Supporting Information

Diphosphines with strongly polarized PP-bonds: Hybrids between covalent molecules and donor-acceptor adducts with flexible molecular structures

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Representations of the molecular structures of crystalline 4a-f

4a

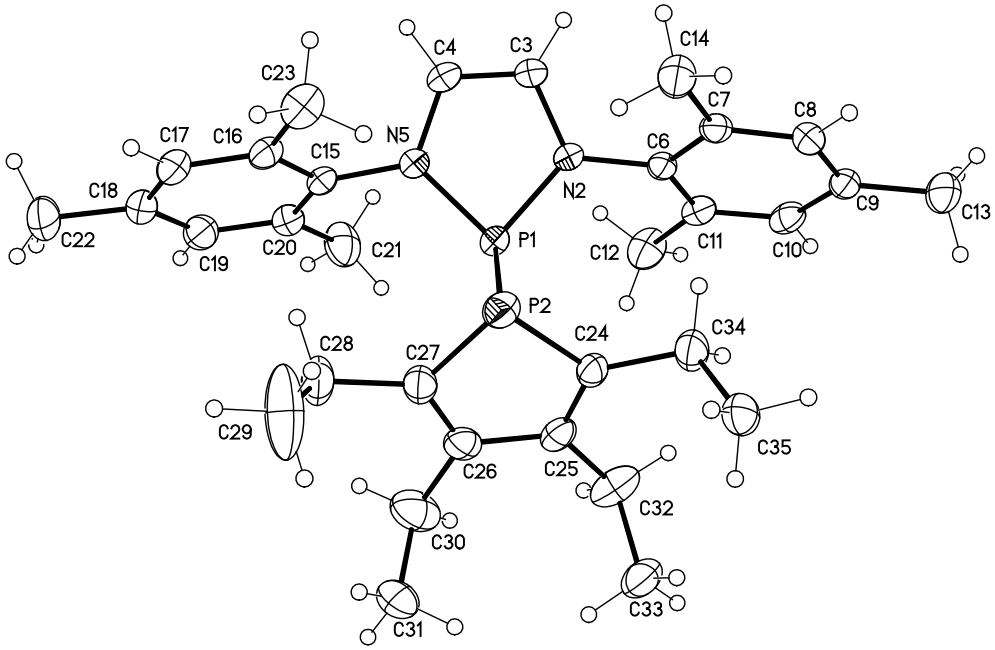

Table 1. Bond lengths [A] and angles [deg] for 4a.

P(1)-N(5)	1.7164(16)
P(1)-N(2)	1.7220(17)
P(1)-P(2)	2.4838(8)
N(2)-C(3)	1.404(2)
N(2)-C(6)	1.440(2)
C(3)-C(4)	1.327(3)
C(4)-N(5)	1.397(3)
N(5)-C(15)	1.438(2)
C(6)-C(7)	1.396(3)
C(6)-C(11)	1.408(3)
C(7)-C(8)	1.388(3)
C(7)-C(14)	1.511(3)
C(8)-C(9)	1.388(3)
C(9)-C(10)	1.385(3)
C(9)-C(13)	1.508(3)
C(10)-C(11)	1.395(3)
C(11)-C(12)	1.501(3)
C(15)-C(20)	1.399(3)
C(15)-C(16)	1.402(3)
C(16)-C(17)	1.392(3)
C(16)-C(23)	1.511(3)
C(17)-C(18)	1.390(3)
C(18)-C(19)	1.381(3)
C(18)-C(22)	1.515(3)
C(19)-C(20)	1.391(3)
C(20)-C(21)	1.511(3)
P(2)-C(27)	1.788(2)
P(2)-C(24)	1.789(2)
C(24)-C(25)	1.371(3)
C(24)-C(34)	1.501(3)
C(25)-C(26)	1.446(3)
C(25)-C(32)	1.514(3)
C(26)-C(27)	1.371(3)
C(26)-C(30)	1.510(3)
C(27)-C(28)	1.515(3)
C(28)-C(29)	1.467(4)
C(30)-C(31)	1.513(4)
C(32)-C(33)	1.514(3)
C(34)-C(35)	1.508(3)
N(5)-P(1)-N(2)	87.10(8)
N(5)-P(1)-P(2)	110.92(6)

N(2)-P(1)-P(2)	109.71(6)
C(3)-N(2)-C(6)	119.96(16)
C(3)-N(2)-P(1)	114.13(13)
C(6)-N(2)-P(1)	125.31(13)
C(4)-C(3)-N(2)	111.57(19)
C(3)-C(4)-N(5)	112.11(18)
C(4)-N(5)-C(15)	119.99(16)
C(4)-N(5)-P(1)	114.36(13)
C(15)-N(5)-P(1)	125.26(14)
C(7)-C(6)-C(11)	120.73(17)
C(7)-C(6)-N(2)	119.80(16)
C(11)-C(6)-N(2)	119.47(17)
C(8)-C(7)-C(6)	118.59(17)
C(8)-C(7)-C(14)	119.07(18)
C(6)-C(7)-C(14)	122.29(17)
C(9)-C(8)-C(7)	122.65(19)
C(10)-C(9)-C(8)	117.35(17)
C(10)-C(9)-C(13)	121.22(18)
C(8)-C(9)-C(13)	121.43(19)
C(9)-C(10)-C(11)	122.85(18)
C(10)-C(11)-C(6)	117.82(19)
C(10)-C(11)-C(12)	119.80(17)
C(6)-C(11)-C(12)	122.37(18)
C(20)-C(15)-C(16)	120.86(18)
C(20)-C(15)-N(5)	120.00(18)
C(16)-C(15)-N(5)	119.10(17)
C(17)-C(16)-C(15)	118.29(19)
C(17)-C(16)-C(23)	119.74(19)
C(15)-C(16)-C(23)	121.97(18)
C(18)-C(17)-C(16)	122.1(2)
C(19)-C(18)-C(17)	117.95(19)
C(19)-C(18)-C(22)	121.5(2)
C(17)-C(18)-C(22)	120.6(2)
C(18)-C(19)-C(20)	122.5(2)
C(19)-C(20)-C(15)	118.32(19)
C(19)-C(20)-C(21)	119.54(19)
C(15)-C(20)-C(21)	122.12(19)
C(27)-P(2)-C(24)	90.50(10)
C(27)-P(2)-P(1)	81.87(8)
C(24)-P(2)-P(1)	81.08(7)
C(25)-C(24)-C(34)	126.61(19)
C(25)-C(24)-P(2)	111.11(15)
C(34)-C(24)-P(2)	122.21(17)
C(24)-C(25)-C(26)	113.54(17)
C(24)-C(25)-C(32)	122.9(2)
C(26)-C(25)-C(32)	123.5(2)
C(27)-C(26)-C(25)	113.47(19)
C(27)-C(26)-C(30)	123.8(2)
C(25)-C(26)-C(30)	122.7(2)
C(26)-C(27)-C(28)	125.7(2)
C(26)-C(27)-P(2)	111.23(15)
C(28)-C(27)-P(2)	123.01(19)
C(29)-C(28)-C(27)	114.5(2)
C(26)-C(30)-C(31)	114.4(2)
C(25)-C(32)-C(33)	116.5(2)
C(24)-C(34)-C(35)	114.01(19)

4b

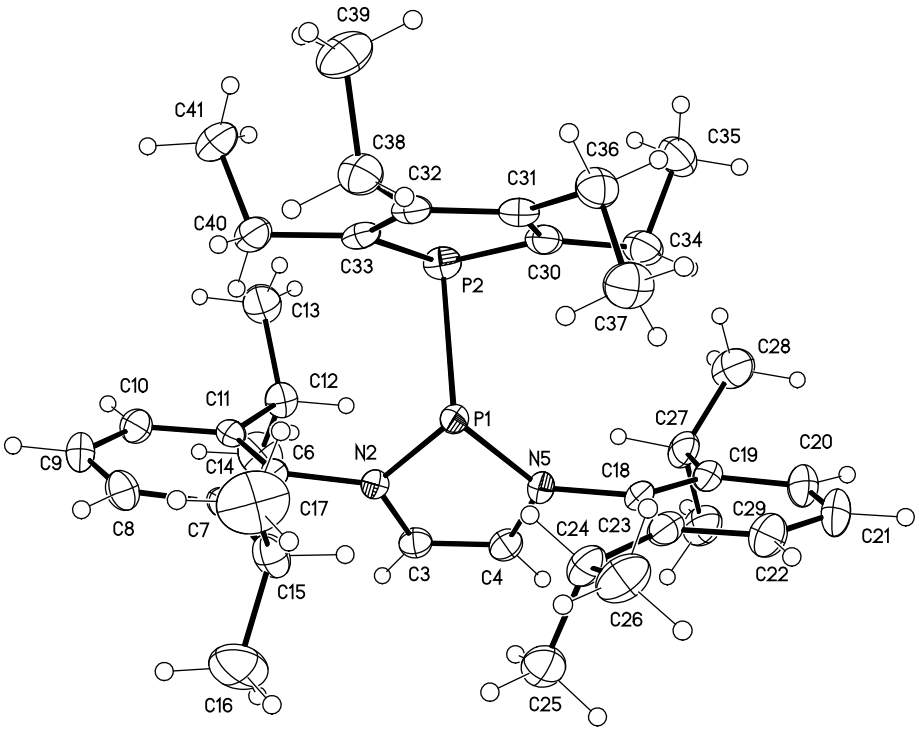

Table 2. Bond lengths [A] and angles [deg] for 4b.

P(1)-N(2)	1.7172(14)
P(1)-N(5)	1.7276(15)
P(1)-P(2)	2.4085(6)
N(2)-C(3)	1.396(2)
N(2)-C(6)	1.438(2)
C(3)-C(4)	1.327(2)
C(4)-N(5)	1.415(2)
N(5)-C(18)	1.443(2)
C(6)-C(11)	1.403(2)
C(6)-C(7)	1.405(2)
C(7)-C(8)	1.389(2)
C(7)-C(15)	1.517(2)
C(8)-C(9)	1.379(2)
C(9)-C(10)	1.380(2)
C(10)-C(11)	1.388(2)
C(11)-C(12)	1.519(2)
C(12)-C(14)	1.526(3)
C(12)-C(13)	1.536(2)
C(15)-C(17)	1.517(3)
C(15)-C(16)	1.526(3)
C(18)-C(19)	1.412(2)
C(18)-C(23)	1.415(2)
C(19)-C(20)	1.394(2)
C(19)-C(27)	1.524(2)
C(20)-C(21)	1.374(3)
C(21)-C(22)	1.380(3)
C(22)-C(23)	1.392(2)
C(23)-C(24)	1.526(2)
C(24)-C(26)	1.529(2)
C(24)-C(25)	1.535(3)
C(27)-C(29)	1.531(3)
C(27)-C(28)	1.534(2)
P(2)-C(30)	1.7940(19)
P(2)-C(33)	1.8037(18)
C(30)-C(31)	1.370(2)
C(30)-C(34)	1.498(2)
C(31)-C(32)	1.445(2)
C(31)-C(36)	1.508(2)
C(32)-C(33)	1.377(2)
C(32)-C(38)	1.509(2)
C(33)-C(40)	1.503(2)

C(34)-C(35)	1.530(2)
C(36)-C(37)	1.530(2)
C(38)-C(39)	1.523(2)
C(40)-C(41)	1.530(2)

