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权利要求书 2 页 说明书 24 页

[54]发明名称 一种具有多种手性中心的二茂铁噁唑啉膦配件、合成方法及用途

[57]摘要

本发明是一种具有多种手性中心的二茂铁噁唑啉膦配体、合成及用途，该配体中含有噁唑啉、膦原子的中心手性和取代反应物的轴或中心手性等，其由二(二胺基)膦取代的二茂铁噁唑啉与手性的二醇、二胺、二酚、二硫醇或二硫酚经催化反应制得。再生的一个手性的膦通常可用柱层析或重结晶分开。该类配体在烯丙基取代反应中对映选择性好，尤其对单取代的反应底物区域选择性好，在氢化，硅氢化等不对称催化反应中亦有较好的应用前景。

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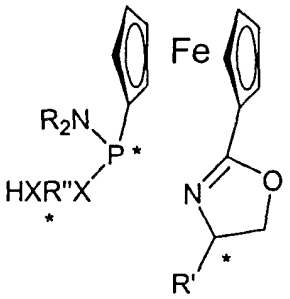
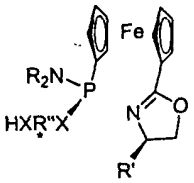
1. 一种具有多种手性中心的二茂铁噁唑啉膦配体，其分子通式为：



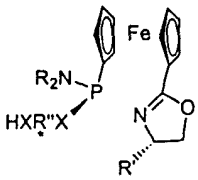
其中：R = 苯基、萘基或1-8个碳的烷基，
R′ = 苯基、萘基或1-8个碳的烷基，
R′′= 5-32个碳的烷基或芳基，
X = NH、O或S。

2. 如权利要求 1 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体，其分子通式为：



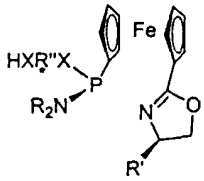
，其中 R、R′ 、R″ 、X 如权利要求 1 所述。

3. 如权利要求 1 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体，其分子通式为：



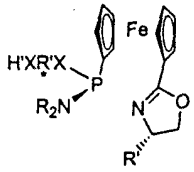
，其中 R、R′ 、R″ 、X 如权利要求 1 所述。

4. 如权利要求 1 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体，其分子通式为：



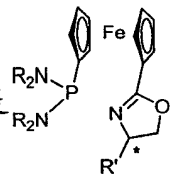
，其中 R、R′ 、R″ 、X 如权利要求 1 所述。

5. 如权利要求 1 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体，其分子通式为：



，其中 R、R′ 、R″ 、X 如权利要求 1 所述。

6. 如权利要求 1 所述一种具有多种手性中心的二茂铁噁唑啉膦配体的合成方法，其特征是

取代的二茂铁-4-取代的噁唑啉具有分子通式是  ，所述的 R′′XH =5-32 个碳的手性二醇、手性二胺、手性二酚、手性二硫醇或手性二硫酚，所述的催化剂是氮原子上含有孤对电子的有机胺化合物，式中 R、R′ 、R′′、X 如权利要求 1 所述。

7. 如权利要求 6 所述一种具有多种手性中心的二茂铁噁唑啉膦配体的合成方法，其特征是所述的有机溶剂是包括苯、四氯化碳、四氢呋喃、乙醚、二氯甲烷、甲苯、环己烷、石油醚、丙酮、吡啶、$CHCl_3$、正己烷、正庚 烷、二氧六环在内的极性或非极性溶剂。

8. 权利要求 6 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体的合成方法，其特征是所述的氮原子上含有孤对电子的有机胺化合物是四甲基二乙胺、联二吡啶、三辛胺、对二甲胺基吡啶，三乙胺，二异丙基乙基胺。

9. 权利要求 6 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体的合成方法，其特征是反应产物可以用柱层析或重结晶的方法拆分。

10. 权利要求 1 所述的一种具有多种手性中心的二茂铁噁唑啉膦配体的用途，其特征是用于制备具有手性的烯丙基羧酸或氨基衍生物。

一种具有多种手性中心的二茂铁噁唑啉膦配体、合成方法及用途

本发明涉及一类手性配体、合成方法及用途，即一种具有多种手性中心的二茂铁噁唑啉膦配体、合成方法及用途。

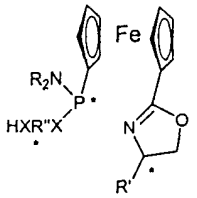
手性噁唑啉膦配体是一类重要的手性配体，G. Helmchen 和 A. Pfaltz 在 *Acc. Chem. Res.* 2000, *33*, 336 中公开了苯环衍生的噁唑啉膦配体（PHOX）在不对称催化反应中的应用。尽管他们这种配体在烯丙基胺化，烯丙基烷基化反应中产物的产率和对映选择性都比较好，但是对于区域选择性的烯丙基化的反应及 Heck 反应则不是很令人满意，而且对于工业上应用意义较大的氢化反应，硅氢化反应等结果也还很不理想。为此寻找新的手性配体使之适用于一些反应或更多反应并能有高的催化活性及对映选择性一直是化学工作者的研究热点之一。

本发明的目的之一就是提供一种具有多种手性中心的二茂铁噁唑啉膦配体。

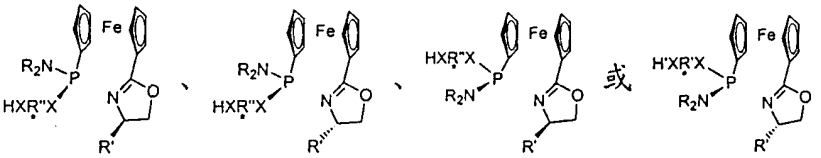
本发明的目的之二是提供该种二茂铁噁唑啉膦配体的合成方法。

本发明的目的之三是提供该种二茂铁噁唑啉膦配体的用途。

本发明提供了一种具有多种手性中心的二茂铁噁唑啉膦配体，其分子通式是



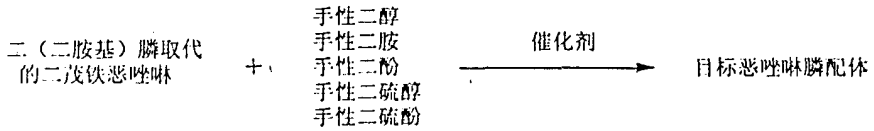
其中：R = 苯基、萘基或1-8个碳的烷基
R′ = 苯基、萘基或1-8个碳的烷基
R′′= 5-32个碳的烷基或芳基
X = NH、O、S

具体来说可以是 

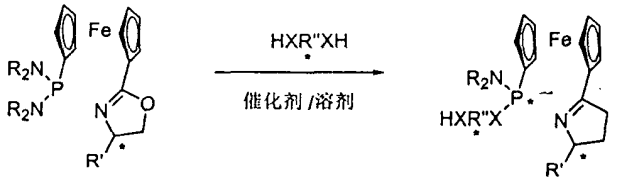
。

这类配体中 R = 苯基、萘基或 1-8 个碳的烷基取代基；R'= 苯基、萘基或 1-8 个碳的烷基取代基；R′′=5-32 个碳的烷基或芳基；X= NH、O 或 S。一般来说，上述配体中的 P 和 N 上具有中心手性，HX R′′X 具有轴手性或中心手性。

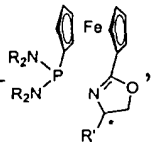
本发明的化合物的合成方法是由二（二胺基）膦取代的二茂铁噁唑啉与分子通式为 HXR"XH 的手性化合物反应制得，反应中还可加入催化剂。其反应式如下：



用结构式可表述为：

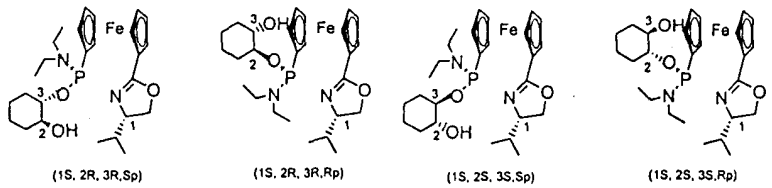


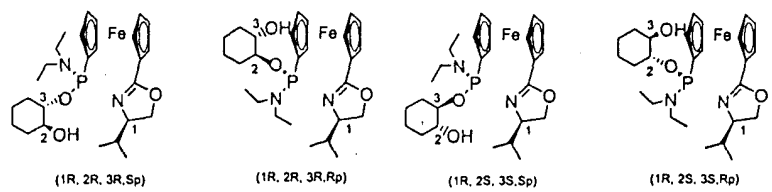
1

具体的合成步骤是：在有机溶剂中和 0-150°C 的温度条件下，二（二胺基）膦取代的二茂铁-4-取代的噁唑啉与分子通式 HXR''XH 的手性化合物及催化剂的摩尔比依次为 1: 0.8-5: 0-0.2，反应 1-50 小时。反应温度越低，反应时间越长。所述的二（二胺基）膦取代的二茂铁-4-取代的噁唑啉具有分子通式是  ，式中 R、R′ 如前所述，HXR''XH 是 5-32 个碳的手性二醇、手性二胺、手性二酚、手性二硫醇或手性二硫酚，例如联二萘酚、带有取代基的联二萘酚、联二萘胺、联二萘硫酚等，上述 R''、X 如前所述。在不加催化剂的条件下，反应仍可进行。所述的有机溶剂为极性或非极性溶剂，如苯、四氯化碳、四氢呋喃、乙醚、二氯甲烷、甲苯、环己烷、石油醚、丙酮、吡啶、$CHCl_3$、正己烷、正庚烷、二氧六环等。所述的催化剂为氮原子上含有孤对电子的有机胺化合物，如四甲基二乙胺、联二吡啶、三辛胺、对二甲胺基吡啶，三乙胺，二异丙基乙基胺等。该配体制备过程中会再生一个手性的膦。反应产生的异构体通常可以用柱层析或重结晶的方法顺利分开。反应产物即本发明的一种具有多种手性中心的二茂铁噁唑啉膦配体。

