

1,2-Disubstituted aryl-based ferrocenyl phosphines

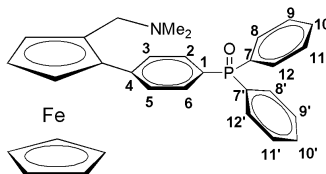
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Detailed assignment of NMR and MS data and IR spectroscopic data for compounds

rac-2 to *rac-9*:

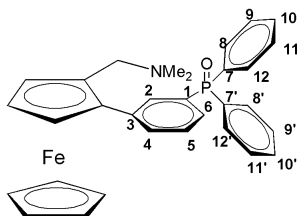
(4-Diphenylphosphine oxide)phenyl-2-N,N-dimethylaminomethylferrocene (*rac-2*)



^1H NMR (CDCl_3 , 400 MHz): δ 2.16 (s, 6H, CH_3), 3.07 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2), 3.64 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2) 4.02 (s, 5H, C_5H_5), 4.27 (s, 1H, C_5H_3), 4.32 (s, 1H, C_5H_3), 4.53 (s, 1H, C_5H_3), 7.47-7.85 (m, 14H, aryl-H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161 MHz): δ 29.4 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 44.6 (s, CH_3), 58.2 (s, CH_2), 67.5 (s, C_5H_3), 70.3 (s, C_5H_5), 71.3 (s, C_5H_3), 72.6 (s, C_5H_3), 82.1 (s, C_5H_3), 86.3 (s, C_5H_3), 128.2 (d, $^3J_{\text{CP}} = 11.9$ Hz, C^9 , $\text{C}^{9'}$, C^{11} or $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 129.0 (d, $^2J_{\text{CP}} = 12.2$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 131.2 (d, $^4J_{\text{CP}} = 2.2$ Hz, C^{10} , $\text{C}^{10'}$ in C_6H_5), 131.2 (d, $^1J_{\text{CP}} = 104.9$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 131.9 (d, $^2J_{\text{CP}} = 9.8$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 132.2 (d, $^3J_{\text{CP}} = 9.6$ Hz, C^9 , $\text{C}^{9'}$, C^{11} or $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 134.4 (d,

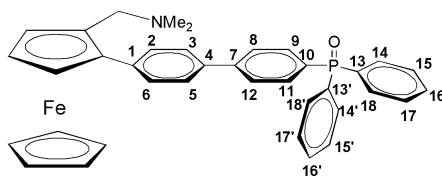
$^1J_{\text{CP}} = 102.6$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 134.5 (d, $^1J_{\text{CP}} = 102.6$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 143.6 (d, $^4J_{\text{CP}} = 3.1$ Hz, C^4 in C_6H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 45.0 (s, CH_3), 58.2 (s, CH_2), 68.2 (s, C_5H_3), 70.6 (s, C_5H_5), 71.0 (s, C_5H_3), 72.9 (s, C_5H_3), 82.5 (s, C_5H_3), 86.2 (s, C_5H_3), 128.5 (d, $^3J_{\text{CP}} = 12.2$ Hz, C^9 , $\text{C}^{9'}$, C^{11} or $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 128.9 (d, $^3J_{\text{CP}} = 12.2$ Hz, C^9 , $\text{C}^{9'}$, C^{11} or $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 129.3 (d, $^1J_{\text{CP}} = 105.9$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 129.4 (d, $^1J_{\text{CP}} = 105.9$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 131.8 (d, $^2J_{\text{CP}} = 9.7$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 131.8 (d, $^4J_{\text{CP}} = 2.2$ Hz, C^{10} , $\text{C}^{10'}$ in C_6H_5), 132.1 (d, $^3J_{\text{CP}} = 9.9$ Hz, C^9 , $\text{C}^{9'}$, C^{11} or $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 132.7 (d, $^1J_{\text{CP}} = 112.8$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 132.8 (2 overlapped signals d, $^1J_{\text{CP}} = 95.0$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 132.9 (d, $^1J_{\text{CP}} = 112.8$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 143.9 (d, $^4J_{\text{CP}} = 2.7$ Hz, C^4 in C_6H_4) ppm. EI MS: m/z (rel. int. %) 519 (100) $[\text{M}]^+$, 504 (14) $[\text{M} - \text{CH}_3]^+$, 475 (90) $[\text{M} - \text{N}(\text{CH}_3)_2]^+$, 462 (7), 438 (12), 409 (20), 355 (28), 257 (9), 238 (27), 229 (21) $[\text{P}(\text{O})\text{Ph}_2 + 2\text{CH}_3]^+$, 201 (23) $[\text{P}(\text{O})\text{Ph}_2]^+$, 183 (20), 152 (40), 133 (13), 121 (72) $[\text{C}_5\text{H}_5\text{Fe}]^+$, 77 (28) $[\text{Ph}]^+$, 58 (64) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3433 s (br), 3073 w ($\nu_{\text{C-H}}$), 2937 w (ν_{CH_3}), 2855 w (ν_{CH_3}), 2814 w, 2768 w, 1636 w (br) ($\nu_{\text{C=C}}$), 1599 m ($\nu_{\text{C=C}}$), 1456 w ($\nu_{\text{P-Ph}}$), 1437 m ($\nu_{\text{P-Ph}}$), 1310 w, 1259 w ($\nu_{\text{C-N}}$), 1190 s ($\nu_{\text{P-O}}$), 1118 s, 1017 w, 972 w, 825 m, 734 s ($\omega_{\text{C-H}}$), 720 m ($\omega_{\text{C-H}}$), 696 s ($\omega_{\text{C=C}}$), 564 s ($\omega_{\text{C=C}}$). Elemental analysis: calculated for $\text{C}_{31}\text{H}_{30}\text{FeNOP}$ 71.69 % C, 5.82 % H, 2.70 % N; found 72.03 % C, 6.21 % H, 2.66 % N.