N(2)-P(1)-N(5)	87.33(7)
N(2)-P(1)-P(2)	105.41(5)
N(5)-P(1)-P(2)	114.92(5)
C(3)-N(2)-C(6)	121.85(14)
C(3)-N(2)-P(1)	114.52(12)
C(6)-N(2)-P(1)	123.46(11)
C(4)-C(3)-N(2)	112.12(16)
C(3)-C(4)-N(5)	111.82(16)
C(4)-N(5)-C(18)	120.18(14)
C(4)-N(5)-P(1)	113.43(11)
C(18)-N(5)-P(1)	125.95(12)
C(11)-C(6)-C(7)	121.82(15)
C(11)-C(6)-N(2)	120.05(14)
C(7)-C(6)-N(2)	118.14(14)
C(8)-C(7)-C(6)	117.69(16)
C(8)-C(7)-C(15)	119.60(15)
C(6)-C(7)-C(15)	122.64(16)
C(9)-C(8)-C(7)	121.58(16)
C(8)-C(9)-C(10)	119.52(17)
C(9)-C(10)-C(11)	121.76(17)
C(10)-C(11)-C(6)	117.56(15)
C(10)-C(11)-C(12)	119.17(15)
C(6)-C(11)-C(12)	123.27(15)
C(11)-C(12)-C(14)	111.31(14)
C(11)-C(12)-C(13)	112.24(15)
C(14)-C(12)-C(13)	109.59(15)
C(7)-C(15)-C(17)	112.56(17)
C(7)-C(15)-C(16)	110.41(15)
C(17)-C(15)-C(16)	111.70(17)
C(19)-C(18)-C(23)	121.42(16)
C(19)-C(18)-N(5)	119.62(15)
C(23)-C(18)-N(5)	118.91(15)
C(20)-C(19)-C(18)	117.59(16)
C(20)-C(19)-C(27)	118.62(16)
C(18)-C(19)-C(27)	123.76(16)
C(21)-C(20)-C(19)	121.84(18)
C(20)-C(21)-C(22)	119.73(18)
C(21)-C(22)-C(23)	121.83(18)
C(22)-C(23)-C(18)	117.48(17)
C(22)-C(23)-C(24)	120.32(16)
C(18)-C(23)-C(24)	122.05(16)
C(23)-C(24)-C(26)	115.28(16)
C(23)-C(24)-C(25)	110.13(15)
C(26)-C(24)-C(25)	109.41(14)
C(19)-C(27)-C(29)	110.67(15)
C(19)-C(27)-C(28)	113.71(15)
C(29)-C(27)-C(28)	108.24(15)
C(30)-P(2)-C(33)	90.32(8)
C(30)-P(2)-P(1)	81.86(6)
C(33)-P(2)-P(1)	84.82(5)
C(31)-C(30)-C(34)	125.92(17)
C(31)-C(30)-P(2)	111.51(14)
C(34)-C(30)-P(2)	122.57(14)
C(30)-C(31)-C(32)	113.57(16)
C(30)-C(31)-C(36)	123.32(17)
C(32)-C(31)-C(36)	123.10(16)
C(33)-C(32)-C(31)	113.91(16)
C(33)-C(32)-C(38)	124.10(17)
C(31)-C(32)-C(38)	121.94(16)
C(32)-C(33)-C(40)	125.45(16)
C(32)-C(33)-P(2)	110.69(13)
C(40)-C(33)-P(2)	123.77(13)
C(30)-C(34)-C(35)	113.07(16)
C(31)-C(36)-C(37)	112.42(15)
C(32)-C(38)-C(39)	113.53(15)
C(33)-C(40)-C(41)	113.64(14)

4c

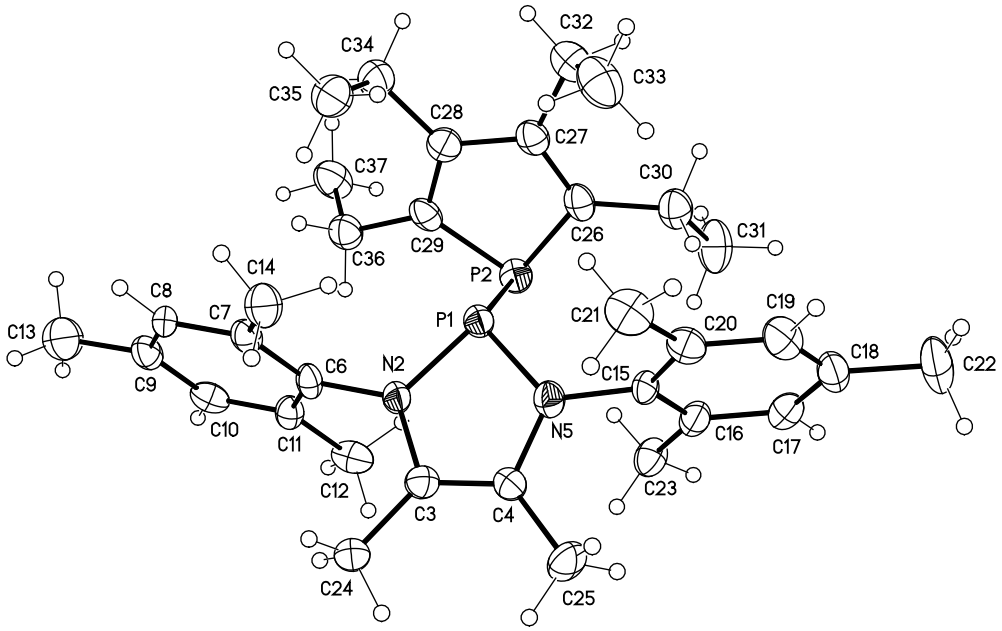

Table 3. Bond lengths [A] and angles [deg] for 4c.

P(1)-N(5)	1.702(4)
P(1)-N(2)	1.707(4)
P(1)-P(2)	2.7011(19)
N(2)-C(3)	1.400(6)
N(2)-C(6)	1.437(6)
C(3)-C(4)	1.335(7)
C(3)-C(24)	1.502(7)
C(4)-N(5)	1.414(6)
C(4)-C(25)	1.496(7)
N(5)-C(15)	1.443(6)
C(6)-C(7)	1.390(7)
C(6)-C(11)	1.400(7)
C(7)-C(8)	1.390(7)
C(7)-C(14)	1.510(7)
C(8)-C(9)	1.385(7)
C(9)-C(10)	1.380(7)
C(9)-C(13)	1.501(7)
C(10)-C(11)	1.384(7)
C(11)-C(12)	1.503(7)
C(15)-C(20)	1.389(7)
C(15)-C(16)	1.392(7)
C(16)-C(17)	1.388(7)
C(16)-C(23)	1.499(7)
C(17)-C(18)	1.382(7)
C(18)-C(19)	1.398(7)
C(18)-C(22)	1.516(7)
C(19)-C(20)	1.385(7)
C(20)-C(21)	1.498(7)
P(2)-C(26)	1.782(5)
P(2)-C(29)	1.786(5)
C(26)-C(27)	1.363(7)
C(26)-C(30)	1.522(7)
C(27)-C(28)	1.434(7)
C(27)-C(32)	1.508(7)
C(28)-C(29)	1.383(7)
C(28)-C(34)	1.526(7)
C(29)-C(36)	1.499(7)
C(30)-C(31)	1.511(8)
C(32)-C(33)	1.528(8)
C(34)-C(35)	1.533(7)
C(36)-C(37)	1.529(7)

N(5)-P(1)-N(2)	86.8(2)
N(5)-P(1)-P(2)	113.93(15)
N(2)-P(1)-P(2)	117.03(15)
C(3)-N(2)-C(6)	121.3(4)

C(3)-N(2)-P(1)	115.9(3)
C(6)-N(2)-P(1)	122.4(3)
C(4)-C(3)-N(2)	110.8(4)
C(4)-C(3)-C(24)	128.9(5)
N(2)-C(3)-C(24)	119.9(4)
C(3)-C(4)-N(5)	111.1(4)
C(3)-C(4)-C(25)	128.9(5)
N(5)-C(4)-C(25)	119.9(4)
C(4)-N(5)-C(15)	120.2(4)
C(4)-N(5)-P(1)	115.3(3)
C(15)-N(5)-P(1)	124.3(3)
C(7)-C(6)-C(11)	121.7(5)
C(7)-C(6)-N(2)	120.2(4)
C(11)-C(6)-N(2)	118.1(4)
C(6)-C(7)-C(8)	117.6(5)
C(6)-C(7)-C(14)	122.1(4)
C(8)-C(7)-C(14)	120.2(5)
C(9)-C(8)-C(7)	122.7(5)
C(10)-C(9)-C(8)	117.5(5)
C(10)-C(9)-C(13)	120.6(5)
C(8)-C(9)-C(13)	121.9(5)
C(9)-C(10)-C(11)	122.7(5)
C(10)-C(11)-C(6)	117.7(5)
C(10)-C(11)-C(12)	120.3(5)
C(6)-C(11)-C(12)	122.0(5)
C(20)-C(15)-C(16)	121.9(5)
C(20)-C(15)-N(5)	119.8(5)
C(16)-C(15)-N(5)	118.3(4)
C(17)-C(16)-C(15)	118.5(5)
C(17)-C(16)-C(23)	120.9(5)
C(15)-C(16)-C(23)	120.6(5)
C(18)-C(17)-C(16)	121.7(5)
C(17)-C(18)-C(19)	117.9(5)
C(17)-C(18)-C(22)	121.4(5)
C(19)-C(18)-C(22)	120.7(5)
C(20)-C(19)-C(18)	122.5(5)
C(19)-C(20)-C(15)	117.5(5)
C(19)-C(20)-C(21)	120.9(5)
C(15)-C(20)-C(21)	121.5(5)
C(26)-P(2)-C(29)	90.5(2)
C(26)-P(2)-P(1)	79.42(16)
C(29)-P(2)-P(1)	78.60(16)
C(27)-C(26)-C(30)	124.4(5)
C(27)-C(26)-P(2)	111.7(4)
C(30)-C(26)-P(2)	123.9(4)
C(26)-C(27)-C(28)	113.3(5)
C(26)-C(27)-C(32)	123.7(5)
C(28)-C(27)-C(32)	123.0(5)
C(29)-C(28)-C(27)	113.9(5)
C(29)-C(28)-C(34)	122.5(5)
C(27)-C(28)-C(34)	123.6(5)
C(28)-C(29)-C(36)	126.0(5)
C(28)-C(29)-P(2)	110.4(4)
C(36)-C(29)-P(2)	123.3(4)
C(31)-C(30)-C(26)	115.9(5)
C(27)-C(32)-C(33)	113.6(5)
C(28)-C(34)-C(35)	112.8(5)
C(29)-C(36)-C(37)	113.1(4)

4d

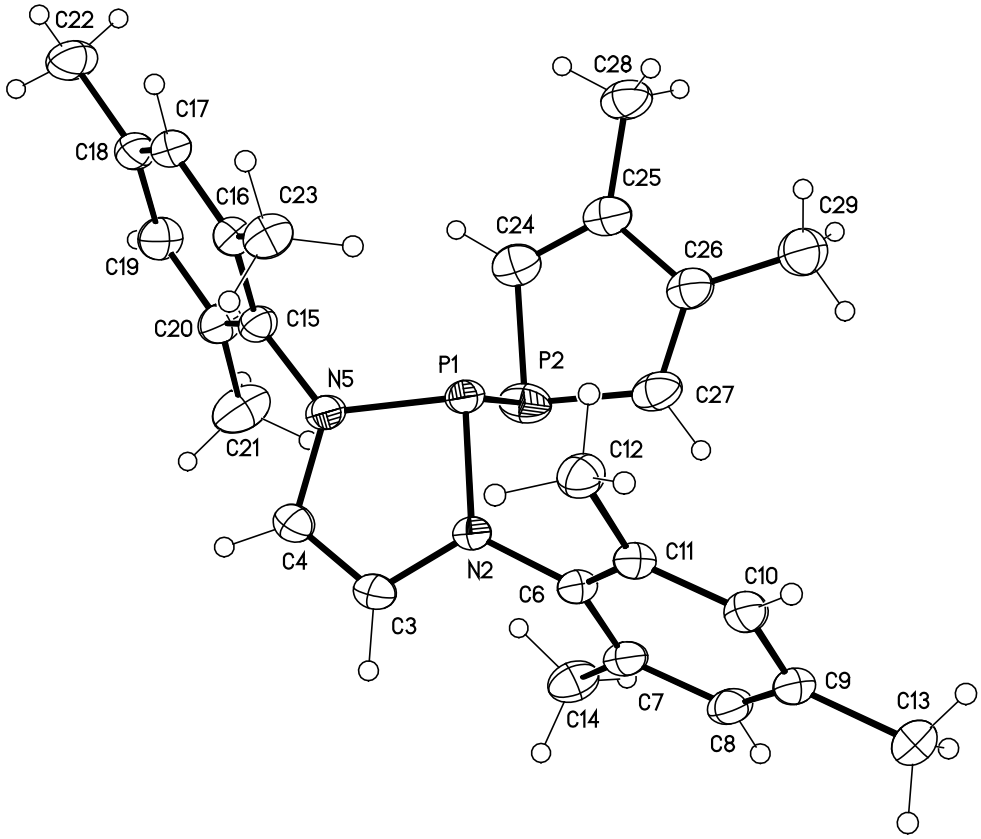

Table 4. Bond lengths [A] and angles [deg] for 4d.

