CDCl_3$, ppm) = 42.34. This product was no isolated. It was dissolved in concentrated formic acid (15 ml) and stirred overnight at room temperature. After this time, distilled water (30 ml) was added. The organic phase was extracted with DCM (4 x 10ml). It was washed with a mixture of 3 ml FA and 12 ml of H_2O and Na_2SO_4 was added. The solution was filtrated via cannula and washed Na_2SO_4 (2x5ml of DCM) and dry under vacuum giving a yellow oil. ^1H NMR (300 MHz, $CDCl_3$, ppm) = 7.49 (dd, J = 9.14, 0.83Hz, 1H), 6.72 (dt, J = 8.15, 2.60, 0.98Hz, 1H), 6.66 (td, J = 9.10, 1.10Hz, 1H), 1.26 (s, 9H), 1.21 (s, 9H). ^{31}P (300 MHz, $CDCl_3$, ppm) = 38.13. This product was distillated under vacuum (0.002 bar) at 110-120 °C). It crystallized in the top part of the distillation Schlenk as colorless to white crystals. At the bottom, an orange/yellow oil was obtained. Then, this oil was washed away with DCM several times and the white crystals were dried under vacuum. 1.39 g were obtained giving a yield of 56%.

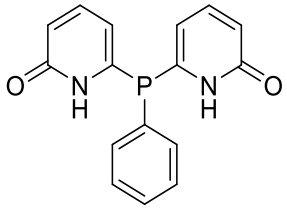
^1H NMR (300 MHz, $CDCl_3$, ppm) = 9.13 (s, 1H), 7.34 (m, 1H), 6.58-6.47 (m, 2H), 1.23 (s, 9H), 1.19 (s, 9H). ^{13}C NMR = (300 MHz, $CDCl_3$, ppm) = 163.51, 146.51, 140.05, 121.83, 115.29, 32.77, 30.26. ^{31}P = (300 MHz, $CDCl_3$, ppm) = 38.28. HR-MS (ESI-TOF) calculated for $C_{13}H_{22}PON$ [M] 239.1439, found [M+H(1)]: 240.1517.

6-Bis-(3,5-di-(trifluormethyl)-phenylphosphanyl-1H-pyridin-2-one (L5)



Synthesis was performed as previously reported by Breit et al. (*Chem. Sci.*, **2013**, *4*, 2418–2422). 2-Tert-butoxy-6-bromo-pyridine (0.37 ml, 2.17 mmol) was dissolved in 18 ml of Et_2O and 1.6 M *n*-BuLi (1.43 ml, 2.28 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 hour and after that time, it was stirred at room temperature for 30 minutes giving an orange suspension. A solution of bis-(3,5-di-(trifluoromethyl)-phenyl)-chlorophosphine (1.12 g, 2.28 mmol) in 2 ml of Et_2O was added at -78°C and stirred an hour at room temperature. Color turned dark purple/brown). Then, 10ml of water were added and the organic phase was extracted with Et_2O (7 x 10 ml), Na_2SO_4 was added and the suspension was washed with Et_2O (2 x 10 ml). It was filtrated and evaporated. 2-Tert-butoxy-6-bis-(3,5-di-(trifluoromethyl)-phenylphosphanyl-pyridine was obtained as brownish solid/oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 7.90-7.77 (m, 3H), 7.55 (ddd, J = 9.36, 3.09, 1.26 Hz, 1H), 7.18 (dt, J = 7.33, 0.82, 0.74 Hz, 1H), 6.66 (qd, J = 8.51, 1.01, 0.44 Hz, 1H), 1.27 (s, 9H). ^{31}P (300 MHz, $CDCl_3$, ppm) = 2.46. This product was not isolated. It was dissolved in concentrated formic acid (8 ml) and stirred overnight at room temperature. After this time, distilled water (16 ml) was added. The organic phase was extracted with DCM (7 x 10 ml). It was washed with a mixture of 1 ml FA and 4 ml of H_2O and Na_2SO_4 was added. The solution was filtrated via cannula, dried over Na_2SO_4 and filtrated again (DCM 3 x 5 ml) and dried further under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 7.94-7.86 (m, 3H), 7.42 (td, J = 8.11, 2.52, 1.86 Hz, 1H), 6.50-6.42 (m, 2H). ^{31}P (300 MHz, $CDCl_3$, ppm) = -7.51. It was recrystallized from acetone (6 ml) and washed several times (4 x 2 ml, 1 x 1 ml). Product was obtained as a white powder (0.300 g). Washes from recrystallization were concentrated under vacuum and let overnight in the freezer. After this time, they were filtrated with a cannula and washed several times with cold acetone (3 x 5 ml) and recrystallized again. An additional 0.270 g were obtained with a final yield of 64%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) = 12.74 (s, 1H), 7.95-7.88 (m, 3H), 7.34 (td, J = 7.86, 2.46, 2.33 Hz 1H), 6.43 (ddd, J = 7.71, 1.12, 1.04 Hz, 1H), 6.24 (dt, J = 9.28, 1.08 Hz, 1H). ^{13}C NMR = (300 MHz, $CDCl_3$, ppm) = 165.24, 142.61, 142.28, 140.29, 140.14, 136.15, 135.95, 133.73, 133.45, 133.04, 132.95, 132.60, 132.51, 132.15, 132.06, 131.70, 131.61, 123.98 (^{13}C-^{19}F : 124.08, 124.03, 123.93, 123.88) 122.91, 121.07 (^{13}C-^{19}F : 128.31, 124.69, 117.45, 116.77), 116.35, 77.43, 77.21, 77.01, 76.58. ^{31}P = (300 MHz, $CDCl_3$, ppm) = -7.13. HR-MS (EI) calculated for $C_{21}H_{10}NF_{12}PON$ [M] 551.03029, found [M]: 551.03032.

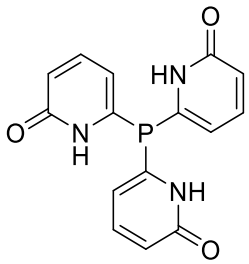
6,6'-(phenylphosphanediyl)bis(pyridin-2(1H)-one) (L6)



2-Tert-butoxy-6-bromo-pyridine (0.75ml, 4.35mmol) was dissolved in 30 ml of Et_2O and 1.6 M *n*-BuLi (2.85 ml, 4.56 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 hour and after that time, it was stirred at room temperature for 30 minutes. A solution of dichlorophenylphosphine in 4 ml of Et_2O was added at 0°C and stirred 1 hour at room temperature. Then, 20ml of water were added and the organic phase was extracted with Et_2O (3x10ml), Na_2SO_4 was added, and it was filtrated and evaporated. 2-Tert-butoxy-6,6'-(phenylphosphanyl)bis-pyridine was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.54-7.46 (m, 2H), 7.39 (ddd, J = 7.74, 2.64, 1.12Hz, 2H), 7.36-7.30 (m, 3H), 6.86 (dd, J = 3.28, 0.87Hz, 1H), 6.48 (dt, J = 8.35, 0.79Hz, H), 1.33 (s, 18H). ^{31}P (300 MHz, $CDCl_3$, ppm) = 0.31. It was dissolved in concentrated formic acid (15 ml) and stirred overnight at room temperature. After this time, distilled water (30 ml) was added, and formation of a precipitate occurred. Complete evaporation was carried out under vacuum (at 50°C), MeOH was added (3x2ml) and evaporated every time. Then, the compound was redispersed in 15 ml of MeOH and filtered through a frit. It was washed several times (1x10 ml, 2x5ml) and dried under vacuum. Off-white powder was obtained (480 mg, 75%).

^{1}H NMR (300 MHz, DMSO, ppm) = 11.80 (s, 2H), 7.59-7.34 (m, 7H), 6.38 (br s, 2H), 5.88 (br s, 2H). ^{31}P (300 MHz, DMSO, ppm) = -15.05, broad signal. ^{13}C NMR = (400 MHz, DMSO, ppm) = 163.18, 146.77, 140.02, 134.21, 131.19, 130.45, 129.20, 119.20, 113.09. HR-MS (ESI-TOF) calculated for $C_{16}H_{13}PO_2N_2$ [M] 296.0715, found [M+H(1)]: 297.0793, [M+Na(23)]: 319.0607.

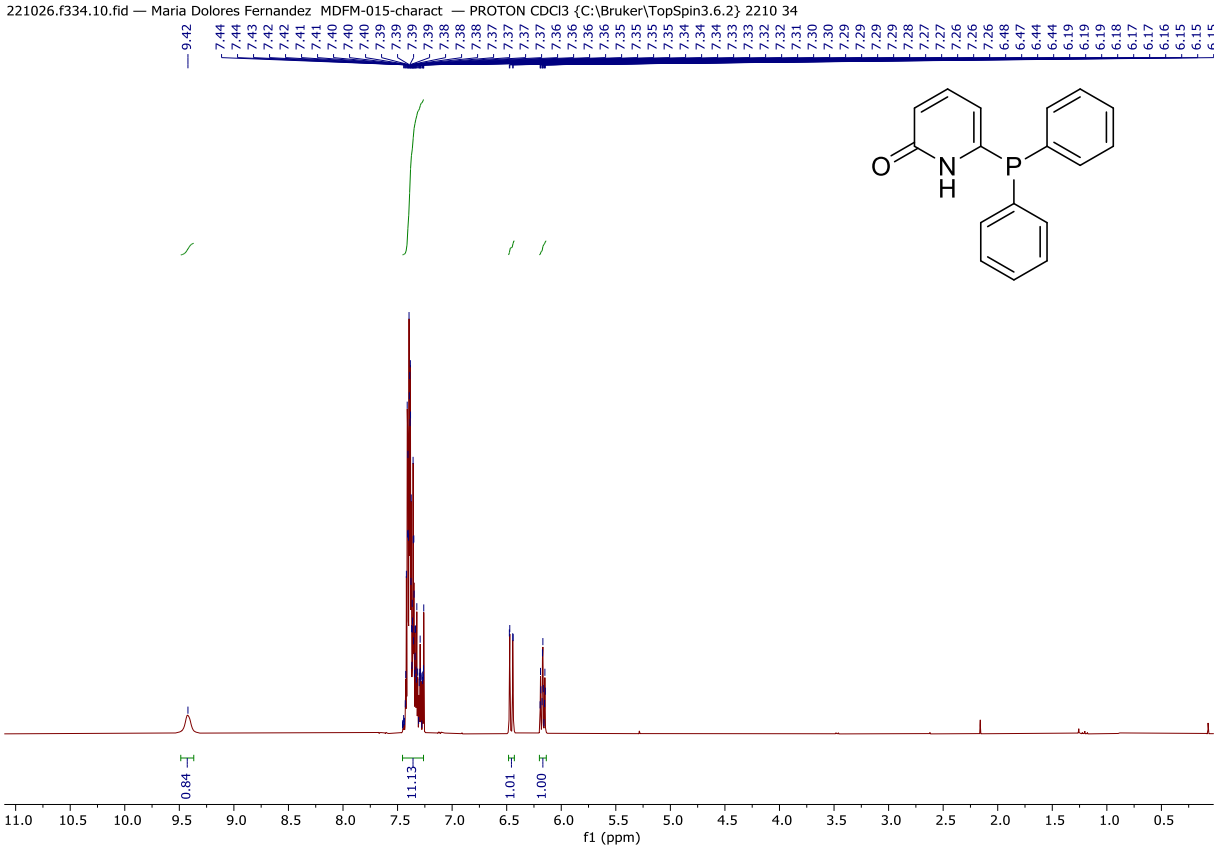
6,6',6''-phosphanetriyltris(pyridin-2(1H)-one) (L7)



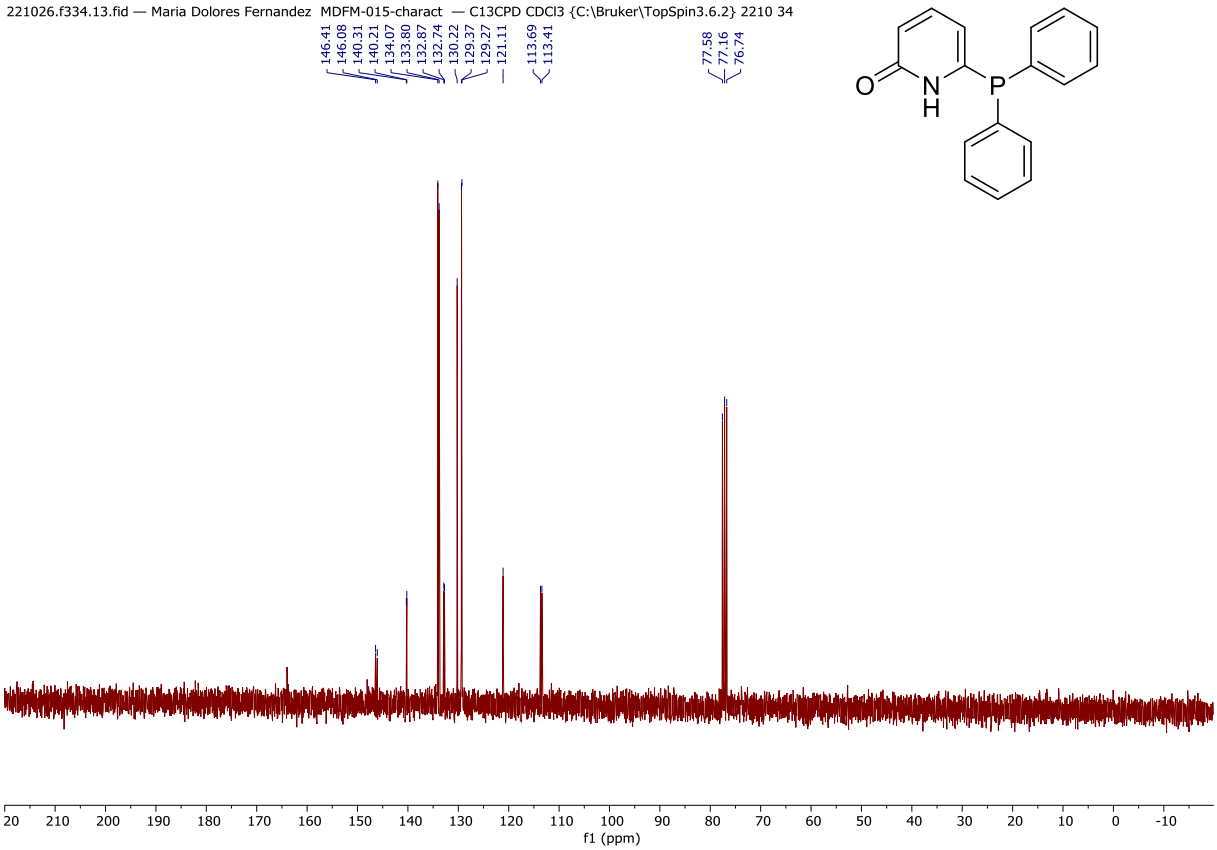
2-Tert-butoxy-6-bromo-pyridine (0.37 ml, 2.17 mmol) was dissolved in 18 ml of Et_2O and 1.6 M *n*-BuLi (1.43 ml, 2.28 mmol) was added dropwise at 0°C. The mixture was stirred at 0°C for 1 hour and after that time, it was stirred at room temperature for 30 minutes. A solution of trichlorophosphine in 2 ml of Et_2O was added at 0°C and stirred an hour at room temperature. Then, 10 ml of water were added, and the organic phase was extracted with Et_2O (3 x 10ml), Na_2SO_4 was added, and it was filtrated and the solution was evaporated. 2-Tert-butoxy-6,6',6''-phosphanetriyltris-pyridine was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) = 7.40 (ddd, J = 6.67, 2.52, 1.09 Hz, 3H), 6.90 (ddd, J = 7.29, 2.67, 1.12 Hz, 3H), 1.35 (s, 21H). ^{31}P (400 MHz, $CDCl_3$, ppm) = 3.14. It was dissolved in concentrated formic acid (8 ml) and stirred overnight at room temperature. After this time, distilled water (16 ml) was added, and formation of a precipitate occurred. Complete evaporation was carried out under vacuum (at 50°C), MeOH was added (3 x 2ml) and evaporated every time. Then, the compound was redispersed in 10 ml of MeOH and filtered through a frit. It was washed several times (3 x 2ml) and dried under vacuum. Off-white powder was obtained (120 mg, 53%).

^{1}H NMR (300 MHz, DMSO, ppm) = 11.79 (s, 3H), 7.48 (br s, 3H), 6.46 (d, J = 8.74, 3H), 6.18 (br s, 3H). ^{31}P (300 MHz, DMSO, ppm) = -18.04, broad signal. ^{13}C NMR = (400 MHz, DMSO, ppm) = 163.62, 145.63, 140.61, 119.78, 115.21. HR-MS (ESI-TOF) calculated for $C_{15}H_{12}PO_3N_3$ [M] 313.0616, found [M+H(1)]: 314.0694, [M+Na(23)]: 336.

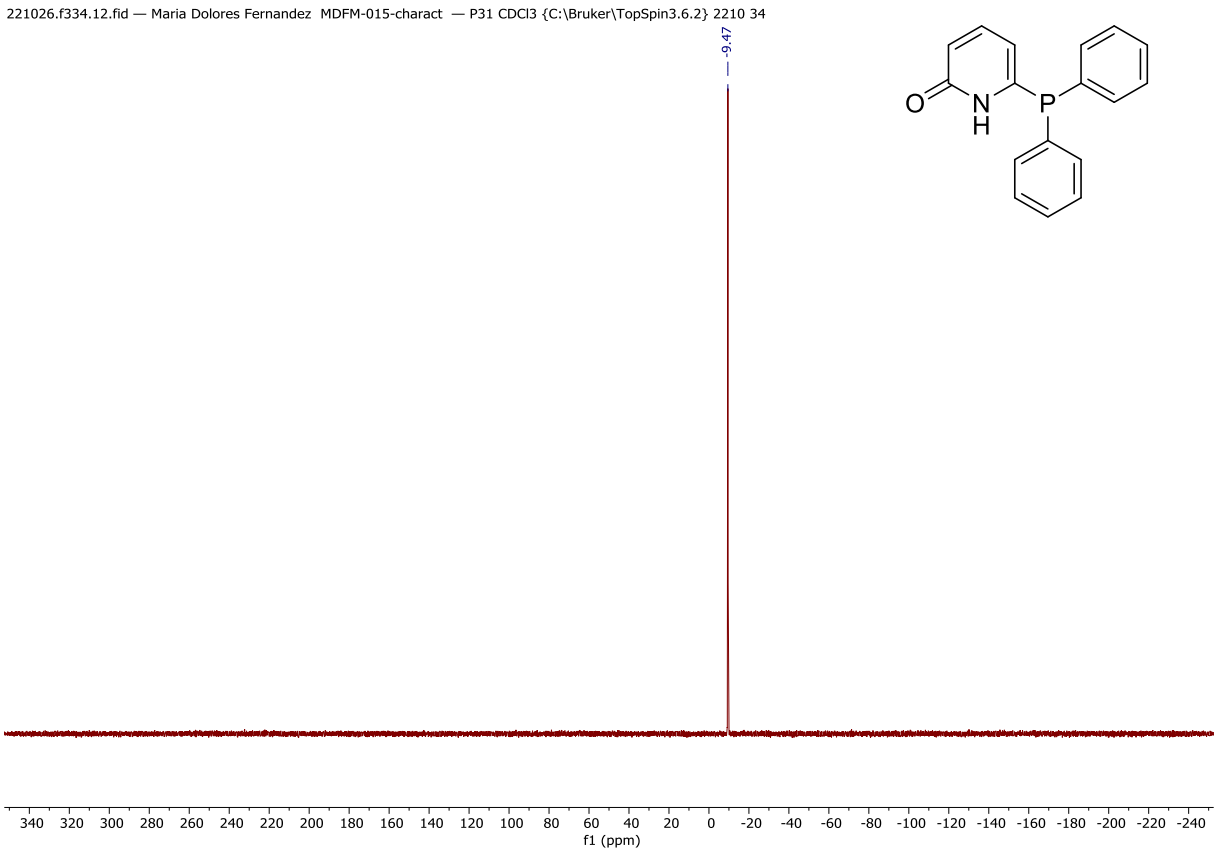
SI-C: NMR Spectra of the phosphine ligands (L1-L7)



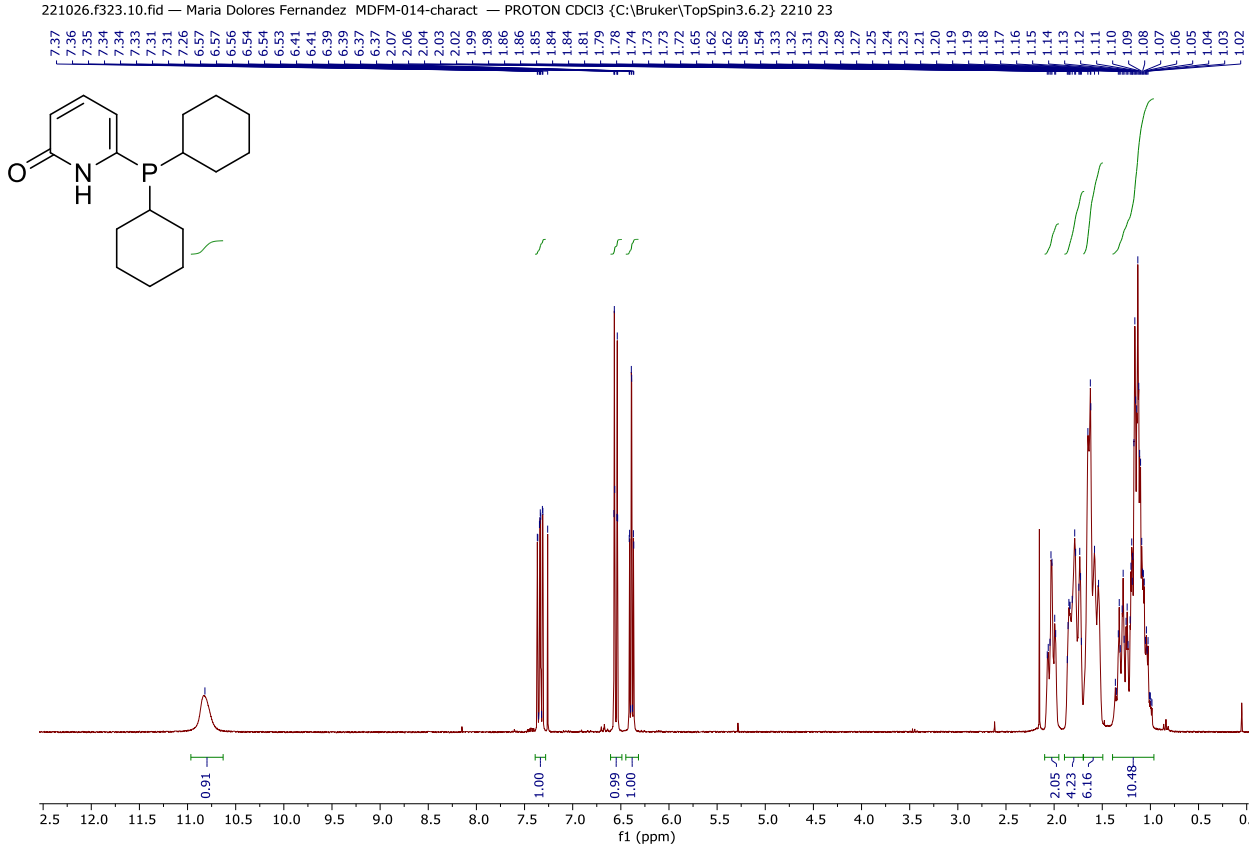
Supplementary Figure 2. ^{1}H NMR spectrum of L1 in $CDCl_3$ at RT and AP.



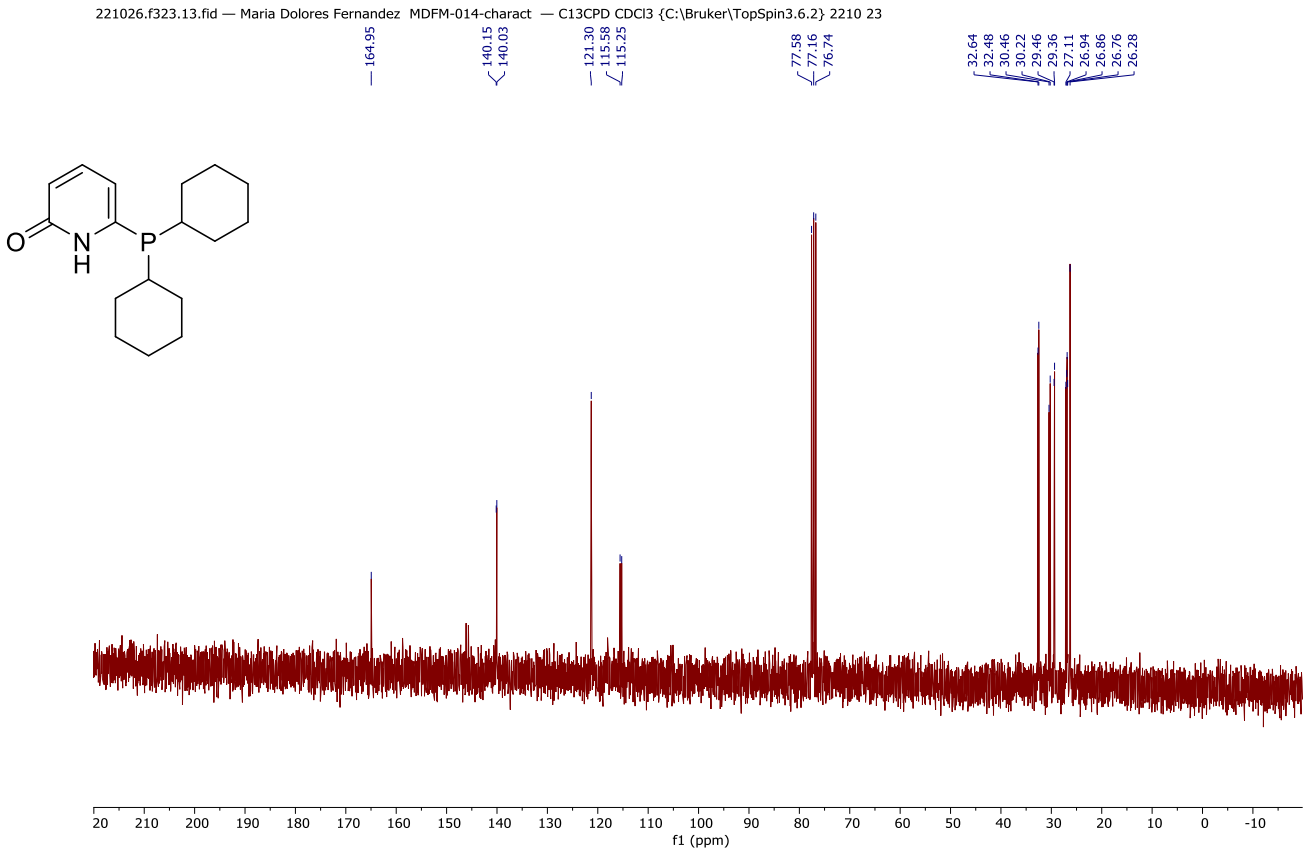
Supplementary Figure 3. ^{13}C NMR spectrum of L1 in $CDCl_3$ at RT and AP.



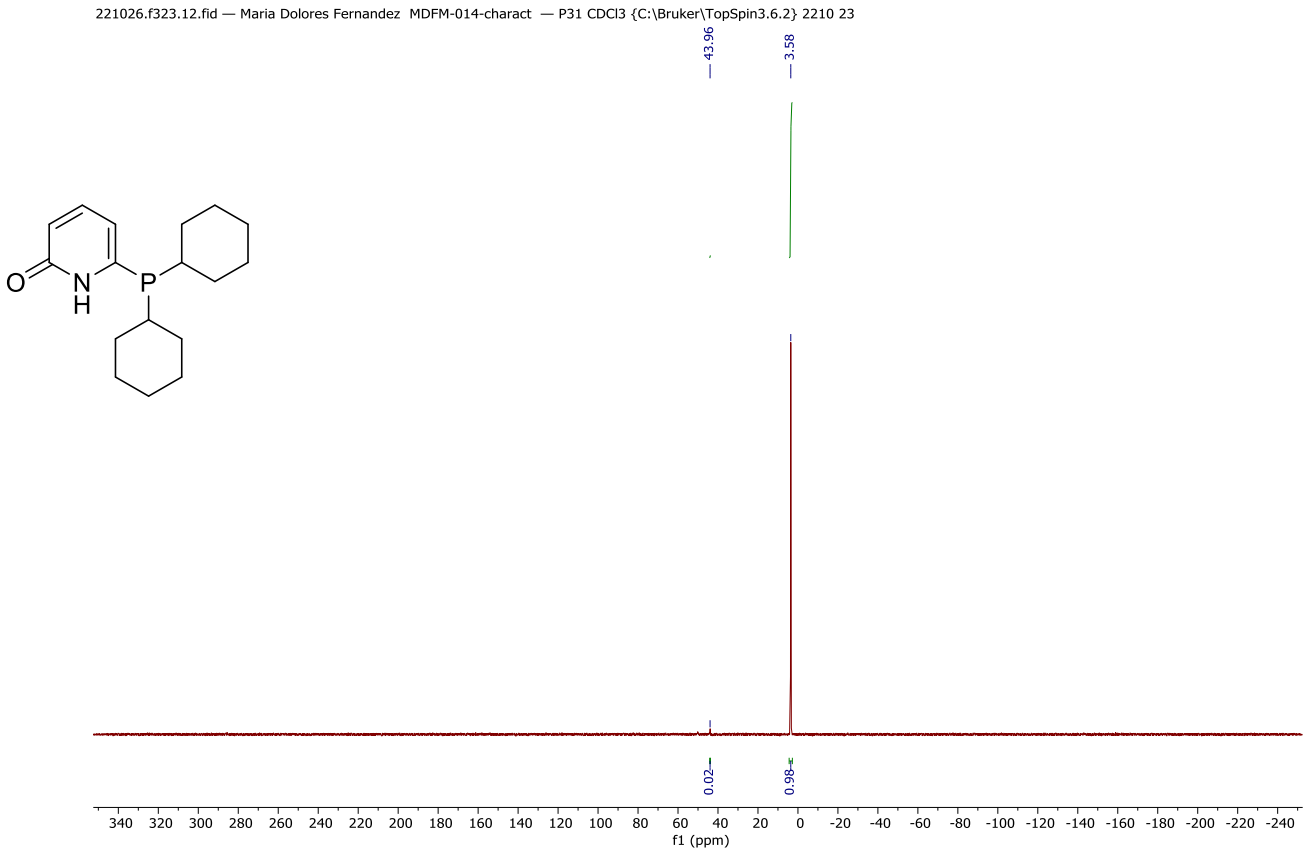
Supplementary Figure 4. ^{31}P NMR spectrum of L1 in $CDCl_3$ at RT and AP.



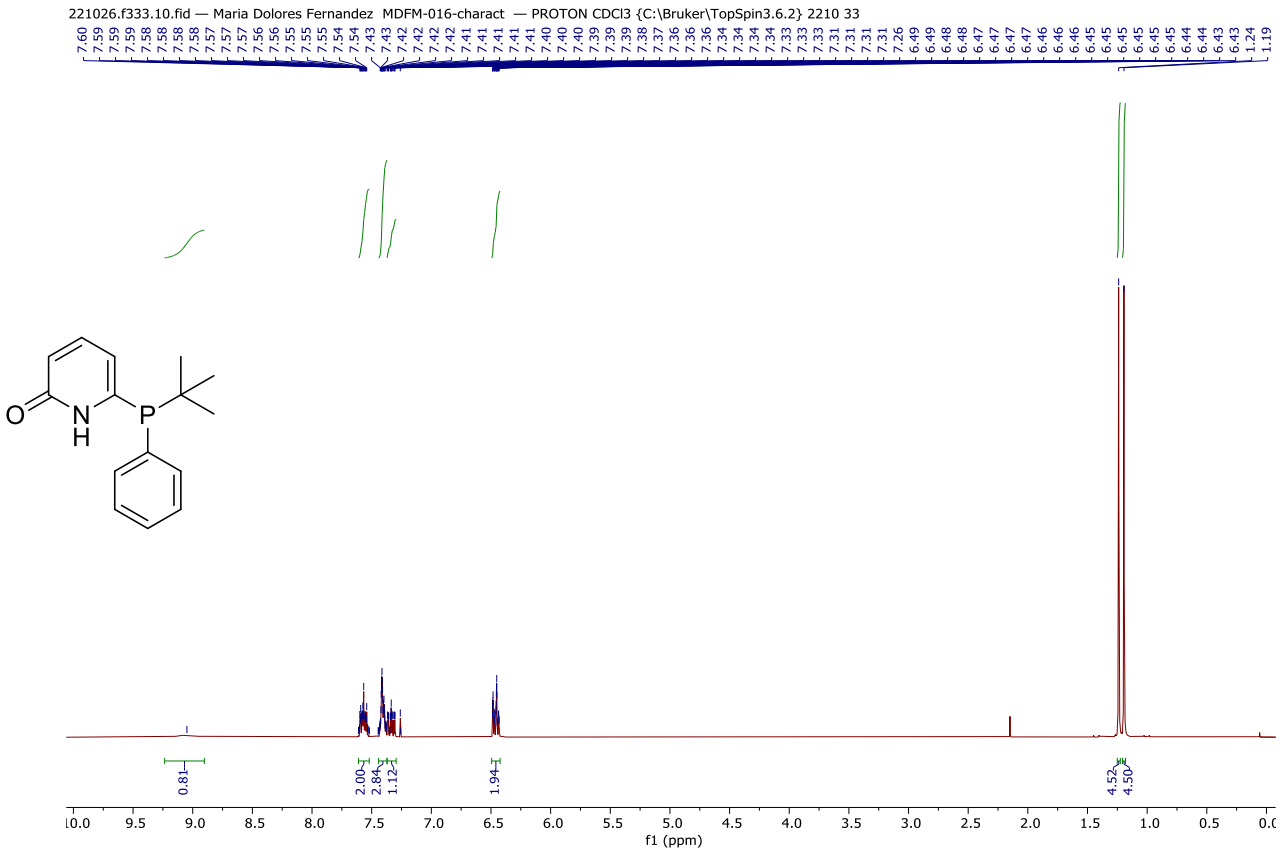
Supplementary Figure 5. ^{1}H NMR spectrum of L2 in $CDCl_3$ at RT and AP.



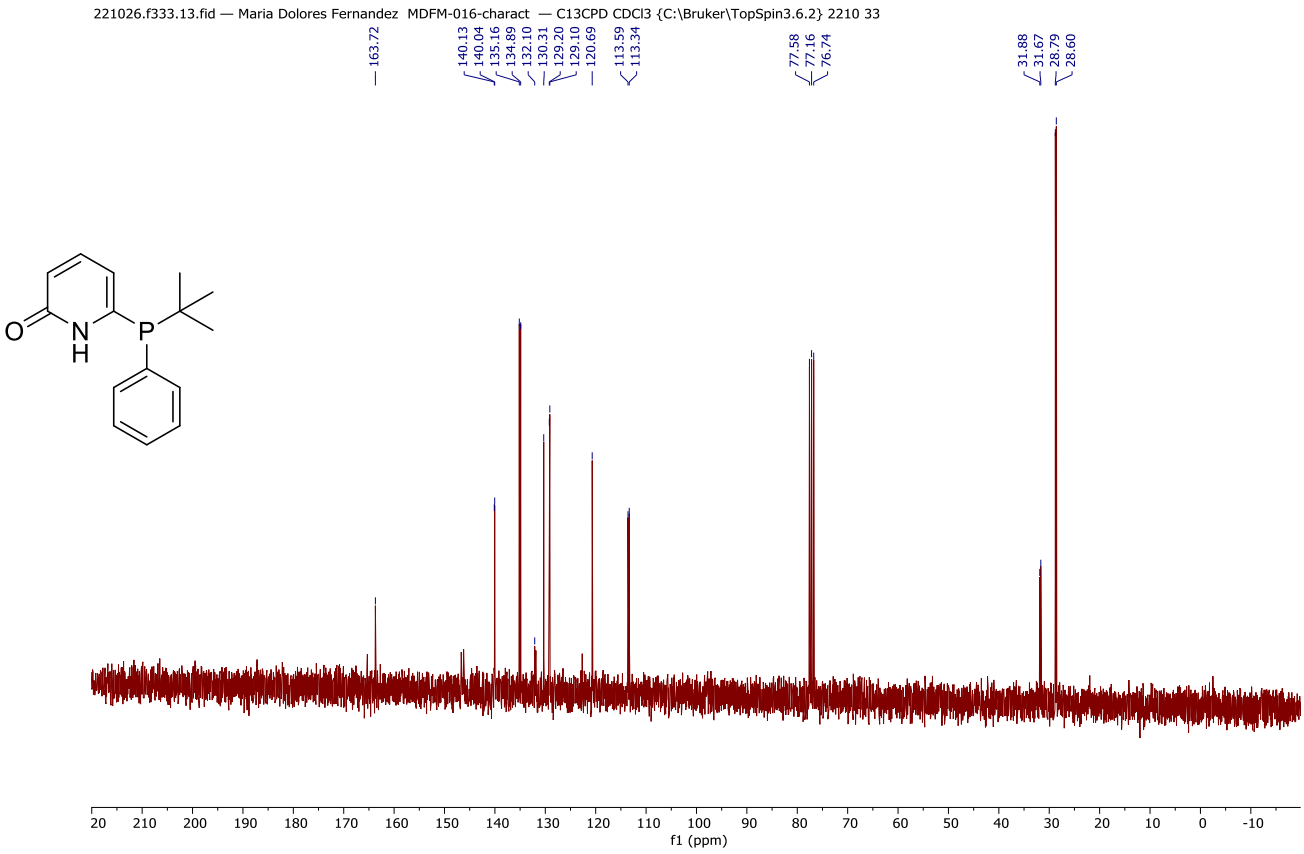
Supplementary Figure 6. ^{13}C NMR spectrum of L2 in $CDCl_3$ at RT and AP.



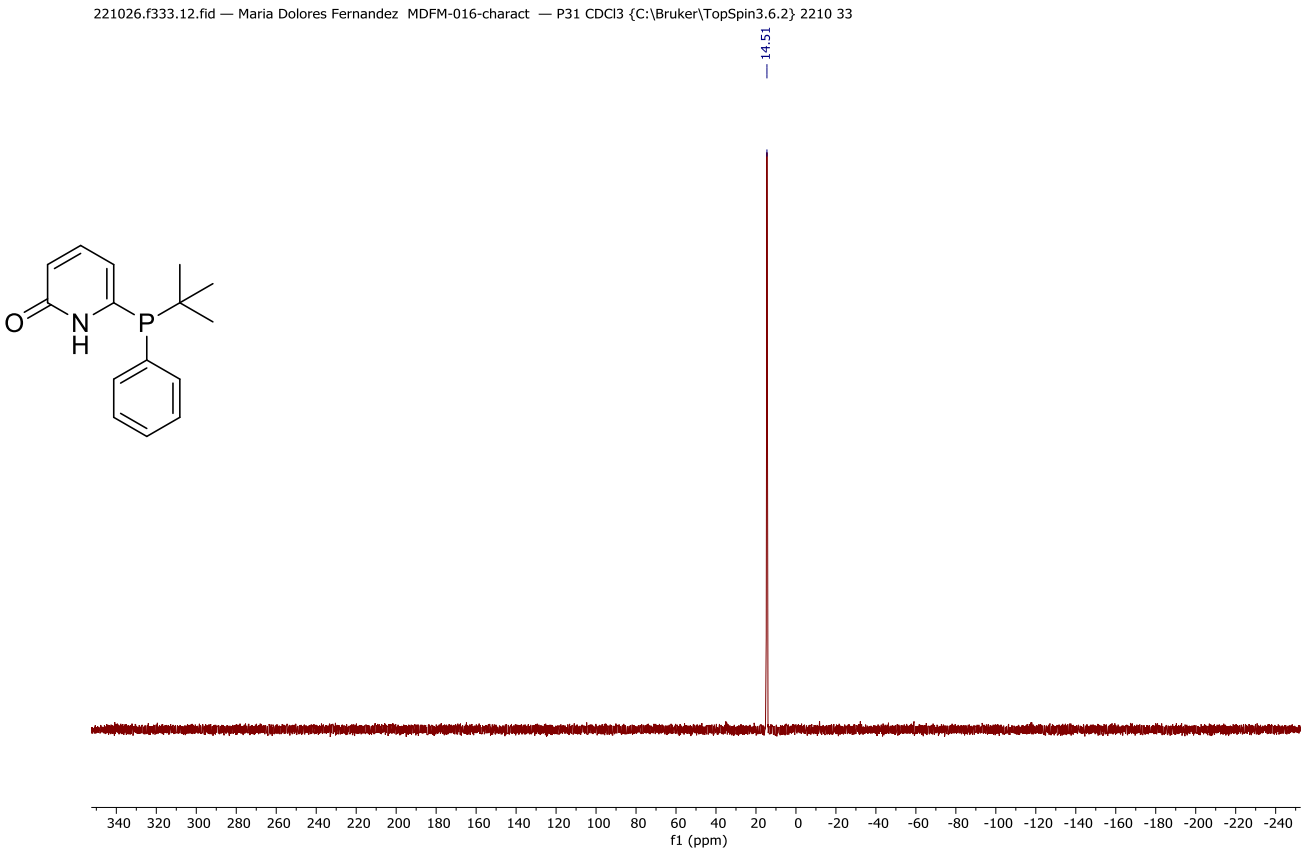
Supplementary Figure 7. ^{31}P NMR spectrum of L2 in $CDCl_3$ at RT and AP.