(3-Diphenylphosphine oxide)phenyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-**3**)



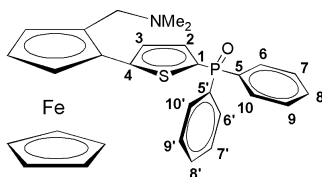
^1H NMR (CDCl_3 , 400 MHz): δ 2.06 (s, 6H, CH_3), 3.02 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2), 3.48 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2), 3.87 (s, 5H, C_5H_5), 4.20 (s, 1H, C_5H_3), 4.26 (s, 1H, C_5H_3), 4.40 (s, 1H), 7.18-7.05 (m, 7H, aryl- H), 7.36 (t, 1H, $^2J_{\text{HH}} = 15.9$ Hz, aryl- H), 7.54-7.46 (m, 4H, aryl- H), 7.94 (d, 1H, $^2J_{\text{HH}} = 7.7$ Hz, aryl- H), 8.01 (d, 1H, $^2J_{\text{HH}} = 7.6$ Hz, aryl- H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161 MHz): δ 29.3 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 44.7 (s, CH_3), 58.1 (s, CH_2), 67.2 (s, C_5H_3), 70.2 (s, C_5H_5), 70.9 (s, C_5H_3), 72.2 (s, C_5H_3), 82.3 (s, C_5H_3), 87.0 (s, C_5H_3), 128.1 (d, overlapped signals, J_{CP} not determined), 128.3 (d, $^2J_{\text{CP}} = 11.8$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 129.7 (d, $^3J_{\text{CP}} = 9.9$ Hz, C^9 , $\text{C}^{9'}$, C^{11} , $\text{C}^{11'}$ in C_6H_5 or C^5 C_6H_4), 131.3 (d, $^4J_{\text{CP}} = 2.5$ Hz, C^{10} , $\text{C}^{10'}$ in C_6H_5 or C^4 in C_6H_4), 131.3 (d, $^4J_{\text{CP}} = 2.8$ Hz, C^{10} , $\text{C}^{10'}$ in C_6H_5 or C^4 in C_6H_4), 132.2 (d, $^3J_{\text{CP}} = 9.6$ Hz, C^9 , $\text{C}^{9'}$, C^{11} , $\text{C}^{11'}$ in C_6H_5 or C^5 C_6H_4), 133.3 (d, $^2J_{\text{CP}} = 10.8$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 133.3 and 134.0 (d, $^1J_{\text{CP}} = 103.3$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 134.2 and 134.3 (d, $^1J_{\text{CP}} = 103.3$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 134.3 and 134.4 (d, $^1J_{\text{CP}} = 102.6$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 140.0 (d, $^2J_{\text{CP}} = 12.3$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 140.0 (d, $^3J_{\text{CP}} = 12.3$ Hz, C^3 in C_6H_4) ppm. EI MS: m/z (rel. int. %) 519 (100) $[\text{M}]^+$, 504 (23) $[\text{M} - \text{CH}_3]^+$, 476 (73) $[\text{M} - \text{N}(\text{CH}_3)_2]^+$, 409 (20), 355 (14), 243 (19), 238 (38), 199 (38), 152 (20), 133 (9), 121 (38) $[\text{P}(\text{O})\text{Ph}_2 + \text{H}]^+$, 77 (10) $[\text{Ph}]^+$, 58 (34) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$, 43 (11). IR (KBr): $\square$ (cm^{-1}) 3426 s (br), 2961 m ($\nu_{\text{C-H}}$), 1586 w ($\nu_{\text{C=C}}$), 1477 w ($\nu_{\text{P-Ph}}$), 1435 m ($\nu_{\text{P-Ph}}$), 1261 s ($\nu_{\text{C-N}}$), 1105 s, 1024 s, 804 s, 744 m ($\omega_{\text{C-H}}$), 698 m ($\omega_{\text{C-H}}$), 662 w ($\omega_{\text{C=C}}$), 496 m ($\omega_{\text{C=C}}$).