P(1)-N(2)	1.7099(11)
P(1)-N(5)	1.7101(11)
P(1)-P(2)	2.3560(5)
N(2)-C(3)	1.4043(17)
N(2)-C(6)	1.4345(16)
C(3)-C(4)	1.3359(19)
C(4)-N(5)	1.4019(17)
N(5)-C(15)	1.4353(16)
C(6)-C(11)	1.4040(18)
C(6)-C(7)	1.4088(18)
C(7)-C(8)	1.3942(19)
C(7)-C(14)	1.5064(19)
C(8)-C(9)	1.388(2)
C(9)-C(10)	1.394(2)
C(9)-C(13)	1.5091(19)
C(10)-C(11)	1.3932(18)
C(11)-C(12)	1.5107(19)
C(15)-C(20)	1.4025(18)
C(15)-C(16)	1.4066(18)
C(16)-C(17)	1.3917(18)
C(16)-C(23)	1.5080(18)
C(17)-C(18)	1.3899(19)
C(18)-C(19)	1.388(2)
C(18)-C(22)	1.5098(19)
C(19)-C(20)	1.3941(19)
C(20)-C(21)	1.506(2)
P(2)-C(27)	1.7832(17)
P(2)-C(24)	1.7879(15)
C(24)-C(25)	1.360(2)
C(25)-C(26)	1.451(2)
C(25)-C(28)	1.509(2)
C(26)-C(27)	1.366(2)
C(26)-C(29)	1.502(2)
N(2)-P(1)-N(5)	88.28(5)
N(2)-P(1)-P(2)	103.27(4)
N(5)-P(1)-P(2)	103.71(4)

C(3)-N(2)-C(6)	123.91(11)
C(3)-N(2)-P(1)	112.45(9)
C(6)-N(2)-P(1)	121.83(9)
C(4)-C(3)-N(2)	111.83(12)
C(3)-C(4)-N(5)	111.93(12)
C(4)-N(5)-C(15)	124.09(11)
C(4)-N(5)-P(1)	112.49(9)
C(15)-N(5)-P(1)	121.97(9)
C(11)-C(6)-C(7)	120.92(12)
C(11)-C(6)-N(2)	118.53(11)
C(7)-C(6)-N(2)	120.52(12)
C(8)-C(7)-C(6)	117.95(12)
C(8)-C(7)-C(14)	118.85(12)
C(6)-C(7)-C(14)	123.18(12)
C(9)-C(8)-C(7)	122.59(13)
C(8)-C(9)-C(10)	118.01(12)
C(8)-C(9)-C(13)	120.73(13)
C(10)-C(9)-C(13)	121.26(13)
C(11)-C(10)-C(9)	121.97(13)
C(10)-C(11)-C(6)	118.56(12)
C(10)-C(11)-C(12)	119.81(12)
C(6)-C(11)-C(12)	121.62(12)
C(20)-C(15)-C(16)	120.84(12)
C(20)-C(15)-N(5)	120.93(12)
C(16)-C(15)-N(5)	118.24(11)
C(17)-C(16)-C(15)	118.40(12)
C(17)-C(16)-C(23)	119.95(12)
C(15)-C(16)-C(23)	121.61(12)
C(18)-C(17)-C(16)	122.26(12)
C(19)-C(18)-C(17)	117.74(12)
C(19)-C(18)-C(22)	121.40(13)
C(17)-C(18)-C(22)	120.86(13)
C(18)-C(19)-C(20)	122.65(13)
C(19)-C(20)-C(15)	118.06(12)
C(19)-C(20)-C(21)	119.45(13)
C(15)-C(20)-C(21)	122.48(13)
C(27)-P(2)-C(24)	89.19(7)
C(27)-P(2)-P(1)	87.95(5)
C(24)-P(2)-P(1)	88.85(5)
C(25)-C(24)-P(2)	112.52(11)
C(24)-C(25)-C(26)	112.94(13)
C(24)-C(25)-C(28)	125.23(14)
C(26)-C(25)-C(28)	121.82(14)
C(27)-C(26)-C(25)	112.65(14)
C(27)-C(26)-C(29)	124.91(14)
C(25)-C(26)-C(29)	122.40(13)
C(26)-C(27)-P(2)	112.60(12)

4e

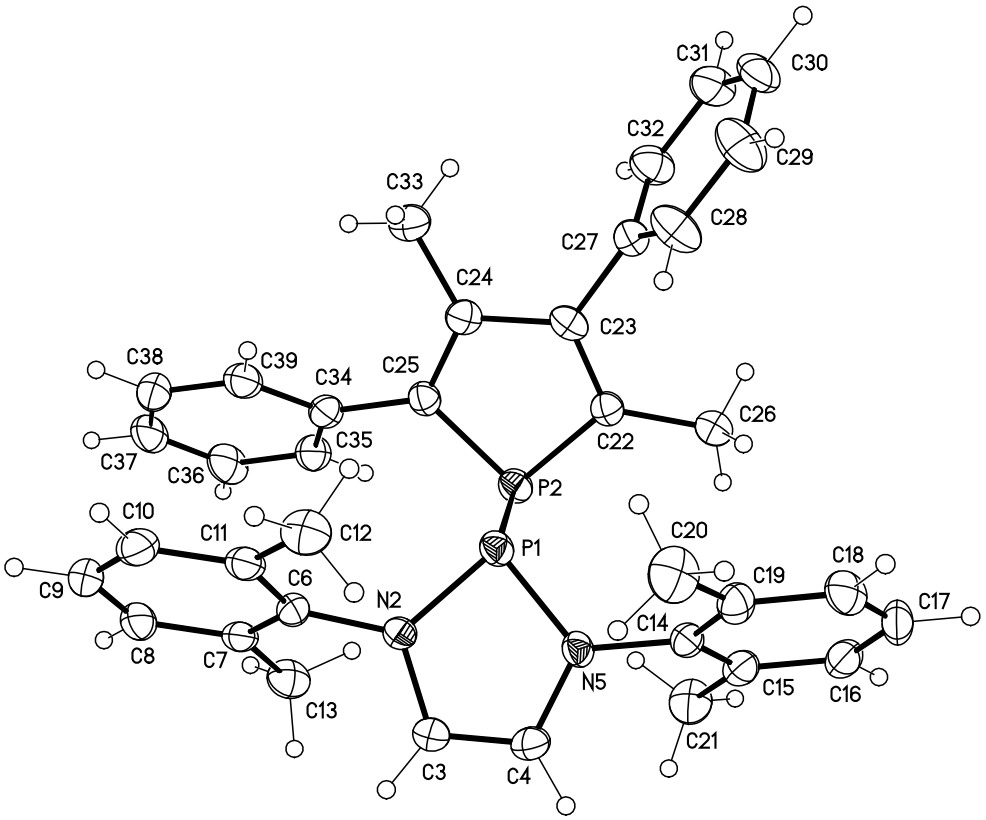

Table 5. Bond lengths [A] and angles [deg] for 4e.

P(1)-N(2)	1.6990(19)
P(1)-N(5)	1.7077(17)
P(1)-P(2)	2.4369(9)
N(2)-C(3)	1.406(3)
N(2)-C(6)	1.444(3)
C(3)-C(4)	1.321(3)
C(4)-N(5)	1.401(3)
N(5)-C(14)	1.439(3)
C(6)-C(11)	1.397(3)
C(6)-C(7)	1.397(3)
C(7)-C(8)	1.389(3)
C(7)-C(13)	1.509(3)
C(8)-C(9)	1.384(3)
C(9)-C(10)	1.373(3)
C(10)-C(11)	1.389(3)
C(11)-C(12)	1.510(3)
C(14)-C(19)	1.389(3)
C(14)-C(15)	1.399(3)
C(15)-C(16)	1.389(3)
C(15)-C(21)	1.509(3)
C(16)-C(17)	1.366(3)
C(17)-C(18)	1.380(3)
C(18)-C(19)	1.397(3)
C(19)-C(20)	1.513(3)
P(2)-C(22)	1.779(2)
P(2)-C(25)	1.805(2)
C(22)-C(23)	1.379(3)
C(22)-C(26)	1.506(3)
C(23)-C(24)	1.449(3)
C(23)-C(27)	1.488(3)
C(24)-C(25)	1.374(3)
C(24)-C(33)	1.508(3)
C(25)-C(34)	1.475(3)
C(27)-C(28)	1.389(3)
C(27)-C(32)	1.393(3)
C(28)-C(29)	1.390(3)
C(29)-C(30)	1.375(3)
C(30)-C(31)	1.374(3)
C(31)-C(32)	1.382(3)

C(34)-C(35)	1.389(3)
C(34)-C(39)	1.399(3)
C(35)-C(36)	1.391(3)
C(36)-C(37)	1.368(3)
C(37)-C(38)	1.387(3)
C(38)-C(39)	1.385(3)

