JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1997, 119(22), 5269-5270, DOI:10.1021/ja970245k

I. Spectroscopic and Analytical Data

NMR, infrared, and analytical data are provided below.

[Cp*Ir(PMe$_3$)(CO)(Me)][OTf] (2a): White powder. (84% yield). mp >250°C. ^{1}H NMR: (CD_2Cl_2, 400 MHz) δ 1.97 (d, J_{PH} = 2.1 Hz, 15H, $C_5(CH_3)_5$), 1.69 (d, J_{PH} = 11.1 Hz, 9H, $P(CH_3)_3$), 0.51 (d, J_{PH} = 6.0 Hz, 3H, $IrCH_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 167.6 (d, J_{PC} = 11.8 Hz, CO), 102.0 (s, $C_5(CH_3)_5$), 14.3 (d, J_{PC} = 42.3 Hz, $P(CH_3)_3$), 8.8 (s, $C_5(CH_3)_5$), -25.6 (d, J_{PC} = 7.0 Hz, CH_3) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -77.7 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -34.9 (s) ppm. IR: (CD_2Cl_2) 2035 (s), 1271 (vs) cm^{-1}. Anal. Calcd for $C_{16}H_{27}O_4F_3IrPS$: C, 32.26; H, 4.57. Found C, 32.38; H, 4.60.

[Cp*Ir(PMe$_3$)(CO)(Et)][OTf] (2b): White powder. mp = 249-251 °C. ^{1}H NMR: (CD_2Cl_2, 400 MHz) δ 2.02 (d, J_{PH} = 2.4 Hz, 15H, $C_5(CH_3)_5$), 1.75 (d, J_{PH} = 11.2 Hz, 9H, $P(CH_3)_3$), 1.58-1.80 (m, 1H, diastereotopic CH_2CH_3), 1.48 (dd, J_{HH} = 7.2 Hz, J_{HH} = 7.2 Hz, 3H, CH_2CH_3), 1.27-1.36 (m, 1H, diastereotopic CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.3 (d, J_{PC} = 11.8 Hz, CO), 102.9 (s, $C_5(CH_3)_5$), 21.7 (s, CH_2CH_3), 15.1 (d, J_{PC} = 40.0 Hz, $P(CH_3)_3$), 9.3 (s, $C_5(CH_3)_5$), -6.9 (d, J_{PC} = 10.0 Hz, CH_2CH_3) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.9 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -34.15 (s) ppm. IR: (KBr) 1997 (s), 1295 (m), 1259 (s), 1222 (s), 1147 (s), 1031 (s), 954 (s), 638 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{29}O_4PSF_3Ir$: C, 33.49; H, 4.79. Found C, 33.21; H, 4.56.

[Cp*Ir(PMe$_3$)(CO)(*n*-Pr)][OTf] (2c): Pale yellow powder. mp = 148-150 °C (decomp). ^{1}H NMR: (CD_2Cl_2, 400 MHz) δ 2.02 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.75 (d, J_{PH} = 10.8 Hz, 9H, $P(CH_3)_3$), 1.48 (m, 2H, CH_2), 1.13 (m, 2H, CH_2) 0.95 (t, J_{HH} = 6.8 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.2 (d, J_{PC} = 11.8 Hz, CO), 102.8 (s, $C_5(CH_3)_5$), 30.9 (s, CH_2CH_3), 19.8 (s, CH_3), 15.0 (d, J_{PC} = 50.0 Hz, $P(CH_3)_3$), 9.3 (s, $C_5(CH_3)_5$), 2.7 (d, J_{PC} = 10.0 Hz, $CH_2CH_2CH_3$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.9 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -33.76 (s) ppm. IR: (KBr) 2015 (s), 1459 (m),

1384 (m), 1265 (s), 1147 (s), 1031 (s), 956 (m), 638 (m), 516 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{31}O_4PSF_3Ir$: C, 34.66; H, 5.01. Found C, 34.26; H, 4.81.

[Cp*Ir(PMe$_3$)(CO)(*c*-Pr)][OTf] (2d): White powder. mp = 205 °C (decomp). ^1H NMR: (CD_2Cl_2, 400 MHz) δ 2.04 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.81 (d, J_{PH} = 11.2 Hz, 9H, $P(CH_3)_3$), 1.00 (m), 0.91 (m), 0.33 (m), 0.21 (m), 0.13 (m) (5 x 1H, *c*-C_3H_5). $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.9 (d, J_{PC} = 11.3 Hz, CO), 104.8 (s, $C_5(CH_3)_5$), 17.0 (d, J_{PC} = 41.1 Hz, $P(CH_3)_3$), 11.3 (d, J_{PC} = 1.3 Hz, CH_2), 10.8 (s, $C_5(CH_3)_5$), 10.2 (d, J_{PC} = 3.3 Hz, CH_2), -16.4 (d, J_{PC} = 10.4 Hz, CH) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.97 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -35.21 (s) ppm. IR: (KBr) 3062 (w), 2989 (w), 2917 (w), 2009 (s), 1492 (w), 1467 (w), 1430 (w), 1384 (w), 1317 (w), 1265 (s), 1145 (s), 1031 (s), 954 (m), 865 (w), 748 (w), 684 (w), 570 (w), 553 (w), 516 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{29}O_4F_3IrPS$: C, 34.78; H, 4.70. Found C, 34.88; H, 4.74.

[Cp*Ir(PMe$_3$)(CO)(*t*-Bu)][OTf] (2e): Colorless powder. mp = 171-172 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 2.02 (d, J_{PH} = 2.4 Hz, 15H, $C_5(CH_3)_5$), 1.84 (d, J_{PH} = 10.4 Hz, 9H, $P(CH_3)_3$), 1.48 (s, 9H, $C(CH_3)_3$)) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.6 (d, J_{PC} = 12.3 Hz, CO), 105.7 (d, J_{PC} = 1.7 Hz, $C_5(CH_3)_5$), 41.0 (s, $C(CH_3)_3$), 18.6 (d, J_{PC} = 39.9 Hz, $P(CH_3)_3$), 15.5 (d, J_{PC} = 4.8 Hz, $C(CH_3)_3$), 10.5 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -77.0 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -47.5 (s) ppm. IR: (KBr) 2015 (s), 1267 (s), 1222 (m), 1145 (s), 1031 (s), 956 (m), 636 (m) cm^{-1}. FAB LRMS: *m/z* 489 ([Cp*Ir(PMe$_3$)(CO)(*t*-Butyl)]$^+$, ^{193}Ir). Anal. Calcd for $C_{19}H_{34}IrPSO_4F_3$: C, 35.73; H, 5.37. Found C, 35.37; H, 5.16.

[Cp*Ir(PMe$_3$)(CO)(*t*-Bu)][BPh$_4$] (2f): Pale yellow crystals. mp = 200-201 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 7.31 (br s, 8H, ortho-C_6H_5), 7.03 (t, 8H, meta-C_6H_5), 6.87 (t, 4H, para-C_6H_5), 1.96 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.69 (d, J_{PH} = 10.6 Hz, 9H, $P(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.7 (d, J_{PC} = 54.6 Hz, CO), 164.5 (1:1:1:1 q, J_{CB} = 48.8 Hz, ipso-C_6H_5), 136.3 (s, C_6H_5), 125.9 (1:1:1:1 q,

J_{CB} = 2.8 Hz, ortho-C_6H_5), 122.1 (s, C_6H_5), 105.7 (d, J_{PC} = 2.1 Hz, $C_5(CH_3)_5$), 41.1 (s, $C(CH_3)_3$), 18.7 (d, J_{PC} = 39.8 Hz, $P(CH_3)_3$), 16.3 (d, J_{PC} = 4.6 Hz, $C(CH_3)_3$), 10.6 (s, $C_5(CH_3)_5$) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -45.9 (s) ppm. IR: (KBr) 3050 (m), 3025 (m), 2996 (m), 2983 (m), 2915 (m), 2850 (m), 2024 (sh), 2005 (vs), 1579 (w), 1479 (m), 1427 (m), 1382 (m), 1363 (w), 1294 (w), 1130 (m), 1029 (w), 954 (s), 732 (s), 707 (s) cm^{-1}. FAB LRMS: *m/z* 489 ($[Cp^*Ir(PMe_3)(CO)(t\text{-Butyl})]^+$, ^{193}Ir). Anal. Calcd for $C_{42}H_{53}IrPOB$: C, 62.43; H, 6.49. Found C, 62.33; H, 6.55.

[Cp*Ir(PMe$_3$)(CO)(1-adamantyl)][OTf] (2g): Pale yellow powder. mp = 125-126 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 2.19 (br m, 6H), 2.03 (br m, 9H), 1.99 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.85 (d, J_{PH} = 10.4 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.1 (d, J_{PC} = 12.2 Hz, CO), 105.6 (s, $C_5(CH_3)_5$), 53.1 (d, J_{PC} = 2.2 Hz, β-CH_2), 37.0 (s, δ-CH_2), 33.6 (s, γ-CH), 29.8 (d, J_{PC} = 4.7 Hz, *ipso*-C), 18.4 (d, J_{PC} = 39.8 Hz, $P(CH_3)_3$), 10.4 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.91 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -47.46 (s) ppm. IR: (KBr) 2915 (m), 2850 (w), 2028 (s), 2021 (s), 1731 (w), 1639 (w), 1450 (m), 1384 (s), 1265 (s), 1149 (s), 1031 (s), 960 (m), 638 (s) cm^{-1}. FAB LRMS: *m/z* 567 ($[Cp^*Ir(PMe_3)(CO)(1\text{-adamantyl})]^+$, ^{193}Ir). This complex was not obtained in sufficiently pure form to perform elemental analysis.

[Cp*Ir(PMe$_3$)(CO)(1-adamantyl)][B(3,5-bistrifluoromethyl)phenyl)$_4$] (2h): mp = 188-191 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 7.72 (br s, 8H, ortho-*Ar*), 7.56 (s, 4H, para-*Ar*), 2.20 (br m, 6H), 1.97 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.88 (br m, 9H), 1.79 (d, J_{PH} = 10.4 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168.5 (d, J_{PC} = 12.1 Hz, *C*O), 162.3 (1:1:1:1 q, J_{BC} = 49.5 Hz, ipso-*Ar*), 135.3 (br s, ortho-*Ar*), 129.4 (qq, *J* = 31.2 Hz, *J* = 2.9 Hz, meta-*Ar*), 125.1 (q, J_{FC} = 270.7 Hz, *C*F_3), 118.0 (m, para-*Ar*), 105.8 (d, J_{PC} = 2.3 Hz, adam-β-*C*), 37.0 (s, adam-δ-*C*), 33.9 (s, adam-γ-*C*), 31.2 (d, J_{PC} = 4.6 Hz, adam-α-*C*), 18.6 (d, J_{PC} = 40.0 Hz, $P(CH_3)_3$), 10.4 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -61.0 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -48.0 (s) ppm. IR: (KBr) 2931 (m), 2910

(m), 2013 (s), 1612 (m), 1456 (m), 1355 (s), 1278 (s), 1137 (s), 1020 (m), 954 (m), 887 (m), 838 (m), 744 (w), 734 (w), 715 (m), 682 (m), 670 (m) cm^{-1}. FAB LRMS: *m/z* 567 ($[Cp^*Ir(PMe_3)(CO)(1\text{-adamantyl})]^+$, ^{193}Ir). FAB HRMS: Calcd for $C_{24}H_{39}{}^{193}IrPO$ 567.2368, found 567.2382.

[Cp*Ir(PMe$_3$)(CO)(1-ethylpropyl)][OTf] (2i): Pale yellow powder. mp = 222-225 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 2.02 (d, J_{PH} = 2.1 Hz, 15H, $C_5(CH_3)_5$), 1.79 (m, 2H, CH_2), 1.78 (d, J_{PH} = 10.8 Hz, 9H, $P(CH_3)_3$), 1.47 (m, 2H, CH_2), 0.95 (t, J_{HH} = 7.2 Hz, 3H, CH_3), 0.93 (t, J_{HH} = 7.2 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 169.0 (d, J_{PC} = 12.0 Hz, CO), 123.0 (q, J_{CF} = 319 Hz, CF_3), 105.0 (s, $C_5(CH_3)_5$), 35.8 (s, CH_2), 24 (s, CH), 18.3 (s, CH_3), 17.8 (d, J_{PC} = 37.1 Hz, $P(CH_3)_3$), 11.3 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.7 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -32.94 (s) ppm. IR: (KBr) 2011 (s), 1269 (s), 1145 (m), 1029 (m), 950 (m), 636 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{35}IrSO_4PF_3$: C, 36.86; H, 5.41. Found C, 36.56; H, 5.30.

[Cp*Ir(PMe$_3$)(CO)(Ph)][OTf] (2j): Pale yellow crystals. mp = 222-225 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 7.10 (m, 5H, Ph), 1.97 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.68 (d, J_{PH} = 11.2 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 169.3 (d, J_{FC} = 12 Hz, CO), 141.0 (s, *o*-aryl), 132.1 (s, *p*-aryl), 127.2 (s, *m*-aryl), 124.3 (d, J_{PC} = 10.4 Hz, *ipso*-aryl), 86.4 (s, $C_5(CH_3)_5$), 17.4 (d, J_{PC} = 42.0 Hz, $P(CH_3)_3$), 11.1 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -77.0 ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -33.0 ppm. IR: (CH_2Cl_2) 2927 (w), 2035 (vs), 1276 (vs), 1164 (s), 1039 (s), 643 (m) cm^{-1}. FAB LRMS: *m/z* 509 ($[Cp^*Ir(PMe_3)(CO)(Ph)]^+$, ^{193}Ir). Anal. Calcd for $C_{21}H_{29}IrPSO_4F_3$: C, 38.35; H, 4.44. Found C, 38.19; H, 4.46.

[Cp*Ir(PMe$_3$)(CO)(*p*-tolyl)][OTf] (2k): Pale yellow powder. mp = 184-185 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 7.03 (d, *J* = 8.0 Hz, 2H, Aryl), 6.92 (d, *J* = 7.6 Hz, 2H, Aryl), 2.28 (s, 3H, *p*-CH_3), 1.98 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.68 (d, J_{PH} = 11.2 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 168 (br s, CO), 139 (s, *o*-aryl), 135 (s,

p-aryl), 131 (s, *m*-aryl), 117 (d, J_{PC} = 10.7 Hz, *ipso*-aryl), 104 (s, $C_5(CH_3)_5$), 20.6 (s, *p*-tolyl methyl), 16.0 (d, J_{PC} = 40.2 Hz, $P(CH_3)_3$), 9.6 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -77.0 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -33.07 (s) ppm. IR: (KBr) 2919 (w), 2017 (s), 1729 (w), 1486 (w), 1270 (s), 1224 (m), 1145 (s), 1031 (m), 945 (m), 636 (m) cm^{-1}. FAB LRMS: *m/z* 523 ($[Cp^*Ir(PMe_3)(CO)(p\text{-tolyl})]^+$, ^{193}Ir). Anal. Calcd for $C_{22}H_{31}O_4F_3IrPS$: C, 39.34; H, 4.65. Found C, 39.17; H, 4.47.