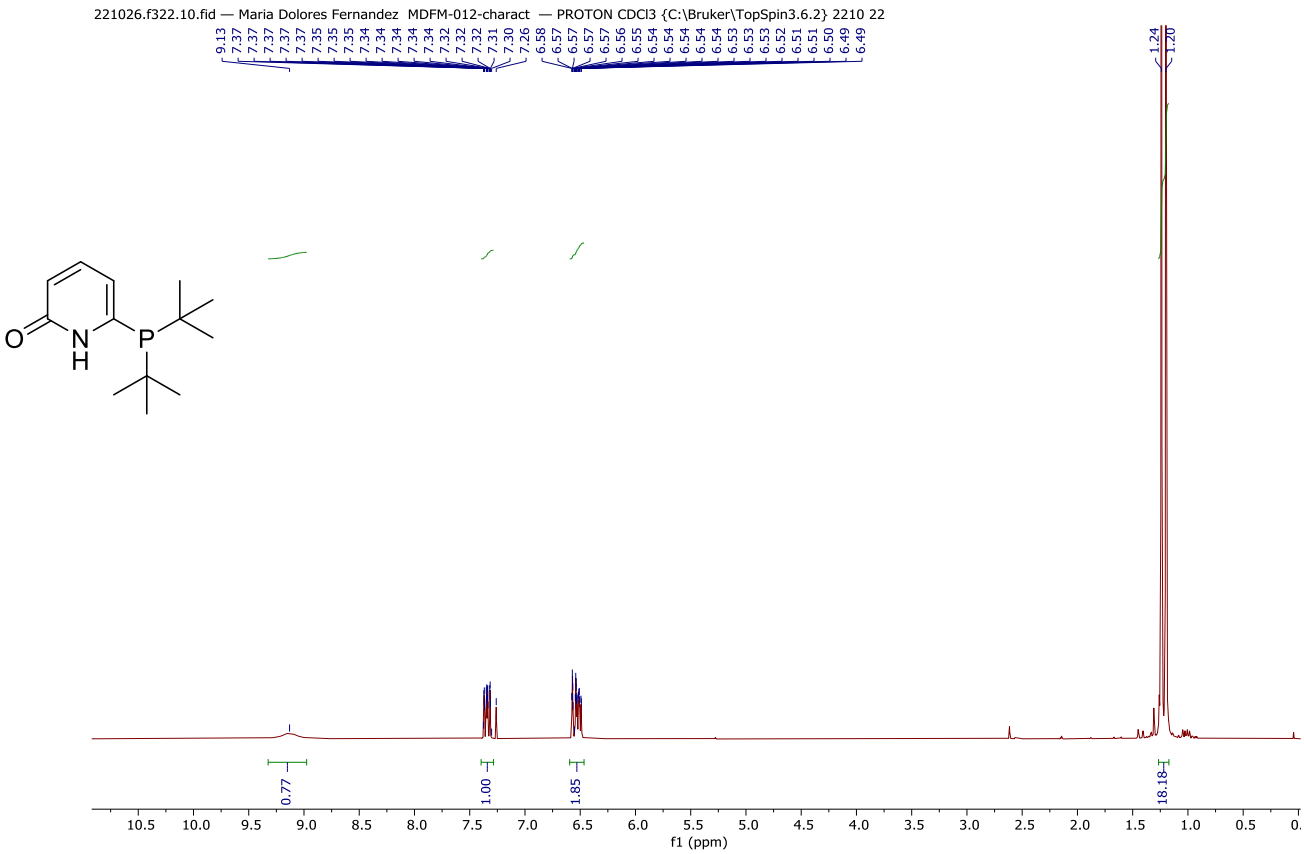
Supplementary Figure 8. ^{1}H NMR spectrum of L3 in $CDCl_3$ at RT and AP.



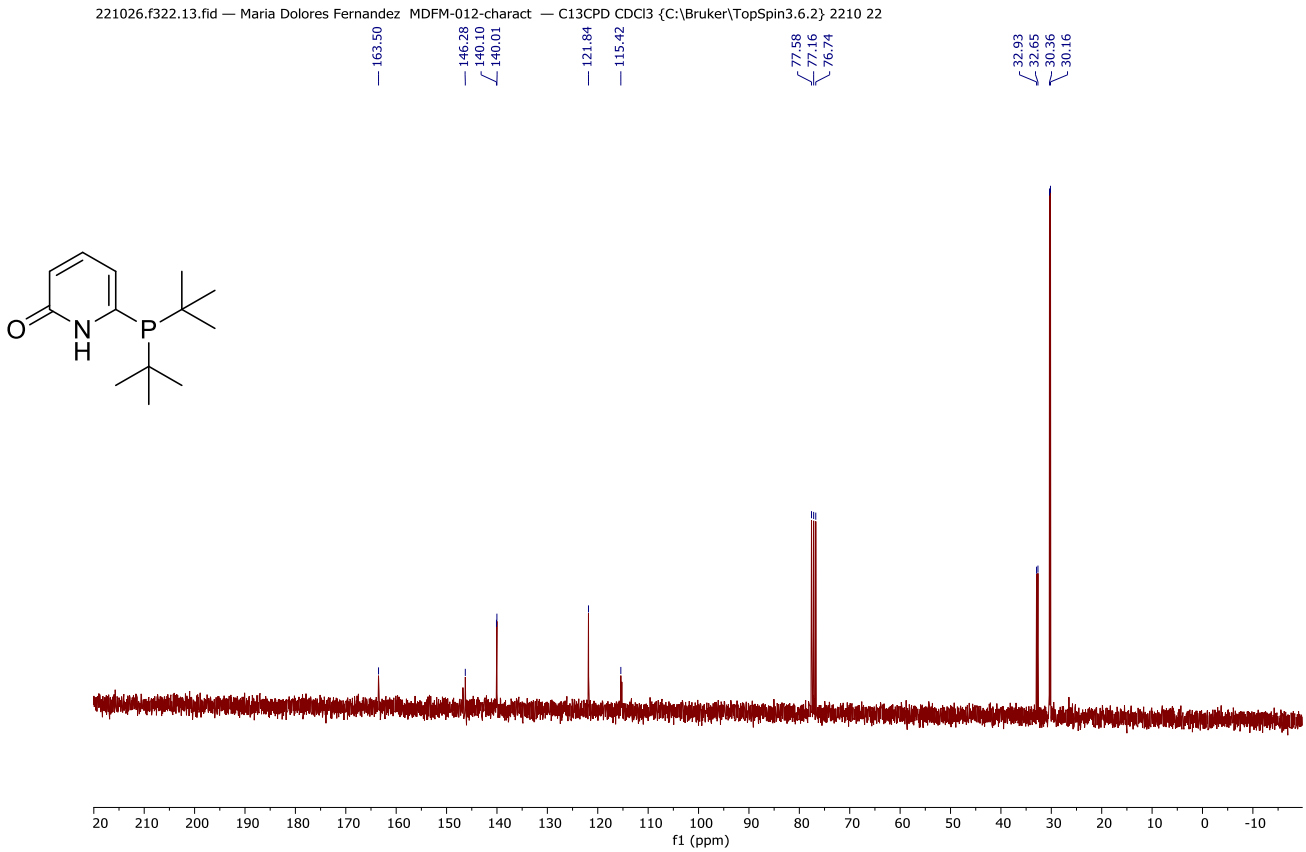
Supplementary Figure 9. ^{13}C NMR spectrum of L3 in $CDCl_3$ at RT and AP.



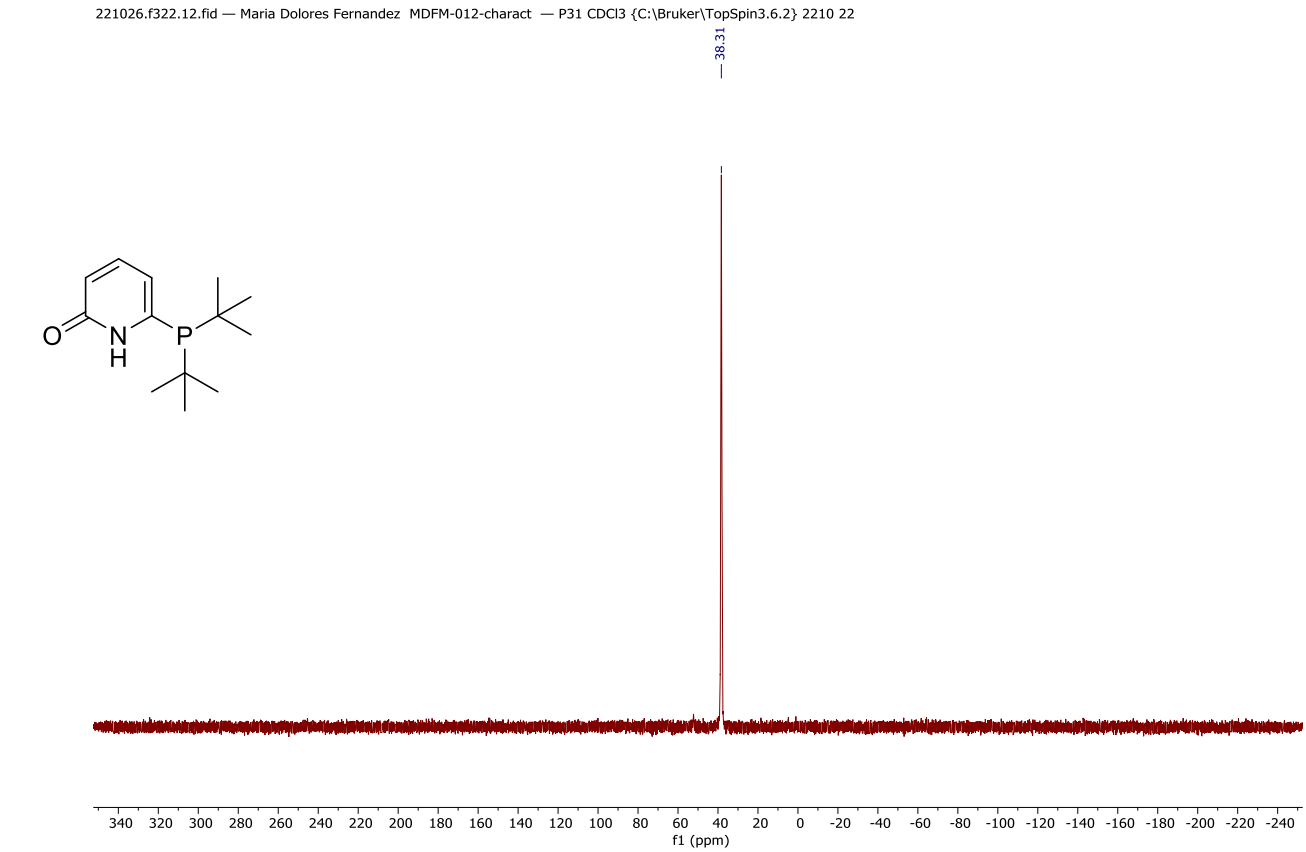
Supplementary Figure 10. ^{31}P NMR spectrum of L3 in $CDCl_3$ at RT and AP.



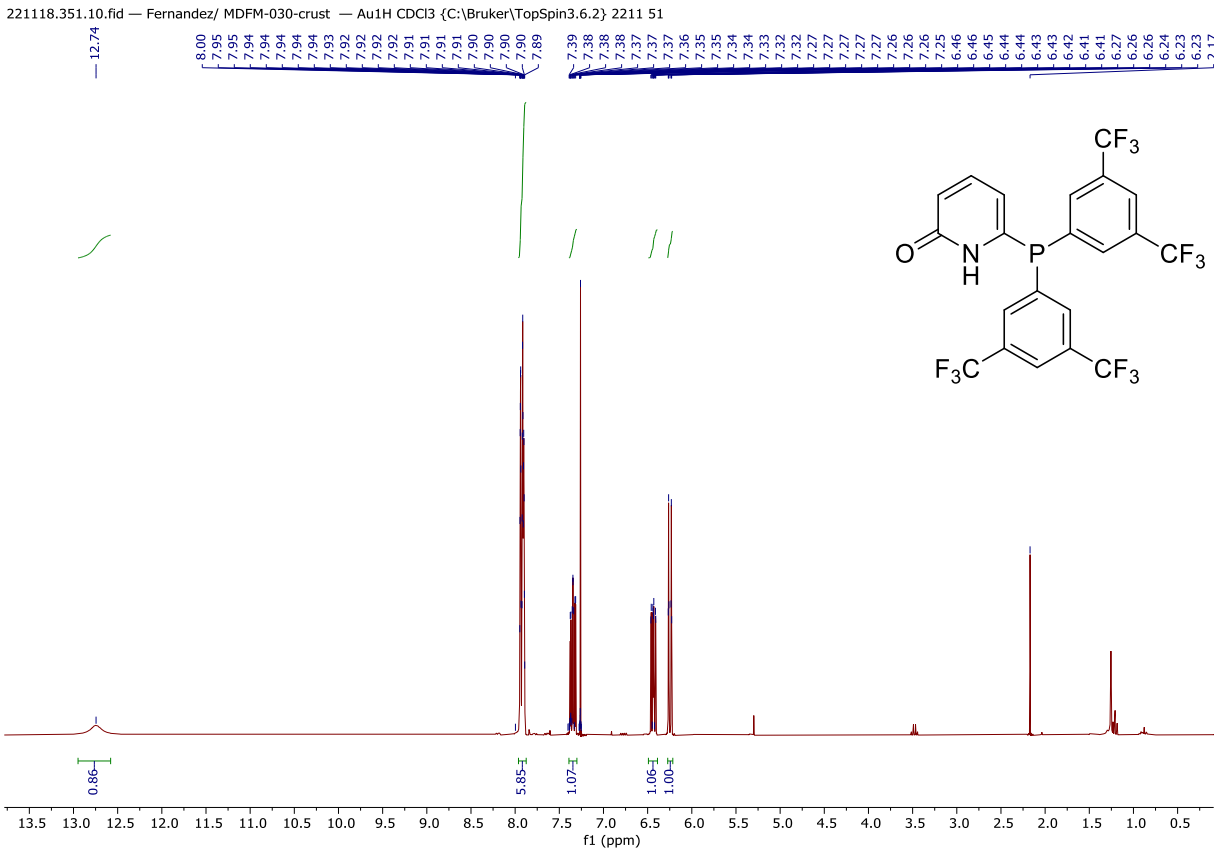
Supplementary Figure 11. ^{1}H NMR spectrum of L4 in $CDCl_3$ at RT and AP.



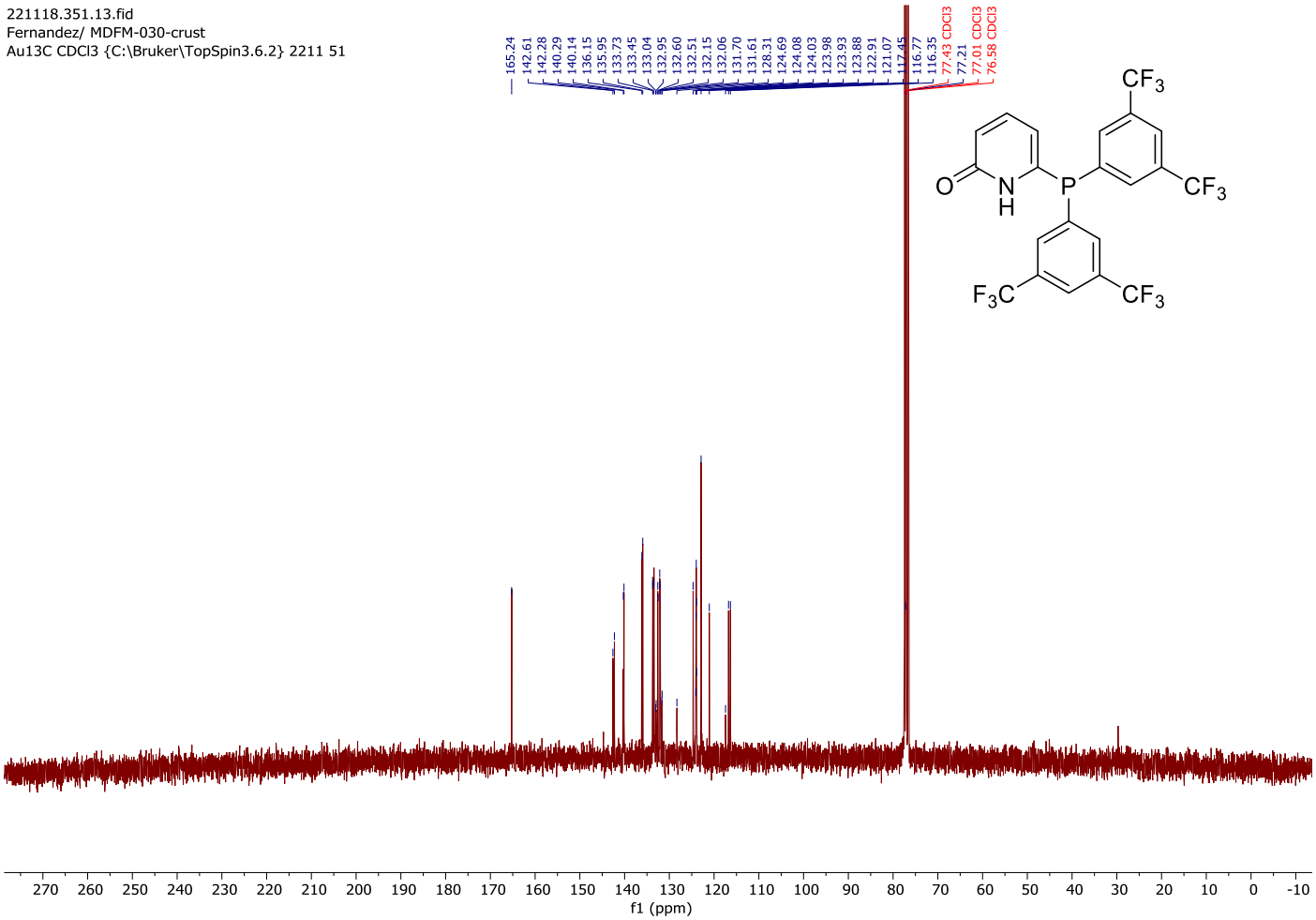
Supplementary Figure 12. ^{13}C NMR spectrum of L4 in $CDCl_3$ at RT and AP.



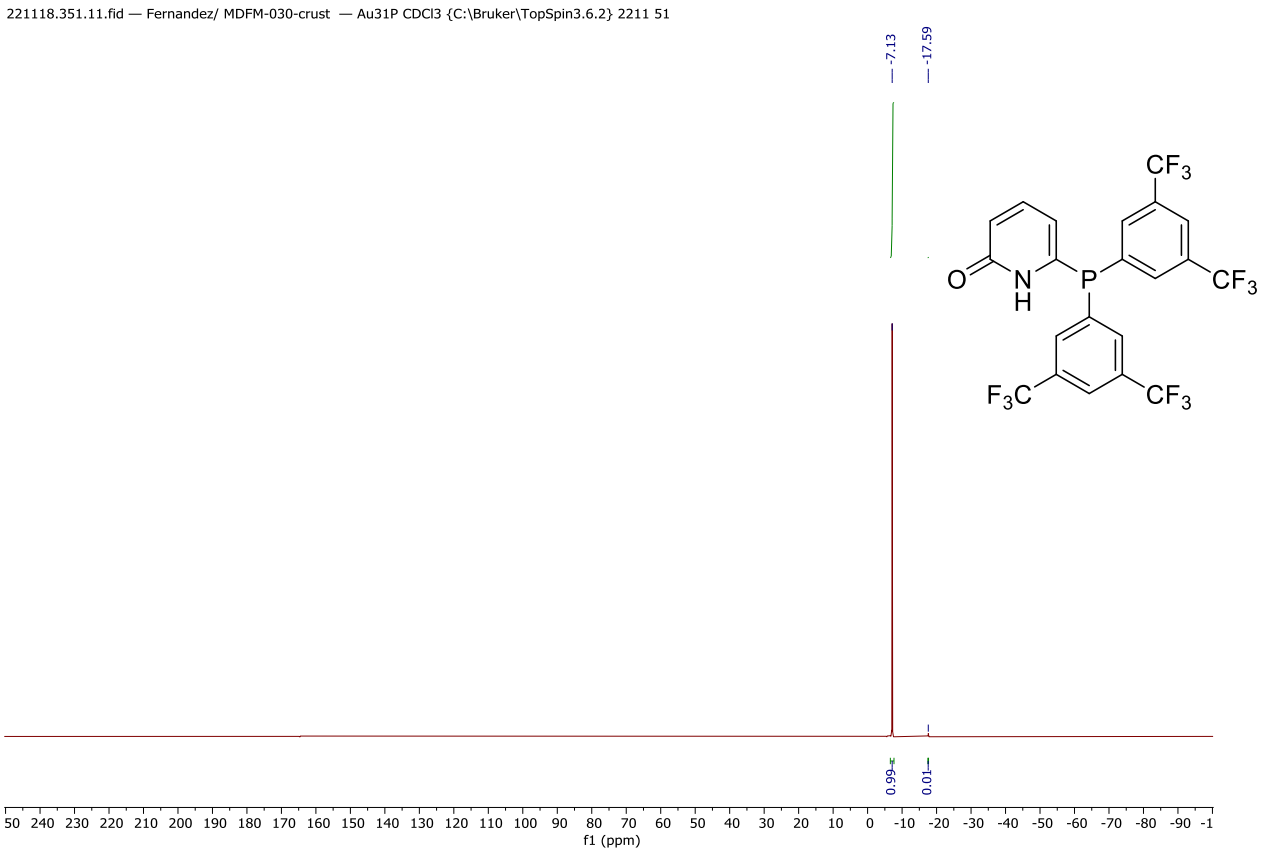
Supplementary Figure 13. ^{31}P NMR spectrum of L4 in $CDCl_3$ at RT and AP.



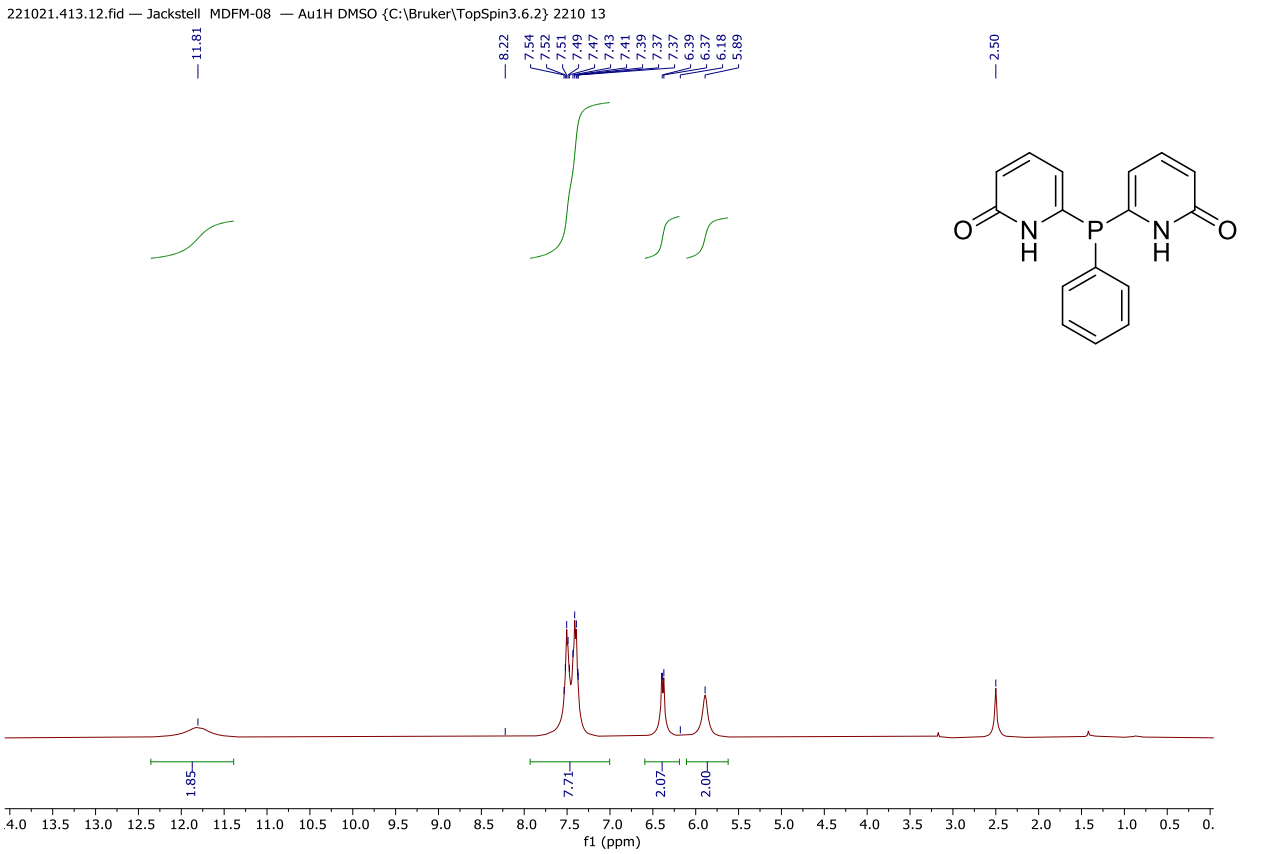
Supplementary Figure 14. ^{1}H NMR spectrum of L5 in $CDCl_3$ at RT and AP.



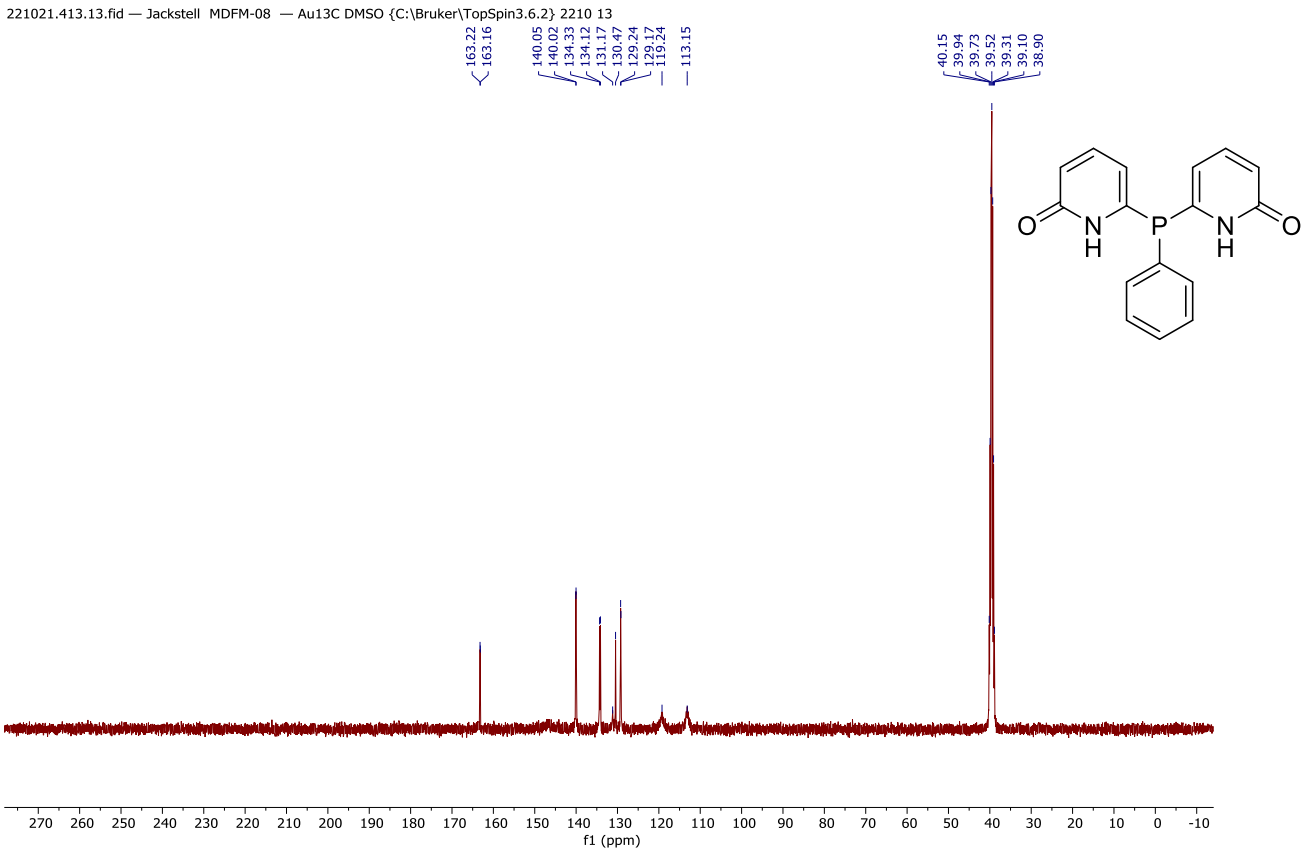
Supplementary Figure 15. ^{13}C NMR spectrum of L5 in $CDCl_3$ at RT and AP.



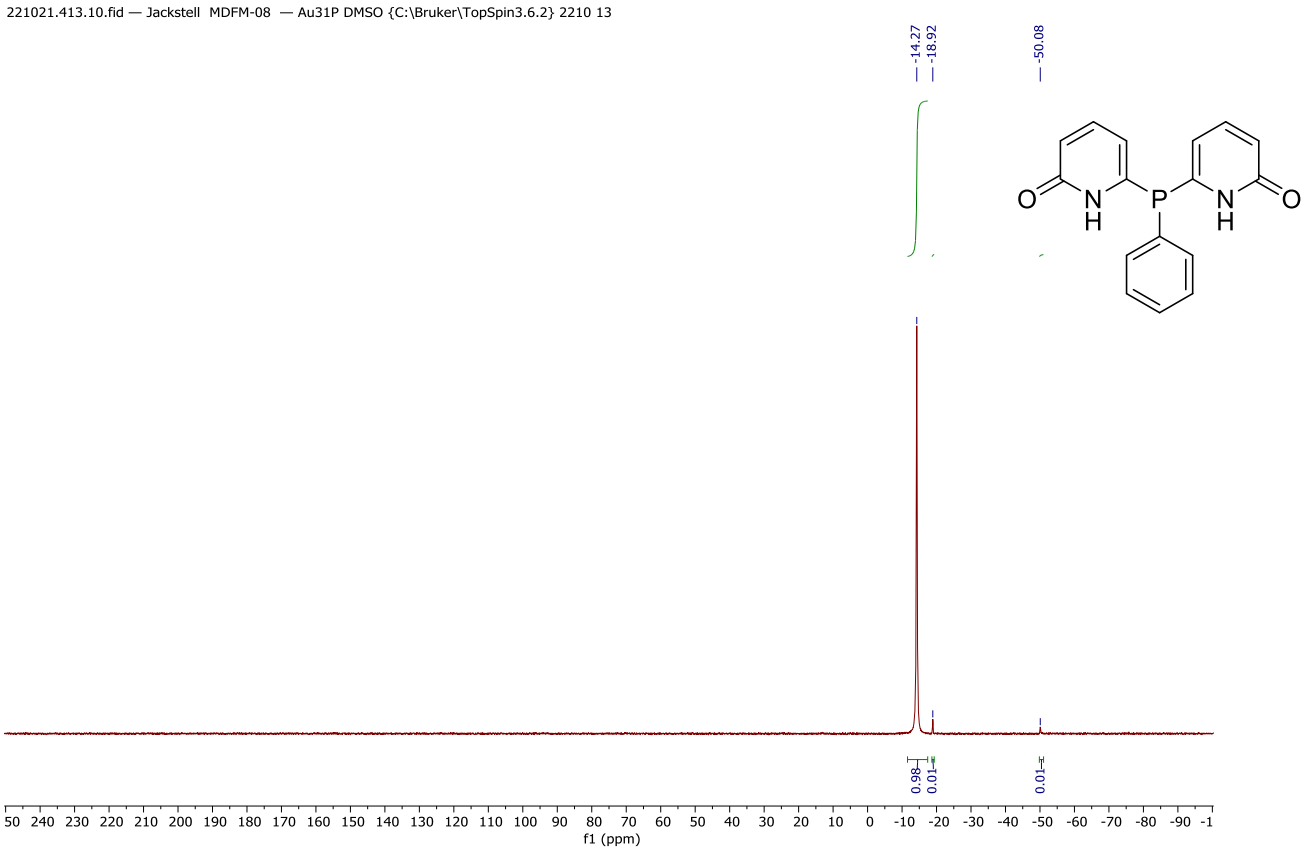
Supplementary Figure 16. ^{31}P NMR spectrum of L5 in $CDCl_3$ at RT and AP.



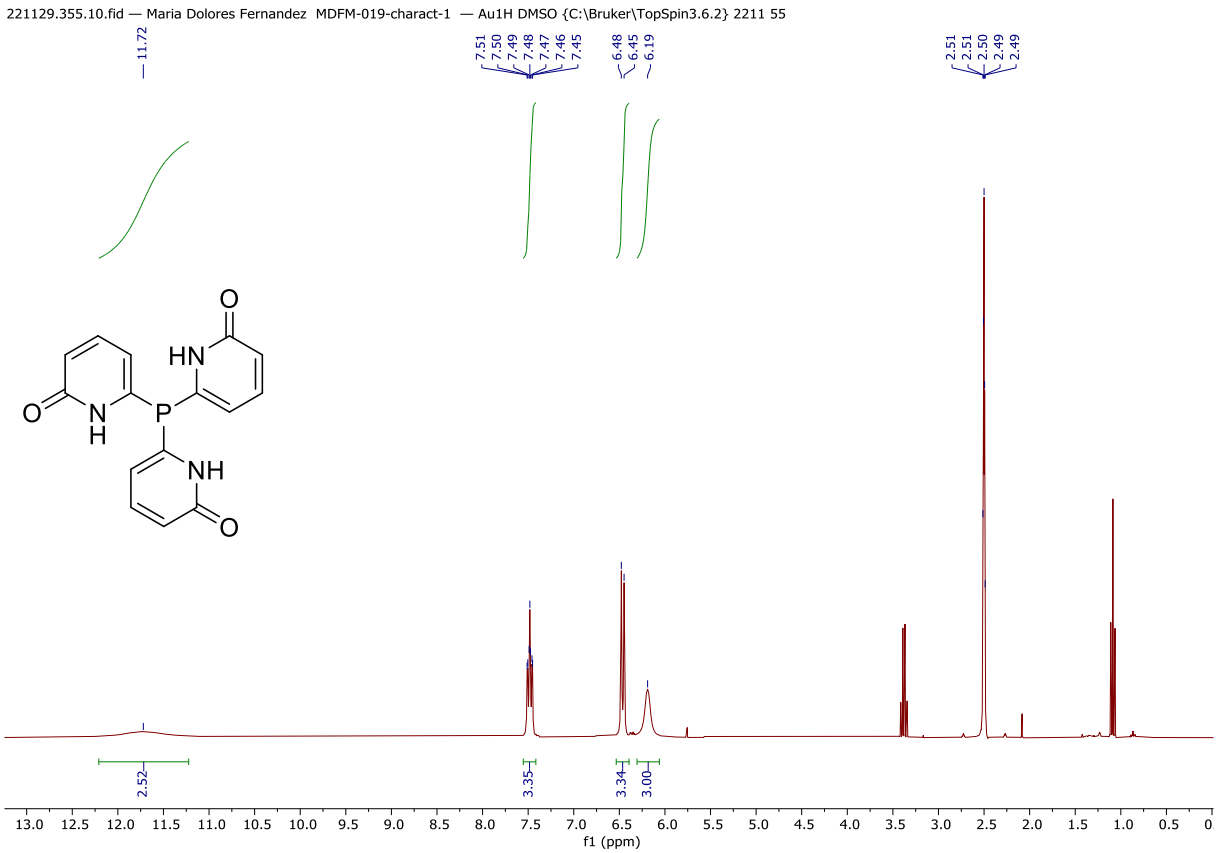
Supplementary Figure 17. ^{1}H NMR spectrum of L6 in DMSO-d6 at RT and AP.



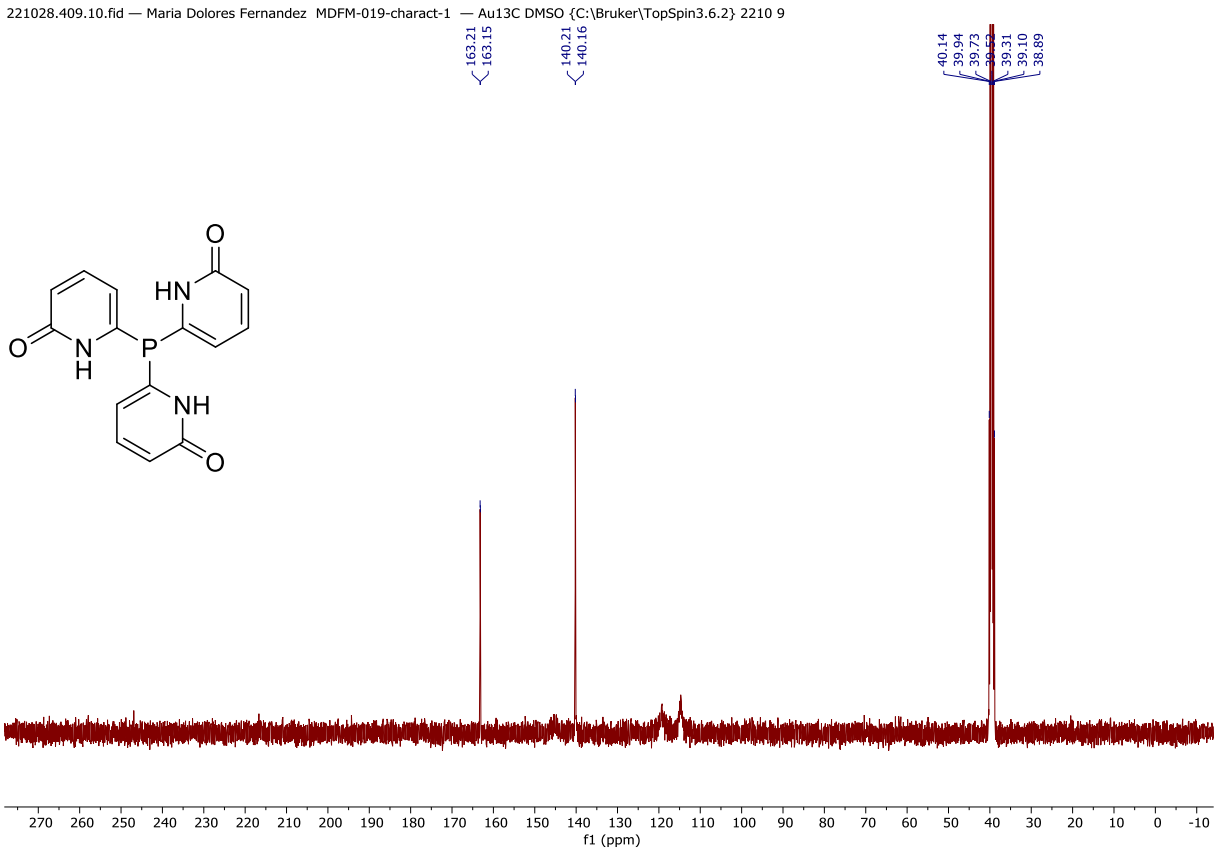
Supplementary Figure 18. ^{13}C NMR spectrum of L6 in DMSO-d6 at RT and AP.



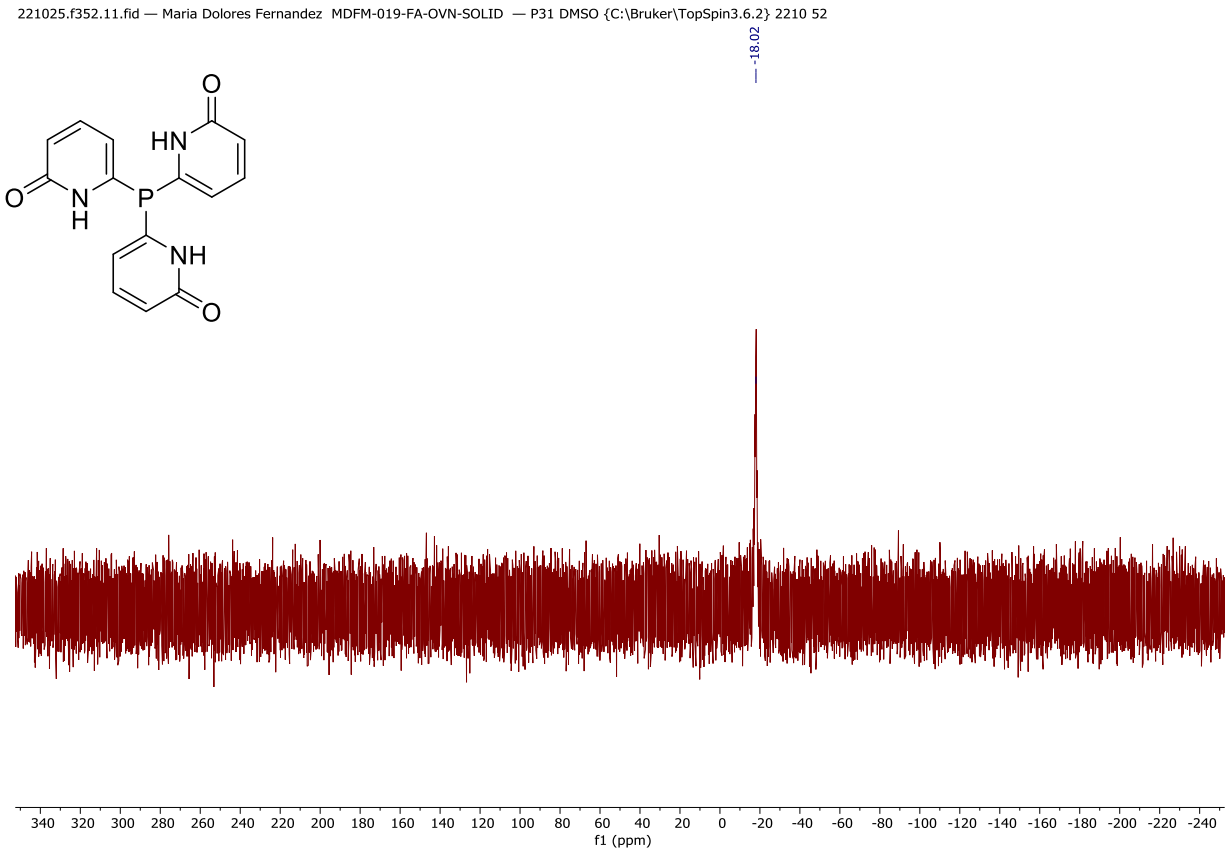
Supplementary Figure 19. ^{31}P NMR spectrum of L6 in DMSO-d6 at RT and AP.



