Supporting Information

Iron-phosphine catalyzed cross-coupling of tetraorgano-borates and related group 13 nucleophiles with alkyl halides.

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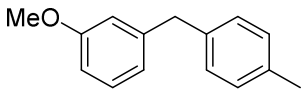
Contents

1. Characterization of cross-coupled products

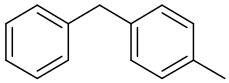
Unless otherwise stated, all products were purified by flash-column chromatography over silica eluting with petroleum ether 40–60.

1-Methoxy-3-(4-methylphenyl)benzene (9b, Table 3, Entry 17)



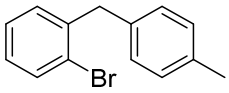
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.24-7.20 (m, 1H), 7.10 (s, 4H), 6.83-6.74 (m, 3H), 3.93 (s, 1H), 3.78 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 159.8, 143.1, 138.0, 135.7, 129.5, 129.3, 128.9, 121.5, 114.9, 111.4, 55.3, 41.7, 21.2. MS (EI) *m/z* (%): 212.1 ($[M+H]^+$, 100).

1-Benzyl-4-methylbenzene (9e, Table 3, Entry 5)



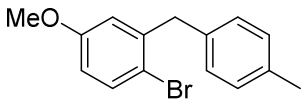
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.33-7.29 (m, 2H), 7.24-7.19 (m, 3H), 7.10 (s, 4H), 3.96 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.4, 138.0, 135.5, 129.1, 128.9, 128.8, 128.4, 125.9, 41.5, 21.0. MS (EI) *m/z* (%): 182.1 ($[M+H]^+$, 85), 167.1 ($[M-CH3]^+$, 100).

1-Bromo-2-(4-methylbenzyl)benzene (9g, Table 3, Entry 7)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.65-7.63 (dd, *J* = 1.22 Hz, 7.57 Hz, 1H), 7.52-7.48 (apparent td, *J* = 1.47 Hz, 7.57 Hz, 1H), 7.32-7.28 (m, 2H), 7.14 (apparent s, 4H) 4.18 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 145.3, 136.3, 135.7, 132.8, 130.0, 129.4, 128.8, 126.7, 118.2, 112.5, 39.8, 21.0. MS (EI) *m/z* (%): 260 ($[M+H]^+$, 65), 181 ($[M-Br]^+$, 100).

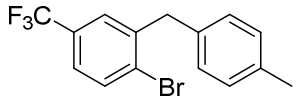
1-Bromo-4-methoxy-2-(4-methylphenyl)benzene (9h, Table 5, Entry 4)



Colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.45 (d, *J* = 8.6 Hz, 1H), 7.15-7.06 (m, 4H), 6.70 (d, *J* = 3.1 Hz, 1H), 6.67-6.63 (dd, *J* = 8.7 Hz, *J* = 3.1 Hz, 1H), 4.04 (s, 2H), 3.74 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl3, 25 °C) δ = 159.1, 141.7, 136.4, 135.9, 133.4, 129.3, 129.0, 117.1, 115.4, 113.4,

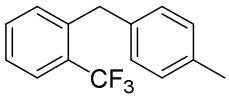
55.5, 41.6, 21.9. HRMS (CI) *m/z*: [M+H]+ calcd. for $C_{15}H_{16}O_2Br$: 307.0334; found: 307.0334. Anal. calcd. for $C_{15}H_{16}O_2Br$: C, 61.87 H, 5.19; found: C, 61.85, H, 5.13.

1-Bromo-2-(4-methylbenzyl)-4-(trifluoromethyl)benzene (9i, Table 3, Entry 9)



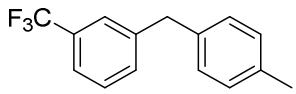
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) = 7.70 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8 Hz, *J* = 2.2 Hz, 1H), 7.17-7.06 (m, 4H), 4.13 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.9, 136.4, 135.3, 133.5, 130.1 (q, *J* = 33.3 Hz), 129.5, 128.9, 128.8, 127.2 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 273.7 Hz), 41.5, 21.2. ^{19}F NMR (376 MHz , $CDCl_3$, 25 °C) δ = -62.6 (s). MS (EI) *m/z* (%): 328 ($[M+H]^+$, 85), 249 ($[M-Br]^+$ 100).