[Cp*Ir(PMe$_3$)(CO)(2,4,6-trimethylphenyl)][OTf] (2l): Ivory powder. mp = 163 °C. ^1H NMR: (CD_2Cl_2, 400 MHz) δ 6.87 (s, 1H, aryl-H), 6.83 (s, 1H, aryl-H), 2.45 (s, 3H, *p*-methyl), 2.22 (s, 3H, *o*-methyl), 2.20 (s, 3H, *o*-methyl) 1.94 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.76 (d, J_{PH} = 10.8 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 169.1 (d, J_{PC} = 17.1 Hz, CO), 145.7 (s, *o*-aryl), 142.8 (d, J_{PC} = 3.0 Hz, *o*-aryl), 134.9 (s, *p*-aryl), 129.6 (s, *m*-aryl), 129.2 (s, *m*-aryl), 123.8 (s, *ipso*-aryl), 104.4 (s, $C_5(CH_3)_5$), 31.1 (s, *o*-methyl), 30.7 (d, J_{PC} = 5.0 Hz, *o*-methyl), 20.0 (s, *p*-methyl), 17.1 (d, J_{PC} = 42.3 Hz, $P(CH_3)_3$), 9.7 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.93 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -43.86 (s) ppm. IR: (KBr) 2015 (s), 1268 (s), 1147 (s), 1031 (s), 638 (s) cm^{-1}. FAB LRMS: *m/z* 551 ($[Cp^*Ir(PMe_3)(CO)(2,4,6\text{-trimethylphenyl})]^+$, ^{193}Ir). Anal. Calcd for $C_{24}H_{35}O_4F_3IrPS$: C, 41.19; H, 5.04. Found C, 40.77; H, 5.04.

[Cp*Ir(PMe$_3$)(CO)(2-(*Z*)-1-phenylpropenyl)][OTf] (2m): Beige powder. mp = 87 °C (decomp). ^1H NMR: (CD_2Cl_2, 400 MHz) δ 7.4-7.1 (m, 5H, phenyl), 6.3 (s, 1H, vinyl), 2.46 (br s, 3H, vinylic-methyl), 2.08 (d, J_{PH} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.86 (d, J_{PH} = 11.2 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 167.5 (d, J_{PC} = 12.7 Hz, CO), 139.6 (s, *ipso*-aryl), 136.7 (s, β-vinyl), 128.6 (s, *o*-aryl), 128.4 (s, *m*-aryl), 126.6 (s, *p*-aryl), 125.4 (d, J_{PC} = 10.6 Hz, α-vinyl), 121.4 (q, J_{CF} = 319 Hz, CF_3), 103.8 (s, $C_5(CH_3)_5$), 34.0 (s, vinylic-methyl), 15.5 (d, J_{PC} = 42.6 Hz, $P(CH_3)_3$), 9.4 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -77.00 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -32.59 (s) ppm.

IR: (KBr) 2019 (s), 1384 (m), 1270 (s), 1222 (s), 1149 (s), 1031 (s), 958 (s), 638 (s) cm^{-1}. FAB HRMS: Calcd for $C_{23}H_{33}{}^{193}IrPO$ 549.1898, found 549.1901.

[Cp*Ir(PMe$_3$)(CH$_3$)(η^2-*C*,*C*-CH$_2$=CHCHO)][OTf] (**3**). Tan powder. mp = 211 °C. ^{1}H NMR: (CD_2Cl_2, 400 MHz) δ 8.23 (br d, 1H, C*H*O), 3.30 (dddd, J_{HH} = 11.6 Hz, J_{HH} = 7.2 Hz, J_{PH} = 11.1 Hz, J_{HH} = 14.4 Hz, 1H, α-H), 2.87 (ddd, J_{HH} = 3.2 Hz, J_{HH} = 11.6 Hz, J_{PH} = 8.0 Hz, 1H, *cis*-β-H), 2.72 (ddd, J_{HH} = 3.2 Hz, J_{HH} = 7.2 Hz, J_{PH} = 10.2 Hz, 1H, *trans*-β-H), 1.85 (d, J_{PH} = 2.0 Hz, 15 H, $C_5(CH_3)_5$), 1.47 (d, J_{PH} = 8.4 Hz, 9H, $P(CH_3)_3$), 0.81 (d, J_{PH} = 6.4 Hz, 3H, Ir-CH_3) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 191.9 (s, *C*HO), 102.9 (d, J_{PC} = 2.3 Hz, $C_5(CH_3)_5$), 59.4 (s, CH), 37.8 (s, CH_2), 11.5 (d, J_{PC} = 42.5 Hz, $P(CH_3)_3$), 9.4 (s, $C_5(CH_3)_5$), -14.5 (d, J_{PC} = 8.9 Hz, Ir-CH_3) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -76.95 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -25.08 (s) ppm. IR: (KBr) 1677 (s), 1481 (w), 1429 (w), 1384 (m), 1268 (s), 1147 (s), 1031 (s), 960 (s), 636 (s) cm^{-1}. FAB LRMS: *m/z* 475 ([Cp*Ir(PMe$_3$)(CH$_3$)(η^2-*C*,*C*-CH$_2$=CHCHO)]$^+$, ^{193}Ir). Anal. Calcd for $C_{18}H_{31}O_4F_3IrPS$: C, 34.66; H, 5.01. Found C, 34.38; H, 5.02.

[Cp*Ir(PMe$_3$)(CO)(CH=CH$_2$)][OTf] (**4**). Tan powder. mp = 158-160 °C (decomp). ^{1}H NMR: (CD_2Cl_2, 400 MHz) δ 6.49 (dd, J_{HH} = 9.2 Hz, J_{HH} = 3.0 Hz, 1H, β-vinylic-*trans*-H), 6.40 (ddd, J_{HH} = 16.3 Hz, J_{HH} = 9.2 Hz, J_{HP} = 6.9 Hz, 1H, α-vinylic-H), 5.47 (dd, J_{HH} = 16.6 Hz, J_{HH} = 3.0 Hz, 1H, β-vinylic-*cis*-H), 2.02 (d, J_{HP} = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.75 (d, J_{HP} = 9.2 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2, 101 MHz) δ 167.6 (d, J_{CP} = 11 Hz, CO), 129.0 (s, β-vinyl), 121.5 (q, J_{CF} = 320 Hz, CF_3), 118.2 (d, J_{CP} = 12.1 Hz, α-vinyl), 103.4 (s, $C_5(CH_3)_5$), 15.2 (d, J_{CP} = 42.7 Hz, $P(CH_3)_3$), 9.4 (s, $C_5(CH_3)_5$) ppm. ^{19}F NMR: (CD_2Cl_2, 376 MHz) δ -77.0 (s) ppm. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, 162 MHz) δ -33.8 (s) ppm. IR: (KBr) 2981 (w), 2973 (w), 2919 (w), 2021 (s), 1575 (w), 1473 (w), 1421 (w), 1384 (m), 1294 (m), 1265 (s), 1224 (m), 1149 (s), 1031 (s), 954 (m), 638 (s), 516 (w) cm^{-1}. FAB LRMS: *m/z* 459 ([Cp*Ir(PMe$_3$)(CO)(CH=CH$_2$)]$^+$, ^{193}Ir). FAB HRMS: Calcd for $C_{16}H_{27}{}^{193}IrPO$ 459.1429, found 459.1423.

Figure S-1. ORTEP diagram of **2f**

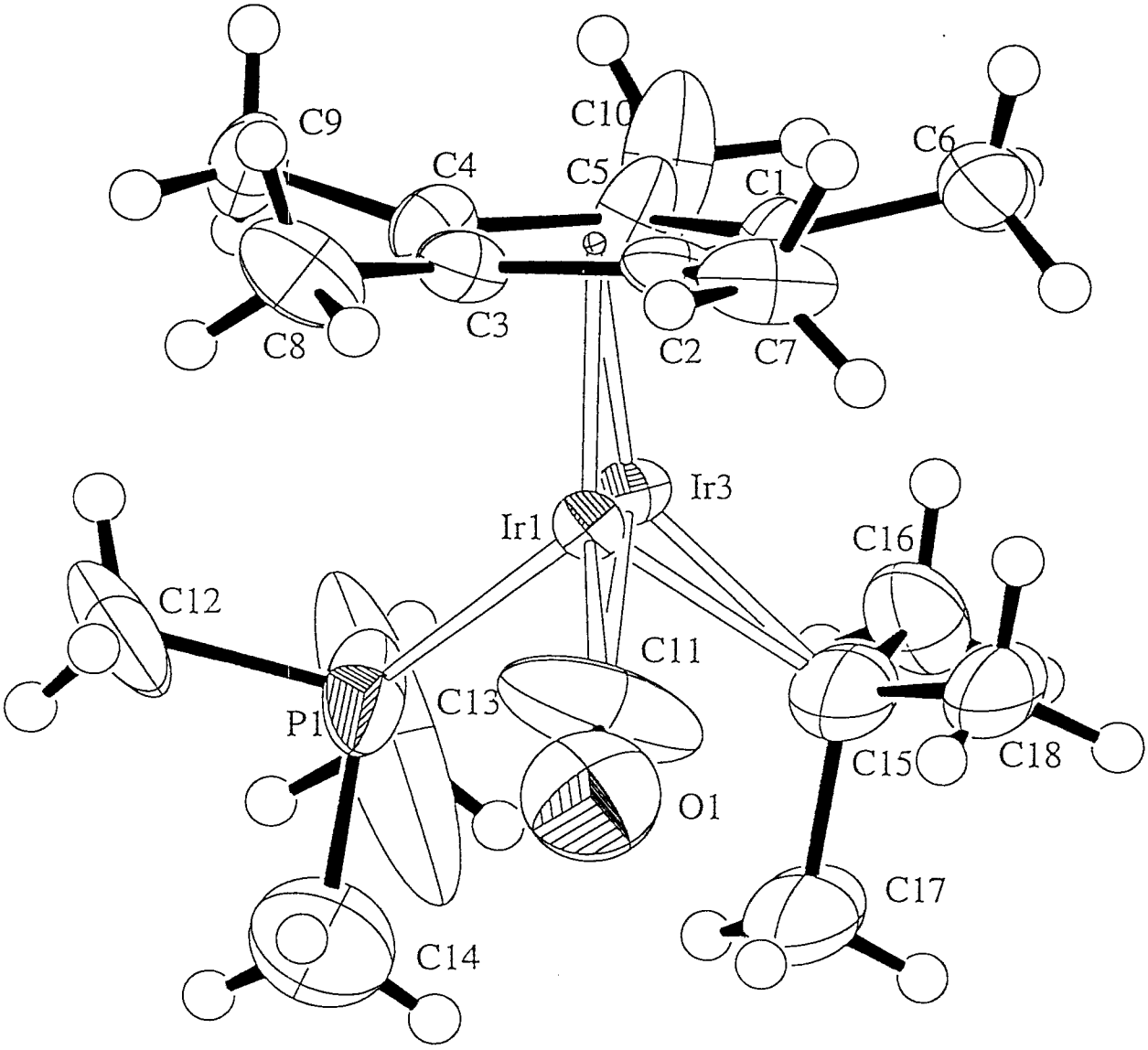

Figure S-2. ORTEP diagram of **2f**

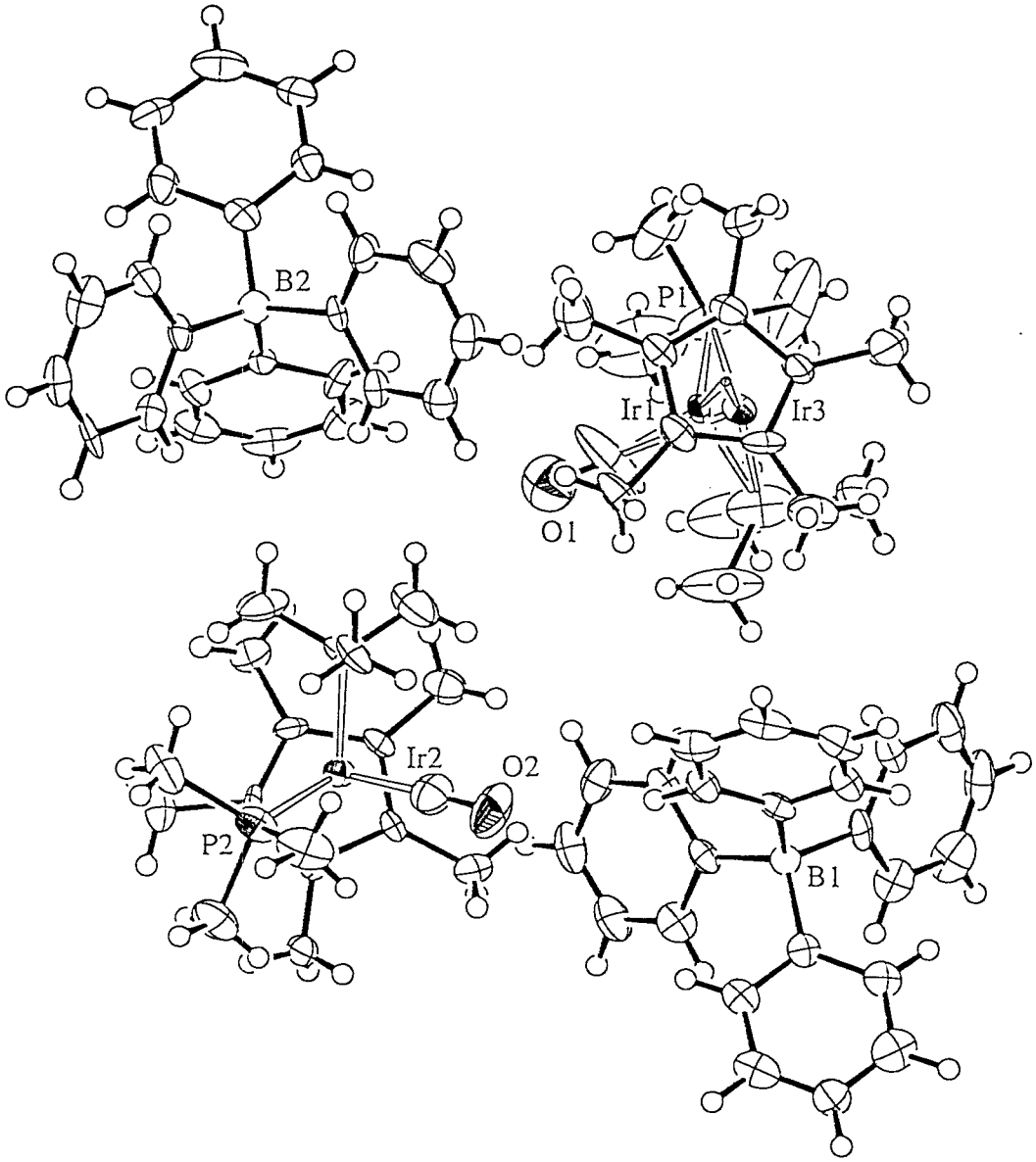

Table S-1. Crystal and Data Collection Parameters for **2f**

a. Crystal Data

Emperical Formula	$IrPOC_{42}BH_{53}$
Formula Weight	807.88
Crystal Color, Habit	pale yellow, columnar
Crystal Dimensions	0.15 X 0.16 X 0.30 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	8192 (3.0 - 45.0°)
Lattice Parameters	a = 20.6674(4) Å b = 12.2900(2) Å c = 29.7698(7) Å V = 7561.6(2) $Å^3$
Space Group	$Pca2_1$ (#29)
Z value	8
Dcalc	1.419 g/cm^3
F_{000}	3280.00
$\mu(MoK_\alpha)$	36.14 cm^{-1}

b. Intensity Measurements

Diffractometer	SMART
Radiation	MoK_α (λ = 0.71069 Å) graphite monochromated
Crystal to Detector Distance	60 mm
Temperature	-121.0 °C
Scan Type	ω (0.3° per frame)
Scan Rate	10.0 seconds per frame
2θ *max*	52.0°
No. of Reflections Measured	Total: 35069 Unique: 14193 (R_{int} = 3.42%)

Corrections	Lorentz-polarization Absorption (T_{max} = 0.69, T_{min} =0.48)

c. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/(\sigma^2(F_o) = 4F_o^2/(\sigma^2(F_o^2))$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No Observations (I>3.00σ(I))	9152
No Variables	828
Reflection/Parameter Ratio	11.05
Residuals: R; R_w; R_{all}	0.027; 0.029; 0.048
Goodness of Fit Indicator	1.01
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.85 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.80e^-/A^3