(4-Diphenylphosphine oxide)biphenyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-**4**)



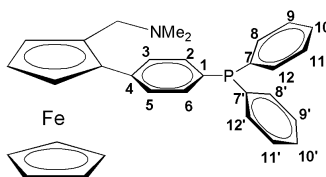
^1H NMR (CDCl_3 , 400 MHz): δ 2.21 (s, 6H, CH_3), 3.13 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2), 3.69 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2), 4.06 (s, 5H, C_5H_5), 4.26 (t br, 1H, $^3J_{\text{HH}} = 2.5$ Hz, C_5H_3), 4.33 (t br, 1H, $^3J_{\text{HH}} = 1.6$ Hz, C_5H_3), 4.53 (t br, 1H, $^3J_{\text{HH}} = 1.85$ Hz, C_5H_3), 7.51-7.47 (m, 4H, aryl- H), 7.58-7.55 (m, 4H, aryl- H), 7.75-7.69 (m, 8H, aryl- H), 7.84-7.82 (m, 2H, aryl- H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161 MHz): δ 28.9 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 45.1 (s, CH_3), 58.1 (s, CH_2), 67.6 (s, C_5H_3), 70.1 (s, C_5H_5), 72.0 (s, C_5H_3), 77.2 (s, C_5H_3), 82.3 (s, C_5H_3), 87.1 (s, C_5H_3), 126.8 (s, C^{16} , $\text{C}^{16'}$ in C_6H_5), 126.8 (d, $^2J_{\text{CP}} = 13.1$ Hz, C^{14} , $\text{C}^{14'}$, C^{18} , $\text{C}^{18'}$ in C_6H_5 or C^9 , C^{11} in C_6H_4), 128.5 (d, $^2J_{\text{CP}} = 12.1$ Hz, C^{14} , $\text{C}^{14'}$, C^{18} , $\text{C}^{18'}$ in C_6H_5 or C^9 , C^{11} in C_6H_4), 129.7 (s), 130.8 and 130.9 (d, $^1J_{\text{CP}} = 105.6$ Hz, C^{13} , $\text{C}^{13'}$ in C_6H_5), 131.9 (d, $^4J_{\text{CP}} = 2.5$ Hz, C^{16} , $\text{C}^{16'}$ in C_6H_5), 132.1 (d, $^3J_{\text{CP}} = 9.6$ Hz, C^{15} , $\text{C}^{15'}$, C^{17} , $\text{C}^{17'}$ in C_6H_5 or C^8 , C^{12} in C_6H_4), 132.6 (d, $^3J_{\text{CP}} = 10.4$ Hz, C^{15} , $\text{C}^{15'}$, C^{17} , $\text{C}^{17'}$ in C_6H_5 or C^8 , C^{12} in C_6H_4), 132.8 (d, $^1J_{\text{CP}} = 104.7$ Hz, C^{10} in C_6H_4), 137.2 (s), 139.4 (s), 144.5 (d, $^4J_{\text{CP}} = 2.7$ Hz, C^7 in C_6H_4) ppm. EI MS: m/z (rel. int. %) 595 (100) $[\text{M}]^+$, 580 (20) $[\text{M} - \text{CH}_3]^+$, 551 (72) $[\text{M} - \text{N}(\text{CH}_3)_2]^+$, 538 (36), 485 (25), 428 (8), 351 (8), 297 (23), 275 (39), 228 (19), 201 (20) $[\text{P}(\text{O})\text{Ph}_2]^+$, 183 (23), 149 (20), 121 (34) $[\text{C}_5\text{H}_5\text{Fe}]^+$, 77 (23) $[\text{Ph}]^+$, 58 (64) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3431 m (br), 3053 w ($\nu_{\text{C-H}}$), 2936 w (ν_{CH_3}), 2854 w (ν_{CH_3}), 2812 w, 2763 w, 1597 w ($\nu_{\text{C=C}}$), 1528 w ($\nu_{\text{C=C}}$), 1490 w ($\nu_{\text{P-Ph}}$), 1455 w ($\nu_{\text{P-Ph}}$), 1436 m, 1385 w, 1305 w, 1259 w ($\nu_{\text{C-N}}$), 1193 s ($\nu_{\text{P-O}}$), 1118 s, 1055 w, 1016 w, 1002 w, 818 s, 753 m ($\omega_{\text{C-H}}$), 727 m ($\omega_{\text{C-H}}$), 707 s ($\omega_{\text{C-H}}$), 562 s ($\omega_{\text{C=C}}$), 540 s ($\omega_{\text{C=C}}$), 513 s ($\omega_{\text{C=C}}$), 470 w ($\omega_{\text{C=C}}$). Elemental analysis: calculated for $\text{C}_{37}\text{H}_{34}\text{FeNOP}$ 74.63 % C, 5.75 % H, 2.35 % N; found 75.13 % C, 5.98 % H, 2.30 % N.