N(2)-P(1)-N(5)	87.78(9)
N(2)-P(1)-P(2)	108.45(7)
N(5)-P(1)-P(2)	105.22(7)
C(3)-N(2)-C(6)	119.54(19)
C(3)-N(2)-P(1)	113.98(15)
C(6)-N(2)-P(1)	126.45(14)
C(4)-C(3)-N(2)	111.8(2)
C(3)-C(4)-N(5)	111.7(2)
C(4)-N(5)-C(14)	121.67(18)
C(4)-N(5)-P(1)	113.97(14)
C(14)-N(5)-P(1)	124.11(16)
C(11)-C(6)-C(7)	122.2(2)
C(11)-C(6)-N(2)	119.3(2)
C(7)-C(6)-N(2)	118.45(19)
C(8)-C(7)-C(6)	117.7(2)
C(8)-C(7)-C(13)	119.7(2)
C(6)-C(7)-C(13)	122.6(2)
C(9)-C(8)-C(7)	121.1(2)
C(10)-C(9)-C(8)	119.8(2)
C(9)-C(10)-C(11)	121.5(2)
C(10)-C(11)-C(6)	117.6(2)
C(10)-C(11)-C(12)	120.1(2)
C(6)-C(11)-C(12)	122.3(2)
C(19)-C(14)-C(15)	122.0(2)
C(19)-C(14)-N(5)	118.3(2)
C(15)-C(14)-N(5)	119.7(2)
C(16)-C(15)-C(14)	117.5(2)
C(16)-C(15)-C(21)	120.6(2)
C(14)-C(15)-C(21)	121.9(2)
C(17)-C(16)-C(15)	121.8(2)
C(16)-C(17)-C(18)	120.1(2)
C(17)-C(18)-C(19)	120.6(2)
C(14)-C(19)-C(18)	118.1(2)
C(14)-C(19)-C(20)	121.8(2)
C(18)-C(19)-C(20)	120.1(2)
C(22)-P(2)-C(25)	90.92(10)
C(22)-P(2)-P(1)	86.85(7)
C(25)-P(2)-P(1)	86.81(7)
C(23)-C(22)-C(26)	123.7(2)
C(23)-C(22)-P(2)	110.85(16)
C(26)-C(22)-P(2)	125.36(16)
C(22)-C(23)-C(24)	114.2(2)
C(22)-C(23)-C(27)	122.7(2)
C(24)-C(23)-C(27)	122.8(2)
C(25)-C(24)-C(23)	113.15(19)
C(25)-C(24)-C(33)	125.9(2)
C(23)-C(24)-C(33)	120.7(2)
C(24)-C(25)-C(34)	127.14(19)
C(24)-C(25)-P(2)	110.82(16)
C(34)-C(25)-P(2)	121.75(17)
C(28)-C(27)-C(32)	117.2(2)
C(28)-C(27)-C(23)	121.9(2)
C(32)-C(27)-C(23)	120.9(2)
C(27)-C(28)-C(29)	121.1(3)
C(30)-C(29)-C(28)	120.7(3)
C(31)-C(30)-C(29)	119.0(3)
C(30)-C(31)-C(32)	120.5(3)
C(31)-C(32)-C(27)	121.5(2)
C(35)-C(34)-C(39)	117.3(2)
C(35)-C(34)-C(25)	119.0(2)
C(39)-C(34)-C(25)	123.7(2)
C(34)-C(35)-C(36)	122.2(2)
C(37)-C(36)-C(35)	119.3(2)
C(36)-C(37)-C(38)	120.2(2)
C(39)-C(38)-C(37)	120.2(2)
C(38)-C(39)-C(34)	120.8(2)

4f

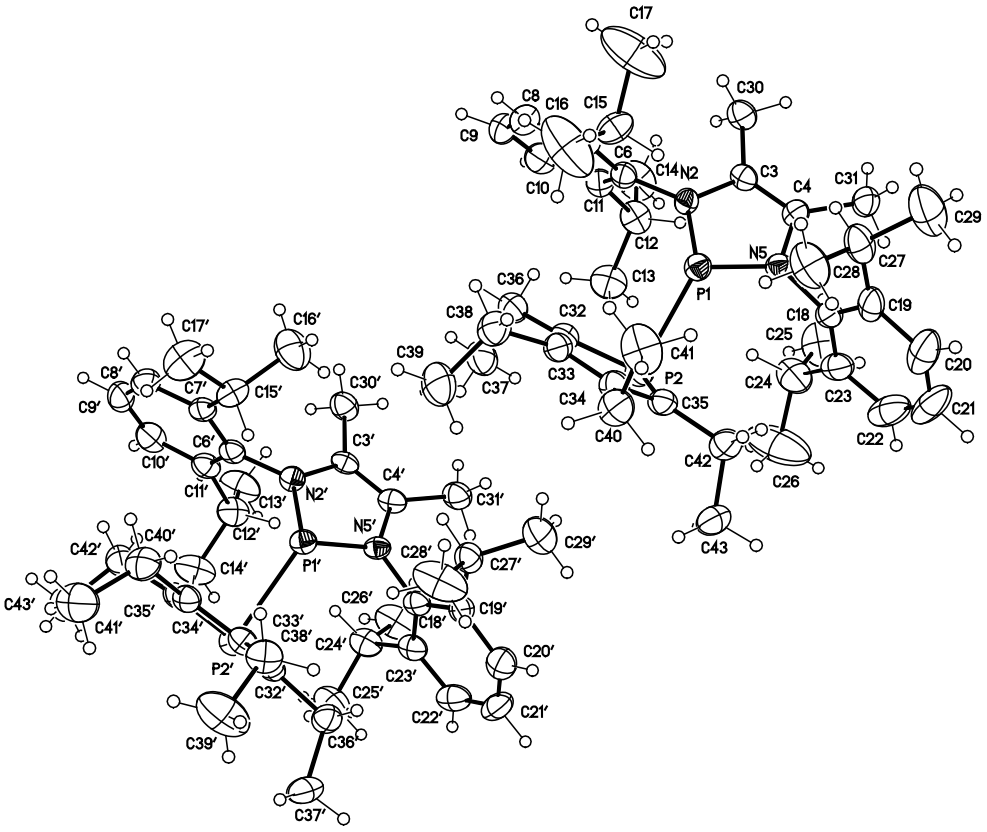

Table 6. Bond lengths [A] and angles [deg] for 4f.

P(1)-N(5)	1.711(2)
P(1)-N(2)	1.715(2)
P(1)-P(2)	2.5205(11)
N(2)-C(3)	1.422(3)
N(2)-C(6)	1.431(3)
C(3)-C(4)	1.330(4)
C(3)-C(30)	1.498(3)
C(4)-N(5)	1.419(3)
C(4)-C(31)	1.501(3)
N(5)-C(18)	1.443(3)
C(6)-C(7)	1.405(4)
C(6)-C(11)	1.414(4)
C(7)-C(8)	1.391(4)
C(7)-C(15)	1.514(4)
C(8)-C(9)	1.377(4)
C(9)-C(10)	1.378(4)
C(10)-C(11)	1.389(4)
C(11)-C(12)	1.520(4)
C(12)-C(13)	1.531(4)
C(12)-C(14)	1.545(4)
C(15)-C(16)	1.493(4)
C(15)-C(17)	1.512(4)
C(18)-C(23)	1.403(4)
C(18)-C(19)	1.407(4)
C(19)-C(20)	1.394(4)
C(19)-C(27)	1.513(4)
C(20)-C(21)	1.386(5)
C(21)-C(22)	1.372(5)
C(22)-C(23)	1.397(4)
C(23)-C(24)	1.508(4)
C(24)-C(25)	1.518(4)
C(24)-C(26)	1.525(4)
C(27)-C(29)	1.524(4)
C(27)-C(28)	1.535(4)
P(2)-C(35)	1.795(3)
P(2)-C(32)	1.797(3)
C(32)-C(33)	1.369(3)
C(32)-C(36)	1.516(4)

C(33)-C(34)	1.450(4)
C(33)-C(38)	1.514(4)
C(34)-C(35)	1.372(3)
C(34)-C(40)	1.521(4)
C(35)-C(42)	1.516(4)
C(36)-C(37)	1.530(4)
C(38)-C(39)	1.529(4)
C(40)-C(41)	1.528(4)
C(42)-C(43)	1.523(4)
P(1')-N(5')	1.709(2)
P(1')-N(2')	1.718(2)
P(1')-P(2')	2.5652(11)
N(2')-C(3')	1.420(3)
N(2')-C(6')	1.439(3)
C(3')-C(4')	1.331(4)
C(3')-C(30')	1.499(3)
C(4')-N(5')	1.413(3)
C(4')-C(31')	1.504(3)
N(5')-C(18')	1.445(3)
C(6')-C(11')	1.405(4)
C(6')-C(7')	1.410(4)
C(7')-C(8')	1.387(4)
C(7')-C(15')	1.514(4)
C(8')-C(9')	1.385(4)
C(9')-C(10')	1.378(4)
C(10')-C(11')	1.391(4)
C(11')-C(12')	1.519(4)
C(12')-C(14')	1.537(4)
C(12')-C(13')	1.539(4)
C(15')-C(16')	1.524(4)
C(15')-C(17')	1.532(4)
C(18')-C(19')	1.396(4)
C(18')-C(23')	1.414(4)
C(19')-C(20')	1.389(4)
C(19')-C(27')	1.520(4)
C(20')-C(21')	1.381(4)
C(21')-C(22')	1.367(4)
C(22')-C(23')	1.392(4)
C(23')-C(24')	1.516(4)
C(24')-C(25')	1.536(4)
C(24')-C(26')	1.537(3)
C(27')-C(28')	1.514(3)
C(27')-C(29')	1.525(4)
P(2')-C(32')	1.787(3)
P(2')-C(35')	1.789(3)
C(32')-C(33')	1.371(4)
C(32')-C(36')	1.519(4)
C(33')-C(34')	1.448(4)
C(33')-C(38')	1.507(4)
C(34')-C(35')	1.370(4)
C(34')-C(40')	1.517(4)
C(35')-C(42')	1.511(4)
C(36')-C(37')	1.506(4)
C(38')-C(39')	1.508(4)
C(40')-C(41')	1.512(4)
C(42')-C(43')	1.516(4)

N(5)-P(1)-N(2)	86.85(11)
N(5)-P(1)-P(2)	112.24(8)
N(2)-P(1)-P(2)	116.20(9)
C(3)-N(2)-C(6)	121.7(2)
C(3)-N(2)-P(1)	115.13(19)
C(6)-N(2)-P(1)	123.08(17)
C(4)-C(3)-N(2)	111.1(2)
C(4)-C(3)-C(30)	128.5(3)
N(2)-C(3)-C(30)	119.7(2)
C(3)-C(4)-N(5)	111.2(2)
C(3)-C(4)-C(31)	128.6(3)
N(5)-C(4)-C(31)	119.9(2)
C(4)-N(5)-C(18)	119.2(2)
C(4)-N(5)-P(1)	115.38(18)
C(18)-N(5)-P(1)	125.45(17)
C(7)-C(6)-C(11)	121.6(3)
C(7)-C(6)-N(2)	118.7(3)
C(11)-C(6)-N(2)	119.6(2)
C(8)-C(7)-C(6)	118.1(3)
C(8)-C(7)-C(15)	119.9(3)
C(6)-C(7)-C(15)	121.8(3)