1-(4-Methylbenzyl)-2-(trifluoromethyl)benzene (9j, Table 3, Entry 10)



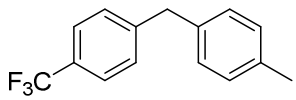
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.69 (d, *J* = 7.8 Hz, 1H), 7.44 (apparent t, *J* = 7.6 Hz, 1H), 7.32 (apparent t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 4.18 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 139.9, 136.9, 136.0, 131.9, 131.8, 129.4, 129.2, 128.9 (q, *J* = 29 Hz), 126.2, 125.9 (q, *J* = 6 Hz), 124.6 (q, *J* = 274 Hz), 196 37.5, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ = -59.5 (s). MS (EI) *m/z* (%): 250.1 ($[M+H]^+$, 100).

1-(4-Methylbenzyl)-3-(trifluoromethyl)benzene (9k, Table 3, Entry 11)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.49-7.40 (m, 2H), 7.42-7.34 (m, 2H), 7.15-7.06 (m, 4H), 4.00 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 142.5, 137.1, 136.2, 132.4, 130.7 (q, *J* = 32 Hz), 129.5, 129.0, 128.9, 126.5 (q, *J* = 274 Hz), 125.7 (q, *J* = 4 Hz), 123.1 (q, *J* = 4 Hz), 41.4, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ = -62.6 (s). MS (EI) *m/z* (%): 250.1 ([M+H]+, 100).

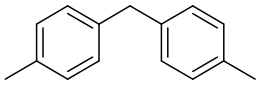
1-(4-Methylbenzyl)-4-(trifluoromethyl)benzene (9l, Table 3, Entry 12)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.55 (d, *J* =8.3 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.17-7.07 (m, 4H), 4.02 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 145.7, 137.1, 136.2,

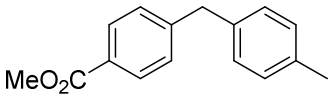
129.5, 129.3, 128.9, 128.7 (q, *J* = 32 Hz, 2C), 128.5 (q, *J* = 274 Hz), 125.5 (q, *J* = 4 Hz), 41.5, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ = -62.4 (s). MS (EI) *m/z* (%): 250.1 ($[M+H]^+$, 100).

Di-*p*-tolylmethane (9m, Table 3, Entry 19)



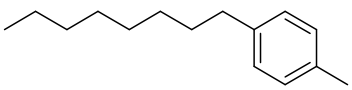
Colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.12 (s, 8H), 3.94 (s, 2H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 138.3, 135.4, 129.1, 128.7, 41.1, 21.0. MS (EI) *m/z* (%): 196.1 ($[M+H]^+$, 100).

Methyl 4-(4-methylbenzyl)benzoate (9o, Table 5, Entry 7)



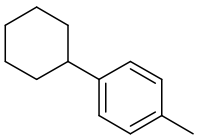
Colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.14-7.03 (m, 4H), 3.99 (s, 2H), 3.89 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.2, 41.7, 52.1, 128.2, 129.0, 129.1, 129.4, 129.9, 136.1, 137.2, 147.0, 167.2. MS (CI) *m/z* (%): 241.1 ($[M+H, 100]^+$.

1-Methyl-4-octylbenzene (9q, Table 5, Entry 14)



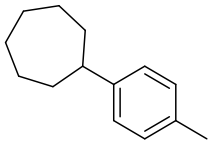
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.11 (s, 4H), 2.65-2.53 (t, *J* = 7.7 Hz, 2H), 2.35 (s, 3H), 1.67-1.57 (m, 2H), 1.40 - 1.25 (m, 10H), 0.95-0.84 (m, 3H). ^{13}C NMR (100 MHz, CDCl3, 25 °C) δ = 140.0, 135.1, 129.0, 201.0, 128.4, 35.7, 32.1, 31.8, 29.7, 29.5, 29.4, 22.8, 21.1, 14.3. MS (EI) *m/z* (%): 204.2 ($[M+H]^+$, 40), 105.1 (100).