(5-Diphenylphosphine oxide)thienyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-5)



^1H NMR (CDCl_3 , 400 MHz): δ 2.16 (s, 6H, CH_3), 3.08 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2), 3.76 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2), 4.04 (s, 5H, C_5H_5), 4.26 (t, 1H, $^3J_{\text{HH}} = 4.9$ Hz, C_5H_5), 4.32 (s br, 1H, C_5H_5), 4.55 (s br, 1H, C_5H_5), 7.21-7.18 (m, 1H, aryl-*H*), 7.34-7.33 (m, 1H, aryl-*H*), 7.50-7.47 (m, 4H, aryl-*H*), 7.56-7.55 (m, 2H, aryl-*H*), 7.81-7.74 (m, 4H, aryl-*H*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161 MHz): δ 21.8 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 45.0 (s, CH_3), 58.0 (s, CH_2), 67.8 (s, C_5H_5), 70.21 (s, C_5H_5), 70.7 (s, C_5H_5), 72.4 (s, C_5H_5), 78.9 (s, C_5H_5), 82.8 (s, C_5H_5), 126.2 (d, $^2J_{\text{CP}} = 12.2$ Hz, C^6 , $\text{C}^{6'}$, C^{10} , $\text{C}^{10'}$ in C_6H_5), 128.4 (d, $^3J_{\text{CP}} = 11.1$ Hz, C^7 , $\text{C}^{7'}$, C^9 , $\text{C}^{9'}$ in C_6H_5), 130.9 (d, $^1J_{\text{CP}} = 113.8$ Hz, C^5 , $\text{C}^{5'}$ in C_6H_5), 131.9 (d, $^2J_{\text{CP}} = 10.2$ Hz, C^2 in $\text{C}_4\text{H}_2\text{S}$), 132.1 (d, $^4J_{\text{CP}} = 2.5$ Hz, C^8 , $\text{C}^{8'}$ in C_6H_5), 133.1 (d, $^1J_{\text{CP}} = 109.5$ Hz, C^1 in $\text{C}_4\text{H}_2\text{S}$), 137.3 (d, $^3J_{\text{CP}} = 10.4$ Hz, C^3 in $\text{C}_4\text{H}_2\text{S}$), 152.7 (d, $^4J_{\text{CP}} = 5.1$ Hz, C^4 in $\text{C}_4\text{H}_2\text{S}$) ppm. EI MS: m/z (rel. int. %) 525 (100) $[\text{M}]^+$, 481 (96) $[\text{M} - \text{N}(\text{CH}_3)_2]^+$, 468 (6), 415 (15), 361 (6), 324 (9) $[\text{M} - \text{P}(\text{O})\text{Ph}_2]^+$, 241 (20) $[\text{M} - \text{C}_4\text{H}_2\text{SP}(\text{O})\text{Ph}_2]^+$, 202 (15) $[\text{P}(\text{O})\text{Ph}_2 + \text{H}]^+$, 133 (6), 121 (15) $[\text{C}_5\text{H}_5\text{Fe}]^+$, 77 (6) $[\text{Ph}]^+$, 58 (22) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3443 s (br), 3076 w ($\nu_{\text{C-H}}$), 2933 w (ν_{CH_3}), 2854 w (ν_{CH_3}), 2813 w, 2765 w, 1634 m (br) ($\nu_{\text{C=C}}$), 1534 w ($\nu_{\text{C=C}}$), 1460 m ($\nu_{\text{P-Ph}}$), 1437 m ($\nu_{\text{P-Ph}}$), 1408 m, 1308 w, 1260 w ($\nu_{\text{C-N}}$), 1194 s ($\nu_{\text{P-O}}$), 1117 s, 1105 s, 1010 s, 909 w ($\nu_{\text{C-S}}$), 814 m ($\nu_{\text{C-S}}$), 752 w ($\omega_{\text{C-H}}$), 723 s ($\omega_{\text{C-H}}$), 700 s ($\omega_{\text{C=C}}$), 558 s ($\omega_{\text{C=C}}$). Elemental analysis: calculated for $\text{C}_{29}\text{H}_{28}\text{FeNOPS}$ 66.29 % C, 5.37 % H, 2.67 % N; found 66.54 % C, 5.48 % H, 2.60 % N.