C(9)-C(8)-C(7)	121.0(3)
C(8)-C(9)-C(10)	120.2(3)
C(9)-C(10)-C(11)	121.7(3)
C(10)-C(11)-C(6)	117.2(3)
C(10)-C(11)-C(12)	119.6(3)
C(6)-C(11)-C(12)	123.1(3)
C(11)-C(12)-C(13)	111.4(2)
C(11)-C(12)-C(14)	112.2(3)
C(13)-C(12)-C(14)	109.6(2)
C(16)-C(15)-C(17)	108.4(3)
C(16)-C(15)-C(7)	114.1(3)
C(17)-C(15)-C(7)	110.4(3)
C(23)-C(18)-C(19)	123.7(3)
C(23)-C(18)-N(5)	117.9(3)
C(19)-C(18)-N(5)	118.2(3)
C(20)-C(19)-C(18)	116.8(3)
C(20)-C(19)-C(27)	121.8(3)
C(18)-C(19)-C(27)	121.4(3)
C(21)-C(20)-C(19)	120.6(4)
C(22)-C(21)-C(20)	121.2(4)
C(21)-C(22)-C(23)	121.2(4)
C(22)-C(23)-C(18)	116.5(4)
C(22)-C(23)-C(24)	120.5(3)
C(18)-C(23)-C(24)	123.0(3)
C(23)-C(24)-C(25)	114.6(3)
C(23)-C(24)-C(26)	114.0(3)
C(25)-C(24)-C(26)	108.7(3)
C(19)-C(27)-C(29)	114.5(3)
C(19)-C(27)-C(28)	110.0(3)
C(29)-C(27)-C(28)	110.1(3)
C(35)-P(2)-C(32)	90.61(13)
C(35)-P(2)-P(1)	83.68(9)
C(32)-P(2)-P(1)	87.25(10)
C(33)-C(32)-C(36)	125.5(3)
C(33)-C(32)-P(2)	110.9(2)
C(36)-C(32)-P(2)	123.3(2)
C(32)-C(33)-C(34)	113.9(2)
C(32)-C(33)-C(38)	124.0(3)
C(34)-C(33)-C(38)	121.8(3)
C(35)-C(34)-C(33)	113.5(2)
C(35)-C(34)-C(40)	124.3(3)
C(33)-C(34)-C(40)	122.1(2)
C(34)-C(35)-C(42)	124.7(3)
C(34)-C(35)-P(2)	111.1(2)
C(42)-C(35)-P(2)	124.2(2)
C(32)-C(36)-C(37)	112.9(3)
C(33)-C(38)-C(39)	113.5(3)
C(34)-C(40)-C(41)	114.3(2)
C(35)-C(42)-C(43)	113.1(3)
N(5')-P(1')-N(2')	86.78(10)
N(5')-P(1')-P(2')	113.19(8)
N(2')-P(1')-P(2')	117.38(9)
C(3')-N(2')-C(6')	119.7(2)
C(3')-N(2')-P(1')	115.08(18)
C(6')-N(2')-P(1')	124.28(17)
C(4')-C(3')-N(2')	111.1(2)
C(4')-C(3')-C(30')	128.0(2)
N(2')-C(3')-C(30')	120.6(2)
C(3')-C(4')-N(5')	111.3(2)
C(3')-C(4')-C(31')	128.5(3)
N(5')-C(4')-C(31')	119.7(2)
C(4')-N(5')-C(18')	119.1(2)
C(4')-N(5')-P(1')	115.59(18)
C(18')-N(5')-P(1')	124.21(16)
C(11')-C(6')-C(7')	121.9(3)
C(11')-C(6')-N(2')	118.9(3)
C(7')-C(6')-N(2')	119.2(3)
C(8')-C(7')-C(6')	117.5(3)
C(8')-C(7')-C(15')	121.2(3)
C(6')-C(7')-C(15')	121.3(3)
C(9')-C(8')-C(7')	121.6(3)
C(10')-C(9')-C(8')	119.8(3)
C(9')-C(10')-C(11')	121.4(3)
C(10')-C(11')-C(6')	117.8(3)
C(10')-C(11')-C(12')	119.1(3)
C(6')-C(11')-C(12')	123.1(3)
C(11')-C(12')-C(14')	111.7(2)
C(11')-C(12')-C(13')	112.7(2)

C(14')-C(12')-C(13')	108.9(2)
C(7')-C(15')-C(16')	112.4(2)
C(7')-C(15')-C(17')	113.9(3)
C(16')-C(15')-C(17')	108.9(3)
C(19')-C(18')-C(23')	122.1(3)
C(19')-C(18')-N(5')	119.2(3)
C(23')-C(18')-N(5')	118.5(3)
C(20')-C(19')-C(18')	117.7(3)
C(20')-C(19')-C(27')	120.4(3)
C(18')-C(19')-C(27')	121.8(3)
C(21')-C(20')-C(19')	121.0(3)
C(22')-C(21')-C(20')	120.6(3)
C(21')-C(22')-C(23')	121.4(3)
C(22')-C(23')-C(18')	117.1(3)
C(22')-C(23')-C(24')	119.9(3)
C(18')-C(23')-C(24')	123.0(3)
C(23')-C(24')-C(25')	112.3(2)
C(23')-C(24')-C(26')	112.4(2)
C(25')-C(24')-C(26')	109.0(2)
C(28')-C(27')-C(19')	111.3(2)
C(28')-C(27')-C(29')	110.3(3)
C(19')-C(27')-C(29')	112.5(2)
C(32')-P(2')-C(35')	90.78(13)
C(32')-P(2')-P(1')	80.94(9)
C(35')-P(2')-P(1')	81.23(9)
C(33')-C(32')-C(36')	125.6(3)
C(33')-C(32')-P(2')	110.9(2)
C(36')-C(32')-P(2')	123.4(2)
C(32')-C(33')-C(34')	113.7(3)
C(32')-C(33')-C(38')	123.6(3)
C(34')-C(33')-C(38')	122.6(3)
C(35')-C(34')-C(33')	113.5(3)
C(35')-C(34')-C(40')	124.0(3)
C(33')-C(34')-C(40')	122.4(3)
C(34')-C(35')-C(42')	124.9(3)
C(34')-C(35')-P(2')	111.0(2)
C(42')-C(35')-P(2')	124.0(2)
C(37')-C(36')-C(32')	115.3(2)
C(33')-C(38')-C(39')	114.6(3)
C(41')-C(40')-C(34')	114.3(3)
C(35')-C(42')-C(43')	113.8(3)

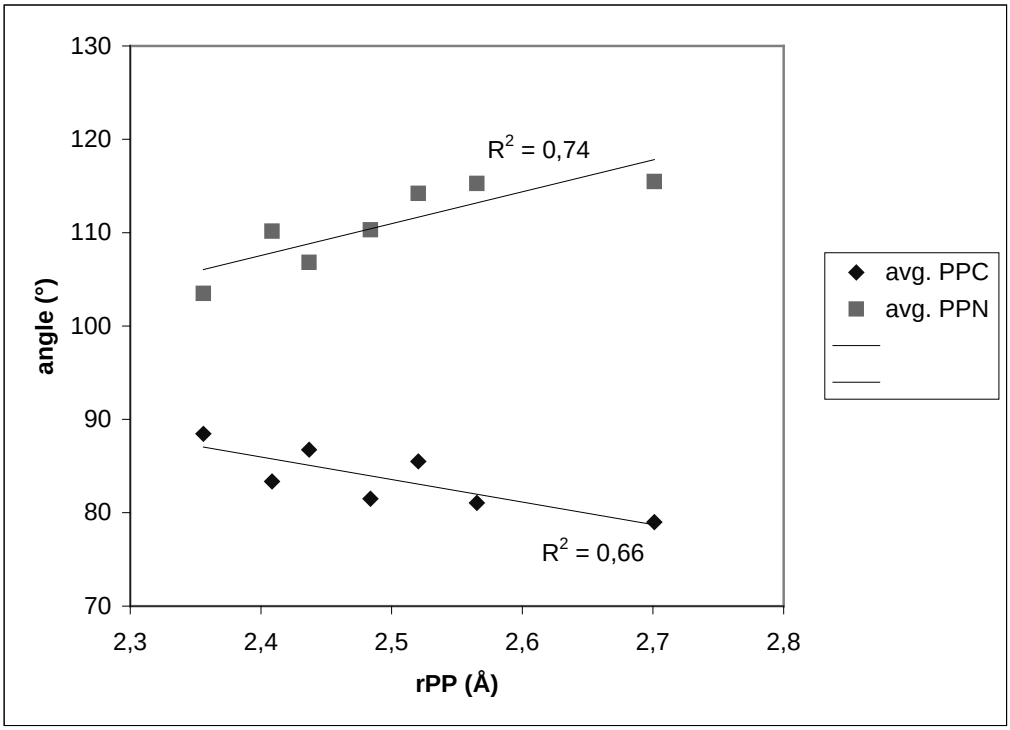

Figure S1: Plot of avgerage P–P(2)–C and P–P(1)–N angles vs. P–P distances. Straight lines indicate the results of linear regression analyses; R^2 denote the appropriate correlation coefficients.

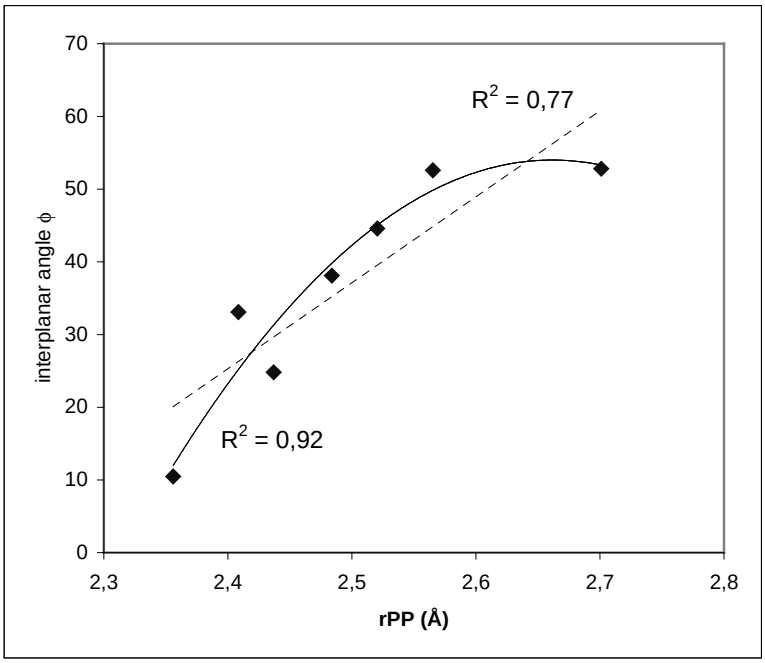

Figure S2: Plot of interplanar angle ϕ vs. P–P distances. Straight and dashed lines indicate the results of linear and quadratic regression analyses; R^2 denote the appropriate correlation coefficients.

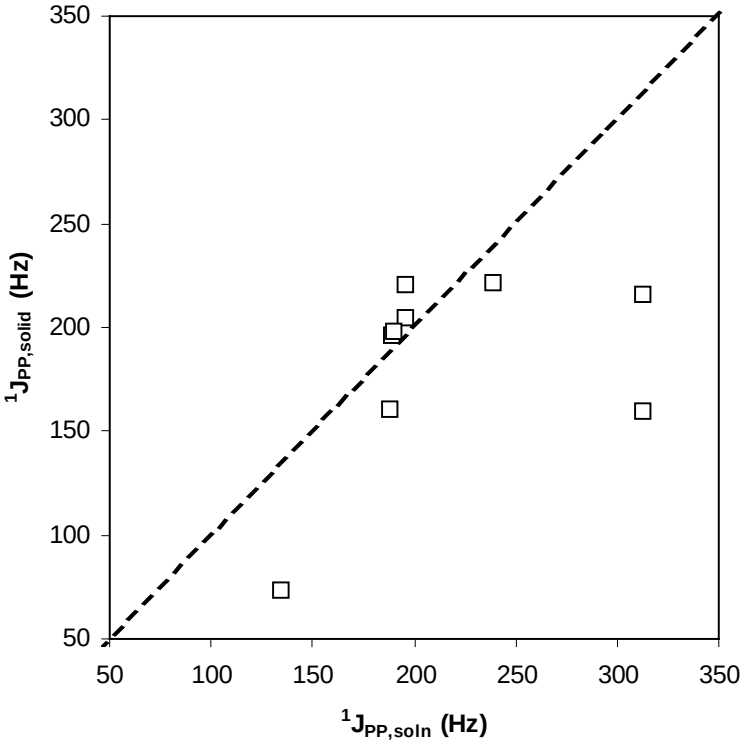

Figure S3: Plot of $^1J_{PP,solid}$ vs. $^1J_{PP,soln}$ for **4a-g**. The dashed line denotes points where $^1J_{PP,solid} = {}^1J_{PP,soln}$.