本发明还提供了此目标化合物－二茂铁噁唑啉膦配体的用途，即应用在钯催化烯丙基化反应中，用各种烯丙基醋酸酯或碳酸酯作为底物，利用丙二酸衍生物及各种胺类化合物作为亲核试剂时，可以得到具有手性的烯丙基羧酸或氨基衍生物。

本发明提供了一种全新的配体，该配体的合成方法简便、条件温和，适于工业化。该配体用于制备具有手性的烯丙基羧酸或氨基衍生物，与现有的技术相比，反应速率、产率、对映选择性及区域选择性都好，并且由于它们具有二茂铁骨架及多手性中心的特点，在过渡金属催化的不对称反应中具有很高的催化活性和手性诱导效果，而且有很强的调节能力。上述特点可以用以下实例给予说明，当 R=-CH_2CH_3，R'=-$CH(CH_3)_3$，和光学纯的反式环己二醇反应时，有三个手性中心，共有 8 个配体，如下：





这类配体很可能在氢化，硅氢化等不对称催化反应中有较好的应用前景。

以下实施例有助于理解本发明，但不限于本发明的内容。

实施例一

（构型为 R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 联二萘酚）

室温，471 mg (1 mmol) (S)-二（二乙基胺基）膦二茂铁 唑啉 1（R = C_2H_5; R'= i-$CH(CH_3)_2$），286-572mg (1-2 mmol) （R）-联萘酚，催化量的对二甲胺基吡啶或四甲基二乙胺(5%)溶于 5 mL 乙醚或四氢呋喃中，所得的黄色溶液在 20-40℃反应 10-48 小时，TLC 跟踪至反应结束，用水洗，饱和食盐水洗，无水硫酸钠干燥，减压除去溶剂，柱层析纯化，得到两个橙黄色固体 588 mg，总产率为 86%。

P1 (S, S_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = 联二萘酚)

mp 136-138 °C; $[\alpha]_D^{25}$ = -410° (c, 0.37, $CHCl_3$);

^{1}H NMR δ 7.83-8.06 (m, 5H), 7.21-7.37 (m, 7H), 5.21 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, J = 7.5 Hz, 4H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.75 (t, J = 7.0 Hz, 6H);

^{31}P NMR (161.92 MHz, $CDCl_3$) δ 127.87;

MS m/z 684 (M^+, 5), 611 (65), 541 (100), 399 (28), 286 (17);

IR (KBr) 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 69.82; H, 6.14; N, 3.87.

P2 (S, R_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = 联二萘酚)

橙色固体: mp 99-101 °C; $[\alpha]_D^{25}$ = 493° (c, 0.54, $CHCl_3$);

^{1}H NMR δ 9.90 (br, 1H), 7.79-7.99 (m, 5H), 7.12-7.41 (m, 7H), 5.17 (t, J = 1.2 Hz, 1H), 4.57 (t, J = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, J = 8.0 Hz, 1H), 4.06 (m, 1H), 4.00 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 1.84 (m, 1H), 1.00 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H), 0.50 (t, J = 6.9 Hz, 6H);

^{31}P NMR (161.92 MHz, $CDCl_3$) δ 117.94;

MS m/z 684 (M^+, 8), 611 (48), 540 (100), 399 (85), 313 (33), 286 (65);

IR (KBr) 3051, 2962, 1640, 1589, 1461, 1232, 1024, 810;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.34; H, 6.31; N, 3.83.

同以上条件，从各种二（二胺基）膦取代的二茂铁噁唑啉出发，和各种手性二醇，手性二胺或手性二酚等在催化剂的催化下可以得到大量的配体。 其数据如下:

P3 (S, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = 联二萘酚);

^{1}H NMR δ 7.80-8.09 (m, 5H), 7.19-7.39 (m, 7H), 5.22 (br, 1H), 4.45 (m, 1H), 4.39 (m, 1H), 4.23 (dd, J = 8.6, 9.1 Hz, 1H), 4.12 (s, 1H), 4.09 (s, 1H), 3.89-4.03 (m, 4H), 3.73 (m, 1H), 3.35 (s, 1H), 2.87 (t, J = 7.5 Hz, 4H), 1.82 (m, 1H), 0.97 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.74 (t, J = 7.0 Hz, 6H);

MS m/z 684;

IR (KBr) 3054, 2965, 1644, 1502, 1466, 1240, 1126;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 69.99; H, 6.11; N, 3.89.

P4 (*S*, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = 联二萘酚);

^1H NMR δ 9.90 (br, 1H), 7.78-7.99 (m, 5H), 7.10-7.41 (m, 7H), 5.16 (t, *J* = 1.2 Hz, 1H), 4.55 (t, *J* = 1.1 Hz, 1H), 4.31-4.40 (m, 4H), 4.21-4.26 (m, 1H), 4.12 (t, *J* = 8.0 Hz, 1H), 4.07 (m, 1H), 4.00 (m, 1H), 3.78 (m, 1H), 2.35-2.60 (m, 4H), 1.83 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.50 (t, *J* = 6.9 Hz, 6H);

MS *m/z* 684; 286;

IR (KBr) 3055, 2968, 1641, 1586, 1460, 1230, 1023;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.14; H, 6.03; N, 3.99.

P5 (*R*, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = 联二萘酚);

^1H NMR δ 7.83-8.09 (m, 5H), 7.23-7.39 (m, 7H), 5.24 (br, 1H), 4.54 (m, 1H), 4.41 (m, 1H), 4.23 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.14 (s, 1H), 4.07 (s, 1H), 3.89-4.03 (m, 4H), 3.73 (m, 1H), 3.37 (s, 1H), 2.85 (t, *J* = 7.5 Hz, 4H), 1.83 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 684, 541, 286;

IR (KBr) 3050, 2964, 1643, 1500, 1468, 1239, 1123;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 69.88; H, 6.10; N, 3.94.

P6 (*R*, S_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 联二萘酚);

^1H NMR δ 9.90 (br, 1H), 7.75-7.98 (m, 5H), 7.10-7.41 (m, 7H), 5.15 (t, *J* = 1.2 Hz, 1H), 4.55 (t, *J* = 1.1 Hz, 1H), 4.34-4.45 (m, 4H), 4.21-4.26 (m, 1H), 4.10 (t, *J* = 8.0 Hz, 1H), 4.07 (m, 1H), 4.01 (m, 1H), 3.79 (m, 1H), 2.39-2.60 (m, 4H), 1.85 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.51 (t, *J* = 6.8 Hz, 6H);

MS *m/z* 684, 611, 286;

IR (KBr) 3050, 2964, 1642, 1582, 1463, 1234, 1021;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.21; H, 6.07; N, 3.91.

P7 (*R*, R_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 联二萘酚);

^1H NMR δ 7.83-8.05 (m, 5H), 7.21-7.39 (m, 7H), 5.20 (br, 1H), 4.54 (m, 1H), 4.39 (m, 1H), 4.21 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.14 (s, 1H), 4.09 (s, 1H), 3.89-4.03 (m, 4H), 3.74 (m, 1H), 3.36 (s, 1H), 2.87 (t, *J* = 7.5 Hz, 4H), 1.83 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 6.7 Hz, 6H);

MS *m/z* 684, 611, 541, 286;

IR (KBr) 3052, 2962, 1641, 1504, 1467, 1236, 1123;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 7.32; H, 6.18; N, 3.89.

P8 (*R*, S_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 联二萘酚);

^1H NMR δ 9.93 (br, 1H), 7.79-8.09 (m, 5H), 7.12-7.45 (m, 7H), 5.15 (t, *J* = 1.2 Hz, 1H), 4.56 (t, *J* = 1.1 Hz, 1H), 4.30-4.45 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H),

4.05 (m, 1H), 4.02 (m, 1H), 3.78 (m, 1H), 2.38-2.56 (m, 4H), 1.85 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H), 0.49 (t, J = 6.9 Hz, 6H);

MS *m/z* 684, 611, 286;

IR (KBr) 3049, 2960, 1639, 1589, 1461, 1232, 1023;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.38; H, 6.20; N, 4.31.

P9 (S, S_{Phos}, R_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 7.85-8.05 (m, 5H), 7.21-7.37 (m, 7H), 5.22 (br, 1H), 4.54 (t, J = 1.2 Hz, 1H), 4.39 (t, J = 1.2 Hz, 1H), 4.08-4.20 (m, 4H), 3.97 (m, 1H), 3.89 (m, 1H), 3.84 (dd, J = 7.7, 10.0 Hz, 1H), 3.70 (m, 1H), 3.37 (m, 1H), 2.85 (m, 4H), 0.93 (s, 9H), 0.75 (t, J = 7.1 Hz, 6H);

MS *m/z* 698, 625, 413, 313, 242;

IR (KBr) 3541, 3055, 2964, 1648, 1589, 1505, 1459, 1123;

元素分析 $C_{41}H_{43}N_2O_3PFe$:

计算值: C, 70.69; H, 6.17; N, 4.02; 实测值: C, 70.96; H, 6.29; N, 3.95.