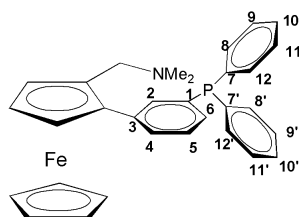
(4-Diphenylphosphino)phenyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-**6**)



^1H NMR (C_6D_6 , 400 MHz): δ 2.09 (s, 6H, CH_3), 2.83 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2) 3.64 (d, 1H, $^2J_{\text{HH}} = 12.8$ Hz, CH_2), 3.85 (s, 5H, C_5H_5), 4.03 (t, 1H, $^3J_{\text{HH}} = 5.0$ Hz, C_5H_3), 4.10 (t, 1H, $^3J_{\text{HH}} = 3.4$ Hz, C_5H_3), 4.38 (s, 1H, C_5H_3), 7.08-7.05 (m, 6H, aryl-*H*), 7.52-7.45 (m, 6H, aryl-*H*), 7.93 (d, 2H, $^2J_{\text{HH}} = 7.1$ Hz, aryl-*H*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161 MHz): δ -5.8 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 44.7 (s, CH_3), 58.2 (s, CH_2), 67.2 (s, C_5H_5), 70.2 (s, C_5H_3), 70.8 (s, C_5H_3), 72.3 (C_5H_3), 82.1 (C_5H_3), 87.2 (C_5H_3), 128.5 (d, $^4J_{\text{CP}} = 5.3$ Hz, C^{10} , $\text{C}^{10'}$ in C_6H_5), 128.5 (d, $^3J_{\text{CP}} = 6.8$ Hz, C^9 , $\text{C}^{9'}$, C^{11} , $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 129.4 (d, $^3J_{\text{CP}} = 6.9$ Hz, C^9 , $\text{C}^{9'}$, C^{11} , $\text{C}^{11'}$ in C_6H_5 or C^3 , C^5 in C_6H_4), 133.7 (d, $^2J_{\text{CP}} = 18.7$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 133.9 (d, $^2J_{\text{CP}} = 19.7$ Hz, C^8 , $\text{C}^{8'}$, C^{12} , $\text{C}^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 134.8 (d, $^1J_{\text{CP}} = 11.5$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 137.9 (d, $^1J_{\text{CP}} = 12.2$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 138.0 (d, $^1J_{\text{CP}} = 12.2$ Hz, C^7 , $\text{C}^{7'}$ in C_6H_5 or C^1 in C_6H_4), 140.3 (s, C^4 in C_6H_4) ppm. EI MS: m/z (rel. int. %) 503 (100) $[\text{M}]^+$, 460 (23) $[\text{M} - \text{N}(\text{CH}_3)_2 + \text{H}]^+$, 274 (41), 183 (33), 163 (12), 152 (18), 121 (41) $[\text{C}_5\text{H}_5\text{Fe}]^+$, 91 (36), 58 (52) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3925 w, 3424 w (br), 3069 w ($\nu_{\text{C-H}}$), 3050 m ($\nu_{\text{C-H}}$), 2967 m (ν_{CH_3}), 2938 m (ν_{CH_3}), 2853 m, 2812 s, 2764 s, 2277 w, 1953 w, 1884 w, 1813 w, 1768 w, 1699 w ($\nu_{\text{C=C}}$), 1595 m ($\nu_{\text{C=C}}$), 1546 w ($\nu_{\text{C=C}}$), 1505 m ($\nu_{\text{C=C}}$), 1477 m ($\nu_{\text{P-Ph}}$), 1454 m ($\nu_{\text{P-Ph}}$), 1433 s ($\nu_{\text{P-Ph}}$), 1386 w, 1362 w, 1338 w, 1305 w, 1258 m ($\nu_{\text{C-N}}$), 1174 m, 1157 w, 1124 m, 1093 s, 1017 s, 1000 m, 971 m, 949 w, 915 w, 830 s, 744 s ($\omega_{\text{C-H}}$), 722 w ($\omega_{\text{C-H}}$), 696 s ($\omega_{\text{C=C}}$), 655 w ($\omega_{\text{C=C}}$), 607 w ($\omega_{\text{C=C}}$).

545 s ($\omega_{C=C}$), 527 s ($\omega_{C=C}$), 499 s ($\omega_{C=C}$), 462 m. Elemental analysis: calculated for $C_{31}H_{30}FeNP$ 73.96 % C, 6.01 % H, 2.78 % N; found 74.25 % C, 6.32 % H, 3.02 % N.