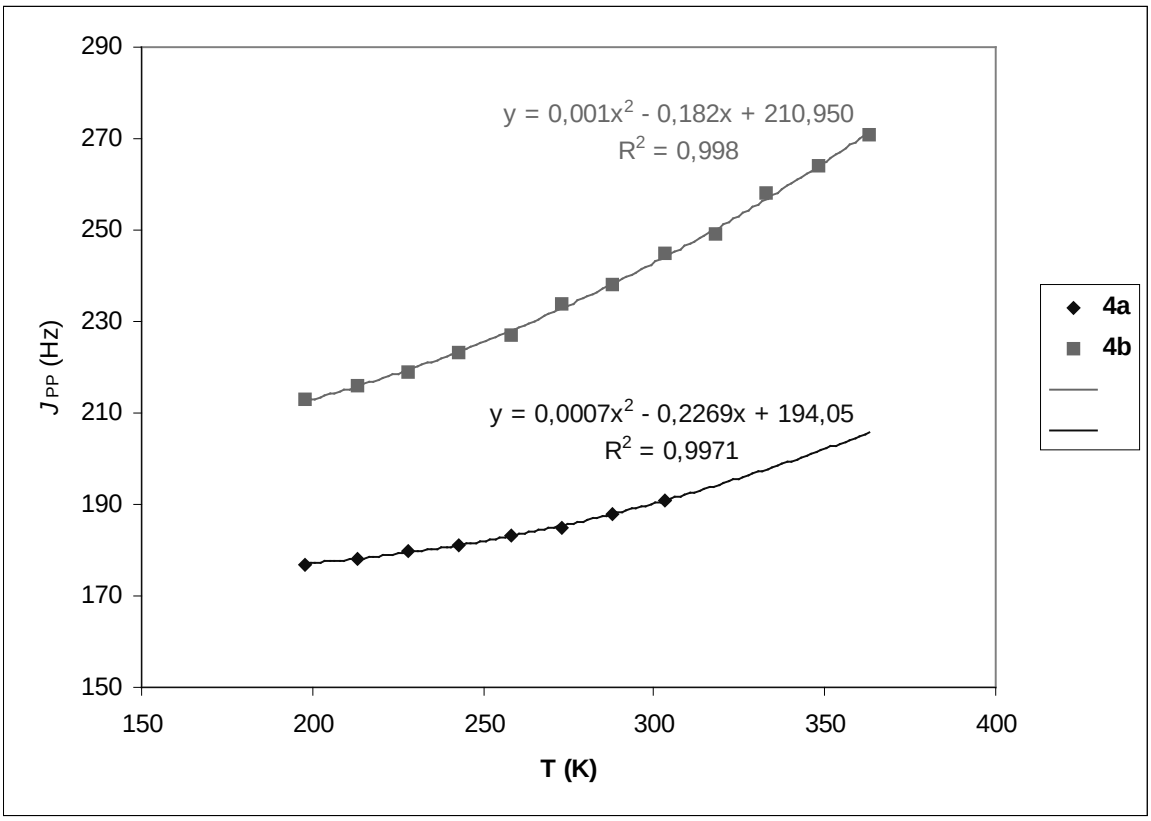

Figure S4: Temperature dependence of $^1J_{PP}$ in **4a,b**.

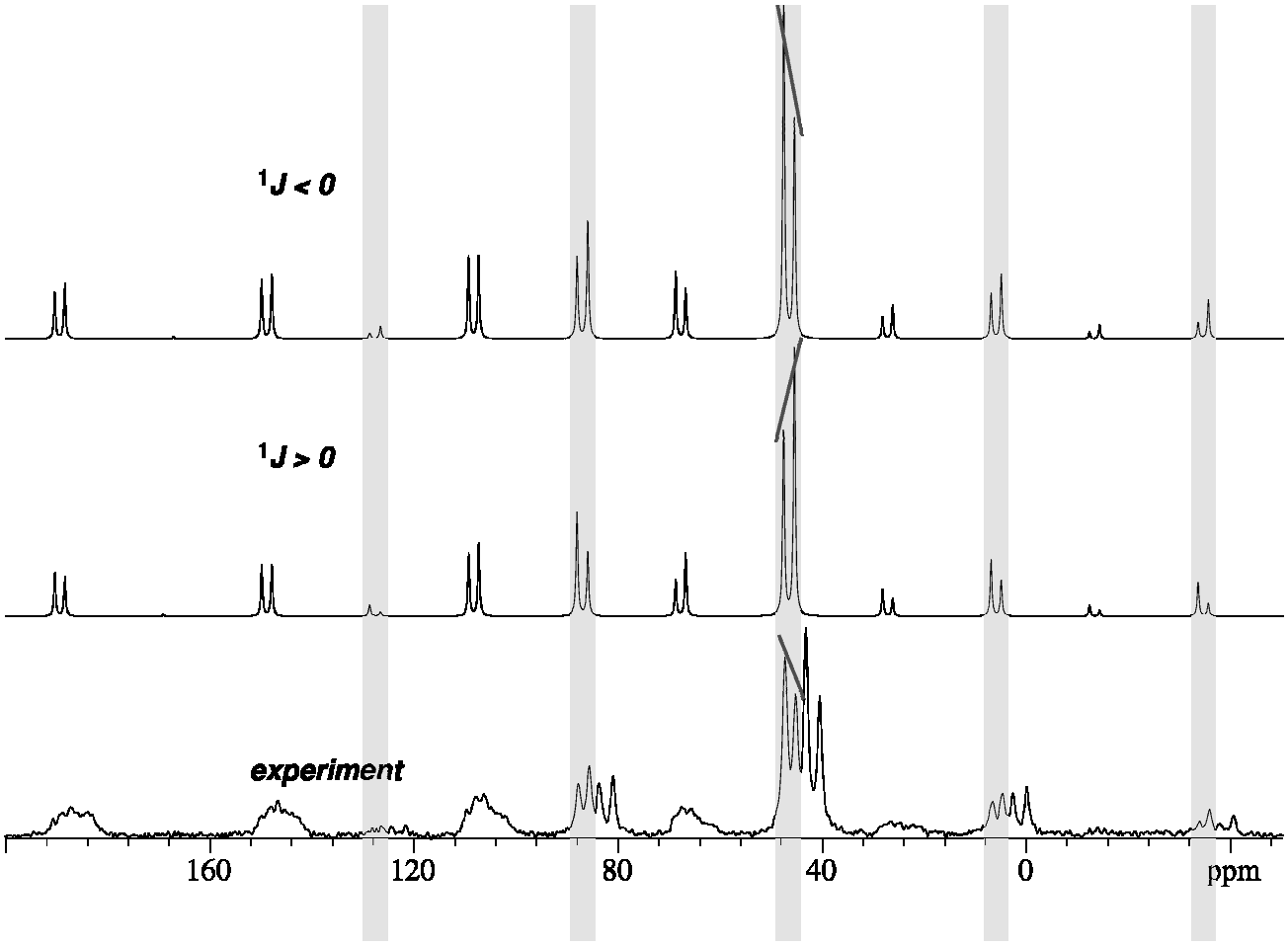

Figure S4: ^{31}P-CP-MAS-NMR spectra for **4f**; bottom: experimental spectrum obtained at 81.0 MHz, sample spinning frequency of 3285 Hz, spinning sidebands from the P atoms in the phosphole rings are highlighted in yellow; anomalous intensities are observed for the doublets caused by $^1J(^{31}\text{P}\text{-}^{31}\text{P})$ coupling which allow to determine the sign of the J-coupling constant; middle: numerically calculated spectrum for **4f#2** using the chemical shift parameters given in table 1, orientations and the direct magnetic dipole-dipole interaction are similar to the theoretically calculated values, the magnitude of $^1J(^{31}\text{P}\text{-}^{31}\text{P})$ was set to the experimentally observed value while the sign was chosen to be positive; top spectrum: the same as the middle spectrum, but with a negative sign of $^1J(^{31}\text{P}\text{-}^{31}\text{P})$; the observed "roof effects" (red lines) in the experimental spectrum agree with the experimental data and that this simulation represents the correct sign of the J-coupling.

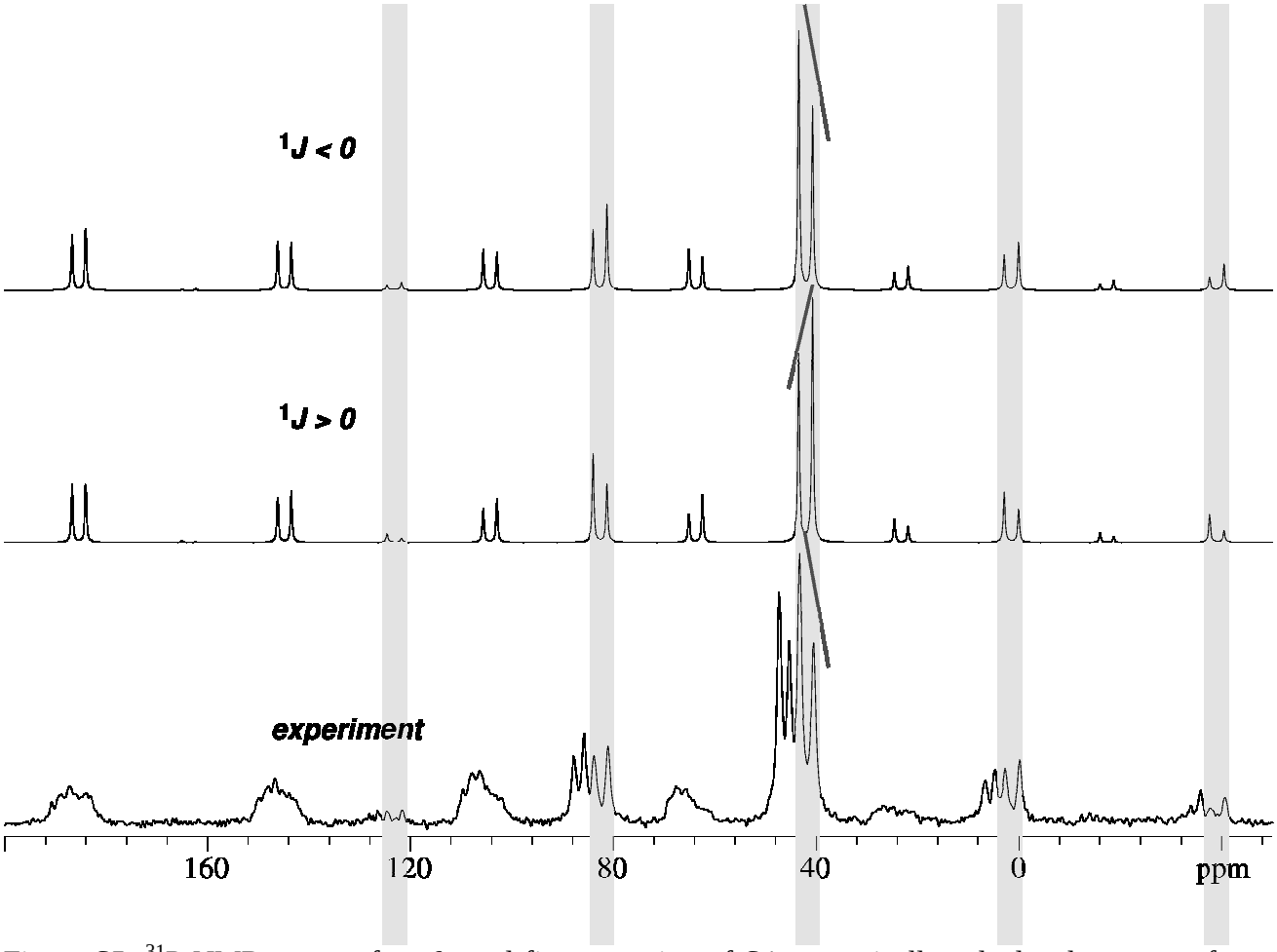

Figure S5: ^{31}P-NMR spectra for **4f**; read figure caption of S4; numerically calculated spectra refer to **4f#1.**

Table S1: Experimental and computed chemical shift tensor data for **4f#1** and **4f#2** in ppm; as often observed when comparing calculated and experimental data the asymmetry parameter η gives the worst agreement while isotropic and anisotropic chemical values agree reasonably well; since the differences in isotropic chemical shift are below 5 ppm (comparing values of **4f#1** and **4f#2**) it is not advisable to base an assignment on the isotropic chemical shift value; our assignment is based on the anisotropic chemical shift values of P1 which both in calculations and experiment show similar values and sufficient separation.

