Supplementary Information for:

# Ferrocene-Based *P*-Chiral Amidophosphinate: Stereoselective Synthesis and X-ray Structural Study

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## Synthesis of *rac*-1 and (*R*)-1

**Starting materials:** *rac*- and *(R)-N,N*-dimethyl-α-ferrocenylethylamine (Ugi's Amine), $^t$BuLi solution are commercially available and used without additional purification. $(Et_2N)P(O)(Ph)Cl$ was prepared according to literature procedure.[1]

**Synthesis of *rac*-$R_C$,$S_{Fc}$,$R_P$/$S_C$,$R_{Fc}$,$S_P$-2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide (1).** A solution of *t*-BuLi (6.45 ml, 12.25 mmol, 1.90 M in *n*-hexane) was slowly added to a solution of *rac-N,N*-dimethyl-1-ferrocenylethylamine (Ugi's Amine) (3.00 g, 11.67 mmol) in diethyl ether (60 ml). The mixture was stirred for 12 h at room temperature and solution of $(Et_2N)P(O)(Ph)Cl$ (3.19 g, 12.25 mmol) in 20 ml of diethyl ether at −80 °C was added slowly. The mixture was warmed to room temperature, strirred overnight. Then the solvent was evaporated at reduced pressure, the dry residue was dissolved in 50 ml of dichloromethane and washed from the impurities with water (3 × 30 ml). Then the solvent was evaporated to obtain 3.44 g of crude 2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide (65% yield). Recrystallization from petroleum ether (b.p. 40-70°C) lead to orange crystals of *rac*-$R_C$,$S_{Fc}$,$R_P$/$S_C$,$R_{Fc}$,$S_P$-2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide (*rac*-**1**) suitable for X-ray diffraction analysis (1.82 g, 35% yield). M.p. 144 ºC. $^1$H NMR ($CDCl_3$, *δ*, ppm, *J*, Hz): 1.08 (t, 6H, $^3J_{HH}$ = 7.14, Et), 1.11 (br.s, 3H, $CH_3$), 1.64 (s, 6H, $NMe_2$), 3.05-3.18 (m, 2H, C$\underline{H}_2$), 3.21-3.34 (m, 2H, C$\underline{H}_2$), 3.84 (br.s, 1H, Cp), 4.30 (s, 5H, Cp), 4.40 (br.s, 2H, Cp), 4.51 (q, 1H, $^3J_{HH}$ = 2.44, CH), 7.30-7.43 (m, 3H, Ph), 7.59-7.67 (m, 2H, Ph). $^{31}$P{$^1$H} NMR ($CDCl_3$, *δ*, ppm, *J*, Hz): 33.8 (s). $^{13}$C{$^1$H} NMR ($CDCl_3$, *δ*, ppm, *J*, Hz): 14.3 (s, $CH_3$), 14.4 (s, $CH_3$), 38.8 (br.s, $NMe_2$), 39.2 (d, $^2J_{CP}$ = 4.2, $\underline{C}H_2$), 55.2 (br.s, CH), 68.5 (br.s, Cp), 70.3 (s, Cp), 70.5 (s, Cp), 73.0 (s, $^1J_{CP}$ = 16.9, Cp), 74.3 (s, Cp), 127.2 (br.s, *p*-Ph), 127.8 (s, *m*-Ph), 131.6 (d, $^2J_{CP}$ = 9.7, *o*-Ph), 135.7 (d, $^1J_{CP}$ = 130.9, *ipso*-Ph). IR (KBr, cm$^{-1}$): 462 (w), 494 (s), 518 (s), 576 (m), 672 (m), 699 (s), 719 (m), 750 (m), 786 (w), 812 (m), 840 (w), 929 (m), 1021 (s), 1041 (w), 1069 (m), 1097 (m), 1115 (m), 1171 (s), 1186 (s), 1210 (s), 1252 (m), 1365 (m), 1378 (m), 1439 (m), 1467(w), 1676 (w), 2771 (m), 2811 (m), 2871 (m), 2926 (m), 2964 (m). Calculated for $C_{24}H_{33}N_2POFe$ (M 452): C 63.72, H, 7.35, Fe 12.35, N 6.19, O 3.54, P 6.85 Found: C 63.64, H 7.34, N 6.32, P 7.01.