1-Cyclohexyl-4-methylbenzene (9r, Table 5, Entry 15)



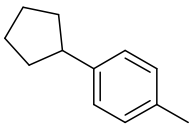
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.13 (s, 4H), 2.53-2.43 (m, 1H), 2.34 (s, 3H), 1.95-1.73 (m, 5H), 1.49-1.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 145.3, 135.3, 129.1, 126.8, 44.3, 34.7, 27.1, 26.4, 21.1. MS (EI) *m/z* (%):175.1 ($[M+H]^+$, 80), 131.1 (100).

***p*-Tolylcycloheptane (9s, Table 5, Entry 16)**



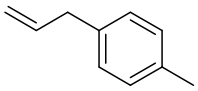
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.13 (s, 4H), 2.71-2.63 (m, 1H), 2.35 (s, 3H), 1.98-1.48 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 147.2, 135.0, 129.1, 126.7, 46.8, 37.1, 28.1, 27.3, 20.0, 21.1. MS (EI) *m/z* (%): 188.1 ($[M+H]^+$, 70), 131.1 (100).

1-Cyclopentyl-4-methylbenzene (9t, Table 5, Entry 17)



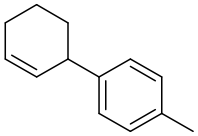
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.20-7.10 (m, 4H), 3.04-2.92 (m, 1H), 2.35 (s, 3H), 2.14-2.02 (m, 2H), 1.90-1.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 143.5, 135.2, 129.1, 127.1, 45.7, 34.8, 25.6, 21.1. MS (EI) *m/z* (%): 160.1 ($[M+H]^+$, 85), 145.1 ($[M-CH_3]^+$, 85), 131.1 (100).

1-Allyl-4-methylbenzene (9u, Table 5, Entry 18)



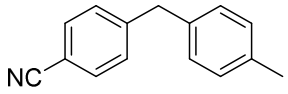
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.13 – 7.08 (m, 4H), 6.03 – 5.91 (m, 1H), 5.11 – 5.04 (m, 2H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 140.0, 137.4, 128.6, 128.4, 126.0, 115.8, 40.2, 21.1. MS (EI) *m/z* (%): 132.1 ($[M+H]^+$, 15), 117.1 ($[M-CH_3]^+$, 30), 84.0 (100).

4'-Methyl-1,2,3,4-tetrahydro-1,1'-biphenyl (9v, Table 5, Entry 19)



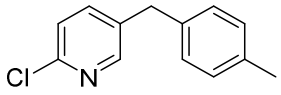
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.15 (app s, 4H), 5.95 – 5.88 (m, 1H), 5.78 – 5.72 (m, 1H), 3.45 – 3.37 (m, 1H), 2.37 (s, 3H), 2.16 – 2.08 (m, 2H), 2.08 – 2.00 (m, 1H), 1.83 – 1.73 (m, 1H), 1.72 – 1.51 (m, 2H). LRMS (EI) *m/z* (%): 172.1 ($[M+H]^+$, 10), 157.1 ($[M-CH_3]^+$, 10), 84.0 (100).

4-(4-Methylbenzyl)benzonitrile (Table 5, Entry 8)



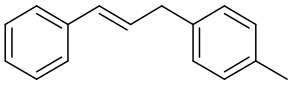
Colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.53-7.45 (m, 4H), 7.13 (s, 4H), 4.17 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 145.1, 136.1, 134.9, 132.7, 130.1, 129.4, 128.8, 117.1, 111.3, 39.8, 21.0. MS (EI) *m/z* (%): 207.1 ($[M+H]^+$, 100).

2-Chloro-5-(4-methylbenzyl)pyridine (Table 5, Entry 13)



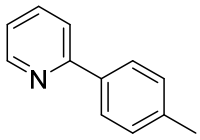
Colorless powder, eluted with hexane/ethyl acetate 9:1. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.27 (d, *J* = 2.4 Hz, 1H), 7.44 – 7.39 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.3 – 7.15 (m, 1H), 7.15 – 7.01 (m, 4H), 3.91 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 149.8, 149.3, 139.3, 136.4, 136.3, 135.9, 129.6, 128.8, 124.2, 37.9, 21.1. MS (EI) *m/z* (%): 217.1 ($[M+H]^+$, 32).