P10 (S, R_{Phos}, R_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 8.89 (br, 1H), 7.79-8.01 (m, 5H), 7.12-7.35 (m, 12H), 5.45 (dd, J = 8.3, 9.6 Hz, 1H), 5.17 (s, 1H), 4.76 (dd, J = 8.6, 9.8 Hz, 1H), 4.68 (s, 1H), 4.48 (m, 1H), 4.36 (m, 2H), 4.19 (t, J = 8.1 Hz, 1H), 4.08-4.11 (m, 2H), 3.80 (s, 1H), 2.63-2.41 (m, 4H), 0.53 (t, J = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;

IR (KBr) 3109, 2927, 1639, 1590, 1504, 1457, 1263, 1129;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.69; H, 5.77; N, 3.66.

P11 (S, R_{Phos}, S_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 7.79-8.04 (m, 5H), 7.12-7.38 (m, 12H), 5.44 (dd, J = 8.3, 9.8 Hz, 1H), 5.22 (br, 1H), 5.16 (s, 1H), 4.76 (dd, J = 8.6, 9.8 Hz, 1H), 4.69 (s, 1H), 4.52 (m, 1H), 4.38 (m, 2H), 4.21 (t, J = 8.1 Hz, 1H), 4.08-4.13 (m, 2H), 3.81 (s, 1H), 2.63-2.42 (m, 4H), 0.75 (t, J = 7.0 Hz, 6H);

MS *m/z* 643, 541, 286;

IR (KBr) 3112, 2926, 1639, 1593, 1502, 1455, 1263;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.79; H, 5.57; N, 3.76.

P12 (S, S_{Phos}, S_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 9.92 (br, 1H), 7.79-8.03 (m, 5H), 7.12-7.38 (m, 12H), 5.44 (dd, J = 8.3, 9.7 Hz, 1H), 5.16 (s, 1H), 4.76 (dd, J = 8.6, 9.8 Hz, 1H), 4.67 (s, 1H), 4.45 (m, 1H), 4.34 (m, 2H), 4.17 (t, J = 8.1 Hz, 1H), 4.07-4.13 (m, 2H), 3.82 (s, 1H), 2.61-2.40 (m, 4H), 0.50 (t, J = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;

IR (KBr) 3109, 2926, 1639, 1591, 1504, 1459, 1265, 1129;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.88; H, 5.52; N, 3.69.

P13 (*R*, R_{Phos}, S_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 7.79-8.01 (m, 5H), 7.12-7.34 (m, 12H), 5.44 (dd, *J* = 8.3, 9.6 Hz, 1H), 5.22 (br, 1H), 5.16 (s, 1H), 4.76 (dd, *J* = 8.6, 9.8 Hz, 1H), 4.70 (s, 1H), 4.45 (m, 1H), 4.37 (m, 2H), 4.189 (t, *J* = 8.1 Hz, 1H), 4.08-4.11 (m, 2H), 3.83 (s, 1H), 2.63-2.40 (m, 4H), 0.74 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;

IR (KBr) 3107, 2926, 1637, 1591, 1503, 1455, 1263, 1127;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.99; H, 5.49; N, 3.75.

P14 (*R*, S_{Phos}, S_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 8.96 (br, 1H), 7.74-8.03 (m, 5H), 7.11-7.33 (m, 12H), 5.42 (dd, *J* = 8.3, 9.9 Hz, 1H), 5.15 (s, 1H), 4.76 (dd, *J* = 8.6, 9.8 Hz, 1H), 4.69 (s, 1H), 4.52 (m, 1H), 4.39 (m, 2H), 4.18 (t, *J* = 8.1 Hz, 1H), 4.08-4.13 (m, 2H), 3.83 (s, 1H), 2.63-2.42 (m, 4H), 0.54 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;

IR (KBr) 3109, 2927, 1642, 1589, 1502, 1457, 1263, 1126;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.82; H, 5.58; N, 3.92.

P15 (*R*, S_{Phos}, R_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 7.79-8.04 (m, 5H), 7.12-7.36 (m, 12H), 5.43 (dd, *J* = 8.3, 9.6 Hz, 1H), 5.23 (br, 1H), 5.17 (s, 1H), 4.75 (dd, *J* = 8.6, 9.8 Hz, 1H), 4.69 (s, 1H), 4.49 (m, 1H), 4.38 (m, 2H), 4.19 (t, *J* = 8.1 Hz, 1H), 4.08-4.11 (m, 2H), 3.82 (s, 1H), 2.63-2.43 (m, 4H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;

IR (KBr) 3111, 2928, 1640, 1590, 1504, 1459, 1263, 1127;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.76; H, 5.62; N, 3.82.

P16 (*R*, R_{Phos}, R_A, R = C_2H_5; R'= $-C(CH_3)_3$; R''XH = 联二萘酚)

^{1}H NMR δ 9.01 (br, 1H), 7.79-8.01 (m, 5H), 7.11-7.35 (m, 12H), 5.46 (dd, *J* = 8.3, 9.6 Hz, 1H), 5.16 (s, 1H), 4.77 (dd, *J* = 8.6, 9.8 Hz, 1H), 4.69 (s, 1H), 4.50 (m, 1H), 4.37 (m, 2H), 4.20 (t, *J* = 8.1 Hz, 1H), 4.08-4.13 (m, 2H), 3.80 (s, 1H), 2.63-2.41 (m, 4H), 0.53 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 643, 435, 286;

IR (KBr) 3109, 2927, 1640, 1593, 1502, 1457, 1263, 1125;

元素分析 $C_{43}H_{39}N_2O_3PFe$:

计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.77; H, 5.67; N, 3.75.

P17 (*S*, S_{Phos}, R_A, R = C_2H_5; R'=$-C_6H_5$; R''XH = 联二萘酚)

^{1}H NMR δ 8.89 (br, 1H), 7.79-8.01 (m, 5H), 7.12-7.35 (m, 12H), 5.45 (dd, *J* = 8.3, 9.6 Hz, 1H), 5.17 (s, 1H), 4.76 (dd, *J* = 8.6, 9.8 Hz, 1H), 4.68 (s, 1H), 4.48 (m, 1H), 4.36 (m, 2H), 4.19 (t, *J* = 8.1 Hz, 1H), 4.08-4.11 (m, 2H), 3.80 (s, 1H), 2.63-2.41 (m, 4H), 0.53 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;

IR (KBr) 3109, 2927, 1639, 1590, 1504, 1457, 1263, 1129;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, C, 71.93; H, 5.43; N, 3.90; 实测值: C, C, 71.69; H, 5.77; N, 3.66.
P18 (*S*, R_{Phos}, R_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^1H NMR δ 7.81-8.05 (m, 5H), 7.22-7.41 (m, 12H), 5.18 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.62 (t, *J* = 8.3, 9.9 Hz, 1H), 4.60 (m, 1H), 4.48 (m, 1H), 4.20-4.11 (m, 3H), 4.01 (m, 1H), 3.90 (m, 1H), 3.77 (m, 1H), 3.41 (m, 1H), 2.80-2.88 (m, 4H), 2.04 (br, 1H), 0.76 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 643, 541, 435, 286;
IR (KBr) 3056, 2966, 1641, 1590, 1503, 1461, 1232, 1125, 1024;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.73; H, 5.68; N, 3.84.
P19 (*S*, R_{Phos}, S_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^1H NMR δ 8.91 (br, 1H), 7.81-8.06 (m, 5H), 7.22-7.43 (m, 12H), 5.18 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.62 (t, *J* = 8.3, 9.9 Hz, 1H), 4.60 (m, 1H), 4.48 (m, 1H), 4.20-4.13 (m, 3H), 4.02 (m, 1H), 3.91 (m, 1H), 3.78 (m, 1H), 3.41 (m, 1H), 2.80-2.89 (m, 4H), 0.49 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 643, 541, 435, 286;
IR (KBr) 3050, 2969, 1644, 1592, 1463, 1231, 1125;
Anal. Calc. For $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.83; H, 5.65; N, 3.86.
P20 (*S*, S_{Phos}, S_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^1H NMR δ 7.81-8.05 (m, 5H), 7.22-7.42 (m, 12H), 5.17 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.63 (t, *J* = 8.3, 9.9 Hz, 1H), 4.60 (m, 1H), 4.48 (m, 1H), 4.20-4.12 (m, 3H), 4.03 (m, 1H), 3.91 (m, 1H), 3.75 (m, 1H), 3.41 (m, 1H), 2.80-2.88 (m, 4H), 2.09 (br, 1H), 0.76 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 643, 541, 435, 286;
IR (KBr) 3056, 2966, 1640, 1592, 1500, 1024;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.99; H, 5.59; N, 3.74.
P21 (*R*, R_{Phos}, S_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^1H NMR δ 8.92 (br, 1H), 7.81-8.02 (m, 5H), 7.20-7.41 (m, 12H), 5.17 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.61 (t, *J* = 8.3, 9.9 Hz, 1H), 4.60 (m, 1H), 4.50 (m, 1H), 4.22-4.11 (m, 3H), 4.02 (m, 1H), 3.91 (m, 1H), 3.78 (m, 1H), 3.41 (m, 1H), 2.80-2.88 (m, 4H), 0.50 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 643, 541, 435, 286;
IR (KBr) 3056, 2966, 1642, 1590, 1501, 1461, 1232, 1125, 1024;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.76; H, 5.62; N, 3.77.
P22 (*R*, S_{Phos}, S_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^1H NMR δ 7.81-8.05 (m, 5H), 7.22-7.41 (m, 12H), 5.17 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.64 (t, *J* = 8.3, 9.9 Hz, 1H), 4.60 (m, 1H), 4.48 (m, 1H), 4.20-4.11 (m, 3H), 4.01 (m, 1H), 3.90 (m, 1H), 3.77 (m, 1H), 3.41 (m, 1H), 2.80-2.88 (m, 4H), 2.06 (br, 1H), 0.76 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 643, 541, 435, 286;
IR (KBr) 3056, 2966, 1640, 1591, 1503, 1232, 1125;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.69; H, 5.70; N, 3.96.