**Synthesis of $R_C$,$S_{Fc}$,$R_P$-2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide ((*R*)-1)**. A solution of *t*-BuLi (6.45 ml, 12.25 mmol, 1.90 M in *n*-hexane) was slowly added to a solution of (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine ((*R*)-Ugi's Amine) (3.00 g, 11.67 mmol) in diethyl ether (60 ml). The mixture was stirred for 12 h at room temperature and solution of $(Et_2N)P(O)(Ph)Cl$ (3.19 g, 12.25 mmol) in 20 ml of diethyl ether at −80 °C was added slowly. The mixture was warmed to room temperature, strirred overnight. Then the solvent was evaporated at reduced pressure, the dry residue was dissolved in 50 ml of dichloromethane and washed from the impurities with water (3 × 30 ml). Then the solvent was evaporated to obtain 3.44 g of crude 2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide (63% yield). Recrystallization from petroleum ether (b.p. 40-70°C) lead to orange crystals of $R_C$,$S_{Fc}$,$R_P$-2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide ((*R*)-**1**) suitable for X-ray diffraction analysis (1.79 g, 34% yield). M.p. 143-144 ºC. $[\alpha]^{25}_D$ = -132° (c 0.25, $CHCl_3$). $^1$H NMR ($CDCl_3$, *δ*, ppm, *J*, Hz): 1.08 (t, 6H, $^3J_{HH}$ =

7.11, Et), 1.11 (br.s, 3H, $CH_3$), 1.65 (s, 6H, $NMe_2$), 3.06-3.18 (m, 2H, C$\underline{H}_2$), 3.23-3.35 (m, 2H, C$\underline{H}_2$), 4.28 (s, 5H, Cp), 4.40 (br.s, 3H, Cp), 4.51 (q, 1H, $^3J_{HH}$ = 2.44, CH), 7.32-7.44 (m, 3H, Ph), 7.60-7.67 (m, 2H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, $\delta$, ppm, $J$, Hz): 34.0 (s).$^{13}C\{^1H\}$ NMR ($CDCl_3$, $\delta$, ppm, $J$, Hz): 14.3 (s, $CH_3$), 14.4 (s, $CH_3$), 38.9 (br.s, $NMe_2$), 39.4 (d, $^2J_{CP}$ = 4.3, $\underline{C}H_2$), 55.2 (br.s, CH), 68.4 (br.s, Cp), 70.2 (s, Cp), 70.4 (s, Cp), 73.1 (s, $^1J_{CP}$ = 16.9, Cp), 74.3 (s, Cp), 127.3 (br.s, *p*-Ph), 127.9 (s, *m*-Ph), 131.5 (d, $^2J_{CP}$ = 9.8, *o*-Ph), 135.7 (d, $^1J_{CP}$ = 130.7, *ipso*-Ph). IR (KBr, $cm^{-1}$): 462 (w), 504 (s), 575 (m), 671 (m), 697 (s), 717 (m), 751 (m), 816 (m), 843 (w), 930 (m), 1022 (s), 1041 (w), 1068 (m), 1096 (m), 1113 (m), 1172 (s), 1193 (s), 1210 (s), 1251 (m), 1364 (m), 1379 (m), 1436 (m), 1467(w), 1674 (w), 2765 (m), 2810 (m), 2867 (m), 2928 (m), 2967 (m). Calculated for $C_{24}H_{33}N_2POFe$ (M 452): C 63.72, H, 7.35, Fe 12.35, N 6.19, O 3.54, P 6.85 Found: C 63.68, H 7.33, N 6.29, P 6.95.

**Experimental $^{31}P$, $^{1}H$, $^{13}C$ NMR and IR spectra for *rac*-$R_C$,$S_{Fc}$,$R_P$/$S_C$,$R_{Fc}$,$S_P$-2-(*N*,*N*-dimethyl-α-aminoethyl)ferrocenylphenyl phosphinic acid *N*,*N*-diethylamide (1)**