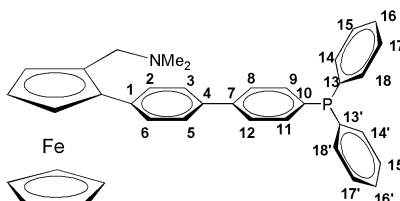
(3-Diphenylphosphino)phenyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-7)



1H NMR (C_6D_6 , 400 MHz): δ 2.09 (s, 6H, CH_3), 2.87 (d, 1H, $^2J_{HH} = 12.8$ Hz, CH_2), 3.61 (d, 1H, $^2J_{HH} = 12.4$ Hz, CH_2), 3.78 (s, 5H, C_5H_5), 3.97 (t, 1H, $^3J_{HH} = 4.9$ Hz, C_5H_3), 4.09 (t, 1H, $^3J_{HH} = 3.4$ Hz, C_5H_3), 4.28 (t, 1H, $^3J_{HH} = 3.5$ Hz, C_5H_3), 7.18-7.04 (m, 7H, aryl-*H*), 7.37 (t, 1H, $^2J_{HH} = 15.5$ Hz, aryl-*H*), 7.54-7.46 (m, 4H, aryl-*H*), 7.94 (d, 1H, $^2J_{HH} = 7.7$ Hz, aryl-*H*), 8.02 (d, 1H, $^2J_{HH} = 7.6$ Hz, aryl-*H*) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6 , 161 MHz): δ -5.1 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6 , 100 MHz): δ 44.7 (s, CH_3), 58.1 (s, CH_2), 67.0 (s, C_5H_3), 70.1 (s, C_5H_5), 70.5 (s, C_5H_3), 71.8 (s, C_5H_3), 82.4 (s, C_5H_3), 87.8 (s, C_5H_3), 128.2 (d, $^3J_{CP} = 8.0$ Hz, C^9 , $C^{9'}$, C^{11} , $C^{11'}$ in C_6H_5 or C^5 in C_6H_4), 128.5 (d, $^3J_{CP} = 7.2$ Hz, C^9 , $C^{9'}$, C^{11} , $C^{11'}$ in C_6H_5 or C^5 in C_6H_4), 128.6 (d, $^3J_{CP} = 6.6$ Hz, C^9 , $C^{9'}$, C^{11} , $C^{11'}$ in C_6H_5 or C^5 in C_6H_4), 129.6 (s, C^{10} , $C^{10'}$ in C_6H_5), 131.7 (d, $^2J_{CP} = 22.8$ Hz, C^8 , $C^{8'}$, C^{12} , $C^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 133.9 (d, $^2J_{CP} = 19.5$ Hz, C^8 , $C^{8'}$, C^{12} , $C^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 134.0 (d, $^2J_{CP} = 19.5$ Hz, C^8 , $C^{8'}$, C^{12} , $C^{12'}$ in C_6H_5 or C^2 , C^6 in C_6H_4), 135.00 (d, $^1J_{CP} = 16.8$ Hz, C^7 , $C^{7'}$ in C_6H_5 or C^1 in C_6H_4), 137.2 (d, $^1J_{CP} = 11.8$ Hz, C^7 , $C^{7'}$ in C_6H_5 or C^1 in C_6H_4), 137.9 (d, $^1J_{CP} = 12.3$ Hz, C^7 , $C^{7'}$ in C_6H_5 or C^1 in C_6H_4), 138.1 (d, $^1J_{CP} = 12.5$ Hz, C^7 , $C^{7'}$ in C_6H_5 or C^1 in C_6H_4), 139.8 (d, $^3J_{CP} = 6.2$ Hz, C^3 in C_6H_4) ppm. EI MS: m/z (rel. int. %) 503 (100) $[M]^+$, 459 (33) $[M - N(CH_3)_2]^+$, 339 (11), 274 (37), 257 (11), 230 (20), 183 (27), 152 (16), 121 (35) $[C_5H_5Fe]^+$, 58 (29) $[CH_2N(CH_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3049 m (ν_{C-H}), 2966 m (ν_{C-H}), 2037 m (ν_{CH_3}), 2853 m