1-Cinnamyl-4-methylbenzene (Table 5, Entry 20)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 7.22 – 7.17 (m, 4H), 6.54 – 6.48 (m, 1H), 6.46 – 6.37 (m, 1H), 3.57 (dd, *J* = 6.5, 1.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 137.7, 137.2, 135.8, 131.0, 129.6, 129.3, 128.7, 128.6, 127.2, 126.3, 39.0, 21.2. LRMS (EI) *m/z* (%): 208.1 ($[M+H]^+$, 20), 193.1 ($[M-CH_3]^+$, 20), 84.0 (100).

2-(4-Methylphenyl)pyridine (Table 5, Entry 21)



Yellow oil, eluted with hexane/ethyl acetate 9:1. ^{1}H NMR (400 MHz, d_8-toluene, 25 °C) δ = 8.57 – 8.50 (ddd, *J* = 4.8, 2.0, 1.0 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.36 – 7.27 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.16 – 7.10 (td, *J* = 7.7, 1.9 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.70 – 6.60 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, d_8-toluene, 25 °C) δ = 157.9, 150.2, 139.2, 137.5, 136.6, 130.0, 137.6, 122.0, 120.0, 21.5. MS (EI) *m/z* (%): 171.9 ($[M+H]^+$, 32), 155.0 ($[M-CH_3]^+$, 100).

2. $^{11}B\{^{1}H\}$ NMR Spectroscopy

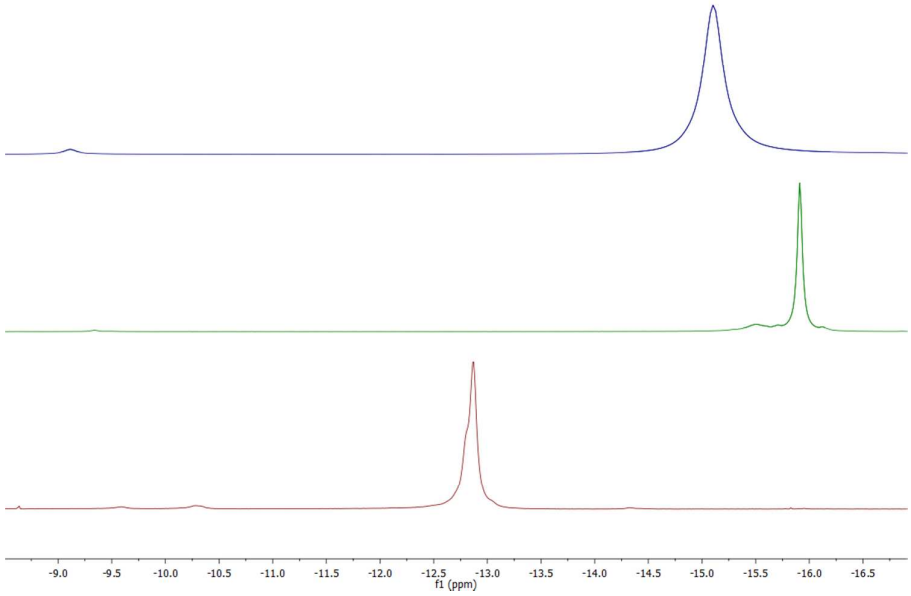


Figure S1: $^{11}B\{^{1}H\}$ NMR spectra (THF) of: **10a** (bottom) **10b** (middle) **10c** (top)