Table S-2. Atomic Coordinates and B_{iso}/B_{eq} for **2f**

atom	x	y	z	$B_{(eq)}$
IR1	0.42446(03)	0.48283(06)	0.2131	1.68(4)
IR2	0.343969(12)	0.00039(02)	0.41194(11)	2.07(1)
IR3	0.42479(06)	0.47946(14)	0.19099(19)	2.2(1)
P1	0.38802(11)	0.66008(13)	0.20782(15)	5.4(1)
P2	0.39421(10)	-0.13148(16)	0.45527(13)	3.2(1)
O1	0.3610(03)	0.4337(06)	0.2974(03)	6.6(4)
O2	0.3863(03)	-0.1100(05)	0.3274(02)	5.7(4)
C1	0.4924(03)	0.3557(05)	0.1750(03)	2.8(4)
C2	0.5046(04)	0.3611(05)	0.2214(03)	2.8(4)
C3	0.5277(04)	0.4695(05)	0.2309(03)	2.5(4)
C4	0.5312(03)	0.5283(05)	0.1928(03)	2.8(4)
C5	0.5051(04)	0.4600(05)	0.1554(03)	3.5(4)
C6	0.4804(04)	0.2544(06)	0.1478(03)	4.4(5)
C7	0.5017(04)	0.2647(06)	0.2534(03)	4.3(4)
C8	0.5547(04)	0.5027(06)	0.2771(03)	4.6(4)
C9	0.5664(04)	0.6331(06)	0.1838(03)	3.7(4)
C10	0.5058(05)	0.4902(06)	0.1066(03)	6.2(6)
C11	0.3783(06)	0.4525(09)	0.2635(04)	9.2(8)
C12	0.4403(05)	0.7512(06)	0.2346(03)	6.4(6)
C13	0.3566(09)	0.7176(08)	0.1630(04)	18(1)
C14	0.3222(06)	0.6897(09)	0.2491(05)	11(1)
C15	0.3362(04)	0.4142(07)	0.1821(04)	6.0(6)
C16	0.3370(05)	0.4260(07)	0.1278(03)	5.0(5)
C17	0.2713(04)	0.4686(07)	0.1988(05)	9.1(7)
C18	0.3298(04)	0.2965(06)	0.2032(05)	6.9(6)
C21	0.2644(03)	0.0408(05)	0.4618(03)	1.8(3)
C22	0.2796(03)	0.1393(05)	0.4407(03)	2.2(3)
C23	0.2685(03)	0.1247(05)	0.3929(03)	2.0(3)
C24	0.2411(03)	0.0187(05)	0.3862(03)	2.2(3)
C25	0.2369(03)	-0.0321(05)	0.4294(03)	2.2(3)
C26	0.2622(04)	0.0313(06)	0.5129(03)	3.1(4)
C27	0.2914(03)	0.2455(05)	0.4626(03)	3.0(4)
C28	0.2680(04)	0.2116(05)	0.3574(03)	3.2(4)
C29	0.2154(04)	-0.0262(05)	0.3438(03)	3.3(4)
C30	0.2006(03)	-0.1356(05)	0.4372(02)	2.5(3)
C31	0.3719(04)	-0.0661(06)	0.3602(03)	3.8(4)
C32	0.4459(04)	-0.2253(06)	0.4264(03)	4.6(5)
C33	0.4424(04)	-0.0895(07)	0.5038(03)	4.7(5)
C34	0.3396(04)	-0.2271(06)	0.4800(03)	4.1(4)
C35	0.4343(03)	0.0964(05)	0.4060(03)	2.8(3)
C36	0.4458(04)	0.1633(06)	0.4501(03)	4.3(4)
C37	0.4958(04)	0.0301(05)	0.3978(02)	3.1(4)
C38	0.4279(04)	0.1752(07)	0.3675(03)	4.9(5)
C39	0.1615(03)	-0.1128(05)	0.1644(03)	2.4(3)
C40	0.1643(03)	-0.1891(05)	0.1991(03)	2.6(3)
C41	0.1584(03)	-0.3003(05)	0.1906(03)	3.3(4)
C42	0.1530(04)	-0.3407(06)	0.1494(03)	3.1(4)
C43	0.1514(04)	-0.2669(06)	0.1151(03)	3.8(4)
C44	0.1556(03)	-0.1556(05)	0.1212(03)	2.7(4)

C45	0.1456(04)	0.0958(05)	0.1334(02)	2.4(4)
C46	0.0817(04)	0.0795(06)	0.1176(03)	3.5(4)
C47	0.0531(04)	0.1461(07)	0.0863(03)	4.6(5)
C48	0.0857(05)	0.2341(07)	0.0706(03)	4.5(5)
C49	0.1469(05)	0.2553(06)	0.0853(03)	4.1(5)
C50	0.1767(03)	0.1854(05)	0.1157(03)	2.7(4)
C51	0.2556(03)	0.0220(04)	0.1755(02)	2.4(4)
C52	0.2930(03)	0.0186(05)	0.1357(02)	2.7(3)
C53	0.3602(04)	0.0129(05)	0.1371(03)	3.4(4)
C54	0.3934(03)	0.0107(05)	0.1771(03)	3.3(4)
C55	0.3584(04)	0.0146(05)	0.2171(03)	3.4(3)
C56	0.2912(03)	0.0203(05)	0.2151(03)	2.5(3)
C57	0.1414(03)	0.0620(05)	0.2200(02)	2.3(3)
C58	0.1622(03)	0.1547(06)	0.2417(03)	2.6(4)
C59	0.1299(04)	0.1983(06)	0.2789(03)	3.3(4)
C60	0.0749(04)	0.1497(07)	0.2957(03)	3.8(4)
C61	0.0528(04)	0.0568(07)	0.2736(03)	3.9(4)
C62	0.0853(04)	0.0149(05)	0.2373(03)	3.3(4)
C63	0.6051(03)	0.6222(05)	0.4562(03)	2.3(3)
C64	0.6097(03)	0.6965(05)	0.4201(03)	2.6(3)
C65	0.6142(03)	0.8066(05)	0.4260(03)	2.9(4)
C66	0.6154(04)	0.8509(06)	0.4688(03)	4.0(4)
C67	0.6113(04)	0.7806(06)	0.5060(03)	3.4(4)
C68	0.6073(04)	0.6704(06)	0.4994(03)	3.0(4)
C69	0.6237(03)	0.4174(05)	0.4892(02)	2.2(3)
C70	0.6855(04)	0.4409(06)	0.5068(03)	2.8(4)
C71	0.7175(04)	0.3739(06)	0.5368(03)	3.9(4)
C72	0.6881(04)	0.2801(06)	0.5525(03)	3.3(4)
C73	0.6280(04)	0.2535(06)	0.5375(03)	3.2(4)
C74	0.5954(03)	0.3205(06)	0.5060(03)	2.7(4)
C75	0.5120(03)	0.4838(05)	0.4481(02)	1.9(3)
C76	0.4752(03)	0.4833(06)	0.4870(02)	2.8(3)
C77	0.4086(04)	0.4901(06)	0.4879(03)	3.4(4)
C78	0.3744(04)	0.4973(05)	0.4484(03)	4.0(4)
C79	0.4085(03)	0.4955(05)	0.4074(04)	3.3(3)
C80	0.4759(03)	0.4912(05)	0.4075(03)	2.9(3)
C81	0.6255(03)	0.4402(05)	0.4032(02)	2.0(3)
C82	0.5999(03)	0.3459(05)	0.3825(03)	2.4(3)
C83	0.6295(04)	0.2952(05)	0.3468(03)	2.9(4)
C84	0.6866(04)	0.3349(06)	0.3300(03)	3.5(4)
C85	0.7149(04)	0.4263(07)	0.3488(03)	4.3(5)
C86	0.6838(04)	0.4760(06)	0.3863(03)	3.0(4)
C101	0.5122	0.4349	0.1951	0.2
C102	0.2576	0.0583	0.4222	0.2
B1	0.1767(04)	0.0177(06)	0.1740(03)	2.1(2)
B2	0.5919(04)	0.4883(07)	0.4496(03)	2.4(2)
H1	0.4727	0.2736	0.1174	4.4
H2	0.4436	0.2173	0.1595	4.4
H3	0.5171	0.2081	0.1496	4.4
H4	0.4593	0.2349	0.2533	3.9
H5	0.5122	0.2884	0.2830	3.9
H6	0.5318	0.2109	0.2442	3.9
H7	0.5373	0.4564	0.2996	4.8

H8	0.6005	0.4963	0.2769	4.8
H9	0.5430	0.5759	0.2833	4.8
H10	0.5756	0.6683	0.2115	3.7
H11	0.5401	0.6791	0.1658	3.7
H12	0.6057	0.6181	0.1685	3.7
H13	0.5483	0.5117	0.0982	6.4
H14	0.4931	0.4291	0.0891	6.4
H15	0.4767	0.5486	0.1015	6.4
H16	0.4457	0.7300	0.2651	7.3
H17	0.4810	0.7507	0.2199	7.3
H18	0.4224	0.8223	0.2335	7.3
H19	0.3486	0.7925	0.1689	12.6
H20	0.3157	0.6831	0.1564	12.6
H21	0.3843	0.7098	0.1384	12.6
H22	0.2833	0.6557	0.2395	9.3
H23	0.3158	0.7661	0.2510	9.3
H24	0.3341	0.6623	0.2778	9.3
H25	0.3333	0.5007	0.1199	5.8
H26	0.3765	0.3978	0.1163	5.8
H27	0.3017	0.3866	0.1154	5.8
H28	0.2707	0.5430	0.1900	7.7
H29	0.2355	0.4321	0.1857	7.7
H30	0.2688	0.4638	0.2305	7.7
H31	0.3691	0.2577	0.1990	7.5
H32	0.2954	0.2586	0.1890	7.5
H33	0.3211	0.3026	0.2345	7.5
H34	0.2450	-0.0377	0.5211	3.2
H35	0.3047	0.0385	0.5247	3.2
H36	0.2354	0.0872	0.5248	3.2
H37	0.3155	0.2347	0.4894	2.7
H38	0.3152	0.2910	0.4428	2.7
H39	0.2513	0.2789	0.4696	2.7
H40	0.2993	0.2654	0.3645	3.2
H41	0.2779	0.1802	0.3291	3.2
H42	0.2263	0.2442	0.3562	3.2
H43	0.2328	0.0133	0.3192	3.4
H44	0.1696	-0.0201	0.3437	3.4
H45	0.2273	-0.1006	0.3413	3.4
H46	0.2121	-0.1871	0.4148	2.7
H47	0.2112	-0.1638	0.4660	2.7
H48	0.1555	-0.1217	0.4357	2.7
H49	0.4213	-0.2651	0.4051	6.1
H50	0.4646	-0.2741	0.4475	6.1
H51	0.4792	-0.1863	0.4114	6.1
H52	0.4633	-0.1513	0.5163	5.4
H53	0.4149	-0.0575	0.5257	5.4
H54	0.4740	-0.0380	0.4945	5.4
H55	0.3187	-0.2674	0.4569	4.8
H56	0.3081	-0.1893	0.4972	4.8
H57	0.3630	-0.2754	0.4989	4.8
H58	0.4088	0.2069	0.4562	4.6
H59	0.4529	0.1148	0.4745	4.6
H60	0.4826	0.2088	0.4464	4.6

H61	0.4921	-0.0079	0.3701	4.0
H62	0.5015	-0.0206	0.4216	4.0
H63	0.5320	0.0776	0.3966	4.0
H64	0.4235	0.1361	0.3402	6.4
H65	0.3908	0.2196	0.3720	6.4
H66	0.4654	0.2199	0.3661	6.4
H67	0.1704	-0.1648	0.2291	3.4
H68	0.1582	-0.3491	0.2154	3.9
H69	0.1505	-0.4168	0.1440	4.2
H70	0.1472	-0.2936	0.0853	4.6
H71	0.1544	-0.1083	0.0960	3.3
H72	0.0576	0.0199	0.1291	3.7
H73	0.0107	0.1308	0.0757	5.4
H74	0.0659	0.2811	0.0494	4.8
H75	0.1693	0.3178	0.0747	4.3
H76	0.2200	0.2000	0.1247	3.0
H77	0.2718	0.0202	0.1074	3.5
H78	0.3838	0.0104	0.1097	4.2
H79	0.4393	0.0067	0.1776	4.1
H80	0.3800	0.0134	0.2452	4.1
H81	0.2681	0.0232	0.2427	3.2
H82	0.1999	0.1904	0.2309	3.1
H83	0.1461	0.2624	0.2928	3.9
H84	0.0531	0.1782	0.3212	4.4
H85	0.0146	0.0218	0.2839	4.6
H86	0.0688	-0.0489	0.2234	4.0
H87	0.6096	0.6686	0.3904	3.4
H88	0.6166	0.8530	0.4006	3.3
H89	0.6188	0.9274	0.4729	4.0
H90	0.6113	0.8095	0.5356	4.2
H91	0.6061	0.6243	0.5251	3.6
H92	0.7062	0.5062	0.4976	3.2
H93	0.7598	0.3924	0.5467	4.6
H94	0.7097	0.2347	0.5736	3.9
H95	0.6076	0.1892	0.5481	3.5
H96	0.5535	0.3000	0.4960	3.4
H97	0.4973	0.4781	0.5149	3.2
H98	0.3863	0.4898	0.5159	4.3
H99	0.3286	0.5035	0.4487	4.6
H100	0.3855	0.4972	0.3798	3.9
H101	0.4984	0.4933	0.3797	3.5
H102	0.5606	0.3163	0.3937	2.9
H103	0.6103	0.2325	0.3337	3.7
H104	0.7068	0.2996	0.3054	4.1
H105	0.7539	0.4552	0.3369	4.8
H106	0.7042	0.5364	0.4003	3.7