Supplementary Figure 20. ^{1}H NMR spectrum of L7 in DMSO-d6 at RT and AP.



Supplementary Figure 21. ^{13}C NMR spectrum of L7 in DMSO-d6 at RT and AP.



Supplementary Figure 22. ^{31}P-NMR spectrum of L7 in DMSO-d6 at RT and AP.

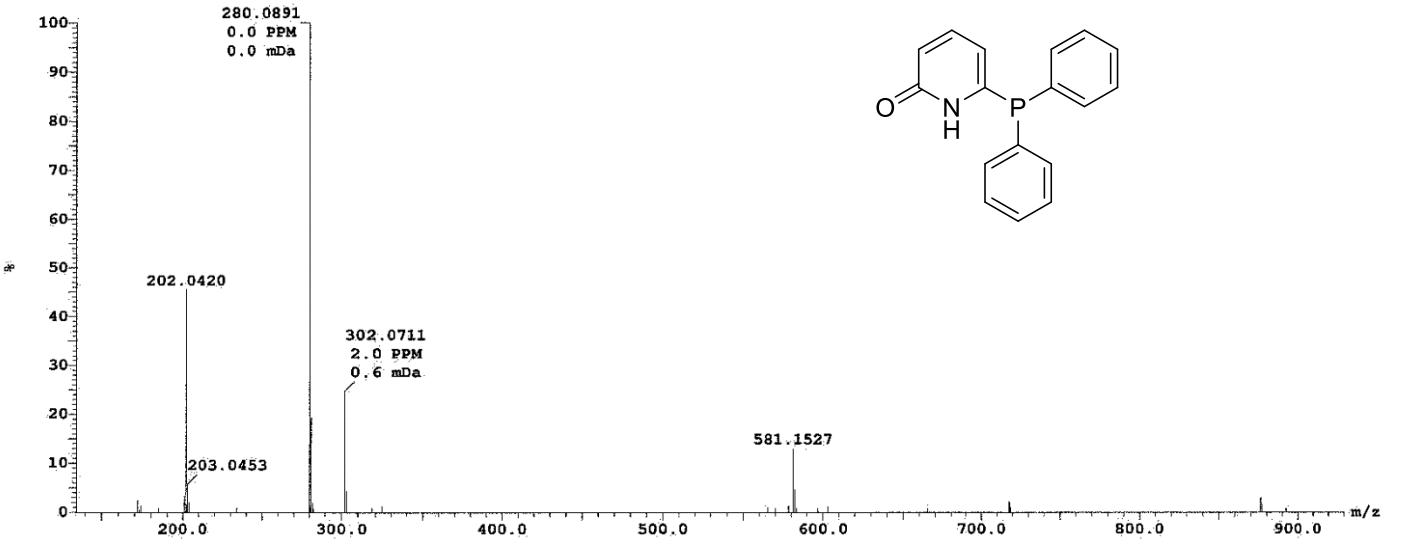
SI-D: HR-MS (ESI) of the phosphine ligands (L1-L7)

ESI-TOF Accurate Mass Report Page 2

File:22101803 Sample Name:MDFM-015 UserName:Fernandez
Vial:1:F,1 Date:18-Oct-2022 Time:12:42:26
Description:MeOH/0.1%HCOOH in H2O 90:10

Sample Report:

(Time: 0.34) Combine (31-79:83) - Dead time test passed 1:TOF MS ES+ 1.5e+008



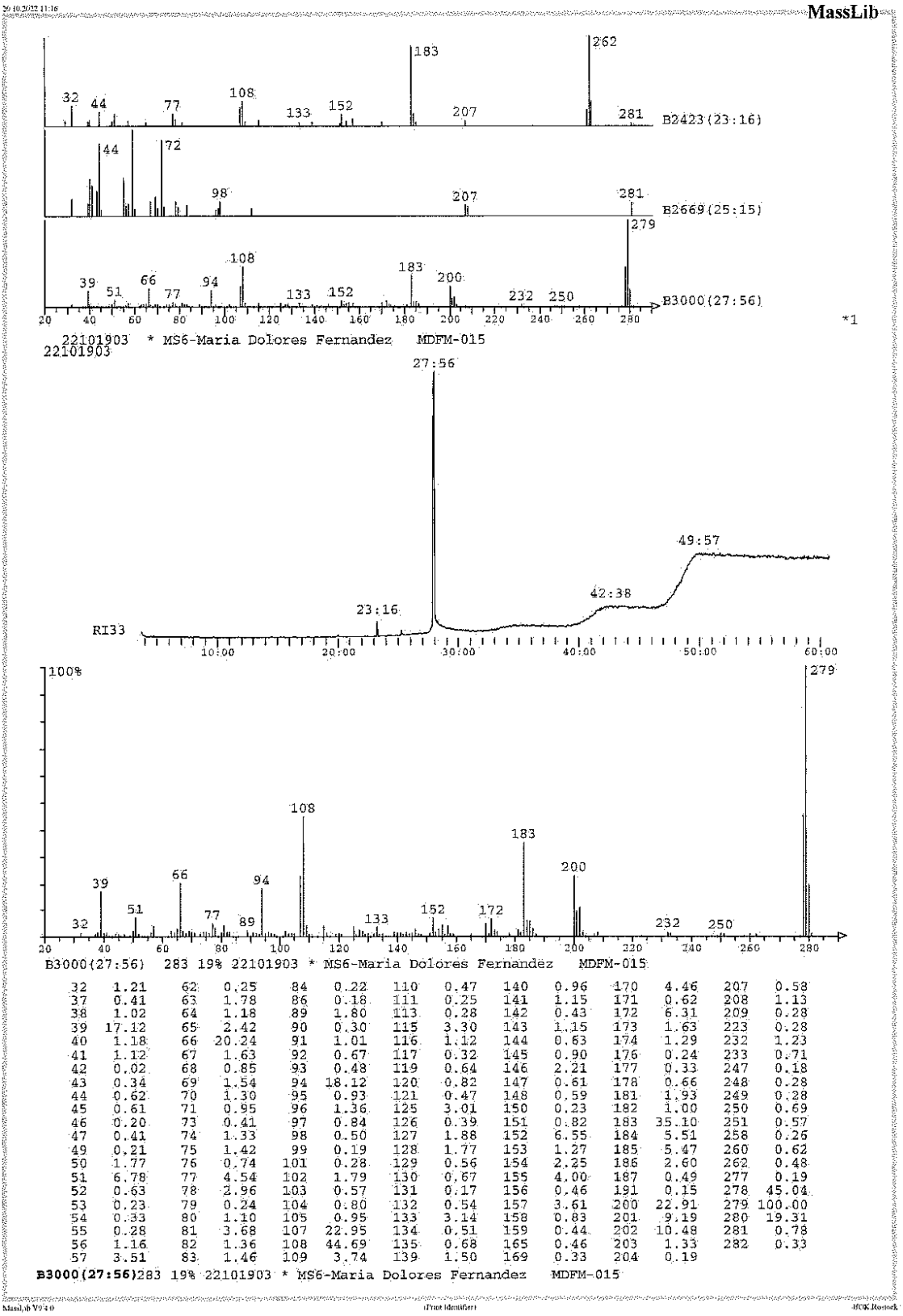
ESI-TOF Accurate Mass Report Page 1

Results file: E:\Projects\2210.PRO\SampleDB\2210.rpt
Last modified: Tuesday, October 18, 2022 12:45:14

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
33	22101803	MDFM-015	Fernandez	279.0813	C17H14PON	280.0891 302.0705	280.0891 302.0711	0.0 2.0	0.0 0.6

Supplementary Figure 23.a Accurate Mass Report of L1



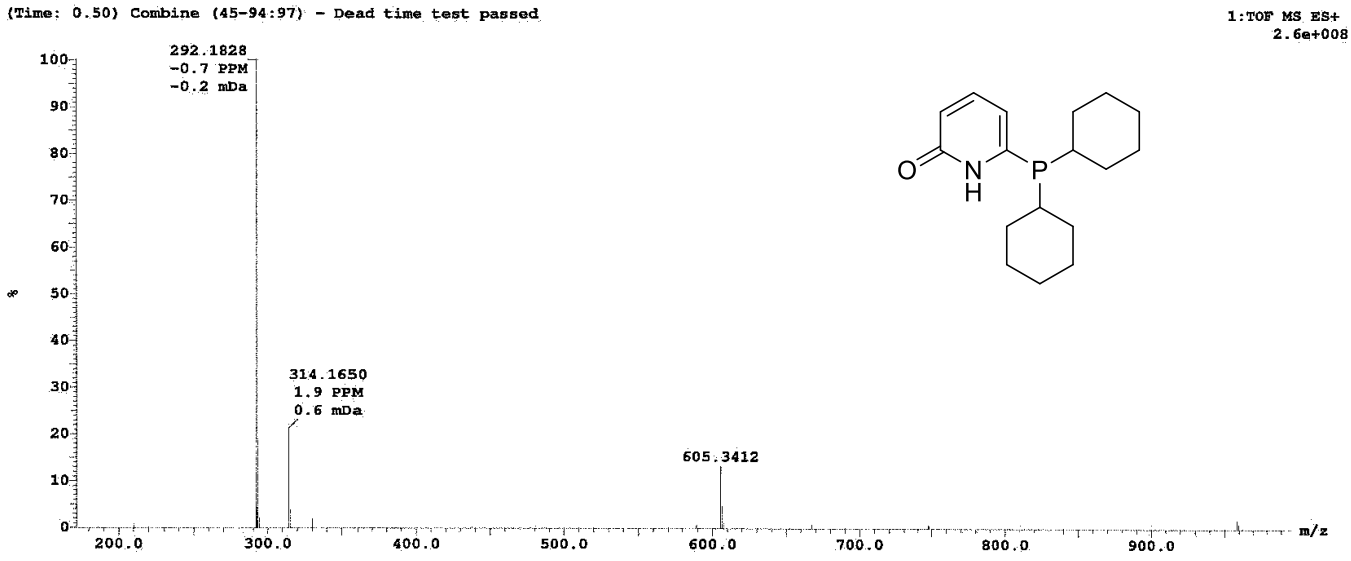
Supplementary Figure 23.b HR-MS spectrum of L1

ESI-TOF Accurate Mass Report
File:22101802
Vial:1:F,1
Description:MeOH/0.1%HCOOH in H2O 90:10

Sample Name:MDFM-014
Date:18-Oct-2022

UserName:Fernandez
Time:11:57:26

Sample Report:



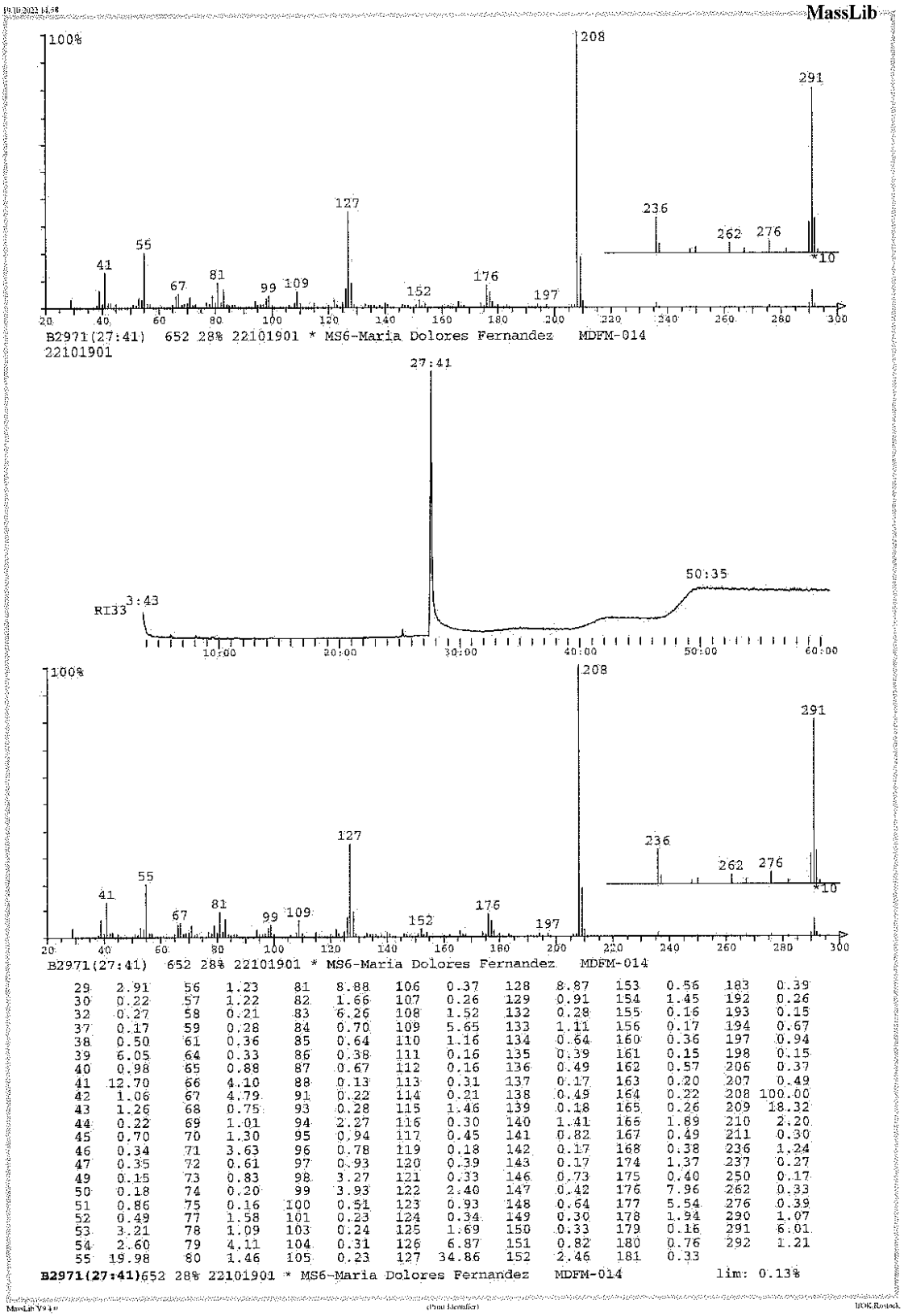
ESI-TOF Accurate Mass Report

Results file: E:\Projects\2210.PRO\SampleDB\2210.rpt
Last modified: Tuesday, October 18, 2022 12:01:04

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
32	22101802	MDFM-014	Fernandez	291.1752	C17H26PON	292.1830	292.1828	-0.7	-0.2
						314.1644	314.1650	1.9	0.6

Supplementary Figure 24.a Accurate Mass Report of L2



29	2.91	56	1.23	81	8.88	106	0.37	128	8.87	153	0.56	183	0.39	
30	0.22	57	1.22	82	1.66	107	0.26	129	0.91	154	1.45	192	0.26	
32	0.27	58	0.21	83	6.26	108	1.52	132	0.28	155	0.16	193	0.15	
37	0.17	59	0.28	84	0.70	109	5.65	133	1.11	156	0.17	194	0.67	
38	0.50	61	0.36	85	0.64	110	1.16	134	0.64	160	0.36	197	0.94	
39	6.05	64	0.33	86	0.38	111	0.16	135	0.39	161	0.15	198	0.15	
40	0.98	65	0.88	87	0.67	112	0.16	136	0.49	162	0.57	206	0.37	
41	12.70	66	4.10	88	0.13	113	0.31	137	0.17	163	0.20	207	0.49	
42	1.06	67	4.79	91	0.22	114	0.21	138	0.49	164	0.22	208	100.00	
43	1.26	68	0.75	93	0.28	115	1.46	139	0.18	165	0.26	209	18.32	
44	0.22	69	1.01	94	2.27	116	0.30	140	1.41	166	1.89	210	2.20	
45	0.70	70	1.30	95	0.94	117	0.45	141	0.82	167	0.49	211	0.30	
46	0.34	71	3.63	96	0.78	119	0.18	142	0.17	168	0.38	236	1.24	
47	0.35	72	0.61	97	0.93	120	0.39	143	0.17	174	1.37	237	0.27	
49	0.15	73	0.83	98	3.27	121	0.33	146	0.73	175	0.40	250	0.17	
50	0.18	74	0.20	99	3.93	122	2.40	147	0.42	176	7.96	262	0.33	
51	0.86	75	0.16	100	0.51	123	0.93	148	0.64	177	5.54	276	0.39	
52	0.49	77	1.58	101	0.23	124	0.34	149	0.30	178	1.94	290	1.07	
53	3.21	78	1.09	103	0.24	125	1.69	150	0.33	179	0.16	291	6.01	
54	2.60	79	4.11	104	0.31	126	6.87	151	0.82	180	0.76	292	1.21	
55	19.98	80	1.46	105	0.23	127	34.86	152	2.46	181	0.33			

B2971(27:41)652 28% 22101901 * MS6-Maria Dolores Fernandez MDFM-014 lim: 0.13%

Supplementary Figure 24.b HR-MS spectrum of L2

ESI-TOF Accurate Mass Report

File:22101804
Vial:1:F,1
Description:MeOH/0.1%HCOOH in H2O 90:10

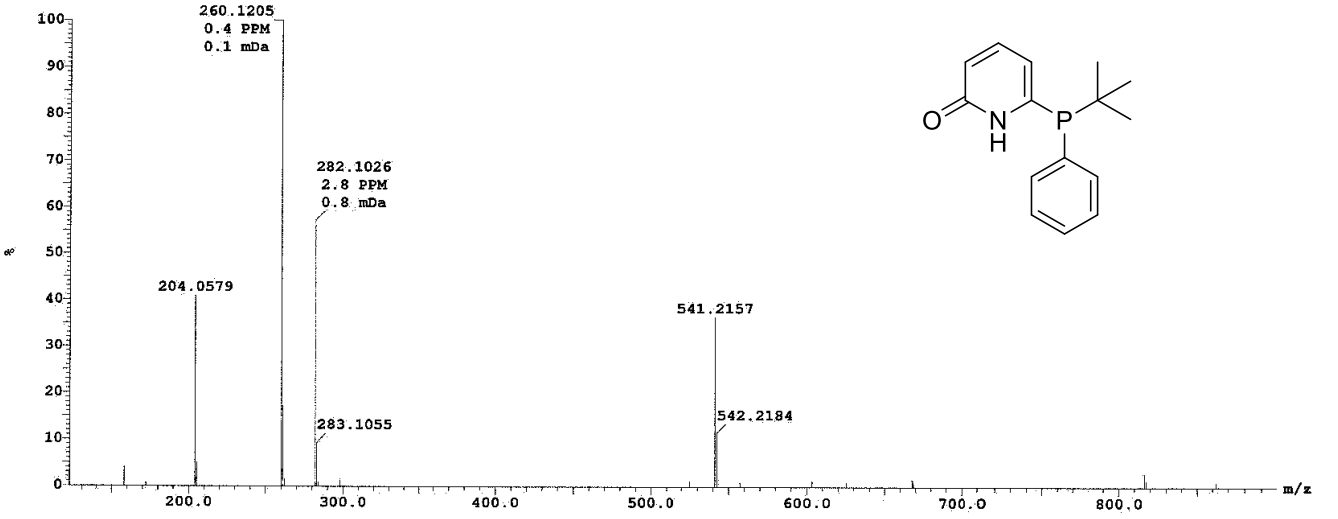
Sample Name:MDFM-016
Date:18-Oct-2022

UserName:Fernandez
Time:12:50:19

Sample Report:

(Time: 0.35) Combine (31:33-80:84) - Dead time test passed

1:TOF MS ES+
2.2e+008



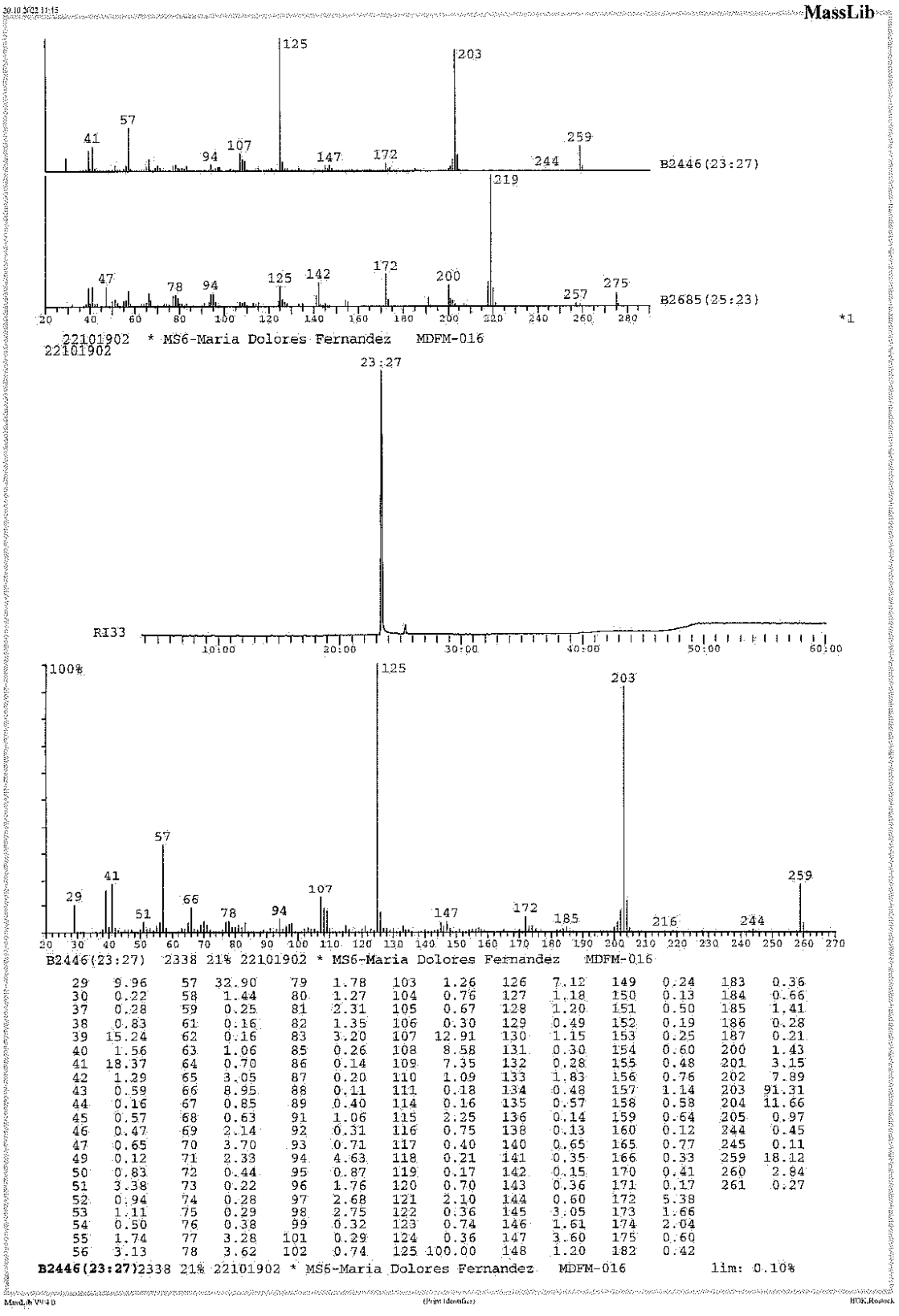
ESI-TOF Accurate Mass Report

Results file: E:\Projects\2210.PRO\SampleDB\2210.rpt
Last modified: Tuesday, October 18, 2022 12:53:13

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
34	22101804	MDFM-016	Fernandez	259.1126	C15H18PON	260.1204 282.1018	260.1205 282.1026	0.4 2.8	0.1 0.8

Supplementary Figure 25.a Accurate Mass Report of L3



29	9.96	57	32.90	79	1.78	103	1.26	126	7.12	149	0.24	183	0.36
30	0.22	58	1.44	80	1.27	104	0.76	127	1.18	150	0.13	184	0.66
37	0.28	59	0.25	81	2.31	105	0.67	128	1.20	151	0.50	185	1.41
38	0.83	61	0.16	82	1.35	106	0.30	129	0.49	152	0.19	186	0.28
39	15.24	62	0.16	83	3.20	107	12.91	130	1.15	153	0.25	187	0.21
40	1.56	63	1.06	85	0.26	108	8.58	131	0.30	154	0.60	200	1.43
41	18.37	64	0.70	86	0.14	109	7.35	132	0.28	155	0.48	201	3.15
42	1.29	65	3.05	87	0.20	110	1.09	133	1.83	156	0.76	202	7.89
43	0.59	66	8.95	88	0.11	111	0.18	134	0.48	157	1.14	203	91.31
44	0.16	67	0.85	89	0.40	114	0.16	135	0.57	158	0.58	204	11.66
45	0.57	68	0.63	91	1.06	115	2.25	136	0.14	159	0.64	205	0.97
46	0.47	69	2.14	92	0.31	116	0.75	138	0.13	160	0.12	244	0.45
47	0.65	70	3.70	93	0.71	117	0.40	140	0.65	165	0.77	245	0.11
49	0.12	71	2.33	94	4.63	118	0.21	141	0.35	166	0.33	259	18.12
50	0.83	72	0.44	95	0.87	119	0.17	142	0.15	170	0.41	260	2.84
51	3.38	73	0.22	96	1.76	120	0.70	143	0.36	171	0.17	261	0.27
52	0.94	74	0.28	97	2.68	121	2.10	144	0.60	172	5.38		
53	1.11	75	0.29	98	2.75	122	0.36	145	3.05	173	1.66		
54	0.50	76	0.38	99	0.32	123	0.74	146	1.61	174	2.04		
55	1.74	77	3.28	101	0.29	124	0.36	147	3.60	175	0.60		
56	3.13	78	3.62	102	0.74	125	100.00	148	1.20	182	0.42		

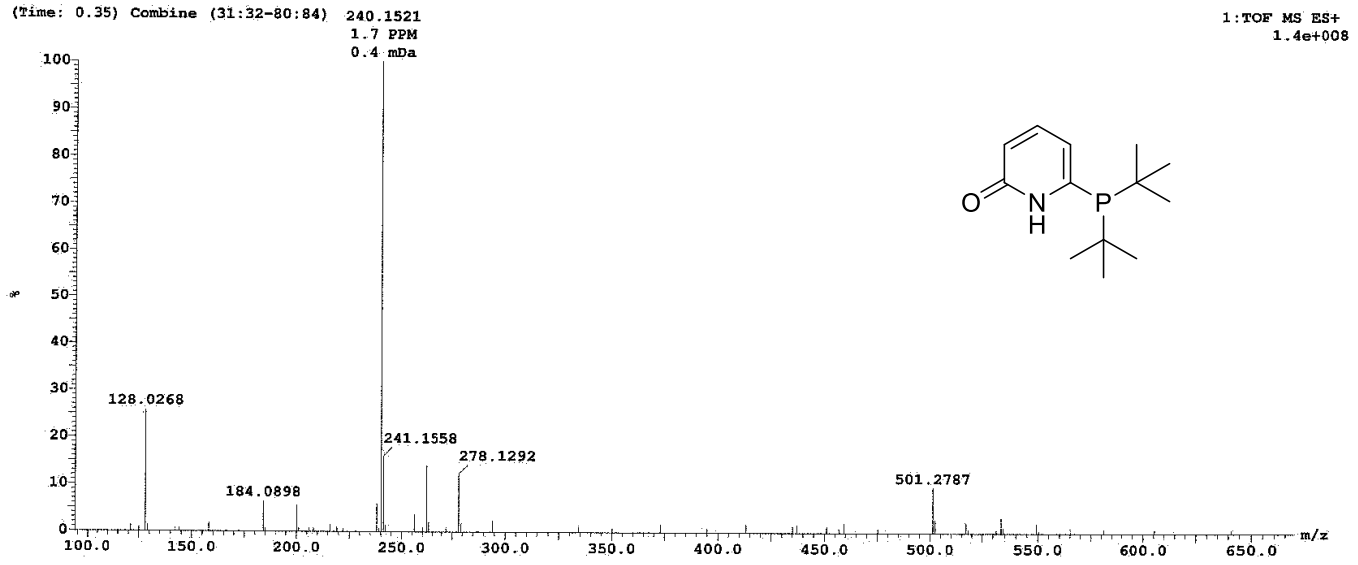
Supplementary Figure 25.b HR-MS spectrum of L3

ESI-TOF Accurate Mass Report
File:22101801
Vial:1:F,1
Description:MeOH/0.1%HCOOH in H2O 90:10

Sample Name:MDFM-012
Date:18-Oct-2022

UserName:Fernandez
Time:11:49:55

Sample Report:



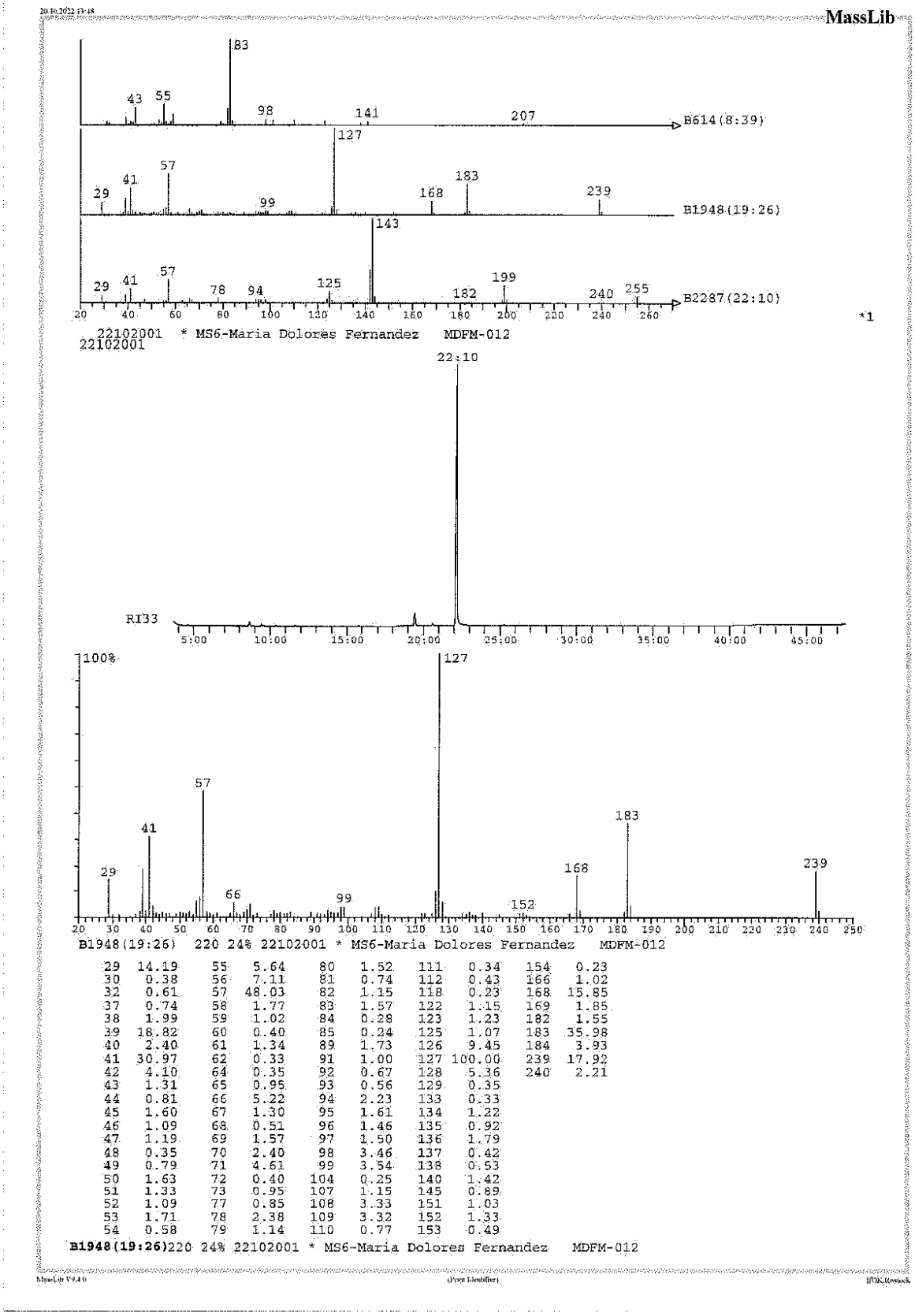
ESI-TOF Accurate Mass Report

Results file: E:\Projects\2210.PRO\SampleDB\2210.rpt
Last modified: Tuesday, October 18, 2022 11:54:50

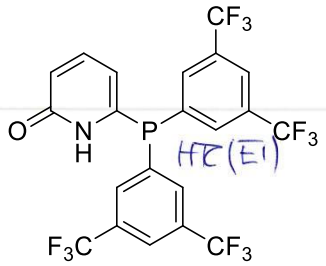
Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
31	22101801	MDFM-012	Fernandez	239.1439	C13H22ONP	240.1517	240.1521	1.7	0.4

Supplementary Figure 26.a Accurate Mass Report of L4



Supplementary Figure 26.b HR-MS spectrum of L4

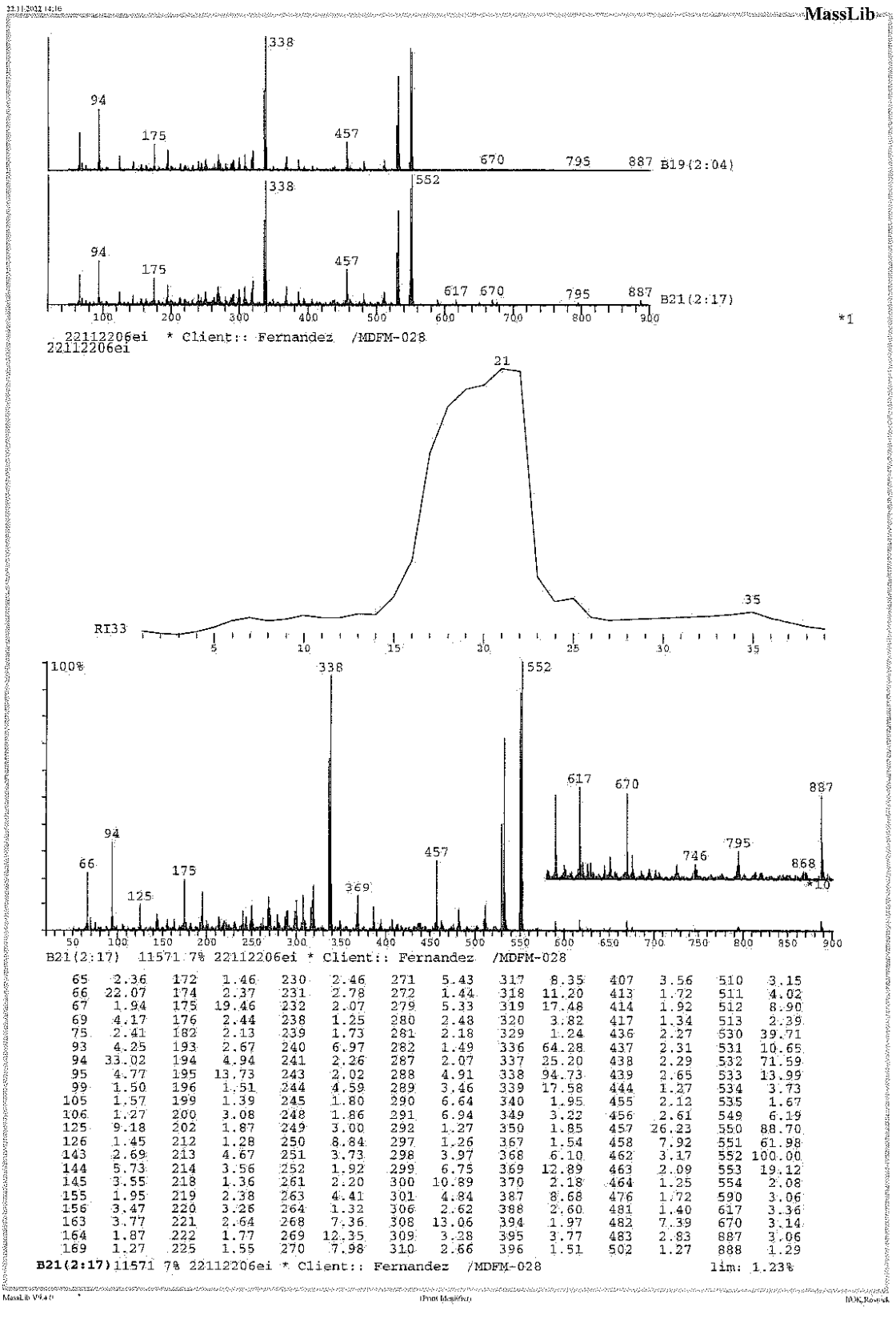


Fernandez HDFM-028 HR(EI)

File : D:\Xcalibur\data\2211\22112206eihr-av2.RAW
Full ms [539.500 - 571.500] - Range: 539.500 - 571.500
Scan No. 1 of 1

Mass	Absolute Intensity	Relative Intensity	Theoretical Mass	Delta [ppm]	Delta [mmu]	RDB	Composition
551.03032	497622	100.0	551.03029	0.0	0.0	12.0	$C_{21}H_{10}O_1N_1F_{12}P_1$

Supplementary Figure 27.a Accurate Mass Report of L5



65	2.36	172	1.46	230	2.46	271	5.43	317	8.35	407	3.56	510	3.15
66	22.07	174	2.37	231	2.78	272	1.44	318	11.20	413	1.72	511	4.02
67	1.94	175	19.46	232	2.07	279	5.33	319	17.48	414	1.92	512	8.90
69	4.17	176	2.44	238	1.25	280	2.48	320	3.82	417	1.34	513	2.39
75	2.41	182	2.13	239	1.73	281	2.18	329	1.24	436	2.27	530	39.71
93	4.25	193	2.67	240	6.97	282	1.49	336	64.28	437	2.31	531	10.65
94	33.02	194	4.94	241	2.26	287	2.07	337	25.20	438	2.29	532	71.59
95	4.77	195	13.73	243	2.02	288	4.91	338	94.73	439	2.65	533	13.99
99	1.50	196	1.51	244	4.59	289	3.46	339	17.58	444	1.27	534	3.73
105	1.57	199	1.39	245	1.80	290	6.64	340	1.95	455	2.12	535	1.67
106	1.27	200	3.08	248	1.86	291	6.94	349	3.22	456	2.61	549	6.19
125	9.18	202	1.87	249	3.00	292	1.27	350	1.85	457	26.23	550	88.70
126	1.45	212	1.28	250	8.84	297	1.26	367	1.54	458	7.92	551	61.98
143	2.69	213	4.67	251	3.73	298	3.97	368	6.10	462	3.17	552	100.00
144	5.73	214	3.56	252	1.92	299	6.75	369	12.89	463	2.09	553	19.12
145	3.55	218	1.36	261	2.20	300	10.89	370	2.18	464	1.25	554	2.08
155	1.95	219	2.38	263	4.41	301	4.84	387	8.68	476	1.72	590	3.06
156	3.47	220	3.26	264	1.32	306	2.62	388	2.60	481	1.40	617	3.36
163	3.77	221	2.64	268	7.36	308	13.06	394	1.97	482	7.39	670	3.14
164	1.87	222	1.77	269	12.35	309	3.28	395	3.77	483	2.83	887	3.06
169	1.27	225	1.55	270	7.98	310	2.66	396	1.51	502	1.27	888	1.29

B21(2:17)11571 7% 22112206ei * Client:: Fernandez /MDFM-028 lim: 1.23%

Supplementary Figure 27.b HR-MS spectrum of L5

ESI-TOF Accurate Mass Report
File:22110102
Vial:1:F,1
Description:MeOH/0.1%HCOOH in H2O 90:10

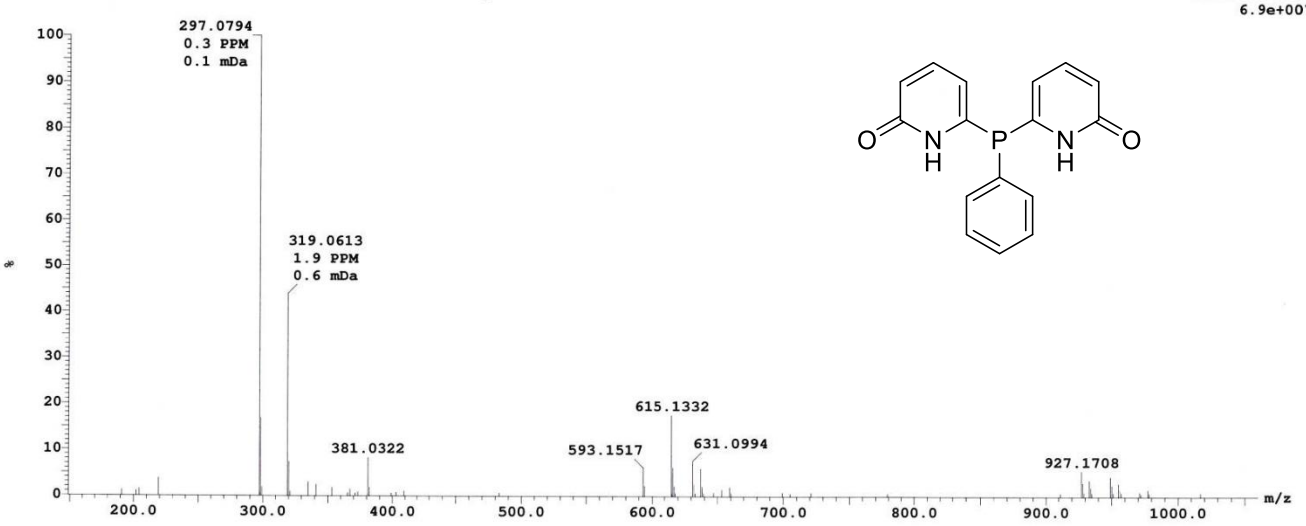
Sample Name:MDFM-018
Date:01-Nov-2022

UserName:Fernandez
Time:16:48:29

Sample Report:

(Time: 0.29) Combine (25:29-78:82) - Dead time test passed

1:TOF MS ES+
6.9e+007



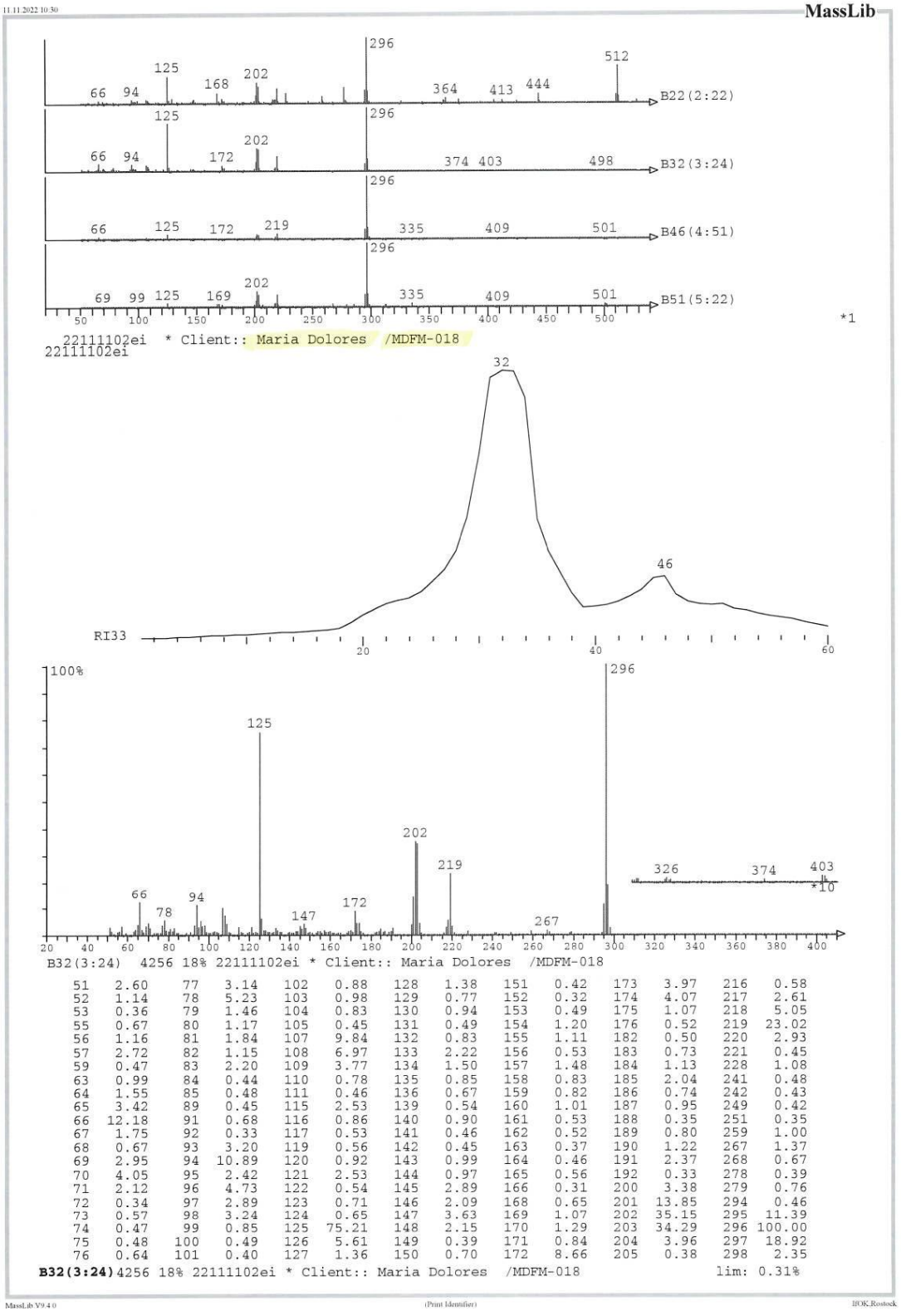
ESI-TOF Accurate Mass Report

Results file: E:\Projects\2211.PRO\SampleDB\2211.rpt
Last modified: Tuesday, November 01, 2022 16:50:36

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
2	22110102	MDFM-018	Fernandez	296.0715	C16H13PO2N2	297.0793 319.0607	297.0794 319.0613	0.3 1.9	0.1 0.6

Supplementary Figure 28.a Accurate Mass Report of L6



51	2.60	77	3.14	102	0.88	128	1.38	151	0.42	173	3.97	216	0.58
52	1.14	78	5.23	103	0.98	129	0.77	152	0.32	174	4.07	217	2.61
53	0.36	79	1.46	104	0.83	130	0.94	153	0.49	175	1.07	218	5.05
55	0.67	80	1.17	105	0.45	131	0.49	154	1.20	176	0.52	219	23.02
56	1.16	81	1.84	107	9.84	132	0.83	155	1.11	182	0.50	220	2.93
57	2.72	82	1.15	108	6.97	133	2.22	156	0.53	183	0.73	221	0.45
59	0.47	83	2.20	109	3.77	134	1.50	157	1.48	184	1.13	228	1.08
63	0.99	84	0.44	110	0.78	135	0.85	158	0.83	185	2.04	241	0.48
64	1.55	85	0.48	111	0.46	136	0.67	159	0.82	186	0.74	242	0.43
65	3.42	89	0.45	115	2.53	139	0.54	160	1.01	187	0.95	249	0.42
66	12.18	91	0.68	116	0.86	140	0.90	161	0.53	188	0.35	251	0.35
67	1.75	92	0.33	117	0.53	141	0.46	162	0.52	189	0.80	259	1.00
68	0.67	93	3.20	119	0.56	142	0.45	163	0.37	190	1.22	267	1.37
69	2.95	94	10.89	120	0.92	143	0.99	164	0.46	191	2.37	268	0.67
70	4.05	95	2.42	121	2.53	144	0.97	165	0.56	192	0.33	278	0.39
71	2.12	96	4.73	122	0.54	145	2.89	166	0.31	200	3.38	279	0.76
72	0.34	97	2.89	123	0.71	146	2.09	168	0.65	201	13.85	294	0.46
73	0.57	98	3.24	124	0.65	147	3.63	169	1.07	202	35.15	295	11.39
74	0.47	99	0.85	125	75.21	148	2.15	170	1.29	203	34.29	296	100.00
75	0.48	100	0.49	126	5.61	149	0.39	171	0.84	204	3.96	297	18.92
76	0.64	101	0.40	127	1.36	150	0.70	172	8.66	205	0.38	298	2.35

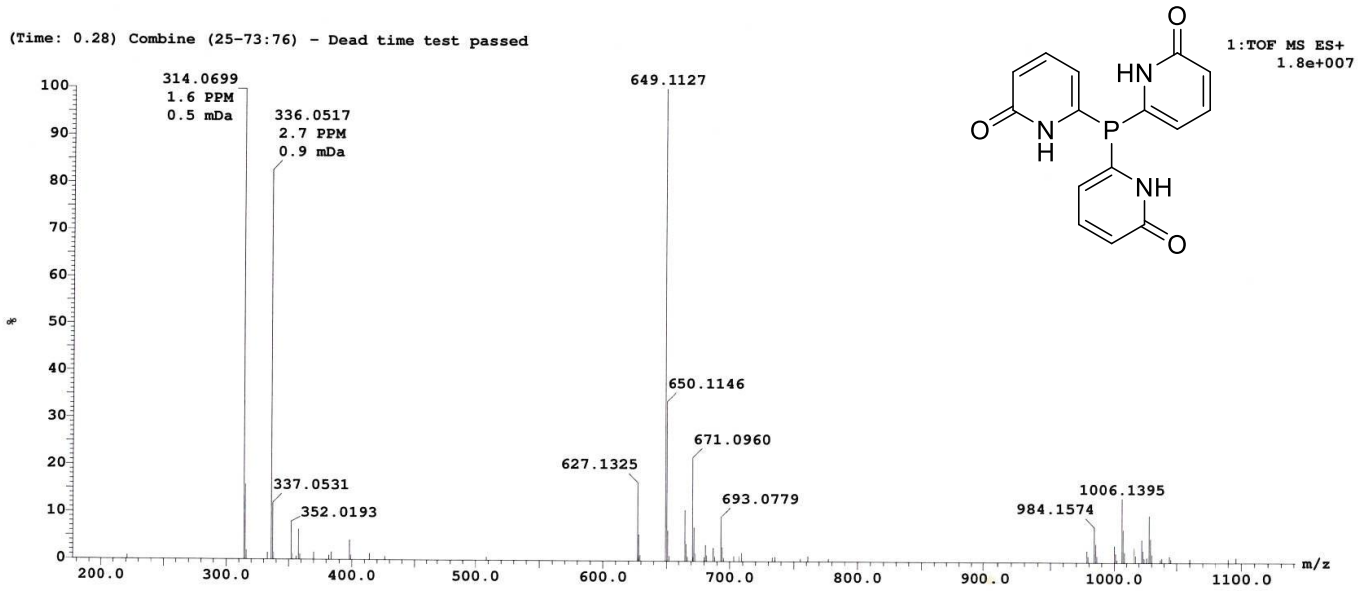
Supplementary Figure 28.b HR-MS spectrum of L6

ESI-TOF Accurate Mass Report
File:22110103
Vial:1:F,2
Description:MeOH/0.1%HCOOH in H2O 90:10

Sample Name:MDFM-019
Date:01-Nov-2022

UserName:Fernandez
Time:16:52:47

Sample Report:



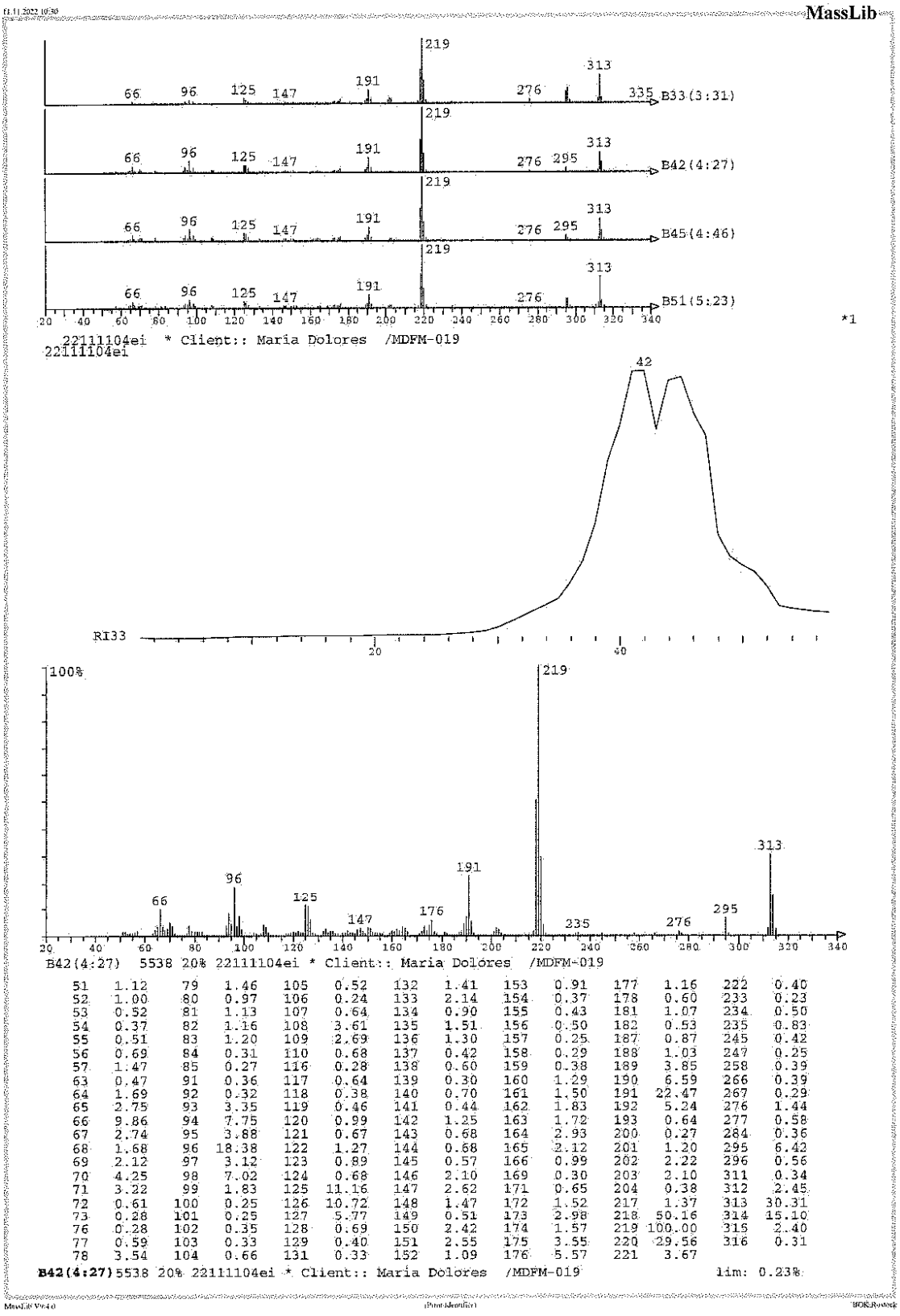
ESI-TOF Accurate Mass Report

Results file: E:\Projects\2211.PRO\SampleDB\2211.rpt
Last modified: Tuesday, November 01, 2022 16:56:12

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
3	22110103	MDFM-019	Fernandez	313.0616	C15H12N3O3P	314.0694 336.0508	314.0699 336.0517	1.6 2.7	0.5 0.9

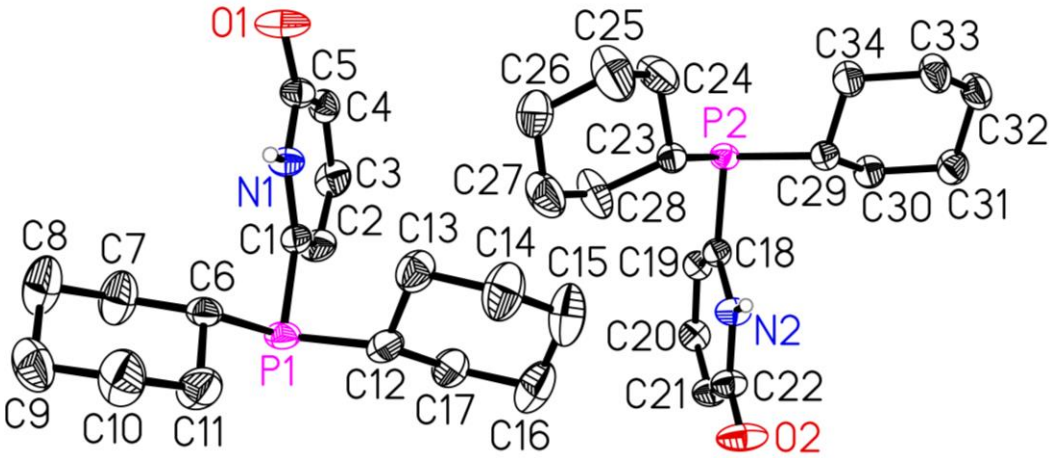
Supplementary Figure 29.a Accurate Mass Report of L7



Supplementary Figure 29.b HR-MS spectrum of L7

SI-E: Single Crystal X-ray Diffraction (SC-XRD) of new phosphine ligands (L2,L3,L4,L5)

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by intrinsic phasing (SHELXT: Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2019: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations.



Supplementary Figure 30. Molecular structure of ligand L2. Displacement ellipsoids correspond to 50% probability. C-bound hydrogen atoms are omitted for clarity.

Empirical formula	$C_{17}H_{26}NOP$
Formula weight	291.36
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 28.2403(7) Å α = 90° b = 12.1632(3) Å β = 116.2798(10)° c = 21.6308(5) Å γ = 90°
Volume	6662.1(3) $Å^3$
Z	16
Density (calculated)	1.162 g/cm^3
Absorption coefficient	1.418 mm^{-1}
F(000)	2528
Crystal size	0.27 x 0.10 x 0.06 mm
Theta range for data collection	3.49 to 67.00°
Index ranges	-33≤h≤31, -14≤k≤14, -25≤l≤25
Reflections collected	35692
Independent reflections	5949 (R_{int} = 0.0439)
Completeness to theta = 67.00°	99.9 %
Max. and min. transmission	0.92 and 0.70
Data / restraints / parameters	5949 / 0 / 369

Goodness-of-fit on F^2	1.030
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0439 wR_2 = 0.1137
R indices (all data)	R_1 = 0.0501 wR_2 = 0.1201
Largest diff. peak and hole	0.829 and -0.536 e·Å^{-3}
CCDC no.	

Supplementary Table 1. Crystal data for L2. Single crystals of the ligand **L2** were obtained from the recrystallization in acetone.

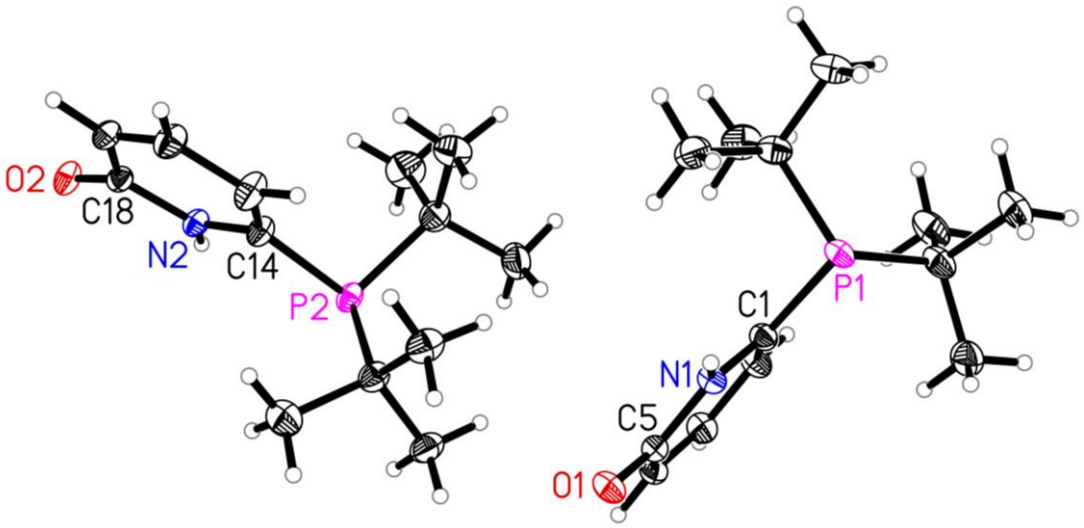
Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1 ^{i}	0.84(2)	1.98(2)	2.805(2)	169(2)
N2—H2*A*···O2^{j}	0.88(2)	1.92(3)	2.798(2)	175(2)
C6—H6···O1i	1.00	2.26	3.223(2)	161
C23—H23···O2^{j}	1.00	2.40	3.317(3)	152

Symmetry codes: (i) 1/2-x, 3/2-y, 1-z; (j) -x, 1-y, -z

Strong intermolecular N-H…O hydrogen bonds are formed resulting in dimeric structures.

For **L2** only dimers by strong intermolecular N-H···O hydrogen bonds stabilized by additional weak intermolecular C-H···O hydrogen bonds were found.



Supplementary Figure 32. Molecular structure of ligand L4. Displacement ellipsoids correspond to 50% probability.

Empirical formula	$C_{13}H_{22}NOP$
Formula weight	239.28
Temperature	110(2) K

Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\overline{1}$
Unit cell dimensions	a = 7.6695(7) Å α = 94.676(2)° b = 13.2632(12) Å β = 101.927(2)° c = 14.0998(12) Å γ = 93.562(2)°
Volume	1394.0(2) Å^3
Z	4
Density (calculated)	1.140 g/cm^3
Absorption coefficient	0.179 mm^{-1}
F(000)	520
Crystal size	0.47 x 0.29 x 0.06 mm
Theta range for data collection	1.48 to 28.99°
Index ranges	-10≤h≤10, -18≤k≤18, -19≤l≤19
Reflections collected	64917
Independent reflections	7434 (R_{int} = 0.0439)
Completeness to theta = 25.24°	100 %
Max. and min. transmission	0.99 and 0.92
Data / restraints / parameters	7434 / 0 / 309
Goodness-of-fit on F^2	1.026
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0373 wR_2 = 0.0924
R indices (all data)	R_1 = 0.0502 wR_2 = 0.1013
Largest diff. peak and hole	0.405 and -0.186 e·Å^{-3}
CCDC no.	

Supplementary Table 3. Crystal data for L4. Single crystals of the ligand **L4** were obtained from the recrystallization in acetone.

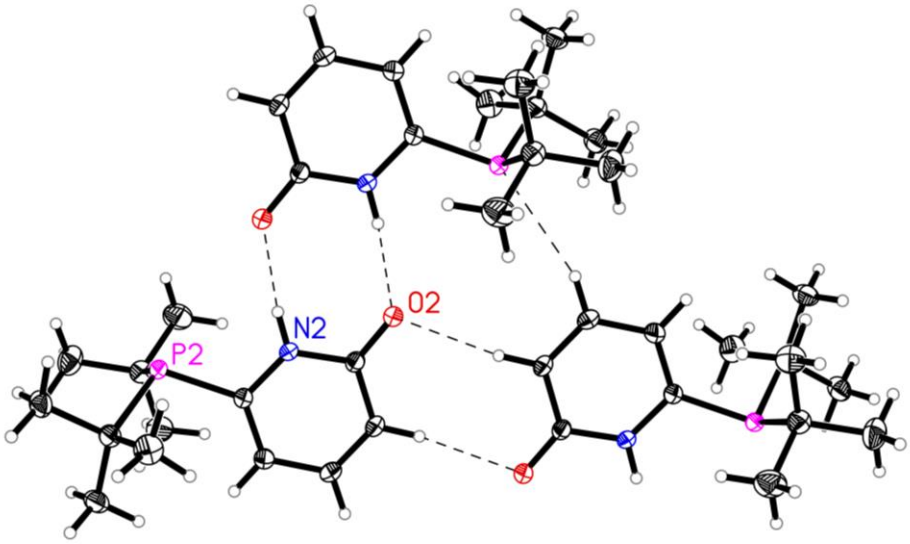
Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.84(2)	2.01(2)	2.8437(14)	173.1(17)
N2—H2*A*···O2^{j}	0.86(2)	1.94(2)	2.7915(13)	173.1(16)
C16— H16···P2^{k}	0.95	2.81	3.7295(14)	163
C17— H17···O2^{l}	0.95	2.38	3.3188(16)	170

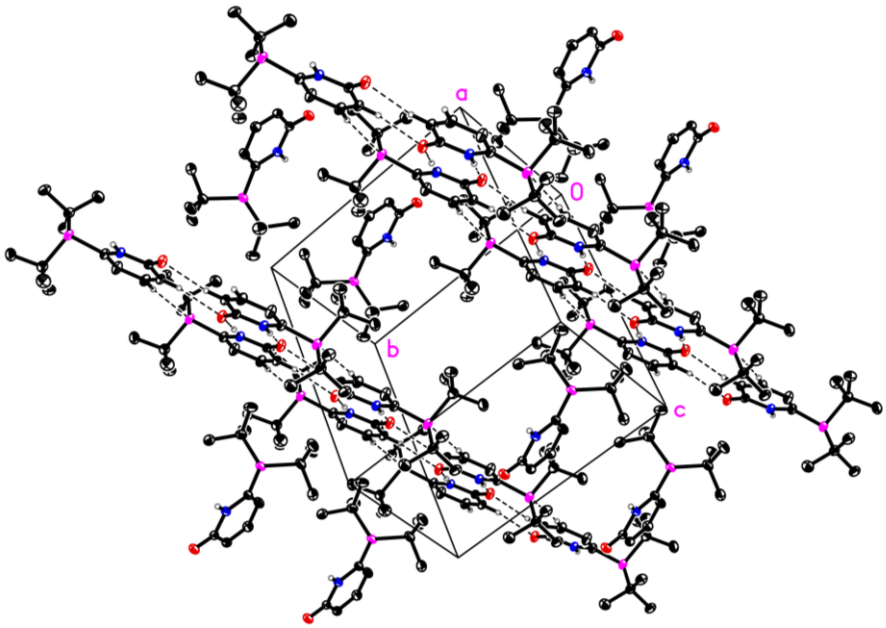
Symmetry codes: (i) 1-x, 1-y, 2-z; (j) 1-x, 2-y, 1-z; (k) 1+x,y,z; (l) 2-x,2-y,1-z

Strong intermolecular N-H…O hydrogen bonds are formed resulting in dimeric structures.

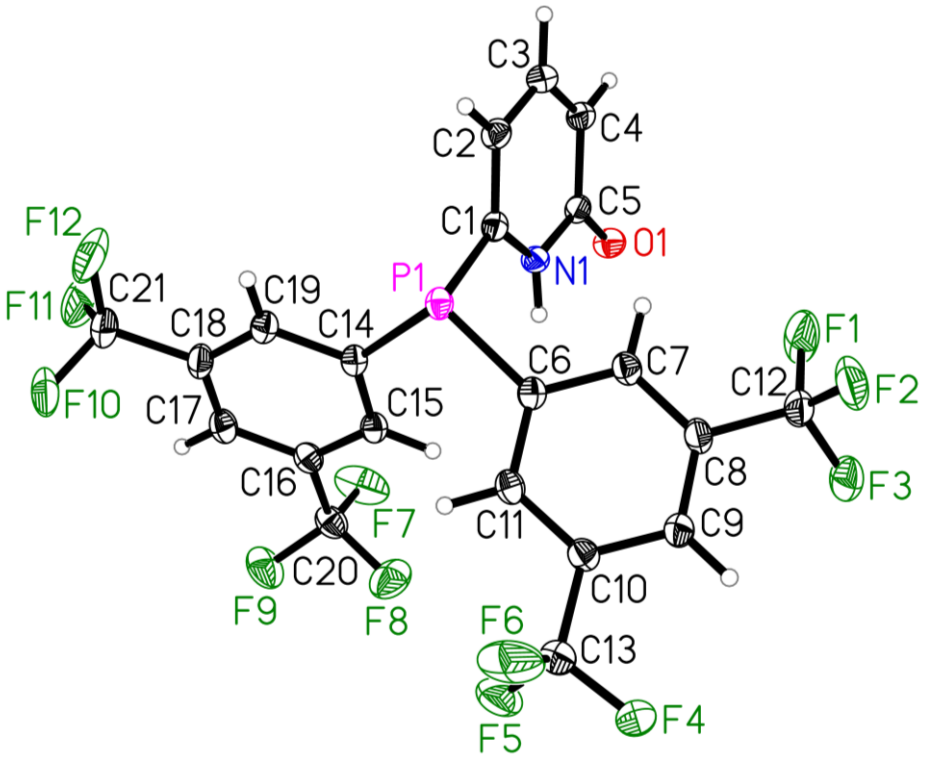
For **L4**, for one molecule of the asymmetric unit, these dimers are linked by further weak intermolecular C-H···O and C-H···P hydrogen bonds.



Supplementary Figure 33. Molecular structure of one molecule of the asymmetric unit of L4 and two further molecules which are generated by symmetry (symmetry codes: 1-x, 2-y, 1-z; 2-x,2-y,1-z). The thermal ellipsoids correspond to 50% probability. Intermolecular hydrogen bonds are depicted as dashed lines.



Supplementary Figure 34. Part of the packing diagram of L4. The thermal ellipsoids correspond to 50% probability. Intermolecular hydrogen bonds are depicted as dashed lines. Hydrogen atoms which are not involved in hydrogen bonds are omitted for clarity.



Supplementary Figure 35. Molecular structure of ligand L5. Displacement ellipsoids correspond to 50% probability.

Empirical formula	$C_{21}H_{10}F_{12}NOP$
Formula weight	551.27
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.8822(10) Å α = 69.592(2)° b = 10.1987(10) Å β = 77.058(3)° c = 11.9192(12) Å γ = 89.014(3)°
Volume	1094.85(19) Å^3
Z	2
Density (calculated)	1.672 g/cm^3
Absorption coefficient	0.243 mm^{-1}
F(000)	548
Crystal size	0.39 x 0.35 x 0.33 mm
Theta range for data collection	1.87 to 30.00°
Index ranges	-13≤h≤13, -14≤k≤14, -16≤l≤16
Reflections collected	57852
Independent reflections	6380 (R_{int} = 0.0279)
Completeness to theta = 25.24°	100 %
Max. and min. transmission	0.92 and 0.91

Data / restraints / parameters	6380/ 0 / 329
Goodness-of-fit on F^2	1.044
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0443 wR_2 = 0.1158
R indices (all data)	R_1 = 0.0512 wR_2 = 0.1226
Largest diff. peak and hole	0.792 and -0.440 e·Å^{-3}
CCDC no.	

Supplementary Table 4. Crystal data for L5. Single crystals of the ligand **L5** were obtained from the recrystallization in acetone.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.85(2)	1.98(2)	2.8211(16)	170(2)
C15—H15···O1^{i}	0.95	2.26	3.1137(17)	150
C17—H17···F5^{j}	0.95	2.42	3.345(2)	163

Symmetry code: (i) 1-x, 2-y, -z; (j) 1-x,1-y,1-z

For **L5**, dimers are formed by strong intermolecular N-H···O hydrogen bonds, which are linked by further weak intermolecular C-H···F interactions. Furthermore, weak intermolecular C-H···O hydrogen bonds are observed.

SI-F: General procedures for hydroformylation experiments

Under argon atmosphere, vials (15 mL) were charged with [$Rh(CO)_2acac$] (0.2 mg, 0.014 mol%), monodentate ligand (0.071 mol%) and a stirring bar. Then **1a** (6.0 mmol) and toluene (4.3 mL) were added. The vials were placed in an alloyed plate, which was then transferred into an argon-flushed autoclave (300 mL). The autoclave was flushed with syngas three times at room temperature and then pressurized with syngas to 10 bar. The reaction was performed at 120 °C for 4 h. After the reaction finished, the autoclave was cooled to room temperature on an ice bath and the pressure was carefully released. Isooctane was added to the reaction mixture as an internal standard and yield and regioselectivity were measured by GC.

a) Influence of temperature

#	Ligand	Conversion (%)	Isomers (%)	Octane (%)	Lin. selec. (%)	Yield 2 (%)	Ligand
1	**L1**	**40**	**1**	**-**	**-**	**>99**	**<1**
2	**L6**	**40**	**1**	**-**	**-**	**>99**	**<1**
3	**L7**	**40**	**1**	**<1**	**-**	**-**	**-**
4	**PPh_3**	**40**	**<1**	**-**	**-**	**-**	**-**
6	**-**	**40**	**<1**	**-**	**-**	**-**	**-**
7	**L1**	**60**	**31**	**1**	**1**	**99**	**29**
8	**L6**	**60**	**11**	**<1**	**<1**	**>99**	**10**
9	**L7**	**60**	**16**	**3**	**9**	**74**	**3**
10	**PPh_3**	**60**	**16**	**<1**	**<1**	**75**	**15**
11	**-**	**60**	**24**	**14**	**4**	**74**	**5**
12	**L1**	**80**	**95**	**4**	**6**	**92**	**85**
13	**L6**	**80**	**38**	**1**	**2**	**99**	**35**
14	**L7**	**80**	**93**	**40**	**37**	**59**	**15**
15	**PPh_3**	**80**	**99**	**10**	**11**	**54**	**77**
16	**-**	**80**	**99**	**44**	**32**	**53**	**21**
17	**L1**	**100**	**98**	**5**	**7**	**89**	**86**
18	**L6**	**100**	**58**	**3**	**3**	**99**	**52**
19	**L7**	**100**	**95**	**48**	**33**	**49**	**13**
20	**PPh_3**	**100**	**>99**	**10**	**9**	**58**	**80**
21	**-**	**100**	**98**	**51**	**35**	**44**	**13**
22	**L1**	**120**	**98**	**4**	**13**	**81**	**80**
23	**L6**	**120**	**90**	**4**	**13**	**99**	**73**
24	**L7**	**120**	**98**	**68**	**29**	**1**	**5**
25	**PPh_3**	**120**	**99**	**3**	**23**	**66**	**73**
26	**-**	**120**	**98**	**7**	**86**	**40**	**5**
27	**L1**	**140**	**98**	**16**	**24**	**81**	**58**
28	**L6**	**140**	**98**	**11**	**18**	**98**	**69**
29	**L7**	**140**	**97**	**65**	**32**	**53**	**4**
30	**PPh_3**	**140**	**98**	**50**	**25**	**62**	**23**
31	**-**	**140**	**98**	**59**	**28**	**39**	**11**

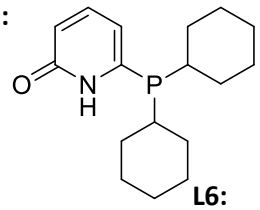
Supplementary Table 5. Temperature screening for the hydroformylation of 1-octene

Variation from general conditions: Temperature was adjusted to the working temperature.

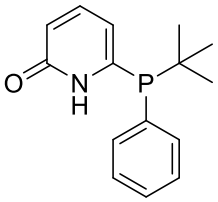
b) Variation of ligands

L1: 6-DPPON

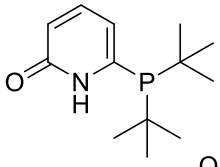
L2:



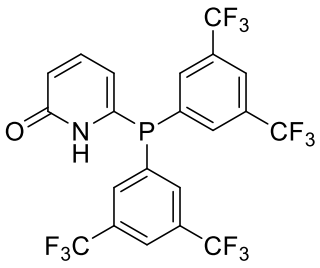
L3:



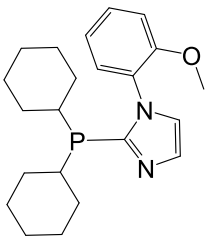
L4:



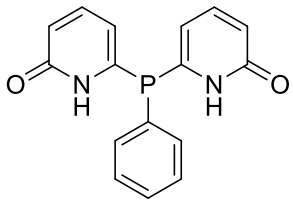
L5:



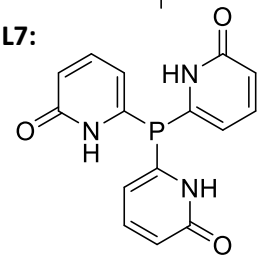
ImidP*:



L6:



L7:



#	Ligand	Conversion (%)	Isomers (%)	Octane (%)	Lin. selec. (%)	Yield 2 (%)
1	**L1**	**95**	**7**	**7**	**99**	**81**
2	**PPh_3**	**34**	**<1**	**1**	**74**	**33**
3	**PCy_3**	**61**	**<1**	**<1**	**57**	**60**
4	**ImidP***	**33**	**<1**	**1**	**50**	**29**
5	**L2**	**12**	**4**	**<1**	**60**	**8**
6	**L3**	**6**	**<1**	**1**	**76**	**5**
7	**L4**	**11**	**<1**	**<1**	**74**	**11**
8	**L6**	**15**	**<1**	**1**	**99**	**14**
9	**L7**	**49**	**7**	**35**	**75**	**7**
10	**-**	**94**	**14**	**60**	**71**	**20**

Supplementary Table 6. Preliminary ligand screening for the hydroformylation of 1-octene

Variation from general conditions: 1-octene (3.5 mmol), [Rh(COD)2BF4](0.05 mol%),L:Rh (20:1), CO/H2 (10 bar), Toluene (2.5 mL), 65 °C, 4h. The conversion, yields and regioselectivity of the products were measured by GC analysis using MeOH as solvent and isooctane as internal standard.

c) Ligand-Metal ratio influence

#	Ligand	L:M	Conv. (%)	L. selec. (%)	Yield (%)
1	L1	10:1	99	81	98
2	L6		90	99	73
3	L1	5:1	99	80	83
4	L6		95	98	77
5	L1	3:1	98	52	32
6	L6		95	98	75
7	L1	2:1	98	48	30
8	L6		71	76	10
9	L1	1:1	98	38	14
10	L6		54	78	7

Supplementary Table 7. Ligand-Metal ratio screening for the hydroformylation of 1-octene

Variation from general conditions: Adjusted ligand loading.

d) Influence of pressure

#	Ligand	$P_{CO/H2}$ (bar)	Conv. (%)	L. selec. (%)	Yield (%)
1	L1	40	99	73	93
2	L6		98	96	94
3	L1	20	98	82	83
4	L6		98	98	87
5	L1	15	98	80	80
6	L6		98	98	85
7	L1	10	99	80	72
8	L6		95	98	77
9	L1	5	99	81	54
10	L6		92	98	54
11	L1	1	8	-	-
12	L6		35	-	-

Supplementary Table 8. Influence of syngas pressure on the hydroformylation of 1-octene

Variation from general conditions: Adjusted syngas pressure.

e) Solvent screening

#	Ligand	solvent	Conv. (%)	L. selec. (%)	Yield (%)
1	**L6**	**Toluene**	**95**	**98**	**77**
2	**L6**	**Dioxane**	**78**	**93**	**57**
3	**L6**	**THF**	**73**	**92**	**57**
4	**L6**	**PC**	**82**	**93**	**55**
5	**L6**	**MeOH**	**30**	**75**	**7**
6	**L6**	**H_2O**	**97**	**73**	**67**
7	**L6**	**NMP**	**21**	**79**	**13**
8	**L6**	**HFIP**	**66**	**81**	**33**
9	**L6**	**Heptane**	**49**	**88**	**35**
10	**L6**	**-**	**[75-98]**	**[85-90]**	**[60-82]**

Supplementary Table 9. Influence of solvents on the hydroformylation of 1-octene

Variation from general conditions: Appropriate solvent used.

f) Ligand screening in optimized conditions

#	Ligand	Conv. (%)	Iso. (%)	L. selec. (%)	Yield (%)
1	**L1**	**95**	**7**	**84**	**81**
2	**L2**	**98**	**8**	**67**	**77**
3	**L3**	**98**	**14**	**66**	**70**
4	**L4**	**44**	**14**	**72**	**3**
5	**L5**	**78**	**18**	**90**	**34**
6	**L6**	**88**	**6**	**99**	**78**
7	**L7**	**98**	**57**	**33**	**1**
8	**PPh_3**	**98**	**49**	**6**	**39**

Supplementary Table 10. Ligand screening for the hydroformylation of 1-octene in optimized conditions

SI-G: Kinetic profile and gas consumption experiments

t(h)	Conv. (%)	Hydrog. (%)	Iso. (%)	Yield (%)	L. selec. (%)	nonanal (%)
0	0	0	0	0	0	0
1	55	8	4	44	97	43
2	70	10	6	53	97	51
3	77	13	6	58	96	56
4	82	13	7	62	96	60
5	84	14	7	63	96	60

Supplementary Table 11. Kinetic profile experiment for the hydroformylation of 1-octene with Rh/L6

t(h)	Conv. (%)	Hydrog. (%)	Iso. (%)	Yield (%)	L. selec. (%)	nonanal (%)
0	0	0	0	0	0	0
1	64	15	7	42	82	34
2	85	20	9	56	80	45
3	92	21	9	62	79	49
4	94	21	9	64	79	51
5	96	22	9	65	79	51

Supplementary Table 12. Kinetic profile experiment for the hydroformylation of 1-octene with Rh/L1

Variation from general conditions: $c_{Rh} = 6 \cdot 10^{-5}$ mol.L^{-1}, **1a** (10.0 mmol) and toluene (24 mL).

A 100 mL was used for those experiments. A pressure probe and a sampling cannula were adapted. The precursor, ligand and solvent were added as a solution along with **1a** under a strong flow of argon. The autoclave was first flushed with N_2, then pressurized to 10 bars of syngas, brought to working temperature (120 °C). Finally, the pressure was adjusted to 25 bars of syngas and stirring was turned on. Samples were collected hourly, including a first one at t = 0 h (approximately one to two minutes after the start of the reaction) and analyzed on GC. Pressure was monitored and provided data points every minute.