P23 (*R*, S_{Phos}, R_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^{1}H NMR δ 8.93 (br, 1H), 7.80-8.05 (m, 5H), 7.22-7.41 (m, 12H), 5.18 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.63 (t, *J* = 8.3, 9.9 Hz, 1H), 4.61 (m, 1H), 4.49 (m, 1H), 4.20-4.11 (m, 3H), 4.02 (m, 1H), 3.91 (m, 1H), 3.77 (m, 1H), 3.41 (m, 1H), 2.80-2.88 (m, 4H), 0.49 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 643, 541, 435, 286;
IR (KBr) 3056, 2969, 1641, 1590, 1464, 1232, 1024;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.75; H, 5.69; N, 3.73.

P24 (*R*, R_{Phos}, R_A, R = C_2H_5; R'= $-C_6H_5$; R''XH = 联二萘酚)
^{1}H NMR δ 7.81-8.04 (m, 5H), 7.22-7.41 (m, 12H), 5.20 (dd, *J* = 8.0, 9.9 Hz, 1H), 4.64 (t, *J* = 8.3, 9.9 Hz, 1H), 4.61 (m, 1H), 4.48 (m, 1H), 4.20-4.13 (m, 3H), 4.02 (m, 1H), 3.91 (m, 1H), 3.77 (m, 1H), 3.41 (m, 1H), 2.80-2.89 (m, 4H), 2.04 (br, 1H), 0.76 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 643, 541, 435, 286;
IR (KBr) 3055, 2967, 1641, 1594, 1503, 1461;
元素分析 $C_{43}H_{39}N_2O_3PFe$:
计算值: C, 71.93; H, 5.43; N, 3.90; 实测值: C, 71.83; H, 5.68; N, 3.79.

P25 (*S*, S_{Phos}, R_A, R = C_2H_5; R'=$-CH_2C_6H_5$; R''XH = 联二萘酚)
^{1}H NMR δ 9.25 (br, 1H), 7.79-8.03 (m, 5H), 7.11-7.41 (m, 12H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.59-4.64 (m, 1H), 4.57 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.33 (m, 3H), 4.07 (dd, *J* = 7.2, 8.1 Hz, 1H), 3.92 (m, 1H), 3.74 (m, 1H), 3.17 (dd, *J* = 5.0, 13.7 Hz, 1H), 2.67 (dd, *J* = 8.9, 13.8 Hz, 1H), 2.41-2.62 (m, 4H), 0.53 (t, *J* = 7.0 Hz, 6H);
MS *m/z* 732, 659, 541, 447, 315, 286;
IR (KBr) 3055, 2967, 1639, 1589, 1504, 1461, 1232, 1023;
元素分析 $C_{44}H_{41}N_2O_3PFe$:
计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 72.00; H, 5.66; N, 3.85.

P26 (*S*, R_{Phos}, R_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)
^{1}H NMR δ 7.82-8.05 (m, 5H), 7.21-7.39 (m, 12H), 5.24 (br, 1H), 4.52 (m, 1H), 4.34-4.42 (m, 2H), 4.18 (t, *J* = 8.6 Hz, 1 H), 4.05-4.13 (m, 2H),), 4.01 (t, *J* = 7.8 Hz, 1 H), 3.94 (m, 1H), 3.88 (m, 1H), 3.73 (m, 1H), 3.39 (m, 1H), 3.18 (dd, *J* = 4.7, 13.7 Hz, 1H), 2.86 (m, 4H), 2.67 (dd, *J* = 9.1, 13.7 Hz, 1H), 0.76 (t, *J* = 7.0 Hz, 6 H);
MS *m/z* 732, 659, 541, 447, 315, 286;
IR (KBr) 3055, 2966, 1641, 1588, 1504, 1458, 1226, 1023;
元素分析 $C_{44}H_{41}N_2O_3PFe$:
计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 71.73; H, 5.94; N, 3.69.

P27 (*S*, R_{Phos}, S_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)
^{1}H NMR δ 9.25 (br, 1H), 7.82-8.04 (m, 5H), 7.21-7.39 (m, 12H), 4.52 (m, 1H), 4.34-4.42 (m, 2H), 4.17 (t, *J* = 8.6 Hz, 1 H), 4.05-4.13 (m, 2H),), 4.02 (t, *J* = 7.8 Hz, 1 H), 3.94 (m,

1H), 3.88 (m, 1H), 3.74 (m, 1H), 3.39 (m, 1H), 3.18 (dd, J = 4.7, 13.7 Hz, 1H), 2.87 (m, 4H), 2.67 (dd, J = 9.1, 13.7 Hz, 1H), 0.51 (t, J = 7.0 Hz, 6 H);

MS m/z 732, 541, 286;

IR (KBr) 3055, 2966, 1640, 1589, 1504, 1458, 1226, 1023;

元素分析 $C_{44}H_{41}N_2O_3PFe$:

计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 71.93; H, 5.89; N, 3.78.

P28 (S, S_{Phos}, S_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)

^{1}H NMR δ 7.81-8.05 (m, 5H), 7.21-7.39 (m, 12H), 5.26 (br, 1H), 4.52 (m, 1H), 4.34-4.44 (m, 2H), 4.18 (t, J = 8.6 Hz, 1 H), 4.05-4.13 (m, 2H),), 4.01 (t, J = 7.8 Hz, 1 H), 3.94 (m, 1H), 3.88 (m, 1H), 3.74 (m, 1H), 3.39 (m, 1H), 3.18 (dd, J = 4.7, 13.7 Hz, 1H), 2.86 (m, 4H), 2.67 (dd, J = 9.1, 13.7 Hz, 1H), 0.73 (t, J = 7.0 Hz, 6 H);

MS m/z 732, 541, 286;

IR (KBr) 3055, 2966, 1641, 1587, 1504, 1458, 1225, 1023;

元素分析 $C_{44}H_{41}N_2O_3PFe$:

计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 71.99; H, 5.79; N, 3.77.

P29 (R, R_{Phos}, S_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)

^{1}H NMR δ 9.22 (br, 1H), 7.82-8.05 (m, 5H), 7.21-7.37 (m, 12H), 4.54 (m, 1H), 4.34-4.42 (m, 2H), 4.18 (t, J = 8.6 Hz, 1 H), 4.05-4.13 (m, 2H),), 4.01 (t, J = 7.8 Hz, 1 H), 3.95 (m, 1H), 3.88 (m, 1H), 3.73 (m, 1H), 3.38 (m, 1H), 3.18 (dd, J = 4.7, 13.7 Hz, 1H), 2.86 (m, 4H), 2.66 (dd, J = 9.1, 13.7 Hz, 1H), 0.52 (t, J = 7.0 Hz, 6 H);

MS m/z 732, 659, 541, 286;

IR (KBr) 3054, 2966, 1640, 1588, 1502, 1458, 1226, 1023;

元素分析 $C_{44}H_{41}N_2O_3PFe$:

计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 71.99; H, 5.81; N, 3.67.

P30 (R, S_{Phos}, S_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)

^{1}H NMR δ 7.82-8.06 (m, 5H), 7.25-7.39 (m, 12H), 5.25 (br, 1H), 4.53 (m, 1H), 4.34-4.42 (m, 2H), 4.18 (t, J = 8.6 Hz, 1 H), 4.05-4.15 (m, 2H),), 4.03 (t, J = 7.8 Hz, 1 H), 3.95 (m, 1H), 3.88 (m, 1H), 3.73 (m, 1H), 3.39 (m, 1H), 3.19 (dd, J = 4.7, 13.7 Hz, 1H), 2.86 (m, 4H), 2.66 (dd, J = 9.1, 13.7 Hz, 1H), 0.76 (t, J = 7.0 Hz, 6 H);

MS m/z 732, 659, 541, 286;

IR (KBr) 3055, 2966, 1641, 1590, 1458, 1226, 1023;

元素分析 $C_{44}H_{41}N_2O_3PFe$:

计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 71.94; H, 5.72; N, 3.99.

P31 (R, S_{Phos}, R_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)

^{1}H NMR δ 9.23 (br, 1H), 7.82-8.05 (m, 5H), 7.21-7.39 (m, 12H), 4.53 (m, 1H), 4.34-4.45 (m, 2H), 4.19 (t, J = 8.6 Hz, 1 H), 4.05-4.13 (m, 2H),), 4.01 (t, J = 7.8 Hz, 1 H), 3.94 (m, 1H), 3.88 (m, 1H), 3.75 (m, 1H), 3.39 (m, 1H), 3.18 (dd, J = 4.7, 13.7 Hz, 1H), 2.86 (m, 4H), 2.66 (dd, J = 9.1, 13.7 Hz, 1H), 0.52 (t, J = 7.0 Hz, 6 H);

MS m/z 732, 659, 541, 286;

IR (KBr) 3055, 2968, 1640, 1588, 1504, 1459, 1228, 1023;

元素分析 $C_{44}H_{41}N_2O_3PFe$:

计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 72.00; H, 5.71; N, 3.82.