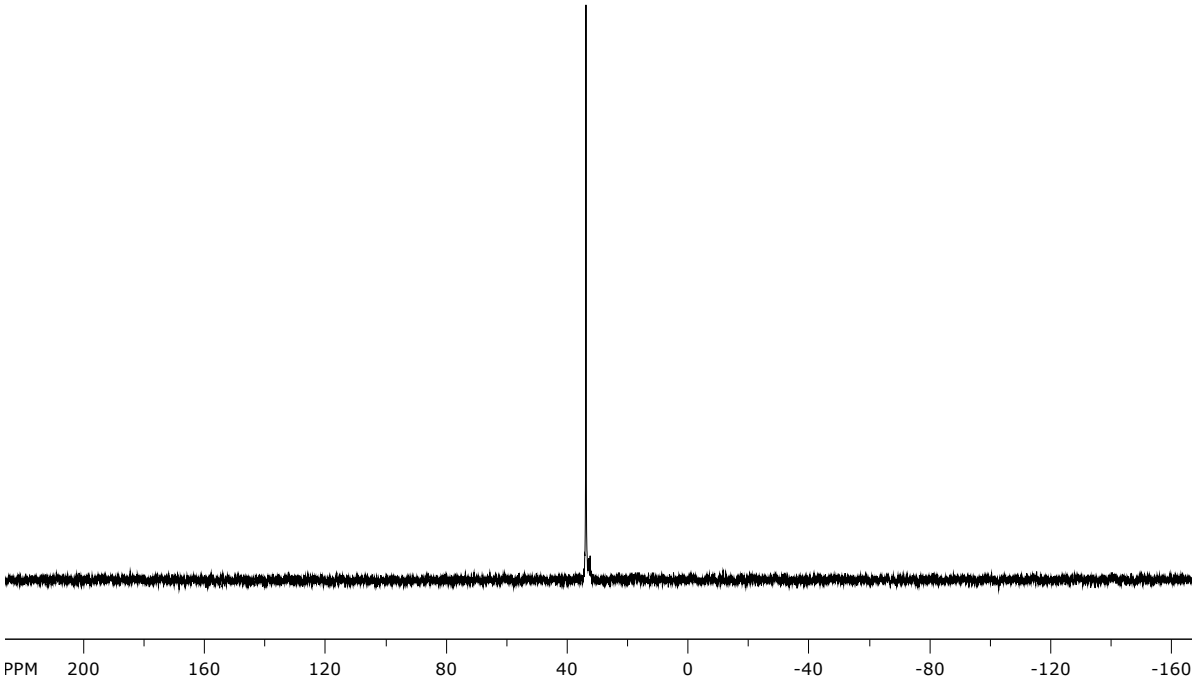



**Figure S1.** $^{31}P\{^{1}H\}$ NMR spectrum of a $CDCl_3$ solution of *rac*-**1.**

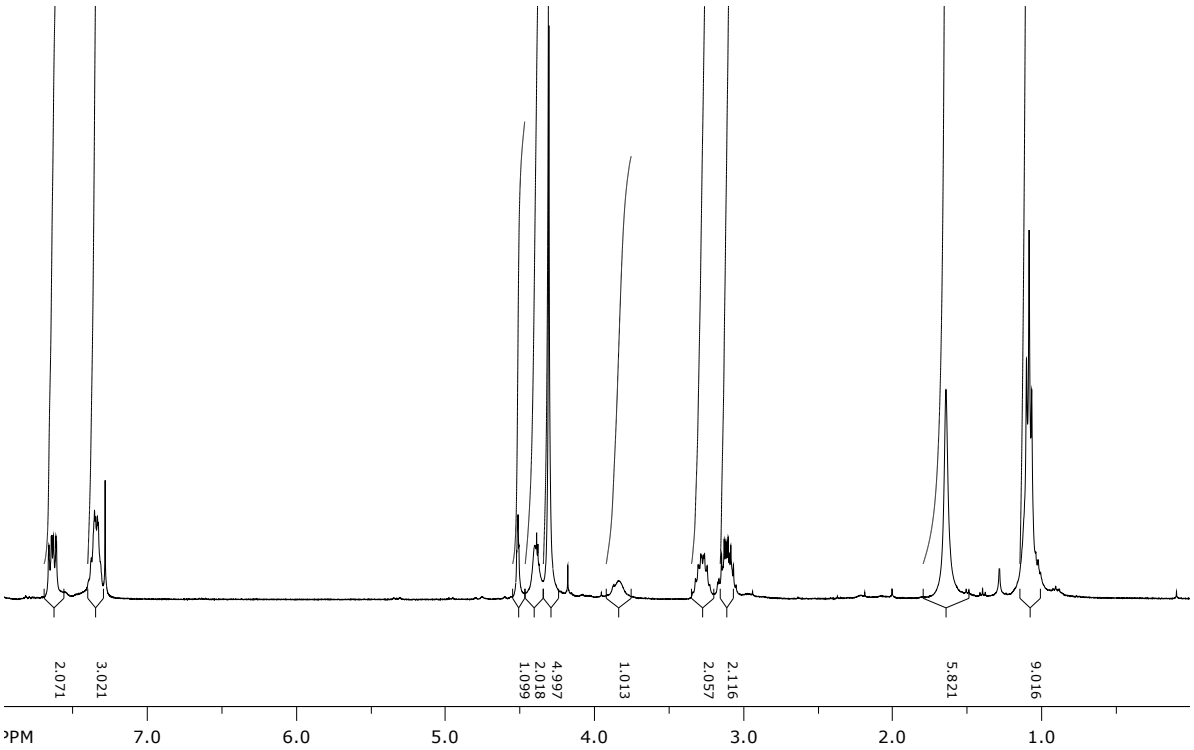



**Figure S2.** $^{1}H$ NMR spectrum of a $CDCl_3$ solution of *rac*-**1** (with integration).

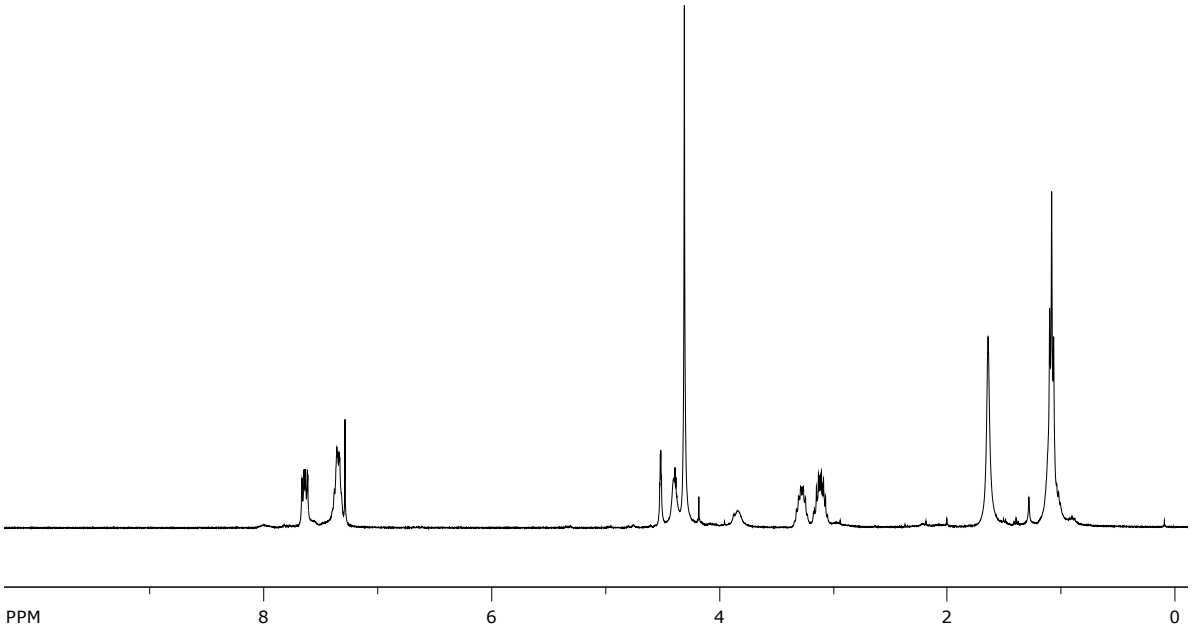



**Figure S3.** $^{1}H$ NMR spectrum of a $CDCl_3$ solution of *rac*-**1.**

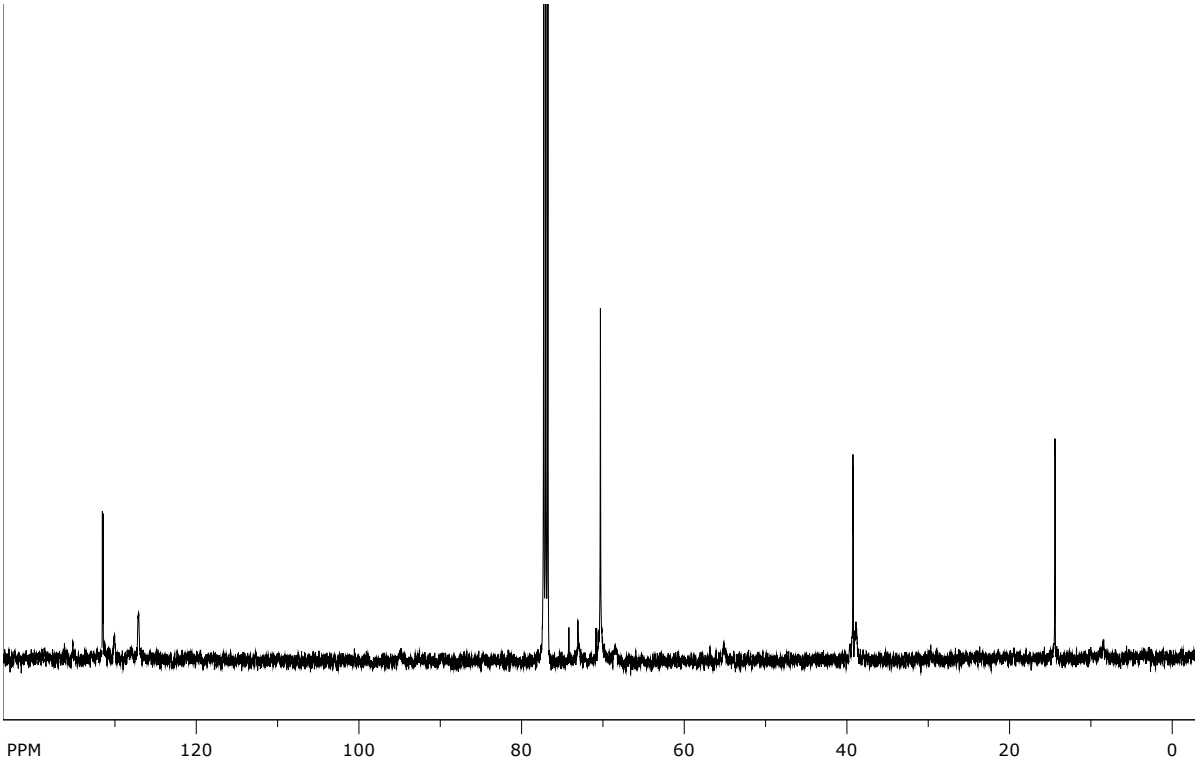