	L1		L6	
t (mn)	**P (bar)**	**Gas consumption (%)**	**P (bar)**	**Gas consumption (%)**
0	25.3	0%	24.1	0%
1	25.2	0%	24	0%
2	25.2	0%	24	0%
3	25.1	1%	24	0%
4	25.1	1%	24	0%
5	25	1%	24.1	0%
6	24.9	2%	24	0%
7	24.9	2%	24	0%
8	24.8	2%	24	0%
9	24.8	2%	23.9	1%
10	24.7	2%	23.8	1%
11	24.7	2%	23.8	1%
12	24.6	3%	23.7	2%
13	24.6	3%	23.7	2%
14	24.6	3%	23.5	2%
15	24.6	3%	23.5	2%
16	24.5	3%	23.4	3%
17	24.5	3%	23.3	3%
18	24.4	4%	23.3	3%
19	24.4	4%	23.2	4%
20	24.4	4%	23.1	4%
21	24.3	4%	23.1	4%
22	24.3	4%	23.1	4%
23	24.3	4%	23	5%
24	24.2	4%	22.9	5%
25	24.2	4%	23	5%
26	24.2	4%	22.9	5%
27	24.2	4%	22.8	5%
28	24.2	4%	22.8	5%
29	24.1	5%	22.7	6%
30	24.1	5%	22.7	6%
31	24	5%	22.7	6%
32	24	5%	22.7	6%
33	24	5%	22.7	6%
34	24	5%	22.6	6%
35	24	5%	22.6	6%
36	23.9	6%	22.6	6%
37	23.9	6%	22.6	6%
38	23.9	6%	22.6	6%
39	23.8	6%	22.5	7%

40	23.9	6%	22.6	6%
41	23.9	6%	22.5	7%
42	23.9	6%	22.5	7%
43	23.8	6%	22.5	7%
44	23.7	6%	22.5	7%
45	23.7	6%	22.5	7%
46	23.7	6%	22.4	7%
47	23.7	6%	22.4	7%
48	23.7	6%	22.4	7%
49	23.6	7%	22.4	7%
50	23.6	7%	22.3	7%
51	23.6	7%	22.3	7%
52	23.5	7%	22.3	7%
53	23.6	7%	22.3	7%
54	23.5	7%	22.2	8%
55	23.5	7%	22.2	8%
56	23.5	7%	22.2	8%
57	23.5	7%	22.2	8%
58	23.4	8%	22.2	8%
59	23.3	8%	22.2	8%
60	23.3	8%	22.2	8%
61	23.2	8%	22.1	8%
62	23.3	8%	22.1	8%
63	23.2	8%	22.2	8%
64	23.2	8%	22	9%
65	23.2	8%	21.9	9%
66	23.2	8%	21.9	9%
67	23.1	9%	21.9	9%
68	23.1	9%	21.8	10%
69	23.1	9%	21.8	10%
70	23.1	9%	21.9	9%
71	23	9%	21.9	9%
72	23.1	9%	21.8	10%
73	23	9%	21.8	10%
74	23	9%	21.8	10%
75	23	9%	21.8	10%
76	23	9%	21.8	10%
77	23	9%	21.8	10%
78	23	9%	21.7	10%
79	23	9%	21.7	10%
80	23	9%	21.7	10%
81	22.9	9%	21.7	10%
82	22.9	9%	21.8	10%
83	22.9	9%	21.7	10%
84	22.8	10%	21.7	10%
85	22.9	9%	21.7	10%

86	22.8	10%	21.7	10%
87	22.9	9%	21.6	10%
88	22.9	9%	21.7	10%
89	22.8	10%	21.7	10%
90	22.9	9%	21.6	10%
91	22.8	10%	21.6	10%
92	22.8	10%	21.6	10%
93	22.8	10%	21.6	10%
94	22.8	10%	21.7	10%
95	22.8	10%	21.6	10%
96	22.7	10%	21.6	10%
97	22.7	10%	21.6	10%
98	22.7	10%	21.6	10%
99	22.7	10%	21.5	11%
100	22.7	10%	21.5	11%
101	22.7	10%	21.6	10%
102	22.7	10%	21.5	11%
103	22.7	10%	21.5	11%
104	22.7	10%	21.5	11%
105	22.6	11%	21.5	11%
106	22.7	10%	21.5	11%
107	22.7	10%	21.5	11%
108	22.7	10%	21.5	11%
109	22.6	11%	21.5	11%
110	22.6	11%	21.4	11%
111	22.6	11%	21.4	11%
112	22.6	11%	21.4	11%
113	22.7	10%	21.4	11%
114	22.6	11%	21.4	11%
115	22.6	11%	21.4	11%
116	22.6	11%	21.3	12%
117	22.6	11%	21.3	12%
118	22.6	11%	21.3	12%
119	22.6	11%	21.2	12%
120	22.5	11%	21.2	12%
121	22.5	11%	21.2	12%
122	22.5	11%	21.2	12%
123	22.6	11%	21.2	12%
124	22.5	11%	21.2	12%
125	22.6	11%	21.1	12%
126	22.6	11%	21.1	12%
127	22.5	11%	21.2	12%
128	22.6	11%	21.1	12%
129	22.5	11%	21.2	12%
130	22.5	11%	21.1	12%
131	22.5	11%	21.1	12%

132	22.5	11%	21.1	12%
133	22.5	11%	21	13%
134	22.5	11%	21.1	12%
135	22.5	11%	21.1	12%
136	22.5	11%	21.1	12%
137	22.5	11%	21.1	12%
138	22.5	11%	21	13%
139	22.4	11%	21	13%
140	22.4	11%	21	13%
141	22.4	11%	21	13%
142	22.5	11%	21	13%
143	22.4	11%	21	13%
144	22.5	11%	21	13%
145	22.4	11%	21	13%
146	22.4	11%	21	13%
147	22.4	11%	21	13%
148	22.4	11%	20.9	13%
149	22.4	11%	21	13%
150	22.4	11%	20.9	13%
151	22.5	11%	21	13%
152	22.4	11%	21	13%
153	22.4	11%	20.9	13%
154	22.5	11%	21	13%
155	22.4	11%	20.9	13%
156	22.4	11%	20.9	13%
157	22.3	12%	20.9	13%
158	22.3	12%	21	13%
159	22.4	11%	20.9	13%
160	22.3	12%	21	13%
161	22.4	11%	21	13%
162	22.4	11%	20.9	13%
163	22.4	11%	20.9	13%
164	22.3	12%	20.9	13%
165	22.2	12%	20.9	13%
166	22.2	12%	20.8	14%
167	22.2	12%	20.8	14%
168	22.2	12%	20.9	13%
169	22.2	12%	20.9	13%
170	22.2	12%	20.8	14%
171	22.2	12%	20.8	14%
172	22.2	12%	20.8	14%
173	22.2	12%	20.8	14%
174	22.3	12%	20.8	14%
175	22.2	12%	20.8	14%
176	22.2	12%	20.8	14%
177	22.1	13%	20.8	14%

178	22.2	12%	20.8	14%
179	22.2	12%	20.8	14%
180	22.1	13%	20.7	14%
181	22.2	12%	20.7	14%
182	22.2	12%	20.8	14%
183	22.1	13%	20.7	14%
184	22.2	12%	20.7	14%
185	22.2	12%	20.7	14%
186	22.2	12%	20.8	14%
187	22.2	12%	20.7	14%
188	22.2	12%	20.8	14%
189	22.2	12%	20.7	14%
190	22.3	12%	20.7	14%
191	22.2	12%	20.8	14%
192	22.2	12%	20.7	14%
193	22.3	12%	20.7	14%
194	22.2	12%	20.8	14%
195	22.2	12%	20.7	14%
196	22.2	12%	20.8	14%
197	22.2	12%	20.8	14%
198	22.2	12%	20.7	14%
199	22.2	12%	20.7	14%
200	22.3	12%	20.7	14%
201	22.2	12%	20.7	14%
202	22.3	12%	20.8	14%
203	22.3	12%	20.7	14%
204	22.2	12%	20.8	14%
205	22.2	12%	20.7	14%
206	22.2	12%	20.7	14%
207	22.2	12%	20.7	14%
208	22.3	12%	20.8	14%
209	22.2	12%	20.7	14%
210	22.2	12%	20.8	14%
211	22.2	12%	20.7	14%
212	22.2	12%	20.8	14%
213	22.3	12%	20.8	14%
214	22.2	12%	20.8	14%
215	22.2	12%	20.8	14%
216	22.2	12%	20.8	14%
217	22.2	12%	20.7	14%
218	22.3	12%	20.8	14%
219	22.2	12%	20.8	14%
220	22.2	12%	20.8	14%
221	22.2	12%	20.8	14%
222	22.2	12%	20.8	14%
223	22.2	12%	20.7	14%

224	22.2	12%	20.7	14%
225	22.2	12%	20.7	14%
226	22.2	12%	20.7	14%
227	22.2	12%	20.7	14%
228	22.1	13%	20.7	14%
229	22.1	13%	20.8	14%
230	22	13%	20.8	14%
231	22	13%	20.7	14%
232	22	13%	20.7	14%
233	22	13%	20.7	14%
234	22	13%	20.8	14%
235	22	13%	20.7	14%
236	22	13%	20.7	14%
237	22	13%	20.6	15%
238	21.9	13%	20.5	15%
239	22	13%	20.5	15%
240	21.9	13%	20.5	15%
241	21.9	13%	20.5	15%
242	22	13%	20.5	15%
243	21.9	13%	20.5	15%
244	22	13%	20.5	15%
245	22	13%	20.5	15%
246	21.9	13%	20.5	15%
247	22	13%	20.5	15%
248	22	13%	20.5	15%
249	22	13%	20.5	15%
250	21.9	13%	20.5	15%
251	21.9	13%	20.5	15%
252	22	13%	20.5	15%
253	21.9	13%	20.5	15%
254	21.9	13%	20.5	15%
255	21.9	13%	20.4	15%
256	21.9	13%	20.4	15%
257	21.9	13%	20.4	15%
258	21.9	13%	20.5	15%
259	21.9	13%	20.4	15%
260	21.9	13%	20.5	15%
261	21.9	13%	20.4	15%
262	21.9	13%	20.4	15%
263	21.9	13%	20.4	15%
264	21.8	14%	20.4	15%
265	21.9	13%	20.4	15%
266	21.8	14%	20.4	15%
267	21.9	13%	20.4	15%
268	21.8	14%	20.4	15%
269	21.8	14%	20.4	15%

270	21.9	13%	20.4	15%
271	21.9	13%	20.5	15%
272	21.8	14%	20.4	15%
273	21.8	14%	20.5	15%
274	21.8	14%	20.4	15%
275	21.8	14%	20.4	15%
276	21.8	14%	20.4	15%
277	21.8	14%	20.5	15%
278	21.8	14%	20.4	15%
279	21.8	14%	20.4	15%
280	21.8	14%	20.5	15%
281	21.8	14%	20.4	15%
282	21.8	14%	20.4	15%
283	21.9	13%	20.5	15%
284	21.8	14%	20.4	15%
285	21.8	14%	20.4	15%
286	21.9	13%	20.4	15%
287	21.9	13%	20.4	15%
288	21.8	14%	20.4	15%
289	21.4	15%	20.4	15%
290	21.3	16%	20.4	15%
291	21.4	15%	20.4	15%
292	21.5	15%	20.5	15%
293	21.4	15%	20.4	15%
294	21.4	15%	20.4	15%
295	21.4	15%	20.5	15%
296	21.4	15%	20.4	15%
297	21.3	16%	20.4	15%
298	21.3	16%	20.4	15%
299	21.4	15%	20.4	15%
300	21.4	15%	20.4	15%
301	21.3	16%	20.3	16%
302	21.3	16%	20.3	16%
303	21.3	16%	20.3	16%
304	21.4	15%	20.3	16%
305	21.4	15%	20.3	16%
306	21.4	15%	20.3	16%
307	21.4	15%	20.3	16%
308	21.4	15%	20.3	16%
309	21.4	15%	20.2	16%
310	21.4	15%	20.2	16%
311	21.4	15%	20.3	16%
312	21.4	15%	20.2	16%
313	21.4	15%	20.2	16%
314	21.3	16%	20.3	16%
315	21.3	16%	20.3	16%

316	21.3	16%	20.3	16%
317	21.3	16%	20.3	16%
318	21.4	15%	20.3	16%
319	21.4	15%	20.3	16%
320	21.3	16%	20.3	16%
321	21.4	15%	20.3	16%
322	21.3	16%	20.3	16%
323	21.4	15%	20.3	16%
324	21.3	16%	20.3	16%
325	21.3	16%	20.3	16%

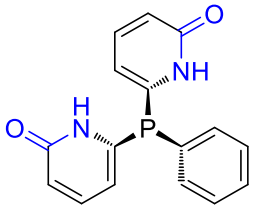
Supplementary Table 13. Gas consumption experiment for **L1** and **L6**

SI-H: DFT and experimental IR spectra

a) Computational details

In our calculation, geometry optimization was carried out using the M06L [1] functional with all electron TZVP[2] basis set in gas phase as well as in the solution of THF and toluene based on solute electron density (SMD[3]). All optimized structures were further characterized either as energy minimums without imaginary frequencies at the corresponding level, which provided zero-point vibrational energies and thermodynamic corrections to enthalpy and Gibbs free energy at 298.15 K under 1 atmosphere. We used the M06L/TZVP computed Gibbs free energies for comparison and discussion. All calculations were carried out using Gaussian 16 program. [4]

Supplementary Table 14. M06L/TZVP computed total electronic energies (HF, au), zero-point vibrational energies (ZPE, au), sum of electronic and thermal enthalpies (Htot, au), sum of electronic and thermal free energies (Gtot, au), number of Imaginary frequencies (NImag) in gas phase as well as in the solution of THF and toluene.

	M06L/TZVP gas phase	M06L-SCRF/TZVP THF	M06L-SCRF/TZVP toluene
	HF=-1219.0098437 ZPE= 0.258939 NImag=0 Htot= -1218.732156 Gtot= -1218.799132	HF=-1219.0383712 ZPE= 0.258935 NImag=0 Htot= -1218.760770 Gtot= -1218.827400	HF=-1219.0334687 ZPE= 0.259066 NImag=0 Htot= -1218.755706 Gtot= -1218.822559

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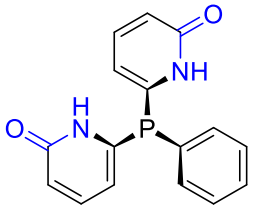
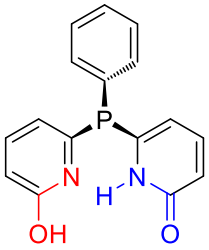
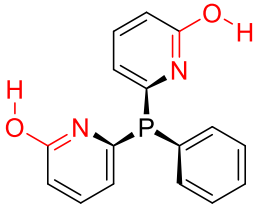
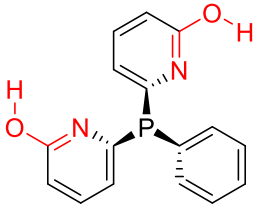
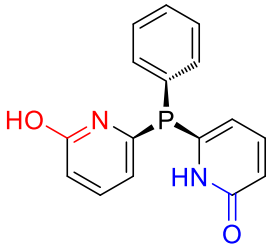
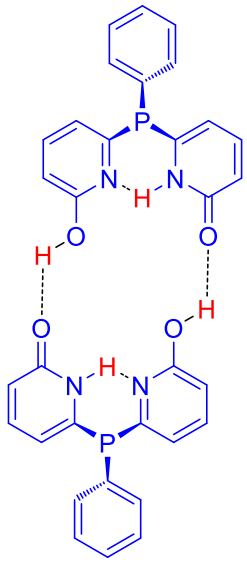
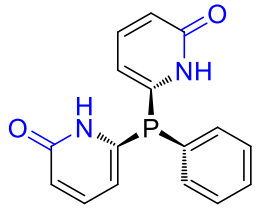
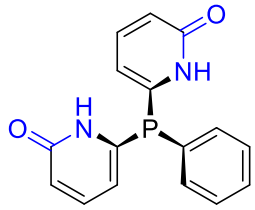
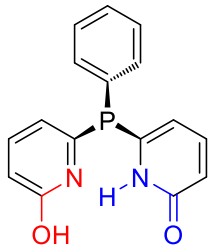
[4] Frisch, M. J. *et al.* Gaussian 16, Revision A.03. *Gaussian Inc. Gaussian, Inc., Wallingford CT, 2016*

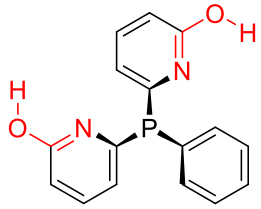
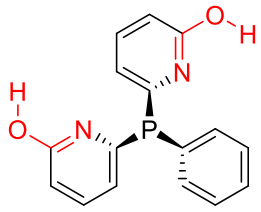
L-a			
 **L-a1**	HF=-1219.0088966 ZPE= 0.258920 NImag=0 Htot= -1218.731107 Gtot= -1218.798952	HF=-1219.0385151 ZPE= 0.259030 NImag=0 Htot= -1218.760762 Gtot= -1218.827572	HF=-1219.0331181 ZPE= 0.259136 NImag=0 Htot= -1218.755213 Gtot= -1218.822400
 **L-b**	HF=-1219.0125129 ZPE= 0.259094 NImag=0 Htot= -1218.734830 Gtot= -1218.800966	HF=-1219.0348591 ZPE= 0.258553 NImag=0 Htot= -1218.757675 Gtot= -1218.824229	HF=-1219.0325556 ZPE= 0.258893 NImag=0 Htot= -1218.755036 Gtot= -1218.821567
 **L-b1**	HF=-1219.0027536 ZPE= 0.258743 NImag=0 Htot= -1218.725313 Gtot= -1218.792855	HF=-1219.0226262 ZPE= 0.258149 NImag=0 Htot= -1218.745742 Gtot= -1218.812676	HF=-1219.0207315 ZPE= 0.258481 NImag=0 Htot= -1218.743520 Gtot= -1218.811180
 **L-b2**	HF=-1219.0027534 ZPE= 0.258743 NImag=0 Htot= -1218.725313 Gtot= -1218.792863	HF=-1219.0226262 ZPE= 0.258149 NImag=0 Htot= -1218.745742 Gtot= -1218.812676	HF=-1219.0207315 ZPE= 0.258481 NImag=0 Htot= -1218.743520 Gtot= -1218.811180
 **L-b3**	HF=-1219.0066152 ZPE= 0.258805 NImag=0 Htot= -1218.729021 Gtot= -1218.797023	HF=-1219.0310499 ZPE= 0.258475 NImag=0 Htot= -1218.753814 Gtot= -1218.821074	HF=-1219.0276058 ZPE= 0.258725 NImag=0 Htot= -1218.750109 Gtot= -1218.817563

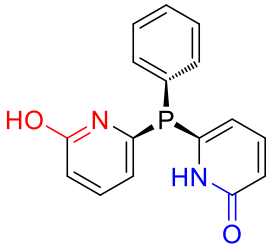
 **L6D**	HF=-2438.059633 ZPE=0.520308 NImag=0 Htot=-2437.501994 Gtot= -2437.613112	HF=-2438.0935405 ZPE=0.519303 NImag=0 Htot=-2437.536832 Gtot= -2437.647851	HF=-2438.0922235 ZPE=0.519860 NImag=0 Htot=-2437.534959 Gtot= -2437.646144

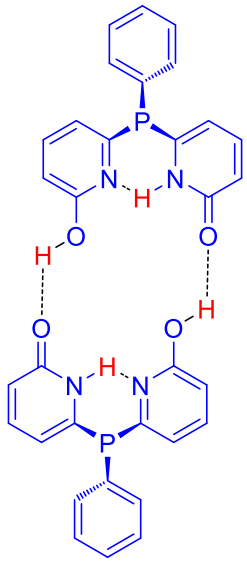
Supplementary Table 15. M06L/TZVP optimized Cartesian Coordinates in gas phase.

	M06L/TZVP gas phase
 **L-a**	P,0,-1.4998236555,-0.0090968569,-0.0364906546 C,0,-0.656695519,-1.2620956111,1.0360675978 C,0,-0.7496115108,1.5546763448,0.5770810162 C,0,-0.5570689886,-0.2755419315,-1.6066894467 C,0,0.3604937439,-3.3400808231,2.5916464873 C,0,0.2762110295,4.0238354804,1.3726591256 C,0,0.8851227174,-0.712348675,-3.9508397406 N,0,-0.1626346545,-2.3943904721,0.4720434692 C,0,0.5357454365,1.6470463748,1.1190694435 N,0,0.5614334751,0.4405484022,-1.892361842 C,0,-0.6582604161,-1.1498779211,2.3986127489 C,0,-1.511766743,2.7159905542,0.4437788373 C,0,-0.9801746998,-1.2240200502,-2.4964587924 C,0,-0.1292378204,-2.2099006135,3.167693738 C,0,-1.0005765606,3.9432657638,0.8380990972 C,0,-0.2244119264,-1.4438183057,-3.6737309222 C,0,0.3728040504,-3.5114374675,1.1628578922 C,0,1.0430399939,2.8753295002,1.5132799014 C,0,1.3564427706,0.3188296208,-3.059135441 H,0,-1.0549548968,-0.2616214894,2.8687213139 H,0,-2.5128074213,2.6537264899,0.0323781924 H,0,-1.8890311847,-1.7763443039,-2.3018414791 H,0,-0.1215229584,-2.1153294221,4.2478173015 H,0,-1.6026250662,4.8366006709,0.730674619 H,0,-0.5506456701,-2.2081372878,-4.3695105622 H,0,0.7615771436,-4.1537582963,3.1787947543 H,0,0.674899477,4.9816564621,1.6820914297 H,0,1.4609894277,-0.8675785948,-4.8520792805 H,0,2.0410828761,2.9350783648,1.9285773901 O,0,2.3221740361,1.0443099768,-3.2096304029 O,0,0.7826528047,-4.4679696459,0.5291065408 H,0,1.135327025,0.7521689019,1.2425203063 H,0,0.8743165258,1.1534856442,-1.2431565305 H,0,-0.139939241,-2.4784286838,-0.5389731081

 **L-a1**	P,0,1.0734432089,0.0047987098,0.0921679136 C,0,0.1563817949,0.7532790365,1.5040905469 C,0,0.2666834221,-1.6413327629,-0.0423747894 C,0,0.2621785368,0.8940148834,-1.3093654239 C,0,-0.9753845816,2.0751248764,3.6833627946 C,0,-0.8619663886,-4.1845250014,-0.1546429505 C,0,-0.7191590117,2.1013153696,-3.6251757229 C,0,-0.7993926358,0.128041634,2.24973567 C,0,-0.9825606477,-1.8317343681,-0.633786419 C,0,-0.7335608238,1.8227231368,-1.2165326598 N,0,0.543949722,2.0145767707,1.8557873413 C,0,0.9471103074,-2.7392075062,0.4839991468 N,0,0.7562305106,0.5837511209,-2.5429451078 C,0,0.0304956116,2.7807207011,2.9293791542 C,0,0.3805547021,-4.0039071548,0.434850791 C,0,0.3268065305,1.1216153593,-3.77965782 C,0,-1.359903104,0.8153745955,3.3530237263 C,0,-1.5406830035,-3.0987972695,-0.6909661388 C,0,-1.2134549542,2.4277300206,-2.4033313277 H,0,-1.1185185145,-0.8706906561,1.9936719403 H,0,-1.5188132405,-0.9838292729,-1.0454702062 H,0,-1.1534788111,2.0784584046,-0.2554240323 H,0,1.26203105,2.4878938054,1.321934659 H,0,1.9240283019,-2.6000920974,0.9331342852 H,0,1.5032557919,-0.0937630995,-2.6296978879 O,0,0.4529603288,3.9059872425,3.1261747335 H,0,0.9144920928,-4.8497527168,0.8491206508 O,0,0.8450325393,0.7446166536,-4.8153176348 H,0,-2.1193300605,0.3167671817,3.9448687133 H,0,-2.5090533458,-3.2388921091,-1.1547641562 H,0,-2.001327427,3.1685148174,-2.3263790313 H,0,-1.4008411063,2.6008874367,4.5263172172 H,0,-1.3001409338,-5.1735402118,-0.2017806107 H,0,-1.0836163611,2.5630808699,-4.5317384648
 **L-b**	P,0,1.3797121937,-0.0878288695,0.0257987431 C,0,0.5178679979,0.5370308392,-1.4931345464 C,0,0.7232222402,1.0407254328,1.3184745504 C,0,0.4278815858,-1.6303263998,0.3890894746 C,0,0.1470917002,1.8660735069,-1.6378648348 H,0,0.2449373966,2.5585250515,-0.8133468139 C,0,-0.3599672463,2.2786002668,-2.8659341859 H,0,-0.6567650648,3.3103834656,-3.0091891844 C,0,-0.4928931928,1.3777416093,-3.899502801 H,0,-0.8859374039,1.6540262268,-4.8671093089 C,0,1.6353886206,1.7828358726,2.0656446803 H,0,2.6967930495,1.6672094043,1.8782493056 C,0,-0.6429680393,1.1928335072,1.5695899656 H,0,-1.3610586665,0.6166702366,0.9972012116 C,0,-1.0812400574,2.0703831345,2.5462163261 C,0,1.194430917,2.6634133037,3.0448345958 H,0,1.9125072448,3.2341571624,3.6201510526 C,0,-0.1624888113,2.8071286669,3.2848199378 H,0,-0.5082740395,3.4920580605,4.0490587745 H,0,-2.1420314197,2.1810213186,2.7342070732 N,0,0.1597122782,-2.4610774656,-0.6491158462 H,0,0.3180710583,-2.101898424,-1.589431848 C,0,-0.4464092316,-3.7314789733,-0.5695439863

	O,0,-0.6781443565,-4.3515677825,-1.5977344847 C,0,0.1390206923,-2.0439853295,1.6617260295 H,0,0.3526610006,-1.4050542925,2.5056733417 C,0,-0.4430114523,-3.318482704,1.835770463 H,0,-0.6731925972,-3.6506799665,2.8422487649 C,0,-0.7221120734,-4.1355016919,0.783146616 H,0,-1.1696216387,-5.1097453394,0.9195653083 N,0,0.4111461129,-0.3461205858,-2.5020509812 C,0,-0.0995728696,0.0621636449,-3.655467787 O,0,-0.2371469462,-0.8432476349,-4.6366650998 H,0,0.0572264183,-1.695318152,-4.2848195064
 **L-b1**	P,0,-0.0769049993,1.0829638443,0.1332712978 C,0,-0.6776437053,0.1236983311,1.5971731291 C,0,-1.0340137878,0.3138388168,-1.2535650848 C,0,1.5714960724,0.309477536,-0.1440954288 C,0,-1.7304378684,-1.031630937,3.8524764825 C,0,-2.2874203089,-0.6088552748,-3.5089443909 C,0,4.1240256732,-0.7855874767,-0.4305558776 C,0,0.1190132846,-0.7257455534,2.3532626207 C,0,-2.1976533593,-0.427908015,-1.1157811417 C,0,1.7417156273,-0.9538459057,-0.7124278197 N,0,-1.946628748,0.4063476276,1.9430765159 N,0,-0.509475042,0.6085268159,-2.4541555799 C,0,2.6984386466,1.0159089664,0.2717764971 C,0,-2.4461207901,-0.1660670825,3.025946669 C,0,-1.1188609447,0.1521926403,-3.5349513679 C,0,3.9674199681,0.4700550203,0.1353783266 C,0,-0.4283273605,-1.3047227053,3.4941435694 C,0,-2.8211896828,-0.8916534111,-2.2703636164 C,0,3.0084796473,-1.4954500692,-0.8565488553 H,0,1.1372868722,-0.935812729,2.057632583 H,0,-2.6057967376,-0.6331219776,-0.1373872414 H,0,0.8750142556,-1.5166448956,-1.0405426485 O,0,-3.7251046485,0.1222369349,3.3393542518 O,0,-0.5652300756,0.4532086261,-4.7263547615 H,0,4.8338355982,1.0303823769,0.4645734841 H,0,0.1699463093,-1.9718744472,4.102941213 H,0,-3.7280882218,-1.4797475932,-2.1960556828 H,0,3.1271956067,-2.4765821789,-1.3001386434 H,0,-2.1955071228,-1.4561500007,4.7306901145 H,0,-2.7379058311,-0.9493155583,-4.4303072615 H,0,5.1135176455,-1.2109171473,-0.5442673287 H,0,-4.0217402724,0.7516323867,2.6667693062 H,0,0.2201747246,0.9797731853,-4.5203394851 H,0,2.5780848754,2.00310495,0.7040333552
 **L-b2**	P,0,0.283971468,1.3789682455,-0.1516510684 C,0,-1.3905073742,0.8410118548,-0.7267930484 C,0,0.3264489005,0.653553195,1.5408104936 C,0,1.3977447596,0.1954238736,-1.040310603 C,0,-3.8783447503,0.3136631498,-1.7573560919 C,0,0.2846799396,-0.3308547895,4.1534383888 C,0,3.3014074239,-1.3979359557,-2.2006405587 N,0,-1.638953653,1.1376462507,-2.0152745235 C,0,0.5125682436,-0.7071771804,1.7892050081 N,0,2.6313199373,0.167177001,-0.5103576813 C,0,-2.358396505,0.2868882326,0.1002460502 C,0,0.1255670042,1.5117028637,2.6202745332

	C,0,1.0578472475,-0.5416558721,-2.164776714 C,0,-3.6153401329,0.0245254238,-0.4361122756 C,0,0.0986281221,1.0226326423,3.9190902913 C,0,2.0347788565,-1.3480679335,-2.7411513129 C,0,-2.8385041357,0.8678344111,-2.5031433345 C,0,0.4942560487,-1.1945028739,3.0857409444 C,0,3.5395828613,-0.6104448468,-1.0743604558 H,0,-2.1369255547,0.0597425173,1.1335734364 H,0,-0.008569958,2.5723809486,2.4390104541 H,0,0.0624323168,-0.4840848526,-2.5792479249 H,0,-4.38981362,-0.4079873603,0.1858039152 H,0,-0.0600247663,1.7015252437,4.7479121493 H,0,1.7987697894,-1.9414751438,-3.6163707639 H,0,-4.8397858282,0.1295026413,-2.2150482814 H,0,0.2708333469,-0.7139863267,5.1663299882 H,0,4.0892861841,-2.0104383039,-2.6151861864 H,0,0.64099507,-2.2526818506,3.2652126663 O,0,4.766093062,-0.628333217,-0.5158720984 O,0,-3.0541937167,1.1601030875,-3.801295736 H,0,4.7161262442,-0.0213001443,0.2361833529 H,0,-2.2299940396,1.5554999446,-4.1188783276 H,0,0.6694747081,-1.3881862758,0.9602406147
 **L-b3**	P,0,1.3265893962,-0.1920703921,0.0505100088 C,0,0.547116639,0.493733924,-1.478461218 C,0,0.7486888259,0.9958361389,1.3370333068 C,0,0.1859917836,-1.6005673535,0.4062885629 C,0,-0.1254144749,1.7046243569,-1.5335398661 H,0,-0.2848763987,2.2912181442,-0.6397702209 C,0,-0.5960295344,2.13773585,-2.7707670859 H,0,-1.1257850723,3.0792201467,-2.8495586879 C,0,-0.3902334166,1.3698721949,-3.8950001119 H,0,-0.7361813283,1.6670399983,-4.8746992439 C,0,1.6572555678,1.9554063788,1.7836558825 H,0,2.6681401413,1.9570559139,1.391003994 C,0,-0.5444213181,0.9928453477,1.8631770352 H,0,-1.2612993827,0.2528295239,1.5239258282 C,0,-0.917620933,1.9316221829,2.8116014477 C,0,1.2784635862,2.9021798014,2.7241881478 H,0,1.9924172597,3.6435588658,3.0606606053 C,0,-0.0084130113,2.8893626935,3.2407520884 H,0,-0.3023326173,3.6212245227,3.9827423211 H,0,-1.9219364936,1.9168376013,3.2165619868 N,0,0.4394827935,-2.2505369784,1.5795509788 H,0,1.1893819228,-1.9288965346,2.1786591278 C,0,-0.2596189231,-3.3671171884,2.0934756998 O,0,0.0664837296,-3.8428102604,3.16798603 C,0,-0.8287889481,-2.056594198,-0.3842956944 H,0,-1.0478729081,-1.5678580939,-1.3203724192 C,0,-1.5748657527,-3.1786992972,0.0450670544 H,0,-2.3800972445,-3.5388144164,-0.5859207597 C,0,-1.3157269049,-3.8096062935,1.2204765729 H,0,-1.8859631303,-4.6670296854,1.5484930732 N,0,0.7672028638,-0.2608001232,-2.5676660144 C,0,0.2984769001,0.1670638911,-3.7284669451 O,0,0.5139509681,-0.6105336808,-4.8053489363 H,0,1.0124177155,-1.3747896812,-4.4827106488



L6D

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P,0,-5.224376534,0.1482336539,-0.2776108794
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C,0,-3.9175720012,-0.2780387115,0.9605469744
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C,0,-6.4323310111,-1.2228181959,-0.0670645532
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C,0,-4.4220382348,-0.3699959836,-1.8614674037
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H,0,5.1761331043,1.3960440727,-2.3027567858
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C,0,7.7515515001,0.8960883615,-0.2387948746
C,0,-7.7515515001,-0.8960883615,0.2387948746
H,0,8.0349328751,-0.1464063225,-0.3287366213
H,0,-8.0349328751,0.1464063225,0.3287366213
C,0,6.0764137883,2.5690764933,0.1819709096
C,0,-6.0764137883,-2.5690764933,-0.1819709096
H,0,5.0519979044,2.8350366436,0.4171737107
H,0,-5.0519979044,-2.8350366436,-0.4171737107
C,0,7.0225529202,3.5619380141,-0.0045795665
C,0,-7.0225529202,-3.5619380141,0.0045795665
C,0,8.7001050821,1.8930379046,-0.4273121416
C,0,-8.7001050821,-1.8930379046,0.4273121416
H,0,9.7226646357,1.6270620316,-0.6643460852
H,0,-9.7226646357,-1.6270620316,0.6643460852
C,0,8.3362377627,3.224627636,-0.3095311217
C,0,-8.3362377627,-3.224627636,0.3095311217
H,0,9.0746768875,4.003392158,-0.4547955792
H,0,-9.0746768875,-4.003392158,0.4547955792
H,0,6.7366587052,4.602581511,0.0863753923
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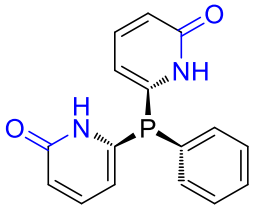
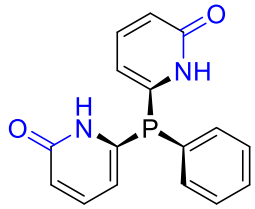
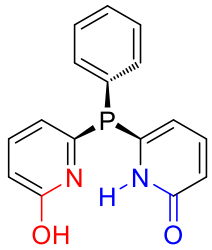
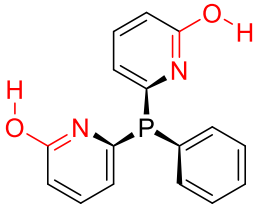
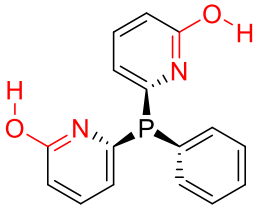
N,0,3.0917885402,0.1530947908,2.0269177542
N,0,-3.0917885402,-0.1530947908,-2.0269177542
H,0,2.5724484392,-0.169169887,1.1969658828
H,0,-2.5724484392,0.169169887,-1.1969658828
C,0,2.3755083712,0.3994570933,3.1950623544
C,0,-2.3755083712,-0.3994570933,-3.1950623544
O,0,1.1463615144,0.2264293116,3.2179257313
O,0,-1.1463615144,-0.2264293116,-3.2179257313
C,0,5.1589263833,0.8293845538,2.9239458777
C,0,-5.1589263833,-0.8293845538,-2.9239458777
H,0,6.2181676873,1.007830485,2.8090404531
H,0,-6.2181676873,-1.007830485,-2.8090404531
C,0,4.5080444625,1.0608732138,4.146660166
C,0,-4.5080444625,-1.0608732138,-4.146660166
H,0,5.0865589802,1.4201170341,4.9903421958
H,0,-5.0865589802,-1.4201170341,-4.9903421958
C,0,3.1677744791,0.8485268794,4.2926858293

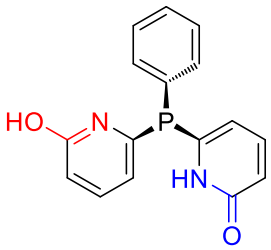
	C,0,-3.1677744791,-0.8485268794,-4.2926858293 H,0,2.6546361934,1.0299241292,5.2259113999 H,0,-2.6546361934,-1.0299241292,-5.2259113999 N,0,2.7232097525,-0.2728202108,-0.7007325991 N,0,-2.7232097525,0.2728202108,0.7007325991 C,0,1.7492545628,-0.1482754179,-1.6047275171 C,0,-1.7492545628,0.1482754179,1.6047275171 O,0,0.6055693476,-0.7310757371,-1.2837755681 O,0,-0.6055693476,0.7310757371,1.2837755681 H,0,-0.0749999648,-0.5298987647,-1.9769267977 H,0,0.0749999648,0.5298987647,1.9769267977

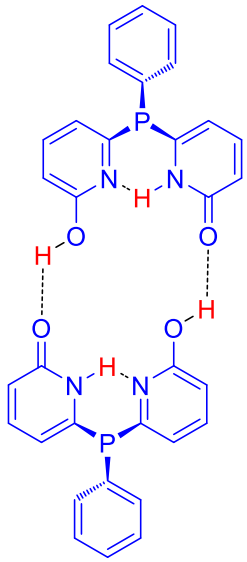
Supplementary Table 16. M06L/TZVP optimized Cartesian Coordinates in THF

	M06L-SCRF/TZVP in THF
 **L-a**	P,0,-1.4895014681,0.0010882126,-0.0509617867 C,0,-0.6701158054,-1.2577128386,1.032702597 C,0,-0.7305021166,1.5572365335,0.5673936671 C,0,-0.5568942447,-0.2862969026,-1.6228462669 C,0,0.3617133277,-3.3099967509,2.6033103994 C,0,0.2965525089,4.0087965737,1.4077696966 C,0,0.8586627663,-0.7236680826,-3.9762788079 N,0,-0.1071606324,-2.3621030718,0.4784532828 C,0,0.554047815,1.6358500493,1.1135033331 N,0,0.553347214,0.4369580523,-1.9259788328 C,0,-0.7363097108,-1.1623654507,2.396096686 C,0,-1.4920273623,2.72098575,0.4501474831 C,0,-0.9837787294,-1.2447611129,-2.5001427953 C,0,-0.1994992262,-2.2073392891,3.1741626372 C,0,-0.9789615209,3.9404168476,0.8670104485 C,0,-0.2428464274,-1.4649204785,-3.683217121 C,0,0.4390256199,-3.4556245884,1.1785837707 C,0,1.0619212854,2.8566227851,1.5302941201 C,0,1.3278082465,0.3101043366,-3.0934384515 H,0,-1.187121741,-0.2953264098,2.8576706922 H,0,-2.4924112496,2.6689746209,0.035448131 H,0,-1.879402021,-1.811410582,-2.2856627213 H,0,-0.2410035046,-2.1283814194,4.2547198541 H,0,-1.579585055,4.8366784633,0.7742075052 H,0,-0.5713802524,-2.2341610633,-4.3724908184 H,0,0.7695577722,-4.1134567499,3.2011237934 H,0,0.6951740273,4.9603131614,1.737361996 H,0,1.4214981711,-0.8798513953,-4.88637858 H,0,2.0586914352,2.907335175,1.9506312147 O,0,2.2951349643,1.0434968345,-3.2654336638 O,0,0.9179523823,-4.3964768138,0.5524288758 H,0,1.1560804599,0.7398293438,1.2165590298 H,0,0.8650311946,1.1557228036,-1.280846648

	H,0,-0.0511745224,-2.4317844434,-0.5332297206
 **L-a1**	P,0,1.0597703333,0.0122395084,0.0953269675 C,0,0.1410320369,0.7605706651,1.5075154337 C,0,0.2619636345,-1.6369463696,-0.0428543111 C,0,0.2574034746,0.9016152176,-1.3120546419 C,0,-0.9763107227,2.0698579975,3.6944938466 C,0,-0.8463840361,-4.1884161558,-0.1635736497 C,0,-0.7079414384,2.0990979526,-3.6329869041 C,0,-0.8090305791,0.1286192141,2.2565438203 C,0,-0.9866534227,-1.8340753451,-0.6341825326 C,0,-0.7123099096,1.8591967862,-1.2228722174 N,0,0.5287227539,2.0206577639,1.8613362316 C,0,0.9527087343,-2.7306144335,0.4792297872 N,0,0.7335192117,0.5610225384,-2.54443869 C,0,0.0223832519,2.7715091746,2.9357662076 C,0,0.3957034518,-3.9999504873,0.4255075131 C,0,0.3078854311,1.0928034353,-3.7738471364 C,0,-1.3636233747,0.8087860243,3.3636029652 C,0,-1.5348093772,-3.105758853,-0.6951728129 C,0,-1.1862286827,2.4580100578,-2.411325818 H,0,-1.1282038957,-0.8705431625,2.0014452219 H,0,-1.5338448964,-0.9911235052,-1.0418910954 H,0,-1.1192437262,2.1413992039,-0.2633646426 H,0,1.2459424399,2.4892274274,1.319264118 H,0,1.9287340347,-2.5859674374,0.9288042655 H,0,1.4595859559,-0.1429395089,-2.6179358481 O,0,0.4466855075,3.9040685152,3.1427769271 H,0,0.9370049351,-4.8429178269,0.8368778742 O,0,0.8073689776,0.6888949631,-4.8192794208 H,0,-2.1186403474,0.3080362653,3.9590822723 H,0,-2.503686675,-3.2513069143,-1.1569093767 H,0,-1.9559813387,3.2182262314,-2.3405367615 H,0,-1.3995619203,2.5894381206,4.5432492518 H,0,-1.2774057962,-5.1808023348,-0.2130256024 H,0,-1.0721045255,2.5572936717,-4.542302342
 **L-b**	P,0,1.3569853073,-0.0761941728,0.0116084657 C,0,0.5015890298,0.5433480118,-1.5093586607 C,0,0.7158486483,1.0454142018,1.3145081424 C,0,0.4142955141,-1.6234150806,0.3806819602 C,0,0.0986123328,1.8622117011,-1.650467294 H,0,0.171330629,2.555582299,-0.8240976242 C,0,-0.405067753,2.2678867709,-2.8826238292 H,0,-0.7286111367,3.2917870517,-3.0239720029 C,0,-0.4961636453,1.3699077264,-3.9235069045 H,0,-0.8802751776,1.6467904473,-4.8951120095 C,0,1.6386170098,1.7561094253,2.0792614298 H,0,2.6993388353,1.627075806,1.8962384223 C,0,-0.6495684545,1.216144629,1.558984928 H,0,-1.3763810743,0.6676575607,0.9701923437 C,0,-1.0774706019,2.0830466959,2.5502378959 C,0,1.2067820982,2.6252770795,3.0730715347 H,0,1.931852108,3.1721019411,3.6631008317 C,0,-0.1493114525,2.7883072725,3.3084735573 H,0,-0.4873138095,3.4647226372,4.0840468414 H,0,-2.1374161445,2.209995388,2.7338187145 N,0,0.1085496613,-2.4513009962,-0.650734365 H,0,0.261206173,-2.0975238993,-1.5964909434