	4f#1 (P1–P2 2.521 Å)		**4f#2** (P1'–P2' 2.565 Å)	
	Exp	Calcd. [a) b)]	Exp.	Calcd. [a) b)]
δ_{iso}(P1)	185.2	152.72	189.2	166.25
δ_{aniso}(P1)	206	203.3	260	284.55
η(P1)	0.93	0.7581	0.47	0.3407
δ_{11}(P1)	391.2	356.00	449.2	450.81
δ_{22}(P1)	178.0	128.13	120.3	72.46
δ_{33}(P1)	-13.6	-25.98	-1.9	-24.50
δ_{iso}(P2)	42.0	30.0	46.4	35.69
δ_{aniso}(P2)	-74	81.06	-77	-80.30
η(P2)	0.13	0.9186	0.09	0.6658
δ_{11}(P2)	83.8	111.06	88.4	102.53
δ_{22}(P2)	81.4	26.70	81.4	49.15
δ_{33}(P2)	-32.0	-47.76	-30.6	-44.61

[a)] mPW1PW/6-311++G(d,p) for the P-atoms, 6-311G(d,p) for the C- and N-atoms in the phospholyl and diazaphospholyl rings and 6-31G(d,p) for all other atoms; [b)] Conversion σ -> δ: δ = (σ-312.48)/-1.1067

Complete Reference 38: Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Computational results / final atomic coordinates and energies for 7:

b3lyp/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.307004	2.084551	1.267223
2	6	0	0.593801	2.964894	0.717837
3	6	0	0.593801	2.964894	-0.717837
4	6	0	-0.307004	2.084551	-1.267223
5	15	0	-1.229338	1.196731	0.000000
6	15	0	0.719363	-0.413448	0.000000
7	7	0	0.305955	-1.588603	1.197998
8	6	0	-0.412917	-2.665757	0.674622
9	6	0	-0.412917	-2.665757	-0.674622
10	7	0	0.305955	-1.588603	-1.197998
11	1	0	-0.843064	-3.406966	1.334875
12	1	0	-0.843064	-3.406966	-1.334875
13	6	0	0.277045	-1.273144	-2.616907
14	6	0	0.277045	-1.273144	2.616907
15	1	0	-0.457316	1.951958	-2.333914
16	1	0	1.240869	3.615991	-1.301607
17	1	0	-0.457316	1.951958	2.333914
18	1	0	1.240869	3.615991	1.301607
19	1	0	1.083205	-0.574077	2.853439
20	1	0	-0.678334	-0.818567	2.916202
21	1	0	0.432224	-2.186012	3.201343
22	1	0	1.083205	-0.574077	-2.853439
23	1	0	0.432224	-2.186012	-3.201343
24	1	0	-0.678334	-0.818567	-2.916202

```
 ---------------------------------------------------------------------
SCF Done:  E(RB+HF-LYP) =  -1104.23662265     A.U. after   16 cycles
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             S**2   =   0.0000
```

b3lyp/6-311G(d,p)

```
 ---------------------------------------------------------------------
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 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0        2.906342    0.672673    0.288757
    2          6             0        2.906829   -0.672189    0.288428
    3          7             0        1.793089   -1.174387   -0.392214
    4         15             0        0.592431   -0.000314   -0.769185
    5         15             0       -0.959120   -0.000577    1.217885
    6          7             0        1.792138    1.174380   -0.391358
    7          1             0        3.650983    1.333983    0.701011
    8          1             0        3.651910   -1.333141    0.700453
    9          1             0        1.583295   -2.159746   -0.377518
   10          1             0        1.582379    2.159735   -0.377491
   11          6             0       -1.842433    1.263866    0.294106
   12          6             0       -1.844060   -1.263813    0.294008
   13          6             0       -2.723625   -0.715940   -0.605116
   14          1             0       -1.707873   -2.327972    0.442061
   15          1             0       -3.367057   -1.299997   -1.254415
   16          6             0       -2.722883    0.717173   -0.604881
   17          1             0       -1.705067    2.327840    0.442449
   18          1             0       -3.365847    1.302095   -1.253866
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SCF Done:  E(RB+HF-LYP) =  -1025.76397688     A.U. after    8 cycles
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             S**2   =   0.0000
```

b3lyp/cc-pVDZ

```
 ---------------------------------------------------------------------
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 Number     Number      Type              X           Y           Z
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    2          6             0        0.624907    2.951779    0.717915
    3          6             0        0.624907    2.951779   -0.717915
    4          6             0       -0.304549    2.096277   -1.268883
    5         15             0       -1.257028    1.231850    0.000000
    6         15             0        0.713715   -0.406790    0.000000
    7          7             0        0.296115   -1.592875    1.202603
    8          6             0       -0.396325   -2.684814    0.676645
    9          6             0       -0.396325   -2.684814   -0.676645
   10          7             0        0.296115   -1.592875   -1.202603
   11          1             0       -0.824802   -3.436010    1.337036
   12          1             0       -0.824802   -3.436010   -1.337036
   13          6             0        0.271085   -1.286776   -2.622869
   14          6             0        0.271085   -1.286776    2.622869
   15          1             0       -0.460316    1.969920   -2.342291
   16          1             0        1.294630    3.585835   -1.305618
   17          1             0       -0.460316    1.969920    2.342291
   18          1             0        1.294630    3.585835    1.305618
   19          1             0        1.027845   -0.522293    2.848602
   20          1             0       -0.715284   -0.904247    2.945178
   21          1             0        0.509260   -2.189829    3.207163
   22          1             0        1.027845   -0.522293   -2.848602
   23          1             0        0.509260   -2.189829   -3.207163
   24          1             0       -0.715284   -0.904247   -2.945178
 ---------------------------------------------------------------------
 SCF Done:  E(RB+HF-LYP) =  -1104.29134196     A.U. after    7 cycles
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```

```
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```

b3lyp/cc-pVTZ

```
 ---------------------------------------------------------------------
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 Number     Number      Type              X           Y           Z
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    1          6             0       -0.304555    2.094949    1.262917
    2          6             0        0.580428    2.983375    0.714792
    3          6             0        0.580428    2.983375   -0.714792
    4          6             0       -0.304555    2.094949   -1.262917
    5         15             0       -1.213729    1.202888    0.000000
    6         15             0        0.717691   -0.428380    0.000000
    7          7             0        0.285349   -1.585390    1.191827
    8          6             0       -0.434123   -2.657470    0.671578
    9          6             0       -0.434123   -2.657470   -0.671578
   10          7             0        0.285349   -1.585390   -1.191827
   11          1             0       -0.878853   -3.387869    1.326330
   12          1             0       -0.878853   -3.387869   -1.326330
   13          6             0        0.305173   -1.297434   -2.613355
   14          6             0        0.305173   -1.297434    2.613355
   15          1             0       -0.453281    1.961901   -2.324454
   16          1             0        1.214309    3.640772   -1.296474
   17          1             0       -0.453281    1.961901    2.324454
   18          1             0        1.214309    3.640772    1.296474
   19          1             0        1.072575   -0.555378    2.824627
   20          1             0       -0.656139   -0.908569    2.962917
   21          1             0        0.542685   -2.202450    3.173416
   22          1             0        1.072575   -0.555378   -2.824627
   23          1             0        0.542685   -2.202450   -3.173416
   24          1             0       -0.656139   -0.908569   -2.962917
 ---------------------------------------------------------------------
 SCF Done:  E(RB+HF-LYP) =  -1104.46137592     A.U. after    6 cycles
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            S**2   =   0.0000
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MP2/6-31g(d)

```
 ---------------------------------------------------------------------
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 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -0.276977    1.994789    1.255860
    2          6             0        0.871231    2.600118    0.710109
    3          6             0        0.871231    2.600118   -0.710109
    4          6             0       -0.276977    1.994789   -1.255860
    5         15             0       -1.422562    1.440530    0.000000
    6         15             0        0.633186   -0.321393    0.000000
    7          7             0        0.263827   -1.533562    1.186970
    8          6             0       -0.319186   -2.684704    0.687235
    9          6             0       -0.319186   -2.684704   -0.687235
   10          7             0        0.263827   -1.533562   -1.186970
   11          1             0       -0.681805   -3.468788    1.354076
   12          1             0       -0.681805   -3.468788   -1.354076
   13          6             0        0.212410   -1.206936   -2.609297
   14          6             0        0.212410   -1.206936    2.609297
   15          1             0       -0.470001    1.924414   -2.332913
   16          1             0        1.682531    3.023682   -1.313701
   17          1             0       -0.470001    1.924414    2.332913
   18          1             0        1.682531    3.023682    1.313701
   19          1             0        0.917127   -0.388536    2.815458
   20          1             0       -0.801851   -0.880334    2.900627
   21          1             0        0.502666   -2.088644    3.202500
   22          1             0        0.917127   -0.388536   -2.815458
   23          1             0        0.502666   -2.088644   -3.202500
   24          1             0       -0.801851   -0.880334   -2.900627
```

```
 -------------------------------------------------------------------
Spin components of T(2) and E(2):
     alpha-alpha T2 =       0.9102416691D-01 E2=     -0.2217160093D+00
     alpha-beta  T2 =       0.4820503640D+00 E2=     -0.1242472252D+01
     beta-beta   T2 =       0.9102416691D-01 E2=     -0.2217160093D+00
 ANorm=    0.1289999495D+01
 E2 =    -0.1685904270D+01 EUMP2 =    -0.11019307755867D+04
```

MP2/cc-pVDZ

```
 -------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
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    1          6             0       -0.276977    1.994789    1.255860
    2          6             0        0.871231    2.600118    0.710109
    3          6             0        0.871231    2.600118   -0.710109
    4          6             0       -0.276977    1.994789   -1.255860
    5         15             0       -1.422562    1.440530    0.000000
    6         15             0        0.633186   -0.321393    0.000000
    7          7             0        0.263827   -1.533562    1.186970
    8          6             0       -0.319186   -2.684704    0.687235
    9          6             0       -0.319186   -2.684704   -0.687235
   10          7             0        0.263827   -1.533562   -1.186970
   11          1             0       -0.681805   -3.468788    1.354076
   12          1             0       -0.681805   -3.468788   -1.354076
   13          6             0        0.212410   -1.206936   -2.609297
   14          6             0        0.212410   -1.206936    2.609297
   15          1             0       -0.470001    1.924414   -2.332913
   16          1             0        1.682531    3.023682   -1.313701
   17          1             0       -0.470001    1.924414    2.332913
   18          1             0        1.682531    3.023682    1.313701
   19          1             0        0.917127   -0.388536    2.815458
   20          1             0       -0.801851   -0.880334    2.900627
   21          1             0        0.502666   -2.088644    3.202500
   22          1             0        0.917127   -0.388536   -2.815458
   23          1             0        0.502666   -2.088644   -3.202500
   24          1             0       -0.801851   -0.880334   -2.900627
 -------------------------------------------------------------------
 Spin components of T(2) and E(2):
     alpha-alpha T2 =       0.9102416691D-01 E2=     -0.2217160093D+00
     alpha-beta  T2 =       0.4820503640D+00 E2=     -0.1242472252D+01
     beta-beta   T2 =       0.9102416691D-01 E2=     -0.2217160093D+00
 ANorm=    0.1289999495D+01
 E2 =    -0.1685904270D+01 EUMP2 =    -0.11019307755867D+04
```

MP4(SDQ)/6-31g(d)