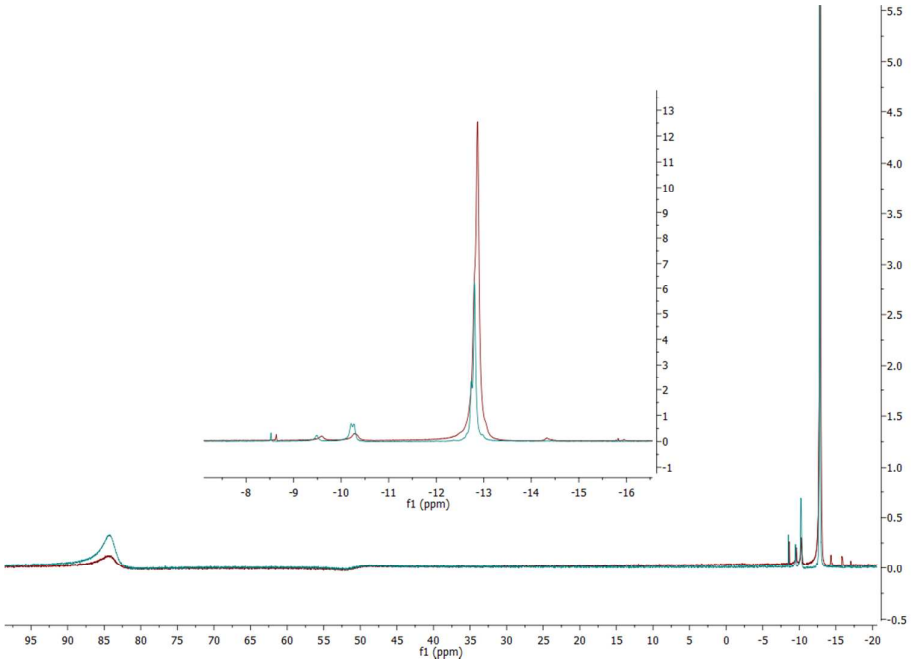


Figure S2: $^{11}B\{^{1}H\}$ NMR spectra (THF) of: **10a** (red line) **10a** + 0.2 equivalents $ZnCl_2$.

3. EPR spectroscopy

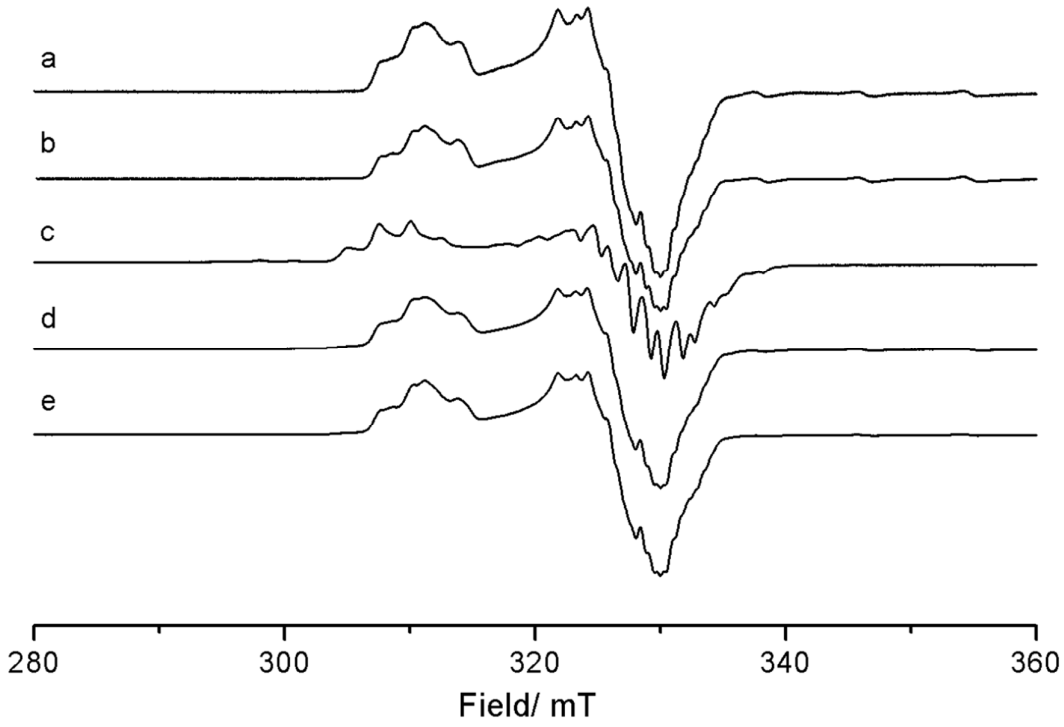


Figure S3: EPR spectra (140 K) of: a) Sample taken from catalytic reaction of **8n** with MgCl[Al(4-tolyl)$_4$] catalyzed by **1**; b) **1** + 20 MgCl[Al(4-tolyl)$_4$]; c) **1** + 20 MgCl[Ga(4-tolyl)$_4$]; d) Sample taken from catalytic reaction of **8n** with MgCl[In(4-tolyl)$_4$] catalyzed by **1**; e) **1** + 20 MgCl[In(4-tolyl)$_4$].