	C,0,-0.4825164191,-3.7203991984,-0.5451966558 O,0,-0.7342680783,-4.3596107564,-1.5656222709 C,0,0.1629929893,-2.0377304475,1.6623858139 H,0,0.4067997525,-1.4006451435,2.4998548198 C,0,-0.4168588621,-3.3067636675,1.856413328 H,0,-0.6194812245,-3.6382934494,2.8689421821 C,0,-0.7272648446,-4.1229728109,0.8092553341 H,0,-1.1711672021,-5.0973249664,0.9616916208 N,0,0.4336813881,-0.3389043999,-2.5233829671 C,0,-0.0651271749,0.0661501544,-3.6833067913 O,0,-0.1479535909,-0.8350011088,-4.6762582101 H,0,0.1985705694,-1.672769602,-4.3320826377
 **L-b1**	P,0,-0.0526533425,1.0783537384,0.1239024189 C,0,-0.6736835321,0.1518224828,1.5982081913 C,0,-1.0171110594,0.2966272479,-1.2488086128 C,0,1.5934330828,0.2988332926,-0.1464473427 C,0,-1.7837955959,-0.9774034297,3.8343819009 C,0,-2.2707959819,-0.6596510576,-3.4882229004 C,0,4.1417868642,-0.8048546486,-0.4309329068 C,0,0.0778616514,-0.7486472499,2.3371909679 C,0,-2.0856728885,-0.5721068394,-1.09613964 C,0,1.7624265474,-0.9441861867,-0.7590218028 N,0,-1.9259622241,0.5000403837,1.9486151857 N,0,-0.581475613,0.6960144101,-2.4565763859 C,0,2.7181909667,0.9825842589,0.3143965152 C,0,-2.4557234531,-0.0619351589,3.023420666 C,0,-1.1895135286,0.2210878279,-3.5314617308 C,0,3.9848182586,0.4309646581,0.1792715818 C,0,-0.4983114792,-1.3141031431,3.4720663477 C,0,-2.7135715716,-1.05016466,-2.2436165746 C,0,3.0287006046,-1.4899478022,-0.9018194951 H,0,1.0837543521,-1.0092852142,2.0382995168 H,0,-2.4202558901,-0.8751186933,-0.1145104035 H,0,0.8990878449,-1.4913510439,-1.1216815951 O,0,-3.7155606845,0.2856962299,3.3464780999 O,0,-0.7305750401,0.6241216038,-4.7312500653 H,0,4.8495486021,0.9718867253,0.5440855761 H,0,0.0636599371,-2.020562245,4.0708712076 H,0,-3.5483713034,-1.7353178457,-2.1585913318 H,0,3.1473603102,-2.4551886429,-1.379376759 H,0,-2.2668428379,-1.3925751884,4.7079694347 H,0,-2.7296612947,-1.0096987076,-4.4024287973 H,0,5.1302214148,-1.2333877176,-0.543761219 H,0,-3.9992049809,0.9307729328,2.6800449863 H,0,0.0095677688,1.2244529784,-4.5511138303 H,0,2.599919396,1.9539418041,0.7822759963
 **L-b2**	P,0,0.2916389029,1.3732199309,-0.1270773748 C,0,-1.3835209612,0.8684323248,-0.7243592888 C,0,0.3257550058,0.6438815808,1.5632609724 C,0,1.3883416687,0.1812599349,-1.0226694276 C,0,-3.8455888736,0.3575700212,-1.8130347345 C,0,0.2792941718,-0.348548876,4.1721092302 C,0,3.2672598173,-1.4397005894,-2.1816881725 N,0,-1.6177343174,1.2298962858,-1.9997926723 C,0,0.5599800584,-0.7100381316,1.8101286465 N,0,2.6587613214,0.2463252537,-0.5870179108 C,0,-2.34944507,0.2583305587,0.0608337564

	C,0,0.0752439013,1.4929030646,2.6409341068 C,0,0.9979390973,-0.6679163008,-2.045565488 C,0,-3.596766407,0.005647247,-0.5048502808 C,0,0.0452698348,0.9984895595,3.937677928 C,0,1.9640517155,-1.4862433269,-2.6256231016 C,0,-2.8065779223,0.9661696509,-2.518222568 C,0,0.5390265607,-1.2010364064,3.1063456647 C,0,3.5561086042,-0.5473170956,-1.1487503087 H,0,-2.1391913317,-0.0186955801,1.0846199879 H,0,-0.0974518785,2.5486435501,2.4619842732 H,0,-0.0285286358,-0.6990169999,-2.3813551162 H,0,-4.3727686688,-0.4691838325,0.0832139541 H,0,-0.1530788628,1.6688008653,4.7651953298 H,0,1.690056873,-2.1655401226,-3.4237693676 H,0,-4.7999366147,0.180057166,-2.2890252458 H,0,0.2635296441,-0.7346130429,5.1840774197 H,0,4.0456211632,-2.0598064914,-2.6041635396 H,0,0.7227370723,-2.253639714,3.2855318 O,0,4.8198566441,-0.4751765096,-0.6901769034 O,0,-3.0147145977,1.3188970655,-3.800667954 H,0,4.8157449979,0.1926317003,0.0131533829 H,0,-2.1919434849,1.7316228749,-4.1063086409 H,0,0.7544880715,-1.3856370152,0.9842969432
 **L-b3**	P,0,1.3092847636,-0.1826531302,0.0625773566 C,0,0.5424554037,0.4946728536,-1.475171298 C,0,0.7434635665,1.0060993397,1.3501500431 C,0,0.1727420497,-1.596757487,0.4100366706 C,0,-0.149612099,1.6921996865,-1.5403964447 H,0,-0.3299842402,2.2803865222,-0.6513612314 C,0,-0.6121837338,2.1151215024,-2.7848346951 H,0,-1.1565071468,3.0473535868,-2.8728191103 C,0,-0.3796444402,1.3476502268,-3.9039106753 H,0,-0.7204031295,1.6407085946,-4.8871988387 C,0,1.6531217761,1.9751093373,1.7745017305 H,0,2.6563049916,1.9866609821,1.3624435039 C,0,-0.5399551611,0.99258619,1.899408058 H,0,-1.2599149306,0.2476233228,1.5778370389 C,0,-0.9037807387,1.9331097298,2.8506611267 C,0,1.28259709,2.9226607652,2.7180017695 H,0,1.9960679581,3.6726598933,3.0367432229 C,0,0.0051688371,2.9007003994,3.258944838 H,0,-0.2819374536,3.6344636598,4.00214025 H,0,-1.9013662371,1.9124321092,3.2723596904 N,0,0.4391860791,-2.2662756785,1.56910544 H,0,1.2026596298,-1.9509818821,2.1570531722 C,0,-0.2567026754,-3.3816562352,2.064529796 O,0,0.0776851735,-3.8846651424,3.1336839855 C,0,-0.8520204555,-2.0368185832,-0.3787641125 H,0,-1.0884226568,-1.5285888106,-1.3008040918 C,0,-1.5962131209,-3.161374825,0.0388128998 H,0,-2.4107038954,-3.5088184995,-0.5871466509 C,0,-1.3226903975,-3.8104464645,1.2033436401 H,0,-1.8944596036,-4.6711770535,1.5223207812 N,0,0.7907314037,-0.25969033,-2.5602825134 C,0,0.3280342147,0.1570429261,-3.7282663382 O,0,0.5685156424,-0.6163410928,-4.802190963 H,0,1.0730658366,-1.3804531131,-4.4822761509



L6D

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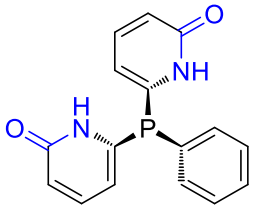
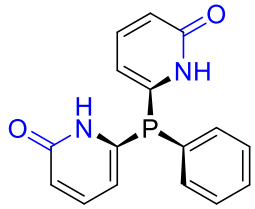
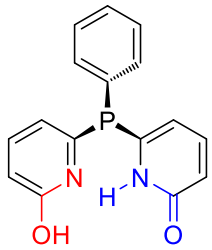
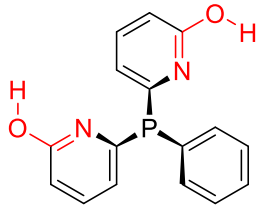
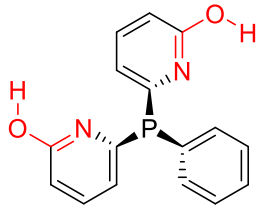
C,0,-8.7237555873,-1.872543235,0.4501498278
H,0,9.7394771565,1.5951460641,-0.7038248251
H,0,-9.7394771565,-1.5951460641,0.7038248251
C,0,8.37944599,3.2080694606,-0.3124381296
C,0,-8.37944599,-3.2080694606,0.3124381296
H,0,9.1266983094,3.9784477447,-0.4589492151
H,0,-9.1266983094,-3.9784477447,0.4589492151
H,0,6.804290926,4.6039453971,0.1212842213
H,0,-6.804290926,-4.6039453971,-0.1212842213
N,0,3.0986795876,0.2009527404,2.0299875766
N,0,-3.0986795876,-0.2009527404,-2.0299875766
H,0,2.5762738826,-0.1265337197,1.2074677711
H,0,-2.5762738826,0.1265337197,-1.2074677711
C,0,2.3876765772,0.4512873956,3.1969409713
C,0,-2.3876765772,-0.4512873956,-3.1969409713
O,0,1.1530517775,0.2831727162,3.2215899671
O,0,-1.1530517775,-0.2831727162,-3.2215899671
C,0,5.1755317727,0.8376099712,2.9325646631
C,0,-5.1755317727,-0.8376099712,-2.9325646631
H,0,6.2390868014,0.9941072071,2.8234305479
H,0,-6.2390868014,-0.9941072071,-2.8234305479
C,0,4.5259352227,1.0821910056,4.1524251657
C,0,-4.5259352227,-1.0821910056,-4.1524251657
H,0,5.1079439061,1.4316184301,4.9975894617
H,0,-5.1079439061,-1.4316184301,-4.9975894617
C,0,3.1803644944,0.8933665638,4.2936295091

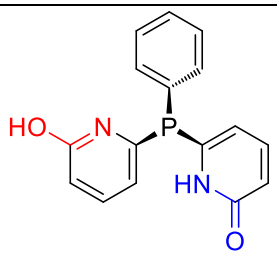
	C,0,-3.1803644944,-0.8933665638,-4.2936295091 H,0,2.6717404698,1.0841888648,5.2281719791 H,0,-2.6717404698,-1.0841888648,-5.2281719791 N,0,2.7436463328,-0.2938582898,-0.7214819065 N,0,-2.7436463328,0.2938582898,0.7214819065 C,0,1.7743179246,-0.165141063,-1.6287190146 C,0,-1.7743179246,0.165141063,1.6287190146 O,0,0.6413313026,-0.7901671153,-1.332908711 O,0,-0.6413313026,0.7901671153,1.332908711 H,0,-0.0498744686,-0.5791688069,-2.0148760652 H,0,0.0498744686,0.5791688069,2.0148760652

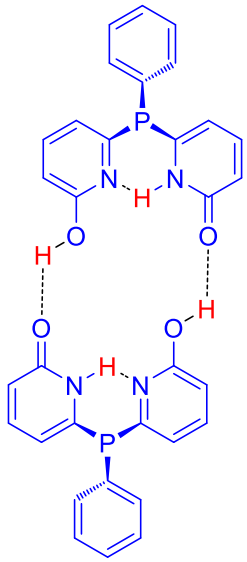
Supplementary Table 17. M06L/TZVP optimized Cartesian Coordinates in toluene.

	M06L-SCRF/TZVP in toluene
 **L-a**	P,0,-1.4915631564,-0.0020982304,-0.0418852146 C,0,-0.6649908197,-1.2598850233,1.0376439834 C,0,-0.7358317399,1.5578140072,0.5723418907 C,0,-0.5560934355,-0.282687855,-1.6137052143 C,0,0.357795041,-3.3276989536,2.5974747251 C,0,0.291257497,4.017693432,1.3888742191 C,0,0.8677432122,-0.7175028357,-3.9653969159 N,0,-0.1261058422,-2.3731968091,0.477129876 C,0,0.5498085947,1.6429583725,1.1150633453 N,0,0.5542203423,0.4410075023,-1.9130961713 C,0,-0.7109301787,-1.1630179235,2.401169371 C,0,-1.4980423243,2.7202081629,0.4474468849 C,0,-0.9793098078,-1.2402462248,-2.4937826969 C,0,-0.1782860779,-2.216545839,3.1730442213 C,0,-0.9852635421,3.9434035637,0.8523819181 C,0,-0.2332134403,-1.4590456436,-3.6753117037 C,0,0.4140348518,-3.4784897892,1.1705448141 C,0,1.0575689495,2.8675511414,1.5200448805 C,0,1.3342931838,0.3192416731,-3.0822176771 H,0,-1.1430168793,-0.2897441451,2.8684852024 H,0,-2.4991906974,2.6630198934,0.0354037728 H,0,-1.8786533105,-1.8033817249,-2.2856950397 H,0,-0.2038319655,-2.1355046511,4.2539772085 H,0,-1.5863168763,4.8384593914,0.7525179231 H,0,-0.5583437855,-2.229032778,-4.3653419995 H,0,0.7620703282,-4.136867775,3.1893006047 H,0,0.6904141144,4.9724426574,1.7077360342 H,0,1.4347612274,-0.8725820913,-4.8726544049 H,0,2.0553971015,2.9230522928,1.9368450003 O,0,2.2968444832,1.0539727948,-3.2480490538 O,0,0.8688227009,-4.4223816252,0.5382908646 H,0,1.151137764,0.7476113127,1.2272340353 H,0,0.8640261041,1.1602694065,-1.2685296603

	H,0,-0.0786880167,-2.4440235861,-0.5346120235
 **L-a1**	P,0,1.0560289831,0.0153859884,0.0977415175 C,0,0.1375915365,0.7610229419,1.5112006469 C,0,0.2627851137,-1.6361699008,-0.0426641411 C,0,0.2523159666,0.9029688864,-1.3094761537 C,0,-0.9804230431,2.071840886,3.6999456292 C,0,-0.8370662712,-4.1907817689,-0.1693594863 C,0,-0.7097258788,2.0972902333,-3.6359809401 C,0,-0.8180064076,0.1333206845,2.2558072132 C,0,-0.9851896281,-1.836459862,-0.6341890073 C,0,-0.7062749499,1.8712419289,-1.2233455459 N,0,0.529464993,2.0189880075,1.8690284395 C,0,0.9569930247,-2.7292318601,0.4759874983 N,0,0.7193937547,0.5495698604,-2.5418369992 C,0,0.024559196,2.7736340091,2.9464815271 C,0,0.4042818264,-3.9998886288,0.4195468975 C,0,0.2953381462,1.0777563313,-3.7775359719 C,0,-1.3719288431,0.8144549582,3.3640253055 C,0,-1.5289768571,-3.1094937967,-0.6981532185 C,0,-1.1778513767,2.468270466,-2.4152410292 H,0,-1.1411824208,-0.8632633615,1.9962039469 H,0,-1.5336284477,-0.9938579694,-1.0407234126 H,0,-1.1052345729,2.1638804829,-0.2637258083 H,0,1.2537194381,2.4861273627,1.3364005905 H,0,1.9331521135,-2.5821152798,0.9244113575 H,0,1.4376316494,-0.1612539517,-2.6169731181 O,0,0.4541066848,3.8998628848,3.1541756331 H,0,0.9484281968,-4.8422195989,0.8280979178 O,0,0.7860073894,0.6608604785,-4.8173857513 H,0,-2.1306262366,0.3155421972,3.9563885884 H,0,-2.4967983172,-3.2574464162,-1.1610198222 H,0,-1.9378173558,3.2383830043,-2.3456992532 H,0,-1.4016127677,2.5918802258,4.54904419 H,0,-1.2643838391,-5.1844705113,-0.2217359049 H,0,-1.0706212995,2.5535794881,-4.5471724349
 **L-b**	P,0,1.3564435174,-0.0737787173,0.0131920341 C,0,0.4995351646,0.5446572163,-1.509002831 C,0,0.7098127429,1.0495114295,1.3137929405 C,0,0.4178897318,-1.6225866945,0.3847284412 C,0,0.1285455022,1.8721994652,-1.6606987614 H,0,0.2231039807,2.5700624952,-0.8403402271 C,0,-0.3722129249,2.2792336748,-2.8932024265 H,0,-0.6701943624,3.3098755332,-3.0419169991 C,0,-0.4940296494,1.3746701825,-3.9248238008 H,0,-0.8784040956,1.6500157304,-4.8965214619 C,0,1.6307716244,1.7520799358,2.088228946 H,0,2.6916716088,1.6167297314,1.9110298434 C,0,-0.6559021128,1.2272150071,1.551169768 H,0,-1.3815399648,0.6835987696,0.9566877642 C,0,-1.0852838398,2.092399955,2.5429248026 C,0,1.1977919058,2.6191239571,3.0829417382 H,0,1.9219140312,3.1589768968,3.6803443784 C,0,-0.1584791429,2.7890712719,3.3099835206 H,0,-0.4977134252,3.4638009874,4.0863578555 H,0,-2.145570312,2.2240132128,2.7205480413 N,0,0.130053532,-2.4546726522,-0.6477404352 H,0,0.2784998452,-2.0964779005,-1.5915607666

	C,0,-0.454510738,-3.7293656914,-0.5500750088 O,0,-0.6938865788,-4.3645003608,-1.5723584523 C,0,0.1579702797,-2.0372990581,1.6639716837 H,0,0.3868452677,-1.396997252,2.5030389247 C,0,-0.4121633263,-3.3128798671,1.8523484791 H,0,-0.6208246602,-3.6455282112,2.8633374861 C,0,-0.7054853616,-4.1330695388,0.8046531642 H,0,-1.1418222811,-5.1111655994,0.952592596 N,0,0.4014620837,-0.3435158572,-2.5148138537 C,0,-0.0964407684,0.0619097587,-3.6748113069 O,0,-0.213843523,-0.8450599833,-4.6570509342 H,0,0.100831649,-1.6915807273,-4.3064001427 HF=-1219.0325556 ZPE= 0.258893 NImag=0 Htot= -1218.755036 Gtot= -1218.821567
 **L-b1**	P,0,-0.0700403309,1.0673043332,0.1351251176 C,0,-0.6767283612,0.1216282542,1.60418471 C,0,-1.0323662599,0.3010303049,-1.2489427307 C,0,1.580429711,0.300553723,-0.1447989668 C,0,-1.750909829,-1.0161762589,3.8561516629 C,0,-2.2868403345,-0.6166835885,-3.5051301227 C,0,4.1376777702,-0.7785287632,-0.4443152653 C,0,0.1050334859,-0.740934455,2.3591264092 C,0,-2.1827229236,-0.4600103543,-1.1109327401 C,0,1.7560637693,-0.9542009862,-0.730681366 N,0,-1.9413269515,0.425935441,1.9480982272 N,0,-0.5201926769,0.6156095065,-2.4503046497 C,0,2.7037078276,1.0073887021,0.2817733928 C,0,-2.4525288522,-0.138279652,3.0300713906 C,0,-1.1296283859,0.1617387071,-3.5324345975 C,0,3.9749878648,0.4686692111,0.1390428563 C,0,-0.4532312239,-1.3109501093,3.4997005903 C,0,-2.8077696548,-0.9206156823,-2.2662873708 C,0,3.0259007939,-1.4877528803,-0.8810477258 H,0,1.1204520818,-0.9682043629,2.0657659016 H,0,-2.5813706333,-0.6863031722,-0.1329211383 H,0,0.893385831,-1.5179267851,-1.0679490062 O,0,-3.7254649307,0.1697638524,3.3422656609 O,0,-0.5897856357,0.48235079,-4.723379993 H,0,4.838658469,1.0285233993,0.4765913563 H,0,0.1330228237,-1.9880389472,4.1091958005 H,0,-3.7051396637,-1.523138338,-2.19218775 H,0,3.1492068722,-2.462189552,-1.338226098 H,0,-2.2216230244,-1.434699934,4.734601081 H,0,-2.7410063038,-0.9555798026,-4.4256376463 H,0,5.1293774983,-1.1976086358,-0.5633190383 H,0,-4.0191588565,0.8016019307,2.6688212557 H,0,0.1919142808,1.0191500676,-4.5237473854 H,0,2.5796110529,1.9882891368,0.7274453779
	P,0,0.2777807398,1.3648301395,-0.1440449914 C,0,-1.397814484,0.8410433621,-0.7258843967 C,0,0.3246902411,0.6452546826,1.5501590635 C,0,1.3897545185,0.1845682724,-1.0381302902 C,0,-3.8775436767,0.3284841243,-1.7785223521 C,0,0.2996117932,-0.327369062,4.166840487 C,0,3.2957025605,-1.404262133,-2.1997093851

L-b2	N,0,-1.6382323199,1.1579351238,-2.0111348969 C,0,0.5299726492,-0.7119636064,1.8037975219 N,0,2.6297848862,0.1746089927,-0.5216251492 C,0,-2.3683555045,0.2734644464,0.0871388963 C,0,0.1136006693,1.5065869816,2.6257434205 C,0,1.0441625381,-0.5703055233,-2.1482122875 C,0,-3.6224767289,0.0190479859,-0.4605282431 C,0,0.0945734736,1.0226350949,3.9265783921 C,0,2.0227750027,-1.3739911241,-2.7262191525 C,0,-2.8346272535,0.8951497047,-2.511049617 C,0,0.519737183,-1.1932129503,3.1030543157 C,0,3.5400582,-0.6010039419,-1.085755713 H,0,-2.153958957,0.030487734,1.1185376384 H,0,-0.0350780562,2.5648433747,2.4408723819 H,0,0.0430862588,-0.5326245728,-2.5520209968 H,0,-4.4004524675,-0.4232612912,0.1499991739 H,0,-0.0722516002,1.7032900603,4.7525207643 H,0,1.7828533921,-1.9808306671,-3.5910778852 H,0,-4.8375328023,0.1498410613,-2.2421104118 H,0,0.2924478605,-0.7059453533,5.1816738984 H,0,4.0832598404,-2.0152083056,-2.6179793291 H,0,0.6812845134,-2.248584927,3.2869991494 O,0,4.7717460728,-0.6006675912,-0.5421401375 O,0,-3.0435499071,1.2061607312,-3.8042416388 H,0,4.7308117667,0.0141998718,0.2057392791 H,0,-2.2177890673,1.6036575723,-4.1190716537 H,0,0.695426165,-1.3961896671,0.9790494451
 **L-b3**	P,0,1.2981789121,-0.1864399027,0.0372380345 C,0,0.5179261491,0.5035399541,-1.4889631406 C,0,0.7431061987,0.996974783,1.3358973563 C,0,0.1701123851,-1.6032582399,0.3999789938 C,0,-0.1375115471,1.7229562471,-1.5457843007 H,0,-0.2903925075,2.3143109672,-0.6538836669 C,0,-0.5980121606,2.1624492403,-2.7846168053 H,0,-1.1132335187,3.111790529,-2.8651251417 C,0,-0.3992635924,1.3919937409,-3.908303148 H,0,-0.7378359332,1.6972883172,-4.8883833879 C,0,1.6690616536,1.9368663121,1.788995656 H,0,2.6777308718,1.9295712513,1.3906051249 C,0,-0.5476739143,1.0059126881,1.8687810505 H,0,-1.2792728739,0.2824320431,1.5253475595 C,0,-0.9013350199,1.9379716076,2.831277944 C,0,1.3091325478,2.8766839572,2.7440081587 H,0,2.0359326741,3.6031300382,3.0859444404 C,0,0.0250287277,2.8760514158,3.2677534259 H,0,-0.2539944481,3.6026475821,4.0208360319 H,0,-1.9040445009,1.9334475611,3.2407988524 N,0,0.3776488395,-2.193337622,1.6131544938 H,0,1.0797848136,-1.812561045,2.2366328703 C,0,-0.308729252,-3.3092323611,2.1302029137 O,0,-0.030648283,-3.7305948856,3.2456978597 C,0,-0.779164552,-2.1307340202,-0.4276847279 H,0,-0.9589863336,-1.6919124227,-1.3964229218 C,0,-1.5093219923,-3.2587070244,0.007660933 H,0,-2.2641457573,-3.6749815241,-0.6504383399 C,0,-1.2957178611,-3.8289078895,1.2239010113 H,0,-1.8558257485,-4.6919551723,1.5559219456

	N,0,0.7300475686,-0.2544456643,-2.5779299254 C,0,0.2710757837,0.1792802762,-3.7407711531 O,0,0.4780209602,-0.6010829764,-4.8160565885 H,0,0.9669040112,-1.3746044615,-4.4970395085
 **L6D**	P,0,5.224376534,-0.1482336539,0.2776108794 P,0,-5.224376534,0.1482336539,-0.2776108794 C,0,3.9175720012,0.2780387115,-0.9605469744 C,0,-3.9175720012,-0.2780387115,0.9605469744 C,0,6.4323310111,1.2228181959,0.0670645532 C,0,-6.4323310111,-1.2228181959,-0.0670645532 C,0,4.4220382348,0.3699959836,1.8614674037 C,0,-4.4220382348,-0.3699959836,-1.8614674037 C,0,4.1986092007,0.9679827406,-2.1287323411 C,0,-4.1986092007,-0.9679827406,2.1287323411 H,0,5.1761331043,1.3960440727,-2.3027567858 H,0,-5.1761331043,-1.3960440727,2.3027567858 C,0,3.1731132338,1.0934739074,-3.062427178 C,0,-3.1731132338,-1.0934739074,3.062427178 H,0,3.3472605192,1.6283354043,-3.9886967078 H,0,-3.3472605192,-1.6283354043,3.9886967078 C,0,1.939934051,0.5358357984,-2.8169694356 C,0,-1.939934051,-0.5358357984,2.8169694356 H,0,1.1232249079,0.6048018909,-3.5229354855 H,0,-1.1232249079,-0.6048018909,3.5229354855 C,0,7.7515515001,0.8960883615,-0.2387948746 C,0,-7.7515515001,-0.8960883615,0.2387948746 H,0,8.0349328751,-0.1464063225,-0.3287366213 H,0,-8.0349328751,0.1464063225,0.3287366213 C,0,6.0764137883,2.5690764933,0.1819709096 C,0,-6.0764137883,-2.5690764933,-0.1819709096 H,0,5.0519979044,2.8350366436,0.4171737107 H,0,-5.0519979044,-2.8350366436,-0.4171737107 C,0,7.0225529202,3.5619380141,-0.0045795665 C,0,-7.0225529202,-3.5619380141,0.0045795665 C,0,8.7001050821,1.8930379046,-0.4273121416 C,0,-8.7001050821,-1.8930379046,0.4273121416 H,0,9.7226646357,1.6270620316,-0.6643460852 H,0,-9.7226646357,-1.6270620316,0.6643460852 C,0,8.3362377627,3.224627636,-0.3095311217 C,0,-8.3362377627,-3.224627636,0.3095311217 H,0,9.0746768875,4.003392158,-0.4547955792 H,0,-9.0746768875,-4.003392158,0.4547955792 H,0,6.7366587052,4.602581511,0.0863753923 H,0,-6.7366587052,-4.602581511,-0.0863753923 N,0,3.0917885402,0.1530947908,2.0269177542 N,0,-3.0917885402,-0.1530947908,-2.0269177542 H,0,2.5724484392,-0.169169887,1.1969658828 H,0,-2.5724484392,0.169169887,-1.1969658828 C,0,2.3755083712,0.3994570933,3.1950623544 C,0,-2.3755083712,-0.3994570933,-3.1950623544 O,0,1.1463615144,0.2264293116,3.2179257313 O,0,-1.1463615144,-0.2264293116,-3.2179257313 C,0,5.1589263833,0.8293845538,2.9239458777 C,0,-5.1589263833,-0.8293845538,-2.9239458777 H,0,6.2181676873,1.007830485,2.8090404531 H,0,-6.2181676873,-1.007830485,-2.8090404531 C,0,4.5080444625,1.0608732138,4.146660166

	C,0,-4.5080444625,-1.0608732138,-4.146660166 H,0,5.0865589802,1.4201170341,4.9903421958 H,0,-5.0865589802,-1.4201170341,-4.9903421958 C,0,3.1677744791,0.8485268794,4.2926858293 C,0,-3.1677744791,-0.8485268794,-4.2926858293 H,0,2.6546361934,1.0299241292,5.2259113999 H,0,-2.6546361934,-1.0299241292,-5.2259113999 N,0,2.7232097525,-0.2728202108,-0.7007325991 N,0,-2.7232097525,0.2728202108,0.7007325991 C,0,1.7492545628,-0.1482754179,-1.6047275171 C,0,-1.7492545628,0.1482754179,1.6047275171 O,0,0.6055693476,-0.7310757371,-1.2837755681 O,0,-0.6055693476,0.7310757371,1.2837755681 H,0,-0.0749999648,-0.5298987647,-1.9769267977 H,0,0.0749999648,0.5298987647,1.9769267977

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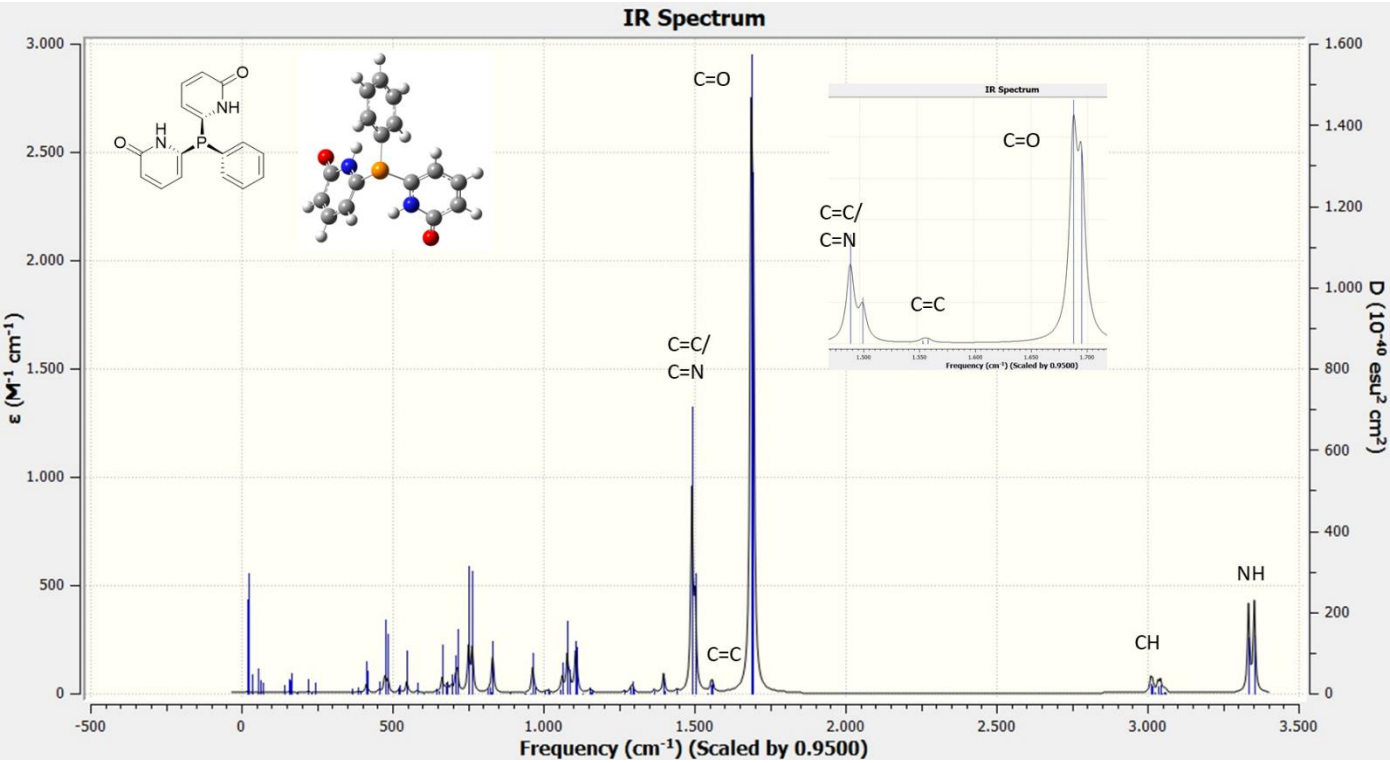
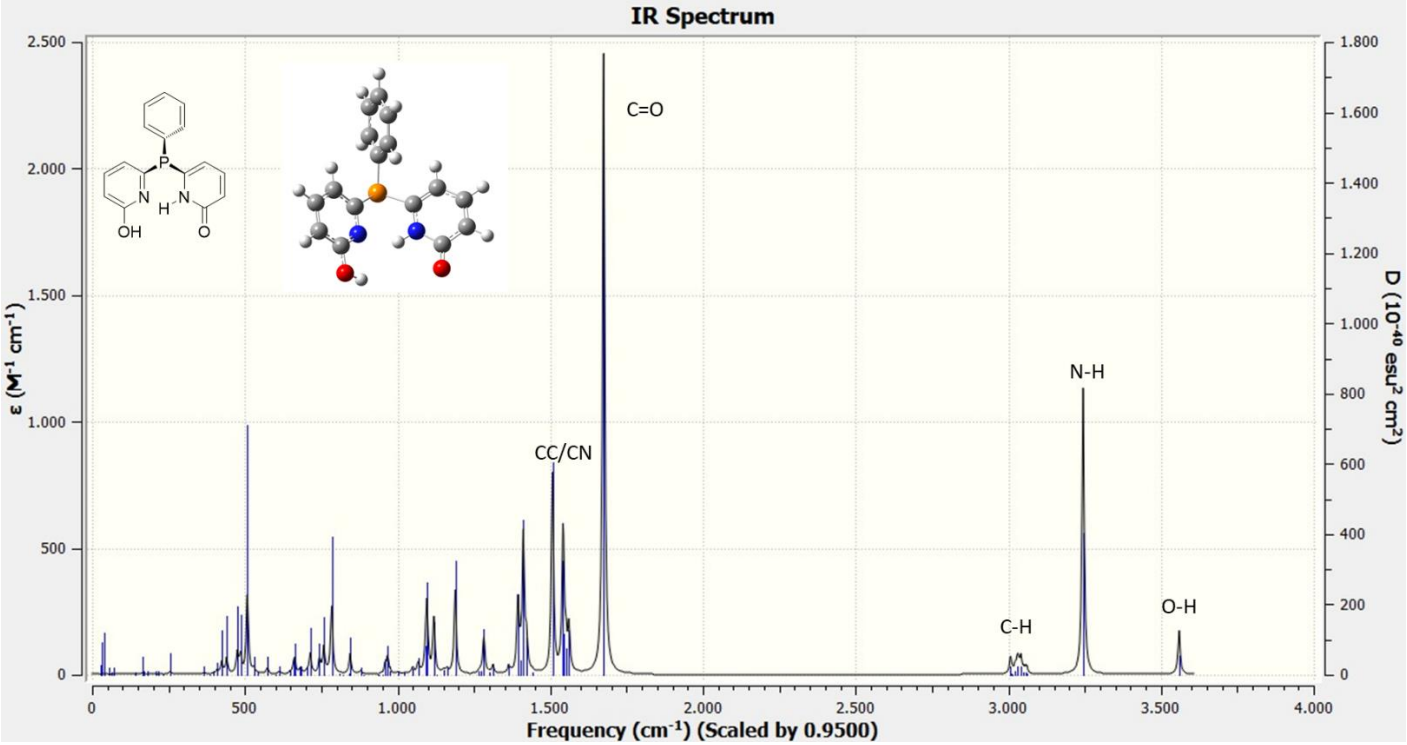
[4] Frisch, M. J. *et al.* Gaussian 16, Revision A.03. *Gaussian Inc. Gaussian, Inc., Wallingford CT, 2016*

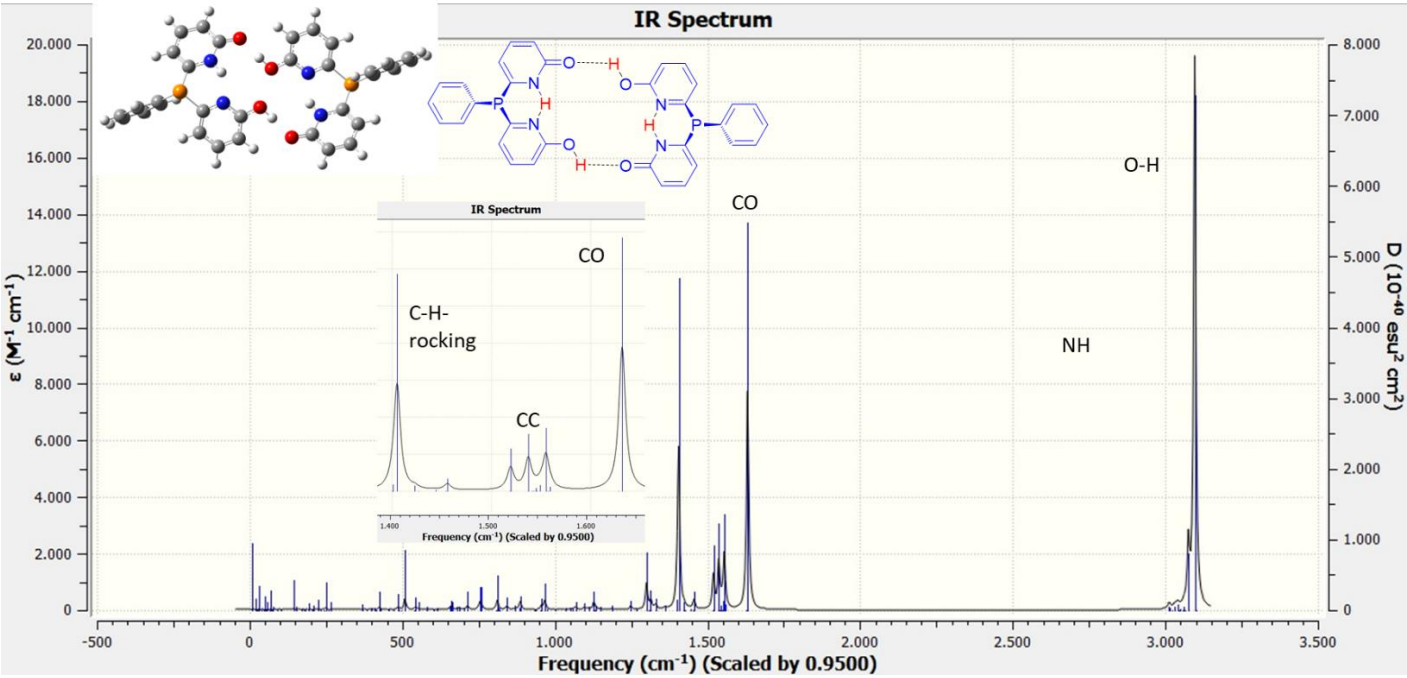
b) IR data



Supplementary Figure 36. Computed IR spectrum for **L6-a**



Supplementary Figure 37. Computed IR spectrum for **L6-b**

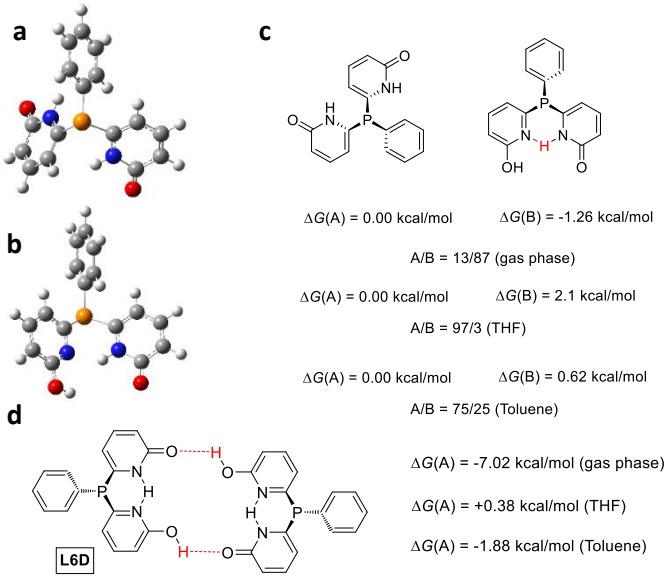


Supplementary Figure 38. Computed IR spectrum of the M06L/TZVP optimized **L6D** dimer structure via N-H and O-H hydrogen bonding

We investigated the structure of the **L6**-**L6** dimer (**L6D**). For this purpose, IR spectroscopy is a powerful tool as it allows for the determination of hydrogen-bonding moieties. In general, upon hydrogen bonding N-H or O-H bonds will display a "*red shift*" or *"bond lengthening"*,[1] and a broadening of their signals.[2] Indeed, this was proven for the 6-DPPON dimer by Breit et al.[3] In agreement with those results, the ATR IR spectrum of **L6** at room temperature showed broad peaks for the stretching of the bond of the donating group O-H ($\nu_{O\text{-}H}$ = 2765 cm^{-1}) and of the accepting C=O group ($\nu_{C=O}$ = 1641 cm^{-1}) as well as the stretching of the accepting group C=N ($\nu_{N=H}$ = 1582 cm^{-1}).[4-6] Notably, no $\nu_{N\text{-}H}$ peak is observed, which was rationalized by DFT calculations for 6-DPPON.[3] To confirm the

structural hypothesis of the **L6**-**L6** dimer, we performed similar DFT studies. Surprisingly, calculations on the free ligand showed an equilibrium of two tautomers L6-a and L6-b, the latter being intramolecularly hydrogen-bonded via its nitrogen atoms (N···H-N). Interestingly, both the tautomerization and the dimerization energy are very dependent on the solvent choice (Supplementary Figure 39c-d). While a transition from L6-bto L6-a is energetically disfavored in solution (endergonic by 2.1 and 0.62 kcal/mol in THF and toluene, respectively), the formation of the dimer L6Doccurs spontaneously in toluene according to calculations (exergonic by 1.88 kcal/mol in toluene). In general, the calculations agree with the observed yields, namely a more energetically favored formation of the catalytically active ligand dimer in toluene than THF leads to better yields and regioselectivities. (Supplementary Table 9, entries 1, 3). Furthermore, the IR vibrational profiles of **L6-a**, **L6-b** and **L6D** were calculated using M06L/TZVP and compared to their experimental counterparts. As usual, DFT obtained vibrations were scaled by a factor of 0,9500.[7, 8] By comparison, in solid-state **L6** exists mainly as the **L6D** dimer. Calculated $\nu_{C=O}$ fit very well to the experimental data, and the lowering of its wavelength provides a strong proof for C=O···H-X hydrogen bonds. Similar lowering of $\nu_{C=N}$ to values close to the experimental ones, confirmed the presence of C=N···H-X hydrogen bonds, too. Moreover, the absence of a non-hydrogen-bonding C=O stretching vibration at ~1700 cm^{-1} and of "free" N-H stretching vibrations at ~3500 cm^{-1} disproved the existence of a hypothetical **L6D2** species.[3] Finally, we could explain the virtual lack of a N-H stretching vibration in the investigated samples as calculations for **L6D** situated it at the same wavelength as the broad O-H stretching vibration, most likely resulting in a coalescence of the two peaks.