```
 -------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 -------------------------------------------------------------------
    1          6             0       -0.316294    2.025642    1.267170
    2          6             0        0.489658    2.986401    0.723442
    3          6             0        0.489658    2.986401   -0.723442
    4          6             0       -0.316294    2.025642   -1.267170
    5         15             0       -1.155056    1.048993    0.000000
    6         15             0        0.772288   -0.410359    0.000000
    7          7             0        0.367520   -1.577142    1.199886
    8          6             0       -0.462369   -2.585851    0.673137
    9          6             0       -0.462369   -2.585851   -0.673137
   10          7             0        0.367520   -1.577142   -1.199886
   11          1             0       -0.937449   -3.299255    1.336944
   12          1             0       -0.937449   -3.299255   -1.336944
   13          6             0        0.266593   -1.207006   -2.603781
   14          6             0        0.266593   -1.207006    2.603781
   15          1             0       -0.458062    1.881753   -2.335458
```

```
  16          1             0        1.070608    3.698353   -1.308307
  17          1             0       -0.458062    1.881753    2.335458
  18          1             0        1.070608    3.698353    1.308307
  19          1             0        1.097787   -0.543698    2.862248
  20          1             0       -0.680500   -0.694245    2.830466
  21          1             0        0.340207   -2.107783    3.222860
  22          1             0        1.097787   -0.543698   -2.862248
  23          1             0        0.340207   -2.107783   -3.222860
  24          1             0       -0.680500   -0.694245   -2.830466
 ---------------------------------------------------------------------
 Spin components of T(2) and E(2):
     alpha-alpha T2 =       0.7961288680D-01 E2=     -0.2074522856D+00
     alpha-beta  T2 =       0.4351906624D+00 E2=     -0.1167278994D+01
     beta-beta   T2 =       0.7961288680D-01 E2=     -0.2074522856D+00
 ANorm=    0.1262702038D+01
 E2=       -0.1582183565D+01 EUMP2=       -0.11017820032658D+04
 MP4(R+Q)=  0.38869540D-01
 E3=       -0.57585039D-01        EUMP3=      -0.11018395883D+04
 E4(DQ)=   -0.46671543D-02        UMP4(DQ)=   -0.11018442555D+04
 E4(SDQ)=  -0.24144281D-01        UMP4(SDQ)=  -0.11018637326D+04
 VARIATIONAL ENERGIES WITH THE FIRST-ORDER WAVEFUNCTION:
 E(VAR1)=  -0.11012282641D+04     E(CISD,4)=  -0.11009621262D+04
```

ccd/6-31G(d)

```
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -0.315438    2.025392    1.266406
    2          6             0        0.485244    2.988565    0.723370
    3          6             0        0.485244    2.988565   -0.723370
    4          6             0       -0.315438    2.025392   -1.266406
    5         15             0       -1.151326    1.047010    0.000000
    6         15             0        0.771633   -0.412978    0.000000
    7          7             0        0.366636   -1.575983    1.197651
    8          6             0       -0.468976   -2.580385    0.672103
    9          6             0       -0.468976   -2.580385   -0.672103
   10          7             0        0.366636   -1.575983   -1.197651
   11          1             0       -0.949738   -3.290284    1.335471
   12          1             0       -0.949738   -3.290284   -1.335471
   13          6             0        0.272797   -1.210159   -2.602283
   14          6             0        0.272797   -1.210159    2.602283
   15          1             0       -0.456434    1.881440   -2.334546
   16          1             0        1.063109    3.702865   -1.308243
   17          1             0       -0.456434    1.881440    2.334546
   18          1             0        1.063109    3.702865    1.308243
   19          1             0        1.104105   -0.545868    2.858143
   20          1             0       -0.673869   -0.700073    2.837054
   21          1             0        0.352316   -2.111911    3.219343
   22          1             0        1.104105   -0.545868   -2.858143
   23          1             0        0.352316   -2.111911   -3.219343
   24          1             0       -0.673869   -0.700073   -2.837054
 ---------------------------------------------------------------------
 DE(Corr)=  -1.6462696     E(CORR)=     -1101.8466587     Delta=-1.00D-09
 NORM(A)=   0.12901115D+01
 Largest amplitude= 5.39D-02
```

ccd/cc-pVDZ

```
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -0.322198    2.019842    1.272038
    2          6             0        0.533838    2.949874    0.725618
    3          6             0        0.533838    2.949874   -0.725618
```

```
   4          6             0       -0.322198    2.019842   -1.272038
   5         15             0       -1.208825    1.072524    0.000000
   6         15             0        0.771696   -0.391267    0.000000
   7          7             0        0.372392   -1.571492    1.204984
   8          6             0       -0.437285   -2.598376    0.677374
   9          6             0       -0.437285   -2.598376   -0.677374
  10          7             0        0.372392   -1.571492   -1.204984
  11          1             0       -0.913710   -3.321438    1.341891
  12          1             0       -0.913710   -3.321438   -1.341891
  13          6             0        0.256275   -1.201971   -2.608847
  14          6             0        0.256275   -1.201971    2.608847
  15          1             0       -0.463659    1.882403   -2.349429
  16          1             0        1.152867    3.635075   -1.316620
  17          1             0       -0.463659    1.882403    2.349429
  18          1             0        1.152867    3.635075    1.316620
  19          1             0        1.059966   -0.493353    2.868957
  20          1             0       -0.719751   -0.727600    2.838378
  21          1             0        0.372233   -2.100287    3.240017
  22          1             0        1.059966   -0.493353   -2.868957
  23          1             0        0.372233   -2.100287   -3.240017
  24          1             0       -0.719751   -0.727600   -2.838378
---------------------------------------------------------------------
DE(Corr)=  -1.7322983     E(CORR)=     -1101.9937393     Delta=-8.18D-10
NORM(A)=   0.13092682D+01
Largest amplitude= 5.25D-02
```

ccsd/6-31G(d)

```
---------------------------------------------------------------------
Center     Atomic     Atomic              Coordinates (Angstroms)
Number     Number      Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.314349    2.030003    1.268032
   2          6             0        0.475101    3.002876    0.724133
   3          6             0        0.475101    3.002876   -0.724133
   4          6             0       -0.314349    2.030003   -1.268032
   5         15             0       -1.139893    1.040608    0.000000
   6         15             0        0.777195   -0.416235    0.000000
   7          7             0        0.368889   -1.581699    1.200558
   8          6             0       -0.468944   -2.584979    0.672535
   9          6             0       -0.468944   -2.584979   -0.672535
  10          7             0        0.368889   -1.581699   -1.200558
  11          1             0       -0.950750   -3.294632    1.335813
  12          1             0       -0.950750   -3.294632   -1.335813
  13          6             0        0.265631   -1.209915   -2.603739
  14          6             0        0.265631   -1.209915    2.603739
  15          1             0       -0.453407    1.883848   -2.336434
  16          1             0        1.044424    3.724830   -1.308423
  17          1             0       -0.453407    1.883848    2.336434
  18          1             0        1.044424    3.724830    1.308423
  19          1             0        1.099172   -0.549567    2.864147
  20          1             0       -0.680089   -0.692882    2.828709
  21          1             0        0.334039   -2.110415    3.224509
  22          1             0        1.099172   -0.549567   -2.864147
  23          1             0        0.334039   -2.110415   -3.224509
  24          1             0       -0.680089   -0.692882   -2.828709
---------------------------------------------------------------------
DE(Corr)=  -1.6632706     E(CORR)=     -1101.8634905     Delta=-5.30D-10
NORM(A)=   0.13104067D+01
Largest amplitude= 6.66D-02
```

Gauche-isomer of 7:

```
---------------------------------------------------------------------
Center     Atomic     Atomic              Coordinates (Angstroms)
Number     Number      Type              X           Y           Z
---------------------------------------------------------------------
```

1	6	0	-2.343402	-0.730967	-0.976755
2	6	0	-3.186393	0.018541	-0.200770
3	6	0	-2.725075	0.207516	1.153536
4	6	0	-1.523999	-0.395979	1.421046
5	15	0	-0.961747	-1.345388	0.000947
6	15	0	0.842159	-0.070004	-1.064272
7	7	0	0.840762	1.489958	-0.340539
8	6	0	-0.139930	2.519733	-0.661577
9	7	0	2.177364	-0.489446	-0.051379
10	6	0	2.680611	-1.851725	0.023787
11	6	0	2.310239	0.401879	1.022314
12	6	0	1.562639	1.512361	0.857785
13	1	0	-2.528163	-0.995985	-2.012180
14	1	0	-1.021031	-0.381373	2.381258
15	1	0	-3.295125	0.772691	1.888000
16	1	0	-4.129524	0.428817	-0.555292
17	1	0	3.006903	0.186766	1.821484
18	1	0	1.524591	2.383409	1.497988
19	1	0	3.680587	-1.847359	0.469180
20	1	0	2.024292	-2.502086	0.620078
21	1	0	2.759097	-2.270635	-0.983633
22	1	0	0.326921	3.508214	-0.584094
23	1	0	-1.006990	2.471576	0.004907
24	1	0	-0.482753	2.385113	-1.690583

SCF Done: E(RB+HF-LYP) = -1104.23405401 A.U. after 1 cycles
Convg = 0.4572D-08 -V/T = 2.0060
S**2 = 0.0000
Full mass-weighted force constant matrix:
Low frequencies --- -4.3908 -0.0003 0.0019 0.0019 2.0551 7.0028
Low frequencies --- 23.6053 57.0862 79.4277
Diagonal vibrational polarizability:
81.5434756 47.6471342 13.8472474

Cisoid isomer of 7 (Transition state):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.047427	1.992666	1.273467
2	6	0	-1.040500	2.617423	0.719263
3	6	0	-1.040500	2.617423	-0.719263
4	6	0	0.047427	1.992666	-1.273467
5	15	0	1.204105	1.457435	0.000000
6	15	0	1.075288	-1.148942	0.000000
7	7	0	-0.083084	-1.566277	1.200337
8	6	0	0.141233	-1.346128	2.619959
9	7	0	-0.083084	-1.566277	-1.200337
10	6	0	0.141233	-1.346128	-2.619959
11	6	0	-1.370540	-1.706765	-0.673914
12	6	0	-1.370540	-1.706765	0.673914
13	1	0	0.248178	1.943839	2.338803
14	1	0	0.248178	1.943839	-2.338803
15	1	0	-1.824537	3.096968	-1.301693
16	1	0	-1.824537	3.096968	1.301693
17	1	0	-2.215283	-1.839345	-1.335898
18	1	0	-2.215283	-1.839345	1.335898
19	1	0	-0.456892	-2.055001	-3.201393
20	1	0	-0.126481	-0.321991	-2.911492
21	1	0	1.195431	-1.517411	-2.856045
22	1	0	-0.456892	-2.055001	3.201393
23	1	0	-0.126481	-0.321991	2.911492
24	1	0	1.195431	-1.517411	2.856045

SCF Done: E(RB+HF-LYP) = -1104.22607444 A.U. after 1 cycles

```
            Convg  =    0.5604D-08             -V/T =  2.0060
            S**2   =   0.0000
Full mass-weighted force constant matrix:
Low frequencies ---  -43.2734   -2.4426   -0.0015    0.0017    0.0019    3.3892
Low frequencies ---    7.6751   69.6799   72.4478
******    1 imaginary frequencies (negative Signs) ******
Diagonal vibrational polarizability:
       9.6120207      99.9336679      14.9963099
```