P32 (*R*, R_{Phos}, R_A, R = C_2H_5; R'= $-CH_2C_6H_5$; R''XH = 联二萘酚)

^{1}H NMR δ 7.82-8.07 (m, 5H), 7.21-7.41 (m, 12H), 5.25 (br, 1H), 4.52 (m, 1H), 4.34-4.42 (m, 2H), 4.18 (t, *J* = 8.6 Hz, 1 H), 4.05-4.13 (m, 2H),), 4.01 (t, *J* = 7.8 Hz, 1 H), 3.92 (m, 1H), 3.89 (m, 1H), 3.75 (m, 1H), 3.40 (m, 1H), 3.18 (dd, *J* = 4.7, 13.7 Hz, 1H), 2.86 (m, 4H), 2.68 (dd, *J* = 9.1, 13.7 Hz, 1H), 0.76 (t, *J* = 7.0 Hz, 6 H);

MS *m/z* 732, 541, 447, 315, 286;

IR (KBr) 3055, 2966, 1641, 1588, 1504, 1023;

元素分析 $C_{44}H_{41}N_2O_3PFe$:

计算值: C, 72.19; H, 5.60; N, 3.83; 实测值: C, 71.93; H, 5.74; N, 3.76.

P33 (*S*, S_{Phos}, R_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);

^{1}H NMR δ 7.83-8.06 (m, 5H), 7.21-7.37 (m, 5H), 5.21 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.5 Hz, 4H), 2.25 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 684 , 611, 286;

IR (KBr) 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 69.88; H, 6.14; N, 3.87.

P34 (*S*, R_{Phos}, R_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);

^{1}H NMR δ 9.90 (br, 1H), 7.79-7.99 (m, 5H), 7.12-7.41 (m, 5H), 5.17 (t, *J* = 1.2 Hz, 1H), 4.57 (t, *J* = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.06 (m, 1H), 4.00 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.50 (t, *J* = 6.9 Hz, 6H);

MS *m/z* 684, 611, 399, 313, 286;

IR (KBr) 3051, 2962, 1640, 1590, 1461, 1232, 1024, 810;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.34; H, 6.31; N, 3.93.

P35 (*S*, R_{Phos}, S_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);

^{1}H NMR δ 7.78-7.98 (m, 5H), 7.12-7.41 (m, 5H), 5.21 (br, 1H), 5.17 (t, *J* = 1.2 Hz, 1H), 4.57 (t, *J* = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.07 (m, 1H), 4.00 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 6.9 Hz, 6H);

MS *m/z* 684, 611, 540, 399, 313, 286;

IR (KBr) 3051, 2962, 1641, 1589, 1462;

元素分析 $C_{40}H_{41}N_2O_3PFe$:

计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.19; H, 6.20; N, 3.93.

P36 (*S*, S_{Phos}, S_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);

^{1}H NMR δ 9.90 (br, 1H), 7.79-7.99 (m, 5H), 7.12-7.41 (m, 5H), 5.17 (t, *J* = 1.2 Hz, 1H), 4.57 (t, *J* = 1.1 Hz, 1H), 4.31-4.45 (m, 4H), 4.21-4.26 (m, 1H), 4.12 (t, *J* = 8.0 Hz, 1H), 4.06 (m, 1H), 4.00 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.50 (t, *J* = 6.9 Hz, 6H);

MS *m/z* 684, 611, 540, 286;

IR (KBr) 3051, 2962, 1642, 1589, 1462, 1232;
元素分析 $C_{40}H_{41}N_2O_3PFe$:
计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.44; H, 5.97; N, 4.01.
P37 (*R*, R_{Phos}, S_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);
^1H NMR δ 7.79-7.99 (m, 5H), 7.11-7.43 (m, 5H), 5.21 (br, 1H), 5.17 (t, *J* = 1.2 Hz, 1H), 4.58 (t, *J* = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.06 (m, 1H), 4.00 (m, 1H), 3.79 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 6.9 Hz, 6H);
MS *m/z* 684, 611, 313, 286;
IR (KBr) 3050, 2962, 1640, 1589, 1461, 1232, 1024, 810;
元素分析 $C_{40}H_{41}N_2O_3PFe$:
计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.21; H, 6.11; N, 3.92.
P38 (*R*, S_{Phos}, S_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);
^1H NMR δ 9.92 (br, 1H), 7.79-7.99 (m, 5H), 7.12-7.41 (m, 5H), 5.18 (t, *J* = 1.2 Hz, 1H), 4.55 (t, *J* = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.06 (m, 1H), 4.02 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.50 (t, *J* = 6.9 Hz, 6H);
MS *m/z* 684, 540, 399, 313, 286;
IR (KBr) 3052, 2962, 1640, 1589, 1460, 1232, 1024;
元素分析 $C_{40}H_{41}N_2O_3PFe$:
计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.28; H, 6.14; N, 3.85.
P39 (*R*, R_{Phos}, S_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);
^1H NMR δ 7.79-7.95 (m, 5H), 7.12-7.41 (m, 5H), 5.21 (br, 1H), 5.17 (t, *J* = 1.2 Hz, 1H), 4.57 (t, *J* = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.05 (m, 1H), 4.00 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 6.9 Hz, 6H);
MS *m/z* 684, 611, 399, 286;
IR (KBr) 3051, 2964, 1640, 1589, 1461, 1233, 1023;
元素分析 $C_{40}H_{41}N_2O_3PFe$:
计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.17; H, 6.01; N, 3.99.
P40 (*R*, S_{Phos}, S_A, R = $-CH_3$; R'= i-$CH(CH_3)_2$; R''XH = 3,3-二甲基联二萘酚);
^1H NMR δ 9.91 (br, 1H), 7.79-7.99 (m, 5H), 7.10-7.42 (m, 5H), 5.18 (t, *J* = 1.2 Hz, 1H), 4.57 (t, *J* = 1.1 Hz, 1H), 4.31-4.43 (m, 4H), 4.20-4.26 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.07 (m, 1H), 4.02 (m, 1H), 3.77 (m, 1H), 2.38-2.61 (m, 4H), 2.21 (s, 6H), 1.84 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.52 (t, *J* = 6.9 Hz, 6H);
MS *m/z* 684, 611, 540, 399, 313, 286;
IR (KBr) 3049, 2962, 1642, 1589, 1462, 1232;
元素分析 $C_{40}H_{41}N_2O_3PFe$:
计算值: C, 70.18; H, 5.99; N, 4.09; 实测值: C, 70.14; H, 6.25; N, 4.11.
P41 (*S*, S_{Phos}, R_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^{1}H NMR δ 7.21-8.37 (m, 22H), 5.21 (br, 3H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 1.52 (m, 3H);

MS *m/z* 750, 611, 541, 399, 286;

IR (KBr) 3440, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.55; H, 5.30; N, 7.52.

P42 (S, R_{Phos}, R_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^{1}H NMR δ 7.23-8.39 (m, 22H), 5.21 (br, 3H), 4.57 (m, 1H), 4.41 (m, 1H), 4.22 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.70 (m, 1H), 3.36 (s, 1H), 1.51 (m, 3H);

MS *m/z* 750, 611, 541, 286;

IR (KBr) 3440, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.59; H, 5.34; N, 7.51.

P43 (S, R_{Phos}, S_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^{1}H NMR δ 7.21-8.37 (m, 22H), 5.22 (br, 3H), 4.55 (m, 1H), 4.41 (m, 1H), 4.20 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 1.52 (m, 3H);

MS *m/z* 750, 611, 541, 399, 286;

IR (KBr) 3440, 3056, 2961, 1645, 1504, 1465, 1237, 1127;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.39; H, 5.45; N, 7.64.

P44 (S, S_{Phos}, S_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^{1}H NMR δ 7.21-8.39 (m, 22H), 5.21 (br, 3H), 4.55 (m, 1H), 4.40 (m, 1H), 4.23 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.70 (m, 1H), 3.37 (s, 1H), 1.50 (m, 3H);

MS *m/z* 750, 611, 541, 286;

IR (KBr) 3440, 3052, 2960, 1645, 1506, 1467, 1127;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.88; H, 5.42; N, 7.38.

P45 (R, R_{Phos}, S_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^{1}H NMR δ 7.21-8.35 (m, 22H), 5.23 (br, 3H), 4.55 (m, 1H), 4.39 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.73 (m, 1H), 3.38 (s, 1H), 1.50 (m, 3H);

MS *m/z* 750, 611, 541, 399, 286;

IR (KBr) 3440, 3050, 2960, 1645, 1500, 1465, 1234;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.75; H, 5.43; N, 7.38.

P46 (R, S_{Phos}, S_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^{1}H NMR δ 7.21-8.35 (m, 22H), 5.21 (br, 3H), 4.55 (m, 1H), 4.41 (m, 1H), 4.22 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.05 (m, 4H), 3.71 (m, 1H), 3.39 (s, 1H), 1.53 (m, 3H);

MS *m/z* 750, 541, 286;

IR (KBr) 3440, 3055, 2960, 1645, 1502, 1465, 1237;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.47; H, 5.39; N, 7.62.