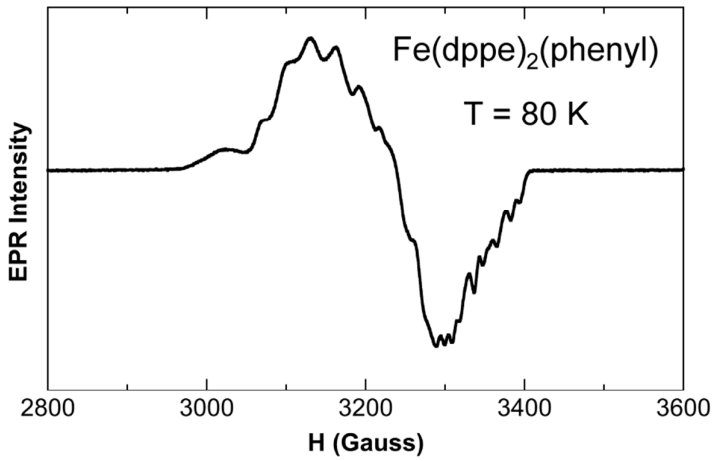


Figure S4: EPR spectrum (80K) of **3d**. The spectrum also shows the presence of a small amount of **3a**.

Table S1: Experimental and DFT calculated spin Hamiltonian parameters of **3c**

	$^{a}g_1$	$^{a}g_2$	$^{a}g_3$	$^{b}A_1$/ MHz	$^{b}A_2$/ MHz	$^{b}A_3$/ MHz
Expt	2.011	2.066	2.151			
DFT	*2.069*	*2.111*	*2.193*			
P (axial)						
Expt				87	58	62.0
DFT				*90*	*98*	*87.0*
Expt				87	87	98.1
DFT				*85*	*94*	*81.7*
P (equatorial)						
Expt				124	87	98.1
DFT				*118*	*111*	*126.6*
Expt				37	35	24.1
DFT				*7*	*11*	*4.4*

[a] ± 0.002; [b] ± 4 MHz

4. Mössbauer Spectroscopy

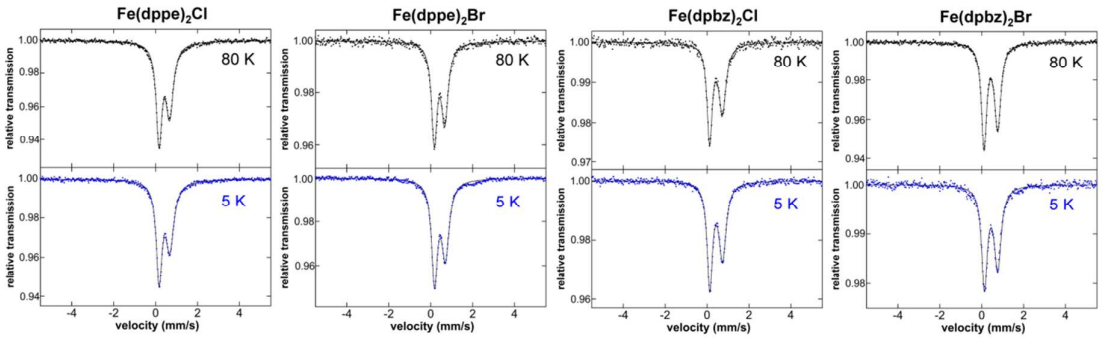


Figure S5. Variable-temperature ^{57}Fe Mössbauer spectra of iron(I)-bisphosphine complexes (left to right) **3a**, **3b**, **12b** and **12c**. For each spectrum the data (dots) and fit (solid line) are given.

Table S2. ^{57}Fe Mössbauer parameters for iron(I)-bisphosphine halide complexes.