Table S-3. Anisotropic Displacement Parameters for **2f**

atom	U11	U22	U33	U12	U13	U23
IR1	0.0263(3)	0.0231(3)	0.0145(10)	0.0009(2)	-0.0001(3)	0.0033(4)
IR2	0.02554(12)	0.02487(11)	0.02828(12)	-0.00185(14)	0.00203(16)	0.00022(15)
IR3	0.0227(06)	0.0291(08)	0.032(03)	0.0009(05)	0.0022(07)	0.0038(09)
P1	0.0540(14)	0.0265(09)	0.125(02)	0.0078(09)	-0.0441(19)	-0.0054(15)
P2	0.0346(13)	0.0357(12)	0.0509(14)	0.0047(09)	0.0107(11)	0.0079(11)
O1	0.081(06)	0.087(05)	0.084(05)	0.010(04)	-0.012(04)	0.009(04)
O2	0.074(05)	0.093(05)	0.049(04)	0.003(04)	0.010(04)	-0.039(04)
C1	0.026(05)	0.025(04)	0.057(06)	-0.011(03)	0.008(04)	-0.003(04)
C2	0.034(05)	0.035(04)	0.036(05)	0.009(03)	0.016(04)	0.009(04)
C3	0.034(04)	0.028(05)	0.033(04)	0.005(03)	0.009(03)	0.007(03)
C4	0.035(04)	0.031(04)	0.040(05)	-0.003(03)	-0.001(04)	0.010(04)
C5	0.054(05)	0.048(04)	0.031(05)	-0.026(04)	-0.016(04)	0.019(04)
C6	0.053(06)	0.040(05)	0.073(06)	-0.006(04)	0.024(05)	-0.006(04)
C7	0.051(06)	0.053(05)	0.058(06)	0.021(04)	0.019(05)	0.039(04)
C8	0.081(06)	0.053(05)	0.042(05)	0.026(05)	0.004(04)	0.007(05)
C9	0.050(05)	0.049(05)	0.043(05)	-0.020(04)	0.002(04)	-0.007(04)
C10	0.127(09)	0.054(06)	0.056(06)	-0.036(06)	-0.040(06)	0.019(05)
C11	0.141(12)	0.082(08)	0.125(11)	0.056(07)	0.105(10)	0.066(08)
C12	0.106(09)	0.053(06)	0.085(07)	0.034(05)	-0.027(06)	-0.042(05)
C13	0.57(03)	0.030(06)	0.098(09)	0.065(12)	-0.185(15)	0.003(06)
C14	0.080(10)	0.078(09)	0.254(17)	0.035(07)	-0.012(10)	-0.031(10)
C15	0.042(06)	0.050(06)	0.134(10)	0.005(04)	0.001(06)	-0.010(06)
C16	0.084(08)	0.053(06)	0.054(06)	-0.008(05)	0.028(05)	-0.005(05)
C17	0.039(05)	0.061(05)	0.248(15)	0.008(04)	0.004(09)	-0.029(08)
C18	0.042(05)	0.035(05)	0.186(12)	-0.006(03)	0.017(08)	-0.013(08)
C21	0.028(05)	0.033(04)	0.008(03)	0.001(03)	0.002(03)	-0.005(03)
C22	0.028(04)	0.020(04)	0.035(05)	-0.010(03)	0.006(04)	-0.008(04)
C23	0.022(04)	0.026(04)	0.027(04)	-0.001(03)	0.011(03)	0.007(03)
C24	0.037(04)	0.029(04)	0.018(04)	-0.003(03)	0.000(03)	0.009(03)
C25	0.024(04)	0.032(04)	0.027(04)	0.006(03)	0.006(03)	-0.006(03)
C26	0.038(05)	0.052(06)	0.026(04)	0.005(04)	-0.004(04)	0.002(03)
C27	0.034(05)	0.030(04)	0.049(05)	0.003(03)	-0.005(04)	-0.003(04)
C28	0.039(05)	0.034(04)	0.049(05)	0.002(03)	-0.001(04)	0.008(04)
C29	0.045(05)	0.038(04)	0.043(05)	-0.016(03)	-0.007(04)	0.001(04)
C30	0.030(05)	0.039(04)	0.028(04)	-0.009(03)	-0.008(04)	0.008(03)
C31	0.040(05)	0.054(05)	0.050(06)	-0.001(04)	-0.001(05)	-0.006(04)
C32	0.048(06)	0.037(04)	0.088(07)	0.015(04)	0.014(05)	0.008(04)
C33	0.053(06)	0.082(06)	0.042(06)	0.001(05)	0.005(05)	0.027(05)
C34	0.063(06)	0.035(04)	0.059(06)	0.008(04)	0.009(05)	0.017(04)
C35	0.021(04)	0.038(04)	0.046(05)	-0.004(03)	0.003(04)	0.022(04)
C36	0.033(05)	0.053(05)	0.077(07)	-0.022(04)	0.011(05)	-0.020(05)
C37	0.032(04)	0.050(04)	0.037(04)	-0.001(03)	0.013(03)	0.020(03)
C38	0.048(06)	0.078(06)	0.060(06)	-0.015(05)	0.004(05)	0.029(05)
C39	0.026(04)	0.033(04)	0.032(05)	0.003(03)	0.004(04)	-0.002(04)
C40	0.024(04)	0.038(04)	0.038(05)	0.005(03)	0.002(04)	0.006(04)
C41	0.025(04)	0.039(04)	0.062(06)	0.006(03)	0.001(04)	0.014(04)
C42	0.046(05)	0.031(04)	0.041(05)	0.006(04)	0.006(05)	-0.002(04)
C43	0.033(05)	0.054(05)	0.057(06)	0.006(04)	0.016(05)	-0.017(05)
C44	0.027(04)	0.037(04)	0.040(05)	0.005(03)	0.015(04)	-0.006(04)

C45	0.041(05)	0.035(04)	0.015(04)	0.017(04)	0.009(04)	-0.002(03)
C46	0.040(05)	0.045(05)	0.046(05)	0.014(04)	-0.004(04)	-0.005(04)
C47	0.058(06)	0.054(06)	0.060(06)	0.027(05)	-0.022(05)	-0.009(05)
C48	0.088(08)	0.057(06)	0.026(05)	0.047(06)	-0.009(05)	-0.003(04)
C49	0.091(08)	0.038(05)	0.028(05)	0.025(05)	0.013(05)	0.002(04)
C50	0.045(06)	0.032(04)	0.026(05)	0.012(03)	0.008(04)	0.006(04)
C51	0.037(04)	0.016(04)	0.039(05)	0.002(03)	0.001(04)	0.010(03)
C52	0.037(05)	0.034(04)	0.032(04)	0.006(03)	0.005(03)	0.009(03)
C53	0.042(05)	0.031(04)	0.057(05)	0.002(04)	0.018(04)	0.006(04)
C54	0.019(04)	0.027(04)	0.081(06)	0.006(03)	0.004(04)	0.012(04)
C55	0.033(04)	0.025(04)	0.070(06)	0.002(03)	-0.009(05)	0.009(04)
C56	0.033(04)	0.031(03)	0.032(04)	0.005(03)	0.001(04)	0.008(04)
C57	0.028(04)	0.033(04)	0.028(04)	0.005(03)	0.000(03)	0.012(03)
C58	0.032(04)	0.036(04)	0.031(05)	0.005(03)	0.003(04)	0.010(04)
C59	0.043(05)	0.046(05)	0.035(05)	0.015(04)	-0.014(04)	-0.009(04)
C60	0.044(06)	0.072(06)	0.027(05)	0.019(05)	0.010(04)	0.008(04)
C61	0.043(06)	0.067(06)	0.037(05)	0.003(04)	0.014(04)	0.010(04)
C62	0.034(05)	0.045(04)	0.045(05)	0.007(04)	0.004(04)	0.002(04)
C63	0.013(04)	0.038(04)	0.038(05)	-0.000(03)	0.004(04)	0.006(04)
C64	0.024(04)	0.046(04)	0.030(05)	-0.000(03)	-0.004(04)	0.004(04)
C65	0.030(05)	0.032(04)	0.046(06)	-0.005(03)	-0.003(04)	0.009(03)
C66	0.020(04)	0.039(05)	0.092(07)	-0.003(04)	0.008(05)	0.002(05)
C67	0.042(05)	0.036(04)	0.052(06)	-0.009(04)	-0.001(04)	-0.015(04)
C68	0.036(05)	0.052(05)	0.027(05)	0.001(04)	0.011(04)	-0.003(04)
C69	0.025(04)	0.044(04)	0.015(04)	0.002(03)	0.007(03)	0.000(03)
C70	0.033(05)	0.040(04)	0.032(05)	-0.001(04)	0.002(04)	0.007(04)
C71	0.042(05)	0.065(05)	0.041(05)	0.025(04)	-0.012(04)	-0.008(04)
C72	0.051(06)	0.054(05)	0.019(05)	0.028(04)	0.003(04)	0.001(04)
C73	0.055(06)	0.053(05)	0.014(04)	0.016(04)	0.016(04)	0.016(04)
C74	0.033(05)	0.046(04)	0.026(05)	0.003(04)	0.001(04)	-0.004(04)
C75	0.029(04)	0.021(04)	0.023(04)	-0.002(03)	0.002(03)	-0.000(03)
C76	0.034(04)	0.043(05)	0.029(04)	-0.000(04)	0.011(03)	0.007(04)
C77	0.033(04)	0.039(04)	0.058(05)	-0.002(04)	0.010(04)	0.010(05)
C78	0.028(04)	0.026(04)	0.098(07)	-0.004(04)	0.006(05)	-0.012(05)
C79	0.033(04)	0.043(03)	0.048(06)	0.011(04)	-0.016(04)	-0.013(04)
C80	0.045(04)	0.037(03)	0.027(04)	0.007(04)	-0.010(04)	-0.017(04)
C81	0.029(04)	0.033(03)	0.012(04)	0.007(03)	0.001(03)	0.007(03)
C82	0.035(05)	0.037(04)	0.018(04)	0.008(03)	-0.002(04)	0.004(03)
C83	0.042(05)	0.038(04)	0.031(05)	0.010(04)	-0.003(04)	0.003(04)
C84	0.056(06)	0.043(05)	0.033(05)	0.022(04)	0.001(04)	-0.007(04)
C85	0.042(06)	0.063(05)	0.058(06)	0.003(04)	0.023(05)	0.012(05)
C86	0.043(05)	0.048(05)	0.025(04)	0.000(04)	0.009(04)	-0.010(04)

Table S-4. Bond Lengths (Å) for **2f**

atom	atom	distance	atom	atom	distance
IR1	IR3	0.659(6)	IR3	C15	2.02(1)
IR1	P1	2.310(2)	IR3	C101	1.892(1)
IR1	C1	2.388(7)	P1	C12	1.749(9)
IR1	C2	2.246(7)	P1	C13	1.64(1)
IR1	C3	2.205(7)	P1	C14	1.87(1)
IR1	C4	2.354(7)	P2	C32	1.791(8)
IR1	C5	2.409(9)	P2	C33	1.828(9)
IR1	C11	1.82(1)	P2	C34	1.787(8)
IR1	C15	2.21(1)	O1	C11	1.09(1)
IR1	C101	1.9803(6)	O2	C31	1.155(8)
IR2	P2	2.317(2)	C1	C2	1.41(1)
IR2	C21	2.270(7)	C1	C5	1.432(9)
IR2	C22	2.328(7)	C1	C6	1.50(1)
IR2	C23	2.256(7)	C2	C3	1.443(9)
IR2	C24	2.271(7)	C2	C7	1.522(9)
IR2	C25	2.308(7)	C3	C4	1.35(1)
IR2	C31	1.837(9)	C3	C8	1.54(1)
IR2	C35	2.215(6)	C4	C5	1.49(1)
IR2	C102	1.9466(6)	C4	C9	1.503(9)
IR3	P1	2.399(3)	C5	C10	1.50(1)
IR3	C1	2.121(7)	C15	C16	1.62(1)
IR3	C2	2.379(8)	C15	C17	1.58(1)
IR3	C3	2.439(9)	C15	C18	1.58(1)
IR3	C4	2.280(7)	C21	C22	1.398(8)
IR3	C5	1.98(1)	C21	C25	1.433(9)
IR3	C11	2.39(1)	C21	C26	1.53(1)
C22	C23	1.455(8)	C51	B1	1.63(1)
C22	C27	1.479(8)	C52	C53	1.39(1)
C23	C24	1.434(9)	C53	C54	1.38(1)
C23	C28	1.502(9)	C54	C55	1.39(1)
C24	C25	1.434(8)	C55	C56	1.39(1)
C24	C29	1.48(1)	C57	C58	1.379(9)
C25	C30	1.494(9)	C57	C62	1.396(9)
C35	C36	1.57(1)	C57	B1	1.64(1)
C35	C37	1.531(9)	C58	C59	1.40(1)
C35	C38	1.51(1)	C59	C60	1.38(1)
C39	C40	1.397(9)	C60	C61	1.39(1)
C39	C44	1.40(1)	C61	C62	1.37(1)
C39	B1	1.66(1)	C63	C64	1.414(9)
C40	C41	1.394(9)	C63	C68	1.42(1)
C41	C42	1.33(1)	C63	B2	1.68(1)
C42	C43	1.37(1)	C64	C65	1.368(9)
C43	C44	1.38(1)	C65	C66	1.39(1)
C45	C46	1.42(1)	C66	C67	1.41(1)
C45	C50	1.380(9)	C67	C68	1.37(1)
C45	B1	1.67(1)	C69	C70	1.41(1)
C46	C47	1.37(1)	C69	C74	1.418(9)
C47	C48	1.36(1)	C69	B2	1.61(1)
C48	C49	1.36(1)	C70	C71	1.38(1)

C49	C50	1.39(1)	C71	C72	1.39(1)
C51	C52	1.42(1)	C72	C73	1.36(1)
C51	C56	1.39(1)	C73	C74	1.42(1)
C75	C76	1.386(9)	C75	C80	1.42(1)
C75	B2	1.65(1)	C76	C77	1.38(1)
C77	C78	1.37(1)	C78	C79	1.41(1)
C79	C80	1.395(9)	C81	C82	1.416(8)
C81	C86	1.378(9)	C81	B2	1.66(1)
C82	C83	1.375(9)	C83	C84	1.37(1)
C84	C85	1.38(1)	C85	C86	1.43(1)

Table S-5. Bond Angles (°) for **2f**

atom	atom	atom	angle	atom	atom	atom	angle
IR3	IR1	P1	89.7(2)	C2	IR1	C5	59.4(2)
IR3	IR1	C1	58.6(3)	C2	IR1	C11	99.2(4)
IR3	IR1	C2	93.5(3)	C2	IR1	C15	113.6(3)
IR3	IR1	C3	103.0(3)	C2	IR1	C101	32.5(2)
IR3	IR1	C4	75.5(3)	C3	IR1	C4	34.2(2)
IR3	IR1	C5	43.5(3)	C3	IR1	C5	59.6(3)
IR3	IR1	C11	144.8(5)	C3	IR1	C11	107.1(5)
IR3	IR1	C15	64.4(3)	C3	IR1	C15	150.5(3)
IR3	IR1	C101	72.7(2)	C3	IR1	C101	32.5(2)
P1	IR1	C1	140.9(2)	C4	IR1	C5	36.6(2)
P1	IR1	C2	151.2(2)	C4	IR1	C11	138.8(5)
P1	IR1	C3	113.7(2)	C4	IR1	C15	139.1(4)
P1	IR1	C4	93.7(2)	C4	IR1	C101	31.0(2)
P1	IR1	C5	106.7(2)	C5	IR1	C11	158.1(4)
P1	IR1	C11	94.5(3)	C5	IR1	C15	103.2(3)
P1	IR1	C15	93.6(2)	C5	IR1	C101	30.6(2)
P1	IR1	C101	124.09(8)	C11	IR1	C15	80.4(6)
C1	IR1	C2	35.2(2)	C11	IR1	C101	130.0(4)
C1	IR1	C3	59.8(2)	C15	IR1	C101	121.9(2)
C1	IR1	C4	58.8(2)	P2	IR2	C21	96.5(2)
C1	IR1	C5	34.7(2)	P2	IR2	C22	124.3(2)
C1	IR1	C11	124.6(4)	P2	IR2	C23	157.5(2)
C1	IR1	C15	92.1(3)	P2	IR2	C24	132.6(2)
C1	IR1	C101	30.5(2)	P2	IR2	C25	100.5(2)
C2	IR1	C3	37.8(2)	P2	IR2	C31	90.9(2)
C2	IR1	C4	59.7(2)	P2	IR2	C35	92.3(2)
P2	IR2	C102	125.37(9)	C31	IR2	C35	84.6(3)
C21	IR2	C22	35.4(2)	C31	IR2	C102	125.6(3)
C21	IR2	C23	61.0(2)	C35	IR2	C102	126.2(2)
C21	IR2	C24	61.4(3)	IR1	IR3	P1	74.3(3)
C21	IR2	C25	36.5(2)	IR1	IR3	C1	106.1(4)
C21	IR2	C31	150.8(3)	IR1	IR3	C2	70.5(3)
C21	IR2	C35	123.1(2)	IR1	IR3	C3	61.7(3)
C21	IR2	C102	32.1(2)	IR1	IR3	C4	88.3(3)
C22	IR2	C23	37.0(2)	IR1	IR3	C5	123.3(4)
C22	IR2	C24	61.1(2)	IR1	IR3	C11	26.1(4)
C22	IR2	C25	59.7(2)	IR1	IR3	C15	98.5(4)
C22	IR2	C31	144.5(3)	IR1	IR3	C101	87.9(3)
C22	IR2	C35	96.9(2)	P1	IR3	C1	156.9(2)
C22	IR2	C102	31.7(2)	P1	IR3	C2	134.9(4)
C23	IR2	C24	36.9(2)	P1	IR3	C3	102.8(3)
C23	IR2	C25	60.7(2)	P1	IR3	C4	93.3(2)
C23	IR2	C31	107.9(3)	P1	IR3	C5	119.2(2)
C23	IR2	C35	101.6(2)	P1	IR3	C11	79.1(3)
C23	IR2	C102	32.6(2)	P1	IR3	C15	96.2(3)
C24	IR2	C25	36.5(2)	P1	IR3	C101	123.8(1)
C24	IR2	C31	93.1(3)	C1	IR3	C2	35.9(2)
C24	IR2	C35	135.2(2)	C1	IR3	C3	59.9(3)