P47 (*R*, R_{Phos}, S_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^1H NMR δ 7.21-8.36 (m, 22H), 5.22 (br, 3H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.06 (m, 4H), 3.71 (m, 1H), 3.37 (s, 1H), 1.51 (m, 3H);

MS *m/z* 750, 541, 399, 286;

IR (KBr) 3440, 3056, 2960, 1645, 1505, 1465, 1238;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.49; H, 5.41; N, 7.63.

P48 (*R*, S_{Phos}, S_A, R = $-C_6H_5$; R'= $-CH_3$; R''XH = 联二萘胺);

^1H NMR δ 7.20-8.37 (m, 22H), 5.20 (br, 3H), 4.57 (m, 1H), 4.41 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.07 (s, 1H), 3.87-4.05 (m, 4H), 3.70 (m, 1H), 3.39 (s, 1H), 1.53 (m, 3H);

MS *m/z* 750, 611, 541, 399, 286;

IR (KBr) 3441, 3055, 2961, 1645, 1506, 1462, 1237;

元素分析 $C_{46}H_{39}N_4OPFe$:

计算值: C, 73.62; H, 5.20; N, 7.46; 实测值: C, 73.54; H, 5.19; N, 7.34.

P49 (*S*, S_{Phos}, R_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^1H NMR δ 9.25 (br, 1H); 7.11-8.20 (m, 29H), 5.07 (t, *J* = 1.2 Hz, 1H), 4.59-4.65 (m, 1H), 4.56 (t, *J* = 1.2 Hz, 1H), 4.42 (m, 1H), 4.29-4.35 (m, 3H), 4.07 (dd, *J* = 7.2, 8.1 Hz, 1H), 3.92 (m, 1H), 3.74 (m, 2H), 2.40-2.62 (m, 4H);

MS *m/z* 924, 659, 541, 447, 286;

IR (KBr) 3055, 2967, 1639, 1589, 1504, 1461, 1232, 1023;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.01; H, 4.90; N, 3.05.

P50 (*S*, R_{Phos}, R_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^1H NMR δ 7.11-8.20 (m, 29H), 5.25 (br, 1H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.59-4.64 (m, 1H), 4.57 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.33 (m, 3H), 4.07 (dd, *J* = 7.2, 8.1 Hz, 1H), 3.92 (m, 1H), 3.74 (m, 2H), 2.41-2.62 (m, 4H);

MS *m/z* 924, 659, 541, 286;

IR (KBr) 3055, 2967, 1640, 1589, 1502, 1461, 1023;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.18; H, 4.95; N, 3.09.

P51 (*S*, R_{Phos}, S_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^1H NMR δ 9.27 (br, 1H), 7.11-8.22 (m, 29H), 5.11 (t, *J* = 1.2 Hz, 1H), 4.59-4.66 (m, 1H), 4.59 (t, *J* = 1.2 Hz, 1H), 4.42 (m, 1H), 4.29-4.35 (m, 3H), 4.07 (m, 1H), 3.90 (m, 1H), 3.71 (m, 2H), 2.41-2.63 (m, 4H);

MS *m/z* 924, 541, 447, 286;

IR (KBr) 3053, 2968, 1639, 1589, 1502, 1460, 1232, 1021;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 73.96; H, 4.62; N, 2.99.

P52 (*S*, S_{Phos}, S_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^{1}H NMR δ 7.11-8.20 (m, 29H), 5.23 (br, 1H), 5.08 (t, *J* = 1.2 Hz, 1H), 4.59-4.64 (m, 1H), 4.57 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.33 (m, 3H), 4.09 (dd, *J* = 7.2, 8.1 Hz, 1H), 3.93 (m, 1H), 3.74 (m, 2H), 2.41-2.60 (m, 4H);

MS *m/z* 924, 659, 541, 286;

IR (KBr) 3055, 2969, 1639, 1589, 1503, 1461, 1230;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.01; H, 4.90; N, 3.05.

P53 (*R*, R_{Phos}, S_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^{1}H NMR δ 9.25 (br, 1H), 7.11-8.22 (m, 29H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.59-4.65 (m, 1H), 4.56 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.34 (m, 3H), 4.07 (m, 1H), 3.92 (m, 1H), 3.76 (m, 2H), 2.40-2.62 (m, 4H);

MS *m/z* 924, 659, 447, 315, 286;

IR (KBr) 3054, 2969, 1640, 1589, 1503, 1460, 1232;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.28; H, 4.95; N, 3.19.

P54 (*R*, S_{Phos}, S_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^{1}H NMR δ 7.11-8.20 (m, 29H), 5.25 (br, 1H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.59-4.63 (m, 1H), 4.57 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.33 (m, 3H), 4.07 (dd, *J* = 7.2, 8.1 Hz, 1H), 3.92 (m, 1H), 3.75 (m, 2H), 2.41-2.62 (m, 4H);

MS *m/z* 924, 659, 315, 286;

IR (KBr) 3053, 2968, 1639, 1589, 1502, 1461, 1023;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.09; H, 4.96; N, 3.15.

P55 (*R*, S_{Phos}, R_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

^{1}H NMR δ 9.25 (br, 1H), 7.10-8.21 (m, 29H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.59-4.65 (m, 1H), 4.57 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.34 (m, 3H), 4.07 (m, 1H), 3.91 (m, 1H), 3.76 (m, 2H), 2.41-2.62 (m, 4H);

MS *m/z* 924, 659, 541, 447, 315, 286;

IR (KBr) 3055, 2967, 1639, 1589, 1503, 1461, 1233, 1023;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.06; H, 4.87; N, 3.24.

P56 (*R*, R_{Phos}, R_A, R = $-CH_2C_6H_5$; R'=萘基 ($-C_{10}H_7$); R''XH = 联二萘硫酚)

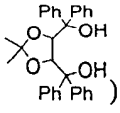
^{1}H NMR δ 7.11-8.20 (m, 29H), 5.25 (br, 1H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.59-4.64 (m, 1H), 4.57 (t, *J* = 1.2 Hz, 1H), 4.41 (m, 1H), 4.29-4.33 (m, 3H), 4.08 (m, 1H), 3.90 (m, 1H), 3.73 (m, 2H), 2.41-2.62 (m, 4H);

MS *m/z* 924, 659, 541, 315;

IR (KBr) 3300, 3052, 2967, 1639, 1587, 1504, 1461, 1232, 1023;

元素分析 $C_{57}H_{45}N_2OS_2PFe$:

计算值: C, 74.04; H, 4.87; N, 3.03; 实测值: C, 74.01; H, 4.68; N, 3.19.

P57 (*S*, S_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

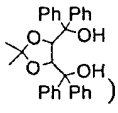
^1H NMR δ 7.21-8.40 (m, 20H), 502 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.5 Hz, 4H), 2.63 (m, 2H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 864, 611, 541;

IR (KBr) 3321, 3056, 2962, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.87; H, 6.54; N, 3.17.

P58 (*S*, R_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

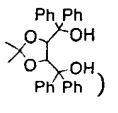
^1H NMR δ 7.21-8.45 (m, 20H), 5.02 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.63 (m, 2H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 964, 611, 541;

IR (KBr) 3299, 3056, 2960, 1643, 1506, 1465, 1237;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.67; H, 6.42; N, 3.09.

P59 (*S*, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

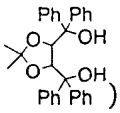
^1H NMR δ 7.21-8.40 (m, 20H), 5.01 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.64 (m, 2H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 864, 611, 541, 399;

IR (KBr) 3320, 3053, 2960, 1643, 1506, 1464, 1239, 1127;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.90; H, 6.72; N, 3.11.

P60 (*S*, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

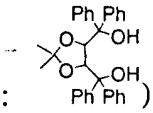
^1H NMR δ 7.21-8.43 (m, 20H), 5.02 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.62 (m, 2H), 2.53 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.73 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 964, 611, 541, 399;

IR (KBr) 3325, 3056, 2961, 1645, 1508, 1465, 1237, 1127;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.62; H, 6.63; N, 3.44.

P61 (*R*, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

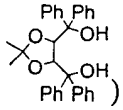
^{1}H NMR δ 7.20-8.42 (m, 20H), 5.00 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (m, 1H), 4.14 (s, 1H), 4.09 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.62 (m, 2H), 2.51 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 864 , 611, 399;

IR (KBr) 3360, 3054, 2961, 1643, 1506, 1465, 1239, 1127;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.98; H, 6.62; N, 3.37.

P62 (*R*, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

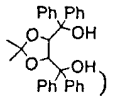
^{1}H NMR δ 7.21-8.41 (m, 20H), 5.01 (br, 1H), 4.55 (m, 1H), 4.42 (m, 1H), 4.22 (m, 1H), 4.14 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.39 (s, 1H), 2.85 (m, 4H), 2.65 (m, 2H), 2.53 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 864, 611, 541;

IR (KBr) 3350, 3054, 2962, 1645, 1505, 1465, 1237, 1127;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.92; H, 6.29; N, 3.01.

P63 (*R*, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

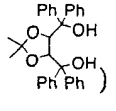
^{1}H NMR δ 7.19-8.40 (m, 20H), 5.02 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.24 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.05 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.86 (m, 4H), 2.63 (m, 2H), 2.52 (s, 6H), 1.82 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 864, 541, 399;

IR (KBr) 3318, 3054, 2960, 1645, 1507, 1465, 1127;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.68; H, 6.72; N, 3.53.