**Figure S4.** $^{13}C$ NMR spectrum of a $CDCl_3$ solution of *rac*-**1.**

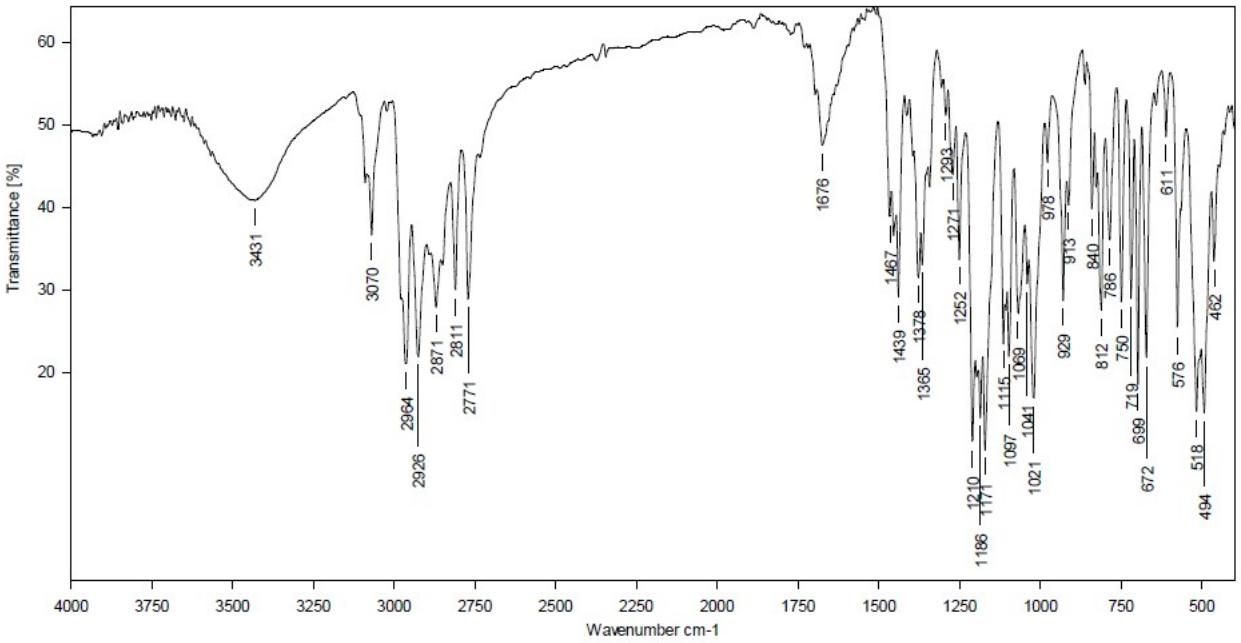



**Figure S5.** IR spectrum of *rac*-**1** in KBr**.**

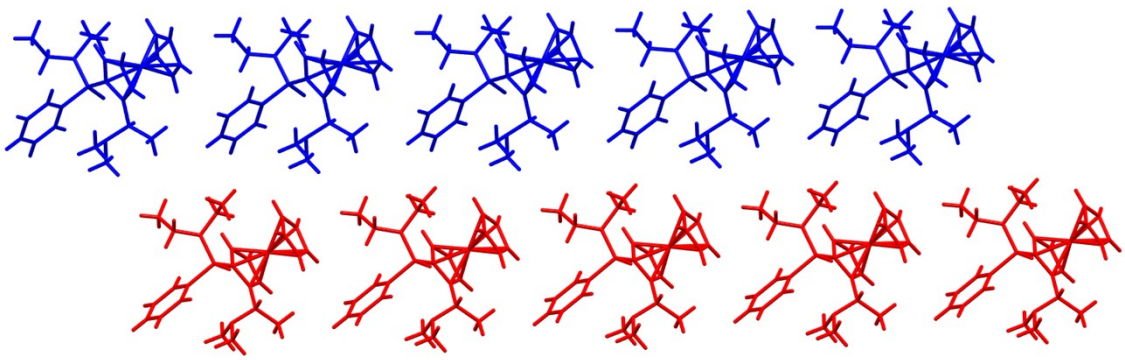


**Fig. S6.** Crystal packing of *rac*-**1** view along *b* axes.

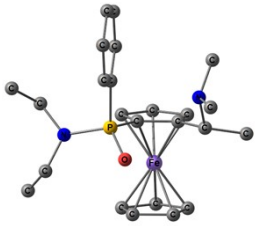
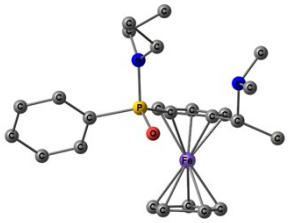
| | Diastereomer 1 | Diastereomer 2 | Δ (kcal/mol) |