(ν_{CH_3}), 2811 m, 2762 s, 1944 w, 1885 w, 1813 w, 1767 w, 1701 w ($\nu_{\text{C}=\text{C}}$), 1587 s ($\nu_{\text{C}=\text{C}}$), 1566 w ($\nu_{\text{C}=\text{C}}$), 1477 m ($\nu_{\text{P-Ph}}$), 1454 m ($\nu_{\text{P-Ph}}$), 1433 s ($\nu_{\text{P-Ph}}$), 1400 w, 1362 w, 1338 w, 1301 w ($\nu_{\text{C-N}}$), 1260 m ($\nu_{\text{C-N}}$), 1174 m, 1157 w, 1103 s, 1019 s, 999 s, 949 w, 912 w, 790 s ($\omega_{\text{C-H}}$), 743 s ($\omega_{\text{C-H}}$), 696 s ($\omega_{\text{C-H}}$), 615 w ($\omega_{\text{C}=\text{C}}$), 572 w ($\omega_{\text{C}=\text{C}}$), 549 w ($\omega_{\text{C}=\text{C}}$), 494 s ($\omega_{\text{C}=\text{C}}$), 458 w ($\omega_{\text{C}=\text{C}}$), 420 w ($\omega_{\text{C}=\text{C}}$). Elemental analysis: calculated for $\text{C}_{31}\text{H}_{30}\text{FeNP}$ 73.96 % C, 6.01 % H, 2.78 % N; found 74.21 % C, 6.35 % H, 2.98 % N.

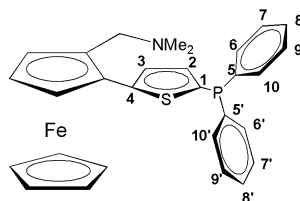
(4-Diphenylphosphino)biphenyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-**8**)



^1H NMR (C_6D_6 , 400 MHz): δ 2.19 (s, 6H, CH_3), 2.91 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2), 3.77 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2), 3.91 (s, 5H, C_5H_5), 7.38-7.34 (m, 12H, aryl- H), 7.55 (d, 2H, $^2J_{\text{HH}} = 8.4$ Hz, aryl- H), 7.60 (d, 2H, $^2J_{\text{HH}} = 7.5$ Hz, aryl- H), 7.79 (d, 2H, $^2J_{\text{HH}} = 8.4$ Hz, aryl- H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161 MHz): δ -6.0 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 45.1 (s, CH_3), 58.1 (s, CH_2), 67.3 (s, C_5H_3), 70.0 (s, C_5H_3), 70.1 (s, C_5H_5), 71.9 (s, C_5H_3), 82.1 (s, C_5H_3), 87.4 (s, C_5H_3), 126.5 (s), 126.86 (d, $^3J_{\text{CP}} = 6.9$ Hz, C^{15} , $\text{C}^{15'}$, C^{17} , $\text{C}^{17'}$ in C_6H_5 or C^8 , C^{12} in C_6H_4), 128.5 (d, $^3J_{\text{CP}} = 7.0$ Hz, C^{15} , $\text{C}^{15'}$, C^{17} , $\text{C}^{17'}$ in C_6H_5 or C^8 , C^{12} in C_6H_4), 128.7 (s), 129.6 (s), 133.8 (d, $^2J_{\text{CP}} = 19.4$ Hz, C^{14} , $\text{C}^{14'}$, C^{18} , $\text{C}^{18'}$ in C_6H_5 or C^9 , C^{11} in C_6H_4), 134.2 (d, $^2J_{\text{CP}} = 19.4$ Hz, C^{14} , $\text{C}^{14'}$, C^{18} , $\text{C}^{18'}$ in C_6H_5 or C^9 , C^{11} in C_6H_4), 135.8 (d, $^1J_{\text{CP}} = 10.8$ Hz, C^{13} , $\text{C}^{13'}$ in C_6H_5 or C^{10} in C_6H_4), 137.2 (d, $^1J_{\text{CP}} = 10.8$ Hz, C^{13} , $\text{C}^{13'}$ in C_6H_5 or C^{10} in C_6H_4), 137.9 (s), 138.6 (s), 141.2 (s) ppm. EI MS: m/z (rel. int. %) 580 (60) $[\text{M}]^+$, 535 (100) $[\text{M} - \text{HN}(\text{CH}_3)_2]^+$, 523 (19), 470 (18), 334 (20), 289 (19), 267 (30), 183 (63), 163 (40), 121 (96) $[\text{C}_5\text{H}_5\text{Fe}]^+$, 58 (98) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3456 s (br), 3069 w ($\nu_{\text{C-H}}$), 2939 w

(ν_{CH_3}), 2854 w (ν_{CH_3}), 2812 w, 2766 w, 1635 m (br) ($\nu_{\text{C}=\text{C}}$), 1528 w ($\nu_{\text{C}=\text{C}}$), 1479 w ($\nu_{\text{P-Ph}}$), 1455 w ($\nu_{\text{P-Ph}}$), 1434 w ($\nu_{\text{P-Ph}}$), 1385 w, 1302 w, 1257 w ($\nu_{\text{C-N}}$), 1175 w, 1105 w, 1018 w, 1002 w, 818 m ($\omega_{\text{C-H}}$), 743 m ($\omega_{\text{C-H}}$), 696 m ($\omega_{\text{C}=\text{C}}$), 502 m ($\omega_{\text{C}=\text{C}}$). Elemental analysis: calculated for $\text{C}_{37}\text{H}_{34}\text{FeNP}$ 76.69 % C, 5.91 % H, 2.42 % N; found 76.38 % C, 6.10 % H, 2.29 % N.