P64 (*R*, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = TADDOL: )

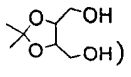
^{1}H NMR δ 7.21-8.45 (m, 20H), 5.00 (br, 1H), 4.53 (m, 1H), 4.41 (m, 1H), 4.24 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.70 (m, 1H), 3.39 (s, 1H), 2.84 (m, 4H), 2.64 (m, 2H), 2.50 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.73 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 864, 611, 541, 399;

IR (KBr) 3350, 3052, 2963, 1645, 1234, 1123;

元素分析 $C_{51}H_{57}N_2O_5PFe$:

计算值: C, 70.85; H, 6.59; N, 3.24; 实测值: C, 70.65; H, 6.44; N, 3.40.

P65 (*S*, S_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

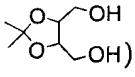
^{1}H NMR δ 4.62 (br, 1H), 4.53 (m, 1H), 4.41 (m, 1H), 4.18 (m, 1H), 4.11 (s, 1H), 4.07 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55-2.64 (m, 6H), 2.54 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 560;

IR (KBr) 3401, 3056, 2963, 1645, 1506, 1465, 1237, 1124;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.99; H, 7.45; N, 5.17.

P66 (*S*, R_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

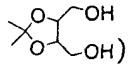
^{1}H NMR δ 4.88 (br, 1H), 4.55 (m, 1H), 4.44 (m, 1H), 4.13-4.15 (m, 2H), 4.07 (s, 1H), 3.87-4.05 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55-2.64 (m, 6H), 2.52 (s, 6H), 1.83 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.72 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 560;

IR (KBr) 3390, 3050, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.77; H, 7.49; N, 5.21.

P67 (*S*, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

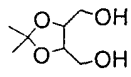
^{1}H NMR δ 4.82 (br, 1H), 4.52 (m, 1H), 4.38 (m, 1H), 4.20 (m, 1H), 4.13 (s, 1H), 4.09 (s, 1H), 3.87-4.06 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55-2.63 (m, 6H), 2.50 (s, 6H), 1.83 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.76 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 560;

IR (KBr) 3450, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.67; H, 7.49; N, 5.18.

P68 (*S*, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

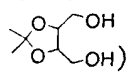
^{1}H NMR δ 4.71 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.5 Hz, 4H), 2.55-2.64 (m, 6H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 560, 399;

IR (KBr) 3410, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.68; H, 7.28; N, 5.00.

P69 (*R*, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

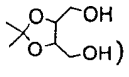
^{1}H NMR δ 4.69 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.19 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, J = 7.5 Hz, 4H), 2.53-2.64 (m, 6H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 6.8 Hz, 6H);

MS *m/z* 560, 399;

IR (KBr) 3400, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.65; H, 7.19; N, 5.23.

P70 (R, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

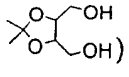
^{1}H NMR δ 4.78 (br, 1H), 4.53 (m, 1H), 4.40 (m, 1H), 4.20 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55-2.64 (m, 6H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.74 (t, J = 6.9 Hz, 6H);

MS *m/z* 560, 399;

IR (KBr) 3399, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.72; H, 7.19; N, 5.20.

P71 (R, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

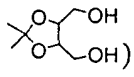
^{1}H NMR δ 4.76 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.19 (m, 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55-2.66 (m, 6H), 2.52 (s, 6H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 6.8 Hz, 6H);

MS *m/z* 560, 399;

IR (KBr) 3420, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.66; H, 7.17; N, 4.88.

P72 (R, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

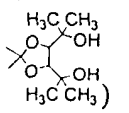
^{1}H NMR δ 4.88 (br, 1H), 4.55 (m, 1H), 4.43 (m, 1H), 4.19 (m, 1H), 4.15 (s, 1H), 4.07 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55-2.64 (m, 6H), 2.53 (s, 6H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.74 (t, J = 7.0 Hz, 6H);

MS *m/z* 560, 399;

IR (KBr) 3414, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{27}H_{41}N_2O_5PFe$:

计算值: C, 57.88; H, 7.32; N, 5.00; 实测值: C, 57.77; H, 7.06; N, 4.92.

P73 (S, S_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

^{1}H NMR δ 4.69 (br, 1H), 4.50 (m, 1H), 4.41 (m, 1H), 4.23 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.39 (s, 1H), 2.86 (t, J = 7.5 Hz, 4H),

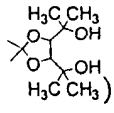
2.55-2.60 (m, 2H), 2.52 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.7 Hz, 3H), 0.72 (t, J = 6.8 Hz, 6H);

MS m/z 616, 399;

IR (KBr) 3380, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.21; H, 7.78; N, 4.63.

P74 (S, R_{Phos}, R_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = ).

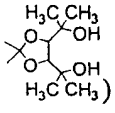
^{1}H NMR δ 4.68 (br, 1H), 4.53 (m, 1H), 4.40 (m, 1H), 4.24 (dd, J = 8.6, 9.2 Hz, 1H), 4.14 (s, 1H), 4.07 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.37 (s, 1H), 2.85 (m, 4H), 2.55-2.60 (m, 2H), 2.51 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.7 Hz, 3H), 0.75 (t, J = 7.0 Hz, 6H);

MS m/z 616;

IR (KBr) 3376, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.47; H, 7.99; N, 4.68.

P75 (S, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = ).

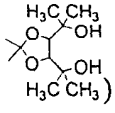
^{1}H NMR δ 4.69 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, J = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.83 (d, 4H), 2.55-2.60 (m, 2H), 2.52 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.74 (t, J = 6.8 Hz, 6H);

MS m/z 616;

IR (KBr) 3387, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.34; H, 7.68; N, 4.28.

P76 (S, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = ).

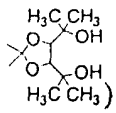
^{1}H NMR δ 4.65 (br, 1H), 4.55 (m, 1H), 4.42 (m, 1H), 4.18 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.36 (s, 1H), 2.85 (t, J = 7.5 Hz, 4H), 2.53-2.60 (m, 2H), 2.52 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.75 (t, J = 7.0 Hz, 6H);

MS m/z 616;

IR (KBr) 3360, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.19; H, 7.99; N, 4.72.

P77 (R, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = ).

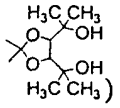
^{1}H NMR δ 4.72 (br, 1H), 4.53 (m, 1H), 4.41 (m, 1H), 4.19 (m, 1H), 4.14 (s, 1H), 4.06 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, J = 7.5 Hz, 4H), 2.55-2.60 (m, 2H), 2.52 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.75 (t, J = 6.8 Hz, 6H);

MS *m/z* 616, 296;

IR (KBr) 3372, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.60; H, 8.12; N, 4.44.

P78 (R, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

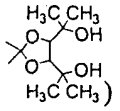
^{1}H NMR δ 4.77 (br, 1H), 4.56 (m, 1H), 4.41 (m, 1H), 4.20 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.05 (m, 4H), 3.73 (m, 1H), 3.38 (s, 1H), 2.85 (t, J = 7.5 Hz, 4H), 2.55-2.62 (m, 2H), 2.50 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.74 (t, J = 7.0 Hz, 6H);

MS *m/z* 616, 296;

IR (KBr) 3382, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.67; H, 7.89; N, 4.31.

P79 (R, R_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

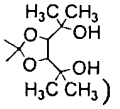
^{1}H NMR δ 4.73 (br, 1H), 4.56 (m, 1H), 4.40 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.72 (m, 1H), 3.37 (s, 1H), 2.83 (m, 4H), 2.55-2.60 (m, 2H), 2.52 (s, 6H), 2.21 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 6.9 Hz, 6H);

MS *m/z* 616, 296;

IR (KBr) 3386, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.28; H, 7.95; N, 4.71.

P80 (R, S_{Phos}, S_A, R = $-C_2H_5$; R'= $-CH(CH_3)_2$; R''XH = )

^{1}H NMR δ 4.80 (br, 1H), 4.56 (m, 1H), 4.42 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.05 (m, 4H), 3.73 (m, 1H), 3.39 (s, 1H), 2.86 (d, 4H), 2.55-2.60 (m, 2H), 2.52 (s, 6H), 2.20 (s, 12H), 1.82 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 7.0 Hz, 6H);

MS *m/z* 616, 296;

IR (KBr) 3380, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{31}H_{49}N_2O_5PFe$:

计算值: C, 60.41; H, 7.95; N, 4.55; 实测值: C, 60.40; H, 7.99; N, 4.24.

实施例二

（构型为 R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH =1,2-反式二苯基乙二醇）

50-100℃时，471 mg (1 mmol) (S)-二（二乙基胺基）膦二茂铁噁唑啉 1（R = C_2H_5; R'= i-$CH(CH_3)_2$），3-5 mmol 的 1,2-反式二苯基乙二醇，溶于 5-20mL 苯或四氯化碳，所得的黄色溶液在 80-120℃下反应 1-10 小时，TLC 跟踪至反应结束，用水洗，饱和食盐水洗，无水硫酸钠干燥，减压除去溶剂，柱层析纯化，得到产品 300mg。

P81 (*S*, S_{Phos}, R_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH =);

^{1}H NMR δ 7.21-8.21 (m, 10H), 5.28 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.7, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.5 Hz, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 612, 296;

IR (KBr) 3300, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.82; H, 6.82; N, 4.68.

P82 (*S*, R_{Phos}, R_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.21 (m, 10H), 5.25 (br, 1H), 4.56 (m, 1H), 4.40 (m, 1H), 4.22 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.07 (s, 1H), 3.87-4.05 (m, 4H), 3.77 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.73 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 612, 296 ;

IR (KBr) 3310, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.88; H, 6.70; N, 4.68.