C24	IR2	C102	32.7(2)	C1	IR3	C4	63.8(2)
C25	IR2	C31	114.4(3)	C1	IR3	C5	40.7(3)
C25	IR2	C35	156.6(2)	C1	IR3	C11	111.7(4)
C25	IR2	C102	31.6(2)	C1	IR3	C15	106.5(3)
C1	IR3	C101	34.6(2)	IR3	P1	C12	119.5(3)
C2	IR3	C3	34.8(2)	IR3	P1	C13	110.7(5)
C2	IR3	C4	58.9(2)	IR3	P1	C14	123.2(4)
C2	IR3	C5	63.2(3)	C12	P1	C13	109.8(6)
C2	IR3	C11	81.4(4)	C12	P1	C14	91.4(5)
C2	IR3	C15	115.9(3)	C13	P1	C14	99.4(8)
C2	IR3	C101	30.2(2)	IR2	P2	C32	116.8(3)
C3	IR3	C4	33.0(2)	IR2	P2	C33	119.1(3)
C3	IR3	C5	61.6(3)	IR2	P2	C34	114.0(3)
C3	IR3	C11	84.5(5)	C32	P2	C33	103.6(4)
C3	IR3	C15	146.7(4)	C32	P2	C34	98.7(4)
C3	IR3	C101	28.5(2)	C33	P2	C34	101.8(4)
C4	IR3	C5	40.3(3)	IR1	C1	IR3	15.4(2)
C4	IR3	C11	113.8(5)	IR1	C1	C2	66.9(4)
C4	IR3	C15	169.6(4)	IR1	C1	C5	73.4(4)
C4	IR3	C101	32.2(2)	IR1	C1	C6	134.3(5)
C5	IR3	C11	143.5(5)	IR1	C1	C101	55.8(3)
C5	IR3	C15	129.9(5)	IR3	C1	C2	82.1(5)
C5	IR3	C101	36.9(2)	IR3	C1	C5	64.5(5)
C11	IR3	C15	72.4(5)	IR3	C1	C6	127.2(6)
C11	IR3	C101	106.6(4)	IR3	C1	C101	62.3(3)
C15	IR3	C101	139.5(3)	C2	C1	C5	109.0(7)
IR1	P1	IR3	15.9(1)	C2	C1	C6	126.6(7)
IR1	P1	C12	111.8(3)	C2	C1	C101	54.3(4)
IR1	P1	C13	126.1(4)	C5	C1	C6	123.6(7)
IR1	P1	C14	112.1(4)	C5	C1	C101	54.7(4)
C6	C1	C101	169.8(7)	C2	C3	C8	122.7(6)
IR1	C2	IR3	16.1(1)	C2	C3	C101	53.6(4)
IR1	C2	C1	77.9(5)	C4	C3	C8	126.2(6)
IR1	C2	C3	69.5(4)	C4	C3	C101	56.8(4)
IR1	C2	C7	124.0(5)	C8	C3	C101	172.5(6)
IR1	C2	C101	61.6(3)	IR1	C4	IR3	16.2(2)
IR3	C2	C1	62.0(5)	IR1	C4	C3	66.8(4)
IR3	C2	C3	74.9(4)	IR1	C4	C5	73.7(4)
IR3	C2	C7	133.4(5)	IR1	C4	C9	134.6(5)
IR3	C2	C101	52.0(3)	IR1	C4	C101	57.2(3)
C1	C2	C3	107.2(6)	IR3	C4	C3	80.0(5)
C1	C2	C7	124.9(7)	IR3	C4	C5	59.1(4)
C1	C2	C101	54.7(4)	IR3	C4	C9	133.5(5)
C3	C2	C7	127.5(7)	IR3	C4	C101	56.0(3)
C3	C2	C101	52.5(4)	C3	C4	C5	107.8(6)
C7	C2	C101	174.4(7)	C3	C4	C9	129.4(7)
IR1	C3	IR3	15.3(1)	C3	C4	C101	55.1(4)
IR1	C3	C2	72.6(4)	C5	C4	C9	121.6(6)
IR1	C3	C4	79.0(4)	C5	C4	C101	52.8(4)
IR1	C3	C8	123.1(5)	C9	C4	C101	167.4(7)
IR1	C3	C101	63.3(3)	IR1	C5	IR3	13.2(2)
IR3	C3	C2	70.3(4)	IR1	C5	C1	71.8(4)
IR3	C3	C4	67.0(4)	IR1	C5	C4	69.7(4)

IR3	C3	C8	137.6(5)	IR1	C5	C10	132.0(7)
IR3	C3	C101	49.3(3)	IR1	C5	C101	55.0(3)
C2	C3	C4	110.3(7)	IR3	C5	C1	74.8(4)
IR3	C5	C4	80.6(5)	C22	C21	C25	109.2(6)
IR3	C5	C10	119.8(7)	C22	C21	C26	121.3(6)
IR3	C5	C101	67.5(4)	C22	C21	C102	55.6(4)
C1	C5	C4	105.4(7)	C25	C21	C26	127.6(6)
C1	C5	C10	128.1(7)	C25	C21	C102	53.7(4)
C1	C5	C101	53.6(4)	C26	C21	C102	169.6(6)
C4	C5	C10	125.3(6)	IR2	C22	C21	70.0(4)
C4	C5	C101	51.8(4)	IR2	C22	C23	68.8(4)
C10	C5	C101	172.5(8)	IR2	C22	C27	135.6(5)
IR1	C11	IR3	9.2(1)	IR2	C22	C102	56.7(3)
IR1	C11	O1	167(1)	C21	C22	C23	107.3(6)
IR3	C11	O1	174(1)	C21	C22	C27	127.2(7)
IR1	C15	IR3	17.1(2)	C21	C22	C102	54.2(4)
IR1	C15	C16	111.9(6)	C23	C22	C27	124.4(6)
IR1	C15	C17	114.0(7)	C23	C22	C102	53.2(4)
IR1	C15	C18	104.6(6)	C27	C22	C102	167.5(6)
IR3	C15	C16	95.0(6)	IR2	C23	C22	74.2(4)
IR3	C15	C17	124.1(6)	IR2	C23	C24	72.1(4)
IR3	C15	C18	112.8(6)	IR2	C23	C28	131.6(5)
C16	C15	C17	106.5(9)	IR2	C23	C102	59.6(3)
C16	C15	C18	118.6(8)	C22	C23	C24	108.0(6)
C17	C15	C18	101.0(7)	C22	C23	C28	127.0(6)
IR2	C21	C22	74.6(4)	C22	C23	C102	53.7(4)
IR2	C21	C25	73.2(4)	C24	C23	C28	123.1(6)
IR2	C21	C26	131.1(5)	C24	C23	C102	54.4(4)
IR2	C21	C102	59.0(3)	C28	C23	C102	168.6(6)
IR2	C24	C23	71.0(4)	C37	C35	C38	107.1(6)
IR2	C24	C25	73.2(4)	C40	C39	C44	115.6(6)
IR2	C24	C29	126.1(5)	C40	C39	B1	121.0(6)
IR2	C24	C102	59.0(3)	C44	C39	B1	122.7(6)
C23	C24	C25	107.2(6)	C39	C40	C41	121.4(7)
C23	C24	C29	126.9(6)	C40	C41	C42	122.7(7)
C23	C24	C102	53.8(4)	C41	C42	C43	116.4(7)
C25	C24	C29	125.7(6)	C42	C43	C44	123.9(8)
C25	C24	C102	53.4(4)	C39	C44	C43	120.0(7)
C29	C24	C102	174.9(7)	C46	C45	C50	114.9(6)
IR2	C25	C21	70.3(4)	C46	C45	B1	121.2(6)
IR2	C25	C24	70.3(4)	C50	C45	B1	123.6(7)
IR2	C25	C30	131.5(5)	C45	C46	C47	122.8(8)
IR2	C25	C102	57.5(3)	C46	C47	C48	119.6(8)
C21	C25	C24	107.9(6)	C47	C48	C49	120.2(8)
C21	C25	C30	128.9(6)	C48	C49	C50	120.1(8)
C21	C25	C102	53.5(4)	C45	C50	C49	122.2(7)
C24	C25	C30	122.6(6)	C52	C51	C56	114.8(6)
C24	C25	C102	54.5(4)	C52	C51	B1	121.5(6)
C30	C25	C102	170.6(6)	C56	C51	B1	123.5(6)
IR2	C31	O2	176.5(7)	C51	C52	C53	121.5(7)
IR2	C35	C36	109.9(5)	C52	C53	C54	121.6(7)
IR2	C35	C37	115.5(4)	C53	C54	C55	118.7(6)
IR2	C35	C38	109.2(5)	C54	C55	C56	119.0(7)

C36	C35	C37	106.7(6)	C51	C56	C55	124.4(7)
C36	C35	C38	108.3(6)	C58	C57	C62	115.3(7)
C58	C57	B1	121.7(6)	C75	C76	C77	124.4(7)
C62	C57	B1	122.7(6)	C76	C77	C78	119.9(7)
C57	C58	C59	122.6(7)	C77	C78	C79	119.0(7)
C58	C59	C60	120.9(7)	C78	C79	C80	120(1)
C59	C60	C61	117.1(7)	C75	C80	C79	122.0(9)
C60	C61	C62	121.2(8)	C82	C81	C86	115.4(6)
C57	C62	C61	122.9(7)	C82	C81	B2	120.0(6)
C64	C63	C68	114.7(6)	C86	C81	B2	123.9(6)
C64	C63	B2	123.7(6)	C81	C82	C83	122.8(7)
C68	C63	B2	121.4(6)	C82	C83	C84	120.2(7)
C63	C64	C65	123.1(7)	C83	C84	C85	120.4(7)
C64	C65	C66	120.6(7)	C84	C85	C86	118.3(7)
C65	C66	C67	118.7(7)	C81	C86	C85	122.9(7)
C66	C67	C68	120.0(7)	IR1	C101	IR3	19.4(2)
C63	C68	C67	122.9(7)	IR1	C101	C1	93.7(3)
C70	C69	C74	114.4(6)	IR1	C101	C2	85.9(3)
C70	C69	B2	122.2(6)	IR1	C101	C3	84.2(3)
C74	C69	B2	123.2(6)	IR1	C101	C4	91.7(3)
C69	C70	C71	123.5(7)	IR1	C101	C5	94.3(4)
C70	C71	C72	120.3(7)	IR3	C101	C1	83.0(4)
C71	C72	C73	119.2(7)	IR3	C101	C2	97.8(4)
C72	C73	C74	120.9(7)	IR3	C101	C3	102.2(4)
C69	C74	C73	121.7(7)	IR3	C101	C4	91.8(3)
C76	C75	C80	114.9(6)	IR3	C101	C5	75.6(5)
C76	C75	B2	121.7(6)	C1	C101	C2	71.0(4)
C80	C75	B2	123.1(6)	C1	C101	C3	144.9(5)
C1	C101	C4	146.9(6)	C45	B1	C51	112.7(6)
C1	C101	C5	71.7(5)	C45	B1	C57	103.9(5)
C2	C101	C3	73.9(5)	C51	B1	C57	114.2(6)
C2	C101	C4	142.0(6)	C63	B2	C69	112.4(6)
C2	C101	C5	142.6(5)	C63	B2	C75	101.4(5)
C3	C101	C4	68.1(5)	C63	B2	C81	112.3(6)
C3	C101	C5	143.4(4)	C69	B2	C75	114.2(6)
C4	C101	C5	75.4(5)	C69	B2	C81	104.3(6)
IR2	C102	C21	88.9(3)	C75	B2	C81	112.5(6)
IR2	C102	C22	91.5(3)	IR2	C102	C23	87.8(3)
IR2	C102	C24	88.4(3)	IR2	C102	C25	90.9(3)
C21	C102	C22	70.2(4)	C21	C102	C23	143.1(4)
C21	C102	C24	144.8(4)	C21	C102	C25	72.8(4)
C22	C102	C23	73.1(4)	C22	C102	C24	144.9(5)
C22	C102	C25	142.9(5)	C23	C102	C24	71.9(5)
C23	C102	C25	144.0(5)	C24	C102	C25	72.1(4)
C39	B1	C45	110.9(6)	C39	B1	C51	103.0(5)
C39	B1	C57	112.3(6)				