(5-Diphenylphosphino)thienyl-2-*N,N*-dimethylaminomethylferrocene (*rac*-**9**)



^1H NMR (C_6D_6 , 400 MHz): δ 2.10 (s, 6H, CH_3), 2.84 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2) 3.77 (d, 1H, $^2J_{\text{HH}} = 12.4$ Hz, CH_2), 3.86 (s 5H, C_5H_5), 3.93 (t, 1H, $^3J_{\text{HH}} = 4.9$ Hz, C_5H_3), 4.04 (s, 1H, C_5H_3), 4.36 (s, 1H, C_5H_3), 7.10-7.04 (m, 6H, aryl-*H*), 7.26-7.23 (m, 1H, aryl-*H*), 7.58-7.52 (m, 5H, aryl-*H*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161 MHz): δ -19.3 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 44.6 (s, CH_3), 58.2 (s, CH_2), 67.2 (s, C_5H_3), 70.1 (s, C_5H_3), 70.6 (s, C_5H_5), 72.0 (s, C_5H_3), 80.7 (s, C_5H_3), 82.8 (s, C_5H_3), 126.7 (d, $^3J_{\text{CP}} = 7.1$ Hz, C^7 , $\text{C}^{7'}$, C^9 , $\text{C}^{9'}$ in C_6H_5), 128.4 (d, $^3J_{\text{CP}} = 6.7$ Hz, C^7 , $\text{C}^{7'}$, C^9 , $\text{C}^{9'}$ in C_6H_5), 128.6 (s, C^8 , $\text{C}^{8'}$ in C_6H_5), 133.3 (2 overlapping doublets, $^1J_{\text{CP}} = 19.6$ Hz and $^1J_{\text{CP}} = 19.7$ Hz, C^5 , $\text{C}^{5'}$ in C_6H_5), 136.2 (d, $^2J_{\text{CP}} = 27.9$ Hz, C^6 , $\text{C}^{6'}$, C^{10} , $\text{C}^{10'}$ in C_6H_5), 136.9 (d, $^1J_{\text{CP}} = 25.6$ Hz, C^1 in $\text{C}_4\text{H}_2\text{S}$), 138.6 (d, $^2J_{\text{CP}} = 9.6$ Hz, C^2 in $\text{C}_4\text{H}_2\text{S}$), 138.7 (d, $^3J_{\text{CP}} = 9.9$ Hz, C^3 in $\text{C}_4\text{H}_2\text{S}$), 150.1 (s, C^4 in $\text{C}_4\text{H}_2\text{S}$) ppm. EI MS: m/z (rel. int. %) 509 (52) $[\text{M}]^+$, 465 (17) $[\text{M} - \text{N}(\text{CH}_3)_2]^+$, 324 (17) $[\text{M} - \text{PPh}_2]^+$, 280 $[\text{M} - \text{NMe}_2 - \text{PPh}_2]^+$ (19), 183 (8), 121 (26) $[\text{C}_5\text{H}_5\text{Fe}]^+$, 91 (100), 58 (29) $[\text{CH}_2\text{N}(\text{CH}_3)_2]^+$. IR (KBr): $\square$ (cm^{-1}) 3427 m (br), 3083 m ($\nu_{\text{C-H}}$), 3067 m ($\nu_{\text{C-H}}$), 3049 m ($\nu_{\text{C-H}}$), 2964 m (ν_{CH_3}), 2937 m (ν_{CH_3}), 2856 m (ν_{CH_3}), 2815 s, 2768 s, 1948 w, 1891 w, 1771 w, 1645

w ($\nu_{C=C}$), 1584 w ($\nu_{C=C}$), 1538 w ($\nu_{C=C}$), 1475 m(ν_{P-Ph}), 1456 m (ν_{P-Ph}), 1433 s, 1409 m, 1383 w, 1344 w, 1313 w, 1278 w (ν_{C-N}), 1258 m (ν_{C-N}), 1215 m, 1173 m, 1120 m, 1104 m, 1070 m, 1044 m, 1017 s, 999 s, 910 m (ν_{C-S}), 846 m (ν_{C-S}), 824 s, 810 s, 746 s (ω_{C-H}), 696 s (ω_{C-H}), 604 w ($\omega_{C=C}$), 541 s ($\omega_{C=C}$), 513 s ($\omega_{C=C}$), 461 m, 439 m. Elemental analysis: calculated for $C_{29}H_{28}FeNPS$ 68.37 %, 5.54 % H, 2.75 % N; found 68.83 % C, 5.90 % H, 2.80 % N.