P83 (*S*, R_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.21 (m, 10H), 5.28 (br, 1H), 4.56 (m, 1H), 4.44 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.37 (s, 1H), 2.83 (t, *J* = 7.5 Hz, 4H), 2.54 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.76 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 612, 296;

IR (KBr) 3312, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.58; H, 6.53; N, 4.69.

P84 (*S*, S_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.21 (m, 10H), 5.27 (br, 1H), 4.57 (m, 1H), 4.40 (m, 1H), 4.18 (dd, *J* = 8.5, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.86 (m, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 6.9 Hz, 6H);

MS *m/z* 612, 296;

IR (KBr) 3308, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.48; H, 6.82; N, 4.49.

P85 (*R*, R_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.24 (m, 10H), 5.24 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.20 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.84 (m, 4H), 2.58 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 6H);

MS *m/z* 612, 296;

IR (KBr) 3321, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.78; H, 6.71; N, 4.41.

P86 (*R*, S_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.21 (m, 10H), 5.28 (br, 1H), 4.55 (m, 1H), 4.41 (m, 1H), 4.23 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.71 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 612;

IR (KBr) 3310, 3056, 2960, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.84; H, 6.92; N, 4.68.

P87 (*R*, R_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.24 (m, 10H), 5.25 (br, 1H), 4.57 (m, 1H), 4.42 (m, 1H), 4.21 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.06 (m, 4H), 3.70 (m, 1H), 3.39 (s, 1H), 2.84 (t, *J* = 7.5 Hz, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.76 (t, *J* = 7.0 Hz, 6H);

MS *m/z* 612, 296;

IR (KBr) 3310, 3056, 2960, 1645, 1506, 1465;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.56; H, 6.48; N, 4.49.

P88 (*R*, S_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 1,2-反式二苯基乙二醇);

^{1}H NMR δ 7.21-8.21 (m, 10H), 5.28 (br, 1H), 4.56 (m, 1H), 4.40 (m, 1H), 4.22 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.72 (m, 1H), 3.39 (s, 1H), 2.87 (m, 4H), 2.56 (m, 2H), 1.81 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 6.8 Hz, 6H);

MS *m/z* 612, 296;

IR (KBr) 3310, 3056, 2964, 1645, 1506, 1465, 1237, 1127;

元素分析 $C_{34}H_{41}N_2O_3PFe$:

计算值: C, 66.69; H, 6.70; N, 4.57; 实测值: C, 66.71; H, 6.58; N, 4.62.

P89 (*S*, S_{Phos}, R_A, R = -$CH(CH_3)_2$; R'= -$CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^{1}H NMR δ 4.77 (br, 1H), 4.52 (m, 1H), 4.40 (m, 1H), 4.17 (dd, *J* = 8.0, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.7 Hz, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.42-1.62 (m, 21H);

MS *m/z* 542, 296;

IR (KBr) 3320, 3050, 2968, 1640, 1501, 1467, 1123;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 62.14; H, 7.82; N, 4.98.

P90 (*S*, R_{Phos}, R_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^1H NMR δ 4.79 (br, 1H), 4.50 (m, 1H), 4.47 (m, 1H), 4.15 (m, 1H), 4.13 (s, 1H), 4.10 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.7 Hz, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.40-1.65 (m, 21H);

MS *m/z* 542, 296;

IR (KBr) 3318, 3049, 2968, 1641, 1501, 1467, 1123;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 62.25; H, 7.99; N, 5.12.

P91 (*S*, R_{Phos}, S_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^1H NMR δ 4.77 (br, 1H), 4.52 (m, 1H), 4.40 (m, 1H), 4.17 (dd, *J* = 8.0, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.7 Hz, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.42-1.62 (m, 21H);

MS *m/z* 542, 296;

IR (KBr) 3320, 3050, 2968, 1640, 1501, 1467, 1123;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 62.21; H, 7.77; N, 4.86.

P92 (*S*, S_{Phos}, S_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^1H NMR δ 4.82 (br, 1H), 4.55 (m, 1H), 4.40 (m, 1H), 4.18 (dd, *J* = 8.2, 9.2 Hz, 1H), 4.14 (s, 1H), 4.08 (s, 1H), 3.87-4.06 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (t, *J* = 7.7 Hz, 4H), 2.58 (m, 2H), 1.83 (m, 1H), 0.42-1.65 (m, 21H);

MS *m/z* 542, 296;

IR (KBr) 3326, 3050, 2968, 1640, 1505, 1467, 1123;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 62.02; H, 7.99; N, 5.05

P93 (*R*, R_{Phos}, S_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^1H NMR δ 4.82 (br, 1H), 4.52 (m, 1H), 4.40 (m, 1H), 4.17 (m, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.38 (s, 1H), 2.85 (m, 4H), 2.55 (m, 2H), 1.82 (m, 1H), 0.40-1.62 (m, 21H);

MS *m/z* 542, 296;

IR (KBr) 3318, 3050, 2967, 1640, 1501, 1467, 1125;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 61.88; H, 7.79; N, 4.92

P94 (*R*, S_{Phos}, S_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^1H NMR δ 4.72 (br, 1H), 4.52 (m, 1H), 4.40 (m, 1H), 4.17 (dd, *J* = 8.0, 9.3 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.72 (m, 1H), 3.38 (s, 1H), 2.87 (t, *J* = 7.8 Hz, 4H), 2.55 (m, 2H), 1.82 (m, 1H), 0.42-1.66 (m, 21H);

MS *m/z* 542, 296;

IR (KBr) 3310, 3050, 2968, 1640, 1501, 1467, 1123;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 61.97; H, 8.10; N, 4.94

P95 (R, R_{Phos}, S_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^{1}H NMR δ 4.77 (br, 1H), 4.52 (m, 1H), 4.40 (m, 1H), 4.17 (dd, J = 8.0, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.87-4.04 (m, 4H), 3.71 (m, 1H), 3.35 (s, 1H), 2.89 (m, 4H), 2.55 (m, 2H), 1.84 (m, 1H), 0.40-1.62 (m, 21H);

MS m/z 542, 296;

IR (KBr) 3308, 3050, 2968, 1644, 1501, 1463, 1123;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 62.18; H, 7.82; N, 4.93

P96 (R, S_{Phos}, S_A, R = $-CH(CH_3)_2$; R'= $-CH(CH_3)_2$; R''XH = 1,2-反式环己二醇);

^{1}H NMR δ 4.79 (br, 1H), 4.54 (m, 1H), 4.41 (m, 1H), 4.17 (dd, J = 8.0, 9.2 Hz, 1H), 4.13 (s, 1H), 4.08 (s, 1H), 3.86-4.04 (m, 4H), 3.73 (m, 1H), 3.39 (s, 1H), 2.89 (m, 4H), 2.56 (m, 2H), 1.82 (m, 1H), 0.42-1.65 (m, 21H);

MS m/z 542, 296;

IR (KBr) 3320, 3051, 2968, 1637, 1501, 1466, 1121;

元素分析 $C_{28}H_{43}N_2O_3PFe$:

计算值: C, 62.01; H, 7.93; N, 5.16; 实测值: C, 62.29; H, 7.93; N, 5.11

实施例三

$[Pd(C_3H_5)Cl]_2$ 3.7 mg (0.01 mmol)和配体 **P3** (S, R_{Phos}, S_A, R = C_2H_5; R'= i-$CH(CH_3)_2$; R''XH = 联二萘酚)(实例一中合成的配体) 13 mg (0.02 mmol)于 4mL 四氢呋喃中络合 0.5-10 小时, 加入 1,3-二苯基烯丙基醋酸酯 252 mg (1 mmol), 苄胺 214 mg(1 mmol), 然后于室温反应, TLC 跟踪至反应结束, 用乙醚提取, 饱和食盐水洗, 无水硫酸钠干燥, 减压除去溶剂, 柱层析纯化, 得到 N-苄基-1,3-二苯基烯丙基胺无色液体 295 mg (99% yield; 95% ee); ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.76 (s, 1H), 3.77 (s, 2H), 4.39 (d, J = 7.4 Hz, 1H), 6.31 (dd, J = 7.4, 15.6 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 7.10-7.53 (m, 15H); MS m/z 299 (M^+).

实施例四

$[Pd(C_3H_5)Cl]_2$ 3.7 mg (0.01 mmol)和配体 **P25** (S, S_{Phos}, R_A, R = C_2H_5; R'=$-CH_2C_6H_5$; R''XH = 联二萘酚) (实例一中合成的配体) 15 mg (0.02 mmol)于 4mL 二氯甲烷中络合 0.5-10 小时, 加入 1-萘基烯丙基醋酸酯 226 mg (1 mmol), 丙二酸二甲酯 (0.34 mL, 3 mmol), N,O-二(三甲硅基)乙酰胺 (0.74 mL, 3 mmol), 然后于室温反应, TLC 跟踪至反应结束, 用乙醚提取, 饱和食盐水洗, 无水硫酸钠干燥, 减压除去溶剂, 柱层析纯化, 得到 3-(1-萘基)-1-丁烯-4,4-二甲酸甲酯无色液体 295 mg (99% yield; 97% ee); ^{1}HNMR (300 MHz, $CDCl_3$) δ 3.99 (s, 3H), 3.79 (s, 3H), 4.17 (d, J = 10.9 Hz, 1H), 5.04 (dd, J = 8.1, 10.9 Hz, 1H), 5.11 (d, J = 10.2 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 6.09 (m, 1H), 7.47-8.25 (m, 7H).