It is important to note that the [Rh(**L6D**)(CO)Cl] ATR-IR spectrum showed similar vibrations as the free dimer, except for a strong shift of the ν_{CO} band all the way to 1992 cm^{-1} testifying for stronger π-accepting properties than Xantphos (1978 cm^{-1}) and PPh_3 (1968 cm^{-1}), but weaker than 6-DPPON (2003 cm^{-1}).[9]



Supplementary Figure 39. Computed IR spectrum of the M06L/TZVP optimized **L6D** dimer structure via N-H and O-H hydrogen bonding **a)** Calculated 3D structures for **L6-a. b)** Calculated 3D structure for **L6-b. c)** Calculated ΔG and equilibrium between **L6-a** and **L-6b** in gas-phase, THF and toluene. **d)** Calculated dimer **L6D** structure and dimerization energy in gas-phase, THF and toluene.

	Exp.	L6-a[b]	L6-b[b]	L6D[b]
N-H bending	1582/1540[a]			
C=O stretching	**1641[a]**	**1706/1700[a]**	**1690[a]**	**1639[a]**
C=N stretching	1250/1315[a]	*1500[a]*	*1520[a]*	*1305[a]*
N-H stretching	2600-	3485/3499[a]	*3250[a]*	3075[a]
O-H stretching	3150[a]		3613[a]	3095[a]

Supplementary Table 18. Calculated and experimental vibrations. [a] Vibrations are given in cm^{-1}. [b] DFT calculations were ran with M06L/TZVP and scaled by a factor of 0,9500. [7, 8]

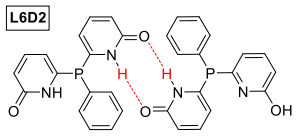
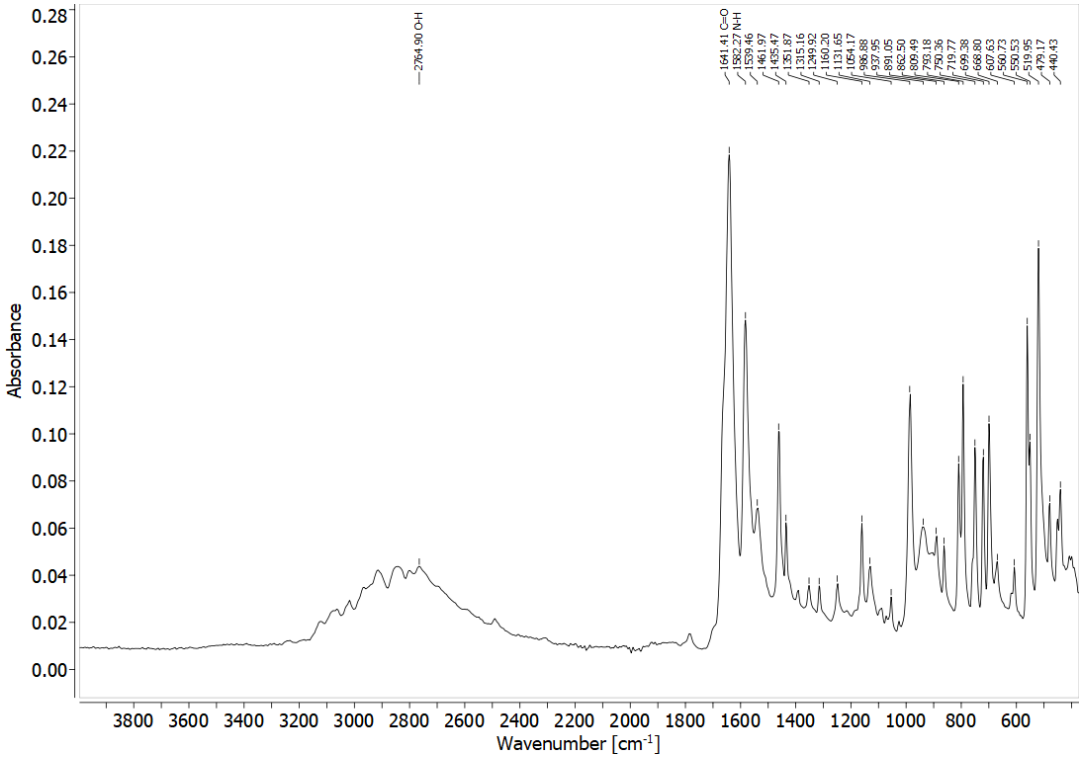
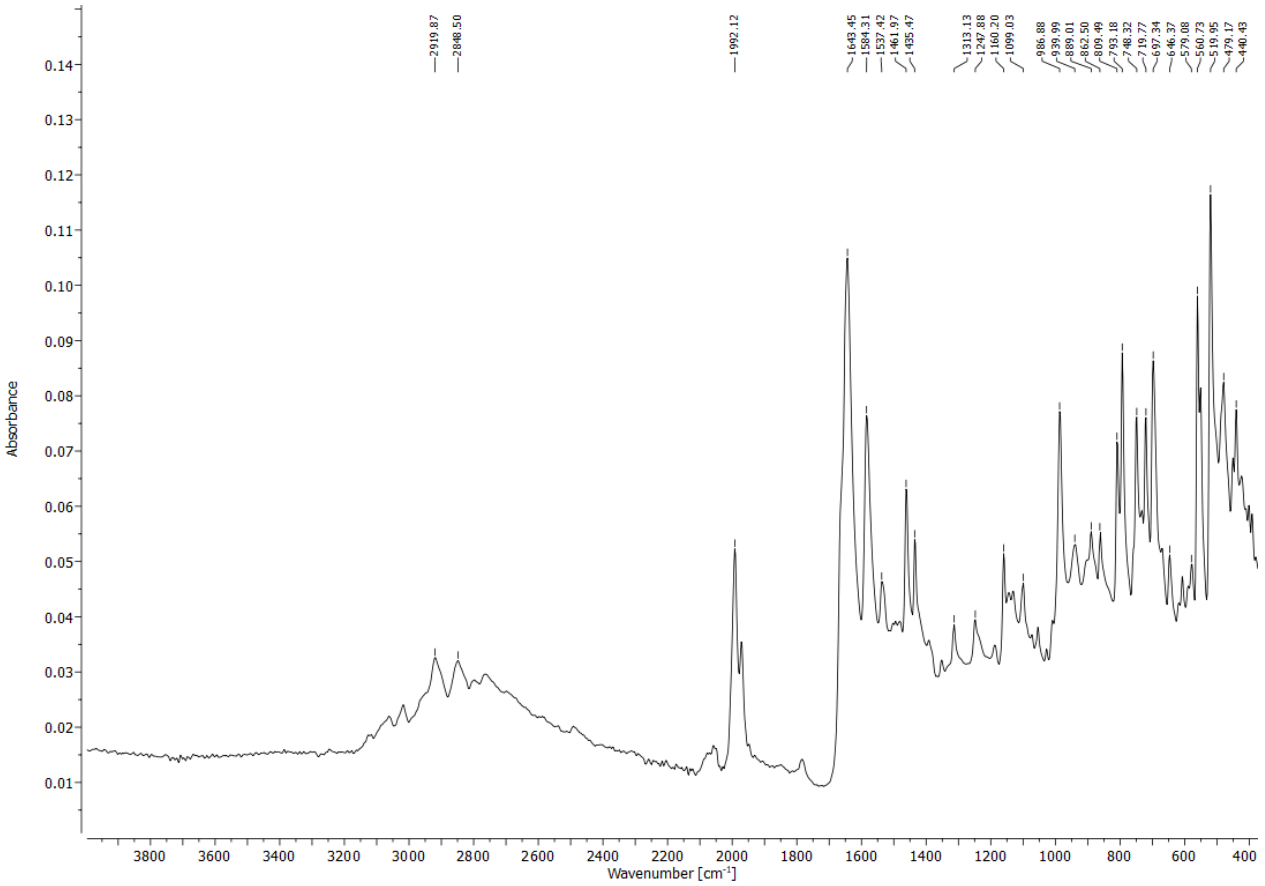


Figure 40. Hypothetical structure of the **L6D2** dimer.



Supplementary Figure 41. ATR IR spectrum of **L6**, at room temperature.



Supplementary Figure 42. ATR IR spectrum of the [Rh(**L6D**)(CO)Cl]

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2. A. A. Howard, G. S. Tschumper and N. I. Hammer, *J Phys Chem A*, 2010, **114**, 6803-6810.
3. U. Gellrich, J. Huang, W. Seiche, M. Keller, M. Meuwly and B. Breit, *J Am Chem Soc*, 2011, **133**, 964-975.
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5. H. I. Abdulla and M. F. El-Bermani, *Spectrochim Acta A*, 2001, **57**, 2659-2671.
6. M. Chevrier, O. Bensaude, J. Guillerez and J. E. Dubois, *Tetrahedron Lett*, 1980, **21**, 3359-3362.
7. J. L. B. S. Kanchanakungwankul, J. Zheng, I. M. Alecu, B. J. Lynch, Y. Zhao, and D. G. Truhlar, Database of Frequency Scale Factors for Electronic Model Chemistries, https://comp.chem.umn.edu/freqscale/210722_Database_of_Freq_Scale_Factors_v5.pdf, (accessed 17/08/2023, 2023).
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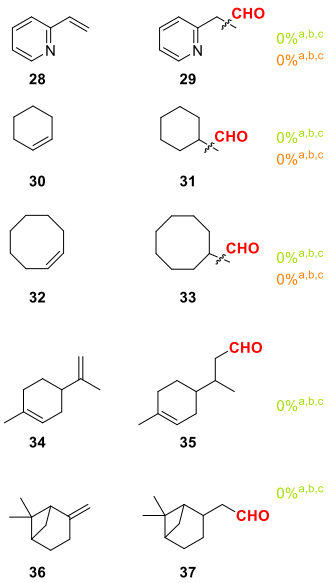
9. F. Bauer, N. Dierenbach and B. Breit, *Asian J Org Chem*, 2023.

SI-I: Addendum to the scope : unreacted olefins



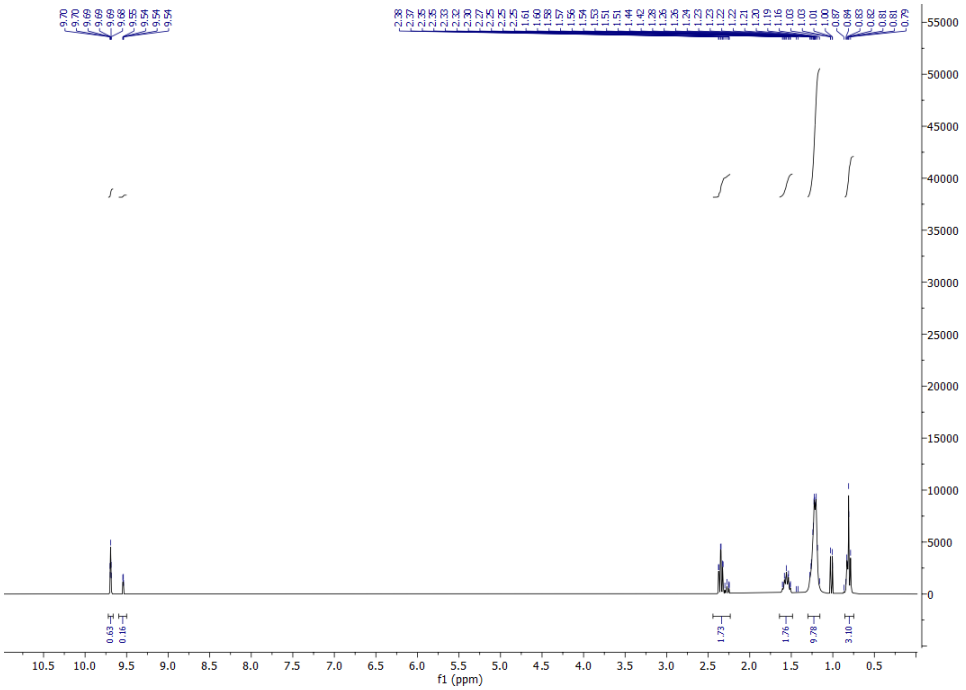
Supplementary Table 18. Rh/**L6**-catalysed hydroformylation of diverse olefins. All shown yields are isolated yields. The regioselectivity is determined by NMR. Displayed in green are the results of the Rh/**L6** system, in orange the ones obtained applying Rh/**L1** (6-DPPON).

Conditions: olefin (6.0 mmol), [$Rh(CO)_2acac$] (0.014 mol%), monodentate ligand (0.071 mol%), $CO:H_2$ (10 bar, 1:1), toluene (4.3 mL), 120 °C, 4 h. [a] $CO:H_2$ (30 bar, 1:1) [b] monodentate ligand (0.142 mol%) [c] monodentate ligand (0.284 mol%).

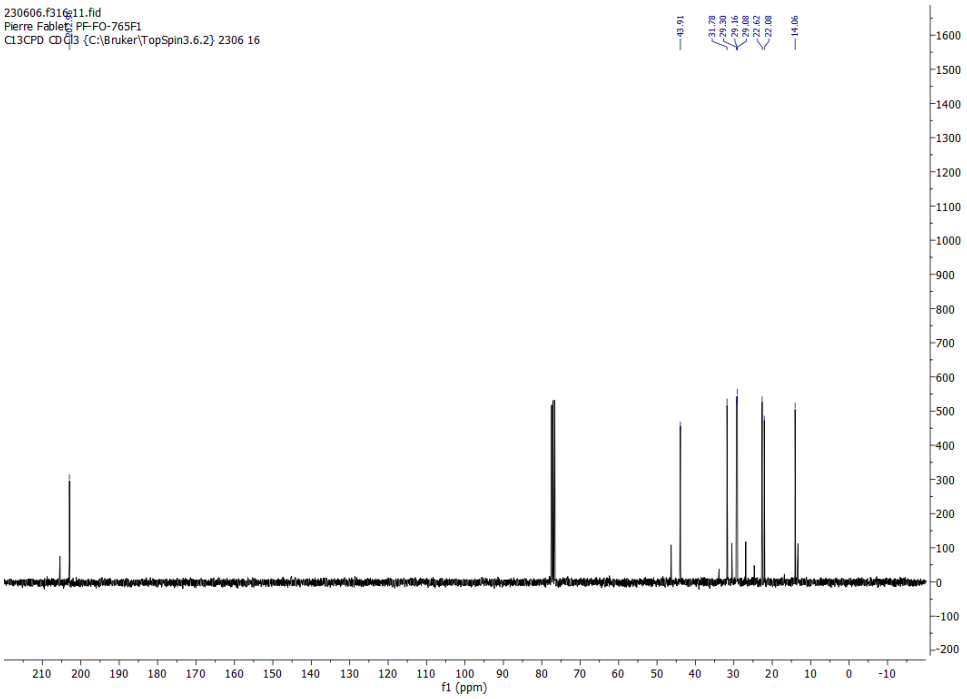
SI-J: NMR attribution and spectra of hydroformylation products

Nonanal (2a) and 2-methyloctanal (2b):

(2a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (td, J = 1.9, 0.6 Hz, 1H), 2.35 (td, J = 7.4, 1.9 Hz, 2H), 1.71 – 1.48 (m, 2H), 1.32 – 1.21 (m, 9H), 0.92 – 0.66 (m, 3H).

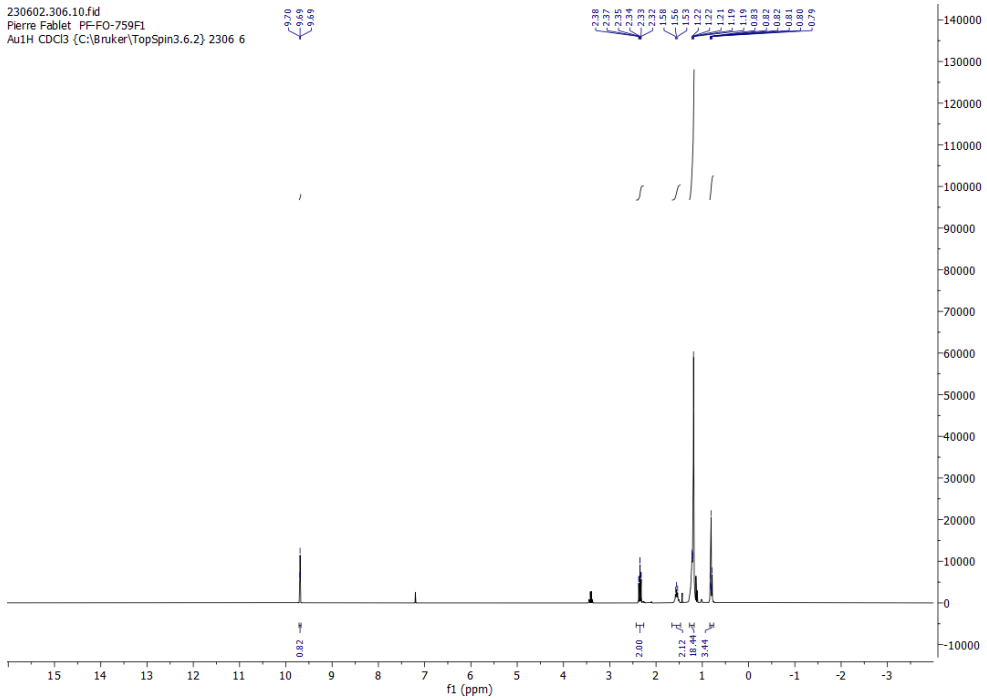


(2a) ^{13}C NMR (75 MHz, CDCl3) δ 202.96, 43.91, 31.78, 29.30, 29.16, 29.08, 22.62, 22.08, 14.06.

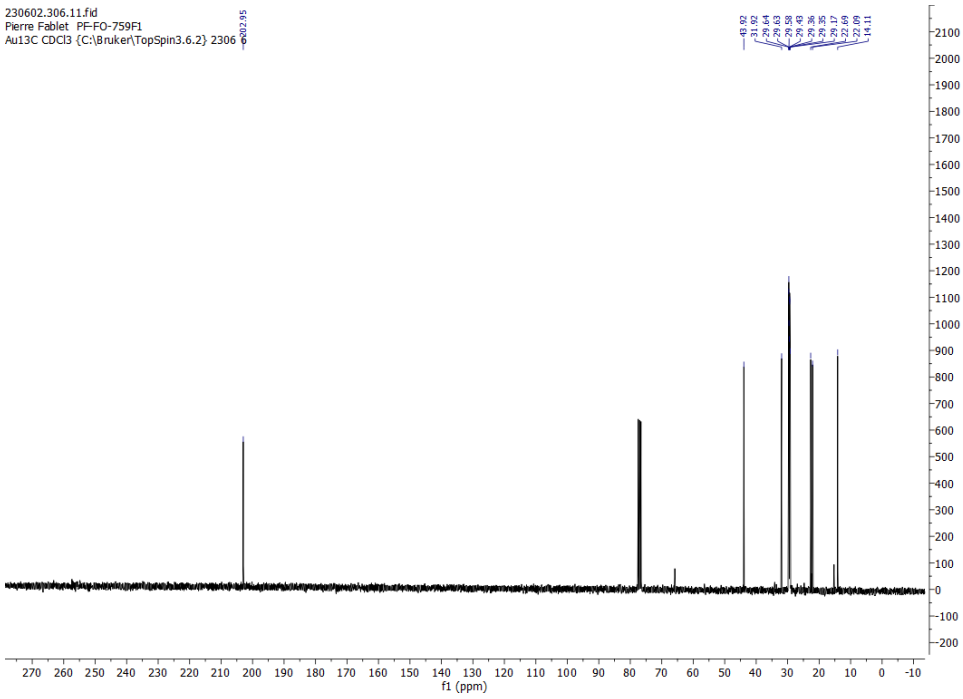


Tridecanal (5a) and 2-methyldodecanal (5b):

(5a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (t, J = 1.9 Hz, 1H), 2.35 (td, *J* = 7.4, 1.9 Hz, 2H), 1.66 – 1.49 (m, 2H), 1.30 – 1.19 (m, 18H), 0.86 – 0.78 (m, 3H).

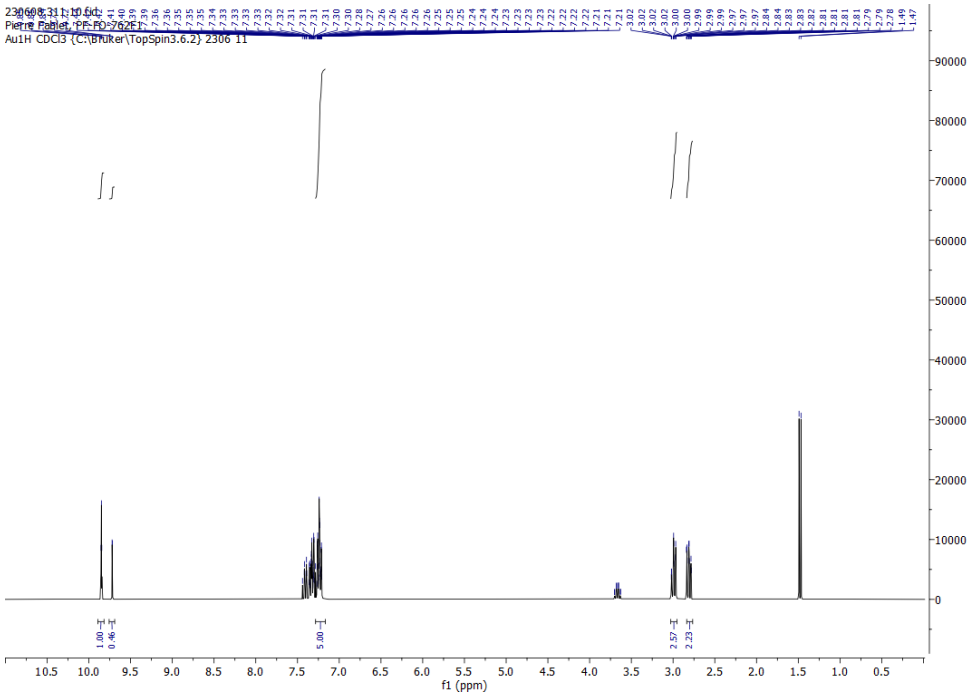


(5a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.95, 43.92, 31.92, 29.64, 29.63, 29.58, 29.43, 29.36, 29.35, 29.17, 22.69, 22.09, 14.11.

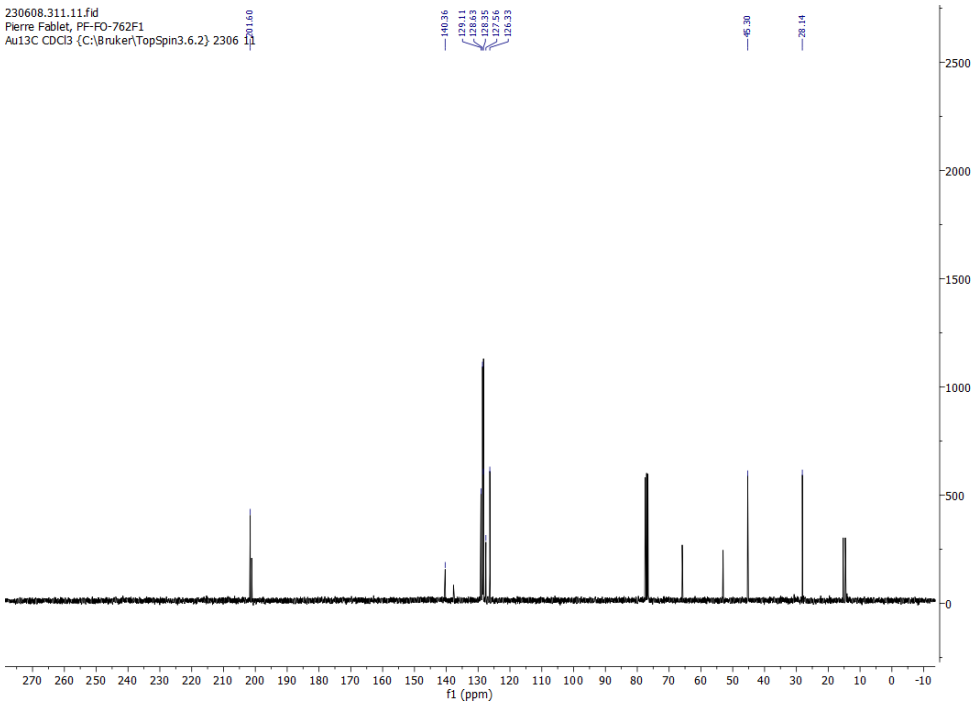


3-phenylpropanal (7a) and 2-phenylpropanal (7b):

(7a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (t, J = 1.4 Hz, 1H), 7.30 – 7.02 (m, 5H), 2.99 (ddt, J = 8.2, 7.1, 0.6 Hz, 2H), 2.88 – 2.67 (m, 2H).

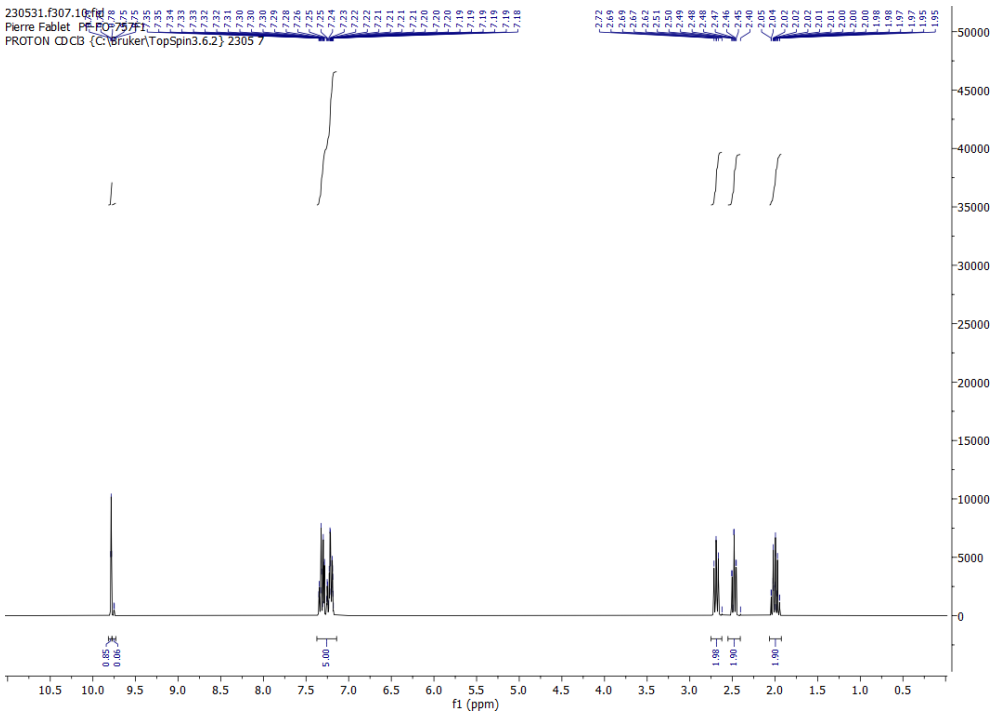


(7a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.60, 140.36, 129.11, 128.63, 128.35, 127.56, 126.33, 45.30, 28.14.

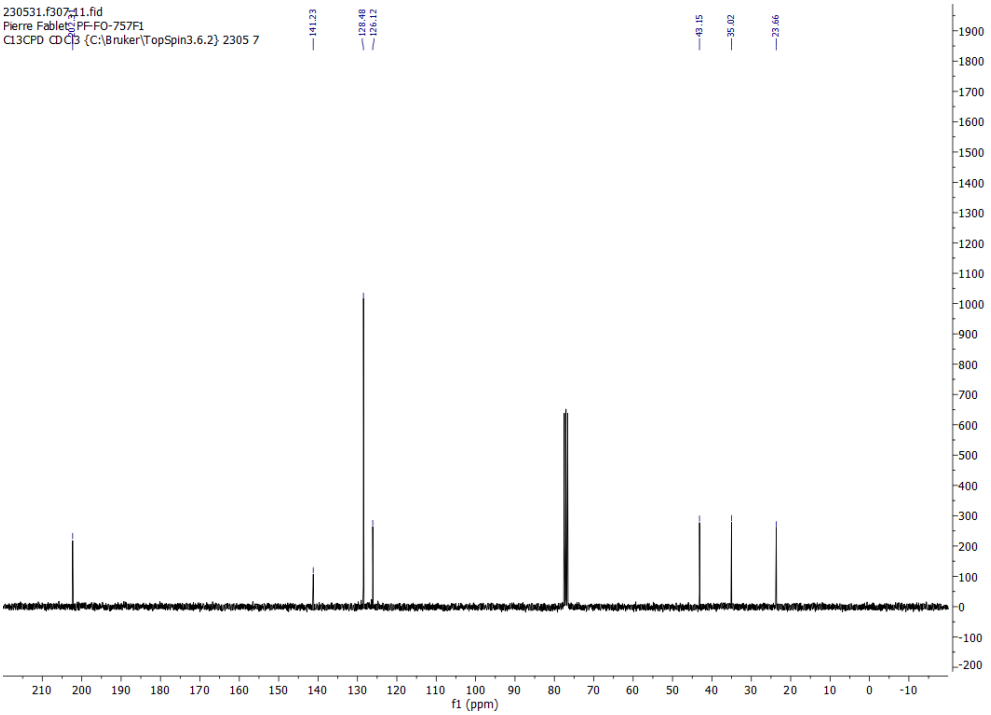


4-phenylbutanal (9a) and 2-methyl-3-phenylpropanal (9b):

(9a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, J = 1.6 Hz, 1H), 7.37 – 7.13 (m, 5H), 2.69 (dd, J = 8.2, 6.9 Hz, 2H), 2.48 (td, J = 7.3, 1.6 Hz, 2H), 2.08 – 1.92 (m, 2H).

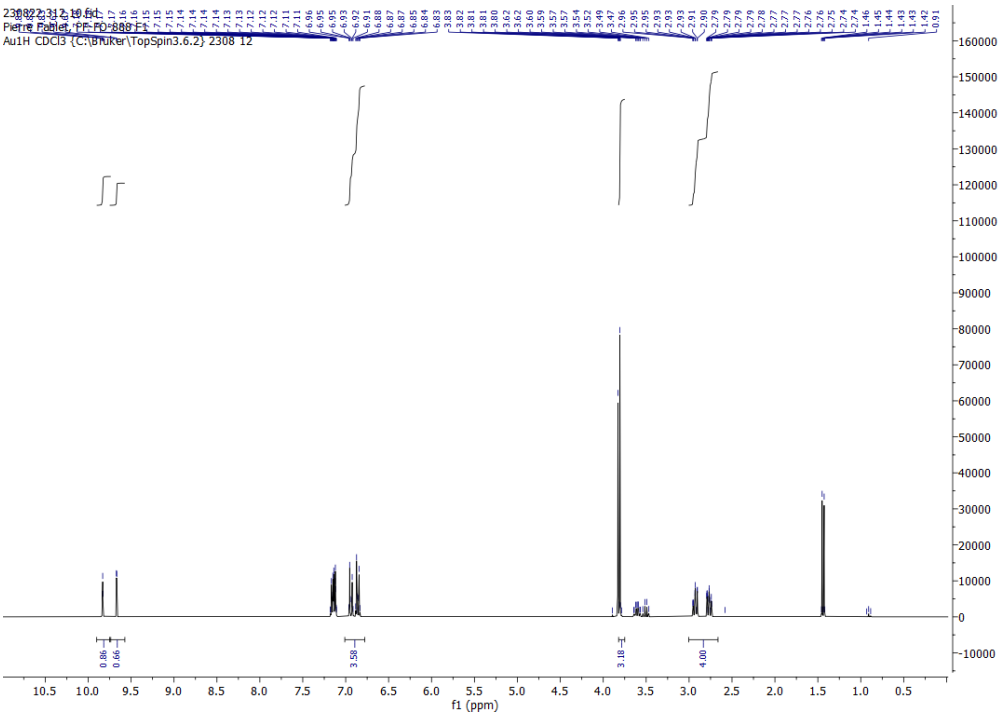


(9a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.31, 141.23, 128.48, 126.12, 43.15, 35.02, 23.66.

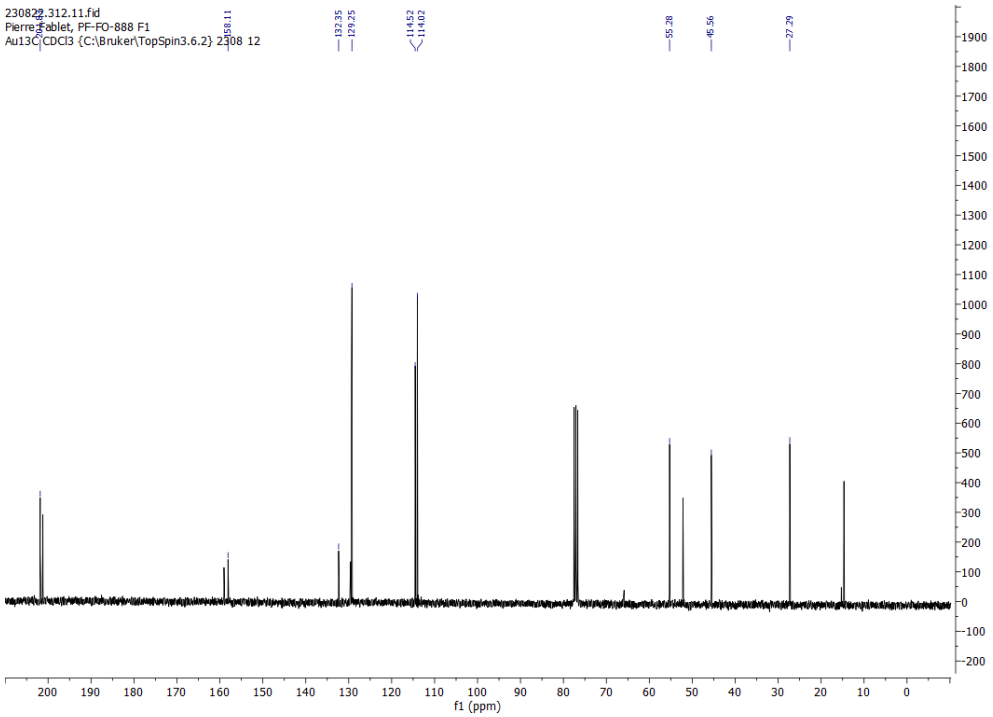


3-(4-methoxyphenyl)propanal (11a) and 2-(4-methoxyphenyl)propanal (11b):

(11a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (t, J = 1. 5 Hz, 1H), 6.99 – 6.80 (m, 4H), 3.81 (s, 3H), 3.02 – 2.54 (m, 4H).

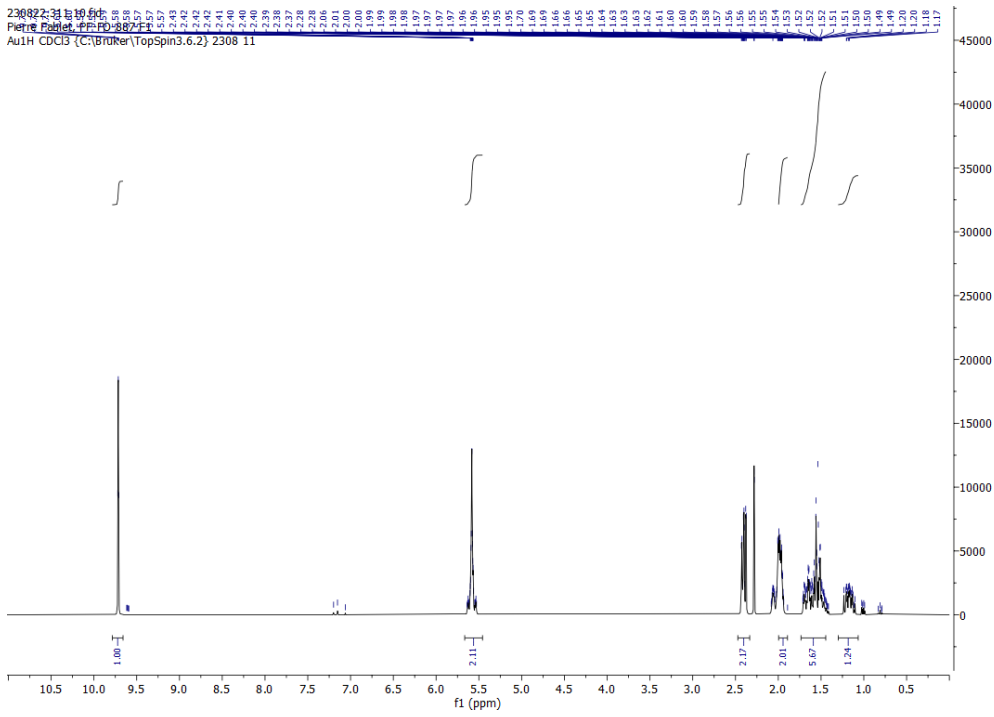


(11a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.83, 158.11, 132.35, 129.25, 114.52, 114.02, 55.28, 45.56, 27.29.

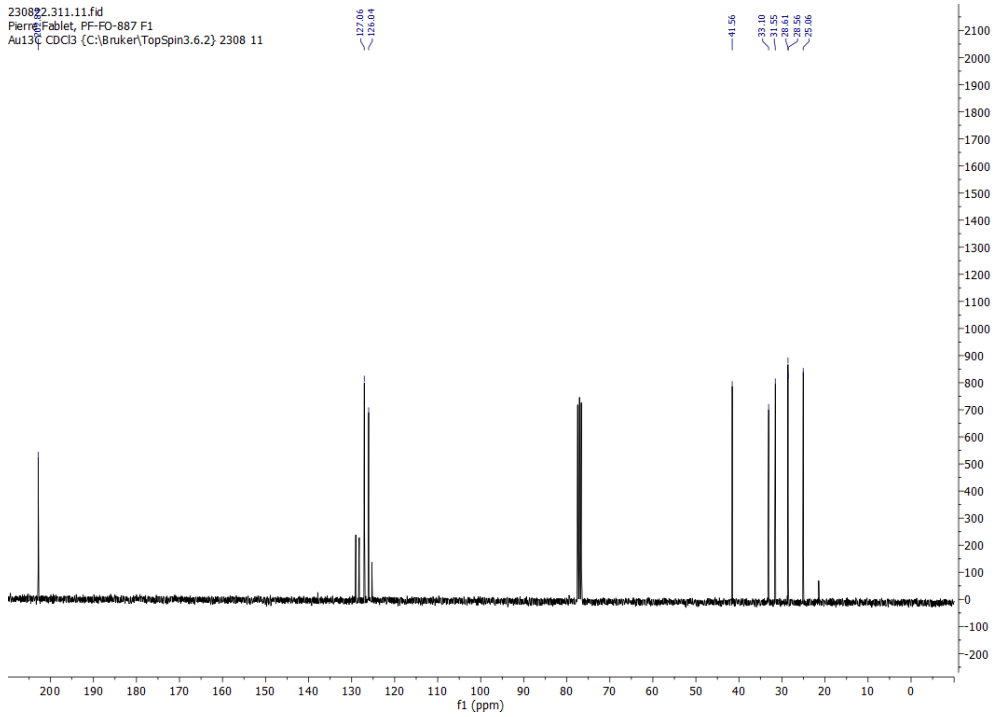


3-(cyclohex-3-en-1-yl)propanal (13a) and 2-(cyclohex-3-en-1-yl)propanal (13b):

(13a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (t, J = 1.8 Hz, 1H), 5.83 – 5.21 (m, 2H), 2.40 (ddd, J = 8.0, 7.0, 1.9 Hz, 2H), 2.02 – 1.88 (m, 2H), 1.74 – 1.38 (m, 6H), 1.17 (dddd, J = 12.7, 10.2, 8.7, 7.4 Hz, 1H).