Figure S-3. ORTEP diagram of **2h**

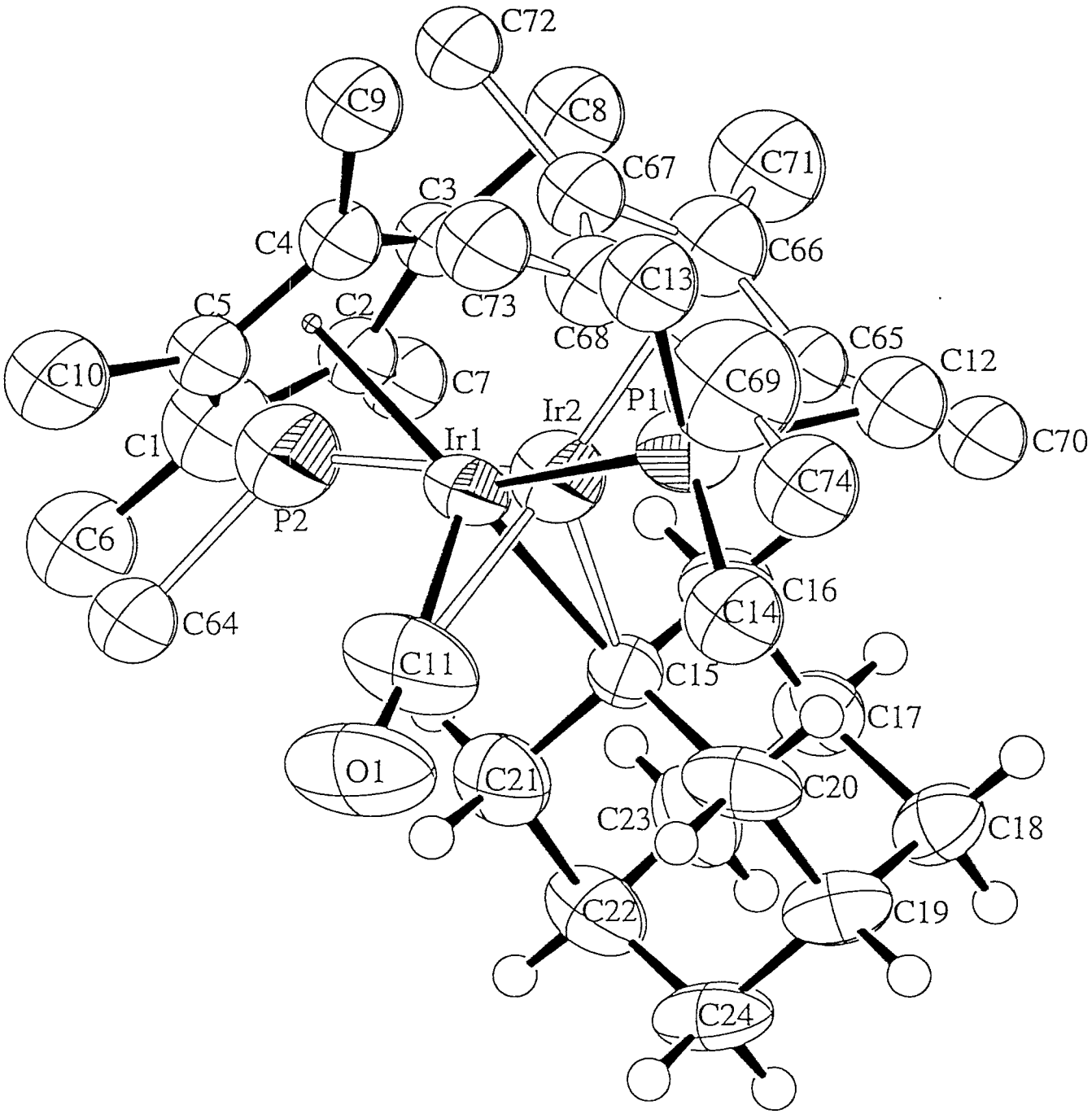

Figure S-4. ORTEP diagram of **2h**

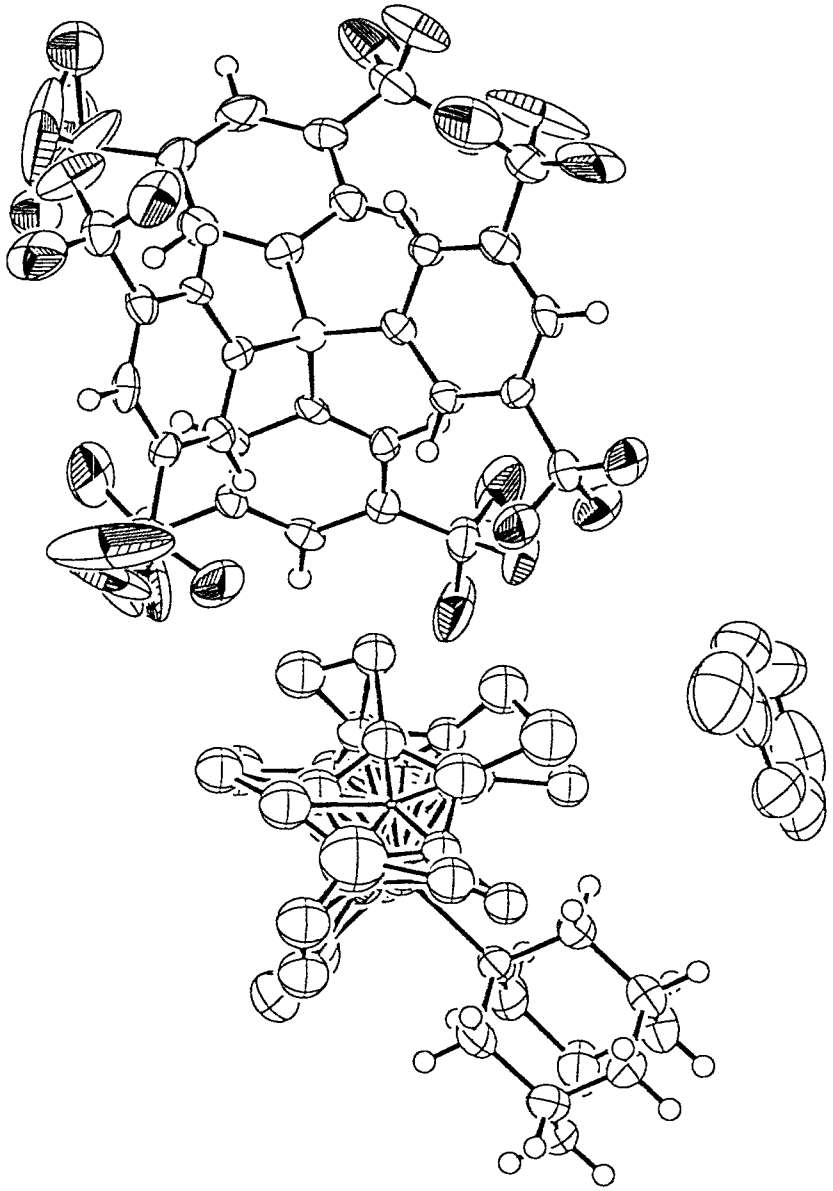

Table S-6. Crystal and Data Collection Parameters for **2h**

a. Crystal Data

Emperical Formula	$IrPOF_{24}C_{63}BH_{59}$
Formula Weight	1522.12
Crystal Color, Habit	pale, bladelike
Crystal Dimensions	0.08 X 0.15 X 0.33 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	599 (3.0 - 45.0°)
Lattice Parameters	a = 41.536(2) Å b = 12.6740(6) Å c = 25.017(1) Å β = 109.960(1)° V = 12378.7(9) Å^3
Space Group	C2/c (#15)
Z value	8
Dcalc	1.633 g/cm^3
F_{000}	6064.00
μ(MoK$_\alpha$)	23.03 cm^{-1}

b. Intensity Measurements

Diffractometer	SMART
Radiation	MoK$_\alpha$ (λ = 0.71069 Å) graphite monochromated
Crystal to Detector Distance	60 mm
Temperature	-130.0 °C
Scan Type	ω (0.3° per frame)
Scan Rate	20.0 seconds per frame
2θ *max*	53.7°
No. of Reflections Measured	Total: 30085 Unique: 11622 (R_{int} = 0.051%)

Corrections	Lorentz-polarization

c. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/(\sigma^2(F_o) = 4F_o^2/(\sigma^2(F_o^2))$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No Observations (I>3.00σ(I))	5376
No Variables	754
Reflection/Parameter Ratio	7.13
Residuals: R; R_w; R_{all}	0.059; 0.064; 0.128
Goodness of Fit Indicator	1.95
Max Shift/Error in Final Cycle	0.08
Maximum peak in Final Diff. Map	1.37 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.11e^-/A^3

Table S-7. Atomic coordinates and B_{iso}/B_{eq} for **2h**

atom	x	y	z	$B_{(eq)}$
IR1	0.398118(17)	0.01206(10)	0.38197(04)	3.14(4)
IR2	0.39340(09)	-0.0317(04)	0.3597(02)	4.7(1)
P1	0.40409(11)	-0.1154(04)	0.3183(02)	4.2(2)
P2	0.3956(05)	0.132(02)	0.4122(08)	5.8(5)
F1	0.2994(03)	0.5609(10)	-0.0627(04)	11.3(7)
F2	0.2771(03)	0.6491(08)	-0.0172(04)	11.9(6)
F3	0.2538(02)	0.5120(07)	-0.0551(04)	10.9(5)
F4	0.26224(17)	0.2198(06)	0.0738(03)	5.3(3)
F5	0.28390(17)	0.2716(05)	0.1580(03)	4.8(3)
F6	0.31187(18)	0.1743(05)	0.1185(03)	5.2(4)
F7	0.3399(02)	0.5555(07)	0.3242(04)	7.5(5)
F8	0.33090(16)	0.3988(06)	0.2966(03)	4.8(3)
F9	0.36650(18)	0.4311(07)	0.3748(03)	7.2(4)
F10	0.48278(16)	0.4796(10)	0.3824(03)	10.3(5)
F11	0.4907(02)	0.3863(09)	0.3187(04)	10.9(6)
F12	0.4943(02)	0.5419(09)	0.3144(04)	10.0(6)
F13	0.4313(02)	0.1157(06)	0.1526(04)	8.5(5)
F14	0.4764(03)	0.1741(07)	0.1859(06)	14.1(7)
F15	0.4661(05)	0.1074(08)	0.1104(06)	18(1)
F16	0.4717(02)	0.3785(07)	-0.0216(03)	6.8(4)
F17	0.4582(02)	0.5342(06)	-0.0078(03)	6.6(5)
F18	0.4218(02)	0.4267(08)	-0.0551(03)	7.9(4)
F22	0.3305(02)	0.9102(06)	0.0622(03)	7.2(4)
F23	0.3568(02)	0.9935(06)	0.1371(03)	6.9(4)
F24	0.3240(02)	0.8685(07)	0.1398(04)	7.1(5)
F25	0.4773(03)	0.9031(12)	0.1713(06)	12.9(8)
F26	0.4935(04)	0.7638(14)	0.1815(06)	5.5(4)
F27	0.4804(03)	0.7863(15)	0.1073(06)	16(1)
F28	0.4636(04)	0.8991(14)	0.0890(07)	6.5(4)
O1	0.4568(02)	-0.0806(09)	0.4669(05)	8.2(6)
C11	0.4339(03)	-0.0507(14)	0.4326(06)	6.9(8)
C12	0.3644(04)	-0.1797(14)	0.2713(07)	4.6(4)
C13	0.4252(04)	-0.0673(14)	0.2683(07)	5.2(4)
C14	0.4322(04)	-0.2283(13)	0.3466(07)	5.0(4)
C15	0.3652(03)	-0.0966(09)	0.4138(05)	3.1(5)
C16	0.3291(03)	-0.0877(09)	0.3793(05)	3.6(5)
C17	0.3066(03)	-0.1543(10)	0.4053(05)	3.9(6)
C18	0.3167(03)	-0.2716(10)	0.4076(05)	3.9(6)
C19	0.3524(03)	-0.2800(10)	0.4422(06)	4.5(6)
C20	0.3756(03)	-0.2138(11)	0.4171(05)	4.8(6)
C21	0.3679(03)	-0.0587(11)	0.4728(05)	4.6(6)
C22	0.3457(03)	-0.1266(12)	0.5002(05)	4.8(7)
C23	0.3092(03)	-0.1147(10)	0.4628(05)	4.5(6)
C24	0.3556(03)	-0.2419(12)	0.5025(05)	4.8(7)
C25	0.3504(02)	0.4771(08)	0.1055(04)	2.6(4)
C26	0.3321(02)	0.5275(08)	0.0551(04)	2.6(4)
C27	0.3004(03)	0.4907(10)	0.0241(04)	3.3(4)
C28	0.2857(02)	0.4018(09)	0.0407(04)	3.0(5)
C29	0.3044(03)	0.3524(09)	0.0887(04)	2.7(5)

C30	0.3355(03)	0.3870(08)	0.1202(04)	2.4(5)
C31	0.2817(03)	0.5507(13)	-0.0271(06)	5.0(7)
C32	0.2905(03)	0.2564(10)	0.1098(05)	3.2(5)
C33	0.3970(02)	0.4953(08)	0.2077(04)	2.1(4)
C34	0.3735(02)	0.4877(08)	0.2367(04)	2.3(4)
C35	0.3822(02)	0.4745(08)	0.2942(04)	2.4(4)
C36	0.4163(03)	0.4691(08)	0.3249(04)	2.5(4)
C37	0.4397(02)	0.4783(08)	0.2974(04)	2.3(4)
C38	0.4310(02)	0.4900(08)	0.2413(04)	2.2(4)
C39	0.3554(03)	0.4658(11)	0.3222(05)	3.7(6)
C40	0.4759(03)	0.4678(12)	0.3300(05)	4.2(6)
C41	0.4132(02)	0.4389(08)	0.1144(04)	2.1(4)
C42	0.4249(03)	0.3385(09)	0.1364(04)	2.3(5)
C43	0.4430(03)	0.2729(08)	0.1124(04)	2.5(5)
C44	0.4511(02)	0.3022(09)	0.0661(04)	2.9(5)
C45	0.4402(03)	0.4016(09)	0.0424(04)	2.7(5)
C46	0.4218(02)	0.4642(07)	0.0661(04)	2.3(4)
C47	0.4542(04)	0.1696(10)	0.1388(07)	4.3(7)
C48	0.4484(03)	0.4371(12)	-0.0096(05)	3.9(6)
C49	0.3952(03)	0.6387(08)	0.1330(04)	2.6(5)
C50	0.4269(03)	0.6786(09)	0.1354(05)	3.5(6)
C51	0.4331(03)	0.7883(09)	0.1325(06)	4.1(6)
C52	0.4066(03)	0.8578(09)	0.1266(05)	4.2(6)
C53	0.3751(03)	0.8231(09)	0.1248(05)	3.2(6)
C54	0.3690(03)	0.7146(09)	0.1282(04)	3.1(5)
C55	0.4694(07)	0.8225(14)	0.1449(14)	12(2)
C56	0.3470(04)	0.8976(12)	0.1152(06)	4.5(7)
C57	0.2379(04)	0.0379(14)	0.3013(08)	7(1)
C58	0.2349(04)	0.083(02)	0.3490(09)	9(1)
C59	0.2359(05)	0.188(02)	0.3576(11)	10(1)
C60	0.2399(06)	0.2536(18)	0.3129(12)	11(1)
C61	0.2439(04)	0.2094(17)	0.2623(09)	8(1)
C62	0.2427(04)	0.101(02)	0.2597(07)	7(1)
C63	0.2471(05)	0.049(02)	0.2074(09)	12(1)
C64	0.4148(14)	0.152(04)	0.488(02)	4(1)
C101	0.3900	0.1652	0.3690	0.2
C102	0.3860	-0.0442	0.2789	0.2
B1	0.3886(03)	0.5132(10)	0.1400(05)	2.4(2)
H1	0.3224	-0.0158	0.3776	4.0
H2	0.3259	-0.1125	0.3420	4.0
H3	0.2834	-0.1477	0.3811	4.8
H4	0.3031	-0.3116	0.4241	4.6
H5	0.3133	-0.2968	0.3704	4.6
H6	0.3592	-0.3519	0.4441	5.5
H7	0.3729	-0.2385	0.3800	5.5
H8	0.3988	-0.2207	0.4408	5.5
H9	0.3913	-0.0627	0.4968	5.0
H10	0.3604	0.0125	0.4702	5.0
H11	0.3486	-0.1014	0.5373	5.4
H12	0.3027	-0.0427	0.4606	5.1
H13	0.2948	-0.1551	0.4774	5.1
H14	0.3409	-0.2822	0.5163	5.2
H15	0.3786	-0.2501	0.5273	5.2

H16	0.3415	0.5868	0.0424	2.9
H17	0.2634	0.3777	0.0186	3.4
H18	0.3480	0.3491	0.1537	3.0
H19	0.3498	0.4922	0.2148	2.9
H20	0.4238	0.4591	0.3650	3.0
H21	0.4483	0.4945	0.2245	2.6
H22	0.4202	0.3146	0.1690	2.7
H23	0.4637	0.2565	0.0504	3.3
H24	0.4142	0.5305	0.0485	2.8
H25	0.4452	0.6304	0.1393	4.3
H26	0.4102	0.9314	0.1238	4.8
H27	0.3470	0.6915	0.1273	3.7
C1	0.39632(16)	0.1819(05)	0.4185(02)	6.6
C5	0.42012(14)	0.1809(05)	0.3901(03)	3.5
C4	0.40248(15)	0.1585(05)	0.3327(02)	3.5
C3	0.36778(14)	0.1457(05)	0.3257(02)	3.0
C2	0.36398(14)	0.1601(05)	0.3787(03)	3.2
C6	0.4035(02)	0.2186(09)	0.4807(02)	6.0
C9	0.4173(02)	0.1727(08)	0.2833(03)	4.8
C10	0.45811(15)	0.2163(08)	0.4157(04)	5.4
C8	0.33810(17)	0.1356(08)	0.2678(03)	5.0
C7	0.32938(17)	0.1688(08)	0.3894(04)	3.9
C66	0.3574(05)	-0.0126(17)	0.2685(09)	5.6
C67	0.3861(05)	0.0485(16)	0.2721(09)	3.9
C68	0.4145(05)	-0.0188(18)	0.2847(09)	4.5
C69	0.4033(05)	-0.1216(17)	0.2890(10)	9.6
C65	0.3680(06)	-0.1178(16)	0.2790(09)	3.2
C71	0.3197(05)	0.026(02)	0.2471(15)	6.9
C73	0.4505(05)	0.012(02)	0.2842(15)	4.5
C72	0.3856(07)	0.1666(16)	0.2552(14)	3.8
C74	0.4248(07)	-0.2236(19)	0.2941(16)	5.7
C70	0.3440(07)	-0.215(02)	0.2711(15)	3.8