Complex	Temperature	Isomer Shift (δ)[a]	ΔE_Q[a]
3a	80 K	0.42 mm/s	0.51 mm/s
	5 K	0.43 mm/s	0.51 mm/s
3b	80 K	0.42 mm/s	0.50 mm/s
	5 K	0.44 mm/s	0.52 mm/s
12b	80 K	0.43 mm/s	0.61 mm/s
	5 K	0.44 mm/s	0.61 mm/s
12c	80 K	0.44 mm/s	0.65 mm/s
	5 K	0.45 mm/s	0.64 mm/s

[a] Isomer shift and ΔE_Q values for each complex are the same at 80 K and 5 K within the error of the fitting analysis ($\delta \pm 0.02$ mm/s, $\Delta E_Q \pm 0.03$ mm/s)

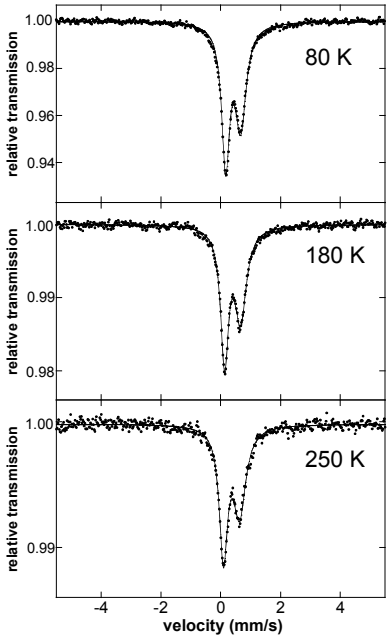


Figure S6. Variable-temperature ^{57}Fe Mössbauer spectra of [FeCl(dppe)$_2$], **3a**. For each spectrum the data (dots) and fit (solid line) are given.

5. Crystallographic Data

X-ray diffraction experiments on single crystals of **3c**, **3d**, **4**, **6**, **7a** and **7b** were carried out at 100 K on a Bruker APEX II diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fiber. Intensities were integrated[S1] from several series of exposures measuring 0.5° in ω or ϕ. Absorption corrections were based on equivalent reflections using SADABS.[S2] The structures were solved using SHELXS and refined against all Fo2 using SHELXL.[S3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Table S3. Crystallographic details.

Compound	**3c**	**3d**	**4**
CCDC Number	1001838	1002921	1001834
Color, habit	Red, plate	Red-orange, block	Colorless, block
Size/mm	0.40×0.35×0.29	0.18x0.16x0.16	0.11×0.11×0.24
Empirical Formula	C59 H55 Fe P4	C58 H53 Fe P4	C24 H28 P2
M	943.76	929.73	378.40
Crystal system	triclinic	monoclinic	monoclinic
Space group	P -1	C 1 2/c 1	P21/n
a/Å	12.4099(2)	19.6913(16)	9.64690(10)
b/Å	13.6448(2)	15.7113(13)	15.5408(2)
c/Å	16.1121(4)	15.2711(12)	14.0872(2)
α/°	79.0780(10)		
β/°	83.438(2)	105.800(1)	91.4840(10)
γ/°	88.8960(10)		
V/Å^3	2661.29(9)	4546.0(6)	2111.25(5)
Z	2	4	4
μ/mm^{-1}	0.439	0.513	0.211
T/K	100(2)	100.0(5)	100(2)
$\vartheta_{min,max}$	1.295, 34.259	2.36, 37.55	1.95, 27.52
Completeness	0.994, 34.259	0.991, 37.78	0.998 to 27.520
Reflections: total/independent	81825/16909	71866/12097	35519/4858
R_{int}	0.0351	0.0745	0.0388
Final *R*1 and *wR*2	0.0380, 0.1034	0.0517, 0.1360	0.0323, 0.0826
Largest peak, hole/eÅ^{-3}	0.738, -0.572	0.809, -0.477	0.39, -0.20
ρ_{calc}/g cm^{-3}	1.178	1.358	1.190