|---|---|---|---|
| |  |  | |
| E | -2723.0049283 | -2723.0029589 | 1.24 |

**Figure S7**. Optimized structures of diastereisomers of **1**.

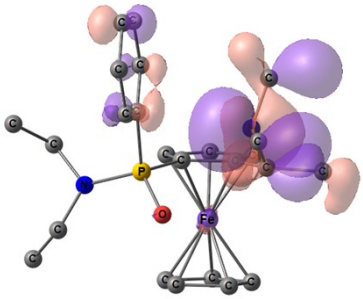
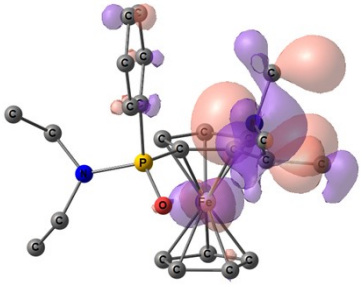
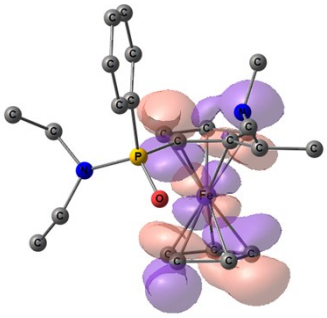
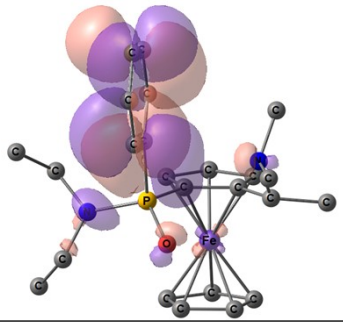
| Cation | Neutral molecule |
|---|---|
|  |  |
| SOMO (-8.75 eV) | HOMO (-5.68 eV) |
|  |  |
| LUMO (-5.82 eV) | LUMO (-0.56 eV) |
| 2.92 eV | 5.13 eV |

**Figure S8**. HOMO of neutral and SOMO of cation forms of **1**.

## References

[1] R.P. Shekurov, V.A. Miluykov, D.R. Islamov, D.B. Krivolapov, O.N. Kataeva, T.P. Gerasimova, S.A. Katsyuba, G.R. Nasybullina, V.V. Yanilkin and O.G. Sinyashin, Synthesis and structure of ferrocenylphosphinic acids, *J. Organomet. Chem.,* 2014, **766**, 40–48.