Table S-8. Anisotropic Displacement Parameters for **2h**

atom	U11	U22	U33	U12	U13	U23
IR1	0.0321(03)	0.0551(07)	0.0318(05)	0.0000(04)	0.0105(03)	0.0054(05)
P1	0.054(03)	0.064(03)	0.053(03)	0.008(02)	0.032(02)	0.006(02)
F1	0.107(08)	0.220(13)	0.079(07)	0.020(08)	0.004(06)	0.086(08)
F2	0.225(13)	0.066(07)	0.081(07)	0.062(07)	-0.051(07)	0.011(05)
F3	0.087(06)	0.127(08)	0.116(07)	-0.044(07)	-0.074(06)	0.078(07)
F4	0.044(04)	0.081(06)	0.057(05)	-0.032(04)	-0.006(04)	0.007(04)
F5	0.070(05)	0.071(05)	0.044(04)	-0.018(04)	0.025(04)	0.001(04)
F6	0.060(05)	0.042(05)	0.100(06)	-0.008(04)	0.031(05)	0.009(04)
F7	0.093(07)	0.080(06)	0.154(09)	0.007(05)	0.094(07)	-0.011(06)
F8	0.043(04)	0.078(05)	0.068(05)	-0.023(04)	0.028(04)	-0.010(04)
F9	0.056(05)	0.171(09)	0.055(05)	-0.034(05)	0.030(04)	0.001(05)
F10	0.038(04)	0.307(14)	0.032(04)	0.027(07)	-0.006(03)	-0.024(07)
F11	0.077(07)	0.162(10)	0.124(09)	0.074(07)	-0.033(06)	-0.057(07)
F12	0.038(05)	0.199(12)	0.105(07)	-0.036(06)	-0.027(05)	0.045(07)
F13	0.088(07)	0.051(06)	0.202(11)	0.008(05)	0.073(07)	0.051(06)
F14	0.129(09)	0.070(07)	0.223(13)	-0.010(07)	-0.086(10)	0.082(08)
F15	0.48(03)	0.079(08)	0.231(15)	0.149(12)	0.281(18)	0.081(09)
F16	0.113(07)	0.096(07)	0.078(06)	0.019(06)	0.071(06)	0.018(05)
F17	0.138(08)	0.063(06)	0.073(06)	-0.028(05)	0.066(05)	-0.001(04)
F18	0.067(05)	0.187(09)	0.034(04)	-0.041(06)	-0.000(04)	0.028(05)
F22	0.102(07)	0.082(06)	0.066(06)	0.044(05)	-0.001(05)	0.019(05)
F23	0.091(06)	0.050(05)	0.103(06)	0.037(05)	0.011(05)	-0.013(05)
F24	0.067(06)	0.093(07)	0.112(07)	0.038(05)	0.034(05)	0.014(05)
F25	0.074(07)	0.171(12)	0.206(14)	-0.055(09)	-0.003(08)	0.032(11)
F27	0.063(07)	0.39(02)	0.169(12)	-0.096(11)	0.053(08)	-0.034(14)
O1	0.049(06)	0.153(11)	0.094(09)	0.004(07)	0.003(06)	0.059(08)
C11	0.027(07)	0.152(16)	0.071(11)	-0.004(09)	0.003(07)	0.028(10)
C15	0.034(07)	0.039(08)	0.040(07)	0.002(06)	0.007(06)	0.002(06)
C16	0.044(07)	0.050(09)	0.046(08)	0.008(06)	0.019(06)	0.009(06)
C17	0.038(07)	0.054(09)	0.053(09)	0.008(06)	0.010(06)	0.005(07)
C18	0.045(08)	0.047(09)	0.060(09)	-0.004(07)	0.022(07)	0.010(07)
C19	0.055(08)	0.055(09)	0.063(09)	0.015(07)	0.026(07)	0.022(07)
C20	0.040(08)	0.089(11)	0.050(08)	0.017(08)	0.013(06)	0.027(07)
C21	0.038(07)	0.076(10)	0.056(09)	-0.006(07)	0.009(07)	0.005(07)
C22	0.049(08)	0.088(12)	0.043(08)	-0.005(08)	0.015(07)	-0.000(07)
C23	0.042(08)	0.072(10)	0.054(09)	0.003(07)	0.012(07)	-0.012(07)
C24	0.042(08)	0.082(11)	0.064(10)	0.006(08)	0.023(07)	0.039(08)
C25	0.029(05)	0.034(07)	0.029(06)	0.002(06)	0.003(05)	-0.002(05)
C26	0.030(06)	0.029(07)	0.035(06)	-0.003(05)	0.004(05)	0.002(05)
C27	0.039(06)	0.047(08)	0.029(06)	0.002(07)	-0.001(05)	-0.002(06)
C28	0.020(06)	0.052(08)	0.032(07)	-0.002(06)	-0.004(05)	-0.004(06)
C29	0.032(07)	0.043(08)	0.029(07)	-0.005(06)	0.011(06)	0.004(06)
C30	0.028(06)	0.032(07)	0.025(06)	-0.001(05)	0.002(05)	0.000(05)
C31	0.041(08)	0.084(13)	0.050(09)	0.000(08)	-0.005(07)	0.028(08)
C32	0.029(07)	0.048(09)	0.039(08)	-0.002(06)	0.005(06)	-0.004(06)
C33	0.027(05)	0.017(06)	0.031(05)	0.006(06)	0.004(04)	0.001(05)
C34	0.025(05)	0.023(06)	0.038(06)	-0.004(05)	0.008(04)	-0.003(05)
C35	0.032(05)	0.026(07)	0.037(06)	-0.000(05)	0.015(05)	-0.005(05)
C36	0.036(06)	0.029(07)	0.023(05)	0.003(05)	0.000(05)	-0.003(05)

C37	0.023(05)	0.037(07)	0.022(05)	-0.001(05)	0.001(04)	-0.002(05)
C38	0.024(05)	0.022(06)	0.037(06)	0.004(05)	0.009(04)	0.004(05)
C39	0.032(07)	0.062(10)	0.049(08)	-0.002(07)	0.018(06)	0.000(07)
C40	0.027(06)	0.091(12)	0.043(08)	-0.002(07)	0.014(06)	-0.018(08)
C41	0.022(05)	0.030(07)	0.020(06)	-0.011(05)	-0.001(05)	-0.004(05)
C42	0.024(07)	0.033(08)	0.027(07)	-0.003(06)	0.002(05)	-0.004(05)
C43	0.029(06)	0.030(07)	0.039(07)	-0.007(05)	0.013(06)	-0.004(05)
C44	0.022(06)	0.054(09)	0.035(07)	-0.011(06)	0.011(05)	-0.023(06)
C45	0.024(06)	0.047(09)	0.027(06)	0.001(06)	0.002(05)	-0.002(06)
C46	0.021(05)	0.015(07)	0.037(06)	-0.008(05)	-0.008(05)	0.004(05)
C47	0.060(10)	0.027(09)	0.074(10)	0.018(08)	0.020(09)	0.011(08)
C48	0.038(07)	0.062(10)	0.044(09)	-0.004(07)	0.011(07)	-0.005(07)
C49	0.036(07)	0.029(07)	0.029(06)	-0.010(06)	0.008(05)	-0.006(05)
C50	0.040(09)	0.039(09)	0.049(09)	0.003(06)	0.009(07)	-0.001(06)
C51	0.051(08)	0.021(08)	0.093(11)	-0.006(07)	0.037(08)	0.001(07)
C52	0.071(10)	0.020(08)	0.077(10)	-0.002(07)	0.035(08)	0.005(06)
C53	0.050(08)	0.031(08)	0.042(07)	0.008(07)	0.017(06)	0.003(06)
C54	0.034(07)	0.041(09)	0.037(07)	0.001(06)	0.005(05)	0.001(06)
C55	0.23(03)	0.024(12)	0.34(04)	-0.018(15)	0.25(03)	-0.009(16)
C56	0.051(09)	0.058(11)	0.057(10)	0.018(08)	0.010(08)	0.011(08)
C57	0.069(11)	0.127(17)	0.063(11)	-0.028(10)	0.004(09)	0.013(12)
C58	0.058(11)	0.18(02)	0.088(16)	-0.015(14)	0.014(11)	0.021(16)
C59	0.071(14)	0.14(02)	0.16(02)	0.012(15)	0.027(14)	-0.05(02)
C60	0.17(02)	0.107(19)	0.14(02)	0.016(15)	0.066(18)	0.032(17)
C61	0.101(14)	0.082(15)	0.117(17)	0.017(12)	0.048(12)	0.017(12)
C62	0.049(10)	0.16(02)	0.061(12)	0.012(12)	0.003(09)	-0.015(13)
C63	0.111(15)	0.21(02)	0.105(16)	-0.037(15)	0.024(13)	-0.022(16)

Table S-9. Bond Lengths (Å) for **2h**

atom	atom	distance	atom	atom	distance
IR1	IR2	0.762(5)	F4	C32	1.30(1)
IR1	P1	2.342(5)	F5	C32	1.34(2)
IR1	C11	1.78(1)	F6	C32	1.34(1)
IR1	C15	2.27(1)	F7	C39	1.32(2)
IR1	C101	1.977(1)	F8	C39	1.31(1)
IR1	C1	2.349(7)	F9	C39	1.31(1)
IR1	C5	2.308(7)	F10	C40	1.25(1)
IR1	C4	2.268(7)	F11	C40	1.28(2)
IR1	C3	2.287(6)	F12	C40	1.35(2)
IR1	C2	2.337(6)	F13	C47	1.31(2)
IR2	P2	2.44(2)	F14	C47	1.22(2)
IR2	C11	2.03(1)	F15	C47	1.27(2)
IR2	C15	2.23(1)	F16	C48	1.33(2)
IR2	C102	1.946(5)	F17	C48	1.29(2)
IR2	C66	2.27(2)	F18	C48	1.29(1)
IR2	C67	2.34(2)	F22	C56	1.28(2)
IR2	C68	2.33(3)	F23	C56	1.34(2)
IR2	C69	2.26(3)	F24	C56	1.35(2)
IR2	C65	2.22(2)	F25	C55	1.20(3)
P1	C12	1.85(2)	F26	C55	1.33(3)
P1	C13	1.86(2)	F27	F28	1.59(2)
P1	C14	1.83(2)	F27	C55	1.26(4)
P2	C64	1.81(5)	F28	C55	1.65(3)
F1	C31	1.34(2)	O1	C11	1.11(2)
F2	C31	1.30(2)	C15	C16	1.46(1)
F3	C31	1.23(2)	C15	C20	1.54(2)
C15	C21	1.52(2)	C37	C38	1.33(1)
C16	C17	1.56(2)	C37	C40	1.45(1)
C17	C18	1.54(2)	C41	C42	1.40(1)
C17	C23	1.49(2)	C41	C46	1.41(2)
C18	C19	1.44(2)	C41	B1	1.67(2)
C19	C20	1.56(2)	C42	C43	1.39(2)
C19	C24	1.55(2)	C43	C44	1.36(2)
C21	C22	1.58(2)	C43	C47	1.47(2)
C22	C23	1.49(2)	C44	C45	1.40(2)
C22	C24	1.51(2)	C45	C46	1.37(2)
C25	C26	1.39(1)	C45	C48	1.52(2)
C25	C30	1.41(2)	C49	C50	1.39(2)
C25	B1	1.59(1)	C49	C54	1.43(2)
C26	C27	1.36(1)	C49	B1	1.63(2)
C27	C28	1.41(2)	C50	C51	1.42(2)
C27	C31	1.47(2)	C51	C52	1.38(2)
C28	C29	1.34(1)	C51	C55	1.49(3)
C29	C30	1.34(1)	C52	C53	1.36(2)
C29	C32	1.52(2)	C53	C54	1.41(2)
C33	C34	1.40(2)	C53	C56	1.46(2)
C33	C38	1.38(1)	C57	C58	1.36(3)
C33	B1	1.62(1)	C57	C62	1.38(3)
C34	C35	1.37(1)	C58	C59	1.35(4)

C35	C36	1.36(1)	C59	C60	1.45(4)
C35	C39	1.51(2)	C60	C61	1.44(4)
C36	C37	1.37(2)	C61	C62	1.38(3)
C62	C63	1.53(3)	C64	C1	1.69(5)
C64	C6	0.95(6)	C1	C5	1.40(1)
C1	C2	1.400(7)	C1	C6	1.553(9)
C5	C4	1.400(8)	C5	C10	1.553(8)
C4	C3	1.400(9)	C4	C9	1.57(1)
C4	C72	1.83(3)	C3	C2	1.40(1)
C3	C8	1.553(7)	C2	C7	1.55(1)
C9	C72	1.27(3)	C8	C71	1.58(3)
C66	C67	1.40(3)	C66	C65	1.40(3)
C66	C71	1.55(3)	C67	C68	1.40(3)
C67	C72	1.55(3)	C68	C69	1.40(3)
C68	C73	1.55(3)	C69	C65	1.40(3)
C69	C74	1.55(3)	C65	C70	1.55(3)

Table S-10. Bond Angles(°) for **2h**

atom	atom	atom	angle	atom	atom	atom	angle
P1	IR1	C11	85.4(6)	IR2	C15	C20	101.2(8)
P1	IR1	C15	92.1(3)	IR2	C15	C21	126.4(8)
P1	IR1	C101	128.1(1)	C16	C15	C20	108.5(9)
C11	IR1	C15	86.3(6)	C16	C15	C21	106(1)
C11	IR1	C101	127.6(5)	C20	C15	C21	109(1)
C15	IR1	C101	124.4(3)	C15	C16	C17	111(1)
C1	IR1	C5	35.0(2)	C16	C17	C18	110(1)
P2	IR2	C11	75.6(7)	C16	C17	C23	111(1)
P2	IR2	C15	85.4(7)	C18	C17	C23	111(1)
P2	IR2	C102	126.2(6)	C17	C18	C19	108(1)
C11	IR2	C15	81.7(6)	C18	C19	C20	112(1)
C11	IR2	C102	135.5(5)	C18	C19	C24	107(1)
C15	IR2	C102	132.3(3)	C20	C19	C24	111(1)
IR1	P1	C12	117.2(6)	C15	C20	C19	110(1)
IR1	P1	C13	114.5(6)	C15	C21	C22	113(1)
IR1	P1	C14	118.5(6)	C21	C22	C23	107(1)
C12	P1	C13	103.9(8)	C21	C22	C24	110(1)
C12	P1	C14	102.3(7)	C23	C22	C24	109(1)
C13	P1	C14	97.6(8)	C17	C23	C22	107(1)
IR2	P2	C64	127(2)	C19	C24	C22	109(1)
IR1	C11	O1	173(2)	C26	C25	C30	117.1(8)
IR2	C11	O1	165(2)	C26	C25	B1	120(1)
IR1	C15	C16	111.5(8)	C30	C25	B1	122.5(8)
IR1	C15	C20	114.4(9)	C25	C26	C27	119(1)
IR1	C15	C21	107.2(7)	C26	C27	C28	123(1)
IR2	C15	C16	105.0(8)	C26	C27	C31	116(1)
C28	C27	C31	121(1)	C36	C37	C38	123.5(8)
C27	C28	C29	117.4(9)	C36	C37	C40	119(1)
C28	C29	C30	121(1)	C38	C37	C40	117(1)
C28	C29	C32	121(1)	C33	C38	C37	120(1)
C30	C29	C32	117.7(9)	F7	C39	F8	106(1)
C25	C30	C29	122.4(9)	F7	C39	F9	105(1)
F1	C31	F2	101(1)	F7	C39	C35	114(1)
F1	C31	F3	107(1)	F8	C39	F9	103(1)
F1	C31	C27	113(1)	F8	C39	C35	113(1)
F2	C31	F3	109(1)	F9	C39	C35	115(1)
F2	C31	C27	114(1)	F10	C40	F11	112(1)
F3	C31	C27	114(1)	F10	C40	F12	106(1)
F4	C32	F5	105(1)	F10	C40	C37	114(1)
F4	C32	F6	103(1)	F11	C40	F12	98(1)
F4	C32	C29	114(1)	F11	C40	C37	116(1)
F5	C32	F6	107(1)	F12	C40	C37	111(1)
F5	C32	C29	115(1)	C42	C41	C46	113(1)
F6	C32	C29	112(1)	C42	C41	B1	122(1)
C34	C33	C38	115.5(8)	C46	C41	B1	124.6(9)
C34	C33	B1	127.4(7)	C41	C42	C43	123(1)
C38	C33	B1	117(1)	C42	C43	C44	122(1)
C33	C34	C35	124.7(8)	C42	C43	C47	118(1)
C34	C35	C36	117(1)	C44	C43	C47	119(1)