Compound	**6**	**7a**	**7b**
CCDC Number	1001835	1001837	1001836
Color, habit	Colorless, block	Colorless, plate	Colorless, block
Size/mm	0.41×0.29×0.11	0.35×0.16×0.04	0.12×0.10×0.08
Empirical Formula	C50 H88 P2 Si8	C35 H42 O0.09 P2	C51 H90 P2 Si8
M	975.86	526.03	989.89
Crystal system	triclinic	orthorhombic	triclinic
Space group	P -1	Pccn	P-1
a/Å	14.0416(3)	29.3603(5)	14.5604(9)
b/Å	15.3613(3)	12.5550(2)	15.1788(9)
c/Å	16.5197(3)	16.3234(3)	15.5199(10)
α/°	74.6830(10)		99.229(4)
β/°	65.0910(10)		110.918(4)
γ/°	84.4340(10)		91.054(4)
V/Å^3	3116.58(11)	6017.11(18)	3151.8(3)
Z	2	8	2
μ/mm^{-1}	0.252	0.166	0.250
T/K	100(2)	100(2)	100(2)
$\vartheta_{min,max}$	1.599, 27.537	2.47, 27.51	1.50, 26.65
Completeness	0.996 to 27.537	0.999 to 27.510	0.965, 26.650
Reflections: total/independent	54214/9859	48271/5350	12821/8404
R_{int}	0.0632	0.0423	0.0750
Final *R*1 and *wR*2	0.0431, 0.0969	0.0409, 0.1070	0.0716, 0.1874
Largest peak, hole/eÅ^{-3}	0.392, -0.295	0.343, -0.241	0.67, -0.45
ρ_{calc}/g cm^{-3}	1.040	1.161	1.043

6. Computational Details

Geometry optimization was carried out for all species in Gaussian 09[S4] at the B3LYP-D2 level of theory, using standard geometry convergence criteria. The B3LYP-D2 functional is based on B3LYP incorporating Grimmes empirical dispersion correction[S5], as implemented in Gaussian 09. The standard 6-31G(d) basis set was used for all atoms except Fe, for which the SDD ECP and associated triple zeta basis set (as implemented in Gaussian 09) was used. This combination of basis sets is referred to as "SB" below. The doublet and quartet species of each complex were described using an unrestricted open-shell (UB3LYP-D2) ansatz. Single point B3LYP-D2 energies were then computed at the optimized structures using a larger basis set, comprised of the 6-311+G(d) basis on all atoms except C, for which the 6-311G(d) basis set was used. This combination of basis sets is referred to as "LB" below. The SOMO of **3c** was plotted (with an isovalue of ± 0.05 (electron/bohr^3)$^{1/2}$) using a single-point calculation with a restricted open-shell (ROB3LYP-D2) ansatz at the previously optimised geometry using basis set combination SB (which used an unrestricted open-shell (UB3LYP-D2) ansatz). The Mulliken spin density was also calculated from the same geometry with ROB3LYP-D2(SB). The use of a restricted open-shell ansatz means the electron spin density is located only in the SOMO. Single-point calculations were performed in Gaussian 09 to obtain the EPR spectral parameters[S6] of **3c**. These calculations on the previously optimised geometry, utilised UB3LYP-D2 with a 6-311G(d) basis on all atoms except C, for which the 6-31G(d) basis set was used.

Table S4. Calculated UB3LYP-D2/SB and UB3LYP-D2/LB total energies for 3c and 14a'-c' (Hartrees).

Complex	$E_{UB3LYP-D2(SB)}$	$E_{UB3LYP-D2(LB)}$
LS-**3c**	-3770.495826	-4911.346836
HS-**3c**	-3770.480791	-4911.324199
LS-**14a'**	-4383.384979	-5526.183221
HS-**14a'**	-4383.413076	-5526.211647
LS-**14b'**	-4535.812735	-5678.647873
HS-**14b'**	-4535.847538	-5678.677264
LS-**14c'**	-2195.973855	-3336.119220
HS-**14c'**	-2196.002173	-3336.142020
LS-**14c''**	-2195.976131	-3336.124029

Optimized Cartesian coordinates (in Å) of all species are provided separately in a file readable by programs such as Mercury.

7. References

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S6. Calculation of NMR and EPR Parameters. Theory and Applications (Eds. M. Kaupp, M. Bühl, V. G. Malkin) Wiley-VCH, Weinheim 2004.