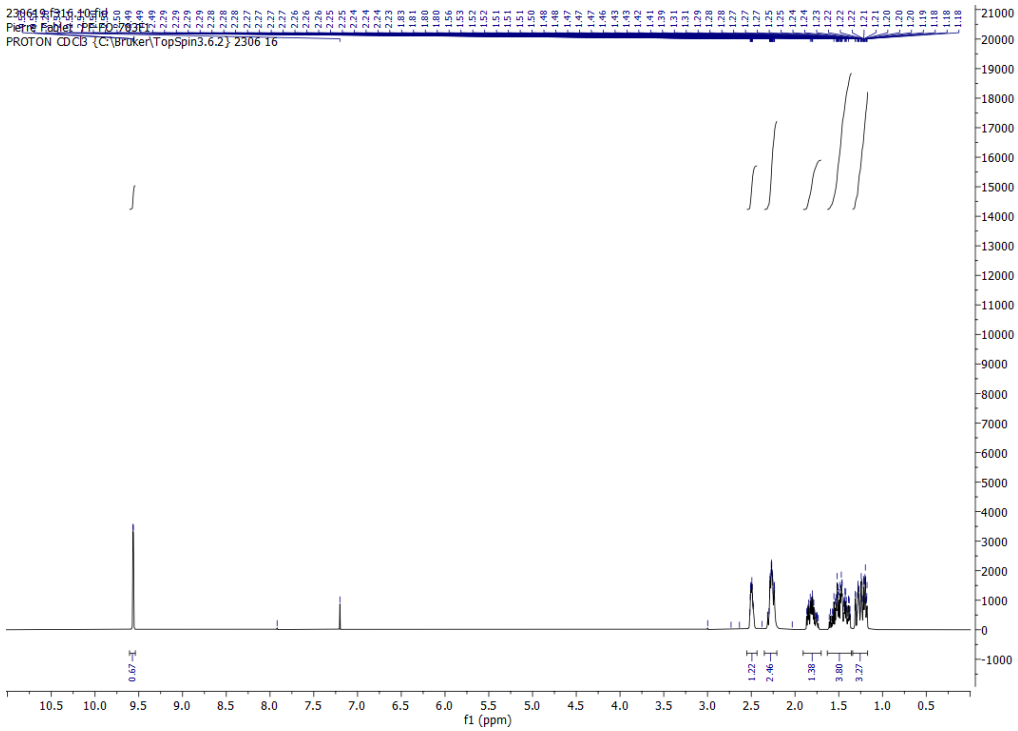


(13a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.84, 127.06, 126.04, 41.56, 33.10, 31.55, 28.61, 28.56, 25.06.

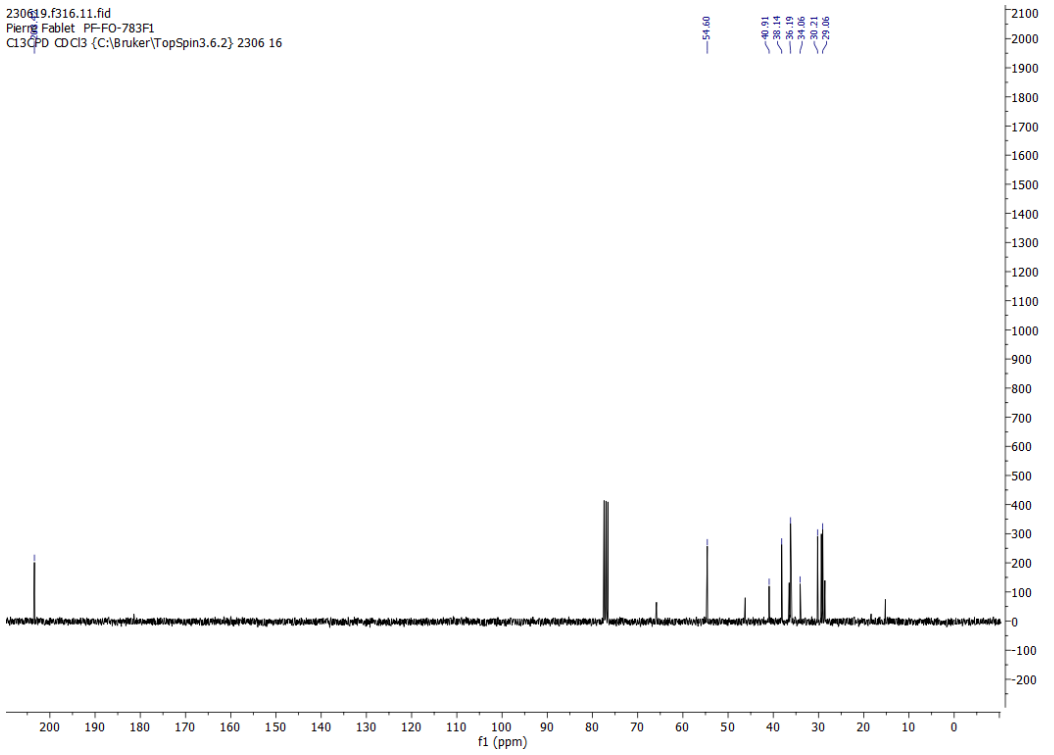


Norbornane-2-carboxaldehyde (15):

(15) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (d, J = 1.6 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.34 – 2.20 (m, 2H), 1.90 – 1.78 (m, 1H), 1.64 – 1.39 (m, 4H), 1.33 – 1.16 (m, 3H).

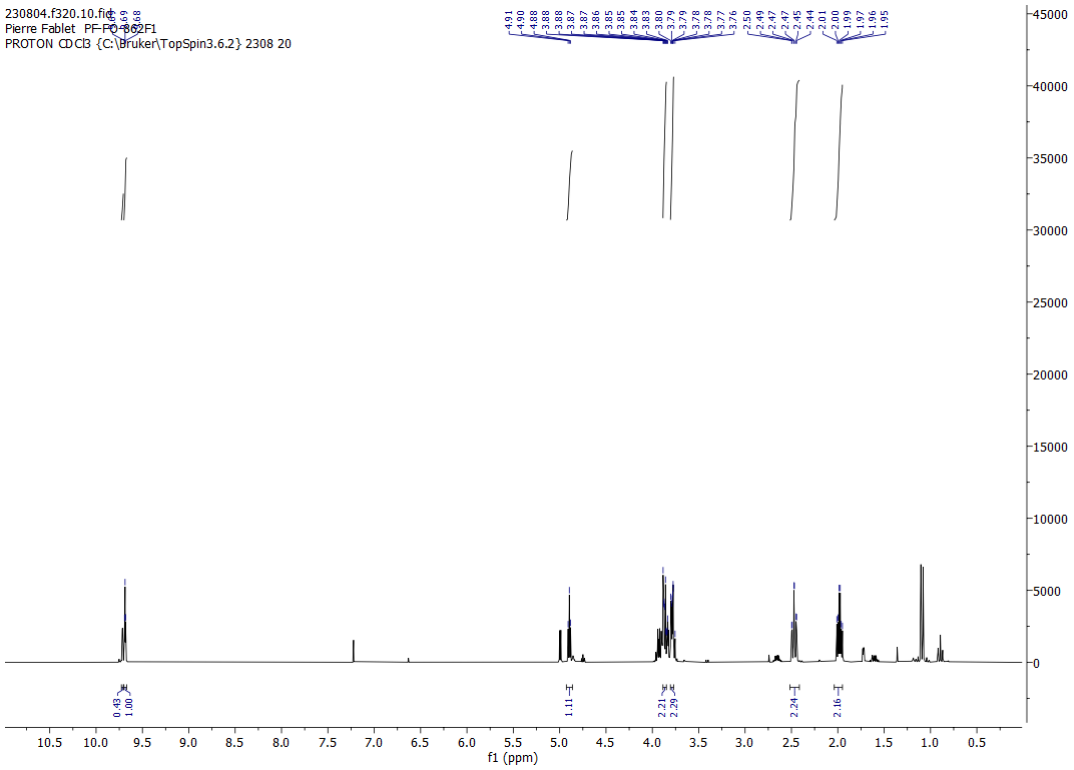


(15) ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.42, 54.60, 40.91, 38.14, 36.19, 34.06, 30.21, 29.06.

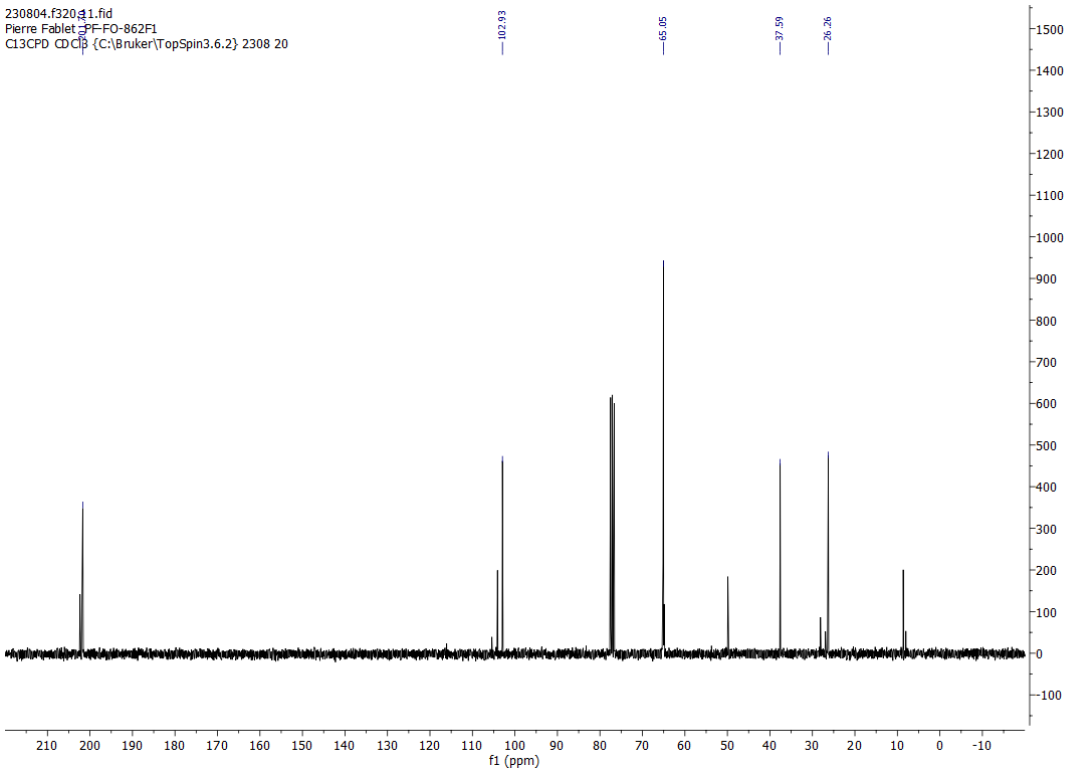


3-(1,3-dioxolan-2-yl)propanal (17a) and 2-(1,3-dioxolan-2-yl)propanal (17b):

(17a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (t, J = 1.7 Hz, 1H), 4.90 (t, J = 3.9 Hz, 1H), 3.86 (ddd, J = 8.1, 3.8, 1.7 Hz, 2H), 3.81 – 3.72 (m, 2H), 2.47 (td, J = 7.1, 1.7 Hz, 2H), 1.98 (td, J = 7.1, 3.9 Hz, 2H).

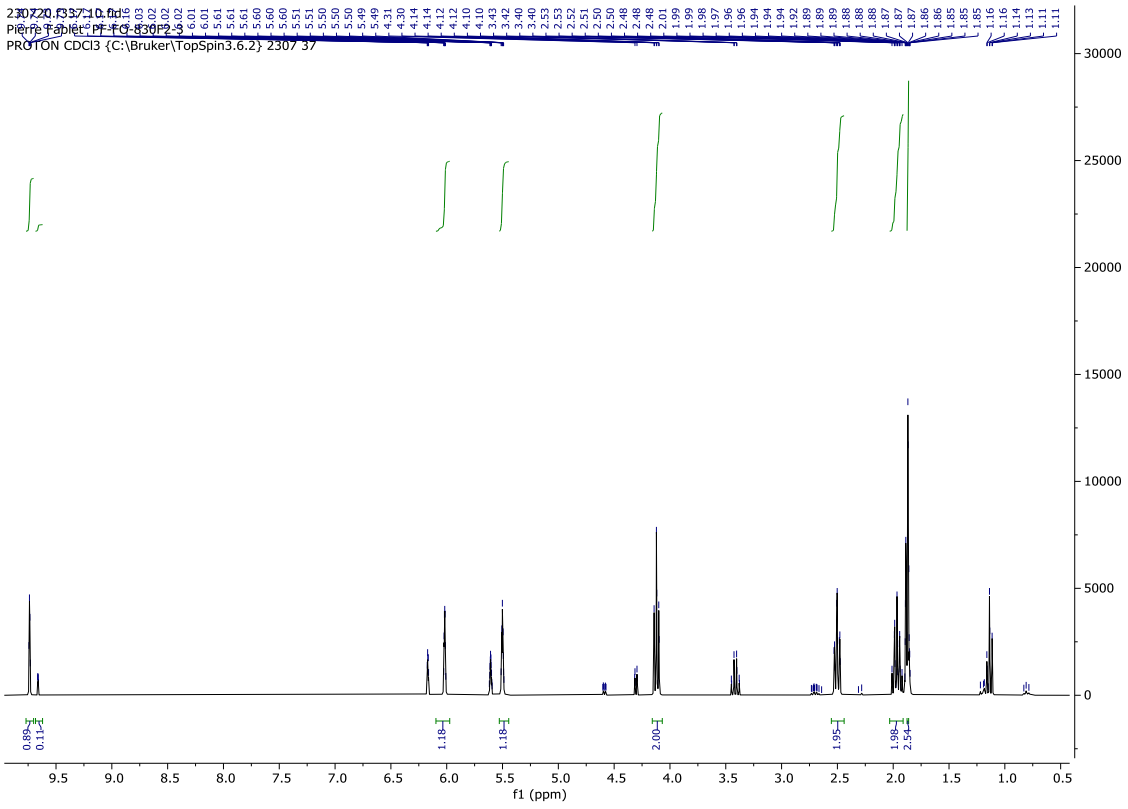


(17a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.70, 102.93, 65.05, 37.59, 26.26.

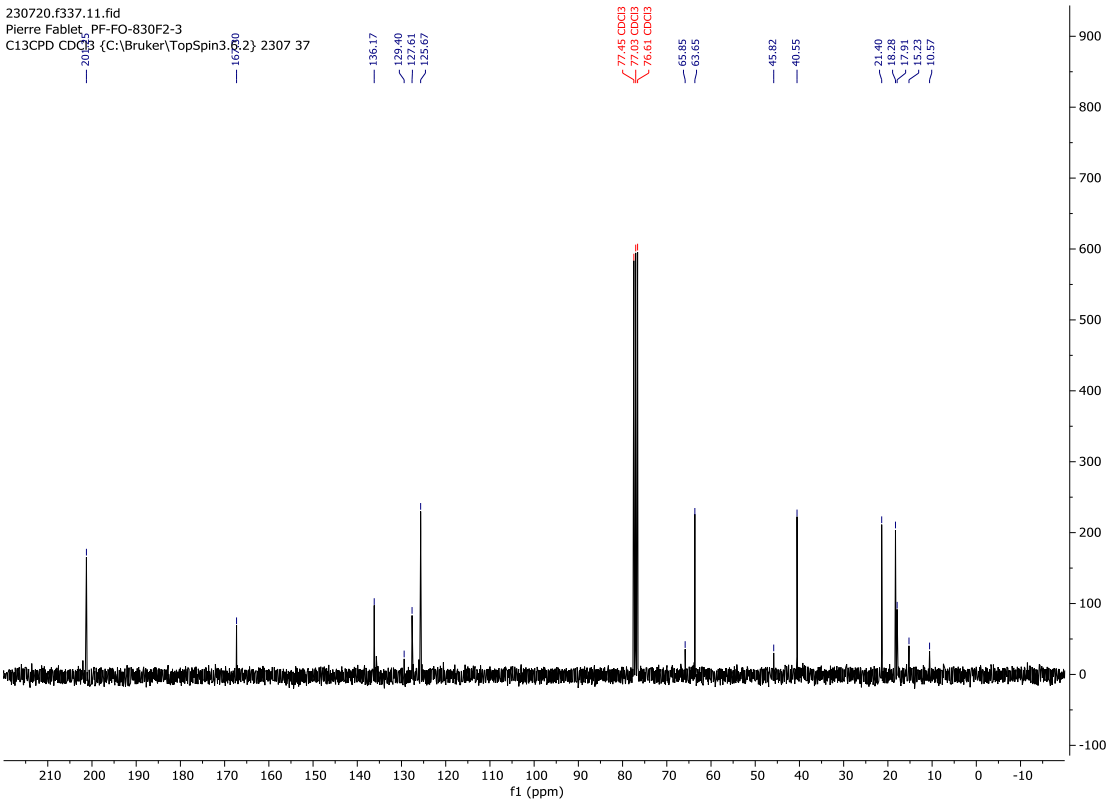


4-oxobutyl methacrylate (19a) and 2-methyl-3-oxopropyl methacrylate (19b):

(19a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (t, J = 1.5 Hz, 1H), 6.02 (m, 1H), 5.51 (m, 1H), 4.12 (t, J = 6.5 Hz, 2H), 2.50 (dt, J = 7.0, 1.5 Hz, 2H), 1.96 (p, J = 6.5 Hz, 2H), 1.87 (m, 3H).

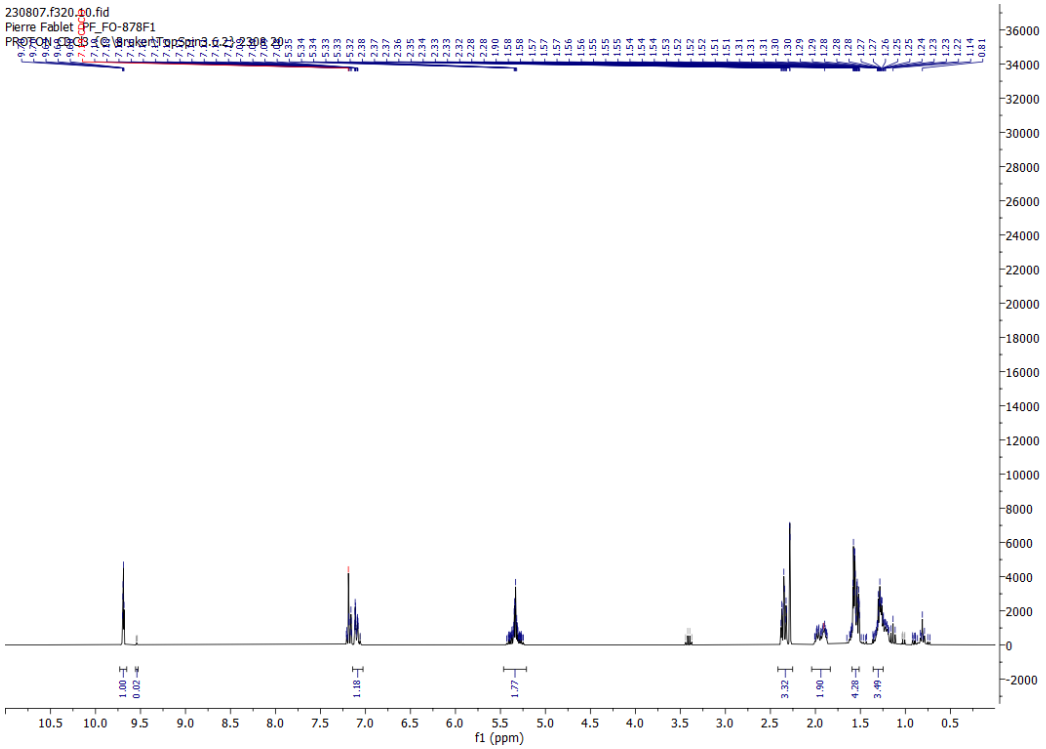


(19a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.9, 167.3, 136.2, 125.7, 63.7, 40.6, 21.4, 18.3.

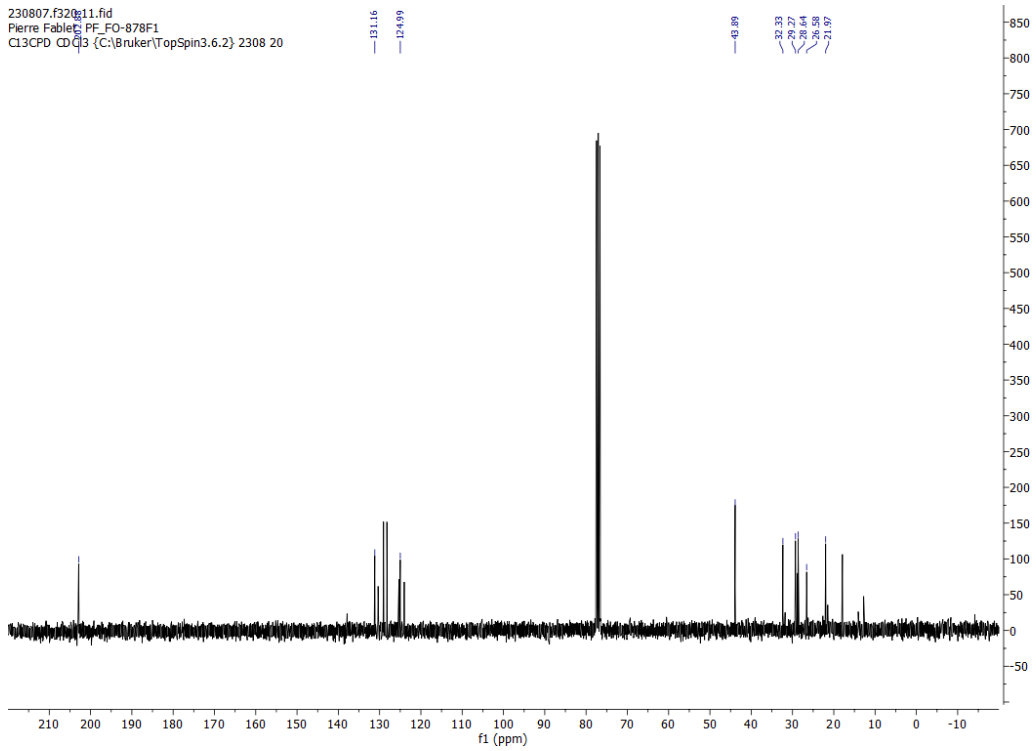


non-8-enal (21a) and 2-methyloct-7-enal (21b):

(21a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (q, J = 1.8 Hz, 1H), 7.14 – 7.03 (m, 1H), 5.47 – 5.21 (m, 2H), 2.35 (tt, J = 7.4, 2.1 Hz, 2H), 2.04 – 1.83 (m, 2H), 1.68 – 1.39 (m, 4H), 1.39 – 1.19 (m, 4H).

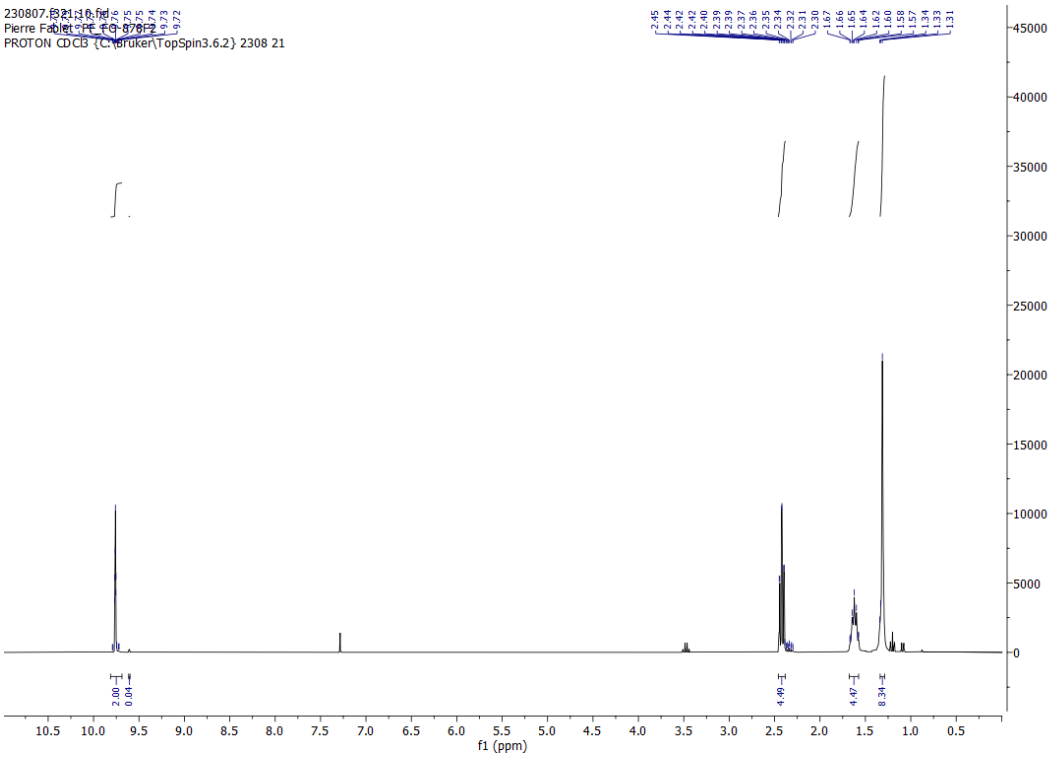


(21a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.88, 131.16, 124.99, 43.89, 32.33, 29.27, 28.64, 26.58, 21.97.

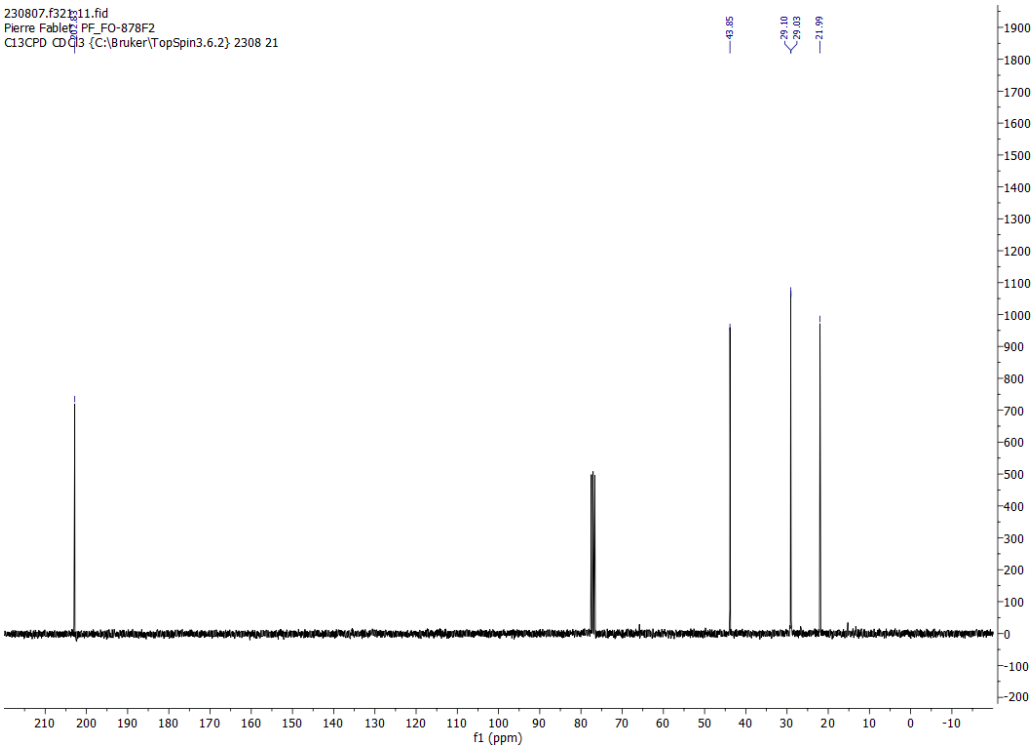


Decanedial (22):

(22) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (td, J = 1.8, 0.5 Hz, 1H), 2.42 (td, J = 7.3, 1.8 Hz, 2H), 1.61 (q, J = 7.3 Hz, 3H), 1.31 (s, 5H).

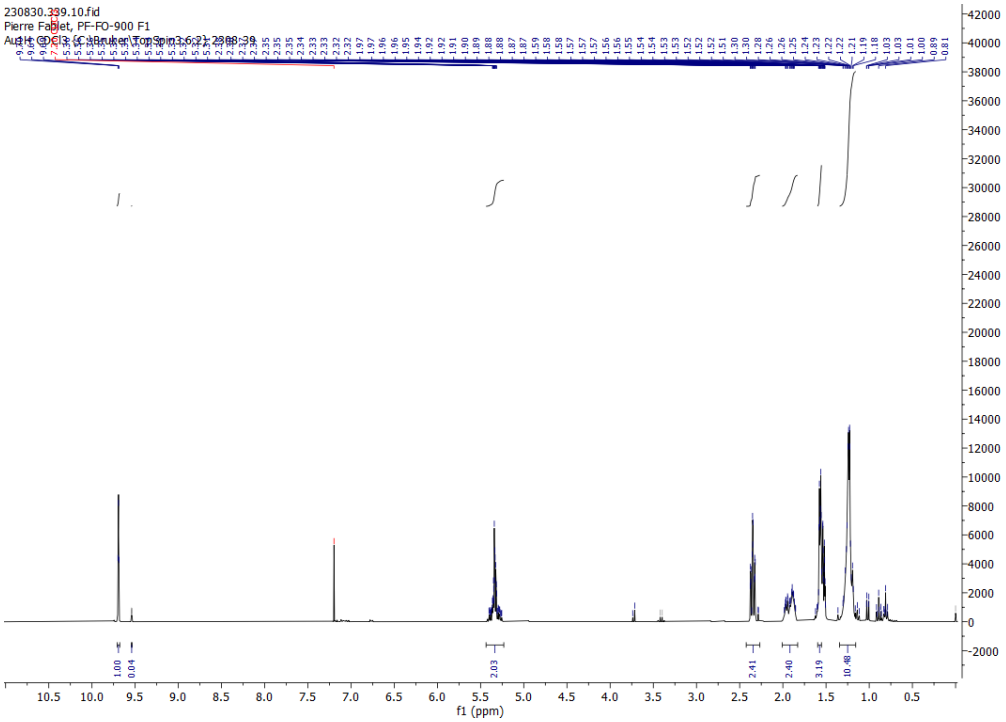


(22) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.83, 43.85, 29.10, 29.03, 21.99.

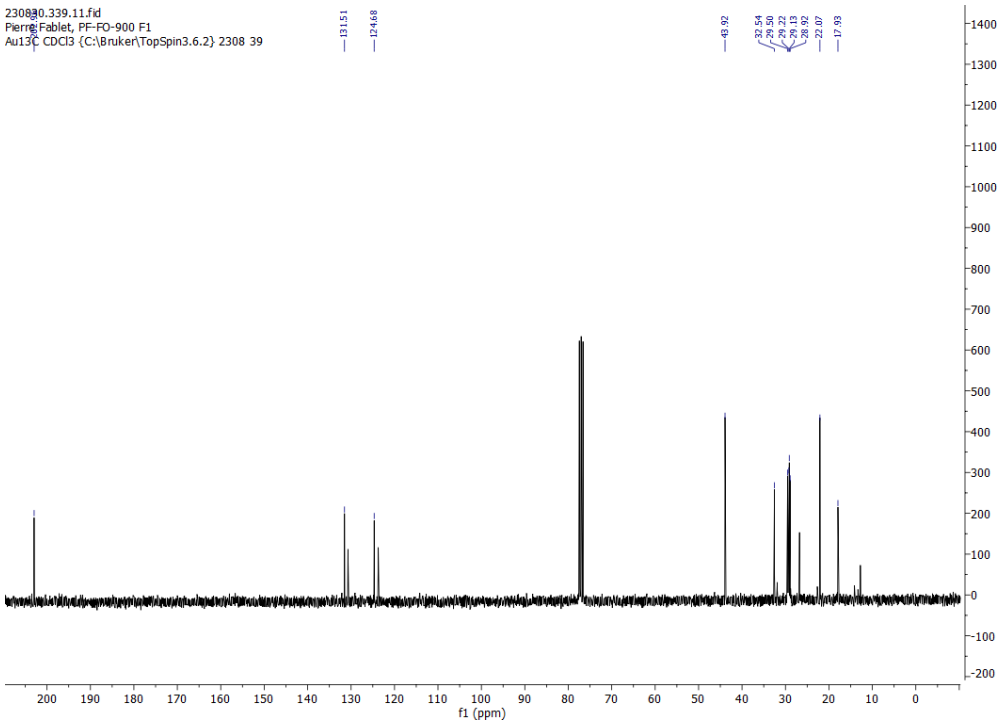


undec-10-enal (24a) and 2-methyldec-9-enal (24b):

(24a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (t, J = 1.8 Hz, 1H), 5.46 – 5.22 (m, 2H), 2.35 (tdd, J = 7.4, 1.9, 1.0 Hz, 2´3H), 2.02 – 1.82 (m, 2H), 1.66 – 1.46 (m, 3H), 1.39 – 1.08 (m, 10H).

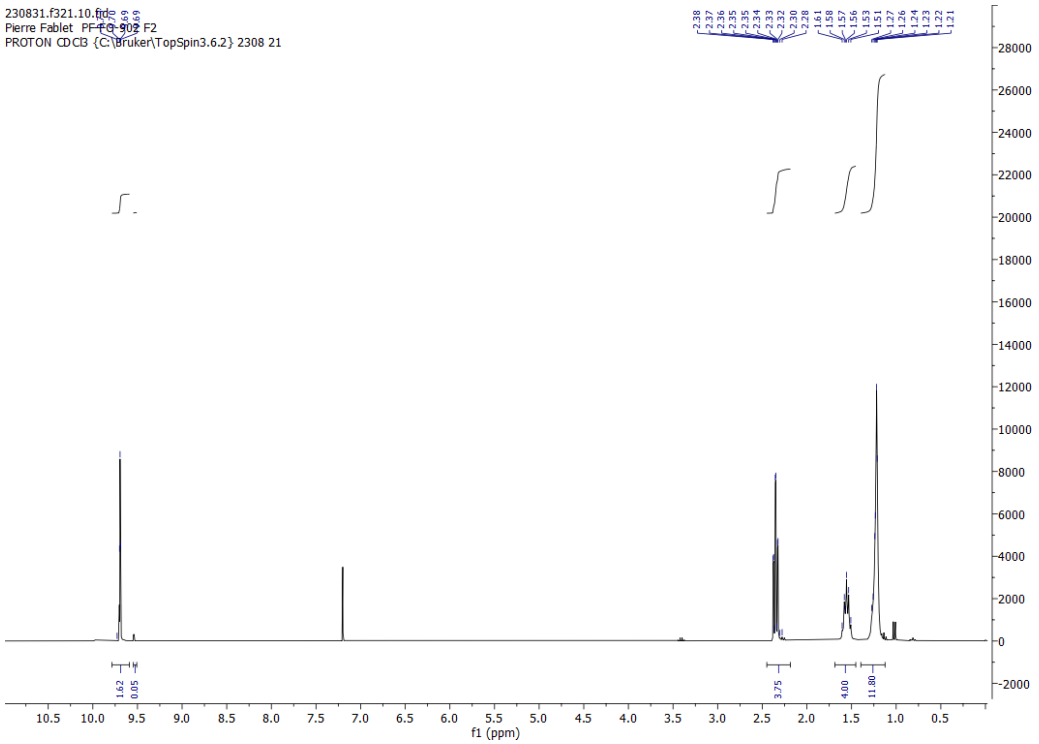


(24a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.96, 131.51, 124.68, 43.92, 32.54, 29.50, 29.22, 29.13, 28.92, 22.07, 17.93.

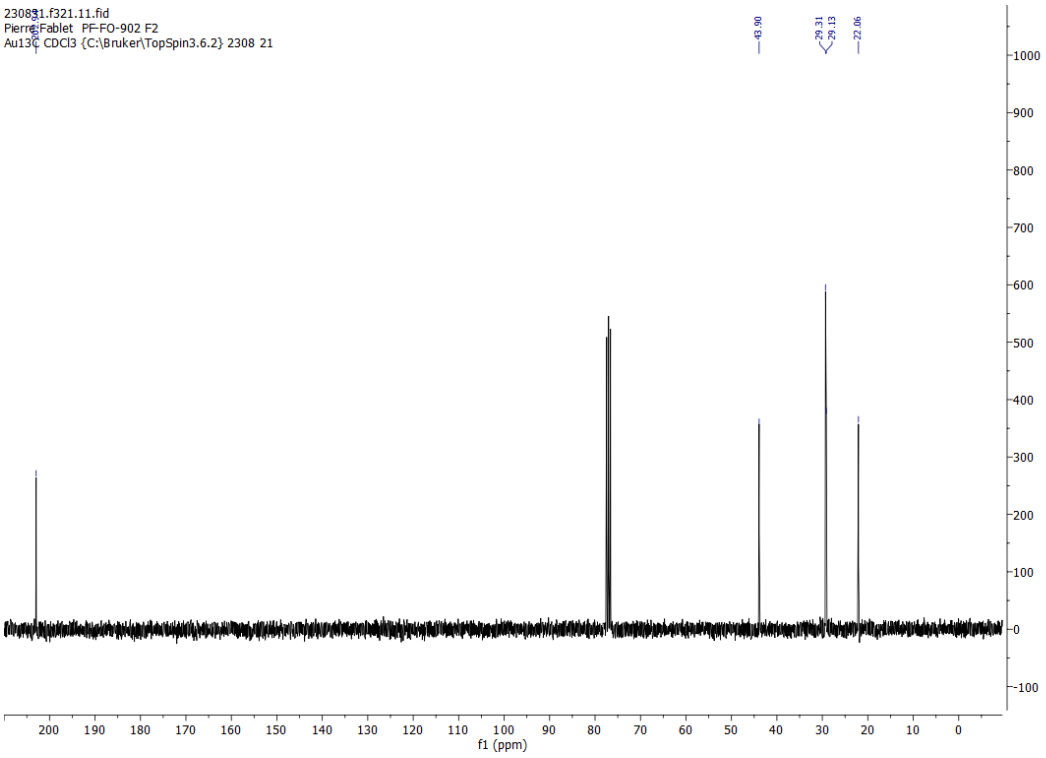


dodecanedial (25):

(25) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (t, J = 1.9 Hz, 1H), 2.35 (td, J = 7.3, 1.9 Hz, 2H), 1.56 (dd, J = 9.2, 5.4 Hz, 3H), 1.30 – 1.17 (m, 9H).

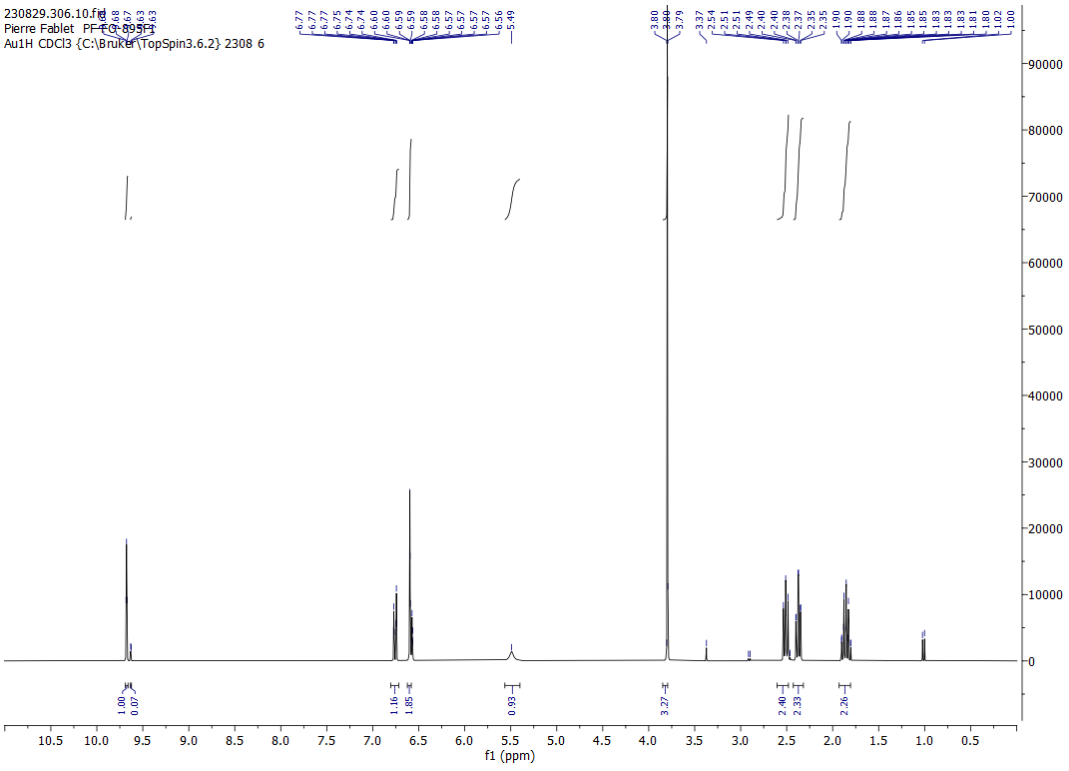


(25) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.94, 43.90, 29.31, 29.13, 22.06.



4-(4-hydroxy-3-methoxyphenyl)butanal (27a) and 3-(4-hydroxy-3-methoxyphenyl)-2-methylpropanal (27b):

(27a) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (t, J = 1.6 Hz, 1H), 6.80 – 6.71 (m, 1H), 6.64 – 6.53 (m, 2H), 3.80 (s, 3H), 2.51 (dd, J = 8.3, 6.9 Hz, 2H), 2.37 (td, J = 7.3, 1.6 Hz, 2H), 1.93 – 1.77 (m, 2H).



(27a) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.52, 146.49, 143.92, 133.15, 121.04, 114.29, 110.99, 55.90, 43.13, 34.71, 23.93.