C34	C35	C39	121.6(8)	C43	C44	C45	118(1)
C36	C35	C39	122(1)	C44	C45	C46	119(1)
C35	C36	C37	119.4(9)	C44	C45	C48	120(1)
C46	C45	C48	121(1)	F25	C55	F26	96(2)
C41	C46	C45	126(1)	F25	C55	F27	128(3)
F13	C47	F14	98(1)	F25	C55	F28	84(2)
F13	C47	F15	106(1)	F25	C55	C51	115(3)
F13	C47	C43	116(1)	F26	C55	F27	86(2)
F14	C47	F15	105(1)	F26	C55	F28	140(3)
F14	C47	C43	114(1)	F26	C55	C51	117(2)
F15	C47	C43	115(1)	F27	C55	F28	64(2)
F16	C48	F17	107(1)	F27	C55	C51	110(2)
F16	C48	F18	102(1)	F28	C55	C51	99(2)
F16	C48	C45	115(1)	F22	C56	F23	107(1)
F17	C48	F18	107(1)	F22	C56	F24	107(1)
F17	C48	C45	114(1)	F22	C56	C53	112(1)
F18	C48	C45	110(1)	F23	C56	F24	103(1)
C50	C49	C54	116(1)	F23	C56	C53	114(1)
C50	C49	B1	123(1)	F24	C56	C53	114(1)
C54	C49	B1	121(1)	C58	C57	C62	120(2)
C49	C50	C51	123(1)	C57	C58	C59	123(2)
C50	C51	C52	119(1)	C58	C59	C60	117(2)
C50	C51	C55	117(1)	C59	C60	C61	122(2)
C52	C51	C55	123(1)	C60	C61	C62	115(2)
C51	C52	C53	121(1)	C57	C62	C61	124(2)
C52	C53	C54	120(1)	C57	C62	C63	119(2)
C52	C53	C56	120(1)	C61	C62	C63	117(2)
C54	C53	C56	120(1)	P2	C64	C1	21(1)
C49	C54	C53	121(1)	P2	C64	C6	84(3)
C1	C64	C6	65(3)	C66	C67	C72	126(2)
C25	B1	C33	110(1)	C68	C67	C72	126(2)
C25	B1	C41	104.9(8)	C67	C68	C69	108(2)
C25	B1	C49	113.2(8)	C67	C68	C73	126(2)
C33	B1	C41	112.3(8)	C69	C68	C73	126(2)
C33	B1	C49	105.3(8)	C68	C69	C65	108(2)
C41	B1	C49	111(1)	C68	C69	C74	126(2)
C5	C1	C2	108.0(5)	C65	C69	C74	126(2)
C5	C1	C6	125.7(6)	C66	C65	C69	108(2)
C2	C1	C6	125.7(7)	C66	C65	C70	126(2)
C1	C5	C4	108.0(5)	C69	C65	C70	126(2)
C1	C5	C10	125.7(6)	C4	C5	C10	125.7(7)
C5	C4	C3	108.0(6)	C5	C4	C9	125.2(6)
C3	C4	C9	125.2(5)	C4	C3	C2	108.0(5)
C4	C3	C8	125.7(6)	C2	C3	C8	125.7(6)
C1	C2	C3	108.0(6)	C1	C2	C7	125.7(6)
C3	C2	C7	125.7(5)	C67	C66	C65	108(2)
C67	C66	C71	126(2)	C65	C66	C71	126(2)
C66	C67	C68	108(2)				

Figure S-5. ORTEP diagram of **21**

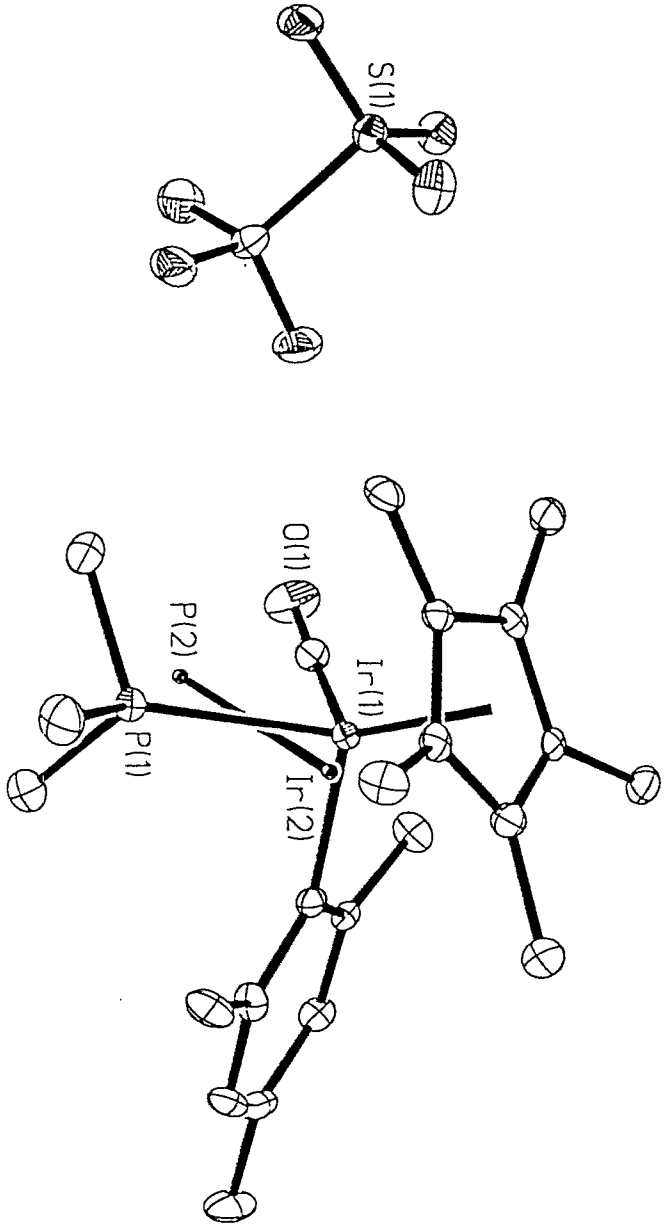

Figure S-6. ORTEP diagram of **21**

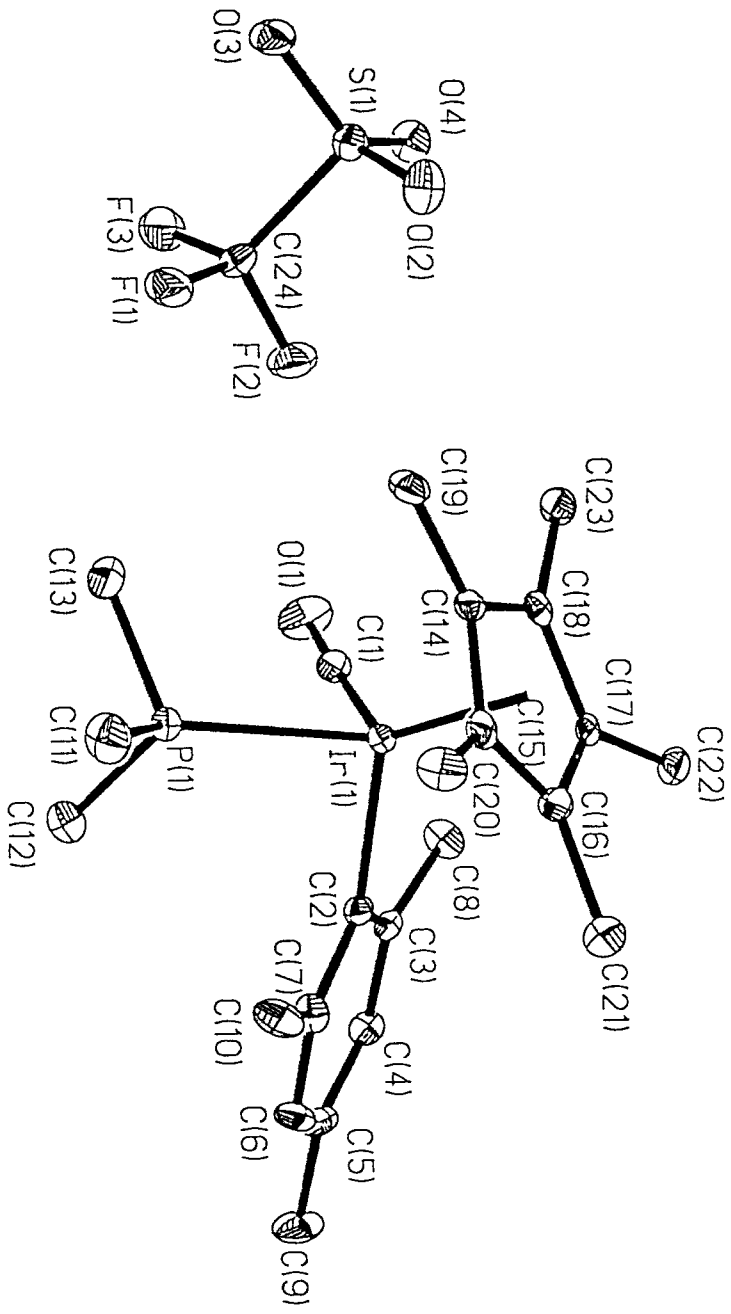

Table S-11. Crystal and Data Collection Parameters for **2l**

a. Crystal Data

Emperical Formula	$IrPSO_4F_3C_{24}H_{35}$
Formula Weight	699.79
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.09 X 0.18 X 0.35 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	5656 (3.0 - 45.0°)
Lattice Parameters	a = 8.5800(2) Å b = 12.7278(6) Å c = 13.0668(6) Å α = 78.050(1)° β = 109.960(1)° γ = 87.312(1)° V = 1319.41(10) Å^3
Space Group	$P\bar{1}$ (#2)
Z value	2
D*calc*	1.761 g/cm^3
F_{000}	692.00
$\mu(MoK_\alpha)$	52.62 cm^{-1}

b. Intensity Measurements

Diffractometer	SMART
Radiation	MoK_α (λ = 0.71069 Å) graphite monochromated
Crystal to Detector Distance	60 mm
Temperature	-148.0 °C
Scan Type	ω (0.3° per frame)
Scan Rate	10.0 seconds per frame
2θ *max*	46.6°

No. of Reflections Measured	Total: 6372
	Unique: 3743 (R_{int} = 0.020%)
Corrections	Lorentz-polarization
	Absorption (T_{max} = 0.49, T_{min} = 0.28)

c. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/(\sigma^2(F_o) = 4F_o^2/(\sigma^2(F_o^2))$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No Observations (I>3.00σ(I))	3518
No Variables	315
Reflection/Parameter Ratio	11.17
Residuals: R; R_w; R_{all}	0.024; 0.033; 0.026
Goodness of Fit Indicator	1.34
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.63 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.67e^-/A^3

Table S-12. Atomic coordinates and B_{iso}/B_{eq} for **2l**

atom	x	y	z	$B_{(eq)}$
Ir(1)	-0.00609(5)	0.29459(1)	0.78215(1)	1.12(2)
Ir(2)	0.0768(8)	0.2947(3)	0.7815(3)	0.4(1)
S(1)	-0.4260(1)	-0.1256(1)	0.7535(1)	1.84(7)
P(1)	0.1661(2)	0.2760(1)	0.6074(1)	1.55(8)
P(2)	0.015(2)	0.307(2)	0.621(2)	0.4
F(1)	-0.1609(3)	-0.0239(3)	0.6052(3)	3.3(2)
F(2)	-0.3447(4)	0.0803(2)	0.6838(3)	3.1(2)
F(3)	-0.3824(4)	0.0031(3)	0.5613(3)	3.5(2)
O(1)	-0.2722(5)	0.3223(3)	0.6762(3)	3.2(3)
O(2)	-0.3369(4)	-0.1334(3)	0.8318(3)	2.9(3)
O(3)	-0.4015(4)	-0.2119(3)	0.6943(3)	2.5(2)
O(4)	-0.5941(4)	-0.0903(3)	0.7908(3)	2.4(2)
C(1)	-0.1704(6)	0.3164(4)	0.7164(4)	2.0(3)
C(2)	0.0495(6)	0.4641(4)	0.7480(4)	1.5(3)
C(3)	-0.0771(6)	0.5399(4)	0.7552(4)	1.5(3)
C(4)	-0.0378(6)	0.6505(4)	0.7259(4)	1.8(3)
C(5)	0.1218(6)	0.6902(4)	0.6921(4)	2.1(3)
C(6)	0.2452(6)	0.6154(4)	0.6925(4)	1.9(3)
C(7)	0.2133(5)	0.5050(4)	0.7181(4)	1.7(3)
C(8)	-0.2615(6)	0.5134(4)	0.7961(5)	2.3(3)
C(9)	0.1600(8)	0.8096(4)	0.6612(5)	3.1(4)
C(10)	0.3614(6)	0.4345(4)	0.7144(5)	2.4(3)
C(11)	0.3620(6)	0.2095(5)	0.5947(5)	2.8(4)
C(12)	0.2163(7)	0.3978(5)	0.5013(5)	2.9(4)
C(13)	0.0696(6)	0.1934(5)	0.5485(5)	2.6(4)
C(14)	-0.0071(5)	0.1253(4)	0.8793(4)	1.4(3)
C(15)	0.1207(6)	0.1846(4)	0.8949(4)	1.7(3)
C(16)	0.0438(6)	0.2697(4)	0.9479(4)	1.8(3)
C(17)	-0.1302(6)	0.2640(4)	0.9660(4)	1.4(3)
C(18)	-0.1611(5)	0.1720(4)	0.9256(4)	1.4(3)
C(19)	0.0166(6)	0.0212(4)	0.8381(4)	1.9(3)
C(20)	0.2958(6)	0.1505(4)	0.8793(5)	2.4(3)
C(21)	0.1264(6)	0.3439(4)	0.9909(4)	2.5(4)
C(22)	-0.2565(7)	0.3291(4)	1.0349(4)	2.3(3)
C(23)	-0.3291(6)	0.1314(4)	0.9360(4)	2.1(3)
C(24)	-0.3226(6)	-0.0115(4)	0.6456(4)	2.2(3)
C(10)	-0.0392	0.2032	0.9228	0.2
H(1)	-0.1250	0.7001	0.7296	2.1
H(2)	0.3553	0.6405	0.6747	2.5
H(3)	-0.2824	0.4456	0.8456	2.4
H(4)	-0.2969	0.5108	0.7349	2.4
H(5)	-0.3199	0.5672	0.8333	2.4
H(6)	0.2586	0.8230	0.6750	3.6
H(7)	0.0716	0.8459	0.7042	3.6
H(8)	0.1740	0.8347	0.5850	3.6
H(9)	0.4319	0.4419	0.6401	2.7
H(10)	0.3255	0.3617	0.7432	2.7
H(11)	0.4197	0.4558	0.7576	2.7
H(12)	0.4144	0.2031	0.5201	3.3